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Site-selective and Stereoselective Functionalization of Non-Activated C–H Bond

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Doctor of Philosophy

Chemistry

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Abstract

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The major challenge for C–H functionalization remains to be selectivity; although considerable progress has been achieved, the established approaches to develop selective transformation rely on the use of substrate control, which inevitably possesses inherent limitation. A more versatile but challenging approach would be catalyst control, in which the sophisticated catalyst can distinguish one C–H bond from others by recognizing the subtle steric and electronic differences. The approach in the Davies group is to develop a rhodium carbene toolbox to control the selectivity at will.

Catalyst Synthesis. In general, systematic study and further catalyst structural modification are required to discover the optimal catalyst. However, current catalyst synthesis has limitations in structural diversification and accessibility. Therefore, a high-throughput Suzuki coupling process was developed to enable rational design and systematic study. So far, three catalyst libraries have been effectively established from three corresponding preformed bromo-containing dirhodium catalyst through a four-, eight- and twelve-fold palladium catalyzed Suzuki coupling reaction.

Catalyst Design. The catalyst design philosophy was inspired by highly selective enzymatic catalysis, in which each enzyme pocket will allow only one specific substrate to fit. Therefore, if a series of sophisticated catalyst pockets can be designed to recognize the unique steric and electronic character of the target C–H bonds, a similar type of selective catalysis could also be viable. The hypothesis is trying to develop a catalyst 1 with a “small” pocket that only 1° C–H bond can fit; a catalyst 2 with “medium” pocket that 2° C–H bond will be sterically preferred over 3° C–H bond and electronically preferred over primary C–H bond; a catalyst 3 with “large” pocket so that tertiary C–H bond will be electronically preferred over other C–H bonds.

This thesis will discuss efforts toward developing three dirhodium catalysts, $\mathrm{Rh_2}[\mathit{tris}(p\text{-}{}^{t}\mathrm{BuC_6H_4})\mathrm{TPCP}]_4$, $\mathrm{Rh_2}[3,5\text{-di}(p\text{-}{}^{t}\mathrm{Bu})\mathrm{C_6H_4TPCP}]_4$, and $\mathrm{Rh_2(TCPTAD)_4}$, to achieve site- and stereoselective C–H functionalization at the most accessible primary, secondary, and tertiary non-activated C–H bonds, respectively. The reaction scope is ranging from alkanes, alkyl halides, alkyl ester, protected alcohols, alkyl silanes to natural products, including steroids, vitamin and phytol derivatives. These three catalysts demonstrated strong catalyst control capability to recognize the target C–H bonds to achieve extremely high site-, diastereo- and enantioselectivity.

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Acknowledgement

Aug. 1st, 2013, my flight landed at the Hartsfield-Jackson Atlanta International Airport, from then I was turning the page to begin a new chapter in my life. At that time, I wasn't clear whether I can make the chapter a better one or not. However, as time goes by, especially at this moment, I believe I have made some progresses during my stay here.

Looking back, there are many people I want to say, "thank you".

The first person I should thank during my stay is Dr. Davies. He has been a well-respected mentor and a beloved friend. He taught me how to master organic chemistry knowledge, identify interesting problem, and develop critical thinking and problem-solving skill. Moreover, he trained me to be a meticulous person which has been the secret of success in my research. He isn't only care about my research, but also care about my life. He shared his wisdom and experience with me quite often, and he was always there to help me whenever I need help.

Along the way to pursue my degree, there are three important professors that have provided invaluable help, who are Dr. Lanny Liebeskind, Dr. Simon Blakey and Dr. Chris Scarborough. I sincerely appreciate their support and guidance in terms of research development and personal growth.

In the last four years, my knowledge and skill have been significantly improved, this is because I learned very hard with the help and guidance from the professors as well as the senior members in the lab. Those include former graduate students Dr. David M. Guptill and Dr. Liangbing Fu, former post-doctoral members Dr. Jeffrey Mighion and Dr. Sandeep Raikar, and the informal post-doctoral member Dr. Daniel Morton.

The achievement I made here is not a sole contribution from me, it is a team work. Therefore, I want to take this opportunity to thank all my collaborators. Catalysts are the key for the success of my study, so the catalyst structure and mechanism study are very important to further develop the research. Dr. Jamal Musaev at Emory University, Dr. Ken Houk and his co-workers, including Dr. Yun-Fang Yang, Ms. Yingzi Li, and Mr. Jacob Sanders, from UCLA, and Dr. Slav Boyarskikh as a former Davies group member have helped to provide a lot of inside about the catalyst structure and reaction mechanism. The X-Ray Crystallography Center member Dr. John Bacsa and Mr. Tom Pickle have provided a lot of help in obtaining the single X-Ray crystal structures of multiple important catalysts. In the study of predictive modelling, Dr. Matt Sigman and Mr. Zach Niemeyer from Utah, and Ms. Wenbin Liu, a current Davies group member, have contributed substantially and made the collaboration successfully. On the way to explore the potential application of the methodologies we developed, I had a great time when I collaborated with Dr. Brian Stoltz, Ms. Elizabeth Goldstein and Mr. Austin Wright from Caltech to explore the total synthesis of Cylindrocyclophanes. To access the non-specific C-H bonds, we worked with the Abbvie scientists to establish a catalyst library that provided me an opportunity to spend a summer at Abbvie which has been a wonderful experience and eventually helped me to work there as a senior scientist I. There are many people I want to thank during my visit at Abbvie, especially Dr. Ying Wang, Dr. Eric Voight, Dr. Mark A Matulenko, Ana Aguirre, Dr. Thaddeus Franczyk II, Dr. Elizabeth Swift, Dr. Vincent Chan, Dr. Michael G Fickes, Dr. Brian J Kotecki, and Alex Nett.

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Most importantly, I want to thank my family. My mom and dad have been very open-mind, patient and supportive parents. I was a troublemaker when I was a kid, I can’t imagine how challenging it has been to raise me. They always gave me the chance to realize and correct my small mistakes but never allow me to have any excuse for making fundamental mistakes. This has provided enough freedom for me to explore various possibilities and develop my life that I enjoy. At the same time, I learned to be independent and take responsibilities. I consider my PhD study is quite successful, behind the success, there is an important woman, who is my wife, Suyuan. Suyuan has been a very patient and supportive soul mate, she is my best friend and my partner. We worked together to overcome all the challenges we encountered, we enjoyed the good time together, and, most amazingly, we are currently cultivating our share interest together!

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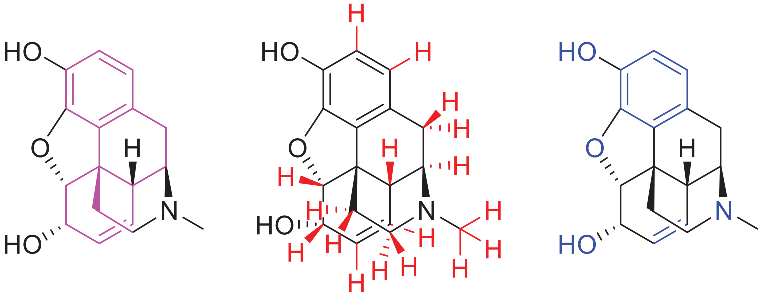
Chapter 1 Introduction

1. C–H Functionalization

Organic compounds consist of C–C bonds, C–H bonds and functional groups. For example, a common organic compound, morphine, is constructed of 18 C–C bonds (marked in pink), 17 C–H bonds (marked in red), and 6 functional groups (marked in blue) (Figure 1.1.1). The standard strategy of organic synthesis relies on developing the most effective way for modification of the functional groups, so that the desired synthetic target is rapidly obtained. However, conducting selective transformations on the ubiquitous C–H bonds was generally not considered to be a viable approach. Recently, it has been recognized and demonstrated that if the C–H bond modification can be controlled and utilized, the logic of organic synthesis will be fundamentally revolutionized.[1-5]



C–C Bond **18**

C–H Bond **17**

Functional Group **6**

Morphine
1.1.1

Figure 1.1.1 Number of C–C bonds, C–H bonds, and functional groups in Morphine

The main reason for the oversight of the importance of C–H bonds in standard organic synthesis was because of the difficulties in developing reagents that are sufficiently reactive to break a C–H bond but still capable of distinguishing among the different C–H bonds. The bond dissociation energy of C–H bonds is relatively high but there are some differences depending on the nature of C–H bonds, as shown for some typical examples in Figure 1.1.2[6]. As can be seen in the first four entries, there is a steady decrease in bond strength going from methyl, primary, secondary and tertiary C–H bonds. The hybridization of the C–H bond plays an important role as sp^2 and sp hybridized C–H bonds are stronger than sp^3 hybridized bonds (entries 5-7). Allylic, benzylic and C–H bonds adjacent to heteroatoms tend to be weaker (entries 8-10) because the resulting radical is resonance stabilized.

entry	bond	bond-dissociation energy at 298 K (kcal/mol)	 (kJ/mol)
1	H_3C–H	105	439
2	C_2H_5–H	101	423
3	$(CH_3)_2CH$–H	98.6	-
4	$(CH_3)_3C$–H	96.5	404
5	CH_2CH–H	111	464
6	C_6H_5–H	113	473
7	HC_2–H	133	556
8	CH_2CHCH_2–H	89	372
9	$C_6H_5CH_2$–H	90	377
10	H–CH_2OH	96.1	385.3

Figure 1.1.2 Bond-dissociation energy of common C–H bonds

The potential of C–H bond modification was recognized in the late 1950s, and "C–H activation" evolved to be a hot topic in organic chemistry.[7] One key example regarding the use of Hofmann–Löffler–Freytag (HLF) reaction for the synthesis of dihydroconessine (**1.1.2**) was reported by Corey (Buchschacher also reported a similar work almost at the same time), the HLF reaction proceeded via an intramolecular C–H halogenation which was essentially a formal C–H amination sequence (Figure 1.1.3, A).[8-9] The first task was the exploration of the appropriate reagents that are reactive enough to break C–H bond without destroying the molecular framework, and the most notable achievement was the utilization of organometallic reagents to assist the bond breaking process. For example, in 1967, the palladium catalyzed C–H alkenylation of benzene with styrene was reported by Moritani and Fujiwara[10] (Figure 1.1.3, B) which was a key foundation to develop the commonly used palladium-catalyzed arene coupling reactions. In 1974, the copper catalyzed carbenoid insertion of cyclohexane reported by Scott[11] (Figure 1.1.3, C) represented a breakthrough in C–H insertion because cyclohexane was commonly regarded as inert and employed as solvent for carbenoid reactions[12-14].

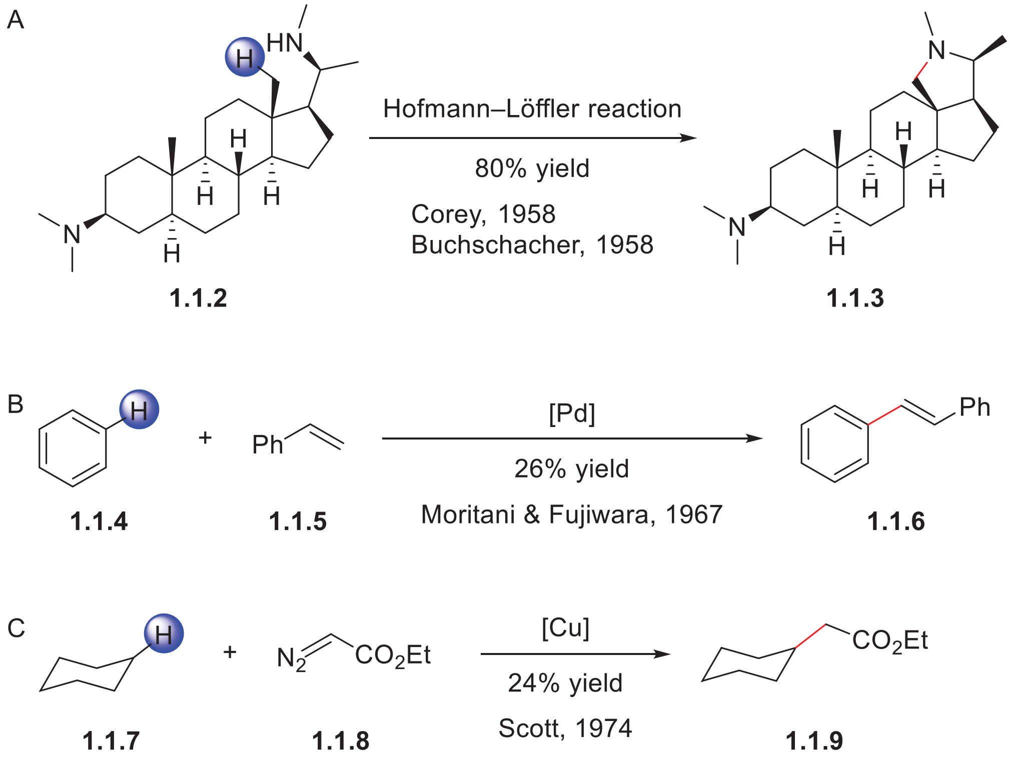


Figure 1.1.3 Early examples of C–H activation

In general, C–H bonds are inert toward direct reaction with common reagents, so an alternative strategy will be needed to transform a C–H bond to a functional group. C–H activation was used to describe metal insertion into the C–H bond with the formation of M-C bond (**1.1.11**). The M-C bond of the newly generated organometallic species (**1.1.11**) is more reactive than the C–H bond of the original compound (**1.1.10**) so it can react with the reagent to form a new compound with an additional functional group (**1.1.12**). The whole process is also known as C–H functionalization.

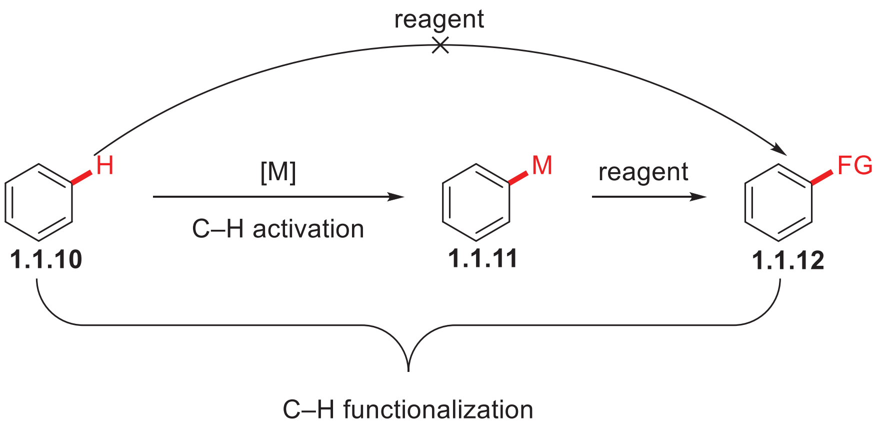
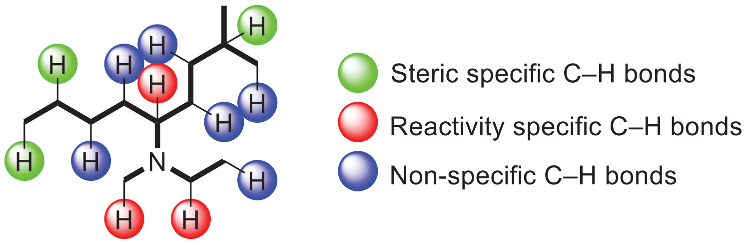


Figure 1.1.4 C–H activation versus C–H functionalization

2. Grand Challenge of C–H Functionalization

Even though considerable progress has been achieved to transform C–H bonds to other useful molecular frameworks, [1-5, 7] the key challenge still exists, which is how to differentiate one C–H bond from the other C–H bonds with similar steric and electronic characteristics. For example, the following hypothetical molecule (**1.2.1**) has 18 different types of C–H bonds, including the steric specific C–H bonds (marked in green), reactivity specific C–H bonds (marked in red), and non-specific C–H bonds (marked in blue). From the standard organic chemistry point of view, it will be fundamentally challenging to precisely functionalize one C–H bond without modifying the rest of them (Figure 1.2.1).



1.2.1

Figure 1.2.1 Grand challenges of C–H functionalization

Over the years, substrate control was developed to tackle the selectivity issue, which is designed to selectively modify the reactivity and/or distance specific C–H bonds. In the early stages, the selectivity was achieved by the careful selection of molecules with reactivity specific C–H bonds. For example, selective functionalization of C–H bonds alpha to nitrogen, oxygen, or pi-bonds can be achieved because those C–H bonds are activated by the functional group so that they are far more reactive than other non-activated C–H bonds. [15-22] Figure 1.2.2-A illustrates a powerful reaction to synthesize *threo*-Methylphenidate (**1.2.4**) from Boc-pyrrolidine (**1.2.2**) through a selective carbene insertion of the C–H bond alpha to nitrogen.[23] The site-selectivity mainly relied on the reactivity preference of the target C–H bond, but the diastereoselectivity and enantioselectivity were caused by the synergistic effects between the catalyst, the carbene and the substrate. The selective C–H arylation reaction shown in Figure 1.2.2-B also uses the same strategy to achieve selectivity by choosing substrates with activated C–H bond, the allylic C–H bond (**1.2.5**).[24]

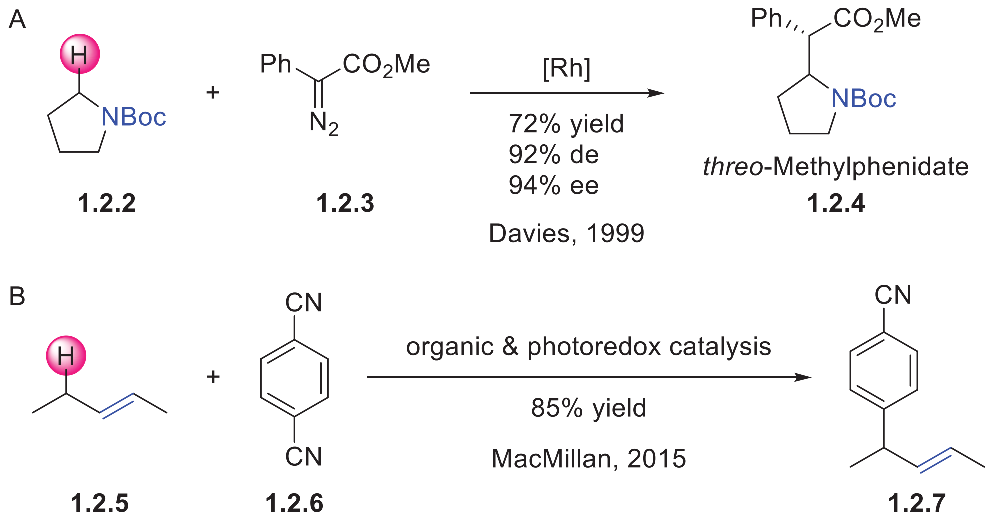


Figure 1.2.2 Selective functionalization of reactivity specific C–H bonds

Another powerful strategy to achieve selectivity at the distance specific C–H bonds relies on the generation of cyclic intermediate or product, which includes intramolecular reactions and the directing group strategies. The use of intramolecular reactions is a standard strategy to functionalize the distance specific C–H bond with the formation of five- or six-membered ring product.[25-29] As shown in Figure 1.2.3-A, a rhodium catalyzed intramolecular carbene insertion of alkyl 2-diazoacetate (**1.2.8**) with the formation of a β-lactone (five-membered ring) product (**1.2.9**) in high selectivity and yield is described.[26] Another example shown in Figure 1.2.3-B is a rhodium-catalyzed intramolecular C–H amination of alkyl sulfamate (**1.2.10**) at the tertiary position of the alkyl chain to form a six membered ring intermediate (**1.2.11**), which can be easily converted N-CBz-(*R*)-β-isoleucine (**1.2.12**) in two steps.[29]

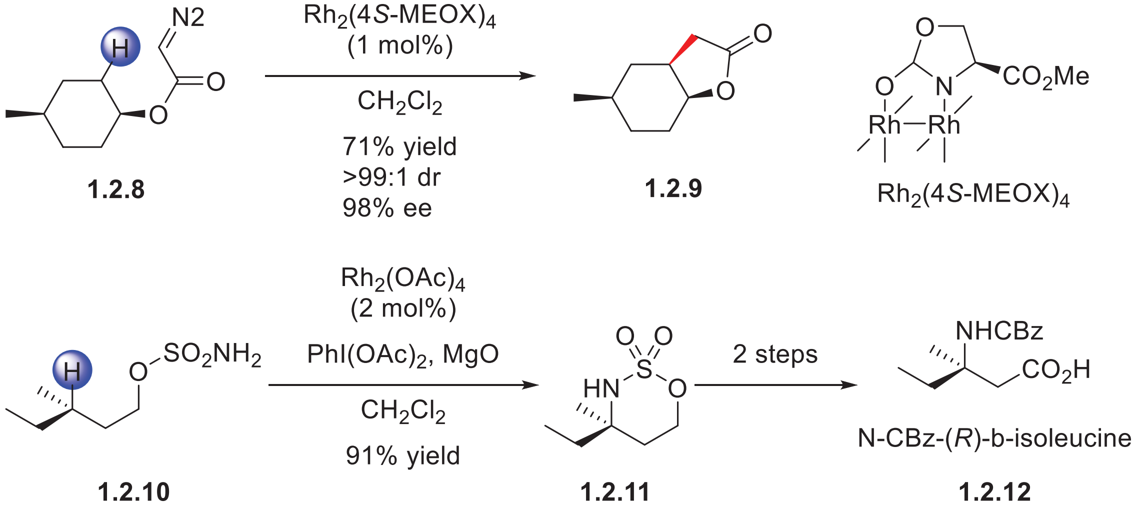


Figure 1.2.3 Selective functionalization of distance specific C–H bonds through intramolecular reaction

Functionalizing the distance specific C–H bond by formation of a metallocyclic intermediate followed by downstream reactions to generate the desired products is well-known as the directing group strategy. This strategy has drawn considerable attention and has been developed into the major strategy to achieve selective C–H functionalization.[30-33] In general, the directing group is pre-installed to guide the catalyst to functionalize the distance specific C–H bond. The early example of Pd-catalyzed ligand-directed sp^2 C–H bond oxygenation used PhI(OAc)$_2$ as oxidant and Pd(OAc)$_2$ as catalyst was reported by Sanford.[34] They demonstrated that a variety of pyridine derivatives served as excellent directing groups to produce *ortho*-acetoxylated products in yields ranging from 54% to 88%. The reaction shown in Figure 1.2.4-A is an interesting example with the formation of a bis acetoxylated product (**1.2.14**) in 78% yield. Inspired by this work, other nitrogen-based directing groups were also explored, including imines, oxime ethers, azobenzene derivatives, and nitrogen heterocycles, and even amides with relatively basic oxygen atoms were shown to be good directing groups.[30, 35-36] A carboxylic acid-derived *N*-methoxy amide directing group was reported by Yu. [37] It also serves as an anionic ligand that localized the reactive PdX$_2$ (X=ArCONOMe) species near the target C–H bond, avoiding interference from any nitrogen or sulfur atoms present in the heterocyclic substrates, which has been a major limitation of directed C–H functionalization. As shown in Figure 1.2.14-B, the reaction could tolerate heteroatom containing substrates (**1.2.15**) to give the desired product (**1.2.16**) in 82% yield. Another type of directed C–H functionalization reported by Hartwig showed a new direction for the development of directing group strategy, using dihydridosilanes to direct the site-selective C–H functionalization of primary C–H bonds. As shown in Figure 1.2.4-C, the (hydrido)silyl ether (**1.2.17**) was formed by dehydrogenative coupling with the alcohol or by hydrosilylation of the ketone, and then the Si–H unit of the silyl ether undergoes iridium catalyzed dehydrogenative functionalization of a primary C–H bond to form a five-membered silyl ether product (**1.2.18**) in 99% yield.[38]

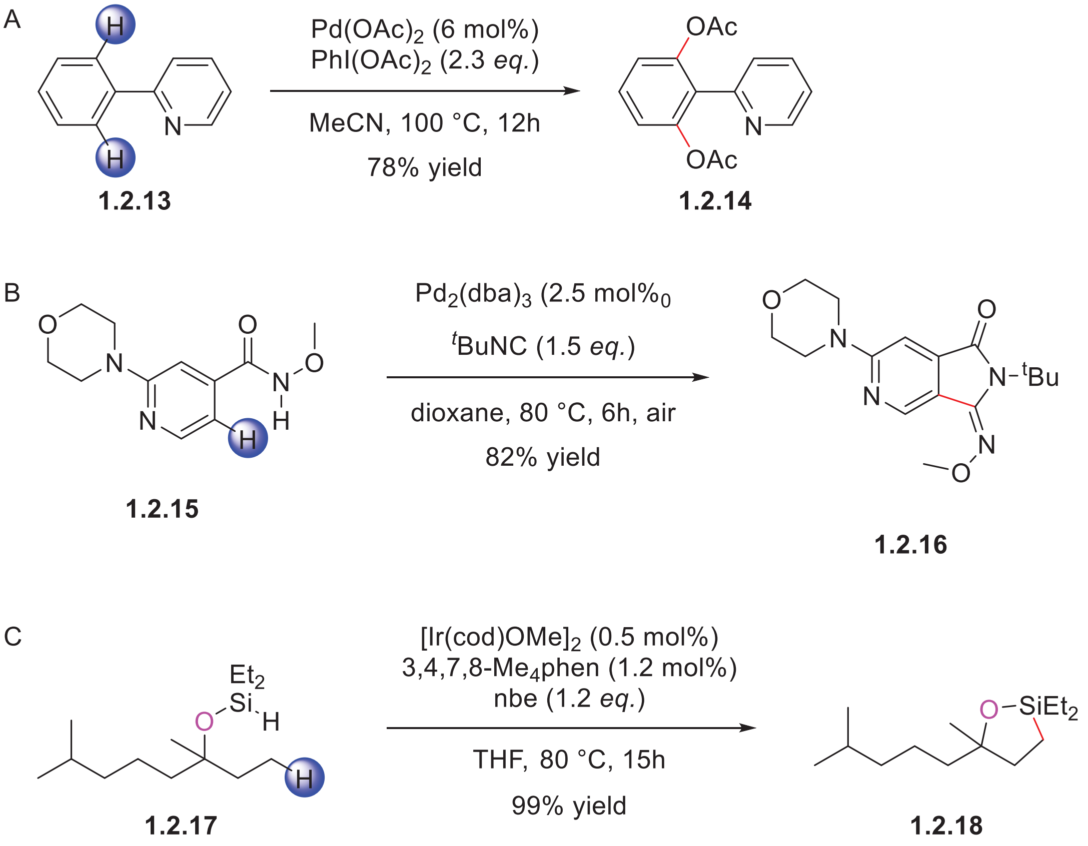


Figure 1.2.4 Selective functionalization of distance specific C–H bonds through directing group strategy

Obviously, the directing group strategy is very powerful in accessing the distance specific C–H bonds because, in an ideal situation, one directing group will functionalize the distance specific C–H bond despite of the changes of substrates. As shown in Figure 1.2.5-A, for the terminally substituted *n*-alkyl compounds, the functional group (FG) can be used to install directing groups. The directing group (DG_1) can always place the catalyst to be close to the *gamma* C–H bond even though the alkyl chains are changing. However, it becomes challenging to achieve selectivity at the steric specific C–H bonds because the directing group will need to be changed according to the changes of substrates. As shown in Figure 1.2.5-B, to achieve selectivity at the most accessible secondary position, DG1 is working for the *n*-butyl compounds because the *gamma* position is the most accessible secondary position. However, a series of new directing groups (DG2, DG3, …) will be needed to access the most accessible secondary position when the alkyl chains are extended. Therefore, the directing group strategy is not suitable to achieve selective functionalization at the steric specific C–H bonds.

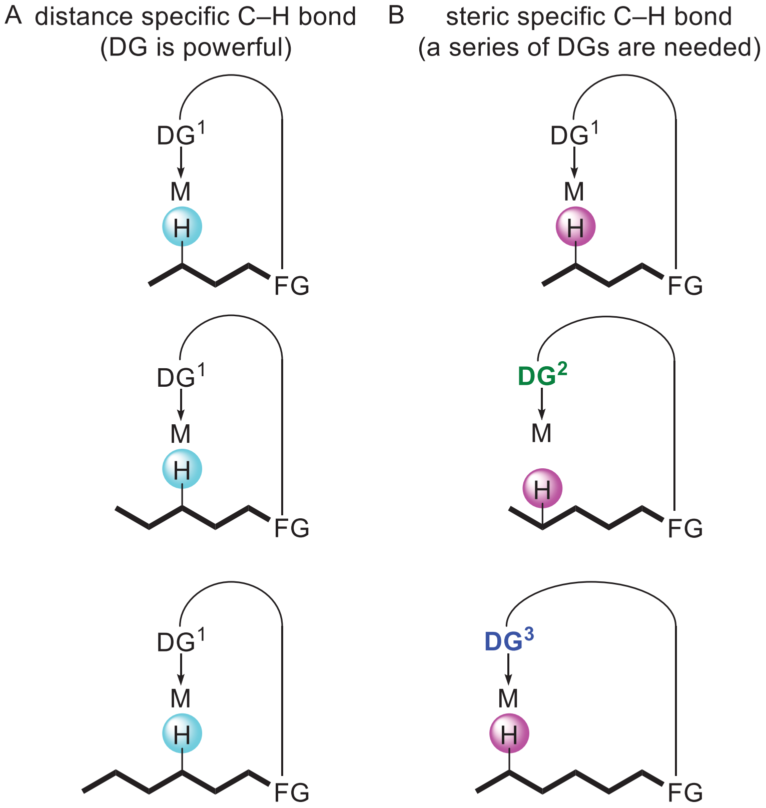


Figure 1.2.5 Advantage and disadvantage of directing group strategy

A more versatile but challenging approach would be catalyst control, where the catalyst can distinguish one C–H bond from others by recognizing the subtle steric and electronic differences. [39-41] This strategy is relatively underdeveloped due to the challenge of designing a series of sophisticated catalysts for each type of C–H bond, but the huge potential has drawn our attention and interest to develop a catalyst toolbox to control the selectivity.

Our group is interested in chiral dirhodium tetracarboxylate [$Rh_2(CO_2R)_4$] catalyzed donor/acceptor carbene induced C–H insertion, and our goal is to develop a catalyst toolbox to control the selectivity at will. Based on the analysis of the unique feature of target C–H bond, an appropriate catalyst will be selected/developed to control the reaction. As shown in Figure 1.2.6, in order to achieve selective functionalization at the most accessible secondary position, an appropriate chiral dirhodium tetracarboxylate ($R=R_1$) catalyst is selected to decompose the donor/acceptor diazo with the formation of a reactive rhodium carbene species, which can undergo a C–H insertion to generate the final product.

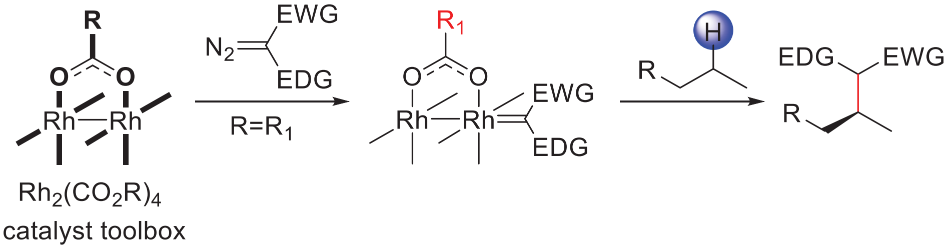
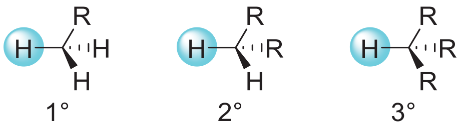


Figure 1.2.6 Catalyst toolbox for selective C–H functionalization

Therefore, detailed comparison and analysis of the nature of different types of C–H bonds are key to develop the catalyst control strategy. Although subtle, nearly every C–H bond is different; therefore, they can be potentially differentiated by enlarging their differences in the unique environments of appropriately designed catalysts. The C–H functionalization proceeds through a concerted but asynchronous process, in which positive charge build-up at carbon occurs in the transition state.[42] Therefore, from the electronic point of view, tertiary is the most reactive, but primary is the least (Figure 1.2.7). However, the carbene species can be sterically demanding so from the steric point of view, primary C–H bond is the most accessible to be preferred for the carbene to approach, but tertiary is the least (Figure 1.2.7). [43]



electronic: 1° < 2° < 3°

steric: 1° > 2° > 3°

Figure 1.2.7 Preference toward C–H functionalization

Therefore, it becomes possible for us to develop a dirhodium catalyst toolbox to control the functionalization at the steric specific C–H bond. As shown in figure 1.2.8, our initial goal is to develop catalyst 1, catalyst 2, and catalyst 3 to control selective functionalization of the most accessible primary (marked in green), secondary (marked in pink), and tertiary (marked in blue) C–H bonds, respectively.

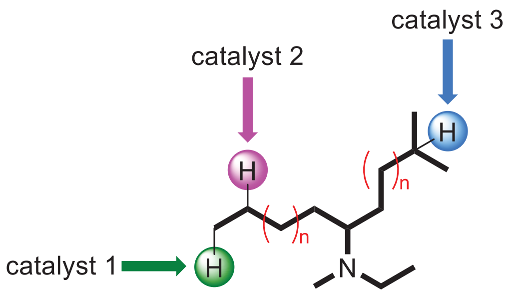


Figure 1.2.8 Concept of catalyst controlled C–H functionalization

Chapter 2 Catalyst Design and Synthesis

1. Catalyst Design Philosophy

The catalyst design philosophy was inspired by highly selective enzymatic catalysis, in which each enzyme pocket will allow only one specific substrate to fit. Therefore, a similar type of selective catalysis could also be viable if a series of sophisticated catalyst pockets can be designed to recognize the unique steric and electronic character of target C–H bonds. A general diagram illustrating this concept is shown in Figure 2.1.1. Assuming a situation in which the C–H functionalization is preferred at the weakest C–H bond electronically (tertiary C–H > secondary C–H > primary C–H), then it may be possible to control site selectivity by modifying the size of the catalysts. For catalyst 1 (marked in green), only primary C–H bond can fit the "*small*" pocket. For the "*medium*" pocket of catalyst 2 (marked in pink), tertiary C–H bond will be sterically blocked; and secondary C–H bond will be electronically preferred over primary C–H bond even though both primary and secondary C–H bond can fit. In terms of the "*large*" pocket of catalyst 3 (marked in blue), tertiary C–H bond will be electronically preferred although other C–H bonds can also fit.

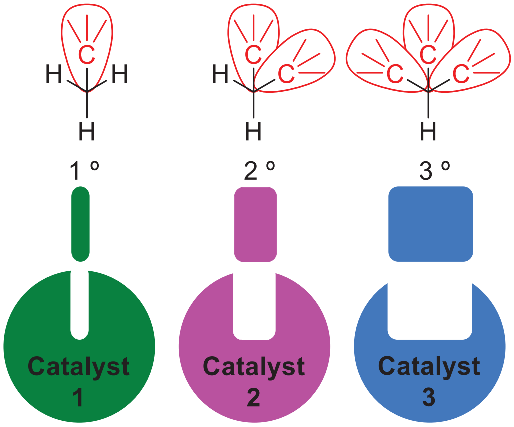


Figure 2.1.1 Catalyst design philosophy

This philosophy represents a simplified guide for catalyst design principles; however, a few critical challenges must be addressed. In terms of catalyst design, the pocket size concept can be used to control the site-selectivity, but the reaction will generate chiral center(s) which presents a further challenge to design chiral catalyst to control the stereoselectivity. In terms of primary and tertiary C–H bond functionalization (Figure 2.1.2-A), there will be a new chiral center generated. The strategy to obtain enantioselectivity will be relying on the chiral environment provided by catalyst structure. Based on the experimental data and computational study,[43-45] we hypothesized that four ligands will synergistically form a chiral pocket centered at each rhodium atom, and groups on each ligand will act as blocking groups (the green bars in Figure 2.1.2-A) to achieve enantioselectivity. Because the substrate will be blocked from approaching the carbene center from other directions (the front, rear, and right sides in Figure 2.1.2-A) but can only approach from the desired direction (the left side in Figure 2.1.2-A). In terms of secondary C–H bond functionalization (Figure 2.1.2-B), there will be two chiral centers generated when two groups attached to the methylene carbon are different. The requirement for the catalyst will further increased because not only the substrate will be forced to approach from one direction (the left side in Figure 2.1.2-B), but also only one C–H bond (marked in blue in Figure 2.1.2-B) of the diastereotopic C–H bonds (as in a chiral environment) at the methylene site will be allowed to approach the carbene center. To control the stereoselectivity, even though in some cases we can empirically predict the appropriate catalyst for the desired transformation, we still rely on catalyst screen strategy to determine and develop the optimum catalyst.[44, 46] So far, neither the pocket size model nor the stereo control model are well understood or developed, but the catalyst design philosophy has guided us to develop the desired catalyst toolbox to achieve selective functionalization at the most accessible primary, secondary and tertiary C–H bonds.

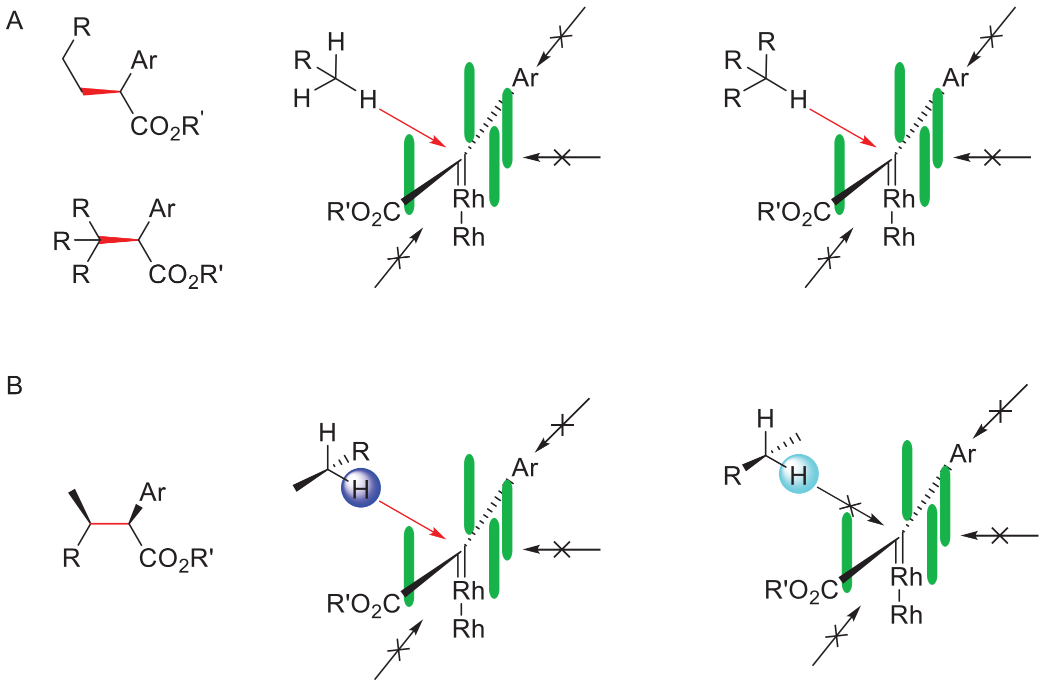
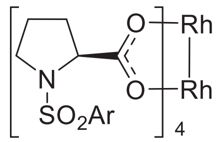


Figure 2.1.2 Proposed model for achieving stereoselective C–H functionalization

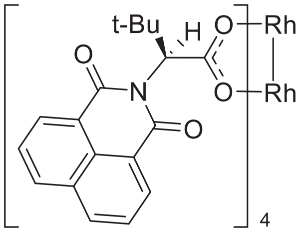
2. Catalyst Development

Chiral dirhodium(II) carboxylate complexes have been proven to be the most effective catalysts for metal-nitrene and metal-carbene induced reactions. The commonly used catalysts listed in Figure 2.2.1 have shown their great utility in C–H insertions,[43, 47] Si-H insertion,[48] tandem O-H insertion/[2,3] sigmatropic rearrangement,[49] cyclopropanation and cyclopropenation reactions,[50-53] aziridinations [54], ylide transformations,[55] and other transformations[45, 56-57]. The proline-derived catalyst, $Rh_2(DOSP)_4$ (**2.2.1**), was developopped in the 1990s and is well known for its application in asymmertic cyclopropanation and C–H insertion reactions, and it is still an important catalyst for asymmetric carbene-induced transformations.[23, 43, 52, 58-60] Another contemporary catalyst, $Rh_2(PTTL)_4$ (**2.2.5**), also played a key role in various types of metal-carbene reactions.[45, 61-63] It is derived from *tert*-leucine and has inspired the development of a collection of similar catalysts, including $Rh_2(NTTL)_4$ (**2.2.2**), $Rh_2(PTAD)_4$ (**2.2.6**), $Rh_2(PTV)_4$ (**2.2.7**), $Rh_2(TCPTTL)_4$ (**2.2.8**), and $Rh_2(TCPTAD)_4$ (**2.2.9**) which all bear a common phthalimide backbone.[63-71] Recently, the triarylcyclopropanecarboxylate catalysts have been reported by the Davies group to show great improvement in controlling the selectivity.[72-74] Rh_2(*p*-BrTPCP)$_4$ (**2.2.3**) and Rh_2(*p*-PhTPCP)$_4$ (**2.2.4**) were the first catalysts reported of this class and they were shown to be sterically very demanding. They were capable of controlling the site- and enantioselectivity of activated primary C–H bond functionalization but they showed poor control in reactions with non-activated C–H bonds.[75] Therefore, more effective catalysts needed to be developed.

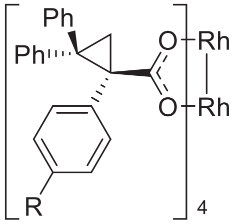


Ar = p-$C_{12}H_{25}C_6H_4$

Rh_2(*S*-DOSP)$_4$ (**2.2.1**)

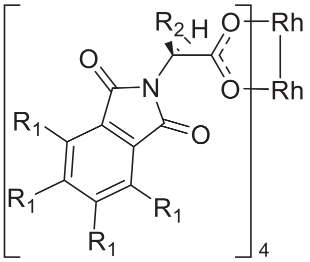


Rh_2(*S*-NTTL)$_4$ (**2.2.2**)



R=Br, Rh_2(*S*-*p*-BrTPCP)$_4$ (**2.2.3**)

R=Ph, Rh_2(*S*-*p*-PhTPCP)$_4$ (**2.2.4**)



R_1 = H, R_2 = ^{t}Bu	Rh_2(*S*-PTTL)$_4$ (**2.2.5**)
R_1 = H, R_2 = adamantyl	Rh_2(*S*-PTAD)$_4$ (**2.2.6**)
R_1 = H, R_2 = ^{i}Pr	Rh_2(*S*-PTV)$_4$ (**2.2.7**)
R_1 = Cl, R_2 = ^{t}Bu	Rh_2(*S*-TCPTTL)$_4$ (**2.2.8**)
R_1 = Cl, R_2 = adamantyl	Rh_2(*S*-TCPTAD)$_4$ (**2.2.9**)

Figure 2.2.1 Structures of commonly used chiral dirhodium(II) carboxylate catalysts

A central focus of this thesis is the development of a variety of new triarylcyclopropanecarboxylate catalysts with varied steric environments. In order to achieve this, a new approach was developed for the synthesis of a library of catalysts. In the next section the standard chiral catalyst synthesis will be described, followed by the new development that enabled a library of catalysts to be readily formed.

The standard method for the synthesis of chiral dirhodium tetracarboxylate catalysts is the ligand exchange reaction in which four of the chiral carboxylate ligands exchange with the ligands in $Rh_2(OAc)_4$ or $Na_4Rh_2(CO_3)_4$.[72, 76] The reactions involve relatively forcing conditions but have been applied for the synthesis of a variety of catalysts. For chiral catalysts, the chiral ligands are either derived from optically pure natural products or prepared by asymmetric synthesis. This approach has been used to generate a lot of useful and well-known catalysts, such as those catalysts listed in Figure 2.2.1. In general, systematic study and further catalyst structural modification are required to discover the optimal catalyst. However, this synthetic pathway has inherent limitations in structural diversification and accessibility. Figure 2.2.2 shows the standard procedure to synthesize the triarylcyclopropane-base catalysts and it was very effective to obtain Rh_2(*p*-BrTPCP)$_4$ and Rh_2(*p*-PhTPCP)$_4$.[72] However, during the development of this catalyst family, a series of limitations were also observed, including the availability of desired starting materials, the variable enantioselectivity of asymmetric reactions (such as the cyclopropanation shown in Figure 2.2.2-A, the enantioselectivity was poor with <5% ee), the bulky ligand exchange issue (such as the ligand exchange reaction shown in Figure 2.2.2-B, the reaction was failed giving lower than 1% yield when a bulky ligand was used), and most importantly, the necessary of multi-step synthesis, which will not be ideal for effective synthesis and screening.

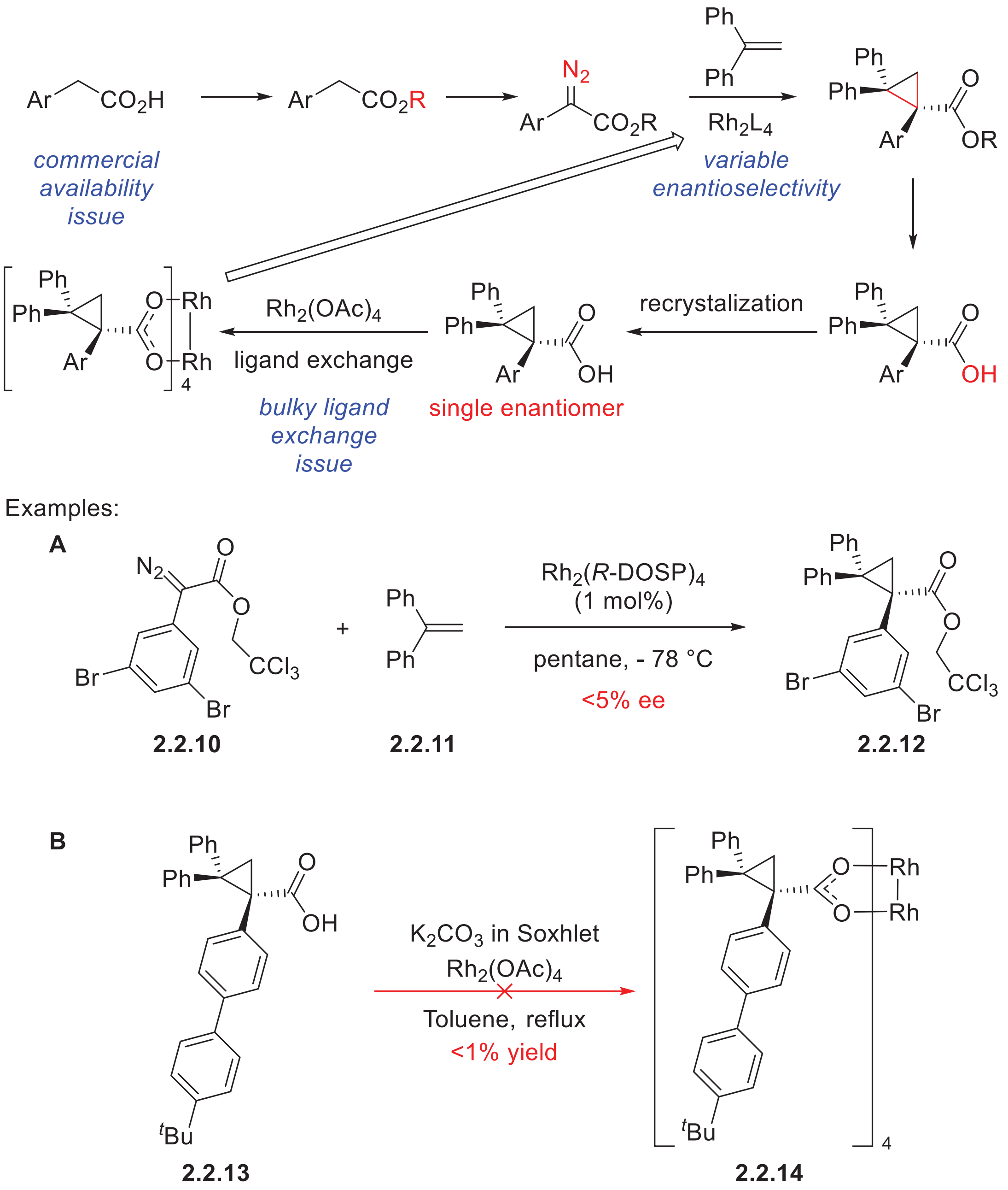


Figure 2.2.2 Standard route and inherent limitation for the synthesis of chiral dirhodium tetra-triarylcyclopropane carboxylate [Rh$_2$(*R*-TPCP)$_4$] catalysts

Due to the challenges of extending the triarylcyclopropane carboxylate catalysts to really bulky ligands, a new approach was developed. Relatively uncrowded bromo-substituted triarylcyclopropane carboxylate complexes were prepared using the conventional chemistry and these were then diversified by multifold Suzuki cross coupling reactions. This approach allowed the synthesis of a library of catalysts from a single brominated complex and introduce severe steric crowding that would not be possible using a preformed sterically hindered ligand.[75]

The synthetic strategy was first developed for the dirhodium catalyst Rh_2(3,5-diBrTPCP)$_4$ (**2.2.16**). As shown in Figure 2.2.3, it was synthesized through a rhodium catalyzed asymmetric cyclopropanation of 2,2,2-trichloroethyl 2-diazo-2-(3,5-dibromophenyl)acetate (**2.2.10**) with 1,1-diphenylethylene (**2.2.11**) to give the enantiopure triarylcyclopropane carboxylate ester (**2.2.12**) in 70% yield. Then 5 equivalent of zinc dust was used to deprotect the ester and then the desired ligand (**2.2.15**) was obtained in 99% yield.[75] The enantiopurity of the ligand was examined again before proceeding to the ligand exchange reactions. The ligand exchange reaction was conducted under standard conditions with dirhodium acetate in toluene under reflux, using a Soxhlet extractor containing potassium carbonate to remove the acetic acid and drive the reaction to completion. The reaction was monitored by TLC and the reaction was stopped when only one green spot was observed.

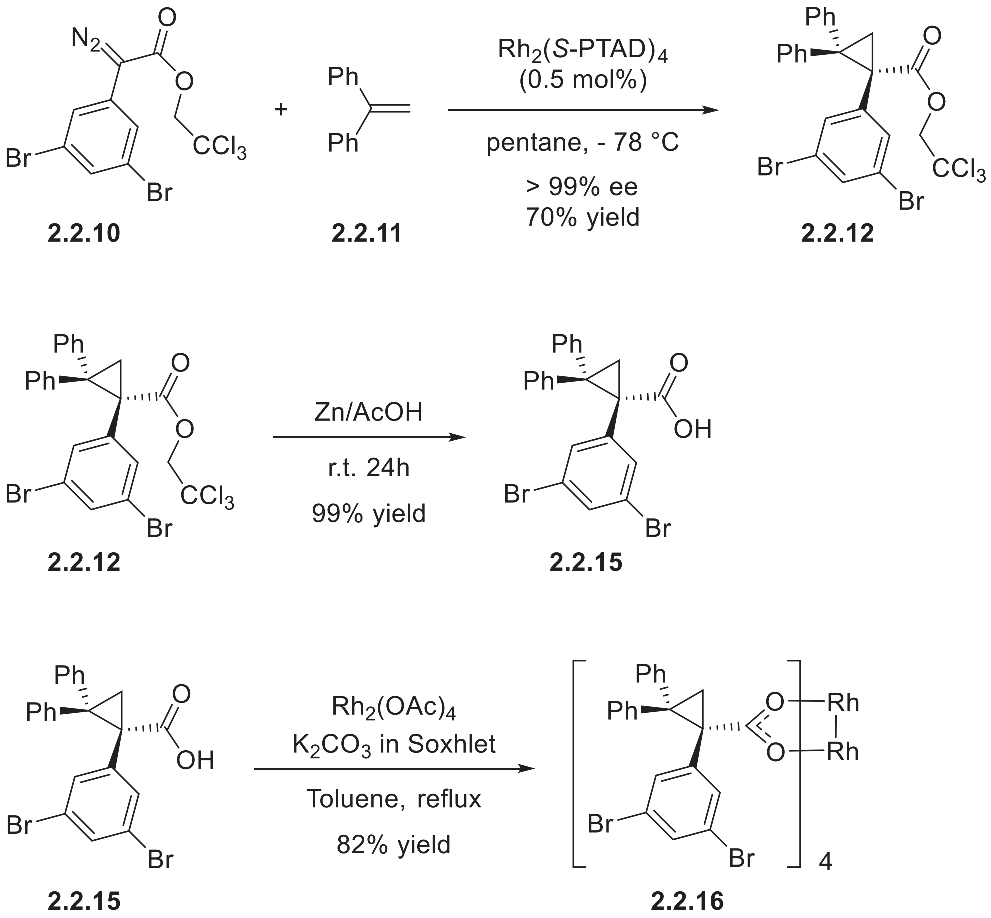


Figure 2.2.3 Synthesis of Rh_2(3,5-diBrTPCP)$_4$

The cyclopropanation to form 2.2.12 is highly enantioselective when Rh_2(S-PTAD)$_4$ is used as catalyst. When the reaction is carried out at -78 °C, only a single enantiomer of the cyclopropane (**2.2.12**) is observed by chiral HPLC. However, the reaction is capricious because at lower temperature, the catalyst has limited solubility, the system can easily condense moisture and the reaction can be slow and side reactions tend to compete with the cyclopropanation. Therefore, it is more practical to carry out the reaction at room temperature and under these conditions (**2.2.12**) is still formed in 99% ee but a tiny peak of the minor enantiomer is observed by HPLC. Further optimization studies revealed that that the crude material from the cyclopropanation reaction can be directly used in the deprotection reaction, and after the non-organic materials were removed by a silica plug, the crude material could be recrystallized to obtain enantiopure ligand (**2.2.15**) for the ligand exchange reaction. The reaction can be conducted using 50 mmol of diazo (**2.2.10**), and the overall yield to give the ligand (**2.2.15**) was 63% (Figure 2.2.4).

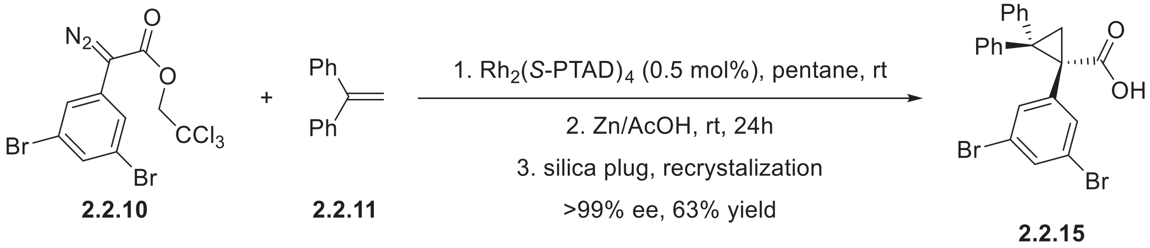


Figure 2.2.4 Synthesis of enantiopure ligand **2.2.15**

The catalyst, Rh$_2$[*tris(p*-Br)TPCP]$_4$ (**2.2.20**), was also synthesized through the same procedure (Figure 2.2.5). The cyclopropanation was conducted in pentane at 0 °C and the cyclopropane was deprotected to give the ligand (**2.2.19**) with >99% ee in 81% overall yield for the two steps. The ligand exchange reaction to form the catalyst (**2.2.20**) tends to be more difficult than that of Rh$_2$(3,5-diBrTPCP)$_4$ (**2.2.16**) because the ligand exchange does not go to completion. Therefore, careful column chromatography was needed to separate the desired product from the byproducts in 55% yield.

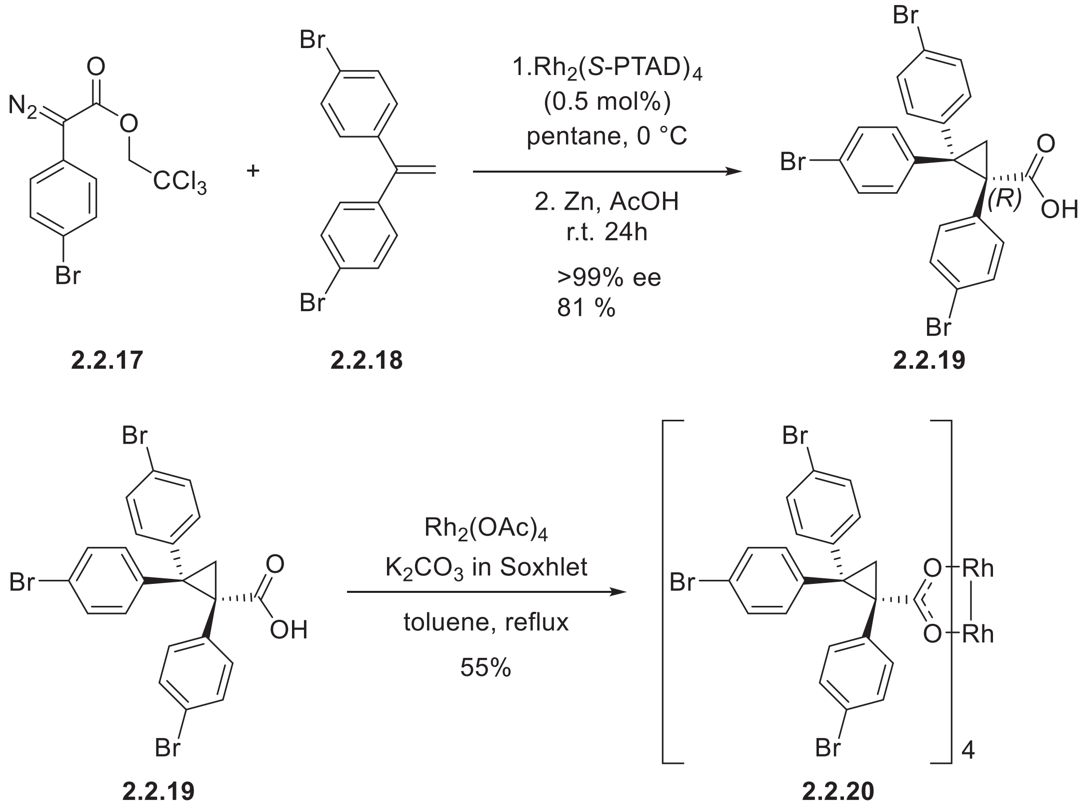
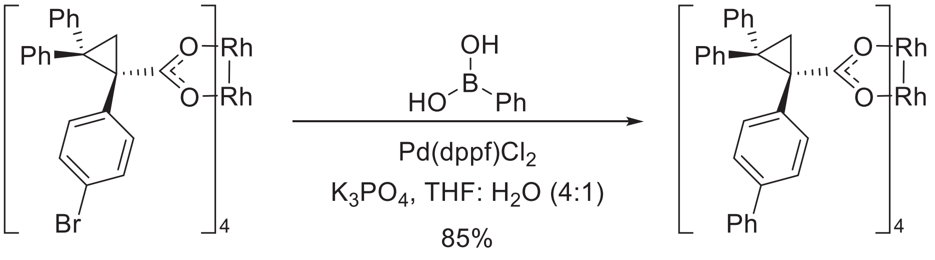


Figure 2.2.5 Synthesis of Rh$_2$[*tris(p*-Br)TPCP]$_4$

After the bromo-containing catalysts were obtained, palladium-catalyzed Suzuki coupling reaction was conducted directly on the dirhodium catalysts to see if it is a viable way to generate the catalyst library. The initial exploration was conducted in the synthesis of Rh$_2$(*p*-PhTPCP)$_4$ (**2.2.4**) from Rh$_2$(*p*-BrTPCP)$_4$ (**2.2.3**) with the classic condition of Pd(dppf)Cl$_2$ and potassium phosphate in THF/water solvent mixture (Figure 2.2.6).



2.2.3 **2.2.4**

Figure 2.2.6 Initial exploration of palladium-catalyzed Suzuki coupling reaction on dirhodium catalyst

The reaction was monitored by TLC, and only one green spot was observed after 12 h. However, the starting material and the desired product were known to be similar in terms of R_f value, and the compounds can also coordinate to other molecules which can change its R_f value. Therefore, the reaction solution was concentrated and passed through a silica plug with ethyl acetate to afford green solution, which was then concentrated and submitted for HRMS analysis. As shown in Figure 2.2.7, the peak correlated to the starting material (**2.2.3**, exact mass: 1769.9445) was not observed indicating that it was fully consumed; peaks correlating to the desired product (**2.2.4**, exact mass: 1762.4271) were observed in addition to a fragment with loss of one ligand (exact mass: 1373.2735) from it were observed.

Elemental composition search on mass 1762.43096

m/z= 1757.43096-1767.43096

m/z	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
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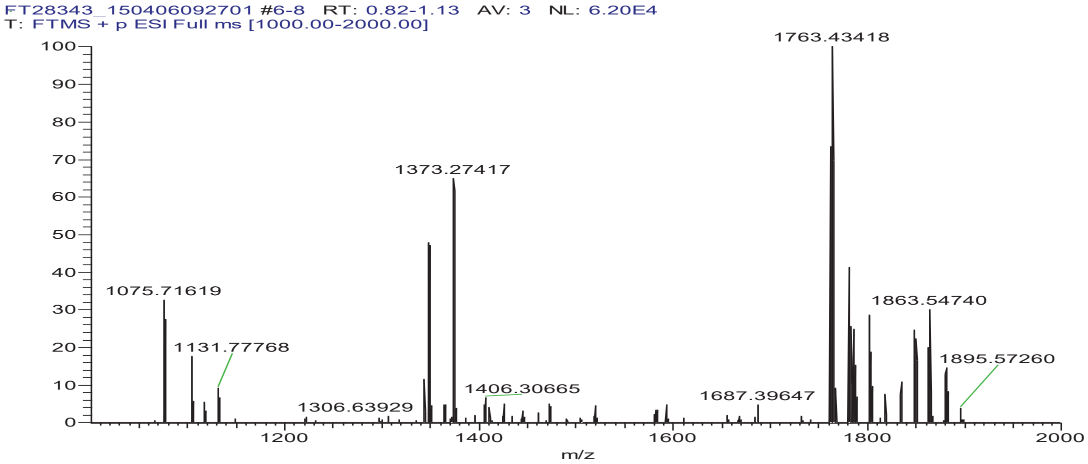
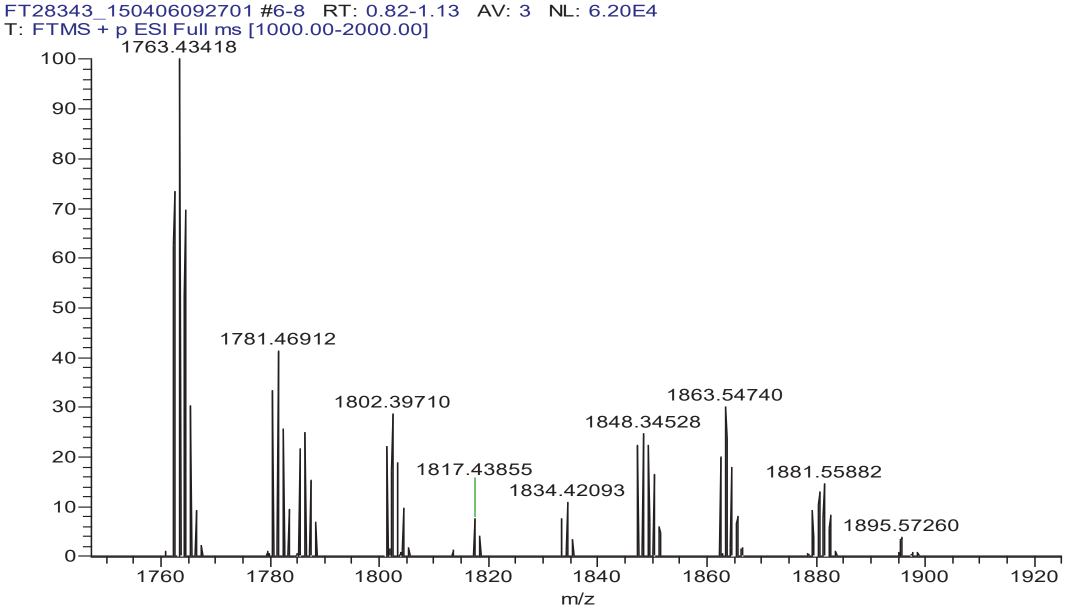
Elemental composition search on mass 1762.43096

m/z= 1757.43096-1767.43096

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1762.43096	1762.42708	2.20	73.0	$C_{112}H_{84}O_8Rh_2$





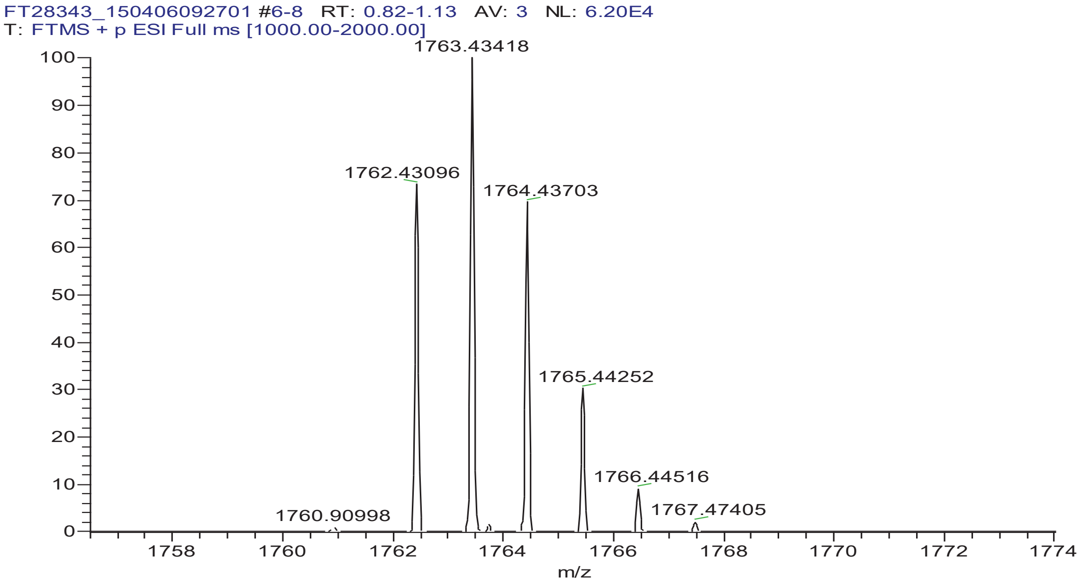
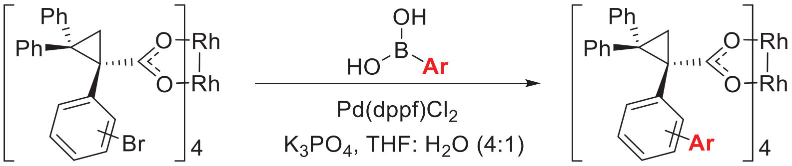


Figure 2.2.7 HRMS data of the crude material from the Suzuki coupling reaction

Since the first condition we tried was effective, we didn't explore other reaction conditions; instead, we quickly used the condition to explore the boronic acid scope in those three catalyst families, including Rh_2(*p*-ArTPCP)$_4$, Rh_2(3,5-diArTPCP)$_4$, and Rh_2[*tris(p*-Ar)TPCP]$_4$ catalysts (Figure 2.2.8). For the reaction with Rh_2(*p*-ArTPCP)$_4$, it involves four-fold cross coupling reaction, various aryl boronic acids were working effectively to give products in 44-96% yield (**2.2.14, 2.2.21**-**2.2.26**). In the case of Rh_2(3,5-diArTPCP)$_4$, the cross coupling becomes more complicated because it requires eight-fold cross coupling reactions to occur, but the reactions still gave 60-96% yield (**2.2.27**-**2.2.33**). Even for the reaction with Rh_2[*tris(p*-Ar)TPCP]$_4$ which involves twelve-fold cross coupling reactions, the reaction can still provide synthetically useful yields ranging from 47 to 70% (**2.2.34**-**2.2.37**). So far, three catalyst libraries have been effectively established from three corresponding preformed bromo-containing dirhodium catalyst through a four-, eight- or twelve-fold palladium-catalyzed Suzuki coupling reaction.[75] Confirmation that the Suzuki coupling had gone fully to completion was obtained from the HRMS data of the catalysts.



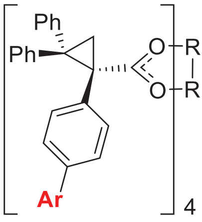
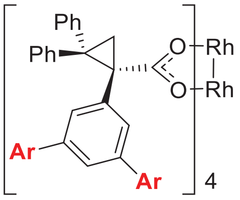
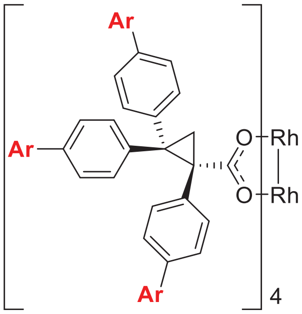
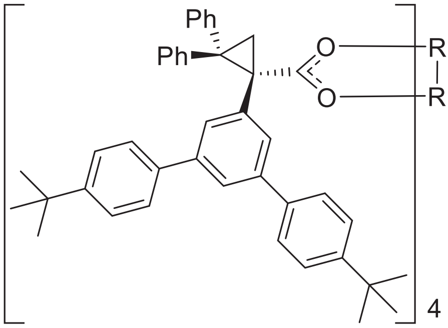
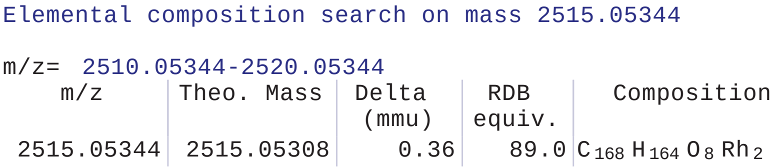
catalyst	Ar	Rh$_2$L$_4$	yield/%
	*p*-^{t}BuC$_6$H$_4$	Rh$_2$(*R*-*p*-^{t}BuC$_6$H$_4$TPCP)$_4$ (**2.2.14**)	85
	p-PhC$_6$H$_4$	Rh$_2$(*R*-*p*-PhC$_6$H$_4$TPCP)$_4$ (**2.2.21**)	44
	p-^{t}BuC$_6$H$_4$C$_6$H$_4$	Rh$_2$(*R*-*p*-^{t}BuC$_6$H$_4$C$_6$H$_4$TPCP)$_4$ (**2.2.22**)	50
	o-CH$_3$C$_6$H$_4$	Rh$_2$(*R*-*o*-CH$_3$C$_6$H$_4$TPCP)$_4$ (**2.2.23**)	96
	2,6-diCH$_3$C$_6$H$_3$	Rh$_2$(*R*-2,6-diCH$_3$C$_6$H$_3$TPCP)$_4$ (**2.2.24**)	69
	2,4,6-triCH$_3$C$_6$H$_2$	Rh$_2$(*R*-2,4,6-triCH$_3$C$_6$H$_2$TPCP)$_4$ (**2.2.25**)	72
	2,4,6-tri(^{i}Pr)C$_6$H$_2$	Rh$_2$[*R*-2,4,6-tri(^{i}Pr)C$_6$H$_2$TPCP]$_4$ (**2.2.26**)	-
	Ph	Rh$_2$(*R*-*3,5*-diPhTPCP)$_4$ (**2.2.27**)	96
	3,5-diCF$_3$C$_6$H$_3$	Rh$_2$[*R*-*3,5*-di(3,5-diCF$_3$C$_6$H$_3$)TPCP]$_4$ (**2.2.28**)	60
	3,5-diCH$_3$C$_6$H$_3$	Rh$_2$[*R*-*3,5*-di(3,5-diCH$_3$C$_6$H$_3$)TPCP]$_4$ (**2.2.29**)	66
	3,5-diPhC$_6$H$_3$	Rh$_2$[*R*-*3,5*-di(3,5-diPhC$_6$H$_3$)TPCP]$_4$ (**2.2.30**)	75
	p-PhC$_6$H$_4$	Rh$_2$[*R*-*3,5*-di(*p*-PhC$_6$H$_4$)TPCP]$_4$ (**2.2.31**)	82
	p-CF$_3$C$_6$H$_4$	Rh$_2$[*R*-*3,5*-di(*p*-CF$_3$C$_6$H$_4$)TPCP]$_4$ (**2.2.32**)	86
	p-^{t}BuC$_6$H$_4$	Rh$_2$[*R*-*3,5*-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$ (**2.2.33**)	81
	Ph	Rh$_2$[*R*-tris(*p*-Ph)TPCP]$_4$ (**2.2.34**)	50
	p-^{t}BuC$_6$H$_4$	Rh$_2$[*R*-tris(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$ (**2.2.35**)	53
	p-PhC$_6$H$_4$	Rh$_2$[*R*-tris(*p*-PhC$_6$H$_4$)TPCP]$_4$ (**2.2.36**)	70
	p-^{t}BuC$_6$H$_4$C$_6$H$_4$	Rh$_2$[*R*-tris(*p*-^{t}BuC$_6$H$_4$C$_6$H$_4$)TPCP]$_4$ (**2.2.37**)	47

Figure 2.2.8 Library synthesis of three catalyst families

The HRMS data of all the catalysts has been included in the supporting information. The HRMS data for the key catalysts, Rh_2[*R*-3,5-di(*p*-^{t}Bu)C_6H_4TPCP]$_4$ (**2.2.32**) and Rh_2[*R-tris(p*-^{t}BuC_6H_4)TPCP]$_4$ (2.2.34), will be discussed in this thesis are shown in Figure 2.2.9 and 2.2.10. The results clearly demonstrate that the eight-fold and twelve-fold crossing coupling reactions went to completion and generated the desired products.





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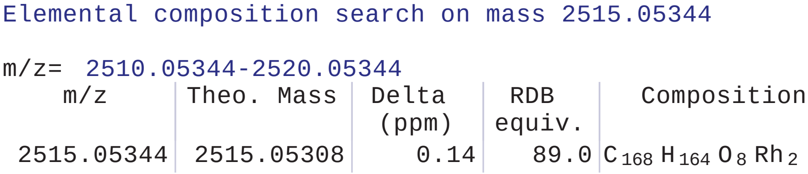

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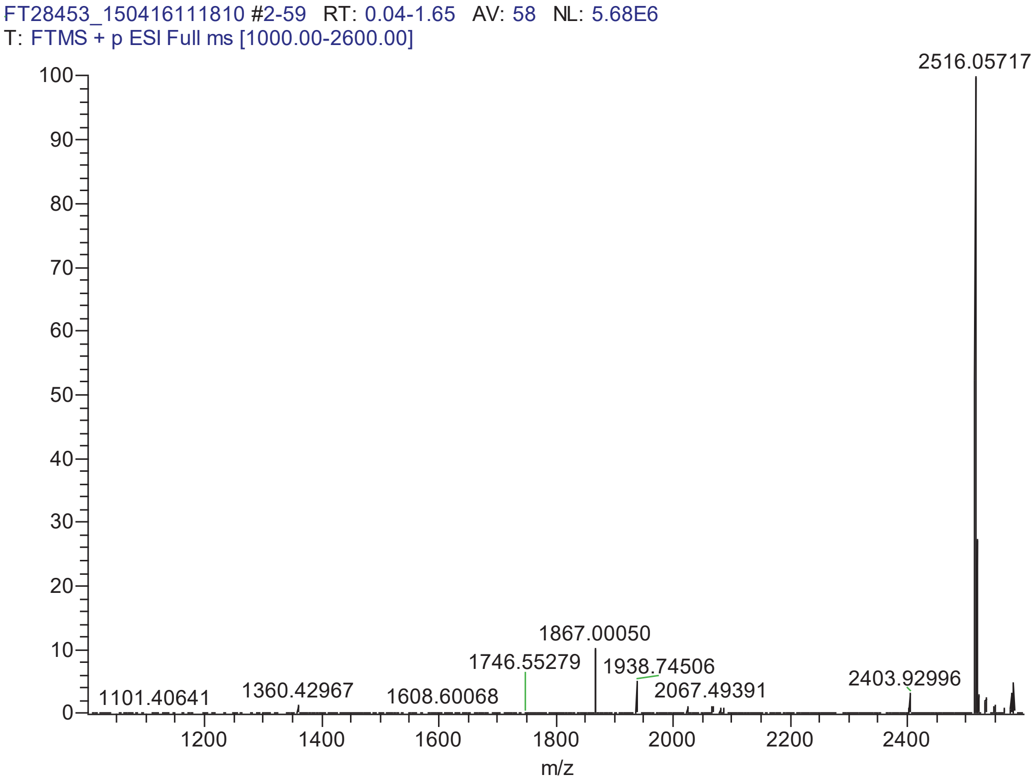
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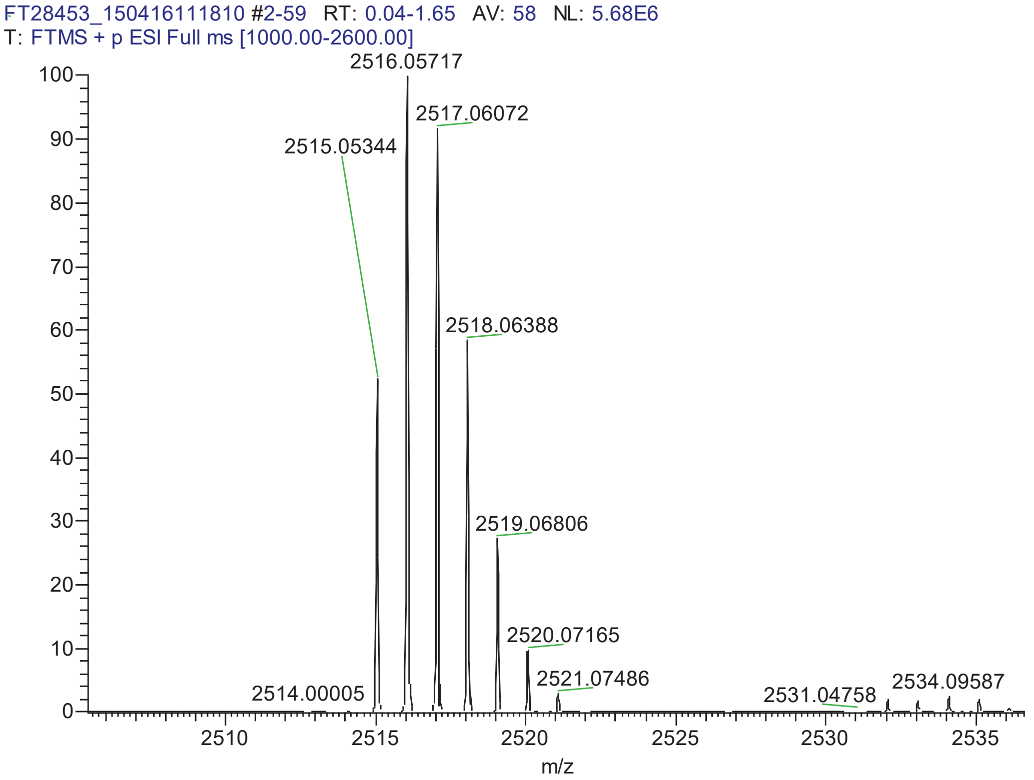
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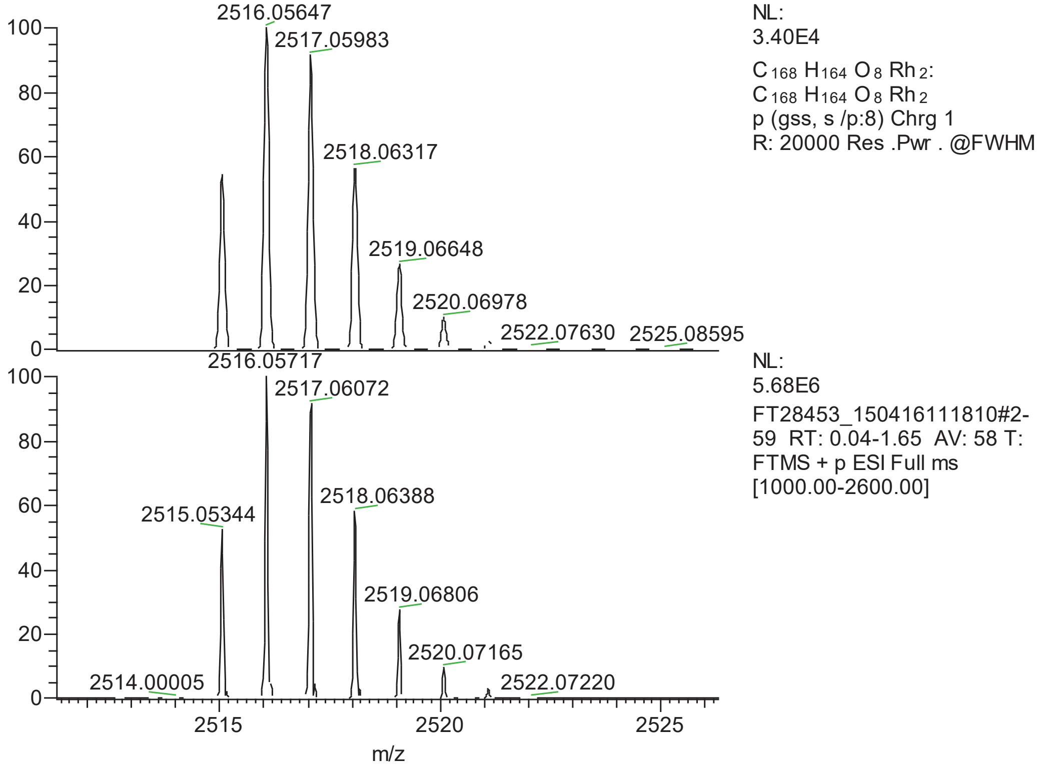
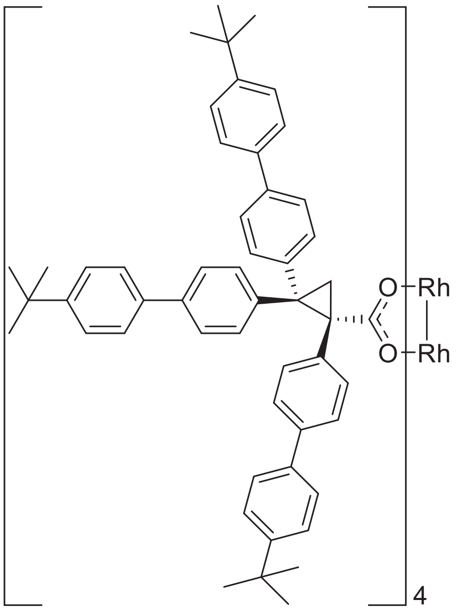


Figure 2.2.9 HRMS data for Rh_2[*R*-3,5-di(*p*-^{t}Bu)C_6H_4TPCP]$_4$ (**2.2.32**)



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Elemental composition search on mass 3043.42029

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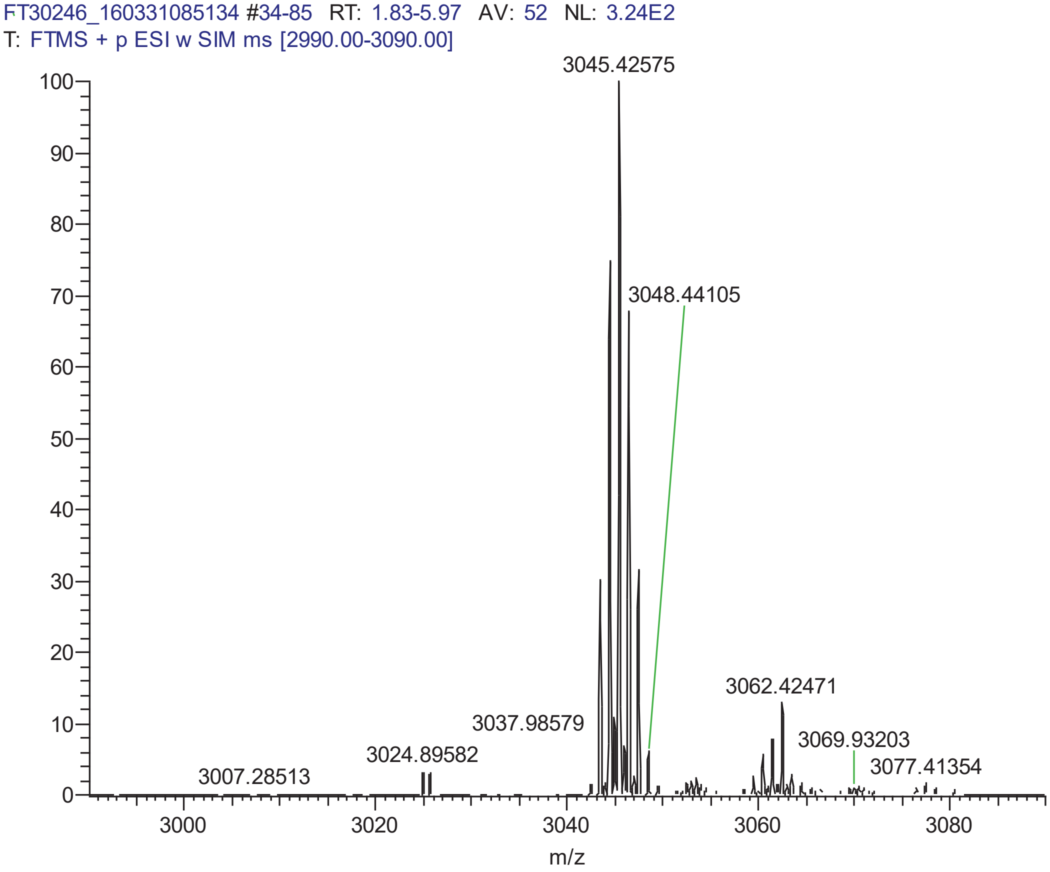

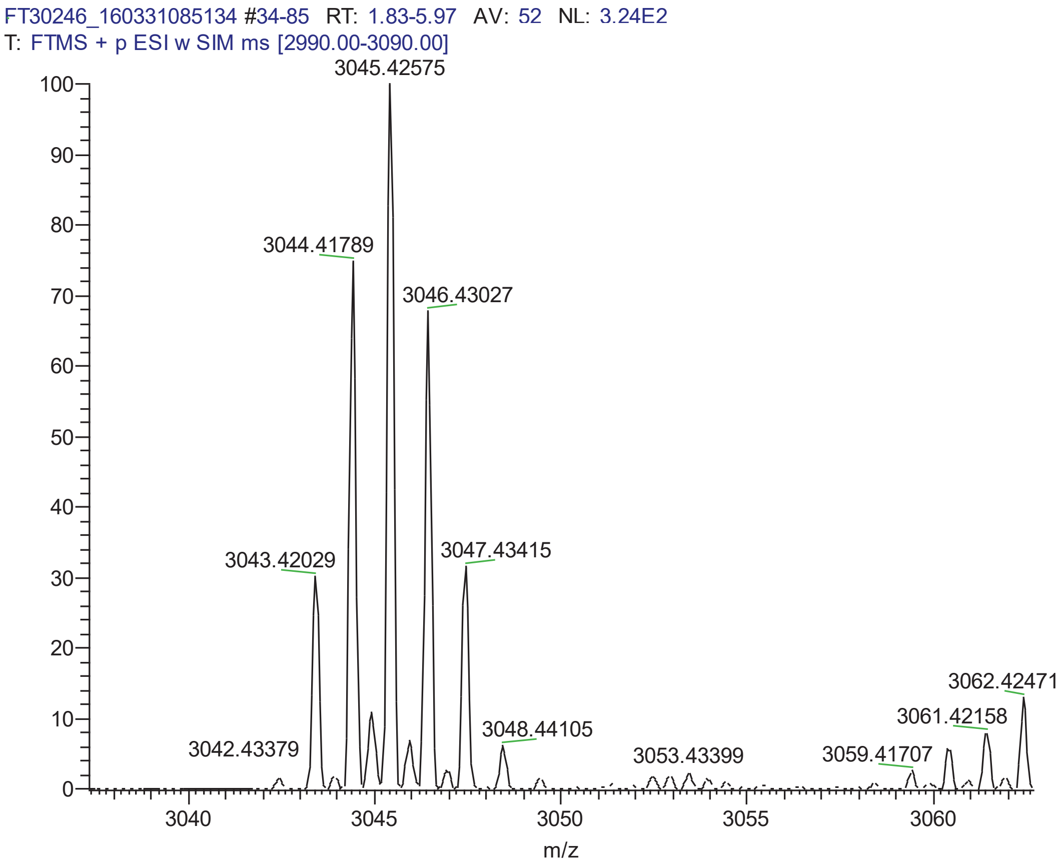
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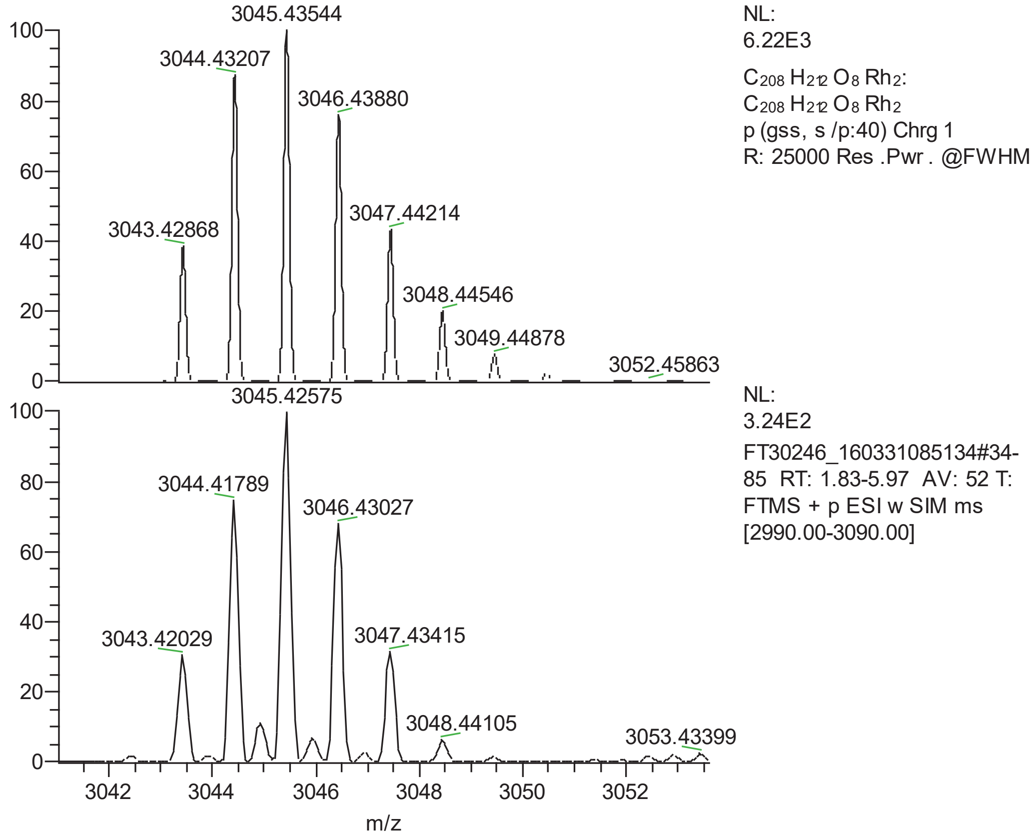

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    m/z     | Theo. Mass | Delta  |  RDB   |   Composition
            |            | (mmu)  | equiv. |
 1521.71407 | 1521.71407 |   0.00 |  105.0 | C 208 H 212 O 8 Rh 2
```

Elemental composition search on mass 1521.71407

m/z= 1516.71407-1526.71407

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
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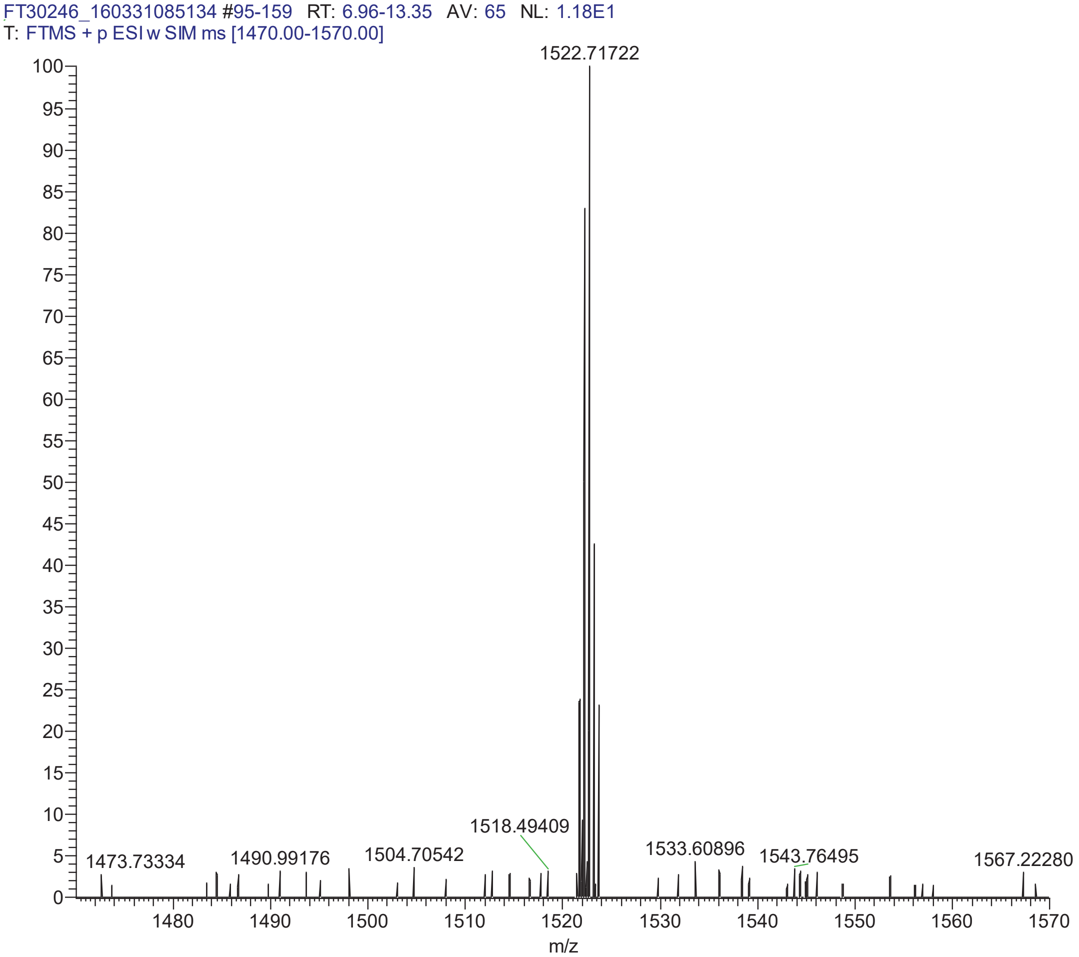

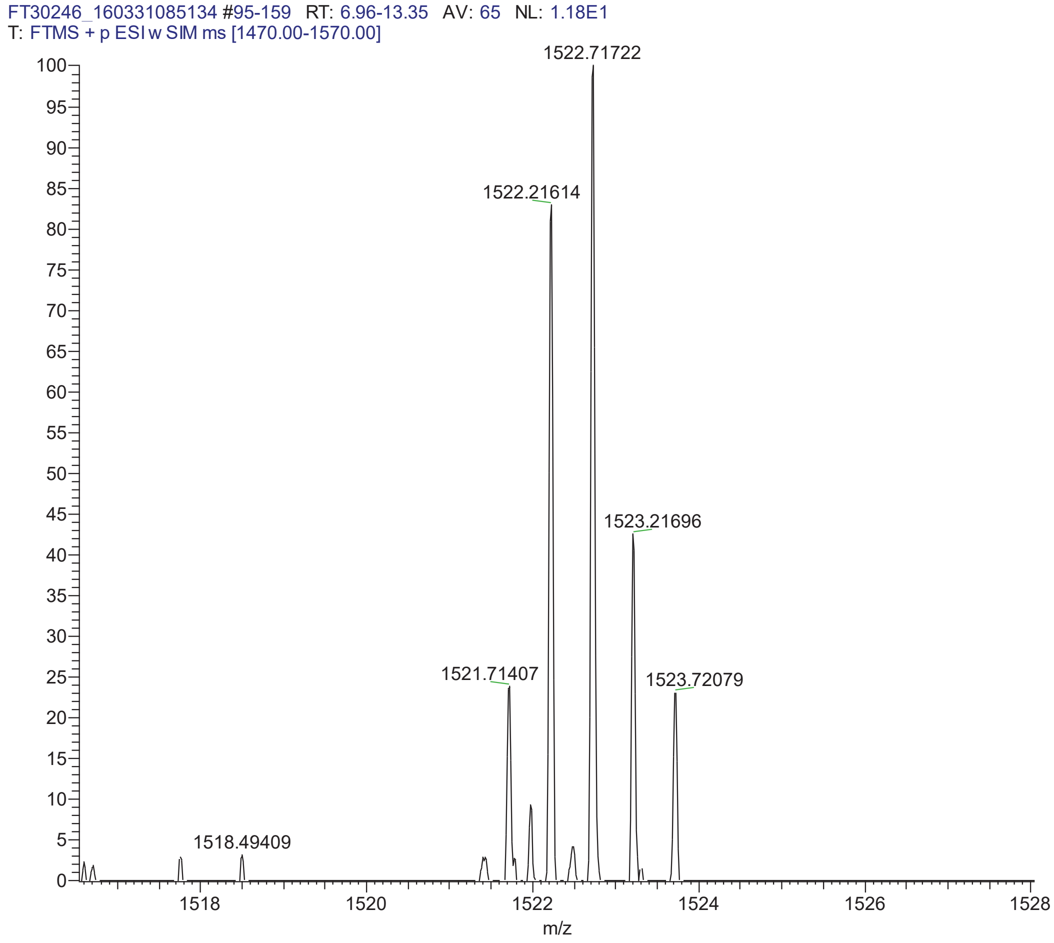
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m/z

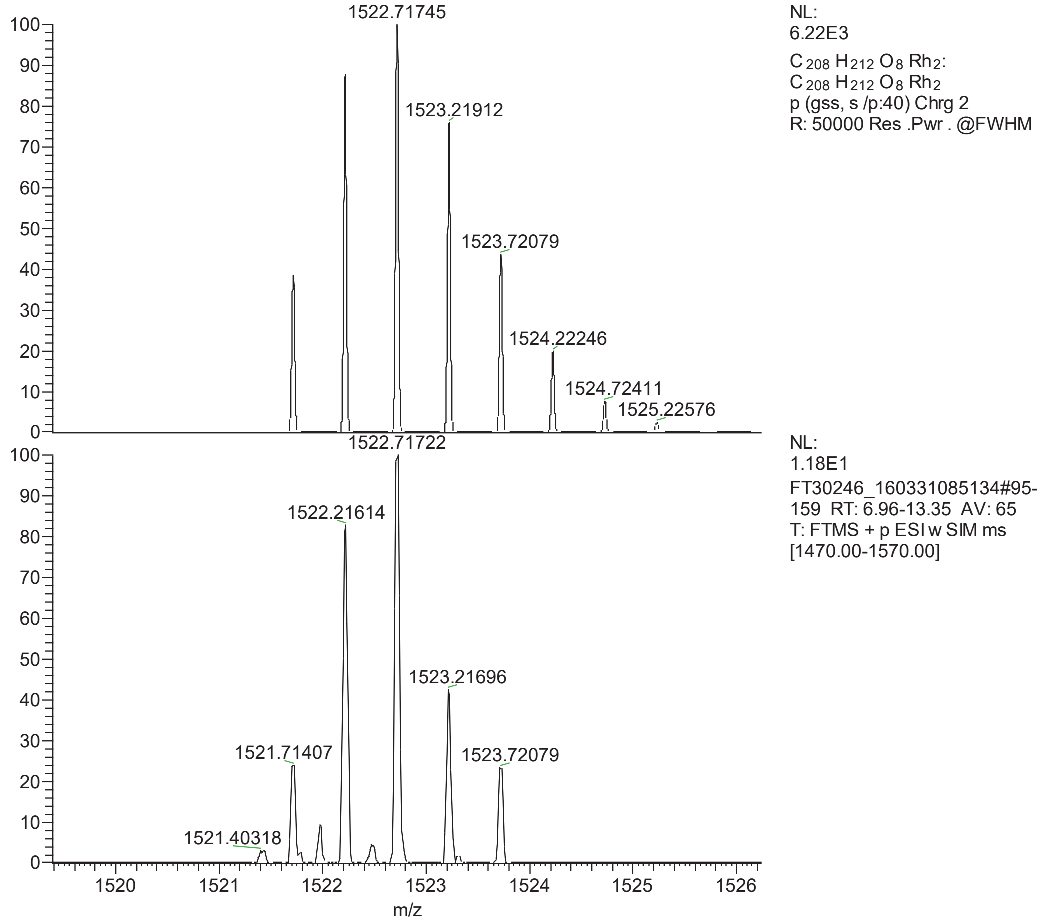


Figure 2.2.10 HRMS data for $Rh_2[R\text{-tris}(p\text{-}^tBuC_6H_4)TPCP]_4$ (**2.2.34**)

Chapter 3 Alkane Reactions

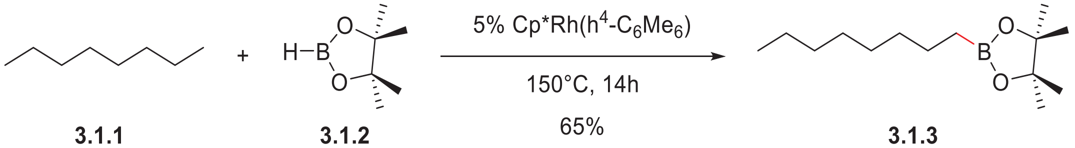
1. Introduction

Alkanes contain only C–H and C–C single bonds. In organic chemistry, alkanes are the simplest molecules and used as the basis for naming most organic compounds. However, from the standard organic chemistry point of view, alkane C–H and C–C bonds are too strong to be cleaved and too similar to be differentiated. Therefore, current major use of alkanes is in combustion as a source of energy, large scale petroleum cracking, conversion to olefins through energy intensive processes, or free radical halogenation.

1.1. C–H Borylation

Even though C–H borylation of alkanes is very difficult, some notable progress has been made. Several important stoichiometric C−H activation reactions were reported in the 1980s demonstrating oxidative addition, typically favored kinetically and thermodynamically, plays a key role in alkane activation with transition metal complexes.[77-79] Thereafter, a series of catalytic reactions have also been established to show the possibility to tackle the challenge of selective alkane functionalization.[43, 60, 80-85]

One milestone study was the C–H bond borylation of alkanes at the terminal position, pioneered by Hartwig and co-workers. They found that rhodium boryl complexes generated *in situ* from Cp*Rh catalyst and pinacolborane (HBpin) (**3.1.2**) or bispinacol diborane (B_2pin_2) can perform regiospecific C–H borylation of *n*-octane (Figure 3.1.1). The selectivity was obtained because the system had a strong preference for the primary C–H bond over secondary and tertiary C–H bond. As shown by Bergman and Jones, oxidative addition of the terminal (primary, in this case) C–H bond is favored thermodynamically, and the formation of primary C–B bond is favored kinetically demonstrated by their computational and experimental studies. [77, 86-89]



3.1.1 **3.1.2** **3.1.3**

Figure 3.1.1 Rhodium(I) catalyzed alkane functionalization

This pioneering work has inspired a lot of scientists to further investigate alkane borylation reaction in various systems, but until now, the substrate scope, the reagent scope, the reaction condition, and the selectivity among different primary C–H bonds is still under developed.[88-91] Moreover, there was limited progress in achieving selective borylation at the secondary or tertiary C–H bonds of alkanes.

1.2. C–H Amination and Azidation

C–H amination of alkanes is also an important topic because transforming C–H bonds to C–N bonds has a lot of synthetic value especially as many pharmaceutical drugs contain nitrogen functionality. In 2004, the Du Bois group reported their progress in C–H amination with trichloroethylsulfamate as nitrene precursor and $Rh_2(esp)_4$ as catalyst. On key example involve the functionalization of cyclooctane (**3.1.4**) to give the amination product (**3.1.6**) in 80% yield with trichloroethylsulfamate (**3.1.5**) as the nitrene precursor (Figure 3.1.2).[92]

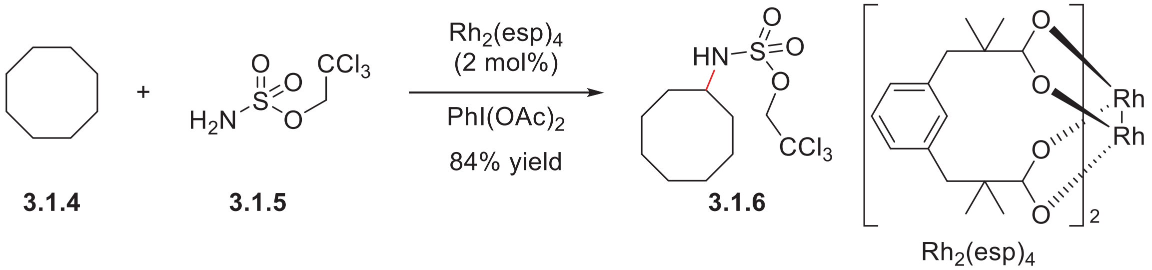
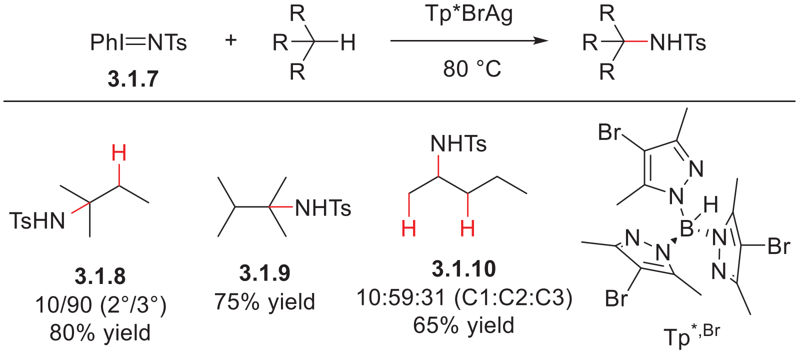


Figure 3.1.2 Rhodium(II) catalyzed C–H amination

In 2008, Pérez and co-workers reported that the silver complex Tp^*Ag (Tp^*=hydrotrispyrazolyborate ligand) can catalyze the thermal (80 °C) nitrene insertion into alkane C–H bonds with PhI=NTs (**3.1.7**) served as nitrene source.[93] The reaction showed similar preference as the carbene reaction but the yield and site-selectivity were improved slightly in the cases of 2-methylbutane (**3.1.8**) and 2,3-dimethylbutane (**3.1.9**) (Figure 3.1.3). In the case of *n*-pentane (**3.1.10**), the reaction gave poor site-selectivity.



3.1.7

3.1.8
10/90 (2°/3°)
80% yield

3.1.9
75% yield

3.1.10
10:59:31 (C1:C2:C3)
65% yield

Figure 3.1.3 Catalytic functionalization of simple alkanes with silver scorpionate catalyst

Other than nitrene transformation, C–H azidation is also a key strategy to transform C–H bond to C–N bond. In 2015, Hartwig and his coworker reported an iron-catalyzed C–H azidation reaction with the hypervalent iodine reagent (**3.1.12**) as the azide source. The reaction showed great potential in synthesis as organic azides play versatile role in modern chemistry and the reaction can be conducted on complex molecules.[94] As shown in Figure 3.1.4, reaction with *cis*-decalin (**3.1.11**) gave the amination product **3.1.14** in 75% yield but only 4.3:1 dr; in the case of α-dihydropinene (**3.1.15**), the reaction yield was 80% but no diastereoselectivity was observed. Overall, the reaction gave good selectivity and yield in functionalizing the tertiary C–H bond but couldn't control the stereoselectivity, so this represented a breakthrough in transforming C–H bond to C–N bond, but further exploration is needed.

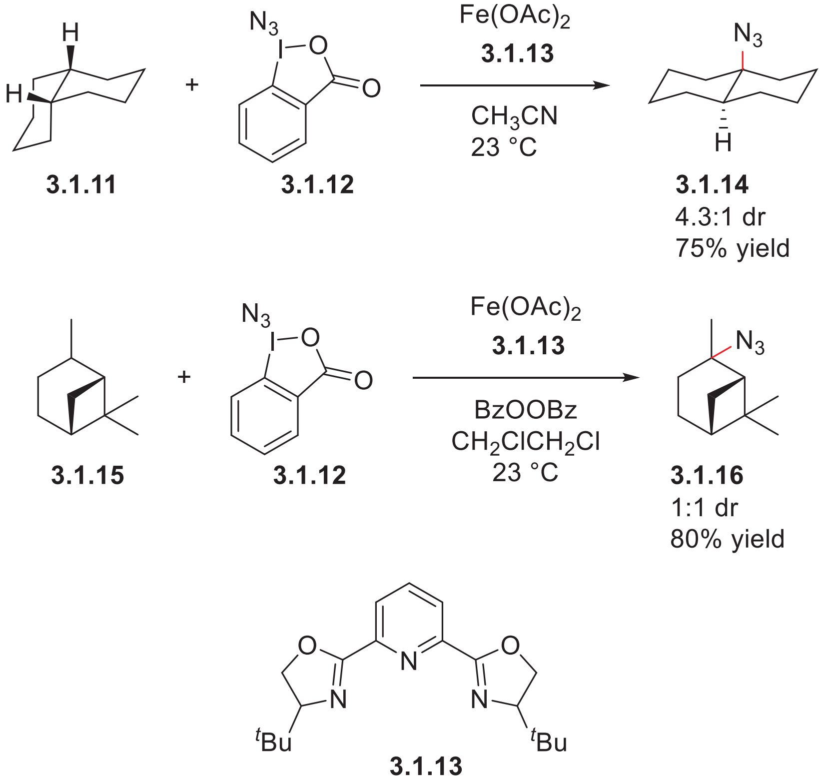


Figure 3.1.4 Iron-catalyzed azidation of tertiary C–H bonds

Soon after the Hartwig paper, the Groves group developed a manganese-catalyzed C–H azidation to effectively convert secondary, tertiary, and benzylic C−H bonds to the corresponding azides.[95] The reactions was conducted under air with sodium azide as the azide source and manganese as catalyst to study various substrates, including a series of alkanes. However, the reaction gave poor to moderate yield in the alkane functionalization (45-67%), and the site-selectivity and stereoselectivity were also very poor. As shown in Figure 3.1.5, the catalyst failed to differentiate the target tertiary C–H bond from other tertiary and secondary C–H bonds (**3.1.20-3.1.24**). Therefore, although significant progress has been achieved, the major challenge in transforming the alkane C–H bond to C–N bond is still how to achieve high site-selectivity and stereoselectivity.

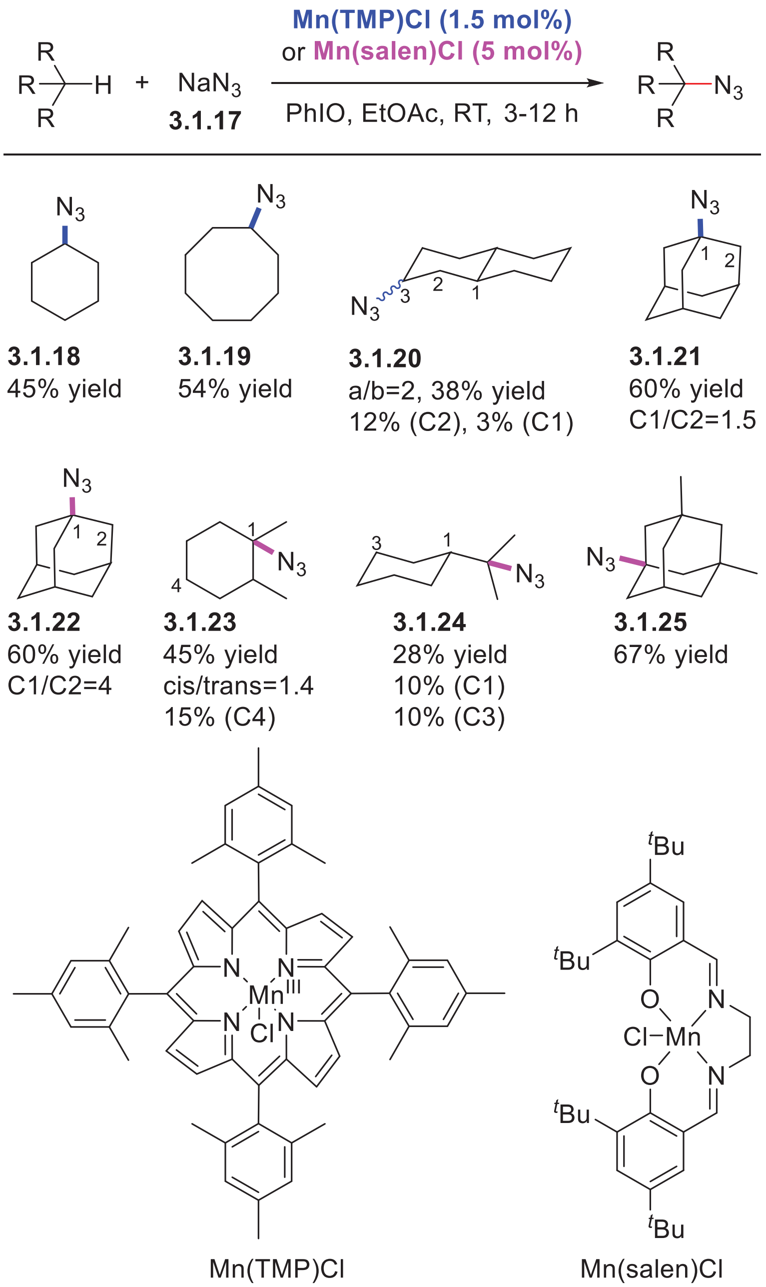
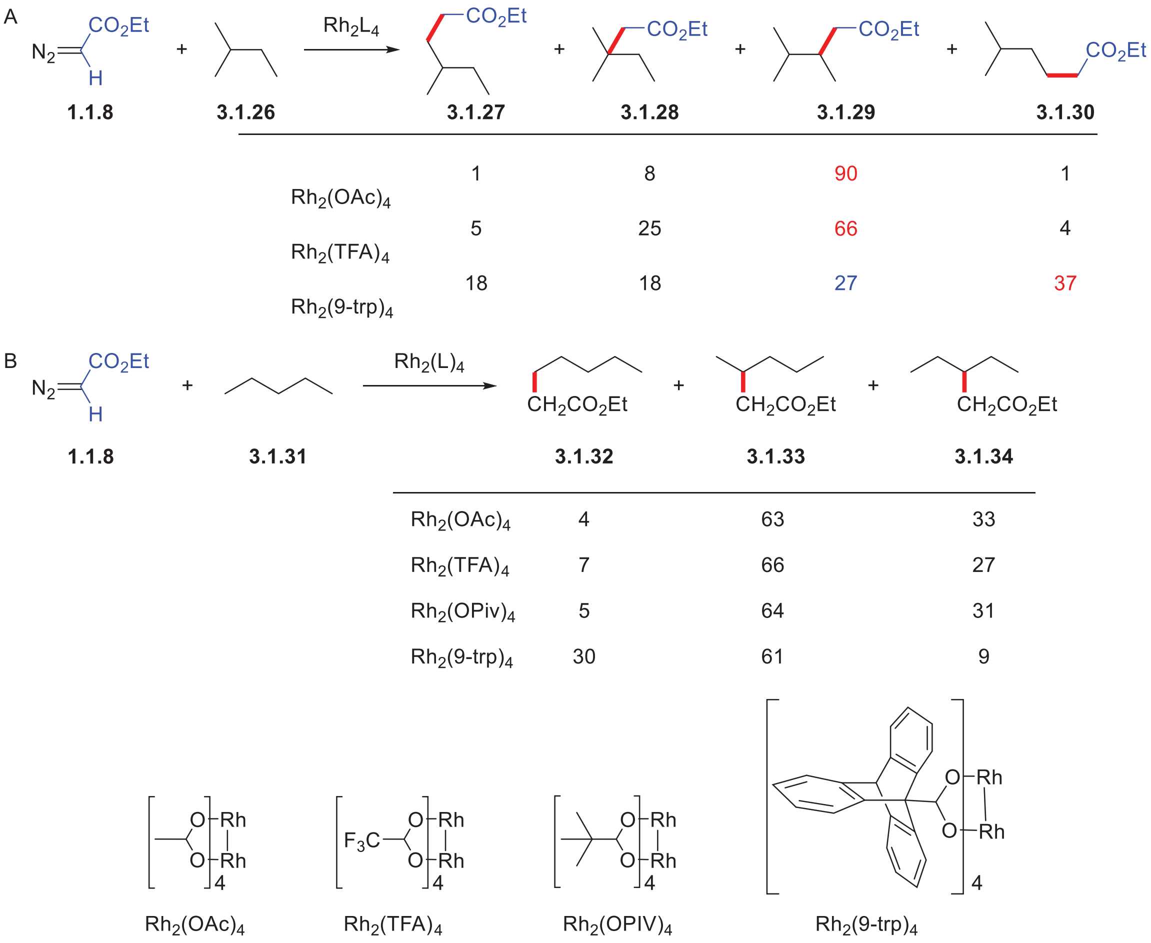


Figure 3.1.5 Rhodium(II) catalyzed C–H amination

1.3. Carbene Insertion

In the case of carbene induced C–H insertion, which is an effective method to transform the C–H bond to C–C bond, selectivity is also a major challenge. Based on the electronic analysis, tertiary C–H bond is preferred over primary C–H bond because the mechanism is different from the borylation reaction and was believed to go through a concerted but asynchronous process,[42-43] in which positive charge build-up at carbon occurs in the transition state. Therefore, sites that can better stabilize the positive charge will be electronically preferred in the reaction.[43]

During the early development of metal carbene insertion reactions, acceptor-only rhodium carbene induced C–H insertion of 2-methylbutane and *n*-pentane were explored.[96] As shown in Figure 3.1.6-A, the reaction with 2-methylbutane gave a mixture of all four possible products (**3.1.23-3.1.26**), but there was some preference for the methylene C–H bond and the catalyst structure did influence the product ratio. The reaction with *n*-pentane gave poor selectivity among all three regioisomers (**3.1.28-3.1.30**). The methyl C–H bond was too electronically disfavored so only small amount of the insertion products were observed both in the 2-methylbutane and *n*-pentane reactions. However, both C2 and C3 of *n*-pentane are methylene positions with similar electronic and steric characteristics and the catalysts failed to differentiate one from the other. The product ratio of C2 and C3 was just a result of the statistical dominance of C2 position (Figure 3.1.6-B). Therefore, more selective transformations are required to be developed to functionalize alkanes.



	3.1.27	3.1.28	3.1.29	3.1.30
$Rh_2(OAc)_4$	1	8	90	1
$Rh_2(TFA)_4$	5	25	66	4
$Rh_2(9\text{-trp})_4$	18	18	27	37

	3.1.32	3.1.33	3.1.34
$Rh_2(OAc)_4$	4	63	33
$Rh_2(TFA)_4$	7	66	27
$Rh_2(OPiv)_4$	5	64	31
$Rh_2(9\text{-trp})_4$	30	61	9

Figure 3.1.6 Rhodium(II) catalyzed intermolecular C–H activation of 2-methylbutane and *n*-pentane

There was no significant improvement until 2003, when the Pérez group reported their progress in the alkane functionalization with the use of a novel perbromohomoscorpionate copper(I) catalyst, $Tp^{Br3}Cu(NCMe)$.[97] As shown in Figure 3.1.3, reaction with cyclohexane, 2,3-dimethylbutane and 2,5-dimethylhexane gave a single regioisomer in high yield (**1.1.9**, **3.1.35** & **3.1.36**). Interestingly, reaction with 2-methylbutane and 2-methylpentane showed preference for the tertiary position (**3.1.28** &

3.1.37) which was opposite to the reaction shown in Figure 3.1.7. However, there was no significant improvement of site-selectivity in the reactions with *n*-pentane and *n*-hexane (**3.1.33 & 3.1.38**). Therefore, selective carbene transformation is still underdeveloped.

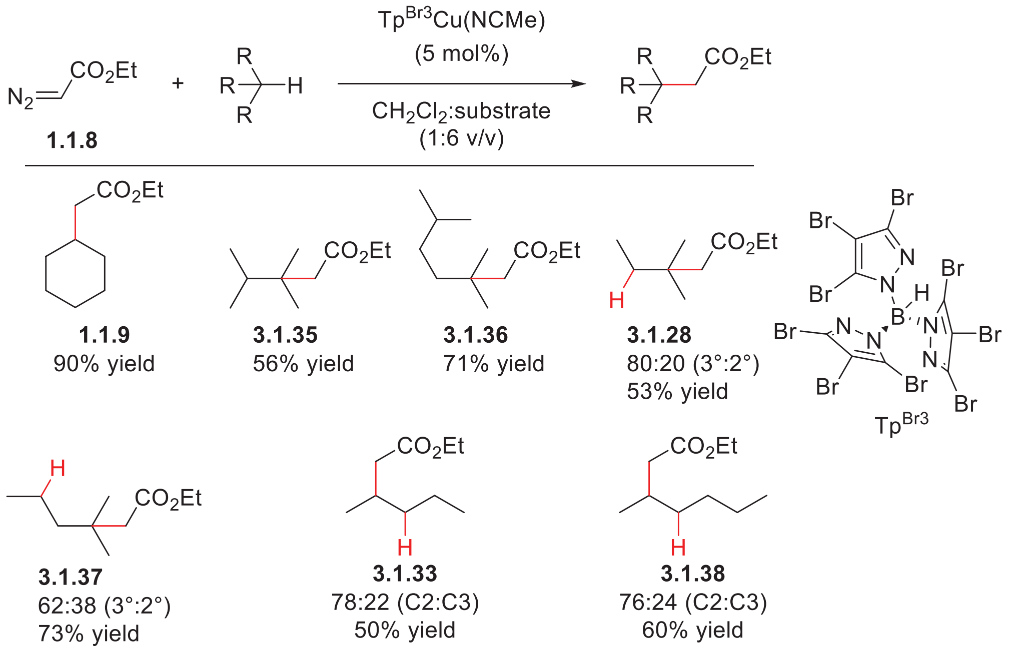


Figure 3.1.7 Functionalization of alkane C–H bond with a perbromohomoscorpionate copper(I) catalyst

Davies has been interested in developing the chemistry of donor/acceptor rhodium carbenes since 1990s; and in 2000, he and his coworkers reported a breakthrough in asymmetric alkane C–H functionalization with donor/acceptor rhodium carbene.[60] However, controlling the selectivity and broadening the substrate scope remained challenging in alkane functionalization. As shown in Figure 3.1.8, the reaction gave good yield and enantioselectivity in the functionalization of cyclohexane reaction (**3.1.39**). The reaction also showed small preference toward tertiary over secondary C–H bonds (**3.1.42**

& **3.1.43**), but strong preference over primary C–H bonds (**3.1.40** & **3.1.41**), but the reactions generally gave poor to moderate yield, site- and enantioselectivity.

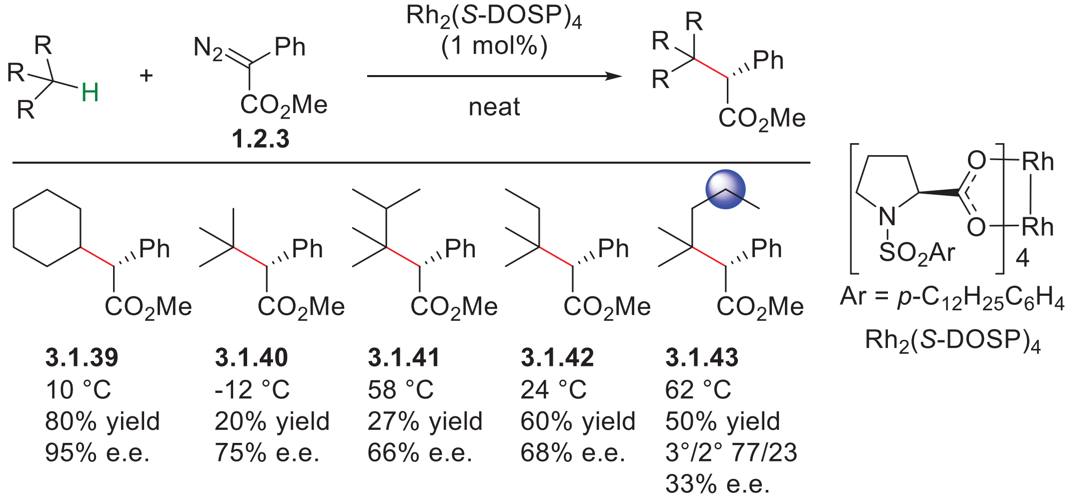


Figure 3.1.8 Catalytic asymmetric C–H activation of alkanes with Rh_2(*S*-DOSP)$_4$

Later in the same year, Che reported a study regarding the donor/acceptor carbene induced primary C–H insertion with a rhodium complex, [Rh(ttppp)(Me)(MeOH)], as catalyst. The catalyst showed great capability to differentiate primary from secondary C–H bonds; however, it failed to differentiate primary from tertiary C–H bond. The enantioselectivity of the reactions were also insufficient.[98] As shown in Figure 3.1.9, the regioselectivity increased from 9.8:1 to 11.4:1 when the alkane chains were extended from hexane to decane (**3.1.44-3.1.46**), but the ratio decreased in the case of 2,2-dimethylbutane (**3.1.47**) and the tertiary site became preferred in the case of 2,3-dimethylbutane and adamantane (**3.1.41** & **3.1.48**).

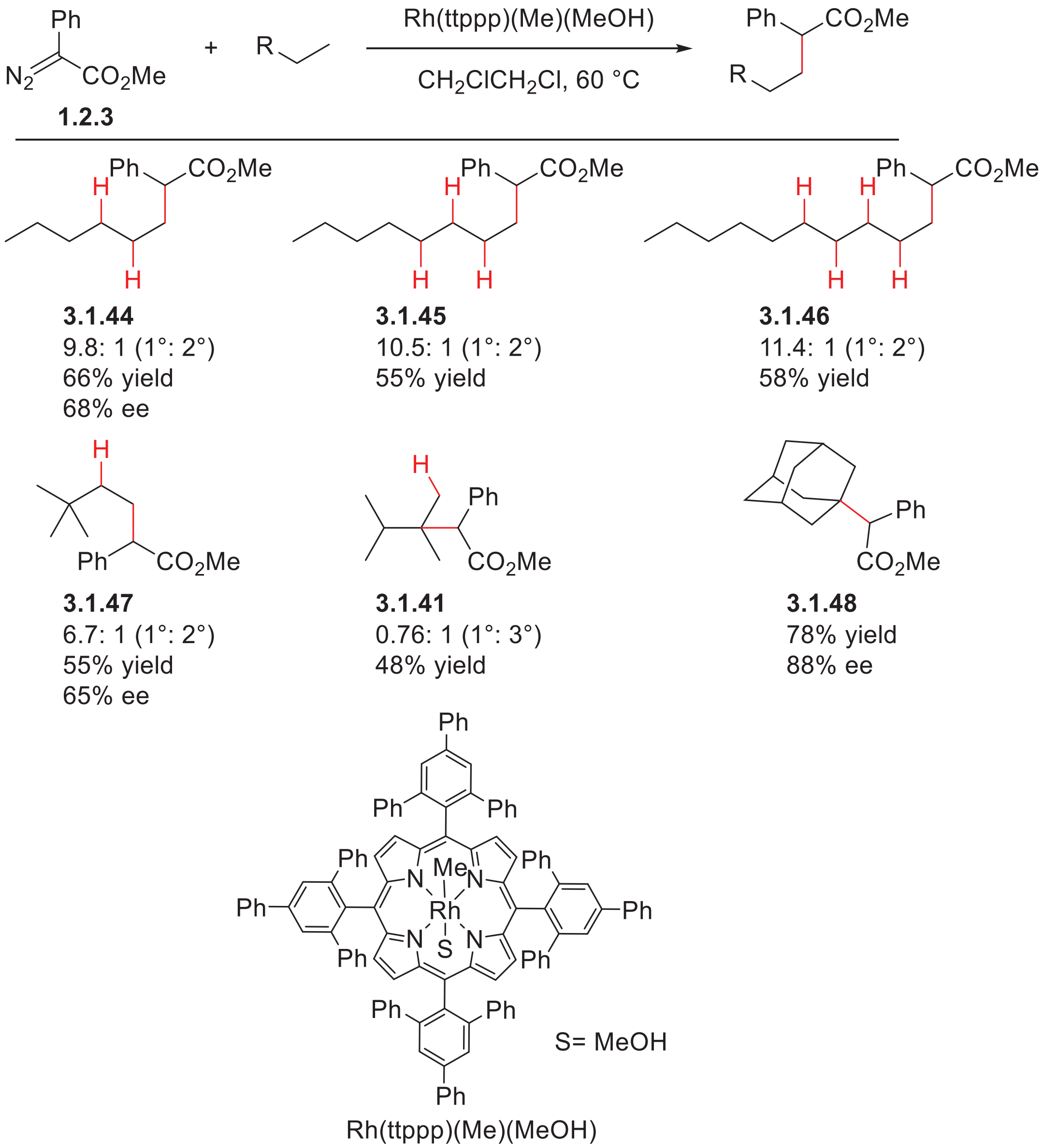
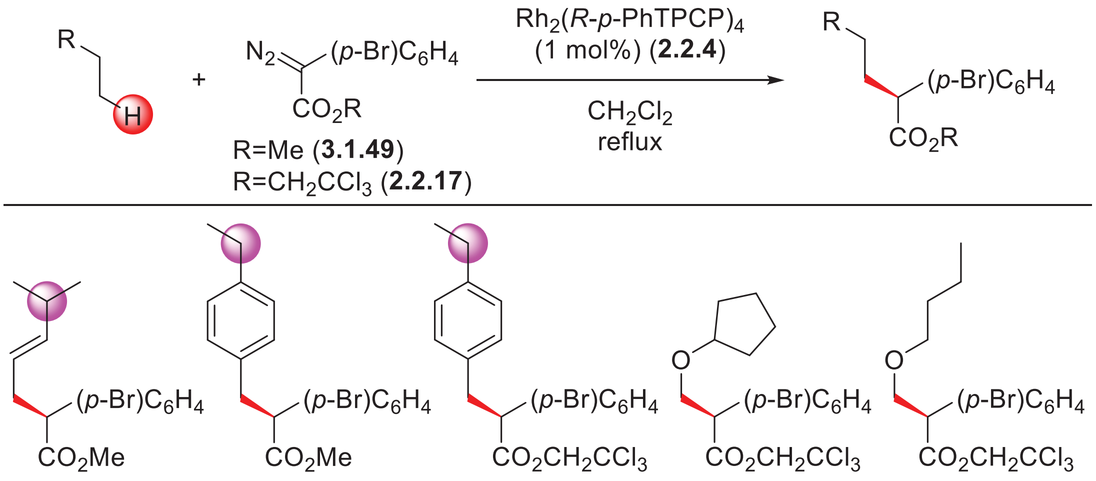


Figure 3.1.9 Rh(I) catalyzed carbanion insertion into primary C–H bonds

Recently, significant progress has been made in understanding the donor/acceptor rhodium carbene, and this newfound understanding has inspired the group to explore the selective functionalization of alkane C–H bond.[72-74] One important advancement was the development of dirhodium tetrakis triarylcyclopropanecarboxylate catalyst because it is a sterically demanding catalyst which can control the functionalization to occur at the activated primary C–H bond. As shown in Figure3.1.10, the reaction of 4-methyl-2-pentene with methyl 2-(4-bromophenyl)-2-diazoacetate (**3.1.49**) as carbene precursor showed preference at C1 over the tertiary position with a ratio of 17:1 although the tertiary C–H bond is more reactive (**3.1.50**). For 4-ethyltoluene, the catalyst also preferred primary over secondary C–H bond with the ratio of 5:1 (**3.1.51**). Another important advancement was the development of 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**2.2.17**) because it can suppress intra-molecular reaction and dimerization, and it has also shown to improve the selectivity in the initial studies. In the reaction with 4-ethyltoluene, the site- and enantioselectivity were significantly improved (**3.1.52**) when 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**2.2.17**) was used. Two examples in Figure 3.1.10 also demonstrate the effectiveness of this type of diazo because the reactions gave very high site-selectivity in the functionalization of the methyl ether C–H bond (**3.1.53** & **3.1.54**).



3.1.50
17: 1 r.r.
94% e.e.
60% yield

3.1.51
5: 1 r.r.
92% e.e.
74% yield

3.1.52
13: 1 r.r.
99% e.e.
75% yield

3.1.53
>20: 1 r.r.
91% e.e.
83% yield

3.1.54
>20: 1 r.r.
84% e.e.
82% yield

Figure 3.1.10 Selective functionalization of activated primary C–H bond

2. Initial Exploration of Pentane Functionalization

To explore the catalyst controlled selective functionalization of alkane C–H bond, *n*-pentane was chosen as the model substrate. It is a simple but challenging substrate because there are three positions in pentane, C1, C2, and C3 with the ratio of number of C–H bonds is 6:4:2, that means the competition will involve primary *vs* secondary C–H bond, and secondary *vs* tertiary C–H bond. To better analyze the result, the methyl ester authentic samples (**3.2.3**, **3.2.6** and **3.2.9**) were synthesized through S$_N$2 reactions with the corresponding bromopentane compounds, the trichloroethyl ester authentic samples (**3.2.4**, **3.2.7** and **3.2.10**) were synthesized by hydrolysis and then esterification of the methyl ester authentic samples (Figure 3.2.1). The ^{1}H NMR spectra of these authentic samples were used to analyze the site- and diastereoselectivity of the *n*-pentane reaction crude.

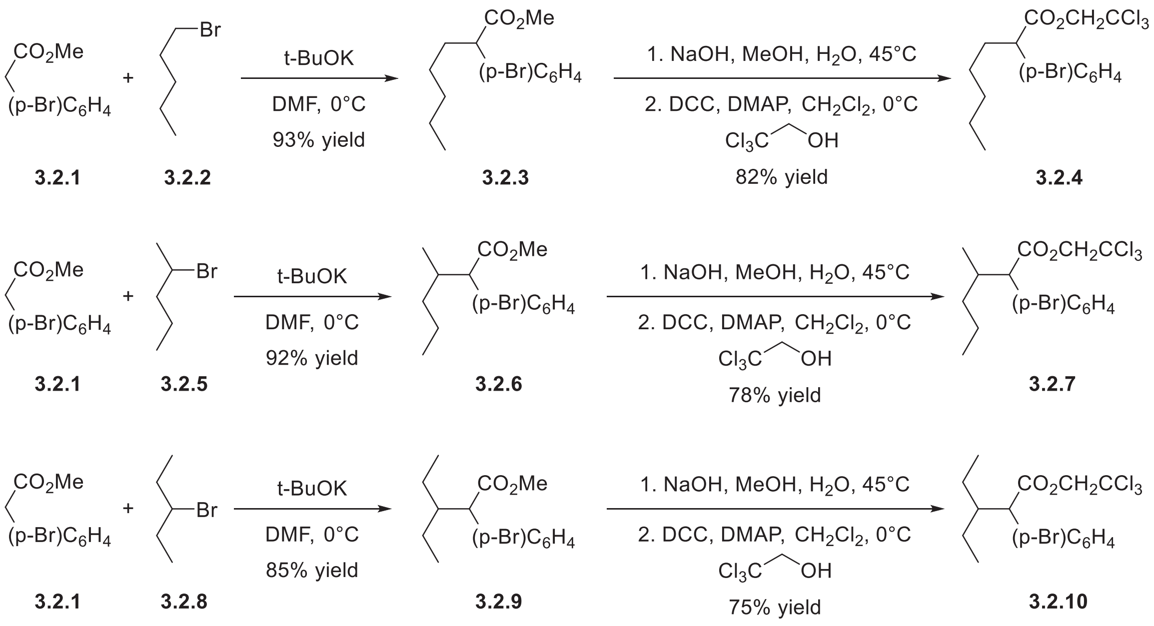
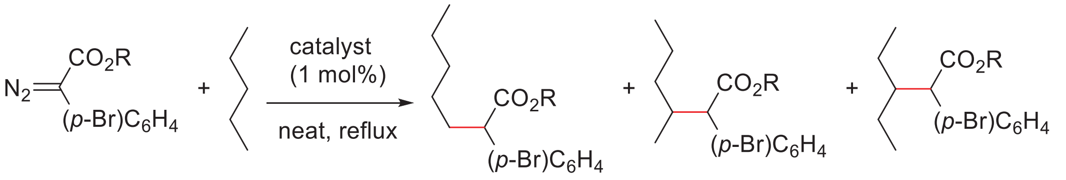


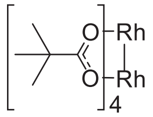
Figure 3.2.1 Synthesis of authentic samples

In the initial study, a series of rhodium catalysts and two diazo compounds (**3.1.49** & **2.2.17**) were screened in pentane functionalization reaction. The result in Figure 3.2.2 showed that in the donor/acceptor rhodium carbene system, the major product was **3.2.6** or **3.2.7** which means the carbene has a preference to react with the most accessible secondary C–H bonds (C2). The combination of Rh_2(*S*-DOSP)$_4$ and 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate gave the best site-, diastereo- and enantioselectivity as well as yield compared to other catalysts. However, to further develop a catalytic system for selective C–H functionalization at the C2 position, this surprisingly good result raised our concerns because there were two major limitations in this result. First, the catalyst has very poor diversification capability which shows poor potential for result improvement. Another more severe limitation is the competition from the internal secondary position, C3; because there will be more internal positions in *n*-hexane, *n*-octane, and other more complex molecules.[75]

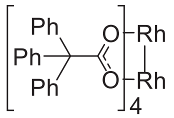


R=CH_3 (**3.1.49**) **3.1.9**
R=CH_2CCl_3 (**2.2.17**)
R=CH_3 (**3.2.3**) R=CH_3 (**3.2.6**) R=CH_3 (**3.2.9**)
R=CH_2CCl_3 (**3.2.4**) R=CH_2CCl_3 (**3.2.7**) R=CH_2CCl_3 (**3.2.10**)

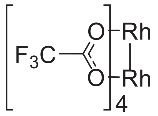
entry	Ligand	R	C1: C2: C3	yield (%)	d.r.	e.e. (major C2, %)	e.e. (minor C2, %)
1	$Rh_2(PIV)_4$	CH_3	n.d.: 11: 1	72	1: 1	-	-
2	$Rh_2(PIV)_4$	CH_2CCl_3	n.d.: 14: 1	98	1: 1	-	-
3	$Rh_2(TPA)_4$	CH_3	n.d.: 47: 1	88	2: 1	-	-
4	$Rh_2(TPA)_4$	CH_2CCl_3	3: 37: 1	99	1: 1	-	-
5	$Rh_2(TFA)_4$	CH_3	n.d.: 9: 1	12	1: 1	-	-
6	$Rh_2(TFA)_4$	CH_2CCl_3	n.d.: 12: 1	93	2: 1	-	-
7	$Rh_2(S\text{-}PTAD)_4$	CH_3	n.d.: 19: 1	47	2: 1	-24	44
8	$Rh_2(S\text{-}PTAD)_4$	CH_2CCl_3	n.d.: 27: 1	95	2: 1	-46	56
9	$Rh_2(S\text{-}DOSP)_4$	CH_3	n.d.: 17: 1	42	2: 1	88	54
10	$Rh_2(S\text{-}DOSP)_4$	CH_2CCl_3	n.d.: 29: 1	98	3: 1	82	68



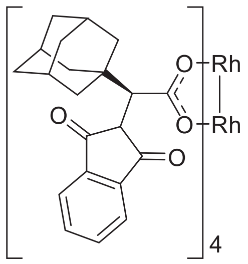
$Rh_2(PIV)_4$



$Rh_2(TPA)_4$



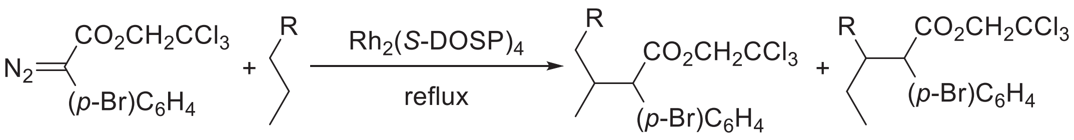
$Rh_2(TFA)_4$



$Rh_2(S\text{-}PTAD)_4$

Figure 3.2.2 Initial catalyst and diazo screen for selective C–H functionalization of *n*-pentane

In order to determine whether the selectivity will vary by the length of the chain, the reactions of *n*-hexane and *n*-octane were examined. The data shown in Figure 3.2.3 revealed that the regioselectivity decreased when the alkane chain becomes longer because there are more internal secondary C–H bonds involved in the competition with the C–H bonds at C2 position.

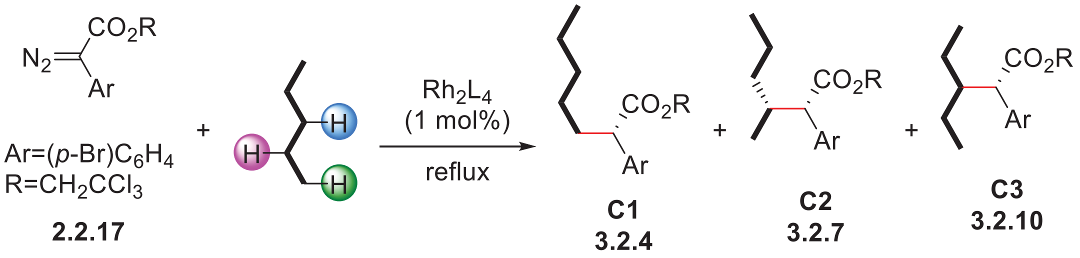


2.2.17

substrate	product	C1: C2: internal 2°	yield (%)	d.r. (C2)
pentane	**3.2.7**	n.d.: 29: 1	98	3: 1
hexane	**3.2.11**	n.d.: 18: 1	84	2: 1
octane	**3.2.12**	n.d.: 10: 1	86	2: 1

Figure 3.2.3 Expanding the substrate scope to longer alkanes

Even though the reactions with the standard catalysts gave reasonable site selectivity, the formation of internal C–H functionalization products will be a problem when extending the chemistry to more elaborate substrates Therefore, we examined the use of more bulky catalysts with the aim of identifying catalysts that will result in selective C–H functionalization at the most accessible methylene site with no reaction at other internal methylene sites. The TPCP catalysts were considered an ideal system to investigate because they have been reported to be sterically demanding to favor the activated primary C–H bond[72-73] and the catalyst family can be synthesized in a high-throughput mode (Figure3.2.4). When the *para*-substituted TPCP catalysts (**2.2.3** and **2.2.4**) were used, the competitions were successfully switched to C1 *vs* C2 without any reaction occurring at the C3 position, and the results also showed good promise for achieving high diastereoselectivity and enantioselectivity. However, when the substituent was moved to the 3,5-position, the TPCP catalysts (**2.2.16** and **2.2.27**) showed significant improvement in terms of site-selectivity at the C2 position. In a simple comparison, 3,5-disubstituted TPCP catalysts should be more sterically demanding than the para-substituted ones, and as the C1 position is more sterically accessible than the C2 position, one would expect these catalysts to have a greater preference for C1 functionalization. However, the data showed opposite result and these catalysts strongly favor C2 functionalization, but no other internal C–H bonds were involved in the reaction. This intriguing result drew our attention to conduct control experiments and computational studies to determine the factors that control the site-selectivity.



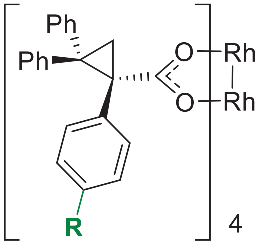
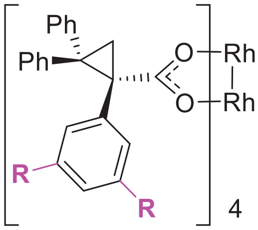
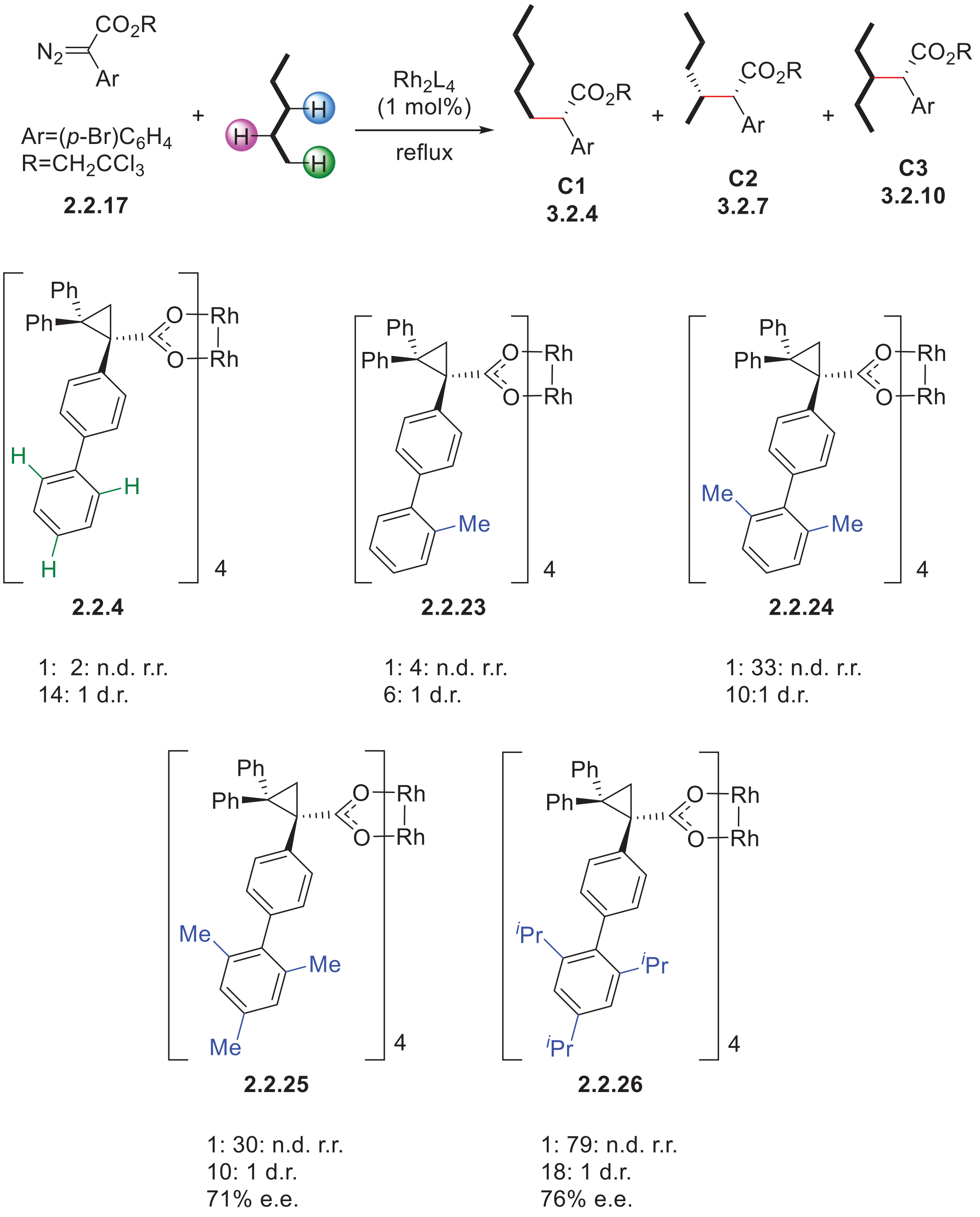
		Rh_2L_4	C1 : **C2** : C3	d.r.	e.e.	yield
	**Br**	Rh_2(*R*-*p*-BrTPCP)$_4$ (**2.2.3**)	1 : 4: n.d.	6: 1	**91**%	98%
	Ph	Rh_2(*R*-*p*-PhTPCP)$_4$ (**2.2.4**)	1 : 2: n.d.	**14**: 1	**92**%	95%
	**Br**	Rh_2(*R*-3,5-diBrTPCP)$_4$ (**2.2.16**)	1 : **26**: n.d.	5: 1	78%	95%
	Ph	Rh_2(*R*-3,5-diPhTPCP)$_4$ (**2.2.27**)	1 : **22**: n.d.	5: 1	**96**%	95%

Figure 3.2.4 Pentane functionalization with *para*- and 3,5-substituted TPCP catalysts

3. Initial exploration of linear and branched TPCP catalysts

A series of *para*-substituted TPCP catalysts were investigated in the pentane reaction under the same condition. When R=Ph (**2.2.4**), the ratio was 1:2: n.d. r.r.; when R=2-methylphenyl (**2.2.23**), the ratios was improved to 1:4: n.d. r.r.; however, when R=2,6-dimethylphenyl (**2.2.24**), the ratio was dramatically improved to 1:33: n.d. r.r. which is similar to the result when R= 2,4,6-trimethylphenyl (**2.2.25**). When R= 2,4,6-triisopropylphenyl (**2.2.26**), the ratio was improved up to 1: 79: n.d. r.r. This controlling experiment showed that not only 3,5-disubstituted TPCP catalyst preferred C2 position, TPCP catalysts with branched substituent at the *para*-position also favored C2 position. However, in order to develop catalyst for selective functionalization at the primary C–H bond, the data showed great potential to explore TPCP catalyst with linear substituent at the *para* position (Figure3.3.1).



2.2.4: 1: 2: n.d. r.r.
14: 1 d.r.

2.2.23: 1: 4: n.d. r.r.
6: 1 d.r.

2.2.24: 1: 33: n.d. r.r.
10:1 d.r.

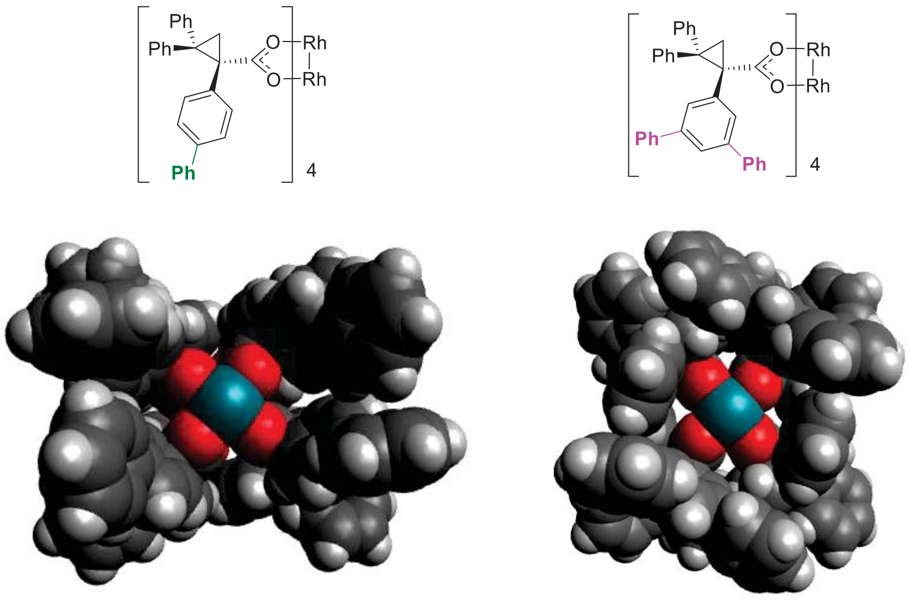
2.2.25: 1: 30: n.d. r.r.
10: 1 d.r.
71% e.e.

2.2.26: 1: 79: n.d. r.r.
18: 1 d.r.
76% e.e.

Figure 3.3.1 Controlling experiments in *n*-pentane functionalization

The *para*-phenyl TPCP, Rh_2(*S*-*p*-PhTPCP)$_4$ (**2.2.4**), and 3,5-diphenyl-TPCP, Rh_2(*S*-3,5-diPhTPCP)$_4$ (**2.2.16**), catalysts were chosen to be studied with the method of

ONION calculation. Our collaborator, Djamaladdin G. Musaev, conducted the computational study and showed that Rh_2(*S*-*p*-PhTPCP)$_4$ (**2.2.4**) favors α, α, α, α orientation by 5.5 kcal/mol over α, β, α, β orientation while Rh_2(*S*-3,5-diPhTPCP)$_4$ (**2.2.16**)prefers α, β, α, β orientation by 5.0 kcal/mol over α, α, α, α orientation. Based on our model for carbene induced C–H insertion, the diazo will approach from the top face to form rhodium carbene, so the C–H bond will be forced to approach the carbene from the side because the top face is blocked. In the Rh_2(*S*-*p*-PhTPCP)$_4$ (**2.2.4**) catalyst structure, the C–H bond can only approach from the narrow channels (left and right sides) between two biphenyls with *π* stacking interaction because the phenyl and ester group of carbene will block the other two sides, and the narrow channel will make C2 relatively less preferred. However, in the Rh_2(*S*-3,5-diPhTPCP)$_4$ (**2.2.16**) catalysts structure, the channel for C–H bond to approach will be relatively larger so that it favors more at C2 but small enough to block C3 (Figure 3.3.2).



α, α, α, α form α, β, α, β form

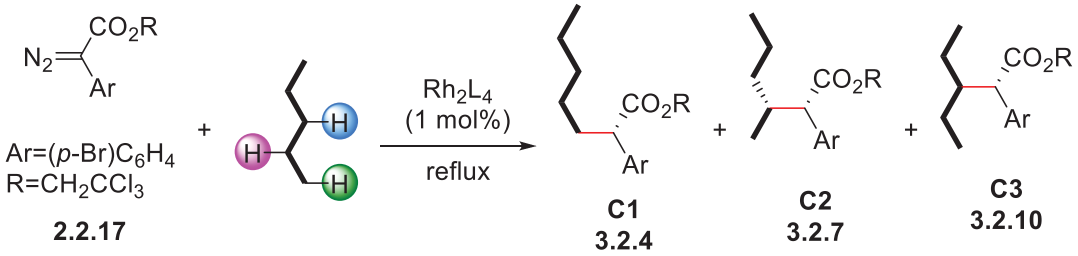
Figure 3.3.2 Computational study of para- and 3,5-substituted catalysts

Although the hypothesis is lacking sufficient computational and experimental support, it helped us to design and obtain the optimum catalysts to achieve selective functionalization at the most accessible primary and secondary C–H bonds.

4. Optimum Catalyst for Selective Functionalization at the Most Accessible Secondary C–H Bond

The previous sections have demonstrated that it will be possible to find an optimum catalyst to achieve selective functionalization at the most accessible secondary C–H bond; the studies shown in section 3 indicate that branched catalysts tend to prefer C2 position of pentane; and the library synthesis described in Chapter 2 strongly enables the ability to quickly conduct catalyst screening and optimization.

As shown in Figure 3.4.1, a library of 3,5-disubstituted catalysts was built to enable systematic study and catalyst screening and they gave moderate to excellent result in terms of site-, diastereo- and enantioselectivity. For **2.2.28**, the site- and diastereoselectivity were good but the enantioselectivity was not high enough (26:1 rr, 26:1 dr, 92% ee); **2.2.29** gave good stereoselectivities but lower site-selectivity (16:1 rr, 29:1 dr, 99% ee); **2.2.30** and **2.2.31** gave poor site- and stereoselectivities (5:1 rr, 16:1 dr, 97% ee & 9:1 rr, 10:1 dr, 89% ee); for **2.3.32**, the site-selectivity was superior but the stereoselectivities were pretty low (30:1 rr, 8:1 dr, 91% ee). Finally, $Rh_2[R\text{-}3,5\text{-di}(p\text{-}{}^tBu)C_6H_4TPCP]_4$ (**2.2.33**) was quickly identified to be the optimum catalyst to give 25: 1 rr, 20: 1 dr, 99% ee and 99% yield. The designing feature includes the use of ^{t}Bu group to provide improved steric bulkiness and enhanced catalyst solubility.



Rh_2L_4	rr	dr	ee (%)	yield (%)
$Rh_2[R\text{-}3,5\text{-di}(3,5\text{-di}CF_3C_6H_3)TPCP]_4$ (**2.2.28**)	1: 26: n.d.	26: 1	92	96
$Rh_2[R\text{-}3,5\text{-di}(3,5\text{-di}CH_3C_6H_3)TPCP]_4$ (**2.2.29**)	1: 16: n.d.	29: 1	99	95
$Rh_2[R\text{-}3,5\text{-di}(3,5\text{-di}PhC_6H_3)TPCP]_4$ (**2.2.30**)	1: 5: n.d.	16: 1	97	98
$Rh_2[R\text{-}3,5\text{-di}(p\text{-}PhC_6H_4)TPCP]_4$ (**2.2.31**)	1: 9: n.d.	10: 1	89	91
$Rh_2[R\text{-}3,5\text{-di}(p\text{-}CF_3C_6H_4)TPCP]_4$ (**2.2.32**)	1: 30: n.d.	8: 1	91	95
$Rh_2[R\text{-}3,5\text{-di}(p\text{-}{}^tBuC_6H_4)TPCP]_4$ (**2.2.33**)	1: 25: n.d.	20: 1	99	99

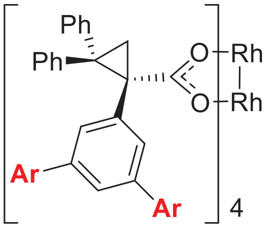
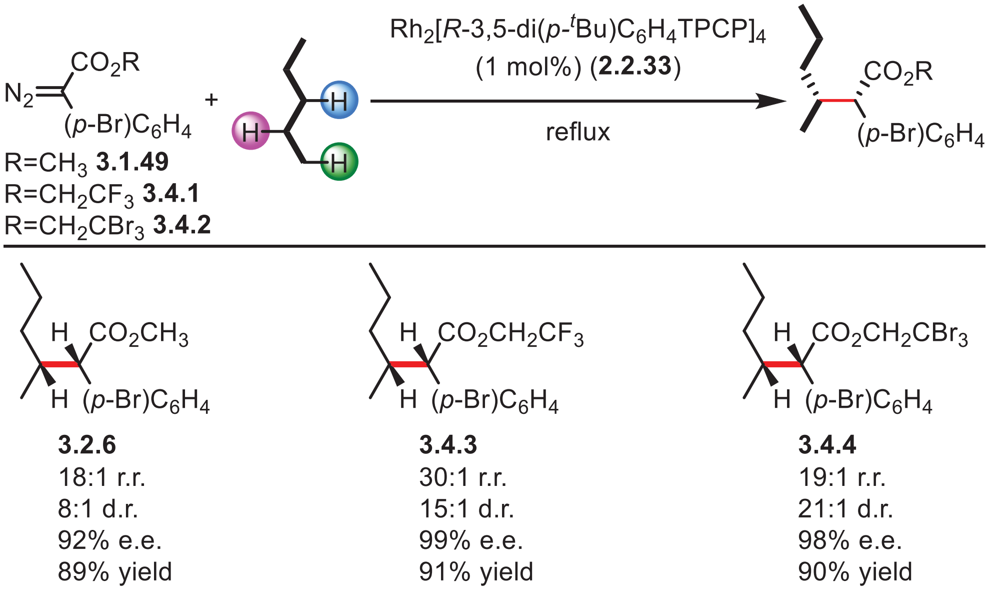


Figure 3.4.1 Catalyst optimization for *n*-pentane functionalization

Followed by the catalyst optimization, three diazo compounds were also screened in the *n*-pentane functionalization with the optimum catalyst, $Rh_2[R\text{-}3,5\text{-di}(p\text{-}{}^tBu)C_6H_4TPCP]_4$ (**2.2.33**), and Figure 3.4.2 showed that different ester groups gave excellent results, but the overall best result was still generated by the trichloroethyl diazo compound (**2.2.17**). Methyl ester diazo worked well in the reaction although the selectivity was lower (**3.2.6**); trifluoroethyl ester diazo gave slightly higher site-selectivity and equivalent enantioselectivity but the diastereoselective was lower (**3.4.3**);

the tribromoethyl ester diazo gave slightly higher diastereoselectivity but the site- and enantioselectivity were lower (**3.4.4**).



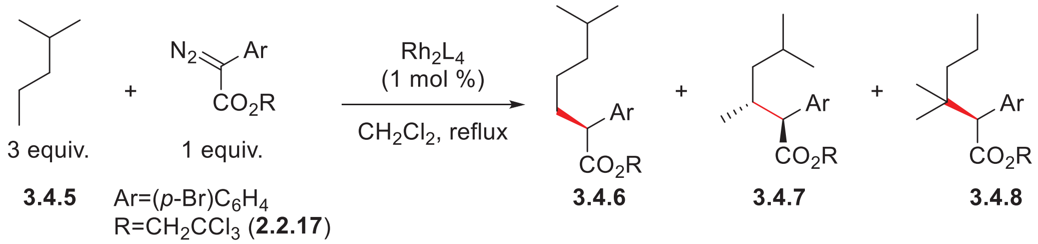
3.2.6
18:1 r.r.
8:1 d.r.
92% e.e.
89% yield

3.4.3
30:1 r.r.
15:1 d.r.
99% e.e.
91% yield

3.4.4
19:1 r.r.
21:1 d.r.
98% e.e.
90% yield

Figure 3.4.2 Diazo screen for *n*-pentane functionalization

To further develop the catalyst control strategy, 2-methylpentane was chosen as a new model substrate to challenge the system. It is a more challenging substrate than *n*-pentane because it has five distinct positions with the ratio of number of C–H bonds 3:2:2:1:6. In order to develop a broadly useful system, dichloromethane was used as solvent and only 3 equiv of substrate was used in the reaction. As shown in Figure 3.4.3, the reaction only occurred at three positions with formation of products **3.4.6**., **3.4.7**, and **3.4.8**; and the major competition was coming from tertiary C–H bond. After catalyst screen, $Rh_2[R\text{-}3,5\text{-di}(p\text{-}^t\text{Bu})C_6H_4TPCP]_4$ (**2.2.33**) was still the best catalyst for the reaction giving 7:75:18 rr, 92% ee, 7:1 dr and 75% yield.

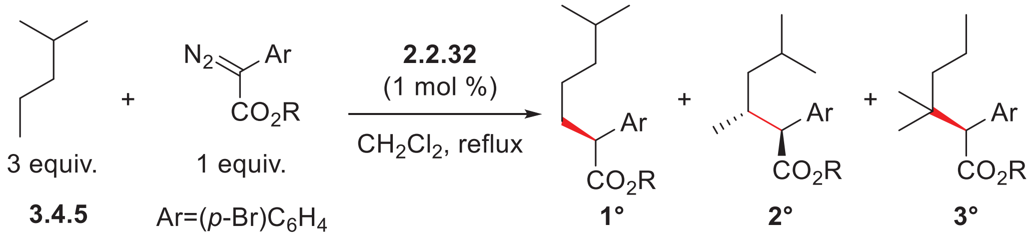


Catalyst	r.r. (**6**:**7**:**8**)	e.e. (**6**,%)	e.e. (**7**,%)	d.r. (**7**,%)	e.e. (**8**,%)	yield (**6+7**,%)	yield (**8**,%)
Rh_2(*R*-2,4,6-tri$CH_3C_6H_2$TPCP)$_4$ (**2.2.25**)	5: 75: 20	94	77	11:1	17	74	18
Rh_2[*R*-3,5-di(3,5-di$CF_3C_6H_3$)TPCP]$_4$ (**2.2.28**)	7: 71: 22	62	>99	4:1	8	70	19
Rh_2[*R*-3,5-di(*p*-$CF_3C_6H_4$)TPCP]$_4$ (**2.2.32**)	7: 64: 29	78	77	4:1	14	35	15
Rh_2[*R*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$ (**2.2.33**)	7: 75: 18	81	92	7:1	23	75	16

Figure 3.4.3 Catalyst screen for 2-methylpentane functionalization

To examine the effect of the ester group, other trihaloethyl diazo compounds (**3.1.49**, **3.4.1** and **3.4.2**) were also tried in the 2-methylpentane reactions. As the major competitor was the tertiary C–H bond, a more sterically demanding carbene would be helpful to block the tertiary C–H bond from the approaching the carbene center. The data indeed showed a strong agreement to this hypothesis (Figure 3.4.4). When methyl diazo (**3.1.49**) was used, the carbene tends to prefer dimerization causing the combined yield to be 23% because the C–H bond is too unreactive. When trifluoroethyl diazo (**3.4.1**) was used, the carbene is less sterically demanding than the trichloroethyl diazo (**2.2.17**) so more functionalization occurred at the tertiary position, but less reaction occurred at the primary position (4:71:26 rr). In the case of tribromoethyl diazo (**3.4.2**), the carbene was believed to be more sterically demanding so primary may be slightly more preferred but tertiary should be sufficiently blocked. Indeed, the site-selectivity was improved to

9:82:10 rr with slight increases at the primary position but significantly lower tertiary functionalization.



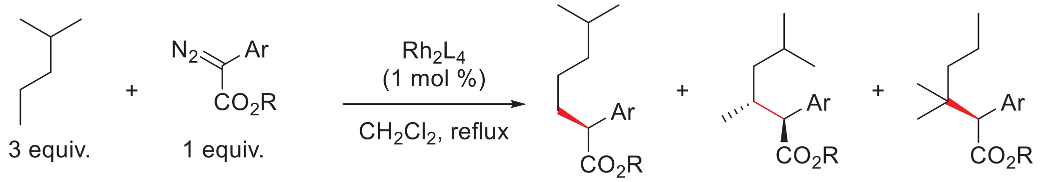
R	r.r. (**1°**:**2°**:**3°**)	e.e. (**1°**, %)	e.e. (**2°**,)	d.r. (**2°**,)	e.e. (**3°**, %)	yield (**1°**+**2°**, %)	yield (**3°**, %)
CH_3 (**3.1.49**)	n.d.: 65: 35	n.d.	n.d.	4:1	-10	15	8
CH_2CF_3 (**3.4.1**)	4: 71: 26	n.d.	93	6:1	67	57	20
CH_2CCl_3 (**2.2.17**)	7: 75: 18	81	92	7:1	23	75	16
CH_2CBr_3 (**3.4.2**)	9: 82: 10	90	92	8:1	12	75	7

Figure 3.4.4 Diazo screen for 2-methylpentane functionalization with Rh_2[*R*-3,5-di(*p*-^{t}Bu)C_6H_4TPCP$]_4$

5. Optimum Catalyst for Selective Functionalization at the Most Accessible Primary C–H Bond

As shown in Figure 3.3.1 and Figure 3.3.2, the potential direction to develop catalyst to achieve selective primary C–H bond functionalization will be exploring the linear type TPCP catalyst, therefore, a series of *para*-substituted TPCP catalysts were tested in the 2-methylpentane reaction. As shown in Figure 3.5.1, Rh_2(*R*-*p*-BrTPCP)$_4$ (**2.2.3**) and Rh_2(*R*-*p*-PhTPCP)$_4$ (**2.2.4**) gave a mixture of three regioisomers with a ratio of 39:48:13 and 39: 45:16. These are not good results but encouraged us to further explore other substituents. When Rh_2[*R*-(*p*-^{t}BuC_6H_4)TPCP]$_4$ was synthesized and tested in the 2-methylpentane reaction, a significant improvement was achieved with the product ratio as 71:25:4. However, when we tested Rh_2[*R*-(*p*-PhC_6H_4)TPCP]$_4$ and Rh_2[*R*-(*p*-^{t}Bu$C_6H_4C_6H_4$)TPCP]$_4$, the ratio didn't change (70:27:4 and 71:26:3). One notable feature of these results was the high asymmetric induction of these reactions, ranging from 96% to 98% ee. We then hypothesized the same improvement may be achieved if the other two phenyl rings at the 2-position of the cyclopropane ring are modified in the same way, so we tried Rh_2[*R*-*tris(p*-Ar)TPCP]$_4$ catalysts in the 2-methylpenatane reaction. When Rh_2[*R*-*tris(p*-Ph)TPCP]$_4$ was used, the reaction gave the ratio of 68:25:7, which was a considerable improvement compared to Rh_2(*R*-*p*-PhTPCP)$_4$ (**2.2.4**). In the case of Rh_2[*R*-*tris(p*-^{t}BuC_6H_4)TPCP]$_4$, the site-selectivity was significantly improved, and no tertiary C–H bond functionalization product was observed in the reaction giving 84:16:nd product ratio. However, the selectivity didn't increase when the bigger substituents were used because Rh_2[*R*-*tris(p*-PhC_6H_4)TPCP]$_4$ and Rh_2[*R*-*tris(p*-

^{t}BuC$_6$H$_4$C$_6$H$_4$)TPCP]$_4$ gave lower selectivity (68:25:7 and 48:35:17). Finally, Rh$_2$[*R-tris(p-*^{t}BuC$_6$H$_4$)TPCP]$_4$ was identified as the best catalyst for selective primary C–H bond functionalization.



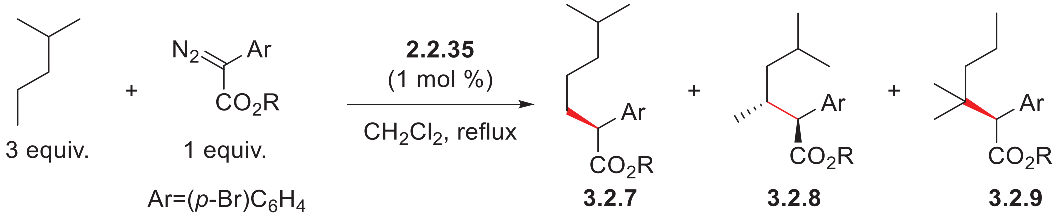
3.2.7 **3.2.8** **3.2.9**

Ar=(*p*-Br)C$_6$H$_4$
R=CH$_2$CCl$_3$ (**2.2.17**)

Catalyst	r.r. (**3.2.7**:**3.2.8**:**3.2.9**)	e.e. (**3.2.7**,%)	e.e. (**3.2.8**,%)	d.r. (**3.2.8**,%)	e.e. (**3.2.9**,%)	yield (**3.2.7**+**3.2.8**,%)	yield (**3.2.9**,%)
Rh$_2$(R-*p*-BrTPCP)$_4$ (**2.2.3**)	39: 48: 13	97	87	3:1	35	75	11
Rh$_2$(R-*p*-PhTPCP)$_4$ (**2.2.4**)	39: 45: 16	97	87	9:1	60	75	14
Rh$_2$(R-*p*-^{t}BuC$_6$H$_4$TPCP)$_4$ (**2.2.14**)	71: 25: 4	96	89	9:1	n.d.	86	4
Rh$_2$(R-*p*-PhC$_6$H$_4$TPCP)$_4$ (**2.2.21**)	70: 27: 4	98	94	11:1	n.d.	83	3
Rh$_2$(R-*p*-^{t}BuC$_6$H$_4$C$_6$H$_4$TPCP)$_4$ (**2.2.22**)	71: 26: 3	97	96	15:1	n.d.	85	3
Rh$_2$[R-tris(*p*-Br)TPCP]$_4$ (**2.2.20**)	21: 49: 30	91	62	2:1	14	62	27
Rh$_2$[R-tris(*p*-Ph)TPCP]$_4$ (**2.2.34**)	68: 25: 7	90	83	5:1	40	71	5
Rh$_2$[R-tris(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$ (**2.2.35**)	84: 16: n.d.	98	92	2:1	n.d.	90	n.d.
Rh$_2$[R-tris(*p*-PhC$_6$H$_4$)TPCP]$_4$ (**2.2.36**)	68: 25: 7	92	82	5:1	35	78	5
Rh$_2$[R-tris(*p*-^{t}BuC$_6$H$_4$C$_6$H$_4$)TPCP]$_4$ (**2.2.37**)	48: 35: 17	97	74	3:1	29	55	12

Figure 3.5.1 Catalyst screen for 2-methylpentane functionalization

Similar to the previous strategy, diazos with different ester groups were studied to find the optimum carbene precursor. As shown in Figure 3.5.2, tribromoethyl diazo was able to improve the selectivity to 87:13:nd rr, >99% ee, and 84% yield because it was believed to form a more sterically demanding carbene with the catalyst. Therefore, Rh$_2$[*R*-*tris(p*-^{t}BuC$_6$H$_4$)TPCP]$_4$ and tribromoethyl diazo (**3.4.2**) became the best combination for selective primary C–H bond functionalization.

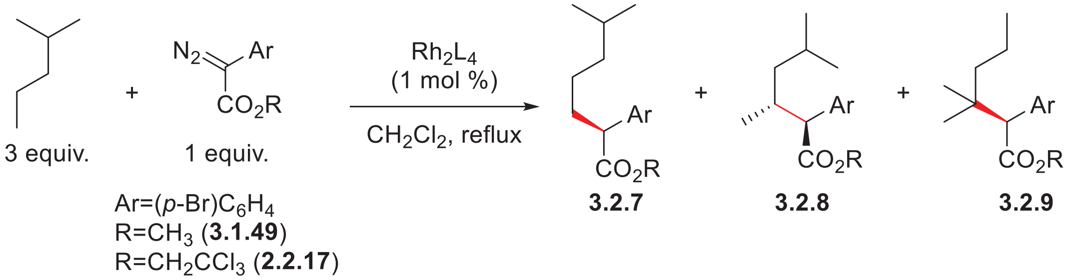


R	r.r. (**3.2.7**: **3.2.8**: **3.2.9**)	e.e. (**3.2.7**, %)	e.e. (**3.2.8**, %)	d.r. (**3.2.8**, %)	e.e. (**3.2.9**, %)	yield (**3.2.7** **+3.2.8**, %)	yield (**3.2.9**, %)
CH$_3$ (**3.1.49**)	51:35:15	n.d.	n.d.	3:1	n.d.	<5	n.d.
CH$_2$CF$_3$ (**3.4.1**)	54: 36: 10	98	94	3:1	n.d.	78	5
CH$_2$CCl$_3$ (**2.2.17**)	84: 16: n.d.	98	92	2:1	n.d.	90	n.d.
CH$_2$CBr$_3$ (**3.4.2**)	87: 13: n.d.	>99	92	7:1	n.d.	84	n.d.

Figure 3.5.2 Diazo screen for 2-methylpentane functionalization with Rh$_2$[*R*-*tris(p*-^{t}BuC$_6$H$_4$)TPCP]$_4$

6. Optimum Catalyst for Selective Functionalization at the Most Accessible Tertiary C–H Bond

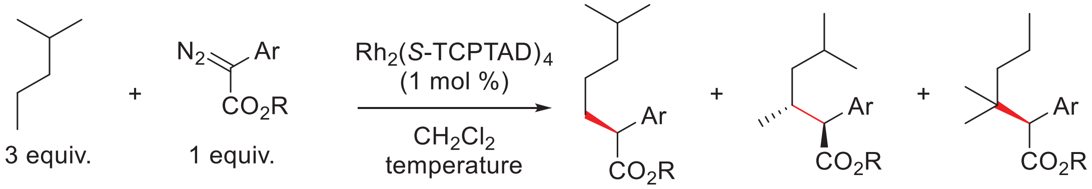
In order to develop a complete toolbox for selective C–H functionalization, we tried to develop the best catalyst for selective tertiary C–H bond functionalization. An extensive catalyst and diazo screen was conducted, and the results were shown in Figure 3.6.1. The classic Rh_2(*R*-DOSP)$_4$ showed preference at the tertiary C–H bond (nd:15:85) but the enantioselectivity was relatively poor (43% ee). Rh_2[*R*-3,5-di(*p*-^{t}Bu)C_6H_4TPCP]$_4$ (**2.2.33**) was also tried but the reaction gave an even poorer product ratio (nd:35:65) and enantioselectivity (10% ee). Rh_2(*S*-PTAD)$_4$ and Rh_2(*S*-PTAD)$_4$ also didn't give good result but their derivatives, Rh_2(*S*-TCPTAD)$_4$ and Rh_2(*S*-TCPTTL)$_4$, showed certain amount of improvement in the site-selectivity (nd:13:87 & nd:14:86) and enantioselectivity (79 & 77). Then Rh_2(*S*-TCPTAD)$_4$ was used to screen different diazos and the result suggested that the combination of Rh_2(*S*-TCPTAD)$_4$ and trifluoroethyl diazo (**3.4.1**) gave the best regioselectivity (nd:11:89) and yield (83%) but the combination of Rh_2(*S*-TCPTAD)$_4$ and trichloroethyl diazo (**2.2.17**) was shown to give better enantioselectivity (84%).



Catalyst	R	r.r. (**3.2.7**:**3.2.8**:**3.2.9**)	e.e. (**3.2.7**,%)	e.e. (**3.2.8**,%)	d.r. (**3.2.8**,%)	e.e. (**3.2.9**,%)	yield (**3.2.7**+**3.2.8**,%)	yield (**3.2.9**,%)
$Rh_2(R\text{-DOSP})_4$	CH_3	n.d.: 15: 85	n.d.	n.d.	3:1	-43	12	71
$Rh_2[R\text{-3,5-di(p-}^t\text{BuC}_6\text{H}_4\text{)TPCP}]_4$	CH_3	n.d.: 35: 65	n.d.	n.d.	4:1	-10	8	15
$Rh_2(S\text{-PTAD})_4$	CH_3	n.d.: 26: 74	n.d.	n.d.	2:1	-34	13	37
$Rh_2(S\text{-PTTL})_4$	CH_3	n.d.: 26: 74	n.d.	n.d.	2:1	-33	21	59
$Rh_2(S\text{-TCPTTL})_4$	CH_3	n.d.: 14: 86	n.d.	n.d.	2:1	77	12	74
$Rh_2(S\text{-TCPTAD})_4$	CH_3	n.d.: 13: 87	n.d.	n.d.	3:1	79	12	77
$Rh_2(R\text{-DOSP})_4$	CH_2CCl_3	n.d.: 19: 81	n.d.	69	2:1	-29	16	72
$Rh_2(R\text{-PTAD})_4$	CH_2CCl_3	n.d.: 32: 68	n.d.	-60	1:1	22	28	59
$Rh_2(S\text{-TCPTAD})_4$	CH_2CCl_3	n.d.: 11: 89	n.d.	77	2:1	84	10	74
$Rh_2(S\text{-TCPTAD})_4$	CH_2CBr_3	n.d.: 13: 87	n.d.	79	2:1	77	11	77
$Rh_2(S\text{-TCPTAD})_4$	CH_2CF_3	n.d.: 10: 90	n.d.	79	2:1	77	9	83

Figure 3.6.1 Catalyst and diazo screen for 2-methylpentane functionalization

To improve the enantioselectivity, a temperature study was conducted with the combination of Rh_2(*S*-TCPTAD)$_4$ and trifluoroethyl diazo (**3.4.1**) in the 2-methylpentane reaction. As shown in Figure 3.6.2, temperature can significantly affect the selectivity, when the temperature was decreased, the site- and enantioselectivity were increased accordingly. However, at lower temperature, the yield was decreased presumably because the substrate became less reactive and side reactions, such as dimerization, tended to be more competitive. When the reaction was cooled down to -78 °C, both the enantioselectivity and yield decreased substantially therefore -40 °C was identified as the optimum temperature to give overall the best site-selectivity (nd:4:96) and enantioselectivity (86%) with reasonable yield (77%).



Ar=(*p*-Br)C_6H_4
R=CH_2CF_3 (**3.4.1**)

3.2.7 **3.2.8** **3.2.9**

temperature (°C)	r.r. (**3.2.8**:**3.2.9**:**3.2.10**)	e.e. (**3.2.10**,%)	yield (**3.2.8**+**3.2.9**,%)	yield (**3.2.10**,%)
24	n.d.: 9: 91	77	8	77
0	n.d.: 7: 93	82	6	79
-10	n.d.: 5: 95	84	4	78
-40	n.d.: 4: 96	86	3	77
-78	n.d.: 4: 96	80	n.d.	65

Figure 3.6.2 Temperature study of 2-methylpentane functionalization with Rh_2(*S*-TCPTAD)$_4$ and trifluoroethyl diazo

7. Conclusion

Reactions with the 2-methylpentane as the model substrate revealed that $\mathrm{Rh_2}[R\text{-}3,5\text{-di}(p\text{-}^t\mathrm{Bu})\mathrm{C_6H_4TPCP}]_4$ has the overall best capability to balance the steric and electronic factors so that one of the most accessible secondary C–H bond is always preferred in the system; $\mathrm{Rh_2}[R\text{-}tris(p\text{-}^t\mathrm{BuC_6H_4})\mathrm{TPCP}]_4$ behaved as the most sterically demanding catalyst to strongly favor the most accessible primary C–H bond with superior enantio-control in the reaction; $\mathrm{Rh_2}(S\text{-}\mathrm{TCPTAD})_4$ represents the best catalyst to achieve site- and enantioselective functionalization of tertiary C–H bond. As shown in the ternary plot of Figure 3.2.15, three catalysts were identified as the best catalyst for selective functionalization at the most accessible primary, secondary and tertiary C–H bonds.

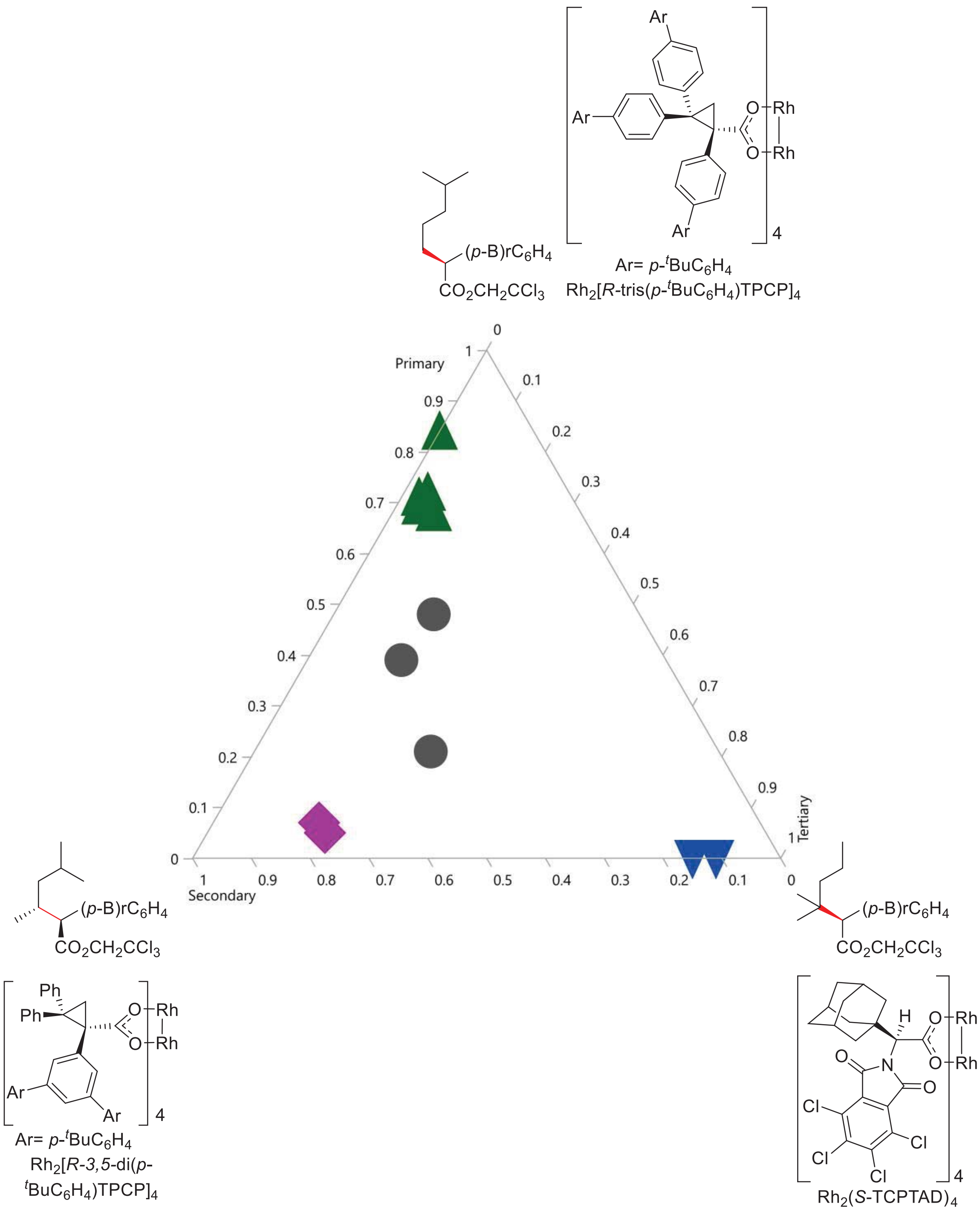


Figure 3.7.1 Catalyst controlled C–H functionalization of 2-methylpentane

Chapter 4 Selective Functionalization of the Most Accessible Secondary C–H bond

1. Catalyst Structure Analysis

In the alkane reactions, Rh_2[*R*-3,5-di(*p*-^{t}Bu)C_6H_4TPCP]$_4$ (**2.2.32**) was identified as the optimal catalyst for selective functionalization at the most accessible secondary C–H bond. Further studies to determine the scope of potential reactions will be described in this chapter.

The single crystal X-ray structure of Rh_2[*S*-3,5-di(*p*-^{t}Bu)C_6H_4TPCP]$_4$ (**2.2.32**) was obtained through slow evaporation of ethyl ether/pentane (1:100), and the analysis conducted by John Bacsa revealed that in the solid state, the catalyst adopts the α,β,α,β-arrangement (Figure 4.1.1), which was consistent with the computational study (Figure 3.3.2).

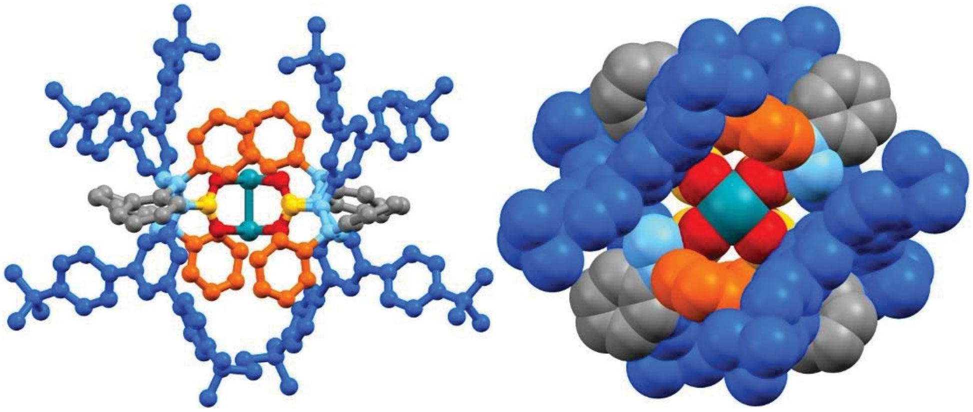


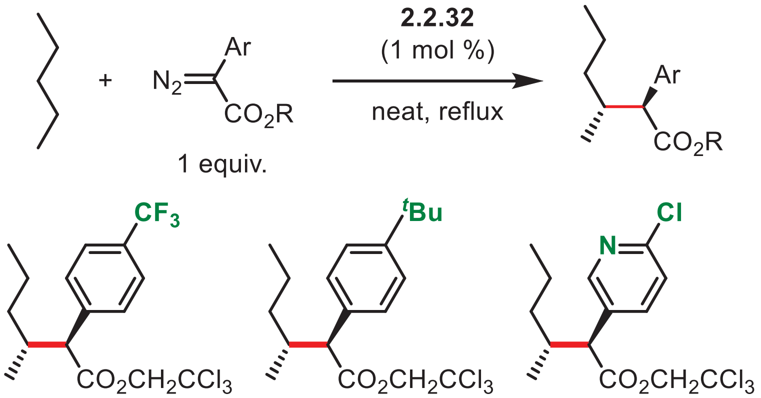
Figure 4.1.1 Single crystal X-ray structure of Rh_2[*S*-3,5-di(*p*-^{t}Bu)C_6H_4TPCP]$_4$ (**2.2.32**) (axially coordinated solvent molecules have been removed)

The catalyst structure is close to D_2 symmetric and both faces of the dirhodium catalysts are the same. In that case, the number of rhodium carbene arrangement will be limited when the carbene binds to the dirhodium core, and the aryl ring of the carbene was believed to π-stacking with the aryl ring of one ligand due to the chiral environment. It has been proposed that C–H functionalization is proceeded through a concerted but asynchronous mechanism where the hydrogen of the C–H bond first approaches the rhodium carbene site.[44] Therefore, in the rhodium carbene structure, one face is blocked and only the opposite face is open for the C–H bond to approach so that the enantioselectivity of the benzylic chiral center can be achieved. The sophisticated rhodium carbene structure can also generate a narrow channel to block more sterically demanding C–H bonds (C3) from approaching the rhodium carbene center and allow the less sterically demanding C–H bonds at C1 and C2 positions to react with the rhodium carbene. As the C–H bond at the C2 position is more reactive than the C–H bond at the C1 position, the majority of the reaction occurred at the C2 position. Another important feature of this catalyst in the *n*-pentane reaction was the ability to control diastereoselectivity of the reaction by forcing only one of the methylene C–H bonds at the C2 position to approach the rhodium carbene center, which was a limitation of previously reported C–H functionalization reactions.[43]

2. Substrate Scope

To further develop the catalyst system to achieve selective functionalization at the most accessible secondary C–H bond, the substrate scope was explored. In order to establish a more applicable system, 3 equiv of substrate were used, and the reactions were conducted in dichloromethane as solvent under reflux condition.

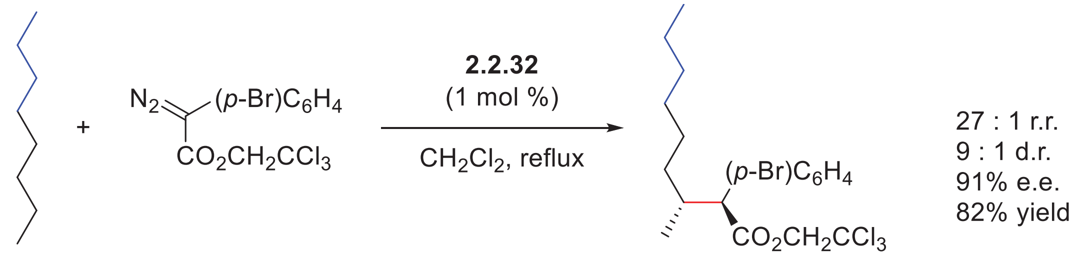
In the initial study of the pentane reaction, 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**3.1.50**) was used as the model carbene precursor. The reaction was extended to a series of aryl-substituted carbenes, including electron withdrawing (CF_3), electron donating (^{t}Bu), and a heterocycle (2-chloropyridine) (Figure 4.2.1). The selectivity was somewhat diminished for the *p*-trifluoromethyl derivative (**4.2.1**: 15: 1 r.r., 14: 1 d.r., 97% e.e.), but the selectivity was improved for the *p*-tertbutyl derivative (**4.2.2**: 22: 1 r.r., 24: 1 d.r., >99% e.e.). The potential breadth of utility of the C–H functionalization is illustrated with a pyridine system, which is an effective substrate for this chemistry. Indeed, the C–H functionalization product **4.2.3** was produced with the highest diastereoselectivity to date (55:1 d.r.).



4.2.1	**4.2.2**	**4.2.3**
15:1 r.r.	22:1 r.r.	28:1 r.r.
14:1 d.r.	24:1 d.r.	55:1 d.r.
97% e.e.	>99% e.e.	91% e.e.
91% yield	91% yield	87% yield

Figure 4.2.1 Evaluation of the scope of Rh_2[*R*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$-catalyzed C–H functionalization of *n*-pentane with different aryl diazo compounds

One of the major concerns about Rh_2(*S*-DOSP)$_4$ catalyzed *n*-pentane functionalization mentioned in Chapter 3 was the potential decrease of selectivity when longer alkane or other complex molecules are used as substrates. Therefore, *n*-octane was examined in the Rh_2[*R*-3,5-di(*p*-^{t}Bu)C_6H_4TPCP]$_4$ (**2.2.32**) catalyzed reaction (**4.2.4**). As shown in Figure 4.2.2, the regioselectivity remained similar to that of *n*-pentane. The data support the hypothesis that no other internal C–H bond will be involved in the reaction when longer alkane substrates are used. Other than alkane, terminally substituted alkane, such as *n*-alkyl halides, silanes and esters, were also tested in the system.

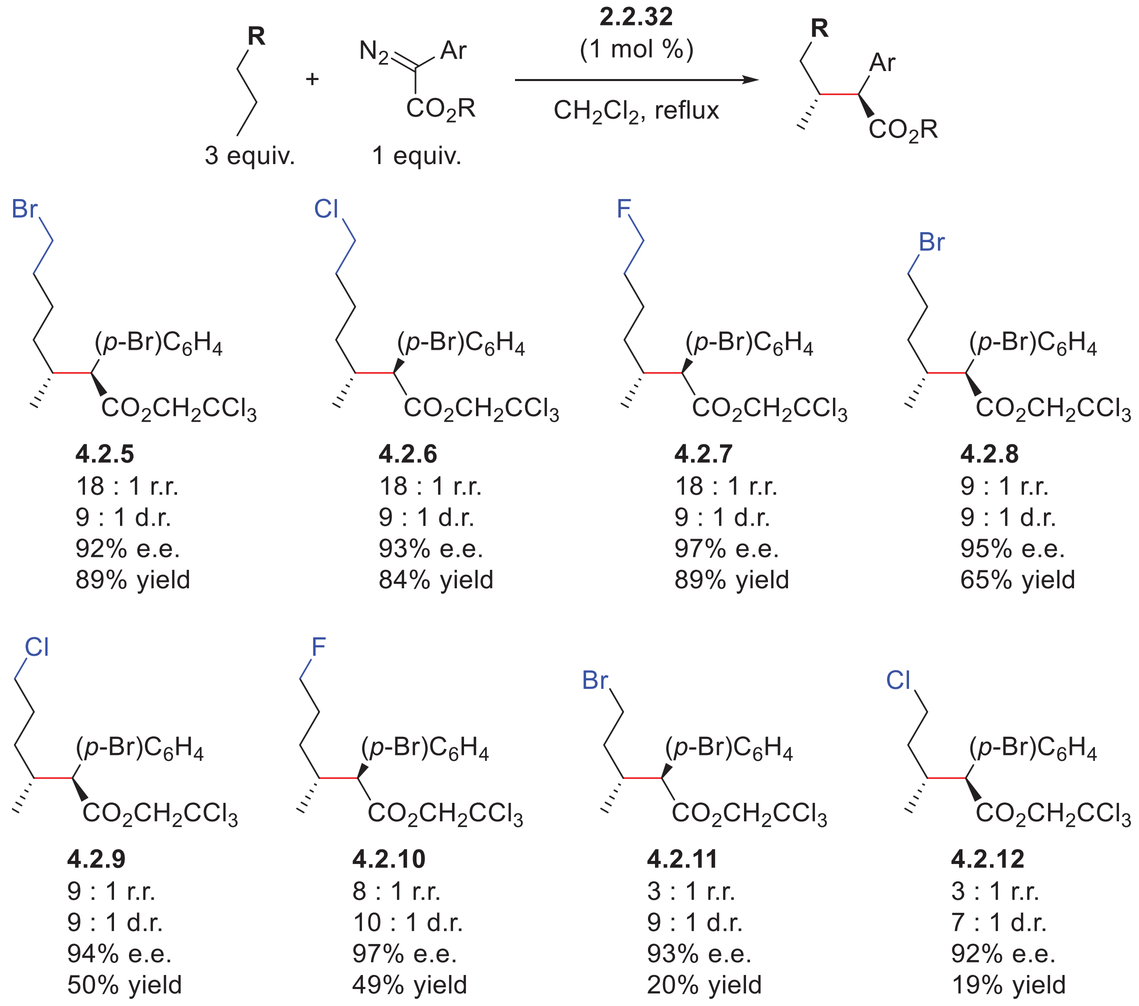


3 equiv. 1 equiv.

3.1.1 **3.1.50** **4.2.4**

Figure 4.2.2 Rh$_2$[*R*-3,5-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$-catalyzed C–H functionalization of *n*-octane

n-Alkyl halides are cheap and versatile feedstock chemicals in organic chemistry, so the corresponding C–H functionalization will be useful because it can generate value added products (Figure 4.2.3). Indeed, products generated from 1-bromo-, 1-chloro- and 1-fluorohexane (**4.2.5-4.2.7**) possessed high site-selectivity (18: 1 r.r.) and enantioselectivity (92-97% e.e.), but the diastereoselectivity was somewhat diminished (9: 1 d.r.). Even though 1-bromo-, 1-chloro- and 1-fluoropentane (**4.2.8-10**) gave high enantioselectivity (94-97% e.e.) and similar diastereoselectivity (9-10: 1 d.r.), the site-selectivity (8-9: 1 r.r.) and yield (49-65%) of the reactions were lowered. In terms of 1-bromo- and 1-chlorobutane (**4.2.11** & **4.2.12**), the site-selectivity (3: 1 r.r.) and yield (19-20%) were significantly decreased, but the diastereoselectivity (7-9: 1 d.r.) and enantioselectivity (92-93% e.e.) remained similar to halogenated hexane and pentane. These results indicate that the halogens are displaying a long-range inductive effect, which slightly deactivates the C2 position inhibiting C–H functionalization. Such a characteristic could become a useful controlling element in more complex systems and the corresponding pattern was studied with a quantitative model which will be discussed in Chapter 7.



4.2.5
18 : 1 r.r.
9 : 1 d.r.
92% e.e.
89% yield

4.2.6
18 : 1 r.r.
9 : 1 d.r.
93% e.e.
84% yield

4.2.7
18 : 1 r.r.
9 : 1 d.r.
97% e.e.
89% yield

4.2.8
9 : 1 r.r.
9 : 1 d.r.
95% e.e.
65% yield

4.2.9
9 : 1 r.r.
9 : 1 d.r.
94% e.e.
50% yield

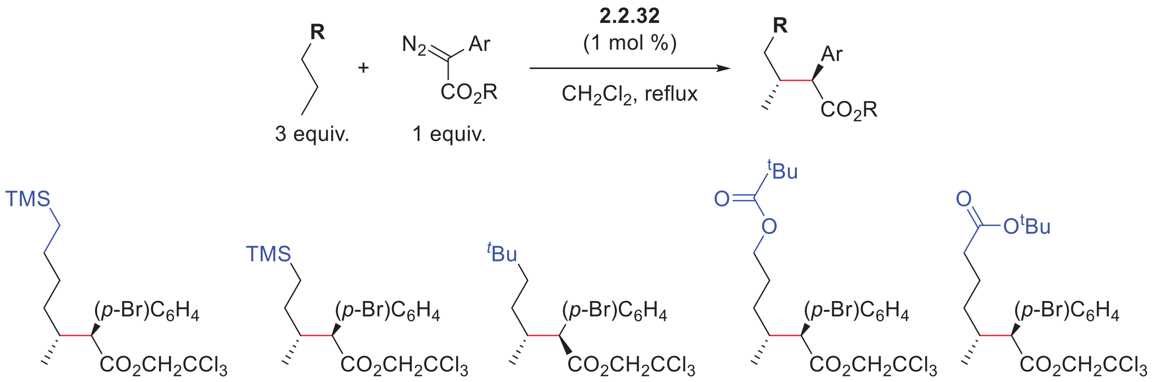
4.2.10
8 : 1 r.r.
10 : 1 d.r.
97% e.e.
49% yield

4.2.11
3 : 1 r.r.
9 : 1 d.r.
93% e.e.
20% yield

4.2.12
3 : 1 r.r.
7 : 1 d.r.
92% e.e.
19% yield

Figure 4.2.3 Rh_2[*R*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$-catalyzed C–H functionalization of *n*-alkyl halides

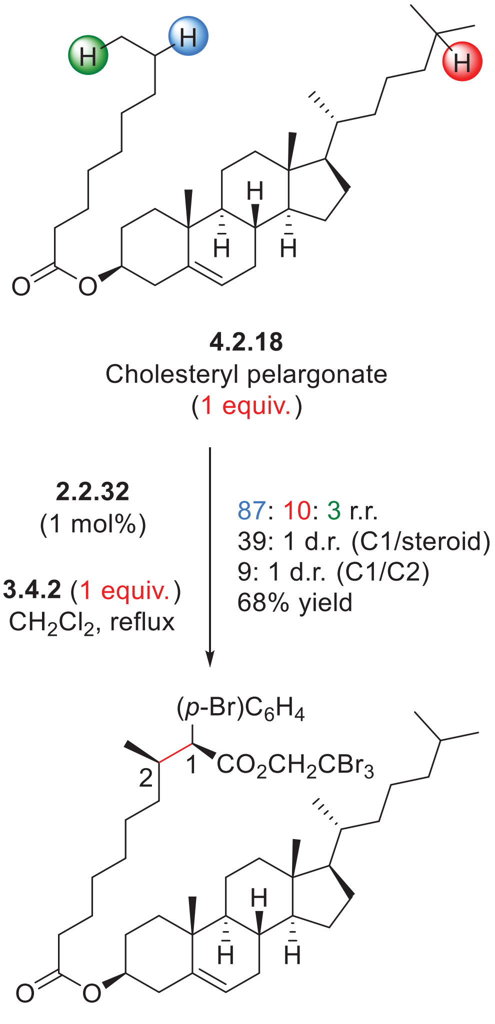
n-Alkyl silanes are interesting substrate and have been substrates for C–H functionalization.[99] However, the selectivity was limited to the *beta* C–H bonds because they are electronically activated by the beta silicon effect. In this system, rhodium carbene generated by the catalyst is sterically demanding so we hypothesize the steric influence can diminish the reaction from occurring at the *beta* position. Hexyltrimethylsilane and butyltrimethylsilane gave very high selectivity at the most accessible secondary C–H bond although the diastereoselectivity of butyltrimethylsilane functionalization was decreased (**4.2.14** & **4.2.15**). Another functional group that is compatible with this chemistry is an ester as illustrated in the formation of **4.2.16** and **4.2.17**, again with strong preference for functionalization of the methylene C–H bond (Figure 4.2.4).



4.2.13	**4.2.14**	**4.2.15**	**4.2.16**	**4.2.17**
20 : 1 r.r.	34 : 1 r.r.	33 : 1 r.r.	21 : 1 r.r.	16 : 1 r.r.
9 : 1 d.r.	4 : 1 d.r.	4 : 1 d.r.	7 : 1 d.r.	9 : 1 d.r.
90% e.e.	99% e.e.	90% e.e.	92% e.e.	91% e.e.
85% yield	40% yield	89% yield	83% yield	84% yield

Figure 4.2.4 Rh_2[*R*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$-catalyzed C–H functionalization of *n*-alkyl silanes and *n*-alkyl ester

A major test for site-selective C–H functionalization is the determination if control can be achieved in elaborate substrates. Therefore, the reactions of a natural product, cholesteryl pelargonate, was examined (Figure 4.2.5). As the substrate is more valuable than simple substituted alkane, the substrate to diazo was set to be 1:1. This was a great improvement because for most of the reported reactions substrate was even used as solvent. There are three positions were involved in the competition, including the most accessible primary (green), secondary (blue) and tertiary (red) C–H bond, so tribromoethyl derivative (**3.4.2**) was used in the reaction and 87% of the reaction occurred at the desired position with high diastereoselectivity. More impressive result was the effectiveness of the reaction because 68% yield was obtained even though only 1 equivalent of substrate was used.



4.2.19

Figure 4.2.5 $Rh_2[R\text{-}3,5\text{-di}(p\text{-}{}^{t}BuC_6H_4)TPCP]_4$-catalyzed C–H functionalization of Cholesteryl pelargonate

3. Conclusion

In conclusion, these studies demonstrate that the Rh_2[*R*-3,5-di(*p*-^{t}BuC_6H_4)TPCP$]_4$-catalyzed reactions of donor/acceptor carbenes have a strong preference for functionalization at the most accessible secondary C–H bond. Presumably, the C–H functionalization at the most accessible primary C–H bond due to electronics, whereas the steric environment around the catalyst is sufficient to distinguish the target C–H from other secondary and tertiary C–H bonds.

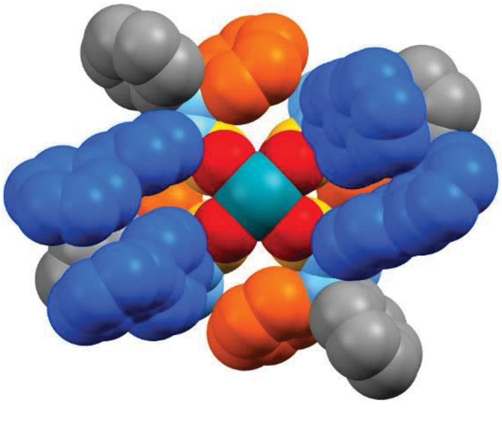
Chapter 5 Selective Functionalization of the Most Accessible Primary C–H bond

1. Introduction

In chapter 3, a milestone study about selective borylation and carbene insertion of methyl C–H bond were described, however, site- and enantioselective methyl C–H bond functionalization was still challenging.[87, 98] In this chapter, site- and enantioselective functionalization of the most accessible primary C–H bond will be discussed in detail.

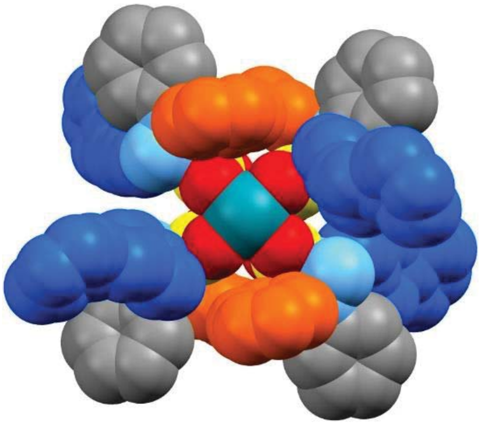
2. Catalyst Structure Analysis

As discussed in chapter 3, in 2-methylpentane reaction, Rh_2[*R-tris(p-*^{t}BuC$_6$H$_4$)TPCP]$_4$ (**2.2.34**) exhibited good control in selective functionalization of the most accessible primary C–H bond. In this chapter, structural investigations of it and related catalysts will be discussed. Suitable crystals of Rh_2[*R-tris(p-*^{t}BuC$_6$H$_4$)TPCP]$_4$ (**2.2.34**) could not be obtained but single crystals of two related catalysts, **2.2.4** and **2.2.20** were obtained and the X-ray crystallographic data were analyzed by John Bacsa. As shown in Figure 5.2.1, catalyst **2.2.20** adopts an α, β, α, β-orientation (close to D_2 symmetric structure), whereas catalyst **2.2.4** adopts an α, α, α, α-orientation (close to C_2 symmetric structure). With two different types of structures observed in the solid state, we decided to investigate the Rh_2[*R-tris(p-*^{t}BuC$_6$H$_4$)TPCP]$_4$ catalyst and rhodium carbene structures with computational methods so that we can understand how selectivity is accomplished.



Rh_2(*S-p*-PhTPCP)$_4$

2.2.4



Rh_2(*S-p*-PhC$_6$H$_4$TPCP)$_4$

2.2.20

α, α, α, α-orientation α, β, α, β-orientation

Figure 5.2.1 Single crystal X-ray structures of Rh_2(*S*-*p*-PhTPCP)$_4$ (**2.2.4**) and Rh_2(*S*-*p*-PhC$_6$H$_4$TPCP)$_4$ (**2.2.20**)

To further understand the catalyst structure and reaction mechanism, collaboration with Ken Houk and his coworkers, Yunfang Yang, Yingzi Li, and Jacob Sanders, was launched. Given that the catalyst contains nearly 500 atoms, Ken Houk and his coworkers employed the two-layer ONIOM (B3LYP:UFF) approach to study the catalyst structure and C–H functionalization selectivity using the partitioning shown in Figure 5.2.2. These ONIOM calculations reveal that Rh_2[*R-tris(p*-^{t}BuC$_6$H$_4$)TPCP]$_4$ (**2.2.34**) can adopt at least four orientations; however, there were only two major conformations. From the energy point of view, the up, side, up, side-orientation (close to C_2-symmetric conformation) favored over the up, up, up, up-orientation (close to C_4-symmetric conformation) by an energy difference of 10.1 kcal/mol.

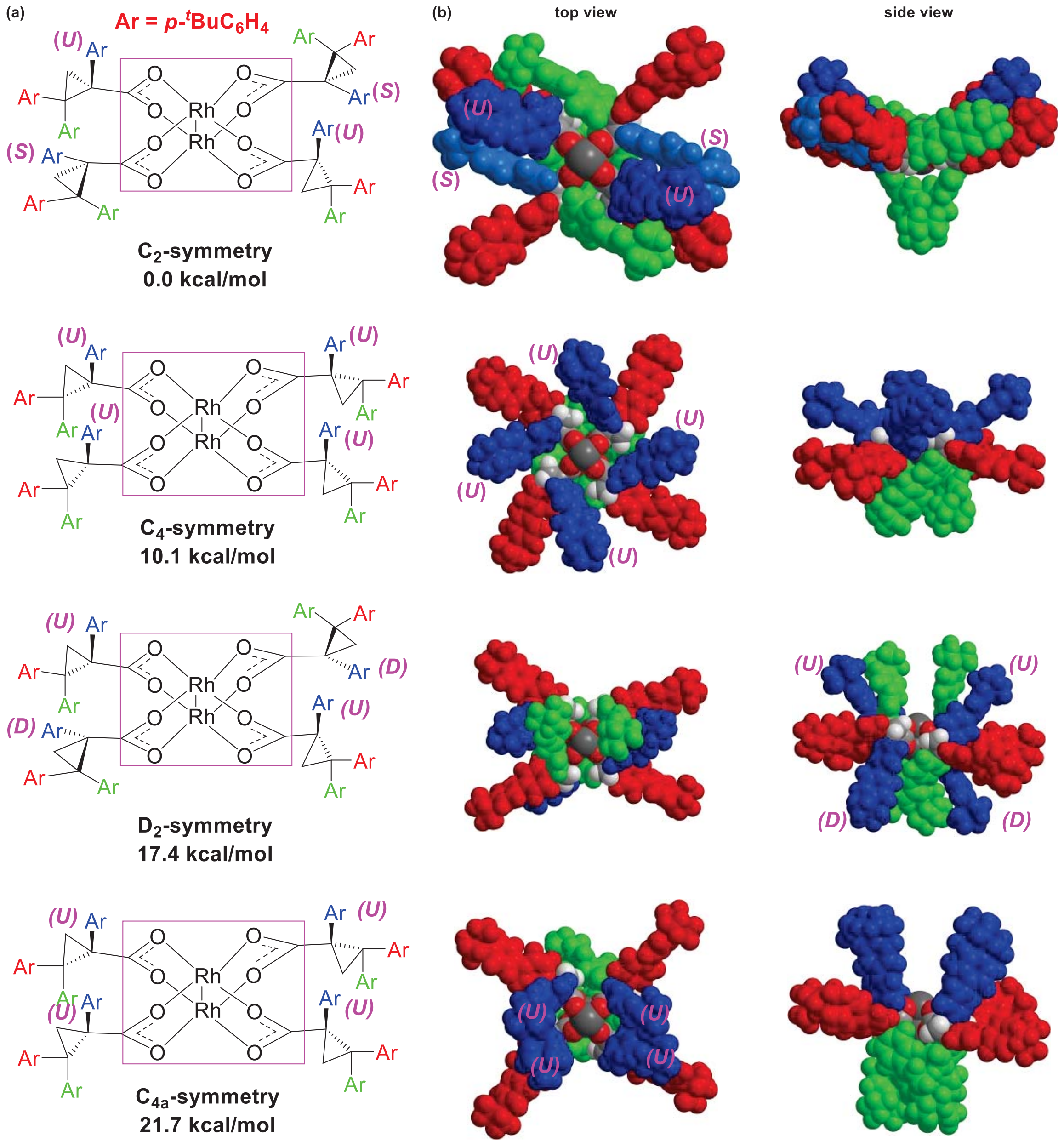
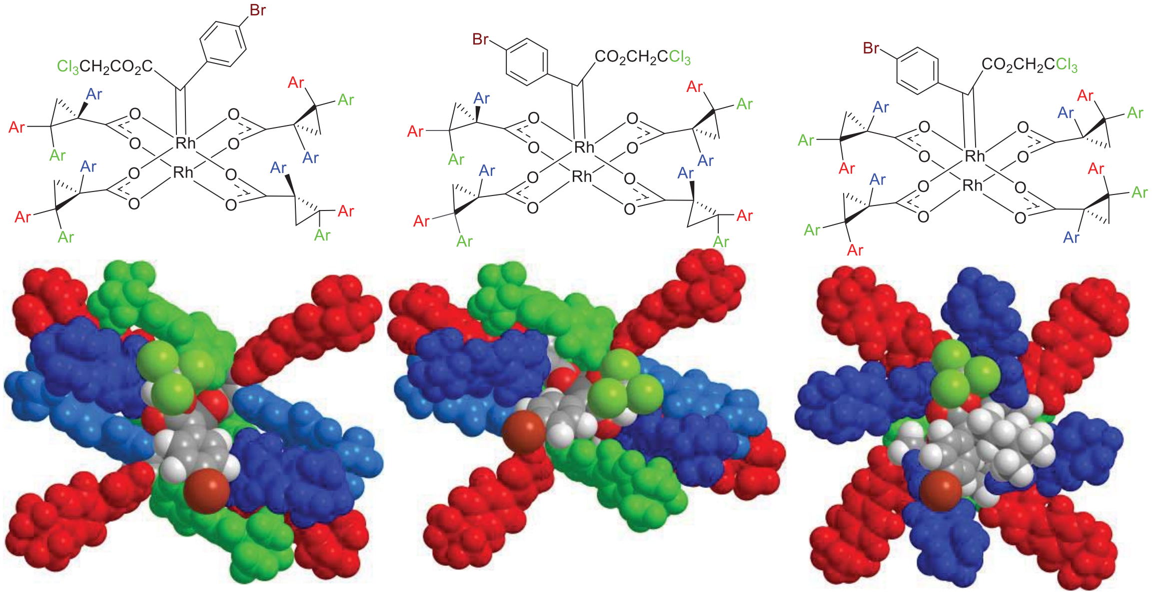


Figure 5.2.2 Structural information about Rh_2[*R-tris(p-*^{t}BuC$_6$H$_4$)TPCP]$_4$ (**2.2.34**)

Based on the calculated catalyst structures, three possible rhodium carbene structures were obtained from the C_2- and C_4-symmetric catalyst structures. As shown in Figure 5.2.3, the energy difference between two rhodium carbenes derived from C_2-symmetric catalyst were very close to each other. Although the rhodium carbene energy derived from C_4-symmetric catalyst was much higher than those derived from C_2-symmetric catalyst, it was still taken into consideration when we conducted the transition state study.



C2-carbene
0.0 kcal/mol

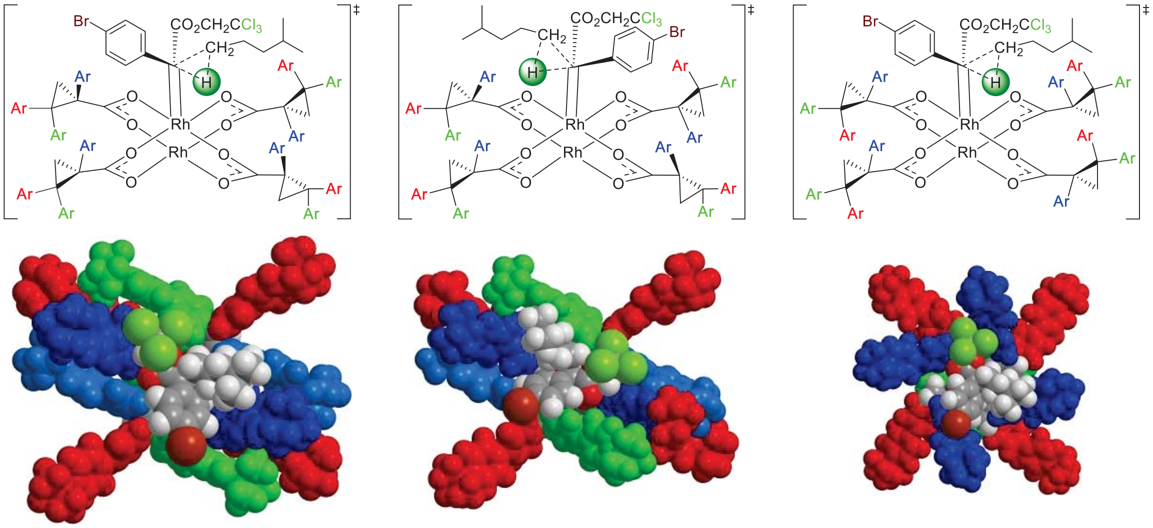
C2a-carbene
-1.5 kcal/mol

C4-carbene
11.7 kcal/mol

Figure 5.2.3 Structural information about rhodium carbene derived from Rh_2[*R-tris(p-*${}^tBuC_6H_4$)TPCP]$_4$ (**2.2.34**) and **3.1.50**

The ONIOM transition structures of the two major catalyst structures for rhodium carbene (derived from **3.1.50**) insertion into the primary C–H bond were calculated and showed in Figure 5.2.4. The substrate fits into the open pocket at the top of the rhodium carbene and binds to the upper rhodium atom. The bottom rhodium atom is blocked by two ^{t}butylbiphenyl groups. The C–H functionalization step is a concerted but asynchronous carbene insertion into the C–H bond, and the transition state predominantly involves movement of the hydrogen in the C–H bond towards the carbene carbon. The energy difference revealed that the energetically favored transition state was **TS1** generated from the C_2-symmetric rhodium carbene structure.

Therefore, for the C_2 catalyst, the transition structure for rhodium carbene insertion into the primary C–H bond from the *Si* face of the rhodium carbene, **TS1**, is energetically favored by 3.1 kcal/mol over **TS2** (primary C–H bond approached from the opposite face of the rhodium carbene), which is in excellent agreement with the experimentally observed enantioselectivity of 98% e.e. The destabilization of **TS2** arises from the alkyl substrate repulsions with the "up" biphenyl moiety. Because there are significant contacts between alkyl and aryl groups, and there are likely a variety of low energy conformations, more extensive computations with dispersion and dynamic averaging are underway.



TS1
$\Delta\Delta E^{\ddagger} = 0.0$ kcal/mol

TS2
$\Delta\Delta E^{\ddagger} = 3.1$ kcal/mol

TS3
$\Delta\Delta E^{\ddagger} = 10.4$ kcal/mol

Figure 5.2.4 Optimized transition structures for rhodium carbene insertion into the primary C–H bond

3. Substrate Scope

In Chapter 3, the optimized reaction condition was obtained, therefore, a set of substrates were tested to further understand the primary C–H functionalization (Figure 5.3.1). Initially several alkanes were examined to determine the influence of the steric environment within the substrate on site-selectivity (**5.3.1-5.3.8**). In contrast to 2-methylpentane, the methylene group in 2-methylbutane is not susceptible to functionalization because the methylene site is sterically blocked by the adjacent isopropyl group. The tribromoethyl product **5.3.1** was formed with better selectivity for the most accessible primary C–H bond (90:10 r.r., >99% e.e.) compared to the trichloroethyl product **5.3.2** (89:11 r.r., 90% e.e.) but the yield was lower (**5.3.1**, 40%; **5.3.2**, 82%). However, in the case of 3-methylpentane the tertiary site is slightly more crowded than 2-methylbutane and this is enough for the reaction to proceed cleanly for the primary C–H insertion product **5.3.3**. In contrast to another study in which only tertiary C–H functionalization product **5.3.3** was observed with Rh_2(*S*-TCPTAD)$_4$ (see Chapter 6), C–H functionalization occurred only at the most accessible primary C–H bond with Rh_2[*R-tris(p-*^{t}BuC$_6$H$_4$)TPCP]$_4$ (**2.2.34**), the more crowded secondary site and the tertiary site were no longer functionalized. Similarly, highly selective reactions were observed in the formation of **5.3.4-5.3.14**. The reaction with 2,2-dimethylbutane to form **5.3.4** was notable because in the past 2,2-dimethylbutane has been extensively used as an "inert" solvent for donor/acceptor carbene C–H functionalization. One interesting case was the reaction with 3,3-dimethylpentane which gave clean formation of **5.3.5** with extremely high site- and enantioselectivity (>98: 2 r.r., >99% e.e.), this presented the superior capability in differentiating ethyl group from methyl group. Similar type of steric subtleties was readily seen in the reactions to form **5.3.8** and **5.3.13**, which demonstrated the catalyst's ability to differentiate propyl group from ethyl group because reaction at the primary C–H bond on the propyl group is favored over ethyl group (marked in green). The formation of **5.3.7** with very high site-selectivity (>98:2 r.r.) and enantioselectivity (98% e.e.) shows the current system is superior to the best previously reported chiral catalyst, a rhodium-porphyrin catalyst, which formed **5.3.7** with relatively poor primary/secondary ratio (3.8:1 r.r.) and enantioselectivity (65% e.e.).[98] The absolute configuration of **5.3.7** was confirmed by the single crystal X-Ray crystallographic data, and the configuration of other products were assigned by analogy.

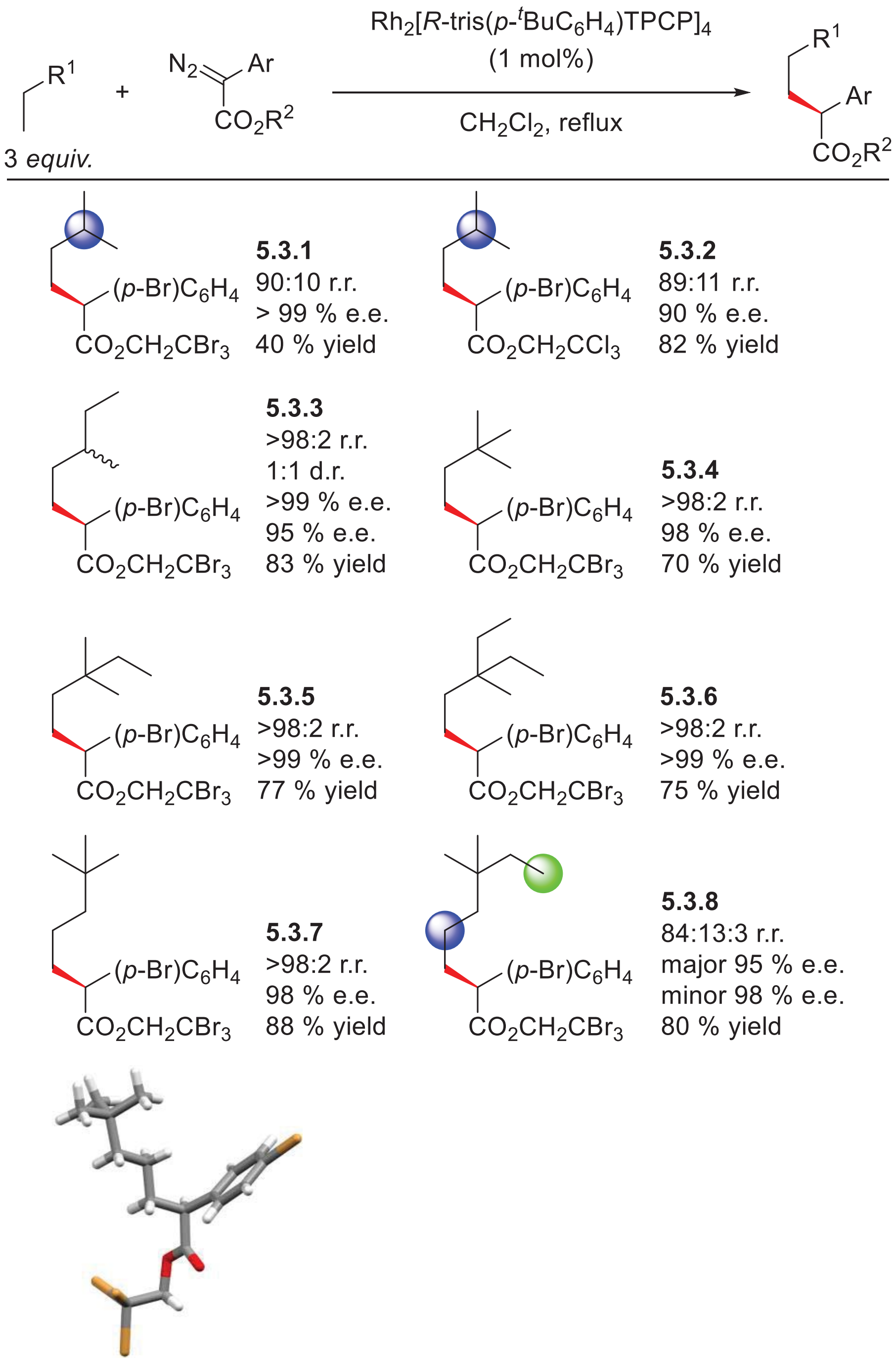


Figure 5.3.1 Rh_2[*tris(p-*^{t}BuC_6H_4)TPCP]$_4$-catalyzed C–H functionalization of alkanes

In terms of the studies conducted with a series of trimethylsilyl (TMS) protected alcohols to form **5.3.9-5.3.13**, the reactions proceeded with excellent selectivity, but the yields were lower when the inductively electron-withdrawing group was too close to the site of C–H functionalization, as seen in the case of **5.3.9** and **5.3.10** (Figure 5.3.2). The reactions with TMS protected 3-ethyl-3-hexanol to form **5.3.9** is a further illustration of the subtle steric effects because reaction at the primary C–H bond of the propyl group is strongly preferred over that of the other two ethyl groups in the substrate. 1-Bromobutane is also a viable substrate, forming **5.3.14** with high enantioselectivity (93% e.e.) but with some competition from C–H functionalization as the secondary C–H bond marked in blue with a ratio of 84:16. As the emphasis of this study has been to determine the subtleties of the site-selectivity, the studies so far have concentrated on a single aryl group in the donor/acceptor carbene. However, the donor group can be varied, and this is illustrated in the reactions of 2,2-dimethylpentane to form the boronic ester and trifluoromethyl derivatives **5.3.15** and **5.3.16**.

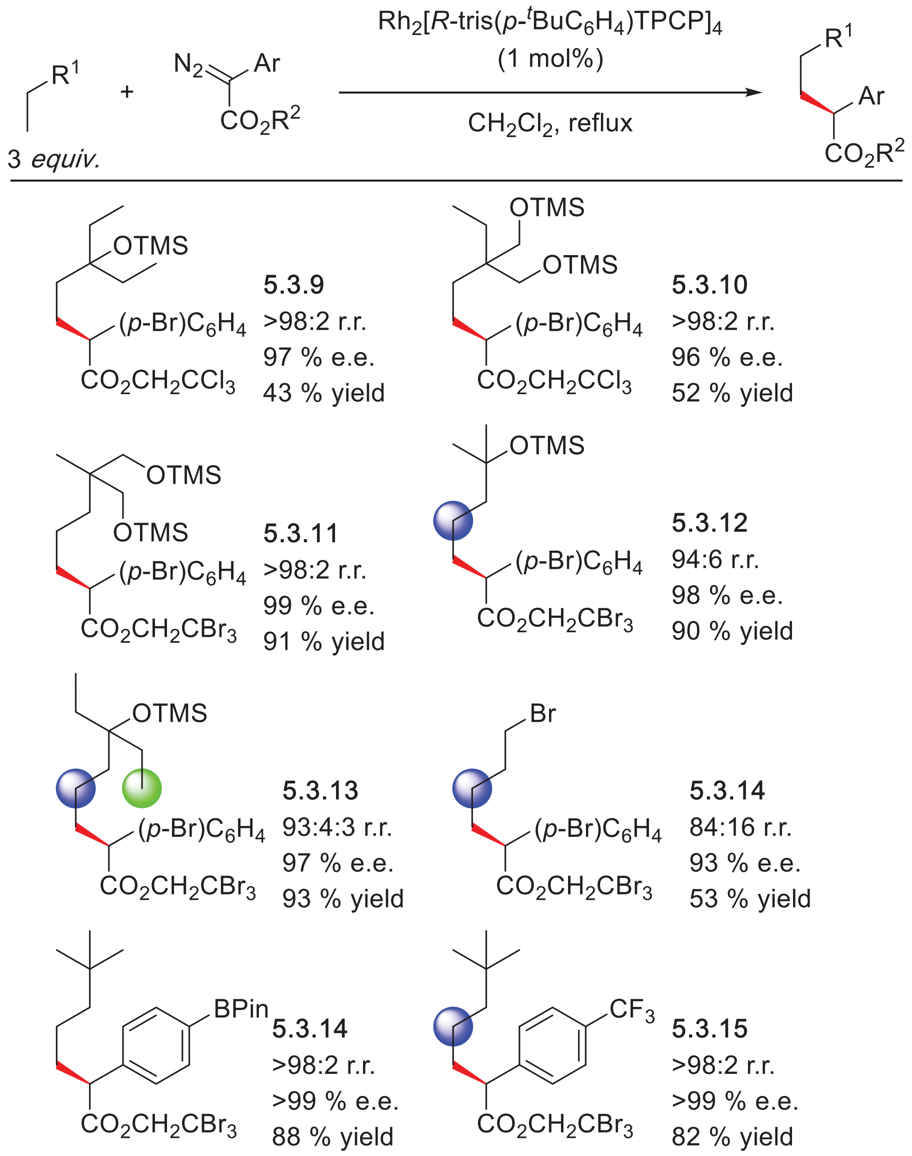


Figure 5.3.2 Evaluation of the scope of Rh$_2$[*tris(p-*^{t}BuC$_6$H$_4$)TPCP]$_4$-catalyzed C–H functionalization

As the reaction gave extremely high asymmetric induction, it was proposed to be an effective way to synthesize diastereo-pure compounds. In Figure 5.3.3, we have also examined the Rh$_2$[*tris(p-*^{t}BuC$_6$H$_4$)TPCP]$_4$-catalyzed reactions with enantiomerically pure substrates **5.3.17-5.3.19**. In these substrates, the internal methyl group is sufficient to block any C–H functionalization reactions at the methylene sites, and all the substrates react cleanly. The reactions are under catalyst control because the reaction with Rh_2[*R*-*tris*(*p*-^{t}BuC_6H_4)TPCP]$_4$ (**2.2.34**) gives one diastereomeric series of the products **5.3.20-5.3.22**, in which the newly formed stereocenter has the *S*-configuration, whereas the reaction with Rh_2[*S*-*tris*(*p*-^{t}BuC_6H_4)TPCP]$_4$ (**2.2.34**) gives the opposite diastereomeric series **5.3.23-5.3.25**.

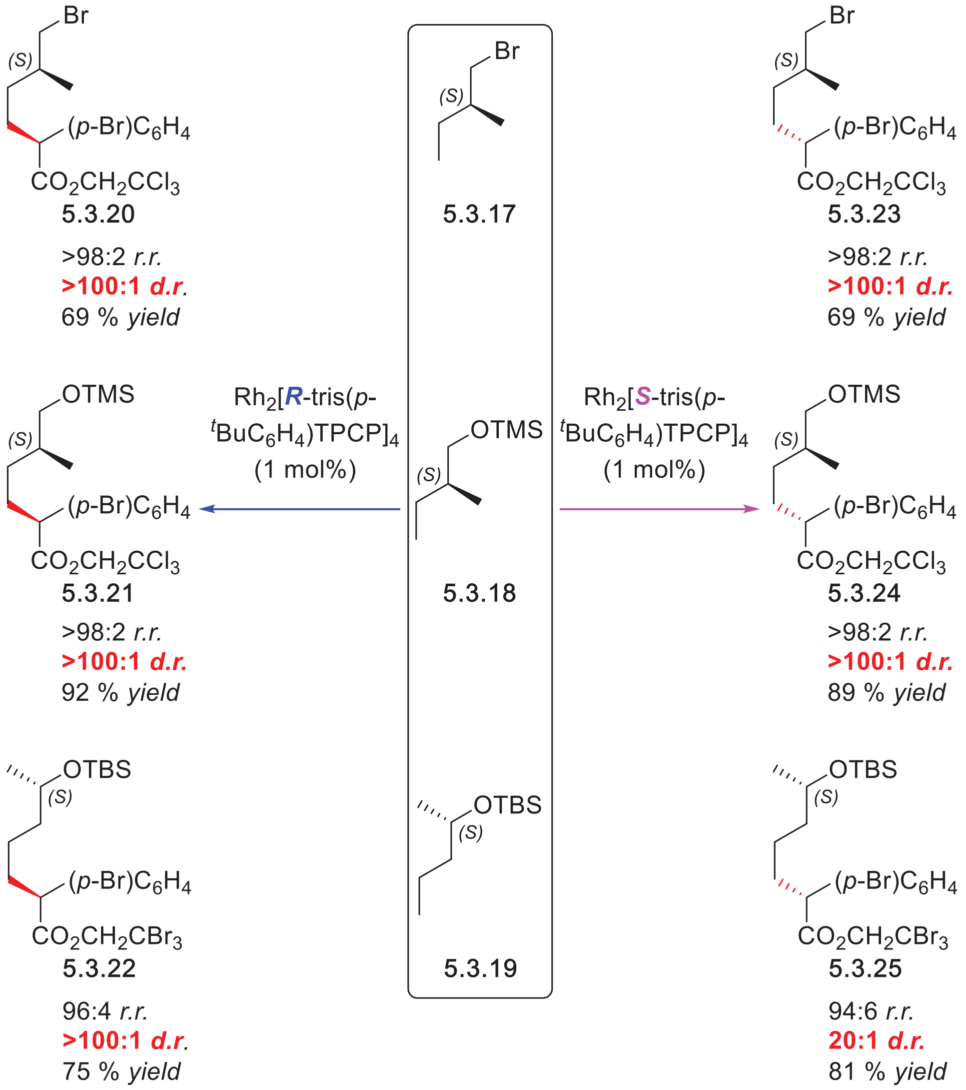


Figure 5.3.3 Catalyst-controlled diastereoselective primary C–H functionalization

4. Conclusion

The study described in this chapter demonstrates that by appropriate design of the catalyst, site-selective C–H functionalization at the most accessible primary C–H bond is also a viable process. Such selectivity is the most challenging for the donor/acceptor carbenes because it goes against the normal electronic preference of these intermediates. Considering that group transfer reactions can be conducted with a range of different types of metal carbenes beyond donor/acceptor carbenes as well as metal nitrene and metal oxo intermediates, these studies are likely to encourage further efforts in catalyst design to control site-selectivity. In conclusion, the discoveries of Rh_2[*S*-*tris(p*-^{t}BuC_6H_4)TPCP]$_4$ (**2.2.34**) and Rh_2[*R*-3,5-di(*p*-^{t}Bu)C_6H_4TPCP]$_4$ (**2.2.32**) demonstrated that it is possible to obtain catalysts to achieve high site-selectivity at either primary or secondary C–H bonds without resorting to the use of directing groups within the substrate.

Chapter 6 Selective Functionalization of the Most Accessible Tertiary C–H bond

1. Introduction

In Figure 3.1.8, a breakthrough in asymmetric alkane C–H functionalization with donor/acceptor rhodium carbene was discussed, several simple alkanes were reported to be suitable for selective C–H carbene insertion. However, the reactions were conducted in neat condition, at various temperature, site- and enantioselectivity were relatively low. Therefore, a tertiary selective catalyst, $Rh_2(TCPTAD)_4$, was developed in the 2-methylpentane system (Figure 3.6.1 and 3.6.2). However, the substrate has only one tertiary C–H bond, to further understand and develop a catalyst to achieve selective functionalization at the most accessible tertiary C–H bond, studies in catalyst structure and substrate scope were conducted.

In 1996, Hashimoto developed Rh_2(*S*-PTTL)$_4$ [61], which was the parent catalyst for the development of Rh_2(*S*-PTAD)$_4$[71]. Later in 2002, Rh_2(*S*-TCPTTL)$_4$ [62] was also developed for enantioselective C–H amidation. Computational and experimental studies[64-69] showed that the tetrachloro functionality rigidifies the structure and generates a chiral crown shape with all phthalimido groups on the same face of the catalyst.[45]

Inspired by the Hashimoto's work, the Davies group developed a similar catalyst, $Rh_2(TCPTAD)_4$, for enantioselective C−H aminations. However, the catalyst wasn't considered as useful in carbene C–H insertion until 2015, where it was used in rhodium(II)-catalyzed double C−H insertion at the C2- and C5-positions of an N-alkylpyrrole.[100] This surprise result brought our attention to further understand this type of catalyst.

In Figure 3.6.1, a dramatic difference was seen between the adamantyl catalysts Rh_2(*S*-PTAD)$_4$ and Rh_2(*S*-TCPTAD)$_4$, in which the former, lacking the chlorine functionality, gave poor site-selectivity as well as relatively low and opposite enantioselectivity.

2. Catalyst Structure Analysis

To understand the catalyst structure and mechanism, single crystal X-ray structure of Rh_2(*R*-TCPTAD)$_4$ was obtained through slow evaporation of acetonitrile/ether/hexane (1:5:10) and the data was analyzed by Thomas C. Pickel and John Bacsa. As shown in Figure 6.2.1, in the solid state, the catalyst adopts the α,α,α,α-arrangement with all the phthalimido groups on the same side but is slightly distorted from a perfect C_4 symmetric structure (Figure 6.2.1).

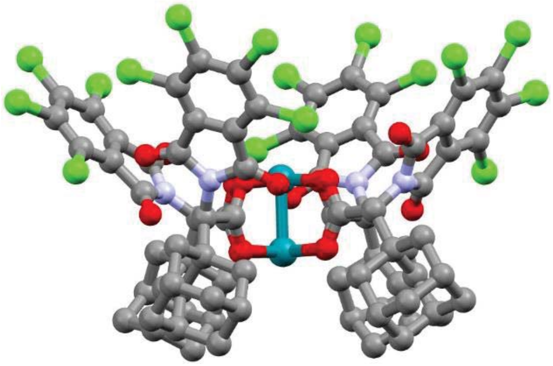


Figure 6.2.1 Single crystal X-ray structure of Rh_2(*R*-TCPTAD)$_4$

Computational studies on Rh_2(*S*-TCPTAD)$_4$ conducted by Vyacheslav Boyarskikh and Djamaladdin G. Musaev revealed that the catalyst adopts a similar orientation to the X-ray structure (Figure 6.2.2). In comparison, a recent X-ray crystallographic study by Ghanem[69] on Rh_2(*S*-PTAD)$_4$ concluded that the adamantyl groups are unable to fully block the carbene from binding to one face of the catalyst, but this argument was made on the basis of limited data, the observation of solvent coordination to both faces of Rh_2(*S*-PTAD)$_4$ in the crystal structure. In the case of Rh_2(*R*-TCPTAD)$_4$, it is clear from the X-ray structure and the computational studies that the gap for the approach of the diazo compound to the rhodium is much wider on the face with the phthalimido groups compared to the face with the adamantyl groups (16.2 Å versus 7.8 Å). Therefore, we conclude that there is a major difference in the steric environment between the two faces of the catalyst with the rhodium face containing the phthalimido groups being much more accessible.

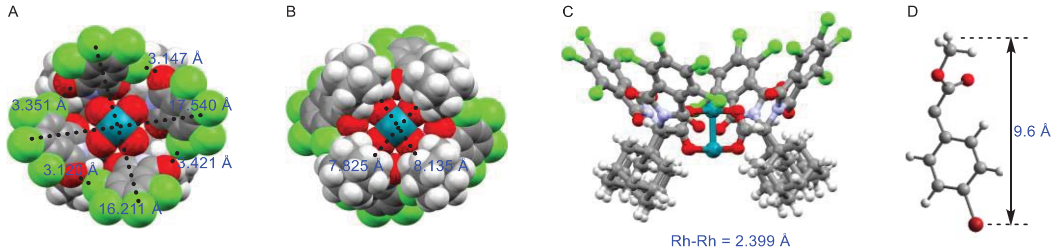


Figure 6.2.2 Calculated structure of Rh_2(*S*-TCPTAD)$_4$

The next level of analysis needs to explain how the catalyst, containing four blocking phthalimido groups controls the favored approach of the substrate to one face of the rhodium carbene, which would lead to an enantioselective reaction. Fox has conducted computational studies on the reactions of Rh_2(*S*-PTTL)$_4$-catalyzed reactions with α-alkyl-α-diazoesters, and suggested that depending on the size of the alkyl group it adopts a certain orientation within the pocket.[66] Computational analysis by Vyacheslav Boyarskikh and Djamaladdin G. Musaev of the Rh_2(*S*-TCPTAD)$_4$-donor/acceptor carbene complex revealed that even though Rh_2(*S*-TCPTAD)$_4$ is quite rigid there is a change in the ligand orientation when the carbene is bound to the complex, in which one of the phthalimido group bends forward to π-stack with the aryl ring of the carbene.

Irrespective of where the carbene is positioned or the orientation of the ester group, the same face of the carbene is involved in the most favorable *π*-stacking interaction (by 2.1 kcal/mol), leading to a preferred attack at the *Re* face of the carbene. Even through the carbene is accessible, the substrate will still need to enter the pocket to react with the carbene; this would explain why the Rh_2(*S*-TCPTAD)$_4$ carbene complex react selectively at only the most accessible tertiary C–H bond (Figure 6.2.3).

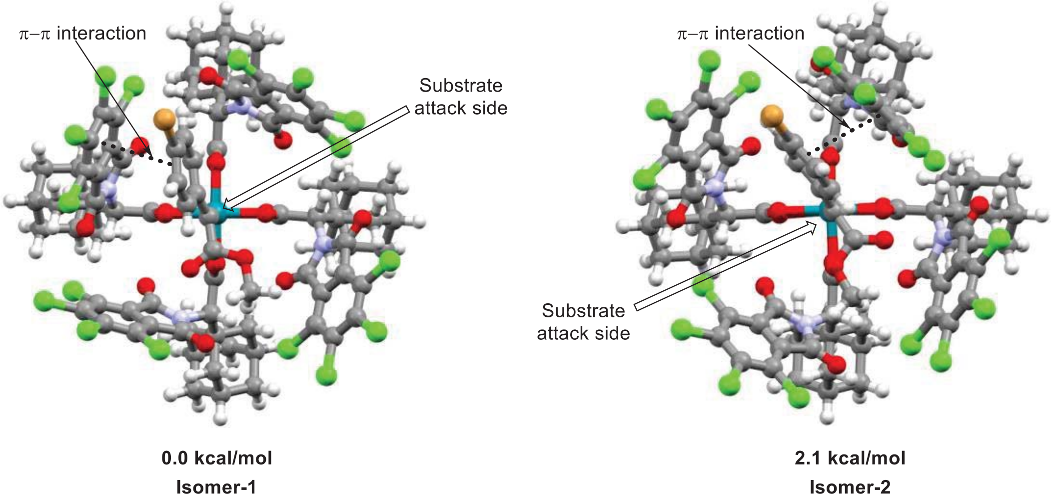


Figure 6.2.3 Calculated carbene structure of Rh_2(*S*-TCPTAD)$_4$

3. Substrate Scope

Based on the results from the 2-methylpentane reactions, we tried to explore more elaborated substrate to develop a selective catalyst for the most accessible tertiary C–H bond. With Rh_2(*S*-TCPTAD)$_4$ as catalyst, highly selective C–H functionalization of the tertiary sites could be achieved in good yields (64-93% yield) and enantioselectivity (77-92% e.e.) with a range of alkane substrates (Figure 6.3.1, **6.3.1-6.3.7**). The system is sensitive to the steric environment around the tertiary site because when the tertiary site becomes crowded another more accessible tertiary or secondary site is preferred (**6.3.1-6.3.4**). For 2-methylbutane, only tertiary product (**6.3.1**) was observed, but for 2-methylpentane (Figure 3.6.2) and 2-methylhexane (**6.3.2**), more competition was observed because the secondary C–H bonds become more accessible. In the case of 3-methylpentane (**6.3.3**), the secondary position is even less accessible than that in 2-methylbutane, but the tertiary also become less accessible than that in 2-methylbutane so certain competition from the secondary C–H bonds was observed. A dramatic change was observed in the case of 4-methylheptane (**6.3.4**) where the major product was formed from the functionalization at the most accessible secondary C–H bond because the tertiary C–H bond was sterically blocked. A delicate competition was conducted to challenge the catalyst in 2-methyl-3-ethylpentane (**6.3.5**) because the substrate has two tertiary C–H bonds, one is adjacent to dimethyl group and another one is adjacent to diethyl group. Although those two tertiary C–H bonds are very similar to each other, only the tertiary C–H bond adjacent to dimethyl group was functionalized.

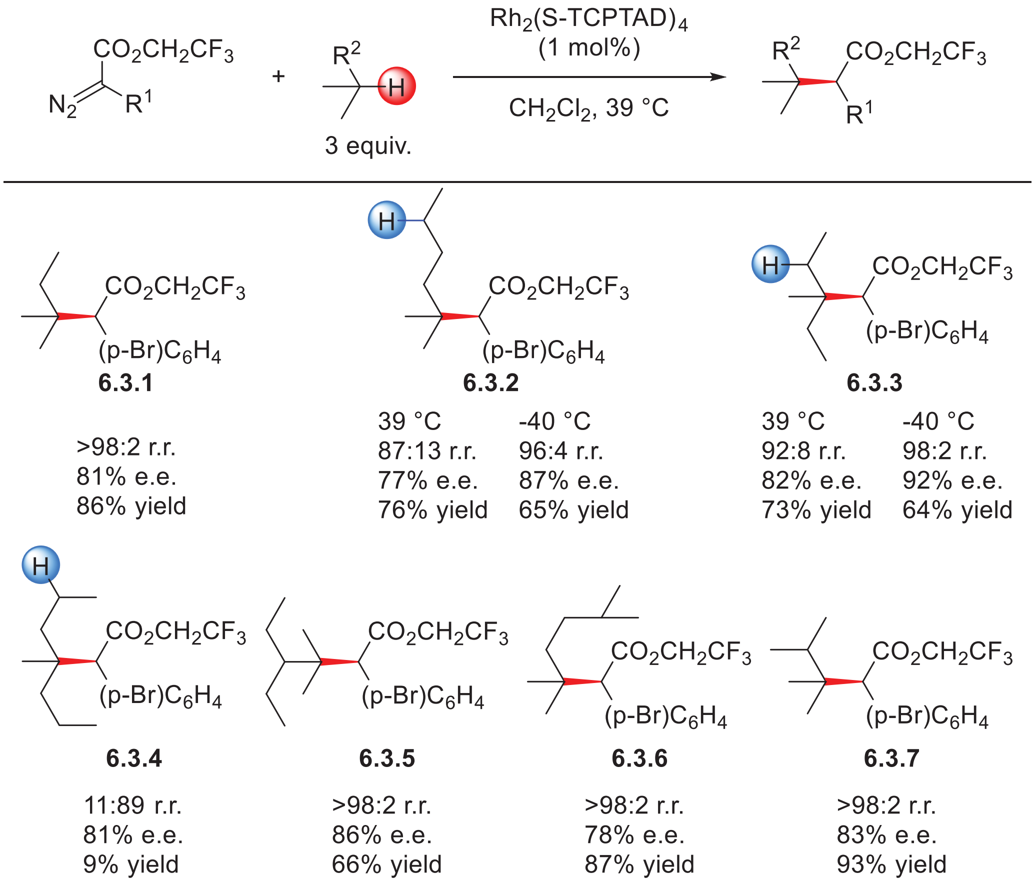


Figure 6.3.1 Rh2(*S*-TCPTAD)4-catalyzed C–H functionalization of alkanes

As shown in Figure 6.3.2, the reaction could be conducted with substrates containing other functionalities such as bromo and ester functional groups (**6.3.8-6.3.10**). In Figure 3.6.2, temperature study revealed that lower temperature can significantly improve the selectivity so for cases with low site-selectivity, the reactions were repeated at -40 °C to improve the site- and enantioselectivity (**6.3.2**, **6.3.3**, **6.3.10**). The reactions have been primarily carried out with the *p*-bromophenyl derivative **3.2.1c** as the carbene precursor, and the products would be readily diversified either by ester modification or metal-catalyzed cross coupling. The reaction can be extended to carbene precursors containing other aryl functionalities and heterocycles (**6.3.11-6.3.14**). Most notable are the examples with the pyridyl and pyrimidyl heterocycles (**6.3.11** and **6.3.12**).

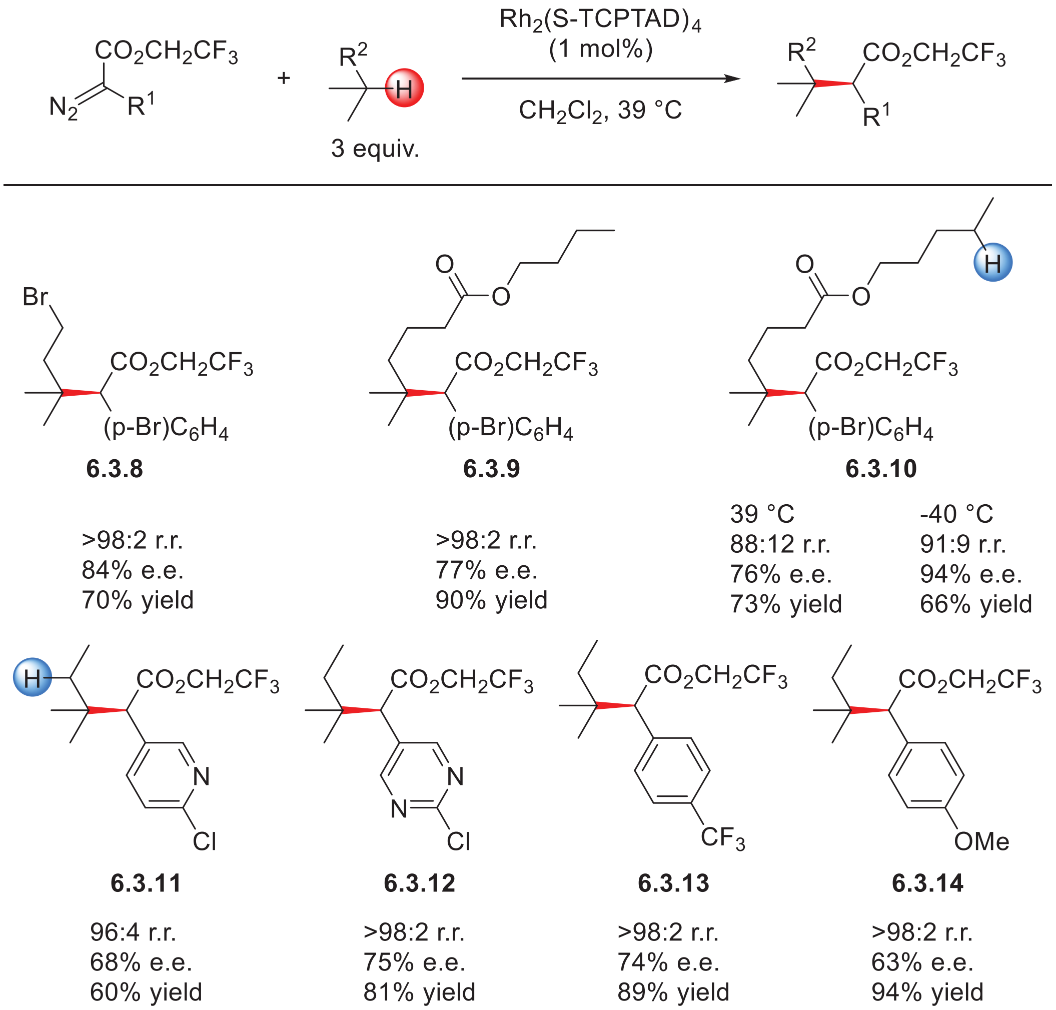
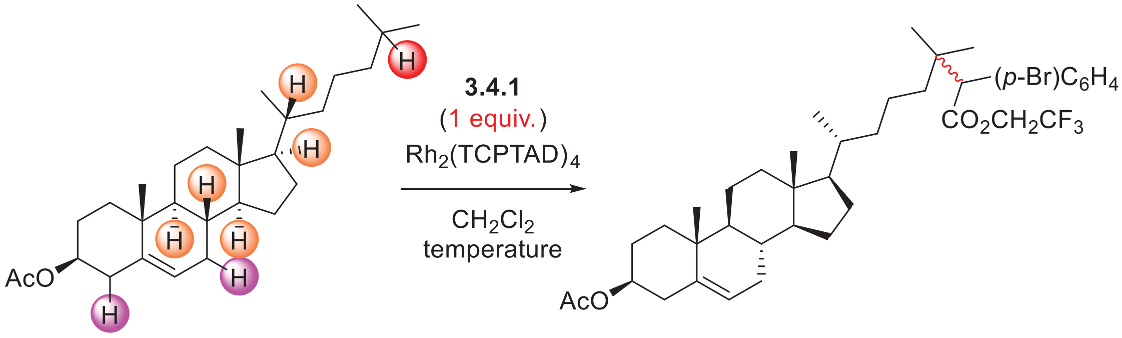


Figure 6.3.2 Evaluation of the scope of Rh_2(*S*-TCPTAD)$_4$-catalyzed C–H functionalization

A major test for site-selective C–H functionalization is the determination if control can be achieved in elaborate substrates. Therefore, the reactions of some representative natural products were examined. As the natural products are valuable substrates, these reactions were conducted with a 1:1 ratio of the substrate to diazo (**3.4.1**). The C–H functionalization of steroids has been of great historical significance because many seminal studies involving radical chemistry have been reported using appropriate directing groups to achieve site-selectivity.[101-102] Therefore, we examined the reaction with the Cholesteryl acetate as a substrate (Figure 6.3.3). Cholesteryl acetate (**6.3.15**) is a challenging substrate because it has forty-eight different C–H bonds including six tertiary C–H bonds (marked in orange and red) and four allylic C–H bonds (marked in pink). Even so, the reaction proceeded cleanly and gave a high yield of the C–H functionalization product **6.3.16** derived from reaction at the most accessible tertiary C–H bond marked in red at the end of the steroid side chain. A particularly intriguing feature of this transformation is the total lack of reactivity at the steroid nucleus, especially the electronically activated allylic positions. The configuration of the reaction is under catalyst control as Rh_2(*R*-TCPTAD)$_4$ and Rh_2(*S*-TCPTAD)$_4$ favored opposite diastereomers by a diastereomeric ratio (d.r.) of 11:1, but the yield of the reaction with Rh_2(*R*-TCPTAD)$_4$ was higher (86% vs 78% isolated *yield*). The higher yield appears to be due to more efficient capture of the carbene by the substrate rather than formation of other regioisomers because no other C–H functionalization products were evident in the ^{1}H NMR spectra of the crude reaction mixtures. When the reaction was conducted at lower temperatures, the diastereoselectivity could be improved (16:1 d.r.), but the yield was lower (60 %). The absolute configuration of **6.3.16** generated by Rh_2(*S*-TCPTAD)$_4$ was confirmed by single crystal X-Ray crystallographic data, the absolute configuration of other tertiary C–H insertion products were assigned by analogy.



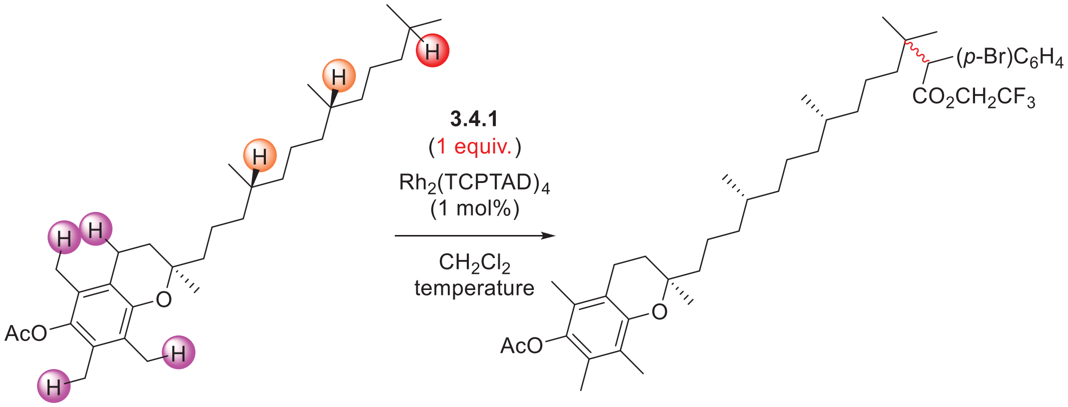
6.3.15
Cholesteryl acetate
(1 equiv.)

6.3.16

Rh$_2$(TCPTAD)$_4$	**6.3.16**	temperature	r.r.	d.r.	yield (%)
S, 1 mol%	*R*	39 °C	>98:2	11:1	78
R, 1 mol%	*S*	39 °C	>98:2	11:1	86
R, 0.1 mol%	*S*	39 °C	>98:2	9:1	83
R, 1 mol%	*S*	24 °C	>98:2	13:1	80
R, 1 mol%	*S*	0 °C	>98:2	16:1	60

Figure 6.3.3 Evaluation of the scope of Rh$_2$(*S*-TCPTAD)$_4$-catalyzed C–H functionalization of Cholesteryl acetate

The site-selectivity was also examined in the case of vitamin E acetate (**6.3.17**) (Figure 6.3.4). This is also a challenging substrate for C–H functionalization because it contains fifty-two C–H bonds, eleven benzylic C–H bonds (marked in pink) and three tertiary C–H bonds (marked in orange and red). Once again, the reaction was selective for the most accessible tertiary C–H bond (marked in red). Rh$_2$(*R*-TCPTAD)$_4$ generated the product **6.3.18** in 84% yield, whereas Rh$_2$(*S*-TCPTAD)$_4$ generated the opposite diastereomer in 64% yield. Both reaction produced the same d.r. as 11:1, indicating that the formation of the new stereogenic center during the reaction is under catalyst control. When the reaction was conducted at room temperature (24 °C), the diastereoselectivity was improved to >20:1 d.r.



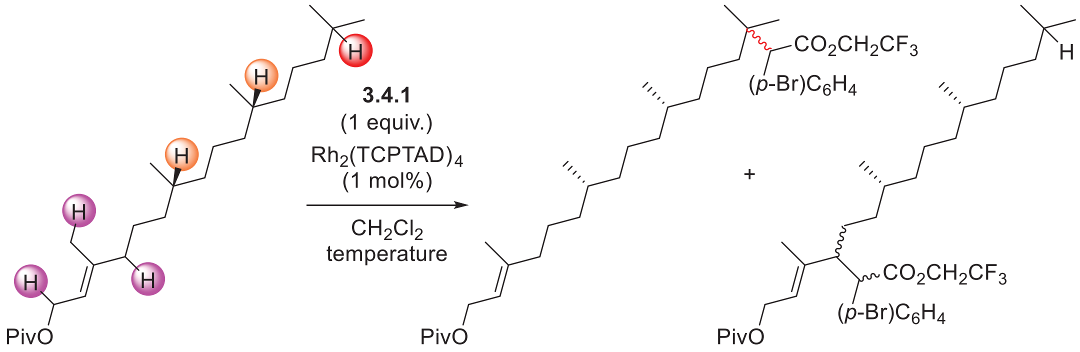
6.3.17
(Vitamin E acetate)
(1 equiv.)

6.3.18

$Rh_2(TCPTAD)_4$	**6.3.18**	temperature	r.r.	d.r.	yield (%)
S	*R*	39 °C	>98:2	11:1	64
R	*S*	39 °C	>98:2	11:1	82
S	*R*	24 °C	>98:2	>20:1	60

Figure 6.3.4 Evaluation of the scope of Rh_2(*S*-TCPTAD)$_4$-catalyzed C–H functionalization of vitamin E acetate

Phytyl pivalate (**6.3.19**) is also a challenging substrate because the allylic C–H bonds would be expected to be electronically activated and in this case, are not sterically constrained within a ring system. Even so, the reaction was still selective for the most accessible tertiary C–H bond to form **6.3.20** over the allylic position to form **6.3.21**. Under refluxing conditions, the ratio of the products was about 3:1 but when the reaction was conducted at room temperature it improved to 89:11, albeit with somewhat decreased yield (Figure 6.3.5).



6.3.19
Phytyl pivalate
(1 equiv.)

6.3.20

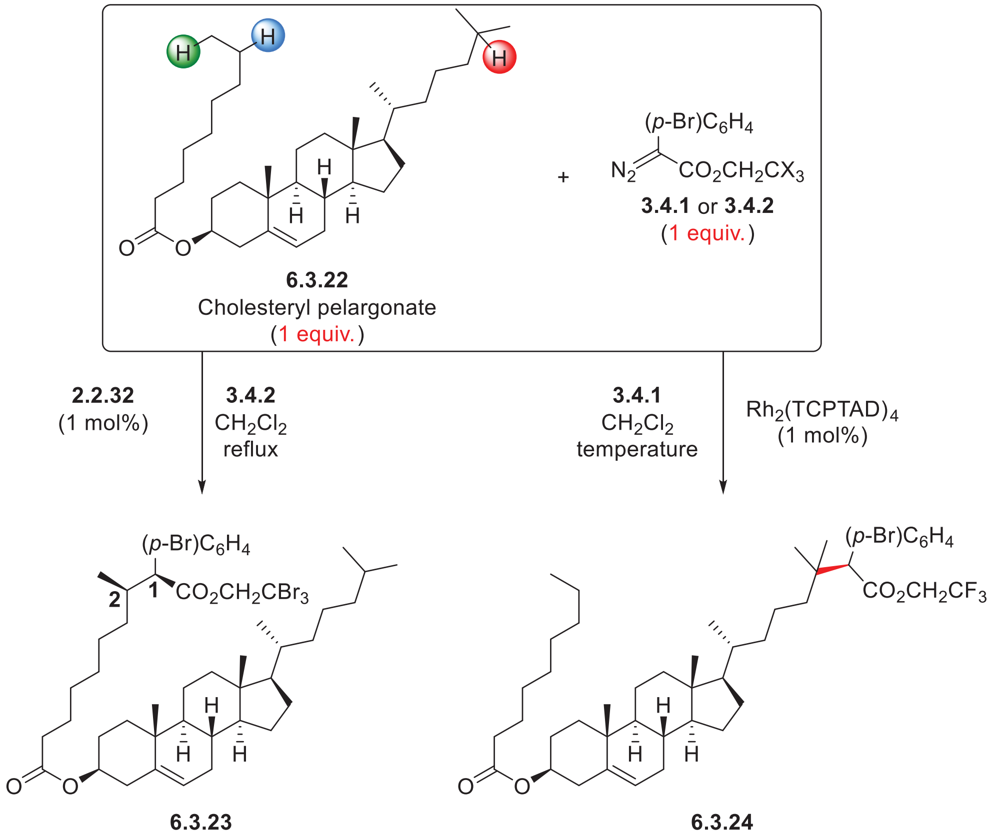
6.3.21

$Rh_2(TCPTAD)_4$	**20**	temperature	r.r. (**20**:**21**)	d.r. (**20**)	yield (**20**, %)
S	*R*	39 °C	77:23	11:1	67
R	*S*	39 °C	78:22	12:1	69
R	*S*	24 °C	89:11	12:1	52

Figure 6.3.5 Evaluation of the scope of Rh_2(*S*-TCPTAD)$_4$-catalyzed C–H functionalization of Phytyl pivalate

The ultimate goal of this program would be to have a collection of catalysts to control site-selectivity at will. In order to demonstrate this concept, the influence of Rh_2(*R*-TCPTAD)$_4$ and Rh_2[*R*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$, on the functionalization of cholesteryl pelargonate (**6.3.22**) was examined. In the Rh_2[*R*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$-catalyzed reaction of **3.4.2**, the methylene C–H functionalization product **6.3.23** became the dominant product by a ratio of 87:10:3. In contrast, the Rh_2(*R*-TCPTAD)$_4$-catalyzed reaction of **3.4.1** gave an 87:13 ratio favoring the tertiary C–H functionalization product **6.3.24** over the methylene position at the terminal side of the *n*-alkyl chain (marked in blue). The regioisomers were readily separated and **6.3.23** was isolated in 68% yield from the Rh_2[*R*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$-catalyzed reaction and **6.3.24** was isolated in 74% yield from the Rh_2(*R*-TCPTAD)$_4$-catalyzed reaction. When the Rh_2(*R*-TCPTAD)$_4$-

catalyzed reaction was conducted at 0 °C, the selectivity was improved to 92:8 r.r. and >20:1 dr (Figure 6.3.6).



r.r.	d.r. (C1/steroid)	d.r. (C1/C2)	yield (%)
87:10:3	39 : 1	9:1	68

$Rh_2(TCPTAD)_4$	**24**	temperature	r.r.	d.r.	yield (%)
R	S	39 °C	87:13	6:1	74
R	S	24 °C	89:11	>20:1	68
R	S	0 °C	92:8	>20:1	65

Figure 6.3.6 Catalyst controlled C–H functionalization of cholesteryl pelargonate

4. Conclusion

These studies demonstrate that highly site-selective catalyst-controlled C–H functionalization of non-activated tertiary C–H bonds is a viable process. The dirhodium catalyst Rh_2(*S*-TCPTAD)$_4$ adopts a structure close to a C_4 symmetric shape with a relatively shallow pocket, enabling the most accessible tertiary C–H bonds to approach the rhodium-bound carbene on the phthalimido face of the dirhodium complex.

So far, we have been able to build a toolbox with three unique catalysts to control the selective functionalization at the most accessible primary, secondary and tertiary C–H bonds (Figure 6.3.7).

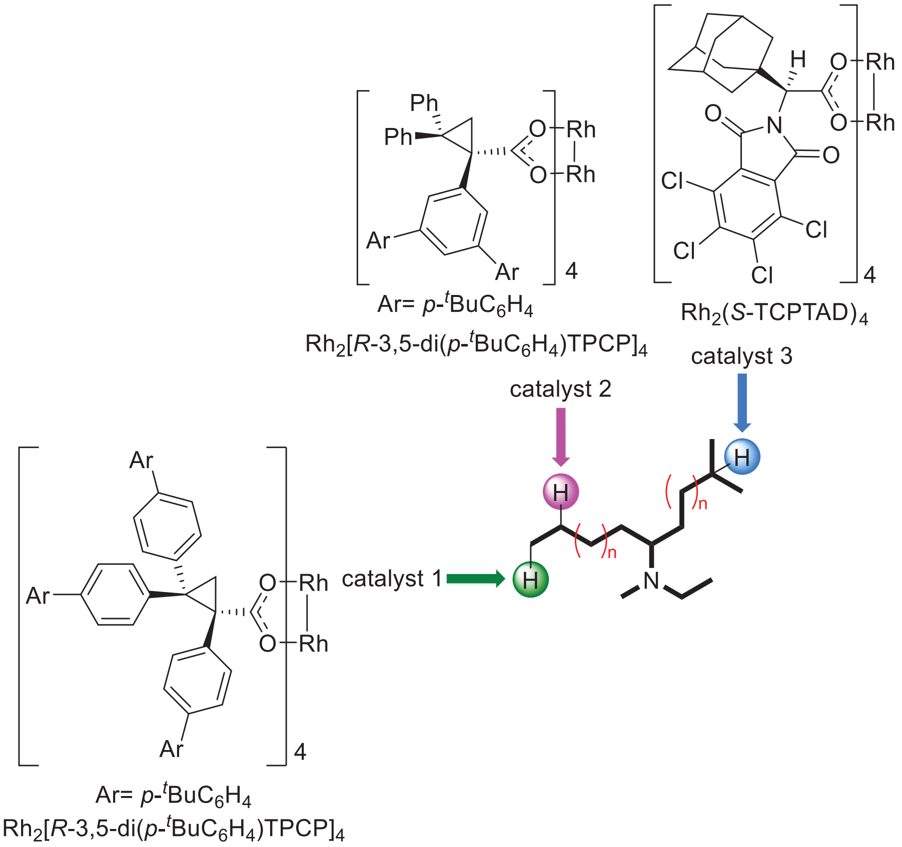


Figure 6.4.1 Catalyst toolbox for selective C–H functionalization

Chapter 7 Catalyst Symmetry & Quantitative Model

1. Introduction

Dirhodium tetracarboxylate catalysts are the key to the success of selective C–H functionalization by means of donor/acceptor rhodium carbenes induced C–H insertion. The catalyst family have attracted more attention in the last two decades because they are capable of controlling a wide variety of selective carbene reactions including intermolecular C–H functionalization of a range of substrates with high levels of site selectivity, diastereoselectivity, and enantioselectivity.

The initial exploration of such reactivity was mainly focusing on the use of as the chiral catalyst, $Rh_2(DOSP)_4$ [103], which demonstrated unique property and broad utility. However, the catalyst has poor diversification capability, so if a particular substrate gave a mixture of products, little could be done to improve the reaction outcome. Recently, a new class of bulky and modular chiral catalyst, dirhodium tetrakis-triarylcyclopropanecarboxylate [$Rh_2(TPCP)_4$] catalysts, were developed and showed great potential in controlling selective C–H functionalization (Figure 7.1.1).

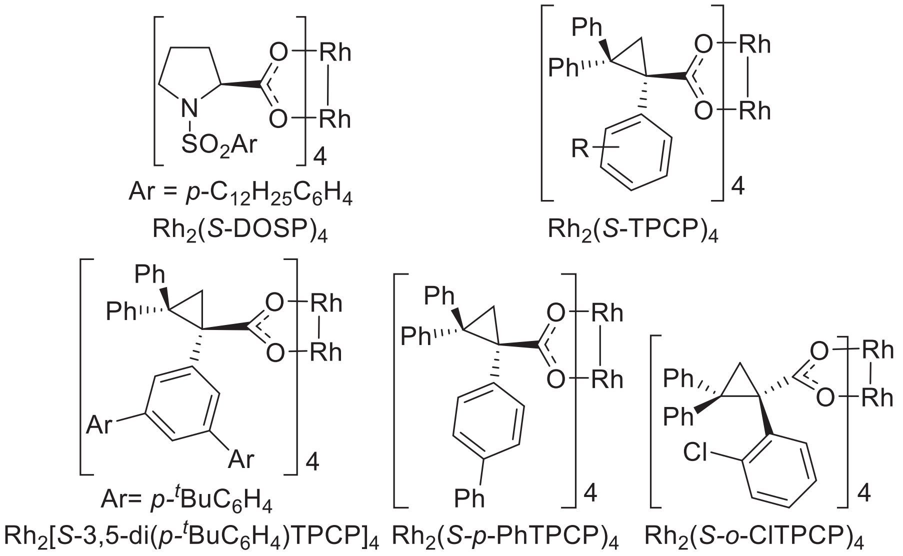


Figure 7.1.1 Structures of dirhodium tetracarboxylate catalysts

Initial exploration of the Rh$_2$(TPCP)$_4$ catalyst was the development of Rh$_2$(*p*-PhTPCP)$_4$, which was capable of site selective reactions at activated primary C–H bonds [73-74], such as benzylic, allylic and sites alpha to oxygen, with a very different reactivity profile to that of Rh$_2$(DOSP)$_4$. Further refinement of these catalyst structures led to the development of the D$_2$-symmetric catalyst, Rh$_2$[3,5-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$ (**2.2.32**),[75] capable of selective functionalization at the C2 position of *n*-alkanes or terminally-substituted *n*-alkanes (Figure 7.1.2).

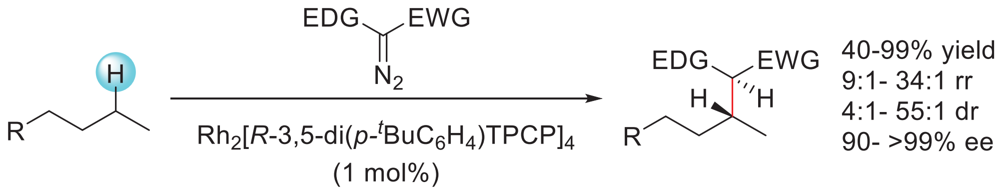


Figure 7.1.2 Site- and stereoselective functionalization of alkanes and alkyl compounds

In this chapter, we will also disclose the structural element of another member of the TPCP dirhodium family, Rh_2(*p*-PhTPCP)$_4$ (**2.2.4**). In addition, we compare the C–H functionalization site selectivity of the two types of catalysts and develop a quantitative model of the electronic effects of substrates for site-selectivity with the different catalysts. These studies identified two distinctive classes of TPCP catalysts that adopt very different shapes, and demonstrate the utility of the quantitative model for the rapid assessment of new dirhodium catalysts.

2. Catalyst Symmetry

A critical component of our design of chiral dirhodium-catalysts is the use of four identical carboxylate ligands, containing a structural feature within the ligand that is too sterically demanding to align in the periphery of the catalyst.[45, 52, 75] Thus, the large component must align on the α face or the β face of the catalyst, leading to four possible structural permutations, α,β,α,β (D_2 symmetric), α,α,α,α (C_4 symmetric), α,α,β,β (C_2 symmetric), and α,α,α,β (C_1 symmetric), each having a different symmetry. Further studies by Fox and Charette have shown that certain dirhodium catalysts adopting an orientation may not be perfectly aligned and thus behave as if they are pseudo C_2 symmetric rather than C_4 symmetric.[64, 66]

The $Rh_2(TPCP)_4$ catalysts have a more sophisticated design element because they share a characteristic structural feature of four identical chiral ligands with cyclopropane backbone. As the ligands are sterically demanding so both the C1 aryl and the cis-C2 (cis to carboxylate group) aryl groups are forced to align away from the periphery of the complex. The ligands will adopt certain orientation to minimize the steric interaction and the substituents on the cyclopropane ring will act as blocking group to form unique chiral pocket for C–H bond recognition.

In the case of $Rh_2[S\text{-}3,5\text{-di}(p\text{-}{}^tBuC_6H_4)TPCP]_4$ (**2.2.32**), the C1 aryl group is so sterically demanding that if the C1 aryl of the first ligand is on the α face, then the C1 aryl ring of the adjacent ligand must be on the β face (Figure 7.2.1, A). The catalyst adopts an orientation in the crystalline form, generating a structure that is D_2 symmetric. Corroboration that this is the preferred conformation was obtained through ONION calculation of the slightly simpler derivative, Rh_2(*S*-3,5-diPhTPCP)$_4$ (**2.2.26**), which revealed that the α,β,α,β form is 5.0 kcal/mol more stable than the α,α,α,α form (Figure 3.3.2).

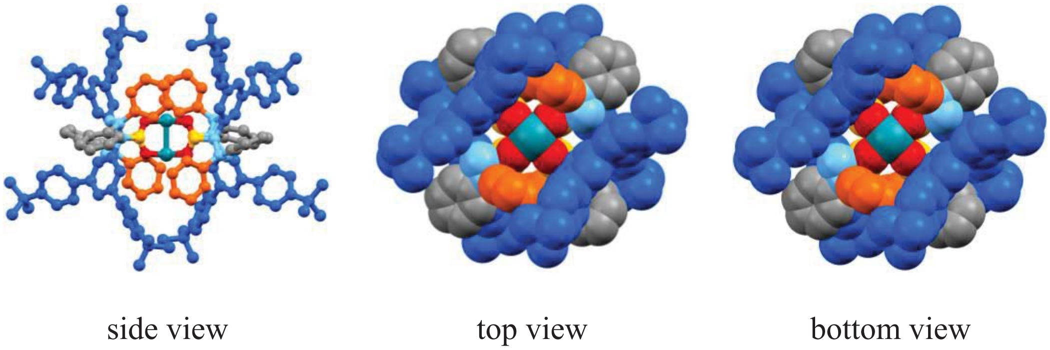

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Figure 7.2.1 X-Ray structures of Rh_2[*S*-3,5-di(*p*-^{t}Bu)C_6H_4]TPCP]$_4$ (**2.2.32**) (lacking axially coordinated solvent molecules)

Encouraged by the remarkable site selectivity exhibited by Rh_2[*S*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$ (**2.2.32**), we continued to explore other members of the TPCP family of catalysts. Surprisingly, we found that depending on the aryl substitution, the complexes adopt different orientations. During the previous catalyst optimization studies on pentane that lead to the discovery of Rh_2[*S*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$ (**2.2.32**), the biphenyl catalyst Rh_2(*S*-*p*-PhTPCP)$_4$ (**2.2.4**) was also evaluated (Figure 3.2.3). Rh_2(*S*-*p*-PhTPCP)$_4$ (**2.2.4**) was expected to be less crowded compared to Rh_2[*S*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$ (**2.2.32**) and was expected to favor C2 functionalization over C1 functionalization of n-alkanes. However, the opposite trend was observed, suggesting that Rh_2(*S*-*p*-PhTPCP)$_4$ (**2.2.4**)was more sterically demanding. The X-ray structure of this catalyst revealed that all of the biphenyl groups occupy the same face. The biaryl rings are involved in π-stacking and this disrupts the C4 symmetry of a regular α,α,α,α orientation and instead the complex is pseudo C2 symmetric (Figure 7.2.2).

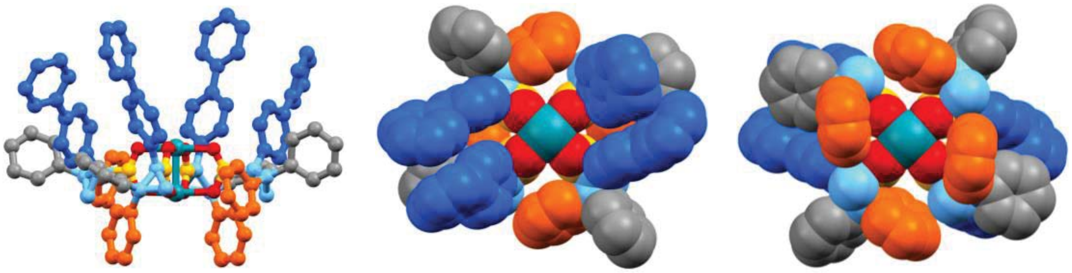
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Figure 7.2.2 X-Ray structures of Rh_2(*S*-*p*-PhTPCP)$_4$ (**2.2.4**) (lacking axially coordinated solvent molecules)

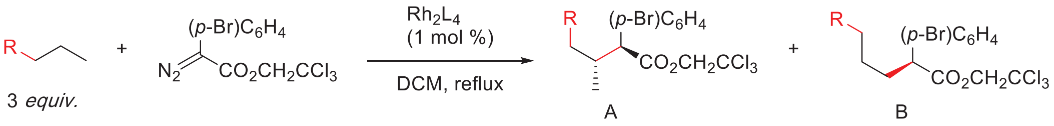
The profound effect of two meta substituents on the C1 aryl group led us to also explore the behavior of ligands containing groups close to the cyclopropane, such as an o-chloro substituent [Rh_2(*S*-*o*-ClTPCP)$_4$] and the study of this type of catalysts are currently being investigated by Wenbin Liu.

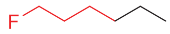
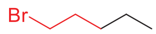
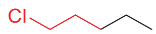
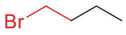
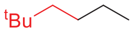
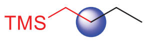
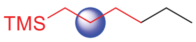
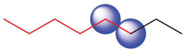
3. Quantitative Model

Having discovered that the $Rh_2(TPCP)_4$ catalysts can adopt three distinct orientations we became interested in determining what would be the influence of the substrate structural changes on the site selectivity of C–H functionalization. C–H functionalization preferentially occurs at electron rich C–H bonds as the C–H insertion is a concerted asynchronous process with build-up of positive charge at carbon. We conducted a study on a range of substrates, with relatively similar steric considerations so that the influence of electronic effects within the substrate on the site-selectivity could be explored. Therefore, a range of terminally-substituted *n*-alkanes were used as substrates and the site-selectivity between C2 and C1 functionalization (and diastereoselectivity) for the three catalysts were determined (Figure 7.3.1). The selectivity of the $Rh_2[R\text{-}3,5\text{-di}(p\text{-}{}^tBuC_6H_4)TPCP]_4$-catalyzed reactions has been described previously (Chapter 4), but a wider range of substrates are reported here. The site selectivity favors C2, but the selectivity decreases progressively from the 1-halohexanes to 1-halobutanes. The C2/C1 site selectivity is 18:1 for 1-bromohexane but is only 3:1 for 1-bromobutane. Similar trends were observed with the chloro and fluoro derivatives, indicating that the inductive effect of the halogen is significant even when the site for C–H functionalization is 3-4 atoms away.

Previously, it was reported that the reaction of pentane with $Rh_2(R\text{-}p\text{-}PhTPCP)_4$ (**2.2.4**) has a greater preference for primary C–H functionalization compared to $Rh_2[R\text{-}3,5\text{-di}(p\text{-}{}^tBuC_6H_4)TPCP]_4$ (**2.2.32**) (Chapter 3). This behavior was observed across the entire substrate series. The highest C2/C1 site selectivity with Rh_2(*R*-*p*-PhTPCP)$_4$ (**2.2.4**)was ~4:1, whereas Rh_2[*R*-3,5-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$ (**2.2.32**) yielded up to 34:1 site selectivity with electron rich substrates. In the case of the silyl-substituted substrates, some C–H functionalization at other internal methylene sites was also observed.

Even though this study is emphasizing the influence of the catalysts structure on site selectivity, these chiral catalysts also alter the diastereoselectivity and enantioselectivity of the reactions. The reactions with two catalysts are moderately diastereoselective, and as previously reported, the reactions catalyzed by Rh_2[*R*-3,5-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$ (**2.2.32**) are highly enantioselective (90->99% ee). Overall, the Rh_2(*R*-*p*-PhTPCP)$_4$- catalyzed reactions were the least regio- and diastereoselective. Most of the enantioselectivity of the Rh_2(*R*-*p*-PhTPCP)$_4$-catalyzed reactions were not determined because of poor HPLC resolution caused by the presence of significant amounts of the second regioisomer.



		$Rh_2[R\text{-}3,5\text{-di}(p\text{-}^tBuC_6H_4)TPCP]_4$				$Rh_2(R\text{-}p\text{-}PhTPCP)_4$		
entry	Substrate	rr (A:B)	dr (A)	ee (A, %)	yield (%)	rr (A:B)	dr (A)	yield (%)
1		18:1	9:1	92	89	3:1	8:1	81
2		18:1	9:1	93	84	3:1	10:1	79
3		18:1	9:1	97	85	2:1	9:1	79
4		9:1	9:1	95	65	1:1	8:1	77
5		9:1	9:1	94	50	2:1	10:1	75
6		8:1	10:1	97	49	2:1	8:1	78
7		3:1	9:1	93	20	1:1	5:1	71
8		3:1	7:1	92	19	1:1	6:1	70
9		33:1	4:1	90	89	2:1	4:1	82
10		34:1	4:1	>99	40	4:1 [a]	4:1	80
11		20:1	9:1	90	85	3:1 [b]	9:1	86
12		27:1	9:1	91	82	2:1	9:1	86

Other internal C–H insertion products was observed by crude ^1H NMR spectra: [a] 10%; [b] 4%. Enantiomeric excess of $Rh_2(R\text{-}p\text{-}PhTPCP)_4$ catalyzed reactions (entry 1-6, 10-12) were not determined due to the low regioisomeric ratio and the corresponding overlap of regioisomer peaks, but enantiomeric excess of the following entries were determined: entry 7: 96% ee, entry 8: 94% ee, entry 9: 88% ee.

Figure 7.3.1 Selective C–H functionalization of terminally-substituted *n*-alkanes

To further investigate the observed site selectivity trends as a function of substrate, we collaborated with Zachary L. Niemeyer and Mathew S. Sigman to examine the ability to correlate the outcomes to various physical organic parameters.[104] Inspired by Hammett σ-values, *para*-substituted benzoic acids were used as a starting point and calculated as simulated substrates since the evaluated substrates were intended to only probe electronic variation. Based on the study conducted by Zachary L. Niemeyer and Mathew S. Sigman, the resultant descriptors were assessed in correlations to the regioisomeric ratio energy preferences (reported as a $\Delta\Delta G^\ddagger$) using various goodness of fit criteria (Figure 7.3.2).

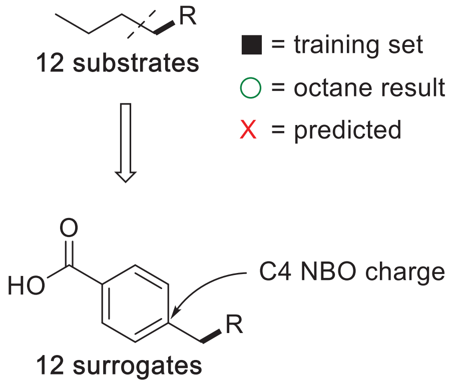
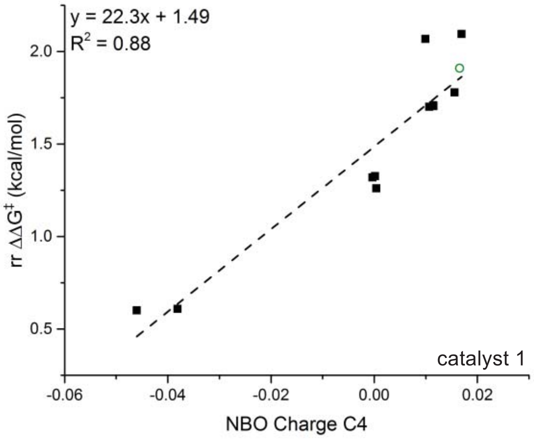


Figure 7.3.2 Substrate surrogate for NBO charge calculation

Of these, the NBO charge of C4 demonstrated a strong correlation to the observed energy differences for Rh$_2$[*R*-3,5-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$ (catalyst 1) and Rh$_2$(*R*-*p*-PhTPCP)$_4$ (catalyst 2). NBO charges of carbonyls next to benzene rings have been correlated to Hammett σ-values previously so this outcome is consistent with the NBO charge reading out[105-107] the relative electronic perturbations of the substrates. While this is somewhat intuitive, the sensitivity of the NBO calculation provides a platform for the rapid assessment of electronics and prediction of similar simple substrates (Figure 7.3.3).



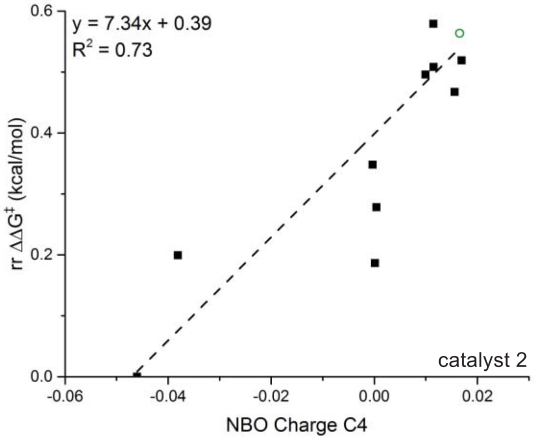


Figure 7.3.3 Simulated charges adequately described the regioisomer outcomes from catalyst 1 & 2

Additionally, as the same parameter is able to describe two catalysts, it was hypothesized that this charge would also correlate to the outcomes from other catalyst in this family and we anticipated that the relative slope of only a few substrates could be used to predict all other substrates relatively well. Therefore, the empirical results using 1-

bromohexane and 1-chloropentane as substrates with Rh_2(*S*-*o*-ClTPCP)$_4$ obtained by Wenbin Liu were applied to define the slope and intercept of a prediction equation. Examining the other data points provided by Wenbin Liu, an excellent agreement is observed between measured and predicted regioisomeric ratio. This provides confidence when new catalysts are evaluated that only a few data points should be required to predict the outcomes of a wide range of functionalized *n*-alkanes. Additionally, the results suggest that this catalyst class functions in a similar manner across different symmetry orientations providing the foundation for future mechanistic interrogation.

4. Conclusion

In conclusion, these studies reveal that the $Rh_2(TPCP)_4$ catalysts can adopt at least three high symmetry orientations, which is dependent on the frame work of the cyclopropane. Rh_2[*S*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$ (**2.2.32**) preferentially adopt a D2 symmetric arrangement, whereas the Rh_2(*S*-*p*-PhTPCP)$_4$ (**2.2.4**) adopts a C4 symmetric structure and the X-ray structure of Rh_2(*S*-*p*-PhTPCP)$_4$ (**2.2.4**) is pseudo C2 symmetric. Rh_2[*S*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$ (**2.2.32**) is selective for C–H functionalization at the most accessible secondary site. Rh_2(*S*-*p*-PhTPCP)$_4$ (**2.2.4**) is not particularly selective but it does represent the catalyst that gives the most preference towards the primary C–H bond before the development of Rh_2[*R-tris(p*-^{t}BuC_6H_4)TPCP]$_4$ (**2.2.34**). Even though the catalysts have different ligand arrangements and selectivity profiles, it is still possible to develop a quantitative model for these catalysts that allows a useful correlation for their behavior without need to evaluate a significant number of substrates. Future work will integrate the information gained in this study to the design of even more site-selective catalysts.

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Supporting Information

Site-selective and Stereoselective Functionalization of Non-Activated C–H Bond

By

Kuangbiao Liao

B.S., Sun Yat-sen University

2013

Advisor: Huw M. L. Davies, Ph.D.

An abstract of

A dissertation submitted to the Faculty of the

James T. Laney School of Graduate Studies of Emory University

in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

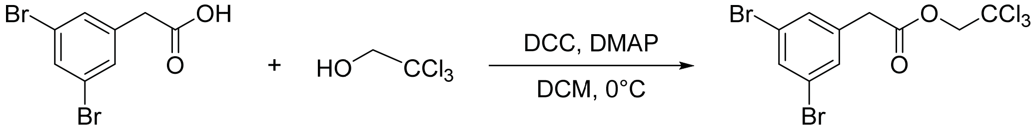
in Chemistry

2018

SI-Chapter 2

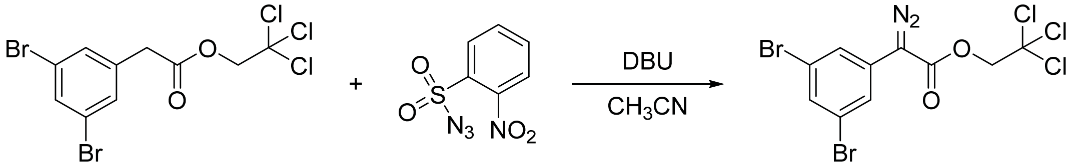
1. Catalyst Synthesis

1.1 3,5-disubstituted catalyst



2,2,2-Trichloroethyl 2-(3,5-dibromophenyl)acetate. A 250-mL flask was charged with 2-(3,5-dibromophenyl)acetic acid (29.4 g, 100 mmol, 1.0 equiv.), DMAP (1.22 g, 10 mmol, 0.1 equiv.), and 2,2,2-trichloroethanol (17.9 g, 120 mmol, 1.2 equiv.) and DCM (150 mL), then the solution was stirred and cooled to 0 °C. A solution of DCC (22.7 g, 110 mmol, 1.1 equiv.) in DCM (50 mL) was poured slowly into the cold reaction mixture. The solution was allowed to stir overnight, at which point it had reached ambient temperature. The precipitate was removed by vacuum filtration, washing once with diethyl ether (50 mL). The filtrate was concentrated to give a crude oil. This was dissolved in pentane and added to a column loaded with 100 mL silica gel, packed and eluted with 1% diethyl ether in pentane. The crude product was purified by flash column chromatography (hexanes/diethyl ether = 50/1) to give a crystalline white solid in 85% overall yield (36.2 g).

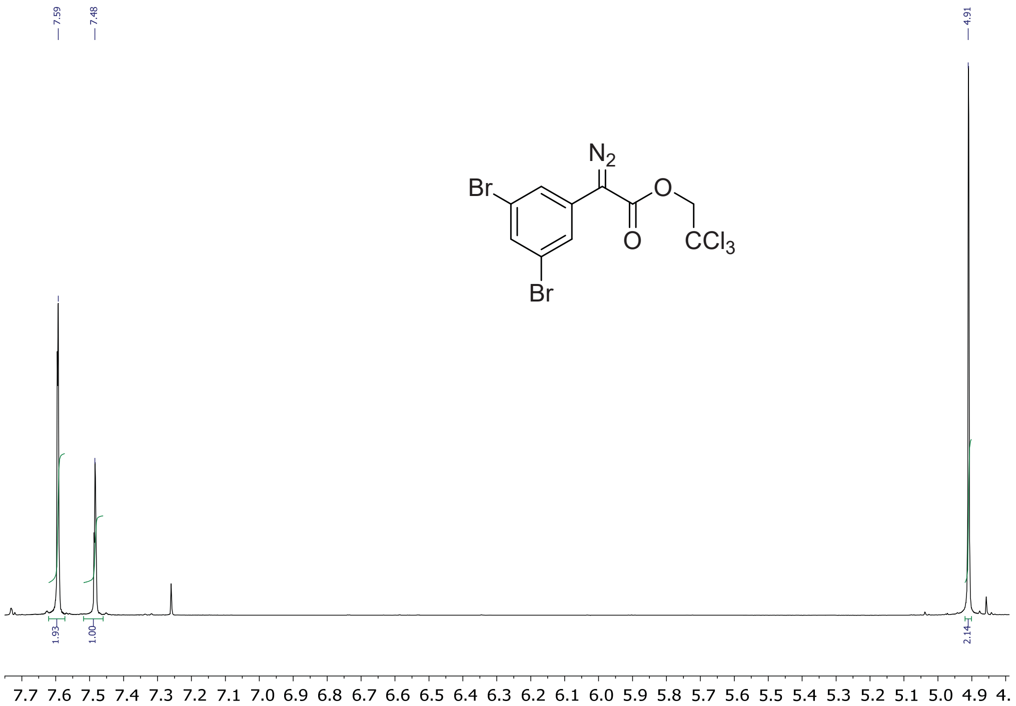
TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.43 (s, 2H), 4.76 (s, 2H), 3.71 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.72, 136.49, 133.35, 131.46, 123.12, 94.68, 74.45, 40.10; HRMS (NSI) calcd for $C_{10}H_6Br_2Cl_3O_2$ ($[M-H]^+$): 420.7805 found 420.7796; IR (neat): 1754, 1557, 1426, 1215, 1132, 1102, 1027, 850, 800, 715, 668.



2,2,2-trichloroethyl 2-diazo-2-(3,5-dibromophenyl)acetate. A 250 mL three-necked flask was equipped with a 100-mL dropping funnel, a rubber septum fitted with N_2 inlet needle and an egg shaped in magnetic stir bar. 1,8-Diazabicycloundec-7-ene (DBU) (28.5

g, 187 mmol, 2.2 equiv.) in acetonitrile (60 mL) was added to the dropping funnel. The flask was charged with 2,2,2-trichloroethyl 2-(3-fluorophenyl)acetate (36.2 g, 85 mmol, 1.00 equiv.), 2-nitrobenzenesulfonyl azide (29.1 g, 128. mmol, 1.5 equiv.) and acetonitrile (120 mL). The DBU solution was added dropwise into reaction mixture. The resulting mixture was stirred over 12 h, and reaction progress was monitored by TLC analysis. The reaction mixture was cooled with an ice bath, and saturated aqueous NH_4Cl (100 mL) was then added to quench the reaction. The mixture was extracted with diethyl ether (3 x 100 mL), and the combined organic layer was washed with saturated NaCl aqueous solution (150 mL), dried over sodium sulfate (10 g) and filtered. Then the filtrate was concentrated by rotary evaporation to afford the crude product. The crude product was purified by flash column chromatography (hexanes/diethyl ether = 50/1) to give an orange solid in 82% overall yield (31.5 g).

TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.48 (s, 2H), 4.91 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.56, 162.26, 131.51, 128.95, 124.92, 123.62, 94.82, 74.04; HRMS (NSI) calcd for $C_{10}H_5Br_2Cl_4N_2O_2$ ([M+Cl]$^-$): 482.7477 found 482.7465; IR (neat): 2097, 1713, 1581, 1545, 1441, 1261, 1233, 1144, 1104, 1046, 843, 789, 744, 706, 666.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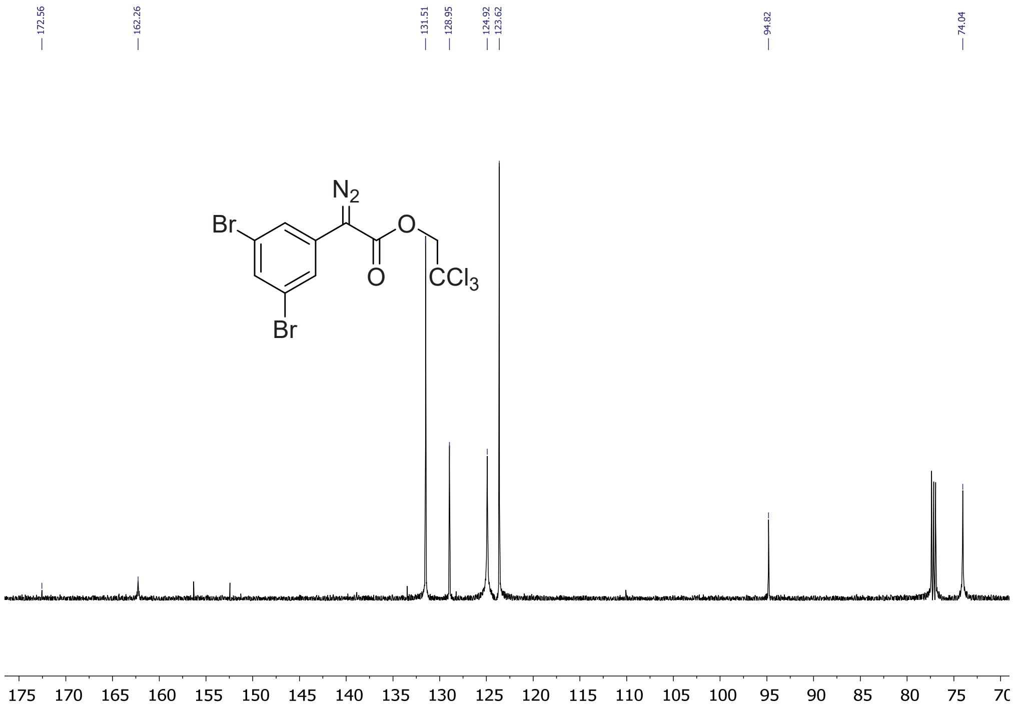
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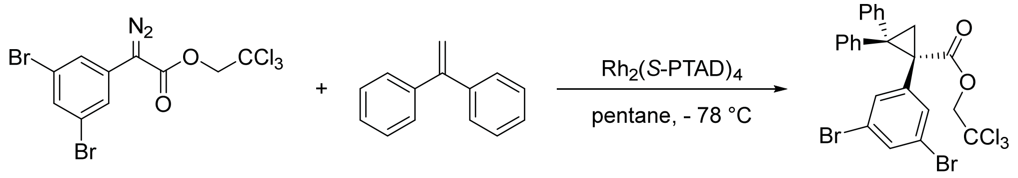
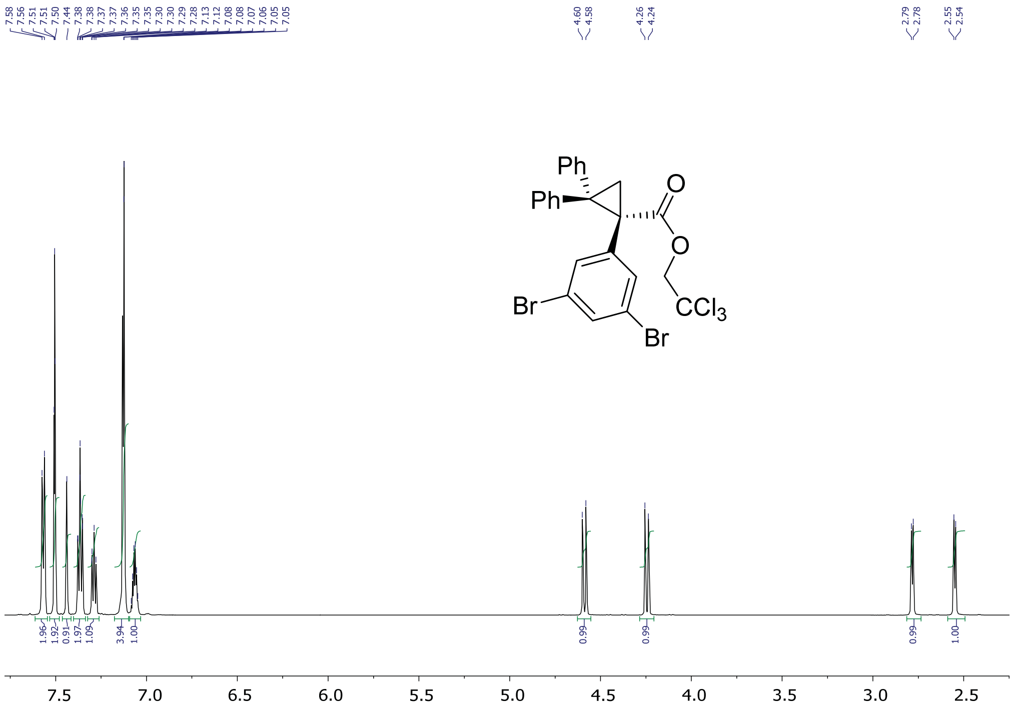
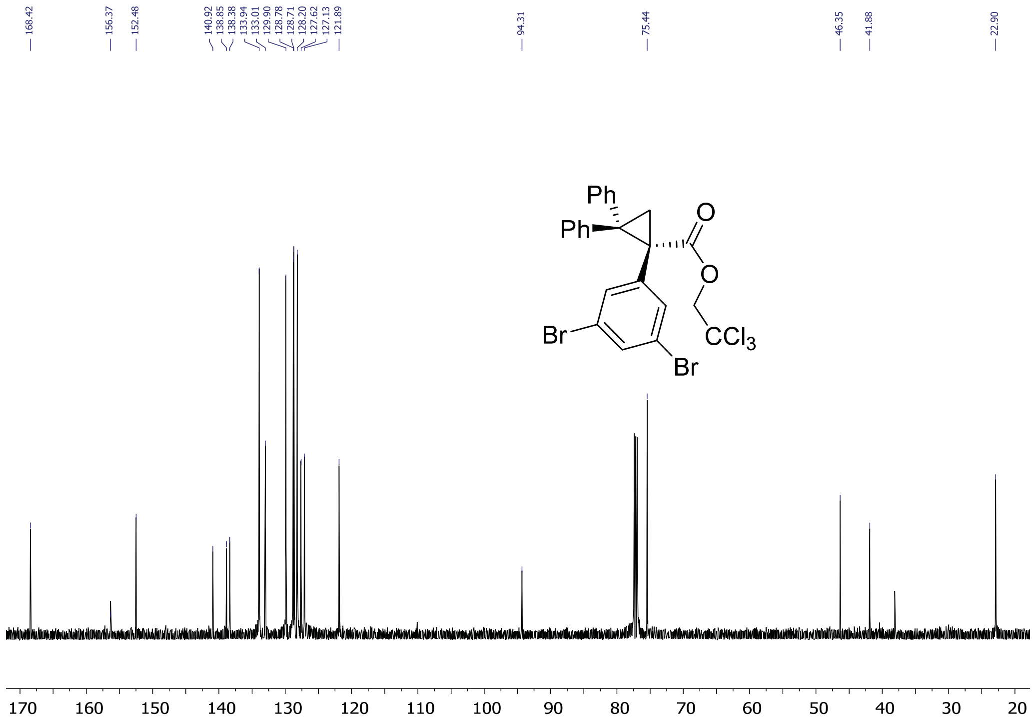


2,2,2-trichloroethyl (*R*)-1-(3,5-dibromophenyl)-2,2-diphenylcyclopropane-1-carboxylate. A flame dried round bottom flask was kept under a dry atmosphere of argon. Rh_2(*S*-PTAD)$_4$ (475 mg, 0.25 mmol, 0.005 equiv.) 1,1-diphenylethlyene (20.9 g, 116 mmol, 2.32 equiv.), and dry degassed pentane (100 mL) were added. A solution of freshly prepared 2,2,2-trichloroethyl 2-diazo-2-(3,5-dibromophenyl)acetate (22.6 g, 50 mmol, 1.0 equiv.) in dry, degassed pentane (150 mL) was added to the former solution drop-wise over 3 hours at -78 °C. The mixture was allowed to warm up to rt and stir overnight, and then concentrated in vacuum. The crude product was purified by flash column chromatography (hexanes/diethyl ether = 30/1) to provide the ester (>99% e.e.) as a white foam in 70% overall yield (21.1 g).

m.p.: 108-100 °C; TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.51 (t, *J* = 1.8 Hz, 2H), 7.44 (s, 1H), 7.37 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 2H), 7.31 – 7.26 (m, 1H), 7.12 (d, *J* = 1.3 Hz, 4H), 7.07 (h, *J* = 4.0 Hz, 1H), 4.59 (d, *J* = 11.8 Hz, 1H), 4.25 (d, *J* = 11.8 Hz, 1H), 2.78 (d, *J* = 5.8 Hz, 1H), 2.55 (d, *J* = 5.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.4, 156.4, 152.5, 140.9, 138.8, 138.4, 133.9, 133.0, 129.9, 128.8, 128.7, 128.2, 127.6, 127.1, 121.9, 94.3, 75.4, 46.4, 41.9, 22.9; HRMS (NSI) calcd for $C_{24}H_{18}Br_2Cl_3O_2$ ($[M+H]^+$): 600.8733 found 600.8750; IR (neat): 1739, 1551, 1202, 1138, 1112, 784, 742, 720, 702; HPLC (S,S-Whelk, 0.5% isopropanol in hexane, 0.5 mL/min, 1 mg/mL, 30 min, UV 210 nm) retention times of 15.8 min (single enantiomer), >99% e.e..

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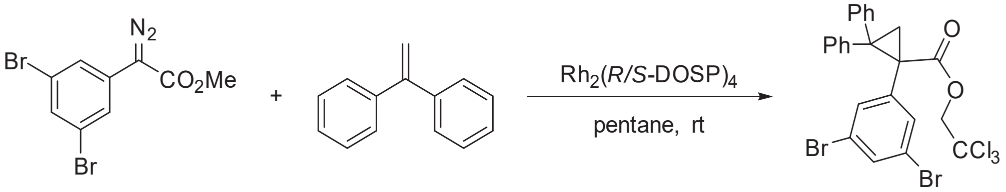

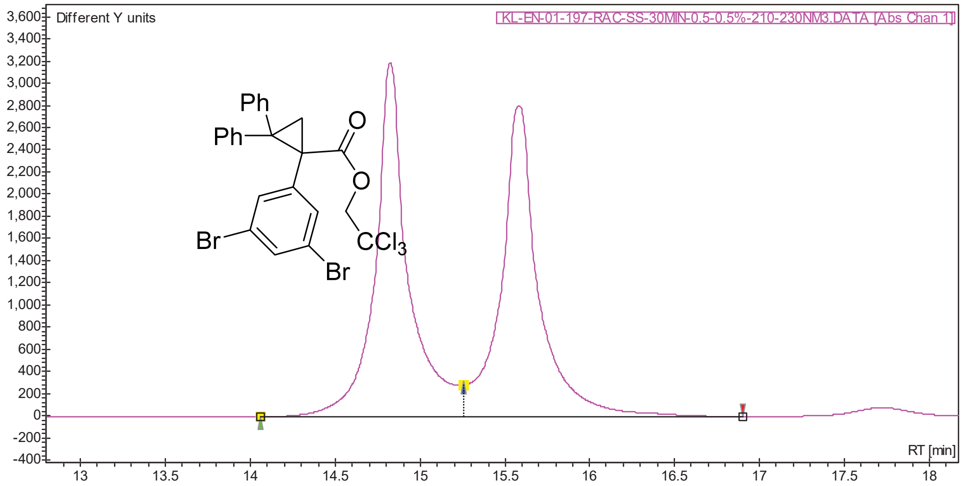

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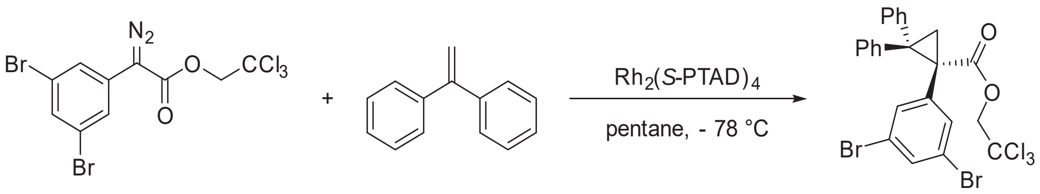

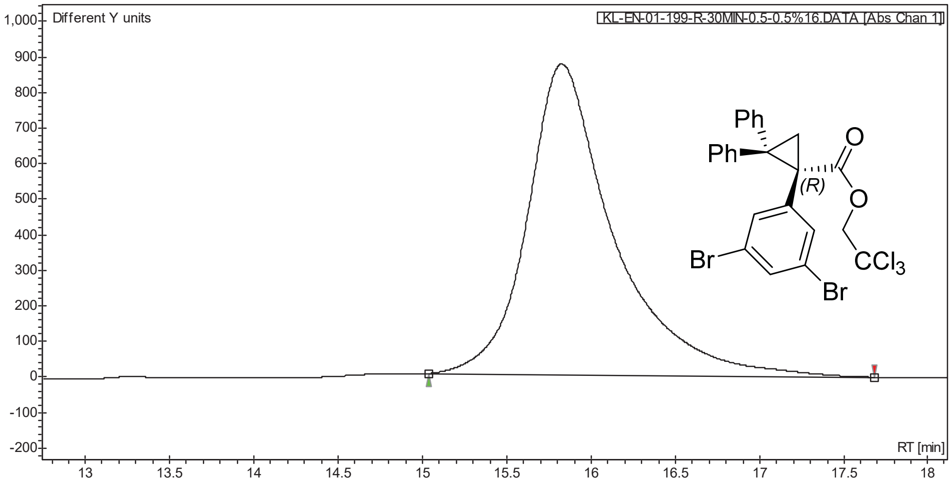

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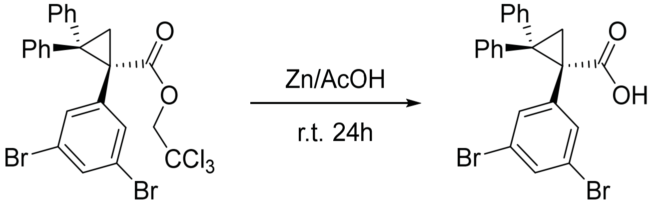
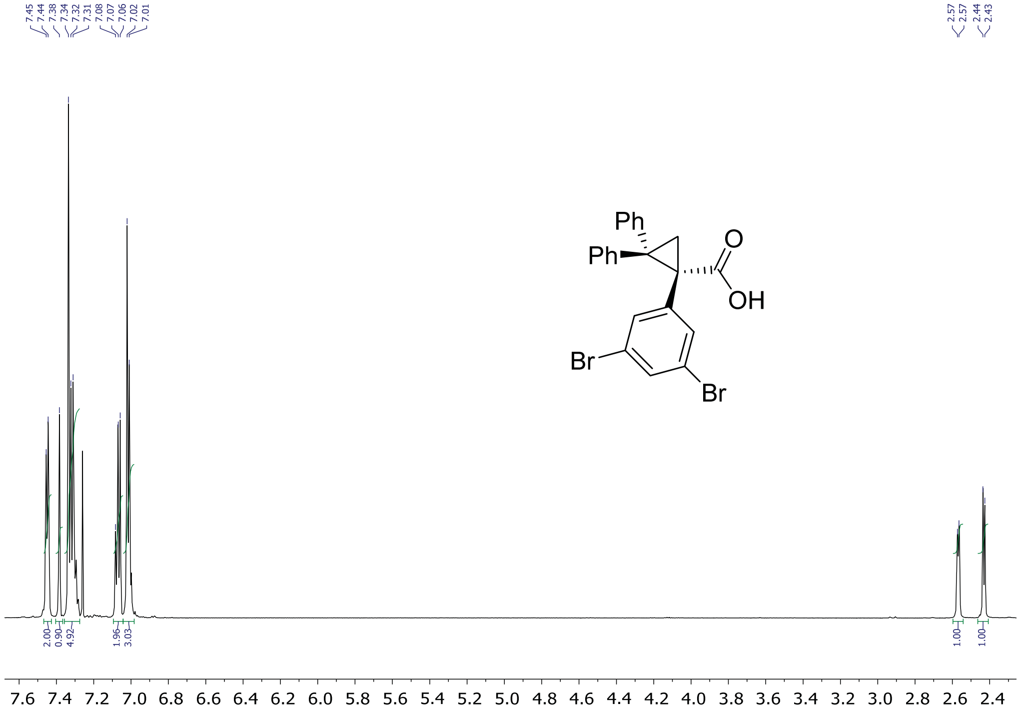
> 99% e.e.



(*R*)-1-(3,5-dibromophenyl)-2,2-diphenylcyclopropane-1-carboxylic acid. The 2,2,2-trichloroethyl (R)-1-(3,5-dibromophenyl)-2,2-diphenylcyclopropane-1-carboxylate (21.0 g, 35 mmol, 1.0 equiv.) was dissolved in 100 mL of glacial acetic acid, and zinc powder (11.4 g, 175 mmol, 5.0 equiv.) was added. The solution was allowed to stir at room temperature for 24 h. The starting material had been fully consumed as indicated by TLC analysis. The solution was diluted with H_2O (100 mL) and extracted with ethyl acetate (3x50 mL). The organic extracts were washed with H_2O and brine, dried over $MgSO_4$ and filtered. Then the filtrate was concentrated to give the crude product. The crude product was transferred to a 100-mL filter funnel loaded with a 3 inches silica plug and flashed with hexane/ethyl acetate (3:2) (100 mL), and then the filtrate was concentrated under reduced pressure to give the product as a white solid in 99% overall yield (16.4 g).

m.p.: 185-187 °C; TLC (ethyl acetate: hexanes, 1:4 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 6.3 Hz, 2H), 7.38 (s, 1H), 7.35 – 7.28 (m, 5H), 7.10 – 7.04 (m, 1H), 7.02 (d, *J* = 6.6 Hz, 3H), 2.57 (d, *J* = 5.6 Hz, 1H), 2.43 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.6, 156.4, 152.5, 141.0, 133.9, 132.9, 129.7, 128.7, 128.6, 128.2, 127.4, 127.1, 121.8, 38.2, 35.0, 23.2; HRMS (NSI) calcd for $C_{22}H_{17}Br_2O_2$ ($[M+H]^+$): 470.9589 found 470.9595; IR (neat): 1693, 1584, 1552, 1448, 1408, 1213, 1098, 863, 741, 693; HPLC (S,S-Whelk, 0.75% isopropanol in hexane, 1 mL/min, 1 mg/mL, 30 min, UV 210 nm) retention times of 20.9 min (single enantiomer), >99% e.e..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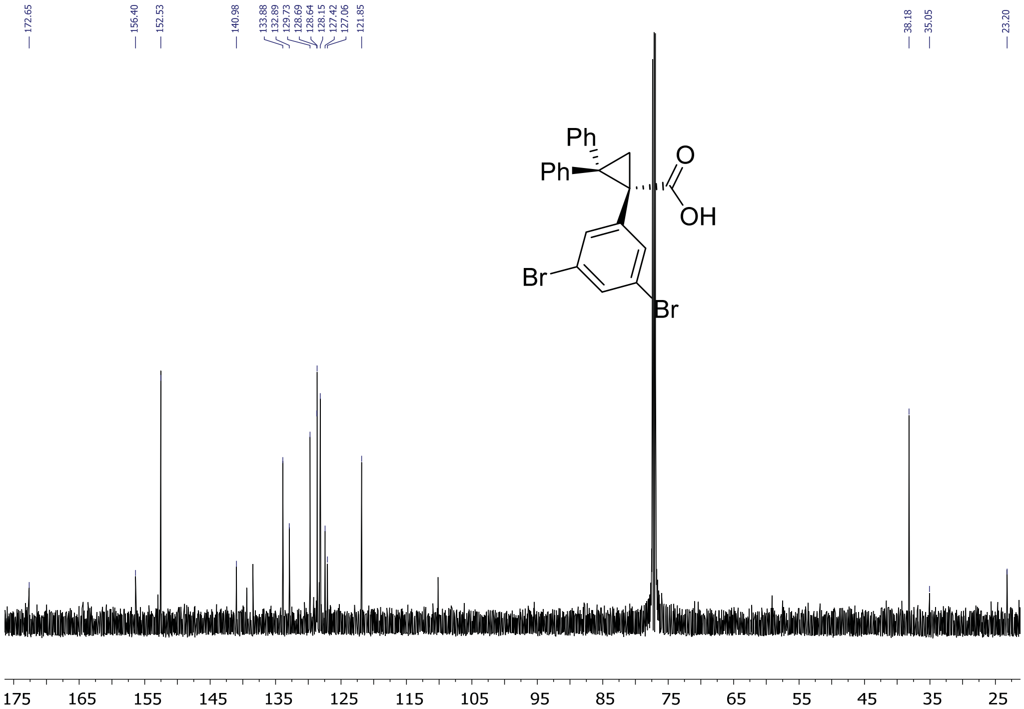

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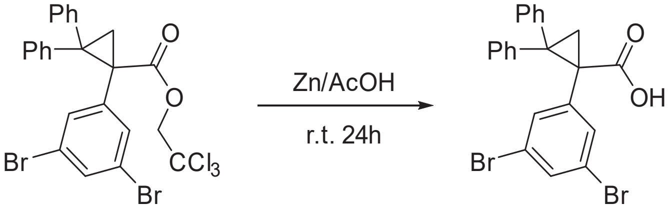

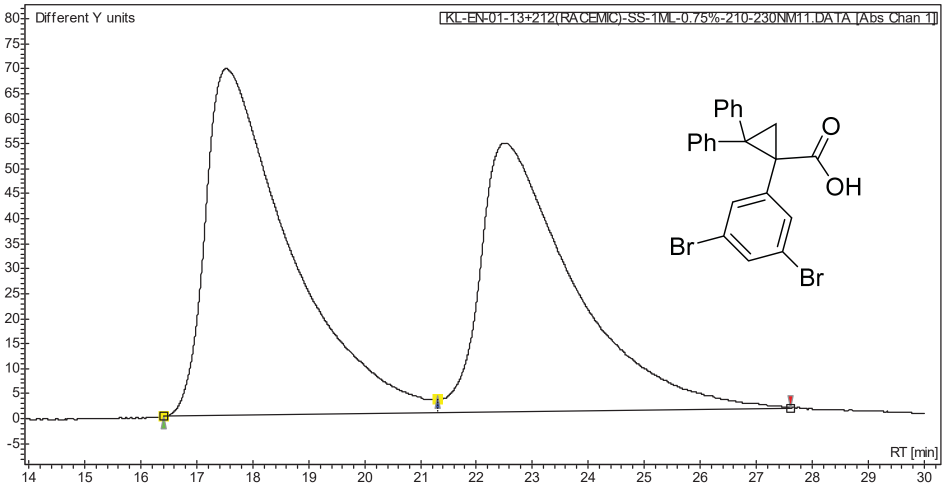

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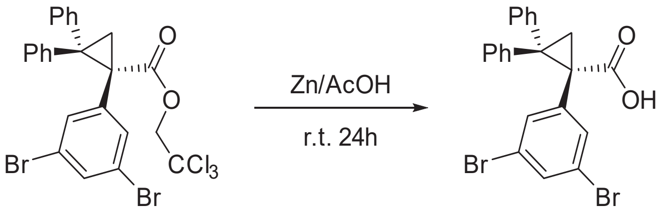

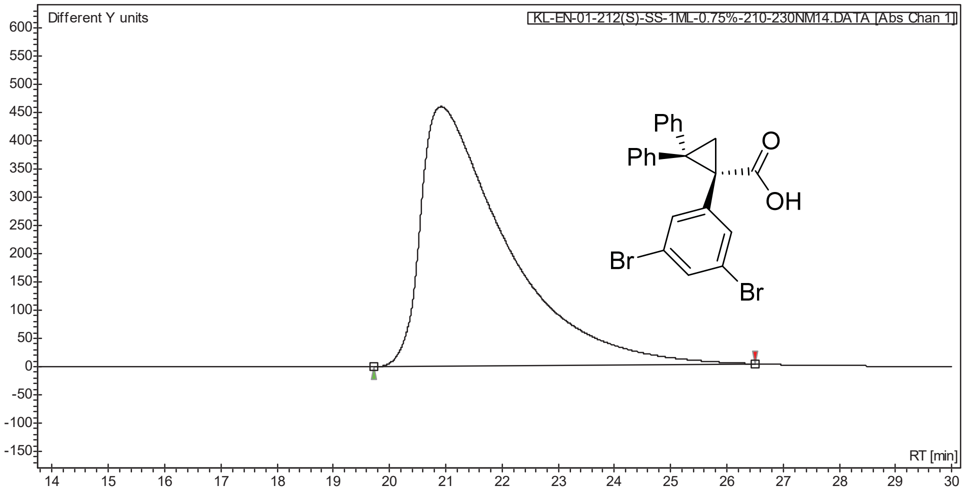

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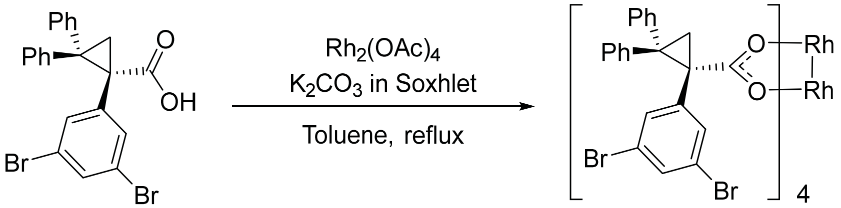
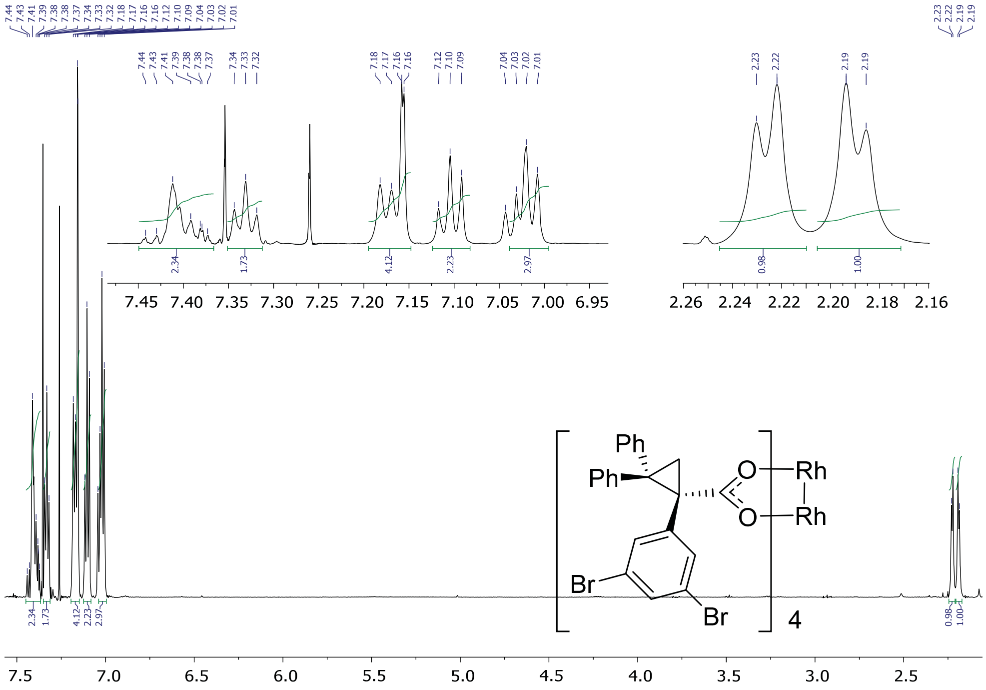
> 99% e.e.



Dirhodium tetrakis((*R*)-1-(3,5-dibromophenyl)-2,2-diphenylcyclopropanecarboxylate) (8). A 50-mL round bottom flask, equipped with a Teflon-coated stirring bar and nitrogen inlet, was flushed with nitrogen and then charged with rhodium(II) acetate (1 mmol, 0.44 g, 1.0 equiv), (*R*)-1-(3,5-dibromophenyl)-2,2-diphenylcyclopropane-1-carboxylic acid (8 mmol, 3.78 g, 8.0 equiv), and 35 mL of toluene. The flask was fitted with a Soxhlet extraction apparatus into which was placed a thimble containing 15 g of an oven-dried mixture of 2 parts sodium carbonate and 1 part of sand. The solution was heated at reflux and monitored by MS; removal of the solvent under reduced pressure using a rotary evaporator and then purified by flash column chromatography (hexanes/diethyl ether = 30/1) to give green solid in 82% overall yield (1.72 g).

m.p.: 203-206 °C; TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.45 – 7.37 (m, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.20 – 7.14 (m, 4H), 7.10 (t, *J* = 7.6 Hz, 2H), 7.02 (t, *J* = 7.0 Hz, 3H), 2.23 (d, *J* = 5.0 Hz, 1H), 2.19 (d, *J* = 5.0 Hz, 1H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 188.6, 156.4, 141.4, 140.9, 139.4, 133.5, 132.2, 129.9, 128.9, 128.2, 128.1, 127.0, 126.8, 121.6, 46.6, 43.4, 38.2, 25.3; HRMS (ESI) calcd for $C_{88}H_{60}Br_8{}^{81}BrO_8Rh_2$ (M$^+$): 2083.5839 found 2083.5794; IR (neat):2924, 1587, 1551, 1408, 1378, 741, 701.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2.23 2.22 2.19 2.19
2.34
1.73
4.12
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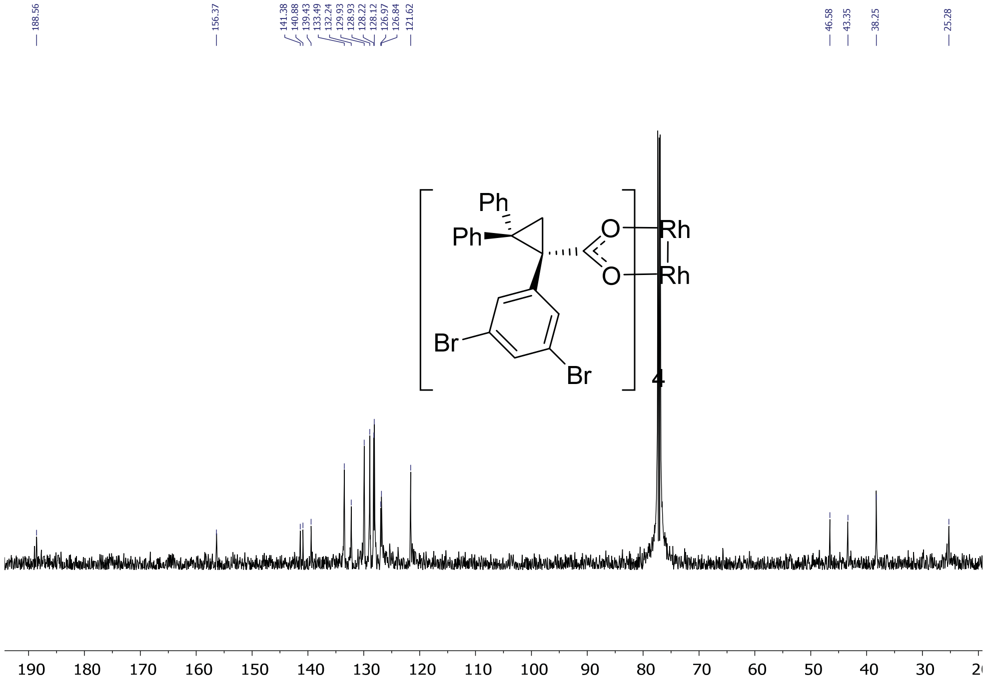
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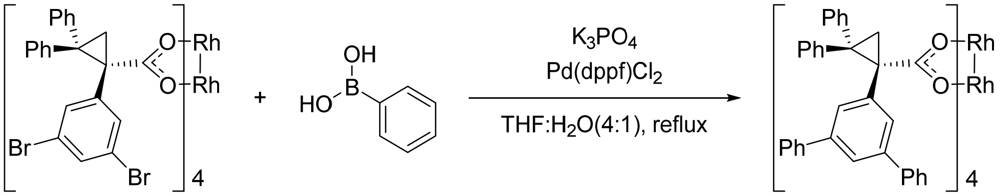
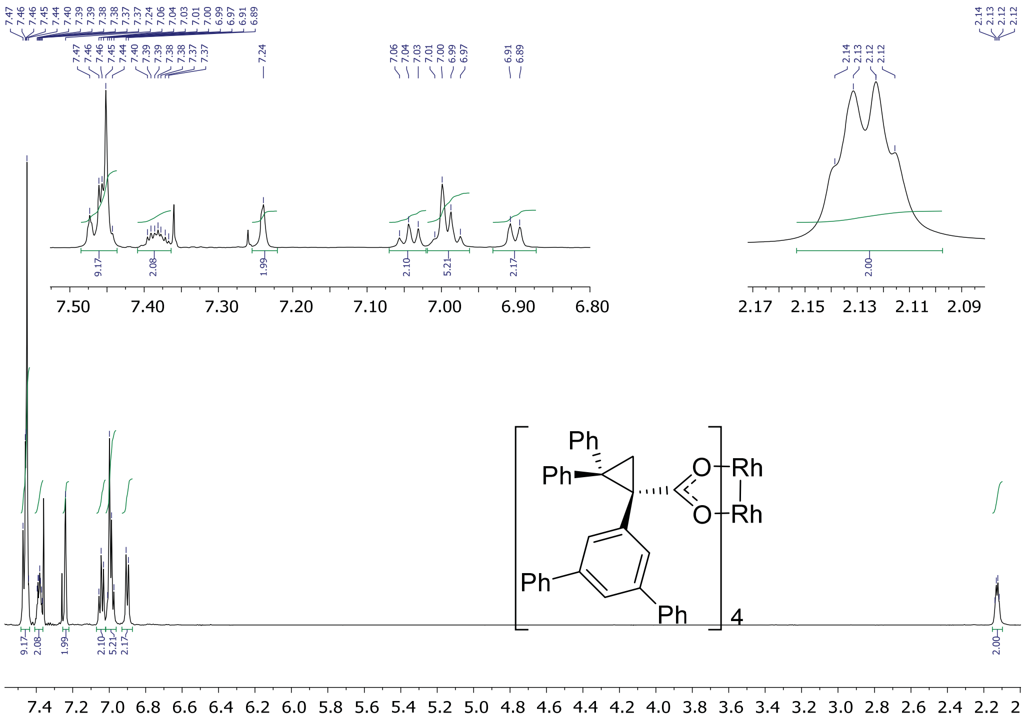


Dirhodium tetrakis((*R*)-1-([1,1':3',1''-terphenyl]-5'-yl)-2,2-diphenylcyclopropanecarboxylate) (9). A 25-mL round bottom flask was charged with dirhodium tetrakis((*R*)-1-(3,5-dibromophenyl)-2,2-diphenylcyclopropanecarboxylate) (73 mg, 0.035 mmol, 1.00 equiv.), boronic acid (68 mg, 0.56 mmol, 16 equiv.). K_3PO_4 (178 mg, 0.84 mmol, 24 equiv.) and THF: H_2O (4:1) (12 mL). The solution was heated to reflux for 10 min to degass and then [1,1'-Bis(diphenylphosphino)ferrocene] dichloropalladium(II) [Pd(dppf)Cl_2] (10 mg, 0.014 mmol, 0.4 equiv.) was added. The resulting red solution was then remained reflux for 12 h. After the allotted time had passed and the starting material had disappeared on TLC, the solution was cooled to room temperature and concentrated under reduced pressure. The residue was redissolved in DCM, washed with water (3x15mL) and brine (3x15mL). The organic layer was dried over sodium sulfate (10 g) and filtered. The filtrate was concentrated by rotary evaporation to afford the crude product. The crude product was purified by flash column chromatography (hexanes/diethyl ether = 30/1) to give a green solid in 96% overall yield (69 mg).

m.p.: 208-211 °C; TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 9H), 7.38 (tt, *J* = 6.3, 2.8 Hz, 2H), 7.24 (s, 2H), 7.04 (t, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 7.0 Hz, 6H), 6.90 (d, *J* = 7.6 Hz, 2H), 2.14 (d, *J* = 4.3 Hz, 1H), 2.12 (d, *J* = 4.3 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 190.2, 156.5, 152.6, 141.8, 141.7, 141.0, 140.8, 138.6, 130.3, 130.2, 129.3, 129.0, 128.2, 127.9, 127.6, 127.5, 126.4, 126.3, 124.7, 45.8, 44.6, 38.3, 31.0, 26.3; HRMS (ESI) calcd for $C_{136}H_{100}O_8Rh_2$ (M^+): 2066.5522 found 2066.5522; IR (neat): 1581, 1496, 1378, 755, 722, 696.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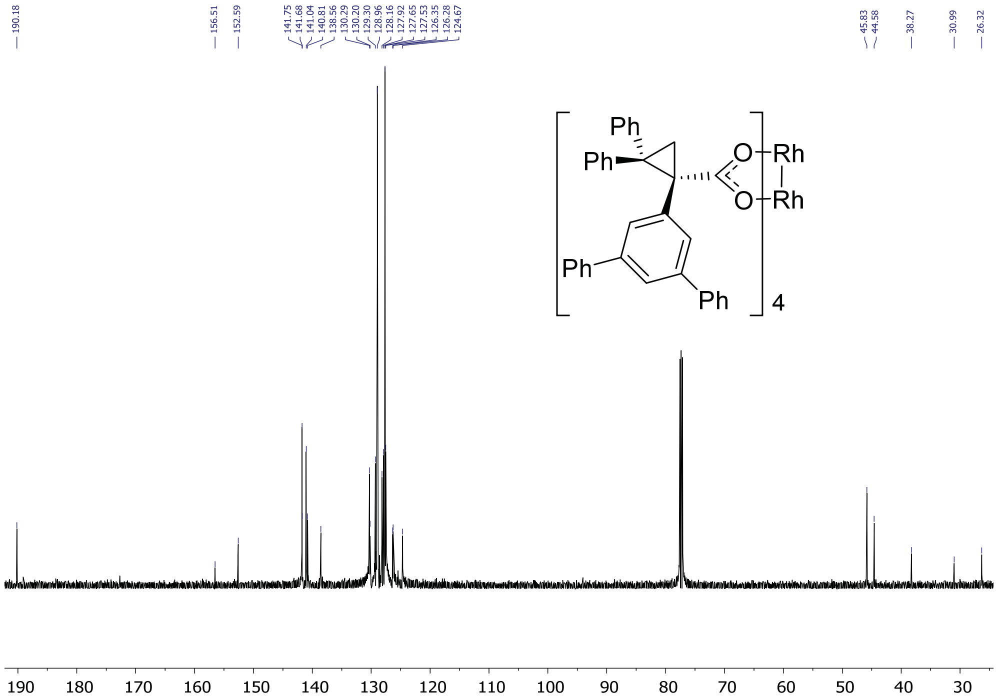
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126.35
126.28
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38.27
30.99
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Rh
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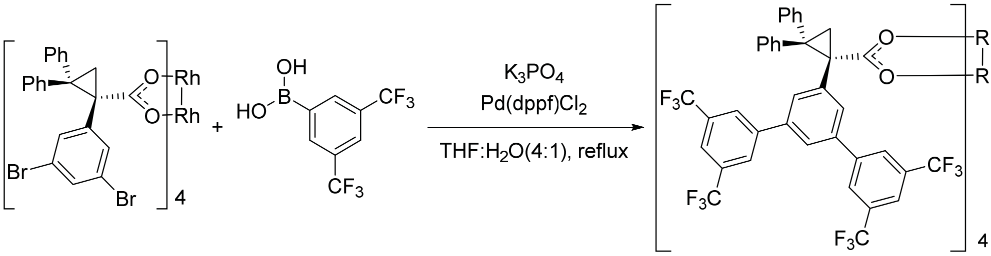
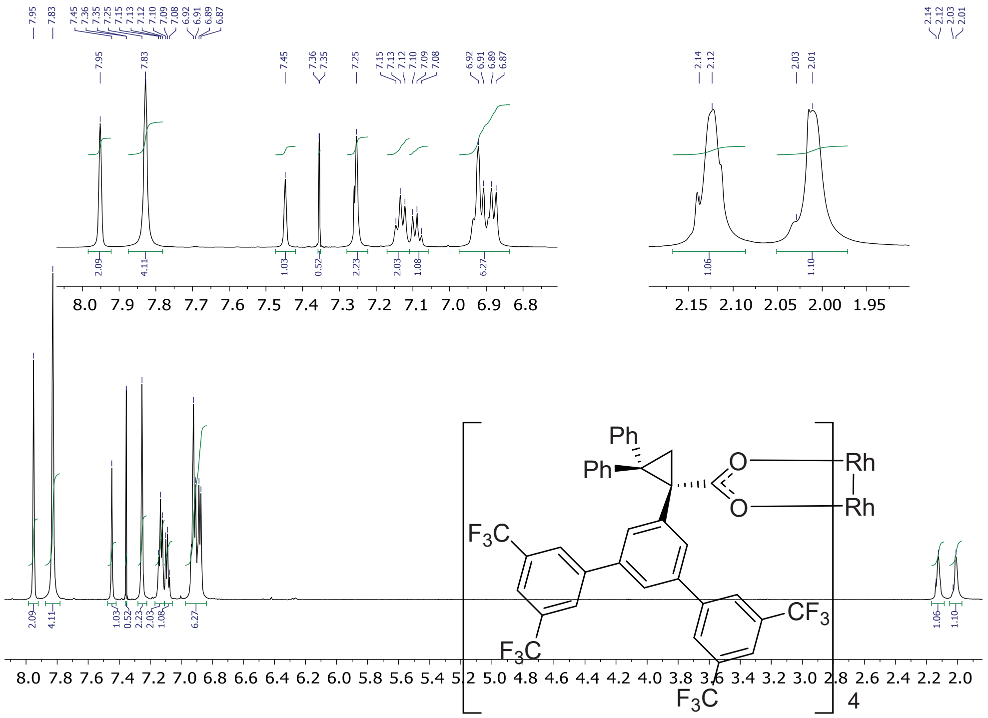


Dirhodium tetrakis((*R*)-2,2-diphenyl-1-(3,3'',5,5''-tetrakis(trifluoromethyl)-[1,1':3',1''-terphenyl]-5'-yl)cyclopropanecarboxylate) (10). A 25-mL round bottom flask was charged with dirhodium tetrakis((*R*)-1-(3,5-dibromophenyl)-2,2-diphenylcyclopropanecarboxylate) (84 mg, 0.04 mmol, 1.00 equiv.), boronic acid (165 mg, 0.64 mmol, 16 equiv.), K_3PO_4 (204 mg, 0.96 mmol, 24.0 equiv.) and THF: H_2O (4:1) (12 mL). The solution was heated to reflux for 10 min to degass and then Pd(dppf)Cl_2 (12 mg, 0.016 mmol, 0.4 equiv.) was added. The resulting red solution was then remained reflux for 12 hours. After the allotted time had passed and the starting material had disappeared on TLC, the solution was cooled to room temperature and concentrated under reduced pressure. The residue was redissolved in DCM, washed with water (3x15mL) and brine (3x15mL). The organic layer was dried over sodium sulfate (10 g) and filtered. The filtrate was concentrated by rotary evaporation to afford the crude product. The crude product was purified by flash column chromatography (hexanes/diethyl ether = 30/1) to give a green solid in 60% overall yield (76 mg).

m.p.: decomposed at 230 °C; TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (s, 2H), 7.83 (s, 4H), 7.45 (s, 1H), 7.35 (d, *J* = 0.6 Hz, 1H), 7.25 (s, 2H), 7.13 (t, *J* = 7.3 Hz, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.97 – 6.86 (m, 6H), 2.13 (d, *J* = 11.0 Hz, 1H), 2.02 (d, *J* = 11.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.4, 189.1, 156.5, 143.0, 140.8, 140.3, 139.4, 139.0, 132.5 (q, *J* = 33.7 Hz), 129.9, 128.8, 128.4, 128.2, 127.9, 127.8-127.5 (m), 127.0, 124.7, 124.3, 122.5, 121.7-121.5 (m), 110.2, 45.8, 44.0, 38.4, 28.2; HRMS (ESI) calcd for $C_{152}H_{84}O_8F_{48}Rh_2$ (M^+): 3154.3504 found 3154.3476; IR (neat): 1585, 1366, 1276, 1173, 1130, 1108, 1072, 901, 877, 844, 754, 721, 706, 682, 674.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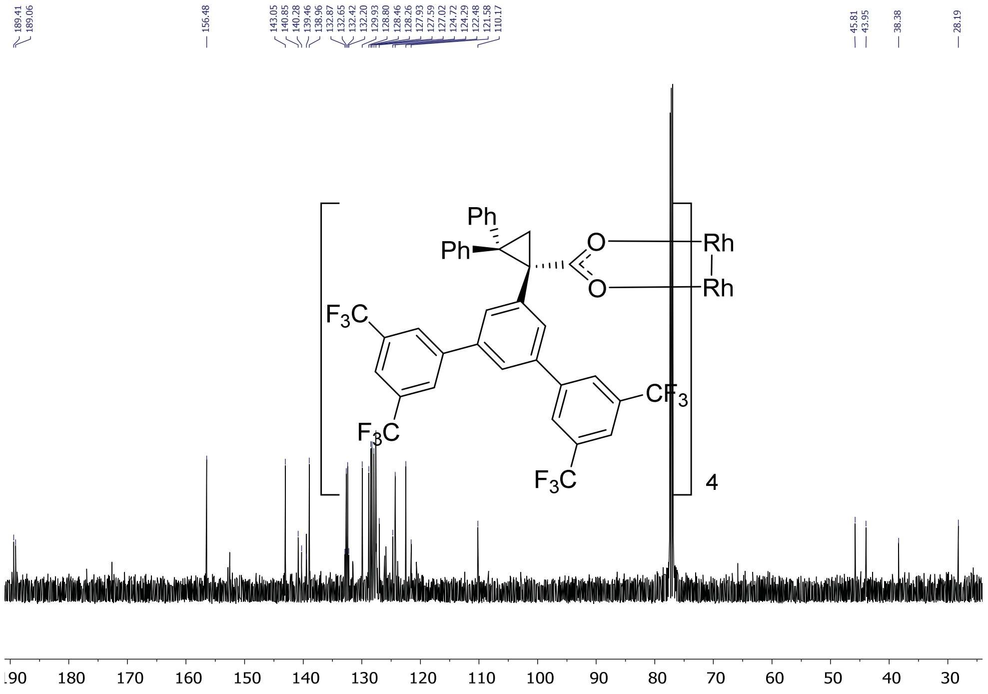
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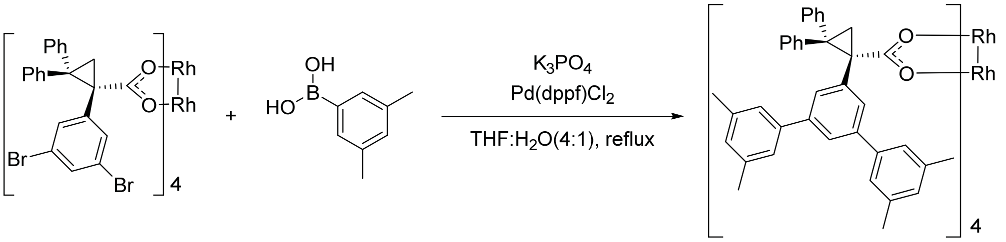
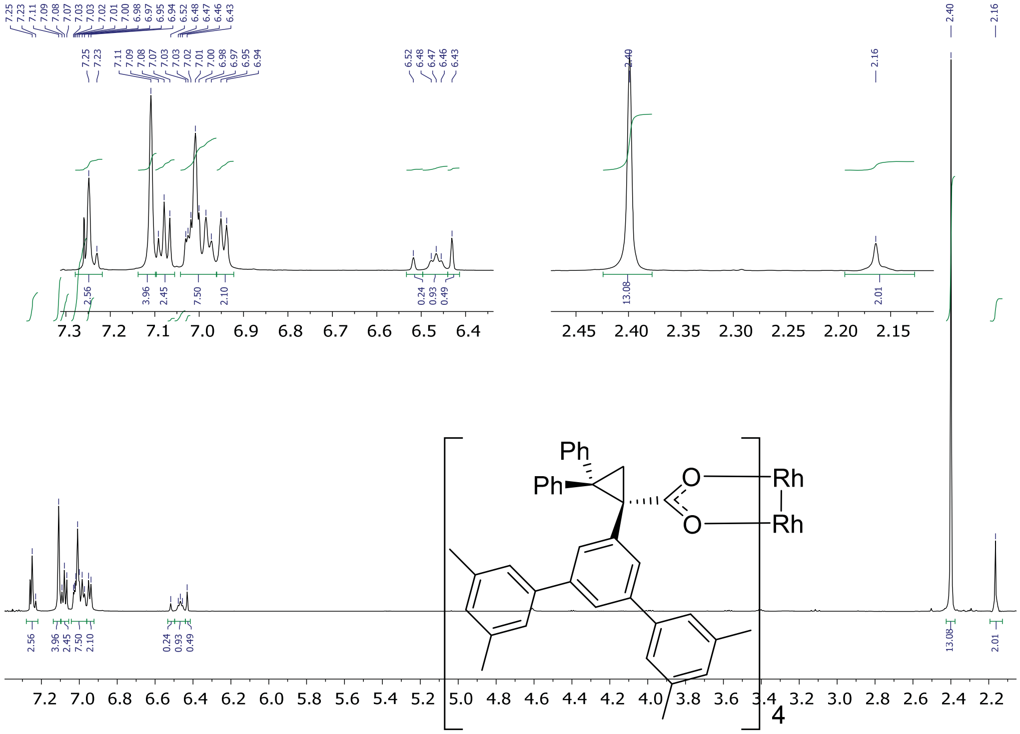


Dirhodium tetrakis((*R*)-2,2-diphenyl-1-(3,3'',5,5''-tetramethyl-[1,1':3',1''-terphenyl]-5'-yl)cyclopropanecarboxylate) (11). A 25-mL round bottom flask was charged with dirhodium tetrakis((*R*)-1-(3,5-dibromophenyl)-2,2-diphenylcyclopropanecarboxylate) (84 mg, 0.04 mmol, 1.00 equiv.), boronic acid (96 mg, 0.64 mmol, 16 equiv.), K_3PO_4 (204 mg, 0.96 mmol, 24 equiv.) and THF: H_2O (4:1) (12 mL). The solution was heated to reflux for 10 min to degass and then Pd(dppf)Cl_2 (12 mg, 0.016 mmol, 0.4 equiv.) was added. The resulting red solution was then remained reflux for 12 hours. After the allotted time had passed and the starting material had disappeared on TLC, the solution was cooled to room temperature and concentrated under reduced pressure. The residue was redissolved in DCM, washed with water (3x15mL) and brine (3x15mL). The organic layer was dried over sodium sulfate (10 g) and filtered. The filtrate was concentrated by rotary evaporation to afford the crude product. The crude product was purified by flash column chromatography (hexanes/diethyl ether = 10/1) to give a green solid in 66% overall yield (61 mg).

m.p.: decomposed at 146 °C; TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 2H), 7.11 (s, 4H), 7.08 (t, *J* = 7.7 Hz, 2H), 7.04 – 6.96 (m, 8H), 6.94 (d, *J* = 7.8 Hz, 2H), 6.47 (t, *J* = 6.7 Hz, 1H), 2.40 (s, 12H), 2.16 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.6, 156.3, 152.4, 141.7, 141.1, 140.7, 138.2, 130.0, 129.3, 128.9, 128.1, 127.7, 125.4, 122.5, 45.6, 44.9, 38.1, 38.1, 21.6; HRMS (ESI) calcd for $C_{152}H_{132}O_8Rh_2$ (M^+): 2290.8026 found 2290.8018; IR (neat): 2919, 1584, 1447, 1378, 846, 752, 700, 676.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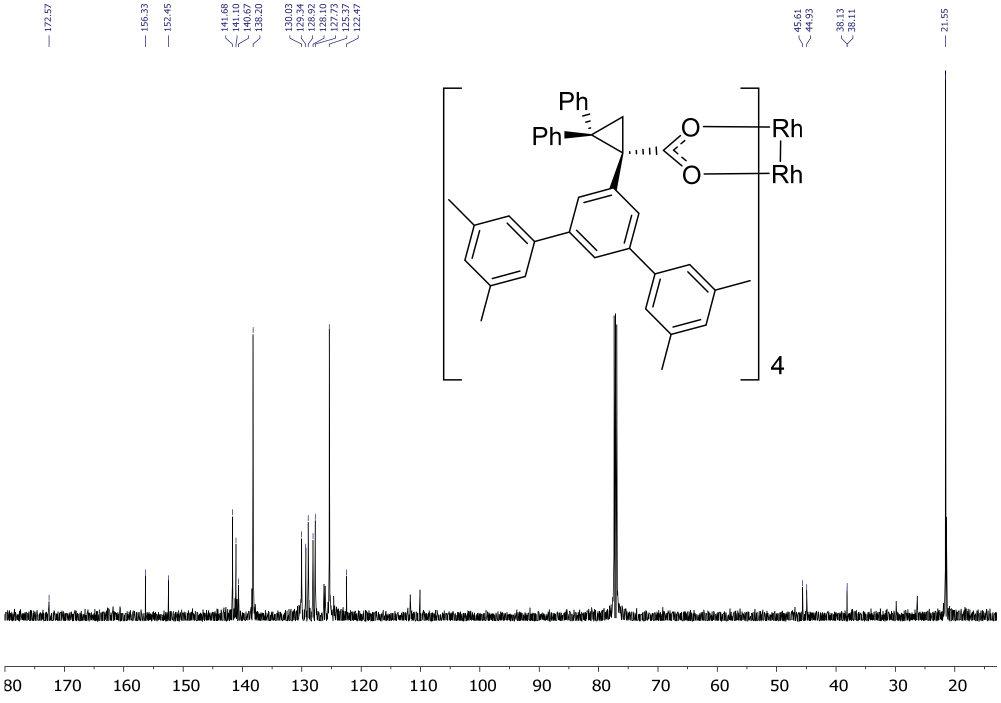
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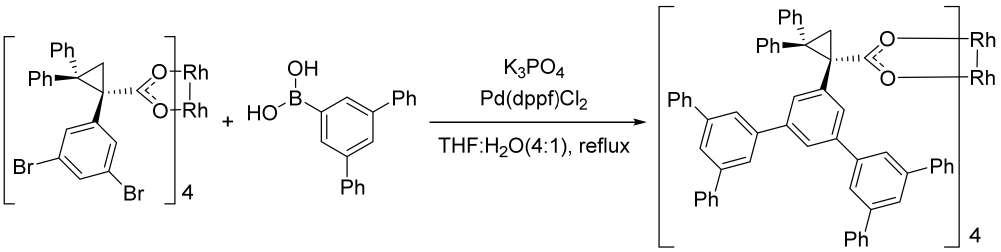
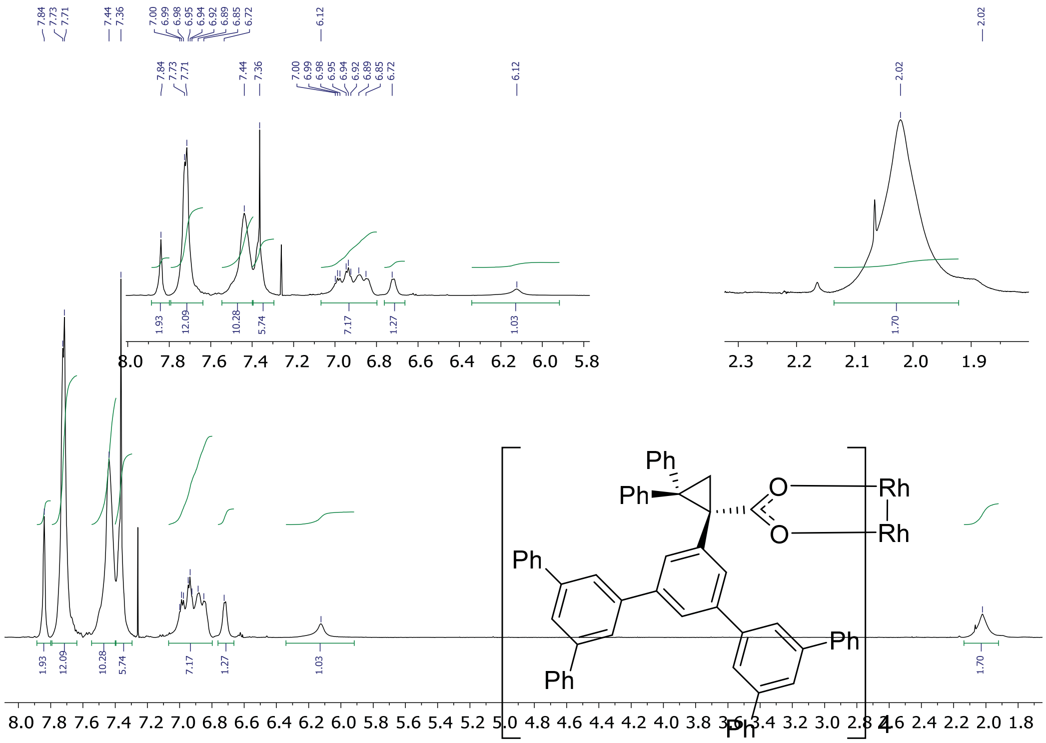


Dirhodium tetrakis((*R*)-1-(5',5'''-diphenyl-[1,1':3',1'':3'',1''':3''',1''''-quinquephenyl]-5''-yl)-2,2-diphenylcyclopropanecarboxylate) (12). A 25-mL round bottom flask was charged with dirhodium tetrakis((*R*)-1-(3,5-dibromophenyl)-2,2-diphenylcyclopropanecarboxylate) (84 mg, 0.04 mmol, 1.00 equiv.), boronic acid (175 mg, 0.64 mmol, 16 equiv.), K_3PO_4 (204 mg, 0.96 mmol, 24 equiv.) and THF: H_2O (4:1) (12 mL). The solution was heated to reflux for 10 min to degass and then Pd(dppf)Cl_2 (12 mg, 0.016 mmol, 0.4 equiv.) was added. The resulting red solution was then remained reflux for 12 hours. After the allotted time had passed and the starting material had disappeared on TLC, the solution was cooled to room temperature and concentrated under reduced pressure. The residue was redissolved in DCM, washed with water (3x15mL) and brine (3x15mL). The organic layer was dried over sodium sulfate (10 g) and filtered. The filtrate was concentrated by rotary evaporation to afford the crude product. The crude product was purified by flash column chromatography (hexanes/diethyl ether = 20/1) to give a green solid in 75% overall yield (98 mg).

m.p.: decomposed at 200 °C; TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (s, 2H), 7.72 (d, *J* = 6.4 Hz, 12H), 7.44 (s, 10H), 7.36 (s, 6H), 7.07 – 6.79 (m, 7H), 6.72 (s, 1H), 6.12 (s, 1H), 2.02 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.0, 156.4, 152.5, 151.3, 142.6, 141.2, 129.1, 129.0, 128.9, 128.4, 127.7, 127.5, 127.5, 125.4, 38.3, 28.1; HRMS (ESI) calcd for $C_{232}H_{164}O_8Rh_2$ (M^+): 3283.0530 found 3283.0598; IR (neat): 2924, 1586, 1496, 1447, 1378, 1114, 1075, 868, 757, 695.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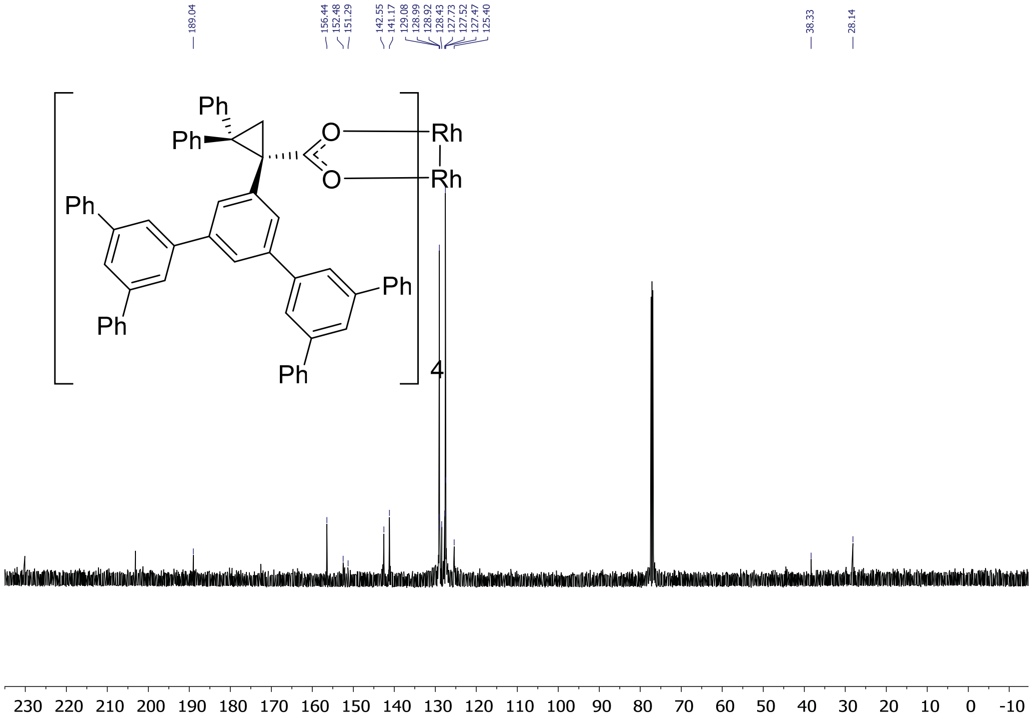
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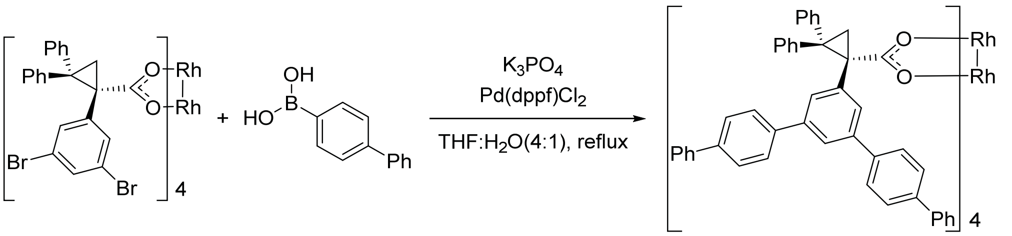
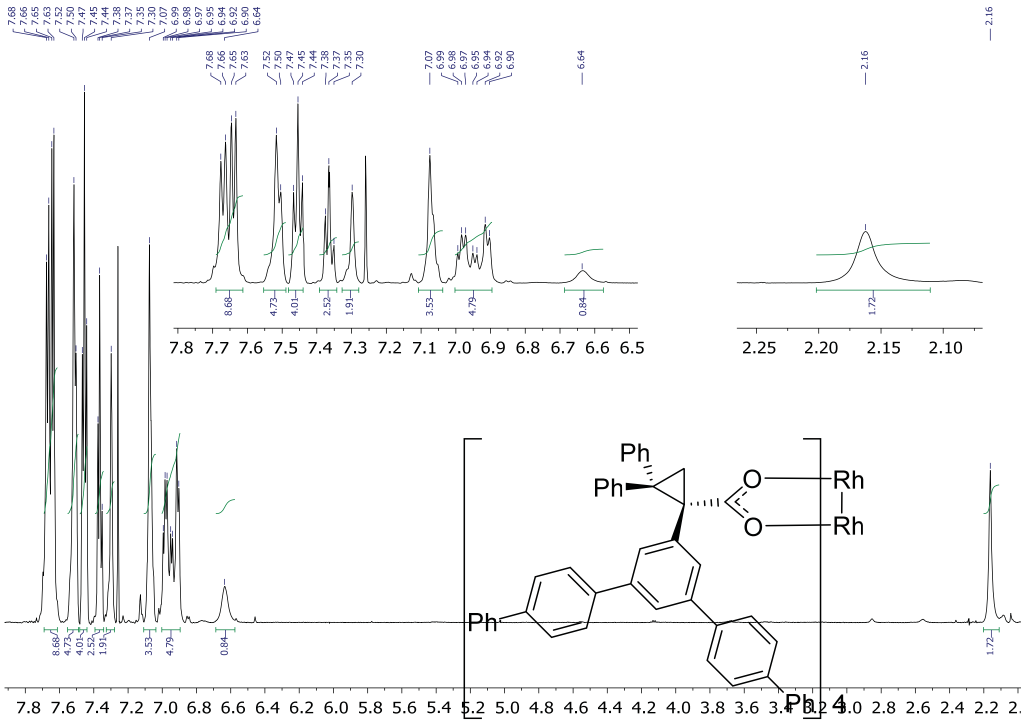


Dirhodium tetrakis((*R*)-1-([1,1':4',1'':3'',1''':4''',1''''-quinquephenyl]-5''-yl)-2,2-diphenylcyclopropanecarboxylate) (13). A 25-mL round bottom flask was charged with dirhodium tetrakis((*R*)-1-(3,5-dibromophenyl)-2,2-diphenylcyclopropanecarboxylate) (84 mg, 0.04 mmol, 1.00 equiv.), boronic acid (127 mg, 0.64 mmol, 16 equiv.) K_3PO_4 (204 mg, 0.96 mmol, 24 equiv.) and THF: H_2O (4:1) (12 mL). The solution was heated to reflux for 10 min to degass and then Pd(dppf)Cl_2 (12 mg, 0.016 mmol, 0.4 equiv.) was added. The resulting red solution was then remained reflux for 12 hours. After the allotted time had passed and the starting material had disappeared on TLC, the solution was cooled to room temperature and concentrated under reduced pressure. The residue was redissolved in DCM, washed with water (3x15mL) and brine (3x15mL). The organic layer was dried over sodium sulfate (10 g) and filtered. The filtrate was concentrated by rotary evaporation to afford the crude product. The crude product was purified by flash column chromatography (hexanes/diethyl ether = 30/1) to give a green solid in 82% overall yield (88 mg).

m.p.: 212-214 °C; TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 18.2, 7.6 Hz, 9H), 7.51 (d, *J* = 7.4 Hz, 5H), 7.45 (t, *J* = 7.7 Hz, 4H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.30 (s, 2H), 7.07 (s, 3H), 7.02 – 6.96 (m, 2H), 6.95 (d, *J* = 7.0 Hz, 1H), 6.91 (d, *J* = 7.4 Hz, 2H), 6.64 (s, 1H), 2.16 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.6, 156.4, 152.5, 140.8, 140.5, 140.4, 140.2, 129.2, 129.0, 128.1, 127.9, 127.8, 127.5, 127.5, 127.2, 38.4, 38.3, 38.2; HRMS (ESI) calcd for $C_{184}H_{132}O_8Rh_2$ (M^+): 2674.8026 found 2674.7965; IR (neat): 2922, 2852, 1582, 1488, 1448, 1378, 1007, 833, 763, 732, 713, 695.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2.16
8.68
4.73
4.01
2.52
1.91
3.53
4.79
0.84
1.72
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5
2.25 2.20 2.15 2.10
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.
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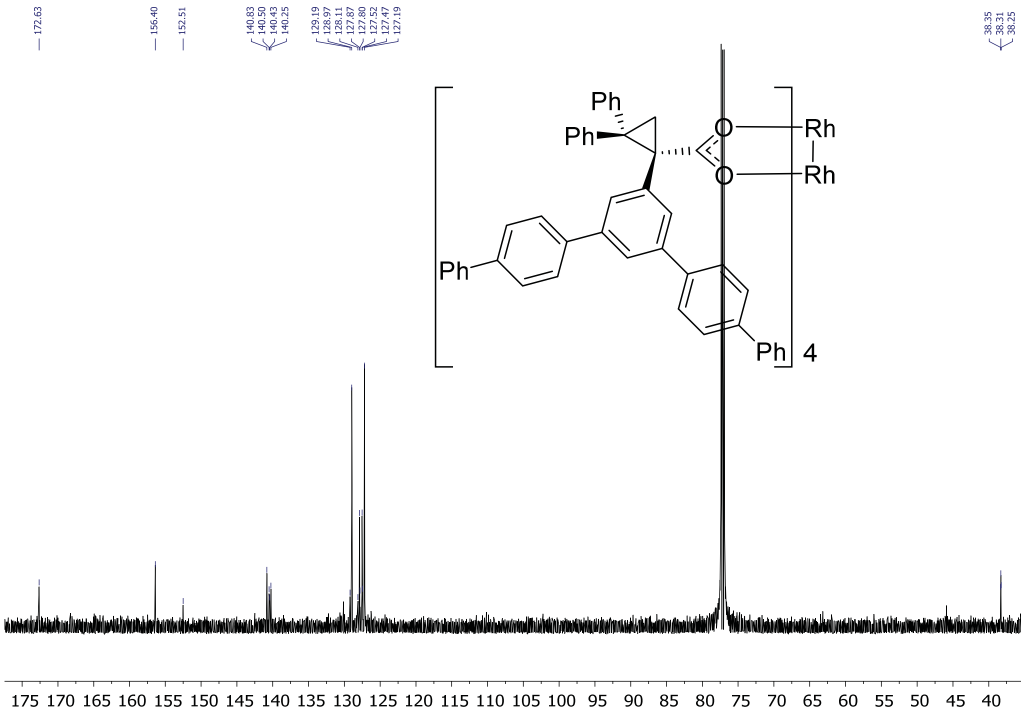

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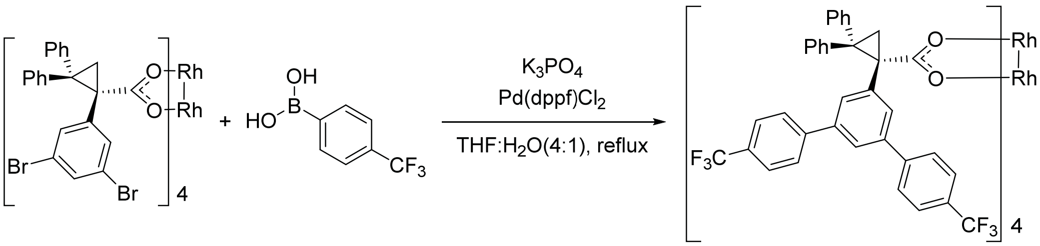
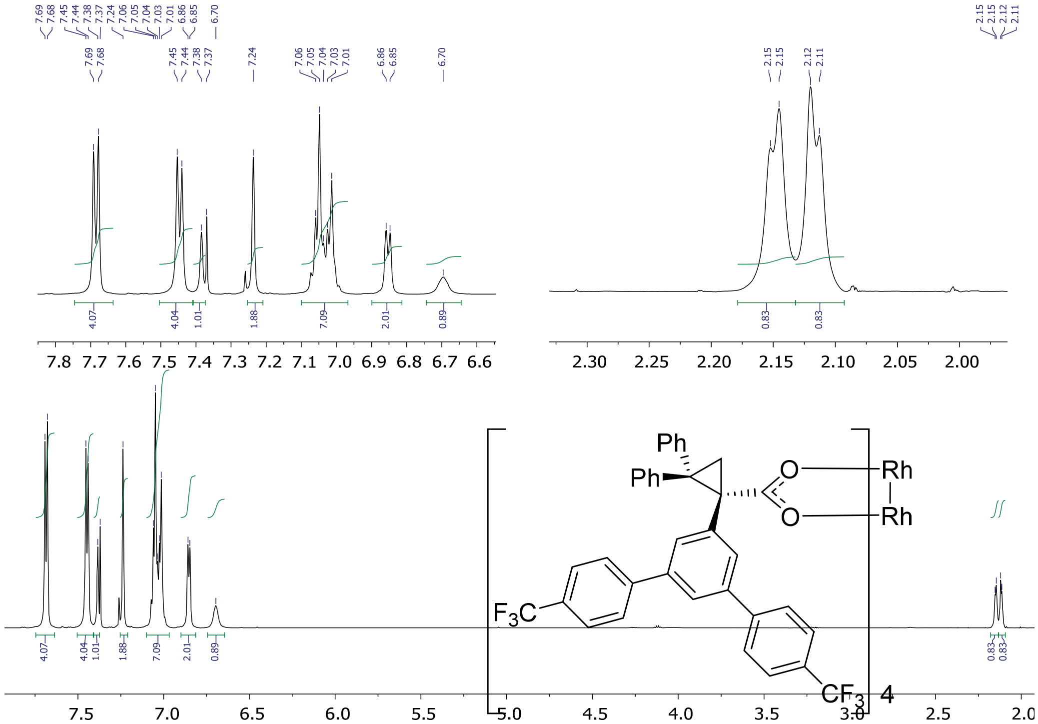


Dirhodium tetrakis((*R*)-1-(4,4''-bis(trifluoromethyl)-[1,1':3',1''-terphenyl]-5'-yl)-2,2-diphenylcyclopropanecarboxylate) (14). A 25-mL round bottom flask was charged with dirhodium tetrakis((*R*)-1-(3,5-dibromophenyl)-2,2-diphenylcyclopropanecarboxylate) (84 mg,0.04 mmol, 1.00 equiv.), boronic acid (122 mg, 0.64 mmol, 16 equiv.), K_3PO_4 (204 mg, 0.96 mmol, 24 equiv.) and THF: H_2O (4:1) (12 mL). The solution was heated to reflux for 10 min to degass and then Pd(dppf)Cl_2 (12 mg, 0.016 mmol, 0.4 equiv.) was added. The resulting red solution was then remained reflux for 12 h. After the allotted time had passed and the starting material had disappeared on TLC, the solution was cooled to room temperature and concentrated under reduced pressure. The residue was redissolved in DCM, washed with water (3x15mL) and brine (3x15mL). The organic layer was dried over sodium sulfate (10 g) and filtered. The filtrate was concentrated by rotary evaporation to afford the crude product. The crude product was purified by flash column chromatography (hexanes/diethyl ether = 20/1) to give a green solid in 86% overall yield (90 mg).

m.p.: 194-195 °C; TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 4H), 7.45 (d, *J* = 7.9 Hz, 4H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.24 (s, 2H), 7.04 (dd, *J* = 20.6, 6.8 Hz, 7H), 6.85 (d, *J* = 6.7 Hz, 2H), 6.70 (s, 1H), 2.15 (d, *J* = 4.3 Hz, 1H), 2.12 (d, *J* = 4.3 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.8, 144.6, 141.4, 140.3, 139.7, 139.1, 130.7, 130.0, 129.8 (d, *J* = 32.2 Hz), 129.1, 128.1, 128.0, 127.7, 126.6, 126.3, 125.8, 125.2, 124.6, 123.4, 45.9, 44.0, 30.8, 26.0; HRMS (ESI) calcd for $C_{144}H_{92}O_8F_{24}Rh_2$ (M^+): 2610.4513 found 2610.4546; IR (neat): 1583, 1378, 1322, 1164, 1123, 1109, 1065, 1016, 835, 757, 720, 700, 670.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4.04
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0.83
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2.30 2.25 2.20 2.15 2.10 2.05 2.00
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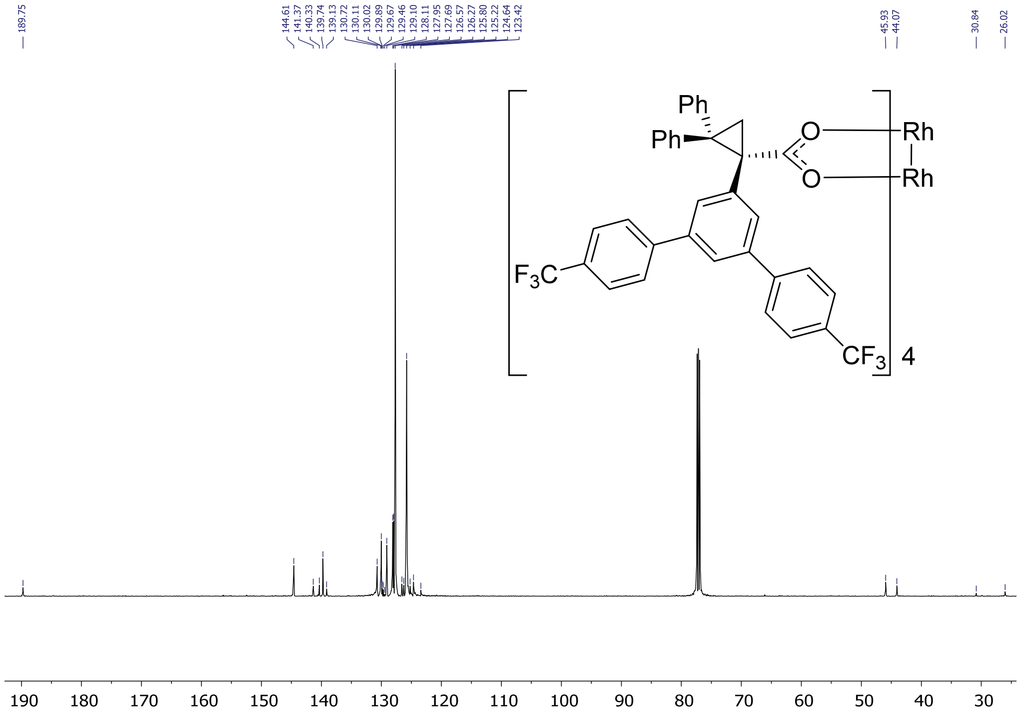
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126.27
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125.22
124.64
123.42
45.93
44.07
30.84
26.02
Ph
Ph
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O
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Rh
F_3C
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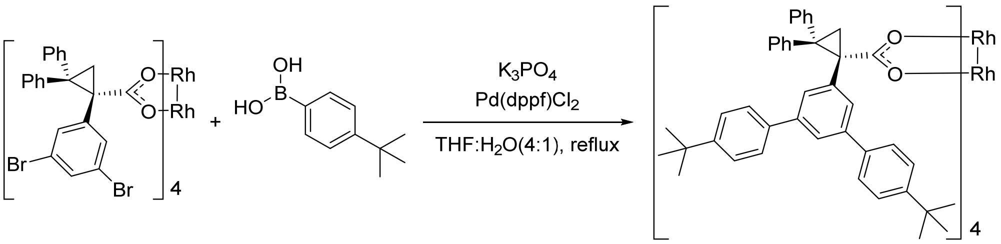
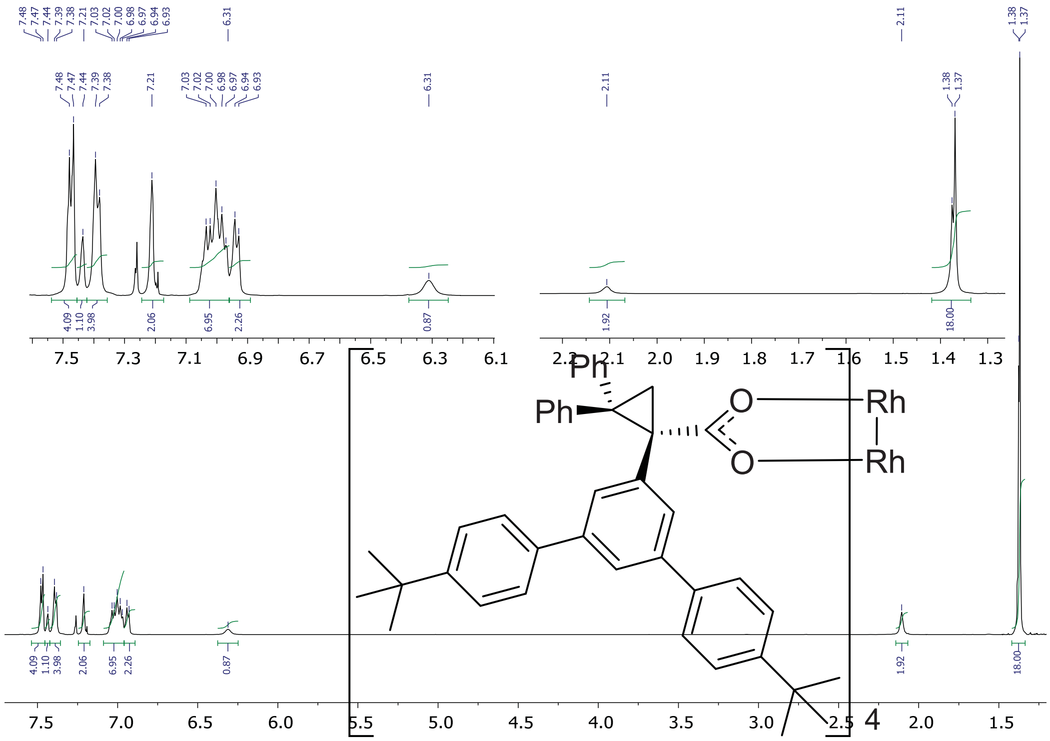


Dirhodium tetrakis((*R*)-1-(4,4''-di-*tert*-butyl-[1,1':3',1''-terphenyl]-5'-yl)-2,2-diphenylcyclopropanecarboxylate) (15). A 25-mL round bottom flask was charged with dirhodium tetrakis((*R*)-1-(3,5-dibromophenyl)-2,2-diphenylcyclopropanecarboxylate) (84 mg, 0.04 mmol, 1.00 equiv.), boronic acid (114 mg, 0.64 mmol, 16 equiv.), K_3PO_4 (204 mg, 0.96 mmol, 24.0 equiv.) and THF: H_2O (4:1) (12 mL). The solution was heated to reflux for 10 min to degass and then and $Pd(dppf)Cl_2$ (12 mg, 0.016 mmol, 0.4 equiv.) was added. The resulting red solution was then remained reflux for 12 h. After the allotted time had passed and the starting material had disappeared on TLC, the solution was cooled to room temperature and concentrated under reduced pressure. The residue was redissolved in DCM, washed with water (3x15mL) and brine (3x15mL). The organic layer was dried over sodium sulfate (10 g) and filtered. The filtrate was concentrated by rotary evaporation to afford the crude product. The crude product was purified by flash column chromatography (hexanes/diethyl ether = 30/1) to give a green solid in 81% overall yield (82 mg).

m.p.: decomposed at 238 °C; TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 4H), 7.44 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 4H), 7.21 (s, 2H), 7.00 (dt, *J* = 19.3, 7.9 Hz, 7H), 6.93 (d, *J* = 7.5 Hz, 2H), 6.31 (s, 1H), 2.11 (s, 2H), 1.37 (s, 18H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 203.1, 189.6, 189.0, 156.4, 152.4, 150.2, 141.7, 140.8, 140.5, 138.9, 138.3, 130.0, 129.2, 128.4, 128.0, 127.7, 127.2, 126.2, 126.1, 125.6, 124.0, 45.7, 44.3, 34.7, 31.6, 28.1, 18.2, 17.8, 12.4; HRMS (ESI) calcd for $C_{168}H_{164}O_8Rh_2$ (M^+): 2515.0530 found 2515.0550; IR (neat): 2960, 2865, 1584, 1515, 1494, 1448, 1378, 1362, 1269, 1114, 1059, 1017, 828, 800, 750, 734, 700.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3.98
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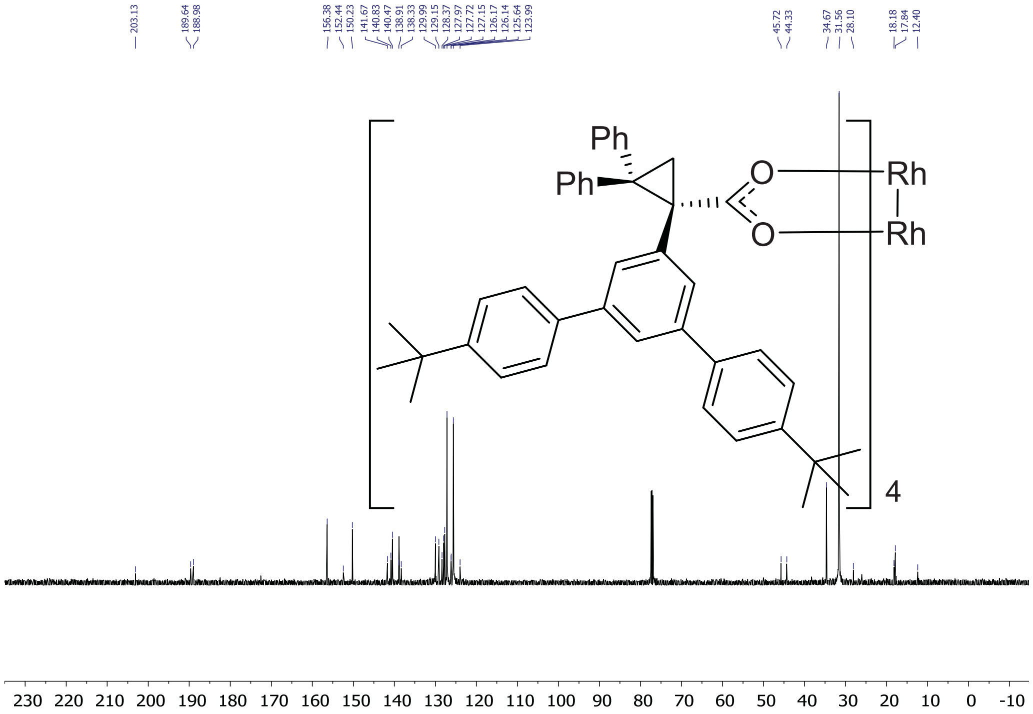
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127.97
127.72
127.15
126.17
126.14
125.64
123.99
45.72
44.33
34.67
31.56
28.10
18.18
17.84
12.40
Ph
Ph
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O
Rh
Rh
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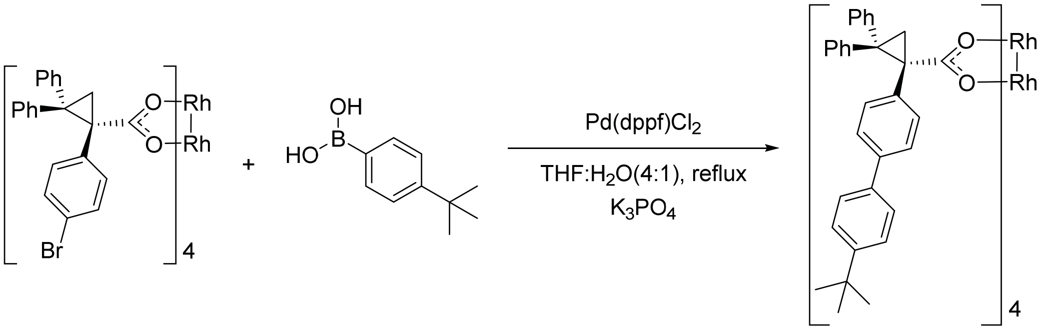
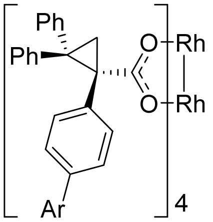
1.2 para-substituted catalyst



Dirhodium tetrakis [(R)-1-(4'-(tert-butyl)-[1,1'-biphenyl]-4-yl)-2,2-diphenylcyclopropane-1-carboxylate] (catalyst E). A 25-mL round-bottom flask was charged with Rh_2(*R*-*p*-BrTPCP)$_4$ (242 mg, 0.136 mmol, 1.00 equiv.), (4-(tert-butyl)phenyl)boronic acid (291 mg, 1.636 mmol, 12 equiv.). K_3PO_4 (521 mg, 2.454 mmol, 18 equiv.) and THF: H_2O (4:1) (15 mL). The flask was then degassed and Pd(dppf)Cl_2 (20 mg, 0.027 mmol, 0.2 equiv.) was added. The resulting red solution was then heated to reflux for 12 hours. After the allotted time had passed and the ester had disappeared on TLC, the solution was cooled to room temperature and concentrated under reduced pressure. The residue was redissolved in DCM and washed with water (3x15ml), brine (3x15ml), dried over sodium sulfate (10 g) and concentrated by rotary evaporation to afford the crude product. The crude product was dissolved by ether (3X30 mL) and transferred to a silica plug (2x2 inch), then further flushed with ether (150 mL) and collect all green solution. The green solution was concentrated and further purified by column chromatography over silica gel to afford the cross-coupling product as green solid in 85% yield (230 mg).

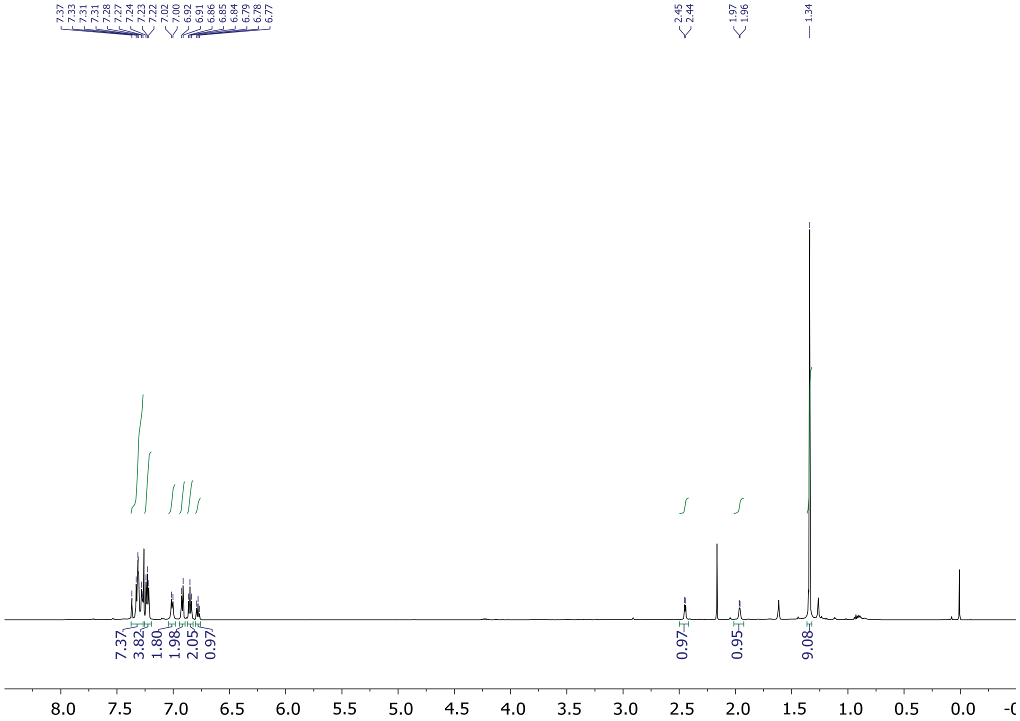
TLC (diethyl ether: hexanes, 1:9 *v/v*); m.p. decomposed at 180 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 7H), 7.25 – 7.20 (m, 4H), 7.01 (d, J = 7.7 Hz, 2H), 6.92 (d, J = 7.8 Hz, 2H), 6.85 (t, J = 7.6 Hz, 2H), 6.78 (t, J = 7.3 Hz, 1H), 2.45 (d, J = 5.0 Hz, 1H), 1.96 (d, J = 4.8 Hz, 1H), 1.34 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.20, 149.98, 142.68, 141.22, 138.56, 137.85, 135.42, 131.51, 130.10, 129.30, 128.48, 128.22, 127.50, 126.58, 126.43, 125.89, 125.76, 125.68, 46.60, 43.03, 34.63, 31.57, 31.06; HRMS (ESI) calcd for $C_{128}H_{116}O_8Rh_2$ ([M]$^+$): 1986.6775 found 1986.6750; IR (neat): 3030, 2961, 1579, 1494, 1448, 1269, 1005, 823, 756, 748, 703, 693, 677.

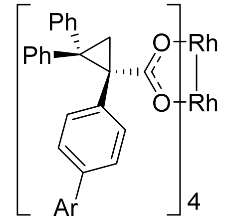


Ar= p-^{t}BuC$_6$H$_4$

Rh$_2$[R-p-^{t}BuC$_6$H$_4$TPCP]$_4$

E

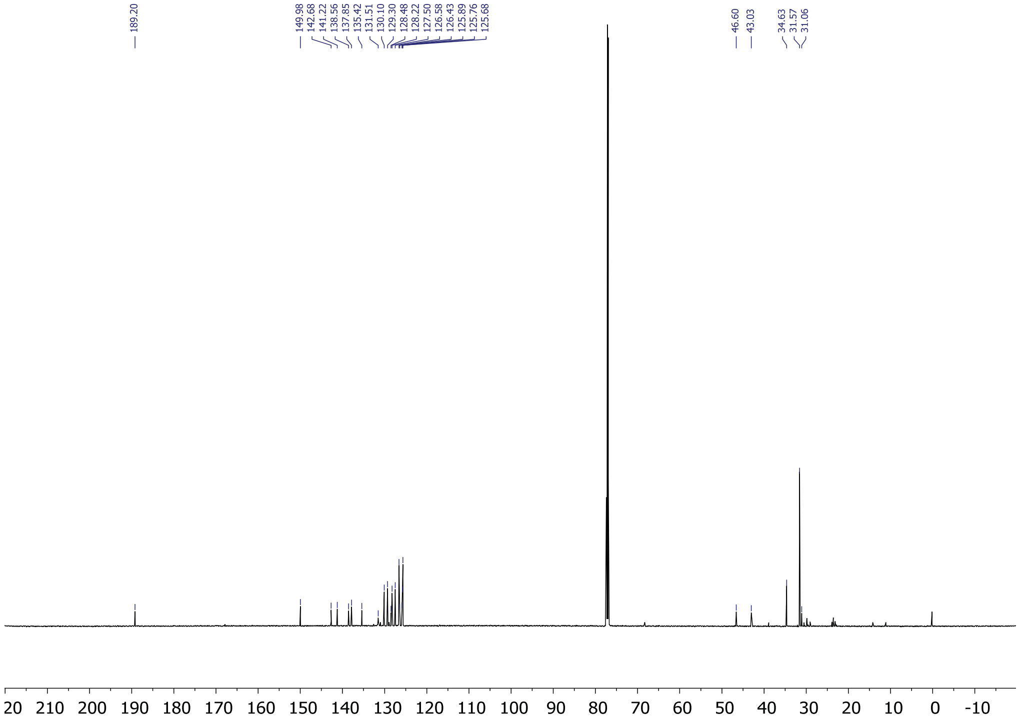


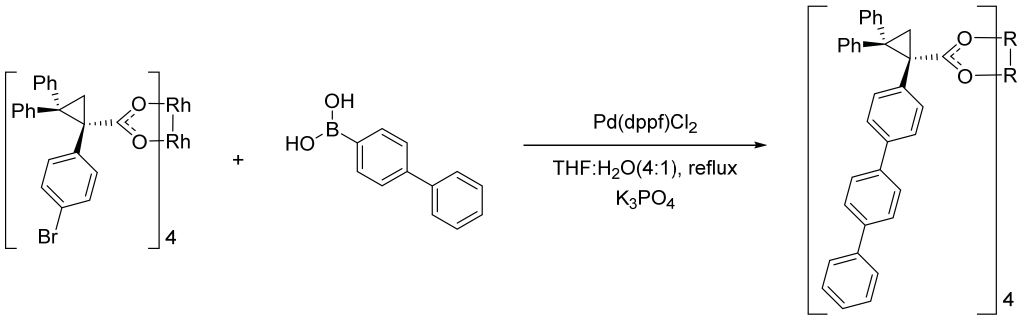


Ar= p-^{t}BuC$_6$H$_4$

Rh$_2$[R-p-^{t}BuC$_6$H$_4$TPCP]$_4$

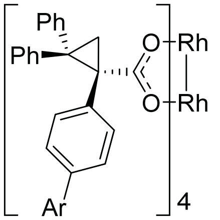
E





Dirhodium tetrakis [(R)-1-([1,1':4',1''-terphenyl]-4-yl)-2,2-diphenylcyclopropane-1-carboxylate] (catalyst F). A 25-mL round-bottom flask was charged with Rh_2(*R*-*p*-BrTPCP)$_4$ (242 mg, 0.136 mmol, 1.00 equiv.), [1,1'-biphenyl]-4-ylboronic acid (324 mg, 1.636 mmol, 12 equiv.). K_3PO_4 (521 mg, 2.454 mmol, 18 equiv.) and THF: H_2O (4:1) (15 mL). The flask was then degassed and Pd(dppf)Cl_2 (20 mg, 0.027 mmol, 0.2 equiv.) was added. The resulting red solution was then heated to reflux for 12 hours. After the allotted time had passed and the ester had disappeared on TLC, the solution was cooled to room temperature and concentrated under reduced pressure. The residue was redissolved in DCM and washed with water (3x15ml), brine (3x15ml), dried over sodium sulfate (10 g) and concentrated by rotary evaporation to afford the crude product. The crude product was dissolved by ether (3X30 mL) and transferred to a silica plug (2x2 inch), then further flushed with ether (150 mL) and collect all green solution. The green solution was concentrated and further purified by column chromatography over silica gel to afford the cross-coupling product as green solid in 44% yield (125 mg).

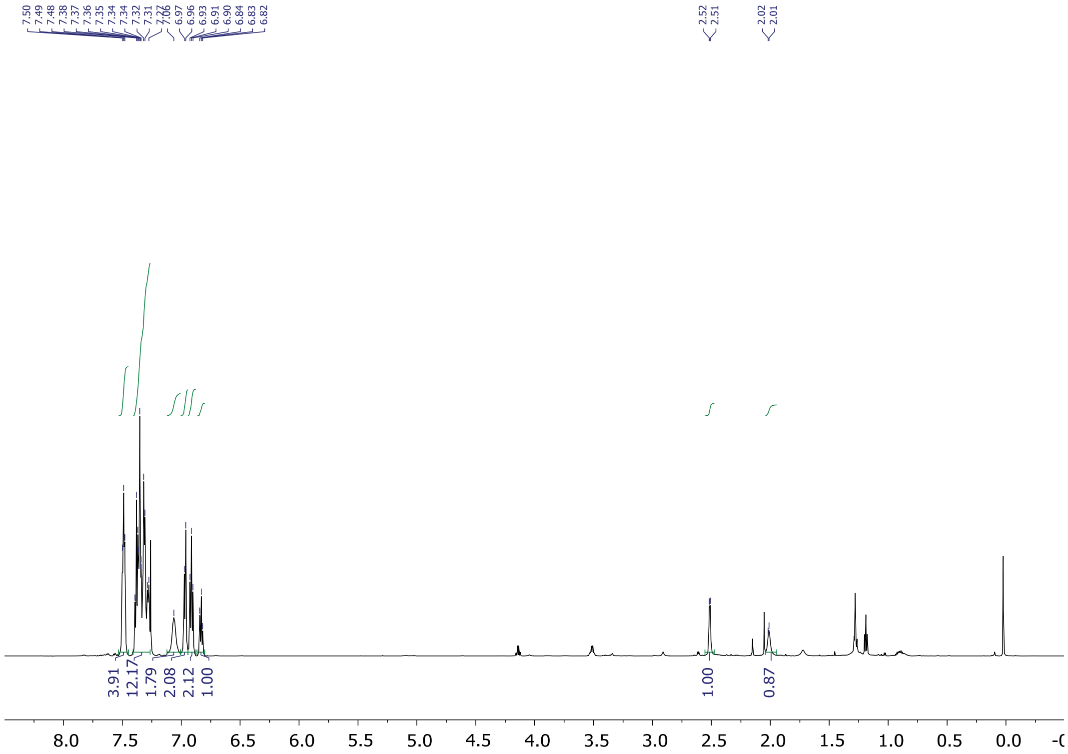
TLC (diethyl ether: hexanes, 1:3 *v/v*); m.p. decomposed at 180 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 4H), 7.41 – 7.26 (m, 12H), 7.06 (s, 2H), 6.97 (d, J = 7.7 Hz, 2H), 6.91 (t, J = 7.7 Hz, 2H), 6.83 (t, J = 7.3 Hz, 1H), 2.51 (d, J = 5.2 Hz, 1H), 2.01 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.09, 142.66, 141.23, 140.50, 139.65, 139.49, 138.07, 135.87, 131.65, 130.07, 129.31, 128.91, 128.47, 128.28, 127.55, 127.42, 127.33, 127.18, 126.97, 126.52, 125.96, 125.74, 66.18, 46.73, 43.00; HRMS (ESI) calcd for $C_{136}H_{100}O_8Rh_2$ ([M]$^+$): 2066.5523 found 2066.5470; IR (neat): 3028, 2925, 2360, 1583, 1484, 1382, 761, 741, 694.

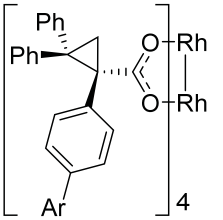


Ar= p-PhC$_6$H$_4$

Rh$_2$[R-p-PhC$_6$H$_4$TPCP]$_4$

F

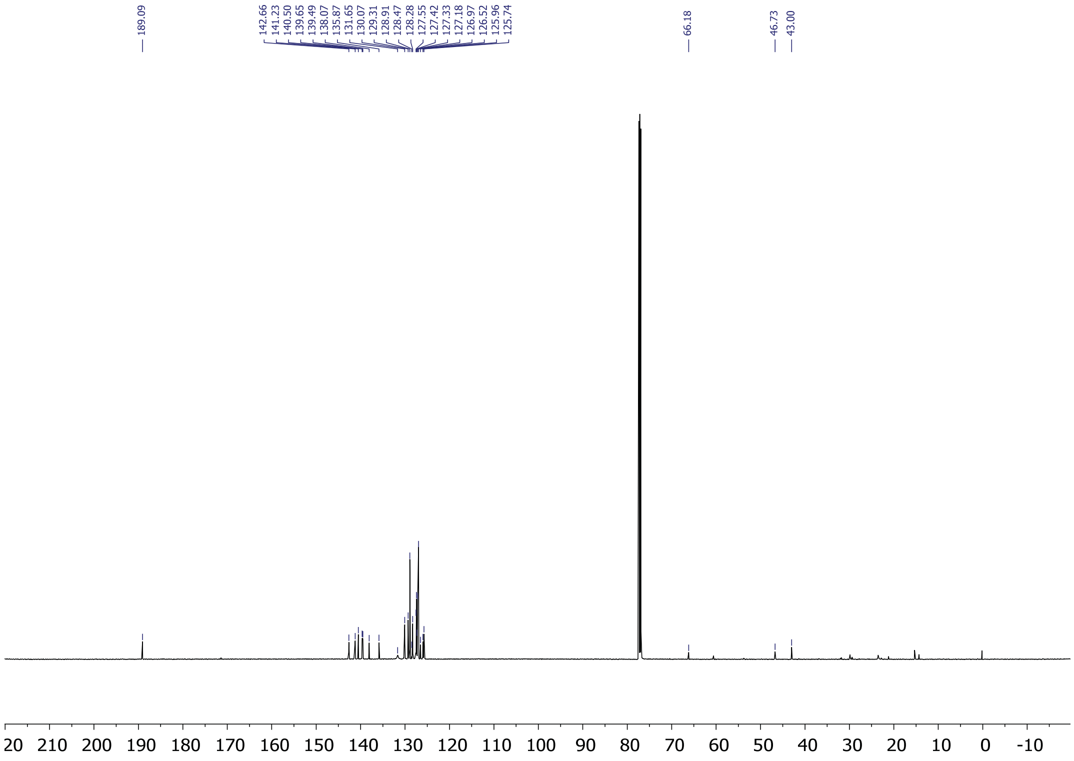


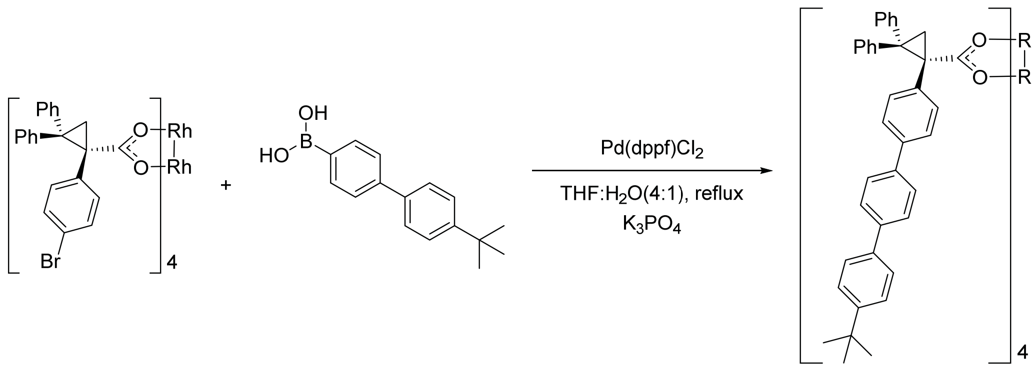


Ar= p-PhC$_6$H$_4$

Rh$_2$[R-p-PhC$_6$H$_4$TPCP]$_4$

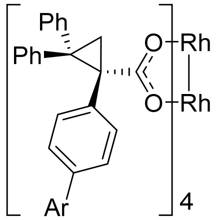
F





Dirhodium tetrakis [(R)-1-(4"-(tert-butyl)-[1,1':4',1"-terphenyl]-4-yl)-2,2-diphenylcyclopropane-1-carboxylate] (catalyst G). A 25-mL round-bottom flask was charged with Rh_2(*R*-*p*-BrTPCP)$_4$ (242 mg, 0.136 mmol, 1.00 equiv.), (4'-(tert-butyl)-[1,1'-biphenyl]-4-yl)boronic acid (415 mg, 1.636 mmol, 12 equiv.). K_3PO_4 (521 mg, 2.454 mmol, 18 equiv.) and THF: H_2O (4:1) (15 mL). The flask was then degassed and Pd(dppf)Cl_2 (20 mg, 0.027 mmol, 0.2 equiv.) was added. The resulting red solution was then heated to reflux for 12 hours. After the allotted time had passed and the ester had disappeared on TLC, the solution was cooled to room temperature and concentrated under reduced pressure. The residue was redissolved in DCM and washed with water (3x15ml), brine (3x15ml), dried over sodium sulfate (10 g) and concentrated by rotary evaporation to afford the crude product. The crude product was dissolved by ether (3X30 mL) and transferred to a silica plug (2x2 inch), then further flushed with ether (150 mL) and collect all green solution. The green solution was concentrated and further purified by column chromatography over silica gel to afford the cross-coupling product as green solid in 50% yield (156 mg).

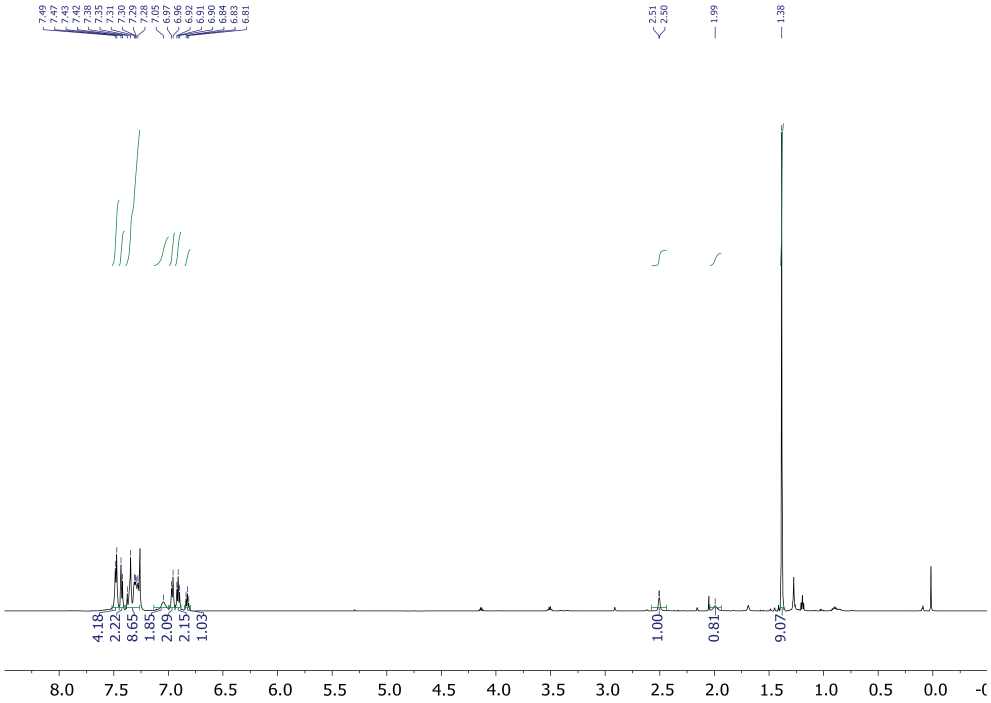
TLC (diethyl ether: hexanes, 1:9 *v/v*); m.p. decomposed at 200 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, J = 8.1 Hz, 4H), 7.43 (d, J = 8.3 Hz, 2H), 7.39 – 7.27 (m, 9H), 7.05 (s, 2H), 6.96 (d, J = 7.6 Hz, 2H), 6.91 (t, J = 7.7 Hz, 2H), 6.83 (t, J = 7.3 Hz, 1H), 2.50 (d, J = 4.7 Hz, 1H), 1.99 (s, 1H), 1.38 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.10, 150.31, 142.68, 141.24, 139.56, 139.24, 138.21, 137.71, 135.73, 131.64, 130.09, 129.31, 128.48, 128.28, 127.54, 127.31, 127.17, 126.70, 126.51, 125.96, 125.81, 125.76, 46.66, 43.00, 34.68, 31.55, 29.85; HRMS (ESI) calcd for $C_{152}H_{132}O_8Rh_2$ ($[M]^+$): 2290.8027 found 2290.8047; IR (neat): 3028, 2961, 2956, 2360, 1583, 1491, 1381, 1005, 818, 703.

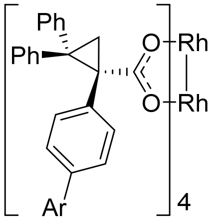


Ar= p-^{t}BuC$_6$H$_4$C$_6$H$_4$

Rh$_2$[R-p-^{t}BuC$_6$H$_4$C$_6$H$_4$TPCP]$_4$

G

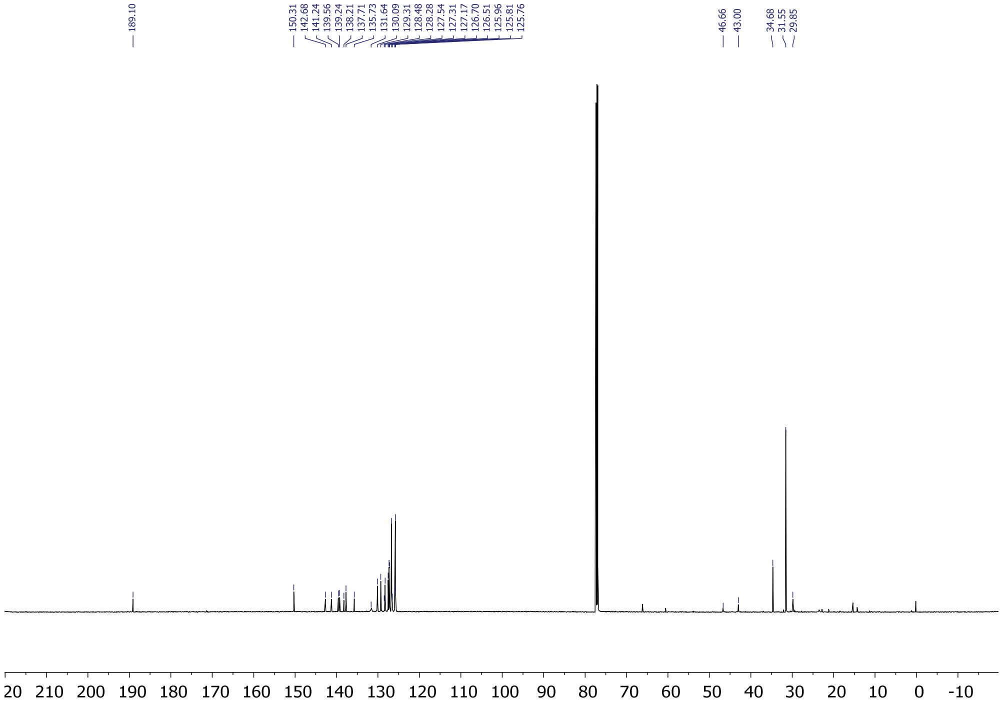




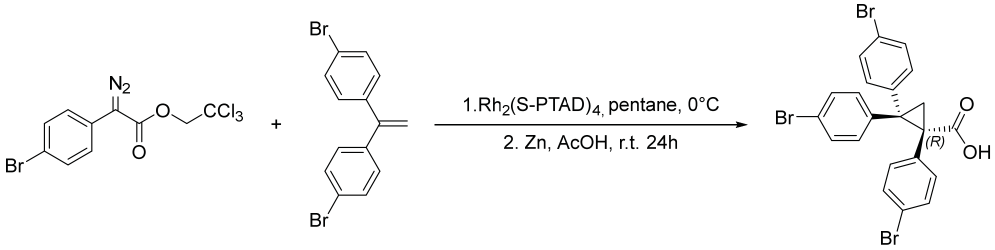
Ar= p-^{t}Bu$C_6H_4C_6H_4$

$Rh_2[R$-p-^{t}Bu$C_6H_4C_6H_4$TPCP$]_4$

G

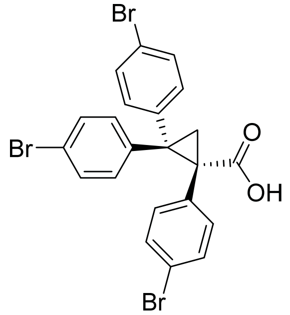


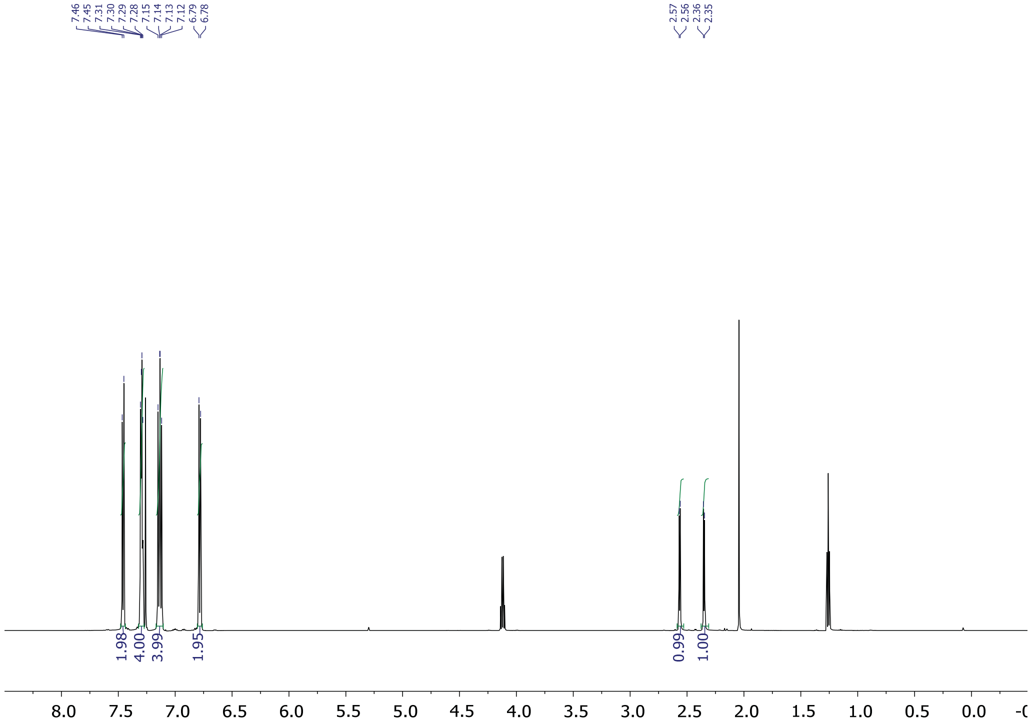
1.3 tris para-substituted catalyst



(R)-1,2,2-tris(4-bromophenyl)cyclopropane-1-carboxylic acid. To a flame-dried 500 mL round-bottom flask kept under a dry atmosphere of argon, was added Rh_2(*S*-PTAD)$_4$ (0.2 g, 0.125 mmol, 0.005 equiv.) 4,4'-(ethene-1,1-diyl)bis(bromobenzene) (10.1 g, 30.0 mmol, 1.2 equiv.), and pentane (100 mL). A solution of freshly prepared 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (9.3 g, 25 mmol, 1.0 equiv.) in CH_2Cl_2 (10 mL) and pentane (300 mL) was added to the former solution drop-wise over 3 hours at room temperature. The mixture was allowed to stir overnight, and then concentrated in vacuum. The crude material was dissolved in 30 mL of glacial acetic acid, and zinc powder (8.2 g, 125 mmol, 5.0 equiv.) was added. The solution was allowed to stir at room temperature for 24 h. The starting material has been fully consumed as indicated by TLC analysis. The solution was diluted with H_2O (10 mL) and extracted with EtOAc (2 x 15 mL). The organic extracts were washed with H_2O and brine, dried over $MgSO_4$ and concentrated to give the product as a white solid in 81% yield (20.2 g).

$[\alpha]^{20}_D$ -235.6° (c = 1.00, $CHCl_3$); TLC (ethyl acetate: hexanes, 1:4 *v/v*); m.p. decomposed at 200 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, J = 8.3 Hz, 2H), 7.29 (dd, J = 8.3, 4.5 Hz, 4H), 7.13 (dd, J = 10.9, 8.5 Hz, 4H), 6.78 (d, J = 8.6 Hz, 2H), 2.56 (d, J = 5.7 Hz, 1H), 2.35 (d, J = 5.7 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.85, 139.99, 137.73, 133.45, 131.93, 131.50, 131.26, 131.19, 130.34, 121.98, 121.58, 121.13, 44.68, 42.21, 23.57; HRMS (ESI) calcd for $C_{22}H_{16}O_2Br_3$ ($[M+H]^+$): 548.8695 found 548.8704; IR (neat): 1694, 1489, 1395, 1239, 1074, 1007, 842, 753.


Br
Br
O
OH
Br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7.45
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7.30
7.29
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7.12
6.79
6.78
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2.56
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2.35
1.98
4.00
3.99
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0.99
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8.0
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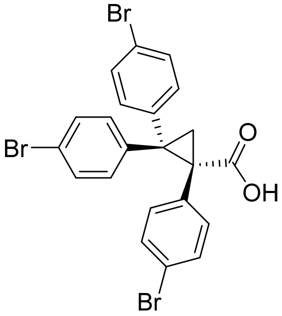
Br
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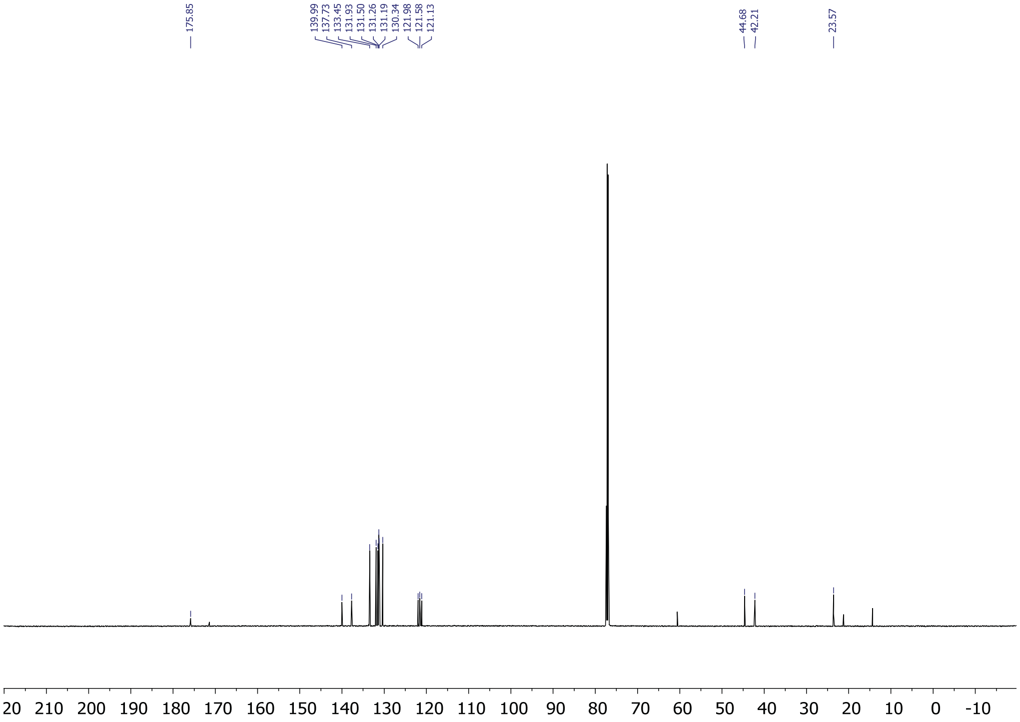
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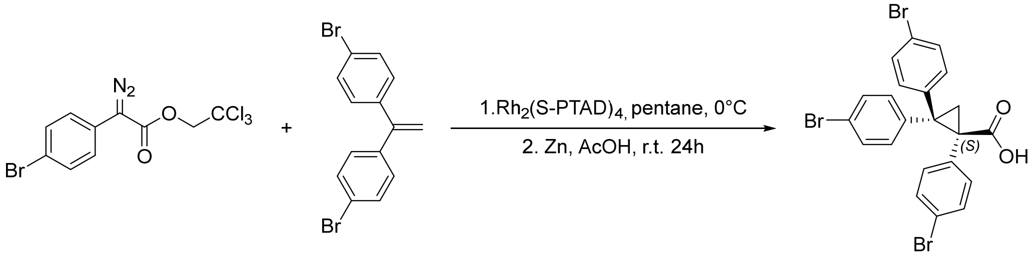

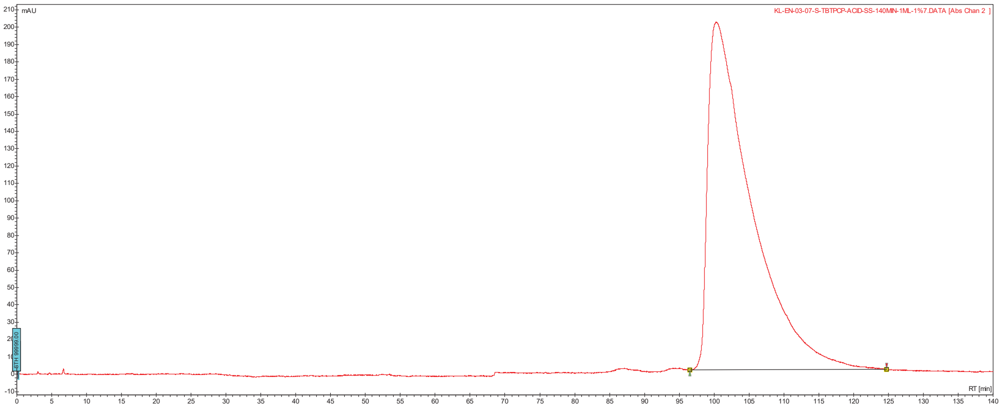

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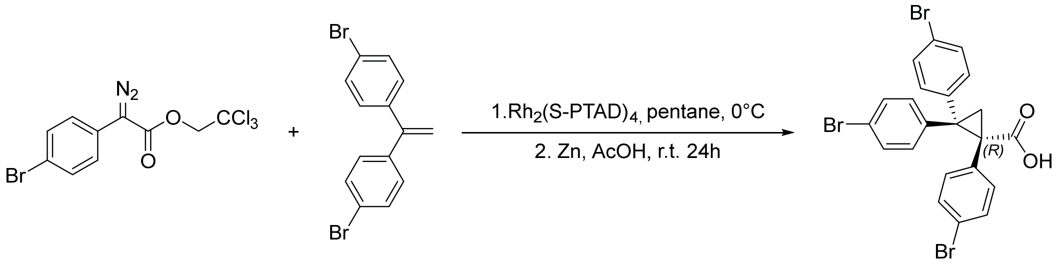

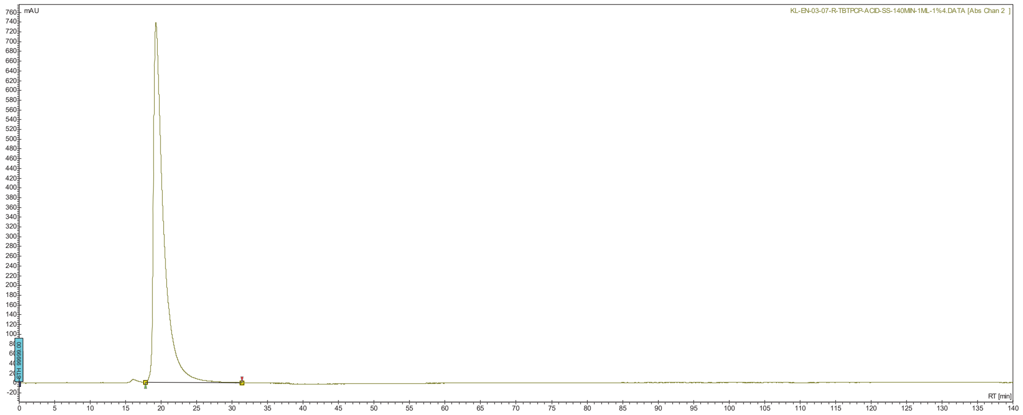

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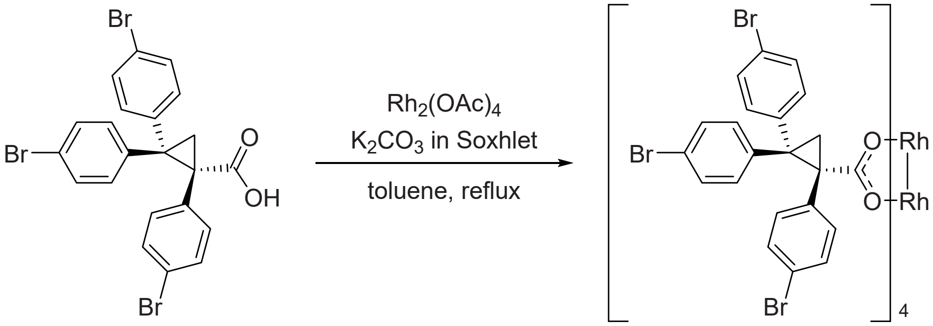
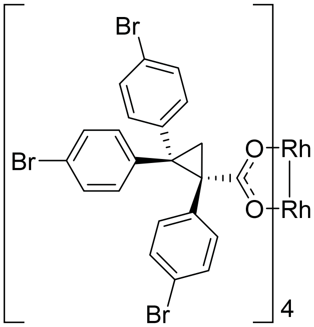


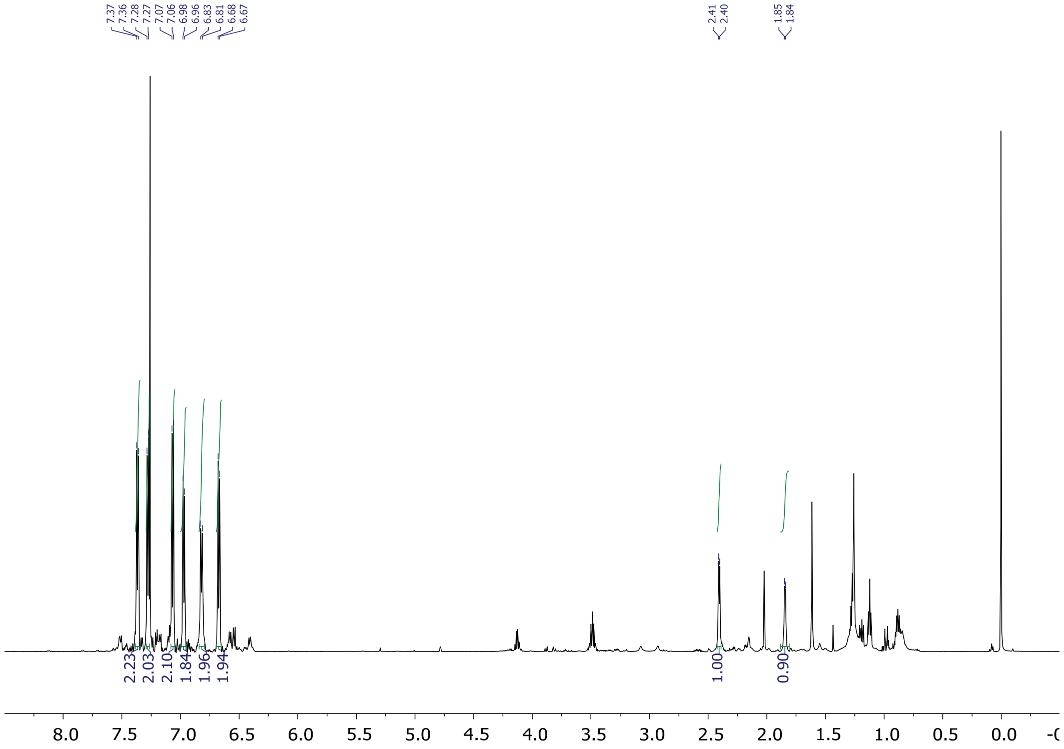
Dirhodium tetrakis[(R)-1,2,2-tris(4-bromophenyl)cyclopropane-1-carboxylate] (catalyst N). A 100-mL round-bottom flask, equipped with a Teflon-coated stirring bar and nitrogen inlet, was flushed with nitrogen and then charged with rhodium(II) acetate (0.625 mmol, 0.276 g, 1.0 *equiv.)*, (R)-1,2,2-tris(4-bromophenyl)cyclopropane-1-carboxylic acid (8 mmol, 2.76 g, 8.0 equiv.), and 75 mL of toluene. The flask was fitted with a Soxhlet extraction apparatus into which was placed a thimble containing 15 g of an oven-dried mixture of 2 parts sodium carbonate and 1 part of sand. The solution was heated at reflux and monitored by TLC and MS; removal of the solvent under reduced pressure using a rotary evaporator and then purified by flash column chromatography (hexanes/diethyl ether = 30/1) to give green solid in 55% overall yield (0.827 g).

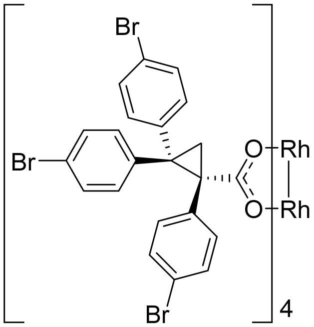
TLC (diethyl ether: hexanes, 1:4 *v/v*); m.p. decomposed at 215 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.5 Hz, 2H), 6.97 (d, J = 8.3 Hz, 2H), 6.82 (d, J = 8.1 Hz, 2H), 6.67 (d, J = 8.5 Hz, 2H), 2.41 (d, J = 5.2 Hz, 1H), 1.84 (d, J = 5.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 188.86, 140.84, 139.18, 134.83, 132.44, 131.57, 131.38, 131.30, 131.01, 130.74, 128.48, 121.60, 120.90, 120.80, 45.55, 42.80, 29.85; HRMS (ESI) calcd for $C_{88}H_{56}O_8Rh_2Br_9{}^{81}Br_3$([M]$^+$): 2399.2219 found 2399.2248; IR (neat): 2360, 2342, 1684, 1653, 1559, 1540, 1507, 1489, 1382, 1010.



Rh_2[*R*-tris(*p*-Br)TPCP]$_4$

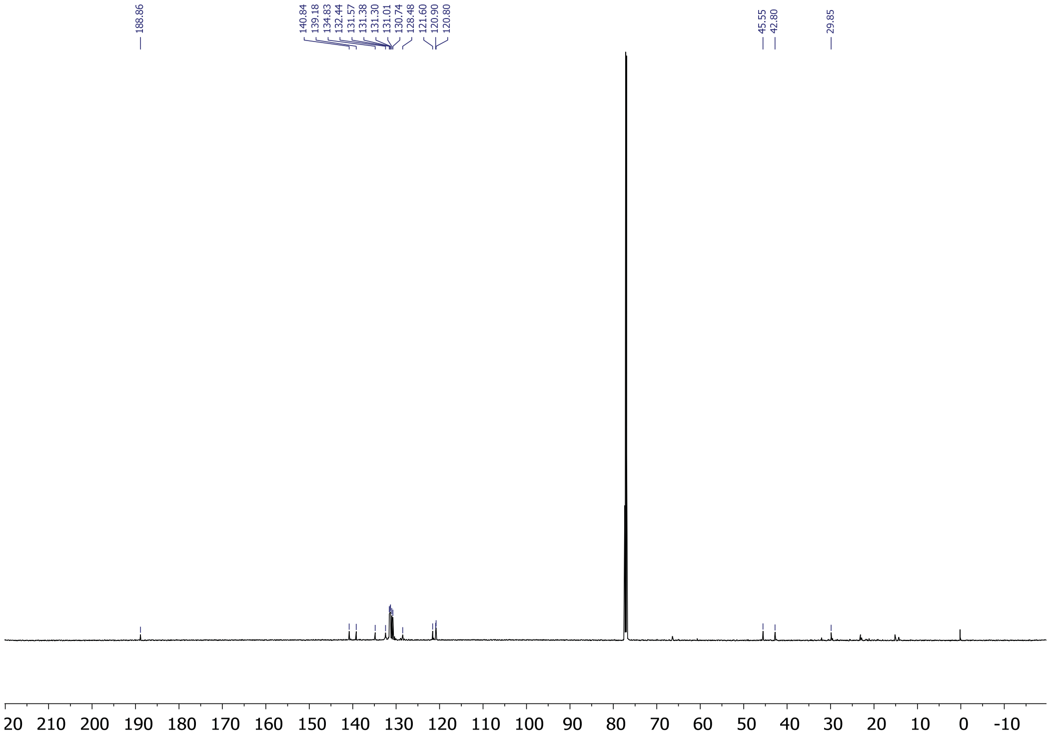
N

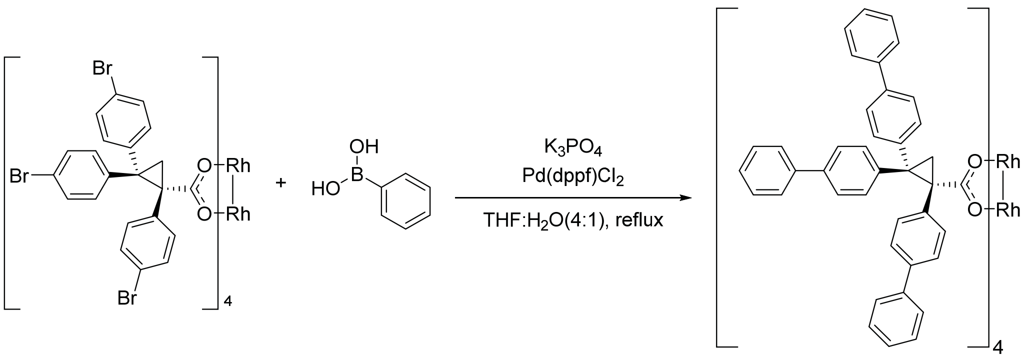




Rh$_2$[*R*-tris(*p*-Br)TPCP]$_4$

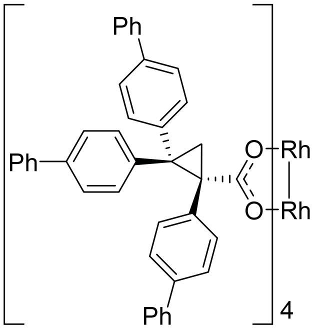
N





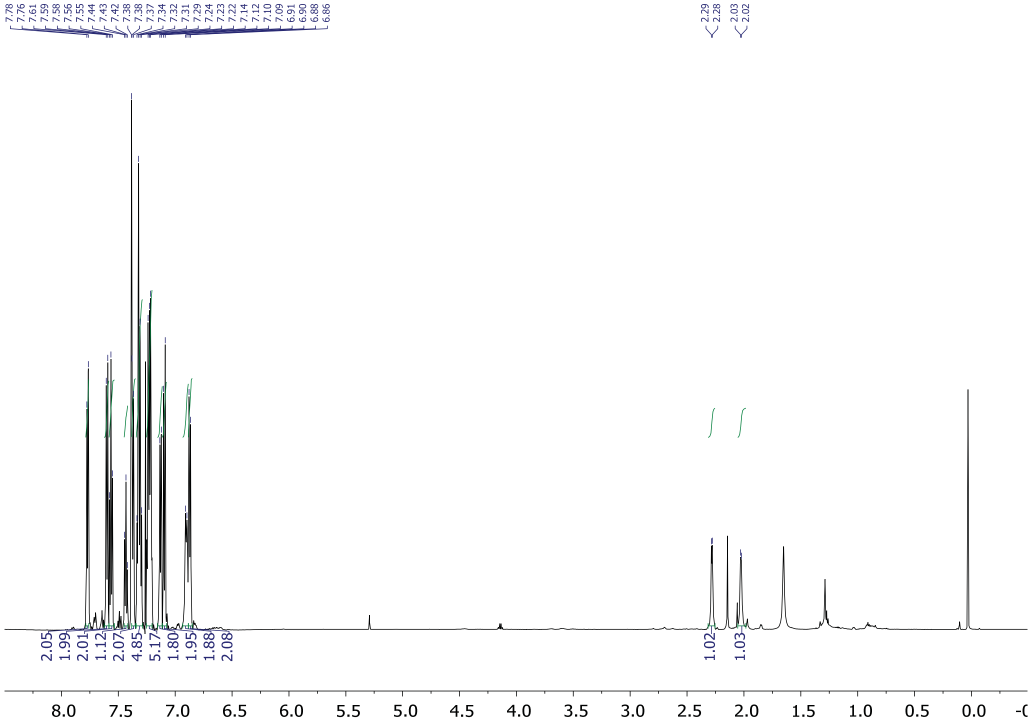
Dirhodium tetrakis [(R)-1,2,2-tri([1,1'-biphenyl]-4-yl)cyclopropane-1-carboxylate] (catalyst H). A 25-mL round-bottom flask was charged with **catalyst N** (241 mg, 0.10 mmol, 1.00 equiv.), phenylboronic acid (439 mg, 3.60 mmol, 36 equiv.). K_3PO_4 (1.146 g, 5.40 mmol, 54 equiv.) and THF: H_2O (4:1) (15 mL). The flask was then degassed and Pd(dppf)Cl_2 (44 mg, 0.06 mmol, 0.6 equiv.) was added. The resulting red solution was then heated to reflux for 12 hours. After the allotted time had passed and the ester had disappeared on TLC, the solution was cooled to room temperature and concentrated under reduced pressure. The residue was redissolved in DCM and washed with water (3x15ml), brine (3x15ml), dried over sodium sulfate (10 g) and concentrated by rotary evaporation to afford the crude product. The crude product was dissolved by ether (3X30 mL) and transferred to a silica plug (2x2 inch), then further flushed with ether (150 mL) and collect all green solution. The green solution was concentrated and further purified by column chromatography over silica gel to afford the cross-coupling product as green solid in 50% yield (119 mg).

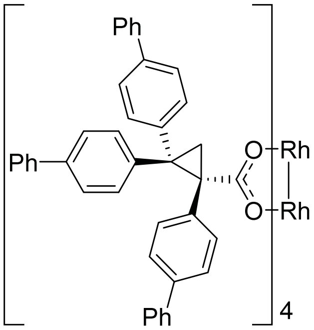
TLC (ethyl acetate: hexanes, 1:4 *v/v*); m.p. decomposed at 205 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, J = 7.4 Hz, 2H), 7.60 (d, J = 8.1 Hz, 2H), 7.56 (t, J = 7.6 Hz, 2H), 7.43 (t, J = 7.3 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.32 (t, J = 8.1 Hz, 5H), 7.26 – 7.19 (m, 5H), 7.13 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 7.4 Hz, 2H), 6.87 (d, J = 8.3 Hz, 2H), 2.28 (d, J = 4.8 Hz, 1H), 2.03 (d, J = 4.1 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.43, 141.66, 141.43, 140.65, 140.02, 139.20, 138.82, 138.51, 135.64, 131.50, 130.57, 129.54, 129.01, 128.68, 128.64, 128.47, 127.54, 127.41, 127.16, 127.08, 126.97, 126.93, 126.91, 126.19, 125.98, 45.91, 43.35, 23.51; HRMS (ESI) calcd for $C_{160}H_{116}O_8Rh_2$ ($[M]^+$): 2370.6775 found 2370.6702; IR (neat): 3027, 2973, 2925, 2869, 1582, 1486, 1379, 1007, 845, 762, 742, 733, 695.



Rh$_2$[*R*-tris(*p*-Ph)TPCP]$_4$

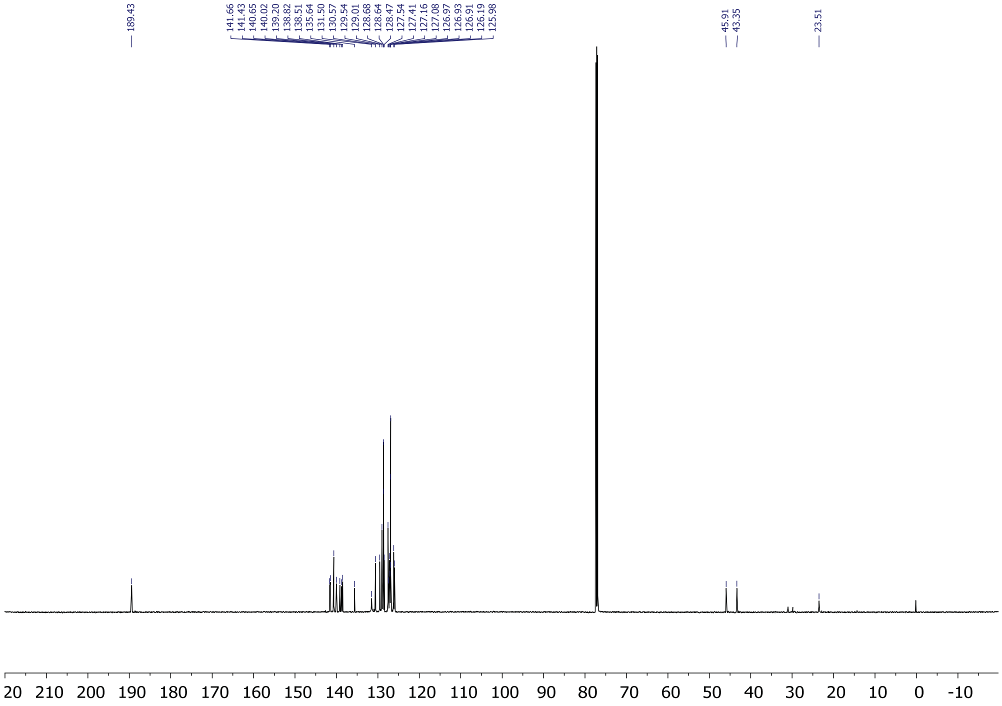
H

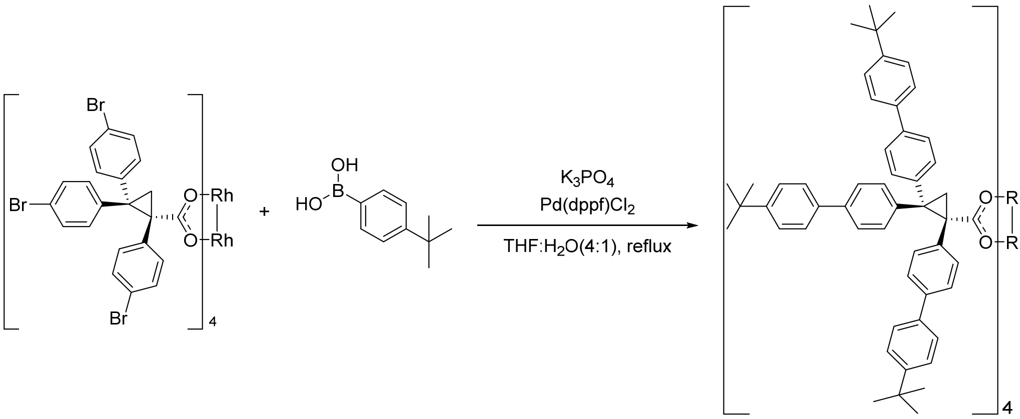




Rh_2[*R*-tris(*p*-Ph)TPCP]$_4$

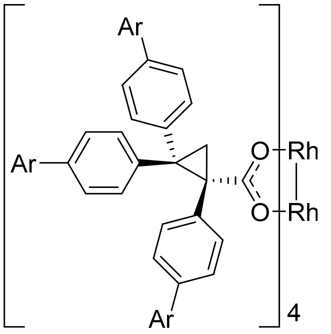
H





Dirhodium tetrakis [(R)-1,2,2-tris(4'-(tert-butyl)-[1,1'-biphenyl]-4-yl)cyclopropane-1-carboxylate] (catalyst I). A 100-mL round-bottom flask was charged with **catalyst N** (1.5 g, 0.623 mmol, 1.00 equiv.), (4-(tert-butyl)phenyl)boronic acid (4.0 g, 22.44 mmol, 36 equiv.). K_3PO_4 (7.15 g, 2.454 mmol, 18 equiv.) and THF: H_2O (4:1) (75 mL). The flask was then degassed and Pd(dppf)Cl_2 (274 mg, 0.374 mmol, 0.6 equiv.) was added. The resulting red solution was then heated to reflux for 12 hours. After the allotted time had passed and the ester had disappeared on TLC, the solution was cooled to room temperature and concentrated under reduced pressure. The residue was redissolved in DCM and washed with water (3x15ml), brine (3x15ml), dried over sodium sulfate (10 g) and concentrated by rotary evaporation to afford the crude product. The crude product was dissolved by ether (3X30 mL) and transferred to a silica plug (2x2 inch), then further flushed with ether (150 mL) and collect all green solution. The green solution was concentrated and further purified by column chromatography over silica gel to afford the cross-coupling product as green solid in 53% yield (1.006 g).

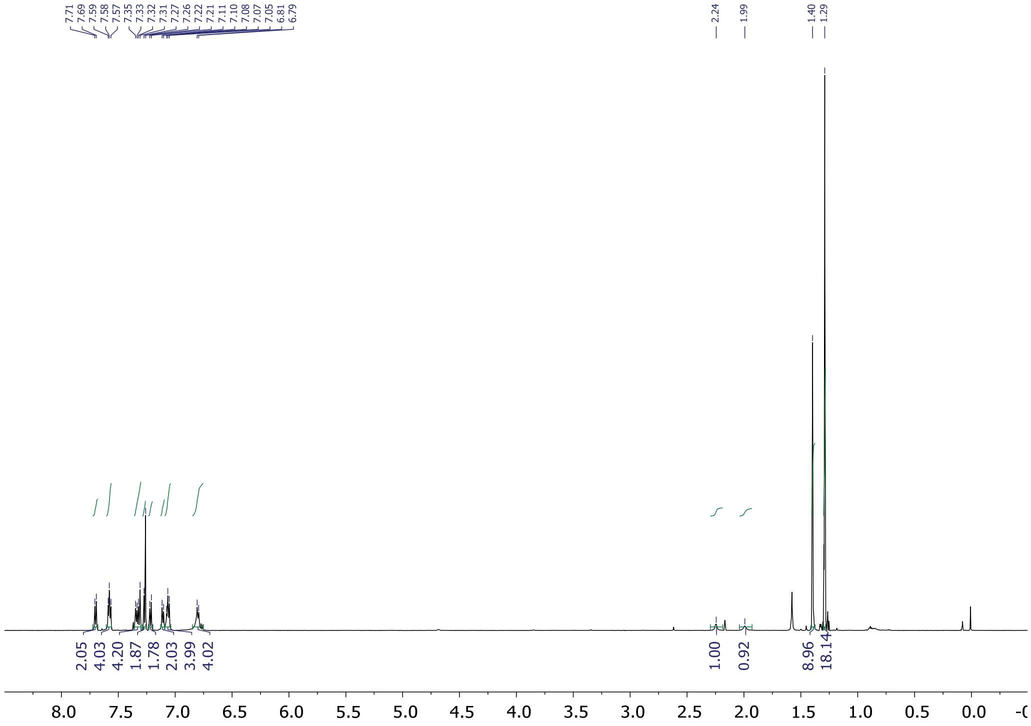
TLC (diethyl ether: hexanes, 1:9 *v/v*); m.p. decomposed at 200 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, J = 8.3 Hz, 2H), 7.58 (t, J = 7.0 Hz, 4H), 7.34 (d, J = 8.0 Hz, 4H), 7.32 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.1 Hz, 2H), 7.06 (t, J = 7.1 Hz, 4H), 6.80 (d, J = 8.1 Hz, 4H), 2.24 (s, 1H), 1.99 (s, 1H), 1.40 (s, 9H), 1.29 (s, 18H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.40, 150.37, 149.93, 149.71, 141.30, 139.70, 139.09, 138.61, 138.10, 138.03, 137.79, 135.37, 131.55, 130.73, 129.39, 128.48, 127.25, 126.99, 126.71, 126.56, 126.52, 125.89, 125.86, 125.56, 125.53, 114.90, 34.75, 34.56, 31.69, 31.63, 31.54, 31.45; HRMS (ESI) calcd for $C_{208}H_{212}O_8Rh_2$ ([M]$^+$): 3043.4287 found 3043.4203; IR (neat): 3028, 2960, 2903, 2867, 2359, 1497, 1383, 1363, 1004, 828, 785.

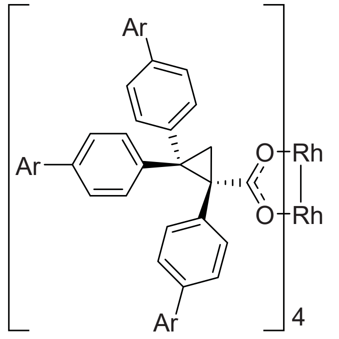


Ar= p-^{t}BuC$_6$H$_4$

Rh$_2$[*R*-tris(p-^{t}BuC$_6$H$_4$)TPCP]$_4$

I

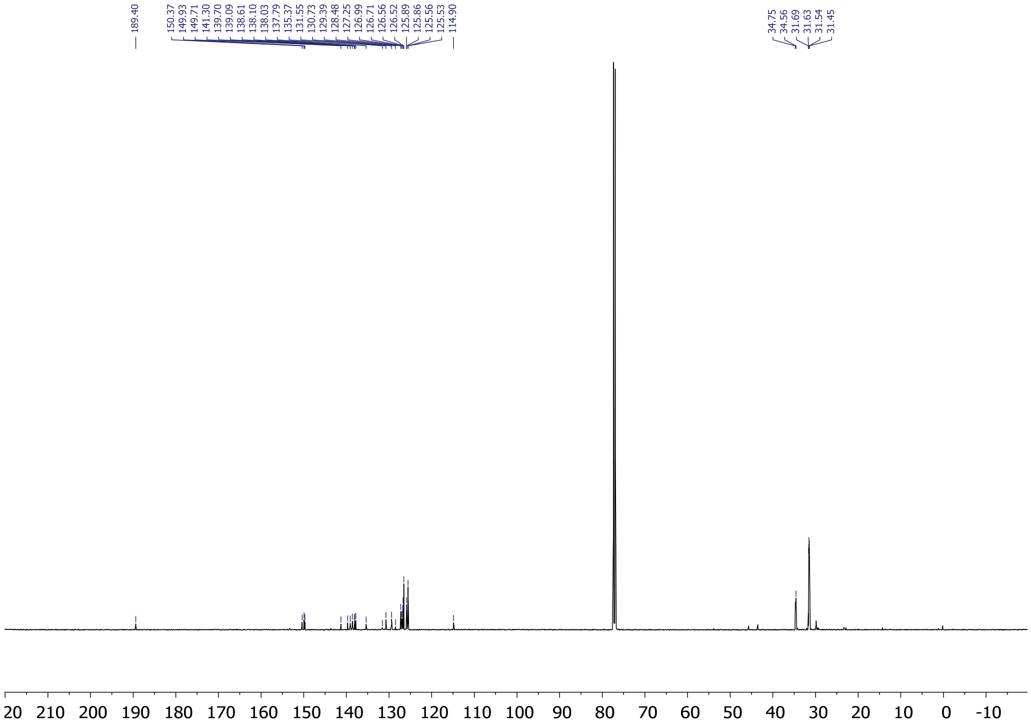


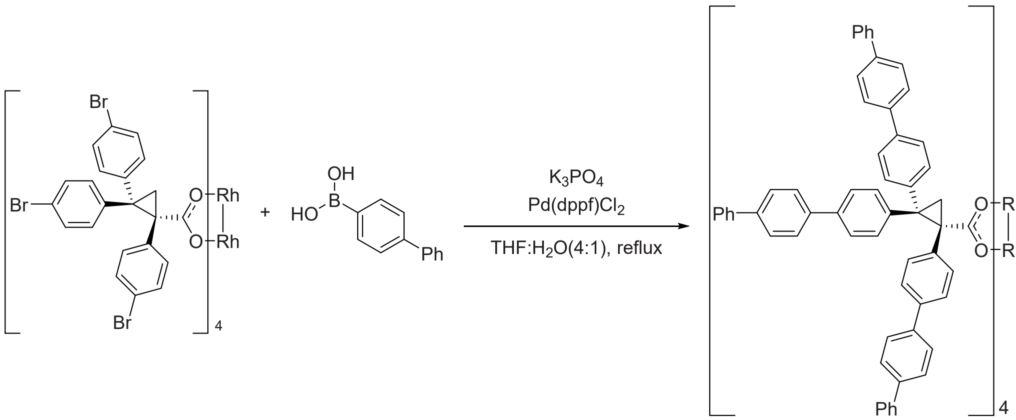


Ar= *p*-^{t}BuC$_6$H$_4$

Rh$_2$[*R*-tris(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$

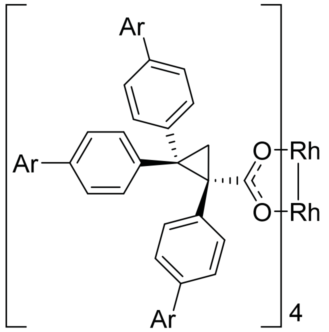
I





Dirhodium tetrakis [(R)-1,2,2-tri([1,1':4',1''-terphenyl]-4-yl)cyclopropane-1-carboxylate] (catalyst J). A 25-mL round-bottom flask was charged with **catalyst N** (241 mg, 0.10 mmol, 1.00 equiv.), [1,1'-biphenyl]-4-ylboronic acid (713 mg, 3.60 mmol, 36 equiv.). K_3PO_4 (1.146 g, 5.40 mmol, 54 equiv.) and THF: H_2O (4:1) (15 mL). The flask was then degassed and Pd(dppf)Cl_2 (44 mg, 0.06 mmol, 0.6 equiv.) was added. The resulting red solution was then heated to reflux for 12 hours. After the allotted time had passed and the ester had disappeared on TLC, the solution was cooled to room temperature and concentrated under reduced pressure. The residue was redissolved in DCM and washed with water (3x15ml), brine (3x15ml), dried over sodium sulfate (10 g) and concentrated by rotary evaporation to afford the crude product. The crude product was dissolved by ether (3X30 mL) and transferred to a silica plug (2x2 inch), then further flushed with ether (150 mL) and collect all green solution. The green solution was concentrated and further purified by column chromatography over silica gel to afford the cross-coupling product as green solid in 70% yield (230 mg).

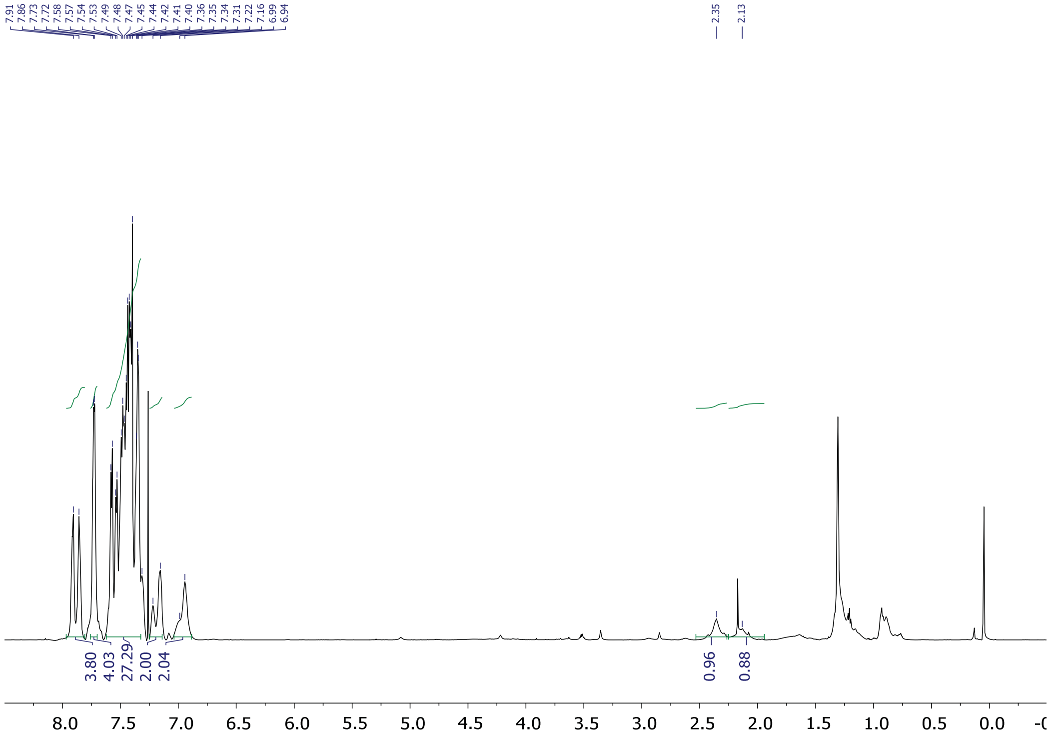
TLC (ethyl ether: hexanes, 1:3 *v/v*); m.p. decomposed at 200 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, J = 28.8 Hz, 4H), 7.78 – 7.68 (m, 4H), 7.45 (dddd, J = 58.5, 29.0, 23.7, 12.9 Hz, 27H), 7.19 (d, J = 37.8 Hz, 2H), 6.97 (d, J = 27.0 Hz, 2H), 2.35 (s, 1H), 2.13 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.44, 141.64, 140.76, 140.74, 140.45, 140.36, 140.29, 140.05, 139.90, 139.57, 139.46, 139.42, 138.74, 138.22, 137.90, 135.88, 131.68, 130.70, 129.62, 129.01, 128.87, 128.46, 127.98, 127.73, 127.38, 127.32, 127.22, 127.18, 127.07, 126.91, 126.07, 125.84, 45.93, 43.51, 29.85; HRMS (ESI) calcd for $C_{232}H_{164}O_8Rh_2$ ([M]$^+$): 3283.0531 found 3283.0432; IR (neat): 3027, 2923, 2852, 1581, 1484, 1380, 1005, 824, 760, 695.

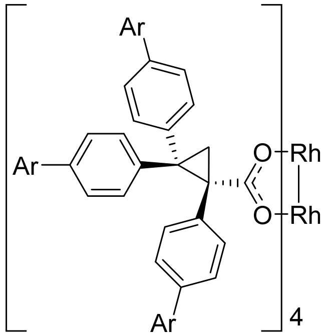


Ar= *p*-PhC_6H_4

Rh_2[*R*-tris(*p*-PhC_6H_4)TPCP$]_4$

J

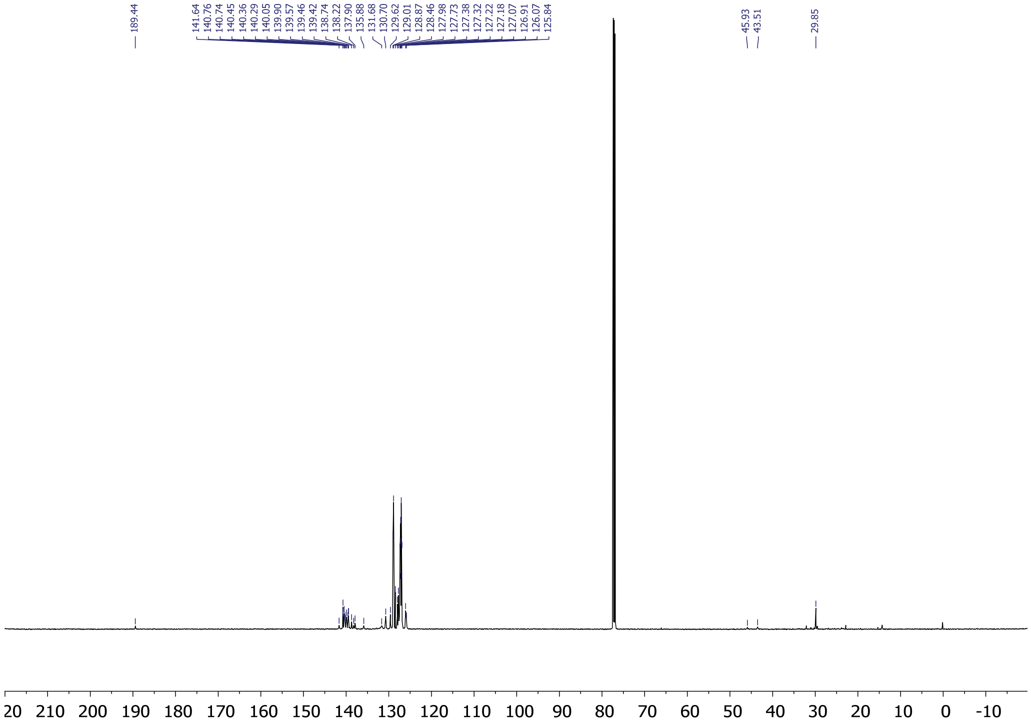


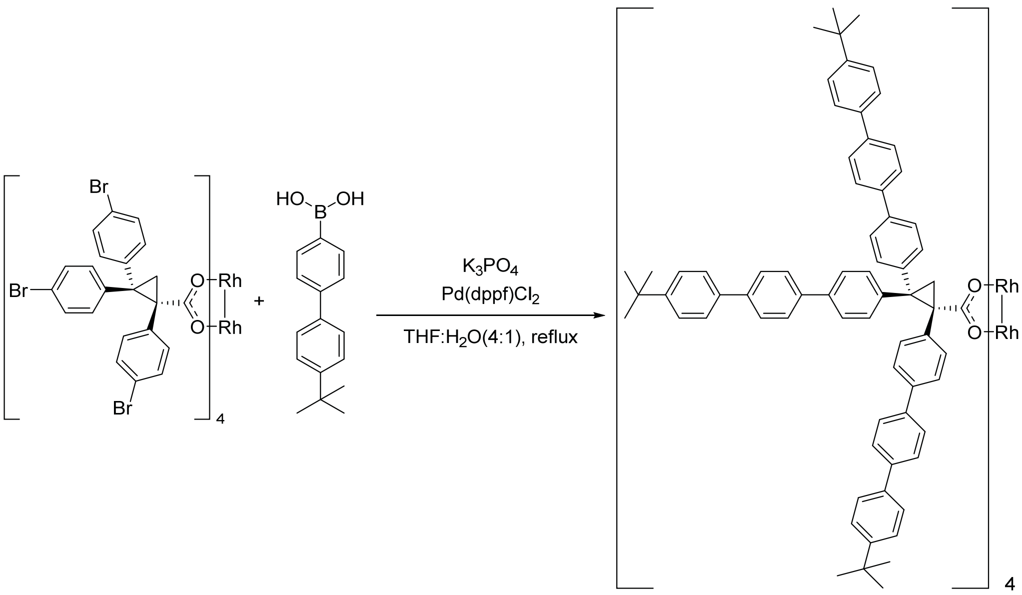


Ar= p-PhC_6H_4

Rh_2[*R*-tris(p-PhC_6H_4)TPCP$]_4$

J

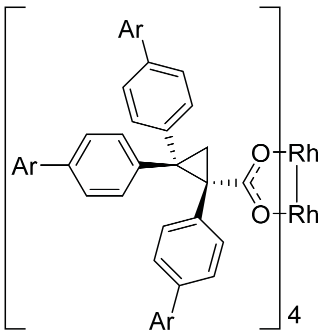




Dirhodium tetrakis [(R)-1,2,2-tris(4''-(tert-butyl)-[1,1':4',1''-terphenyl]-4-yl)cyclopropane-1-carboxylate] (catalyst K). A 25-mL round-bottom flask was charged with **catalyst N** (170 mg, 0.71 mmol, 1.00 equiv.), (4'-(tert-butyl)-[1,1'-biphenyl]-4-yl)boronic acid (646 mg, 2.54 mmol, 36 equiv.). K_3PO_4 (810 mg, 3.82 mmol, 54 equiv.) and THF: H_2O (4:1) (15 mL). The flask was then degassed and Pd(dppf)Cl_2 (31 mg, 0.042 mmol, 0.6 equiv.) was added. The resulting red solution was then heated to reflux for 12 hours. After the allotted time had passed and the ester had disappeared on TLC, the solution was cooled to room temperature and concentrated under reduced pressure. The residue was redissolved in DCM and washed with water (3x15ml), brine (3x15ml), dried over sodium sulfate (10 g) and concentrated by rotary evaporation to afford the crude product. The crude product was dissolved by ether (3X30 mL) and transferred to a silica plug (2x2 inch), then further flushed with ether (150 mL) and collect all green solution. The green solution was concentrated and further purified by column chromatography over silica gel to afford the cross-coupling product as green solid in 47% yield (131 mg).

TLC (diethyl ether: hexanes, 1:3 *v/v*); m.p. decomposed at 205 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 7.9 Hz, 2H), 7.71 (d, J = 7.9 Hz, 2H), 7.64 (d, J = 7.9 Hz, 2H), 7.56 – 7.51 (m, 4H), 7.49 (d, J = 8.1 Hz, 4H), 7.42 (ddd, J = 28.9, 14.8, 7.3 Hz, 13H), 7.28 (d, J = 7.4 Hz, 1H), 7.22 – 7.15 (m, 3H), 6.96 (d, J = 29.0 Hz, 3H), 2.34 (s, 1H), 2.13 (s, 1H), 1.38 (s, 9H), 1.37 (s, 9H), 1.37 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$)

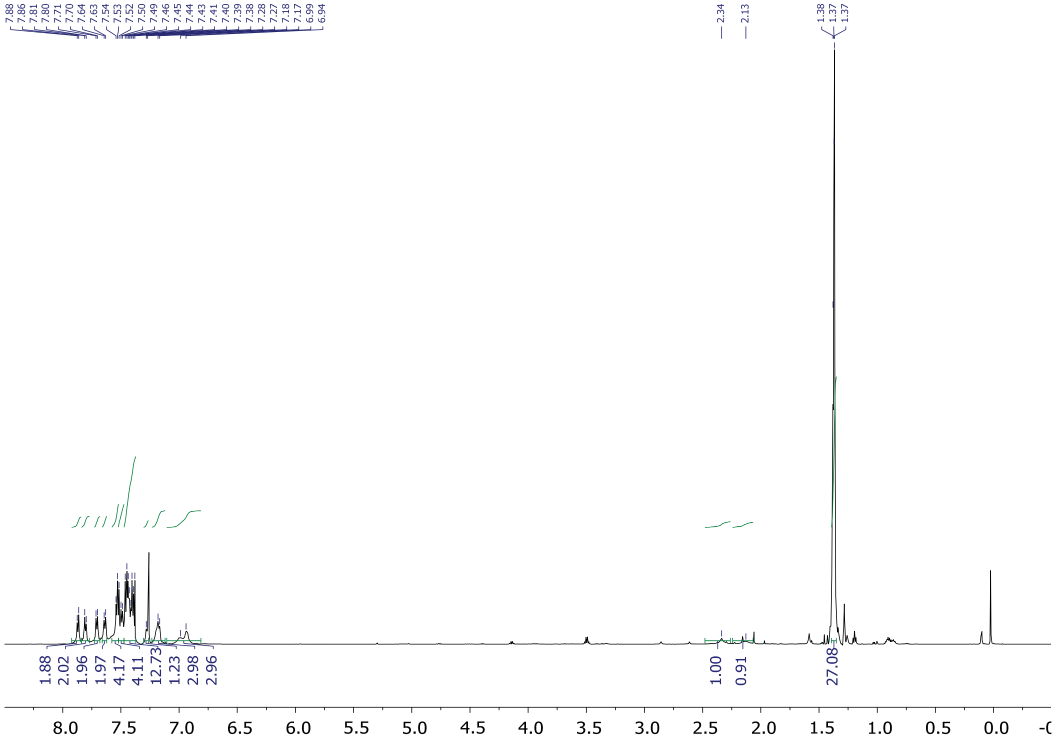
δ 189.54, 150.53, 150.36, 150.21, 141.53, 140.11, 140.04, 139.99, 139.75, 139.48, 139.29, 139.17, 138.84, 138.38, 137.95, 137.90, 137.86, 137.74, 135.80, 131.69, 130.73, 129.58, 128.48, 127.93, 127.55, 127.27, 127.22, 127.14, 127.06, 126.88, 126.72, 126.66, 126.07, 125.92, 125.84, 125.78, 45.97, 43.60, 34.70, 34.66, 34.66, 31.54, 31.50, 29.86; HRMS (ESI) calcd for $C_{279}{}^{13}CH_{262}O_8NRh_2$ ($[M+NH_2]^-$): 3972.8264 found 3972.8234; IR (neat): 3027, 2959, 2867, 2360, 1583, 1491, 1379, 1004, 816.

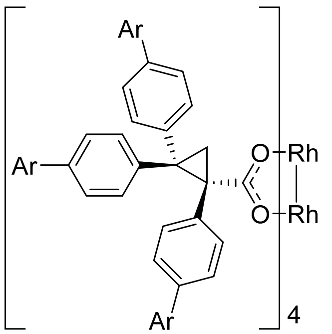


Ar= *p*-^{t}BuC$_6$H$_4$C$_6$H$_4$

Rh$_2$[*R*-tris(*p*-^{t}BuC$_6$H$_4$C$_6$H$_4$)TPCP]$_4$

K

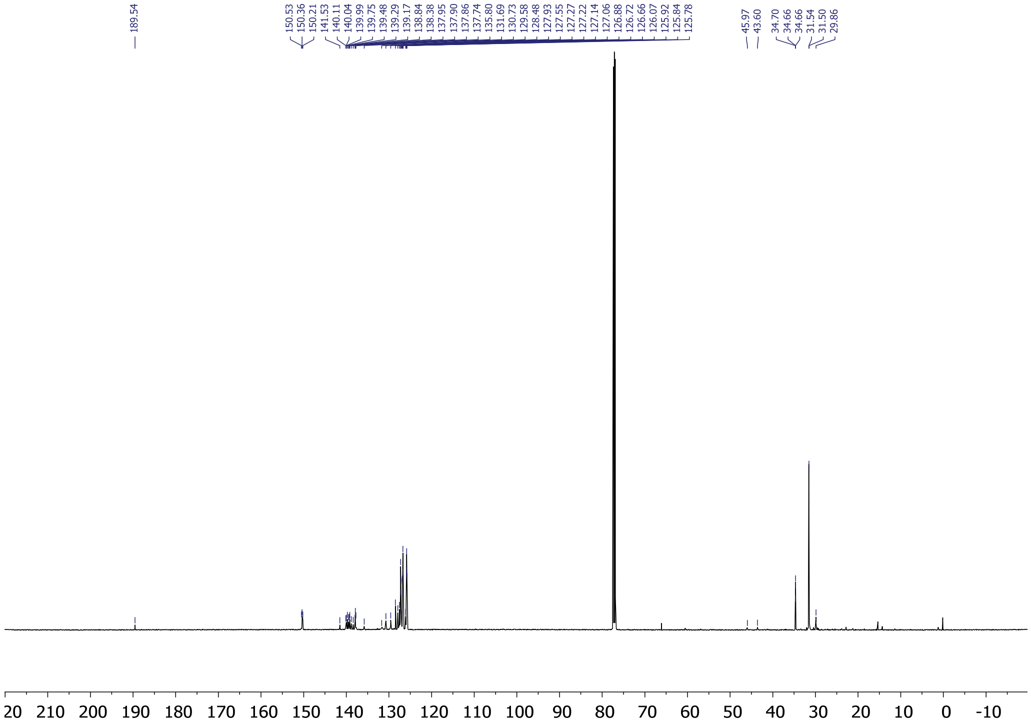


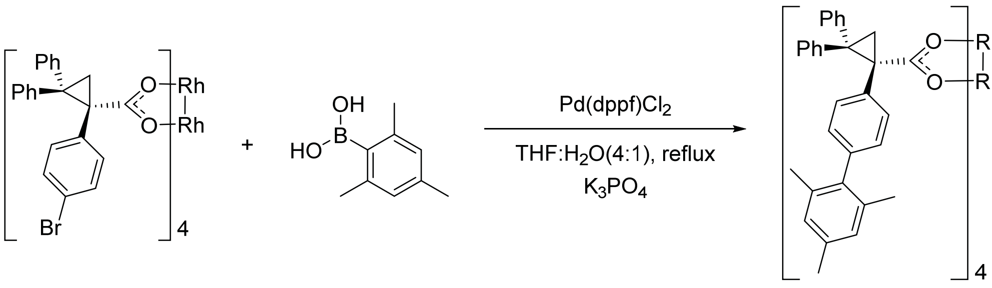


Ar= p-^{t}BuC$_6$H$_4$C$_6$H$_4$

Rh$_2$[R-tris(p-^{t}BuC$_6$H$_4$C$_6$H$_4$)TPCP]$_4$

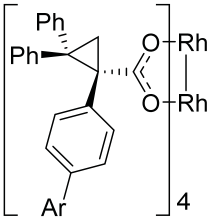
K





Dirhodium tetrakis [(R)-2,2-diphenyl-1-(2',4',6'-trimethyl-[1,1'-biphenyl]-4-yl)cyclopropane-1-carboxylate] (catalyst Q). A 25-mL round-bottom flask was charged with Rh_2(*R*-*p*-BrTPCP)$_4$ (242 mg, 0.136 mmol, 1.00 equiv.), mesitylboronic acid (268 mg, 1.636 mmol, 12 equiv.). K_3PO_4 (521 mg, 2.454 mmol, 18 equiv.) and THF: H_2O (4:1) (15 mL). The flask was then degassed and Pd(dppf)Cl_2 (20 mg, 0.027 mmol, 0.2 equiv.) was added. The resulting red solution was then heated to reflux for 12 hours. After the allotted time had passed and the ester had disappeared on TLC, the solution was cooled to room temperature and concentrated under reduced pressure. The residue was redissolved in DCM and washed with water (3x15ml), brine (3x15ml), dried over sodium sulfate (10 g) and concentrated by rotary evaporation to afford the crude product. The crude product was dissolved by ether (3X30 mL) and transferred to a silica plug (2x2 inch), then further flushed with ether (150 mL) and collect all green solution. The green solution was concentrated and further purified by column chromatography over silica gel to afford the cross-coupling product as green solid in 78% yield (206 mg).

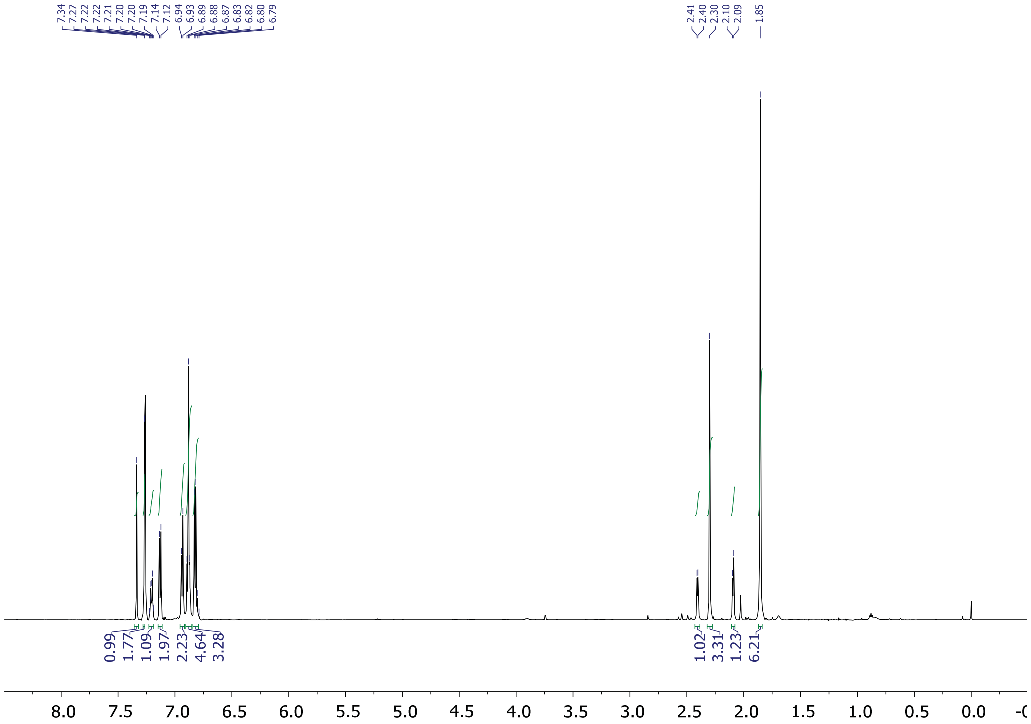
TLC (diethyl ether: hexanes, 1:9 *v/v*); m.p. decomposed at 200 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.27 (s, 2H), 7.21 (dq, J = 8.5, 5.0, 4.4 Hz, 1H), 7.13 (d, J = 7.9 Hz, 2H), 6.94 (d, J = 7.6 Hz, 2H), 6.90 – 6.86 (m, 5H), 6.82 (d, J = 8.0 Hz, 3H), 2.41 (d, J = 4.9 Hz, 1H), 2.30 (s, 3H), 2.09 (d, J = 6.8 Hz, 3H), 1.85 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.78, 142.42, 141.27, 138.91, 138.84, 136.46, 136.08, 135.32, 131.19, 130.12, 129.31, 128.44, 128.12, 128.08, 128.02, 127.54, 126.21, 125.72, 46.61, 43.31, 29.83, 24.74, 21.14, 20.94; HRMS (ESI) calcd for $C_{124}H_{108}O_8Rh_2$ ($[M]^+$): 1930.6149 found 1930.6121; IR (neat): 3023, 2921, 1583, 1494, 1448, 1382, 1005, 849, 783, 747, 701.

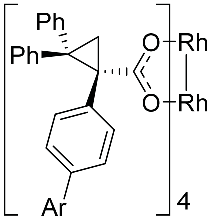


Ar= 2,4,6-tri-MeC_6H_2

Rh_2(*R*-2,4,6-tri-MeC_6H_2-TPCP$)_4$

Q

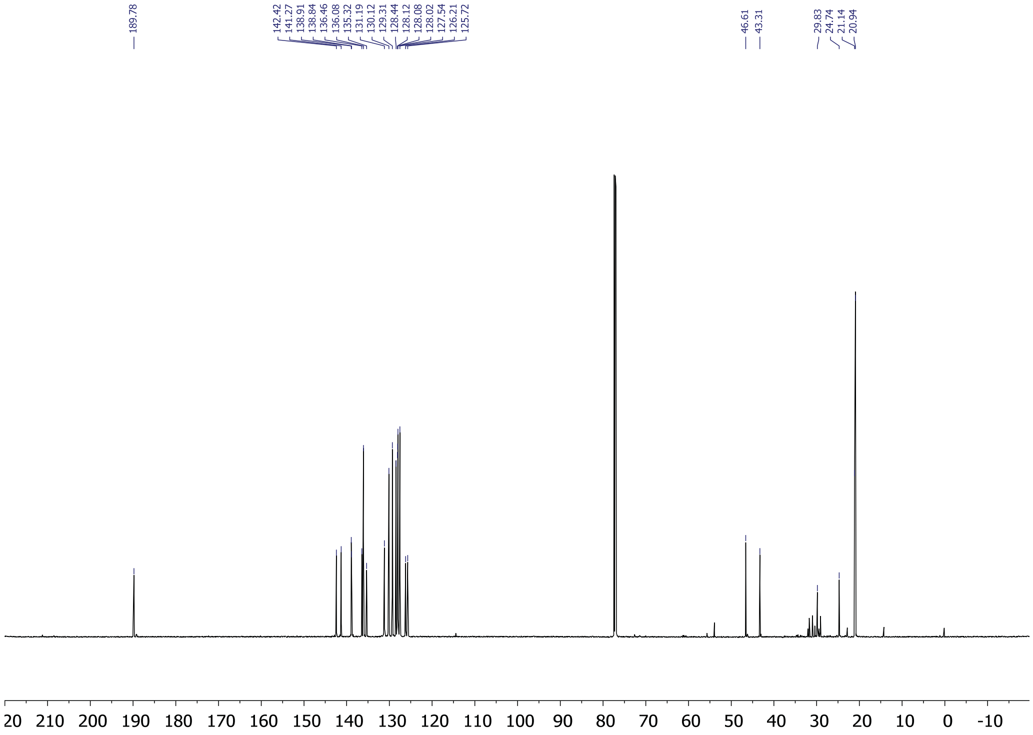




Ar= 2,4,6-tri-MeC$_6$H$_2$

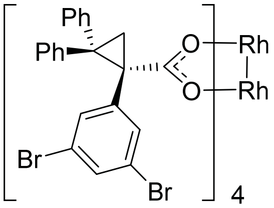
Rh$_2$(*R*-2,4,6-tri-MeC$_6$H$_2$-TPCP)$_4$

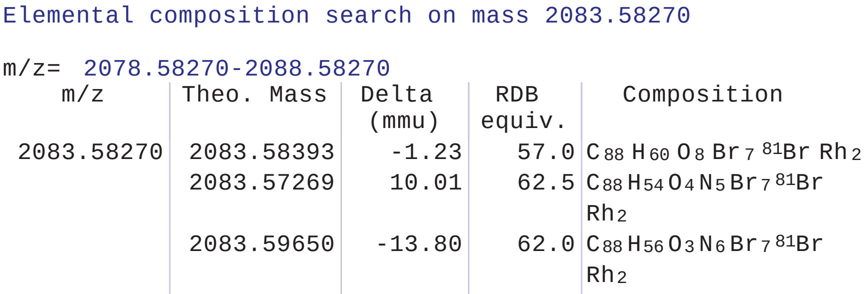
Q



2. High Resolution Mass Spectrometry (HRMS) spectra of catalysts

2.1 3,5-disubstituted catalyst





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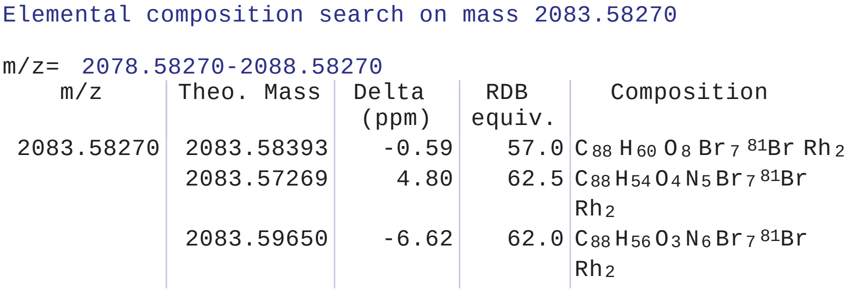
Elemental composition search on mass 2083.58270

m/z=  2078.58270-2088.58270
     m/z      | Theo. Mass | Delta  |  RDB   |    Composition
              |            | (mmu)  | equiv. |
 2083.58270   2083.58393     -1.23     57.0  C88 H60 O8 Br7 81Br Rh2
              2083.57269     10.01     62.5  C88 H54 O4 N5 Br7 81Br
                                             Rh2
              2083.59650    -13.80     62.0  C88 H56 O3 N6 Br7 81Br
                                             Rh2
```



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Elemental composition search on mass 2083.58270

m/z=  2078.58270-2088.58270
     m/z      | Theo. Mass | Delta  |  RDB   |    Composition
              |            | (ppm)  | equiv. |
 2083.58270   2083.58393     -0.59     57.0  C88 H60 O8 Br7 81Br Rh2
              2083.57269      4.80     62.5  C88 H54 O4 N5 Br7 81Br
                                             Rh2
              2083.59650     -6.62     62.0  C88 H56 O3 N6 Br7 81Br
                                             Rh2
```

M+CH3N

Elemental composition search on mass 2124.61169

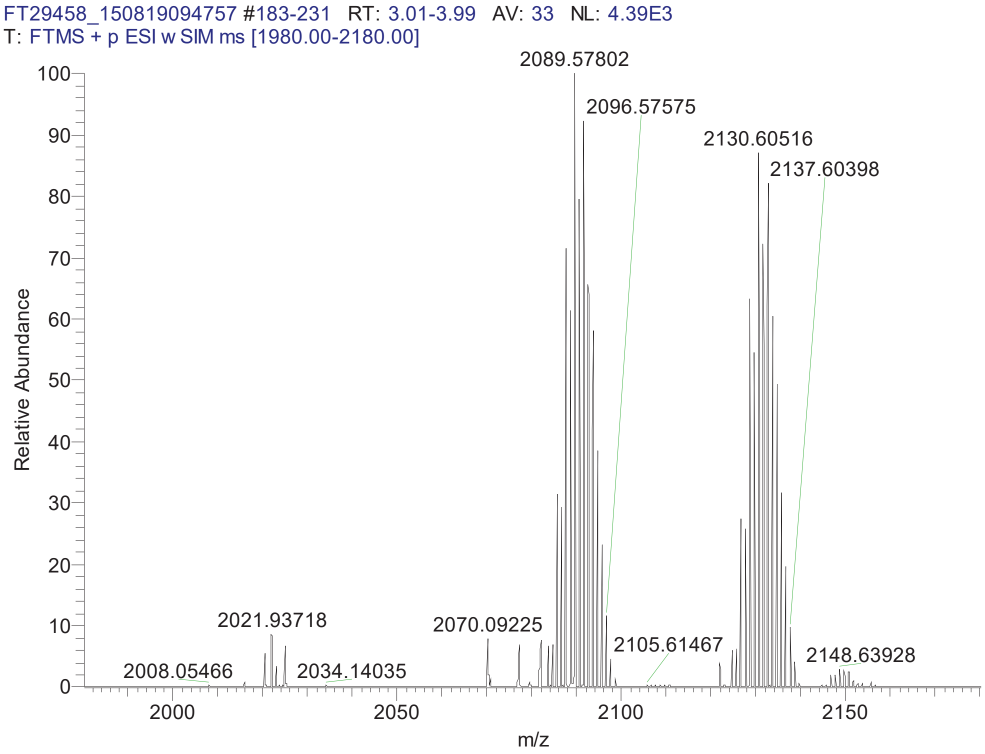
m/z= 2119.61169-2129.61169

m/z	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
2124.61169	2124.61048	1.21	58.0	$C_{90}H_{63}O_{8}NBr_{7}{}^{81}BrRh_{2}$
	2124.61048	1.21	63.5	$C_{89}H_{57}O_{3}N_{8}Br_{7}{}^{81}BrRh_{2}$
	2124.60914	2.55	58.5	$C_{88}H_{61}O_{7}N_{4}Br_{7}{}^{81}BrRh_{2}$
	2124.62171	-10.02	63.5	$C_{88}H_{57}O_{2}N_{10}Br_{7}{}^{81}BrRh_{2}$
	2124.62171	-10.02	58.0	$C_{89}H_{63}O_{7}N_{3}Br_{7}{}^{81}BrRh_{2}$
	2124.62305	-11.36	63.0	$C_{90}H_{59}O_{3}N_{7}Br_{7}{}^{81}BrRh_{2}$
	2124.59924	12.45	63.5	$C_{90}H_{57}O_{4}N_{6}Br_{7}{}^{81}BrRh_{2}$
	2124.59791	13.78	58.5	$C_{89}H_{61}O_{8}N_{2}Br_{7}{}^{81}BrRh_{2}$
	2124.59790	13.79	64.0	$C_{88}H_{55}O_{3}N_{9}Br_{7}{}^{81}BrRh_{2}$

Elemental composition search on mass 2124.61169

m/z= 2119.61169-2129.61169

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
2124.61169	2124.61048	0.57	58.0	$C_{90}H_{63}O_{8}NBr_{7}{}^{81}BrRh_{2}$
	2124.61048	0.57	63.5	$C_{89}H_{57}O_{3}N_{8}Br_{7}{}^{81}BrRh_{2}$
	2124.60914	1.20	58.5	$C_{88}H_{61}O_{7}N_{4}Br_{7}{}^{81}BrRh_{2}$
	2124.62171	-4.72	63.5	$C_{88}H_{57}O_{2}N_{10}Br_{7}{}^{81}BrRh_{2}$
	2124.62171	-4.72	58.0	$C_{89}H_{63}O_{7}N_{3}Br_{7}{}^{81}BrRh_{2}$
	2124.62305	-5.35	63.0	$C_{90}H_{59}O_{3}N_{7}Br_{7}{}^{81}BrRh_{2}$
	2124.59924	5.86	63.5	$C_{90}H_{57}O_{4}N_{6}Br_{7}{}^{81}BrRh_{2}$
	2124.59791	6.49	58.5	$C_{89}H_{61}O_{8}N_{2}Br_{7}{}^{81}BrRh_{2}$
	2124.59790	6.49	64.0	$C_{88}H_{55}O_{3}N_{9}Br_{7}{}^{81}BrRh_{2}$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2034.14035
Relative Abundance
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20
30
40
50
60
70
80
90
100
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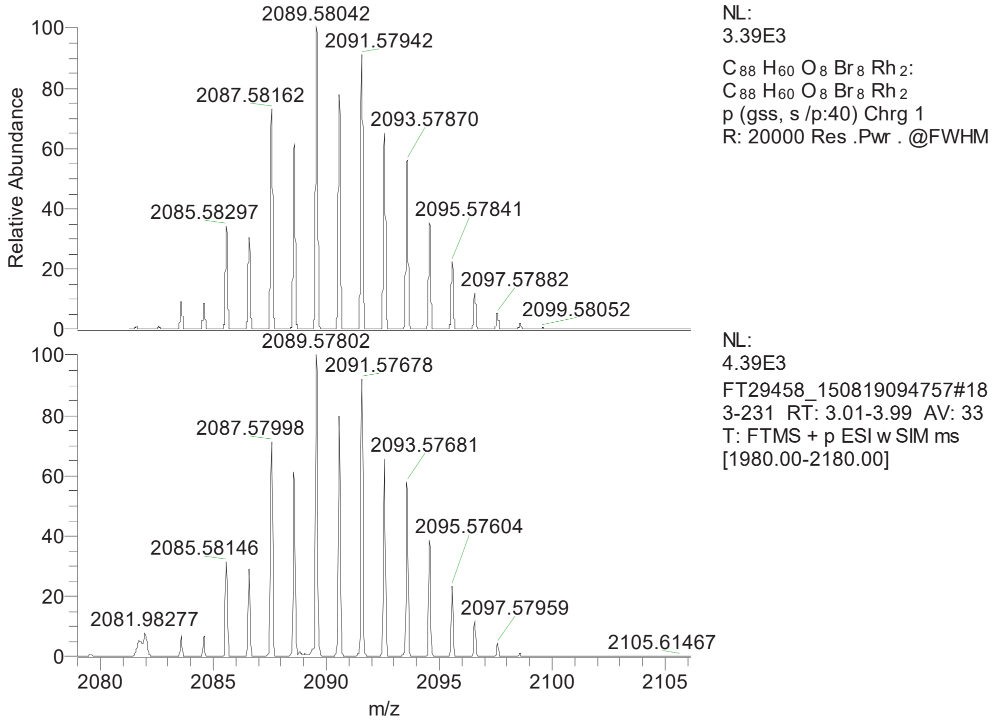
2050
2100
2150
m/z


NL:
3.39E3
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$C_{88}H_{60}O_8Br_8Rh_2$
p (gss, s /p:40) Chrg 1
R: 20000 Res .Pwr . @FWHM
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Relative Abundance
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60
80
100
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2085
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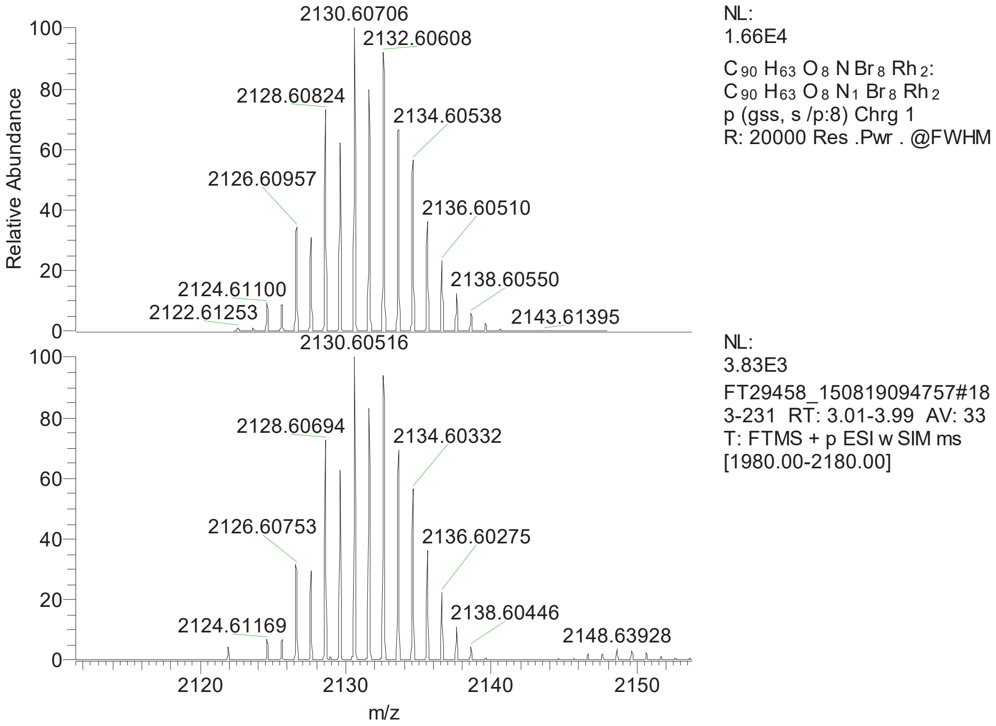
2100
2105
m/z

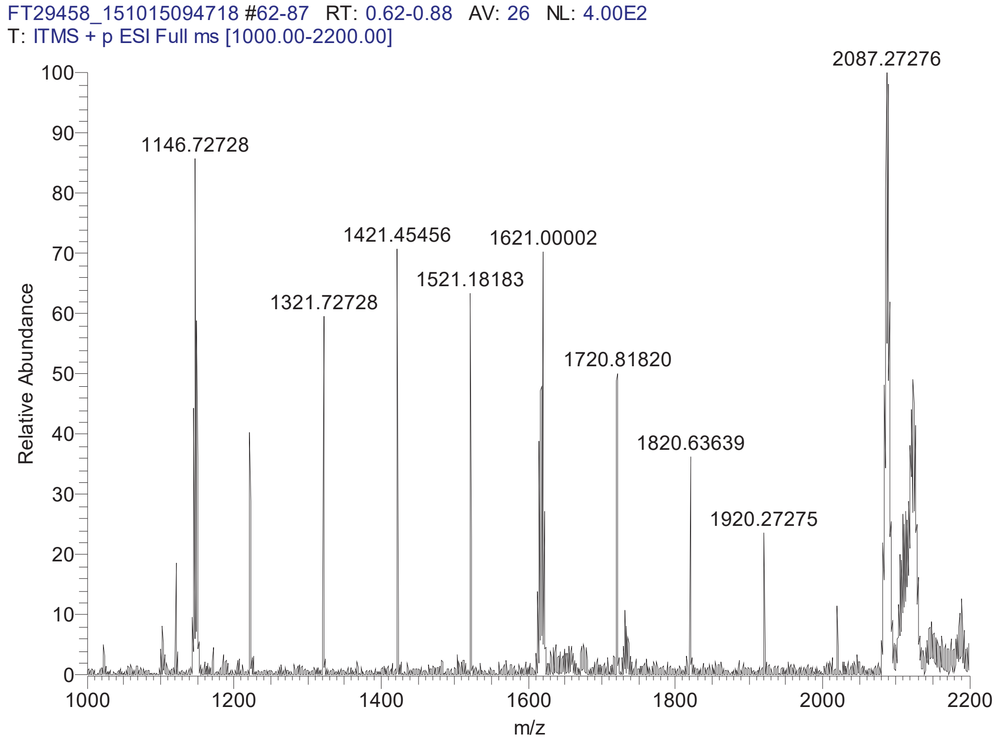


m/z

Intensity Relative

2085.58146	1398.4	31.42
2086.58368	1285.2	28.88
2087.57998	3144.2	70.65
2088.58180	2741.1	61.59
2089.57802	4450.6	100.00
2090.58034	3613.9	81.20
2091.57678	4139.3	93.00
2092.57858	2968.8	66.71
2093.57681	2594.5	58.30
2094.57787	1714.6	38.52
2126.60753	1225.9	27.54
2127.61159	1147.5	25.78
2128.60694	2797.5	62.86
2129.60897	2468.5	55.46
2130.60516	3835.4	86.18
2131.60755	3200.5	71.91
2132.60364	3646.2	81.93
2133.60556	2661.9	59.81
2134.60332	2199.2	49.41
2135.60507	1399.4	31.44

Ion trap (peaks at xx21 are from calibration peaks).



m/z	Intensity	Relative
1146.72728	343.2	85.87
2087.00003	322.3	80.65
2087.09094	349.5	87.46
2087.18185	384.5	96.22
2087.27276	399.6	100.00
2087.36367	379.1	94.86
2087.45458	330.8	82.77
2087.63640	334.2	83.62
2087.81821	322.6	80.73
2088.09094	345.2	86.39
2088.18185	372.3	93.16
2088.27276	381.7	95.50
2088.36367	338.7	84.76
2088.45458	321.9	80.55
2089.00003	322.3	80.65
2089.09094	348.4	87.19
2089.18185	364.0	91.08
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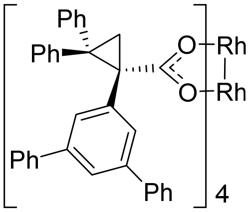


Elemental composition search on mass 2066.55229

m/z= 2061.55229-2071.55229

m/z	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
2066.55229	2066.55228	0.01	89.0	$C_{136}H_{100}O_{8}Rh_{2}$
	2066.45838	93.91	96.0	$C_{137}H_{88}O_{8}Rh_{2}$
	2066.44580	106.49	96.5	$C_{136}H_{86}O_{8}NRh_{2}$
	2066.42199	130.30	97.0	$C_{136}H_{84}O_{9}Rh_{2}$

Elemental composition search on mass 2066.55229

m/z= 2061.55229-2071.55229

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
2066.55229	2066.55228	0.01	89.0	$C_{136}H_{100}O_{8}Rh_{2}$
	2066.45838	45.44	96.0	$C_{137}H_{88}O_{8}Rh_{2}$
	2066.44580	51.53	96.5	$C_{136}H_{86}O_{8}NRh_{2}$
	2066.42199	63.05	97.0	$C_{136}H_{84}O_{9}Rh_{2}$

Elemental composition search on mass 2084.58681

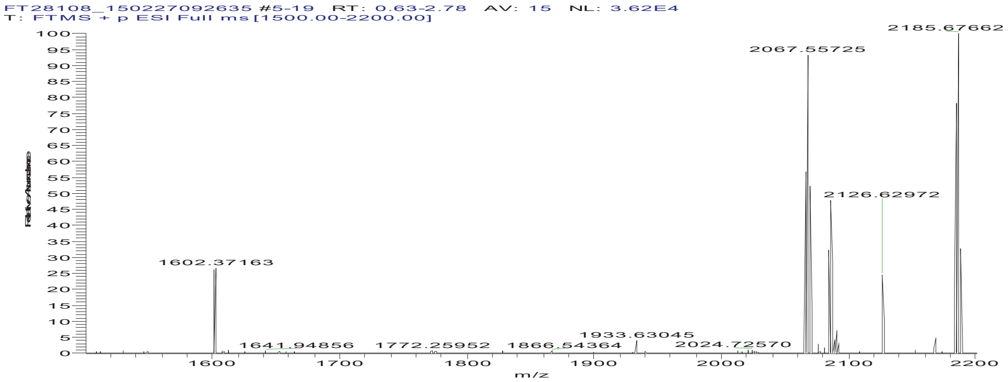
m/z= 2079.58681-2089.58681

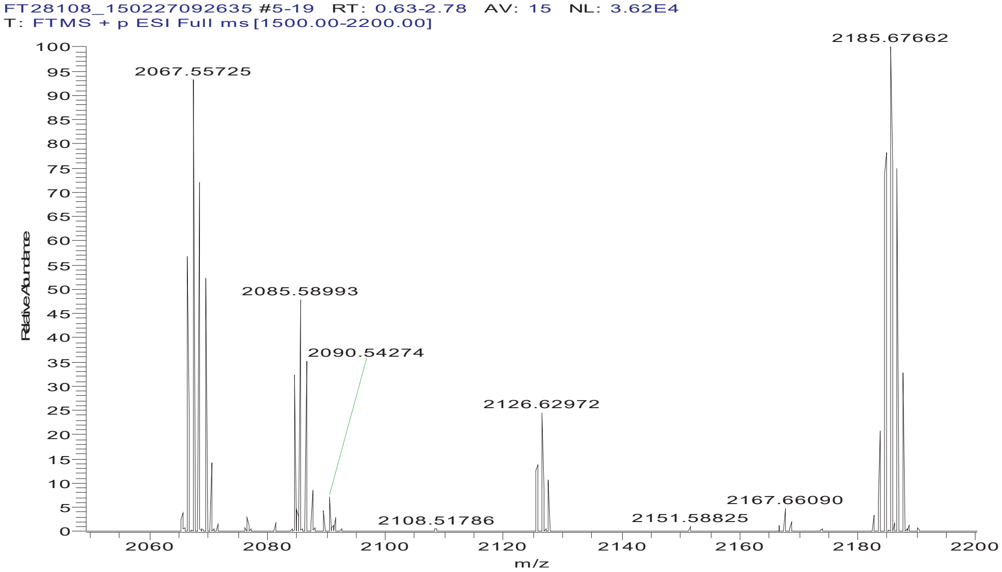
m/z	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
2084.58681	2084.58665	0.16	87.5	$C_{136}H_{104}O_8NRh_2$
	2084.59923	-12.42	87.0	$C_{137}H_{106}O_8Rh_2$
	2084.56284	23.97	88.0	$C_{136}H_{102}O_9Rh_2$
	2084.50533	81.48	94.0	$C_{138}H_{94}O_8Rh_2$
	2084.49275	94.06	94.5	$C_{137}H_{92}O_8NRh_2$
	2084.69313	-106.32	80.0	$C_{136}H_{118}O_8Rh_2$
	2084.46894	117.87	95.0	$C_{137}H_{90}O_9Rh_2$
	2084.45637	130.44	95.5	$C_{136}H_{88}O_9NRh_2$
	2084.43256	154.25	96.0	$C_{136}H_{86}O_{10}Rh_2$

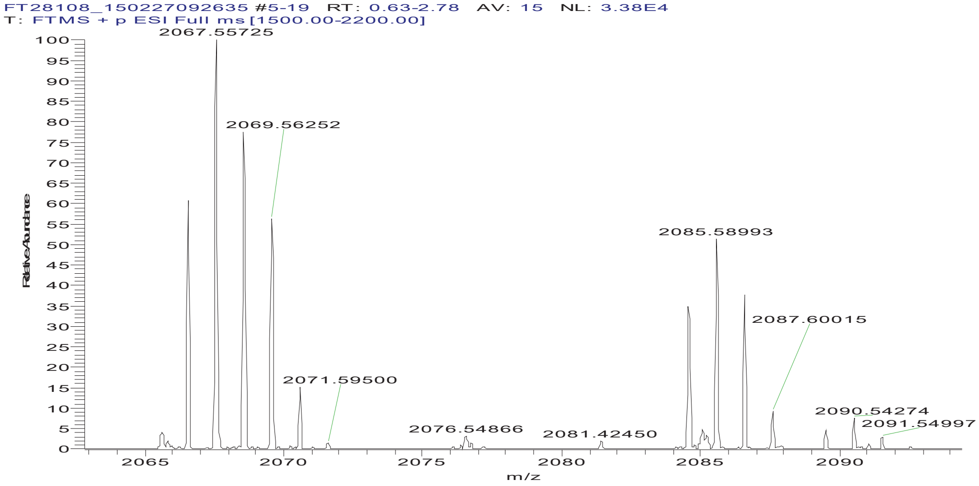
Elemental composition search on mass 2084.58681

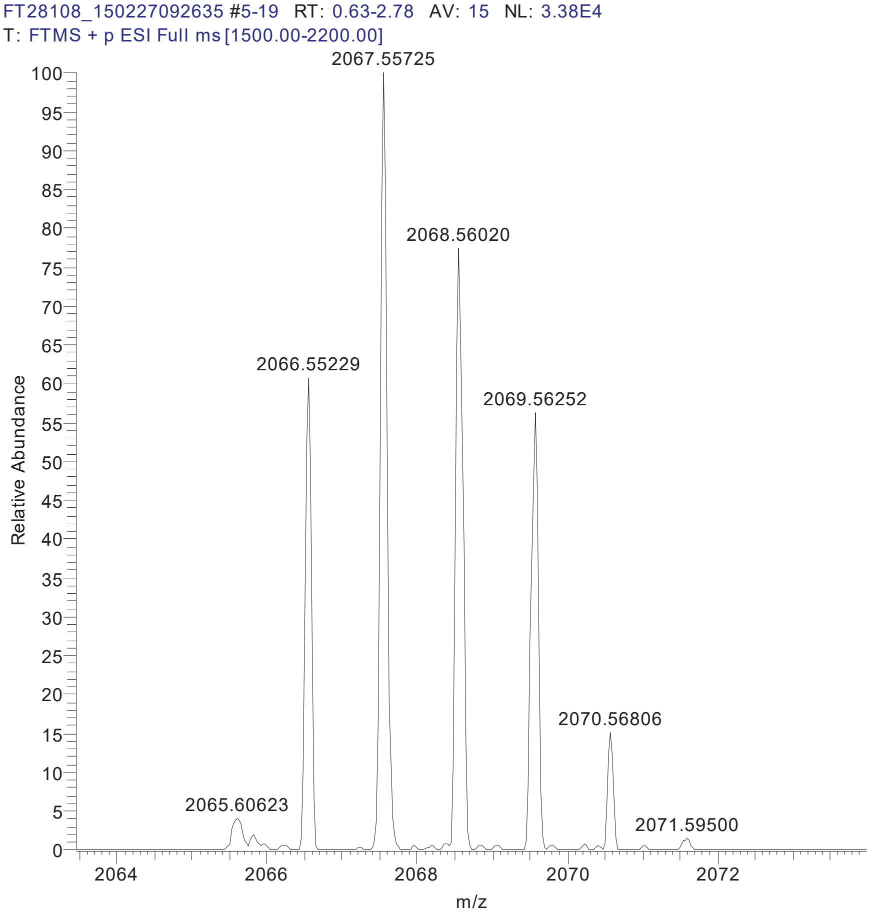
m/z= 2079.58681-2089.58681

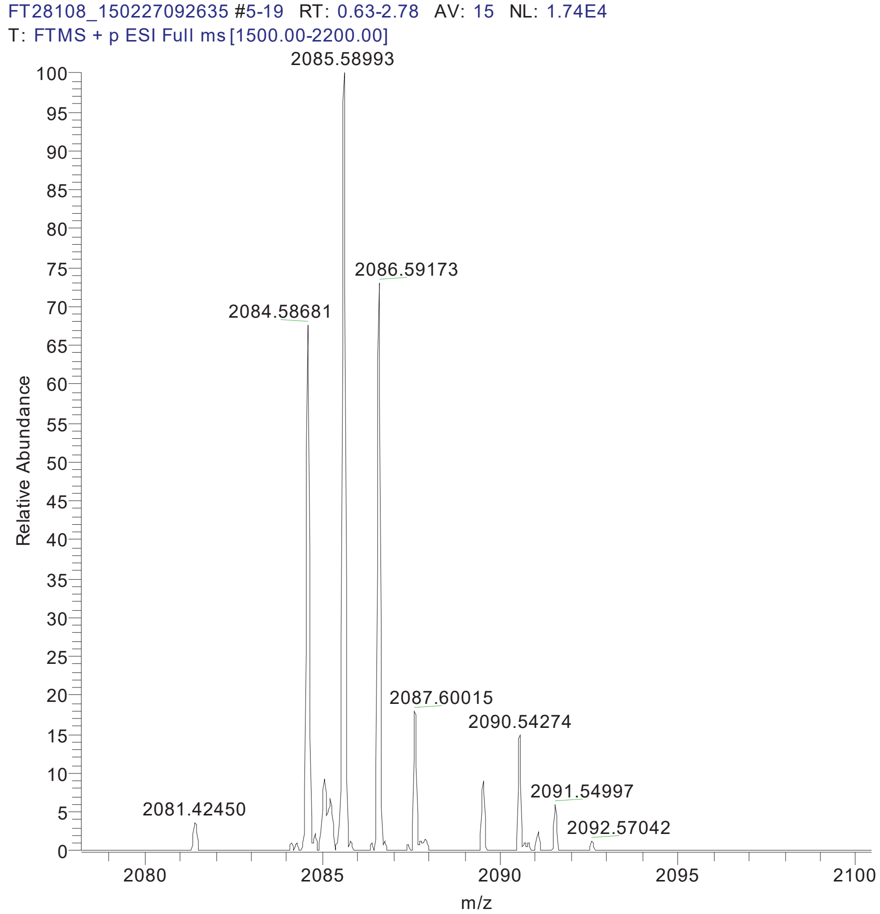
m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
2084.58681	2084.58665	0.08	87.5	$C_{136}H_{104}O_8NRh_2$
	2084.59923	-5.96	87.0	$C_{137}H_{106}O_8Rh_2$
	2084.56284	11.50	88.0	$C_{136}H_{102}O_9Rh_2$
	2084.50533	39.09	94.0	$C_{138}H_{94}O_8Rh_2$
	2084.49275	45.12	94.5	$C_{137}H_{92}O_8NRh_2$
	2084.69313	-51.00	80.0	$C_{136}H_{118}O_8Rh_2$
	2084.46894	56.54	95.0	$C_{137}H_{90}O_9Rh_2$
	2084.45637	62.57	95.5	$C_{136}H_{88}O_9NRh_2$
	2084.43256	74.00	96.0	$C_{136}H_{86}O_{10}Rh_2$


FT28108_150227092635 #5-19 RT: 0.63-2.78 AV: 15 NL: 3.62E4
T: FTMS + p ESI Full ms [1500.00-2200.00]
Relative Abundance
m/z
2185.67662
2067.55725
2126.62972
1602.37163
1641.94856
1772.25952
1866.54364
1933.63045
2024.72570
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
1600
1700
1800
1900
2000
2100
2200


FT28108_150227092635 #5-19 RT: 0.63-2.78 AV: 15 NL: 3.62E4
T: FTMS + p ESI Full ms [1500.00-2200.00]
Relative Abundance
m/z
2185.67662
2067.55725
2085.58993
2090.54274
2126.62972
2167.66090
2108.51786
2151.58825
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
2060
2080
2100
2120
2140
2160
2180
2200

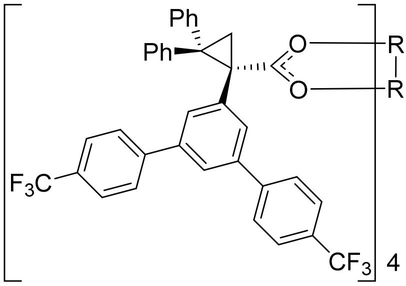

FT28108_150227092635 #5-19 RT: 0.63-2.78 AV: 15 NL: 3.38E4
T: FTMS + p ESI Full ms [1500.00-2200.00]
Relative Abundance
m/z
2067.55725
2069.56252
2071.59500
2076.54866
2081.42450
2085.58993
2087.60015
2090.54274
2091.54997
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
2065
2070
2075
2080
2085
2090


FT28108_150227092635 #5-19 RT: 0.63-2.78 AV: 15 NL: 3.38E4
T: FTMS + p ESI Full ms [1500.00-2200.00]
2067.55725
2068.56020
2066.55229
2069.56252
2070.56806
2065.60623
2071.59500
Relative Abundance
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
2064
2066
2068
2070
2072
m/z



m/z	Intensity	Relative
1601.36816	9548.0	26.00
1602.37163	9682.5	26.36
2066.55229	20580.3	56.03
2067.55725	33765.6	91.93
2068.56020	26150.0	71.20
2069.56252	18988.0	51.70
2070.56806	5134.6	13.98
2084.58681	11868.3	32.31
2085.58993	17770.2	48.38
2086.59173	12727.0	34.65
2087.60015	3244.2	8.83
2090.54274	2690.2	7.32
2125.62519	4996.0	13.60
2126.62972	9046.0	24.63
2127.63399	3934.8	10.71
2183.66050	7745.4	21.09
2184.67213	28679.5	78.09

2185.67662	36727.8	100.00
2186.67930	27810.3	75.72
2187.68368	12344.7	33.61



Elemental composition search on mass 2610.45468

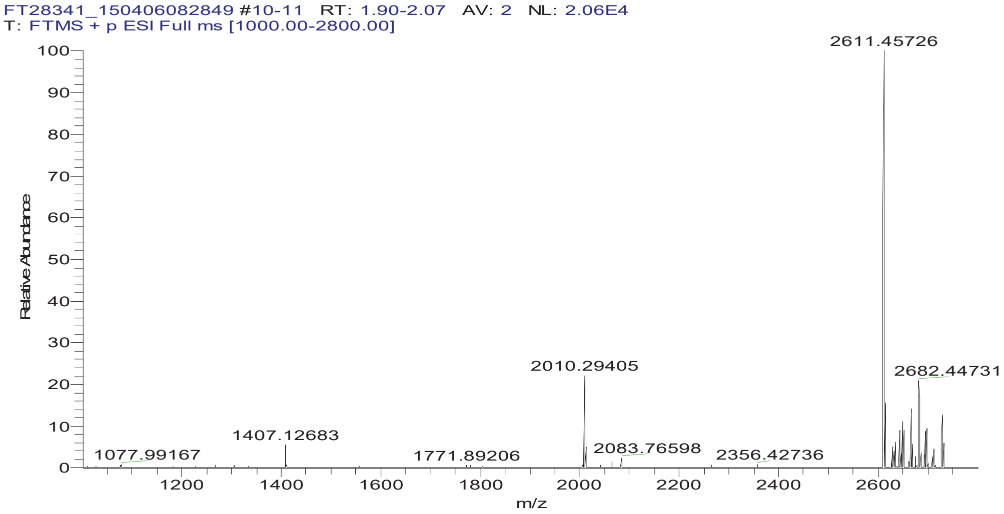
m/z= 2605.45468-2615.45468

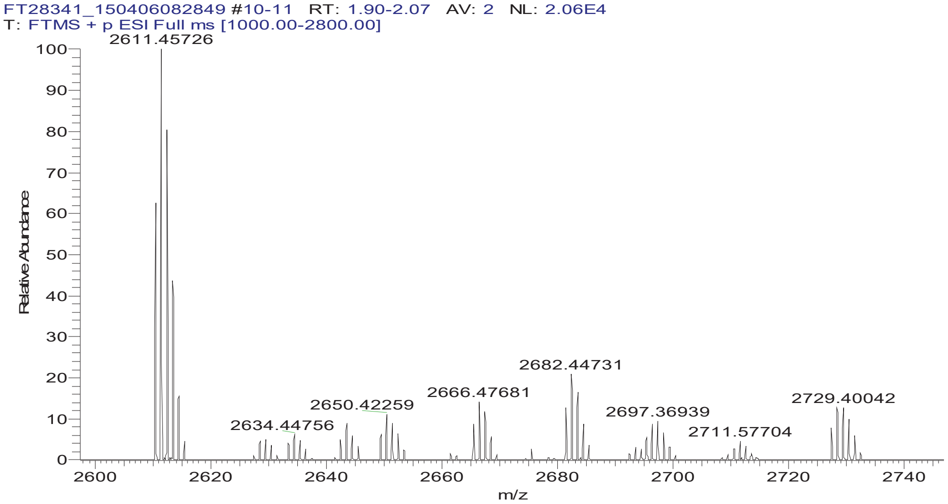
m/z	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
2610.45468	2610.45136	3.32	89.0	$C_{144}H_{92}O_8F_{24}Rh_2$

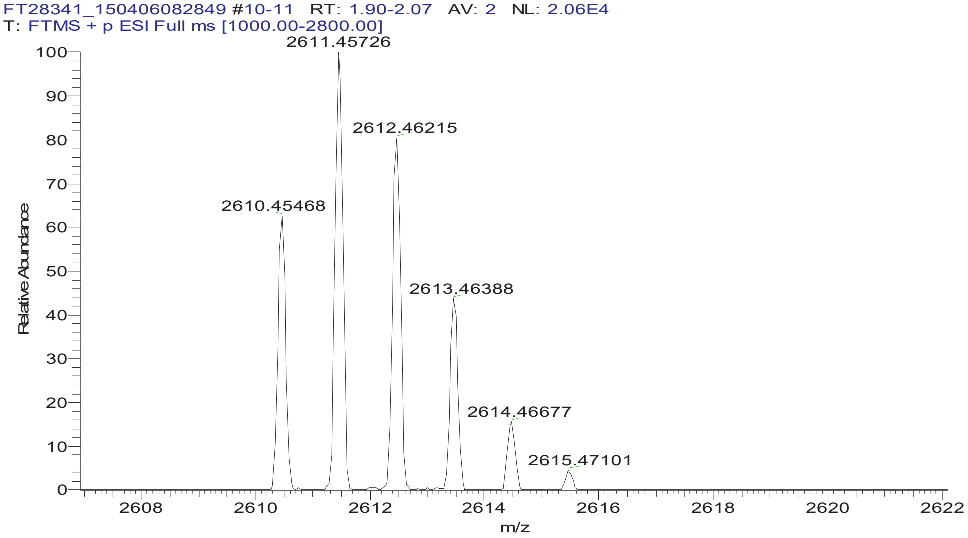
Elemental composition search on mass 2610.45468

m/z= 2605.45468-2615.45468

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
2610.45468	2610.45136	1.27	89.0	$C_{144}H_{92}O_8F_{24}Rh_2$

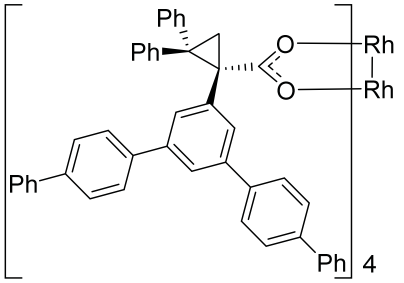




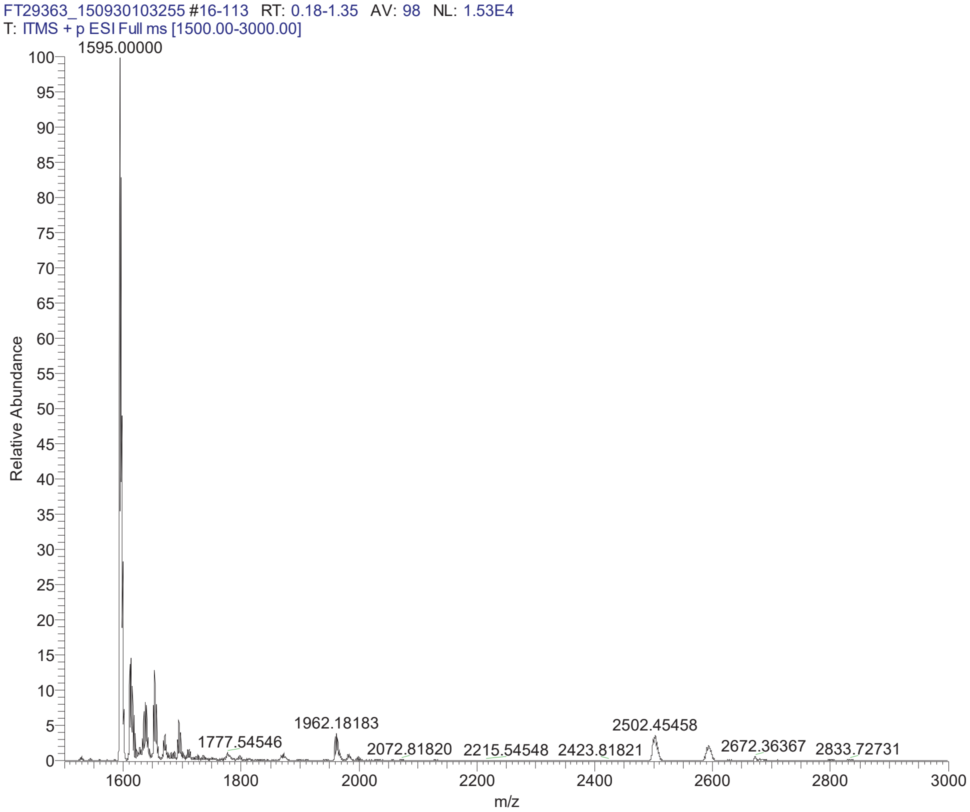


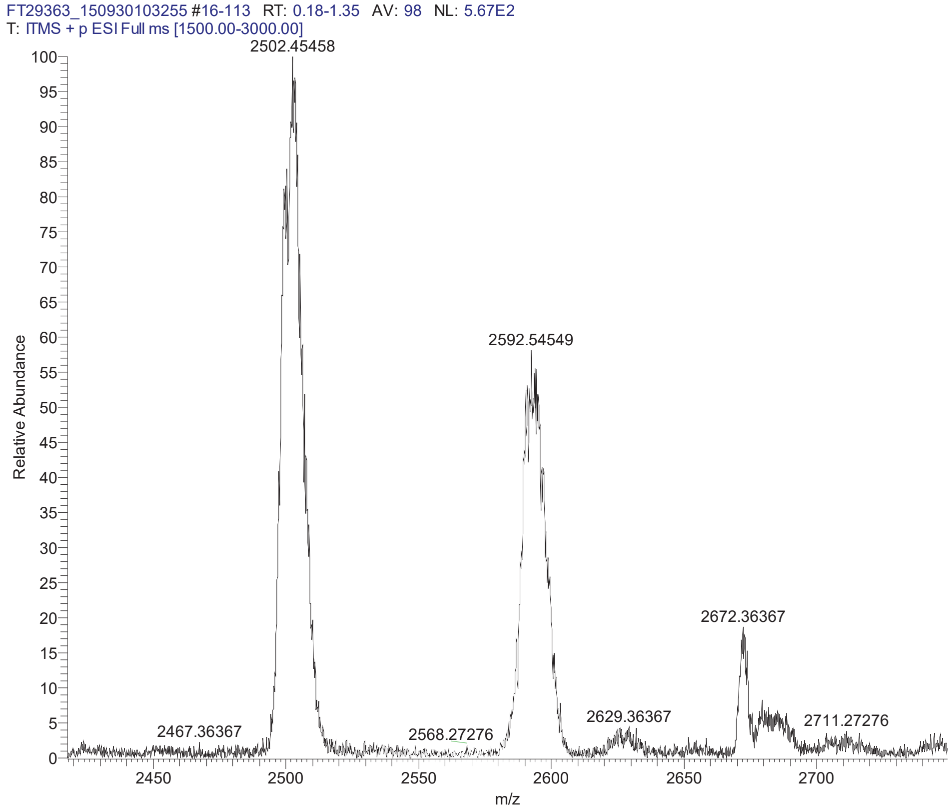
m/z	Intensity	Relative
2009.28937	3837.1	18.31
2010.29405	4625.1	22.07
2011.29603	2696.2	12.86
2610.45468	12971.0	61.88
2611.45726	20961.4	100.00
2612.46215	16653.9	79.45
2613.46388	9067.7	43.26
2614.46677	3293.6	15.71
2650.42259	2319.6	11.07
2651.42968	1905.7	9.09
2666.47681	2993.3	14.28
2667.47524	2416.3	11.53
2681.44613	2666.9	12.72

2682.44731	4299.5	20.51
2683.45079	3414.0	16.29
2684.45598	1856.5	8.86
2697.36939	1943.1	9.27
2728.39726	2634.8	12.57
2729.40042	2691.4	12.84
2730.39977	2057.3	9.81



Ion trap


FT29363_150930103255 #16-113 RT: 0.18-1.35 AV: 98 NL: 1.53E4
T: ITMS + p ESI Full ms [1500.00-3000.00]
1595.00000
1777.54546
1962.18183
2072.81820
2215.54548
2423.81821
2502.45458
2672.36367
2833.72731
Relative Abundance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
1600
1800
2000
2200
2400
2600
2800
3000
m/z



FTMS Sim Mode

Elemental composition search on mass 2674.79651

m/z= 2669.79651-2679.79651

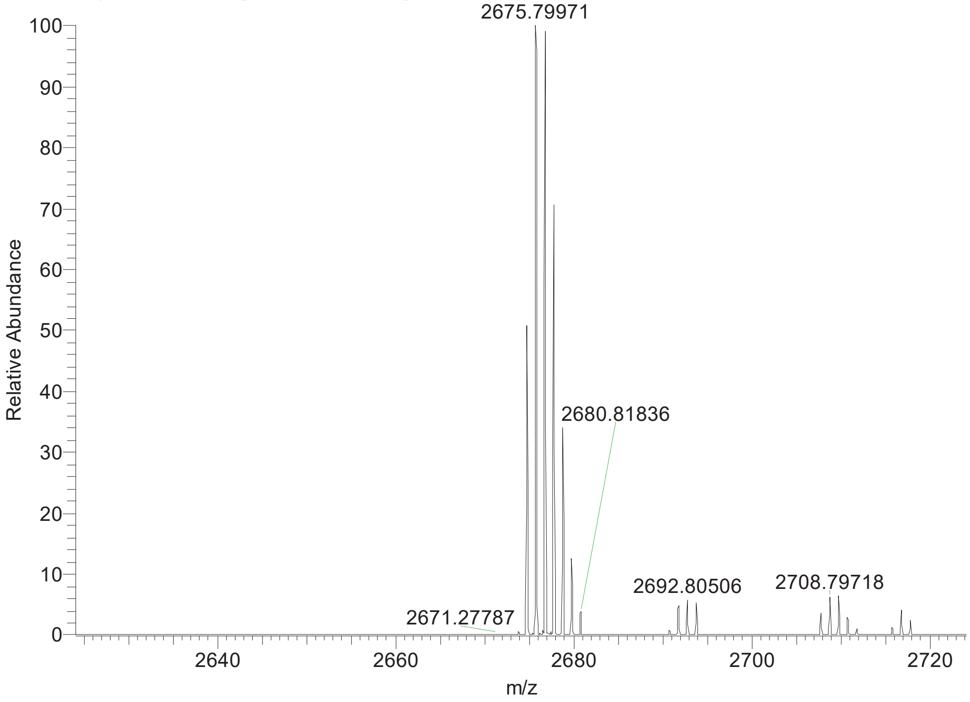
m/z	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
2674.79651	2674.80268	-6.17	121.0	$C_{184}H_{132}O_{8}Rh_{2}$

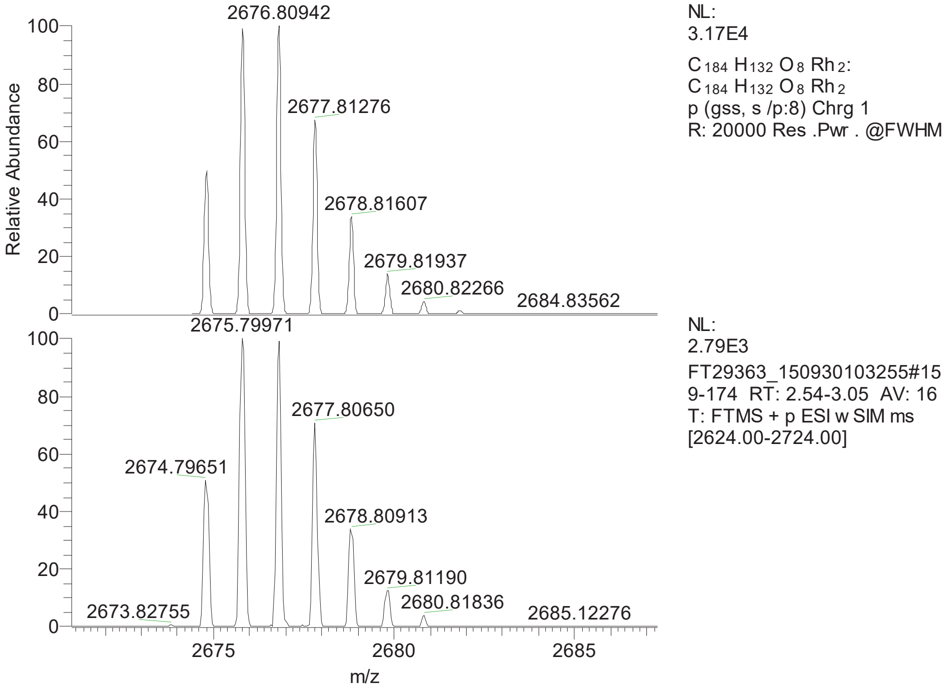
Elemental composition search on mass 2674.79651

m/z= 2669.79651-2679.79651

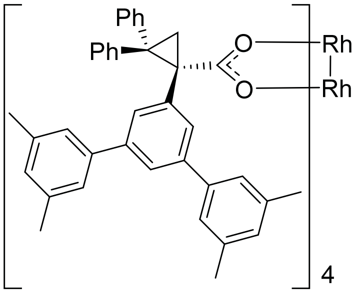
m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
2674.79651	2674.80268	-2.31	121.0	$C_{184}H_{132}O_{8}Rh_{2}$

FT29363_150930103255 #159-174 RT: 2.54-3.05 AV: 16 NL: 2.79E3
T: FTMS + p ESI w SIM ms [2624.00-2724.00]





m/z	Intensity	Relative
2674.79651	1419.2	49.61
2675.79971	2860.7	100.00
2676.60229	21.8	0.76
2676.80460	2809.2	98.20
2677.80650	1976.7	69.10
2678.80913	958.7	33.51
2679.81190	368.4	12.88
2680.81836	112.9	3.95
2690.80688	22.2	0.78
2691.79388	138.1	4.83
2692.80506	163.5	5.71
2693.81047	146.0	5.10
2707.79594	104.8	3.66
2708.79718	183.0	6.40
2709.80115	182.7	6.39
2710.80808	84.8	2.96
2711.81086	29.0	1.01
2715.81941	35.2	1.23
2716.83098	114.4	4.00
2717.83311	68.8	2.41

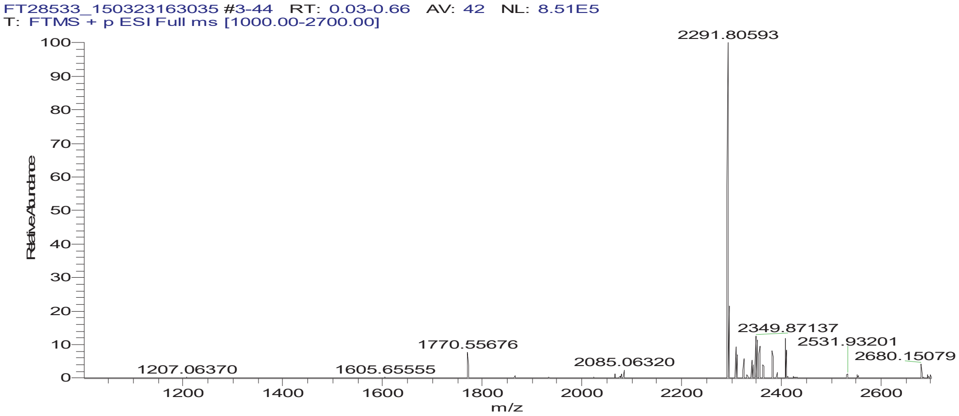


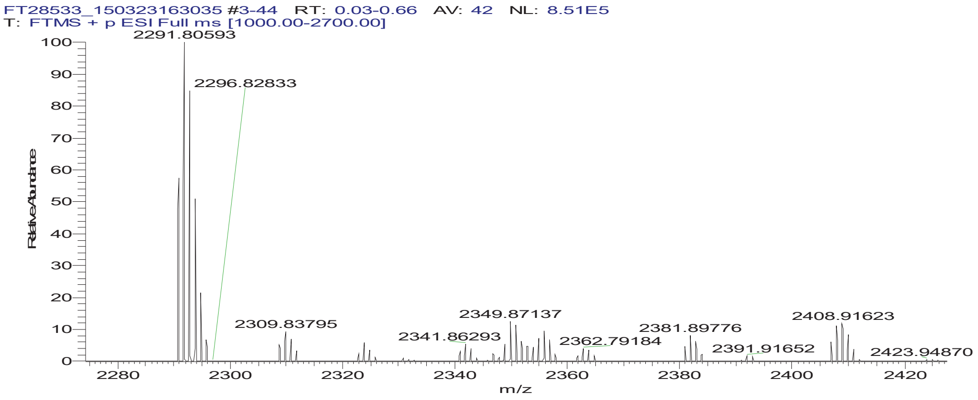
```
Elemental composition search on mass 2290.80189

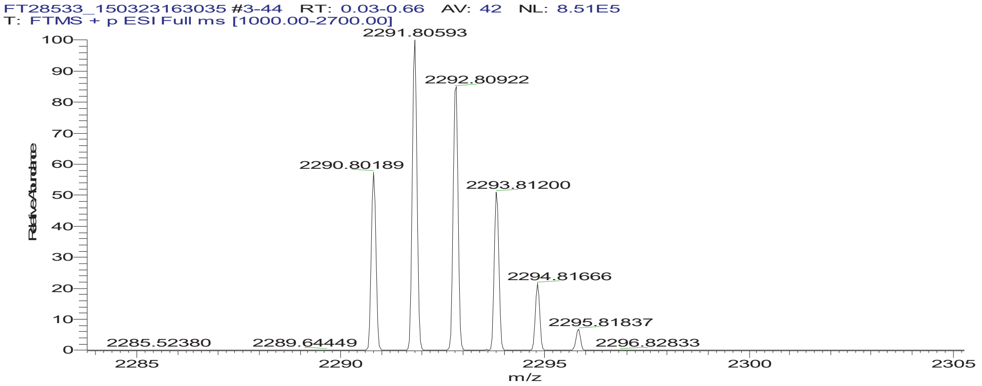
m/z= 2285.80189-2295.80189
    m/z      | Theo. Mass | Delta   | RDB    |   Composition
             |            | (mmu)   | equiv. |
 2290.80189  | 2290.80268 |   -0.79 |   89.0 | C152 H132 O8 Rh2
```

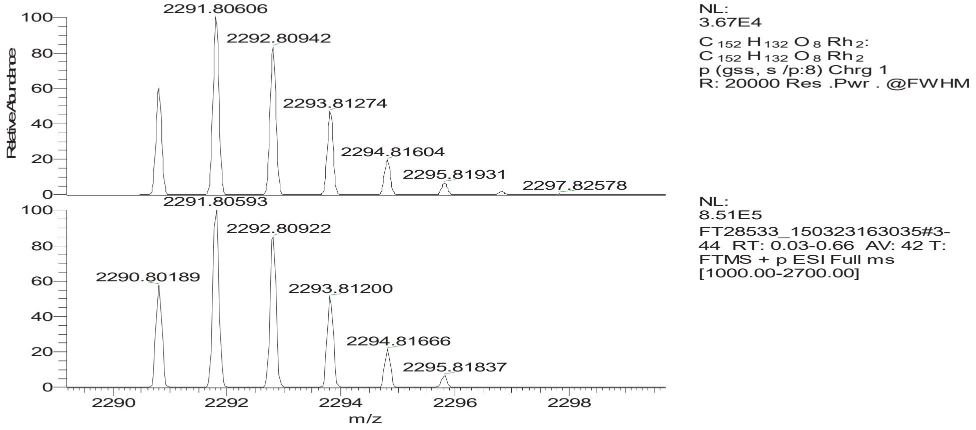
```
Elemental composition search on mass 2290.80189

m/z= 2285.80189-2295.80189
    m/z      | Theo. Mass | Delta   | RDB    |   Composition
             |            | (ppm)   | equiv. |
 2290.80189  | 2290.80268 |   -0.35 |   89.0 | C152 H132 O8 Rh2
```



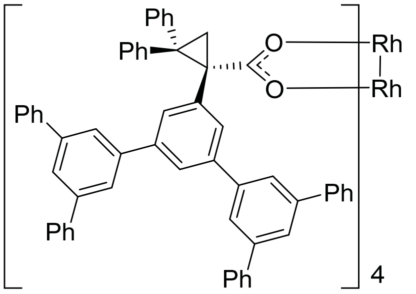






m/z	Intensity	Relative
1769.55253	58056.8	6.78
1770.55676	67757.4	7.91
2290.80189	488864.1	57.05
2291.80593	856914.6	100.00
2292.80922	745951.6	87.05

2293.81200	439347.9	51.27
2294.81666	182884.3	21.34
2295.81837	58774.5	6.86
2309.83795	81813.9	9.55
2310.84285	61449.6	7.17
2349.87137	108314.2	12.64
2350.87526	99618.9	11.63
2354.86188	61180.2	7.14
2355.86138	81278.1	9.48
2356.86103	58720.1	6.85
2381.89776	70012.3	8.17
2382.90201	55896.5	6.52
2407.91367	96803.4	11.30
2408.91623	100435.5	11.72
2409.92183	71792.4	8.38

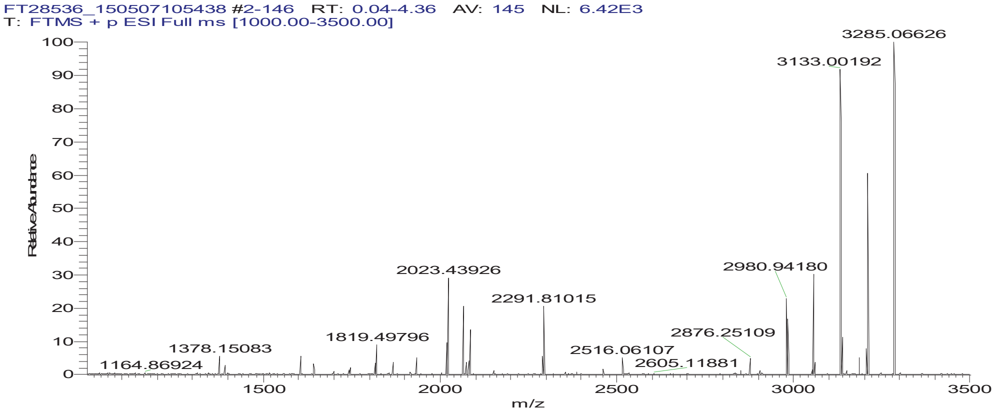


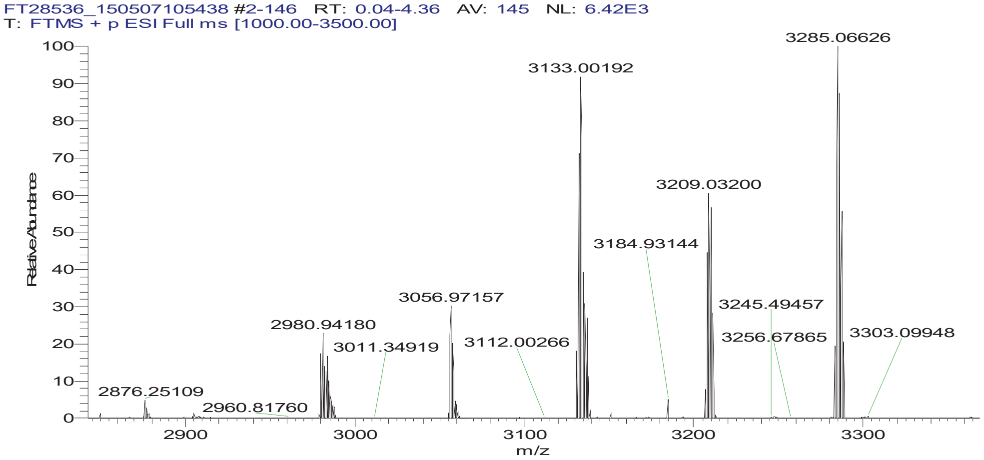
```
Elemental composition search on mass 3283.05980

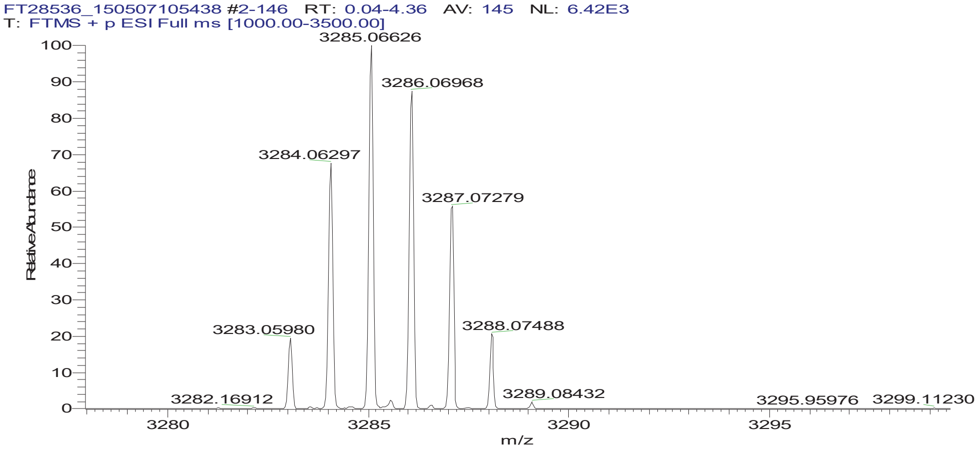
m/z=  3278.05980-3288.05980
     m/z       Theo. Mass   Delta     RDB      Composition
                            (mmu)   equiv.
 3283.05980   3283.05308     6.72    153.0  C 232 H 164 O 8 Rh 2
```

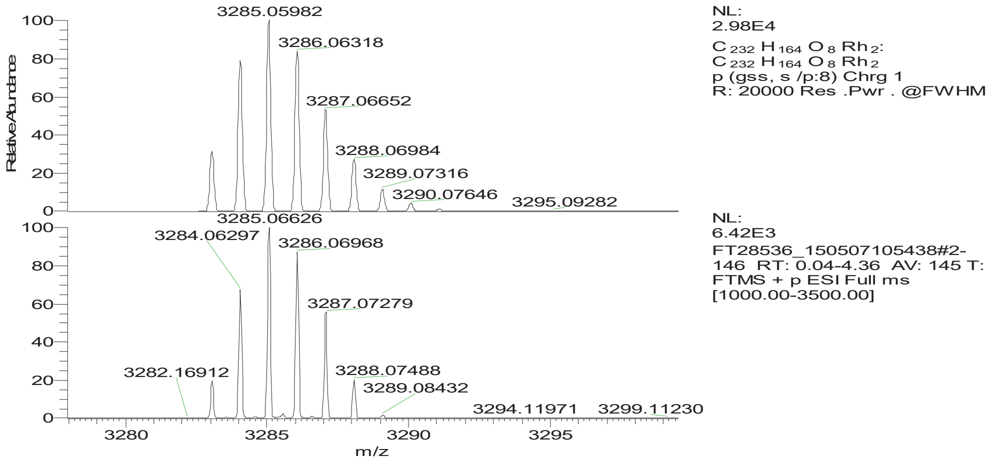
```
Elemental composition search on mass 3283.05980

m/z=  3278.05980-3288.05980
     m/z       Theo. Mass   Delta     RDB      Composition
                            (ppm)   equiv.
 3283.05980   3283.05308     2.05    153.0  C 232 H 164 O 8 Rh 2
```



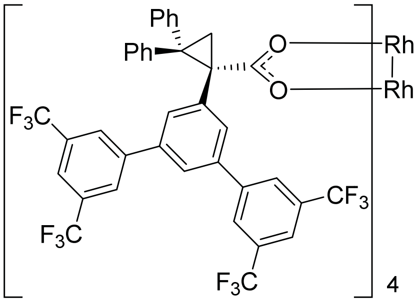






m/z Intensity Relative

2023.43926	1875.1	28.80
2980.94180	1496.7	22.99
3055.96677	1431.8	21.99
3056.97157	1954.7	30.02
3131.99860	4680.0	71.88
3133.00192	6017.6	92.42
3134.00612	4953.4	76.08
3134.88609	1544.4	23.72
3135.00927	2585.6	39.71
3135.87964	1994.4	30.63
3136.88005	1732.5	26.61
3208.02847	2863.7	43.98
3209.03200	3978.5	61.11
3210.03720	3671.4	56.39
3211.04127	1839.2	28.25
3284.06297	4376.1	67.21
3285.06626	6510.9	100.00
3286.06968	5745.0	88.24
3287.07279	3732.0	57.32
3288.07488	1361.4	20.91



Elemental composition search on mass 3154.34761

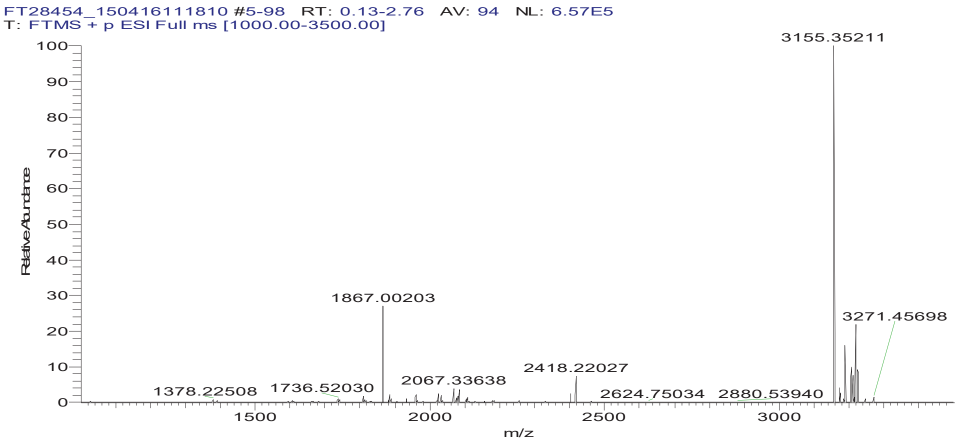
m/z= 3149.34761-3159.34761

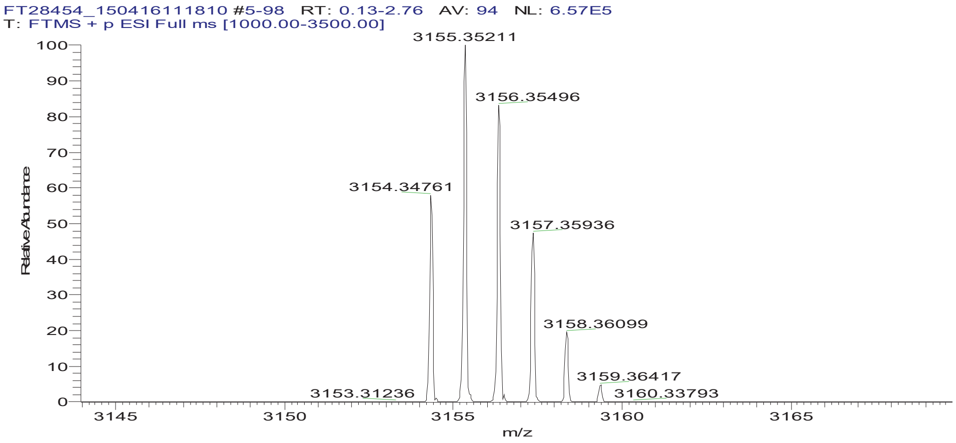
m/z	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
3154.34761	3154.35043	-2.82	89.0	$C_{152} H_{84} O_8 F_{48} Rh_2$

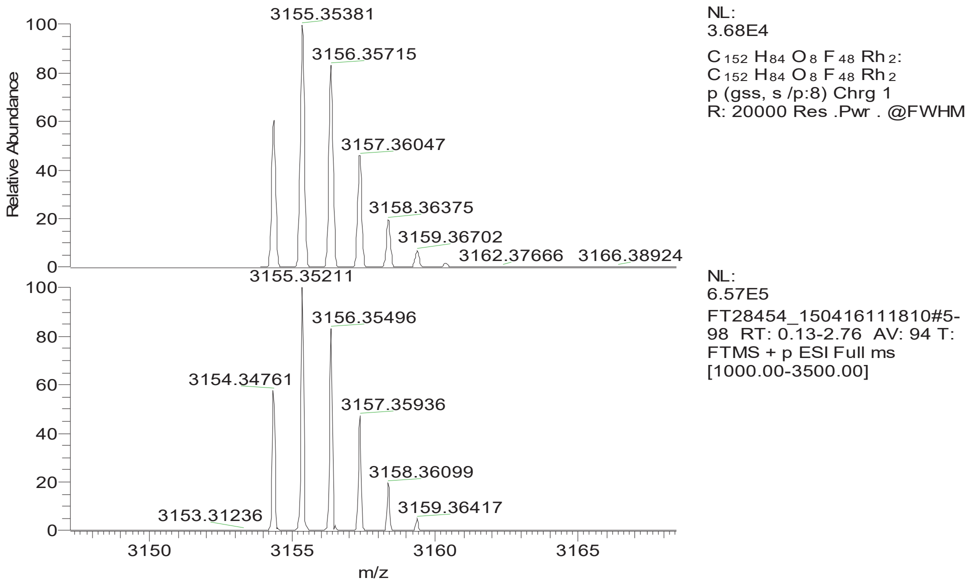
Elemental composition search on mass 3154.34761

m/z= 3149.34761-3159.34761

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
3154.34761	3154.35043	-0.89	89.0	$C_{152} H_{84} O_8 F_{48} Rh_2$

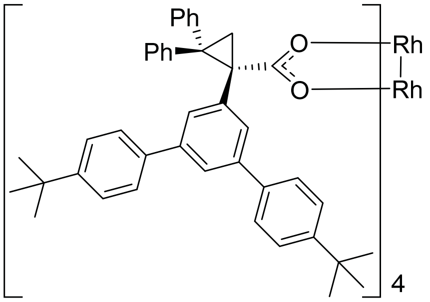






m/z	Intensity	Relative
1867.00203	179691.5	27.14
2418.22027	49653.8	7.50
3154.34761	384221.5	58.02
3155.35211	662198.9	100.00
3156.35496	555073.1	83.82
3157.35936	313540.3	47.35
3158.36099	129060.6	19.49
3186.37318	54909.0	8.29
3187.37690	104901.5	15.84
3188.38038	83243.6	12.57
3189.38567	43116.5	6.51

3205.41387	67808.0	10.24
3206.41980	48892.7	7.38
3210.36961	52387.2	7.91
3211.36909	43450.1	6.56
3218.40351	105345.9	15.91
3219.40499	147775.4	22.32
3220.40734	119608.8	18.06
3221.41148	61695.1	9.32
3226.34086	56899.2	8.59

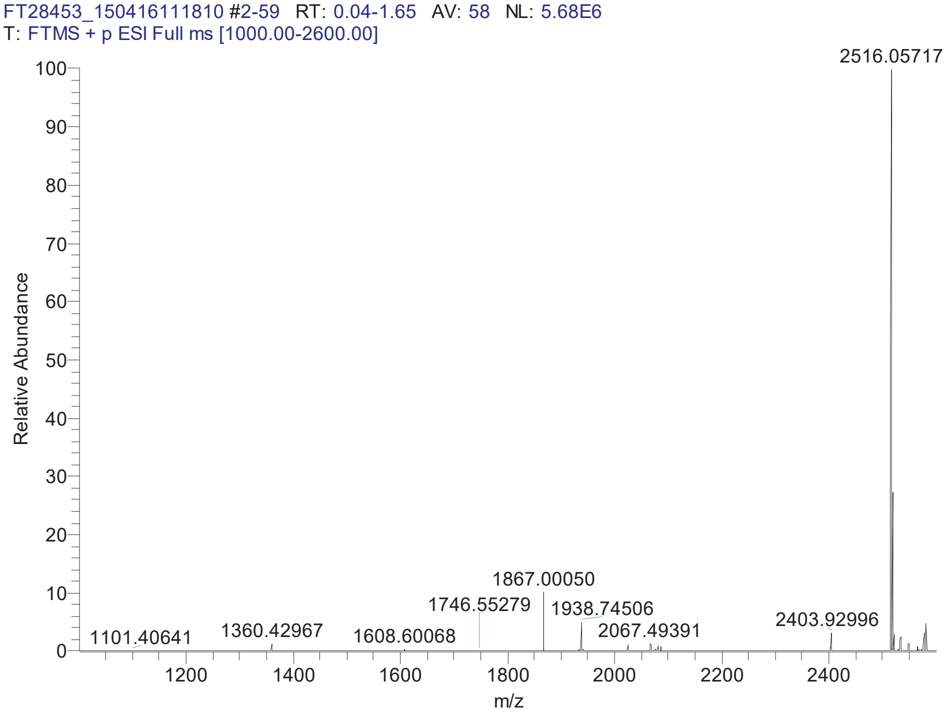


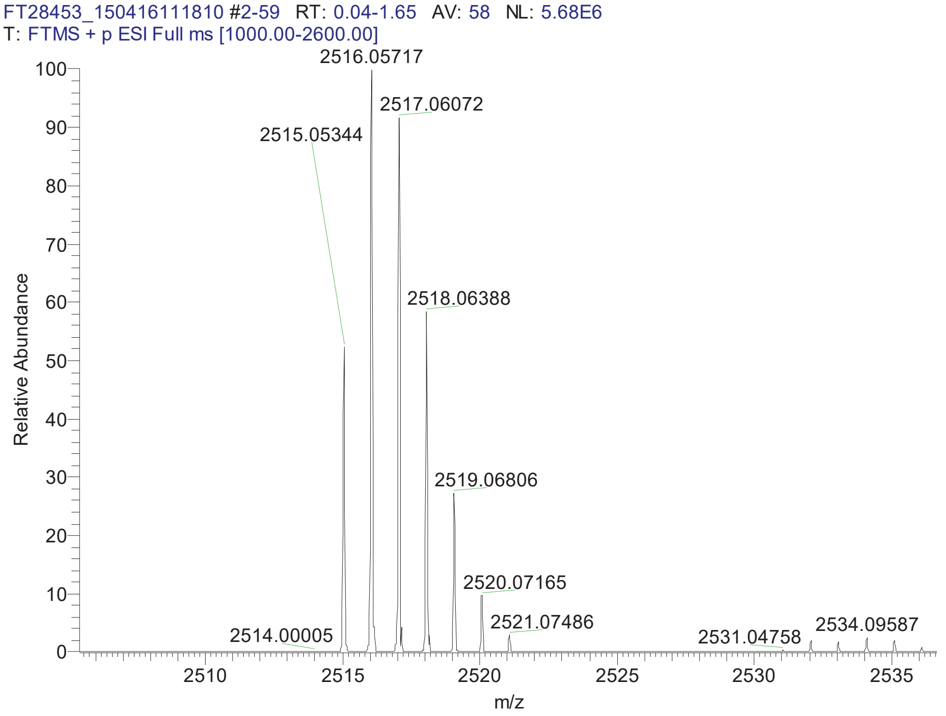
```
Elemental composition search on mass 2515.05344

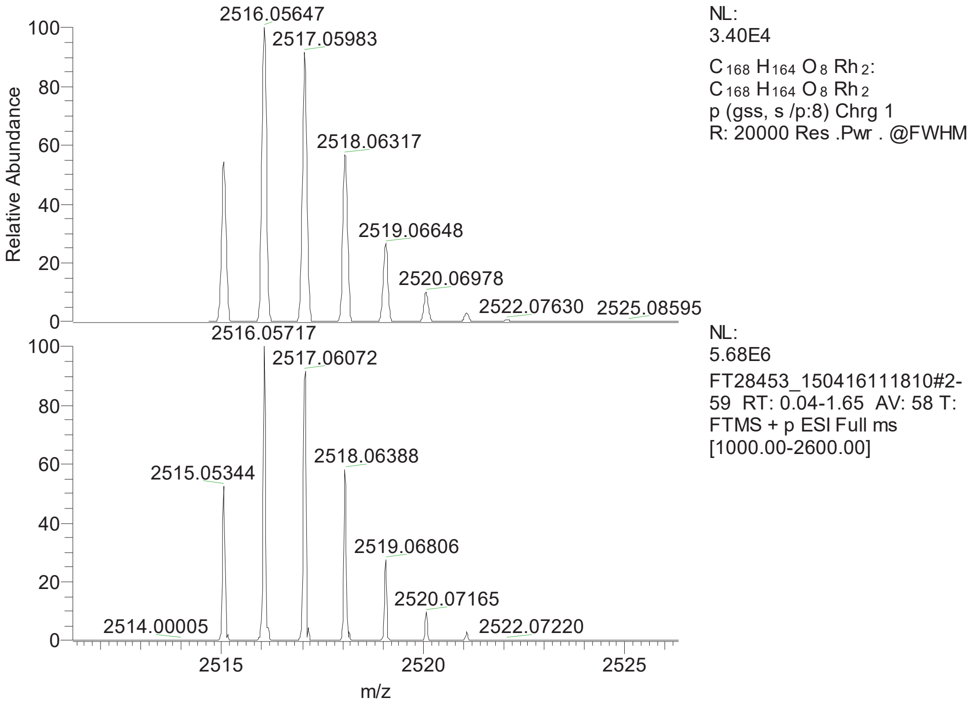
m/z= 2510.05344-2520.05344
    m/z       Theo. Mass   Delta      RDB        Composition
                           (mmu)     equiv.
 2515.05344   2515.05308     0.36      89.0  C 168 H 164 O 8 Rh 2
```

```
Elemental composition search on mass 2515.05344

m/z= 2510.05344-2520.05344
    m/z       Theo. Mass   Delta      RDB        Composition
                           (ppm)     equiv.
 2515.05344   2515.05308     0.14      89.0  C 168 H 164 O 8 Rh 2
```

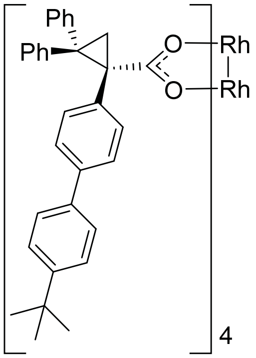

FT28453_150416111810 #2-59 RT: 0.04-1.65 AV: 58 NL: 5.68E6
T: FTMS + p ESI Full ms [1000.00-2600.00]
2516.05717
1867.00050
1746.55279
1938.74506
2067.49391
2403.92996
1101.40641
1360.42967
1608.60068
Relative Abundance
100
90
80
70
60
50
40
30
20
10
0
1200
1400
1600
1800
2000
2200
2400
m/z

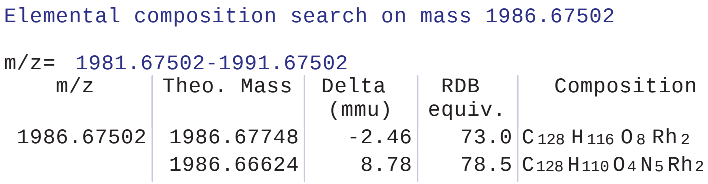

FT28453_150416111810 #2-59 RT: 0.04-1.65 AV: 58 NL: 5.68E6
T: FTMS + p ESI Full ms [1000.00-2600.00]
2516.05717
2517.06072
2515.05344
2518.06388
2519.06806
2520.07165
2521.07486
2514.00005
2531.04758
2534.09587
Relative Abundance
100
90
80
70
60
50
40
30
20
10
0
2510
2515
2520
2525
2530
2535
m/z



m/z	Intensity	Relative
1867.00050	577306.3	10.13
1937.73992	215131.6	3.78
1938.74506	292463.5	5.13
1939.74994	170802.3	3.00
2403.92996	175134.5	3.07
2404.93363	134827.3	2.37
2515.05344	2982963.8	52.35
2516.05717	5697734.0	100.00
2517.06072	5358020.5	94.04
2517.14995	258186.2	4.53
2518.06388	3348929.3	58.78
2518.15681	162663.9	2.85
2519.06806	1557678.1	27.34
2520.07165	574278.4	10.08
2521.07486	162481.1	2.85
2534.09587	144042.0	2.53
2535.09869	114857.8	2.02
2579.11095	177261.3	3.11
2580.11210	276901.2	4.86
2581.11322	206339.8	3.62

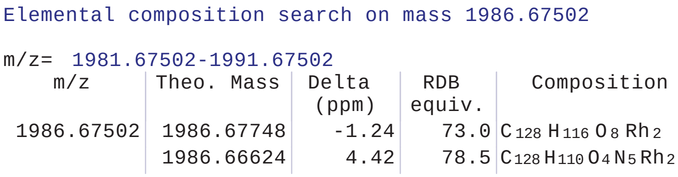
2.2 para-substituted catalyst





```
Elemental composition search on mass 1986.67502

m/z=  1981.67502-1991.67502
    m/z      | Theo. Mass | Delta   | RDB    |   Composition
             |            |  (mmu)  | equiv. |
 1986.67502  | 1986.67748 |   -2.46 |   73.0 | C128 H116 O8 Rh2
             | 1986.66624 |    8.78 |   78.5 | C128 H110 O4 N5 Rh2
```



```
Elemental composition search on mass 1986.67502

m/z=  1981.67502-1991.67502
    m/z     | Theo. Mass | Delta  | RDB    |   Composition
            |            | (ppm)  | equiv. |
 1986.67502 | 1986.67748 |  -1.24 |   73.0 | C128 H116 O8 Rh2
            | 1986.66624 |   4.42 |   78.5 | C128 H110 O4 N5 Rh2
```

```
Elemental composition search on mass 1854.58310

m/z= 1849.58310-1859.58310
    m/z     | Theo. Mass | Delta  | RDB   |   Composition
            |            | (mmu)  | equiv.|
 1854.58310 | 1854.58358 |  -0.48 |  69.0 | C118 H104 O8 Rh2
            | 1854.57771 |   5.39 |  78.0 | C125 H100 O3 Rh2
```

```
Elemental composition search on mass 1854.58310

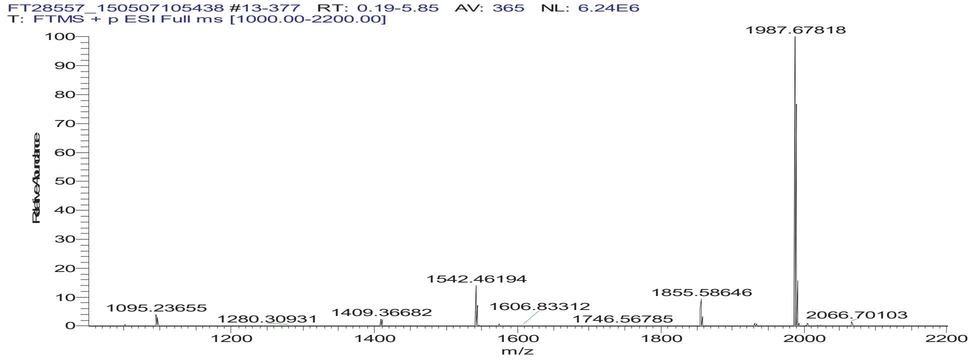
m/z= 1849.58310-1859.58310
    m/z     | Theo. Mass | Delta  | RDB   |   Composition
            |            | (ppm)  | equiv.|
 1854.58310 | 1854.58358 |  -0.26 |  69.0 | C118 H104 O8 Rh2
            | 1854.57771 |   2.91 |  78.0 | C125 H100 O3 Rh2
```

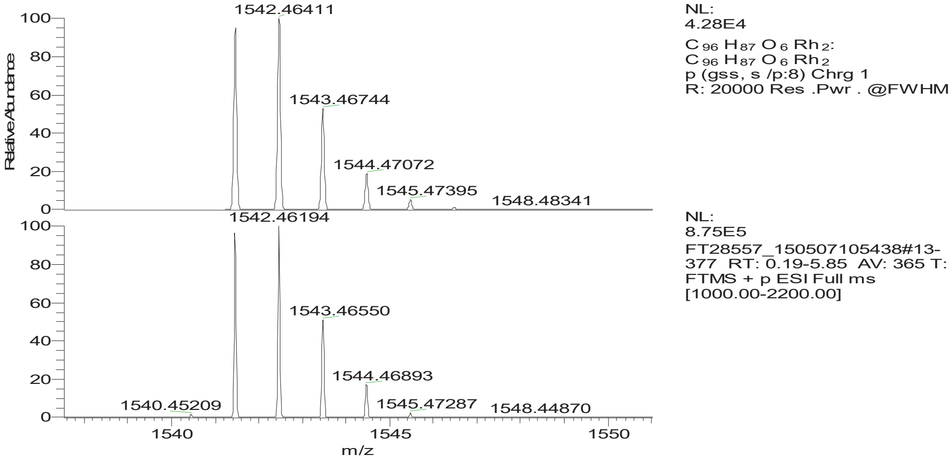
```
Elemental composition search on mass 1541.45864

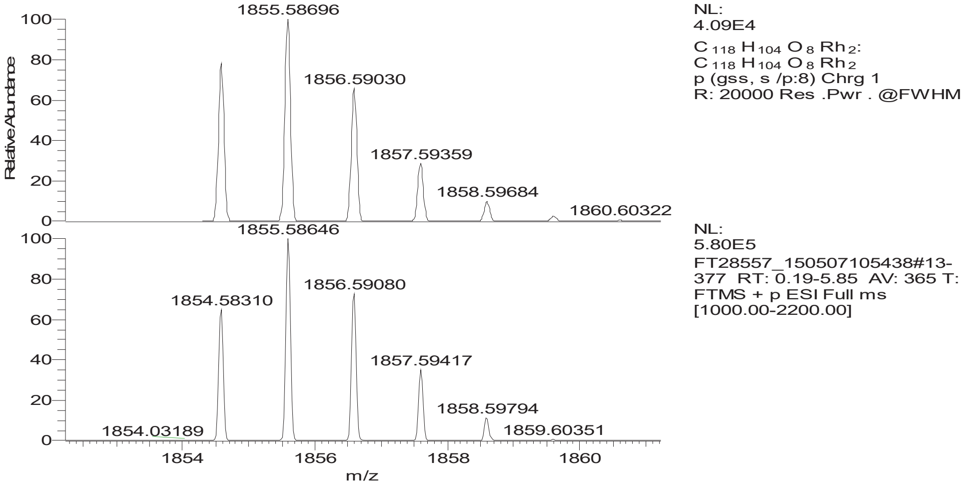
m/z= 1536.45864-1546.45864
    m/z     | Theo. Mass | Delta  | RDB   |   Composition
            |            | (mmu)  | equiv.|
 1541.45864 | 1541.46072 |  -2.08 |  55.5 | C96 H87 O6 Rh2
            | 1541.45485 |   3.79 |  64.5 | C103 H83 O Rh2
```

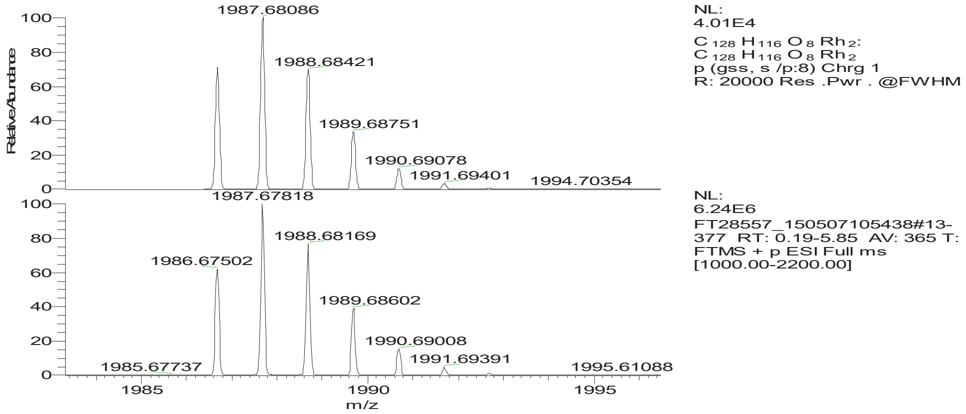
```
Elemental composition search on mass 1541.45864

m/z= 1536.45864-1546.45864
    m/z       Theo. Mass    Delta      RDB       Composition
                            (ppm)     equiv.
 1541.45864  1541.46072     -1.35      55.5  C96 H87 O6 Rh2
             1541.45485      2.46      64.5  C103 H83 O Rh2
```



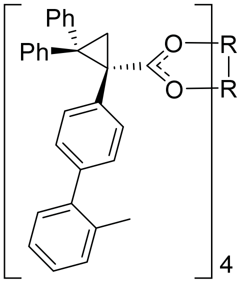






m/z	Intensity	Relative
1095.23655	256198.7	4.10
1096.24053	193485.0	3.09
1409.36682	147069.2	2.35
1410.37002	140586.1	2.25
1541.45864	848433.1	13.56
1542.46194	886502.6	14.17
1543.46550	460015.0	7.35
1544.46893	155616.9	2.49
1854.58310	383653.8	6.13
1855.58646	582176.0	9.31
1856.59080	430619.2	6.88
1857.59417	204721.8	3.27
1986.67502	3905512.3	62.44
1987.67818	6254829.0	100.00
1988.68169	4880430.0	78.03
1989.68602	2514232.8	40.20
1990.69008	985243.6	15.75

1991.69391	296299.0	4.74
2065.69518	80447.8	1.29
2066.70103	94709.6	1.51



Elemental composition search on mass 1818.49033

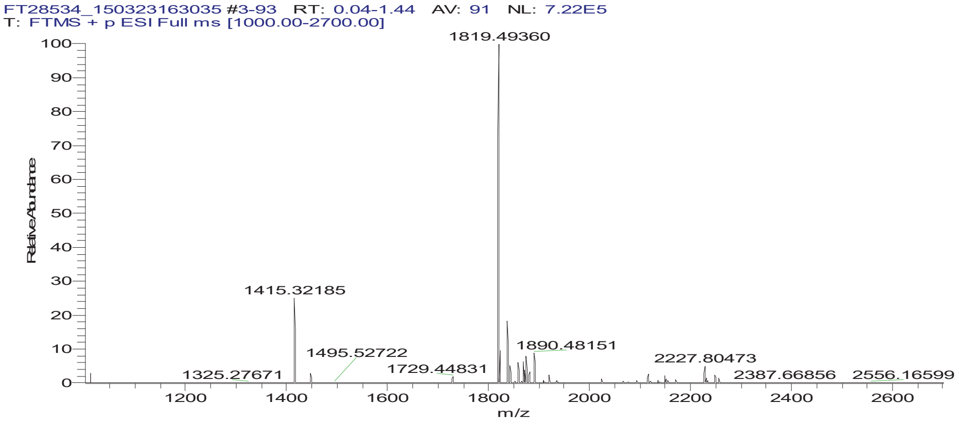
m/z= 1813.49033-1823.49033

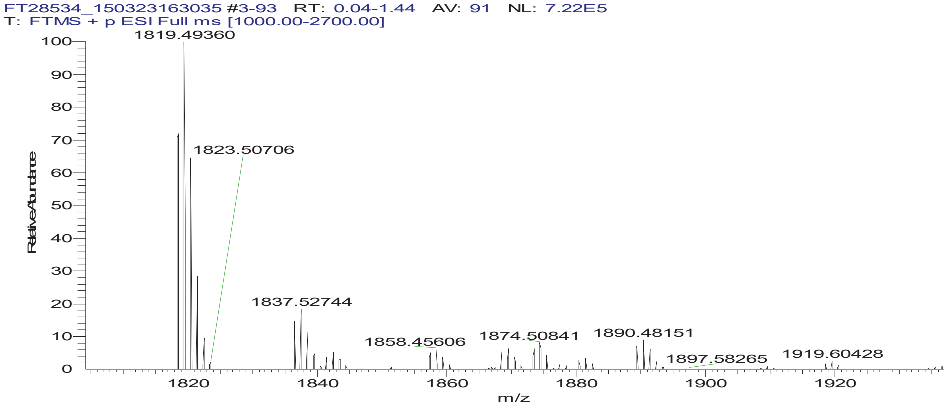
m/z	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
1818.49033	1818.48968	0.65	73.0	$C_{116}H_{92}O_8Rh_2$

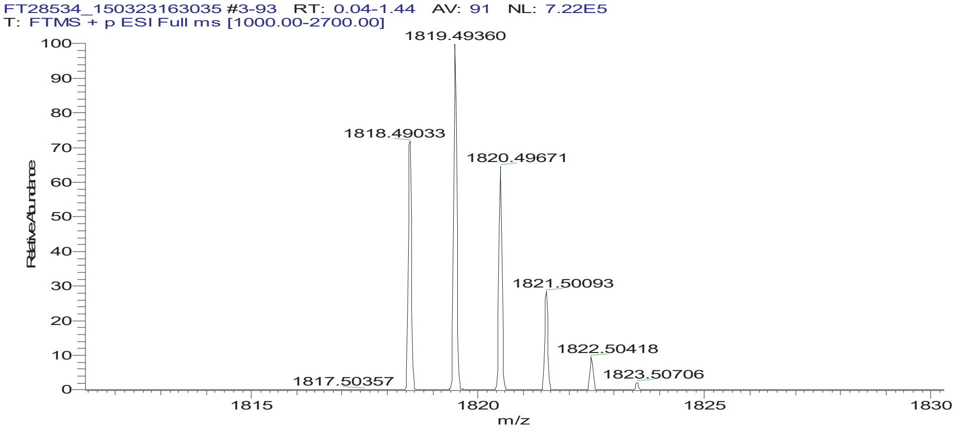
Elemental composition search on mass 1818.49033

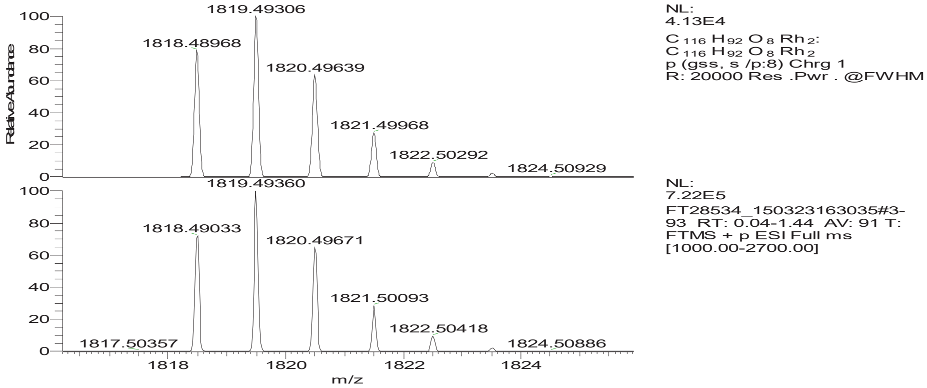
m/z= 1813.49033-1823.49033

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1818.49033	1818.48968	0.36	73.0	$C_{116}H_{92}O_8Rh_2$



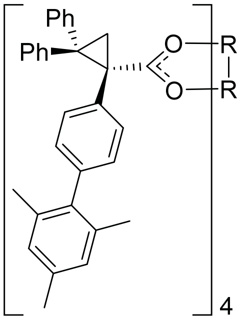






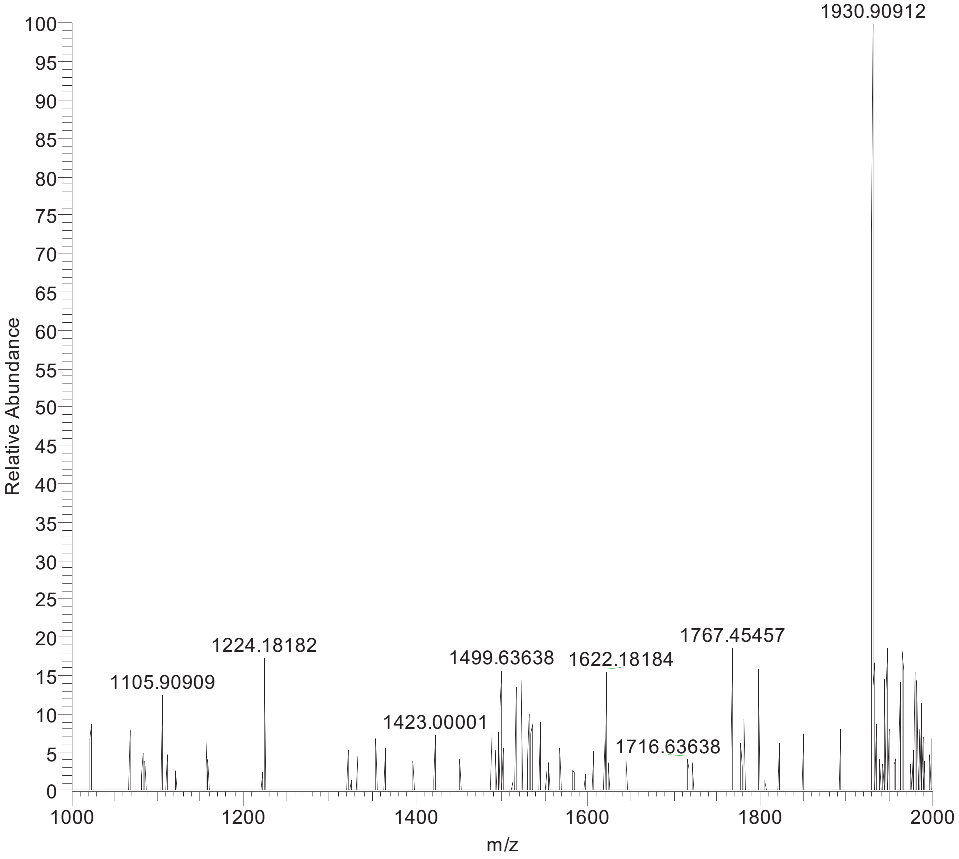
m/z	Intensity	Relative
1415.32185	182659.1	25.31
1416.32566	172910.1	23.96
1417.32908	79739.7	11.05
1818.49033	535442.6	74.19
1819.49360	721756.3	100.00
1820.49671	474936.8	65.80
1821.50093	208089.0	28.83

1822.50418	69043.0	9.57
1836.52476	106672.3	14.78
1837.52744	133251.0	18.46
1838.53102	84470.6	11.70
1842.48271	37866.2	5.25
1858.45606	45282.7	6.27
1868.54943	39101.1	5.42
1869.55373	45286.0	6.27
1873.50420	43179.2	5.98
1874.50841	56599.4	7.84
1889.47812	51155.5	7.09
1890.48151	64857.7	8.99
1891.48374	44591.0	6.18

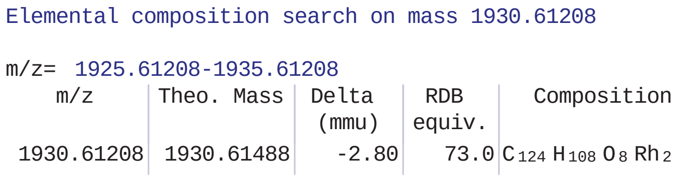


Ion Trap

FT31957_170119095924 #4-14 RT: 0.02-0.09 AV: 11 NL: 1.49E1
T: ITMS + p ESI Full ms [1000.00-2000.00]

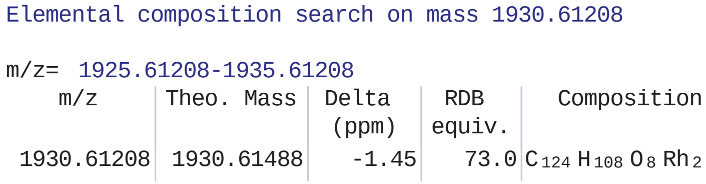


FTMS



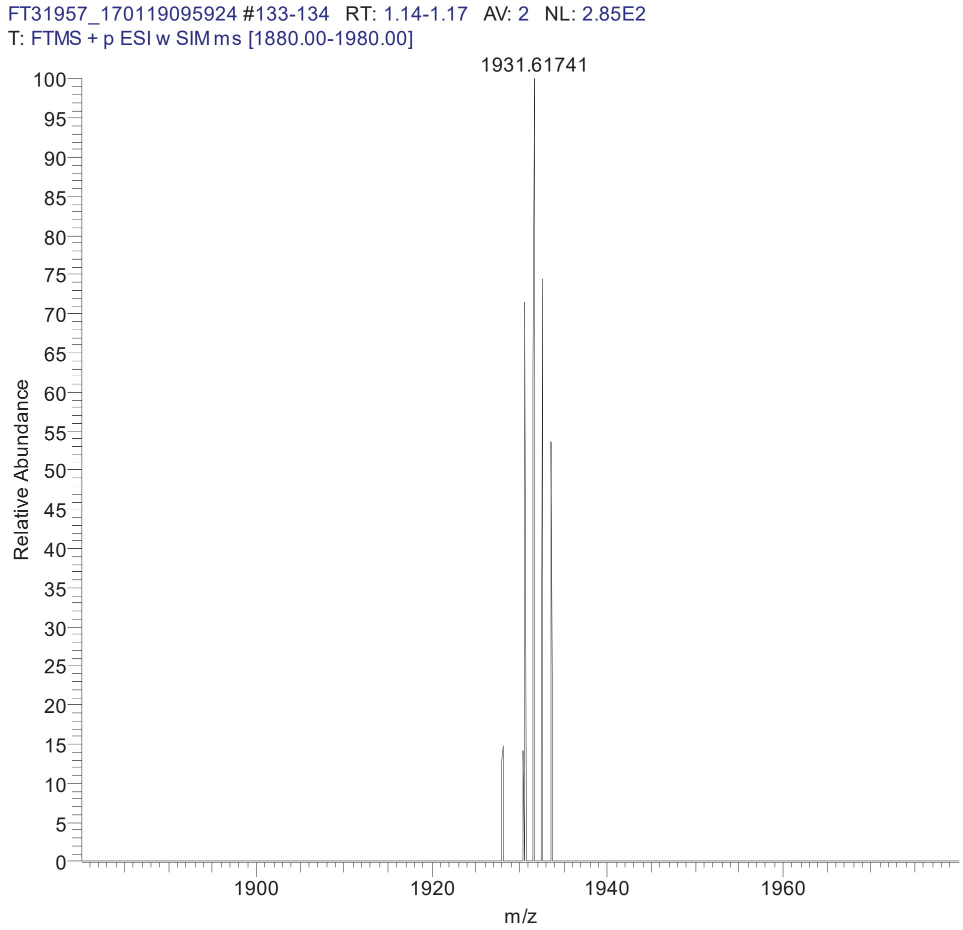
```
Elemental composition search on mass 1930.61208

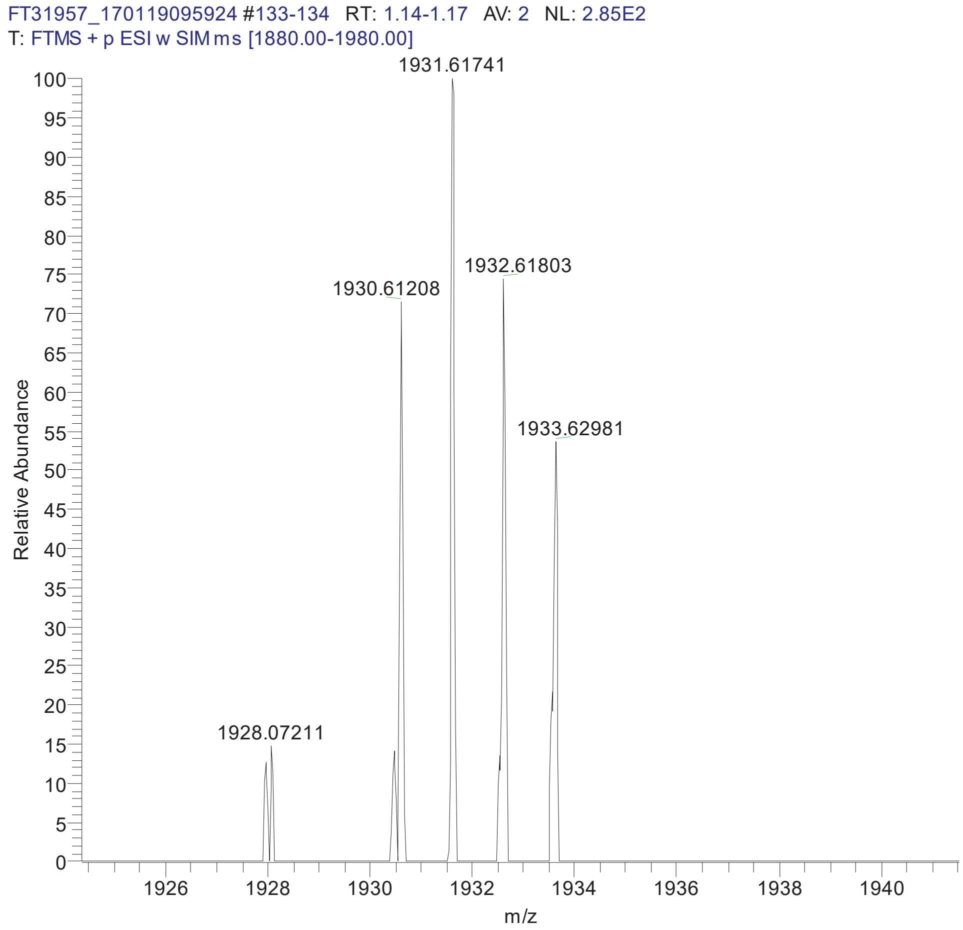
m/z= 1925.61208-1935.61208
    m/z     | Theo. Mass | Delta  |  RDB   |   Composition
            |            | (mmu)  | equiv. |
 1930.61208 | 1930.61488 |  -2.80 |   73.0 | C124 H108 O8 Rh2
```

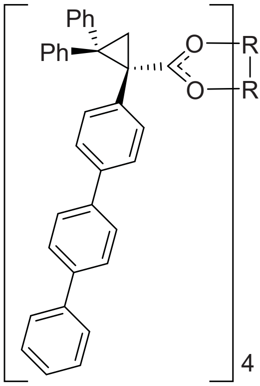


```
Elemental composition search on mass 1930.61208

m/z= 1925.61208-1935.61208
    m/z     | Theo. Mass | Delta  |  RDB   |   Composition
            |            | (ppm)  | equiv. |
 1930.61208 | 1930.61488 |  -1.45 |   73.0 | C124 H108 O8 Rh2
```


FT31957_170119095924 #133-134 RT: 1.14-1.17 AV: 2 NL: 2.85E2
T: FTMS + p ESI w SIM ms [1880.00-1980.00]
1931.61741
Relative Abundance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
1900
1920
1940
1960
m/z


FT31957_170119095924 #133-134 RT: 1.14-1.17 AV: 2 NL: 2.85E2
T: FTMS + p ESI w SIM ms [1880.00-1980.00]
1931.61741
1930.61208
1932.61803
1933.62981
1928.07211
Relative Abundance
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
1926
1928
1930
1932
1934
1936
1938
1940
m/z



Elemental composition search on mass 2066.54704

m/z= 2061.54704-2071.54704

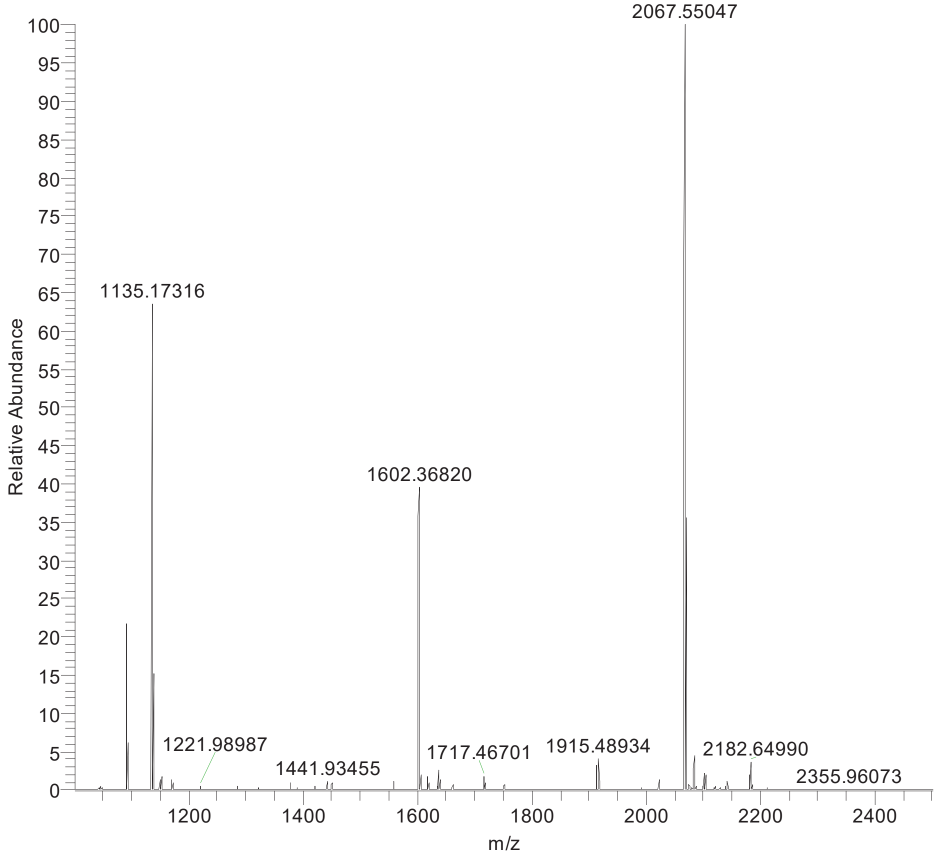
m/z	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
2066.54704	2066.55228	-5.24	89.0	$C_{136}H_{100}O_8Rh_2$
	2066.54104	6.00	94.5	$C_{136}H_{94}O_4N_5Rh_2$
	2066.52980	17.24	100.0	$C_{136}H_{88}N_{10}Rh_2$
	2066.56485	-17.81	94.0	$C_{136}H_{96}O_3N_6Rh_2$

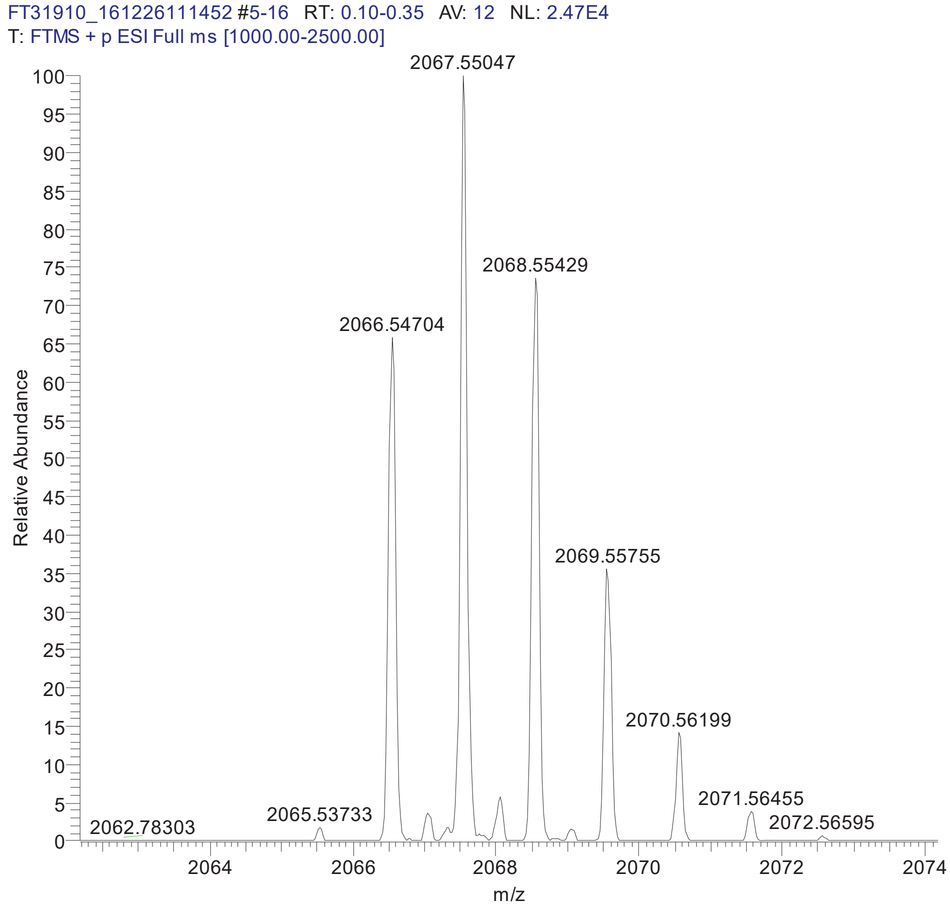
Elemental composition search on mass 2066.54704

m/z= 2061.54704-2071.54704

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
2066.54704	2066.55228	-2.54	89.0	$C_{136}H_{100}O_8Rh_2$
	2066.54104	2.90	94.5	$C_{136}H_{94}O_4N_5Rh_2$
	2066.52980	8.34	100.0	$C_{136}H_{88}N_{10}Rh_2$
	2066.56485	-8.62	94.0	$C_{136}H_{96}O_3N_6Rh_2$

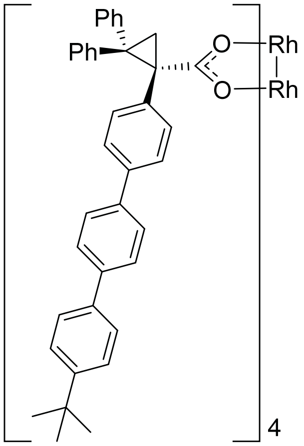
FT31910_161226111452 #5-16 RT: 0.10-0.35 AV: 12 NL: 2.47E4
T: FTMS + p ESI Full ms [1000.00-2500.00]

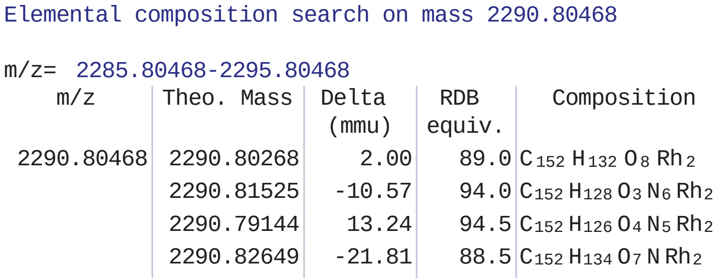




m/z	Intensity	Relative
1091.18341	5339.6	21.32
1092.18703	4174.4	16.67
1093.19100	1505.9	6.01
1135.17316	15699.0	62.68
1136.17710	13475.1	53.80
1137.18456	7083.3	28.28
1138.19131	3883.9	15.51
1139.19536	1205.0	4.81
1601.36498	9035.2	36.07
1602.36820	10052.6	40.14
1603.37173	5828.1	23.27
1604.37555	2182.0	8.71
1915.48934	1018.4	4.07
2066.54704	16394.0	65.45
2067.55047	25046.3	100.00
2068.05466	1421.3	5.67
2068.55429	18529.0	73.98

2069.55755	8927.3	35.64
2070.56199	3541.1	14.14
2083.54721	1123.6	4.49



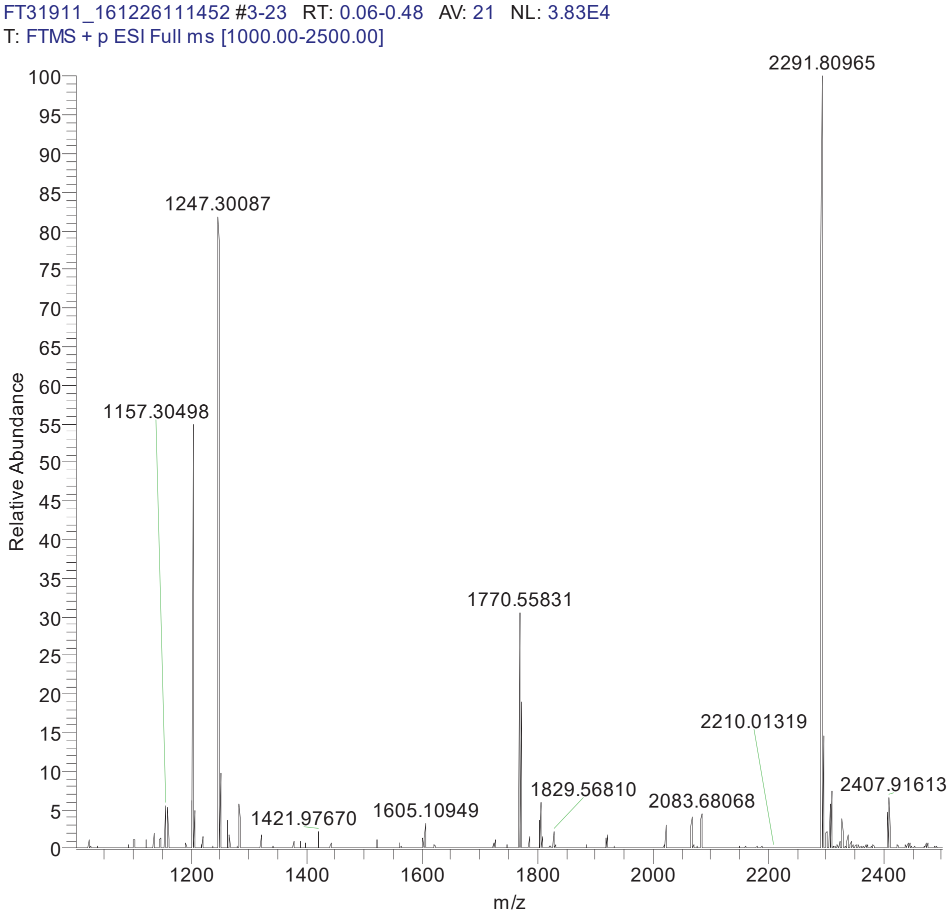


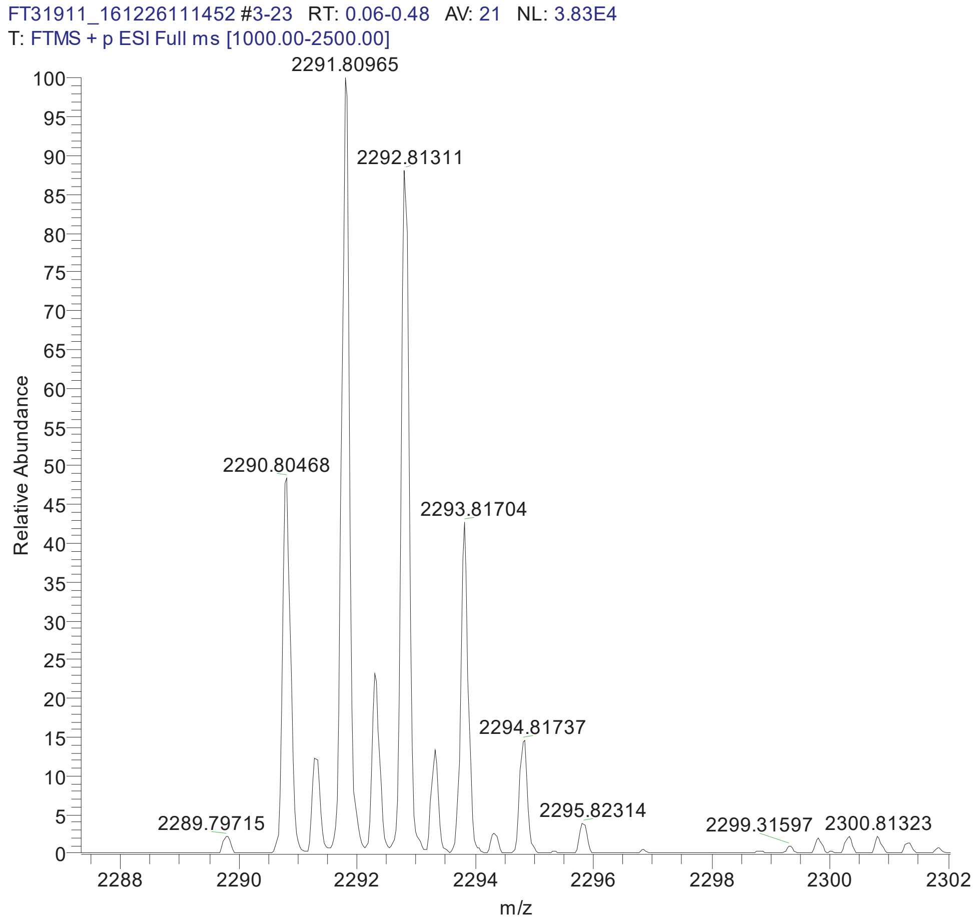
```
Elemental composition search on mass 2290.80468

m/z=  2285.80468-2295.80468
    m/z     | Theo. Mass | Delta  |  RDB   |    Composition
            |            | (mmu)  | equiv. |
 2290.80468 | 2290.80268 |   2.00 |   89.0 | C152 H132 O8 Rh2
            | 2290.81525 | -10.57 |   94.0 | C152 H128 O3 N6 Rh2
            | 2290.79144 |  13.24 |   94.5 | C152 H126 O4 N5 Rh2
            | 2290.82649 | -21.81 |   88.5 | C152 H134 O7 N Rh2
```

```
Elemental composition search on mass 2290.80468

m/z= 2285.80468-2295.80468
    m/z      Theo. Mass   Delta     RDB       Composition
                          (ppm)    equiv.
 2290.80468  2290.80268    0.87     89.0 C152 H132 O8 Rh2
             2290.81525   -4.61     94.0 C152 H128 O3 N6 Rh2
             2290.79144    5.78     94.5 C152 H126 O4 N5 Rh2
             2290.82649   -9.52     88.5 C152 H134 O7 N Rh2
```

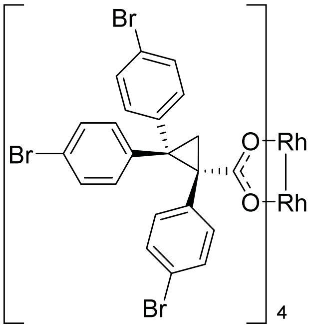




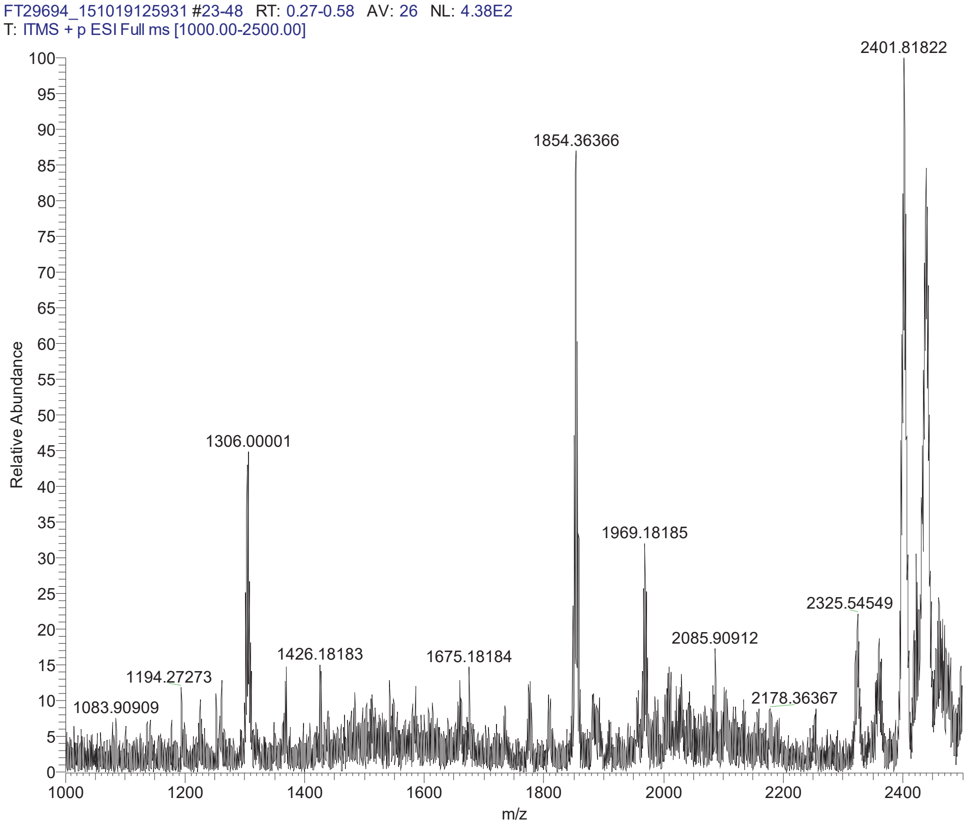
m/z	Intensity	Relative
1203.30984	21177.9	54.20
1204.31394	17280.2	44.22
1205.31719	7949.0	20.34
1247.30087	31347.7	80.22
1248.30473	30244.4	77.40
1249.31320	21153.3	54.13
1250.31803	11236.0	28.75
1251.32140	3832.0	9.81
1769.55512	9642.6	24.68
1770.55831	11703.1	29.95
1771.56056	7301.7	18.69
2290.80468	18992.0	48.60
2291.30682	4830.2	12.36
2291.80965	39077.0	100.00
2292.31311	8994.7	23.02
2292.81311	33844.1	86.61
2293.31565	5077.6	12.99

2293.81704	16357.7	41.86
2294.81737	5724.6	14.65
2308.80828	2892.1	7.40

2.3 tris para-substituted catalyst



Ion trap



FTMS

Elemental composition search on mass 2399.22453

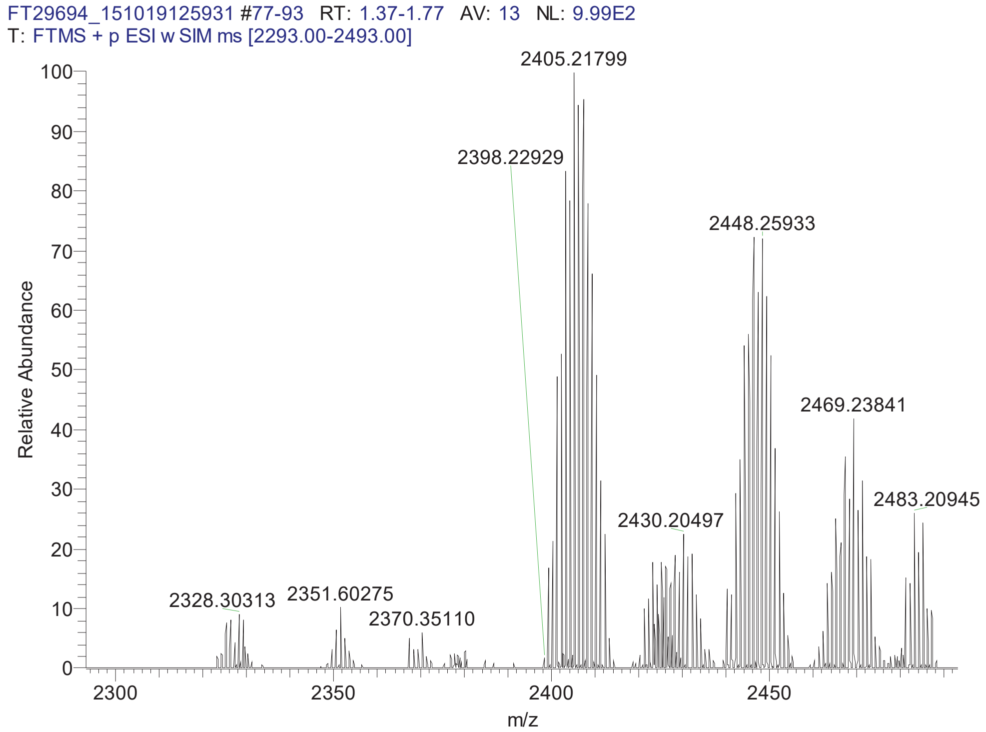
m/z= 2394.22453-2404.22453

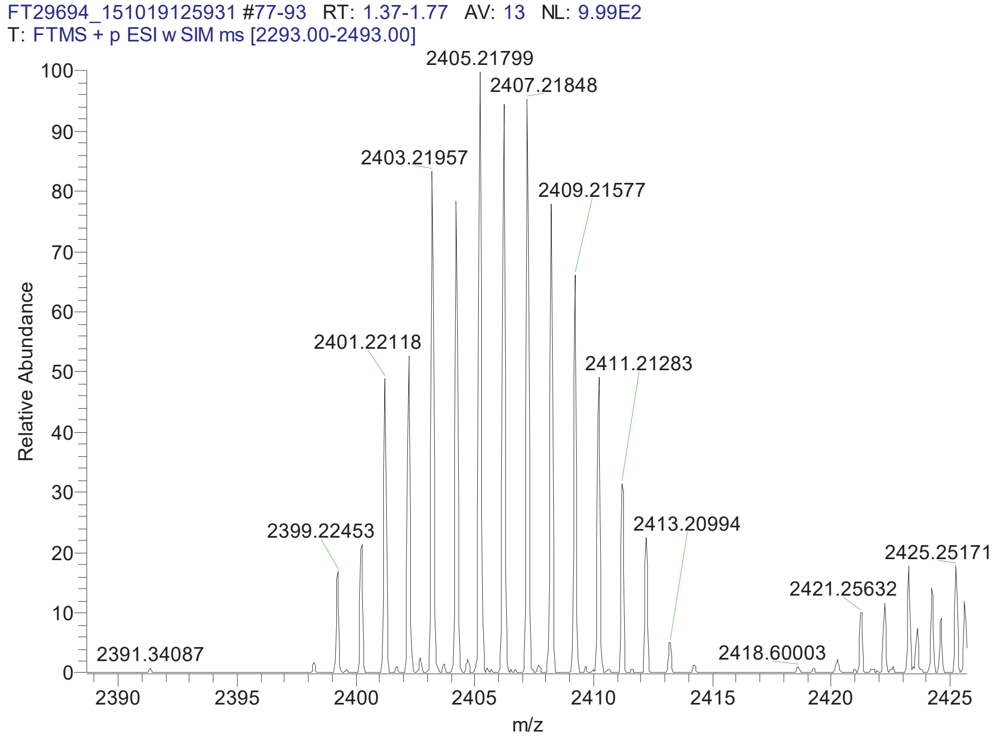
m/z	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
2399.22453	2399.22358	0.95	60.5	$C_{90}H_{54}O_{6}NBr_{11}{}^{81}BrRh_{2}$
	2399.22677	-2.24	47.0	$C_{80}H_{60}O_{14}Br_{11}{}^{81}BrRh_{2}$
	2399.22090	3.63	56.0	$C_{87}H_{56}O_{9}Br_{11}{}^{81}BrRh_{2}$
	2399.22945	-4.92	51.5	$C_{83}H_{58}O_{11}NBr_{11}{}^{81}BrRh_{2}$
	2399.23028	-5.75	69.0	$C_{98}H_{52}OBr_{11}{}^{81}BrRh_{2}$
	2399.21770	6.83	69.5	$C_{97}H_{50}ONBr_{11}{}^{81}BrRh_{2}$
	2399.21502	9.51	65.0	$C_{94}H_{52}O_{4}Br_{11}{}^{81}BrRh_{2}$
	2399.23615	-11.62	60.0	$C_{91}H_{56}O_{6}Br_{11}{}^{81}BrRh_{2}$
	2399.23883	-14.30	64.5	$C_{94}H_{54}O_{3}NBr_{11}{}^{81}BrRh_{2}$
	2399.20832	16.21	56.5	$C_{86}H_{54}O_{9}NBr_{11}{}^{81}BrRh_{2}$

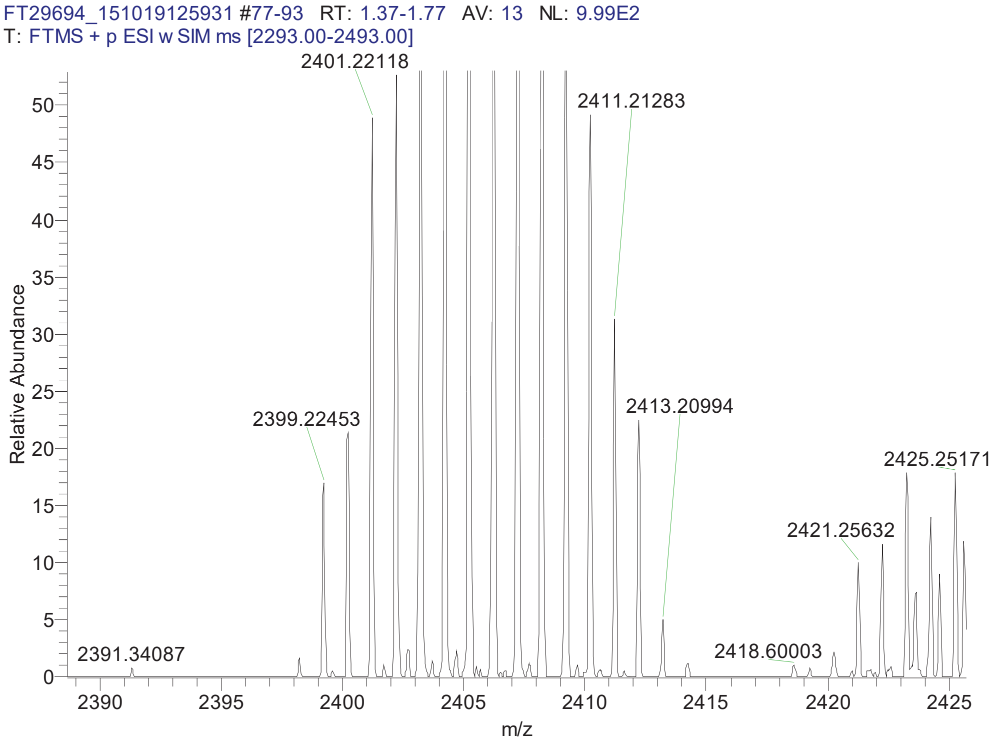
Elemental composition search on mass 2399.22453

m/z= 2394.22453-2404.22453

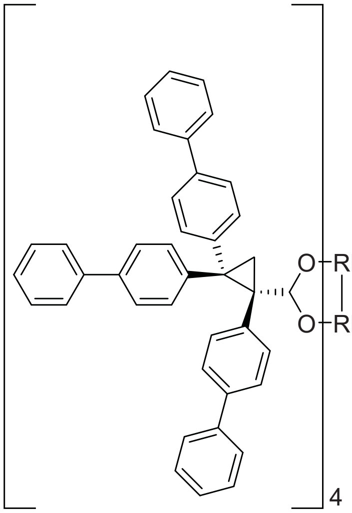
m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
2399.22453	2399.22358	0.40	60.5	$C_{90}H_{54}O_{6}NBr_{11}{}^{81}BrRh_{2}$
	2399.22677	-0.93	47.0	$C_{80}H_{60}O_{14}Br_{11}{}^{81}BrRh_{2}$
	2399.22090	1.51	56.0	$C_{87}H_{56}O_{9}Br_{11}{}^{81}BrRh_{2}$
	2399.22945	-2.05	51.5	$C_{83}H_{58}O_{11}NBr_{11}{}^{81}BrRh_{2}$
	2399.23028	-2.40	69.0	$C_{98}H_{52}OBr_{11}{}^{81}BrRh_{2}$
	2399.21770	2.84	69.5	$C_{97}H_{50}ONBr_{11}{}^{81}BrRh_{2}$
	2399.21502	3.96	65.0	$C_{94}H_{52}O_{4}Br_{11}{}^{81}BrRh_{2}$
	2399.23615	-4.84	60.0	$C_{91}H_{56}O_{6}Br_{11}{}^{81}BrRh_{2}$
	2399.23883	-5.96	64.5	$C_{94}H_{54}O_{3}NBr_{11}{}^{81}BrRh_{2}$
	2399.20832	6.76	56.5	$C_{86}H_{54}O_{9}NBr_{11}{}^{81}BrRh_{2}$

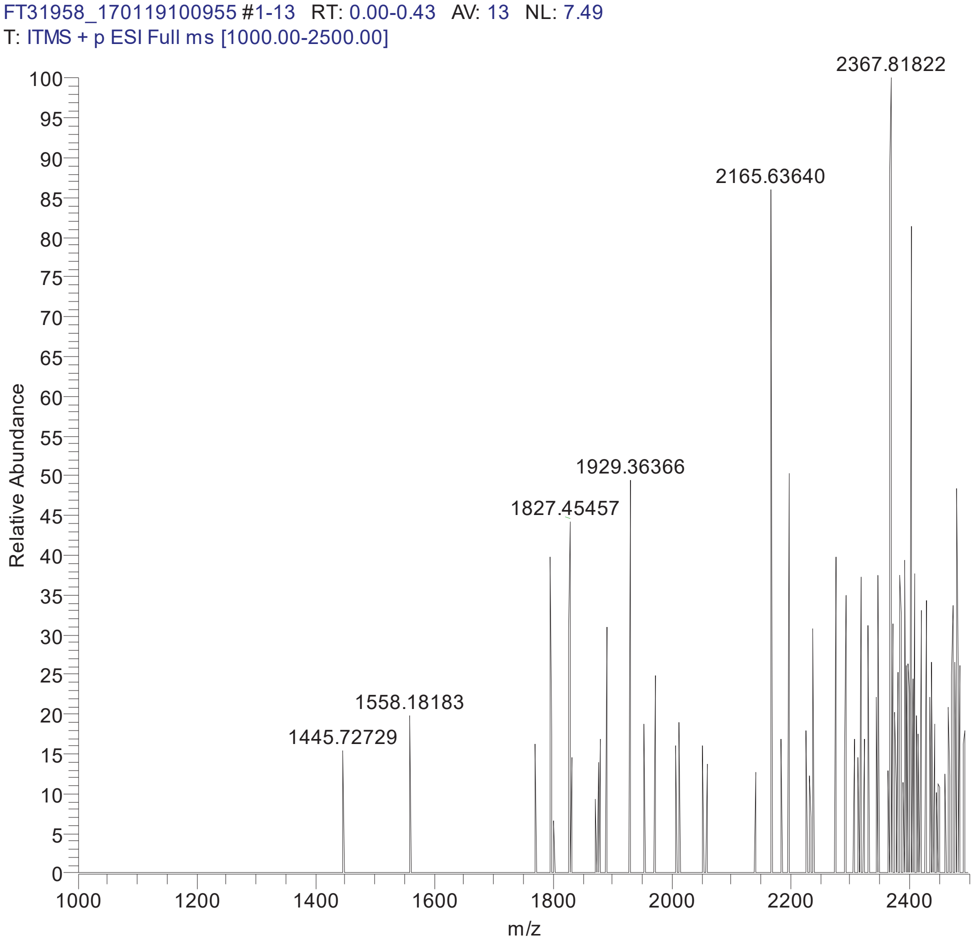

FT29694_151019125931 #77-93 RT: 1.37-1.77 AV: 13 NL: 9.99E2
T: FTMS + p ESI w SIM ms [2293.00-2493.00]
2405.21799
2398.22929
2448.25933
2469.23841
2483.20945
2430.20497
2328.30313
2351.60275
2370.35110
Relative Abundance
0
10
20
30
40
50
60
70
80
90
100
2300
2350
2400
2450
m/z


FT29694_151019125931 #77-93 RT: 1.37-1.77 AV: 13 NL: 9.99E2
T: FTMS + p ESI w SIM ms [2293.00-2493.00]
2405.21799
2407.21848
2403.21957
2409.21577
2401.22118
2411.21283
2399.22453
2413.20994
2425.25171
2421.25632
2391.34087
2418.60003
Relative Abundance
0
10
20
30
40
50
60
70
80
90
100
2390
2395
2400
2405
2410
2415
2420
2425
m/z

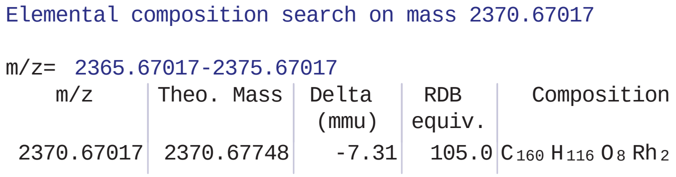


m/z	Intensity	Relative
2401.22118	499.3	48.24
2402.22159	529.6	51.16
2403.21957	833.9	80.56
2404.22188	788.0	76.12
2405.21799	1035.1	100.00
2406.21872	950.5	91.82
2407.21848	952.9	92.06
2408.21815	800.5	77.33
2409.21577	665.8	64.32
2410.21595	492.8	47.61
2444.26709	547.3	52.87
2445.26518	560.8	54.18
2446.16914	400.7	38.71
2446.26523	725.6	70.10
2447.26485	648.9	62.68
2448.25933	728.0	70.32
2449.26240	622.3	60.12
2450.25927	535.1	51.70
2451.25788	377.9	36.51
2469.23841	433.0	41.83


O
Rh
O
Rh
4

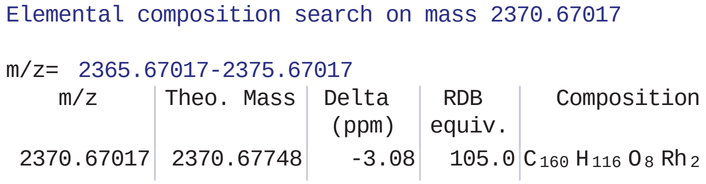

FT31958_170119100955 #1-13 RT: 0.00-0.43 AV: 13 NL: 7.49
T: ITMS + p ESI Full ms [1000.00-2500.00]
2367.81822
2165.63640
1929.36366
1827.45457
1558.18183
1445.72729
Relative Abundance
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
1000
1200
1400
1600
1800
2000
2200
2400
m/z

FTMS



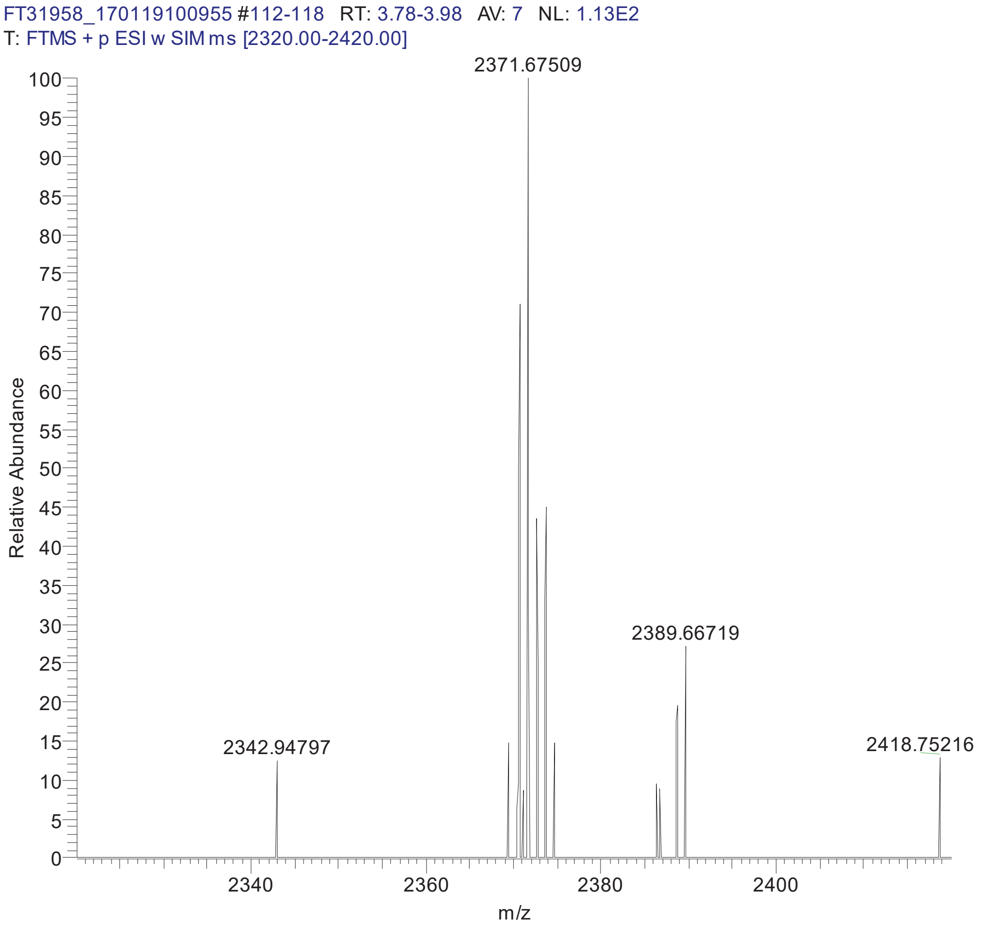
```
Elemental composition search on mass 2370.67017

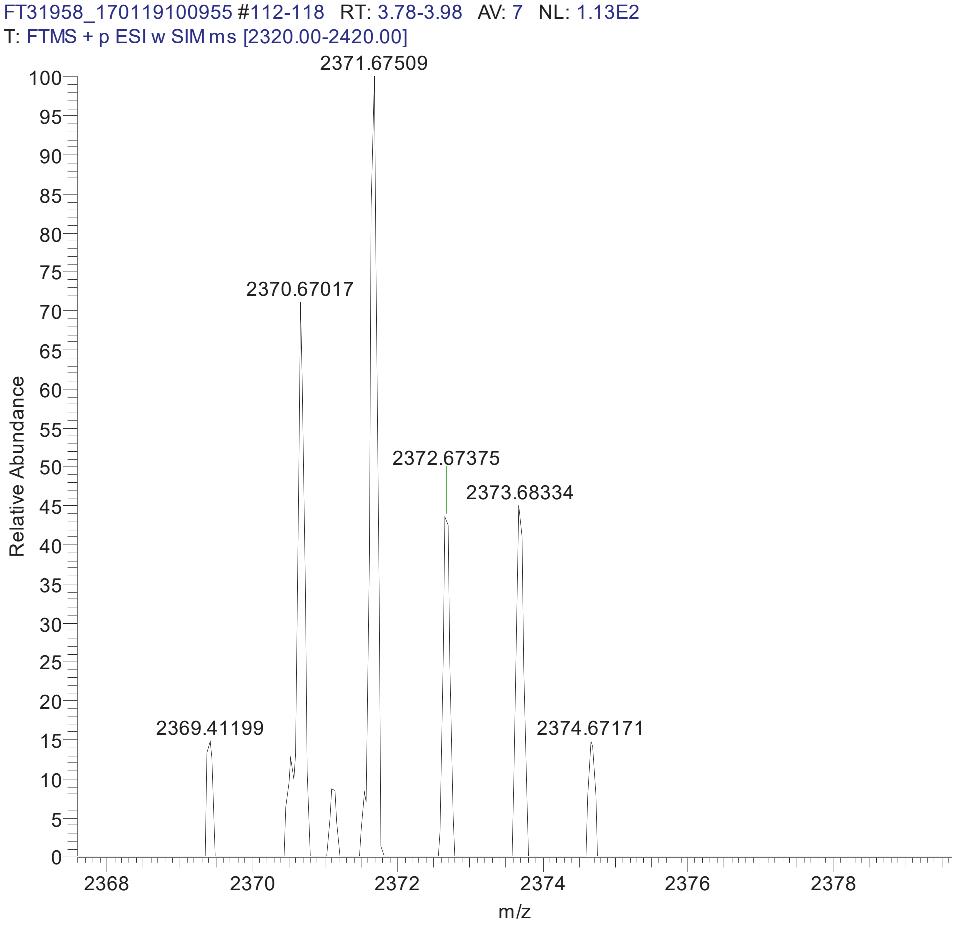
m/z= 2365.67017-2375.67017
    m/z     | Theo. Mass | Delta  | RDB   |  Composition
            |            | (mmu)  |equiv. |
 2370.67017 | 2370.67748 |  -7.31 |  105.0| C160 H116 O8 Rh2
```

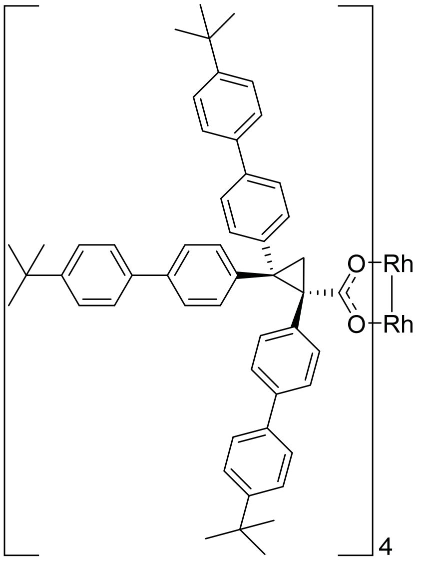


```
Elemental composition search on mass 2370.67017

m/z= 2365.67017-2375.67017
    m/z     | Theo. Mass | Delta  | RDB   |  Composition
            |            | (ppm)  |equiv. |
 2370.67017 | 2370.67748 |  -3.08 |  105.0| C160 H116 O8 Rh2
```

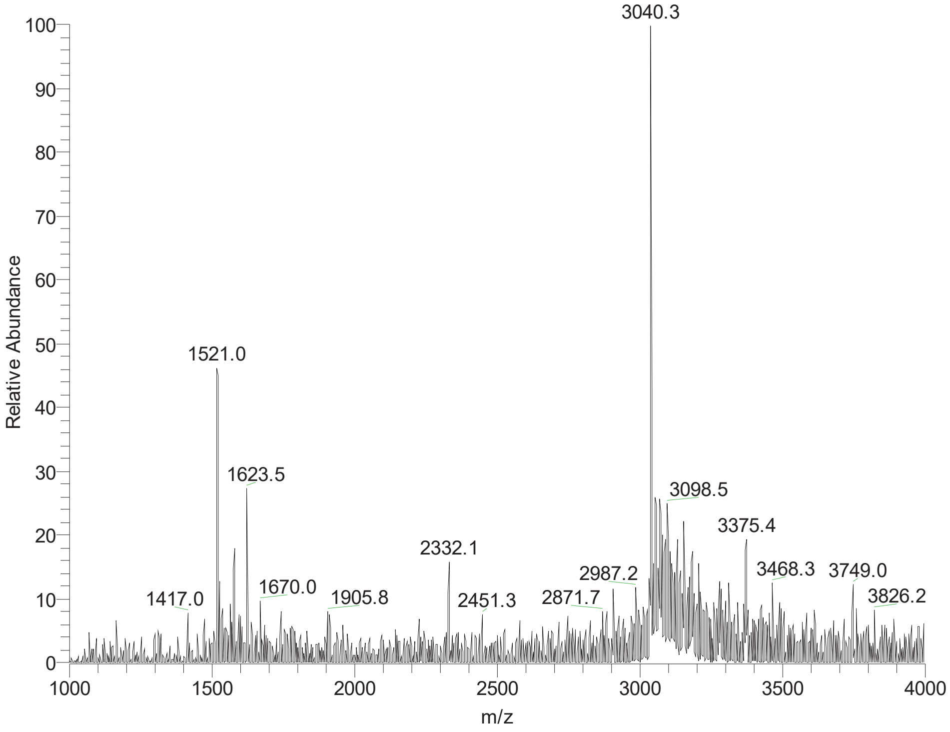

FT31958_170119100955 #112-118 RT: 3.78-3.98 AV: 7 NL: 1.13E2
T: FTMS + p ESI w SIM ms [2320.00-2420.00]
2371.67509
2389.66719
2342.94797
2418.75216
Relative Abundance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
2340
2360
2380
2400
m/z


FT31958_170119100955 #112-118 RT: 3.78-3.98 AV: 7 NL: 1.13E2
T: FTMS + p ESI w SIM ms [2320.00-2420.00]
2371.67509
2370.67017
2372.67375
2373.68334
2369.41199
2374.67171
Relative Abundance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
2368
2370
2372
2374
2376
2378
m/z



Low resolution

C208 H212 O8 Rh2: C208 H212 O8 Rh2 p(gss, s/p:40) Ch...



High resolution on 3040

Elemental composition search on mass 3043.42029

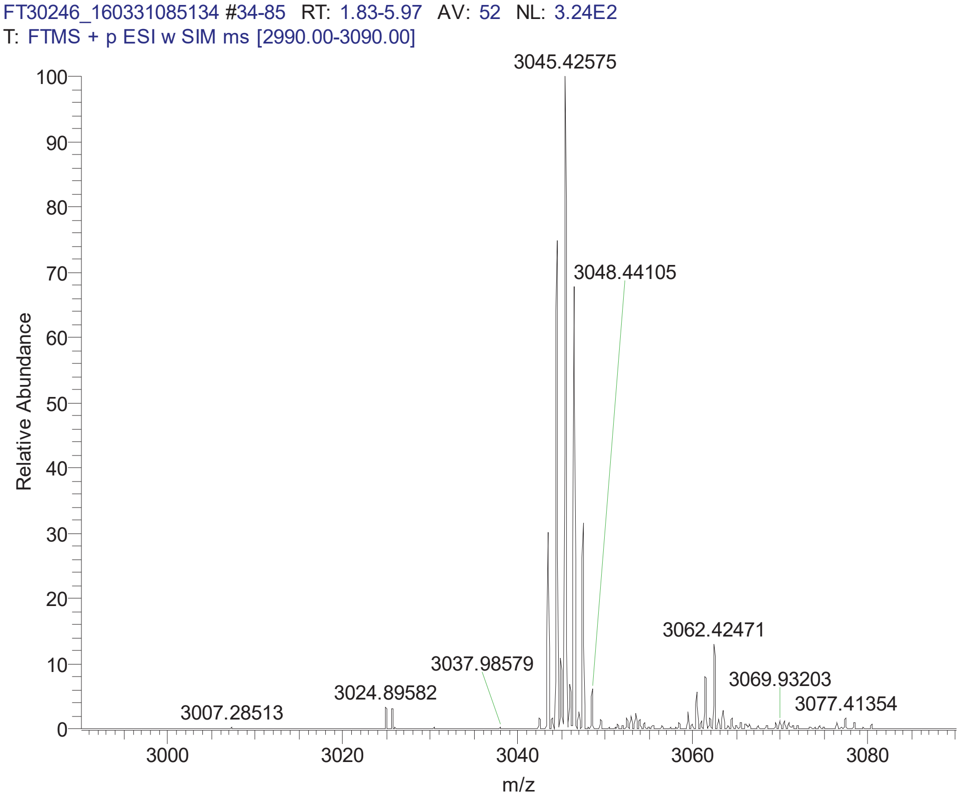
m/z= 3038.42029-3048.42029

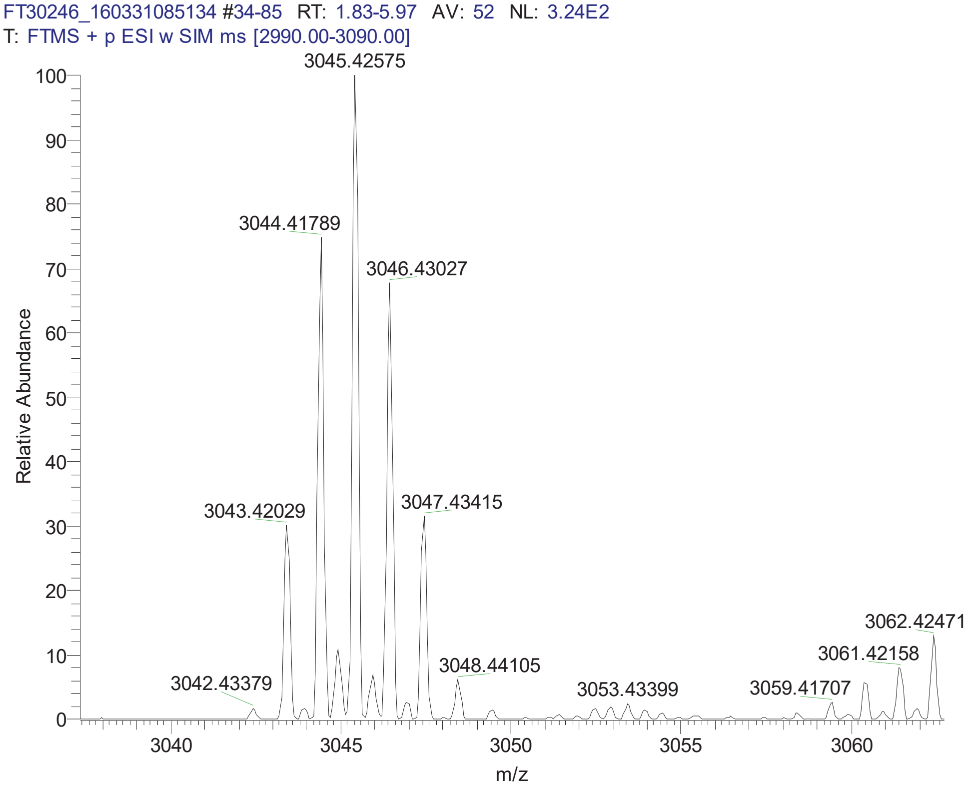
m/z	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
3043.42029	3043.42868	-8.39	105.0	$C_{208} H_{212} O_8 Rh_2$

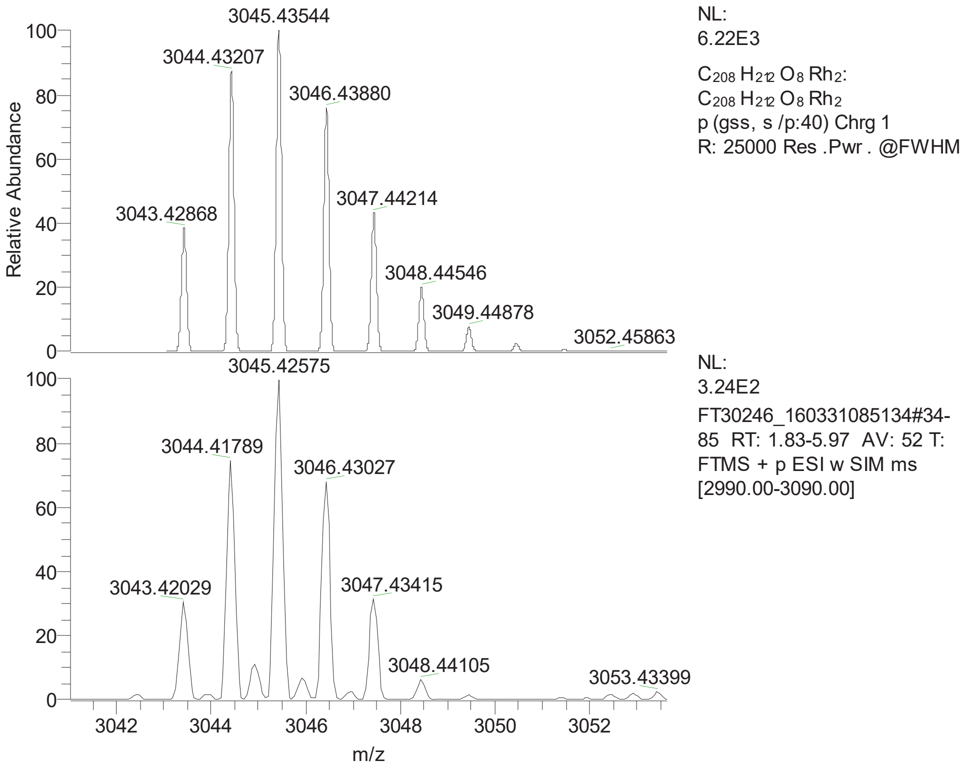
Elemental composition search on mass 3043.42029

m/z= 3038.42029-3048.42029

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
3043.42029	3043.42868	-2.76	105.0	$C_{208} H_{212} O_8 Rh_2$

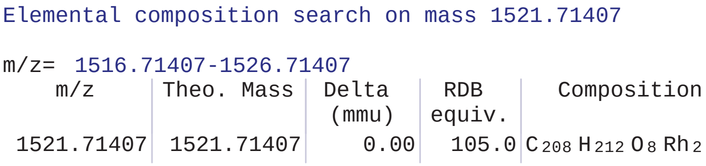

FT30246_160331085134 #34-85 RT: 1.83-5.97 AV: 52 NL: 3.24E2
T: FTMS + p ESI w SIM ms [2990.00-3090.00]
3045.42575
3048.44105
3062.42471
3069.93203
3077.41354
3037.98579
3024.89582
3007.28513
Relative Abundance
0
10
20
30
40
50
60
70
80
90
100
3000
3020
3040
3060
3080
m/z


FT30246_160331085134 #34-85 RT: 1.83-5.97 AV: 52 NL: 3.24E2
T: FTMS + p ESI w SIM ms [2990.00-3090.00]
3045.42575
3044.41789
3046.43027
3043.42029
3047.43415
3048.44105
3042.43379
3053.43399
3059.41707
3061.42158
3062.42471
Relative Abundance
0
10
20
30
40
50
60
70
80
90
100
3040
3045
3050
3055
3060
m/z



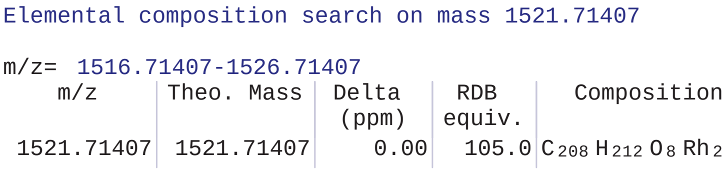
m/z	**Intensity**	**Relative**
3024.89582	**11.5**	**3.54**
3025.62596	**10.6**	**3.27**
3043.42029	**98.4**	**30.34**
3044.41789	**243.4**	**75.03**
3044.91943	**35.7**	**11.00**
3045.42575	**324.5**	**100.00**
3045.93036	**22.1**	**6.82**
3046.43027	**220.4**	**67.92**
3046.94127	**8.6**	**2.66**
3047.43415	**102.6**	**31.63**
3048.44105	**20.0**	**6.17**
3052.92879	**6.6**	**2.04**
3053.43399	**8.0**	**2.47**
3059.41707	**8.7**	**2.67**
3060.41350	**19.3**	**5.94**
3061.42158	**27.1**	**8.35**
3061.92029	**5.8**	**1.78**
3062.42471	**42.8**	**13.19**
3063.42735	**9.9**	**3.05**
3064.43549	**5.9**	**1.80**

High resolution on 1520 (doubly charged)



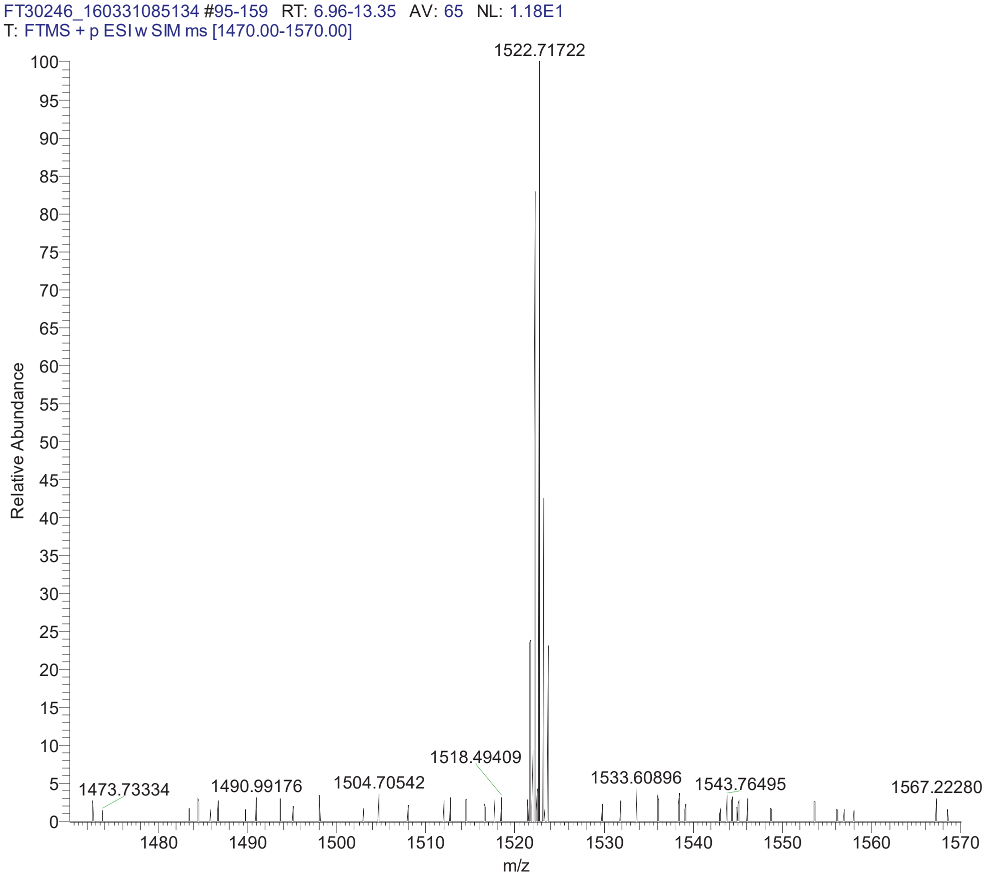
```
Elemental composition search on mass 1521.71407

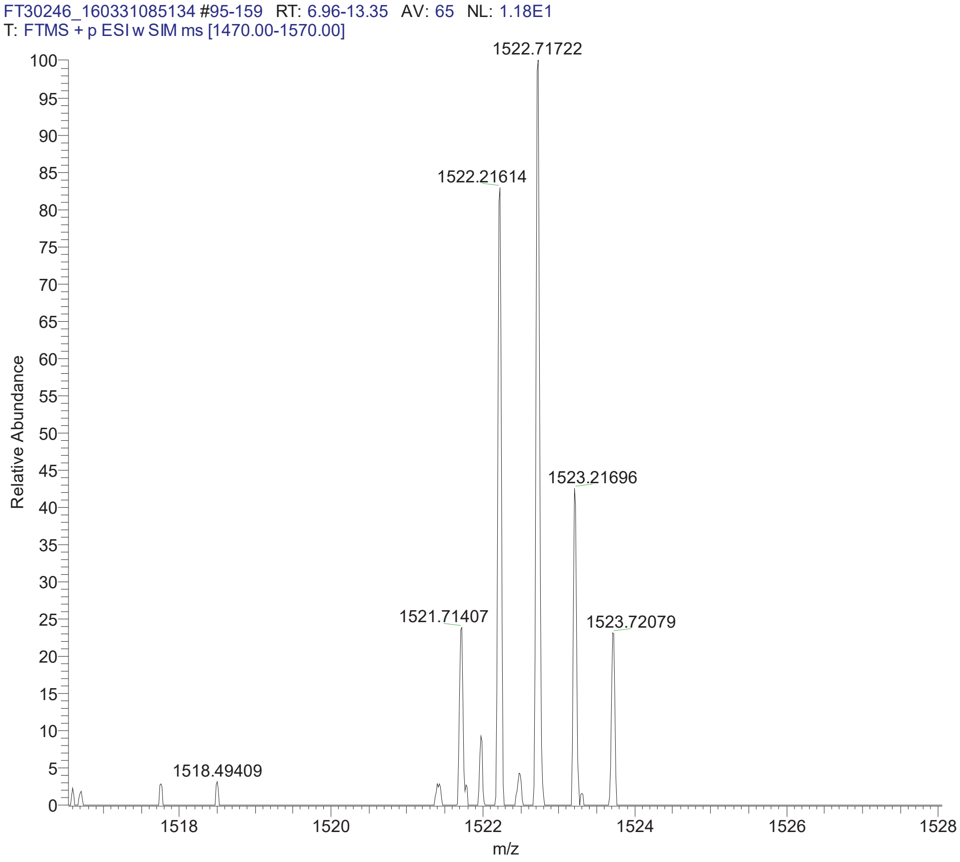
m/z= 1516.71407-1526.71407
    m/z     Theo. Mass  Delta     RDB       Composition
                        (mmu)    equiv.
 1521.71407 1521.71407     0.00   105.0 C208 H212 O8 Rh2
```

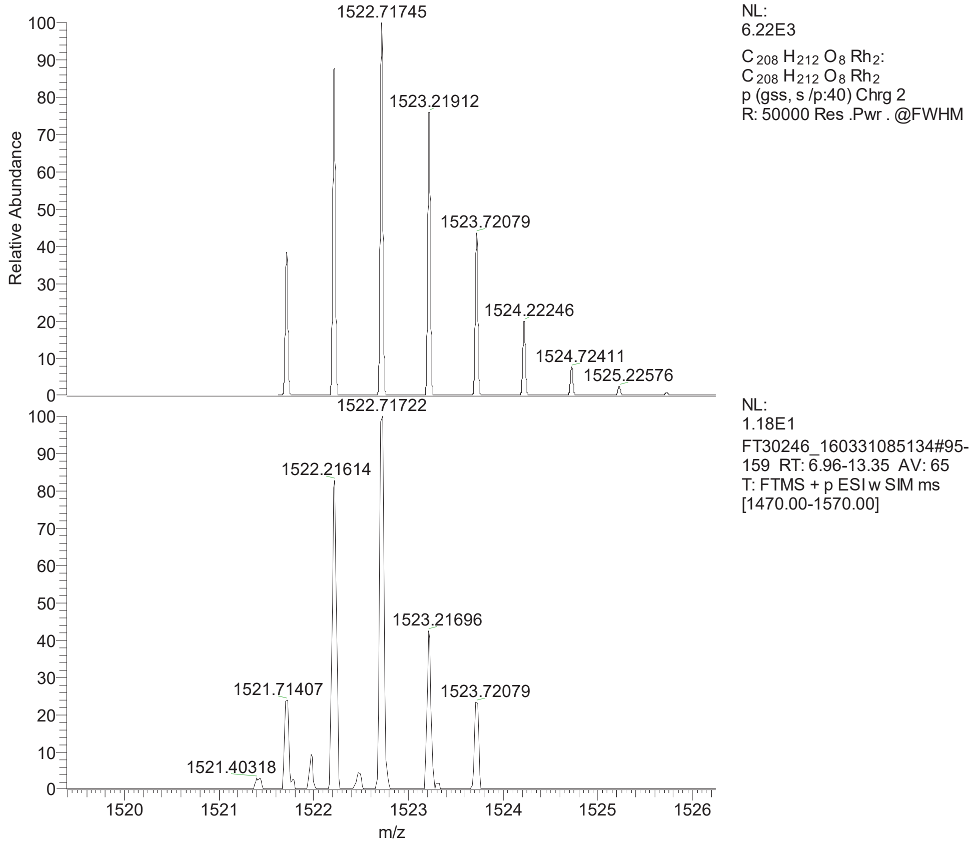


```
Elemental composition search on mass 1521.71407

m/z= 1516.71407-1526.71407
    m/z     Theo. Mass  Delta     RDB       Composition
                        (ppm)    equiv.
 1521.71407 1521.71407     0.00   105.0 C208 H212 O8 Rh2
```

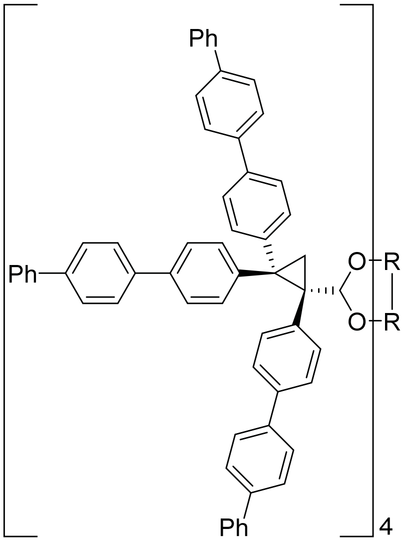

FT30246_160331085134 #95-159 RT: 6.96-13.35 AV: 65 NL: 1.18E1
T: FTMS + p ESI w SIM ms [1470.00-1570.00]
1522.71722
1518.49409
1473.73334
1490.99176
1504.70542
1533.60896
1543.76495
1567.22280
Relative Abundance
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
1480
1490
1500
1510
1520
1530
1540
1550
1560
1570
m/z


FT30246_160331085134 #95-159 RT: 6.96-13.35 AV: 65 NL: 1.18E1
T: FTMS + p ESI w SIM ms [1470.00-1570.00]
1522.71722
1522.21614
1523.21696
1521.71407
1523.72079
1518.49409
Relative Abundance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
1518
1520
1522
1524
1526
1528
m/z

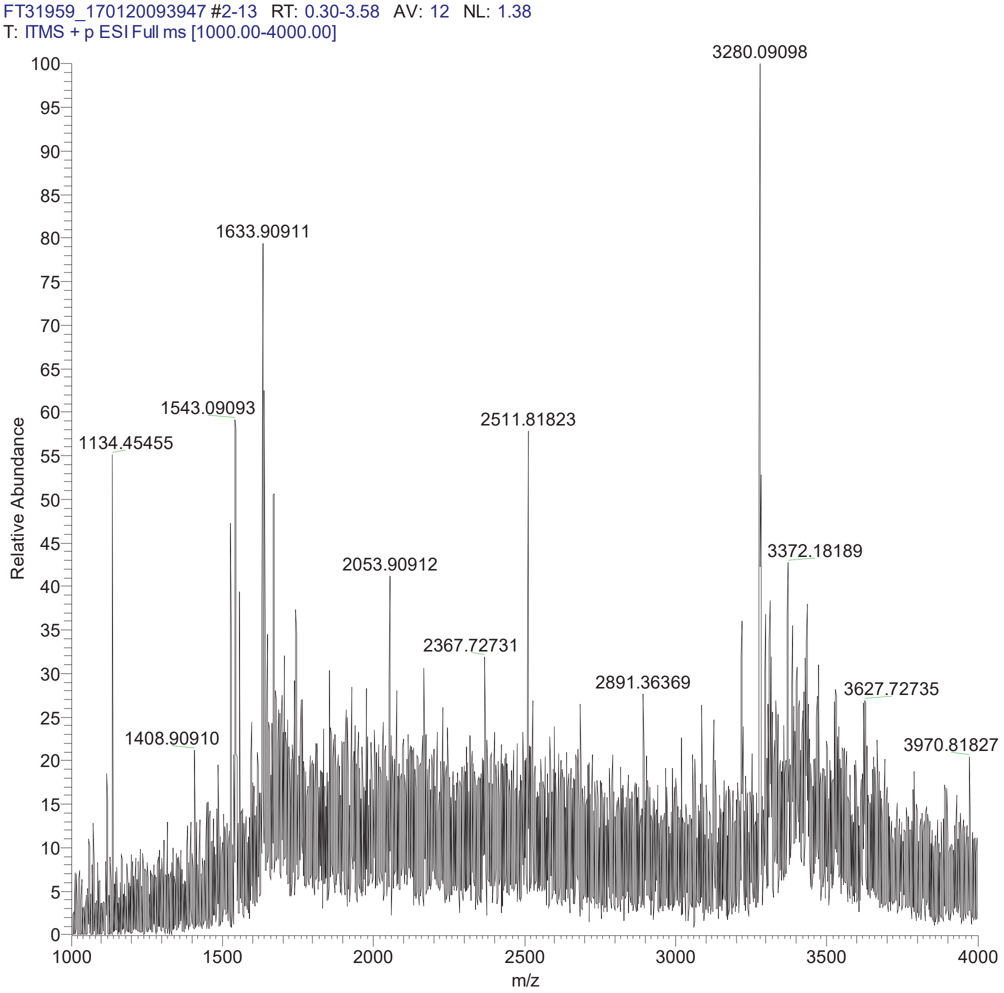


m/z	**Intensity**	**Relative**
1484.48115	**0.4**	**3.00**
1490.99176	**0.4**	**3.06**
1493.67454	**0.4**	**3.00**
1498.08913	**0.4**	**3.31**
1504.70542	**0.4**	**3.51**
1512.76655	**0.4**	**3.06**
1518.49409	**0.4**	**3.11**
1521.71407	**3.0**	**24.07**
1521.97530	**1.1**	**9.15**
1522.21614	**10.1**	**82.09**
1522.47841	**0.5**	**4.25**
1522.71722	**12.3**	**100.00**
1523.21696	**5.2**	**42.21**
1523.72079	**2.9**	**23.28**
1533.60896	**0.5**	**4.21**
1536.06428	**0.4**	**3.22**
1538.39720	**0.4**	**3.64**
1543.76495	**0.4**	**3.44**
1544.42194	**0.4**	**3.14**

1567.22280 0.4 3.13



Ion trap


FT31959_170120093947 #2-13 RT: 0.30-3.58 AV: 12 NL: 1.38
T: ITMS + p ESI Full ms [1000.00-4000.00]

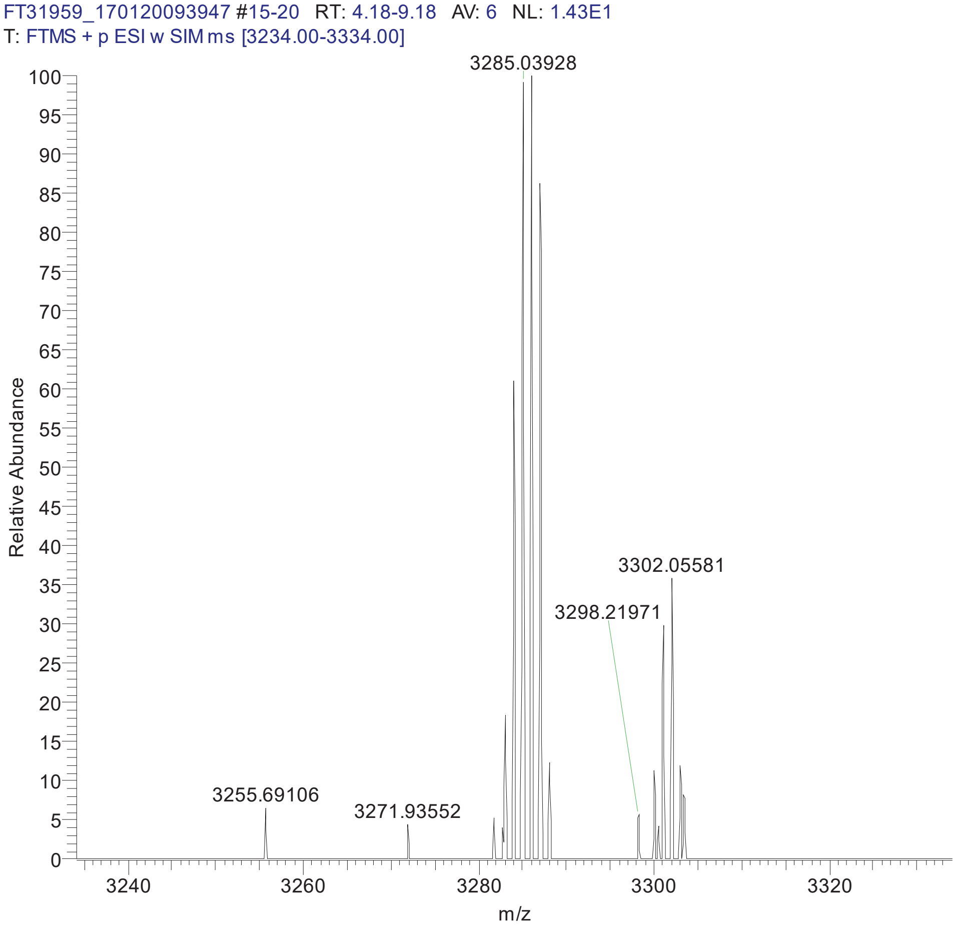
FTMS

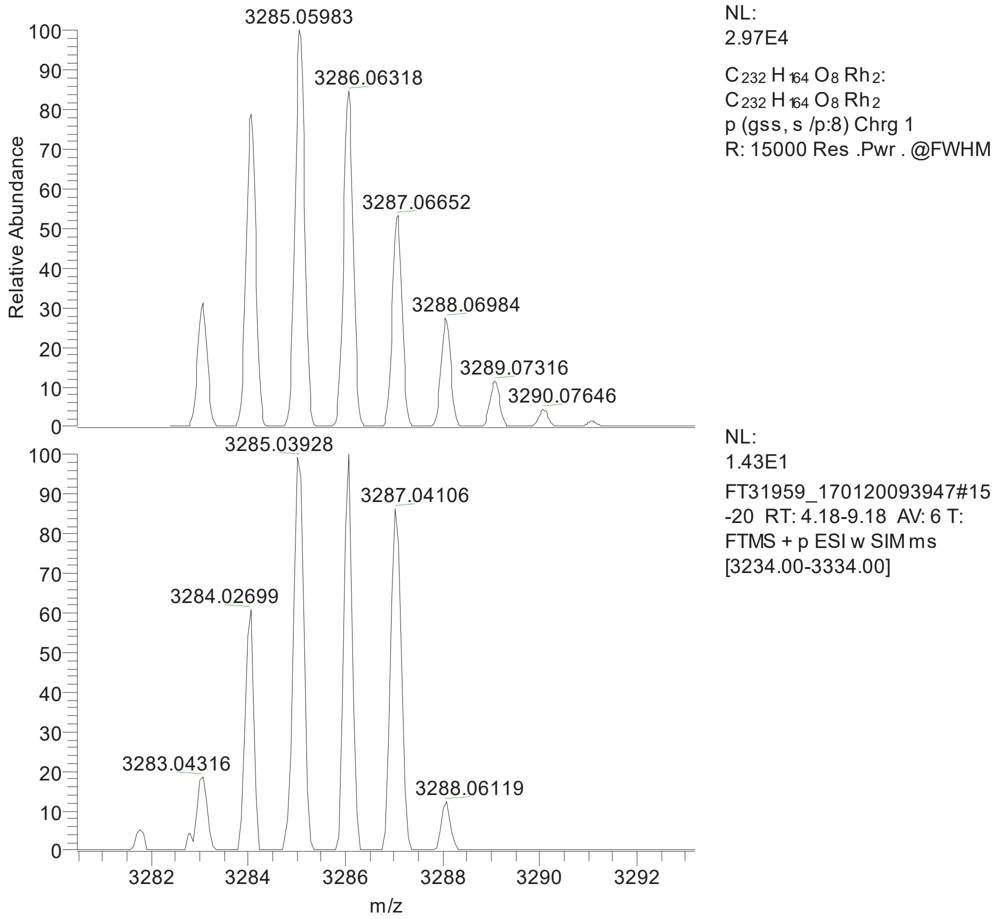
```
Elemental composition search on mass 3283.04316

m/z= 3278.04316-3288.04316
    m/z      | Theo. Mass | Delta  |  RDB   |   Composition
             |            | (mmu)  | equiv. |
  3283.04316 | 3283.05308 |  -9.92 |  153.0 | C232 H164 O8 Rh2
```

```
Elemental composition search on mass 3283.04316

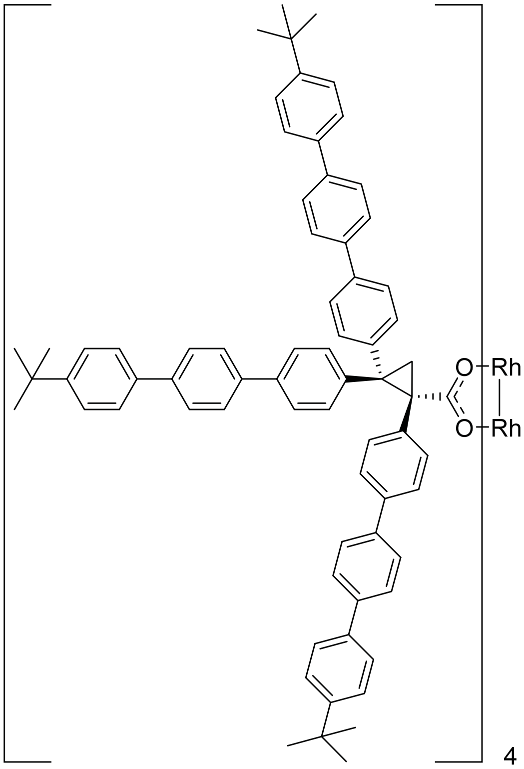
m/z= 3278.04316-3288.04316
    m/z      | Theo. Mass | Delta  |  RDB   |   Composition
             |            | (ppm)  | equiv. |
  3283.04316 | 3283.05308 |  -3.02 |  153.0 | C232 H164 O8 Rh2
```


FT31959_170120093947 #15-20 RT: 4.18-9.18 AV: 6 NL: 1.43E1
T: FTMS + p ESI w SIM ms [3234.00-3334.00]
3285.03928
3302.05581
3298.21971
3255.69106
3271.93552
Relative Abundance
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
3240
3260
3280
3300
3320
m/z

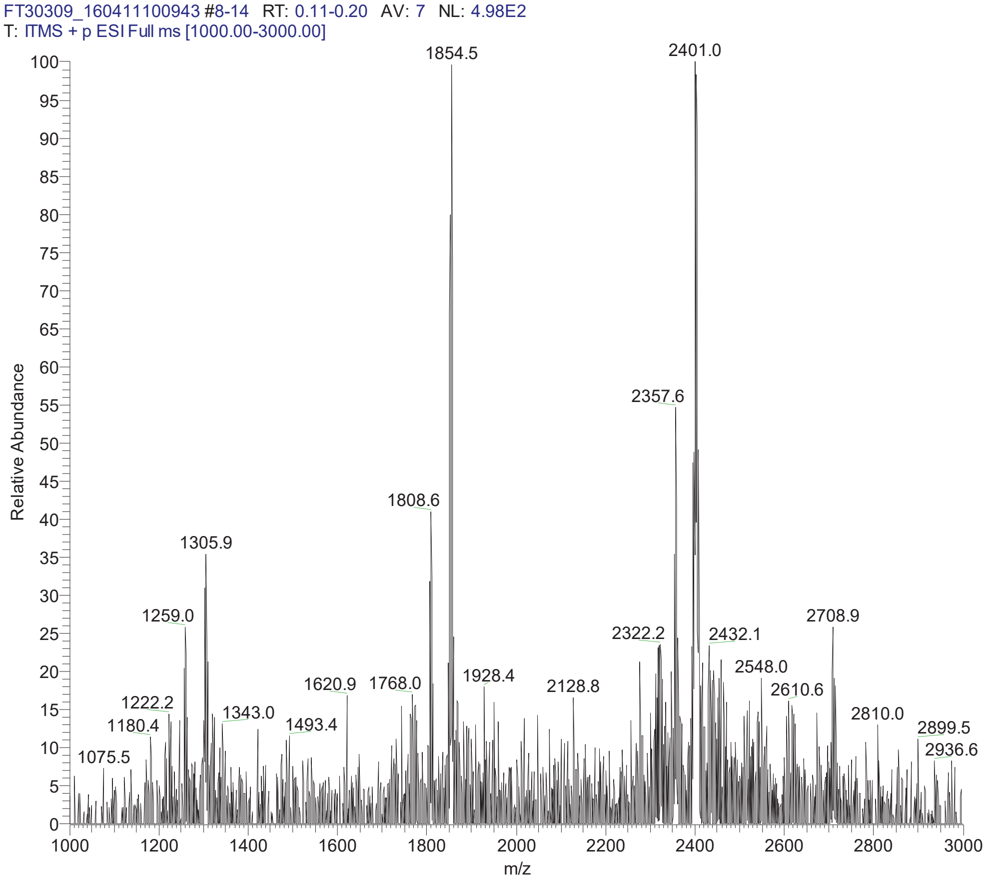


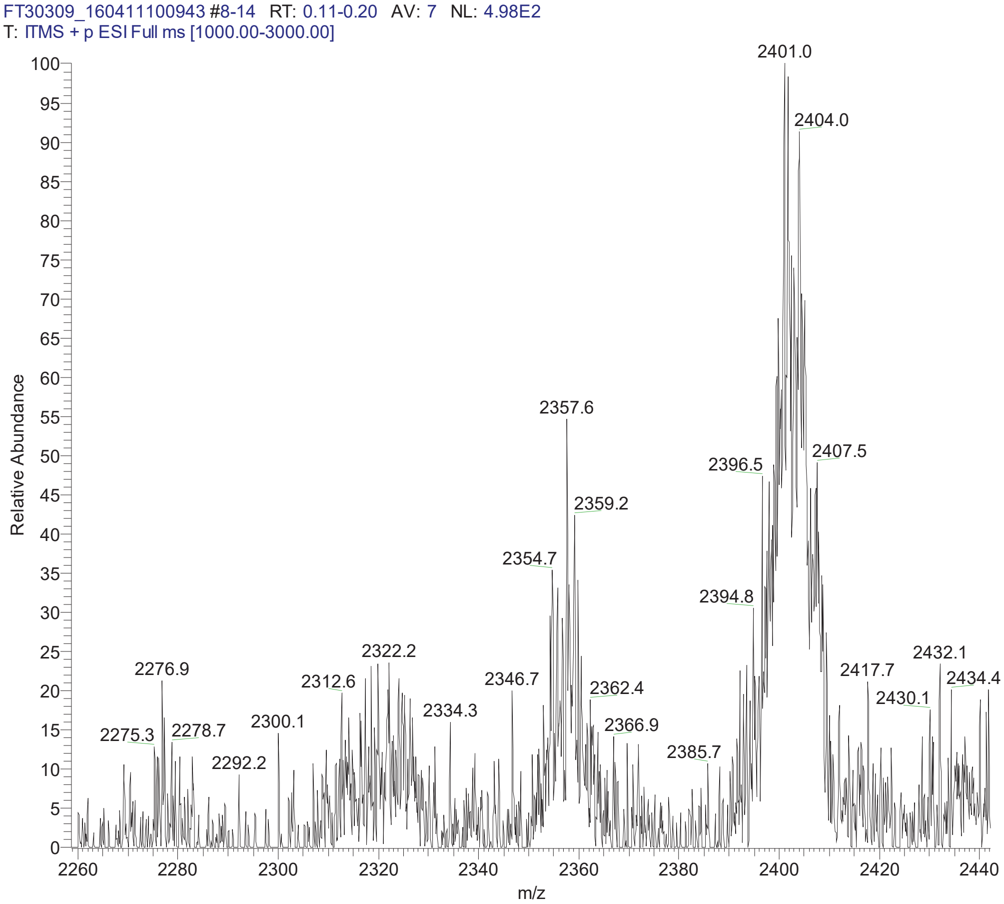
m/z	Intensity	Relative	
3255.69106	0.9	6.39	
3271.93552	0.7	4.56	
3281.77171	0.8	5.24	
3282.78541	0.7	4.55	
3283.04316	2.7	18.58	
3284.02699	8.8	60.49	
3285.03928	14.6		100.00
3286.05035	14.3		98.07
3287.04106	12.4		85.35
3288.06119	1.8	12.23	
3298.21971	0.8	5.75	
3300.07092	1.6	11.06	
3300.50126	0.6	4.41	
3301.05953	4.3	29.34	
3302.05581	5.2	35.91	
3303.01453	1.7	11.68	

3303.43364	1.2	8.24



Low resolution


FT30309_160411100943 #8-14 RT: 0.11-0.20 AV: 7 NL: 4.98E2
T: ITMS + p ESI Full ms [1000.00-3000.00]
Relative Abundance
m/z
1854.5
2401.0
2357.6
1808.6
1305.9
1259.0
2322.2
2432.1
2708.9
2548.0
1620.9
1768.0
1928.4
2128.8
2610.6
1222.2
1180.4
1343.0
1493.4
2810.0
2899.5
2936.6
1075.5
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800
3000



FT30309_160411100943 #8-14 RT: 0.11-0.20 AV: 7 NL: 4.98E2
T: ITMS + p ESI Full ms [1000.00-3000.00]

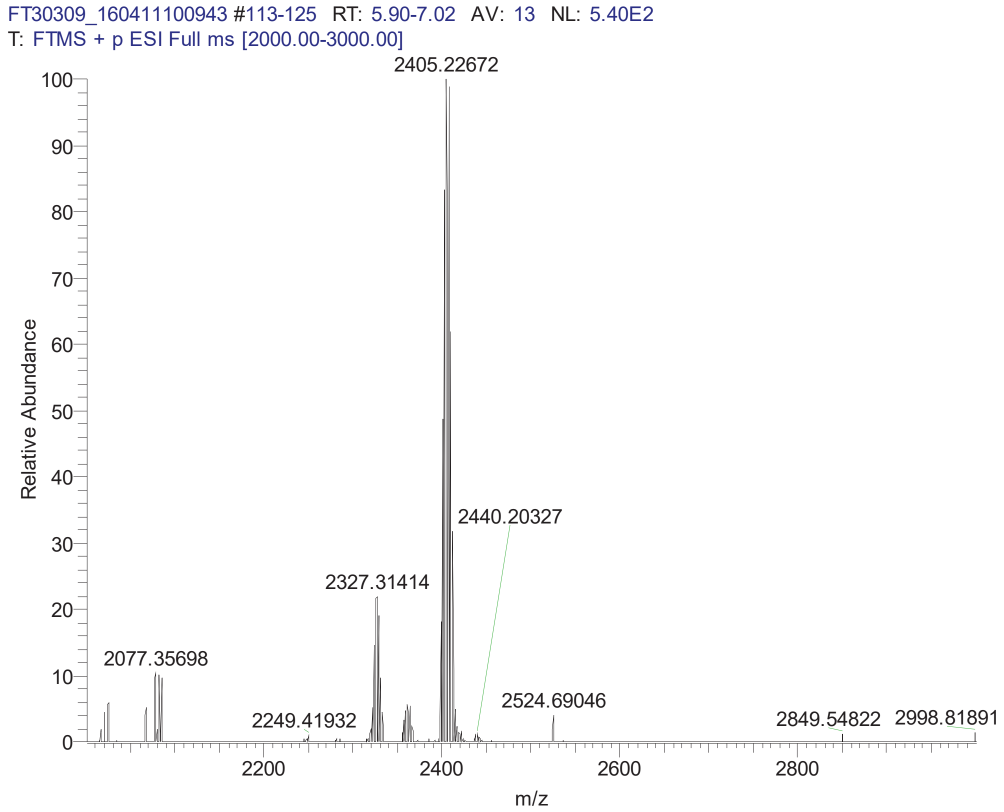
High resolution

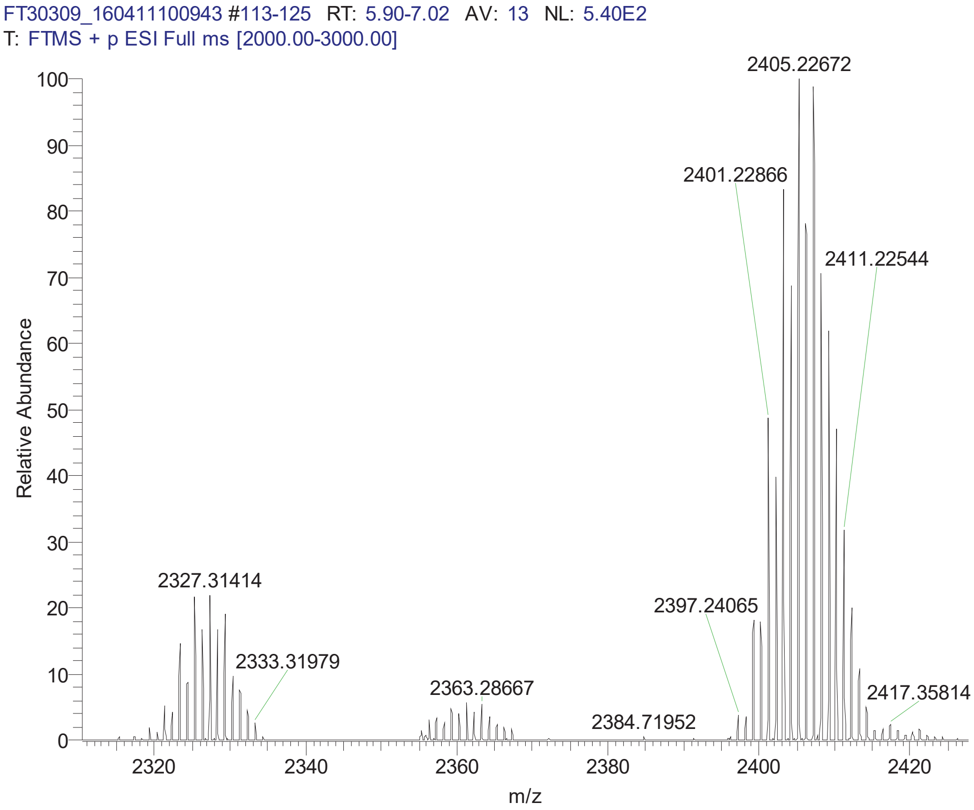
```
Elemental composition search on mass 2397.24065

m/z= 2392.24065-2402.24065
     m/z      | Theo. Mass | Delta  |  RDB   |   Composition
              |            | (mmu)  | equiv. |
  2397.24065  | 2397.22394 |  16.71 |   57.0 | C88 H56 O8 Br10 81Br2 Rh2
```

```
Elemental composition search on mass 2397.24065

m/z= 2392.24065-2402.24065
    m/z     | Theo. Mass | Delta  |  RDB  |   Composition
            |            | (ppm)  | equiv.|
 2397.24065 | 2397.22394 |   6.97 |  57.0 | C88 H56 O8 Br10 81Br2 Rh2
```


FT30309_160411100943 #113-125 RT: 5.90-7.02 AV: 13 NL: 5.40E2
T: FTMS + p ESI Full ms [2000.00-3000.00]
2405.22672
2440.20327
2327.31414
2077.35698
2524.69046
2249.41932
2849.54822
2998.81891
Relative Abundance
0
10
20
30
40
50
60
70
80
90
100
2200
2400
2600
2800
m/z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T: FTMS + p ESI Full ms [2000.00-3000.00]
Relative Abundance
m/z
0
10
20
30
40
50
60
70
80
90
100
2320
2340
2360
2380
2400
2420
2405.22672
2401.22866
2411.22544
2327.31414
2333.31979
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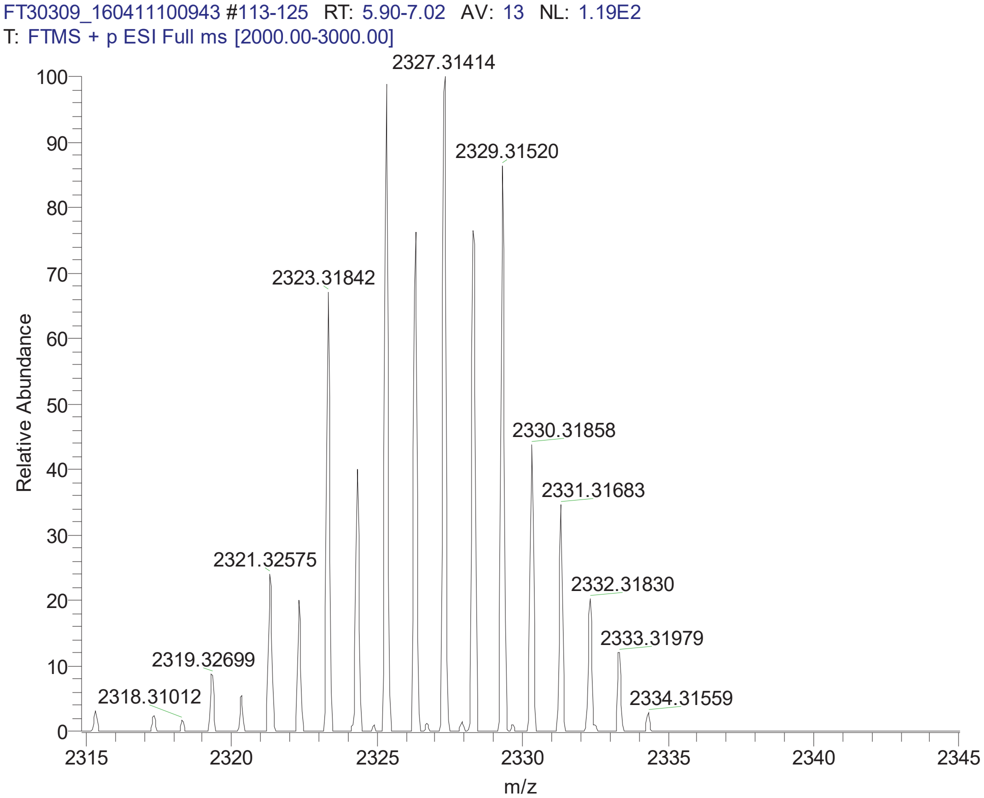
2384.71952
2397.24065
2417.35814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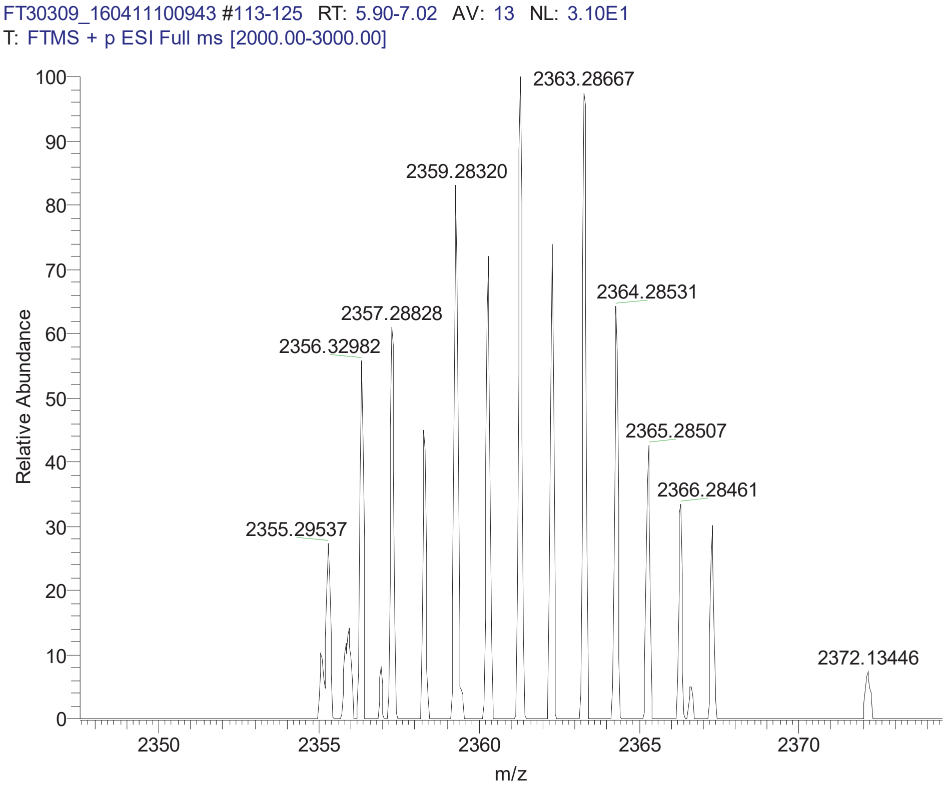
2329.31520
2323.31842
2330.31858
2331.31683
2321.32575
2332.31830
2333.31979
2319.32699
2318.31012
2334.31559
Relative Abundance
0
10
20
30
40
50
60
70
80
90
100
2315
2320
2325
2330
2335
2340
2345
m/z


FT30309_160411100943 #113-125 RT: 5.90-7.02 AV: 13 NL: 3.10E1
T: FTMS + p ESI Full ms [2000.00-3000.00]
Relative Abundance
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80
70
60
50
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30
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10
0
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2350
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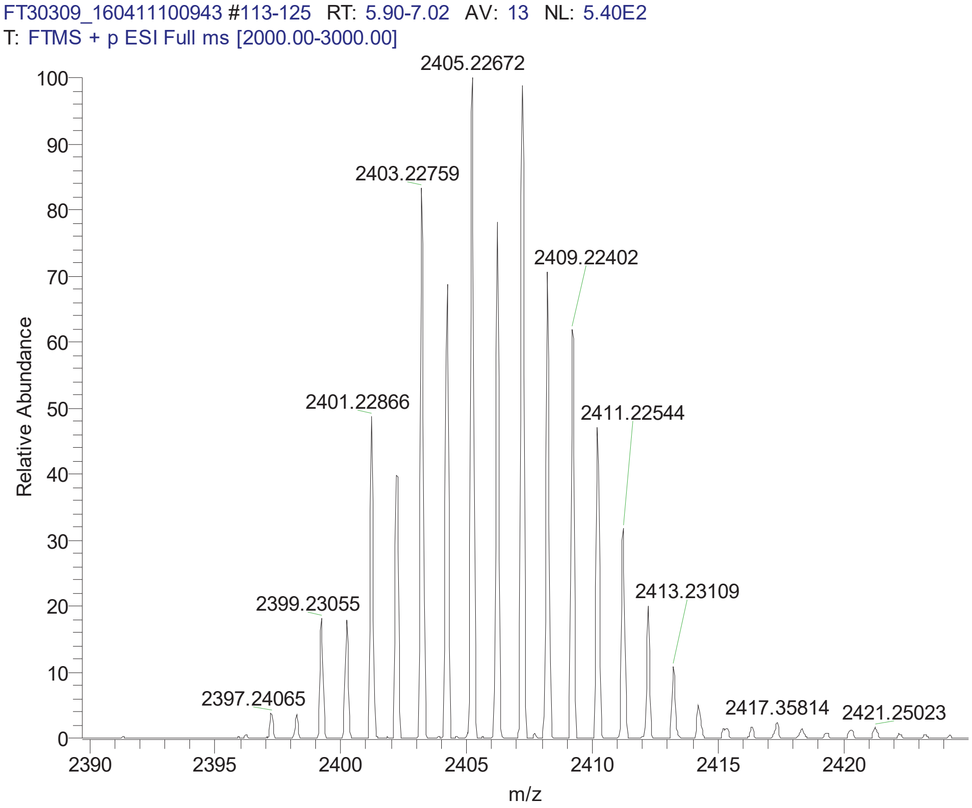
2360
2365
2370
m/z



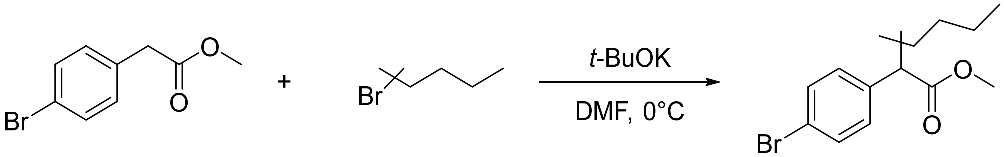
m/z	Intensity	Relative
2323.31842	81.4	14.84
2325.31737	118.6	21.63
2326.31583	91.0	16.59
2327.31414	122.2	22.29
2328.31840	93.1	16.99
2329.31520	103.0	18.80
2399.23055	99.0	18.06
2400.23390	97.4	17.77
2401.22866	271.8	49.59
2402.23206	222.3	40.55
2403.22759	451.8	82.42
2404.22957	371.3	67.73
2405.22672	548.2	100.00
2406.22699	433.8	79.13
2407.22496	535.7	97.72
2408.22700	383.2	69.90
2409.22402	343.6	62.69
2410.22464	255.4	46.59
2411.22544	174.6	31.85
2412.22571	109.7	20.02

SI-Chapter 3

1. Characterization of Pentane Functionalization Products

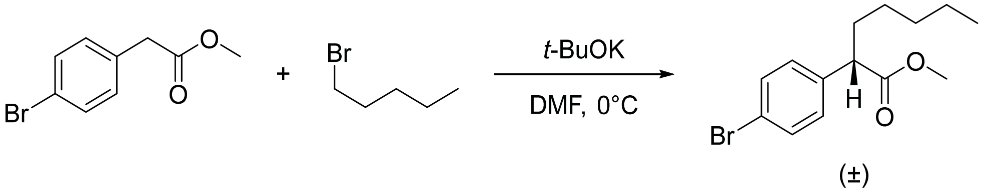
The mixtures of products formed from reaction with *n*-alkanes and *n*-alkyl compounds were inseparable by chromatography. Therefore, authentic samples of the products from functionalization at the C1, C2 and C3 positions of *n*-pentane were prepared independently by an alternative method for characterization. Products from functionalizing other *n*-alkanes and *n*-alkyl compounds are reasonably assigned by analogy from the *n*-pentane reactions, and confirmed by ^{1}H NMR, ^{13}C NMR, IR and MS.

1.1 General Procedure for SN2 Reaction



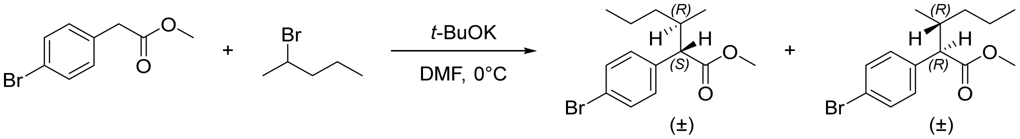
A sample of potassium *tert*-butoxide (*t*-BuOK) (808 mg, 7.2 mmol, 1.2 equiv.) was suspended in 10 mL of dry dimethylformamide (DMF) at 0 °C under an N_2 atmosphere, and 2-(4-bromophenyl)acetate (1.37 g, 6.0 mmol, 1 equiv.) was added at once, followed by the corresponding *n*-pentyl bromide (1.088 g, 7.2 mmol, 1.2 equiv.) after 10 min. The reaction solution was allowed to warm up to room temperature, and magnetic stirring was continued for 1h. Water (10 mL) was added and the solution was extracted with DCM (2x10 mL). The combined organic layer was washed with saturated, aqueous solution of NH_4Cl (10 mL) and water (10 mL), dried over $MgSO_4$ (5 g) and filtered. Then the filtrate was concentrated, and the resulting crude mixture was separated by flash chromatography on silica gel to obtain pure compound.

Below is shown the experimental data for each reaction:



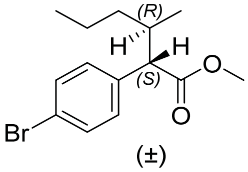
Methyl 2-(4-bromophenyl)heptanoate. This compound was prepared according to the general procedure for S_N2 reaction. *t*-BuOK (804 mg, 7.2 mmol, 1.2 equiv.), methyl 2-(4-bromophenyl)acetate (1.38 g, 6.0 mmol, 1 equiv.) and 1-bromopentane (1.09 g, 7.2 mmol, 1.2 equiv.) were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as colorless oil in 93% overall yield (1.67 g).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 3.64 (s, 3H), 3.50 (t, *J* = 7.7 Hz, 1H), 2.09 – 1.98 (m, 1H), 1.77 – 1.68 (m, 1H), 1.32 – 1.16 (m, 6H), 0.85 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.2, 138.3, 131.7, 129.7, 121.2, 52.0, 51.1, 33.5, 31.5, 27.2, 22.5, 14.0; HRMS (NSI) calcd for $C_{14}H_{20}BrO_2$ ($[M+H]^+$): 299.0641 found 299.0641; IR (neat): 2952, 2928, 2858, 1733, 1488, 1434, 1239, 1158, 1010, 820, 756.

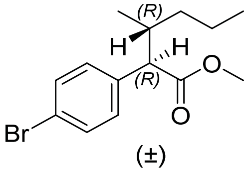


Methyl 2-(4-bromophenyl)-3-methylhexanoate. The compounds were prepared according to the general procedure for S_N2 reaction. *t*-BuOK (807 mg, 7.2 mmol, 1.2 equiv.), methyl 2-(4-bromophenyl)acetate (1.37 g, 6.0 mmol, 1 equiv.) and 2-bromopentane (1.09 g, 7.2 mmol, 1.2 equiv.) were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil in 92% overall yield (1.65 g).

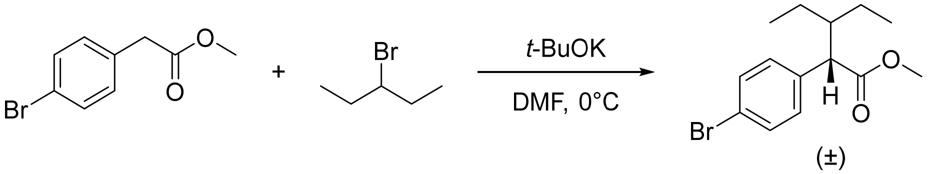
HRMS (NSI) calcd for $C_{14}H_{20}BrO_2$ ($[M+H]^+$): 299.0641 found 299.0649; IR (neat):2956, 2930, 2871, 1733, 1487, 1196, 1161, 1145, 1073, 1010, 818, 761.



^{1}H NMR (600 MHz, CDCl$_3$) δ 7.43 (d, *J* = 7.4 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 2H), 3.65 (s, 3H), 3.23 (d, *J* = 10.6 Hz, 1H), 2.23 – 2.10 (m, 1H), 1.36 – 1.30 (m, 1H), 1.19 – 1.11 (m, 1H), 1.08 (ddd, *J* = 10.0, 8.2, 4.7 Hz, 1H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.87 (dtd, *J* = 14.7, 10.0, 4.7 Hz, 1H), 0.77 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 174.2, 137.3, 131.7, 130.4, 121.3, 58.3, 52.0, 36.3, 35.7, 19.6, 17.9, 14.2.



^{1}H NMR (600 MHz, CDCl$_3$) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 3.65 (s, 3H), 3.21 (d, *J* = 10.5 Hz, 1H), 2.23 – 2.10 (m, 1H), 1.36 – 1.30 (m, 1H), 1.19 – 1.11 (m, 1H), 1.08 (ddd, *J* = 10.0, 8.2, 4.7 Hz, 1H), 0.91 (t, *J* = 7.1 Hz, 3H), 0.87 (dtd, *J* = 14.7, 10.0, 4.7 Hz, 1H), 0.66 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 174.2, 137.3, 131.7, 130.4, 121.3, 58.3, 52, 36.3, 35.7, 19.6, 17.9, 14.2.

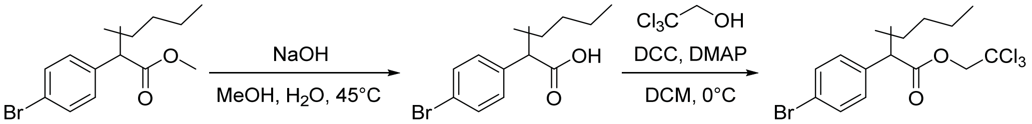


Methyl 2-(4-bromophenyl)-3-ethylpentanoate. This compound was prepared according to the general procedure for S_N2 reaction. *t*-BuOK (805 mg, 7.2 mmol, 1.2 equiv.), methyl 2-(4-bromophenyl)acetate (1.38 g, 6.0 mmol, 1 equiv.) and 3-bromopentane (1.09 g, 7.2 mmol, 1.2 equiv.) were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil in 85% overall yield (1.53 g).

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 3.64 (s, 3H), 3.41 (d, *J* = 11.0 Hz, 1H), 2.08 (m, 1H), 1.54 – 1.32 (m, 2H), 1.22 (m, 1H), 1.01 (m, 1H), 0.90 (t, *J* = 7.5 Hz, 3H), 0.70 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ

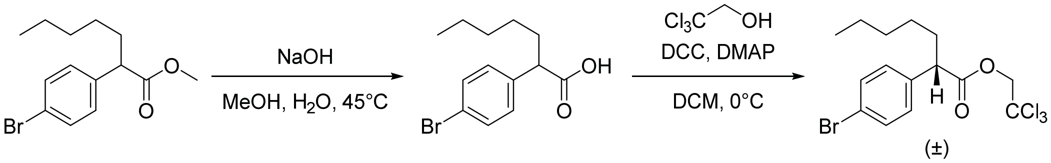
174.4, 137.3, 131.7, 130.5, 121.3, 55.0, 52.0, 42.9, 22.8, 20.9, 10.3, 9.5; HRMS (NSI) calcd for $C_{14}H_{20}BrO_2$ ($[M+H]^+$): 299.0641 found 299.0645; IR (neat): 2962, 2875, 1733, 1487, 1159, 1141, 1073, 1010, 817, 763.

1.2 General Procedure for Trichloroethyl Ester Synthesis



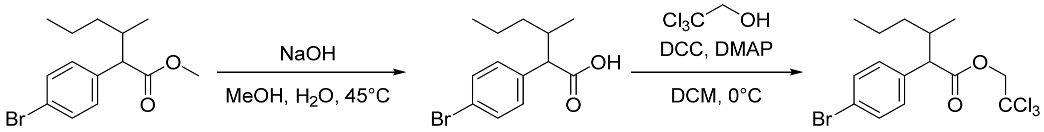
Ester (299 mg, 1 mmol, 1.0 equiv.), 3 mL of methanol and 5mL of water were placed in a 25 mL round bottomed flask mounted over a magnetic stirrer and maintained at 45°C. NaOH (88 mg, 2.2 mmol, 2.2 equiv.) was added and the mixture were stirred. The reactions were quenched invariably after 60 min by addition of 5 mL of water and acidified to pH = 2 with 6 N hydrochloric acid and extracted with diethyl ether (3x10 mL). The combined organic phase was washed by water (3x10 mL), saturated NaCl aqueous solution (3x10 mL) and dried with Na_2SO_4 and then concentrated to obtain the crude without further purification. To a stirred solution of crude acid in dry DCM (4 mL) cooled in an ice bath was added 2,2,2-trichloroethanol (179 mg, 1.2 mmol, 1.2 equiv.) and 4-Dimethylaminopyridine (DMAP) (37 mg, 0.3 mmol, 0.3 equiv.). A solution of N,N-Dicyclohexylcarbodiimide (DCC) (227 mg, 1.1 mmol, 1.1 equiv.) in DCM (5 mL) was added slowly into the cold solution, then the reaction mixture was stirred overnight and allowed to warm up to room temperature. The mixture was transferred to a 25-mL filter funnel loaded with a 2 inches silica plug, then the mixture was flashed with diethyl ether (30 mL). The filtrate was concentrated, and the resulting crude mixture was separated by flash chromatography on silica gel to obtain pure compound.

Below shown the experimental data for each reaction:



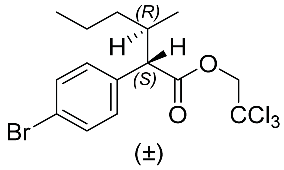
2,2,2-trichloroethyl 2-(4-bromophenyl)heptanoate. The compounds were prepared according to the general procedure for trichloroethyl ester synthesis. Methyl 2-(4-bromophenyl)heptanoate (297 mg, 1 mmol, 1.0 equiv.), NaOH (89 mg, 2.2 mmol, 2.2 equiv.), 2,2,2–trichloroethanol (180 mg, 1.2 mmol, 1.2 equiv.), DMAP (38 mg, 0.3 mmol, 0.3 equiv.) and DCC (228 mg, 1.1 mmol, 1.1 equiv.) were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil in 82% overall yield (342 mg).

^{1}H NMR (600 MHz, Chloroform–*d*) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 3.65 (t, *J* = 7.7 Hz, 1H), 2.15 – 2.05 (m, 1H), 1.92 (d, *J* = 9.5 Hz, 2H), 1.85 – 1.77 (m, 1H), 1.77 – 1.70 (m, 2H), 1.61 – 1.53 (m, 1H), 1.22 – 1.17 (m, 1H), 0.88 – 0.84 (t, *J* = 3.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.1, 137.3, 131.9, 130.0, 121.6, 94.9, 77.4, 77.2, 77.0, 74.2, 51.1, 33.2, 31.6, 27.2, 22.6, 14.1; HRMS (NSI) calcd for $C_{15}H_{18}NaBrCl_3O_2$ ([M+Na]$^+$): 436.9448 found 436.9488; IR (neat):2953, 2928, 2858, 1749, 1487, 1371, 1205, 1138, 1073, 1011, 822, 801, 753, 716.

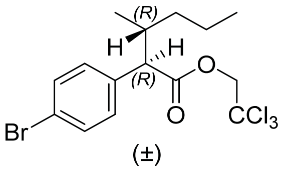


2,2,2-trichloroethyl-2-(4-bromophenyl)-3-methylhexanoate. The compounds were prepared according to the general procedure for trichloroethyl ester synthesis. Methyl 2-(4-bromophenyl)heptanoate (298 mg, 1 mmol, 1.0 equiv.), NaOH (90 mg, 2.2 mmol, 2.2 equiv.), 2,2,2–trichloroethanol (178 mg, 1.2 mmol, 1.2 equiv.), DMAP (38 mg, 0.3 mmol, 0.3 equiv.) and DCC (229 mg, 1.1 mmol, 1.1 equiv.) were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil in 78% overall yield (325 mg).

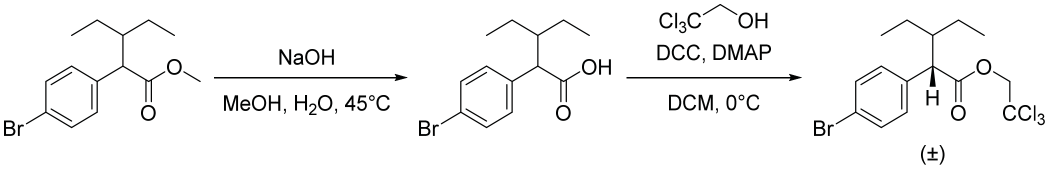
HRMS (NSI) calcd for $C_{15}H_{18}NaBrCl_3O_2$ ([M+Na]$^+$): 436.9448 found 436.9489; IR (neat):2957, 2931, 2872, 1747, 1487, 1116, 1073, 1010, 824, 758, 714;



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 0.9 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 3.38 (d, *J* = 10.6 Hz, 1H), 2.33 – 2.19 (m, 1H), 1.40 – 1.30 (m, 1H), 1.21 – 1.09 (m, 2H), 1.05 (d, *J* = 7.6 Hz, 3H), 0.99-0.83 (m, 1H), 0.77 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 136.3, 131.8, 130.6, 121.7, 94.9, 74.2, 58.2, 36.0, 35.6, 19.6, 17.9, 14.2.



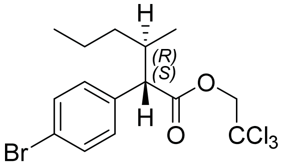
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 3.37 (d, *J* = 10.5 Hz, 1H), 2.34 – 2.19 (m, 1H), 1.52 – 1.42 (m, 1H), 1.26 – 1.08 (m, 2H), 0.91 (t, *J* = 7.1 Hz, 3H), 0.99 – 0.83 (m, 1H), 0.70 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.0, 136.4, 131.8, 130.6, 121.7, 94.9, 74.3, 58.2, 37.6, 36.1, 20.0, 16.7, 14.4.



2,2,2-trichloroethyl 2-(4-bromophenyl)-3-ethylpentanoate(19). The compounds were prepared according to the general procedure for trichloroethyl ester synthesis. Methyl 2-(4-bromophenyl)heptanoate (300 mg, 1 mmol, 1.0 equiv.), NaOH (89 mg, 2.2 mmol, 2.2 equiv.), 2,2,2-trichloroethanol (179 mg, 1.2 mmol, 1.2 equiv.), DMAP (39 mg, 0.3 mmol, 0.3 equiv.) and DCC (228 mg, 1.1 mmol, 1.1 equiv.) were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford **19** as a colorless oil in 75% overall yield (312 mg).

^{1}H NMR (600 MHz, Chloroform–*d*) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 4.76 (d, *J* = 12.1 Hz, 1H), 4.62 (d, *J* = 12.1 Hz, 1H), 3.55 (d, *J* = 11.1 Hz, 1H), 2.22 – 2.11 (m, 1H), 1.54 – 1.41 (m, 2H), 1.26-1.15 (m, 1H), 1.10 – 1.03 (m, 1H), 0.92 (t, *J* = 7.5 Hz, 3H), 0.73 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.1, 136.3, 131.8, 130.6, 121.7, 94.9, 74.3, 55.9, 35.1, 25.6, 24.8, 10.2, 9.5; HRMS (NSI) calcd for $C_{15}H_{18}NaBrCl_3O_2$ ([M-H]$^+$): 436.9448 found 436.9487; IR (neat): 2964, 2876, 1734, 1488, 1160, 1142, 1674, 1011, 818, 764.

1.3 Characterization of the pentane C2 insertion product



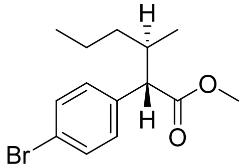
2,2,2-trichloroethyl (2*S*,3*R*)-2-(4-bromophenyl)-3-methylhexanoate.

This compound was prepared according to the general procedure A for Rh_2[*R-3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 3 mL *n*-pentane and Rh_2[*R-3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$ (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL n-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (144 mg, 99% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 25, C3 was not detected; and the dr of C2 was 20: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.5% isopropanol in hexane, 0.7 mL/min, 1 mg/mL, 160 min, UV 210 nm) retention times of 84.0 min (major) and 142.4 min (minor), 99% e.e..

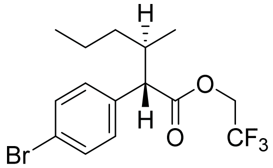
$[\alpha]^{20}_D$ 15.2° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 0.9 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 3.38 (d, *J* = 10.6 Hz, 1H), 2.33 – 2.19 (m, 1H), 1.40 – 1.30 (m, 1H), 1.21 – 1.09 (m, 2H), 1.05 (d, *J* = 7.6 Hz, 3H), 0.99 – 0.83 (m, 1H), 0.77 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 136.3, 131.8, 130.6, 121.7, 94.9, 74.2, 58.2, 36.0, 35.6, 19.6, 17.9, 14.2; HRMS (NSI) calcd for $C_{15}H_{18}NaBrCl_3O_2$ ($[M+Na]^+$): 436.9448 found 436.9489; IR (neat):2957, 2931, 2872, 1747, 1487, 1116, 1073, 1010, 824, 758, 714;



Methyl (2*S*,3*R*)-2-(4-bromophenyl)-3-methylhexanoate. This compound was prepared according to the general procedure A for Rh_2[*R*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$-catalyzed C–H functionalization. Methyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 89 mg, 1.0 equiv.) in 3 mL *n*-pentane and Rh_2[*R*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$ (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL n-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (98 mg, 94% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 18, C3 was not detected; and the dr of C2 was 8: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

$[\alpha]^{20}_D$ 35.5° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.4 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 2H), 3.64 (s, 3H), 3.23 (d, *J* = 10.6 Hz, 1H), 2.22 – 2.10 (m, 1H), 1.36 – 1.28 (m, 1H), 1.10 (m, 1H), 0.98 (d, *J* = 6.6 Hz, 3H), 0.86 (m, 1H), 0.76 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.2, 137.3, 131.7, 130.4, 121.3, 58.3, 52.0, 36.3, 35.7, 19.6, 17.9, 14.2; HRMS (NSI) calcd for $C_{14}H_{20}BrO_2$ ($[M+H]^+$): 299.0641 found 299.0649; IR (neat):2956, 2930, 2871, 1733, 1487, 1196, 1161, 1145, 1073, 1010, 818, 761; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.5% isopropanol in hexane, 0.7 mL/min, 1 mg/mL, 160 min, UV 210 nm) retention times of 86.2 min (major) and 141.5 min (minor), 92% e.e..

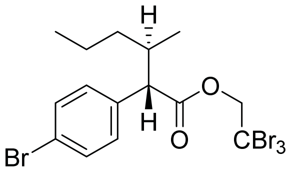


2,2,2-Trifluoroethyl (2*S*,3*R*)-2-(4-bromophenyl)-3-methylhexanoate. This compound was prepared according to the general procedure A for Rh_2[*R*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$-catalyzed C–H functionalization. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate

(0.35 mmol, 113 mg, 1.0 equiv.) in 3 mL *n*-pentane and Rh_2[*R*-*3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$ (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL n-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (123 mg, 96% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 30, C3 was not detected; and the dr of C2 was 15: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

$[\alpha]^{20}_D$ 26.1° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 4.55 (dd, *J* = 12.7, 8.4 Hz, 1H), 4.33 (dd, *J* = 12.7, 8.4 Hz, 1H), 3.35 (d, *J* = 10.6 Hz, 1H), 2.25 – 2.16 (m, 1H), 1.40 – 1.31 (m, 1H), 1.20 – 1.13 (m, 1H), 1.10 (m, 1H), 1.01 (d, *J* = 6.5 Hz, 3H), 0.94 – 0.85 (m, 1H), 0.77 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.1, 136.2, 131.9 130.4, 121.8, 60.4 (q, *J* = 36.7 Hz), 57.8, 36.3, 35.6, 19.5, 17.6, 14.1; HRMS (APCI) calcd for $C_{15}H_{17}O_2BrF_3$ ($[M-H]^+$): 365.0369 found 365.0370; IR (neat): 2961, 2932, 1753, 1489, 1279, 1164, 1122, 1074, 1011, 979, 819; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.5% isopropanol in hexane, 0.7 mL/min, 1 mg/mL, 160 min, UV 210 nm) retention times of 84.8 min (major) and 141.4 min (minor), 99% e.e..



2,2,2-Tribromoethyl (*2S,3R*)-2-(4-bromophenyl)-3-methylhexanoate.This compound was prepared according to the general procedure A for Rh_2[*R*-*3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$-catalyzed C–H functionalization. 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 177mg, 1.0 equiv.) in 3 mL *n*-pentane and Rh_2[*R*-*3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$ (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL *n*-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (183 mg, 95% yield).

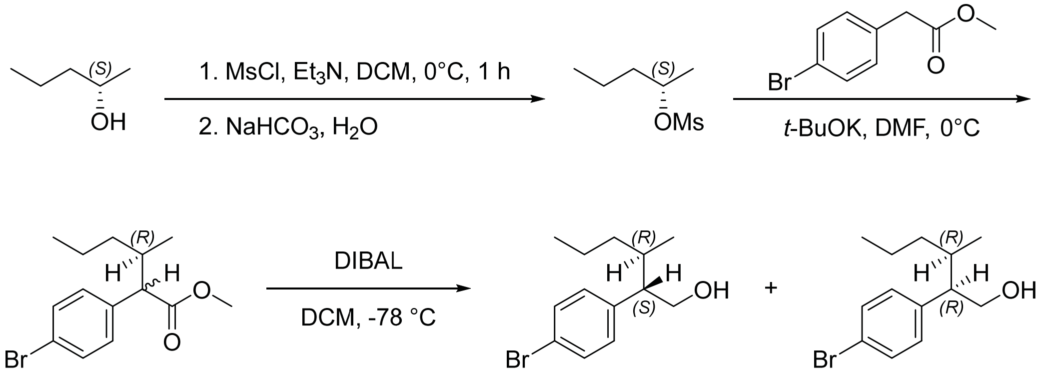
Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 19, C3 was not detected; and the dr of C2 was 21: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

$[\alpha]^{20}_{D}$ 6.8° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 4.92 (d, *J* = 12.3 Hz, 1H), 4.84 (d, *J* = 12.3 Hz, 1H), 3.40 (d, *J* = 10.6 Hz, 1H), 2.28 (m, 1H), 1.41 – 1.30 (m, 1H), 1.22 – 1.10 (m, 2H), 1.08 (d, *J* = 6.5 Hz, 3H), 0.97 – 0.89 (m, 1H), 0.78 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 136.4, 131.8, 130.7, 121.6, 58.4, 35.9, 35.6, 35.4, 19.5, 18.0, 14.2; IR (neat): 2958, 2929, 1745, 1712, 1488, 1361, 1220, 1115, 1073, 1010, 715, 630; HRMS (NSI) calcd for $C_{15}H_{19}O_2Br_3{}^{81}Br$ ($[M+H]^+$): 548.8092 found 548.8105; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.5% isopropanol in hexane, 0.7 mL/min, 1 mg/mL, 160 min, UV 210 nm) retention times of 84.4 min (major) and 144.6 min (minor), 98% e.e..

1.4 Determination of the Absolute Stereochemistry of the C–H Functionalization Products.

The absolute stereochemistry of the 2,2,2-trichloroethyl-2-(4-bromophenyl)-3-methylhexanoate was determined by the ^{1}H NMR spectra and the HPLC spectra of the authentic product derived from (*S*)-2-pentanol. Diastereomers were determined from ^{1}H NMR spectra; then the absolute stereochemistry was further determined by comparing the HPLC spectra of each derivatives of the authentic sample, racemic sample and the C–H insertion product of *n*-pentane.

Procedure for the synthesis of authentic sample derived from (*S*)-2-pentanol



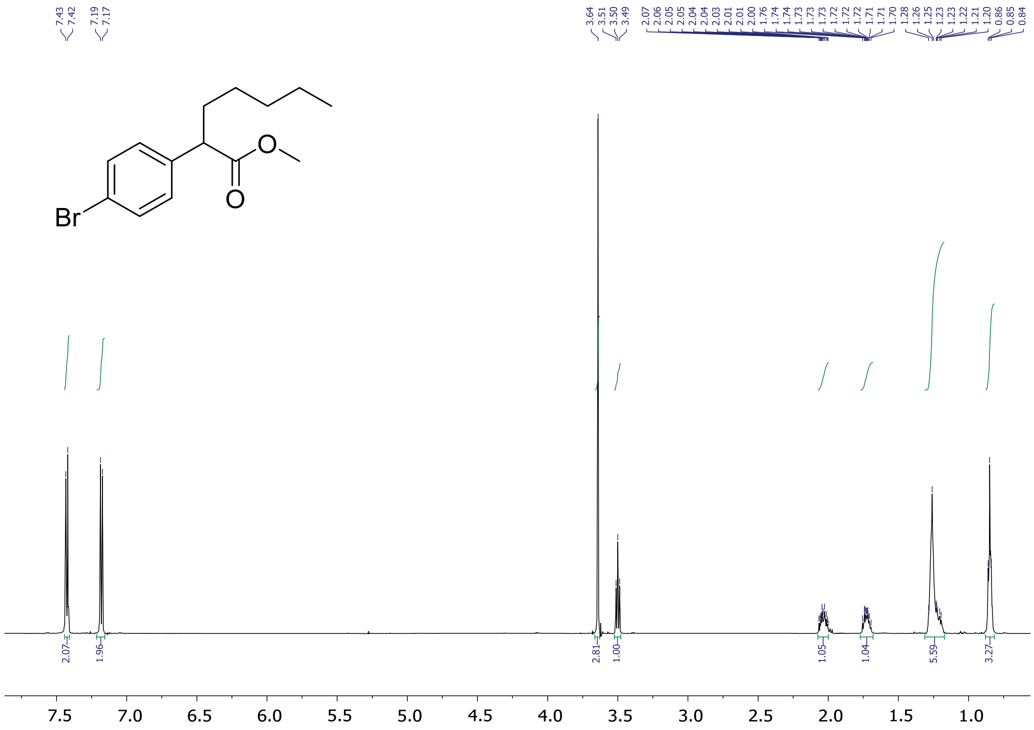
At room temperature, a three-neck flask with internal thermometer, dropping funnel and stirrer under N_2 atmosphere; (*S*)-2-pentanol (882 mg, 10 mmol, 1.0 equiv.), triethylamine (1.32 g, 13 mmol, 1.3 equiv.) and dried DCM (10 mL) were placed. To the mixture, methanesulfonyl chloride (MsCl) (1.49 g, 13 mol, 1.3 equiv.) was added undiluted within 5 min at 0 °C, where a precipitate was formed. Subsequently, the mixture was stirred for 60 min at 0 °C, hydrolyzed with 30 mL of saturated sodium hydrogencarbonate solution and stirred for 15 min. After phase separation, the mixture was washed with 30 mL of water and the organic phase was then dried over sodium sulfate and solvent was distilled to give colorless oil, the crude was used directly for the next step without further purification.

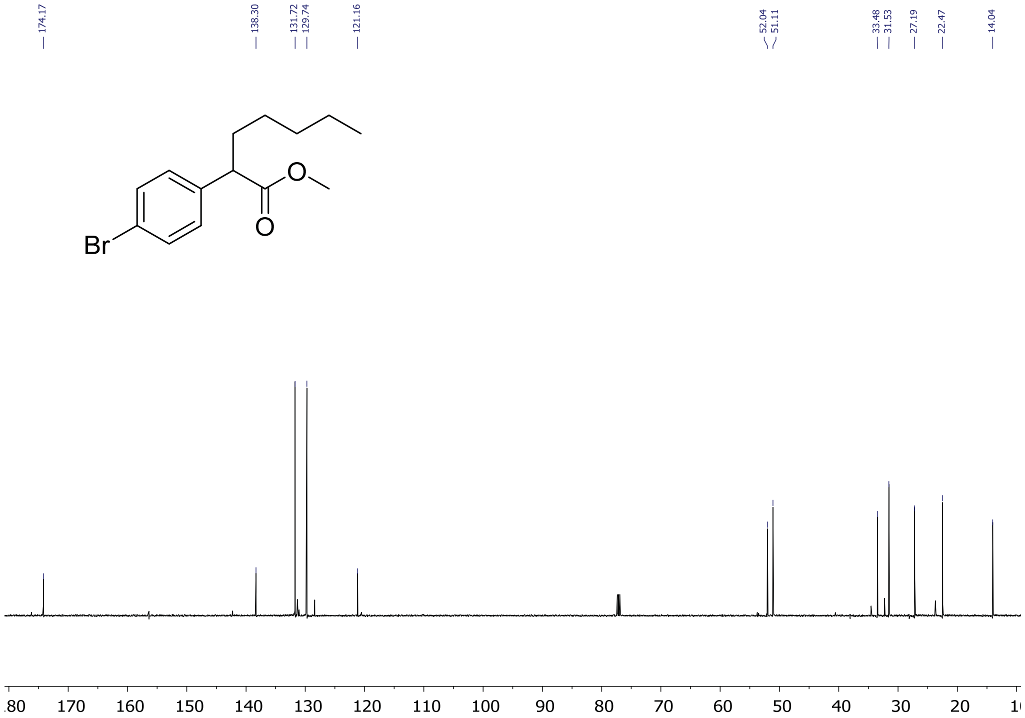
A round bottom flask with stirrer was initially charged with *t*-BuOK (817 mg, 7.3 mmol, 1.2 equiv.) and cooled down to 0 °C, vacuum/N_2 three times to maintain N_2 atmosphere, then 10 mL of dry DMF was added and maintain at 0 °C for 10 min. Subsequently, methyl 2-(4-bromophenyl)acetate (1.39 g, 6.1 mmol, 1.0 equiv.) was added dropwise at 0 °C. The clear mixture was stirred at 0°C for 10 min, and (*S*)-pentan-2-yl methanesulfonate (1.21 g, 7.3 mmol, 1.2 equiv.) was added undiluted. The mixture was cooled to 0°C and stirred for

2 h. After warmed up to 25°C, the suspension was added with 10 mL of water and extracted with 25 mL of ethyl acetate, the organic phase was washed with 15 mL of saturated NaCl aqueous solution and then dried over magnesium sulfate. After solvent had been distilled, the crude mixture was purified by silica gel column chromatography (hexanes/diethyl ether = 65/1) to give colorless oil.

To a stirred solution of the ester (0.1 mmol, 1.0 equiv.) in DCM (3 mL) was added 1 M DIBAL in DCM (0.22 mL, 0.22 mmol, 2.2 equiv.) slowly at -78 °C. The mixture was stirred for 2 h and allowed to warm up to rt. Methanol (0.5 mL) was added into the reaction solution and stirred for 20 min. The reaction mixture was extracted by DCM, the organic layer was washed with saturated NaCl (10 mL). The organic layer was dried ($MgSO_4$) and filtered. Then the filtrate was concentrated, and the resulting crude residue was analyzed by ^1H NMR and purified by flash column chromatography (hexanes/diethyl ether = 9/1) to give white solid.

1.5 NMR Spectra

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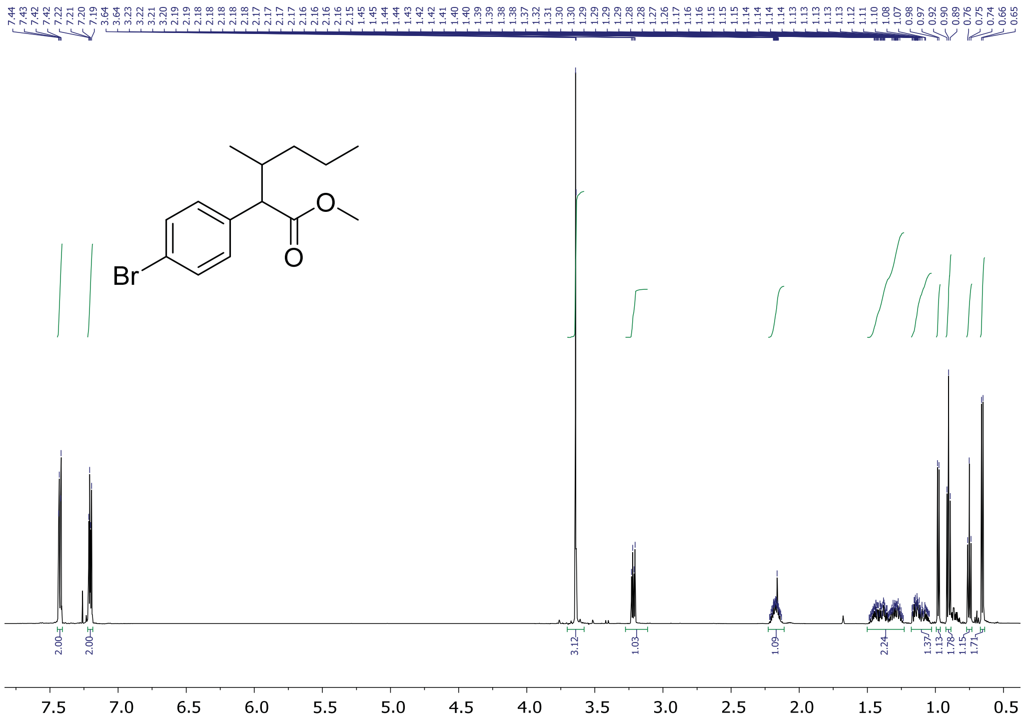
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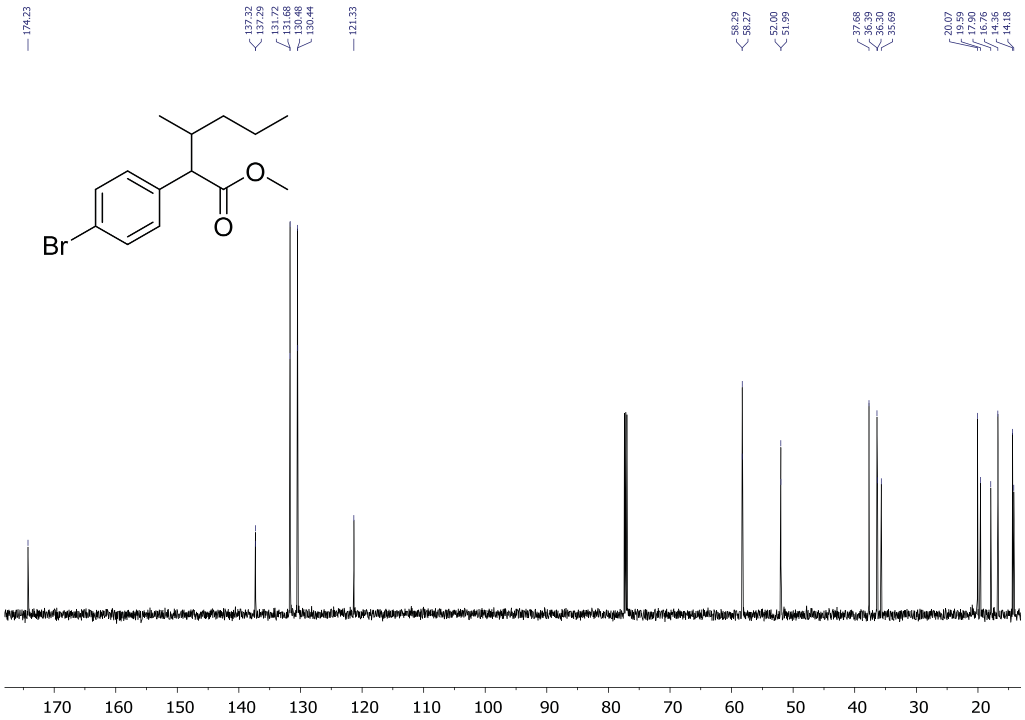
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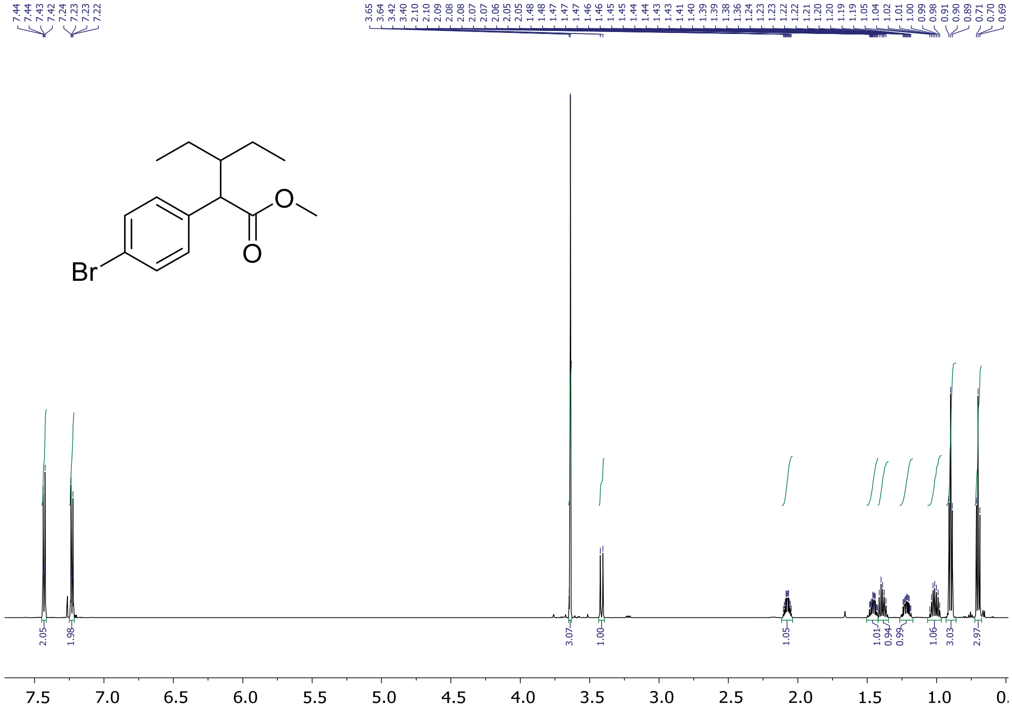
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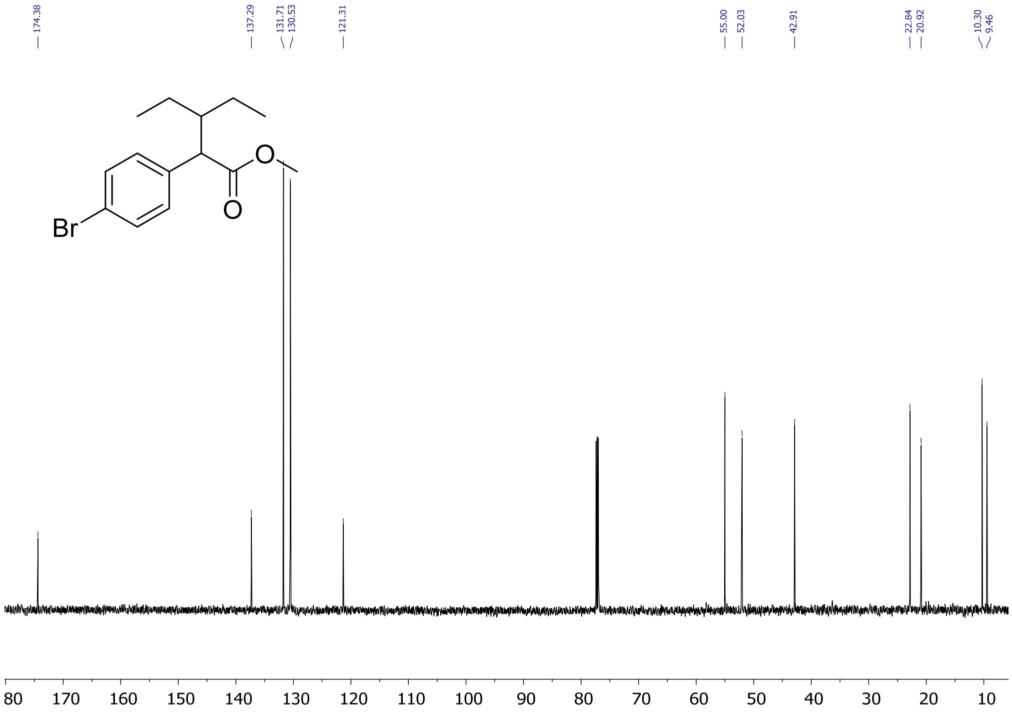
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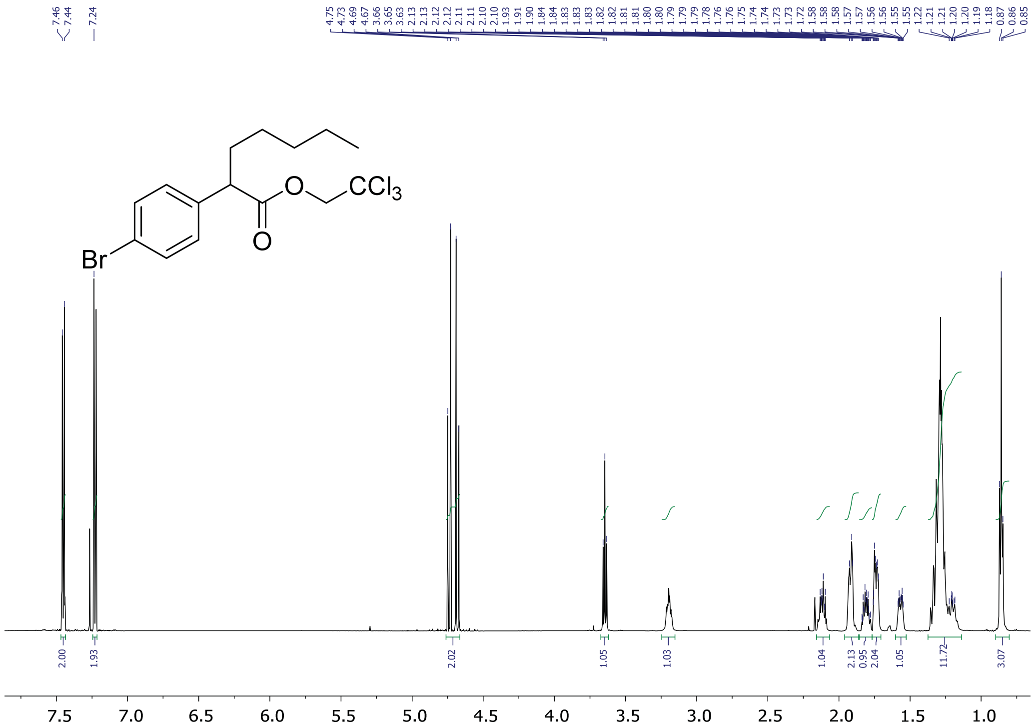
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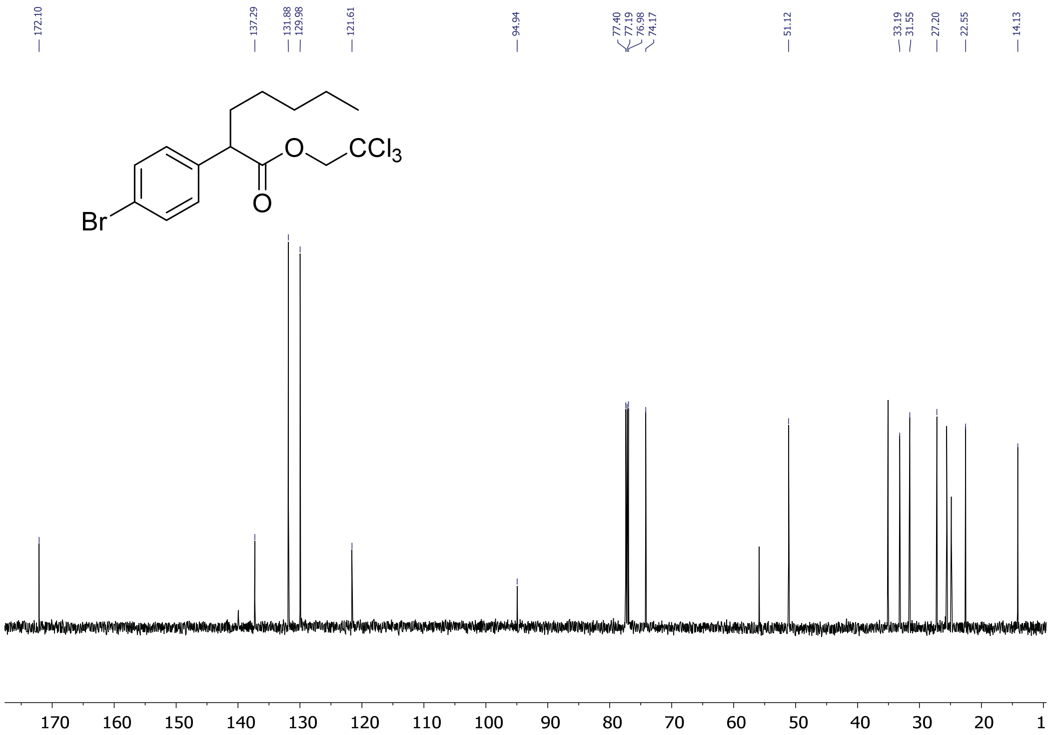
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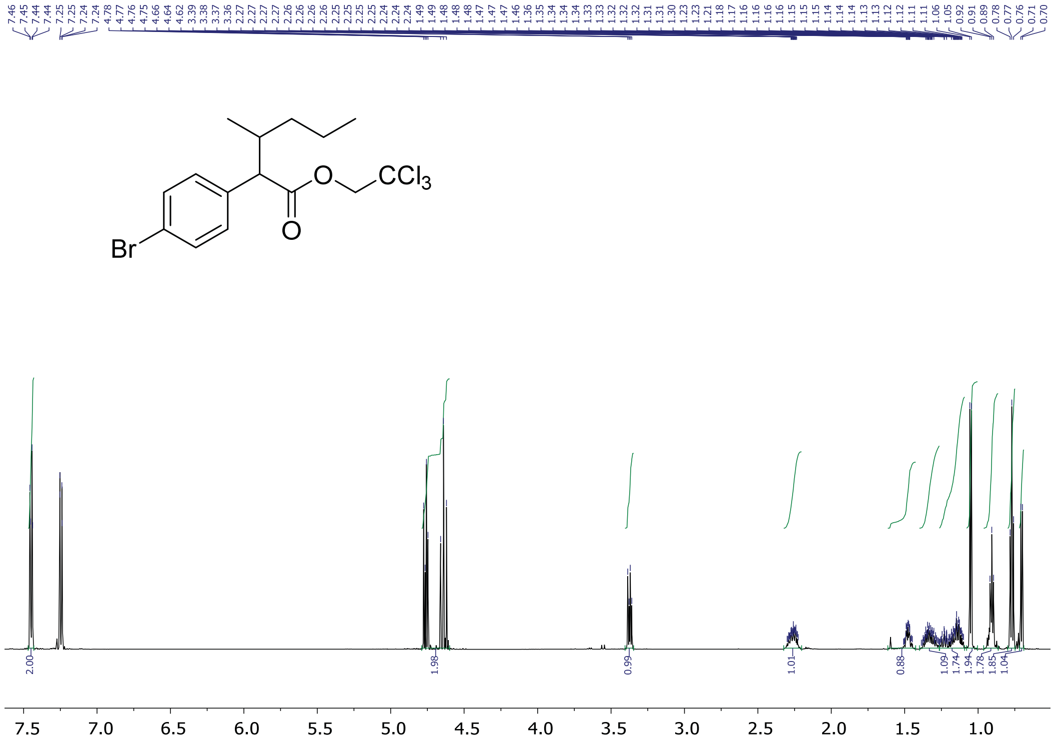
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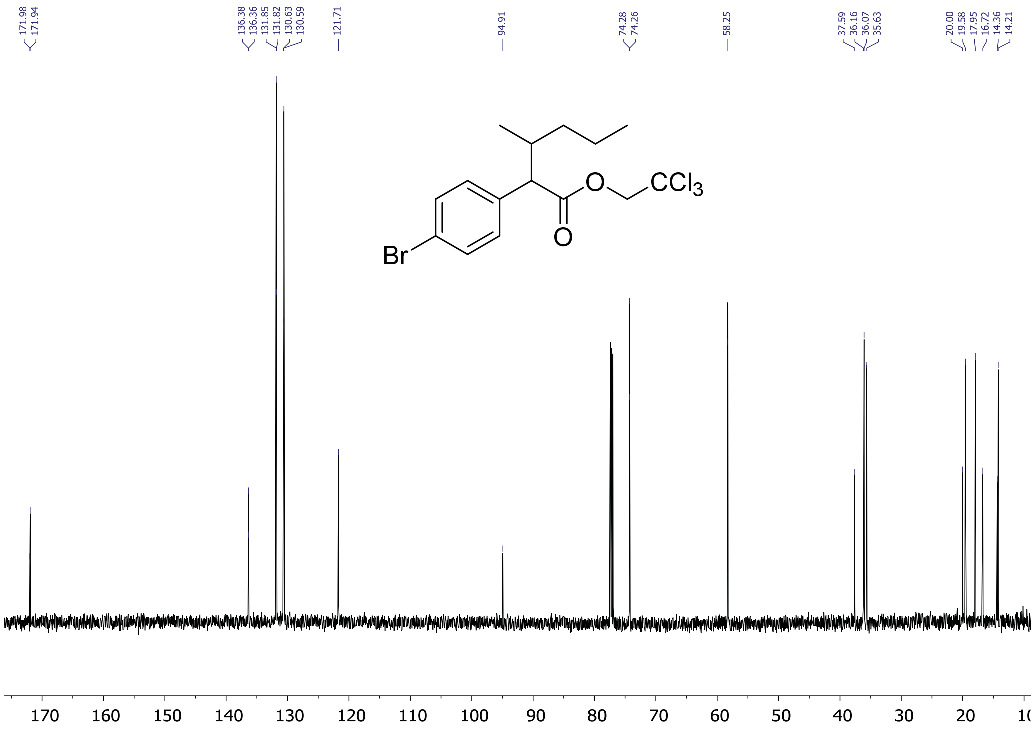
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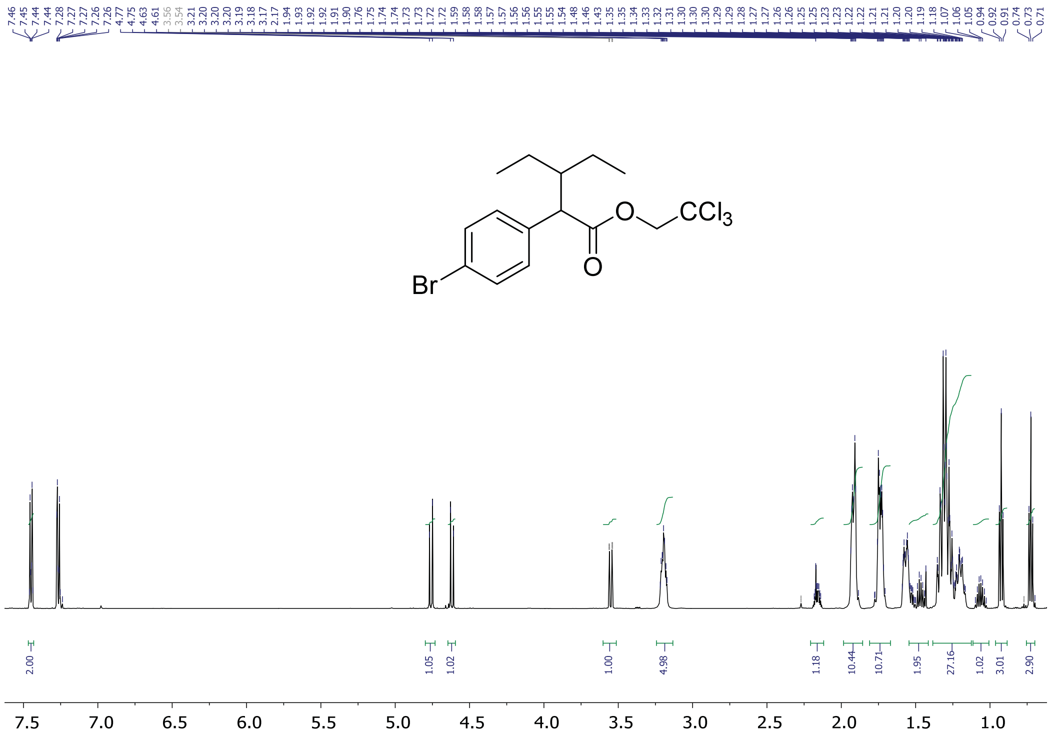
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1.02
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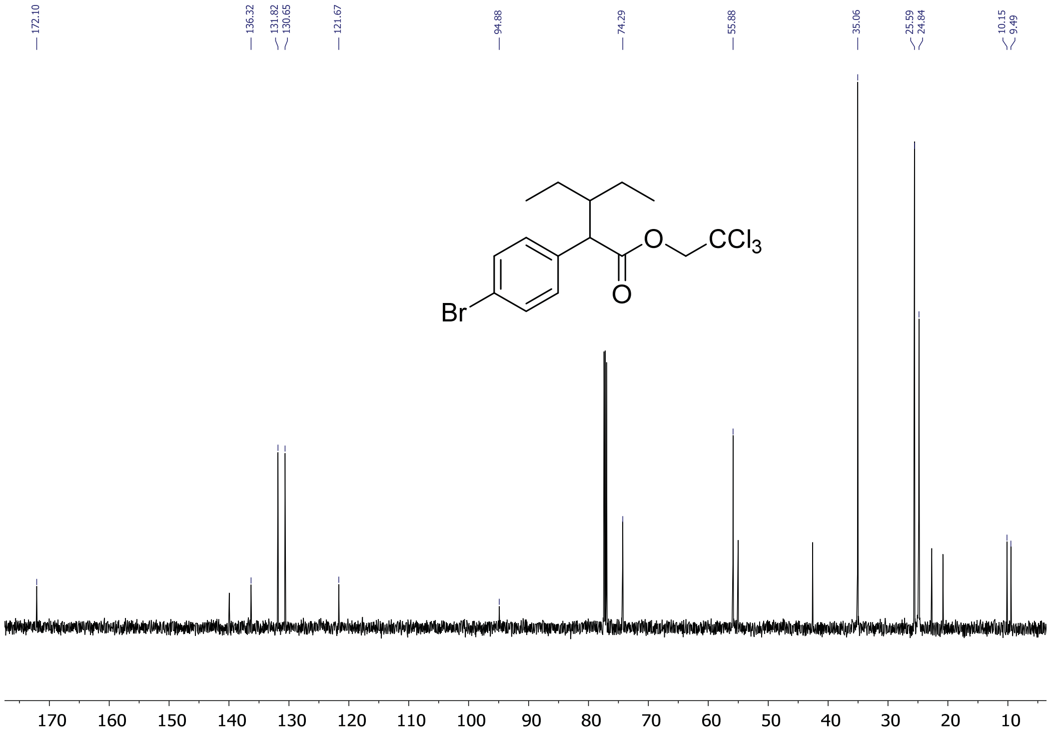
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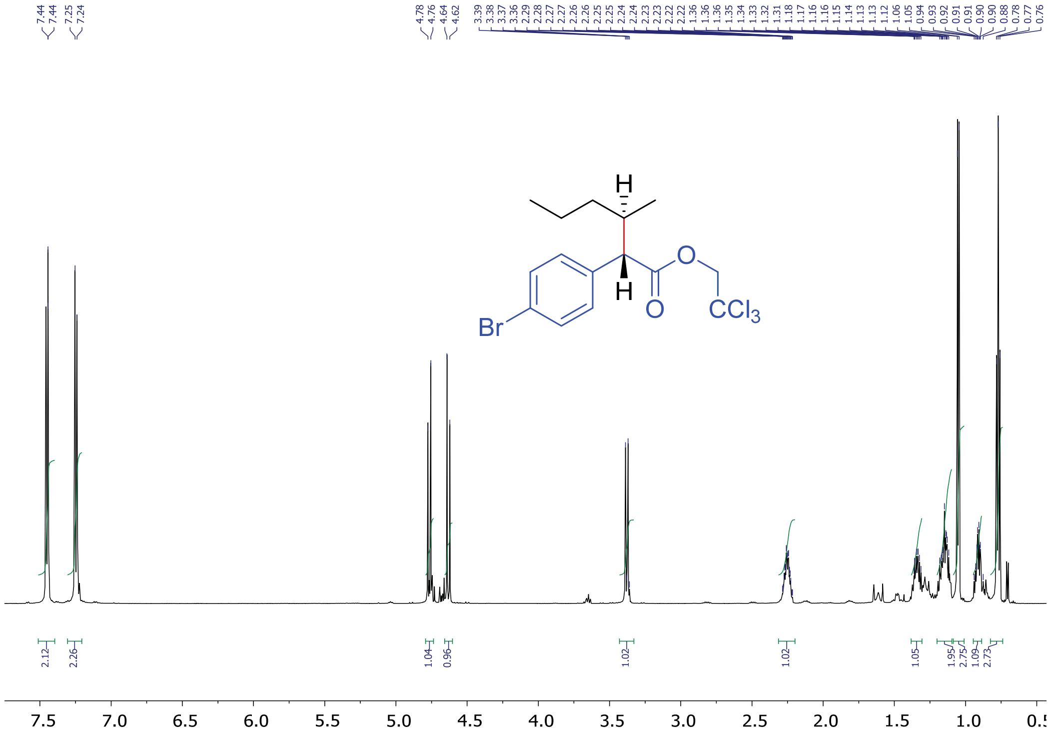
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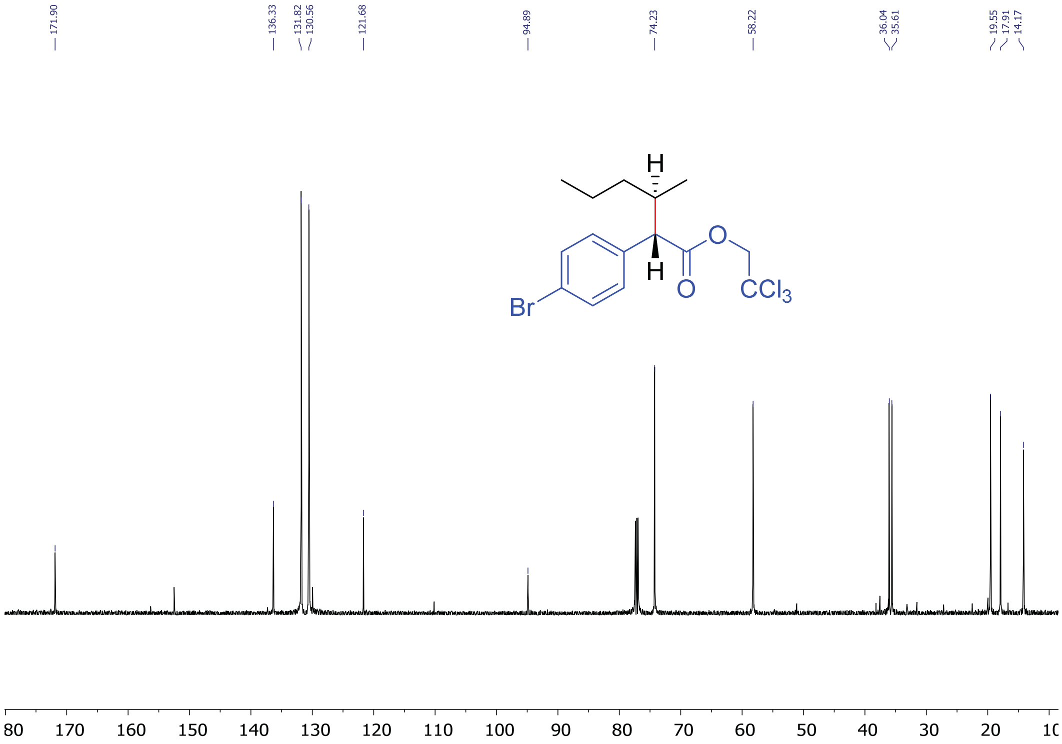
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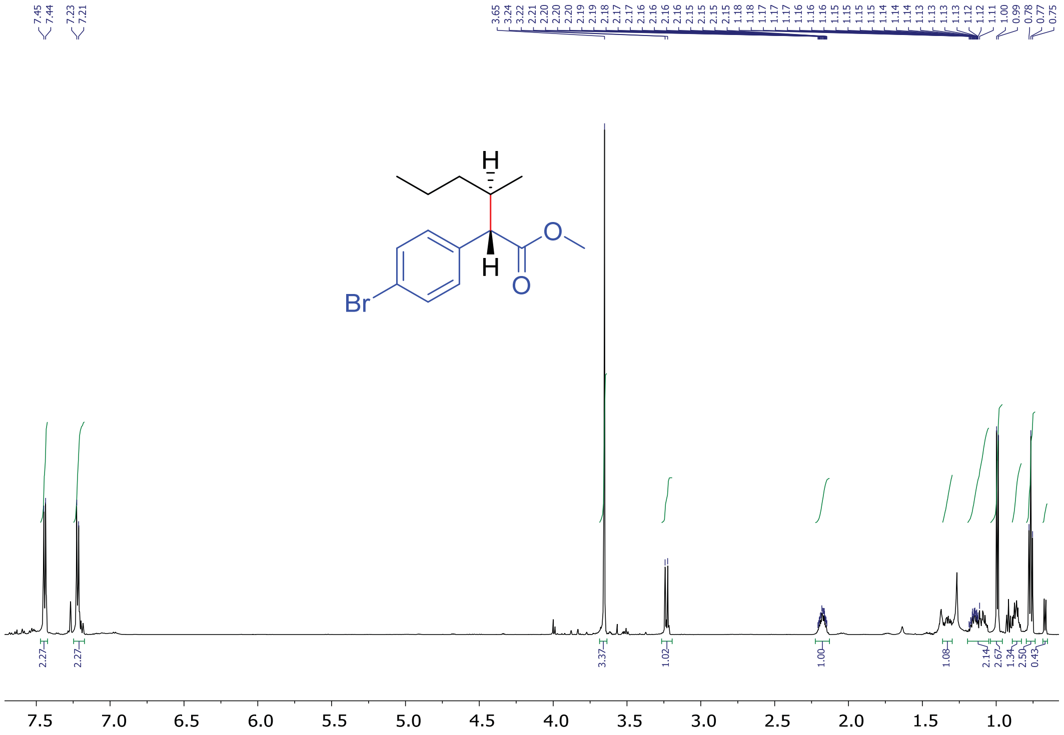
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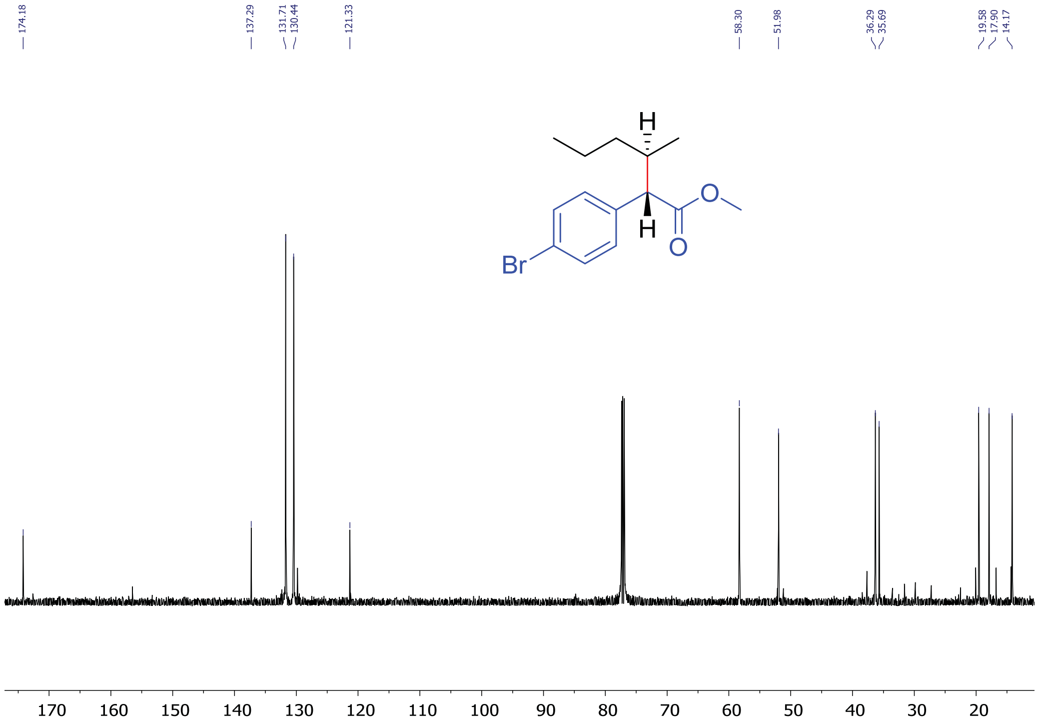
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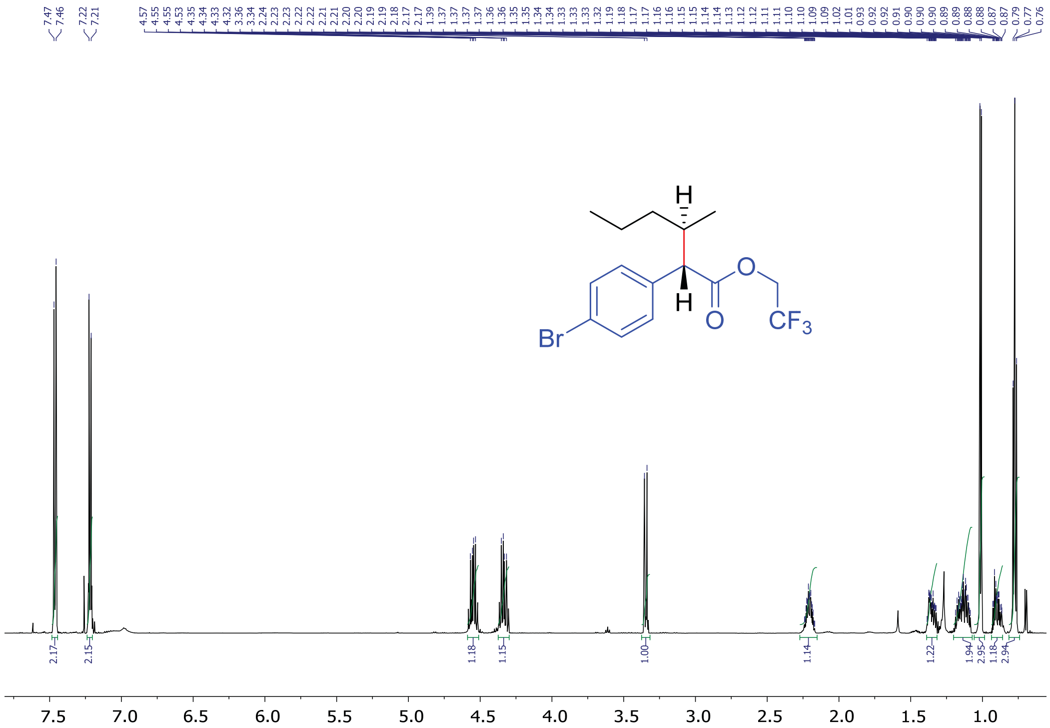
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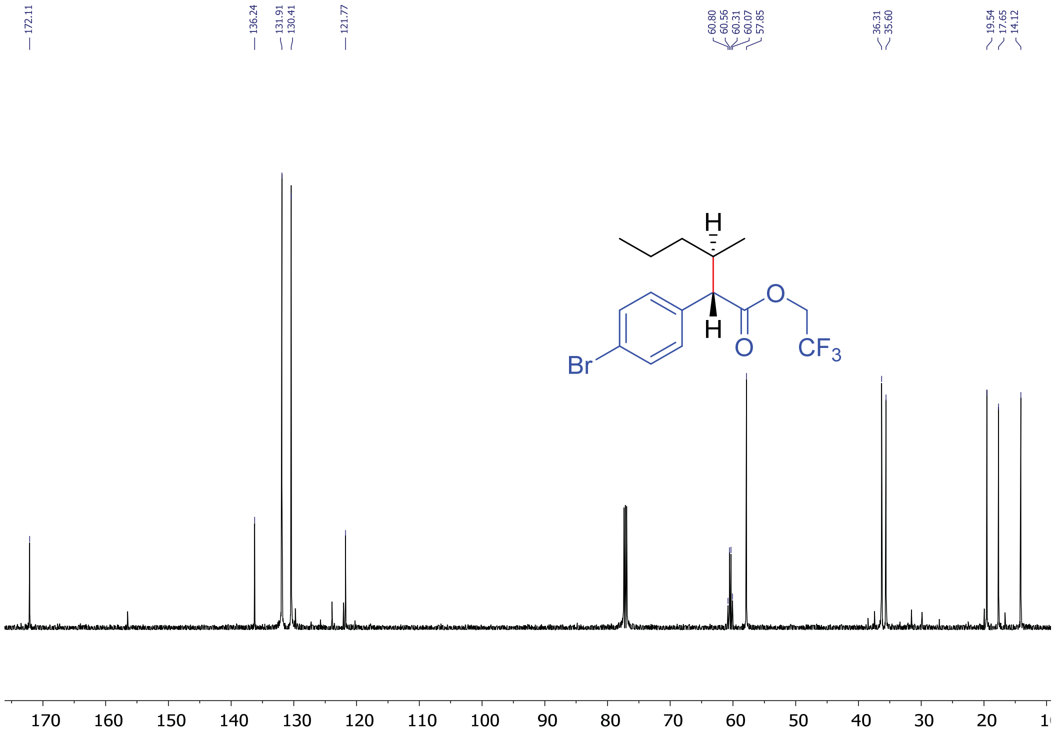
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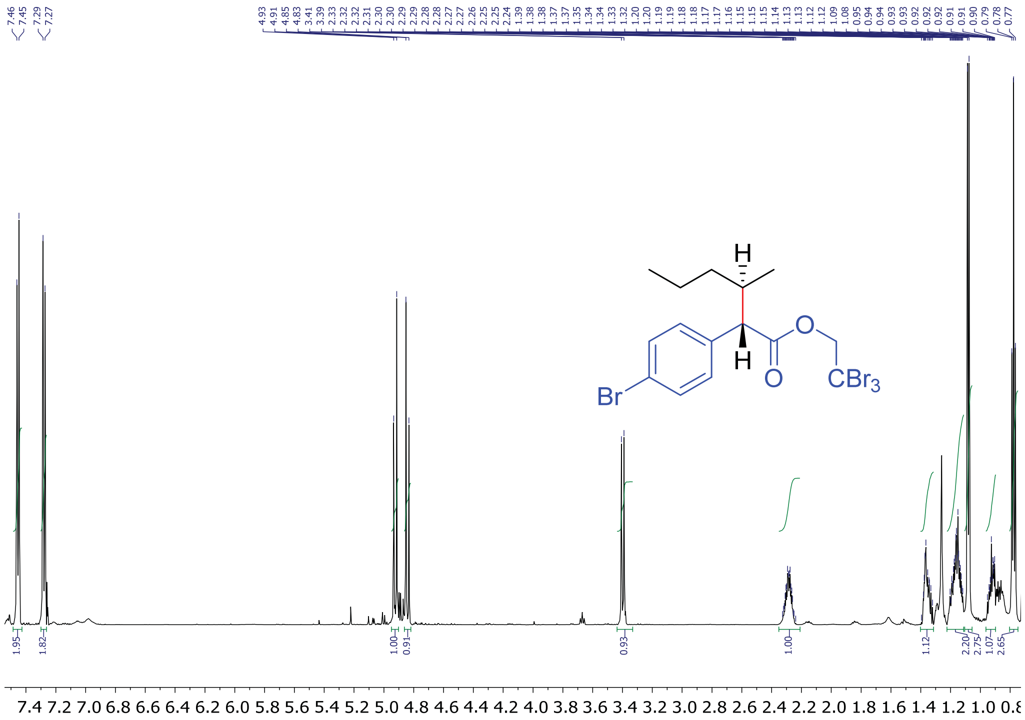
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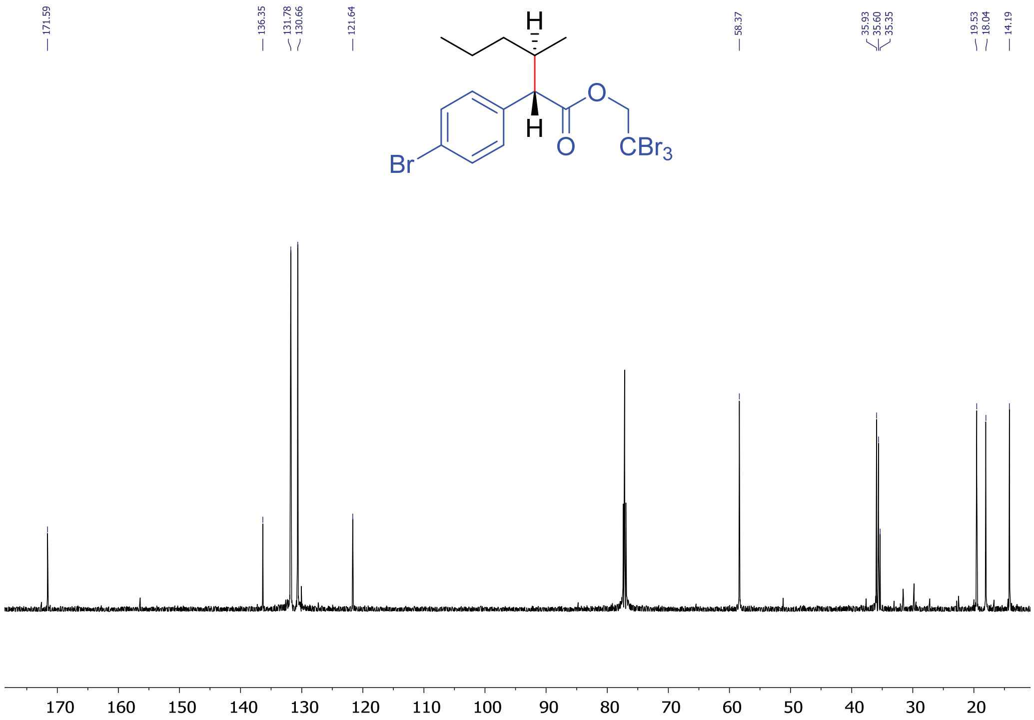
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CBr3
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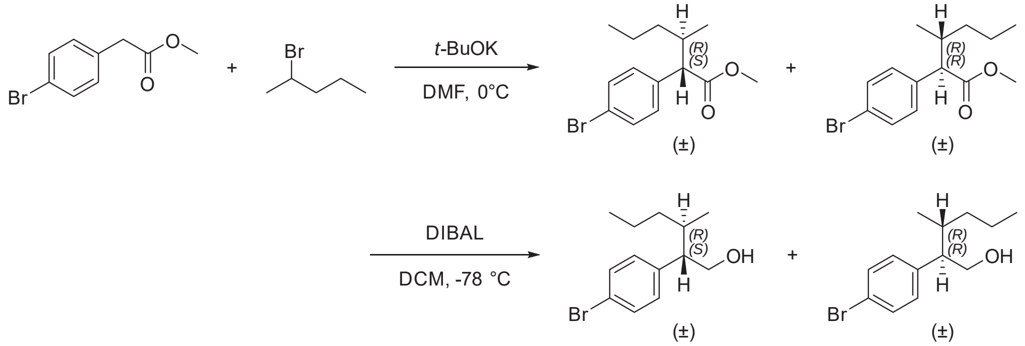
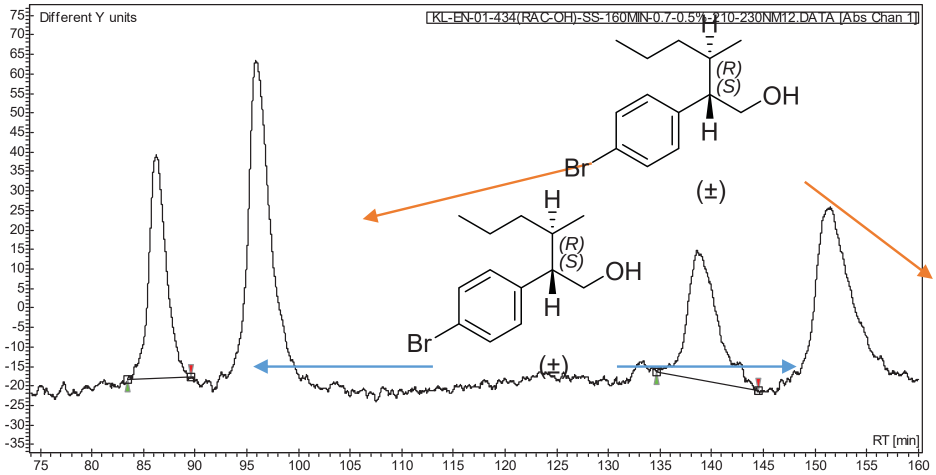
1.6 HPLC Spectra

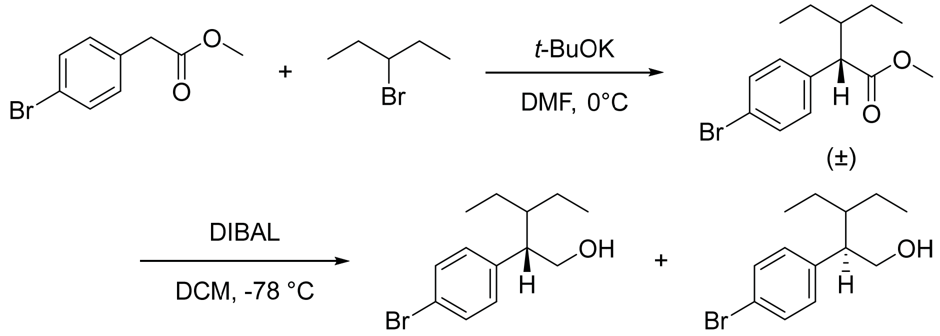
Authentic samples of C2 insertion products of pentane were synthesized, and the corresponding derivatives were separated on the HPLC. Then the diastereomers were differentiated and assigned by dr which was obtained from 1H NMR spectrum.

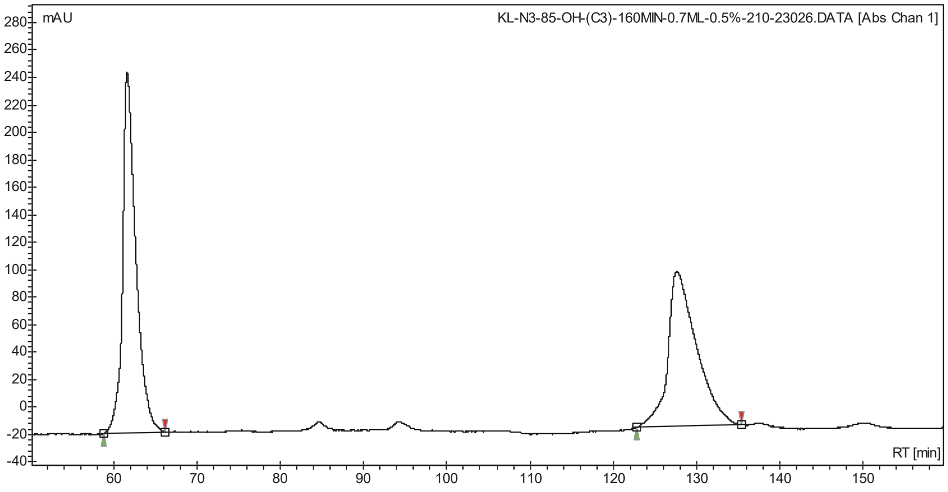




#	Time [Min]	Area % [%]
1	86.20	50.191
2	138.60	49.809

Authentic samples of C3 and C1 insertion products of pentane were synthesized. In order to confirm the assignments of the peaks of C2 insertion products on the HPLC, the corresponding derivatives of C3 and C1 insertion products were run on the HPLC under the same condition as C2 insertion products'. From the following HPLC spectra, the retention times of the derivatives of C3 and C1 insertion products were different from the retention times of the derivatives of C2 insertion products. In conclusion, the assignments of the peaks of C2 insertion products were confirmed.





#	Time [Min]	Area % [%]
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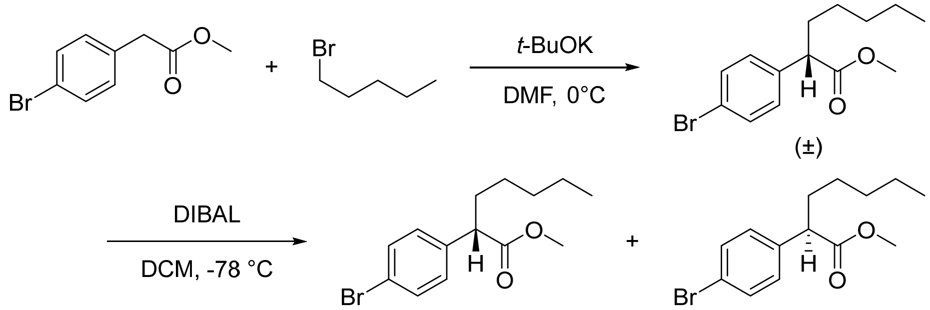
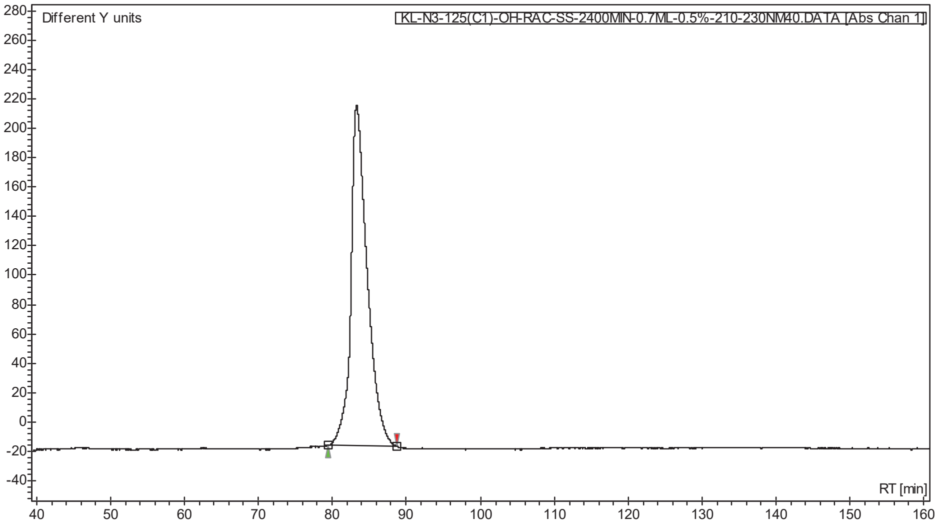
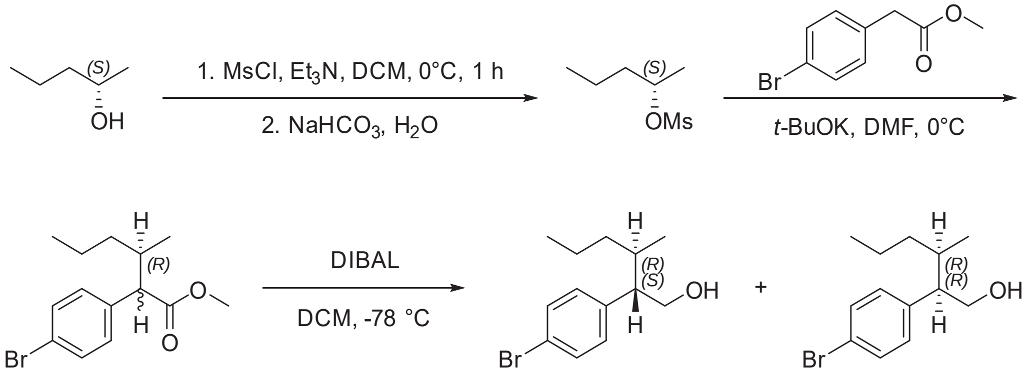
1	127.64	48.108

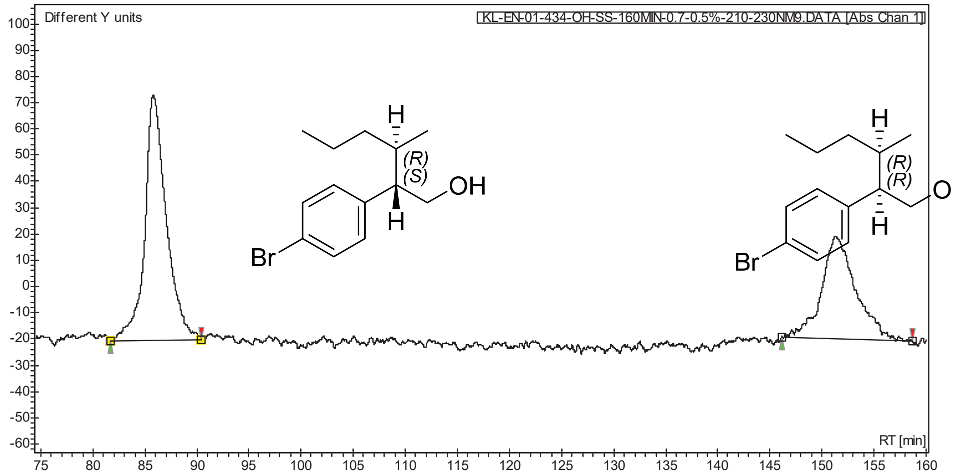




#	Time [Min]	Area % [%]
1	83.27	100.000

The enantiomers cannot be separated under this condition

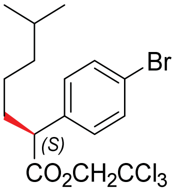




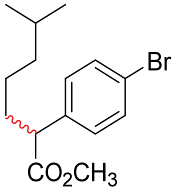
#	Time [Min]	Area % [%]	
1	85.83	60.072	> 99% e.e.
2	151.33	39.928	> 99% e.e.

2. Characterization of 2-Methylpentane Functionalization Products

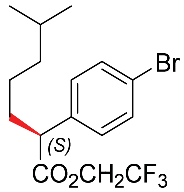
2.1 Characterization



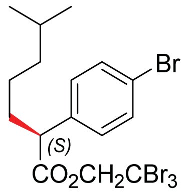
2,2,2-Trichloroethyl (*S*)-2-(4-bromophenyl)-6-methylheptanoate. $[\alpha]^{20}_{D}$ +5.9° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:20 v/v); ^1H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 3.65 (t, *J* = 7.7 Hz, 1H), 2.10 (dddd, *J* = 13.7, 9.9, 8.1, 5.6 Hz, 1H), 1.79 (dddd, *J* = 13.3, 10.1, 7.4, 5.4 Hz, 1H), 1.50 (tt, *J* = 13.2, 6.6 Hz, 1H), 1.36 – 1.25 (m, 2H), 1.22 – 1.13 (m, 2H), 0.84 (d, *J* = 6.5 Hz, 3H), 0.83 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.14, 137.32, 131.90, 129.98, 121.63, 94.95, 74.21, 51.17, 38.64, 33.47, 27.90, 25.35, 22.72, 22.62; HRMS (NSI) calcd for $C_{16}H_{19}BrCl_3O_2$ ($[M-H]^-$): 426.9629 found 426.9635; IR (neat): 2954, 2926, 2868, 1752, 1488, 1466, 1368, 1261, 1142, 1121, 1074, 1012, 823, 800, 758, 720.



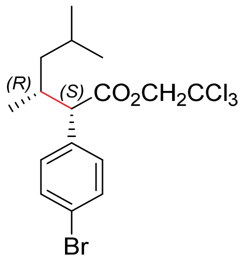
Methyl 2-(4-bromophenyl)-6-methylheptanoate. TLC (diethyl ether: hexanes, 1:20 v/v); ^1H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 3.65 (s, 3H), 3.50 (t, *J* = 7.7 Hz, 1H), 2.01 (dt, *J* = 13.9, 6.8 Hz, 1H), 1.71 (td, *J* = 13.9, 7.2 Hz, 1H), 1.49 (dp, *J* = 13.2, 6.6 Hz, 1H), 1.20 (m, 4H), 0.84 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.32, 138.38, 131.82, 129.82, 121.26, 77.37, 77.16, 76.95, 52.18, 51.21, 38.67, 33.80, 27.86, 25.38, 22.69, 22.66; HRMS (NSI) calcd for $C_{15}H_{22}BrO_2$ ($[M+H]^+$): 313.0798 found 313.0799; IR (neat): 2951, 2867, 1735, 1488, 1434, 1213, 1192, 1159, 1074, 1011, 820, 759.



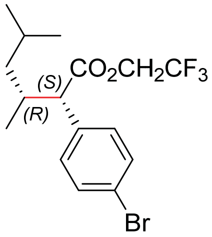
2,2,2-Trifluoroethyl (*S*)-2-(4-bromophenyl)-6-methylheptanoate. $[\alpha]^{20}_{D}$ +29.6° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:20 v/v); ^1H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, J = 7.2 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 4.53 (ddq, J = 16.9, 12.8, 8.4 Hz, 1H), 4.35 (ddq, J = 29.5, 12.8, 8.5 Hz, 1H), 3.61 (t, J = 7.7 Hz, 1H), 2.04 (ddt, J = 14.2, 8.3, 4.3 Hz, 1H), 1.80 – 1.70 (m, 1H), 1.49 (dq, J = 13.2, 6.6 Hz, 1H), 1.32 – 1.26 (m, 2H), 1.20 – 1.15 (m, 2H), 0.84 (d, J = 6.2 Hz, 3H), 0.84 (d, J = 6.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.30, 137.21, 131.99, 130.47, 129.78, 125.72, 123.88, 122.05, 120.21, 60.95, 60.71, 60.47, 60.23, 50.83, 38.58, 33.64, 27.87, 25.24, 22.66, 22.60; HRMS (NSI) calcd for $C_{16}H_{20}BrF_3O_2$ ($[M]^+$): 380.0593 found 380.0594; IR (neat): 2956, 2928, 2870, 1755, 1489, 1407, 1281, 1167, 1143, 1075, 1012, 978, 819.



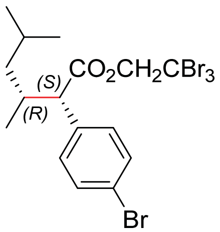
2,2,2-Tribromoethyl (*S*)-2-(4-bromophenyl)-6-methylheptanoate. $[\alpha]^{20}_{D}$ +9.7° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:20 v/v); ^1H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 4.89 (d, *J* = 6.2 Hz, 2H), 3.67 (t, *J* = 7.7 Hz, 1H), 2.14 (dddd, *J* = 13.6, 10.0, 8.0, 5.5 Hz, 1H), 1.81 (dddd, *J* = 13.3, 10.2, 7.5, 5.4 Hz, 1H), 1.50 (dp, *J* = 13.2, 6.6 Hz, 1H), 1.37 – 1.25 (m, 3H), 1.21 (m, 2H), 0.84 (d, *J* = 6.7 Hz, 3H), 0.83 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.86, 137.35, 131.88, 130.10, 121.61, 77.10, 51.32, 38.66, 33.40, 27.91, 25.41, 22.75, 22.64; HRMS (NSI) calcd for $C_{16}H_{21}Br_4O_2$ ($[M+H]^+$): 560.8270 found 560.8278; IR (neat): 2952, 2867, 1747, 1488, 1466, 1366, 1140, 1117, 1073, 1011, 821, 727.



2,2,2-Trichloroethyl (2*S*,3*R*)-2-(4-bromophenyl)-3,5-dimethylhexanoate.$[\alpha]^{20}_{D}$ +14° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:20 v/v); ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 3.33 (d, *J* = 10.5 Hz, 1H), 2.29 (dddd, *J* = 16.8, 10.4, 6.5, 3.6 Hz, 1H), 1.03 (d, *J* = 6.5 Hz, 3H), 0.93 – 0.81 (m, 3H), 0.79 (d, *J* = 6.6 Hz, 3H), 0.74 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.97, 136.31, 131.83, 130.61, 121.70, 74.24, 58.79, 43.02, 34.25, 25.08, 24.18, 21.06, 18.04; HRMS (NSI) calcd for $C_{16}H_{21}BrCl_3O_2$ ($[M+H]^+$): 428.9785 found 428.9793; IR (neat): 2956, 2928, 2869, 1750, 1488, 1368, 1142, 1118, 1074, 1011, 825, 805, 759, 719.

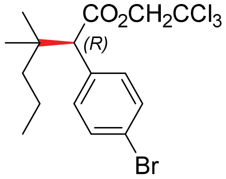


2,2,2-Trifluoroethyl (2*S,3R*)-2-(4-bromophenyl)-3,5-dimethylhexanoate.$[\alpha]^{20}_{D}$ +30.7° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:20 v/v); ^1H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 4.55 (dd, *J* = 12.7, 8.5 Hz, 1H), 4.33 (dd, *J* = 12.7, 8.4 Hz, 1H), 3.30 (d, *J* = 10.4 Hz, 1H), 2.23 (ddtd, *J* = 16.7, 10.2, 6.5, 3.9 Hz, 1H), 0.99 (d, *J* = 6.5 Hz, 3H), 0.93 – 0.81 (m, 3H), 0.79 (d, *J* = 6.6 Hz, 3H), 0.73 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.11, 136.16, 131.89, 130.45, 121.77, 60.87, 60.58, 60.29, 60.00, 58.38, 43.00, 34.50, 25.07, 24.14, 21.02, 17.79; HRMS (NSI) calcd for $C_{16}H_{21}BrF_3O_2$ ($[M+H]^+$): 381.0672 found 381.0676; IR (neat): 2958, 2931, 2872, 1753, 1489, 1407, 1280, 1165, 1141, 1123, 1074, 1012, 979, 818, 758.



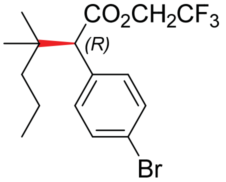
2,2,2-Tribromoethyl (2S,3R)-2-(4-bromophenyl)-3,5-dimethylhexanoate.

[α]$^{20}_{D}$ +12.7° (c = 1.00, CHCl$_3$); TLC (diethyl ether: hexanes, 1:20 v/v); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 3H), 4.92 (d, *J* = 12.3 Hz, 1H), 4.84 (d, *J* = 12.3 Hz, 1H), 3.35 (d, *J* = 10.6 Hz, 1H), 2.41 – 2.25 (m, 1H), 1.06 (d, *J* = 6.4 Hz, 3H), 0.94 – 0.82 (m, 3H), 0.79 (d, *J* = 6.6 Hz, 3H), 0.75 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 171.69, 136.37, 131.81, 130.72, 121.68, 58.98, 43.04, 34.17, 25.10, 24.20, 21.08, 18.19; HRMS (NSI) calcd for $C_{16}H_{21}Br_4O_2$ ([M+H]$^+$): 560.8270 found 560.8280; IR (neat): 2954, 2926, 2868, 1747, 1488, 1385, 1366, 1142, 1116, 1074, 1011, 821, 715.

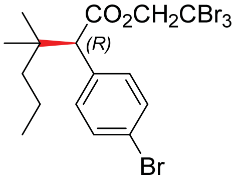


2,2,2-Trichloroethyl *(R)*-2-(4-bromophenyl)-3,3-dimethylhexanoate.

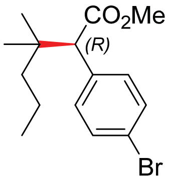
[α]$^{20}_{D}$ -4.0° (c = 1.00, CHCl$_3$); TLC (diethyl ether: hexanes, 1:20 v/v); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.44 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 4.84 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 3.63 (s, 1H), 1.35 (tdd, *J* = 11.5, 8.9, 5.2 Hz, 3H), 1.25 – 1.16 (m, 1H), 1.04 (s, 3H), 0.92 (s, 3H), 0.87 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 171.21, 134.32, 131.95, 131.16, 121.76, 94.89, 74.26, 59.78, 43.19, 37.53, 24.70, 24.37, 17.16, 14.92; HRMS (NSI) calcd for $C_{16}H_{19}BrCl_3O_2$ ([M-H]$^-$): 426.9629 found 426.9633; IR (neat): 2959, 2872, 1748, 1489, 1370, 1118, 1076, 1011, 826, 761, 716.



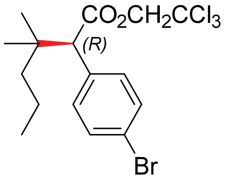
2,2,2-Trifluoroethyl *(R)*-2-(4-bromophenyl)-3,3-dimethylhexanoate.$[\alpha]^{20}_{D}$ -13.6° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:20 v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 4.62 (dq, *J* = 12.7, 8.5 Hz, 1H), 4.26 (dq, *J* = 12.7, 8.5 Hz, 1H), 3.59 (s, 1H), 1.37 – 1.26 (m, 3H), 1.21 – 1.11 (m, 1H), 1.00 (s, 3H), 0.89 (s, 3H), 0.87 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.26, 134.13, 131.83, 131.20, 121.82, 60.16 (q, *J* = 36.5 Hz), 59.31, 43.07, 37.55, 24.54, 24.24, 17.13, 14.81; HRMS (NSI) calcd for $C_{16}H_{21}BrF_3O_2$ ($[M+H]^+$): 381.0673 found 381.0673; IR (neat): 2963, 2935, 2874, 1752, 1489, 1414, 1278, 1164, 1122, 1076, 1012, 980, 825.



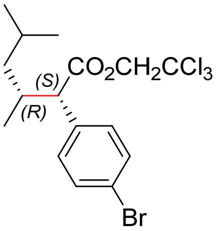
2,2,2-Tribromoethyl *(R)*-2-(4-bromophenyl)-3,3-dimethylhexanoate.$[\alpha]^{20}_{D}$ -8.3° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:20 v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 4.98 (d, *J* = 12.3 Hz, 1H), 4.81 (d, *J* = 12.3 Hz, 1H), 3.64 (s, 1H), 1.44 – 1.30 (m, 3H), 1.25 – 1.17 (m, 1H), 1.06 (s, 3H), 0.93 (s, 3H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.05, 134.41, 132.04, 131.16, 121.74, 60.04, 43.24, 37.54, 24.76, 24.46, 17.19, 14.97; HRMS (NSI) calcd for $C_{16}H_{21}Br_4O_2$ ($[M+H]^+$): 560.8270 found 560.8276; IR (neat): 2963, 2935, 2874, 1752, 1489, 1414, 1278, 1164, 1122, 1076, 1012, 980, 825.



Methyl *(R)*-2-(4-bromophenyl)-3,3-dimethylhexanoate.$[\alpha]^{20}_{D}$ -12.1° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:20 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 3.64 (s, 3H), 3.48 (s, 1H), 1.29 (m, 3H), 1.14 (td, *J* = 9.9, 3.4 Hz, 1H), 0.98 (s, 3H), 0.88 (s, 3H), 0.86 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 173.27, 135.01, 131.80, 130.89, 121.29, 59.60, 51.47, 42.99, 37.15, 24.47, 24.18, 17.03, 14.83; HRMS (NSI) calcd for $C_{15}H_{22}BrO_2$ ($[M+H]^+$):313.0798 found 313.0797; IR (neat):2957, 2930, 2872, 1734, 1457, 1434, 1195, 1168, 1143, 1076, 1011, 825.

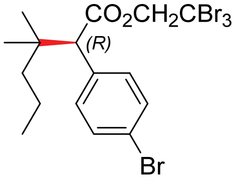


2,2,2-Trichloroethyl *(R)*-2-(4-bromophenyl)-3,3-dimethylhexanoate.[α]$^{20}_{D}$ -4.0° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:20 v/v); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.44 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 4.84 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 3.63 (s, 1H), 1.35 (tdd, *J* = 11.5, 8.9, 5.2 Hz, 3H), 1.25 – 1.16 (m, 1H), 1.04 (s, 3H), 0.92 (s, 3H), 0.87 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 171.21, 134.32, 131.95, 131.16, 121.76, 94.89, 74.26, 59.78, 43.19, 37.53, 24.70, 24.37, 17.16, 14.92; HRMS (NSI) calcd for $C_{16}H_{19}BrCl_3O_2$ ($[M-H]^-$):426.9629 found 426.9633; IR (neat):2959, 2872, 1748, 1489, 1370, 1118, 1076, 1011, 826, 761, 716.

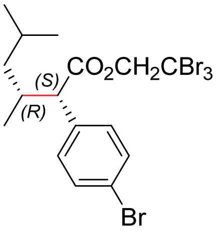


2,2,2-Trichloroethyl (2S,3R)-2-(4-bromophenyl)-3,5-dimethylhexanoate.[α]$^{20}_{D}$ +14° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:20 v/v); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.45 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 3.33 (d, *J* = 10.5 Hz, 1H), 2.29 (dddd, *J* = 16.8, 10.4, 6.5, 3.6 Hz, 1H), 1.03 (d, *J* = 6.5 Hz, 3H), 0.93 – 0.81 (m, 3H), 0.79 (d, *J* = 6.6 Hz, 3H), 0.74 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 171.97, 136.31, 131.83, 130.61, 121.70, 74.24, 58.79, 43.02, 34.25, 25.08, 24.18, 21.06, 18.04; HRMS (NSI) calcd for $C_{16}H_{21}BrCl_3O_2$

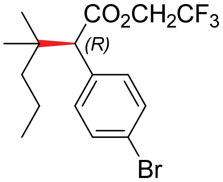
([M+H]$^+$):428.9785 found 428.9793; IR (neat):2956, 2928, 2869, 1750, 1488, 1368, 1142, 1118, 1074, 1011, 825, 805, 759, 719.



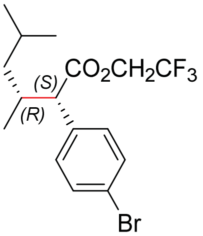
2,2,2-Tribromoethyl *(R)*-2-(4-bromophenyl)-3,3-dimethylhexanoate.$[\alpha]^{20}_{D}$ -8.3° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:20 v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 4.98 (d, *J* = 12.3 Hz, 1H), 4.81 (d, *J* = 12.3 Hz, 1H), 3.64 (s, 1H), 1.44 – 1.30 (m, 3H), 1.25 – 1.17 (m, 1H), 1.06 (s, 3H), 0.93 (s, 3H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.05, 134.41, 132.04, 131.16, 121.74, 60.04, 43.24, 37.54, 24.76, 24.46, 17.19, 14.97; HRMS (NSI) calcd for $C_{16}H_{21}Br_4O_2$ ([M+H]$^+$):560.8270 found 560.8276; IR (neat):2963, 2935, 2874, 1752, 1489, 1414, 1278, 1164, 1122, 1076, 1012, 980, 825.



2,2,2-Tribromoethyl (2S,3R)-2-(4-bromophenyl)-3,5-dimethylhexanoate.$[\alpha]^{20}_{D}$ +12.7° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:20 v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 3H), 4.92 (d, *J* = 12.3 Hz, 1H), 4.84 (d, *J* = 12.3 Hz, 1H), 3.35 (d, *J* = 10.6 Hz, 1H), 2.41 – 2.25 (m, 1H), 1.06 (d, *J* = 6.4 Hz, 3H), 0.94 – 0.82 (m, 3H), 0.79 (d, *J* = 6.6 Hz, 3H), 0.75 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.69, 136.37, 131.81, 130.72, 121.68, 58.98, 43.04, 34.17, 25.10, 24.20, 21.08, 18.19; HRMS (NSI) calcd for $C_{16}H_{21}Br_4O_2$ ([M+H]$^+$):560.8270 found 560.8280; IR (neat):2954, 2926, 2868, 1747, 1488, 1385, 1366, 1142, 1116, 1074, 1011, 821, 715.

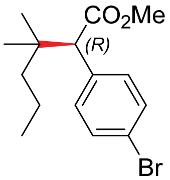


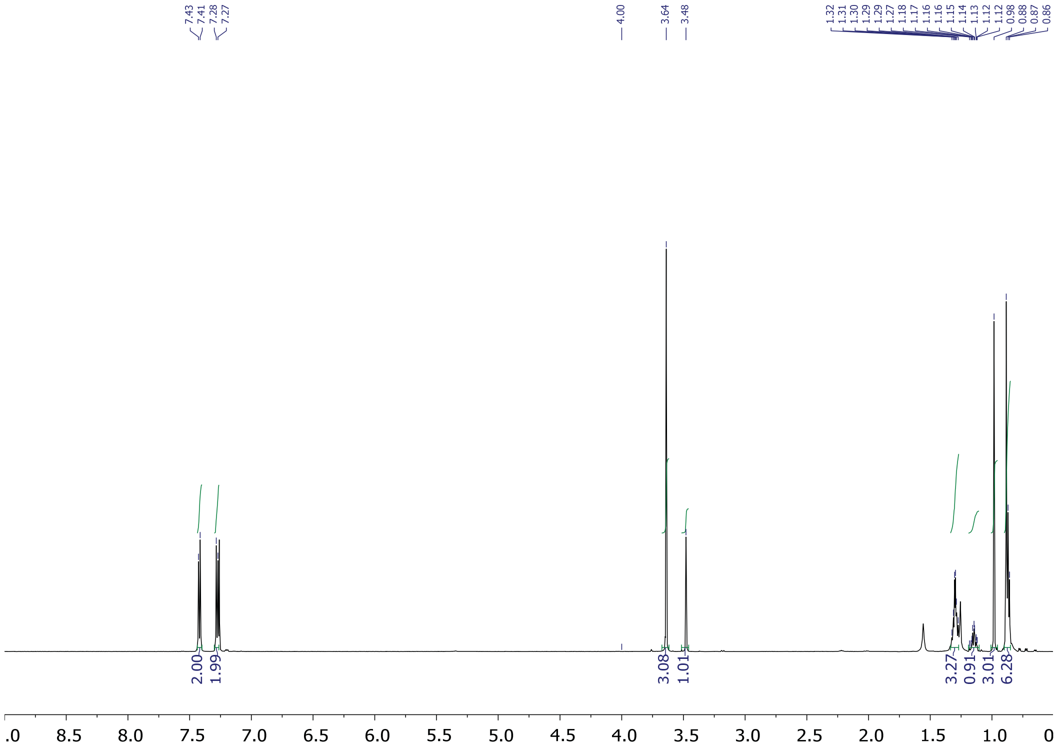
2,2,2-Trifluoroethyl *(R)*-2-(4-bromophenyl)-3,3-dimethylhexanoate.[α]$^{20}_{D}$ -13.6° (c = 1.00, CHCl$_3$); TLC (diethyl ether: hexanes, 1:20 v/v); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.44 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 4.62 (dq, *J* = 12.7, 8.5 Hz, 1H), 4.26 (dq, *J* = 12.7, 8.5 Hz, 1H), 3.59 (s, 1H), 1.37 – 1.26 (m, 3H), 1.21 – 1.11 (m, 1H), 1.00 (s, 3H), 0.89 (s, 3H), 0.87 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 171.26, 134.13, 131.83, 131.20, 121.82, 60.16 (q, *J* = 36.5 Hz), 59.31, 43.07, 37.55, 24.54, 24.24, 17.13, 14.81; HRMS (NSI) calcd for $C_{16}H_{21}BrF_3O_2$ ([M+H]$^+$):381.0672 found 381.0673; IR (neat):2963, 2935, 2874, 1752, 1489, 1414, 1278, 1164, 1122, 1076, 1012, 980, 825.

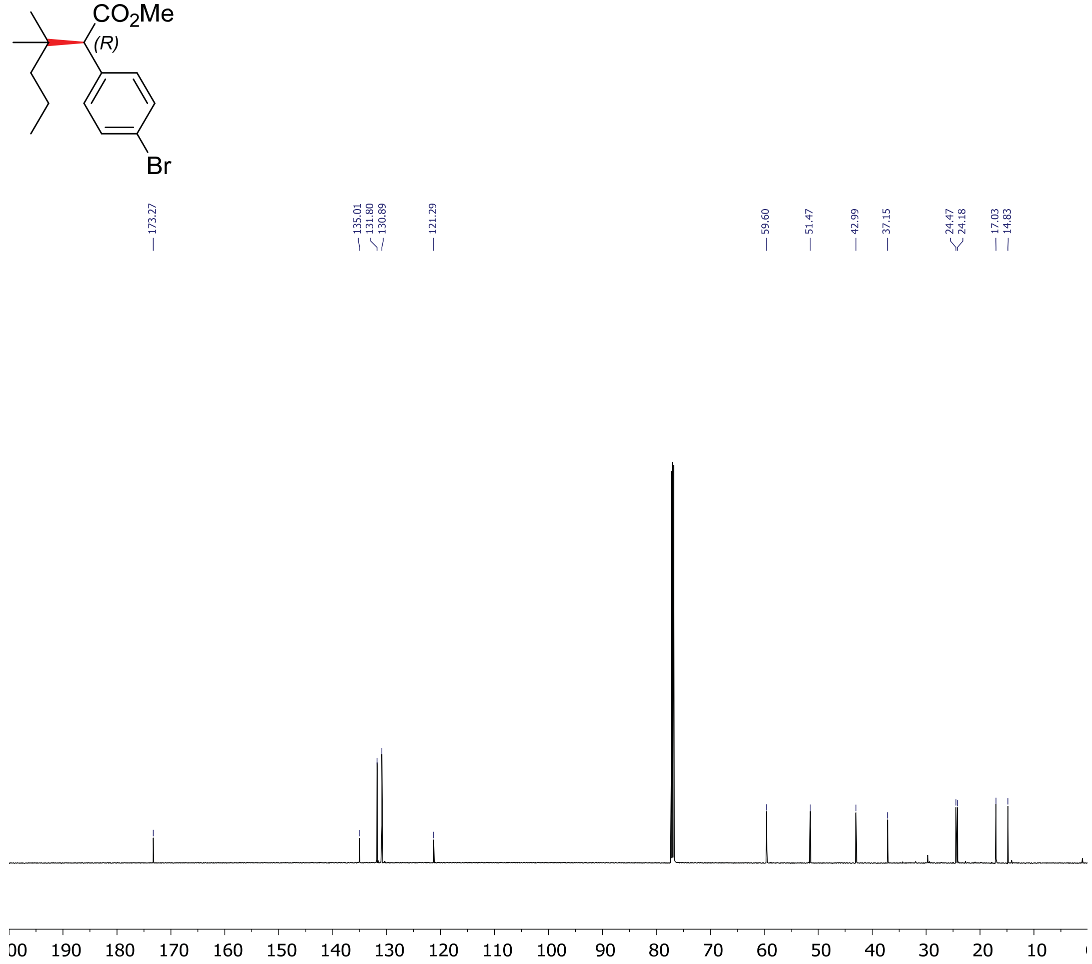


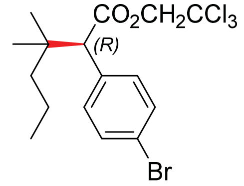
2,2,2-Trifluoroethyl (*2S,3R*)-2-(4-bromophenyl)-3,5-dimethylhexanoate.[α]$^{20}_{D}$ +30.7° (c = 1.00, CHCl$_3$); TLC (diethyl ether: hexanes, 1:20 v/v); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 4.55 (dd, *J* = 12.7, 8.5 Hz, 1H), 4.33 (dd, *J* = 12.7, 8.4 Hz, 1H), 3.30 (d, *J* = 10.4 Hz, 1H), 2.23 (ddtd, *J* = 16.7, 10.2, 6.5, 3.9 Hz, 1H), 0.99 (d, *J* = 6.5 Hz, 3H), 0.93 – 0.81 (m, 3H), 0.79 (d, *J* = 6.6 Hz, 3H), 0.73 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 172.11, 136.16, 131.89, 130.45, 121.77, 60.87, 60.58, 60.29, 60.00, 58.38, 43.00, 34.50, 25.07, 24.14, 21.02, 17.79; HRMS (NSI) calcd for $C_{16}H_{21}BrF_3O_2$ ([M+H]$^+$):381.0672 found 381.0676; IR (neat):2958, 2931, 2872, 1753, 1489, 1407, 1280, 1165, 1141, 1123, 1074, 1012, 979, 818, 758.

2.2 NMR Spectra

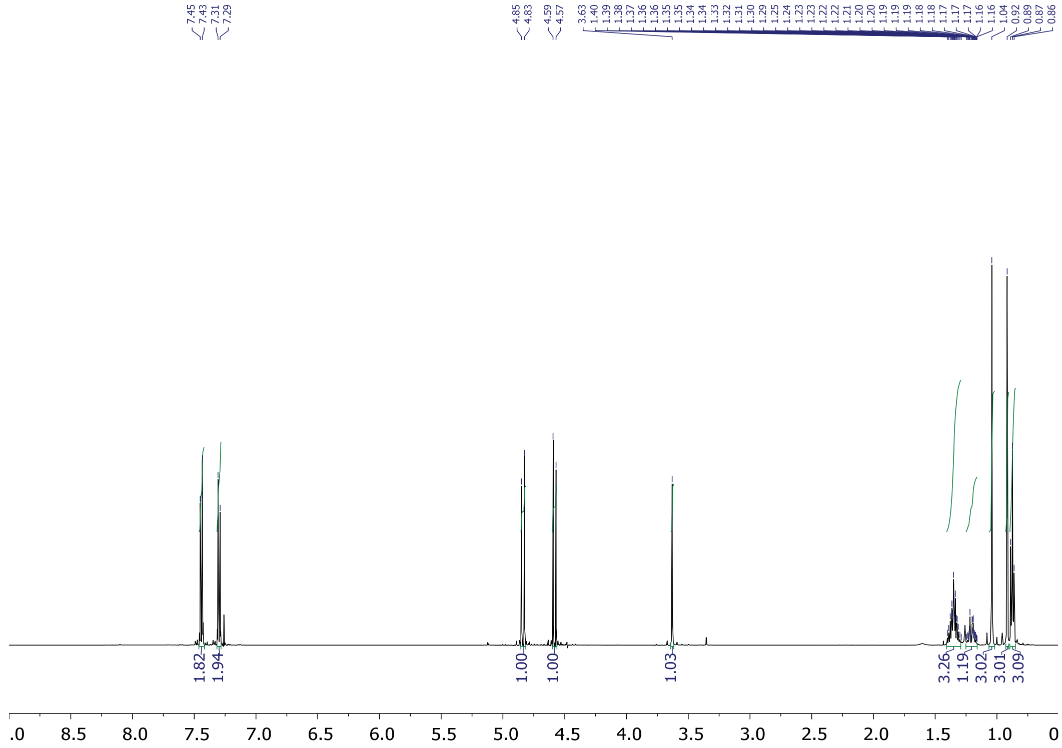





CO2Me
(R)
Br
173.27
135.01
131.80
130.89
121.29
59.60
51.47
42.99
37.15
24.47
24.18
17.03
14.83
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10



$CO_2CH_2CCl_3$
(R)
Br



7.45
7.43
7.31
7.29
4.85
4.83
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4.57
3.63
1.40
1.39
1.38
1.37
1.36
1.36
1.35
1.35
1.34
1.33
1.32
1.31
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1.29
1.25
1.24
1.23
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1.22
1.21
1.20
1.20
1.19
1.19
1.19
1.18
1.18
1.17
1.17
1.17
1.16
1.16
1.04
0.92
0.89
0.87
0.86
1.82
1.94
1.00
1.00
1.03
3.26
1.19
3.02
3.01
3.09
.0
8.5
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7.5
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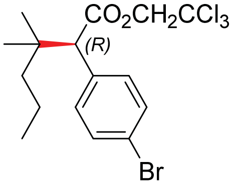
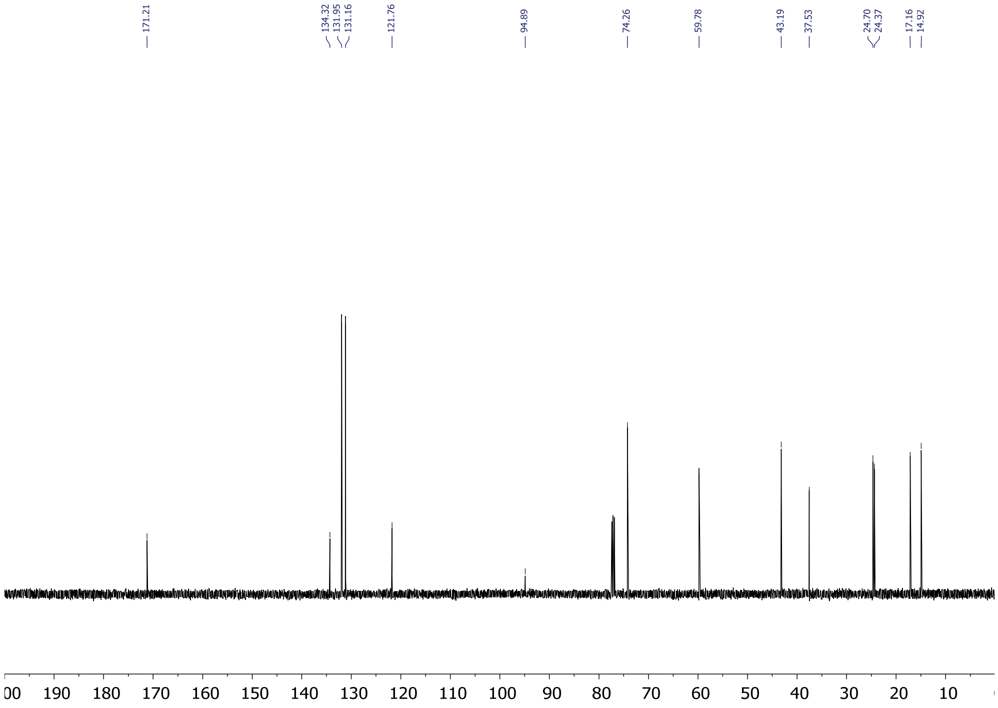

$CO_2CH_2CCl_3$
(R)
Br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134.32
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131.16
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94.89
74.26
59.78
43.19
37.53
24.70
24.37
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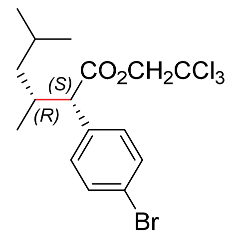
14.92
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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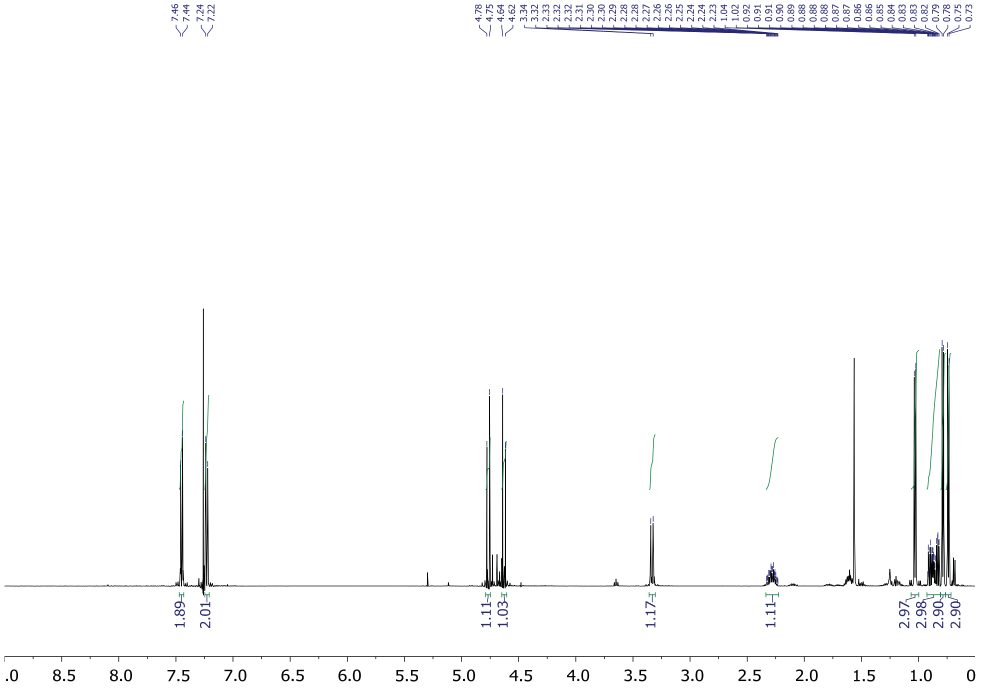
(R)
Br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2.25
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2.24
2.23
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1.02
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0.88
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0.86
0.86
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0.82
0.79
0.78
0.75
0.73
1.89
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1.11
1.03
1.17
1.11
2.97
2.98
2.90
2.90
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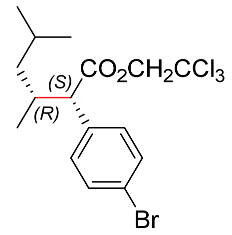
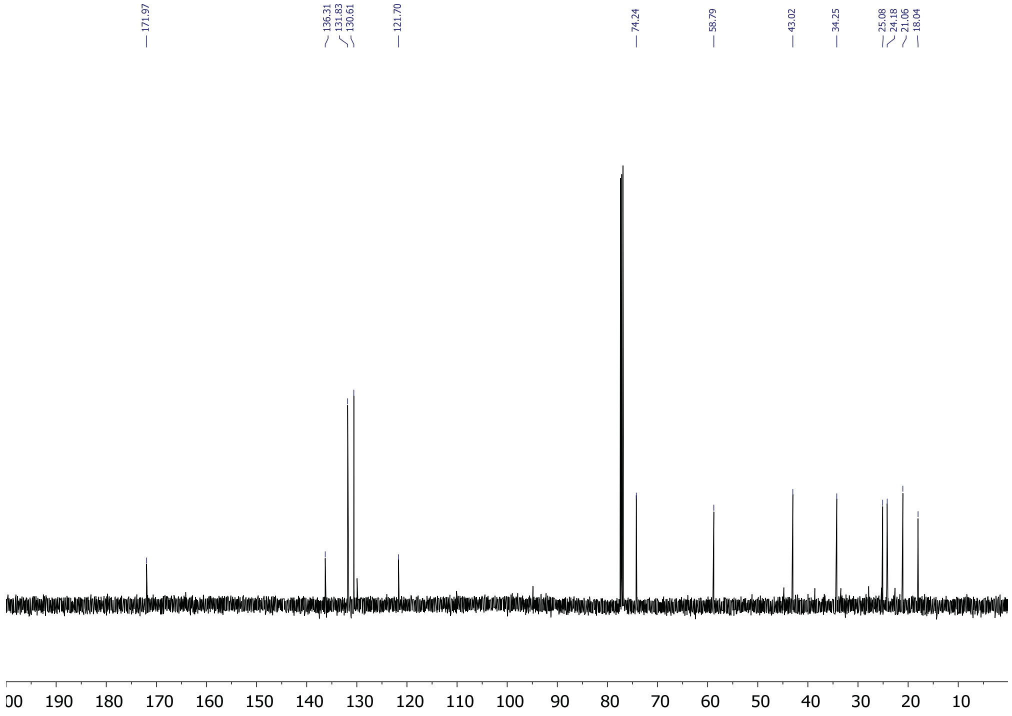

(S)
(R)
CO2CH2CCl3
Br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18.04
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80
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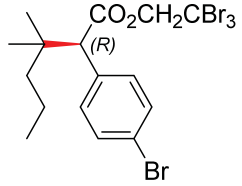
10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(R)
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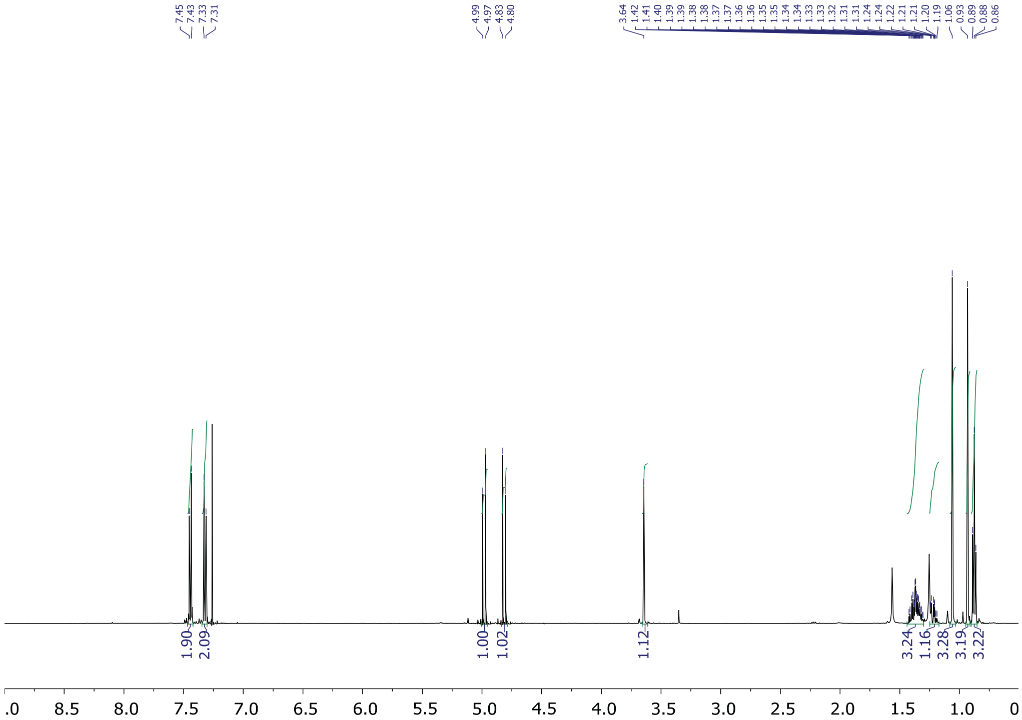
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1.31
1.24
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1.22
1.21
1.21
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0.88
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1.00
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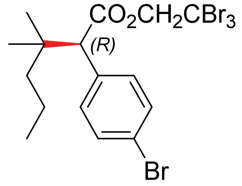
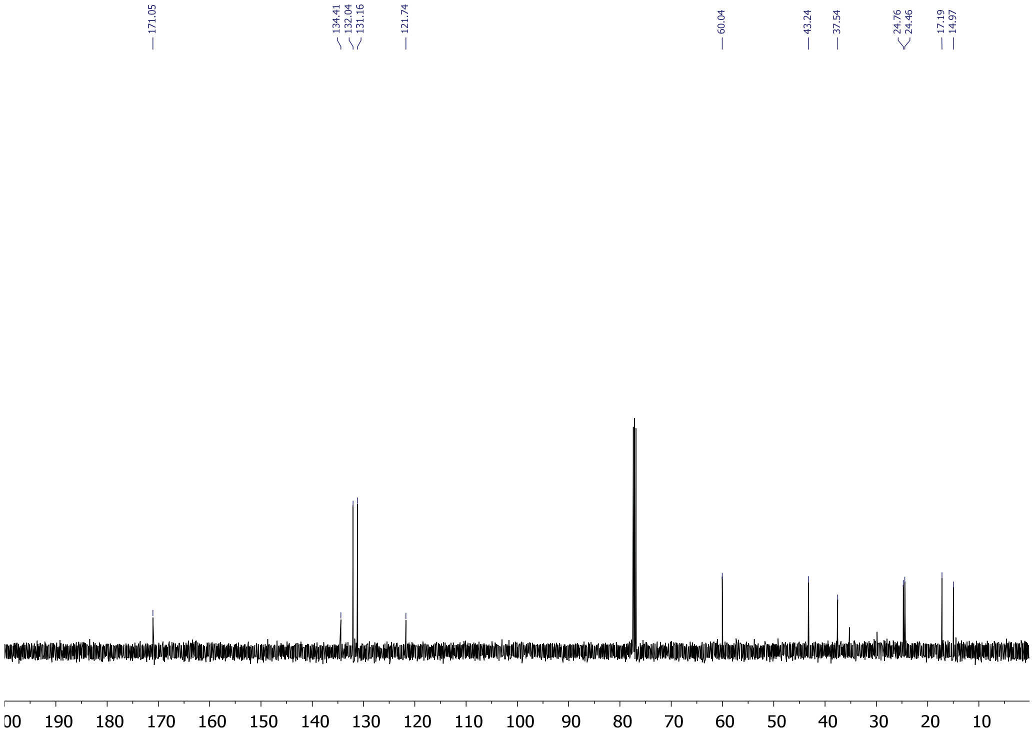


CO2CH2CBr3
(R)
Br



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37.54
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17.19
14.97
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160
150
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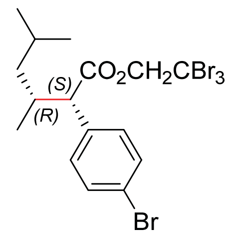
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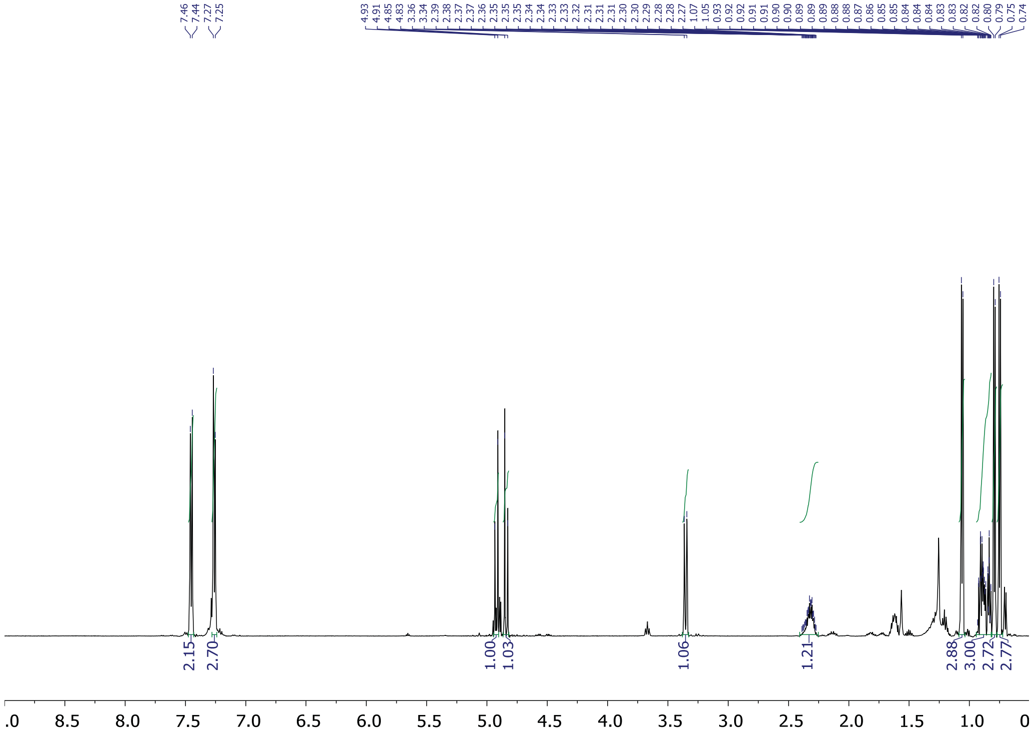
(S)
(R)
Br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2.31
2.30
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2.27
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1.05
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0.92
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0.89
0.89
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0.87
0.86
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0.83
0.82
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0.80
0.79
0.75
0.74
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1.03
1.06
1.21
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3.00
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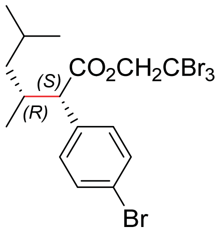
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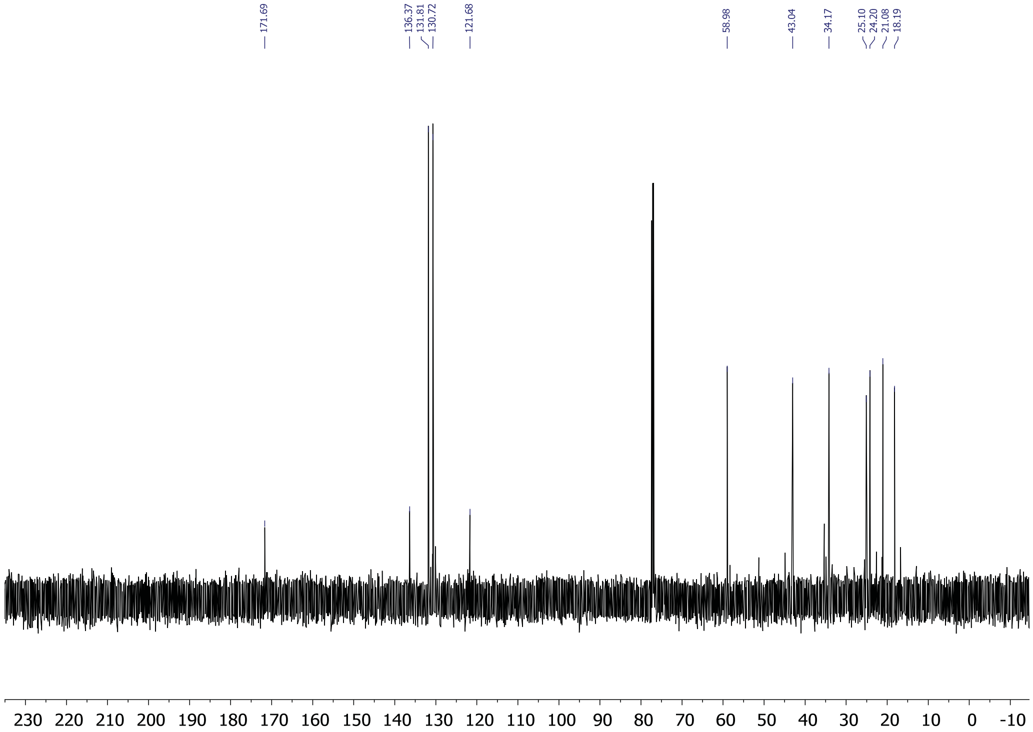
(S)
(R)
Br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24.20
21.08
18.19
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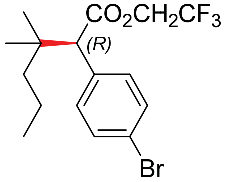
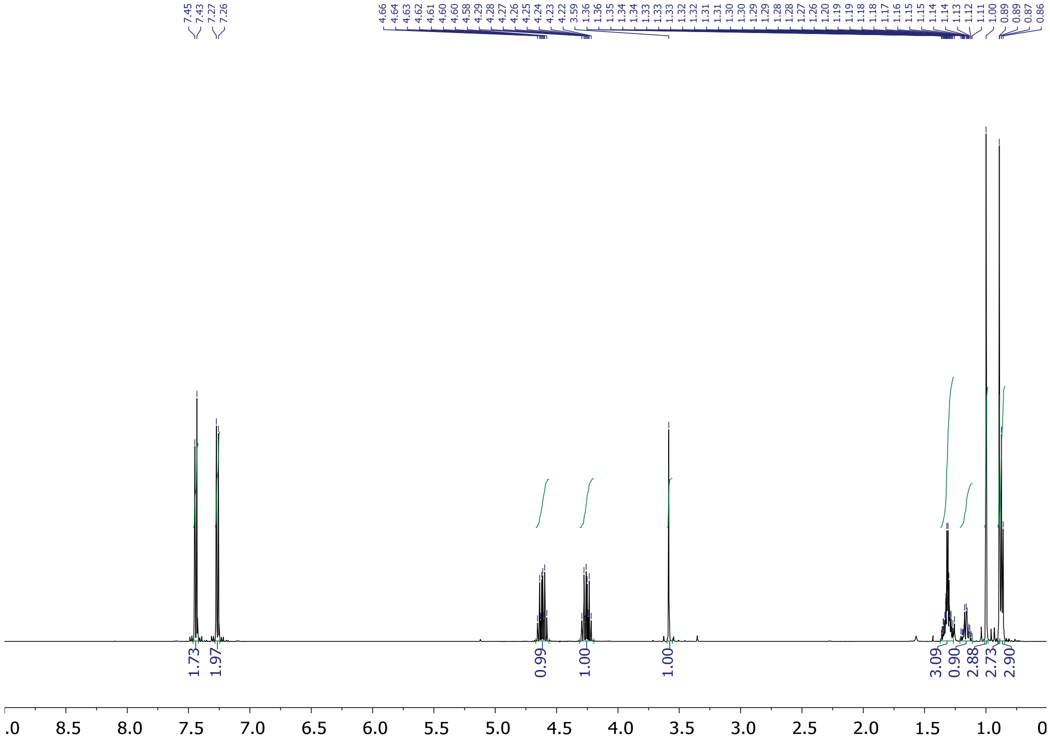

CO2CH2CF3
(R)
Br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1.28
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1.19
1.19
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1.18
1.17
1.16
1.15
1.15
1.14
1.14
1.13
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1.00
3.09
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2.90
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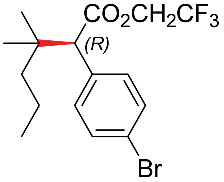
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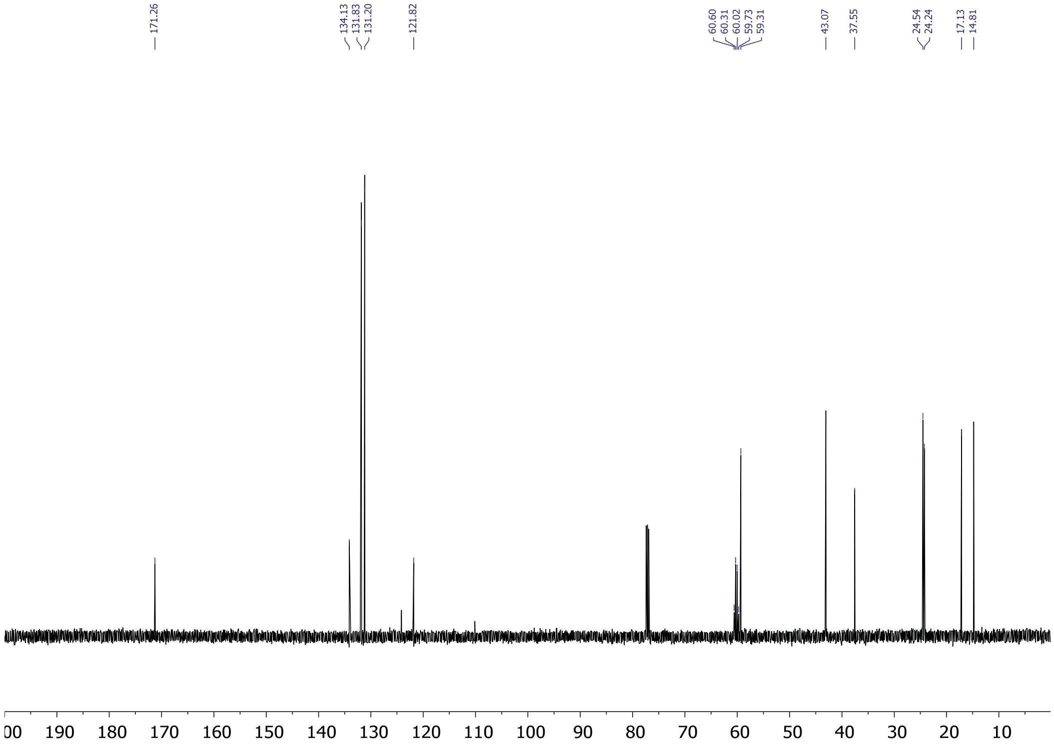
(R)
Br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17.13
14.81
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150
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80
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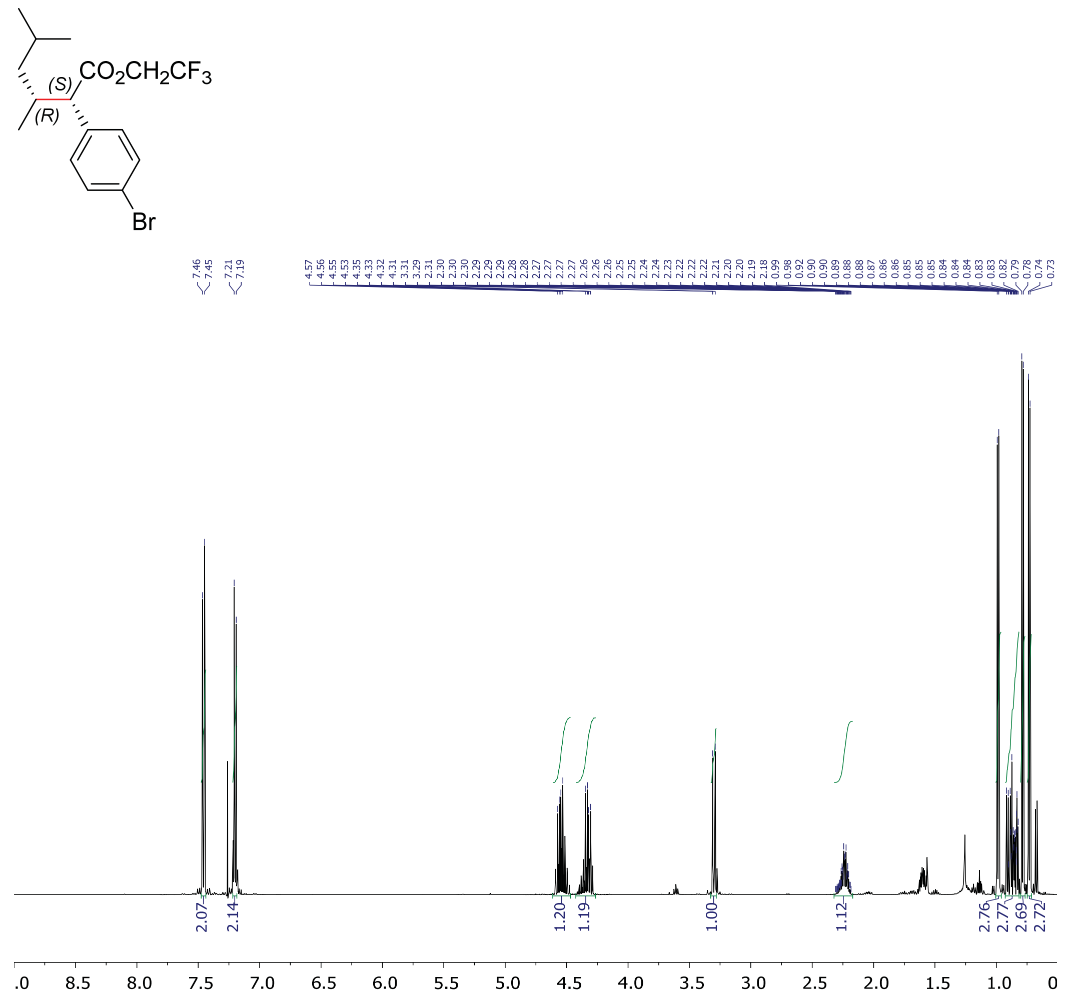
20
10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CO2CH2CF3
(R)
Br
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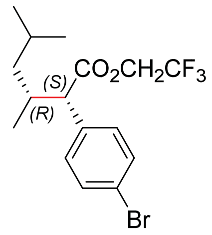
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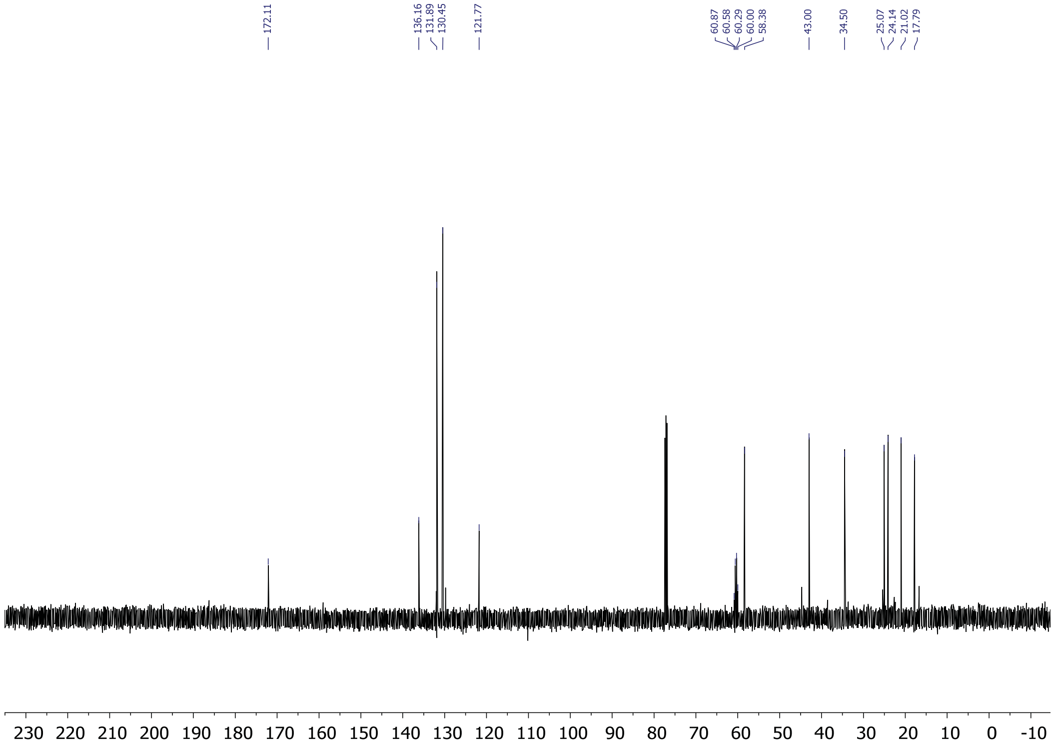
(S)
(R)
Br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60.58
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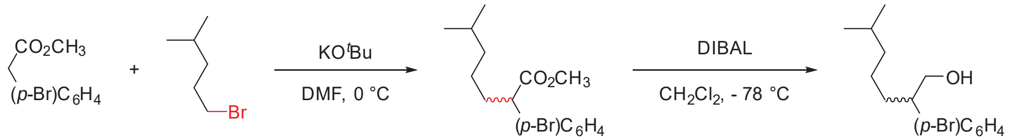
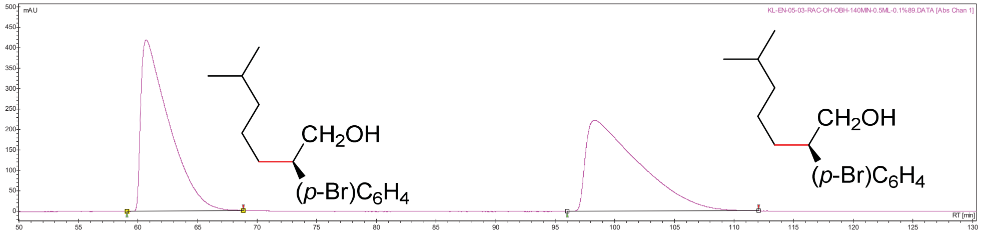
58.38
43.00
34.50
25.07
24.14
21.02
17.79
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

2.3 HPLC Spectra





#	Time [Min]	Area% [%]
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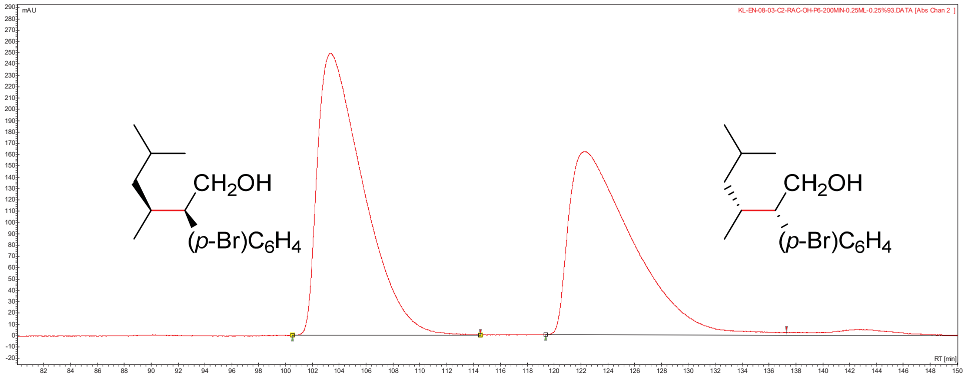
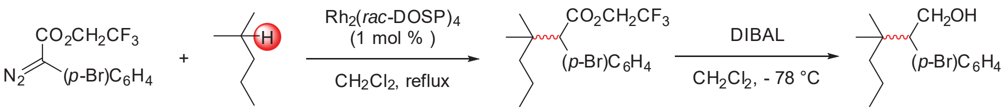
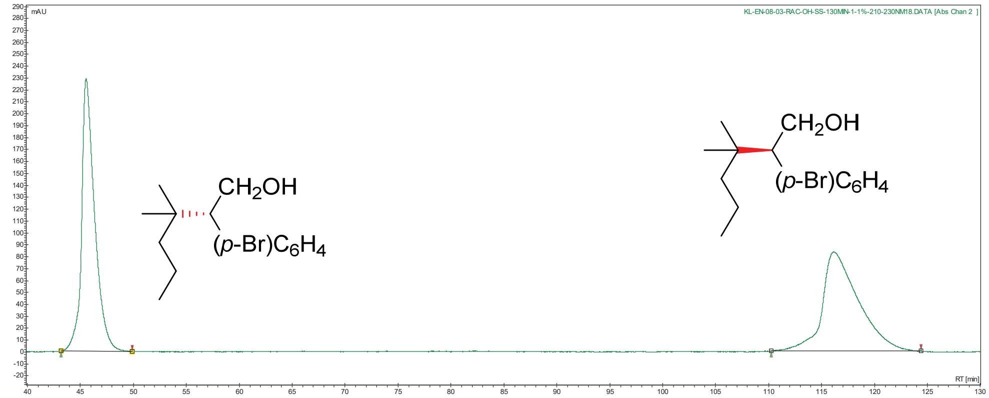
2	98.29	50.093

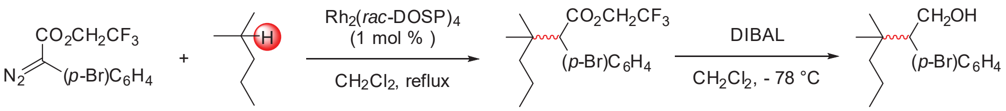


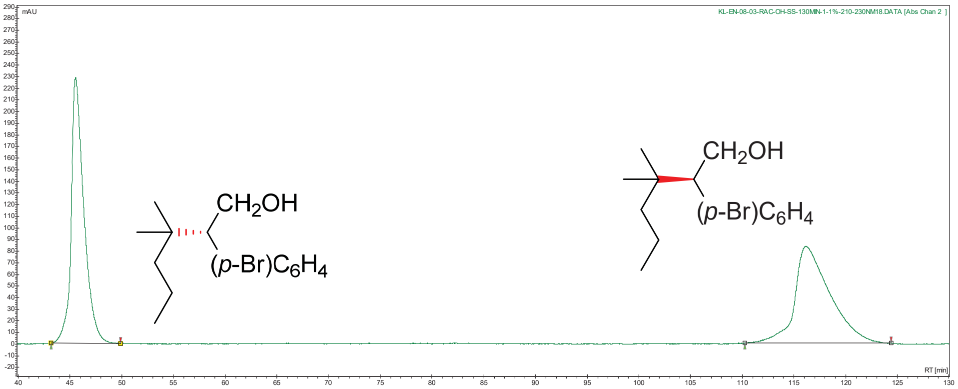
#	Time [Min]	Area% [%]
1	103.34	52.556
2	122.27	47.444



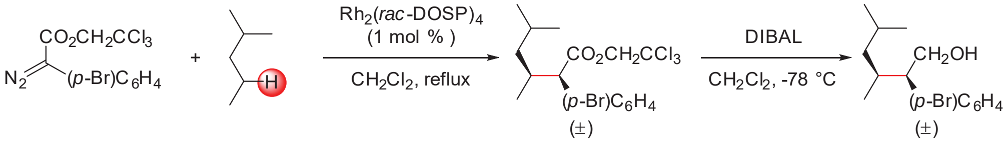


#	Time [Min]	Area% [%]
1	45.54	49.859
2	116.15	50.141

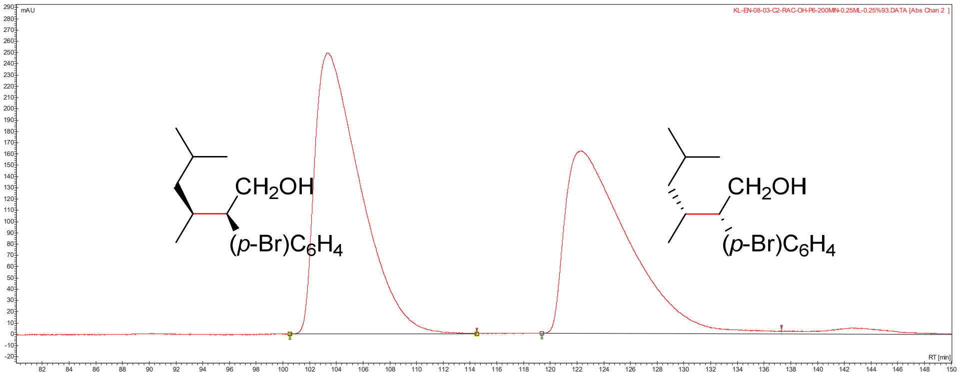




#	Time [Min]	Area % [%]
1	45.54	49.859
2	116.15	50.141



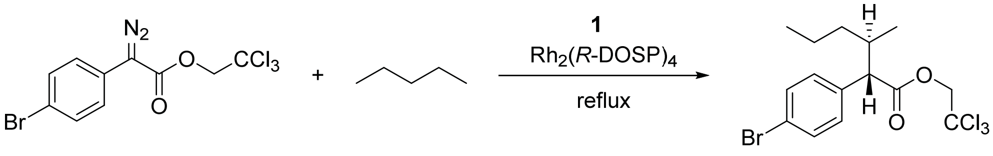
1c 3 *equiv.* **3b**



#	Time [Min]	Area % [%]
1	103.34	52.556
2	122.27	47.444

3. Catalyst Screen for Secondary Selective Catalyst

3.1 Catalyst and Diazo Screen

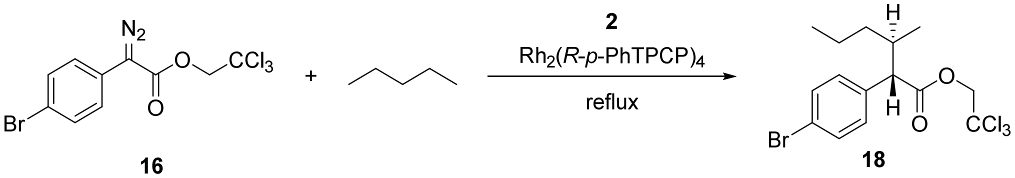


16 **18**

This compound was prepared according to the general procedure A for Rh_2(*R*-DOSP)$_4$ catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 3 mL *n*-pentane and Rh_2(*R*-DOSP)$_4$ (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL *n*-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (143 mg, 98% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C2: C3 ratio was 29: 1, C1 was not detected; and the dr of C2 was 3: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.5% isopropanol in hexane, 0.7 mL/min, 1 mg/mL, 160 min, UV 210 nm) retention times of 82.7 min (major) and 136.7 min (minor), 82% e.e..

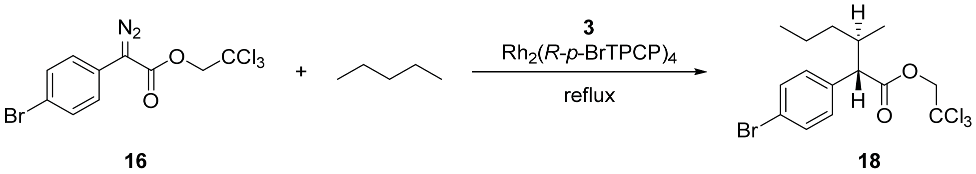


16 **18**

This compound was prepared according to the general procedure A for Rh_2(*R*-*p*-PhTPCP)$_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 3 mL *n*-pentane and Rh_2(*R*-*p*- PhTPCP)$_4$ (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL n-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (141 mg, 97% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 2, C3 was not detected; and the dr of C2 was 14: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

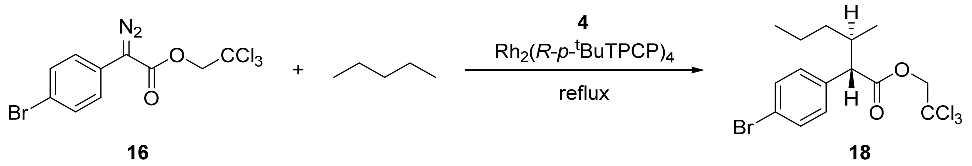
HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.5% isopropanol in hexane, 0.7 mL/min, 1 mg/mL, 160 min, UV 210 nm) retention times of 84.8 min (major) and 140.0 min (minor), 92% e.e..



This compound was prepared according to the general procedure A for Rh$_2$(*R*-*p*-BrTPCP)$_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 3 mL *n*-pentane and Rh$_2$(*R*-*p*-BrTPCP)$_4$ (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL n-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (143 mg, 98% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 4, C3 was not detected; and the dr of C2 was 6: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.5% isopropanol in hexane, 0.7 mL/min, 1 mg/mL, 160 min, UV 210 nm) retention times of 84.7 min (major) and 139.0 min (minor), 91% e.e..

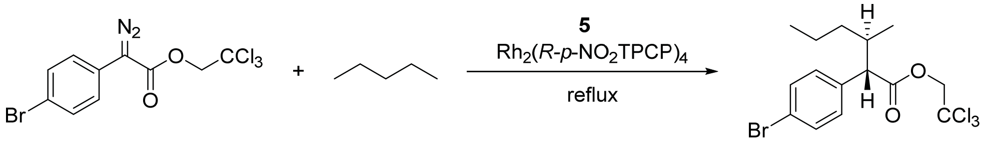


This compound was prepared according to the general procedure A for Rh$_2$(*R*-*p*-^{t}BuTPCP)$_4$ **(4)**-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-

diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 3 mL *n*-pentane and Rh_2(*R*-*p*-^{t}BuTPCP)$_4$ (**4**) (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL n-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (139 mg, 95% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 5, C3 was not detected; and the dr of C2 was 15: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.5% isopropanol in hexane, 0.7 mL/min, 1 mg/mL, 160 min, UV 210 nm) retention times of 85.3 min (major) and 140.4 min (minor), 92% e.e..

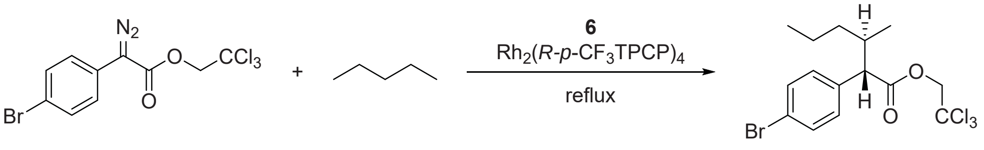


16 **18**

This compound was prepared according to the general procedure A for Rh_2(*R*-*p*-NO_2TPCP)$_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 3 mL *n*-pentane and Rh_2(*R*-*p*-NO_2TPCP)$_4$(0.0035 mmol, 9 mg, 1 mol%.) in 5 mL n-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (112 mg, 82% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2: C3 ratio was 12: 36: 1; and the dr of C2 was 3: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.5% isopropanol in hexane, 0.7 mL/min, 1 mg/mL, 160 min, UV 210 nm) retention times of 81.2 min (major) and 133.6 min (minor), 79% e.e..

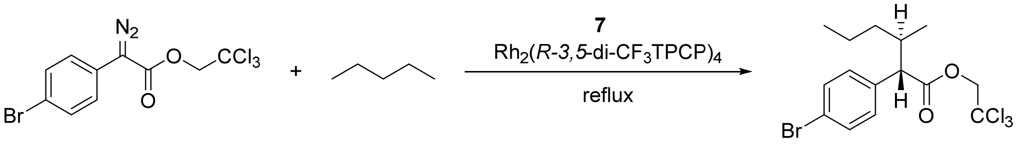


16 **18**

This compound was prepared according to the general procedure A for Rh$_2$(*R*-*p*-CF$_3$TPCP)$_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 3 mL *n*-pentane and Rh$_2$(*R*-*p*-CF$_3$TPCP)$_4$ (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL n-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (127 mg, 87% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 7, C3 was not detected; and the dr of C2 was 5: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.5% isopropanol in hexane, 0.7 mL/min, 1 mg/mL, 160 min, UV 210 nm) retention times of 85.2 min (major) and 140.7 min (minor), 94% e.e..

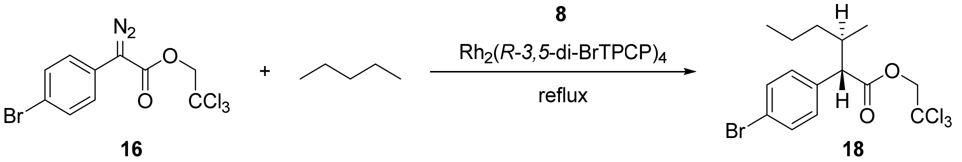


16 **18**

This compound was prepared according to the general procedure A for Rh$_2$(*R*-*3*,*5*-di-CF$_3$TPCP)$_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 3 mL *n*-pentane and Rh$_2$(*R*-*3*,*5*-di-CF$_3$TPCP)$_4$ (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL n-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (134 mg, 92% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 11, C3 was not detected; and the dr of C2 was 8: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

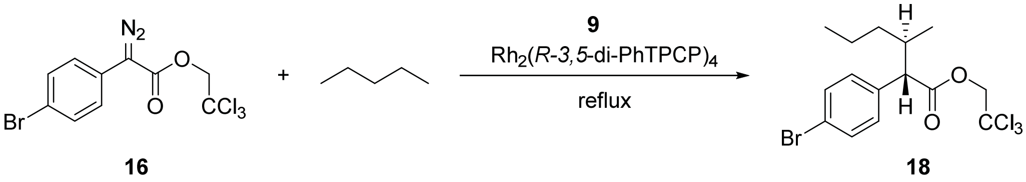
HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.5% isopropanol in hexane, 0.7 mL/min, 1 mg/mL, 160 min, UV 210 nm) retention times of 84.6 min (major) and 138.8 min (minor), 81% e.e..



This compound was prepared according to the general procedure A for Rh_2(*R-3,5*-di-BrTPCP)$_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 3 mL *n*-pentane and Rh_2(*R-3,5*-di-BrTPCP)$_4$ (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL n-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (139 mg, 95% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 26, C3 was not detected; and the dr of C2 was 5: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

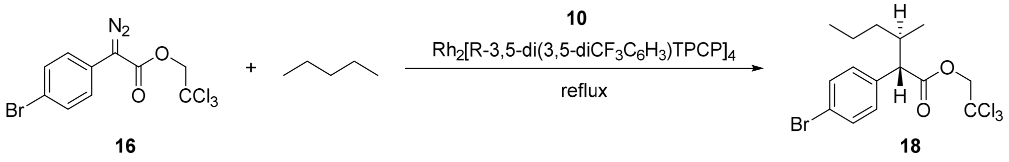
HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.5% isopropanol in hexane, 0.7 mL/min, 1 mg/mL, 160 min, UV 210 nm) retention times of 85.0 min (major) and 139.5 min (minor), 78% e.e..



This compound was prepared according to the general procedure A for Rh_2(*R-3,5*-di-PhTPCP)$_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 3 mL *n*-pentane and Rh_2(*R-3,5*-di-PhTPCP)$_4$ (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL n-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (139 mg, 95% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 22, C3 was not detected; and the dr of C2 was 5: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

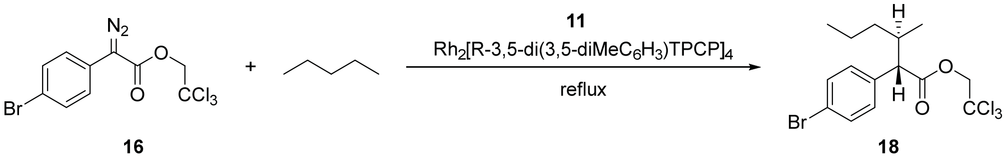
HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.5% isopropanol in hexane, 0.7 mL/min, 1 mg/mL, 160 min, UV 210 nm) retention times of 84.6 min (major) and 139.1 min (minor), 96% e.e..



This compound was prepared according to the general procedure A for Rh_2[*R*-*3,5*-di(*3,5*-diCF$_3$C$_6$H$_3$)TPCP]$_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 3 mL *n*-pentane and Rh_2[*R*-*3,5*-di(*3,5*-diCF$_3$C$_6$H$_3$)TPCP]$_4$ (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL *n*-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (140 mg, 96% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 26, C3 was not detected; and the dr of C2 was 26: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

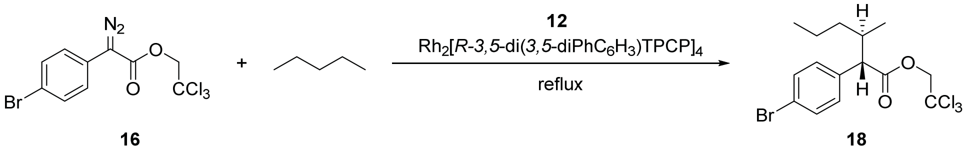
HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.5% isopropanol in hexane, 0.7 mL/min, 1 mg/mL, 160 min, UV 210 nm) retention times of 84.3 min (major) and 140.5 min (minor), 92% e.e..



This compound was prepared according to the general procedure A for Rh_2[*R*-3,5-di(3,5-diMeC_6H_3)TPCP]$_4$ -catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 3 mL *n*-pentane and Rh_2[*R*-3,5-di(3,5-diMeC_6H_3)TPCP]$_4$ (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL n-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (139 mg, 95% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 16, C3 was not detected; and the dr of C2 was 29: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

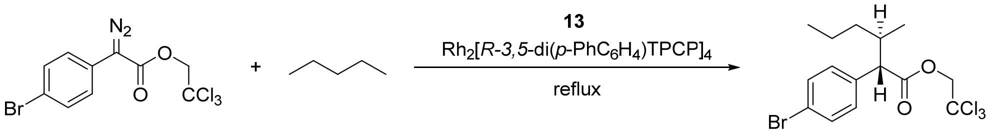
HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.5% isopropanol in hexane, 0.7 mL/min, 1 mg/mL, 160 min, UV 210 nm) retention times of 84.2 min (minor) and 139.1 min (major), >99% e.e..



This compound was prepared according to the general procedure A for Rh_2[*R*-3,5-di(3,5-diPhC_6H_3)TPCP]$_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 3 mL n-pentane and Rh_2[*R*-3,5-di(3,5-diPhC_6H_3)TPCP]$_4$ (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL *n*-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (143 mg, 98% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 5, C3 was not detected; and the dr of C2 was 16: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.5% isopropanol in hexane, 0.7 mL/min, 1 mg/mL, 160 min, UV 210 nm) retention times of 85.2 min (major) and 139.2 min (minor), 97% e.e..

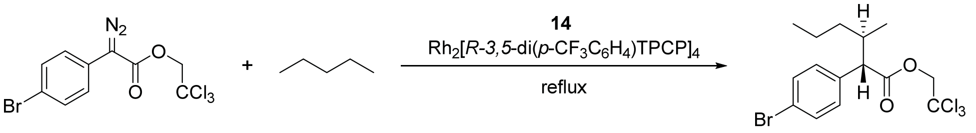


16 **18**

This compound was prepared according to the general procedure A for Rh$_2$[*R*-3,5-di(*p*-PhC$_6$H$_4$)TPCP]$_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 3 mL *n*-pentane and Rh$_2$[*R*-3,5-di(*p*-PhC$_6$H$_4$)TPCP]$_4$ (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL *n*-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (133 mg, 91% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 9, C3 was not detected; and the dr of C2 was 10: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.5% isopropanol in hexane, 0.7 mL/min, 1 mg/mL, 160 min, UV 210 nm) retention times of 84.1 min (major) and 138.1 min (minor), 89% e.e..



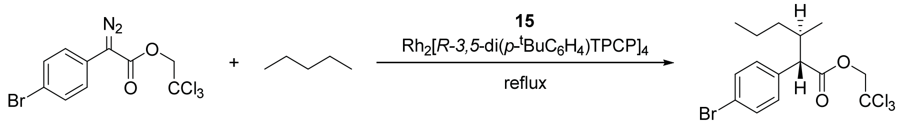
16 **18**

This compound was prepared according to the general procedure A for Rh$_2$[*R*-3,5-di(*p*-CF$_3$C$_6$H$_4$)TPCP]$_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-

bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 3 mL n-pentane and Rh_2[*R-3,5*-di(*p*-$CF_3C_6H_4$)TPCP]$_4$ (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL *n*-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (139 mg, 95% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 30, C3 was not detected; and the dr of C2 was 8: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.5% isopropanol in hexane, 0.7 mL/min, 1 mg/mL, 160 min, UV 210 nm) retention times of 84.6 min (minor) and 138.3 min (major), 91% e.e..

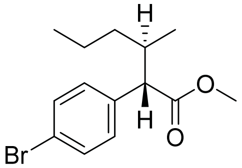


16 **18**

This compound was prepared according to the general procedure A for Rh_2[*R-3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 3 mL *n*-pentane and Rh_2[*R-3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$ (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL n-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (144 mg, 99% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 25, C3 was not detected; and the dr of C2 was 20: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

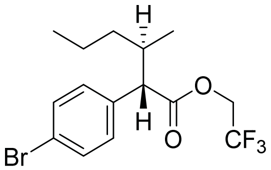
HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.5% isopropanol in hexane, 0.7 mL/min, 1 mg/mL, 160 min, UV 210 nm) retention times of 84.0 min (major) and 142.4 min (minor), 99% e.e..



Methyl (*2S,3R*)-2-(4-bromophenyl)-3-methylhexanoate. This compound was prepared according to the general procedure A for Rh$_2$[*R*-*3,5*-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$-catalyzed C–H functionalization. Methyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 89 mg, 1.0 equiv.) in 3 mL *n*-pentane and Rh$_2$[*R*-*3,5*-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$ (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL n-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (98 mg, 94% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 18, C3 was not detected; and the dr of C2 was 8: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

$[\alpha]^{20}_D$ 35.5° (c = 1.00, CHCl$_3$); TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.44 (d, *J* = 7.4 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 2H), 3.64 (s, 3H), 3.23 (d, *J* = 10.6 Hz, 1H), 2.22 – 2.10 (m, 1H), 1.36 – 1.28 (m, 1H), 1.10 (m, 1H), 0.98 (d, *J* = 6.6 Hz, 3H), 0.86 (m, 1H), 0.76 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 174.2, 137.3, 131.7, 130.4, 121.3, 58.3, 52.0, 36.3, 35.7, 19.6, 17.9, 14.2; HRMS (NSI) calcd for $C_{14}H_{20}BrO_2$ ([M+H]$^+$): 299.0641 found 299.0649; IR (neat):2956, 2930, 2871, 1733, 1487, 1196, 1161, 1145, 1073, 1010, 818, 761; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.5% isopropanol in hexane, 0.7 mL/min, 1 mg/mL, 160 min, UV 210 nm) retention times of 86.2 min (major) and 141.5 min (minor), 92% e.e..

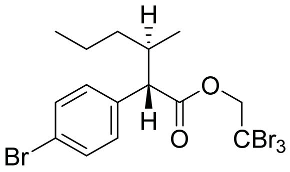


2,2,2-Trifluoroethyl (*2S,3R*)-2-(4-bromophenyl)-3-methylhexanoate. This compound was prepared according to the general procedure A for Rh$_2$[*R*-*3,5*-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$-catalyzed C–H functionalization. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate

(0.35 mmol, 113 mg, 1.0 equiv.) in 3 mL *n*-pentane and Rh_2[*R*-*3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$ (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL n-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (123 mg, 96% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 30, C3 was not detected; and the dr of C2 was 15: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

$[\alpha]^{20}_D$ 26.1° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 4.55 (dd, *J* = 12.7, 8.4 Hz, 1H), 4.33 (dd, *J* = 12.7, 8.4 Hz, 1H), 3.35 (d, *J* = 10.6 Hz, 1H), 2.25 – 2.16 (m, 1H), 1.40 – 1.31 (m, 1H), 1.20 – 1.13 (m, 1H), 1.10 (m, 1H), 1.01 (d, *J* = 6.5 Hz, 3H), 0.94 – 0.85 (m, 1H), 0.77 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.1, 136.2, 131.9 130.4, 121.8, 60.4 (q, *J* = 36.7 Hz), 57.8, 36.3, 35.6, 19.5, 17.6, 14.1; HRMS (APCI) calcd for $C_{15}H_{17}O_2BrF_3$ ($[M-H]^+$): 365.0369 found 365.0370; IR (neat): 2961, 2932, 1753, 1489, 1279, 1164, 1122, 1074, 1011, 979, 819; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.5% isopropanol in hexane, 0.7 mL/min, 1 mg/mL, 160 min, UV 210 nm) retention times of 84.8 min (major) and 141.4 min (minor), 99% e.e..

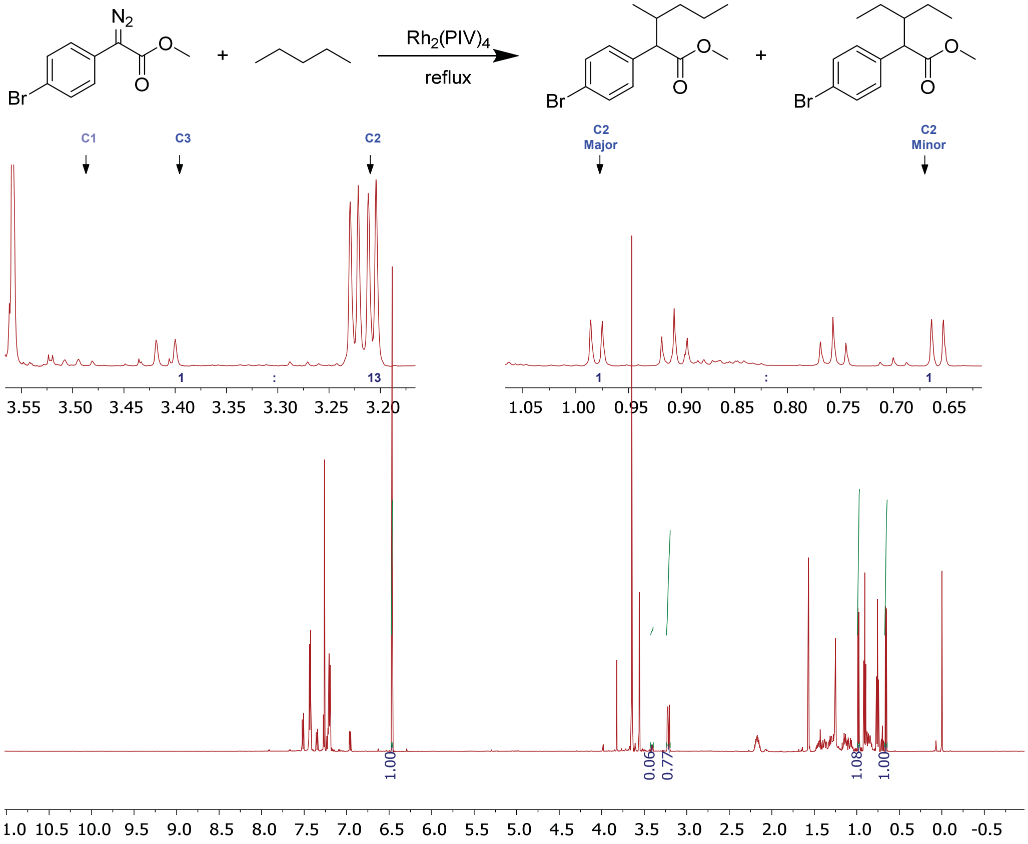


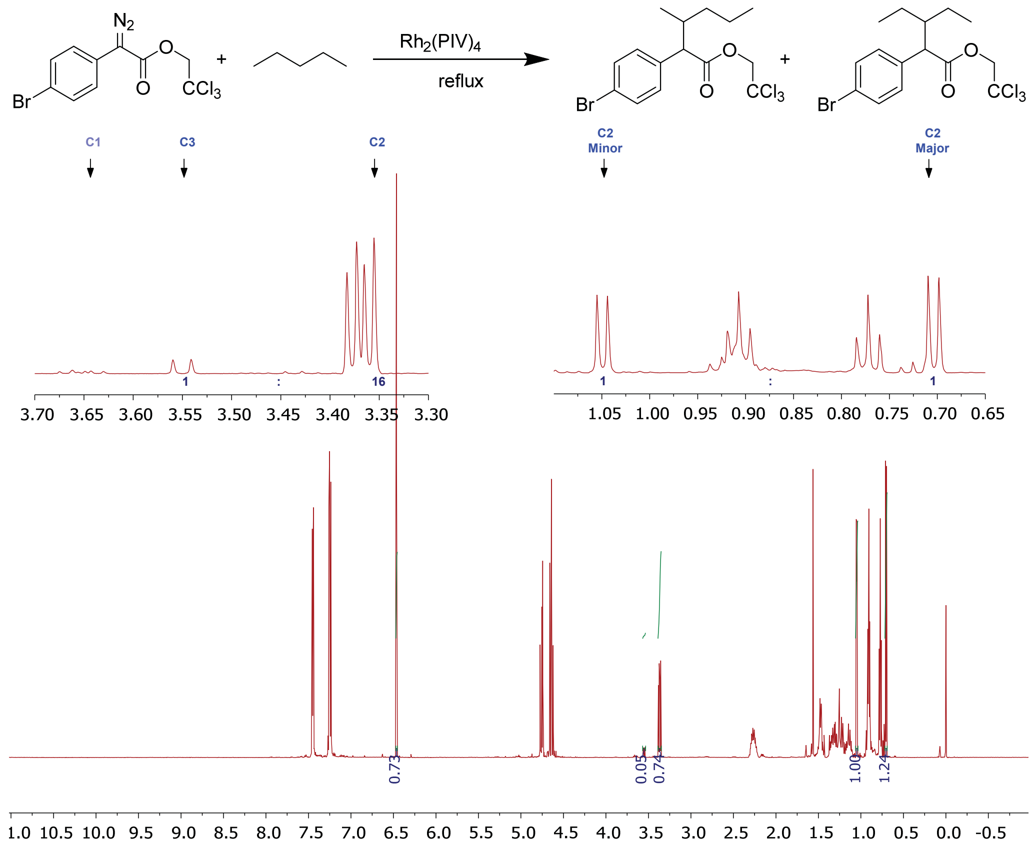
2,2,2-Tribromoethyl (*2S,3R*)-2-(4-bromophenyl)-3-methylhexanoate.This compound was prepared according to the general procedure A for Rh_2[*R*-*3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$-catalyzed C–H functionalization. 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 177mg, 1.0 equiv.) in 3 mL *n*-pentane and Rh_2[*R*-*3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$ (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL *n*-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (183 mg, 95% yield).

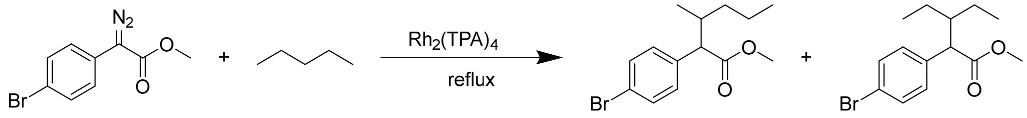
Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 19, C3 was not detected; and the dr of C2 was 21: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

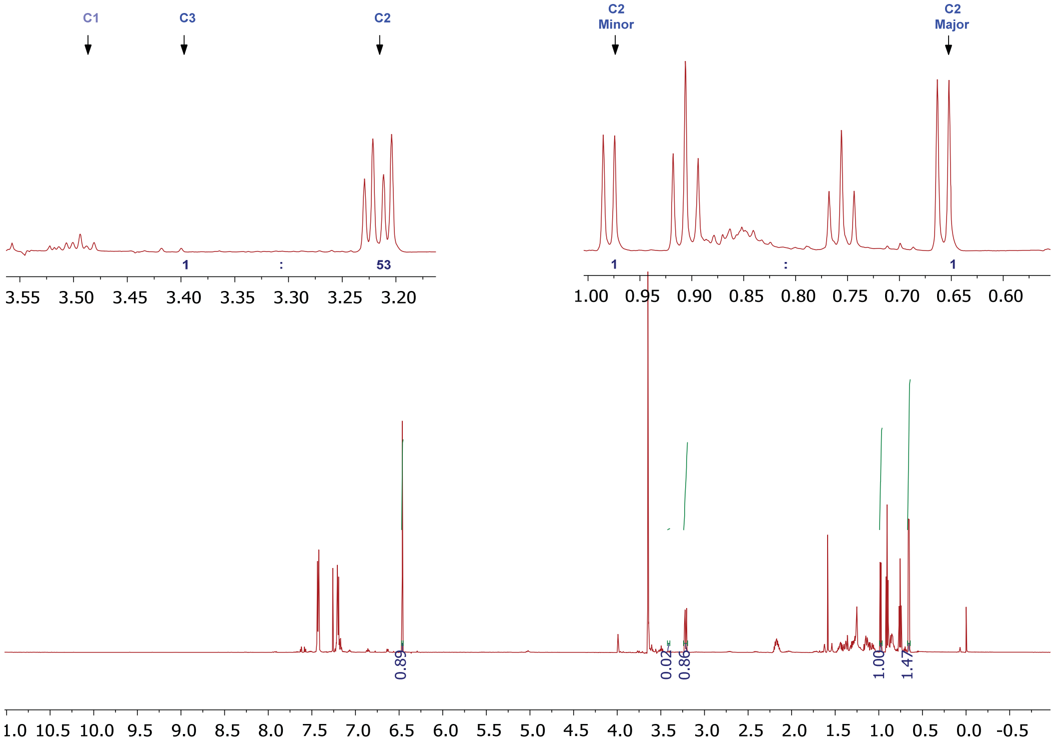
$[\alpha]^{20}{}_{D}$ 6.8° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 4.92 (d, *J* = 12.3 Hz, 1H), 4.84 (d, *J* = 12.3 Hz, 1H), 3.40 (d, *J* = 10.6 Hz, 1H), 2.28 (m, 1H), 1.41 – 1.30 (m, 1H), 1.22 – 1.10 (m, 2H), 1.08 (d, *J* = 6.5 Hz, 3H), 0.97 – 0.89 (m, 1H), 0.78 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 136.4, 131.8, 130.7, 121.6, 58.4, 35.9, 35.6, 35.4, 19.5, 18.0, 14.2; IR (neat): 2958, 2929, 1745, 1712, 1488, 1361, 1220, 1115, 1073, 1010, 715, 630; HRMS (NSI) calcd for $C_{15}H_{19}O_2Br_3{}^{81}Br$ ($[M+H]^+$): 548.8092 found 548.8105; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.5% isopropanol in hexane, 0.7 mL/min, 1 mg/mL, 160 min, UV 210 nm) retention times of 84.4 min (major) and 144.6 min (minor), 98% e.e..

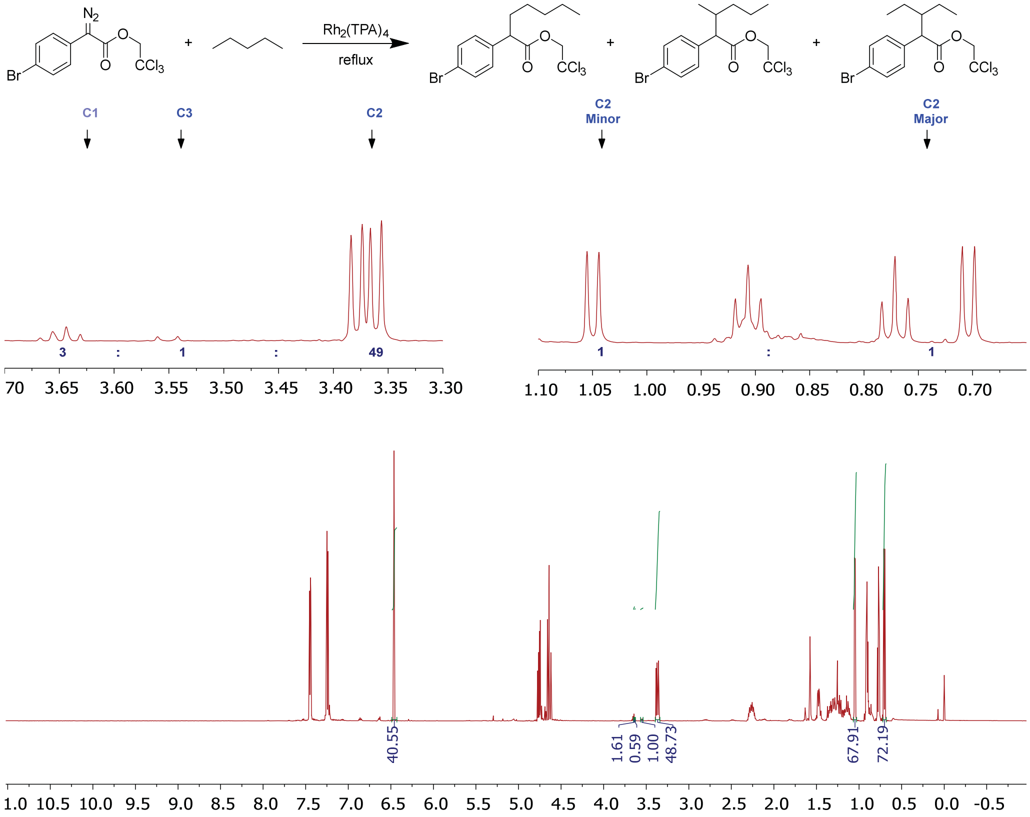
3.2 Crude ^{1}H NMR Spectra

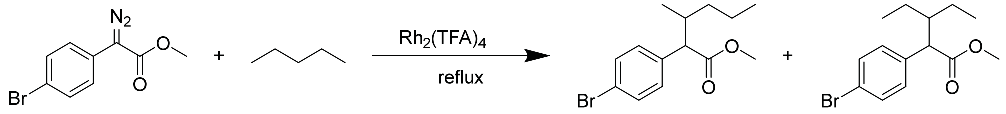


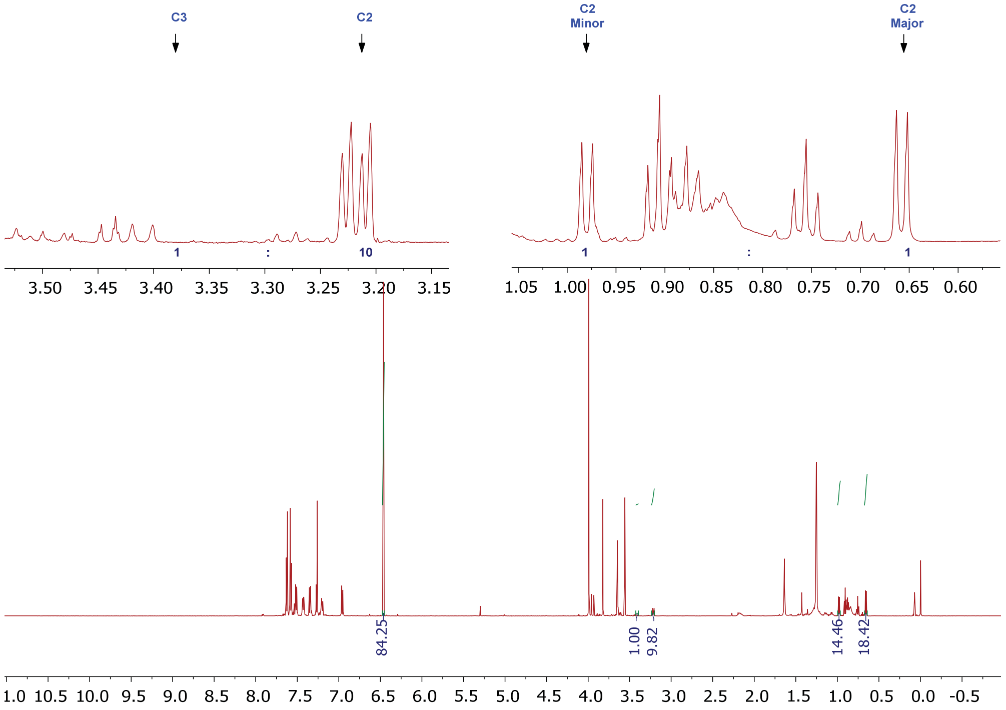

N2
Br
O
O
CCl3
+
Rh2(PIV)4
reflux
Br
O
O
CCl3
+
Br
O
O
CCl3
C1
C3
C2
C2
Minor
C2
Major
1
:
16
3.70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30
1
:
1
1.05 1.00 0.95 0.90 0.85 0.80 0.75 0.70 0.65
0.73
0.05
0.74
1.00
1.24
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

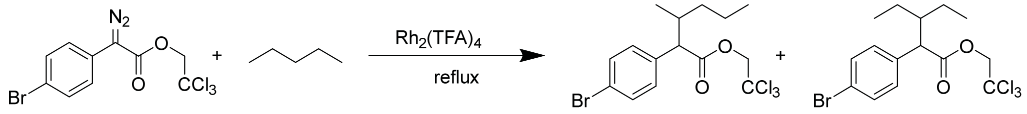

N$_2$
O
O
Br
+
Rh$_2$(TPA)$_4$
reflux
+

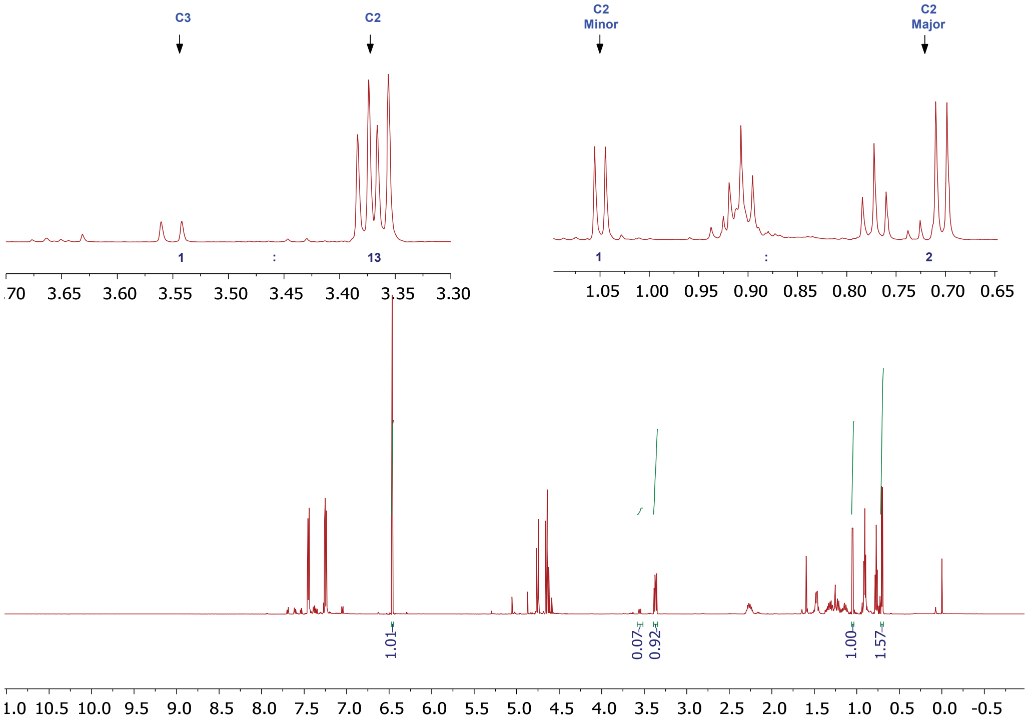

C1
C3
C2
C2
Minor
C2
Major
1 : 53
1 : 1
3.55 3.50 3.45 3.40 3.35 3.30 3.25 3.20
1.00 0.95 0.90 0.85 0.80 0.75 0.70 0.65 0.60
0.89
0.02
0.86
1.00
1.47
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

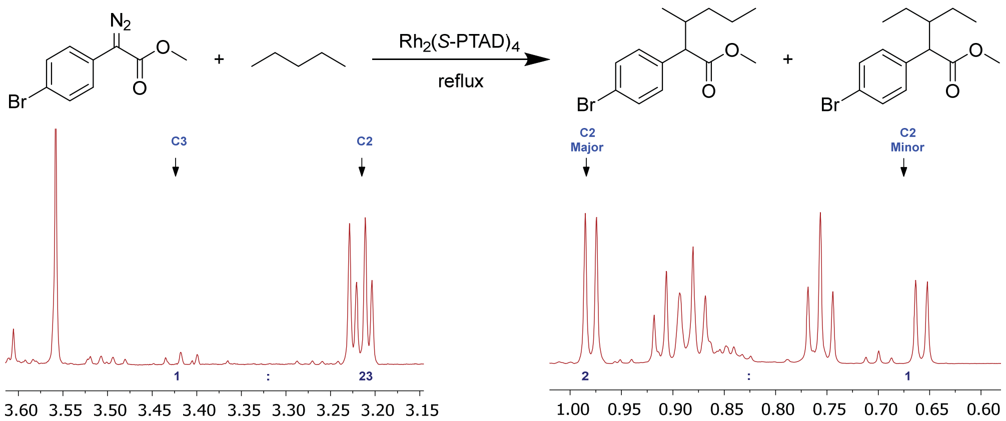

N2
Br
O
CCl3
+
Rh2(TPA)4
reflux
C1
C3
C2
C2 Minor
C2 Major
3 : 1 : 49
1 : 1
70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30
1.10 1.05 1.00 0.95 0.90 0.85 0.80 0.75 0.70
40.55
1.61
0.59
1.00
48.73
67.91
72.19
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

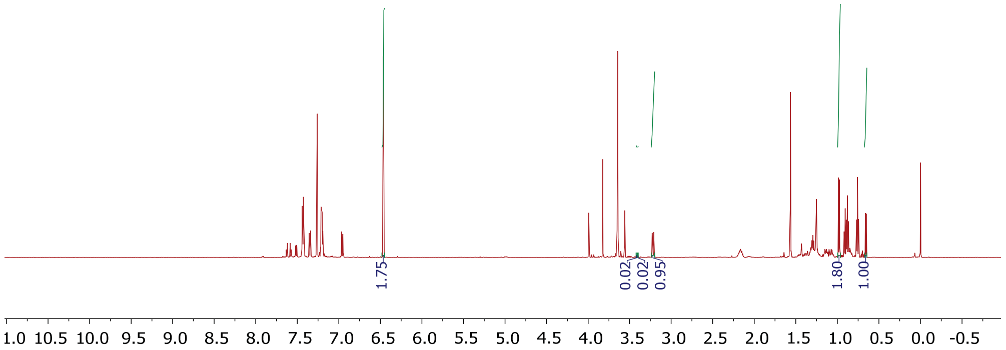

N2
Br
+
Rh2(TFA)4
reflux
Br
O
O
+
Br
O
O

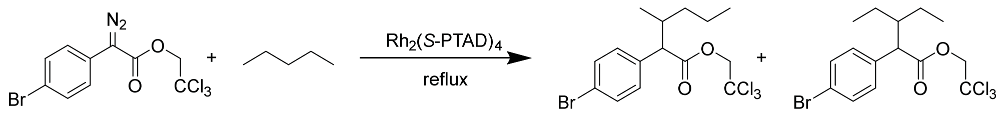

C3
C2
C2
Minor
C2
Major
1
:
10
1
:
1
3.50
3.45
3.40
3.35
3.30
3.25
3.20
3.15
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
84.25
1.00
9.82
14.46
18.42
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

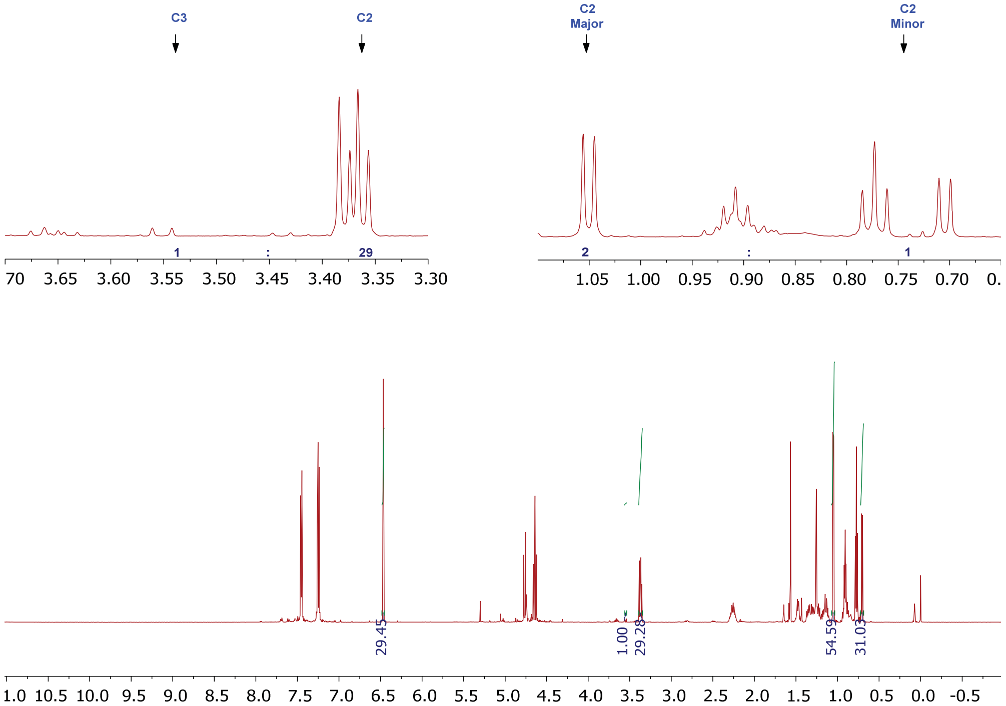

N2
Br
O
O
CCl3
+
Rh2(TFA)4
reflux
Br
O
O
CCl3
+
Br
O
O
CCl3

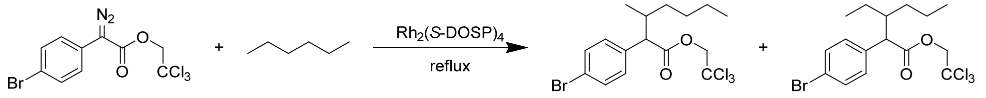

C3
C2
C2
Minor
C2
Major
1
:
13
1
:
2
.70
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
1.01
0.07
0.92
1.00
1.57
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

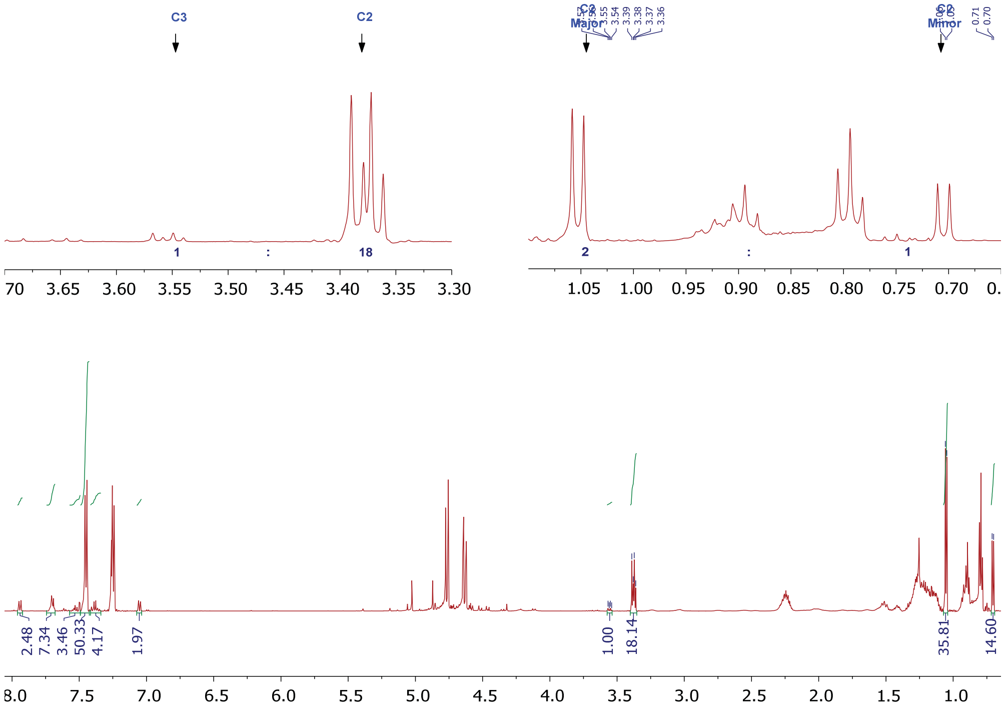

N2
Br
O
+
Rh2(S-PTAD)4
reflux
Br
O
+
Br
O
C3
C2
C2
Major
C2
Minor
1
:
23
2
:
1
3.60 3.55 3.50 3.45 3.40 3.35 3.30 3.25 3.20 3.15
1.00 0.95 0.90 0.85 0.80 0.75 0.70 0.65 0.60

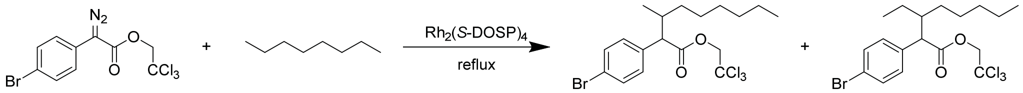

1.75
0.02
0.02
0.95
1.80
1.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

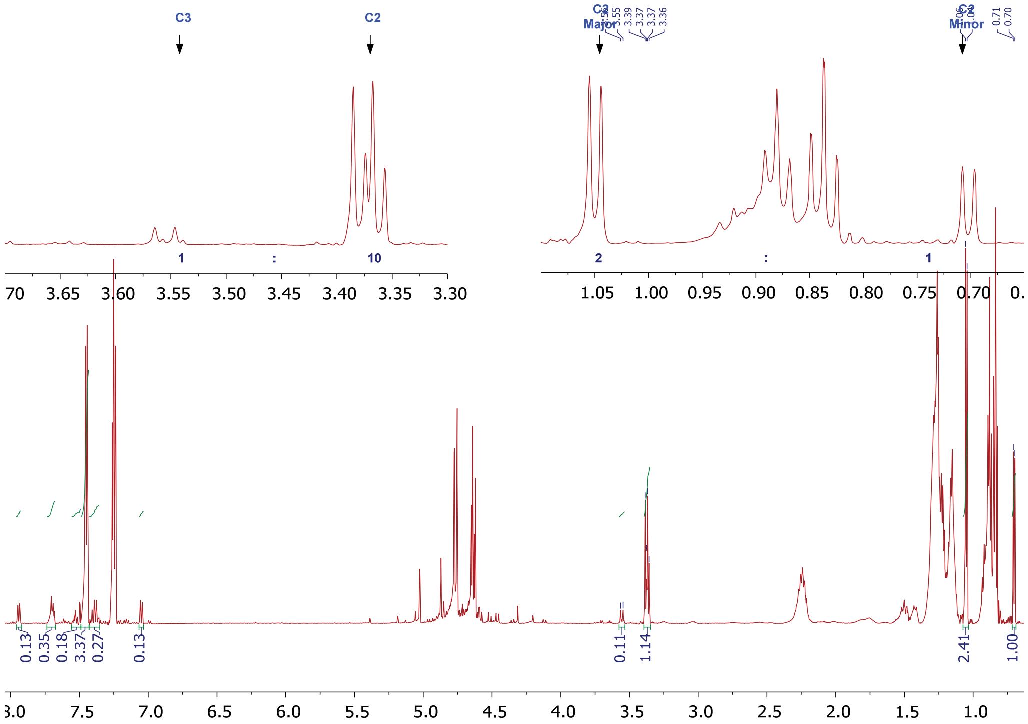

N$_2$
O
Br
O
CCl$_3$
+
Rh$_2$(S-PTAD)$_4$
reflux
Br
O
O
CCl$_3$
+
Br
O
O
CCl$_3$

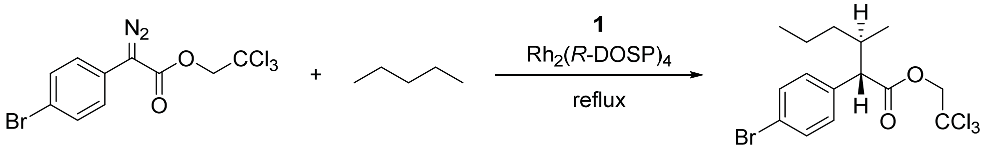

C3
C2
C2
Major
C2
Minor
1
:
29
70
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
2
:
1
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.
29.45
1.00
29.28
54.59
31.03
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


N2
Br
O
CCl3
+
Rh2(S-DOSP)4
reflux
+


C3
C2
C2
Major
C2
Minor
3.55
3.54
3.39
3.38
3.37
3.36
0.71
0.70
1
:
18
2
:
1
70
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
2.48
7.34
3.46
50.33
4.17
1.97
1.00
18.14
35.81
14.60
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

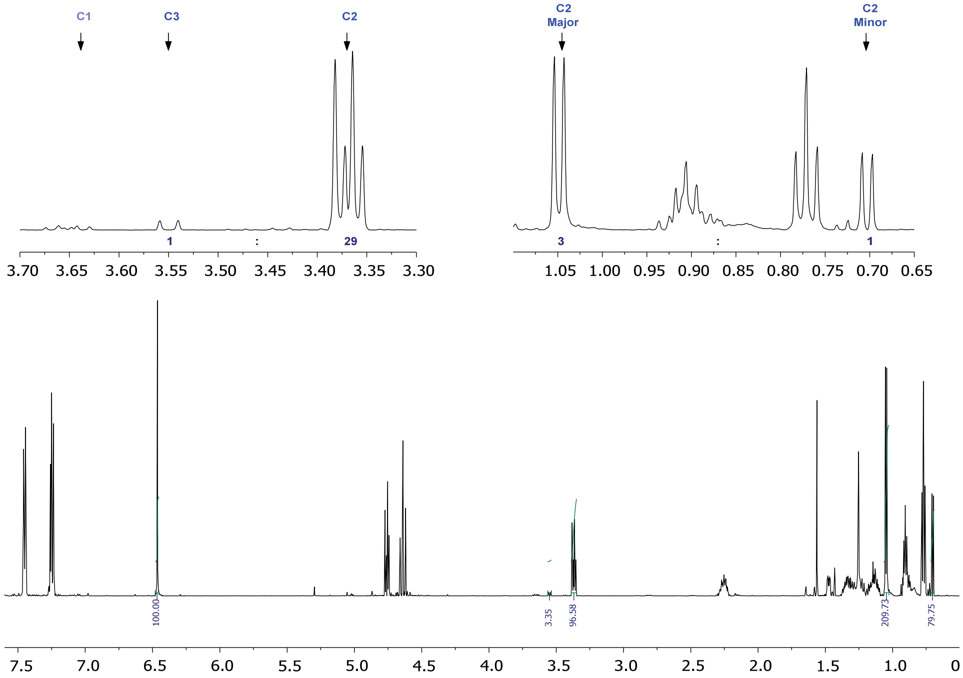

N2
Br
O
CCl3
Rh2(S-DOSP)4
reflux
+

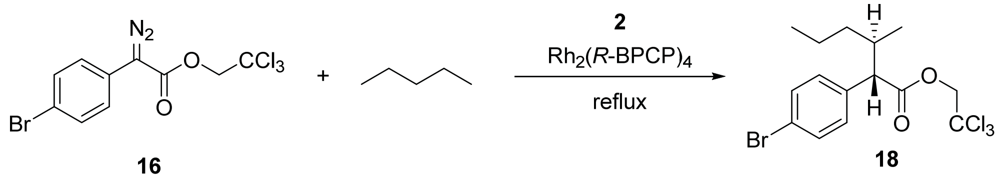

C3
C2
C3 Major
C2 Minor
3.55
3.39
3.37
3.37
3.36
0.71
0.70
1 : 10
2 : 1
3.70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30
1.05 1.00 0.95 0.90 0.85 0.80 0.75 0.70
0.13
0.35
0.18
3.37
0.27
0.13
0.11
1.14
2.41
1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0

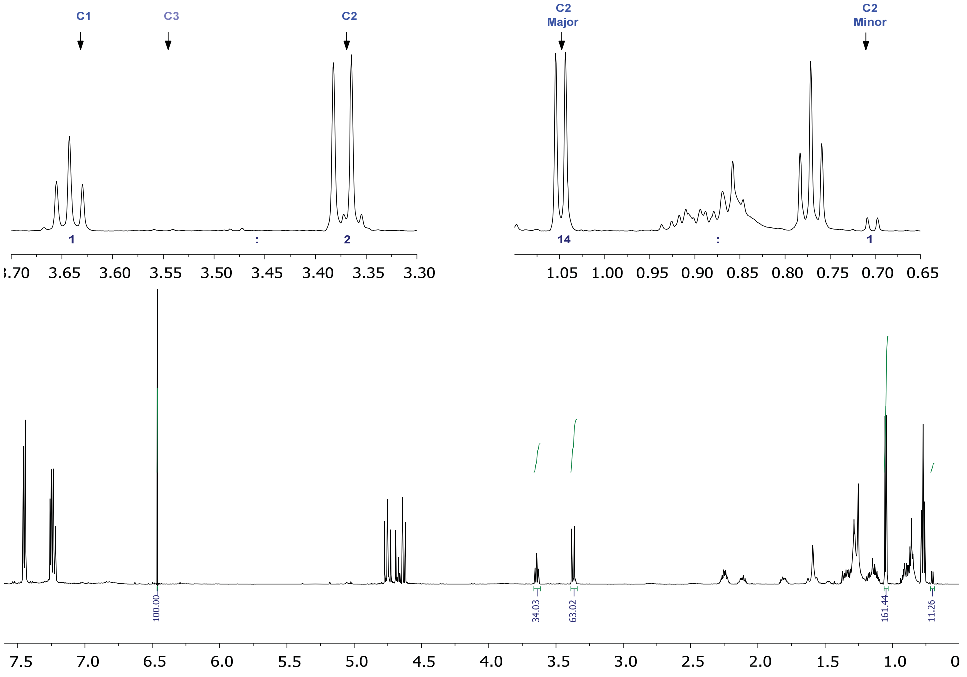

N2
CCl3
Br
1
Rh2(R-DOSP)4
reflux
H
H
CCl3
Br

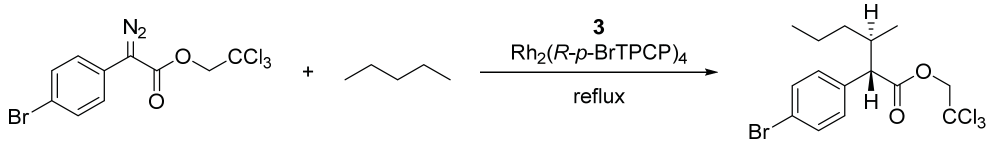
16

18


C1
C3
C2
1
:
29
3.70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30
C2
Major
C2
Minor
3
:
1
1.05 1.00 0.95 0.90 0.85 0.80 0.75 0.70 0.65
100.00
3.35
96.58
209.73
79.75
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

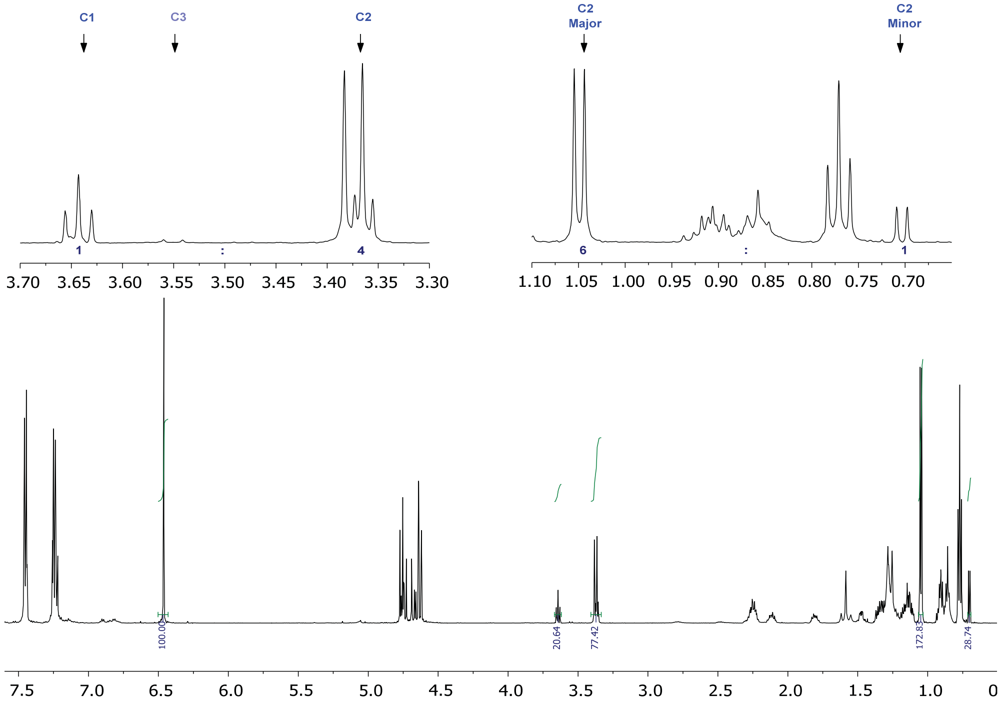

N2
CCl3
Br
16
+
2
Rh2(R-BPCP)4
reflux
H
H
O
CCl3
Br
18


C1
C3
C2
1
2
3.70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30
C2
Major
C2
Minor
14
1
1.05 1.00 0.95 0.90 0.85 0.80 0.75 0.70 0.65
100.00
34.03
63.02
161.44
11.26
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

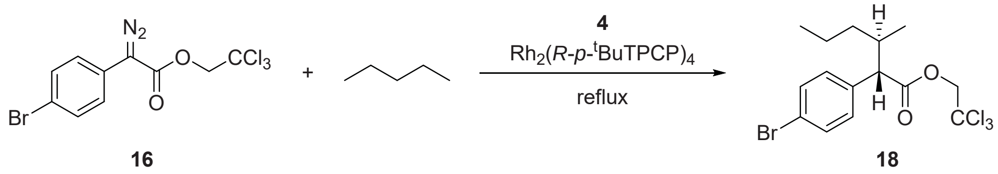


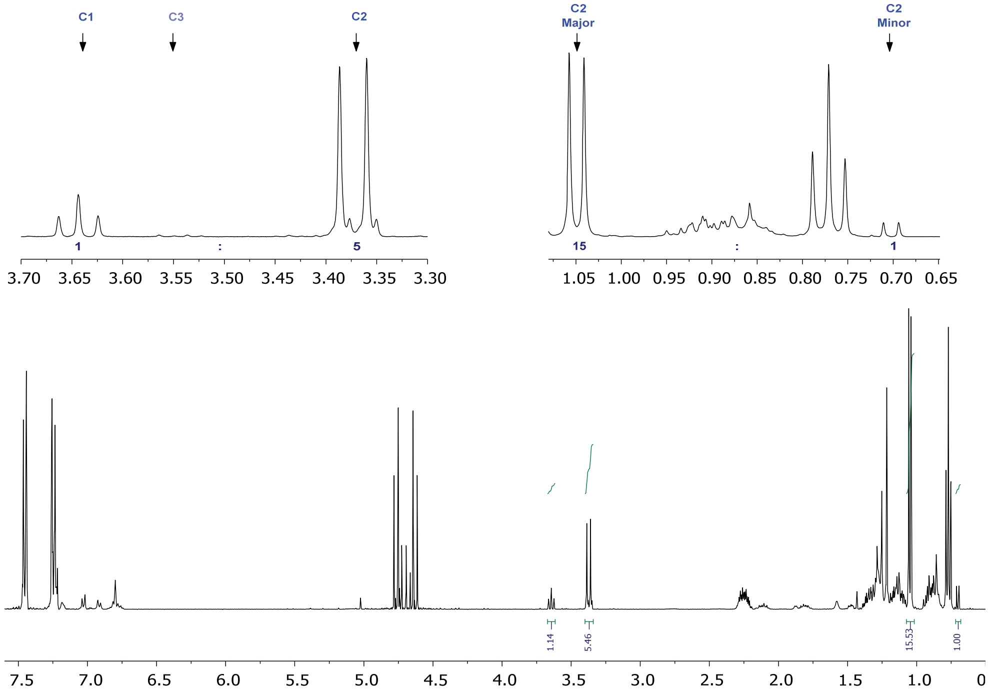
N_2
O
CCl_3
Br
+
3
Rh_2(*R*-*p*-BrTPCP)$_4$
reflux
H
H
O
O
CCl_3
Br

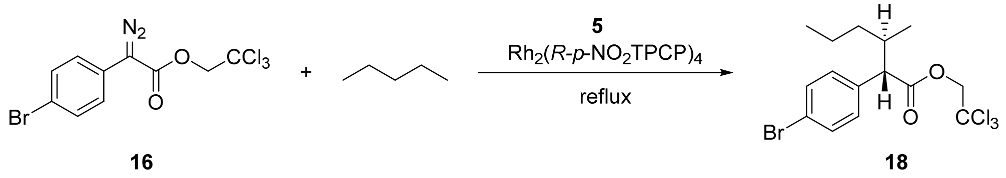
16 **18**

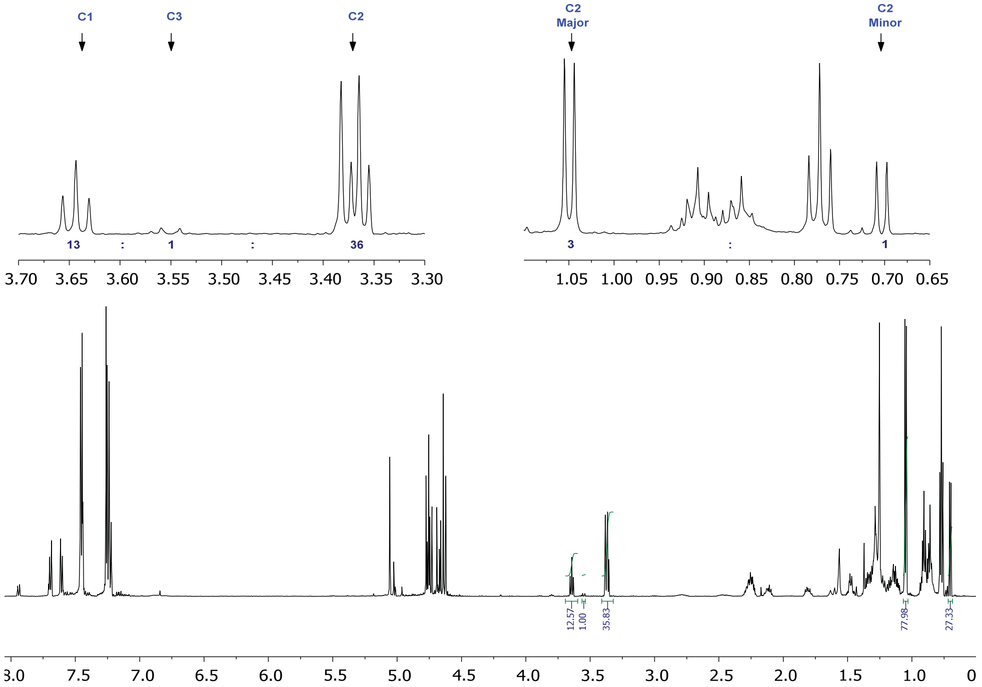


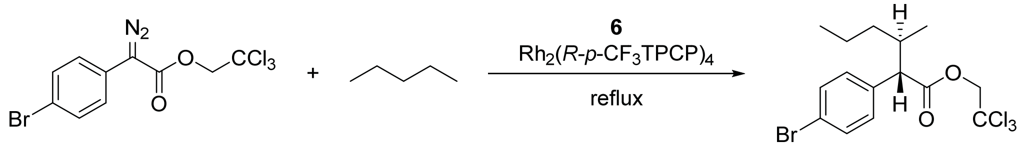
C1
C3
C2
1
:
4
3.70
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
C2 Major
C2 Minor
6
:
1
1.10
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
100.00
20.64
77.42
172.83
28.74
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0


N2
O
CCl3
O
Br
16
+
4
Rh2(R-p-tBuTPCP)4
reflux
H
H
O
O
CCl3
Br
18


C1
C3
C2
C2 Major
C2 Minor
1 : 5
15 : 1
3.70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30
1.05 1.00 0.95 0.90 0.85 0.80 0.75 0.70 0.65
1.14
5.46
15.53
1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

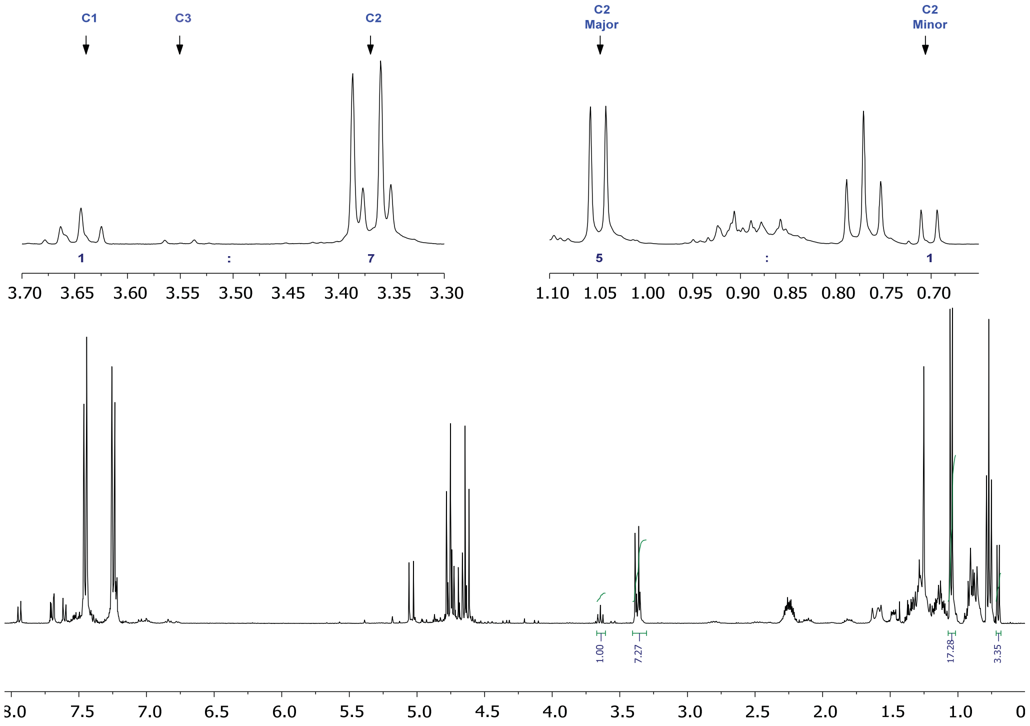

N2
CCl3
Br
16
+
5
Rh2(R-p-NO2TPCP)4
reflux
H
H
O
CCl3
Br
18

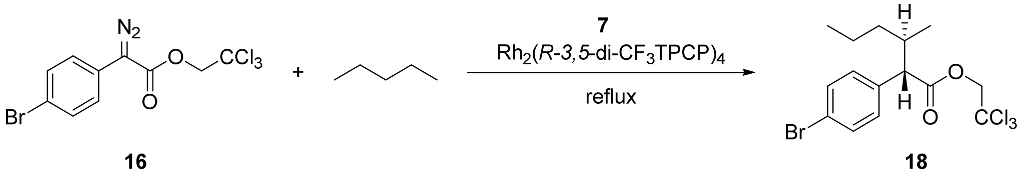

C1
C3
C2
13 : 1 : 36
3.70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30
C2 Major
C2 Minor
3 : 1
1.05 1.00 0.95 0.90 0.85 0.80 0.75 0.70 0.65
12.57
1.00
35.83
77.98
27.33
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

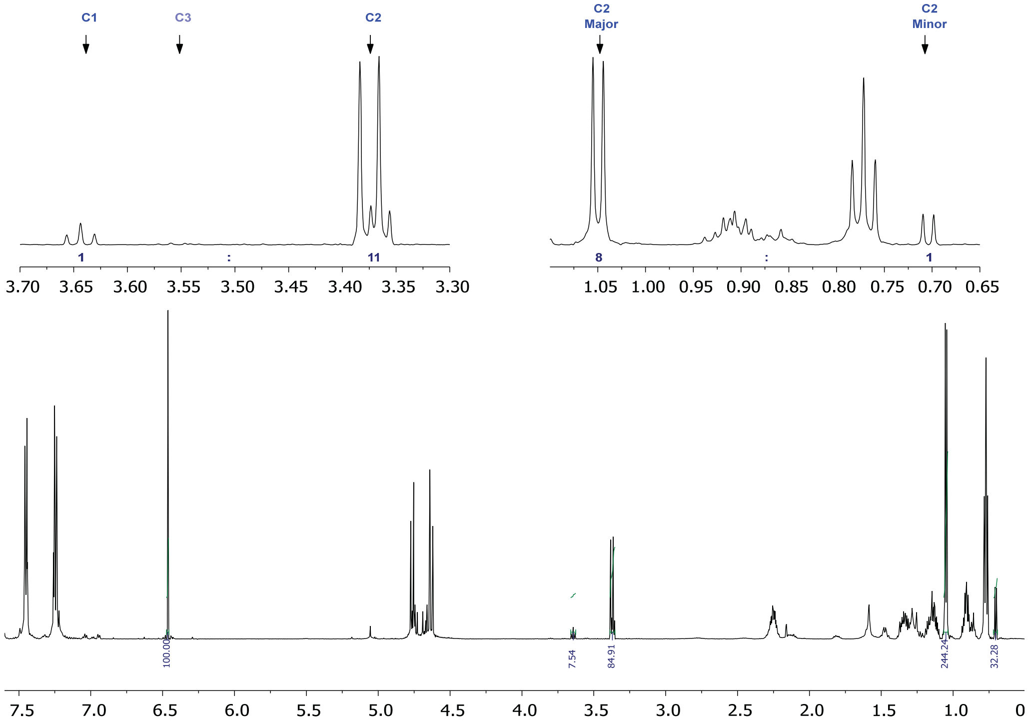

N2
CCl3
Br
O
6
Rh2(R-p-CF3TPCP)4
reflux
H
H
O
CCl3
Br

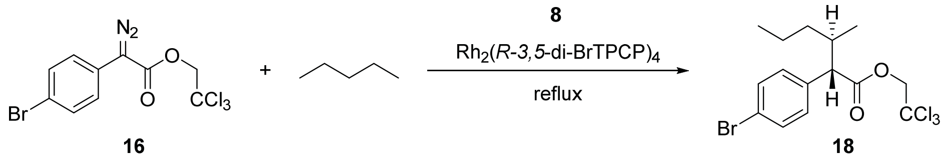
16

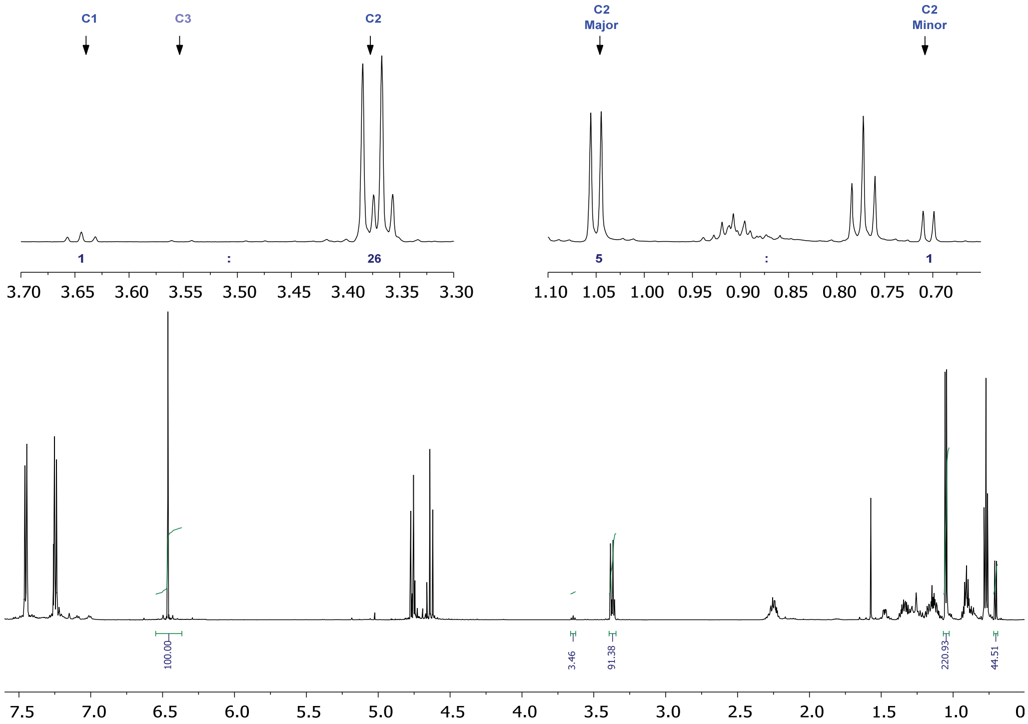
18

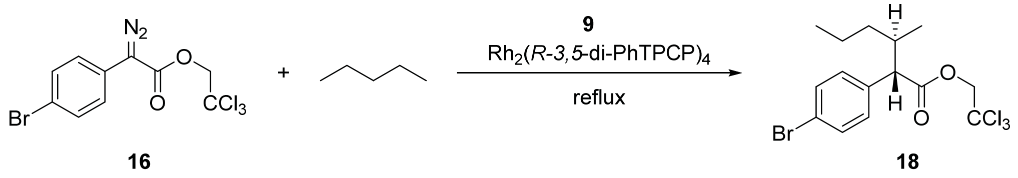

C1
C3
C2
1
:
7
3.70
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
C2 Major
C2 Minor
5
:
1
1.10
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
1.00
7.27
17.28
3.35
3.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

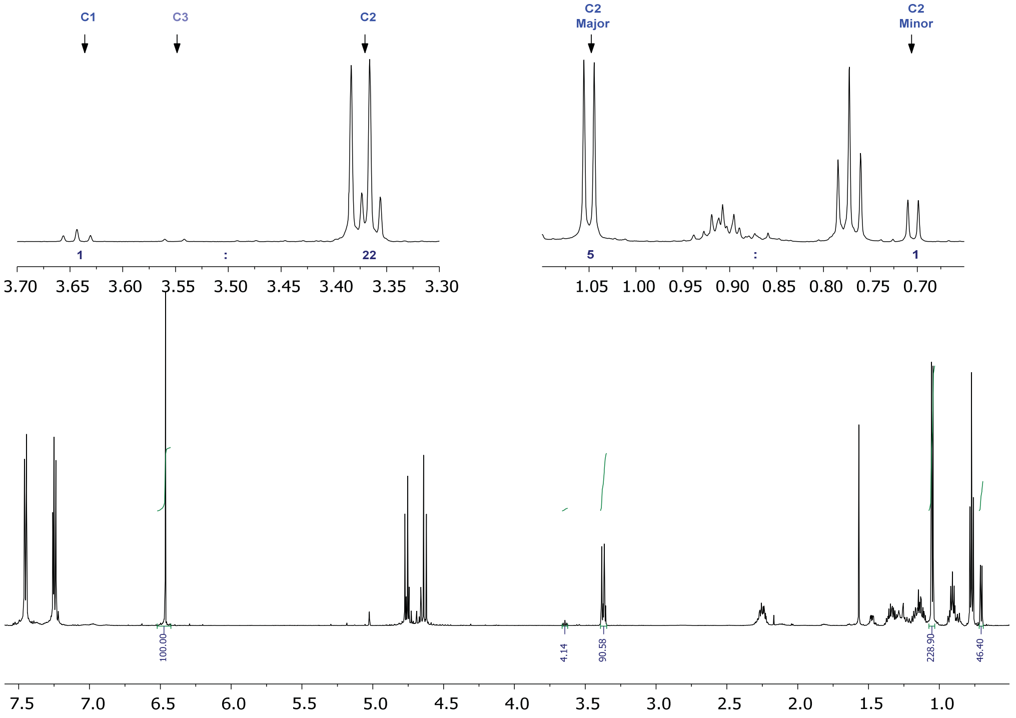

N2
CCl3
Br
O
16
+
7
Rh2(R-3,5-di-CF3TPCP)4
reflux
H
H
O
CCl3
Br
18

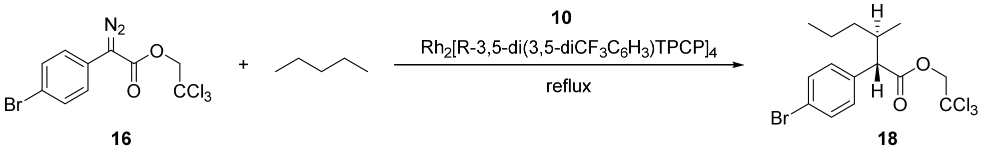

C1
C3
C2
1
:
11
3.70
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
C2 Major
C2 Minor
8
:
1
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
100.00
7.54
84.91
244.24
32.28
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0


N2
+
8
Rh2(R-3,5-di-BrTPCP)4
reflux
Br
CCl3
O
H
16
18

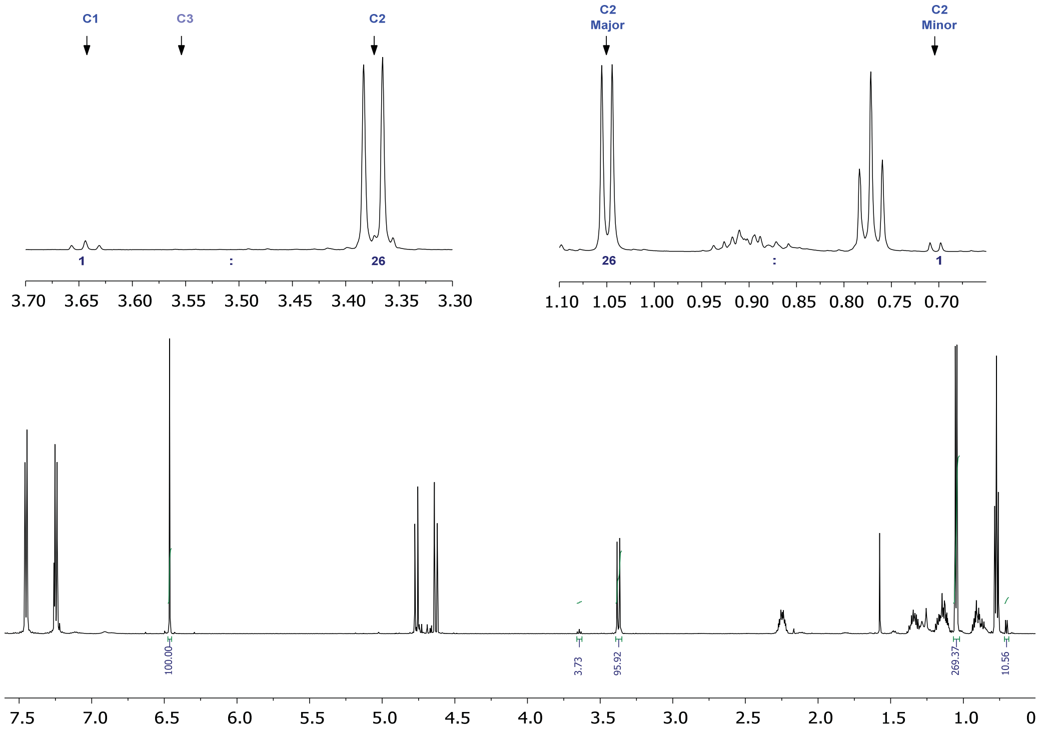

C1
C3
C2
1
:
26
3.70
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
C2 Major
C2 Minor
5
:
1
1.10
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
100.00
3.46
91.38
220.93
44.51
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0


N2
O
CCl3
Br
16
+
9
Rh2(R-3,5-di-PhTPCP)4
reflux
H
H
O
O
CCl3
Br
18

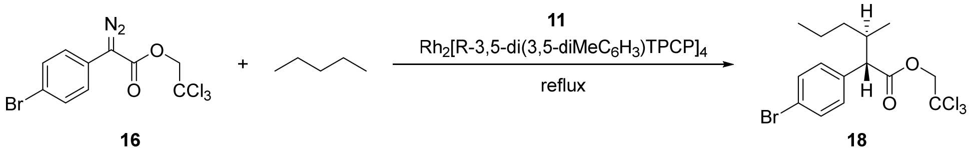

C1
C3
C2
C2 Major
C2 Minor
1
:
22
5
:
1
3.70
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
100.00
4.14
90.58
228.90
46.40
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0



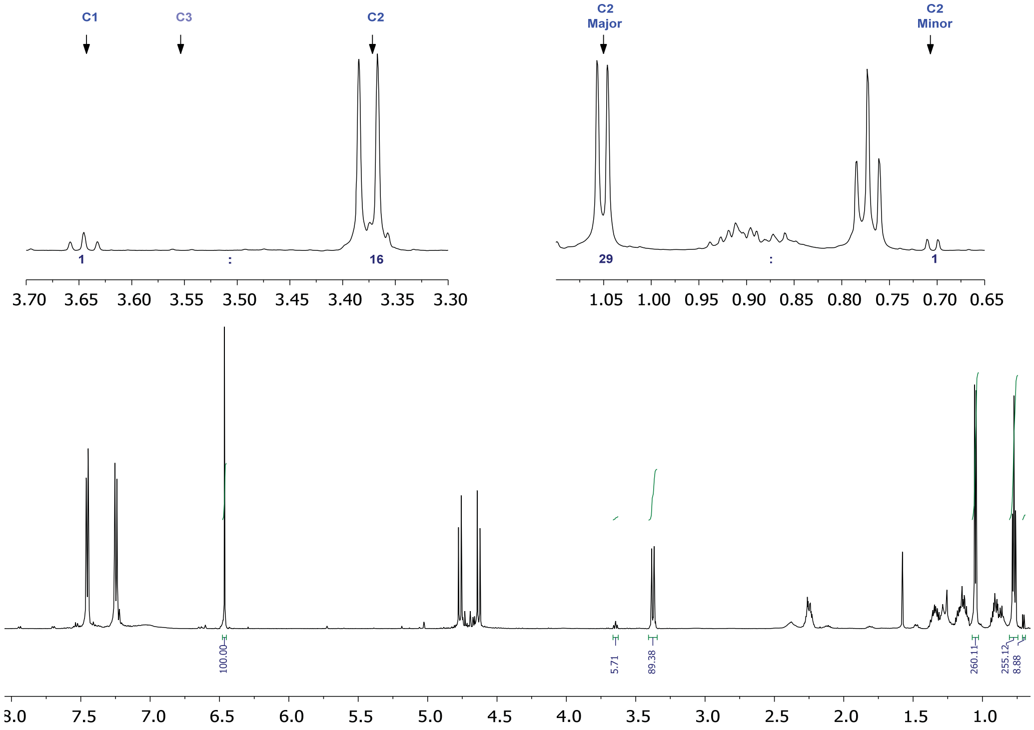
N2
O
CCl3
Br
16
10
Rh2[R-3,5-di(3,5-diCF3C6H3)TPCP]4
reflux
H
O
CCl3
Br
18



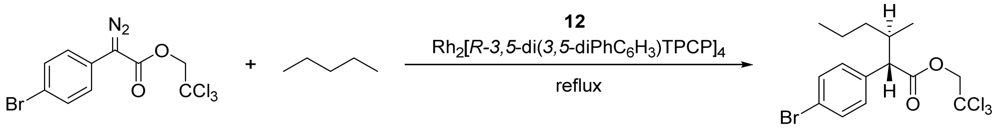
C1
C3
C2
1
:
26
3.70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30
C2 Major
C2 Minor
26
:
1
1.10 1.05 1.00 0.95 0.90 0.85 0.80 0.75 0.70
100.00
3.73
95.92
269.37
10.56
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0



N$_2$
O
CCl$_3$
Br
16
+
11
Rh$_2$[R-3,5-di(3,5-diMeC$_6$H$_3$)TPCP]$_4$
reflux
H
H
O
CCl$_3$
Br
18

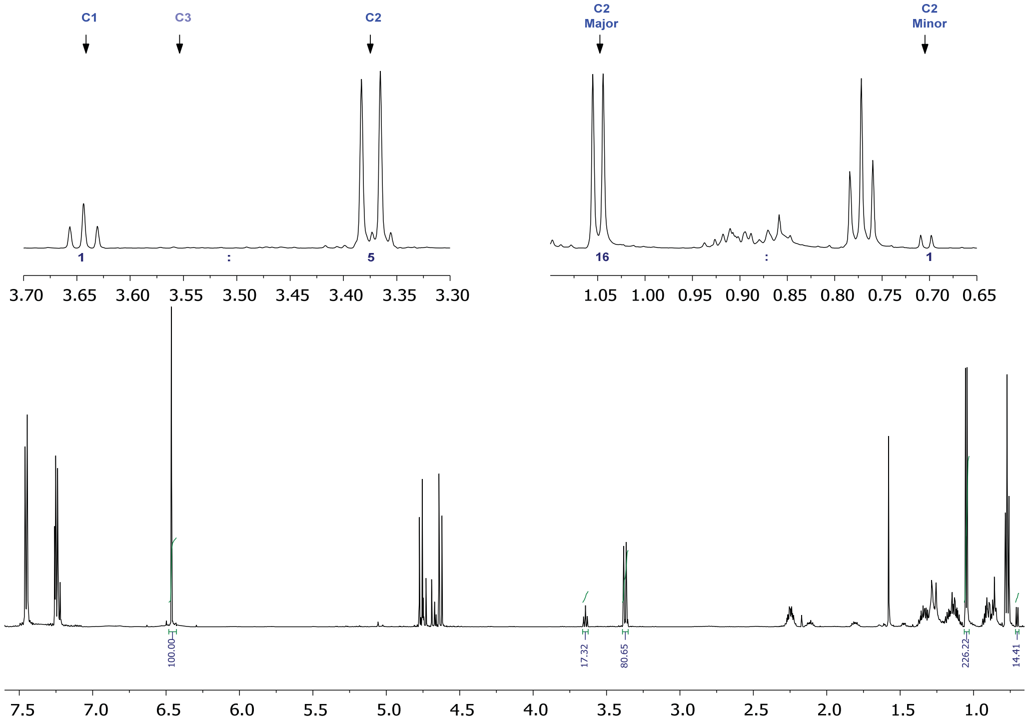


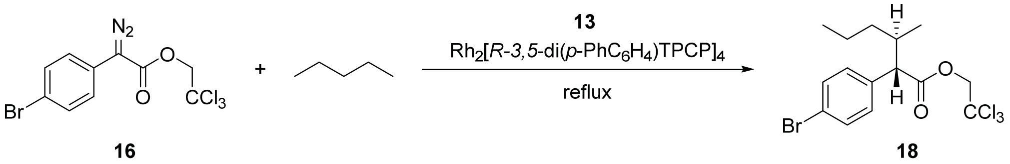
C1
C3
C2
1
:
16
3.70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30
C2 Major
C2 Minor
29
:
1
1.05 1.00 0.95 0.90 0.85 0.80 0.75 0.70 0.65
100.00
5.71
89.38
260.11
255.12
8.88
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0

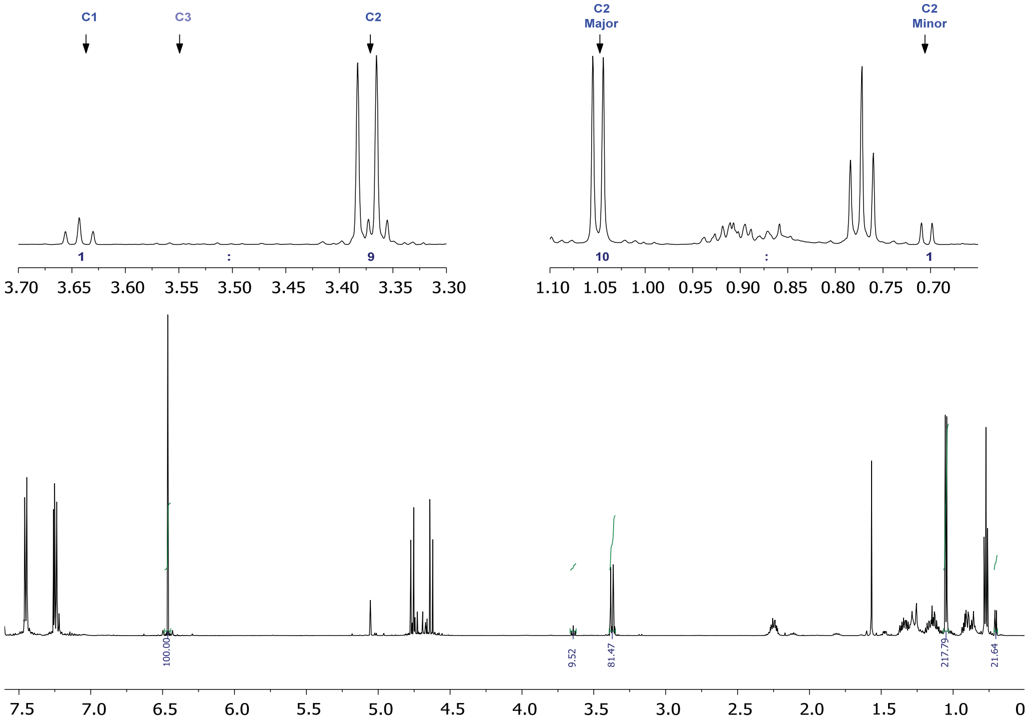

N2
O
CCl3
Br
+
12
Rh2[R-3,5-di(3,5-diPhC6H3)TPCP]4
reflux
H
H
O
CCl3
Br

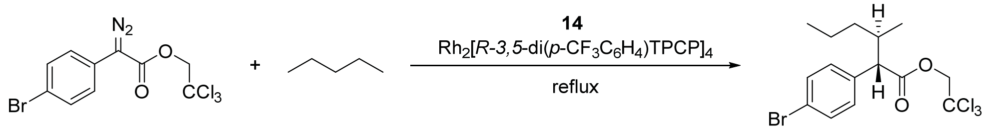
16

18


C1
C3
C2
C2 Major
C2 Minor
1
:
5
16
:
1
3.70
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
100.00
17.32
80.65
226.22
14.41
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

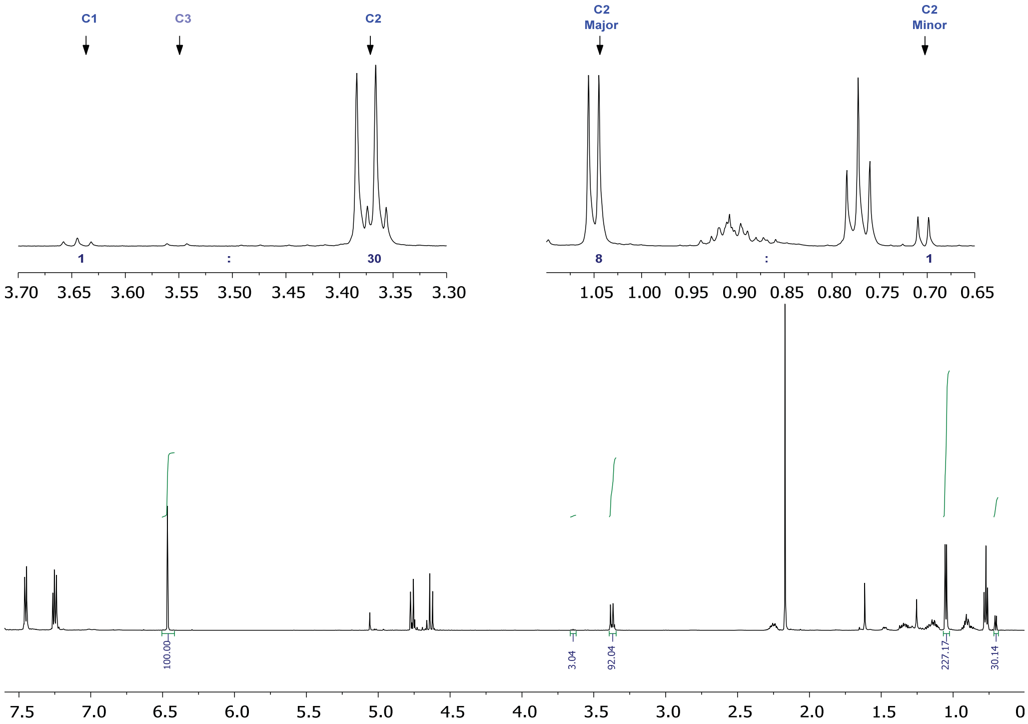

N$_2$
Br
O
O
CCl$_3$
16
+
13
Rh$_2$[*R-3,5*-di(*p*-PhC$_6$H$_4$)TPCP]$_4$
reflux
H
H
Br
O
O
CCl$_3$
18

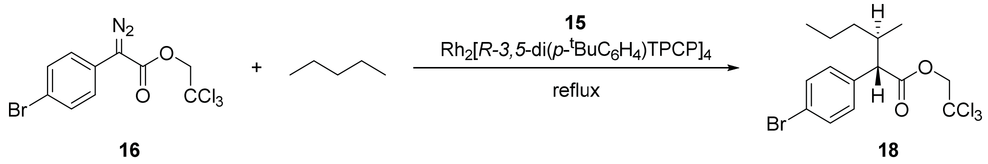

C1
C3
C2
1
:
9
3.70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30
C2 Major
C2 Minor
10
:
1
1.10 1.05 1.00 0.95 0.90 0.85 0.80 0.75 0.70
100.00
9.52
81.47
217.79
21.64
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0


N$_2$
Br
O
O
CCl$_3$
+
14
Rh$_2$[*R-3,5*-di(*p*-CF$_3$C$_6$H$_4$)TPCP]$_4$
reflux
H
H
O
O
CCl$_3$
Br

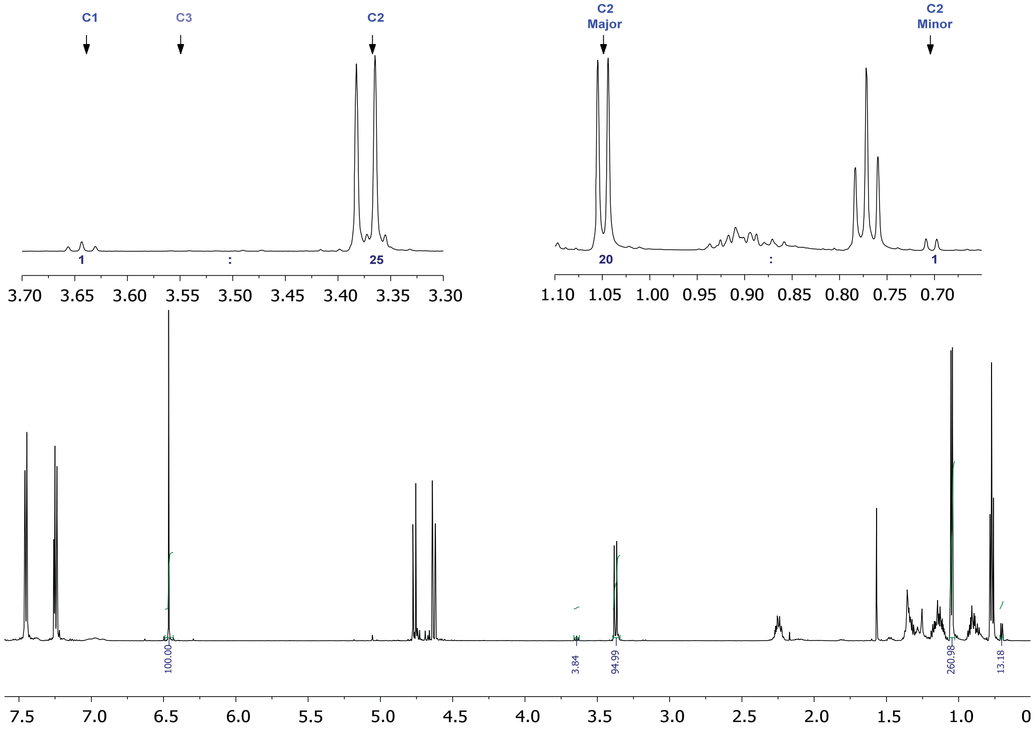
16

18

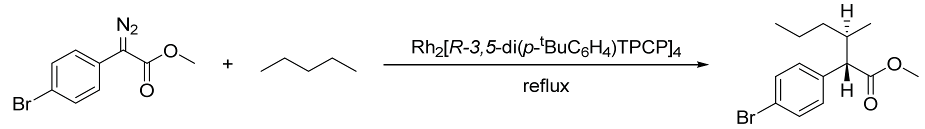

C1
C3
C2
1
:
30
3.70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30
C2
Major
C2
Minor
8
:
1
1.05 1.00 0.95 0.90 0.85 0.80 0.75 0.70 0.65
100.00
3.04
92.04
227.17
30.14
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

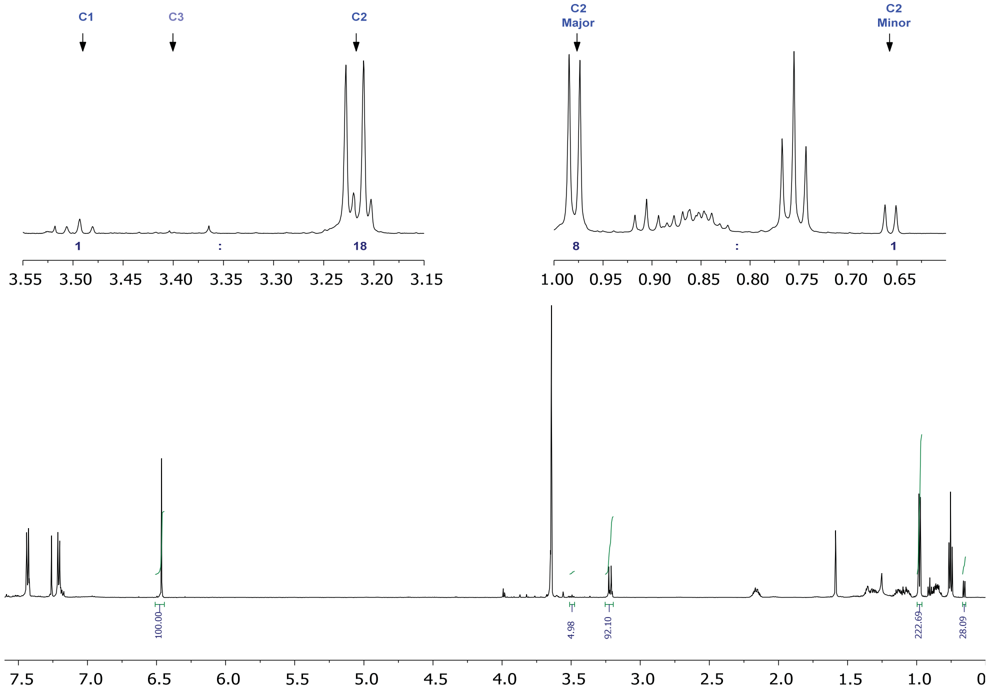


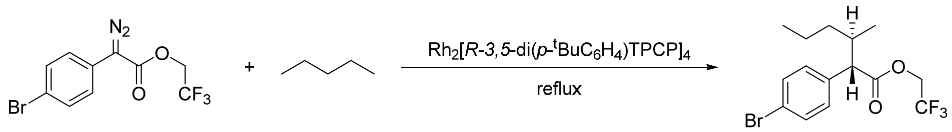
N2
Br
O
CCl3
16
+
15
Rh2[R-3,5-di(p-tBuC6H4)TPCP]4
reflux
H
H
O
Br
CCl3
18

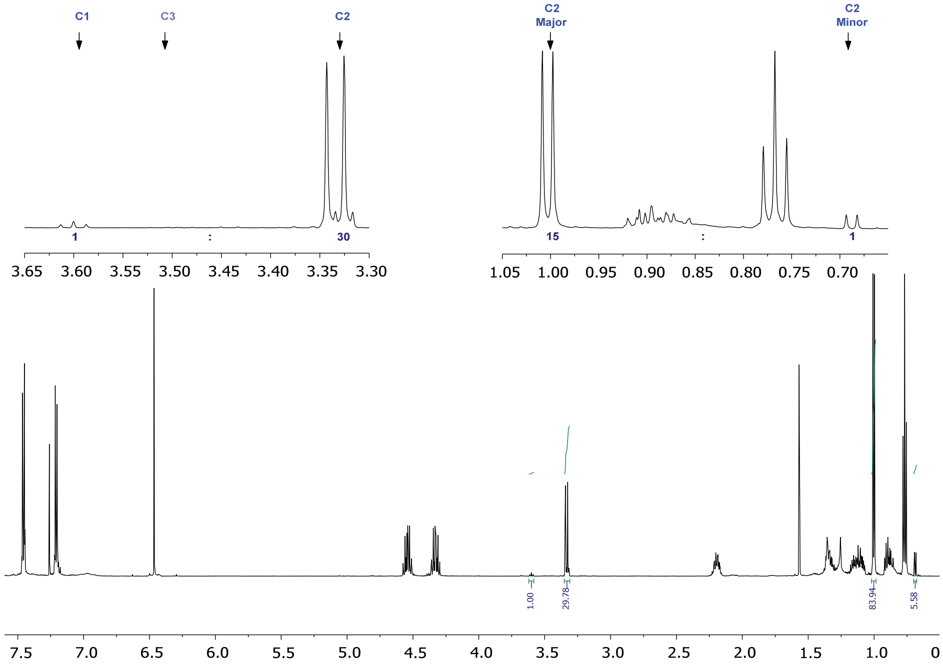


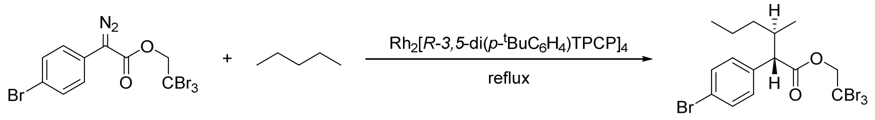
C1
C3
C2
1
:
25
3.70
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
C2 Major
C2 Minor
20
:
1
1.10
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
100.00
3.84
94.99
260.98
13.18
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

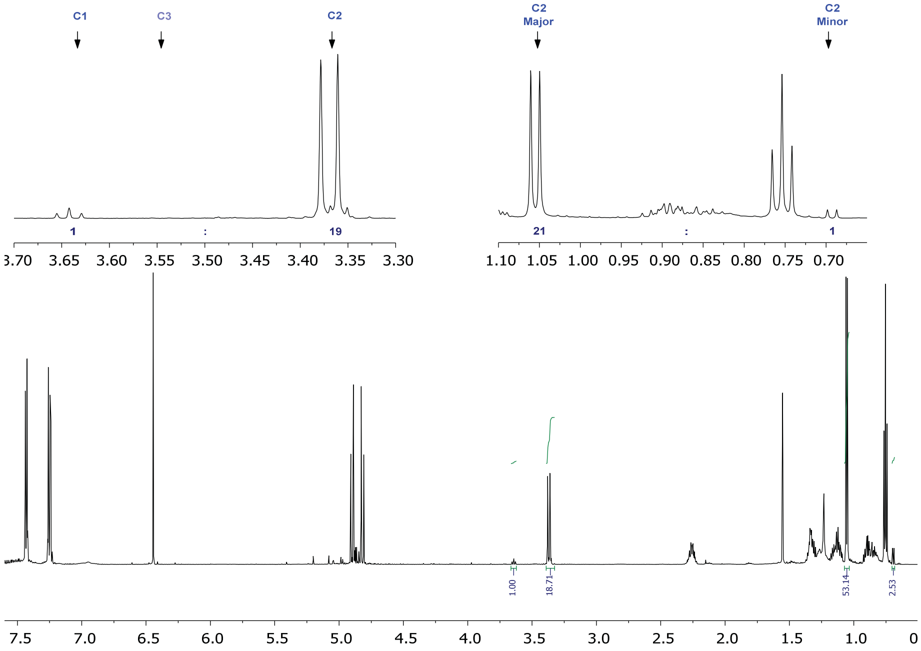

N2
Br
+
Rh2[R-3,5-di(p-tBuC6H4)TPCP]4
reflux
H
H
O
Br


C1
C3
C2
C2 Major
C2 Minor
1
:
18
8
:
1
3.55 3.50 3.45 3.40 3.35 3.30 3.25 3.20 3.15
1.00 0.95 0.90 0.85 0.80 0.75 0.70 0.65
100.00
4.98
92.10
222.69
28.09
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

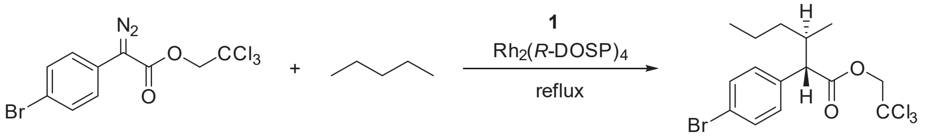

N2
Br
O
O
CF3
+
Rh2[R-3,5-di(p-tBuC6H4)TPCP]4
reflux
H
H
Br
O
O
CF3


C1
C3
C2
1
:
30
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
C2 Major
C2 Minor
15
:
1
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
1.00
29.78
83.94
5.58
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

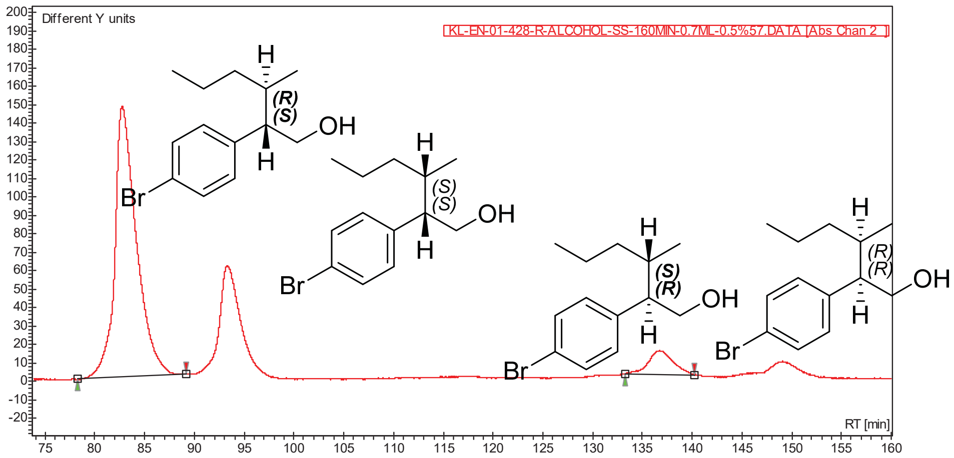

N2
Br
O
CBr3
+
Rh2[R-3,5-di(p-tBuC6H4)TPCP]4
reflux
H
H
O
CBr3
Br


C1
C3
C2
1
:
19
3.70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30
C2 Major
C2 Minor
21
:
1
1.10 1.05 1.00 0.95 0.90 0.85 0.80 0.75 0.70
1.00
18.71
53.14
2.53
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

3.3 HPLC Spectra

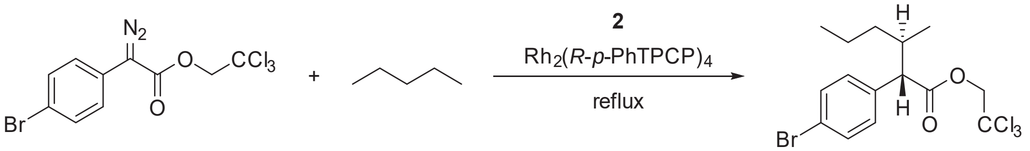


16 **18**

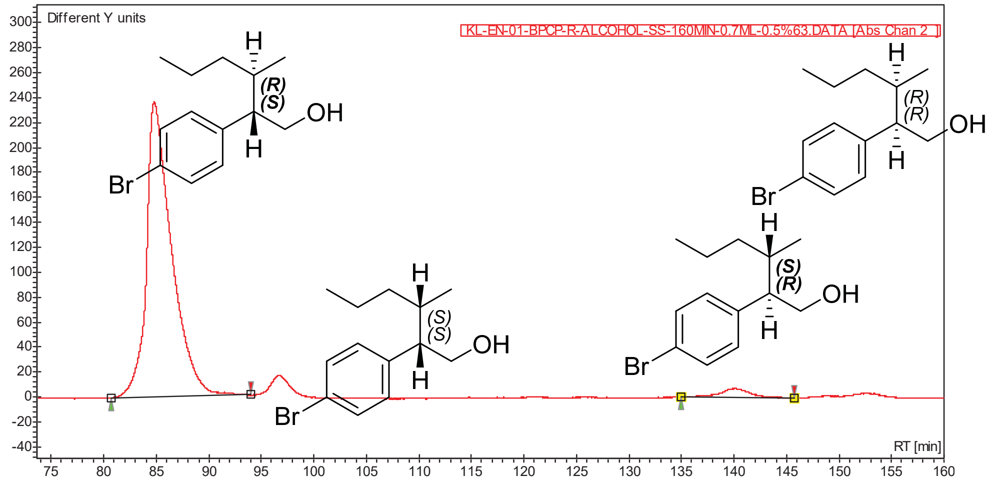


#	Time [Min]	Area % [%]
1	82.74	91.118
2	136.73	8.882

82% e.e.

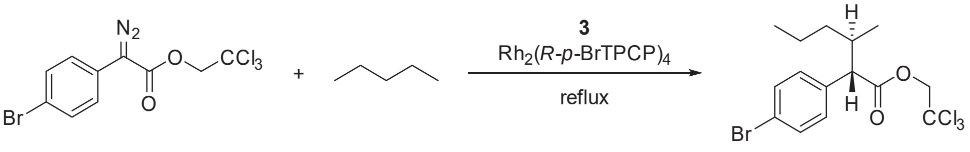


16 **18**

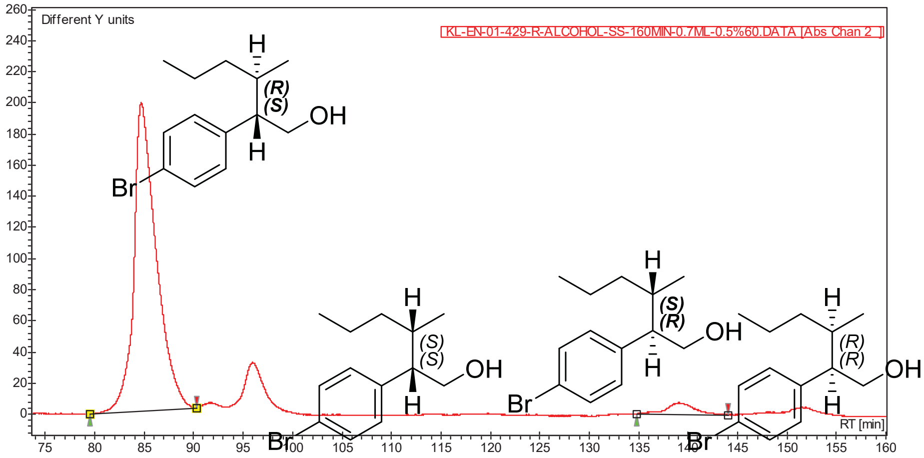


#	Time [Min]	Area % [%]
1	84.79	96.211
2	140.01	3.789

92% e.e.

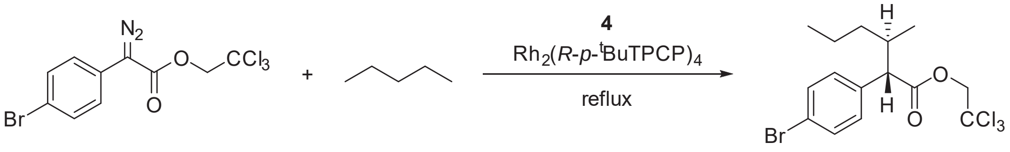


16 **18**

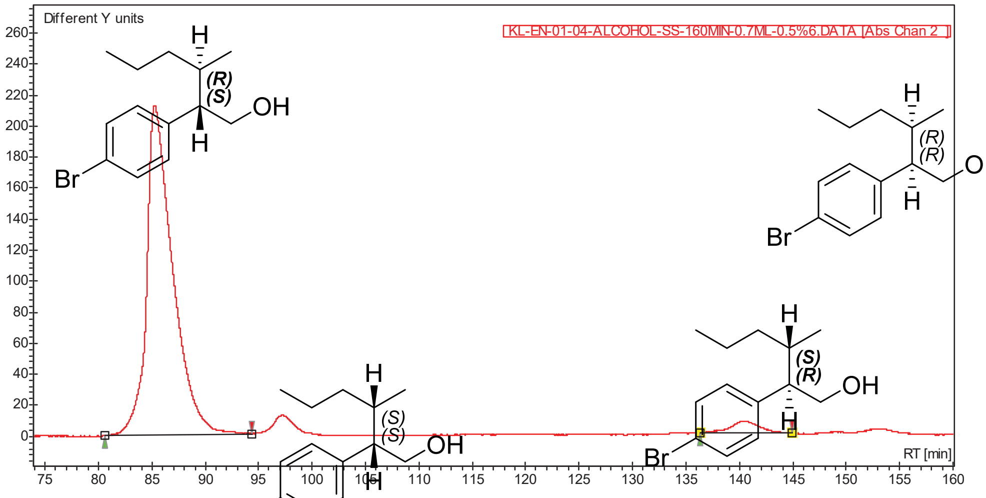


#	Time [Min]	Area % [%]
1	84.70	95.443
2	139.03	4.557

91% e.e.

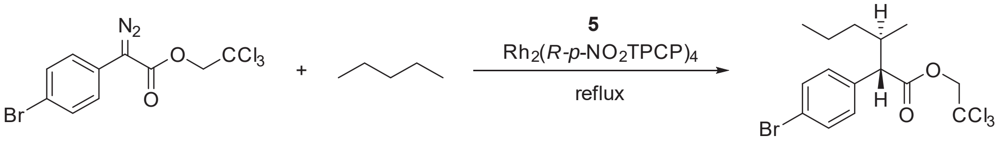


16 **18**

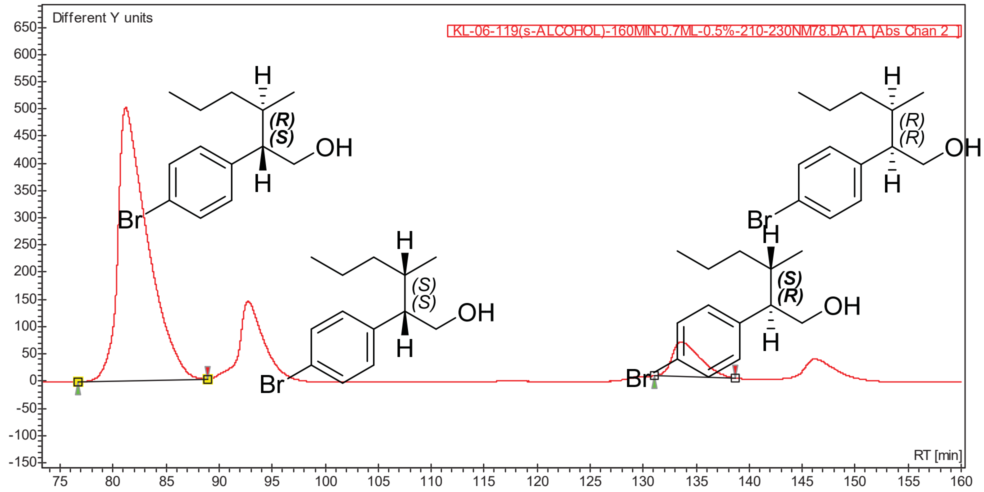


#	Time [Min]	Area % [%]
1	85.26	96.182
2	140.41	3.818

92% e.e.

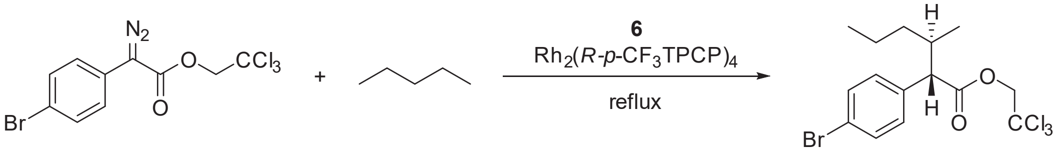


16 **18**

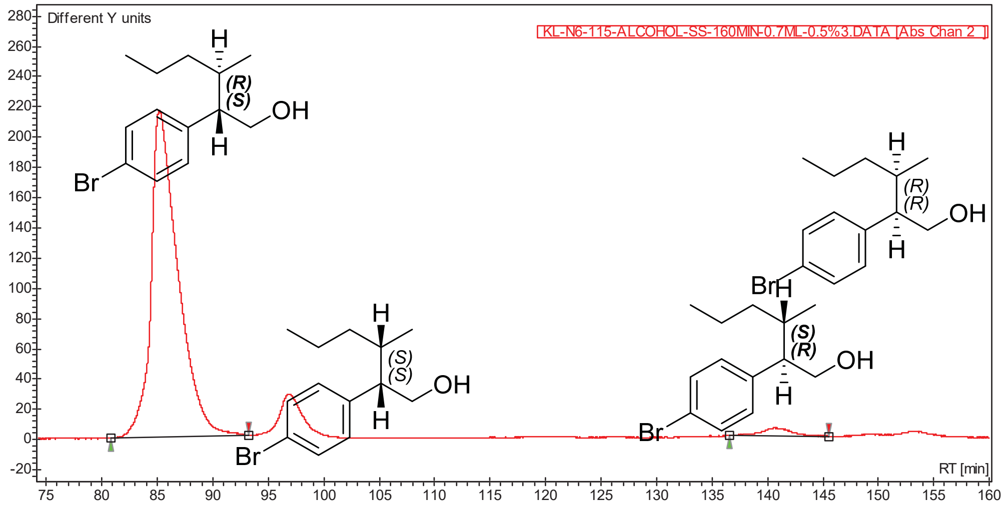


#	Time [Min]	Area % [%]
1	81.17	89.291
2	133.62	10.709

79% e.e.

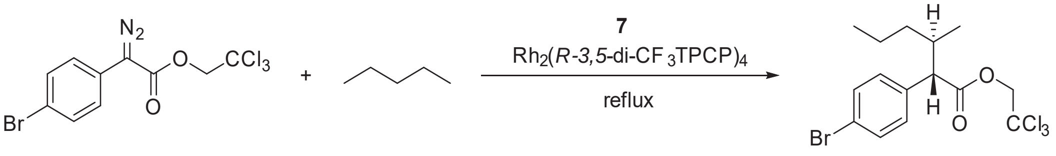


16 **18**

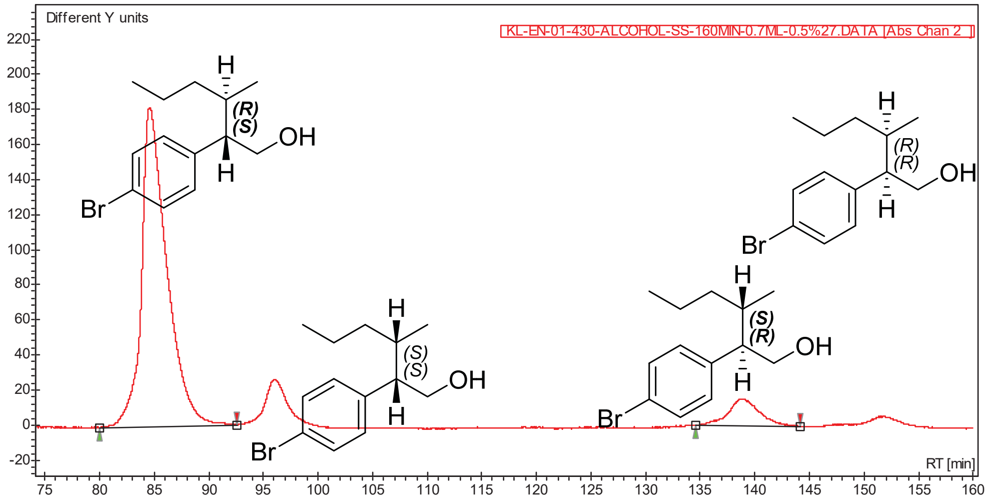


#	Time [Min]	Area % [%]
1	85.16	97.121
2	140.73	2.879

94% e.e.

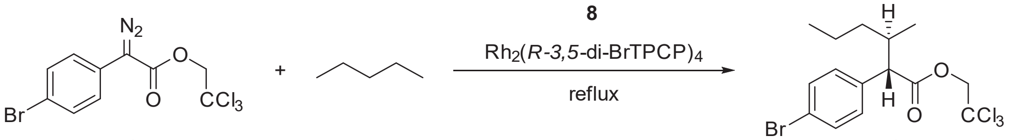


16 **18**

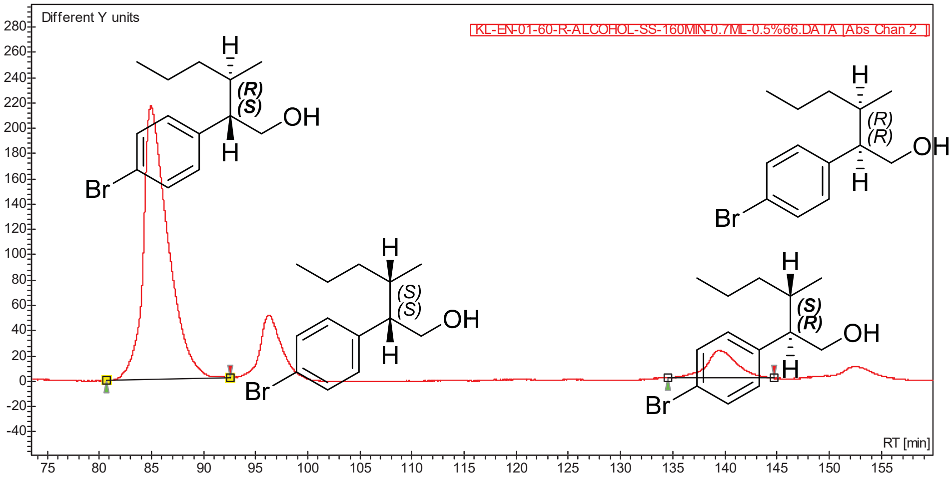


#	Time [Min]	Area % [%]
1	84.58	90.564
2	138.78	9.436

81% e.e.

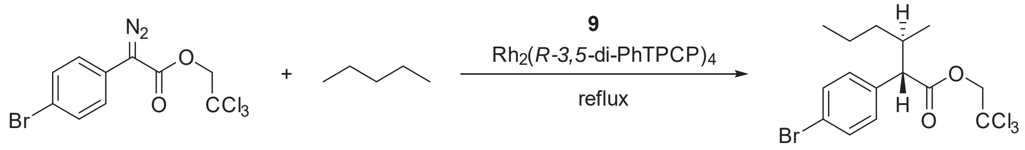


16 **18**

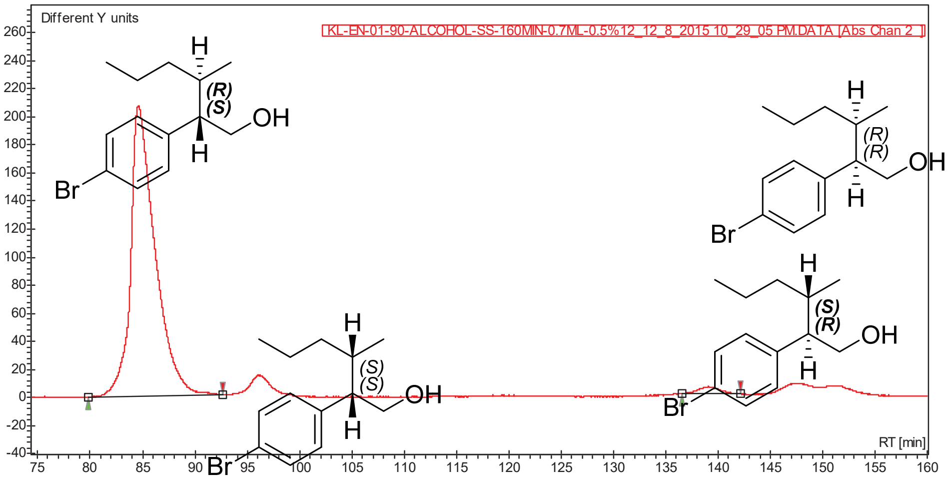


#	Time [Min]	Area % [%]
1	84.95	89.026
2	139.49	10.974

78% e.e.

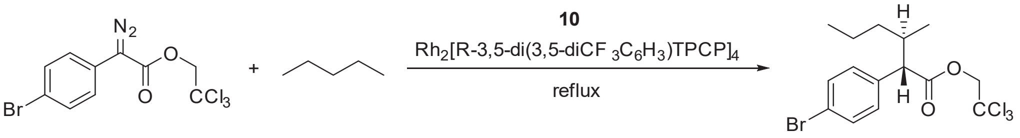


16 **18**

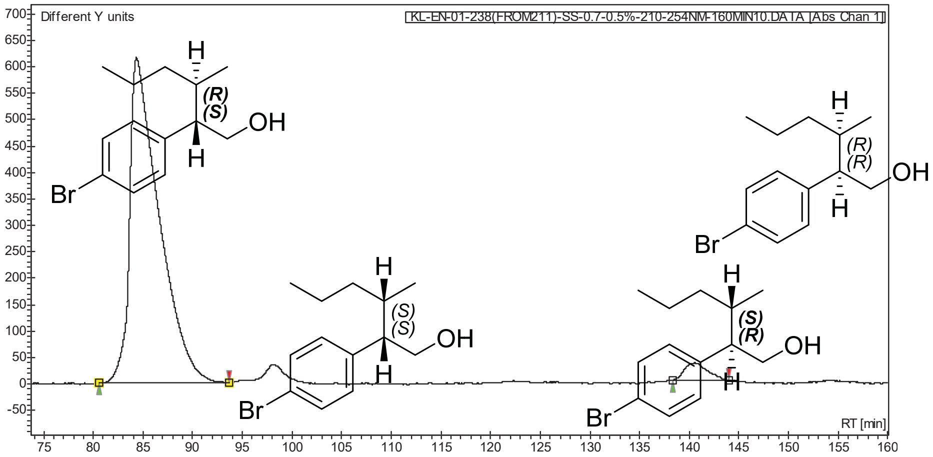


#	Time [Min]	Area % [%]
1	84.62	97.905
2	139.08	2.095

96% e.e.



16 **18**



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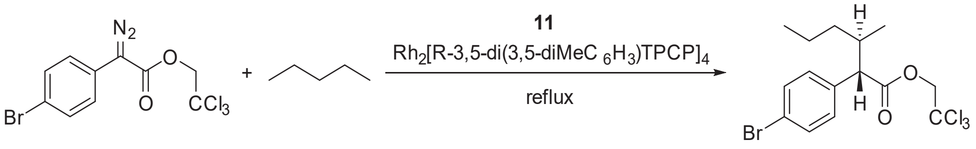
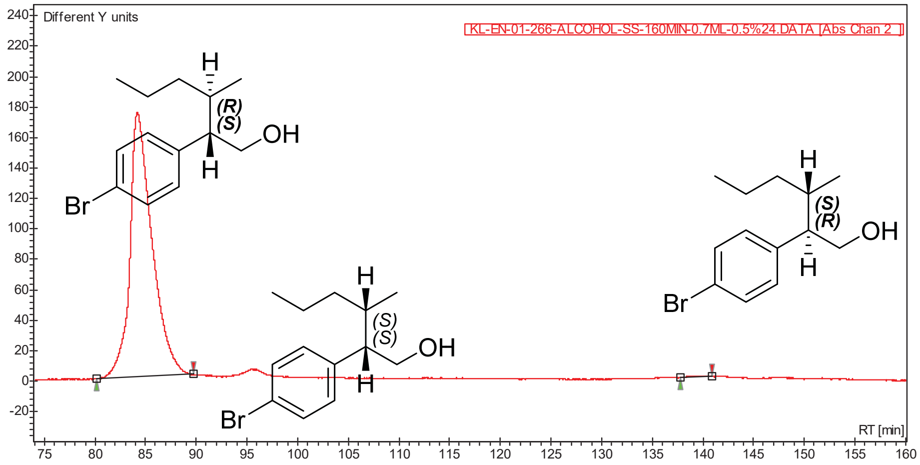
2	140.51	4.019

92% e.e.



16 **18**



#	Time [Min]	Area % [%]
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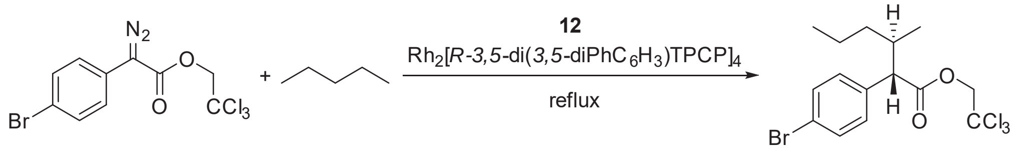
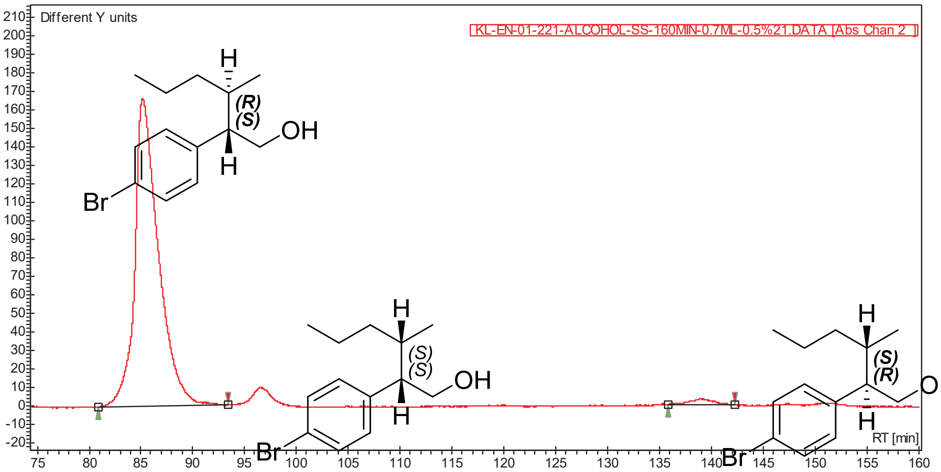
2	139.06	0.354

>99% e.e.

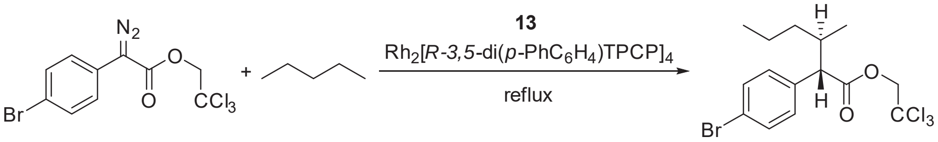


16 18

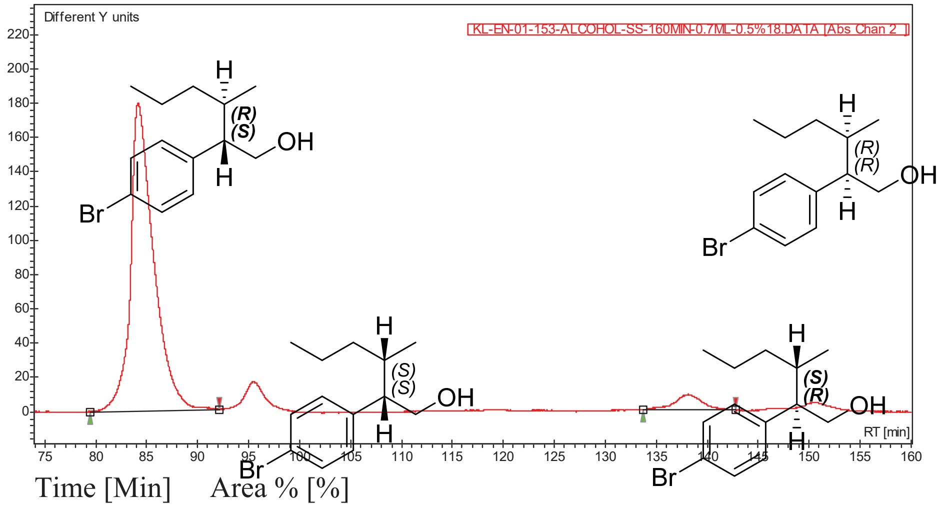


#	Time [Min]	Area % [%]
1	85.16	98.273
2	139.17	1.727

97% e.e.



16 **18**



#	Time [Min]	Area % [%]
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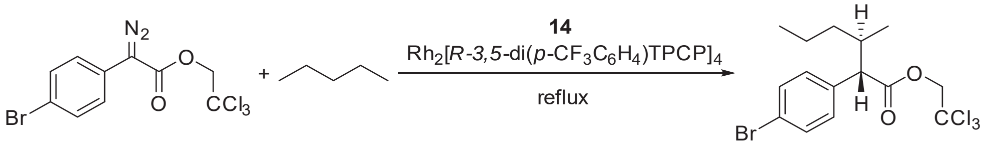
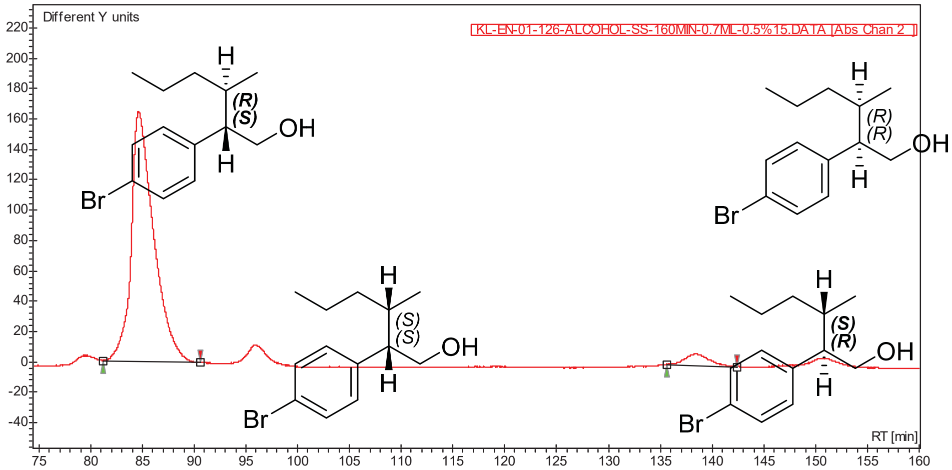
2	138.11	5.674

89% e.e.



16 **18**



#	Time [Min]	Area % [%]
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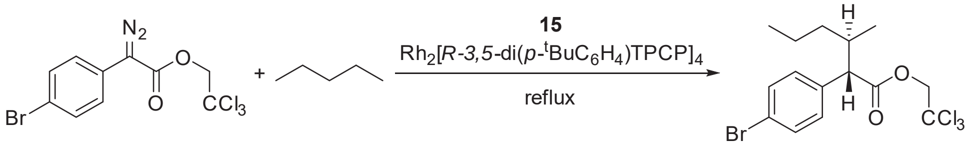
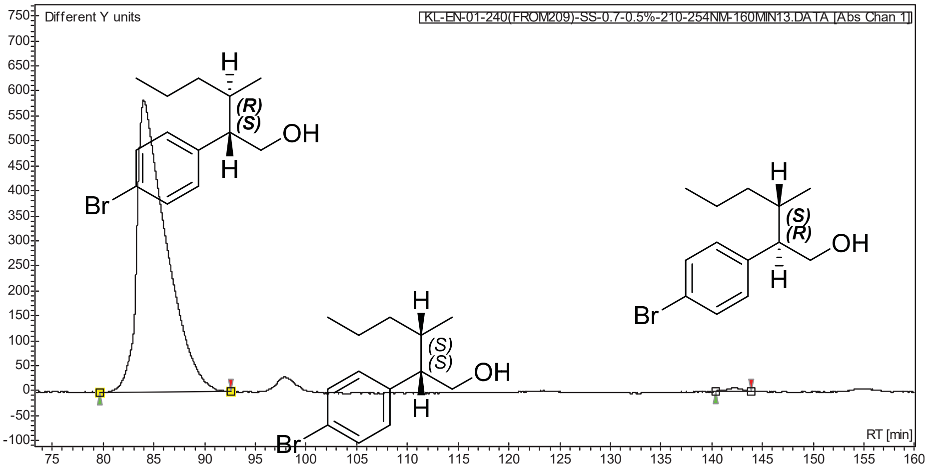
2	138.29	4.549

91% e.e.



16 **18**



#	Time [Min]	Area % [%]
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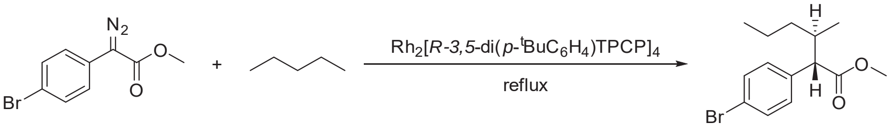
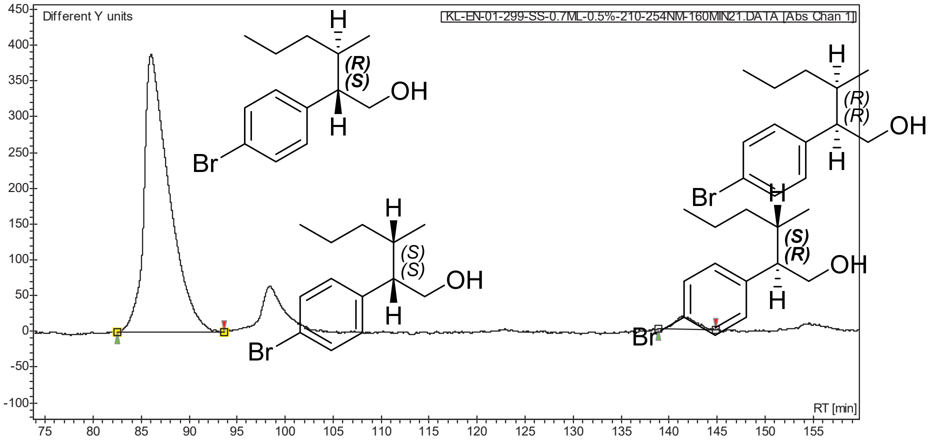
2	142.41	0.527

99% e.e.





#	Time [Min]	Area % [%]
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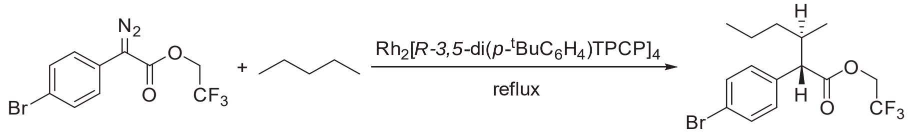
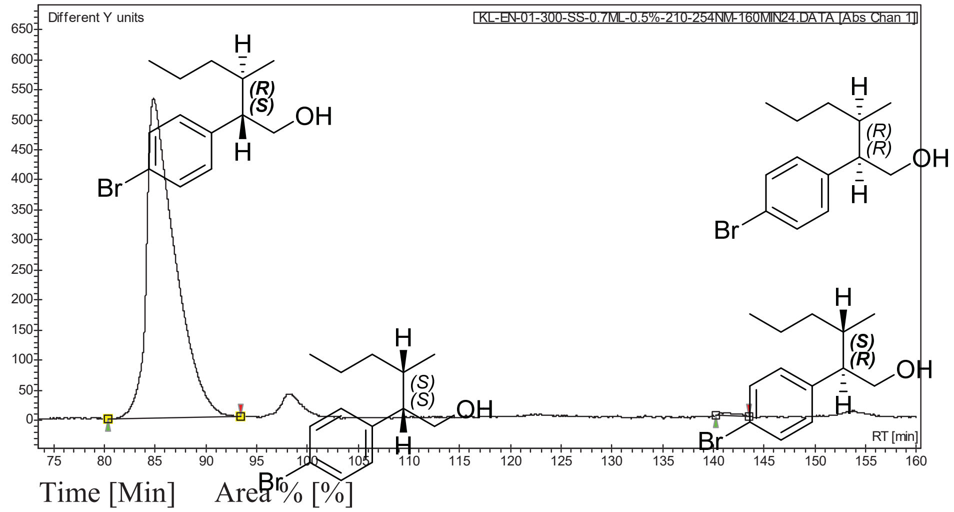
2	141.49	3.814

92% e.e.





#	Time [Min]	Area % [%]
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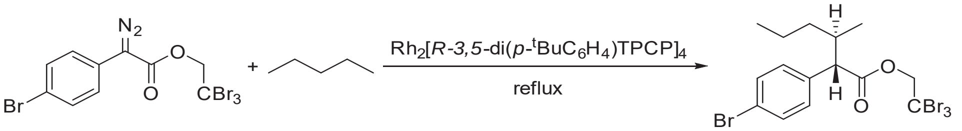
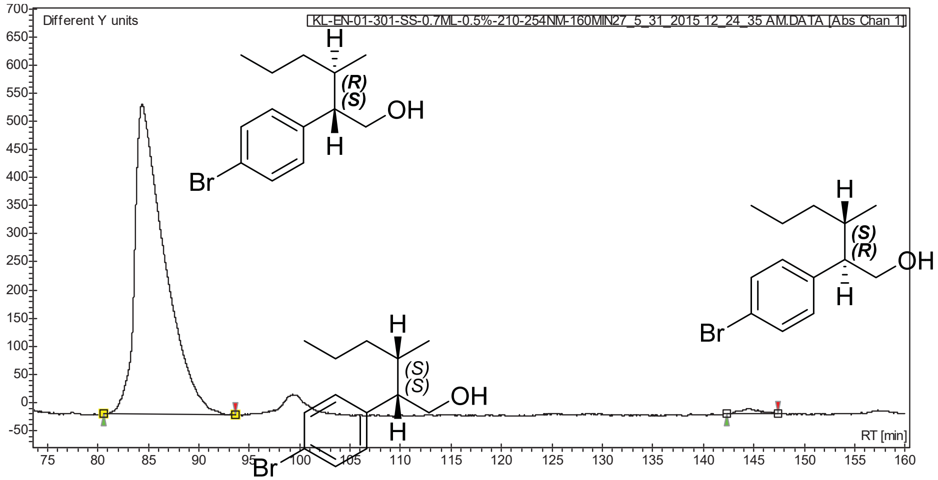
2	141.42	0.637

99% e.e.



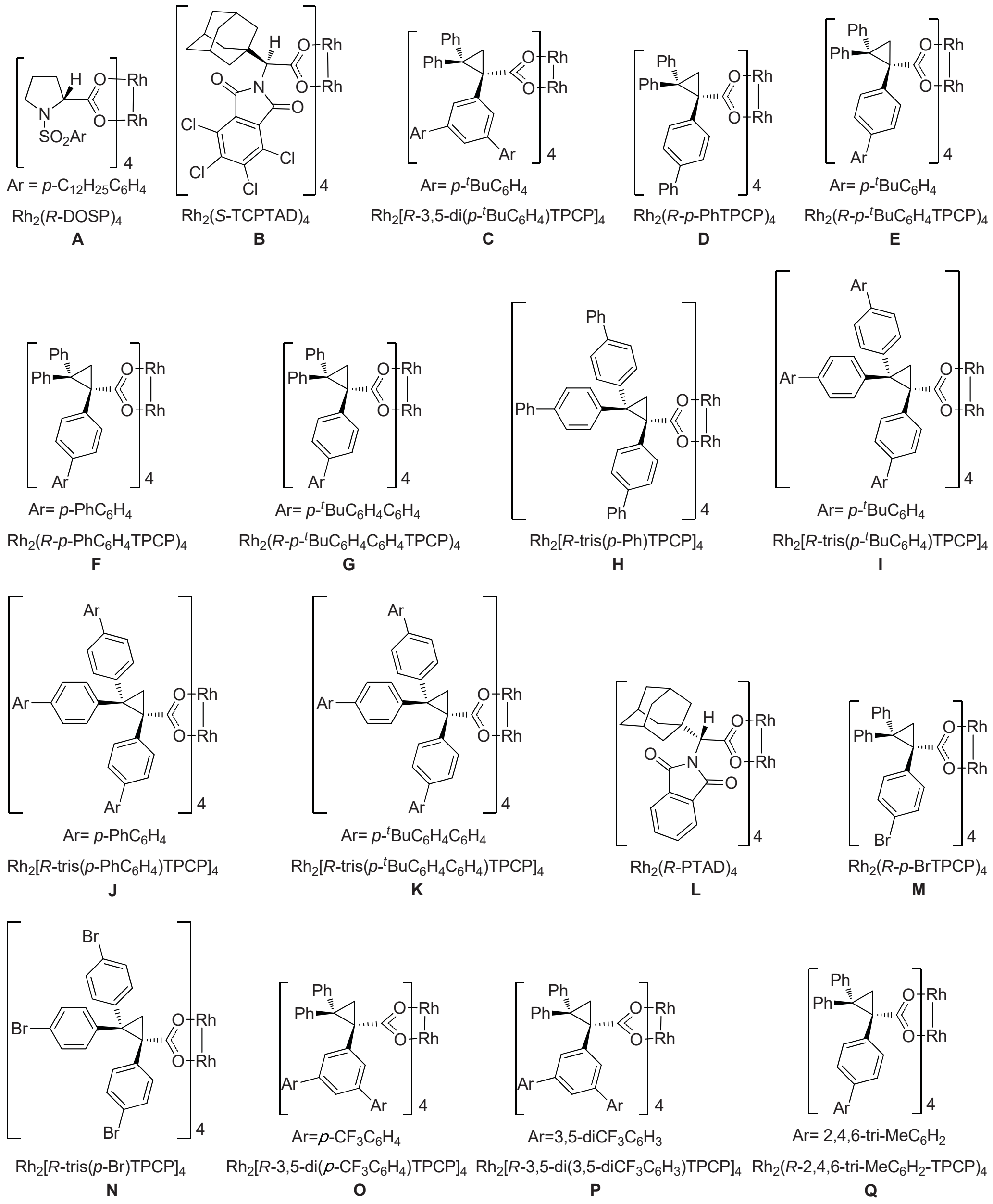


#	Time [Min]	Area % [%]
1	84.38	98.929
2	144.57	1.071

98% e.e.

4. Catalyst Screen for Primary Selective Catalyst

4.1 Catalysts Structures



Ar = p-$C_{12}H_{25}C_6H_4$
Rh_2(*R*-DOSP)$_4$
A

Rh_2(*S*-TCPTAD)$_4$
B

Ar= p-$^tBuC_6H_4$
Rh_2[*R*-3,5-di(p-$^tBuC_6H_4$)TPCP]$_4$
C

Rh_2(*R*-p-PhTPCP)$_4$
D

Ar= p-$^tBuC_6H_4$
Rh_2(*R*-p-$^tBuC_6H_4$TPCP)$_4$
E

Ar= p-PhC_6H_4
Rh_2(*R*-p-PhC_6H_4TPCP)$_4$
F

Ar= p-$^tBuC_6H_4C_6H_4$
Rh_2(*R*-p-$^tBuC_6H_4C_6H_4$TPCP)$_4$
G

Rh_2[*R*-tris(p-Ph)TPCP]$_4$
H

Ar= p-$^tBuC_6H_4$
Rh_2[*R*-tris(p-$^tBuC_6H_4$)TPCP]$_4$
I

Ar= p-PhC_6H_4
Rh_2[*R*-tris(p-PhC_6H_4)TPCP]$_4$
J

Ar= p-$^tBuC_6H_4C_6H_4$
Rh_2[*R*-tris(p-$^tBuC_6H_4C_6H_4$)TPCP]$_4$
K

Rh_2(*R*-PTAD)$_4$
L

Rh_2(*R*-p-BrTPCP)$_4$
M

Rh_2[*R*-tris(p-Br)TPCP]$_4$
N

Ar=p-$CF_3C_6H_4$
Rh_2[*R*-3,5-di(p-$CF_3C_6H_4$)TPCP]$_4$
O

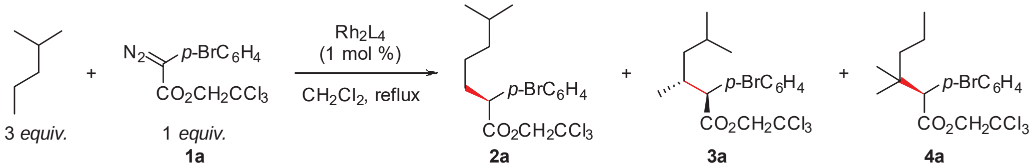
Ar=3,5-di$CF_3C_6H_3$
Rh_2[*R*-3,5-di(3,5-di$CF_3C_6H_3$)TPCP]$_4$
P

Ar= 2,4,6-tri-MeC_6H_2
Rh_2(*R*-2,4,6-tri-MeC_6H_2-TPCP)$_4$
Q

Figure S1. Catalysts Structure

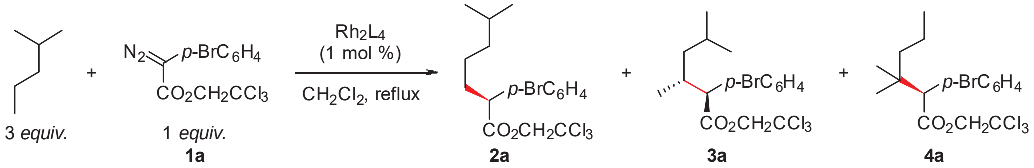
4.2 Result Summary

Table S1. Catalyst Screen Data Summary



Catalyst	r.r. (**2a**: **3a**: **4a**)	e.e. (**2a**,%)	e.e. (**3a**,%)	d.r. (**3a**,%)	e.e. (**4a**,%)	yield (**2a+3a**,%)	yield (**4a**,%)
Rh$_2$(*R*-DOSP)$_4$ **(A)**	0: 19: 81	n.d.	69	2:1	29	16	72
Rh$_2$(*S*-TCPTAD)$_4$ **(B)** 5	0: 11: 89	n.d.	-77	2:1	-84	10	74
Rh$_2$[*R*-3,5-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$ **(C)**	7: 75: 18	81	92	7:1	23	75	16
Rh$_2$(*R*-*p*-PhTPCP)$_4$ **(D)**	39: 45: 16	97	87	9:1	60	75	14
Rh$_2$(*R*-*p*-^{t}BuC$_6$H$_4$TPCP)$_4$ **(E)**	71: 25: 4	96	89	9:1	n.d.	86	4
Rh$_2$(*R*-*p*-PhC$_6$H$_4$TPCP)$_4$ **(F)**	70: 27: 4	98	94	11:1	n.d.	83	3
Rh$_2$(*R*-*p*-^{t}BuC$_6$H$_4$C$_6$H$_4$TPCP)$_4$ **(G)**	71: 26: 3	97	96	15:1	n.d.	85	3
Rh$_2$[*R*-tris(*p*-Ph)TPCP]$_4$ **(H)**	68: 25: 7	90	83	5:1	40	71	5
Rh$_2$[*R*-tris(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$ **(I)**	84: 16: 0	98	92	2:1	n.d.	90	n.d.
Rh$_2$[*R*-tris(*p*-PhC$_6$H$_4$)TPCP]$_4$ **(J)**	68: 25: 7	92	82	5:1	35	78	5
Rh$_2$[*R*-tris(*p*-^{t}BuC$_6$H$_4$C$_6$H$_4$)TPCP]$_4$ **(K)**	48: 35: 17	97	74	3:1	29	55	12

Table S2. Data Summary for Extended Catalysts Screen (not presented in the paper)



Catalyst	r.r. (**2a**: **3a**: **4a**)	e.e. (**2a**,%)	e.e. (**3a**,%)	d.r. (**3a**,%)	e.e. (**4a**,%)	yield (**2a+3a**,%)	yield (**4a**,%)
Rh$_2$(*R*-PTAD)$_4$ **(L)**	0: 32: 68	n.d.	-60	1:1	-22	28	59
Rh$_2$(*R*-*p*-BrTPCP)$_4$ **(M)**	39: 48: 13	97	87	3:1	35	75	11
Rh$_2$[*R*-tris(*p*-Br)TPCP]$_4$ **(N)**	21: 49: 30	91	62	2:1	14	62	27
Rh$_2$[*R*-3,5-di(*p*-CF$_3$C$_6$H$_4$)TPCP]$_4$ **(O)**	7: 64: 29	78	77	4:1	14	35	15
Rh$_2$[*R*-3,5-di(3,5-diCF$_3$C$_6$H$_3$)TPCP]$_4$ **(P)**	7: 71: 22	62	>99	4:1	8	70	19
Rh$_2$(*R*-2,4,6-tri-MeC$_6$H$_2$-TPCP)$_4$ **(Q)**	5: 75: 20	94	77	11:1	17	74	18

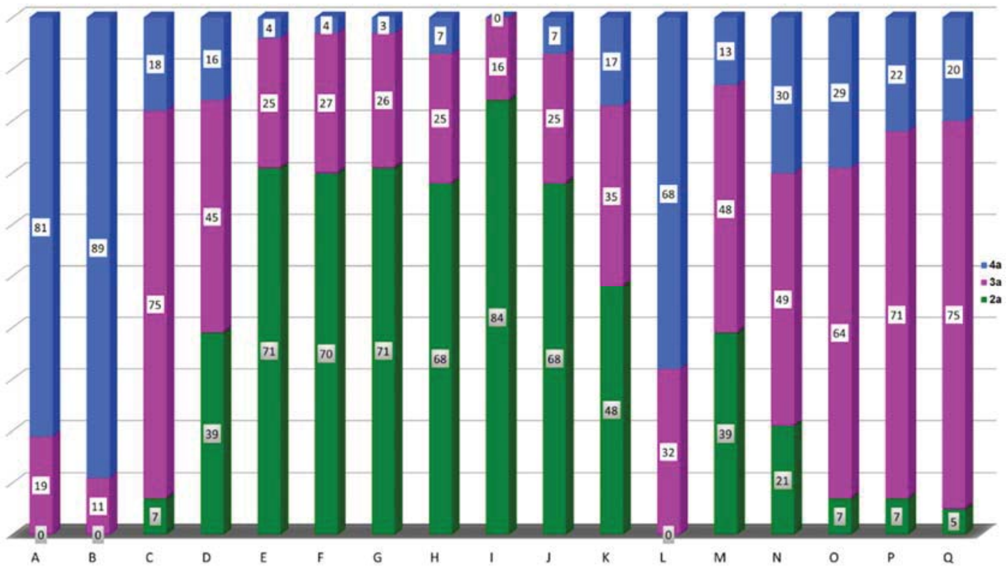
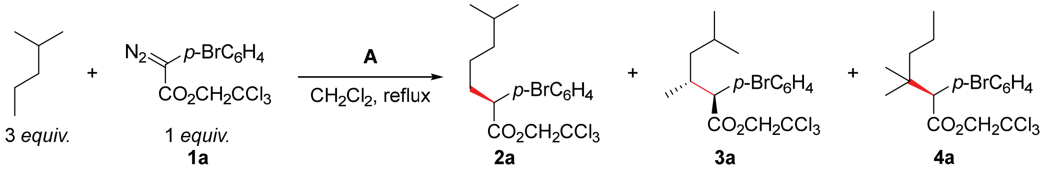


Figure S2. Bar Graph for Catalyst Screen Data Summary

Table S3. Diazo Screen Data Summary

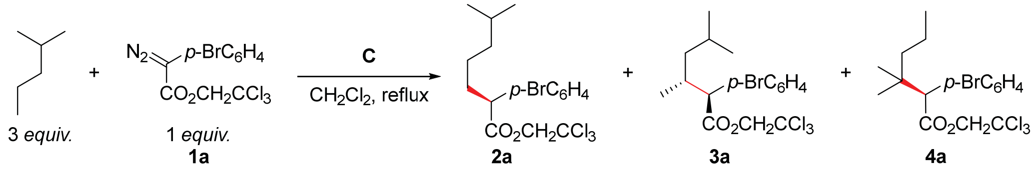
	R	*r.r.* (**2**: **3**: **4**)	*e.e.* (**2**, %)	*e.e.* (**3**, %)	*d.r.* (**3**, %)	*e.e.* (**4**, %)	*yield* (**2+3**, %)	*yield* (**4**, %)
PTAD)$_4$ (**B**) [5]	CH_2CF_3 (**1c**)	*n.d.*: 10: 90	*n.d.*	79	2:1	77	9	83
PTAD)$_4$ (**B**) [5]	CH_2CBr_3(**1d**)	*n.d.*: 13: 87	*n.d.*	79	2:1	77	11	77
-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$ (**C**)	CH_2CF_3 (**1c**)	4: 71: 26	*n.d.*	93	6:1	67	57	20
-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$ (**C**)	CH_2CBr_3(**1d**)	9: 82: 10	90	92	8:1	12	75	7
(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$ (**I**)	CH_3(**1b**)	51:35:15	*n.d.*	*n.d.*	3:1	*n.d.*	<5	*n.d.*
(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$ (**I**)	CH_2CF_3 (**1c**)	54: 36: 10	98	94	3:1	*n.d.*	78	5
(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$ (**I**)	CH_2CBr_3(**1d**)	87: 13: *n.d.*	>99	92	7:1	*n.d.*	84	*n.d.*

4.3 Catalyst and Diazo Screen



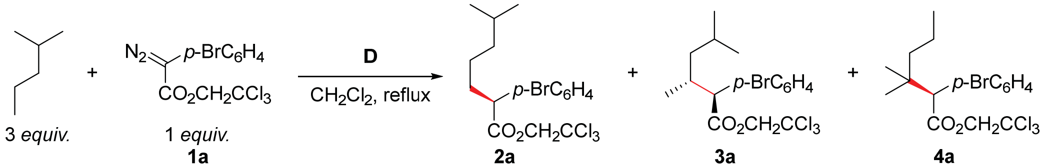
This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 74 mg, 1.0 equiv.) in 3 mL distilled CH_2Cl_2, **catalyst A** (0.002 mmol, 4 mg, 1 mol%.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **3a** as a colorless oil (14 mg, 16% combined yield) and **4a** as a colorless oil (62 mg, 72% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a**, **3a** and **4a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a**: **3a: 4a**) of this reaction was *n.d.*: 19: 81 *r.r.* and the diastereoselectivity for **3a** was 2: 1 *d.r.*. The enantioselectivity of this reaction for compound **2a** was not determined. The enantioselectivity of this reaction for compound **3a** was 69% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "ASH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 101.4 min (minor) and 118.5 min (major). The enantioselectivity of this reaction for compound **4a** was 29% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "S, S-Whelk, 1% isopropanol in hexane, 1 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 46.6 min (major) and 121.5 min (minor).



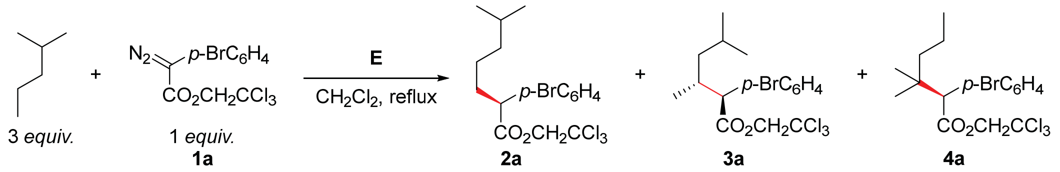
This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 74 mg, 1.0 equiv.) in 3 mL distilled CH_2Cl_2, **catalyst C** (0.002 mmol, 4 mg, 1 mol%.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^1H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2a** and **3a** as a colorless oil (65 mg, 75% combined yield) and **4a** as a colorless oil (14 mg, 16% yield).

Analysis of the ^1H NMR spectrum of the crude reaction mixture revealed that only compound **2a**, **3a** and **4a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a** : **3a : 4a**) of this reaction was 7: 75: 18 *r.r.* and the diastereoselectivity for **3a** was 7: 1 *d.r.*. The enantioselectivity of this reaction for compound **2a** was 81% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "OBH, 0.1% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 140 min, UV 230 nm, with the retention times at 62.3 min (major) and 102.7 min (minor). The enantioselectivity of this reaction for compound **3a** was 92% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "ASH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 102.0 min (minor) and 113.2 min (major). The enantioselectivity of this reaction for compound **4a** was 23% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "S, S-Whelk, 1% isopropanol in hexane, 1 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 47.8 min (major) and 123.4 min (minor).



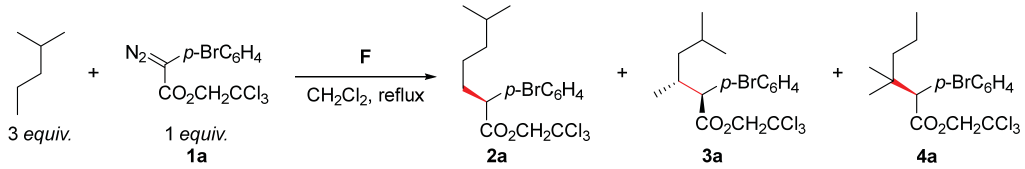
This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 74 mg, 1.0 equiv.) in 3 mL distilled CH_2Cl_2, **catalyst D** (0.002 mmol, 4 mg, 1 mol%.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2a** and **3a** as a colorless oil (65 mg, 75% combined yield) and **4a** as a colorless oil (12 mg, 14% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a**, **3a** and **4a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a** : **3a : 4a**) of this reaction was 39: 45: 16 *r.r.* and the diastereoselectivity for **3a** was 9: 1 *d.r.*. The enantioselectivity of this reaction for compound **2a** was 97% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "OBH, 0.1% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 140 min, UV 230 nm, with the retention times at 60.3 min (major) and 105.2 min (minor). The enantioselectivity of this reaction for compound **3a** was 87% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "ASH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 102.7 min (minor) and 115.3 min (major). The enantioselectivity of this reaction for compound **4a** was 60% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "S, S-Whelk, 1% isopropanol in hexane, 1 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 47.0 min (major) and 122.9 min (minor).



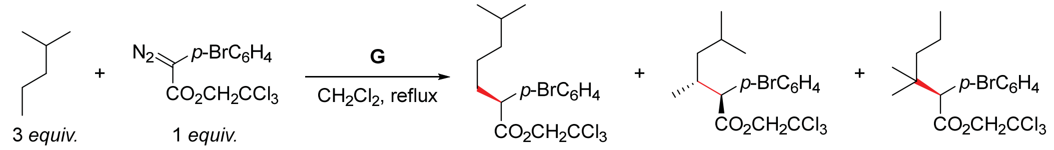
This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 74 mg, 1.0 equiv.) in 3 mL distilled CH_2Cl_2, **catalyst E** (0.002 mmol, 4 mg, 1 mol%.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2a** and **3a** as a colorless oil (74 mg, 86% combined yield) and **4a** as a colorless oil (3 mg, 4% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a**, **3a** and **4a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a** : **3a : 4a**) of this reaction was 71: 25: 4 *r.r.* and the diastereoselectivity for **3a** was 9: 1 *d.r.*. The enantioselectivity of this reaction for compound **2a** was 96% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "OBH, 0.1% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 140 min, UV 230 nm, with the retention times at 58.1 min (major) and 106.3 min (minor). The enantioselectivity of this reaction for compound **3a** was 89% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "ASH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 103.8 min (minor) and 114.9 min (major). The enantioselectivity of this reaction for compound **4a** was not determined.



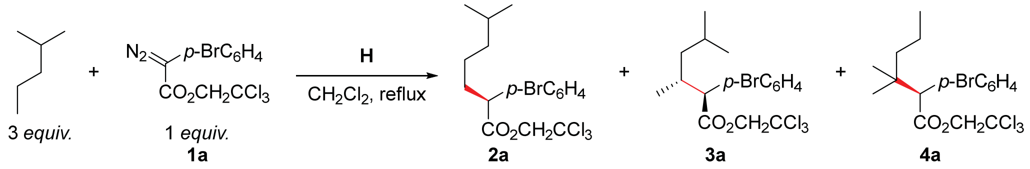
This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 74 mg, 1.0 equiv.) in 3 mL distilled CH_2Cl_2, **catalyst F** (0.002 mmol, 4 mg, 1 mol%.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2a** and **3a** as a colorless oil (71 mg, 83% combined yield) and **4a** as a colorless oil (3 mg, 3% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a**, **3a** and **4a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a** : **3a : 4a**) of this reaction was 70: 27: 4 *r.r.* and the diastereoselectivity for **3a** was 11: 1 *d.r.*. The enantioselectivity of this reaction for compound **2a** was 98% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "OBH, 0.1% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 140 min, UV 230 nm, with the retention times at 56.8 min (major) and 104.8 min (minor). The enantioselectivity of this reaction for compound **3a** was 94% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "ASH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 102.4 min (minor) and 114.4 min (major). The enantioselectivity of this reaction for compound **4a** was not determined due to the low yielding.



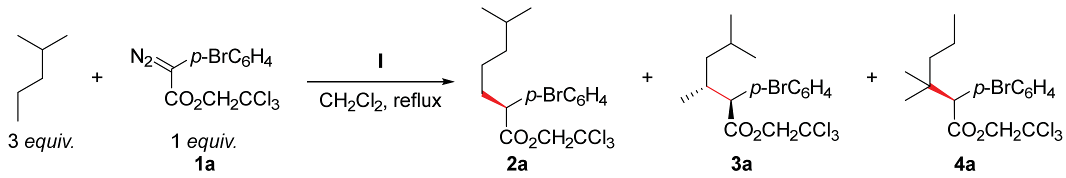
This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 74 mg, 1.0 equiv.) in 3 mL distilled CH_2Cl_2, **catalyst G** (0.002 mmol, 4 mg, 1 mol%.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2a** and **3a** as a colorless oil (73 mg, 85% combined yield) and **4a** as a colorless oil (3 mg, 3% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a**, **3a** and **4a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a** : **3a : 4a**) of this reaction was 71: 26: 3 *r.r.* and the diastereoselectivity for **3a** was 15: 1 *d.r.*. The enantioselectivity of this reaction for compound **2a** was 97% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "OBH, 0.1% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 140 min, UV 230 nm, with the retention times at 56.0 min (major) and 104.2 min (minor). The enantioselectivity of this reaction for compound **3a** was 96% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "ASH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 100.2 min (minor) and 112.7 min (major). The enantioselectivity of this reaction for compound **4a** was not determined due to the low yielding.



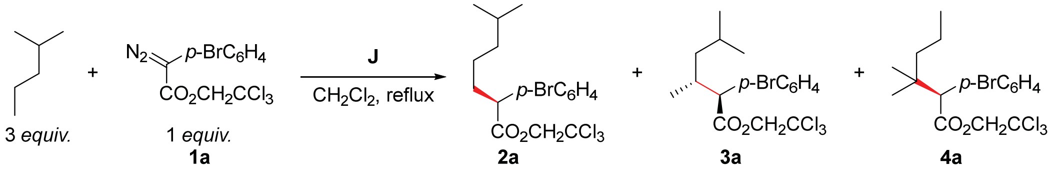
This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 74 mg, 1.0 equiv.) in 3 mL distilled CH_2Cl_2, **catalyst H** (0.002 mmol, 4 mg, 1 mol%.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2a** and **3a** as a colorless oil (61 mg, 71% combined yield) and **4a** as a colorless oil (4 mg, 5% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a**, **3a** and **4a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a** : **3a : 4a**) of this reaction was 68: 25: 7 *r.r.* and the diastereoselectivity for **3a** was 5: 1 *d.r.*. The enantioselectivity of this reaction for compound **2a** was 90% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "OBH, 0.1% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 140 min, UV 230 nm, with the retention times at 56.3 min (major) and 93.4 min (minor). The enantioselectivity of this reaction for compound **3a** was 83% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "ASH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 99.7 min (minor) and 115.5 min (major). The enantioselectivity of this reaction for compound **4a** was 40% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "S, S-Whelk, 1% isopropanol in hexane, 1 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 47.0 min (major) and 123.0 min (minor).



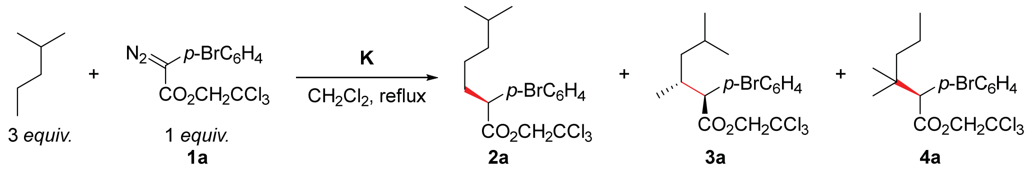
This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 74 mg, 1.0 equiv.) in 3 mL distilled CH_2Cl_2, **catalyst I** (0.002 mmol, 4 mg, 1 mol%.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2a** and **3a** as a colorless oil (77 mg, 90% combined yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a**, **3a** and **4a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a** : **3a : 4a**) of this reaction was 84: 16: *n.d. r.r.* and the diastereoselectivity for **3a** was 2: 1 *d.r.*. The enantioselectivity of this reaction for compound **2a** was 98% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was “OBH, 0.1% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 140 min, UV 230 nm, with the retention times at 59.7 min (major) and 106.8 min (minor). The enantioselectivity of this reaction for compound **3a** was 92% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was “ASH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 105.4 min (minor) and 119.9 min (major). The enantioselectivity of this reaction for compound **4a** was not determined due to the low yielding.



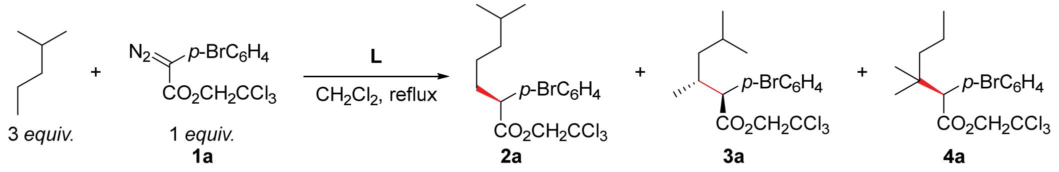
This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 74 mg, 1.0 equiv.) in 3 mL distilled CH_2Cl_2, **catalyst J** (0.002 mmol, 4 mg, 1 mol%.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2a** and **3a** as a colorless oil (67 mg, 78% combined yield) and **4a** as a colorless oil (4 mg, 5% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a**, **3a** and **4a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a** : **3a : 4a**) of this reaction was 68: 25: 7 *r.r.* and the diastereoselectivity for **3a** was 5: 1 *d.r.*. The enantioselectivity of this reaction for compound **2a** was 92% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "OBH, 0.1% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 140 min, UV 230 nm, with the retention times at 56.0 min (major) and 95.2 min (minor). The enantioselectivity of this reaction for compound **3a** was 82% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "ASH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 88.5 min (major) and 100.2 min (minor). The enantioselectivity of this reaction for compound **4a** was 35% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "S, S-Whelk, 1% isopropanol in hexane, 1 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 46.9 min (major) and 122.3 min (minor).



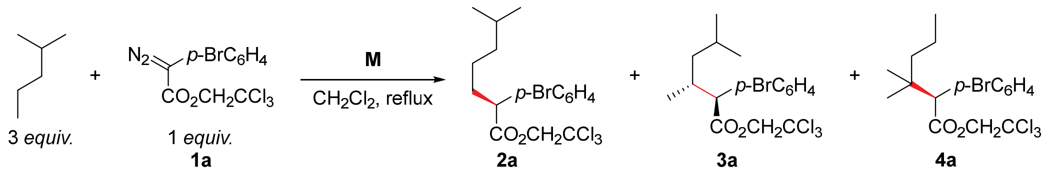
This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 74 mg, 1.0 equiv.) in 3 mL distilled CH_2Cl_2, **catalyst K** (0.002 mmol, 4 mg, 1 mol%.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2a** and **3a** as a colorless oil (47 mg, 55% combined yield) and **4a** as a colorless oil (10 mg, 12% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a**, **3a** and **4a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a** : **3a : 4a**) of this reaction was 48: 35: 17 *r.r.* and the diastereoselectivity for **3a** was 3: 1 *d.r.*. The enantioselectivity of this reaction for compound **2a** was 97% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was “OBH, 0.1% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 140 min, UV 230 nm, with the retention times at 58.2 min (major) and 105.2 min (minor). The enantioselectivity of this reaction for compound **3a** was 74% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was “ASH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 98.9 min (minor) and 113.0 min (major). The enantioselectivity of this reaction for compound **4a** was 29% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was “S, S-Whelk, 1% isopropanol in hexane, 1 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 47.5 min (major) and 123.4 min (minor).



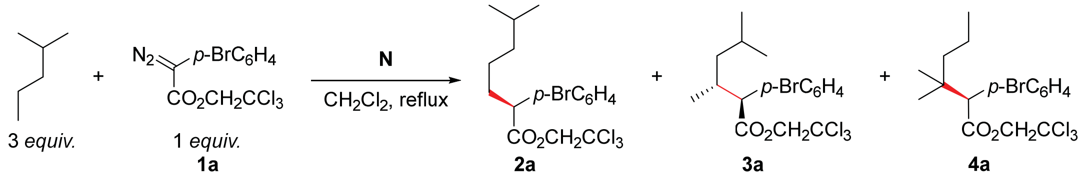
This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 74 mg, 1.0 equiv.) in 3 mL distilled CH_2Cl_2, **catalyst L** (0.002 mmol, 4 mg, 1 mol%.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **3a** as a colorless oil (24 mg, 28% combined yield) and **4a** as a colorless oil (50 mg, 59% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a**, **3a** and **4a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a** : **3a : 4a**) of this reaction was *n.d.:* 32: 68 *r.r.* and the diastereoselectivity for **3a** was 1: 1 *d.r.*. The enantioselectivity of this reaction for compound **2a** was not determined. The enantioselectivity of this reaction for compound **3a** was 60% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "ASH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 101.3 min (major) and 122.1 min (minor). The enantioselectivity of this reaction for compound **4a** was 22% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "S, S-Whelk, 1% isopropanol in hexane, 1 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 47.0 min (major) and 119.8 min (minor).



This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 74 mg, 1.0 equiv.) in 3 mL distilled CH_2Cl_2, **catalyst M** (0.002 mmol, 4 mg, 1 mol%.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2a** and **3a** as a colorless oil (65 mg, 75% combined yield) and **4a** as a colorless oil (9 mg, 11% yield).

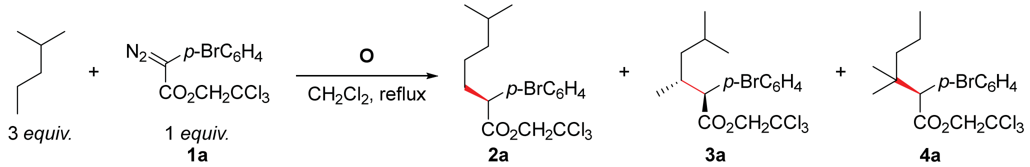
Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a**, **3a** and **4a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a** : **3a : 4a**) of this reaction was 39: 48: 13 *r.r.* and the diastereoselectivity for **3a** was 3: 1 *d.r.*. The enantioselectivity of this reaction for compound **2a** was 97% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "OBH, 0.1% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 140 min, UV 230 nm, with the retention times at 61.9 min (major) and 100.8 min (minor). The enantioselectivity of this reaction for compound **3a** was 87% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was “ASH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 102.1 min (minor) and 121.1 min (major). The enantioselectivity of this reaction for compound **4a** was 35% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was “S, S-Whelk, 1% isopropanol in hexane, 1 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 59.6 min (major) and 124.5 min (minor).



This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 74 mg, 1.0 equiv.) in 3 mL distilled CH_2Cl_2, **catalyst N** (0.002 mmol, 4 mg, 1 mol%.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2a** and **3a** as a colorless oil (53 mg, 62% combined yield) and **4a** as a colorless oil (23 mg, 27% yield).

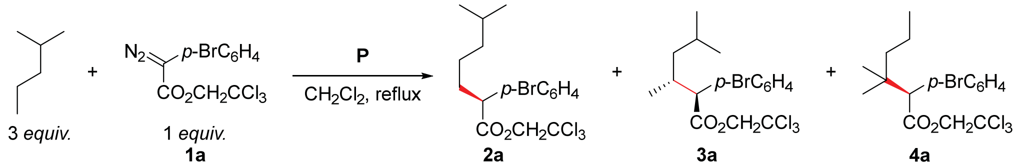
Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a**, **3a** and **4a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a** : **3a : 4a**) of this reaction was 21: 49: 30 *r.r.* and the diastereoselectivity for **3a** was 11: 1 *d.r.*. The enantioselectivity of this reaction for compound **2a** was 98% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was “OBH, 0.1% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 140 min, UV 230 nm, with the retention times at 59.4 min (major) and 104.0 min (minor). The enantioselectivity of this reaction for compound **3a** was 94% *e.e.*; the HPLC

(in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "ASH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 100.4 min (minor) and 116.1 min (major). The enantioselectivity of this reaction for compound **4a** was 14% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "S, S-Whelk, 1% isopropanol in hexane, 1 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 47.9 min (major) and 124.2 min (minor).



This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 74 mg, 1.0 equiv.) in 3 mL distilled CH_2Cl_2, **catalyst O** (0.002 mmol, 4 mg, 1 mol%.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2a** and **3a** as a colorless oil (30 mg, 35% combined yield) and **4a** as a colorless oil (13 mg, 15% yield).

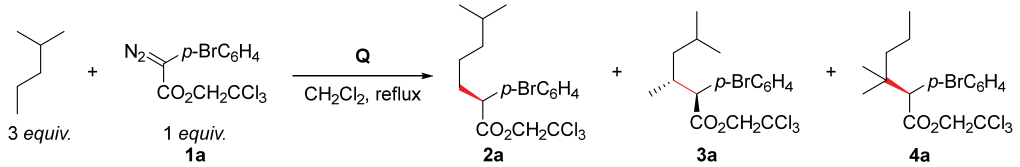
Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a**, **3a** and **4a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a** : **3a : 4a**) of this reaction was 7: 64: 29 *r.r.* and the diastereoselectivity for **3a** was 4: 1 *d.r.*. The enantioselectivity of this reaction for compound **2a** was 78% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "OBH, 0.1% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 140 min, UV 230 nm, with the retention times at 62.3 min (major) and 103.3 min (minor). The enantioselectivity of this reaction for compound **3a** was 77% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "ASH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 103.4 min (major) and 121.2 min (minor). The enantioselectivity of this reaction for compound **4a** was 14% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "S, S-Whelk, 1% isopropanol in hexane, 1 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 47.8 min (major) and 124.3 min (minor).



This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 74 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, **catalyst P** (0.002 mmol, 4 mg, 1 mol%.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2a** and **3a** as a colorless oil (60 mg, 70% combined yield) and **4a** as a colorless oil (16 mg, 19% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a**, **3a** and **4a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a** : **3a : 4a**) of this reaction was 7: 71: 22 *r.r.* and the diastereoselectivity for **3a** was 4: 1 *d.r.*. The enantioselectivity of this reaction for compound **2a** was 62% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "OBH, 0.1% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 140 min, UV 230 nm, with the retention times at 61.4 min (major) and 102.9 min (minor). The enantioselectivity of this reaction for compound **3a** was >99% *e.e.*; the HPLC

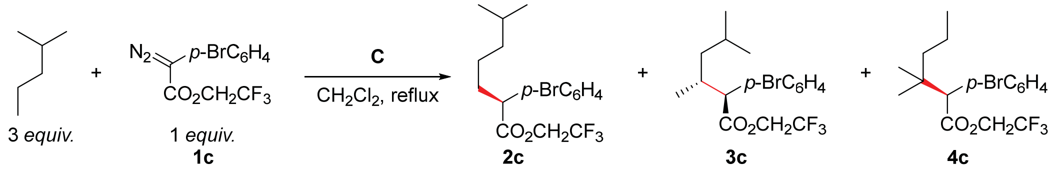
(in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "ASH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 114.4 min (minor) and 132.0 min (major). The enantioselectivity of this reaction for compound **4a** was 8% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "S, S-Whelk, 1% isopropanol in hexane, 1 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 46.7 min (major) and 119.8 min (minor).



This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 74 mg, 1.0 equiv.) in 3 mL distilled CH_2Cl_2, **catalyst Q** (0.002 mmol, 4 mg, 1 mol%.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2a** and **3a** as a colorless oil (64 mg, 74% combined yield) and **4a** as a colorless oil (16 mg, 18% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a**, **3a** and **4a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a** : **3a** : **4a**) of this reaction was 5: 75: 20 *r.r.* and the diastereoselectivity for **3a** was 11: 1 *d.r.*. The enantioselectivity of this reaction for compound **2a** was 94% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "OBH, 0.1% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 140 min, UV 230 nm, with the retention times at 62.9 min (minor) and 103.6 min (major). The enantioselectivity of this reaction for compound **3a** was 77% *e.e.*; the HPLC

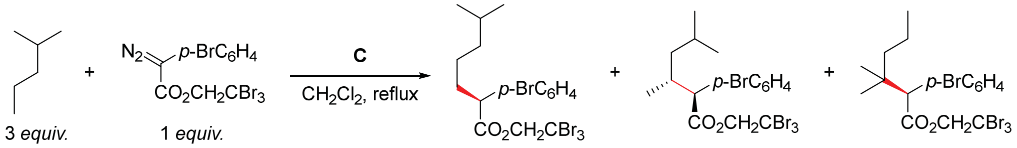
(in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "ASH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 101.2 min (minor) and 115.8 min (major). The enantioselectivity of this reaction for compound **4a** was 17% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "S, S-Whelk, 1% isopropanol in hexane, 1 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 59.0 min (major) and 123.5 min (minor).



This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1c** (0.2 mmol, 65 mg, 1.0 equiv.) in 3 mL distilled CH_2Cl_2, **catalyst C** (0.002 mmol, 4 mg, 1 mol%.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2c** and **3c** as a colorless oil (43 mg, 57% combined yield) and **4c** as a colorless oil (15 mg, 20% yield).

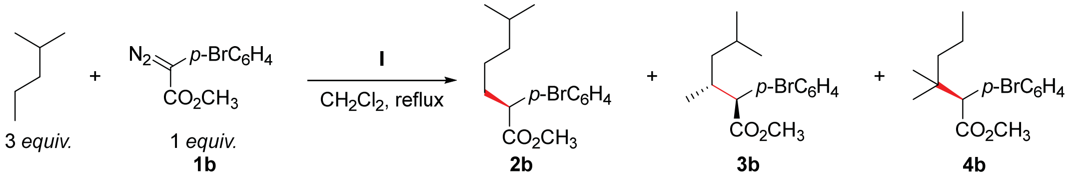
Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2c**, **3c** and **4c** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2c** : **3c : 4c**) of this reaction was 4: 71: 26 *r.r.* and the diastereoselectivity for **3c** was 6: 1 *d.r.*. The enantioselectivity of this reaction for compound **2c** was not determined due to the low yielding. The enantioselectivity of this reaction for compound **3c** was 93% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "ASH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 105.6 min (minor) and 119.1 min (major). The enantioselectivity of this reaction for compound **4c** was 67%

e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "S, S-Whelk, 1% isopropanol in hexane, 1 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 47.2 min (major) and 123.0 min (minor).

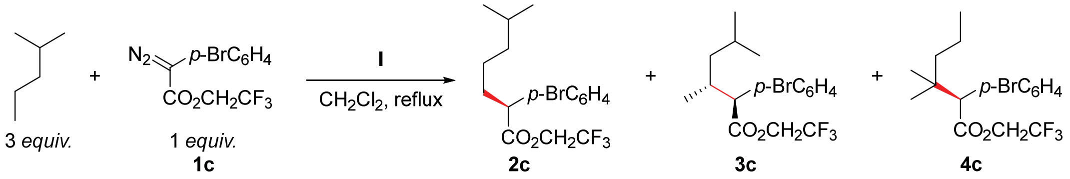


This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 101 mg, 1.0 equiv.) in 3 mL distilled CH_2Cl_2, **catalyst C** (0.002 mmol, 4 mg, 1 mol%.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^1H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2d** and **3d** as a colorless oil (85 mg, 75% combined yield) and **4d** as a colorless oil (8 mg, 7% yield).

Analysis of the ^1H NMR spectrum of the crude reaction mixture revealed that only compound **2d**, **3d** and **4d** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2d** : **3d : 4d**) of this reaction was 9: 82: 9 *r.r.* and the diastereoselectivity for **3d** was 8: 1 *d.r.*. The enantioselectivity of this reaction for compound **2d** was 90% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "OBH, 0.1% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 140 min, UV 230 nm, with the retention times at 62.0 min (major) and 103.4 min (minor). The enantioselectivity of this reaction for compound **3d** was 92% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "ASH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 104.1 min (minor) and 117.7 min (major). The enantioselectivity of this reaction for compound **4d** was 12% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was “S, S-Whelk, 1% isopropanol in hexane, 1 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 47.1 min (major) and 122.3 min (minor).

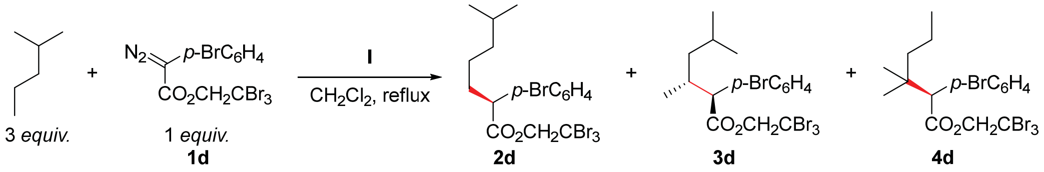


This reaction was conducted according to the general procedure for C–H functionalization reactions. Methyl 2-(4-bromophenyl)-2-diazoacetate **1b** (0.2 mmol, 51 mg, 1.0 equiv.) in 3 mL distilled CH_2Cl_2, **catalyst I** (0.002 mmol, 4 mg, 1 mol%.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and only trace amount of C–H functionalization product was observed (<5%), the regioselectivity (**2b** : **3b : 4b**) of this reaction was 51: 35: 15 *r.r.* and the diastereoselectivity for **3b** was 3: 1 *d.r.*.



This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1c** (0.2 mmol, 65 mg, 1.0 equiv.) in 3 mL distilled CH_2Cl_2, **catalyst I** (0.002 mmol, 4 mg, 1 mol%.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2c** and **3c** as a colorless oil (59 mg, 78% combined yield) and **4c** as a colorless oil (4 mg, 5% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2c**, **3c** and **4c** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2c** : **3c : 4c**) of this reaction was 54: 36: 10 *r.r.* and the diastereoselectivity for **3c** was 3: 1 *d.r.*. The enantioselectivity of this reaction for compound **2c** was 98% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "OBH, 0.1% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 140 min, UV 230 nm, with the retention times at 64.1 min (major) and 105.7 min (minor). The enantioselectivity of this reaction for compound **3c** was 94% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was "ASH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 100.9 min (minor) and 116.7 min (major). The enantioselectivity of this reaction for compound **4c** was not determined due to the low yielding.

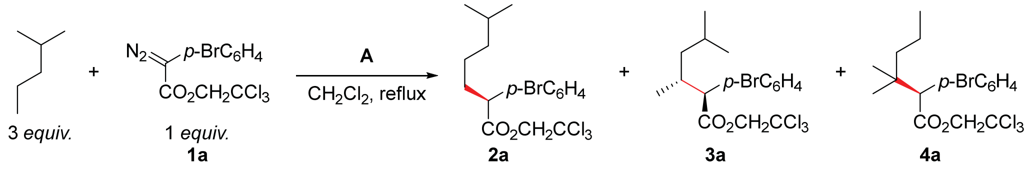


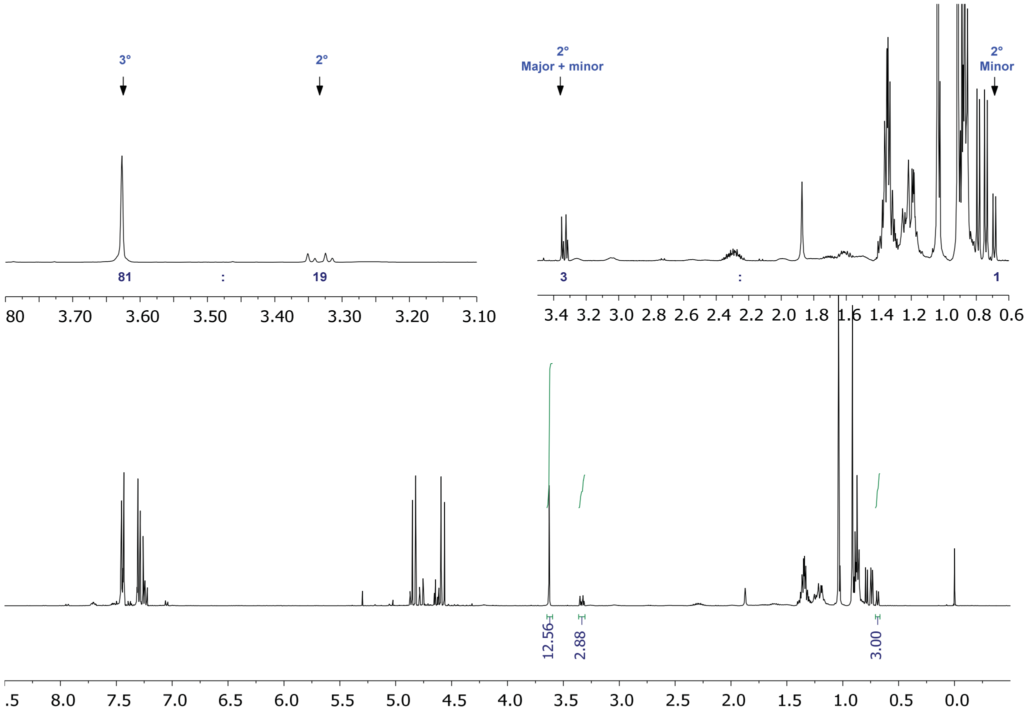
This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 101 mg, 1.0 equiv.) in 3 mL distilled CH_2Cl_2, **catalyst I** (0.002 mmol, 4 mg, 1 mol%.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2d** and **3d** as a colorless oil (95 mg, 84% combined yield).

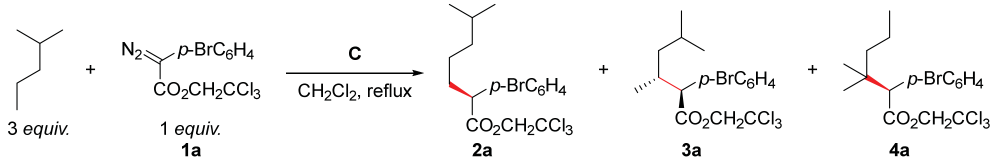
Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2d**, **3d** and **4d** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2d** : **3d : 4d**) of this reaction was 87: 13: *n.d. r.r.* and the diastereoselectivity for **3d** was 7: 1 *d.r.*. The enantioselectivity of this reaction for compound **2d** was >99% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in

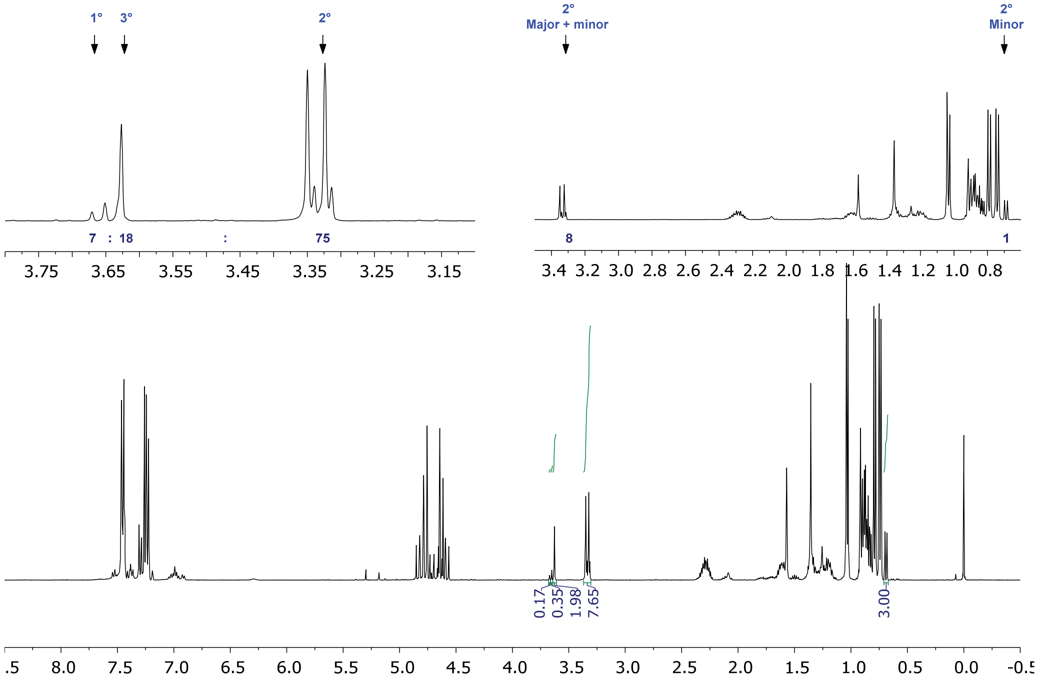
DCM at -78 °C) condition was “OBH, 0.1% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 140 min, UV 230 nm, with the retention times at 58.0 min (major) and 105.5 min (minor). The enantioselectivity of this reaction for compound **3d** was 92% *e.e.*; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was “ASH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 230 nm, with the retention times at 103.5 min (minor) and 120.5 min (major). The enantioselectivity of this reaction for compound **4d** was not determined due to the low yielding.

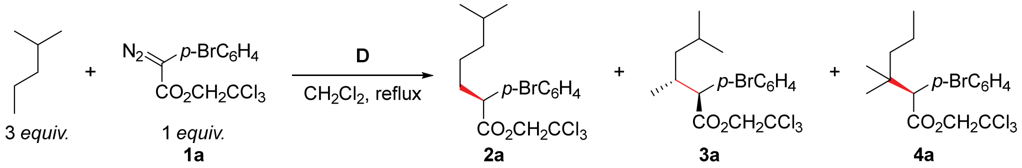
4.4 Crude ^{1}H NMR Spectra

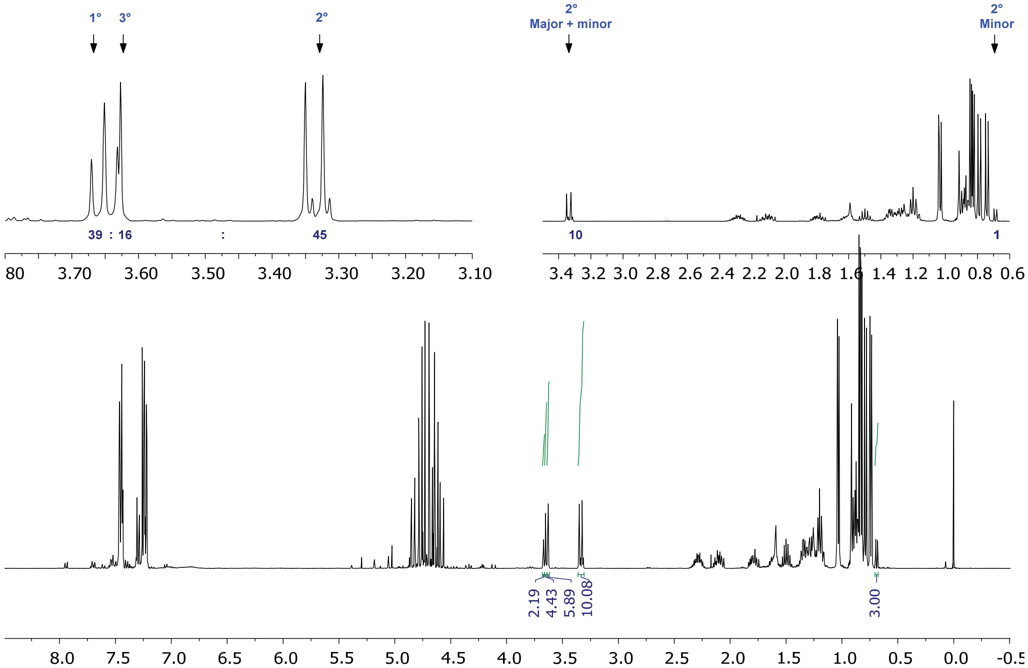


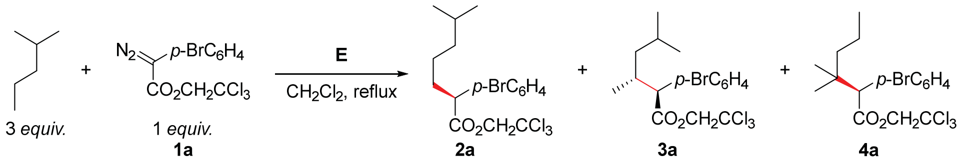



3 *equiv.*
+
N_2
p-BrC_6H_4
$CO_2CH_2CCl_3$
1 *equiv.*
1a
C
CH_2Cl_2, reflux
p-BrC_6H_4
$CO_2CH_2CCl_3$
2a
+
p-BrC_6H_4
$CO_2CH_2CCl_3$
3a
+
p-BrC_6H_4
$CO_2CH_2CCl_3$
4a

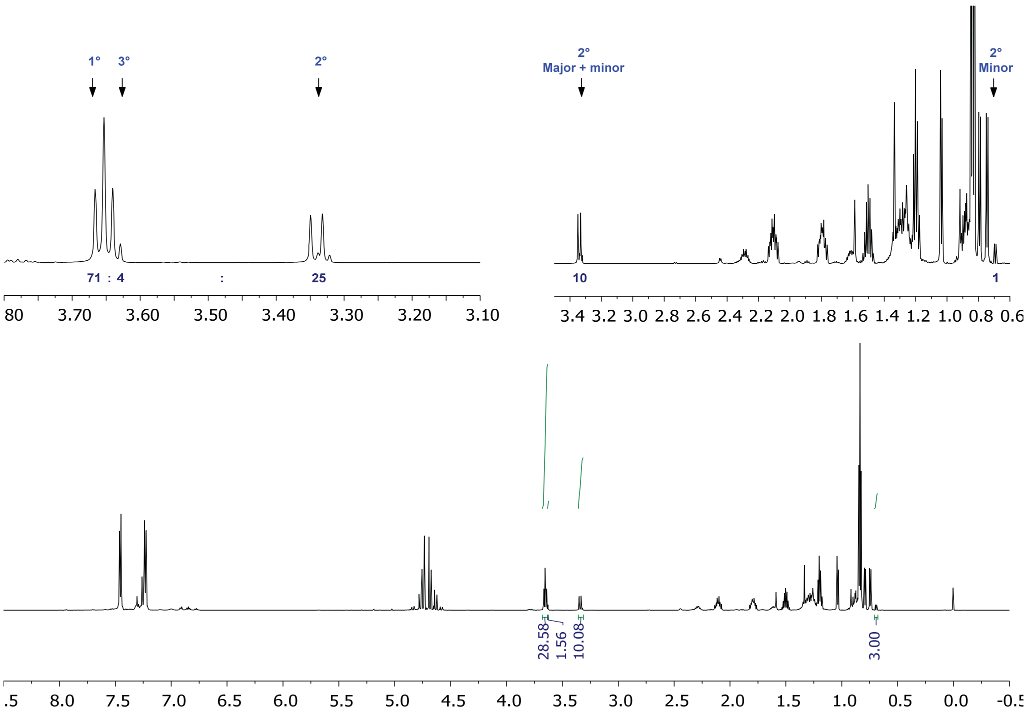

1°
3°
2°
7 : 18 : 75
3.75
3.65
3.55
3.45
3.35
3.25
3.15
2°
Major + minor
2°
Minor
8
1
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
0.17
0.35
1.98
7.65
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

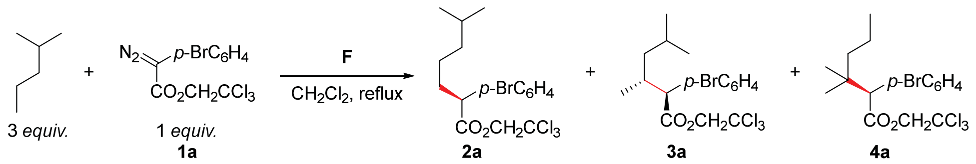

3 equiv.
N2
p-BrC6H4
CO2CH2CCl3
1 equiv.
1a
D
CH2Cl2, reflux
p-BrC6H4
CO2CH2CCl3
2a
p-BrC6H4
CO2CH2CCl3
3a
p-BrC6H4
CO2CH2CCl3
4a

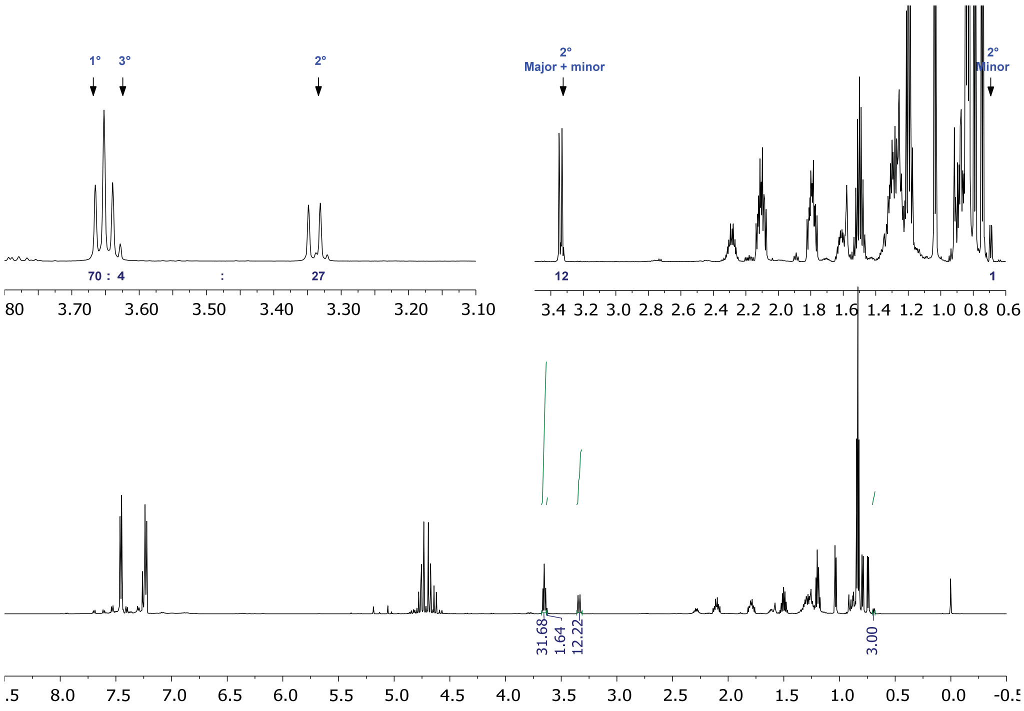

1°
3°
2°
39 : 16 : 45
80
3.70
3.60
3.50
3.40
3.30
3.20
3.10
2°
Major + minor
2°
Minor
10
1
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
2.19
4.43
5.89
10.08
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

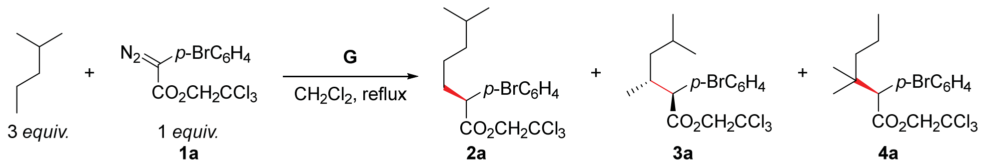

3 *equiv.*
N_2
p-BrC$_6$H$_4$
CO$_2$CH$_2$CCl$_3$
1 *equiv.*
E
CH$_2$Cl$_2$, reflux
p-BrC$_6$H$_4$
CO$_2$CH$_2$CCl$_3$
p-BrC$_6$H$_4$
CO$_2$CH$_2$CCl$_3$
p-BrC$_6$H$_4$
CO$_2$CH$_2$CCl$_3$

1a **2a** **3a** **4a**

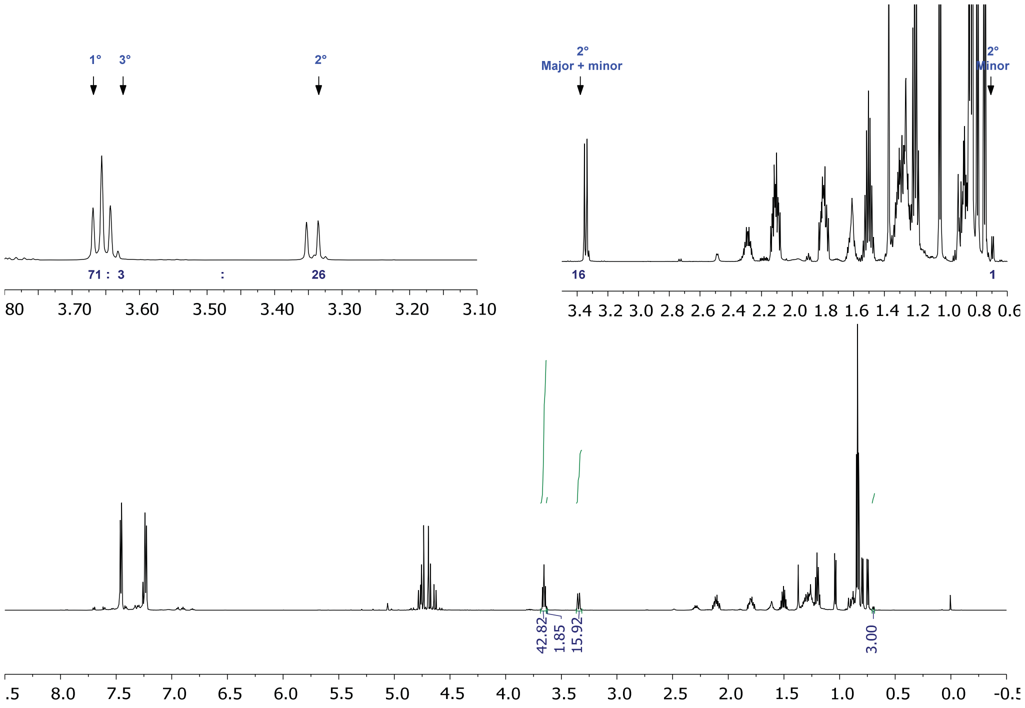

1°
3°
2°
71 : 4 : 25
80
3.70
3.60
3.50
3.40
3.30
3.20
3.10
2°
Major + minor
2°
Minor
10
1
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
28.58
1.56
10.08
3.00
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


3 equiv.
+
N_2
p-BrC_6H_4
$CO_2CH_2CCl_3$
1 equiv.
1a
F
CH_2Cl_2, reflux
p-BrC_6H_4
$CO_2CH_2CCl_3$
2a
+
p-BrC_6H_4
$CO_2CH_2CCl_3$
3a
+
p-BrC_6H_4
$CO_2CH_2CCl_3$
4a

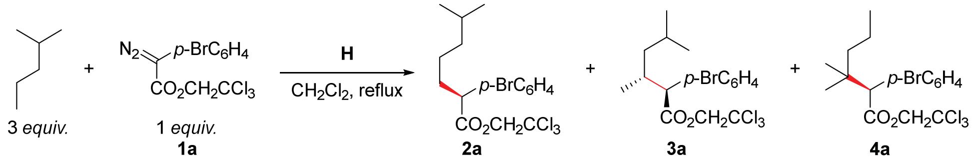

1°
3°
2°
70 : 4 : 27
80 3.70 3.60 3.50 3.40 3.30 3.20 3.10
2° Major + minor
2° Minor
12
1
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
31.68
1.64
12.22
3.00
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

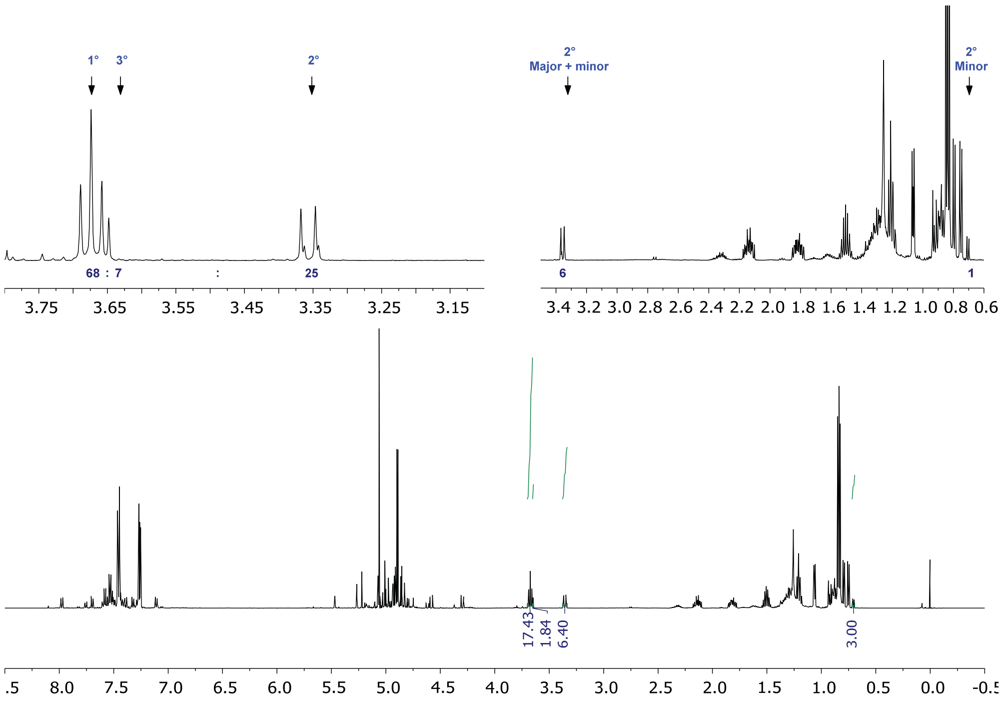


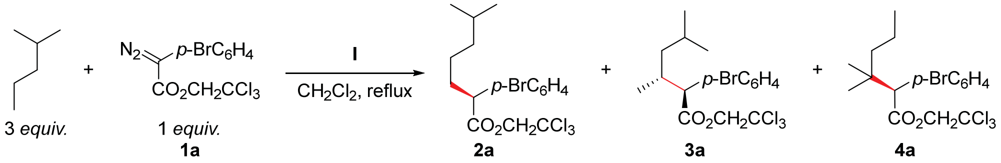
3 equiv.
N2
p-BrC6H4
CO2CH2CCl3
1 equiv.
1a
G
CH2Cl2, reflux
2a
3a
4a

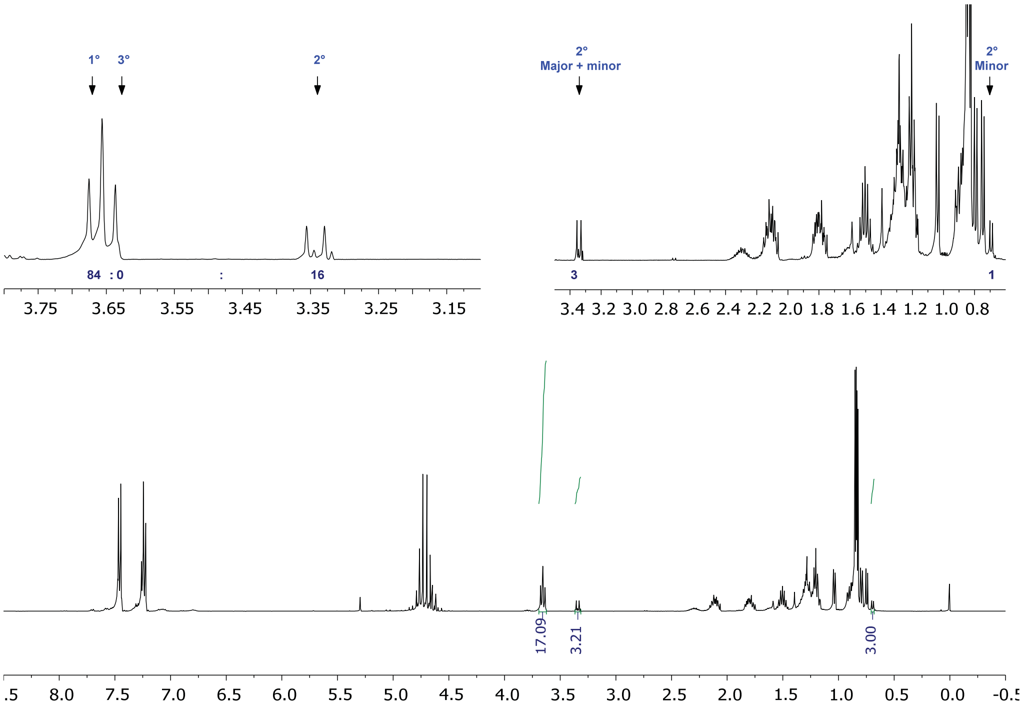


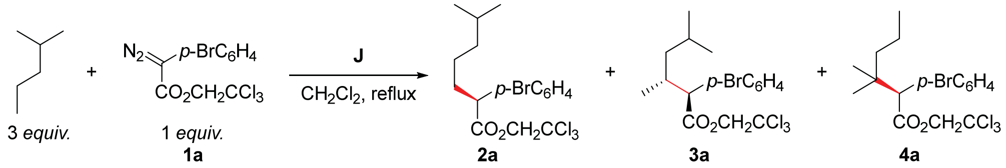
1°
3°
2°
71 : 3 : 26
80 3.70 3.60 3.50 3.40 3.30 3.20 3.10
2° Major + minor
2° Minor
16
1
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
42.82
1.85
15.92
3.00
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


3 equiv.
+
N_2
p-BrC$_6$H$_4$
CO$_2$CH$_2$CCl$_3$
1 equiv.
1a
H
CH$_2$Cl$_2$, reflux
p-BrC$_6$H$_4$
CO$_2$CH$_2$CCl$_3$
2a
+
p-BrC$_6$H$_4$
CO$_2$CH$_2$CCl$_3$
3a
+
p-BrC$_6$H$_4$
CO$_2$CH$_2$CCl$_3$
4a

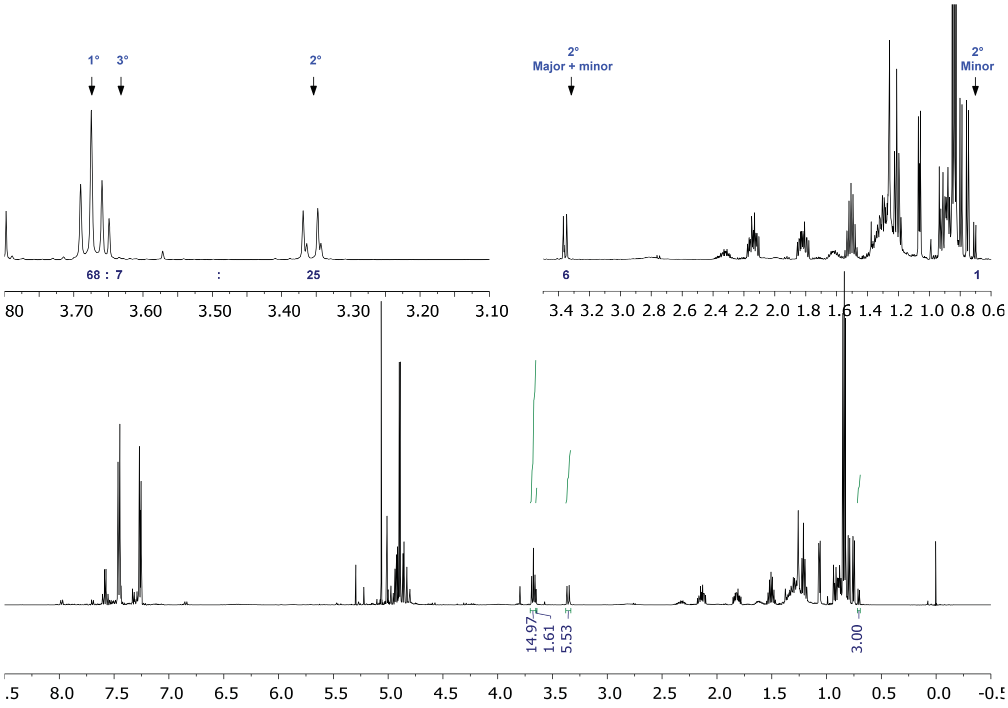

1°
3°
2°
68 : 7 : 25
3.75
3.65
3.55
3.45
3.35
3.25
3.15
2°
Major + minor
2°
Minor
6
1
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
17.43
1.84
6.40
3.00
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.


3 equiv.
+
N_2
p-BrC_6H_4
$CO_2CH_2CCl_3$
1 equiv.
1a
I
CH_2Cl_2, reflux
p-BrC_6H_4
$CO_2CH_2CCl_3$
2a
+
p-BrC_6H_4
$CO_2CH_2CCl_3$
3a
+
p-BrC_6H_4
$CO_2CH_2CCl_3$
4a

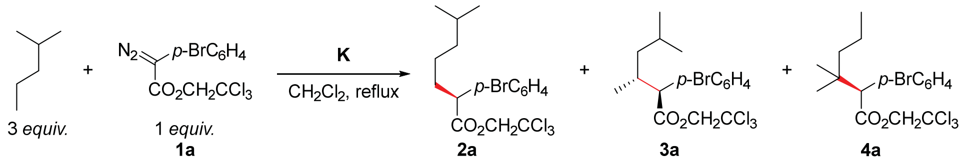

1°
3°
2°
84 : 0 : 16
3.75 3.65 3.55 3.45 3.35 3.25 3.15
2°
Major + minor
2°
Minor
3
1
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
17.09
3.21
3.00
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5



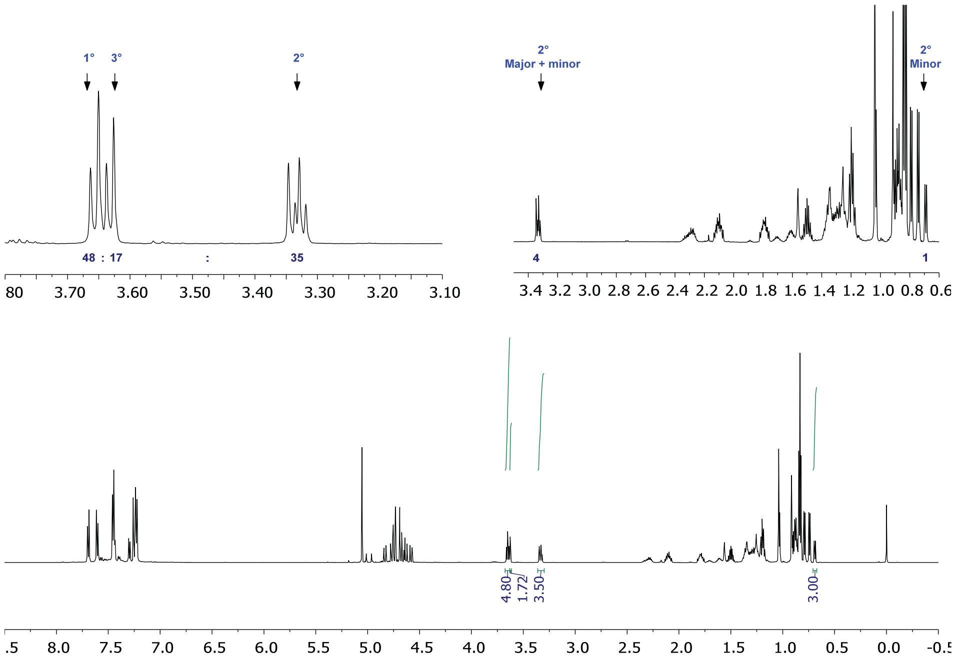
3 equiv.
N_2
p-BrC_6H_4
$CO_2CH_2CCl_3$
1 equiv.
1a
J
CH_2Cl_2, reflux
2a
3a
4a



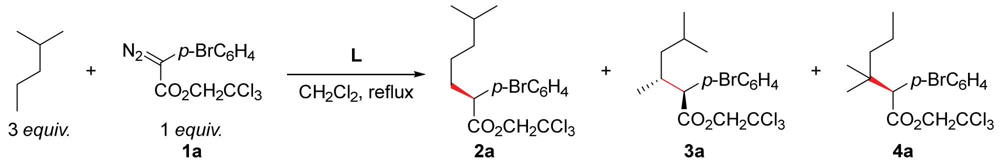
1°
3°
2°
2° Major + minor
2° Minor
68 : 7 : 25
6
1
80 3.70 3.60 3.50 3.40 3.30 3.20 3.10
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
14.97
1.61
5.53
3.00
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

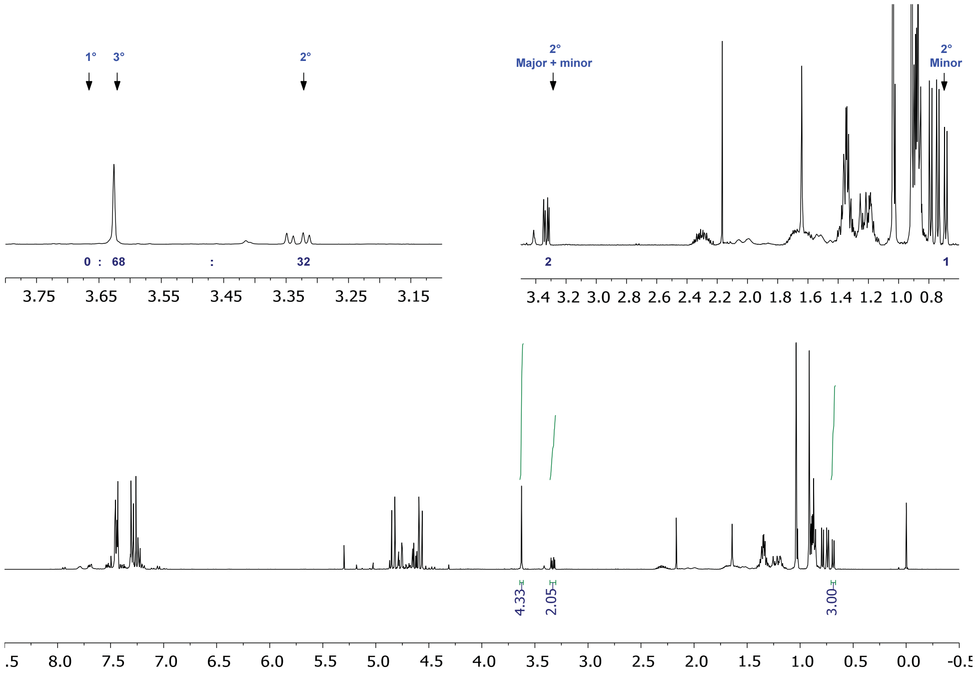


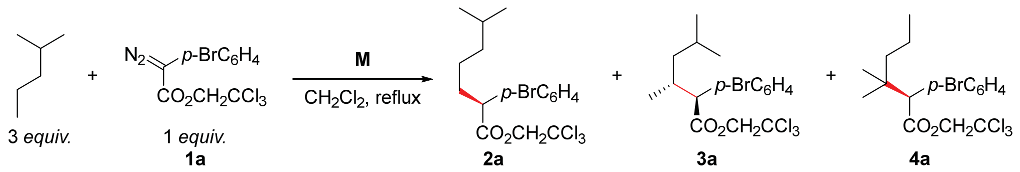
3 equiv.
N2
p-BrC6H4
CO2CH2CCl3
1 equiv.
1a
K
CH2Cl2, reflux
2a
3a
4a

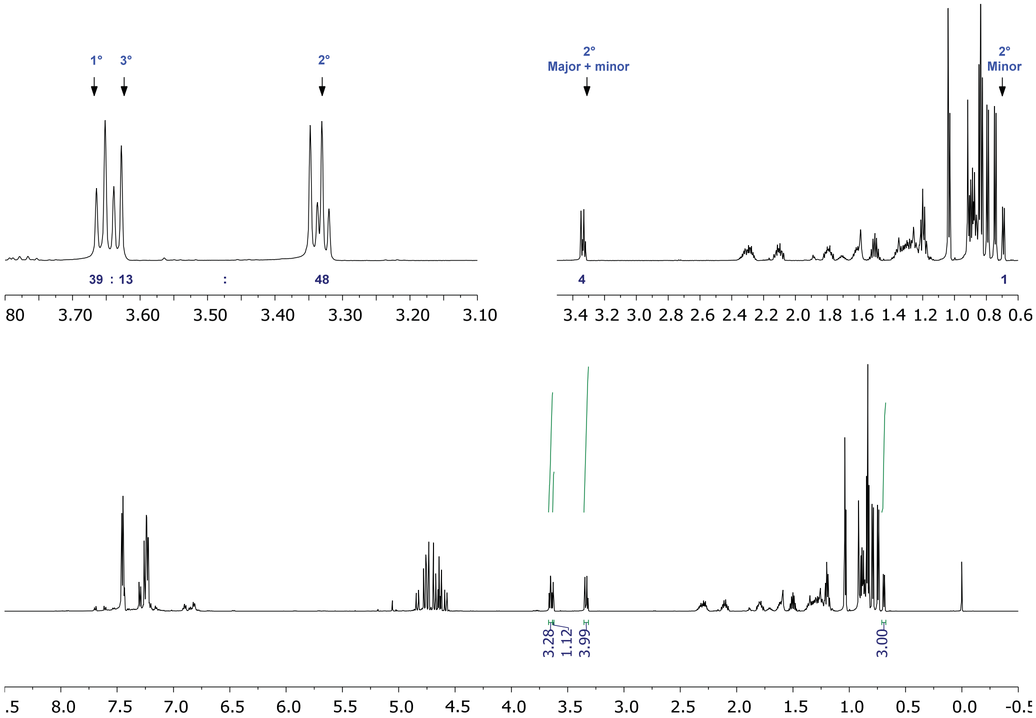


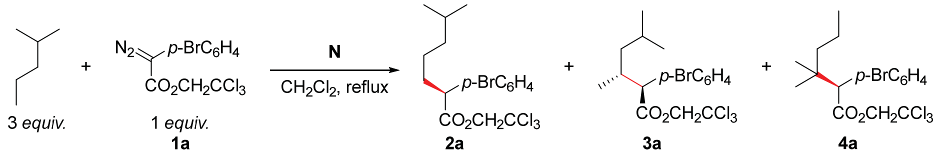
1°
3°
2°
48 : 17 : 35
80
3.70
3.60
3.50
3.40
3.30
3.20
3.10
2°
Major + minor
2°
Minor
4
1
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
4.80
1.72
3.50
3.00
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

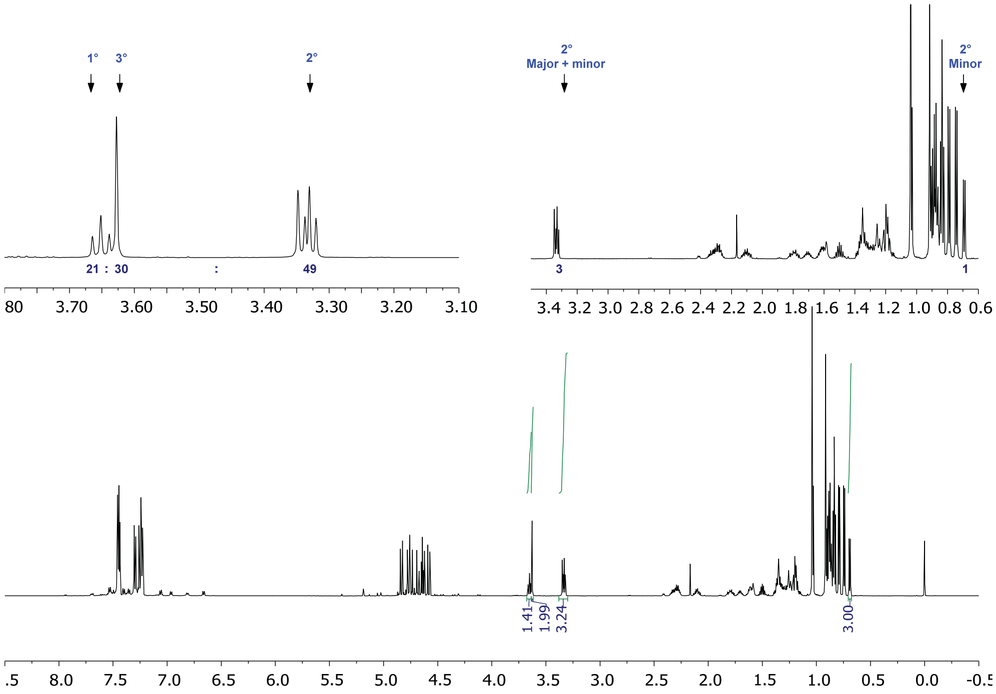

3 *equiv.*
+
N_2
p-BrC_6H_4
$CO_2CH_2CCl_3$
1 *equiv.*
1a
L
CH_2Cl_2, reflux
p-BrC_6H_4
$CO_2CH_2CCl_3$
2a
+
p-BrC_6H_4
$CO_2CH_2CCl_3$
3a
+
p-BrC_6H_4
$CO_2CH_2CCl_3$
4a

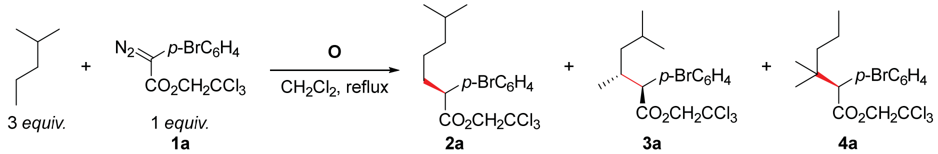

1°
3°
2°
0 : 68 : 32
3.75 3.65 3.55 3.45 3.35 3.25 3.15
2°
Major + minor
2°
Minor
2
1
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
4.33
2.05
3.00
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

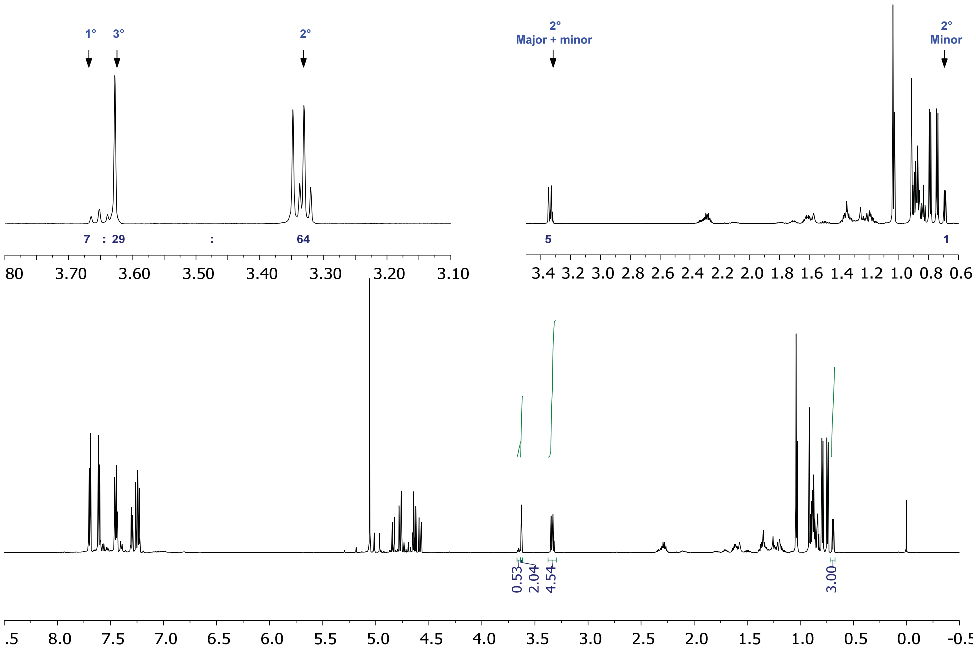

3 *equiv.*
+
N_2
p-BrC_6H_4
$CO_2CH_2CCl_3$
1 *equiv.*
1a
M
CH_2Cl_2, reflux
p-BrC_6H_4
$CO_2CH_2CCl_3$
2a
+
p-BrC_6H_4
$CO_2CH_2CCl_3$
3a
+
p-BrC_6H_4
$CO_2CH_2CCl_3$
4a

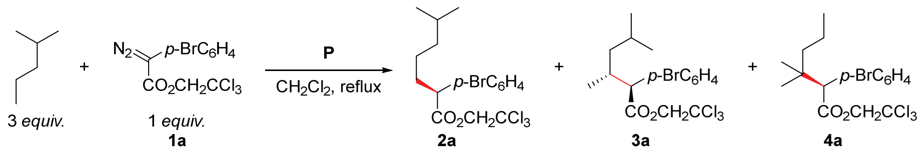

1°
3°
2°
39 : 13 : 48
80
3.70
3.60
3.50
3.40
3.30
3.20
3.10
2°
Major + minor
2°
Minor
4
1
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
3.28
1.12
3.99
3.00
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

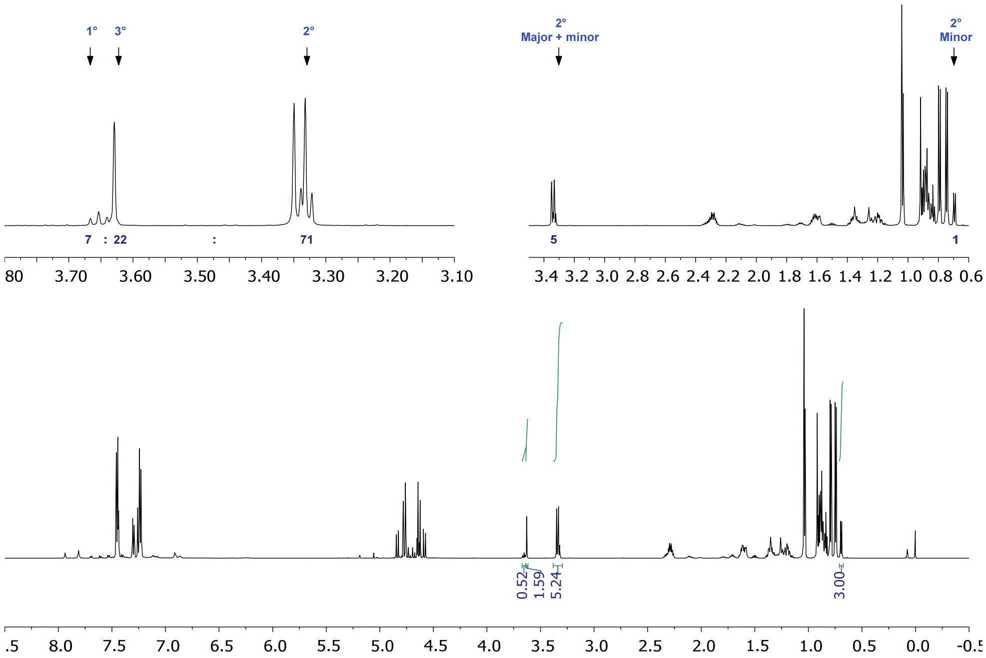

3 equiv.
N₂
p-BrC₆H₄
CO₂CH₂CCl₃
1 equiv.
1a
N
CH₂Cl₂, reflux
p-BrC₆H₄
CO₂CH₂CCl₃
2a
p-BrC₆H₄
CO₂CH₂CCl₃
3a
p-BrC₆H₄
CO₂CH₂CCl₃
4a

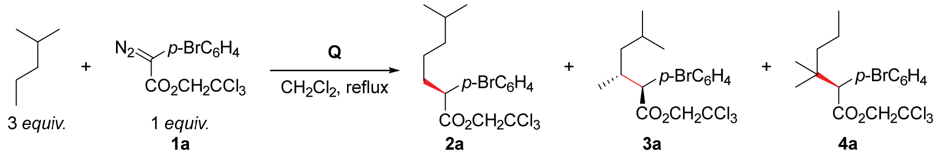

1°
3°
2°
21 : 30 : 49
80
3.70
3.60
3.50
3.40
3.30
3.20
3.10
2°
Major + minor
2°
Minor
3
1
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
1.41
1.99
3.24
3.00
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

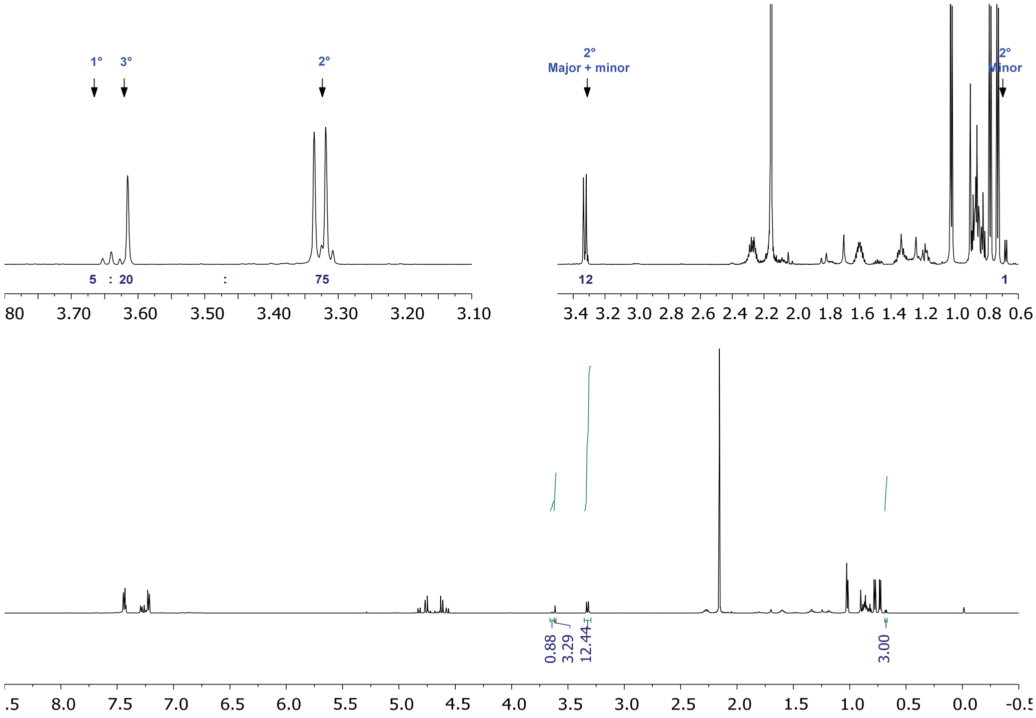

3 equiv.
N$_2$
p-BrC$_6$H$_4$
CO$_2$CH$_2$CCl$_3$
1 equiv.
1a
O
CH$_2$Cl$_2$, reflux
2a
3a
4a

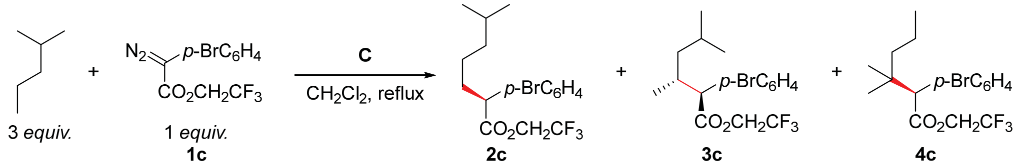

1°
3°
2°
7 : 29 : 64
80 3.70 3.60 3.50 3.40 3.30 3.20 3.10
2° Major + minor
2° Minor
5
1
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
0.53
2.04
4.54
3.00
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

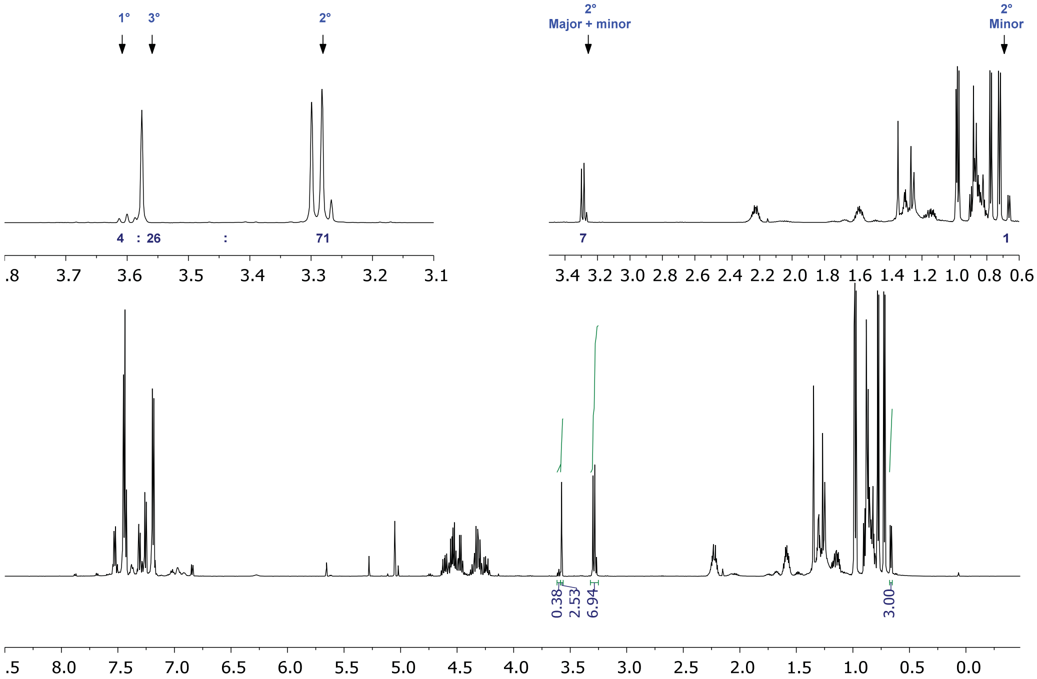

3 *equiv.*
+
N_2
p-BrC_6H_4
$CO_2CH_2CCl_3$
1 *equiv.*
1a
P
CH_2Cl_2, reflux
p-BrC_6H_4
$CO_2CH_2CCl_3$
2a
+
p-BrC_6H_4
$CO_2CH_2CCl_3$
3a
+
p-BrC_6H_4
$CO_2CH_2CCl_3$
4a

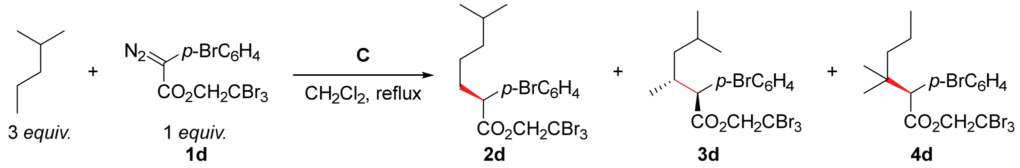

1°
3°
2°
7 : 22 : 71
80
3.70
3.60
3.50
3.40
3.30
3.20
3.10
2°
Major + minor
2°
Minor
5
1
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
0.52
1.59
5.24
3.00
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


3 equiv.
N2
p-BrC6H4
CO2CH2CCl3
1 equiv.
1a
Q
CH2Cl2, reflux
p-BrC6H4
CO2CH2CCl3
2a
p-BrC6H4
CO2CH2CCl3
3a
p-BrC6H4
CO2CH2CCl3
4a

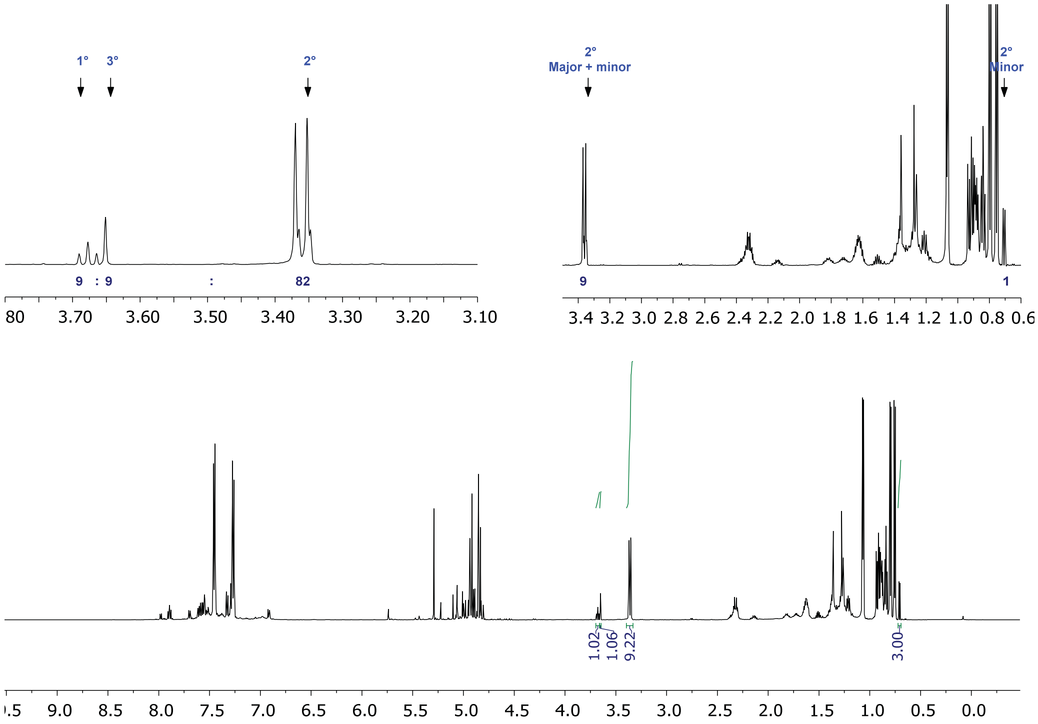

1°
3°
2°
5 : 20 : 75
80 3.70 3.60 3.50 3.40 3.30 3.20 3.10
2°
Major + minor
2°
Minor
12
1
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
0.88
3.29
12.44
3.00
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


3 equiv.
+
N_2
p-BrC$_6$H$_4$
CO$_2$CH$_2$CF$_3$
1 equiv.
1c
C
CH$_2$Cl$_2$, reflux
2c
+
3c
+
4c

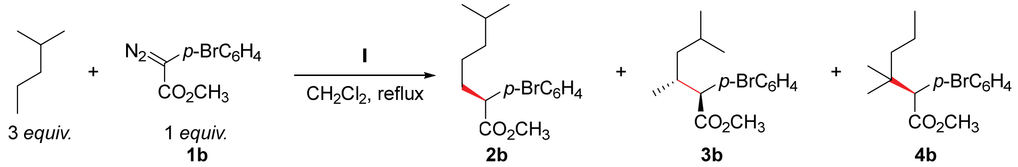

1°
3°
2°
2° Major + minor
2° Minor
4 : 26 : 71
7
1
.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
0.38
2.53
6.94
3.00
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

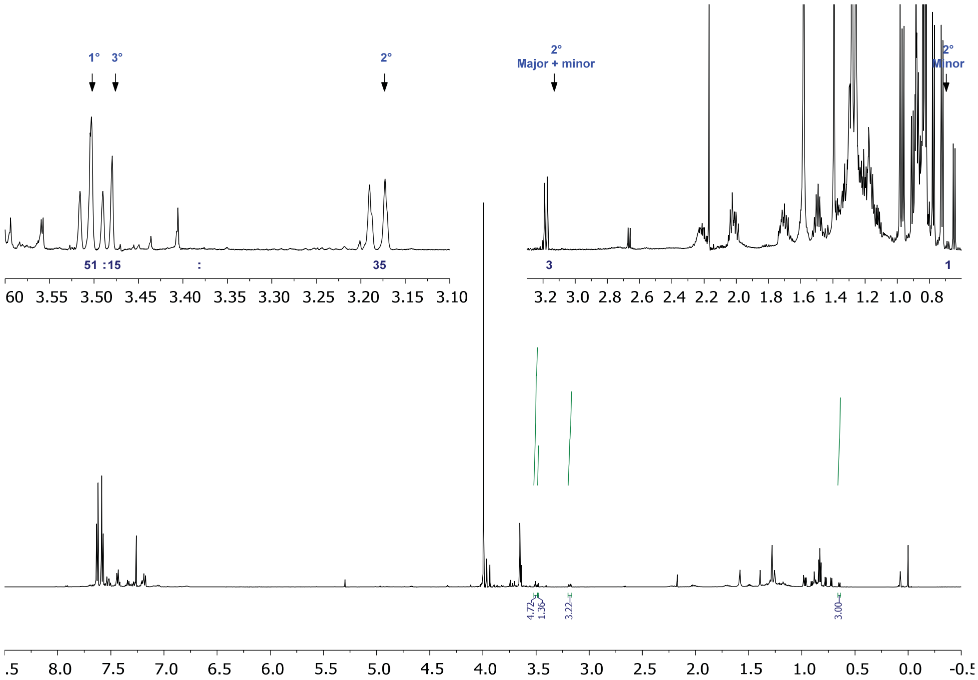


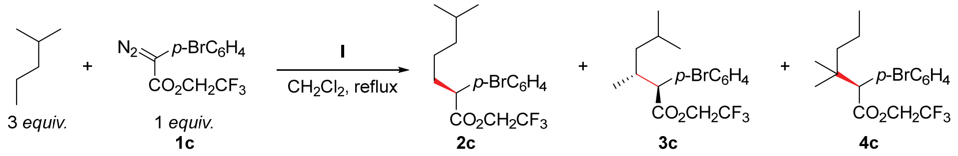
3 *equiv.*
+
N_2
p-BrC_6H_4
$CO_2CH_2CBr_3$
1 *equiv.*
1d
C
CH_2Cl_2, reflux
p-BrC_6H_4
$CO_2CH_2CBr_3$
2d
+
p-BrC_6H_4
$CO_2CH_2CBr_3$
3d
+
p-BrC_6H_4
$CO_2CH_2CBr_3$
4d

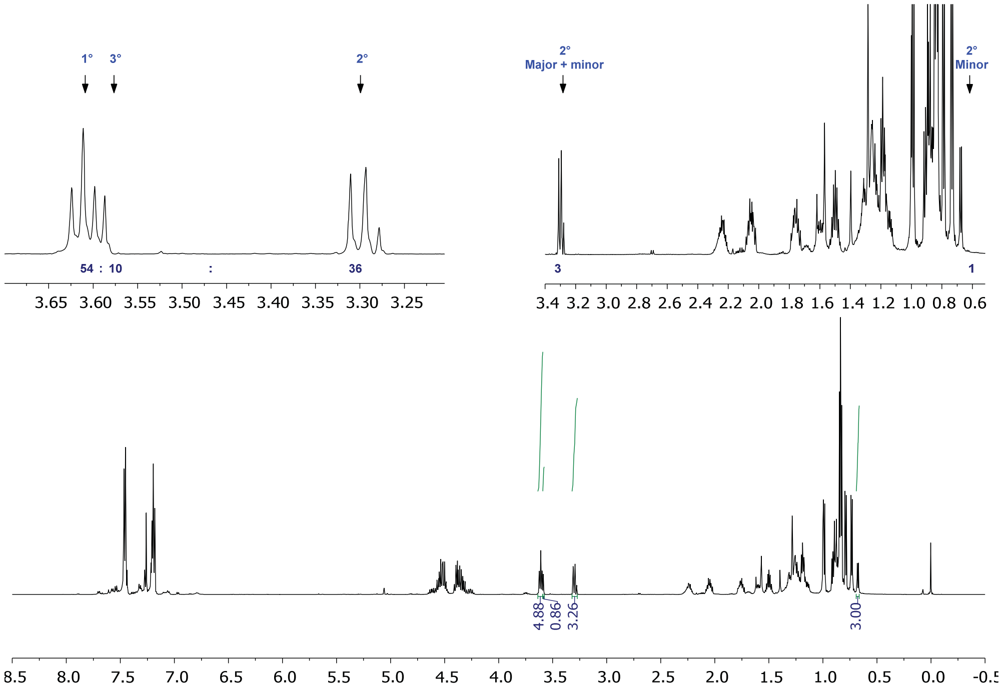


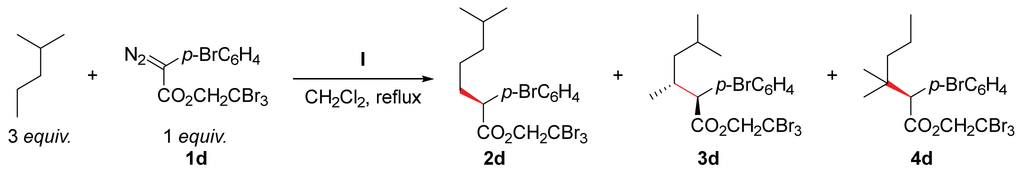
1°
3°
2°
9 : 9 : 82
80
3.70
3.60
3.50
3.40
3.30
3.20
3.10
2°
Major + minor
2°
Minor
9
1
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
1.02
1.06
9.22
3.00
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

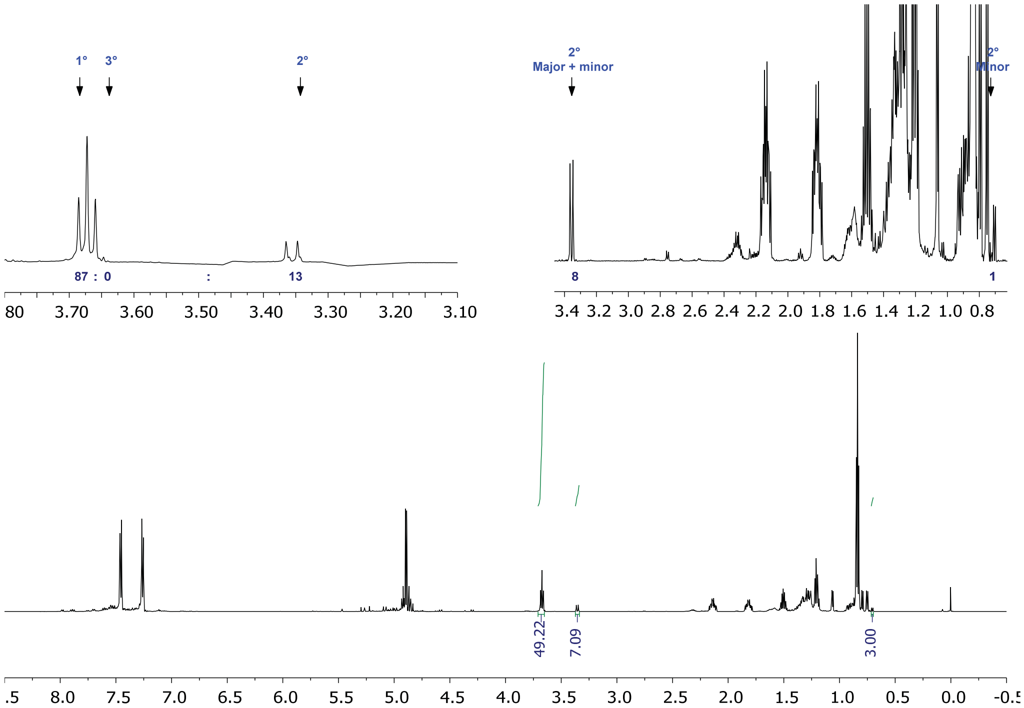

3 equiv.
N2
p-BrC6H4
CO2CH3
1 equiv.
1b
I
CH2Cl2, reflux
p-BrC6H4
CO2CH3
2b
p-BrC6H4
CO2CH3
3b
p-BrC6H4
CO2CH3
4b


1°
3°
2°
51 :15
:
35
60 3.55 3.50 3.45 3.40 3.35 3.30 3.25 3.20 3.15 3.10
2°
Major + minor
2°
Minor
3
1
3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
4.72
1.36
3.22
3.00
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

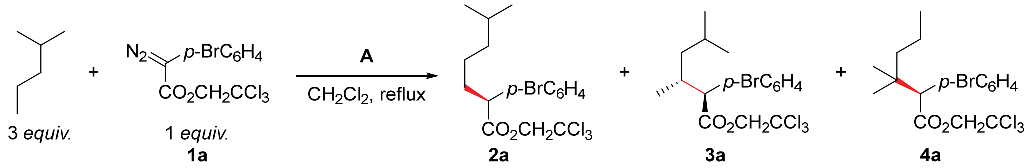

3 equiv.
N2
p-BrC6H4
CO2CH2CF3
1 equiv.
1c
I
CH2Cl2, reflux
p-BrC6H4
CO2CH2CF3
2c
p-BrC6H4
CO2CH2CF3
3c
p-BrC6H4
CO2CH2CF3
4c

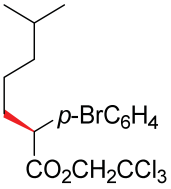

1°
3°
2°
54 : 10 : 36
3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30 3.25
2°
Major + minor
2°
Minor
3
1
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
4.88
0.86
3.26
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


3 *equiv.*
+
N_2
p-BrC_6H_4
$CO_2CH_2CBr_3$
1 *equiv.*
1d
I
CH_2Cl_2, reflux
p-BrC_6H_4
$CO_2CH_2CBr_3$
2d
+
p-BrC_6H_4
$CO_2CH_2CBr_3$
3d
+
p-BrC_6H_4
$CO_2CH_2CBr_3$
4d

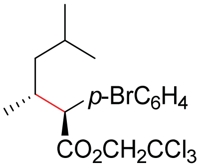

1°
3°
2°
87 : 0 : 13
80
3.70
3.60
3.50
3.40
3.30
3.20
3.10
2° Major + minor
2° Minor
8
1
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
49.22
7.09
3.00
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

4.5 HPLC

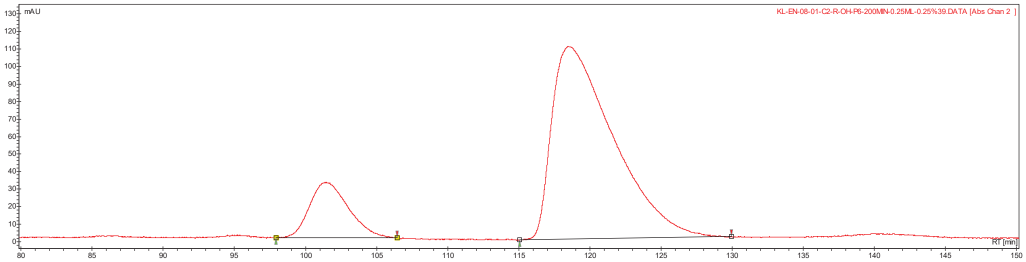




2a was not detected.

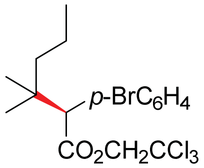


3a

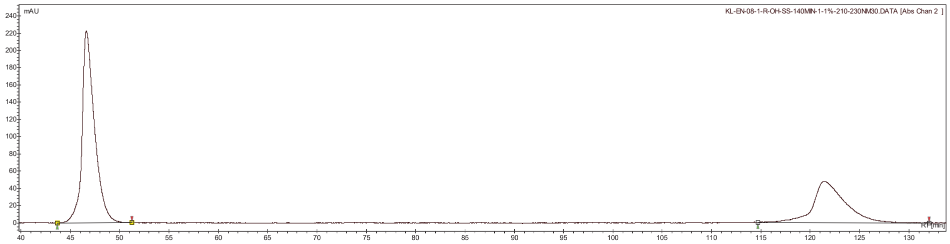


#	Time [Min]	Area% [%]
1	101.37	15.397
2	118.49	84.603

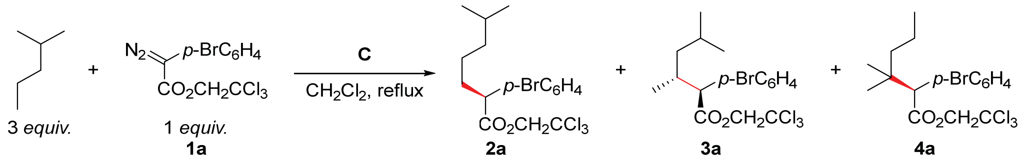
69% *e.e.*

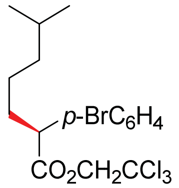


4a

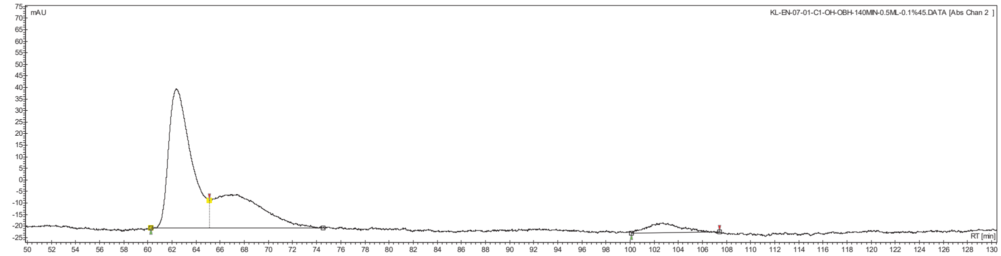


#	Time [Min]	Area% [%]
1	46.62	64.676
2	121.53	35.324
		29% *e.e.*

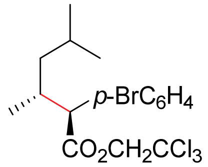




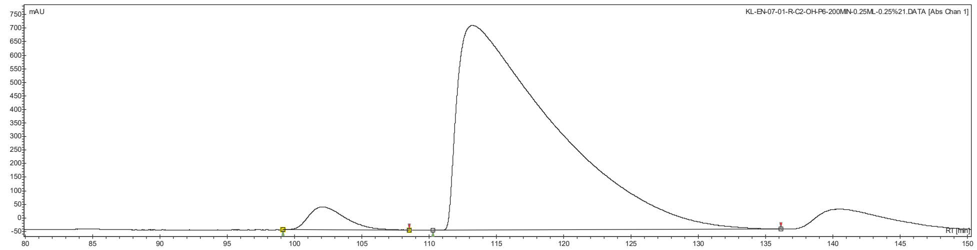
2a



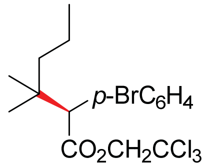
#	Time [Min]	Area% [%]
1	62.34	90.562
2	102.71	9.438
		81% *e.e.*



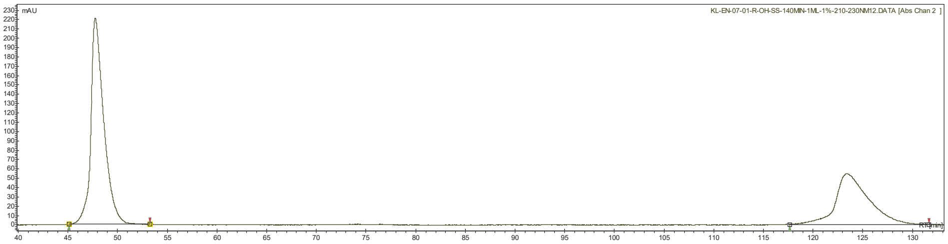
3a



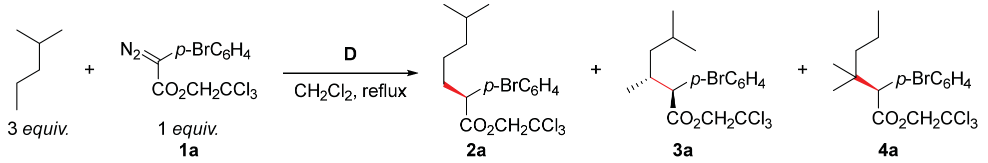
#	Time [Min]	Area% [%]
1	102.01	4.095
2	113.17	95.905
		92% *e.e.*

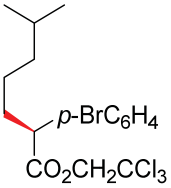


4a

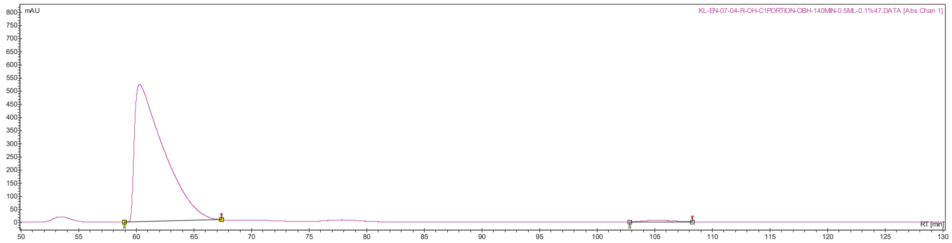


#	Time [Min]	Area% [%]
1	47.75	61.453
2	123.37	38.547
		23% *e.e.*

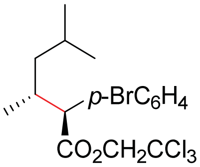




2a



#	Time [Min]	Area% [%]
1	60.25	98.781
2	105.23	1.219
		97% *e.e.*



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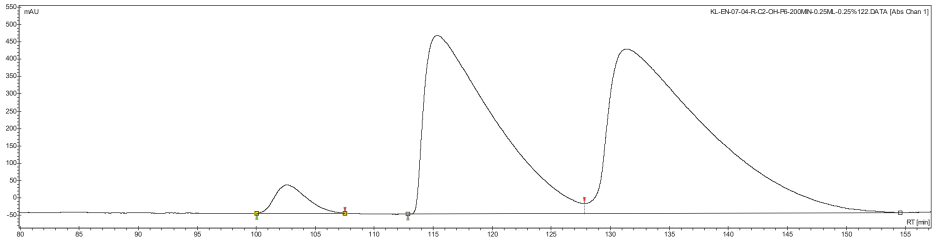
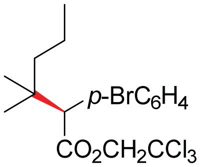
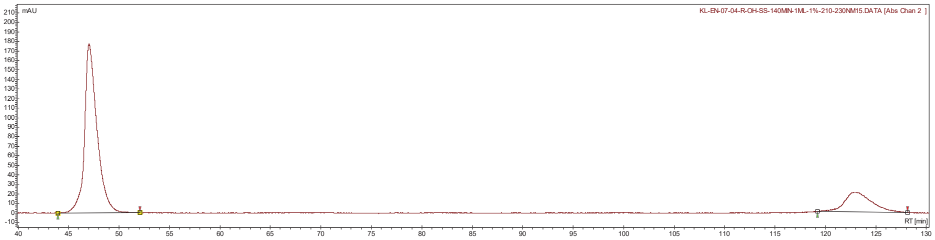


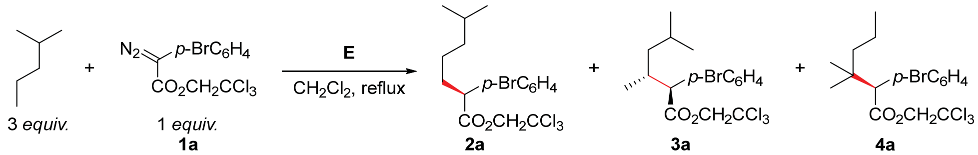
#	Time [Min]	Area% [%]
1	102.66	6.656
2	115.31	93.344
		87% *e.e.*

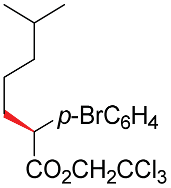


4a

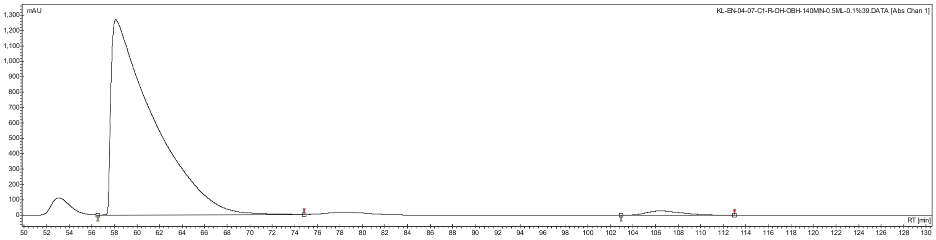


#	Time [Min]	Area% [%]
1	47.03	80.156
2	122.92	19.844
		60% *e.e.*

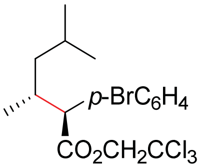




2a



#	Time [Min]	Area% [%]
1	58.12	98.197
2	106.27	1.803
		96% *e.e.*



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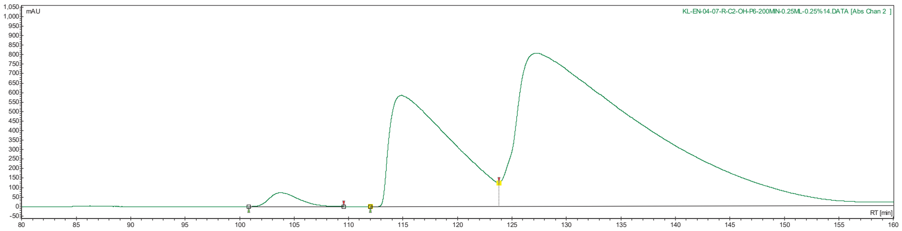
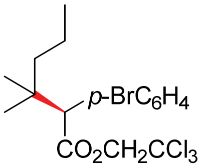
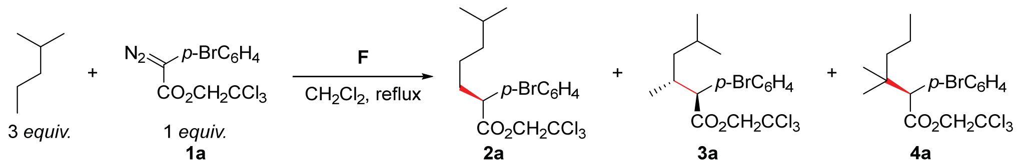


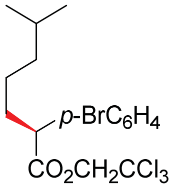
#	Time [Min]	Area% [%]
1	103.79	5.526
2	114.86	94.474
		89% *e.e.*



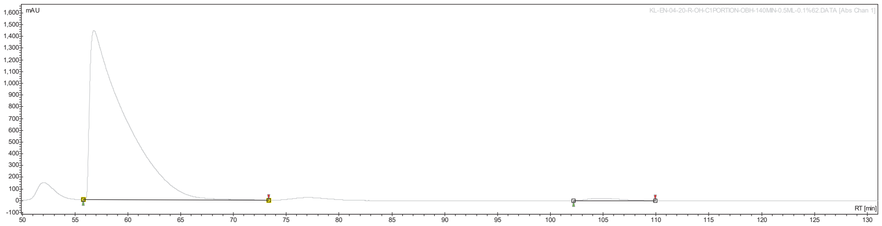
4a

Enantiomeric excess was not determined.

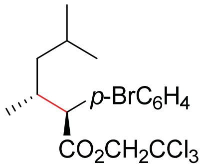




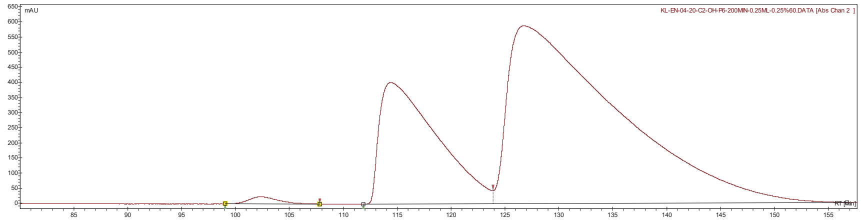
2a



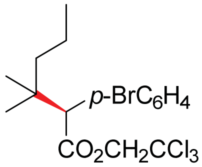
#	Time [Min]	Area% [%]
1	56.76	98.764
2	104.75	1.236
		98% *e.e.*



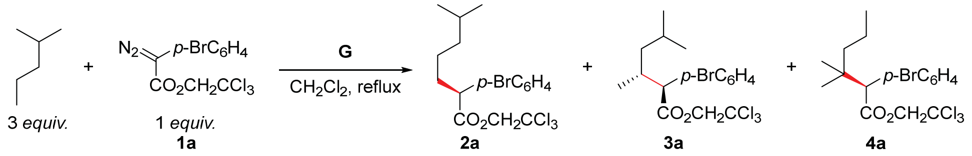
3a

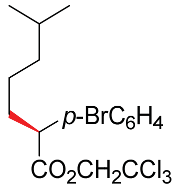


#	Time [Min]	Area% [%]
1	102.44	2.897
2	114.39	97.103
		94% *e.e.*

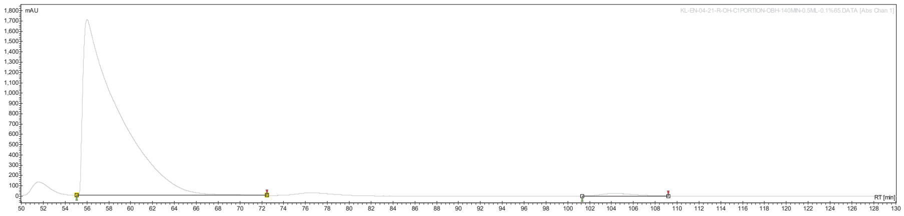


4a Enantiomeric excess was not determined.

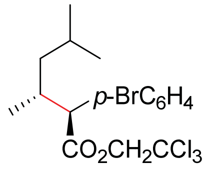




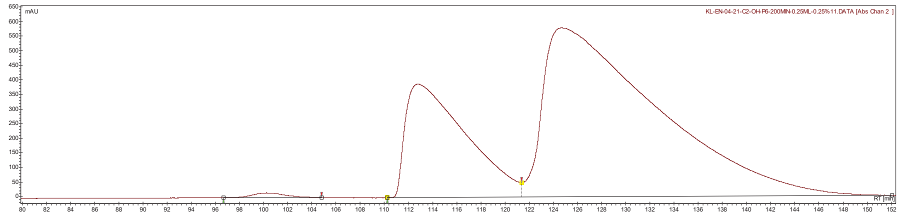
2a



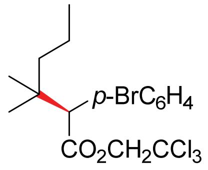
#	Time [Min]	Area% [%]
1	55.99	98.696
2	104.16	1.304
		97% *e.e.*



3a

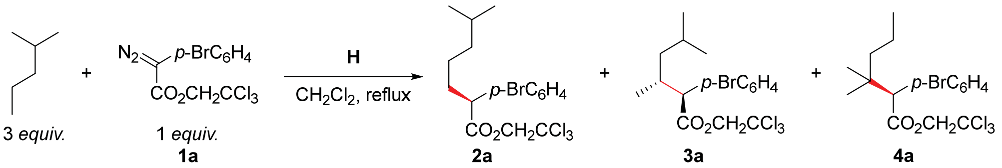


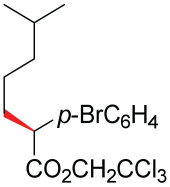
#	Time [Min]	Area% [%]
1	100.24	2.160
2	112.72	97.840
		96% *e.e.*



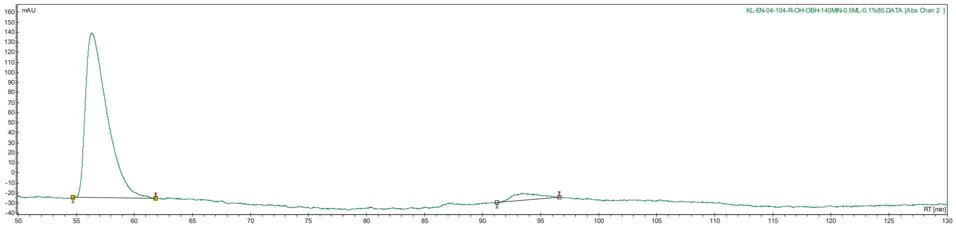
4a

Enantiomeric excess was not determined.

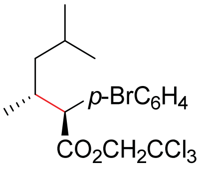




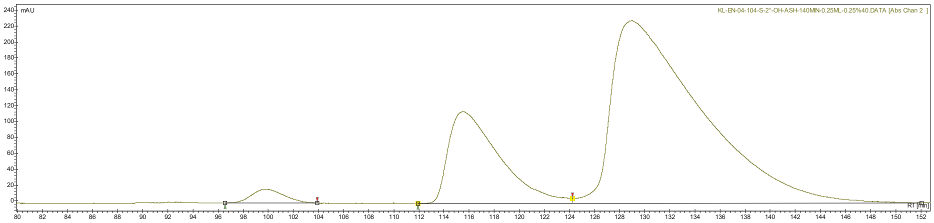
2a



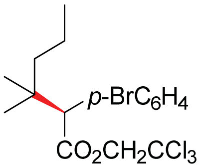
#	Time [Min]	Area% [%]
1	56.33	94.934
2	93.42	5.066
		90% *e.e.*



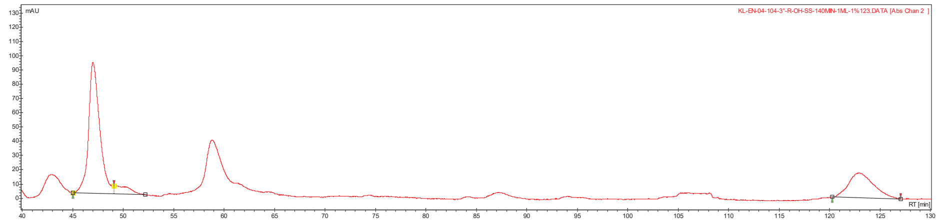
3a



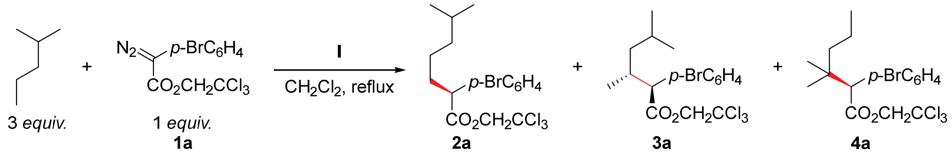
#	Time [Min]	Area% [%]
1	99.71	8.744
2	115.51	91.256
		83% *e.e.*

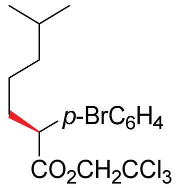


4a

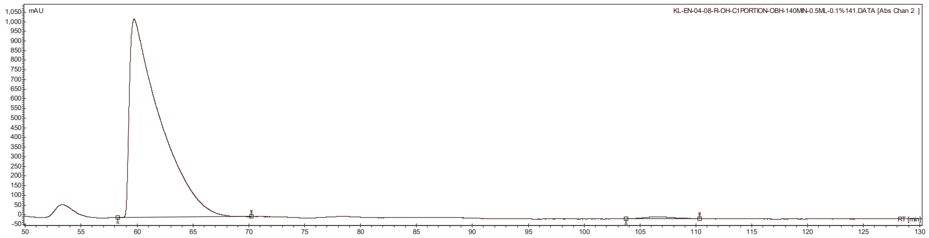


#	Time [Min]	Area% [%]
1	47.00	70.105
2	122.98	29.895
		40% *e.e.*

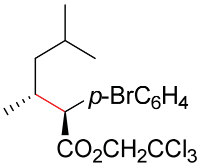




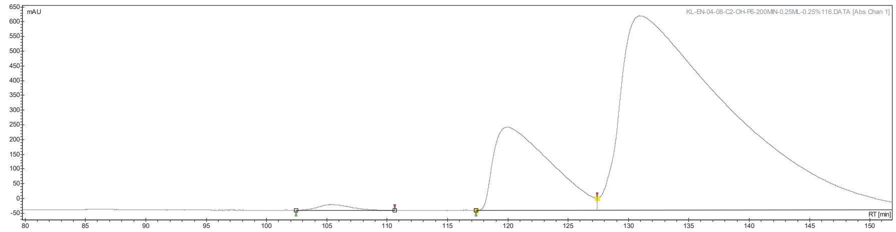
2a



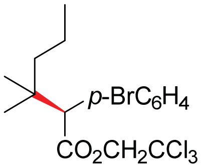
#	Time [Min]	Area% [%]
1	59.71	98.998
2	106.82	1.002
		98% *e.e.*



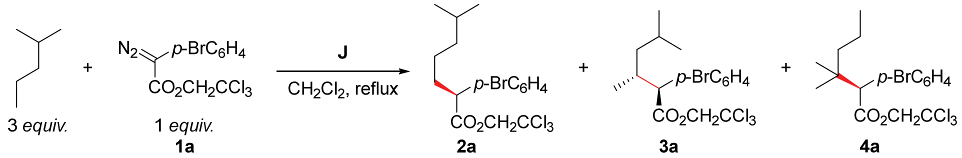
3a

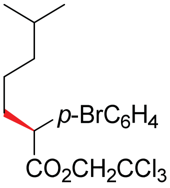


#	Time [Min]	Area% [%]
1	105.43	3.856
2	119.91	96.144
		92% *e.e.*

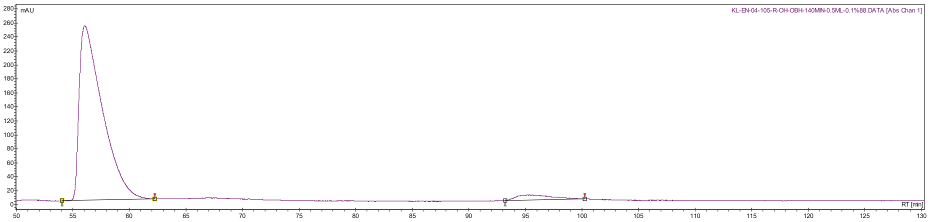


4a was not detected.

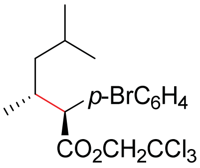




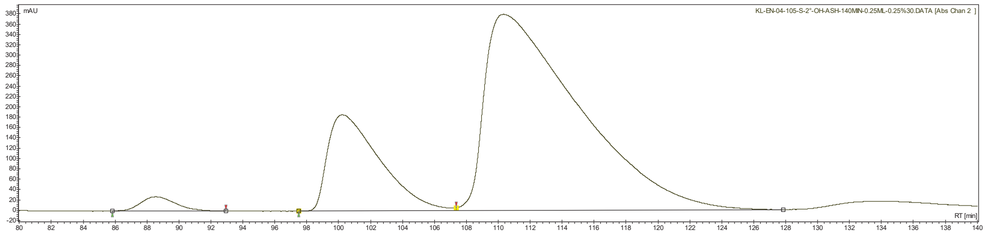
2a



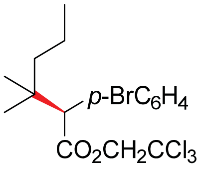
#	Time [Min]	Area% [%]
1	56.04	95.943
2	95.22	4.057
		92% *e.e.*



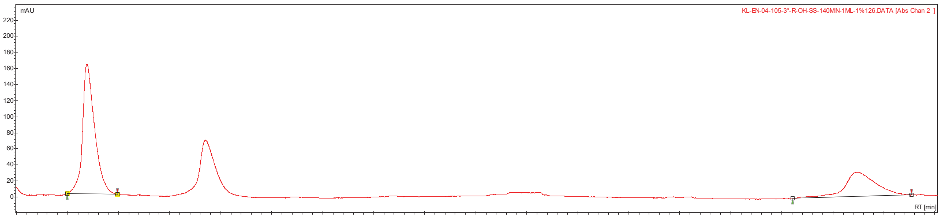
3a



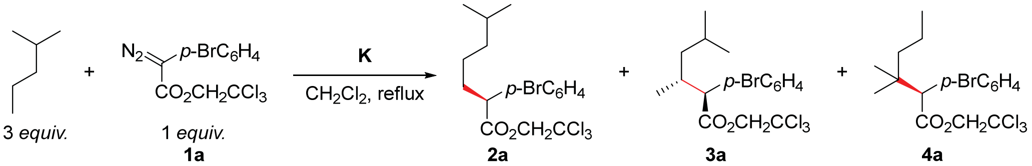
#	Time [Min]	Area% [%]
1	88.52	8.914
2	100.24	91.086
		82% *e.e.*

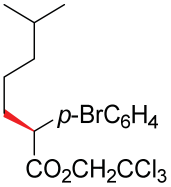


4a

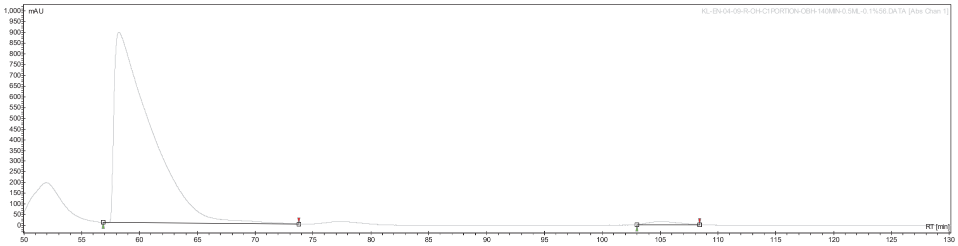


#	Time [Min]	Area% [%]
1	46.90	67.555
2	122.34	32.445
		35% *e.e.*

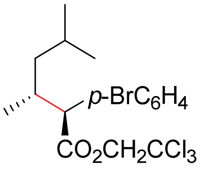




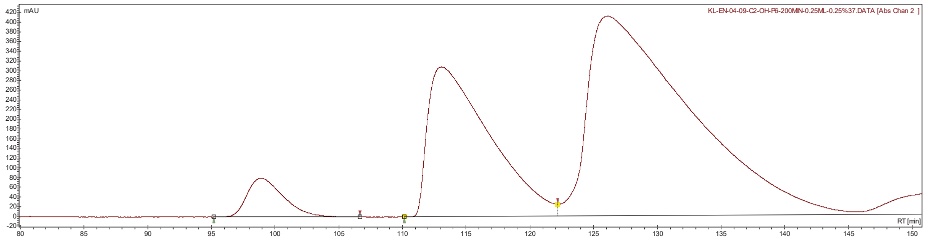
2a



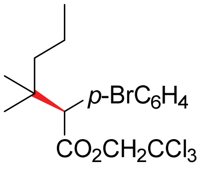
#	Time [Min]	Area% [%]
1	58.21	98.697
2	105.24	1.303
		97% *e.e.*



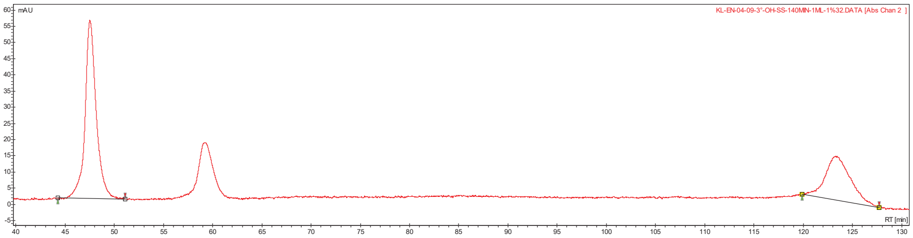
3a



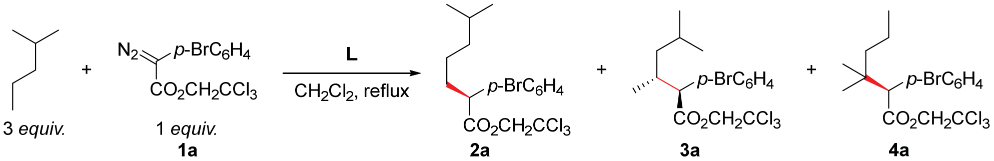
#	Time [Min]	Area% [%]
1	98.86	13.101
2	113.05	86.899
		74% *e.e.*

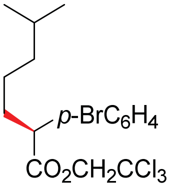


4a



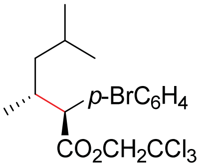
#	Time [Min]	Area% [%]
1	47.51	64.303
2	123.44	35.697
		29% *e.e.*



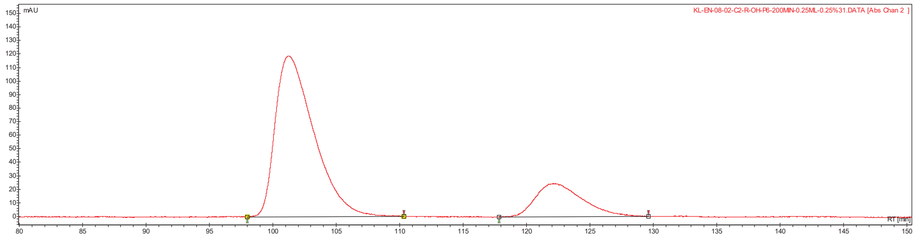


2a

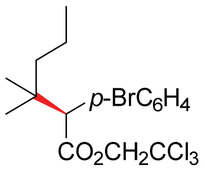
Enantiomeric excess was not determined.



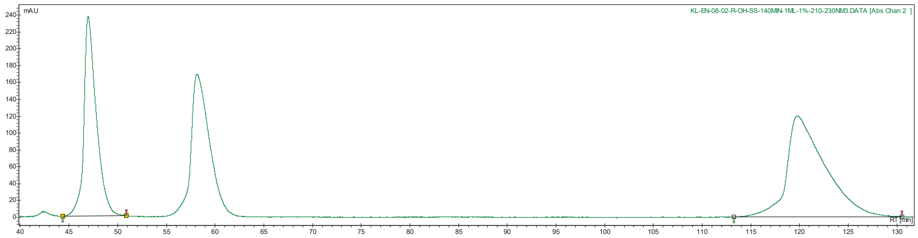
3a



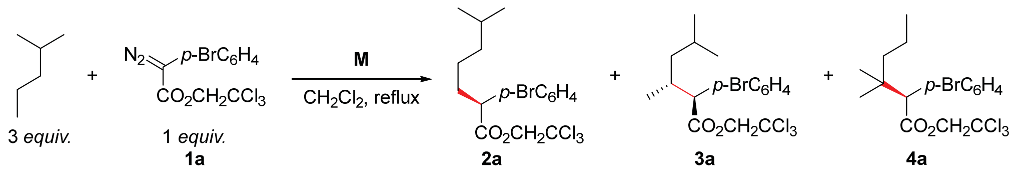
#	Time [Min]	Area% [%]
1	101.27	80.057
2	122.10	19.943
		-60% *e.e.*

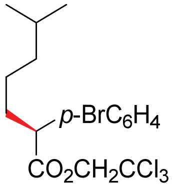


4a

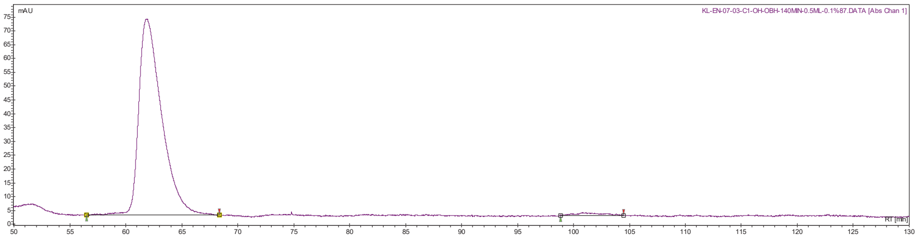


#	Time [Min]	Area% [%]
1	46.97	39.225
2	119.75	60.775
		-22% *e.e.*

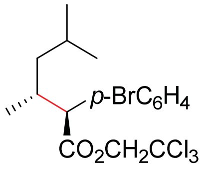




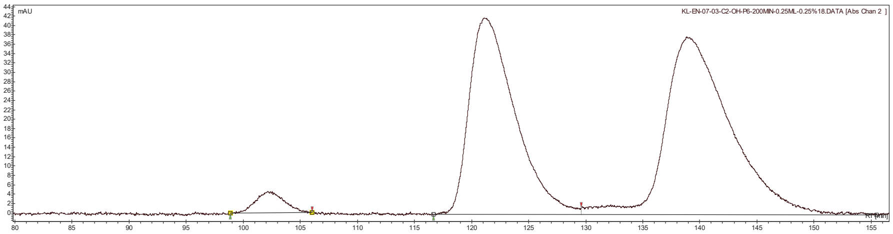
2a



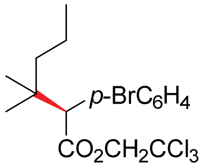
#	Time [Min]	Area% [%]
1	61.85	98.526
2	100.84	1.474
		97% *e.e.*



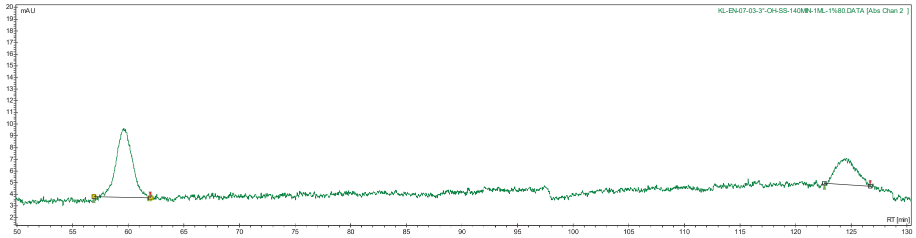
3a



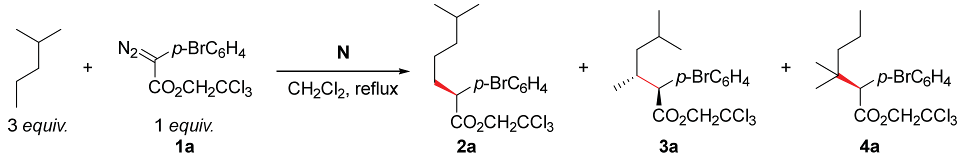
#	Time [Min]	Area% [%]
1	102.13	6.405
2	121.11	93.595
		87% *e.e.*

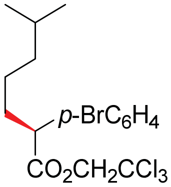


4a



#	Time [Min]	Area% [%]
1	59.61	67.637
2	124.52	32.363
		35% *e.e.*





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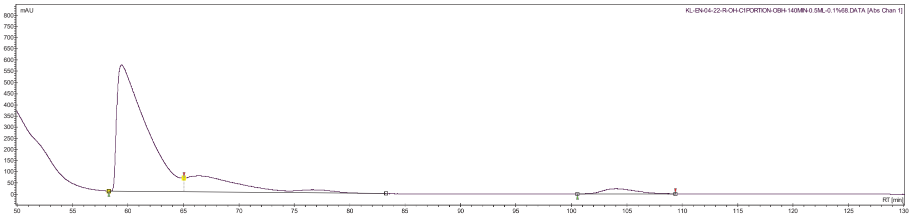
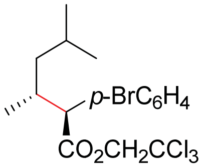
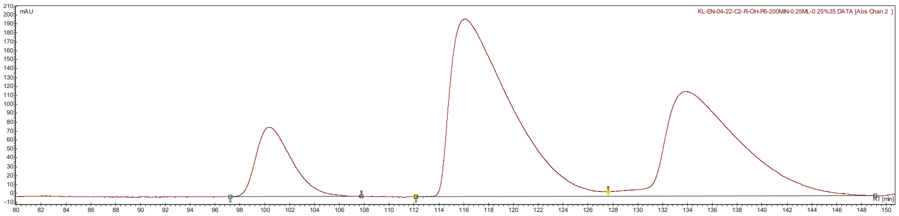


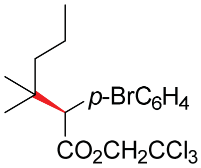
#	Time [Min]	Area% [%]
1	59.41	95.704
2	103.97	4.296
		91% *e.e.*



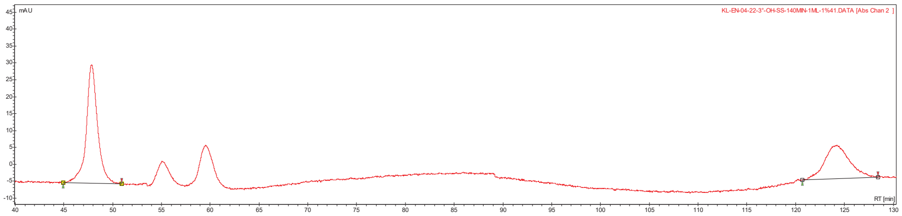
3a



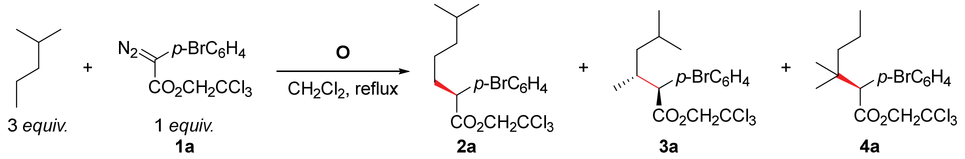
#	Time [Min]	Area% [%]
1	100.41	18.840
2	116.14	81.160
		62% *e.e.*

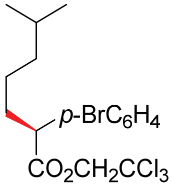


4a

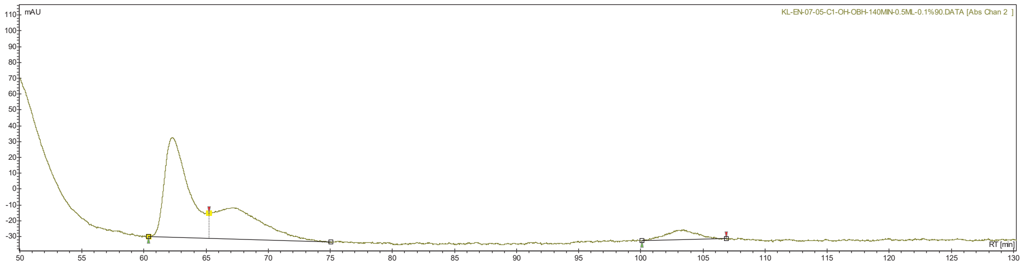


#	Time [Min]	Area% [%]
1	47.87	61.089
2	124.24	38.911
		14% *e.e.*

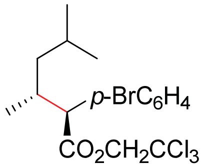




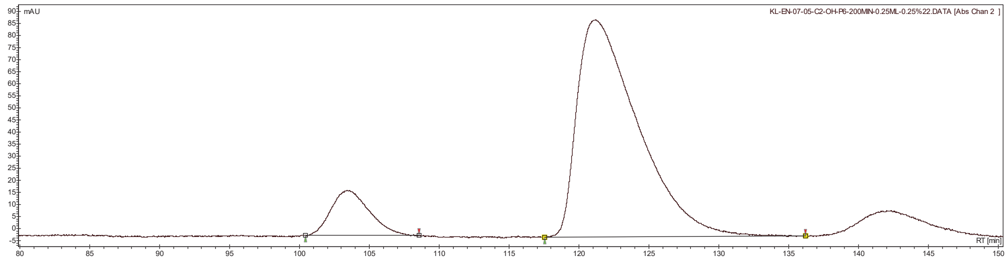
2a



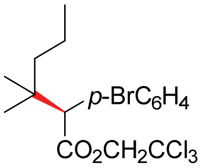
#	Time [Min]	Area% [%]
1	62.32	88.857
2	103.33	11.143
		78% *e.e.*



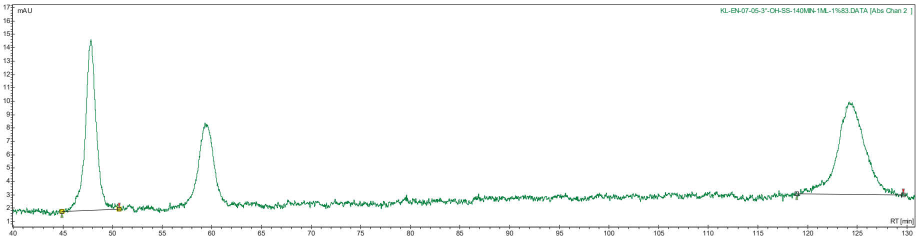
3a



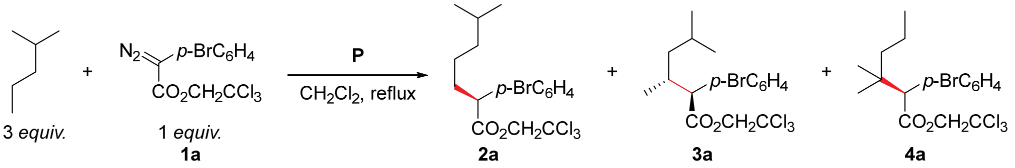
#	Time [Min]	Area% [%]
1	103.41	11.565
2	121.23	88.435
		77% *e.e.*

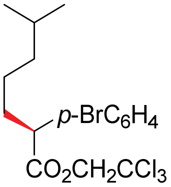


4a

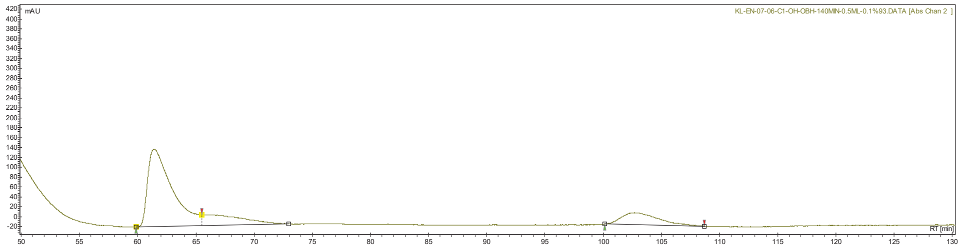


#	Time [Min]	Area% [%]
1	47.80	42.773
2	124.26	57.227
		14% *e.e.*

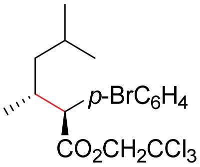




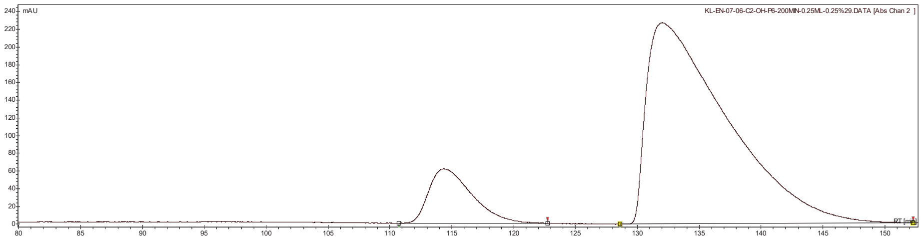
2a



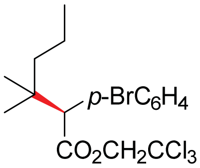
#	Time [Min]	Area% [%]
1	61.43	80.721
2	102.87	19.279
		62% *e.e.*



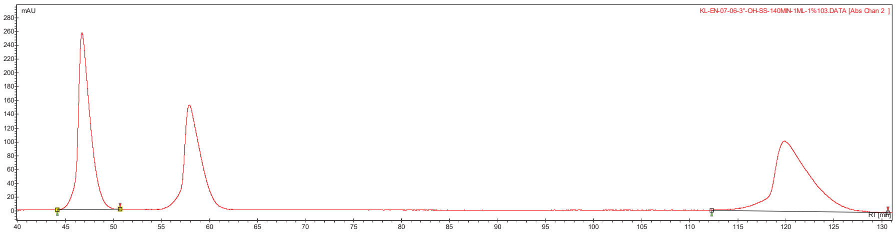
3a



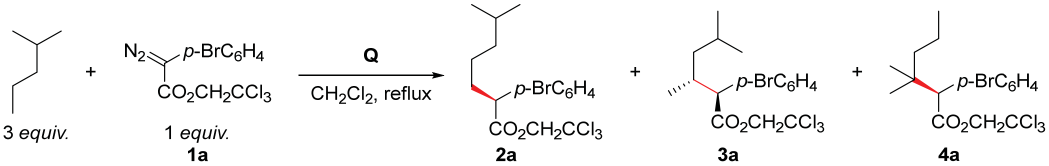
#	Time [Min]	Area% [%]
1	114.39	12.615
2	132.02	87.385
		>99% *e.e.*

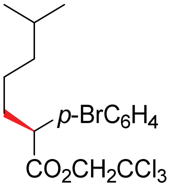


4a

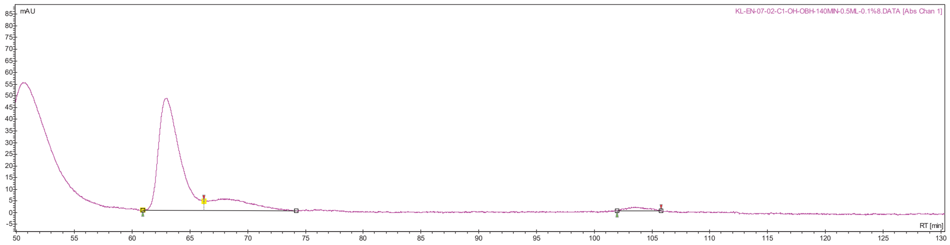


#	Time [Min]	Area% [%]
1	46.72	45.911
2	119.82	54.089
		8% *e.e.*

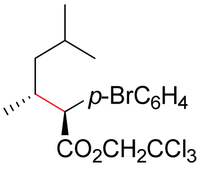




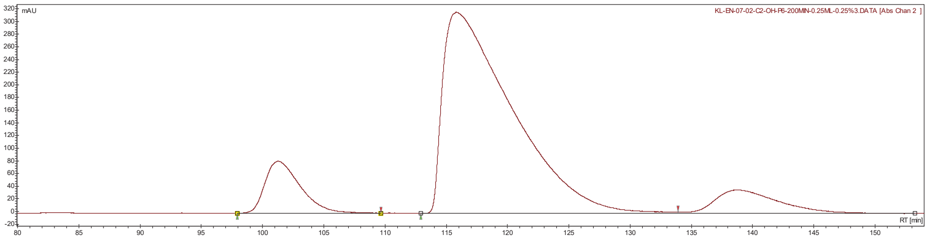
2a



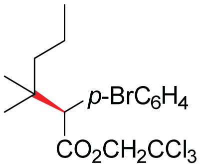
#	Time [Min]	Area% [%]
1	62.94	97.034
2	103.61	2.966
		94% *e.e.*



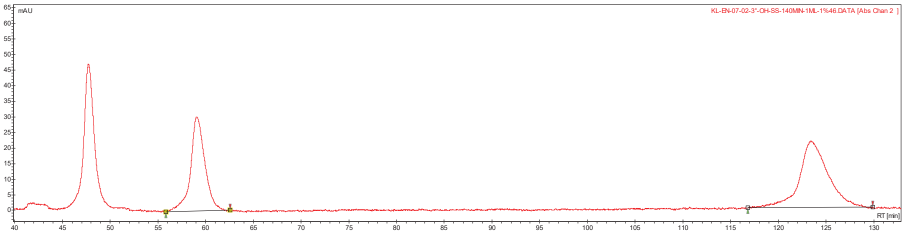
3a



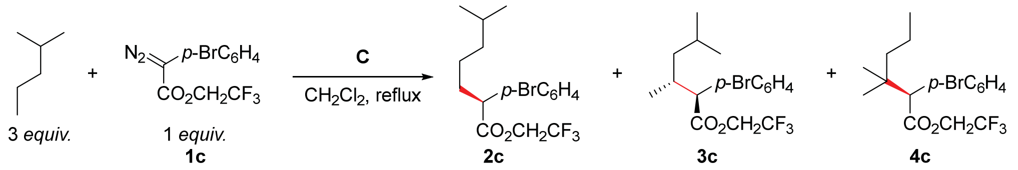
#	Time [Min]	Area% [%]
1	101.22	11.581
2	115.80	88.419
		77% *e.e.*

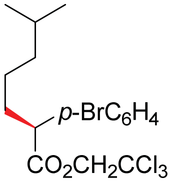


4a

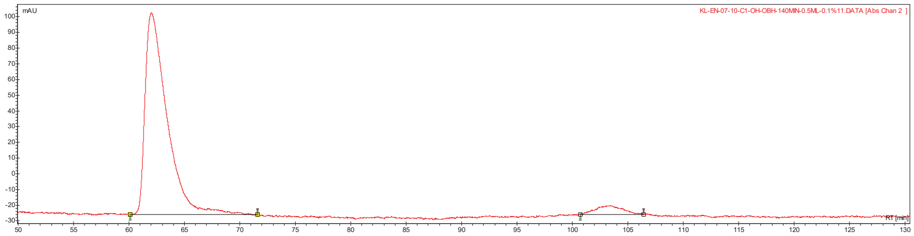


#	Time [Min]	Area% [%]
1	59.04	41.367
2	123.46	58.633
		17% *e.e.*



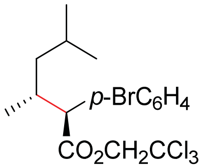


2c

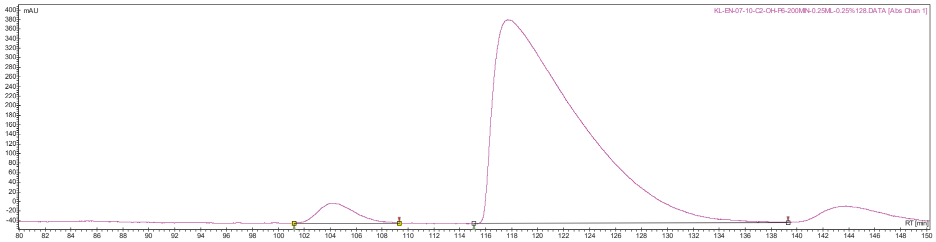


#	Time [Min]	Area% [%]
1	62.04	95.021
2	103.39	4.979

90% *e.e.*

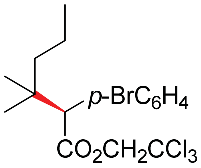


3c

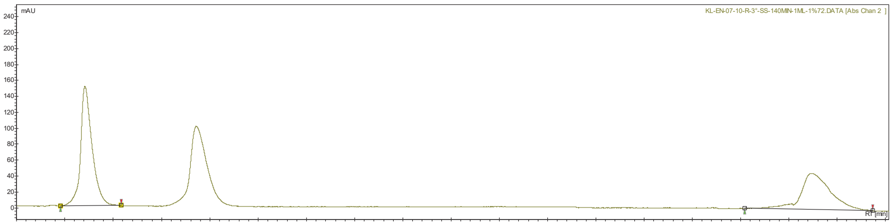


#	Time [Min]	Area% [%]
1	104.10	4.084
2	117.69	95.916

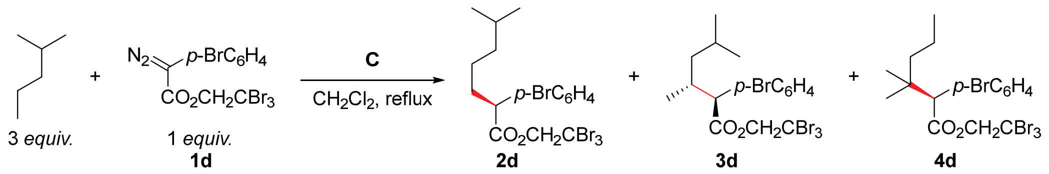
92 *e.e.*

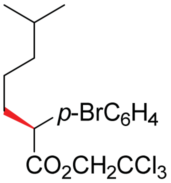


4c



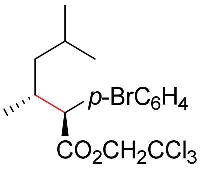
#	Time [Min]	Area% [%]
1	47.06	56.009
2	122.30	43.991
		12% *e.e.*



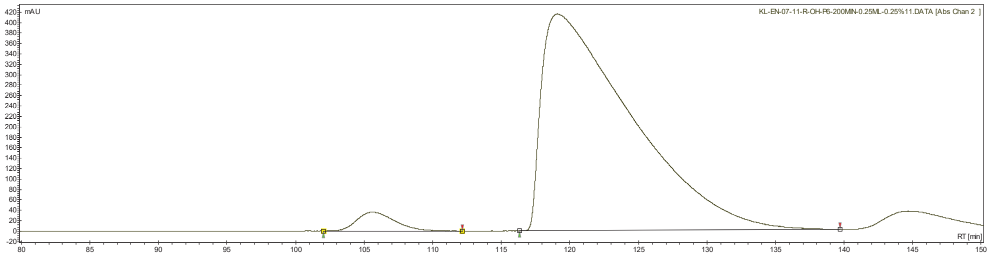


2d

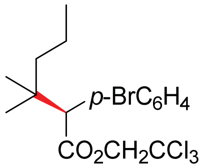
Enantiomeric excess was not determined.



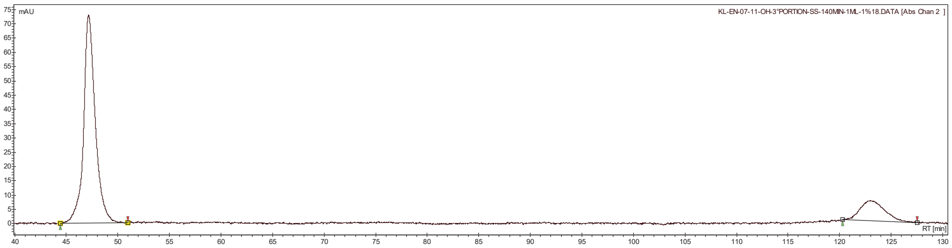
3d



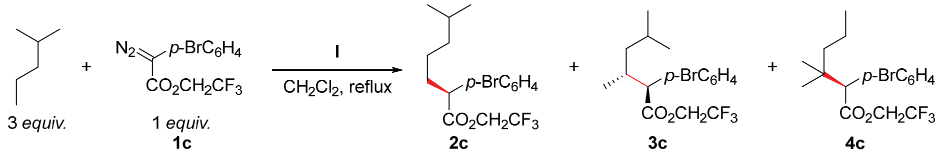
#	Time [Min]	Area% [%]
1	105.57	3.571
2	119.10	96.429
		93% *e.e.*

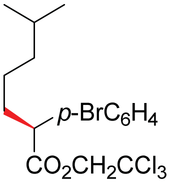


4d

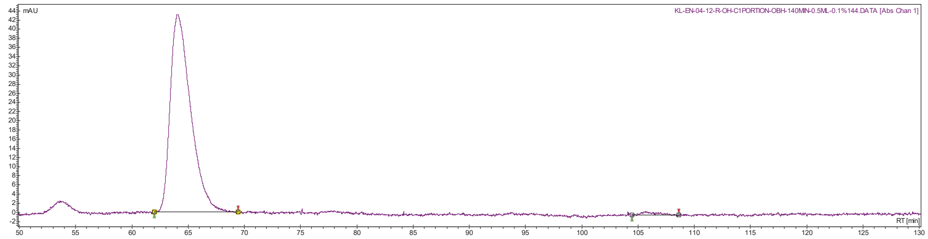


#	Time [Min]	Area% [%]
1	47.16	83.653
2	123.00	16.347
		67% *e.e.*

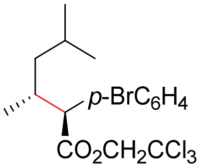




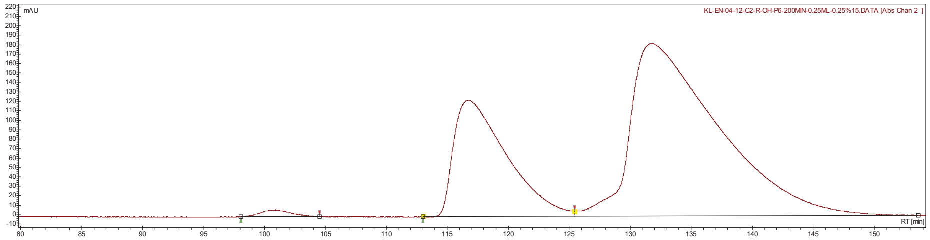
2c



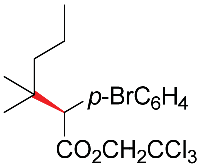
#	Time [Min]	Area% [%]
1	64.10	98.917
2	105.68	1.083
		98% *e.e.*



3c

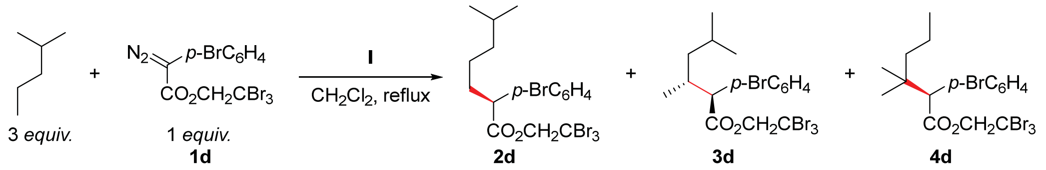


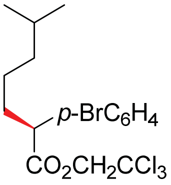
#	Time [Min]	Area% [%]
1	100.92	2.986
2	116.70	97.014
		94% *e.e.*



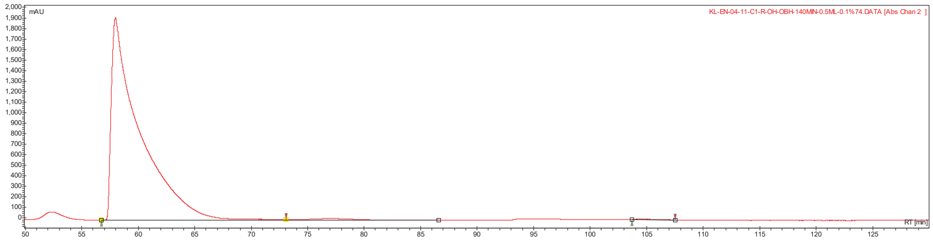
4c

Enantiomeric excess was not determined.



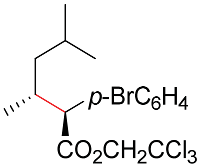


2d

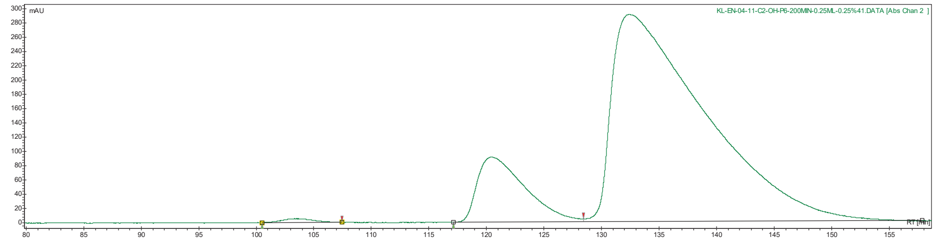


#	Time [Min]	Area% [%]
1	58.01	99.856
2	105.51	0.144

>99% *e.e.*

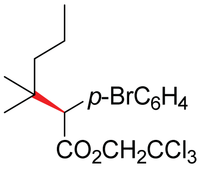


3d



#	Time [Min]	Area% [%]
1	103.51	3.791
2	120.46	96.209

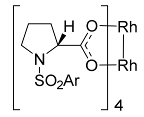
92% *e.e.*



4d was not detected.

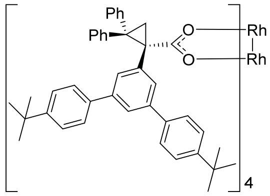
5. Catalyst Screen for Tertiary Selective Catalyst

5.1 Catalysts Structures

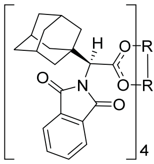


Ar = *p*-$C_{12}H_{25}C_6H_4$

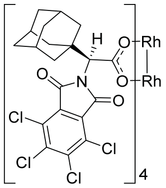
Rh$_2$(*R*-DOSP)$_4$



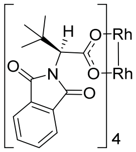
Rh$_2$[*R*-3,5-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$



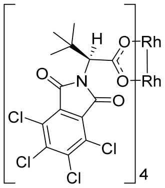
Rh$_2$(*S*-PTAD)$_4$



Rh$_2$(*S*-TCPTAD)$_4$

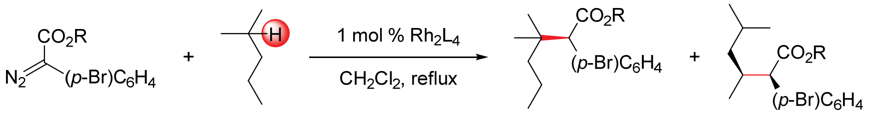


Rh$_2$(*S*-PTTL)$_4$



Rh$_2$(*S*-TCPTTL)$_4$

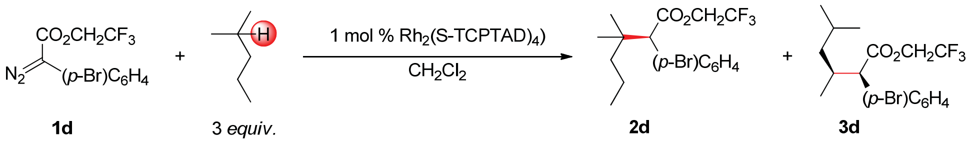
5.2 Data Summary



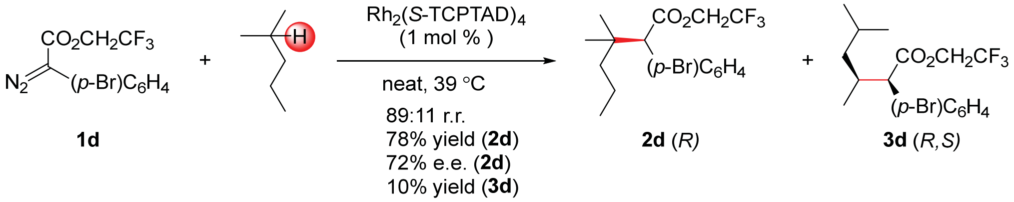
1a-e 3 *equiv.* **2a-e** **3a-e**

Catalyst	**1**	R	yield (%)[a]	r.r. (**2**:**3**)	e.e. (**2**, %)	d.r. (**3**)	e.e. (**3**, %)
$Rh_2(R\text{-DOSP})_4$	**1a**	CH_3	83	85:15	-43	3: 1	-
$Rh_2[R\text{-3,5-di}(p\text{-}^tBuC_6H_4)TPCP]_4$	**1a**	CH_3	23	35:65	-10	4: 1	-
$Rh_2(S\text{-PTAD})_4$	**1a**	CH_3	50	74:26	-34	2: 1	-
$Rh_2(S\text{-PTTL})_4$	**1a**	CH_3	80	74:26	-33	2: 1	-
$Rh_2(S\text{-TCPTTL})_4$	**1a**	CH_3	86	86:14	77	2: 1	-
$Rh_2(S\text{-TCPTAD})_4$	**1a**	CH_3	89	87:13	79	3: 1	-
$Rh_2(S\text{-TCPTAD})_4$	**1b**	CH_2CCl_3	84 (74)[b]	89:11	84	2: 1	77
$Rh_2(S\text{-TCPTAD})_4$	**1c**	CH_2CBr_3	88 (77)	87:13	77	2: 1	79
$Rh_2(S\text{-TCPTAD})_4$	**1d**	CH_2CF_3	92 (83)	90:10	77	2: 1	79

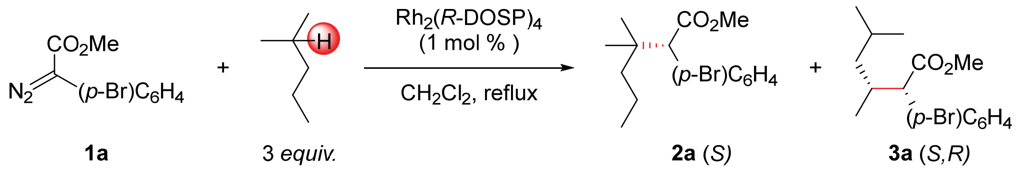
[a] Combined yield of **2** and **3**. [b] Isolated yield of **2** shown in parenthesis.



#	Temperature (°C)	r.r. (%)	e.e. (**2d**,%)	Yield (**2d**, %)	d.r. (**3d**,%)	Yield (**3d**, %)
1	39 (reflux)	90:10	77	83	2:1	9
2	*r.t.*	91:9	80	77	3:1	8
3	0	93:7	82	79	4:1	6
4	-10	95:5	84	78	5:1	4
5	-40	96:4	86	77	9:1	3
6	-78	96:4	80	65	7:1	0

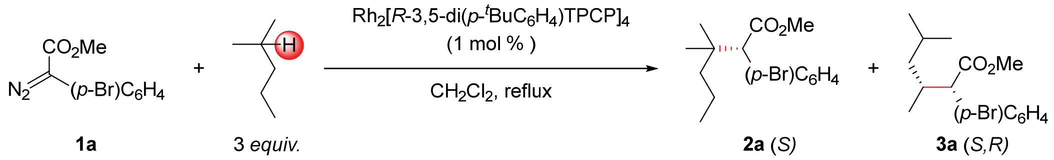


5.3 Catalyst and Diazo Screen



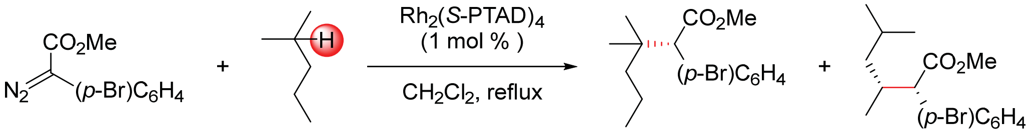
This reaction was conducted according to the general procedure for C–H functionalization reactions. Methyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 51 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, $Rh_2(R\text{-DOSP})_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford mixture of **2a** and **3a** as a colorless oil (52 mg, 83% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a** and **3a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a**:**3a**) of this reaction was 85:15 r.r. and the diastereoselectivity for **3a** was 3:1 d.r.. The enantioselectivity of this reaction for compound **2a** was -43 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm, with the retention times at 46.0 min (major) and 121.0 min (minor).



This reaction was conducted according to the general procedure for C–H functionalization reactions. Methyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 51 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, $Rh_2[R\text{-}3,5\text{-di}(p\text{-}^t\text{BuC}_6\text{H}_4)\text{TPCP}]_4$ (0.002 mmol, 5 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford mixture of **2a** and **3a** as a colorless oil (14 mg, 23% yield).

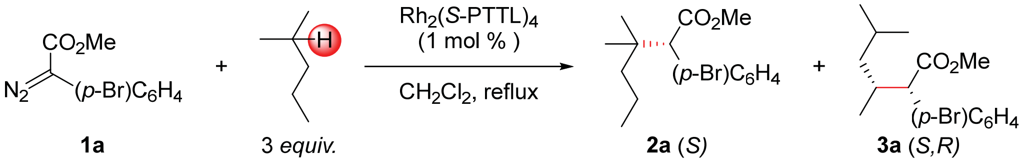
Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a** and **3a** were observed and no evident signal of other regioisomer was detected, the major reason for the yield lost is the formation of carbene dimers. The regioselectivity (**2a**:**3a**) of this reaction was 35:65 r.r. and the diastereoselectivity for **3a** was 4:1 d.r.. The enantioselectivity of this reaction for compound **2a** was -10 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm, with the retention times at 47.9 min (major) and 125.5 min (minor).



1a 3 *equiv.* **2a** (*S*) **3a** (*S*,*R*)

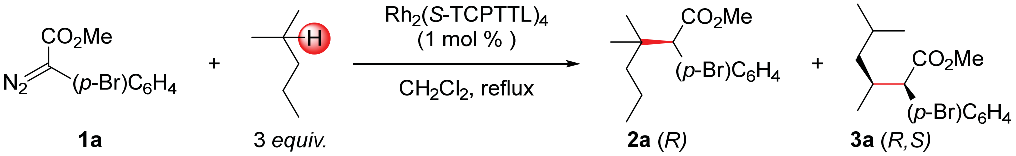
This reaction was conducted according to the general procedure for C–H functionalization reactions. Methyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 51 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-PTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford mixture of **2a** and **3a** as a colorless oil (31 mg, 50% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a** and **3a** were observed and no evident signal of other regioisomer was detected, the major reason for the yield lost is the formation of carbene dimers. The regioselectivity (**2a**:**3a**) of this reaction was 74:26 r.r. and the diastereoselectivity for **3a** was 2:1 d.r.. The enantioselectivity of this reaction for compound **2a** was -34 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm, with the retention times at 46.9 min (major) and 122.4 min (minor).



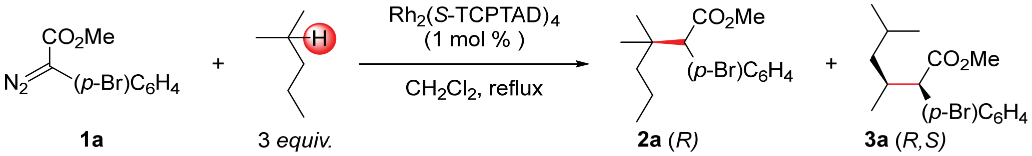
This reaction was conducted according to the general procedure for C–H functionalization reactions. Methyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 51 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-PTTL)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford mixture of **2a** and **3a** as a colorless oil (50 mg, 80 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a** and **3a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a**:**3a**) of this reaction was 74:26 r.r. and the diastereoselectivity for **3a** was 2:1 d.r.. The enantioselectivity of this reaction for compound **2a** was -33 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm, with the retention times at 46.4 min (major) and 120.7 min (minor).



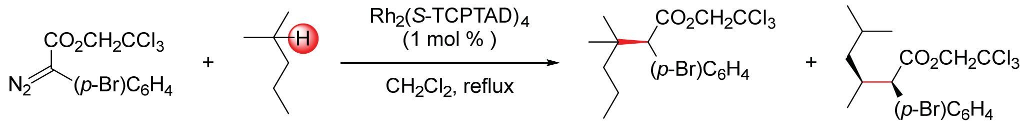
This reaction was conducted according to the general procedure for C–H functionalization reactions. Methyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 51 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTTL)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford mixture of **2a** and **3a** as a colorless oil (54 mg, 86 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a** and **3a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a**:**3a**) of this reaction was 86:14 r.r. and the diastereoselectivity for **3a** was 2:1 d.r.. The enantioselectivity of this reaction for compound **2a** was 77 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm, with the retention times at 47.1 min (minor) and 117.1 min (major).



This reaction was conducted according to the general procedure for C–H functionalization reactions. Methyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 51 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford mixture of **2a** and **3a** as a colorless oil (56 mg, 89 % yield).

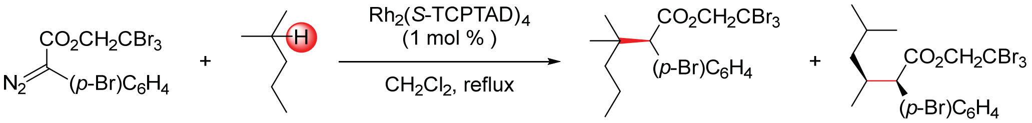
Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2a** and **3a** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2a**:**3a**) of this reaction was 87:13 r.r. and the diastereoselectivity for **3a** was 3:1 d.r.. The enantioselectivity of this reaction for compound **2a** was 79 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm, with the retention times at 47.5 min (minor) and 119.8 min (major).



1b 3 *equiv.* **2b** (*R*) **3b** (*R,S*)

This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate **1b** (0.2 mmol, 74 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2b** as a colorless oil (64 mg, 74 % yield), and **3b** as a colorless oil (9 mg, 10 % yield).

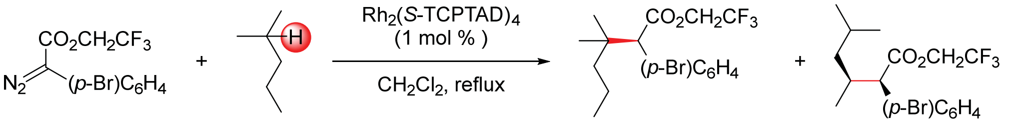
Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2b** and **3b** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2b**:**3b**) of this reaction was 89:11 r.r. and the diastereoselectivity for **3b** was 2:1 d.r.. The enantioselectivity of this reaction for compound **2b** was 84 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm, with the retention times at 47.6 min (minor) and 91.9 min (major). The enantioselectivity of this reaction for compound **3b** was 77 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was ASH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 210 nm, with the retention times at 93.4 min (major) and 113.0 min (minor).



1c 3 *equiv.* **2c** (*R*) **3c** (*R*,*S*)

This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate **1c** (0.2 mmol, 101 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2c** as a colorless oil (87 mg, 77 % yield), and **3c** as a colorless oil (12 mg, 11 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2c** and **3c** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2c**:**3c**) of this reaction was 87:13 r.r. and the diastereoselectivity for **3c** was 2:1 d.r.. The enantioselectivity of this reaction for compound **2c** was 77 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm, with the retention times at 47.4 min (minor) and 122.6 min (major). The enantioselectivity of this reaction for compound **3c** was 79 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was ASH, 0.25 % isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 210 nm, with the retention times at 105.2 min (major) and 126.1 min (minor).

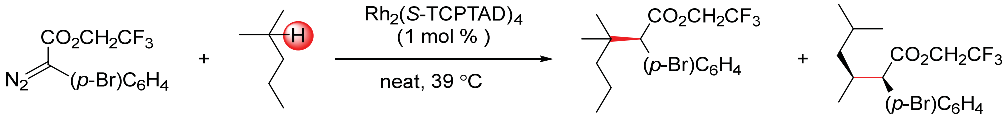


1d 3 *equiv.* **2d** (*R*) **3d** (*R*,*S*)

This reaction was conducted according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2d** as a colorless oil (63 mg, 83 % yield), and **3d** as a colorless oil (7 mg, 9 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2d** and **3d** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2d**:**3d**) of this reaction was 90:10 r.r. and the diastereoselectivity for **3d** was 2:1 d.r.. The enantioselectivity of this reaction for compound **2d** was 77 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm, with the retention times at 47.3 min (minor) and 116.3 min (major). The enantioselectivity of this reaction for compound **3d** was 79 % e.e.; the HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,5-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was ASH, 0.25 % isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 150 min, UV 210 nm, with the retention times at 104.8 min (major) and 126.9 min (minor).

5.4 Reaction Condition Screen



1d

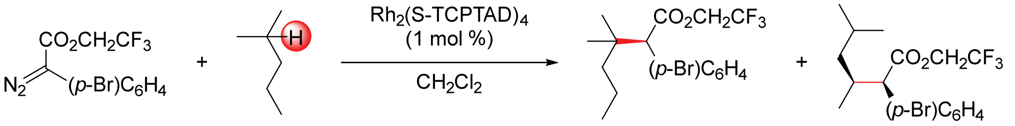
89:11 *r.r.*
2d: 78% *yield*; 72% *e.e.*
3d: 10% *yield;* 1:1 *d.r.*

2d (*R*)

3d (*R*,*S*)

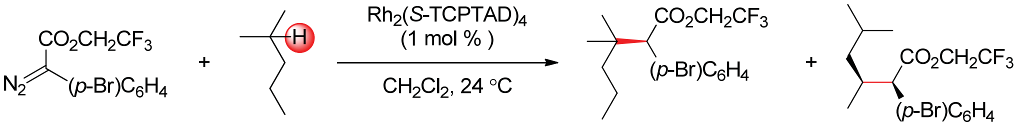
This reaction was conducted according to the general procedure for C–H functionalization reactions but the temperature was maintained at 39 °C. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL 2-methylpentane, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2d** as a colorless oil (59 mg, 78 % yield) , and **3d** as a colorless oil (8 mg, 10 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2d** and **3d** were observed and no evident signal of other regioisomer was detected but **3d** wasn't isolated. The regioselectivity (**2d**:**3d**) of this reaction was 89:11 r.r. and the diastereoselectivity for **3d** was 1:1 d.r.. The enantioselectivity of this reaction for compound **2d** was 72 % e.e.. The enantioselectivity analysis was conducted in a different HPLC instrument with a different S,S-whelk chiral column, the enantiomers' peaks were re-determined with the products generated by Rh_2(*R*-TCPTAD)$_4$ and Rh_2(*S*-TCPTAD)$_4$. For **2d** The HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 80 min, UV 210 nm, with the retention times at 25.8 min (minor) and 64.0 min (major). The enantioselectivity of this reaction for compound **3d** was not determined due to the low yielding.



1d 3 *equiv.* **2d** **3d**

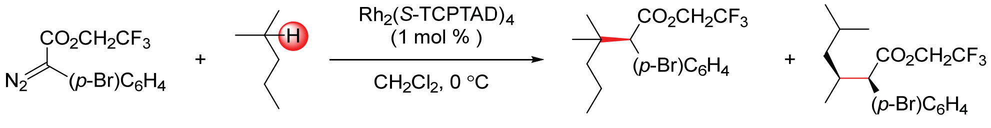
#	Temperature (°C)	r.r. (%)	e.e. (**2d**,%)	Yield (**2d**, %)	d.r. (**3d**,%)	Yield (**3d**, %)
1	39 (reflux)	90:10	77	83	2:1	9
2	r.t.	91:9	80	77	3:1	8
3	0	93:7	82	79	4:1	6
4	-10	95:5	84	78	5:1	4
5	-40	96:4	86	77	9:1	3
6	-78	96:4	80	65	7:1	0



1d 3 *equiv.* **2d** (*R*) **3d** (*R,S*)

This reaction was conducted according to the general procedure for C–H functionalization reactions but the temperature was maintained at room temperature (24 °C). 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2d** as a colorless oil (59 mg, 77 % yield), and **3d** as a colorless oil (6 mg, 8 % yield).

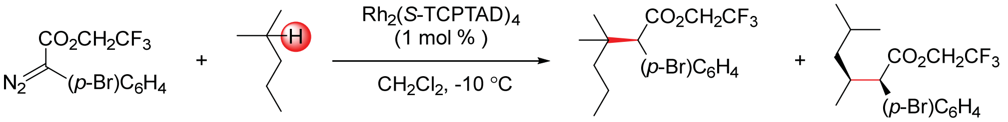
Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2d** and **3d** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2d**:**3d**) of this reaction was 91:9 r.r. and the diastereoselectivity for **3d** was 3:1 d.r.. The enantioselectivity of this reaction for compound **2d** was 80 % e.e.. The enantioselectivity analysis for the temperature study were conducted in a different HPLC instrument with a different S,S-whelk chiral column, both of the retention time of enantiomers' peaks were re-determined with the products generated by Rh_2(*R*-TCPTAD)$_4$ and Rh_2(*S*-TCPTAD)$_4$. For **2d** The HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 80 min, UV 210 nm, with the retention times at 25.8 min (minor) and 64.0 min (major). The enantioselectivity of this reaction for compound **3d** was not determined due to the low yielding.



1d 3 *equiv.* **2d** (*R*) **3d** (*R*,*S*)

This reaction was conducted according to the general procedure for C–H functionalization reactions but the temperature was maintained at 0 °C. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2d** as a colorless oil (60 mg, 79 % yield), and **3d** as a colorless oil (5 mg, 6 % yield).

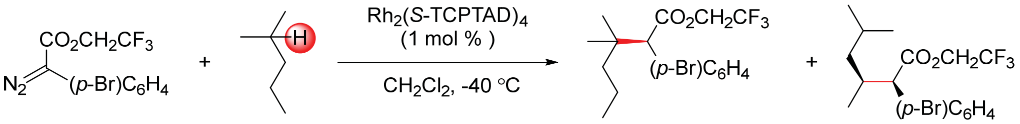
Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2d** and **3d** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2d**:**3d**) of this reaction was 91:9 r.r. and the diastereoselectivity for **3d** was 4:1 d.r.. The enantioselectivity of this reaction for compound **2d** was 82 % e.e.. The enantioselectivity analysis was conducted in a different HPLC instrument with a different S,S-whelk chiral column, the enantiomers' peaks were re-determined with the products generated by Rh_2(*R*-TCPTAD)$_4$ and Rh_2(*S*-TCPTAD)$_4$. For **2d** The HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 80 min, UV 210 nm, with the retention times at 27.4 min (minor) and 68.5 min (major). The enantioselectivity of this reaction for compound **3d** was not determined due to the low yielding.



1d 3 *equiv.* **2d** (*R*) **3d** (*R*,*S*)

This reaction was conducted according to the general procedure for C–H functionalization reactions but the temperature was maintained at -10 °C. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^1H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2d** as a colorless oil (59 mg, 78 % yield), and **3d** as a colorless oil (3 mg, 4 % yield).

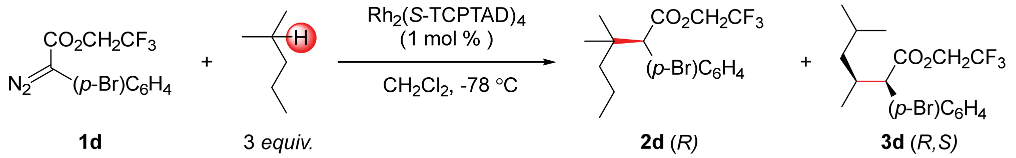
Analysis of the ^1H NMR spectrum of the crude reaction mixture revealed that only compound **2d** and **3d** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2d**:**3d**) of this reaction was 95:5 r.r. and the diastereoselectivity for **3d** was 5:1 d.r.. The enantioselectivity of this reaction for compound **2d** was 84 % e.e.. The enantioselectivity analysis was conducted in a different HPLC instrument with a different S,S-whelk chiral column, the enantiomers' peaks were re-determined with the products generated by Rh_2(*R*-TCPTAD)$_4$ and Rh_2(*S*-TCPTAD)$_4$. For **2d** The HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 80 min, UV 210 nm, with the retention times at 27.5 min (minor) and 69.0 min (major). The enantioselectivity of this reaction for compound **3d** was not determined due to the low yielding.



1d 3 *equiv.* **2d** (*R*) **3d** (*R*,*S*)

This reaction was conducted according to the general procedure for C–H functionalization reactions but the temperature was maintained at -40 °C. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^1H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2d** as a colorless oil (59 mg, 77 % yield), and **3d** as a colorless oil (2 mg, 3 % yield).

Analysis of the ^1H NMR spectrum of the crude reaction mixture revealed that only compound **2d** and **3d** were observed and no evident signal of other regioisomer was detected. The regioselectivity (**2d**:**3d**) of this reaction was 96:4 r.r. and the diastereoselectivity for **3d** was 9:1 d.r.. The enantioselectivity of this reaction for compound **2d** was 86 % e.e.. The enantioselectivity analysis was conducted in a different HPLC instrument with a different S,S-whelk chiral column, the enantiomers' peaks were re-determined with the products generated by Rh_2(*R*-TCPTAD)$_4$ and Rh_2(*S*-TCPTAD)$_4$. For **2d** The HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 80 min, UV 210 nm, with the retention times at 27.6 min (minor) and 68.4 min (major). The enantioselectivity of this reaction for compound **3d** was not determined due to the low yielding.

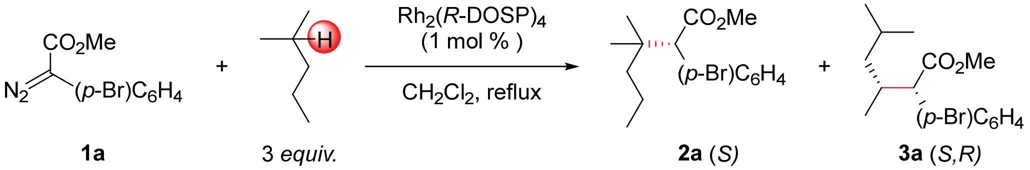


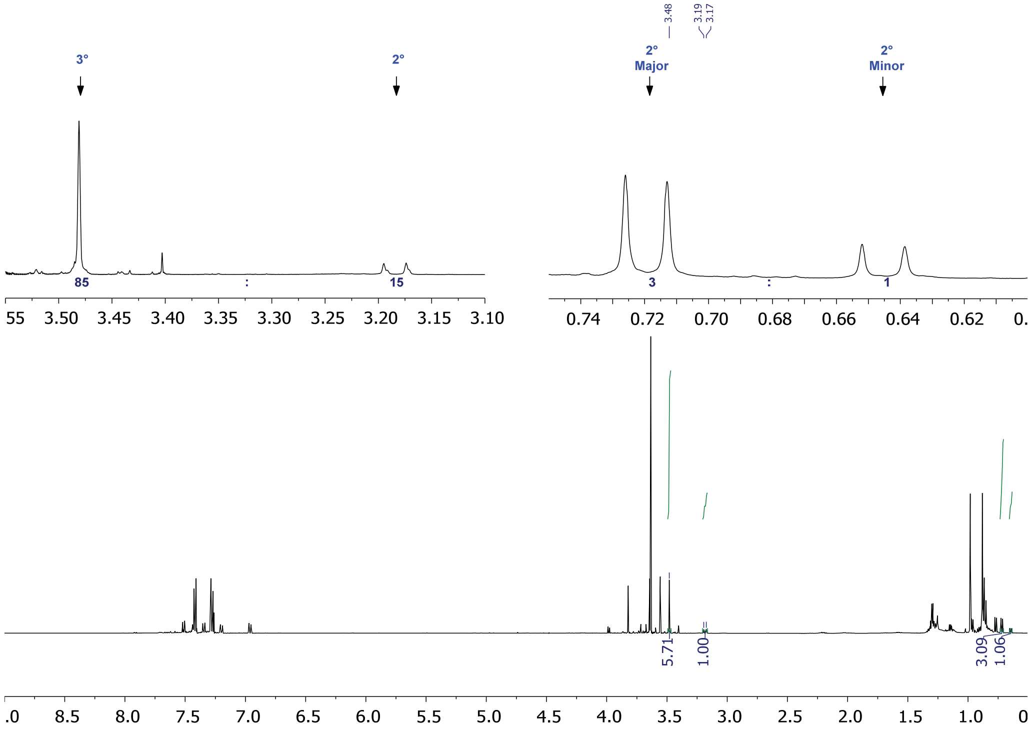
This reaction was conducted according to the general procedure for C–H functionalization reactions but the temperature was maintained at -78 °C. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^1H

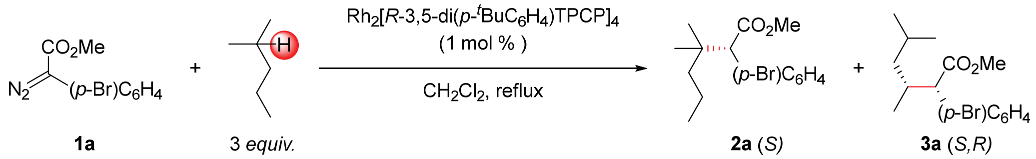
NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **2d** as a colorless oil (50 mg, 65 % yield).

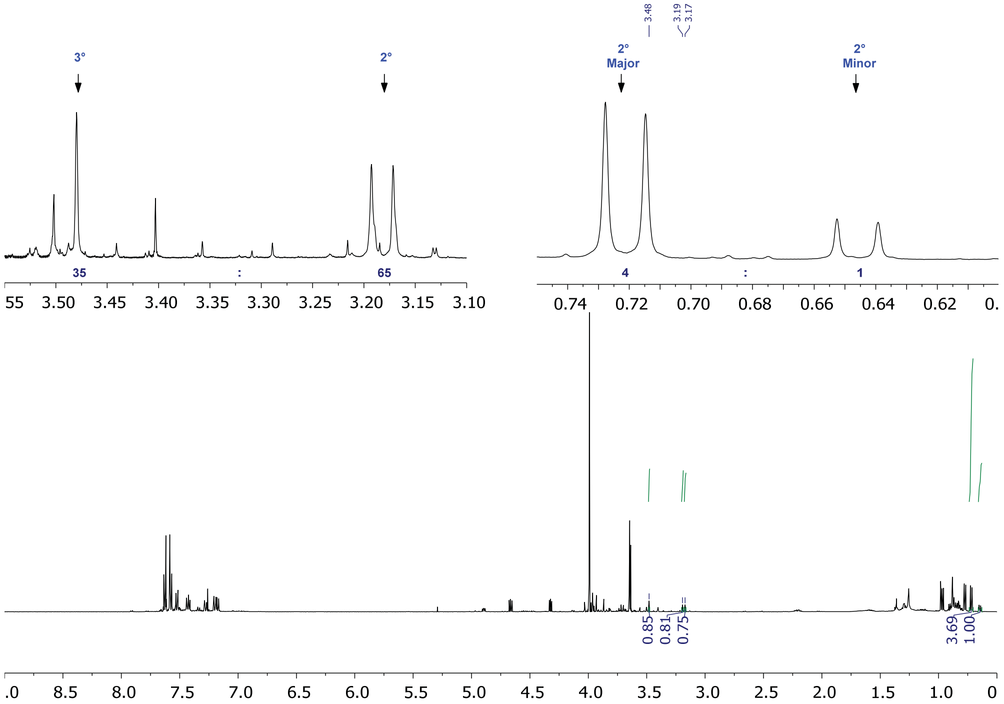
Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **2d** and **3d** were observed and no evident signal of other regioisomer was detected but **3d** wasn't isolated. The regioselectivity (**2d**:**3d**) of this reaction was 96:4 r.r. and the diastereoselectivity for **3d** was 7:1 d.r.. The enantioselectivity of this reaction for compound **2d** was 80 % e.e.. The enantioselectivity analysis was conducted in a different HPLC instrument with a different S,S-whelk chiral column, the enantiomers' peaks were re-determined with the products generated by Rh_2(*R*-TCPTAD)$_4$ and Rh_2(*S*-TCPTAD)$_4$. For **2d** The HPLC (in order to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylhexan-1-ol prepared by using DIBAL in DCM at -78 °C) condition was S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 80 min, UV 210 nm, with the retention times at 28.8 min (minor) and 68.2 min (major). The enantioselectivity of this reaction for compound **3d** was not determined due to the low yielding.

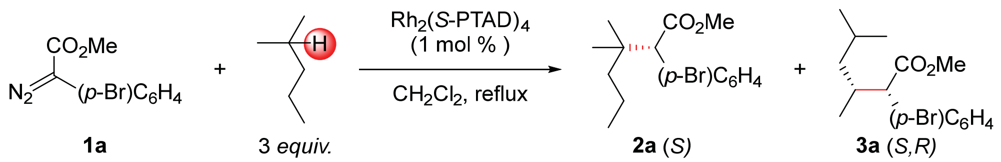
5.5 Crude ^1H NMR Spectra for Catalyst and Diazo Screen

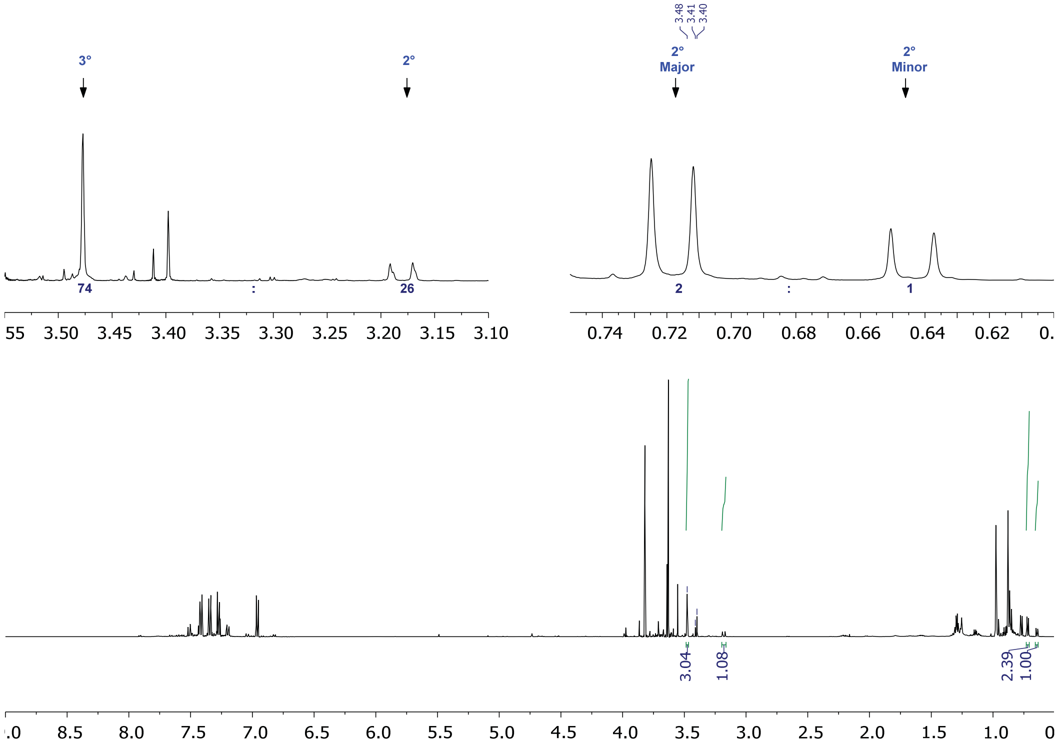


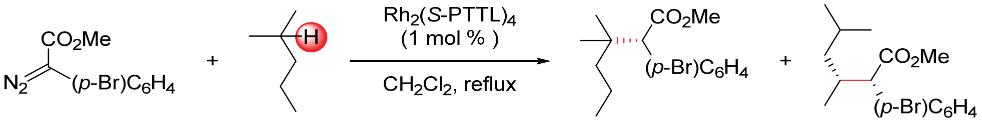



CO$_2$Me
N$_2$
(p-Br)C$_6$H$_4$
1a
+
H
3 equiv.
Rh$_2$[R-3,5-di(p-^{t}BuC$_6$H$_4$)TPCP]$_4$
(1 mol %)
CH$_2$Cl$_2$, reflux
CO$_2$Me
(p-Br)C$_6$H$_4$
2a (S)
+
CO$_2$Me
(p-Br)C$_6$H$_4$
3a (S,R)

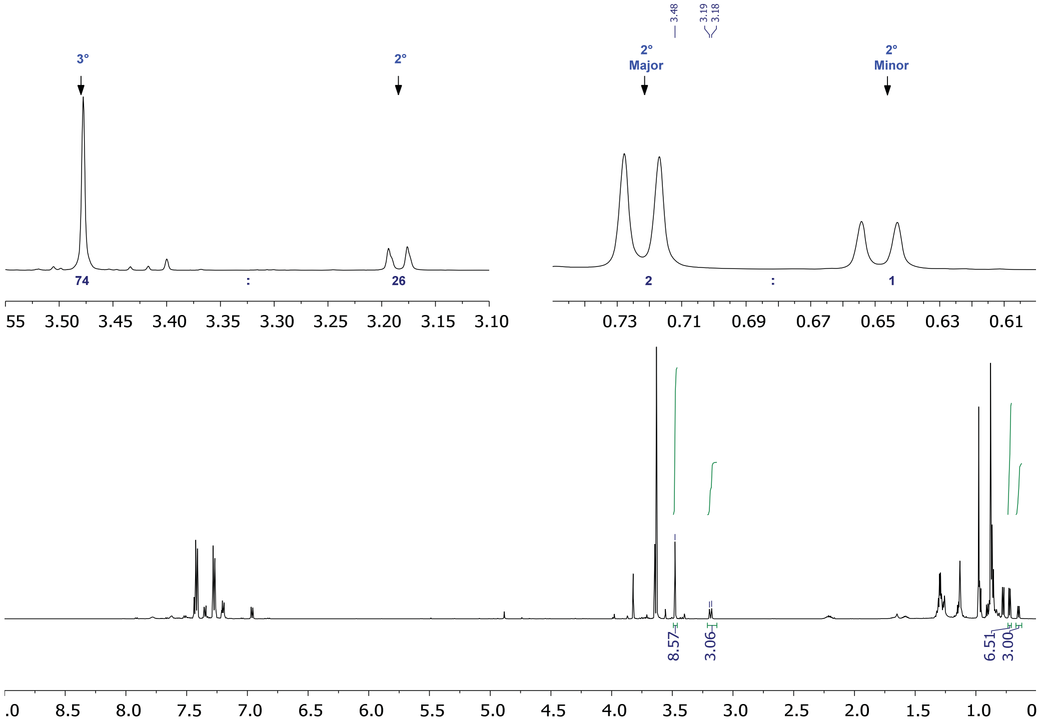

3.48
3.19
3.17
3°
2°
35
:
65
55
3.50
3.45
3.40
3.35
3.30
3.25
3.20
3.15
3.10
2°
Major
2°
Minor
4
:
1
0.74
0.72
0.70
0.68
0.66
0.64
0.62
0.
0.85
0.81
0.75
3.69
1.00
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

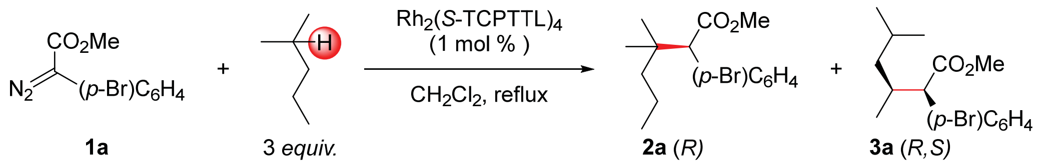

CO2Me
N2
(p-Br)C6H4
1a
+
H
3 equiv.
Rh2(S-PTAD)4
(1 mol %)
CH2Cl2, reflux
CO2Me
(p-Br)C6H4
2a (S)
+
CO2Me
(p-Br)C6H4
3a (S,R)

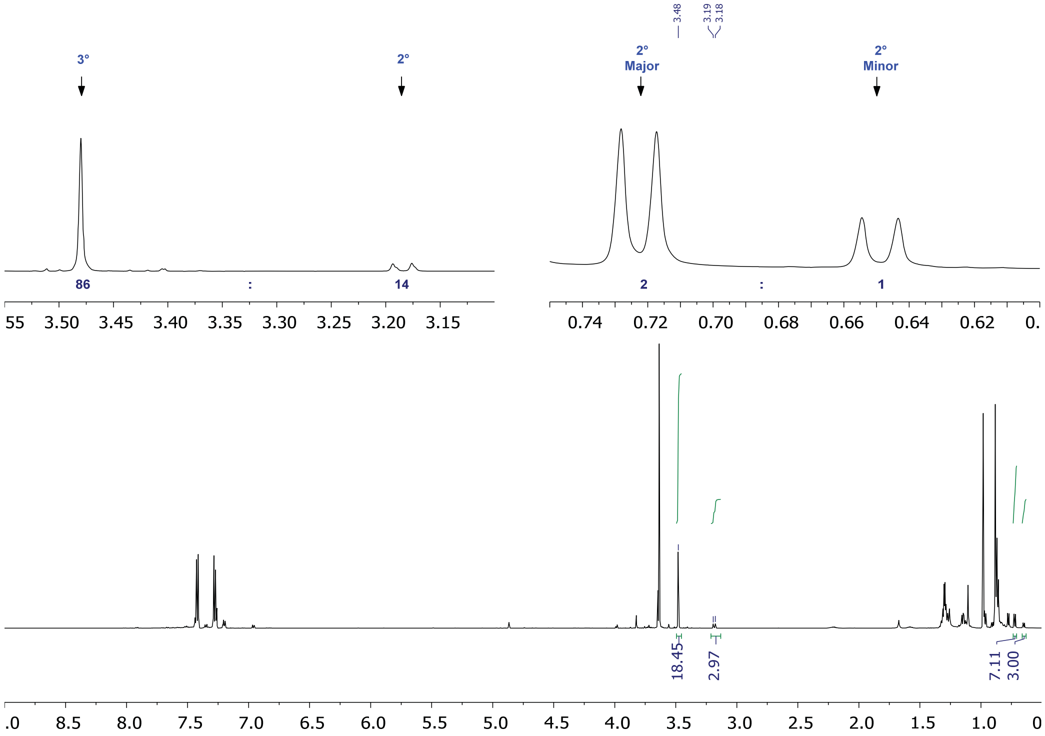

3.48
3.41
3.40
3°
2°
2°
Major
2°
Minor
74
:
26
2
:
1
55
3.50
3.45
3.40
3.35
3.30
3.25
3.20
3.15
3.10
0.74
0.72
0.70
0.68
0.66
0.64
0.62
0.
3.04
1.08
2.39
1.00
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

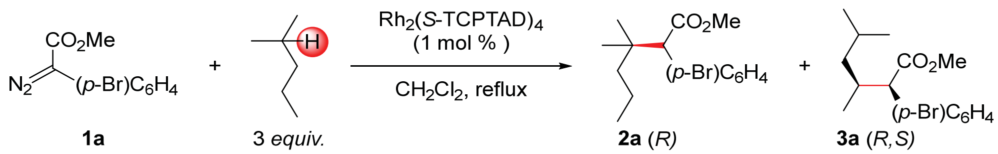


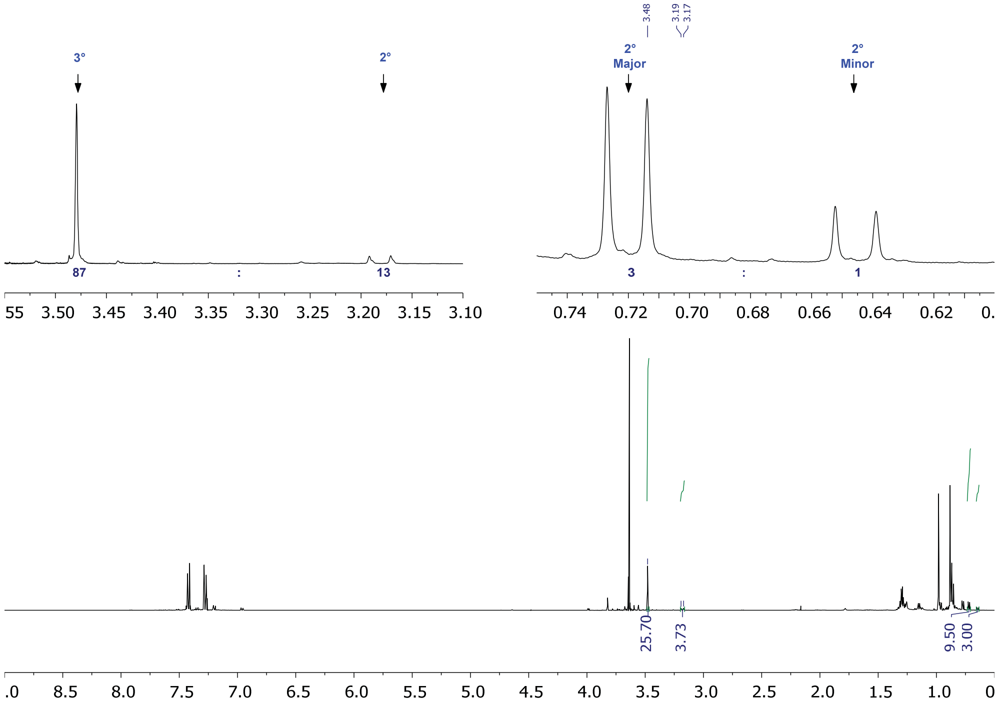
1a 3 *equiv.* **2a** (*S*) **3a** (*S,R*)

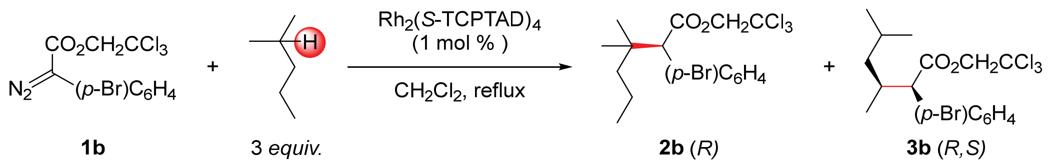


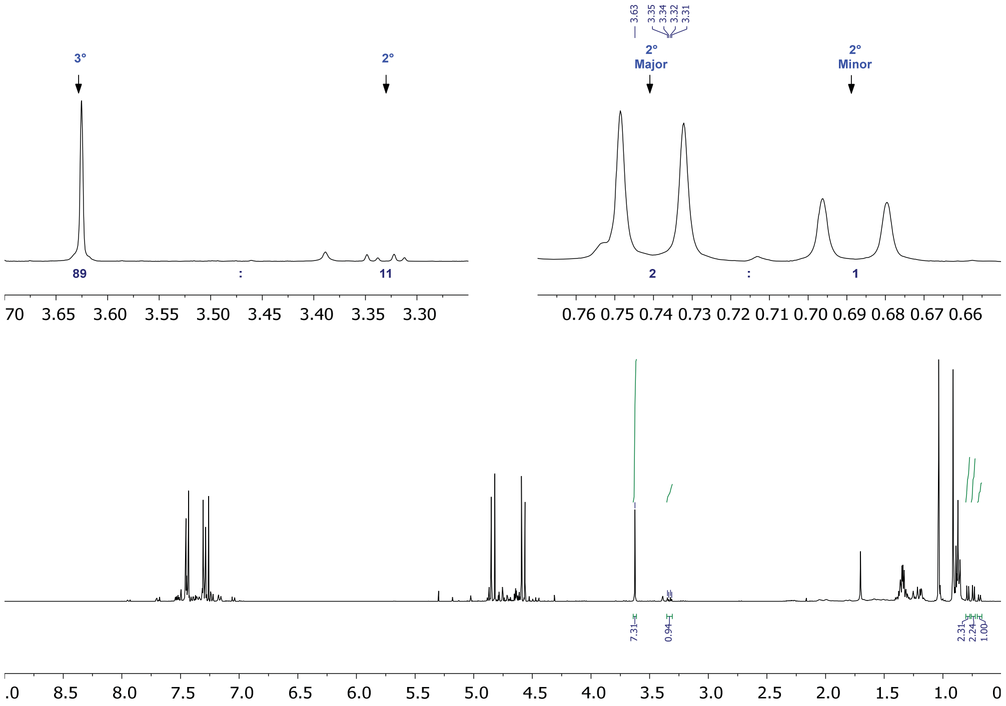

CO2Me
N2
(p-Br)C6H4
1a
+
3 equiv.
H
Rh2(S-TCPTTL)4
(1 mol %)
CH2Cl2, reflux
CO2Me
(p-Br)C6H4
2a (R)
+
CO2Me
(p-Br)C6H4
3a (R,S)

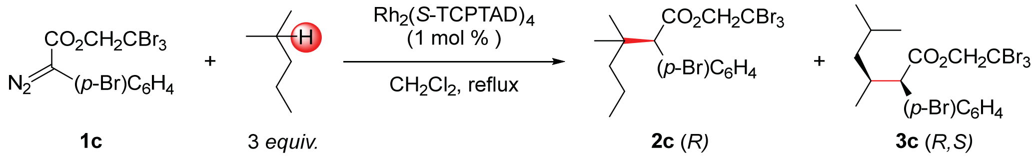

3°
2°
86
:
14
3.48
3.19
3.18
2°
Major
2°
Minor
2
:
1
55
3.50
3.45
3.40
3.35
3.30
3.25
3.20
3.15
0.74
0.72
0.70
0.68
0.66
0.64
0.62
18.45
2.97
7.11
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

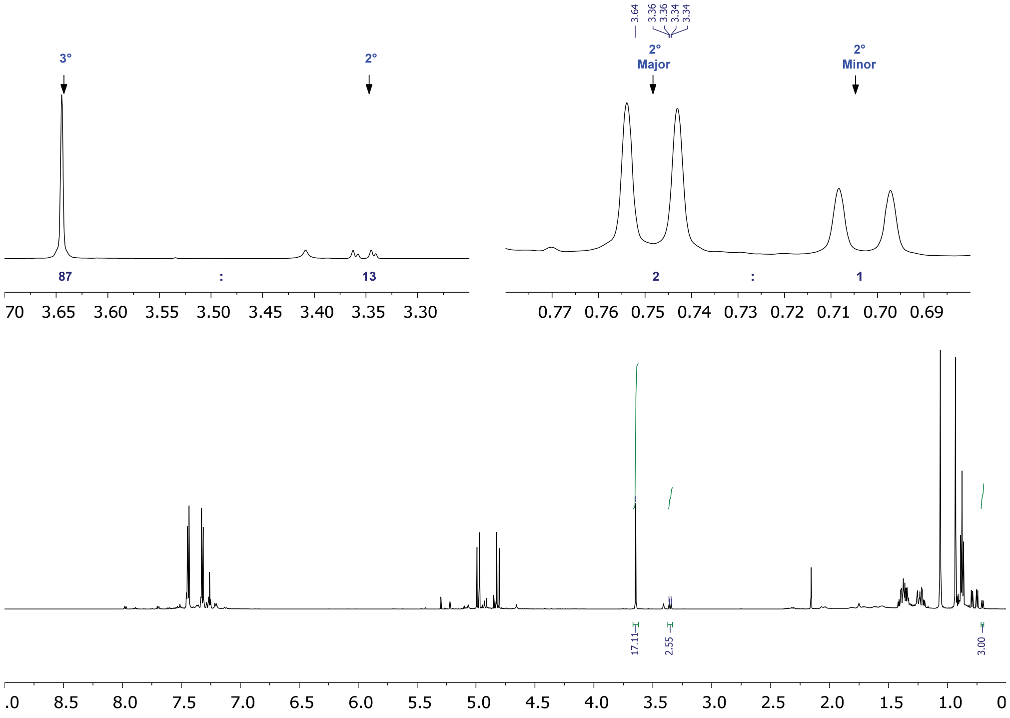

CO2Me
N2
(p-Br)C6H4
1a
+
H
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
CO2Me
(p-Br)C6H4
2a (R)
+
CO2Me
(p-Br)C6H4
3a (R,S)

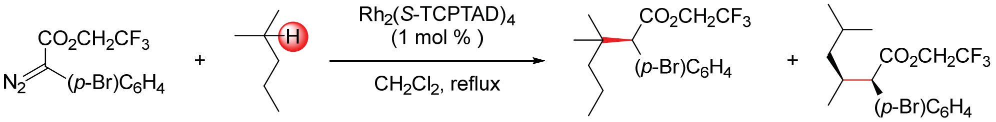

3°
2°
87
:
13
55
3.50
3.45
3.40
3.35
3.30
3.25
3.20
3.15
3.10
3.48
3.19
3.17
2°
Major
2°
Minor
3
:
1
0.74
0.72
0.70
0.68
0.66
0.64
0.62
0.
25.70
3.73
9.50
3.00
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0


$CO_2CH_2CCl_3$
N_2
(p-Br)C_6H_4
1b
+
H
3 equiv.
Rh$_2$(S-TCPTAD)$_4$
(1 mol %)
CH_2Cl_2, reflux
$CO_2CH_2CCl_3$
(p-Br)C_6H_4
2b (R)
+
$CO_2CH_2CCl_3$
(p-Br)C_6H_4
3b (R,S)

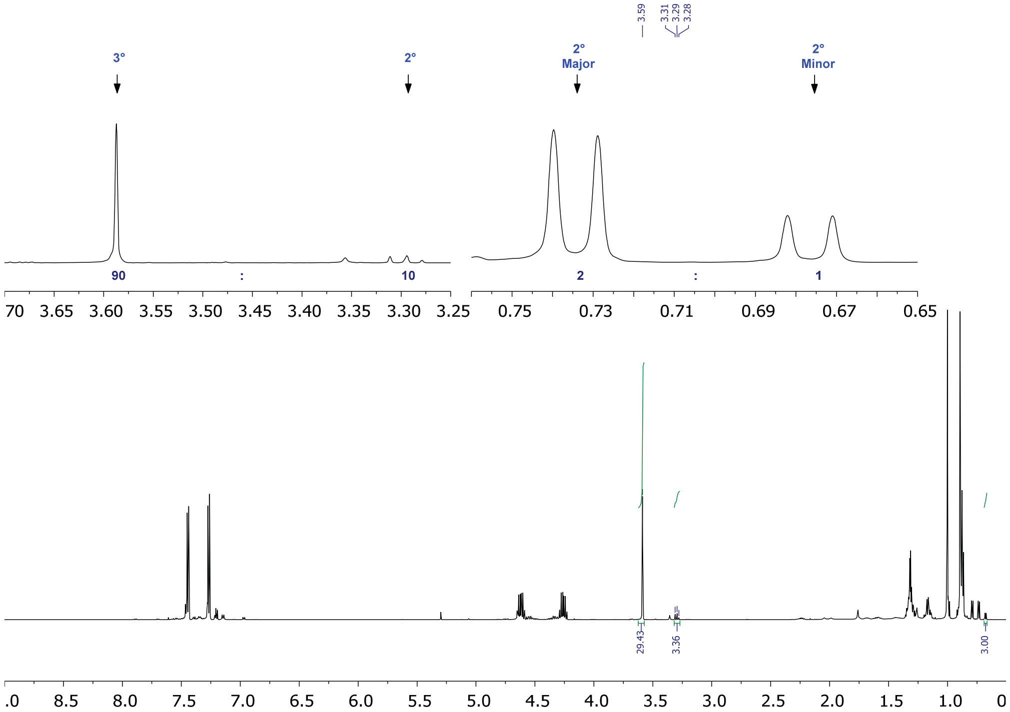

3.63
3.35
3.34
3.32
3.31
3°
2°
89
:
11
70
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
2°
Major
2°
Minor
2
:
1
0.76
0.75
0.74
0.73
0.72
0.71
0.70
0.69
0.68
0.67
0.66
7.31
0.94
2.31
2.24
1.00
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0


CO$_2$CH$_2$CBr$_3$
N$_2$
(p-Br)C$_6$H$_4$
+
H
Rh$_2$(S-TCPTAD)$_4$
(1 mol %)
CH$_2$Cl$_2$, reflux
CO$_2$CH$_2$CBr$_3$
(p-Br)C$_6$H$_4$
+
CO$_2$CH$_2$CBr$_3$
(p-Br)C$_6$H$_4$
1c
3 equiv.
2c (R)
3c (R,S)

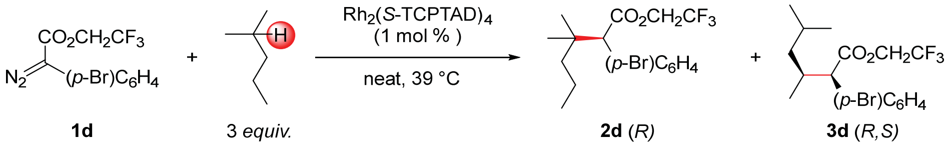

3.64
3.36
3.36
3.34
3.34
3°
2°
87
:
13
70
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
2°
Major
2°
Minor
2
:
1
0.77
0.76
0.75
0.74
0.73
0.72
0.71
0.70
0.69
17.11
2.55
3.00
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

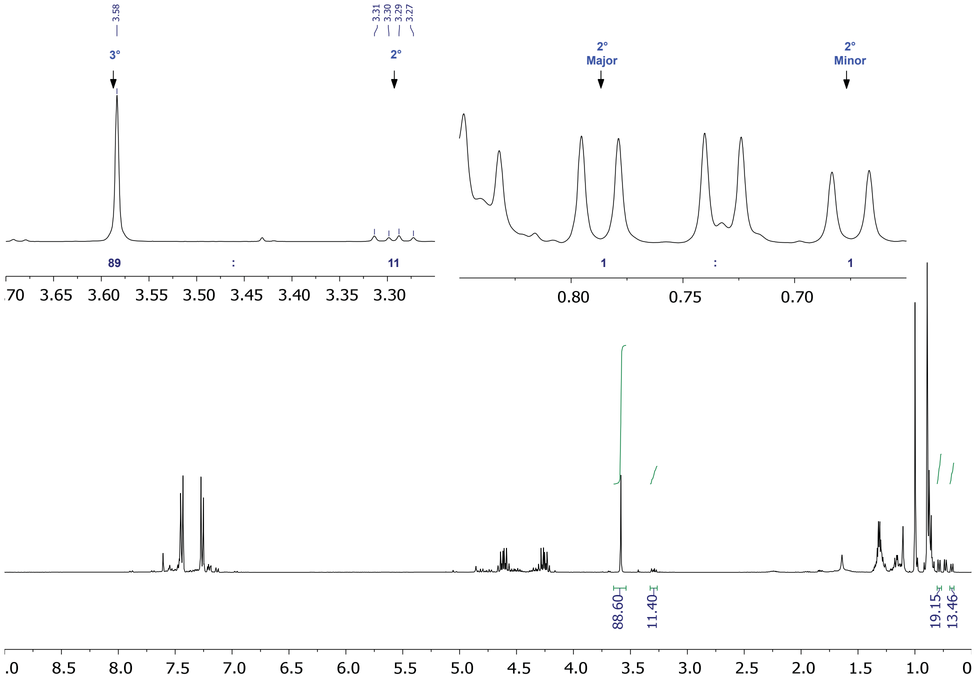


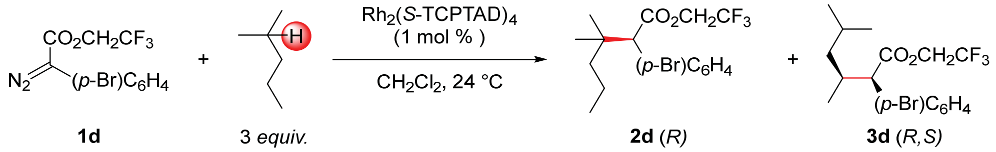
1d 3 *equiv.* **2d** (*R*) **3d** (*R,S*)

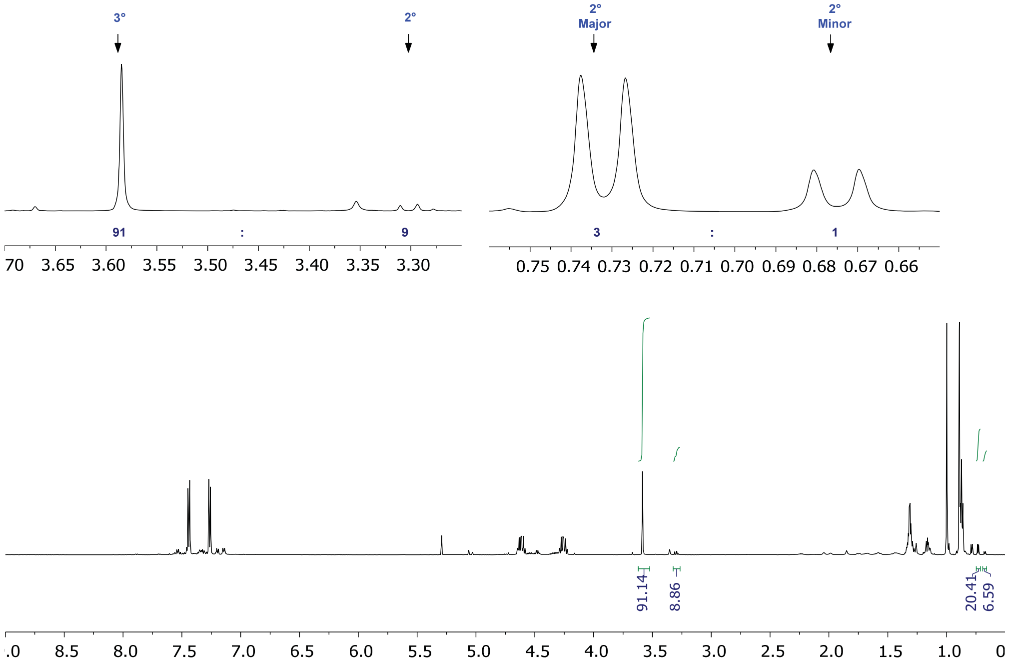


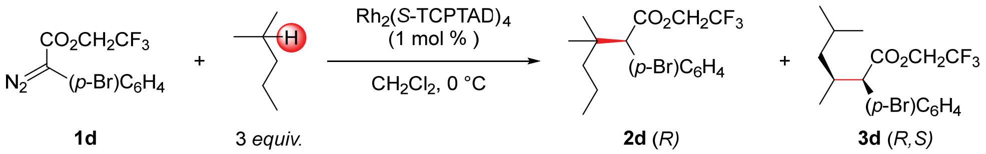
5.6 Crude ^{1}H NMR Spectra for Reaction Condition Screen

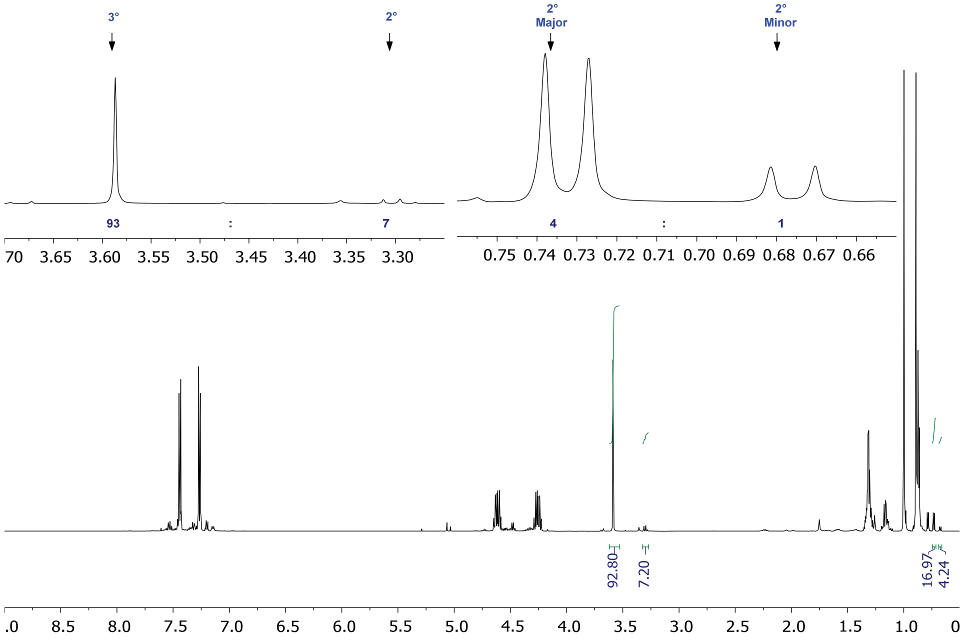


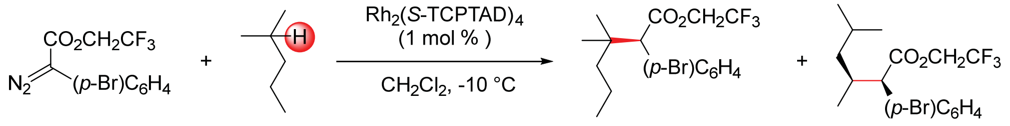



CO2CH2CF3
N2
(p-Br)C6H4
1d
+
H
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, 24 °C
CO2CH2CF3
(p-Br)C6H4
2d (R)
+
CO2CH2CF3
(p-Br)C6H4
3d (R,S)

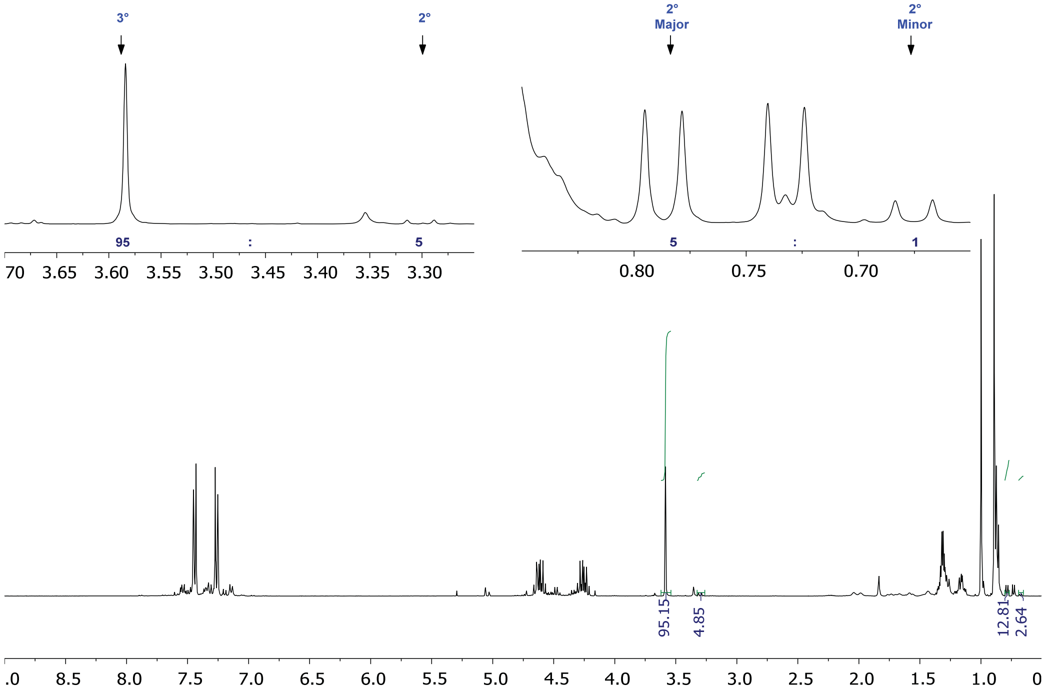

3°
2°
91
:
9
70
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
2°
Major
2°
Minor
3
:
1
0.75
0.74
0.73
0.72
0.71
0.70
0.69
0.68
0.67
0.66
91.14
8.86
20.41
6.59
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

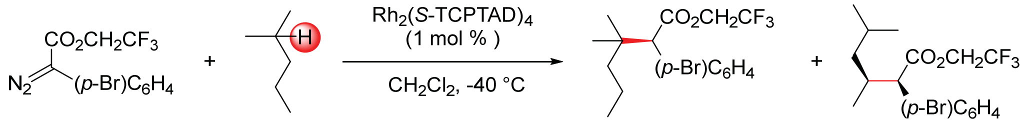

CO2CH2CF3
N2
(p-Br)C6H4
1d
+
H
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, 0 °C
CO2CH2CF3
(p-Br)C6H4
2d (R)
+
CO2CH2CF3
(p-Br)C6H4
3d (R,S)


3°
2°
2°
Major
2°
Minor
93
:
7
4
:
1
70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30
0.75 0.74 0.73 0.72 0.71 0.70 0.69 0.68 0.67 0.66
92.80
7.20
16.97
4.24
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

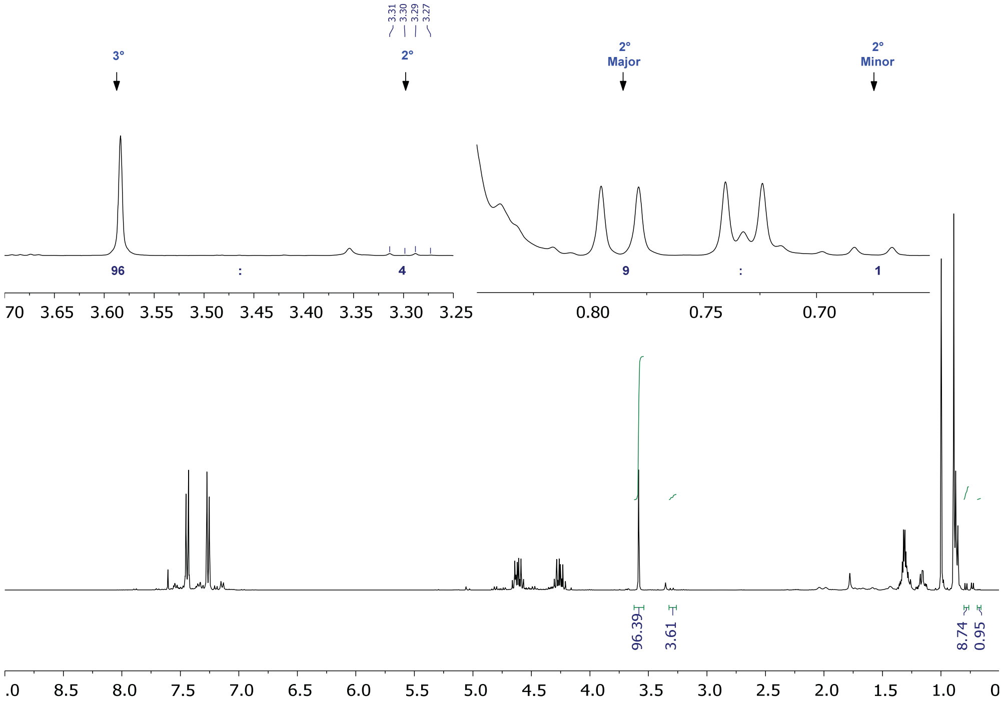


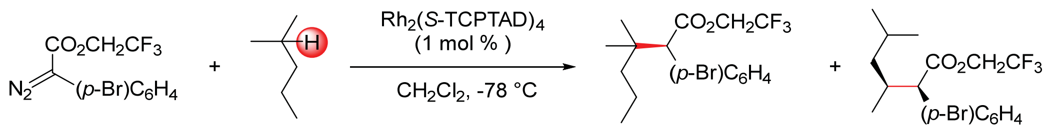
1d 3 *equiv.* **2d** (*R*) **3d** (*R,S*)



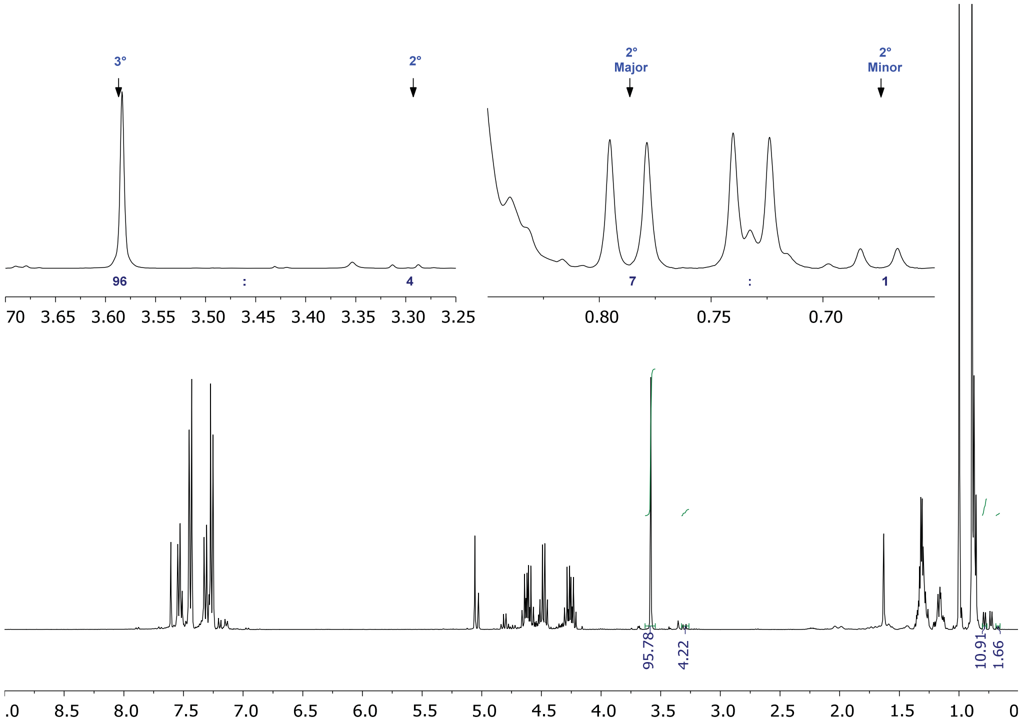


1d 3 *equiv.* **2d** (*R*) **3d** (*R*,*S*)



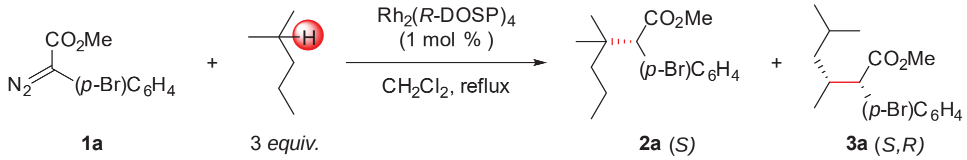


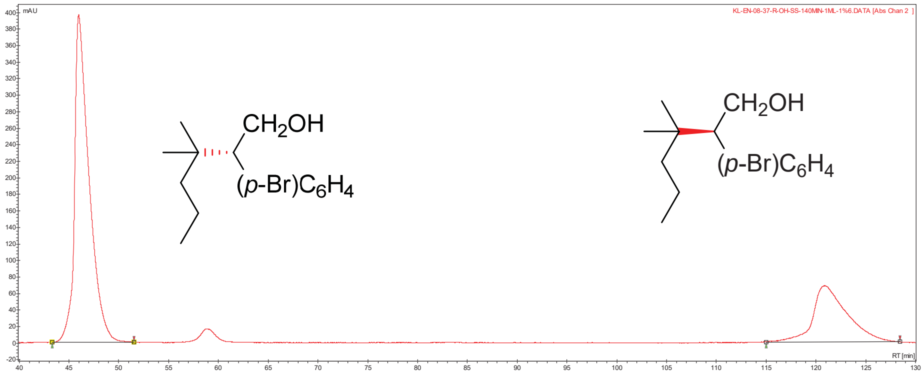
1d 3 *equiv.* **2d** (*R*) **3d** (*R,S*)



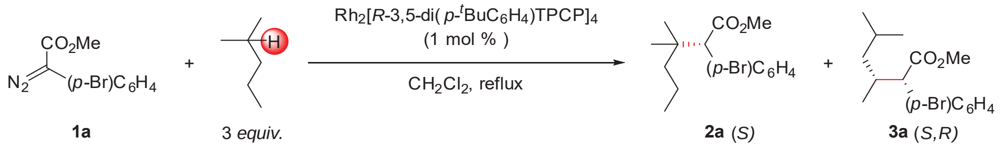
5.7 HPLC

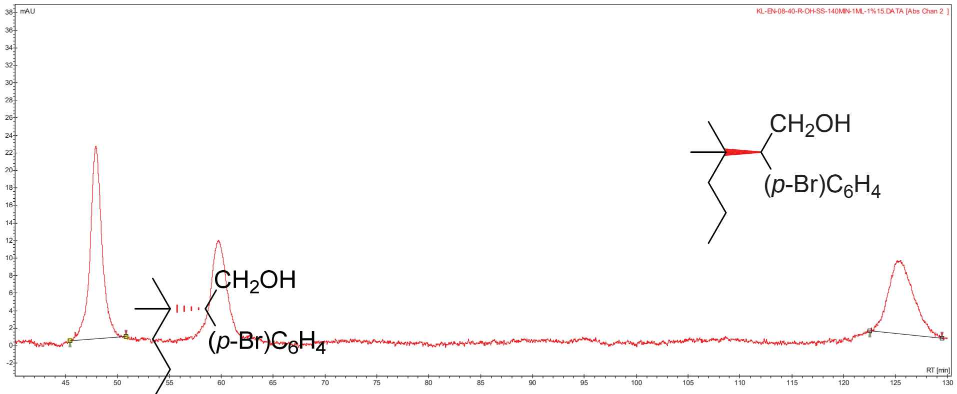
5.7.1 Catalyst and Diazo Screen



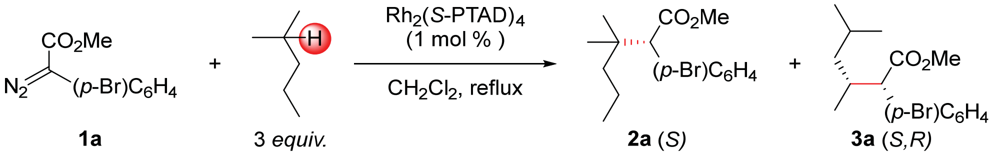


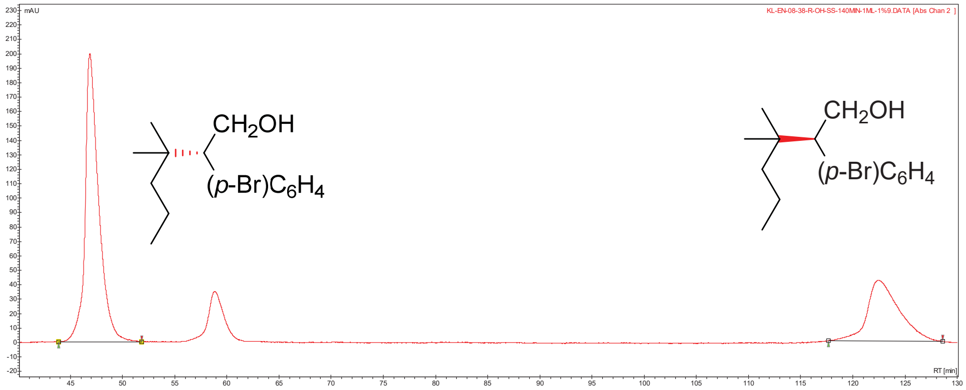
#	Time [Min]	Area % [%]
1	45.98	71.449
2	120.82	28.551
		-43 % e.e.





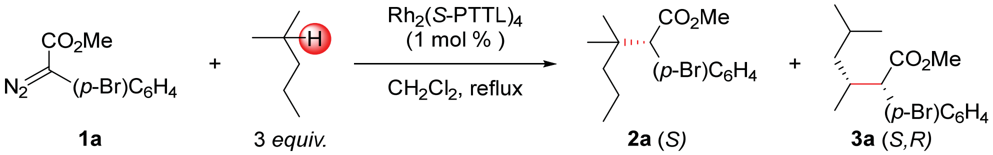
#	Time [Min]	Area % [%]
1	47.91	54.986
2	125.47	45.014
		-10 % e.e.

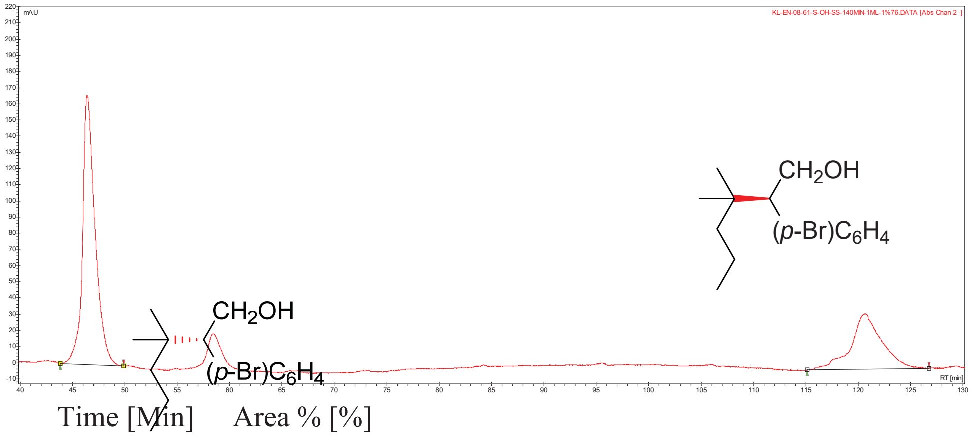




#	Time [Min]	Area % [%]
1	46.86	66.765
2	122.38	33.235

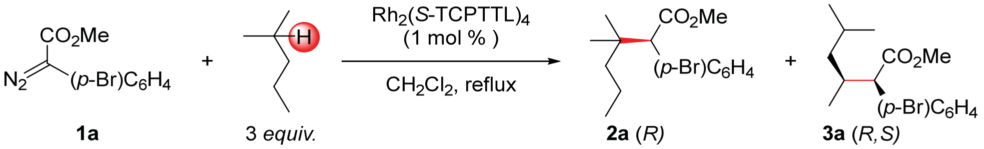
-34 % e.e.

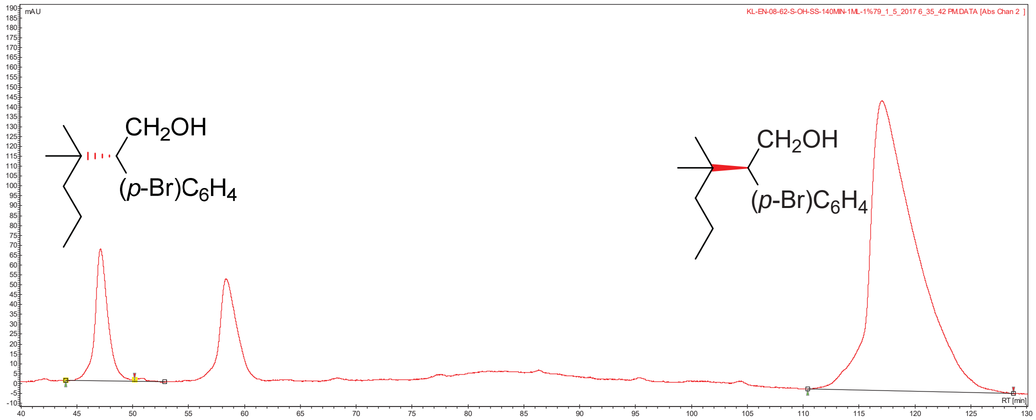




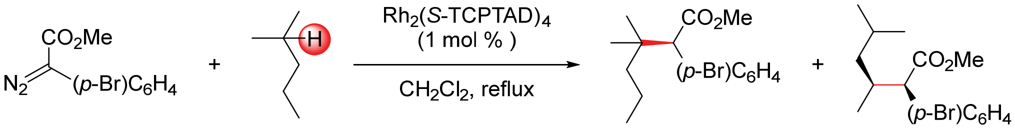
#	Time [Min]	Area % [%]
1	46.40	66.565
2	120.66	33.435

-33 % e.e.

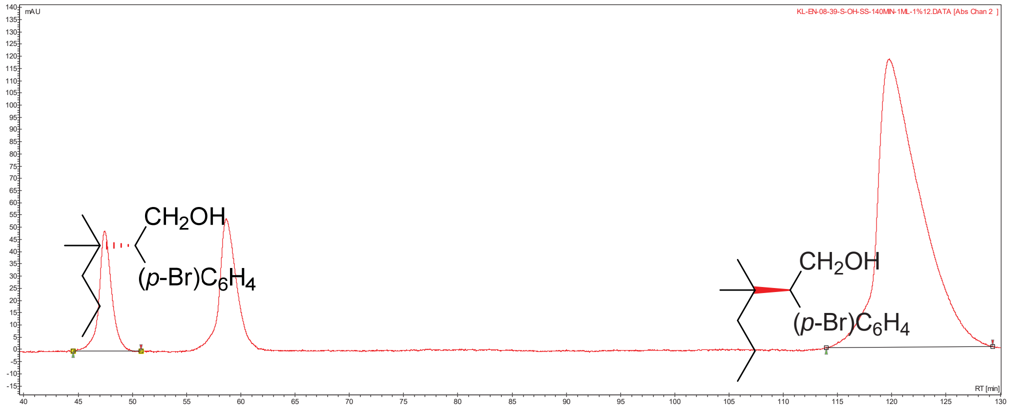




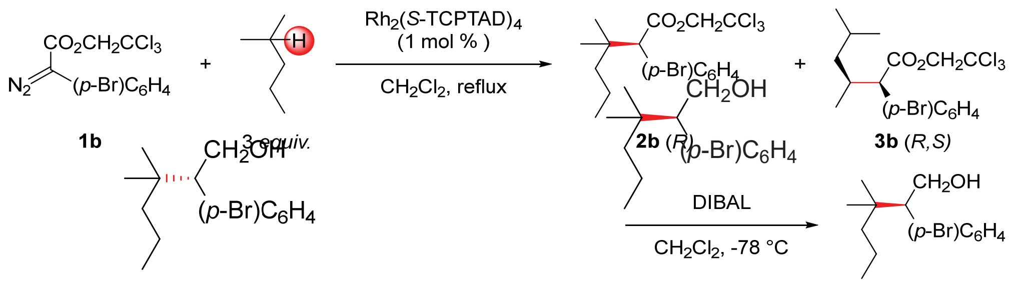
#	Time [Min]	Area % [%]
1	47.13	11.286
2	117.05	88.714
		77 % e.e.



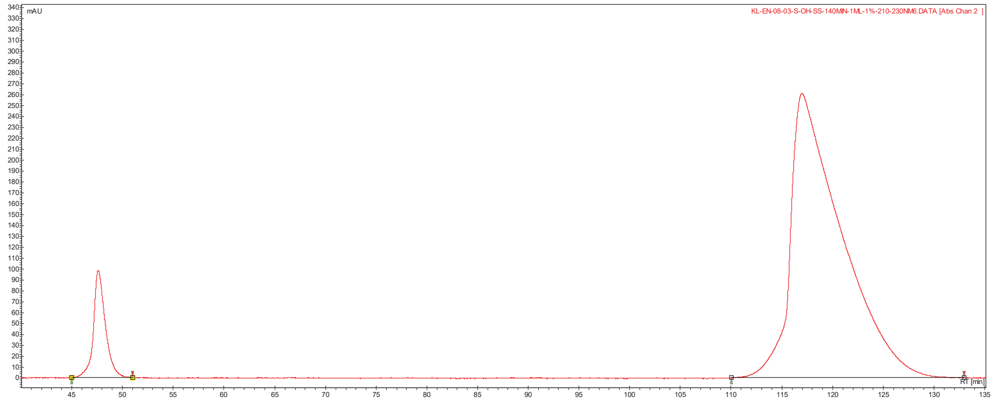
1a 3 *equiv.* **2a** (*R*) **3a** (*R*,*S*)



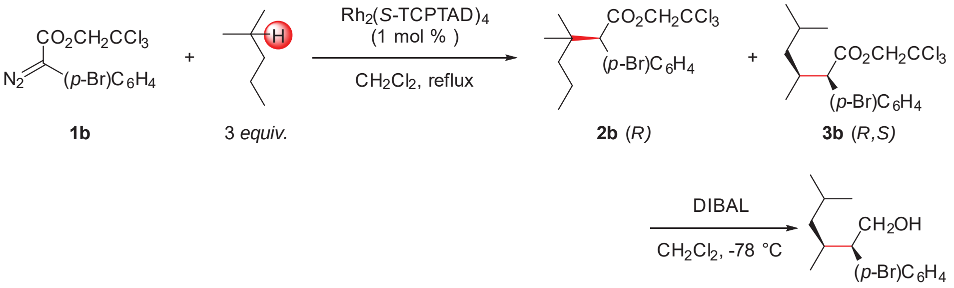
#	Time [Min]	Area % [%]
1	47.46	10.742
2	119.78	89.258
		79 % e.e.

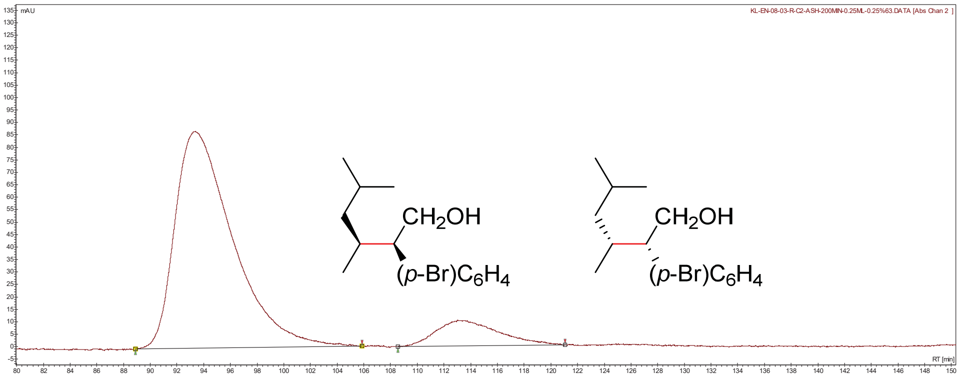


1b **2b** (*R*) **3b** (*R,S*)

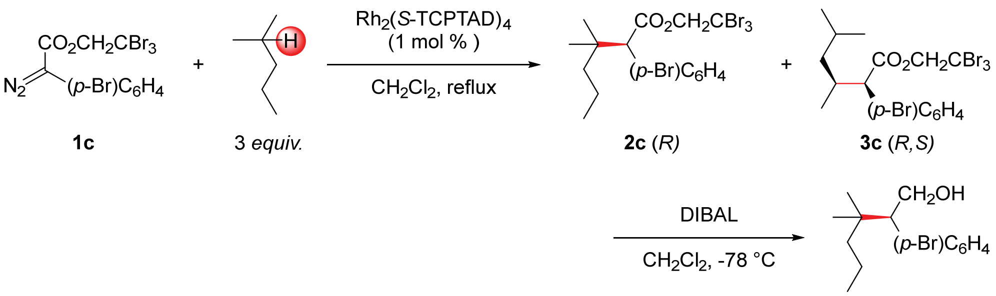


#	Time [Min]	Area % [%]
1	47.61	8.069
2	91.93	91.931
		84 % e.e.

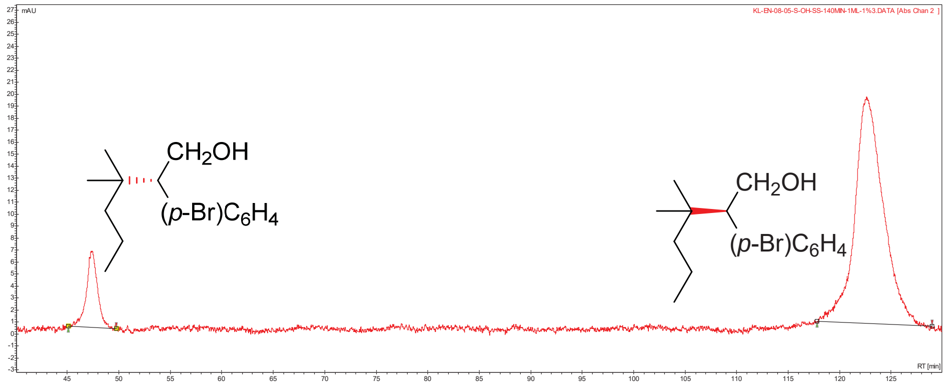




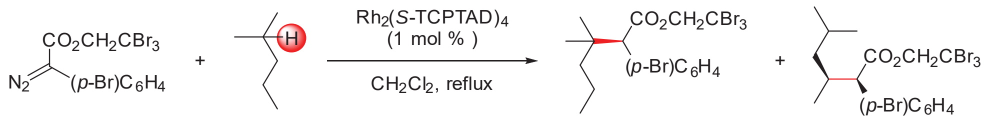
#	Time [Min]	Area % [%]
1	93.38	88.720
2	113.03	11.280
		77 % e.e.



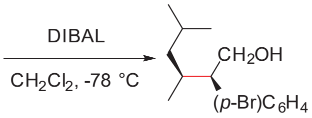
1c 3 *equiv.* **2c** (*R*) **3c** (*R*,*S*)

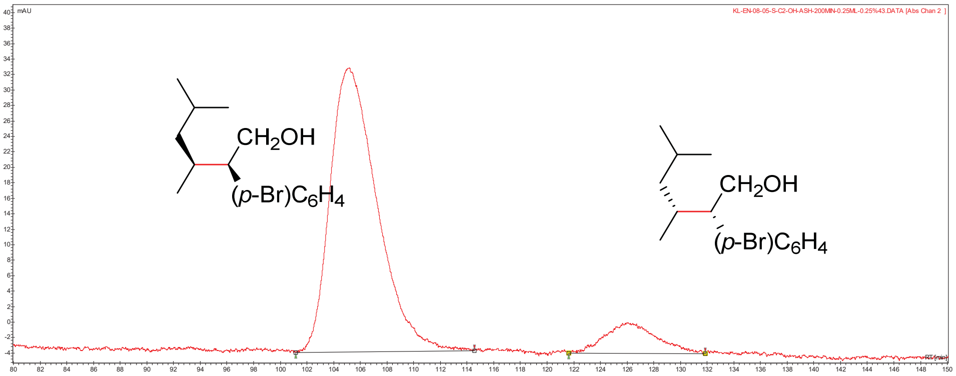


#	Time [Min]	Area % [%]
1	47.39	11.589
2	122.62	88.411
		77 % e.e.

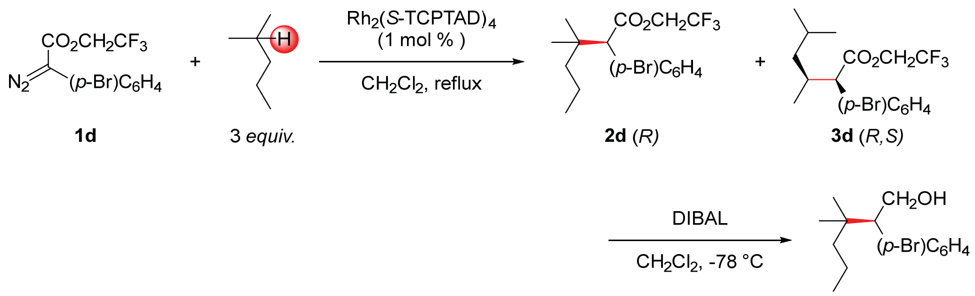


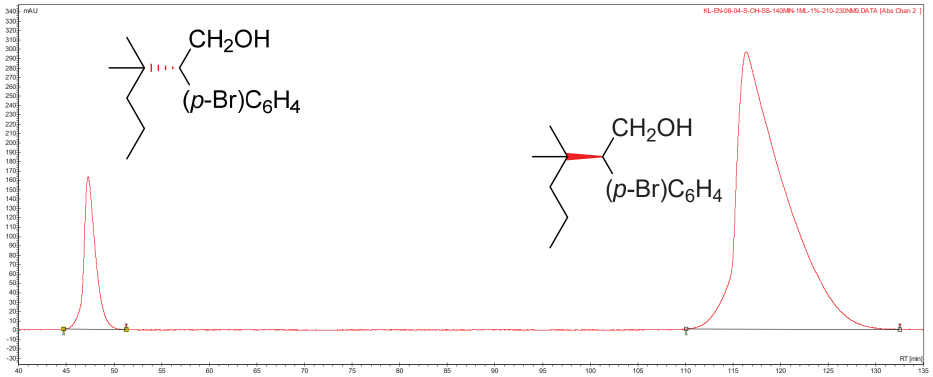
1c 3 *equiv.* **2c** (*R*) **3c** (*R*,*S*)



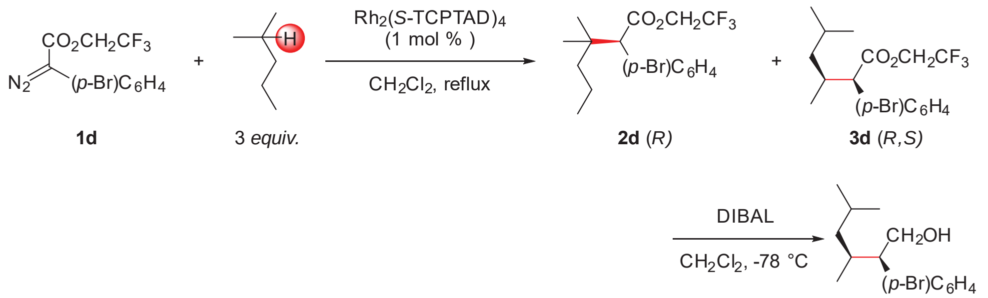


#	Time [Min]	Area % [%]
1	105.17	89.476
2	126.09	10.524
		79 % e.e.

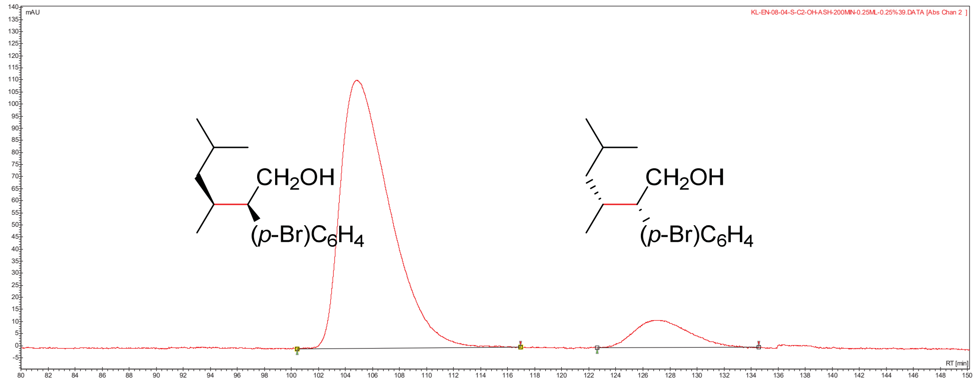




#	Time [Min]	Area % [%]
1	47.28	11.694
2	116.33	88.306
		77 % e.e.



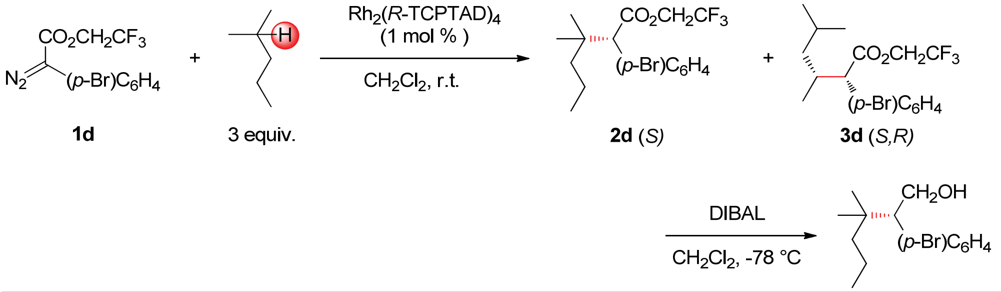
1d 3 *equiv.* **2d** (*R*) **3d** (*R*,*S*)

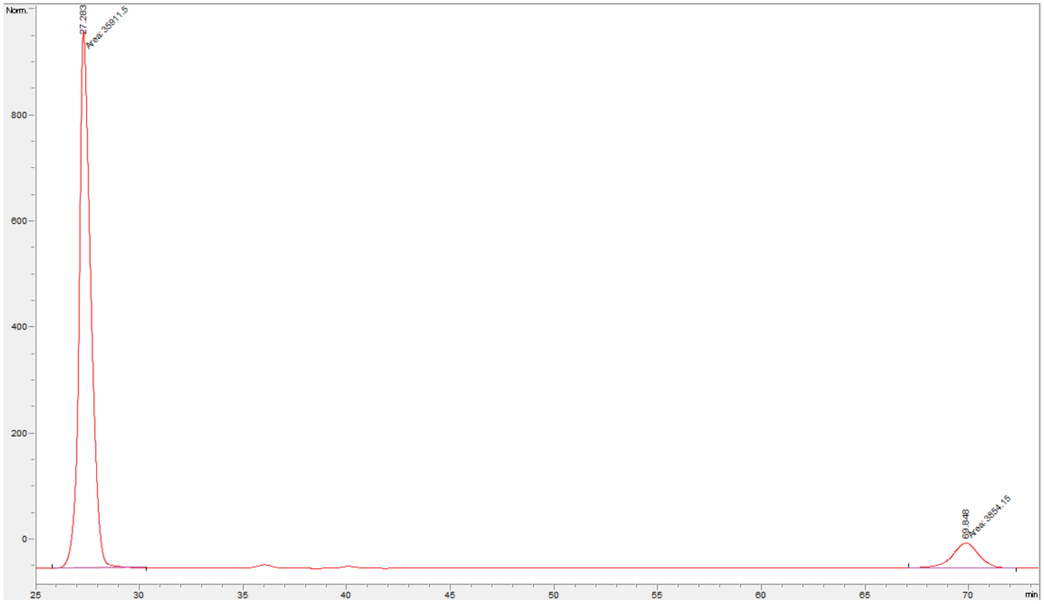


#	Time [Min]	Area % [%]
1	104.83	89.640
2	126.85	10.360
		79 % e.e.

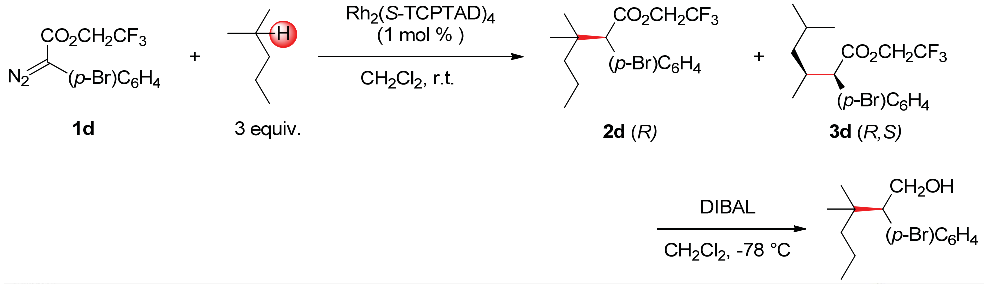
5.7.2 Reaction Condition Screen

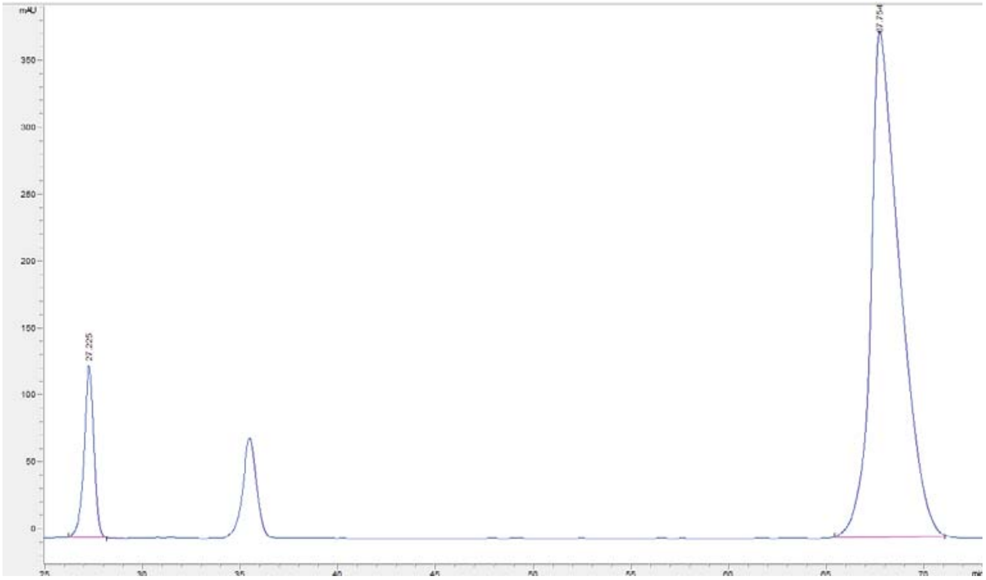
A different HPLC machine with a different S,S-whelk chiral column was used, so the enantiomers' peaks were re-determined with the products generated by Rh2(*R*-TCPTAD)4 and Rh2(*S*-TCPTAD)4.



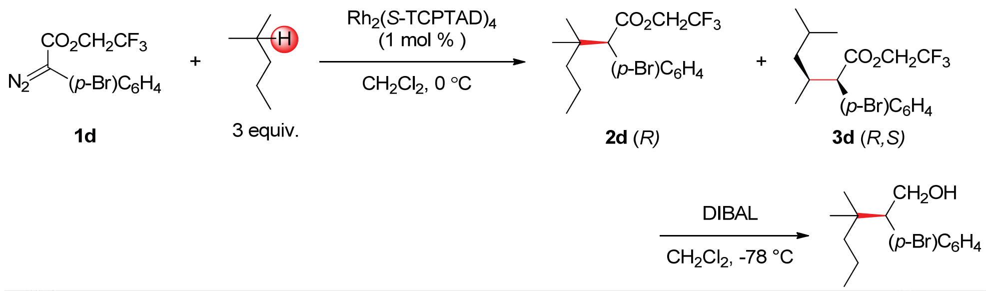


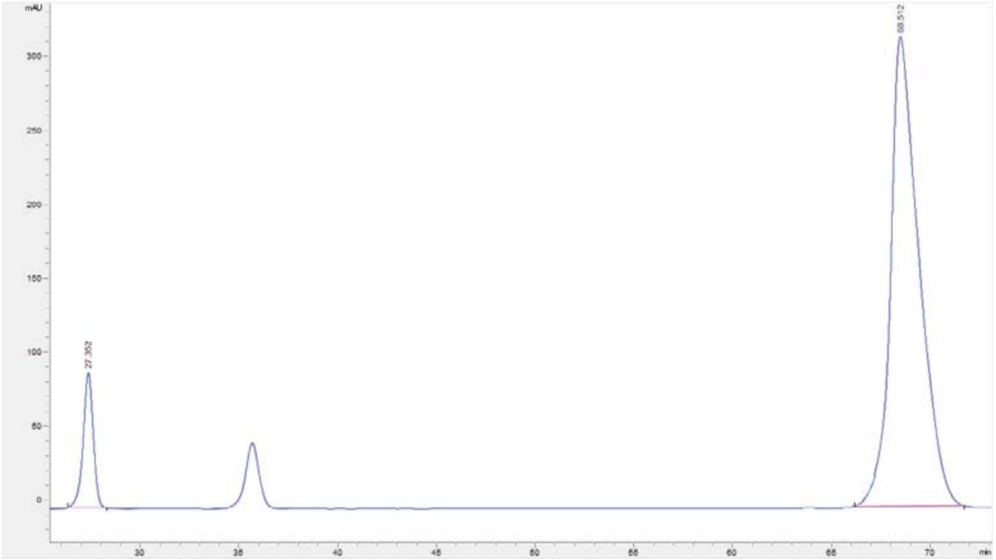
#	Time [Min]	Area% [%]
1	27.283	90.308
2	69.848	9.692 n
		-80% e.e.



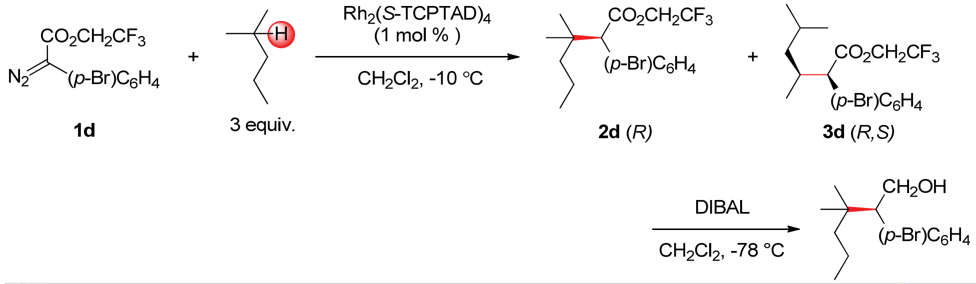


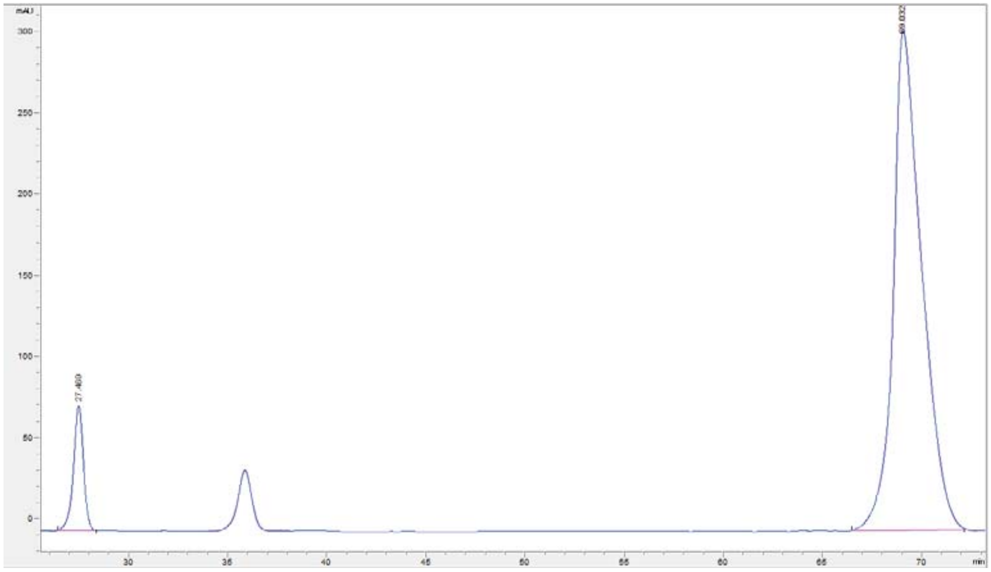
#	Time [Min]	Area% [%]
1	25.830	10.208
2	63.988	89.794
		80% e.e.



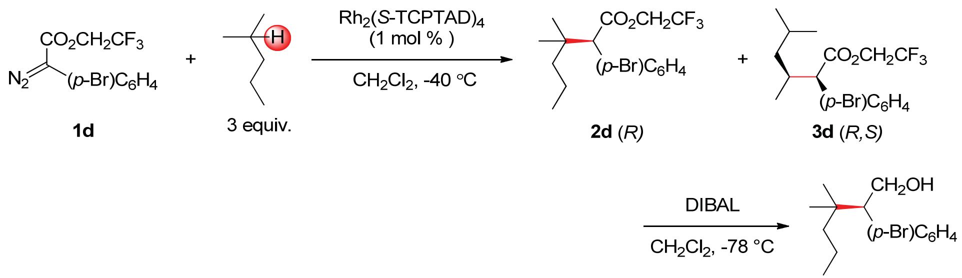


#	Time [Min]	Area% [%]
1	27.352	9.261
2	68.512	90.739
		82% e.e.

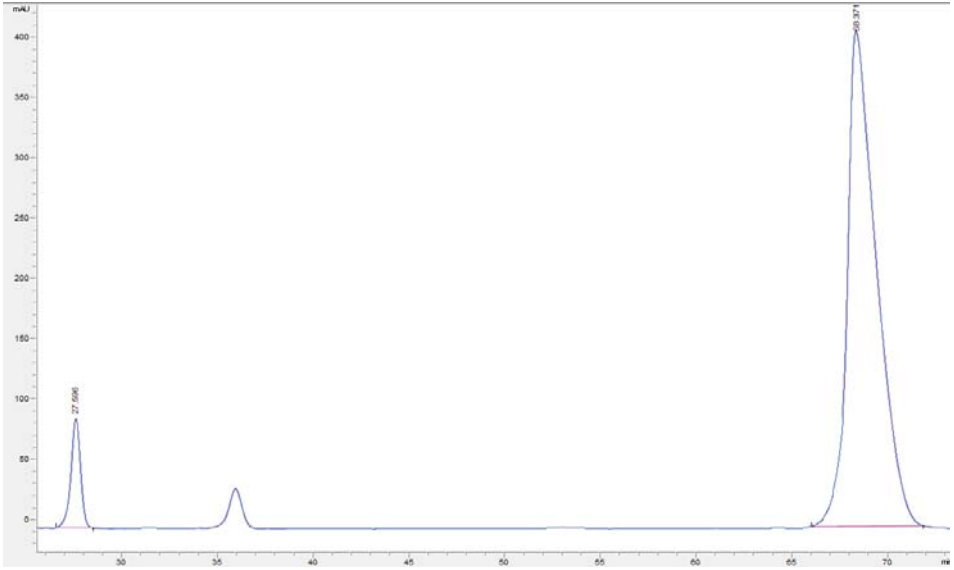




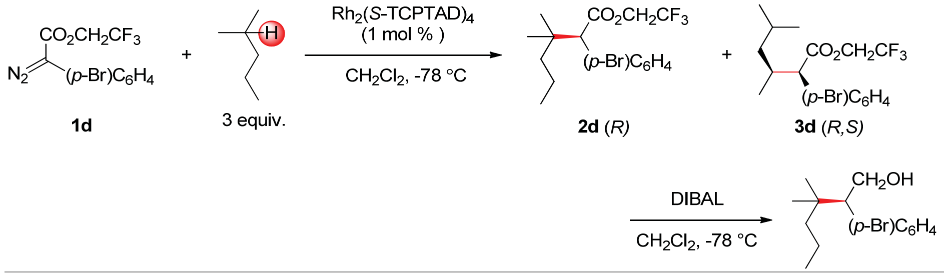
#	Time [Min]	Area% [%]
1	27.469	8.071
2	69.032	91.929
		84% e.e.



1d + 3 equiv. → **2d** (*R*) + **3d** (*R,S*)



#	Time [Min]	Area% [%]
1	27.596	6.745
2	68.371	93.255
		86% e.e.

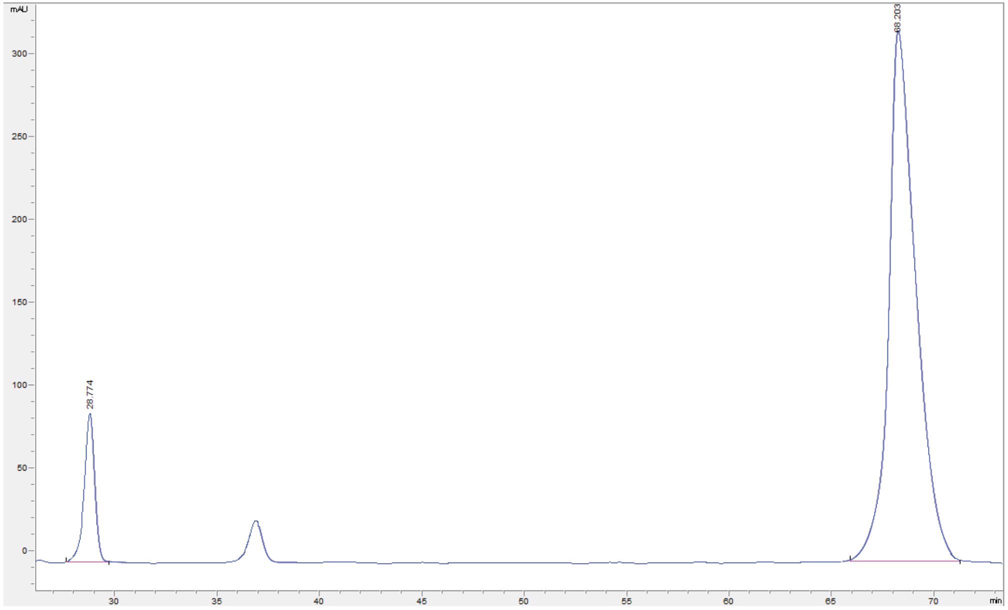


1d

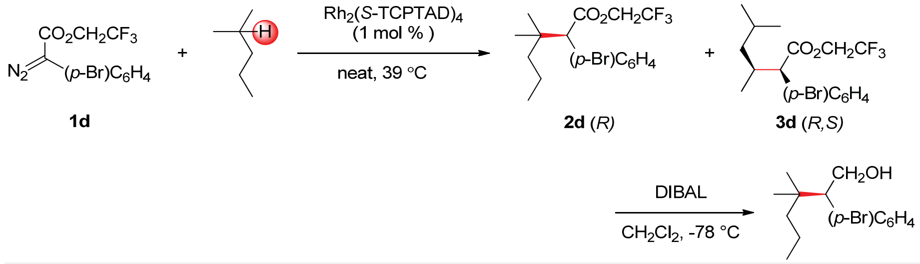
3 equiv.

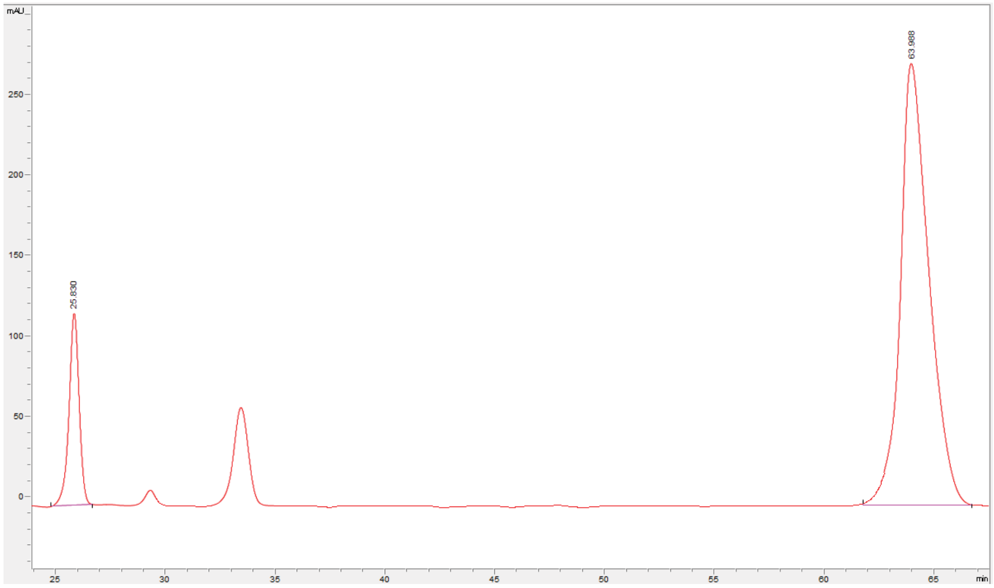
2d (*R*)

3d (*R*,*S*)



#	Time [Min]	Area% [%]
1	28.774	9.729
2	68.203	90.271
		80% e.e.





#	Time [Min]	Area% [%]
1	25.830	13.436
2	63.988	86.564
		73% e.e.

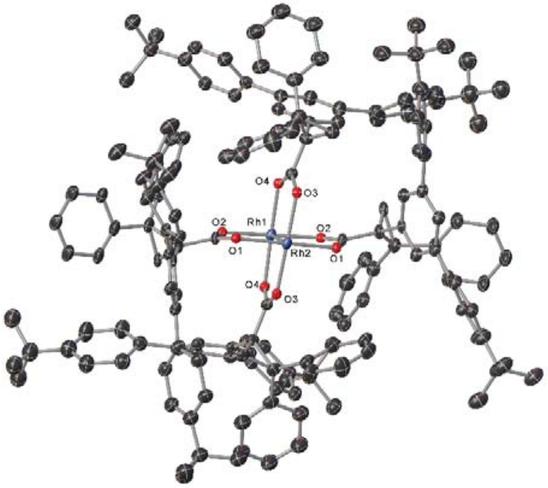
6. X-Ray Crystallographic Data

6.1 Rh$_2$[*S*-3,5-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$

Rh$_2$[*S*-3,5-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$

Submitted by: **Kuangbiao Liao**
Solved by: **John Bacsa**
Sample ID: **Rh$_2$[*S*-3,5-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$**

Crystal Data and Experimental



Experimental. Single green prism-shaped crystals of (**Rh$_2$[*S*-3,5-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$**) were recrystallized from hexane by slow evaporation. A suitable crystal (0.68×0.30×0.28 mm) was selected and mounted on a loop with paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was cooled to T = 100(2) K during the data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program using combined Patterson and dual-space recycling methods and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The crystal structure was refined with **ShelXL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{176}H_{184}O_{10}Rh_2$, M_r = 2665.04, orthorhombic, C222$_1$ (No. 20), a = 19.2803(19) Å, b = 26.114(3) Å, c = 34.545(3) Å, = = = 90°, V = 17393(3) Å^3, T = 100(2) K, Z = 4, Z' = 0.5, (MoK) = 0.240, 36677 reflections measured, 14514 unique (R_{int} = 0.0549) which were used in all calculations. The final wR_2 was 0.3764 (all data) and R_1 was 0.1305 (I > 2(I)).

Compound	**Rh_2[*S*-3,5-di(*p*-$^tBuC_6H_4$)TPCP]$_4$**
Formula	$C_{176}H_{184}O_{10}Rh_2$
$D_{calc.}$/ g cm^{-3}	1.018
/mm^{-1}	0.240
Formula Weight	2665.04
Colour	green
Shape	prism
Max Size/mm	0.68
Mid Size/mm	0.30
Min Size/mm	0.28
T/K	100(2)
Crystal System	orthorhombic
Flack Parameter	0.12(12)
Hooft Parameter	0.067(16)
Space Group	$C222_1$
a/Å	19.2803(19)
b/Å	26.114(3)
c/Å	34.545(3)
/°	90
/°	90
/°	90
V/Å^3	17393(3)
Z	4
Z'	0.5
$_{min}$/°	1.313
$_{max}$/°	24.712
Measured Refl.	36677
Independent Refl.	14514
$I > 2 \quad (I)$	8183
R_{int}	0.0549
Parameters	931
Restraints	1696
Largest Peak	1.411
Deepest Hole	-1.111
GooF	1.087
wR_2 (all data)	0.3764
wR_2	0.3253
R_1 (all data)	0.1905
R_1	0.1305

Structure Quality Indicators

Reflections:	d min 0.85	I/σ 8.1	Rint 5.49%	complete 98%
Refinement:	Shift -0.006	Max Peak 1.4	Min Peak -1.1	GooF 1.087

A green prism-shaped crystal with dimensions 0.68×0.30×0.28mm was mounted on a loop with paratone oil.X-ray diffraction data were collected using a Bruker APEX-II CCD diffractometer equipped with an Oxford Cryosystems low-temperature apparatus operating at *T* = 100(2) K.

Data were measured using and scans with a narrow frame width scans of 0.50° per frame for 119.97 s using MoK radiation (fine-focus sealed tube, 45 kV, 35 mA). The total number of runs and images was based on the strategy calculation from the program **APEX2** (Bruker, 2014). The maximum resolution achieved was = 24.712.

Unit cell indexing was performed by using the **APEX2** (Bruker, 2014) software and refined using **SAINT** (Bruker, V8.34A, 2013) on 9898 reflections, 27% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **SAINT** (Bruker, V8.34A, 2013) and **SADABS-2014/5** (Bruker, 2014) was used for absorption correction.wR_2(int) was 0.1074 before and 0.0544 after the correction. The ratio of minimum to maximum transmission is 0.7157.The /2 correction factor is 0.00150. The final completeness is 98.9% out to 24.712 in . The absorption coefficient ( ) of this material is 0.240 mm^{-1} and the minimum and maximum transmissions are 0.5333 and 0.7451.

The structure was solved in the space group P1 with the **ShelXT** (Sheldrick, 2015) structure solution program using combined Patterson and dual-space recycling methods. The space group C222$_1$ (# 20) was determined by the **ShelXT** (Sheldrick, 2015) structure solution program. The crystal structure was refined by Least Squares using **ShelXL** (Sheldrick, 2008). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Refined as a 2-component inversion twin.

The molecule packs rather uneasily in the crystal with extensive disorder affecting the phenyl groups and the axial ligands. For most atoms, the disorder appears in large elongated ellipsoids but there are two groups where the ellipsoids were especially large, and this disorder was modeled using two disorder components corresponding to two displacements with respect to the overall structure. However, the absolute and relative structure was unequivocally established from the diffraction data.

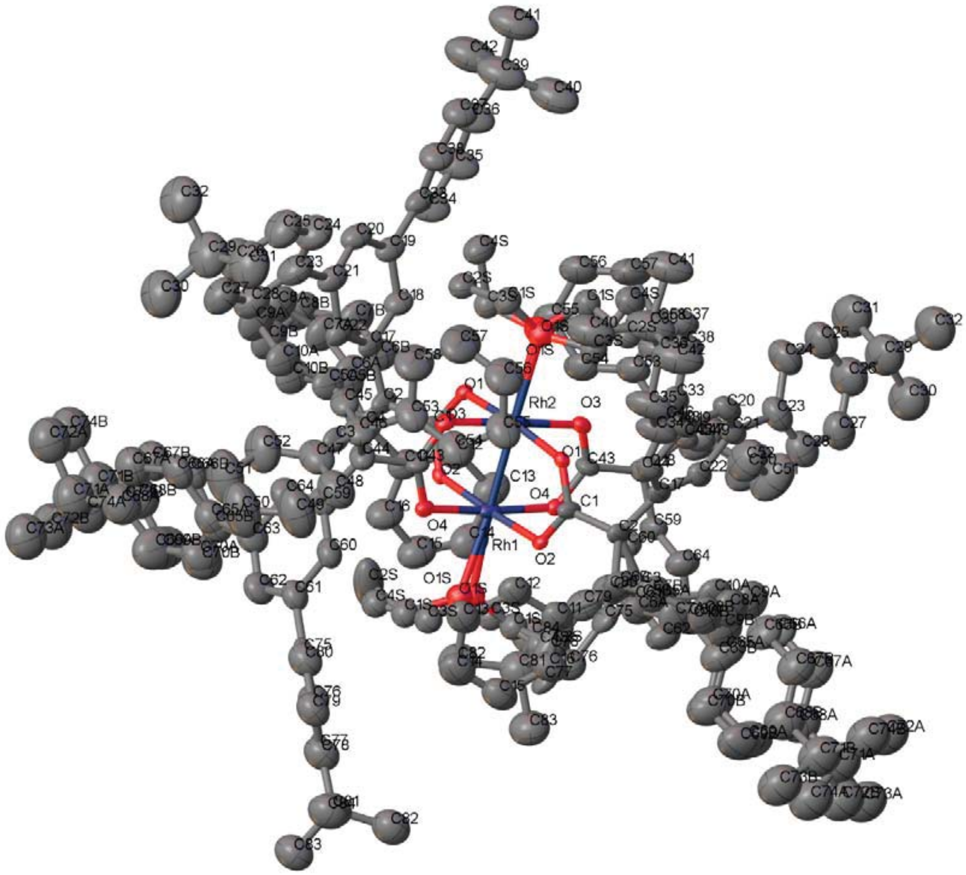


Figure 1: Plot of the asymmetric unit with both components of the disorder and the disordered axial ligands.

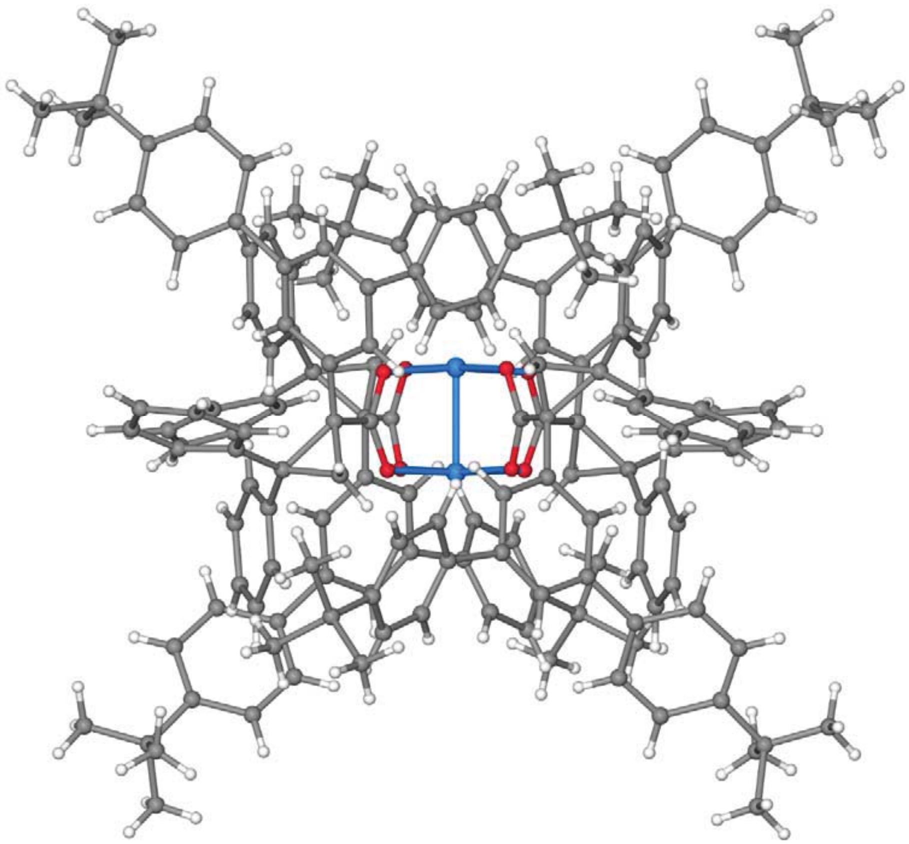


Figure 2: Plot of one of the two components of the disorder without axial ligands.

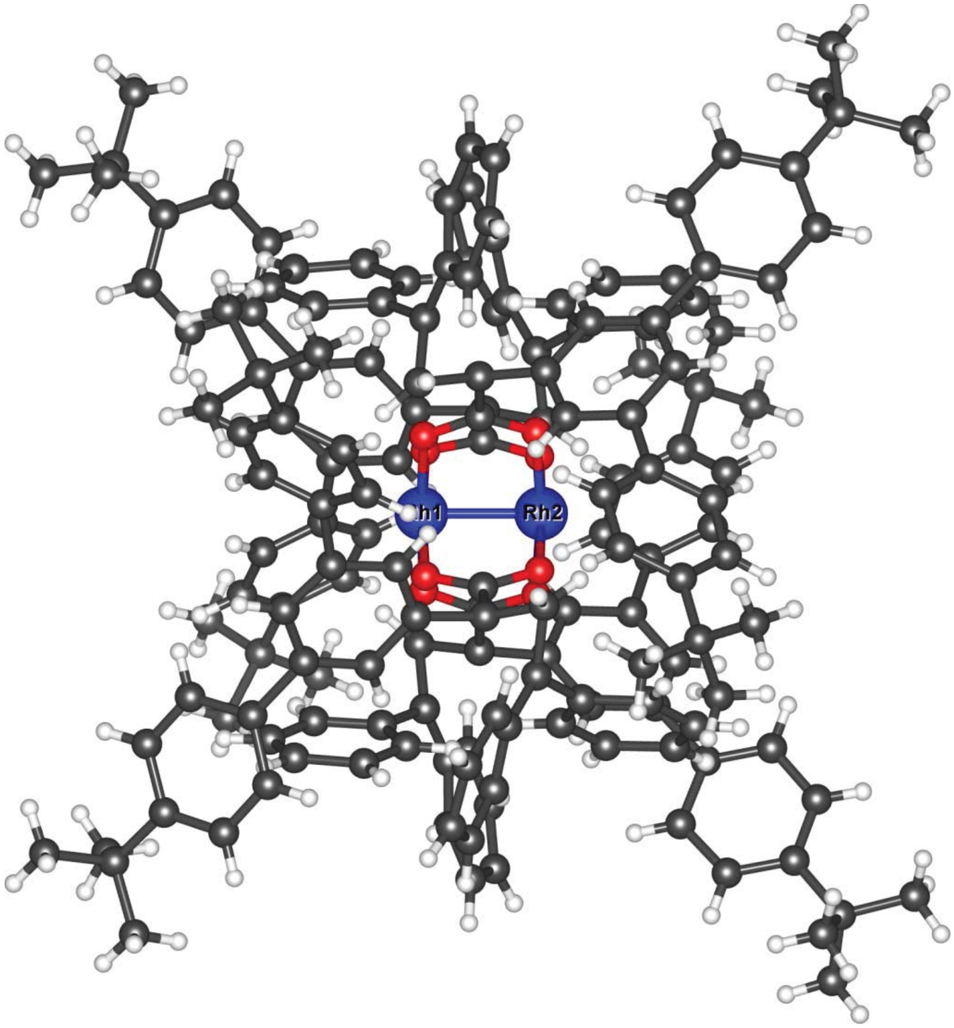


Figure 3: Plot of one of the two components of the disorder without axial ligands.

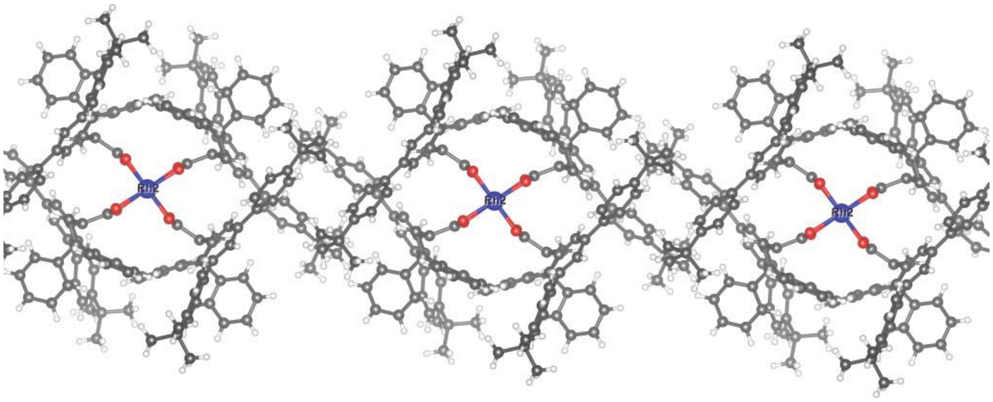


Figure 1: Plot of the molecular packing viewed along the b-axis. The methyl-phenyl groups ‘embrace’ each other forming infinite one-dimensional chains along the a-axis.

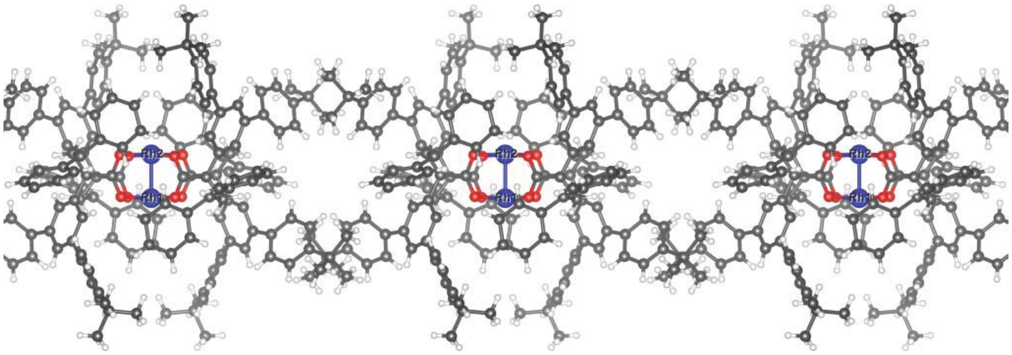


Figure 2: Plot of the molecular packing viewed along the c-axis. The methyl-phenyl groups ‘embrace’ each other forming infinite one-dimensional chains along the a-axis.

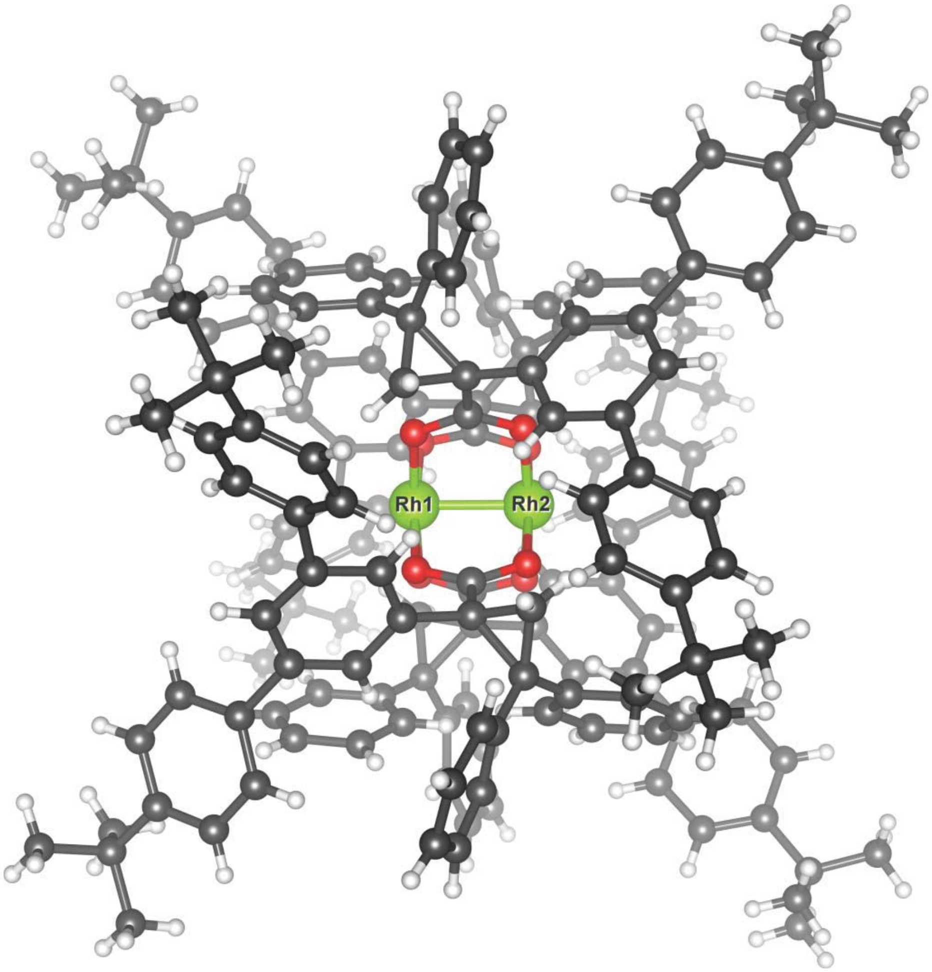


Figure 3: Perspective plot without axial ligands.

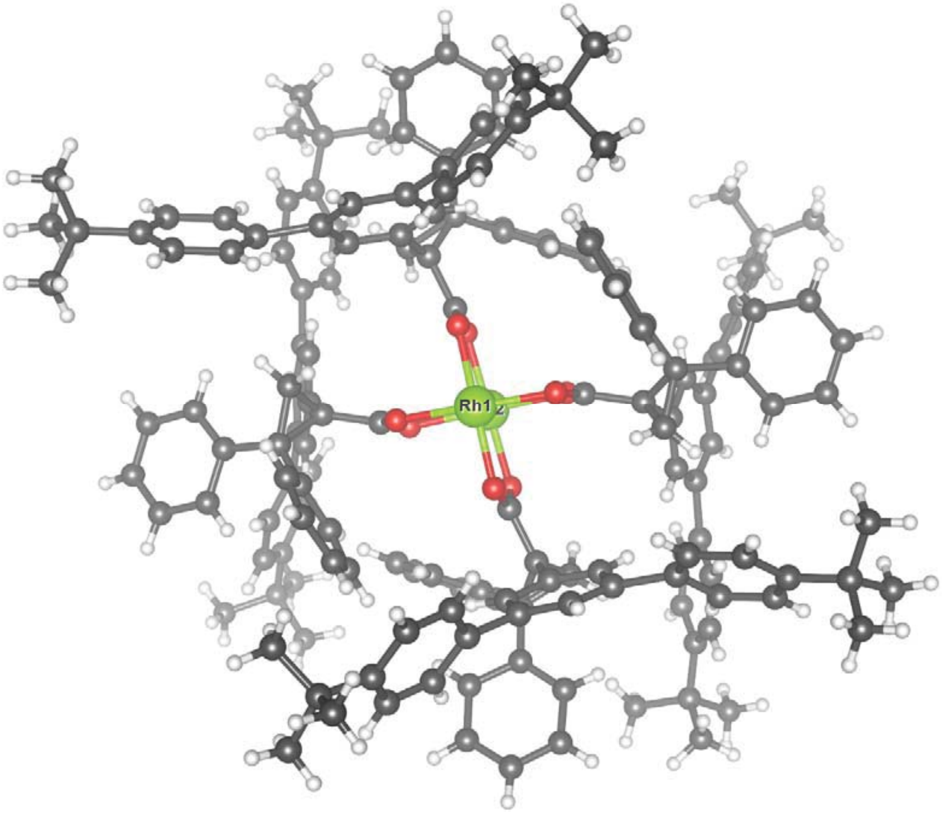


Figure 4: Perspective plot without axial ligands.

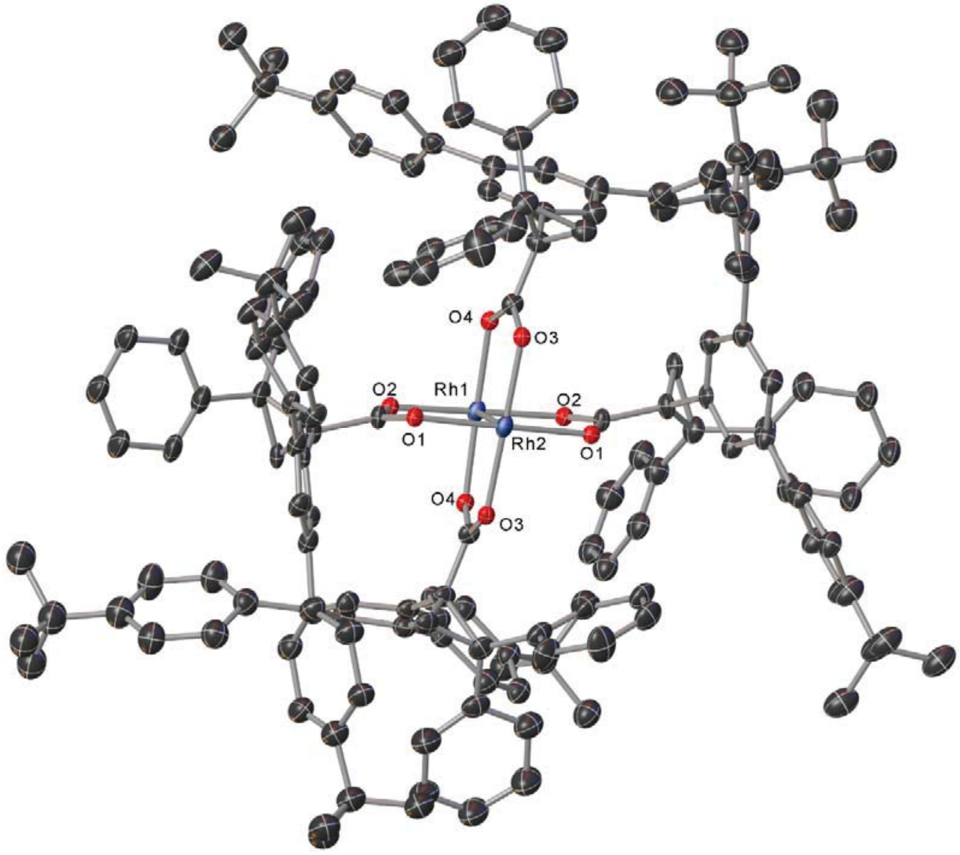
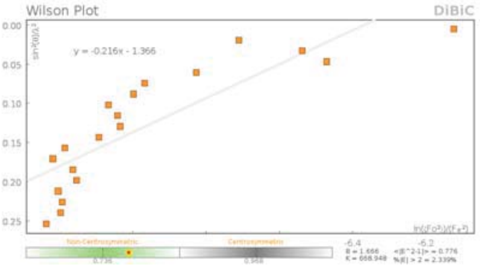


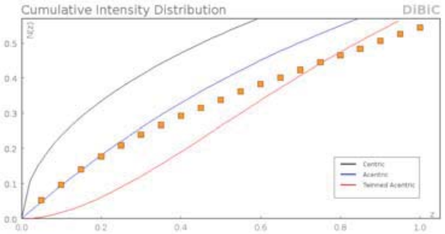
Figure 8: Perspective plot without axial ligands.

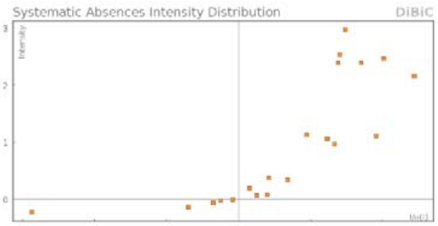
The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

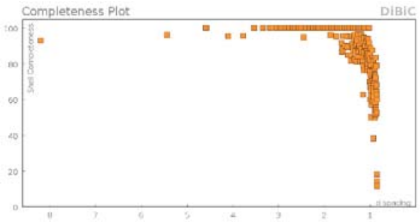
The Flack parameter was refined to 0.12(12). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in 0.067(16). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong, and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

Data Plots: Diffraction Data

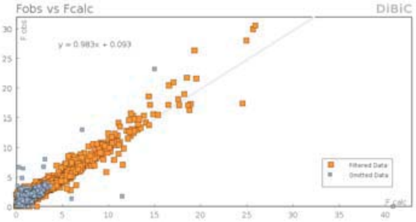


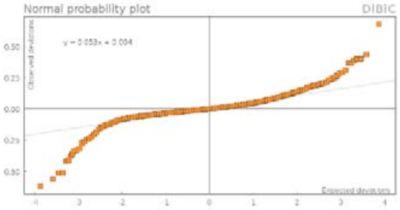






Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	36844	Unique reflections	14514
Completeness	0.979	Mean I/	8.14
hklsub>max</sub> collected	(17, 30, 40)	hklsub>min</sub> collected	(-22, -28, -30)
hkl$_{max}$ used	(22, 30, 40)	hkl$_{min}$ used	(-22, 0, 0)
Lim d$_{max}$ collected	20.0	Lim d$_{min}$ collected	0.85
d$_{max}$ used	17.27	d$_{min}$ used	0.85
Friedel pairs	6003	Friedel pairs merged	0
Inconsistent equivalents	2	R$_{int}$	0.0549
R$_{sigma}$	0.0837	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	124
Multiplicity	(29186, 3688, 110)	Maximum multiplicity	9
Removed systematic absences	43	Filtered off (Shel/OMIT)	48

Images of the Crystal on the Diffractometer

Table 1: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **Rh_2[*S*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	**x**	**y**	**z**	U_{eq}
Rh1	5000	3990.9(6)	7500	50.7(5)
Rh2	5000	4908.4(6)	7500	51.3(5)
O1	4343(6)	4870(5)	7032(3)	45(2)
O2	4323(6)	4007(5)	7058(3)	45(2)
O3	5872(6)	4896(4)	7169(3)	46(2)
O4	5846(6)	4017(5)	7134(3)	45(3)
C1	4099(10)	4432(8)	6952(5)	57(4)
C2	3441(10)	4437(8)	6706(5)	64(3)
C3	2990(11)	3966(7)	6747(6)	67(4)
C4	3363(13)	4025(8)	6371(6)	81(4)
C5B	2990(14)	4202(7)	5986(5)	95(6)
C6B	3387(12)	4402(5)	5677(6)	90(6)
C7B	3037(16)	4559(6)	5338(5)	110(8)
C8B	2330(16)	4522(10)	5303(7)	117(7)
C9B	1955(13)	4328(11)	5605(8)	121(8)
C10B	2296(14)	4168(10)	5948(7)	101(7)
C5A	2804(16)	4199(19)	6062(7)	95(6)
C6A	3085(14)	4203(18)	5684(9)	90(6)
C7A	2663(18)	4380(20)	5377(7)	110(8)
C8A	1992(19)	4540(20)	5436(7)	117(7)
C9A	1723(14)	4510(20)	5801(9)	121(8)
C10A	2152(16)	4372(18)	6117(6)	101(7)
C14	5068(10)	3029(7)	6084(6)	109(6)
C13	5152(9)	3566(7)	6054(7)	108(6)
C12	4590(10)	3883(6)	6159(6)	93(5)
C11	3967(9)	3685(7)	6280(7)	94(5)
C16	3897(9)	3166(7)	6310(7)	101(6)
C15	4453(12)	2840(6)	6202(8)	114(7)
C17	3091(8)	4933(5)	6671(4)	60(3)
C18	3331(9)	5282(6)	6388(5)	73(5)
C19	3041(10)	5778(5)	6382(4)	73(4)
C20	2551(10)	5931(5)	6646(5)	74(4)
C21	2363(9)	5600(6)	6934(4)	74(4)
C22	2637(9)	5096(5)	6941(4)	69(4)
C23	1833(11)	5728(7)	7240(5)	93(5)
C24	1892(12)	6214(7)	7419(6)	107(7)
C25	1469(12)	6319(7)	7743(6)	105(7)
C26	979(13)	5979(9)	7872(6)	119(6)
C27	941(11)	5507(8)	7702(6)	110(7)
C28	1380(12)	5385(6)	7386(6)	99(6)
C29	563(12)	6111(11)	8230(6)	132(6)
C30	95(17)	5677(11)	8363(9)	144(8)
C31	1053(16)	6261(15)	8555(8)	141(8)
C32	67(19)	6546(12)	8135(9)	147(8)
C33	3295(10)	6161(5)	6073(4)	68(4)
C34	3493(14)	5973(5)	5705(5)	91(7)
C35	3704(16)	6329(6)	5421(4)	107(9)
C36	3737(16)	6845(6)	5494(5)	106(6)
C37	3524(12)	7020(5)	5847(5)	83(6)
C38	3323(12)	6670(6)	6140(4)	82(6)
C39	3995(13)	7201(7)	5180(5)	122(6)
C40	4729(14)	7053(11)	5065(9)	137(8)

Atom	x	y	z	U_{eq}
C41	3950(20)	7764(8)	5291(8)	126(8)
C42	3598(18)	7138(12)	4802(7)	135(8)
C43	6112(8)	4463(8)	7070(5)	59(4)
C44	6833(9)	4471(8)	6903(6)	70(3)
C45	7241(13)	4939(8)	6965(6)	76(4)
C46	6990(14)	4874(9)	6570(6)	84(4)
C47	7481(11)	4655(9)	6278(5)	102(5)
C48	7197(10)	4549(11)	5908(6)	119(8)
C49	7645(13)	4362(14)	5617(5)	152(13)
C50	8316(13)	4221(13)	5698(7)	151(12)
C51	8592(10)	4353(13)	6049(7)	146(11)
C52	8164(12)	4575(13)	6337(6)	138(11)
C56	5479(11)	5940(6)	6152(8)	109(7)
C55	5308(9)	5414(6)	6159(6)	99(6)
C54	5814(10)	5063(5)	6289(6)	93(6)
C53	6442(10)	5222(7)	6432(7)	94(5)
C58	6601(10)	5732(7)	6421(9)	120(9)
C57	6110(13)	6089(6)	6277(11)	148(13)
C59	7168(10)	3955(5)	6901(5)	71(4)
C60	6956(10)	3590(6)	6622(5)	77(5)
C61	7242(11)	3093(6)	6641(5)	80(5)
C62	7655(12)	2943(5)	6944(6)	92(7)
C63	7879(11)	3305(6)	7201(5)	89(6)
C64	7606(11)	3809(6)	7184(5)	83(6)
C65B	8302(8)	3180(8)	7570(4)	99(6)
C66B	8809(7)	3544(6)	7680(4)	112(8)
C67B	9265(7)	3419(7)	7985(4)	136(14)
C68B	9229(9)	2958(8)	8175(5)	137(8)
C69B	8737(13)	2611(8)	8065(6)	123(14)
C70B	8273(12)	2729(8)	7759(6)	121(10)
C71B	9727(13)	2838(12)	8500(7)	155(9)
C72B	10090(30)	2370(18)	8316(16)	157(9)
C73B	9270(30)	2620(20)	8831(14)	157(9)
C74B	10300(20)	3160(20)	8695(16)	157(9)
C76	6683(12)	2223(7)	6442(4)	84(4)
C75	6966(11)	2701(6)	6330(4)	79(5)
C80	6991(13)	2820(6)	5932(5)	95(6)
C79	6754(13)	2488(7)	5655(4)	92(6)
C78	6492(12)	2025(7)	5767(4)	92(5)
C77	6459(11)	1898(6)	6166(5)	83(5)
C81	6192(11)	1642(7)	5484(5)	104(5)
C82	5409(12)	1596(12)	5539(8)	113(6)
C83	6522(16)	1112(9)	5535(8)	113(7)
C84	6298(17)	1806(11)	5065(6)	118(7)
C65A	8393(8)	3226(9)	7541(4)	99(6)
C66A	8925(8)	3579(7)	7632(4)	112(8)
C67A	9455(7)	3423(8)	7887(4)	136(14)
C68A	9469(9)	2941(8)	8047(4)	137(8)
C69A	8951(12)	2605(8)	7955(7)	123(14)
C70A	8412(12)	2754(9)	7700(7)	121(10)
C71A	10046(11)	2787(11)	8319(7)	155(9)
C73A	10560(20)	2408(18)	8124(11)	157(9)
C74A	9780(20)	2514(19)	8684(9)	157(9)
C72A	10490(20)	3242(14)	8456(13)	157(9)

Atom	x	y	z	U_{eq}
O1S	5025(12)	5820(4)	7441(5)	30(2)
C2S	6091(17)	6066(15)	7608(10)	66(9)
C1S	5570(12)	6132(12)	7317(9)	55(5)
C3S	4339(12)	5916(11)	7333(10)	54(5)
C4S	4000(20)	6437(13)	7316(16)	89(10)
O1S	5011(11)	3094(4)	7435(5)	30(2)
C2S	6169(13)	2923(14)	7611(10)	56(7)
C1S	5626(13)	2844(14)	7335(9)	53(5)
C3S	4560(20)	2900(30)	7714(10)	125(16)
C4S	3901(16)	2720(20)	7519(19)	125(16)

Table 2: Anisotropic Displacement Parameters (×10^4) **Rh_2[*S*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$**. The anisotropic displacement factor exponent takes the form: *-2* ^{2}*[h^2a^{*2} × U_{11}+ ... +2hka* × b* × U_{12}]*

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh1	72.4(13)	31.1(8)	48.5(10)	0	-13.4(13)	0
C2S_2	52(6)	58(9)	59(8)	1(5)	-2(5)	4(4)
O1S_2	31(3)	26(3)	33(4)	-1(2)	-5(2)	-3(2)
O1S_1	31(3)	26(3)	33(4)	-1(2)	-5(2)	-3(2)
C4S_1	82(13)	69(9)	117(19)	-5(9)	-22(12)	26(9)
C3S_2	125(17)	125(17)	125(17)	0(5)	1(5)	0(5)
C2S_1	51(9)	64(19)	84(15)	1(14)	-19(10)	-15(10)
C1S_1	49(6)	53(7)	62(7)	3(5)	-2(4)	-13(5)
C3S_1	46(5)	56(7)	59(8)	0(5)	-6(4)	5(4)
C1S_2	49(5)	51(7)	59(7)	2(5)	1(4)	7(4)
C4S_2	125(17)	125(17)	125(17)	0(5)	1(5)	0(5)
Rh2	74.2(13)	31.8(8)	47.9(10)	0	-17.3(13)	0
O1	50(4)	41(3)	45(4)	0(3)	-8(3)	1(3)
O2	50(4)	41(3)	46(4)	0(3)	-5(3)	-2(3)
O3	52(4)	34(3)	51(5)	5(3)	-5(4)	-6(3)
O4	54(5)	33(3)	47(5)	1(3)	-4(4)	1(3)
C1	68(6)	44(4)	59(8)	-2(4)	-26(6)	0(4)
C2	69(6)	57(5)	68(7)	-11(4)	-31(5)	3(4)
C3	72(8)	56(6)	71(8)	-16(5)	-34(6)	2(6)
C4	99(7)	74(6)	71(6)	-21(5)	-26(5)	-5(5)
C5B	112(11)	103(13)	70(7)	-22(7)	-30(7)	3(9)
C6B	112(12)	88(15)	70(7)	-22(8)	-29(8)	9(10)
C7B	119(13)	139(18)	72(8)	-14(8)	-27(8)	24(12)
C8B	119(13)	158(18)	75(10)	-18(10)	-28(8)	25(12)
C9B	118(12)	170(20)	74(10)	-20(10)	-30(8)	17(11)
C10B	111(11)	120(17)	73(9)	-28(9)	-31(7)	4(9)
C5A	112(11)	103(13)	70(7)	-22(7)	-30(7)	3(9)
C6A	112(12)	88(15)	70(7)	-22(8)	-29(8)	9(10)
C7A	119(13)	139(18)	72(8)	-14(8)	-27(8)	24(12)
C8A	119(13)	158(18)	75(10)	-18(10)	-28(8)	25(12)
C9A	118(12)	170(20)	74(10)	-20(10)	-30(8)	17(11)
C10A	111(11)	120(17)	73(9)	-28(9)	-31(7)	4(9)
C14	142(12)	116(9)	71(13)	-19(9)	-15(10)	16(8)
C13	128(9)	117(9)	80(14)	-17(9)	-11(8)	17(7)
C12	116(8)	101(9)	62(11)	-20(8)	-19(7)	4(6)
C11	111(7)	90(6)	82(9)	-14(5)	-15(6)	9(5)
C16	135(11)	88(7)	80(15)	-16(6)	-13(9)	10(6)
C15	143(12)	103(9)	95(17)	-14(8)	-8(11)	22(7)
C17	65(7)	61(5)	53(6)	-12(4)	-28(5)	2(4)
C18	97(10)	64(6)	59(8)	-13(5)	-8(7)	8(6)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C19	97(10)	67(6)	56(6)	-14(5)	-13(6)	10(5)
C20	97(10)	66(7)	60(7)	-16(5)	-12(7)	8(6)
C21	89(9)	72(6)	62(7)	-12(5)	-14(7)	10(6)
C22	74(7)	69(6)	63(6)	-12(4)	-16(5)	1(5)
C23	103(10)	99(9)	78(9)	-8(7)	-1(8)	19(7)
C24	116(13)	107(9)	97(13)	-18(8)	14(11)	10(9)
C25	104(14)	124(11)	89(11)	-20(8)	3(10)	14(9)
C26	117(12)	140(11)	100(10)	-18(8)	10(9)	0(9)
C27	110(13)	134(11)	84(10)	-9(8)	-3(9)	7(9)
C28	104(12)	113(10)	80(11)	-1(7)	-9(8)	11(8)
C29	126(12)	164(13)	106(10)	-25(9)	18(9)	0(9)
C30	133(15)	177(15)	123(14)	-16(11)	18(12)	-4(12)
C31	133(15)	180(19)	110(12)	-27(11)	16(10)	-2(13)
C32	141(14)	176(14)	123(15)	-20(11)	20(12)	11(12)
C33	79(11)	69(6)	55(6)	-12(4)	-18(6)	13(6)
C34	136(19)	74(7)	61(6)	-14(5)	1(8)	11(8)
C35	180(20)	79(7)	65(7)	-12(6)	11(10)	4(9)
C36	163(17)	80(7)	74(7)	-12(5)	8(9)	4(8)
C37	106(15)	75(7)	68(7)	-10(5)	-11(8)	8(7)
C38	111(16)	70(6)	64(7)	-15(5)	-5(8)	10(6)
C39	201(16)	86(9)	79(8)	-8(7)	19(9)	-5(9)
C40	204(16)	101(14)	108(14)	-9(11)	27(10)	-3(10)
C41	200(20)	88(8)	88(13)	-8(8)	14(12)	-4(9)
C42	219(19)	101(14)	86(9)	-7(8)	9(10)	-8(12)
C43	77(6)	37(4)	64(9)	5(4)	3(5)	-1(4)
C44	77(5)	60(5)	73(7)	12(5)	7(5)	0(4)
C45	90(8)	61(6)	77(7)	17(5)	9(6)	-4(6)
C46	106(8)	68(7)	78(6)	19(5)	7(5)	-8(5)
C47	129(10)	85(11)	92(7)	19(7)	23(7)	0(9)
C48	139(12)	120(20)	99(9)	7(11)	17(9)	12(11)
C49	153(15)	200(30)	106(10)	-8(13)	17(10)	37(17)
C50	151(15)	190(30)	110(13)	7(16)	21(9)	34(17)
C51	146(12)	180(30)	108(13)	14(16)	24(9)	26(13)
C52	134(11)	180(30)	106(11)	9(13)	19(8)	15(11)
C56	152(13)	88(9)	88(16)	29(9)	0(12)	11(8)
C55	135(10)	87(9)	76(13)	27(9)	3(9)	15(8)
C54	131(10)	82(9)	66(12)	24(8)	8(8)	11(7)
C53	126(9)	84(8)	72(10)	23(7)	10(7)	11(6)
C58	155(13)	85(8)	120(20)	31(9)	-13(13)	3(8)
C57	167(14)	89(9)	190(30)	45(10)	-38(16)	3(8)
C59	81(8)	63(5)	69(8)	13(4)	10(6)	1(5)
C60	82(11)	74(7)	75(9)	7(6)	7(8)	2(7)
C61	84(11)	77(6)	79(8)	5(5)	5(7)	3(6)
C62	106(14)	78(8)	92(10)	4(6)	-11(10)	8(8)
C63	108(13)	74(8)	84(10)	9(6)	-11(10)	8(8)
C64	97(12)	74(8)	78(9)	12(6)	-2(9)	4(7)
C65B	105(10)	96(9)	97(10)	2(8)	-3(8)	16(7)
C66B	117(14)	109(10)	109(14)	-4(9)	-3(12)	6(9)
C67B	140(20)	137(11)	130(20)	10(13)	-27(19)	-1(13)
C68B	146(11)	136(10)	128(11)	8(8)	-14(8)	4(7)
C69B	140(20)	122(11)	110(20)	12(13)	-15(19)	16(13)
C70B	140(16)	107(10)	116(16)	14(10)	-18(14)	5(11)
C71B	160(14)	163(16)	143(15)	19(12)	-22(11)	8(11)
C72B	162(14)	164(15)	144(14)	17(12)	-20(11)	6(11)
C73B	162(14)	164(15)	144(14)	17(12)	-20(11)	6(11)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C74B	162(14)	164(15)	144(14)	17(12)	-20(11)	6(11)
C76	87(6)	83(5)	82(5)	1(3)	0(4)	6(4)
C75	74(11)	80(6)	82(7)	0(5)	2(6)	14(6)
C80	111(15)	93(8)	82(7)	0(5)	5(6)	15(9)
C79	105(14)	90(8)	82(7)	-2(5)	-2(7)	26(8)
C78	104(12)	90(7)	83(6)	-3(5)	-2(6)	27(7)
C77	84(12)	82(7)	84(6)	-3(5)	-5(6)	17(7)
C81	122(11)	102(8)	89(7)	-10(6)	-6(7)	20(8)
C82	124(10)	117(14)	97(13)	-12(10)	-7(8)	17(8)
C83	131(15)	105(9)	105(13)	-8(8)	0(11)	22(9)
C84	145(16)	118(14)	92(8)	-7(7)	-3(8)	17(11)
C65A	105(10)	96(9)	97(10)	2(8)	-3(8)	16(7)
C66A	117(14)	109(10)	109(14)	-4(9)	-3(12)	6(9)
C67A	140(20)	137(11)	130(20)	10(13)	-27(19)	-1(13)
C68A	146(11)	136(10)	128(11)	8(8)	-14(8)	4(7)
C69A	140(20)	122(11)	110(20)	12(13)	-15(19)	16(13)
C70A	140(16)	107(10)	116(16)	14(10)	-18(14)	5(11)
C71A	160(14)	163(16)	143(15)	19(12)	-22(11)	8(11)
C73A	162(14)	164(15)	144(14)	17(12)	-20(11)	6(11)
C74A	162(14)	164(15)	144(14)	17(12)	-20(11)	6(11)
C72A	162(14)	164(15)	144(14)	17(12)	-20(11)	6(11)

Table 3: Bond Lengths in Å for **$Rh_2[S\text{-}3,5\text{-di}(p\text{-}^tBuC_6H_4)TPCP]_4$**.

Atom	Atom	Length/Å
Rh1	O1S_2	2.352(12)
C2S_1	H2SC_1	0.9600
C3S_1	H3SA_1	0.9700
C4S_1	H4SC_1	0.9600
C1S_1	H1SB_1	0.9700
C1S_2	H1SB_2	0.9700
C4S_1	H4SB_1	0.9600
C4S_2	H4SA_2	0.9600
C1S_1	H1SA_1	0.9700
C2S_2	H2SA_2	0.9600
C3S_1	C4S_1	1.51(2)
C4S_2	H4SC_2	0.9600
C3S_1	H3SB_1	0.9700
C4S_1	H4SA_1	0.9600
O1S_2	C3S_2	1.397(7)
O1S_1	C1S_1	1.396(7)
C2S_2	C1S_2	1.43(2)
O1S_2	C1S_2	1.397(6)
C2S_2	H2SB_2	0.9600
O1S_1	C3S_1	1.396(7)
C1S_2	H1SA_2	0.9700
C2S_2	H2SC_2	0.9600
C3S_2	C4S_2	1.51(2)
C2S_1	C1S_1	1.43(2)
C3S_2	H3SB_2	0.9700
C3S_2	H3SA_2	0.9700
C4S_2	H4SB_2	0.9600
C2S_1	H2SA_1	0.9600
C2S_1	H2SB_1	0.9600
Rh1	Rh2	2.396(2)
Rh1	O2[1]	2.010(11)
Rh1	O2	2.010(11)
Rh1	O4	2.065(11)
Rh1	O4[1]	2.065(11)
Rh2	O1S_1	2.390(11)
Rh2	O1	2.056(10)
Rh2	O1[1]	2.056(10)
Rh2	O3[1]	2.033(11)
Rh2	O3	2.033(11)
O1	C1	1.27(2)
O2	C1	1.25(2)
O3	C43	1.27(2)
O4	C43	1.29(2)
C1	C2	1.53(2)
C2	C3	1.51(3)
C2	C4	1.59(2)
C2	C17	1.47(2)
C3	C4	1.49(3)
C4	C5B	1.58(3)
C4	C5A	1.58(3)
C4	C11	1.50(3)
C5B	C6B	1.415(10)
C5B	C10B	1.348(11)

Atom	Atom	Length/Å
C6B	C7B	1.411(10)
C7B	C8B	1.372(12)
C8B	C9B	1.366(12)
C9B	C10B	1.418(11)
C5A	C6A	1.415(11)
C5A	C10A	1.349(11)
C6A	C7A	1.410(10)
C7A	C8A	1.373(12)
C8A	C9A	1.367(12)
C9A	C10A	1.418(11)
C14	C13	1.414(10)
C14	C15	1.348(11)
C13	C12	1.411(10)
C12	C11	1.372(12)
C11	C16	1.366(12)
C16	C15	1.417(11)
C17	C18	1.415(10)
C17	C22	1.348(11)
C18	C19	1.412(10)
C19	C20	1.373(12)
C19	C33	1.541(17)
C20	C21	1.367(12)
C21	C22	1.418(11)
C21	C23	1.510(19)
C23	C24	1.415(10)
C23	C28	1.349(11)
C24	C25	1.411(10)
C25	C26	1.373(12)
C26	C27	1.366(12)
C26	C29	1.513(8)
C27	C28	1.418(11)
C29	C30	1.520(6)
C29	C31	1.520(6)
C29	C32	1.520(6)
C33	C34	1.416(10)
C33	C38	1.348(11)
C34	C35	1.410(10)
C35	C36	1.373(12)
C36	C37	1.367(12)
C36	C39	1.513(8)
C37	C38	1.417(11)
C39	C40	1.522(6)
C39	C41	1.522(6)
C39	C42	1.522(6)
C43	C44	1.505(13)
C44	C45	1.47(3)
C44	C46	1.59(2)
C44	C59	1.49(2)
C45	C46	1.46(3)
C46	C47	1.50(3)
C46	C53	1.47(3)
C47	C48	1.415(10)
C47	C52	1.349(11)
C48	C49	1.412(10)

Atom	Atom	Length/Å
C49	C50	1.375(12)
C50	C51	1.367(12)
C51	C52	1.417(11)
C56	C55	1.415(10)
C56	C57	1.348(11)
C55	C54	1.411(10)
C54	C53	1.372(12)
C53	C58	1.366(12)
C58	C57	1.418(11)
C59	C60	1.416(10)
C59	C64	1.349(11)
C60	C61	1.411(10)
C61	C62	1.374(12)
C61	C75	1.575(18)
C62	C63	1.367(12)
C63	C64	1.418(11)
C63	C65B	1.549(17)
C63	C65A	1.551(17)
C65B	C66B	1.415(10)
C65B	C70B	1.348(11)
C66B	C67B	1.411(10)
C67B	C68B	1.372(12)
C68B	C69B	1.366(12)
C68B	C71B	1.511(8)
C69B	C70B	1.418(11)
C71B	C72B	1.547(14)
C71B	C73B	1.544(14)
C71B	C74B	1.540(14)
C76	C75	1.415(10)
C76	C77	1.348(11)
C75	C80	1.411(10)
C80	C79	1.371(12)
C79	C78	1.367(12)
C78	C77	1.418(11)
C78	C81	1.513(8)
C81	C82	1.526(13)
C81	C83	1.532(13)
C81	C84	1.524(13)
C65A	C66A	1.415(10)
C65A	C70A	1.348(11)
C66A	C67A	1.411(10)
C67A	C68A	1.373(12)
C68A	C69A	1.366(12)
C68A	C71A	1.512(8)
C69A	C70A	1.418(11)
C71A	C73A	1.555(14)
C71A	C74A	1.539(14)
C71A	C72A	1.535(14)

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[1] 1-X, +Y, 3/2-

Table 4: Bond Angles in ° for **Rh$_2$[*S*-3,5-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$**.

Atom	**Atom**	**Atom**	**Angle/°**
C4S_1	C3S_1	H3SB_1	106.0
O2^1	Rh1	Rh2	88.8(4)
O2	Rh1	Rh2	88.8(4)
O2	Rh1	O2^1	177.7(7)
O2	Rh1	O4^1	87.2(5)
O2^1	Rh1	O4^1	92.7(5)
H2SB_2	C2S_2	H2SC_2	109.5
O2	Rh1	O4	92.7(5)
O2^1	Rh1	O4	87.2(5)
O4	Rh1	Rh2	88.1(3)
O1S_2	C3S_2	C4S_2	109.2(14)
C2S_1	C1S_1	H1SA_1	110.9
H4SB_2	C4S_2	H4SC_2	109.5
C1S_1	C2S_1	H2SA_1	109.5
C2S_1	C1S_1	H1SB_1	110.9
O1S_1	C3S_1	C4S_1	125(3)
O4^1	Rh1	Rh2	88.1(3)
O4^1	Rh1	O4	176.3(7)
C3S_1	C4S_1	H4SA_1	109.5
C3S_2	C4S_2	H4SC_2	109.5
C1S_2	C2S_2	H2SA_2	109.5
C1S_1	O1S_1	C3S_1	121.8(17)
C2S_2	C1S_2	H1SB_2	109.0
O1	Rh2	Rh1	87.2(3)
C4S_2	C3S_2	H3SA_2	109.8
H2SA_1	C2S_1	H2SB_1	109.5
H4SA_2	C4S_2	H4SC_2	109.5
H2SA_1	C2S_1	H2SC_1	109.5
O1S_1	C1S_1	C2S_1	104(3)
O1^1	Rh2	Rh1	87.2(3)
O1^1	Rh2	O1	174.4(7)
O3^1	Rh2	Rh1	89.1(3)
O3	Rh2	Rh1	89.1(3)
O3^1	Rh2	O1	86.1(5)
O3	Rh2	O1^1	86.1(5)
O3	Rh2	O1	93.8(5)
O3^1	Rh2	O1^1	93.8(5)
O3^1	Rh2	O3	178.2(6)
C1S_1	C2S_1	H2SB_1	109.5
C3S_2	O1S_2	Rh1	107(3)
C1S_1	C2S_1	H2SC_1	109.5
C1	O1	Rh2	116.4(10)
H2SB_1	C2S_1	H2SC_1	109.5
C1	O2	Rh1	117.8(11)
O1S_1	C1S_1	H1SA_1	110.9
C43	O3	Rh2	117.9(10)
O1S_1	C1S_1	H1SB_1	110.9
C43	O4	Rh1	116.6(10)
H1SA_1	C1S_1	H1SB_1	109.0
O1S_1	C3S_1	H3SA_1	106.0
C4S_1	C3S_1	H3SA_1	106.0
O1	C1	C2	115.0(16)

Atom	**Atom**	**Atom**	**Angle/°**
O2	C1	O1	127.6(15)
O2	C1	C2	117.3(16)
O1S_1	C3S_1	H3SB_1	106.0
H4SA_1	C4S_1	H4SB_1	109.5
H3SA_1	C3S_1	H3SB_1	106.3
C3S_1	C4S_1	H4SC_1	109.5
C3S_1	C4S_1	H4SB_1	109.5
H4SB_1	C4S_1	H4SC_1	109.5
C1	C2	C4	118.6(17)
C3	C2	C1	114.8(16)
C3	C2	C4	57.5(13)
C17	C2	C1	115.8(15)
C17	C2	C3	117.5(16)
C17	C2	C4	119.7(15)
H4SA_1	C4S_1	H4SC_1	109.5
C3S_2	O1S_2	C1S_2	122(3)
C1S_2	O1S_2	Rh1	119.8(19)
H2SA_2	C2S_2	H2SB_2	109.5
C1S_2	C2S_2	H2SB_2	109.5
C1S_2	C2S_2	H2SC_2	109.5
C4	C3	C2	63.7(13)
H2SA_2	C2S_2	H2SC_2	109.5
O1S_2	C1S_2	H1SA_2	109.0
O1S_2	C1S_2	C2S_2	112.8(15)
C2S_2	C1S_2	H1SA_2	109.0
C3	C4	C2	58.7(12)
C3	C4	C5B	123(2)
C3	C4	C5A	107(2)
C3	C4	C11	120(2)
O1S_2	C1S_2	H1SB_2	109.0
C4S_2	C3S_2	H3SB_2	109.8
H1SA_2	C1S_2	H1SB_2	107.8
C3S_2	C4S_2	H4SA_2	109.5
O1S_2	C3S_2	H3SA_2	109.8
C3S_2	C4S_2	H4SB_2	109.5
O1S_2	C3S_2	H3SB_2	109.8
H4SA_2	C4S_2	H4SB_2	109.5
H3SA_2	C3S_2	H3SB_2	108.3
C1S_1	O1S_1	Rh2	128.5(18)
O1S_2	Rh1	Rh2	174.5(4)
C3S_1	O1S_1	Rh2	100.4(13)
O1S_1	Rh2	Rh1	174.9(4)
O1	Rh2	O1S_1	89.6(6)
O1^1	Rh2	O1S_1	95.9(6)
O2^1	Rh1	O1S_2	95.0(6)
O2	Rh1	O1S_2	87.3(6)
O3^1	Rh2	O1S_1	94.6(6)
O3	Rh2	O1S_1	87.2(6)
O4	Rh1	O1S_2	88.1(6)
O4^1	Rh1	O1S_2	95.6(6)
C5B	C4	C2	117.3(17)
C5A	C4	C2	111(2)
C11	C4	C2	118.7(18)
C11	C4	C5B	110.6(19)

Atom	Atom	Atom	Angle/°
C11	C4	C5A	124(2)
C6B	C5B	C4	120(2)
C10B	C5B	C4	121(2)
C10B	C5B	C6B	119.1(8)
C7B	C6B	C5B	118.3(8)
C8B	C7B	C6B	122.0(8)
C9B	C8B	C7B	118.9(8)
C8B	C9B	C10B	120.1(9)
C5B	C10B	C9B	121.6(9)
C6A	C5A	C4	111(2)
C10A	C5A	C4	130(2)
C10A	C5A	C6A	118.9(8)
C7A	C6A	C5A	118.4(8)
C8A	C7A	C6A	122.1(8)
C9A	C8A	C7A	118.7(8)
C8A	C9A	C10A	120.0(9)
C5A	C10A	C9A	121.5(9)
C15	C14	C13	119.0(8)
C12	C13	C14	118.3(8)
C11	C12	C13	122.0(8)
C12	C11	C4	121.4(16)
C16	C11	C4	119.8(16)
C16	C11	C12	118.8(8)
C11	C16	C15	120.1(9)
C14	C15	C16	121.6(9)
C18	C17	C2	118.4(14)
C22	C17	C2	121.5(14)
C22	C17	C18	119.0(8)
C19	C18	C17	118.3(8)
C18	C19	C33	118.8(12)
C20	C19	C18	121.9(8)
C20	C19	C33	119.3(12)
C21	C20	C19	118.9(8)
C20	C21	C22	120.0(9)
C20	C21	C23	123.4(13)
C22	C21	C23	116.4(13)
C17	C22	C21	121.6(9)
C24	C23	C21	116.7(15)
C28	C23	C21	123.6(14)
C28	C23	C24	119.0(8)
C25	C24	C23	118.3(8)
C26	C25	C24	122.0(8)
C25	C26	C29	118.9(18)
C27	C26	C25	118.8(8)
C27	C26	C29	121.9(18)
C26	C27	C28	120.1(9)
C23	C28	C27	121.6(9)
C26	C29	C30	113(2)
C26	C29	C31	109(2)
C26	C29	C32	109(2)
C31	C29	C30	110(2)
C32	C29	C30	104(2)
C32	C29	C31	111(3)
C34	C33	C19	118.8(11)

Atom	Atom	Atom	Angle/°
C38	C33	C19	122.2(12)
C38	C33	C34	118.9(8)
C35	C34	C33	118.3(8)
C36	C35	C34	122.1(8)
C35	C36	C39	119.1(14)
C37	C36	C35	118.7(8)
C37	C36	C39	122.2(14)
C36	C37	C38	120.1(9)
C33	C38	C37	121.7(9)
C36	C39	C40	110(2)
C36	C39	C41	113.2(17)
C36	C39	C42	113(2)
C40	C39	C42	102(2)
C41	C39	C40	111(2)
C41	C39	C42	107(2)
O3	C43	O4	127.7(15)
O3	C43	C44	115.3(16)
O4	C43	C44	116.4(16)
C43	C44	C46	117.6(17)
C45	C44	C43	116.7(19)
C45	C44	C46	56.7(13)
C45	C44	C59	121.3(17)
C59	C44	C43	112.9(16)
C59	C44	C46	120.8(17)
C46	C45	C44	65.7(14)
C45	C46	C44	57.6(13)
C45	C46	C47	118(2)
C45	C46	C53	118(2)
C47	C46	C44	110.8(19)
C53	C46	C44	120(2)
C53	C46	C47	118.1(19)
C48	C47	C46	116.0(18)
C52	C47	C46	125.0(18)
C52	C47	C48	119.0(8)
C49	C48	C47	118.2(8)
C50	C49	C48	121.6(9)
C51	C50	C49	118.5(9)
C50	C51	C52	120.0(9)
C47	C52	C51	121.6(9)
C57	C56	C55	119.1(8)
C54	C55	C56	118.3(8)
C53	C54	C55	122.0(8)
C54	C53	C46	124.3(16)
C58	C53	C46	116.7(16)
C58	C53	C54	118.8(8)
C53	C58	C57	120.1(9)
C56	C57	C58	121.7(9)
C60	C59	C44	119.0(14)
C64	C59	C44	121.5(14)
C64	C59	C60	119.1(8)
C61	C60	C59	118.2(8)
C60	C61	C75	115.7(13)
C62	C61	C60	121.8(8)
C62	C61	C75	121.9(13)

Atom	Atom	Atom	Angle/°
C63	C62	C61	118.6(8)
C62	C63	C64	120.0(9)
C62	C63	C65B	123.6(14)
C62	C63	C65A	126.9(14)
C64	C63	C65B	115.1(14)
C64	C63	C65A	113.1(15)
C59	C64	C63	121.6(9)
C66B	C65B	C63	116.2(13)
C70B	C65B	C63	124.2(14)
C70B	C65B	C66B	119.1(8)
C67B	C66B	C65B	118.3(8)
C68B	C67B	C66B	122.0(8)
C67B	C68B	C71B	120.4(9)
C69B	C68B	C67B	118.9(8)
C69B	C68B	C71B	120.7(9)
C68B	C69B	C70B	120.1(9)
C65B	C70B	C69B	121.6(9)
C68B	C71B	C72B	98(3)
C68B	C71B	C73B	105(3)
C68B	C71B	C74B	132(3)
C73B	C71B	C72B	106.0(13)
C74B	C71B	C72B	106.2(13)
C74B	C71B	C73B	106.4(13)
C77	C76	C75	119.2(8)
C76	C75	C61	121.2(13)
C80	C75	C61	120.6(13)
C80	C75	C76	118.2(8)
C79	C80	C75	122.1(8)
C78	C79	C80	119.0(8)
C79	C78	C77	119.9(9)
C79	C78	C81	122.8(15)
C77	C78	C81	117.1(15)
C76	C77	C78	121.7(9)
C78	C81	C82	110.4(19)
C78	C81	C83	111.3(19)
C78	C81	C84	112.2(18)
C82	C81	C83	109(2)
C84	C81	C82	106(2)
C84	C81	C83	107.8(19)
C66A	C65A	C63	122.9(15)
C70A	C65A	C63	116.7(16)
C70A	C65A	C66A	119.0(8)
C67A	C66A	C65A	118.3(8)
C68A	C67A	C66A	122.0(8)
C67A	C68A	C71A	120.5(9)
C69A	C68A	C67A	118.8(8)
C69A	C68A	C71A	120.7(9)
C68A	C69A	C70A	120.2(9)
C65A	C70A	C69A	121.6(9)
C68A	C71A	C73A	111.8(11)
C68A	C71A	C74A	112.9(11)
C68A	C71A	C72A	113.1(11)
C74A	C71A	C73A	105.8(11)
C72A	C71A	C73A	105.9(11)

Atom	Atom	Atom	Angle/°
C72A	C71A	C74A	106.8(11)

Table 5: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **Rh$_2$[*S*-3,5-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	**x**	**y**	**z**	***U*$_{eq}$**
H3A	3150	3699	6921	80
H3B	2492	4016	6746	80
H6B	3867	4430	5696	108
H7B	3293	4691	5133	132
H8B	2110	4628	5077	141
H9B	1475	4300	5585	145
H10B	2034	4037	6151	121
H6A	3537	4094	5638	108
H7A	2844	4383	5128	132
H8A	1726	4655	5230	141
H9A	1259	4593	5843	145
H10A	1979	4398	6368	121
H14	5432	2810	6023	131
H13	5567	3706	5968	130
H12	4643	4236	6146	111
H16	3485	3026	6402	121
H15	4391	2487	6214	137
H18	3671	5187	6211	88
H20	2350	6254	6629	89
H22	2500	4874	7137	82
H24	2201	6457	7325	128
H25	1525	6629	7873	127
H27	627	5266	7794	131
H28	1354	5060	7277	119
H30A	-374	5747	8288	217
H30B	120	5647	8640	217
H30C	245	5362	8247	217
H31A	1461	6050	8544	212
H31B	826	6213	8800	212
H31C	1183	6614	8526	212
H32A	327	6839	8051	220
H32B	-196	6633	8361	220
H32C	-242	6440	7932	220
H34	3484	5624	5651	109
H35	3824	6210	5176	128
H37	3510	7370	5896	99
H38	3207	6793	6384	98
H40A	5045	7146	5268	206
H40B	4855	7229	4831	206
H40C	4752	6690	5022	206
H41A	3478	7848	5356	188
H41B	4097	7971	5077	188
H41C	4242	7828	5510	188
H42A	3626	6788	4718	203
H42B	3797	7356	4608	203
H42C	3121	7229	4841	203
H45A	7029	5208	7118	91
H45B	7735	4899	7008	91
H48	6728	4601	5859	143
H49	7481	4333	5365	182
H50	8577	4040	5518	181
H51	9060	4298	6098	175

Atom	x	y	z	U_{eq}
H52	8359	4667	6573	166
H56	5161	6181	6063	131
H55	4873	5301	6079	119
H54	5719	4715	6277	112
H58	7031	5845	6507	145
H57	6226	6435	6270	177
H60	6636	3676	6430	93
H62	7779	2601	6974	110
H64	7732	4045	7374	100
H66B	8840	3858	7554	134
H67B	9599	3656	8059	164
H69B	8706	2298	8191	147
H70B	7940	2489	7688	145
H72A	10045	2386	8040	235
H72B	9881	2061	8411	235
H72C	10574	2373	8384	235
H73A	9201	2885	9022	235
H73B	9501	2336	8947	235
H73C	8832	2518	8728	235
H74A	10595	3304	8500	235
H74B	10573	2940	8860	235
H74C	10095	3425	8846	235
H76	6652	2135	6702	101
H80	7173	3134	5856	114
H79	6772	2576	5394	111
H77	6279	1582	6239	100
H82A	5314	1416	5776	169
H82B	5213	1412	5325	169
H82C	5208	1932	5552	169
H83A	7010	1133	5480	170
H83B	6308	875	5360	170
H83C	6456	998	5796	170
H84A	6133	2150	5031	177
H84B	6045	1580	4897	177
H84C	6783	1791	5002	177
H66A	8924	3907	7526	134
H67A	9807	3652	7948	164
H69A	8952	2278	8061	147
H70A	8063	2521	7640	145
H73D	10317	2105	8045	235
H73E	10918	2317	8305	235
H73F	10768	2568	7902	235
H74D	9535	2753	8844	235
H74E	10167	2377	8826	235
H74F	9476	2240	8611	235
H72D	10764	3365	8245	235
H72E	10782	3135	8664	235
H72F	10186	3511	8544	235
H2SA	6542	6102	7493	100
H2SB	6049	5731	7721	100
H2SC	6033	6321	7806	100
H1SA	5425	6487	7301	66
H1SB	5740	6023	7066	66
H3SA	4054	5712	7505	64

Atom	x	y	z	U_{eq}
H3SB	4284	5768	7077	64
H4SA	4348	6691	7258	134
H4SB	3792	6513	7561	134
H4SC	3654	6439	7117	134
H2SA	6494	3169	7511	84
H2SB	6404	2605	7658	84
H2SC	5975	3049	7848	84
H1SA	5779	2966	7084	64
H1SB	5536	2480	7312	64
H3SA	4450	3165	7902	150
H3SB	4775	2617	7849	150
H4SA	3980	2689	7246	187
H4SB	3538	2965	7564	187
H4SC	3768	2395	7623	187

Citations

APEX2 suite for crystallographic software, Bruker axs, Madison, WI (2014).

O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

SAINT-8.34A-2013 - Software for the Integration of CCD Detector System Bruker Analytical X-ray Systems, Bruker axs, Madison, WI (2013).

Sheldrick, G.M., A short history of ShelX, *Acta Cryst.*, (2008), **A64**, 339-341.

Sheldrick, G.M., ShelXT, *Acta Cryst.*, (2014), **A71**, 3-8.

6.2 Rh$_2$(R-p-PhTPCP)$_4$

The X-Ray Crystallographic Data of **Catalyst D [Rh$_2$(*R*-*p*-PhTPCP)$_4$]** was reported previously,[6] below is the side, top and bottom view of the structure.

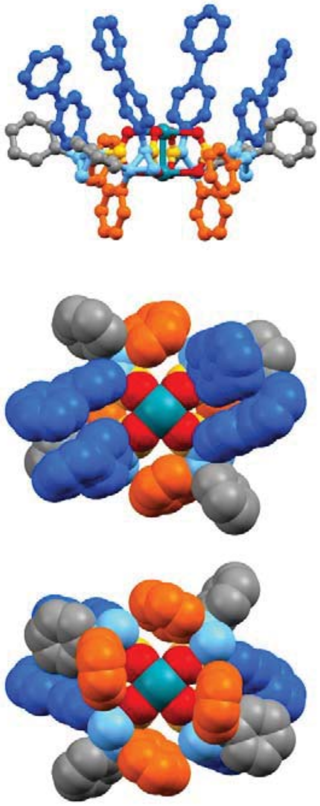


Figure S3. Side, top and bottom view of the Catalyst D [Rh$_2$(*R*-*p*-PhTPCP)$_4$]

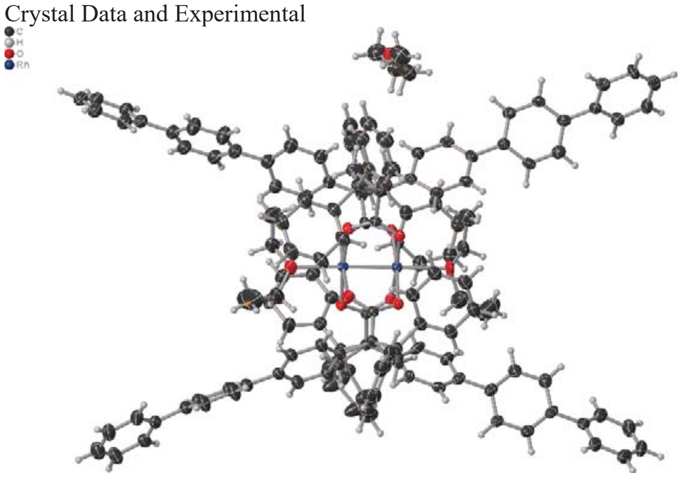
6.3 Rh$_2$(R-p-PhC$_6$H$_4$TPCP)$_4$

Submitted by: **Kuangbiao Liao**
Davies Group, Emory University

Solved by: **John Bacsa**

Sample ID: **Rh$_2$(*R*-*p*-PhC$_6$H$_4$TPCP)$_4$**

Crystal Data and Experimental



Experimental. Single light green plate-shaped crystals of **{Rh$_2$[*R*-*p*-PhC$_6$H$_4$TPCP]$_4$}** was chosen from the sample as supplied.. A suitable crystal (0.10×0.05×0.02 mm^3) was selected and mounted on a loop with paratone oil on an Bruker D8 VENTURE diffractometer diffractometer. The crystal was cooled to T = 100(2) K during data collection. The structure was solved with the XT (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2014/7 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{148}H_{130}O_{11}Rh_2$, M_r = 2290.33, trigonal, P3$_1$ (No. 144), a = 14.66084(10) Å, b = 14.66084(10) Å, c = 48.6185(3) Å, = 90.0°, = 90.0°, = 120.0°, V = 9050.03(11) Å^3, T = 100(2) K, Z = 3, Z' = 1, (CuK) = 2.696 mm^{-1}, 67340 reflections measured, 21512 unique (R_{int} = 0.0743) which were used in all calculations. The final wR_2 was 0.1472 (all data) and R_1 was 0.0565 (I > 2σ(I)).

Compound	**$Rh_2[R\text{-}p\text{-}PhC_6H_4TPCP]_4$**
Formula	$C_{148}H_{130}O_{11}Rh_2$
$D_{calc.}$/ g cm^{-3}	1.261
/mm^{-1}	2.696
Formula Weight	2290.33
Colour	light green
Shape	plate
Size/mm^3	0.10×0.05×0.02
T/K	100(2)
Crystal System	trigonal
Flack Parameter	-0.034(6)
Hooft Parameter	-0.017(5)
Space Group	$P3_1$
a/Å	14.66084(10)
b/Å	14.66084(10)
c/Å	48.6185(3)
/°	90.0
/°	90.0
/°	120.0
V/Å^3	9050.03(11)
Z	3
Z'	1
Wavelength/Å	1.541840
Radiation type	CuK
$_{min}$/°	1.817
$_{max}$/°	67.078
Measured Refl.	67340
Independent Refl.	21512
Reflections with I > 2σ(I)	19806
R_{int}	0.0743
Parameters	1457
Restraints	850
Largest Peak	1.120
Deepest Hole	-0.702
GooF	1.019
wR_2 (all data)	0.1472
wR_2	0.1423
R_1 (all data)	0.0621
R_1	0.0565

Structure Quality Indicators

Reflections:

Refinement:

d min (Cu) 0.84

complete at 2θ=134° 100%

I/σ 8.0

Rint 7.43%

Shift -0.005

-0.034(6)

Max Peak 1.1

Min Peak -0.7

GooF 1.019

A light green plate-shaped crystal with dimensions 0.10×0.05×0.02 mm^3 was mounted on a loop with paratone oil. Data were collected using a Bruker D8 VENTURE diffractometer diffractometer equipped with an Oxford Cryosystems low-temperature device, operating at T = 100(2) K.

Data were measured using and scans with a narrow frame width of 0.5° per frame for 5.0 s using CuK radiation (microfocus sealed tube, 50 kV, 1 mA).The total number of runs and images was based on the strategy calculation from the program **APEX2** (Bruker). The maximum resolution that was achieved was = 67.078°.

The diffraction patterns were indexed using CrysAlisPro (Agilent) and the unit cells were refined using CrysAlisPro (Agilent) on 18119 reflections, 27% of the observed reflections. Data reduction, scaling and absorption corrections were performed using CrysAlisPro (Agilent) and CrysAlisPro 1.171.39.9g (Rigaku Oxford Diffraction, 2015)Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.. The final completeness is 100.00 out to 67.078° in . The absorption coefficient of this material is 2.696 at this wavelength (= 1.54184) and the minimum and maximum transmissions are 0.81432 and 1.00000.

The structure was solved and the space group P3$_1$ (# 144) determined by the XT (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2014/7 of **XL** (Sheldrick, 2008). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_refine_special_details: Refined as a 2-component twin.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 3 and Z' is 1.

The Flack parameter was refined to -0.034(6). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in -0.017(5). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong, and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

Figure 1:

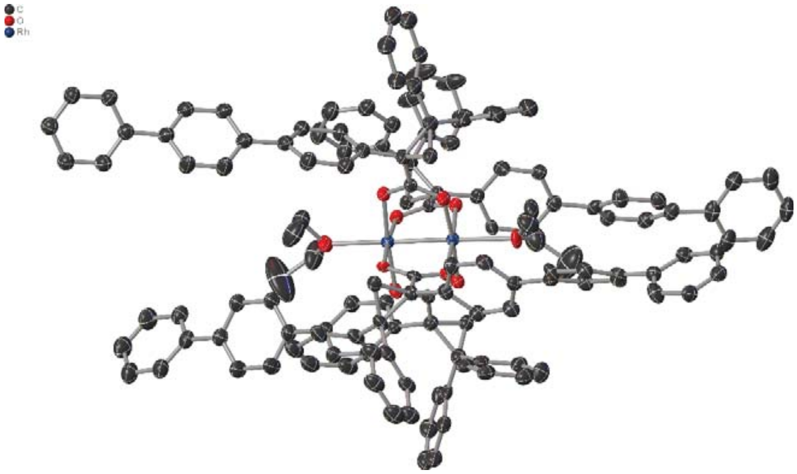


Figure 2:

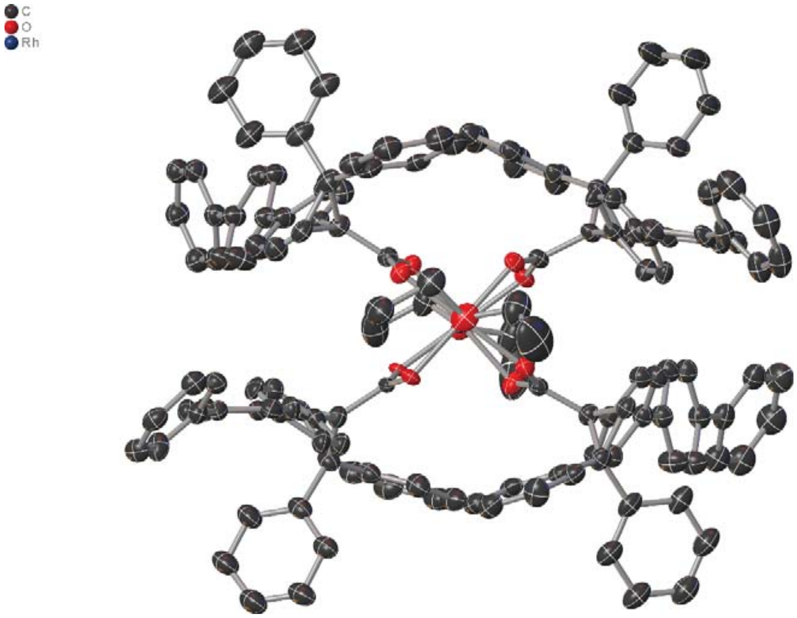


Figure 3:

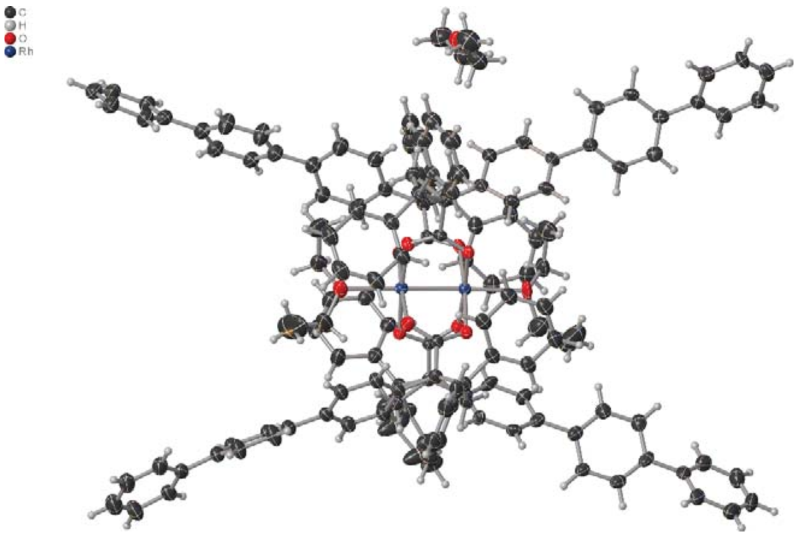
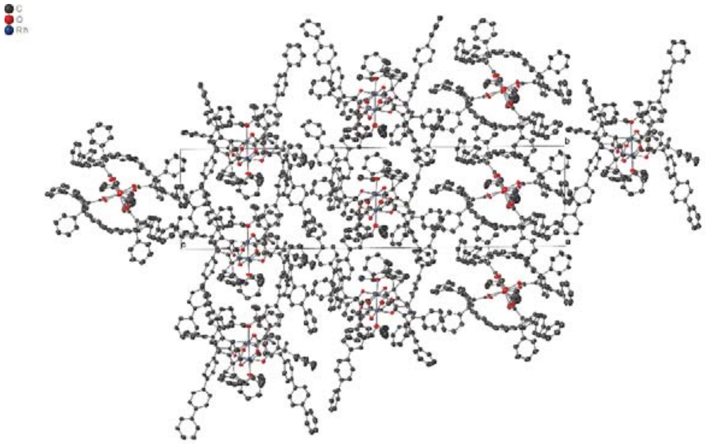
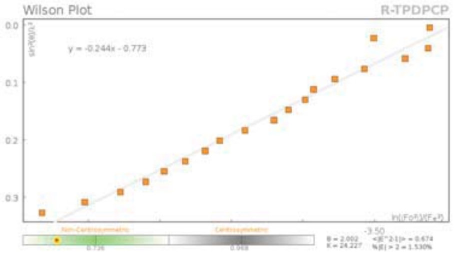
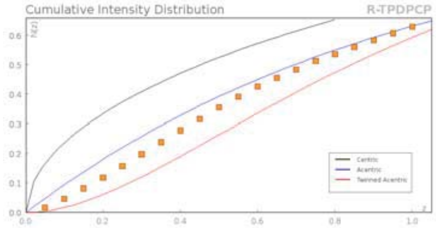


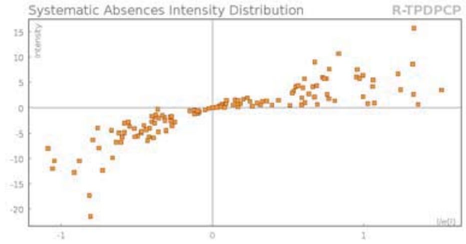
Figure 4:

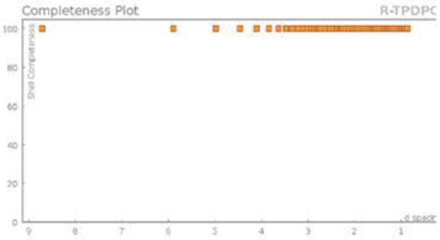


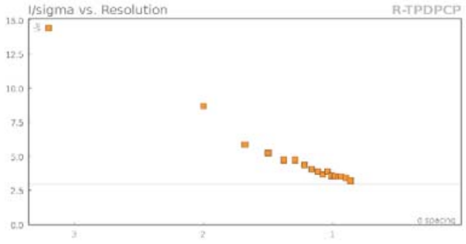
Data Plots: Diffraction Data



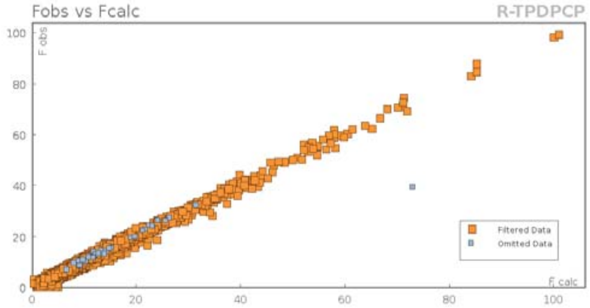


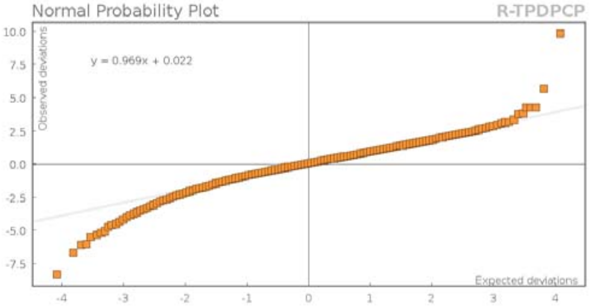

Systematic Absences Intensity Distribution
R-TPDPCP
Intensity
15
10
5
0
-5
-10
-15
-20
-1
0
1
I/σ(I)


Completeness Plot
R-TPDPC
Shell Completeness
100
80
60
40
20
0
9
8
7
6
5
4
3
2
1
d spacing


I/sigma vs. Resolution
R-TPDPCP
15.0
12.5
10.0
7.5
5.0
2.5
0.0
3
2
1
d spacing

Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	67519	Unique reflections	21512
Completeness	0.997	Mean I/	8.04
hkl_{max} collected	(16, 17, 58)	hkl_{min} collected	(-17, -17, -58)
hkl_{max} used	(8, 17, 57)	hkl_{min} used	(-17, 0, -57)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.77
d_{max} used	24.31	d_{min} used	0.84
Friedel pairs	17646	Friedel pairs merged	0
Inconsistent equivalents	3	R_{int}	0.0743
R_{sigma}	0.0977	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	179
Multiplicity	(28168, 14615, 3166, 137, 15)	Maximum multiplicity	10
Removed systematic absences	135	Filtered off (Shel/OMIT)	0

Table 1: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **Rh_2[*R*-*p*-PhC_6H_4TPCP]$_4$**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Rh1	4426.9(5)	3708.2(5)	4929.1(2)	24.40(15)
Rh2	4350.6(6)	5287.3(6)	4914.8(2)	24.87(15)
O2	5726(5)	5948(5)	4695.8(12)	30.3(13)
O3	5940(6)	4555(6)	4788.5(13)	31.0(13)
O4	5070(5)	5670(5)	5285.3(11)	26.7(13)

Atom	x	y	z	*U*$_{eq}$
O5	4831(5)	4032(5)	5331.8(11)	23.9(13)
O6	2983(5)	4516(5)	5131.9(13)	31.2(13)
O7	2923(5)	2958(5)	5063.2(12)	30.4(13)
O8	3640(5)	4827(5)	4543.7(12)	27.6(13)
O9	4023(5)	3513(5)	4522.9(11)	26.5(12)
O1	4314(6)	6845(6)	4895.1(15)	43.3(17)
O10	4523(6)	2194(6)	4935.8(14)	40.2(16)
C7	8047(8)	6962(8)	4500.8(19)	33.5(14)
C5	6190(7)	5421(8)	4668.5(16)	27.4(14)
C6	7100(8)	5802(8)	4470.8(18)	31.0(14)
C8	7265(8)	6677(8)	4273.3(18)	33.2(16)
C9	7999(8)	7628(8)	4731(2)	33.5(16)
C10	7916(8)	7322(9)	5003(2)	38(2)
C11	7979(9)	8007(10)	5212(2)	43(2)
C12	8127(10)	8981(10)	5146(2)	46(2)
C13	8196(10)	9289(10)	4877(2)	50(3)
C14	8129(9)	8609(9)	4668(2)	41(2)
C15	9146(9)	7162(8)	4442(2)	37.2(18)
C16	9434(10)	6970(10)	4184(2)	47(2)
C17	10447(10)	7174(10)	4134(3)	52(2)
C18	11206(11)	7578(10)	4336(3)	54(2)
C19	10946(10)	7772(10)	4592(3)	52(2)
C20	9913(9)	7573(9)	4643(2)	42(2)
C21	7306(8)	4958(8)	4373.7(19)	31.6(15)
C22	6786(8)	4367(8)	4140.2(19)	34.5(18)
C23	6901(9)	3525(8)	4057(2)	35.9(19)
C24	7548(8)	3248(8)	4201.1(18)	31.9(16)
C25	8066(8)	3837(8)	4437.5(19)	33.8(18)
C26	7959(8)	4689(8)	4518.0(19)	34.4(18)
C27	7692(8)	2365(8)	4112.1(19)	34.5(17)
C28	6876(9)	1485(9)	3991(2)	38.3(19)
C29	7003(9)	638(9)	3900(2)	37.2(18)
C30	7979(9)	697(8)	3922.5(19)	35.1(17)
C31	8806(10)	1598(9)	4046(2)	44(2)
C32	8642(9)	2397(9)	4141(2)	45(2)
C33	8162(9)	-126(9)	3804(2)	39.1(18)
C34	8907(10)	-345(9)	3920(2)	44(2)
C35	9129(12)	-1085(10)	3800(3)	56(3)
C36	8560(12)	-1623(11)	3564(3)	61(3)
C37	7843(11)	-1418(10)	3448(3)	54(3)
C38	7627(9)	-676(9)	3569(2)	41(2)
C39	5038(7)	4925(7)	5424.1(16)	22.9(18)
C40	5265(8)	5119(8)	5730.9(18)	29(2)
C42	4867(8)	4129(8)	5904.3(18)	32(2)
C41	6034(8)	4803(8)	5860.8(18)	31.9(16)
C43	6554(9)	4347(9)	5685.7(19)	36.3(17)
C44	6458(9)	3400(10)	5766(2)	43(2)
C45	6999(11)	2991(11)	5615(3)	56(3)
C46	7600(10)	3537(11)	5391(3)	52(2)
C47	7710(9)	4493(10)	5312(2)	46(2)
C48	7176(9)	4898(10)	5461(2)	40(2)
C49	6739(9)	5442(9)	6096.3(19)	36.0(17)
C50	7686(9)	6339(9)	6047(2)	40(2)
C51	8414(10)	6871(11)	6253(2)	50(2)
C52	8163(11)	6486(12)	6519(2)	54(3)

Atom	x	y	z	*U_{eq}*
C53	7230(11)	5603(12)	6575(2)	54(3)
C54	6508(10)	5069(11)	6363(2)	46(2)
C55	5140(8)	6002(8)	5838.9(17)	30(2)
C56	5817(8)	7052(8)	5770.6(18)	35(2)
C57	5629(8)	7855(9)	5855.8(19)	36(2)
C58	4746(8)	7616(8)	6018.2(17)	32(2)
C59	4086(8)	6582(9)	6089.5(19)	34(2)
C60	4268(8)	5793(9)	6001.2(19)	34(2)
C61	4541(8)	8468(8)	6112.4(19)	33(2)
C62	4756(9)	9326(9)	5946.6(18)	36(2)
C63	4611(9)	10149(9)	6041.9(19)	36(2)
C64	4245(8)	10120(9)	6312.5(19)	32(2)
C65	4011(8)	9256(9)	6470.8(19)	34(2)
C66	4137(8)	8427(9)	6376.6(19)	35(2)
C67	4138(8)	10999(9)	6420.3(19)	34(2)
C68	3685(8)	11471(8)	6272(2)	37(2)
C69	3559(9)	12270(8)	6380(2)	40(2)
C70	3935(9)	12655(9)	6643(2)	42(3)
C71	4409(9)	12221(9)	6793(2)	41(2)
C72	4508(9)	11390(9)	6688(2)	38(2)
C73	2572(8)	3524(8)	5163.7(17)	28.3(14)
C74	1617(8)	2973(8)	5347.4(19)	33.7(15)
C76	1436(8)	3654(9)	5545(2)	36.0(18)
C75	683(9)	3187(9)	5309(2)	36.9(15)
C77	742(8)	3945(9)	5081(2)	36.5(18)
C78	979(8)	3835(9)	4816(2)	40(2)
C79	933(9)	4474(9)	4611(2)	43(2)
C80	676(10)	5246(10)	4680(3)	49(2)
C81	476(10)	5365(10)	4950(3)	49(2)
C82	513(8)	4718(9)	5151(2)	40.2(19)
C83	-442(9)	2297(9)	5358(3)	43.2(19)
C84	-814(10)	1831(10)	5613(3)	51(2)
C85	-1846(10)	1084(10)	5659(3)	57(3)
C86	-2551(11)	782(10)	5440(3)	57(2)
C87	-2214(10)	1209(10)	5181(3)	56(3)
C88	-1174(9)	1952(9)	5142(3)	47(2)
C89	1371(8)	1906(9)	5443(2)	35.2(16)
C90	1578(10)	1730(9)	5708(2)	45(2)
C91	1403(10)	741(9)	5796(2)	44(2)
C92	1033(9)	-102(9)	5606(2)	38.9(19)
C93	821(9)	78(9)	5339(2)	37(2)
C94	976(9)	1055(8)	5260(2)	37(2)
C95	900(9)	-1134(9)	5691(2)	40(2)
C96	173(9)	-2052(9)	5561(2)	41(2)
C97	45(9)	-3026(9)	5642(2)	40(2)
C98	637(9)	-3111(9)	5850(2)	39.1(18)
C99	1393(10)	-2178(9)	5975(2)	47(3)
C100	1516(11)	-1219(10)	5899(3)	52(3)
C101	478(9)	-4148(9)	5942.1(19)	37.0(17)
C102	-522(9)	-5030(9)	5952(2)	38.9(19)
C103	-660(10)	-5977(9)	6046(2)	41.7(19)
C104	192(9)	-6076(10)	6128(2)	42.1(19)
C105	1189(9)	-5195(9)	6115(2)	41.3(19)
C106	1342(9)	-4242(9)	6019(2)	39.7(18)
C107	3766(7)	4138(7)	4418.0(17)	26.4(16)

Atom	x	y	z	U_{eq}
C108	3637(8)	4105(8)	4105.9(17)	29.1(15)
C110	4028(8)	3467(8)	3949.0(17)	30.4(15)
C109	2867(8)	3028(8)	3974.5(17)	31.1(14)
C111	2245(8)	2124(8)	4167.2(19)	36.0(17)
C112	1484(9)	2123(9)	4337.5(19)	37.1(18)
C113	862(9)	1266(9)	4502(2)	42(2)
C114	979(11)	388(10)	4498(3)	52(3)
C115	1733(12)	379(11)	4335(3)	59(3)
C116	2366(11)	1238(10)	4165(3)	51(3)
C117	2253(8)	2980(9)	3715.0(18)	37(2)
C118	2652(9)	3659(10)	3501(2)	43(2)
C119	2082(10)	3571(11)	3267(2)	51(3)
C120	1101(12)	2774(15)	3235(3)	87(6)
C121	674(13)	1948(15)	3438(3)	97(7)
C122	1242(11)	2091(12)	3677(2)	67(4)
C123	3796(8)	5123(8)	3991.0(17)	28.9(18)
C124	4781(8)	5901(8)	3904.0(18)	31(2)
C125	4959(9)	6876(8)	3816.2(18)	33(2)
C126	4134(8)	7103(8)	3819.6(18)	31(2)
C127	3153(9)	6323(9)	3914.2(19)	37(2)
C128	2983(8)	5368(9)	3999(2)	36(2)
C129	4307(8)	8154(8)	3727.2(19)	34(2)
C130	4824(8)	8593(8)	3478.5(19)	33(2)
C131	4951(8)	9550(8)	3391.8(19)	37(2)
C132	4556(9)	10087(8)	3542(2)	38(2)
C133	4053(9)	9638(9)	3789(2)	39(2)
C134	3931(10)	8702(9)	3880(2)	42(3)
C135	4636(10)	11066(9)	3437.1(18)	40(3)
C136	3767(11)	11200(9)	3433(2)	47(3)
C137	3805(12)	12084(10)	3313(2)	55(3)
C138	4755(13)	12856(10)	3207(3)	59(4)
C139	5624(12)	12762(10)	3216(2)	53(3)
C140	5574(10)	11862(9)	3328(2)	45(3)
C1	3398(9)	6831(11)	5005(2)	51(3)
C2	3513(12)	6971(13)	5310(3)	65(4)
C3	4521(15)	7247(12)	4618(2)	82(4)
C4	5252(19)	8421(12)	4594(4)	122(8)
C141	5044(16)	2048(12)	4707(3)	94(5)
C142	5550(30)	1370(30)	4715(7)	242(17)
C143	3695(10)	1269(9)	5061(3)	54(3)
C144	3840(14)	1348(14)	5366(3)	79(5)
O11	3609(8)	4669(8)	6878.2(17)	55.6(19)
C145	4605(11)	5574(13)	6823(3)	64(3)
C146	5332(13)	5654(15)	7049(3)	78(4)
C147	2836(10)	4482(11)	6678(2)	56(3)
C148	1842(11)	3472(11)	6735(3)	63(3)

Table 2: Anisotropic Displacement Parameters (×10^4) **Rh_2[*R*-*p*-PhC_6H_4TPCP]$_4$**. The anisotropic displacement factor exponent takes the form: $-2\ {}^{2}[h^2a^{*2} \times U_{11} + \ldots + 2hka^{*} \times b^{*} \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh1	24.8(3)	25.0(3)	24.1(3)	-0.2(2)	0.2(2)	13.0(3)
Rh2	26.6(4)	25.6(4)	24.0(2)	-1.4(2)	-1.1(2)	14.3(3)
O2	32(3)	32(3)	30(3)	-2(2)	-1(2)	18(3)
O3	32(3)	35(3)	33(3)	2(2)	4(2)	22(2)
O4	31(4)	29(3)	20(2)	-4(2)	-2(2)	15(3)
O5	25(3)	27(3)	19(2)	-6(2)	-8(2)	12(3)
O6	33(3)	33(2)	35(3)	-2(2)	4(2)	22(2)
O7	30(3)	28(3)	36(3)	1(2)	5(2)	17(3)
O8	32(4)	27(3)	25(2)	-3(2)	-7(2)	16(3)
O9	31(3)	27(3)	21(2)	-5.1(19)	-7(2)	14(3)
O1	48(4)	38(4)	56(3)	-6(3)	-3(3)	31(3)
O10	42(4)	31(3)	53(3)	3(3)	9(3)	23(3)
C7	32(2)	30(3)	38(2)	0.3(19)	5.4(18)	16(2)
C5	29(3)	30(3)	25(3)	-2(2)	-3(2)	16(2)
C6	32(3)	30(3)	31(3)	0.3(19)	3(2)	16(2)
C8	35(4)	31(3)	34(3)	2(2)	5(2)	17(3)
C9	22(4)	33(3)	44(2)	-6(2)	1(2)	12(3)
C10	31(5)	38(4)	43(3)	-5(2)	1(2)	14(4)
C11	33(6)	46(4)	49(3)	-11(3)	-1(3)	18(4)
C12	39(6)	45(4)	53(3)	-11(3)	-1(3)	20(4)
C13	53(7)	44(4)	54(3)	-10(3)	1(3)	27(4)
C14	38(6)	37(3)	48(3)	-5(2)	2(3)	20(3)
C15	33(3)	25(4)	55(3)	7(3)	13(2)	15(3)
C16	44(4)	40(6)	58(3)	5(3)	19(2)	22(3)
C17	45(4)	41(6)	72(4)	12(3)	24(3)	24(4)
C18	47(4)	42(6)	78(4)	10(4)	19(3)	24(4)
C19	39(3)	44(6)	76(4)	8(4)	13(3)	24(3)
C20	36(3)	31(5)	60(3)	2(3)	8(2)	18(3)
C21	32(4)	29(3)	33(3)	1(2)	5(2)	15(3)
C22	36(4)	33(3)	35(3)	-2(3)	2(3)	18(3)
C23	37(4)	35(4)	37(3)	-5(3)	0(3)	19(3)
C24	29(4)	30(3)	35(3)	-2(2)	4(3)	13(3)
C25	33(4)	33(3)	36(3)	-4(3)	1(3)	17(3)
C26	38(4)	35(4)	33(3)	-4(3)	2(3)	20(3)
C27	35(3)	33(3)	37(4)	-7(3)	-2(3)	18(3)
C28	37(3)	35(3)	45(4)	-10(3)	-5(3)	19(3)
C29	40(3)	33(3)	39(4)	-7(3)	-3(3)	19(3)
C30	41(3)	31(3)	34(3)	-2(3)	0(3)	19(3)
C31	41(3)	39(3)	57(5)	-14(3)	-7(3)	23(3)
C32	38(3)	39(4)	62(6)	-19(4)	-11(3)	22(3)
C33	46(4)	30(3)	42(3)	1(3)	6(3)	20(3)
C34	49(5)	35(4)	52(4)	3(3)	4(3)	23(4)
C35	65(6)	43(5)	68(4)	-4(4)	3(4)	33(5)
C36	68(6)	51(6)	71(5)	-9(4)	1(5)	36(5)
C37	62(6)	45(5)	59(4)	-10(4)	5(4)	30(5)
C38	44(4)	33(4)	43(3)	-1(3)	7(3)	17(4)
C39	17(4)	34(5)	21(4)	-5(3)	-4(3)	15(4)
C40	34(5)	32(5)	27(4)	0(4)	2(4)	22(5)
C42	35(6)	31(5)	31(4)	2(4)	-1(4)	17(5)
C41	37(3)	37(4)	29(2)	0(2)	-4(2)	24(3)
C43	36(4)	42(3)	37(3)	-9(2)	-6(3)	24(3)
C44	40(5)	43(4)	54(4)	-6(3)	-8(3)	26(4)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C45	50(6)	56(4)	71(4)	-12(3)	-3(4)	34(4)
C46	42(5)	54(4)	64(4)	-18(3)	-9(4)	27(4)
C47	39(5)	55(4)	48(4)	-19(3)	-6(3)	26(4)
C48	42(4)	47(4)	38(3)	-6(3)	-2(3)	26(4)
C49	40(3)	48(4)	34(2)	-9(2)	-7(2)	33(3)
C50	41(3)	49(4)	39(3)	-10(3)	-5(2)	30(3)
C51	49(4)	62(5)	46(3)	-17(3)	-13(3)	34(3)
C52	57(4)	72(5)	46(3)	-15(3)	-12(3)	40(4)
C53	57(4)	75(5)	39(3)	-11(3)	-13(3)	40(4)
C54	51(4)	63(5)	34(2)	-4(3)	-6(2)	35(4)
C55	30(5)	37(5)	25(4)	-1(4)	-1(4)	20(5)
C56	34(6)	40(6)	31(4)	-1(4)	6(4)	20(5)
C57	34(6)	45(6)	31(4)	-1(4)	8(4)	21(5)
C58	38(6)	35(5)	27(4)	-4(4)	-2(4)	21(5)
C59	24(5)	45(6)	37(4)	1(4)	5(4)	20(5)
C60	34(6)	35(6)	38(4)	-2(4)	2(4)	19(5)
C61	30(5)	39(6)	33(4)	-1(4)	0(4)	20(5)
C62	47(6)	46(6)	27(4)	0(4)	2(4)	31(6)
C63	38(6)	39(6)	33(4)	1(4)	-3(4)	21(5)
C64	26(5)	39(6)	33(4)	0(4)	-2(4)	17(5)
C65	35(6)	42(6)	33(4)	5(4)	9(4)	25(5)
C66	37(6)	44(6)	30(4)	3(4)	4(4)	25(5)
C67	32(6)	38(6)	33(4)	4(4)	7(4)	17(5)
C68	32(6)	35(6)	39(5)	-1(4)	-1(4)	13(5)
C69	41(6)	30(5)	49(5)	8(4)	1(5)	17(5)
C70	36(6)	34(6)	56(6)	0(5)	8(5)	16(5)
C71	38(6)	42(6)	45(5)	-9(5)	1(5)	22(5)
C72	36(6)	46(6)	39(5)	1(5)	5(4)	26(5)
C73	28(3)	33(2)	28(3)	-2(2)	-1(2)	19(2)
C74	32(3)	36(3)	36(3)	0(2)	5(2)	20(2)
C76	33(4)	36(4)	41(3)	0(3)	8(3)	19(3)
C75	33(3)	35(3)	47(3)	-2(2)	4.0(19)	20(2)
C77	23(5)	33(3)	52(3)	-1(2)	-3(2)	13(3)
C78	31(5)	40(4)	52(3)	-2(2)	-3(3)	19(4)
C79	30(5)	44(4)	56(3)	1(3)	-5(3)	18(4)
C80	38(6)	47(5)	65(3)	3(3)	-2(3)	23(5)
C81	41(6)	43(4)	66(3)	4(3)	0(3)	25(5)
C82	26(5)	33(4)	61(3)	-3(3)	-2(3)	14(4)
C83	32(3)	34(4)	69(3)	-2(3)	10(2)	21(3)
C84	42(4)	41(4)	70(3)	2(3)	15(3)	22(3)
C85	42(4)	44(5)	85(4)	3(3)	18(3)	21(3)
C86	43(4)	43(5)	89(4)	-1(3)	15(3)	24(3)
C87	36(3)	43(5)	87(4)	-1(3)	9(3)	18(3)
C88	35(3)	38(4)	73(4)	-2(3)	6(2)	21(3)
C89	31(4)	36(3)	41(3)	0.7(19)	2(2)	18(2)
C90	49(6)	40(3)	44(3)	0(2)	-4(3)	21(3)
C91	47(6)	40(3)	42(3)	0(2)	-7(3)	20(3)
C92	35(5)	38(3)	41(3)	2(2)	-3(3)	16(3)
C93	35(5)	36(3)	39(3)	2(2)	-3(3)	17(3)
C94	37(5)	36(3)	38(3)	3(2)	0(3)	18(3)
C95	35(4)	38(3)	43(3)	3(2)	-6(3)	16(2)
C96	36(4)	39(3)	44(4)	2(2)	-6(3)	16(3)
C97	35(4)	40(3)	43(3)	4(2)	-3(3)	16(3)
C98	36(4)	38(3)	42(3)	1(2)	-5(3)	17(2)
C99	47(5)	37(3)	53(4)	1(2)	-16(4)	18(3)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C100	54(5)	38(3)	59(5)	-1(3)	-23(5)	19(3)
C101	38(3)	38(3)	34(4)	1(2)	-2(2)	19(2)
C102	39(3)	39(3)	38(4)	-1(3)	0(3)	18(2)
C103	43(4)	39(3)	42(4)	0(3)	-1(3)	20(3)
C104	44(4)	44(4)	39(4)	1(3)	1(3)	23(3)
C105	43(4)	44(3)	38(4)	3(3)	-1(3)	23(3)
C106	41(3)	43(3)	37(4)	1(3)	-1(3)	22(3)
C107	28(4)	25(3)	25(2)	-2.6(18)	-4(2)	12(3)
C108	32(4)	28(3)	25(2)	-2.9(17)	-4.7(19)	14(3)
C110	36(3)	29(3)	25(3)	-3(2)	-4(2)	16(3)
C109	35(3)	29(3)	27(2)	-4.8(17)	-5.1(18)	15(2)
C111	39(4)	33(3)	31(3)	-2(2)	-6(2)	14(3)
C112	40(4)	34(3)	32(3)	-1(3)	-4(3)	14(3)
C113	43(4)	37(4)	37(3)	3(3)	-3(3)	14(3)
C114	56(5)	41(4)	55(5)	9(3)	7(4)	21(4)
C115	67(6)	43(4)	68(6)	15(4)	18(5)	28(4)
C116	58(5)	38(3)	57(5)	8(3)	11(4)	25(4)
C117	34(3)	44(4)	29(2)	0(2)	-4(2)	17(3)
C118	36(4)	51(4)	35(3)	5(3)	-5(2)	16(3)
C119	37(4)	65(6)	35(3)	11(3)	-5(3)	14(4)
C120	49(5)	101(7)	50(5)	29(5)	-17(4)	-7(5)
C121	62(6)	101(7)	53(5)	30(5)	-25(5)	-17(6)
C122	49(4)	68(5)	41(4)	13(4)	-14(3)	-2(4)
C123	33(5)	28(3)	23(3)	-4(2)	-5(3)	14(3)
C124	32(5)	28(5)	32(4)	3(4)	5(4)	15(4)
C125	34(6)	35(5)	28(4)	-1(4)	2(4)	15(5)
C126	33(5)	27(5)	28(4)	-2(4)	-4(4)	12(4)
C127	40(6)	38(6)	37(5)	6(4)	2(4)	23(5)
C128	24(5)	37(6)	40(5)	7(4)	1(4)	10(5)
C129	33(5)	33(6)	34(4)	-1(4)	-5(4)	14(5)
C130	34(6)	27(5)	38(4)	-2(4)	-3(4)	16(5)
C131	34(6)	34(6)	32(4)	2(4)	-2(4)	9(5)
C132	45(6)	26(5)	37(4)	-3(4)	-9(4)	12(5)
C133	45(6)	37(6)	37(5)	-7(4)	-5(4)	23(5)
C134	49(7)	43(7)	33(5)	0(4)	0(4)	22(6)
C135	50(7)	31(6)	27(4)	-6(4)	-5(4)	12(5)
C136	58(8)	32(6)	50(6)	-1(5)	-5(5)	23(6)
C137	76(10)	42(7)	53(6)	-5(5)	-9(6)	35(7)
C138	90(11)	32(7)	54(6)	2(5)	-4(7)	30(7)
C139	74(9)	29(6)	47(6)	-3(5)	3(6)	19(6)
C140	58(8)	34(6)	37(5)	0(4)	3(5)	18(6)
C1	54(5)	53(7)	59(4)	-6(4)	-3(3)	38(5)
C2	68(8)	80(10)	60(4)	-10(4)	-2(4)	46(8)
C3	101(9)	89(8)	69(4)	14(4)	13(4)	58(7)
C4	155(17)	86(7)	98(9)	24(6)	8(10)	41(8)
C141	118(11)	46(7)	111(7)	5(5)	70(8)	37(7)
C142	370(40)	260(30)	240(20)	121(19)	200(20)	280(30)
C143	55(5)	40(4)	67(5)	10(4)	17(4)	24(4)
C144	82(10)	69(9)	65(4)	13(4)	15(4)	21(8)
O11	62(4)	70(5)	50(3)	-4(3)	0(3)	45(3)
C145	61(4)	73(6)	68(5)	-11(4)	6(3)	41(4)
C146	72(6)	95(9)	78(6)	-18(6)	-6(5)	52(6)
C147	60(4)	72(6)	46(4)	3(4)	4(3)	42(4)
C148	62(5)	78(6)	53(6)	7(5)	0(4)	38(4)

Table 3: Bond Lengths in Å for **Rh$_2$[*R*-*p*-PhC$_6$H$_4$TPCP]$_4$**.

Atom	**Atom**	**Length/Å**
Rh1	Rh2	2.3740(9)
Rh1	O3	2.043(7)
Rh1	O5	2.032(5)
Rh1	O7	2.017(7)
Rh1	O9	2.041(5)
Rh1	O10	2.294(7)
Rh2	O2	2.046(7)
Rh2	O4	2.020(6)
Rh2	O6	2.036(7)
Rh2	O8	2.023(6)
Rh2	O1	2.313(7)
O2	C5	1.266(12)
O3	C5	1.273(12)
O4	C39	1.264(11)
O5	C39	1.268(11)
O6	C73	1.275(12)
O7	C73	1.273(12)
O8	C107	1.271(11)
O9	C107	1.258(11)
O1	C1	1.436(8)
O1	C3	1.439(6)
O10	C141	1.424(10)
O10	C143	1.427(10)
C7	C6	1.575(14)
C7	C8	1.495(14)
C7	C9	1.511(13)
C7	C15	1.514(14)
C5	C6	1.507(13)
C6	C8	1.522(13)
C6	C21	1.488(14)
C9	C10	1.383(15)
C9	C14	1.388(15)
C10	C11	1.395(15)
C11	C12	1.370(17)
C12	C13	1.371(17)
C13	C14	1.394(15)
C15	C16	1.398(15)
C15	C20	1.380(16)
C16	C17	1.383(16)
C17	C18	1.38(2)
C18	C19	1.373(18)
C19	C20	1.415(16)
C21	C22	1.400(14)
C21	C26	1.394(14)
C22	C23	1.388(14)
C23	C24	1.393(15)
C24	C25	1.410(13)
C24	C27	1.477(14)
C25	C26	1.391(14)
C27	C28	1.378(15)
C27	C32	1.377(16)
C28	C29	1.415(15)

Atom	Atom	Length/Å
C29	C30	1.394(15)
C30	C31	1.404(15)
C30	C33	1.478(15)
C31	C32	1.388(15)
C33	C34	1.403(16)
C33	C38	1.390(15)
C34	C35	1.405(17)
C35	C36	1.406(19)
C36	C37	1.351(19)
C37	C38	1.405(16)
C39	C40	1.524(11)
C40	C42	1.520(13)
C40	C41	1.552(13)
C40	C55	1.491(13)
C42	C41	1.502(15)
C41	C43	1.503(14)
C41	C49	1.512(13)
C43	C44	1.380(16)
C43	C48	1.394(15)
C44	C45	1.416(17)
C45	C46	1.379(19)
C46	C47	1.383(19)
C47	C48	1.397(15)
C49	C50	1.375(17)
C49	C54	1.383(15)
C50	C51	1.387(15)
C51	C52	1.383(17)
C52	C53	1.36(2)
C53	C54	1.401(16)
C55	C56	1.392(15)
C55	C60	1.399(14)
C56	C57	1.399(15)
C57	C58	1.403(14)
C58	C59	1.374(15)
C58	C61	1.496(14)
C59	C60	1.378(15)
C61	C62	1.390(14)
C61	C66	1.403(13)
C62	C63	1.405(15)
C63	C64	1.413(13)
C64	C65	1.372(15)
C64	C67	1.470(15)
C65	C66	1.394(15)
C67	C68	1.377(15)
C67	C72	1.417(14)
C68	C69	1.378(16)
C69	C70	1.395(16)
C70	C71	1.365(16)
C71	C72	1.395(15)
C73	C74	1.510(13)
C74	C76	1.501(13)
C74	C75	1.561(14)
C74	C89	1.492(14)
C76	C75	1.499(14)

Atom	Atom	Length/Å
C75	C77	1.540(15)
C75	C83	1.525(16)
C77	C78	1.367(15)
C77	C82	1.376(15)
C78	C79	1.393(15)
C79	C80	1.401(17)
C80	C81	1.375(17)
C81	C82	1.383(16)
C83	C84	1.388(17)
C83	C88	1.404(18)
C84	C85	1.371(18)
C85	C86	1.39(2)
C86	C87	1.384(19)
C87	C88	1.374(17)
C89	C90	1.381(14)
C89	C94	1.399(15)
C90	C91	1.406(16)
C91	C92	1.414(15)
C92	C93	1.394(14)
C92	C95	1.482(15)
C93	C94	1.387(15)
C95	C96	1.383(15)
C95	C100	1.405(15)
C96	C97	1.400(15)
C97	C98	1.378(14)
C98	C99	1.398(16)
C98	C101	1.487(15)
C99	C100	1.375(17)
C101	C102	1.388(15)
C101	C106	1.393(16)
C102	C103	1.378(16)
C103	C104	1.386(16)
C104	C105	1.386(17)
C105	C106	1.380(16)
C107	C108	1.527(11)
C108	C110	1.523(13)
C108	C109	1.547(13)
C108	C123	1.500(13)
C110	C109	1.495(14)
C109	C111	1.502(14)
C109	C117	1.531(12)
C111	C112	1.389(15)
C111	C116	1.396(16)
C112	C113	1.379(15)
C113	C114	1.382(17)
C114	C115	1.366(19)
C115	C116	1.399(17)
C117	C118	1.356(15)
C117	C122	1.414(17)
C118	C119	1.379(14)
C119	C120	1.332(19)
C120	C121	1.44(2)
C121	C122	1.384(17)
C123	C124	1.384(14)

Atom	**Atom**	**Length/Å**
C123	C128	1.407(15)
C124	C125	1.385(14)
C125	C126	1.406(15)
C126	C127	1.394(15)
C126	C129	1.499(14)
C127	C128	1.357(15)
C129	C130	1.401(14)
C129	C134	1.394(15)
C130	C131	1.386(15)
C131	C132	1.393(16)
C132	C133	1.392(15)
C132	C135	1.473(15)
C133	C134	1.366(16)
C135	C136	1.383(18)
C135	C140	1.390(16)
C136	C137	1.396(16)
C137	C138	1.38(2)
C138	C139	1.35(2)
C139	C140	1.395(17)
C1	C2	1.495(17)
C3	C4	1.510(7)
C141	C142	1.506(7)
C143	C144	1.495(18)
O11	C145	1.424(18)
O11	C147	1.411(15)
C145	C146	1.494(15)
C147	C148	1.494(15)

Table 4: Bond Angles in ° for **Rh_2[*R*-*p*-PhC_6H_4TPCP]$_4$**.

Atom	Atom	Atom	Angle/°
O3	Rh1	Rh2	87.9(2)
O3	Rh1	O10	91.1(3)
O5	Rh1	Rh2	87.17(18)
O5	Rh1	O3	94.5(3)
O5	Rh1	O9	174.6(3)
O5	Rh1	O10	93.5(3)
O7	Rh1	Rh2	88.25(19)
O7	Rh1	O3	176.1(3)
O7	Rh1	O5	85.9(3)
O7	Rh1	O9	94.3(3)
O7	Rh1	O10	92.7(3)
O9	Rh1	Rh2	87.48(18)
O9	Rh1	O3	85.0(3)
O9	Rh1	O10	91.9(3)
O10	Rh1	Rh2	178.88(17)
O2	Rh2	Rh1	87.75(19)
O2	Rh2	O1	90.9(3)
O4	Rh2	Rh1	88.38(19)
O4	Rh2	O2	94.5(3)
O4	Rh2	O6	85.7(3)
O4	Rh2	O8	176.6(3)
O4	Rh2	O1	91.7(3)
O6	Rh2	Rh1	87.51(19)
O6	Rh2	O2	175.2(3)
O6	Rh2	O1	93.9(3)
O8	Rh2	Rh1	88.18(19)
O8	Rh2	O2	85.1(3)
O8	Rh2	O6	94.4(3)
O8	Rh2	O1	91.7(3)
O1	Rh2	Rh1	178.6(2)
C5	O2	Rh2	118.0(6)
C5	O3	Rh1	116.3(6)
C39	O4	Rh2	116.6(5)
C39	O5	Rh1	118.3(5)
C73	O6	Rh2	118.0(6)
C73	O7	Rh1	117.2(6)
C107	O8	Rh2	116.0(6)
C107	O9	Rh1	117.5(5)
C1	O1	Rh2	117.0(7)
C1	O1	C3	111.0(11)
C3	O1	Rh2	109.8(8)
C141	O10	Rh1	115.5(7)
C141	O10	C143	117.1(10)
C143	O10	Rh1	119.4(7)
C8	C7	C6	59.4(6)
C8	C7	C9	116.9(9)
C8	C7	C15	120.6(8)
C9	C7	C6	117.8(8)
C9	C7	C15	113.8(9)
C15	C7	C6	118.0(9)
O2	C5	O3	125.9(9)

Atom	Atom	Atom	Angle/°
O2	C5	C6	119.1(9)
O3	C5	C6	115.0(9)
C5	C6	C7	118.7(8)
C5	C6	C8	116.9(9)
C8	C6	C7	57.7(6)
C21	C6	C7	119.4(9)
C21	C6	C5	113.8(9)
C21	C6	C8	119.2(8)
C7	C8	C6	63.0(7)
C10	C9	C7	121.7(10)
C10	C9	C14	119.5(10)
C14	C9	C7	118.6(9)
C9	C10	C11	119.8(11)
C12	C11	C10	120.0(11)
C13	C12	C11	120.8(11)
C12	C13	C14	119.6(12)
C9	C14	C13	120.2(11)
C16	C15	C7	121.9(10)
C20	C15	C7	120.5(9)
C20	C15	C16	117.6(11)
C17	C16	C15	121.0(12)
C18	C17	C16	121.1(12)
C19	C18	C17	119.3(12)
C18	C19	C20	119.7(13)
C15	C20	C19	121.4(11)
C22	C21	C6	119.8(9)
C26	C21	C6	121.9(9)
C26	C21	C22	118.1(9)
C23	C22	C21	121.1(10)
C22	C23	C24	121.1(9)
C23	C24	C25	117.9(9)
C23	C24	C27	121.6(9)
C25	C24	C27	120.4(9)
C26	C25	C24	120.7(10)
C25	C26	C21	121.0(9)
C28	C27	C24	120.6(10)
C32	C27	C24	121.7(10)
C32	C27	C28	117.7(10)
C27	C28	C29	121.4(10)
C30	C29	C28	120.2(10)
C29	C30	C31	117.9(10)
C29	C30	C33	121.3(10)
C31	C30	C33	120.7(10)
C32	C31	C30	120.3(11)
C27	C32	C31	122.4(11)
C34	C33	C30	120.6(10)
C38	C33	C30	121.0(10)
C38	C33	C34	118.4(10)
C33	C34	C35	121.1(12)
C34	C35	C36	118.0(13)
C37	C36	C35	121.7(13)
C36	C37	C38	119.9(12)
C33	C38	C37	120.9(12)
O4	C39	O5	126.1(7)

Atom	Atom	Atom	Angle/°
O4	C39	C40	116.8(8)
O5	C39	C40	117.1(8)
C39	C40	C41	117.8(8)
C42	C40	C39	114.9(8)
C42	C40	C41	58.6(7)
C55	C40	C39	113.4(8)
C55	C40	C42	118.6(8)
C55	C40	C41	122.6(8)
C41	C42	C40	61.8(7)
C42	C41	C40	59.7(6)
C42	C41	C43	116.8(9)
C42	C41	C49	120.1(8)
C43	C41	C40	120.5(8)
C43	C41	C49	111.3(9)
C49	C41	C40	119.8(8)
C44	C43	C41	117.9(10)
C44	C43	C48	120.8(10)
C48	C43	C41	121.1(10)
C43	C44	C45	118.8(12)
C46	C45	C44	119.7(13)
C45	C46	C47	121.5(12)
C46	C47	C48	118.9(12)
C43	C48	C47	120.2(11)
C50	C49	C41	120.7(9)
C50	C49	C54	118.2(10)
C54	C49	C41	120.6(11)
C49	C50	C51	122.4(11)
C52	C51	C50	118.2(13)
C53	C52	C51	120.8(12)
C52	C53	C54	120.1(12)
C49	C54	C53	120.1(13)
C56	C55	C40	123.2(9)
C56	C55	C60	116.4(9)
C60	C55	C40	120.3(9)
C55	C56	C57	121.9(9)
C56	C57	C58	120.1(10)
C57	C58	C61	120.6(10)
C59	C58	C57	118.0(10)
C59	C58	C61	121.3(9)
C58	C59	C60	121.5(9)
C59	C60	C55	122.1(10)
C62	C61	C58	121.9(8)
C62	C61	C66	118.0(10)
C66	C61	C58	120.1(9)
C61	C62	C63	121.5(9)
C62	C63	C64	120.0(10)
C63	C64	C67	120.7(9)
C65	C64	C63	117.8(10)
C65	C64	C67	121.5(9)
C64	C65	C66	122.7(9)
C65	C66	C61	120.0(10)
C68	C67	C64	123.0(9)
C68	C67	C72	117.4(10)
C72	C67	C64	119.7(9)

Atom	Atom	Atom	Angle/°
C67	C68	C69	122.2(10)
C68	C69	C70	119.9(10)
C71	C70	C69	119.5(11)
C70	C71	C72	120.8(10)
C71	C72	C67	120.3(10)
O6	C73	C74	117.7(8)
O7	C73	O6	125.6(9)
O7	C73	C74	116.6(9)
C73	C74	C75	119.5(9)
C76	C74	C73	116.6(9)
C76	C74	C75	58.6(7)
C89	C74	C73	114.7(9)
C89	C74	C76	117.9(8)
C89	C74	C75	118.1(9)
C75	C76	C74	62.7(7)
C76	C75	C74	58.7(6)
C76	C75	C77	117.2(9)
C76	C75	C83	120.4(9)
C77	C75	C74	119.5(9)
C83	C75	C74	119.4(9)
C83	C75	C77	112.1(9)
C78	C77	C75	121.2(10)
C78	C77	C82	120.8(11)
C82	C77	C75	118.0(10)
C77	C78	C79	119.8(11)
C78	C79	C80	119.6(11)
C81	C80	C79	119.5(12)
C80	C81	C82	120.3(12)
C77	C82	C81	119.9(11)
C84	C83	C75	123.5(11)
C84	C83	C88	116.7(11)
C88	C83	C75	119.7(11)
C85	C84	C83	123.0(13)
C84	C85	C86	118.4(14)
C87	C86	C85	120.8(13)
C88	C87	C86	119.3(14)
C87	C88	C83	121.8(13)
C90	C89	C74	121.7(10)
C90	C89	C94	117.2(10)
C94	C89	C74	120.9(9)
C89	C90	C91	122.1(11)
C90	C91	C92	119.8(10)
C91	C92	C95	120.6(9)
C93	C92	C91	117.8(10)
C93	C92	C95	121.5(10)
C94	C93	C92	121.0(10)
C93	C94	C89	121.9(9)
C96	C95	C92	120.8(10)
C96	C95	C100	117.4(11)
C100	C95	C92	121.8(10)
C95	C96	C97	120.5(10)
C98	C97	C96	122.1(11)
C97	C98	C99	117.2(11)
C97	C98	C101	122.0(10)

Atom	Atom	Atom	Angle/°
C99	C98	C101	120.8(10)
C100	C99	C98	121.2(11)
C99	C100	C95	121.5(11)
C102	C101	C98	121.0(10)
C102	C101	C106	119.2(11)
C106	C101	C98	119.8(10)
C103	C102	C101	120.3(11)
C102	C103	C104	121.0(11)
C103	C104	C105	118.3(11)
C106	C105	C104	121.4(11)
C105	C106	C101	119.7(11)
O8	C107	C108	116.0(8)
O9	C107	O8	126.8(8)
O9	C107	C108	117.2(8)
C107	C108	C109	117.3(8)
C110	C108	C107	116.0(8)
C110	C108	C109	58.3(6)
C123	C108	C107	112.5(8)
C123	C108	C110	120.4(8)
C123	C108	C109	122.2(8)
C109	C110	C108	61.7(6)
C110	C109	C108	60.1(6)
C110	C109	C111	119.4(9)
C110	C109	C117	117.9(8)
C111	C109	C108	117.0(7)
C111	C109	C117	113.0(8)
C117	C109	C108	119.9(8)
C112	C111	C109	120.3(10)
C112	C111	C116	118.6(10)
C116	C111	C109	120.9(10)
C113	C112	C111	120.7(11)
C112	C113	C114	120.5(12)
C115	C114	C113	119.7(12)
C114	C115	C116	120.6(13)
C111	C116	C115	119.8(12)
C118	C117	C109	125.0(10)
C118	C117	C122	116.4(9)
C122	C117	C109	118.1(9)
C117	C118	C119	123.2(11)
C120	C119	C118	120.9(11)
C119	C120	C121	119.0(12)
C122	C121	C120	118.1(14)
C121	C122	C117	121.6(12)
C124	C123	C108	120.8(9)
C124	C123	C128	117.8(9)
C128	C123	C108	121.0(9)
C123	C124	C125	121.7(10)
C124	C125	C126	120.0(10)
C125	C126	C129	121.1(9)
C127	C126	C125	117.8(10)
C127	C126	C129	121.1(10)
C128	C127	C126	121.9(10)
C127	C128	C123	120.9(10)
C130	C129	C126	120.3(9)

Atom	Atom	Atom	Angle/°
C134	C129	C126	121.4(9)
C134	C129	C130	118.3(10)
C131	C130	C129	119.7(10)
C130	C131	C132	122.0(9)
C131	C132	C135	121.2(10)
C133	C132	C131	117.2(10)
C133	C132	C135	121.6(10)
C134	C133	C132	121.7(10)
C133	C134	C129	121.1(10)
C136	C135	C132	121.0(11)
C136	C135	C140	118.1(11)
C140	C135	C132	120.9(11)
C135	C136	C137	121.7(13)
C138	C137	C136	118.2(14)
C139	C138	C137	121.4(12)
C138	C139	C140	120.2(13)
C135	C140	C139	120.4(13)
O1	C1	C2	109.1(10)
O1	C3	C4	115.1(13)
O10	C141	C142	123.8(16)
O10	C143	C144	109.3(11)
C147	O11	C145	113.6(11)
O11	C145	C146	107.0(13)
O11	C147	C148	110.9(11)

Table 5: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **Rh_2[*R*-*p*-PhC_6H_4TPCP]$_4$**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H8A	7502	6649	4084	40
H8B	6766	6945	4285	40
H10	7815	6648	5049	46
H11	7921	7798	5399	51
H12	8181	9448	5289	56
H13	8290	9963	4834	59
H14	8171	8818	4481	49
H16	8925	6696	4041	57
H17	10623	7032	3957	62
H18	11901	7721	4299	65
H19	11459	8038	4735	62
H20	9743	7726	4819	50
H22	6346	4546	4037	41
H23	6534	3132	3899	43
H25	8493	3650	4543	41
H26	8336	5093	4674	41
H28	6214	1447	3967	46
H29	6421	27	3824	45
H31	9481	1661	4064	53
H32	9205	2988	4230	54
H34	9268	12	4083	53
H35	9648	-1219	3876	67
H36	8682	-2143	3484	73

Atom	x	y	z	U_{eq}
H37	7486	-1776	3285	65
H38	7109	-550	3490	49
H42A	4588	4132	6090	38
H42B	4501	3442	5808	38
H44	6036	3029	5920	52
H45	6948	2343	5668	67
H46	7948	3249	5288	63
H47	8141	4869	5160	55
H48	7238	5551	5408	48
H50	7848	6605	5864	48
H51	9068	7484	6213	59
H52	8648	6842	6663	65
H53	7067	5347	6758	65
H54	5859	4451	6403	55
H56	6424	7228	5663	41
H57	6101	8563	5804	43
H59	3492	6406	6202	41
H60	3786	5086	6052	41
H62	5005	9355	5765	44
H63	4759	10725	5925	43
H65	3754	9221	6652	41
H66	3948	7834	6491	42
H68	3452	11238	6090	45
H69	3216	12559	6276	48
H70	3862	13214	6717	51
H71	4675	12488	6972	49
H72	4826	11084	6796	45
H76A	1172	3366	5731	43
H76B	1939	4421	5540	43
H78	1174	3324	4772	49
H79	1076	4387	4425	52
H80	641	5684	4541	59
H81	312	5894	4998	58
H82	379	4807	5338	48
H84	-333	2040	5762	61
H85	-2074	780	5836	68
H86	-3272	277	5469	68
H87	-2696	990	5032	67
H88	-944	2241	4963	57
H90	1847	2295	5836	54
H91	1533	639	5982	52
H93	565	-478	5208	45
H94	810	1149	5077	44
H96	-243	-2023	5415	49
H97	-466	-3646	5551	49
H99	1830	-2207	6115	56
H100	2030	-600	5990	62
H102	-1113	-4980	5894	47
H103	-1349	-6571	6055	50
H104	95	-6731	6192	51
H105	1780	-5248	6173	50
H106	2034	-3654	6005	48
H11A	4352	3732	3766	36
H11B	4348	3126	4057	36

Atom	x	y	z	U_{eq}
H112	1391	2720	4341	45
H113	348	1279	4618	50
H114	538	-206	4608	62
H115	1829	-216	4336	71
H116	2878	1219	4049	61
H118	3358	4223	3512	51
H119	2393	4085	3126	61
H120	691	2751	3082	104
H121	19	1323	3408	117
H122	946	1578	3819	80
H124	5348	5762	3904	37
H125	5639	7390	3754	40
H127	2587	6464	3920	45
H128	2306	4858	4064	43
H130	5086	8235	3370	39
H131	5319	9849	3225	45
H133	3787	9992	3898	46
H134	3584	8420	4050	50
H136	3127	10678	3514	56
H137	3194	12151	3303	65
H138	4797	13468	3127	71
H139	6272	13311	3145	63
H140	6184	11793	3329	54
H1A	2760	6153	4961	61
H1B	3321	7406	4922	61
H2A	4187	7600	5353	98
H2B	3491	6352	5393	98
H2C	2935	7053	5384	98
H3A	3842	7066	4530	98
H3B	4828	6884	4514	98
H4A	5787	8562	4453	183
H4B	5597	8702	4771	183
H4C	4847	8759	4541	183
H14A	5600	2759	4650	112
H14B	4523	1771	4556	112
H14C	5209	803	4581	363
H14D	5473	1073	4900	363
H14E	6301	1805	4671	363
H14F	3706	639	4993	65
H14G	3006	1197	5013	65
H14H	4557	1510	5411	119
H14I	3333	676	5451	119
H14J	3724	1908	5437	119
H14K	4539	6214	6818	77
H14L	4877	5499	6643	77
H14M	5684	5259	6998	116
H14N	4927	5359	7218	116
H14O	5860	6395	7078	116
H14P	3105	4450	6494	67
H14Q	2688	5071	6679	67
H14R	1308	3374	6599	95
H14S	1587	3495	6919	95
H14T	1979	2884	6723	95

Citations

APEX2 suite for crystallographic software, Bruker axs, Madison, WI (2015).

O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

Sheldrick, G.M., A short history of ShelX, *Acta Cryst.*, (2008), **A64**, 339-341.

```
#==============================================================================
====
# PLATON/CHECK-( 70414) versus check.def version of 310314   for Entry: r-tpdpcp
# Data: R-TPDPCP.cif - Type: CIF                Bond Precision   C-C = 0.0175 A
# Refl: R-TPDPCP.fcf - Type: LIST4                           Temp = 100 K
#                                   X-Ray        Nref/Npar =   7.4
# Cell14.66084(10)14.66084(10)  48.6185(3)          90          90         120
# Wavelength 1.54184    Volume Reported   9050.03(11)   Calculated   9050.03(16)
# SpaceGroup from Symmetry P 31       Hall: P 31                trigonal
#               Reported P 31             P 31                trigonal
# MoietyFormula C144 H120 O10 Rh2, C4 H10 O
#      Reported C144 H120 O10 Rh2, C4 H10 O
#    SumFormula C148 H130 O11 Rh2
#      Reported C148 H130 O11 Rh2
# Mr        =   2290.35[Calc],   2290.33[Rep]
# Dx,gcm-3  =     1.261[Calc],     1.261[Rep]
# Z         =         3[Calc],         3[Rep]
# Mu (mm-1) =     2.696[Calc],     2.696[Rep]
# F000      =    3588.0[Calc],    3588.0[Rep]  or F000' =   3597.90[Calc]
# Reported   T Limits: Tmin=0.814             Tmax=1.000  AbsCorr=MULTI-SCAN
# Calculated T Limits: Tmin=0.851 Tmin'=0.764  Tmax=0.948
# Reported   Hmax= 17, Kmax= 17, Lmax= 58, Nref=  21512        , Th(max)= 67.078
# Obs in FCF Hmax= 17, Kmax= 17, Lmax= 57, Nref=  21512[ 10774], Th(max)= 67.077
# Calculated Hmax= 17, Kmax= 17, Lmax= 58, Nref=  21580[ 10790], Ratio=1.99/1.00
# Reported   Rho(min) = -0.70, Rho(max) =  1.12 e/Ang**3 (From CIF)
# w=1/[sigma**2(Fo**2)+(0.0711P)**2], P=(Fo**2+2*Fc**2)/3
# R= 0.0565( 19806), wR2= 0.1472( 21512), S = 1.019      (From FCF data only)
# R= 0.0565( 19806), wR2= 0.1472( 21512), S = 1.019, Npar= 1457, Flack -0.034(6)
#==============================================================================
====
For Documentation: http://http://www.platonsoft.nl/CIF-VALIDATION.pdf
#==============================================================================
====

#==============================================================================
====
>>> The Following Improvement and Query ALERTS were generated - (Acta-Mode) <<<
#==============================================================================
====
Format: alert-number_ALERT_alert-type_alert-level text

222_ALERT_3_A Large Non-Solvent    H    Uiso(max)/Uiso(min) ..       10.0 Ratio
#==============================================================================
====
220_ALERT_2_B Large Non-Solvent  C     Ueq(max)/Ueq(min) Range       10.0 Ratio
601_ALERT_2_B Structure Contains Solvent Accessible VOIDS of .       104 Ang3
#==============================================================================
====
090_ALERT_3_C Poor Data / Parameter Ratio (Zmax > 18) ........       7.39 Note
213_ALERT_2_C Atom C142           has ADP max/min Ratio .....        3.7 prolat
241_ALERT_2_C High       Ueq as Compared to Neighbors for .....       C121 Check
242_ALERT_2_C Low        Ueq as Compared to Neighbors for .....        O10 Check
242_ALERT_2_C Low        Ueq as Compared to Neighbors for .....       C141 Check
342_ALERT_3_C Low Bond Precision on  C-C Bonds ..............     0.0175 Ang.
```

```
911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L=  0.597        16 Why ?
#=========================================================================
====
002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         12 Note
003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...        119 Why ?
008_ALERT_5_G No _iucr_refine_reflections_details   in the CIF     Please Do !
033_ALERT_4_G Flack x Value Deviates > 2*sigma from Zero .....     -0.034
143_ALERT_4_G su on c - Axis Small or Missing ...............    0.00030 Ang.
152_ALERT_1_G The Supplied and Calc. Volume s.u. Differ by ...          5 Units
760_ALERT_1_G CIF Contains no Torsion Angles ................          ? Info
791_ALERT_4_G The Model has Chirality at C6      ............          R Verify
791_ALERT_4_G The Model has Chirality at C40     ............          R Verify
791_ALERT_4_G The Model has Chirality at C74     ............          R Verify
791_ALERT_4_G The Model has Chirality at C108    ............          R Verify
802_ALERT_4_G CIF Input Record(s) with more than 80 Characters          ! Info
860_ALERT_3_G Number of Least-Squares Restraints ............        850 Note
870_ALERT_4_G ALERTS Related to Twinning Effects Suppressed ..          ! Info
909_ALERT_3_G Percentage of Observed Data at Theta(Max) still          78%
931_ALERT_5_G Found Twin Law ( 1-2  0)[       ] Estimated BASF       0.12 Check
#=========================================================================
====

ALERT_Level and ALERT_Type Summary
=================================
1 ALERT_Level_A = Most Likely a Serious Problem - Resolve or Explain
2 ALERT_Level_B = A Potentially Serious Problem - Consider Carefully
7 ALERT_Level_C = Check. Ensure it is Not caused by an Omission or Oversight
16 ALERT_Level_G = General Info/Check that it is not Something Unexpected

2 ALERT_Type_1 CIF Construction/Syntax Error, Inconsistent or Missing Data.
8 ALERT_Type_2 Indicator that the Structure Model may be Wrong or Deficient.
6 ALERT_Type_3 Indicator that the Structure Quality may be Low.
8 ALERT_Type_4 Improvement, Methodology, Query or Suggestion.
2 ALERT_Type_5 Informative Message, Check.
#=========================================================================
====

2 Missing  Experimental  Info Issue(s) (Out of  54 Tests) -   96% Satisfied
1 Experimental  Data  Related Issue(s) (Out of  28 Tests) -   96% Satisfied
12 Structural  Model   Related Issue(s) (Out of 117 Tests) -   90% Satisfied
9 Unresolved or to be Checked Issue(s) (Out of 223 Tests) -   96% Satisfied

#=========================================================================
====
```

6.4 Rh_2(R-TCPTAD)$_4$

Rh_2(*R*-TCPTAD)$_4$

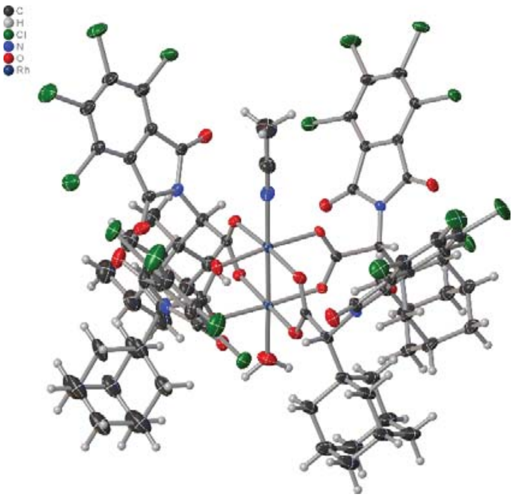
Submitted by: **Kuangbiao Liao**

Emory University

Solved by: **Thomas C. Pickel**

Sample ID: **Rh_2(*R*-TCPTAD)$_4$**

Crystal Data and Experimental



Experimental. Single violet needle-shaped crystals of [**Rh_2(*R*-TCPTAD)$_4$**] were crystallised by vapour diffusion. The major component was MeCN and ethyl ether; the minor methylene chloride and MeOH. A suitable crystal (0.70×0.50×0.40 mm^3) was selected and mounted on a loop with paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was cooled to T = 100(2) K during data collection. The structure was solved with the **XT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2014/7 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{86}H_{77}Cl_{24}N_5O_{17}Rh_2$, M_r = 2509.14, monoclinic, P2_1 (No. 4), a = 13.9309(2) Å, b = 23.4777(4) Å, c = 19.4295(4) Å, = 90.0°, = 97.9250(17)°, = 90.0°, V = 6294.0(2) Å^3, T = 100(2) K, Z = 2, Z' = 1, (MoK) = 0.824 mm^{-1}, 157466 reflections measured, 38220 unique (R_{int} = 0.0523) which were used in all calculations. The final wR_2 was 0.1590 (all data) and R_1 was 0.0641 (I > 2σ(I)).

Compound	**Rh_2(*R*-TCPTAD)$_4$**
Formula	$C_{86}H_{77}Cl_{24}N_5O_{17}Rh_2$
$D_{calc.}$/ g cm^{-3}	1.324
/mm^{-1}	0.824
Formula Weight	2509.14
Colour	violet
Shape	needle
Size/mm^3	0.70×0.50×0.40
T/K	100(2)
Crystal System	monoclinic
Flack Parameter	-0.007(8)
Hooft Parameter	-0.005(5)
Space Group	$P2_1$
a/Å	13.9309(2)
b/Å	23.4777(4)
c/Å	19.4295(4)
/°	90.0
/°	97.9250(17)
/°	90.0
V/Å^3	6294.0(2)
Z	2
Z'	1
Wavelength/Å	0.710730
Radiation type	MoK
$_{min}$/°	1.693
$_{max}$/°	30.508
Measured Refl.	157466
Independent Refl.	38220
Reflections with I > 2σ(I)	32915
R_{int}	0.0523
Parameters	1203
Restraints	1130
Largest Peak	1.919
Deepest Hole	-1.069
GooF	1.043

wR_2 (all data)	0.1590
wR_2	0.1513
R_1 (all data)	0.0770
R_1	0.0641

Structure Quality Indicators

Reflections:
d min (Mo) 0.70
I/σ 22.9
Rint 5.23%
complete 100%

Refinement:
Shift 0.000
Max Peak 1.9
Min Peak -1.1
GooF 1.043
-0.007(8)

A violet needle-shaped crystal with dimensions 0.70×0.50×0.40 mm^3 was mounted on a loop with paratone oil. Data were collected using a APEX2 Mo source diffractometer equipped with an Oxford Cryosystems low-temperature device, operating at T = 100(2) K.

Data were measured using scans of 0.5° per frame for 20.0 s using MoK radiation (fine-focus sealed tube, 45 kV, 35 mA).The total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Agilent). The maximum resolution that was achieved was = 30.508°.

The diffraction patterns were indexed using CrysAlisPro (Agilent) and the unit cells were refined using CrysAlisPro (Agilent) on 65720 reflections, 42 % of the observed reflections. Data reduction, scaling and absorption corrections were performed using CrysAlisPro (Agilent) and CrysAlisPro 1.171.39.9g (Rigaku Oxford Diffraction, 2015). An empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm was used. The final completeness is 99.8% out to 30.508° in . The absorption coefficient of this material is 0.824 mm^{-1} at this wavelength (= 0.71073 Å) and the minimum and maximum transmissions are 0.72898 and 1.00.

The structure was solved and the space group P2$_1$ (# 4) determined by the **XT** (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2014/7 of **XL** (Sheldrick, 2008). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

The structure contains regions of diffuse and disordered solvent. These volumes were treated using Platon SQUEEZE (Spek, 2015).

The Flack parameter was refined to -0.007(8). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in -0.005(5). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

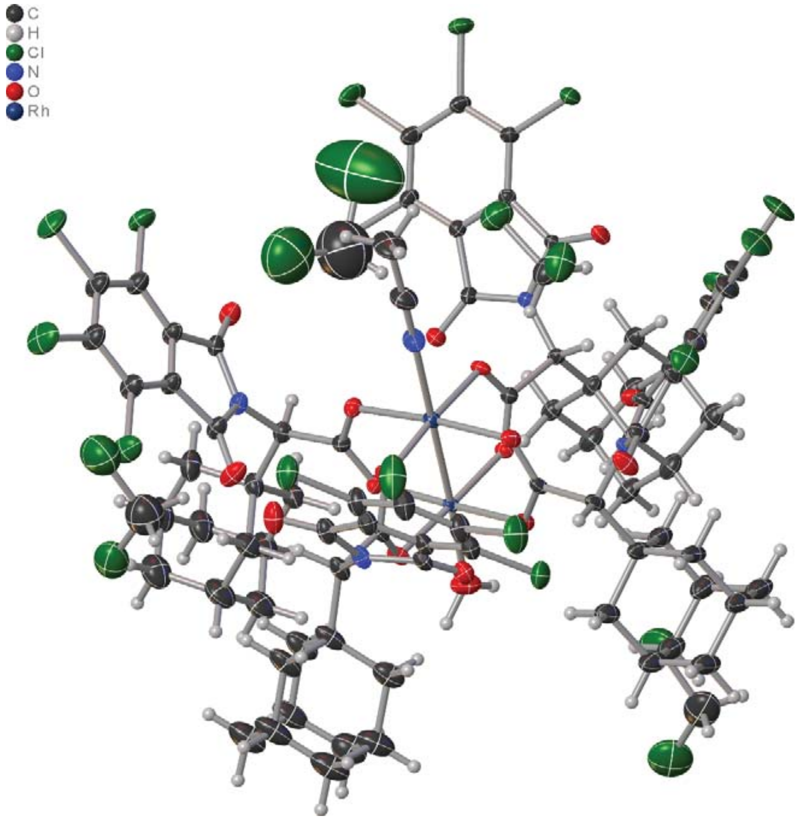


Figure 1:

Plot of the asymmetric unit with solvent molecules.

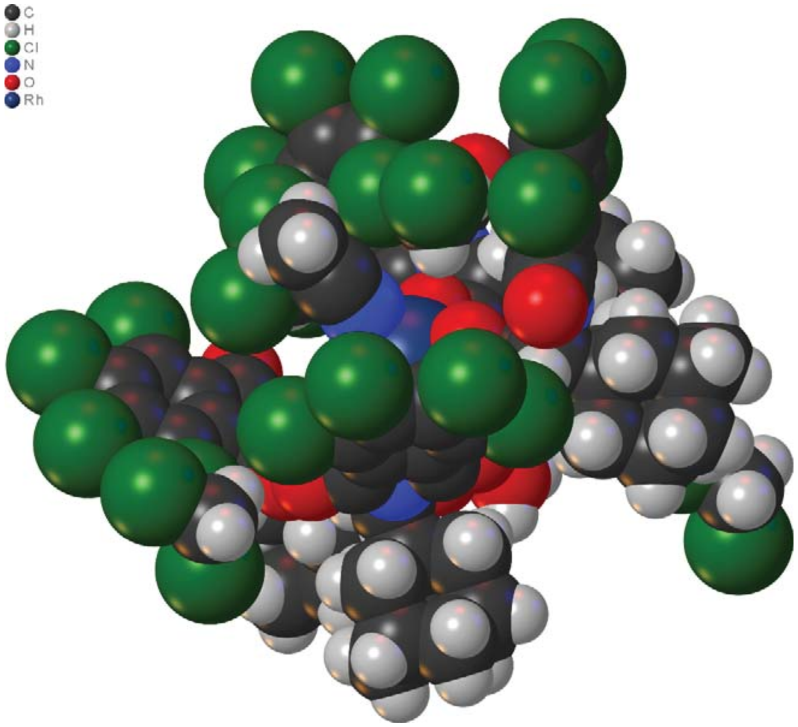


Figure 2:

Space filling plot of the asymmetric unit with solvent molecules.

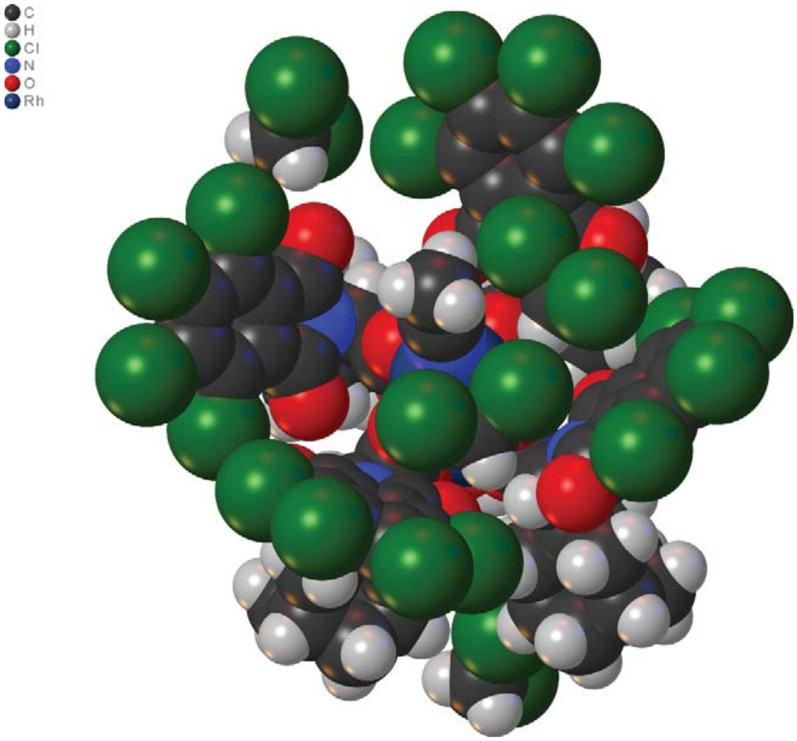


Figure 3:

Space filling plot of the asymmetric unit showing how the cup shaped cavity encapsulates solvent molecules.

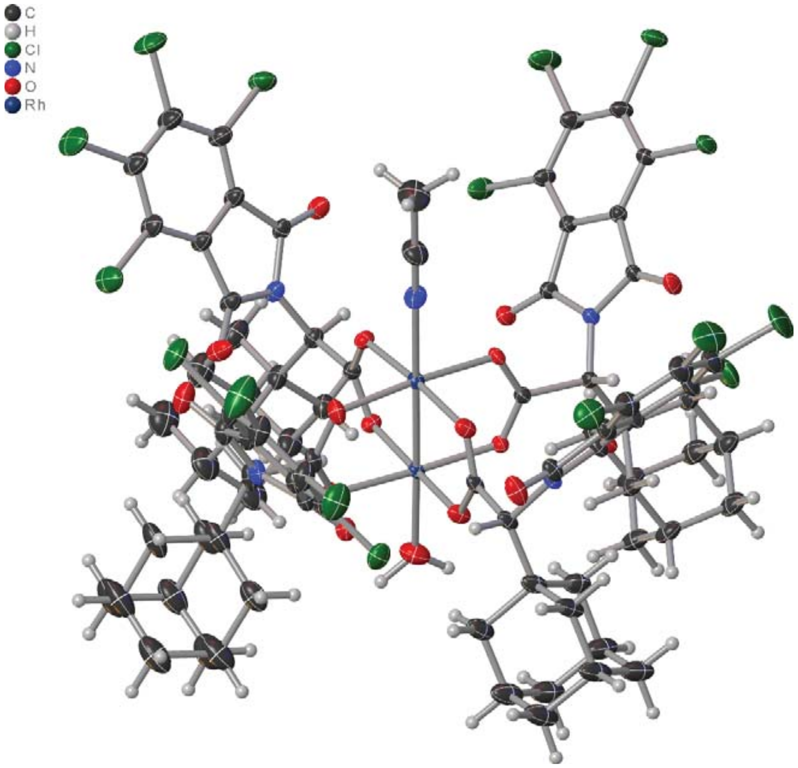


Figure 4:

Thermal ellipsoid plot of the asymmetric unit without solvent molecules for clarity.

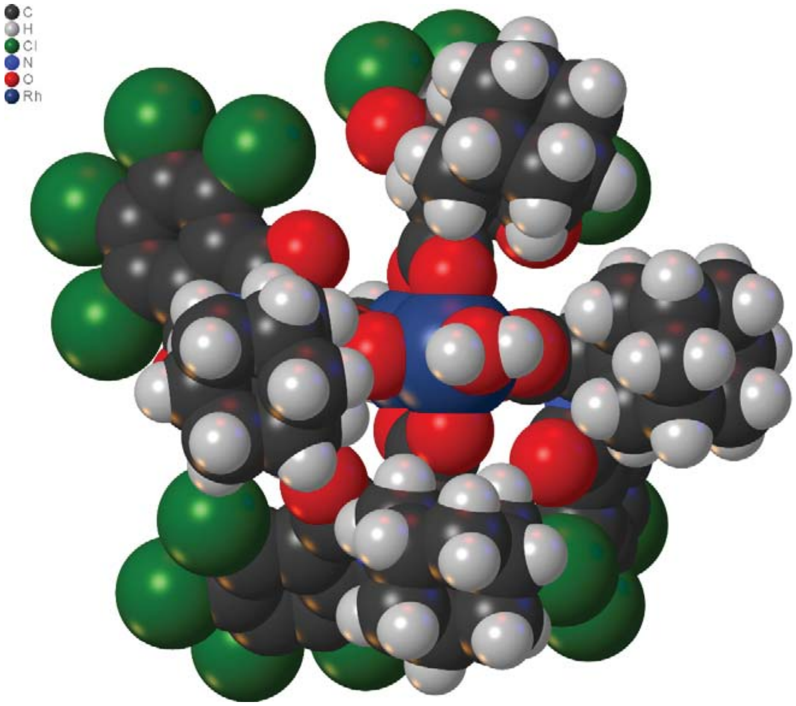


Figure 5:

Space filling plot of the asymmetric unit without solvent molecules for clarity.

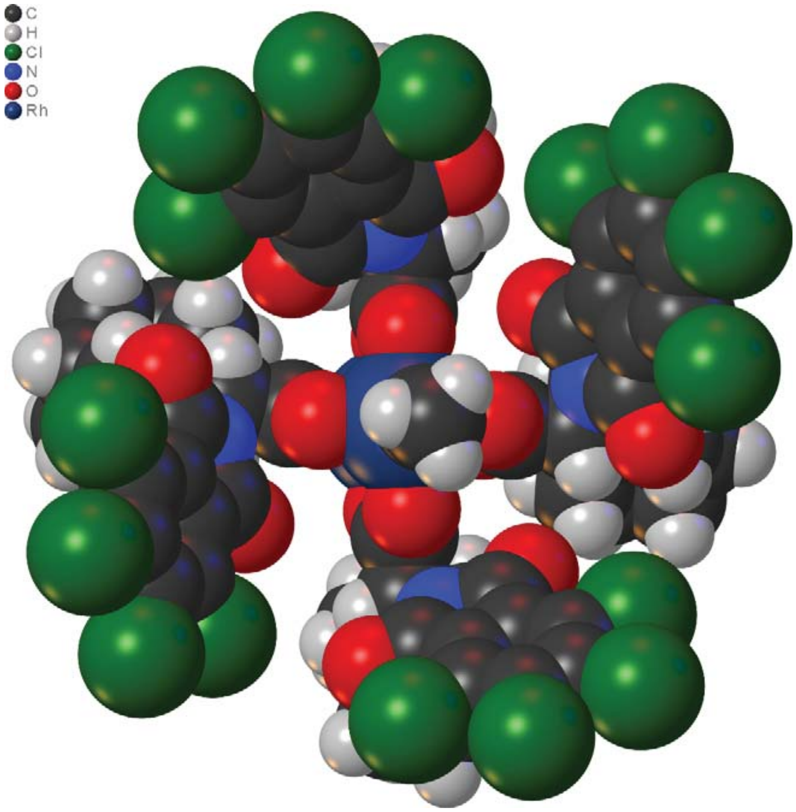
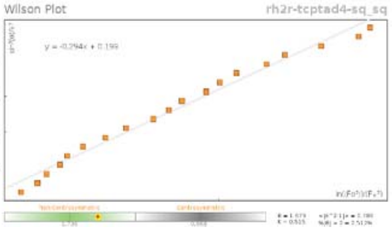
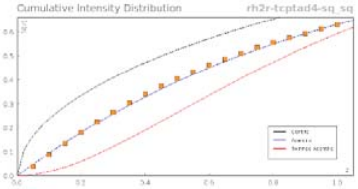


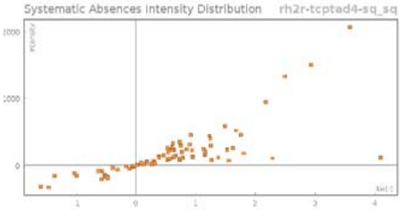
Figure 6:

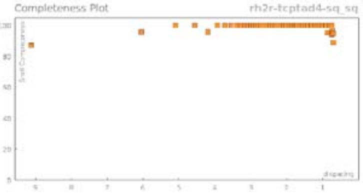
Space filling plot of the asymmetric unit showing the large cup shaped cavity.

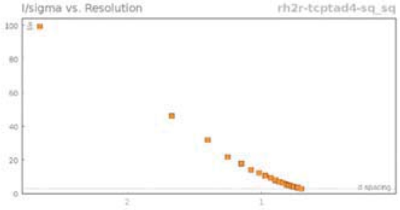
Data Plots: Diffraction Data



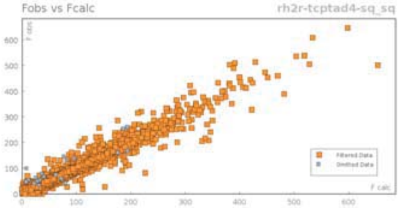


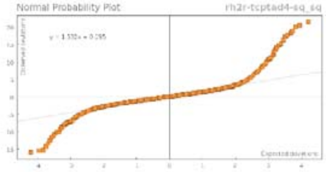






Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	157727	Unique reflections	38220
Completeness	0.996	Mean I/	22.86
hkl$_{max}$ collected	(19, 33, 27)	hkl$_{min}$ collected	(-19, -33, -27)
hkl$_{max}$ used	(19, 33, 27)	hkl$_{min}$ used	(-19, -33, 0)
Lim d$_{max}$ collected	20.0	Lim d$_{min}$ collected	0.7
d$_{max}$ used	12.03	d$_{min}$ used	0.7
Friedel pairs	35805	Friedel pairs merged	0
Inconsistent equivalents	308	R$_{int}$	0.0523
R$_{sigma}$	0.0449	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	189
Multiplicity	(16366, 38122, 14845, 3422, 438, 784)	Maximum multiplicity	10
Removed systematic absences	72	Filtered off (Shel/OMIT)	0

Images of the Crystal on the Diffractometer

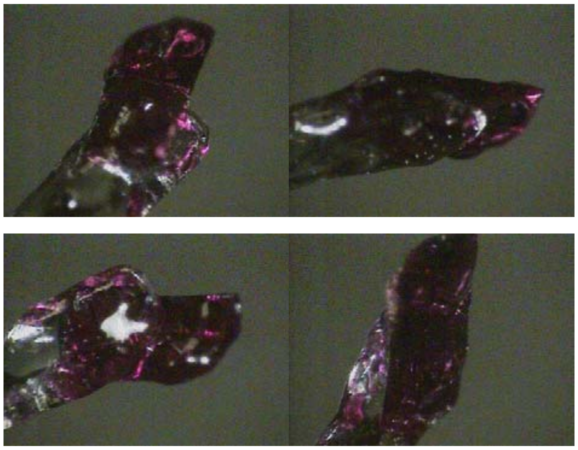


Table 6: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **Rh_2(*R*-TCPTAD)$_4$**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	**x**	**y**	**z**	U_{eq}
Rh1	4977	5309	3544	13.18(8)
Rh2	6309	5341	2883	14.90(8)
Cl1	7410.8(18)	9029.2(9)	2023.6(12)	45.3(5)
Cl1B	12155.2(15)	6127.1(14)	5584.3(15)	62.5(7)
Cl1C	8754.6(14)	1748.9(9)	2735.7(12)	41.0(5)
Cl1D	5147(2)	4648.7(12)	-1780.8(11)	53.3(6)
Cl3	6342.1(13)	8281.6(8)	3010.9(9)	30.9(3)
Cl3B	10161.4(15)	5515.1(10)	5626.6(13)	45.2(5)
Cl3C	6871.5(12)	2441.4(8)	2885.4(10)	31.1(4)
Cl3D	4152.6(17)	5232.9(9)	-617.2(10)	42.9(5)
Cl4	7453(2)	8657.0(12)	499.4(12)	57.7(7)
Cl4B	12251.6(13)	7245.7(12)	4741.7(15)	55.2(6)
Cl4C	10751.8(12)	2153.2(8)	3466(1)	30.7(3)
Cl4D	6304.0(18)	3527.6(10)	-1479.1(11)	43.8(5)
Cl7	6245.2(17)	7596.8(10)	-110.9(10)	39.9(5)
Cl7B	10348.5(14)	7829.6(9)	4039.1(12)	40.1(4)
Cl7C	10911.4(10)	3235.8(7)	4415.5(9)	25.4(3)
Cl7D	6439.3(15)	2947.0(8)	-20.7(10)	34.2(4)
O1	5515(3)	5896(2)	2231(3)	23.4(9)
O1B	6863(3)	6003.3(19)	3500(3)	19.9(8)
O1C	7027(3)	4789.6(19)	3599(2)	17.1(8)

Atom	x	y	z	U_{eq}
O1D	5644(3)	4690(2)	2295(2)	19.0(8)
O1W	3695(4)	5247(3)	4141(3)	38.1(13)
O2	4219(3)	5821.2(19)	2807(3)	21.4(9)
O2B	5547(3)	6004.6(19)	4057(3)	21.5(9)
O2C	5817(3)	4817.4(19)	4253(2)	16.8(8)
O2D	4452(3)	4631.3(19)	2973(2)	18.6(8)
O3	5180(3)	7130(2)	2824(3)	25.9(9)
O3B	8020(3)	5782(2)	4943(3)	24.4(9)
O3C	6447(3)	3542(2)	3725(2)	22.9(9)
O3D	4106(4)	4960(2)	977(3)	31.6(11)
O4	4831(4)	6734(2)	506(3)	35.4(11)
O4B	8131(3)	7556(2)	3992(3)	30.3(11)
O4C	9388(3)	4105(2)	4871(3)	22.6(9)
O4D	5515(4)	3206(2)	1331(2)	26.1(9)
N1	4732(4)	6877(2)	1670(3)	22.9(9)
N1B	7817(4)	6686(2)	4479(3)	17.6(8)
N1C	7779(4)	3903(2)	4413(3)	17.0(8)
N1D	4675(4)	4059(2)	1299(3)	20.3(8)
N2	7545(4)	5366(4)	2271(3)	29.6(12)
C1	5215(4)	7202(3)	2221(3)	20.6(9)
C1B	8342(4)	6227(3)	4793(3)	19.5(10)
C1C	7292(4)	3530(3)	3940(3)	17.7(9)
C1D	4482(5)	4519(3)	847(3)	22.7(11)
C2	5796(4)	7629(3)	1878(3)	21.4(9)
C2B	9376(4)	6420(3)	4868(4)	21(1)
C2C	8055(4)	3119(3)	3750(3)	16.8(9)
C2D	4852(5)	4342(3)	194(3)	23.5(11)
C3	6309(5)	8099(3)	2150(3)	23.7(10)
C3B	10224(5)	6151(3)	5204(4)	30.3(12)
C3C	7973(4)	2646(3)	3329(3)	20.9(10)
C3D	4777(6)	4607(3)	-445(4)	28.7(13)
C4	6802(5)	8425(3)	1712(4)	30.5(13)
C4B	11109(5)	6428(4)	5166(4)	35.7(13)
C4C	8820(5)	2352(3)	3249(4)	24.2(11)
C4D	5218(6)	4341(3)	-967(4)	31.7(13)
C5	6788(6)	8273(3)	1024(4)	32.1(13)

Atom	x	y	z	U_{eq}
C5B	11149(5)	6937(4)	4798(5)	36.6(14)
C5C	9716(4)	2530(3)	3580(4)	22.4(11)
C5D	5748(6)	3833(3)	-835(4)	33.0(14)
C6	6263(5)	7794(3)	751(4)	28.3(12)
C6B	10293(5)	7204(3)	4483(4)	29.9(12)
C6C	9800(4)	3011(2)	4010(3)	17.8(9)
C6D	5803(5)	3574(3)	-182(4)	27.6(12)
C7	5755(5)	7485(3)	1179(3)	23.5(10)
C7B	9423(4)	6937(3)	4547(4)	22.2(10)
C7C	8954(4)	3294(2)	4092(3)	16.2(9)
C7D	5330(5)	3821(3)	315(3)	23.1(11)
C8	5067(5)	6992(3)	1045(4)	26.0(11)
C8B	8405(4)	7126(3)	4293(4)	21.6(11)
C8C	8805(4)	3817(2)	4516(3)	15.3(9)
C8D	5219(5)	3631(3)	1028(3)	19.5(10)
C9	4095(5)	6396(3)	1775(4)	24.5(9)
C9B	6745(4)	6721(3)	4355(4)	20.5(9)
C9C	7337(4)	4390(2)	4724(3)	16.5(8)
C9D	4393(5)	4005(3)	2002(3)	20.5(9)
C10	4658(4)	6007(3)	2338(4)	21.3(10)
C10B	6361(4)	6192(3)	3940(3)	17.6(9)
C10C	6658(4)	4693(2)	4138(3)	15.3(9)
C10D	4858(4)	4491(3)	2455(3)	16.8(9)
C11	3039(5)	6592(3)	1862(5)	34.5(11)
C11B	6290(4)	6880(3)	5009(4)	26.3(10)
C11C	6927(5)	4230(3)	5405(3)	19.9(9)
C11D	3288(5)	3894(3)	1984(4)	25.8(10)
C12	2982(6)	6957(3)	2508(5)	37.9(13)
C12B	6286(5)	6392(3)	5529(4)	30.9(11)
C12C	6039(5)	3833(3)	5291(3)	22.3(10)
C12D	2636(5)	4417(4)	1855(5)	36.8(13)
C13	1921(6)	7142(4)	2551(6)	50.9(15)
C13B	5819(6)	6588(4)	6164(5)	41.8(13)
C13C	5681(6)	3704(3)	5994(4)	28.8(11)
C13D	1580(6)	4256(5)	1845(5)	47.5(14)
C14	1527(7)	7477(4)	1886(6)	54.2(16)

Atom	x	y	z	U_{eq}
C14B	6418(6)	7089(4)	6520(5)	44.4(14)
C14C	6482(6)	3398(3)	6473(4)	34.4(12)
C14D	1291(7)	3799(5)	1264(6)	53.4(16)
C15	1570(6)	7123(4)	1263(6)	52.1(15)
C15B	6432(5)	7579(4)	6010(5)	40.7(13)
C15C	7363(6)	3788(3)	6593(4)	33.3(12)
C15D	1896(7)	3284(5)	1397(5)	46.8(14)
C16	2622(6)	6926(4)	1211(5)	42.3(14)
C16B	6863(5)	7382(3)	5368(4)	31.8(12)
C16C	7718(5)	3921(3)	5899(3)	25.8(11)
C16D	2977(6)	3446(4)	1418(4)	37.4(13)
C17	2389(6)	6055(4)	1905(5)	41.1(14)
C17B	5238(5)	7100(3)	4783(4)	33.0(12)
C17C	6672(5)	4784(3)	5767(3)	22.6(10)
C17D	3119(5)	3621(3)	2692(4)	27.4(11)
C18	1324(6)	6251(4)	1962(5)	47.7(14)
C18B	4800(5)	7285(4)	5439(5)	42.2(13)
C18C	6297(6)	4649(3)	6465(4)	29.2(11)
C18D	2050(5)	3464(4)	2683(4)	36.4(13)
C19	957(7)	6583(5)	1328(6)	54.8(17)
C19B	5394(6)	7790(4)	5769(6)	46.6(15)
C19C	7120(6)	4338(3)	6939(4)	33.3(12)
C19D	1739(7)	3029(4)	2108(5)	44.1(15)
C20	1321(8)	6620(4)	2598(6)	53.2(16)
C20B	4782(6)	6787(4)	5930(5)	44.5(14)
C20C	5408(6)	4266(3)	6324(4)	30.6(12)
C20D	1422(6)	4006(5)	2560(6)	46.5(15)
C21	8180(5)	5364(4)	1951(4)	34.9(15)
C22	8970(5)	5344(6)	1538(5)	55(2)
Cl1S	1944(3)	5333.5(16)	7402(2)	85.7(9)
Cl2S	3702(3)	5287(2)	6749.3(18)	94.7(12)
C1S	3111(10)	5606(5)	7374(7)	71(2)
Cl3S	4878(3)	6611(2)	-1818(2)	98.4(12)
Cl4S	3146(3)	6530.0(14)	-1132.4(17)	71.7(8)
C2S	4275(11)	6832(7)	-1143(8)	83(3)
Cl5S	7457(6)	4169(3)	1120(4)	157(2)

Atom	x	y	z	U_{eq}
Cl6S	8720(8)	3456(7)	2070(7)	291(7)
C3S	7605(13)	3833(12)	2004(12)	174(5)
Cl7S	9462(2)	4546.6(11)	3228.9(14)	53.3(6)
Cl8S	9864(2)	5753.3(13)	3424.6(14)	60.5(7)
C4S	9245(7)	5166(4)	3694(5)	43(2)

Table 7: Anisotropic Displacement Parameters (×10^4) **Rh_2(*R*-TCPTAD)$_4$**. The anisotropic displacement factor exponent takes the form: $-2\quad{}^{2}[h^2a^{*2} \times U_{11} + \ldots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh1	9.56(14)	12.57(16)	17.47(18)	-0.52(18)	2.04(12)	-0.41(16)
Rh2	11.81(15)	16.48(18)	16.62(18)	2.20(19)	2.70(13)	-0.96(18)
Cl1	56.0(12)	37.3(10)	40.1(11)	0.2(8)	-2.1(9)	-25.8(9)
Cl1B	21.9(8)	89.4(19)	69.1(16)	-7.0(14)	-18.2(9)	18.6(10)
Cl1C	36.4(9)	31.2(9)	56.1(12)	-26.4(9)	9.1(8)	-1.8(7)
Cl1D	78.0(16)	62.3(14)	22.4(9)	15.2(9)	17.4(9)	17.4(12)
Cl3	36.8(9)	29.2(8)	25.4(8)	-5.5(6)	-0.4(6)	-6.7(7)
Cl3B	35.4(9)	45.9(10)	51.7(12)	14.0(9)	-3.0(8)	17.3(8)
Cl3C	22.9(7)	33.8(8)	36.5(9)	-16.8(7)	4.3(6)	-7.7(6)
Cl3D	63.1(12)	38.0(11)	29.4(8)	15.1(7)	12.6(8)	18.1(9)
Cl4	72.7(16)	66.7(15)	34(1)	7.4(10)	8.1(10)	-43.5(13)
Cl4B	15.4(7)	76.6(16)	73.3(16)	-19.7(13)	5.1(8)	-17.4(8)
Cl4C	24.4(7)	29.4(8)	39.2(9)	-8.6(7)	7.4(6)	8.9(6)
Cl4D	61.5(13)	45.6(11)	29.4(9)	-3.7(8)	24.4(9)	4.4(9)
Cl7	54.6(12)	45.8(11)	18.8(8)	3.4(7)	3.5(7)	-14.1(9)
Cl7B	34.2(9)	37.8(9)	49.4(11)	-1.8(8)	9.7(8)	-18.6(7)
Cl7C	14.8(6)	30.7(8)	29.6(8)	-6.4(6)	-0.6(5)	3.8(5)
Cl7D	45.1(10)	26.6(8)	32.8(9)	-3.3(7)	12.7(8)	9.5(7)
O1	18.3(15)	24(2)	26(2)	8.2(18)	-2.0(14)	-1.5(14)
O1B	14.4(17)	17.3(19)	28(2)	-3.3(15)	2.0(14)	-3.5(14)
O1C	12.5(16)	21(2)	18.0(16)	5.1(14)	3.0(13)	4.8(14)
O1D	19.9(16)	22(2)	16.2(19)	-1.1(15)	5.1(14)	-2.4(14)
O1W	30(2)	37(3)	50(3)	-1(3)	14(2)	6(2)
O2	17.4(17)	17(2)	28.4(19)	7.4(15)	-0.4(14)	2.5(14)
O2B	15.2(15)	17.1(19)	32(2)	-6.6(17)	2.8(14)	-3.5(13)
O2C	15.3(14)	19.8(19)	15.7(19)	2.5(15)	3.2(12)	2.1(13)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2D	16.8(17)	21(2)	18.9(17)	-3.1(14)	4.5(14)	-5.4(15)
O3	24(2)	27(2)	24.8(16)	2.3(14)	-0.3(13)	-0.4(17)
O3B	20.1(18)	18.7(15)	35(2)	1.7(15)	6.3(17)	2.6(13)
O3C	16.9(14)	27(2)	24(2)	-2.9(17)	0.6(13)	0.9(13)
O3D	53(3)	20.6(17)	24(2)	4.7(15)	13(2)	9.9(17)
O4	49(3)	31(2)	24.0(18)	2.3(16)	-5.5(17)	-10(2)
O4B	22(2)	21.6(17)	44(3)	6.3(17)	-5.7(19)	-4.5(14)
O4C	17.1(16)	20.9(18)	28(2)	-3.7(16)	-4.2(15)	1.7(14)
O4D	38(2)	19.6(17)	21(2)	2.4(14)	3.9(17)	3.7(16)
N1	22.5(17)	19.6(17)	24.1(16)	4.6(12)	-4.9(13)	-2.7(14)
N1B	12.5(12)	15.0(14)	24.6(19)	-1.5(12)	-0.5(11)	0.2(10)
N1C	15.0(14)	17.9(16)	17.5(18)	-1.7(14)	0.1(12)	2.6(11)
N1D	29(2)	15.2(15)	16.5(15)	0.8(11)	2.4(13)	-0.6(14)
N2	22(2)	44(4)	23(3)	1(3)	6.1(19)	-3(3)
C1	17(2)	19.4(19)	23.8(15)	3.4(13)	-3.4(13)	0.4(16)
C1B	13.0(15)	19.1(15)	26(3)	0.3(15)	0.0(14)	2.2(11)
C1C	16.6(14)	18.7(18)	18(2)	-2.3(16)	1.5(12)	0.4(12)
C1D	34(3)	17.8(16)	17.0(17)	1.5(13)	5.7(16)	2.3(16)
C2	19(2)	21.2(17)	22.0(16)	3.0(12)	-3.4(13)	-1.0(15)
C2B	14.3(13)	24.1(16)	24(2)	-2.3(14)	0.8(12)	1.1(11)
C2C	17.1(15)	17.5(16)	16(2)	-0.6(15)	2.7(13)	0.2(11)
C2D	32(3)	21.3(18)	17.1(15)	1.6(12)	4.9(15)	3.7(17)
C3	25(2)	22.2(19)	22.1(17)	1.4(13)	-3.7(14)	-3.6(17)
C3B	17.2(16)	38(2)	34(3)	-2(2)	-4.9(15)	8.1(13)
C3C	20.3(16)	19.6(18)	24(2)	-6.6(17)	5.9(14)	-2.5(13)
C3D	40(3)	28(2)	18.3(17)	6.2(14)	6.3(17)	5(2)
C4	33(3)	31(2)	26.3(17)	3.4(14)	-2.4(16)	-12(2)
C4B	15.5(16)	50(2)	40(3)	-9(2)	-2.8(16)	1.7(14)
C4C	21.9(15)	20.7(19)	31(3)	-8.1(19)	6.1(14)	-0.3(13)
C4D	44(3)	34(2)	19.4(18)	2.8(15)	9.2(18)	4(2)
C5	38(3)	31(2)	25.5(18)	5.1(15)	-1.6(16)	-12(2)
C5B	15.5(16)	50(2)	43(3)	-10(2)	-1.8(16)	-3.6(14)
C5C	20.1(16)	18.6(18)	29(2)	-6.3(18)	5.4(14)	2.0(13)
C5D	46(3)	34(2)	21.1(18)	1.0(15)	10.5(18)	6(2)
C6	33(3)	31(2)	19.8(17)	4.6(14)	-0.7(15)	-10(2)
C6B	15.9(16)	36(2)	38(3)	-6.4(19)	3.2(15)	-9.7(13)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C6C	16.8(15)	16.8(17)	20(2)	-0.2(16)	2.8(13)	3.2(12)
C6D	37(3)	25(2)	21.7(17)	-1.0(14)	7.9(17)	3.5(19)
C7	26(2)	22.5(19)	20.1(16)	3.8(13)	-2.8(13)	-3.6(17)
C7B	13.7(14)	24.4(17)	27(3)	-2.5(16)	-1.0(13)	-2.5(11)
C7C	16.4(14)	14.7(16)	17(2)	0.5(15)	1.8(12)	0.9(11)
C7D	32(3)	20.5(18)	16.9(16)	1.4(13)	4.3(15)	3.4(17)
C8	28(2)	24(2)	23.8(16)	5.1(13)	-4.2(14)	-5.4(19)
C8B	14.6(15)	18.9(16)	30(3)	-0.1(16)	-0.9(14)	-4.0(12)
C8C	13.5(14)	15.4(17)	16(2)	0.1(15)	0.2(12)	2.0(11)
C8D	25(2)	16.5(16)	15.9(16)	-1.1(12)	0.4(15)	-2.0(15)
C9	22.0(14)	21.0(16)	27.7(18)	6.9(13)	-6.8(12)	-3.5(11)
C9B	12.9(13)	16.8(16)	30.6(17)	-4.4(13)	-0.5(11)	0.3(11)
C9C	17.9(17)	16.7(17)	14.8(15)	0.4(12)	2.3(12)	3.7(13)
C9D	24.9(17)	19.5(19)	17.2(16)	0.9(13)	2.4(12)	-1.9(14)
C10	16.4(16)	21(2)	25(2)	4.6(17)	-4.7(14)	-3.9(14)
C10B	11.9(15)	15.1(18)	25(2)	-1.0(16)	-1.5(14)	0.4(13)
C10C	14.8(16)	15(2)	15.8(17)	0.9(14)	2.5(12)	0.5(14)
C10D	17.5(17)	16(2)	17.0(18)	2.1(15)	2.6(14)	0.9(15)
C11	19.7(16)	27(2)	54(3)	16.3(18)	-3.1(15)	-1.1(14)
C11B	15.6(17)	24(2)	39.7(19)	-12.5(15)	5.0(14)	-2.1(14)
C11C	27.7(19)	17.9(18)	14.8(15)	0.5(12)	5.8(13)	2.5(14)
C11D	23.7(17)	34(2)	19(2)	2.3(16)	1.2(13)	-6.8(14)
C12	29(2)	29(3)	55(3)	14(2)	1.6(18)	-0.5(17)
C12B	27(2)	28(2)	39(2)	-11.1(17)	9.1(18)	-1.0(17)
C12C	30(2)	19(2)	19.5(19)	0.5(15)	8.3(15)	1.0(16)
C12D	25(2)	40(2)	45(3)	5(2)	0.9(18)	-3.0(16)
C13	30(2)	44(3)	78(3)	16(2)	6(2)	4.4(19)
C13B	34(2)	48(3)	47(3)	-20.3(19)	15.5(19)	-5.1(19)
C13C	43(2)	25(2)	22(2)	-0.1(16)	14.9(17)	-1.5(17)
C13D	26(2)	61(3)	55(3)	7(2)	0.6(19)	-7.8(19)
C14	30(3)	48(3)	82(3)	22(2)	2(2)	1(2)
C14B	31(3)	47(3)	57(3)	-26(2)	14(2)	-1(2)
C14C	50(3)	30(2)	25(2)	3.5(18)	12.2(19)	3.1(18)
C14D	41(3)	66(3)	53(3)	6(2)	4(2)	-17(2)
C15	27(2)	47(3)	79(3)	24(2)	-4(2)	2.7(19)
C15B	22(2)	44(3)	58(3)	-28(2)	9.8(18)	-3.5(18)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C15C	49(3)	33(2)	20(2)	4.1(16)	9.7(17)	3.7(18)
C15D	40(3)	61(3)	37(3)	1(2)	1.5(19)	-20(2)
C16	27(2)	37(3)	58(3)	21(2)	-8.7(18)	-0.5(19)
C16B	17(2)	27(2)	51(3)	-19.2(19)	4.1(17)	-1.2(16)
C16C	35(2)	25(2)	16.8(18)	2.6(16)	2.8(15)	5.6(17)
C16D	40(2)	45(3)	27(2)	-4(2)	3.7(17)	-16.0(19)
C17	26(2)	32(2)	62(4)	15(2)	-3.8(19)	-6.8(16)
C17B	20.8(16)	31(2)	47(2)	-11.0(16)	3.6(14)	1.1(14)
C17C	32(2)	20.1(18)	16.4(19)	-0.2(14)	6.7(16)	3.0(16)
C17D	24(2)	35(3)	23(2)	3.0(18)	4.2(15)	-4.8(17)
C18	25(2)	44(3)	71(3)	17(2)	-1.1(19)	-3.6(18)
C18B	21(2)	48(3)	59(3)	-23(2)	9.6(18)	-4.0(18)
C18C	45(2)	27(2)	18(2)	0.3(16)	11.7(17)	-0.6(17)
C18D	23(2)	53(3)	34(3)	2(2)	3.8(17)	-10.6(18)
C19	34(3)	51(3)	76(3)	21(2)	-4(2)	-1(2)
C19B	23(2)	46(3)	71(4)	-28(2)	8(2)	-0.7(18)
C19C	49(3)	34(2)	19(2)	2.4(17)	10.4(18)	2.8(19)
C19D	38(3)	57(3)	37(3)	0(2)	3(2)	-16(2)
C20	42(2)	49(2)	67(3)	13.4(18)	4.4(18)	-2.3(18)
C20B	32(2)	48(3)	56(3)	-24(2)	14(2)	-4.8(19)
C20C	45(2)	26(2)	24(3)	-2.0(18)	15.1(19)	-0.7(17)
C20D	26(3)	57(3)	56(3)	4(2)	4(2)	-7(2)
C21	21(3)	44(4)	40(4)	5(4)	8(2)	-1(3)
C22	25(3)	91(7)	53(5)	6(6)	19(3)	-7(5)
Cl1S	98(2)	52.6(14)	105(2)	13.9(18)	9.8(17)	23.1(17)
Cl2S	105(2)	111(3)	64.6(18)	4(2)	0.4(16)	50(2)
C1S	92(4)	57(5)	61(4)	10(4)	0(3)	26(3)
Cl3S	88(2)	122(3)	83(2)	5(2)	2.2(18)	15(2)
Cl4S	84.3(19)	61.1(16)	65.1(18)	5.6(13)	-5.5(14)	14.1(14)
C2S	87(3)	80(4)	80(3)	3(2)	4(2)	0(2)
Cl5S	165(6)	137(5)	167(5)	-16(4)	19(4)	-19(4)
Cl6S	237(7)	368(15)	284(11)	155(11)	94(7)	82(10)
C3S	174(6)	174(6)	172(5)	3(3)	18(3)	-10(3)
Cl7S	61.6(14)	48.2(13)	51.7(14)	-3.6(10)	13.4(11)	9.9(11)
Cl8S	71.9(17)	60.9(15)	50.4(14)	-2.2(12)	14.7(12)	-24.8(13)
C4S	47(5)	46(5)	39(5)	-5(3)	18(4)	-7(3)

Table 8: Bond Lengths in Å for **Rh_2(*R*-TCPTAD)$_4$**.

Atom	**Atom**	**Length/Å**
Rh1	Rh2	2.39913(4)
Rh1	O1W	2.265(5)
Rh1	O2	2.048(4)
Rh1	O2B	2.018(4)
Rh1	O2C	2.038(4)
Rh1	O2D	2.018(4)
Rh2	O1	2.036(5)
Rh2	O1B	2.049(4)
Rh2	O1C	2.055(4)
Rh2	O1D	2.051(5)
Rh2	N2	2.224(5)
Cl1	C4	1.720(7)
Cl1B	C4B	1.719(8)
Cl1C	C4C	1.728(7)
Cl1D	C4D	1.729(7)
Cl3	C3	1.721(7)
Cl3B	C3B	1.711(8)
Cl3C	C3C	1.721(6)
Cl3D	C3D	1.716(7)
Cl4	C5	1.723(8)
Cl4B	C5B	1.716(8)
Cl4C	C5C	1.733(6)
Cl4D	C5D	1.716(8)
Cl7	C6	1.734(7)
Cl7B	C6B	1.710(8)
Cl7C	C6C	1.720(6)
Cl7D	C6D	1.724(7)
O1	C10	1.268(8)
O1B	C10B	1.256(8)
O1C	C10C	1.250(7)
O1D	C10D	1.268(7)
O2	C10	1.243(8)
O2B	C10B	1.266(7)
O2C	C10C	1.258(7)

Atom	Atom	Length/Å
O2D	C10D	1.265(7)
O3	C1	1.192(8)
O3B	C1B	1.188(8)
O3C	C1C	1.193(7)
O3D	C1D	1.203(8)
O4	C8	1.214(9)
O4B	C8B	1.202(8)
O4C	C8C	1.199(7)
O4D	C8D	1.201(8)
N1	C1	1.408(8)
N1	C8	1.385(10)
N1	C9	1.469(8)
N1B	C1B	1.395(8)
N1B	C8B	1.397(8)
N1B	C9B	1.483(7)
N1C	C1C	1.379(8)
N1C	C8C	1.430(7)
N1C	C9C	1.468(8)
N1D	C1D	1.395(8)
N1D	C8D	1.403(8)
N1D	C9D	1.479(8)
N2	C21	1.150(9)
C1	C2	1.501(9)
C1B	C2B	1.499(8)
C1C	C2C	1.519(8)
C1D	C2D	1.493(9)
C2	C3	1.380(9)
C2	C7	1.393(9)
C2B	C3B	1.418(9)
C2B	C7B	1.369(9)
C2C	C3C	1.374(8)
C2C	C7C	1.396(8)
C2D	C3D	1.380(9)
C2D	C7D	1.396(9)
C3	C4	1.393(10)
C3B	C4B	1.405(10)

Atom	Atom	Length/Å
C3C	C4C	1.394(9)
C3D	C4D	1.404(10)
C4	C5	1.382(11)
C4B	C5B	1.397(13)
C4C	C5C	1.388(9)
C4D	C5D	1.407(11)
C5	C6	1.405(10)
C5B	C6B	1.410(10)
C5C	C6C	1.400(8)
C5D	C6D	1.400(10)
C6	C7	1.371(10)
C6B	C7B	1.386(9)
C6C	C7C	1.380(8)
C6D	C7D	1.371(9)
C7	C8	1.503(9)
C7B	C8B	1.504(8)
C7C	C8C	1.509(8)
C7D	C8D	1.485(9)
C9	C10	1.552(9)
C9	C11	1.573(10)
C9B	C10B	1.536(8)
C9B	C11B	1.542(10)
C9C	C10C	1.548(8)
C9C	C11C	1.558(8)
C9D	C10D	1.530(9)
C9D	C11D	1.557(9)
C11	C12	1.531(13)
C11	C16	1.532(11)
C11	C17	1.562(10)
C11B	C12B	1.528(11)
C11B	C16B	1.536(9)
C11B	C17B	1.559(9)
C11C	C12C	1.540(9)
C11C	C16C	1.539(9)
C11C	C17C	1.543(9)
C11D	C12D	1.527(11)

Atom	Atom	Length/Å
C11D	C16D	1.539(10)
C11D	C17D	1.563(10)
C12	C13	1.555(12)
C12B	C13B	1.544(11)
C12C	C13C	1.546(9)
C12D	C13D	1.517(11)
C13	C14	1.548(14)
C13	C20	1.494(14)
C13B	C14B	1.548(12)
C13B	C20B	1.527(12)
C13C	C14C	1.530(11)
C13C	C20C	1.539(10)
C13D	C14D	1.569(15)
C13D	C20D	1.550(14)
C14	C15	1.476(17)
C14B	C15B	1.520(15)
C14C	C15C	1.522(12)
C14D	C15D	1.476(16)
C15	C16	1.553(12)
C15	C19	1.542(14)
C15B	C16B	1.529(11)
C15B	C19B	1.539(11)
C15C	C16C	1.531(10)
C15C	C19C	1.516(11)
C15D	C16D	1.548(12)
C15D	C19D	1.549(13)
C17	C18	1.572(12)
C17B	C18B	1.549(12)
C17C	C18C	1.553(9)
C17D	C18D	1.531(10)
C18	C19	1.489(14)
C18	C20	1.510(11)
C18B	C19B	1.534(11)
C18B	C20B	1.513(10)
C18C	C19C	1.551(11)
C18C	C20C	1.523(11)

Atom	Atom	Length/Å
C18D	C19D	1.533(12)
C18D	C20D	1.543(14)
C21	C22	1.449(10)
Cl1S	C1S	1.755(16)
Cl2S	C1S	1.729(14)
Cl3S	C2S	1.731(16)
Cl4S	C2S	1.728(16)
Cl5S	C3S	1.88(2)
Cl6S	C3S	1.778(3)
Cl7S	C4S	1.761(9)
Cl8S	C4S	1.744(9)

Table 9: Bond Angles in ° for **Rh_2(*R*-TCPTAD)$_4$**.

Atom	Atom	Atom	Angle/°
O1W	Rh1	Rh2	177.58(16)
O2	Rh1	Rh2	88.25(13)
O2	Rh1	O1W	91.7(2)
O2B	Rh1	Rh2	87.60(13)
O2B	Rh1	O1W	94.8(2)
O2B	Rh1	O2	90.01(19)
O2B	Rh1	O2C	88.5(2)
O2C	Rh1	Rh2	87.99(12)
O2C	Rh1	O1W	92.1(2)
O2C	Rh1	O2	176.01(18)
O2D	Rh1	Rh2	88.79(12)
O2D	Rh1	O1W	88.8(2)
O2D	Rh1	O2	88.0(2)
O2D	Rh1	O2B	175.95(19)
O2D	Rh1	O2C	93.21(18)
O1	Rh2	Rh1	87.66(15)
O1	Rh2	O1B	90.4(2)
O1	Rh2	O1C	175.2(2)
O1	Rh2	O1D	87.97(18)

Atom	Atom	Atom	Angle/°
O1	Rh2	N2	92.5(2)
O1B	Rh2	Rh1	88.11(13)
O1B	Rh2	O1C	88.49(19)
O1B	Rh2	O1D	175.12(19)
O1B	Rh2	N2	92.1(2)
O1C	Rh2	Rh1	87.64(12)
O1C	Rh2	N2	92.2(2)
O1D	Rh2	Rh1	87.24(13)
O1D	Rh2	O1C	92.80(18)
O1D	Rh2	N2	92.6(2)
N2	Rh2	Rh1	179.7(2)
C10	O1	Rh2	118.2(4)
C10B	O1B	Rh2	117.7(4)
C10C	O1C	Rh2	117.6(4)
C10D	O1D	Rh2	118.5(4)
C10	O2	Rh1	117.4(4)
C10B	O2B	Rh1	119.6(4)
C10C	O2C	Rh1	118.3(4)
C10D	O2D	Rh1	118.3(4)
C1	N1	C9	123.1(6)
C8	N1	C1	112.2(5)
C8	N1	C9	123.7(6)
C1B	N1B	C8B	113.3(5)
C1B	N1B	C9B	124.7(5)
C8B	N1B	C9B	122.0(5)
C1C	N1C	C8C	113.2(5)
C1C	N1C	C9C	125.0(5)
C8C	N1C	C9C	121.4(5)
C1D	N1D	C8D	112.7(5)
C1D	N1D	C9D	126.5(5)
C8D	N1D	C9D	120.8(5)
C21	N2	Rh2	178.2(8)
O3	C1	N1	126.3(6)
O3	C1	C2	129.0(6)
N1	C1	C2	104.7(5)
O3B	C1B	N1B	126.4(5)

Atom	Atom	Atom	Angle/°
O3B	C1B	C2B	129.3(6)
N1B	C1B	C2B	104.2(5)
O3C	C1C	N1C	126.2(6)
O3C	C1C	C2C	128.2(6)
N1C	C1C	C2C	105.6(5)
O3D	C1D	N1D	125.9(6)
O3D	C1D	C2D	129.1(6)
N1D	C1D	C2D	105.1(5)
C3	C2	C1	130.3(6)
C3	C2	C7	121.1(6)
C7	C2	C1	108.7(5)
C3B	C2B	C1B	129.6(6)
C7B	C2B	C1B	109.3(5)
C7B	C2B	C3B	121.1(6)
C3C	C2C	C1C	130.8(5)
C3C	C2C	C7C	121.1(5)
C7C	C2C	C1C	108.0(5)
C3D	C2D	C1D	130.2(6)
C3D	C2D	C7D	121.5(6)
C7D	C2D	C1D	108.3(6)
C2	C3	Cl3	121.0(5)
C2	C3	C4	118.6(6)
C4	C3	Cl3	120.5(5)
C2B	C3B	Cl3B	121.1(6)
C4B	C3B	Cl3B	122.2(5)
C4B	C3B	C2B	116.8(7)
C2C	C3C	Cl3C	121.3(5)
C2C	C3C	C4C	117.6(6)
C4C	C3C	Cl3C	121.0(5)
C2D	C3D	Cl3D	122.4(6)
C2D	C3D	C4D	117.5(6)
C4D	C3D	Cl3D	120.1(5)
C3	C4	Cl1	119.9(6)
C5	C4	Cl1	119.6(6)
C5	C4	C3	120.5(6)
C3B	C4B	Cl1B	118.5(7)

Atom	**Atom**	**Atom**	**Angle/°**
C5B	C4B	Cl1B	120.2(6)
C5B	C4B	C3B	121.3(7)
C3C	C4C	Cl1C	119.5(5)
C5C	C4C	Cl1C	119.1(5)
C5C	C4C	C3C	121.4(6)
C3D	C4D	Cl1D	119.9(6)
C3D	C4D	C5D	121.2(7)
C5D	C4D	Cl1D	118.9(6)
C4	C5	Cl4	120.0(6)
C4	C5	C6	120.6(7)
C6	C5	Cl4	119.4(6)
C4B	C5B	Cl4B	119.5(6)
C4B	C5B	C6B	120.8(7)
C6B	C5B	Cl4B	119.7(7)
C4C	C5C	Cl4C	119.9(5)
C4C	C5C	C6C	121.0(6)
C6C	C5C	Cl4C	119.1(5)
C4D	C5D	Cl4D	119.9(6)
C6D	C5D	Cl4D	120.4(6)
C6D	C5D	C4D	119.7(7)
C5	C6	Cl7	121.0(6)
C7	C6	Cl7	120.3(5)
C7	C6	C5	118.7(7)
C5B	C6B	Cl7B	120.4(6)
C7B	C6B	Cl7B	122.3(6)
C7B	C6B	C5B	117.2(7)
C5C	C6C	Cl7C	121.1(4)
C7C	C6C	Cl7C	121.9(5)
C7C	C6C	C5C	117.0(5)
C5D	C6D	Cl7D	119.9(6)
C7D	C6D	Cl7D	121.3(5)
C7D	C6D	C5D	118.8(7)
C2	C7	C8	107.1(6)
C6	C7	C2	120.6(6)
C6	C7	C8	132.2(6)
C2B	C7B	C6B	122.6(6)

Atom	Atom	Atom	Angle/°
C2B	C7B	C8B	108.0(5)
C6B	C7B	C8B	129.3(6)
C2C	C7C	C8C	108.5(5)
C6C	C7C	C2C	121.9(5)
C6C	C7C	C8C	129.6(5)
C2D	C7D	C8D	108.2(6)
C6D	C7D	C2D	121.1(6)
C6D	C7D	C8D	130.7(6)
O4	C8	N1	125.0(6)
O4	C8	C7	128.6(7)
N1	C8	C7	106.4(6)
O4B	C8B	N1B	126.2(6)
O4B	C8B	C7B	129.0(6)
N1B	C8B	C7B	104.8(5)
O4C	C8C	N1C	125.8(5)
O4C	C8C	C7C	129.8(5)
N1C	C8C	C7C	104.4(5)
O4D	C8D	N1D	125.3(6)
O4D	C8D	C7D	129.3(6)
N1D	C8D	C7D	105.4(5)
N1	C9	C10	107.1(5)
N1	C9	C11	112.4(5)
C10	C9	C11	119.0(6)
N1B	C9B	C10B	108.1(5)
N1B	C9B	C11B	113.4(5)
C10B	C9B	C11B	118.4(5)
N1C	C9C	C10C	107.6(5)
N1C	C9C	C11C	112.6(5)
C10C	C9C	C11C	118.5(5)
N1D	C9D	C10D	108.8(5)
N1D	C9D	C11D	112.5(5)
C10D	C9D	C11D	118.5(5)
O1	C10	C9	113.6(6)
O2	C10	O1	128.2(6)
O2	C10	C9	118.2(6)
O1B	C10B	O2B	126.6(6)

Atom	Atom	Atom	Angle/°
O1B	C10B	C9B	117.1(5)
O2B	C10B	C9B	116.2(5)
O1C	C10C	O2C	127.4(5)
O1C	C10C	C9C	114.9(5)
O2C	C10C	C9C	117.7(5)
O1D	C10D	C9D	116.5(5)
O2D	C10D	O1D	126.6(6)
O2D	C10D	C9D	116.8(5)
C12	C11	C9	114.0(6)
C12	C11	C16	109.6(7)
C12	C11	C17	108.2(7)
C16	C11	C9	108.4(7)
C16	C11	C17	107.5(6)
C17	C11	C9	109.1(6)
C9B	C11B	C17B	109.0(6)
C12B	C11B	C9B	113.7(5)
C12B	C11B	C16B	108.9(6)
C12B	C11B	C17B	110.2(6)
C16B	C11B	C9B	108.3(5)
C16B	C11B	C17B	106.4(5)
C12C	C11C	C9C	113.9(5)
C12C	C11C	C17C	110.1(5)
C16C	C11C	C9C	109.2(5)
C16C	C11C	C12C	107.2(5)
C16C	C11C	C17C	107.7(5)
C17C	C11C	C9C	108.5(5)
C9D	C11D	C17D	108.5(5)
C12D	C11D	C9D	115.6(6)
C12D	C11D	C16D	109.2(6)
C12D	C11D	C17D	108.4(6)
C16D	C11D	C9D	108.0(6)
C16D	C11D	C17D	106.7(6)
C11	C12	C13	111.0(7)
C11B	C12B	C13B	110.2(6)
C11C	C12C	C13C	110.0(5)
C13D	C12D	C11D	110.9(7)

Atom	Atom	Atom	Angle/°
C14	C13	C12	109.1(9)
C20	C13	C12	108.5(8)
C20	C13	C14	109.3(9)
C12B	C13B	C14B	108.9(7)
C20B	C13B	C12B	109.8(7)
C20B	C13B	C14B	109.3(7)
C14C	C13C	C12C	109.4(6)
C14C	C13C	C20C	110.5(6)
C20C	C13C	C12C	109.2(6)
C12D	C13D	C14D	109.3(8)
C12D	C13D	C20D	109.9(7)
C20D	C13D	C14D	109.3(8)
C15	C14	C13	110.4(9)
C15B	C14B	C13B	109.8(8)
C15C	C14C	C13C	108.4(6)
C15D	C14D	C13D	110.6(8)
C14	C15	C16	111.5(8)
C14	C15	C19	108.1(9)
C19	C15	C16	107.4(8)
C14B	C15B	C16B	110.2(7)
C14B	C15B	C19B	110.2(7)
C16B	C15B	C19B	107.9(7)
C14C	C15C	C16C	109.8(6)
C19C	C15C	C14C	110.8(7)
C19C	C15C	C16C	109.6(6)
C14D	C15D	C16D	109.5(8)
C14D	C15D	C19D	108.9(9)
C16D	C15D	C19D	109.1(7)
C11	C16	C15	110.6(8)
C15B	C16B	C11B	111.4(6)
C15C	C16C	C11C	110.8(6)
C11D	C16D	C15D	111.3(7)
C11	C17	C18	109.2(7)
C18B	C17B	C11B	108.9(6)
C11C	C17C	C18C	110.7(5)
C18D	C17D	C11D	110.6(6)

Atom	Atom	Atom	Angle/°
C19	C18	C17	108.3(8)
C19	C18	C20	109.7(9)
C20	C18	C17	109.5(8)
C19B	C18B	C17B	108.1(7)
C20B	C18B	C17B	110.2(7)
C20B	C18B	C19B	112.9(8)
C19C	C18C	C17C	107.6(6)
C20C	C18C	C17C	109.0(6)
C20C	C18C	C19C	110.2(6)
C17D	C18D	C19D	110.2(7)
C17D	C18D	C20D	109.5(7)
C19D	C18D	C20D	109.8(7)
C18	C19	C15	111.6(8)
C18B	C19B	C15B	108.0(7)
C15C	C19C	C18C	109.3(6)
C18D	C19D	C15D	109.4(8)
C13	C20	C18	111.0(9)
C18B	C20B	C13B	109.0(7)
C18C	C20C	C13C	109.9(6)
C18D	C20D	C13D	107.7(8)
N2	C21	C22	178.2(12)
Cl2S	C1S	Cl1S	113.4(8)
Cl4S	C2S	Cl3S	115.0(9)
Cl6S	C3S	Cl5S	105.0(9)
Cl8S	C4S	Cl7S	111.8(5)

Table 10: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **Rh$_2$(*R*-TCPTAD)$_4$**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	**x**	**y**	**z**	U_{eq}
H1WA	3689	5075	4594	57
H1WB	3056	5399	3990	57
H9	4030	6171	1333	29
H9B	6596	7049	4028	25
H9C	7878	4664	4867	20
H9D	4719	3650	2201	25
H12A	3394	7299	2492	45
H12B	3234	6736	2929	45
H12C	6959	6264	5682	37
H12D	5917	6066	5303	37
H12E	6214	3473	5075	27
H12F	5513	4017	4973	27
H12G	2822	4701	2225	44
H12H	2727	4591	1404	44
H13	1899	7387	2970	61
H13B	5816	6265	6500	50
H13C	5096	3453	5912	35
H13D	1166	4603	1745	57
H14A	848	7593	1907	65
H14B	1917	7827	1856	65
H14C	6129	7218	6931	53
H14D	7089	6961	6679	53
H14E	6255	3308	6922	41
H14F	6653	3037	6257	41
H14G	600	3696	1253	64
H14H	1376	3960	806	64
H15	1305	7340	836	62
H15B	6830	7899	6239	49
H15C	7892	3589	6902	40
H15D	1710	2998	1020	56
H16A	2624	6682	795	51

Atom	x	y	z	U_{eq}
H16B	3034	7262	1158	51
H16C	7545	7266	5506	38
H16D	6857	7703	5036	38
H16E	7895	3562	5681	31
H16F	8304	4163	5982	31
H16G	3383	3101	1511	45
H16H	3085	3600	960	45
H17A	2643	5824	2316	49
H17B	2396	5817	1484	49
H17C	5247	7427	4463	40
H17D	4837	6795	4538	40
H17E	6168	4994	5459	27
H17F	7255	5029	5855	27
H17G	3523	3274	2778	33
H17H	3317	3893	3074	33
H18	903	5909	1996	57
H18B	4119	7416	5293	51
H18C	6124	5011	6691	35
H18D	1959	3295	3142	44
H19A	276	6695	1346	66
H19B	972	6341	912	66
H19C	5102	7938	6170	56
H19D	5403	8101	5426	56
H19E	7702	4585	7017	40
H19F	6911	4255	7395	40
H19G	1046	2931	2103	53
H19H	2125	2676	2197	53
H20A	648	6732	2642	64
H20B	1581	6401	3017	64
H20C	4397	6471	5693	53
H20D	4475	6902	6339	53
H20E	4895	4462	6007	37
H20F	5153	4186	6765	37
H20G	1616	4288	2933	56
H20H	730	3911	2560	56
H22A	8756	5147	1099	82

Atom	x	y	z	U_{eq}
H22B	9520	5140	1795	82
H22C	9169	5733	1440	82
H1SA	3063	6021	7281	85
H1SB	3504	5554	7835	85
H2SA	4684	6743	-698	99
H2SB	4199	7251	-1170	99
H3SA	7629	4127	2371	209
H3SB	7062	3570	2049	209
H4SA	8541	5248	3628	51
H4SB	9452	5101	4196	51

Table 11: Solvent masking (PLATON/SQUEEZE) information for **Rh_2(*R*-TCPTAD)$_4$**.

No	x	y	z	V	e	Content
1	0.000	-0.008	0.000	1738	410	

Citations

O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

Rigaku Oxford Diffraction, (2015), CrysAlisPro Software system, version 1.171.39.9g,

Rigaku Corporation, Oxford, UK.

Sheldrick, G.M., A short history of ShelX, *Acta Cryst.*, (2008), **A64**, 339-341.

Spek, A. L. (1980-2014). PLATON. Version 191114. Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands.

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#==============================================================================
# PLATON/CHECK-( 70414) versus check.def version of 310314   for Entry: rh2r-tcp
# Data: rh2r-tcptad4-sq_sq.cif - Type: CIF       Bond Precision   C-C = 0.0109 A
# Refl: rh2r-tcptad4-sq_sq.fcf - Type: LIST4                      Temp = 100 K
#                                       X-Ray        Nref/Npar =  16.3
# Cell  13.9309(2)  23.4777(4)  19.4295(4)          90  97.9250(17)          90
# Wavelength 0.71073    Volume Reported     6294.0(2)   Calculated   6294.03(19)
# SpaceGroup from Symmetry P 21       Hall: P 2yb                monoclinic
#               Reported P 1 21 1          P 2yb               monoclinic
# MoietyFormula C82 H69 Cl16 N5 O17 Rh2, 4(C H2 Cl2)
#      Reported C82 H69 Cl16 N5 O17 Rh2, 4(C H2 Cl2)
#    SumFormula C86 H77 Cl24 N5 O17 Rh2
#      Reported C86 H77 Cl24 N5 O17 Rh2
# Mr        =   2509.15[Calc],   2509.14[Rep]
# Dx,gcm-3  =     1.324[Calc],     1.324[Rep]
# Z         =         2[Calc],         2[Rep]
# Mu (mm-1) =     0.824[Calc],     0.824[Rep]
# F000      =    2524.0[Calc],    2524.0[Rep]  or F000' =   2527.46[Calc]
# Reported   T Limits: Tmin=0.729            Tmax=1.000  AbsCorr=MULTI-SCAN
# Calculated T Limits: Tmin=0.616 Tmin'=0.556  Tmax=0.719
# Reported   Hmax= 19, Kmax= 33, Lmax= 27, Nref=  38220        , Th(max)= 30.508
# Obs in FCF Hmax= 19, Kmax= 33, Lmax= 27, Nref=  38220[ 19594], Th(max)= 30.508
# Calculated Hmax= 19, Kmax= 33, Lmax= 27, Nref=  38391[ 19624], Ratio=1.95/1.00
# PLATON/Squeeze:      1738.0 Ang**3, Total El.Count =   410.0 e-
# Reported   Rho(min) = -1.07, Rho(max) =  1.92 e/Ang**3 (From CIF)
# w=1/[sigma**2(Fo**2)+(0.0808P)**2+ 14.7866P], P=(Fo**2+2*Fc**2)/3
# R= 0.0641( 32914), wR2= 0.1590( 38220), S = 1.040      (From FCF data only)
# R= 0.0641( 32915), wR2= 0.1590( 38220), S = 1.043, Npar= 1203, Flack -0.007(8)
# Number Bijvoet Pairs =18626 ( 99%)     (13732 Selected for:  Parsons  0.040(4)
# P2(tr) 1.000, P3(tr) 1.000, P3(tw) 0.000,  Student-T Nu  9.28, Hooft -0.013(6)
#==============================================================================
For Documentation: http://http://www.platonsoft.nl/CIF-VALIDATION.pdf
#==============================================================================

#==============================================================================
>>> The Following Improvement and Query ALERTS were generated - (Acta-Mode) <<<
#==============================================================================
Format: alert-number_ALERT_alert-type_alert-level text

420_ALERT_2_B D-H Without Acceptor       O1W    -   H1WA   ...     Please Check
```

```
420_ALERT_2_B D-H Without Acceptor      O1W   -  H1WB  ...    Please Check
#==================================================================================
161_ALERT_4_C Missing or Zero su (esd) on x-coordinate for ...       RH1
161_ALERT_4_C Missing or Zero su (esd) on x-coordinate for ...       RH2
162_ALERT_4_C Missing or Zero su (esd) on y-coordinate for ...       RH1
162_ALERT_4_C Missing or Zero su (esd) on y-coordinate for ...       RH2
163_ALERT_4_C Missing or Zero su (esd) on z-coordinate for ...       RH1
163_ALERT_4_C Missing or Zero su (esd) on z-coordinate for ...       RH2
220_ALERT_2_C Large Non-Solvent  C     Ueq(max)/Ueq(min) Range       3.6 Ratio
222_ALERT_3_C Large Non-Solvent    H    Uiso(max)/Uiso(min) ..       4.1 Ratio
244_ALERT_4_C Low   'Solvent' Ueq as Compared to Neighbors of        C1S Check
244_ALERT_4_C Low   'Solvent' Ueq as Compared to Neighbors of        C3S Check
342_ALERT_3_C Low Bond Precision on  C-C Bonds ...............     0.0109 Ang.
411_ALERT_2_C Short Inter H...H Contact  H15B   ..  H18D    ..       2.14 Ang.
731_ALERT_1_C Bond    Calc 2.39910(10), Rep  2.39913(4) ......         3 su-Rat
RH1  -RH2     1.555   1.555                   #         1
911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L=  0.600        19 Why ?
913_ALERT_3_C Missing # of Very Strong Reflections in FCF ....         1 Note
#==================================================================================
002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         7 Note
003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...       125 Why ?
007_ALERT_5_G Number of Unrefined Donor-H Atoms .............          2 Why ?
008_ALERT_5_G No _iucr_refine_reflections_details   in the CIF     Please Do !
063_ALERT_4_G Crystal Size Likely too Large for Beam Size ....       0.70 mm
083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large.      14.79 Why ?
232_ALERT_2_G Hirshfeld Test Diff (M-X)  Rh1     --  O1W     ..        5.3 su
434_ALERT_2_G Short Inter HL..HL Contact  Cl1     ..  Cl1S    .      3.34 Ang.
606_ALERT_4_G VERY LARGE Solvent Accessible VOID(S) in Structure        ! Info
720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........         10 Note
760_ALERT_1_G CIF Contains no Torsion Angles .................         ? Info
790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #         3 Note
C H2 Cl2
791_ALERT_4_G The Model has Chirality at C9      ............          R Verify
791_ALERT_4_G The Model has Chirality at C9B     ............          R Verify
791_ALERT_4_G The Model has Chirality at C9C     ............          R Verify
791_ALERT_4_G The Model has Chirality at C9D     ............          R Verify
791_ALERT_4_G The Model has Chirality at C18     ............          R Verify
791_ALERT_4_G The Model has Chirality at C18B    ............          R Verify
791_ALERT_4_G The Model has Chirality at C18C    ............          R Verify
791_ALERT_4_G The Model has Chirality at C18D    ............          R Verify
```

```
802_ALERT_4_G CIF Input Record(s) with more than 80 Characters          ! Info
860_ALERT_3_G Number of Least-Squares Restraints ............       1130 Note
869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed           ! Info
910_ALERT_3_G Missing # of FCF Reflections Below Th(Min) .....          3 Why ?
912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600          9 Note
#==============================================================================

ALERT_Level and ALERT_Type Summary
==================================
2 ALERT_Level_B = A Potentially Serious Problem - Consider Carefully
15 ALERT_Level_C = Check. Ensure it is Not caused by an Omission or Oversight
25 ALERT_Level_G = General Info/Check that it is not Something Unexpected

2 ALERT_Type_1 CIF Construction/Syntax Error, Inconsistent or Missing Data.
9 ALERT_Type_2 Indicator that the Structure Model may be Wrong or Deficient.
6 ALERT_Type_3 Indicator that the Structure Quality may be Low.
23 ALERT_Type_4 Improvement, Methodology, Query or Suggestion.
2 ALERT_Type_5 Informative Message, Check.
#==============================================================================

1 Missing  Experimental  Info Issue(s) (Out of  54 Tests) -   98 % Satisfied
0 Experimental  Data  Related Issue(s) (Out of  28 Tests) -  100 % Satisfied
11 Structural  Model   Related Issue(s) (Out of 117 Tests) -   91 % Satisfied
30 Unresolved or to be Checked Issue(s) (Out of 223 Tests) -   87 % Satisfied

#==============================================================================
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7. Computational Study

7.1 Rh$_2$[S-3,5-diPhTPCP]$_4$

In this paper we employ a two-layer ONIOM (QM:MM) approach.[1] This method divides the whole system into two subsystems (called as "model" and "real" layers) and treat them at the best possible level of theory. The ONIOM partitioning of the complex that was used is shown in Figure S1. In these studies, the M06L[2] and UFF[3] methods were used for the calculations of the "model" (in red) and "real" (in blue) layers, respectively. Such partition provided an accurate description for the central rhodium tetra-carboxylate complex and accounted for the steric influence of the surrounding ligands.

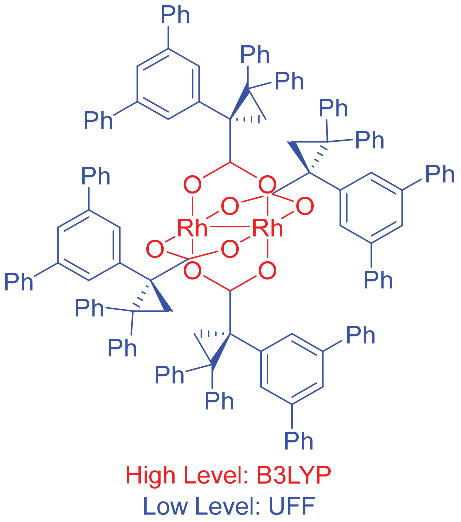
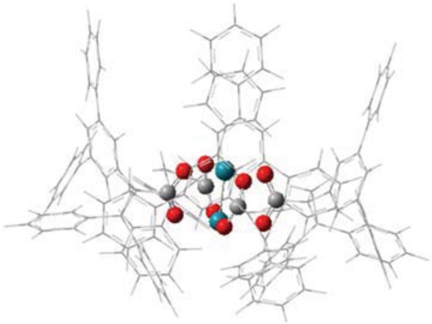


Figure S1. ONIOM partitioning scheme the form of Rh$_2$[*S*-3,5-diPhTPCP]$_4$ complex.

All calculations were performed with the Gaussian 09 software package.[4] Geometries of the studied systems were located using Stuttgart relativistic effective core potential and associated basis sets for rhodium.[5] These basis sets were extended by the polarization 4f-function (ζ_f (Rh) = 1.350).[6] The split-valence 6-31G(d) basis sets were used on all other atoms. Below, these basis sets will be called as BS1.

Cartesian Coordinates (in Å):

-CONFORMATION:



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O       -2.02552000   -0.30476900   -1.26942500 H
O       -0.92974500    1.83805200    0.88698200 H
O       -0.30255700    2.02325600   -1.27503000 H
C       -2.46753700   -0.82666100   -0.20458700 H
C       -3.90778300   -1.29719200   -0.19934300 L H-H_ 7   0.0000
C       -4.02253800   -2.79550800    0.09417100 L
H       -3.05640700   -3.34506600    0.12446600 L
H       -4.84947100   -3.09322200    0.77210400 L
C       -4.44742000   -2.27549100   -1.28652900 L
C       -5.93759100   -2.31494500   -1.56688900 L
C       -6.54806500   -1.27304100   -2.28936200 L
H       -5.97090500   -0.43459100   -2.65114300 L
C       -7.91893200   -1.33394300   -2.57170400 L
H       -8.39335400   -0.52648900   -3.11485300 L
C       -8.64127000   -2.39949300   -2.18138500 L
H       -9.69942400   -2.44126500   -2.40731800 L
C       -8.05834100   -3.42236900   -1.52762600 L
H       -8.64911000   -4.28164200   -1.23643200 L
C       -6.68660400   -3.38925900   -1.22721200 L
H       -6.24299800   -4.24046000   -0.72701600 L
C       -1.95123800   -3.36947600   -4.59790200 L
H       -1.31696400   -3.64452100   -5.43084900 L
C       -2.41540400   -2.05578900   -4.47125700 L
H       -2.14878700   -1.30766300   -5.20663100 L
C       -3.23436100   -1.71957200   -3.38469600 L
H       -3.60472300   -0.70606400   -3.30009700 L
C       -3.54757400   -2.64619300   -2.44877400 L
C       -3.12638100   -3.92343300   -2.60416000 L
H       -3.42302000   -4.68174500   -1.89525600 L
C       -2.30678400   -4.28759100   -3.68503600 L
H       -1.96451500   -5.31013900   -3.78180600 L
C       -4.87253200   -0.40094400    0.54710400 L
C       -5.36486300    0.74780200   -0.08526000 L
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H	-6.50350700	1.70842900	6.98399500	L			
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C     -0.58737200    5.12437500    1.86569600 L
H     -1.42168200    4.67290100    2.38820600 L
C      4.12762500    6.57478900    0.57926700 L
H      4.23505400    6.09942400    1.54670000 L
C      2.85943000    6.70952400   -0.01776700 L
C      2.77389200    7.31457400   -1.28835100 L
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C      3.88699800    7.74606800   -1.91089600 L
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C      4.87715200    0.40215700    0.54991400 L
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H	4.70893800	1.42995600	2.38601500	L		
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C	6.24259800	-1.13022600	4.92864800	L		
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H	6.49932800	-1.69008700	6.99446300	L		
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H	4.26139900	-8.66736900	-1.21140900	L		
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H	4.22381800	-6.25955400	-0.71074000	L		
C	3.35328400	-1.97000200	-4.60056100	L		
H	3.62652700	-1.33574600	-5.43411700	L		
C	2.04030100	-2.43564900	-4.47202300	L		
H	1.29084800	-2.17005700	-5.20641700	L		
C	1.70630100	-3.25394100	-3.38426400	L		
H	0.69300200	-3.62386100	-3.29693200	L		
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C	3.91107900	-3.14386300	-2.60712400	L		
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H	5.29505400	-1.98099000	-3.78711300	L		
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C	-0.75059600	-5.38092500	-0.06542900	L		
H	-0.96590200	-5.10962300	-1.08903300	L		
C	-1.65212000	-6.18296200	0.65331300	L		

C	-1.41799000	-6.43742400	1.95995400	L
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C	-5.22009100	-7.01794100	-0.07978400	L
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H	-2.11906900	-5.88351400	4.61538800	L
H	7.06755900	0.54890900	7.72455300	L
H	7.93181100	-6.01784800	-1.87874900	L
H	5.98212500	7.95731000	-1.85002300	L
H	0.52758400	-6.88390200	7.78024500	L
H	-0.58047800	6.93631900	7.75557500	L
H	-5.97290000	-7.96788800	-1.86212600	L
H	-7.92853200	6.01085700	-1.90279600	L
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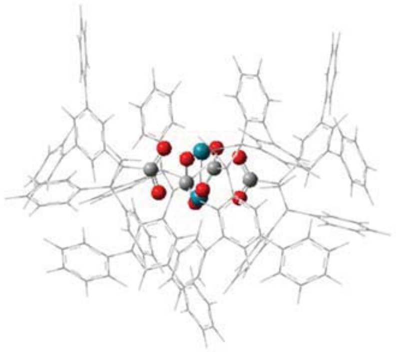
-CONFORMATION:



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O	-0.98750700	1.77398300	-0.59135400	H
O	1.43799500	1.47815900	1.61997600	H
O	1.81602400	0.96399500	-0.54483000	H

C	-1.66721100	2.01313300	0.45694500	H	
C	-2.81134800	3.00262800	0.25424000	L	H-H_ 7 0.0000
C	-2.56458800	4.32539500	0.97957900	L	
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H	-2.81813600	5.25112500	0.42333500	L	
C	-3.76710600	3.46385400	1.39638300	L	
C	-5.11930800	4.04677200	1.03146500	L	
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C	-7.35358100	3.78936700	0.12045100	L	
H	-8.11133400	3.17359400	-0.34365300	L	
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H	-6.88290700	6.91123700	1.13702600	L	
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H	-4.68519800	5.99057500	1.76155700	L	
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H	-4.17601200	-0.15529000	4.26403800	L	
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C	-3.68172900	2.81171700	2.75702200	L	
C	-3.35918100	3.54720200	3.84912100	L	
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C	-3.30824500	2.95747300	5.12306000	L	
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C	-3.33422800	3.07043400	-1.17096700	L	
C	-4.08009900	1.98607800	-1.65977400	L	
H	-4.32969600	1.16248400	-1.00078800	L	
C	-4.43762300	1.93016300	-3.01620000	L	
C	-4.04916900	2.92380800	-3.84637300	L	
H	-4.34107900	2.88347200	-4.88988600	L	
C	-3.30619800	3.96505700	-3.39989200	L	
C	-2.92920700	4.02184100	-2.03988200	L	
H	-2.26347700	4.80957200	-1.71270800	L	
C	-2.85002400	5.02164800	-4.34099000	L	
C	-2.35494900	4.68268500	-5.61699300	L	
H	-2.29462700	3.64960000	-5.93577500	L	
C	-1.90377500	5.69342100	-6.47635000	L	
H	-1.51640800	5.43608700	-7.45394300	L	
C	-1.94661400	6.98020300	-6.08648800	L	
C	-2.42022100	7.31509900	-4.87120200	L	
H	-2.44871900	8.35549600	-4.57307700	L	
C	-2.87741200	6.32620900	-3.98427700	L	
H	-3.25791200	6.62859200	-3.01610800	L	
C	-5.20288500	0.77021400	-3.52926700	L	
C	-6.37637100	0.34691100	-2.87778200	L	
H	-6.74487800	0.87024500	-2.00412600	L	
C	-7.08659000	-0.75187400	-3.38160300	L	
H	-7.99824400	-1.07452400	-2.89735300	L	
C	-6.63447500	-1.41047500	-4.46423500	L	
C	-5.50664900	-1.01792900	-5.08667600	L	
H	-5.15432800	-1.56004800	-5.95497000	L	
C	-4.78250400	0.09146700	-4.62005500	L	
H	-3.87566800	0.38242600	-5.13662500	L	
C	2.04434500	1.61914000	0.51379100	H	
C	3.15289900	2.65456600	0.48379000	L	H-H_ 64 0.0000

C	2.57703400	4.07362500	0.58670600	L
H	1.46867800	4.13883400	0.51822200	L
H	3.13024600	4.78661400	1.23322400	L
C	3.30163900	3.66388900	-0.69810000	L
C	4.65449100	4.30904400	-0.93033300	L
C	5.70778000	3.55684600	-1.48080200	L
H	5.57014000	2.51689600	-1.73500000	L
C	6.94430000	4.16762700	-1.72676200	L
H	7.76012100	3.58753400	-2.13848800	L
C	7.11407900	5.47554200	-1.46335000	L
H	8.07162200	5.94156700	-1.65931800	L
C	6.10056900	6.21467000	-0.97336800	L
H	6.24764500	7.27024100	-0.78304900	L
C	4.84917000	5.63024700	-0.71546100	L
H	4.04636000	6.25804100	-0.35021400	L
C	0.88541900	3.24644200	-4.21891600	L
H	0.27992800	3.14222600	-5.10995500	L
C	1.87935700	2.30527100	-3.93054600	L
H	2.04933600	1.46881200	-4.59575200	L
C	2.65676900	2.45985800	-2.77468100	L
H	3.43000100	1.73224700	-2.56134700	L
C	2.43169000	3.49404300	-1.92929200	L
C	1.48653300	4.41768300	-2.23571200	L
H	1.32789100	5.27752700	-1.59683700	L
C	0.69864200	4.28608700	-3.39051900	L
H	-0.05356600	5.03018800	-3.61447600	L
C	4.31781300	2.39063500	1.42065600	L
C	5.36931700	1.55710200	1.01025000	L
H	5.34598400	1.10076000	0.02945700	L
C	6.42389200	1.26762700	1.89590000	L
C	6.40023300	1.77944600	3.14700100	L
H	7.22620200	1.57509500	3.81892500	L
C	5.37234800	2.54980600	3.57406500	L
C	4.30779300	2.83863200	2.69587700	L
H	3.46268700	3.40729300	3.06353100	L
C	8.05111700	-0.60849900	2.29135500	L
H	7.58996100	-0.81595500	3.24942800	L
C	7.55283500	0.41394600	1.45993300	L
C	8.17438900	0.62999800	0.21474100	L
H	7.82333800	1.41647300	-0.44062800	L
C	9.22741100	-0.12115800	-0.15897600	L
H	9.70060300	0.05860900	-1.11604500	L
C	9.70420500	-1.08888300	0.64728500	L
C	9.10396600	-1.34060800	1.89122600	L
H	9.48837200	-2.12887100	2.52581400	L
C	5.34589400	3.07460100	4.96498200	L
C	4.95458300	4.40470600	5.21750100	L
H	4.68815800	5.07052000	4.40596700	L
C	4.92562000	4.88051600	6.53553600	L
H	4.62860200	5.90271700	6.73288000	L
C	5.26746600	4.07034500	7.55374700	L
C	5.64104700	2.79714400	7.32380200	L
H	5.90976000	2.15703500	8.15459700	L
C	5.68205500	2.28913700	6.01468600	L
H	5.97191800	1.25607500	5.86541900	L
O	1.46953100	-1.46334100	1.59402900	H
O	0.98392900	-1.77138300	-0.58304000	H
O	-1.44084700	-1.46270800	1.62984000	H
O	-1.81929800	-0.96220800	-0.53807000	H

C	1.66268600	-2.00504100	0.46704000	H	
C	2.80484200	-2.99818300	0.27152800	L	H-H_ 125 0.0000
C	2.55256800	-4.31728400	1.00181000	L	
H	1.69571500	-4.30831900	1.71051100	L	
H	2.80481600	-5.24610100	0.45021900	L	
C	3.75641500	-3.45742100	1.41803700	L	
C	5.10846900	-4.04405700	1.05816100	L	
C	6.11380400	-3.22825700	0.50773400	L	
H	5.95242800	-2.16996000	0.36012500	L	
C	7.34641200	-3.79242300	0.15441300	L	
H	8.10715700	-3.17868900	-0.30751600	L	
C	7.58718800	-5.09375000	0.39355600	L	
H	8.54600700	-5.51926200	0.12510200	L	
C	6.65176300	-5.86989300	0.97277400	L	
H	6.86509600	-6.91253900	1.17135800	L	
C	5.39753100	-5.33964300	1.31748200	L	
H	4.66763800	-5.98636700	1.78835000	L	
C	3.57960300	-1.62814400	5.28512500	L	
H	3.53792900	-1.16336400	6.26193400	L	
C	3.94152200	-0.87456300	4.16422100	L	
H	4.17235800	0.17394500	4.26893300	L	
C	3.99627000	-1.49204000	2.90766000	L	
H	4.28463500	-0.90917200	2.04210300	L	
C	3.66986200	-2.79834500	2.77519800	L	
C	3.34169700	-3.52723200	3.87002100	L	
H	3.11674600	-4.58294300	3.77945900	L	
C	3.28990300	-2.93108000	5.14094100	L	
H	3.01726600	-3.52417100	6.00453800	L	
C	3.33231500	-3.07311500	-1.15163900	L	
C	4.08323500	-1.99304700	-1.64206800	L	
H	4.33167700	-1.16685000	-0.98591900	L	
C	4.44900500	-1.94559300	-2.99659000	L	
C	4.06312100	-2.94287000	-3.82356200	L	
H	4.36153200	-2.90918400	-4.86548100	L	
C	3.31544800	-3.98009500	-3.37564600	L	
C	2.93041800	-4.02861600	-2.01755900	L	
H	2.26206200	-4.81383700	-1.68973700	L	
C	2.86412500	-5.04169700	-4.31333700	L	
C	2.37591000	-4.70959300	-5.59374300	L	
H	2.31709500	-3.67818500	-5.91821100	L	
C	1.93017700	-5.72502900	-6.45040300	L	
H	1.54826100	-5.47299800	-7.43152000	L	
C	1.97166000	-7.00977000	-6.05369500	L	
C	2.43859400	-7.33809200	-4.83403000	L	
H	2.46614700	-8.37693400	-4.53043600	L	
C	2.89020500	-6.34434500	-3.94966400	L	
H	3.26557000	-6.64141900	-2.97785200	L	
C	5.22160500	-0.79128500	-3.51115000	L	
C	6.39331700	-0.36963100	-2.85542600	L	
H	6.75482800	-0.88996600	-1.97705700	L	
C	7.11105700	0.72336100	-3.36112300	L	
H	8.02145300	1.04457700	-2.87357100	L	
C	6.66769400	1.37821500	-4.44964100	L	
C	5.54155800	0.98729500	-5.07616500	L	
H	5.19634100	1.52635100	-5.94920000	L	
C	4.81012600	-0.11655900	-4.60777700	L	
H	3.90500900	-0.40654600	-5.12789200	L	
C	-2.04619900	-1.61190200	0.52419400	H	
C	-3.15163100	-2.65075300	0.49907800	L	H-H_ 182 0.0000

C	-2.57321000	-4.06756500	0.61552400	L
H	-1.46443800	-4.13055600	0.55206500	L
H	-3.12749100	-4.77634400	1.26571500	L
C	-3.29371600	-3.66951400	-0.67538000	L
C	-4.64446200	-4.31909300	-0.90778200	L
C	-5.69682300	-3.57342600	-1.46885700	L
H	-5.56003900	-2.53538600	-1.73115300	L
C	-6.93125300	-4.18842100	-1.71472100	L
H	-7.74633700	-3.61320700	-2.13469700	L
C	-7.09986200	-5.49435900	-1.44092500	L
H	-8.05579600	-5.96370300	-1.63683900	L
C	-6.08710200	-6.22753600	-0.94054900	L
H	-6.23314900	-7.28171600	-0.74189400	L
C	-4.83776700	-5.63876400	-0.68249000	L
H	-4.03540600	-6.26203900	-0.30862500	L
C	-0.86499100	-3.27382700	-4.19002800	L
H	-0.25632700	-3.17513700	-5.07952400	L
C	-1.86219000	-2.33277200	-3.91284200	L
H	-2.03158800	-1.50196800	-4.58523400	L
C	-2.64371300	-2.48020000	-2.75883500	L
H	-3.41952700	-1.75281700	-2.55428000	L
C	-2.41944500	-3.50718500	-1.90448600	L
C	-1.47097300	-4.43094300	-2.20002800	L
H	-1.31277500	-5.28535900	-1.55379800	L
C	-0.67906000	-4.30657500	-3.35288200	L
H	0.07558000	-5.05071600	-3.56826000	L
C	-4.32171100	-2.38113300	1.42804700	L
C	-5.37220700	-1.55206600	1.00588100	L
H	-5.34431300	-1.10308500	0.02180400	L
C	-6.43220000	-1.25780500	1.88354300	L
C	-6.41445200	-1.76026600	3.13851800	L
H	-7.24444500	-1.55250800	3.80445000	L
C	-5.38781800	-2.52591800	3.57677300	L
C	-4.31808900	-2.81979800	2.70653500	L
H	-3.47436000	-3.38471300	3.08297000	L
C	-8.06810600	0.61556400	2.25677900	L
H	-7.61411500	0.83034200	3.21665000	L
C	-7.56077700	-0.41012400	1.43481400	L
C	-8.17332200	-0.63560800	0.18681200	L
H	-7.81541100	-1.42482300	-0.46148100	L
C	-9.22620300	0.10985400	-0.19848300	L
H	-9.69224800	-0.07709500	-1.15768600	L
C	-9.71167500	1.08066300	0.59882500	L
C	-9.12075700	1.34164100	1.84531800	L
H	-9.51208200	2.13230000	2.47266100	L
C	-5.36852500	-3.04054200	4.97154000	L
C	-4.97834200	-4.36865600	5.23580400	L
H	-4.70710300	-5.04016100	4.43057100	L
C	-4.95703700	-4.83504300	6.55735400	L
H	-4.66109800	-5.85577100	6.76372200	L
C	-5.30499800	-4.01768900	7.56773900	L
C	-5.67734700	-2.74621000	7.32653500	L
H	-5.95105300	-2.10023000	8.15113500	L
C	-5.71081400	-2.24759800	6.01361000	L
H	-6.00003200	-1.21571300	5.85518500	L
H	1.62506100	-7.78807700	-6.72200700	L
H	7.22285200	2.22834600	-4.82583500	L
H	10.55175400	-1.68387200	0.33176500	L
H	-5.28492700	-4.38607400	8.58581200	L

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 H        5.24138800    4.44596400    8.56903700 L
 H      -10.55903000    1.67094900    0.27408100 L
 H       -7.18390800   -2.26495100   -4.83899800 L
 H       -1.59564300    7.75483100   -6.75678400 L
---------------------------------------------------------------------
```

7.2 $Rh_2[R\text{-}tris(p\text{-}{}^tBuC_6H_4)TPCP]_4$

All calculations were performed using Gaussian 09.[7] Performing DFT calculations on the complete dirhodium complex (approximately 500 atoms) is impractical, so we employed a two-layer ONIOM[7] (B3LYP[9-11]:UFF[3]) approach to study this reaction. The ONIOM partitioning of the catalyst system that was used is shown in Figure S3. ONIOM partitioning of the catalyst with the atoms inside the purple rectangle modeled with DFT and the atoms outside modeled with the UFF. The carbene and the 2-methylpentane substrate are also included in the QM part. For the QM part, the LANL2DZ basis set[12-13] was used for Rh, Br, and Cl atoms, and the 6-31G(d)[14-16] basis set was used for all other atoms. The solvation free-energy corrections were computed with the SMD model[17] on gas-phase optimized geometries, and dichloromethane was chosen as the solvent for consistency with the experiment. Extensive conformational searches for catalysts and transition states have been conducted, but only the most stable conformers are discussed here.

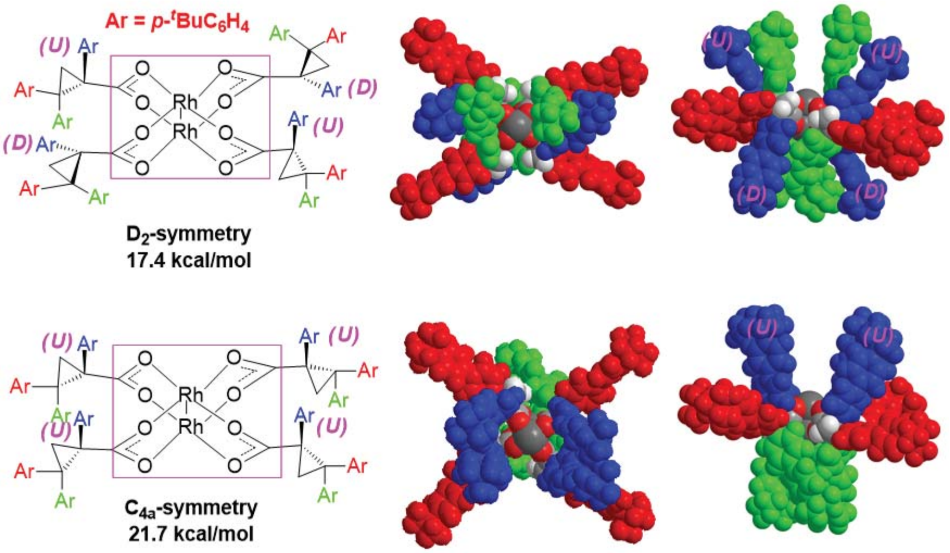
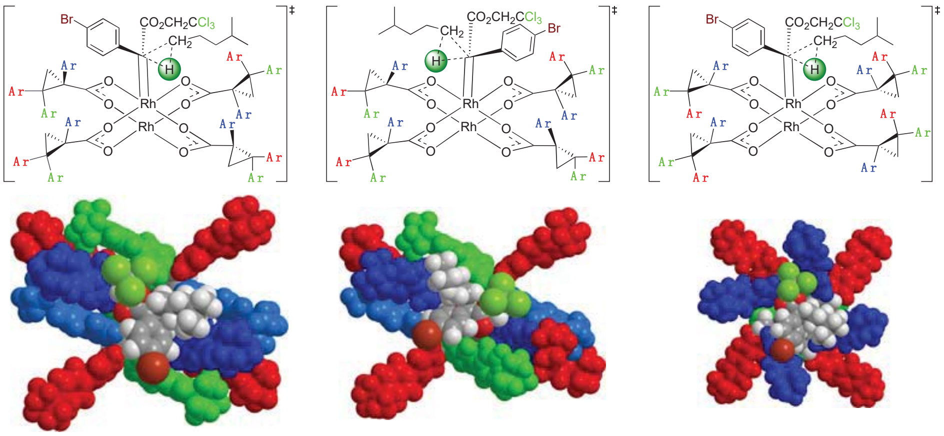


Figure S4. Structural information about the dirhodium catalyst I. a, ONIOM partitioning of the catalyst with the atoms inside the purple rectangle modeled with DFT and the atoms outside modeled with the UFF, along with the relative energies of the D2 and C4a conformations. b, Top and side views of the D2 and C4a conformations.

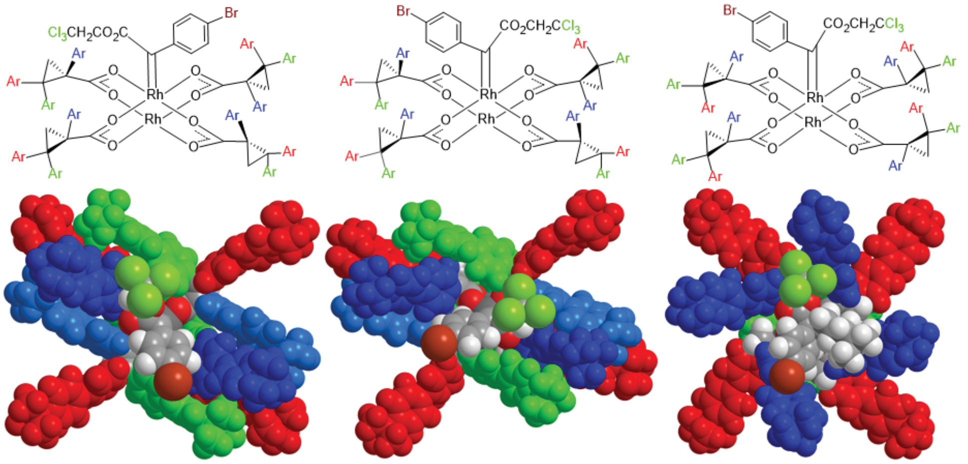


TS1
ΔΔE‡= 0.0 kcal/mol

TS2
ΔΔE‡= 3.1 kcal/mol

TS3
ΔΔE‡= 10.4 kcal/mol

Figure S5. ONIOM transition structures for carbene insertion into the least hindered primary C–H bond with C_2 and C_4-catalyst.

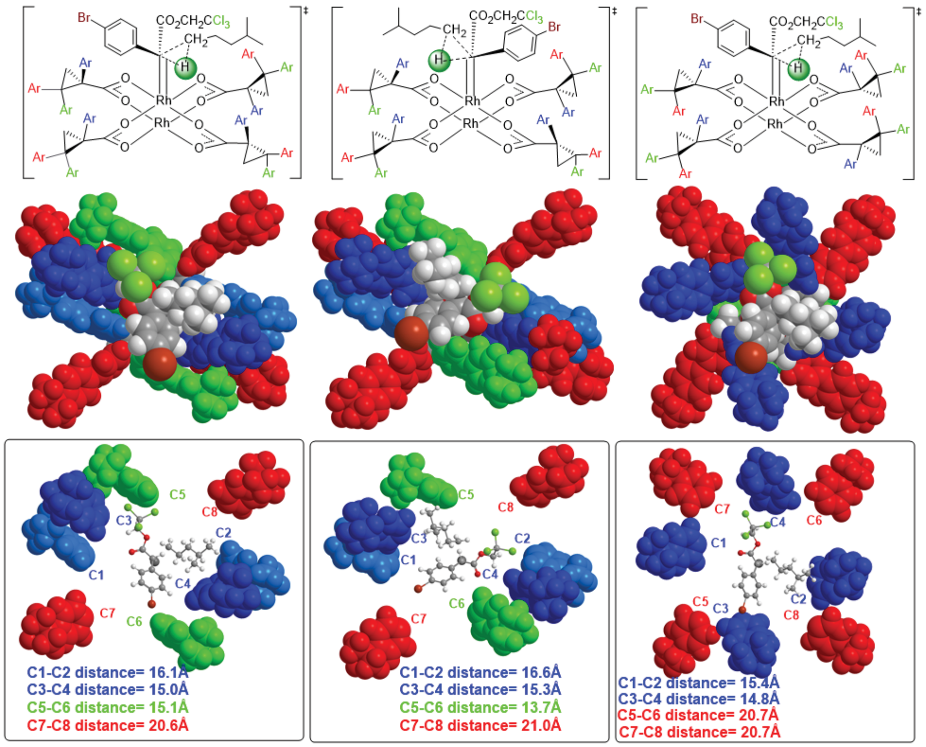


C2-carbene
0.0 kcal/mol

C2a-carbene
-1.5 kcal/mol

C4-carbene
11.7 kcal/mol

Figure S6. Structural information about the dirhodium catalyst I. a, ONIOM partitioning of the catalyst with the atoms inside the purple rectangle modeled with DFT and the atoms outside modeled with the UFF, along with the relative energies of the C2-carbene, C2a-carbene, and C4-carbene conformations. b, Top views of the C2-carbene, C2a-carbene, and C4-carbene conformations.



TS-1
$\Delta\Delta E^{\ddagger}$= 0.0 kcal/mol

TS-2
$\Delta\Delta E^{\ddagger}$= 3.1 kcal/mol

TS-3
$\Delta\Delta E^{\ddagger}$= 10.4 kcal/mol

Figure S7. Optimized geometries of the primary and primary enantiomeric C–H bond activation transition states.

Cartesian coordinates of the structures

catalyst I (*C_2*) (E = -973.3576356 a.u. ; Esol = -973.46376139 a.u.)

C	-2.3845	-1.09716	0.773495	H
C	-3.7764	-1.72575	0.80406	L
C	-3.76185	-3.05216	1.573852	L
H	-4.35373	-3.8901	1.17446	L
H	-2.83663	-3.27817	2.147002	L
C	-4.59135	-1.88782	2.131799	L
C	-4.06959	-1.17053	3.351925	L
C	-3.62471	-1.8889	4.471446	L
H	-3.72905	-2.96614	4.507735	L
C	-2.98727	-1.22602	5.524292	L
H	-2.61111	-1.80466	6.357754	L
C	-2.7877	0.164534	5.472675	L
C	-3.29938	0.888645	4.382782	L
H	-3.18029	1.963791	4.331722	L
C	-3.95402	0.227792	3.341235	L
H	-4.30578	0.795215	2.490087	L
C	-6.09548	-2.04461	2.007165	L
C	-6.86988	-0.9772	1.532331	L
H	-6.43311	0.005277	1.412443	L
C	-8.17098	-1.20195	1.08303	L
H	-8.71649	-0.39381	0.620771	L
C	-8.74064	-2.48115	1.15901	L
C	-8.02758	-3.50592	1.802622	L
H	-8.45031	-4.49751	1.89808	L
C	-6.71568	-3.28639	2.232266	L
H	-6.1591	-4.11095	2.65929	L
C	-4.60959	-1.60196	-0.46787	L
C	-5.08777	-2.71273	-1.17719	L
H	-4.78905	-3.70291	-0.91595	L
C	-6.0066	-2.55985	-2.21429	L
H	-6.39837	-3.44898	-2.68655	L
C	-6.45259	-1.28311	-2.59071	L
C	-5.89479	-0.16351	-1.94959	L
H	-6.18346	0.833919	-2.24325	L
C	-4.98127	-0.32191	-0.90362	L
H	-4.60755	0.552957	-0.38816	L
C	1.116363	-2.40601	0.799821	H
C	1.921154	-3.6915	0.832104	L
C	1.240882	-5.06775	0.569446	L
C	1.592083	-4.62863	1.997338	L
H	0.725421	-4.32146	2.622935	L

H	2.451432	-5.15057	2.463728	L
C	3.382275	-3.55727	0.455368	L
C	3.725787	-3.35351	-0.88761	L
H	2.954178	-3.2666	-1.64146	L
C	5.062786	-3.25309	-1.27221	L
H	5.28486	-3.08055	-2.31717	L
C	6.091651	-3.31676	-0.31408	L
C	5.741285	-3.47002	1.040422	L
H	6.501251	-3.51986	1.80897	L
C	4.401136	-3.56988	1.422535	L
H	4.167076	-3.65516	2.475171	L
C	2.086354	-6.18925	-0.00288	L
C	2.395064	-6.18767	-1.3709	L
H	2.032565	-5.39516	-2.01178	L
C	3.164029	-7.21116	-1.92787	L
H	3.39139	-7.17726	-2.98601	L
C	3.608647	-8.28163	-1.13387	L
C	3.243737	-8.31751	0.223305	L
H	3.562334	-9.13402	0.858971	L
C	2.477377	-7.28955	0.779668	L
H	2.191462	-7.35805	1.821019	L
C	-0.24275	-5.2012	0.31915	L
C	-1.00088	-6.08133	1.109208	L
H	-0.5582	-6.55332	1.977623	L
C	-2.3119	-6.41035	0.753475	L
H	-2.85578	-7.11515	1.368897	L
C	-2.89322	-5.87332	-0.40825	L
C	-2.13495	-4.97489	-1.18672	L
H	-2.55491	-4.51855	-2.07361	L
C	-0.81983	-4.65587	-0.83458	L
H	-0.2381	-4.0223	-1.49057	L
C	2.425238	1.058223	0.697434	H
C	3.826622	1.672136	0.728661	L
C	3.815123	3.024488	1.447607	L
H	4.41606	3.827071	0.988635	L
H	2.878985	3.288931	1.985324	L
C	4.615104	1.871506	2.069572	L
C	4.056419	1.196461	3.29823	L
C	3.581744	1.951055	4.381176	L
H	3.685939	3.028875	4.38474	L
C	2.916975	1.322533	5.438746	L
H	2.520448	1.928265	6.243301	L
C	2.719867	-0.06968	5.4289	L

C	3.258293	-0.82857	4.375762	L
H	3.142772	-1.90536	4.356823	L
C	3.938235	-0.20213	3.329436	L
H	4.310599	-0.79967	2.50712	L
C	6.122972	2.037121	2.000781	L
C	6.720354	3.295686	2.191511	L
H	6.134267	4.139783	2.531939	L
C	8.05714	3.500391	1.844727	L
H	8.463563	4.501446	1.905005	L
C	8.823339	2.443583	1.326747	L
C	8.270288	1.153791	1.297579	L
H	8.857037	0.317062	0.945489	L
C	6.937726	0.947764	1.659647	L
H	6.521698	-0.04814	1.590941	L
C	4.69122	1.510477	-0.51529	L
C	5.040612	2.591087	-1.33845	L
H	4.595443	3.554626	-1.19454	L
C	6.005706	2.445416	-2.33768	L
H	6.272946	3.309909	-2.932	L
C	6.629868	1.204192	-2.55179	L
C	6.196985	0.099038	-1.80022	L
H	6.652134	-0.868	-1.94098	L
C	5.224362	0.248139	-0.80679	L
H	4.944034	-0.60538	-0.20416	L
C	-1.1384	2.37637	0.696433	H
C	-1.96493	3.652054	0.694375	L
C	-1.30467	5.034606	0.415861	L
C	-1.64507	4.609124	1.848448	L
H	-0.77294	4.325085	2.477474	L
H	-2.51174	5.122266	2.312045	L
C	-3.43925	3.491211	0.376408	L
C	-3.85533	3.357171	-0.95476	L
H	-3.1262	3.32895	-1.75324	L
C	-5.21276	3.248188	-1.26937	L
H	-5.48954	3.146089	-2.30993	L
C	-6.18726	3.215108	-0.25258	L
C	-5.75883	3.30846	1.085716	L
H	-6.46907	3.303804	1.90138	L
C	-4.40278	3.427219	1.395715	L
H	-4.11122	3.472289	2.436521	L
C	-2.16067	6.14393	-0.16477	L
C	-2.57499	7.238954	0.613663	L
H	-2.29975	7.313462	1.65736	L

C	-3.33957	8.262187	0.0471	L
H	-3.64684	9.091815	0.671466	L
C	-3.67553	8.231334	-1.31737	L
C	-3.20901	7.166279	-2.10663	L
H	-3.44237	7.117192	-3.1627	L
C	-2.44477	6.144889	-1.53825	L
H	-2.06819	5.354897	-2.17422	L
C	0.176944	5.178138	0.168597	L
C	0.766634	4.614098	-0.96899	L
H	0.190663	3.973295	-1.62333	L
C	2.089271	4.918808	-1.30388	L
H	2.515925	4.452237	-2.18183	L
C	2.844479	5.815052	-0.5193	L
C	2.245225	6.377197	0.621509	L
H	2.780752	7.089289	1.235694	L
C	0.926149	6.065906	0.957284	L
H	0.472781	6.55277	1.811959	L
O	0.936376	-1.81779	1.910242	H
O	0.782395	-1.95619	-0.33949	H
O	1.806407	0.956651	1.798357	H
O	1.949056	0.723957	-0.43292	H
O	-0.9358	1.834276	1.826983	H
O	-0.79539	1.892887	-0.4264	H
O	-1.78195	-0.93458	1.875385	H
O	-1.90454	-0.8053	-0.36733	H
C	-7.63427	3.036648	-0.58049	L
C	-8.48522	2.343274	0.295314	L
C	-8.17839	3.541456	-1.77449	L
C	-9.83209	2.149265	-0.01439	L
H	-8.11063	1.922398	1.217898	L
C	-9.52785	3.343714	-2.08993	L
H	-7.56689	4.106921	-2.46518	L
C	-10.3858	2.638483	-1.21454	L
H	-10.4401	1.603649	0.694224	L
H	-9.8805	3.754496	-3.02402	L
C	7.514225	-3.15254	-0.72408	L
C	8.421049	-2.46436	0.096826	L
C	7.962402	-3.62475	-1.9687	L
C	9.732449	-2.23623	-0.32285	L
H	8.111914	-2.06866	1.054753	L
C	9.269896	-3.38437	-2.39764	L
H	7.300938	-4.18313	-2.61859	L
C	10.18279	-2.67288	-1.58647	L

H	10.39114	-1.69834	0.345021	L
H	9.544635	-3.76408	-3.37013	L
C	7.757827	1.073946	-3.51615	L
C	8.686682	2.115229	-3.66573	L
C	7.941757	-0.10028	-4.26445	L
C	9.767481	1.990555	-4.53876	L
H	8.597479	3.021806	-3.08459	L
C	9.020638	-0.226	-5.14553	L
H	7.240899	-0.92151	-4.18477	L
C	9.955149	0.823157	-5.30833	L
H	10.46034	2.818201	-4.60602	L
H	9.102615	-1.15299	-5.69282	L
C	-7.53484	-1.12347	-3.60074	L
C	-8.48063	-0.0946	-3.47039	L
C	-7.66616	-2.02264	-4.67201	L
C	-9.5301	0.027899	-4.37943	L
H	-8.43588	0.599112	-2.64168	L
C	-8.73032	-1.91362	-5.57175	L
H	-6.94363	-2.81433	-4.82206	L
C	-9.69399	-0.88801	-5.4381	L
H	-10.2264	0.839448	-4.23927	L
H	-8.78042	-2.64466	-6.36457	L
C	4.437328	-9.36228	-1.72503	L
C	5.461939	-9.05756	-2.6334	L
C	4.209562	-10.7045	-1.38876	L
C	6.242062	-10.0709	-3.19644	L
H	5.672794	-8.02873	-2.89842	L
C	4.986314	-11.7199	-1.95115	L
H	3.415313	-10.9735	-0.70365	L
C	6.019804	-11.4285	-2.86839	L
H	7.015923	-9.76831	-3.88565	L
H	4.769421	-12.7403	-1.66598	L
C	-4.29669	-6.20935	-0.7872	L
C	-4.67797	-6.27544	-2.13736	L
C	-5.29315	-6.33645	0.195411	L
C	-6.02373	-6.3888	-2.4951	L
H	-3.93715	-6.20766	-2.92367	L
C	-6.6402	-6.4515	-0.16033	L
H	-5.04292	-6.28014	1.2469	L
C	-7.03912	-6.4499	-1.51666	L
H	-6.26867	-6.39652	-3.54833	L
H	-7.35639	-6.51074	0.644978	L
C	-10.0137	-2.76812	0.458722	L

C	-10.9959	-3.57977	1.040678	L
C	-10.2165	-2.28287	-0.84061	L
C	-12.1554	-3.90983	0.331965	L
H	-10.8645	-3.96427	2.044494	L
C	-11.3642	-2.61954	-1.55492	L
H	-9.46372	-1.67442	-1.3231	L
C	-12.3606	-3.44174	-0.98812	L
H	-12.873	-4.54263	0.831778	L
H	-11.4602	-2.24147	-2.56341	L
C	-4.49326	9.315876	-1.91765	L
C	-5.59291	9.84573	-1.22645	L
C	-4.18143	9.828864	-3.1852	L
C	-6.36589	10.86557	-1.78812	L
H	-5.86844	9.458188	-0.25339	L
C	-4.95106	10.84884	-3.74878	L
H	-3.32835	9.453948	-3.73676	L
C	-6.06092	11.39163	-3.06506	L
H	-7.20052	11.22579	-1.20582	L
H	-4.66902	11.2146	-4.7266	L
C	4.255258	6.142884	-0.87722	L
C	5.224434	6.332037	0.122328	L
C	4.662337	6.193372	-2.22061	L
C	6.567278	6.520281	-0.21083	L
H	4.95712	6.28791	1.170071	L
C	6.007468	6.369014	-2.55601	L
H	3.941177	6.083405	-3.02018	L
C	6.994898	6.516281	-1.55545	L
H	7.276193	6.647842	0.595723	L
H	6.25374	6.378158	-3.60695	L
C	10.13451	2.710751	0.692186	L
C	11.05651	3.590739	1.27491	L
C	10.41798	2.168425	-0.56854	L
C	12.23255	3.936558	0.601568	L
H	10.8614	4.021834	2.249023	L
C	11.57815	2.529288	-1.25239	L
H	9.715306	1.500013	-1.04992	L
C	12.51155	3.422552	-0.68728	L
H	12.8998	4.624038	1.099022	L
H	11.73355	2.117235	-2.2392	L
C	1.94897	-0.73028	6.508254	L
C	0.984318	-1.70109	6.204188	L
C	2.186259	-0.40768	7.849761	L
C	0.291946	-2.35738	7.224791	L

H	0.766336	-1.95497	5.17376	L
C	1.494012	-1.0601	8.873535	L
H	2.937088	0.328284	8.108303	L
C	0.541379	-2.06473	8.584109	L
H	-0.42842	-3.11297	6.943158	L
H	1.737489	-0.77868	9.886629	L
C	-2.03515	0.857072	6.543916	L
C	-1.04846	1.800558	6.226183	L
C	-2.30554	0.585502	7.890137	L
C	-0.36169	2.4763	7.23766	L
H	-0.80672	2.015536	5.192187	L
C	-1.61695	1.254981	8.905151	L
H	-3.07629	-0.12637	8.157425	L
C	-0.63765	2.229386	8.600988	L
H	0.377845	3.208816	6.945175	L
H	-1.88228	1.008766	9.922051	L
C	6.852022	-12.5799	-3.47007	L
C	5.92032	-13.539	-4.24254	L
H	5.371933	-12.9881	-5.03715	L
H	6.503783	-14.3548	-4.72204	L
H	5.175524	-14.0145	-3.57077	L
C	7.557429	-13.3536	-2.335	L
H	8.199892	-12.6677	-1.74136	L
H	6.826072	-13.8282	-1.64797	L
H	8.19824	-14.1627	-2.74815	L
C	7.942654	-12.0912	-4.45365	L
H	8.666039	-11.4203	-3.94166	L
H	8.517689	-12.9501	-4.86334	L
H	7.488249	-11.5543	-5.31434	L
C	-8.51978	-6.48422	-1.9537	L
C	-9.5032	-6.55612	-0.7616	L
H	-10.5568	-6.56954	-1.11725	L
H	-9.33721	-7.47925	-0.16552	L
H	-9.38808	-5.67021	-0.10413	L
C	-8.84957	-5.20374	-2.7523	L
H	-8.24738	-5.13521	-3.68228	L
H	-9.92144	-5.18421	-3.04614	L
H	-8.64313	-4.30325	-2.13614	L
C	-8.77037	-7.72126	-2.84241	L
H	-8.17937	-7.67724	-3.78077	L
H	-8.49398	-8.65007	-2.29802	L
H	-9.84242	-7.78962	-3.12905	L
C	-13.6052	-3.80467	-1.8217	L

C	-13.1664	-4.58136	-3.08225	L
H	-12.5068	-3.96917	-3.73141	L
H	-12.6121	-5.50135	-2.79536	L
H	-14.049	-4.87936	-3.68875	L
C	-14.34	-2.51219	-2.24201	L
H	-15.2677	-2.75129	-2.80578	L
H	-14.6188	-1.91739	-1.3453	L
H	-13.7103	-1.87607	-2.89774	L
C	-14.6139	-4.68931	-1.05095	L
H	-14.1514	-5.65752	-0.76063	L
H	-14.9806	-4.16886	-0.13984	L
H	-15.4986	-4.92039	-1.68336	L
C	-10.9033	-0.74412	-6.38408	L
C	-10.9405	-1.82759	-7.4882	L
H	-11.01	-2.84397	-7.04338	L
H	-11.8268	-1.69033	-8.14537	L
H	-10.036	-1.76847	-8.1315	L
C	-12.2096	-0.86117	-5.56798	L
H	-12.2974	-0.05067	-4.81447	L
H	-13.0978	-0.79469	-6.23294	L
H	-12.2446	-1.83595	-5.03699	L
C	-10.855	0.634357	-7.07836	L
H	-10.9432	1.464414	-6.34653	L
H	-9.89797	0.755334	-7.6305	L
H	-11.6921	0.740699	-7.80218	L
C	-11.8817	2.400991	-1.51172	L
C	-12.3324	2.990371	-2.87006	L
H	-13.4118	2.79139	-3.0472	L
H	-12.1895	4.092385	-2.89039	L
H	-11.7696	2.534739	-3.71082	L
C	-12.7344	3.065797	-0.40933	L
H	-13.8187	2.943809	-0.62222	L
H	-12.5389	2.614995	0.586071	L
H	-12.51	4.15285	-0.34982	L
C	-12.1734	0.883361	-1.53356	L
H	-11.5257	0.373437	-2.2751	L
H	-11.9945	0.416717	-0.54245	L
H	-13.2333	0.687191	-1.80514	L
C	0.089933	3.048058	9.688692	L
C	-0.33473	2.659455	11.12554	L
H	0.217637	3.264716	11.87702	L
H	-1.41956	2.843842	11.28227	L
H	-0.11038	1.589603	11.32878	L

C	-0.22592	4.546987	9.494476	L
H	-1.32393	4.717642	9.524346	L
H	0.243811	5.157069	10.2964	L
H	0.159321	4.921645	8.52303	L
C	1.614066	2.831477	9.580364	L
H	1.863649	1.765891	9.758021	L
H	2.003485	3.124843	8.583672	L
H	2.151674	3.438885	10.34048	L
C	-0.18201	-2.86941	9.685235	L
C	0.214566	-2.43144	11.11594	L
H	-0.33344	-3.02862	11.87703	L
H	1.301202	-2.58588	11.29134	L
H	-0.0373	-1.36198	11.28651	L
C	0.170271	-4.36552	9.537205	L
H	-0.29618	-4.96378	10.34988	L
H	-0.19348	-4.77579	8.571859	L
H	1.271358	-4.50999	9.585678	L
C	-1.7089	-2.69146	9.552078	L
H	-1.98431	-1.62708	9.694525	L
H	-2.07854	-3.02453	8.560552	L
H	-2.24229	-3.28782	10.32382	L
C	8.495076	6.673774	-1.8798	L
C	8.808132	6.522656	-3.38814	L
H	9.901186	6.604703	-3.575	L
H	8.47655	5.52961	-3.76165	L
H	8.313339	7.322666	-3.9798	L
C	9.305705	5.595767	-1.12731	L
H	10.37002	5.599322	-1.44666	L
H	9.297154	5.769709	-0.03227	L
H	8.882754	4.58876	-1.32337	L
C	8.968868	8.071485	-1.43185	L
H	8.386337	8.862282	-1.95219	L
H	8.841451	8.210066	-0.33734	L
H	10.04562	8.215941	-1.66795	L
C	11.14731	0.740017	-6.28439	L
C	12.46889	0.83172	-5.49254	L
H	13.34264	0.776537	-6.17738	L
H	12.54339	1.785443	-4.93019	L
H	12.54386	-0.00664	-4.76946	L
C	11.07286	1.909443	-7.29155	L
H	11.88917	1.836715	-8.04271	L
H	10.10065	1.894088	-7.8302	L
H	11.17788	2.892653	-6.78749	L

C	11.17411	-0.57484	-7.10015	L
H	11.28193	-1.45636	-6.43403	L
H	10.24779	-0.68347	-7.7048	L
H	12.0363	-0.58544	-7.80202	L
C	11.62754	-2.36414	-2.02778	L
C	11.9395	-2.8508	-3.4626	L
H	11.8495	-3.95605	-3.53616	L
H	11.25105	-2.37679	-4.19382	L
H	12.97792	-2.58171	-3.75483	L
C	12.61661	-3.05567	-1.06638	L
H	13.66644	-2.87241	-1.38294	L
H	12.5081	-2.67508	-0.02901	L
H	12.4409	-4.15317	-1.0551	L
C	11.86194	-0.83916	-1.99241	L
H	11.11214	-0.3201	-2.62796	L
H	11.78551	-0.43875	-0.96084	L
H	12.8779	-0.58504	-2.36424	L
C	-6.88473	12.51802	-3.72305	L
C	-7.47134	12.01353	-5.05947	L
H	-8.09782	11.11107	-4.8901	L
H	-8.105	12.79516	-5.53218	L
H	-6.67194	11.75192	-5.78379	L
C	-8.06433	13.00007	-2.84452	L
H	-7.69753	13.40779	-1.87771	L
H	-8.63015	13.81022	-3.35417	L
H	-8.7767	12.16991	-2.64742	L
C	-5.97197	13.73463	-3.99041	L
H	-5.50695	14.08415	-3.04321	L
H	-5.16065	13.48743	-4.70648	L
H	-6.55369	14.57621	-4.42545	L
C	13.76489	3.815426	-1.49434	L
C	14.57335	2.54659	-1.84612	L
H	14.84046	1.989978	-0.92185	L
H	14.00082	1.866005	-2.51027	L
H	15.51248	2.812088	-2.37833	L
C	14.70447	4.773803	-0.72453	L
H	15.59947	5.023091	-1.33522	L
H	14.1887	5.72937	-0.48709	L
H	15.06165	4.304466	0.217625	L
C	13.33209	4.524811	-2.79613	L
H	12.72783	5.427925	-2.56224	L
H	14.2195	4.841397	-3.38596	L
H	12.7227	3.858728	-3.44154	L

Rh	0.010128	-0.03252	-0.47018	H
Rh	0.01106	0.015653	1.910576	H

catalyst I (*C_4*) (E = -973.3335121 a.u. ; Esol = -973.44765145 a.u.)

C	2.567274	0.550416	-1.63035	H
C	4.057398	0.825628	-1.61683	L
C	4.393344	2.292991	-1.88974	L
H	5.274984	2.486308	-2.53476	L
H	3.519912	2.978396	-1.91954	L
C	4.712108	1.705711	-0.50846	L
C	3.869722	2.211853	0.641697	L
C	3.715913	3.586551	0.869276	L
H	4.174565	4.304749	0.201254	L
C	2.972315	4.046081	1.962253	L
H	2.885311	5.114155	2.108203	L
C	2.363036	3.137962	2.852973	L
C	2.567394	1.760562	2.642131	L
H	2.107892	1.020539	3.282247	L
C	3.348374	1.310232	1.577169	L
H	3.520013	0.248338	1.461026	L
C	6.186381	1.537107	-0.21053	L
C	7.095656	2.575871	-0.46939	L
H	6.759626	3.501482	-0.91956	L
C	8.447811	2.430004	-0.14816	L
H	9.131236	3.23447	-0.38894	L
C	8.913063	1.252783	0.463999	L
C	7.992316	0.234019	0.763111	L
H	8.311718	-0.66805	1.269894	L
C	6.642086	0.38306	0.441139	L
H	5.949438	-0.3977	0.715792	L
C	4.90695	-0.22464	-2.29777	L
C	5.060884	-1.46879	-1.67194	L
H	4.614851	-1.64567	-0.70329	L
C	5.767431	-2.49834	-2.29396	L
H	5.888153	-3.43855	-1.77097	L
C	6.308915	-2.31534	-3.57694	L
C	6.123141	-1.08007	-4.22286	L
H	6.495539	-0.92274	-5.22734	L
C	5.414452	-0.04998	-3.59669	L
H	5.243827	0.868487	-4.14171	L
C	-0.55332	2.548168	-1.62526	H
C	-0.83411	4.037285	-1.60849	L
C	-1.70753	4.688055	-0.49238	L
C	-2.3053	4.366926	-1.86843	L
H	-2.98674	3.490338	-1.89256	L

H	-2.50867	5.248124	-2.51096	L
C	0.204123	4.890436	-2.30289	L
C	0.013761	5.389395	-3.60294	L
H	-0.90978	5.212168	-4.13723	L
C	1.034863	6.096712	-4.2449	L
H	0.865626	6.461767	-5.25018	L
C	2.276821	6.289097	-3.61421	L
C	2.475252	5.757234	-2.32954	L
H	3.421331	5.882923	-1.81828	L
C	1.454248	5.052662	-1.69129	L
H	1.64325	4.612932	-0.72212	L
C	-1.54281	6.162886	-0.1959	L
C	-2.58819	7.067392	-0.44474	L
H	-3.5165	6.727232	-0.88619	L
C	-2.44556	8.420137	-0.12447	L
H	-3.25543	9.099907	-0.35743	L
C	-1.26481	8.890632	0.476849	L
C	-0.23906	7.974458	0.766135	L
H	0.666116	8.29781	1.264705	L
C	-0.38485	6.623592	0.445168	L
H	0.4013	5.934234	0.712761	L
C	-2.20363	3.844043	0.661156	L
C	-3.57642	3.689735	0.900333	L
H	-4.30037	4.14899	0.238983	L
C	-4.02659	2.945204	1.996701	L
H	-5.09334	2.858177	2.152122	L
C	-3.11079	2.335617	2.879309	L
C	-1.73531	2.539708	2.65634	L
H	-0.98992	2.079826	3.289832	L
C	-1.29416	3.321845	1.588367	L
H	-0.23353	3.494519	1.463714	L
C	-2.54834	-0.567	-1.6138	H
C	-4.03857	-0.842	-1.59129	L
C	-4.37461	-2.31099	-1.85524	L
H	-5.25765	-2.50708	-2.49755	L
H	-3.50048	-2.99512	-1.88513	L
C	-4.68871	-1.71712	-0.47603	L
C	-3.84149	-2.21737	0.673268	L
C	-3.68879	-3.59091	0.908867	L
H	-4.1524	-4.31254	0.248014	L
C	-2.94017	-4.04476	2.000975	L
H	-2.85468	-5.112	2.153762	L
C	-2.32436	-3.13194	2.882429	L

C	-2.52671	-1.75562	2.663008	L
H	-2.06181	-1.01224	3.295158	L
C	-3.31329	-1.31081	1.599941	L
H	-3.48412	-0.24951	1.478228	L
C	-6.16149	-1.54524	-0.17282	L
C	-6.61105	-0.39173	0.484044	L
H	-5.91457	0.385173	0.760048	L
C	-7.95994	-0.2383	0.809445	L
H	-8.27444	0.663382	1.319888	L
C	-8.88557	-1.25219	0.508793	L
C	-8.4263	-2.42954	-0.1077	L
H	-9.11343	-3.23054	-0.34948	L
C	-7.07537	-2.57993	-0.4322	L
H	-6.74423	-3.50583	-0.88537	L
C	-4.89109	0.200356	-2.28023	L
C	-5.38588	0.018559	-3.58304	L
H	-5.20441	-0.90065	-4.12347	L
C	-6.09538	1.042167	-4.2187	L
H	-6.45746	0.879437	-5.22612	L
C	-6.29467	2.278161	-3.57831	L
C	-5.76608	2.468349	-2.291	L
H	-5.89679	3.40958	-1.77213	L
C	-5.05863	1.445122	-1.65953	L
H	-4.62095	1.628376	-0.68847	L
C	0.566757	-2.56654	-1.61984	H
C	0.833305	-4.05824	-1.60352	L
C	1.70899	-4.71794	-0.4944	L
C	2.299091	-4.40234	-1.87499	L
H	2.988991	-3.53246	-1.90464	L
H	2.486192	-5.28406	-2.52182	L
C	-0.21612	-4.90035	-2.29438	L
C	-1.45984	-5.06447	-1.67066	L
H	-1.63591	-4.63608	-0.69418	L
C	-2.49307	-5.75169	-2.30803	L
H	-3.4343	-5.87809	-1.78807	L
C	-2.31449	-6.26169	-3.6044	L
C	-1.07811	-6.06887	-4.24595	L
H	-0.92365	-6.41706	-5.25955	L
C	-0.04417	-5.3802	-3.60411	L
H	0.87458	-5.20017	-4.14585	L
C	1.525911	-6.1903	-0.1956	L
C	0.371695	-6.63216	0.465188	L
H	-0.39648	-5.9296	0.749892	L

C	0.205478	-7.98165	0.781506	L
H	-0.69696	-8.29029	1.294205	L
C	1.207181	-8.91602	0.467498	L
C	2.386427	-8.46474	-0.15133	L
H	3.178388	-9.15874	-0.40309	L
C	2.54962	-7.11307	-0.46669	L
H	3.47624	-6.78863	-0.92318	L
C	2.217944	-3.87699	0.655828	L
C	1.317784	-3.346	1.58718	L
H	0.255284	-3.51272	1.470314	L
C	1.770383	-2.5593	2.646942	L
H	1.031634	-2.09125	3.282198	L
C	3.148367	-2.35939	2.857974	L
C	4.054784	-2.98006	1.973269	L
H	5.123058	-2.89716	2.12009	L
C	3.593101	-3.7288	0.88455	L
H	4.309879	-4.19463	0.220038	L
O	-0.12011	2.028056	-0.55657	H
O	-0.70291	1.941916	-2.73291	H
O	-2.02196	-0.13794	-0.5465	H
O	-1.94714	-0.71738	-2.72415	H
O	0.14499	-2.04105	-0.54922	H
O	0.71313	-1.96368	-2.72981	H
O	2.047105	0.125686	-0.55827	H
O	1.960186	0.695829	-2.73808	H
C	-3.42568	-6.96	-4.29767	L
C	-3.17947	-8.10609	-5.06743	L
C	-4.74072	-6.48197	-4.19795	L
C	-4.22414	-8.76392	-5.72248	L
H	-2.17663	-8.50657	-5.15038	L
C	-5.78643	-7.13616	-4.85221	L
H	-4.96071	-5.5878	-3.62754	L
C	-5.55436	-8.29201	-5.62941	L
H	-3.96797	-9.64259	-6.29496	L
H	-6.78246	-6.72784	-4.74883	L
C	3.371947	7.013541	-4.30596	L
C	4.693029	6.547844	-4.23245	L
C	3.104158	8.173674	-5.04694	L
C	5.72369	7.227784	-4.88443	L
H	4.929284	5.643924	-3.68437	L
C	4.133716	8.857499	-5.6992	L
H	2.096159	8.564918	-5.10887	L
C	5.469931	8.398333	-5.63237	L

H	6.72518	6.828118	-4.8022	L
H	3.861233	9.745966	-6.24856	L
C	-7.0243	3.375352	-4.2617	L
C	-8.18068	3.10725	-5.0085	L
C	-6.56846	4.699004	-4.17295	L
C	-8.87052	4.13882	-5.65121	L
H	-8.56474	2.097282	-5.08207	L
C	-7.25471	5.731763	-4.81499	L
H	-5.66765	4.936072	-3.62013	L
C	-8.42166	5.477623	-5.56838	L
H	-9.75573	3.865845	-6.20557	L
H	-6.86299	6.735305	-4.72042	L
C	7.03891	-3.41898	-4.24972	L
C	6.574534	-4.7397	-4.16133	L
C	8.204753	-3.16013	-4.98501	L
C	7.261894	-5.77869	-4.7921	L
H	5.666513	-4.9697	-3.6174	L
C	8.895776	-4.19803	-5.61632	L
H	8.595375	-2.15265	-5.058	L
C	8.43862	-5.53403	-5.53333	L
H	6.863498	-6.77966	-4.6982	L
H	9.78856	-3.93217	-6.16191	L
Rh	0.006047	-0.01074	-2.83561	H
Rh	0.013203	-0.00628	-0.46515	H
C	10.34989	1.092253	0.802444	L
C	10.99686	-0.13544	0.599663	L
C	11.0846	2.163767	1.331429	L
C	12.34808	-0.28846	0.917373	L
H	10.46145	-0.97676	0.177341	L
C	12.43658	2.013556	1.651777	L
H	10.6082	3.118547	1.516385	L
C	13.10029	0.780869	1.450871	L
H	12.80401	-1.25279	0.739446	L
H	12.94275	2.875646	2.059243	L
C	1.494243	3.615629	3.972891	L
C	1.347401	2.858949	5.148827	L
C	0.75814	4.807182	3.856816	L
C	0.463555	3.255142	6.154925	L
H	1.91853	1.955332	5.303085	L
C	-0.12586	5.205672	4.860333	L
H	0.825515	5.419911	2.971156	L
C	-0.31093	4.429405	6.022864	L
H	0.39427	2.619303	7.024695	L

H	-0.67884	6.123073	4.711787	L
C	3.628229	-1.48302	3.971179	L
C	4.823857	-0.75418	3.851144	L
C	2.869772	-1.32142	5.144127	L
C	5.224673	0.137022	4.847375	L
H	5.438483	-0.83324	2.96786	L
C	3.268092	-0.43004	6.142765	L
H	1.963265	-1.88688	5.302011	L
C	4.446737	0.336965	6.006307	L
H	6.145383	0.683659	4.695951	L
H	2.630762	-0.34951	7.01046	L
C	1.02574	-10.3529	0.79506	L
C	2.089521	-11.1104	1.307242	L
C	-0.21433	-10.9775	0.59723	L
C	1.919685	-12.4629	1.615655	L
H	3.053728	-10.6517	1.488022	L
C	-0.38701	-12.329	0.903179	L
H	-1.05035	-10.4243	0.187526	L
C	0.674422	-13.1041	1.419274	L
H	2.776837	-12.9873	2.010224	L
H	-1.36036	-12.7671	0.72956	L
C	-1.45169	-3.6034	4.002058	L
C	-1.29731	-2.83773	5.171249	L
C	-0.71968	-4.79812	3.892479	L
C	-0.41003	-3.22818	6.176513	L
H	-1.86545	-1.93158	5.321089	L
C	0.167493	-5.19112	4.89546	L
H	-0.79296	-5.41803	3.012345	L
C	0.360168	-4.40587	6.050718	L
H	-0.33508	-2.58549	7.040726	L
H	0.716809	-6.11154	4.752214	L
C	-10.3212	-1.08631	0.849758	L
C	-11.0604	-2.15653	1.375165	L
C	-10.9627	0.1452	0.652661	L
C	-12.4114	-2.00136	1.697372	L
H	-10.5883	-3.11424	1.555839	L
C	-12.3129	0.303227	0.97242	L
H	-10.4239	0.98576	0.233178	L
C	-13.0695	-0.7648	1.502143	L
H	-12.9212	-2.86276	2.101764	L
H	-12.7644	1.27042	0.798998	L
C	-3.57865	1.468388	4.004547	L
C	-2.81219	1.324439	5.174494	L

C	-4.77123	0.732131	3.900319	L
C	-3.20063	0.444258	6.186781	L
H	-1.90728	1.895768	5.319581	L
C	-5.16221	-0.14801	4.910307	L
H	-5.39114	0.797149	3.019462	L
C	-4.37685	-0.32925	6.067374	L
H	-2.55774	0.377605	7.051517	L
H	-6.0814	-0.70049	4.771471	L
C	-1.10775	10.3281	0.814083	L
C	0.114899	10.98086	0.599707	L
C	-2.1777	11.0578	1.353113	L
C	0.264452	12.3329	0.915727	L
H	0.954732	10.44939	0.169542	L
C	-2.03092	12.41057	1.671801	L
H	-3.12841	10.57693	1.547129	L
C	-0.8034	13.08013	1.459091	L
H	1.22485	12.7934	0.728597	L
H	-2.89154	12.91271	2.08727	L
C	-14.5587	-0.54826	1.842546	L
C	-15.3244	-0.13789	0.565795	L
H	-15.2058	-0.91341	-0.22169	L
H	-16.4091	-0.01799	0.777713	L
H	-14.9568	0.828327	0.16153	L
C	-15.2415	-1.81481	2.412871	L
H	-14.7518	-2.13789	3.356982	L
H	-16.3108	-1.61624	2.643679	L
H	-15.2089	-2.6477	1.677514	L
C	-14.6878	0.570009	2.899642	L
H	-14.1065	0.309401	3.81054	L
H	-14.3146	1.541758	2.51421	L
H	-15.7504	0.714954	3.192762	L
C	-9.15091	6.647521	-6.26108	L
C	-10.4094	6.200437	-7.04329	L
H	-10.1414	5.481974	-7.84794	L
H	-11.1527	5.730904	-6.36311	L
H	-10.9038	7.071549	-7.526	L
C	-8.19417	7.329677	-7.26308	L
H	-8.7116	8.149882	-7.80663	L
H	-7.31519	7.774092	-6.75123	L
H	-7.82736	6.592582	-8.0099	L
C	-9.59955	7.675318	-5.19947	L
H	-10.2557	7.189822	-4.44492	L
H	-8.73176	8.122042	-4.67077	L

H	-10.1657	8.507847	-5.67095	L
C	-4.82541	-1.33995	7.142683	L
C	-6.18031	-0.8914	7.729499	L
H	-6.97348	-0.87434	6.952701	L
H	-6.51147	-1.58571	8.532074	L
H	-6.09499	0.12873	8.162718	L
C	-4.98172	-2.7413	6.509322	L
H	-4.0316	-3.06201	6.033294	L
H	-5.25499	-3.49415	7.280176	L
H	-5.77902	-2.75749	5.7377	L
C	-3.81936	-1.46617	8.312133	L
H	-2.82401	-1.79577	7.942903	L
H	-3.71086	-0.49933	8.849473	L
H	-4.16799	-2.21839	9.052831	L
C	-1.32753	4.884838	7.089662	L
C	-0.88493	6.245785	7.666913	L
H	-0.8662	7.032398	6.883523	L
H	-1.58377	6.582069	8.463391	L
H	0.133372	6.166656	8.105573	L
C	-2.72618	5.03236	6.448282	L
H	-3.04207	4.077646	5.978223	L
H	-3.48349	5.309807	7.213244	L
H	-2.74063	5.823384	5.670178	L
C	-1.45682	3.888596	8.267112	L
H	-1.78287	2.889451	7.905148	L
H	-0.49208	3.786655	8.809496	L
H	-2.21295	4.242068	9.001495	L
C	1.379798	-4.85575	7.11695	L
C	2.77517	-5.01348	6.470891	L
H	3.534749	-5.2874	7.234868	L
H	2.783507	-5.81085	5.699206	L
H	3.092367	-4.06369	5.991783	L
C	1.517632	-3.84995	8.285298	L
H	2.275866	-4.19966	9.019319	L
H	1.845331	-2.85499	7.913279	L
H	0.555678	-3.74021	8.831093	L
C	0.935007	-6.2102	7.70765	L
H	-0.08112	-6.12379	8.149966	L
H	0.910147	-7.00333	6.931028	L
H	1.636091	-6.54218	8.503962	L
C	4.90544	1.360591	7.06496	L
C	5.062439	2.752542	6.411323	L
H	5.341951	3.515269	7.170123	L

H	5.855698	2.755538	5.635366	L
H	4.11083	3.069366	5.935636	L
C	3.90726	1.506128	8.238894	L
H	3.798703	0.546945	8.789767	L
H	4.263291	2.266903	8.967228	L
H	2.910771	1.834432	7.871727	L
C	6.262522	0.915541	7.649427	L
H	6.17658	-0.09827	8.097108	L
H	7.050823	0.885215	6.868097	L
H	6.600966	1.619659	8.440329	L
C	0.441747	-14.5944	1.743964	L
C	1.702738	-15.2985	2.300464	L
H	1.492535	-16.3679	2.520181	L
H	2.532491	-15.2674	1.561509	L
H	2.036026	-14.8234	3.248444	L
C	-0.67305	-14.7222	2.804873	L
H	-0.40135	-14.1543	3.721003	L
H	-1.64209	-14.3332	2.428313	L
H	-0.82925	-15.7862	3.086688	L
C	0.016345	-15.3406	0.460646	L
H	-0.94734	-14.9571	0.065219	L
H	0.789489	-15.2223	-0.3292	L
H	-0.11543	-16.4262	0.660883	L
C	-6.73788	-8.98453	-6.33645	L
C	-7.40168	-7.99455	-7.31831	L
H	-8.23156	-8.48494	-7.87211	L
H	-7.82928	-7.11797	-6.78833	L
H	-6.6577	-7.6265	-8.05766	L
C	-7.77404	-9.43527	-5.2839	L
H	-8.61716	-9.97567	-5.7666	L
H	-7.30111	-10.1159	-4.54314	L
H	-8.20424	-8.57018	-4.73735	L
C	-6.31475	-10.2349	-7.14454	L
H	-5.59141	-9.96399	-7.94385	L
H	-5.85928	-11.0007	-6.47998	L
H	-7.1951	-10.7027	-7.6369	L
C	9.169093	-6.71071	-6.21305	L
C	10.43919	-6.27389	-6.98224	L
H	10.93421	-7.14969	-7.45571	L
H	10.18465	-5.55716	-7.79279	L
H	11.17707	-5.80582	-6.29525	L
C	9.599487	-7.73699	-5.1424	L
H	8.723083	-8.17686	-4.62224	L

H	10.16641	-8.5745	-5.60403	L
H	10.24948	-7.25229	-4.38202	L
C	8.220114	-7.39124	-7.2235	L
H	7.866346	-6.65495	-7.97736	L
H	8.738968	-8.2166	-7.75783	L
H	7.332623	-7.82847	-6.72021	L
C	6.637352	9.11978	-6.33724	L
C	7.298844	8.160215	-7.3503	L
H	8.11695	8.67208	-7.90219	L
H	7.741502	7.275712	-6.84648	L
H	6.549536	7.802241	-8.08922	L
C	7.681968	9.556555	-5.28713	L
H	8.513183	10.11736	-5.7672	L
H	7.211325	10.2142	-4.52451	L
H	8.128195	8.683467	-4.76681	L
C	6.191365	10.38438	-7.1102	L
H	5.461279	10.12479	-7.90712	L
H	5.735983	11.12919	-6.42216	L
H	7.060722	10.87311	-7.60168	L
C	14.59077	0.569836	1.788981	L
C	15.26802	1.836964	2.364625	L
H	16.33846	1.642363	2.59376	L
H	15.23097	2.673054	1.63313	L
H	14.7775	2.153392	3.310546	L
C	15.35717	0.169091	0.509646	L
H	16.44263	0.053216	0.720057	L
H	14.99371	-0.79689	0.101123	L
H	15.23436	0.947772	-0.27404	L
C	14.72622	-0.55271	2.840743	L
H	14.14437	-0.29922	3.753313	L
H	14.35751	-1.52448	2.451079	L
H	15.7897	-0.69382	3.132335	L
C	-0.59641	14.57173	1.79475	L
C	0.535363	14.71299	2.835806	L
H	1.50518	14.34886	2.437067	L
H	0.674062	15.77723	3.125759	L
H	0.293335	14.13021	3.750891	L
C	-0.21151	15.33965	0.511454	L
H	-0.99702	15.21288	-0.26476	L
H	-0.09884	16.42571	0.720458	L
H	0.752253	14.98068	0.093855	L
C	-1.8613	15.24306	2.382158	L
H	-2.70409	15.20174	1.658614	L

H	-2.1664	14.75133	3.33117	L
H	-1.66973	16.31451	2.609137	L

catalyst I (*C4a*) (E = -973.31373745 a.u. ; Esol = -973.42920947 a.u.)

C	1.69699	-0.08292	2.076376	H
C	2.77181	-0.162	3.161899	L
C	2.291863	-0.97636	4.364202	L
H	2.516664	-0.52913	5.354296	L
H	1.359631	-1.56	4.215004	L
C	3.495814	-1.48365	3.560389	L
C	3.325553	-2.65458	2.626562	L
C	2.783595	-3.86702	3.071783	L
H	2.436463	-3.96916	4.092042	L
C	2.720782	-4.96634	2.208911	L
H	2.328683	-5.90159	2.581439	L
C	3.213104	-4.87607	0.893318	L
C	3.763494	-3.66061	0.45718	L
H	4.150436	-3.5602	-0.54841	L
C	3.827671	-2.56577	1.321019	L
H	4.279009	-1.64451	0.982095	L
C	4.82093	-1.42239	4.299641	L
C	5.99895	-1.07821	3.618633	L
H	5.979233	-0.85812	2.561588	L
C	7.222533	-1.03322	4.290667	L
H	8.112424	-0.75974	3.737688	L
C	7.301373	-1.36791	5.653037	L
C	6.132748	-1.77306	6.320243	L
H	6.160808	-2.04432	7.368043	L
C	4.909467	-1.81477	5.646693	L
H	4.031203	-2.15232	6.181944	L
C	3.532701	1.122117	3.415172	L
C	4.502386	1.509249	2.479849	L
H	4.740079	0.864564	1.643714	L
C	5.135572	2.745864	2.581355	L
H	5.870036	3.020648	1.834666	L
C	4.776428	3.645988	3.595575	L
C	3.782333	3.274935	4.518412	L
H	3.478234	3.957645	5.302016	L
C	3.15929	2.024882	4.424908	L
H	2.363159	1.782971	5.116345	L
C	-2.17647	-0.05565	1.643602	H
C	-3.5086	-0.05357	2.399543	L
C	-3.94904	-1.28642	3.238472	L
C	-4.56318	-1.02054	1.858193	L
H	-4.22191	-1.6996	1.054385	L
H	-5.61132	-0.65605	1.862578	L

C	-4.064	1.318885	2.749102	L
C	-4.93701	1.981961	1.869973	L
H	-5.30736	1.487461	0.983631	L
C	-5.30948	3.306917	2.098994	L
H	-5.96122	3.789872	1.384119	L
C	-4.79987	4.014605	3.200929	L
C	-3.92613	3.350007	4.082189	L
H	-3.51654	3.858917	4.945047	L
C	-3.54798	2.024701	3.845824	L
H	-2.81203	1.567138	4.492084	L
C	-4.86573	-1.07356	4.424219	L
C	-4.337	-0.57587	5.623561	L
H	-3.28362	-0.34119	5.699906	L
C	-5.15547	-0.39723	6.741283	L
H	-4.71811	-0.00913	7.652616	L
C	-6.51539	-0.74894	6.693118	L
C	-7.03137	-1.30297	5.50868	L
H	-8.07271	-1.59186	5.442122	L
C	-6.21128	-1.47834	4.391124	L
H	-6.63056	-1.93493	3.504134	L
C	-3.09488	-2.5284	3.284737	L
C	-3.63576	-3.7627	2.893933	L
H	-4.6562	-3.82451	2.536101	L
C	-2.86731	-4.92492	2.961215	L
H	-3.31628	-5.86208	2.657019	L
C	-1.54538	-4.87947	3.438546	L
C	-1.01785	-3.64368	3.858291	L
H	-0.00437	-3.57338	4.225944	L
C	-1.78918	-2.48006	3.790584	L
H	-1.36647	-1.53992	4.123093	L
C	-1.74616	0.391846	-1.89316	H
C	-2.79075	0.56003	-2.99874	L
C	-2.27674	0.05861	-4.3497	L
H	-2.50904	0.705328	-5.22033	L
H	-1.32856	-0.51756	-4.32361	L
C	-3.47544	-0.64938	-3.70394	L
C	-3.27181	-2.0099	-3.08571	L
C	-3.79489	-2.27157	-1.81105	L
H	-4.29533	-1.48571	-1.26197	L
C	-3.68463	-3.54396	-1.24537	L
H	-4.09353	-3.72162	-0.25914	L
C	-3.05567	-4.58106	-1.95091	L
C	-2.53973	-4.31907	-3.2334	L

H	-2.08375	-5.11127	-3.8116	L
C	-2.65842	-3.04683	-3.80182	L
H	-2.29232	-2.87646	-4.80612	L
C	-4.79689	-0.44606	-4.42216	L
C	-4.8718	-0.53028	-5.82318	L
H	-3.98471	-0.726	-6.41195	L
C	-6.09254	-0.35924	-6.48086	L
H	-6.11128	-0.39175	-7.56292	L
C	-7.27101	-0.13036	-5.75002	L
C	-7.20405	-0.10399	-4.34666	L
H	-8.1009	0.027098	-3.75423	L
C	-5.98297	-0.27793	-3.69122	L
H	-5.97047	-0.29535	-2.61134	L
C	-3.5725	1.858601	-2.96849	L
C	-3.23422	2.959043	-3.77478	L
H	-2.43777	2.888739	-4.50324	L
C	-3.89634	4.182001	-3.61383	L
H	-3.60905	5.020867	-4.23545	L
C	-4.88091	4.334647	-2.62136	L
C	-5.20335	3.237163	-1.80865	L
H	-5.96283	3.322528	-1.04254	L
C	-4.54419	2.019979	-1.97182	L
H	-4.77179	1.202528	-1.30124	L
C	2.096141	0.477258	-1.42775	H
C	3.413094	0.735977	-2.16515	L
C	3.927468	-0.24884	-3.25408	L
C	4.529176	-0.25989	-1.8433	L
H	4.237949	-1.12978	-1.22547	L
H	5.552846	0.159377	-1.757	L
C	3.869574	2.186704	-2.21794	L
C	3.271484	3.069096	-3.12943	L
H	2.528187	2.710505	-3.82829	L
C	3.590602	4.429581	-3.11786	L
H	3.125843	5.080156	-3.84789	L
C	4.491875	4.944807	-2.16938	L
C	5.065856	4.067589	-1.23414	L
H	5.733742	4.439683	-0.46708	L
C	4.746312	2.70742	-1.24888	L
H	5.16832	2.067989	-0.48647	L
C	4.830485	0.276085	-4.35043	L
C	6.194778	-0.05864	-4.39442	L
H	6.634816	-0.68867	-3.63242	L
C	7.007801	0.416161	-5.42664	L

H	8.062727	0.172804	-5.41366	L
C	6.467425	1.209013	-6.45393	L
C	5.090978	1.492999	-6.43892	L
H	4.63695	2.064062	-7.23903	L
C	4.279626	1.01486	-5.40718	L
H	3.216161	1.209338	-5.44153	L
C	3.131168	-1.48387	-3.59435	L
C	1.83793	-1.37297	-4.12241	L
H	1.384476	-0.39851	-4.25642	L
C	1.120611	-2.51974	-4.4737	L
H	0.118405	-2.40731	-4.86149	L
C	1.688663	-3.79727	-4.31432	L
C	2.995415	-3.90011	-3.80532	L
H	3.473788	-4.86544	-3.69619	L
C	3.713025	-2.75378	-3.46128	L
H	4.725891	-2.85587	-3.09153	L
O	-1.76288	-1.11709	1.080092	H
O	-1.57799	1.064663	1.603055	H
O	-1.21727	-0.74609	-1.70571	H
O	-1.46244	1.441156	-1.23388	H
O	1.73458	-0.71372	-1.17061	H
O	1.45563	1.518106	-1.08061	H
O	1.213361	-1.15299	1.597103	H
O	1.344966	1.090387	1.734764	H
C	4.805732	6.39666	-2.13436	L
C	3.794999	7.349153	-2.33155	L
C	6.116124	6.841317	-1.9039	L
C	4.086818	8.715386	-2.31402	L
H	2.769502	7.03798	-2.48743	L
C	6.412222	8.207064	-1.89051	L
H	6.920388	6.131035	-1.75792	L
C	5.406701	9.176269	-2.1011	L
H	3.262882	9.394141	-2.47446	L
H	7.439419	8.50173	-1.72426	L
C	-5.12945	5.455212	3.388003	L
C	-6.39629	5.954555	3.043318	L
C	-4.16584	6.351933	3.876098	L
C	-6.68892	7.315266	3.169317	L
H	-7.17178	5.291242	2.682208	L
C	-4.46063	7.70933	4.017218	L
H	-3.16952	6.012097	4.127742	L
C	-5.72376	8.225646	3.657547	L
H	-7.67966	7.63278	2.880827	L

H	-3.68594	8.357959	4.402578	L
C	-5.54708	5.641286	-2.40461	L
C	-5.7361	6.134327	-1.10514	L
C	-6.007	6.398468	-3.49041	L
C	-6.38461	7.352005	-0.89422	L
H	-5.36821	5.583604	-0.24871	L
C	-6.66214	7.61598	-3.28284	L
H	-5.88021	6.036458	-4.50336	L
C	-6.87155	8.117666	-1.97631	L
H	-6.50457	7.691573	0.125559	L
H	-7.00212	8.146007	-4.15971	L
C	5.390785	4.992894	3.633015	L
C	4.593637	6.134843	3.790532	L
C	6.769885	5.148707	3.438462	L
C	5.157702	7.411467	3.719016	L
H	3.523388	6.041805	3.928612	L
C	7.338332	6.421721	3.37768	L
H	7.410189	4.282089	3.327451	L
C	6.543706	7.583062	3.49326	L
H	4.487537	8.251012	3.826104	L
H	8.405843	6.492665	3.220351	L
Rh	-0.0091	-1.01319	-0.05915	H
Rh	-0.06391	1.340286	0.266684	H
C	-8.56703	0.0689	-6.44703	L
C	-9.47465	1.040566	-5.99983	L
C	-8.90476	-0.70664	-7.56572	L
C	-10.6929	1.236014	-6.65597	L
H	-9.23426	1.666508	-5.14929	L
C	-10.122	-0.51475	-8.22292	L
H	-8.23377	-1.47683	-7.92506	L
C	-11.0445	0.460726	-7.78536	L
H	-11.3435	2.003135	-6.26395	L
H	-10.3394	-1.13914	-9.0787	L
C	-2.99074	-5.94925	-1.38346	L
C	-1.82413	-6.71194	-1.5074	L
C	-4.11252	-6.5241	-0.76931	L
C	-1.79874	-8.0469	-1.10123	L
H	-0.93202	-6.27387	-1.93057	L
C	-4.08449	-7.85525	-0.34494	L
H	-5.02858	-5.95792	-0.65591	L
C	-2.93812	-8.65833	-0.53404	L
H	-0.8873	-8.59259	-1.26761	L
H	-4.97993	-8.26386	0.10278	L

C	-7.38655	-0.55529	7.880001	L
C	-8.32929	-1.52859	8.241821	L
C	-7.28095	0.605753	8.660114	L
C	-9.14746	-1.34579	9.358779	L
H	-8.4231	-2.44389	7.670871	L
C	-8.0993	0.792533	9.777461	L
H	-6.57405	1.382501	8.395633	L
C	-9.05298	-0.18207	10.15298	L
H	-9.85597	-2.12617	9.600586	L
H	-7.97036	1.709744	10.33202	L
C	-0.71875	-6.1137	3.485217	L
C	0.188517	-6.33496	4.532867	L
C	-0.81576	-7.07187	2.465684	L
C	1.002054	-7.47076	4.541698	L
H	0.274271	-5.62808	5.348214	L
C	-0.00826	-8.21005	2.476153	L
H	-1.48916	-6.92349	1.631694	L
C	0.931406	-8.42883	3.506824	L
H	1.7043	-7.5845	5.35595	L
H	-0.10899	-8.88687	1.645082	L
C	3.205227	-6.06576	0.00522	L
C	4.318521	-6.37622	-0.7897	L
C	2.10465	-6.93076	-0.01071	L
C	4.345079	-7.54994	-1.54789	L
H	5.18785	-5.73083	-0.79692	L
C	2.137497	-8.11542	-0.7481	L
H	1.216589	-6.68882	0.553901	L
C	3.264364	-8.45886	-1.52651	L
H	5.231961	-7.75721	-2.13077	L
H	1.27886	-8.75978	-0.68015	L
C	8.599617	-1.30504	6.371221	L
C	8.95812	-2.30173	7.29051	L
C	9.48817	-0.24326	6.145404	L
C	10.17673	-2.23772	7.969755	L
H	8.3024	-3.14371	7.473932	L
C	10.70772	-0.17559	6.824321	L
H	9.231505	0.550158	5.454278	L
C	11.07988	-1.17376	7.754604	L
H	10.41029	-3.03104	8.666574	L
H	11.34289	0.670209	6.608427	L
C	0.926627	-5.018	-4.68301	L
C	1.017536	-6.17674	-3.8991	L
C	0.101191	-5.03492	-5.81792	L

C	0.289832	-7.31975	-4.2324	L
H	1.628362	-6.19189	-3.00583	L
C	-0.62505	-6.18036	-6.15614	L
H	0.025085	-4.16402	-6.45661	L
C	-0.54912	-7.35031	-5.36536	L
H	0.375818	-8.17935	-3.58562	L
H	-1.24066	-6.1277	-7.04131	L
C	7.332656	1.726414	-7.54425	L
C	7.169284	3.034396	-8.02411	L
C	8.330386	0.919234	-8.10992	L
C	7.98611	3.52801	-9.04501	L
H	6.418562	3.686784	-7.59537	L
C	9.147291	1.408915	-9.13132	L
H	8.469978	-0.10075	-7.77421	L
C	8.996427	2.72417	-9.6225	L
H	7.811745	4.544345	-9.36454	L
H	9.9004	0.748016	-9.53813	L
C	-6.00288	9.734423	3.816966	L
C	-7.40785	10.14715	3.315544	L
H	-7.53114	9.900926	2.239507	L
H	-8.2042	9.640024	3.901913	L
H	-7.56139	11.24244	3.428434	L
C	-4.96134	10.54376	3.011827	L
H	-5.19632	11.62995	3.038778	L
H	-3.9383	10.4196	3.423665	L
H	-4.94923	10.21396	1.951913	L
C	-5.90301	10.11637	5.308915	L
H	-4.88459	9.928162	5.709229	L
H	-6.12721	11.19537	5.455129	L
H	-6.62742	9.523958	5.908836	L
C	-7.60138	9.448103	-1.69884	L
C	-8.83898	9.18193	-0.81362	L
H	-8.55412	8.766264	0.175224	L
H	-9.40121	10.12287	-0.62831	L
H	-9.52118	8.459095	-1.31118	L
C	-8.08857	10.15409	-2.98689	L
H	-7.23196	10.4085	-3.64792	L
H	-8.80482	9.511814	-3.54363	L
H	-8.61264	11.10352	-2.74159	L
C	-6.64654	10.41459	-0.96706	L
H	-5.73422	10.59307	-1.57635	L
H	-7.14058	11.39266	-0.77978	L
H	-6.33402	10.00646	0.014467	L

C	5.778623	10.67418	-2.11278	L
C	6.431427	11.05974	-0.76783	L
H	7.401903	10.54162	-0.62576	L
H	6.635124	12.15168	-0.72491	L
H	5.760506	10.79633	0.078224	L
C	6.775972	10.94342	-3.25996	L
H	6.333823	10.6436	-4.23475	L
H	7.036049	12.02307	-3.31104	L
H	7.721225	10.37846	-3.11857	L
C	4.557012	11.60115	-2.32283	L
H	4.072267	11.40345	-3.30332	L
H	3.812419	11.46374	-1.50901	L
H	4.866229	12.66911	-2.31643	L
C	7.201535	8.970125	3.350184	L
C	6.186223	10.13504	3.437056	L
H	5.681288	10.14847	4.427071	L
H	6.697746	11.11431	3.312457	L
H	5.421363	10.05311	2.634604	L
C	7.903394	9.063527	1.977435	L
H	8.754031	8.354662	1.902174	L
H	7.184402	8.828462	1.163477	L
H	8.309454	10.08437	1.808106	L
C	8.241939	9.164421	4.473318	L
H	8.709214	10.17097	4.40712	L
H	7.757634	9.068084	5.469162	L
H	9.05638	8.412766	4.408492	L
C	12.41434	-1.13872	8.528135	L
C	13.28654	0.091228	8.178606	L
H	13.55308	0.094164	7.099511	L
H	12.75783	1.036158	8.429782	L
H	14.23655	0.077851	8.75611	L
C	12.12901	-1.09482	10.04516	L
H	11.59739	-2.00711	10.38757	L
H	13.07631	-1.02589	10.62291	L
H	11.50238	-0.21132	10.29491	L
C	13.23485	-2.40433	8.197091	L
H	13.41252	-2.47394	7.102024	L
H	14.22075	-2.38066	8.71028	L
H	12.71261	-3.32733	8.524848	L
C	9.922115	3.227415	-10.7496	L
C	9.627879	4.687541	-11.1704	L
H	8.589479	4.787762	-11.554	L
H	9.773358	5.383164	-10.3157	L

H	10.31534	5.009923	-11.9826	L
C	9.745665	2.335396	-11.9977	L
H	10.37204	2.705064	-12.8385	L
H	10.04699	1.286258	-11.7962	L
H	8.683768	2.336564	-12.3263	L
C	11.39084	3.163063	-10.2768	L
H	12.07446	3.561509	-11.0577	L
H	11.52609	3.766476	-9.35314	L
H	11.70552	2.120637	-10.0613	L
C	-12.3773	0.642481	-8.54108	L
C	-13.2722	1.750837	-7.93576	L
H	-13.5417	1.512188	-6.88414	L
H	-12.7597	2.736569	-7.9698	L
H	-14.2202	1.848755	-8.50836	L
C	-12.0887	1.023248	-10.0096	L
H	-11.5402	0.217409	-10.5404	L
H	-13.0355	1.201624	-10.5642	L
H	-11.4771	1.950319	-10.0551	L
C	-13.1761	-0.6785	-8.50131	L
H	-13.3554	-0.98986	-7.44942	L
H	-14.1609	-0.55926	-9.00322	L
H	-12.6366	-1.49812	-9.02025	L
C	-9.97548	-0.01931	11.37894	L
C	-9.74681	1.309678	12.13863	L
H	-8.70587	1.372123	12.52339	L
H	-9.94894	2.18219	11.48033	L
H	-10.4298	1.38681	13.01257	L
C	-11.4501	-0.04976	10.92153	L
H	-11.7157	-1.02502	10.46277	L
H	-12.1339	0.108751	11.78365	L
H	-11.6392	0.750695	10.1738	L
C	-9.72229	-1.17553	12.37077	L
H	-10.3459	-1.05613	13.28335	L
H	-9.97385	-2.15993	11.92377	L
H	-8.65405	-1.1943	12.67753	L
C	1.889718	-9.63681	3.514446	L
C	1.71029	-10.4348	4.824607	L
H	2.355472	-11.3401	4.826832	L
H	1.987692	-9.83202	5.714053	L
H	0.653006	-10.759	4.936928	L
C	1.648662	-10.6133	2.33734	L
H	0.61088	-11.0111	2.358923	L
H	1.8306	-10.1136	1.363203	L

H	2.34228	-11.4801	2.39506	L
C	3.343748	-9.12859	3.413759	L
H	4.057893	-9.97995	3.384803	L
H	3.479374	-8.52677	2.4884	L
H	3.613057	-8.49337	4.283641	L
C	3.357759	-9.78061	-2.31682	L
C	2.095	-10.6669	-2.17563	L
H	1.19247	-10.1428	-2.55273	L
H	2.203338	-11.6039	-2.76399	L
H	1.930142	-10.9576	-1.11561	L
C	4.560004	-10.5998	-1.79946	L
H	5.519641	-10.068	-1.96811	L
H	4.454979	-10.7931	-0.70961	L
H	4.625529	-11.5782	-2.32324	L
C	3.555271	-9.4745	-3.81728	L
H	4.508017	-8.93594	-4.00197	L
H	3.583086	-10.4138	-4.41108	L
H	2.72338	-8.84732	-4.19932	L
C	-1.33247	-8.63719	-5.69579	L
C	-2.22793	-8.4952	-6.94963	L
H	-2.7794	-9.43966	-7.14964	L
H	-2.98196	-7.69098	-6.80696	L
H	-1.6166	-8.27183	-7.85059	L
C	-0.33706	-9.78915	-5.95376	L
H	0.275281	-10.0087	-5.05397	L
H	-0.87643	-10.7222	-6.22633	L
H	0.351049	-9.52624	-6.78613	L
C	-2.24603	-9.00843	-4.50695	L
H	-2.89962	-8.15104	-4.23531	L
H	-2.89283	-9.87663	-4.75869	L
H	-1.6517	-9.2952	-3.61651	L
C	-2.97535	-10.1513	-0.1475	L
C	-1.65856	-10.9002	-0.47246	L
H	-1.73389	-11.9718	-0.18669	L
H	-1.43759	-10.8599	-1.56095	L
H	-0.8023	-10.4714	0.086712	L
C	-4.10863	-10.8536	-0.92765	L
H	-4.12528	-11.9427	-0.70509	L
H	-5.10538	-10.4467	-0.65797	L
H	-3.96227	-10.7228	-2.02205	L
C	-3.23749	-10.2845	1.367534	L
H	-2.45211	-9.75447	1.94593	L
H	-4.22262	-9.85721	1.648912	L

H	-3.23549	-11.3527	1.675289	L

catalyst I (*D*$_2$) (E = -973.32267634 a.u. ; Esol = -973.43603127 a.u.)

C	1.885099	-0.50154	-2.21495	H
C	2.915017	-1.06182	-3.19961	L
C	2.754694	-0.52566	-4.62553	L
H	2.864445	-1.28333	-5.42784	L
H	2.031734	0.309862	-4.74662	L
C	4.024727	-0.1741	-3.83803	L
C	4.159352	1.263404	-3.40854	L
C	4.234093	2.287143	-4.36627	L
H	4.143062	2.055679	-5.42029	L
C	4.455432	3.610802	-3.96858	L
H	4.521091	4.385723	-4.72207	L
C	4.577624	3.929058	-2.6054	L
C	4.483799	2.901887	-1.6569	L
H	4.554844	3.124026	-0.60816	L
C	4.329038	1.577012	-2.054	L
H	4.314188	0.797026	-1.30234	L
C	5.309491	-0.83237	-4.30517	L
C	6.311791	-1.1266	-3.36836	L
H	6.169885	-0.88786	-2.32266	L
C	7.510689	-1.71877	-3.77056	L
H	8.261585	-1.93919	-3.02219	L
C	7.749628	-1.99453	-5.12733	L
C	6.772806	-1.64027	-6.07393	L
H	6.931409	-1.83008	-7.12802	L
C	5.572299	-1.05058	-5.66899	L
H	4.855333	-0.76242	-6.42603	L
C	3.213875	-2.54579	-3.07186	L
C	4.086741	-2.98507	-2.06481	L
H	4.553923	-2.27218	-1.3988	L
C	4.339013	-4.34636	-1.88499	L
H	5.016259	-4.65598	-1.09869	L
C	3.67802	-5.30093	-2.67388	L
C	2.766238	-4.86529	-3.65048	L
H	2.23448	-5.58163	-4.26427	L
C	2.526122	-3.50083	-3.83919	L
H	1.790902	-3.19483	-4.57206	L
C	-1.84699	-0.20768	-1.82108	H
C	-3.03383	-0.56158	-2.71142	L
C	-3.34979	-2.03496	-3.12479	L
C	-2.52578	-1.12944	-4.04266	L
H	-1.43266	-1.32797	-4.08413	L
H	-3.04867	-0.7597	-4.95061	L

C	-4.04121	0.558058	-2.90225	L
C	-3.74447	1.629191	-3.76481	L
H	-2.86289	1.60233	-4.39279	L
C	-4.53096	2.781056	-3.76786	L
H	-4.23838	3.608644	-4.40206	L
C	-5.61566	2.90475	-2.88519	L
C	-5.93777	1.822714	-2.04932	L
H	-6.76961	1.890056	-1.35927	L
C	-5.15302	0.665563	-2.05388	L
H	-5.37842	-0.11131	-1.34298	L
C	-4.73497	-2.38506	-3.6333	L
C	-5.81814	-2.47812	-2.74559	L
H	-5.68642	-2.28893	-1.69178	L
C	-7.08746	-2.83678	-3.2047	L
H	-7.90769	-2.86763	-2.49857	L
C	-7.2963	-3.1422	-4.56012	L
C	-6.20188	-3.0998	-5.44051	L
H	-6.32195	-3.36886	-6.48247	L
C	-4.93278	-2.74142	-4.97868	L
H	-4.1032	-2.75241	-5.67399	L
C	-2.60835	-3.1191	-2.37044	L
C	-1.53105	-3.80501	-2.95386	L
H	-1.27867	-3.65713	-3.99588	L
C	-0.72477	-4.63659	-2.17473	L
H	0.131636	-5.11578	-2.62941	L
C	-1.00228	-4.82389	-0.81086	L
C	-2.15298	-4.24106	-0.26033	L
H	-2.39497	-4.3786	0.785732	L
C	-2.95186	-3.39962	-1.03656	L
H	-3.78137	-2.89352	-0.56749	L
C	-1.48043	1.157275	1.473545	H
C	-2.70131	1.403387	2.350767	L
C	-2.44404	2.406886	3.473814	L
H	-2.87584	2.152566	4.462451	L
H	-1.47502	2.947622	3.407633	L
C	-3.45967	2.763477	2.378467	L
C	-3.08039	3.857601	1.413037	L
C	-3.3525	3.697124	0.04667	L
H	-3.711	2.747969	-0.3301	L
C	-3.19115	4.763987	-0.83701	L
H	-3.43378	4.616935	-1.87979	L
C	-2.79041	6.0257	-0.36781	L
C	-2.5052	6.181848	1.001135	L

H	-2.18374	7.138798	1.392199	L
C	-2.65674	5.108726	1.884604	L
H	-2.48224	5.264806	2.941805	L
C	-4.91108	2.785887	2.816151	L
C	-5.29317	3.408509	4.015819	L
H	-4.54972	3.839015	4.674326	L
C	-6.64195	3.495008	4.371034	L
H	-6.90472	3.957066	5.314278	L
C	-7.63885	2.986365	3.519975	L
C	-7.25655	2.398443	2.302383	L
H	-8.00193	2.033485	1.606851	L
C	-5.90864	2.313276	1.949827	L
H	-5.64671	1.899695	0.986825	L
C	-3.54203	0.173096	2.631641	L
C	-3.55765	-0.47367	3.878767	L
H	-2.98336	-0.091	4.710549	L
C	-4.29461	-1.65164	4.053704	L
H	-4.26965	-2.14347	5.01776	L
C	-5.01434	-2.21244	2.981128	L
C	-4.9794	-1.56708	1.734379	L
H	-5.53489	-1.95679	0.891516	L
C	-4.2288	-0.40683	1.559569	L
H	-4.17264	0.046849	0.581688	L
C	2.173251	1.054212	1.296334	H
C	3.010127	1.486858	2.489336	L
C	2.857308	0.79095	3.874999	L
C	2.122182	2.101568	3.578707	L
H	1.029112	2.018771	3.396106	L
H	2.520527	2.981653	4.123993	L
C	4.277661	2.254877	2.165748	L
C	5.375159	1.560067	1.634926	L
H	5.338456	0.483396	1.527863	L
C	6.498747	2.250167	1.170693	L
H	7.318944	1.688179	0.74187	L
C	6.535866	3.655188	1.203594	L
C	5.449876	4.351541	1.757029	L
H	5.436919	5.434337	1.763907	L
C	4.322067	3.661999	2.207363	L
H	3.467321	4.239718	2.530493	L
C	3.984478	0.906883	4.879707	L
C	3.77714	1.556992	6.10727	L
H	2.81631	1.999563	6.338469	L
C	4.808652	1.647414	7.045333	L

H	4.629215	2.184419	7.968193	L
C	6.062382	1.067002	6.785508	L
C	6.252816	0.377035	5.575857	L
H	7.194264	-0.11378	5.363181	L
C	5.219254	0.286063	4.640605	L
H	5.382131	-0.28285	3.73714	L
C	2.024593	-0.47169	3.948293	L
C	2.560037	-1.68354	3.478446	L
H	3.550893	-1.71707	3.044578	L
C	1.799067	-2.85214	3.537474	L
H	2.208928	-3.77832	3.153071	L
C	0.504241	-2.81019	4.074337	L
C	0.004117	-1.59405	4.572992	L
H	-0.98025	-1.55957	5.022553	L
C	0.741094	-0.47169	4.528307	L
H	0.328283	0.437689	4.945866	L
O	-1.23339	0.869488	-2.10274	H
O	-1.55144	-0.98345	-0.86432	H
O	-1.16237	1.99755	0.582405	H
O	-0.88372	0.05167	1.678154	H
O	1.701486	1.982013	0.568246	H
O	1.976302	-0.18647	1.12057	H
O	1.622097	0.73999	-2.21612	H
O	1.344703	-1.35621	-1.4433	H
C	7.635773	4.398322	0.544164	L
C	8.18745	5.540547	1.139971	L
C	8.09975	4.000833	-0.7178	L
C	9.194068	6.264616	0.495088	L
H	7.846169	5.869629	2.113745	L
C	9.098709	4.726764	-1.36839	L
H	7.669901	3.140939	-1.21686	L
C	9.670979	5.874646	-0.77821	L
H	9.583872	7.128951	1.011044	L
H	9.420251	4.384147	-2.34229	L
C	-6.31806	4.20463	-2.75332	L
C	-6.62493	4.969464	-3.88749	L
C	-6.59624	4.733708	-1.48444	L
C	-7.18044	6.244942	-3.75892	L
H	-6.42754	4.582135	-4.87948	L
C	-7.14049	6.012408	-1.35205	L
H	-6.34821	4.177874	-0.58865	L
C	-7.43923	6.801378	-2.48471	L
H	-7.3856	6.784556	-4.67108	L

H	-7.30919	6.389298	-0.35259	L
C	-5.78193	-3.47506	3.147358	L
C	-5.8238	-4.42532	2.114463	L
C	-6.48903	-3.73599	4.330429	L
C	-6.56966	-5.59652	2.252933	L
H	-5.26578	-4.27268	1.199342	L
C	-7.23604	-4.90921	4.472424	L
H	-6.48906	-3.0182	5.140986	L
C	-7.29977	-5.86404	3.430553	L
H	-6.57696	-6.29201	1.425016	L
H	-7.76632	-5.04319	5.403069	L
C	3.908994	-6.74716	-2.44889	L
C	2.830351	-7.64029	-2.38736	L
C	5.210162	-7.24318	-2.29404	L
C	3.047242	-9.00692	-2.19194	L
H	1.813494	-7.27841	-2.47931	L
C	5.431615	-8.60993	-2.11056	L
H	6.06135	-6.57518	-2.34327	L
C	4.357354	-9.5256	-2.06093	L
H	2.174624	-9.64121	-2.15469	L
H	6.45445	-8.9493	-2.02244	L
Rh	0.264207	1.473185	-0.82834	H
Rh	0.236536	-0.69728	0.136804	H
C	7.16409	1.171079	7.775891	L
C	8.480726	1.410999	7.355333	L
C	6.907962	1.033947	9.147984	L
C	9.519841	1.513978	8.284063	L
H	8.706828	1.538361	6.303848	L
C	7.944378	1.135021	10.07864	L
H	5.905668	0.830336	9.503661	L
C	9.274053	1.378158	9.670207	L
H	10.50857	1.704223	7.894643	L
H	7.698247	1.018711	11.12524	L
C	-0.31512	-4.03511	4.152811	L
C	-1.62286	-4.04411	3.656271	L
C	0.189602	-5.1846	4.77066	L
C	-2.42241	-5.18001	3.793824	L
H	-2.02446	-3.16923	3.16074	L
C	-0.60935	-6.32097	4.916003	L
H	1.19155	-5.18795	5.180136	L
C	-1.93947	-6.34159	4.434902	L
H	-3.42958	-5.14035	3.40965	L
H	-0.17306	-7.16502	5.427147	L

C	-0.0501	-5.56064	0.04609	L
C	-0.49535	-6.53405	0.947714	L
C	1.317708	-5.27345	-0.02627	L
C	0.417871	-7.24142	1.735524	L
H	-1.55053	-6.76248	1.024327	L
C	2.232011	-5.97348	0.759224	L
H	1.677768	-4.49687	-0.68851	L
C	1.806793	-6.98301	1.648816	L
H	0.017227	-7.99259	2.399023	L
H	3.279557	-5.72691	0.657442	L
C	-8.64589	-3.52051	-5.05112	L
C	-9.47447	-4.35937	-4.29144	L
C	-9.11561	-3.04405	-6.28406	L
C	-10.7438	-4.71369	-4.7538	L
H	-9.13444	-4.75877	-3.3441	L
C	-10.3857	-3.39571	-6.749	L
H	-8.50552	-2.38116	-6.88511	L
C	-11.2302	-4.2408	-5.99222	L
H	-11.3444	-5.36587	-4.13462	L
H	-10.6878	-2.9914	-7.70328	L
C	9.019155	-2.63594	-5.55319	L
C	9.687771	-2.20299	-6.70741	L
C	9.570479	-3.68857	-4.80767	L
C	10.88106	-2.80852	-7.10729	L
H	9.297349	-1.38121	-7.29463	L
C	10.76349	-4.29764	-5.20587	L
H	9.067818	-4.05586	-3.92136	L
C	11.44731	-3.86983	-6.36764	L
H	11.36214	-2.43752	-8.00193	L
H	11.1312	-5.10484	-4.59054	L
C	-9.07352	3.090609	3.88769	L
C	-9.95242	2.025285	3.642183	L
C	-9.57604	4.258004	4.480606	L
C	-11.3045	2.121968	3.982361	L
H	-9.59021	1.105468	3.199713	L
C	-10.9268	4.358393	4.820444	L
H	-8.92748	5.105258	4.665335	L
C	-11.8232	3.294184	4.580151	L
H	-11.926	1.265122	3.770468	L
H	-11.2683	5.280116	5.271307	L
C	-2.74386	7.185384	-1.29453	L
C	-3.21294	8.442174	-0.88514	L
C	-2.28578	7.032508	-2.61204	L

C	-3.2378	9.516712	-1.77568	L
H	-3.5973	8.589018	0.116327	L
C	-2.31637	8.104306	-3.50774	L
H	-1.90128	6.079576	-2.9539	L
C	-2.80649	9.370156	-3.11164	L
H	-3.62455	10.46112	-1.41798	L
H	-1.95887	7.917146	-4.50903	L
C	4.846246	5.31602	-2.16172	L
C	4.159011	5.856022	-1.06583	L
C	5.834976	6.08477	-2.78901	L
C	4.458255	7.137065	-0.59776	L
H	3.386861	5.283282	-0.5664	L
C	6.138828	7.36531	-2.32173	L
H	6.396258	5.682898	-3.62358	L
C	5.460739	7.921012	-1.21413	L
H	3.896216	7.491279	0.253048	L
H	6.91459	7.918919	-2.83093	L
C	-2.87714	-7.55052	4.627575	L
C	-4.07283	-7.1241	5.505676	L
H	-4.69414	-6.35731	4.998131	L
H	-4.72617	-7.99276	5.735055	L
H	-3.71349	-6.69983	6.468118	L
C	-2.18473	-8.74945	5.319194	L
H	-1.31309	-9.09896	4.723978	L
H	-1.84656	-8.47695	6.342277	L
H	-2.88682	-9.60564	5.419949	L
C	-3.39446	-8.03981	3.256866	L
H	-4.05556	-8.92462	3.379497	L
H	-3.98293	-7.2578	2.733831	L
H	-2.54461	-8.33555	2.606629	L
C	2.85731	-7.77056	2.456077	L
C	2.232139	-8.83262	3.39163	L
H	3.021993	-9.37547	3.955019	L
H	1.55951	-8.35674	4.135777	L
H	1.660607	-9.58769	2.809689	L
C	3.680394	-6.7991	3.329819	L
H	4.416577	-7.35468	3.950295	L
H	4.249423	-6.0729	2.712976	L
H	3.012805	-6.23023	4.00933	L
C	3.800808	-8.50301	1.4793	L
H	3.216473	-9.1813	0.82103	L
H	4.359478	-7.79103	0.836201	L
H	4.549257	-9.1091	2.034162	L

C	-8.1462	-7.15071	3.525474	L
C	-7.24193	-8.38767	3.334407	L
H	-7.83351	-9.32496	3.419569	L
H	-6.75517	-8.39315	2.337236	L
H	-6.44971	-8.40823	4.11011	L
C	-9.22556	-7.13353	2.421737	L
H	-9.87764	-8.03108	2.493297	L
H	-9.86431	-6.22909	2.519828	L
H	-8.77159	-7.13116	1.40856	L
C	-8.8657	-7.30359	4.887034	L
H	-8.13067	-7.34073	5.720199	L
H	-9.57411	-6.46439	5.058185	L
H	-9.45438	-8.24629	4.918206	L
C	4.646993	-11.0337	-1.90504	L
C	3.361859	-11.8933	-1.83612	L
H	2.769948	-11.7988	-2.77212	L
H	3.61324	-12.969	-1.71015	L
H	2.732189	-11.593	-0.97052	L
C	5.446567	-11.2873	-0.6079	L
H	6.424134	-10.7627	-0.6166	L
H	4.871908	-10.9434	0.276502	L
H	5.655016	-12.3719	-0.481	L
C	5.474229	-11.5192	-3.11465	L
H	5.662591	-12.613	-3.05084	L
H	4.930927	-11.3133	-4.06231	L
H	6.461048	-11.0126	-3.16168	L
C	-12.6388	-4.65526	-6.46617	L
C	-13.6885	-4.17933	-5.43849	L
H	-14.7165	-4.42944	-5.77998	L
H	-13.5408	-4.66215	-4.44995	L
H	-13.6239	-3.07804	-5.30215	L
C	-13.0192	-4.05185	-7.83982	L
H	-13.0206	-2.9411	-7.79798	L
H	-12.314	-4.38955	-8.6299	L
H	-14.0388	-4.37473	-8.14363	L
C	-12.7072	-6.19262	-6.59468	L
H	-11.9283	-6.55631	-7.29939	L
H	-12.5519	-6.69194	-5.61557	L
H	-13.7009	-6.51269	-6.9767	L
C	-13.3081	3.446181	4.970387	L
C	-13.9221	4.638865	4.205341	L
H	-15.0044	4.741684	4.437965	L
H	-13.4318	5.596295	4.479285	L

H	-13.8128	4.492003	3.108949	L
C	-13.4178	3.700353	6.489618	L
H	-12.9231	4.650104	6.781827	L
H	-14.4824	3.770693	6.801995	L
H	-12.9417	2.870423	7.055425	L
C	-14.1535	2.192077	4.641741	L
H	-14.1397	1.979667	3.550781	L
H	-13.7769	1.304336	5.194478	L
H	-15.2145	2.343092	4.937994	L
C	10.38948	1.48549	10.73074	L
C	10.07019	2.646187	11.69797	L
H	9.128718	2.46479	12.25731	L
H	10.88256	2.770653	12.44662	L
H	9.964044	3.599264	11.13584	L
C	10.4734	0.164106	11.52543	L
H	10.6605	-0.68894	10.83776	L
H	11.29993	0.202191	12.26794	L
H	9.535377	-0.03743	12.08363	L
C	11.78533	1.754818	10.1186	L
H	12.08446	0.930136	9.43601	L
H	11.79453	2.716139	9.560667	L
H	12.55823	1.824773	10.91482	L
C	12.76647	-4.5123	-6.84454	L
C	13.24988	-5.65995	-5.92535	L
H	14.20096	-6.09414	-6.3037	L
H	13.44014	-5.28893	-4.89499	L
H	12.50093	-6.48046	-5.88873	L
C	13.87777	-3.44067	-6.87997	L
H	14.84946	-3.88983	-7.17996	L
H	13.64599	-2.63539	-7.60791	L
H	14.00127	-2.979	-5.87637	L
C	12.57212	-5.09655	-8.26071	L
H	11.74562	-5.83985	-8.26179	L
H	12.3296	-4.30463	-8.99975	L
H	13.49832	-5.60332	-8.6089	L
C	-8.0045	8.224047	-2.29512	L
C	-6.97751	9.081755	-1.52625	L
H	-7.3485	10.12154	-1.3965	L
H	-6.77347	8.669314	-0.51596	L
H	-6.02007	9.12142	-2.08681	L
C	-8.3061	8.941252	-3.63321	L
H	-7.38056	9.062719	-4.2364	L
H	-9.05862	8.375576	-4.2241	L

H	-8.71807	9.957827	-3.45151	L
C	-9.32235	8.156395	-1.49276	L
H	-10.055	7.498571	-2.00855	L
H	-9.15875	7.761537	-0.46851	L
H	-9.77317	9.167239	-1.38868	L
C	-2.90305	10.56836	-4.0777	L
C	-2.06016	11.74137	-3.5319	L
H	-1.00312	11.42612	-3.3945	L
H	-2.07965	12.6018	-4.23556	L
H	-2.44597	12.10293	-2.55601	L
C	-2.3898	10.24306	-5.50111	L
H	-2.47546	11.13175	-6.16372	L
H	-1.31875	9.946718	-5.4777	L
H	-2.98769	9.426631	-5.96109	L
C	-4.37853	11.00851	-4.2006	L
H	-5.00571	10.16132	-4.55339	L
H	-4.78349	11.35899	-3.22825	L
H	-4.48172	11.84525	-4.92509	L
C	5.832924	9.334853	-0.7222	L
C	7.31168	9.352186	-0.28145	L
H	7.990558	9.103771	-1.12255	L
H	7.599906	10.35775	0.094472	L
H	7.47801	8.615811	0.533258	L
C	4.979615	9.803152	0.481195	L
H	3.901386	9.835486	0.213038	L
H	5.121777	9.129868	1.354244	L
C	5.626278	10.35111	-1.86651	L
H	5.8401	11.38531	-1.51928	L
H	6.300413	10.14478	-2.72378	L
H	4.576532	10.31483	-2.23024	L
C	10.7822	6.641137	-1.52501	L
C	10.24665	7.136336	-2.88612	L
H	11.02615	7.713058	-3.42973	L
H	9.3674	7.797169	-2.73817	L
C	11.98383	5.700575	-1.76059	L
H	12.81688	6.241941	-2.25946	L
H	12.35705	5.300748	-0.79289	L
H	11.70933	4.842753	-2.40952	L
C	11.29678	7.87564	-0.74608	L
H	10.47631	8.604171	-0.57017	L
H	11.73568	7.574074	0.229528	L
H	12.09106	8.400817	-1.32003	L
H	5.275532	10.82643	0.799802	L

H	9.942311	6.29243	-3.53948	L

C2-carbene (E = -1566.43496410 a.u. ; Esol = -1566.54538324 a.u.)

C	-2.42202	-0.97019	1.230636
C	-3.81127	-1.60652	1.242971
C	-3.76994	-2.97776	1.928052
H	-4.35048	-3.79513	1.471283
H	-2.83432	-3.22538	2.475081
C	-4.6086	-1.86389	2.567701
C	-4.08386	-1.20522	3.819499
C	-3.6008	-1.97482	4.888173
H	-3.67821	-3.05464	4.864289
C	-2.95999	-1.35693	5.966338
H	-2.55511	-1.97188	6.75946
C	-2.79365	0.038667	5.989875
C	-3.3438	0.81081	4.953165
H	-3.25096	1.889807	4.961483
C	-4.00303	0.19456	3.887713
H	-4.38353	0.802496	3.077373
C	-6.11211	-2.04083	2.453435
C	-6.91427	-0.95529	2.076369
H	-6.49747	0.041321	2.02739
C	-8.21934	-1.16886	1.632874
H	-8.78776	-0.33687	1.245434
C	-8.76343	-2.4614	1.617221
C	-8.02122	-3.51922	2.166359
H	-8.42491	-4.52339	2.187372
C	-6.70672	-3.30796	2.592418
H	-6.12935	-4.15202	2.947413
C	-4.66496	-1.41343	-0.00472
C	-5.10296	-2.48268	-0.79593
H	-4.7395	-3.47051	-0.62746
C	-6.05576	-2.2922	-1.79545
H	-6.40963	-3.15735	-2.33566
C	-6.57013	-1.01187	-2.05695
C	-6.04651	0.076906	-1.33831
H	-6.38175	1.079721	-1.54832
C	-5.09981	-0.12149	-0.32909
H	-4.7496	0.724995	0.246322
C	1.039412	-2.34829	1.298432
C	1.817226	-3.65053	1.302915
C	1.124751	-5.00592	0.972073
C	1.439062	-4.61845	2.424804
H	0.559047	-4.31461	3.033118
H	2.289411	-5.14276	2.904957

C	3.28051	-3.53634	0.937387
C	3.630035	-3.33768	-0.40372
H	2.861324	-3.2453	-1.15866
C	4.967537	-3.25942	-0.78579
H	5.193484	-3.09535	-1.83133
C	5.992459	-3.3365	0.17478
C	5.637525	-3.48604	1.529083
H	6.396001	-3.54823	2.29829
C	4.294496	-3.57107	1.907816
H	4.053182	-3.66457	2.958161
C	1.966607	-6.13086	0.396167
C	2.279921	-6.12441	-0.97134
H	1.92043	-5.32955	-1.61096
C	3.053593	-7.14388	-1.52939
H	3.287278	-7.10402	-2.58594
C	3.497103	-8.21667	-0.73811
C	3.122951	-8.2611	0.61606
H	3.439009	-9.08047	1.249324
C	2.352039	-7.23741	1.173571
H	2.059048	-7.31549	2.212052
C	-0.34836	-5.09317	0.652318
C	-1.15608	-5.98573	1.374248
H	-0.7621	-6.49526	2.244991
C	-2.45166	-6.28236	0.943868
H	-3.03183	-7.00104	1.507727
C	-2.97187	-5.69336	-0.22249
C	-2.16318	-4.78271	-0.93402
H	-2.53297	-4.286	-1.82187
C	-0.86031	-4.50173	-0.51095
H	-0.23719	-3.86216	-1.12171
C	2.438302	1.110873	1.2092
C	3.847205	1.712288	1.263768
C	3.837003	3.051369	2.011438
H	4.445331	3.869049	1.590871
H	2.90112	3.306541	2.5541
C	4.625888	1.879887	2.613751
C	4.055568	1.167519	3.816237
C	3.574955	1.888099	4.919612
H	3.679023	2.965261	4.957069
C	2.907418	1.226482	5.955576
H	2.508371	1.806471	6.777832
C	2.713655	-0.16541	5.9032
C	3.253503	-0.89016	4.827367

H	3.140022	-1.96593	4.775328
C	3.934491	-0.23118	3.802418
H	4.307437	-0.80323	2.962723
C	6.13729	2.014605	2.543414
C	6.76182	3.25932	2.736797
H	6.196194	4.113048	3.087605
C	8.098737	3.440201	2.376049
H	8.523107	4.434096	2.434589
C	8.841266	2.370934	1.847573
C	8.259798	1.093398	1.812209
H	8.825375	0.246283	1.450733
C	6.924665	0.912952	2.177389
H	6.484134	-0.07088	2.088334
C	4.73045	1.54366	0.032317
C	5.220735	2.63113	-0.70525
H	4.874853	3.624326	-0.51392
C	6.180492	2.447203	-1.70203
H	6.535275	3.313718	-2.24411
C	6.670808	1.163301	-1.995
C	6.12339	0.066687	-1.30779
H	6.480398	-0.9316	-1.50139
C	5.154005	0.254356	-0.31752
H	4.783573	-0.60041	0.232457
C	-1.1113	2.482036	1.166453
C	-1.92074	3.7669	1.149535
C	-1.24923	5.134268	0.82549
C	-1.56765	4.745563	2.274145
H	-0.68999	4.45926	2.894731
H	-2.42564	5.267051	2.745202
C	-3.40641	3.612368	0.891126
C	-3.88407	3.519724	-0.42242
H	-3.19346	3.509848	-1.25444
C	-5.25511	3.427618	-0.67582
H	-5.58148	3.359531	-1.70489
C	-6.18054	3.361672	0.384615
C	-5.68946	3.404209	1.703752
H	-6.36116	3.368386	2.550813
C	-4.31969	3.510697	1.952759
H	-3.97585	3.521632	2.978983
C	-2.10387	6.235911	0.228506
C	-2.5346	7.335211	0.992149
H	-2.2668	7.426046	2.036266
C	-3.30861	8.342317	0.409942

H	-3.63113	9.17407	1.023695
C	-3.63763	8.291554	-0.95557
C	-3.14976	7.22617	-1.73136
H	-3.37676	7.162282	-2.78802
C	-2.37595	6.220852	-1.14741
H	-1.9874	5.42701	-1.7719
C	0.231751	5.262361	0.562391
C	0.820963	4.646112	-0.54923
H	0.242381	3.987585	-1.18283
C	2.150632	4.918582	-0.88525
H	2.580817	4.409181	-1.73665
C	2.908204	5.842548	-0.13696
C	2.308524	6.460895	0.97351
H	2.847736	7.194434	1.558644
C	0.986012	6.175758	1.316073
H	0.534354	6.700997	2.148705
O	0.8734	-1.77149	2.40871
O	0.715223	-1.88866	0.156816
O	1.812752	0.994865	2.294263
O	1.975131	0.805771	0.057827
O	-0.92221	1.94582	2.293256
O	-0.77149	1.99993	0.035949
O	-1.83422	-0.81443	2.330377
O	-1.9384	-0.67601	0.084836
C	-7.64067	3.191547	0.118476
C	-8.44611	2.450688	0.998423
C	-8.24102	3.74601	-1.02523
C	-9.80461	2.260916	0.741266
H	-8.02692	1.990712	1.882223
C	-9.60184	3.55104	-1.28907
H	-7.66372	4.346228	-1.71621
C	-10.4146	2.798345	-0.41003
H	-10.377	1.679243	1.450811
H	-9.99859	4.000247	-2.18707
C	7.416936	-3.19995	-0.23571
C	8.335469	-2.52061	0.578794
C	7.856748	-3.69531	-1.4741
C	9.652322	-2.32474	0.158857
H	8.031896	-2.10991	1.532244
C	9.16984	-3.48946	-1.90243
H	7.184837	-4.24754	-2.1186
C	10.09665	-2.78975	-1.0971
H	10.32094	-1.79183	0.820891

H	9.437916	-3.88731	-2.86949
C	7.76814	0.974171	-2.9865
C	8.774646	1.942449	-3.12711
C	7.836862	-0.1811	-3.78286
C	9.818947	1.764849	-4.03374
H	8.775791	2.832352	-2.51566
C	8.884125	-0.36333	-4.69176
H	7.069945	-0.94237	-3.72089
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C	-3.63524	8.113915	0.751532
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C	-2.79743	7.065007	1.1399
H	-2.22935	7.162958	2.056122
C	-0.40722	4.770017	0.065788
C	0.716371	5.350443	0.673354
H	0.665459	5.714628	1.691292
C	1.906487	5.510448	-0.04247
H	2.754081	5.952904	0.463731
C	1.988654	5.135996	-1.3983
C	0.866683	4.529896	-1.99407
H	0.875695	4.246202	-3.03788
C	-0.31389	4.348101	-1.26939
H	-1.17222	3.916837	-1.76767
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O	1.448869	1.295532	2.391208
O	1.770194	1.284599	0.167905
O	-1.36572	1.521014	2.225169
O	-1.11815	1.808804	-0.00534
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C	-8.05207	2.267135	1.042152
C	-8.59839	1.394288	1.99519
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C	-10.1855	2.264514	-0.12666
H	-8.49051	3.415049	-0.74063
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C	9.166166	-2.1333	0.726596
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H	7.69664	-0.70897	-1.99129
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C	-1.39849	4.714184	-1.01625
H	-1.40505	5.604702	-1.67884
H	-2.25062	4.001956	-1.02976
C	-0.73972	4.918817	0.353362
C	-1.39835	4.206509	1.51487
C	-2.77316	4.340069	1.754637
H	-3.38516	4.94548	1.097723
C	-3.36987	3.692753	2.842879
H	-4.43093	3.831002	2.998786
C	-2.60395	2.88839	3.71291
C	-1.2159	2.803761	3.489268

H	-0.5836	2.18514	4.110069
C	-0.61937	3.493733	2.433355
H	0.453551	3.438821	2.306686
C	-0.25429	6.323987	0.632175
C	0.965088	6.525303	1.293268
H	1.568561	5.682282	1.594203
C	1.4064	7.815638	1.59368
H	2.351432	7.937736	2.107959
C	0.620351	8.933078	1.263277
C	-0.62488	8.727586	0.64361
H	-1.25557	9.56695	0.379199
C	-1.06382	7.435292	0.344596
H	-2.03719	7.304465	-0.11111
C	1.135948	4.672034	-1.51154
C	1.020831	5.027751	-2.8658
H	0.064278	4.988647	-3.37006
C	2.153546	5.376579	-3.60441
H	2.034471	5.619469	-4.65227
C	3.430121	5.339353	-3.01629
C	3.542202	4.979887	-1.66272
H	4.509655	4.938337	-1.17853
C	2.408806	4.632362	-0.92703
H	2.530929	4.276202	0.085852
C	-2.64502	-0.05606	-0.72346
C	-4.15853	-0.00757	-0.72813
C	-4.99697	-0.75941	0.348353
C	-4.78692	-1.36639	-1.0426
H	-4.0724	-2.21347	-1.08317
H	-5.67899	-1.35432	-1.70249
C	-4.75323	1.185671	-1.44053
C	-4.71734	2.434966	-0.80736
H	-4.32361	2.524215	0.195119
C	-5.14662	3.584047	-1.47235
H	-5.12336	4.530429	-0.94687
C	-5.58795	3.512577	-2.80404
C	-5.59017	2.265525	-3.4534
H	-5.88641	2.185584	-4.49185
C	-5.16052	1.116085	-2.78434
H	-5.11846	0.182579	-3.32992
C	-6.40755	-0.297	0.638694
C	-6.62352	0.907326	1.321491
H	-5.78831	1.520059	1.623013
C	-7.91761	1.320079	1.644273

H	-8.05019	2.252941	2.177873
C	-9.02441	0.519462	1.313717
C	-8.80429	-0.70925	0.666563
H	-9.63548	-1.35006	0.400648
C	-7.50774	-1.11927	0.344948
H	-7.36403	-2.08123	-0.1308
C	-4.28547	-1.45427	1.488441
C	-3.59969	-0.69943	2.446711
H	-3.55166	0.377497	2.355369
C	-2.93276	-1.32342	3.501325
H	-2.33877	-0.70457	4.158636
C	-3.00946	-2.71924	3.678333
C	-3.77699	-3.46487	2.758475
H	-3.9074	-4.53189	2.874851
C	-4.40151	-2.83937	1.673344
H	-4.98271	-3.4358	0.98103
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O	2.037759	0.318603	-1.87662
O	0.264093	1.976351	0.296941
O	-0.37719	2.016394	-1.87024
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C	-6.00836	4.739952	-3.52461
C	-7.12439	4.722388	-4.37359
C	-5.29286	5.936818	-3.37249
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H	-7.70424	3.8163	-4.4992
C	-5.68589	7.091114	-4.05282
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H	-8.39121	5.796678	-5.68889
H	-5.10078	7.988781	-3.90682
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C	5.945337	-7.19976	-3.8546
H	4.445294	-6.02624	-2.87787
C	8.033292	-6.08153	-4.34202
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C	7.245724	-7.2548	-4.40253
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C	5.770823	6.815325	-5.61376
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C	6.93479	6.027375	-5.45829
H	5.705856	7.599709	-6.35261
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H	-7.6393	-3.17894	-4.94114
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C	-3.79593	-11.838	1.22137
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C	-1.60715	-12.6834	1.80501
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C	-2.99235	-12.9192	1.644654
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H	-0.92899	-13.4582	2.129237
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C	4.460419	-2.09059	4.470811
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C	5.085212	-1.28814	5.42587
H	5.015751	-2.34104	3.579986
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H	2.505307	-1.07663	7.649666
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C	-0.64923	-4.59082	6.810979
H	-0.66879	-6.31177	5.484754
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C	-10.7842	2.296616	1.495536
C	-12.6341	0.452945	2.483995
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C	-12.0776	2.710668	1.821083
H	-10.0875	3.024487	1.098586
C	-13.0331	1.800241	2.32313
H	-13.3061	-0.30069	2.865888
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C	-2.52158	1.771463	5.978976
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C	-3.08843	0.970566	6.972878
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H	-5.1708	1.892698	3.848316
C	-4.4087	0.48314	6.850354
H	-2.47023	0.738304	7.826976
H	-6.16317	0.538707	5.5695
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C	2.43492	10.66028	1.377387
C	0.646323	12.5668	2.359359
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C	2.129713	3.127049	4.860454
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H	0.882613	2.329178	7.9143
H	0.493932	6.001636	5.647716
C	10.32192	-1.05583	1.64156
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C	11.23554	-0.17588	2.240538
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C	12.53428	-0.59265	2.544535
H	10.94065	0.835468	2.491511
C	12.96309	-1.90921	2.256366
H	12.30554	-3.80121	1.409181
H	13.1862	0.132515	3.007761
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H	2.321926	15.00371	0.378052
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H	1.008573	14.92906	3.953132
H	1.858152	16.31752	3.203552
H	0.618721	15.43582	2.255896
C	3.6415	14.26983	3.529513
H	3.256592	13.78524	4.452882
H	4.511992	13.68493	3.16584
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H	7.197769	7.114302	-8.08486
H	7.861269	8.313351	-6.89681
H	8.96029	7.427762	-8.00116
C	8.475296	4.892412	-7.09703
H	9.348939	5.010244	-7.77429
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H	-1.5716	6.107888	6.630841
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H	-1.3393	4.40629	9.935682
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H	7.100646	-0.90387	7.359336
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H	6.307491	1.149365	6.097682
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C	-5.06458	-0.42957	7.90669
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H	-6.32682	-1.55758	6.483014
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H	-7.05396	0.512564	7.758159
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H	1.1462	-3.41443	8.672694
C	-0.45225	-6.49992	8.438207
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H	-13.8447	2.997858	4.660869
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C	-3.64215	-14.2927	1.912789
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C	1.53485	-0.09367	-4.4846

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H	14.54636	-3.71006	0.791293
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C	14.30889	-3.60861	3.542711
H	15.32675	-3.96094	3.817883
H	13.77683	-3.31597	4.47377
H	13.77171	-4.46786	3.089678
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TS-1 (E = -1803.50394123 a.u. ; Esol = -1803.61965564 a.u.)

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C	2.911153	1.412304	6.265268	L
H	2.57019	2.041658	7.076341	L
C	2.615562	0.038389	6.254468	L
C	3.079647	-0.75247	5.189005	L
H	2.885456	-1.81785	5.167658	L
C	3.781251	-0.1693	4.130789	L
H	4.093236	-0.78464	3.29711	L
C	6.068833	1.939541	2.735427	L
C	6.779613	0.818442	2.283838	L
H	6.295579	-0.14727	2.216404	L
C	8.067058	0.969677	1.768032	L
H	8.558044	0.122265	1.315747	L
C	8.684677	2.228699	1.749432	L
C	8.050744	3.303697	2.394624	L
H	8.515511	4.27881	2.432941	L
C	6.752986	3.157672	2.892789	L
H	6.250453	4.022787	3.306427	L
C	4.573965	1.554425	0.269446	L
C	5.091677	2.631889	-0.46759	L
H	4.853485	3.644459	-0.2166	L
C	5.956819	2.412788	-1.54006	L
H	6.372673	3.27103	-2.05011	L
C	6.301838	1.106649	-1.92342	L
C	5.738253	0.0301	-1.21997	L
H	5.97186	-0.98546	-1.49101	L
C	4.878858	0.25084	-0.14524	L
H	4.482377	-0.59825	0.396914	L
C	-1.16263	2.468154	1.39686	H
C	-1.97271	3.750432	1.346488	L
C	-1.27417	5.124179	1.132369	L
C	-1.75173	4.702141	2.527266	L
H	-0.94031	4.412468	3.23013	L
H	-2.64689	5.233677	2.906479	L

C	-3.38064	3.609408	0.806688	L
C	-3.56159	3.328408	-0.55478	L
H	-2.70596	3.202398	-1.20603	L
C	-4.84238	3.199913	-1.09049	L
H	-4.9355	2.96062	-2.14155	L
C	-5.97902	3.324182	-0.26985	L
C	-5.79253	3.570594	1.103916	L
H	-6.6374	3.678246	1.770796	L
C	-4.50826	3.690176	1.639348	L
H	-4.40454	3.840703	2.705164	L
C	-2.06412	6.235063	0.467802	L
C	-2.26614	6.203795	-0.92004	L
H	-1.86028	5.395743	-1.51392	L
C	-2.98479	7.217265	-1.55686	L
H	-3.12972	7.160881	-2.62844	L
C	-3.48555	8.305641	-0.82262	L
C	-3.2278	8.369368	0.557996	L
H	-3.59284	9.199234	1.149853	L
C	-2.51136	7.351849	1.194065	L
H	-2.30898	7.439881	2.253477	L
C	0.222859	5.227192	0.977543	L
C	0.956667	6.09115	1.809274	L
H	0.47913	6.56785	2.656295	L
C	2.289611	6.402754	1.514856	L
H	2.81767	7.098074	2.154384	L
C	2.909173	5.866547	0.37281	L
C	2.176412	4.976668	-0.43262	L
H	2.631377	4.52659	-1.29755	L
C	0.846464	4.672019	-0.14489	L
H	0.289723	4.048572	-0.83204	L
C	-2.49958	-1.00241	1.412888	H
C	-3.91553	-1.59303	1.46624	L
C	-3.96305	-2.84909	2.347201	L
H	-4.58698	-3.69506	2.018324	L
H	-3.05219	-3.06757	2.945086	L
C	-4.74342	-1.60394	2.795791	L
C	-4.19622	-0.82391	3.965844	L
C	-3.81157	-1.48023	5.143853	L
H	-3.97914	-2.54402	5.257757	L
C	-3.15232	-0.77889	6.156541	L
H	-2.82232	-1.31653	7.035604	L
C	-2.87335	0.591162	6.00933	L
C	-3.32708	1.260621	4.859383	L

H	-3.14901	2.321461	4.732232	L
C	-3.99932	0.561317	3.853977	L
H	-4.30414	1.083962	2.956494	L
C	-6.25309	-1.70509	2.678913	L
C	-6.92377	-2.90018	2.99133	L
H	-6.40054	-3.71821	3.469958	L
C	-8.24636	-3.09127	2.585555	L
H	-8.70325	-4.05947	2.74303	L
C	-8.9268	-2.07884	1.888011	L
C	-8.30669	-0.82924	1.73116	L
H	-8.82852	-0.02218	1.237857	L
C	-6.98646	-0.63699	2.141828	L
H	-6.50919	0.316023	1.953664	L
C	-4.74742	-1.55295	0.185899	L
C	-5.27683	-2.70689	-0.41416	L
H	-5.00843	-3.6831	-0.07179	L
C	-6.17123	-2.6164	-1.48012	L
H	-6.54976	-3.53272	-1.91347	L
C	-6.55748	-1.36506	-1.98738	L
C	-5.98194	-0.21096	-1.42791	L
H	-6.25704	0.767135	-1.78889	L
C	-5.0824	-0.30547	-0.36046	L
H	-4.68844	0.59906	0.083381	L
C	1.054654	-2.33647	1.480638	H
C	1.871938	-3.61727	1.533494	L
C	1.192382	-5.00628	1.357501	L
C	1.5904	-4.50607	2.750771	L
H	0.743272	-4.18234	3.39417	L
H	2.472793	-4.99562	3.209186	L
C	3.323986	-3.49732	1.119652	L
C	3.651826	-3.43638	-0.24001	L
H	2.871175	-3.42706	-0.98789	L
C	4.985397	-3.39454	-0.64871	L
H	5.19198	-3.3547	-1.70756	L
C	6.028199	-3.35833	0.296746	L
C	5.689304	-3.37164	1.664544	L
H	6.452027	-3.36244	2.430923	L
C	4.35406	-3.42045	2.069785	L
H	4.131346	-3.40878	3.128635	L
C	2.019428	-6.14564	0.790745	L
C	2.497078	-7.18752	1.604668	L
H	2.282994	-7.20665	2.664899	L
C	3.250892	-8.22751	1.054148	L

H	3.611132	-9.0136	1.705916	L
C	3.512768	-8.26732	-0.3263	L
C	2.979177	-7.25942	-1.14716	L
H	3.155316	-7.26499	-2.21544	L
C	2.225527	-6.22176	-0.59521	L
H	1.803138	-5.47381	-1.25304	L
C	-0.29541	-5.1355	1.150327	L
C	-0.8879	-4.64792	-0.02007	L
H	-0.31396	-4.05645	-0.7213	L
C	-2.20707	-4.98112	-0.33188	L
H	-2.63178	-4.59566	-1.24413	L
C	-2.9607	-5.8206	0.510042	L
C	-2.36798	-6.29115	1.694362	L
H	-2.90729	-6.95433	2.358074	L
C	-1.04657	-5.95879	2.005567	L
H	-0.59131	-6.38618	2.890445	L
O	-1.03194	1.917352	2.529497	H
O	-0.77713	1.992384	0.283443	H
O	-1.88771	-0.87081	2.509755	H
O	-2.01857	-0.71166	0.269666	H
O	0.852122	-1.74989	2.580748	H
O	0.72476	-1.90389	0.327398	H
O	1.696513	1.059207	2.59144	H
O	1.890843	0.776085	0.367593	H
C	7.453893	-3.25743	-0.14023	L
C	8.397436	-2.58309	0.651105	L
C	7.884215	-3.81223	-1.35884	L
C	9.72295	-2.45236	0.23552	L
H	8.113442	-2.13424	1.591762	L
C	9.21262	-3.68194	-1.77869	L
H	7.200746	-4.36626	-1.98852	L
C	10.16347	-2.9962	-0.98812	L
H	10.40539	-1.91922	0.883255	L
H	9.475509	-4.13022	-2.72502	L
C	-7.34486	3.136267	-0.83623	L
C	-8.36131	2.543249	-0.07152	L
C	-7.63247	3.502129	-2.16176	L
C	-9.62343	2.308636	-0.61831	L
H	-8.17885	2.235022	0.948185	L
C	-8.89074	3.25606	-2.71631	L
H	-6.8862	3.98842	-2.77642	L
C	-9.91501	2.647221	-1.95625	L
H	-10.3713	1.850205	0.014102	L

H	-9.04119	3.555613	-3.74246	L
C	-7.56259	-1.26995	-3.08453	L
C	-8.60873	-2.20251	-3.17605	L
C	-7.48909	-0.25188	-4.04949	L
C	-9.54385	-2.13157	-4.20816	L
H	-8.72027	-2.9853	-2.43941	L
C	-8.42853	-0.17499	-5.08261	L
H	-6.68805	0.475602	-4.02674	L
C	-9.47222	-1.12327	-5.19169	L
H	-10.3256	-2.87838	-4.23342	L
H	-8.31059	0.627917	-5.79458	L
C	7.268645	0.865802	-3.0274	L
C	8.156168	-0.21952	-2.97047	L
C	7.327961	1.724357	-4.13679	L
C	9.07879	-0.43936	-3.99057	L
H	8.163002	-0.88707	-2.12012	L
C	8.26782	1.517943	-5.15035	L
H	6.639394	2.554195	-4.2315	L
C	9.172994	0.433357	-5.09307	L
H	9.732404	-1.2933	-3.90373	L
H	8.267806	2.219395	-5.97092	L
C	-4.26318	9.37482	-1.49827	L
C	-5.21527	9.052792	-2.4769	L
C	-4.06069	10.72324	-1.17061	L
C	-5.95008	10.05507	-3.11577	L
H	-5.40611	8.019151	-2.7383	L
C	-4.79228	11.72754	-1.80844	L
H	-3.32102	11.00549	-0.43184	L
C	-5.75379	11.41858	-2.79549	L
H	-6.66951	9.739376	-3.85617	L
H	-4.59772	12.75304	-1.52566	L
C	4.318476	6.201467	0.019616	L
C	4.71363	6.270416	-1.32658	L
C	5.303285	6.326815	1.013035	L
C	6.061342	6.368836	-1.67155	L
H	3.981482	6.212356	-2.12144	L
C	6.655584	6.433533	0.66957	L
H	5.038959	6.273481	2.061348	L
C	7.066597	6.42605	-0.68394	L
H	6.314815	6.367015	-2.72273	L
H	7.366456	6.4854	1.480371	L
C	9.906277	2.442169	0.936571	L
C	10.9481	3.262603	1.388011	L

C	9.994079	1.87942	-0.34547	L
C	12.05568	3.518185	0.572564	L
H	10.90575	3.709157	2.373629	L
C	11.08764	2.145189	-1.16734	L
H	9.192333	1.264771	-0.73179	L
C	12.14707	2.966388	-0.72814	L
H	12.82489	4.159037	0.976147	L
H	11.09273	1.711711	-2.15815	L
C	4.328791	-9.36277	-0.90835	L
C	5.479173	-9.82162	-0.24979	L
C	3.967397	-9.9541	-2.12765	L
C	6.254024	-10.8479	-0.79679	L
H	5.793007	-9.37253	0.684437	L
C	4.738726	-10.981	-2.6763	L
H	3.07553	-9.63448	-2.65204	L
C	5.90008	-11.452	-2.02564	L
H	7.129184	-11.1507	-0.24194	L
H	4.417929	-11.4082	-3.61651	L
C	-4.36247	-6.18117	0.155296	L
C	-5.35284	-6.27486	1.146782	L
C	-4.74508	-6.32457	-1.1891	L
C	-6.69571	-6.43994	0.799167	L
H	-5.10228	-6.15949	2.193292	L
C	-6.08772	-6.48113	-1.5391	L
H	-4.00706	-6.29242	-1.98048	L
C	-7.09831	-6.5123	-0.55199	L
H	-7.42453	-6.47906	1.59715	L
H	-6.31409	-6.55674	-2.59188	L
C	-10.2094	-2.36863	1.202734	L
C	-11.192	-3.16569	1.806604	L
C	-10.4047	-1.93784	-0.1174	L
C	-12.3357	-3.54537	1.09656	L
H	-11.0701	-3.5069	2.82704	L
C	-11.5329	-2.33293	-0.83451	L
H	-9.65663	-1.33569	-0.61735	L
C	-12.5222	-3.14908	-0.24921	L
H	-13.0517	-4.16636	1.613353	L
H	-11.6175	-2.01237	-1.86296	L
C	-2.09799	1.314912	7.044727	L
C	-1.07312	2.200102	6.681328	L
C	-2.37797	1.124054	8.403537	L
C	-0.35822	2.897413	7.658539	L
H	-0.8207	2.350539	5.638582	L

C	-1.66297	1.81651	9.383739	L
H	-3.17475	0.457169	8.707864	L
C	-0.64413	2.732184	9.032199	L
H	0.413309	3.580533	7.330814	L
H	-1.9381	1.633908	10.41132	L
C	1.804184	-0.56039	7.339574	L
C	0.755228	-1.44144	7.042872	L
C	2.066855	-0.24499	8.678301	L
C	-0.00568	-2.00843	8.068127	L
H	0.517642	-1.68658	6.014669	L
C	1.303795	-0.8041	9.706196	L
H	2.8834	0.419401	8.931639	L
C	0.2554	-1.71075	9.424302	L
H	-0.79611	-2.69286	7.792834	L
H	1.562739	-0.52429	10.71608	L
C	-6.54008	12.55797	-3.47662	L
C	-5.55456	13.50711	-4.19254	L
H	-4.94727	12.94506	-4.93476	L
H	-6.10173	14.3135	-4.72756	L
H	-4.86304	13.99552	-3.47465	L
C	-7.32974	13.34786	-2.41026	L
H	-8.01414	12.66994	-1.85563	L
H	-6.65263	13.83497	-1.67788	L
H	-7.9387	14.14872	-2.88321	L
C	-7.55321	12.0506	-4.53107	L
H	-8.31219	11.38638	-4.06386	L
H	-8.09697	12.9013	-4.99675	L
H	-7.03482	11.50086	-5.34629	L
C	8.549103	6.432978	-1.11182	L
C	9.526978	6.531839	0.082329	L
H	10.5816	6.543659	-0.27019	L
H	9.353206	7.465001	0.660334	L
H	9.417348	5.658005	0.754919	L
C	8.861586	5.123523	-1.86838	L
H	8.272595	5.042947	-2.8061	L
H	9.936507	5.070782	-2.1424	L
H	8.620371	4.246198	-1.23138	L
C	8.821688	7.639407	-2.03674	L
H	8.242927	7.572768	-2.98112	L
H	8.548736	8.587491	-1.52486	L
H	9.897317	7.688349	-2.31368	L
C	13.33729	3.234364	-1.67129	L
C	12.83601	3.966296	-2.93482	L

H	12.08777	3.361204	-3.48841	L
H	12.36622	4.934852	-2.65913	L
H	13.67883	4.174138	-3.62917	L
C	13.98532	1.892774	-2.08078	L
H	14.88918	2.064395	-2.70463	L
H	14.28688	1.317416	-1.17878	L
H	13.28944	1.267803	-2.6782	L
C	14.43704	4.109353	-1.02402	L
H	14.03933	5.11154	-0.75391	L
H	14.8474	3.619043	-0.11478	L
H	15.28117	4.267599	-1.73009	L
C	10.24987	0.181476	-6.16665	L
C	10.22834	1.230923	-7.30341	L
H	10.41591	2.251095	-6.90375	L
H	11.02042	1.015823	-8.05338	L
H	9.25283	1.217686	-7.83603	L
C	11.64798	0.228369	-5.51023	L
H	11.77503	-0.57831	-4.7585	L
H	12.44647	0.099331	-6.27263	L
H	11.80406	1.204594	-5.00218	L
C	10.02726	-1.20771	-6.80339	L
H	10.14495	-2.02281	-6.05898	L
H	9.005217	-1.27507	-7.23545	L
H	10.76367	-1.39157	-7.61555	L
C	11.64365	-2.84409	-1.3972	L
C	11.96169	-3.47688	-2.77352	L
H	13.03336	-3.33604	-3.03375	L
H	11.76371	-4.57046	-2.7621	L
H	11.36014	-3.00561	-3.57863	L
C	12.53743	-3.53699	-0.34608	L
H	13.60858	-3.47601	-0.63739	L
H	12.43653	-3.06164	0.652099	L
H	12.26157	-4.60956	-0.25072	L
C	12.0139	-1.34589	-1.46978	L
H	11.34653	-0.81442	-2.17797	L
H	11.92908	-0.85232	-0.47931	L
H	13.06219	-1.21523	-1.81513	L
C	-0.5717	-2.39871	10.53094	L
C	-0.14785	-1.97368	11.95767	L
H	-0.76976	-2.48719	12.723	L
H	0.912187	-2.24453	12.15364	L
H	-0.28037	-0.87905	12.10052	L
C	-0.39454	-3.92902	10.42482	L

H	0.681325	-4.19931	10.49599	L
H	-0.93948	-4.4476	11.24337	L
H	-0.78978	-4.31946	9.463726	L
C	-2.06474	-2.04594	10.36508	L
H	-2.21328	-0.95125	10.46518	L
H	-2.45693	-2.36758	9.37829	L
H	-2.67603	-2.54755	11.14638	L
C	0.119448	3.57054	10.07943	L
C	-0.31651	3.26776	11.53353	L
H	0.261956	3.884778	12.25522	L
H	-1.39232	3.5039	11.68271	L
H	-0.13527	2.200326	11.78662	L
C	-0.13416	5.070393	9.814946	L
H	0.367431	5.697428	10.5838	L
H	0.258579	5.381065	8.824079	L
H	-1.2237	5.28888	9.842788	L
C	1.632426	3.285047	9.979658	L
H	1.833026	2.211386	10.17203	L
H	2.035679	3.54918	8.9807	L
H	2.195225	3.879666	10.73161	L
C	-8.59826	-6.61035	-0.8986	L
C	-8.87378	-6.56366	-2.42122	L
H	-9.96595	-6.60257	-2.62641	L
H	-8.48247	-5.62173	-2.86376	L
H	-8.41142	-7.433	-2.93641	L
C	-9.35563	-5.42851	-0.25543	L
H	-10.4158	-5.40569	-0.58765	L
H	-9.36435	-5.50357	0.850806	L
H	-8.87778	-4.46648	-0.53615	L
C	-9.16345	-7.93705	-0.35179	L
H	-8.61761	-8.79979	-0.79132	L
H	-9.06873	-7.99246	0.753242	L
H	-10.2415	-8.03863	-0.60385	L
C	-10.5016	-1.10922	-6.34093	L
C	-11.9261	-0.96061	-5.76383	L
H	-12.6813	-0.94959	-6.57933	L
H	-12.1843	-1.7974	-5.08174	L
H	-12.016	-0.01019	-5.19966	L
C	-10.4069	-2.43455	-7.12823	L
H	-11.1038	-2.43011	-7.99444	L
H	-9.37425	-2.58331	-7.51175	L
H	-10.6725	-3.30612	-6.49402	L
C	-10.2763	0.048372	-7.34302	L

H	-10.363	1.034028	-6.83808	L
H	-9.27655	-0.03153	-7.82215	L
H	-11.0375	0.021968	-8.15296	L
C	-11.3181	2.358204	-2.52601	L
C	-11.4487	2.719914	-4.02458	L
H	-11.2955	3.808763	-4.1858	L
H	-10.7109	2.151711	-4.6305	L
H	-12.4629	2.469322	-4.40489	L
C	-12.3656	3.180226	-1.74634	L
H	-13.3846	3.009979	-2.15692	L
H	-12.385	2.898701	-0.6724	L
H	-12.1362	4.265501	-1.81755	L
C	-11.6364	0.855236	-2.37793	L
H	-10.8457	0.244178	-2.86306	L
H	-11.7052	0.557362	-1.31186	L
H	-12.613	0.60762	-2.84693	L
C	6.725434	-12.587	-2.66671	L
C	7.223594	-12.1387	-4.05796	L
H	7.82718	-11.2093	-3.9711	L
H	7.857649	-12.9251	-4.52215	L
H	6.378853	-11.9422	-4.75072	L
C	7.965262	-12.9836	-1.82935	L
H	7.663882	-13.349	-0.8238	L
H	8.530538	-13.8025	-2.32542	L
H	8.65856	-12.1223	-1.71549	L
C	5.841256	-13.8438	-2.81901	L
H	5.439092	-14.1552	-1.83062	L
H	4.985294	-13.6611	-3.50168	L
H	6.427136	-14.6896	-3.24006	L
C	-13.7362	-3.58561	-1.0931	L
C	-14.5009	-2.33569	-1.58178	L
H	-14.8145	-1.7119	-0.7169	L
H	-13.8767	-1.71071	-2.25422	L
H	-15.4102	-2.62722	-2.15093	L
C	-14.7322	-4.47112	-0.30723	L
H	-15.5931	-4.76045	-0.94851	L
H	-14.2431	-5.40848	0.035963	L
H	-15.1388	-3.92508	0.571387	L
C	-13.247	-4.39652	-2.31379	L
H	-12.6571	-5.27815	-1.98159	L
H	-14.1077	-4.75913	-2.91652	L
H	-12.6082	-3.78347	-2.98366	L
Rh	-0.04874	0.051439	0.198556	H

Rh	-0.09953	0.085851	2.624969	H
C	-0.0099	0.171152	-2.15703	H
C	-1.39416	-0.20125	-2.51448	H
O	-2.31011	0.587289	-2.62318	H
O	-1.56592	-1.55638	-2.65974	H
C	-2.88011	-1.98681	-2.95958	H
H	-3.23078	-2.61843	-2.14752	H
H	-3.54442	-1.1291	-3.08073	H
C	0.584934	1.379698	-2.75931	H
C	1.949655	1.672237	-2.5485	H
C	-0.1513	2.259348	-3.58278	H
C	2.574523	2.731317	-3.20073	H
H	2.521964	1.069821	-1.85649	H
C	0.450515	3.361053	-4.18573	H
H	-1.20937	2.094005	-3.73349	H
C	1.813924	3.571499	-4.00735	H
H	3.630498	2.923561	-3.054	H
H	-0.138	4.034306	-4.79892	H
Br	2.684829	5.100931	-4.88362	H
C	-2.88805	-2.80997	-4.24209	H
Cl	-2.34862	-1.79638	-5.66676	H
Cl	-1.78526	-4.26481	-4.10324	H
Cl	-4.59865	-3.38735	-4.52421	H
H	0.714519	-0.73087	-1.99676	H
C	1.17301	-1.60527	-3.09259	H
H	0.535525	-1.54153	-3.9679	H
H	0.914453	-2.44128	-2.44271	H
C	2.622361	-1.29178	-3.28285	H
H	2.730023	-0.32377	-3.77925	H
H	3.137448	-1.23415	-2.31689	H
C	3.307669	-2.38169	-4.15265	H
H	2.754096	-2.50639	-5.09364	H
H	3.251284	-3.34312	-3.62642	H
C	4.787225	-2.06174	-4.47185	H
C	5.4851	-3.30072	-5.05264	H
H	6.545496	-3.09567	-5.24084	H
H	5.424984	-4.15313	-4.3657	H
H	5.029805	-3.60239	-6.00456	H
C	4.948978	-0.85548	-5.40877	H
H	6.009038	-0.67732	-5.62315	H
H	4.442104	-1.02924	-6.3667	H
H	4.54579	0.067268	-4.97706	H
H	5.288824	-1.8161	-3.5282	H

TS-2 (E = -1803.4996243 a.u. ; Esol = -1803.61469965 a.u.)

C	-2.08631	-1.36432	0.970013
C	-3.4411	-2.07569	0.94436
C	-3.40391	-3.39941	1.713471
H	-3.96462	-4.24796	1.296634
H	-2.4867	-3.59861	2.308588
C	-4.28473	-2.26385	2.251021
C	-3.82444	-1.55309	3.497462
C	-3.76307	-0.15289	3.514211
H	-4.08989	0.416851	2.653326
C	-3.20693	0.512561	4.607738
H	-3.13057	1.590799	4.582699
C	-2.73598	-0.20801	5.718071
C	-2.89035	-1.60538	5.738045
H	-2.55923	-2.18418	6.58948
C	-3.42905	-2.27356	4.634204
H	-3.50362	-3.35374	4.651068
C	-5.77626	-2.50724	2.119048
C	-6.33506	-3.75584	2.442774
H	-5.72945	-4.52706	2.90205
C	-7.66003	-4.04402	2.10477
H	-8.05143	-5.033	2.307095
C	-8.44141	-3.08939	1.434196
C	-7.91211	-1.81017	1.20797
H	-8.50087	-1.0547	0.705071
C	-6.60773	-1.50682	1.596744
H	-6.22283	-0.51209	1.418329
C	-4.26618	-1.95543	-0.33327
C	-4.76616	-3.0685	-1.02949
H	-4.44267	-4.06273	-0.7955
C	-5.77348	-2.91554	-1.98395
H	-6.20617	-3.80323	-2.42459
C	-6.27825	-1.64084	-2.28882
C	-5.66641	-0.51874	-1.70787
H	-5.99797	0.478036	-1.96102
C	-4.6745	-0.67575	-0.7383
H	-4.29262	0.200286	-0.23051
C	1.651726	-2.02982	1.080922
C	2.613829	-3.21423	1.115008
C	2.123601	-4.67741	0.896142
C	2.387174	-4.15106	2.309613
H	1.474258	-3.9524	2.912976

H	3.309204	-4.5069	2.811936
C	4.068121	-2.89977	0.817097
C	4.513386	-2.85868	-0.5084
H	3.825983	-3.07214	-1.31242
C	5.840488	-2.53758	-0.80935
H	6.149216	-2.55251	-1.84595
C	6.747102	-2.19874	0.213384
C	6.290235	-2.228	1.545375
H	6.93783	-1.94177	2.363315
C	4.971469	-2.58058	1.842196
H	4.654047	-2.58368	2.876104
C	3.111066	-5.70353	0.369111
C	3.71877	-6.65299	1.210256
H	3.493777	-6.68649	2.2675
C	4.618673	-7.58719	0.690465
H	5.076578	-8.30162	1.363103
C	4.902362	-7.6177	-0.68578
C	4.24019	-6.7144	-1.53421
H	4.427184	-6.71768	-2.60063
C	3.340507	-5.78295	-1.01229
H	2.820857	-5.11911	-1.68901
C	0.673653	-4.98413	0.610876
C	-0.00174	-5.93566	1.391716
H	0.471371	-6.35228	2.27242
C	-1.26289	-6.40439	1.011071
H	-1.73585	-7.16449	1.618534
C	-1.87715	-5.93334	-0.16389
C	-1.19942	-4.96568	-0.93172
H	-1.64249	-4.56539	-1.8306
C	0.067972	-4.51068	-0.55808
H	0.596736	-3.82555	-1.20705
C	2.226872	1.669424	1.279938
C	3.585672	2.377244	1.420341
C	3.529263	3.607462	2.339134
H	4.145633	4.492818	2.106897
H	2.572669	3.757617	2.884362
C	4.335067	2.38185	2.793206
C	3.764674	1.557638	3.921617
C	3.310662	2.157107	5.105946
H	3.405652	3.226097	5.249631
C	2.689548	1.383066	6.09264
H	2.312511	1.87234	6.980591
C	2.517623	-0.00146	5.909228

C	3.043792	-0.6039	4.754188
H	2.956883	-1.67207	4.599297
C	3.670109	0.169477	3.777186
H	4.021744	-0.29666	2.870326
C	5.846087	2.498688	2.758198
C	6.495264	3.636329	3.260996
H	5.926195	4.442781	3.705559
C	7.886353	3.747025	3.183025
H	8.363882	4.638039	3.571345
C	8.655703	2.708531	2.62927
C	8.00813	1.550129	2.171254
H	8.575852	0.736141	1.739066
C	6.617766	1.44436	2.24423
H	6.13837	0.548419	1.877654
C	4.487314	2.395314	0.186406
C	4.712293	1.180394	-0.48398
H	4.221996	0.271151	-0.15814
C	5.59089	1.112331	-1.5613
H	5.725182	0.167975	-2.06275
C	6.324208	2.237838	-1.95508
C	6.112466	3.453408	-1.28989
H	6.651491	4.343495	-1.5877
C	5.177991	3.542868	-0.25623
H	5.029961	4.511053	0.190943
C	-1.41202	2.287367	1.194428
C	-2.23085	3.560133	1.279458
C	-1.64838	4.917306	0.793177
C	-1.64759	4.55738	2.283628
H	-0.65854	4.278399	2.707969
H	-2.38843	5.095782	2.910026
C	-3.73277	3.372887	1.298921
C	-4.47009	3.331787	2.495113
H	-3.9902	3.511779	3.446839
C	-5.83571	3.021932	2.475664
H	-6.37899	2.994472	3.411543
C	-6.48784	2.744278	1.26011
C	-5.74511	2.793445	0.06978
H	-6.20674	2.56462	-0.88095
C	-4.38182	3.079086	0.097159
H	-3.81767	3.041012	-0.81853
C	-2.60445	6.028364	0.399504
C	-3.31366	5.958906	-0.81008
H	-3.187	5.119326	-1.47679

C	-4.18321	6.984835	-1.18565
H	-4.71726	6.899281	-2.12383
C	-4.33712	8.122184	-0.37531
C	-3.58304	8.219602	0.806844
H	-3.67403	9.085896	1.449888
C	-2.71526	7.190585	1.182001
H	-2.13174	7.303791	2.086675
C	-0.31453	4.909277	0.078009
C	0.817502	5.509127	0.651481
H	0.781665	5.899302	1.660466
C	1.99732	5.647654	-0.08699
H	2.854432	6.105511	0.38905
C	2.059277	5.223857	-1.42832
C	0.925317	4.614217	-1.99278
H	0.922186	4.307697	-3.02938
C	-0.24503	4.458014	-1.24784
H	-1.11281	4.019164	-1.72091
O	1.372032	-1.50334	2.196723
O	1.273542	-1.60223	-0.05761
O	1.557793	1.457677	2.332567
O	1.864283	1.323698	0.109261
O	-1.24565	1.663475	2.283244
O	-1.00096	1.925294	0.049381
O	-1.49394	-1.25431	2.074846
O	-1.63618	-0.93681	-0.14728
C	-7.91736	2.338655	1.225558
C	-8.4402	1.472844	2.197679
C	-8.75231	2.758683	0.178992
C	-9.74808	0.989183	2.093621
H	-7.82001	1.121402	3.012755
C	-10.061	2.284084	0.077147
H	-8.39126	3.452855	-0.56952
C	-10.5768	1.357663	1.008366
H	-10.0792	0.301193	2.856798
H	-10.6631	2.633283	-0.75028
C	8.146292	-1.77828	-0.10245
C	8.445667	-1.0951	-1.29374
C	9.194743	-2.02712	0.800274
C	9.736264	-0.63469	-1.55287
H	7.685932	-0.8947	-2.03086
C	10.49094	-1.57338	0.539766
H	9.021249	-2.58379	1.711663
C	10.78874	-0.85795	-0.64218

H	9.904816	-0.09615	-2.47545
H	11.24521	-1.79181	1.280571
C	7.319834	2.136212	-3.04443
C	7.014515	1.448149	-4.2262
C	8.589475	2.70938	-2.89978
C	7.956597	1.343003	-5.25196
H	6.036303	1.005586	-4.36508
C	9.532625	2.609295	-3.92356
H	8.858717	3.225603	-1.98637
C	9.238528	1.927719	-5.12498
H	7.657613	0.805341	-6.13896
H	10.49896	3.068461	-3.76765
C	-7.5071	-1.48976	-3.11128
C	-8.48089	-0.54087	-2.75859
C	-7.7587	-2.33842	-4.19878
C	-9.68144	-0.45177	-3.46551
H	-8.33608	0.109759	-1.90472
C	-8.95747	-2.24912	-4.90972
H	-7.02932	-3.07543	-4.50271
C	-9.95339	-1.31452	-4.55141
H	-10.3874	0.295294	-3.13835
H	-9.10379	-2.92391	-5.74194
C	5.875683	-8.59629	-1.23389
C	5.623863	-9.25475	-2.44639
C	7.067827	-8.87499	-0.54902
C	6.542998	-10.171	-2.96239
H	4.705244	-9.0749	-2.99072
C	7.989894	-9.79056	-1.06297
H	7.298524	-8.36898	0.38032
C	7.747319	-10.4609	-2.28439
H	6.3033	-10.656	-3.89877
H	8.889021	-9.95577	-0.48876
C	-3.22848	-6.41775	-0.57631
C	-3.5871	-6.4762	-1.93443
C	-4.20705	-6.72842	0.38402
C	-4.90532	-6.7371	-2.3172
H	-2.85367	-6.29483	-2.7095
C	-5.52644	-6.98382	0.003118
H	-3.97779	-6.7002	1.441031
C	-5.91528	-6.95274	-1.35274
H	-5.11632	-6.74669	-3.37535
H	-6.2512	-7.17379	0.782993
C	-9.78148	-3.43827	0.9168

C	-10.7096	-4.11578	1.717057
C	-10.1308	-3.10494	-0.39727
C	-11.9764	-4.43507	1.218655
H	-10.4613	-4.38212	2.737056
C	-11.3894	-3.42822	-0.90063
H	-9.42062	-2.60678	-1.04332
C	-12.3457	-4.09362	-0.10445
H	-12.652	-4.94788	1.886333
H	-11.6111	-3.14855	-1.91987
C	-5.27116	9.20723	-0.76946
C	-6.52796	8.903027	-1.31343
C	-4.91498	10.55354	-0.60374
C	-7.41175	9.920504	-1.68289
H	-6.83784	7.87268	-1.4376
C	-5.7953	11.57282	-0.97345
H	-3.94521	10.82158	-0.20342
C	-7.0641	11.28179	-1.52071
H	-8.36452	9.618364	-2.0908
H	-5.47447	12.59559	-0.83039
C	3.27383	5.471685	-2.25657
C	4.038498	6.635329	-2.077
C	3.663984	4.563101	-3.25404
C	5.160314	6.88266	-2.8712
H	3.757099	7.374629	-1.33847
C	4.784017	4.809111	-4.05269
H	3.115114	3.646378	-3.40899
C	5.557717	5.979364	-3.88017
H	5.712207	7.79608	-2.69686
H	5.030946	4.064414	-4.79441
C	10.13046	2.830283	2.547541
C	10.95755	1.765928	2.931969
C	10.72043	4.02364	2.109121
C	12.34747	1.90548	2.912546
H	10.52856	0.83447	3.280484
C	12.11025	4.160348	2.071706
H	10.10318	4.854016	1.78844
C	12.95721	3.1061	2.486154
H	12.94542	1.068418	3.245574
H	12.50041	5.105386	1.725449
C	1.774847	-0.8173	6.901534
C	0.882112	-1.81223	6.475232
C	1.964141	-0.62367	8.276125
C	0.214763	-2.61677	7.401065

H	0.695874	-1.96889	5.419533
C	1.293302	-1.42359	9.204942
H	2.657026	0.127078	8.634361
C	0.408692	-2.44318	8.790482
H	-0.44173	-3.3766	7.005671
H	1.486958	-1.25283	10.25471
C	-2.06627	0.500099	6.836179
C	-1.15127	1.530777	6.574956
C	-2.34418	0.163938	8.167394
C	-0.54689	2.230576	7.62146
H	-0.89801	1.79572	5.555418
C	-1.73917	0.86078	9.216565
H	-3.05515	-0.61921	8.398467
C	-0.8324	1.914743	8.969632
H	0.13395	3.023227	7.351418
H	-2.00111	0.582381	10.22779
C	8.736698	-11.4785	-2.88926
C	9.193673	-10.9877	-4.28024
H	9.659099	-9.98139	-4.201
H	9.940662	-11.6847	-4.71864
H	8.343107	-10.9234	-4.99054
C	8.041684	-12.8501	-3.03213
H	7.667645	-13.1982	-2.04495
H	7.182458	-12.8019	-3.73319
H	8.74923	-13.6117	-3.42609
C	10.00349	-11.6821	-2.02348
H	9.736897	-12.0686	-1.01599
H	10.68768	-12.4218	-2.49351
H	10.56674	-10.7299	-1.91527
C	-7.39952	-7.14742	-1.72773
C	-7.84886	-8.56347	-1.31285
H	-8.90956	-8.73855	-1.59595
H	-7.22094	-9.3308	-1.81526
H	-7.76501	-8.70958	-0.2153
C	-8.26606	-6.10032	-0.991
H	-7.90635	-5.07279	-1.21015
H	-9.3298	-6.17061	-1.30672
H	-8.24322	-6.25118	0.107257
C	-7.66698	-6.98532	-3.2438
H	-7.35617	-5.97653	-3.59364
H	-7.12684	-7.76068	-3.82864
H	-8.74998	-7.09959	-3.46782
C	-13.7296	-4.42242	-0.69924

C	-13.5553	-5.34892	-1.92218
H	-12.9774	-4.85467	-2.73041
H	-13.0195	-6.27791	-1.62967
H	-14.5432	-5.63315	-2.34548
C	-14.4249	-3.11568	-1.1403
H	-15.4424	-3.32472	-1.53619
H	-14.5222	-2.42103	-0.27811
H	-13.8575	-2.5998	-1.94312
C	-14.666	-5.13706	0.304177
H	-14.2337	-6.10896	0.626701
H	-14.8482	-4.50081	1.197263
H	-15.6531	-5.35009	-0.161
C	-11.2744	-1.26216	-5.34671
C	-10.9717	-0.89328	-6.81434
H	-10.3355	-1.66072	-7.30319
H	-11.9115	-0.81302	-7.40267
H	-10.4425	0.082842	-6.86603
C	-11.9676	-2.64194	-5.29878
H	-12.1649	-2.93889	-4.24787
H	-12.9389	-2.61411	-5.83866
H	-11.3485	-3.43054	-5.77438
C	-12.2752	-0.21987	-4.79147
H	-12.5396	-0.44976	-3.73622
H	-11.854	0.80693	-4.85041
H	-13.2177	-0.22521	-5.38113
C	-11.9978	0.790104	0.811498
C	-12.3469	-0.32939	1.821848
H	-13.3571	-0.74643	1.6173
H	-11.6172	-1.16426	1.749809
H	-12.3579	0.06085	2.862157
C	-12.1289	0.190353	-0.60736
H	-13.1038	-0.32658	-0.73352
H	-12.0774	0.97383	-1.39103
H	-11.3157	-0.54133	-0.79271
C	-13.0259	1.926597	0.980145
H	-12.9381	2.380494	1.99096
H	-12.87	2.72656	0.225632
H	-14.0615	1.541267	0.857412
C	-0.22318	2.691942	10.15549
C	-1.35708	3.349479	10.97153
H	-0.94264	3.957861	11.8046
H	-1.96464	4.015803	10.32152
H	-2.03098	2.589096	11.41879

C	0.748284	3.812097	9.711388
H	0.22319	4.569509	9.090086
H	1.170316	4.340496	10.5939
H	1.600982	3.391173	9.135586
C	0.565299	1.725952	11.0654
H	-0.08152	0.920115	11.46973
H	1.398121	1.258975	10.50064
H	1.000786	2.269658	11.93167
C	-0.27619	-3.33649	9.846089
C	0.802418	-4.07932	10.66381
H	0.334878	-4.76883	11.39993
H	1.454046	-4.67736	9.9905
H	1.442632	-3.3719	11.23129
C	-1.21247	-4.40088	9.224518
H	-1.69144	-5.0157	10.01743
H	-2.02567	-3.91929	8.639169
H	-0.64468	-5.09243	8.565126
C	-1.12684	-2.46646	10.79594
H	-0.51085	-1.7097	11.32425
H	-1.92079	-1.93974	10.22765
H	-1.61842	-3.095	11.56987
C	6.793383	6.300131	-4.74643
C	7.094268	5.209624	-5.80162
H	7.988907	5.47984	-6.4031
H	7.302862	4.236006	-5.31289
H	6.242463	5.091865	-6.50563
C	8.038305	6.435577	-3.84296
H	8.950625	6.616133	-4.45197
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H	8.192034	5.507655	-3.25425
C	6.561663	7.627929	-5.49966
H	5.645036	7.562403	-6.12504
H	6.444738	8.480453	-4.79846
H	7.422289	7.859925	-6.16407
C	10.30622	1.847143	-6.23451
C	9.815383	1.096123	-7.49558
H	10.61093	1.067639	-8.27177
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H	8.932576	1.604742	-7.94016
C	11.54699	1.102526	-5.69795
H	12.32717	1.018316	-6.48528
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H	11.2674	0.077006	-5.37434

C	10.70982	3.273516	-6.66816
H	9.819007	3.835502	-7.02176
H	11.17234	3.840942	-5.83402
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C	12.1974	-0.3192	-0.96281
C	12.1429	1.220374	-1.06544
H	11.47112	1.548718	-1.88483
H	11.77122	1.659687	-0.11482
H	13.15092	1.637825	-1.27546
C	12.68522	-0.90631	-2.30525
H	13.71753	-0.56337	-2.53458
H	12.68604	-2.01704	-2.26412
H	12.03888	-0.59021	-3.1481
C	13.24556	-0.68797	0.112542
H	12.96854	-0.25902	1.097488
H	13.34182	-1.79102	0.209078
H	14.24637	-0.28767	-0.15884
C	-8.00741	12.43741	-1.91464
C	-9.35635	11.94888	-2.49549
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H	-9.19687	11.35052	-3.41855
C	-8.31725	13.29653	-0.66939
H	-7.40044	13.77177	-0.26231
H	-9.03048	14.11164	-0.92001
H	-8.76963	12.66978	0.12944
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H	16.10986	4.649256	2.022539
C	15.12006	2.139934	1.61492
H	16.22575	2.2472	1.57485
H	14.90293	1.123049	2.001652
H	14.72558	2.216864	0.57956
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C	-0.52364	2.131272	-4.16011
C	-3.16833	2.10636	-3.25783
H	-2.50876	0.612938	-1.86362
C	-1.44782	3.017645	-4.7068
H	0.497275	2.156479	-4.51783
C	-2.76339	2.989621	-4.25322
H	-4.20128	2.085962	-2.92994
H	-1.14384	3.7118	-5.48228
C	1.459989	0.29055	-2.98081
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C	3.377413	-0.96149	-3.54762
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H	0.208298	-2.18482	-3.48703
H	-1.07578	-2.25692	-2.19484
C	-1.84363	-1.60615	-4.13671
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H	-4.8347	-4.53222	-4.41701
H	-5.38305	-4.15588	-6.05897
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C	-3.42294	-2.34396	-6.73673
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C	-2.25423	4.700375	2.634012
H	-3.23822	5.137447	2.736654
C	-1.78336	3.744243	3.557304
C	-0.46941	3.261786	3.404365
H	-0.06552	2.514103	4.072481
C	0.337895	3.710301	2.358254
H	1.352972	3.344652	2.281769
C	1.596023	6.207145	0.494192
C	1.188443	7.509076	0.160889
H	0.237158	7.680474	-0.32666
C	2.004304	8.604143	0.458811
H	1.679025	9.593357	0.1624
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H	4.533643	6.950859	2.039255
C	2.797737	6.029475	1.193388
H	3.09553	5.046225	1.526105
C	2.436844	4.186675	-1.61137
C	3.64792	3.806151	-1.01757
H	3.665597	3.451289	0.003095
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H	5.75249	3.501902	-1.2685
C	4.827369	4.169536	-3.11006
C	3.614807	4.548264	-3.70883
H	3.575224	4.800719	-4.76074
C	2.427432	4.532322	-2.97444
H	1.499113	4.74808	-3.48671
C	-2.52176	0.654823	-0.80076
C	-3.97754	1.080538	-0.84635
C	-4.97056	0.637236	0.269163
C	-4.93831	-0.08682	-1.08368
H	-4.46675	-1.09156	-1.06726
H	-5.82347	0.096922	-1.72441

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H	-3.15423	3.525753	-0.0875
C	-6.20199	1.478864	0.52001
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H	-5.09766	3.163294	1.295581
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H	-5.6581	-1.90805	1.044198
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C	-3.58741	-1.57618	3.740969
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C	-3.6203	0.453593	2.392576
H	-3.29707	1.47601	2.2488
C	-0.59863	-2.53146	-0.65367
C	-1.02371	-3.98379	-0.60899
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H	-0.06312	-5.85626	-1.41873
H	1.146539	-4.48809	-0.8127
C	-0.58133	-4.92245	0.552807
C	0.208546	-4.35504	1.712009
C	1.498831	-4.82245	1.999757
H	1.958876	-5.57606	1.372704
C	2.204024	-4.32615	3.102164
H	3.191184	-4.72231	3.297505
C	1.634496	-3.34532	3.940683
C	0.322101	-2.9151	3.665169

H	-0.1539	-2.14892	4.26079
C	-0.39338	-3.44848	2.592728
H	-1.41363	-3.12824	2.428669
C	-1.43131	-6.13341	0.868957
C	-2.68372	-5.96918	1.476349
H	-3.05327	-4.98141	1.706552
C	-3.46317	-7.07799	1.810321
H	-4.42476	-6.91722	2.281527
C	-2.99193	-8.37959	1.567954
C	-1.71547	-8.54499	1.001558
H	-1.32258	-9.5346	0.805274
C	-0.93764	-7.43269	0.667994
H	0.050347	-7.58772	0.253195
C	-2.30321	-4.28652	-1.35348
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H	-1.37006	-5.10088	-3.13527
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C	-4.7082	-4.52308	-2.81261
C	-4.70687	-3.97032	-1.52141
H	-5.62531	-3.62213	-1.06613
C	-3.51472	-3.83959	-0.80997
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C	2.559807	-0.62479	-0.56451
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H	5.151133	-1.42298	-3.00338
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C	4.714407	-6.02281	-3.38396
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H	2.741377	-6.71036	-2.81737
C	4.79382	-8.36641	-4.98877
H	6.771057	-7.61939	-5.55095
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C	3.547596	10.78689	1.897377
C	6.312993	10.58	1.595427
H	5.949398	8.580189	0.925325
C	4.365632	11.87806	2.202926
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C	5.770351	11.79858	2.058477
H	7.379814	10.46287	1.46261
H	3.87695	12.77396	2.555035
C	-2.6633	3.22071	4.646762
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C	-4.05421	3.131465	4.468241
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H	-1.06041	2.828865	6.054454
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H	-5.92784	2.485686	5.242268

C	2.756883	2.767139	4.95281
C	2.636858	4.158023	4.788709
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H	2.997985	4.648001	3.896957
C	1.603158	2.973921	7.09271
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C	1.443603	4.366171	6.912774
H	1.918176	6.004008	5.565583
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C	9.586648	-3.63167	2.26456
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C	11.8003	-3.75397	3.269084
H	10.68767	-1.93922	3.04262
C	10.72618	-5.76934	2.474706
H	8.788276	-5.5297	1.598284
C	11.84323	-5.15528	3.082182
H	12.61349	-3.21344	3.729484
H	10.70511	-6.8369	2.303387
C	2.408395	-2.74831	5.073131
C	1.753093	-2.23616	6.206937
C	3.807708	-2.63294	5.009675
C	2.464707	-1.59099	7.220634
H	0.683685	-2.3337	6.32213
C	4.521566	-1.989	6.021171
H	4.359391	-2.99922	4.157683
C	3.866341	-1.4337	7.139513
H	1.894189	-1.21267	8.055471
H	5.594941	-1.91387	5.913133
C	-3.82474	-9.55841	1.916746
C	-3.24727	-10.6951	2.501601
C	-5.20504	-9.5541	1.668171
C	-4.03067	-11.8043	2.83215
H	-2.18741	-10.7212	2.722425
C	-5.9904	-10.6613	1.995836
H	-5.67795	-8.69833	1.202506
C	-5.42337	-11.8122	2.585526
H	-3.5253	-12.6447	3.28363
H	-7.04919	-10.6125	1.781254
C	-3.05982	-2.34894	4.907501
C	-2.63453	-1.69418	6.076753
C	-2.92988	-3.74706	4.847311

C	-2.06251	-2.40588	7.133502
H	-2.74616	-0.62555	6.186929
C	-2.36022	-4.4611	5.902277
H	-3.22937	-4.2975	3.968577
C	-1.8946	-3.80693	7.061451
H	-1.75025	-1.83613	7.995724
H	-2.2735	-5.53393	5.797816
C	-9.69361	3.854894	1.363596
C	-9.70823	5.220903	1.046068
C	-10.8347	3.28475	1.947138
C	-10.8385	5.999285	1.304618
H	-8.84925	5.686905	0.57932
C	-11.9669	4.061233	2.208555
H	-10.847	2.236839	2.22006
C	-11.9943	5.439358	1.891558
H	-10.8037	7.046782	1.038133
H	-12.8096	3.562237	2.662698
C	-6.32652	-13.014	2.93281
C	-6.99991	-13.5405	1.646749
H	-6.23052	-13.8259	0.896951
H	-7.62317	-14.4347	1.865554
H	-7.66422	-12.7769	1.191114
C	-5.55141	-14.1909	3.572771
H	-5.07181	-13.8781	4.52546
H	-6.23746	-15.0341	3.806698
H	-4.77393	-14.5774	2.878721
C	-7.41348	-12.5686	3.935253
H	-6.94504	-12.1466	4.85073
H	-8.08114	-11.7971	3.498107
H	-8.05113	-13.4289	4.233775
C	-9.61279	-4.63524	-6.03311
C	-9.77421	-5.90225	-6.90711
H	-8.92845	-6.00114	-7.62156
H	-9.83081	-6.81483	-6.27505
H	-10.7105	-5.85234	-7.5046
C	-9.58841	-3.41375	-6.9779
H	-10.4843	-3.40611	-7.63601
H	-9.5845	-2.45889	-6.41181
H	-8.68215	-3.44094	-7.62107
C	-10.8455	-4.54374	-5.10761
H	-10.8545	-5.39353	-4.39112
H	-10.8513	-3.59793	-4.52665
H	-11.7861	-4.57556	-5.69935

C	-1.24066	-4.62965	8.1904
C	-2.2766	-5.61873	8.764672
H	-2.61779	-6.34187	7.994258
H	-1.84068	-6.20299	9.603981
H	-3.1653	-5.06991	9.145022
C	-0.03554	-5.41967	7.630979
H	0.699546	-4.73085	7.164876
H	0.479366	-5.97953	8.441586
H	-0.34834	-6.16173	6.867563
C	-0.72289	-3.75307	9.356198
H	0.034452	-3.02368	8.995347
H	-1.5583	-3.20552	9.843598
H	-0.23942	-4.38018	10.13658
C	-5.24964	1.352648	7.663282
C	-6.28226	2.379325	8.174771
H	-6.93185	2.74695	7.352847
H	-6.94227	1.924276	8.944939
H	-5.76619	3.253118	8.628389
C	-5.99005	0.171525	6.99566
H	-5.26406	-0.55322	6.570916
H	-6.62467	-0.3644	7.734348
H	-6.65624	0.514343	6.176968
C	-4.48849	0.794401	8.889909
H	-3.73792	0.036185	8.578495
H	-3.9781	1.610384	9.445766
H	-5.18942	0.300107	9.597267
C	4.688258	-0.69444	8.215035
C	5.475134	0.465759	7.563864
H	6.033224	1.043799	8.332011
H	6.218071	0.096256	6.827035
H	4.784376	1.160174	7.041383
C	3.811449	-0.09103	9.338781
H	4.438437	0.449621	10.08079
H	3.081962	0.637225	8.922764
H	3.263933	-0.88785	9.887062
C	5.679872	-1.68133	8.86632
H	5.133177	-2.53983	9.313233
H	6.404211	-2.0783	8.12434
H	6.262977	-1.18134	9.669964
C	0.708123	5.261589	7.930836
C	-0.45039	6.007501	7.230164
H	-1.0234	6.619865	7.959783
H	-0.08022	6.696539	6.443107

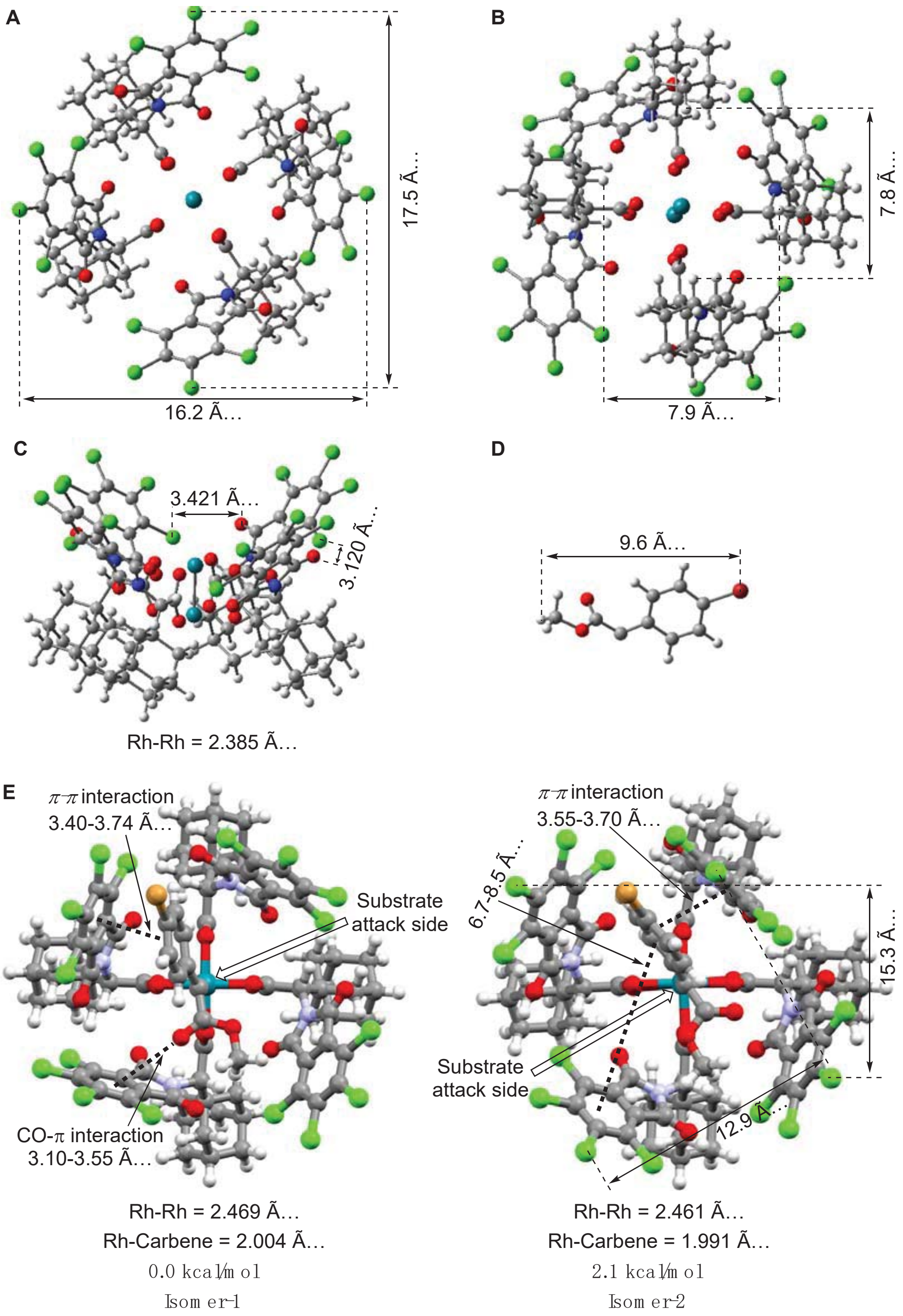
H	-1.1499	5.285896	6.759009
C	0.102536	4.464499	9.111325
H	0.897935	3.954541	9.696607
H	-0.43759	5.141496	9.808436
H	-0.62652	3.709391	8.744819
C	1.699531	6.291054	8.512508
H	2.556127	5.772533	8.995217
H	2.09889	6.961093	7.722294
H	1.202599	6.929668	9.274793
C	13.04721	-6.01888	3.512315
C	14.18416	-5.1944	4.162858
H	15.03011	-5.85309	4.457315
H	14.58268	-4.43889	3.451607
H	13.82602	-4.68192	5.081886
C	12.58375	-7.07196	4.542368
H	12.11818	-6.57443	5.420607
H	11.84218	-7.77266	4.105099
H	13.44363	-7.67916	4.899901
C	13.63515	-6.73437	2.276598
H	12.90185	-7.43204	1.82093
H	13.93499	-5.99116	1.506319
H	14.53155	-7.33006	2.555066
C	4.791594	-9.64315	-5.85468
C	3.615482	-9.58721	-6.85387
H	3.608609	-10.4884	-7.50468
H	2.636518	-9.54633	-6.33247
H	3.702595	-8.69038	-7.5039
C	4.633141	-10.8812	-4.94551
H	4.674978	-11.8177	-5.54319
H	5.447831	-10.9124	-4.18994
H	3.660872	-10.8731	-4.41003
C	6.093079	-9.824	-6.67239
H	6.241351	-8.97464	-7.37399
H	6.974938	-9.90482	-6.00062
H	6.050705	-10.754	-7.28023
C	9.650606	3.685606	-6.40612
C	9.883169	4.870375	-7.37443
H	10.80021	4.708813	-7.98199
H	9.031248	4.978319	-8.08022
H	10.01878	5.820051	-6.81299
C	10.89393	3.571625	-5.49743
H	10.84459	2.672823	-4.84795
H	11.82095	3.491135	-6.10574

H	10.97992	4.468434	-4.84634
C	9.517542	2.403934	-7.25729
H	8.601386	2.45076	-7.8852
H	10.39563	2.282993	-7.92825
H	9.458089	1.495678	-6.62192
C	-5.03459	10.00236	-5.68726
C	-3.97399	10.06217	-6.80808
H	-4.05384	11.01435	-7.37629
H	-2.9436	10.00542	-6.3992
H	-4.11458	9.218661	-7.51825
C	-4.78315	11.14704	-4.68172
H	-4.89126	12.13699	-5.17592
H	-5.51242	11.09289	-3.84458
H	-3.75926	11.09923	-4.2557
C	-6.41857	10.24351	-6.33697
H	-6.6396	9.46509	-7.09903
H	-7.22196	10.2453	-5.56882
H	-6.44674	11.22931	-6.8504
C	6.711705	12.97665	2.384764
C	5.959665	14.2354	2.880333
H	6.672992	15.05862	3.103277
H	5.2548	14.60664	2.105192
H	5.398422	14.01928	3.815107
C	7.501292	13.37111	1.117637
H	8.155869	14.24717	1.317534
H	8.152945	12.54338	0.767899
H	6.803058	13.63719	0.294686
C	7.699768	12.55423	3.493832
H	7.145965	12.22615	4.400069
H	8.352741	11.71967	3.163277
H	8.361462	13.40172	3.776393
C	0.079513	-0.0563	-4.27424
C	1.114889	0.737552	-4.96927
C	0.802516	1.592147	-6.04694
C	2.466435	0.639693	-4.576
C	1.795417	2.30609	-6.71338
H	-0.22752	1.717073	-6.35666
C	3.470271	1.335347	-5.24758
H	2.731035	0.034924	-3.71773
C	3.121543	2.154315	-6.31707
H	1.536483	2.960772	-7.53794
H	4.503774	1.246759	-4.93137
C	-1.34879	0.183832	-4.57156

O	-1.83008	1.283737	-4.73527
O	-2.10104	-0.96962	-4.55717
C	-3.50637	-0.79935	-4.56199
H	-3.75185	0.251061	-4.41272
H	-3.9221	-1.41392	-3.76039
C	-4.12699	-1.25209	-5.8832
Cl	-3.48931	-0.28434	-7.29261
Cl	-5.93465	-0.99891	-5.75051
Cl	-3.7956	-3.02384	-6.20133
Br	4.533228	3.110727	-7.29739
H	0.340915	-1.18685	-4.05954
C	0.315342	-2.12355	-5.12523
H	-0.12465	-1.75172	-6.0451
C	1.735261	-2.59405	-5.2221
H	2.379277	-1.77565	-5.56023
H	2.098732	-2.92771	-4.24263
C	1.808269	-3.76553	-6.23652
H	1.135459	-4.56616	-5.90183
C	3.225682	-4.34843	-6.412
H	-0.37831	-2.74271	-4.55779
H	1.430776	-3.42605	-7.21153
C	3.172929	-5.64879	-7.22712
H	2.789944	-5.46752	-8.23953
H	4.173029	-6.08701	-7.32363
H	2.525147	-6.39385	-6.75044
H	3.592416	-4.60293	-5.41164
C	4.206554	-3.34801	-7.04008
H	3.875004	-3.05076	-8.04353
H	4.316223	-2.4376	-6.4407
H	5.202494	-3.79487	-7.13843
C	-13.2221	6.334136	2.160397
C	-13.7255	6.931484	0.828276
H	-14.6371	7.546555	0.99124
H	-12.9622	7.587589	0.360252
H	-13.9752	6.11989	0.110967
C	-12.8255	7.478706	3.118147
H	-13.7057	8.112919	3.360801
H	-12.4204	7.065323	4.067158
H	-12.0548	8.139128	2.668642
C	-14.4016	5.568263	2.806945
H	-14.7537	4.749295	2.143014
H	-14.1064	5.143439	3.790752
H	-15.2637	6.24786	2.983116

7.3 Rh_2(S-TCPTAD)$_4$

Computational Procedure. Geometry of the Rh_2(*S*-TCPTAD)$_4$, and their carbenes, [(*p*-Br-C_6H_4)C(COOMe)], complexes were optimized in the gas phase with no geometry constraints. Vibrational analyses were performed to ensure that all reported structures are true minima. In these calculations we used the Density Functional Theory with M06L-functional in conjunction with the 6-31G(d) basis sets for all atoms, except Rh: For Rh we used the lanl2dz basis set with the associated Hay-Wadt ECPs. Previously, we have shown that this approach describes both geometries and relative energies of the transition metal systems with reasonable accuracy. All calculations were carried out with the Gaussian 09 software package.[18-19]



Triplet Carbene: CCOOMe_PhBr

C	0.09888200	1.59108200	0.48702400
C	-1.19936900	1.11870200	0.25213300
C	-2.29189900	1.70156200	0.94602600
C	-1.47617100	0.06568200	-0.66399700
C	-3.58585900	1.26158200	0.74345100
H	-2.09693800	2.50878400	1.64957200
C	-2.77210200	-0.37149600	-0.86425100
H	-0.64815200	-0.38867000	-1.20114600
C	-3.82315300	0.22366400	-0.16140200
H	-4.41566900	1.71479500	1.27919500
H	-2.97837400	-1.17571600	-1.56598600
Br	-5.58917700	-0.38613200	-0.43193800
C	1.38810300	1.23879100	-0.03553700
O	1.58247300	0.36261300	-0.86955900
O	2.37263700	1.99203000	0.50272800
C	3.67899900	1.67808100	0.01910700
H	3.73035000	1.80478500	-1.06682100
H	4.35239800	2.37384000	0.52056500
H	3.94297500	0.64370800	0.26246000

Rh_2(*S*-TCPTAD)$_4$

Rh	0.06610900	0.31393900	-1.87950400
O	-2.00557500	0.31054000	-1.93610000
O	2.12384900	0.31139600	-1.71101900
O	-2.12498200	0.20319800	0.32587200
O	2.01489300	0.02460400	0.53587700
O	0.09178300	2.36133600	-1.64949700
O	0.02944400	-1.74718600	-2.00870200
O	-0.11778800	-1.95914600	0.24301300
O	-0.01359000	2.18256000	0.60785500
C	-0.10541600	-2.41456500	-0.94346000
C	0.09578600	2.83497600	-0.47667700
C	-2.62970700	0.29434400	-0.83656700
C	2.63519600	0.13721400	-0.56644700
Rh	-0.06461500	0.10326000	0.49244900
C	0.21350500	4.35193000	-0.30570200
C	0.42735200	5.20811800	-1.57356600
N	1.21455800	4.59256400	0.73416800
C	-0.79459200	5.06423200	-2.50328100
C	0.51823300	6.69290700	-1.16195000
C	1.71503700	4.84494100	-2.33091900
C	2.39740500	3.86380900	0.87478000
C	0.98571200	5.45468500	1.81398400
H	-0.92817500	4.01936400	-2.80292000
H	-1.70462300	5.35011700	-1.95112800
C	-0.62474800	5.94733100	-3.74232100
C	0.68081300	7.58865400	-2.39349500
H	-0.38154800	6.97778500	-0.59430200
H	1.37472000	6.84462300	-0.48685000
C	1.86492100	5.73123400	-3.57147900
H	2.58556500	4.98317800	-1.67071900

H	1.70040200	3.78651400	-2.61669400
O	2.79420600	3.01737500	0.09791600
C	3.01822900	4.34843300	2.13675300
O	-0.00432800	6.13757100	1.96477000
C	2.18248200	5.32177700	2.68552100
C	-0.52547200	7.41325300	-3.31779700
C	0.65131000	5.54053800	-4.48562600
H	-1.49526600	5.80920800	-4.39967800
H	0.74848100	8.63577800	-2.06465200
C	1.95630400	7.19771000	-3.14330500
H	2.78107900	5.44306900	-4.10777200
C	4.20089200	3.97896300	2.75727500
C	2.50297100	5.97656700	3.86215400
H	-0.42168600	8.06190400	-4.20088100
H	-1.44731600	7.72062000	-2.80075900
H	0.58260000	4.49011500	-4.80672400
H	0.76603600	6.14711600	-5.39684600
H	2.08894600	7.84512400	-4.02333300
H	2.83670400	7.34941600	-2.49992200
Cl	5.19999600	2.73675700	2.12042800
C	4.54803800	4.63559100	3.95859000
C	3.71030600	5.62740900	4.50331200
Cl	1.47232100	7.18034300	4.51970500
Cl	6.00596400	4.21660800	4.76097400
Cl	4.15606500	6.41623200	5.96154500
C	-4.15763700	0.36122900	-0.85176500
C	-4.87427300	0.33514400	-2.21771900
N	-4.55896600	1.47796700	0.00668100
C	-4.51709100	-0.97853800	-2.94063100
C	-6.39714000	0.32627900	-1.97139200
C	-4.54444800	1.53816300	-3.11684700

C	-3.90204900	2.71046900	0.07975900
C	-5.54376200	1.34067200	0.99324300
H	-3.43726700	-1.03665100	-3.11538500
H	-4.77628600	-1.82925400	-2.29101900
C	-5.26846300	-1.07899200	-4.26890600
C	-7.16249100	0.21743200	-3.29294500
H	-6.66011200	-0.50901900	-1.30387400
H	-6.69861600	1.24912900	-1.45145800
C	-5.30171900	1.41981700	-4.44491400
H	-4.83339200	2.47138900	-2.60750800
H	-3.46375000	1.59546800	-3.29428400
O	-2.94873600	3.04129600	-0.59718400
C	-4.60552700	3.47337200	1.14785000
O	-6.19246600	0.33749000	1.20085100
C	-5.59274000	2.65112100	1.69185000
C	-6.77516700	-1.07968100	-4.00633700
C	-4.90216300	0.11967300	-5.14964800
H	-4.97594100	-2.01260500	-4.77260000
H	-8.24137600	0.21718800	-3.08029900
C	-6.80919200	1.41270000	-4.18109400
H	-5.04156900	2.27845400	-5.08069700
C	-4.40885300	4.76473400	1.60990900
C	-6.42026400	3.08439000	2.71438200
H	-7.32908300	-1.16876700	-4.95329100
H	-7.05113900	-1.94823300	-3.38951400
H	-3.82103100	0.11937700	-5.35579200
H	-5.41330200	0.04589000	-6.12165100
H	-7.36157900	1.35499800	-5.13135000
H	-7.11274500	2.35150800	-3.69258400
Cl	-3.18224500	5.77579900	0.96356000
C	-5.24651700	5.23058700	2.64755300

C	-6.24225400	4.39917500	3.19396100
Cl	-7.62679700	2.06134400	3.37814800
Cl	-7.24859700	4.98736800	4.45375900
C	-0.23770800	-3.93601700	-1.05435500
C	-0.28760000	-4.55329500	-2.46991900
N	-1.34395000	-4.34516300	-0.18987400
C	1.05235300	-4.27277600	-3.17989900
C	-0.42780200	-6.08553400	-2.34109100
C	-1.45864000	-4.04182400	-3.32744800
C	-2.53457800	-3.63271400	-0.03467800
C	-1.21919800	-5.38702500	0.73839700
H	1.21677000	-3.19493700	-3.27635000
H	1.87760600	-4.66175400	-2.56213900
C	1.07164700	-4.92581400	-4.56210200
C	-0.40282900	-6.75097000	-3.71966100
H	0.38107600	-6.48173600	-1.70754600
H	-1.37329000	-6.33493000	-1.83411900
C	-1.41820100	-4.69571200	-4.71271900
H	-2.41370500	-4.28045300	-2.83260900
H	-1.41449500	-2.95032900	-3.41907700
O	-2.85281100	-2.65267900	-0.67906900
C	-3.27560400	-4.32525900	1.05442800
O	-0.24348100	-6.09500200	0.86470500
C	-2.49729500	-5.39542300	1.49758500
C	0.92333800	-6.44089600	-4.41562400
C	-0.08675400	-4.37156500	-5.39695500
H	2.02692200	-4.69173600	-5.05393300
H	-0.51089600	-7.83771500	-3.59144000
C	-1.55859700	-6.21297700	-4.56686800
H	-2.24990900	-4.30229000	-5.31578400
C	-4.50983600	-4.04736400	1.61972600

C	-2.92924200	-6.24091400	2.50566600
H	0.95505900	-6.92751800	-5.40234300
H	1.76293200	-6.84729800	-3.83102900
H	0.02163700	-3.28277600	-5.51508700
H	-0.06745600	-4.80685700	-6.40774800
H	-1.55581200	-6.69353700	-5.55709500
H	-2.52246400	-6.46000000	-4.09561900
Cl	-5.43645500	-2.68884800	1.13144800
C	-4.97184300	-4.90022200	2.64659800
C	-4.19260000	-5.98940400	3.08113500
Cl	-1.96262800	-7.55326900	3.04160800
Cl	-6.49580200	-4.59791000	3.37437500
Cl	-4.77766900	-7.01214300	4.32900500
C	4.15959800	0.06929400	-0.44383200
C	5.00394900	0.30744800	-1.71373800
N	4.48625700	-1.17969800	0.24756900
C	4.71806900	1.72396700	-2.25328100
C	6.49786700	0.25835000	-1.32945900
C	4.76300300	-0.73621400	-2.81789100
C	3.84243600	-2.40081000	0.02983000
C	5.37894200	-1.23193700	1.32543300
H	3.66028400	1.82577500	-2.51820100
H	4.91490400	2.45984800	-1.45761200
C	5.59097700	2.01691300	-3.47444600
C	7.38330600	0.55718300	-2.54171300
H	6.69693100	0.97855800	-0.52086000
H	6.75122500	-0.73725700	-0.93304500
C	5.63750700	-0.42280200	-4.03582500
H	5.01116600	-1.73968400	-2.43735500
H	3.70355300	-0.75711900	-3.09881400
O	2.96308400	-2.59510400	-0.78570700

C	4.45432100	-3.35195100	0.99719500
O	5.99634300	-0.28815100	1.77087300
C	5.38114300	-2.65152900	1.77008800
C	7.06689500	1.95463100	-3.07836000
C	5.30613300	0.97711400	-4.56244400
H	5.34791100	3.02218600	-3.84983800
H	8.43749500	0.50711500	-2.23305300
C	7.11360500	-0.47914700	-3.63523200
H	5.43871000	-1.16847700	-4.81919800
C	4.23228100	-4.70642100	1.18534900
C	6.12226400	-3.27761600	2.75851400
H	7.70685800	2.18132400	-3.94462200
H	7.28445500	2.71370400	-2.31174000
H	4.24862800	1.02615700	-4.86339600
H	5.90496400	1.19411300	-5.46008700
H	7.75328100	-0.28145400	-4.50885300
H	7.36910600	-1.48769300	-3.27510000
Cl	3.08124100	-5.57057800	0.25102700
C	4.98074400	-5.36591300	2.18466000
C	5.91777600	-4.65894700	2.96222500
Cl	7.26143800	-2.40822800	3.70257800
Cl	4.74660800	-7.04453800	2.44974300
Cl	6.81960100	-5.48369000	4.16709300
H	4.42091400	0.85785800	0.27808200
H	0.65755800	-4.34134200	-0.55607600
H	-4.48065400	-0.53486500	-0.30027400
H	-0.73949600	4.66583700	0.14939500
Cl	-5.04558100	6.82649100	3.24476200

{Rh$_2$(*S*-TCPTAD)$_4$}-Carbene: Isomer-1

E$_{tot}$ = -15160.3365089 a. u.

Rh	0.21143400	0.29777500	-2.00790200
O	-1.88258100	0.30667300	-2.08571400
O	2.29015900	0.29034500	-1.81030400
O	-2.03511500	0.11470000	0.17389900
O	2.09592000	-0.00360500	0.42933300
O	0.23931800	2.37356800	-1.76836600
O	0.20022900	-1.78238300	-2.08582000
O	0.00548700	-2.00923800	0.16508600
O	0.00723200	2.12461300	0.47809700
C	0.04647700	-2.44942800	-1.02909000
C	0.16310000	2.80397300	-0.58989700
C	-2.51298700	0.26409100	-1.00029500
C	2.75233100	0.10150700	-0.65764500
Rh	0.01424700	0.05699500	0.44097700
C	0.20986200	4.30140700	-0.28651900
C	0.55779500	5.29779200	-1.40588800
C	-0.51806800	5.21965200	-2.50894800
C	0.51544800	6.71685300	-0.80088100
C	1.94700600	5.08352900	-2.02825000
C	2.26824400	3.83073300	1.09076900
C	0.46087000	4.81779400	2.15021300
H	-0.52791400	4.21722000	-2.95225600
H	-1.51224400	5.37132500	-2.06042100
C	-0.25222300	6.27226900	-3.58628800
C	0.77423900	7.77226400	-1.87630100
H	-0.46165300	6.88535400	-0.31980000
H	1.27479600	6.80498000	-0.00862600
C	2.20094100	6.13312600	-3.11480400

H	2.72132000	5.16923600	-1.25271900
H	2.02677700	4.06722100	-2.43784500
O	2.85773700	3.18500200	0.24599200
C	2.64517700	4.08188600	2.50772500
O	-0.67567100	5.20680600	2.30905600
C	1.53645100	4.62148900	3.15810600
C	-0.29777700	7.66916500	-2.96362900
C	1.12851000	6.02781000	-4.20230800
H	-1.02465800	6.18768100	-4.36412200
H	0.74170800	8.77005400	-1.41467800
C	2.15478800	7.53247400	-2.49404900
H	3.19318500	5.95797300	-3.55524700
C	3.83664800	3.85547200	3.17393600
C	1.55995400	4.90628800	4.51316400
H	-0.13216500	8.43804400	-3.73350800
H	-1.29362800	7.85743900	-2.53214900
H	1.16106800	5.03237900	-4.66993000
H	1.32373100	6.76291400	-4.99803700
H	2.36314500	8.29512400	-3.25972900
H	2.93535200	7.63149600	-1.72403700
Cl	5.18844800	3.17404500	2.37003500
C	3.90150800	4.19060700	4.54366800
C	2.76739100	4.69128100	5.21252600
Cl	0.16603300	5.50619900	5.31656000
Cl	5.37888100	3.98046500	5.39213500
Cl	2.85366600	5.06088600	6.88588700
C	-4.03736800	0.40308800	-0.95461400
C	-4.83991000	0.39725800	-2.26441300
N	-4.32031600	1.53588800	-0.06524500
C	-4.51840600	-0.90185000	-3.02791800
C	-6.33820100	0.37549300	-1.89732900

C	-4.59044000	1.60705000	-3.17937900
C	-3.65832700	2.76633900	-0.14030300
C	-4.90685400	1.34259400	1.19782800
H	-3.45448900	-0.92931000	-3.29113900
H	-4.69966500	-1.76522900	-2.37061100
C	-5.37621300	-1.00765600	-4.28879600
C	-7.20196000	0.26275100	-3.15512900
H	-6.54181600	-0.46807500	-1.21716500
H	-6.59865300	1.29081200	-1.34290200
C	-5.44587800	1.48778900	-4.44644200
H	-4.85067800	2.53470500	-2.64801100
H	-3.52459900	1.67883100	-3.43070100
O	-2.87999300	3.09553700	-1.01442500
C	-4.04056400	3.50533500	1.08903800
O	-5.45299500	0.32124300	1.55699800
C	-4.71722300	2.62246900	1.92933800
C	-6.85559500	-1.02859700	-3.89946300
C	-5.09624100	0.19707300	-5.19151100
H	-5.11890400	-1.93617000	-4.81928100
H	-8.26206900	0.25126800	-2.86272700
C	-6.92861500	1.46454000	-4.06433700
H	-5.24503200	2.35385600	-5.09333300
C	-3.77830800	4.81147300	1.46779500
C	-5.07621600	2.98816700	3.21524500
H	-7.48732600	-1.12824300	-4.79519400
H	-7.06508200	-1.90122800	-3.26066900
H	-4.03689300	0.20683800	-5.48829600
H	-5.68835700	0.12527900	-6.11673700
H	-7.55310100	1.40297500	-4.96854000
H	-7.20251000	2.39822800	-3.54952300
Cl	-3.13651600	5.95025300	0.35164500

C	-4.11072600	5.19758900	2.78149800
C	-4.73832400	4.28580400	3.65247200
Cl	-5.88510900	1.88870900	4.25762200
Cl	-5.11681400	4.76296600	5.25814900
C	-0.07952700	-3.97505200	-1.12499800
C	-0.02067200	-4.61177000	-2.52920200
N	-1.26286600	-4.36862700	-0.35559700
C	1.35511800	-4.31735100	-3.16226800
C	-0.13955200	-6.14433400	-2.38664000
C	-1.14847800	-4.13306800	-3.45911300
C	-2.47144600	-3.67001700	-0.34797600
C	-1.24093300	-5.40325300	0.58627800
H	1.51068900	-3.23752400	-3.25696500
H	2.14697500	-4.69081200	-2.49208700
C	1.46277600	-4.98604200	-4.53417600
C	-0.02594700	-6.82735000	-3.75158600
H	0.64076200	-6.51602300	-1.70376500
H	-1.10694200	-6.40626300	-1.93001300
C	-1.01808900	-4.80323900	-4.82928400
H	-2.12429400	-4.39016900	-3.01719800
H	-1.12374500	-3.04197600	-3.55851600
O	-2.70920100	-2.66929800	-0.99366500
C	-3.34857800	-4.39636400	0.61048900
O	-0.29362200	-6.12306900	0.81829900
C	-2.59882000	-5.41726600	1.19422200
C	1.33138300	-6.50213500	-4.37813900
C	0.34431600	-4.46346000	-5.44160100
H	2.44052300	-4.74075300	-4.97353900
H	-0.12208100	-7.91423100	-3.61469000
C	-1.14121000	-6.32036100	-4.66933300
H	-1.81970500	-4.43412400	-5.48537800

C	-4.67548100	-4.19007200	0.95067400
C	-3.13779700	-6.25463500	2.15694400
H	1.42417400	-6.99754000	-5.35665700
H	2.14435700	-6.88874700	-3.74494200
H	0.43988400	-3.37467800	-5.56901100
H	0.42997800	-4.91195900	-6.44313900
H	-1.07567300	-6.81442400	-5.65071300
H	-2.12571300	-6.57685600	-4.24824300
Cl	-5.60773200	-2.94499700	0.22022700
C	-5.24710000	-5.03255400	1.92770100
C	-4.48409400	-6.05173300	2.52900100
Cl	-2.20382900	-7.49730300	2.88248200
Cl	-6.88254200	-4.80422600	2.39341400
Cl	-5.19427500	-7.06161000	3.72113700
C	4.26301000	0.00607500	-0.42406500
C	5.20608000	0.00047900	-1.63604200
N	4.46885100	-1.11038600	0.50579300
C	5.08154200	1.34654600	-2.37991400
C	6.65343900	-0.11160200	-1.11681500
C	4.94928600	-1.15917800	-2.61189500
C	3.76281400	-2.31854700	0.42905900
C	5.03547000	-0.91500200	1.76937700
H	4.05814100	1.48182900	-2.74896500
H	5.27707600	2.17061900	-1.67335100
C	6.07333100	1.40046900	-3.54419500
C	7.65057800	-0.05772700	-2.27502900
H	6.85324800	0.70049600	-0.39886600
H	6.77896100	-1.05679500	-0.56652500
C	5.93991000	-1.08927100	-3.77858200
H	5.06326200	-2.11935300	-2.08635600
H	3.91446900	-1.12240500	-2.97631500

O	3.07836300	-2.66593600	-0.51181300
C	4.01651000	-3.01256700	1.72087800
O	5.59312900	0.09901900	2.13684000
C	4.77741300	-2.16522700	2.52724900
C	7.50237400	1.27494900	-3.01302200
C	5.78235700	0.24741900	-4.50943000
H	5.95517200	2.35999100	-4.06799600
H	8.67037100	-0.14968600	-1.87377900
C	7.36911300	-1.21021800	-3.24302500
H	5.73328000	-1.91645800	-4.47297400
C	3.60534900	-4.25678500	2.16984700
C	5.14459600	-2.52090500	3.81433100
H	8.22420300	1.33164400	-3.84204400
H	7.72856100	2.11098800	-2.33385900
H	4.76209500	0.34014300	-4.91113200
H	6.46920700	0.29159500	-5.36854300
H	8.09065400	-1.18919400	-4.07391000
H	7.49996600	-2.17572600	-2.73074400
Cl	2.63628000	-5.28503300	1.20183400
C	3.98717300	-4.64897000	3.47201000
C	4.74699600	-3.78894600	4.28714000
Cl	6.04420300	-1.45032700	4.81252700
Cl	3.51110900	-6.18656700	4.06491200
Cl	5.19317600	-4.27848100	5.86990100
H	4.51127000	0.89754500	0.17483000
H	0.76660100	-4.37541400	-0.54647700
H	-4.37197800	-0.47287200	-0.37802900
H	-0.80984400	4.54357700	0.05228900
Cl	-3.75025300	6.78679600	3.31422000
C	-0.25624200	0.06220400	2.42619100
C	-1.67485600	-0.16354200	2.76715900

C	0.60830500	0.47388100	3.48871300
C	2.00914200	0.62283200	3.30527200
C	0.09830900	0.67735000	4.80160500
C	2.85461000	0.86977000	4.37267200
H	2.42584200	0.52155300	2.30674000
C	0.93251300	0.95818900	5.86470800
H	-0.97448700	0.62189200	4.97144000
C	2.31336300	1.02264800	5.65258000
H	3.93149400	0.93644600	4.21491900
H	0.53003000	1.10902400	6.86288800
Br	3.44867300	1.31665900	7.12150200
O	-2.43823700	0.76478600	2.97686200
O	-2.01342200	-1.45764900	2.77188600
C	-3.40363100	-1.71574700	3.02547300
H	-3.99550300	-1.47853100	2.13570400
H	-3.46204600	-2.77870800	3.26692600
H	-3.76756600	-1.10713600	3.85823100
N	1.02844200	4.45387600	0.91910600

{Rh$_2$(*S*-TCPTAD)$_4$}-Carbene: Isomer-2

E_{tot} = -15160.3331428 a. u.

Rh	0.21297200	0.14964000	-2.08776600
O	-1.86082800	0.07241500	-2.27686900
O	2.25502800	0.23796500	-1.75551700
O	-2.09173900	-0.03503100	-0.02247400
O	2.03585900	-0.10592900	0.47729600
O	0.11306500	2.19298700	-1.77615100
O	0.23245400	-1.92635100	-2.27051500
O	-0.05078600	-2.16208300	-0.03379700
O	-0.09557000	1.99114200	0.47372900
C	-0.02469000	-2.59127500	-1.23601000
C	0.04522000	2.65158300	-0.60722900
C	-2.53292100	0.07027800	-1.21059300
C	2.70643100	0.06525800	-0.59356500
Rh	-0.05910900	-0.09890600	0.34581300
C	0.10358200	4.17178600	-0.40665400
C	0.35201100	5.04145000	-1.65823800
N	1.03399700	4.43698000	0.69366800
C	-0.83738500	4.87530500	-2.62657100
C	0.39745800	6.52577500	-1.23961700
C	1.67380600	4.70953300	-2.37072300
C	2.22770000	3.74254800	0.90540700
C	0.72445700	5.29830200	1.75060900
H	-0.94244300	3.82812300	-2.93001700
H	-1.76864100	5.14432200	-2.10096800
C	-0.64537600	5.76455400	-3.85706700
C	0.58343300	7.42828300	-2.46372300
H	-0.52736200	6.78998900	-0.70329100
H	1.22706900	6.69192200	-0.53459200

C	1.84280700	5.59941900	-3.60623400
H	2.51643400	4.87060900	-1.67984000
H	1.69700800	3.65209500	-2.65652800
O	2.70550200	2.92676300	0.14265300
C	2.74453200	4.22506900	2.21596800
O	-0.27997900	5.97339600	1.83522600
C	1.85471800	5.17939100	2.70924100
C	-0.58866000	7.23118300	-3.42705200
C	0.66239800	5.38386000	-4.55817900
H	-1.49065600	5.61089800	-4.54349700
H	0.61875100	8.47553500	-2.13014400
C	1.88988300	7.06644900	-3.17409400
H	2.78120500	5.33047900	-4.11354400
C	3.88145500	3.86588100	2.92121000
C	2.07217800	5.82027400	3.91732300
H	-0.46815600	7.88332800	-4.30543600
H	-1.53268200	7.51987700	-2.94032900
H	0.62518600	4.33227600	-4.88011300
H	0.79437200	5.99250700	-5.46569500
H	2.03523100	7.71894300	-4.04842400
H	2.74672600	7.23578700	-2.50376500
Cl	4.93684700	2.64195500	2.35170300
C	4.12703100	4.51380400	4.15208300
C	3.23403600	5.48405800	4.64417300
Cl	0.96393200	6.98590300	4.51928900
Cl	5.52819600	4.10756800	5.05436000
Cl	3.55281200	6.26124700	6.14100000
C	-4.06006700	0.16399300	-1.27267200
C	-4.72379500	0.38612900	-2.64639100
N	-4.48038900	1.12460100	-0.25031900
C	-4.42606100	-0.82187000	-3.55709800

C	-6.25047500	0.44787200	-2.43693300
C	-4.28138400	1.68186700	-3.34747200
C	-3.84395700	2.33817300	0.01903700
C	-5.40724500	0.78288400	0.74041200
H	-3.34709300	-0.90802400	-3.72654500
H	-4.74686800	-1.74756000	-3.05061700
C	-5.15020200	-0.66934300	-4.89741000
C	-6.97854700	0.59844800	-3.77382700
H	-6.59049600	-0.45726300	-1.91097300
H	-6.50101700	1.30071200	-1.78748000
C	-5.00209700	1.82206700	-4.69238800
H	-4.51623800	2.54852300	-2.71088200
H	-3.19306400	1.68060400	-3.49049400
O	-2.92476400	2.80921200	-0.62281000
C	-4.50084800	2.86843800	1.24403600
O	-6.07039600	-0.23334700	0.75081600
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C	-6.66032700	-0.60162800	-4.66767600
C	-4.67580700	0.61746800	-5.58027600
H	-4.90886600	-1.53451000	-5.53224400
H	-8.06121200	0.64689000	-3.58702000
C	-6.51405500	1.88516300	-4.46211100
H	-4.66319400	2.74562200	-5.18382600
C	-4.29530200	4.05211800	1.92995500
C	-6.07714400	2.06513800	2.90370800
H	-7.18891900	-0.50967400	-5.62876700
H	-7.01395300	-1.53064900	-4.19533800
H	-3.59227600	0.56805200	-5.76649100
H	-5.16450600	0.72814300	-6.56035100
H	-7.03932400	2.01192100	-5.42110600
H	-6.76598400	2.75854600	-3.84128600

Cl	-3.23180100	5.26277900	1.33702900
C	-4.97637600	4.23576300	3.15227300
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Cl	-7.14268600	0.85466000	3.49230400
Cl	-6.65840200	3.48047900	5.13762900
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C	-0.73194100	-4.61452200	-2.77270800
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C	-1.16393800	-6.08668000	-2.62732100
C	-1.88987000	-3.83600500	-3.42022600
C	-2.28059000	-3.65640400	0.13766700
C	-0.74533200	-5.28702800	0.75308100
H	0.85776300	-3.54547500	-3.80842500
H	1.31888700	-5.15079200	-3.23251300
C	0.16159900	-5.16755100	-5.06796900
C	-1.50276000	-6.68564800	-3.99505200
H	-0.36124700	-6.66412100	-2.14095200
H	-2.04323300	-6.15105600	-1.96901900
C	-2.21307900	-4.42692300	-4.79664300
H	-2.77715600	-3.88845000	-2.77457900
H	-1.63042600	-2.77249700	-3.50940500
O	-2.86624100	-2.86173500	-0.56763100
C	-2.49235700	-3.97940200	1.57348600
O	0.17656500	-6.07041800	0.65448900
C	-1.57847800	-4.96725300	1.93830700
C	-0.27229400	-6.62499700	-4.90175400
C	-0.97656000	-4.35849500	-5.69662800
H	1.05230800	-5.11591100	-5.71074300
H	-1.81300300	-7.73202000	-3.85928900
C	-2.64305200	-5.88699100	-4.63343000

H	-3.03267800	-3.84783000	-5.24845000
C	-3.33746100	-3.39324000	2.50330100
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H	-0.66488500	-3.31173300	-5.83168600
H	-1.21397200	-4.75431200	-6.69596900
H	-2.90356400	-6.31983300	-5.61129700
H	-3.54569500	-5.94703100	-4.00650800
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Cl	-4.19787300	-3.06513300	5.04783600
Cl	-2.17410400	-5.29736800	5.85705900
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N	4.58356400	-1.08853400	0.40761900
C	4.80982100	1.71167900	-2.21108300
C	6.59662900	0.34658100	-1.15771200
C	4.97389900	-0.76276700	-2.69044600
C	3.96060600	-2.33376500	0.27916000
C	5.38905100	-1.01276000	1.54963100
H	3.76279000	1.76575400	-2.52652400
H	4.94489100	2.47781500	-1.43022400
C	5.72781500	2.00021300	-3.39991300
C	7.52765600	0.64244500	-2.33757000
H	6.72830500	1.09856900	-0.36444700
H	6.86680400	-0.62533800	-0.71618500
C	5.89490300	-0.45430300	-3.87547300
H	5.23607300	-1.74291300	-2.26107900

H	3.93132900	-0.83143000	-3.02182400
O	3.16332400	-2.63463200	-0.58683100
C	4.45464500	-3.14605900	1.42463200
O	5.99079500	-0.02792600	1.92251100
C	5.31750300	-2.35568100	2.18302800
C	7.18416600	2.00904200	-2.93442100
C	5.53551100	0.91469500	-4.46333700
H	5.46400000	2.98210800	-3.82056400
H	8.56686300	0.64437000	-1.97772300
C	7.35120100	-0.43830400	-3.40648100
H	5.76162300	-1.23071000	-4.64269000
C	4.12875800	-4.43552600	1.81011100
C	5.89787700	-2.82761000	3.34898500
H	7.85545200	2.23247500	-3.77759700
H	7.33730600	2.79989800	-2.18449000
H	4.49253700	0.91188100	-4.81433500
H	6.16820600	1.12658000	-5.33865700
H	8.02283800	-0.24223400	-4.25621700
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C	4.69742400	-4.93244000	3.00367200
C	5.57733500	-4.13870800	3.76302100
Cl	6.96347300	-1.85051000	4.27298200
Cl	4.27705600	-6.50591900	3.54637700
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H	4.39963000	0.93933400	0.30522900
H	0.62921200	-4.60304300	-1.12650400
H	-4.41892800	-0.80462900	-0.88768000
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C	-0.39361700	-0.26563800	2.30086500

C	-1.21414600	0.85107800	2.80494500
C	-0.01625000	-1.31454000	3.18455400
C	0.90945000	-2.31450900	2.78521600
C	-0.51391300	-1.36473500	4.51526500
C	1.33969300	-3.27782200	3.67846200
H	1.29283900	-2.30385300	1.76797300
C	-0.08514000	-2.32642500	5.40985700
H	-1.25254000	-0.62974700	4.83376400
C	0.86159600	-3.26803000	4.99199300
H	2.04381800	-4.04709200	3.37260700
H	-0.46491400	-2.35132700	6.42832000
Br	1.53193700	-4.52266900	6.21942000
O	-0.45587100	1.83262100	3.32647300
O	-2.42760200	0.89291500	2.70681500
C	-1.16665300	3.04959800	3.58969100
H	-2.05793300	2.85833600	4.19578500
H	-0.47062600	3.69437800	4.12813500
H	-1.46176600	3.51373200	2.64104600

SI-Chapter 4

1. General Considerations

1.1 Equipment and methods

^{1}H and ^{13}C NMR spectra were recorded at either 400 MHz (^{13}C at 100 MHz) or 600 MHz (^{13}C at 150 MHz) on Varian-400 or INOVA-600 spectrometer, as indicated. NMR spectra were run in solutions of deuterated chloroform ($CDCl_3$) with residual chloroform taken as an internal standard (7.26 ppm for ^{1}H, and 77.16 ppm for ^{13}C), and were reported in parts per million (ppm).

Abbreviations for signal multiplicity are as follow: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, etc. Coupling constants (*J* values) were calculated directly from the spectra. IR spectra were collected on a Nicolet iS10 FT-IR spectrometer. Mass spectra were taken on a Thermo Finnigan LTQ-FTMS spectrometer with APCI, ESI or NSI. Thin layer chromatographic (TLC) analysis was performed with glass-backed silica gel plates, visualizing with UV light and/or staining with aqueous $KMnO_4$ stain.

1.2 Solvents for reaction

Tetrahydrofuran and *n*-pentane was purified and dried by a Glass Contour Solvent System. The dichloromethane(DCM) used for the carbenoid transformations was dried and degassed at reflux over activated 4Å molecular sieves in a 250mL round bottom flask for 3 hours under N_2, then stored with 4Å molecular sieves under N_2 atmosphere and then was directly used.

1.3 Substrates and reagents

The substrates and reagents were purchased from the following suppliers and used without further purification:

Sigma-Aldrich: (*S*)-(+)-2-pentanol; 1-chlorohexane; phenylboronic acid; (4-(*tert*-butyl)phenyl)boronic acid; [1,1'-biphenyl]-4-ylboronic acid; (4-(trifluoromethyl)phenyl)boronic acid.

Alfa-Aesar: 1-bromohexane.

Combi-Blocks: (3,5-dimethylphenyl)boronic acid; (3,5-bis(trifluoromethyl)phenyl)boronic acid; [1,1':3',1''-terphenyl]-5'-ylboronic acid.

Synquest Laboratory: 1-Fluorohexane.

The following substrates were prepared according to reported procedures[20-21]:

Butyltrimethylsilane; hexyltrimethylsilane; pentyl pivalate; *tert*-butyl hexanoate.

The following reagents were prepared according to reported procedures[22-24]:

methyl 2-(4-bromophenyl)-2-diazoacetate; 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate; 2,2,2-trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate; 2,2,2-tribromoethyl 2-(4-bromophenyl)-2-diazoacetate; 2,2,2-trichloroethyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate; 2,2,2-trichloroethyl 2-(4-(*tert*-butyl)phenyl)-2-diazoacetate; 2,2,2-trichloroethyl 2-(6-chloropyridin-3-yl)-2-diazoacetate; (*R*)-1-(4-nitrophenyl)-2,2-diphenylcyclopropane-1-carboxylic acid.

2. C–H Functionalization Reactions

2.1 General Procedures for C–H Functionalization Reactions

General procedure A for C–H insertion reaction (for reaction in *n*-pentane):

A 25-mL flask was equipped with a reflux condenser and an egg shaped magnetic stir bar. The flask was charged with $Rh_2(R\text{-}L)_4$ (0.0035 mmol, 1 mol%) and treated by vacuum/ N_2 to remove the air. Degassed *n*-pentane (3 mL) was added, then the catalyst solution was heated to reflux under N_2 for 5 minutes. Diazo (0.35 mmol, 1.0 equiv.) was dissolved in 5 mL of degassed *n*-pentane and then the diazo solution was added dropwise to the catalyst solution over 3h with a syringe pump under reflux condition and N_2 atmosphere. After addition, the reaction mixture was stirred for another 30 min, and then concentrated under vacuum. Trichloroethylene (0.35 mmol, 1.0 equiv.) was added into the crude mixture as an internal standard to obtain the crude ^1H NMR yield. Then crude mixture was separated by flash chromatography on silica gel to obtain the product.

General procedure B for C–H insertion reaction (for reaction in DCM):

A 5-mL flask was equipped with a reflux condenser and an egg shaped magnetic stir bar. The flask was charged with $Rh_2(R\text{-}L)_4$ (0.0035 mmol, 1 mol%) and treated by vacuum/ N_2 to remove the air. Substrate (1.05 mmol, 3 equiv.) and degassed DCM (0.5 mL) were added, then the catalyst solution was heated to reflux under N_2 for 5 minutes. Diazo (0.35 mmol, 1.0 equiv.) was dissolved in 1 mL of degassed DCM and then the diazo solution was added dropwise to the catalyst solution over 3h with a syringe pump under reflux condition and N_2 atmosphere. After addition, the reaction mixture was stirred for another 30 min, and then concentrated under vacuum. Then crude mixture was separated by flash chromatography on silica gel to obtain the product.

2.2 Procedure for the Product Ratios Determination

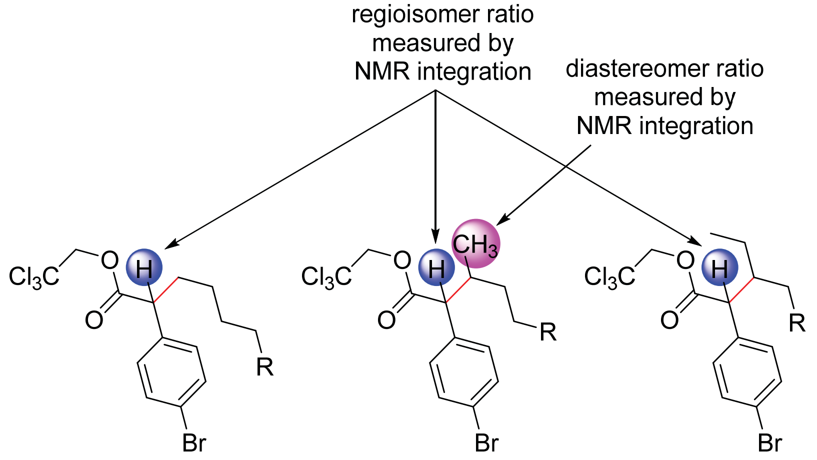
To measure the product ratios, the mixtures obtained as described in section 2.1 were analyzed by ^{1}H NMR using the following settings:

Instrument: 600 MHz INOVA equipped with an ID probe with sensitivity of 1000:1

Number of scans: 16

Relaxation time: 5 seconds

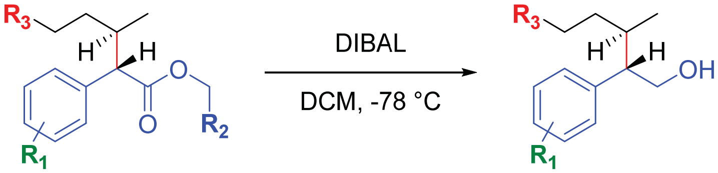
The crude ^{1}H NMR spectra data was processed using MestReNova 9.1.0 (Mestrelab Research S.L.), applying an auto-phase correction as well as a Segments Smoother baseline correction. The baseline was manually inspected before integration. The ratios were measured by integration of the ^{1}H NMR peaks resulting from the indicated hydrogens below.



3. General Procedure for Enantiomeric Excess (e.e.) Determination on HPLC

As the enantiomers of the C–H functionalization products are difficult to be separated on the HPLC, most of the C–H functionalization products were converted to other derivatives, which will have better separation on the HPLC, without changing the e.e of the products. Therefore, the e.e. of the products were determined from the corresponding derivatives.

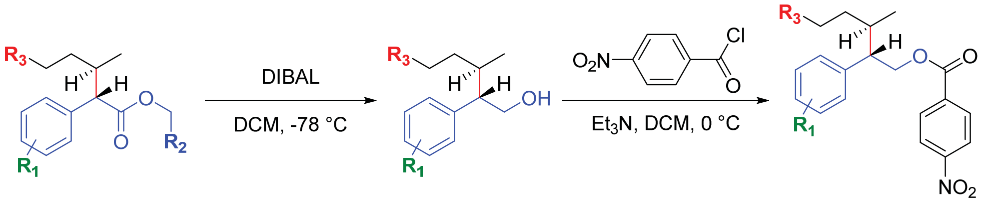
3.1 Reduction of the C–H Functionalization Products



To a stirred solution of the ester (0.1 mmol, 1.0 equiv.) in DCM (3 mL) was added 1 M diisobutylaluminum hydride (DIBAL) in DCM (0.22 mL, 0.22 mmol, 2.2 equiv.) slowly at -78 °C. The mixture was stirred for 2 h and allowed to warm up to r.t. Methanol (0.5 mL) was added into the reaction solution and stirred for 20 min. The reaction mixture was extracted by DCM, the organic layer was washed with saturated NaCl aqueous solution (10 mL). The organic layer was dried ($MgSO_4$) and filtered. Then the filtrate was concentrated. The resulting crude residue was analyzed by ^1H NMR and purified by flash column chromatography (hexanes/diethyl ether = 9/1) to afford white solid or colorless oil. The sample was dissolved in hexanes (1 mg/mL) and the e.e. was determined on the HPLC.

The e.e. of the C–H functionalization products are determined from the e.e. of the corresponding alcohol.

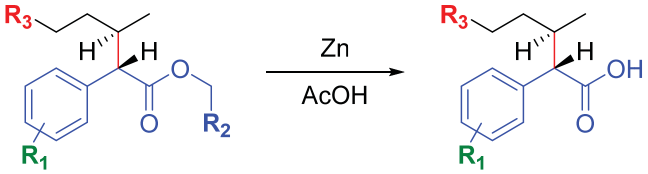
3.2 Reduction of the C–H Functionalization Products and Followed by Esterification



To a stirred solution of the ester (0.1 mmol, 1.0 equiv.) in DCM (3 mL) was added 1 M DIBAL in DCM (0.22 mL, 0.22 mmol, 2.2 equiv.) slowly at -78 °C. The mixture was stirred for 2 h and allowed to warm up to r.t. Methanol (0.5 mL) was added into the reaction solution and stirred for 20 min. The reaction mixture was extracted by DCM, the organic layer was washed with saturated NaCl aqueous solution (10 mL). The organic layer was dried ($MgSO_4$) and filtered. Then the filtrate was concentrated and directly used for the next step without further purification. To a solution of the crude alcohol and Et_3N (0.15 mmol, 1.5 equiv.) in DCM (3 mL) was added 4-nitrobenzoyl chloride (1.2 equiv.) portion wise at 0 °C. The reaction was allowed to warm up to room temperature and stirred for 12 h. The reaction mixture was diluted with DCM (3 mL) and then washed successively by $NaHCO_3$, H_2O and saturated NaCl aqueous solution. The organic phase was dried ($MgSO_4$), filtered, and the filtrate was concentrated. The resulting crude mixture was purified by silica gel column chromatography (hexanes/diethyl ether = 20/1) to afford colorless oil. The sample was dissolved in hexanes (1 mg/mL) and the e.e. was determined on the HPLC.

The e.e. of the C–H functionalization products are determined from the e.e. of the corresponding ester.

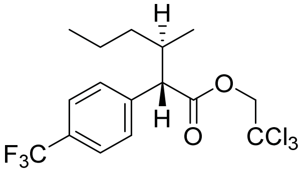
3.3 Deprotection of the Trichloroethyl Ester of the C–H Functionalization Products



The ester (0.1 mmol, 1.0 equiv.) was dissolved in 2 mL of glacial acetic acid, and zinc powder (33 mg, 0.5 mmol, 5.0 equiv.) was added. The solution was allowed to stir at room temperature for 24 h. The starting material had been fully consumed as indicated by TLC analysis. The solution was diluted with H_2O (10 mL) and extracted with ethyl acetate (2 x 15 mL). The organic extracts were washed with H_2O (10 mL) and saturated NaCl (10 mL). Then the organic layer was dried over $MgSO_4$ and filtered. The filtrate was concentrated to give the product as colorless oil or white solid. Crude product was purified by silica gel column chromatography (hexanes/diethyl ether = 20/1) to afford colorless oil. The sample was dissolved in hexanes (1 mg/mL) and the e.e. was determined on the HPLC.

The e.e. of the products are determined from the e.e. of the corresponding carboxylic acid.

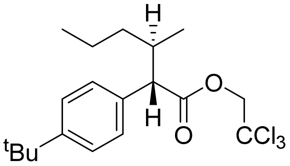
4. Substrate Screen



2,2,2-Trichloroethyl (*2S,3R*)-3-methyl-2-(4-(trifluoromethyl)phenyl)hexanoate (23). This compound was prepared according to the general procedure A for Rh_2[*R-3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate (0.35 mmol, 127 mg, 1.0 equiv.) in 3 mL n-pentane and Rh_2[*R-3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$ (**15**) (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL *n*-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (136 mg, 96% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 15, C3 was not detected; and the dr of C2 was 14: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

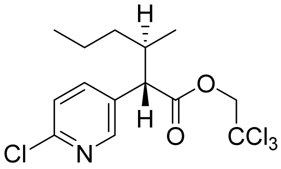
$[\alpha]^{20}_D$ 18.1° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.64 (s, 1H), 3.51 (d, *J* = 10.5 Hz, 1H), 2.33 (m, 1H), 1.37 (m, 1H), 1.23 – 1.09 (m, 2H), 1.08 (d, *J* = 6.5 Hz, 3H), 0.98 – 0.90 (m, 1H), 0.78 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.7, 141.4, 129.3, 125.6 (q, *J* = 4.2 Hz), 94.8, 74.3, 58.6, 36.2, 35.7, 19.6, 17.9, 14.1; HRMS (APCI) calcd for $C_{16}H_{17}Cl_3F_3O_2$ ($[M-H]^+$): 403.0251 found 403.0239; IR (neat): 2960, 2932, 1750, 1421, 1323, 1261, 1224, 1165, 1123, 1068, 1019, 839, 808, 780, 760, 717; HPLC (to improve the separation, the product was converted to 3-methyl-2-(4-(trifluoromethyl)phenyl)hexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.5% isopropanol in hexane, 0.5 mL/min, 1 mg/mL, 130 min, UV 210 nm) retention times of 63.6 min (major) and 107.2 min (minor), 97% e.e..



2,2,2-Trichloroethyl (2S,3R)-2-(4-(*tert*-butyl)phenyl)-3-methylhexanoate (24). This compound was prepared according to the general procedure A for Rh_2[*R-3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-(*tert*-butyl)phenyl)-2-diazoacetate (0.35 mmol, 122 mg, 1.0 equiv.) in 3 mL *n*-pentane and Rh_2[*R-3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$ (**15**) (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL *n*-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (132 mg, 96% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 22, C3 was not detected; and the dr of C2 was 24: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

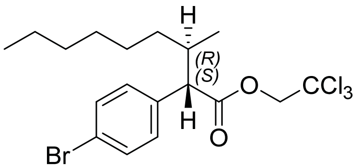
$[\alpha]^{20}_D$ 21.4° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 4.81 (d, *J* = 12.0 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 3.41 (d, *J* = 10.5 Hz, 1H), 2.30 (m, 1H), 1.42 – 1.33 (m, 1H), 1.32 (s, 9H), 1.25 – 1.15 (m, 2H), 1.07 (d, *J* = 6.6 Hz, 3H), 0.97 – 0.89 (m, 1H), 0.79 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.6, 150.4, 134.2, 128.5, 125.6, 95.1, 74.2, 58.4, 35.9, 35.7, 34.6, 31.5, 19.63, 18.0, 14.2; HRMS (NSI) calcd for $C_{19}H_{28}Cl_3O_2$ ($[M+H]^+$): 393.1149 found 393.1150; IR (neat): 2958, 2930, 1750, 1269, 1201, 1117, 1019, 830, 808, 769, 721; HPLC (to improve the separation, the product was converted to 2-(4-(*tert*-butyl)phenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.2% isopropanol in hexane, 0.2 mL/min, 1 mg/mL, 130 min, UV 210 nm) retention times of 61.3 min (single enantiomer), >99% e.e..



2,2,2-Trichloroethyl (2S,3R)-2-(6-chloropyridin-3-yl)-3-methylhexanoate (25). This compound was prepared according to the general procedure A for Rh_2[*R-3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-(*tert*-butyl)phenyl)-2-diazoacetate (0.35 mmol, 115 mg, 1.0 equiv.) in 3 mL *n*-pentane and Rh_2[*R-3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$ (**15**) (0.0035 mmol, 9 mg, 1 mol%.) in 5 mL n-pentane were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (114 mg, 87% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 28, C3 was not detected; and the dr of C2 was 55: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

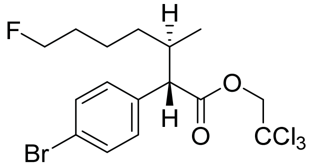
$[\alpha]^{20}_D$ -3.6° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (d, *J* = 2.6 Hz, 1H), 7.74 (dd, *J* = 8.3, 2.6 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 4.77 (d, *J* = 11.9 Hz, 1H), 4.66 (d, *J* = 11.9 Hz, 1H), 3.45 (d, *J* = 10.1 Hz, 1H), 2.25 (dtd, *J* = 10.1, 6.6, 3.3 Hz, 1H), 1.41 – 1.29 (m, 1H), 1.23 – 1.08 (m, 2H), 1.06 (d, *J* = 6.6 Hz, 3H), 0.93 (dtd, *J* = 13.5, 9.7, 3.3 Hz, 1H), 0.78 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 152.5, 150.2, 138.8, 132.0, 124.4, 110.2, 74.4, 55.3, 36.3, 35.6, 19.5, 17.8, 14.1; HRMS (NSI) calcd for $C_{14}H_{18}Cl_4NO_2$ ($[M+H]^+$): 372.0086 found 372.0089. IR(neat): 2959, 2927, 1750, 1459, 1384, 1194, 1138, 1103, 1022, 834, 810, 772, 742, 719; HPLC (S,S-Whelk, 0.2% isopropanol in hexane, 0.2 mL/min, 1 mg/mL, 100 min, UV 210 nm) retention times of 56.5 min (major) and 78.4 min (minor), 91% e.e..



2,2,2-Trichloroethyl (2S,3R)-2-(4-bromophenyl)-3-methylnonanoate (26). This compound was prepared according to the general procedure B for Rh_2[*R-3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 1 mL DCM, Rh_2[*R-3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$ (0.0035 mmol, 9 mg, 1 mol%.) and *n*-octane (1.05 mmol, 120 mg, 3.0 equiv.) in 0.5 mL DCM were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford the product as a colorless oil (132 mg, 82% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the C1: C2 ratio was 1: 27, C3 was not detected; and the dr of C2 was 9: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

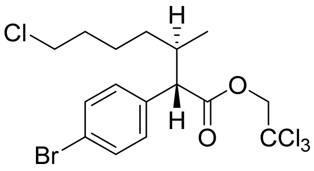
$[\alpha]^{20}_D$ 5.6° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.4, 1.7 Hz, 2H), 7.27 – 7.22 (m, 2H), 4.77 (dd, *J* = 11.8, 1.4 Hz, 1H), 4.63 (dd, *J* = 11.8, 1.4 Hz, 1H), 3.38 (d, *J* = 10.1 Hz, 1H), 2.24 (ttd, *J* = 10.1, 6.5, 3.1 Hz, 1H), 1.34 – 1.18 (m, 5H), 1.20 – 1.11 (m, 4H), 1.05 (d, *J* = 6.5 Hz, 3H), 0.96 – 0.86 (m, 1H), 0.84 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 136.4, 131.8, 130.6, 121.7, 94.9, 74.2, 58.2, 36.2, 33.4, 31.9, 29.4, 26.3, 22.7, 18.0, 14.2; HRMS (NSI) calcd for $C_{18}H_{24}Cl_3O_2BrNa$ ($[M+Na]^+$): 478.9917 found 478.9925; IR (neat): 2928, 2855, 2118, 1749, 1488, 1370, 1216, 1118, 1073, 1046, 1011, 825, 759, 715. HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methylnonyl 4-nitrobenzoate prepared using (1)DIBAL in dichloromethane at -78 °C, (2) 4-nitrobenzoyl chloride and triethylamine in dichloromethane at 0 °C), (S,S-Whelk, 0.35% isopropanol in hexane, 0.3 mL/min, 1 mg/mL, 100 min, UV 210 nm) retention times of 57.4 min (major) and 77.0 min (minor), 91% e.e..



2,2,2-Trichloroethyl (*2S,3R*)-2-(4-bromophenyl)-7-fluoro-3-methylheptanoate (27). This compound was prepared according to the general procedure B for Rh_2[*R-3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 1 mL DCM, Rh_2[*R-3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$ (0.0035 mmol, 9 mg, 1 mol%.) and 1-florohexane (1.05 mmol, 109 mg, 3.0 equiv.) in 0.5 mL DCM were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford **27** as a colorless oil (133 mg, 85% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the regioisomers ratio was 18: 1, and the dr of the major product was 9: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

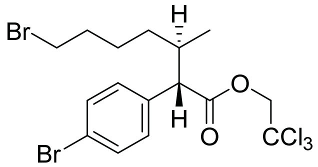
$[\alpha]^{20}_{D}$ 8.0° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 6.9 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.38 (t, *J* = 6.0 Hz, 1H), 4.33 – 4.27 (m, 1H), 3.40 (d, *J* = 10.6 Hz, 1H), 2.27 (m, 1H), 1.66 – 1.49 (m, 1H), 1.52 – 1.39 (m, 2H), 1.27 (m, 1H), 1.20 (m, 1H), 1.07 (d, *J* = 6.5 Hz, 3H), 0.97 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.7, 136.1, 131.9, 131.9, 131.8, 130.5, 121.8, 94.8, 83.90 (d, *J* = 164.5 Hz), 74.2, 58.0, 36.2, 32.9, 30.5, 30.4, 22.1, 22.1, 17.8; HRMS (NSI) calcd for $C_{16}H_{19}Cl_4O_2BrF$ ($[M+Cl]^-$): 480.9312 found 480.9317; IR (neat): 2936, 1748, 1488, 1371, 1266, 1184, 1131, 1073, 1010, 912, 826, 759, 714; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-7-fluoro-3-methylheptan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 1% isopropanol in hexane, 1 mL/min, 1 mg/mL, 100 min, UV 210 nm) retention times of 51.9 min (major) and 85.4 min (minor), 97% e.e..



2,2,2-Trichloroethyl (*2S,3R*)-2-(4-bromophenyl)-7-chloro-3-methylheptanoate (28). This compound was prepared according to the general procedure B for Rh_2[*R*-*3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 1 mL DCM, Rh_2[*R*-*3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$ (0.0035 mmol, 9 mg, 1 mol%.) and 1-chlorohexane (1.05 mmol, 127 mg, 3.0 equiv.) in 0.5 mL DCM were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford **28** as a colorless oil (137 mg, 84% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the regioisomers ratio was 18: 1, and the dr of the major product was 9: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

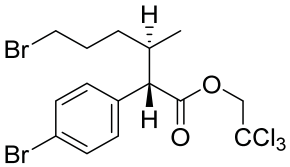
$[\alpha]^{20}_{D}$ 7.1° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:9 v/v); ^1H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 3.43 (td, *J* = 6.6, 3.7 Hz, 2H), 3.39 (d, *J* = 10.6 Hz, 1H), 2.26 (m, 1H), 1.70 – 1.62 (m, 1H), 1.57 (m, 1H), 1.52 – 1.42 (m, 1H), 1.35 – 1.25 (m, 1H), 1.18 (m, 1H), 1.07 (d, *J* = 6.4 Hz, 3H), 0.99 – 0.89 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.7, 136.1, 131.9, 130.5, 121.8, 94.8, 74.2, 58.0, 44.95, 36.12, 32.57, 32.53, 23.64, 17.88; HRMS (NSI) calcd for $C_{16}H_{19}Cl_5O_2Br$ ($[M+Cl]^-$): 496.9016 found 496.9016. IR (neat): 2935, 1748, 1488, 1371, 1269, 1213, 1126, 1073, 1011, 912, 826, 759, 715; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-7-chloro-3-methylheptan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.7% isopropanol in hexane, 0.7 mL/min, 1 mg/mL, 240 min, UV 210 nm) retention times of 118.7 min (minor) and 179.1 min (major), 93% e.e..



2,2,2-Trichloroethyl (*2S,3R*)-7-bromo-2-(4-bromophenyl)-3-methylheptanoate (29). This compound was prepared according to the general procedure B for Rh_2[*R-3,5*-di(*p*-$^tBuC_6H_4$)TPCP$]_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 1 mL DCM, Rh_2[*R-3,5*-di(*p*-$^tBuC_6H_4$)TPCP$]_4$ (0.0035 mmol, 9 mg, 1 mol%.) and 1-bromohexane (1.05 mmol, 173.3 mg, 3.0 equiv.) in 0.5 mL DCM were used. The crude residue was analyzed by ^1H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford **29** as a colorless oil (159 mg, 89% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the regioisomers ratio was 18: 1, and the dr of the major product was 9: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

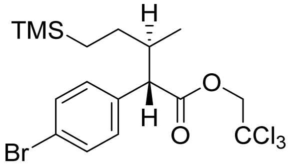
$[\alpha]^{20}_{D}$ 6.5° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 6.9 Hz, 2H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 3.39 (d, *J* = 10.2 Hz, 1H), 3.31 (q, *J* = 6.7 Hz, 1H), 2.27 (m, 1H), 1.79 – 1.71 (m, 1H), 1.66 (m, 1H), 1.47 (m, 1H), 1.29 (m, 1H), 1.19 (m, 1H), 1.08 (d, *J* = 6.5 Hz, 3H), 1.00 – 0.91 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.7, 136.1, 131.9, 130.5, 121.8, 94.8, 74.2, 58.0, 36.1, 33.8, 32.7, 32.4, 24.9, 17.9; HRMS (NSI) calcd for $C_{16}H_{19}Cl_4O_2Br_2$ ($[M+Cl]^-$): 540.8511 found 540.8512; IR (neat): 2933, 1748, 1488, 1371, 1259, 1211, 1125, 1073, 1011, 911, 825, 759, 714; HPLC (to improve the separation, the product was converted to 7-bromo-2-(4-bromophenyl)-3-methylheptan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.8% isopropanol in hexane, 0.8 mL/min, 1 mg/mL, 180 min, UV 210 nm) retention times of 91.4 min (minor) and 138.3 min (major), 92% e.e..



2,2,2-Trichloroethyl (*2S,3R*)-6-bromo-2-(4-bromophenyl)-3-methylhexanoate (30). This compound was prepared according to the general procedure B for Rh_2[*R-3,5*-di(*p*-^{t}BuC_6H_4)TPCP$]_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 1 mL DCM, Rh_2[*R-3,5*-di(*p*-^{t}BuC_6H_4)TPCP$]_4$ (0.0035 mmol, 9 mg, 1 mol%.) and 1-bromopentane (1.05 mmol, 159 mg, 3.0 equiv.) in 0.5 mL DCM were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford **30** as a colorless oil (113 mg, 65% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the regioisomers ratio was 9: 1, and the dr of the major product was 9: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

$[\alpha]^{20}_{D}$ 8.4° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 6.9 Hz, 2H), 7.25 (d, *J* = 6.9 Hz, 2H), 4.77 (d, *J* = 12.1 Hz, 1H), 4.63 (d, *J* = 12.1 Hz, 1H), 3.39 (d, *J* = 11.8 Hz, 1H), 3.32 – 3.26 (m, 1H), 3.24 – 3.18 (m, 1H), 2.29 (m 1H), 1.92 – 1.78 (m, 1H), 1.78 – 1.67 (m, 1H), 1.36 – 1.27 (m, 1H), 1.11 – 1.04 (m, 1H), 1.08 (dd, *J* = 6.6, 1.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 135.8, 132.0, 130.5, 129.9, 121.9, 94.8, 74.2, 58.0, 35.6, 33.4, 32.0, 29.8, 18.0; HRMS (NSI) calcd for $C_{15}H_{17}Cl_4O_2Br_2$ ($[M+Cl]^-$): 526.8354 found 526.8356; IR (neat): 2927, 1748, 1488, 1449, 1408, 1371, 1256, 1215, 1125, 1073, 1011, 913, 826, 759, 714; HPLC (to improve the separation, the product was converted to 6-bromo-2-(4-bromophenyl)-3-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.8% isopropanol in hexane, 0.8 mL/min, 1 mg/mL, 180 min, UV 210 nm) retention times of 99.4 min (minor) and 139.9 min (major), 95% e.e..

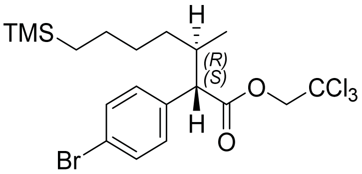


2,2,2-Trichloroethyl (*2S,3R*)-2-(4-bromophenyl)-3-methyl-5-(trimethylsilyl)pentanoate (31). This compound was prepared according to the general procedure B for Rh_2[*R*-*3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 1 mL DCM, Rh_2[*R*-*3,5*-di(*p*-^{t}BuC_6H_4)TPCP]$_4$ (0.0035 mmol, 9 mg, 1 mol%.) and butyltrimethylsilane (1.05 mmol, 137 mg, 3.0 equiv.) in 0.5 mL DCM were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford **31** as a colorless oil (67 mg, 40% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the regioisomers ratio was 34: 1, and the dr of the major product was 4: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

$[\alpha]^{20}_D$ 12.2° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 3.44 (d, *J* = 10.8 Hz, 1H), 2.23 (m, 1H), 1.24 (m, 1H), 1.06 (d, *J* = 6.7 Hz, 3H), 0.99 – 0.90 (m, 1H), 0.46 (m Hz, 1H), 0.32 (m, 1H) , -0.14 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.0, 136.3, 131.8, 130.6, 121.6, 94.9, 74.3, 57.3, 38.5, 27.2, 17.3, 12.1, -1.8; HRMS (APCI) calcd for $C_{17}H_{23}Cl_3O_2BrSi$ ($[M-H]^+$): 470.9721 found 470.9709;

IR (neat): 2953, 1749, 1488, 1260, 1247, 1215, 1183, 1124, 1073, 1037, 1011, 894, 861, 826, 757, 715; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methyl-5-(trimethylsilyl)pentanoic acid prepared using Zn/acetic acid), (ADH, 0.65% isopropanol in hexane, 0.65 mL/min, 1 mg/mL, 35 min, UV 210 nm) retention times of 25.1 min (minor) and 28.3 min (major), >99% e.e..

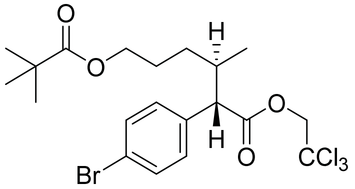


2,2,2-Trichloroethyl (*2S,3R*)-2-(4-bromophenyl)-3-methyl-7-(trimethylsilyl)heptanoate (32). This compound was prepared according to the general procedure B for Rh_2[*R*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 1 mL DCM, Rh_2[*R*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$ (0.0035 mmol, 9 mg, 1 mol%.) and hexyltrimethylsilane (1.05 mmol, 166 mg, 3.0 equiv.) in 0.5 mL DCM were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford **32** as a colorless oil (150 mg, 85% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the regioisomers ratio was 20: 1, and the dr of the major product was 9: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

$[\alpha]^{20}_D$ 4.5° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 3.38 (d, *J* = 10.6 Hz, 1H), 2.24 (m, 1H), 1.36 – 1.22 (m, 2H), 1.17 (m, 3H), 1.05 (d, *J* = 6.5 Hz, 3H), 0.90 (m, 1H), 0.37 (m, 2H), -0.07 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 136.4, 131.8, 130.6, 121.7, 94.9, 74.3, 58.2, 36.2, 33.1, 30.4, 24.0, 18.0, 16.8, -1.5; HRMS (NSI) calcd for $C_{19}H_{27}Cl_3O_2BrSi$ ($[M-H]^+$): 499.0034 found 499.0023; IR (neat): 2928, 1750, 1488, 1258, 1246, 1124, 1074, 1011, 858, 830, 758, 718, 692; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methyl-7-(trimethylsilyl)heptanoic acid prepared using Zn/acetic acid), (ADH, 0.5%

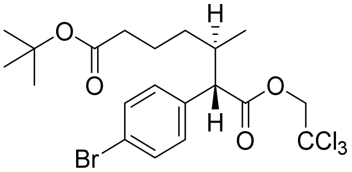
isopropanol in hexane, 0.5 mL/min, 1 mg/mL, 100 min, UV 210 nm) retention times of 59.9 min (minor) and 63.1 min (major), 90% e.e..



2,2,2-Trichloroethyl (*2S,3R*)-2-(4-bromophenyl)-3-methyl-6-(pivaloyloxy)hexanoate (33). This compound was prepared according to the general procedure B for Rh$_2$[*R*-3,5-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 1 mL DCM, Rh$_2$[*R*-3,5-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$ (0.0035 mmol, 9 mg, 1 mol%.) and pentyl pivalate (1.05 mmol, 181 mg, 3.0 equiv.) in 0.5 mL DCM were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford **33** as a colorless oil (150 mg, 83% yield).

Analysis of the NMR spectrum of the crude reaction mixture revealed that the regioisomers ratio was 21: 1, and the dr of the major product was 7: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

$[\alpha]^{20}_D$ 7.1° (c = 1.00, CHCl$_3$); TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 4.76 (d, *J* = 12.1 Hz, 1H), 4.63 (d, *J* = 12.1 Hz, 1H), 3.95 – 3.87 (m, 2H), 3.36 (d, *J* = 10.8 Hz, 1H), 2.26 (m, 1H), 1.64 (m, 1H), 1.46 (m, 1H), 1.28 – 1.21 (m, 1H), 1.08 (d, *J* = 6.5 Hz, 3H), 1.07 (s, 9H), 0.94 (m, 1H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 178.5, 171.7, 136.1, 132.0, 130.5, 121.9, 94.8, 74.3, 64.0, 58.1, 36.0, 29.7, 27.2, 25.7, 17.9; HRMS (NSI) calcd for $C_{20}H_{26}Cl_4O_4Br$ ([M+Cl]$^-$): 548.9755 found 548.9757; IR (neat): 2958, 1749, 1724, 1488, 1480, 1283, 1210, 1150, 1073, 1033, 1011, 826, 760, 715; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-3-methyl-6-(pivaloyloxy)hexanoic acid prepared using Zn/acetic acid), (ADH, 0.5% isopropanol in hexane, 0.65 mL/min, 1 mg/mL, 240 min, UV 210 nm) retention times of 193.8 min (minor) and 204.3 min (major), 92% e.e..

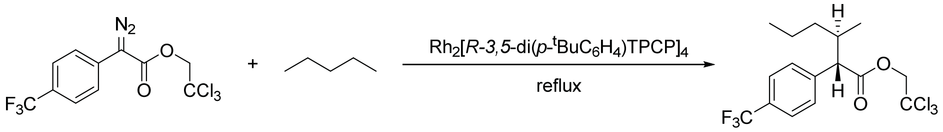


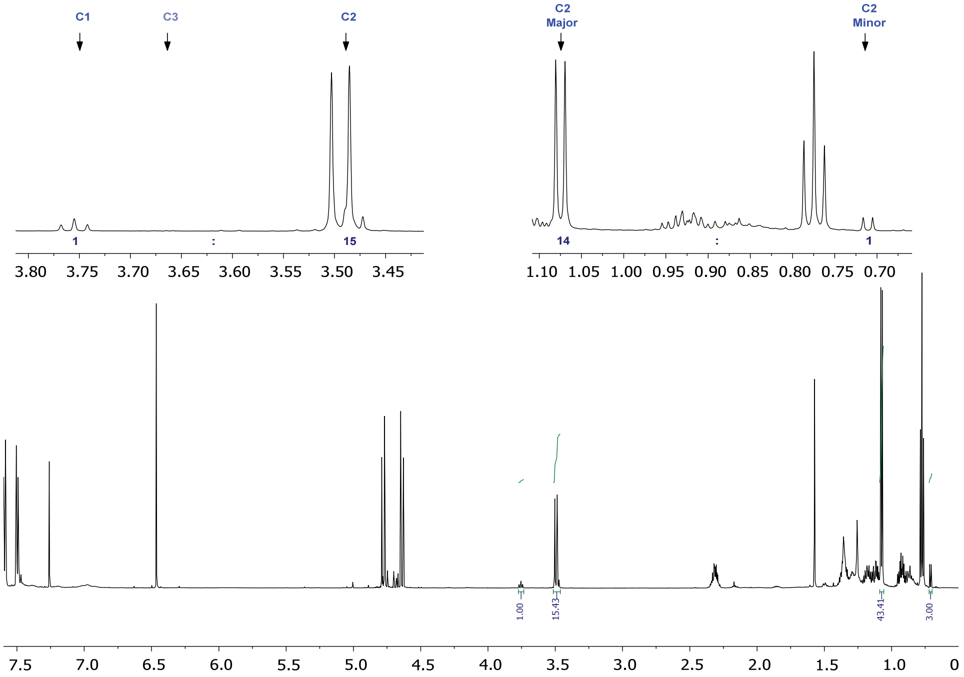
7-(*tert*-Butyl) 1-(2,2,2-trichloroethyl) (2*S*,3*R*)-2-(4-bromophenyl)-3-methylheptanedioate (34). This compound was prepared according to the general procedure B for Rh_2[*R*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$-catalyzed C–H functionalization. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (0.35 mmol, 130 mg, 1.0 equiv.) in 1 mL DCM, Rh_2[*R*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$ (0.0035 mmol, 9 mg, 1 mol%.) and *tert*-butyl hexanoate (1.05 mmol, 181 mg, 3.0 equiv.) in 0.5 mL DCM were used. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford **34** as a colorless oil (152 mg, 84% yield).

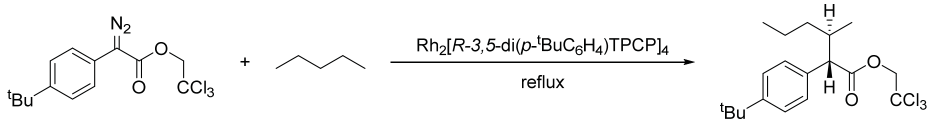
Analysis of the NMR spectrum of the crude reaction mixture revealed that the regioisomers ratio was 16: 1, and the dr of the major product was 9: 1, favoring the (2*S*, 3*R*) and (2*R*, 3*S*) over the (2*S*, 3*S*) and (2*R*, 3*R*).

$[\alpha]^{20}_D$ 6.2° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:9 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 3.37 (d, *J* = 10.8 Hz, 1H), 2.24 (m, 1H), 2.12 – 2.00 (m, 2H), 1.67 – 1.58 (m, 1H), 1.48 – 1.39 (m, 1H), 1.36 (d, *J* = 1.0 Hz, 9H), 1.15 (m, 1H), 1.07 (d, *J* = 6.5 Hz, 3H), 0.92 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.8, 171.8, 136.1, 131.9, 130.5, 121.8, 94.8, 80.2, 74.2, 58.1, 36.1, 35.6, 32.8, 28.1, 22.1, 17.9; HRMS (NSI) calcd for $C_{20}H_{26}Cl_4O_4Br$ ($[M+Cl]^-$): 548.9755 found 548.9760; IR (neat): 2929, 1750, 1726, 1488, 1456, 1366, 1255, 1150, 1128, 1074, 1011, 826, 760, 716; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-7-(*tert*-butoxy)-3-methyl-7-oxoheptanoic acid prepared using Zn/acetic acid), (ADH, 0.5% isopropanol in hexane, 0.65 mL/min, 1 mg/mL, 240 min, UV 210 nm) retention times of 168.3 min (minor) and 175.7 min (major), 91% e.e..

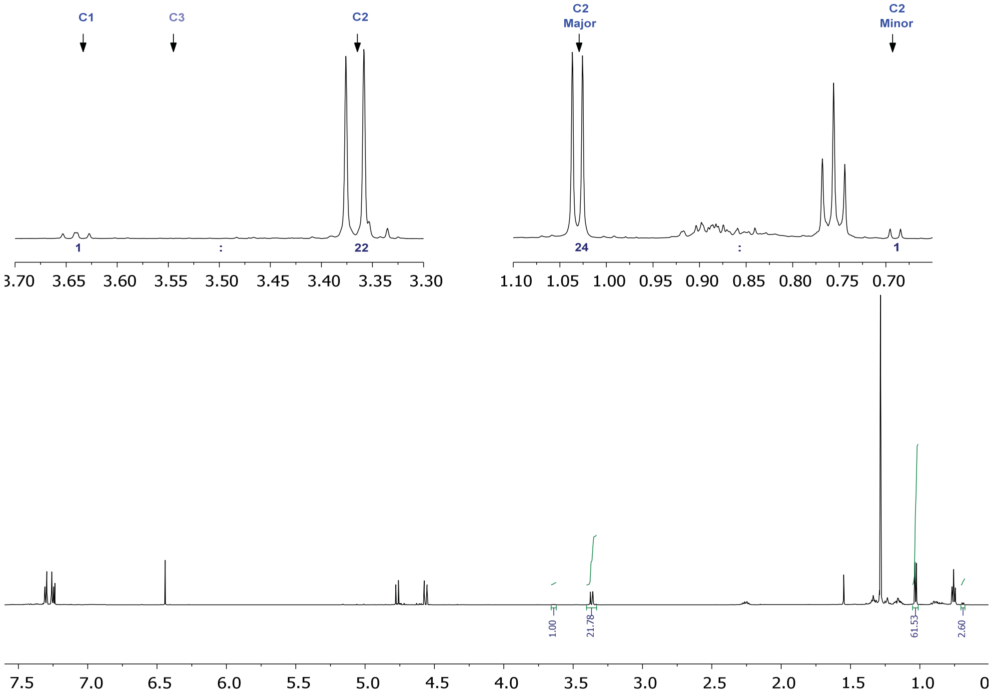
4.1 Crude 1H NMR Spectra of Substrate Screen



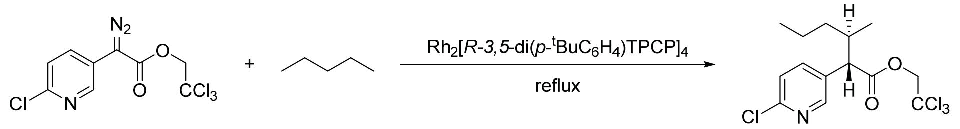


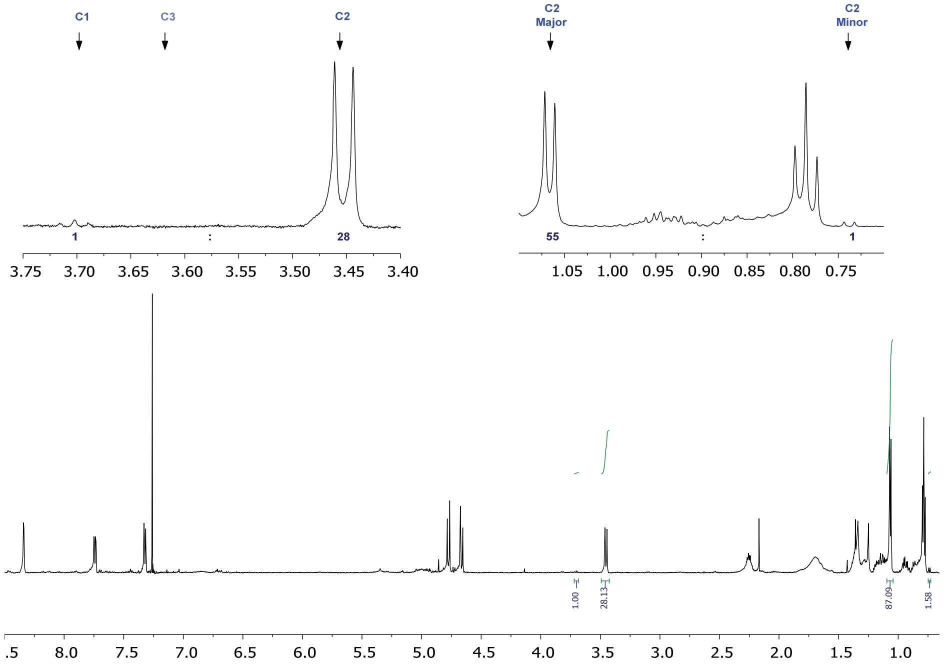


N_2
^tBu
O
CCl_3
+
$Rh_2[R\text{-}3,5\text{-di}(p\text{-}^tBuC_6H_4)TPCP]_4$
reflux
H
H
O
CCl_3
^tBu



C1
C3
C2
1
:
22
3.70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30
C2 Major
C2 Minor
24
:
1
1.10 1.05 1.00 0.95 0.90 0.85 0.80 0.75 0.70
1.00
21.78
61.53
2.60
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0


N2
Cl
N
O
CCl3
+
Rh2[R-3,5-di(p-tBuC6H4)TPCP]4
reflux
H
H
O
O
Cl
N
CCl3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C3
C2
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3.75 3.70 3.65 3.60 3.55 3.50 3.45 3.40
C2 Major
C2 Minor
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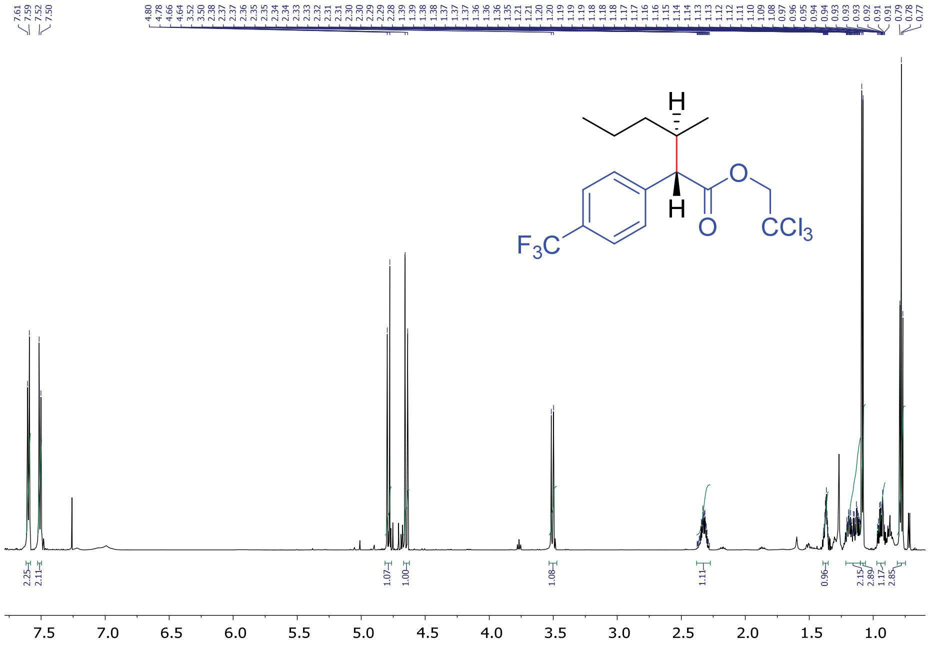
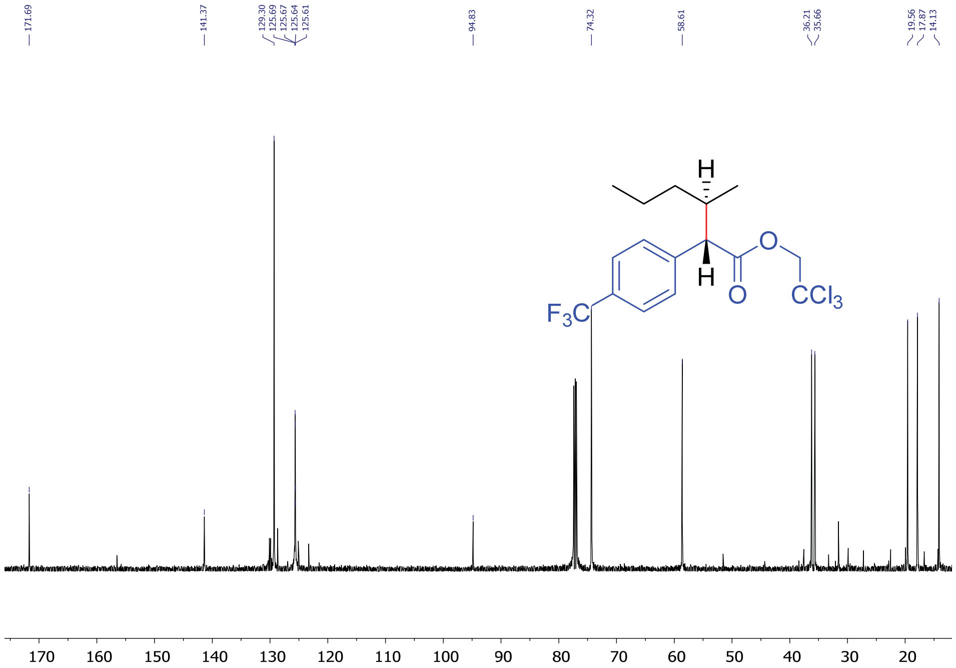
1.00
28.13
87.09
1.58
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0

4.2 NMR Spectra for Product Characterization

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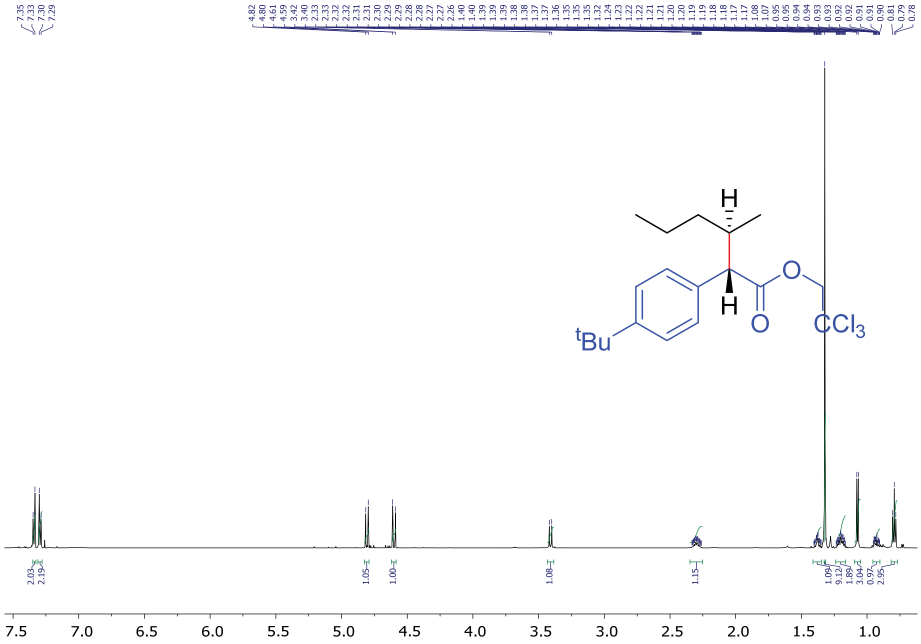
129.30
125.69
125.67
125.64
125.61
94.83
74.32
58.61
36.21
35.66
19.56
17.87
14.13
H
H
O
O
F_3C
CCl_3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20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1.36
1.35
1.35
1.35
1.32
1.24
1.23
1.22
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1.21
1.21
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1.19
1.18
1.18
1.17
1.17
1.08
1.07
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0.95
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0.93
0.93
0.93
0.92
0.92
0.91
0.91
0.90
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0.79
0.78
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H
O
O
CCl_3
^tBu
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2.19
1.05
1.00
1.08
1.15
1.09
9.12
1.89
3.04
0.97
2.95
7.5
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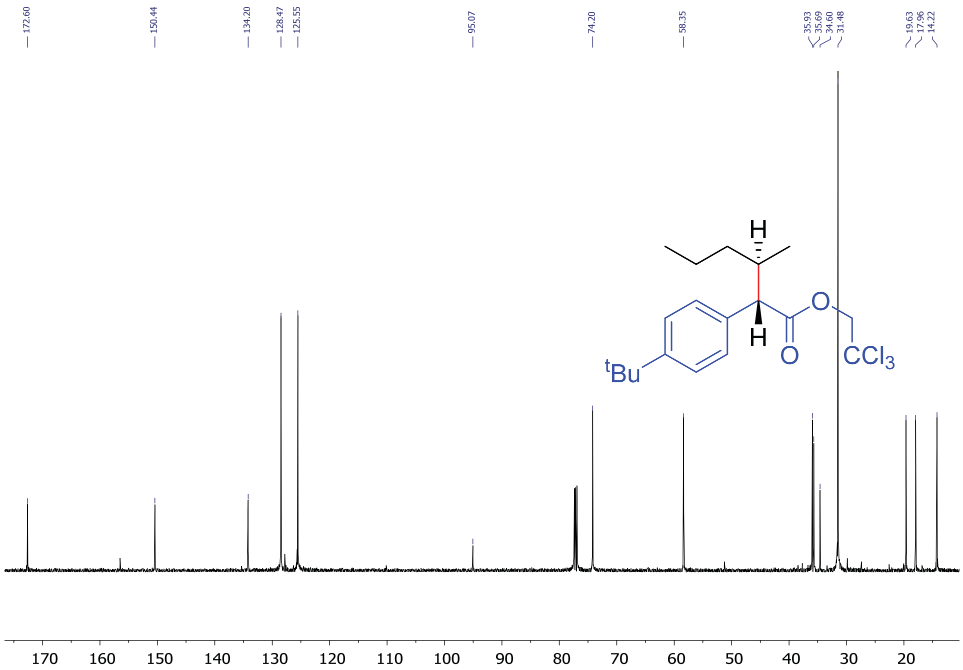
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H
H
O
O
CCl3
tBu
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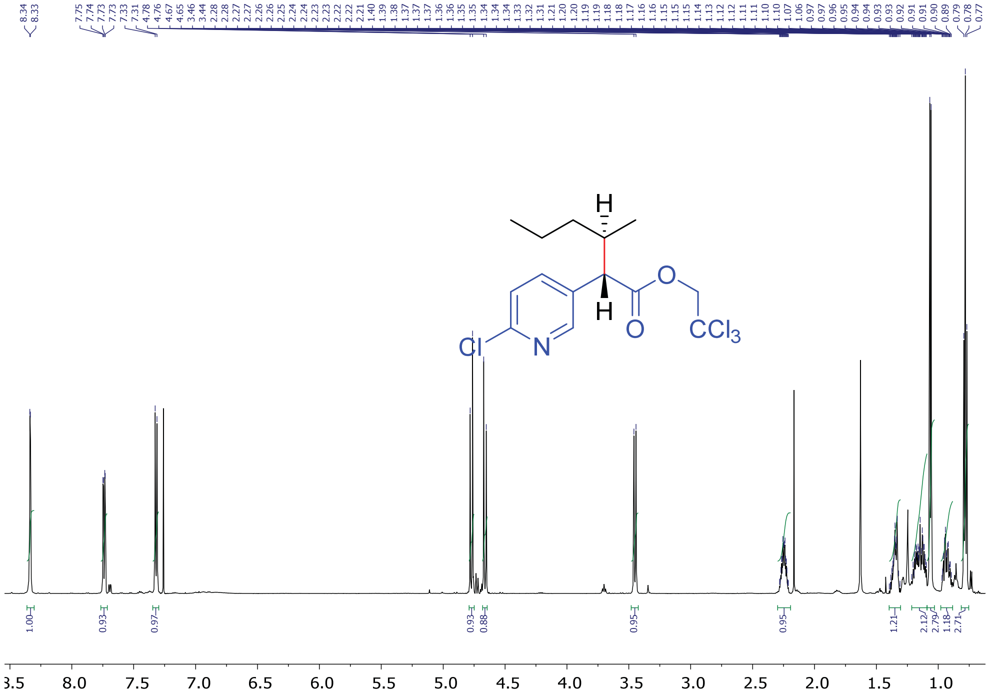
150
140
130
120
110
100
90
80
70
60
50
40
30
20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2.27
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2.24
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1.15
1.15
1.14
1.13
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H
O
O
CCl3
Cl
N
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7.0
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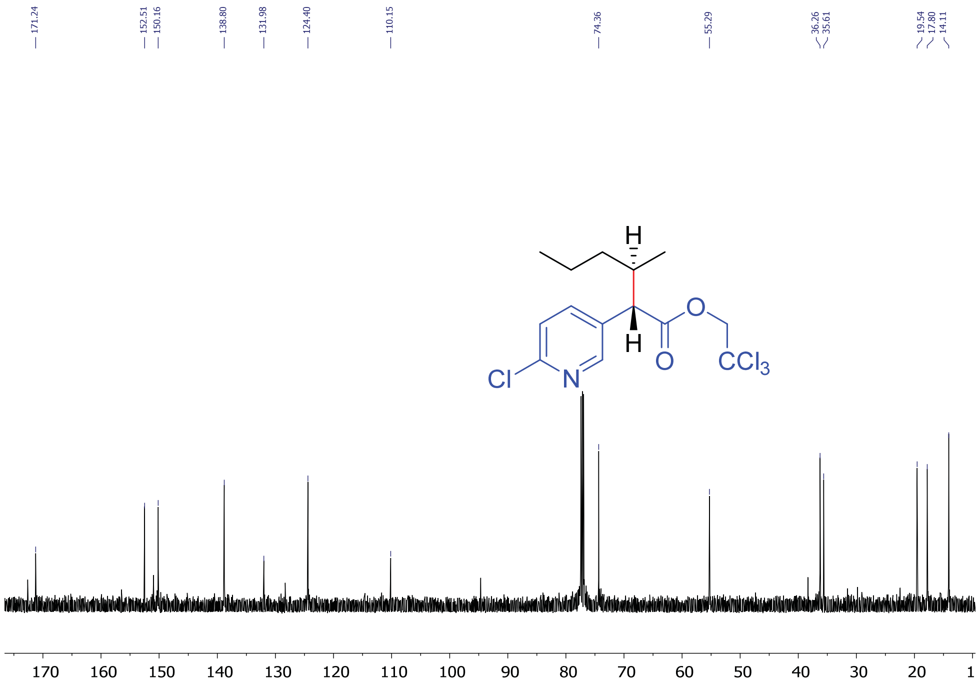
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Cl
N
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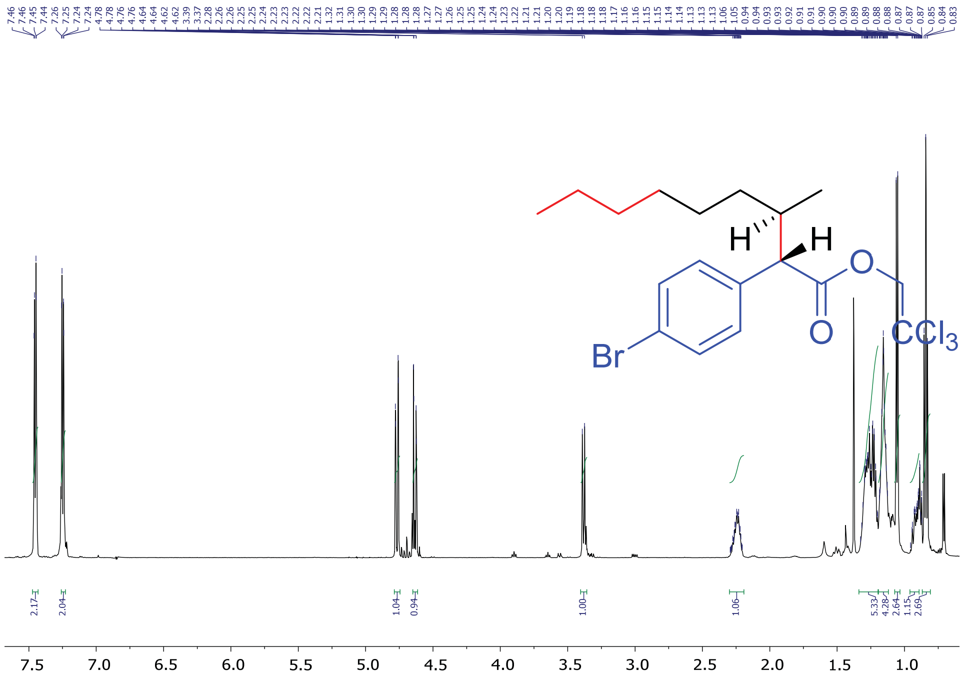
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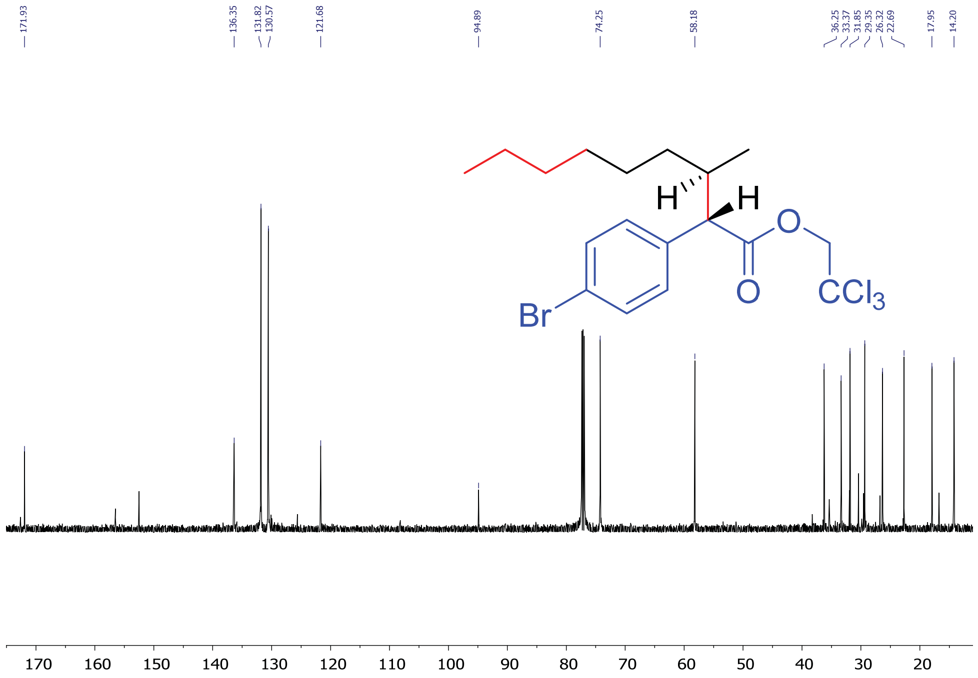
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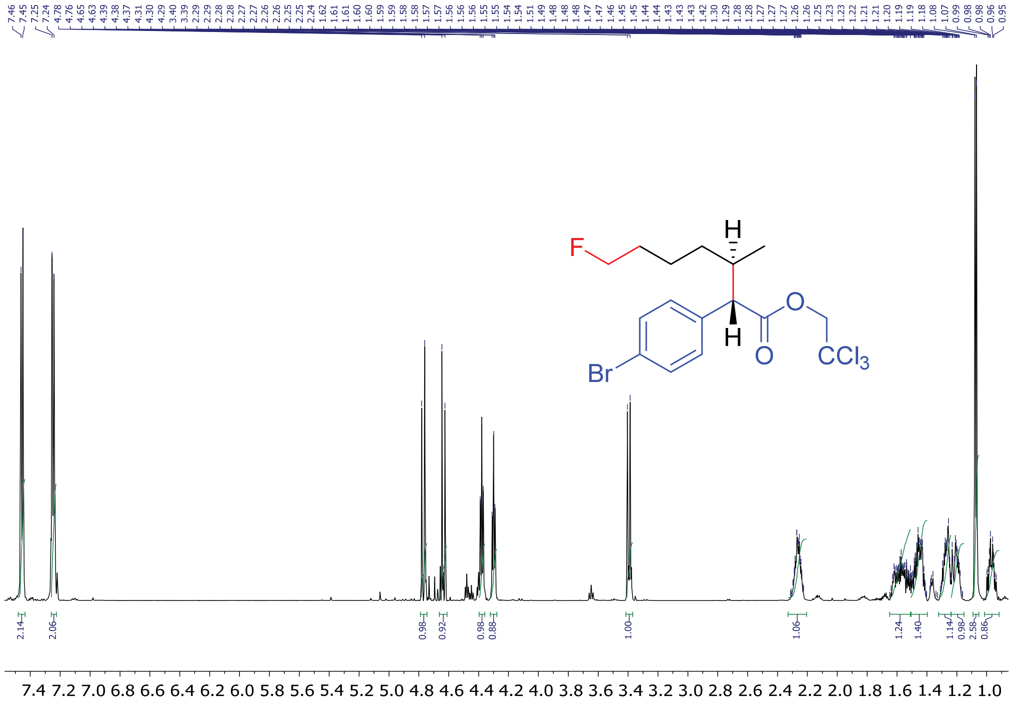
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0.98
0.88
1.00
1.06
1.24
1.40
1.14
0.98
2.58
0.86
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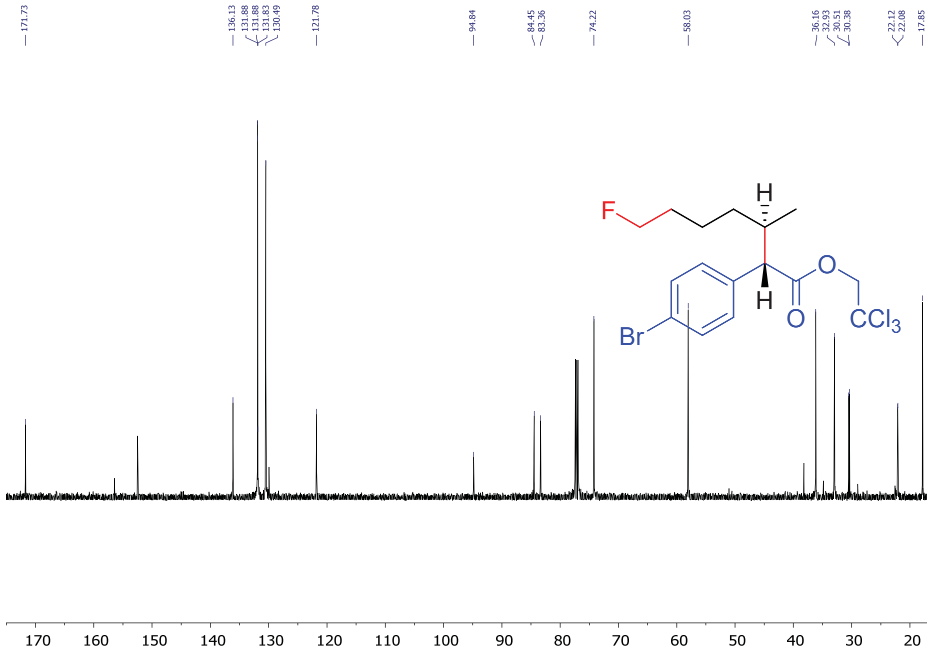

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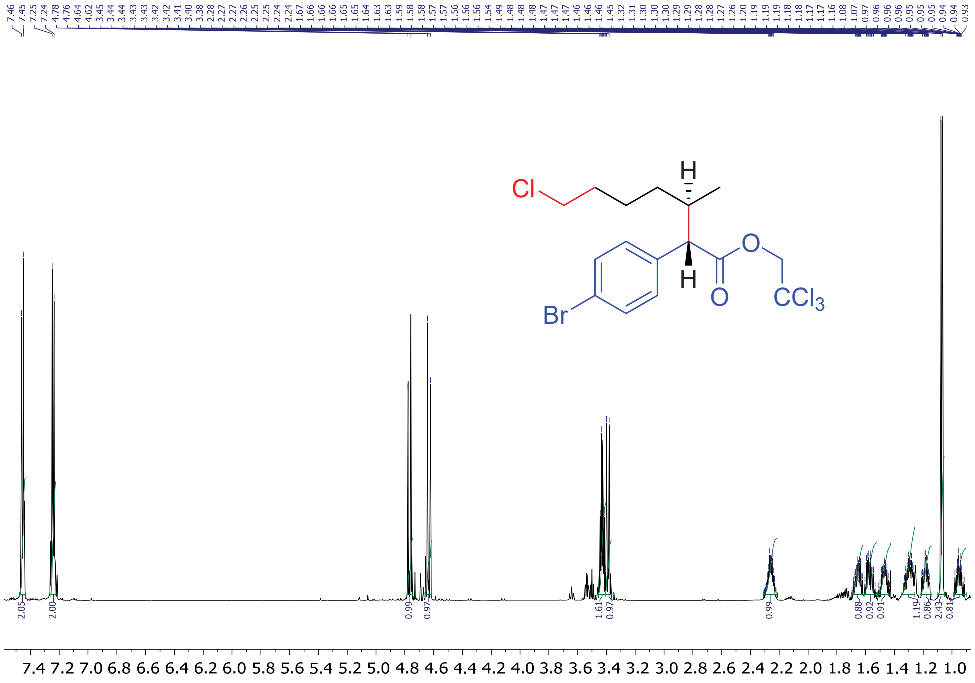
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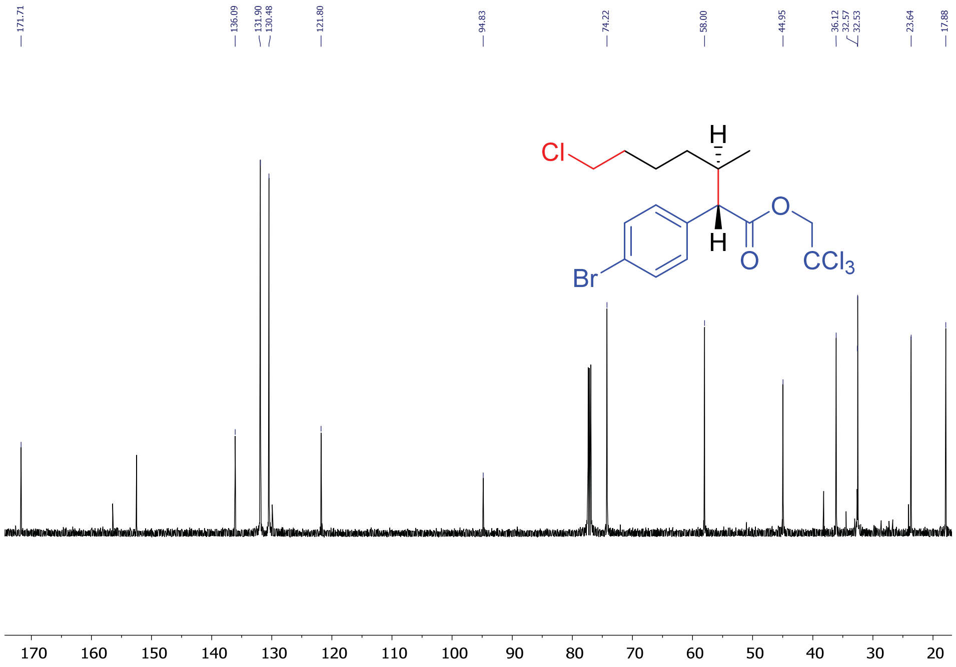
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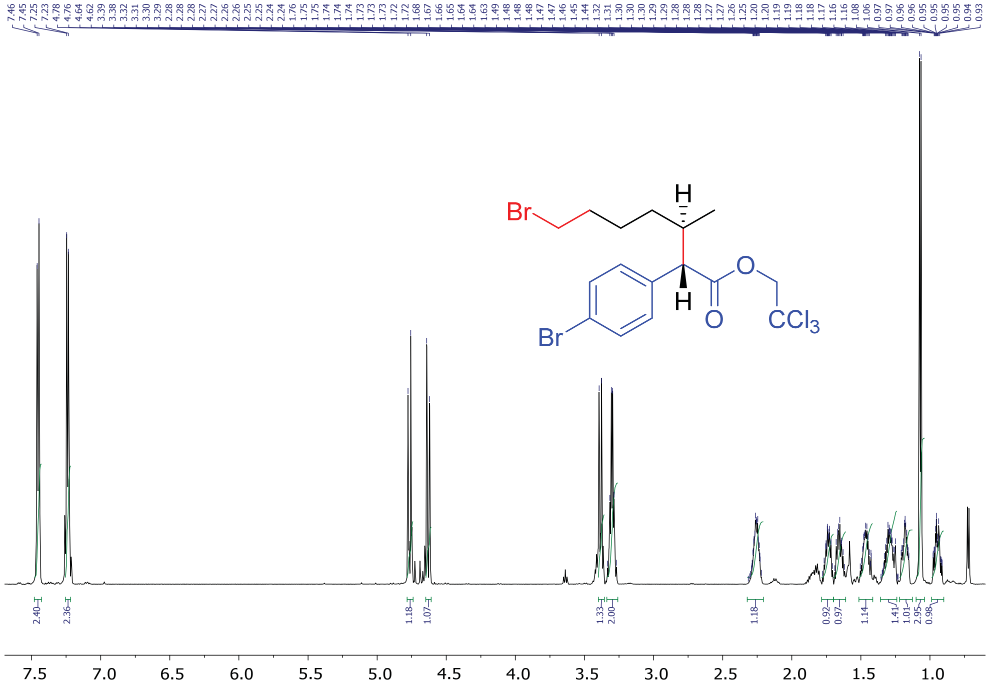
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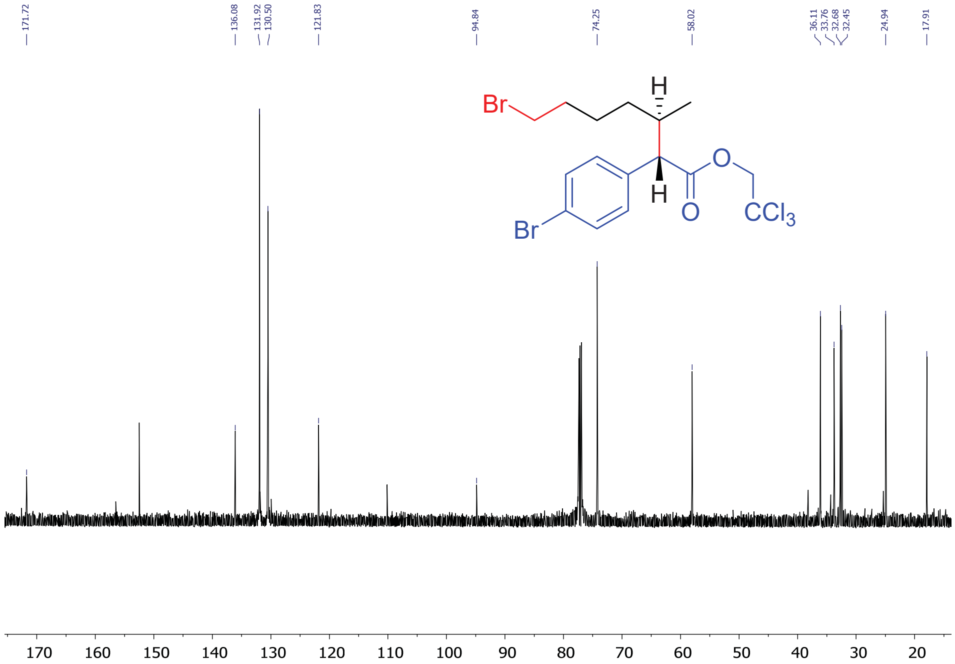
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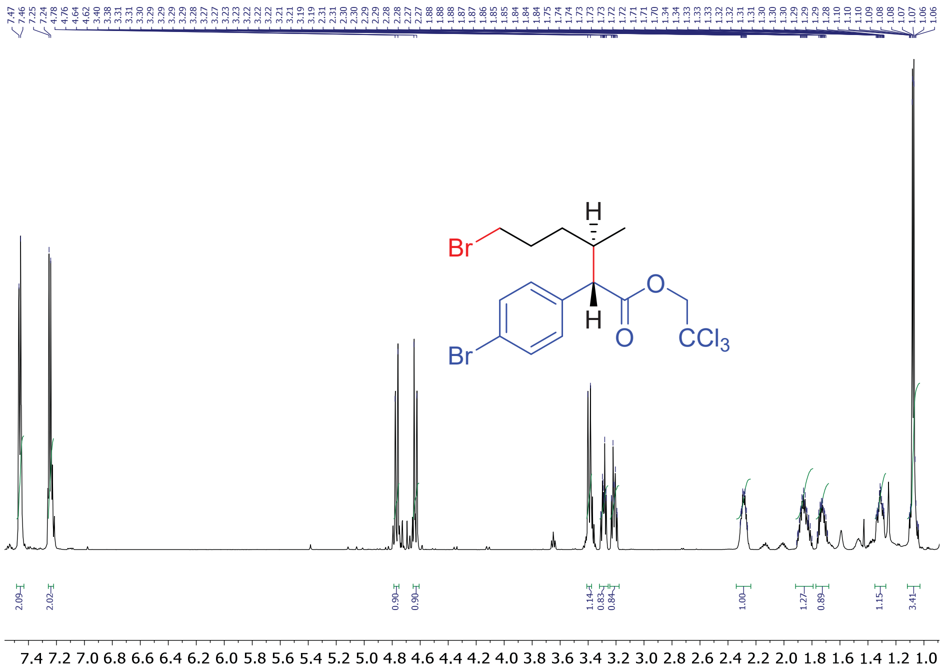
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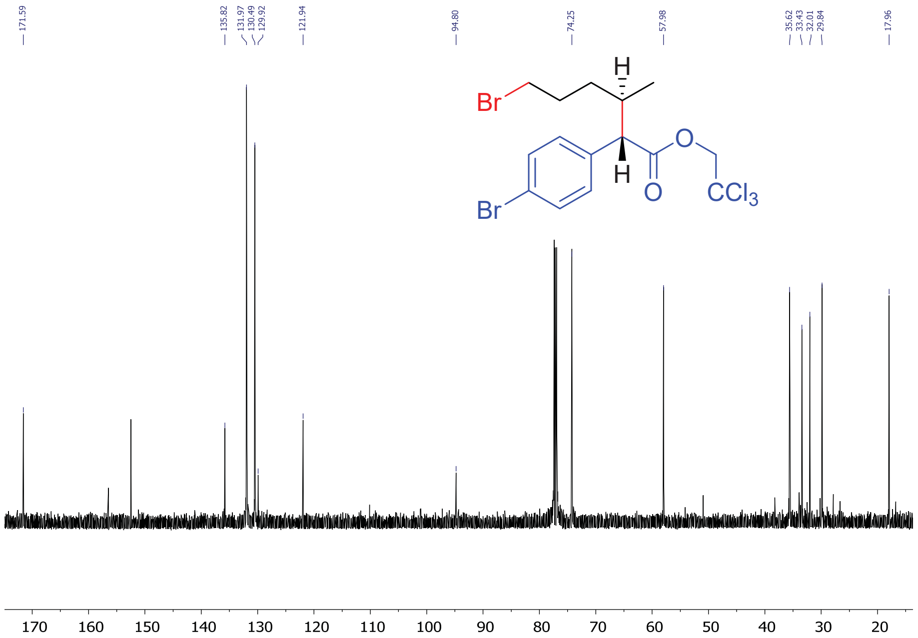
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Br
Br
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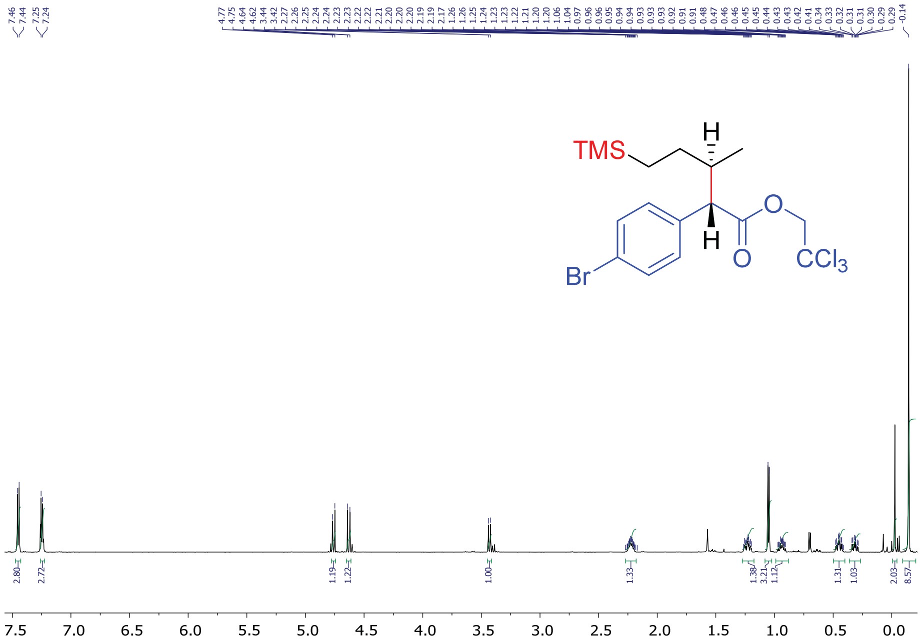
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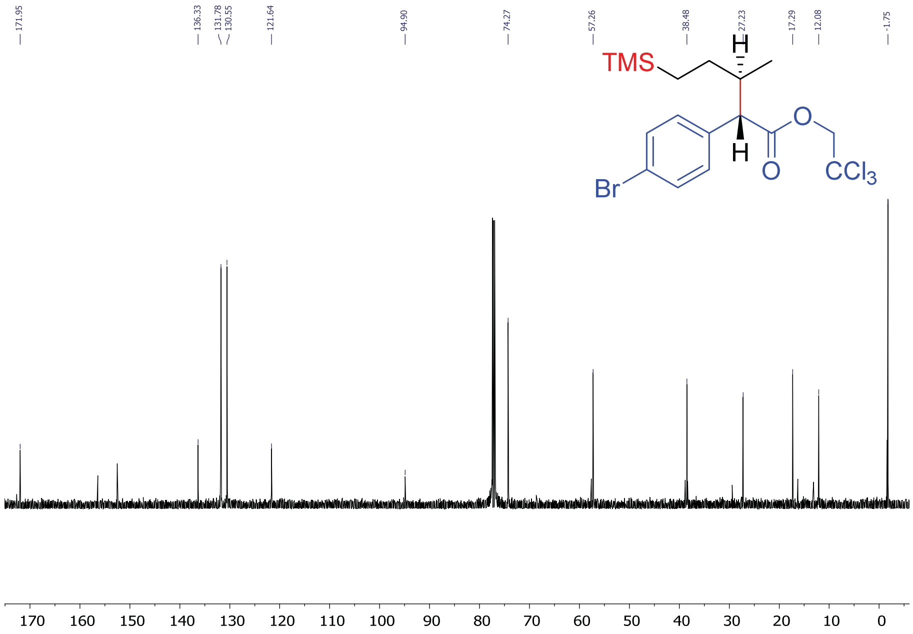
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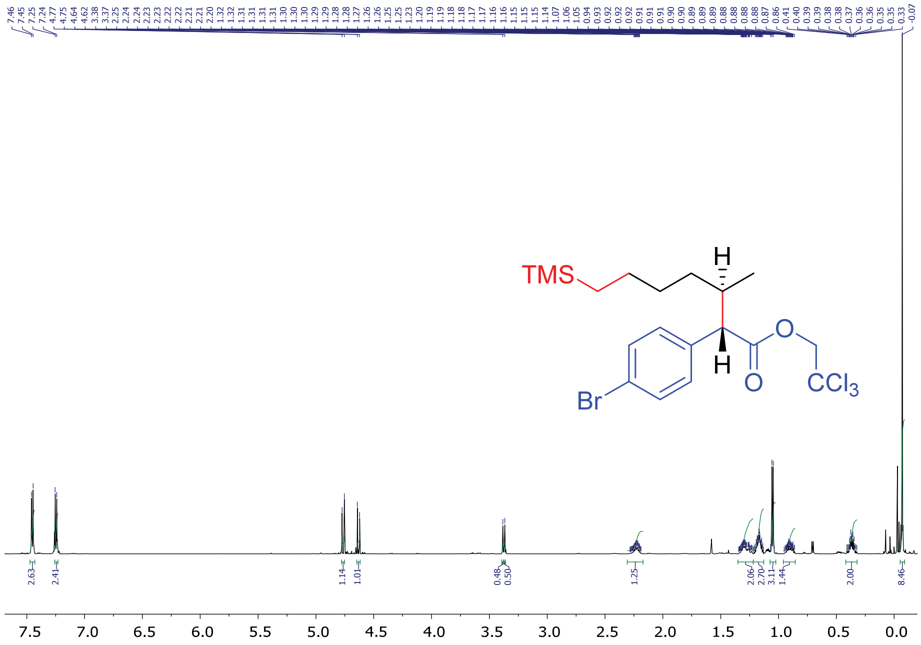
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0.33
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O
CCl_3
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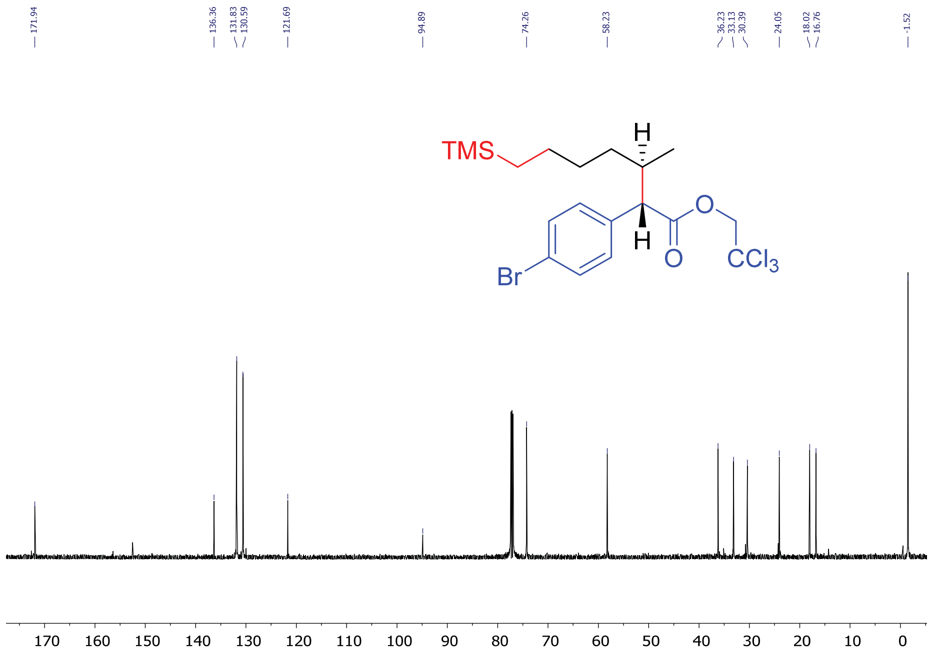
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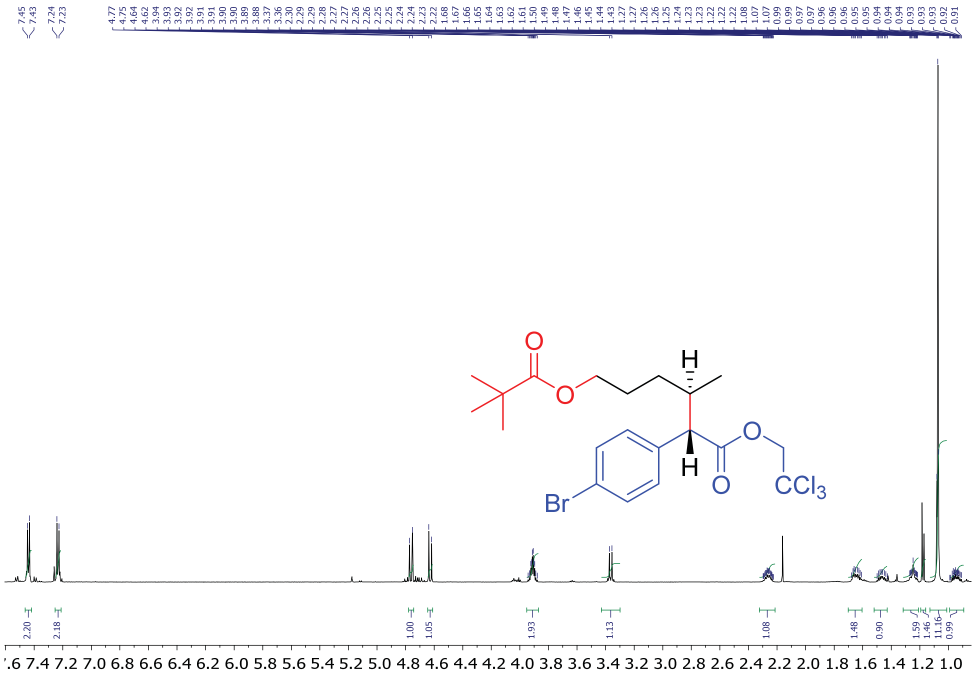
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Br
CCl3
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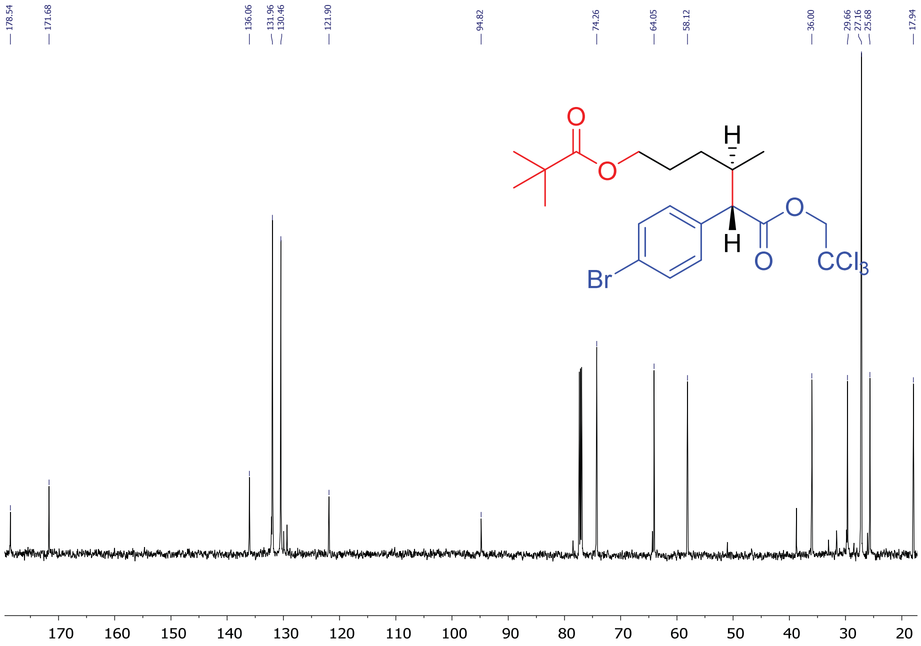
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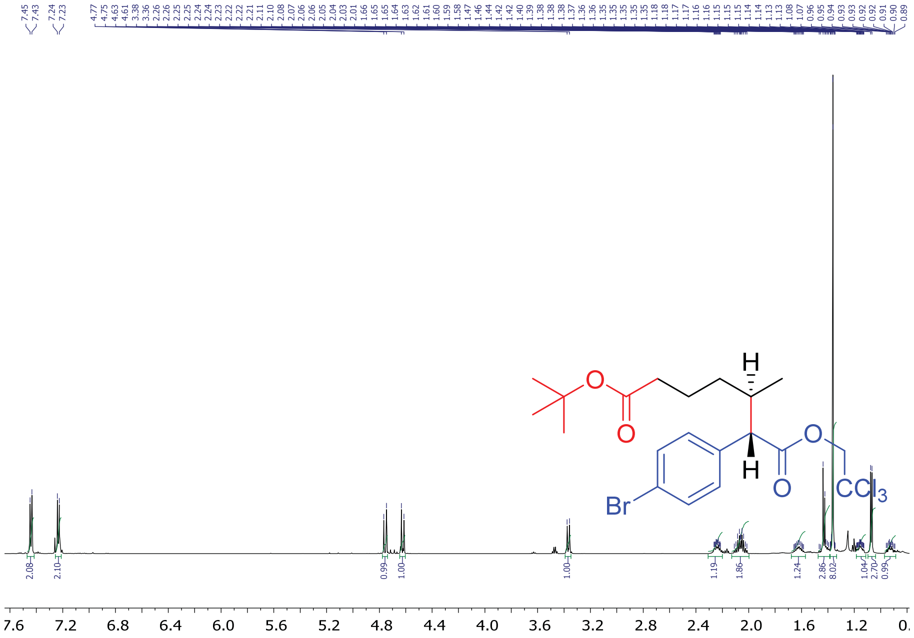
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O
Br
CCl3
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1.00
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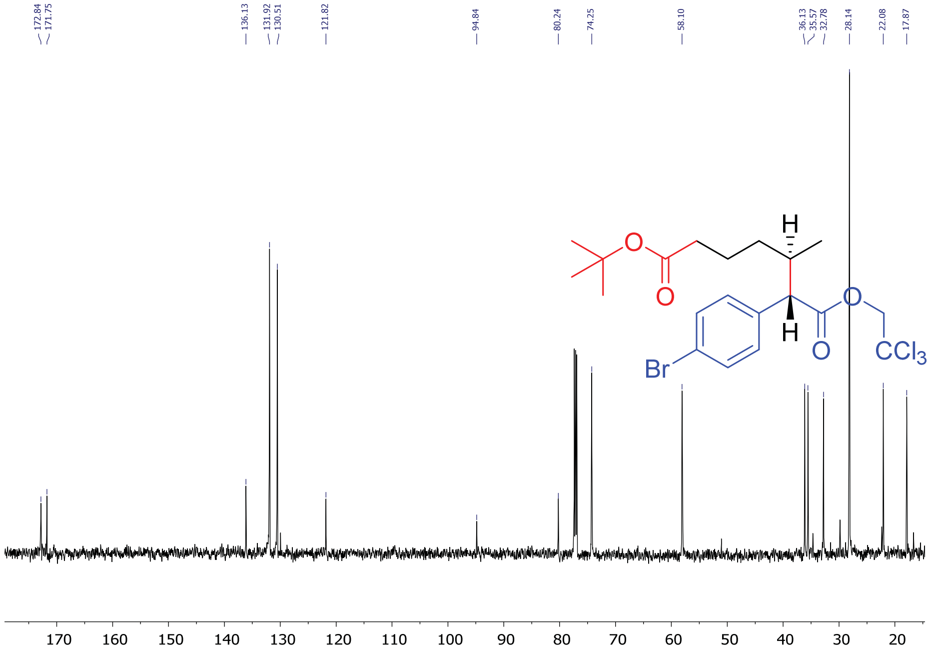
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22.08
17.87
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Br
CCl3
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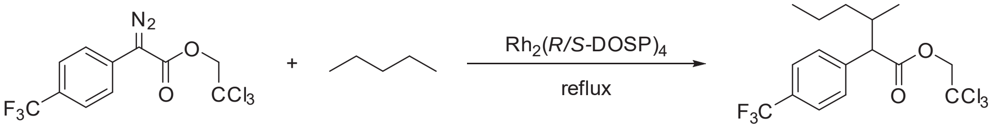
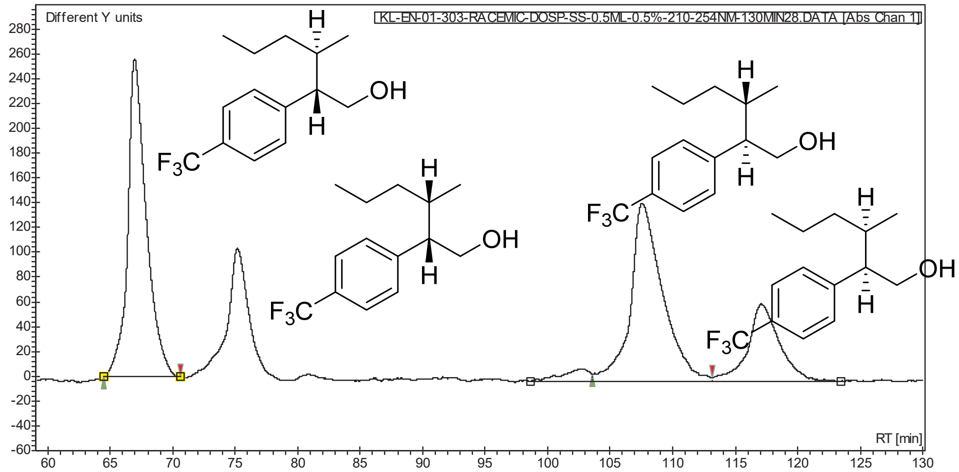
4.3 HPLC Spectra for Substrate Screen





#	Time [Min]	Area % [%]
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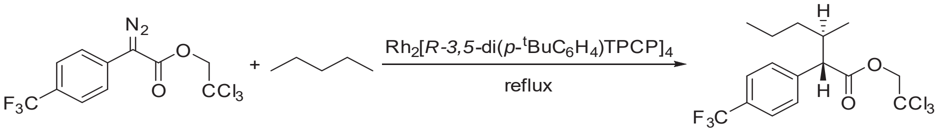

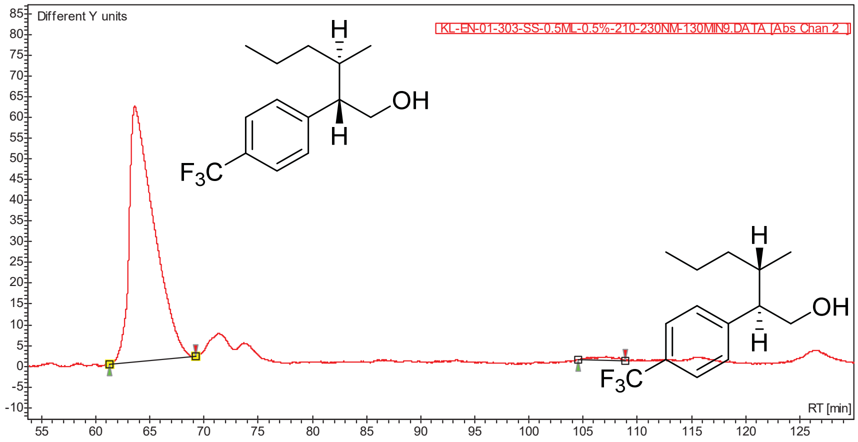

#	Time [Min]	Area % [%]
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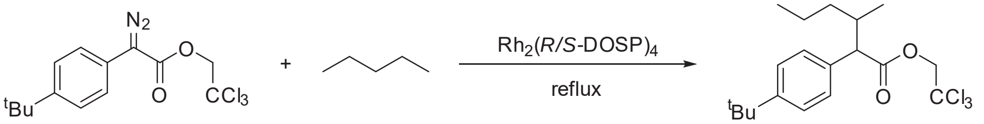
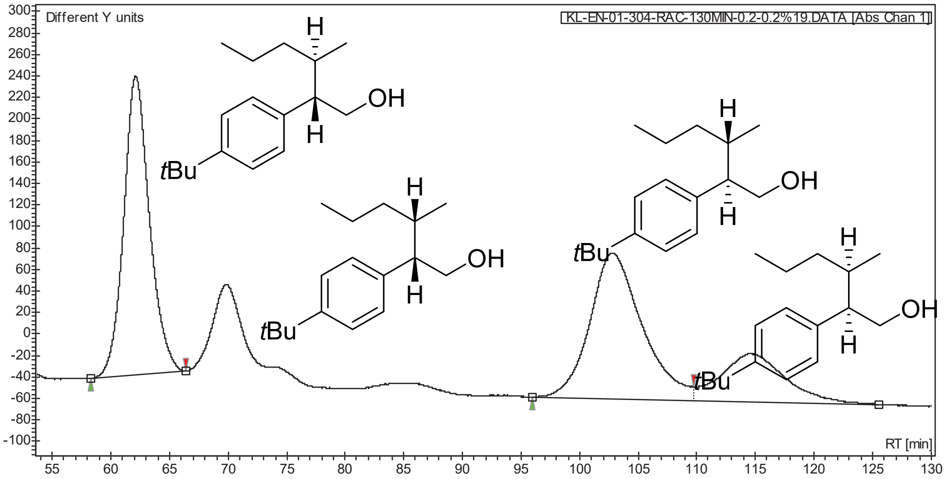
97% e.e.





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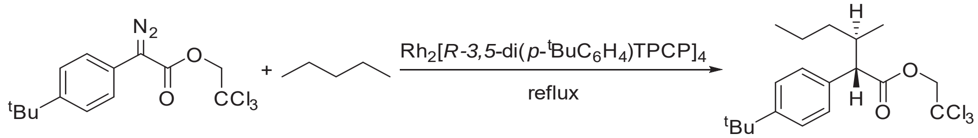

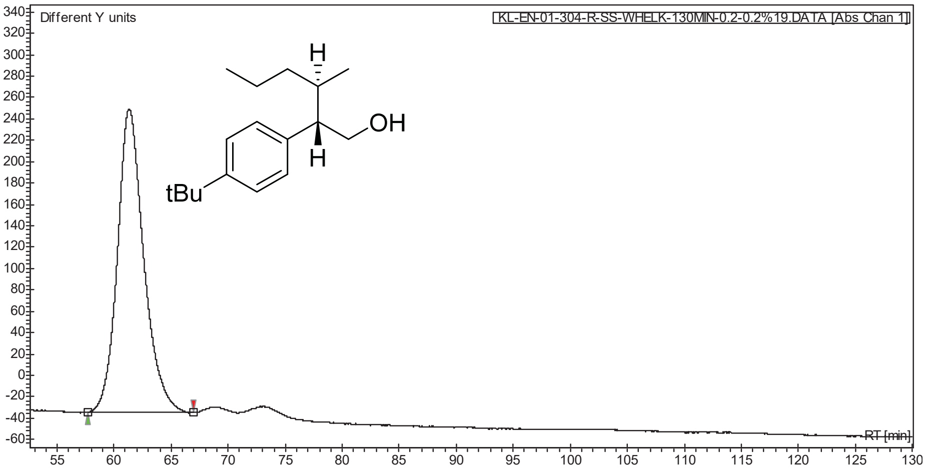

#	Time [Min]	Area % [%]
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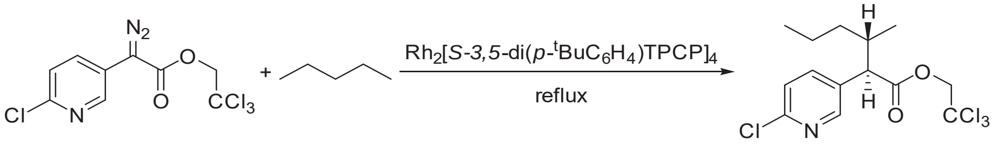
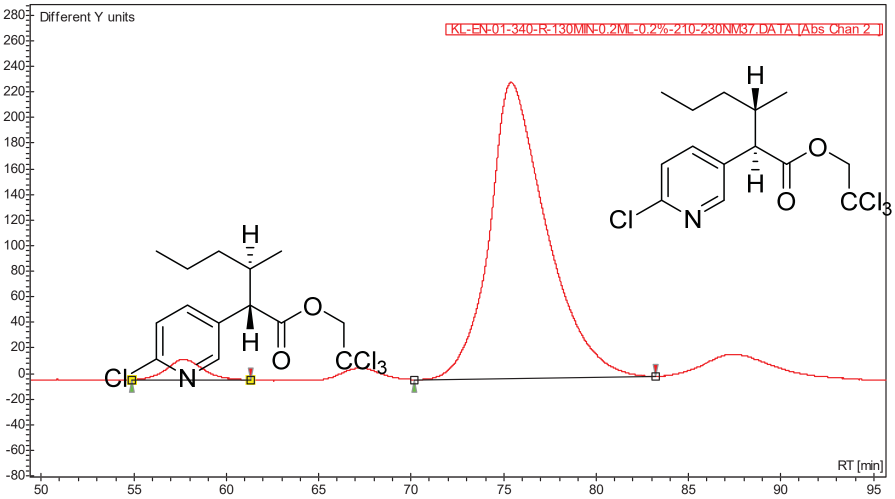
>99% e.e.





#	Time [Min]	Area % [%]
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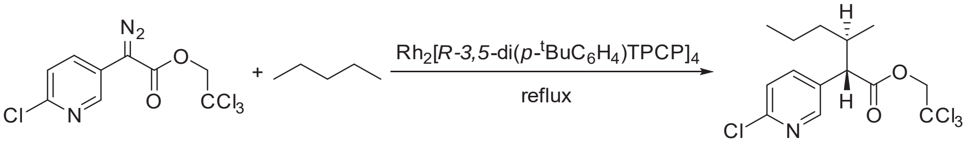
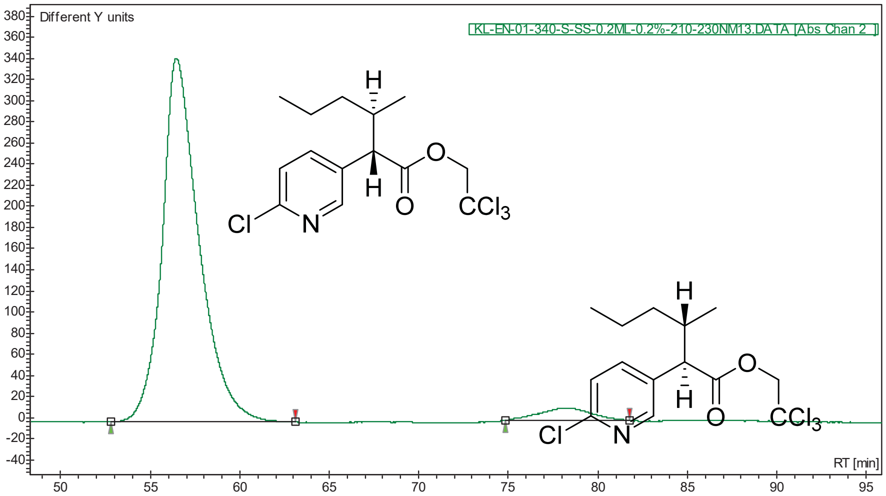
91% e.e.





#	Time [Min]	Area % [%]
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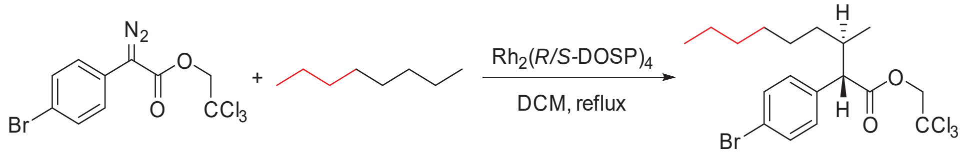
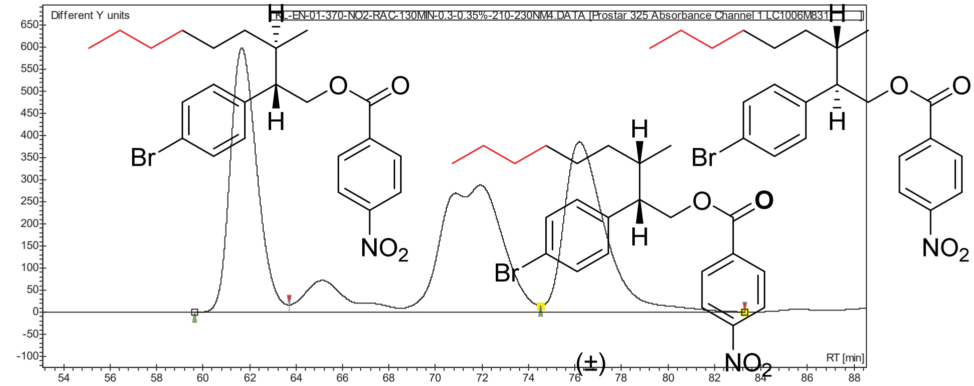
2	78.41	4.668

91% e.e.





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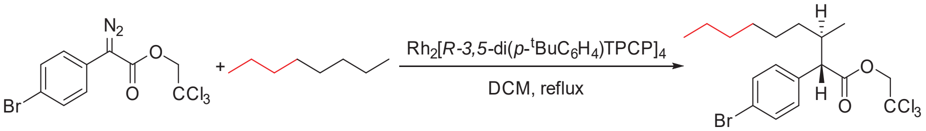
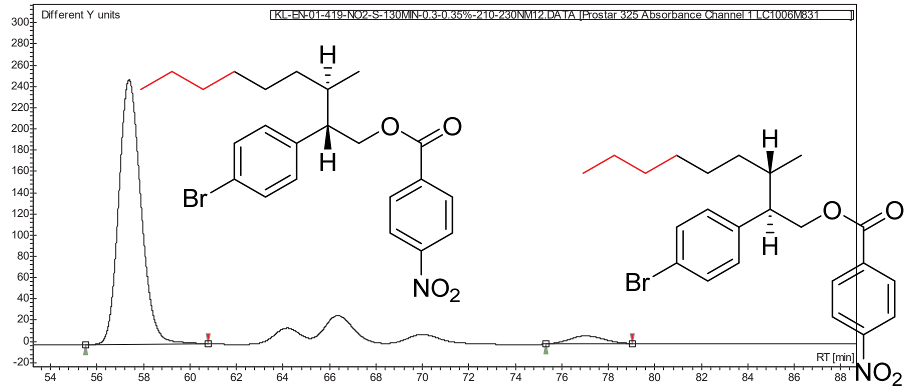
2	76.19	49.705





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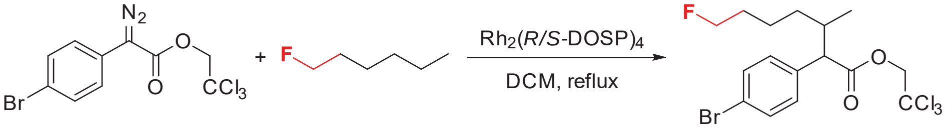
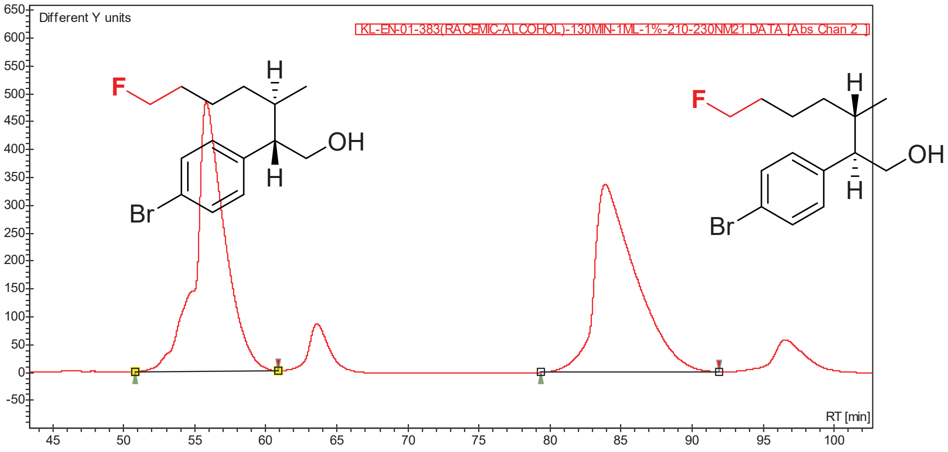
2	76.98	4.432

91% e.e.





#	Time [Min]	Area % [%]
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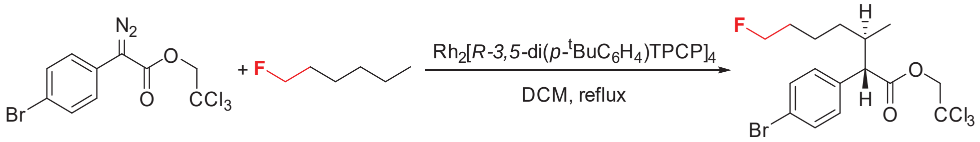
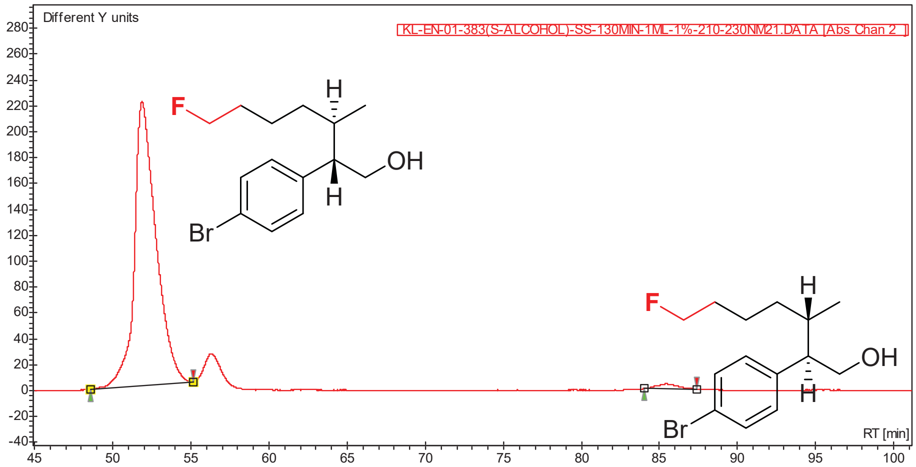
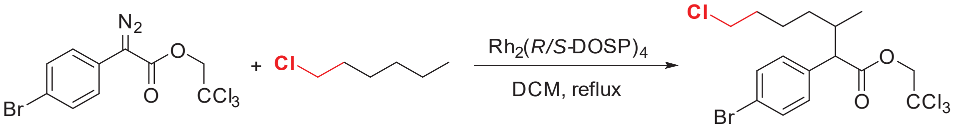
2	83.90	49.594

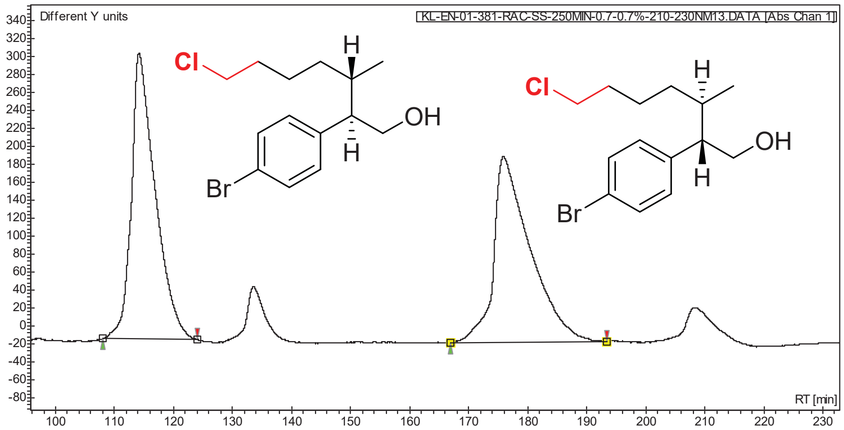




#	Time [Min]	Area % [%]
1	51.88	98.290
2	85.44	1.710

97% e.e.





#	Time [Min]	Area % [%]
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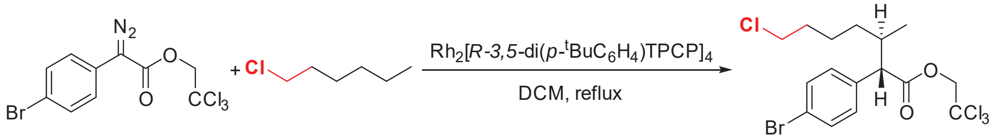
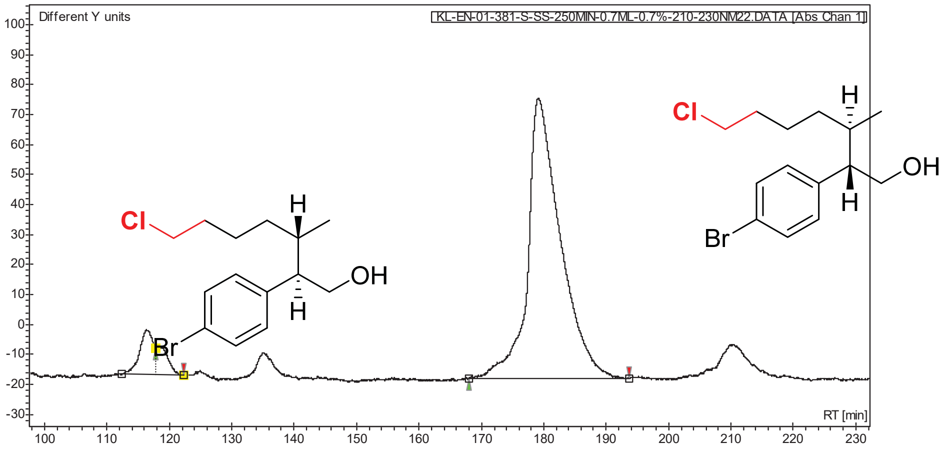
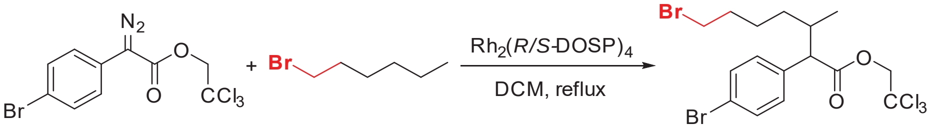
2	175.93	49.711

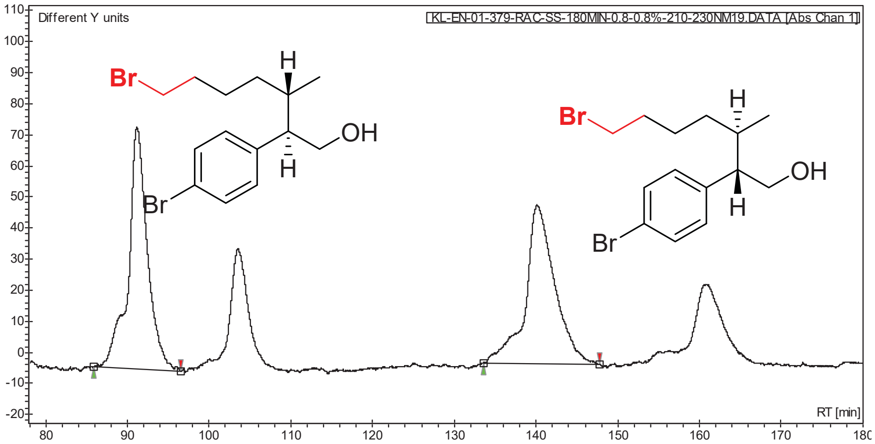




#	Time [Min]	Area % [%]
1	118.73	3.531
2	179.12	96.469

93% e.e.





#	Time [Min]	Area % [%]
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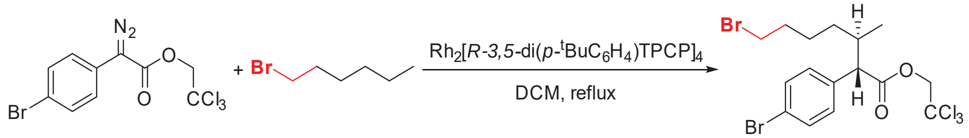
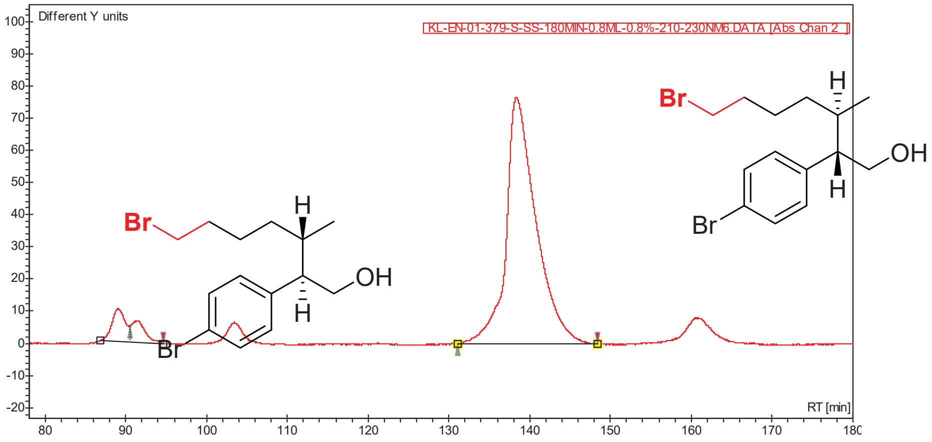
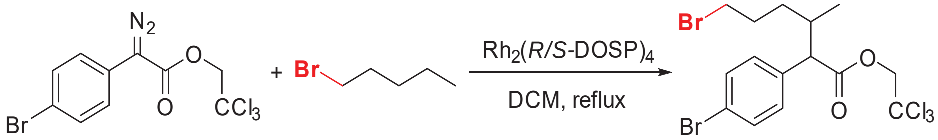
2	140.09	49.877

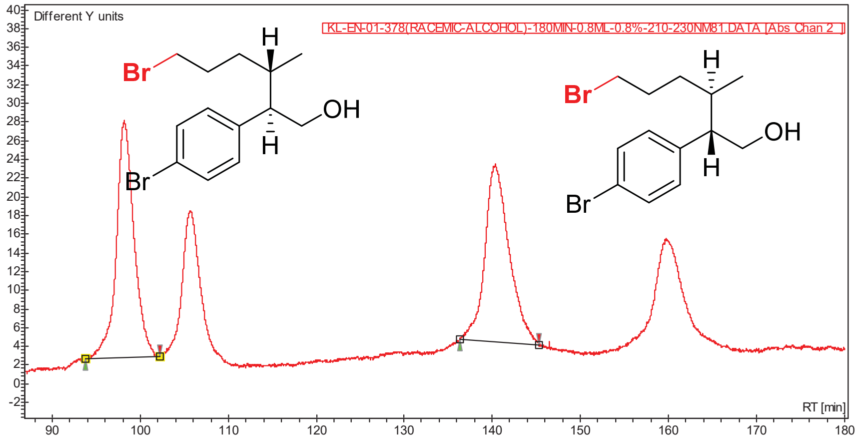




#	Time [Min]	Area % [%]
1	91.43	3.928
2	138.33	96.072

92% e.e.





#	Time [Min]	Area % [%]
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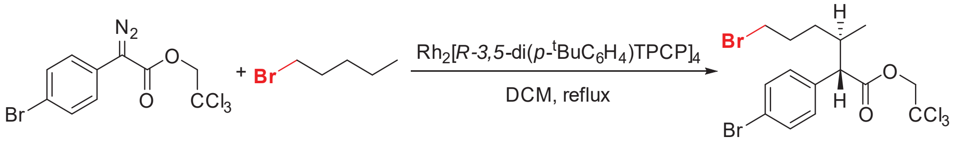
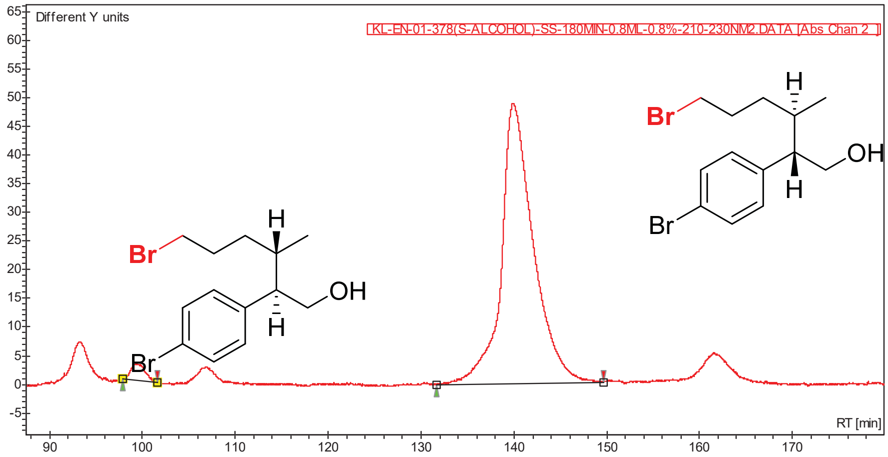
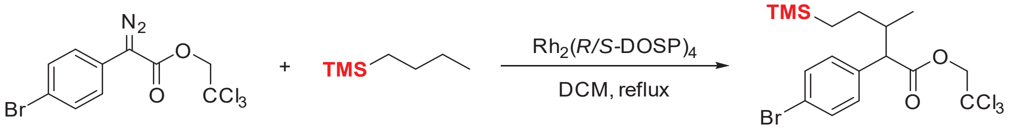
2	140.33	50.537

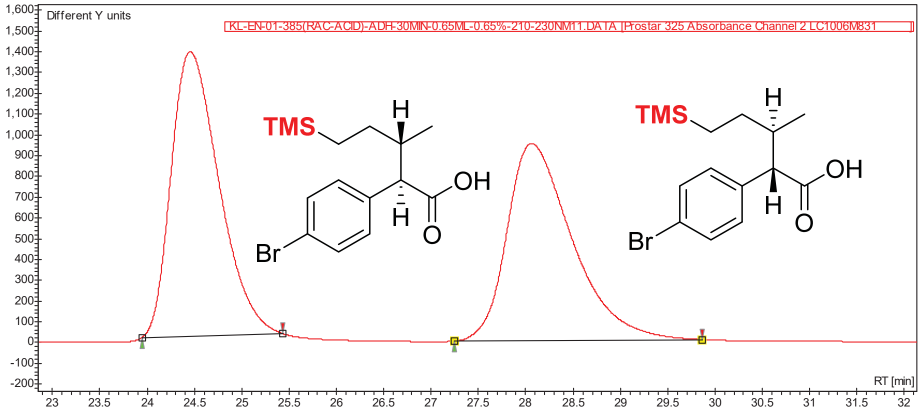




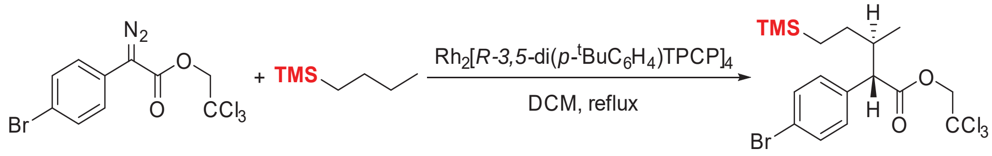
#	Time [Min]	Area % [%]
1	99.44	2.673
2	139.86	97.327

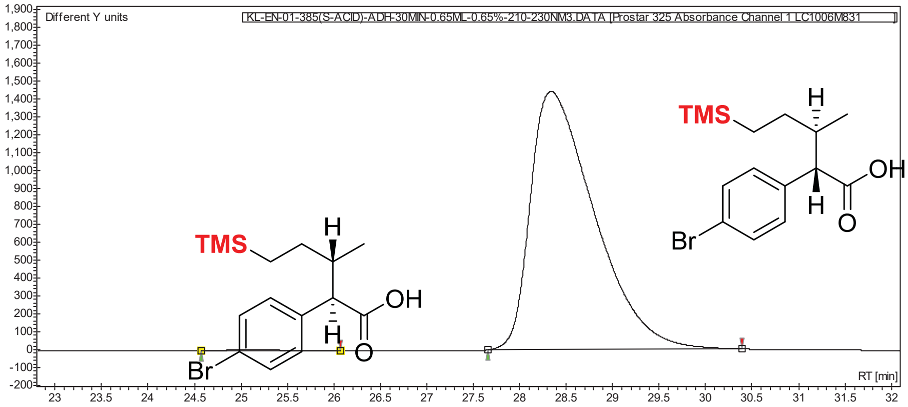
95% e.e.





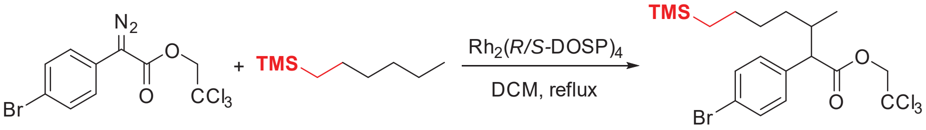
#	Time [Min]	Area % [%]
1	24.46	51.350
2	28.06	48.650

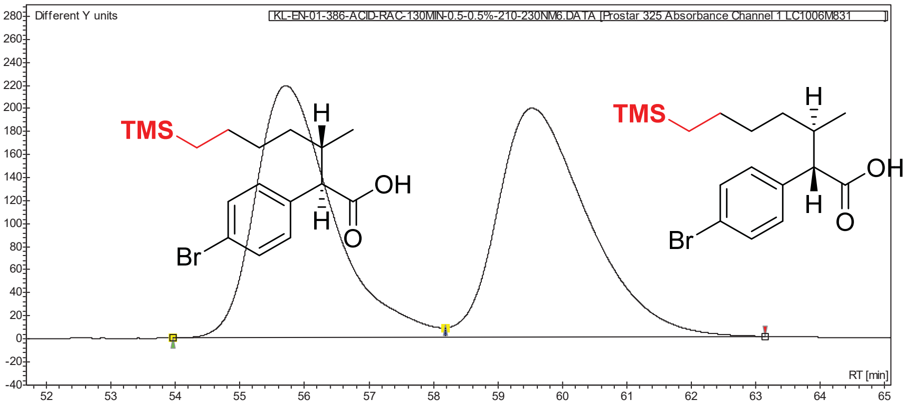




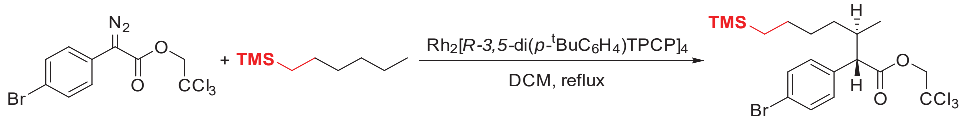
#	Time [Min]	Area % [%]
1	25.10	0.164
2	28.34	99.836

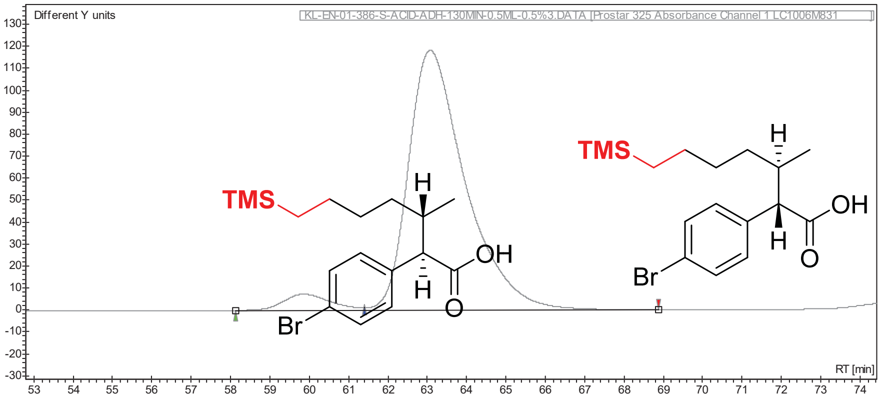
>99% e.e.





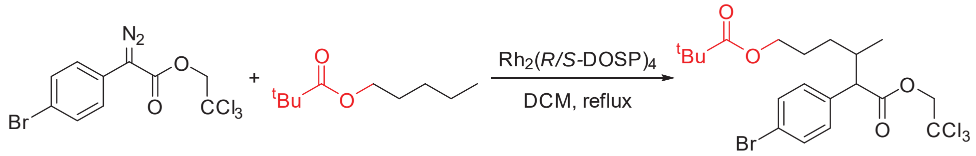
#	Time [Min]	Area % [%]
1	55.71	48.693
2	59.53	51.307

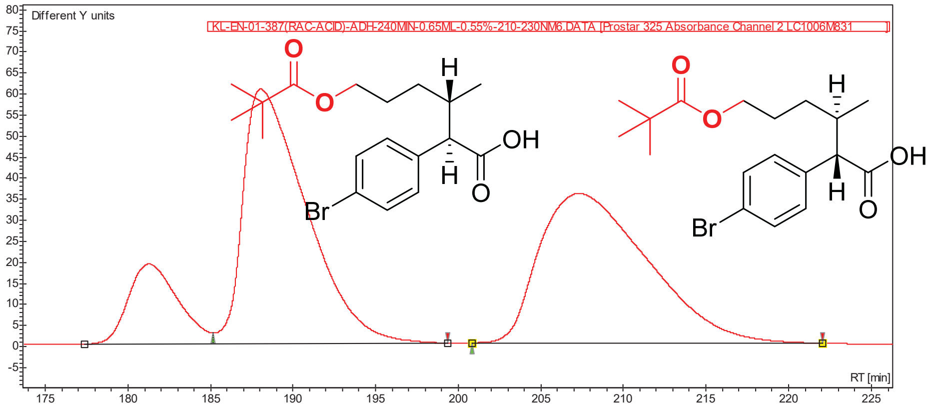




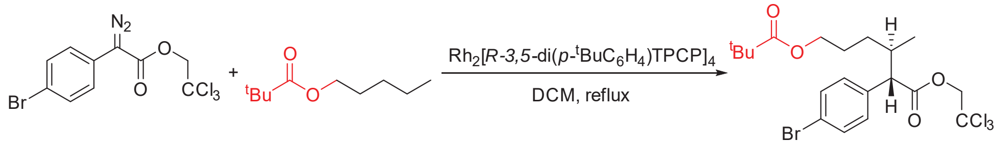
#	Time [Min]	Area % [%]
1	59.86	4.917
2	63.07	95.083

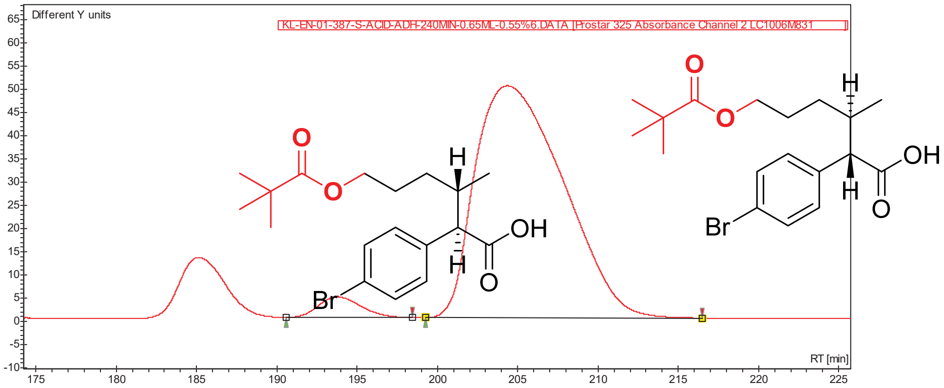
90% e.e.





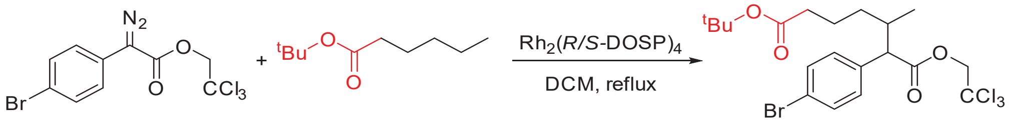
#	Time [Min]	Area % [%]
1	188.04	49.951
2	207.40	50.049

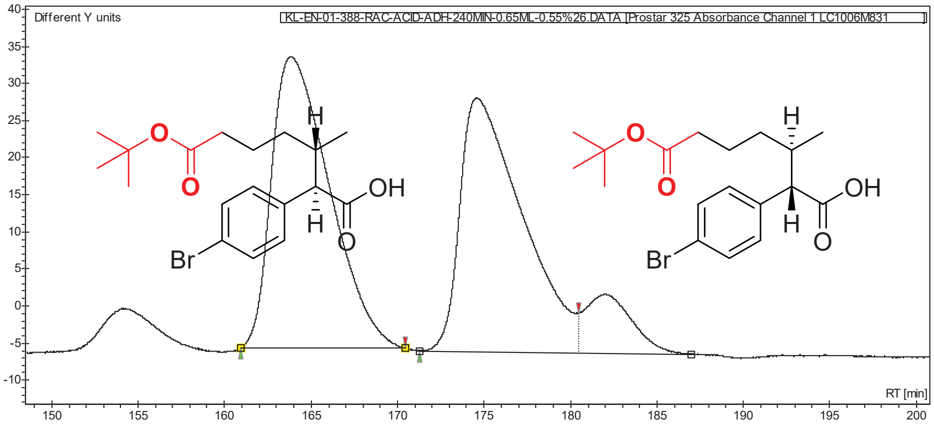




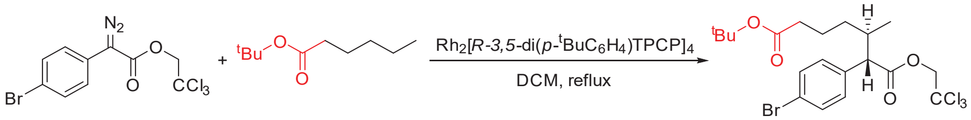
#	Time [Min]	Area % [%]
1	193.75	4.166
2	204.34	95.834

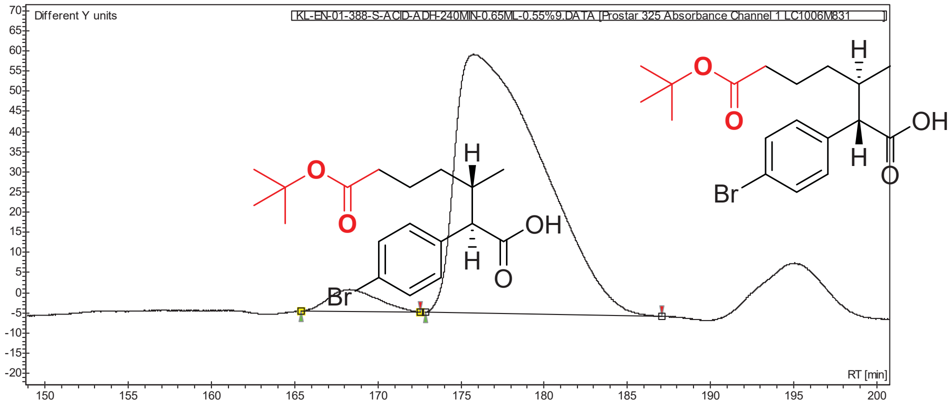
92% e.e.





#	Time [Min]	Area % [%]
1	163.85	51.634
2	174.57	48.366





#	Time [Min]	Area % [%]
1	168.28	4.651
2	175.74	95.349

91% e.e.

SI-Chapter 5 Selective Functionalization of the Most Accessible Primary C-H bond

1. General Considerations

1.1 Equipment and Methods

^{1}H and ^{13}C NMR spectra were recorded at either 500 MHz (^{13}C at 126 MHz) or 600 MHz (^{13}C at 151 MHz) on INOVA-500 or Bruker-600 spectrometer, as indicated. NMR spectra were run in solutions of deuterated chloroform ($CDCl_3$) with residual chloroform taken as an internal standard (7.26 ppm for ^{1}H, and 77.16 ppm for ^{13}C), and were reported in parts per million (ppm).

Abbreviations for signal multiplicity are as follow: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, etc. Coupling constants (*J* values) were calculated directly from the spectra. IR spectra were collected on a Nicolet iS10 FT-IR spectrometer. Mass spectra were taken on a Thermo Finnigan LTQ-FTMS spectrometer with APCI, ESI or NSI. Thin layer chromatographic (TLC) analysis was performed with glass-backed silica gel plates, visualizing with UV light (254 nm) and/or staining with aqueous $KMnO_4$ stain.

1.2 Solvents for Reaction

The dichloromethane(CH_2Cl_2) used for the carbene transformations was dried at reflux over calcium hydride in a 250mL round-bottom flask for 12 hours under argon, then distilled and stored under argon atmosphere and then used directly.

1.3 Substrates and Reagents

The substrates and reagents were purchased from the following suppliers and used without further purification:

Acros: 2-Methylbutane (1 LT, 99+% purity).

Sigma-Aldrich: 3-Methylpentane (1 LT, ≥99% purity); 2,2-Dimethylbutane (100 mL, ≥99% purity); 3,3-Dimethylpentane (5 g, 99% purity); 2,2-Diethyl-1,3-propanediol (100 g, ≥99% purity); 1-Bromobutane (500 mL, 99% purity); (*S*)-(+)-1-Bromo-2-methylbutane (1g, >99% purity); (*S*)-(-)-2-Methylbutanol (10g, ≥99% purity); (*S*)-(+)-2-Pentanol (5g, 98% purity).

Alfa-Aesar: 2-Methylpentane (100 mL, 99+% purity); 3-Ethyl-3-hexanol (5g, 98% purity).

TCI: 3-Ethyl-3-methylpentane (5 mL, >99% purity); 2,2-Dimethylpentane (5 mL, 97% purity); 3,3-Dimethylhexane (1 mL, >99% purity); 3-Ethyl-3-pentanol (10 mL, ≥99% purity); 2-Methyl-2-propyl-1,3-propanediol (25 g, >98% purity);

The following reagents were prepared according to reported procedures [20-23]:

Methyl 2-(4-bromophenyl)-2-diazoacetate; 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate; 2,2,2-trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate; 2,2,2-tribromoethyl 2-(4-bromophenyl)-2-diazoacetate.

2. General Procedures for C–H Functionalization Reactions

A 5-mL flask was equipped with a reflux condenser and an octagonal magnetic stir bar. The flask was charged with Rh_2L_4 (0.002 mmol, 1 mol%) and treated by vacuum/argon to replace the air in the flask to argon. Substrate (0.6 mmol, 3 *equiv.*) and distilled CH_2Cl_2 (0.5 mL) were added, then the catalyst/substrate solution was heated to reflux under argon for 5 minutes. Diazo (0.2 mmol, 1.0 *equiv.*) was dissolved in 3 mL of distilled CH_2Cl_2 and then the diazo solution was added dropwise to the catalyst solution over 6h with a syringe pump under reflux condition and argon atmosphere. After addition, 0.5 mL distilled CH_2Cl_2 was used to dilute the left over diazo in the syringe needle and then the diazo solution was added dropwise to the reaction solution. Then the rest of the diazo solution in the syringe needle was further pushed into the reaction solution. Then the reaction mixture was allowed to stir for another 1 min, then the reaction mixture was transferred into a 25-mL round-bottom flask with diethyl ether (5 mL x 3) and concentrated under vacuum, and crude ^{1}H NMR spectrum was obtained to analyze the reaction and measure the selectivity. Then the crude was purified by flash chromatography on silica gel to obtain the product.

3. General Procedure for Data Analysis

3.1 Regioisomeric Ratios (r.r.) and Diastereomeric Ratios (d.r.) Determination

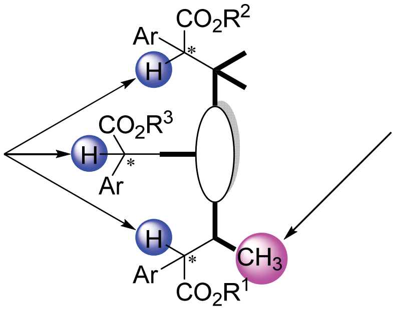
To measure the regioisomeric ratios and diastereomeric ratios, the mixtures obtained as described in section 2.1 were analyzed by ^{1}H NMR using the following settings:

Instrument: 600 MHz Bruker equipped with a prodigy probe with sensitivity over 1500:1

Number of scans: 32

Relaxation time: 5 seconds

The crude ^{1}H NMR spectra data was processed using MestReNova 11.0.2 (Mestrelab Research S.L.), applying an auto-phase correction as well as a Smooth Segment baseline correction. The baseline was manually inspected before integration. The ratios were measured by integrating the ^{1}H NMR peaks resulting from the indicated hydrogens below.

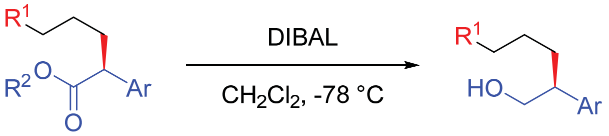


The regioisomeric ratios (*r.r.*) were measured by integrating the proton peaks of each regioisomers in the crude ^{1}H NMR spectra

The diastereoisomeric ratios (*d.r.*) were measured by integrating the proton peaks of each diastereomers in the crude ^{1}H NMR spectra

3.2 Enantiomeric Excess (e.e.) Determination

As most of the enantiomers of the C–H functionalization products were difficult to be separated on the HPLC, they were reduced to the corresponding alcohol derivatives, which will have better separation on the HPLC, without changing the *e.e.* of the products. Therefore, the *e.e.* of the products were determined from the corresponding alcohol derivatives. [4]

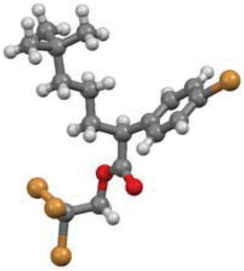


To a 25-mL round-bottom flask with a stirred solution of the ester (0.1 mmol, 1.0 *equiv.*) in CH_2Cl_2 (3 mL) was added 1 M diisobutylaluminum hydride (DIBAL) in CH_2Cl_2 (0.5 mL, 0.5 mmol, 5 *equiv.*) slowly at -78 °C. The mixture was stirred overnight and allowed to warm up to room temperature. Once the starting material was fully consumed and confirmed by TLC, the solution was cooled down to 0 °C, then methanol (0.5 mL) was added dropwise to quench the reaction and then stirred for 20 min. The reaction mixture was concentrated to dry solid mixture, then 10 mL of ethyl acetate (EA) was added into the flask to extract the organic compound. Then mixture in the flask was poured onto and filtered through a silica plug (3 *cm* height, 2 *cm* wide), and the solid residue was further extracted and washed by EA (10 mL x 4). Then the filtrate was concentrated and purified by flash column chromatography to afford the corresponding alcohol derivatives as white solid or colorless oil. The sample was dissolved in hexanes/isopropanol (5~30 mg/mL) and the *e.e.* value of the corresponding alcohol derivatives were determined on the HPLC.

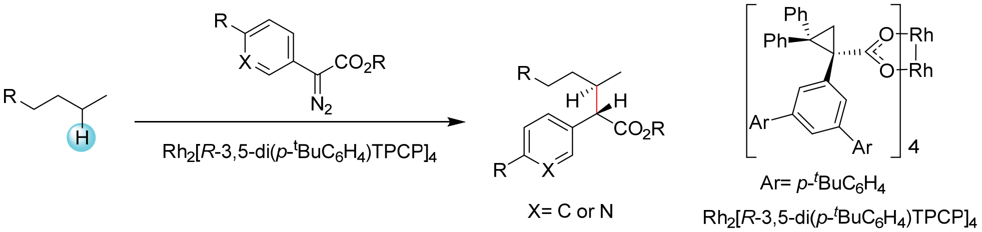
The *e.e.* of the C–H functionalization products were then obtained from the *e.e.* of the corresponding alcohol derivatives, in which the *e.e.* values were considered equal to each other.

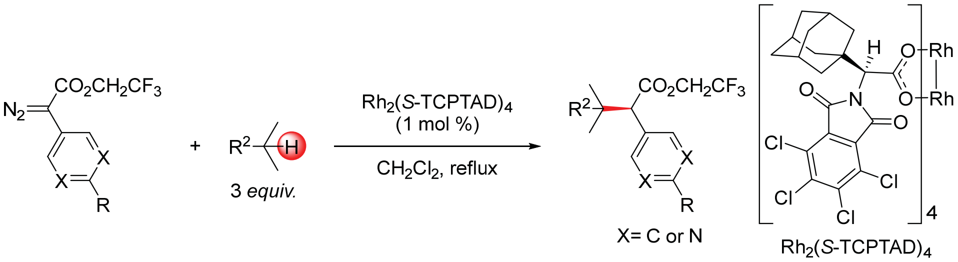
4. Absolute Stereochemistry Determination

The absolute stereochemistry of Rh2[*R*-tris(*p*-^{t}BuC6H4)TPCP]4 catalyzed primary C–H insertion reaction of 2,2-dimethylpentane was determined by the X-Ray single crystal structure analysis of product **11** (see section 10 for detail), the absolute stereochemistry of the secondary C–H insertion products were determined by the known asymmetric induction of Rh2[*R*-3,5-di(*p*-^{t}BuC6H4)TPCP]4,[4] and the absolute stereochemistry of the tertiary C–H insertion products were determined by the known asymmetric induction of Rh2(*S*-TCPTAD)4,[5] Based on these data, the absolute stereochemistry of the rest of the reactions were tentatively assigned accordingly.



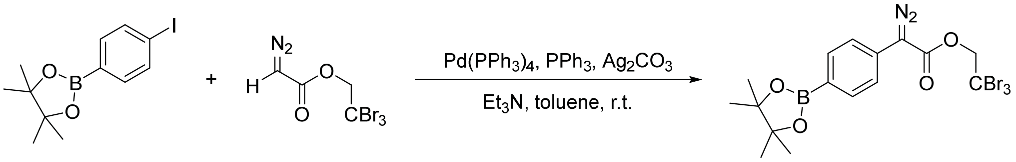
The single crystal X-ray structure of **11**





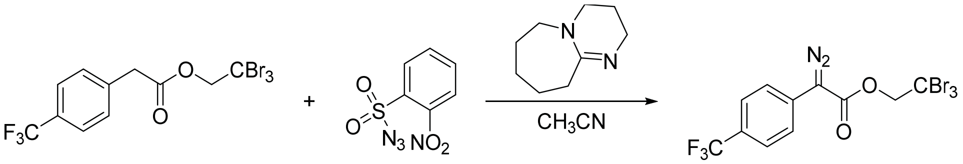
5. Diazo Compounds Preparation

5.1 Procedure



2,2,2-Tribromoethyl 2-diazo-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetate. 2-(4-Iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.0 g, 6.0 mmol, 1.0 *equiv.*), tetrakis(triphenylphosphine)palladium(0) [Pd(PPh$_3$)$_4$] (347 mg, 0.30 mmol, 0.05 *equiv.*), triphenylphosphine (PPh$_3$) (157 mg, 0.6 mmol, 0.1 *equiv.*), silver carbonate (Ag$_2$CO$_3$) (827 mg, 3.0 mmol, 0.5 *equiv.*) and triethylamine (Et$_3$N) (789 mg, 7.8 mmol, 1.3 *equiv.*) were suspended in toluene (20 mL) in a round-bottomed flask under nitrogen. Then 2,2,2-trichloroethyl 2-diazoacetate (2.74 g, 7.8 mmol, 1.3 *equiv.*) was added. After stirring at r.t. for 12 h, the mixture was filtered through a short silica plug (3 *cm* height, 2 *cm* wide), eluting with ethyl acetate. The solvents were removed under reduced pressure and the crude residue was purified by column chromatography on silica gel eluting with gradient diethyl ether/hexanes (1% to 5%) to give the diazo as a yellow solid in 20% yield (663 mg).

TLC (diethyl ether: hexanes, 1:9 *v/v*); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.83 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 8.3 Hz, 2H), 5.10 (s, 2H), 1.35 (s, 12H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 162.90, 135.43, 129.08, 127.74, 122.83, 84.47, 83.89, 35.81, 24.87; HRMS (NSI) calcd for $C_{16}H_{19}O_4BBr_3$ ([M-N$_2$+H]$^-$): 522.8932 found 522.8930; IR (neat): 2978, 2095, 1752, 1717, 1608, 1399, 1359, 1270, 1166, 1143, 1090, 857.

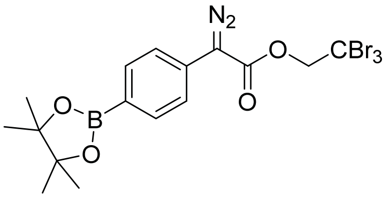


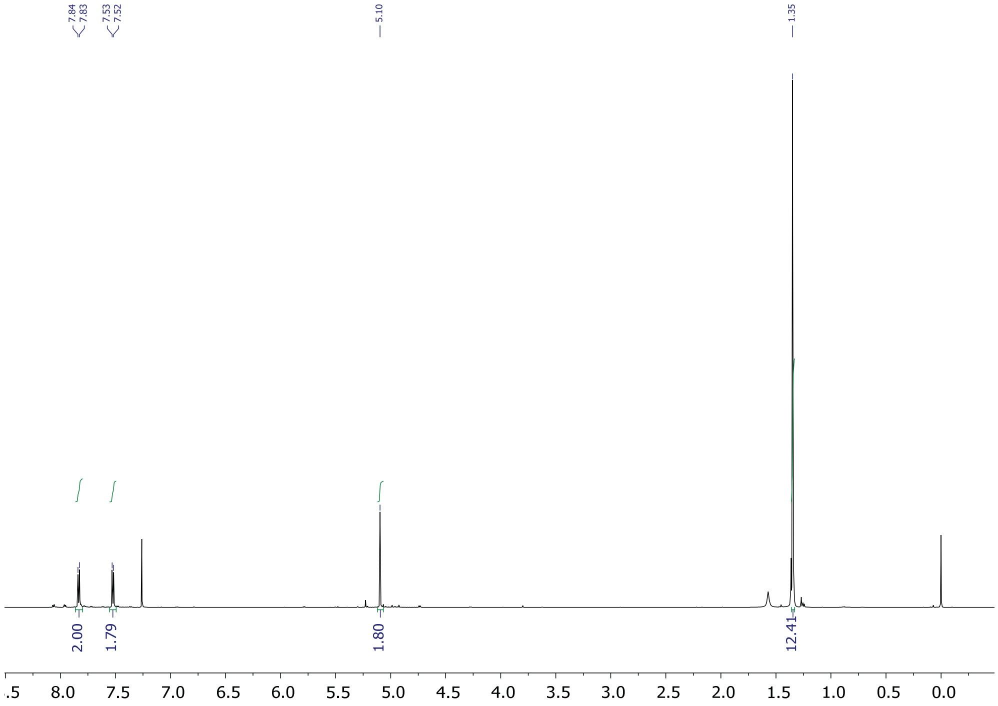
2,2,2-Tribromoethyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate. A 100-mL three-necked flask is equipped with a 100-mL dropping funnel, a rubber septum fitted with argon inlet needle and an egg-shaped in magnetic stir bar. 1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU) (457 mg, 3 mmol, 1.5 equiv.) in CH$_3$CN (60 mL) is added to the dropping funnel.

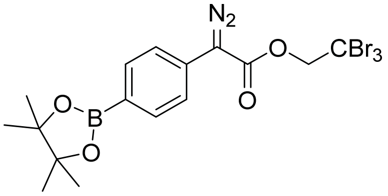
The flask is charged with 2,2,2-tribromoethyl 2-(4-(trifluoromethyl)phenyl)acetate (938 mg, 2 mmol, 1.0 equiv.), 2-nitrobenzenesulfonyl azide (593 mg, 2.6 mmol, 1.3 equiv.) and CH_3CN (120 mL). The DBU solution is added dropwise into reaction mixture. The resulting mixture is stirred over 12 h, and reaction progress is monitored by TLC analysis. The reaction mixture is cooled with an ice bath, and saturated aqueous NH_4Cl (100 mL) is then added to quench the reaction. The mixture is extracted with ethyl ether (3 x 100 mL), and the combined organic layers are washed with saturated brine (150 mL), dried over sodium sulfate (10 g) and concentrated by rotary evaporation to afford the crude product. Column chromatography purification of the crude product over silica gel affords the diazo compounds as an orange solid in 85% yield (541 mg).

TLC (diethyl ether: hexanes, 1:9 *v/v*); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (s, 4H), 5.11 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.58, 130.66, 129.41, 128.21 (q, J = 32.8 Hz), 126.13 (q, J = 3.8 Hz), 124.11 (q, J = 271.8 Hz), 123.70, 35.69.; HRMS (NSI) calcd for $C_{11}H_6O_2N_2Br_3F_3$ ($[M]^-$): 491.7937 found 491.7941; IR (neat): 2095, 1712, 1616, 1372, 1322, 1234, 1113, 1071, 1015, 924, 839, 824, 737, 721.

5.2 NMR Spectra



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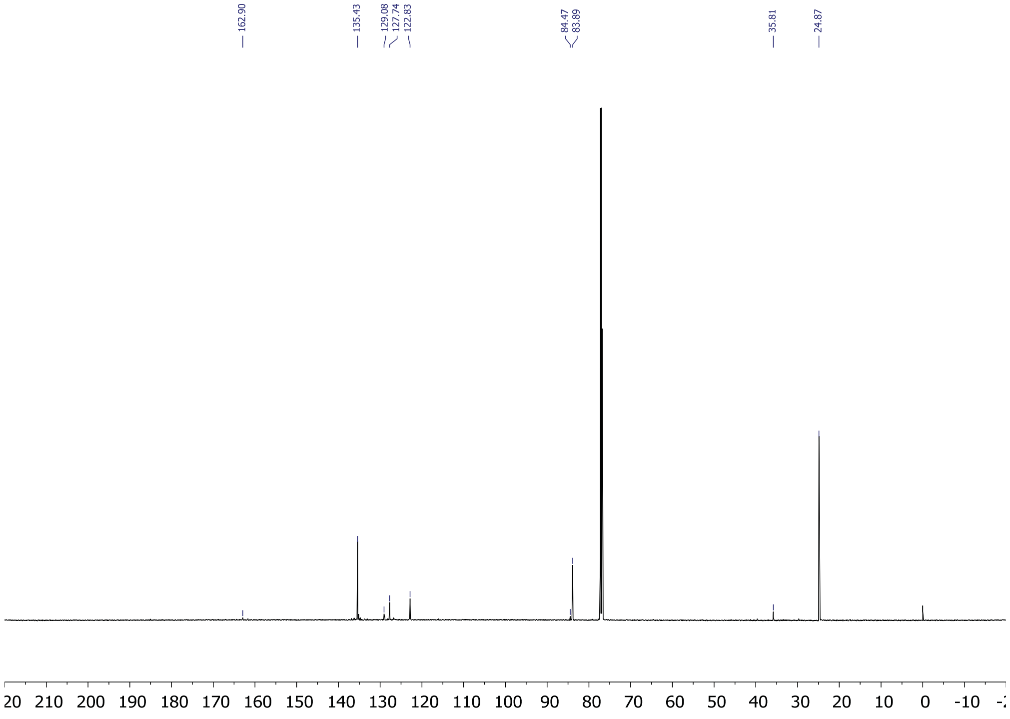
O
O
B
O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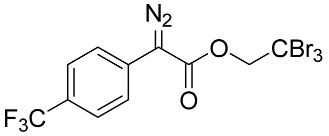
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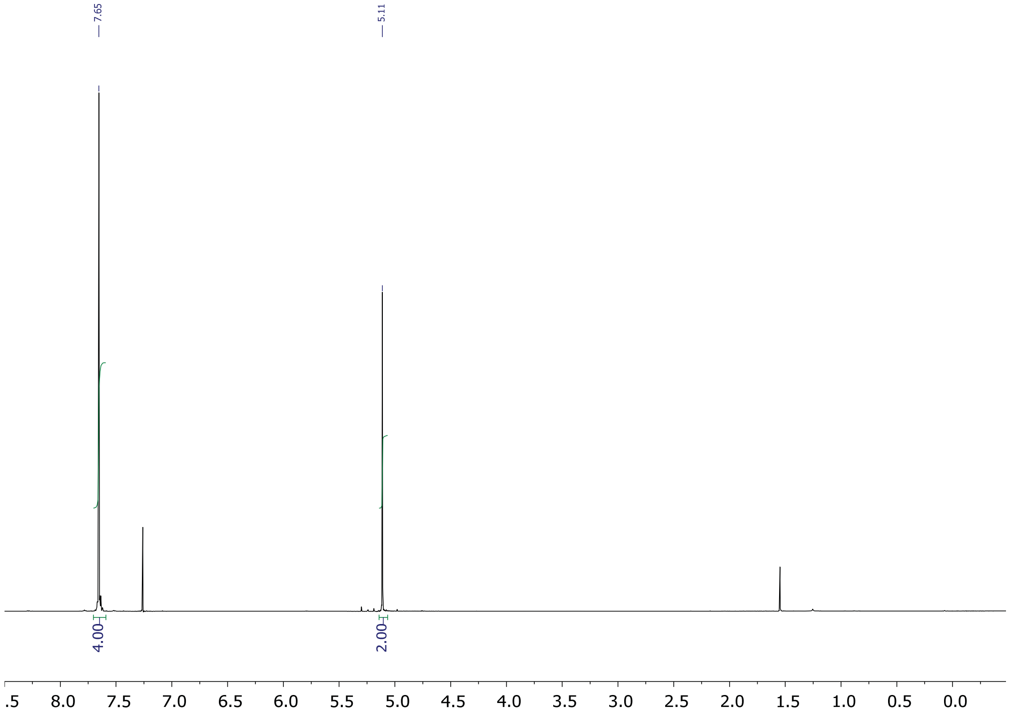
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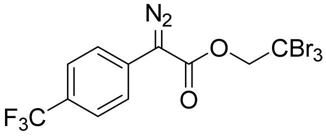
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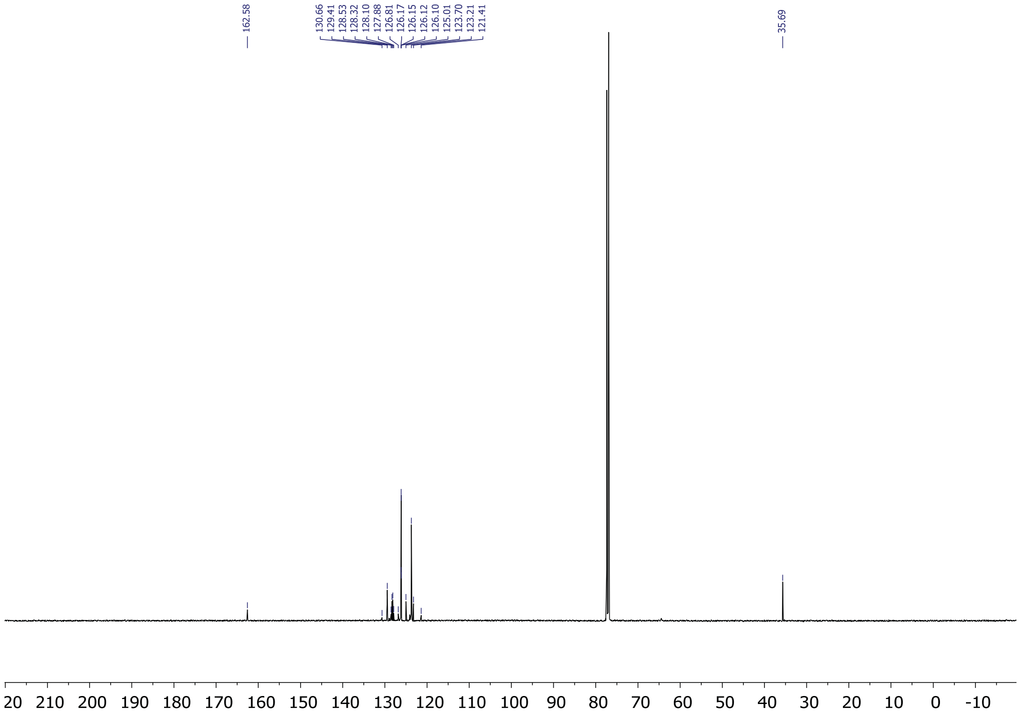
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200
190
180
170
160
150
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10
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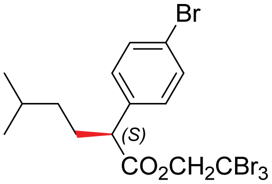
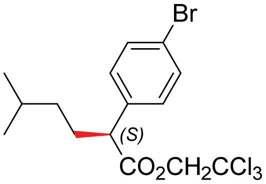
6. Characterization of C–H Functionalization Products



2,2,2-Tribromoethyl (*S*)-2-(4-bromophenyl)-5-methylhexanoate (**5**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 101 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, **catalyst I**, $Rh_2[R\text{-tris}(p\text{-}^tBuC_6H_4)TPCP]_4$, (0.002 mmol, 6 mg, 1 mol%.) and 2-methylbutane (0.6 mmol, 43 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^1H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **5** as a colorless oil (44 mg, 40% yield).

Analysis of the ^1H NMR spectrum of the crude reaction mixture revealed that only compound **5** and the tertiary C–H insertion product, 2,2,2-tribromoethyl (*S*)-2-(4-bromophenyl)-3,3-dimethylpentanoate, were observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as 90: 10 *r.r.*

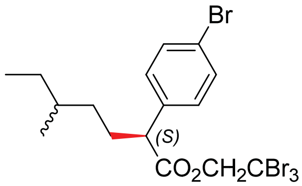
$[\alpha]^{20}_D$ +6.3° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:10 v/v); ^1H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 6.3 Hz, 2H), 4.89 (d, J = 2.3 Hz, 2H), 3.62 (t, J = 7.7 Hz, 1H), 2.16 (tdd, J = 13.4, 7.9, 5.2 Hz, 1H), 1.84 (tdd, J = 13.2, 7.6, 5.1 Hz, 1H), 1.61 – 1.55 (m, 1H), 1.24 – 1.19 (m, 1H), 1.18 – 1.10 (m, 1H), 0.87 (d, J = 4.8 Hz, 3H), 0.86 (d, J = 5.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.86, 137.36, 131.89, 130.12, 121.62, 77.10, 51.54, 36.67, 35.48, 31.09, 28.01, 22.65, 22.52; HRMS (NSI) calcd for $C_{15}H_{19}Br_4O_2$ ($[M+H]^+$): 546.8113 found 546.8121; IR (neat): 2953, 2923, 2853, 1750, 1488, 1458, 1122, 1074, 1012, 825, 727; HPLC (to improve the separation, the product was converted to (*S*)-2-(4-bromophenyl)-5-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (OBH, 0.1% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 140 min, UV 230 nm) retention times of 80.0 min (minor) and 122.2 min (major), >99% *e.e.*.



2,2,2-Trichloroethyl (*S*)-2-(4-bromophenyl)-5-methylhexanoate (**6**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 74 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, **catalyst I**, Rh_2[*R*-tris(*p*-^{t}BuC_6H_4)TPCP]$_4$, (0.002 mmol, 6 mg, 1 mol%.) and 2-methylbutane (0.6 mmol, 43 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **6** as a colorless oil (68 mg, 82% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **6** and the tertiary C–H insertion product, 2,2,2-trichloroethyl (*S*)-2-(4-bromophenyl)-3,3-dimethylpentanoate, were observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as 89: 11 *r.r.*

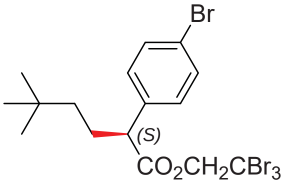
$[\alpha]^{20}_D$ +14° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 1H NMR (600 MHz, Chloroform-d) δ 7.45 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 4.73 (d, J = 12.0 Hz, 1H), 4.69 (d, J = 12.0 Hz, 1H), 3.61 (t, J = 7.7 Hz, 1H), 2.18 – 2.07 (m, 1H), 1.81 (dddd, J = 13.5, 11.2, 7.5, 5.1 Hz, 1H), 1.56 (dq, J = 13.3, 6.7 Hz, 1H), 1.20 (dddd, J = 13.3, 11.5, 6.7, 5.1 Hz, 1H), 1.13 (dddd, J = 13.2, 11.0, 6.9, 5.1 Hz, 1H), 0.87 (d, J = 5.3 Hz, 3H), 0.86 (d, J = 5.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 172.10, 137.31, 131.90, 129.98, 121.63, 94.94, 74.20, 51.39, 36.62, 31.15, 27.98, 22.61, 22.51; HRMS (NSI) calcd for $C_{15}H_{17}BrCl_3O_2$ ($[M-H]^-$): 412.9472 found 412.9481; IR (neat): 2955, 2928, 2870, 1753, 1489, 1144, 1075, 1012, 827, 720; HPLC (to improve the separation, the product was converted to (*S*)-2-(4-bromophenyl)-5-methylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (OBH, 0.1% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 140 min, UV 230 nm) retention times of 73.3 min (minor) and 109.6 min (major), 90% *e.e.*.



2,2,2-Tribromoethyl (2*S*)-2-(4-bromophenyl)-5-methylheptanoate (**7**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 101 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, **catalyst I**, $Rh_2[R\text{-tris}(p\text{-}^tBuC_6H_4)TPCP]_4$, (0.002 mmol, 6 mg, 1 mol%.) and 3-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^1H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **7** as a colorless oil (94 mg, 83% yield).

Analysis of the ^1H NMR spectrum of the crude reaction mixture revealed that only compound **7** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as >98:2 *r.r.* The diastereoselectivity of this reaction is 1:1.

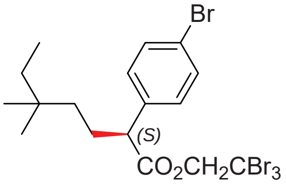
$[\alpha]^{20}_D$ +8.7° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:10 v/v); ^1H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, J = 8.3 Hz, 2H), 7.26 (dd, J = 8.4, 1.6 Hz, 2H), 4.96 – 4.84 (m, 2H), 3.62 (td, J = 7.7, 2.3 Hz, 1H), 2.19 (dddd, J = 13.3, 11.1, 8.1, 5.0 Hz, 0.5H), 2.12 (dddd, J = 12.4, 11.0, 7.7, 4.9 Hz, 0.5H), 1.87 (tdd, J = 12.6, 9.3, 4.8 Hz, 0.5H), 1.84 – 1.75 (m, 0.5H), 1.40 – 1.23 (m, 4H), 1.22 – 1.03 (m, 2H), 0.86 (d, J = 6.5 Hz, 1.5H), 0.85 (d, J = 6.6 Hz, 1.5H), 0.83 (t, *J* = 7.3 Hz, 1.5H), 0.83 (t, *J* = 7.4 Hz, 1.5H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.89, 171.85, 137.43, 137.33, 131.88, 130.13, 130.09, 121.61, 77.11, 77.10, 51.64, 51.59, 35.51, 35.49, 34.41, 34.36, 34.34, 34.31, 30.84, 30.75, 29.43, 29.29, 19.21, 19.17, 11.49, 11.42; HRMS (NSI) calcd for $C_{16}H_{20}Br_4O_2$ ($[M+H]^+$): 560.8270 found 560.8281; IR (neat): 2956, 2925, 2871, 1747, 1488, 1458, 1367, 1139, 1120, 1073, 1011, 823, 728; HPLC (to improve the separation, the product was converted to (2S)-2-(4-bromophenyl)-5-methylheptan-1-ol prepared using DIBAL in DCM at -78 °C), (OBH, 0% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 160 min, UV 230 nm) retention times of one diastereomer is 65.9 min (major) and 144.7 min (minor), >99% *e.e.*, and retention times of another diastereomer is 74.3 min (major) and 100.3 min (minor), 95% *e.e.*.



2,2,2-Tribromoethyl (S)-2-(4-bromophenyl)-5,5-dimethylhexanoate (**8**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 101 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, **catalyst I**, Rh_2[*R*-tris(*p*-^{t}BuC_6H_4)TPCP]$_4$, (0.002 mmol, 6 mg, 1 mol%.) and 2,2-dimethylbutane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **8** as a colorless oil (79 mg, 70% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **8** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as >98:2 *r.r.*

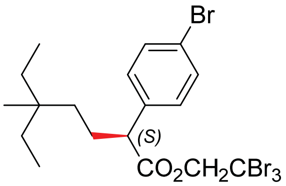
$[\alpha]^{20}_D$ +4.4° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 4.89 (s, 2H), 3.58 (t, J = 7.7 Hz, 1H), 2.14 (tdd, J = 12.5, 7.8, 4.4 Hz, 1H), 1.81 (tdd, J = 13.0, 7.6, 4.3 Hz, 1H), 1.24 (td, J = 13.0, 4.5 Hz, 1H), 1.12 (td, J = 12.9, 4.3 Hz, 1H), 0.87 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.87, 137.38, 131.90, 130.13, 121.64, 52.03, 41.81, 35.47, 30.43, 29.39, 28.46.; HRMS (NSI) calcd for $C_{16}H_{21}Br_4O_2$ ($[M+H]^+$): 560.8270 found 560.8271; IR (neat): 2954, 2931, 2868, 2110, 1748, 1488, 1364, 1130, 1074, 1011, 824, 731; HPLC (to improve the separation, the product was converted to (S)-2-(4-bromophenyl)-5,5-dimethylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (OJH, 0.3% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 30 min, UV 230 nm) retention times of 12.1 min (minor) and 18.3 min (major), 98 % *e.e.*.



2,2,2-Tribromoethyl (S)-2-(4-bromophenyl)-5,5-dimethylheptanoate (**9**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 101 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, **catalyst I**, Rh_2[*R*-tris(*p*-^{t}BuC_6H_4)TPCP]$_4$, (0.002 mmol, 6 mg, 1 mol%.) and 3,3-dimethylpentane (0.6 mmol, 60 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **9** as a colorless oil (89 mg, 77% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **9** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as >98:2 *r.r.*

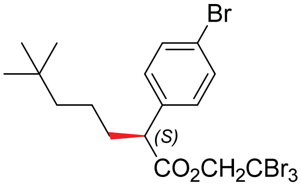
$[\alpha]^{20}_D$ +9.9° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 4.91 (d, J = 12.3 Hz, 1H), 4.88 (d, J = 12.3 Hz, 1H), 3.58 (t, J = 7.7 Hz, 1H), 2.10 (tdd, J = 12.7, 7.9, 4.4 Hz, 1H), 1.77 (tdd, J = 13.1, 7.5, 4.2 Hz, 1H), 1.21 (m, 3H), 1.10 (td, J = 13.0, 4.2 Hz, 1H), 0.81 (s, 6H), 0.76 (t, J = 7.5 Hz, 3H).; ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.90, 137.40, 131.88, 130.12, 121.63, 77.09, 52.07, 39.17, 35.49, 34.01, 32.82, 27.99, 26.76, 26.71, 8.49; HRMS (NSI) calcd for $C_{17}H_{23}Br_4O_2$ ($[M+H]^+$): 574.8426 found 574.8440; IR (neat): 2958, 1747, 1488, 1364, 1126, 1073, 1011, 821, 727; HPLC (to improve the separation, the product was converted to (*S*)-2-(4-bromophenyl)-5,5-dimethylheptan-1-ol prepared using DIBAL in DCM at -78 °C), (OJH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 140 min, UV 230 nm) retention times of 95.1 min (minor) and 97.6 min (major), >99% *e.e.*.



2,2,2-Tribromoethyl (*S*)-2-(4-bromophenyl)-5-ethyl-5-methylheptanoate (**10**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 101 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, **catalyst I**, Rh_2[*R*-tris(*p*-^{t}BuC_6H_4)TPCP]$_4$, (0.002 mmol, 6 mg, 1 mol%.) and 3-ethyl-3-methylpentane (0.6 mmol, 69 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **10** as a colorless oil (89 mg, 75% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **10** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as >98:2 *r.r.*

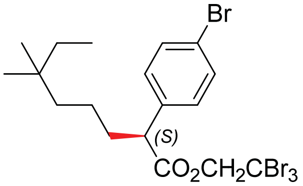
$[\alpha]^{20}_D$ +11.3° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.3 Hz, 2H), 4.92 (d, J = 12.3 Hz, 1H), 4.87 (d, J = 12.3 Hz, 1H), 3.57 (t, J = 7.6 Hz, 1H), 2.07 (tdd, J = 12.6, 7.9, 4.4 Hz, 1H), 1.73 (tdd, J = 12.9, 7.4, 4.2 Hz, 1H), 1.19 (q, J = 7.6 Hz, 5H), 1.09 (td, J = 13.1, 4.2 Hz, 1H), 0.76 (s, 3H), 0.72 (t, J = 7.5 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.93, 137.43, 131.87, 130.11, 121.63, 77.07, 52.09, 36.22, 35.51, 35.09, 30.99, 30.97, 27.57, 24.03, 8.03; HRMS (NSI) calcd for $C_{18}H_{25}Br_4O_2$ ($[M+H]^+$): 588.8583 found 588.8596; IR (neat): 2960, 2876, 1747, 1488, 1462, 1371, 1258, 1126, 1073, 1011, 822, 730; HPLC (to improve the separation, the product was converted to (*S*)-2-(4-bromophenyl)-5-ethyl-5-methylheptan-1-ol prepared using DIBAL in DCM at -78 °C), (OJH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 140 min, UV 230 nm) retention times of 90.6 min (minor) and 96.3 min (major), >99% *e.e.*.



2,2,2-Tribromoethyl (S)-2-(4-bromophenyl)-6,6-dimethylheptanoate (**11**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 101 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, **catalyst I**, Rh_2[*R*-tris(*p*-^{t}BuC_6H_4)TPCP]$_4$, (0.002 mmol, 6 mg, 1 mol%.) and 2,2-dimethylpentane (0.6 mmol, 60 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **11** as a colorless oil (102 mg, 88% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **11** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as >98:2 *r.r*.

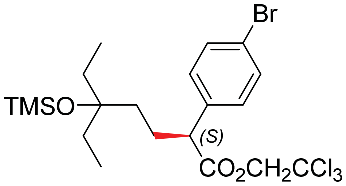
$[\alpha]^{20}_D$ +7.9° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 4.89 (d, J = 2.7 Hz, 2H), 3.69 (t, J = 7.7 Hz, 1H), 2.13 (ddt, J = 14.0, 8.9, 4.2 Hz, 1H), 1.85 – 1.75 (m, 1H), 1.24 (dtdt, J = 41.8, 24.4, 12.6, 6.0 Hz, 4H), 0.83 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.86, 137.38, 131.88, 130.08, 121.61, 77.12, 51.33, 43.90, 35.50, 34.08, 30.47, 29.50, 22.73; HRMS (NSI) calcd for $C_{17}H_{23}Br_4O_2$ ($[M+H]^+$): 586.8426 found 586.8442; IR (neat): 2950, 2864, 1748, 1488, 1364, 1126, 1074, 1011, 823, 728; HPLC (to improve the separation, the product was converted to (S)-2-(4-bromophenyl)-6,6-dimethylheptan-1-ol prepared using DIBAL in DCM at -78 °C), (OJH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 140 min, UV 230 nm) retention times of 100 min (minor) and 112.7 min (major), 98% *e.e.*.



2,2,2-Tribromoethyl (S)-2-(4-bromophenyl)-6,6-dimethyloctanoate (**12**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 101 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, **catalyst I**, $Rh_2[R\text{-tris}(p\text{-}^tBuC_6H_4)TPCP]_4$, (0.002 mmol, 6 mg, 1 mol%.) and 3,3-dimethylhexane (0.6 mmol, 69 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^1H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **12** as a colorless oil (95 mg, 80% yield).

Analysis of the ^1H NMR spectrum of the crude reaction mixture revealed that only compound **12**, another primary C–H functionalization product, 2,2,2-tribromoethyl (S)-2-(4-bromophenyl)-5,5-dimethyloctanoate, and the secondary C–H functionalization product, 2,2,2-tribromoethyl (2*S*,3*R*)-2-(4-bromophenyl)-3,5,5-trimethylheptanoate, were observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as 84:13:3 *r.r.*

$[\alpha]^{20}_D$ +9.0° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:10 v/v); ^1H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 4.93 – 4.85 (m, 2H), 3.69 (t, J = 7.7 Hz, 1H), 2.12 (dqd, J = 17.2, 8.3, 2.8 Hz, 1H), 1.80 (dddd, J = 17.0, 13.6, 6.1, 3.3 Hz, 1H), 1.32 – 1.17 (m, 4H), 1.16 (q, J = 7.5 Hz, 2H), 0.77 (s, 6H), 0.76 (4, J = 7.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.85, 137.37, 131.87, 130.09, 121.61, 77.12, 51.33, 41.24, 35.50, 34.16, 34.11, 32.84, 26.77, 22.17, 8.53; HRMS (NSI) calcd for $C_{18}H_{25}Br_4O_2$ ($[M+H]^+$): 588.8583 found 588.8586; IR (neat): 2956, 2866, 1748, 1488, 1458, 1364, 1125, 1074, 1011, 822, 727; HPLC (to improve the separation, compound **12** was converted to (S)-2-(4-bromophenyl)-6,6-dimethyloctan-1-ol prepared using DIBAL in DCM at -78 °C), (OJH, 0.2% isopropanol in hexane, 0.2 mL/min, 10 mg/mL, 140 min, UV 230 nm) retention times of 82.2 min (minor) and 92.8 min (major), 98% *e.e.*. HPLC (to improve the separation, another primary C–H functionalization product, 2,2,2-tribromoethyl (S)-2-(4-bromophenyl)-5,5-dimethyloctanoate was converted to (*S*)-2-(4-bromophenyl)-5,5-dimethyloctan-1-ol prepared using DIBAL in DCM at -78 °C), (OJH, 0.2% isopropanol in hexane, 0.2 mL/min, 10 mg/mL, 140 min, UV 230 nm) retention times of 102.4 min (minor) and 111.6 min (major), 95% *e.e.*.

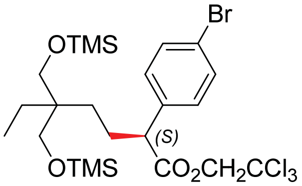


2,2,2-Trichloroethyl (S)-2-(4-bromophenyl)-5-ethyl-5-((trimethylsilyl)oxy)heptanoate (**13**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 74 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, **catalyst I**, Rh_2[*R*-tris(*p*-^{t}BuC_6H_4)TPCP]$_4$, (0.002 mmol, 6 mg, 1 mol%.) and ((3-ethylpentan-3-yl)oxy)trimethylsilane (0.6 mmol, 113 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **13** as a colorless oil (46 mg, 43% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **13** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as >98:2 *r.r.*

$[\alpha]^{20}_D$ +17.1° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 4.76 (d, J = 12.0 Hz, 1H), 4.67 (d, J = 12.0 Hz, 1H), 3.59 (t, J = 7.7 Hz, 1H), 2.12 (dddd, J = 13.4, 12.3, 7.7, 4.6 Hz, 1H), 1.81 (dddd, J = 13.2, 12.2, 7.7, 4.3 Hz, 1H), 1.50 – 1.40 (m, 5H), 1.30 (ddd, J = 13.5, 12.3, 4.3 Hz, 1H), 0.78 (t, J = 7.5 Hz, 3H), 0.77 (t, J = 7.5 Hz, 3H), 0.07 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.99, 137.15, 131.77, 129.86, 121.54, 94.80, 78.49, 74.05, 51.42, 35.94, 31.46, 31.35, 29.71, 27.47, 8.23, 8.20, 2.70; HRMS (NSI) calcd for

$C_{16}H_{18}BrNCl_3O_2$ ([M-$C_4H_{16}O$+NH_4]$^+$): 439.9582 found 439.9581; IR (neat): 2963, 2880, 1752, 1488, 1456, 1373, 1249, 1141, 1126, 1061, 1012, 880, 836; HPLC (R, R-Whelk, 0.5% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 30 min, UV 230 nm) retention times of 18.3 min (minor) and 20.3 min (major), 97% *e.e.*.

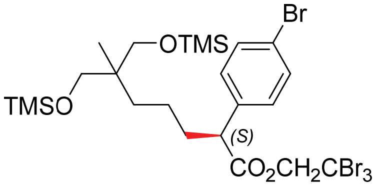


2,2,2-Trichloroethyl (S)-2-(4-bromophenyl)-5,5-bis(((trimethylsilyl)oxy)methyl)heptanoate (**14**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 74 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, **catalyst I**, Rh_2[*R*-tris(*p*-^{t}BuC_6H_4)TPCP]$_4$, (0.002 mmol, 6 mg, 1 mol%.) and 5,5-diethyl-2,2,8,8-tetramethyl-3,7-dioxa-2,8-disilanonane (0.6 mmol, 166 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **14** as a colorless oil (65 mg, 52% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **14** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as >98:2 *r.r.*

$[\alpha]^{20}_D$ +10.1° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 4.74 (d, J = 12.0 Hz, 1H), 4.67 (d, J = 12.0 Hz, 1H), 3.56 (t, J = 7.7 Hz, 1H), 3.28 – 3.20 (m, 4H), 2.04 (tdd, J = 12.6, 7.2, 4.5 Hz, 1H), 1.79 (tdd, J = 12.7, 8.1, 4.4 Hz, 1H), 1.18 (q, J = 7.5 Hz, 2H), 1.13 (td, J = 13.1, 4.5 Hz, 1H), 1.05 (td, J = 13.2, 4.4 Hz, 1H), 0.71 (t, J = 7.5 Hz, 3H), 0.06 (s, 9H), 0.04 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.21, 137.23, 131.84, 130.07, 121.61, 94.97, 74.17, 63.66, 63.58, 51.90, 41.92, 29.86, 27.80, 26.64, 22.48, 7.30, -0.43, -0.44; HRMS (NSI) calcd for $C_{23}H_{39}BrCl_3Si_2O_4$ ([M+H]$^+$): 619.0630 found 619.0619; IR (neat):

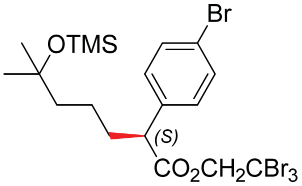
2956, 2925, 2868, 1754, 1488, 1250, 1128, 1086, 1012, 873, 839, 721; HPLC (R, R-Whelk, 0.5% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 30 min, UV 230 nm)-retention times of 14.8 min (minor) and 17.4 min (major), 96% *e.e.*.



2,2,2-Tribromoethyl (S)-2-(4-bromophenyl)-6-methyl-7-((trimethylsilyl)oxy)-6-(((trimethylsilyl)oxy)methyl)heptanoate (**15**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 101 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, **catalyst I**, Rh_2[*R*-tris(*p*-^{t}BuC_6H_4)TPCP]$_4$, (0.002 mmol, 6 mg, 1 mol%.) and 2,2,5,8,8-pentamethyl-5-propyl-3,7-dioxa-2,8-disilanonane (0.6 mmol, 166 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **15** as a colorless oil (137 mg, 91% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **15** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as >98:2 *r.r.*

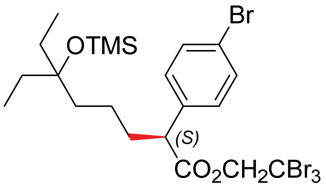
$[\alpha]^{20}_D$ +9.1° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 4.89 (s, 2H), 3.68 (t, J = 7.7 Hz, 1H), 3.23 (d, J = 5.8 Hz, 4H), 2.16 – 2.07 (m, 1H), 1.81 (dddd, J = 14.0, 11.5, 5.8, 2.8 Hz, 1H), 1.30 – 1.16 (m, 5H), 0.69 (s, 2H), 0.05 (s, 9H), 0.04 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.84, 137.32, 131.87, 130.14, 121.61, 77.09, 66.30, 66.21, 51.28, 39.62, 35.52, 34.12, 33.63, 21.40, 18.63, -0.39, -0.42; HRMS (NSI) calcd for $C_{23}H_{39}Br_4Si_2O_4$ ($[M+H]^+$): 750.9115 found 750.9117; IR (neat): 2924, 2854, 1745, 1488, 1260, 1123, 1073, 1027, 1011, 819, 797, 728; HPLC (OD, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 30 min, UV 230 nm) retention times of 22.2 min (minor) and 24.6 min (major), 99% *e.e.*.



2,2,2-Tribromoethyl (S)-2-(4-bromophenyl)-6-methyl-6-((trimethylsilyl)oxy)heptanoate (**16**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 101 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, **catalyst I**, $Rh_2[R\text{-tris}(p\text{-}^tBuC_6H_4)TPCP]_4$, (0.002 mmol, 6 mg, 1 mol%.) and trimethyl((2-methylpentan-2-yl)oxy)silane (0.6 mmol, 105 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **16** as a colorless oil (117 mg, 90% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **16** and the secondary C–H functionalization product, 2,2,2-tribromoethyl (2*S*,3*R*)-2-(4-bromophenyl)-3,5-dimethyl-5-((trimethylsilyl)oxy)hexanoate, were observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as 94:6 *r.r.*

$[\alpha]^{20}_D$ +9.5° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 4.91 (d, J = 12.3 Hz, 1H), 4.88 (d, J = 12.3 Hz, 1H), 3.68 (t, J = 7.7 Hz, 1H), 2.15 (dddd, J = 13.5, 9.9, 8.0, 5.6 Hz, 1H), 1.82 (dddd, J = 13.3, 9.2, 7.5, 5.7 Hz, 1H), 1.49 – 1.29 (m, 4H), 1.16 (s, 3H), 1.16 (s, 3H), 0.06 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.82, 137.32, 131.87, 130.11, 121.61, 77.09, 73.83, 51.33, 44.49, 35.51, 33.64, 30.04, 29.92, 22.43, 2.73; HRMS (NSI) calcd for $C_{19}H_{29}Br_4SiO_3$ ($[M+H]^+$): 648.8614 found 648.8609; IR (neat): 2966, 2943, 2868, 1745, 1366, 1247, 1184, 1142, 1123, 1073, 1043, 1011, 905, 823, 728; HPLC (R, R-Whelk, 0.5% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 40 min, UV 230 nm) retention times of 24.6 min (minor) and 27.4 min (major), 98% *e.e.*.

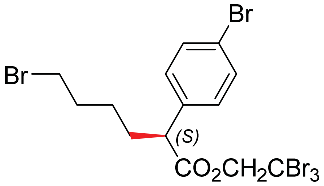


2,2,2-Tribromoethyl (S)-2-(4-bromophenyl)-6-ethyl-6-((trimethylsilyl)oxy)octanoate (**17**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 101 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, **catalyst I**, Rh_2[*R*-tris(*p*-^{t}BuC_6H_4)TPCP]$_4$, (0.002 mmol, 6 mg, 1 mol%.) and trimethyl((2-methylpentan-2-yl)oxy)silane (0.6 mmol, 105 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **17** as a colorless oil (127 mg, 93% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **17**, another primary C–H functionalization product, 2,2,2-tribromoethyl (2S)-2-(4-bromophenyl)-5-ethyl-5-((trimethylsilyl)oxy)octanoate, and the secondary C–H functionalization product, 2,2,2-tribromoethyl (2S,3R)-2-(4-bromophenyl)-5-ethyl-3-methyl-5-((trimethylsilyl)oxy)heptanoate, were observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as 93: 4: 3 *r.r.*

$[\alpha]^{20}_{D}$ +9.0° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ
7.45 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 4.89 (d, J = 1.2 Hz, 2H), 3.68 (t, J = 7.7 Hz, 1H), 2.14 (dddd, J = 13.6, 9.9, 7.9, 5.9 Hz, 1H), 1.82 (dddd, J = 13.4, 9.6, 7.6, 5.7 Hz, 1H), 1.48 – 1.35 (m, 6H), 1.35 – 1.21 (m, 2H), 0.78 (t, J = 7.5 Hz, 3H), 0.77 (t, J = 7.5 Hz, 3H), 0.04 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.75, 137.24, 131.87, 130.11, 121.63, 78.73, 77.08, 51.34, 38.27, 35.50, 33.73, 31.52, 31.32, 21.74, 8.41, 8.36, 2.83; HRMS (NSI) calcd for $C_{18}H_{23}Br_4O_3$ ($[M-C_3H_9]^-$): 586.8426 found 586.8417; IR (neat): 2961,

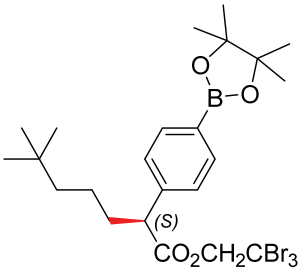
2943, 2877, 1749, 1488, 1458, 1367, 1248, 1140, 1123, 1072, 1011, 835, 751, 728; HPLC (OD, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 40 min, UV 230 nm) retention times of 25.2 min (minor) and 29.2 min (major), 97% *e.e.*.



2,2,2-Tribromoethyl (S)-6-bromo-2-(4-bromophenyl)hexanoate (**18**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 101 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, **catalyst I**, Rh_2[*R*-tris(*p*-^{t}BuC_6H_4)TPCP]$_4$, (0.002 mmol, 6 mg, 1 mol%.) and 1-bromobutane (0.6 mmol, 82 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **18** as a colorless oil (65 mg, 53% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **18**, and the secondary C–H functionalization product, 2,2,2-tribromoethyl (2S,3R)-5-bromo-2-(4-bromophenyl)-3-methylpentanoate, were observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as 84: 16 r.r.

$[\alpha]^{20}_D$ +14.3° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.9 Hz, 2H), 4.91 (d, J = 12.2 Hz, 1H), 4.88 (d, J = 12.3 Hz, 1H), 3.68 (t, J = 7.7 Hz, 1H), 3.38 (tq, J = 6.8, 3.2 Hz, 2H), 2.19 (dtt, J = 10.5, 7.9, 5.4 Hz, 1H), 1.94 – 1.82 (m, 3H), 1.54 – 1.48 (m, 1H), 1.47 – 1.39 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.53, 136.90, 132.01, 130.06, 121.83, 77.12, 51.10, 35.38, 33.32, 32.45, 32.22, 26.20; HRMS (NSI) calcd for $C_{14}H_{16}Br_4{}^{81}BrO_2$ ($[M+H]^+$): 612.7041 found 612.7036; IR (neat): 2924, 2854, 1746, 1488, 1260, 1123, 1073, 1011, 804, 728; HPLC (OJH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 40 min, UV 230 nm) retention times of 26.9 min (minor) and 29.3 min (major), 93% *e.e.*.

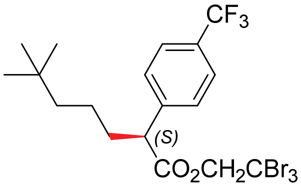


2,2,2-Tribromoethyl (S)-6,6-dimethyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)heptanoate (**19**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-tribromoethyl 2-diazo-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetate (0.2 mmol, 111 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, **catalyst I**, Rh_2[*R*-tris(*p*-^{t}BuC_6H_4)TPCP]$_4$, (0.002 mmol, 6 mg, 1 mol%.) and 2,2-dimethylpentane (0.6 mmol, 60 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 50/1) to afford compound **19** as a colorless oil (110 mg, 88% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **19** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as >98:2 r.r.

$[\alpha]^{20}_D$ +6.8° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:5 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, J = 8.1 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 4.91 (d, J = 12.3 Hz, 1H), 4.86 (d, J = 12.3 Hz, 1H), 3.74 (t, J = 7.7 Hz, 1H), 2.15 (ddt, J = 14.0, 8.6, 4.3 Hz, 1H), 1.88 – 1.78 (m, 1H), 1.34 (s, 12H), 1.32 – 1.14 (m, 4H), 0.82 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.09, 141.50, 135.22, 127.74, 83.95, 77.11, 52.08, 43.94, 35.65, 34.14, 30.47, 29.85, 29.51, 25.03, 22.77; HRMS (NSI) calcd for $C_{23}H_{35}BBr_3O_4$ ($[M+H]^+$): 623.0179 found 623.0191; IR (neat): 2950, 2866, 1750, 1610, 1359, 1141, 1121, 1090, 1021, 858, 724;

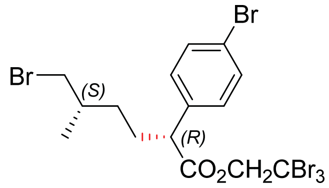
HPLC (S, S-Whelk, 0.1% isopropanol in hexane, 0.1 mL/min, 10 mg/mL, 120 min, UV 230 nm) retention times of 58.9 min (minor) and 91.2 min (major), >99% *e.e.*.



2,2,2-Tribromoethyl (S)-6,6-dimethyl-2-(4-(trifluoromethyl)phenyl)heptanoate (**20**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-tribromoethyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate (0.2 mmol, 99 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, **catalyst I**, Rh_2[*R*-tris(*p*-^{t}BuC_6H_4)TPCP]$_4$, (0.002 mmol, 6 mg, 1 mol%.) and 2,2-dimethylpentane (0.6 mmol, 60 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 50/1) to afford compound **20** as a colorless oil (93 mg, 82% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **20** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as >98:2 r.r.

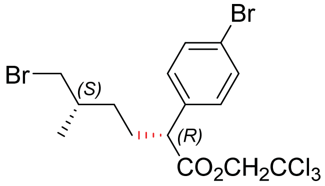
$[\alpha]^{20}_D$ +10.7° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:5 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, J = 8.1 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 4.92 (d, J = 12.3 Hz, 1H), 4.89 (d, J = 12.3 Hz, 1H), 3.80 (t, J = 7.7 Hz, 1H), 2.24 – 2.14 (m, 1H), 1.90 – 1.79 (m, 1H), 1.38 – 1.17 (m, 4H), 0.83 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.59, 142.34, 129.96 (q, J = 32.5 Hz), 128.77, 125.72 (q, J = 3.7 Hz), 124.20 (q, J = 272.0 Hz), 51.73, 43.88, 35.35, 34.15, 30.47, 29.49, 22.76; HRMS (NSI) calcd for $C_{18}H_{21}Br_3F_3O_2$ ($[M-H]^-$): 562.9049 found 562.9061; IR (neat): 2950, 2867, 1750, 1618, 1364, 1324, 1165, 1125, 1068, 1019, 842, 720; HPLC (OJH, 0.15% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 40 min, UV 230 nm) retention times of 19.7 min (minor) and 25.8 min (major), >99% *e.e.*.



2,2,2-Tribromoethyl (2R,5S)-6-bromo-2-(4-bromophenyl)-5-methylhexanoate (**24**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 101 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, **catalyst I**, Rh_2[*S*-tris(*p*-^{t}BuC_6H_4)TPCP]$_4$, (0.002 mmol, 6 mg, 1 mol%.) and (S)-1-bromo-2-methylbutane (0.6 mmol, 91 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **24** as a colorless oil (49 mg, 39% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **24** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as >98: 2 r.r.

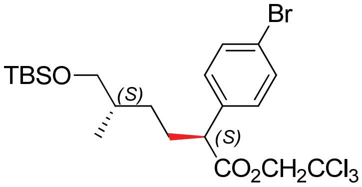
$[\alpha]^{20}_D$ -17.7° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 4.92 (d, J = 12.3 Hz, 1H), 4.88 (d, J = 12.2 Hz, 1H), 3.64 (t, J = 7.7 Hz, 1H), 3.33 (d, J = 5.6 Hz, 2H), 2.20 – 2.10 (m, 1H), 1.89 (ddt, J = 18.9, 8.0, 5.0 Hz, 1H), 1.82 (dt, J = 12.6, 6.3 Hz, 1H), 1.52 (td, J = 12.2, 11.1, 5.8 Hz, 1H), 1.20 (tdd, J = 12.5, 7.7, 4.8 Hz, 1H), 1.01 (d, J = 6.6 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.54, 136.88, 131.99, 130.07, 121.82, 77.10, 51.29, 40.82, 35.40, 35.14, 32.62, 30.41, 29.85, 18.77; HRMS (NSI) calcd for $C_{15}H_{18}Br_5O_2$ ($[M+H]^+$): 624.7218 found 624.7224; IR (neat): 2960, 2925, 2853, 1746, 1488, 1260, 1124, 1073, 1011, 907, 803, 731; HPLC (ODH, 0.5% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 40 min, UV 230 nm) retention times of 22.1 min (minor) and 26.6 min (major), >100:1 d.*r*..



2,2,2-Trichloroethyl (2R,5S)-6-bromo-2-(4-bromophenyl)-5-methylhexanoate (**27**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 101 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, **catalyst I**, Rh_2[*S*-tris(*p*-^{t}BuC_6H_4)TPCP]$_4$, (0.002 mmol, 6 mg, 1 mol%.) and (S)-1-bromo-2-methylbutane (0.6 mmol, 91 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **27** as a colorless oil (68 mg, 69% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **27** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as >98: 2 r.r.

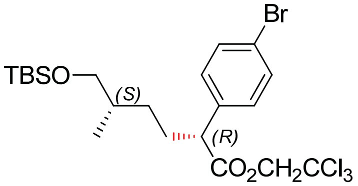
$[\alpha]^{20}_D$ -25.2° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, J = 8.5 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 4.75 (d, J = 12.0 Hz, 1H), 4.69 (d, J = 12.0 Hz, 1H), 3.62 (t, J = 7.7 Hz, 1H), 3.32 (dd, J = 5.6, 1.1 Hz, 2H), 2.11 (tdd, J = 12.8, 7.0, 3.8 Hz, 1H), 1.91 – 1.77 (m, 2H), 1.50 (ddt, J = 13.4, 11.0, 5.3 Hz, 1H), 1.23 – 1.12 (m, 1H), 1.00 (d, J = 6.7 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.80, 136.83, 132.01, 129.94, 121.83, 94.87, 74.22, 51.13, 40.75, 35.11, 32.54, 30.44, 18.76; HRMS (NSI) calcd for $C_{15}H_{18}Br_2Cl_3O_2$ ($[M+H]^+$): 492.8724 found 492.8748; IR (neat): 2955, 2927, 2854, 1751, 1488, 1131, 1074, 1012, 827, 766, 719; HPLC (ODH, 0.3% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 40 min, UV 230 nm) retention times of 20.3 min (minor) and 25.6 min (major), >100:1 d.*r*..



(2S,5S)-2,2,2-Trichloroethyl 2-(4-bromophenyl)-6-((tert-butyldimethylsilyl)oxy)-5-methylhexanoate (**25**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 101 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, **catalyst I**, Rh_2[*R*-tris(*p*-^{t}BuC_6H_4)TPCP]$_4$, (0.002 mmol, 6 mg, 1 mol%.) and (S)-trimethyl(2-methylbutoxy)silane (0.6 mmol, 96 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **25** as a colorless oil (93 mg, 92% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **25** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as >98: 2 r.r.

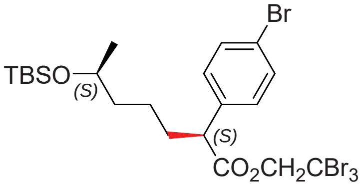
$[\alpha]^{20}_D$ +11.7° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 4.73 (d, J = 12.0 Hz, 1H), 4.69 (d, J = 12.0 Hz, 1H), 3.62 (t, J = 7.7 Hz, 1H), 3.37 (dd, J = 6.0, 3.7 Hz, 2H), 2.19 (tdd, J = 12.9, 7.3, 3.9 Hz, 1H), 1.79 (dddd, J = 12.9, 11.5, 7.6, 5.0 Hz, 1H), 1.59 (h, J = 6.3 Hz, 1H), 1.39 (ddt, J = 13.2, 10.9, 5.2 Hz, 1H), 1.13 – 1.04 (m, 1H), 0.87 (d, J = 6.8 Hz, 3H), 0.86 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.03, 137.25, 131.90, 129.97, 121.65, 94.93, 74.20, 68.02, 51.48, 35.77, 31.13, 30.91, 26.04, 18.42, 16.75, -5.25; HRMS (NSI) calcd for $C_{21}H_{33}BrCl_3SiO_3$ ($[M+H]^+$): 545.0442 found 545.0437; IR (neat): 2954, 2928, 2856, 1752, 1488, 1471, 1462, 1250, 1139, 1094, 1075, 1012, 834, 773, 719; HPLC (R, R-Whelk, 0.5% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 30 min, UV 230 nm) retention times of 17.5 min (minor) and 19.8 min (major), >100:1 d.*r*..



(2R,5S)-2,2,2-Trichloroethyl 2-(4-bromophenyl)-6-((tert-butyldimethylsilyl)oxy)-5-methylhexanoate (**28**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate **1a** (0.2 mmol, 101 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, **catalyst I**, $Rh_2[S$-tris(p-$^tBuC_6H_4$)TPCP$]_4$, (0.002 mmol, 6 mg, 1 mol%.) and (S)-trimethyl(2-methylbutoxy)silane (0.6 mmol, 96 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **28** as a colorless oil (90 mg, 89% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **28** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as >98: 2 r.r.

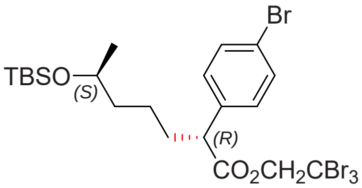
$[\alpha]^{20}_D$ -19..9° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, J = 8.5 Hz, 2H), 7.22 (d, J = 8.5 Hz, 2H), 4.73 (d, J = 12.0 Hz, 1H), 4.69 (d, J = 12.0 Hz, 1H), 3.61 (t, J = 7.7 Hz, 1H), 3.37 (dd, J = 6.1, 3.2 Hz, 2H), 2.18 (tdd, J = 12.9, 7.3, 3.9 Hz, 1H), 1.79 (dddd, J = 12.8, 11.5, 7.6, 5.0 Hz, 1H), 1.64 – 1.52 (m, 1H), 1.39 (ddt, J = 13.3, 10.7, 5.2 Hz, 1H), 1.08 (dddd, J = 13.0, 11.7, 7.9, 4.9 Hz, 1H), 0.86 (d, J = 6.8 Hz, 3H), 0.85 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.06, 137.26, 131.91, 129.98, 121.66, 94.94, 74.21, 68.03, 51.50, 35.78, 31.14, 30.92, 26.04, 18.43, 16.75, -5.26; HRMS (NSI) calcd for $C_{21}H_{33}BrCl_3SiO_3$ ($[M+H]^+$): 545.0442 found 545.0437; IR (neat): 2954, 2928, 2856, 1752, 1488, 1471, 1462, 1251, 1138, 1094, 1075, 1011, 834, 773, 719; HPLC (R, R-Whelk, 0.5% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 30 min, UV 230 nm) retention times of 18.0 min (minor) and 19.0 min (major), >100:1 d.*r*..



2,2,2-Tribromoethyl (2S,6S)-2-(4-bromophenyl)-6-((tert-butyldimethylsilyl)oxy)heptanoate (**26**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 101 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, **catalyst I**, $Rh_2[R\text{-tris}(p\text{-}^tBuC_6H_4)TPCP]_4$, (0.002 mmol, 6 mg, 1 mol%.) and (S)-tert-butyldimethyl(pentan-2-yloxy)silane (0.6 mmol, 121 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **26** as a colorless oil (102 mg, 75% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **26,** and the secondary C–H insertion product, (5S)-2,2,2-tribromoethyl 2-(4-bromophenyl)-5-((tert-butyldimethylsilyl)oxy)-3-methylhexanoate , were observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as 96: 4 *r.r.*

$[\alpha]^{20}_D$ +15.1° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 4.89 (s, 2H), 3.77 – 3.69 (m, 1H), 3.66 (t, J = 7.7 Hz, 1H), 2.14 (dtt, J = 10.0, 7.8, 5.0 Hz, 1H), 1.84 (dddd, J = 13.3, 9.6, 6.1, 3.8 Hz, 1H), 1.50 – 1.44 (m, 0H), 1.44 – 1.35 (m, 2H), 1.08 (d, J = 6.1 Hz, 3H), 0.85 (s, 9H), 0.01 (s, 3H), -0.02 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.76, 137.22, 131.89, 130.11, 121.64, 77.11, 68.37, 51.30, 39.34, 35.47, 33.25, 29.86, 26.02, 23.95, 23.78, 18.25, -4.20, -4.60; HRMS (NSI) calcd for $C_{17}H_{23}Br_4SiO_3$ ($[M-C_4H_9]^-$): 618.8144 found 618.8138; IR (neat): 2951, 2926, 2855, 1749, 1488, 1461, 1371, 1254, 1133, 1094, 1074, 1042, 1011, 833, 773, 727; HPLC (R, R-Whelk, 0.5% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 40 min, UV 230 nm) retention times of 25.2 min (minor) and 27.7 min (major), >100:1 d.*r*..

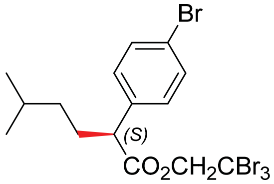


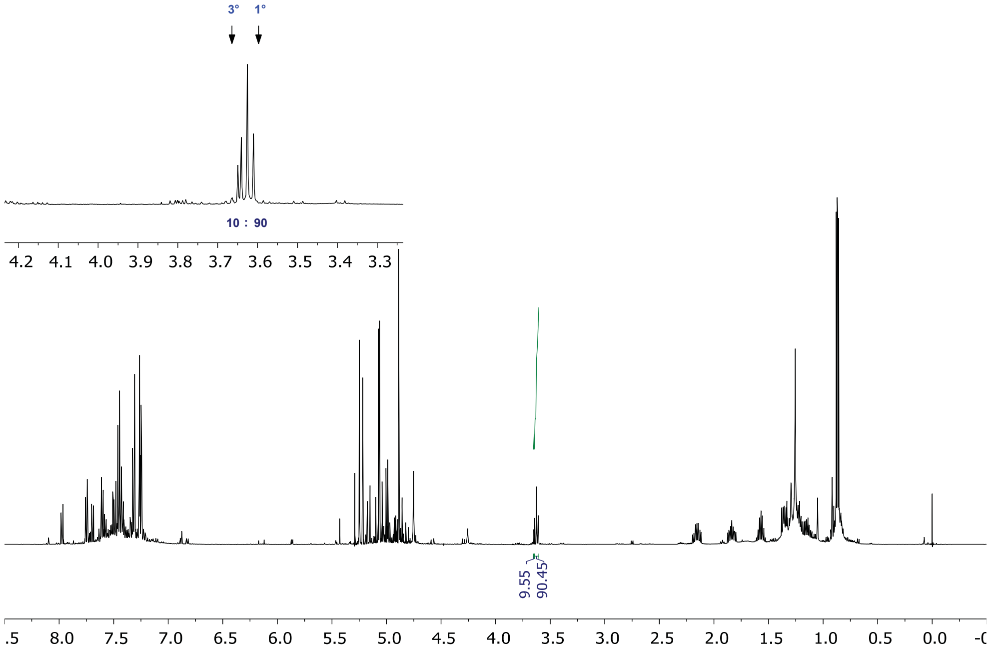
2,2,2-Tribromoethyl (2R,6S)-2-(4-bromophenyl)-6-((tert-butyldimethylsilyl)oxy)heptanoate (**29**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Tribromoethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 101 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, **catalyst I**, $Rh_2[S\text{-tris}(p\text{-}^tBuC_6H_4)TPCP]_4$, (0.002 mmol, 6 mg, 1 mol%.) and (S)-tert-butyldimethyl(pentan-2-yloxy)silane (0.6 mmol, 121 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **29** as a colorless oil (110 mg, 81% yield).

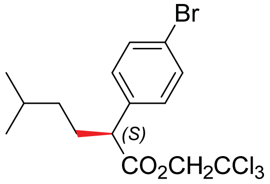
Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **29,** and the secondary C–H insertion product, (5S)-2,2,2-tribromoethyl 2-(4-bromophenyl)-5-((tert-butyldimethylsilyl)oxy)-3-methylhexanoate , were observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as 94: 6 *r.r.*

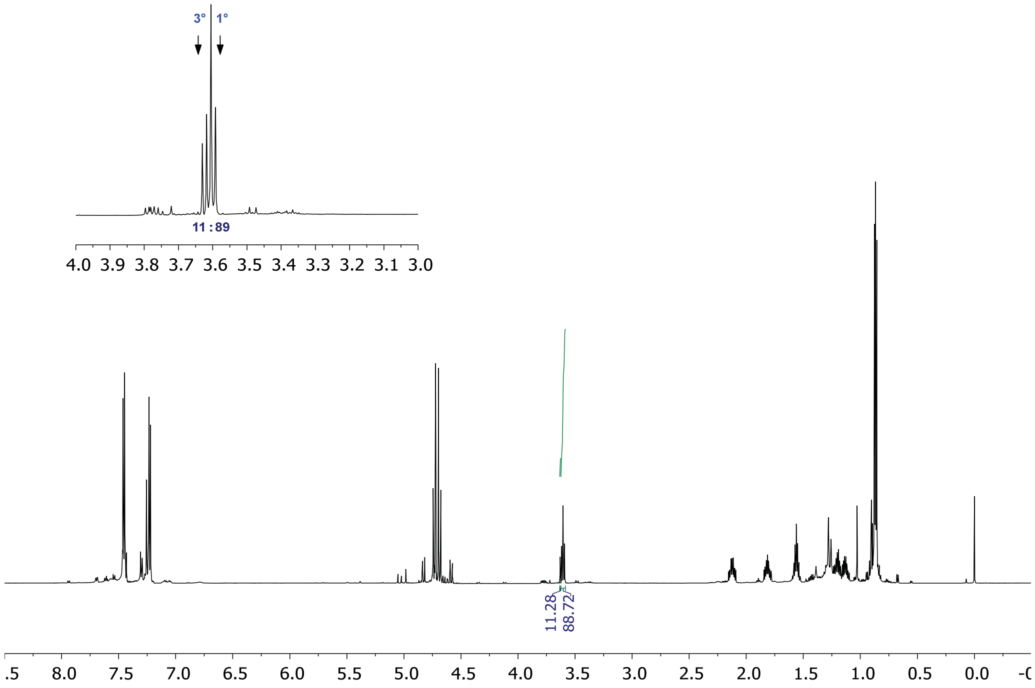
$[\alpha]^{20}_D$ -6.2° (c = 1.00, $CHCl_3$); TLC (diethyl ether: hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 4.90 (d, J = 12.3 Hz, 1H), 4.87 (d, J = 12.3 Hz, 1H), 3.73 (h, J = 6.1 Hz, 1H), 3.66 (t, J = 7.7 Hz, 1H), 2.15 (dddd, J = 13.1, 9.8, 7.5, 5.5 Hz, 1H), 1.83 (dtt, J = 10.3, 8.1, 5.0 Hz, 1H), 1.44 – 1.38 (m, 2H), 1.38 – 1.31 (m, 1H), 1.31 – 1.21 (m, 1H), 1.07 (d, J = 6.1 Hz, 3H), 0.83 (s, 9H), 0.01 (s, 3H), -0.02 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.77, 137.16, 131.89, 130.12, 121.64, 77.08, 68.44, 51.31, 39.46, 35.51, 33.26, 26.00, 23.99, 23.92, 18.23, -4.19, -4.63; HRMS (NSI) calcd for $C_{17}H_{23}Br_4SiO_3$ ($[M-C_4H_9]^-$): 618.8144 found 618.8138; IR (neat): 2952, 2927, 2855, 1749, 1488, 1461, 1371, 1254, 1133, 1094, 1074, 1042, 1011, 833, 773, 728; HPLC (R, R-Whelk, 0.5% isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 30 min, UV 230 nm) retention times of 25.0 min (minor) and 26.8 min (major), 20:1 d.*r*..

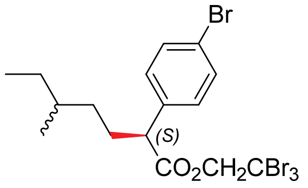
7. Crude ^{1}H NMR Spectra for C–H Functionalization Products 5-29

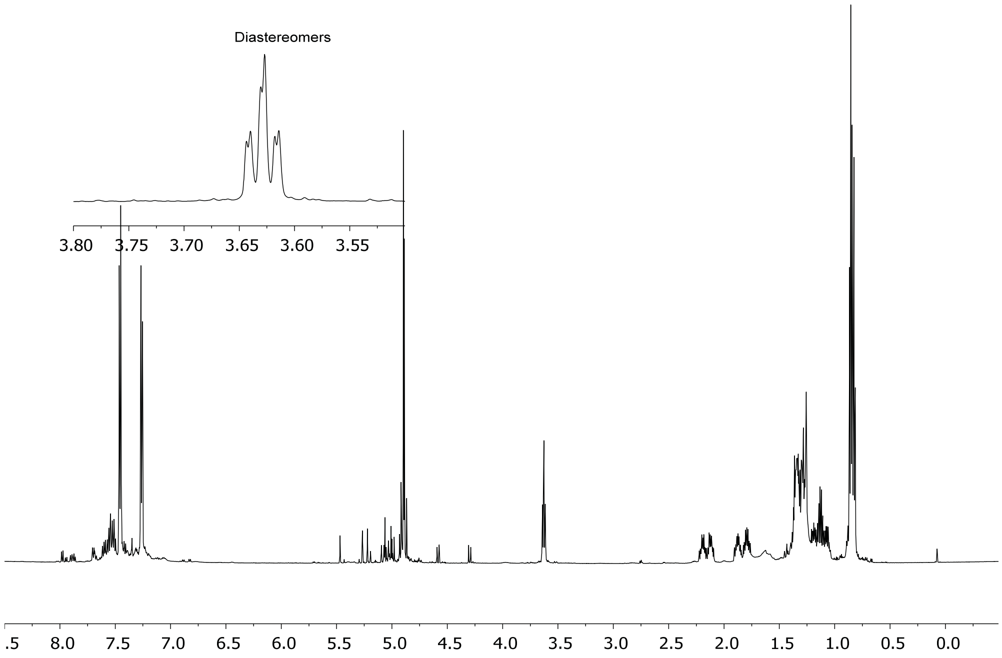


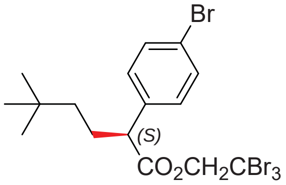


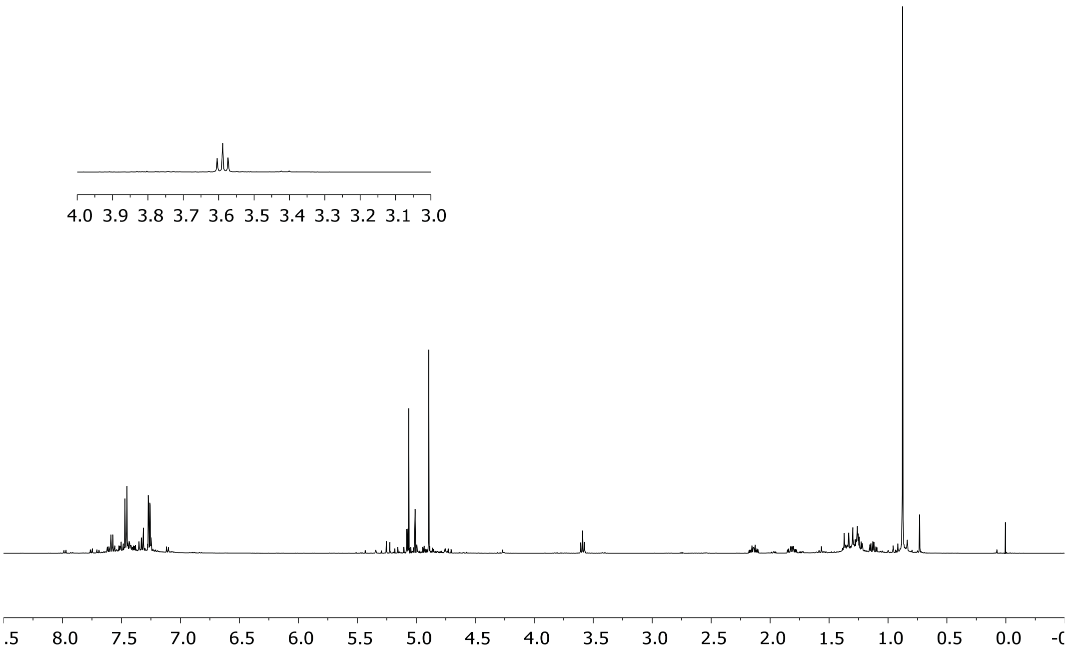

Br
(S)
CO2CH2CCl3

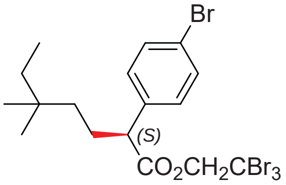

3°
1°
11 : 89
4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0
11.28
88.72
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

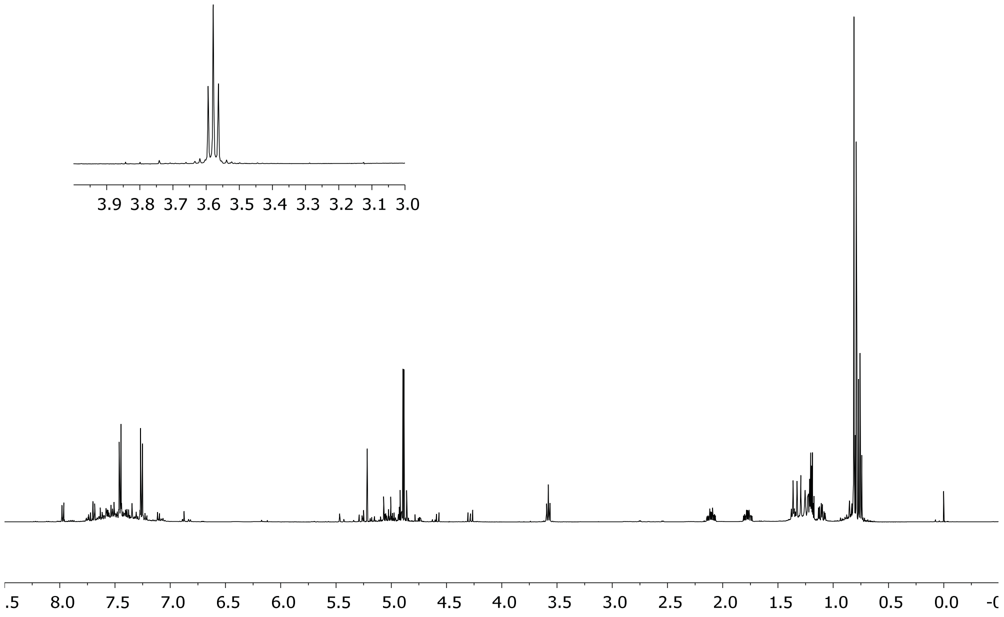

Br
(S)
CO2CH2CBr3

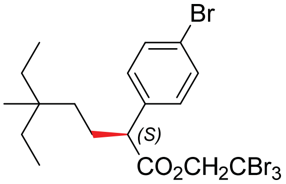

Diastereomers
3.80
3.75
3.70
3.65
3.60
3.55
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

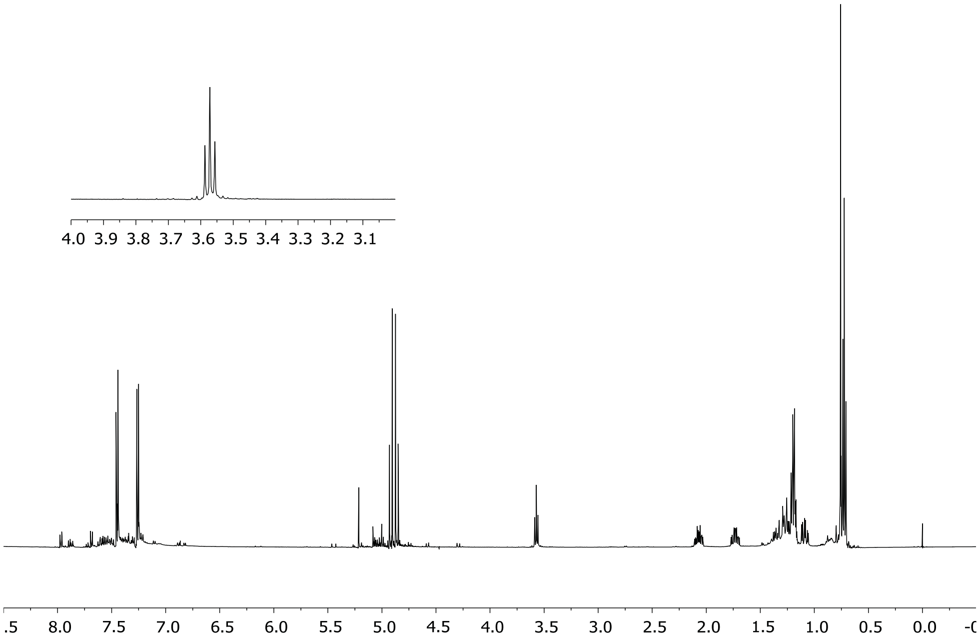

Br
(S)
CO2CH2CBr3

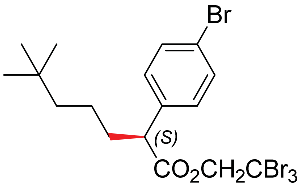

4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -(

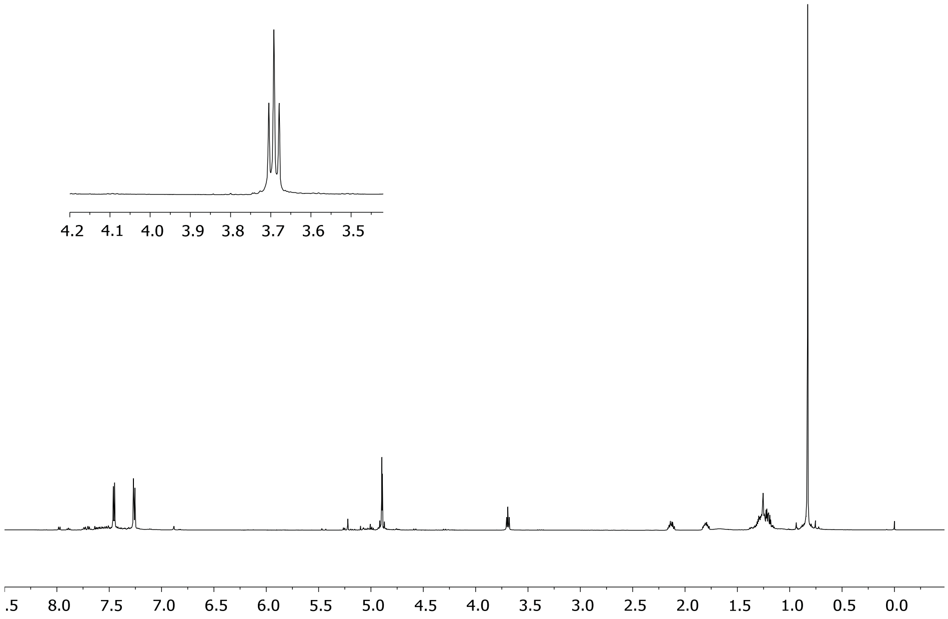

Br
(S)
CO2CH2CBr3

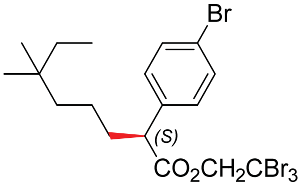

3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -(

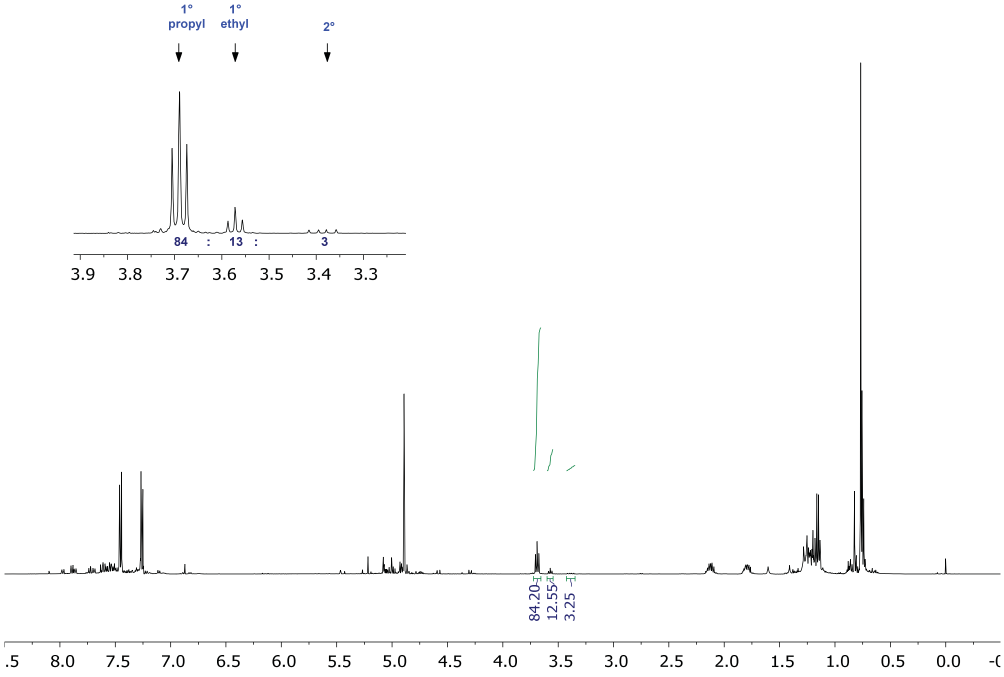

Br
(S)
CO2CH2CBr3

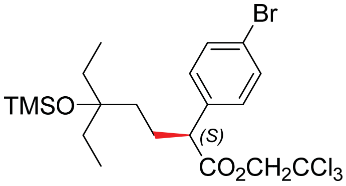

4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -(

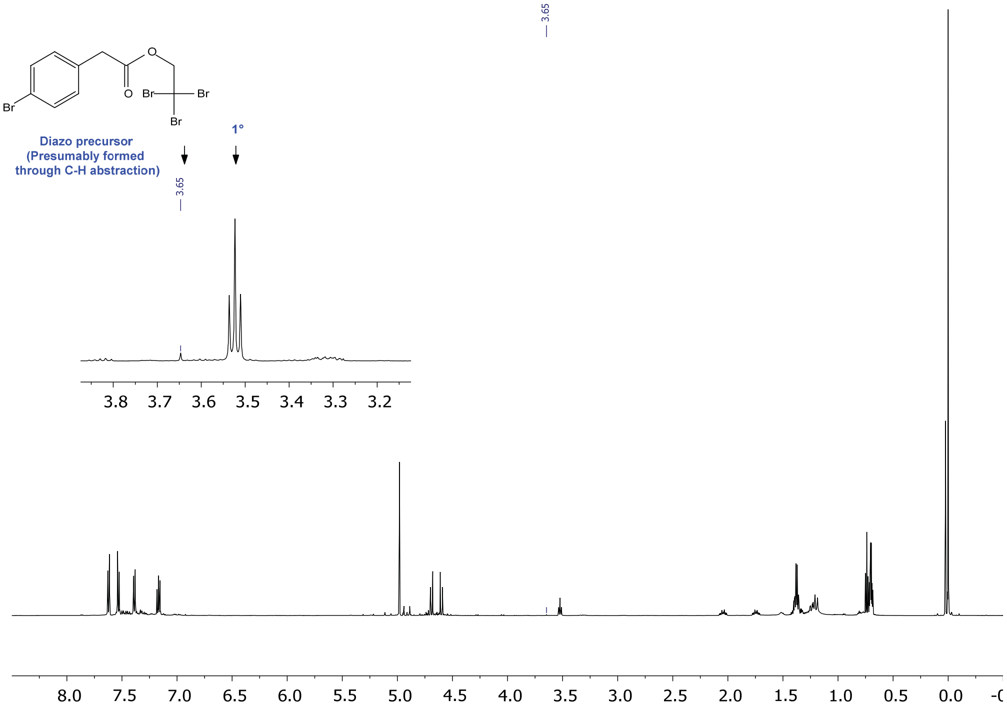

Br
(S)
CO2CH2CBr3

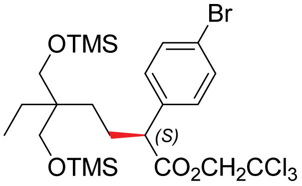

4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

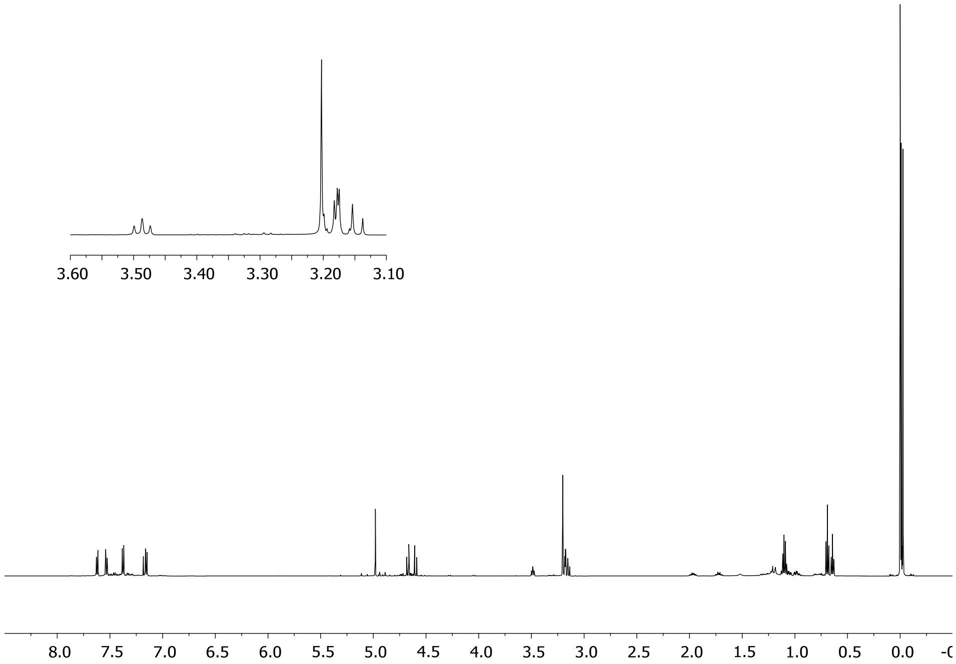

Br
(S)
CO2CH2CBr3

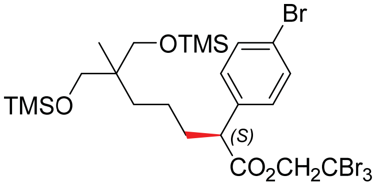

1°
propyl
1°
ethyl
2°
84 : 13 : 3
3.9
3.8
3.7
3.6
3.5
3.4
3.3
84.20
12.55
3.25
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

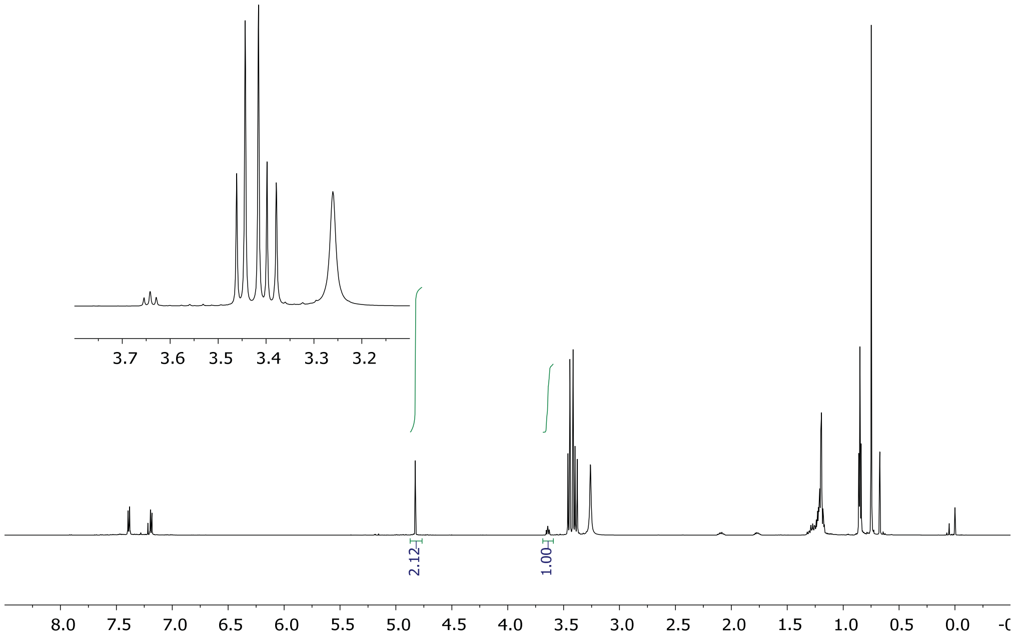

Br
TMSO
(S)
CO2CH2CCl3

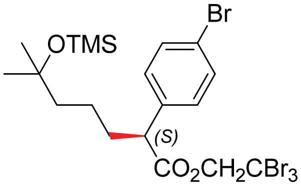

3.65
Br
O
Br
Br
Br
Diazo precursor
(Presumably formed
through C-H abstraction)
1°
3.65
3.8
3.7
3.6
3.5
3.4
3.3
3.2
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

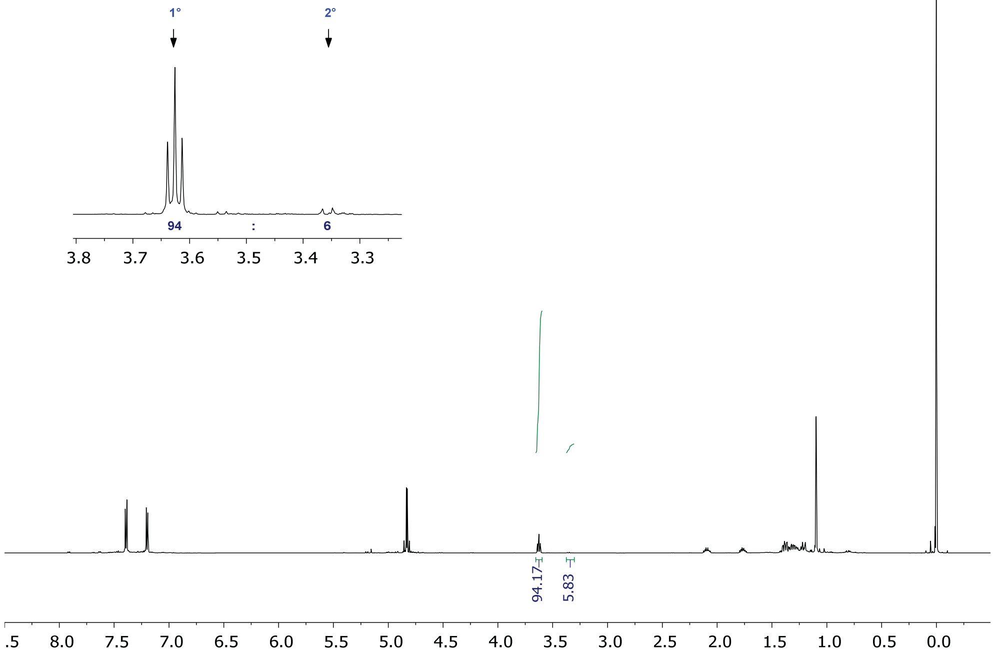

Br
OTMS
(S)
OTMS
CO2CH2CCl3

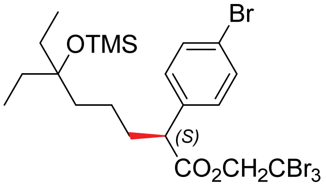

3.60
3.50
3.40
3.30
3.20
3.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(

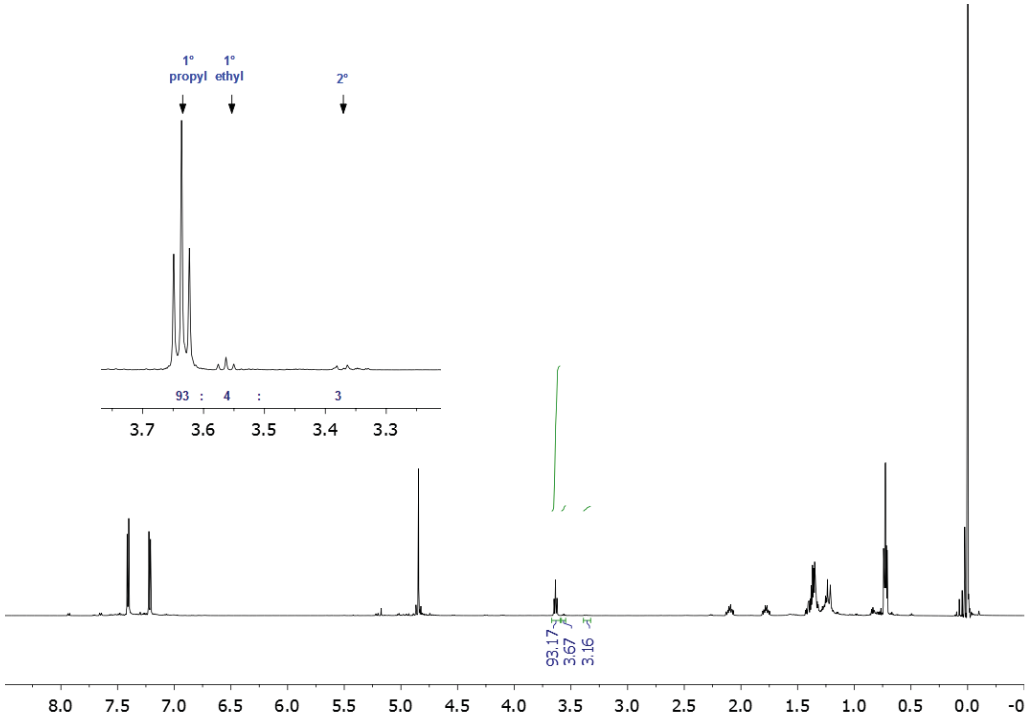

Br
OTMS
TMSO
(S)
CO2CH2CBr3

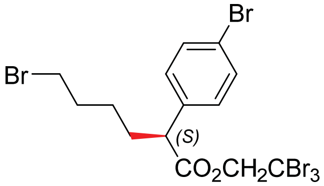

3.7
3.6
3.5
3.4
3.3
3.2
2.12
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(

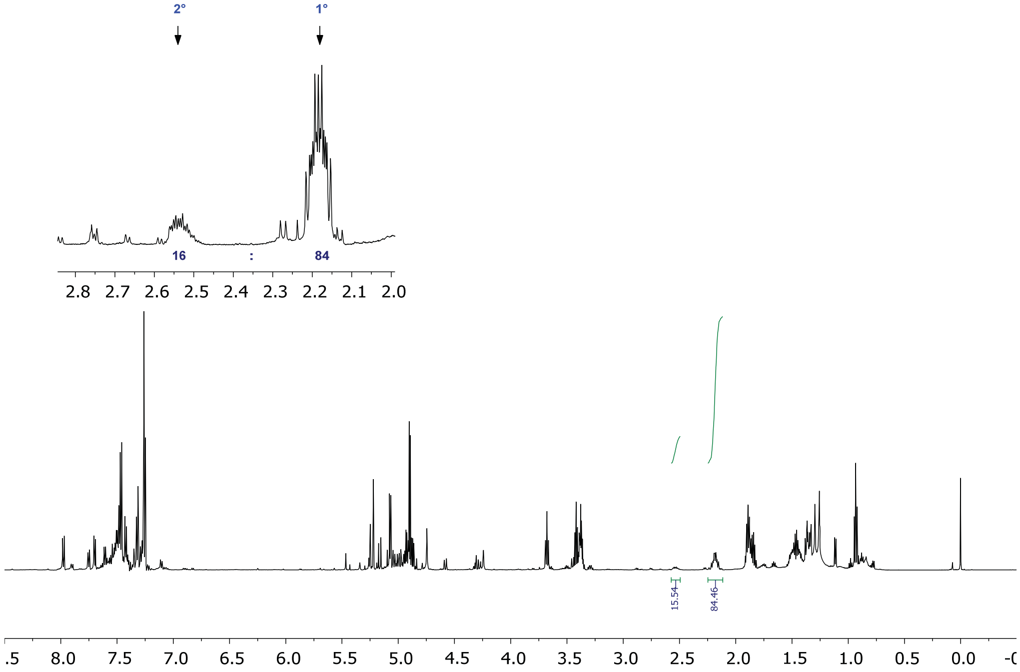

Br
OTMS
(S)
$CO_2CH_2CBr_3$

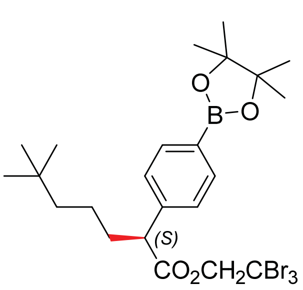

1°
2°
94
:
6
3.8
3.7
3.6
3.5
3.4
3.3
94.17
5.83
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

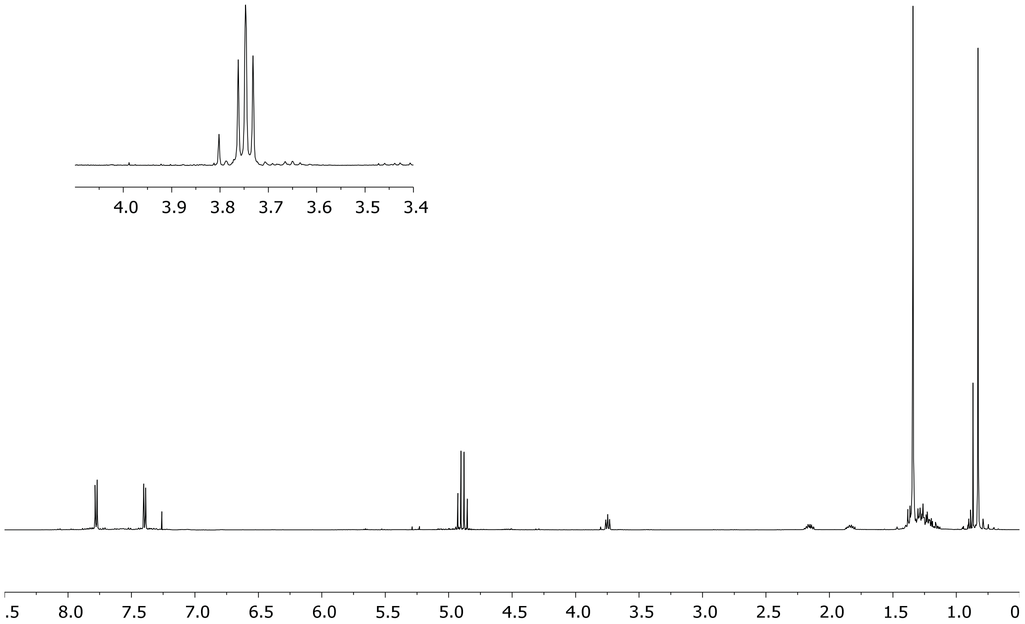

Br
OTMS
(S)
CO2CH2CBr3

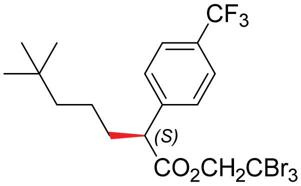

1°
propyl
1°
ethyl
2°
93 : 4 : 3
3.7
3.6
3.5
3.4
3.3
93.17
3.67
3.16
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0

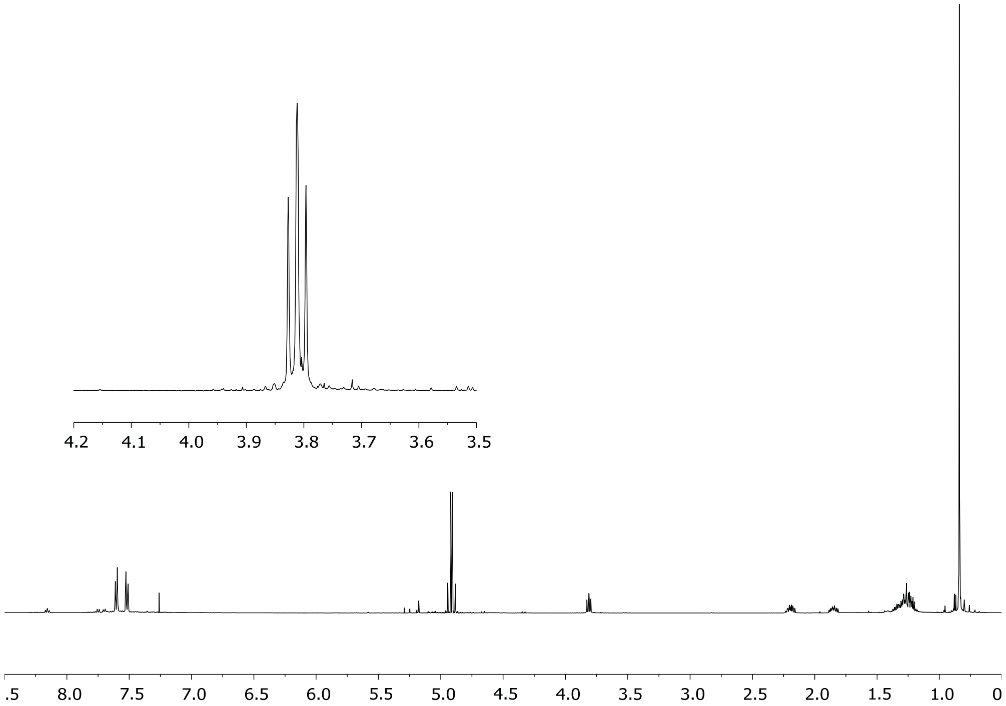

Br
Br
(S)
CO2CH2CBr3

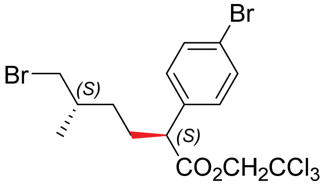

2°
1°
16
:
84
2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0
15.54
84.46
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

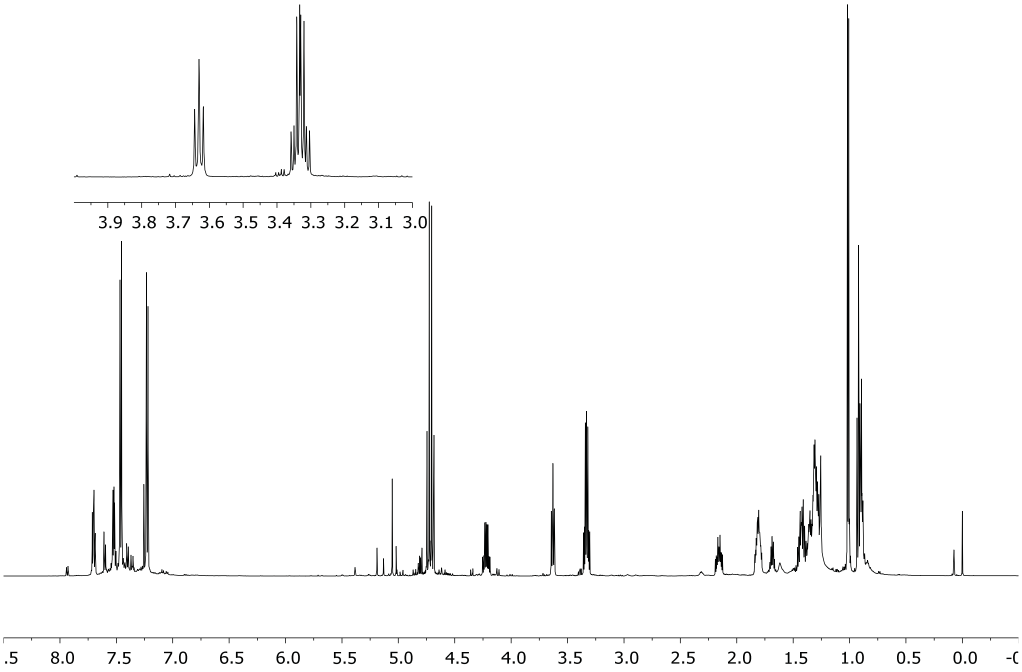

O
B
O
(S)
CO2CH2CBr3

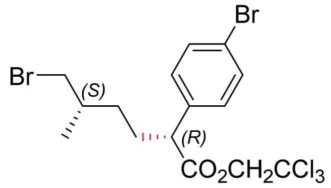

4.0
3.9
3.8
3.7
3.6
3.5
3.4
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

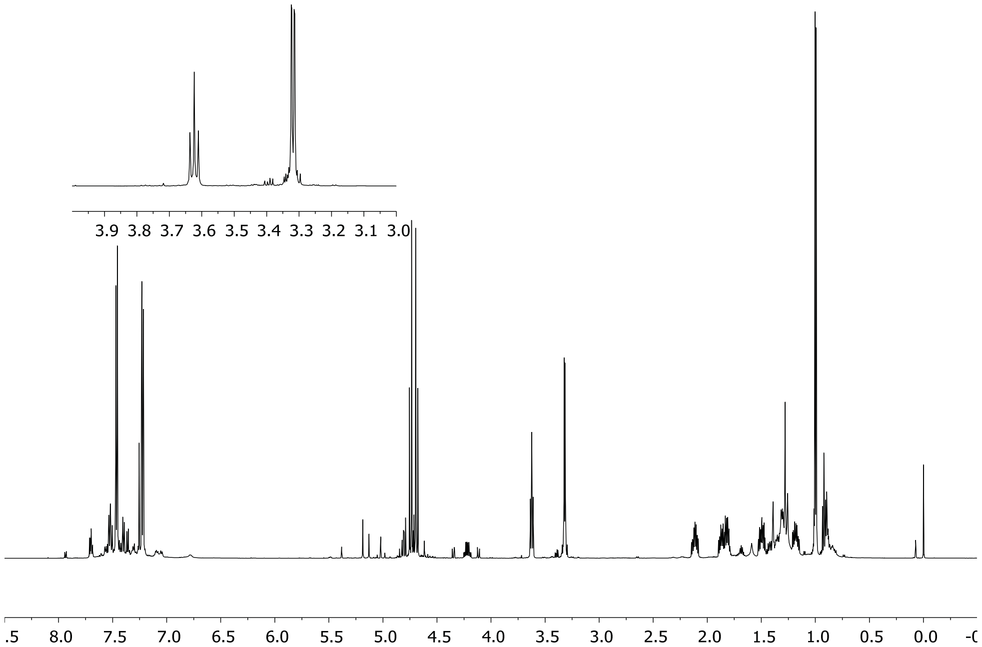

CF3
(S)
CO2CH2CBr3

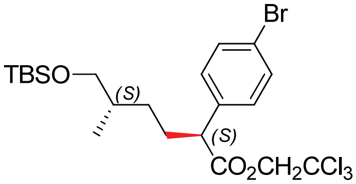

4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

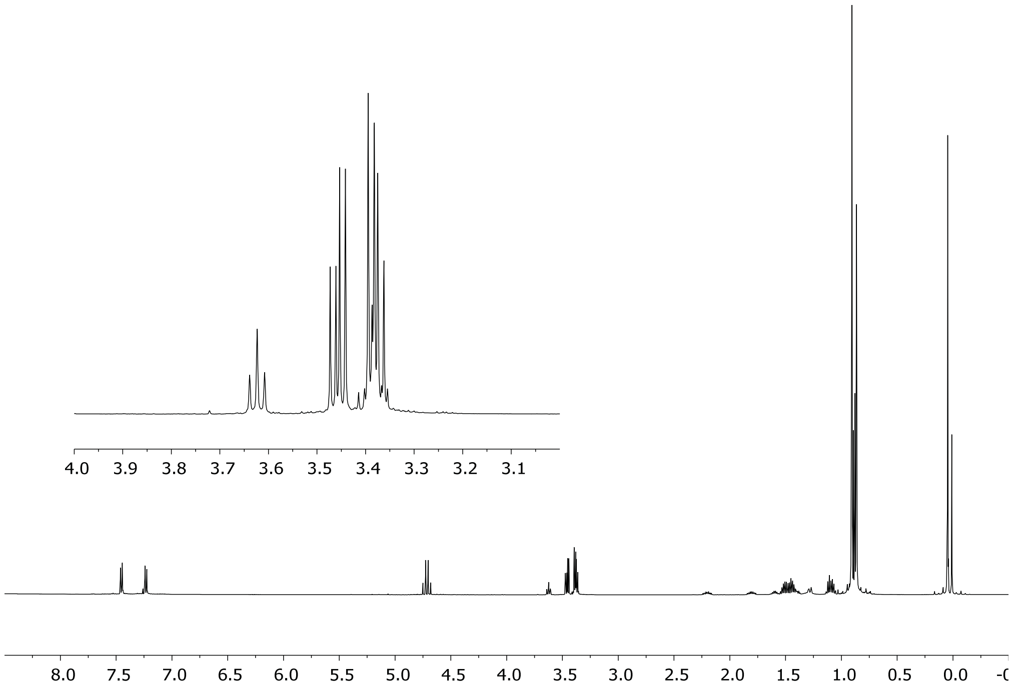

Br
Br
(S)
(S)
CO2CH2CCl3

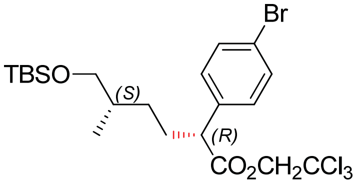

3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -(

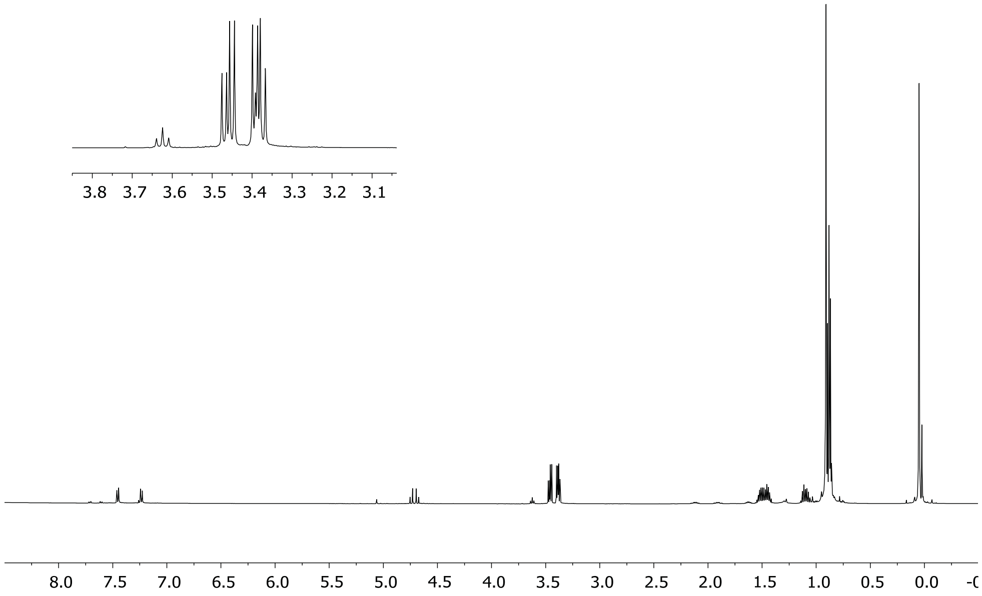

Br
Br
(S)
(R)
CO2CH2CCl3

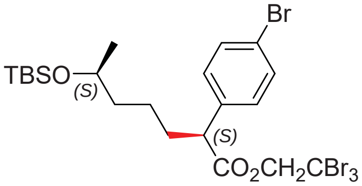

3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -(


Br
TBSO
(S)
(S)
$CO_2CH_2CCl_3$

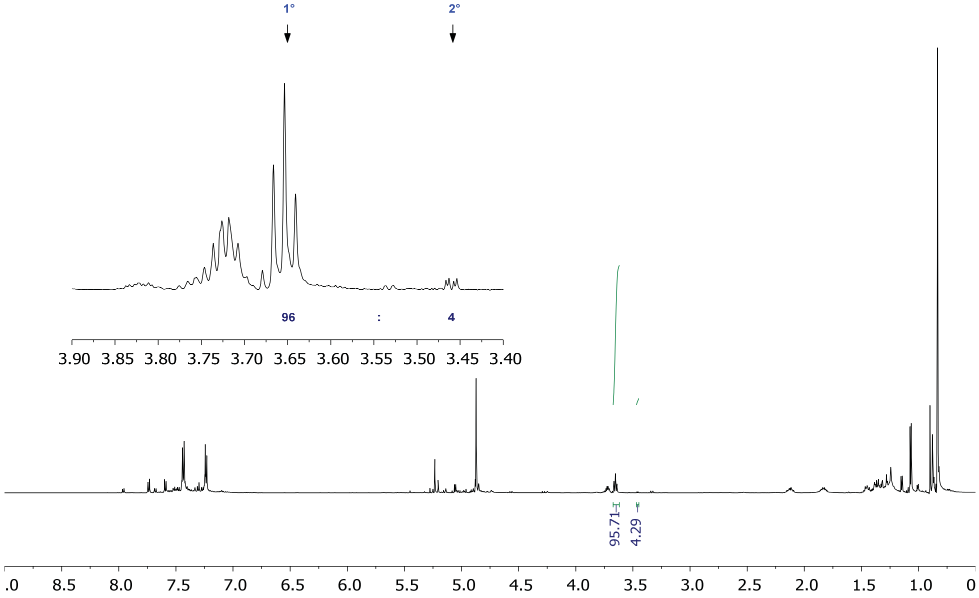

4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


Br
TBSO
(S)
(R)
CO2CH2CCl3

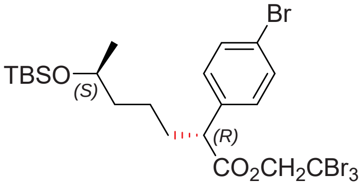

3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -(

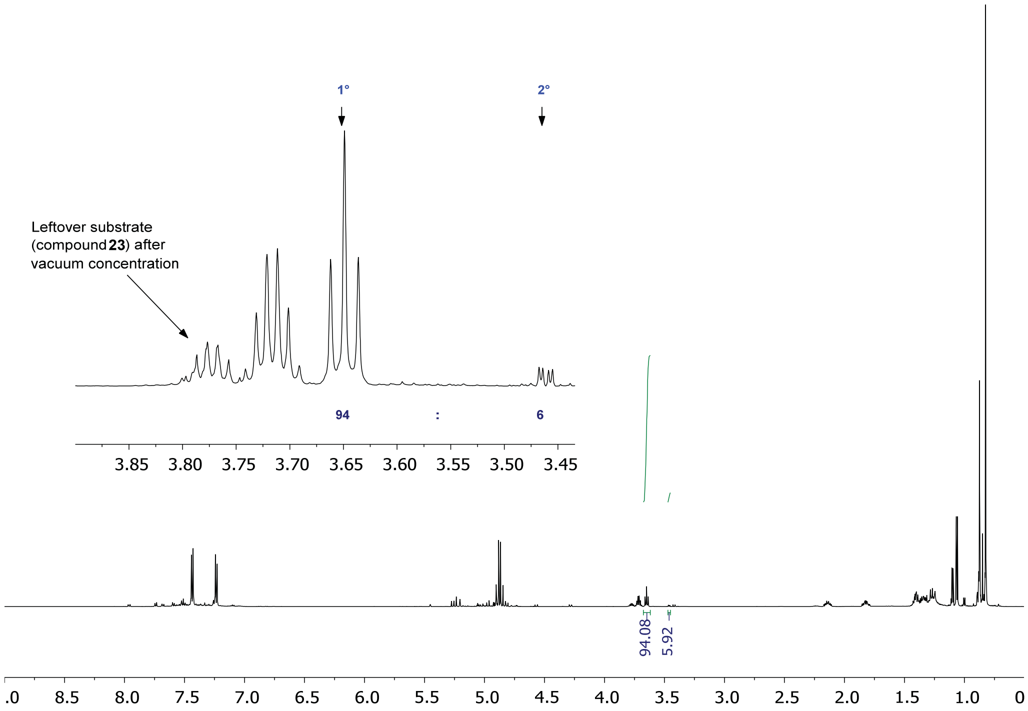


Br
TBSO
(S)
(S)
$CO_2CH_2CBr_3$

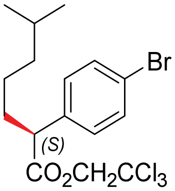


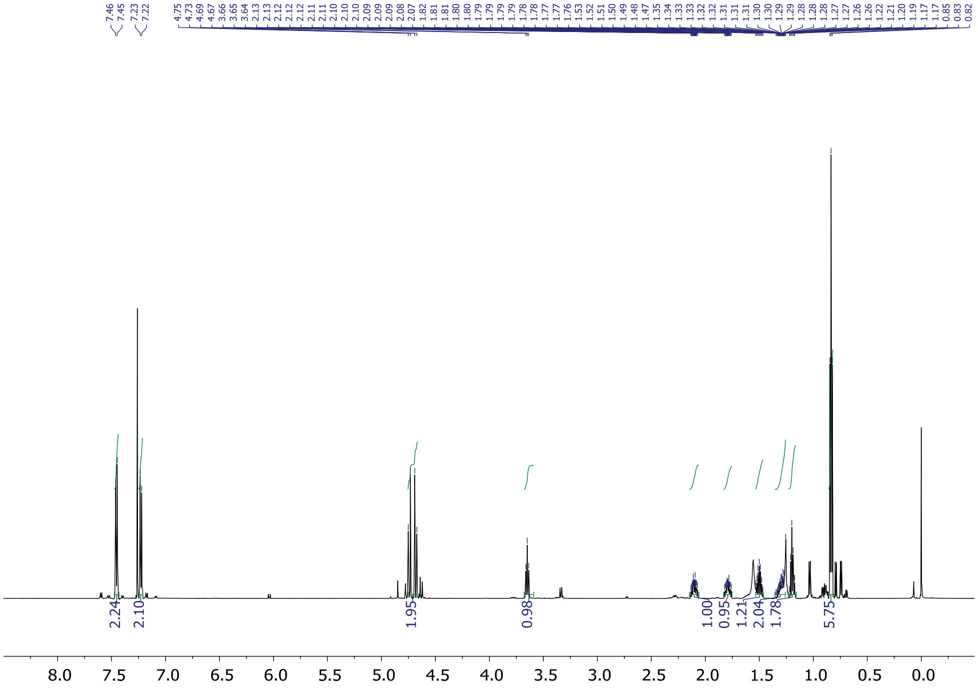
1°
2°
96
:
4
3.90 3.85 3.80 3.75 3.70 3.65 3.60 3.55 3.50 3.45 3.40
95.71
4.29
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

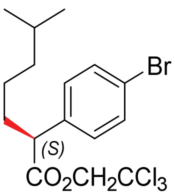

Br
TBSO
(S)
(R)
CO2CH2CBr3

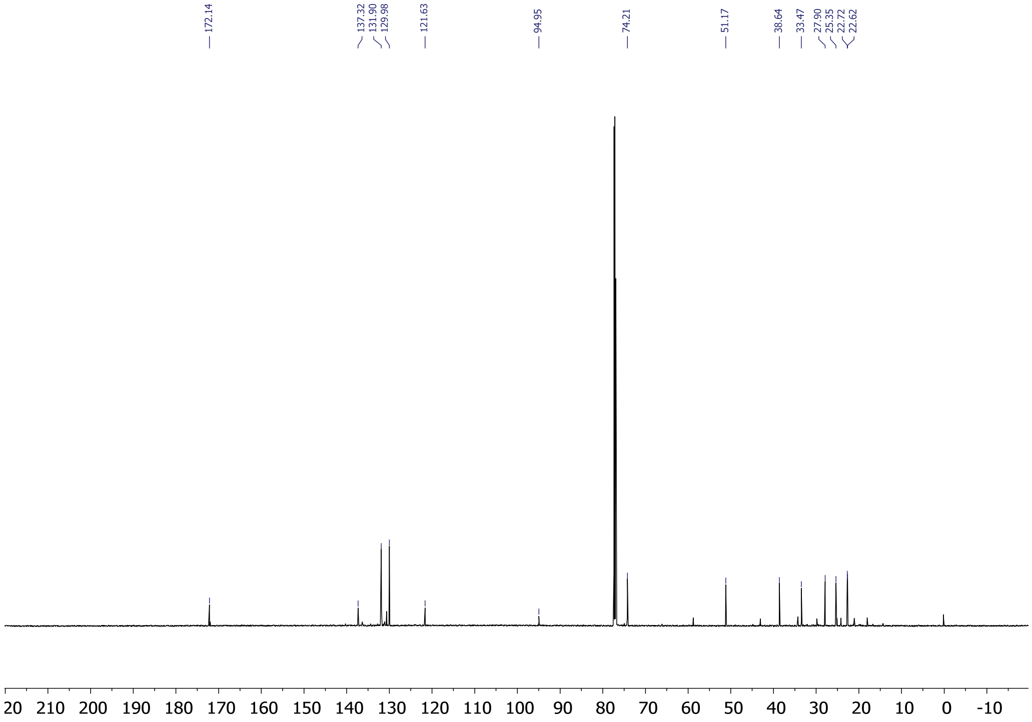

1°
2°
Leftover substrate
(compound **23**) after
vacuum concentration
94
:
6
3.85
3.80
3.75
3.70
3.65
3.60
3.55
3.50
3.45
94.08
5.92
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

8. NMR Spectra for C–H Functionalization Products






Br
(S)
CO$_2$CH$_2$CCl$_3$


172.14
137.32
131.90
129.98
121.63
94.95
74.21
51.17
38.64
33.47
27.90
25.35
22.72
22.62
20
210
200
190
180
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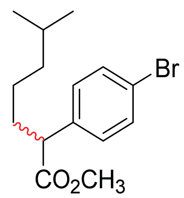
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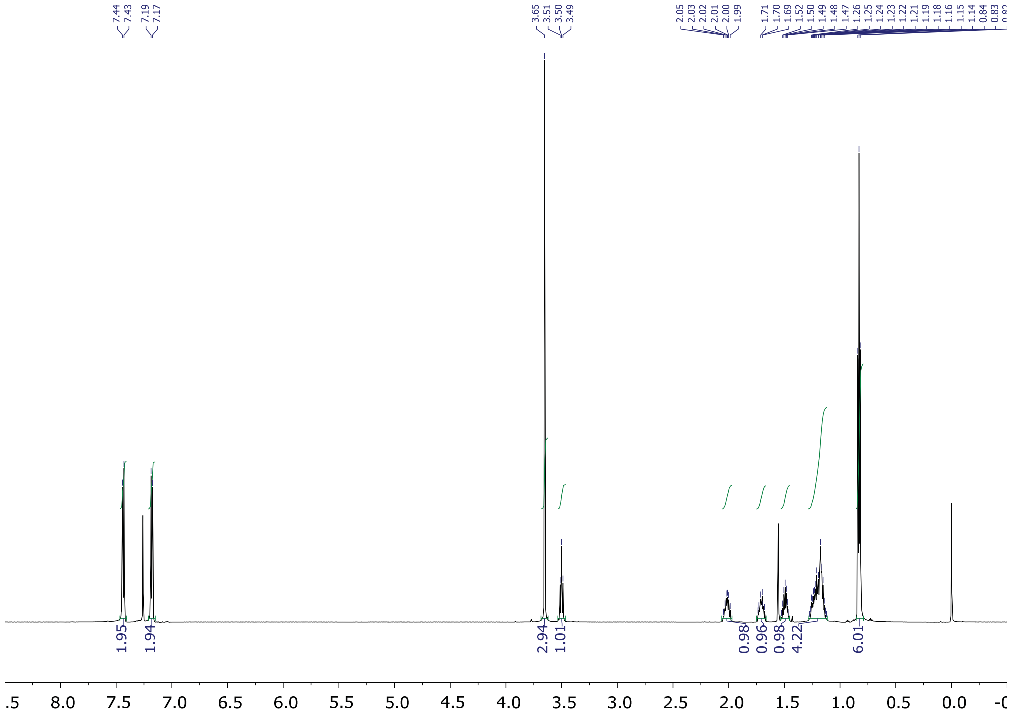
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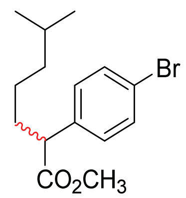
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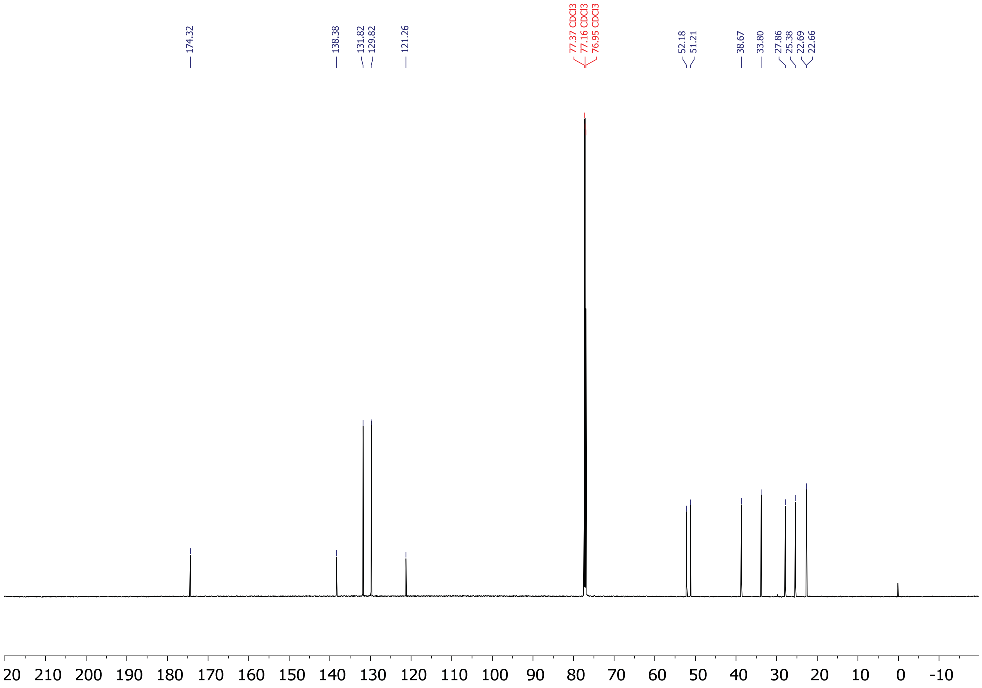
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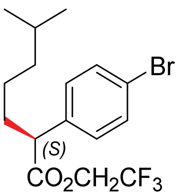
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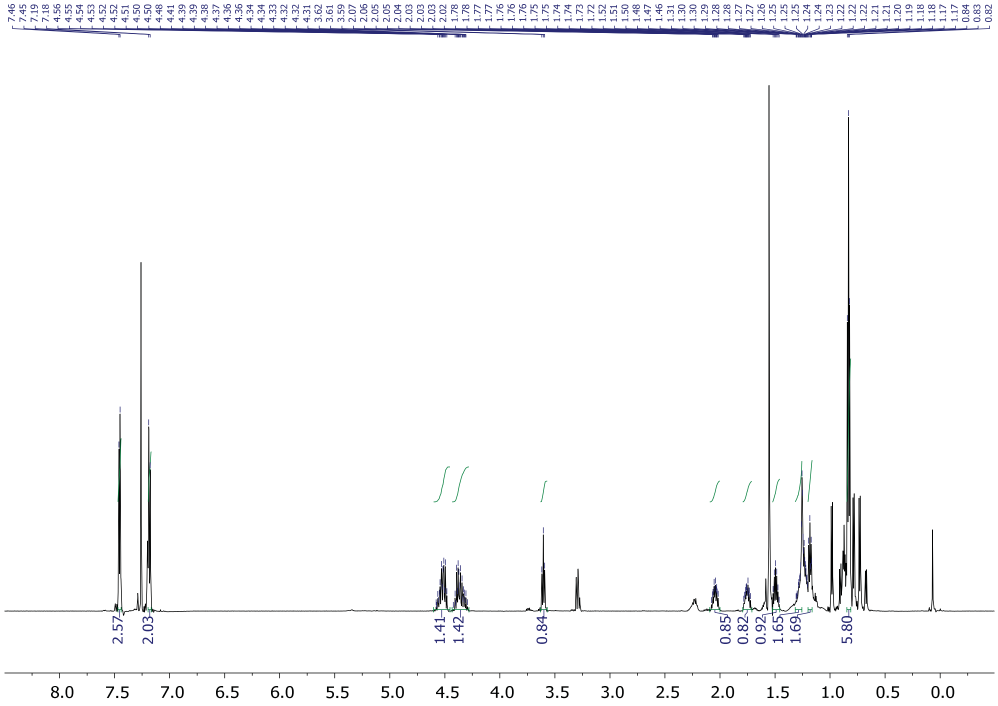
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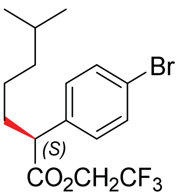
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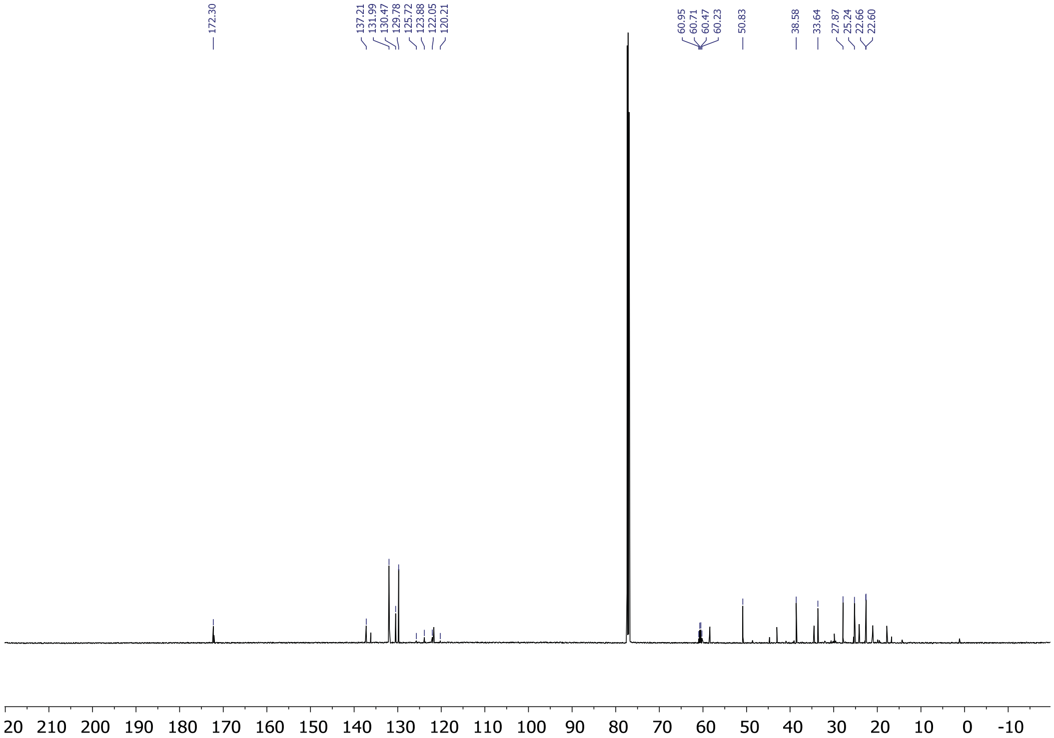
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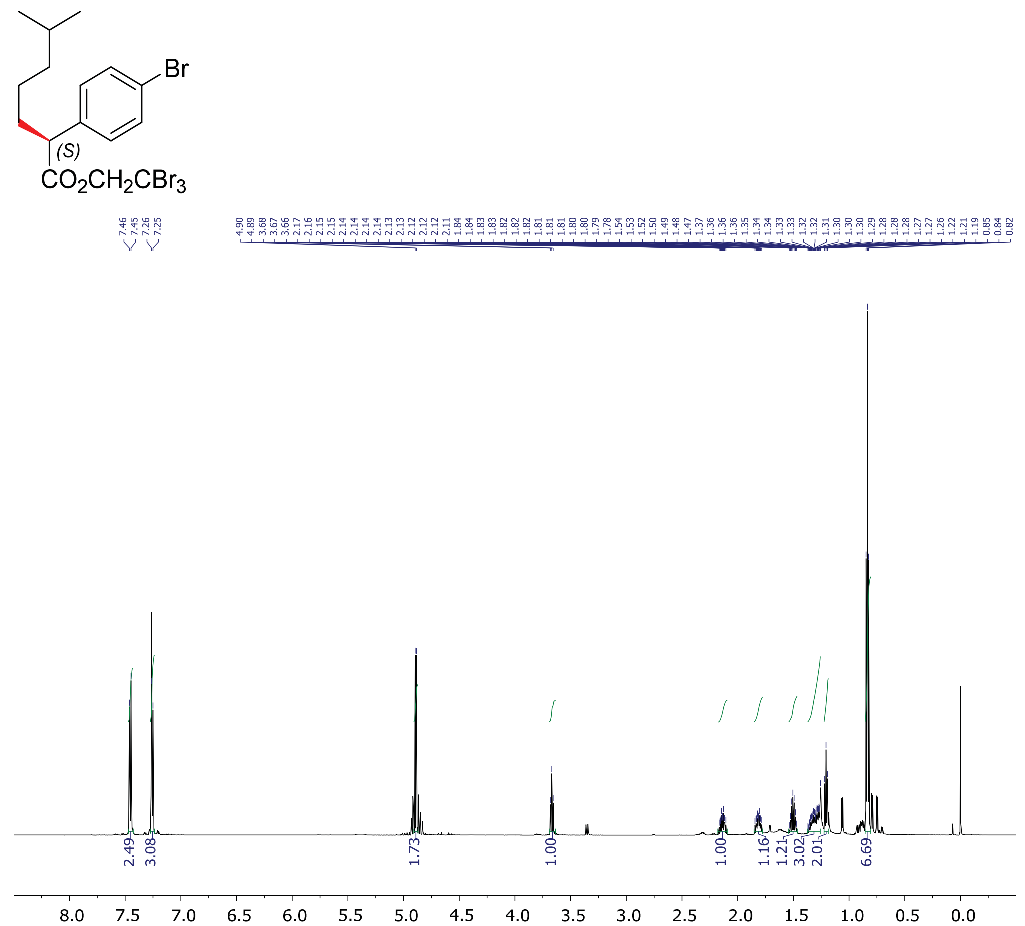
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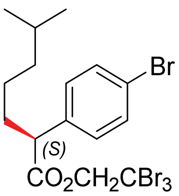
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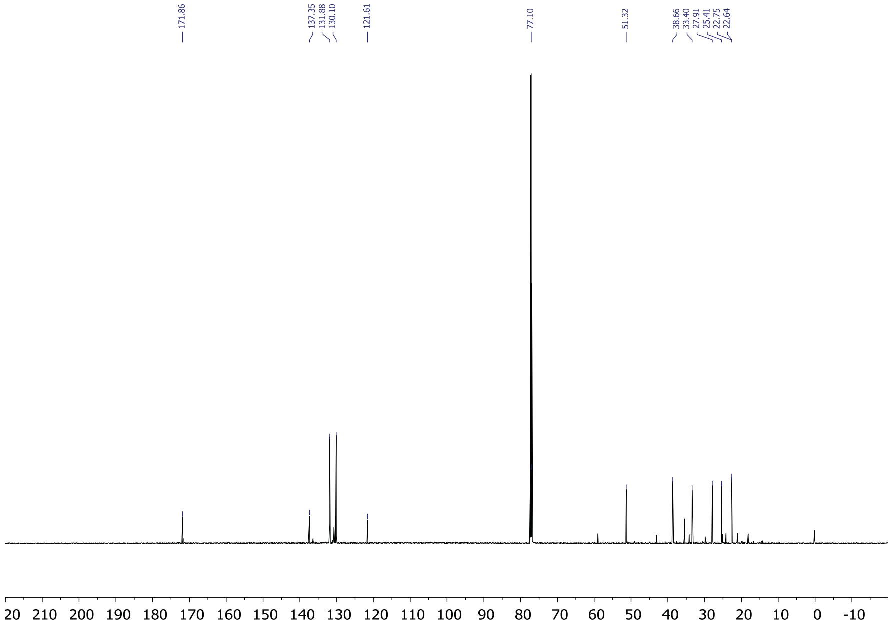
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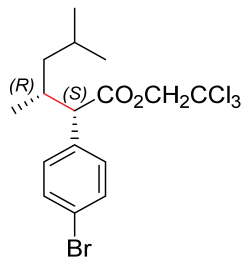
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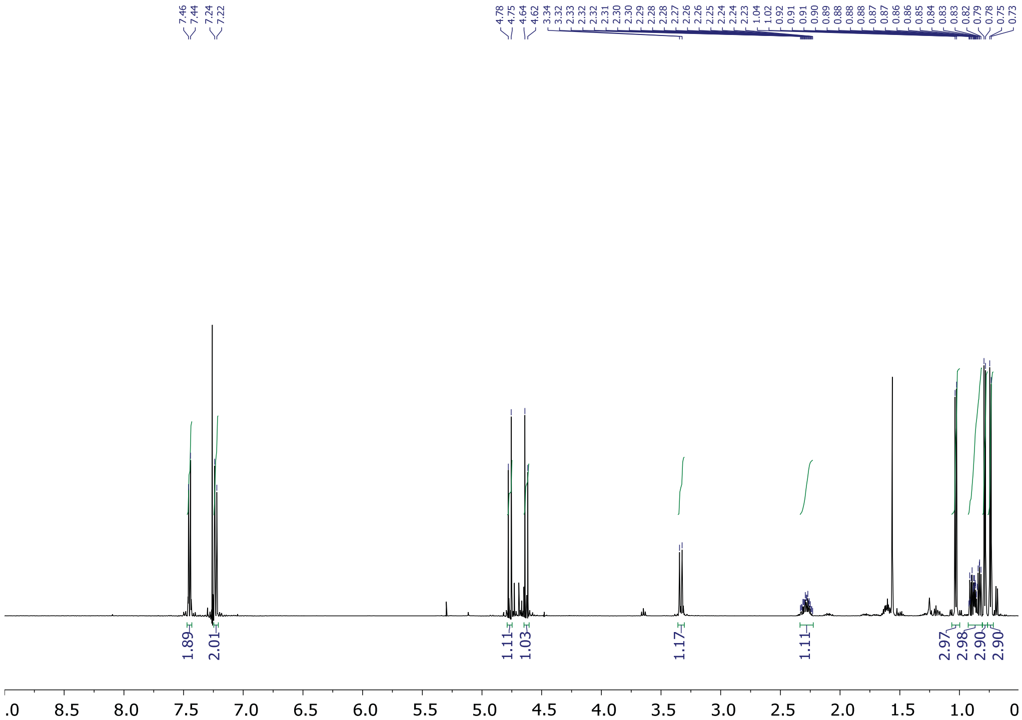
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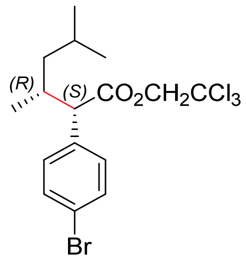
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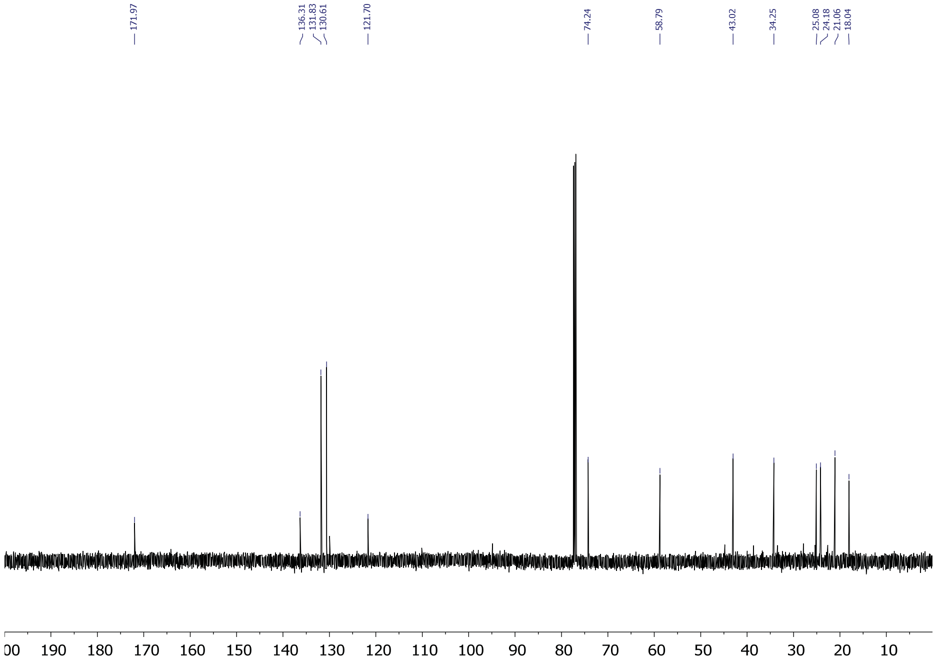
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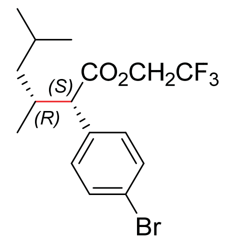
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(R)
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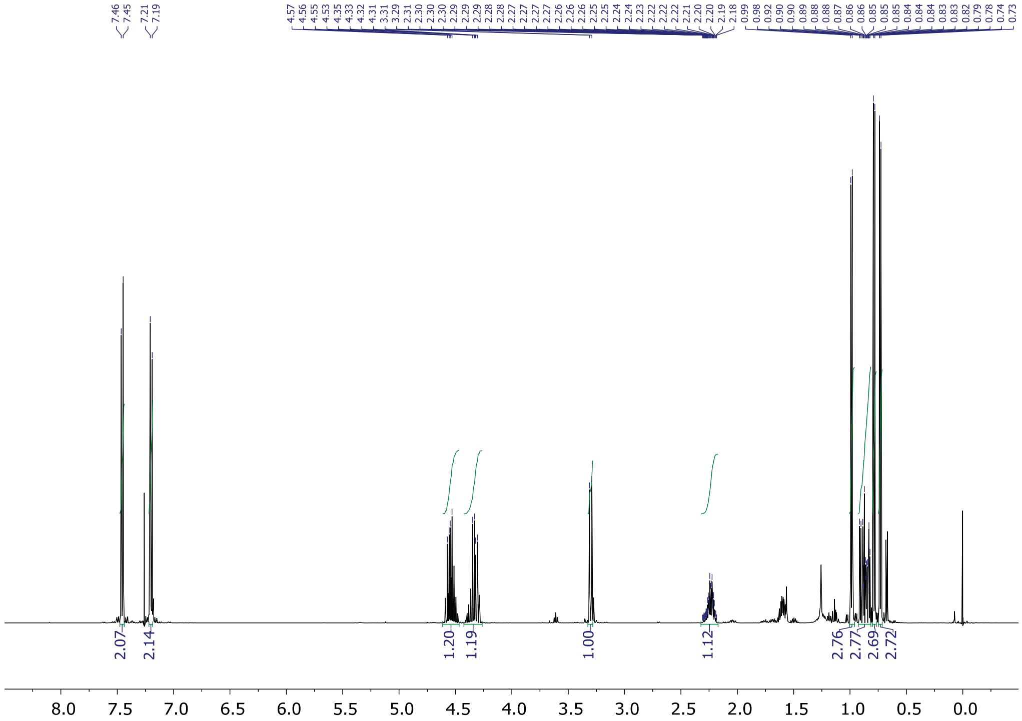
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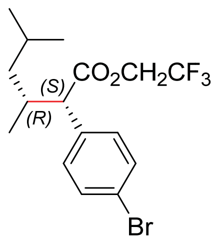
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(R)
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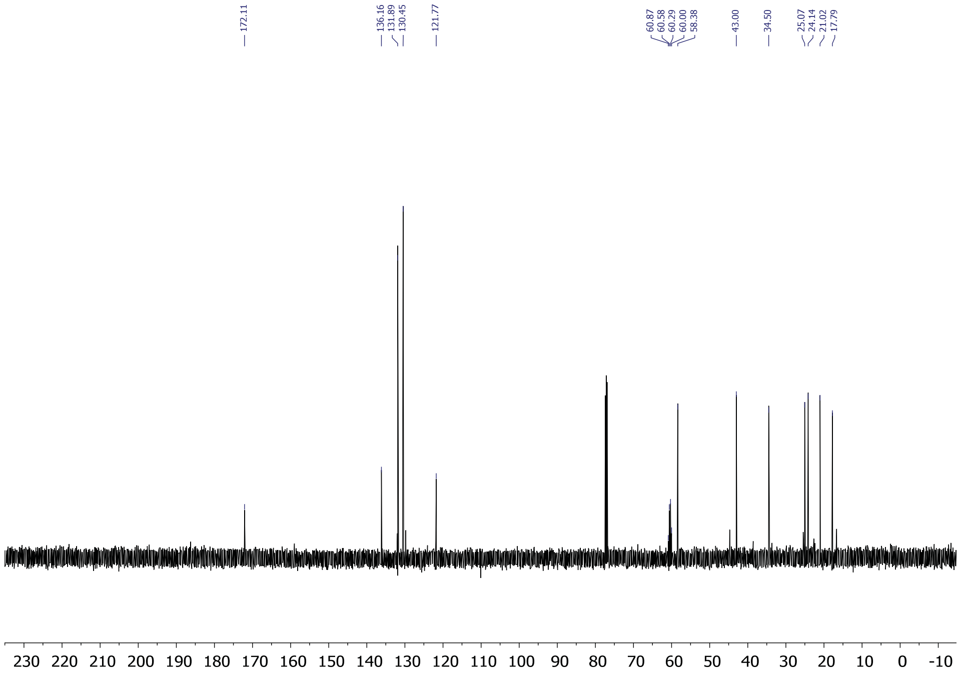
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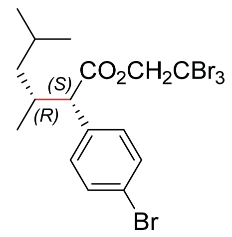
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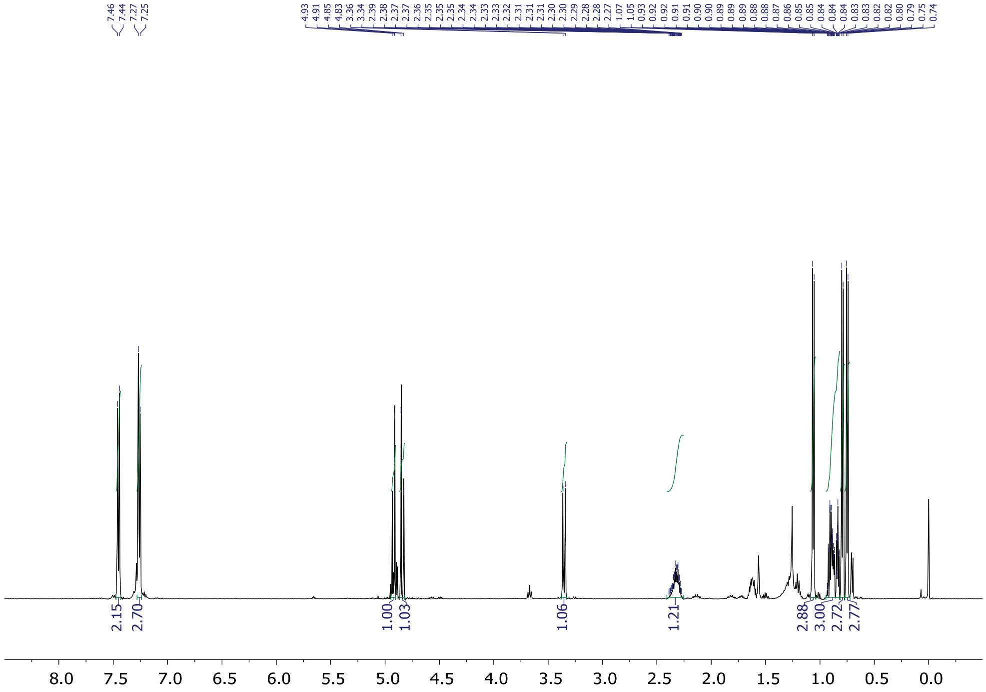
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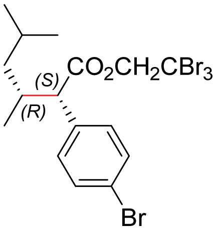
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(R)
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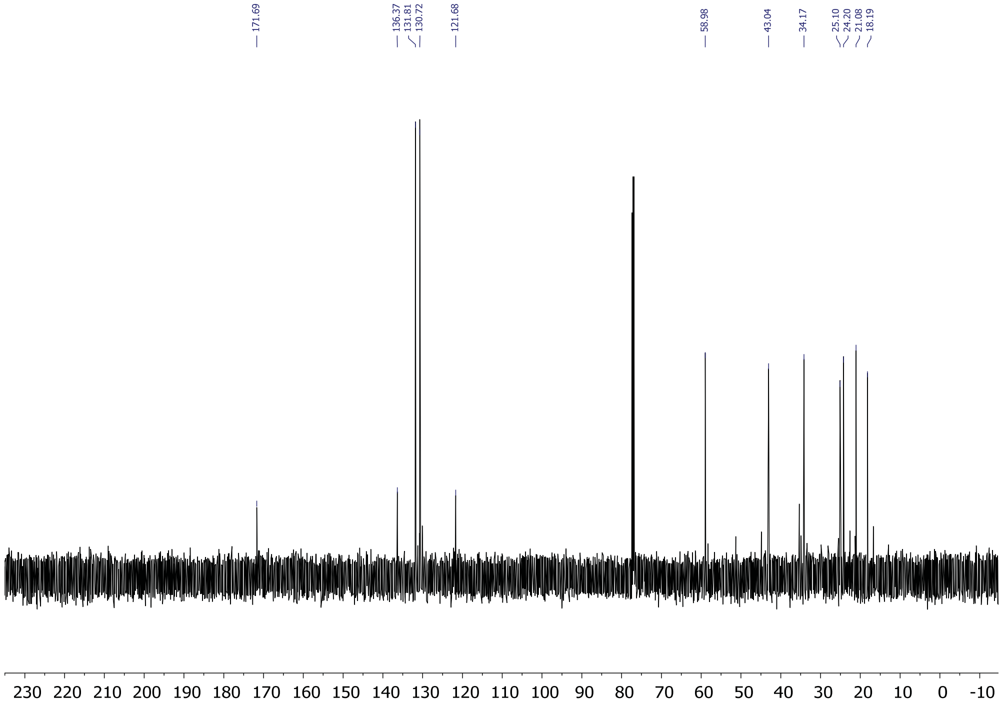
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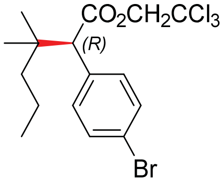
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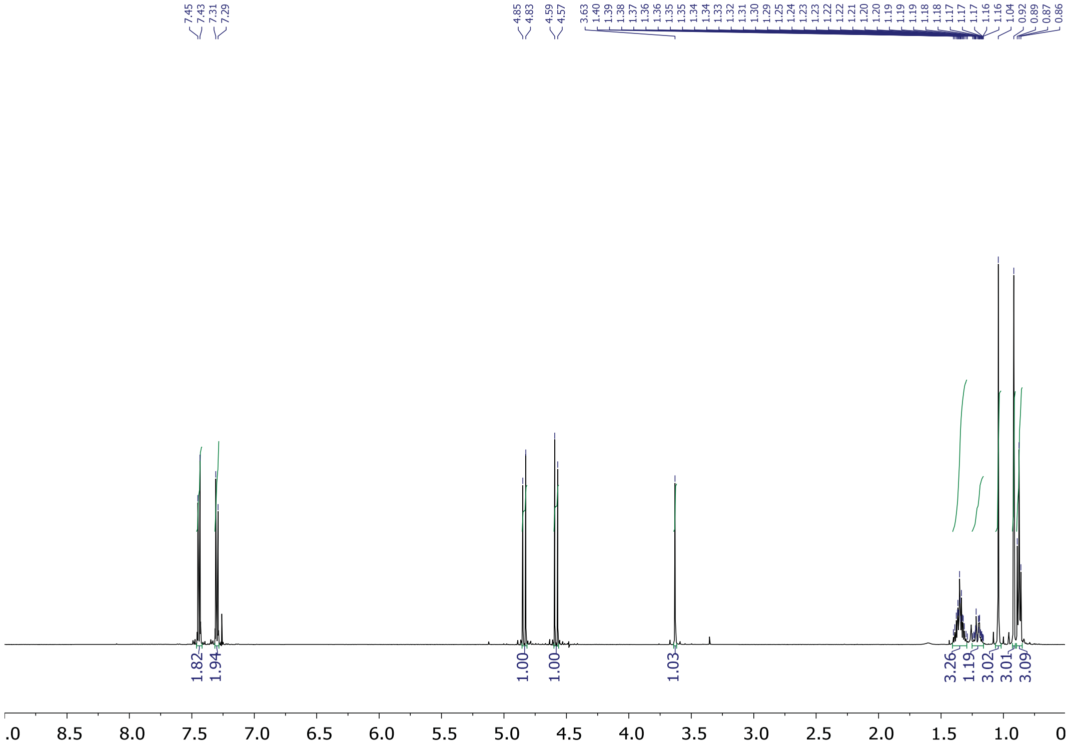
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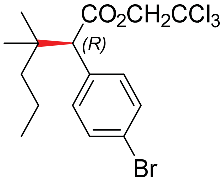
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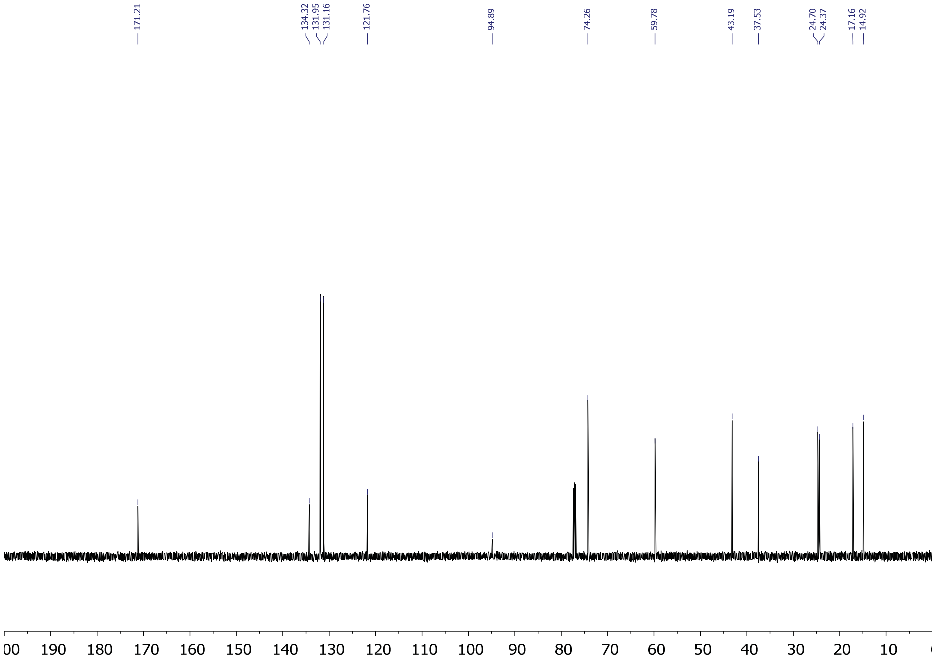
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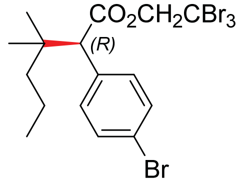
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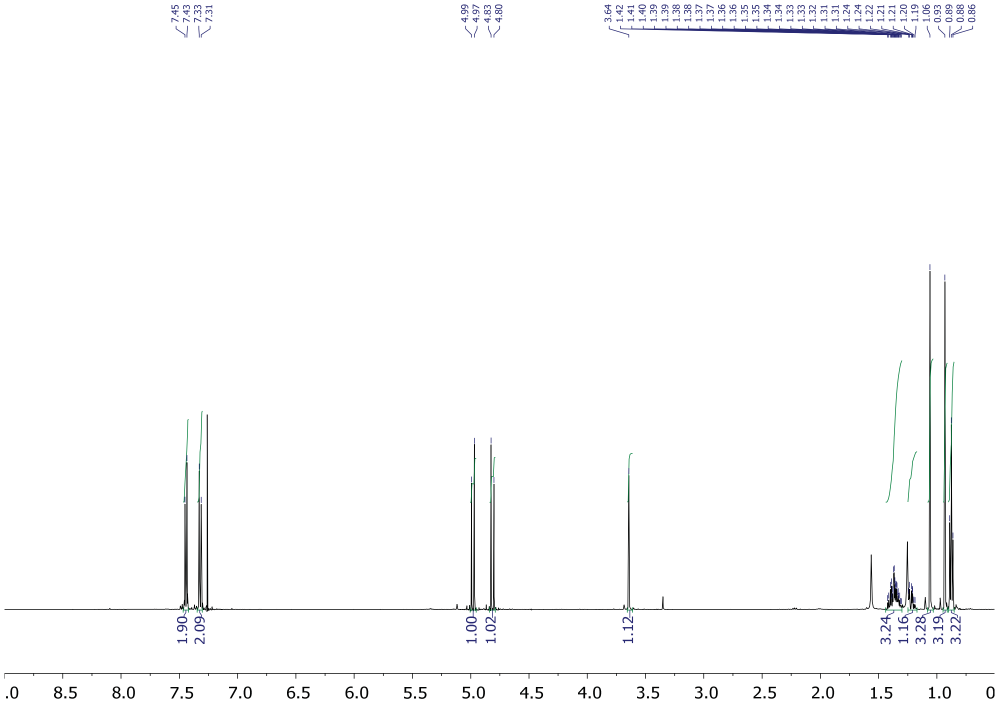
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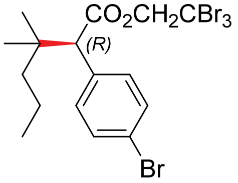
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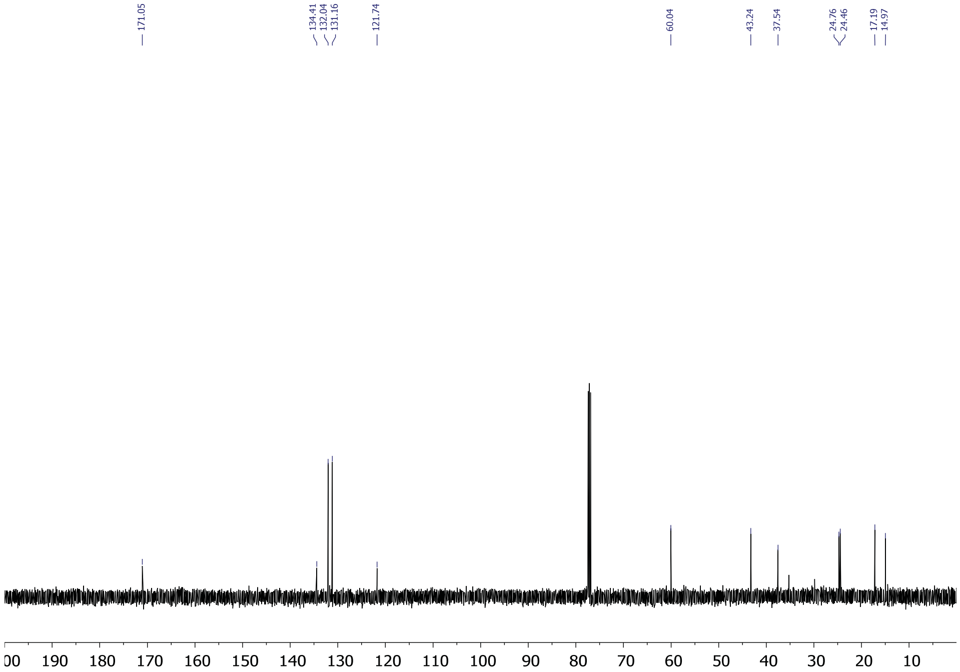
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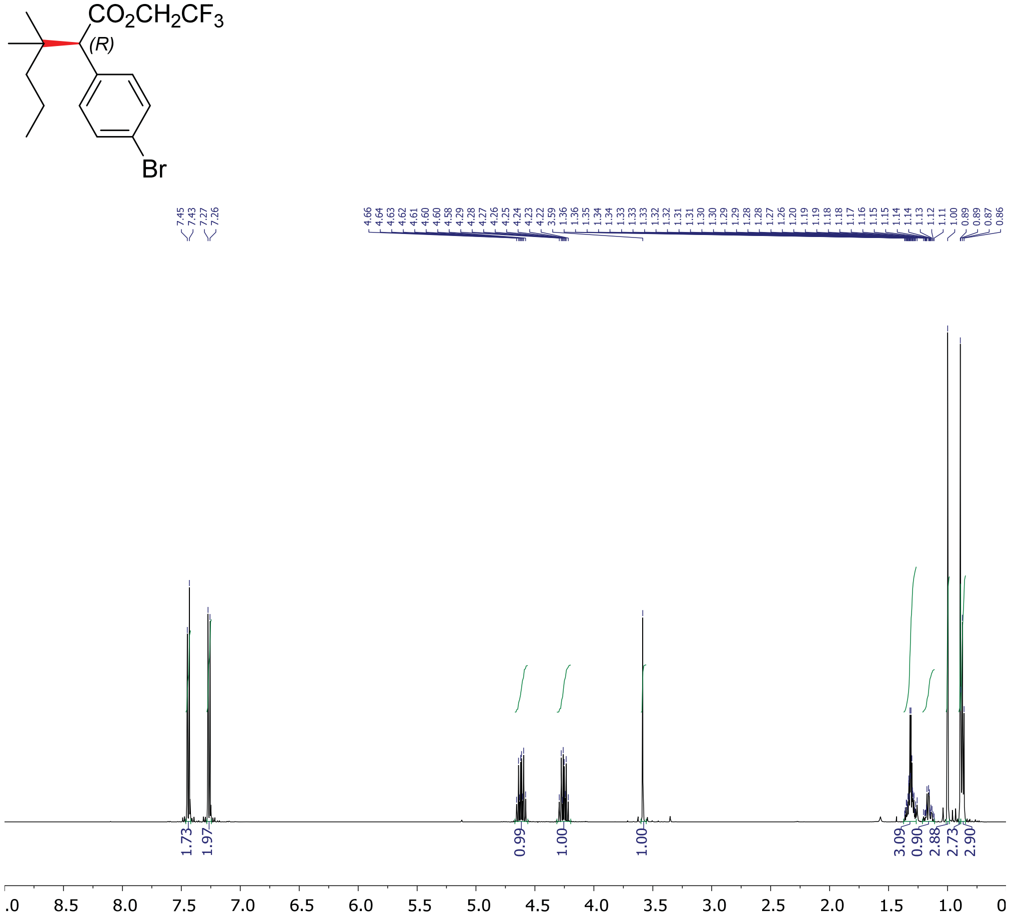
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(R)
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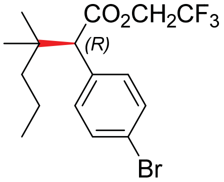
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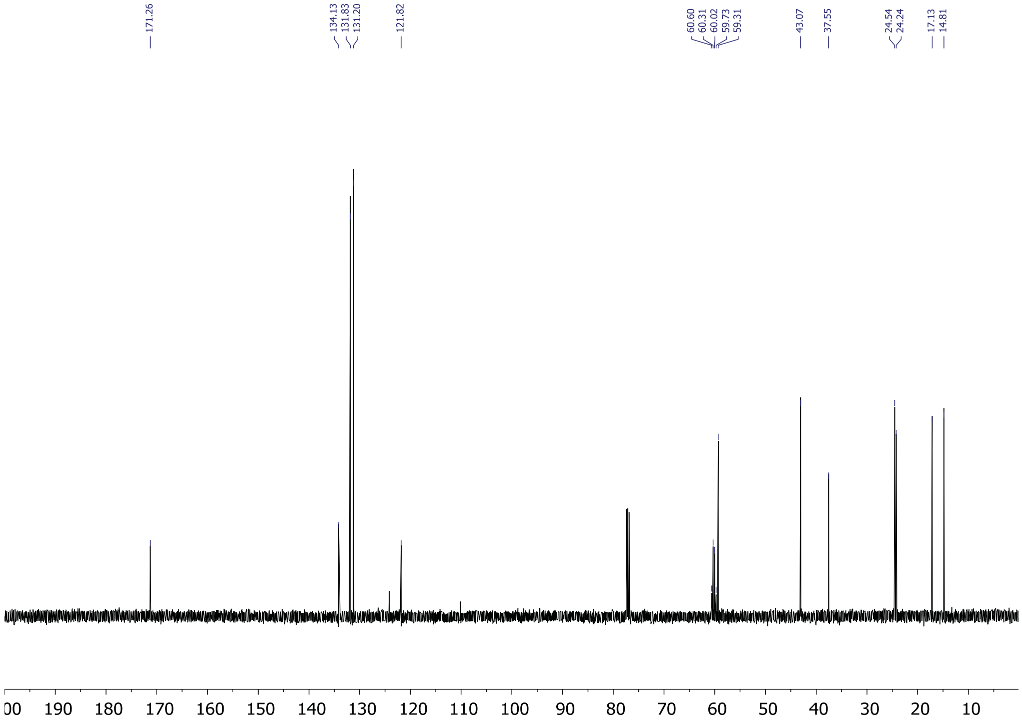
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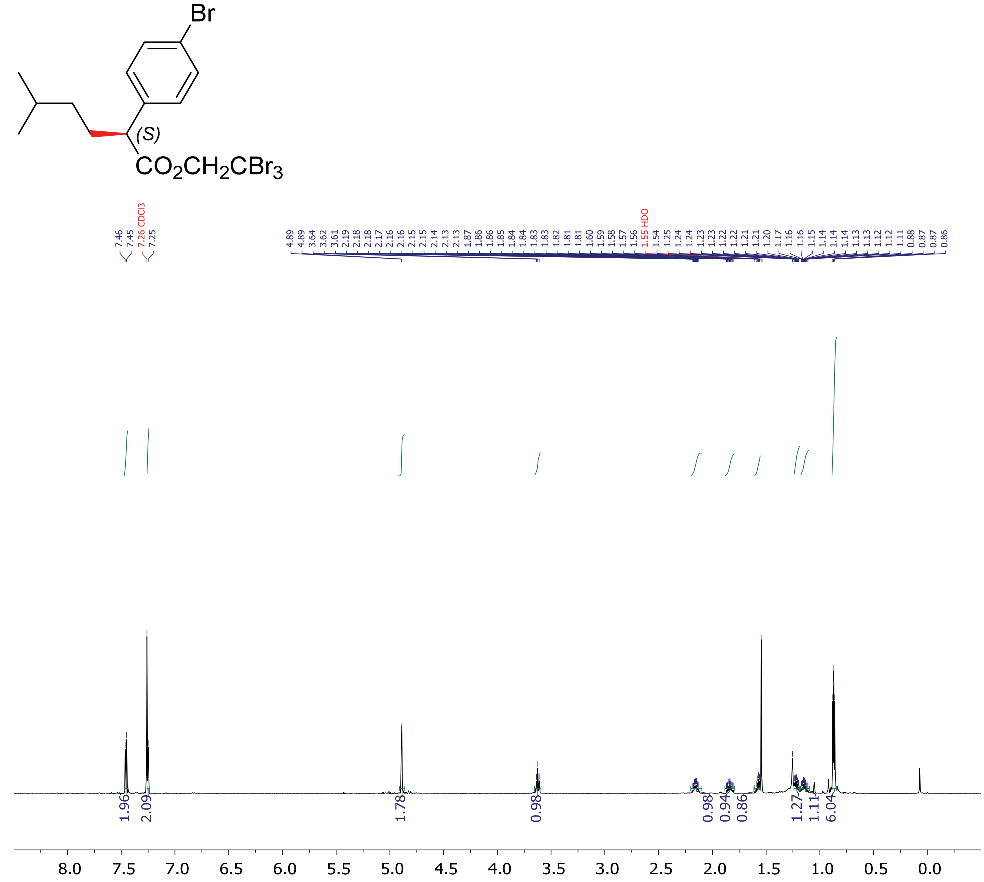

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7.25
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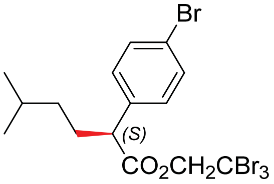
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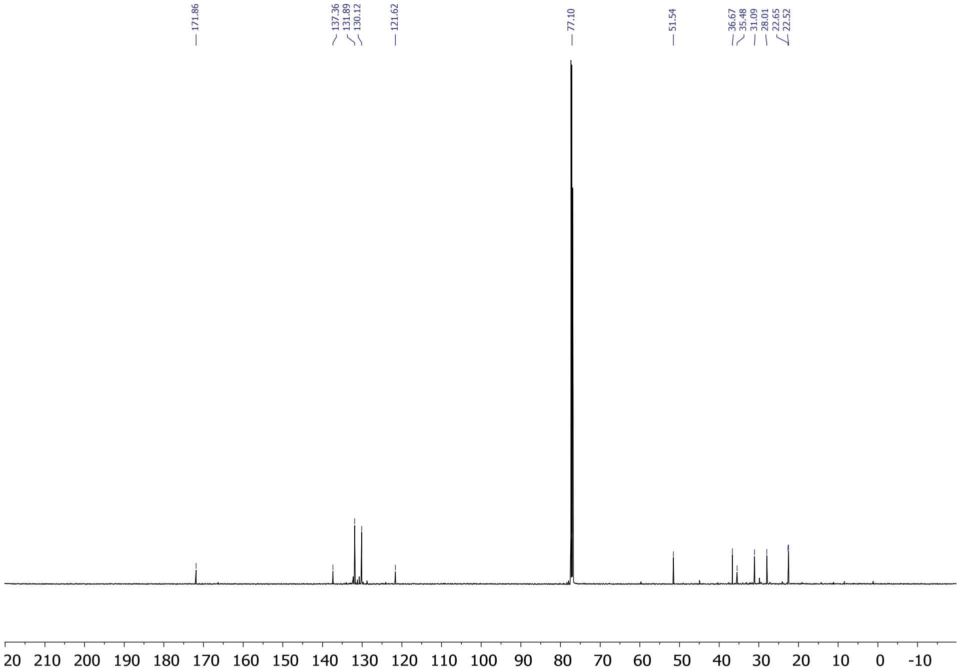
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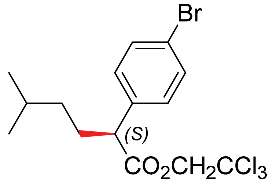
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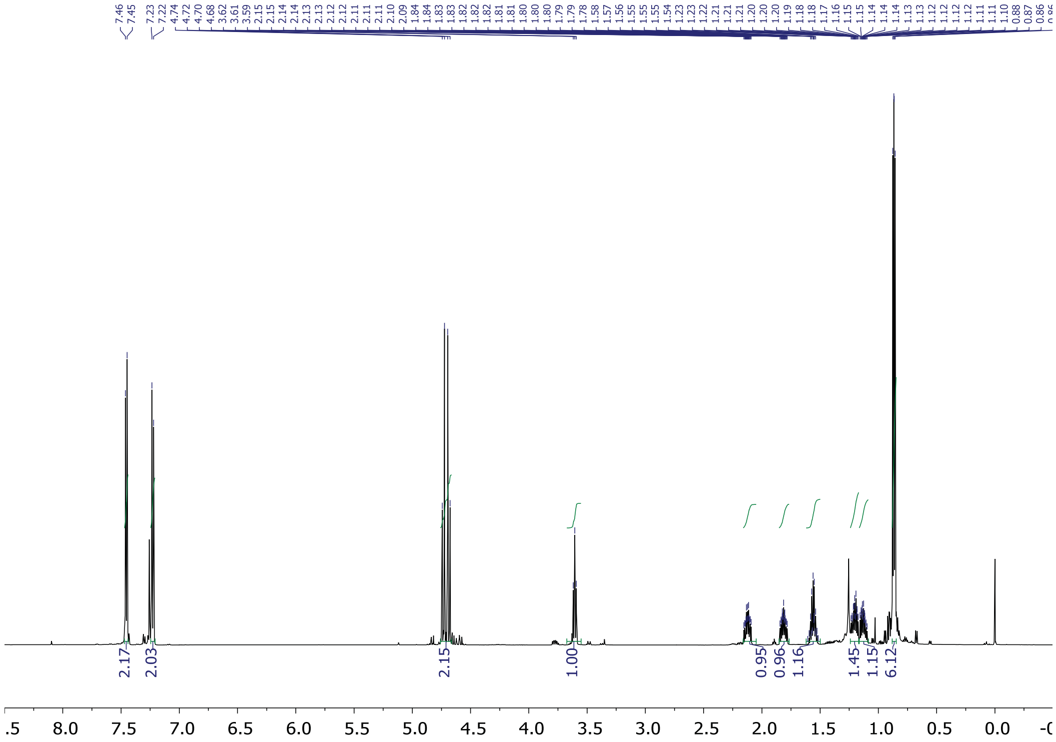
CO₂CH₂CCl₃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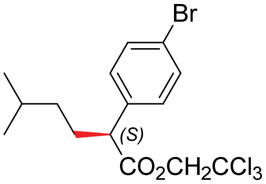
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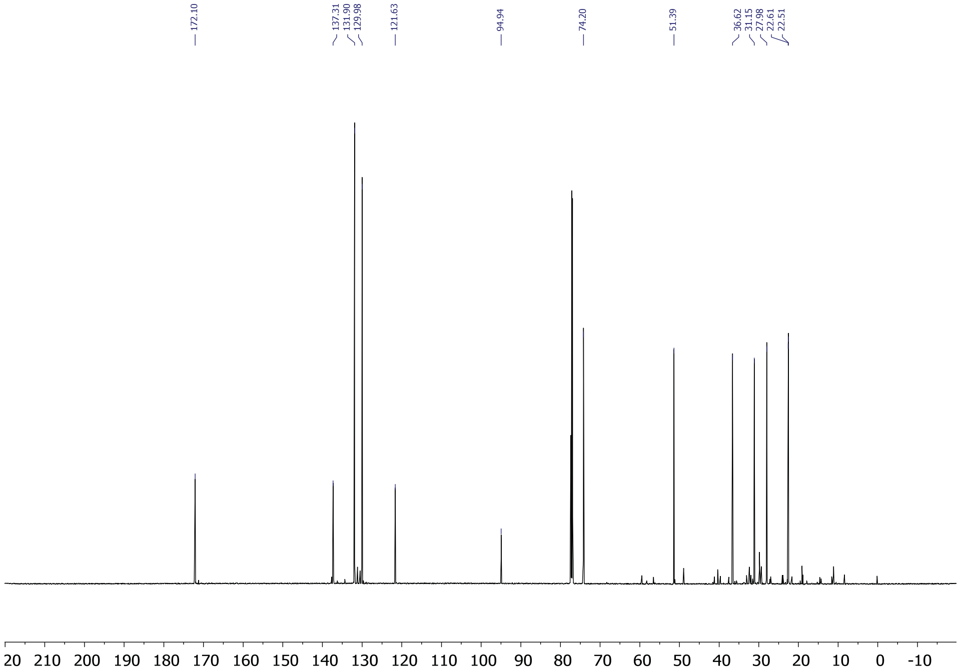
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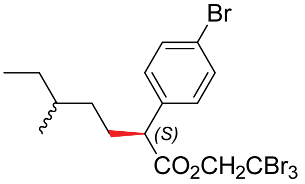
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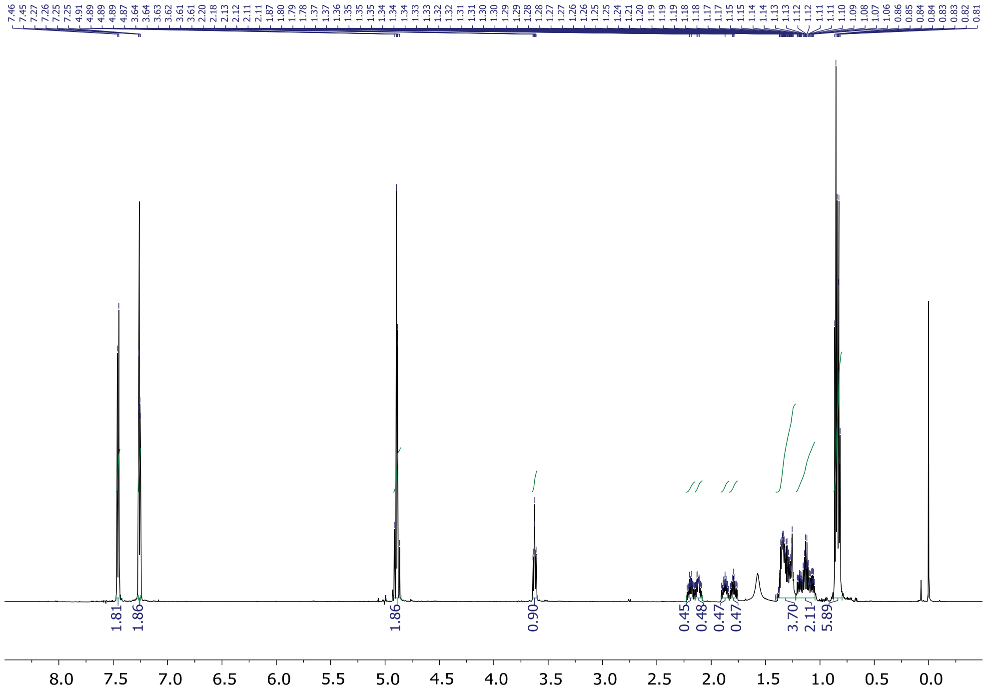
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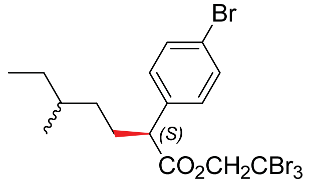
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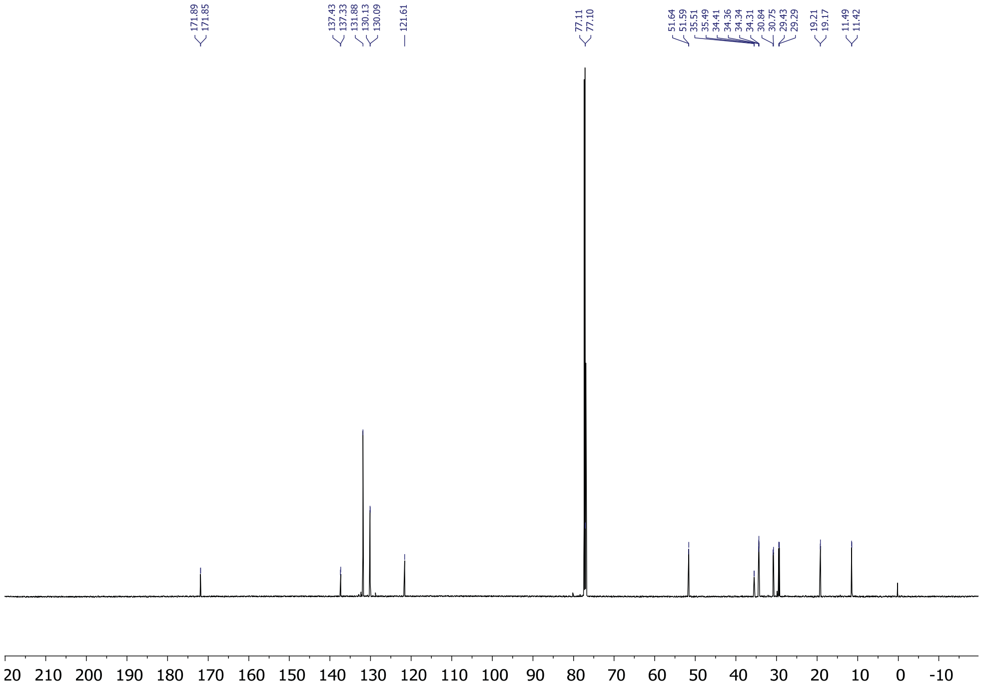
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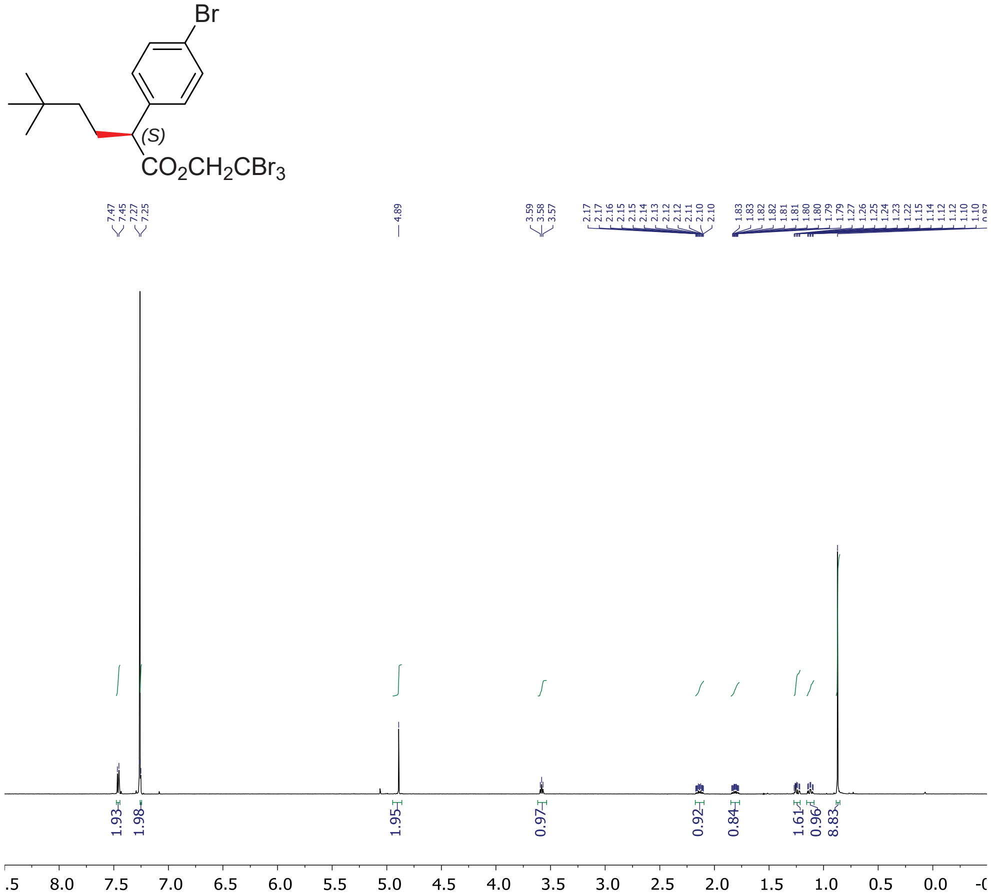
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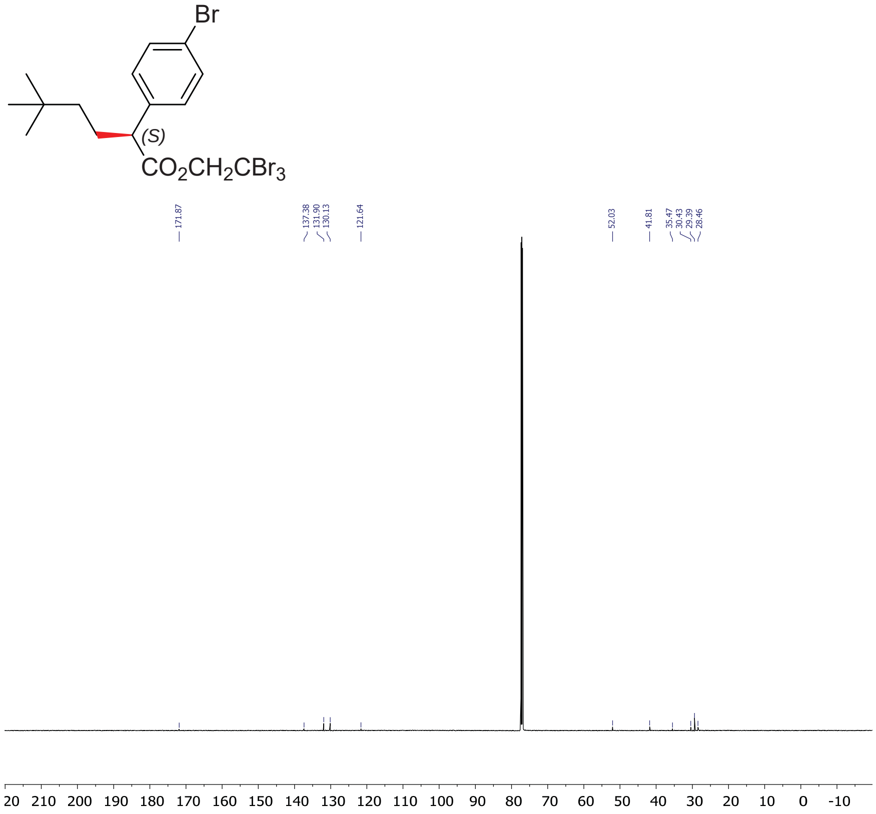
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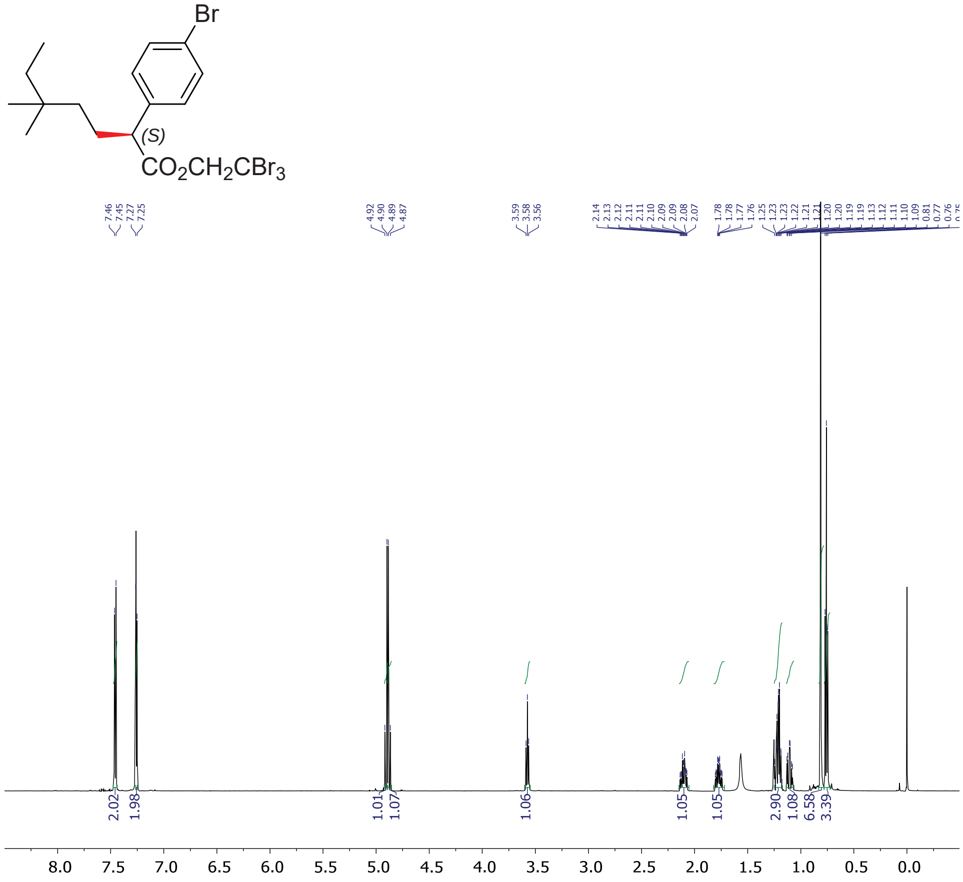
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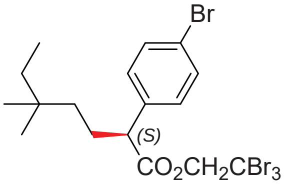
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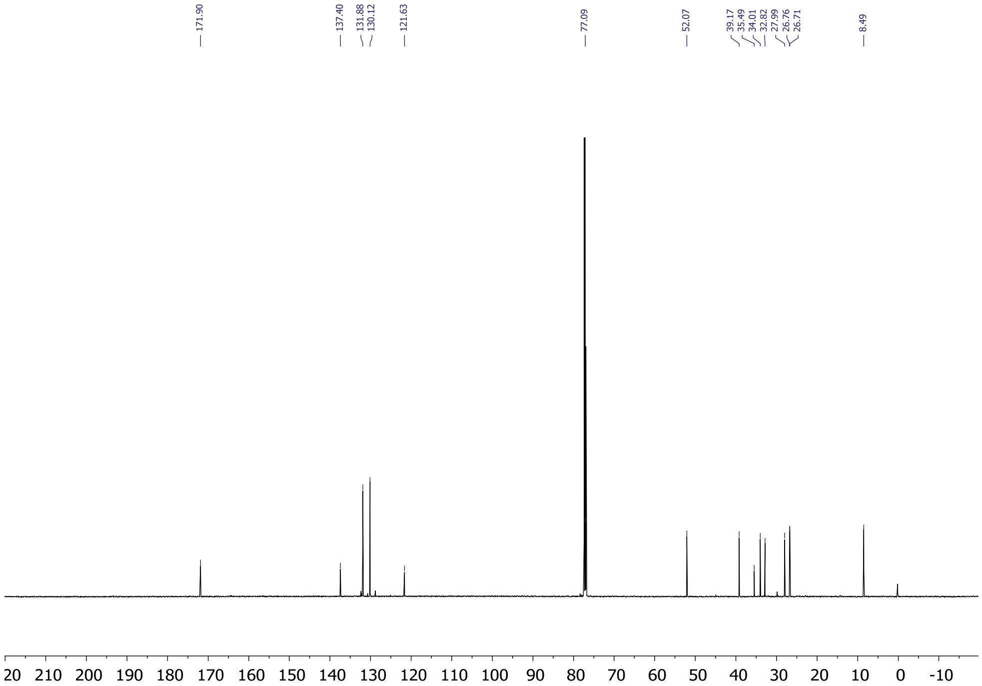
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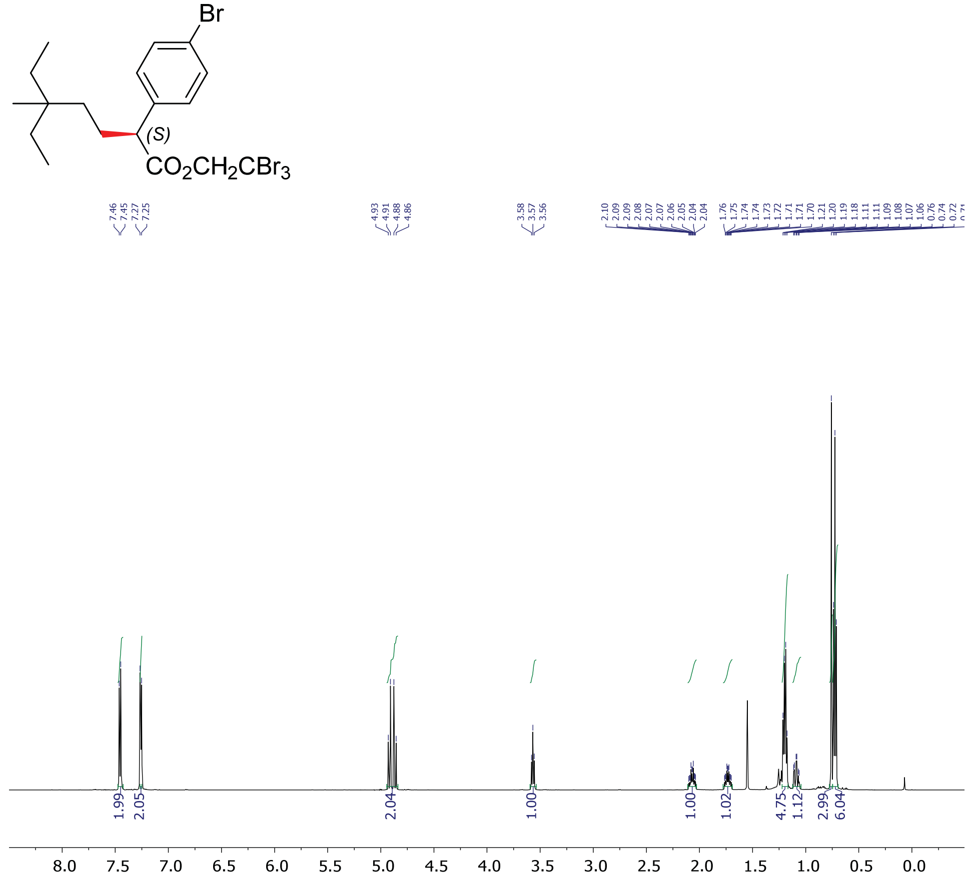
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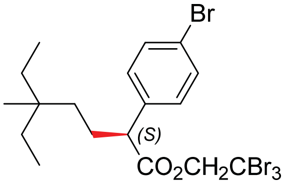
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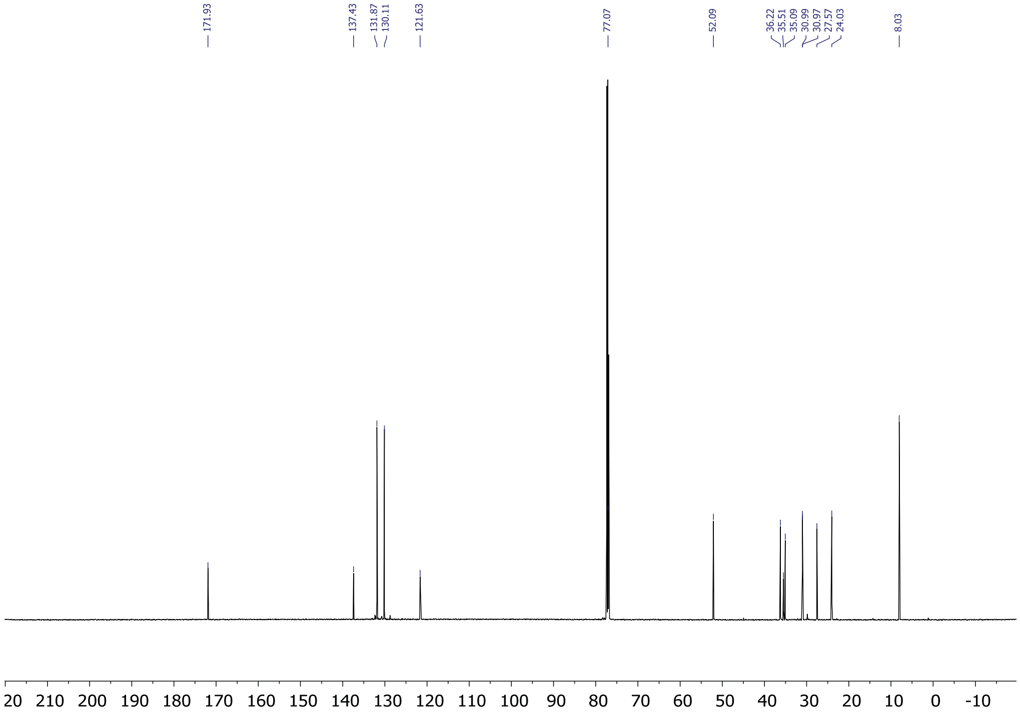
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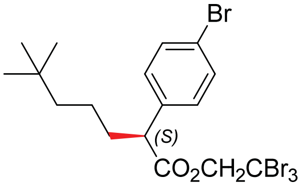
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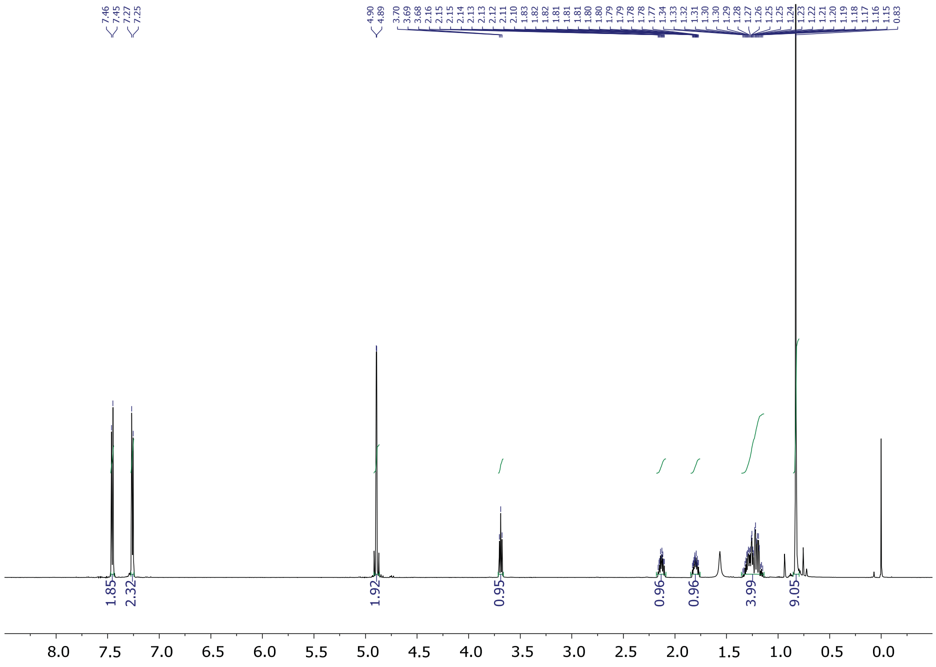
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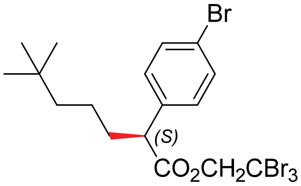
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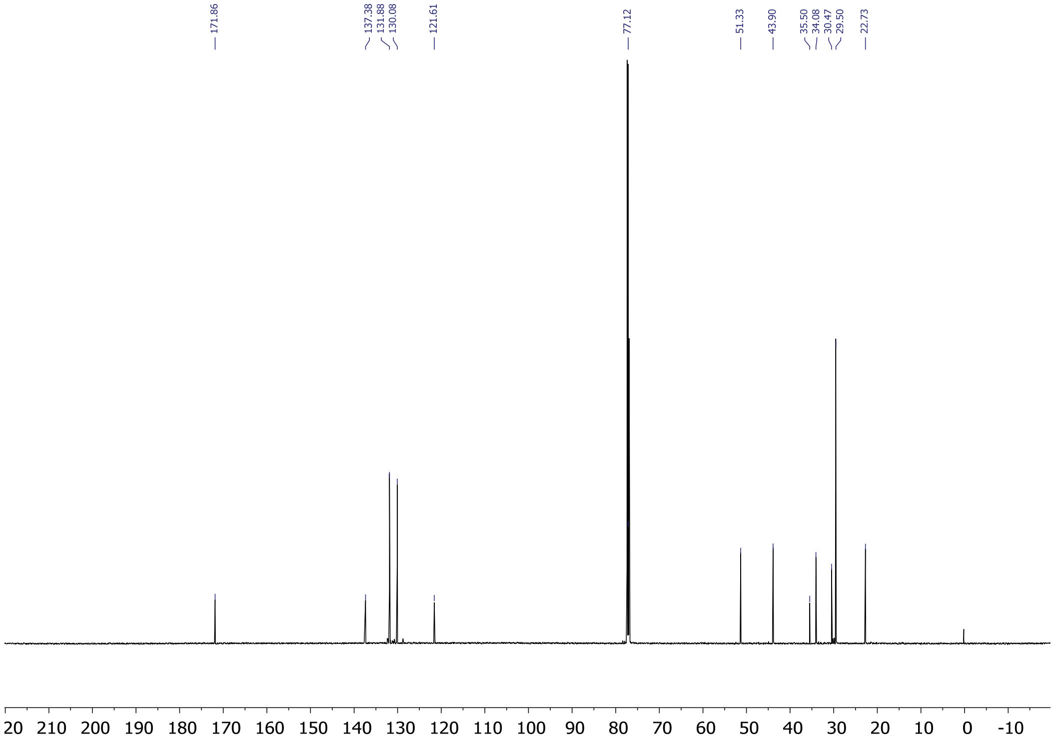
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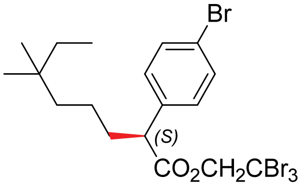
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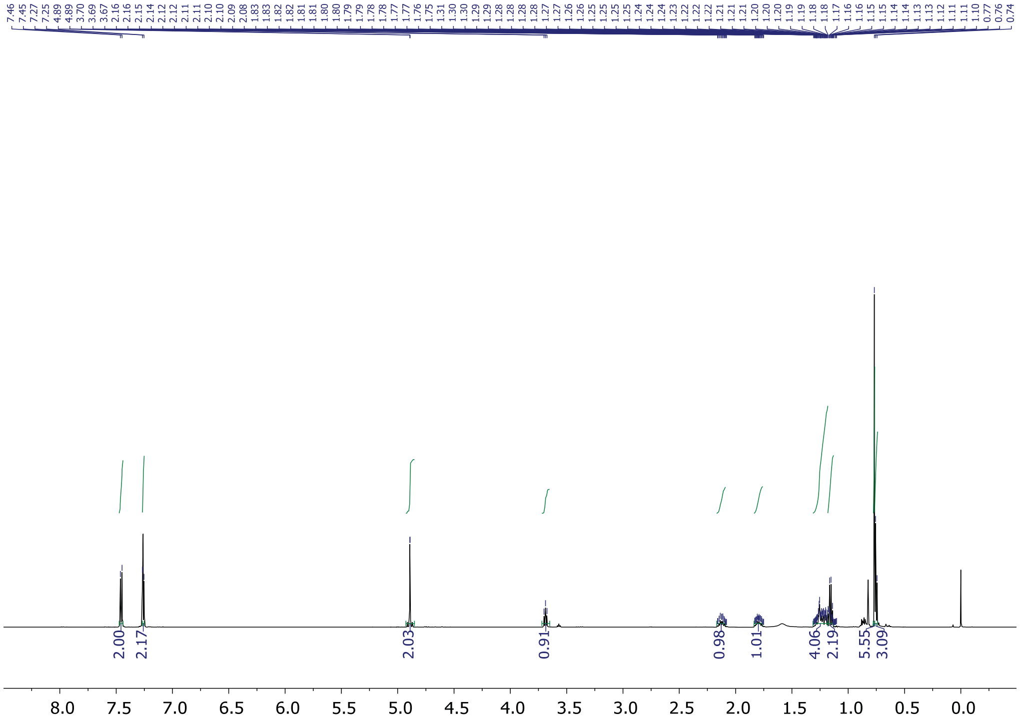
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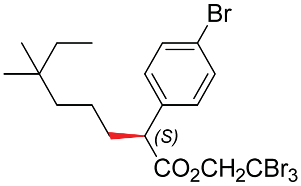
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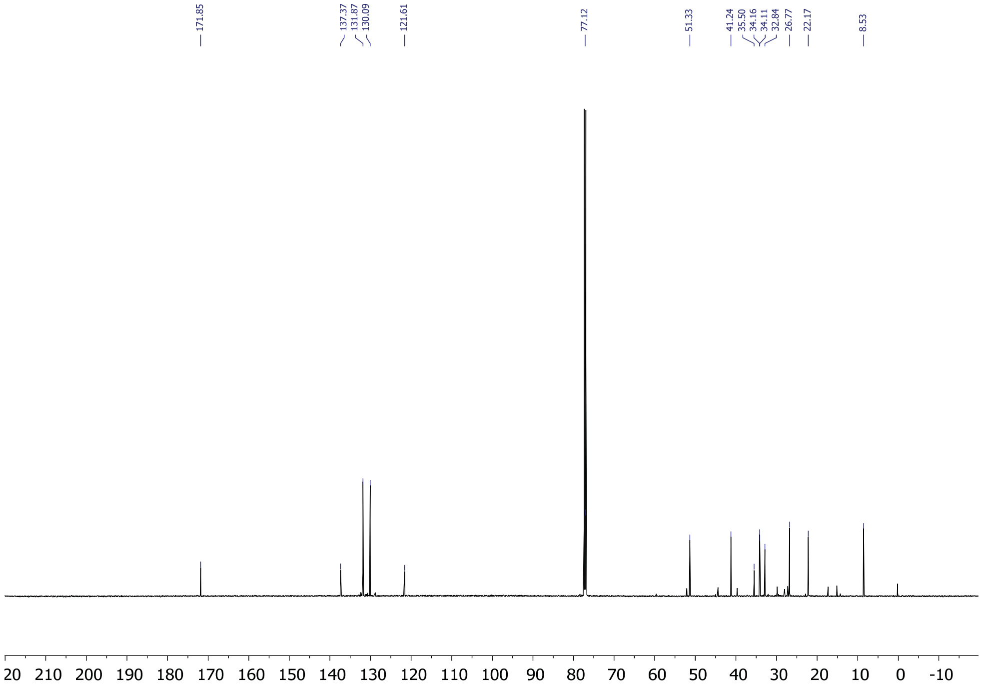
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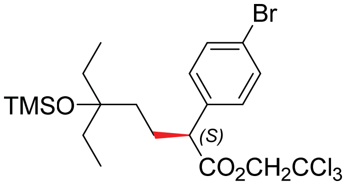
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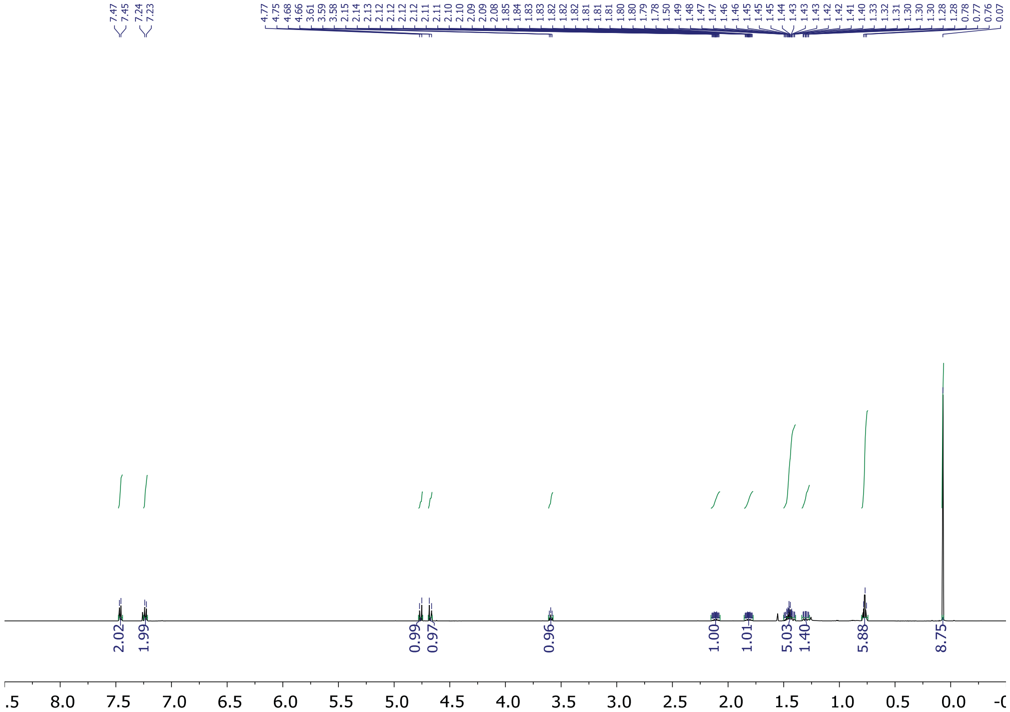
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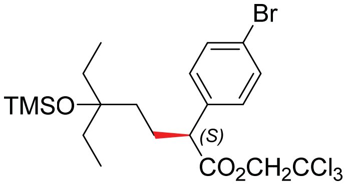
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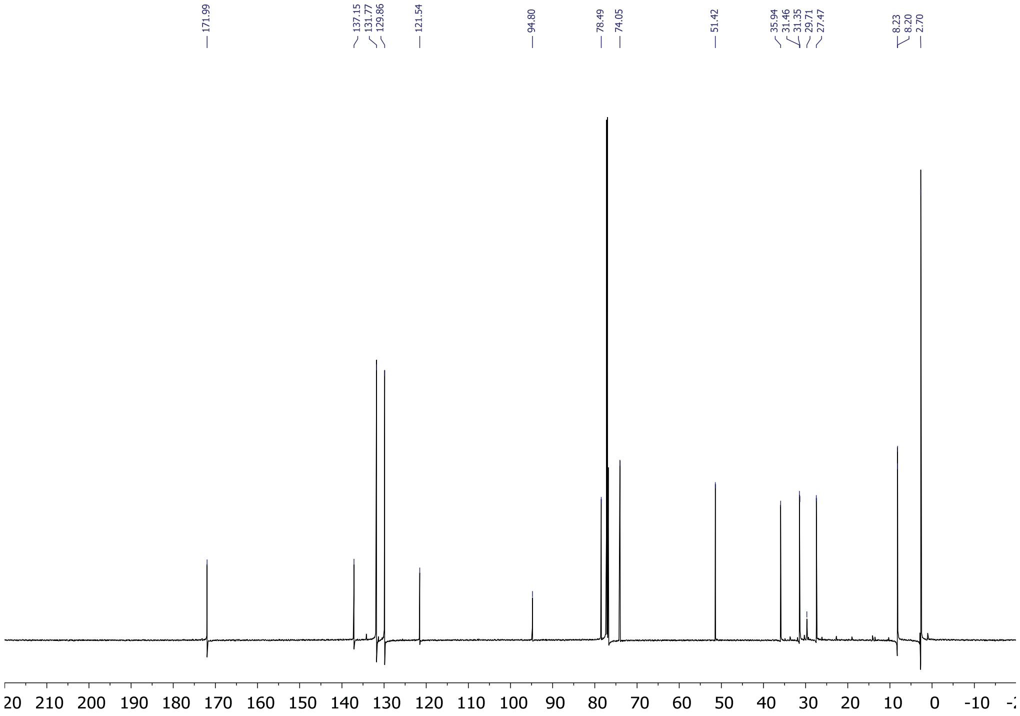
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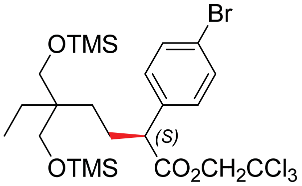
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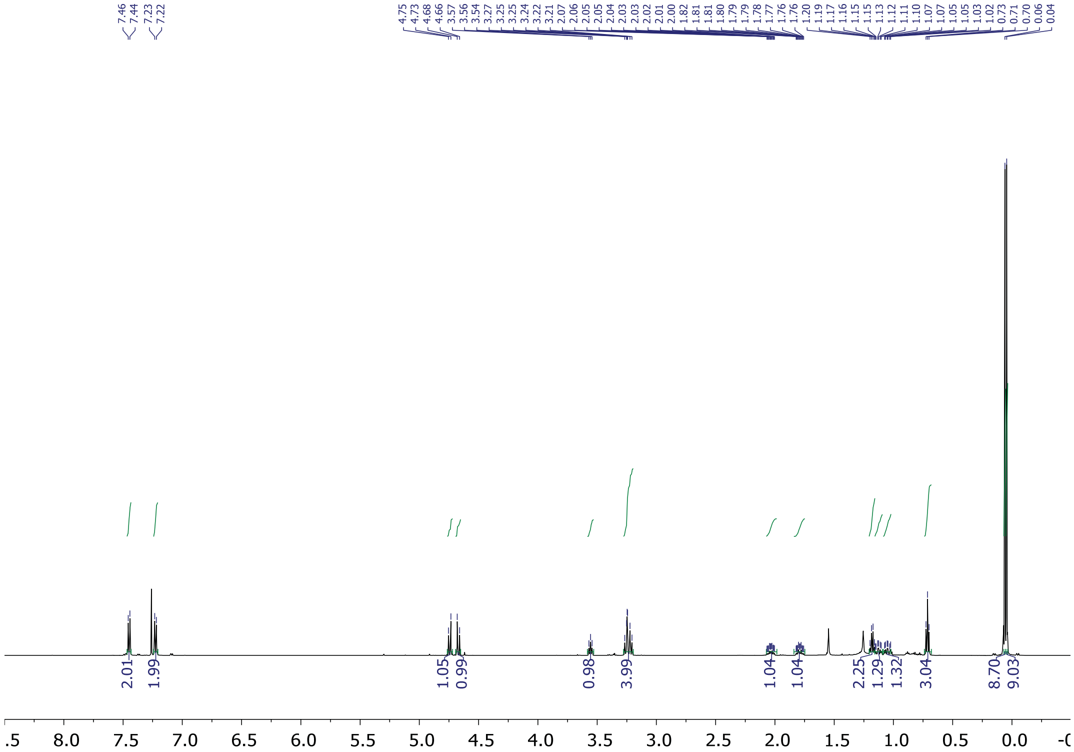
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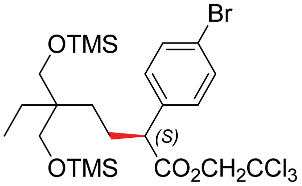
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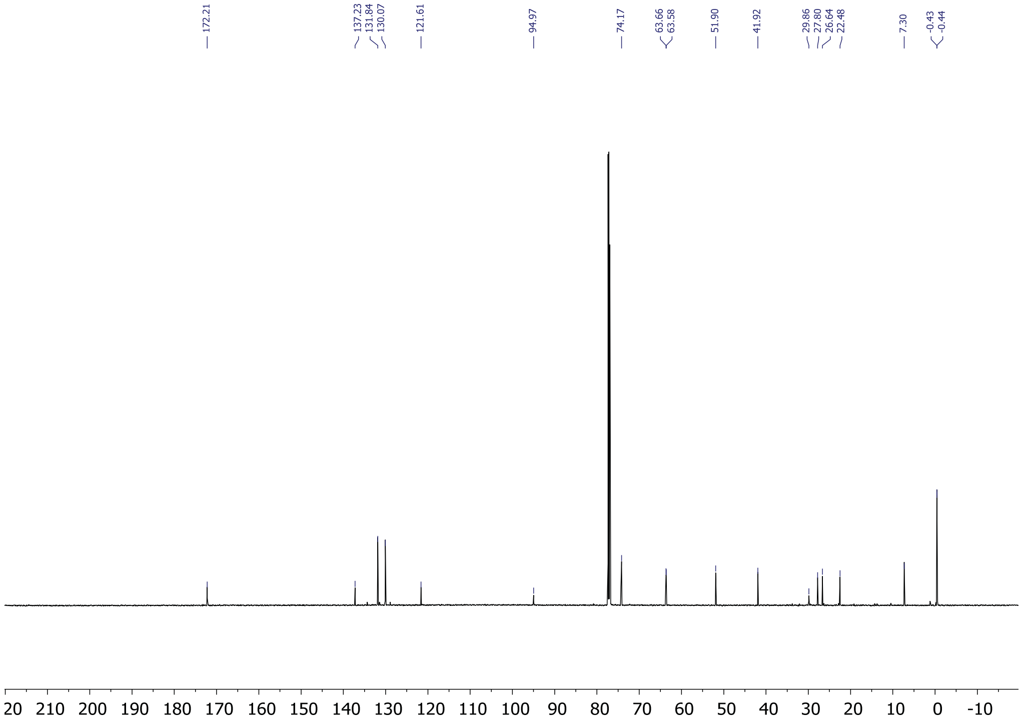
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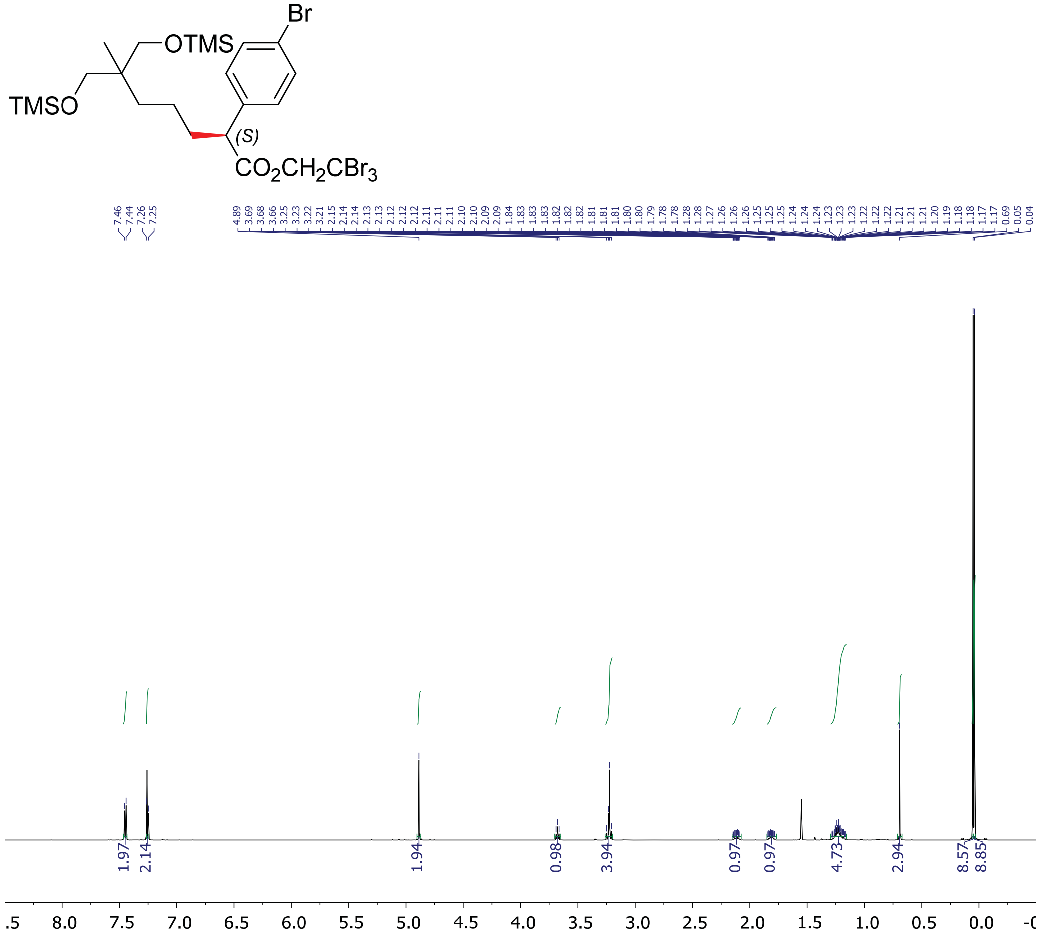
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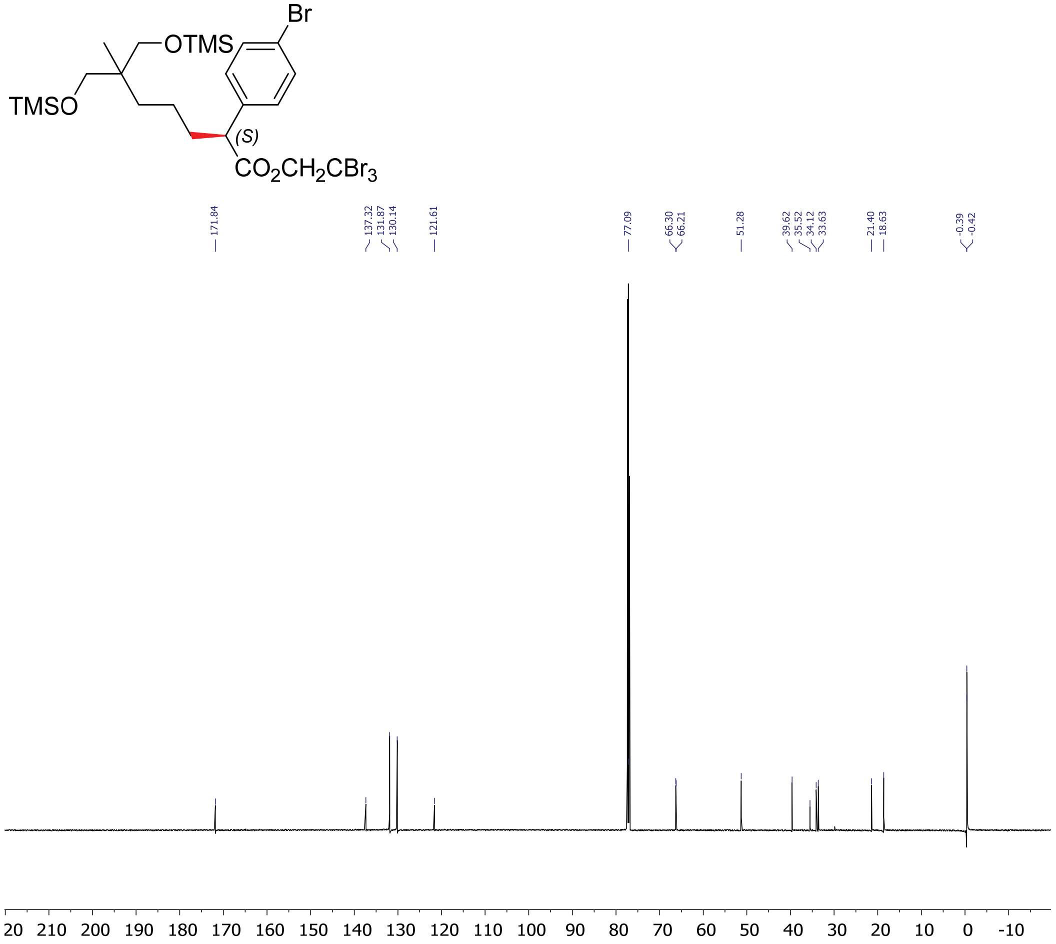
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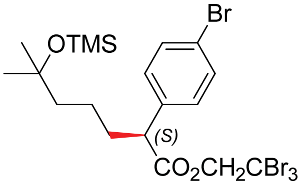
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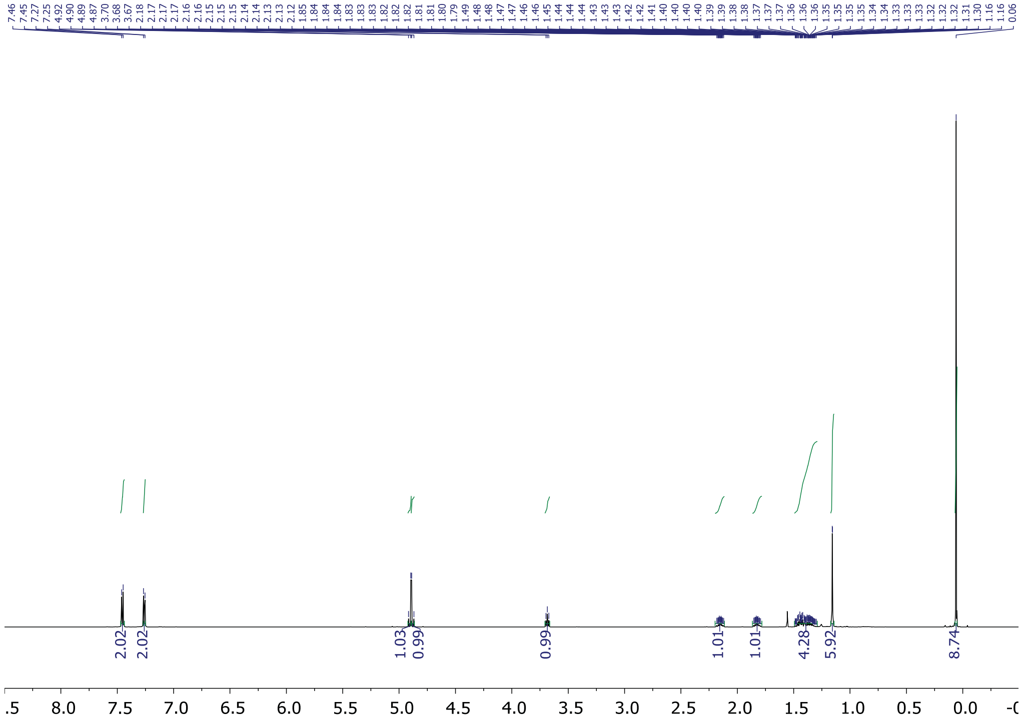
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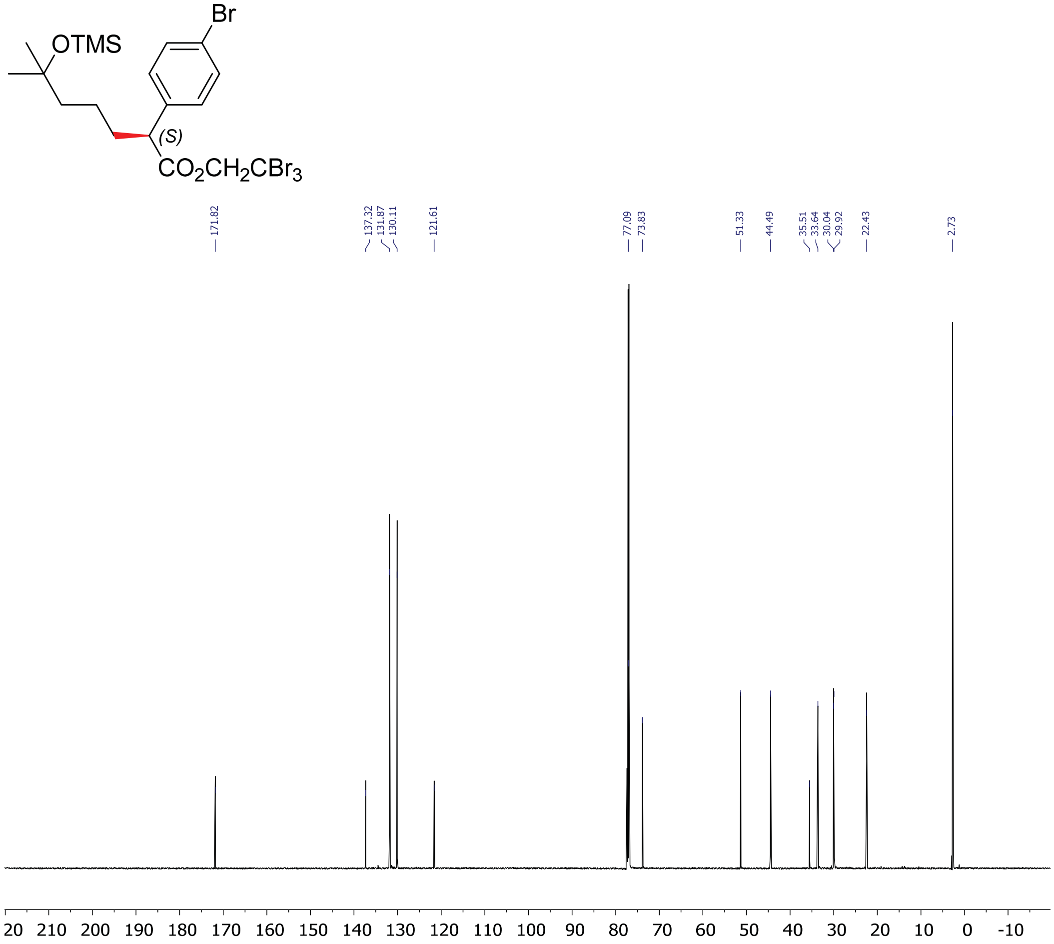
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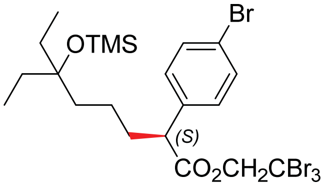
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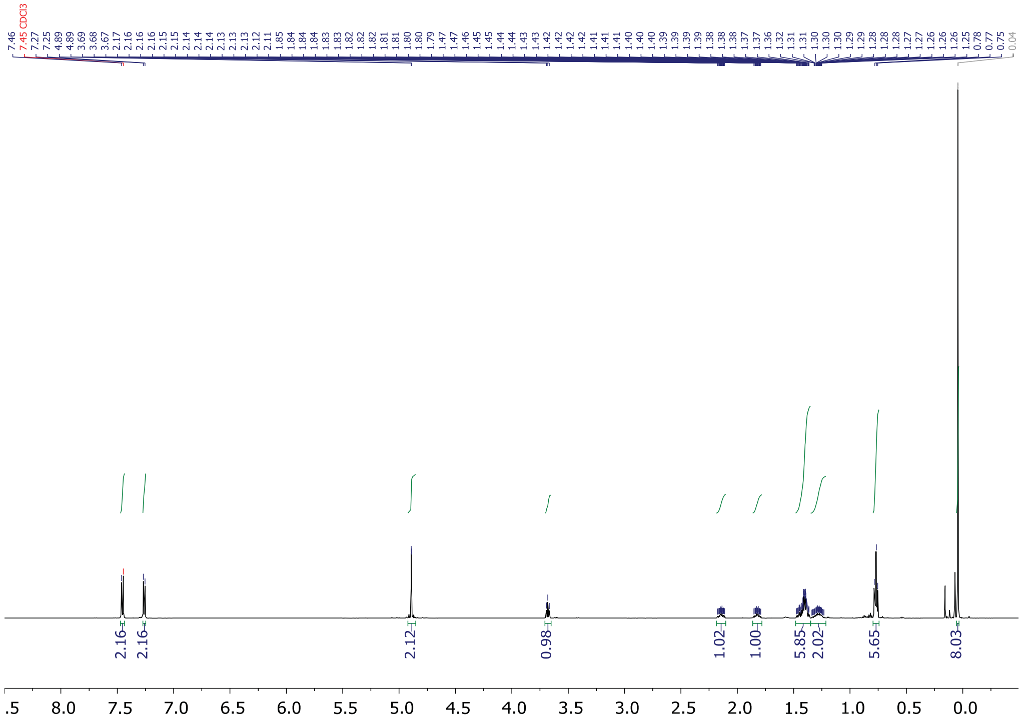
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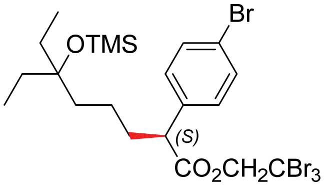
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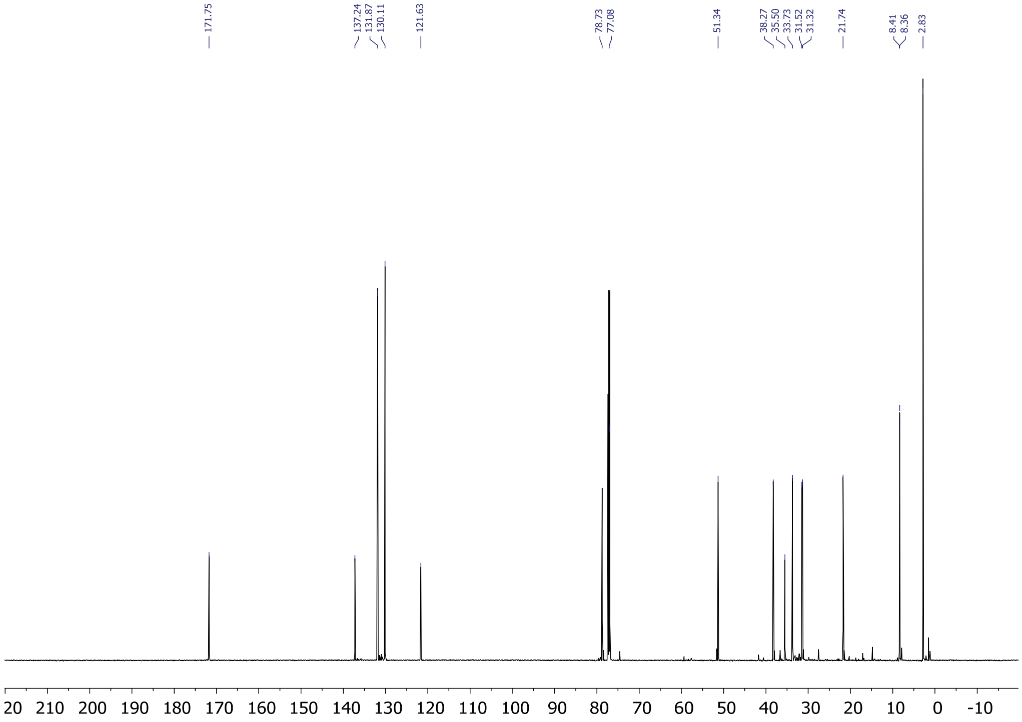
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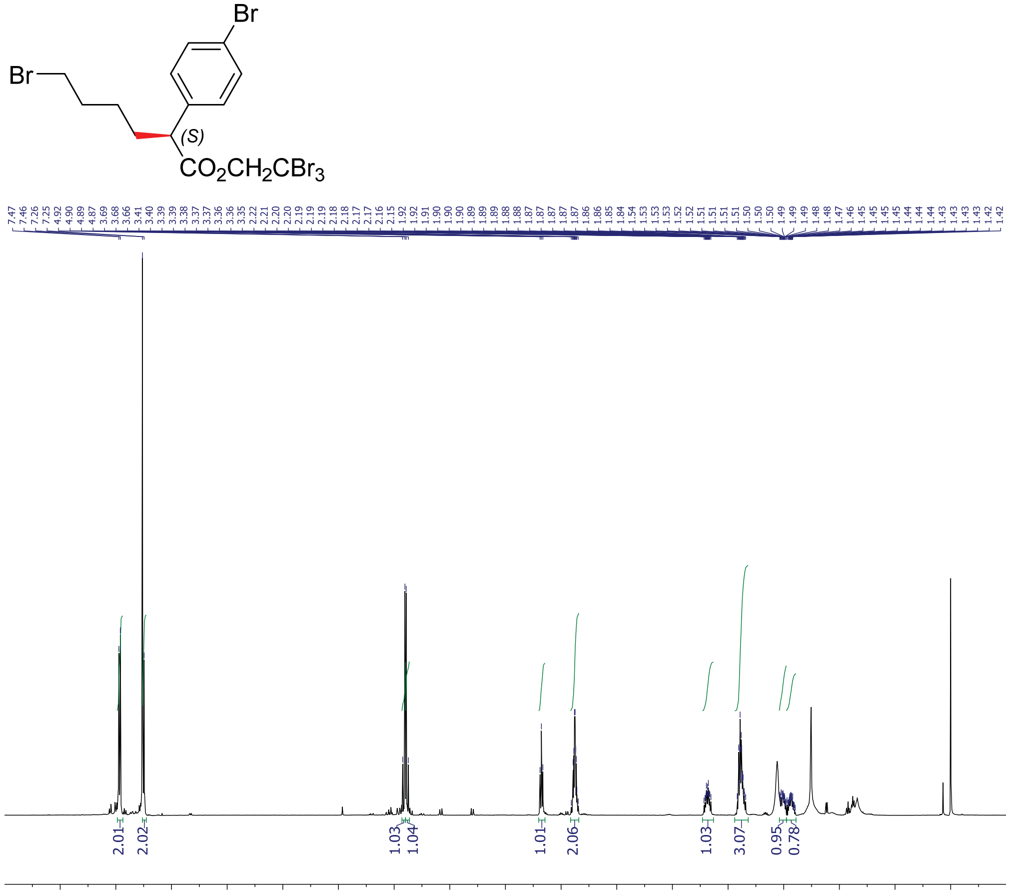
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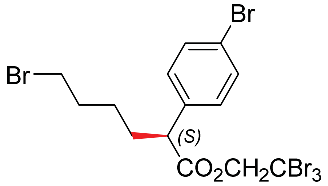
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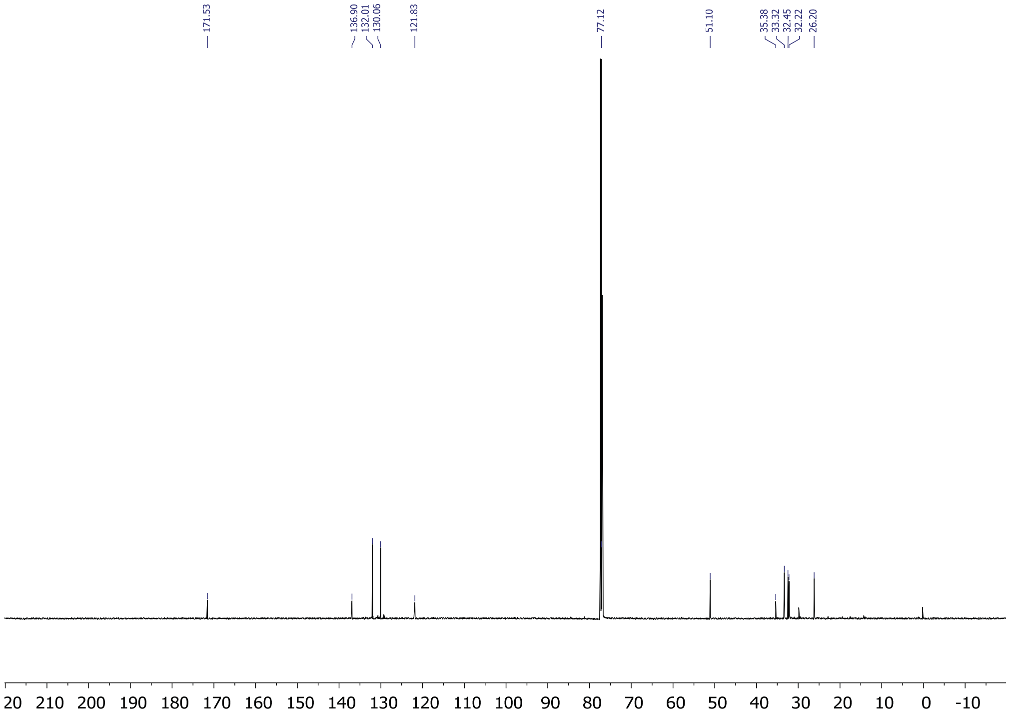
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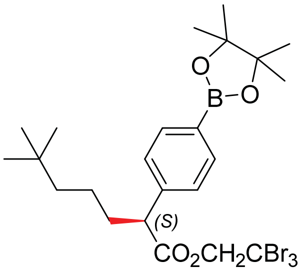
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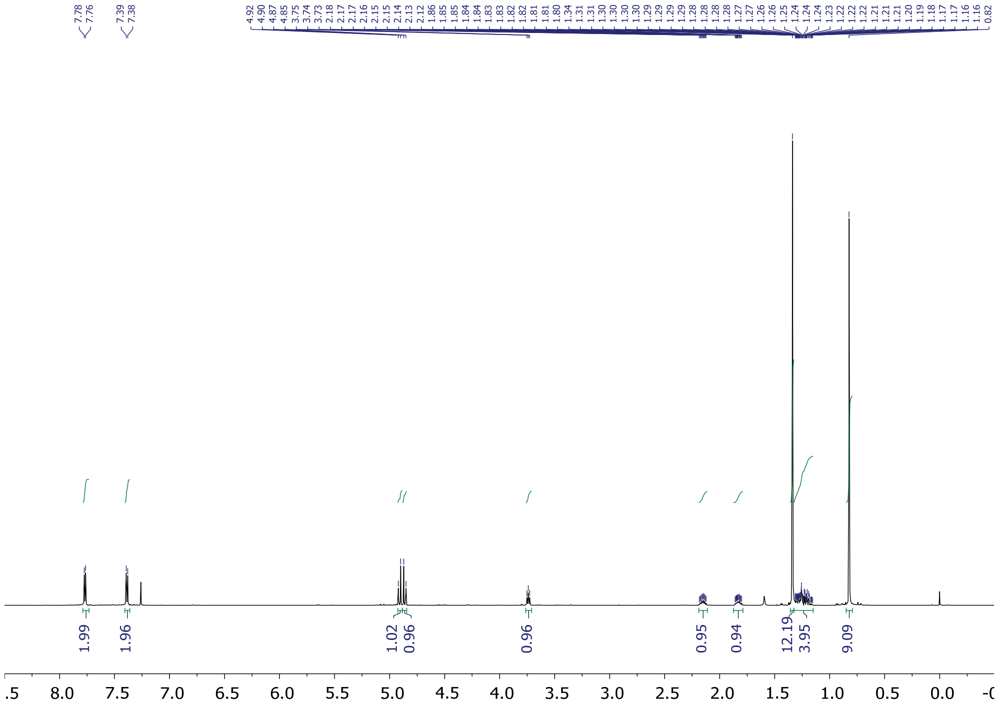
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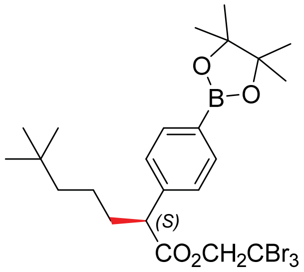
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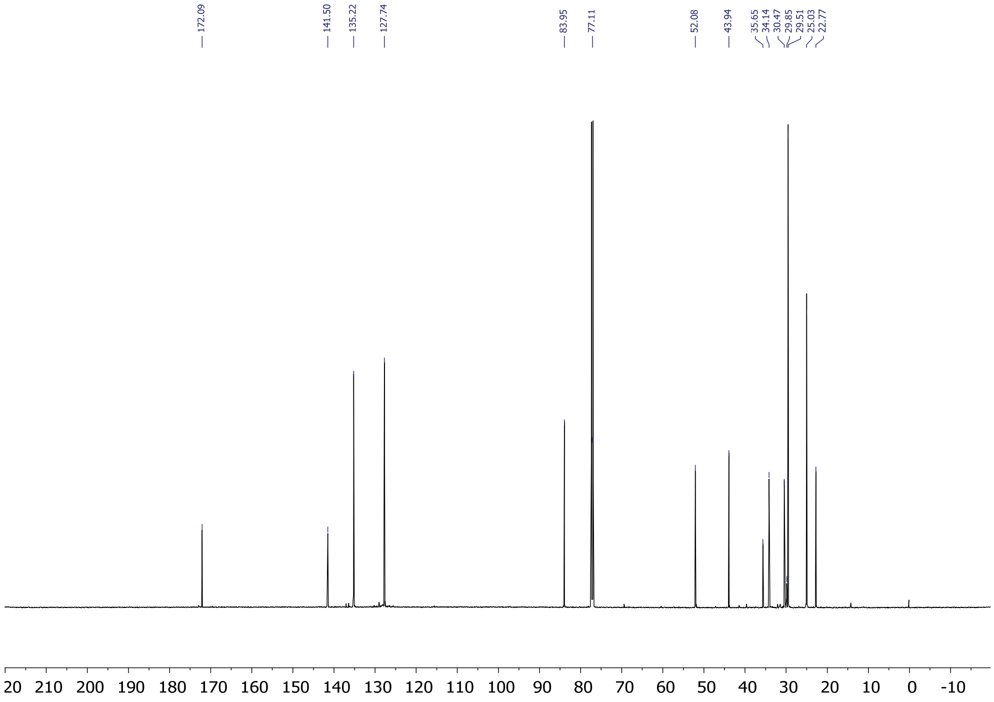
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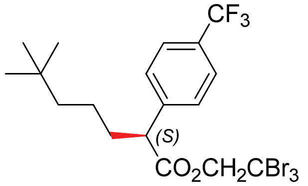
CF$_3$
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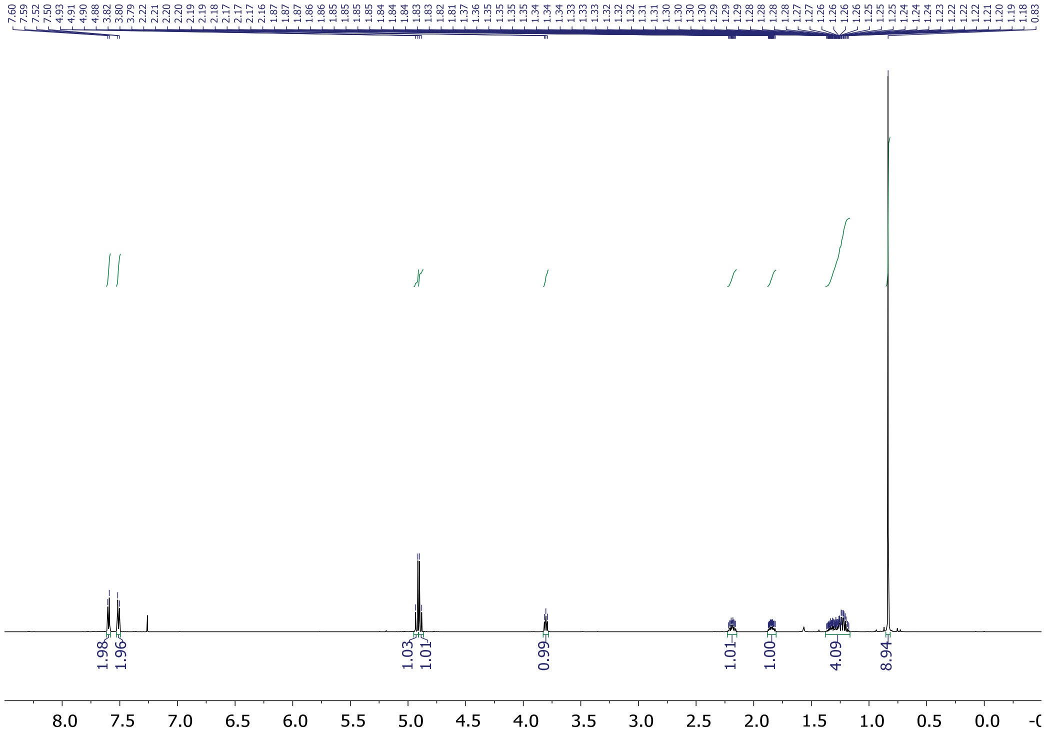
CO$_2$CH$_2$CBr$_3$


7.60 7.59 7.52 7.50 4.93 4.91 4.90 4.88 3.82 3.80 3.79 2.22 2.21 2.20 2.20 2.19 2.19 2.18 2.17 2.17 2.17 2.16 1.87 1.87 1.87 1.86 1.86 1.85 1.85 1.85 1.84 1.84 1.84 1.83 1.83 1.82 1.81 1.37 1.36 1.35 1.35 1.35 1.34 1.34 1.34 1.33 1.33 1.33 1.32 1.32 1.32 1.31 1.31 1.30 1.30 1.30 1.29 1.29 1.28 1.28 1.28 1.28 1.27 1.27 1.26 1.26 1.26 1.26 1.25 1.25 1.25 1.24 1.24 1.24 1.23 1.22 1.22 1.22 1.21 1.20 1.19 1.18 0.83
1.98
1.96
1.03
1.01
0.99
1.01
1.00
4.09
8.94
8.0
7.5
7.0
6.5
6.0
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4.0
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2.5
2.0
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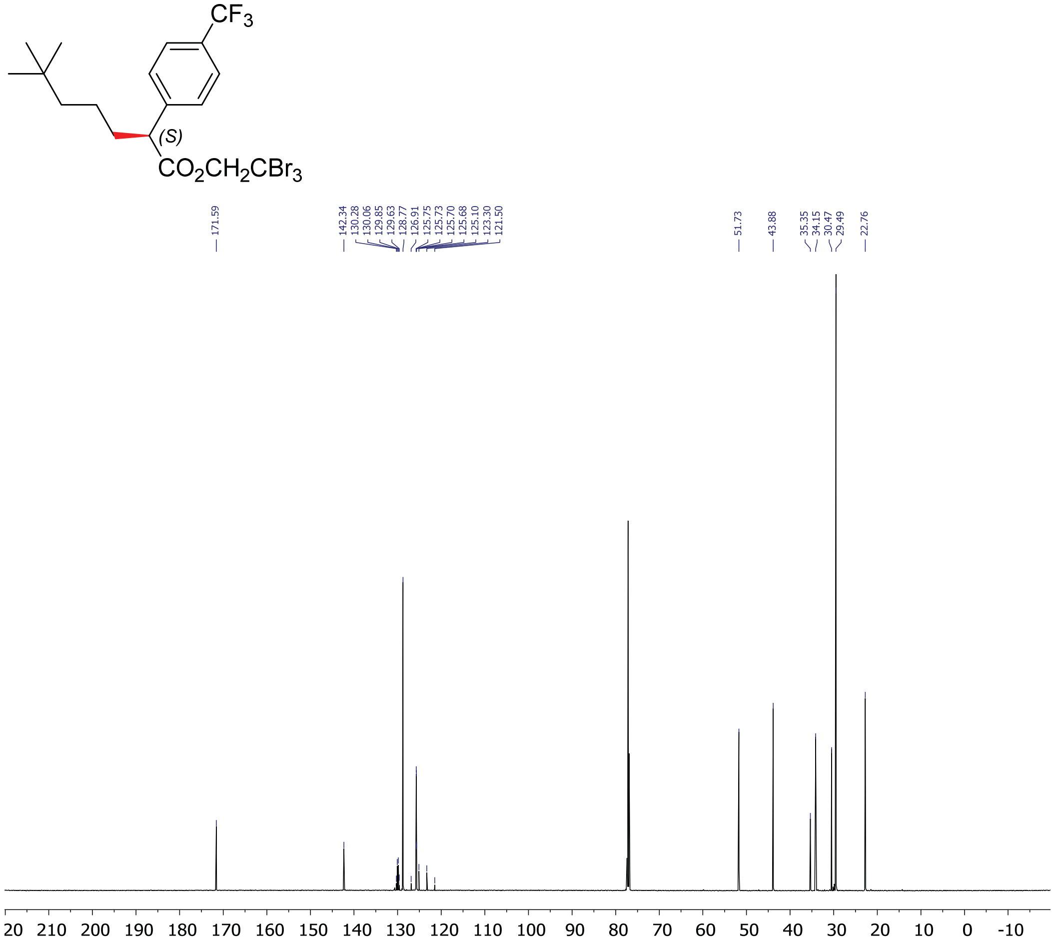
CF3
(S)
CO2CH2CBr3
171.59
142.34
130.28
130.06
129.85
129.63
128.77
126.91
125.75
125.73
125.70
125.68
125.10
123.30
121.50
51.73
43.88
35.35
34.15
30.47
29.49
22.76
20
210
200
190
180
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140
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120
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100
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80
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60
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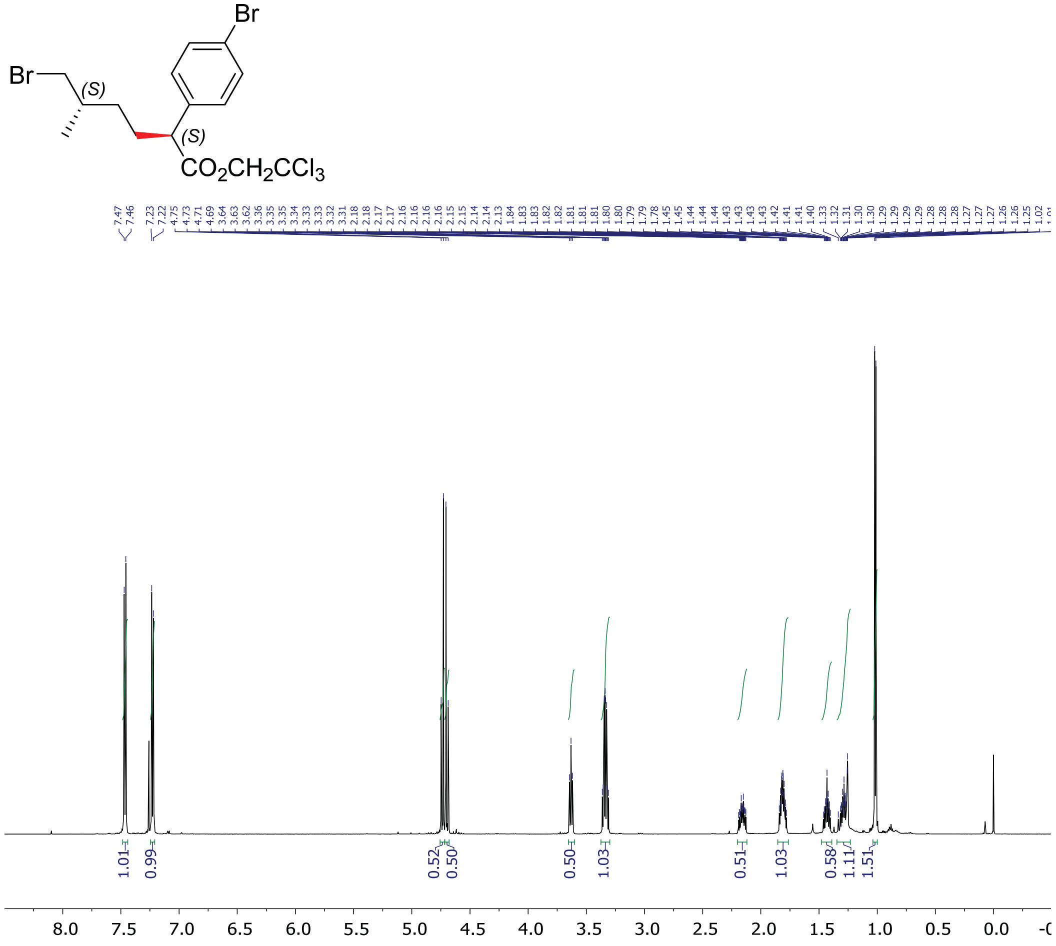
0
-10


Br
Br
(S)
(S)
CO2CH2CCl3
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7.23
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4.73
4.71
4.69
3.64
3.63
3.62
3.36
3.35
3.35
3.34
3.33
3.33
3.32
3.31
2.18
2.18
2.17
2.17
2.16
2.16
2.16
2.15
2.15
2.14
2.14
2.13
1.84
1.83
1.83
1.82
1.82
1.81
1.81
1.81
1.80
1.79
1.79
1.78
1.45
1.45
1.44
1.44
1.43
1.43
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1.43
1.42
1.41
1.41
1.40
1.33
1.32
1.31
1.31
1.30
1.30
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1.29
1.28
1.28
1.28
1.27
1.27
1.27
1.26
1.25
1.02
1.01
0.99
0.52
0.50
0.50
1.03
0.51
1.03
0.58
1.11
1.51
8.0
7.5
7.0
6.5
6.0
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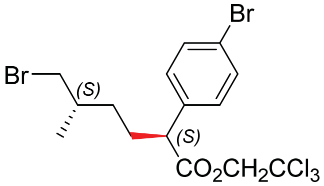
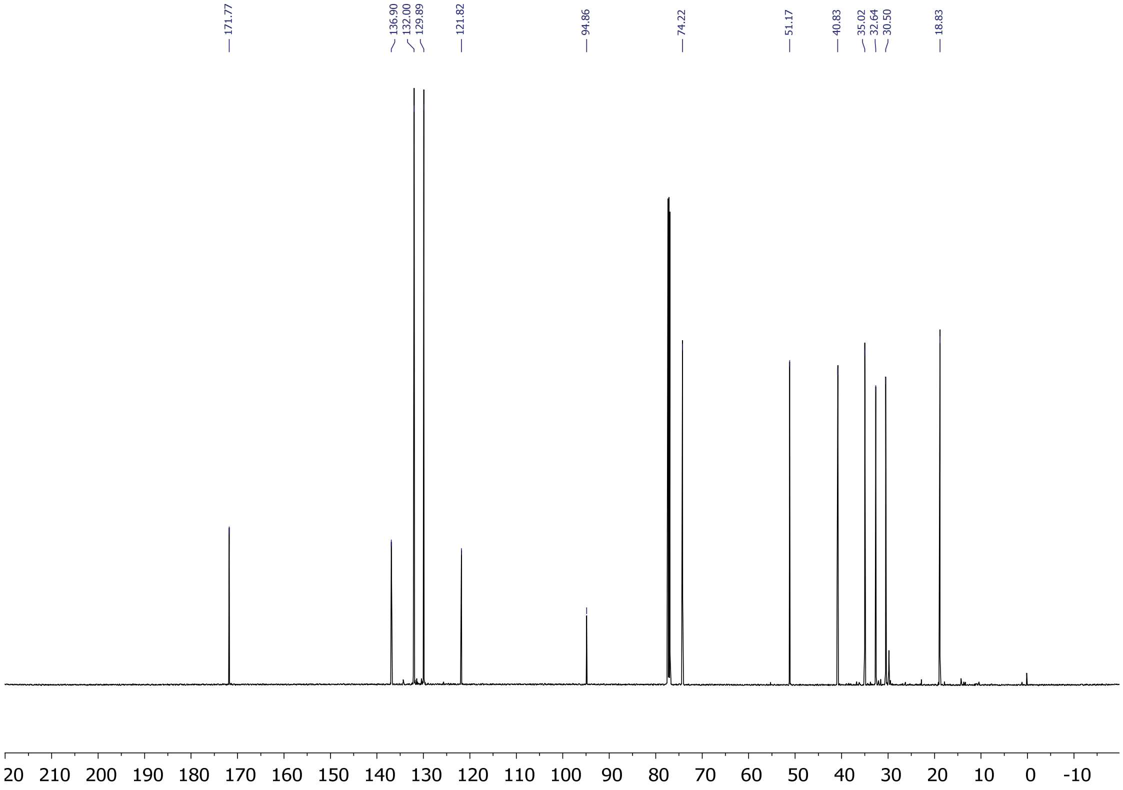
0.0



Br
Br
(S)
(S)
$CO_2CH_2CCl_3$



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129.89
121.82
94.86
74.22
51.17
40.83
35.02
32.64
30.50
18.83
20
210
200
190
180
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150
140
130
120
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100
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60
50
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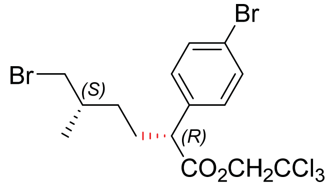
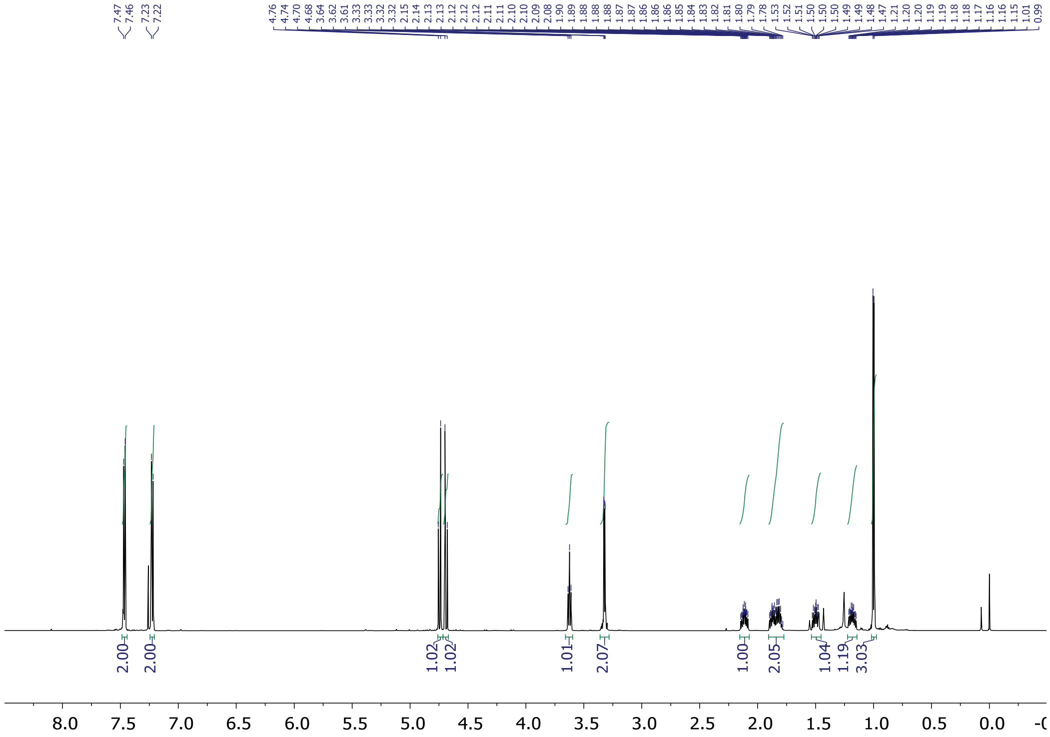
20
10
0
-10


Br
Br
(S)
(R)
CO2CH2CCl3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7.46
7.23
7.22
4.76
4.74
4.70
4.68
3.64
3.62
3.61
3.33
3.33
3.32
3.32
2.15
2.14
2.13
2.13
2.12
2.12
2.11
2.11
2.10
2.10
2.09
2.08
1.90
1.89
1.88
1.88
1.88
1.87
1.87
1.86
1.86
1.86
1.85
1.84
1.83
1.82
1.81
1.80
1.79
1.78
1.53
1.52
1.51
1.50
1.50
1.50
1.49
1.49
1.48
1.47
1.21
1.20
1.20
1.19
1.19
1.18
1.18
1.17
1.16
1.16
1.15
1.01
0.99
2.00
2.00
1.02
1.02
1.01
2.07
1.00
2.05
1.04
1.19
3.03
8.0
7.5
7.0
6.5
6.0
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4.5
4.0
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3.0
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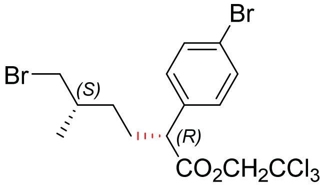
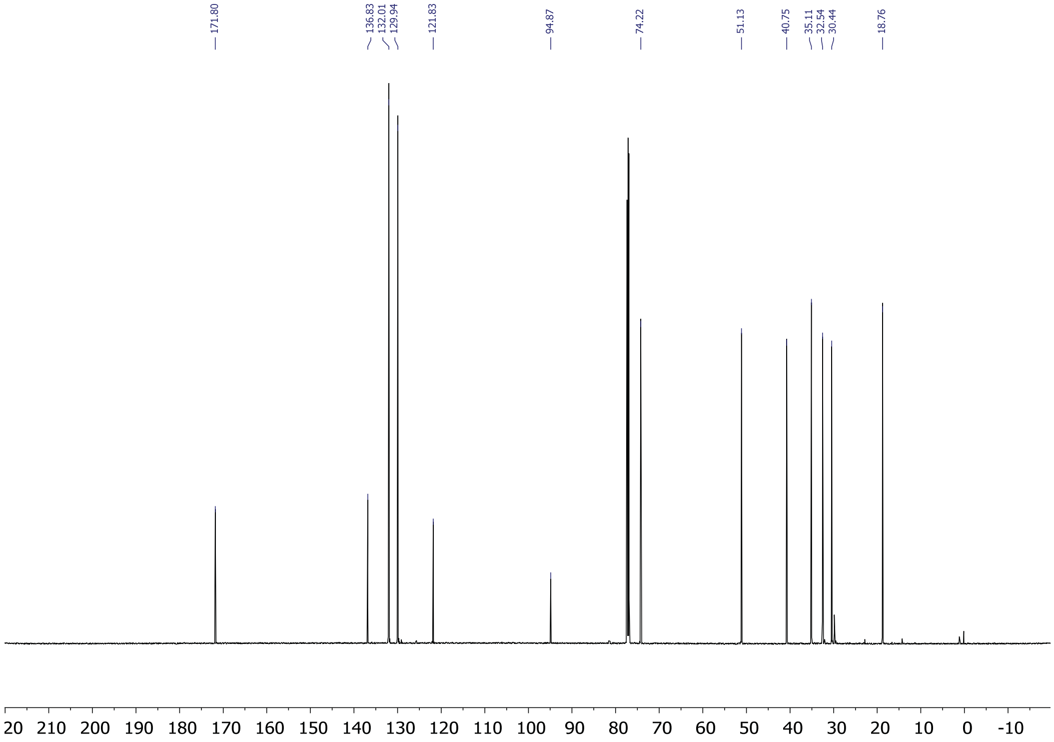
2.0
1.5
1.0
0.5
0.0


Br
Br
(S)
(R)
CO2CH2CCl3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35.11
32.54
30.44
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20
210
200
190
180
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160
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140
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120
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100
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60
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20
10
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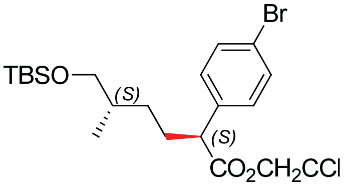
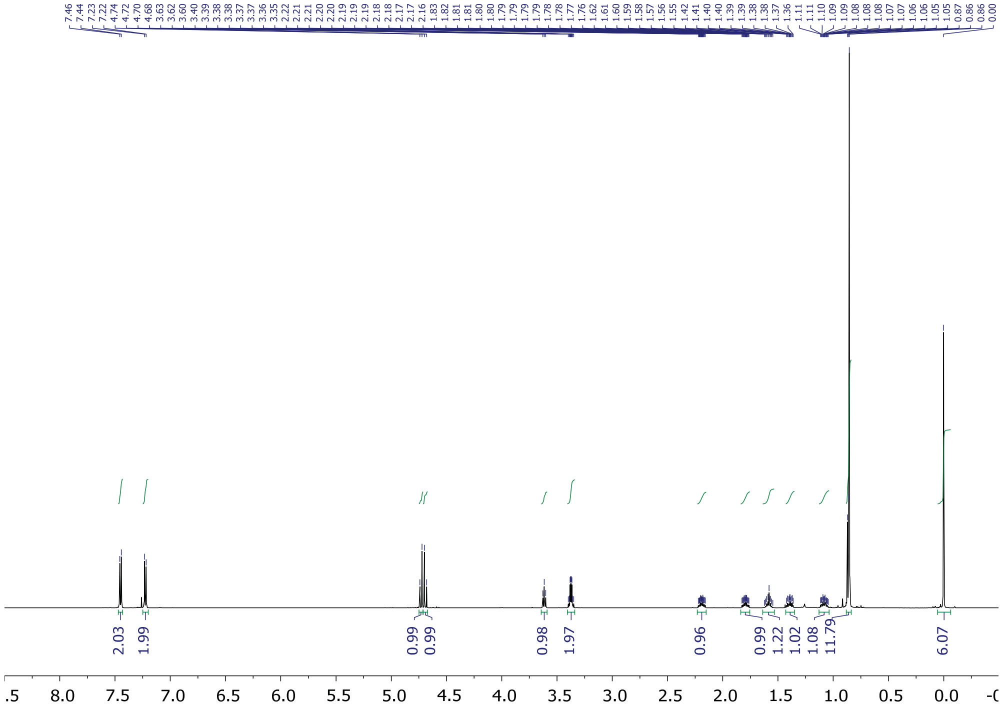
-10


Br
TBSO
(S)
(S)
CO_2CH_2CCl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7.23
7.22
4.74
4.72
4.70
4.68
3.63
3.62
3.60
3.40
3.39
3.38
3.38
3.37
3.37
3.36
3.35
2.22
2.21
2.21
2.20
2.20
2.19
2.19
2.18
2.18
2.17
2.17
2.16
1.83
1.82
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1.81
1.80
1.80
1.79
1.79
1.79
1.78
1.78
1.77
1.76
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1.60
1.59
1.58
1.57
1.56
1.55
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1.40
1.39
1.39
1.38
1.38
1.37
1.36
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1.10
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1.09
1.08
1.08
1.08
1.07
1.07
1.06
1.06
1.05
1.05
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0.86
0.86
0.00
2.03
1.99
0.99
0.99
0.98
1.97
0.96
0.99
1.22
1.02
1.08
11.79
6.07
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
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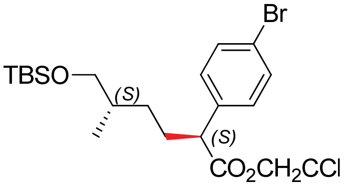
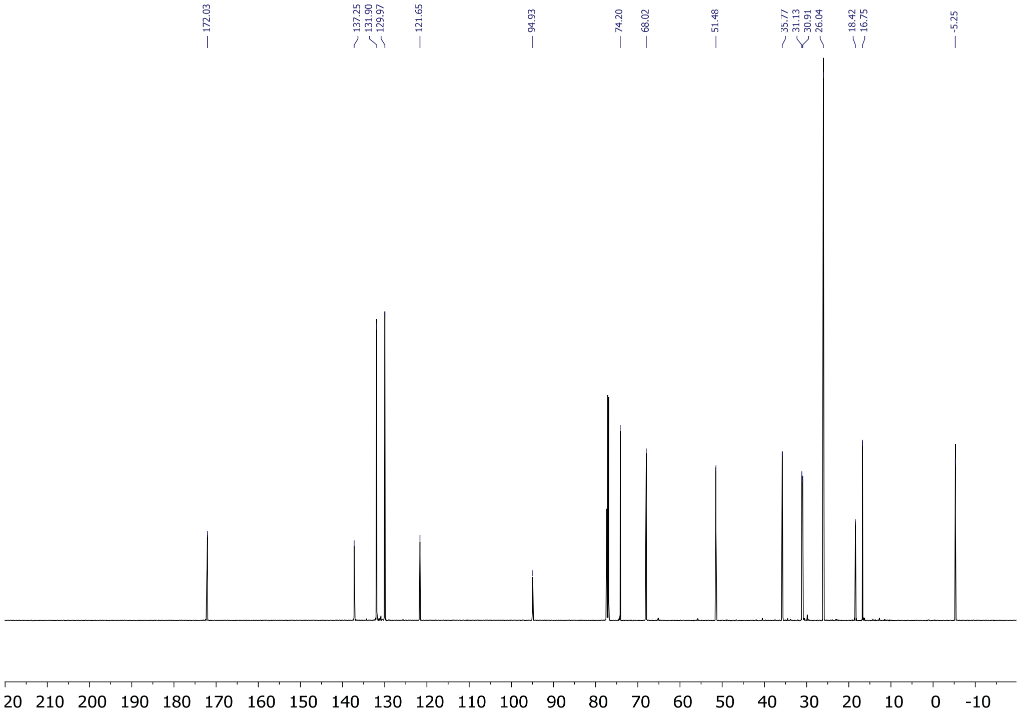

Br
TBSO
(S)
(S)
CO_2CH_2CCl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68.02
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30.91
26.04
18.42
16.75
-5.25
20
210
200
190
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100
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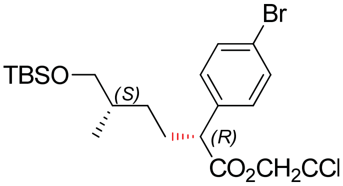
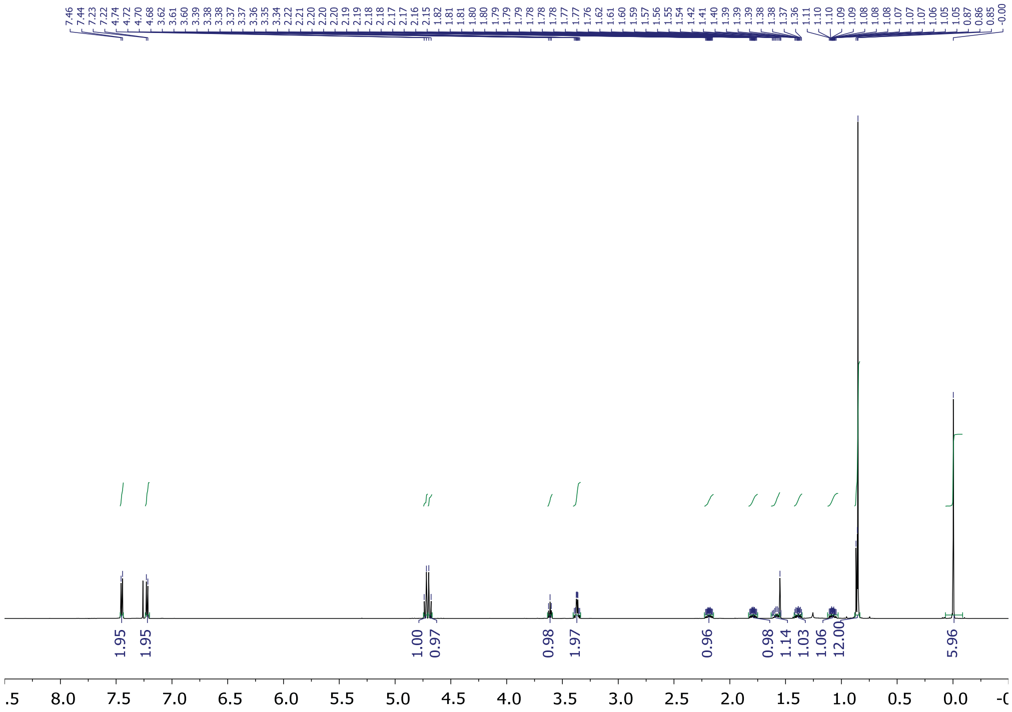
20
10
0
-10


Br
TBSO
(S)
(R)
CO2CH2CCl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1.05
1.05
0.87
0.86
0.85
-0.00
1.95
1.95
1.00
0.97
0.98
1.97
0.96
0.98
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1.06
12.00
5.96
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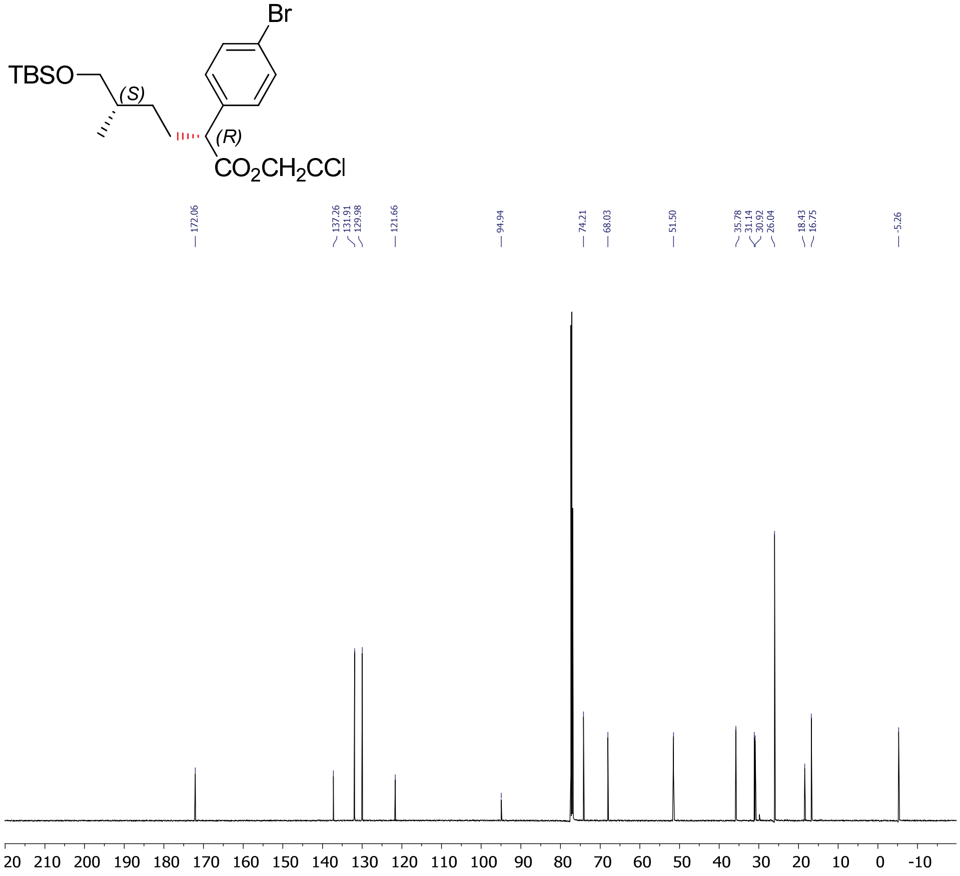
Br
TBSO
(S)
(R)
CO2CH2CCl
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137.26
131.91
129.98
121.66
94.94
74.21
68.03
51.50
35.78
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26.04
18.43
16.75
-5.26
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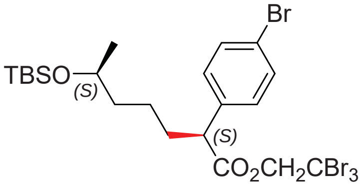
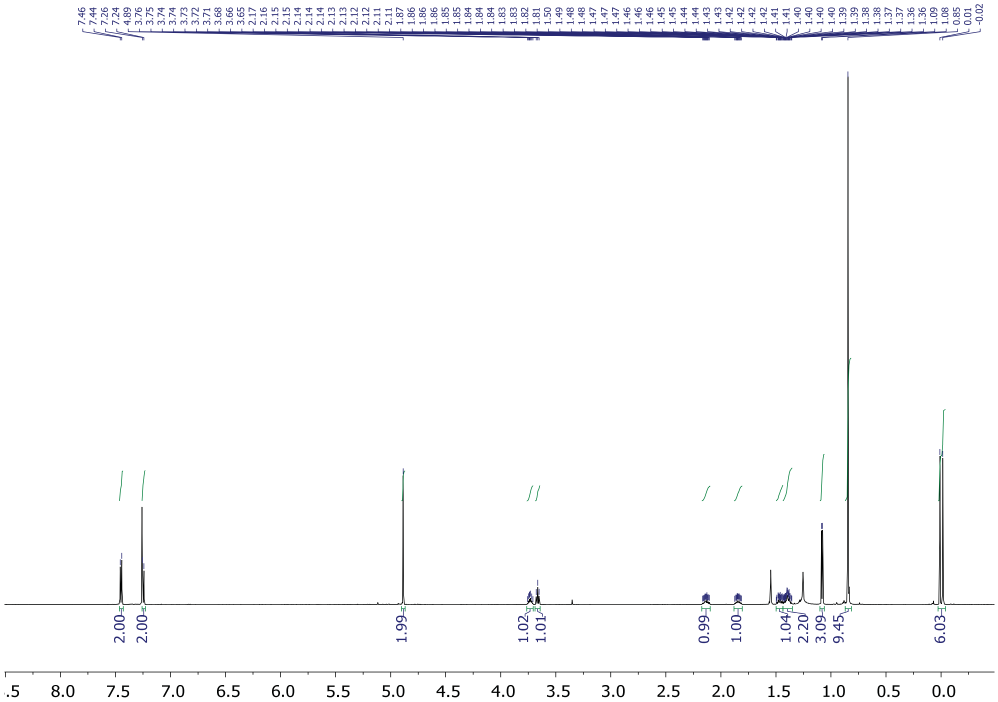

Br
TBSO
(S)
(S)
$CO_2CH_2CBr_3$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3.68
3.66
3.65
2.17
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2.15
2.14
2.14
2.14
2.13
2.13
2.12
2.12
2.11
2.11
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1.09
1.08
0.85
0.01
-0.02
2.00
2.00
1.99
1.02
1.01
0.99
1.00
1.04
2.20
3.09
9.45
6.03
.5
8.0
7.5
7.0
6.5
6.0
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2.0
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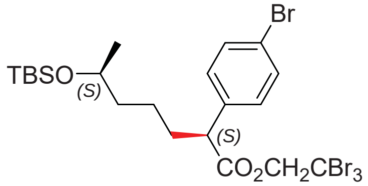
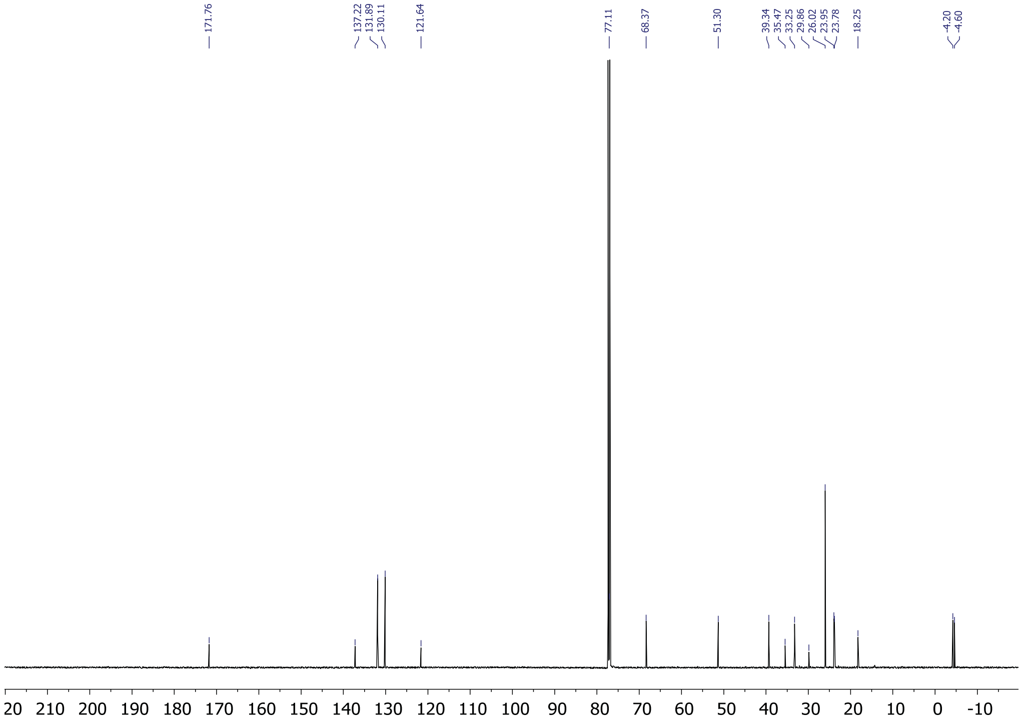
0.0


Br
TBSO
(S)
(S)
CO$_2$CH$_2$CBr$_3$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77.11
68.37
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35.47
33.25
29.86
26.02
23.95
23.78
18.25
-4.20
-4.60
20
210
200
190
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100
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60
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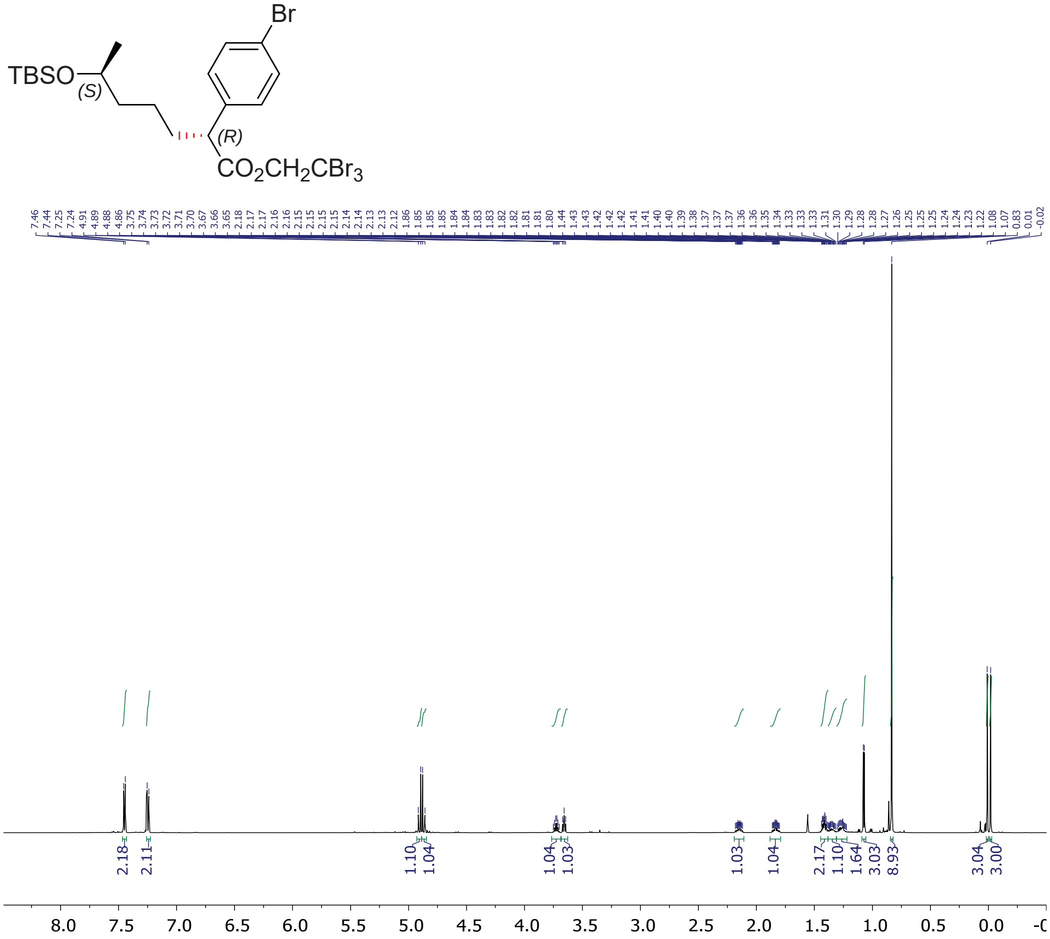
-10


TBSO
(S)
Br
(R)
CO2CH2CBr3
2.18
2.11
1.10
1.04
1.04
1.03
1.03
1.04
2.17
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1.64
3.03
8.93
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6.5
6.0
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2.0
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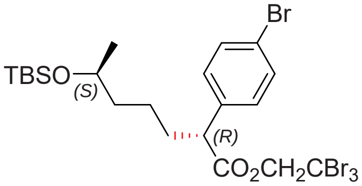
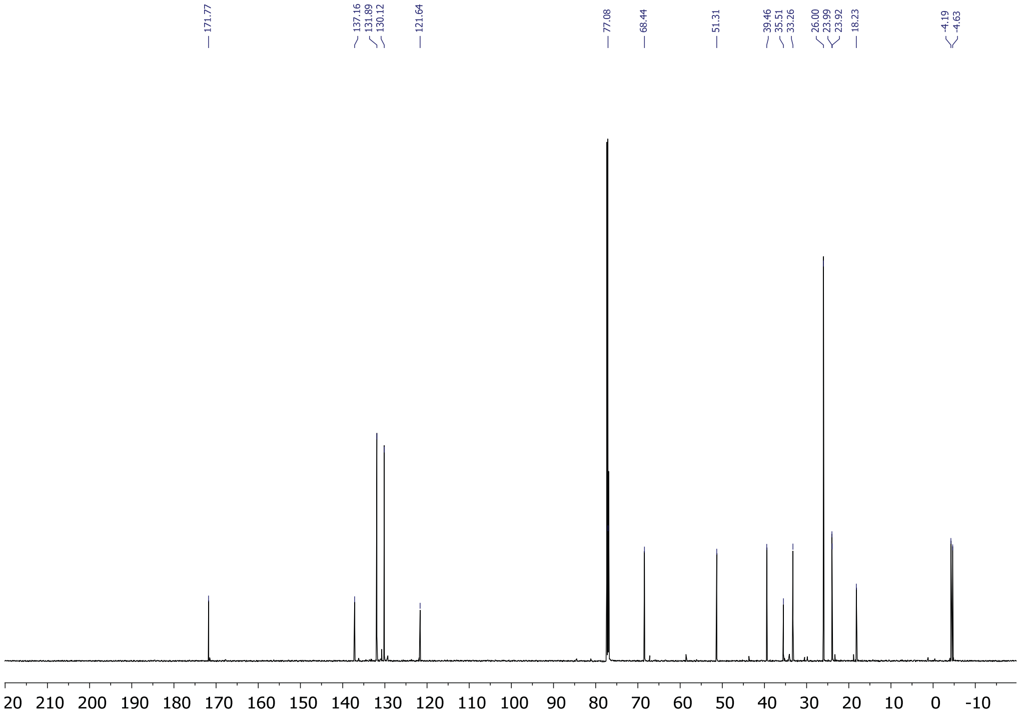
0.0


Br
TBSO
(S)
(R)
CO2CH2CBr3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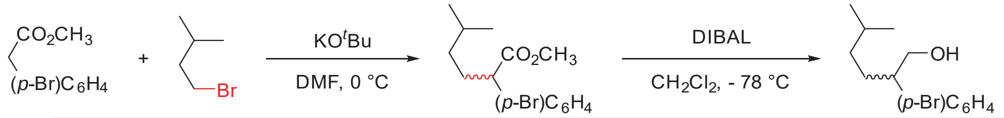
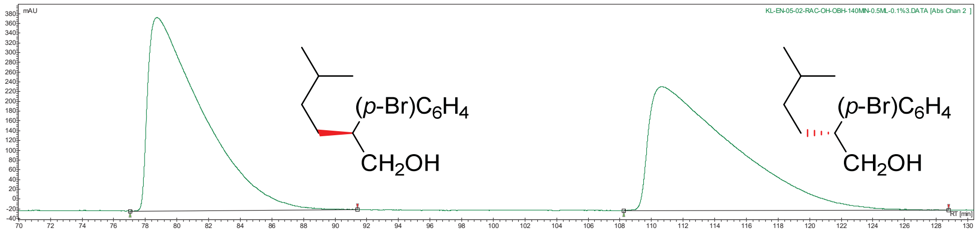
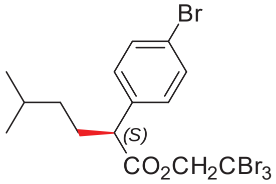
131.89
130.12
121.64
77.08
68.44
51.31
39.46
35.51
33.26
26.00
23.99
23.92
18.23
-4.19
-4.63
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

9. HPLC for C–H Functionalization Products

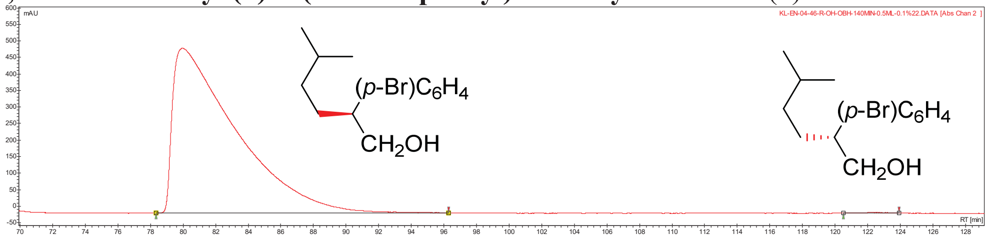




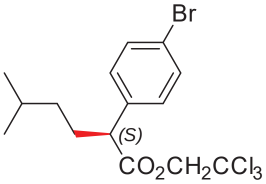
#	Time [Min]	Area% [%]
1	78.74	50.180
2	110.64	49.820



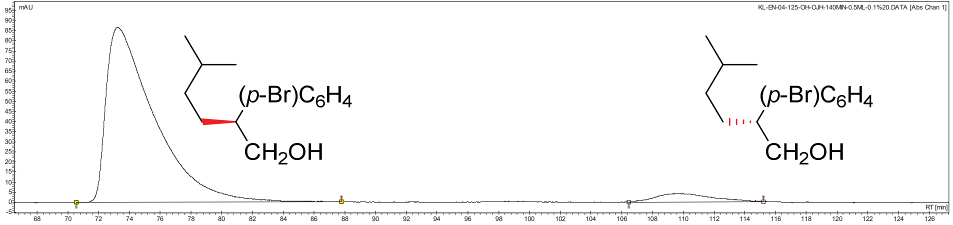
2,2,2-Tribromoethyl (*S*)-2-(4-bromophenyl)-5-methylhexanoate (5).



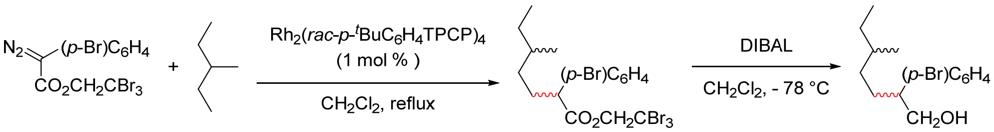
#	Time [Min]	Area% [%]
1	79.95	99.841
2	122.19	0.159
		>99% *e.e.*.

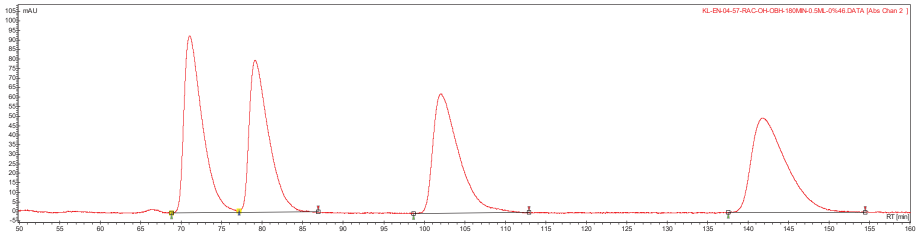


2,2,2-Trichloroethyl (*S*)-2-(4-bromophenyl)-5-methylhexanoate (6).

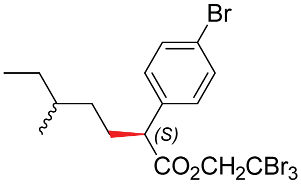


#	Time [Min]	Area% [%]
1	73.27	94.783
2	109.60	5.217
		90% *e.e.*.

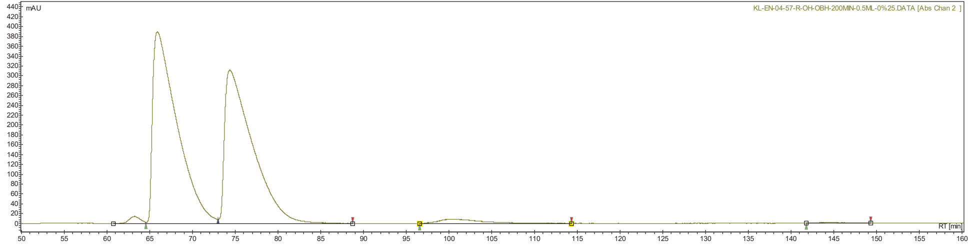




#	Time [Min]	Area% [%]
1	70.99	26.025
2	79.11	23.516
3	102.01	24.404
4	141.75	26.055



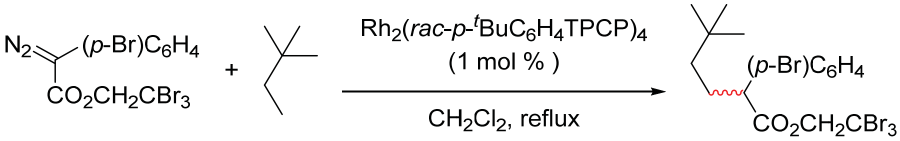
2,2,2-Tribromoethyl (2*S*)-2-(4-bromophenyl)-5-methylheptanoate (7).

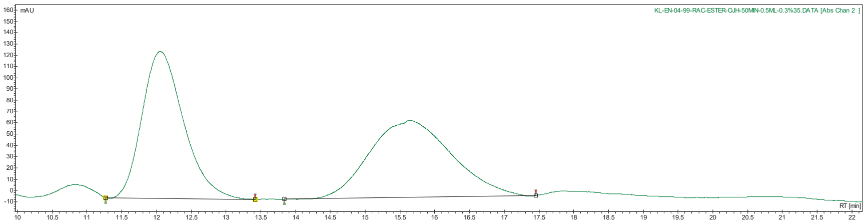


#	Time [Min]	Area% [%]
1	65.89	50.915
2	74.33	46.611
3	100.31	2.320
4	144.66	0.154

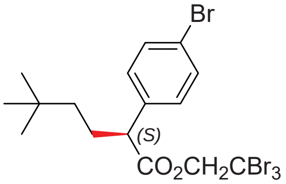
>99% *e.e.*

95% *e.e.*.

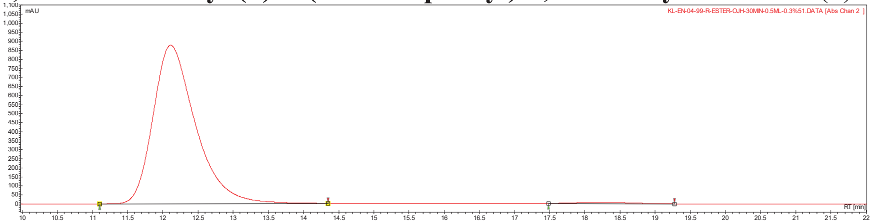




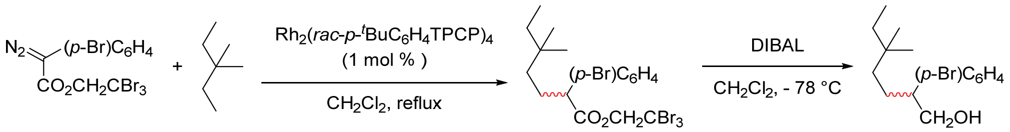
#	Time [Min]	Area% [%]
1	12.05	49.266
2	15.64	50.734

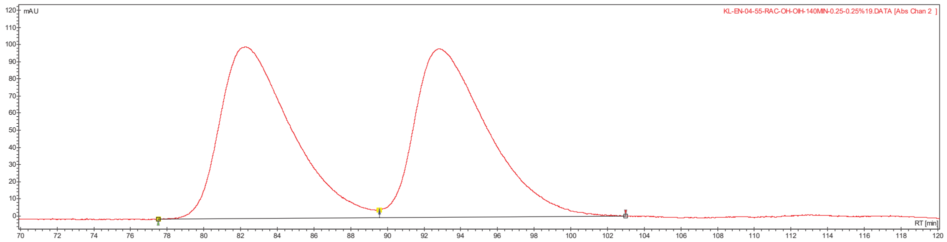


2,2,2-Tribromoethyl (S)-2-(4-bromophenyl)-5,5-dimethylhexanoate (8).

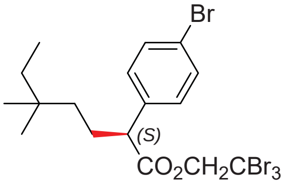


#	Time [Min]	Area% [%]
1	12.11	98.920
2	18.29	1.080
		98% *e.e.*.

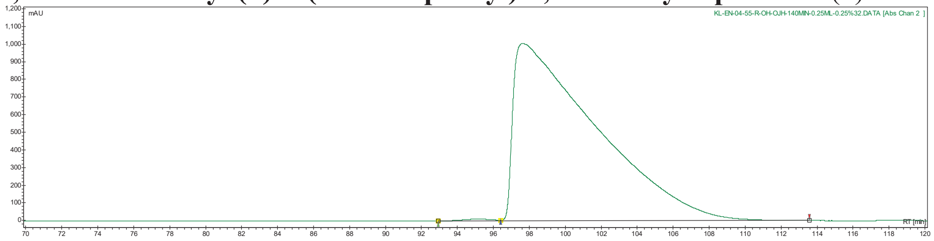




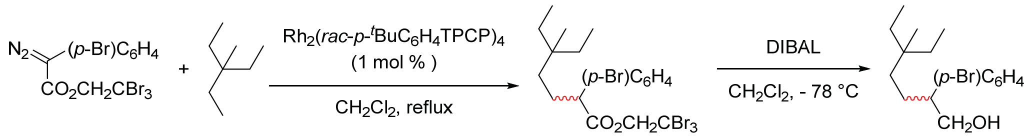
#	Time [Min]	Area% [%]
1	82.29	50.004
2	92.80	49.996

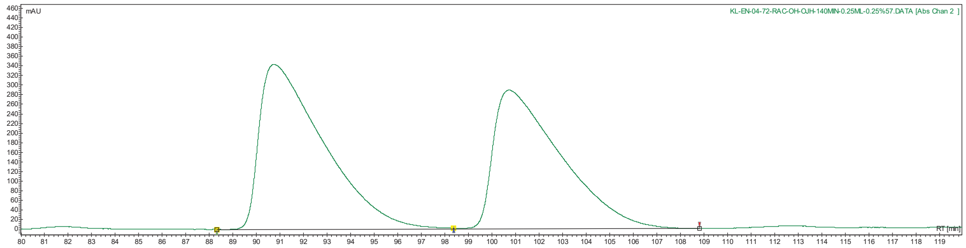


2,2,2-Tribromoethyl (S)-2-(4-bromophenyl)-5,5-dimethylheptanoate (9).

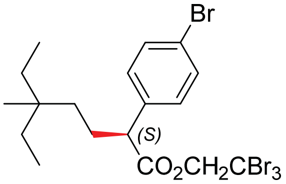


#	Time [Min]	Area% [%]
1	95.06	0.341
2	97.61	99.659
		>99% *e.e.*.

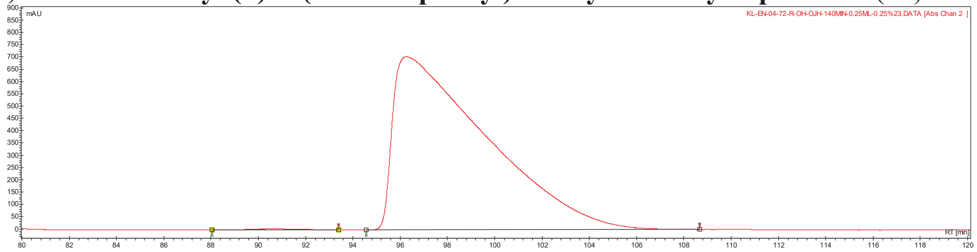




#	Time [Min]	Area% [%]
1	90.73	53.081
2	100.73	46.919

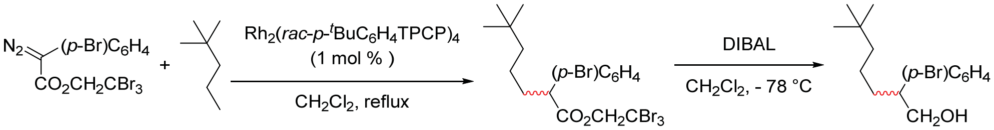


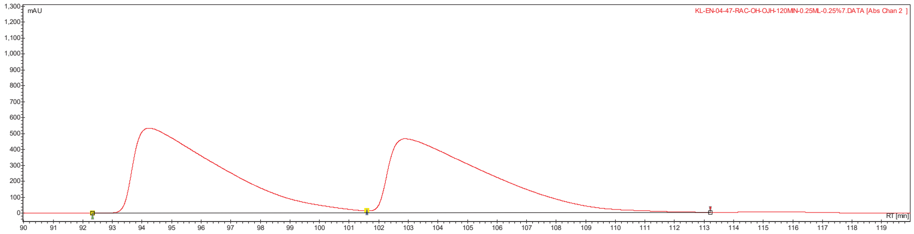
2,2,2-Tribromoethyl (*S*)-2-(4-bromophenyl)-5-ethyl-5-methylheptanoate (10).



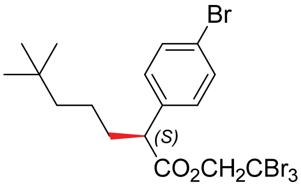
#	Time [Min]	Area% [%]
1	90.64	0.342
2	96.25	99.658

>99% *e.e.*.

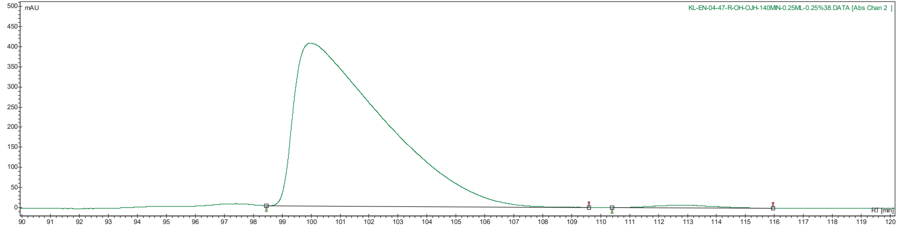




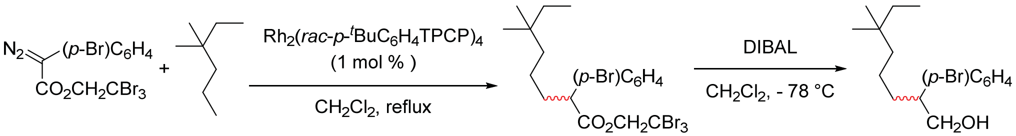
#	Time [Min]	Area% [%]
1	94.21	50.792
2	102.90	49.208

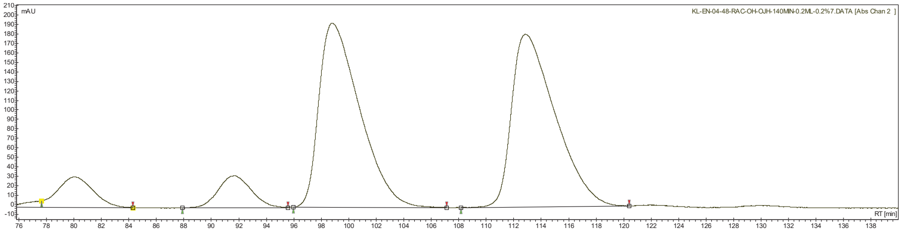


2,2,2-Tribromoethyl (S)-2-(4-bromophenyl)-6,6-dimethylheptanoate (11).

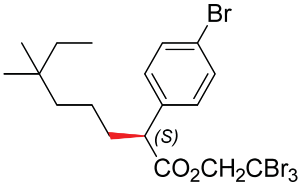


#	Time [Min]	Area% [%]
1	99.96	98.842
2	112.72	1.158
		98% *e.e.*.

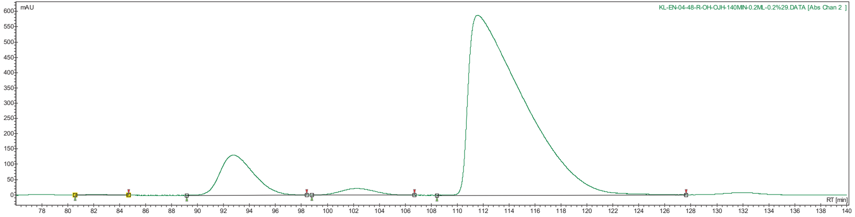




#	Time [Min]	Area% [%]
1	80.11	6.389
2	91.75	6.185
3	98.78	43.622
4	112.84	43.804



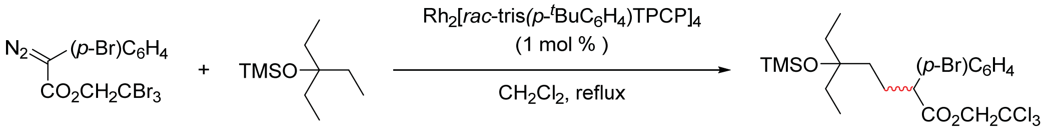
2,2,2-Tribromoethyl (S)-2-(4-bromophenyl)-6,6-dimethyloctanoate (12).

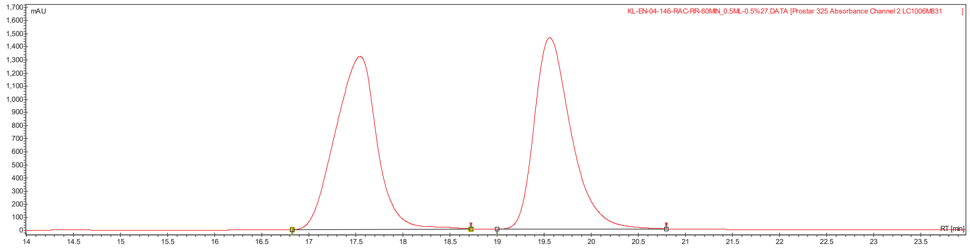


#	Time [Min]	Area% [%]
1	82.19	0.117
2	92.76	11.692
3	102.39	2.018
4	111.60	86.173

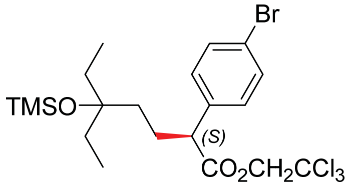
98% *e.e.*.

95% *e.e.*.

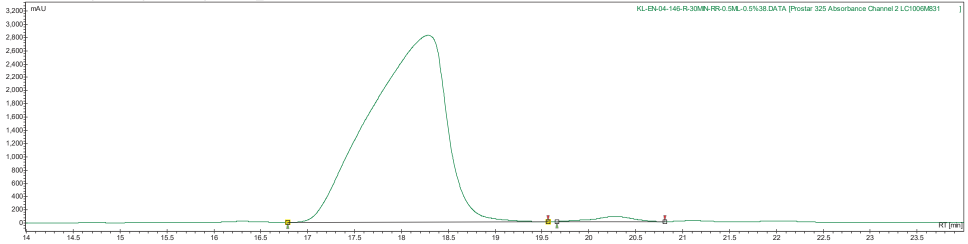




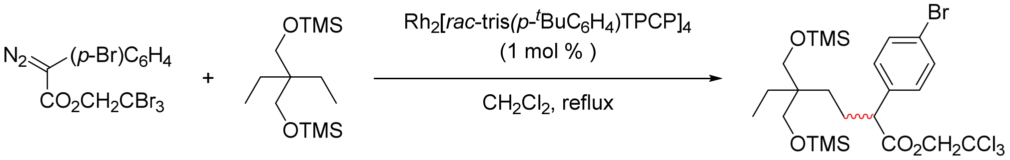
#	Time [Min]	Area% [%]
1	17.54	50.434
2	19.56	49.566

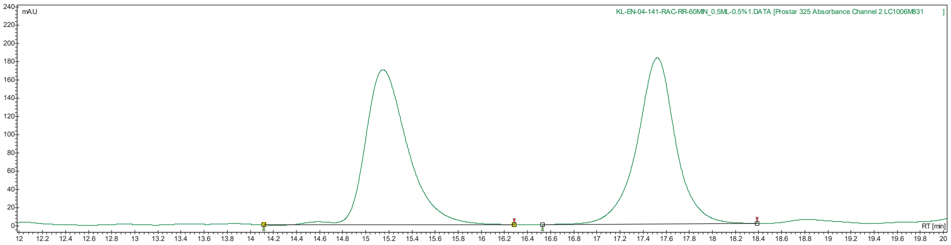


2,2,2-Trichloroethyl (S)-2-(4-bromophenyl)-5-ethyl-5-((trimethylsilyl)oxy)heptanoate (13).

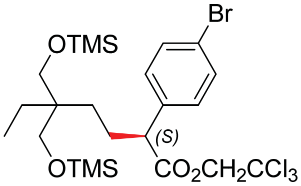


#	Time [Min]	Area% [%]
1	18.29	98.626
2	20.28	1.374
		97% *e.e.*.

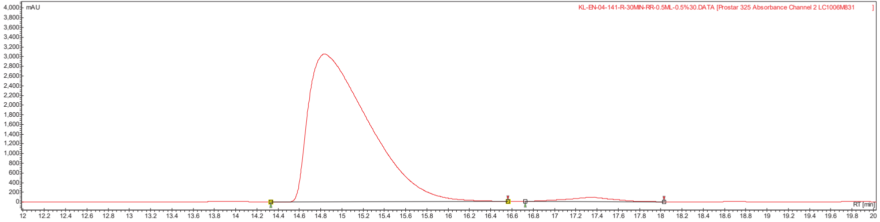




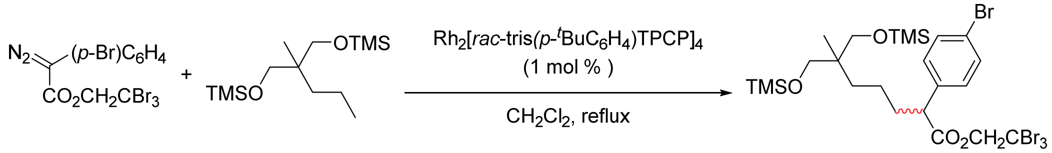
#	Time [Min]	Area% [%]
1	15.15	50.447
2	17.52	49.553

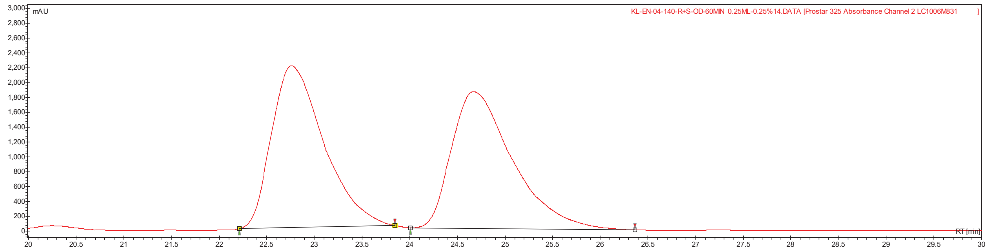


2,2,2-Trichloroethyl (S)-2-(4-bromophenyl)-5,5-bis(((trimethylsilyl)oxy)methyl)heptanoate (14).

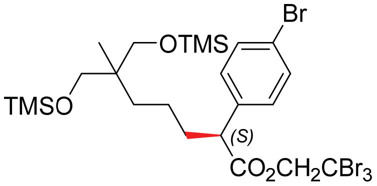


#	Time [Min]	Area% [%]
1	14.84	97.886
2	17.35	2.114
		96% *e.e.*.

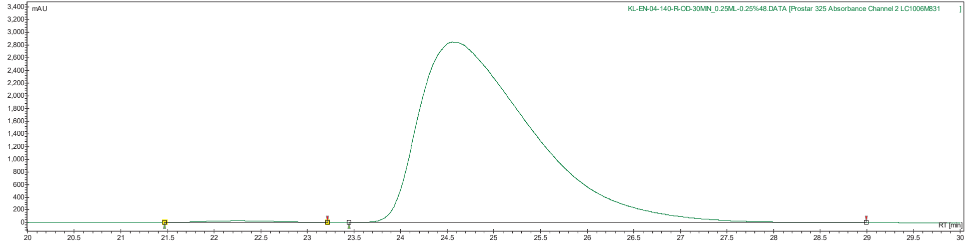




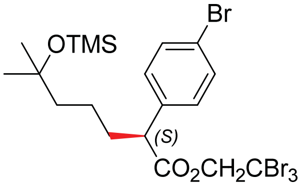
#	Time [Min]	Area% [%]
1	22.76	50.387
2	24.67	49.613



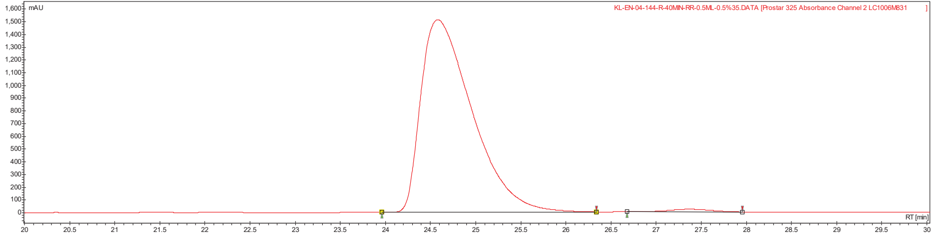
2,2,2-Tribromoethyl (S)-2-(4-bromophenyl)-6-methyl-7-((trimethylsilyl)oxy)-6-(((trimethylsilyl)oxy)methyl)heptanoate (15).



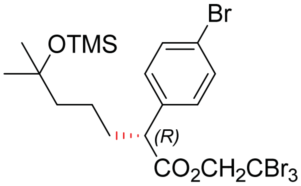
#	Time [Min]	Area% [%]
1	22.24	0.592
2	24.55	99.408
		99% *e.e.*.



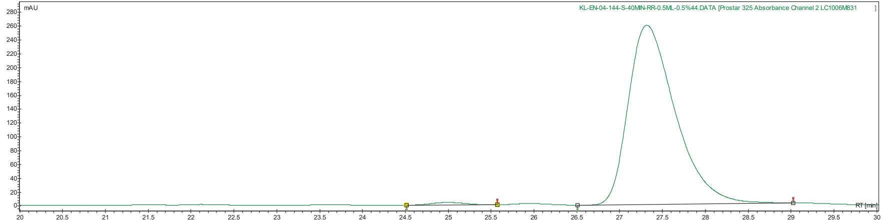
2,2,2-Tribromoethyl (S)-2-(4-bromophenyl)-6-methyl-6-((trimethylsilyl)oxy)heptanoate (16).



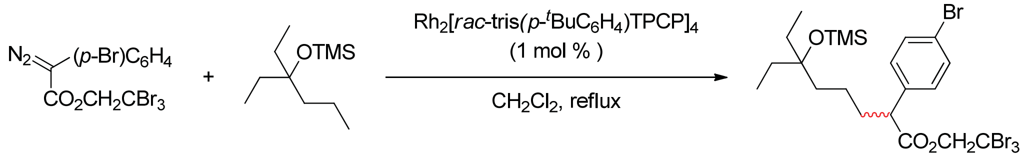
#	Time [Min]	Area% [%]
1	24.58	98.942
2	27.37	1.058
		98% *e.e.*.

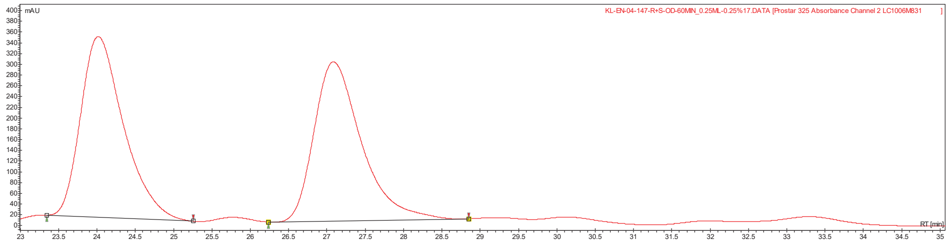


2,2,2-Tribromoethyl (R)-2-(4-bromophenyl)-6-methyl-6-((trimethylsilyl)oxy)heptanoate.

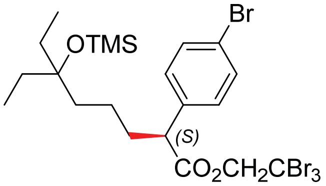


#	Time [Min]	Area% [%]
1	24.98	0.984
2	27.32	99.016
		98% *e.e.*.

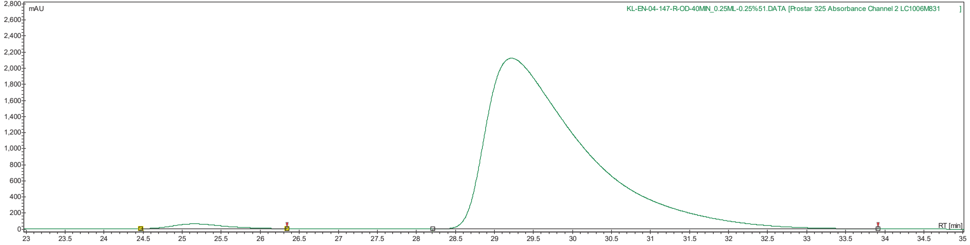




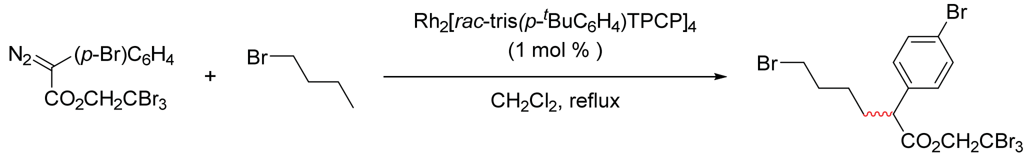
#	Time [Min]	Area% [%]
1	24.02	50.742
2	27.08	49.258

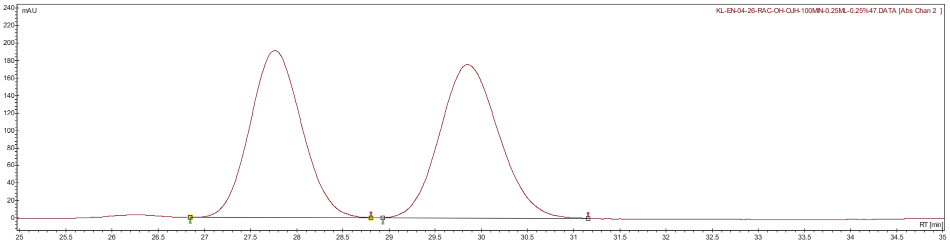


2,2,2-Tribromoethyl (S)-2-(4-bromophenyl)-6-ethyl-6-((trimethylsilyl)oxy)octanoate (17).

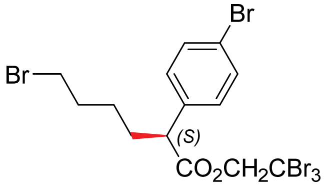


#	Time [Min]	Area% [%]
1	25.16	1.472
2	29.22	98.528
		97% *e.e.*.

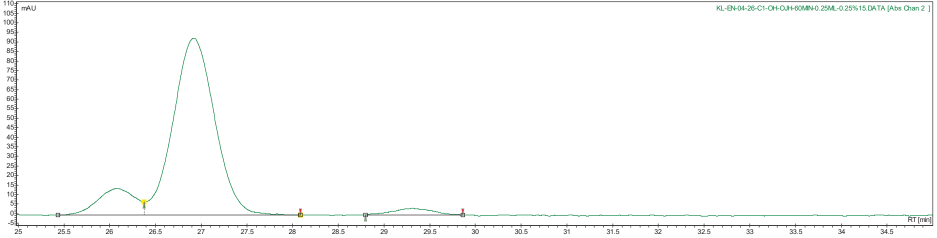




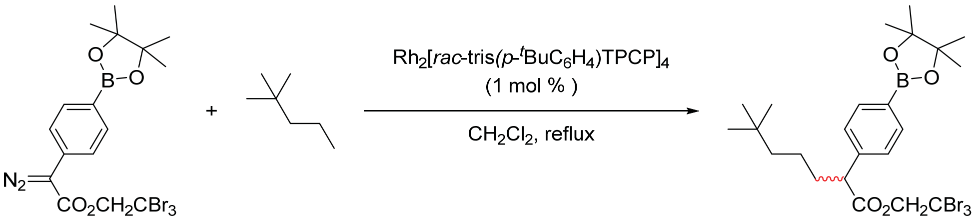
#	Time [Min]	Area% [%]
1	27.76	48.741
2	29.85	51.259

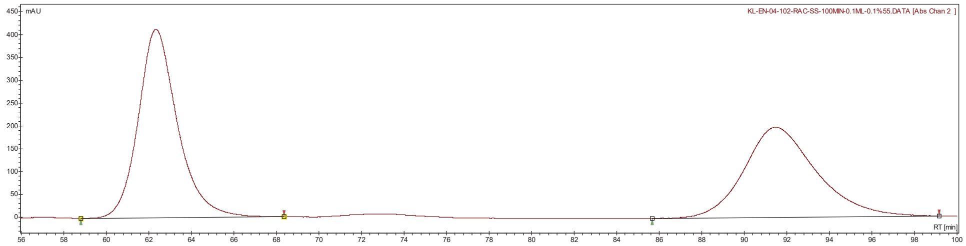


2,2,2-Tribromoethyl (S)-6-bromo-2-(4-bromophenyl)hexanoate (18).

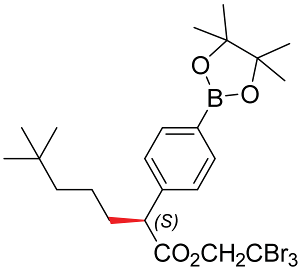


#	Time [Min]	Area% [%]
1	26.92	96.452
2	29.31	3.548
		93% *e.e.*.

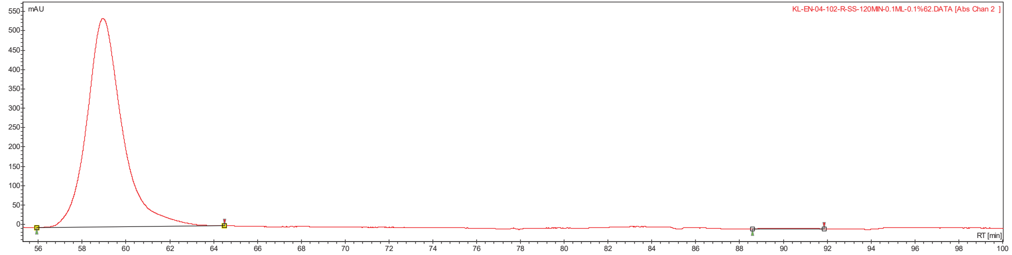




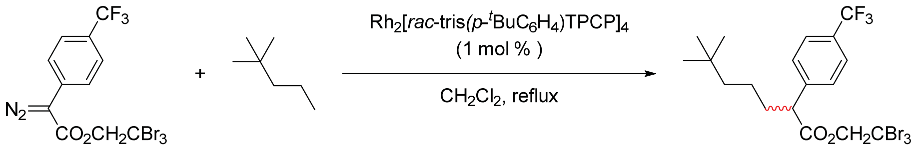
#	Time [Min]	Area% [%]
1	62.31	53.209
2	91.46	46.791

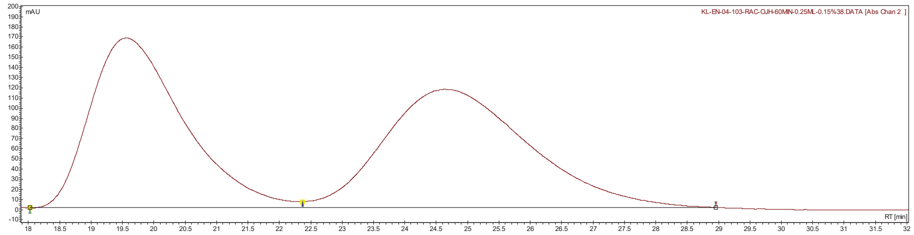


2,2,2-Tribromoethyl (S)-6,6-dimethyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)heptanoate (19).

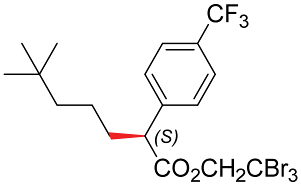


#	Time [Min]	Area% [%]
1	58.94	99.661
2	91.19	0.339
		>99% *e.e.*.

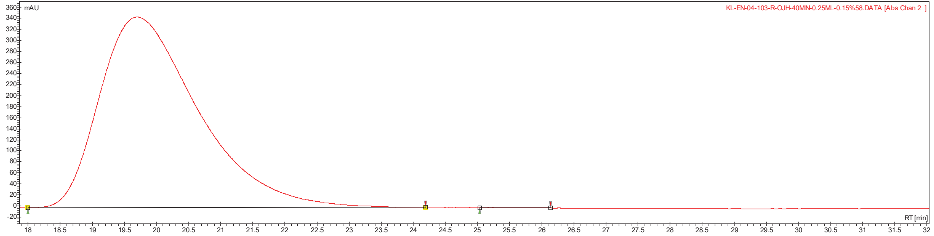




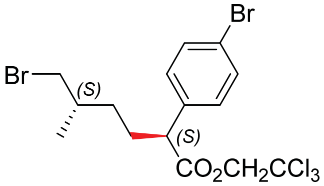
#	Time [Min]	Area% [%]
1	19.56	48.144
2	24.63	51.856



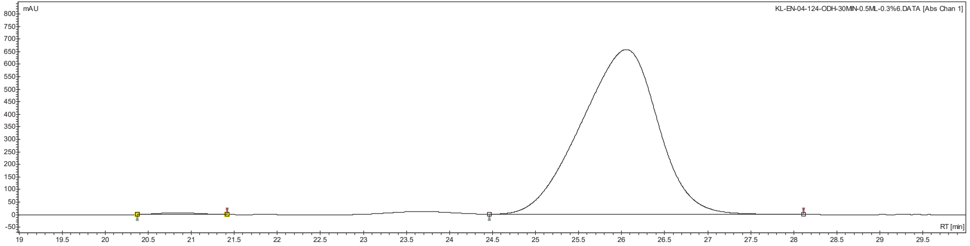
2,2,2-Tribromoethyl (S)-6,6-dimethyl-2-(4-(trifluoromethyl)phenyl)heptanoate (20).



#	Time [Min]	Area% [%]
1	19.70	99.957
2	25.77	0.043
		>99% *e.e.*.

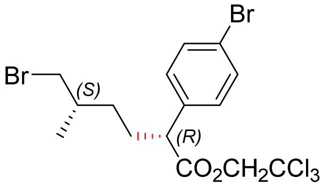


2,2,2-Trichloroethyl (2S,5S)-6-bromo-2-(4-bromophenyl)-5-methylhexanoate (**24**).

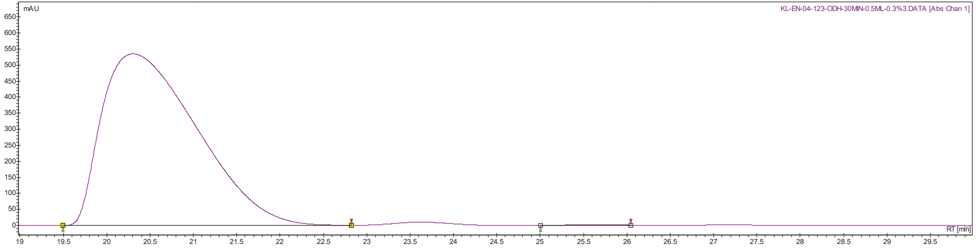


#	Time [Min]	Area% [%]
1	20.83	0.542
2	26.05	99.458

>100:1 d.*r*..

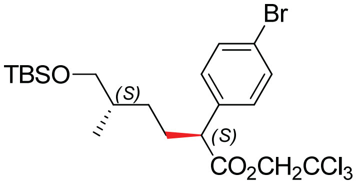


2,2,2-Trichloroethyl (2R,5S)-6-bromo-2-(4-bromophenyl)-5-methylhexanoate (**27**).

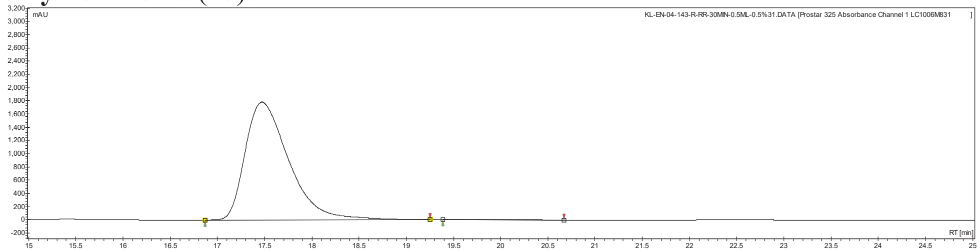


#	Time [Min]	Area% [%]
1	20.30	99.775
2	25.59	0.225

>100:1 d.*r*..

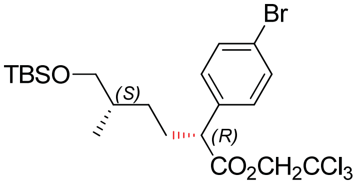


(2S,5S)-2,2,2-Trichloroethyl 2-(4-bromophenyl)-6-((tert-butyldimethylsilyl)oxy)-5-methylhexanoate (25).

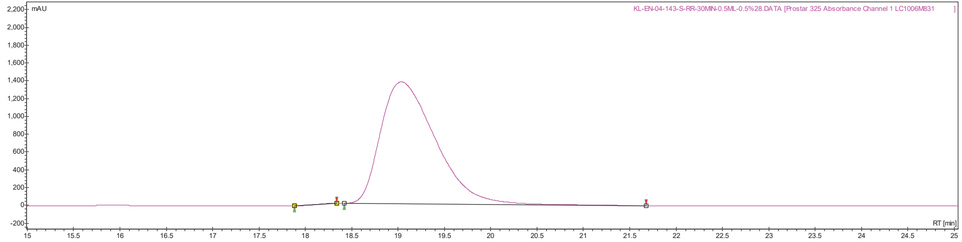


#	Time [Min]	Area% [%]
1	17.47	99.749
2	19.79	0.251

>100:1 d.*r*..

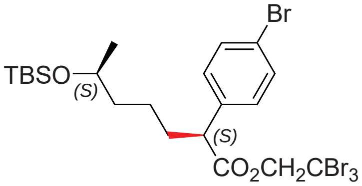


(2R,5S)-2,2,2-Trichloroethyl 2-(4-bromophenyl)-6-((tert-butyldimethylsilyl)oxy)-5-methylhexanoate (28).

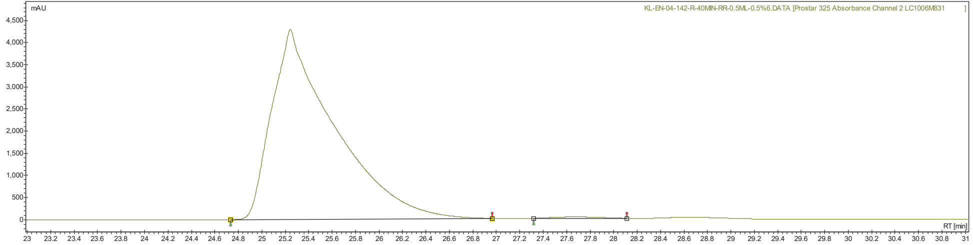


#	Time [Min]	Area% [%]
1	18.01	0.035
2	19.04	99.965

>100:1 d.*r*..

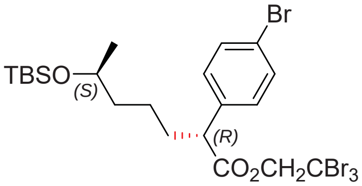


2,2,2-Tribromoethyl (2S,6S)-2-(4-bromophenyl)-6-((tert-butyldimethylsilyl)oxy)heptanoate (26).

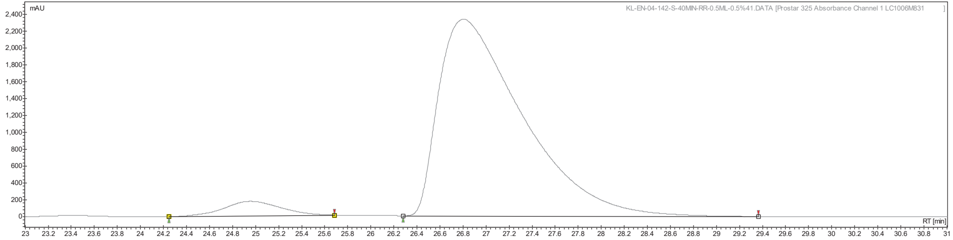


#	Time [Min]	Area% [%]
1	25.24	99.397
2	27.67	0.603

>100:1 d.*r*..



2,2,2-Tribromoethyl (2R,6S)-2-(4-bromophenyl)-6-((tert-butyldimethylsilyl)oxy)heptanoate (29).



#	Time [Min]	Area% [%]
1	24.95	4.833
2	26.81	95.167

20:1 d.*r*..

10. X-Ray Crystallographic Data of Product 5.3.7

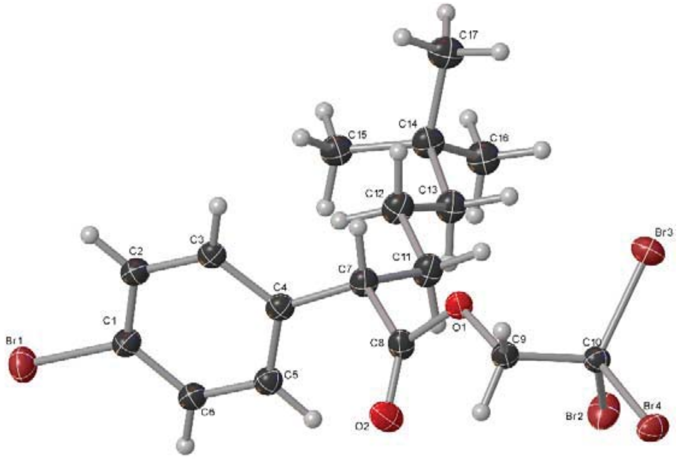
Submitted by: **Kuangbiao Liao**

Davies Group, Emory University

Solved by: **John Bacsa**

Sample ID: **11**

Crystal Data and Experimental



Experimental. Single colorless needle-shaped crystals of (**11**) were recrystallized from hexane by slow evaporation. A suitable crystal ($0.46\times0.08\times0.06$ mm^3) was selected and mounted on a loop with paratone oil on a Bruker D8 Venture diffractometer. The crystal was cooled to $T = 100(2)$ K during data collection. The structure was solved with the **XT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2014/7 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{17}H_{22}Br_4O_2$, $M_r = 577.98$, monoclinic, $P2_1$ (No. 4), a = 12.3961(10) Å, b = 5.9063(5) Å, c = 14.7231(11) Å, = 110.981(4)°, = = 90°, $V = 1006.48(14)$ Å^3, $T = 100(2)$ K, $Z = 2$, $Z' = 1$, (CuK) = 9.807 mm^{-1}, 5488 reflections measured, 3186 unique ($R_{int} = 0.0390$) which were used in all calculations. The final wR_2 was 0.1304 (all data) and R_1 was 0.0512 ($I > 2\sigma(I)$).

Compound	**11**
Formula	$C_{17}H_{22}Br_4O_2$
$D_{calc.}$/ g cm^{-3}	1.907
/mm^{-1}	9.807
Formula Weight	577.98
Colour	colourless
Shape	needle
Size/mm^3	0.46×0.08×0.06
T/K	100(2)
Crystal System	monoclinic
Flack Parameter	0.18(8)
Hooft Parameter	0.24(3)
Space Group	$P2_1$
a/Å	12.3961(10)
b/Å	5.9063(5)
c/Å	14.7231(11)
/°	90
/°	110.981(4)
/°	90
V/Å^3	1006.48(14)
Z	2
Z'	1
Wavelength/Å	1.541840
Radiation type	CuK
$_{min}$/°	3.215
$_{max}$/°	70.313
Measured Refl.	5488
Independent Refl.	3186
Reflections with $I > 2\sigma(I)$	2871
R_{int}	0.0390
Parameters	212
Restraints	145
Largest Peak	1.366
Deepest Hole	-0.973
GooF	1.048
wR_2 (all data)	0.1304
wR_2	0.1216
R_1 (all data)	0.0630
R_1	0.0512

Structure Quality Indicators

Reflections:	d min (Cu) 0.82	I/σ 14.3	Rint 3.90%	
Refinement:	Shift 0.000	Max Peak 1.4	Min Peak -1.0	GooF 1.048

A colourless needle-shaped crystal with dimensions 0.46×0.08×0.06 mm^3 was mounted on a loop with paratone oil. Data were collected using a 'Bruker D8 Venture diffractometer equipped with an Oxford Cryosystems low-temperature device, operating at *T* = 100(2) K.

Data were measured using and scans with a narrow frame width of 0.50° per frame for 10.00 s using CuK radiation (microfocus sealed tube, 50 kV, 1 mA).The total number of runs and images was based on the strategy calculation from the program **APEX3** (Bruker). The maximum resolution that was achieved was = 70.313°.

The diffraction patterns were indexed using **APEX3** (Bruker) and the unit cells were refined using SAINT (Bruker, V8.37A, 2015) on 8987 reflections. Data reduction, scaling and absorption corrections were performed using SAINT (Bruker, V8.37A, 2015) and SADABS-2016/2 (Bruker, 2016). The final completeness is 97.7% out to 70.313° in . The absorption coefficient of this material is 9.807 mm^{-1} at this wavelength (= 1.54178 Å) and the minimum and maximum transmissions are 0.4475 and 0.7533.

The structure was solved and the space group $P2_1$ (# 4) determined by the XT (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2014/7 of **XL** (Sheldrick, 2008). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

The Flack parameter was refined to 0.18(8). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in 0.24(3). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

Images of the Crystal on the Diffractometer

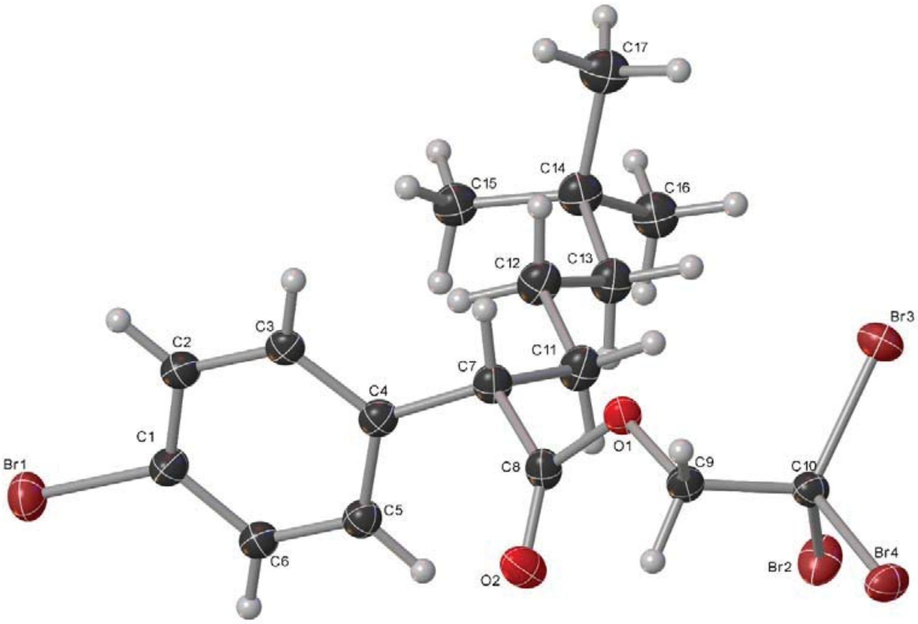


Figure 1:

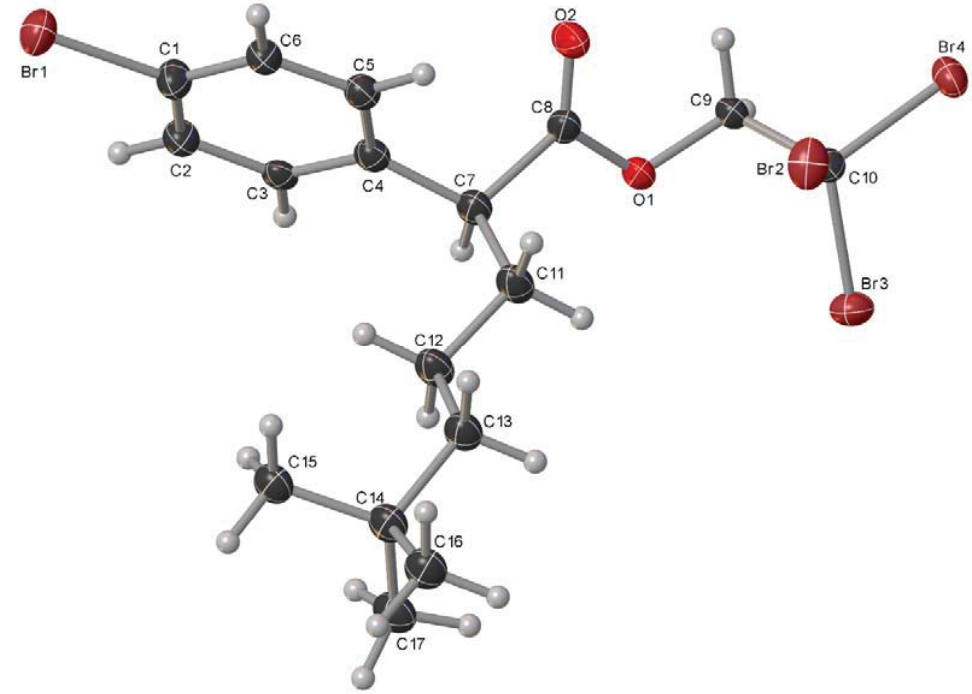
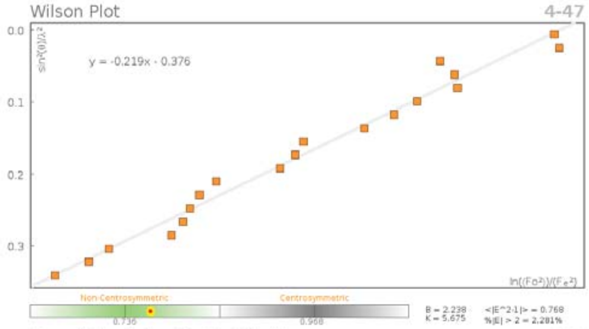
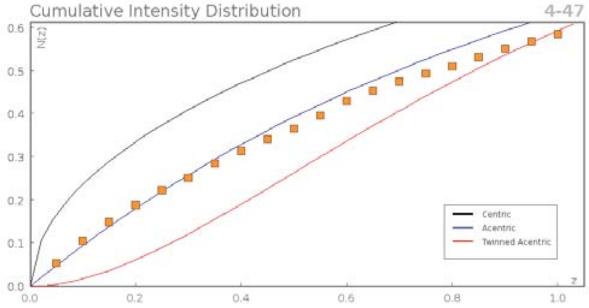
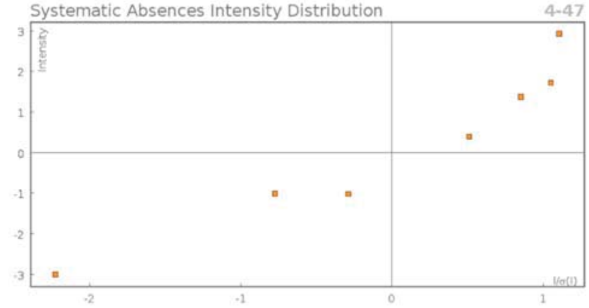


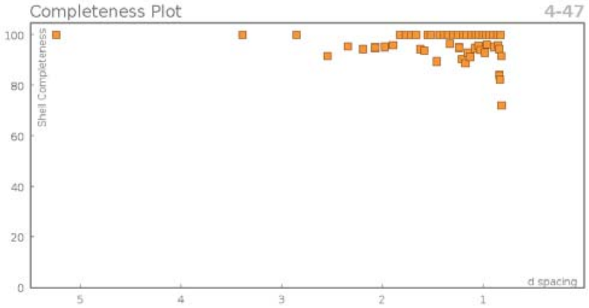
Figure 2:

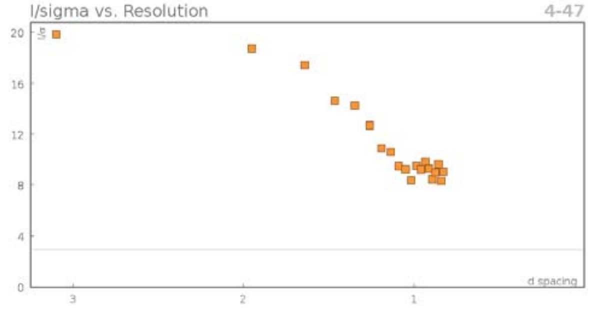
Data Plots: Diffraction Data



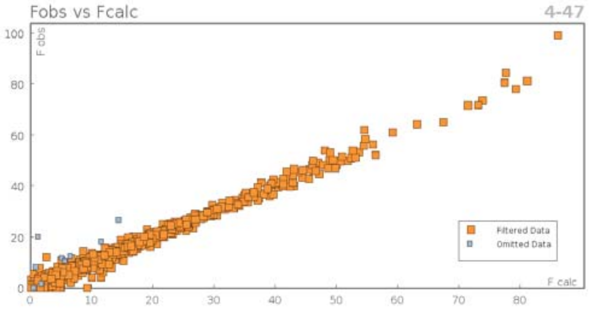


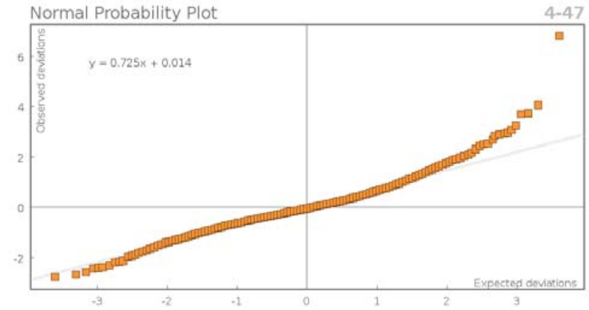






Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	5510	Unique reflections	3186
Completeness	0.831	Mean I/	14.29
hkl_{max} collected	(15, 7, 17)	hkl_{min} collected	(-15, -7, -14)
hkl_{max} used	(14, 7, 17)	hkl_{min} used	(-15, -7, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.77
d_{max} used	13.75	d_{min} used	0.82
Friedel pairs	765	Friedel pairs merged	0
Inconsistent equivalents	10	R_{int}	0.039
R_{sigma}	0.0571	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	15
Multiplicity	(2347, 1330, 154, 9, 1)	Maximum multiplicity	5
Removed systematic absences	7	Filtered off (Shel/OMIT)	0

Table 1: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **11**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Br3	3984.8(10)	-678(2)	4758.1(9)	27.1(3)
Br4	1697.8(11)	-719(2)	2882.2(8)	26.7(3)
Br1	12.6(12)	9973(2)	9050.1(10)	31.5(4)
Br2	2662.0(13)	3883(2)	3988.5(10)	30.7(3)
O2	808(7)	3900(20)	5343(6)	30.7(19)
O1	2199(7)	1231(16)	5674(6)	21.6(15)
C3	1691(9)	4720(20)	8263(8)	19.8(19)
C9	1682(10)	280(20)	4727(8)	21(2)
C7	2409(10)	3990(20)	6901(8)	22.3(18)
C4	1722(10)	5320(20)	7360(8)	21(2)
C11	3426(11)	5360(30)	6792(9)	27(3)
C15	5392(11)	9950(20)	9245(9)	27(2)
C10	2486(11)	690(20)	4146(8)	20.5(14)
C16	6699(12)	10740(30)	8323(10)	29(2)
C1	678(12)	8070(30)	8350(9)	27(2)
C6	673(10)	8700(20)	7449(8)	24(2)
C12	4224(12)	6250(20)	7756(9)	27(3)
C5	1171(11)	7380(20)	6944(9)	23(2)
C8	1666(11)	3060(20)	5885(9)	22(2)
C13	5097(11)	7940(20)	7653(9)	26(2)
C14	5993(11)	8910(30)	8597(8)	26.6(17)
C17	6826(12)	6950(30)	9154(10)	30(2)
C2	1177(11)	6060(20)	8764(9)	25(2)

Table 2: Anisotropic Displacement Parameters (×10^4) **11**. The anisotropic displacement factor exponent takes the form: $-2\ {}^2[h^2a^{*2} \times U_{11} + \ldots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br3	20.6(6)	26.6(8)	31.0(6)	0.7(6)	5.4(5)	2.2(6)
Br4	32.4(7)	25.3(7)	19.3(5)	-2.1(5)	5.5(5)	5.1(6)
Br1	35.1(8)	32.1(9)	32.0(7)	-2.5(6)	17.8(6)	3.4(6)
Br2	45.3(8)	17.8(7)	34.3(6)	2.2(6)	20.7(6)	-0.4(6)
O2	26(3)	36(5)	25(3)	-10(3)	3(2)	5(3)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	19(3)	26(3)	18(2)	-4(2)	4(2)	-2(2)
C3	15(4)	22(3)	19(3)	-2(3)	3(3)	-5(3)
C9	18(4)	25(5)	17(3)	-3(3)	4(3)	-2(3)
C7	21(3)	24(4)	21(3)	-4(3)	6(2)	-3(2)
C4	20(4)	22(4)	20(3)	-2(3)	5(3)	-3(3)
C11	25(4)	32(6)	23(4)	-5(3)	8(3)	-9(4)
C15	28(4)	26(5)	24(4)	-4(3)	7(3)	-3(4)
C10	21(3)	20(2)	20(2)	-0.4(17)	6.4(18)	2.4(18)
C16	28(4)	28(4)	30(4)	-5(3)	9(4)	-5(3)
C1	30(6)	29(3)	22(3)	2(3)	10(3)	6(4)
C6	23(5)	26(4)	20(3)	0(3)	6(3)	1(3)
C12	25(4)	30(5)	23(4)	-4(3)	6(3)	-8(4)
C5	22(5)	24(4)	21(3)	0(3)	7(3)	-1(3)
C8	19(3)	27(4)	22(3)	-5(2)	8(2)	-3(3)
C13	25(3)	27(4)	25(3)	-5(3)	8(3)	-6(3)
C14	26(3)	26(4)	25(3)	-5(3)	6(3)	-5(3)
C17	30(4)	26(4)	28(4)	-6(3)	4(3)	-3(3)
C2	25(5)	28(3)	21(3)	1(3)	7(3)	3(3)

Table 3: Bond Lengths in Å for **11**.

Atom	**Atom**	**Length/Å**
Br3	C10	1.928(12)
Br4	C10	1.951(12)
Br1	C1	1.902(13)
Br2	C10	1.924(13)
O2	C8	1.185(16)
O1	C9	1.427(13)
O1	C8	1.360(15)
C3	C4	1.389(15)
C3	C2	1.383(17)
C9	C10	1.546(15)
C7	C4	1.486(16)
C7	C11	1.554(17)
C7	C8	1.550(16)
C4	C5	1.421(19)
C11	C12	1.504(17)
C15	C14	1.531(17)
C16	C14	1.531(19)
C1	C6	1.377(16)
C1	C2	1.38(2)
C6	C5	1.369(16)
C12	C13	1.519(18)
C13	C14	1.548(17)
C14	C17	1.57(2)

Table 4: Bond Angles in ° for **11**.

Atom	Atom	Atom	Angle/°
C8	O1	C9	116.9(9)
C2	C3	C4	122.7(12)
O1	C9	C10	109.0(9)
C4	C7	C11	113.1(11)
C4	C7	C8	112.8(10)
C8	C7	C11	107.9(9)
C3	C4	C7	121.1(12)
C3	C4	C5	117.2(11)
C5	C4	C7	121.4(10)
C12	C11	C7	111.5(10)
Br3	C10	Br4	109.7(6)
Br2	C10	Br3	109.5(6)
Br2	C10	Br4	110.0(6)
C9	C10	Br3	112.3(8)
C9	C10	Br4	105.0(8)
C9	C10	Br2	110.1(8)
C6	C1	Br1	120.5(11)
C2	C1	Br1	118.9(9)
C2	C1	C6	120.6(12)
C5	C6	C1	121.3(13)
C11	C12	C13	112.7(11)
C6	C5	C4	119.8(11)
O2	C8	O1	124.9(11)
O2	C8	C7	125.5(12)
O1	C8	C7	109.4(10)
C12	C13	C14	117.6(11)
C15	C14	C16	109.5(12)
C15	C14	C13	110.8(10)
C15	C14	C17	110.1(10)
C16	C14	C13	108.7(10)
C16	C14	C17	109.1(11)
C13	C14	C17	108.6(12)
C1	C2	C3	118.5(12)

Table 5: Torsion Angles in ° for **11**.

Atom	Atom	Atom	Atom	Angle/°
Br1	C1	C6	C5	178.5(10)
Br1	C1	C2	C3	-177.9(9)
O1	C9	C10	Br3	60.1(12)
O1	C9	C10	Br4	179.3(8)
O1	C9	C10	Br2	-62.3(11)
C3	C4	C5	C6	2.0(18)
C9	O1	C8	O2	0.4(18)
C9	O1	C8	C7	-174.7(9)
C7	C4	C5	C6	-171.5(11)
C7	C11	C12	C13	-169.6(12)
C4	C3	C2	C1	0(2)
C4	C7	C11	C12	56.9(15)
C4	C7	C8	O2	28.1(18)
C4	C7	C8	O1	-156.7(11)
C11	C7	C4	C3	-114.8(13)
C11	C7	C4	C5	58.5(15)

Atom	Atom	Atom	Atom	Angle/°
C11	C7	C8	O2	-97.5(15)
C11	C7	C8	O1	77.7(13)
C11	C12	C13	C14	-178.0(12)
C1	C6	C5	C4	-1.0(19)
C6	C1	C2	C3	1(2)
C12	C13	C14	C15	-53.8(17)
C12	C13	C14	C16	-174.2(12)
C12	C13	C14	C17	67.2(15)
C8	O1	C9	C10	112.0(11)
C8	C7	C4	C3	122.5(13)
C8	C7	C4	C5	-64.2(15)
C8	C7	C11	C12	-177.7(12)
C2	C3	C4	C7	172.1(11)
C2	C3	C4	C5	-1.4(18)
C2	C1	C6	C5	-1(2)

Table 6: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **11**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H3	2039	3333	8549	24
H9A	921	988	4387	25
H9B	1563	-1369	4778	25
H7	2745	2664	7331	27
H11A	3867	4372	6506	32
H11B	3115	6642	6342	32
H15A	5972	10622	9822	40
H15B	4972	8759	9446	40
H15C	4848	11115	8881	40
H16A	6179	11928	7944	44
H16B	7112	10064	7934	44
H16C	7257	11401	8916	44
H6	317	10089	7171	28
H12A	4641	4962	8162	32
H12B	3759	6987	8096	32
H5	1148	7829	6319	27
H13A	4665	9219	7255	31
H13B	5525	7194	7281	31
H17A	7511	7597	9653	45
H17B	7062	6068	8692	45
H17C	6423	5960	9463	45
H2	1168	5598	9380	30

Citations

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O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

SAINT-8.37A-2015 - Software for the Integration of CCD Detector System Bruker Analytical X-ray Systems, Bruker axs, Madison, WI (2015).

Sheldrick, G.M., A short history of ShelX, *Acta Cryst.*, (2008), **A64**, 339-341.

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# Wavelength 1.54178    Volume Reported   1006.48(14)   Calculated   1006.48(14)
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#      Reported C17 H22 Br4 O2
#    SumFormula C17 H22 Br4 O2
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# F000      =     560.0[Calc],     560.0[Rep]  or F000' =    555.42[Calc]
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# Calculated T Limits: Tmin=0.428 Tmin'=0.009  Tmax=0.555
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# Calculated Hmax= 15, Kmax=  7, Lmax= 17, Nref=   3833[  2115], Ratio=1.51/0.83
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For Documentation: http://http://www.platonsoft.nl/CIF-VALIDATION.pdf
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#==============================================================================
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>>> The Following Improvement and Query ALERTS were generated - (Acta-Mode) <<<
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090_ALERT_3_C Poor Data / Parameter Ratio (Zmax > 18) ........      9.71 Note
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083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large.       8.78 Why ?
434_ALERT_2_G Short Inter HL..HL Contact  Br2    ..  Br4     .       3.59 Ang.
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ALERT_Level and ALERT_Type Summary
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1 ALERT_Level_B = A Potentially Serious Problem - Consider Carefully
3 ALERT_Level_C = Check. Ensure it is Not caused by an Omission or Oversight
11 ALERT_Level_G = General Info/Check that it is not Something Unexpected

3 ALERT_Type_2 Indicator that the Structure Model may be Wrong or Deficient.
5 ALERT_Type_3 Indicator that the Structure Quality may be Low.
6 ALERT_Type_4 Improvement, Methodology, Query or Suggestion.
1 ALERT_Type_5 Informative Message, Check.
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1 Missing  Experimental  Info Issue(s) (Out of  54 Tests) -   98% Satisfied
1 Experimental  Data  Related Issue(s) (Out of  28 Tests) -   96% Satisfied
5 Structural  Model   Related Issue(s) (Out of 117 Tests) -   96% Satisfied
7 Unresolved or to be Checked Issue(s) (Out of 223 Tests) -   97% Satisfied

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SI-Chapter 6

1. General Considerations

1.1 Equipment and Methods

^{1}H and ^{13}C NMR spectra were recorded at either 500 MHz (^{13}C at 126 MHz) or 600 MHz (^{13}C at 151 MHz) on INOVA-500 or Bruker-600 spectrometer, as indicated. NMR spectra were run in solutions of deuterated chloroform ($CDCl_3$) with residual chloroform taken as an internal standard (7.26 ppm for ^{1}H, and 77.16 ppm for ^{13}C), and were reported in parts per million (ppm).

Abbreviations for signal multiplicity are as follow: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, etc. Coupling constants (*J* values) were calculated directly from the spectra. IR spectra were collected on a Nicolet iS10 FT-IR spectrometer. Mass spectra were taken on a Thermo Finnigan LTQ-FTMS spectrometer with APCI, ESI or NSI. Thin layer chromatographic (TLC) analysis was performed with glass-backed silica gel plates, visualizing with UV light (254 nm) and/or staining with aqueous $KMnO_4$ stain.

1.2 Solvents for Reaction

The dichloromethane(CH_2Cl_2) used for the carbenoid transformations was dried at reflux over calcium hydride in a 250-mL round bottom flask for 12 hours under argon, then distilled and stored under argon atmosphere and then used directly.

1.3 Substrates and Reagents

The substrates and reagents were purchased from the following suppliers and used without further purification:

Acros:2-Methylbutane (1 LT, 99+ % purity);

Sigma-Aldrich:3-Methylpentane (1 LT, ≥99 % purity); 2,5-Dimethylhexane (5 g, 99 % purity); 1-Bromo-3-methylbutane (100 g, 96 % purity); Cholesteryl acetate (100 g, 97 % purity); Cholesteryl pelargonate (100 g, 97 % purity); 2-Methylhexane (5g, 99% purity)

Alfa-Aesar:2-Methylpentane (100 mL, 99+ % purity); 2,3-Dimethylbutane (100 g, 99 % purity)

TCI:3-Ethyl-2-methylpentane (5 mL, >99 % purity); D-α-Tocopherol Acetate (Vitamin E) (25 g, >96 % purity)

The following substrates were prepared according to reported procedures[20]:

Butyl 5-methylhexanoate; pentyl 5-methylhexanoate; phytyl pivalate.

The following reagents were prepared according to reported procedures [21-24]:

Methyl 2-(4-bromophenyl)-2-diazoacetate; 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate; 2,2,2-trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate; 2,2,2-tribromoethyl 2-(4-bromophenyl)-2-diazoacetate.

2. General Procedures for C–H Functionalization Reactions

A 5-mL flask was equipped with a reflux condenser and an octagonal magnetic stir bar. The flask was charged with Rh_2L_4 (0.002 mmol, 1 mol%) and treated by vacuum/argon to replace the air in the flask to argon. Substrate (0.6 mmol, 3 *equiv.*) and distilled CH_2Cl_2 (0.5 mL) were added, then the catalyst/substrate solution was heated to reflux (39 °C) under argon for 5 minutes [or the reaction was conducted at room temperature(24 °C), 0° C, -10 °C, -40 °C, -78 °C]. Diazo (0.2 mmol, 1.0 *equiv.*) was dissolved in 3 mL of distilled CH_2Cl_2 and then the diazo solution was added dropwise to the catalyst solution over 6h with a syringe pump under reflux condition [or the reaction was conducted at room temperature(24 °C), 0° C, -10 °C, -40 °C, -78 °C] and argon atmosphere. After addition, 0.5 mL distilled CH_2Cl_2 was used to dilute the left over diazo in the syringe needle and then the diazo solution was added dropwise to the reaction solution. Then the rest of the diazo solution in the syringe needle was further pushed into the reaction solution. Then the reaction mixture was allowed to stir for another 1 min, then the reaction mixture was transferred into a 25-mL round bottom flask with diethyl ether (5 mL x 3) and concentrated under vacuum, and crude ^1H NMR spectrum was obtained to analyze the reaction and measure the selectivity. Then the crude was purified by flash chromatography on silica gel to obtain the product.

3. General Procedure of Data Analysis

3.1 General Procedure for the Regioisomeric Ratios (r.r.) and Diastereomeric Ratios (d.r.) Determination

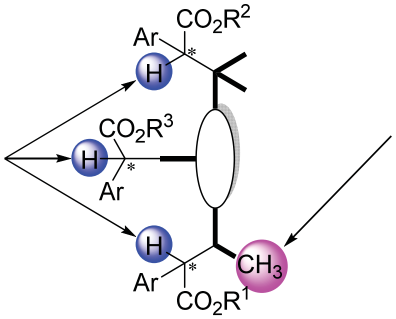
To measure the regioisomeric ratios and diastereomeric ratios, the mixtures obtained as described in section 2.1 were analyzed by ^{1}H NMR using the following settings:

Instrument:600 MHz Bruker equipped with a prodigy probe with sensitivity over 1500:1

Number of scans:32

Relaxation time:5 seconds

The crude ^{1}H NMR spectra data was processed using MestReNova 11.0.2 (Mestrelab Research S.L.), applying an auto-phase correction as well as a Smooth Segment baseline correction. The baseline was manually inspected before integration. The ratios were measured by integrating the ^{1}H NMR peaks resulting from the indicated hydrogens below.



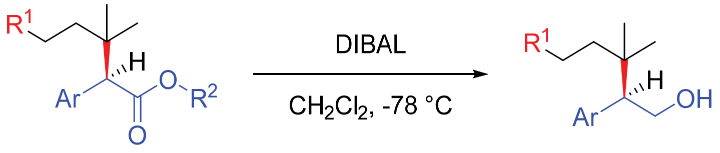
The regioisomeric ratios (*r.r.*) were measured by integrating the proton peaks of each regioisomers in the crude ^{1}H NMR spectra

The diastereoisomeric ratios (*d.r.*) were measured by integrating the proton peaks of each diastereomers in the crude ^{1}H NMR spectra

In terms of the functionalization of cholesteryl acetate and Vitamin E, no other regioisomer was detected in the crude ^{1}H NMR spectra, LC-MS technique was used to confirm the results.

3.2 General Procedure for Enantiomeric Excess (e.e.) Determination on HPLC

As most of the enantiomers of the C–H functionalization products were difficult to be separated on the HPLC, they were reduced to the corresponding alcohol derivatives, which will have better separation on the HPLC, without changing the e.e. of the products. Therefore, the e.e. of the products were determined from the corresponding alcohol derivatives. [5]

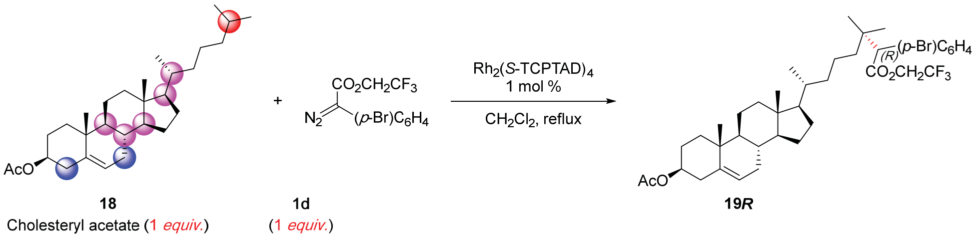


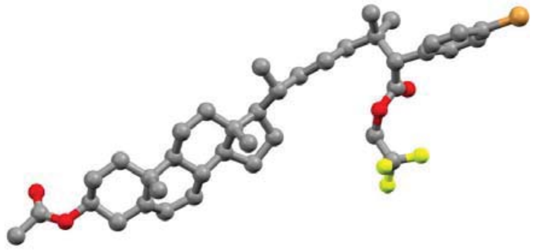
To a 25-mL round bottom flask with a stirred solution of the ester (0.1 mmol, 1.0 *equiv.*) in CH_2Cl_2 (3 mL) was added 1 M diisobutylaluminum hydride (DIBAL) in CH_2Cl_2 (0.5 mL, 0.5 mmol, 5 *equiv.*) slowly at -78 °C. The mixture was stirred overnight and allowed to warm up to room temperature. Once the starting material was fully consumed and confirmed by TLC, the solution was cooled down to 0 °C, then methanol (0.5 mL) was added dropwise to quench the reaction and then stirred for 20 min. The reaction mixture was concentrated to dry solid mixture, then 10 mL of ethyl acetate (EA) was added into the flask to extract the organic compound. Then mixture in the flask was poured onto and filtered through a silica plug (3 *cm* height, 2 *cm* wide), and the solid residue was further extracted and washed by EA (10 mL x 4). Then the filtrate was concentrated and purified by flash column chromatography to afford the corresponding alcohol derivatives as white solid or colorless oil. The sample was dissolved in hexanes/isopropanol (5~30 mg/mL) and the e.e. value of the corresponding alcohol derivatives were determined on the HPLC.

The e.e. of the C–H functionalization products were then obtained from the e.e. of the corresponding alcohol derivatives, in which the e.e. values were considered equal to each other.

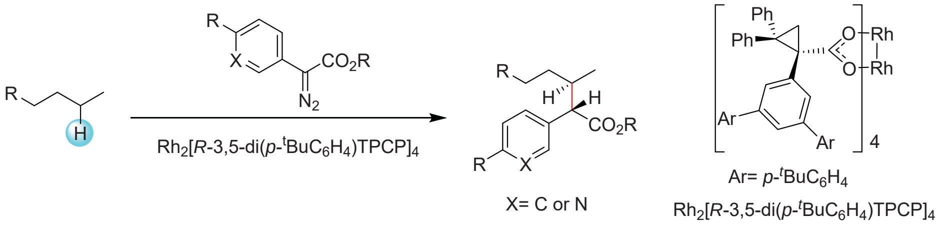
4. Determination of the Absolute Stereochemistry

The absolute stereochemistry of $Rh_2(S\text{-TCPTAD})_4$ catalyzed tertiary C-H insertion reaction of substrate **17** was determined by the X-Ray single crystal structure analysis of product **18*R*** (see section 10 for detail), the absolute stereochemistry of the secondary C-H insertion products was determined by the known asymmetric induction of $Rh_2[R\text{-3,5-di}(p\text{-}{}^tBuC_6H_4)TPCP]_4$.[5] Based on these data, the absolute stereochemistry of the rest of the reactions were tentatively assigned accordingly.



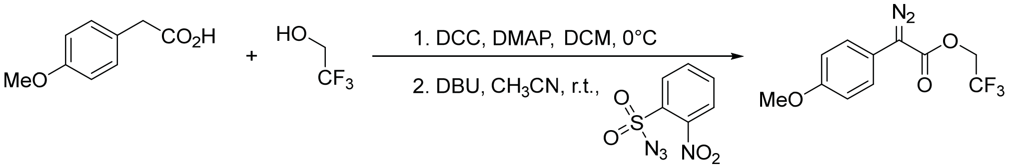


The single crystal X-ray structure of **19*R***



5. Preparation of Diazo Compounds

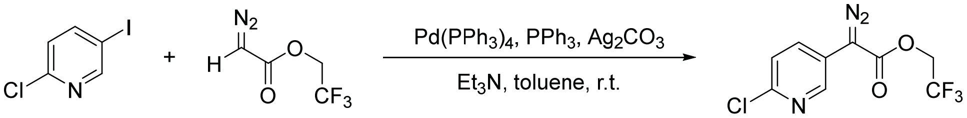
5.1 Procedures



2,2,2-Trifluoroethyl 2-diazo-2-(4-methoxyphenyl)acetate. [3] A 250-mL flask was charged with 2-(4-methoxyphenyl)acetic acid (1.7 g, 10 mmol, 1.0 *equiv.*), N,N-dimethylpyridin-4-amine (DMAP) (0.1 g, 10 mmol, 0.1 *equiv.*), and 2,2,2-trifluoroethan-1-ol (1.2 g, 12 mmol, 1.2 *equiv.*) and CH_2Cl_2 (150 mL), then the solution was stirred and cooled to 0 °C. A solution of N,N'-Dicyclohexylcarbodiimide (DCC) (2.3 g, 11 mmol, 1.1 *equiv.*) in CH_2Cl_2 (50 mL) was poured slowly into the cold reaction mixture. The solution was allowed to stir overnight, at which point it had reached ambient temperature. The precipitate was removed by vacuum filtration on a silica plug (5 *cm* height, 5 *cm* wide), washing once with diethyl ether (50 mL). The filtrate was concentrated to give a crude oil. The crude was dissolved in acetonitrile (CH_3CN) (40 mL) in a 250 mL three-necked flask equipped with a 50-mL dropping funnel, a rubber septum fitted with argon inlet needle, an egg shaped in magnetic stir bar and 2-nitrobenzenesulfonyl azide (3.4 g, 15 mmol, 1.5 *equiv.*). Then 1,8-Diazabicycloundec-7-ene (DBU) (3.4 g, 22 mmol, 2.2 *equiv.*) in acetonitrile (20 mL) was transferred to the dropping funnel and added dropwise into reaction mixture at room temperature. The resulting mixture was stirred over 4 h, and reaction progress was monitored by TLC analysis. The reaction mixture was cooled with an ice bath, and saturated aqueous NH_4Cl (50 mL) was then added to quench the reaction. The mixture was extracted with diethyl ether (3 x 30 mL), and the combined organic layer was washed with saturated NaCl aqueous solution (50 mL), dried over sodium sulfate (10 g) and filtered. Then the filtrate was concentrated by rotary evaporation to afford the crude product. The crude product was purified by flash column chromatography (hexanes/diethyl ether = 50/1) to give an orange solid in 47% overall yield (1.3 g).

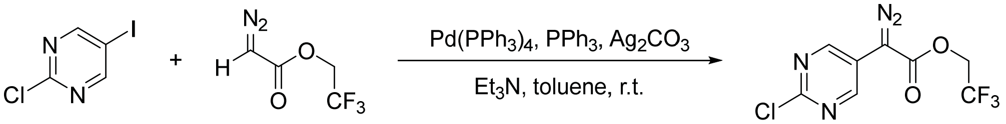
TLC (diethyl ether:hexanes, 1:9 *v/v*); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, J = 8.9 Hz, 2H), 6.96 (d, J = 9.0 Hz, 2H), 4.64 (q, J = 8.4 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.76, 158.50, 126.18, 122.94 (q, J = 277.5 Hz), 115.82, 114.76, 60.27 (q, J = 36.8 Hz), 55.36; HRMS (NSI) calcd for $C_{11}H_{10}O_3F_3$ ($[M-N_2+H]^+$):247.0577 found

247.0577; IR (neat):2976, 2089, 1709, 1610, 1514, 1281, 1255, 1138, 1076, 1032, 974, 828, 733.



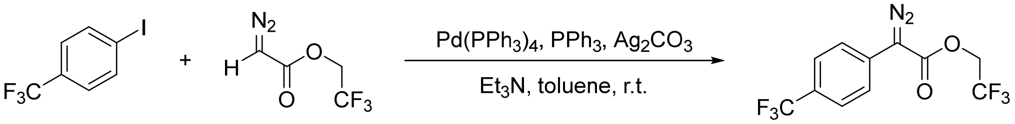
2,2,2-Trifluoroethyl 2-(6-chloropyridin-3-yl)-2-diazoacetate. [6] 2-Chloro-5-iodopyridine (718 mg, 0.3 mmol, 1.0 *equiv.*), tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] (173 mg, 0.15 mmol, 0.05 *equiv.*), triphenylphosphine (PPh_3) (79 mg, 0.3 mmol, 0.1 *equiv.*), silver carbonate (Ag_2CO_3) (414 mg, 1.5 mmol, 0.5 *equiv.*) and triethylamine (Et_3N) (395 mg, 3.9 mmol, 1.3 *equiv.*) were suspended in toluene (20 mL) in a round-bottomed flask under nitrogen. Then 2,2,2-trichloroethyl 2-diazoacetate (504 mg, 3 mmol, 1.0 *equiv.*) was added. After stirring at r.t. for 12 h, the mixture was filtered through a short silica plug (3 *cm* height, 2 *cm* wide), eluting with ethyl acetate. The solvents were removed under reduced pressure and the crude residue was purified by column chromatography on silica gel eluting with gradient diethyl ether/hexanes (1% to 10%) to give the diazo as a yellow solid in 61 % yield (512 mg).

TLC (diethyl ether:hexanes, 1:7 *v/v*); ^1H NMR (600 MHz, $CDCl_3$) δ 8.45 (d, J = 2.5 Hz, 1H), 7.83 (d, J = 6.7 Hz, 1H), 7.37 (d, J = 8.5 Hz, 1H), 4.67 (q, J = 8.3 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.40, 149.16, 144.50, 133.95, 124.47, 122.71 (q, J = 277.4 Hz), 120.85, 60.62 (q, J = 37.1 Hz); HRMS (NSI) calcd for $C_9H_6O_2N_3ClF_3$ ($[M+H]^+$):280.0106 found 280.0098; IR (neat):2976, 2099, 1685, 1482, 1418, 1274, 1248, 1225, 1166, 1115, 1071, 1020, 959, 841, 725.



2,2,2-Trifluoroethyl 2-(2-chloropyrimidin-5-yl)-2-diazoacetate. 2-Chloro-5-iodopyrimidine (721 mg, 0.3 mmol, 1.0 *equiv.*), tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] (173 mg, 0.15 mmol, 0.05 *equiv.*), triphenylphosphine (PPh_3) (79 mg, 0.3 mmol, 0.1 *equiv.*), silver carbonate (Ag_2CO_3) (414 mg, 1.5 mmol, 0.5 *equiv.*) and triethylamine (Et_3N) (395 mg, 3.9 mmol, 1.3 *equiv.*) were suspended in toluene (20 mL) in a round-bottomed flask under nitrogen. Then 2,2,2-trichloroethyl 2-diazoacetate (504 mg, 3 mmol, 1.0 *equiv.*) was added. After stirring at r.t. for 12 h, the mixture was filtered through a short silica plug (3 *cm* height, 2 *cm* wide), eluting with ethyl acetate. The solvents were removed under reduced pressure and the crude residue was purified by column chromatography on silica gel eluting with gradient diethyl ether/hexanes (1% to 20%) to give the diazo as a yellow solid in 25 % yield (210 mg).

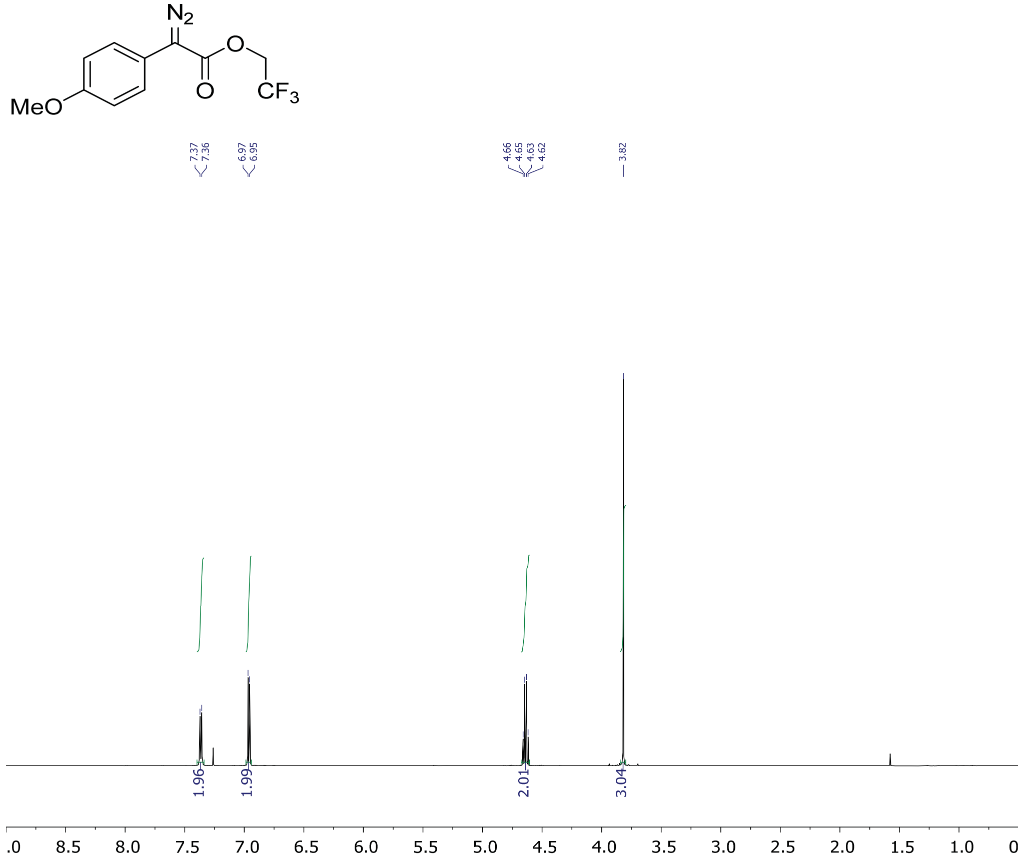
TLC (diethyl ether:hexanes, 1:3 *v/v*); ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.76 (s, 2H), 4.70 (q, J = 8.2 Hz, 2H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 161.76, 158.80, 153.83, 121.67 (q, J = 277.6 Hz), 119.83, 60.87 (q, J = 37.3 Hz); HRMS (NSI) calcd for $C_8H_5O_2N_4ClF_3$ ([M+H]$^+$):281.0059 found 281.0048; IR (neat):2923, 2102, 1702, 1528, 1424, 1358, 1288, 1244, 1145, 1080, 972, 731.



2,2,2-Trifluoroethyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate. 1-Iodo-4-(trifluoromethyl)benzene (816 mg, 0.3 mmol, 1.0 *equiv.*), tetrakis(triphenylphosphine)palladium(0) [Pd(PPh$_3$)$_4$] (173 mg, 0.15 mmol, 0.05 *equiv.*), triphenylphosphine (PPh$_3$) (79 mg, 0.3 mmol, 0.1 *equiv.*), silver carbonate (Ag$_2$CO$_3$) (414 mg, 1.5 mmol, 0.5 *equiv.*) and triethylamine (Et$_3$N) (395 mg, 3.9 mmol, 1.3 *equiv.*) were suspended in toluene (20 mL) in a round-bottomed flask under nitrogen. Then 2,2,2-trichloroethyl 2-diazoacetate (504 mg, 3 mmol, 1.0 *equiv.*) was added. After stirring at r.t. for 12 h, the mixture was filtered through a short silica plug (3 *cm* height, 2 *cm* wide), eluting with ethyl acetate. The solvents were removed under reduced pressure and the crude residue was purified by column chromatography on silica gel eluting with gradient diethyl ether/hexanes (1% to 5%) to give the diazo as a yellow solid in 41 % yield (384 mg).

TLC (diethyl ether:hexanes, 1:9 *v/v*); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.63 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 4.67 (q, J = 8.3 Hz, 2H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 162.55, 129.17, 128.26 (q, J = 32.9 Hz), 126.09 (q, J = 3.8 Hz), 124.07 (q, J = 272.0 Hz), 123.62, 122.92 (q, J = 277.5 Hz), 60.54 (q, J = 36.9 Hz); HRMS (NSI) calcd for $C_{11}H_6O_2N_2ClF_6$ ([M+Cl]$^-$):347.0028 found 347.0030; IR (neat):2979, 2098, 1717, 1618, 1411, 1356, 1325, 1280, 1240, 1115, 1074, 1016, 975, 840.

5.2 NMR Spectra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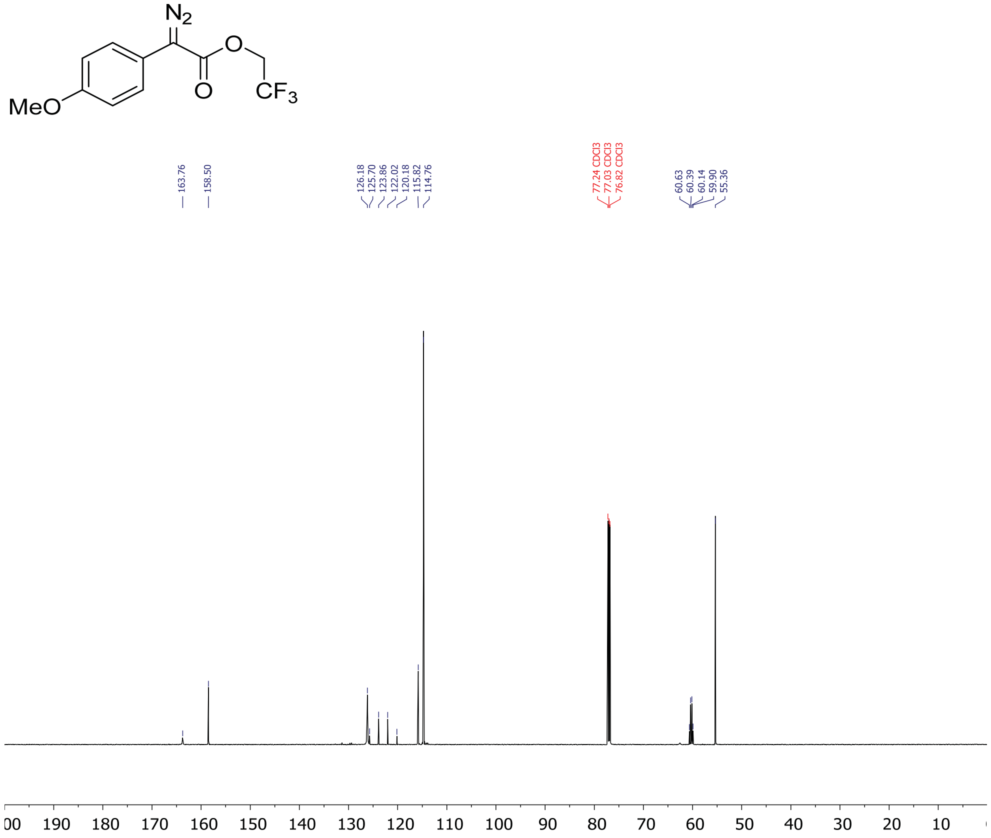
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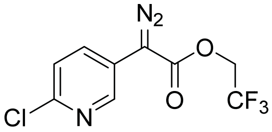
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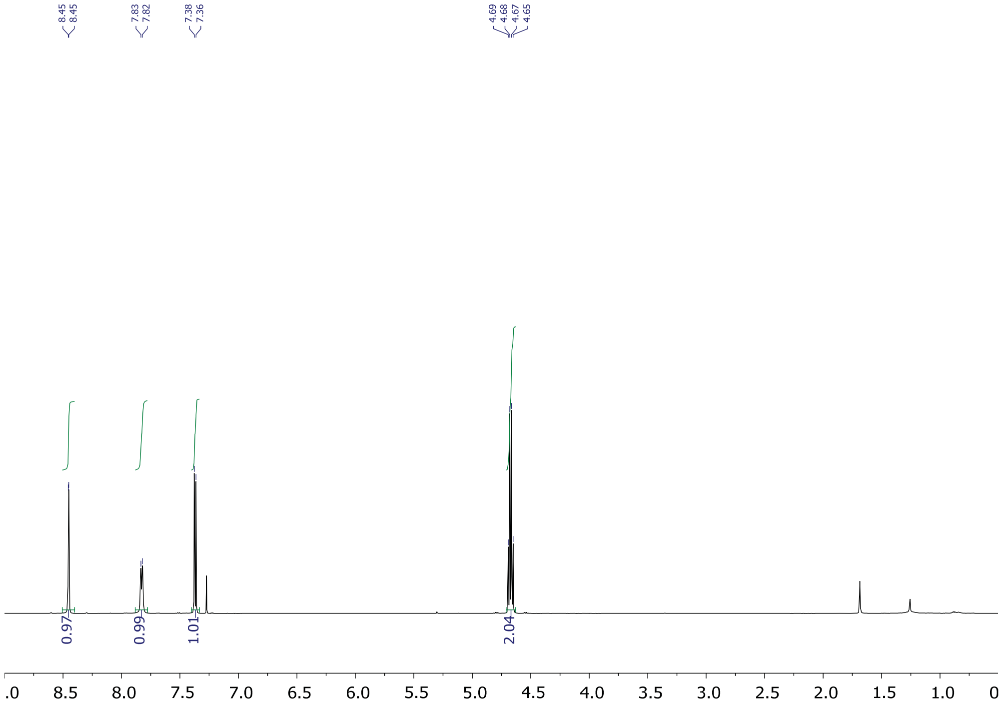
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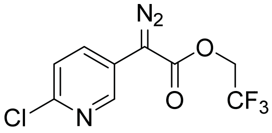
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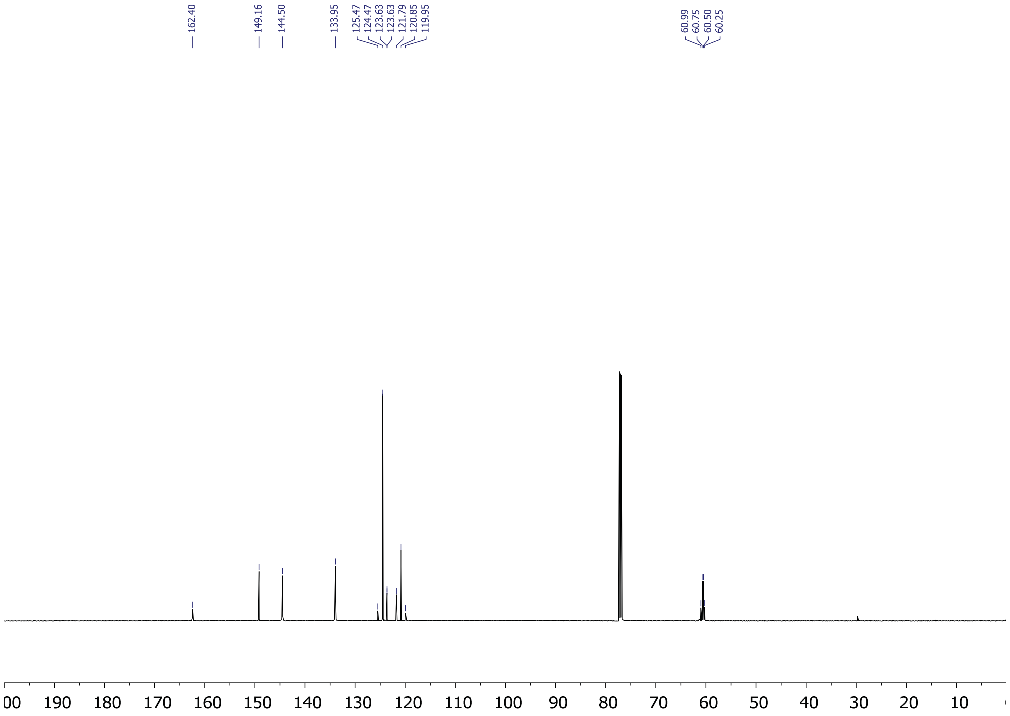
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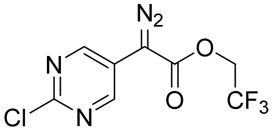
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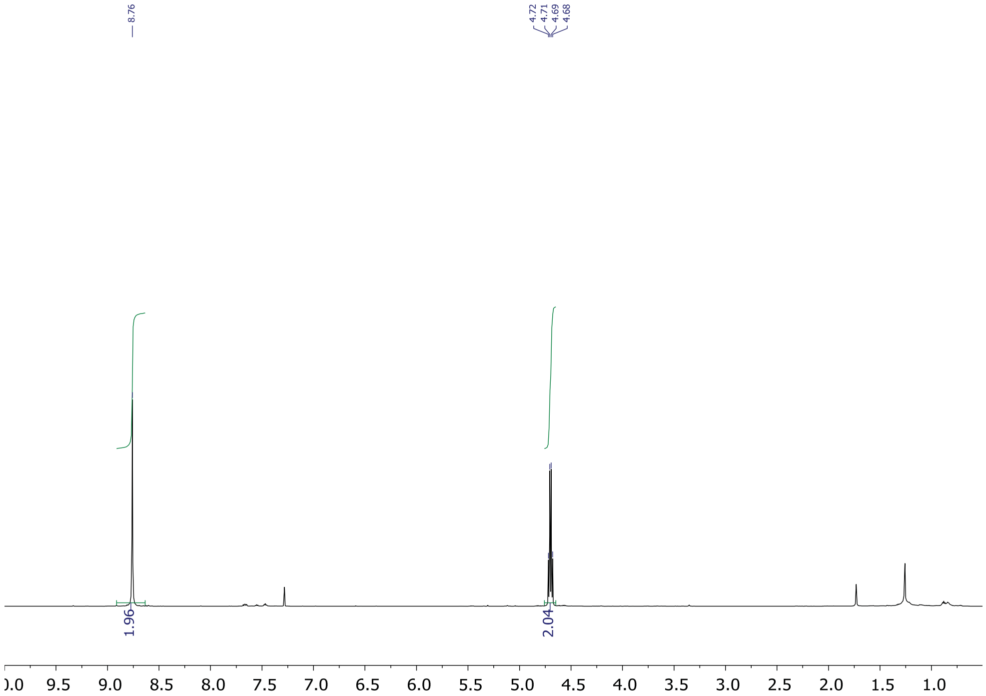
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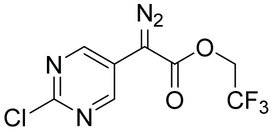
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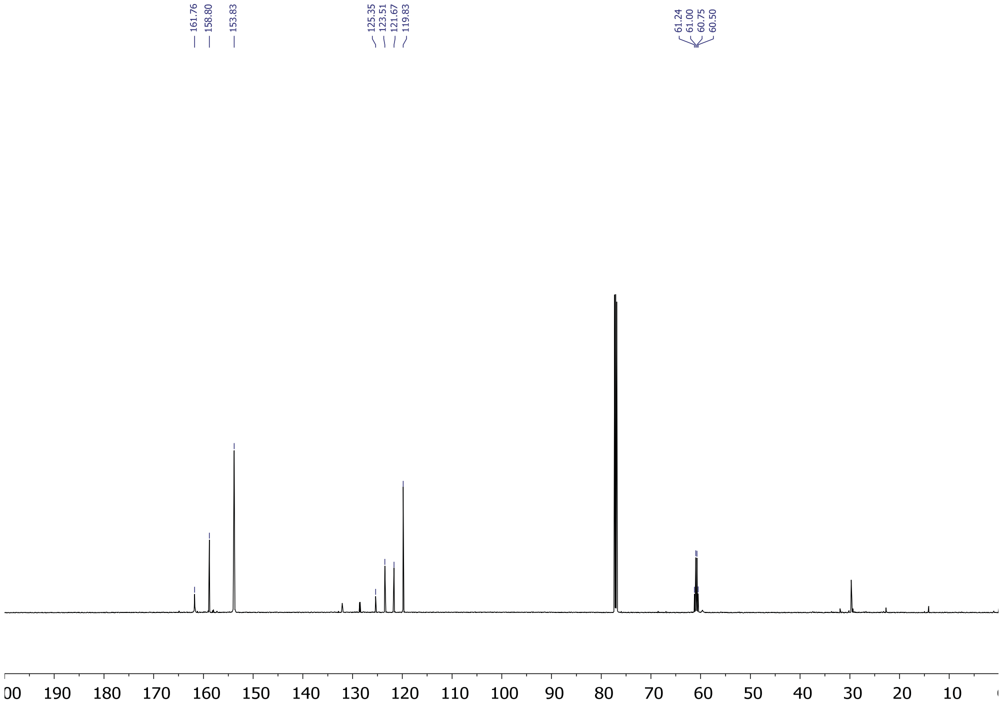
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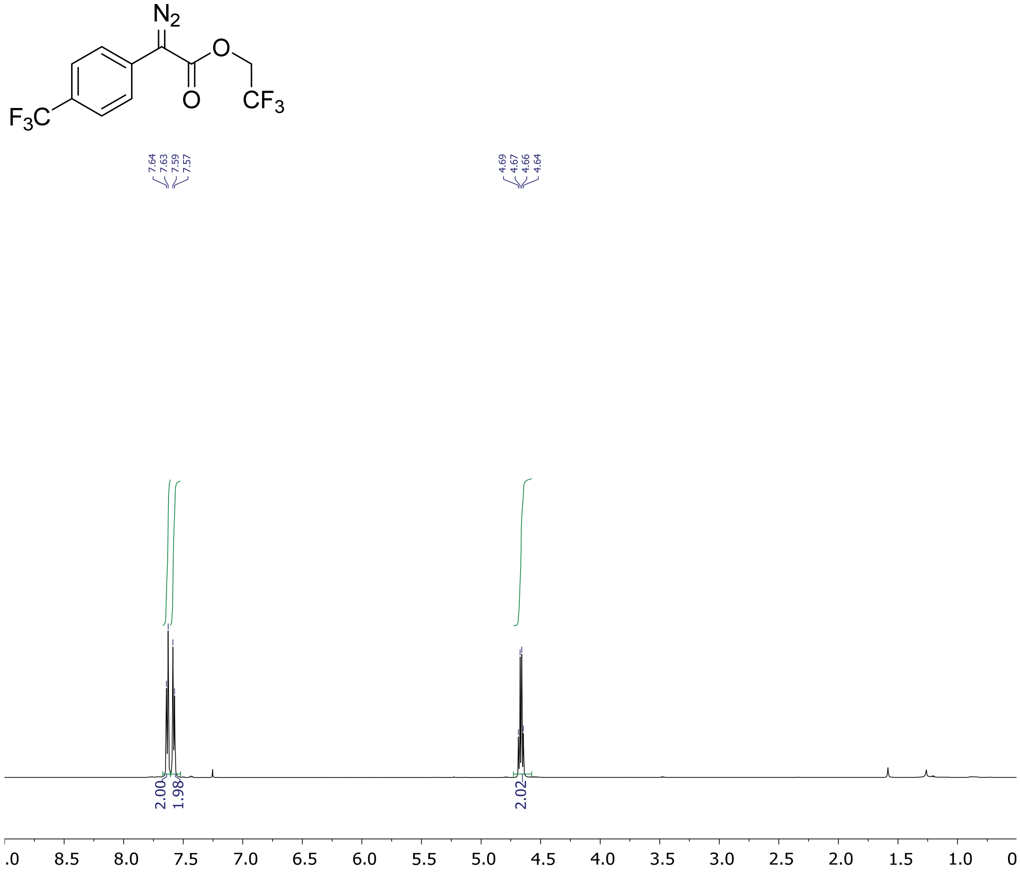
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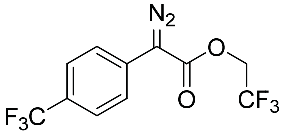
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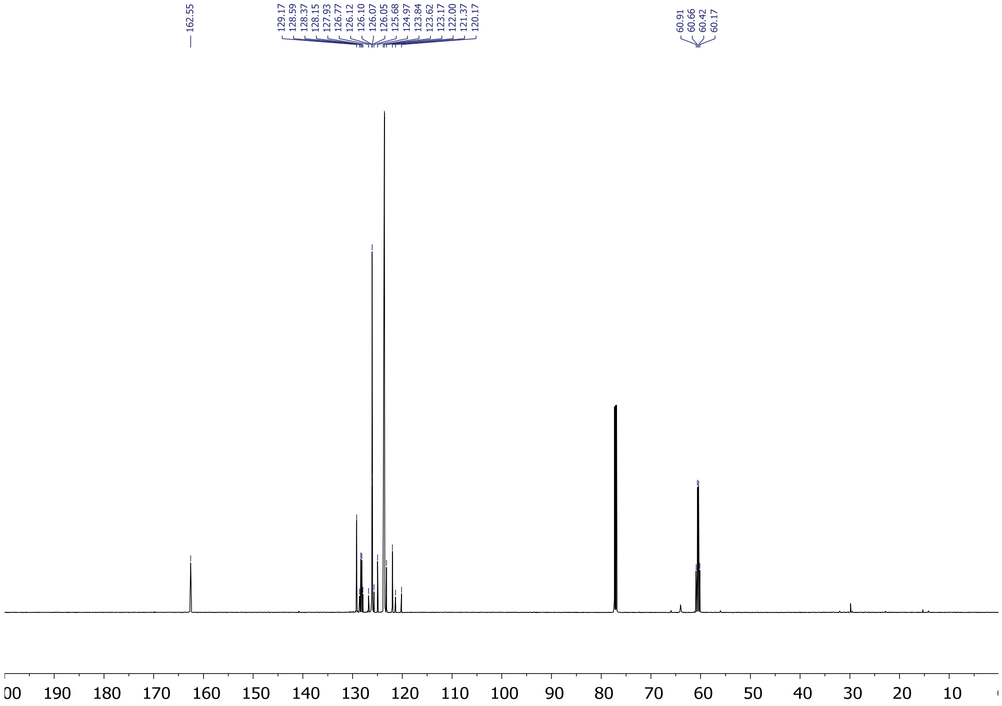
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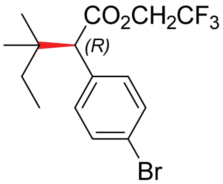
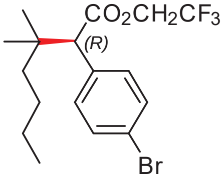
6. Characterization of C–H Functionalization Products



2,2,2-Trifluoroethyl *(R)*-2-(4-bromophenyl)-3,3-dimethylpentanoate (**4**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylbutane (0.6 mmol, 43 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **4** as a colorless oil (63 mg, 86% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **4** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

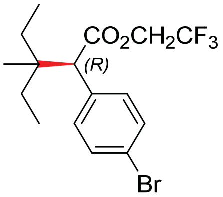
$[\alpha]^{20}_D$ -12.1° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 4.61 (dq, *J* = 12.7, 8.5 Hz, 1H), 4.27 (dq, *J* = 12.7, 8.5 Hz, 1H), 3.59 (s, 1H), 1.42 – 1.34 (m, 1H), 1.25 (dq, J = 14.8, 7.5 Hz, 1H), 0.99 (s, 3H), 0.88 (s, 4H), 0.88 (t, *J* = 7.5 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.27, 134.13, 131.83, 131.20, 121.81, 60.18 (q, *J* = 36.7 Hz), 59.04, 37.58, 32.94, 23.88, 23.71, 8.27; HRMS (NSI) calcd for $C_{15}H_{19}BrF_3O_2$ ($[M+H]^+$):367.0515 found 367.0522; IR (neat):2969, 1752, 1489, 1414, 1276, 1164, 1122, 1076, 1012, 979, 822; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylpentan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm) retention times of 45.2 min (minor) and 119.0 min (major), 81 % e.e..



2,2,2-Trifluoroethyl (R)-2-(4-bromophenyl)-3,3-dimethylheptanoate (**5**). This compound was prepared according to the general procedure (at 39 °C and -40 °C) for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylhexane (0.6 mmol, 60 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **5** as a colorless oil (39 °C: 60 mg, 76% yield; -40 °C: 51 mg, 65% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **5** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as 87:13 r.r. (39 °C) and 96:4 r.r. (-40 °C).

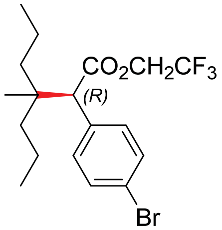
$[\alpha]^{20}_D$ -15.8° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 4.62 (dq, *J* = 12.7, 8.5 Hz, 1H), 4.25 (dq, *J* = 12.7, 8.5 Hz, 1H), 3.59 (s, 1H), 1.36 – 1.14 (m, 6H), 1.00 (s, 3H), 0.89 (t, *J* = 7.1 Hz, 3H), 0.89 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ
171.28, 134.15, 131.84, 131.21, 121.82, 60.18 (q, *J* = 36.5 Hz), 59.23, 40.49, 37.45, 26.14, 24.61, 24.23, 23.52, 14.23; HRMS (NSI) calcd for $C_{17}H_{23}BrF_3O_2$ ($[M+H]^+$):395.0828 found 395.0830; IR (neat):2961, 2933, 2872, 1753, 1489, 1414, 1278, 1165, 1122, 1076, 1012, 980, 827; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3-dimethylheptan-1-ol prepared using DIBAL in DCM at -78 °C), at 39 °C, (S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm) retention times of 45.5 min (minor) and 117.4 min (major), 77 % e.e.; at -40 °C, a different instrument was used, (S,S-Whelk, 1.5 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 130 min, UV 210 nm) retention times of 40.8 min (minor) and 102.7 min (major), 87 % e.e..



2,2,2-Trifluoroethyl *(R)*-2-(4-bromophenyl)-3-ethyl-3-methylpentanoate (**6**). This compound was prepared according to the general procedure (at 39 °C and -40 °C) for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 3-methylpentane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **6** as a colorless oil (39 °C: 56 mg, 73% yield; -40 °C: 49 mg, 64% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **6** and the secondary C-H functionalization product, 2,2,2-trifluoroethyl (2R,3S)-2-(4-bromophenyl)-3,4-dimethylhexanoate, were observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as 92:8 r.r. (39 °) and 98:2 r.r. (-40 °C).

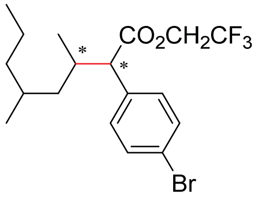
$[\alpha]^{20}_D$ -10.2° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 4.62 (dq, *J* = 12.7, 8.5 Hz, 1H), 4.24 (dq, *J* = 12.7, 8.5 Hz, 1H), 3.71 (s, 1H), 1.48 (dq, *J* = 14.8, 7.5 Hz, 1H), 1.34 (dq, *J* = 14.6, 7.4 Hz, 1H), 1.17 (ddt, *J* = 26.7, 14.1, 7.2 Hz, 2H), 0.95 (s, 3H), 0.87 (t, *J* = 7.5 Hz, 3H), 0.79 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.28, 134.04, 131.95, 131.17, 124.16, 121.78, 60.18 (q, *J* = 36.5 Hz), 56.82, 40.02, 28.65, 28.38, 20.49, 7.88, 7.71; HRMS (NSI) calcd for $C_{16}H_{21}BrF_3O_2$ ($[M+H]^+$):381.0672 found 381.0672; IR (neat):2969, 1752, 1489, 1414, 1383, 1275, 1161, 1121, 1077, 1012, 979, 828, 772, 717; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-3-ethyl-3-methylpentan-1-ol prepared using DIBAL in DCM at -78 °C), at 39 °C, (S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm) retention times of 32.7 min (minor) and 119.9 min (major), 82 % e.e.; at -40 °C, a different instrument was used, (S,S-Whelk, 1.5 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 130 min, UV 210 nm) retention times of 29.7 min (minor) and 105.3 min (major), 92 % e.e..



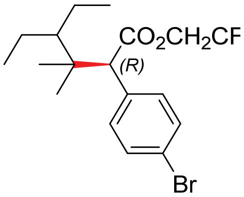
2,2,2-Trifluoroethyl (R)-2-(4-bromophenyl)-3-methyl-3-propylhexanoate (**7**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 4-methylheptane (0.6 mmol, 69 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **7** as a colorless oil (7 mg, 9% yield), however, the major product of this reaction was 2,2,2-trifluoroethyl 2-(4-bromophenyl)-3,5-dimethyloctanoate and the compound was also isolated as a colorless oil (64 mg, 79% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **7** and the secondary C-H functionalization product, 2,2,2-trifluoroethyl 2-(4-bromophenyl)-3,5-dimethyloctanoate, were observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as 11:89 r.r..

$[\alpha]^{20}_D$ -14.9° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.6 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 4.63 (dq, J = 12.7, 8.5 Hz, 1H), 4.23 (dq, J = 12.7, 8.5 Hz, 1H), 3.71 (s, 1H), 1.43 – 1.14 (m, 6H), 1.14 – 1.01 (m, 2H), 0.96 (s, 3H), 0.89 (t, J = 7.0 Hz, 3H), 0.83 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.31, 134.10, 131.96, 131.20, 125.67, 124.18, 121.81, 60.20 (*q, J* = 36.6 Hz), 57.53, 39.57, 39.24, 30.48, 21.49, 16.83, 16.62, 14.82, 14.79; HRMS (NSI) calcd for $C_{18}H_{23}BrF_3O_2$ ($[M-H]^-$):407.0839 found 407.0839; IR (neat): 2964, 1489, 1420, 1379, 1278, 1151, 1123, 1079, 1013, 979, 828, 772, 717; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3,6-trimethylheptan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 1% isopropanol in hexane, 1 mL/min, 10 mg/mL, 30 min, UV 210 nm) retention times of 17.8 min (major) and 25.1 min (minor), 81 % e.e..



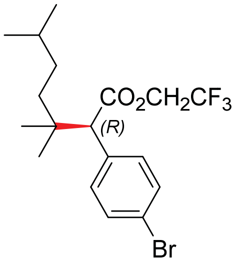
2,2,2-trifluoroethyl 2-(4-bromophenyl)-3,5-dimethyloctanoate. TLC (diethyl ether:hexanes, 1:10 v/v); the isolated material was a mixture of diastereomers, please see the 1H and 13C NMR spectra on Page 131-132 for detail; HRMS (NSI) calcd for C18H23BrF3O2 ([M-H]-):407.0839 found 407.0839; IR (neat): 2969, 1485, 1425, 1376, 1279, 1156, 1123, 1077, 1012, 978, 829, 770, 719.



2,2,2-Trifluoroethyl *(R)*-2-(4-bromophenyl)-4-ethyl-3,3-dimethylhexanoate (**8**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 3-ethyl-2-methylpentane (0.6 mmol, 69 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **8** as a colorless oil (54 mg, 66% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **8** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

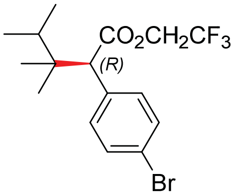
$[\alpha]^{20}_D$ -13.4° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 4.57 (dq, *J* = 12.7, 8.5 Hz, 1H), 4.27 (dq, *J* = 12.7, 8.5 Hz, 1H), 3.89 (s, 1H), 1.59 (dpt, *J* = 17.9, 7.5, 3.3 Hz, 3H), 1.15 (tp, *J* = 14.7, 7.4 Hz, 2H), 1.01 (s, 3H), 0.93 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.5 Hz, 4H), 0.80 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.42, 134.43, 132.14, 131.17, 121.79, 60.26 (q, *J* = 36.6 Hz), 57.07, 48.97, 41.43, 23.44, 23.17, 21.75, 21.56, 14.49, 14.03; HRMS (NSI) calcd for $C_{18}H_{23}BrF_3O_2$ ($[M-H]^-$):407.0828 found 407.0836; IR (neat):2967, 2932, 2878, 1752, 1489, 1414, 1277, 1165, 1138, 1115, 1076, 1012, 980, 823; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-4-ethyl-3,3-dimethylhexan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm) retention times of 34.3 min (minor) and 109.6 min (major), 86 % e.e..



2,2,2-Trifluoroethyl *(R)*-2-(4-bromophenyl)-3,3,6-trimethylheptanoate (**9**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2,5-dimethylhexane (0.6 mmol, 69 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **9** as a colorless oil (71 mg, 87% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **9** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

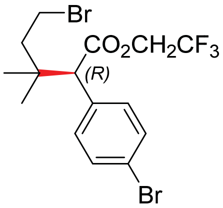
$[\alpha]^{20}_{D}$ -14.9° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 4.61 (dq, *J* = 12.7, 8.5 Hz, 1H), 4.26 (dq, *J* = 12.7, 8.5 Hz, 1H), 3.60 (s, 1H), 1.43 (dp, *J* = 12.8, 6.5 Hz, 1H), 1.36 – 1.27 (m, 1H), 1.24 – 1.13 (m, 3H), 1.00 (s, 3H), 0.88 (s, 4H), 0.86 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.26, 134.15, 131.83, 131.20, 124.17, 121.96, 121.82, 60.18 (q, *J* = 36.5 Hz), 59.12, 38.52, 37.35, 32.87, 28.81, 24.66, 24.17, 22.76; HRMS (NSI) calcd for $C_{18}H_{23}BrF_3O_2$ ($[M-H]^-$):407.0828 found 407.0840; IR (neat):2960, 2871, 1753, 1489, 1469, 1414, 1369, 1278, 1165, 1124, 1077, 1012, 978, 825; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3,6-trimethylheptan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 1% isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm) retention times of 44.1 min (minor) and 108.8 min (major), 78 % e.e..



2,2,2-Trifluoroethyl *(R)*-2-(4-bromophenyl)-3,3,4-trimethylpentanoate (**10**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2,3-dimethylbutane (0.6 mmol, 52 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **10** as a colorless oil (71 mg, 93% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **10** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

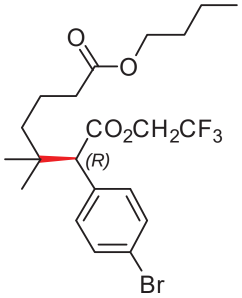
[α]^{20}$_D$ -11.4° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 4.61 (dq, *J* = 12.7, 8.5 Hz, 1H), 4.24 (dq, *J* = 12.7, 8.5 Hz, 1H), 3.82 (s, 1H), 1.54 (hept, *J* = 6.7 Hz, 1H), 0.98 (s, 3H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.78 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.34, 134.32, 132.04, 131.19, 124.16, 121.81, 60.17 (q, J = 36.7 Hz), 57.06, 40.13, 34.30, 20.48, 20.45, 17.99, 17.26; HRMS (NSI) calcd for $C_{16}H_{21}BrF_3O_2$ ([M+H]$^+$):381.0672 found 381.0675; IR (neat):2970, 1752, 1489, 1277, 1166, 1146, 1117, 1076, 1012, 979, 834; HPLC (to improve the separation, the product was converted to 2-(4-bromophenyl)-3,3,4-trimethylpentan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 140 min, UV 210 nm) retention times of 33.0 min (minor) and 109.6 min (major), 83 % e.e..



2,2,2-Trifluoroethyl *(R)*-5-bromo-2-(4-bromophenyl)-3,3-dimethylpentanoate (**11**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 1-bromo-3-methylbutane (0.6 mmol, 91 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **11** as a colorless oil (62 mg, 70% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **11** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

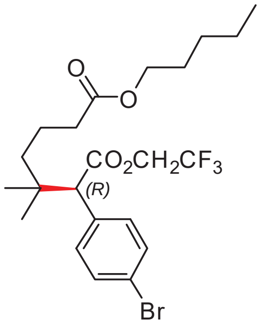
$[\alpha]^{20}_{D}$ -17.6° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 4.61 (dq, *J* = 12.6, 8.4 Hz, 1H), 4.30 (dq, *J* = 12.6, 8.4 Hz, 1H), 3.55 (s, 1H), 3.42 – 3.32 (m, 2H), 2.07 – 1.98 (m, 1H), 1.89 – 1.80 (m, 1H), 1.04 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.63, 133.10, 131.70, 131.51, 124.01, 122.30, 60.33 (q, *J* = 36.7 Hz), 59.58, 43.54, 38.51, 28.06, 24.24, 24.07; HRMS (NSI) calcd for $C_{15}H_{18}Br_2F_3O_2$ ($[M-H]^-$):444.9620 found 444.9622; IR (neat):2970, 1752, 1489, 1414, 1277, 1166, 1126, 1076, 1055, 1012, 977, 826; HPLC (to improve the separation, the product was converted to 5-bromo-2-(4-bromophenyl)-3,3-dimethylpentan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 0.3 % isopropanol in hexane, 0.3 mL/min, 10 mg/mL, 60 min, UV 210 nm) retention times of 30.5 min (minor) and 34.7 min (major), 84 % e.e..



7-Butyl 1-(2,2,2-trifluoroethyl) *(R)*-2-(4-bromophenyl)-3,3-dimethylheptanedioate (**12**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and butyl 5-methylhexanoate (0.6 mmol, 112 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **12** as a colorless oil (87 mg, 90% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **12** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

$[\alpha]^{20}_{D}$ -12.4° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.6 Hz, 2H), 7.26 (d, J = 8.6 Hz, 2H), 4.62 (dq, J = 12.7, 8.5 Hz, 1H), 4.27 (dq, J = 12.7, 8.5 Hz, 1H), 4.06 (t, J = 6.7 Hz, 2H), 3.59 (s, 1H), 2.35 – 2.19 (m, 2H), 1.68 – 1.62 (m, 2H), 1.62 – 1.56 (m, 2H), 1.41 – 1.31 (m, 3H), 1.24 – 1.16 (m, 1H), 1.02 (s, 3H), 0.93 (t, J = 7.4 Hz, 3H), 0.92 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.62, 171.06, 133.82, 131.79, 131.25, 121.92, 121.90, 64.36, 60.17 (q, J = 36.5 Hz), 59.19, 39.85, 37.38, 34.73, 30.78, 29.82, 24.42, 24.15, 19.54, 19.25, 13.82; HRMS (NSI) calcd for $C_{21}H_{29}BrF_3O_4$ ($[M-H]^-$):481.1196 found 481.1201; IR (neat):2962, 2874, 1732, 1489, 1415, 1277, 1165, 1119, 1076, 1012, 978, 827; HPLC (ODH, 0.5 % isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 30 min, UV 210 nm) retention times of 17.4 min (minor) and 22.4 min (major), 77 % e.e..

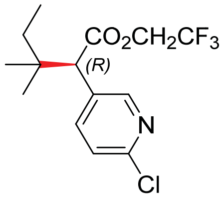


7-Pentyl 1-(2,2,2-trifluoroethyl) *(R)*-2-(4-bromophenyl)-3,3-dimethylheptanedioate (**13**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and pentyl 5-methylhexanoate (0.6 mmol, 120 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^1H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **13** as a colorless oil (39 °C: 72 mg, 73% yield; -40 °C: 65 mg, 66% yield).

Analysis of the ^1H NMR spectrum of the crude reaction mixture revealed that only compound **13** and the most accessible secondary C-H insertion product, 2,2,2-trifluoroethyl 2-(4-bromophenyl)-3-methyl-6-((5-methylhexanoyl)oxy)hexanoate, were observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as 88:12 r.r. (39 °C) and 96:4 r.r. (-40 °C).

$[\alpha]^{20}_D$ -11.9° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.6 Hz, 2H), 7.25 (d, J = 8.5 Hz, 2H), 4.62 (dq, J = 12.7, 8.5 Hz, 1H), 4.26 (dq, J = 12.7, 8.5 Hz, 1H), 4.05 (t, J = 6.8 Hz, 2H), 3.58 (s, 1H), 2.32 – 2.18 (m, 2H), 1.69 – 1.56 (m, 5H), 1.41 – 1.27 (m, 5H), 1.25 – 1.15 (m, 1H), 1.01 (s, 3H), 0.92 (s, 3H), 0.90 (t, J = 7.1 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.65, 171.08, 133.84, 131.80, 131.27, 121.95, 64.68, 60.19 (q, J = 36.7 Hz), 59.20, 39.88, 37.41, 34.76, 28.45, 28.20, 24.44, 24.18, 22.46, 19.57, 14.10; HRMS (NSI) calcd for $C_{22}H_{31}BrF_3O_4$ ($[M+H]^+$):495.1352 found 495.1354; IR (neat):2960, 2873, 1732, 1489, 1278, 1166, 1119, 1076, 1012, 978, 827; HPLC (ODH, 0.5 % isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 30 min, UV 210 nm) retention times of 18.0 min (minor) and 22.7 min (major),

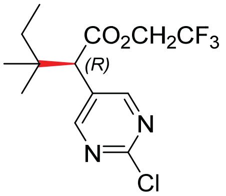
HPLC: at 39 °C, (ODH, 0.5 % isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 30 min, UV 210 nm) retention times of 18.0 min (minor) and 22.7 min (major), 76 % e.e.; at -40 °C, (ODH, 0.5 % isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 30 min, UV 210 nm) retention times of 18.1 min (minor) and 24.2 min (major), 94 % e.e..



2,2,2-Trifluoroethyl *(R)*-2-(6-chloropyridin-3-yl)-3,3-dimethylpentanoate (**14**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(6-chloropyridin-3-yl)-2-diazoacetate (0.2 mmol, 56 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylbutane (0.6 mmol, 43 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^1H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **14** as a colorless oil (39 mg, 60% yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **14** the secondary C-H insertion product, 2,2,2-trifluoroethyl 2-(6-chloropyridin-3-yl)-3,4-dimethylpentanoate, were observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as 96:4 r.r.

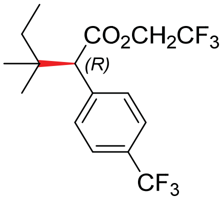
$[\alpha]^{20}_D$ +5.3° (c = 0.50, $CHCl_3$); TLC (diethyl ether:hexanes, 1:4 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.30 (d, J = 8.2 Hz, 1H), 4.61 (p, J = 9.4, 8.7 Hz, 1H), 4.32 (p, J = 8.9 Hz, 1H), 3.63 (s, 1H), 1.37 (tt, J = 18.4, 8.7 Hz, 1H), 0.99 (s, 3H), 0.93 – 0.76 (m, 7H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.65, 150.86, 150.81, 139.71, 129.92, 123.61, 122.79 (q, J = 277.2 Hz), 60.29 (q, J = 36.7 Hz), 56.20, 37.75, 32.77, 23.67, 23.58, 8.10; HRMS (NSI) calcd for $C_{14}H_{18}ClF_3NO_2$ ($[M+H]^+$):324.0983 found 324.0977; IR (neat):2967, 2926, 2855, 1753, 1460, 1279, 1170, 1130, 1107, 1024, 980; HPLC (ODH, 0.5 % isopropanol in hexane, 0.5 mL/min, 5 mg/mL, 30 min, UV 210 nm) retention times of 18.3 min (major) and 25.6 min (minor), 68 % e.e..



2,2,2-Trifluoroethyl *(R)*-2-(2-chloropyrimidin-5-yl)-3,3-dimethylpentanoate (**15**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(2-chloropyrimidin-5-yl)-2-diazoacetate (0.2 mmol, 56 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylbutane (0.6 mmol, 43 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **15** as a colorless oil (53 mg, 81 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **15** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

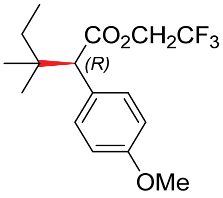
$[\alpha]^{20}_D$ +10.7° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:3 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (s, 2H), 4.65 (dq, *J* = 12.7, 8.3 Hz, 1H), 4.38 (dq, *J* = 12.7, 8.4 Hz, 1H), 3.64 (s, 1H), 1.41 (dq, *J* = 14.9, 7.5 Hz, 1H), 1.27 (dq, *J* = 7.5 Hz, 1H), 1.03 (s, 3H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.93 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.98, 160.82, 160.18, 127.72, 122.69 (q, J = 277.4 Hz), 60.60 (q, J = 36.8 Hz), 54.61, 38.00, 32.75, 29.71, 23.65, 23.61, 8.07; HRMS (NSI) calcd for $C_{13}H_{17}ClF_3N_2O_2$ ($[M+H]^+$):325.0936 found 325.0930; IR (neat):2969, 2926, 1752, 1576, 1546, 1401, 1278, 1162, 1130, 980; HPLC (ODH, 1 % isopropanol in hexane, 1 mL/min, 5 mg/mL, 20 min, UV 210 nm) retention times of 9.4 min (minor) and 10.5 min (major), 75 % e.e..



2,2,2-Trifluoroethyl *(R)*-3,3-dimethyl-2-(4-(trifluoromethyl)phenyl)pentanoate (**16**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate (0.2 mmol, 62 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylbutane (0.6 mmol, 43 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **16** as a colorless oil (63 mg, 89 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **16** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

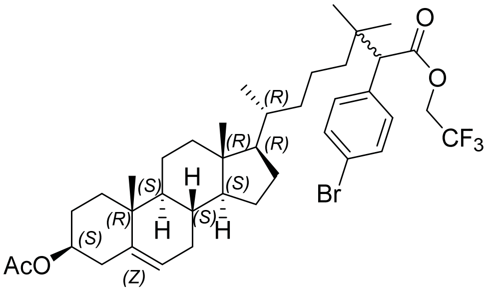
$[\alpha]^{20}_D$ -2.0° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 4.62 (dq, *J* = 12.7, 8.5 Hz, 1H), 4.28 (dq, *J* = 12.7, 8.5 Hz, 1H), 3.70 (s, 1H), 1.45 – 1.35 (dq, *J* = 14.8, 7.5 Hz, 1H), 1.27 (dq, *J* = 14.8, 7.5 Hz, 1H), 1.01 (s, 3H), 0.90 (s, 3H), 0.90 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.94, 139.08, 130.40, 129.78 (q, *J* = 32.5 Hz), 124.84 (q, *J* = 3.7 Hz), 124.12 (q, *J* = 272.1 Hz), 122.90 (q, *J* = 277.4 Hz), 60.15 (q, *J* = 36.7 Hz), 59.33, 37.72, 32.88, 23.81, 23.65, 8.14; HRMS (NSI) calcd for $C_{16}H_{17}F_6O_2$ ($[M-H]^-$):355.1138 found 355.1137; IR (neat):2972, 1753, 1620, 1325, 1277, 1163, 1122, 1112, 1070, 1020, 980, 839; HPLC (to improve the separation, the product was converted to 3,3-dimethyl-2-(4-(trifluoromethyl)phenyl)pentan-1-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 1 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 70 min, UV 210 nm) retention times of 23.5 min (minor) and 58.5 min (major), 74 % e.e..



2,2,2-Trifluoroethyl *(R)*-2-(4-methoxyphenyl)-3,3-dimethylpentanoate (**17**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-diazo-2-(4-methoxyphenyl)acetate (0.2 mmol, 55 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and 2-methylbutane (0.6 mmol, 43 mg, 3.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **17** as a colorless oil (60 mg, 94 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **17** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

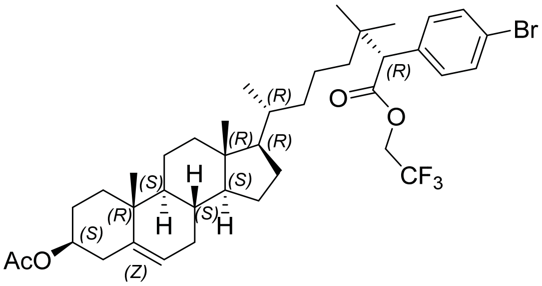
$[\alpha]^{20}_D$ -17.2° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 4.61 (dq, *J* = 12.7, 8.5 Hz, 1H), 4.24 (dq, *J* = 12.7, 8.5 Hz, 1H), 3.80 (s, 3H), 3.57 (s, 1H), 1.38 (dq, *J* = 15.0, 7.5 Hz, 1H), 1.26 (dq, *J* = 14.8, 7.5 Hz, 1H), 0.99 (s, 3H), 0.89 (s, 3H), 0.87 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.71, 158.95, 131.09, 127.04, 123.04 (q, *J* = 277.4 Hz), 113.31, 59.91 (q, *J* = 36.5 Hz), 58.74, 55.21, 37.36, 32.81, 23.79, 23.62, 8.18; HRMS (NSI) calcd for $C_{16}H_{20}F_3O_3$ ($[M-H]^-$):317.1370 found 317.1366; IR (neat):2969, 1752, 1611, 1512, 1277, 1249, 1166, 1123, 1037, 979, 832; HPLC (ODH, 0.3 % isopropanol in hexane, 0.5 mL/min, 10 mg/mL, 50 min, UV 210 nm) retention times of 11.7 min (major) and 45.6 min (minor), 63 % e.e..



2,2,2-Trifluoroethyl (7*R*)-7-((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-3-acetoxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-2-(4-bromophenyl)-3,3-dimethyloctanoate (**19**)

The diastereomers have no evident difference in the ^{1}H NMR and ^{13}C NMR spectra, presumably due to the fact that the newly generated chiral center is too far away from the existing chiral centers.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 5.37 (d, *J* = 4.8 Hz, 1H), 4.66 – 4.56 (m, 2H), 4.26 (dq, *J* = 12.7, 8.5 Hz, 1H), 3.59 (s, 1H), 2.32 (d, *J* = 6.8 Hz, 2H), 2.03 (s, 3H), 2.01 – 1.93 (m, 2H), 1.86 (d, *J* = 10.1 Hz, 2H), 1.80 (ddt, *J* = 13.2, 9.5, 4.9 Hz, 1H), 1.62 – 1.43 (m, 6H), 1.37 – 1.05 (m, 12H), 1.02 (s, 3H), 1.01 (s, 3H), 0.99 – 0.94 (m, 2H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.89 (s, 3H), 0.67 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.25, 170.65, 139.76, 134.14, 131.80, 131.20, 124.15, 122.75, 121.94, 121.81, 74.09, 60.17 (q, *J* = 36.6 Hz), 59.21, 56.79, 56.14, 50.14, 42.45, 41.21, 39.85, 38.25, 37.56, 37.13, 36.71, 35.90, 32.01, 31.98, 28.32, 27.90, 24.64, 24.40, 24.30, 21.58, 21.15, 20.33, 19.44, 18.87, 11.96; HRMS (NSI) calcd for $C_{37}H_{51}BrF_3O_2$ ([M-$C_2H_3O_2$]$^+$):663.3019 found 663.3030.

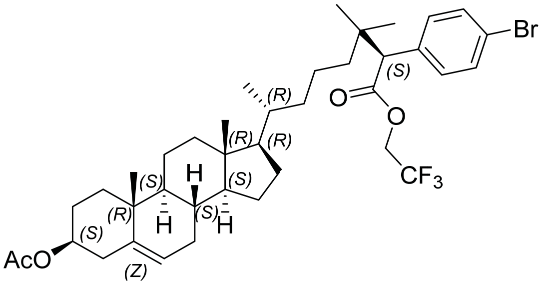


2,2,2-Trifluoroethyl (2*R*,7*R*)-7-((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-3-acetoxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-2-(4-bromophenyl)-3,3-dimethyloctanoate (**19*R***). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-(*(R)*-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (cholesteryl acetate) **18** (0.2 mmol, 86 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **19*R*** as a white solid (113 mg, 78 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **19*R*** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

m.p.:143-145 °C; $[\alpha]^{20}_D$ -41.9° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); IR (neat):2941, 2869, 1752, 1732, 1489, 1467, 1373, 1278, 1242, 1167, 1123, 1033, 1012, 979, 831; HPLC (to improve the separation, the product was converted to (3S,8S,9S,10R,13R,14S,17R)-17-((2R,7S)-7-(4-bromophenyl)-8-hydroxy-6,6-dimethyloctan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-

1H-cyclopenta[a]phenanthren-3-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 20 % isopropanol in hexane, 1 mL/min, 30 mg/mL, 30 min, UV 210 nm) retention times of 10.0 min (minor) and 21.3 min (major), 11:1 d.r.

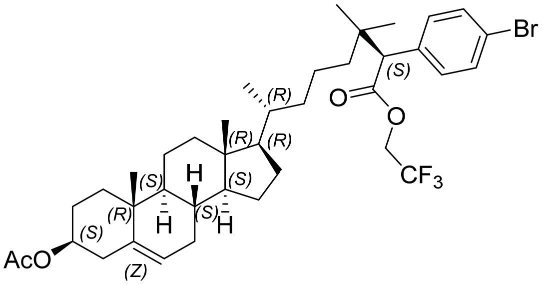


2,2,2-Trifluoroethyl (2*S*,7*R*)-7-((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-3-acetoxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-2-(4-bromophenyl)-3,3-dimethyloctanoate (**19*S***). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-(*(R)*-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (cholesteryl acetate) **18** (0.2 mmol, 86 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **19*S*** as a white solid (124 mg, 86 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **19*S*** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

m.p.:144-146 °C; $[\alpha]^{20}_D$ -9.2° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); IR (neat):2941, 2868, 1752, 1732, 1489, 1374, 1279, 1246, 1168, 1125, 1033, 1012, 979, 758; HPLC (to improve the separation, the product was converted to (3S,8S,9S,10R,13R,14S,17R)-17-((2R,7R)-7-(4-bromophenyl)-8-hydroxy-6,6-

dimethyloctan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 20 % isopropanol in hexane, 1 mL/min, 30 mg/mL, 30 min, UV 210 nm) retention times of 9.9 min (major) and 21.5 min (minor), 11:1 d.r.

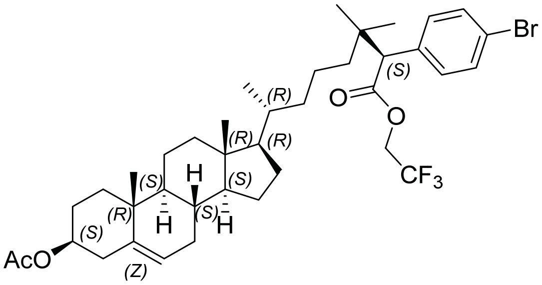


2,2,2-Trifluoroethyl (2*S*,7*R*)-7-((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-3-acetoxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-2-(4-bromophenyl)-3,3-dimethyloctanoate (**19*S***). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*R*-TCPTAD)$_4$ (0.0002 mmol, 0.4 mg, 0.1 mol %.) and (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-(*(R)*-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (cholesteryl acetate) **18** (0.2 mmol, 86 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **19*S*** as a white solid (120 mg, 83 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **19*S*** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

HPLC (to improve the separation, the product was converted to (3S,8S,9S,10R,13R,14S,17R)-17-((2R,7R)-7-(4-bromophenyl)-8-hydroxy-6,6-dimethyloctan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-

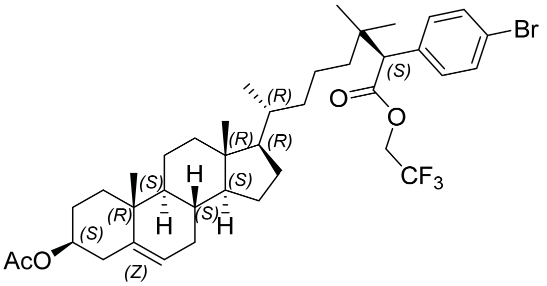
1H-cyclopenta[a]phenanthren-3-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 20 % isopropanol in hexane, 1 mL/min, 30 mg/mL, 30 min, UV 210 nm) retention times of 9.9 min (major) and 21.5 min (minor), 9:1 d.r.



2,2,2-Trifluoroethyl (2*S*,7*R*)-7-((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-3-acetoxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-2-(4-bromophenyl)-3,3-dimethyloctanoate (19*S*). This compound was prepared according to the general procedure for C–H functionalization reactions at **<u>room temperature (24 °C)</u>**. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-(*(R)*-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (cholesteryl acetate) **18** (0.2 mmol, 86 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **19*S*** as a white solid (117 mg, 80 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **19*S*** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

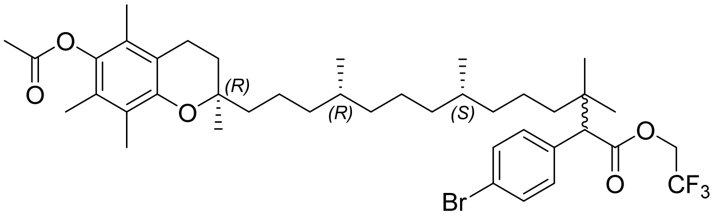
HPLC (to improve the separation, the product was converted to (3S,8S,9S,10R,13R,14S,17R)-17-((2R,7R)-7-(4-bromophenyl)-8-hydroxy-6,6-dimethyloctan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 20 % isopropanol in hexane, 1 mL/min, 30 mg/mL, 30 min, UV 210 nm) retention times of 10.9 min (major) and 24.2 min (minor), 13:1 d.r.



2,2,2-Trifluoroethyl (2*S*,7*R*)-7-((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-3-acetoxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-2-(4-bromophenyl)-3,3-dimethyloctanoate (**19*S***). This compound was prepared according to the general procedure for C–H functionalization reactions at **0 °C**. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-(*(R)*-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (cholesteryl acetate) **18**(0.2 mmol, 86 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **19*S*** as a white solid (88 mg, 60 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **19*S*** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

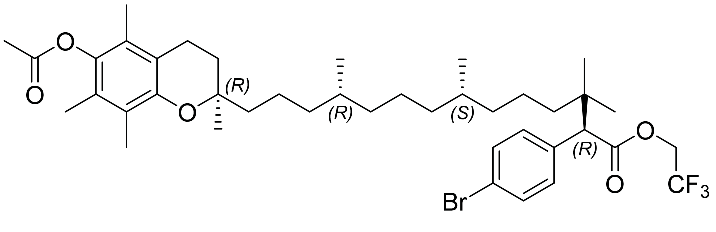
HPLC (to improve the separation, the product was converted to (3S,8S,9S,10R,13R,14S,17R)-17-((2R,7R)-7-(4-bromophenyl)-8-hydroxy-6,6-dimethyloctan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 20 % isopropanol in hexane, 1 mL/min, 30 mg/mL, 30 min, UV 210 nm) retention times of 10.9 min (major) and 24.1 min (minor), 16:1 d.r.



2,2,2-Trifluoroethyl (7*S*,11*R*)-14-((*R*)-6-acetoxy-2,5,7,8-tetramethylchroman-2-yl)-2-(4-bromophenyl)-3,3,7,11-tetramethyltetradecanoate (21)

The diastereomers have no evident difference in the ^{1}H NMR and ^{13}C NMR spectra, presumably due to the fact that the newly generated chiral center is too far away from the existing chiral centers.

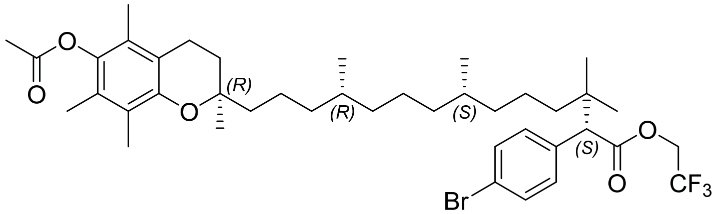
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.3 Hz, 3H), 4.60 (dq, J = 12.7, 8.5 Hz, 1H), 4.26 (dq, J = 12.8, 8.5 Hz, 1H), 3.59 (s, 1H), 2.59 (t, J = 6.7 Hz, 2H), 2.33 (s, 3H), 2.09 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.81 (dt, J = 13.9, 7.1 Hz, 1H), 1.78 – 1.70 (m, 1H), 1.55 (d, J = 11.4 Hz, 2H), 1.44 (ddt, J = 25.1, 13.6, 6.9 Hz, 1H), 1.40 – 1.35 (m, 2H), 1.35 – 1.26 (m, 7H), 1.23 (s, 5H), 1.15 – 1.02 (m, 4H), 1.00 (s, 3H), 0.90 (s, 3H), 0.86 (d, J = 5.7 Hz, 3H), 0.85 (d, J = 6.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.10, 168.74, 148.39, 139.49, 133.00, 130.66, 130.05, 125.63, 123.87, 122.00, 121.89 (q, J = 277.1 Hz), 120.66, 116.33, 74.02, 59.03 (q, J = 36.6 Hz), 58.14, 39.88, 36.67, 36.42, 36.39, 36.38, 31.78, 31.70, 30.91, 28.69, 28.35, 23.44, 23.14, 21.68, 20.18, 20.00, 19.57, 19.55, 18.70, 18.61, 13.11, 11.93, 11.08, 10.81, -1.02.; HRMS (NSI) calcd for $C_{37}H_{51}BrF_3O_2$ ([M-$C_4H_7O_3$]$^+$):663.3019 found 663.3019.



2,2,2-Trifluoroethyl (2*R*,7*S*,11*R*)-14-((*R)*-6-acetoxy-2,5,7,8-tetramethylchroman-2-yl)-2-(4-bromophenyl)-3,3,7,11-tetramethyltetradecanoate (**21*R***). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and *(R)*-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl acetate (D-alpha-tocopheryl acetate or Vitamin E) **20** (0.2 mmol, 95 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **21*R*** as a colorless oil (98 mg, 64 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **21*R*** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

$[\alpha]^{20}_D$ -7.1° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); IR (neat):2927, 2868, 1754, 1489, 1459, 1414, 1368, 1278, 1208, 1166, 1127, 1076, 1011, 979; HPLC (OJH, 0.25 % isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 80 min, UV 254 nm) retention times of 25.7 min (major) and 37.9 min (minor), 11:1 d.r.



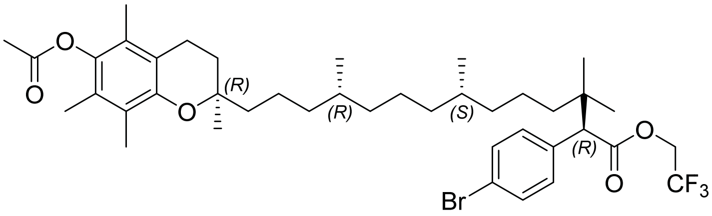
2,2,2-Trifluoroethyl (*2S,7S,11R*)-14-((*R*)-6-acetoxy-2,5,7,8-tetramethylchroman-2-yl)-2-(4-bromophenyl)-3,3,7,11-tetramethyltetradecanoate (**21*S***). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and *(R)*-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl acetate (D-alpha-tocopheryl acetate or Vitamin E) **20** (0.2 mmol, 95 mg, 1.0 *equiv.*) in 0.5 mL distilled

CH_2Cl_2 were used. The crude residue was analyzed by ^1H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **21*S*** as a colorless oil (126 mg, 82 % yield).

Analysis of the ^1H NMR spectrum of the crude reaction mixture revealed that only compound **21*S*** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

$[\alpha]^{20}_D$ +5.3° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); IR (neat):2927, 2867, 1755, 1489, 1457, 1417, 1368, 1279, 1208, 1167, 1128, 1076, 1012, 979; HPLC (OJH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 80 min, UV 254 nm) retention times of 26.9 min (minor) and 39.9 min (major), 11:1 d.r.

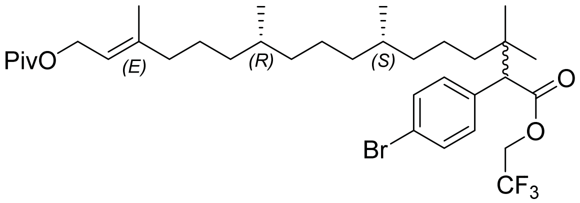
In the functionalization of compound **20** (Vitamin E acetate), even though Rh_2(*S*-TCPTAD)$_4$ and Rh_2(*R*-TCPTAD)$_4$ gave the same calculated d.r. at 39 °C (reflux CH_2Cl_2), actually in the HPLC spectra Rh_2(*S*-TCPTAD)$_4$ gave slightly higher ratio, so we used Rh_2(*S*-TCPTAD)$_4$ to conduct the temperature study.



2,2,2-Trifluoroethyl (2*R*,7*S*,11*R*)-14-((*R*)-6-acetoxy-2,5,7,8-tetramethylchroman-2-yl)-2-(4-bromophenyl)-3,3,7,11-tetramethyltetradecanoate (**21*R***). This compound was prepared according to the general procedure for C–H functionalization reactions at **room temperature (24 °C)**. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and *(R)*-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl acetate (D-alpha-tocopheryl acetate or Vitamin E) **20** (0.2 mmol, 95 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^1H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **21*R*** as a colorless oil (92 mg, 60 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **21*R*** was observed and no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as > *98:2* r.r..

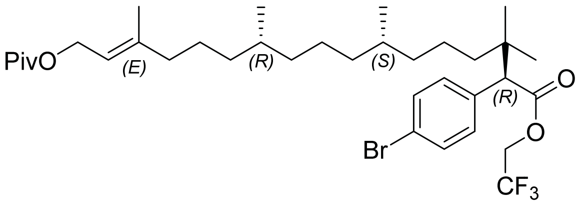
HPLC (OJH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 80 min, UV 254 nm) retention times of 24.5 min (minor) and 39.3 min (major), >20:1 d.r.



2,2,2-Trifluoroethyl (7*S*,11*R*,*E*)-2-(4-bromophenyl)-3,3,7,11,15-pentamethyl-17-(pivaloyloxy)heptadec-15-enoate (23).

The diastereomers have no evident difference in the ^{1}H NMR and ^{13}C NMR spectra, presumably due to the fact that the newly generated chiral center is too far away from the existing chiral centers.

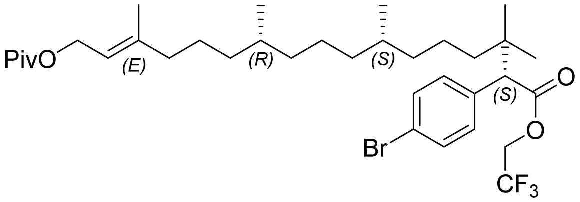
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.44 (d, J = 8.6 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 5.31 (tq, J = 6.9, 1.2 Hz, 1H), 4.61 (dq, J = 12.7, 8.5 Hz, 1H), 4.57 (d, J = 6.9 Hz, 2H), 4.26 (dq, J = 12.7, 8.5 Hz, 1H), 3.59 (s, 1H), 2.00 (dp, J = 15.1, 7.7, 7.2 Hz, 2H), 1.68 (s, 3H), 1.40 – 1.21 (m, 12H), 1.19 (s, 9H), 1.15 – 1.01 (m, 4H), 1.00 (s, 3H), 0.89 (s, 3H), 0.85 (d, J = 6.6 Hz, 3H), 0.84 (d, J = 6.6 Hz, 3H), 0.85 – 0.83 (m, 1H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 178.73, 171.26, 142.29, 134.13, 131.81, 131.20, 121.82, 118.62, 61.46, 60.17 (q, J = 36.7 Hz), 59.27, 41.02, 39.94, 38.87, 37.84, 37.53, 37.49, 36.68, 32.93, 32.82, 29.84, 27.35, 25.16, 24.62, 24.60, 24.28, 21.34, 19.86, 19.83, 16.48; HRMS (NSI) calcd for $C_{35}H_{58}O_4BrF_3N$ ([M+NH$_4$]$^+$):692.3496 found 692.3516.



2,2,2-Trifluoroethyl (2*R*,7*S*,11*R*,*E*)-2-(4-bromophenyl)-3,3,7,11,15-pentamethyl-17-(pivaloyloxy)heptadec-15-enoate (**23*R***). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (7R,11R,E)-3,7,11,15-tetramethylhexadec-2-en-1-yl pivalate (phytyl pivalate) **22** (0.2 mmol, 76 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **23*R*** as a colorless oil (91 mg, 67 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **23*R* and compound 24** were observed, no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as 77:23 r.r..

$[\alpha]^{20}_D$ -10.0° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); IR (neat):2929, 2869, 1754, 1725, 1489, 1480, 1461, 1279, 1152, 1125, 1076, 1032, 1012, 979, 830, 770; HPLC (OJH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 30 min, UV 210 nm) retention times of 16.1 min (major) and 19.4 min (minor), 11:1 d.r.

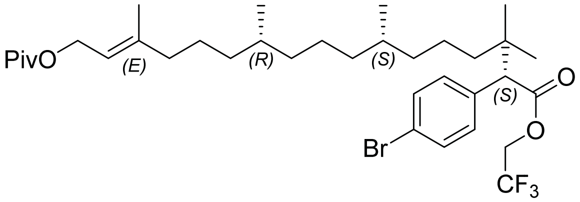


2,2,2-Trifluoroethyl (2*S*,7*S*,11*R*,*E*)-2-(4-bromophenyl)-3,3,7,11,15-pentamethyl-17-(pivaloyloxy)heptadec-15-enoate (**23*S***). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-

bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (7R,11R,E)-3,7,11,15-tetramethylhexadec-2-en-1-yl pivalate (phytyl pivalate) **22** (0.2 mmol, 76 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^1H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **23*S*** as a colorless oil (93 mg, 69 % yield).

Analysis of the ^1H NMR spectrum of the crude reaction mixture revealed that only compound **23*S* and compound 24** were observed, no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as 78:22 r.r..

$[\alpha]^{20}_D$ +11.6° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); IR (neat):2930, 2869, 1755, 1726, 1489, 1458, 1280, 1165, 1126, 1077, 1012, 980; HPLC (OJH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 30 min, UV 210 nm) retention times of 16.1 min (major) and 19.2 min (minor), 12:1 d.r.

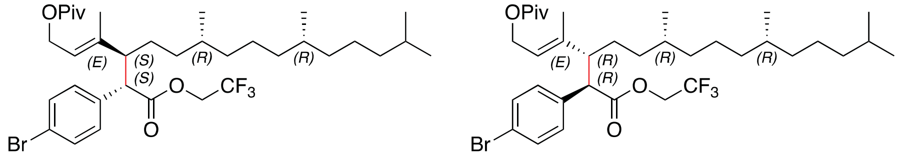


2,2,2-Trifluoroethyl (2*S*,7*S*,11*R*,*E*)-2-(4-bromophenyl)-3,3,7,11,15-pentamethyl-17-(pivaloyloxy)heptadec-15-enoate (**23*S***). This compound was prepared according to the general procedure for C–H functionalization reactions at room temperature (24 °C). 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (7R,11R,E)-3,7,11,15-tetramethylhexadec-2-en-1-yl pivalate (phytyl pivalate) **22** (0.2 mmol, 76 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^1H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **23*S*** as a colorless oil (70 mg, 52 % yield).

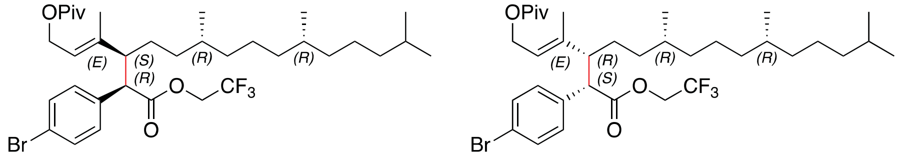
Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that only compound **23*S* and compound 24** were observed, no evident signal of other regioisomer was detected, so the regioselectivity of this reaction was recoded as 89:11 r.r..

HPLC (OJH, 0.25% isopropanol in hexane, 0.25 mL/min, 10 mg/mL, 30 min, UV 210 nm) retention times of 16.1 min (major) and 19.2 min (minor), 12:1 d.r.

22A

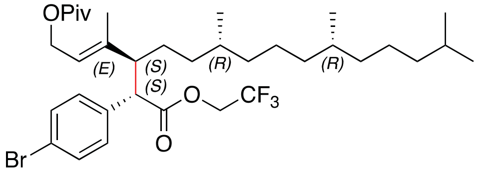


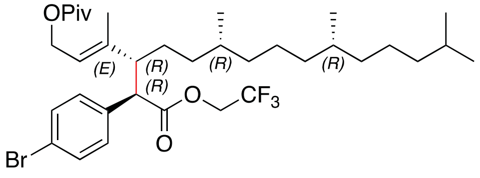
22B



2,2,2-Trifluoroethyl (6*R*,10*R*)-2-(4-bromophenyl)-6,10,14-trimethyl-3-(4-(pivaloyloxy)but-2-en-2-yl)pentadecanoate (**24**). These compounds were prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ or Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (7R,11R,E)-3,7,11,15-tetramethylhexadec-2-en-1-yl pivalate (phytyl pivalate) **22**(0.2 mmol, 76 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **24** as a colorless oil (27 mg, 20 % yield for Rh_2(*S*-TCPTAD)$_4$ and 28 mg, 21 % yield for Rh_2(*R*-TCPTAD)$_4$).

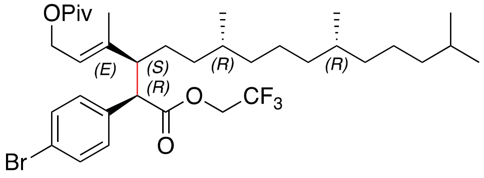
Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that the diastereomeric ratio (d.r.) between **(±) 24** (***S*, *S***) and **(±) 24** (***S*, *R***) was 2:1 for both Rh_2(*S*-TCPTAD)$_4$ and Rh_2(*R*-TCPTAD)$_4$.

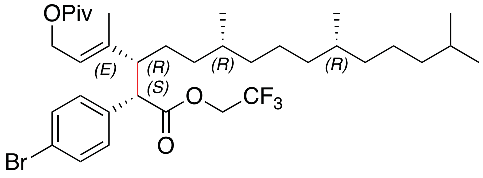




(±)2,2,2-Trifluoroethyl (2*S*,3*S*,6*R*,10*R*)-2-(4-bromophenyl)-6,10,14-trimethyl-3-((*E*)-4-(pivaloyloxy)but-2-en-2-yl)pentadecanoate [(±) **24** (***S*, *S***)]**.** These compounds were prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ or Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (7R,11R,E)-3,7,11,15-tetramethylhexadec-2-en-1-yl pivalate (phytyl pivalate) **22** (0.2 mmol, 76 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford **(±) 24** (***S*, *S***) as colorless oil (18 mg, 13 % yield for Rh_2(*S*-TCPTAD)$_4$ and 19 mg, 14 % yield for Rh_2(*R*-TCPTAD)$_4$).

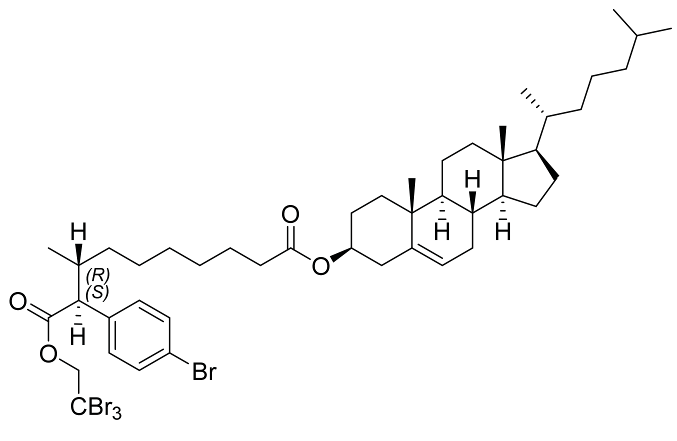
TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 5.25 (t, *J* = 7.1 Hz, 1H), 4.56 (dq, *J* = 12.7, 8.4 Hz, 1H), 4.39 – 4.26 (m, 3H), 3.60 (d, *J* = 11.6 Hz, 1H), 2.80 (td, *J* = 11.3, 3.3 Hz, 1H), 1.54 (s, 3H), 1.58 – 1.47 (m, 1H), 1.42 (s, 3H), 1.36 (ddt, *J* = 9.8, 6.6, 3.2 Hz, 2H), 1.34 – 1.26 (m, 2H), 1.26 – 1.20 (m, 3H), 1.22 – 1.17 (m, 3H), 1.15 (dddt, *J* = 12.0, 9.2, 6.4, 2.7 Hz, 2H), 1.10 (s, 9H), 1.09 – 1.00 (m, 2H), 1.02 – 0.93 (m, 1H), 0.87 (d, *J* = 6.6 Hz, 6H), 0.84 (d, *J* = 6.6 Hz, 3H), 0.82 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.20, 171.71, 138.98, 135.29, 131.56, 130.25, 124.26, 122.79 (q, *J* = 277.6 Hz), 121.70, 60.49 (q, *J* = 36.5 Hz), 60.12, 54.92, 51.78, 39.37, 38.66, 37.64, 37.38, 37.31, 34.36, 32.78, 32.41, 29.71, 28.45, 27.98, 27.11, 24.80, 24.53, 22.72, 22.62, 19.72, 19.28, 12.25; HRMS (NSI) calcd for $C_{35}H_{53}BrO_4F_3$ ($[M-H]^-$):673.3085 found 673.3091; IR (neat):2954, 2925, 2854, 1756, 1727, 1489, 1462, 1281, 1168, 1147, 1075, 1012, 980.





(±)2,2,2-Trifluoroethyl (2*S*,3*R*,6*R*,10*R*)-2-(4-bromophenyl)-6,10,14-trimethyl-3-((*E*)-4-(pivaloyloxy)but-2-en-2-yl)pentadecanoate [(±) **24** (***S*, *R***)]. These compounds were prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*S*-TCPTAD)$_4$ or Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (7R,11R,E)-3,7,11,15-tetramethylhexadec-2-en-1-yl pivalate (phytyl pivalate) **22** (0.2 mmol, 76 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford **(±) 24 (*S*, *R*)** as colorless oil (9 mg, 7 % yield for both Rh_2(*S*-TCPTAD)$_4$ and Rh_2(*R*-TCPTAD)$_4$).

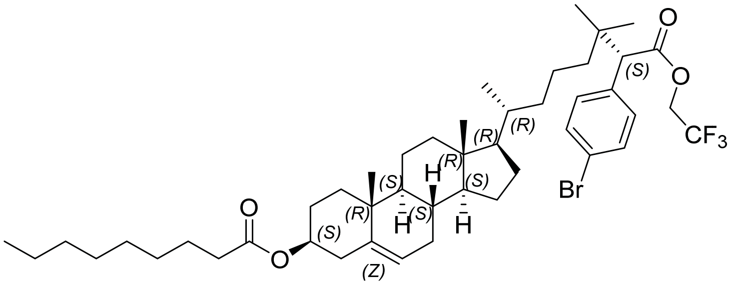
TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 9.1 Hz, 5H), 5.49 (t, *J* = 6.7 Hz, 1H), 4.57 (qd, *J* = 12.7, 6.7 Hz, 2H), 4.44 (dq, *J* = 12.6, 8.5 Hz, 1H), 4.24 (dq, *J* = 12.7, 8.4 Hz, 1H), 3.63 (d, *J* = 11.6 Hz, 1H), 2.72 – 2.63 (m, 1H), 1.70 (s, 3H), 1.58 – 1.47 (m, 1H), 1.36 – 1.19 (m, 9H), 1.19 (s, 9H), 1.17 – 1.00 (m, 4H), 1.02 – 0.92 (m, 1H), 0.87 (d, *J* = 6.6 Hz, 6H), 0.91 – 0.82 (m, 4H), 0.81 (d, *J* = 6.6 Hz, 3H), 0.70 (d, *J* = 6.6 Hz, 3H).; ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.34, 170.86, 139.93, 135.17, 131.89, 130.34, 123.63, 122.89 (q, *J* = 277.3 Hz), 121.94, 60.69, 60.53 (q, J = 36.7 Hz), 55.11, 52.22, 39.37, 38.73, 37.40, 37.29, 36.43, 33.97, 32.75, 32.39, 29.71, 27.98, 27.18, 26.72, 24.80, 24.18, 22.73, 22.63, 19.95, 19.71, 14.13, 12.56; HRMS (NSI) calcd for $C_{35}H_{53}BrO_4F_3$ ($[M-H]^-$):673.3085 found 673.3074; IR (neat):2954, 2924, 2854, 1756, 1730, 1488, 1461, 1281, 1168, 1149, 1075, 1012.



10-((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl) 1-(2,2,2-tribromoethyl) (2*S*,3*R*)-2-(4-bromophenyl)-3-methyldecanedioate (**26**). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1c** (0.2 mmol, 101 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-(*(R)*-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl nonanoate (cholesteryl pelargonate) **25** (0.6 mmol, 105 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **26** as a colorless oil (137 mg, 68 % yield).

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that the regioselectivity of this reaction was 3:87:10 r.r.. 3% of product was the C-H insertion at the most accessible primary position (the last primary carbon) of the *n*-alkyl chain, another 10% of the product was the C-H insertion at the most accessible tertiary position (the isopropyl tertiary carbon) of another alkyl chain. For this reaction, two new chiral centers will be generated, compound **26** is (*S*,*R*), other potential diastereomers are (*R*,*S*), (*S*,*S*) and (*R*,*R*), the ratio of [(*S*,*R*) + (*R*,*S*)] to [(*S*,*S*) + (*R*,*R*)] is 9.27:1.

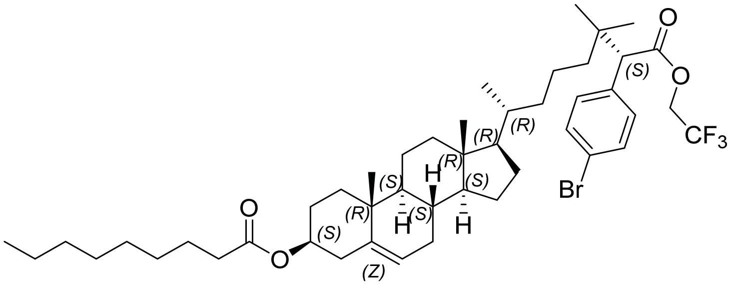
$[\alpha]^{20}_D$ -4.6° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 5.37 (d, *J* = 4.7 Hz, 1H), 4.92 (d, *J* = 12.3 Hz, 1H), 4.84 (d, *J* = 12.3 Hz, 1H), 3.39 (d, *J* = 10.6 Hz, 1H), 2.33 – 2.24 (m, 3H), 2.22 (t, *J* = 7.5 Hz, 2H), 2.03 – 1.93 (m, 2H), 1.88 – 1.78 (m, 3H), 1.52 (dddd, *J* = 50.3, 26.9, 12.9, 5.1 Hz, 10H), 1.40 – 1.26 (m, 6H), 1.25 – 1.09 (m, 12H), 1.07 (d, *J* = 6.5 Hz, 3H), 1.02 (s, 3H), 1.01 – 0.93 (m, 3H), 0.91 (d, *J* = 6.5 Hz, 4H), 0.87 (d, *J* = 2.7 Hz, 3H), 0.86 (d, *J* = 2.7 Hz, 3H), 0.68 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.15, 171.45, 139.66, 136.20, 131.68, 130.52, 122.59, 121.54, 77.06, 73.68, 58.19, 56.67, 56.11, 50.00, 42.30, 39.71, 39.50, 38.15, 36.98, 36.58, 36.17, 36.00, 35.78, 35.18, 34.58, 33.19, 31.89, 31.85, 29.69, 29.19, 28.95, 28.22, 28.00, 27.80, 26.06, 24.88, 24.27, 23.82, 22.82, 22.56, 21.02, 19.33, 18.71, 17.93, 14.12, 11.85; HRMS (NSI) calcd for $C_{46}H_{69}Br_4O_4$ ($[M+H]^+$):1003.1903 found 1003.1937; IR (neat):2932, 2853, 2361, 1733, 1488, 1466, 1365, 1256, 1173, 1128, 1074, 1011, 756, 719; HPLC (to improve the separation, the product was converted to 3-methyl-2-(4-(trifluoromethyl)phenyl)decane-1,10-diol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 4 % isopropanol in hexane, 1 mL/min, 10 mg/mL, 90 min, UV 210 nm) retention times of 47.5 min (major) and 78.8 min (minor), the ratio of (*S*,*R*) to (*R*,*S*) is 39:1. Combined with the ratio measured by crude ^1H NMR spectrum, the calculated d.r. of this reaction is 9:1.



(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-17-((2*R*,7*S*)-7-(4-Bromophenyl)-6,6-dimethyl-8-oxo-8-(2,2,2-trifluoroethoxy)octan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl nonanoate (27). This compound was prepared according to the general procedure for C–H functionalization reactions. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-(*(R)*-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl nonanoate (cholesteryl pelargonate) **25** (0.6 mmol, 105 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^1H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **27** as a white solid (122 mg, 74 % yield).

Analysis of the ^1H NMR spectrum of the crude reaction mixture revealed that the regioselectivity of this reaction was 87:13 r.r., and the minor regioisomer was the C-H insertion at the most accessible secondary position (the second last secondary carbon) of the *n*-alkyl chain.

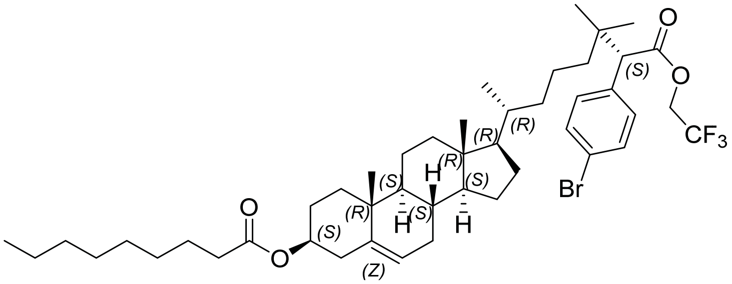
$[\alpha]^{20}_{D}$ -5.1° (c = 1.00, $CHCl_3$); TLC (diethyl ether:hexanes, 1:10 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 5.37 (d, *J* = 4.8 Hz, 1H), 4.66 – 4.55 (m, 2H), 4.27 (dq, *J* = 12.7, 8.5 Hz, 1H), 3.59 (s, 1H), 2.36 – 2.29 (m, 2H), 2.27 (t, *J* = 7.5 Hz, 2H), 2.03 – 1.94 (m, 2H), 1.90 – 1.75 (m, 3H), 1.68 – 1.54 (m, 5H), 1.54 – 1.42 (m, 3H), 1.42 – 1.33 (m, 2H), 1.33 – 1.23 (m, 15H), 1.23 – 1.04 (m, 6H), 1.01 (d, *J* = 10.7 Hz, 6H), 0.98 – 0.95 (m, 1H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.89 (s, 3H), 0.88 (t, *J* = 7.0 Hz, 3H), 0.67 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.31, 171.12, 139.72, 134.03, 131.68, 131.07, 122.92 (q, *J* = 277.3 Hz), 122.55, 121.69, 73.66, 60.06 (q, *J* = 36.6 Hz), 59.12, 56.66, 56.07, 50.02, 42.33, 41.10, 39.72, 38.16, 37.44, 37.01, 36.60, 35.82, 34.73, 31.89, 31.86, 31.81, 29.71, 29.23, 29.13, 28.23, 27.82, 25.07, 24.47, 24.27, 24.21, 22.65, 21.03, 20.30, 19.33, 18.74, 14.10, 11.84; HRMS (NSI) calcd for $C_{37}H_{51}BrF_3O_2$ ($[M-C_9H_{17}O_2]^-$):663.3019 found 663.3037; IR (neat):2930, 2853, 1751, 1734, 1489, 1457, 1279, 1168, 1124, 1012, 980; HPLC (to improve the separation, the product was converted to (3S,8S,9S,10R,13R,14S,17R)-17-((2R,7R)-7-(4-bromophenyl)-8-hydroxy-6,6-dimethyloctan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 20 % isopropanol in hexane, 1 mL/min, 30 mg/mL, 30 min, UV 210 nm) retention times of 9.9 min (major) and 21.3 min (minor), 6:1 d.r.



(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-17-((2*R*,7*S*)-7-(4-Bromophenyl)-6,6-dimethyl-8-oxo-8-(2,2,2-trifluoroethoxy)octan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl nonanoate (27). This compound was prepared according to the general procedure for C–H functionalization reactions at **room temperature (24 °C)**. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, $Rh_2(R\text{-TCPTAD})_4$ (0.002 mmol, 4 mg, 1 mol %.) and (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-(*(R)*-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl nonanoate (cholesteryl pelargonate) **25** (0.6 mmol, 105 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^1H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **27** as a white solid (112 mg, 68 % yield).

Analysis of the ^1H NMR spectrum of the crude reaction mixture revealed that the regioselectivity of this reaction was 89:11 r.r., and the minor regioisomer was the C-H insertion at the most accessible secondary position (the second last secondary carbon) of the *n*-alkyl chain.

HPLC (to improve the separation, the product was converted to (3S,8S,9S,10R,13R,14S,17R)-17-((2R,7R)-7-(4-bromophenyl)-8-hydroxy-6,6-dimethyloctan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 20 % isopropanol in hexane, 1 mL/min, 30 mg/mL, 30 min, UV 210 nm) retention times of 11.8 min (major) and 24.06 min (minor), >20:1 d.r.

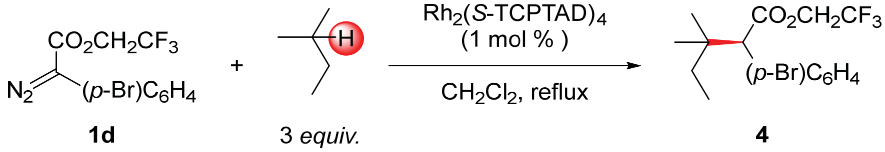


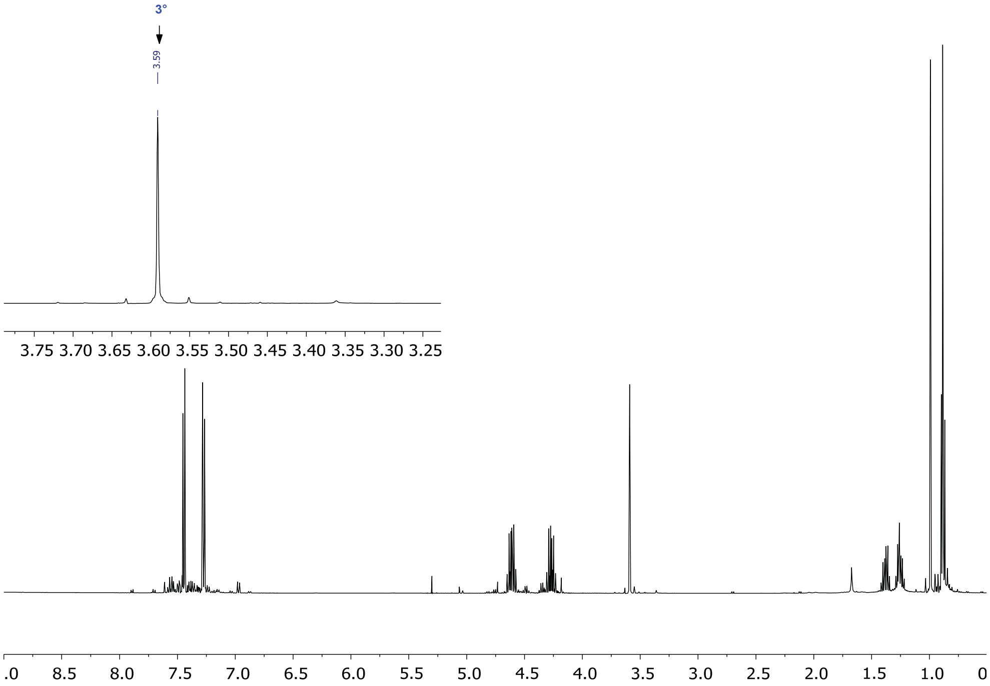
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-17-((2*R*,7*S*)-7-(4-Bromophenyl)-6,6-dimethyl-8-oxo-8-(2,2,2-trifluoroethoxy)octan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl nonanoate (27). This compound was prepared according to the general procedure for C–H functionalization reactions at **0 °C**. 2,2,2-Trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate **1d** (0.2 mmol, 65 mg, 1.0 *equiv.*) in 3 mL distilled CH_2Cl_2, Rh_2(*R*-TCPTAD)$_4$ (0.002 mmol, 4 mg, 1 mol %.) and (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((*R)*-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl nonanoate (cholesteryl pelargonate) **25** (0.6 mmol, 105 mg, 1.0 *equiv.*) in 0.5 mL distilled CH_2Cl_2 were used. The crude residue was analyzed by ^{1}H NMR and then purified by flash column chromatography (hexanes/diethyl ether = 65/1) to afford compound **27** as a white solid (107 mg, 65 % yield).

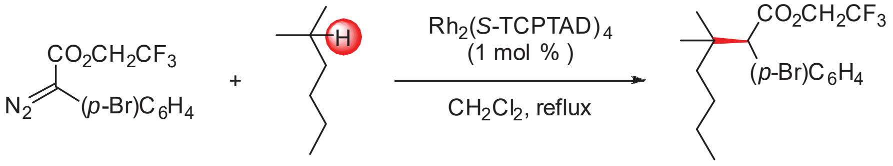
Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that the regioselectivity of this reaction was 92:8 r.r., and the minor regioisomer was the C-H insertion at the most accessible secondary position (the second last secondary carbon) of the *n*-alkyl chain.

HPLC (to improve the separation, the product was converted to (3S,8S,9S,10R,13R,14S,17R)-17-((2R,7R)-7-(4-bromophenyl)-8-hydroxy-6,6-dimethyloctan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol prepared using DIBAL in DCM at -78 °C), (S,S-Whelk, 20 % isopropanol in hexane, 1 mL/min, 30 mg/mL, 30 min, UV 210 nm) retention times of 11.9 min (major) and 24.5 min (minor), >20:1 d.r.

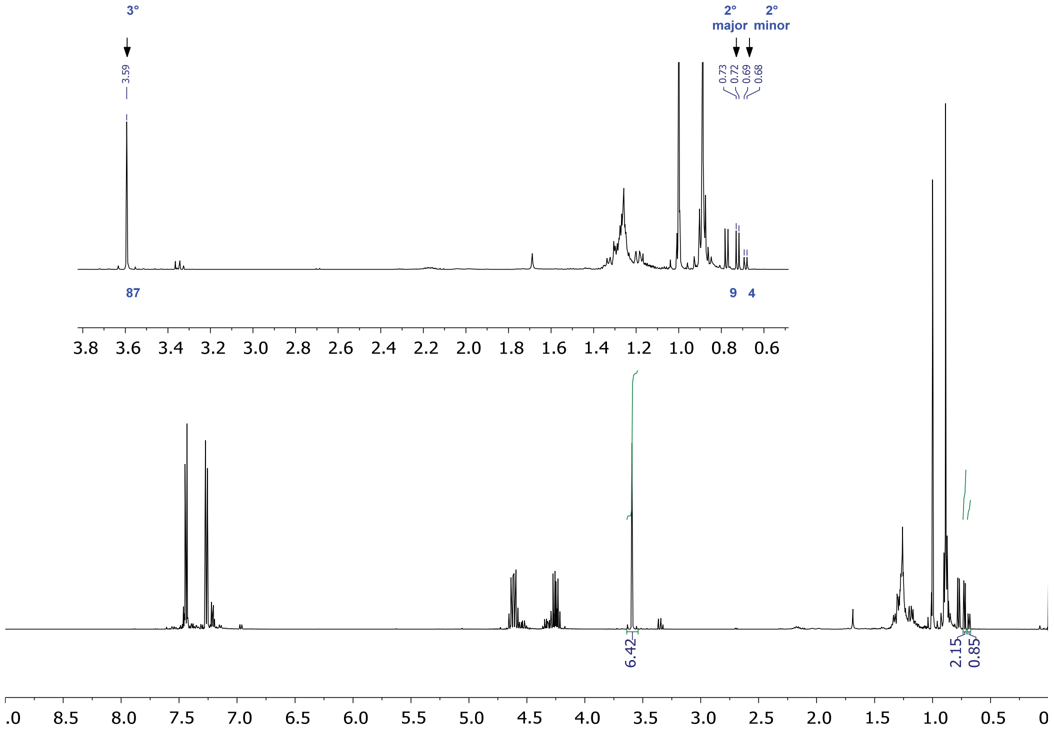
7. Crude ^{1}H NMR Spectra

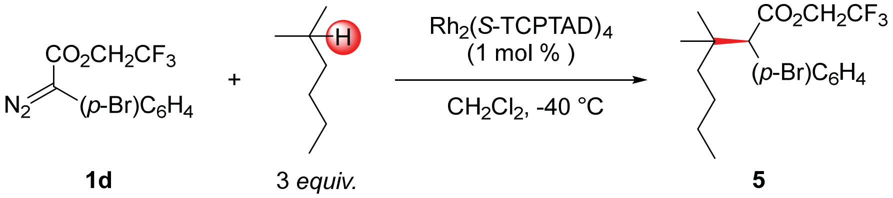


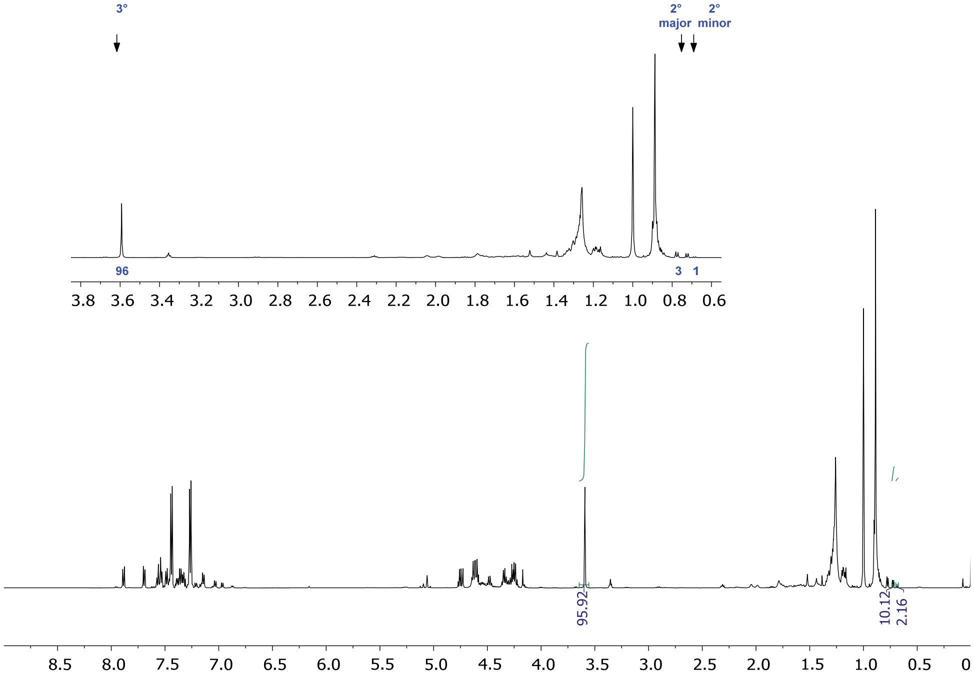


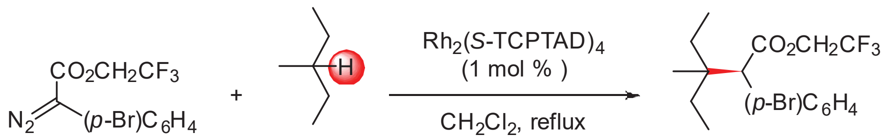

CO$_2$CH$_2$CF$_3$
N$_2$
(p-Br)C$_6$H$_4$
+
H
Rh$_2$(S-TCPTAD)$_4$
(1 mol %)
CH$_2$Cl$_2$, reflux
3 equiv.
CO$_2$CH$_2$CF$_3$
(p-Br)C$_6$H$_4$

1d **5**

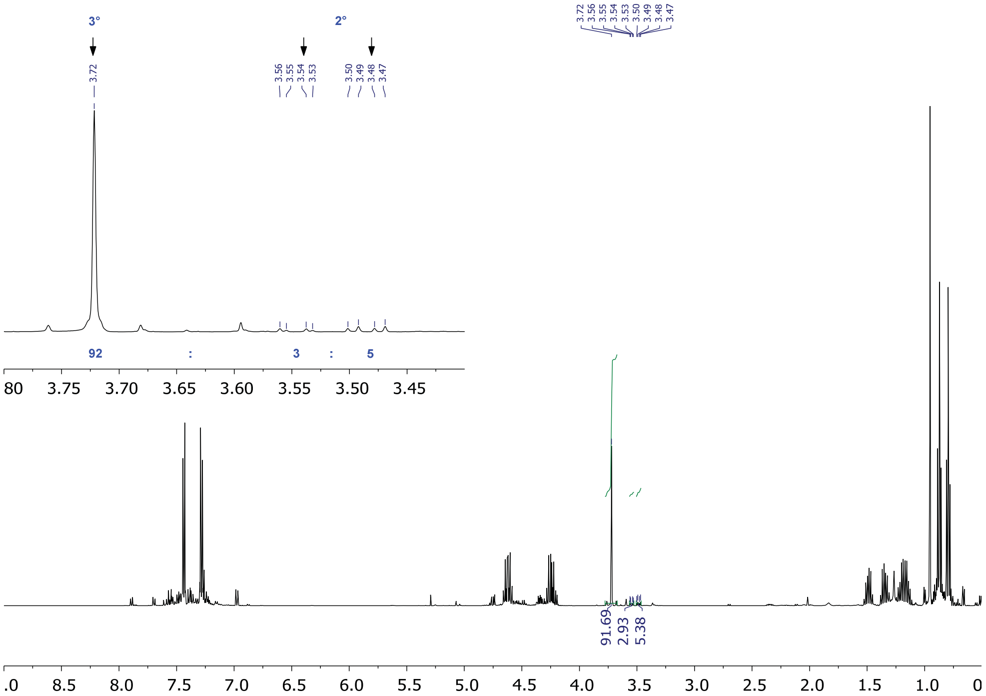

3°
2° major
2° minor
3.59
0.73
0.72
0.69
0.68
87
9
4
3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
6.42
2.15
0.85
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0

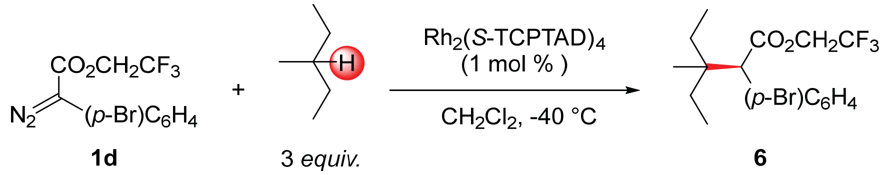

$CO_2CH_2CF_3$
N_2
(p-Br)C_6H_4
1d
+
H
3 equiv.
Rh_2(S-TCPTAD)$_4$
(1 mol %)
CH_2Cl_2, -40 °C
$CO_2CH_2CF_3$
(p-Br)C_6H_4
5


3°
2° major
2° minor
96
3
1
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
95.92
10.12
2.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0


CO2CH2CF3
N2
(p-Br)C6H4
+
H
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
CO2CH2CF3
(p-Br)C6H4

1d 3 *equiv.* **6**

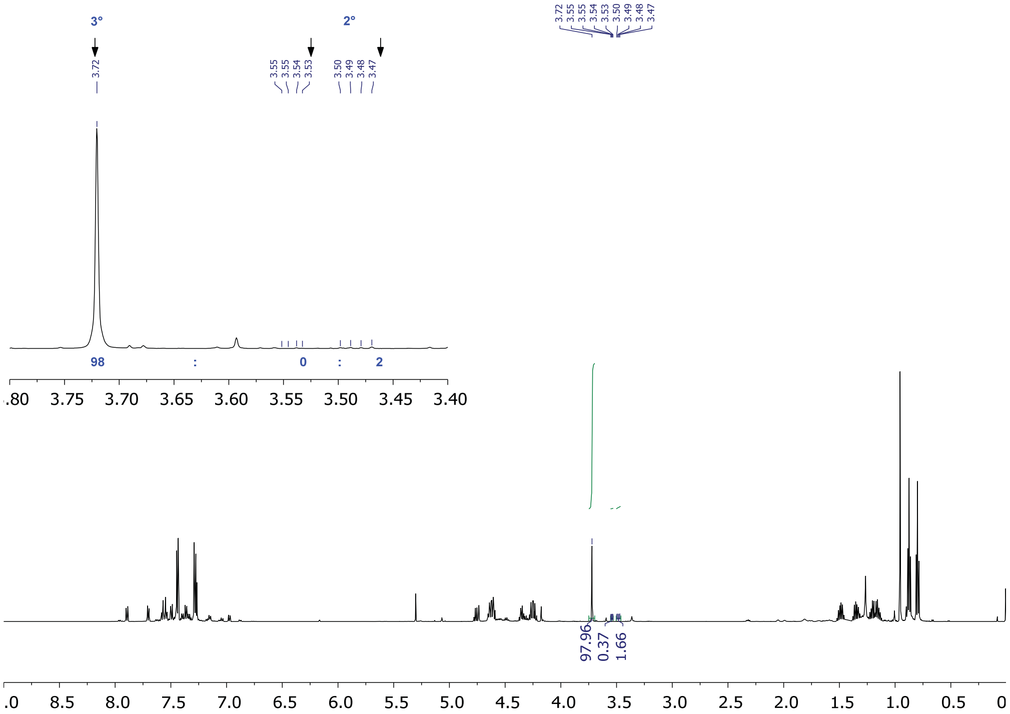

3°
2°
3.72
3.56
3.55
3.54
3.53
3.50
3.49
3.48
3.47
92 : 3 : 5
80
3.75
3.70
3.65
3.60
3.55
3.50
3.45
91.69
2.93
5.38
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

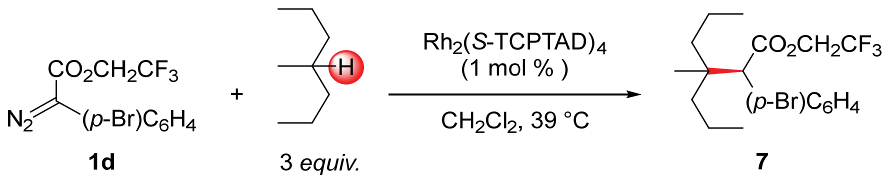

$CO_2CH_2CF_3$
N_2
$(p\text{-Br})C_6H_4$
+
H
$Rh_2(S\text{-TCPTAD})_4$
(1 mol %)
CH_2Cl_2, -40 °C
$CO_2CH_2CF_3$
$(p\text{-Br})C_6H_4$

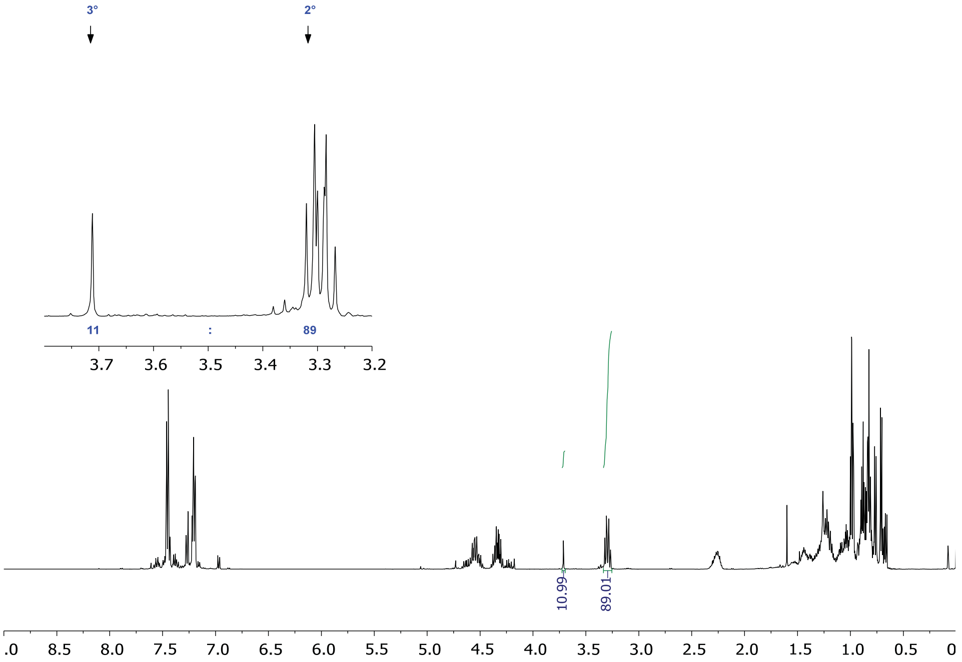
1d

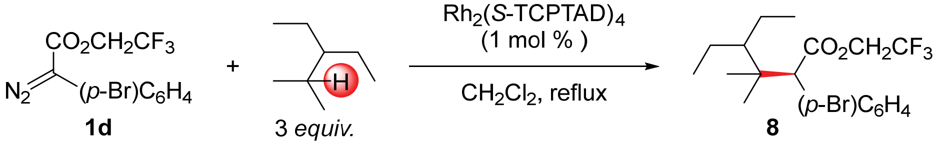
3 *equiv.*

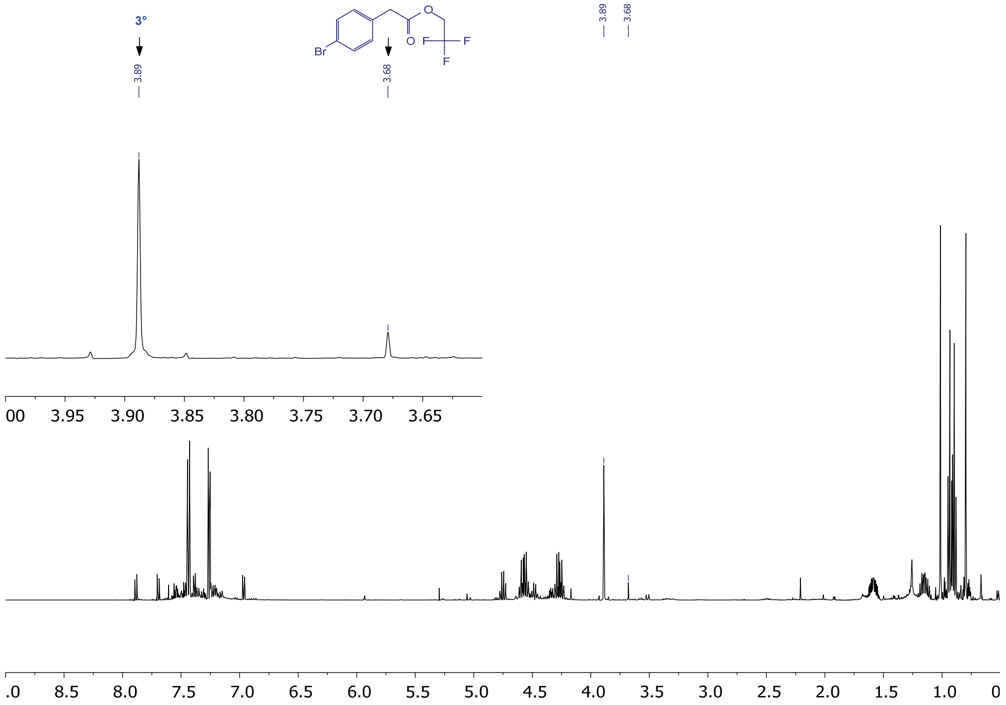
6

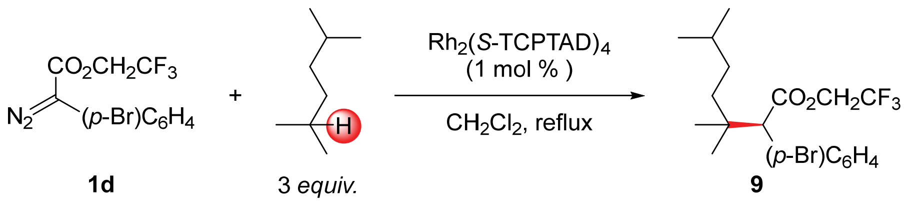

3°
2°
3.72
3.55
3.55
3.54
3.53
3.50
3.49
3.48
3.47
98
:
0
:
2
.80
3.75
3.70
3.65
3.60
3.55
3.50
3.45
3.40
3.72
3.55
3.55
3.54
3.53
3.50
3.49
3.48
3.47
97.96
0.37
1.66
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0

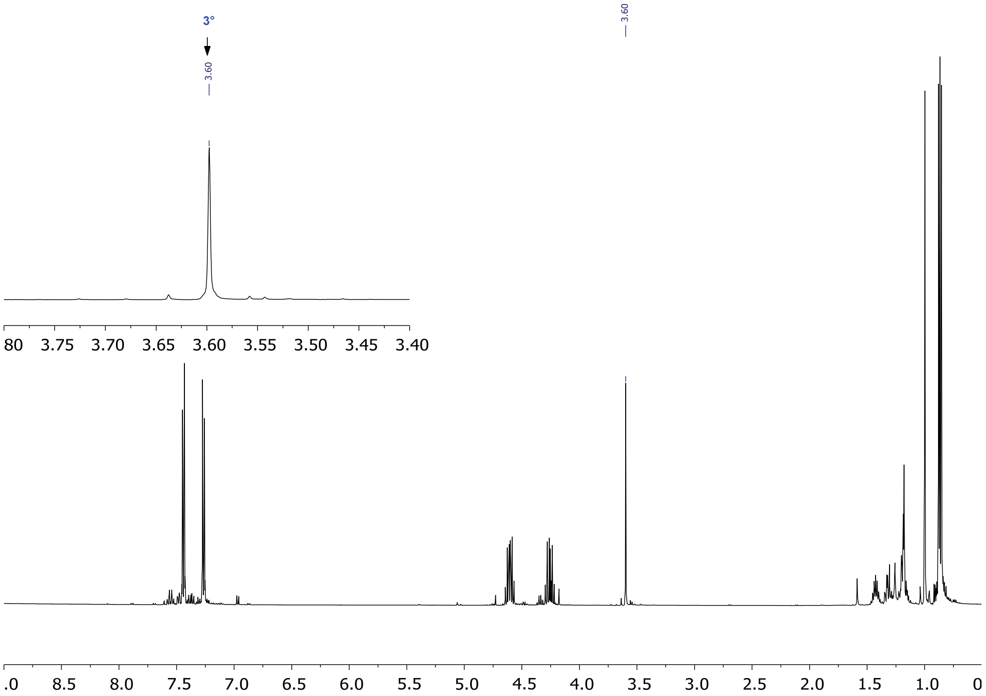

CO2CH2CF3
N2
(p-Br)C6H4
1d
+
H
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, 39 °C
CO2CH2CF3
(p-Br)C6H4
7

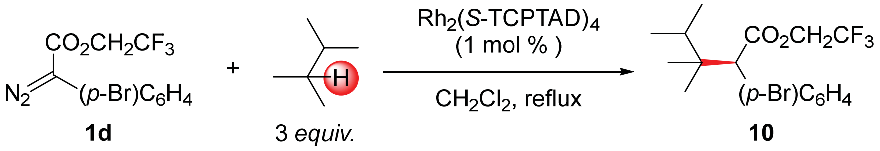

3°
2°
11
:
89
3.7
3.6
3.5
3.4
3.3
3.2
10.99
89.01
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0

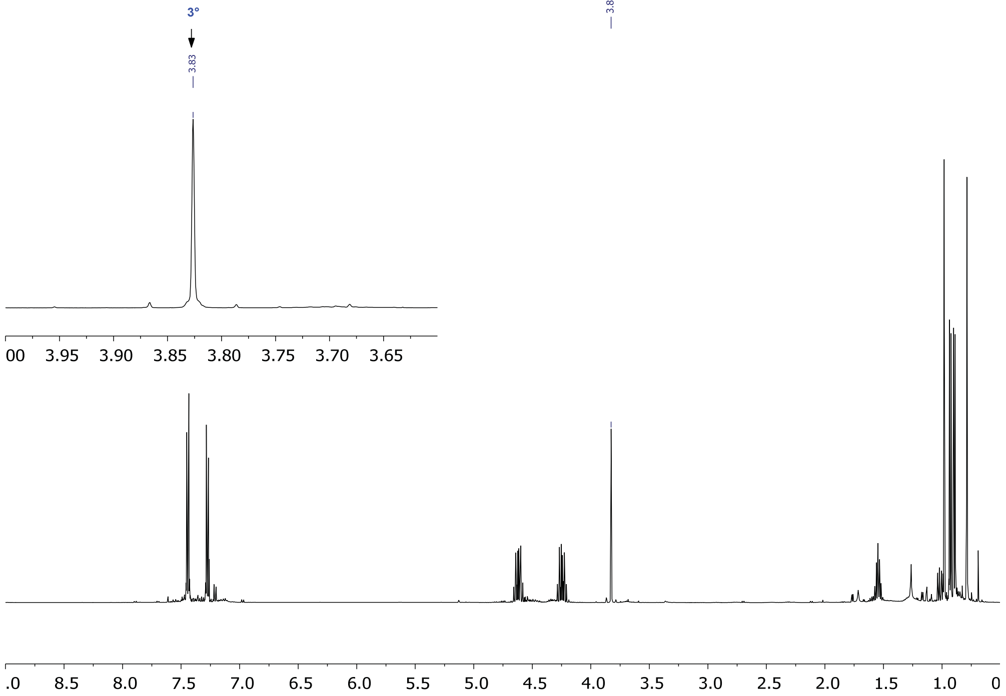

CO2CH2CF3
N2
(p-Br)C6H4
1d
+
H
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
CO2CH2CF3
(p-Br)C6H4
8


3°
3.89
Br
O
O
F
F
F
3.68
3.89
3.68
00
3.95
3.90
3.85
3.80
3.75
3.70
3.65
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0


CO2CH2CF3
N2
(p-Br)C6H4
1d
+
H
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
CO2CH2CF3
(p-Br)C6H4
9


3°
3.60
80 3.75 3.70 3.65 3.60 3.55 3.50 3.45 3.40
3.60
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0


CO2CH2CF3
N2
(p-Br)C6H4
1d
+
H
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
CO2CH2CF3
(p-Br)C6H4
10


3°
3.83
3.83
00
3.95
3.90
3.85
3.80
3.75
3.70
3.65
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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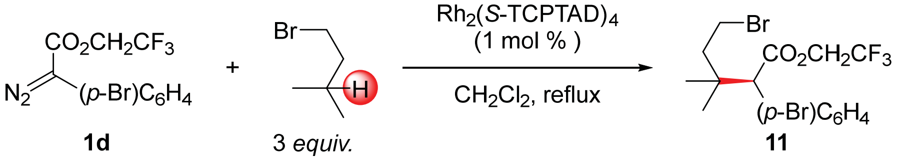
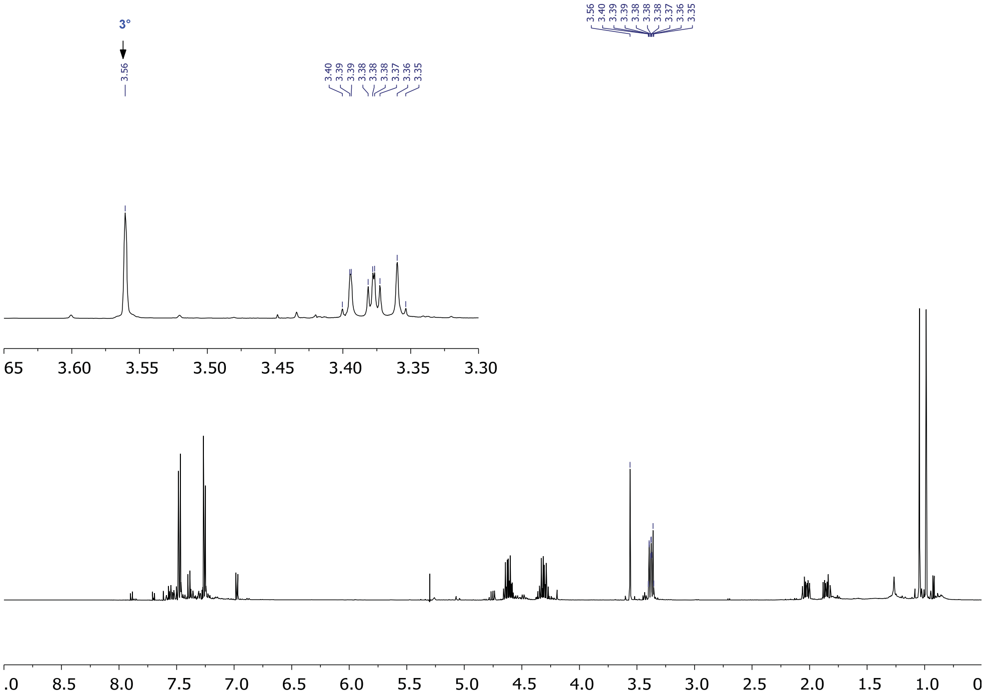
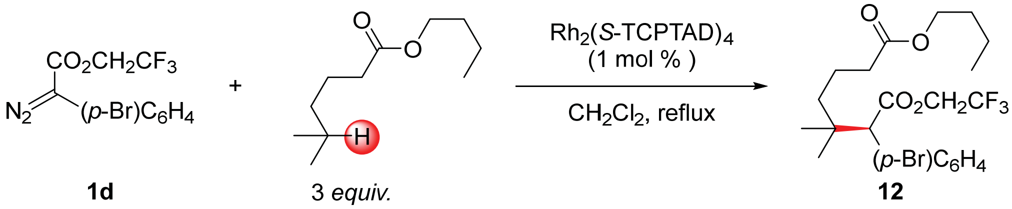
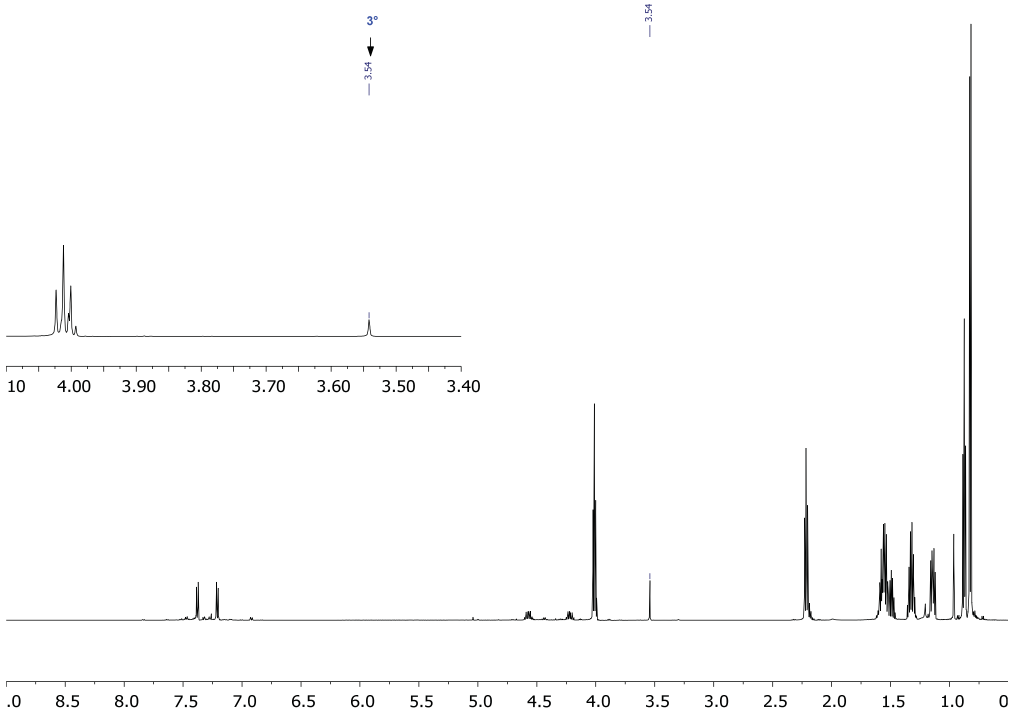
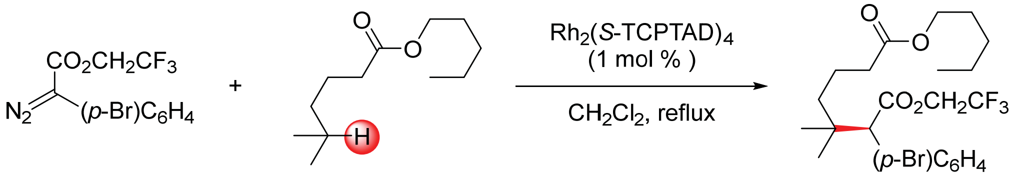
2.5
2.0
1.5
1.0
0


$CO_2CH_2CF_3$
N_2
$(p\text{-Br})C_6H_4$
1d
+
Br
H
3 equiv.
$Rh_2(S\text{-TCPTAD})_4$
(1 mol %)
CH_2Cl_2, reflux
Br
$CO_2CH_2CF_3$
$(p\text{-Br})C_6H_4$
11

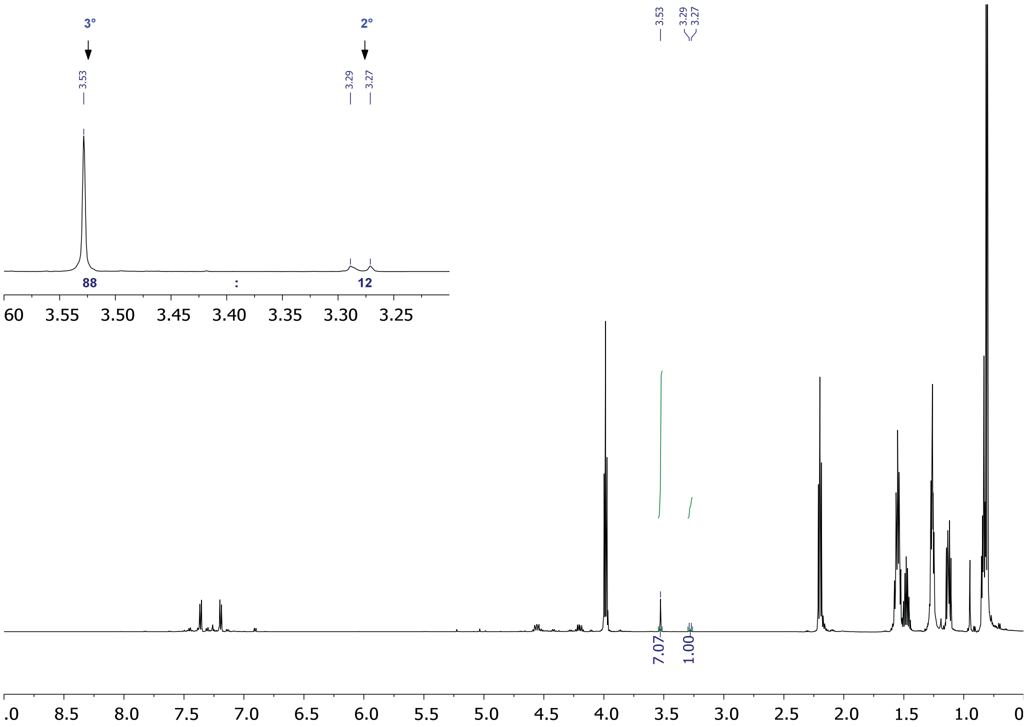

3.56
3.40
3.39
3.39
3.38
3.38
3.38
3.37
3.36
3.35
3°
3.56
3.40
3.39
3.39
3.38
3.38
3.38
3.37
3.36
3.35
65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

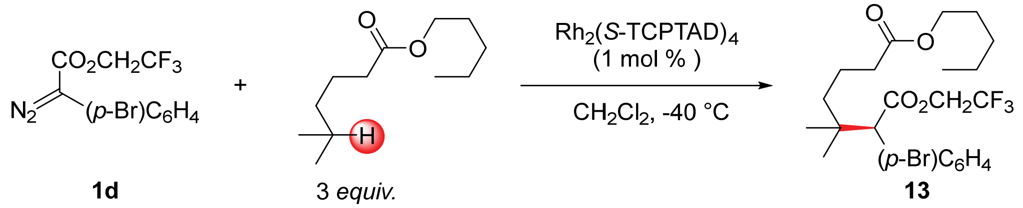

$CO_2CH_2CF_3$
N_2
$(p\text{-Br})C_6H_4$
1d
+
H
3 equiv.
$Rh_2(S\text{-TCPTAD})_4$
(1 mol %)
CH_2Cl_2, reflux
$CO_2CH_2CF_3$
$(p\text{-Br})C_6H_4$
12

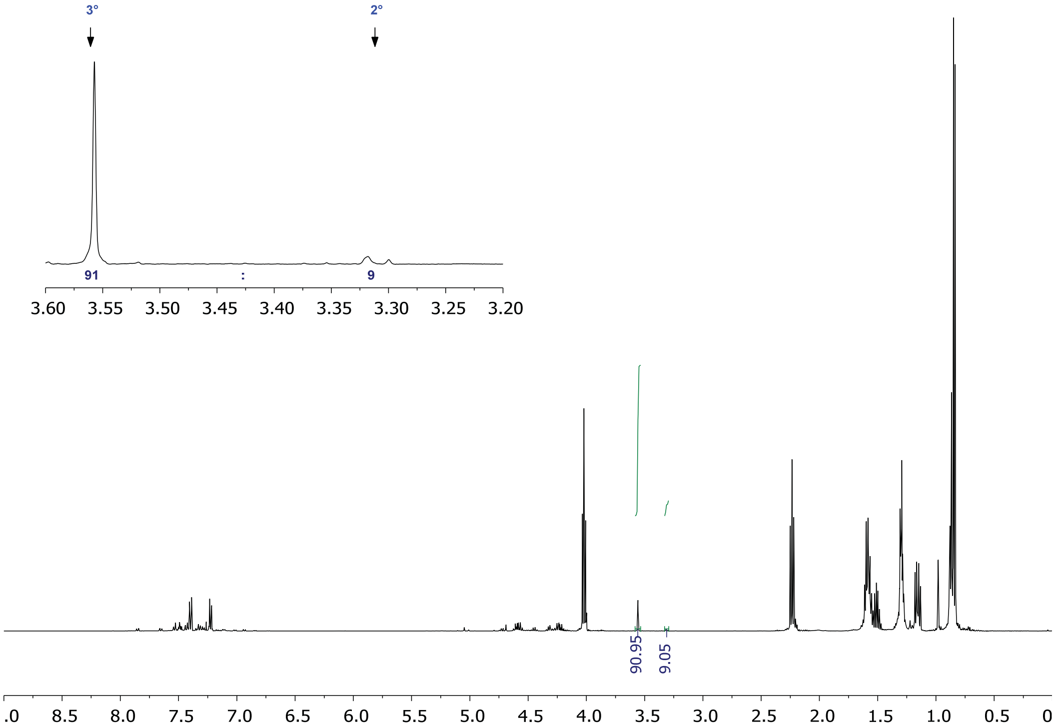

3°
3.54
3.54
10
4.00
3.90
3.80
3.70
3.60
3.50
3.40
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

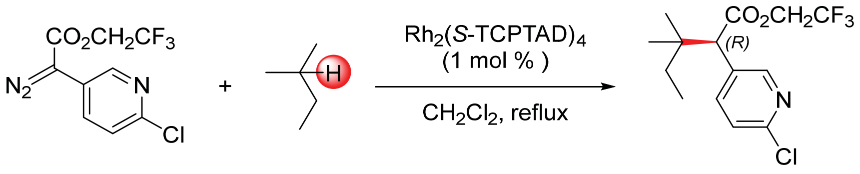

$CO_2CH_2CF_3$
N_2
$(p\text{-Br})C_6H_4$
+
O
O
H
$Rh_2(S\text{-TCPTAD})_4$
(1 mol %)
CH_2Cl_2, reflux
$CO_2CH_2CF_3$
$(p\text{-Br})C_6H_4$

1d 3 *equiv.* **13**

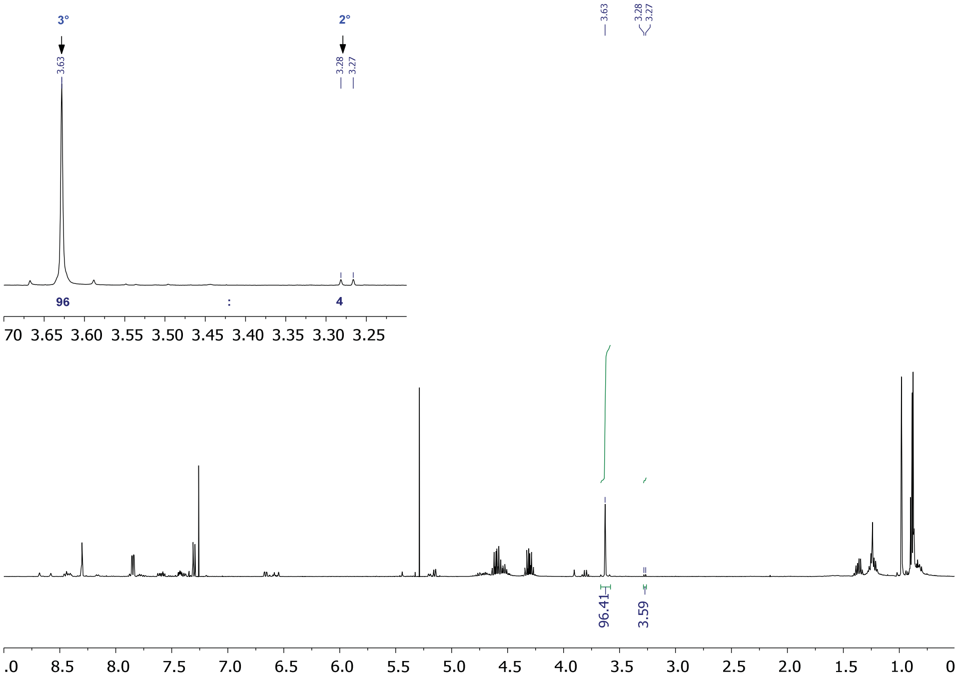

3°
2°
3.53
3.29
3.27
88
:
12
60
3.55
3.50
3.45
3.40
3.35
3.30
3.25
3.53
3.29
3.27
7.07
1.00
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

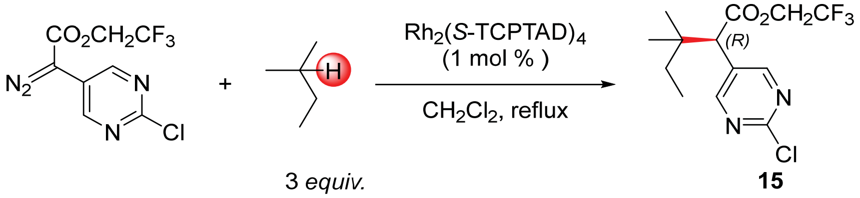

CO2CH2CF3
N2
(p-Br)C6H4
1d
+
O
O
H
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, -40 °C
O
O
CO2CH2CF3
(p-Br)C6H4
13


3°
2°
91
:
9
3.60
3.55
3.50
3.45
3.40
3.35
3.30
3.25
3.20
90.95
9.05
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0

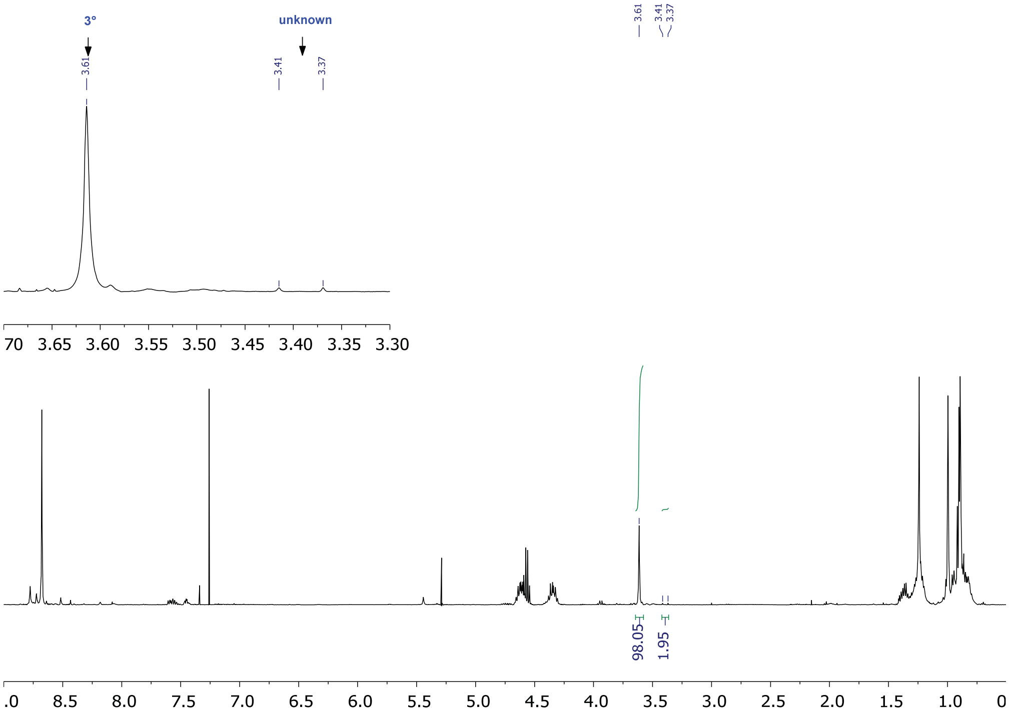

$CO_2CH_2CF_3$
N_2
N
Cl
+
H
$Rh_2(S\text{-}TCPTAD)_4$
(1 mol %)
CH_2Cl_2, reflux
$CO_2CH_2CF_3$
(R)
N
Cl
3 equiv.

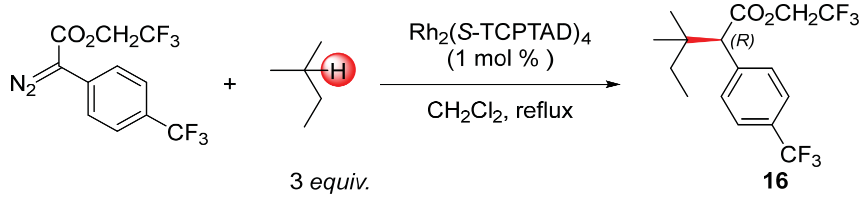
14

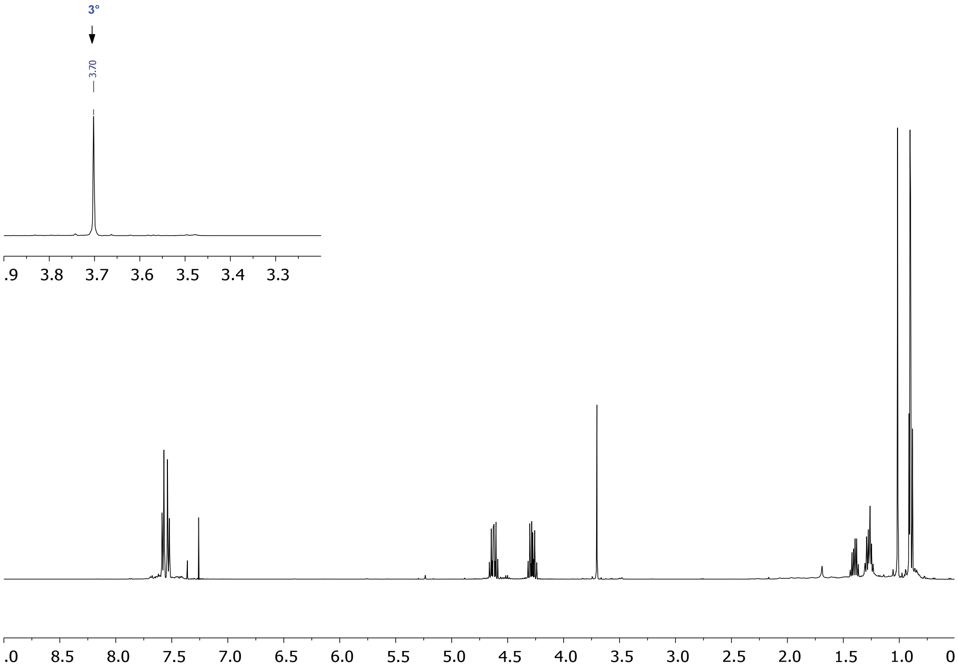

3°
2°
3.63
3.28
3.27
96
:
4
70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30 3.25
96.41
3.59
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

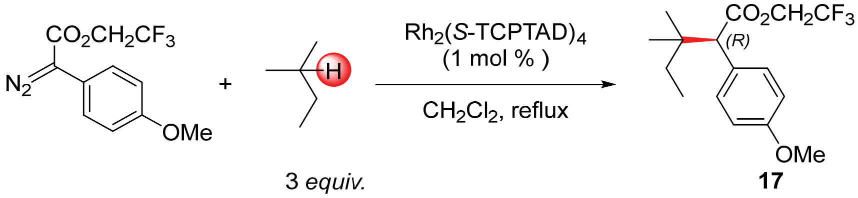

CO2CH2CF3
N2
N
N
Cl
+
H
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
CO2CH2CF3
(R)
N
N
Cl

15

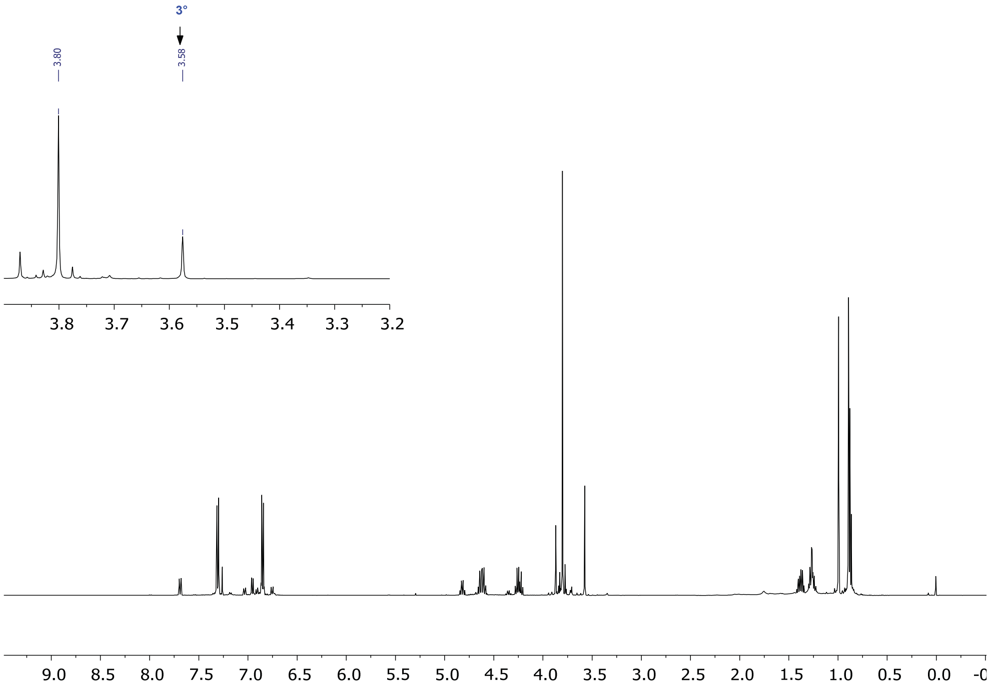

3°
unknown
3.61
3.41
3.37
70
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
3.61
3.41
3.37
98.05
1.95
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

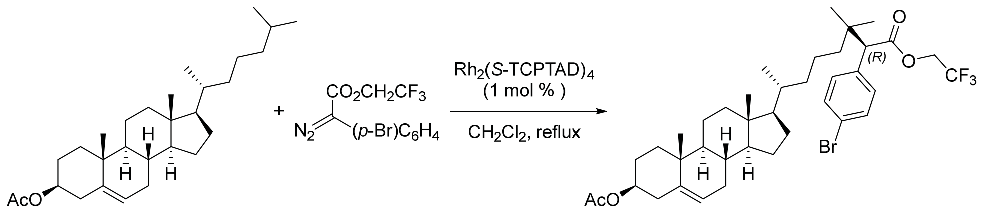

CO2CH2CF3
N2
CF3
+
H
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
CO2CH2CF3
(R)
CF3
16


3°
3.70
.9
3.8
3.7
3.6
3.5
3.4
3.3
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0


CO2CH2CF3
N2
OMe
+
H
3 equiv.
Rh2(S-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
CO2CH2CF3
(R)
OMe

17

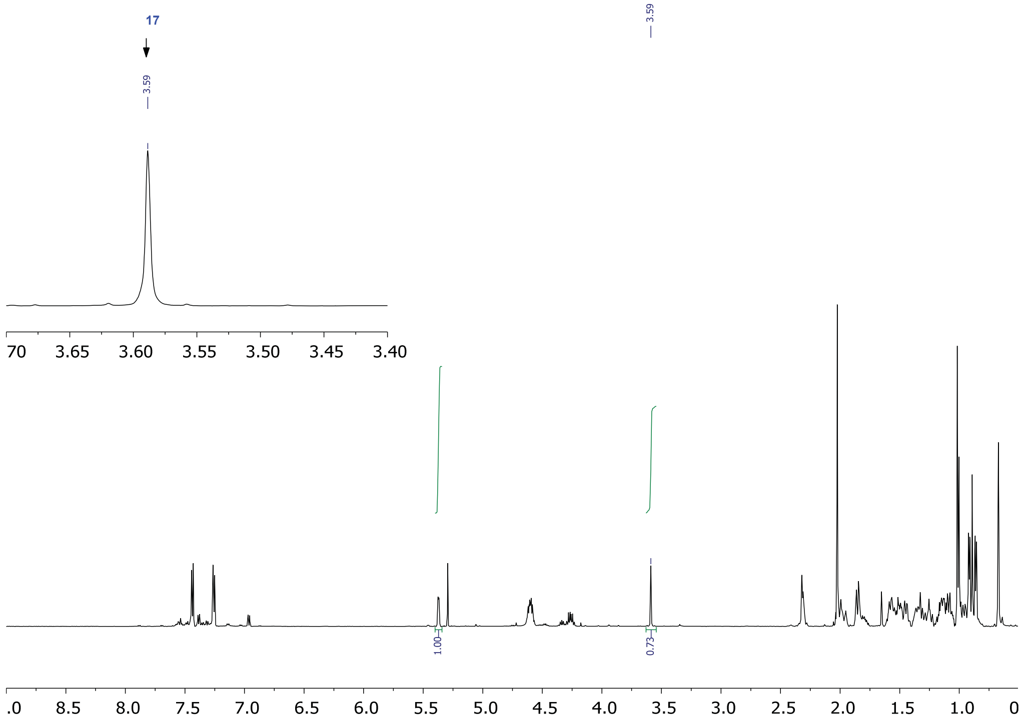

3°
3.80
3.58
3.8
3.7
3.6
3.5
3.4
3.3
3.2
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

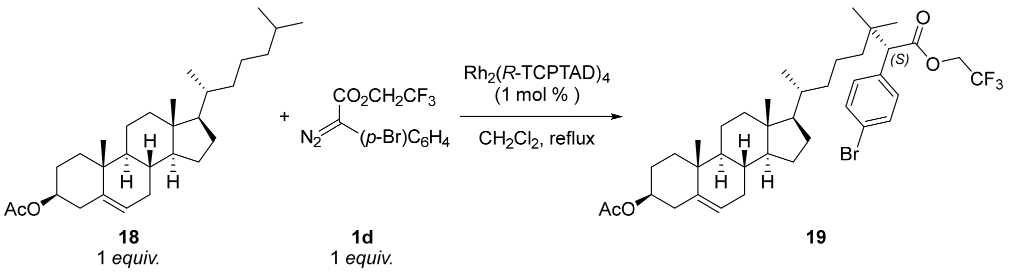


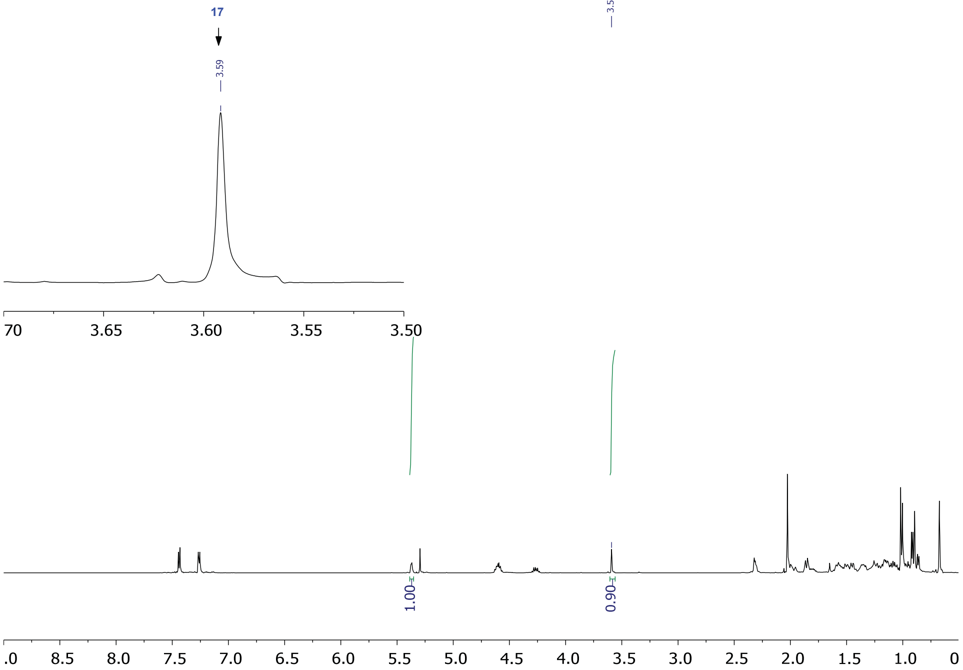
18
1 *equiv.*

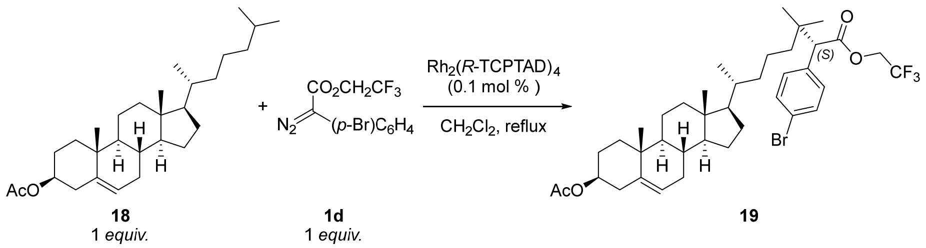
1d
1 *equiv.*

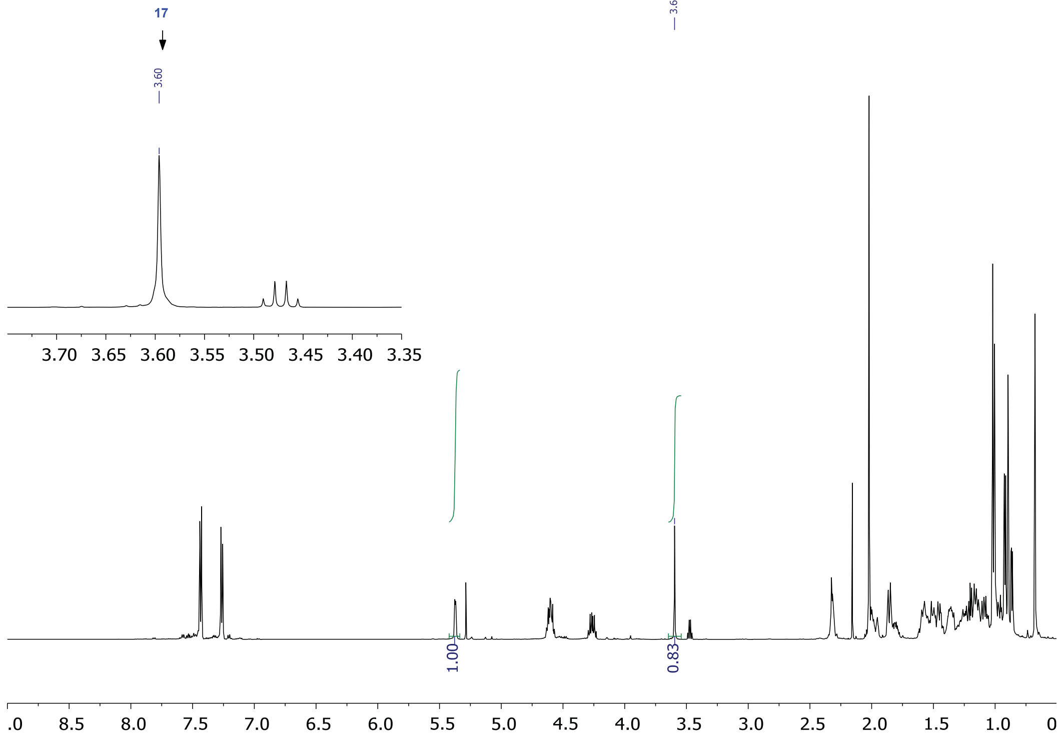
19

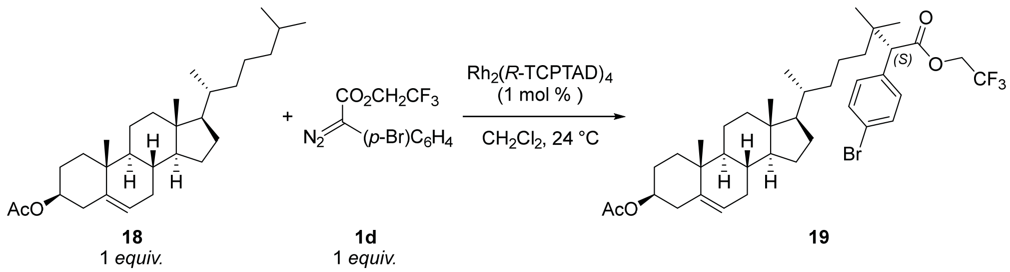


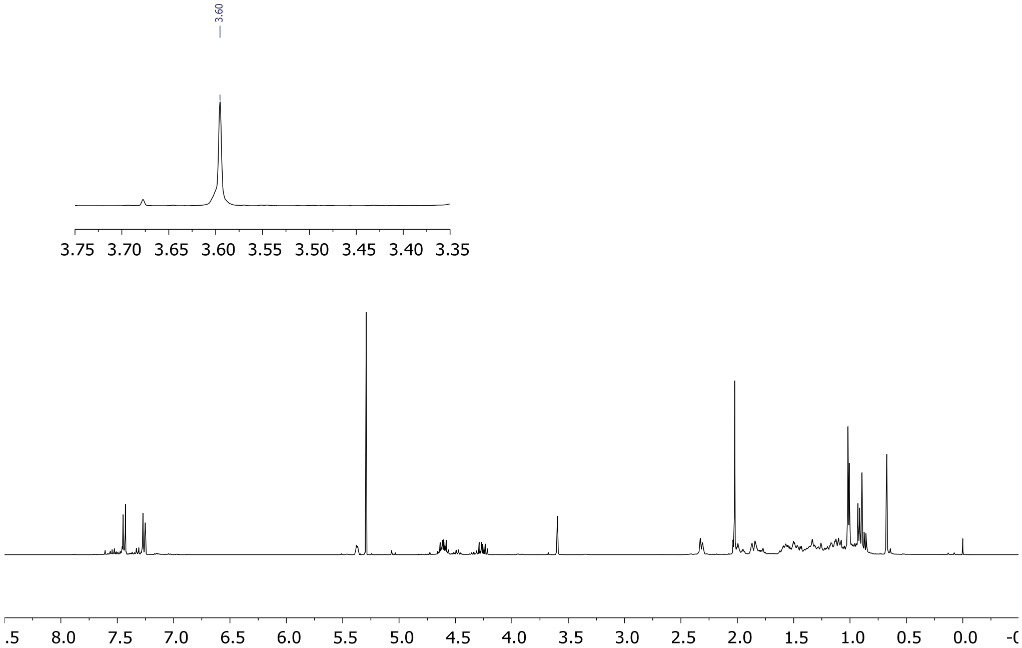

AcO
18
1 equiv.
+
CO2CH2CF3
N2
(p-Br)C6H4
1d
1 equiv.
Rh2(R-TCPTAD)4
(1 mol %)
CH2Cl2, reflux
AcO
(S)
O
O
CF3
Br
19

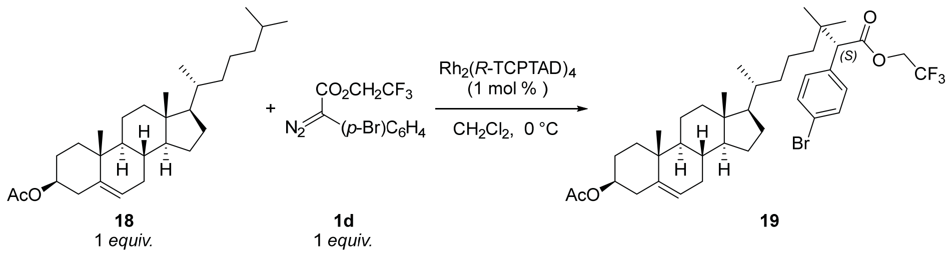

17
3.59
70
3.65
3.60
3.55
3.50
3.59
1.00
0.90
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

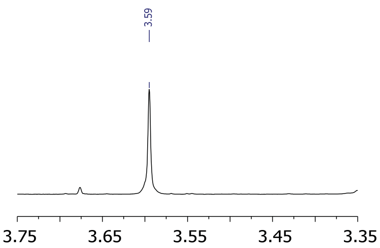

Rh$_2$(R-TCPTAD)$_4$
(0.1 mol %)
CH$_2$Cl$_2$, reflux
CO$_2$CH$_2$CF$_3$
N$_2$
(p-Br)C$_6$H$_4$
AcO
H
(S)
CF$_3$
Br
18
1 equiv.
1d
1 equiv.
19

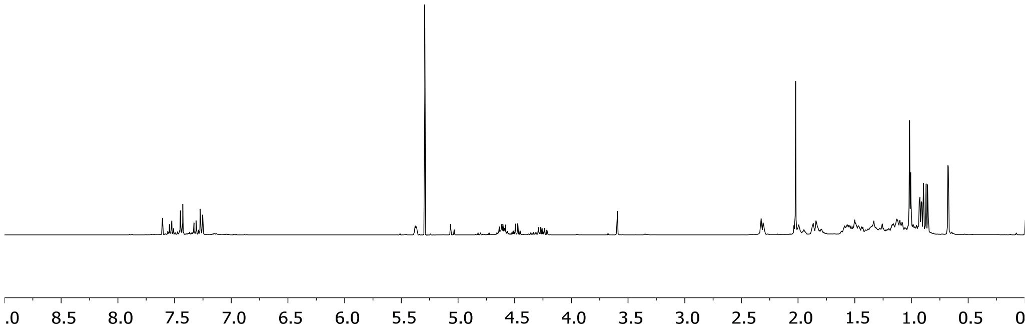

17
3.60
3.60
3.70 3.65 3.60 3.55 3.50 3.45 3.40 3.35
1.00
0.83
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0

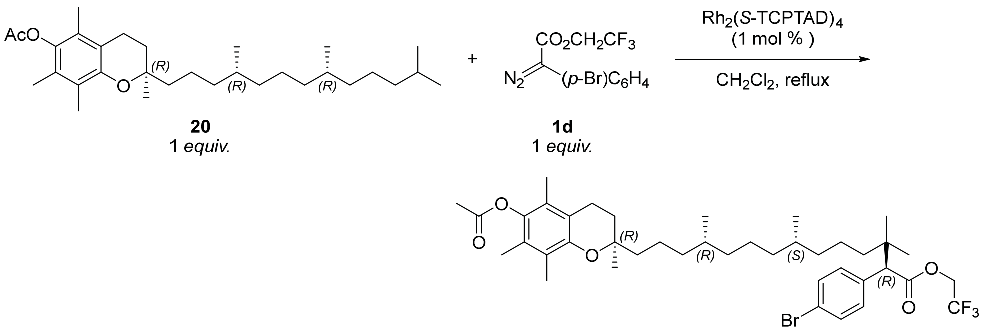

AcO
18
1 equiv.
+
$CO_2CH_2CF_3$
N_2
(p-Br)C_6H_4
1d
1 equiv.
Rh_2(R-TCPTAD)$_4$
(1 mol %)
CH_2Cl_2, 24 °C
AcO
(S)
O
O
CF_3
Br
H
H
H
19


3.60
3.75 3.70 3.65 3.60 3.55 3.50 3.45 3.40 3.35
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


AcO
18
1 equiv.
+
$CO_2CH_2CF_3$
N_2
$(p\text{-Br})C_6H_4$
1d
1 equiv.
$Rh_2(R\text{-TCPTAD})_4$
(1 mol %)
CH_2Cl_2, 0 °C
(S)
CF_3
Br
AcO
19


3.59
3.75
3.65
3.55
3.45
3.35

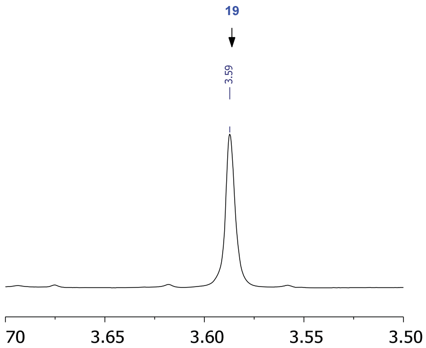

.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0

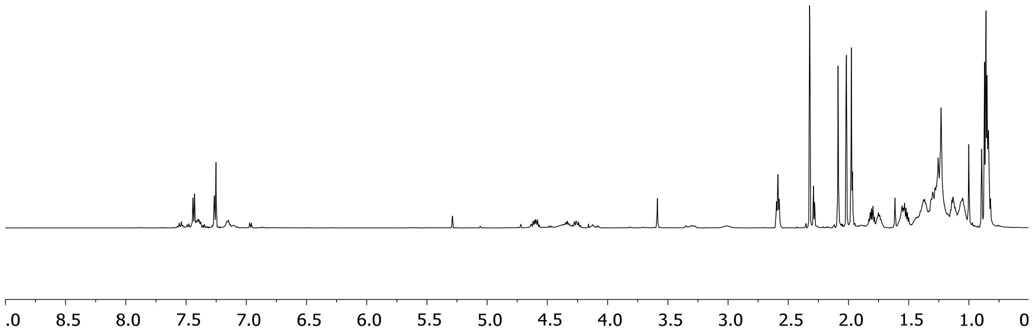


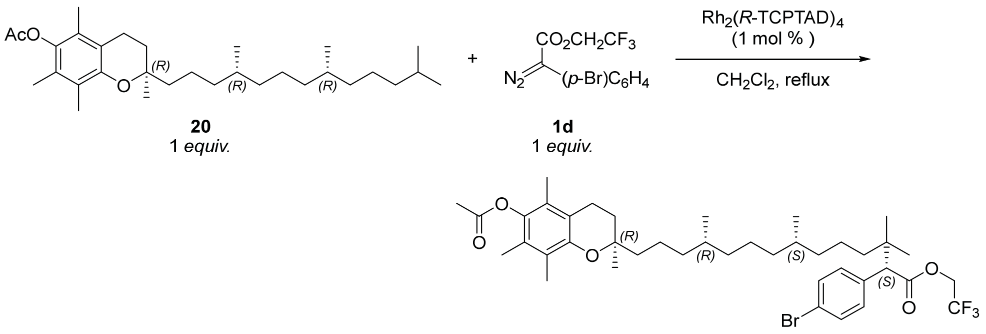
20
1 *equiv.*

1d
1 *equiv.*

21



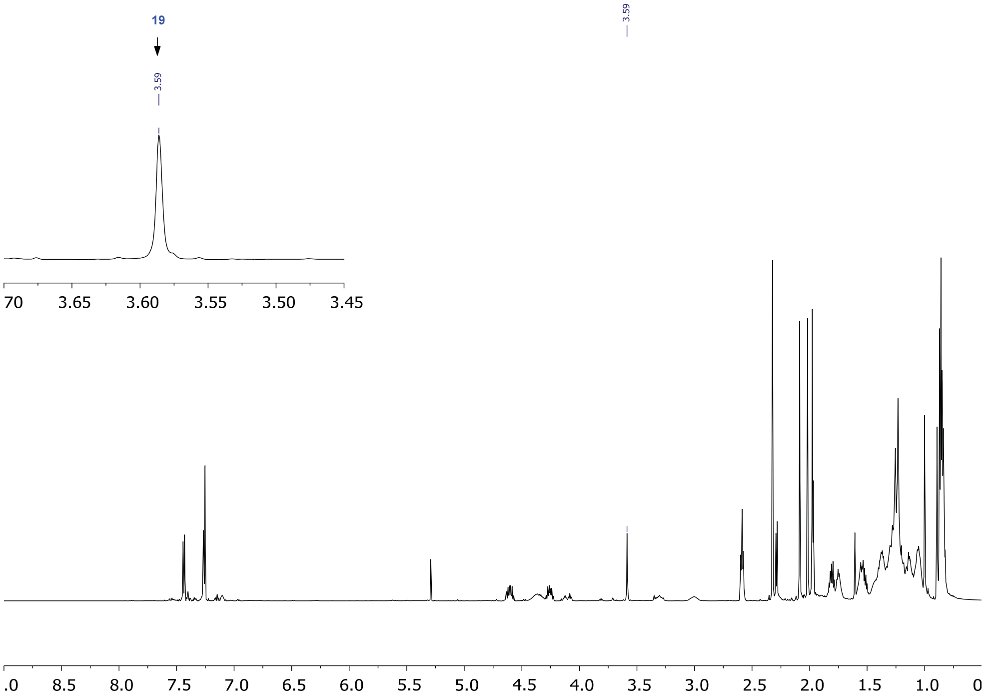


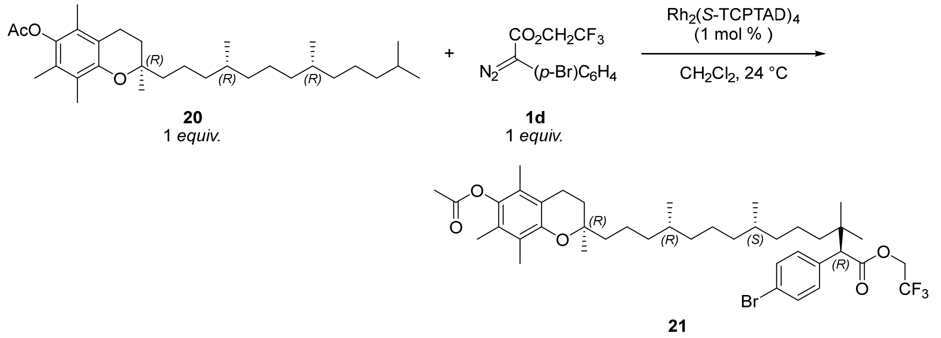


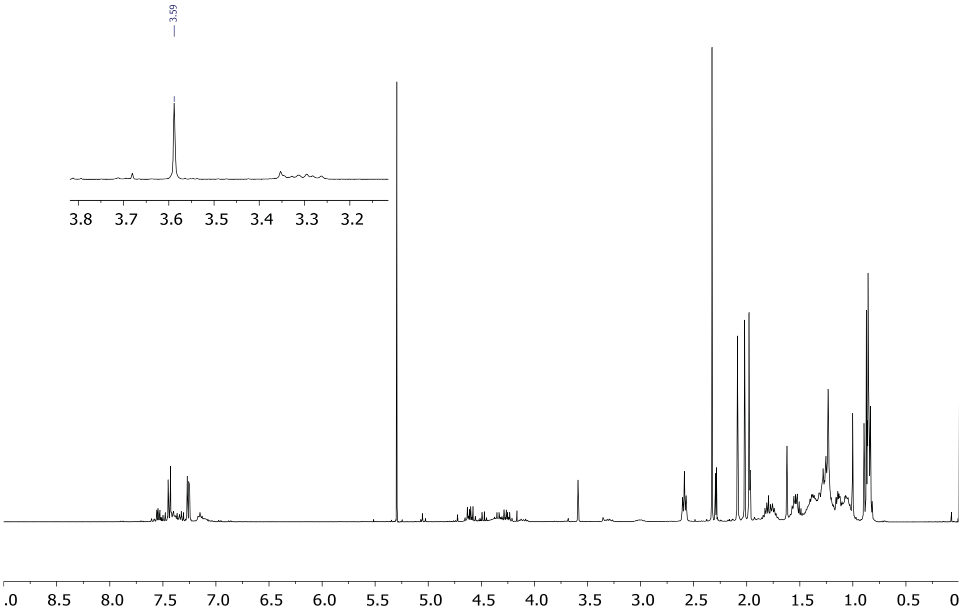
20
1 *equiv.*

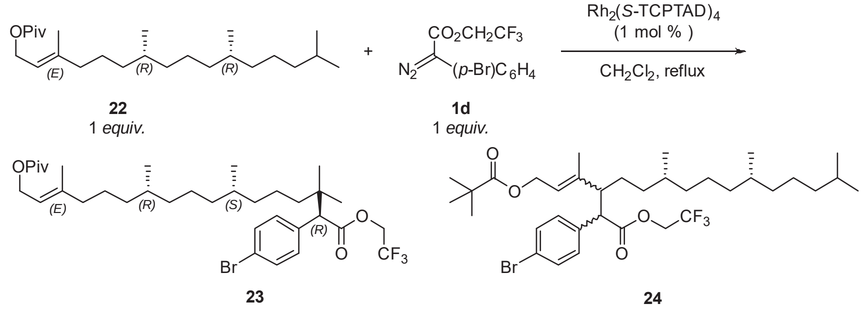
1d
1 *equiv.*

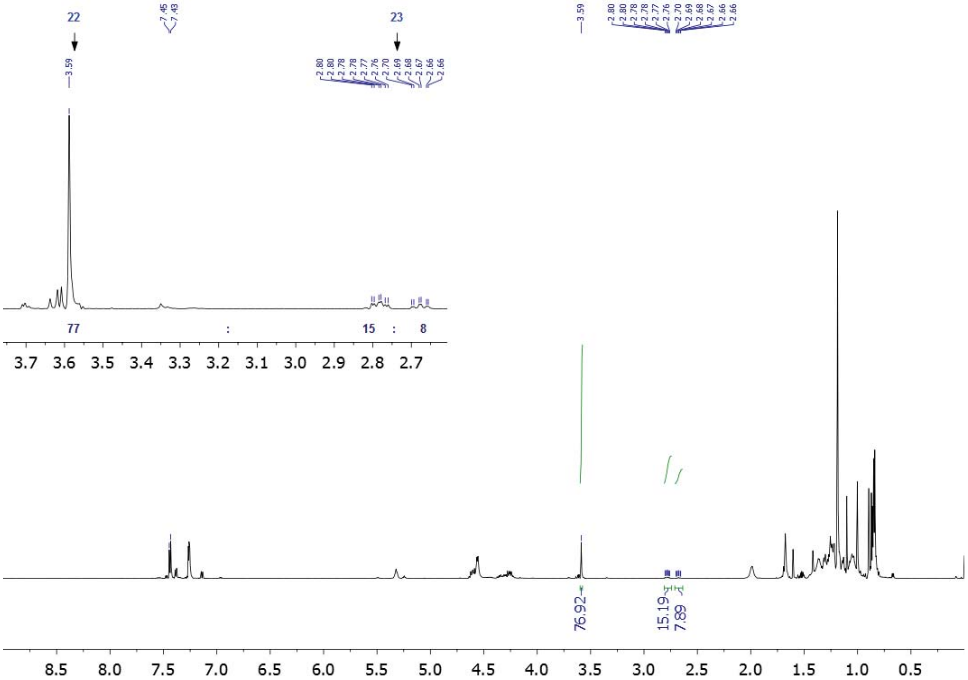
21

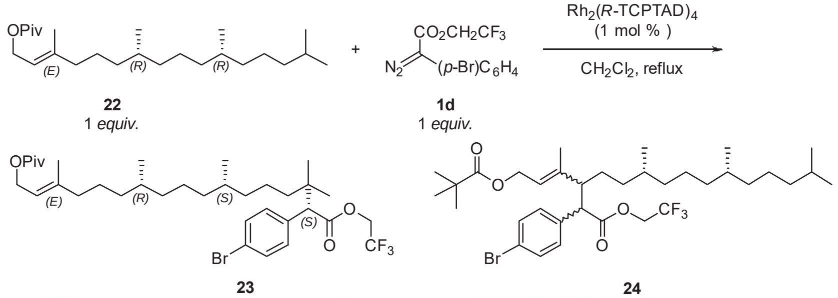



Rh$_2$(*S*-TCPTAD)$_4$
(1 mol %)
CH$_2$Cl$_2$, 24 °C
AcO
(R)
CO$_2$CH$_2$CF$_3$
N$_2$
(*p*-Br)C$_6$H$_4$
+
20
1 *equiv.*
1d
1 *equiv.*
(S)
CF$_3$
Br
21


3.59
3.8 3.7 3.6 3.5 3.4 3.3 3.2
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0


OPiv
(E)
(R)
(R)
+
$CO_2CH_2CF_3$
N_2
(p-Br)C_6H_4
Rh_2(S-TCPTAD)$_4$
(1 mol %)
CH_2Cl_2, reflux
22
1 equiv.
1d
1 equiv.
OPiv
(E)
(R)
(S)
(R)
O
Br
O
CF_3
23
O
O
O
CF_3
Br
O
24


22
23
7.45
7.43
3.59
2.80
2.80
2.78
2.78
2.77
2.76
2.70
2.69
2.68
2.67
2.66
2.66
77
:
15
:
8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
76.92
15.19
7.89
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

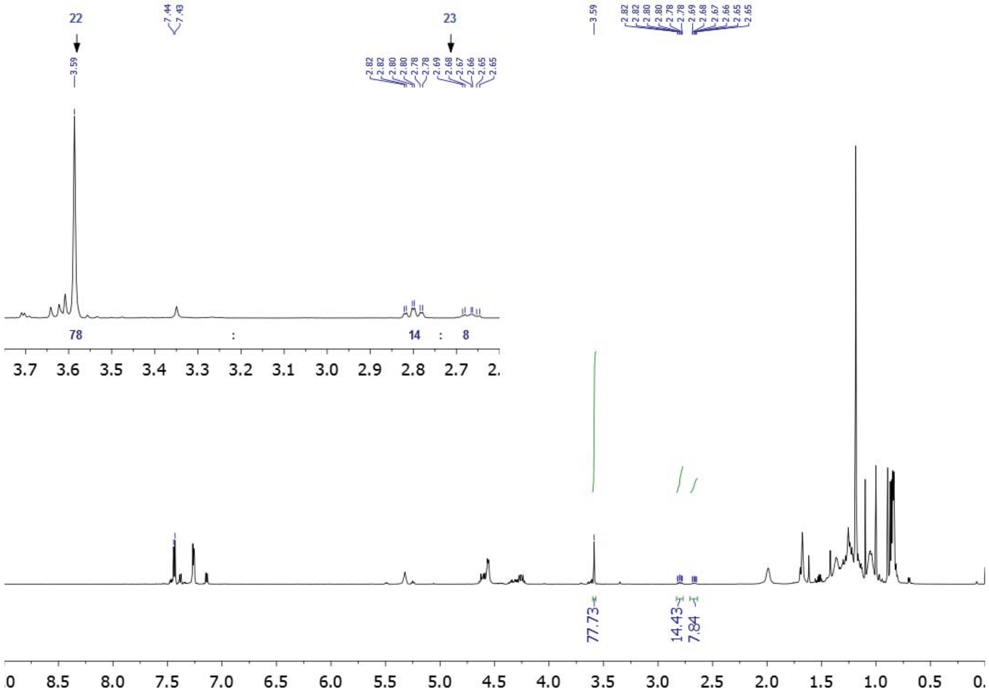


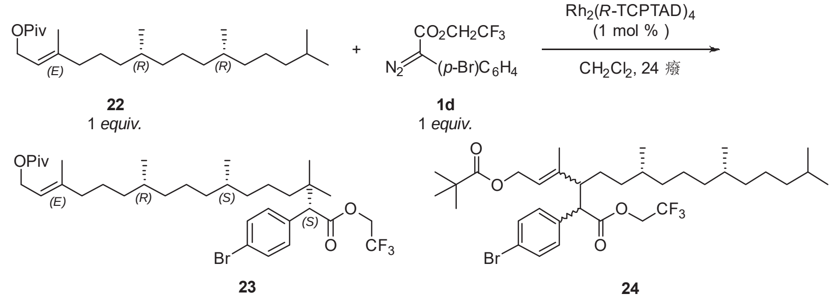
22
1 *equiv.*

1d
1 *equiv.*

23

24



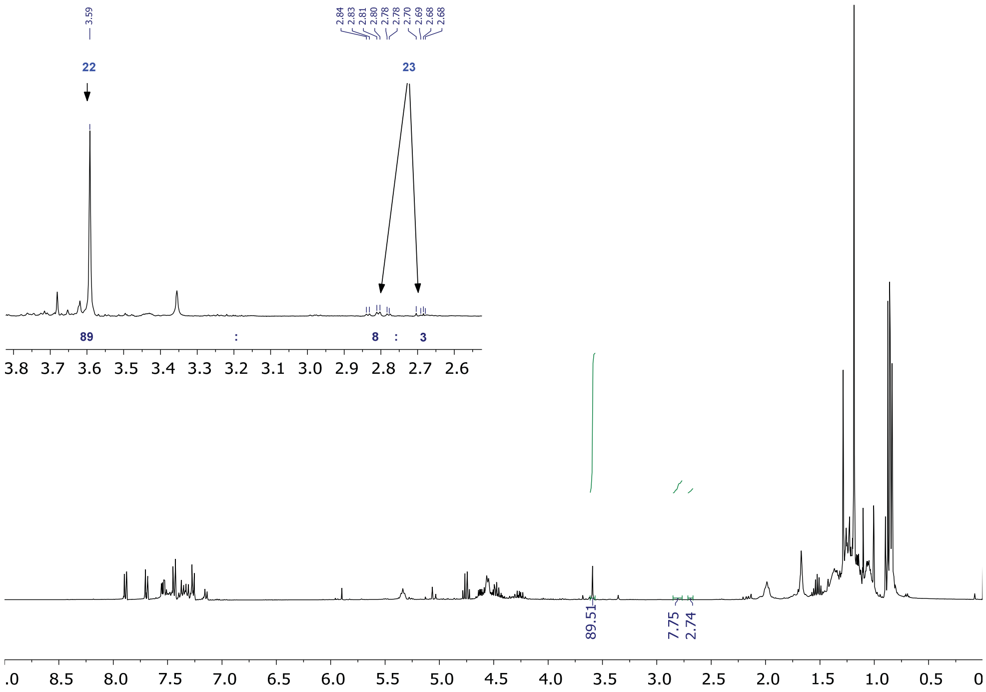


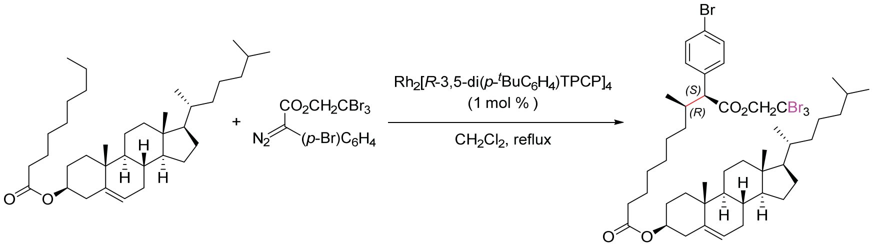
22
1 *equiv.*

1d
1 *equiv.*

23

24

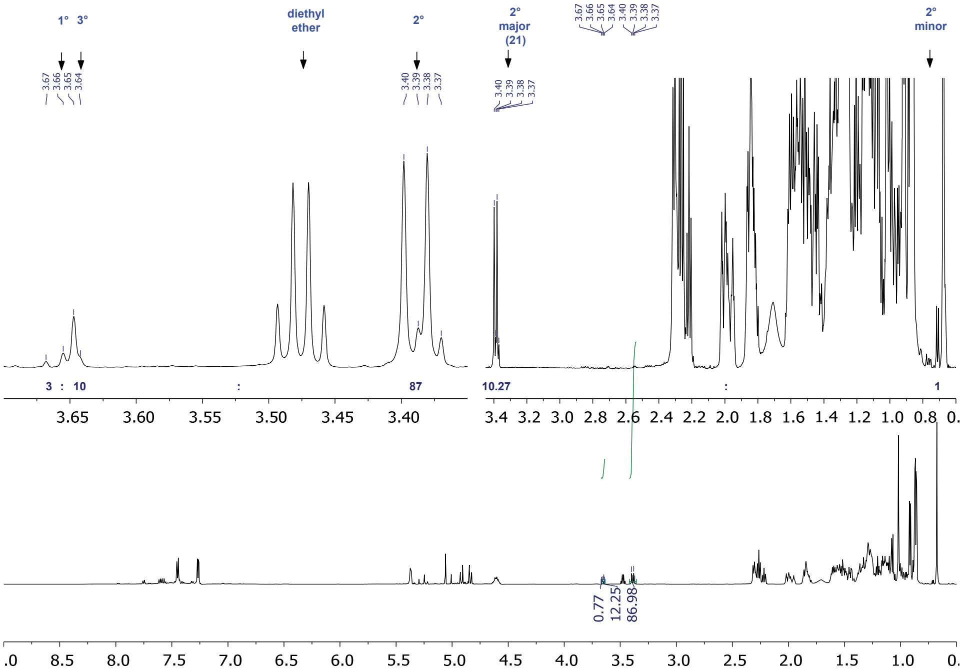


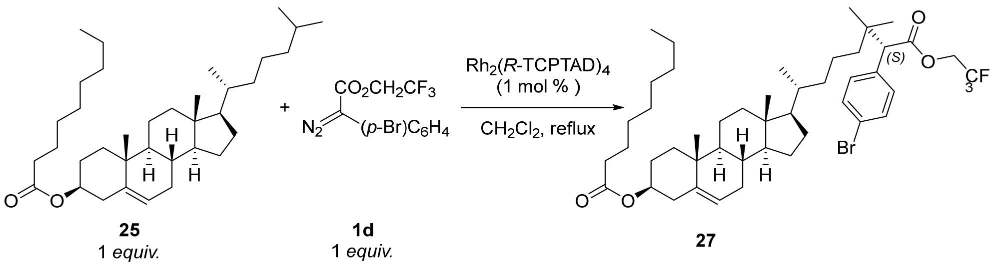


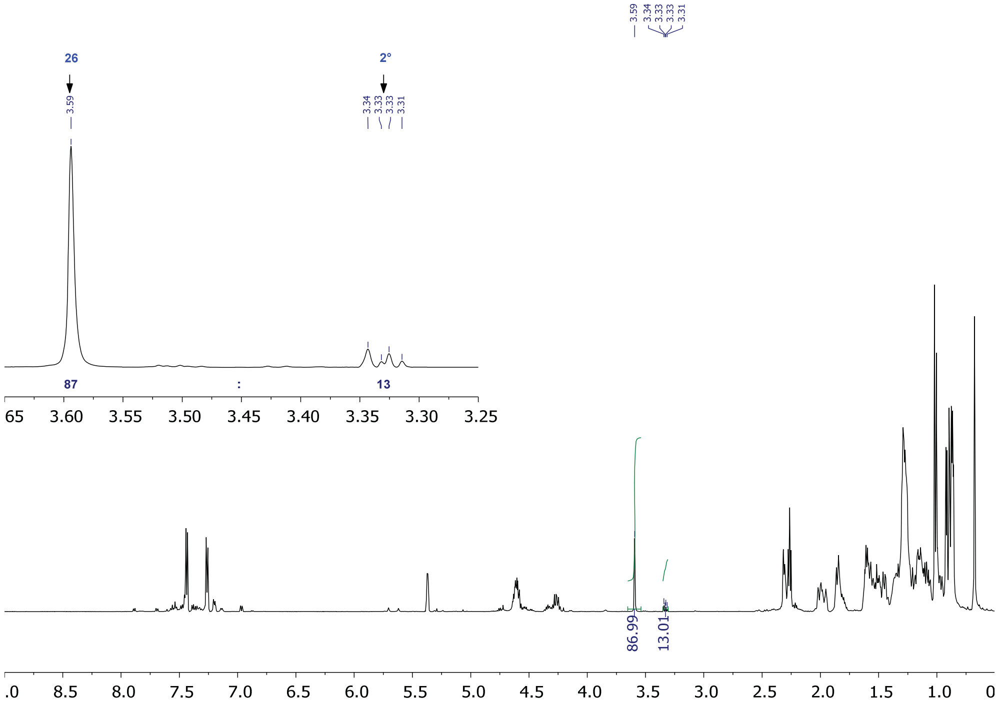
25 1 *equiv.*

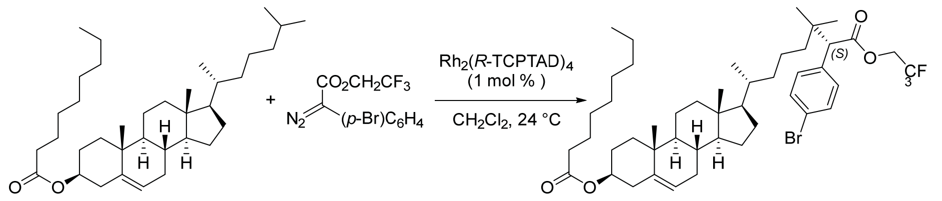
1c 1 *equiv.*

26




Rh$_2$(*R*-TCPTAD)$_4$
(1 mol %)
CH$_2$Cl$_2$, reflux
+
CO$_2$CH$_2$CF$_3$
N$_2$
(*p*-Br)C$_6$H$_4$
H
H
H
O
O
Br
(*S*)
O
O
CF$_3$
25
1 *equiv.*
1d
1 *equiv.*
27

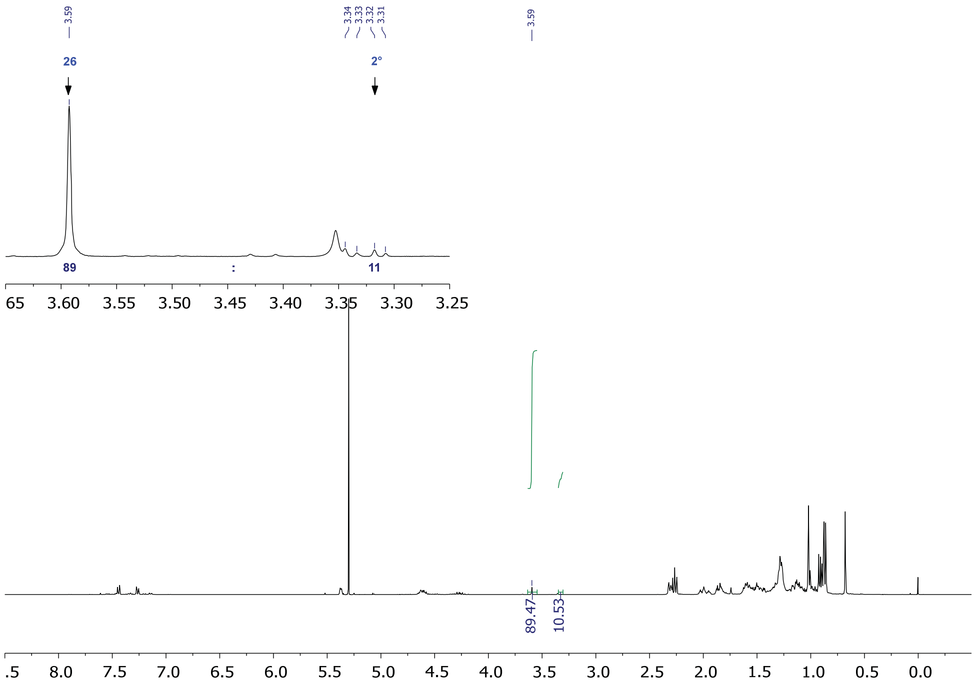

3.59
3.34
3.33
3.33
3.31
26
2°
87
:
13
65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
3.25
86.99
13.01
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0

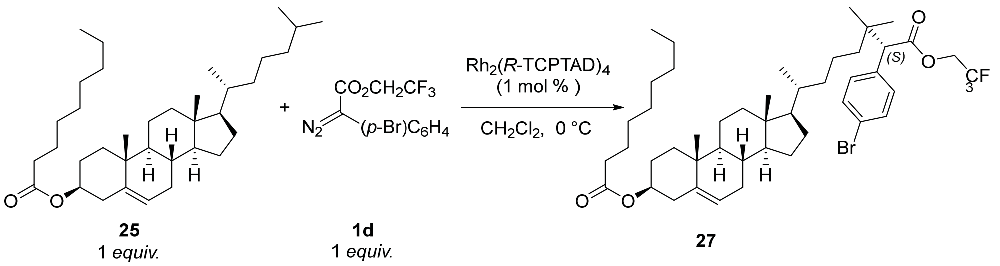


25
1 *equiv.*

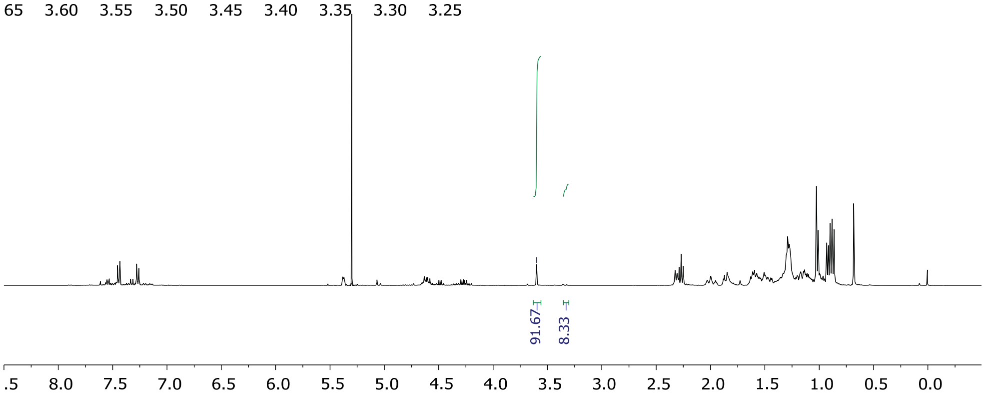
1d
1 *equiv.*

27




Rh$_2$(*R*-TCPTAD)$_4$
(1 mol %)
CH$_2$Cl$_2$, 0 °C
CO$_2$CH$_2$CF$_3$
N$_2$
(*p*-Br)C$_6$H$_4$
+
(*S*)
Br
CF$_3$
25
1 *equiv.*
1d
1 *equiv.*
27


3.59
3.35
3.34
3.32
3.31
26
2°
92
:
8
65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
3.25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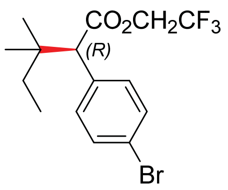
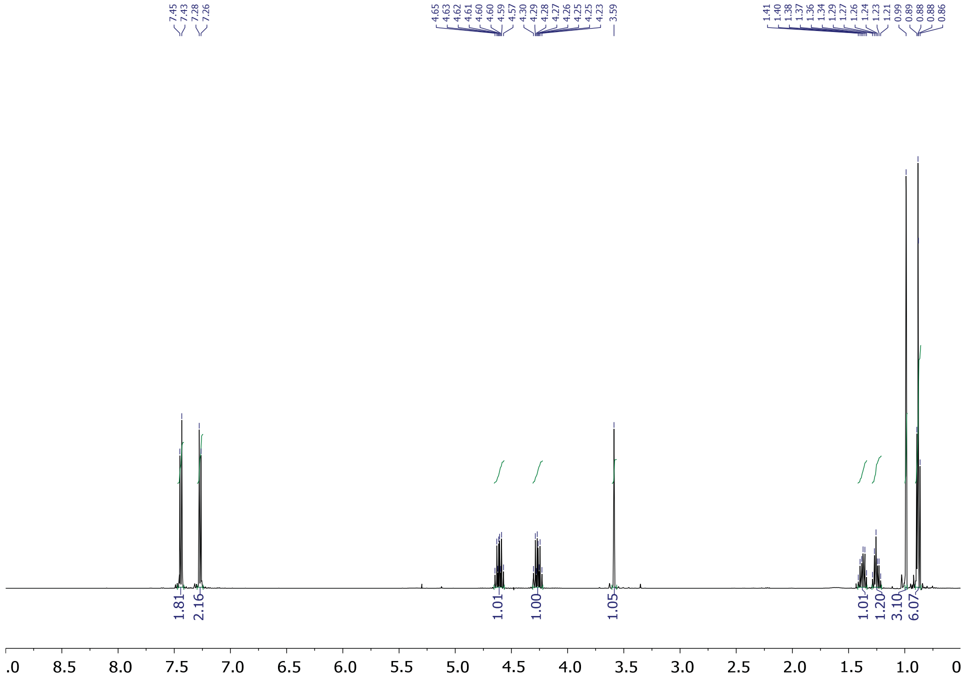
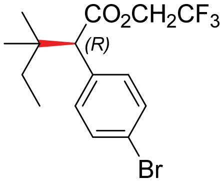
8. NMR Spectra



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(R)
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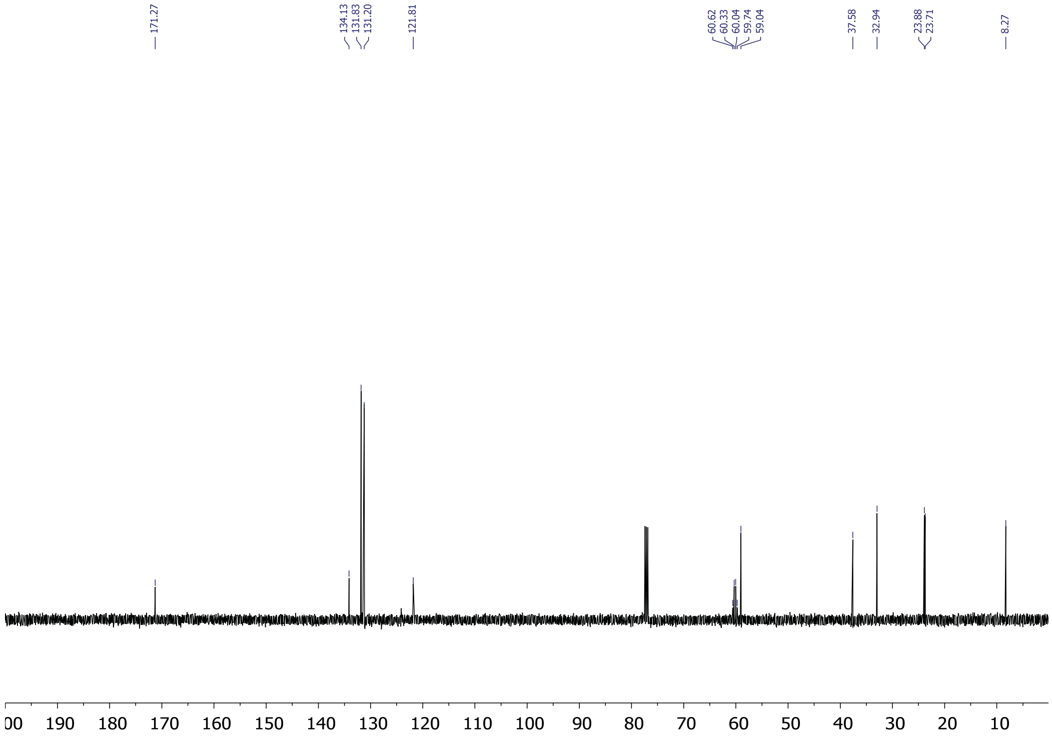
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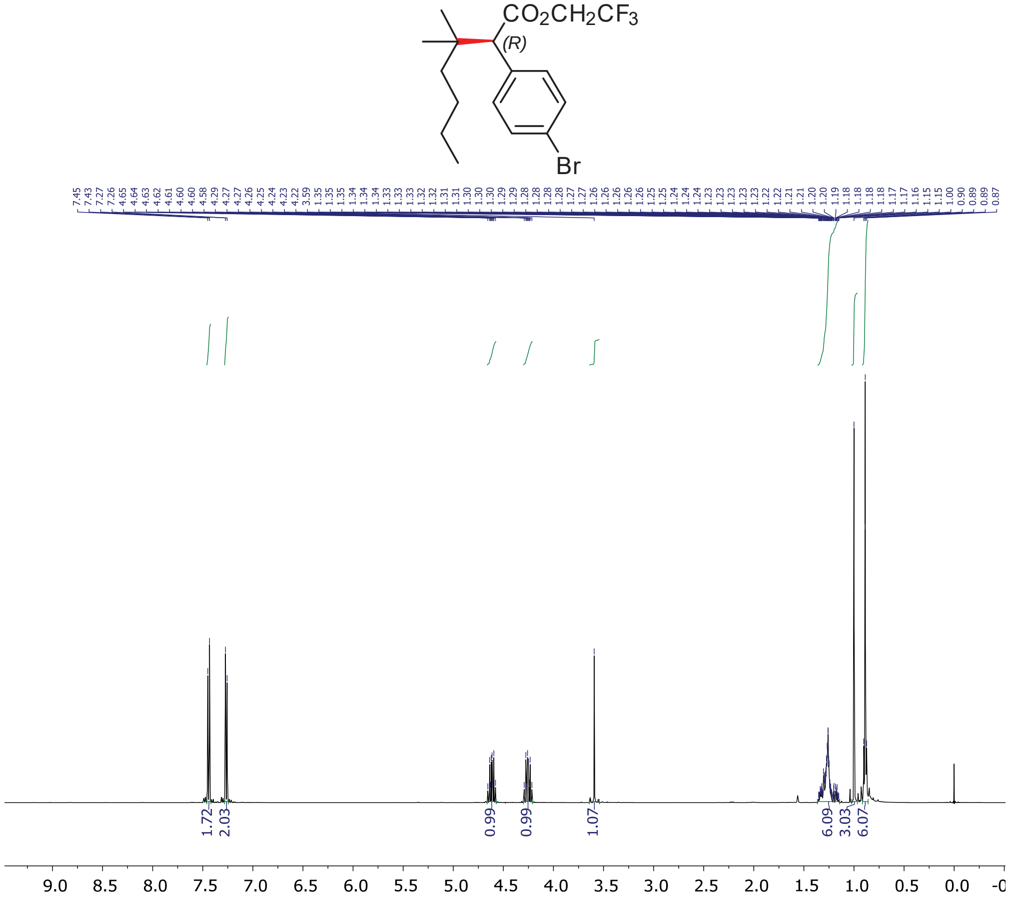
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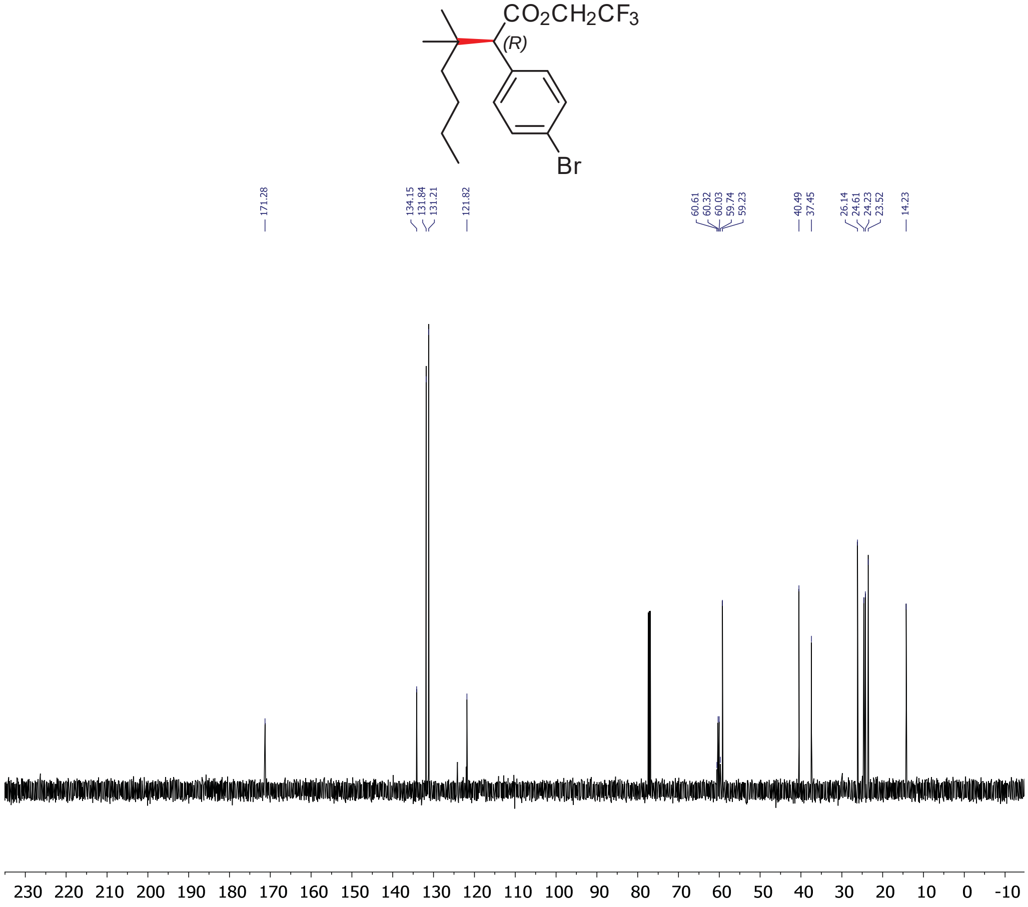
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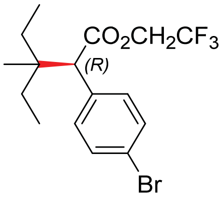
CO$_2$CH$_2$CF$_3$
(R)
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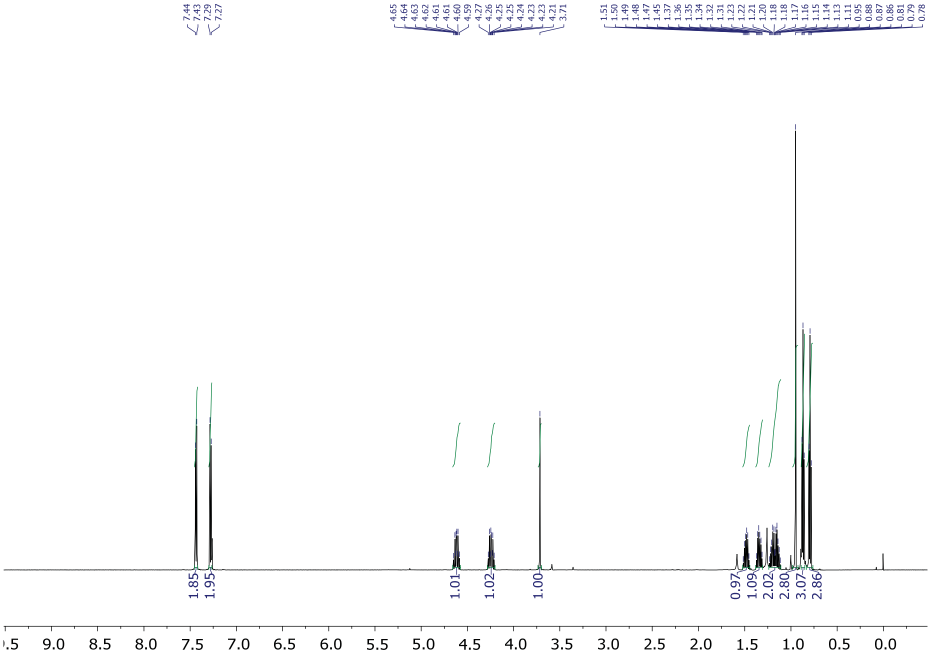
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1.09
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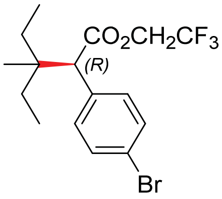
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(R)
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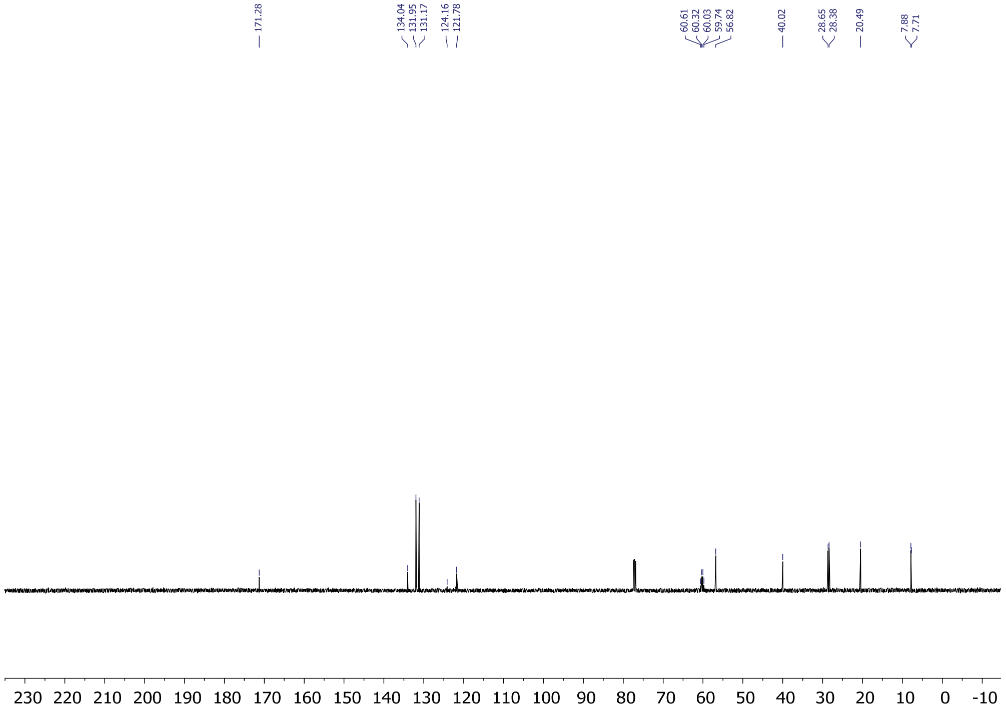
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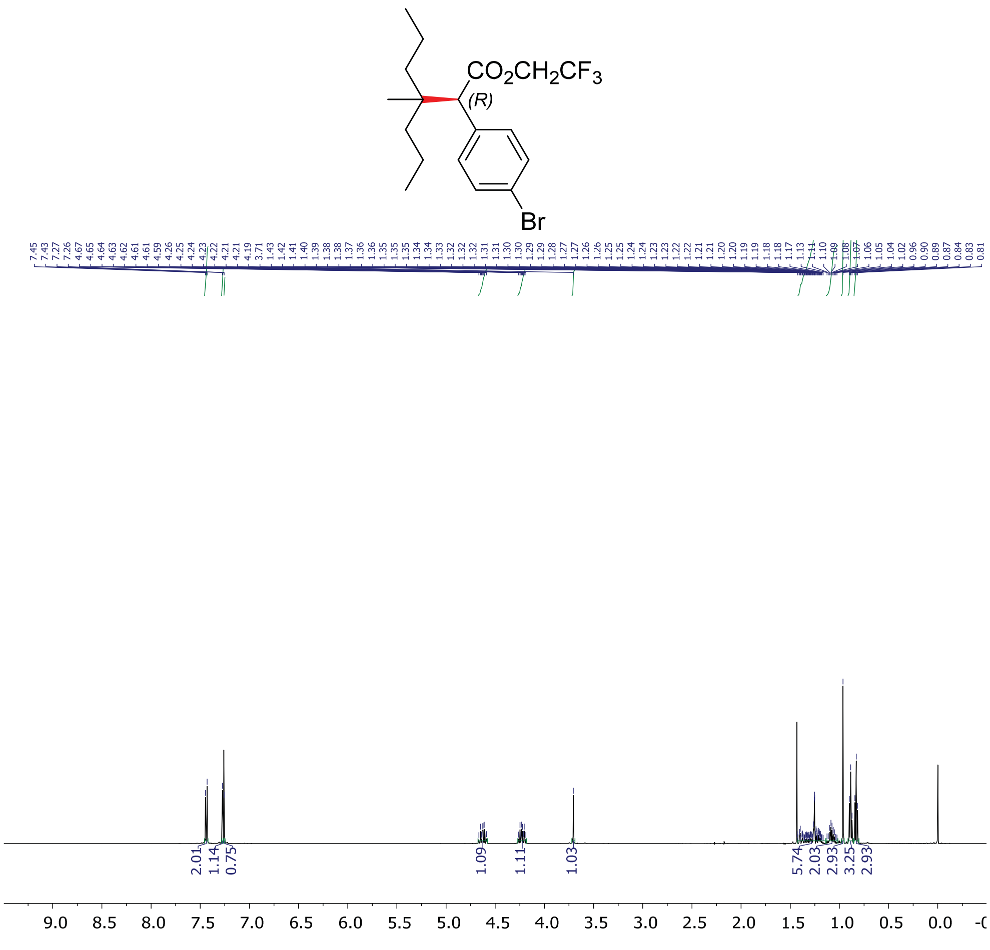
CO2CH2CF3
(R)
Br
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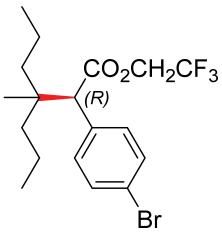
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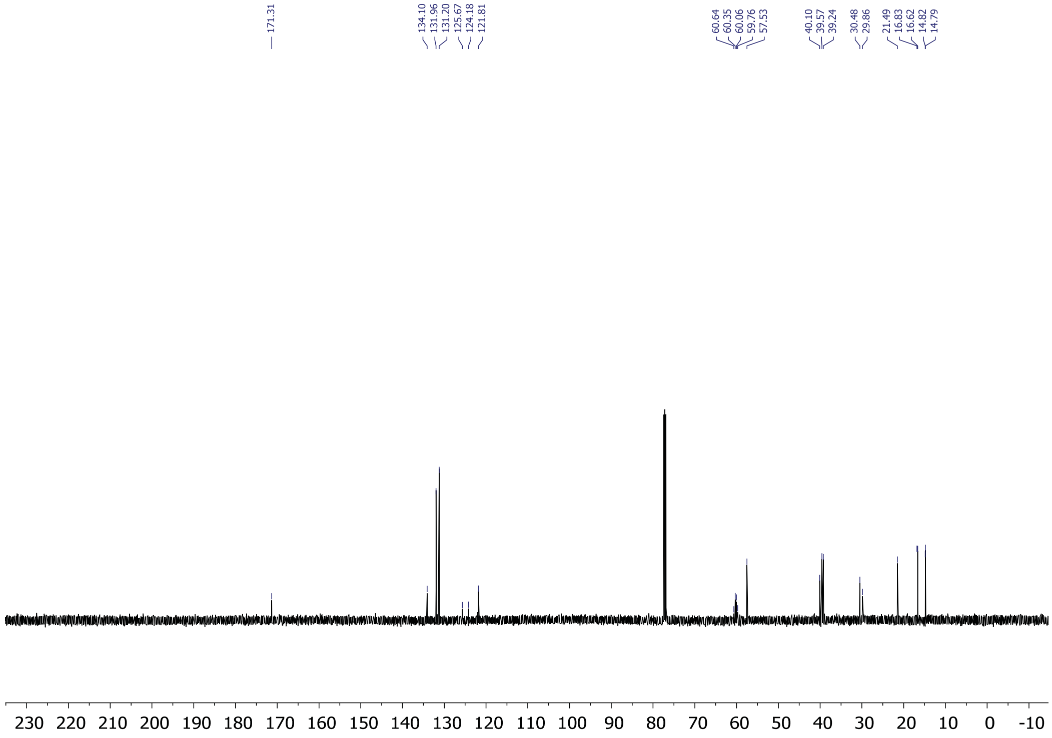
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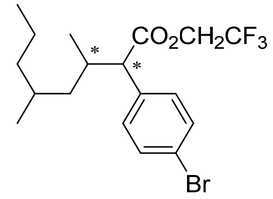
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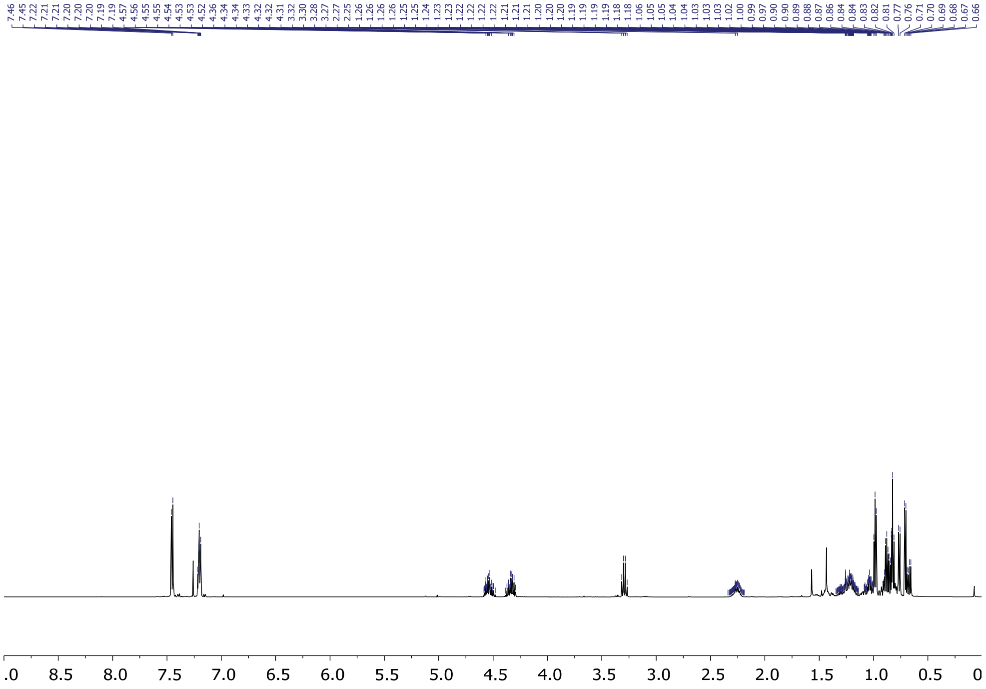
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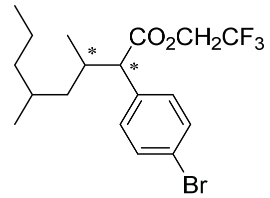
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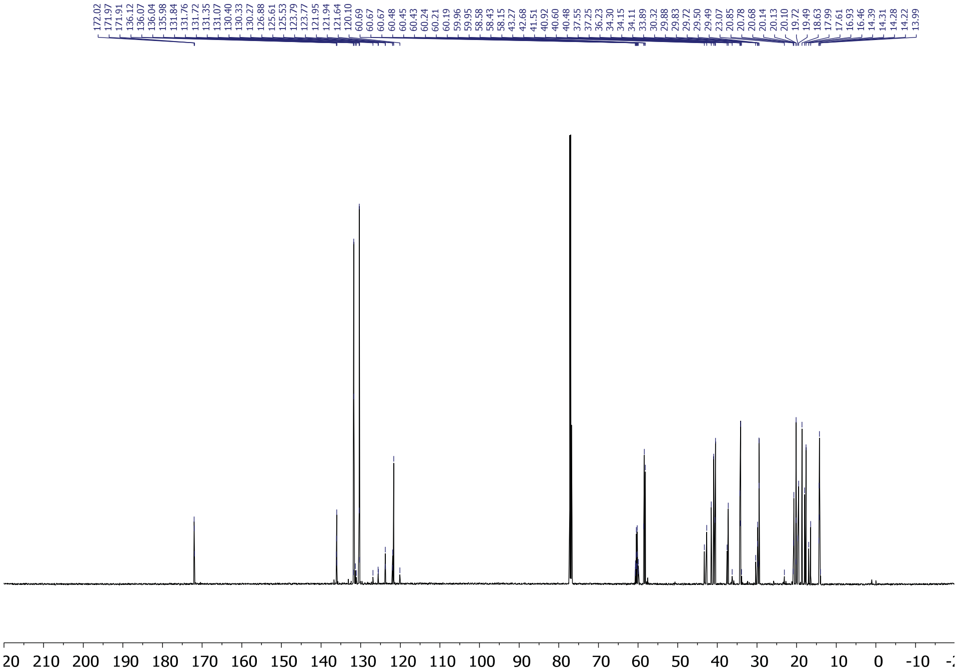
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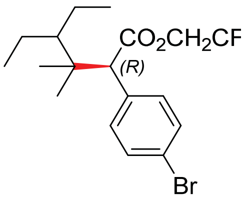
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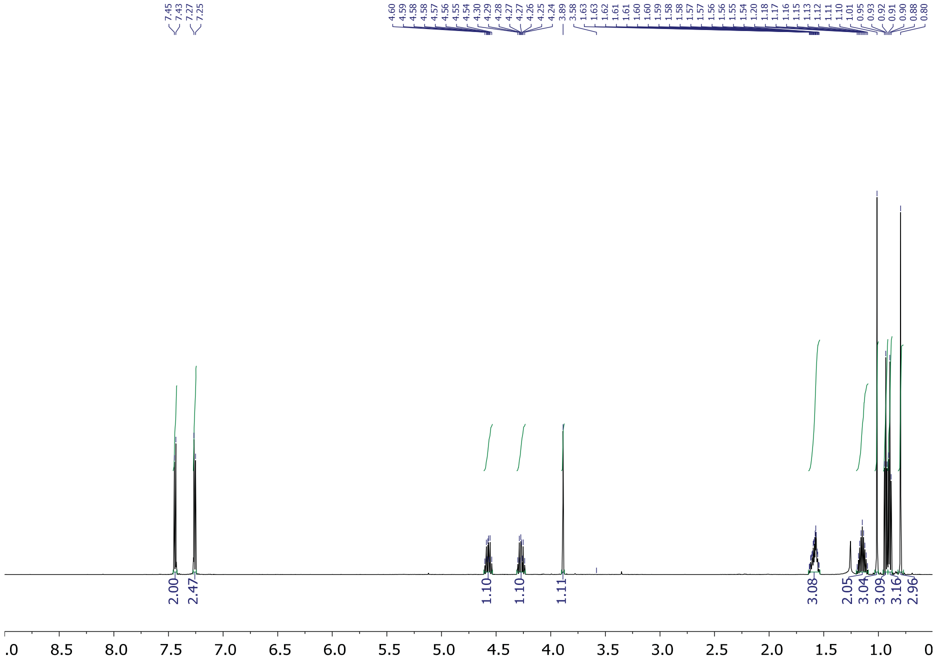
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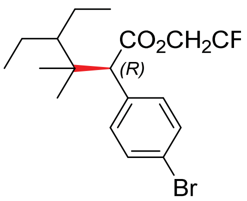
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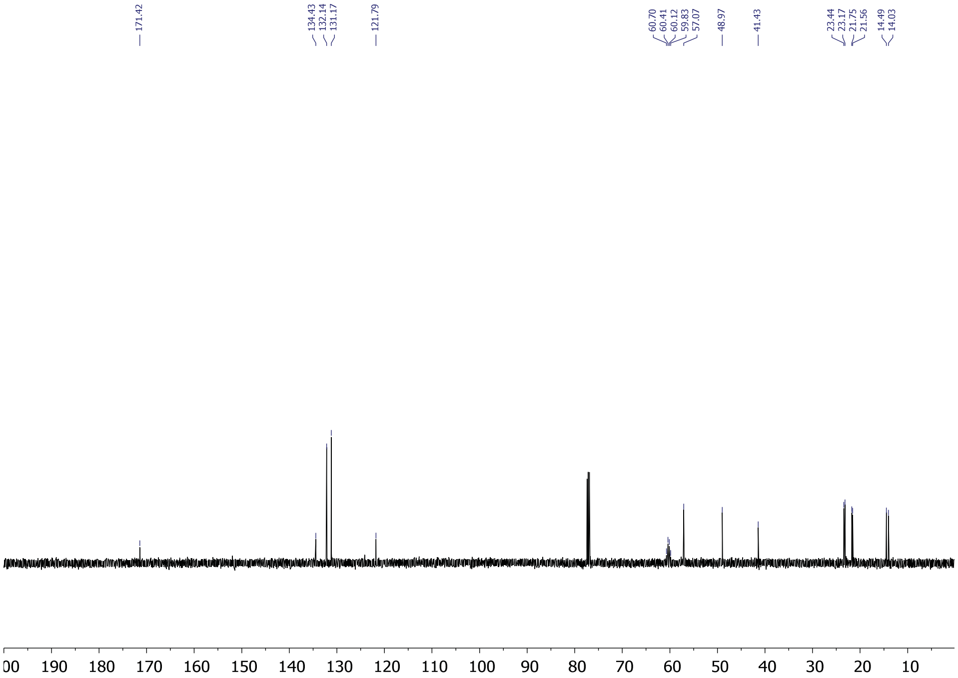
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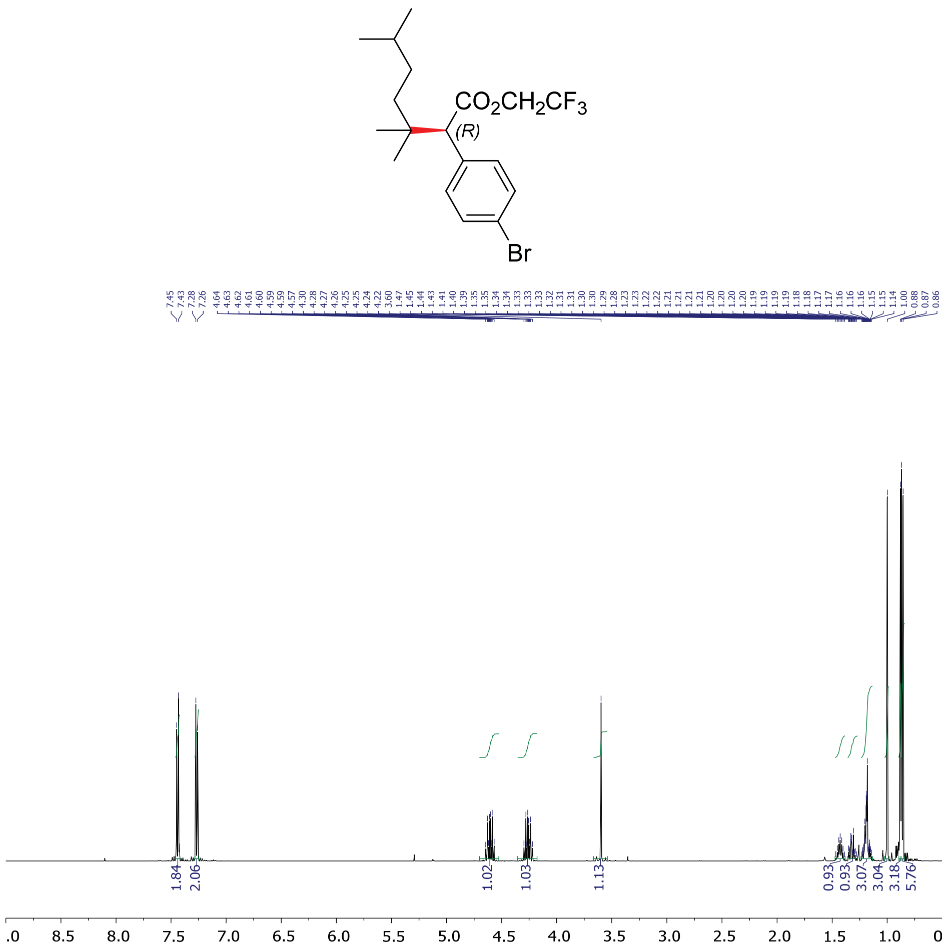
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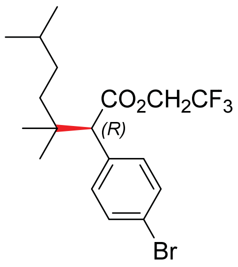
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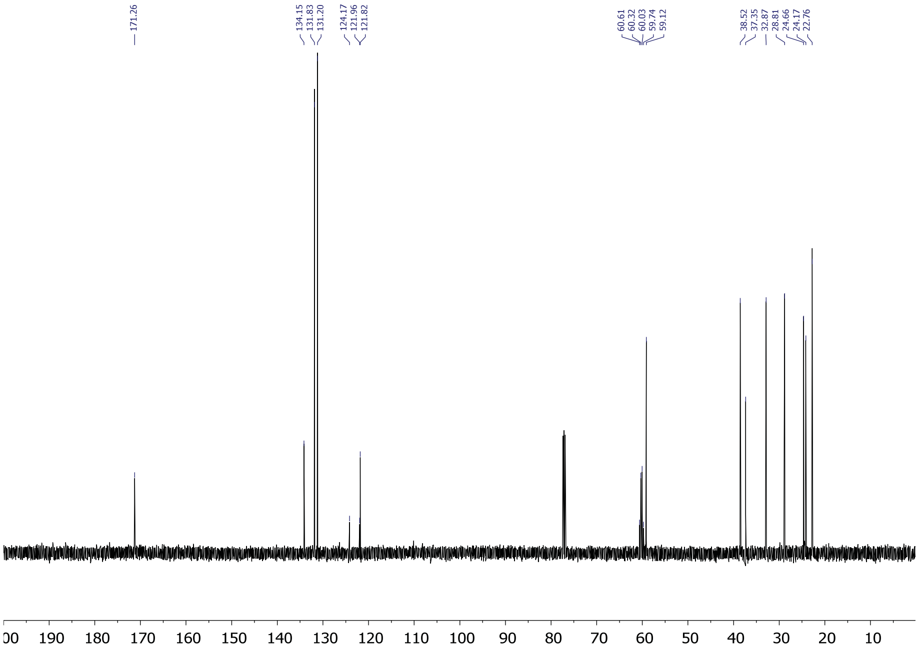
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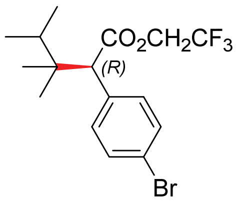
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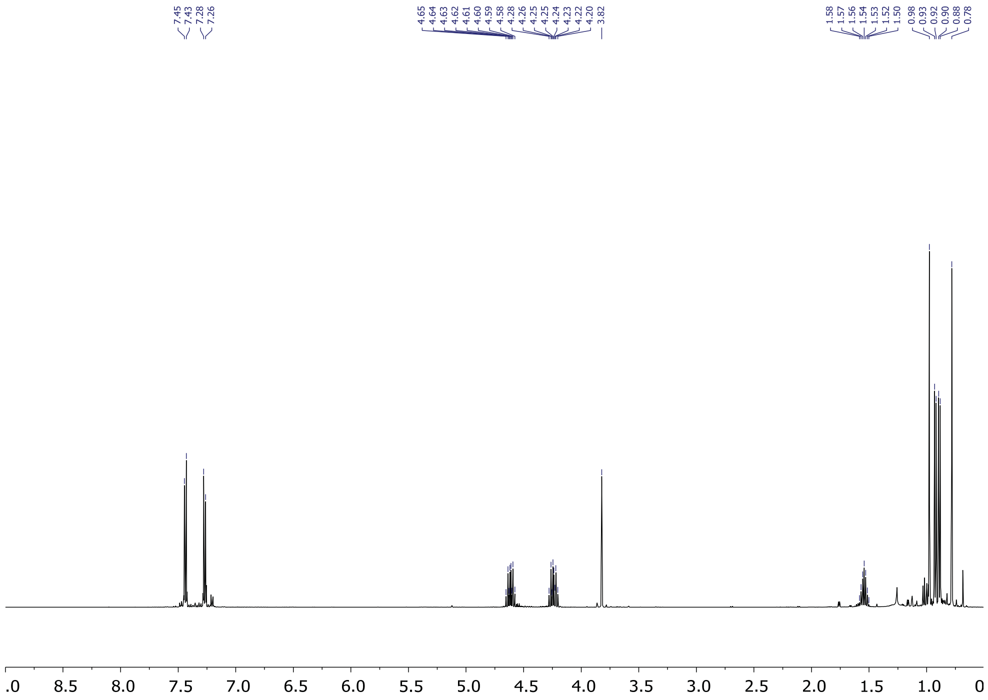
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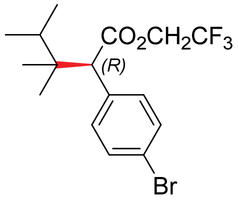
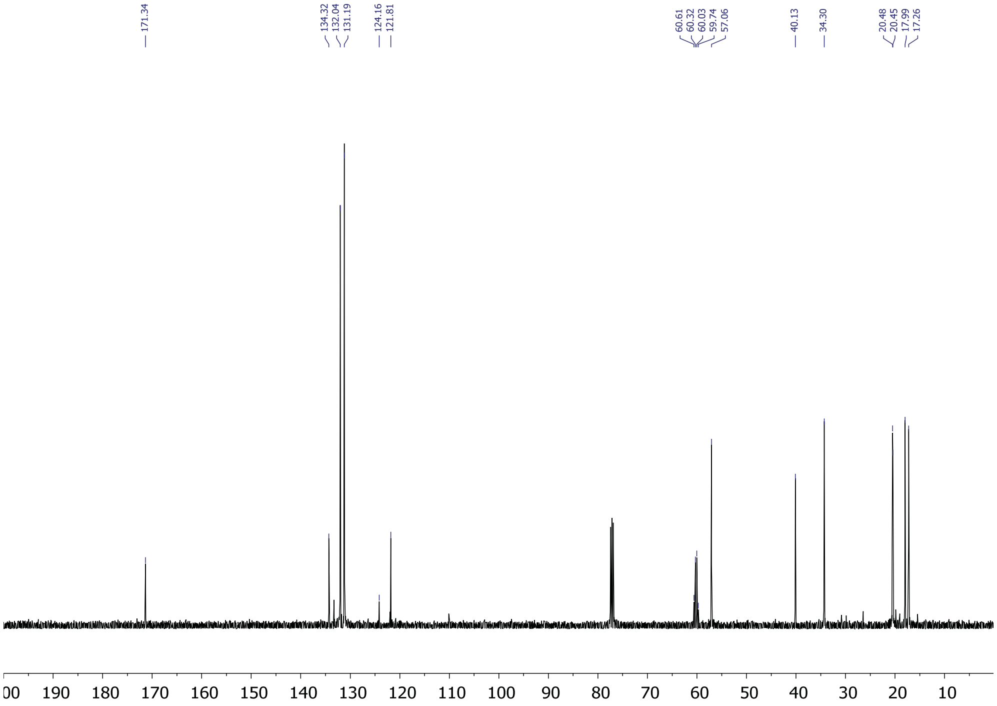

CO$_2$CH$_2$CF$_3$
(R)
Br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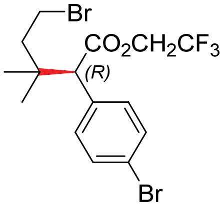
Br
CO2CH2CF3
(R)
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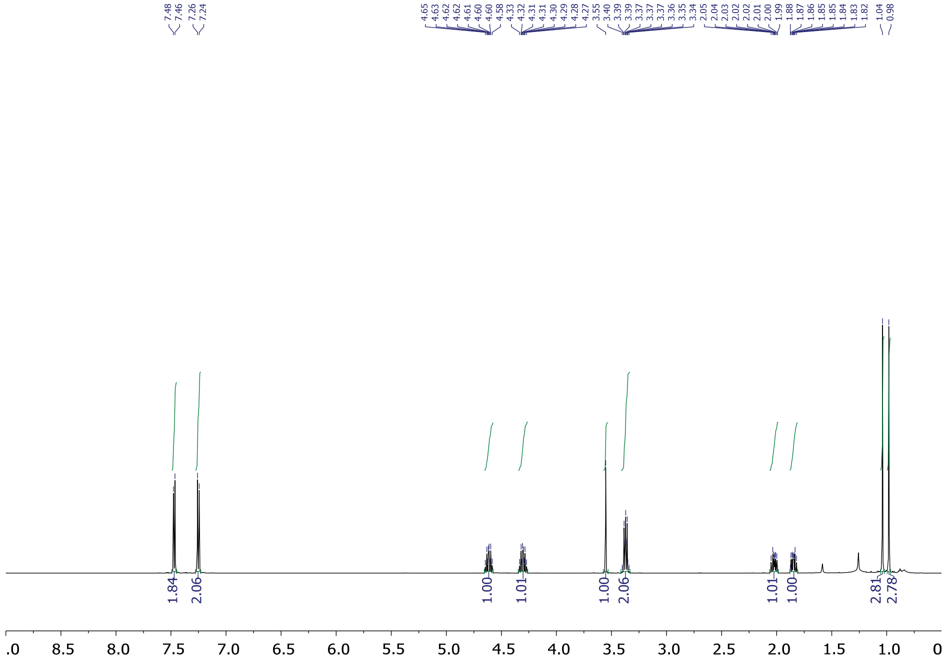
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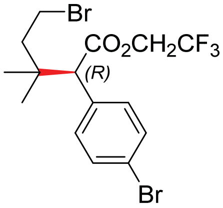
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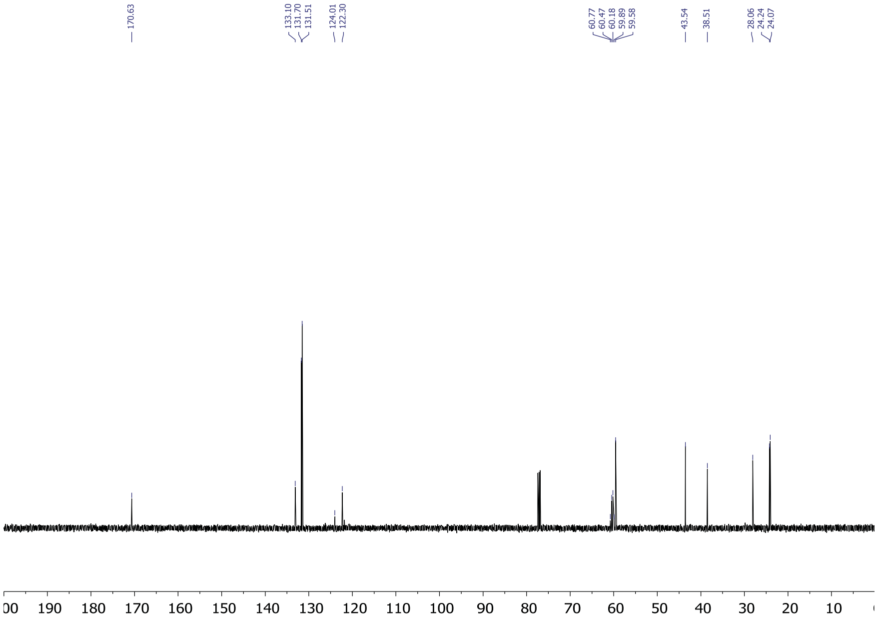
CO2CH2CF3
(R)
Br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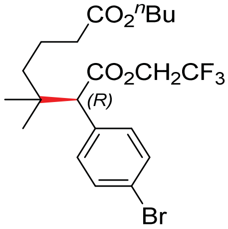

CO$_2$^{n}Bu
CO$_2$CH$_2$CF$_3$
(R)
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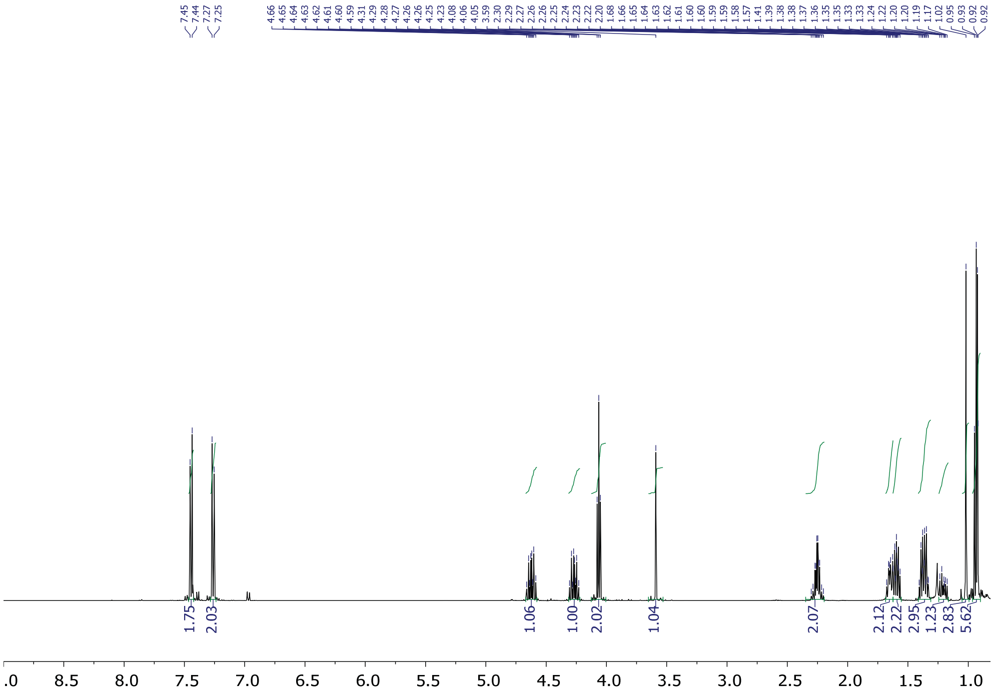

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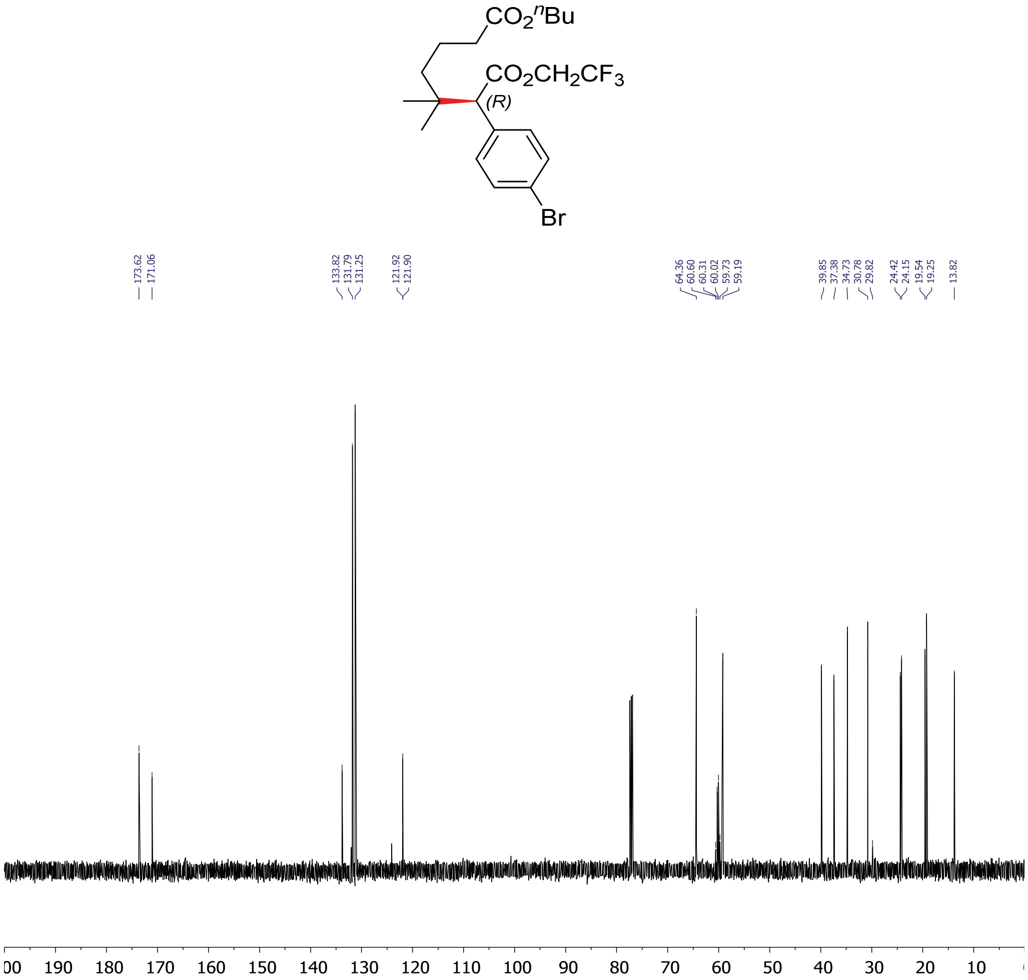
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(R)
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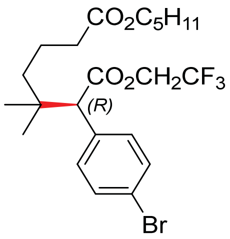
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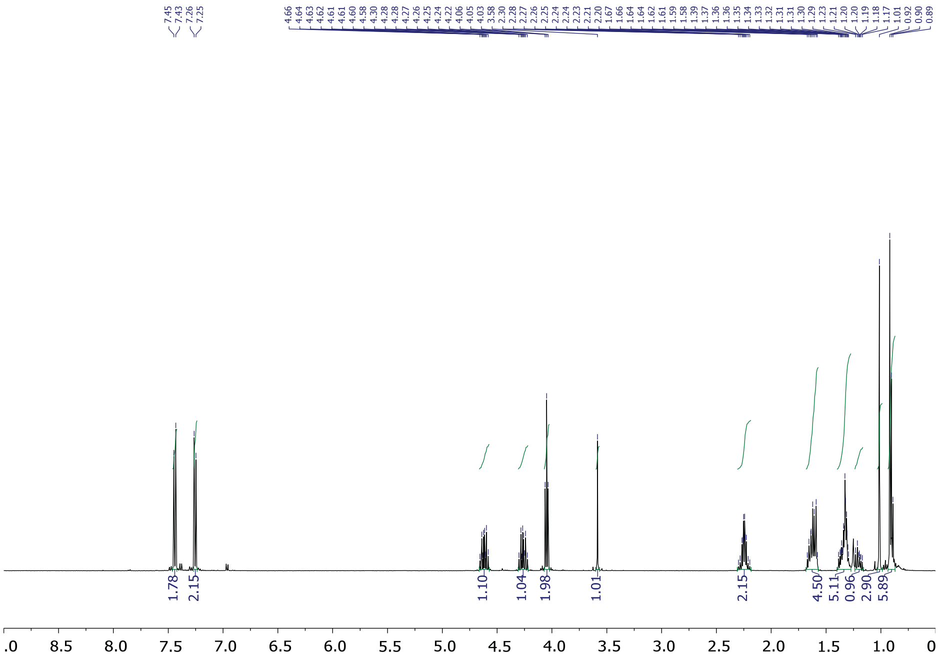
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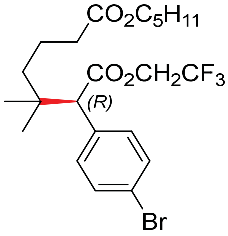
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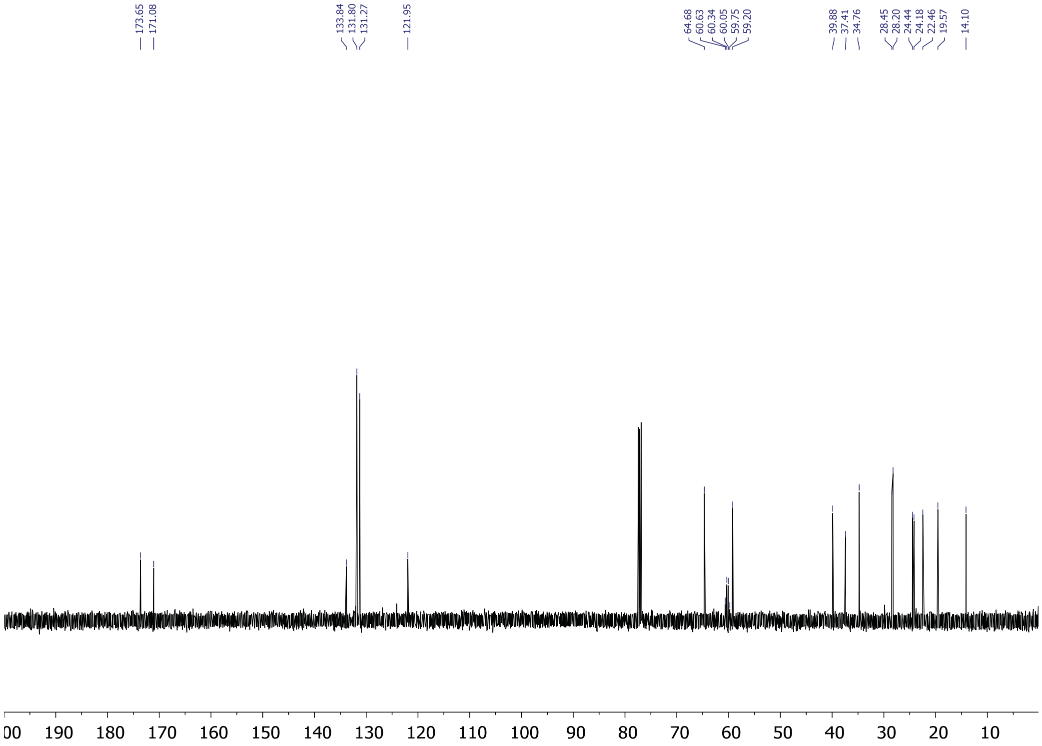
CO$_2$CH$_2$CF$_3$
(R)
Br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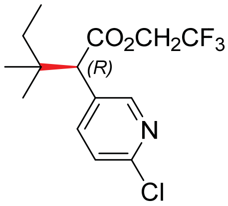
CO2CH2CF3
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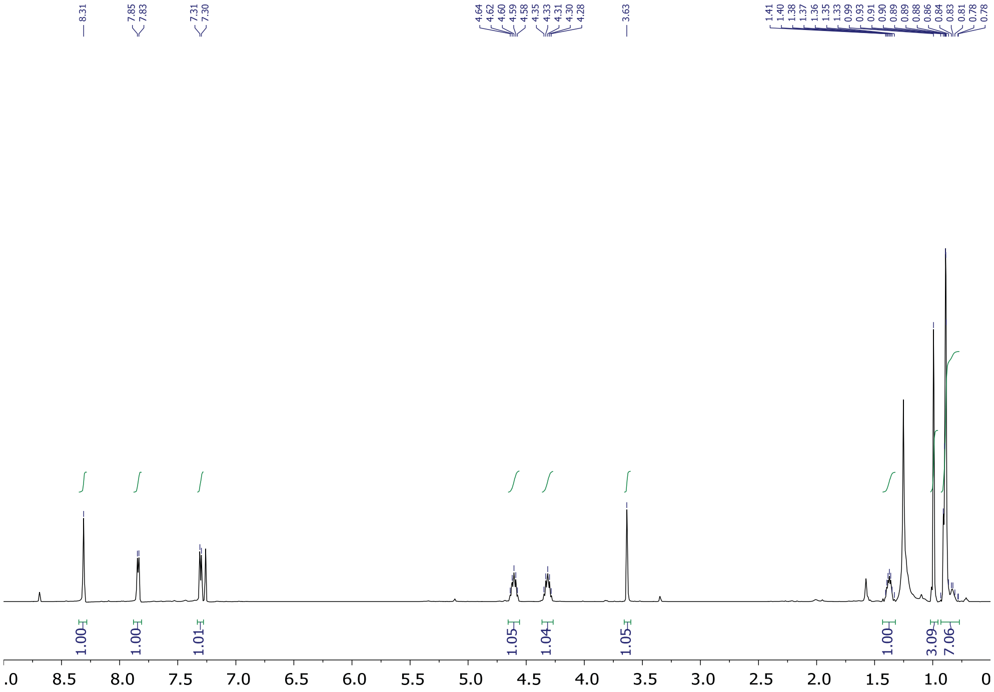
Cl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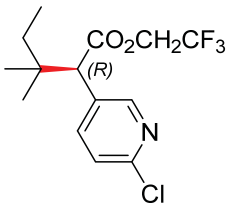
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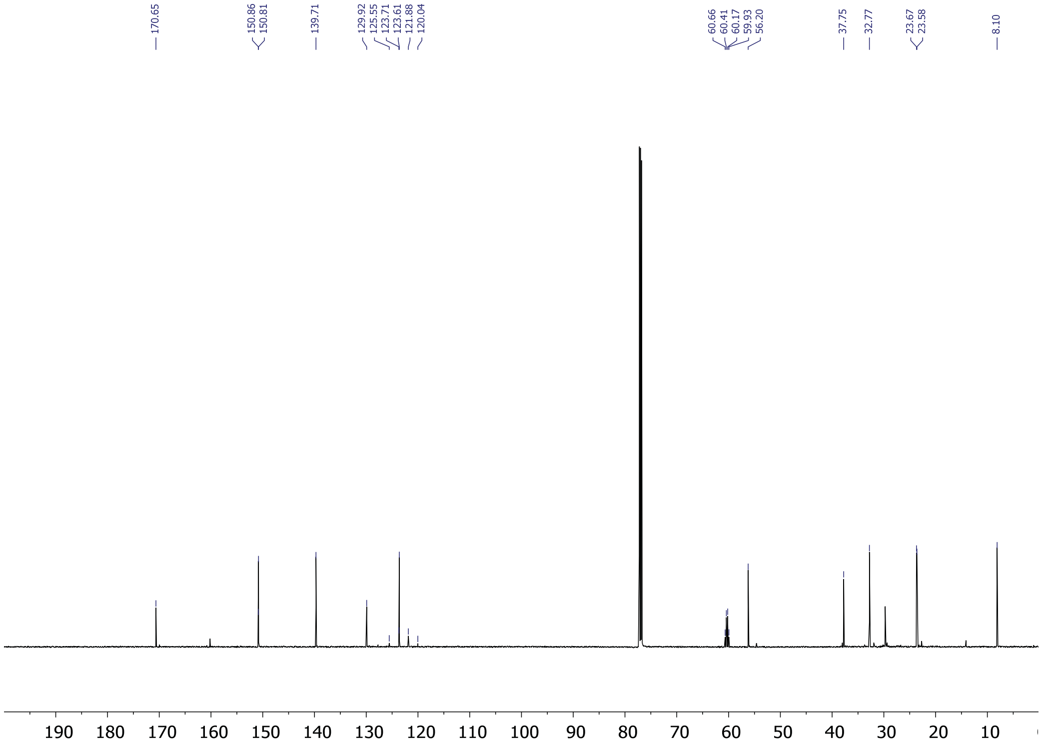
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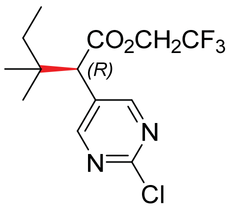
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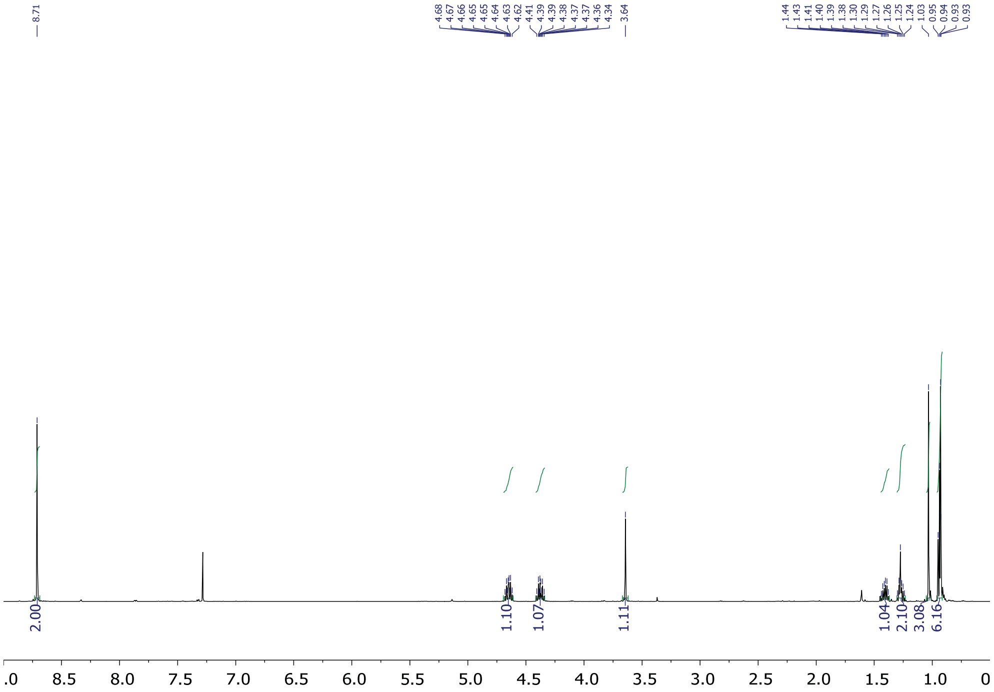
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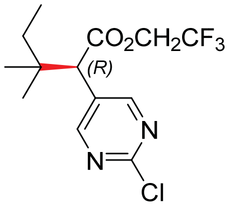
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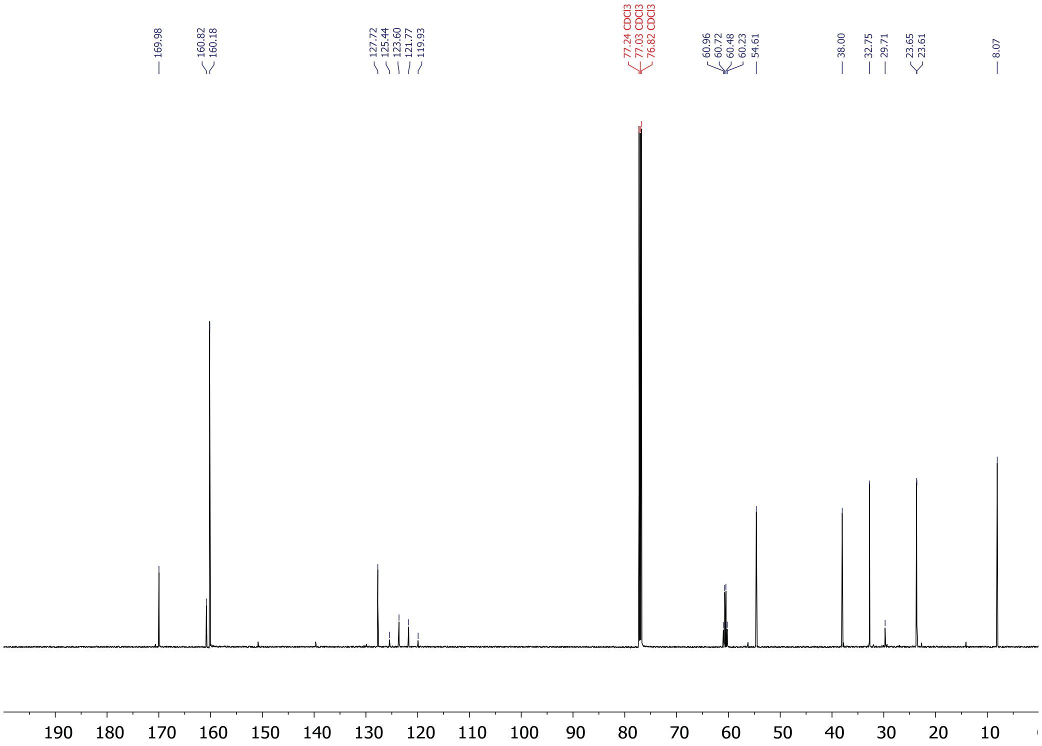
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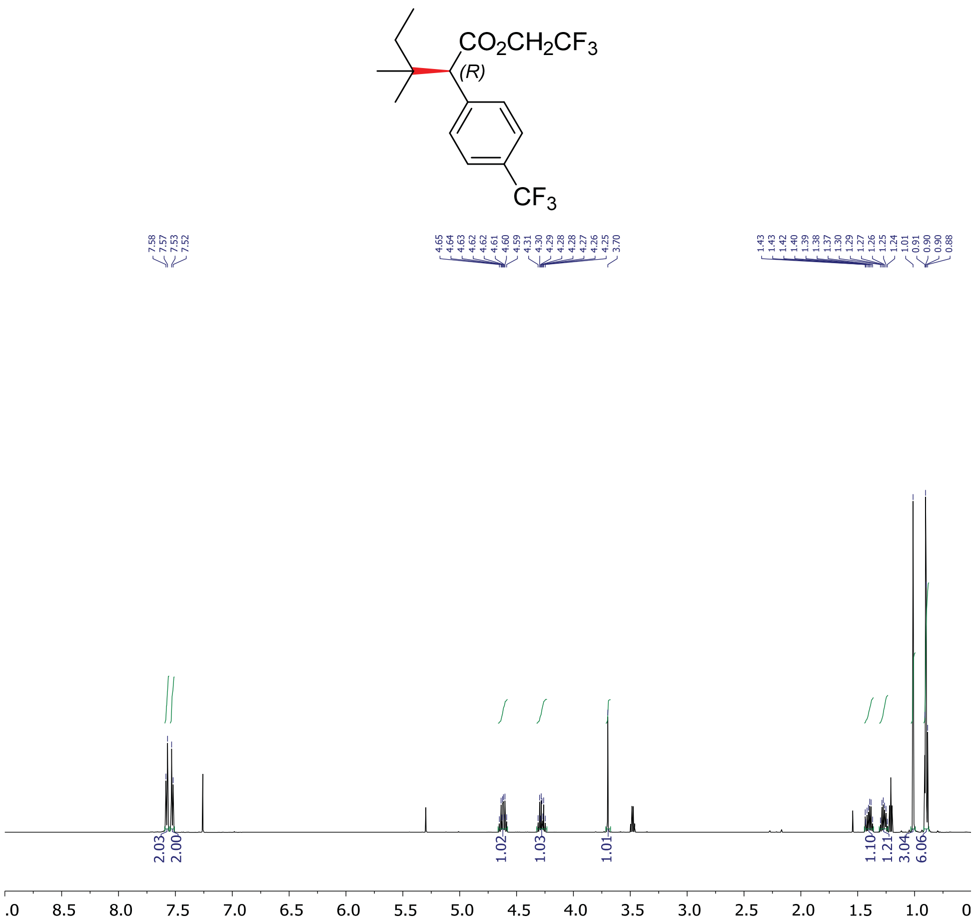
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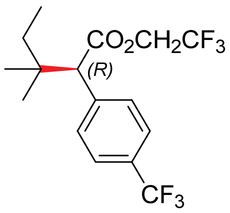
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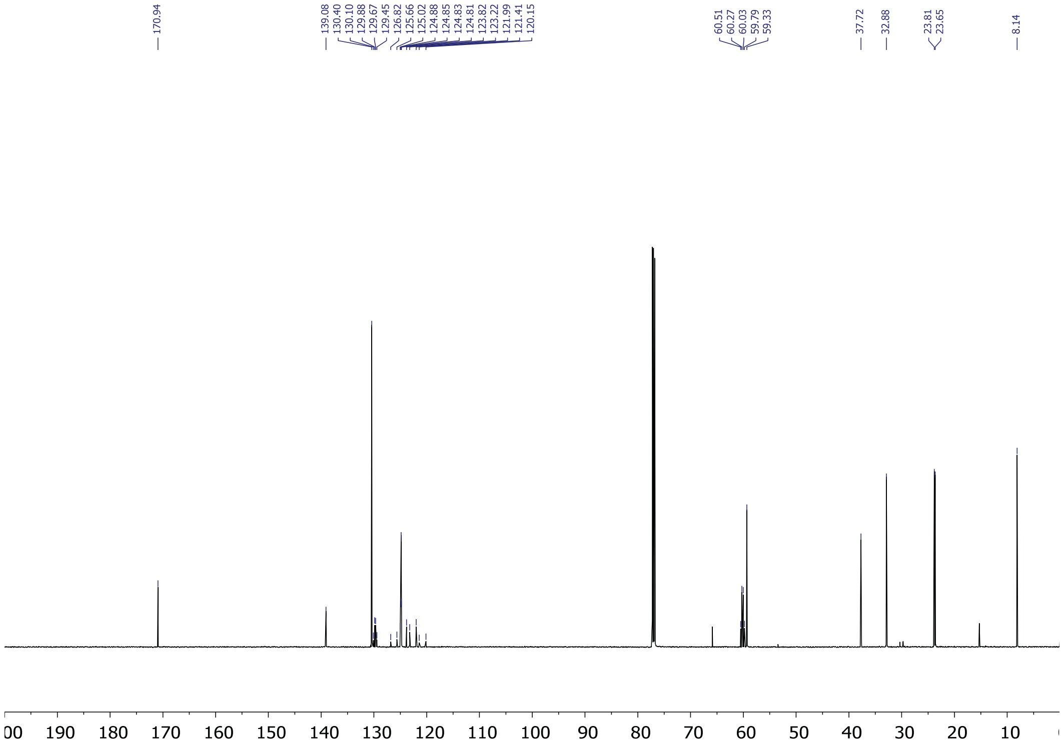
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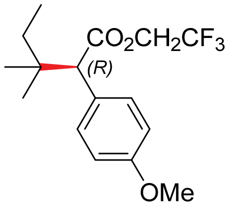
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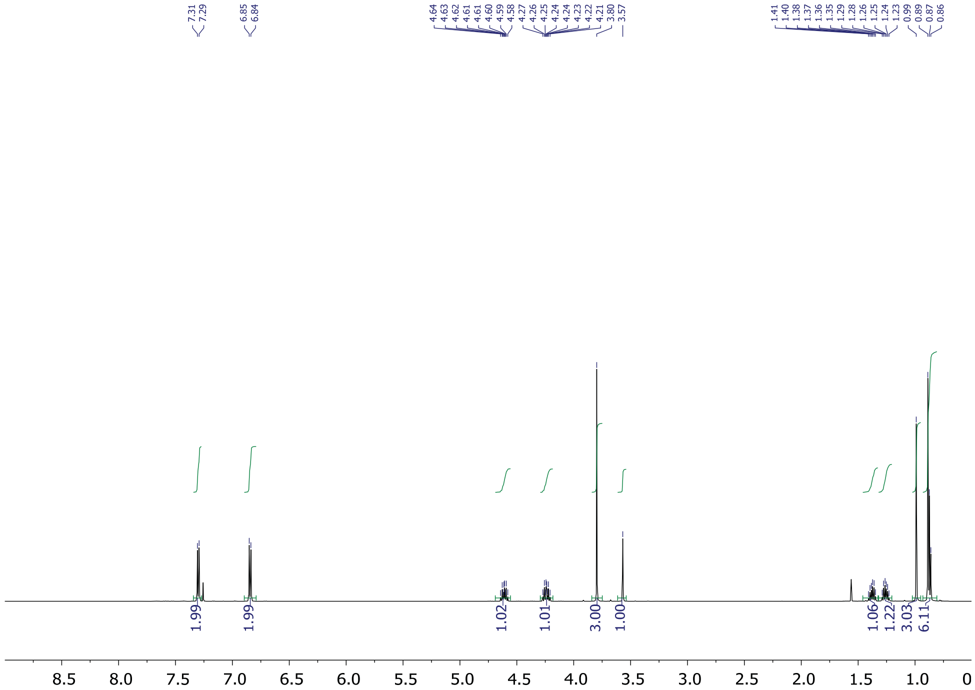
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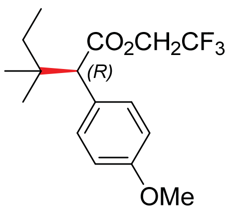
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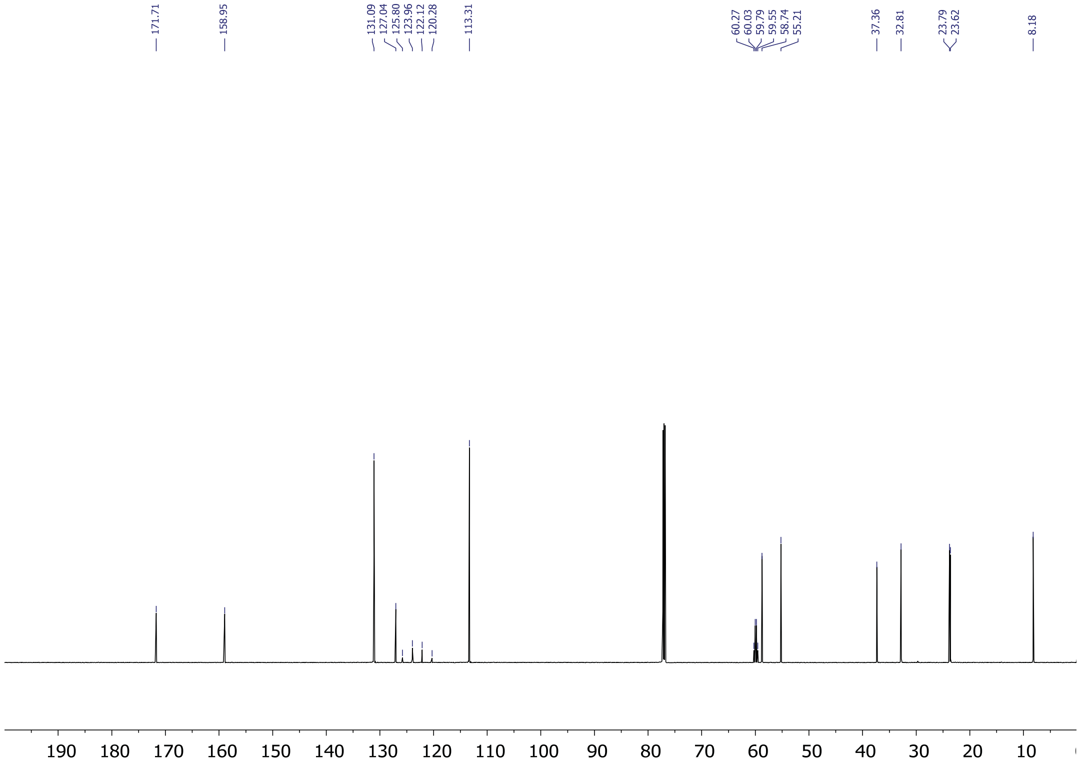
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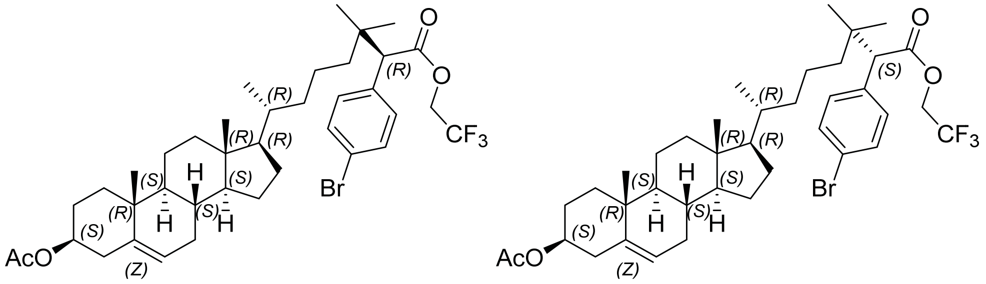
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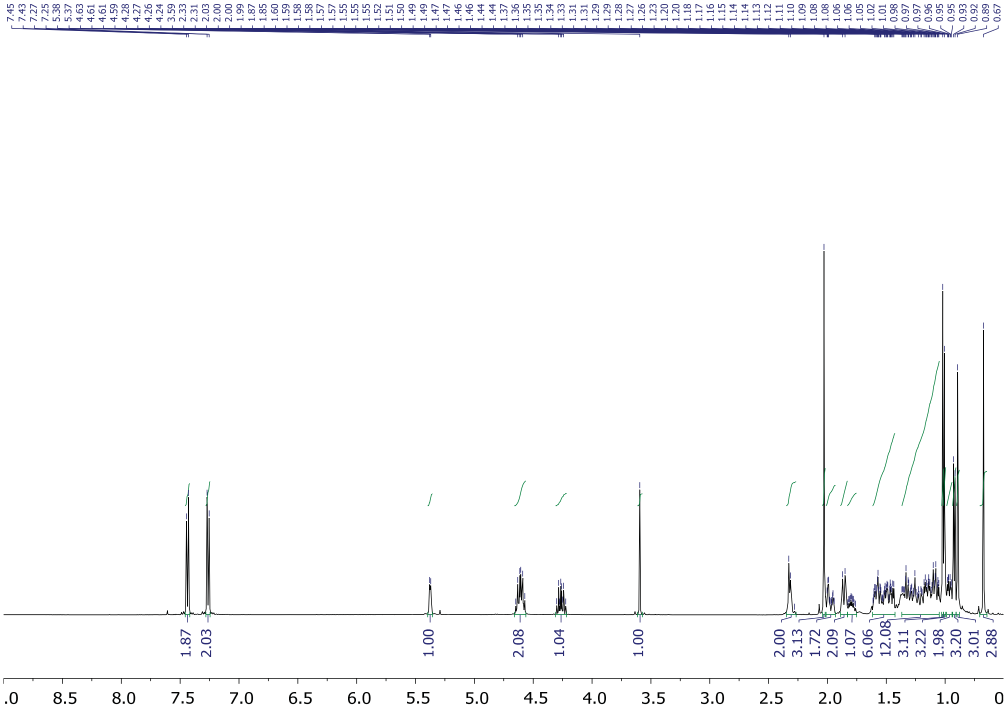
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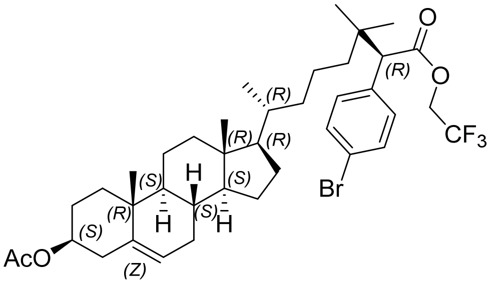
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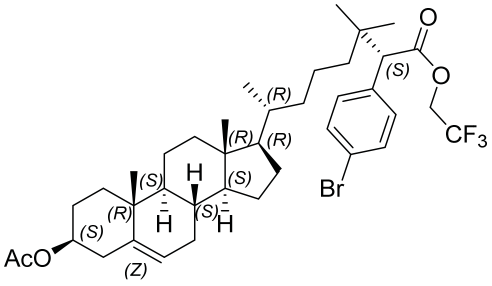
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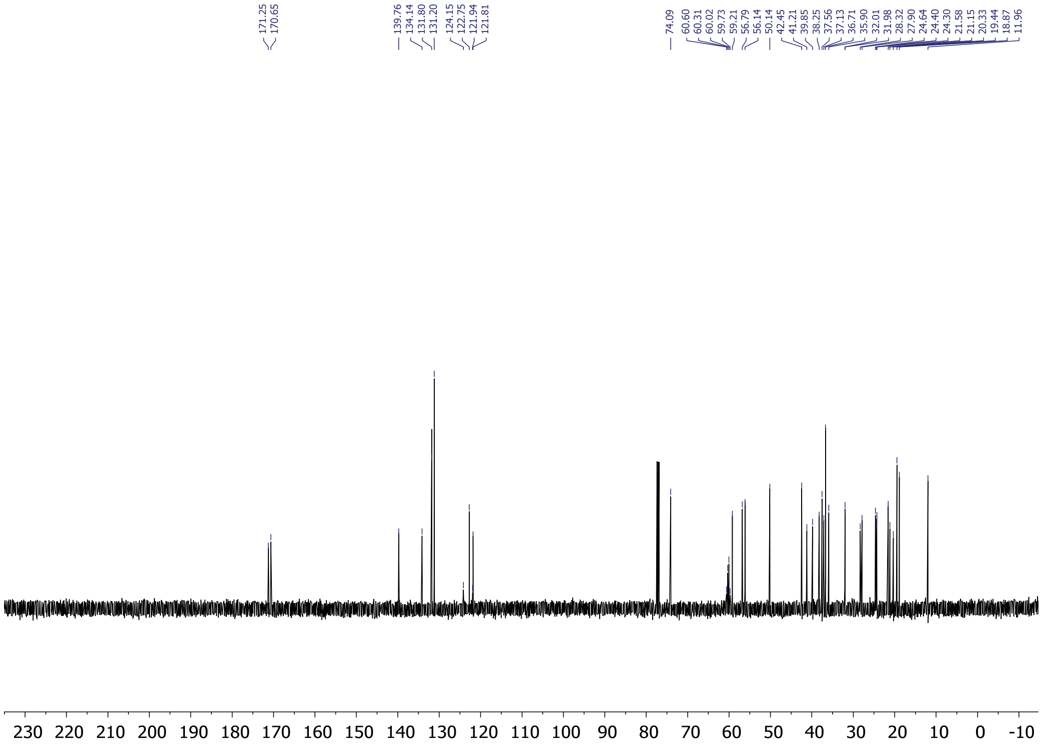
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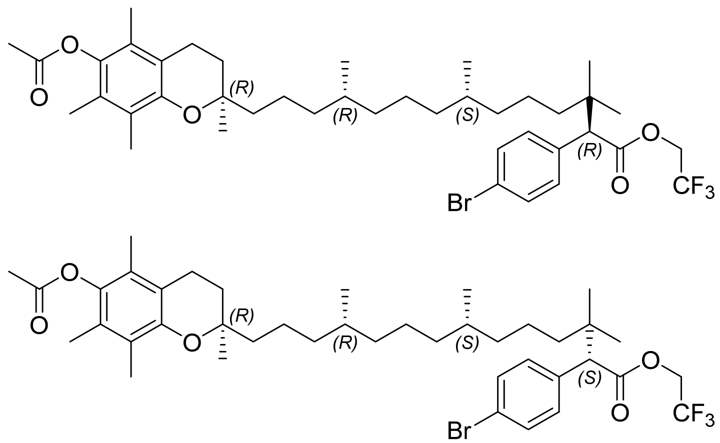
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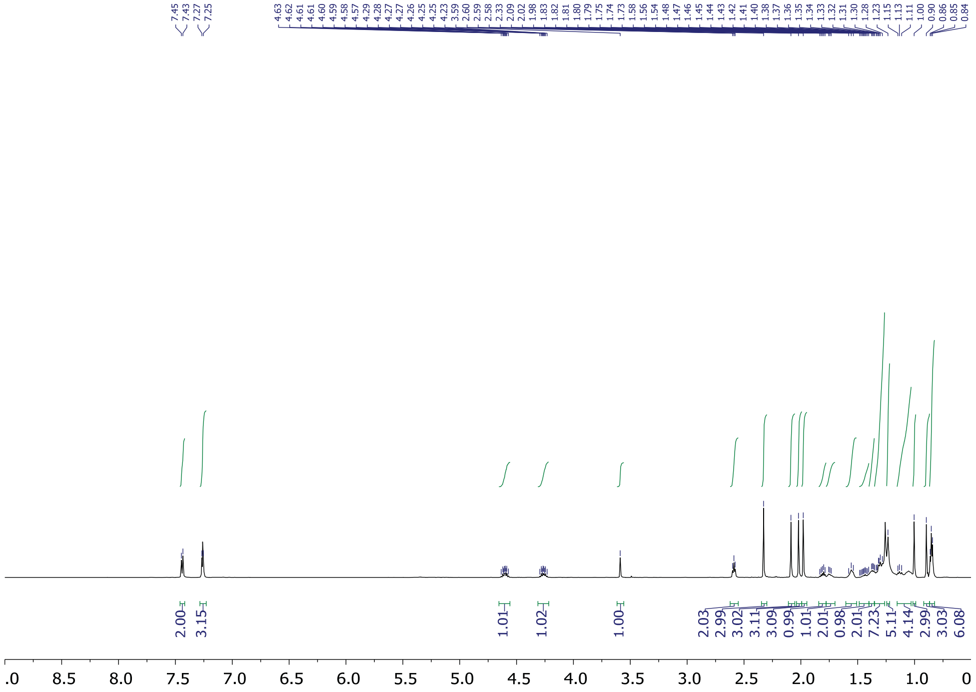
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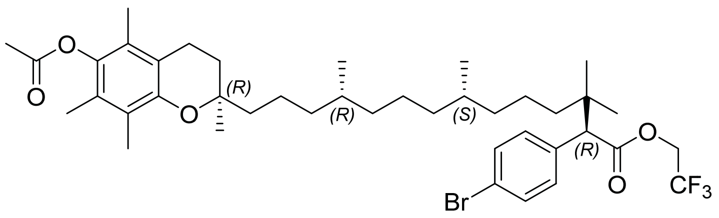
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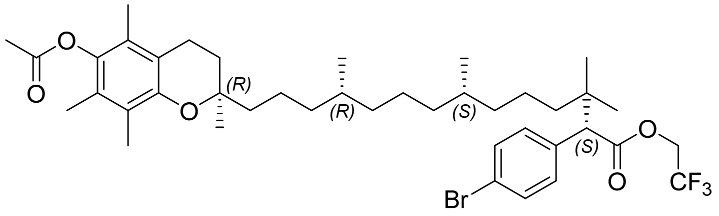
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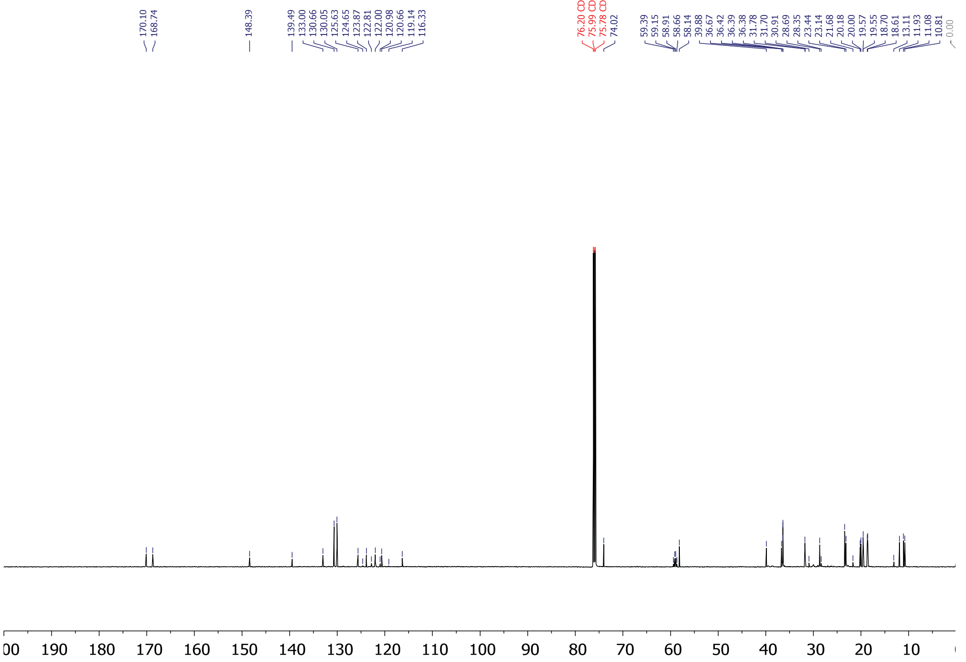
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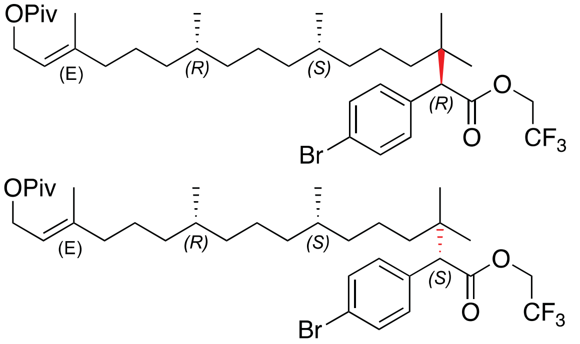
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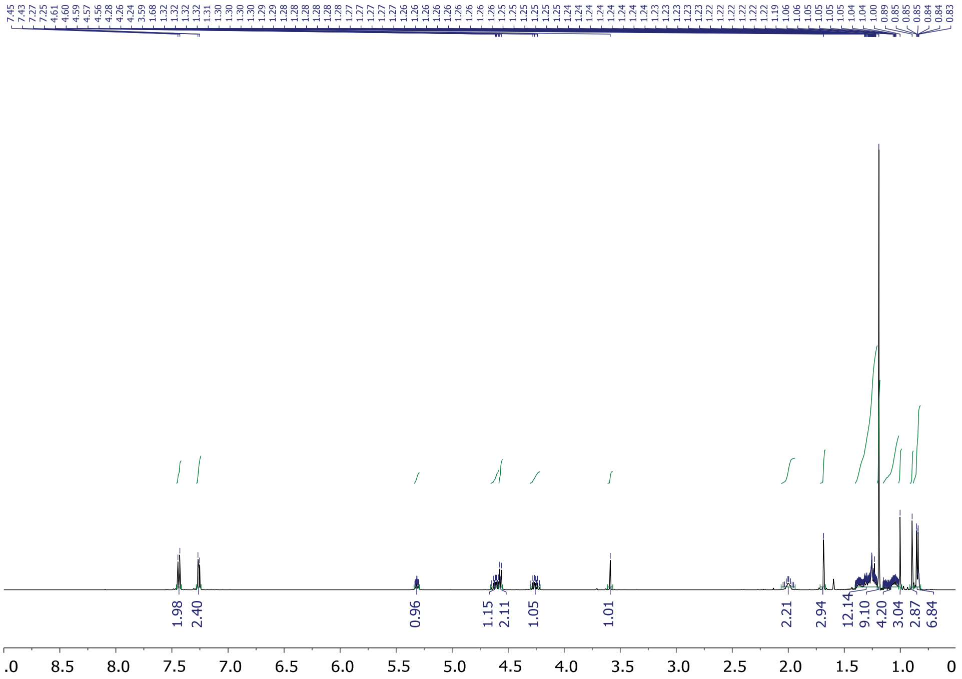
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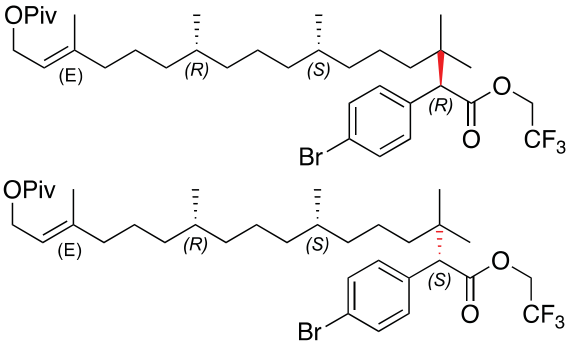
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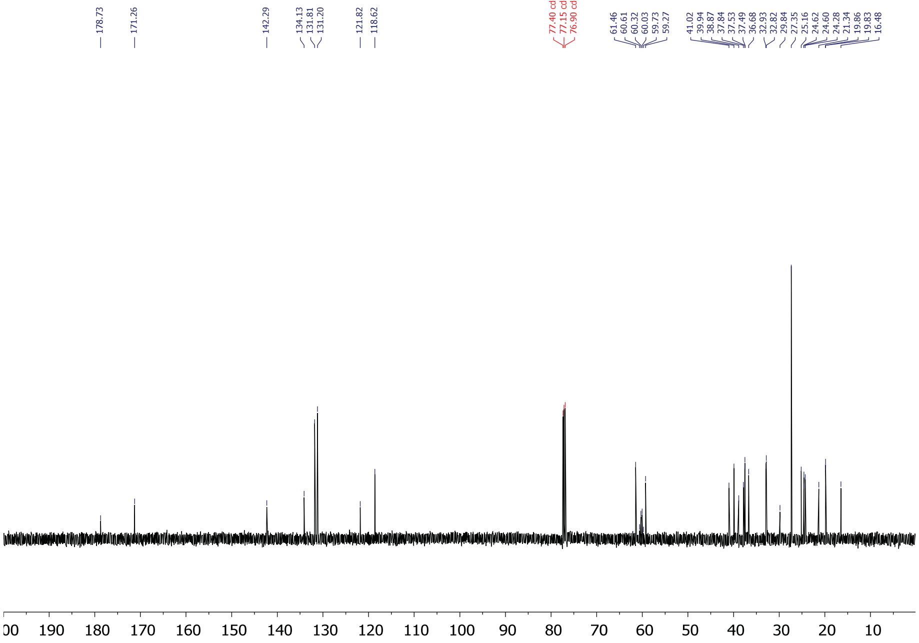
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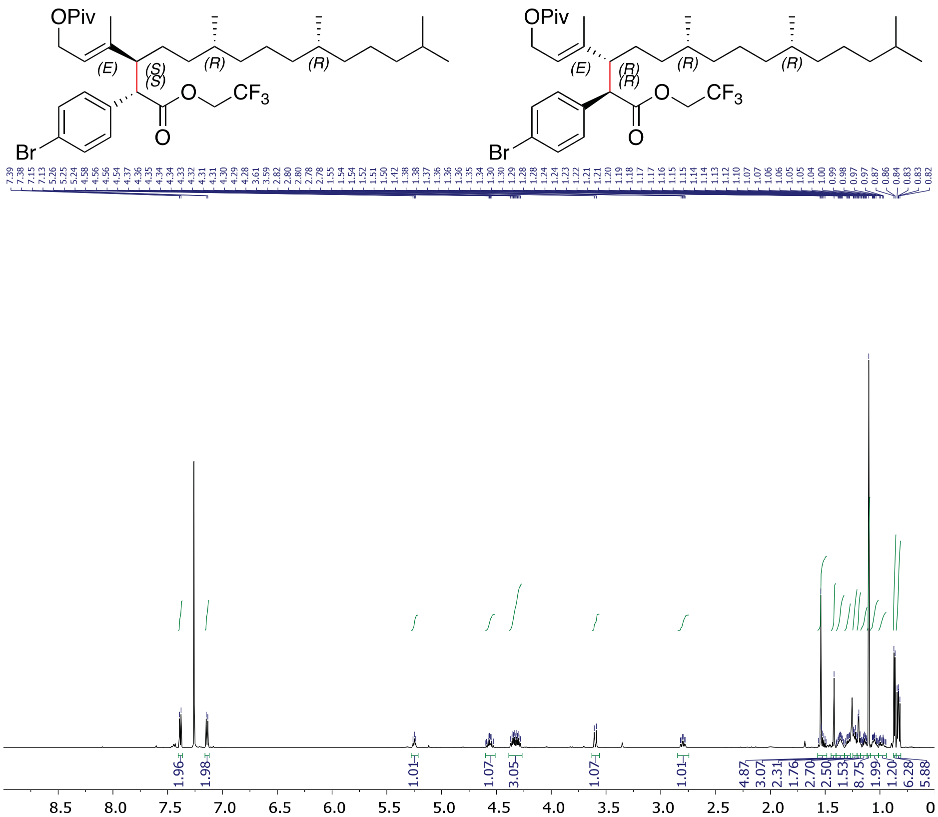
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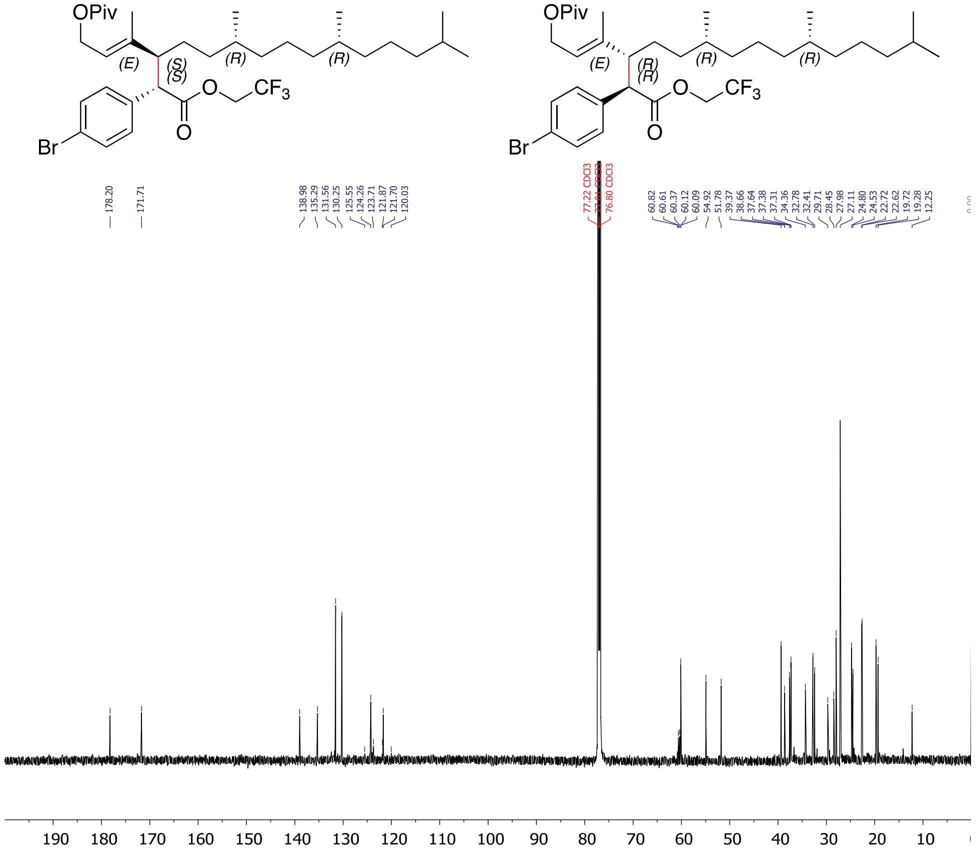
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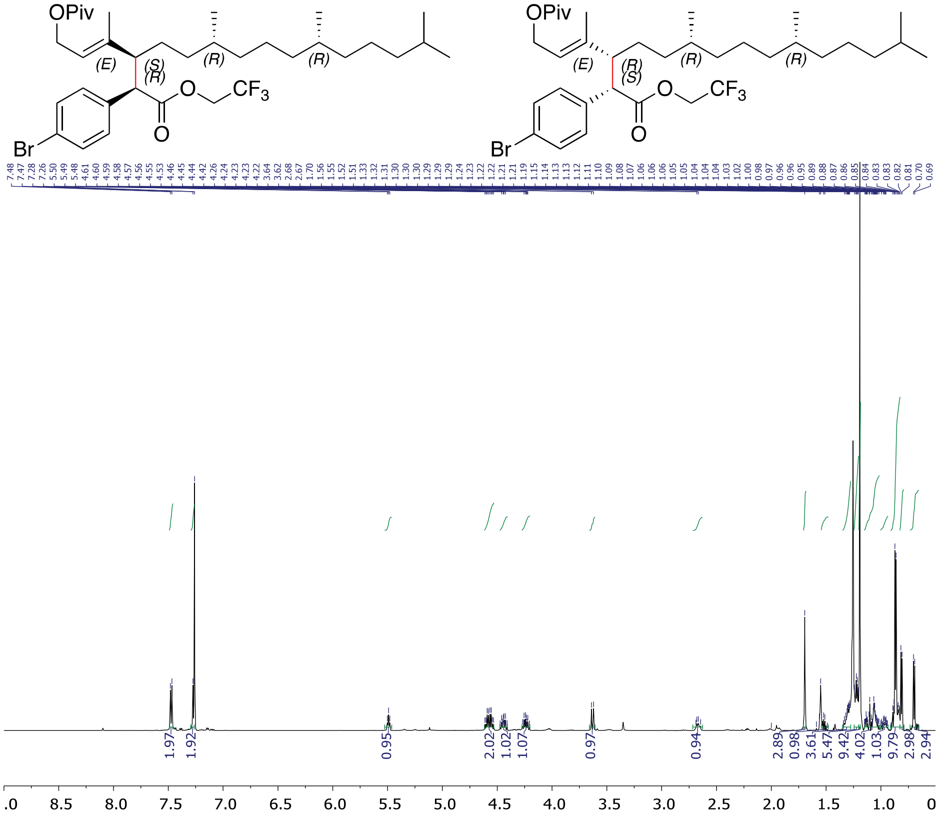
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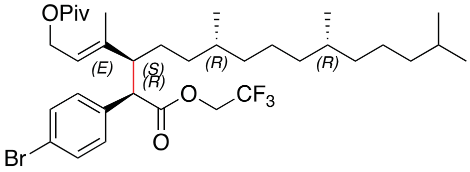
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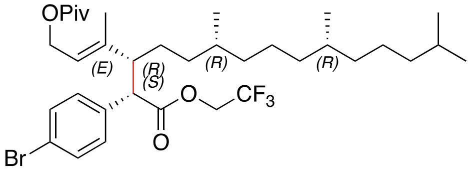
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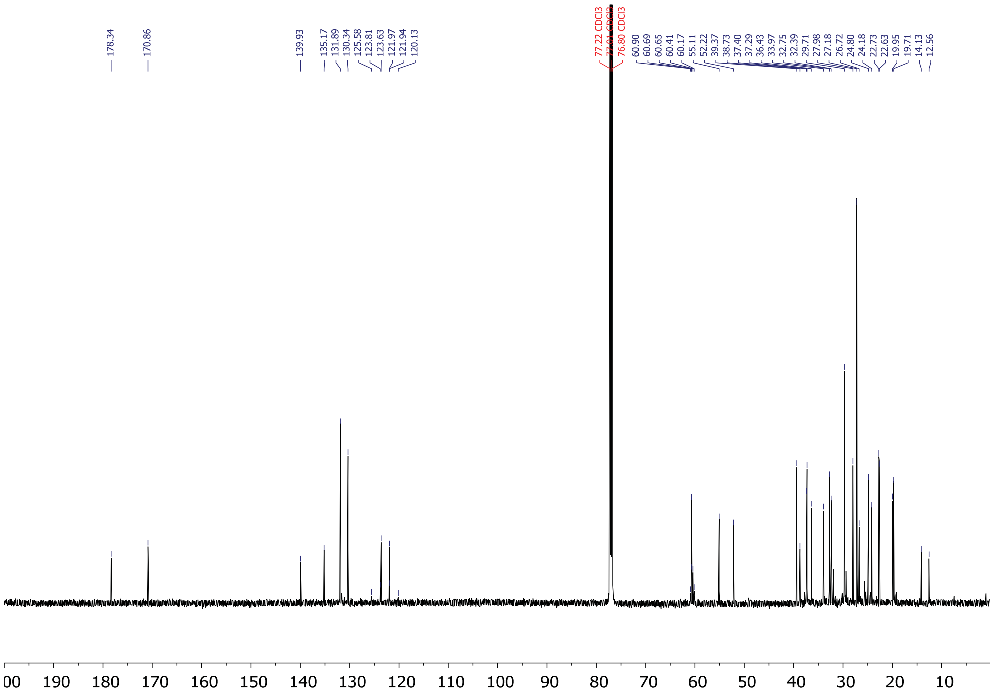
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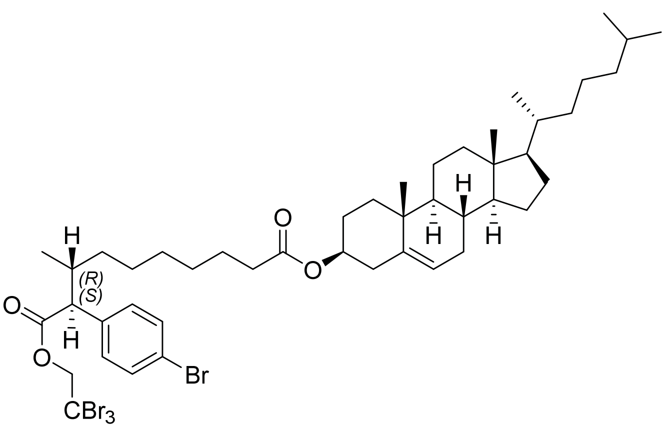
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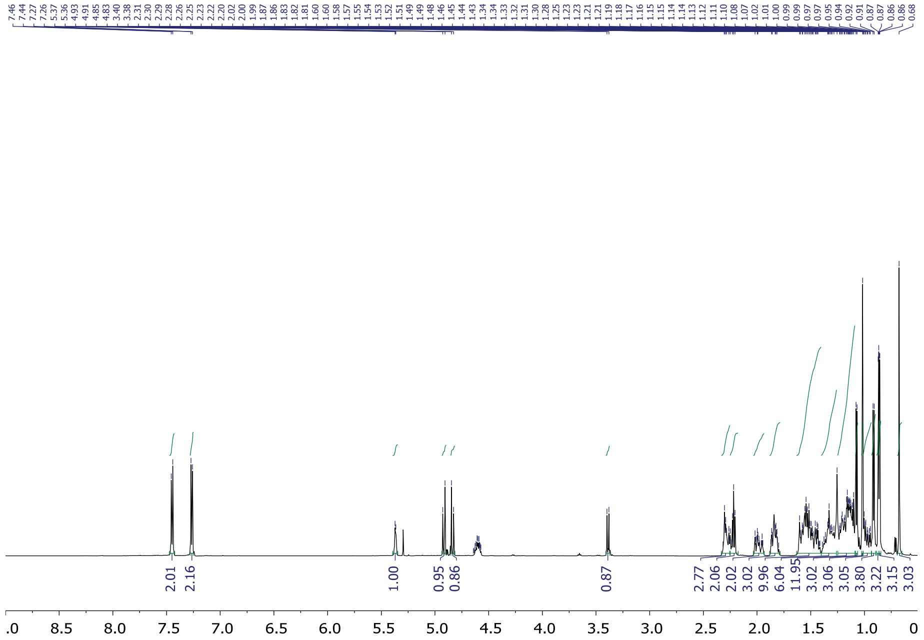
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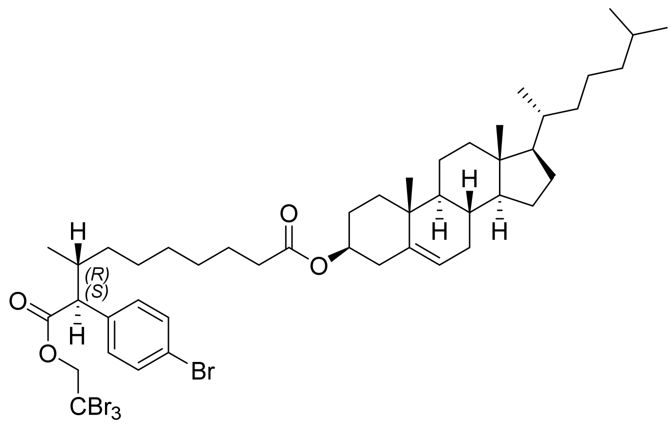
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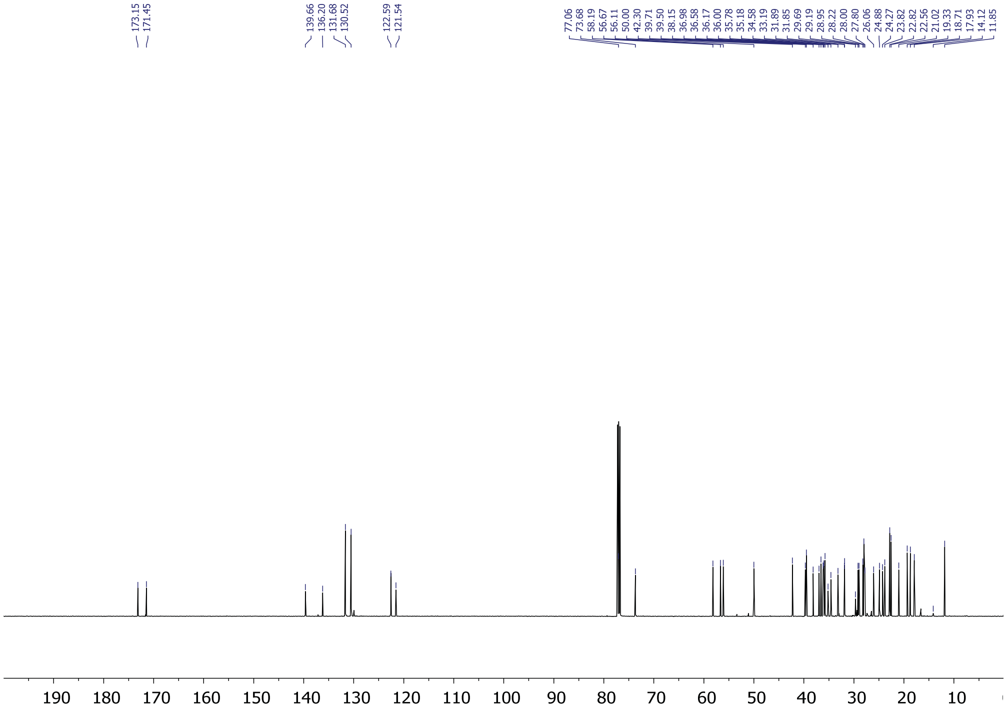
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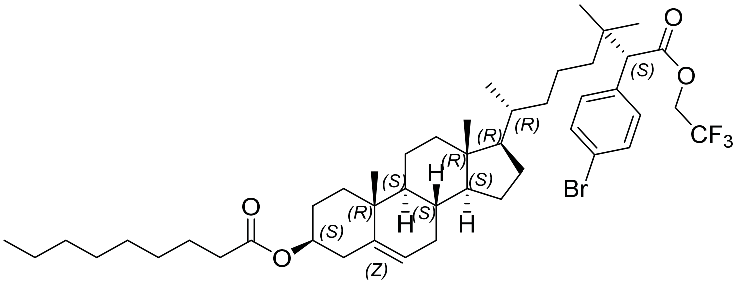
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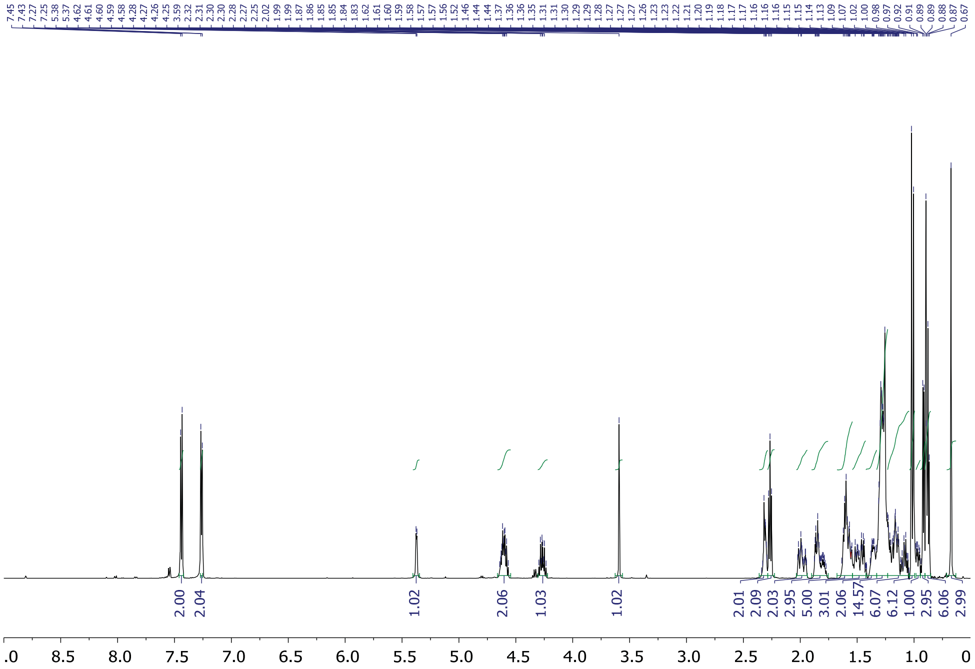
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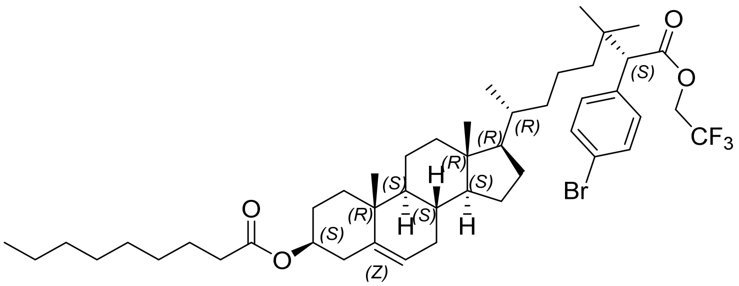
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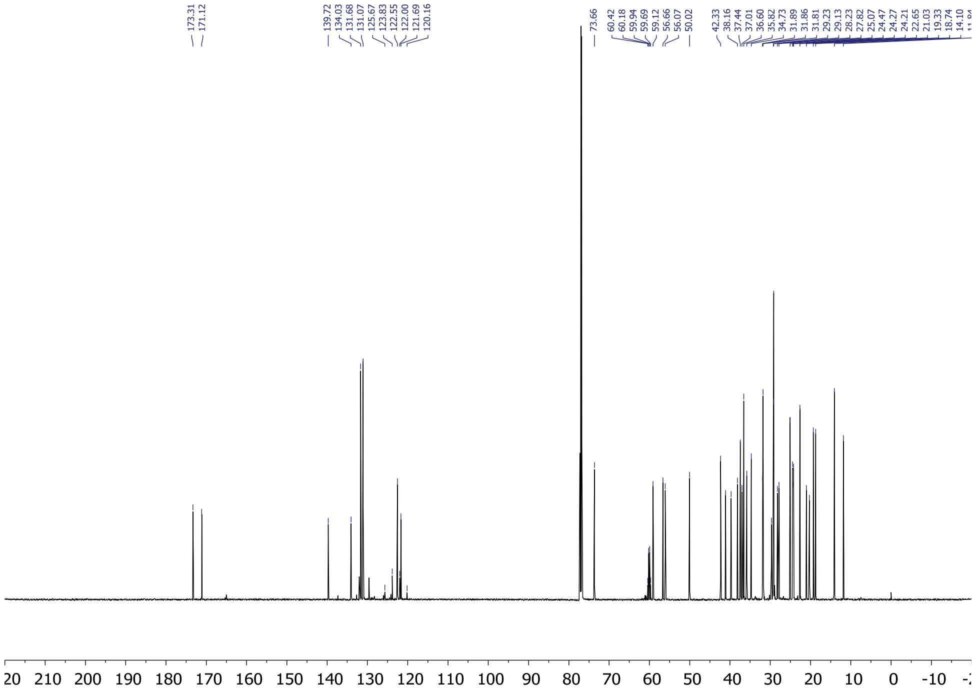
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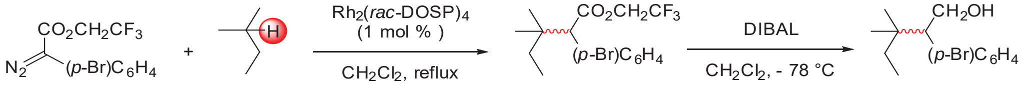
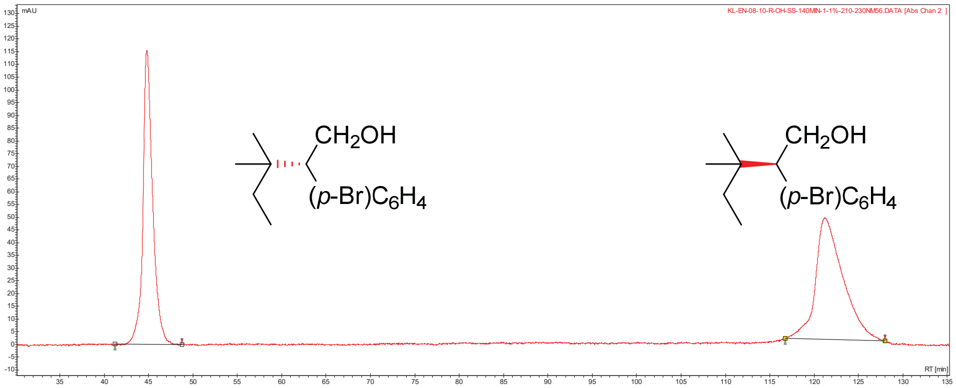
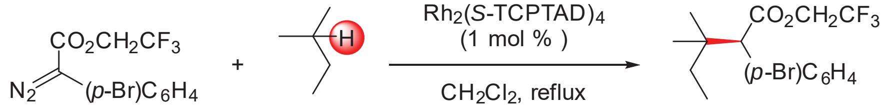
14.10
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

9. HPLC

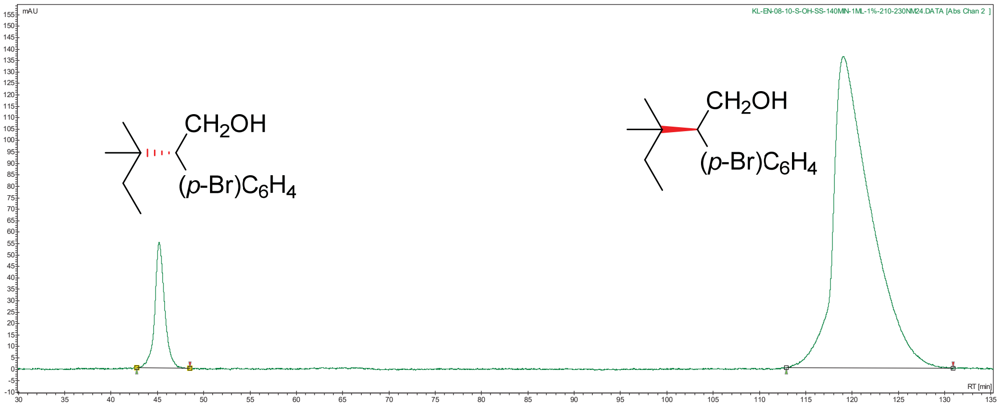




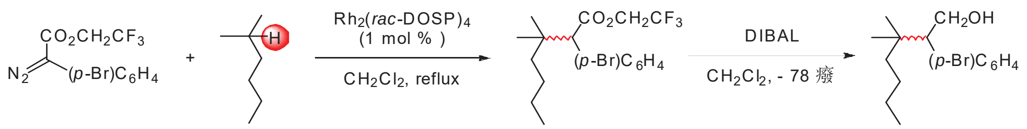
#	Time [Min]	Area % [%]
1	44.81	46.077
2	121.22	53.92

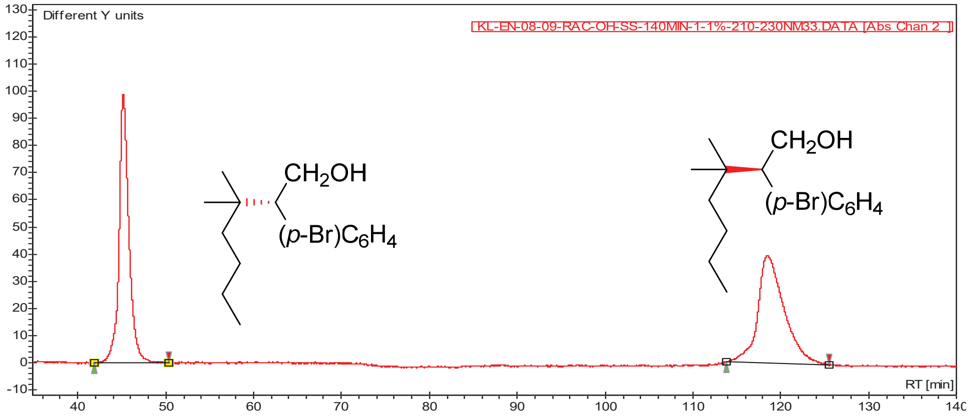


1d 3 *equiv.* **4**

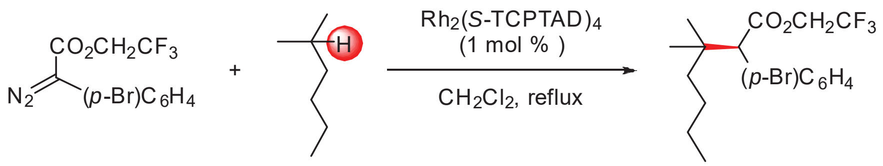


#	Time [Min]	Area % [%]
1	45.20	9.435
2	119.00	90.565
		81 % e.e.

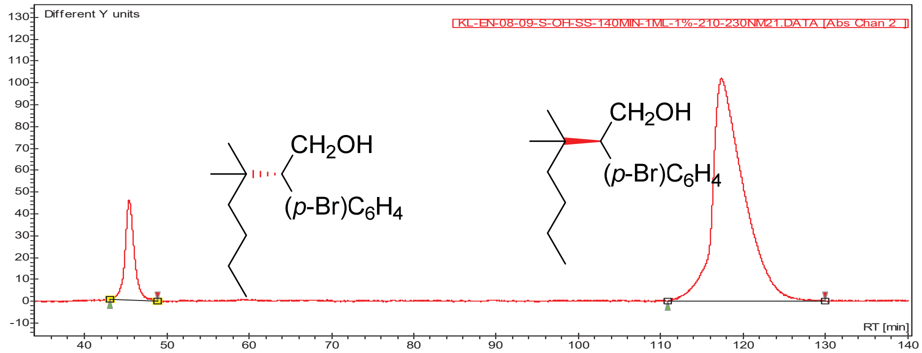




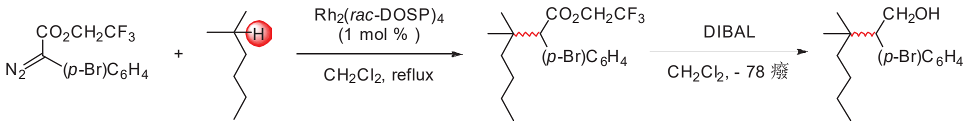
#	Time [Min]	Area % [%]
1	45.15	48.468
2	118.51	51.532

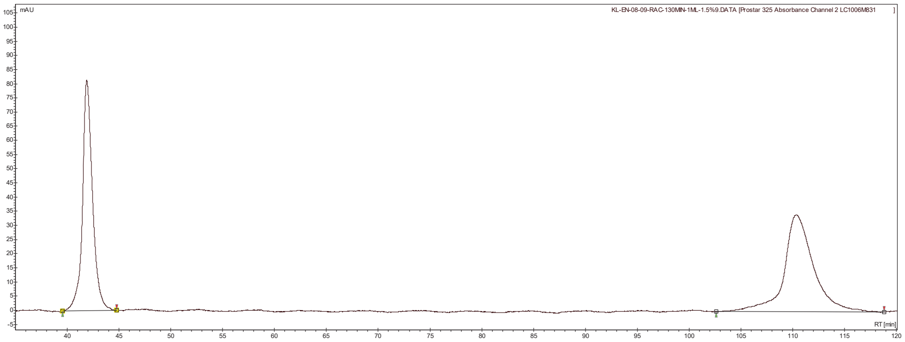


1d 3 *equiv.* **5**

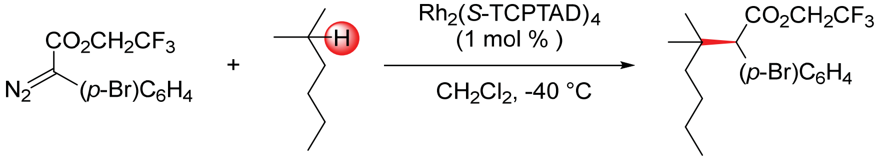


#	Time [Min]	Area % [%]
1	45.48	11.597
2	117.39	88.403
		77 % e.e.

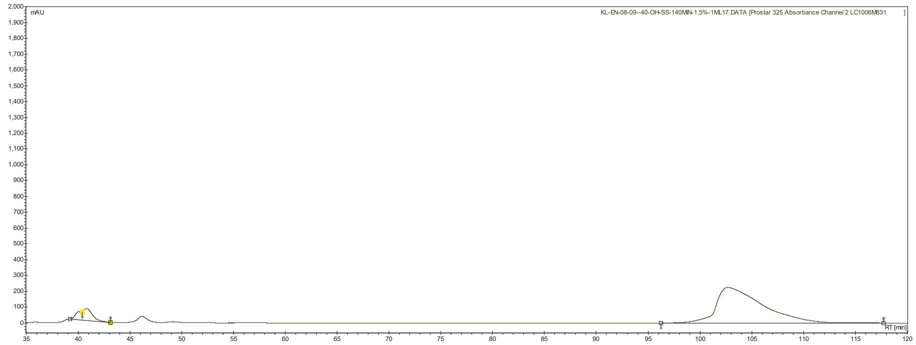




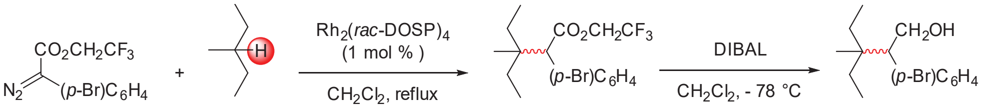
#	Time [Min]	Area % [%]
1	41.88	44.963
2	110.38	55.037

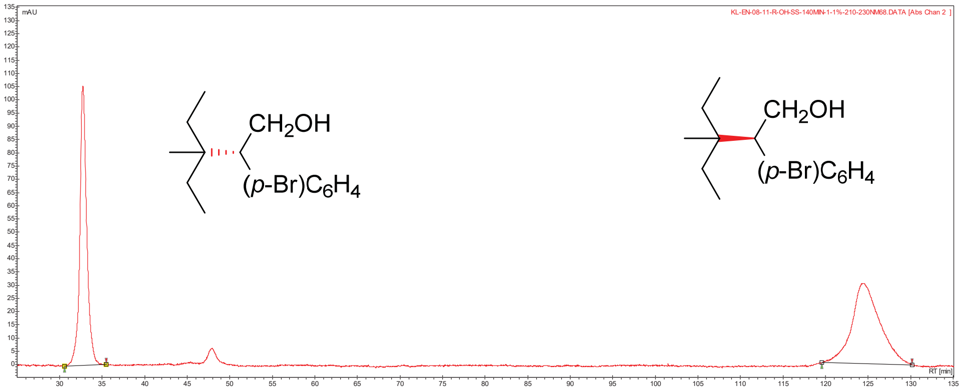


1d 3 *equiv.* **5**

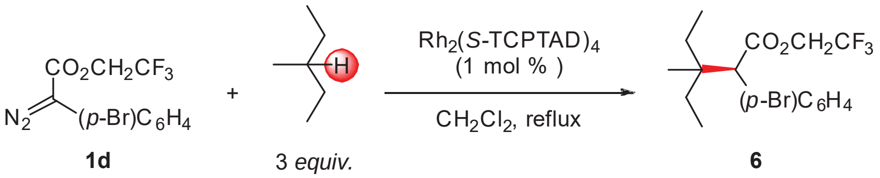


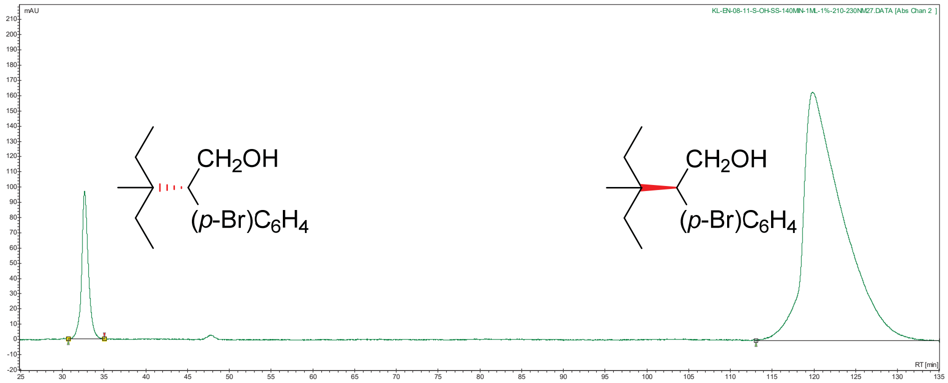
#	Time [Min]	Area % [%]
1	40.81	6.286
2	102.67	93.714
		87 % e.e.



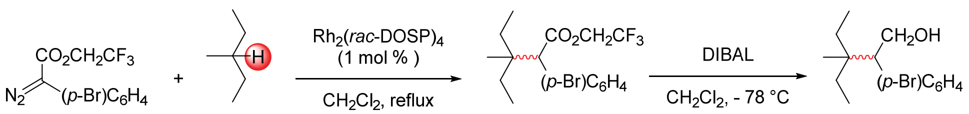


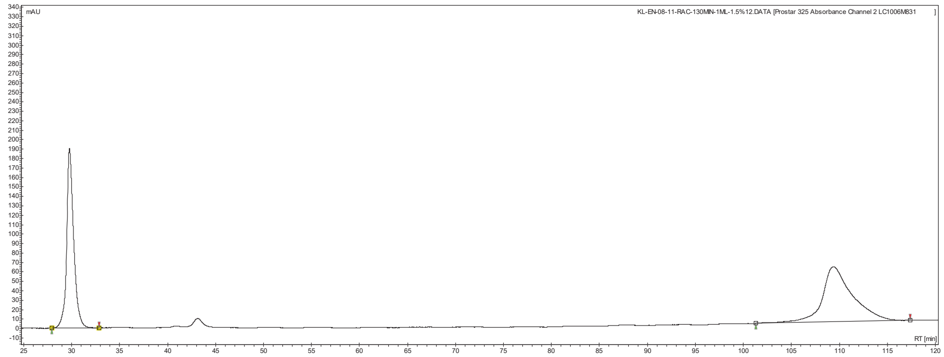
#	Time [Min]	Area % [%]
1	32.73	46.258
2	124.52	53.742



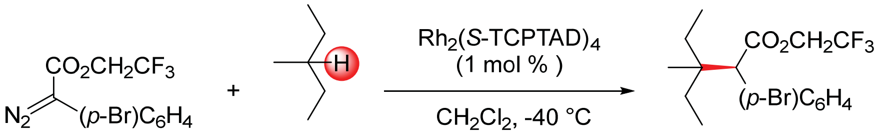


#	Time [Min]	Area % [%]
1	32.67	9.096
2	119.86	90.904
		82 % e.e.

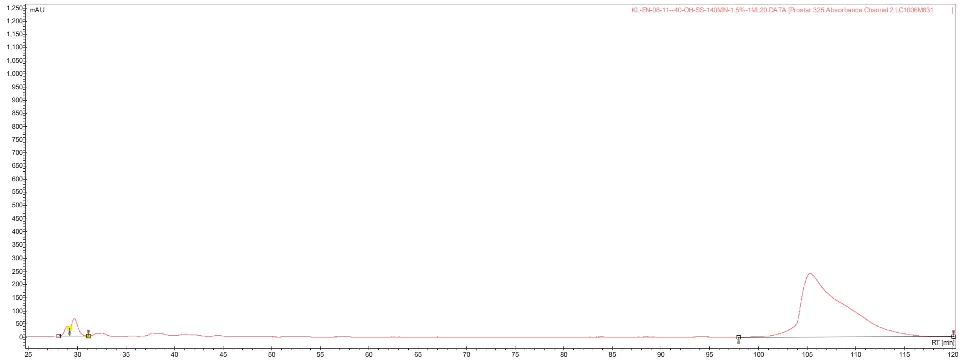




#	Time [Min]	Area % [%]
1	29.77	43.020
2	109.43	56.980

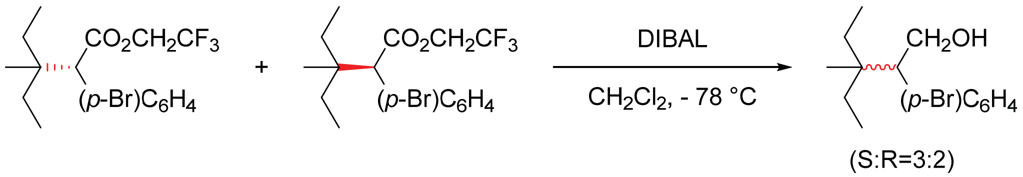


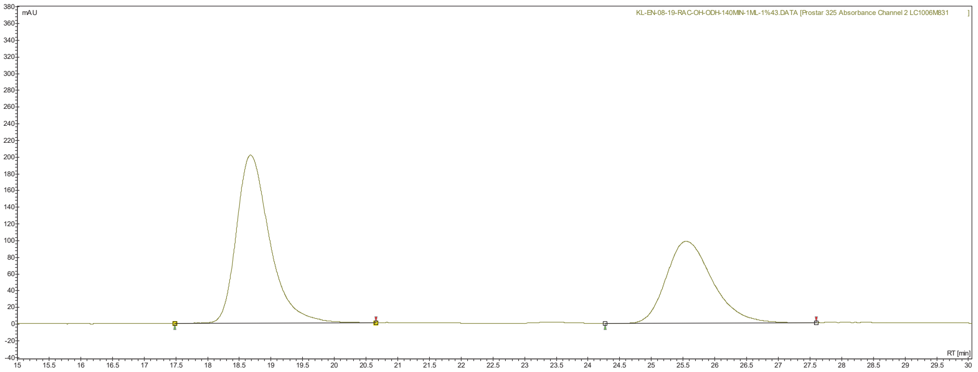
1d 3 *equiv.* **6**



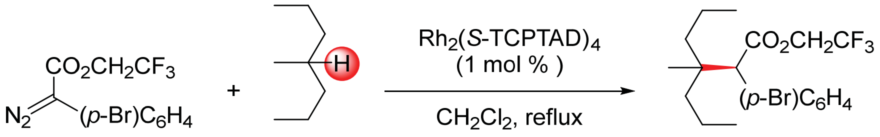
#	Time [Min]	Area % [%]
1	29.70	3.977
2	105.31	96.023

92 % e.e.

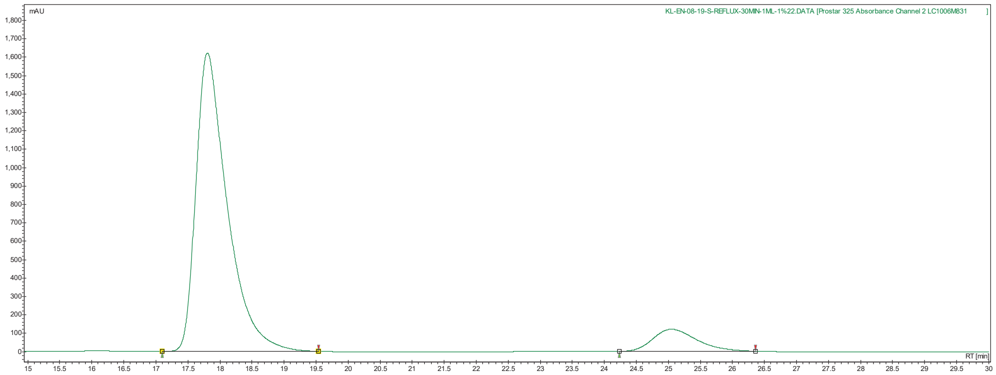




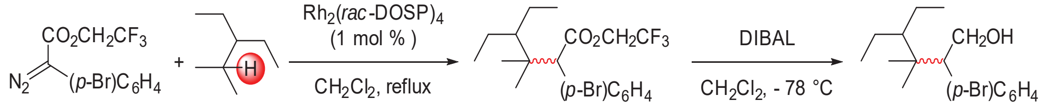
#	Time [Min]	Area % [%]
1	18.68	59.566
2	25.55	40.434

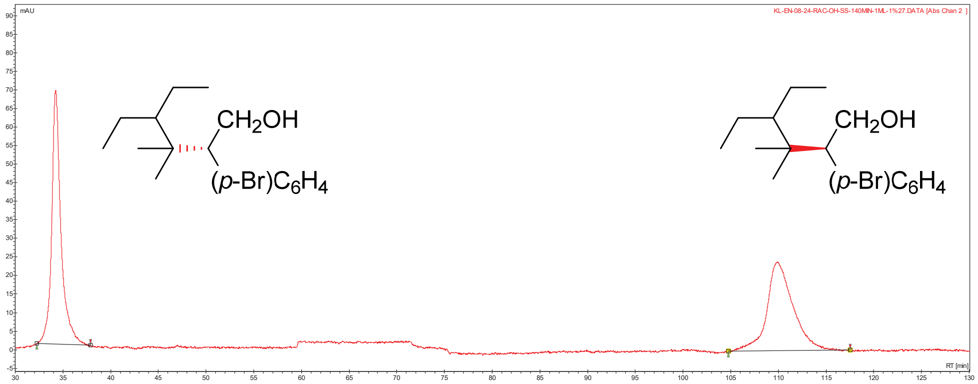


1d 3 *equiv.* **7**

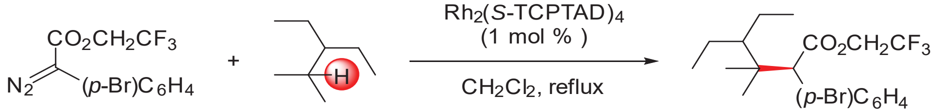


#	Time [Min]	Area % [%]
1	17.81	90.547
2	25.05	9.453
		81% e.e.

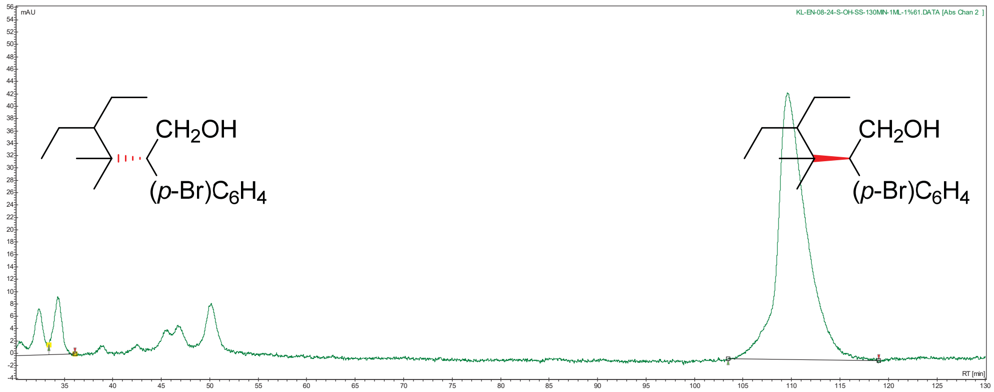




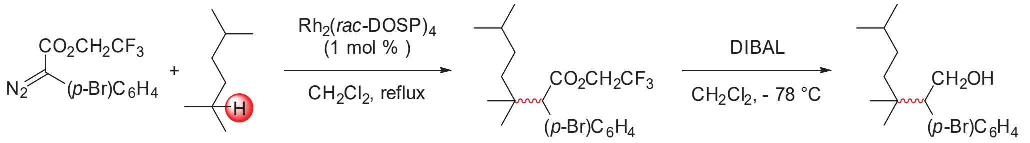
#	Time [Min]	Area % [%]
1	34.21	50.646
2	109.84	49.354

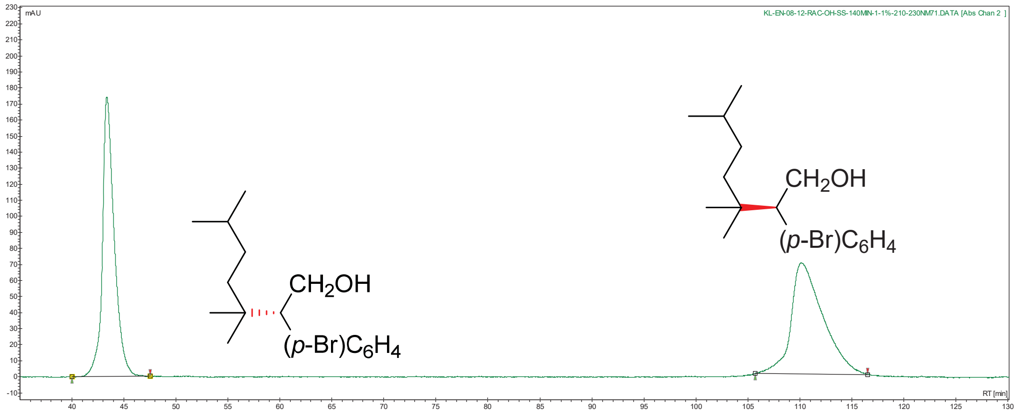


1d 3 *equiv.* **8**

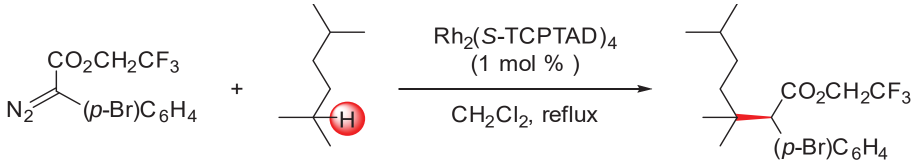


#	Time [Min]	Area % [%]
1	34.32	5.859
2	109.62	94.141
		86 % e.e.

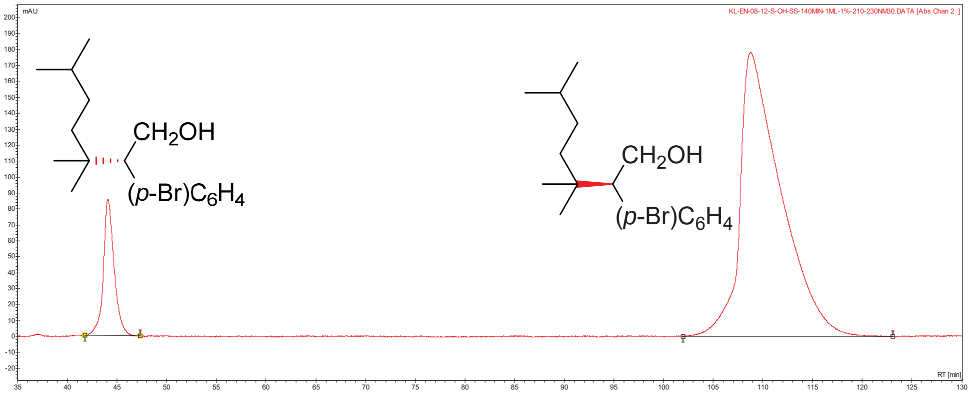




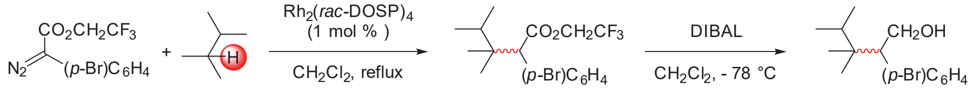
#	Time [Min]	Area % [%]
1	43.35	48.322
2	110.12	51.678

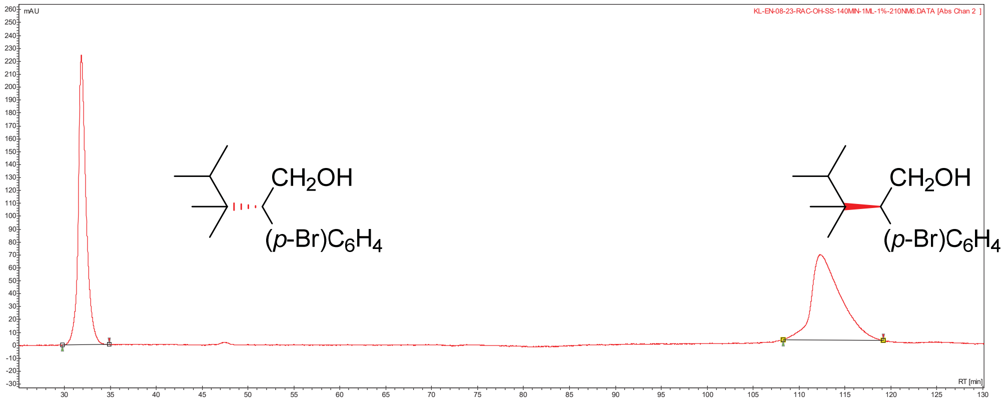


1d 3 *equiv.* **9**

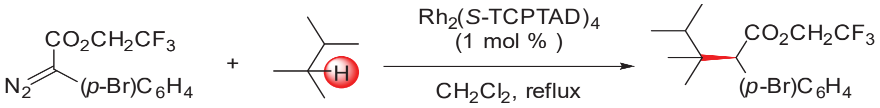


#	Time [Min]	Area % [%]
1	44.08	11.204
2	108.78	88.796
		78 % e.e.

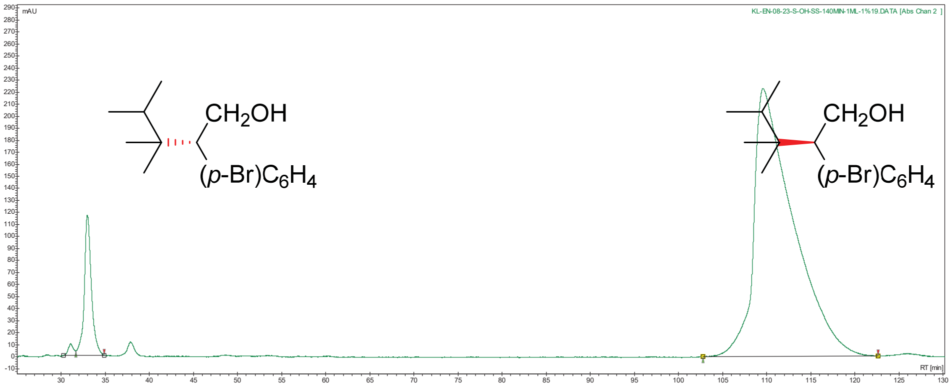




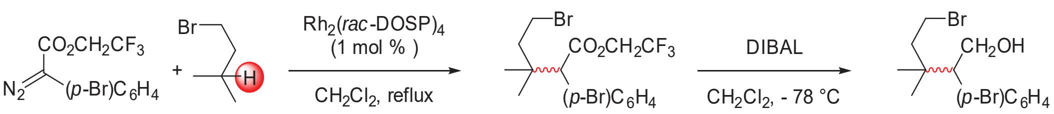
#	Time [Min]	Area % [%]
1	31.84	47.542
2	112.29	52.458

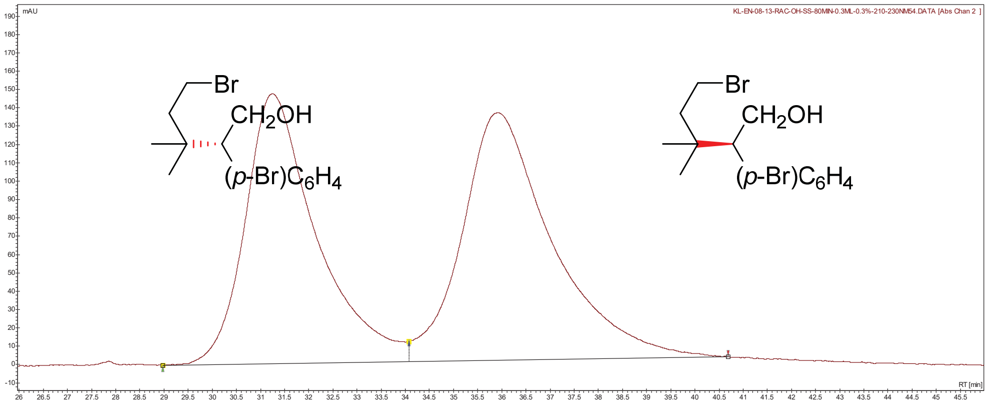


1d 3 *equiv.* **10**

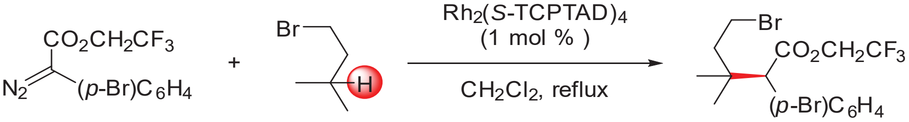


#	Time [Min]	Area % [%]
1	32.97	8.688
2	109.63	91.312
		83 % e.e.

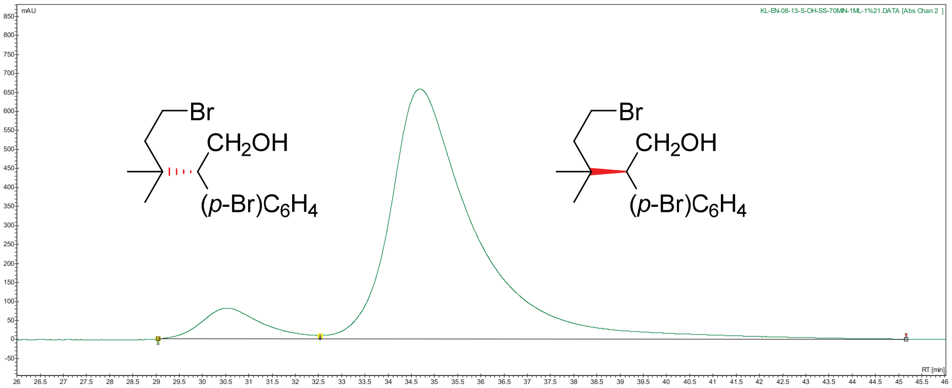




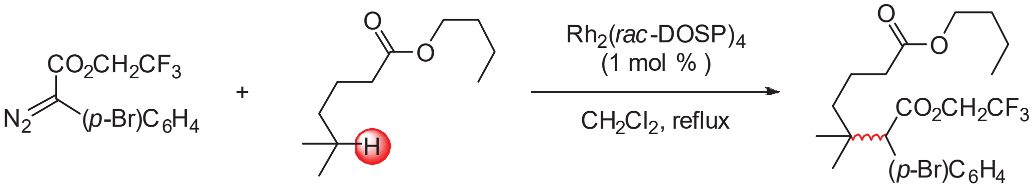
#	Time [Min]	Area % [%]
1	31.25	46.375
2	35.92	53.625

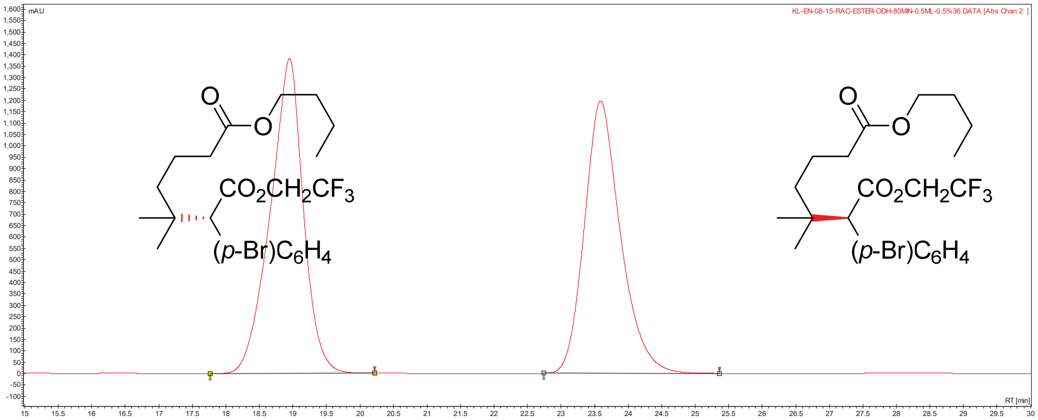


1d 3 *equiv.* **11**

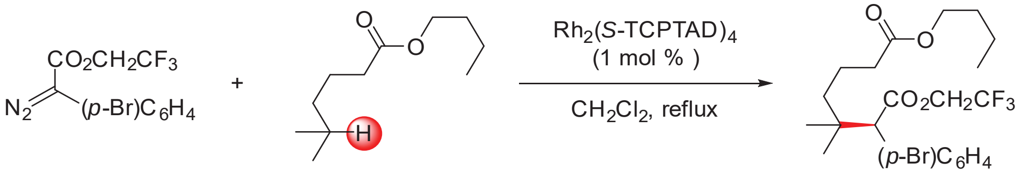


#	Time [Min]	Area % [%]
1	30.53	8.153
2	34.69	91.847
		84 % e.e.

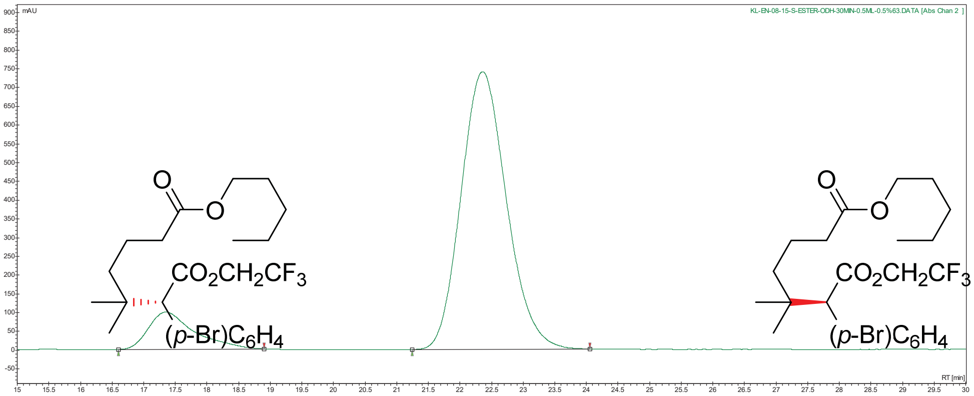




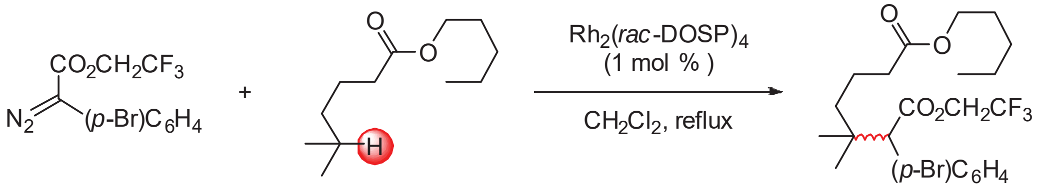
#	Time [Min]	Area % [%]
1	18.95	51.328
2	23.59	48.672

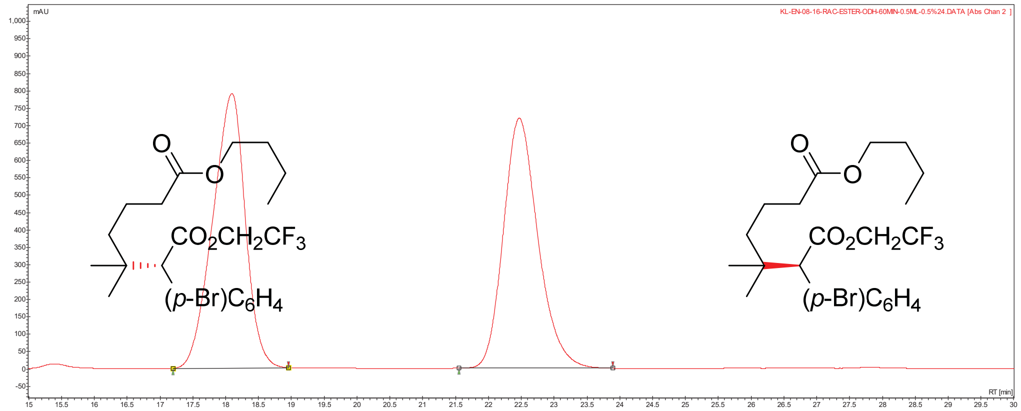


1d 3 *equiv.* **12**

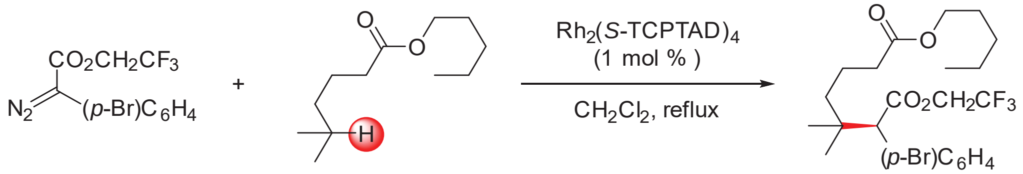


#	Time [Min]	Area % [%]
1	17.35	11.928
2	22.36	88.072
		77 % e.e.

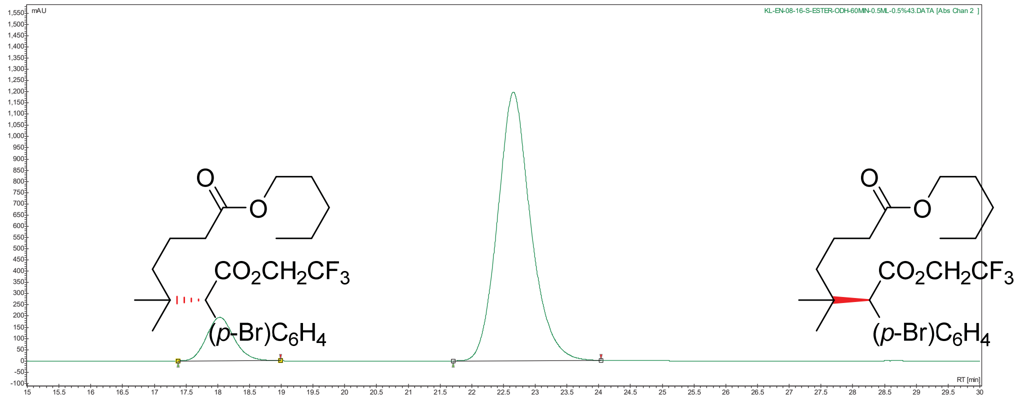




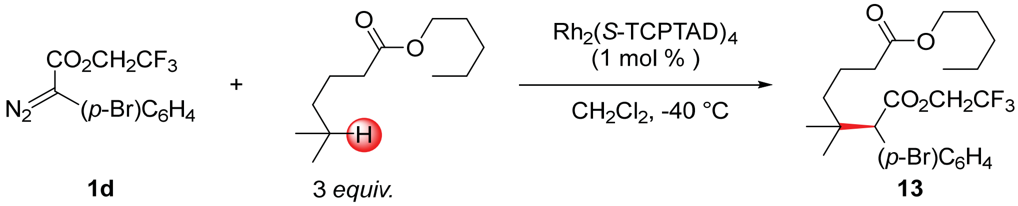
#	Time [Min]	Area % [%]
1	18.09	50.801
2	22.47	49.199

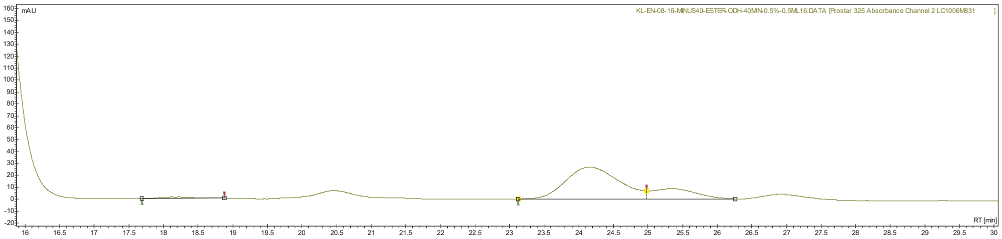


1d 3 *equiv.* **13**

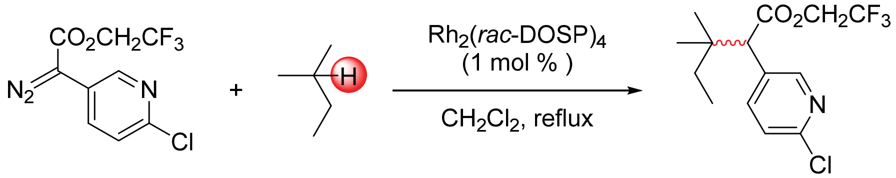


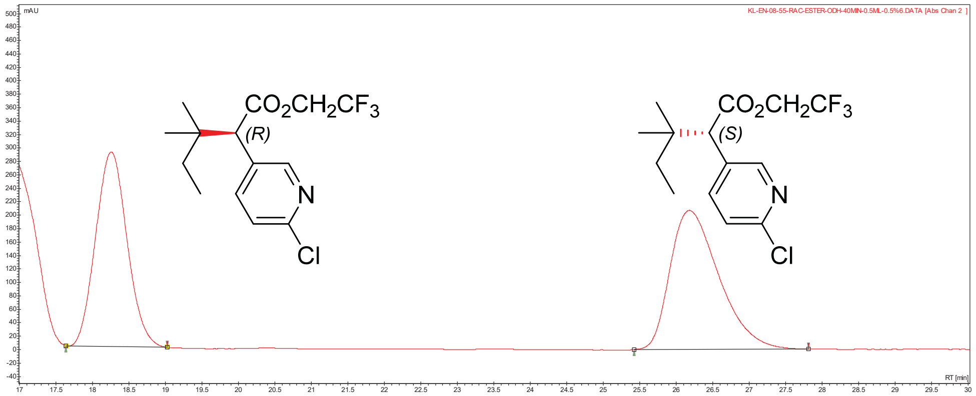
#	Time [Min]	Area % [%]
1	18.03	11.871
2	22.66	88.129
		76 % e.e.



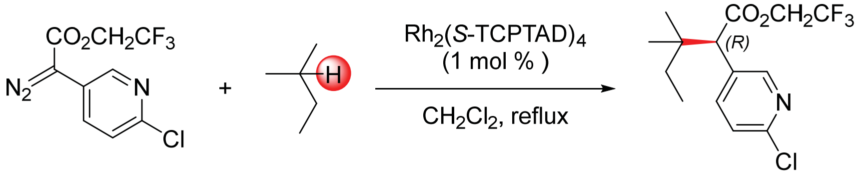


#	Time [Min]	Area % [%]
1	18.11	2.954
2	24.17	97.046
		94 % e.e.



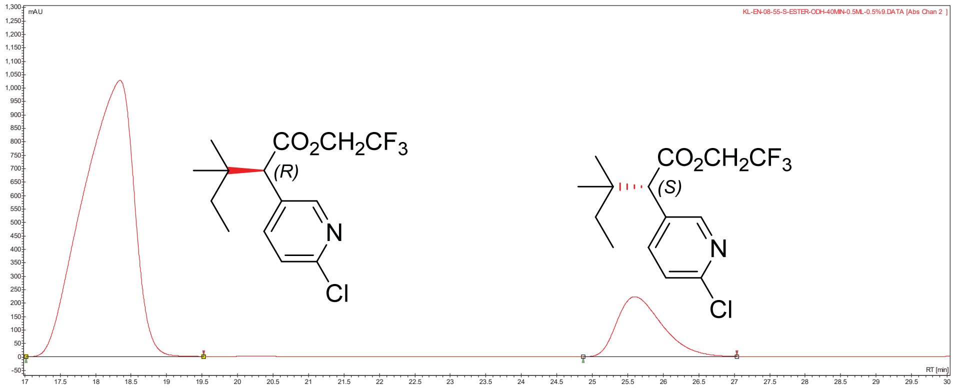


#	Time [Min]	Area % [%]
1	18.26	47.418
2	26.18	52.582

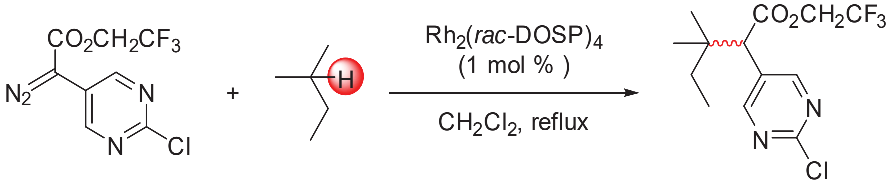


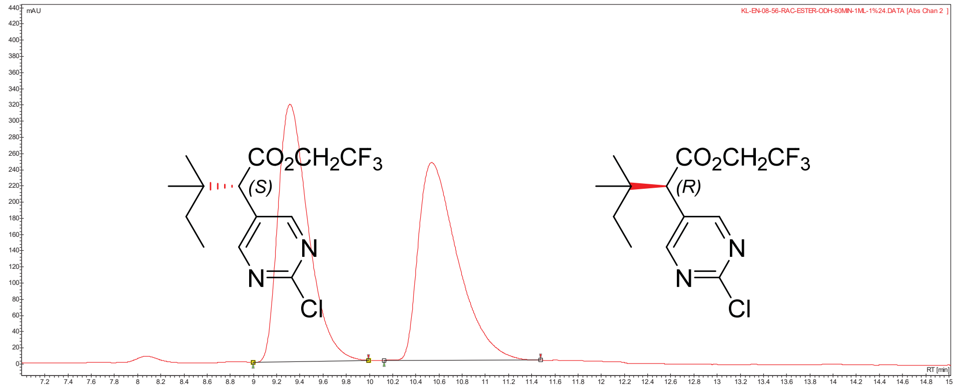
3 *equiv.*

14

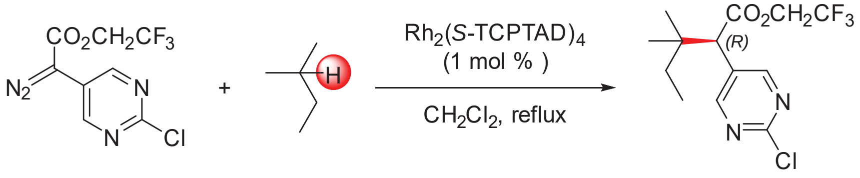


#	Time [Min]	Area % [%]
1	18.34	83.806
2	25.60	16.194
		68 % e.e.

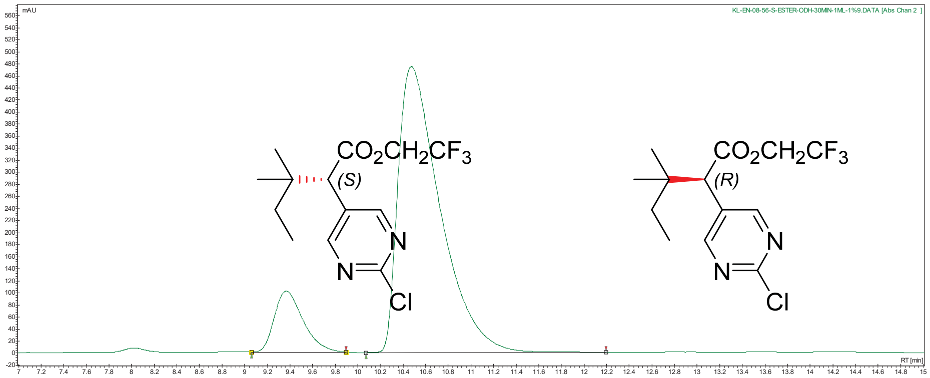




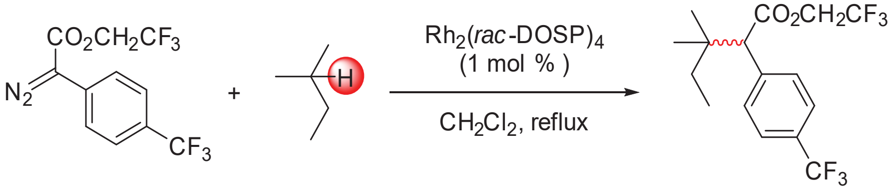
#	Time [Min]	Area % [%]
1	9.31	50.138
2	10.54	49.862

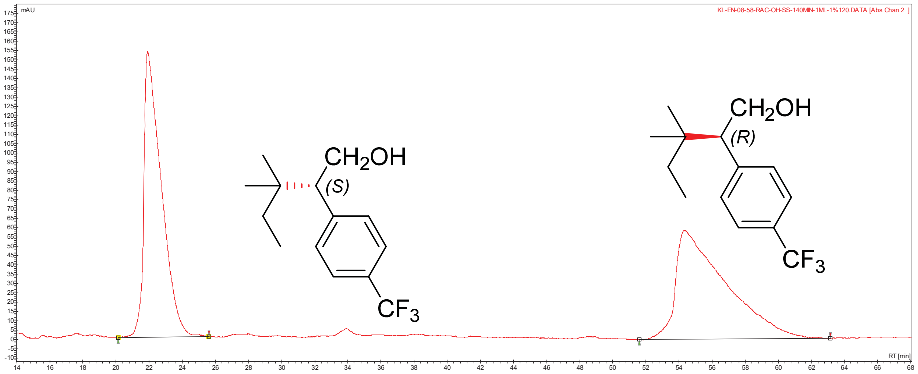


15

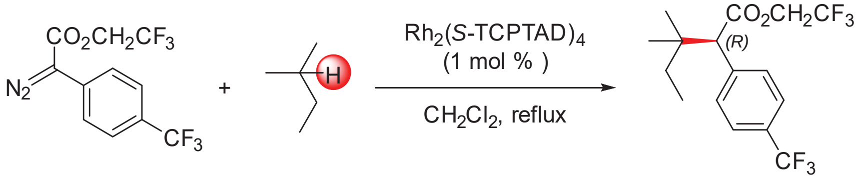


#	Time [Min]	Area % [%]
1	9.37	12.701
2	10.47	87.299
		75 % e.e.

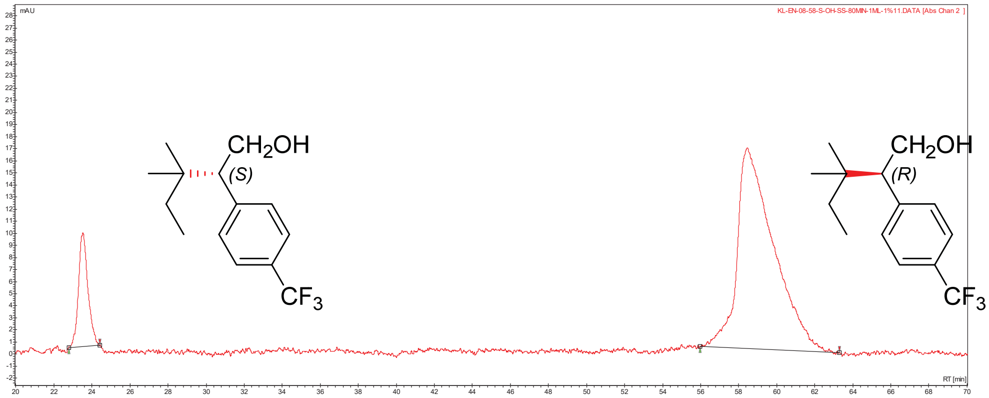




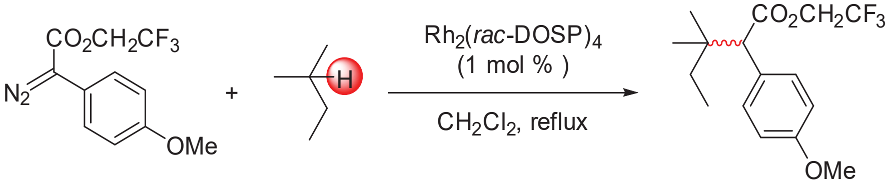
#	Time [Min]	Area % [%]
1	21.91	47.862
2	54.41	52.138

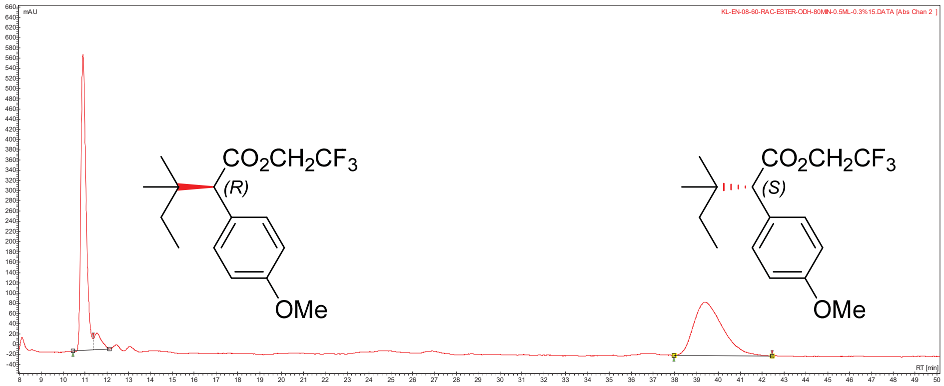


16

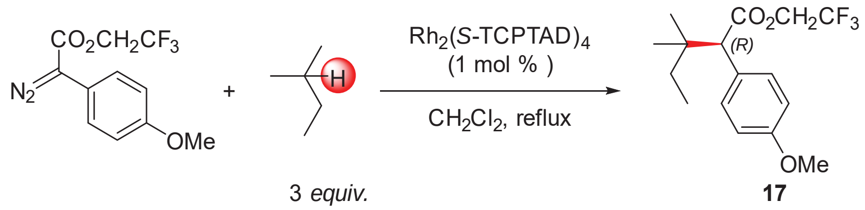


#	Time [Min]	Area % [%]
2	23.53	12.822
1	58.45	87.178
		74 % e.e.

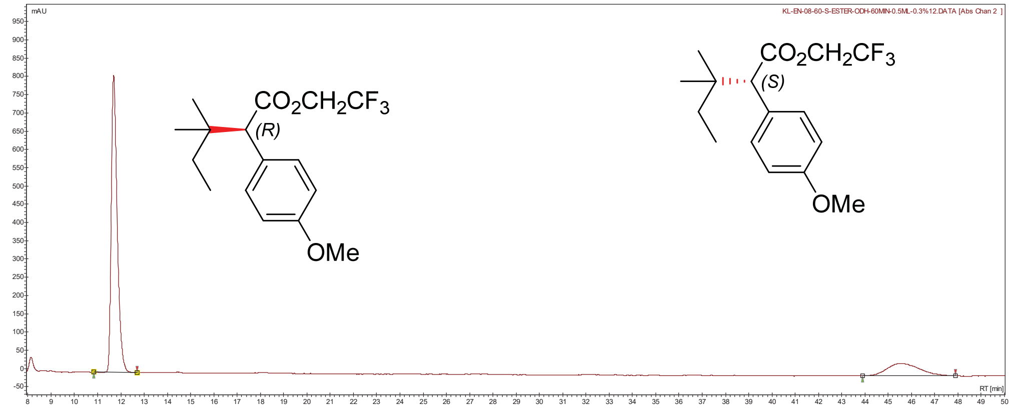




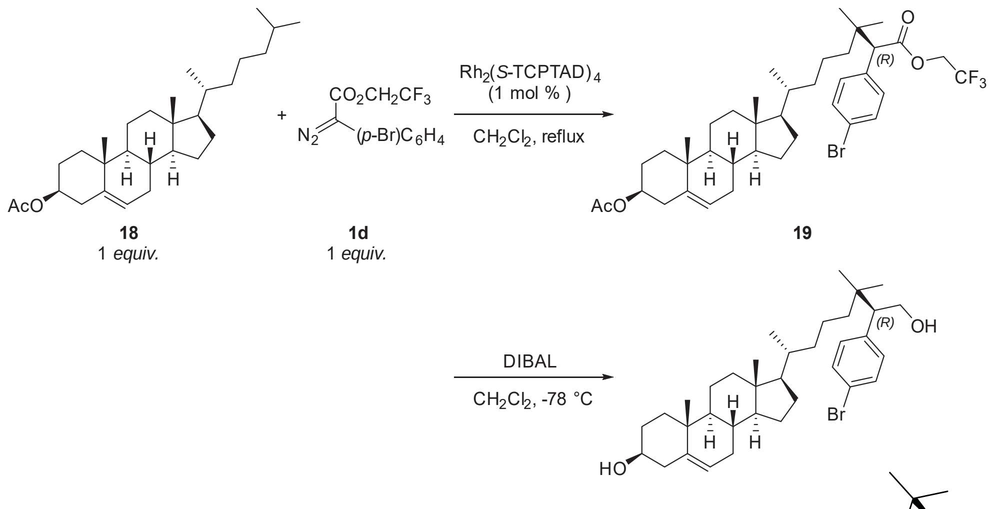
#	Time [Min]	Area % [%]
1	21.91	47.862
2	54.41	52.138



17



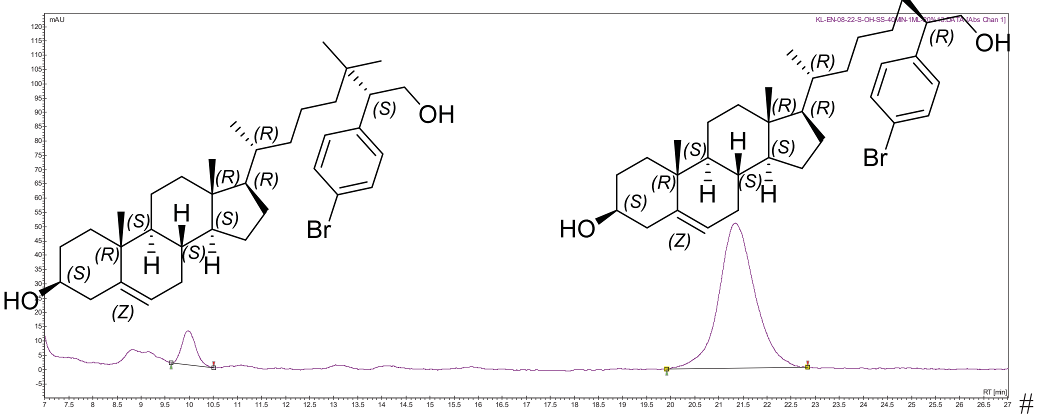
#	Time [Min]	Area % [%]
1	11.69	81.477
2	45.61	18.523
		63 % e.e.



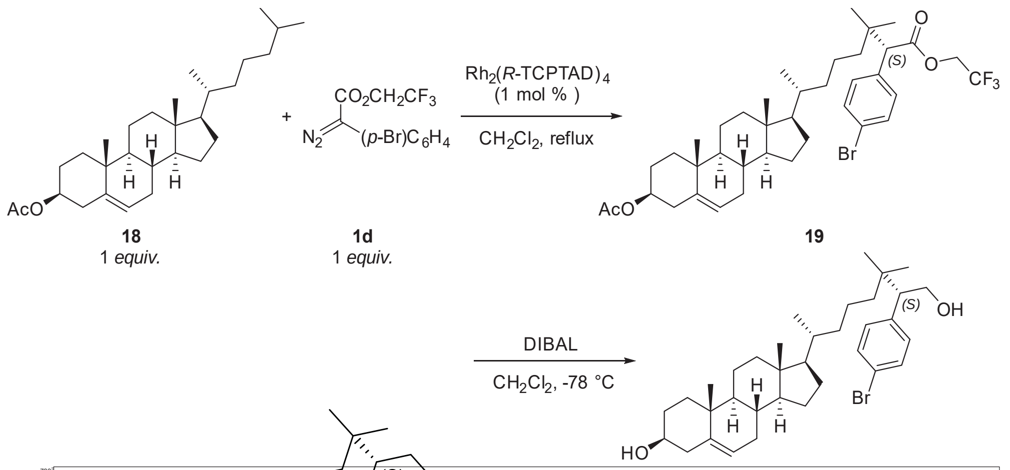
18 1 *equiv.*

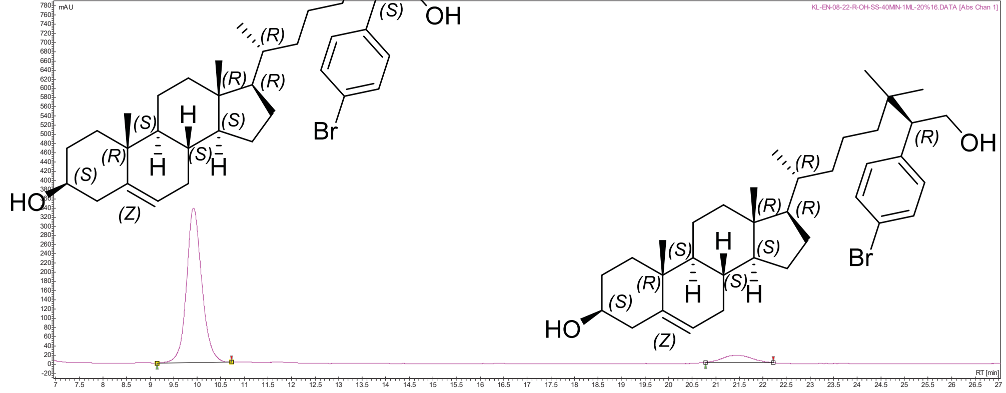
1d 1 *equiv.*

19

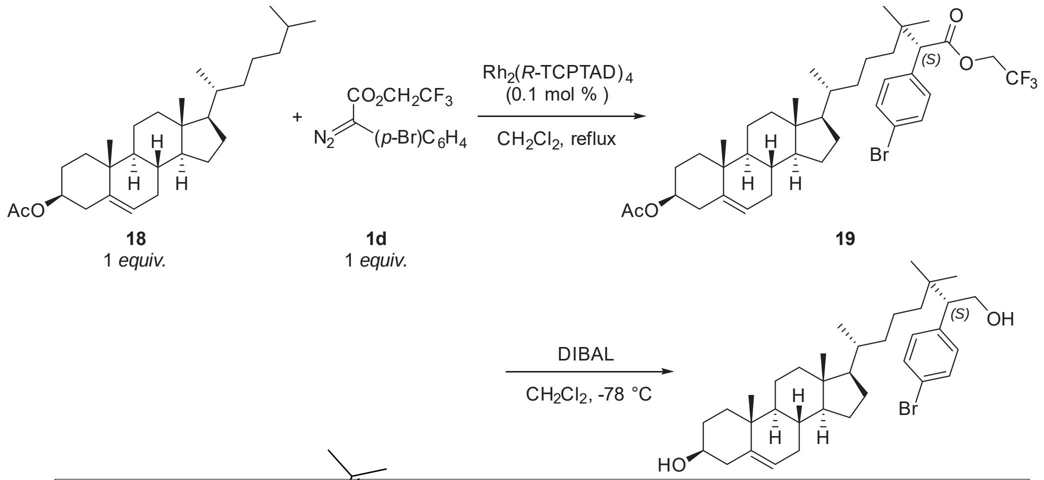


	Time [Min]	Area % [%]
1	9.97	8.250
2	21.34	91.750
		11:1 d.r.





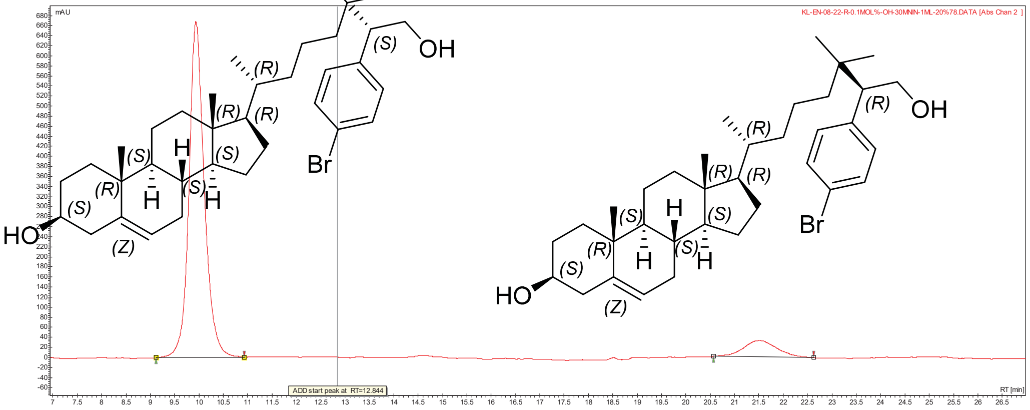
#	Time [Min]	Area % [%]
1	9.92	91.762
2	21.46	8.238
		11:1 d.r.



18
1 *equiv.*

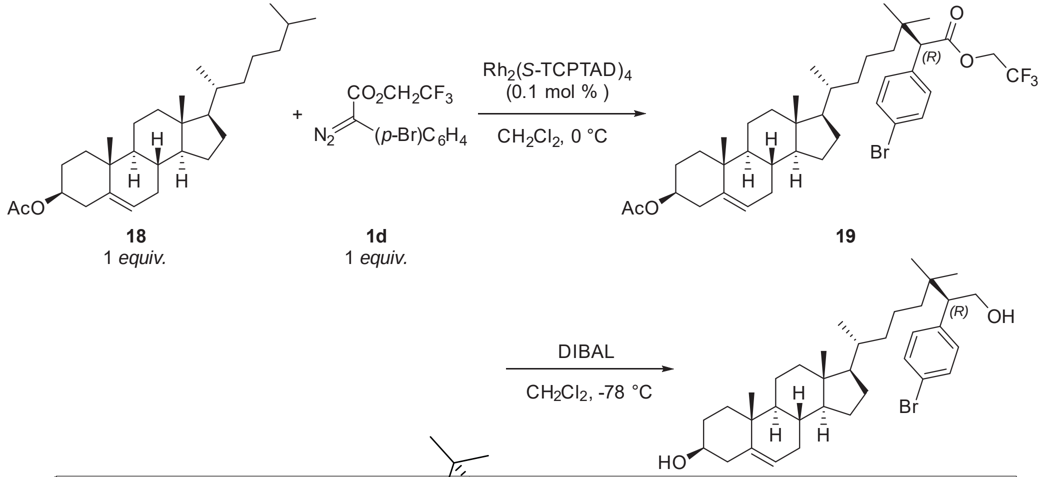
1d
1 *equiv.*

19



#	Time [Min]	Area % [%]
1	9.94	90.311
2	21.51	9.689
		9:1 d.r.

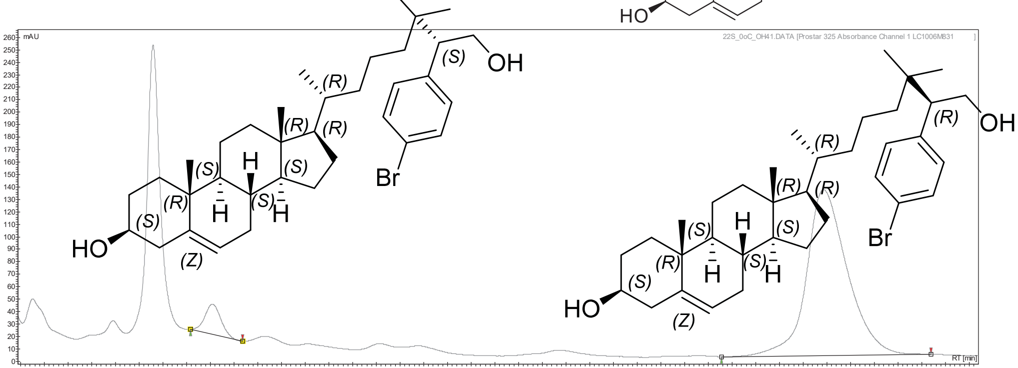
A different HPLC machine with a different S,S-whelk chiral column was used, so the enantiomers' peaks were re-determined with the products generated by Rh_2(*R*-TCPTAD)$_4$ and Rh_2(*S*-TCPTAD)$_4$.



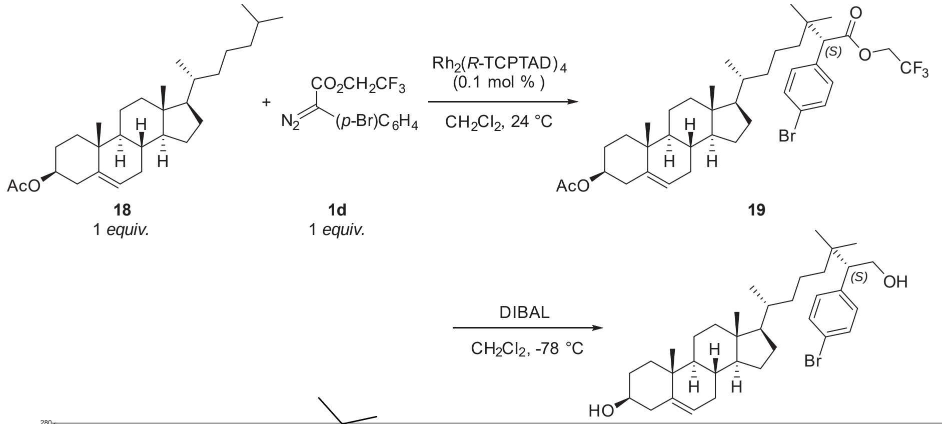
18
1 *equiv.*

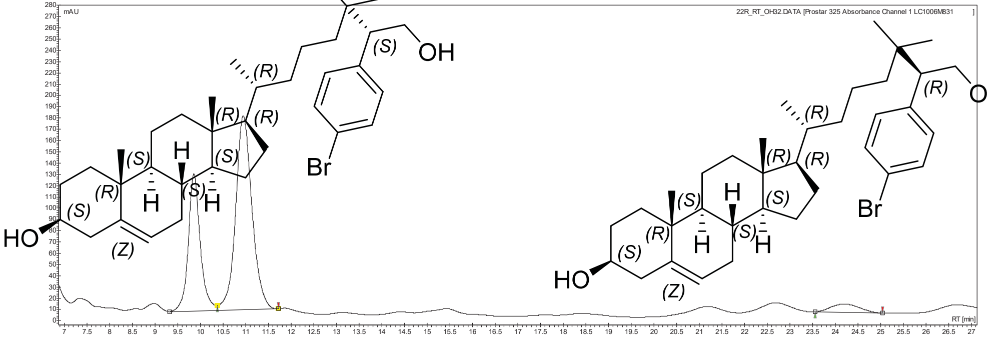
1d
1 *equiv.*

19

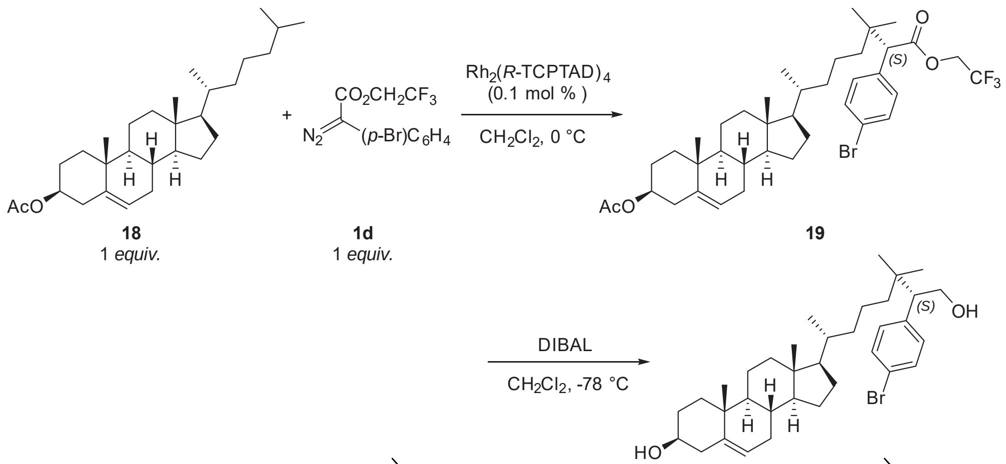


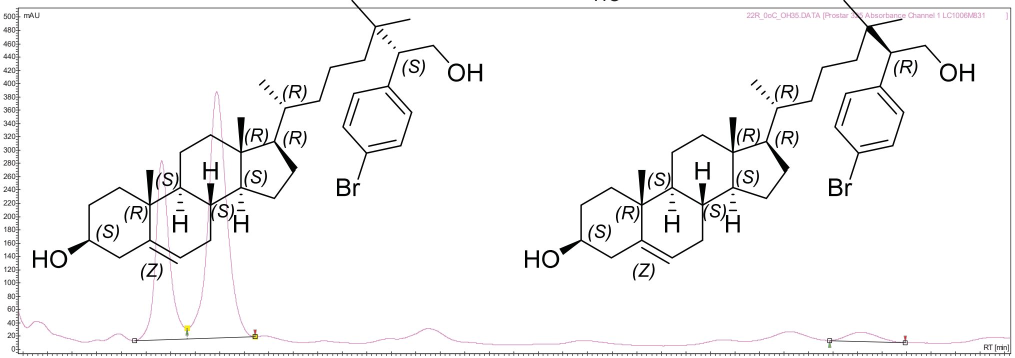
#	Time [Min]	Area % [%]
1	11.05	6.709
2	23.92	93.291
		14:1 d.r.



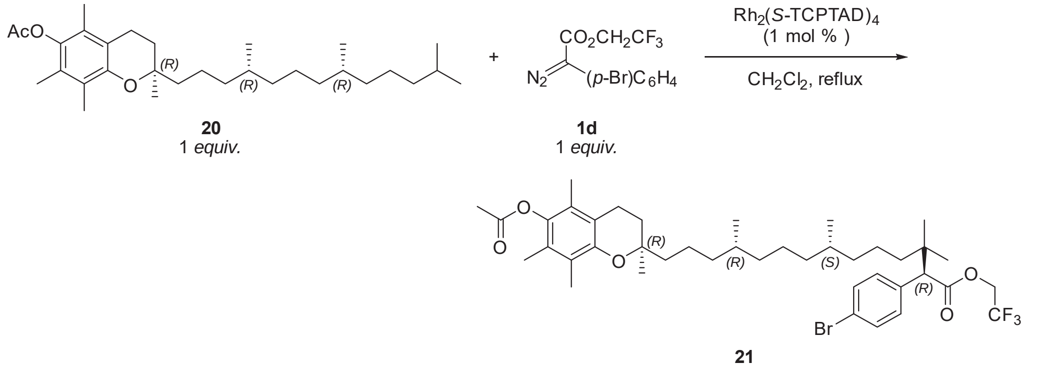


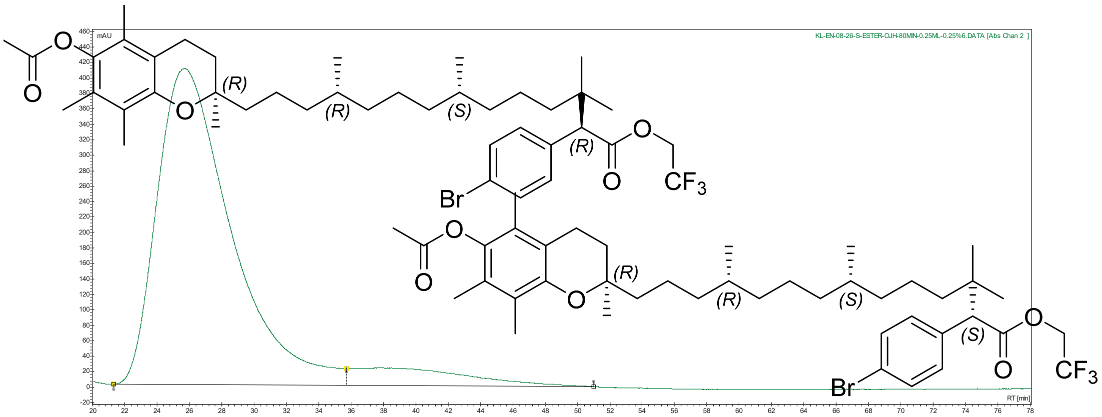
#	Time [Min]	Area % [%]
1	10.94	92.926
2	24.19	7.074
		13:1 d.r.



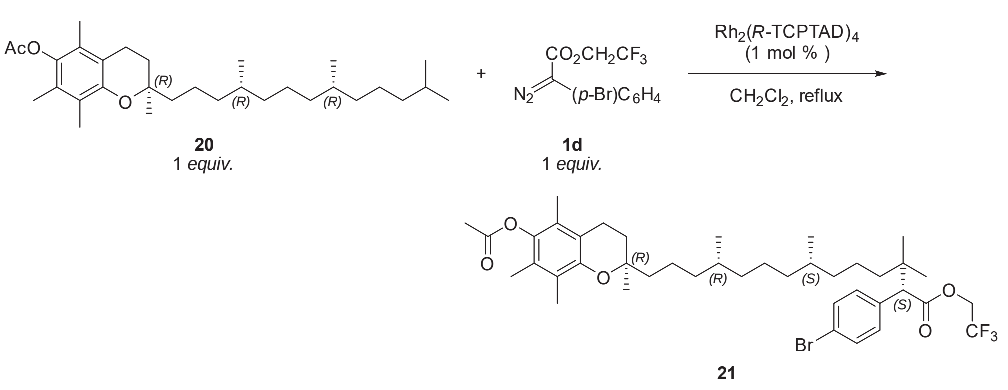


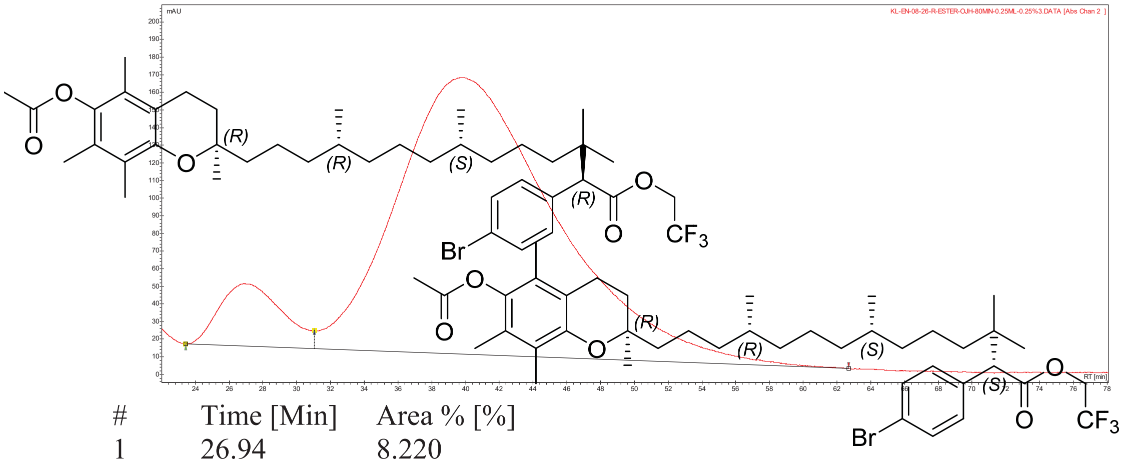
#	Time [Min]	Area % [%]
1	10.94	94.267
2	24.08	5.733
		16:1 d.r.



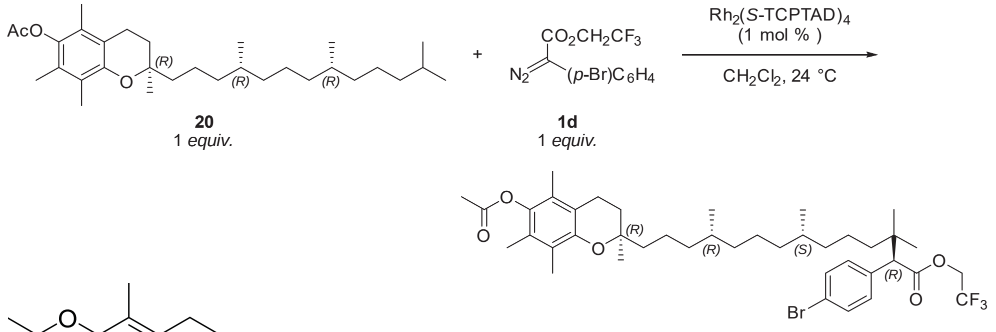


#	Time [Min]	Area % [%]
1	25.74	91.846
2	37.89	8.154
		11:1 d.r.





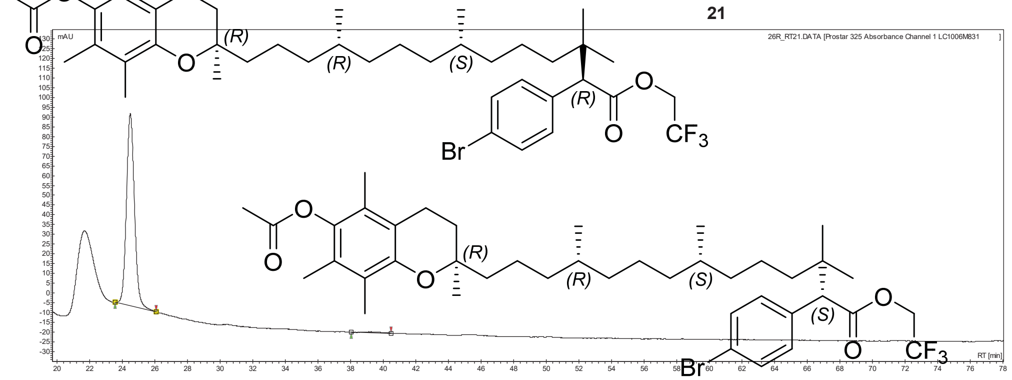
#	Time [Min]	Area % [%]
1	26.94	8.220
2	39.92	91.780
		11:1 d.r.



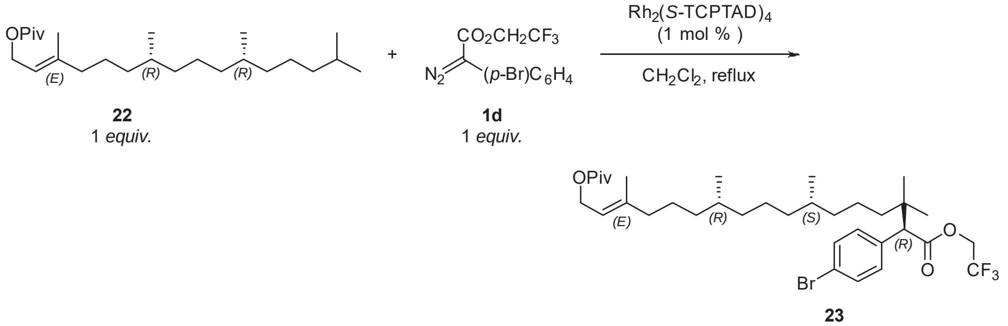
20
1 *equiv.*

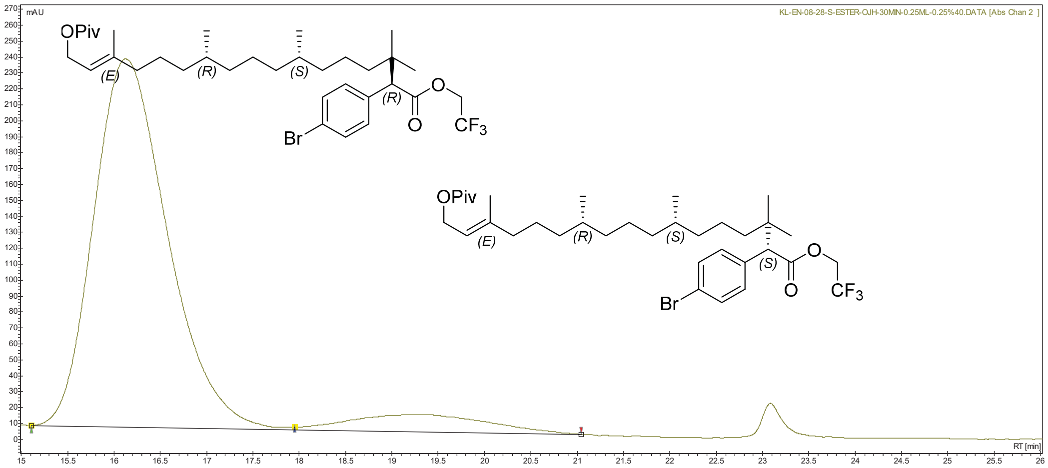
1d
1 *equiv.*

21

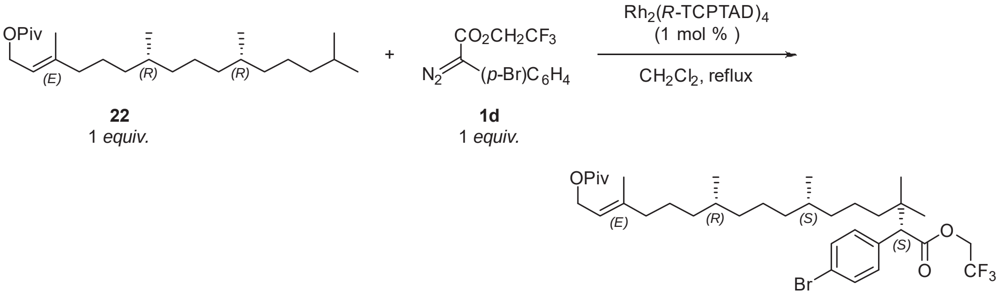


#	Time [Min]	Area % [%]
1	24.49	99.363
2	39.25	0.637
		>20:1 d.r.

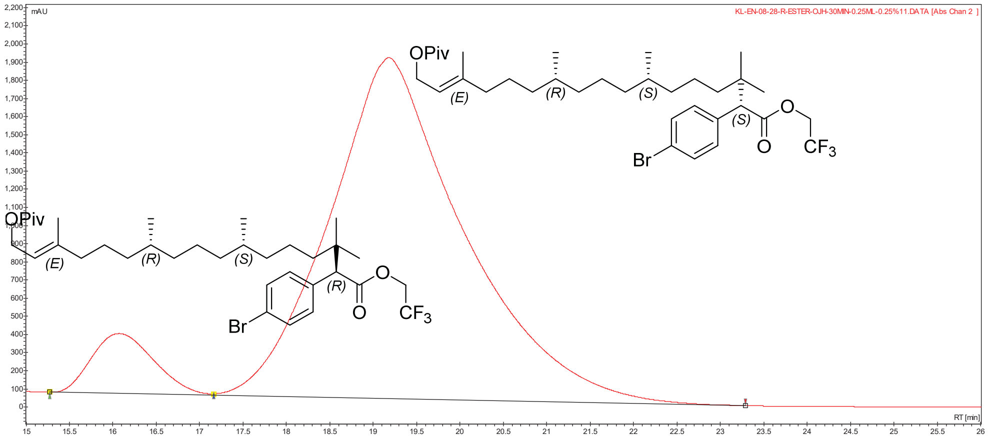




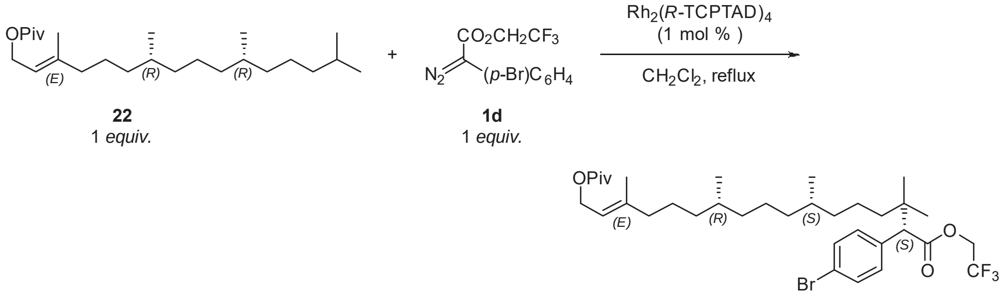
#	Time [Min]	Area % [%]
1	16.12	91.930
2	19.36	8.070
		11:1 d.r.



23



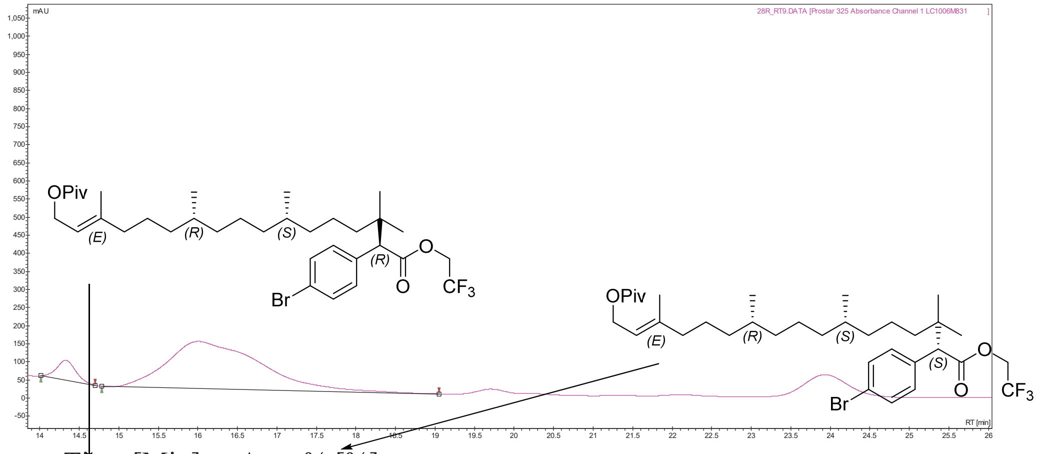
#	Time [Min]	Area % [%]
1	16.07	7.550
2	19.18	92.450
		12:1 d.r.



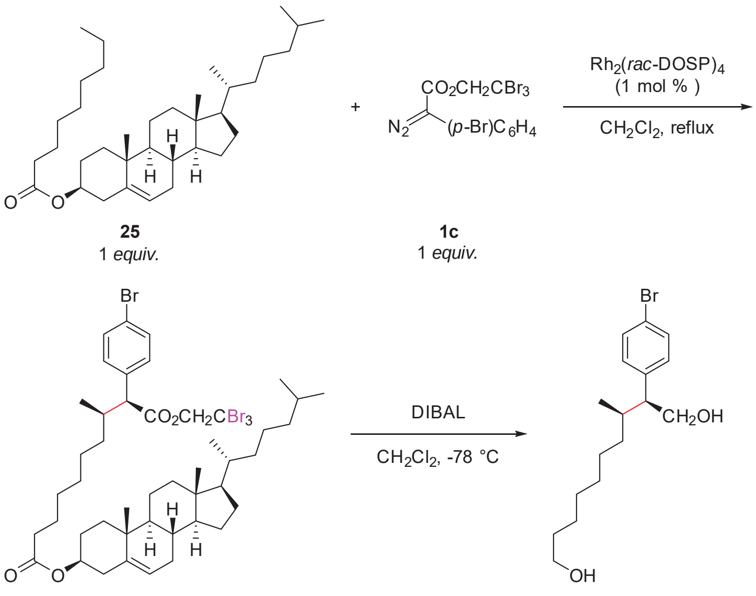
22 1 *equiv.*

1d 1 *equiv.*

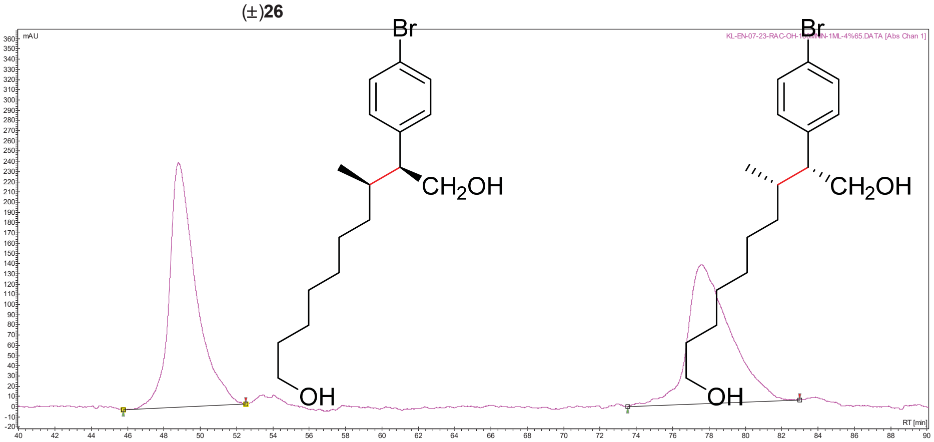
23



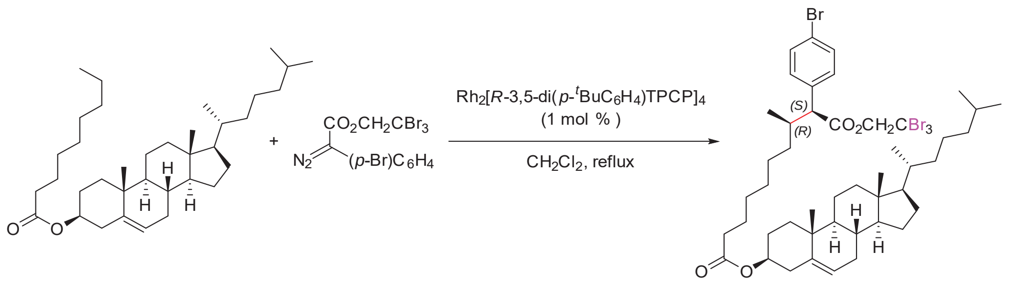
#	Time [Min]	Area % [%]
1	14.34	7.905
2	16.01	92.096
		12:1 d.r.



(±)**26**



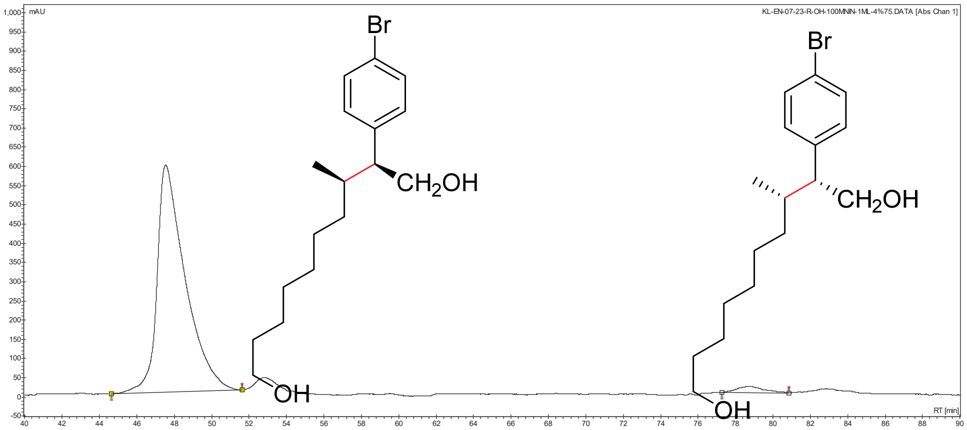
#	Time [Min]	Area % [%]
1	48.80	52.343
2	77.61	47.657



25 1 *equiv.*

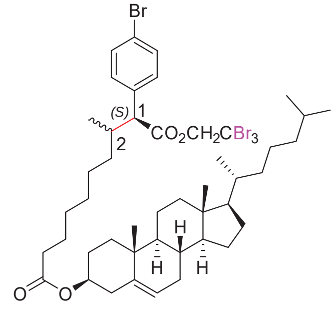
1c 1 *equiv.*

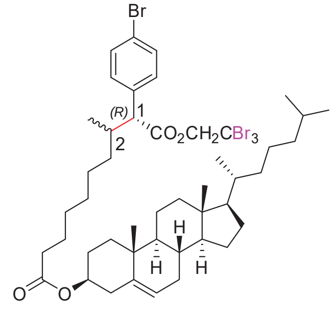
26



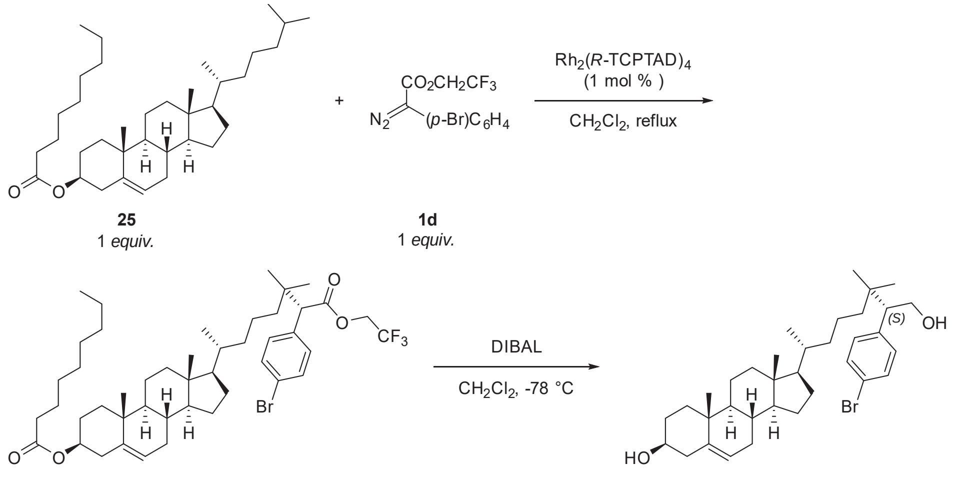
#	Time [Min]	Area % [%]
1	47.53	97.512
2	78.83	2.488
		39:1 d.r.

The 39:1 d.r. represents the ratio of C1 chiral center to the steroid, as shown below:





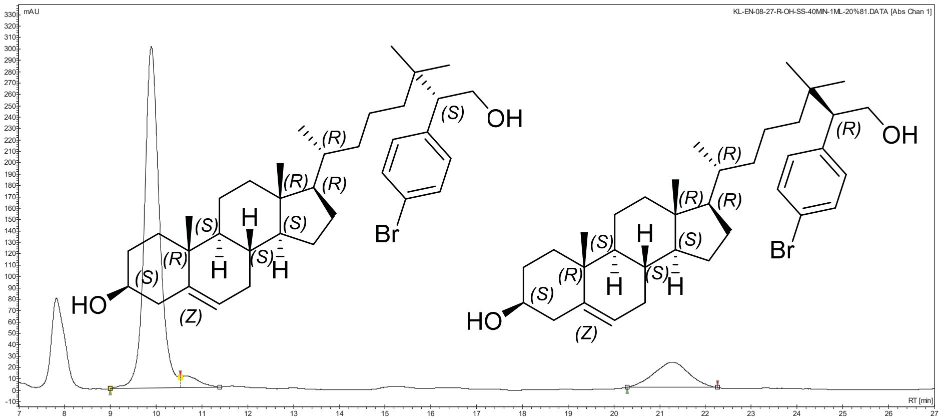
39 : 1



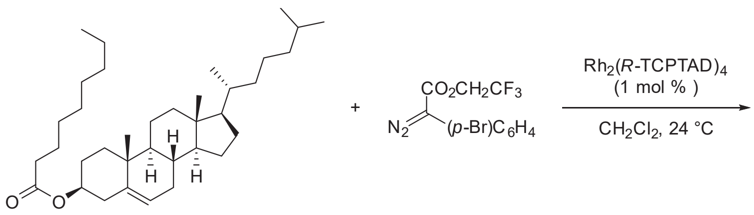
25
1 *equiv.*

1d
1 *equiv.*

27

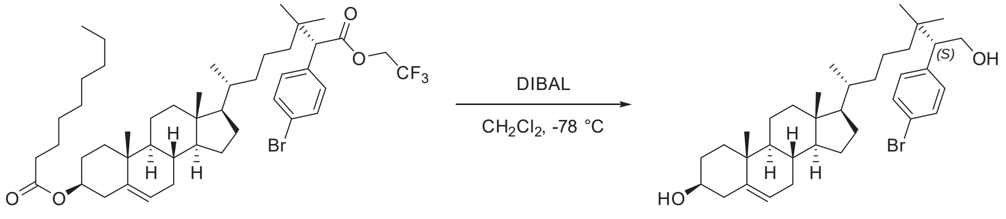


#	Time [Min]	Area % [%]
1	9.89	85.363
2	21.30	14.637
		6:1 d.r.

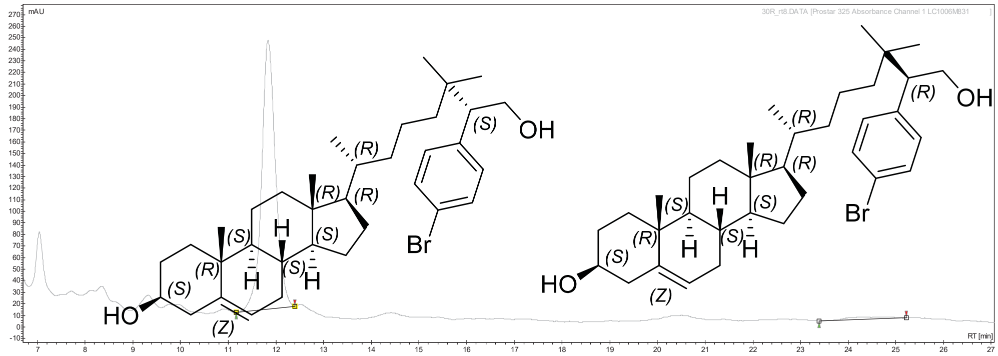


25
1 *equiv.*

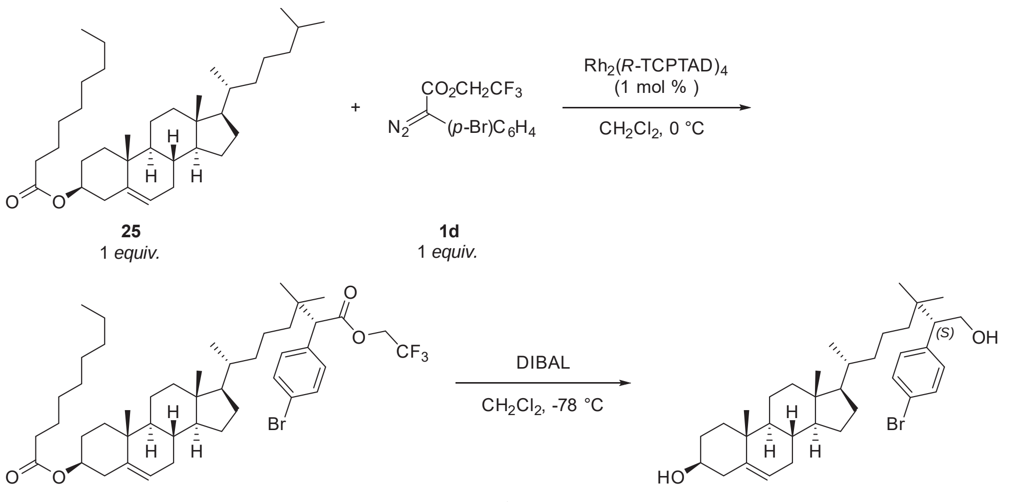
1d
1 *equiv.*



27



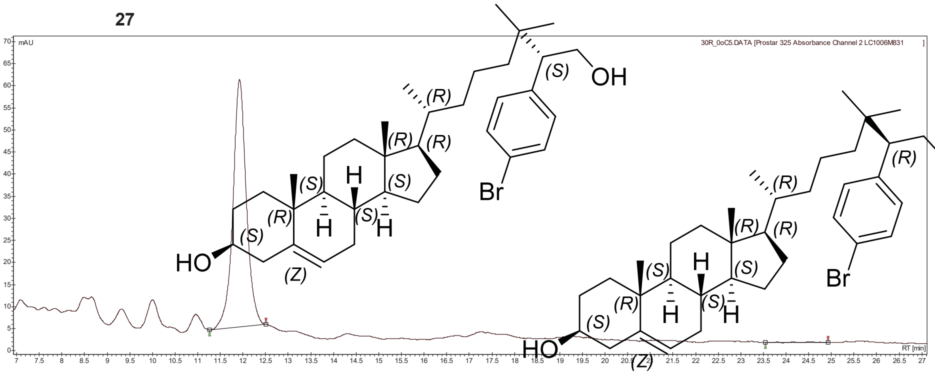
#	Time [Min]	Area % [%]
1	11.84	97.333
2	24.06	2.667
		>20:1 d.r.



25 1 *equiv.*

1d 1 *equiv.*

27



#	Time [Min]	Area % [%]
1	11.92	99.457
2	24.47	0.543
		>20:1 d.r.

10. X-Ray Crystallographic Data for **6.3.16**

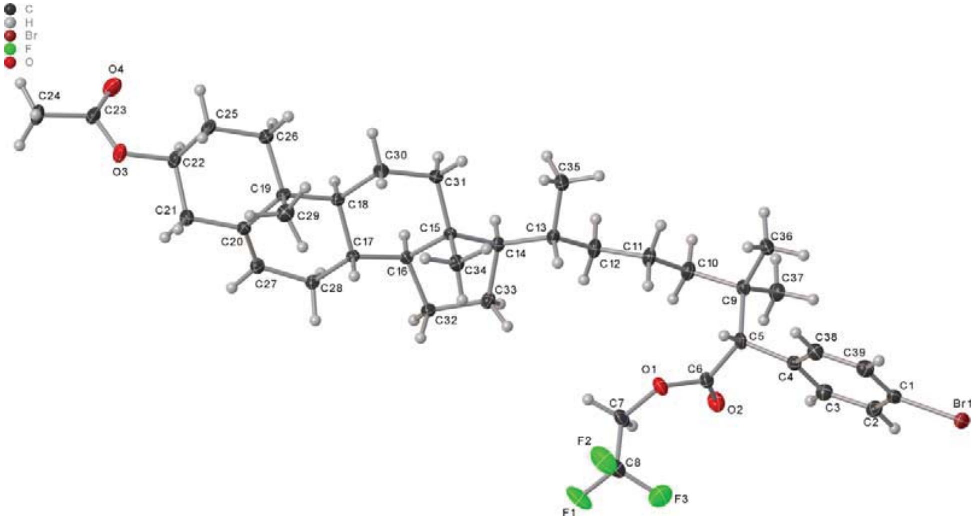


Table 1 Crystal data and structure refinement for 19*R*.

Identification code	19*R*
Empirical formula	$C_{39}H_{54}BrF_3O_4$
Formula weight	723.72
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.8637(16)
b/Å	15.308(4)
c/Å	30.278(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3644.8(15)
Z	4
ρ_{calc}g/cm^3	1.319
μ/mm^{-1}	1.182
F(000)	1528.0

Crystal size/mm^3	1.165 × 0.591 × 0.296
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.69 to 61.016
Index ranges	$-11 \leq h \leq 11$, $-21 \leq k \leq 21$, $-43 \leq l \leq 38$
Reflections collected	48851
Independent reflections	11132 [R_{int} = 0.0465, R_{sigma} = 0.0280]
Data/restraints/parameters	11132/2/440
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0377, wR_2 = 0.0903
Final R indexes [all data]	R_1 = 0.0442, wR_2 = 0.0941
Largest diff. peak/hole / e Å^{-3}	0.74/-0.22
Flack parameter	-0.013(3)

Table 2 Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2\times10^3$) for 19*R*. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	7538.3(3)	1662.9(2)	10528.5(2)	23.74(7)
F1	1005(2)	3514.1(13)	7763.3(7)	40.8(5)
F2	3364(3)	4127.9(12)	7955.9(8)	42.1(5)
F3	2072(3)	3277.1(14)	8410.0(6)	43.5(5)
O3	7622(3)	5249.5(11)	3254.1(5)	21.2(3)
O1	4985(2)	2514.2(12)	8024.4(6)	21.4(4)
O2	3982(2)	1302.8(13)	8366.9(7)	25.2(4)
O4	8464(3)	4073.4(13)	2861.8(7)	29.3(4)
C6	5133(3)	1802.9(16)	8299.4(8)	18.0(4)
C27	4866(3)	4318.7(16)	4574.3(8)	16.8(4)
C28	4698(3)	3896.7(16)	5020.3(8)	15.8(4)
C1	7333(3)	1684.8(15)	9902.6(7)	17.5(4)
C2	6065(3)	1193.9(17)	9699.7(8)	19.6(5)
C20	6310(3)	4647.4(14)	4407.8(8)	15.2(4)
C32	4783(3)	3220.2(16)	5975.7(8)	16.1(4)
C23	8036(3)	4829.5(17)	2879.0(8)	20.3(5)
C15	7878(3)	3351.5(15)	5979.7(7)	13.0(4)
C18	7928(3)	3901.1(15)	5021.4(7)	14.0(4)
C19	8022(3)	4605.0(14)	4649.0(8)	14.3(4)
C22	7694(3)	4747.0(15)	3662.8(7)	17.8(4)

C39	8423(3)	2206.0(17)	9656.9(9)	20.3(5)
C14	7437(3)	2600.1(13)	6307.3(6)	14.2(3)
C34	7949(3)	4228.6(15)	6227.4(8)	16.6(4)
C13	8458(3)	2525.9(16)	6741.1(7)	16.4(4)
C17	6306(3)	3985.8(14)	5305.1(7)	12.4(4)
C25	9428(3)	4846.8(18)	3880.4(8)	19.9(5)
C10	7672(4)	973.7(15)	7750.4(7)	19.2(4)
C11	8398(3)	1757.0(17)	7494.2(8)	19.4(4)
C16	6332(3)	3294.1(14)	5666.5(7)	12.4(4)
C35	10392(3)	2465.4(19)	6663.5(9)	23.7(5)
C9	7936(3)	972.1(15)	8257.4(8)	16.7(4)
C4	6995(3)	1735.4(15)	8982.4(7)	15.6(4)
C33	5487(3)	2723.8(16)	6384.4(8)	18.0(4)
C36	9836(3)	1092.7(17)	8367.2(9)	20.2(5)
C38	8243(3)	2224.0(16)	9199.2(8)	18.7(4)
C26	9433(3)	4331.8(17)	4316.5(8)	18.8(4)
C31	9490(3)	3228.2(17)	5697.3(8)	18.3(4)
C12	7830(3)	1737.0(16)	7010.0(8)	19.8(5)
C21	6292(3)	5100.5(17)	3961.8(8)	19.7(5)
C7	3409(3)	2613.3(18)	7794.4(9)	22.1(5)
C3	5893(3)	1224.7(16)	9241.1(8)	19.0(5)
C8	2464(4)	3388.3(16)	7983.2(9)	24.4(5)
C37	7337(4)	82.4(15)	8429.8(8)	20.9(4)
C24	7861(4)	5426(2)	2487.1(9)	27.5(6)
C30	9553(3)	3874.5(17)	5307.6(8)	19.4(5)

C29	8438(3)	5522.3(16)	4837.7(9)	20.5(5)
C5	6942(3)	1753.8(15)	8477.5(8)	15.5(4)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for 19*R*. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+…].

Atom	U$_{11}$	U$_{22}$	U$_{33}$	U$_{23}$	U$_{13}$	U$_{12}$
Br1	22.33(11)	33.72(13)	15.17(10)	-1.42(9)	-0.75(10)	7.24(12)
F1	25.0(9)	37.5(10)	59.8(13)	-1.1(9)	-17.8(9)	10.1(7)
F2	37.9(10)	21.5(8)	67.0(14)	5.7(8)	-14.3(10)	-2.4(7)
F3	50.1(12)	49.9(11)	30.4(9)	-4.9(8)	5.9(8)	9.7(10)
O3	29.7(9)	19.5(7)	14.3(7)	3.6(6)	1.2(8)	1.7(8)
O1	17.9(8)	22.0(8)	24.4(9)	6.7(7)	-5.4(7)	1.3(7)
O2	16.8(8)	30.4(10)	28.4(10)	8.9(8)	-3.6(7)	-5.8(7)
O4	40.0(12)	26.9(10)	20.9(9)	-0.1(7)	7.1(8)	5.3(9)
C6	16.7(10)	21.1(11)	16.2(10)	2.8(8)	-1.8(8)	0.4(8)
C27	15.9(10)	19.5(10)	15(1)	0.4(8)	-1.7(8)	-0.2(8)
C28	12.4(9)	19.7(10)	15.1(10)	2.1(8)	0.7(8)	-2.4(8)
C1	17.6(10)	18.7(9)	16.1(9)	-1.4(8)	-0.3(8)	4.9(10)
C2	18.4(11)	22.0(11)	18.4(11)	2.0(9)	2.1(9)	-2.0(9)
C20	15.6(10)	15.3(9)	14.5(11)	0.4(8)	0.3(8)	1.5(8)
C32	13.5(9)	20.1(11)	14.8(10)	1.3(8)	1.3(8)	0.1(8)
C23	21.0(11)	26.2(12)	13.8(10)	1.8(9)	2.0(8)	-0.5(9)
C15	13.8(9)	12.4(8)	12.8(9)	0.0(7)	0.5(7)	1.0(7)
C18	12.4(9)	15.8(9)	13.8(9)	0.2(7)	0.6(7)	-0.2(7)
C19	13.5(9)	15.4(9)	14.1(10)	0.1(8)	2.0(8)	0.0(8)
C22	23.1(12)	17.2(9)	13.0(9)	3.5(7)	1.8(9)	-0.4(9)
C39	18.1(11)	20.7(11)	22.2(12)	-1.6(9)	-2.2(9)	-2.6(9)
C14	15.7(8)	14.2(8)	12.6(8)	0.0(7)	-1.1(9)	-0.3(9)
C34	17.8(10)	15.0(9)	16.8(10)	-2.4(8)	-3.1(8)	-2.1(8)
C13	19.4(10)	17.2(10)	12.5(10)	1.0(8)	0.0(8)	0.9(8)
C17	11.8(9)	13.2(9)	12.1(9)	-0.7(7)	0.3(7)	-0.1(8)

C25	19.4(11)	25.7(12)	14.5(11)	4.2(9)	4.1(9)	-2.0(9)
C10	24.3(12)	17.4(10)	15.8(9)	2.7(7)	-0.6(10)	-3.5(10)
C11	23.8(11)	19.9(11)	14.5(10)	4.3(8)	-1.3(8)	-4.6(10)
C16	13.4(9)	12.1(9)	11.9(9)	-1.2(7)	0.8(7)	-0.7(8)
C35	19.0(11)	32.2(13)	19.8(12)	7.8(10)	-0.4(9)	3.5(10)
C9	17.2(10)	15.6(10)	17.2(10)	4.2(8)	-1.0(8)	-1.3(8)
C4	15.8(9)	14.6(10)	16.5(10)	1.7(8)	0.1(7)	0.6(8)
C33	17.9(10)	21.3(11)	14.9(10)	2.1(8)	0.4(8)	-3.0(9)
C36	17.6(11)	23.7(12)	19.2(11)	4.9(9)	-1.2(9)	2.4(9)
C38	17.7(10)	17.2(10)	21.1(11)	1.6(8)	-0.4(9)	-1.9(9)
C26	16.3(10)	23.4(11)	16.9(11)	3.4(9)	3.2(9)	2.8(9)
C31	15.1(9)	24.0(12)	15.7(10)	1.7(9)	0.9(8)	4.4(9)
C12	25.8(12)	19(1)	14.6(9)	3.3(8)	-1.8(8)	-2.1(9)
C21	20.2(11)	21.8(11)	17.2(11)	4.9(9)	0.9(9)	2.6(9)
C7	18.3(11)	25.9(12)	22.1(12)	1.6(10)	-6.9(9)	3.9(9)
C3	17.1(10)	19.3(11)	20.7(12)	1.2(9)	0.4(9)	-4.4(9)
C8	20.3(10)	23.5(11)	29.3(12)	0.3(9)	-6.4(11)	2.5(13)
C37	24.8(12)	16.0(9)	21.8(10)	5.3(8)	1.1(10)	-2.8(10)
C24	32.1(16)	34.9(14)	15.5(11)	8.1(10)	1.1(10)	3.6(11)
C30	11.5(10)	27.2(12)	19.5(12)	4.6(9)	1.7(9)	0.5(9)
C29	20.5(11)	18.8(11)	22.1(12)	-0.1(9)	1.1(9)	-5.1(9)
C5	15.4(8)	15.2(10)	16(1)	4.6(8)	-4.0(7)	-3.5(8)

Table 4 Bond Lengths for 19*R*.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C1	1.902(2)	C18	C19	1.562(3)
F1	C8	1.340(3)	C18	C17	1.544(3)
F2	C8	1.338(3)	C18	C30	1.544(3)
F3	C8	1.339(3)	C19	C26	1.556(3)
O3	C23	1.345(3)	C19	C29	1.551(3)
O3	C22	1.458(3)	C22	C25	1.522(4)
O1	C6	1.376(3)	C22	C21	1.526(3)
O1	C7	1.429(3)	C39	C38	1.393(4)
O2	C6	1.203(3)	C14	C13	1.543(3)
O4	C23	1.206(3)	C14	C33	1.563(4)
C6	C5	1.523(3)	C13	C35	1.542(4)
C27	C28	1.503(3)	C13	C12	1.538(3)
C27	C20	1.340(3)	C17	C16	1.523(3)
C28	C17	1.536(3)	C25	C26	1.538(3)
C1	C2	1.391(3)	C10	C11	1.538(3)
C1	C39	1.387(3)	C10	C9	1.549(3)
C2	C3	1.396(4)	C11	C12	1.533(3)
C20	C19	1.533(3)	C9	C36	1.542(3)
C20	C21	1.518(3)	C9	C37	1.533(3)
C32	C16	1.540(3)	C9	C5	1.577(3)
C32	C33	1.554(3)	C4	C38	1.398(3)
C23	C24	1.503(4)	C4	C3	1.405(3)
C15	C14	1.558(3)	C4	C5	1.530(3)
C15	C34	1.539(3)	C31	C30	1.541(3)
C15	C16	1.544(3)	C7	C8	1.512(4)
C15	C31	1.541(3)			

Table 5 Bond Angles for 19*R*.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C23	O3	C22	117.06(19)	C35	C13	C14	112.8(2)
C6	O1	C7	116.9(2)	C12	C13	C14	109.97(19)
O1	C6	C5	109.4(2)	C12	C13	C35	110.5(2)
O2	C6	O1	122.9(2)	C28	C17	C18	111.13(18)
O2	C6	C5	127.7(2)	C16	C17	C28	110.66(18)
C20	C27	C28	125.0(2)	C16	C17	C18	109.27(18)
C27	C28	C17	113.19(19)	C22	C25	C26	108.8(2)
C2	C1	Br1	119.42(18)	C11	C10	C9	116.8(2)
C39	C1	Br1	119.47(18)	C12	C11	C10	111.0(2)
C39	C1	C2	121.1(2)	C32	C16	C15	104.69(17)
C1	C2	C3	119.4(2)	C17	C16	C32	118.49(18)
C27	C20	C19	123.3(2)	C17	C16	C15	114.36(18)
C27	C20	C21	119.9(2)	C10	C9	C5	110.55(19)
C21	C20	C19	116.8(2)	C36	C9	C10	110.1(2)
C16	C32	C33	103.78(18)	C36	C9	C5	107.35(19)
O3	C23	C24	110.7(2)	C37	C9	C10	107.31(19)
O4	C23	O3	124.2(2)	C37	C9	C36	109.3(2)
O4	C23	C24	125.0(2)	C37	C9	C5	112.22(19)
C34	C15	C14	110.00(18)	C38	C4	C3	118.0(2)
C34	C15	C16	112.20(18)	C38	C4	C5	118.6(2)
C34	C15	C31	110.30(19)	C3	C4	C5	123.4(2)
C16	C15	C14	100.02(17)	C32	C33	C14	106.85(18)
C31	C15	C14	116.47(19)	C39	C38	C4	121.9(2)
C31	C15	C16	107.47(18)	C25	C26	C19	114.6(2)
C17	C18	C19	112.51(18)	C30	C31	C15	111.88(19)

C17	C18	C30	111.96(18)	C11	C12	C13	113.4(2)
C30	C18	C19	112.60(18)	C20	C21	C22	111.0(2)
C20	C19	C18	109.37(18)	O1	C7	C8	109.0(2)
C20	C19	C26	109.26(19)	C2	C3	C4	120.9(2)
C20	C19	C29	108.81(19)	F1	C8	C7	110.2(2)
C26	C19	C18	108.39(18)	F2	C8	F1	107.5(2)
C29	C19	C18	111.63(19)	F2	C8	F3	106.8(2)
C29	C19	C26	109.3(2)	F2	C8	C7	112.4(2)
O3	C22	C25	110.5(2)	F3	C8	F1	107.5(2)
O3	C22	C21	106.74(19)	F3	C8	C7	112.2(2)
C25	C22	C21	110.8(2)	C31	C30	C18	114.8(2)
C1	C39	C38	118.8(2)	C6	C5	C9	110.52(19)
C15	C14	C33	102.92(18)	C6	C5	C4	112.3(2)
C13	C14	C15	118.73(19)	C4	C5	C9	113.26(19)
C13	C14	C33	113.07(18)				

Table 6 Torsion Angles for 19*R*.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C1	C2	C3	178.68(19)	C34	C15	C31	C30	-68.6(2)
Br1	C1	C39	C38	-179.19(19)	C13	C14	C33	C32	153.10(19)
O3	C22	C25	C26	178.24(19)	C17	C18	C19	C20	-47.2(2)
O3	C22	C21	C20	-177.34(19)	C17	C18	C19	C26	-166.28(19)
O1	C6	C5	C9	-107.8(2)	C17	C18	C19	C29	73.2(2)
O1	C6	C5	C4	124.6(2)	C17	C18	C30	C31	48.7(3)
O1	C7	C8	F1	177.9(2)	C25	C22	C21	C20	-57.0(3)
O1	C7	C8	F2	58.1(3)	C10	C11	C12	C13	177.6(2)
O1	C7	C8	F3	-62.3(3)	C10	C9	C5	C6	46.9(3)

O2	C6	C5	C9	70.1(3)	C10	C9	C5	C4	173.94(19)
O2	C6	C5	C4	-57.5(4)	C11	C10	C9	C36	-53.4(3)
C6	O1	C7	C8	109.9(2)	C11	C10	C9	C37	-172.3(2)
C27	C28	C17	C18	-37.7(3)	C11	C10	C9	C5	65.0(3)
C27	C28	C17	C16	-159.28(19)	C16	C32	C33	C14	4.3(2)
C27	C20	C19	C18	17.3(3)	C16	C15	C14	C13	-167.80(19)
C27	C20	C19	C26	135.8(2)	C16	C15	C14	C33	-42.0(2)
C27	C20	C19	C29	-104.9(3)	C16	C15	C31	C30	54.0(3)
C27	C20	C21	C22	-130.3(2)	C35	C13	C12	C11	71.0(3)
C28	C27	C20	C19	2.3(4)	C9	C10	C11	C12	-172.0(2)
C28	C27	C20	C21	-176.8(2)	C33	C32	C16	C15	-31.4(2)
C28	C17	C16	C32	-53.9(3)	C33	C32	C16	C17	-160.26(19)
C28	C17	C16	C15	-178.12(18)	C33	C14	C13	C35	-176.2(2)
C1	C2	C3	C4	0.8(4)	C33	C14	C13	C12	60.0(2)
C1	C39	C38	C4	0.3(4)	C36	C9	C5	C6	166.98(19)
C2	C1	C39	C38	-0.8(4)	C36	C9	C5	C4	-66.0(2)
C20	C27	C28	C17	8.1(3)	C38	C4	C3	C2	-1.2(4)
C20	C19	C26	C25	48.4(3)	C38	C4	C5	C6	-139.1(2)
C23	O3	C22	C25	92.6(3)	C38	C4	C5	C9	94.8(3)
C23	O3	C22	C21	-146.9(2)	C31	C15	C14	C13	76.8(3)
C15	C14	C13	C35	-55.5(3)	C31	C15	C14	C33	-157.42(19)
C15	C14	C13	C12	-179.30(19)	C31	C15	C16	C32	168.07(19)
C15	C14	C33	C32	23.8(2)	C31	C15	C16	C17	-60.6(2)
C15	C31	C30	C18	-51.0(3)	C21	C20	C19	C18	-163.58(19)
C18	C19	C26	C25	167.5(2)	C21	C20	C19	C26	-45.1(3)
C18	C17	C16	C32	-176.59(19)	C21	C20	C19	C29	74.2(2)
C18	C17	C16	C15	59.2(2)	C21	C22	C25	C26	60.2(3)
C19	C20	C21	C22	50.6(3)	C7	O1	C6	O2	-3.8(4)
C19	C18	C17	C28	59.0(2)	C7	O1	C6	C5	174.3(2)

C19	C18	C17	C16	-178.55(18)	C3	C4	C38	C39	0.7(4)
C19	C18	C30	C31	176.6(2)	C3	C4	C5	C6	43.5(3)
C22	O3	C23	O4	-0.2(4)	C3	C4	C5	C9	-82.6(3)
C22	O3	C23	C24	178.7(2)	C37	C9	C5	C6	-72.9(2)
C22	C25	C26	C19	-57.2(3)	C37	C9	C5	C4	54.2(3)
C39	C1	C2	C3	0.2(4)	C30	C18	C19	C20	-174.91(19)
C14	C15	C16	C32	46.1(2)	C30	C18	C19	C26	66.0(2)
C14	C15	C16	C17	177.35(17)	C30	C18	C19	C29	-54.4(3)
C14	C15	C31	C30	165.1(2)	C30	C18	C17	C28	-172.96(19)
C14	C13	C12	C11	-163.8(2)	C30	C18	C17	C16	-50.6(2)
C34	C15	C14	C13	-49.6(3)	C29	C19	C26	C25	-70.6(3)
C34	C15	C14	C33	76.2(2)	C5	C4	C38	C39	-176.8(2)
C34	C15	C16	C32	-70.5(2)	C5	C4	C3	C2	176.2(2)
C34	C15	C16	C17	60.8(2)					

Table 7 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for 19*R*.

Atom	***x***	***y***	***z***	**U(eq)**
H28A	4439	3269	4980	19
H28B	3729	4165	5179	19
H2	5324	841	9872	24
H32A	3852	2888	5834	19
H32B	4356	3805	6060	19
H18	7855	3322	4870	17
H39	9276	2545	9798	24
H14	7589	2037	6144	17

H34A	6871	4326	6382	25
H34B	8141	4703	6016	25
H34C	8882	4216	6442	25
H13	8233	3064	6919	20
H17	6301	4575	5447	15
H25A	9661	5472	3939	24
H25B	10326	4621	3682	24
H10A	8188	435	7629	23
H10B	6435	943	7691	23
H11A	8007	2307	7633	23
H11B	9656	1744	7509	23
H16	6427	2718	5512	15
H35A	10620	2061	6420	36
H35B	10947	2252	6932	36
H35C	10837	3045	6589	36
H33A	4921	2149	6415	22
H33B	5283	3065	6657	22
H36A	10511	671	8198	30
H36B	10017	997	8684	30
H36C	10188	1687	8289	30
H38	8990	2578	9030	22
H26A	10555	4408	4460	23
H26B	9298	3703	4248	23
H31A	10507	3314	5885	22
H31B	9520	2623	5582	22
H12A	6573	1720	6999	24

H12B	8260	1195	6871	24
H21A	6454	5736	4004	24
H21B	5174	5009	3819	24
H7A	2715	2078	7828	27
H7B	3626	2706	7476	27
H3	5020	896	9102	23
H37A	6108	25	8383	31
H37B	7589	37	8746	31
H37C	7930	-384	8270	31
H24A	6654	5534	2429	41
H24B	8382	5151	2228	41
H24C	8434	5981	2549	41
H30A	10528	3718	5116	23
H30B	9766	4468	5426	23
H29A	8285	5963	4606	31
H29B	9619	5533	4941	31
H29C	7674	5650	5085	31
H22	7490(40)	4123(7)	3590(9)	19
H5	7460(50)	2290(20)	8398(10)	19
H27	3770(20)	4370(20)	4420(10)	26(8)

Experimental

Single crystals of $C_{39}H_{54}BrF_3O_4$ **[18*R*]** were **[The material was recrystallised from --- by as supplied]**. A suitable crystal was selected and **[The crystal was mounted on a loop with paratone oil]** on a **Saxi-CrysAlisPro-abstract goniometer imported SAXI images** diffractometer. The crystal was kept at 100(2) K during data collection. Using Olex2 [1], the structure was solved with the XT [2] structure solution program using Intrinsic Phasing and refined with the XL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal structure determination of [19*R*]

Crystal Data for $C_{39}H_{54}BrF_3O_4$ (M =723.72 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 7.8637(16) Å, b = 15.308(4) Å, c = 30.278(7) Å, V = 3644.8(15) Å^3, Z = 4, T = 100(2) K, μ(MoKα) = 1.182 mm^{-1}, *Dcalc* = 1.319 g/cm^3, 48851 reflections measured (2.69° ≤ 2Θ ≤ 61.016°), 11132 unique (R_{int} = 0.0465, R_{sigma} = 0.0280) which were used in all calculations. The final R_1 was 0.0377 (I > 2σ(I)) and wR_2 was 0.0941 (all data).

Refinement model description

Number of restraints - 2, number of constraints - unknown.

Details:

1. Fixed Uiso
At 1.2 times of:
All C(H) groups, All C(H,H) groups
At 1.5 times of:
All C(H,H,H) groups
2. Restrained distances
C27-H27
0.99 with sigma of 0.005
C22-H22
0.995 with sigma of 0.005
3.a Ternary CH refined with riding coordinates:
C18(H18), C14(H14), C13(H13), C17(H17), C16(H16)
3.b Secondary CH2 refined with riding coordinates:
C28(H28A,H28B), C32(H32A,H32B), C25(H25A,H25B), C10(H10A,H10B), C11(H11A, H11B), C33(H33A,H33B), C26(H26A,H26B), C31(H31A,H31B), C12(H12A,H12B), C21(H21A,H21B), C7(H7A,H7B), C30(H30A,H30B)
3.c Aromatic/amide H refined with riding coordinates:
C2(H2), C39(H39), C38(H38), C3(H3)
3.d Idealised Me refined as rotating group:
C34(H34A,H34B,H34C), C35(H35A,H35B,H35C), C36(H36A,H36B,H36C), C37(H37A,H37B, H37C), C24(H24A,H24B,H24C), C29(H29A,H29B,H29C)

This report has been created with Olex2, compiled on 2016.08.25 svn.r3337 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

SI-Chapter 7

1. General Considerations

All solvents were purified and dried by a *Glass Contour Solvent System* unless otherwise stated. The dichloromethane used for the C–H Functionalization was dried and degassed at reflux over 4Å molecular sieves for 2 hours under argon, then stored with 4Å molecular sieves under argon atmosphere and was used directly.

^{1}H and ^{13}C NMR spectra were recorded at either 400 MHz (^{13}C at 100 MHz) on Varian-400 spectrometer or 600 MHz (^{13}C at 150 MHz) on INOVA-600 spectrometer. NMR spectra were run in solutions of deuterated chloroform ($CDCl_3$) with residual chloroform taken as an internal standard (7.26 ppm for ^{1}H, and 77.16 ppm for ^{13}C), and were reported in parts per million (ppm). Abbreviations for signal multiplicity are as follow: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, etc. Coupling constants (*J* values) were calculated directly from the spectra.

IR spectra were collected on a Nicolet iS10 FT-IR spectrometer.

Mass spectra were taken on a Thermo Finnigan LTQ-FTMS spectrometer with APCI, ESI or NSI. Thin layer chromatographic (TLC) analysis was performed with aluminum-sheet silica gel plates, visualizing with UV light and/or staining with aqueous $KMnO_4$ stain.

Melting points (mp) were measured in open capillary tubes with a Mel-Temp Electrothermal melting points apparatus and are uncorrected.

Optical rotations were measured on Jasco P-2000 polarimeters.

Analytical enantioselective chromatographies were measured on Varian Prostar instrument and used isopropanol/hexane as gradient. Chiral HPLC conditions were determined by obtaining separation of the racemic products using Rh_2(*R/S*-DOSP)$_4$ as catalyst.

2. Acquisition and Preparation of Substrates

The substrates and reagents were purchased from the following suppliers and used without further purification (unless otherwise stated):

Sigma-Aldrich: 1-Bromobutane; 1-Chlorohexane; 1-Chloropentane; 1-Fluoropentane; n-Octane; 2,2-dimethylhexane; Diisobutylaluminum hydride (DIBAl); 4-Nitrobenzoyl chloride.

Alfa-Aesar: 1-Bromohexane; 1-Bromopentane.

Synquest Laboratory: 1-Fluorohexane.

TCI America: 1-Chlorobutane; 1,1-diphenylethylene.

Oakwood Chemical: 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU).

Combi-Blocks: Potassium trimethylsilanolate (heated under vacuum before use).

Acros Organics: Methyl 2-(2-chlorophenyl)acetate.

The following substrates were prepared according to reported procedures: Butyltrimethylsilane[1]; Hexyltrimethylsilane[1]; *p*-Acetamidobenzenesulfonyl azide (*p*-ABSA)[2]; 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate[3]; Rh_2(*S*-PTAD)$_4$[4]; Rh_2(*R*-*p*-PhTPCP)$_4$[5]; Rh_2[*R*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$[6].

3. C-H Functionalization Reactions

3.1 General Procedure for C–H Functionalization Reactions

A 5-mL round-bottom flask equipped with reflux condenser was charged with $Rh_2(R\text{-}L)_4$ (0.002 mmol, 1 mol%) and flushed with argon gas (3 times). After the addition of corresponding substrate (0.6 mmol, 3.0 equiv.) and 0.5 mL of dry degassed CH_2Cl_2, the solution was heated to reflux under argon atmosphere for 5 min. 2,2,2-Trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (74.5 mg, 0.2 mmol, 1.0 equiv.) was weighed in a 20 mL scintillation vial and flushed with argon gas (3 times), then it was dissolved in 3 mL dry degassed CH_2Cl_2 and transferred to the reaction solution dropwise over 3 h via syringe pump under reflux condition and argon atmosphere. After addition, the reaction mixture was allowed to stir for another 30 min, then concentrated under vacuum for crude ^1H NMR. Finally, the crude product was purified by flash column chromatography.

3.2 Regioisomeric and Diastereomeric Ratios Determination

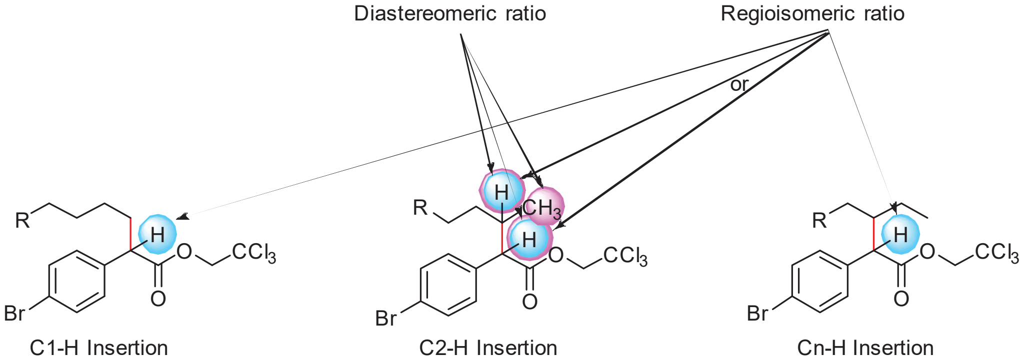
The crude ^1H NMR in general procedure was employed for regioisomeric and diastereomeric ratios determination, and it was obtained using the following settings:

Instrument: INOVA-600 MHz spectrometer with an ID probe, which has a sensitivity of 1000:1

Number of scans: 16

Relaxation time: 5 seconds

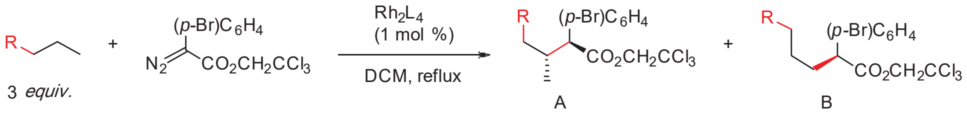
The crude ^1H NMR spectra data was analyzed using MestReNova 11.0.2 (Mestrelab Research S.L.). Before integration, spectra were processed through an auto-phase correction and a Segments Smoother baseline correction manually. The ratios were measured by integration of the peaks corresponding to the hydrogens indicated below.

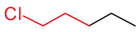
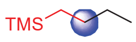
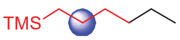
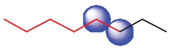


rr = C2-H insertion/ C1-H insertion
dr = [(2S, 3R)+(2R, 3S)]/[(2S, 3S)+(2R, 3R)]

Figure S1 Method for ratio determination in the crude ^{1}H NMR spectra

Tables S1 Result summary for C–H insertion reactions



entry	Substrate	Rh$_2$[R-3,5-di(p-^{t}BuC$_6$H$_4$)TPCP]$_4$ rr (A:B)	dr (A)	ee (A, %)	yield (A, %)	Rh$_2$(R-p-PhTPCP)$_4$ rr (A:B)	dr (A)	yield (A, %)
1		18:1	9:1	92	89	3:1	8:1	81
2		18:1	9:1	93	84	3:1	10:1	79
3		18:1	9:1	97	85	2:1	9:1	79
4		9:1	9:1	95	65	1:1	8:1	77
5		9:1	9:1	94	50	2:1	10:1	75
6		8:1	10:1	97	49	2:1	8:1	78
7		3:1	9:1	93	20	1:1	5:1	71
8		3:1	7:1	92	19	1:1	6:1	70
9		33:1	4:1	90	89	2:1	4:1	82
10		34:1	4:1	>99	40	4:1 [a]	4:1	80
11		20:1	9:1	90	85	3:1 [b]	9:1	86
12		27:1	9:1	91	82	2:1	9:1	86

Other internal C–H insertion products was observed by crude ^{1}H NMR spectra: [a] 10%; [b] 4%. Enantiomeric excess of Rh$_2$(R-p-PhTPCP)$_4$ catalyzed reactions (entry 1-6, 10-12) were not determined due to the low regioisomeric ratio and the corresponding overlap of regioisomer peaks, but enantiomeric excess of the following entries were determined: entry 7: 96% ee, entry 8: 94% ee, entry 9: 88% ee.

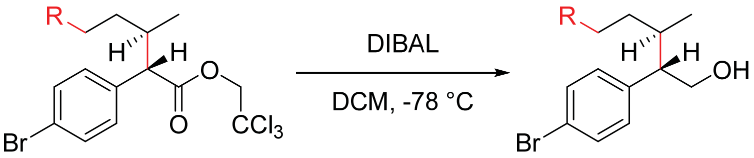
3.3 Enantiomeric Excess Determination

Due to the difficulty in separation of the enantiomers from the C–H functionalization reactions on our available HPLC columns, the C–H functionalization products were converted to their derivatives, which gave better separations, without influence on their enantiomeric ratios and used for enantiomeric excess (*ee*) determination of corresponding C–H functionalization products.

(Note: The HPLC condition for *ee* determination of C–H functionalization products of 1-bromohexane, 1-bromopentane, 1-chlorohexane, 1-fluorohexane, butyltrimethylsilane, hexyltrimethylsilane and octane were adapted from reported methods[6].)

3.3.1 Reduction to Alcohols

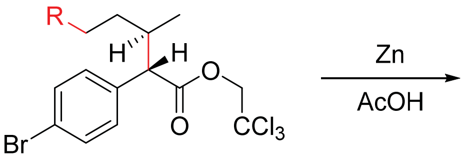
(The following procedure is for the C–H functionalization products of 1-bromohexane; 1-bromopentane; 1-bromobutane; 1-chlorohexane; 1-chloropentane; 1-chlorobutane; 1-fluorohexane; 1-fluoropentane; 2,2-dimethylhexane)



A flask with solution of 1 M diisobutylaluminum hydride (DIBAl) in CH_2Cl_2 (0.22 mL, 0.22 mmol, 2.2 equiv.) was flushed with argon gas and cooled to -78 ºC via dry ice/acetone bath. Under argon atmosphere, a solution of corresponding ester (0.1 mmol, 1.0 equiv.) in CH_2Cl_2 (1 mL) was added dropwise into the flask and stirred for 2 h at -78 ºC. Then, the mixture was warmed back to room temperature (23 ºC) and stirred for another 1 h. The reaction was quenched by adding 2 mL of 2 M aqueous HCl solution dropwise. The resulted solution was extracted by ethyl acetate (3 mL x 3) and dried over Na_2SO_4. The crude product was concentrated and purified by flash column chromatography (hexane/diethyl ether = 9/1) to afford colorless oil or white solid. After confirmed by ^1H NMR, the alcohol product was dissolved in hexane/*i*-propanol = 50/1 (1 mg/mL) for HPLC.

3.3.2 Hydrolysis to Carboxylic Acids

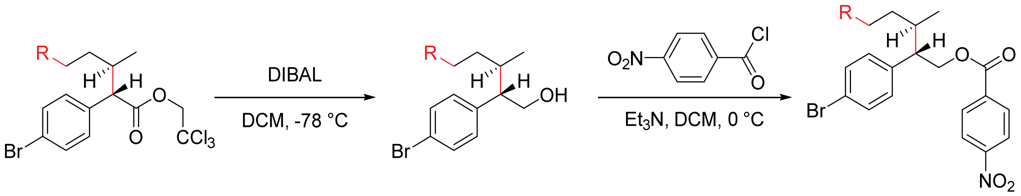
(The following procedure is for the C–H functionalization products of butyltrimethylsilane and hexyltrimethylsilane)



To a solution of corresponding ester (0.1 mmol, 1.0equiv.) in 3 mL of glacial acetic acid, zinc duct (33 mg, 0.5 mmol, 5.0 equiv.) was added. The mixture was stirred under room temperature overnight (15 h) and monitored by TLC. After diluted with DI H_2O (10 mL), the resulted mixture was extracted by ethyl acetate (10 mL x 3) and dried over Na_2SO_4. The crude product was concentrated and purified by flash column chromatography (hexane/diethyl ether = 9/1) to afford colorless oil. After confirmed by ^{1}H NMR, the carboxylic acid product was dissolved in hexane/*i*-propanol = 50/1 (1 mg/mL) for HPLC.

3.3.3 Reduction and Esterification to Ester

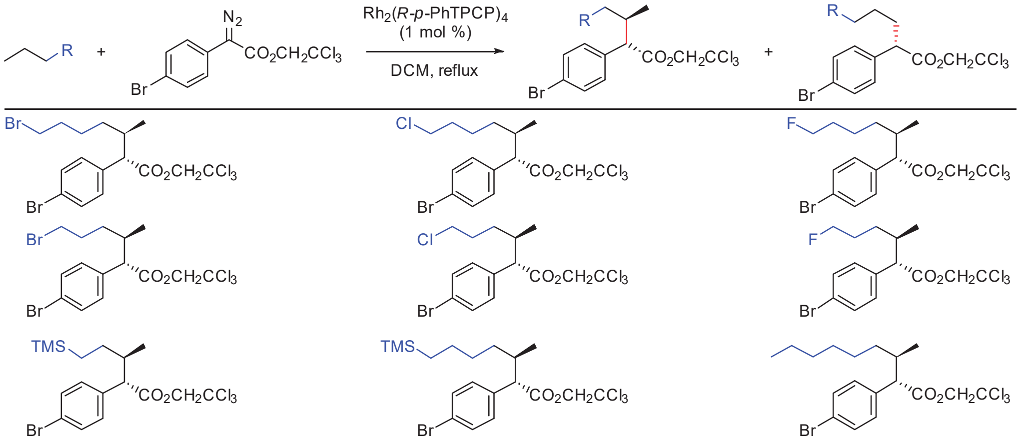
(The following procedure is for the C–H functionalization products of octane)



A flask with solution of 1 M diisobutylaluminum hydride (DIBAl) in CH_2Cl_2 (0.22 mL, 0.22 mmol, 2.2 equiv.) was flushed with argon gas and cooled to -78 °C via dry ice/acetone bath. Under argon atmosphere, a solution of corresponding ester (0.1 mmol, 1.0 equiv.) in CH_2Cl_2 (1 mL) was added dropwise into the flask and stirred for 2 h at -78 °C. Then, the mixture was warmed back to room temperature (23 °C) and stirred for another 1 h. The reaction was quenched by adding 2 mL of 2 M aqueous HCl solution dropwise. The resulted solution was extracted by ethyl acetate (3 mL x 3) and dried over Na_2SO_4. The crude product was concentrated and employed for next step without further purification. Another flask was charged with the crude alcohol and Et_3N (0.15 mmol, 1.5 equiv.), as well as 3 mL of CH_2Cl_2. After cooled to 0 °C via ice bath, 4-nitrobenzoyl chloride (1.2 equiv.) was added to the flask in 3 portions. The resulted mixture was stirred overnight (15 h) and at which point it warmed up to room temperature (23 °C). After diluted with CH_2Cl_2 (5 mL), the solution was washed with 1M aqueous $NaHCO_3$ solution, DI H_2O and brine successively, then dried over Na_2SO_4. The crude product was concentrated and purified by flash column chromatography (hexane/diethyl ether = 9/1) to afford colorless oil. After confirmed by ^{1}H NMR, the carboxylic acid product was dissolved in hexane/*i*-propanol = 50/1 (1 mg/mL) for HPLC.

3.3.4 Enantiomeric Excess Determination for Rh_2(R-PhTPCP)$_4$ Catalyzed Reaction

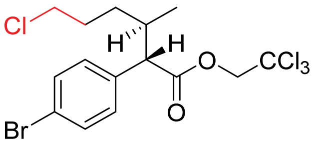
The Rh_2(*R*-PhTPCP)$_4$ catalyzed reactions gave poor ratio of the primary and secondary C-H insertion products, and the regio- and stereoisomers peaks were overlapped on HPLC spectra, therefore, the *ee* of the following products were not determined:



Schemes S1 Products without enantioselectivity data from reactions catalyzed by Rh_2(*R*-PhTPCP)$_4$

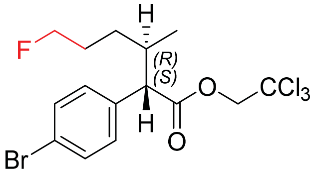
3.4. Experimental Data of C–H Functionalization Products

The C–H functionalization products of 1-bromohexane, 1-bromopentane, 1-chlorohexane, 1-fluorohexane, butyltrimethylsilane, hexyltrimethylsilane and octane were confirmed by ^{1}H NMR comparing to reported experimental data[6]. The C–H functionalization products of 1-bromobutane, 1-chloropentane and 1-fluoropentane, catalyzed by Rh_2[*R*-3,5-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$, were used for characterization due to its higher selectivity, while characterization of C–H functionalization products of 2,2-dimethylhexane was obtained from reaction catalyzed by Rh_2(*S*-*o*-ClTPCP)$_4$.



2,2,2-Trichloroethyl (2*S*,3*R*)-2-(4-bromophenyl)-6-chloro-3-methylhexanoate. This compound was obtained according to general procedure from C–H functionalization reaction catalyzed by $Rh_2[R\text{-}3,5\text{-di}(p\text{-}^tBuC_6H_4)TPCP]_4$ (50% yield).

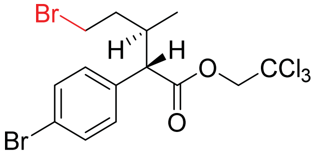
Rf = 0.6 (hexane/ether = 9/1); **[α]$^{20}_{D}$**: 6.7° (c = 1.00, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$) *δ*** 7.46 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 11.9 Hz, 0H), 3.39 (d, *J* = 10.7 Hz, 1H), 3.45 – 3.32 (m, 2H), 2.29 (tqd, *J* = 9.9, 6.5, 3.2 Hz, 1H), 1.84 – 1.70 (m, 1H), 1.69 – 1.57 (m, 1H), 1.32 (dddd, *J* = 14.0, 11.0, 5.4, 3.3 Hz, 1H), 1.08 (d, *J* = 6.5 Hz, 3H), 1.11 – 1.01 (m, 1H); **^{13}C NMR (151 MHz, $CDCl_3$) *δ*** 171.62, 135.85, 131.98, 130.49, 121.93, 94.81, 74.26, 58.02, 44.87, 35.71, 29.67, 17.95; **IR (neat)** 2928, 1748, 1488, 1446, 1408, 1371, 1268, 1207, 1127, 1073, 1029, 1011, 915, 825, 759, 715; **HRMS (+p NSI)** calcd for $C_{15}H_{18}Cl_4O_2Br$ ($[M+H]^+$): 448.9249 found 448.9245; **HPLC** (the ester product was reduced to 5-bromo-2-(4-bromophenyl)-3-methylpentan-1-ol for better separation)(S,S-Whelk column, 0.8 % *i*-propanol in hexane, 0.8 mL min^{-1}, 1 mg mL^{-1}. 180 min, UV 230 nm) retention times of 96.43 min (minor) and 138.06 min (major) 94 % ee (81 % ee for $Rh_2(S\text{-}o\text{-ClTPCP})_4$).



2,2,2-Trichloroethyl (2*S*,3*R*)-2-(4-bromophenyl)-6-fluoro-3-methylhexanoate. This compound was obtained according to general procedure from C–H functionalization reaction catalyzed by $Rh_2[R\text{-}3,5\text{-di}(p\text{-}^tBuC_6H_4)TPCP]_4$ (49 % yield).

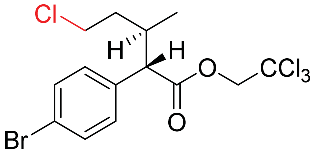
Rf = 0.4 (hexane/ether = 9/1); **[α]$^{20}_{D}$**: 5.1° (c = 1.00, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$) *δ*** 7.46 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.34 (td, *J* = 5.4, 4.1 Hz, 1H), 4.27 (td, *J* = 6.0, 4.3 Hz, 1H), 3.40 (d, *J* = 10.5 Hz, 1H), 2.29 (ddtd, *J* = 16.5, 10.0, 6.6, 3.3 Hz, 1H), 1.79 – 1.65 (m, 1H), 1.53 (dddt, *J* = 25.5, 19.8, 11.4, 5.9 Hz, 1H), 1.30 (dddd, *J* = 14.0, 11.1, 5.5, 3.4 Hz, 1H), 1.08 (d, *J* = 6.5

Hz, 3H), 1.02 (dddd, *J* = 14.0, 11.1, 9.5, 4.7 Hz, 1H); **^{13}C NMR (151 MHz, CDCl$_3$) *δ*** 171.67, 135.92, 131.98, 130.49, 121.92, 94.83, 74.26, 58.10, 38.26, 35.94, 29.09, 29.05, 27.52, 27.39, 17.90; **IR (neat)** 2960, 2927, 1748, 1488, 1371, 1273, 1208, 1132, 1037, 1046, 1011, 888, 825, 760, 715; **HRMS (+p NSI)** calcd for $C_{15}H_{16}Cl_3FO_2Br$ ([M-H]$^+$): 430.9388 found 430.9392; **HPLC** (the ester product was reduced to 5-bromo-2-(4-bromophenyl)-3-methylpentan-1-ol for better separation)(S,S-Whelk column, 1 % *i*-propanol in hexane, 1 mL min^{-1}, 1 mg mL^{-1}. 180 min, UV 230 nm) retention times of 53.50 min (major) and 87.55 min (minor) 97 % ee (81 % ee for Rh$_2$(*S*-*o*-ClTPCP)$_4$).



2,2,2-Trichloroethyl (2S,3R)-5-bromo-2-(4-bromophenyl)-3-methylpentanoate. This compound was obtained according to general procedure from C–H functionalization reaction catalyzed by Rh$_2$[*R*-3,5-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$ (20% yield).

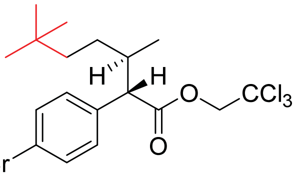
Rf = 0.5 (hexane/ether = 9/1); **[α]$^{20}_{D}$**: 5.1° (c = 1.00, CHCl$_3$); **^{1}H NMR (600 MHz, CDCl$_3$) *δ*** 7.47 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 11.9 Hz, 1H), 3.42 (d, *J* = 10.6 Hz, 1H), 3.40 – 3.34 (m, 1H), 3.27 (ddd, *J* = 10.1, 9.1, 6.7 Hz, 1H), 2.49 (ddpd, *J* = 16.3, 10.2, 6.6, 3.5 Hz, 1H), 1.74 (dddd, *J* = 14.3, 8.9, 7.6, 3.5 Hz, 1H), 1.48 (dddd, *J* = 14.4, 9.8, 6.7, 4.6 Hz, 1H), 1.08 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR (125 MHz, CDCl$_3$) *δ*** 171.28, 135.41, 132.09, 132.00, 130.55, 130.53, 129.91, 122.15, 94.76, 74.27, 57.74, 36.52, 34.91, 30.93, 17.37; **IR (neat)** 2926, 1748, 1488, 1127, 1073, 1011, 825, 759, 715; **HRMS (+p NSI)** calcd for $C_{13}H_{13}Br_2Cl_4O_2$ (M-CH$_2$+Cl)$^+$ 498.8040 found 499.2708; **HPLC** (the ester product was reduced to 5-bromo-2-(4-bromophenyl)-3-methylpentan-1-ol for better separation)(S,S-Whelk column, 1% *i*-propanol in hexane, 1 mL min^{-1}, 1 mg mL^{-1}. 130 min, UV 230 nm) retention times of 57.7 min (major) and 101.5 min (minor) 93 % ee (79% ee for Rh$_2$(*S*-*o*-ClTPCP)$_4$, 96 % for Rh$_2$(*R*-*p*-PhTPCP)$_4$).



2,2,2-Trichloroethyl (2*S*,3*R*)-2-(4-bromophenyl)-5-chloro-3-methylpentanoate

This compound was obtained according to general procedure from C–H functionalization reaction catalyzed by $Rh_2[R\text{-}3,5\text{-di}(p\text{-}^tBuC_6H_4)TPCP]_4$ (19% yield).

Rf = 0.6 (hexane/ether = 9/1); **$[\alpha]^{20}_D$**: 6.1° (c = 1.00, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$) *δ*** 7.47 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 11.9 Hz, 1H), 3.55 – 3.48 (m, 1H), 3.48 – 3.41 (m, 1H), 3.43 (d, *J* = 10.4 Hz, 1H), 2.52 (dtq, *J* = 14.8, 8.1, 3.4 Hz, 1H), 1.72 – 1.63 (m, 1H), 1.43 – 1.36 (m, 1H), 1.10 (d, *J* = 6.5 Hz, 3H).; **^{13}C NMR (151 MHz, $CDCl_3$) *δ*** 171.21, 135.34, 131.95, 130.39, 122.00, 94.64, 74.15, 57.74, 42.28, 36.19, 33.60, 17.37; **IR (neat)** 2928, 1750, 1489, 1457, 1373, 1295, 1217, 1130, 1074, 1011, 828, 761, 722; **HRMS (+p NSI)** calcd for $C_{14}H_{15}BrCl_4O_2$ $(M+H)^+$ 434.9082 found 434.9085; **HPLC** (the ester product was reduced to 2-(4-bromophenyl)-5-chloro-3-methylpentan-1-ol for better separation)(S,S-Whelk column, 1% *i*-propanol in hexane, 1 mL min^{-1}, 1 mg mL^{-1}. 130 min, UV 230 nm) retention times of 55.94 min (major) and 95.03 min (minor) 92 % ee (83% ee for $Rh_2(S\text{-}o\text{-}ClTPCP)_4$, 94 % for $Rh_2(R\text{-}p\text{-}PhTPCP)_4$).

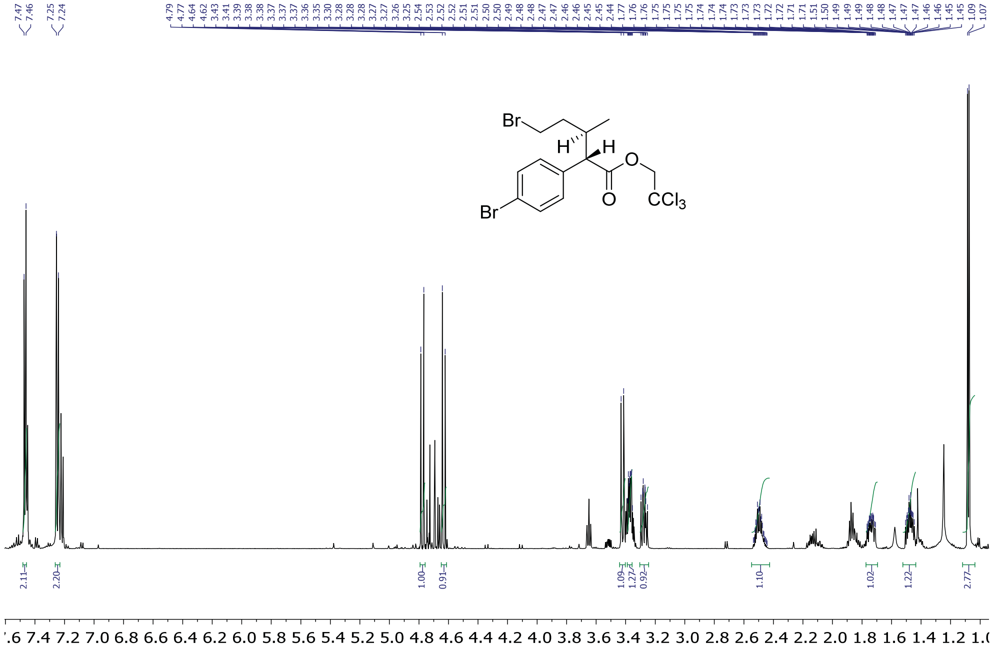


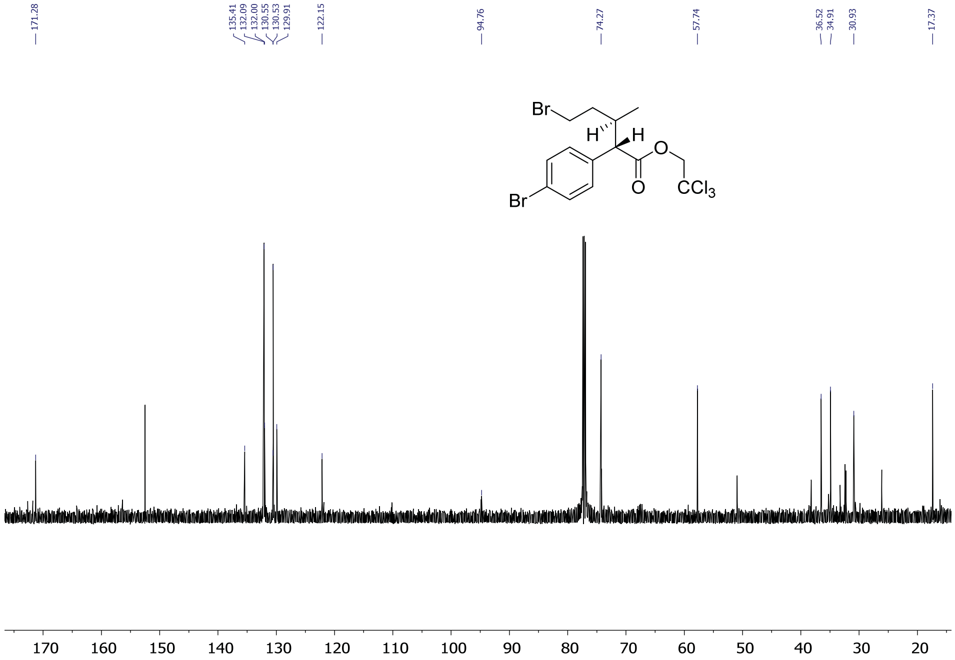
2,2,2-Trichloroethyl (2*S*,3*R*)-2-(4-bromophenyl)-3,6,6-trimethylheptanoate

This compound was obtained according to general procedure from C–H functionalization reaction catalyzed by $Rh_2(S\text{-}o\text{-}ClTPCP)_4$ (72% yield).

Rf = 0.85 (pentane/ether = 9/1); **$[\alpha]^{20}_D$**: +2.2° (c = 1.00, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$) *δ*** 7.45 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 3.42 (d, *J* = 10.6 Hz, 1H), 2.26 – 2.16 (m, 1H), 1.22 – 1.18 (m, 2H), 1.05 (d, *J* = 6.6 Hz, 3H), 1.02 – 0.97 (m, 1H), 0.93 – 0.86 (m, 1H), 0.73 (s, 9H); **^{13}C NMR (125 MHz, $CDCl_3$) *δ*** 171.81, 136.2, 131.7, 130.5, 121.5, 94.8, 74.2, 57.7, 40.1, 36.6, 30.1, 29.2, 27.8, 17.8; **IR (neat)** 2954, 1750, 1488, 1365, 1128,1074, 1011, 827, 761, 720; **HRMS (+p NSI)** calcd for $C_{18}H_{25}O_2BrCl_3$ $(M+H)^+$ 457.0098 found 457.01004; **HPLC** (the ester product was reduced to 2-(4-bromophenyl)-3,6,6-trimethylheptan-1-ol for better separation)(OJH column, 1% *i*-propanol in hexane, 0.5 mL min^{-1}, 1 mg mL^{-1}. 30 min, UV 230 nm) retention times of 15.8 min (minor) and 17.1 min (major) 76% ee (90 % ee for Rh_2[*R*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$, 88 % for Rh_2(*R*-*p*-PhTPCP)$_4$).

4. NMR Spectra for Characterizations

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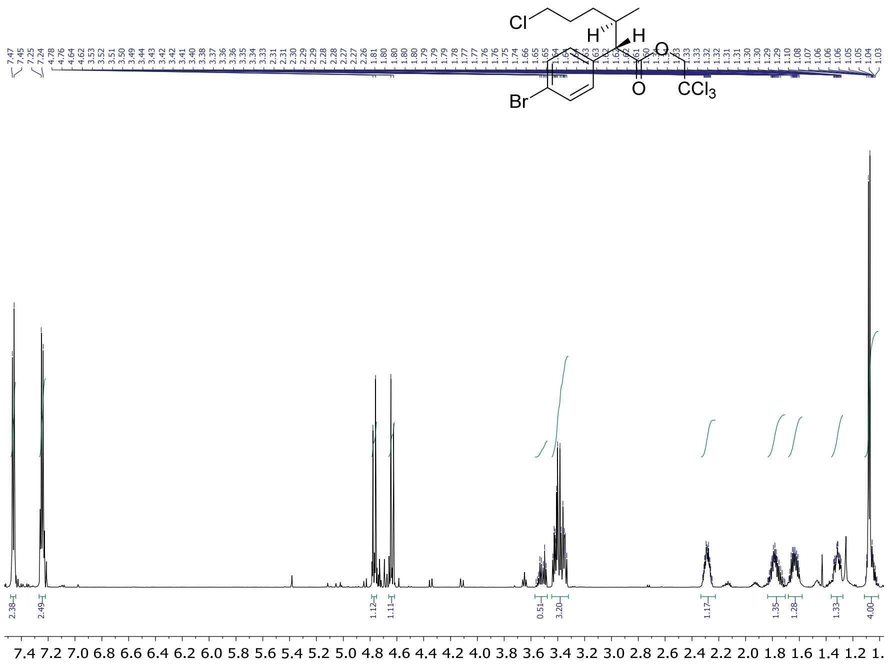
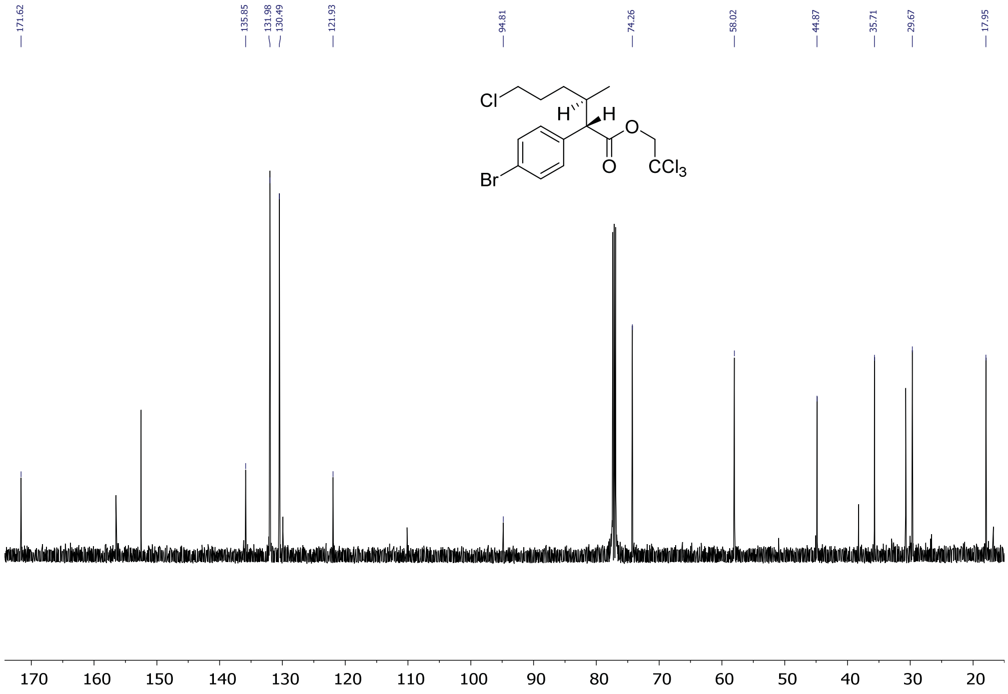
135.41
132.09
132.00
130.55
130.53
129.91
122.15
94.76
74.27
57.74
36.52
34.91
30.93
17.37
Br
H
H
O
O
CCl3
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20


Cl
H
H
O
O
CCl3
Br
2.38
2.49
1.12
1.11
0.51
3.20
1.17
1.35
1.28
1.33
4.00
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.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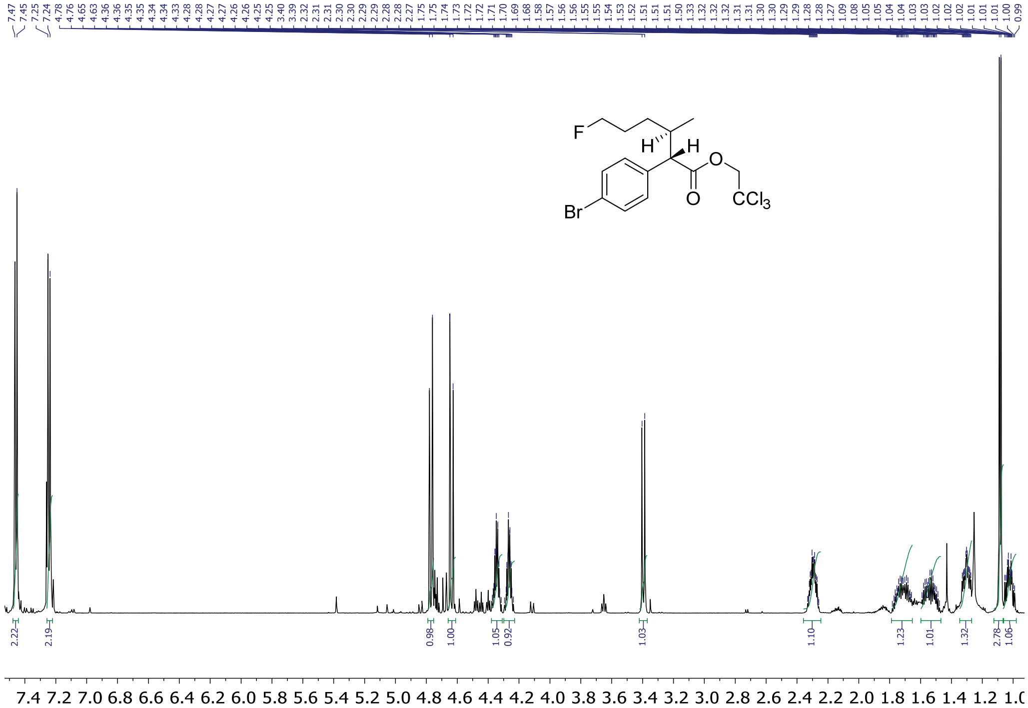
135.85
131.98
130.49
121.93
94.81
74.26
58.02
44.87
35.71
29.67
17.95
Cl
H
H
O
O
CCl3
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20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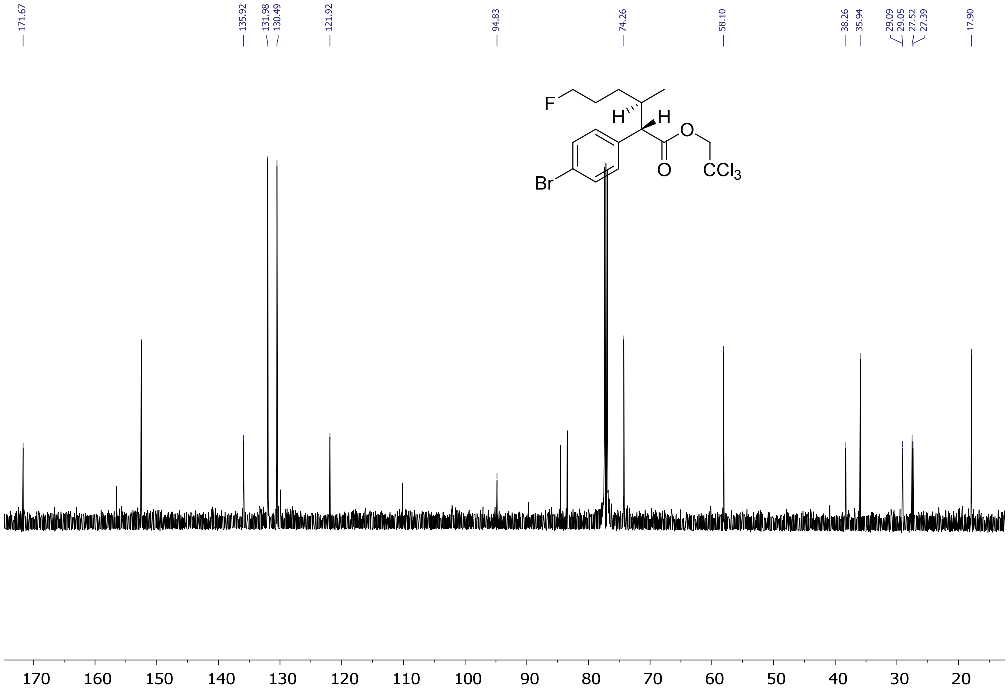
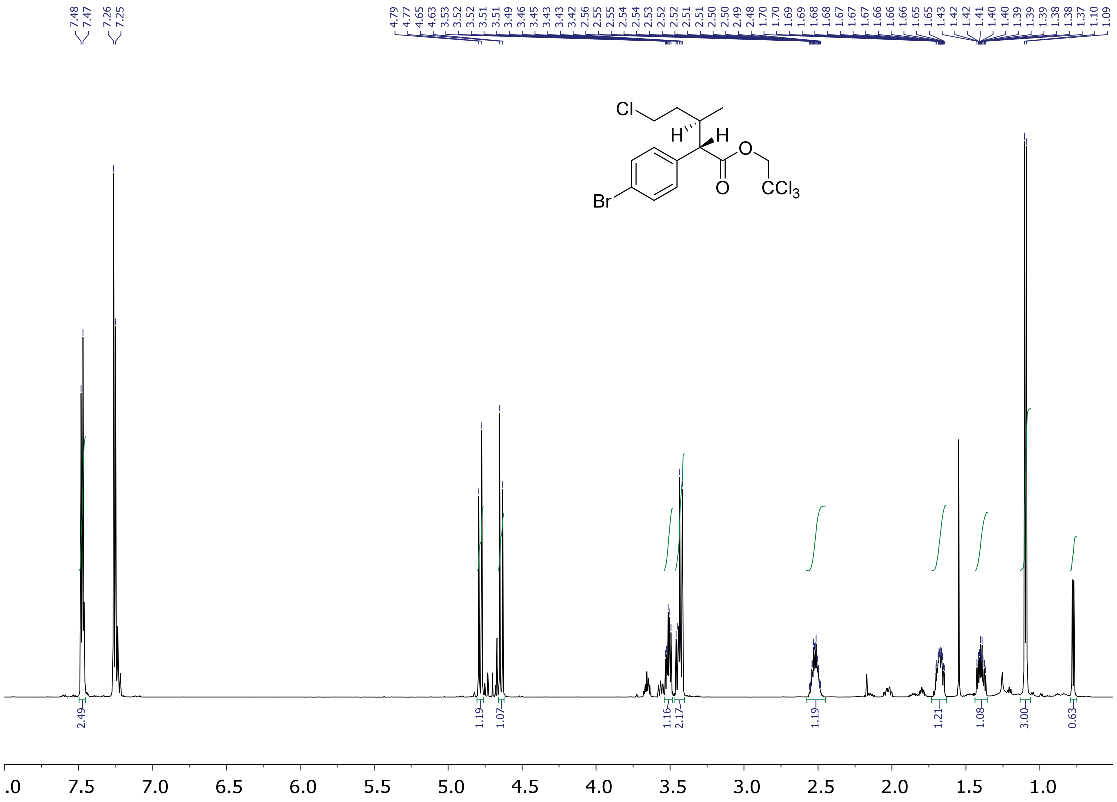
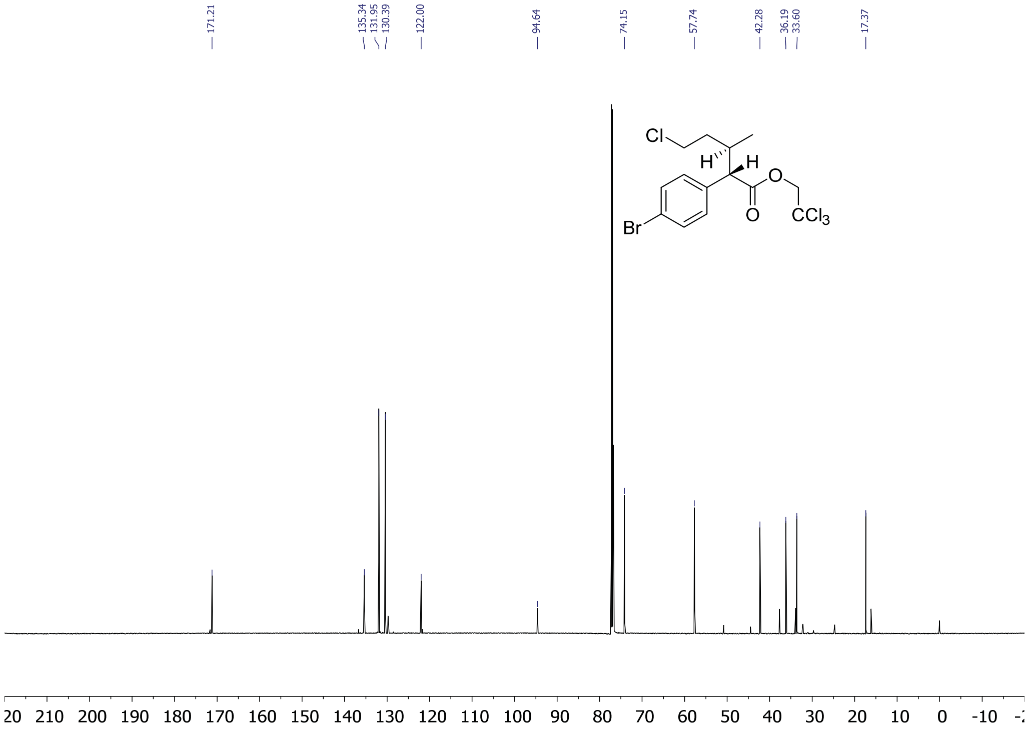
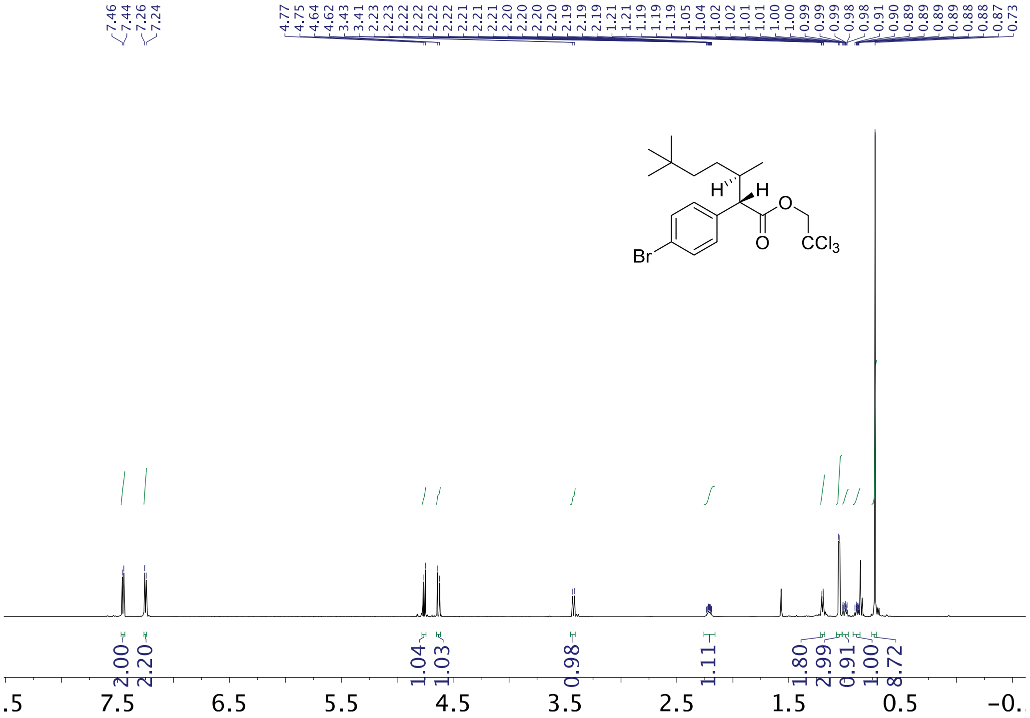
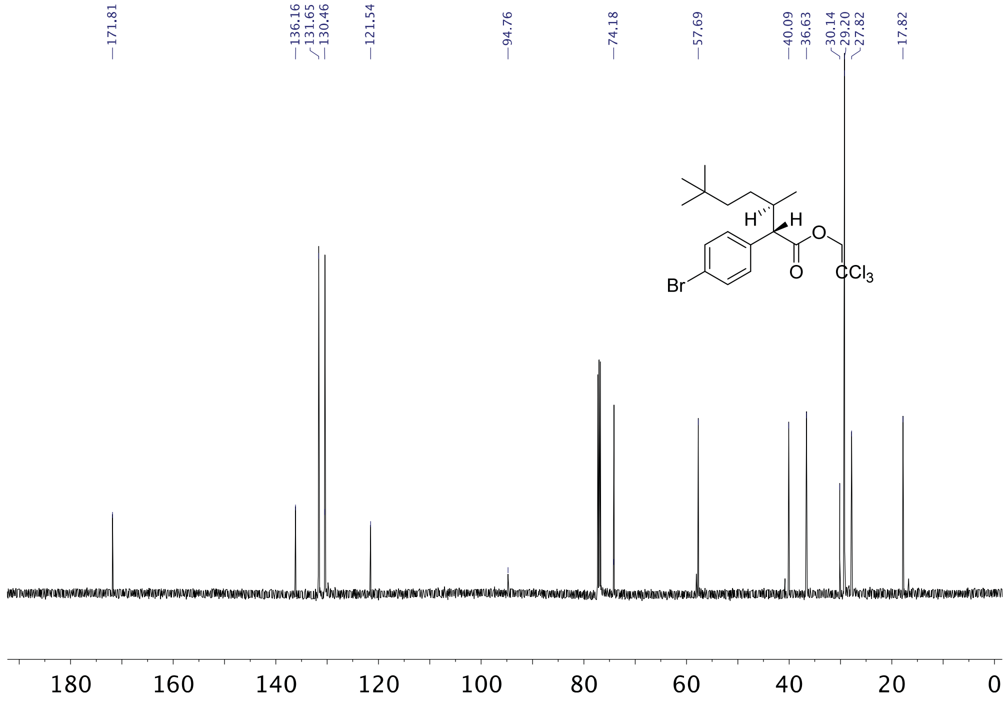
7.45
7.25
7.24
4.78
4.76
4.65
4.63
4.36
4.36
4.35
4.34
4.34
4.33
4.28
4.28
4.27
4.27
4.26
4.26
4.25
4.25
3.40
3.39
2.32
2.32
2.31
2.31
2.30
2.30
2.29
2.29
2.28
2.28
2.27
1.75
1.75
1.74
1.73
1.72
1.72
1.71
1.70
1.69
1.68
1.58
1.57
1.56
1.56
1.55
1.55
1.54
1.53
1.52
1.51
1.51
1.51
1.50
1.33
1.32
1.32
1.32
1.31
1.31
1.30
1.30
1.29
1.29
1.28
1.28
1.27
1.09
1.08
1.05
1.05
1.04
1.04
1.03
1.03
1.02
1.02
1.02
1.01
1.01
1.01
1.00
0.99
F
H
H
O
O
Br
CCl3
2.22
2.19
0.98
1.00
1.05
0.92
1.03
1.10
1.23
1.01
1.32
2.78
1.06
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0


171.67
135.92
131.98
130.49
121.92
94.83
74.26
58.10
38.26
35.94
29.09
29.05
27.52
27.39
17.90
F
H
H
O
O
CCl3
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

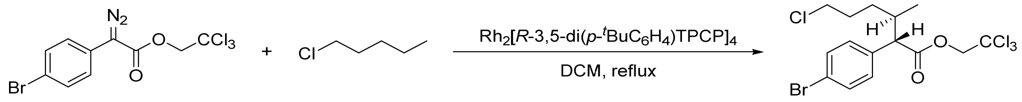

7.48
7.47
7.26
7.25
4.79
4.77
4.65
4.63
3.53
3.52
3.52
3.51
3.51
3.49
3.46
3.45
3.43
3.43
3.42
2.56
2.55
2.55
2.54
2.54
2.53
2.52
2.52
2.51
2.51
2.50
2.50
2.49
2.48
1.70
1.69
1.69
1.68
1.68
1.67
1.67
1.66
1.66
1.66
1.65
1.65
1.43
1.42
1.42
1.41
1.40
1.40
1.39
1.39
1.38
1.38
1.37
1.10
1.09
Cl
H
H
O
Br
O
CCl$_3$
2.49
1.19
1.07
1.16
2.17
1.19
1.21
1.08
3.00
0.63
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

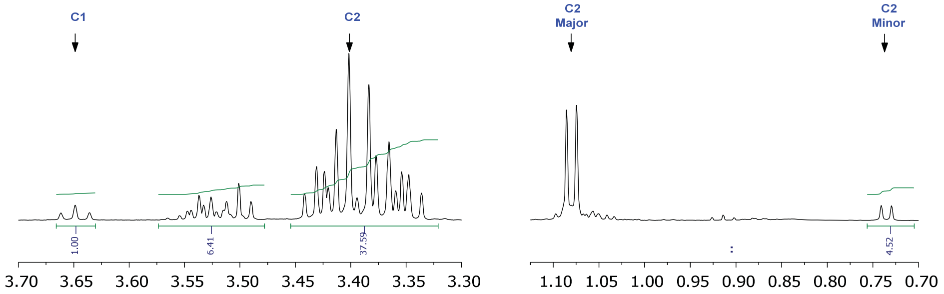

171.21
135.34
131.95
130.39
122.00
94.64
74.15
57.74
42.28
36.19
33.60
17.37
Cl
H
H
O
Br
O
CCl3
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

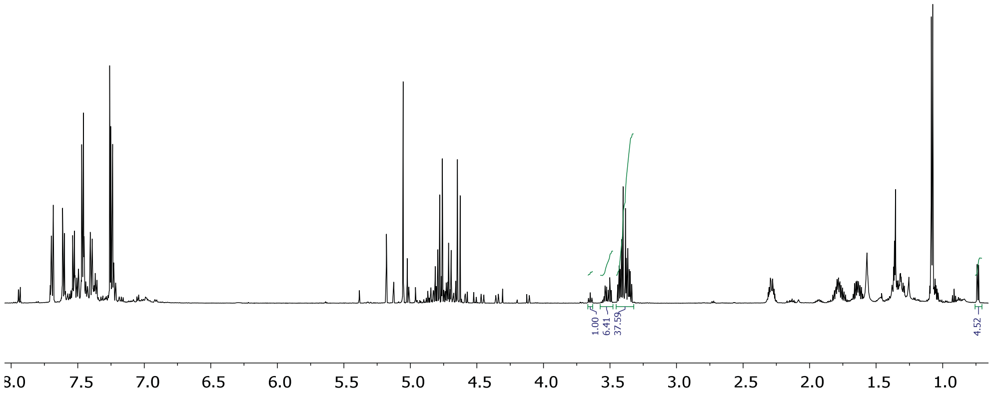

7.46
7.44
7.26
7.24
4.77
4.75
4.64
4.62
3.43
3.41
2.23
2.23
2.22
2.22
2.22
2.22
2.21
2.21
2.21
2.20
2.20
2.20
2.19
2.19
2.19
1.21
1.21
1.19
1.19
1.19
1.05
1.04
1.02
1.02
1.01
1.01
1.00
1.00
0.99
0.99
0.99
0.98
0.98
0.91
0.90
0.89
0.89
0.89
0.89
0.88
0.87
0.73
H
H
O
O
CCl_3
Br
2.00
2.20
1.04
1.03
0.98
1.11
1.80
2.99
0.91
1.00
8.72
.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
–0.

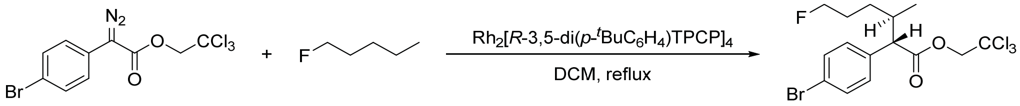

171.81
136.16
131.65
130.46
121.54
94.76
74.18
57.69
40.09
36.63
30.14
29.20
27.82
17.82
H
H
O
O
CCl$_3$
Br
180
160
140
120
100
80
60
40
20
0

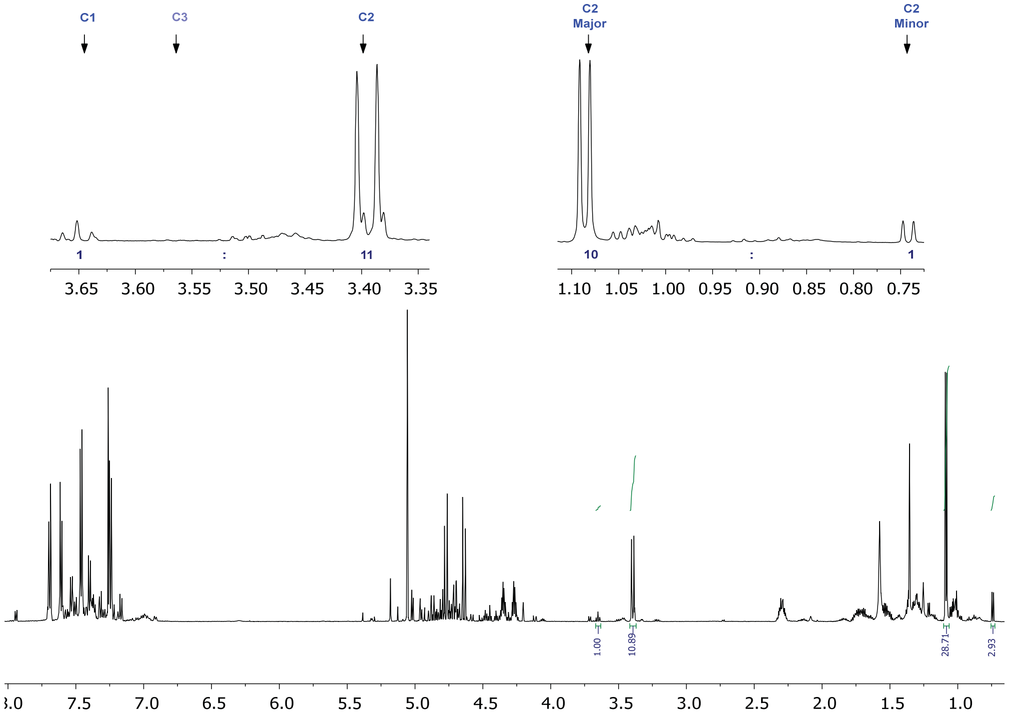
5. Crude ^{1}H NMR Spectra for the Ratio Determination

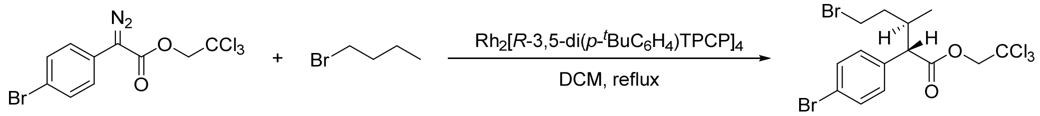


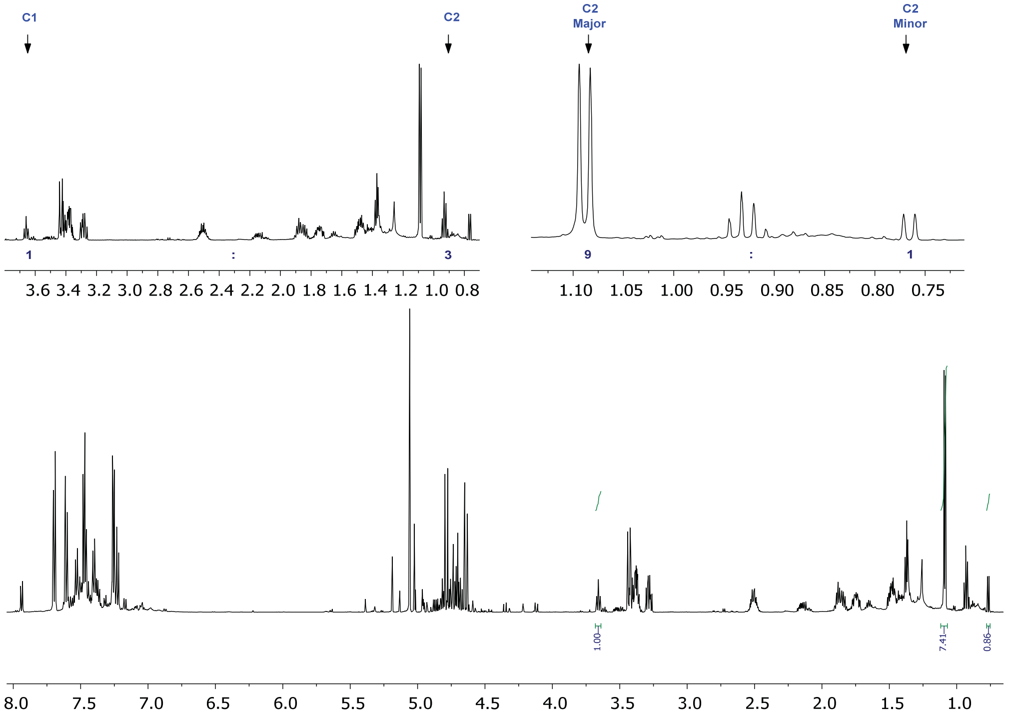


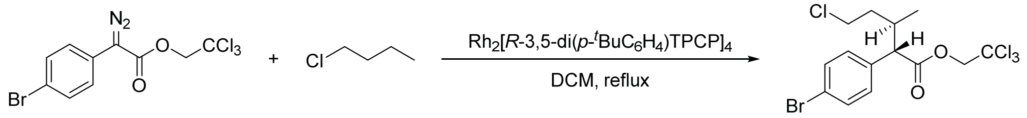


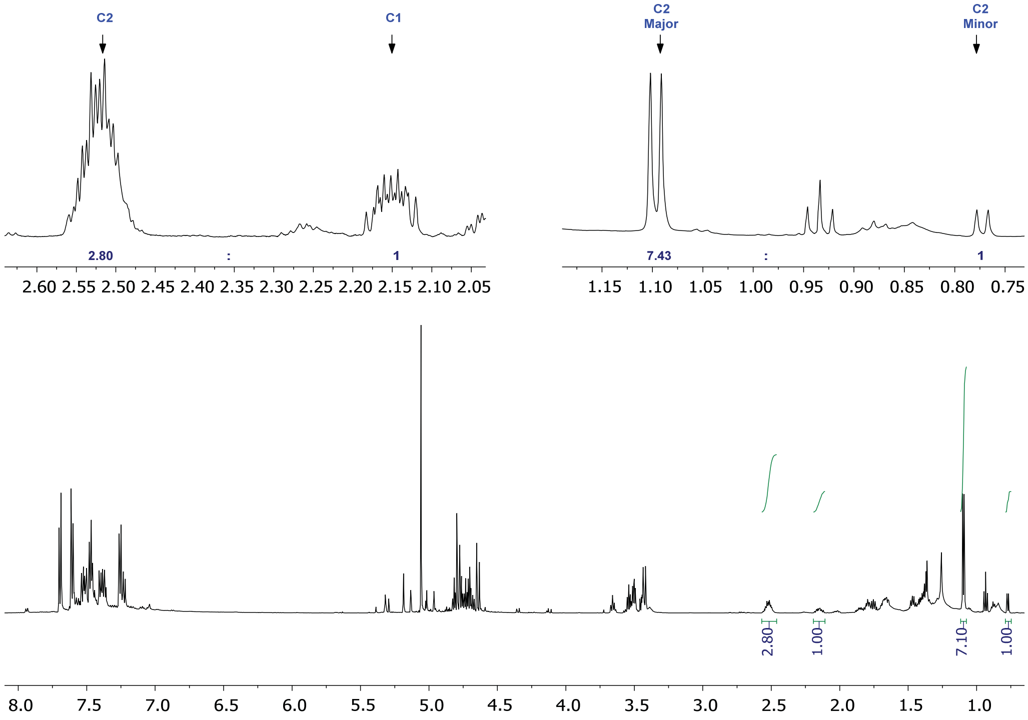

N2
CCl3
Br
O
F
Rh2[R-3,5-di(p-tBuC6H4)TPCP]4
DCM, reflux
H
H
O
CCl3
Br

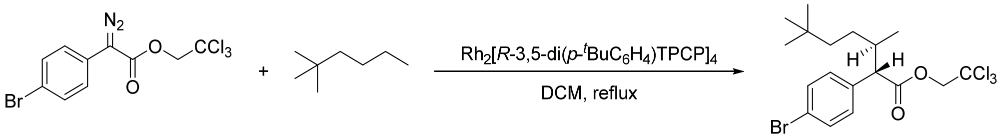

C1
C3
C2
C2 Major
C2 Minor
1 : 11
10 : 1
3.65 3.60 3.55 3.50 3.45 3.40 3.35
1.10 1.05 1.00 0.95 0.90 0.85 0.80 0.75
1.00
10.89
28.71
2.93
.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0

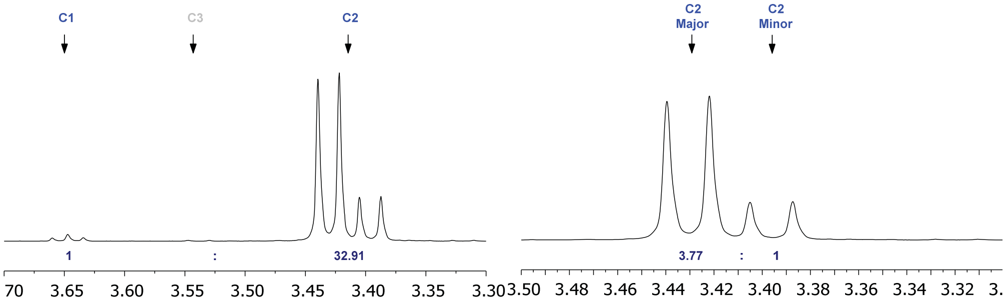

N2
CCl3
Br
+
Br
Rh2[R-3,5-di(p-tBuC6H4)TPCP]4
DCM, reflux
Br
H
H
O
CCl3
Br
O

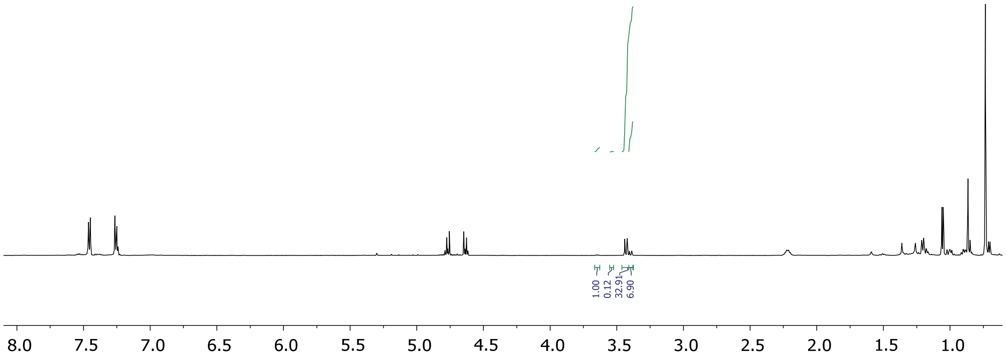

C1
C2
1
:
3
3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
C2 Major
C2 Minor
9
:
1
1.10 1.05 1.00 0.95 0.90 0.85 0.80 0.75
1.00
7.41
0.86
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0


N2
Br
O
CCl3
+
Cl
Rh2[R-3,5-di(p-tBuC6H4)TPCP]4
DCM, reflux
Cl
H
H
O
CCl3
Br


C2
C1
2.80
:
1
2.60 2.55 2.50 2.45 2.40 2.35 2.30 2.25 2.20 2.15 2.10 2.05
C2
Major
C2
Minor
7.43
:
1
1.15 1.10 1.05 1.00 0.95 0.90 0.85 0.80 0.75
2.80
1.00
7.10
1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0


N2
Br
O
CCl3
+
Rh2[R-3,5-di(p-tBuC6H4)TPCP]4
DCM, reflux
H
H
O
CCl3
Br
O


C1
C3
C2
1
:
32.91
70
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
C2 Major
C2 Minor
3.77
:
1
3.50
3.48
3.46
3.44
3.42
3.40
3.38
3.36
3.34
3.32
3.


1.00
0.12
32.91
6.90
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
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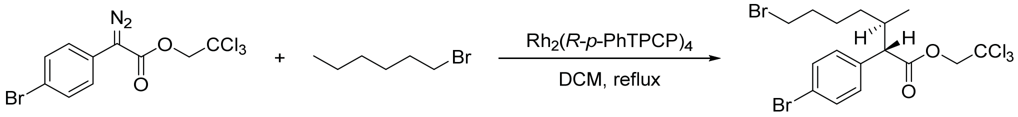
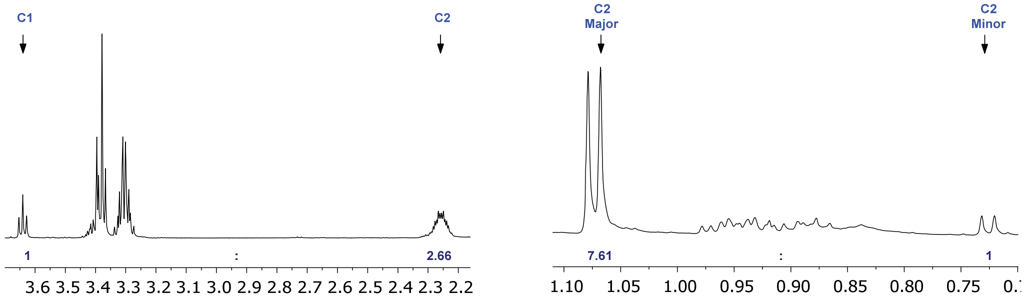
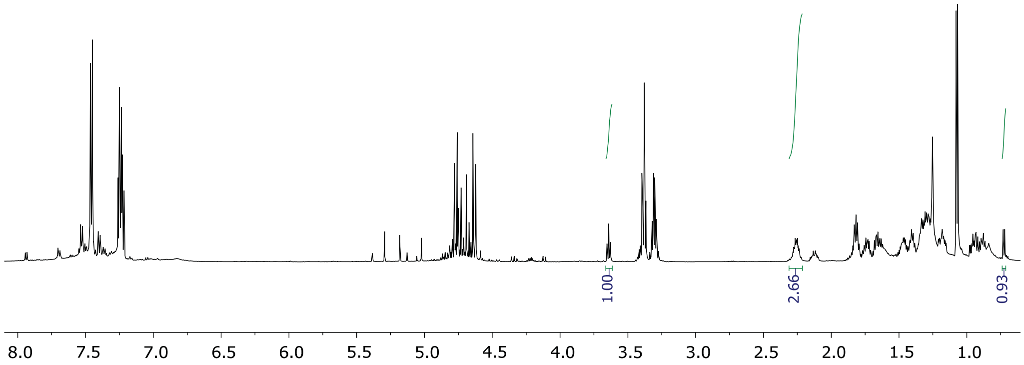
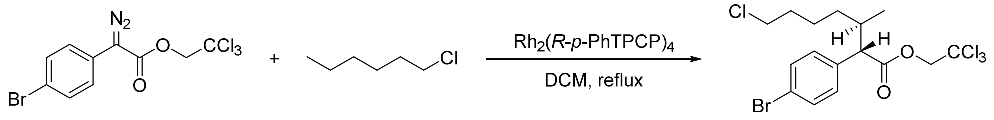
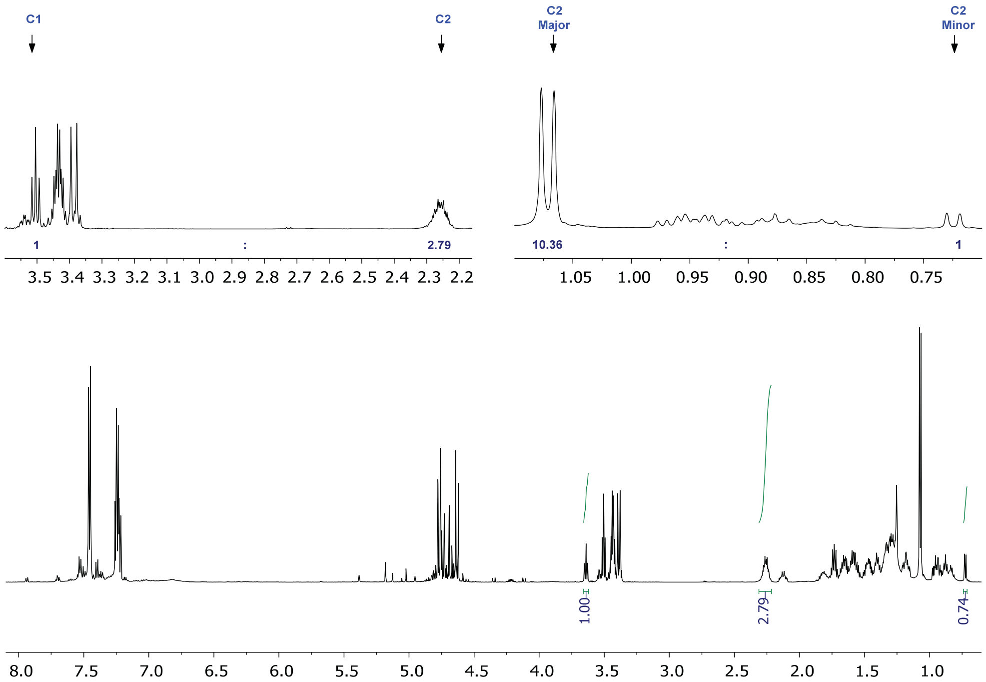
2.5
2.0
1.5
1.0

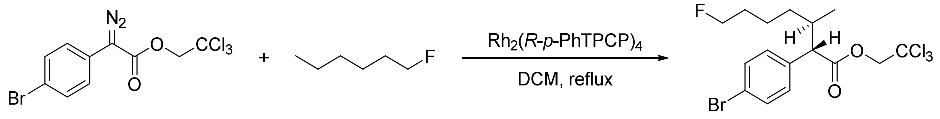

N2
Br
O
O
CCl3
+
Br
Rh2(R-p-PhTPCP)4
DCM, reflux
Br
H
H
O
O
CCl3
Br

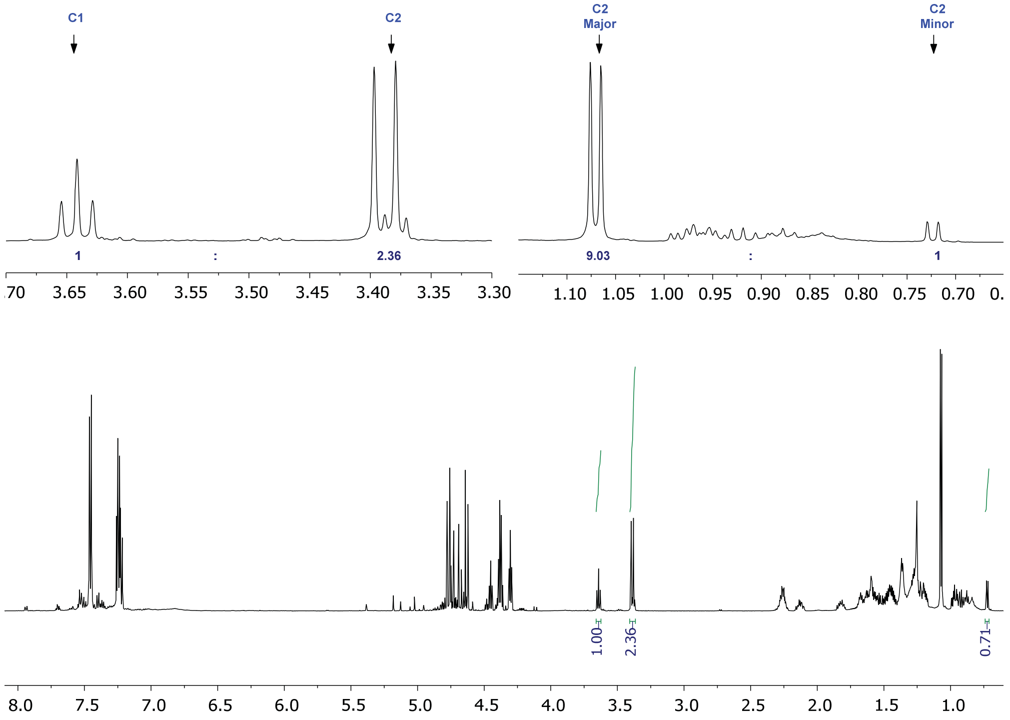

C1
C2
C2
Major
C2
Minor
1
:
2.66
7.61
:
1
3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2
1.10 1.05 1.00 0.95 0.90 0.85 0.80 0.75


1.00
2.66
0.93
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0


N2
CCl3
Br
+
Cl
Rh2(R-p-PhTPCP)4
DCM, reflux
Cl
H
H
O
CCl3
Br
O


C1
C2
C2 Major
C2 Minor
1
:
2.79
10.36
:
1
3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2
1.05 1.00 0.95 0.90 0.85 0.80 0.75
1.00
2.79
0.74
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0


N2
CCl3
Br
+
F
Rh2(R-p-PhTPCP)4
DCM, reflux
F
H
H
O
CCl3
Br


C1
C2
C2
Major
C2
Minor
1
:
2.36
9.03
:
1
.70
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
1.10
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.
1.00
2.36
0.71
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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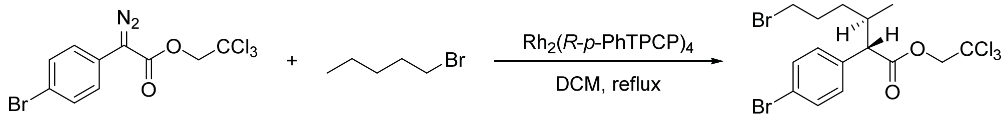
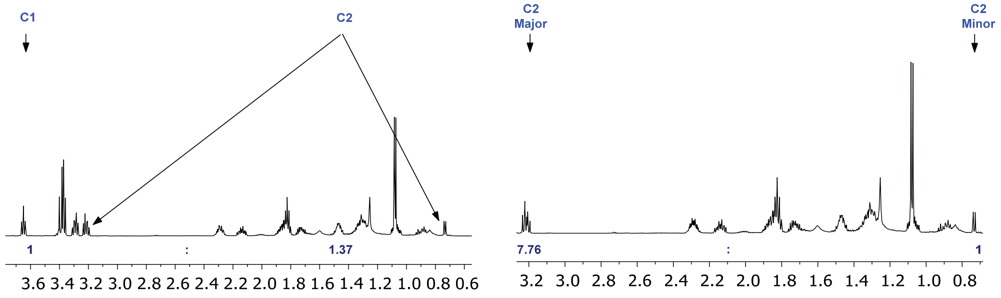
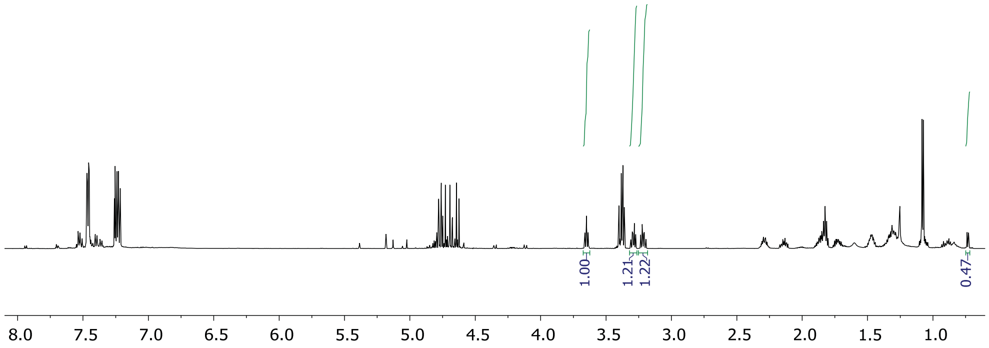
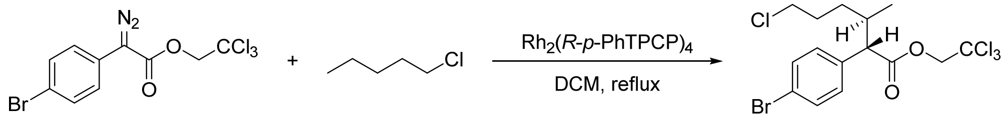
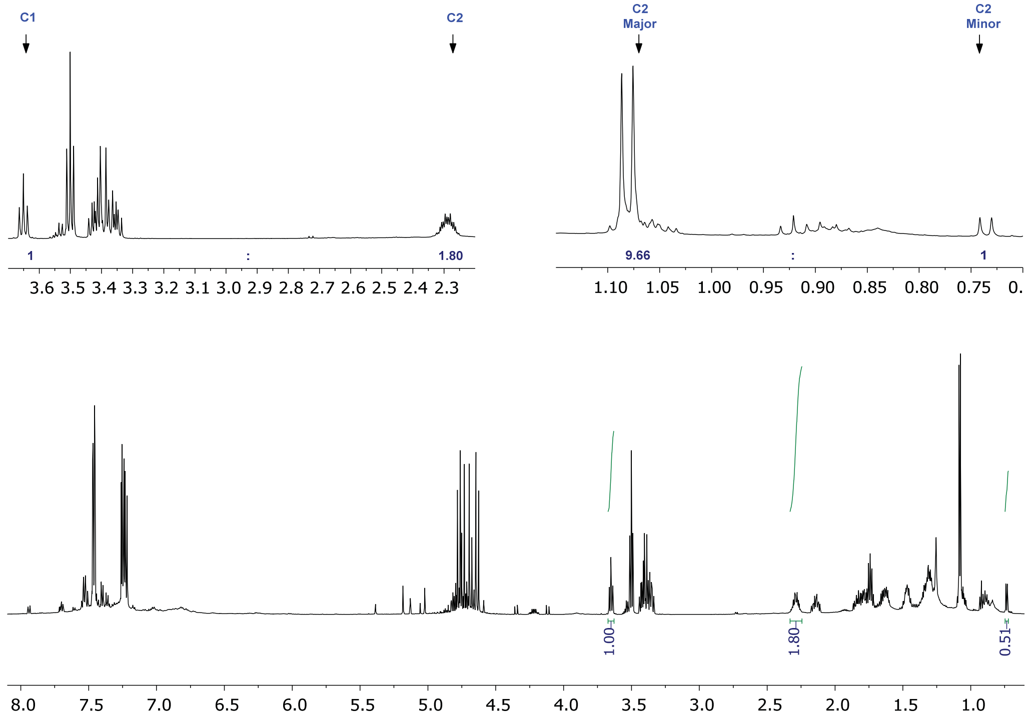
2.5
2.0
1.5
1.0

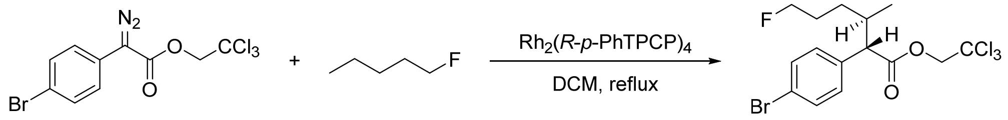

N2
CCl3
Br
O
+
Br
Rh2(R-p-PhTPCP)4
DCM, reflux
Br
H
H
O
CCl3
Br
O

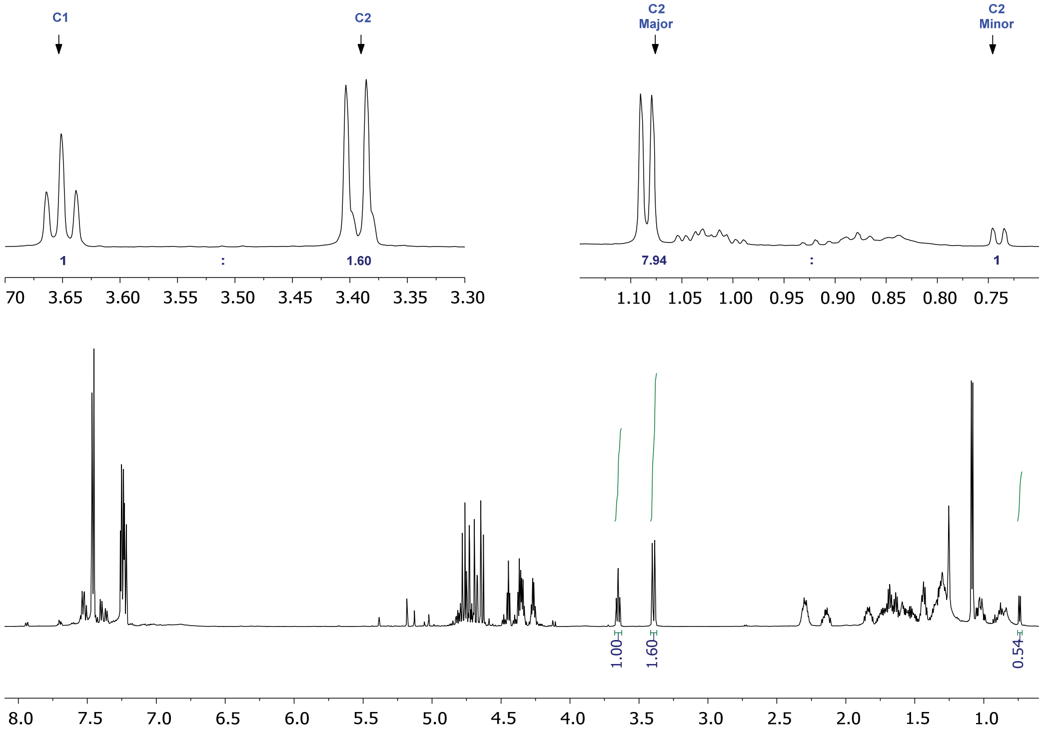

C1
C2
1
:
1.37
3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
C2
Major
C2
Minor
7.76
:
1
3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8

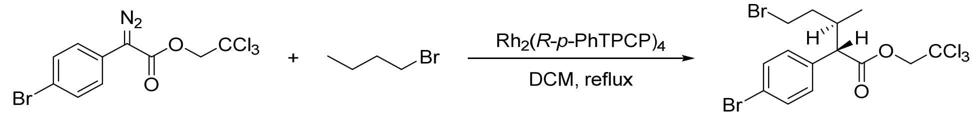

1.00
1.21
1.22
0.47
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0

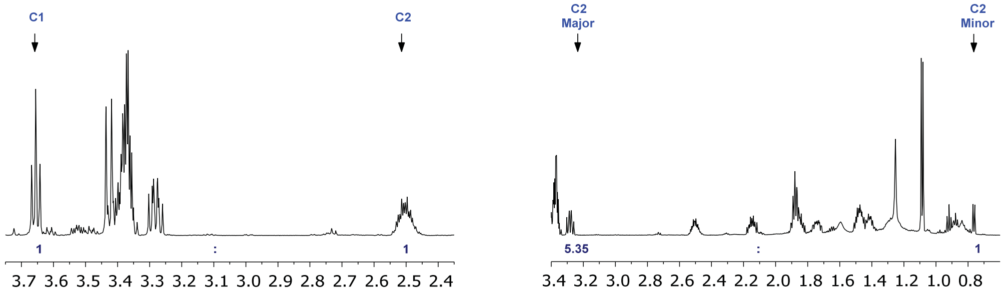

N$_2$
O
CCl$_3$
Br
O
+
Cl
Rh$_2$(R-p-PhTPCP)$_4$
DCM, reflux
Cl
H
H
O
CCl$_3$
Br
O

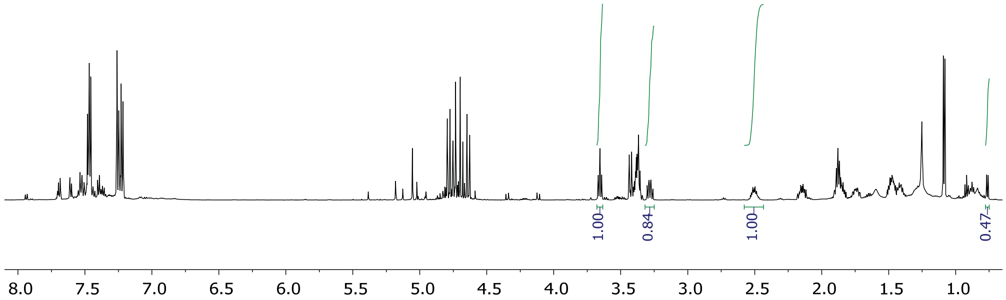

C1
C2
1
:
1.80
3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3
C2
Major
C2
Minor
9.66
:
1
1.10 1.05 1.00 0.95 0.90 0.85 0.80 0.75 0.
1.00
1.80
0.51
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0

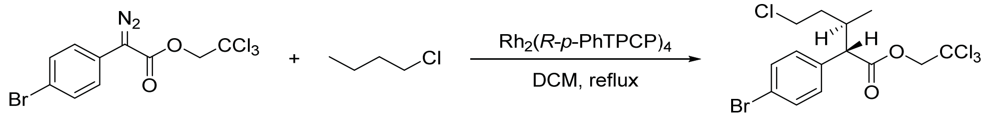

N2
CCl3
Br
F
Rh2(R-p-PhTPCP)4
DCM, reflux
H
H
O

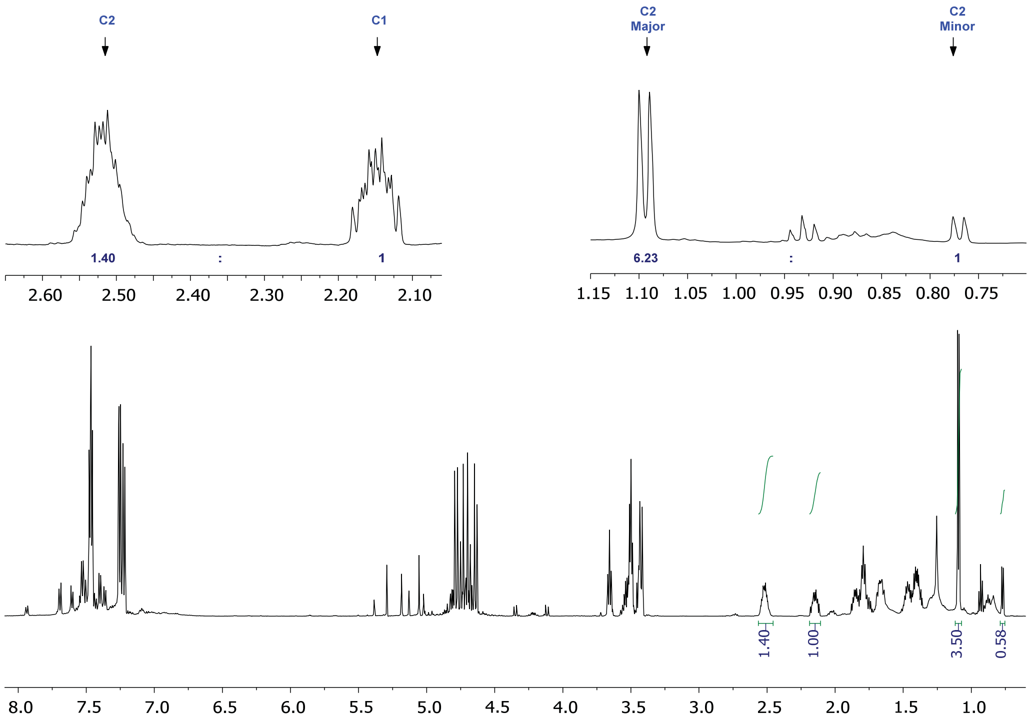

C1
C2
1
:
1.60
70
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
C2 Major
C2 Minor
7.94
:
1
1.10
1.05
1.00
0.95
0.90
0.85
0.80
0.75
1.00
1.60
0.54
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

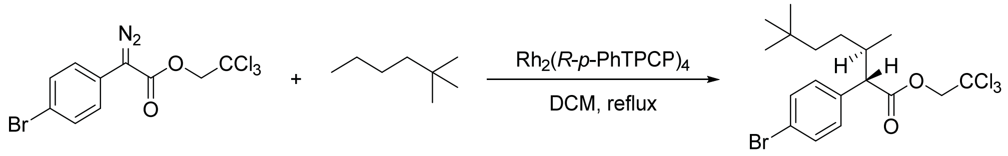

N2
CCl3
Br
O
+
Br
Rh2(R-p-PhTPCP)4
DCM, reflux
Br
H
H
O
CCl3
Br
O

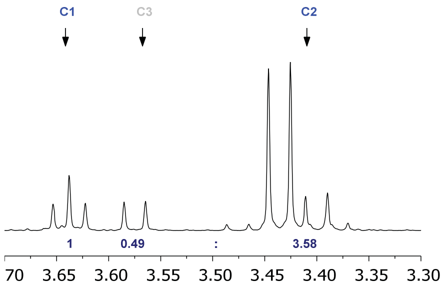

C1
C2
C2
Major
C2
Minor
1
:
1
5.35
:
1
3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8

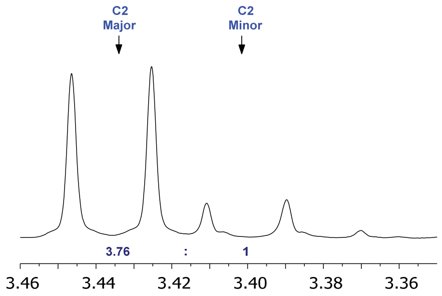

1.00
0.84
1.00
0.47
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

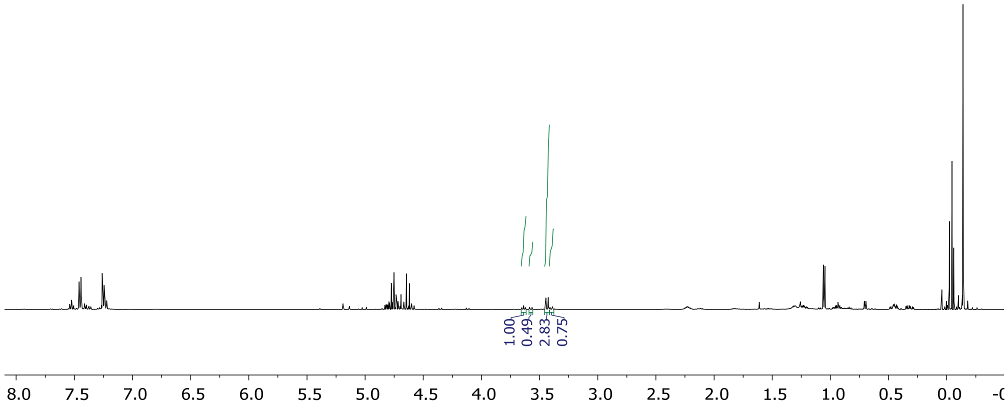

N$_2$
CCl$_3$
Br
O
Cl
Rh$_2$(*R*-*p*-PhTPCP)$_4$
DCM, reflux
Cl
H
H
CCl$_3$
Br
O

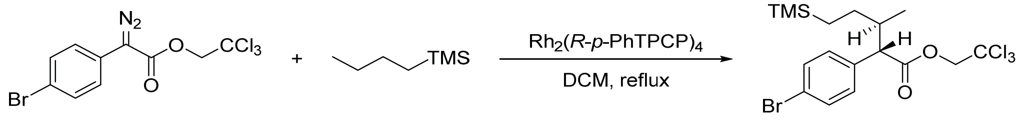

C2
C1
1.40
:
1
2.60
2.50
2.40
2.30
2.20
2.10
C2 Major
C2 Minor
6.23
:
1
1.15
1.10
1.05
1.00
0.95
0.90
0.85
0.80
0.75
1.40
1.00
3.50
0.58
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

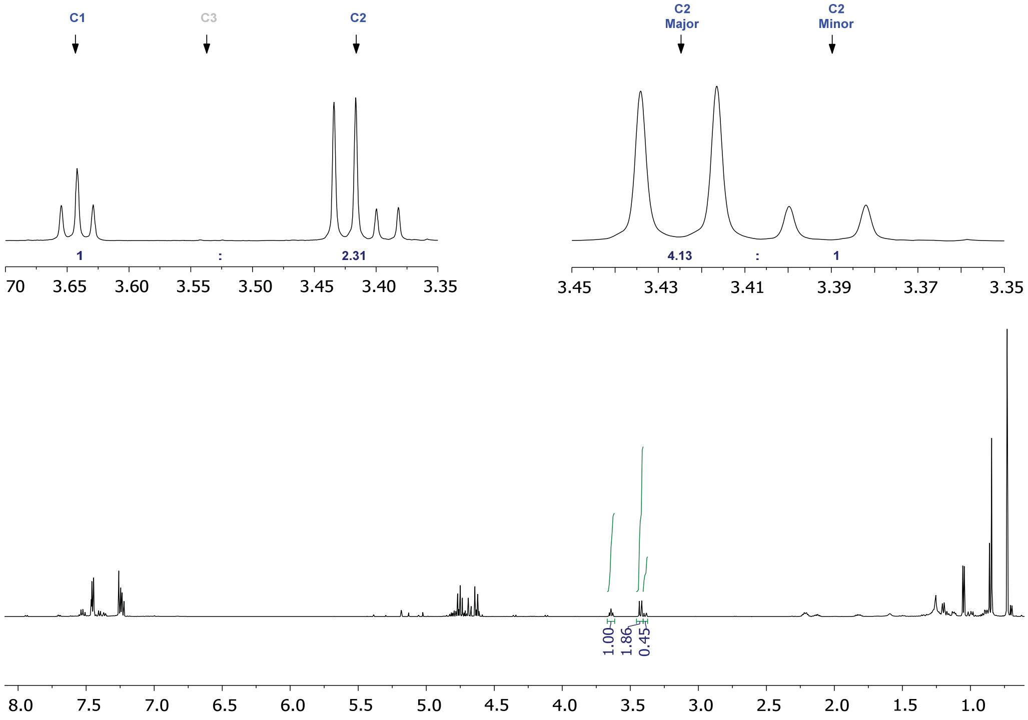

N2
CCl3
Br
O
+
Rh2(R-p-PhTPCP)4
DCM, reflux
H
H
O
CCl3
Br
O

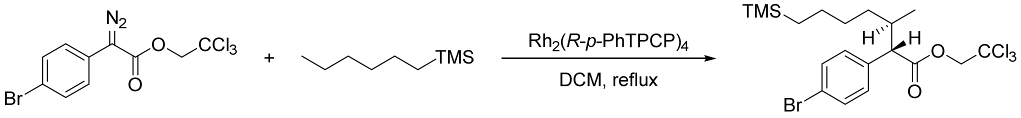

C1
C3
C2
1
0.49
:
3.58
70
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30

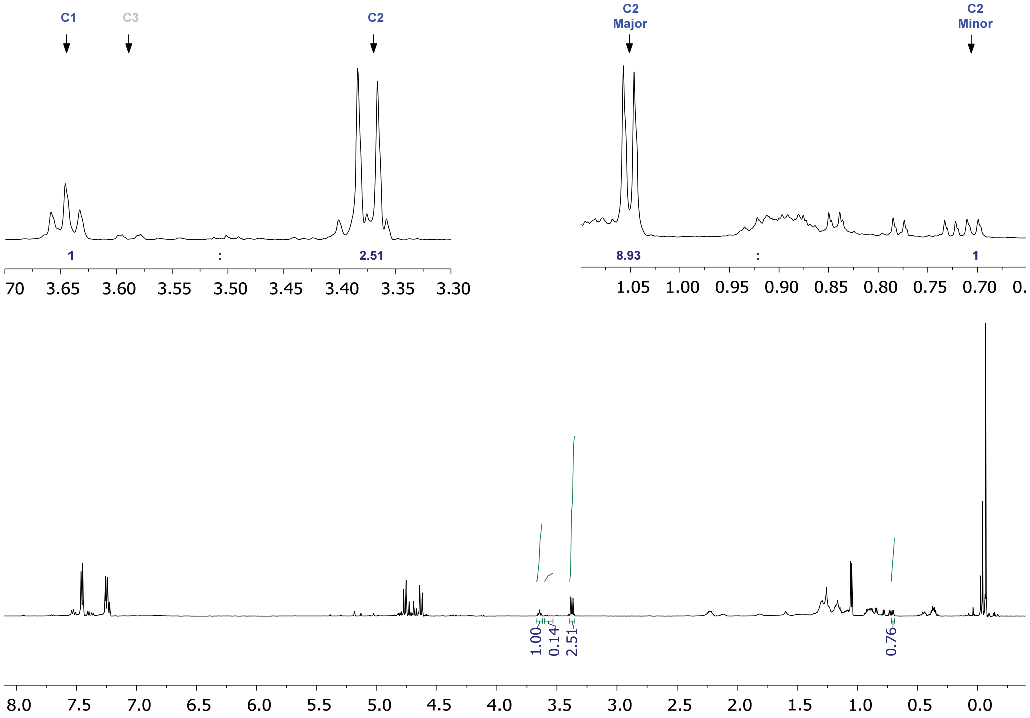

C2
Major
C2
Minor
3.76
:
1
3.46
3.44
3.42
3.40
3.38
3.36

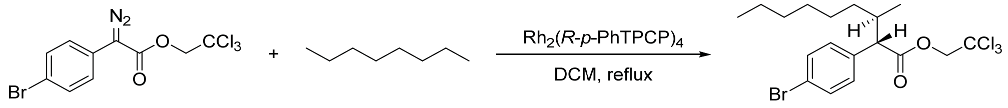

1.00
0.49
2.83
0.75
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

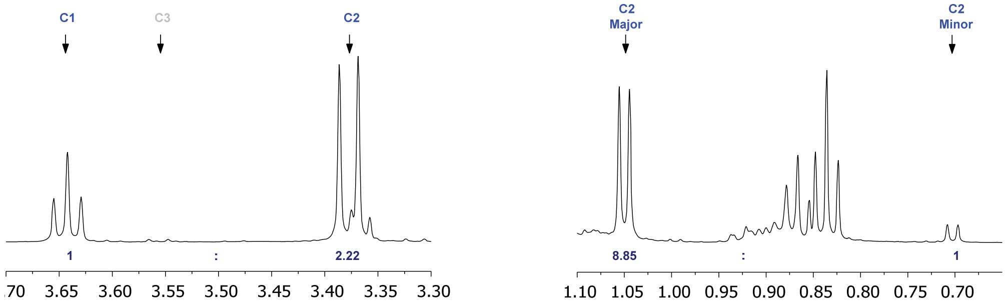

N2
CCl3
Br
TMS
Rh2(R-p-PhTPCP)4
DCM, reflux
H
O

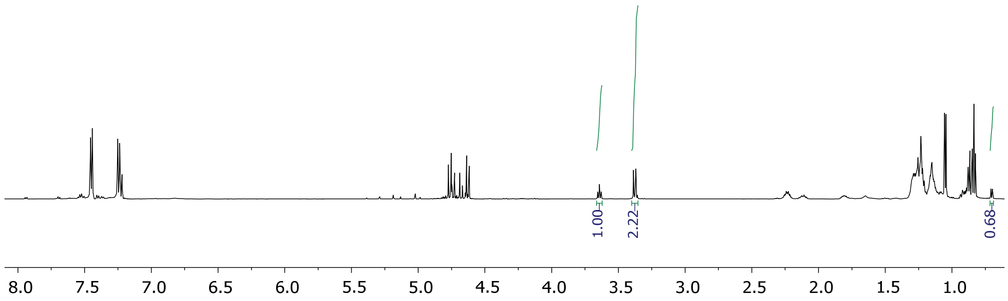

C1
C3
C2
C2 Major
C2 Minor
1
:
2.31
4.13
1
70
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.43
3.41
3.39
3.37
1.00
1.86
0.45
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.0
2.5
2.0
1.5
1.0


N2
O
CCl3
Br
+
TMS
Rh2(R-p-PhTPCP)4
DCM, reflux
TMS
H
H
O
CCl3
O
Br

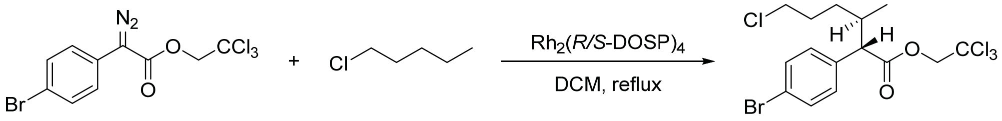

C1
C3
C2
1
:
2.51
70
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
C2 Major
C2 Minor
8.93
:
1
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.
1.00
0.14
2.51
0.76
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

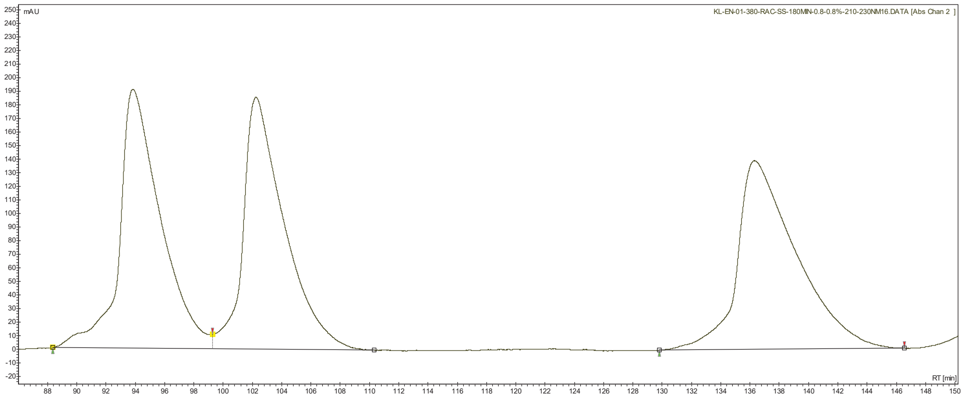

N2
O
CCl3
Br
O
+
Rh2(R-p-PhTPCP)4
DCM, reflux
H
H
O
CCl3
Br
O


C1
C3
C2
1
:
2.22
.70
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
C2
Major
C2
Minor
8.85
:
1
1.10
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70

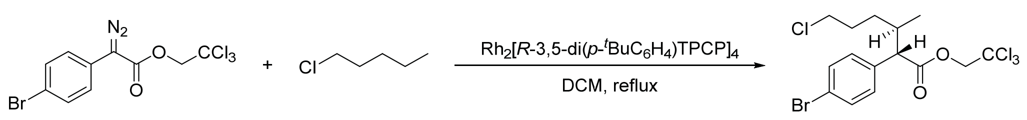

1.00
2.22
0.68
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

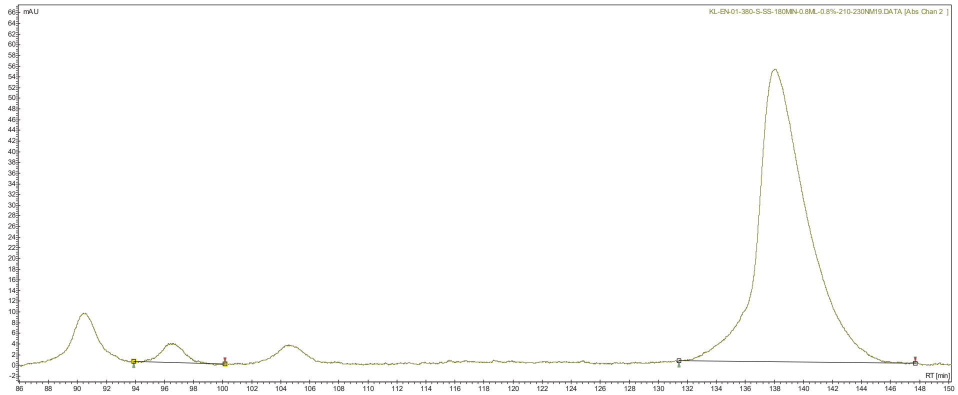
6. HPLC Spectra for C–H Functionalization Reactions



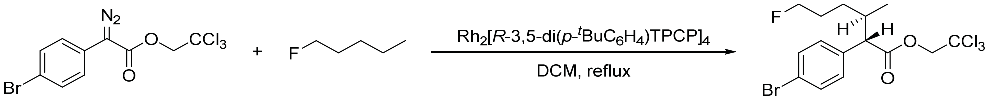


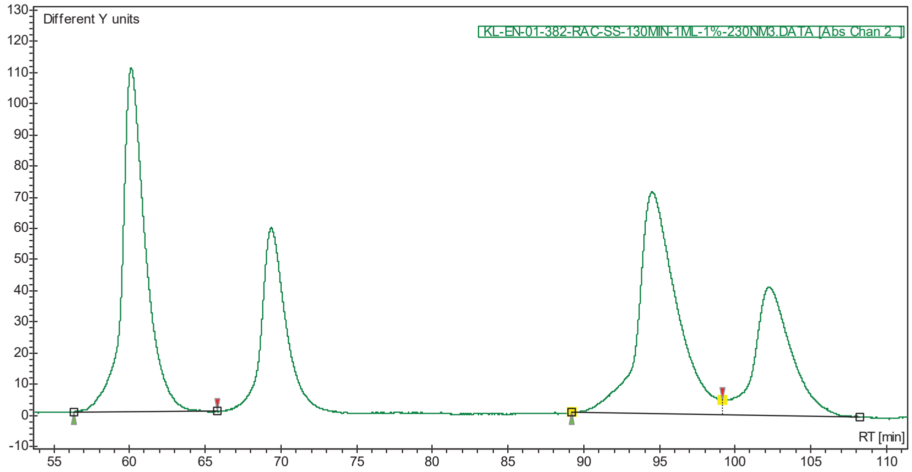
#	Time [Min]	Area % [%]
1	93.84	48.985
2	136.26	51.015



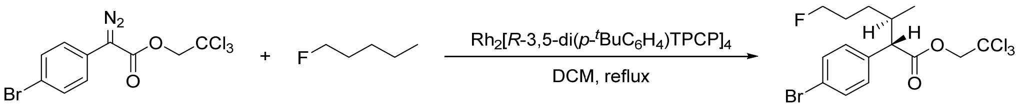


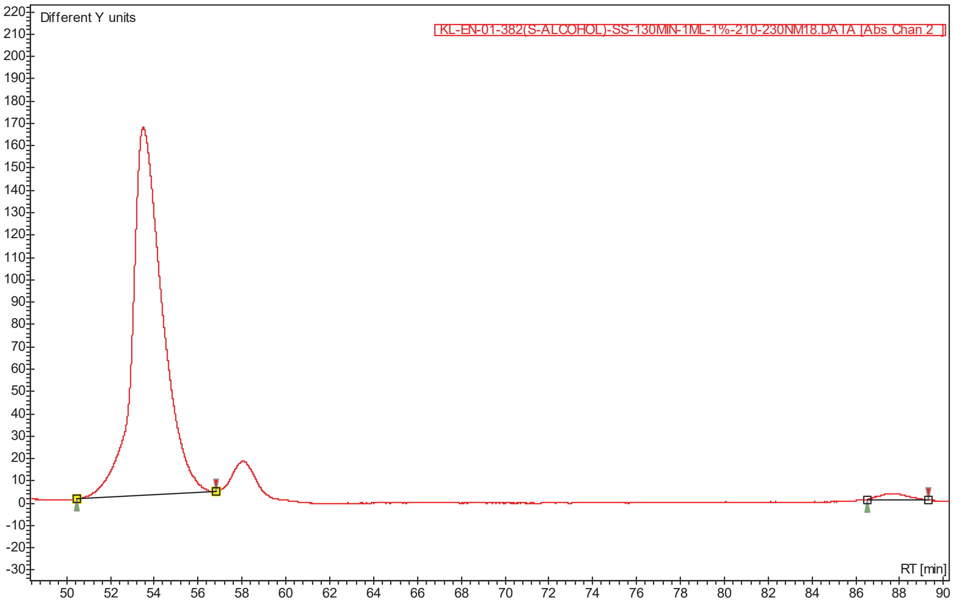
#	Time [Min]	Area % [%]
1	96.43	2.928
2	138.06	97.072
		94 % ee



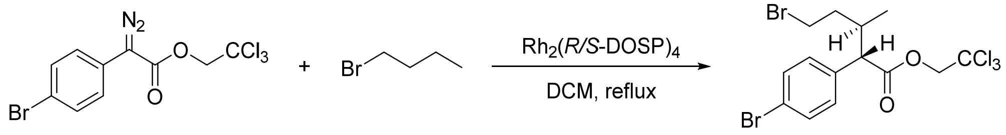


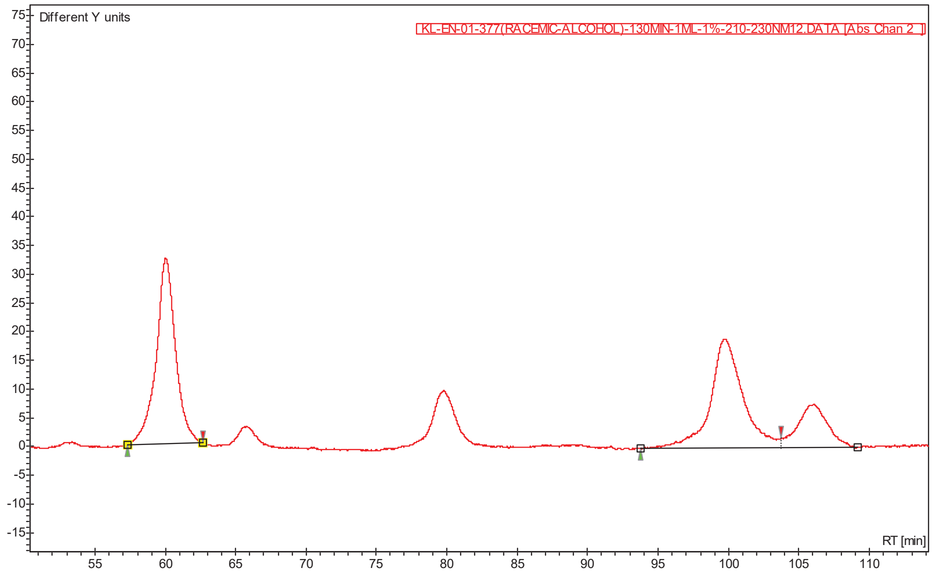
#	Time [Min]	Area % [%]
1	60.10	48.262
2	94.56	51.738



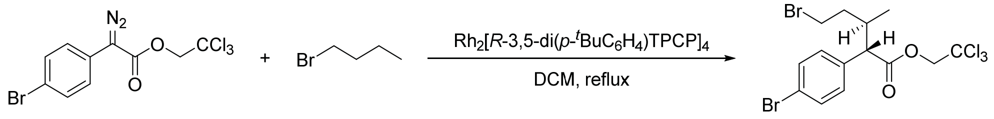


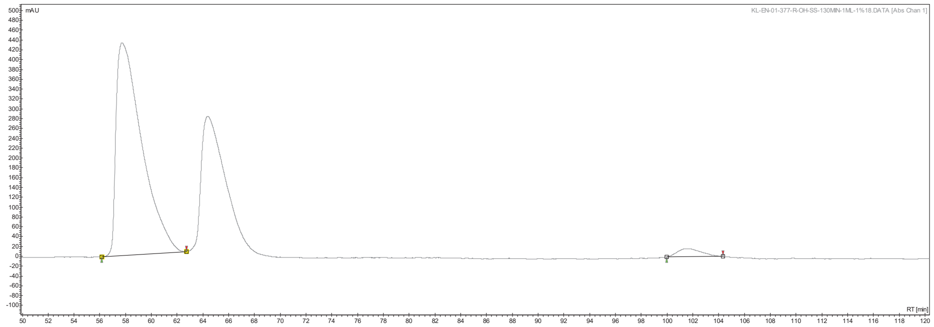
#	Time [Min]	Area % [%]
1	53.50	98.437
2	87.55	1.563
		97 % ee



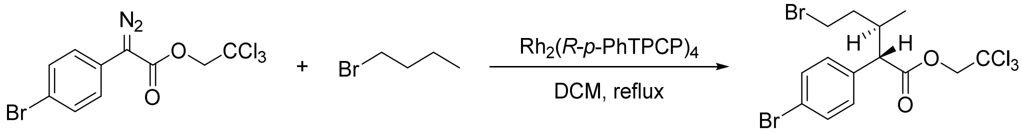


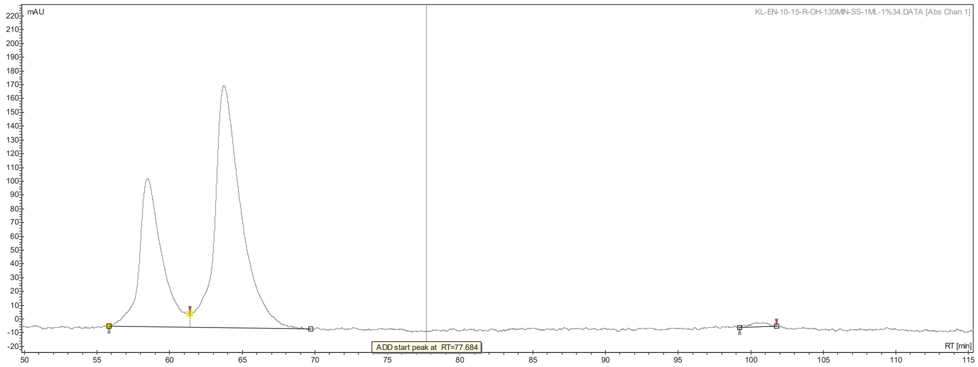
#	Time [Min]	Area % [%]
1	60.03	50.166
2	99.71	49.834



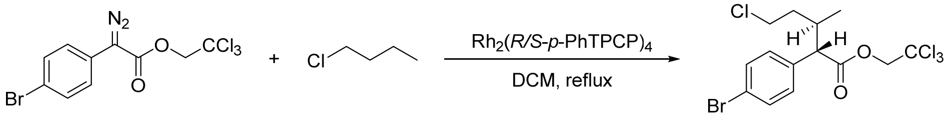


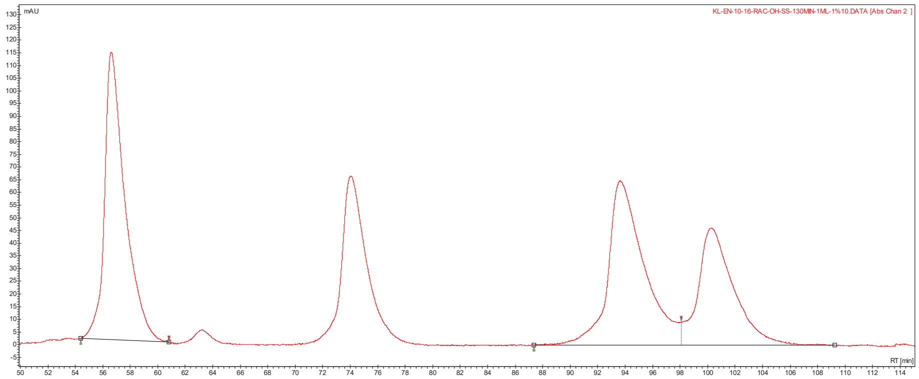
#	Time [Min]	Area % [%]
1	57.73	96.548
2	101.48	3.452
		93 % ee



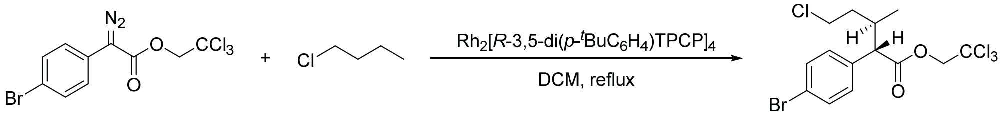


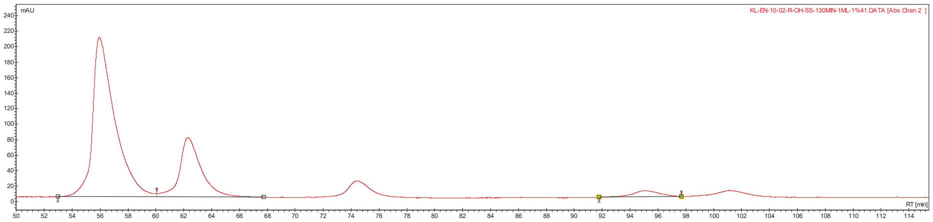
#	Time [Min]	Area % [%]
1	58.50	98.081
2	100.36	1.919
		96 % ee



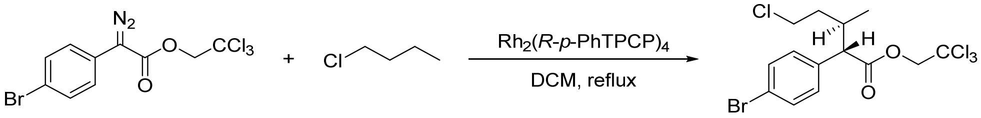


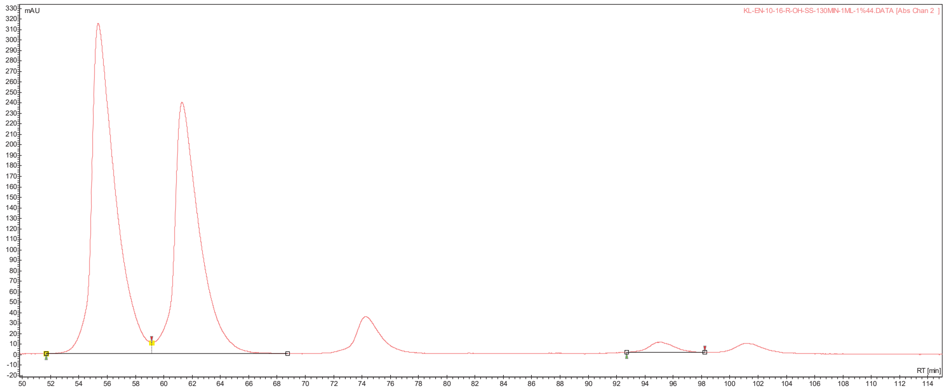
#	Time [Min]	Area % [%]
1	56.61	49.963
2	93.63	50.037



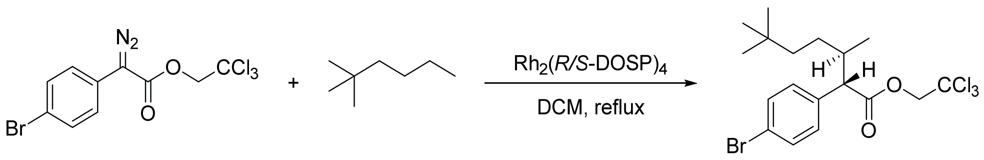


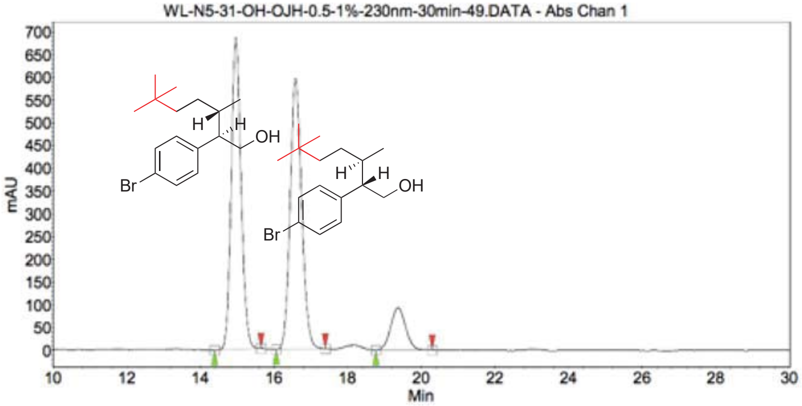
#	Time [Min]	Area % [%]
1	55.94	95.790
2	95.03	4.210
		92 % ee



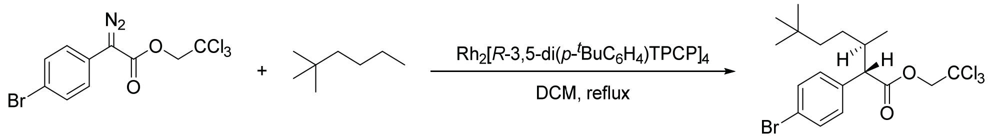


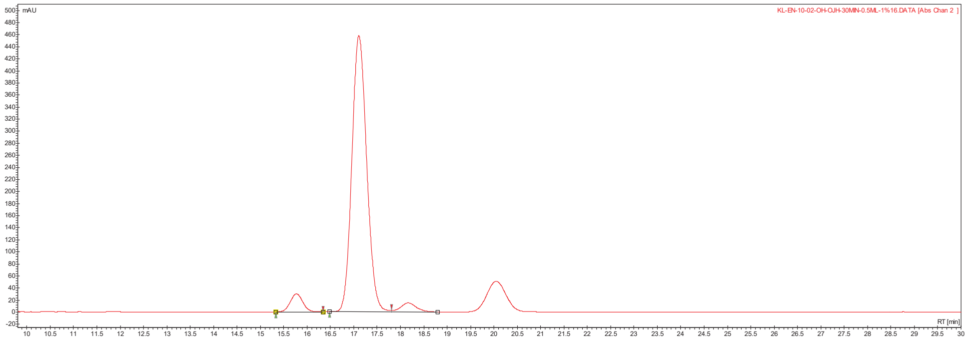
#	Time [Min]	Area % [%]
1	55.36	96.827
2	95.10	3.173
		94 % ee



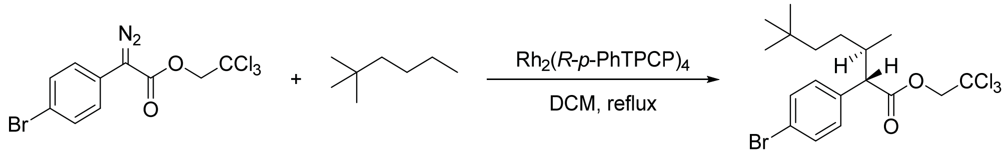


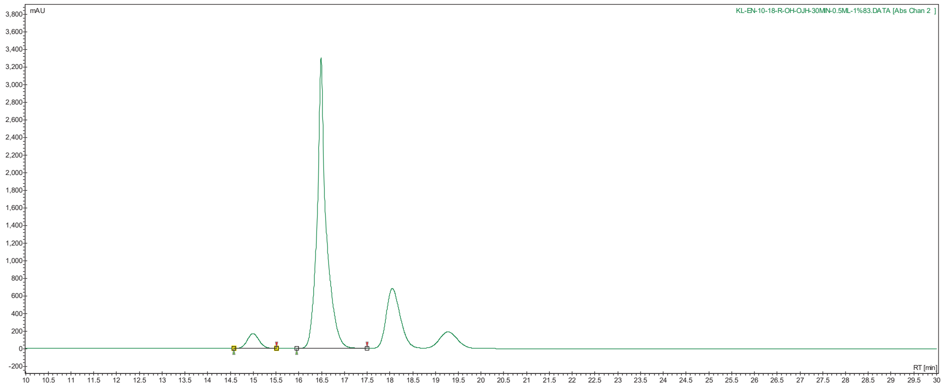
Index	Time (min)	Area (%)
1	14.96	49.441
2	16.59	50.559





#	Time [Min]	Area % [%]
1	15.77	5.318
2	17.11	94.682
		90 % ee





#	Time [Min]	Area % [%]
1	14.99	6.264
2	16.49	93.736
		88 % ee

7. X-Ray Crystallographic Data for Rh$_2$(*S*-*p*-PhTPCP)$_4$

Rh$_2$(*S*-*p*-PhTPCP)$_4$

Submitted by: **Kuangbiao Liao**
Davies Group, Emory University
Solved by: **John Bacsa**
Sample ID: **S-BPCP**

Crystal Data and Experimental

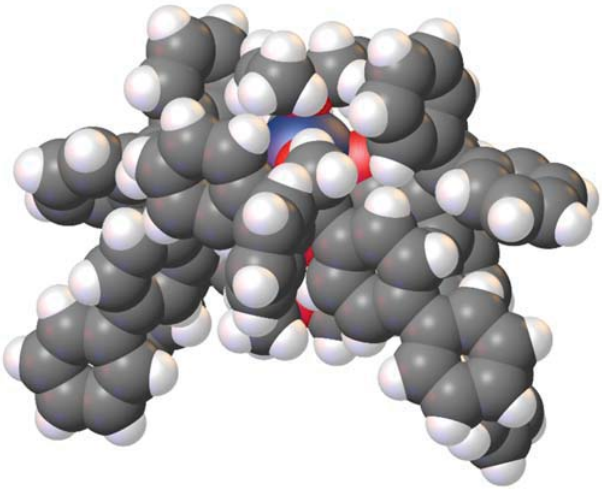


Figure S2

Experimental. Single greenish blue plate-shaped crystals of (**S-BPCP**) were obtained by recrystallisation from ether by slow evaporation. A suitable crystal (0.55×0.48×0.20 mm^3) was selected and mounted on a loop with paratone oil on a Bruker APEXII diffractometer. The crystal was cooled to T = 100(2) K during data collection. The structure was solved with the **Superflip** (Palatinus et al., 2012) structure solution program using the Charge Flipping solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2014/7 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{124}H_{114}O_{11}Rh_2$, M_r = 1985.97, monoclinic, P2$_1$ (No. 4), a = 11.764(3) Å, b = 17.436(4) Å, c = 26.079(7) Å, = 91.389(6)°, = = 90°, V = 5347(2) Å^3, T = 100(2) K, Z = 2, Z' = 1, (MoK) = 0.368 mm^{-1}, 19801 reflections measured, 15161 unique (R_{int} = 0.0531) which were used in all calculations. The final wR_2 was 0.2181 (all data) and R_1 was 0.0987 (I > 2σ(I)).

Compound	**S-BPCP**
Formula	$C_{124}H_{114}O_{11}Rh_2$
$D_{calc.}$/ g cm^{-3}	1.233
/mm^{-1}	0.368
Formula Weight	1985.97
Colour	greenish blue
Shape	plate
Size/mm^3	0.55×0.48×0.20
T/K	100(2)
Crystal System	monoclinic
Flack Parameter	0.11(3)
Hooft Parameter	0.13(2)
Space Group	$P2_1$
a/Å	11.764(3)
b/Å	17.436(4)
c/Å	26.079(7)
/°	90
/°	91.389(6)
/°	90
V/Å^3	5347(2)
Z	2
Z'	1
Wavelength/Å	0.710730
Radiation type	MoK
$_{min}$/°	1.562
$_{max}$/°	24.713
Measured Refl.	19801
Independent Refl.	15161
Reflections with I > 2σ(I)	10889
R_{int}	0.0531
Parameters	1240
Restraints	1416
Largest Peak	1.398
Deepest Hole	-1.430
GooF	1.104
wR_2 (all data)	0.2181
wR_2	0.1964
R_1 (all data)	0.1395
R_1	0.0987

Structure Quality Indicators

Reflections: d min (Mo) 0.85 | I/σ 6.5 | Rint 5.31%

Refinement: Shift -0.003 | Max Peak 1.4 | Min Peak -1.4 | GooF 1.104 | 0.11(3)

A greenish blue plate-shaped crystal with dimensions 0.55×0.48×0.20 mm^3 was mounted on a loop with paratone oil. Data were collected using an Bruker D8 diffractometer with APEX2 detector diffractometer equipped with a Oxford Cryosystems low-temperature device, operating at T = 100(2) K. Data were measured using and scans with a narrow frame width of 0.50° per frame for 10.00 s using MoK radiation (fine-focus sealed tube, 45 kV, 35 mA).The total number of runs and images was based on the strategy calculation from the program **APEX2** (Bruker). The maximum resolution that was achieved was = 24.713°.

The diffraction patterns were indexed using **SAINT** (Bruker, V8.34A, 2013) and the unit cells were refined using **SAINT** (Bruker, V8.34A, 2013) on 9996 reflections, 50 % of the observed reflections. Data reduction, scaling and absorption corrections were performed using **SAINT** (Bruker, V8.34A, 2013) and **SADABS-2014/5** (Bruker, 2014) was used for absorption correction. The value of wR_2(int) was 0.0922 before and 0.0599 after correction. The ratio of minimum to maximum transmission is 0.8066. The /2 correction factor is 0.00150. The final completeness is 96.7% out to 24.713° in . The absorption coefficient of this material is 0.368 mm^{-1} at this wavelength (= 0.71073 Å) and the minimum and maximum transmissions are 0.6011 and 0.7452.

The structure was solved and the space group P2$_1$ (# 4) determined by the Superflip (Palatinus & Chapuis, 2007;Palatinus & van der Lee, 2008;Palatinus et al., 2012) structure solution program using Charge Flipping and refined by Least Squares using version 2014/7 of **XL** (Sheldrick, 2008). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

Images of the Crystal on the Diffractometer

Figure S3

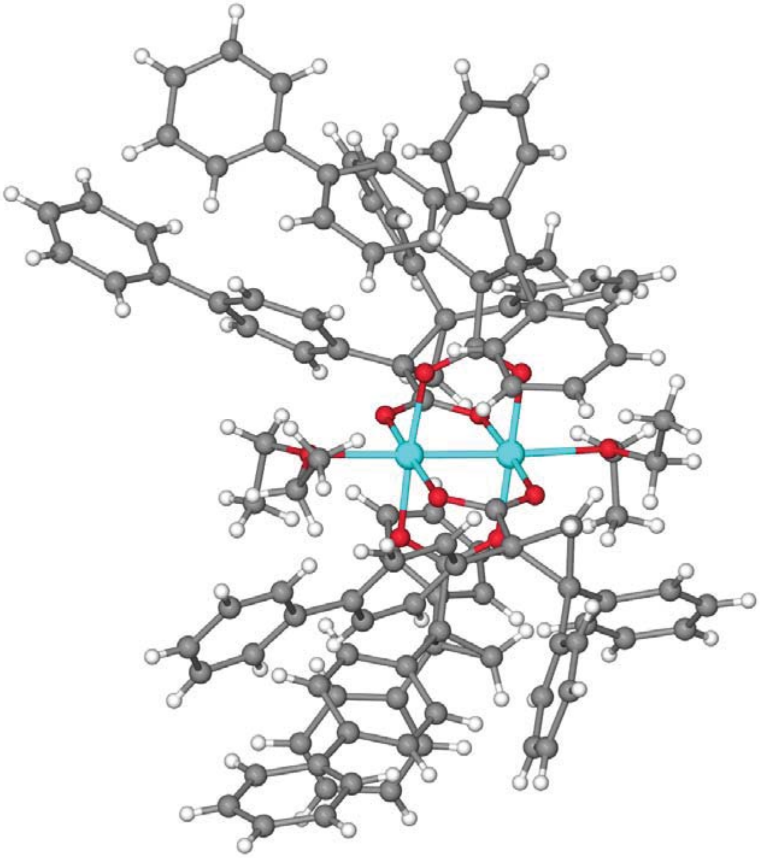


Figure S4

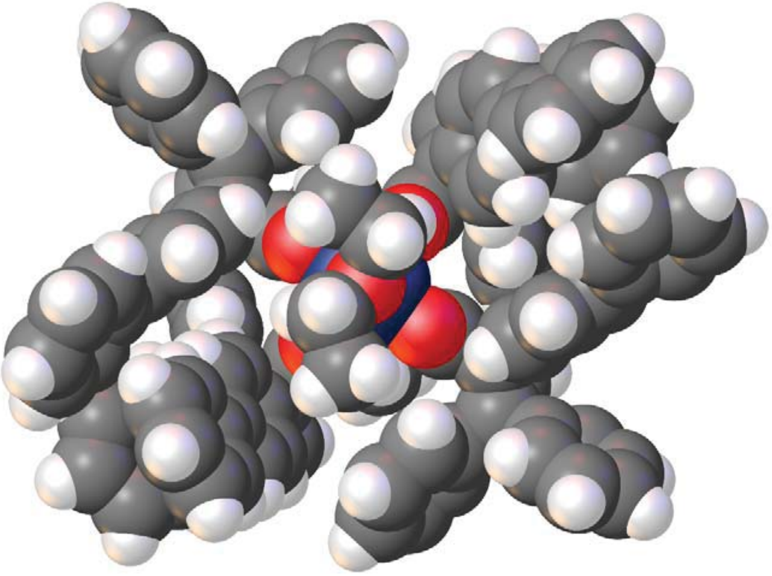


Figure S5

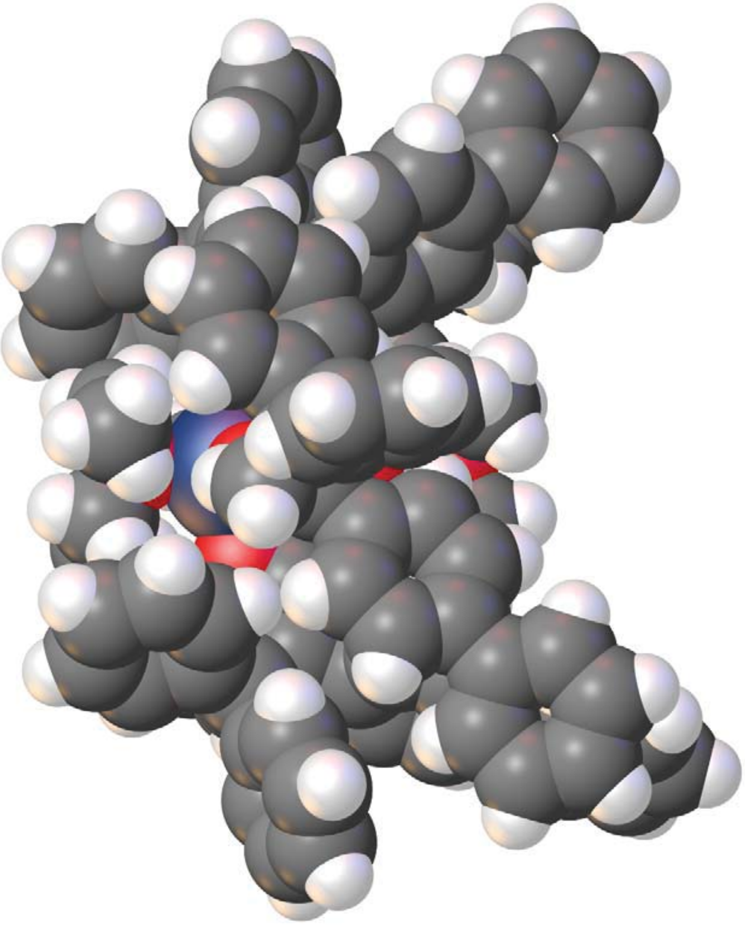


Figure S6

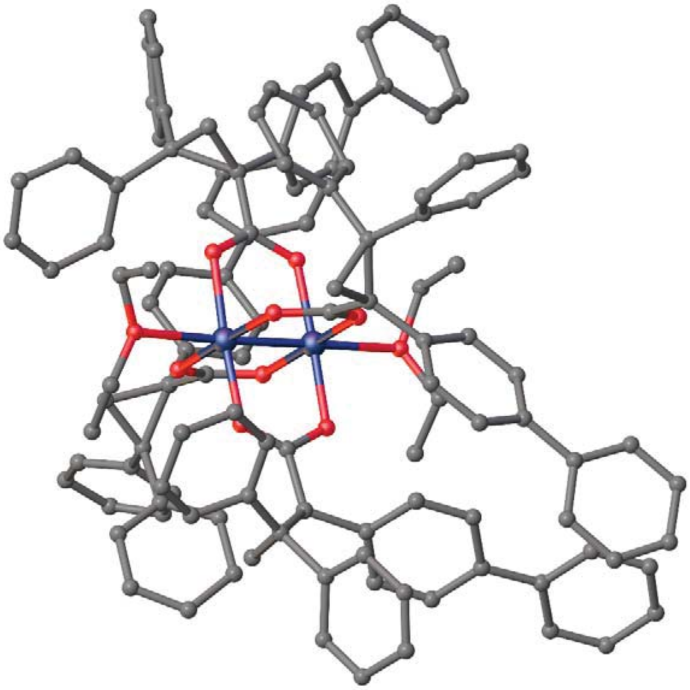


Figure S7

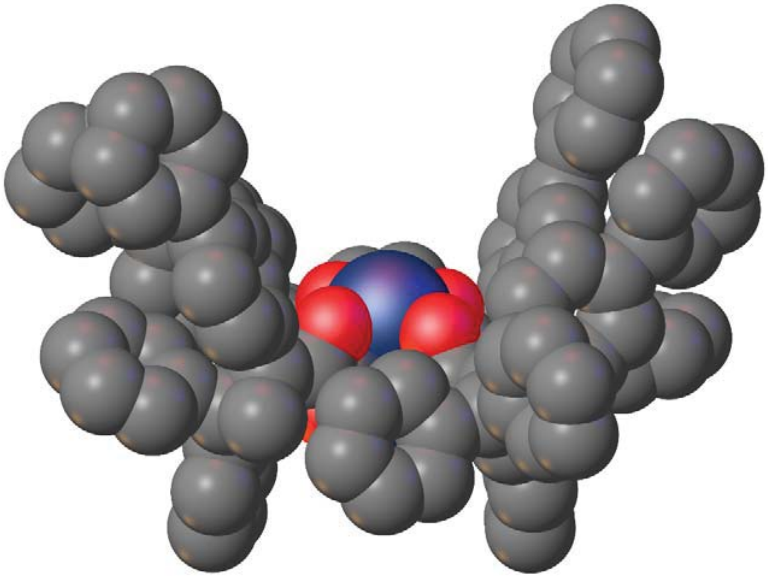


Figure S8

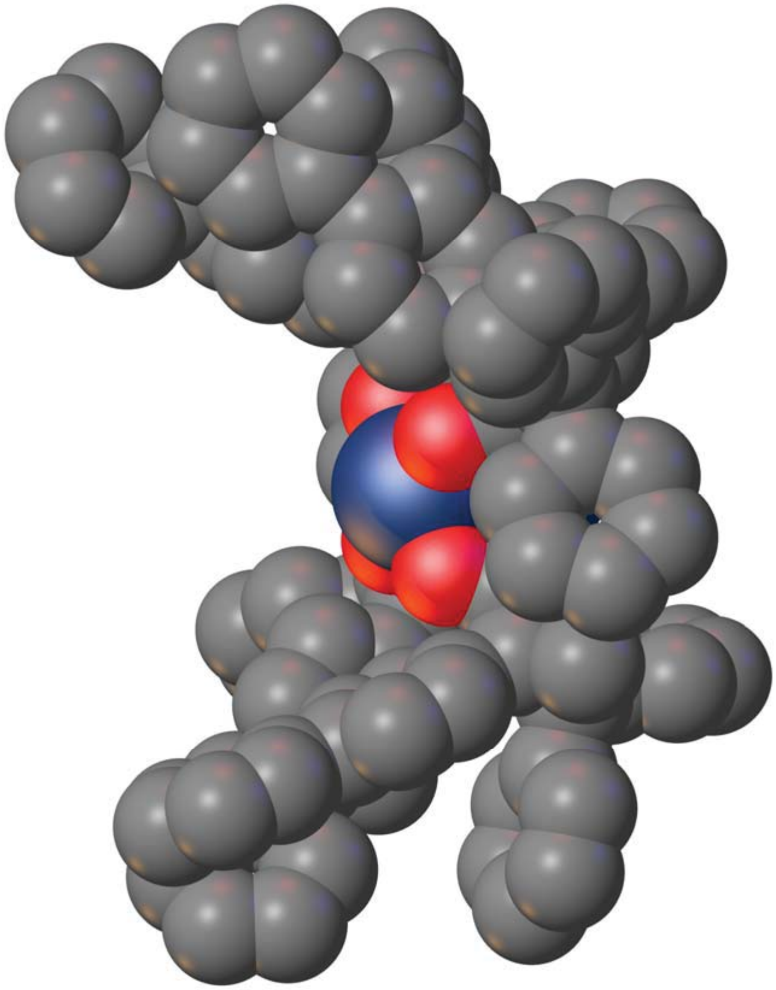


Figure S9

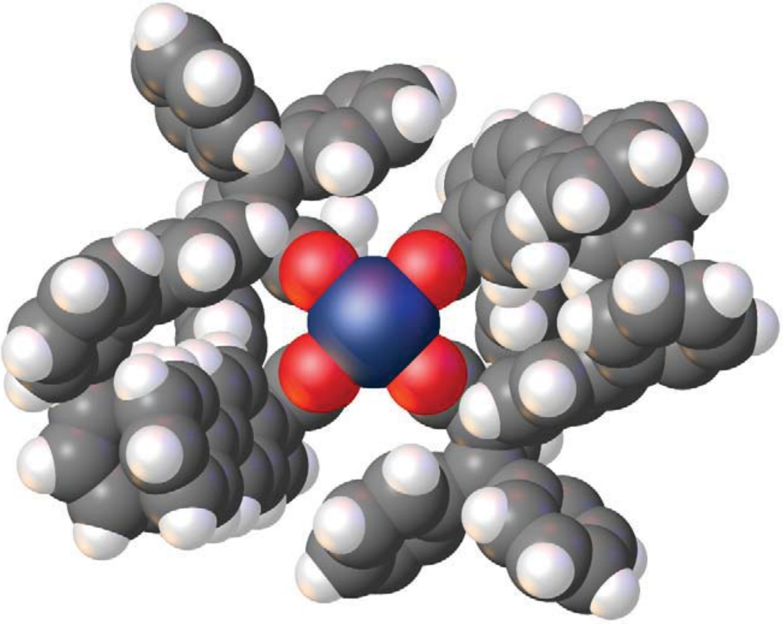


Figure S10

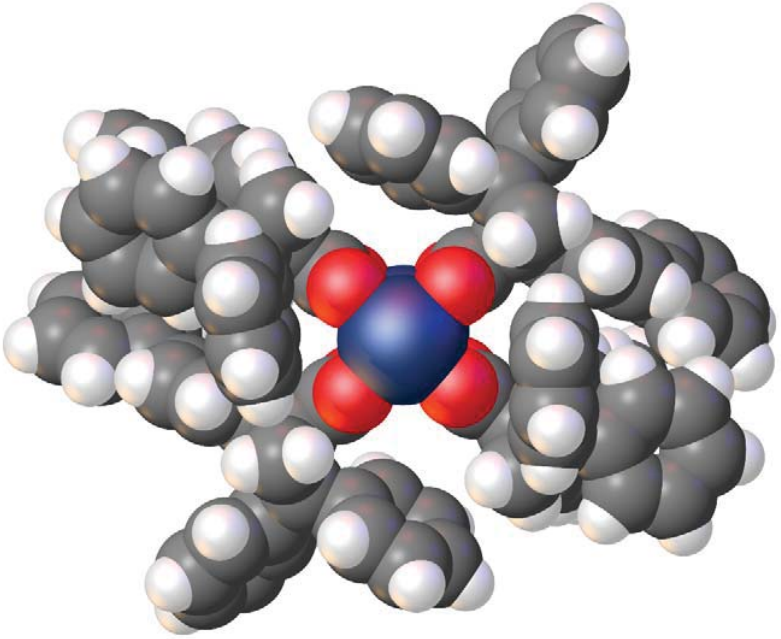


Figure S11

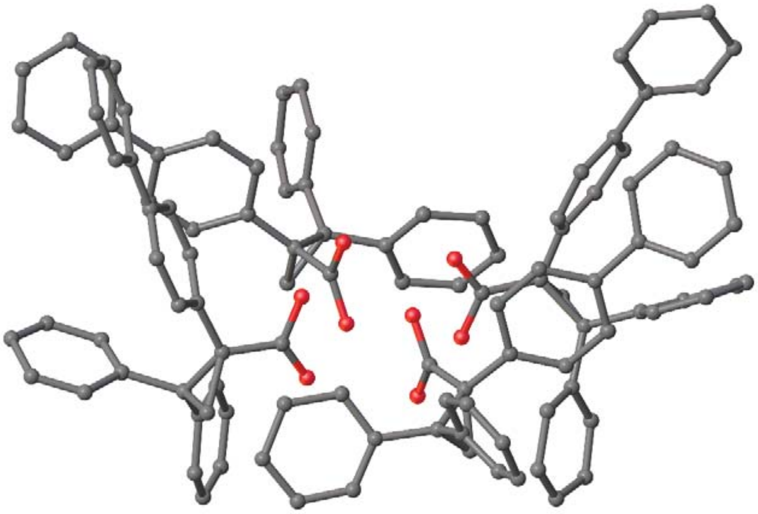


Figure S12

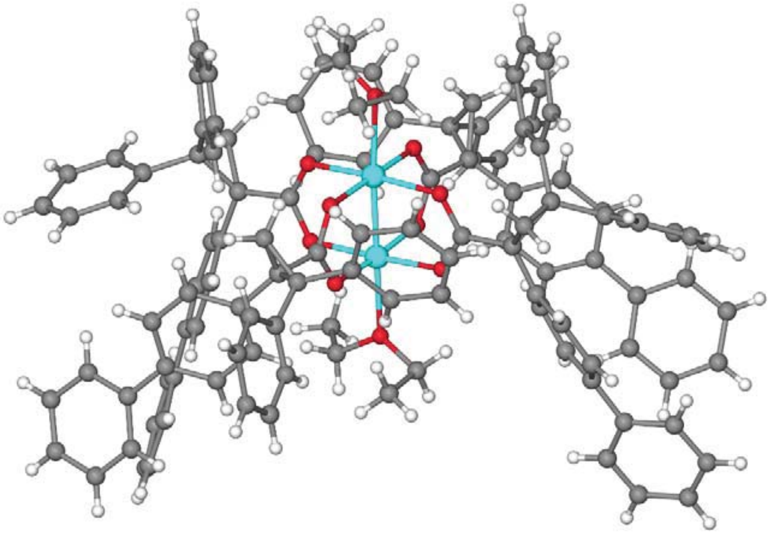


Figure S13

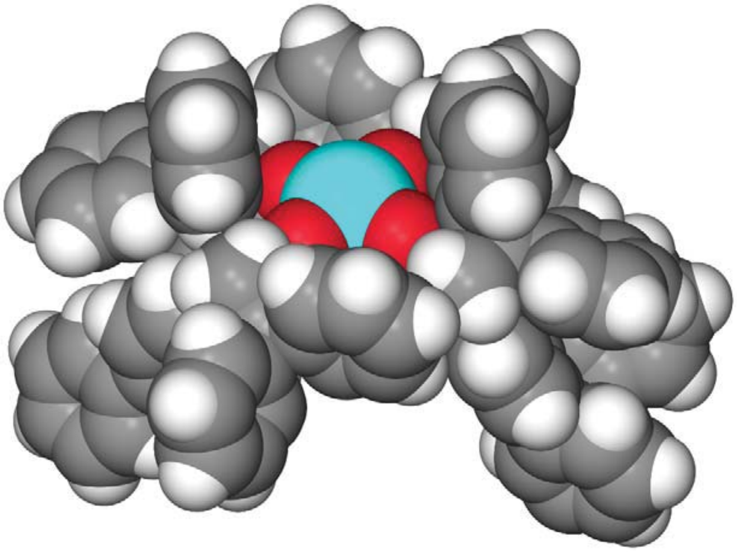


Figure S14

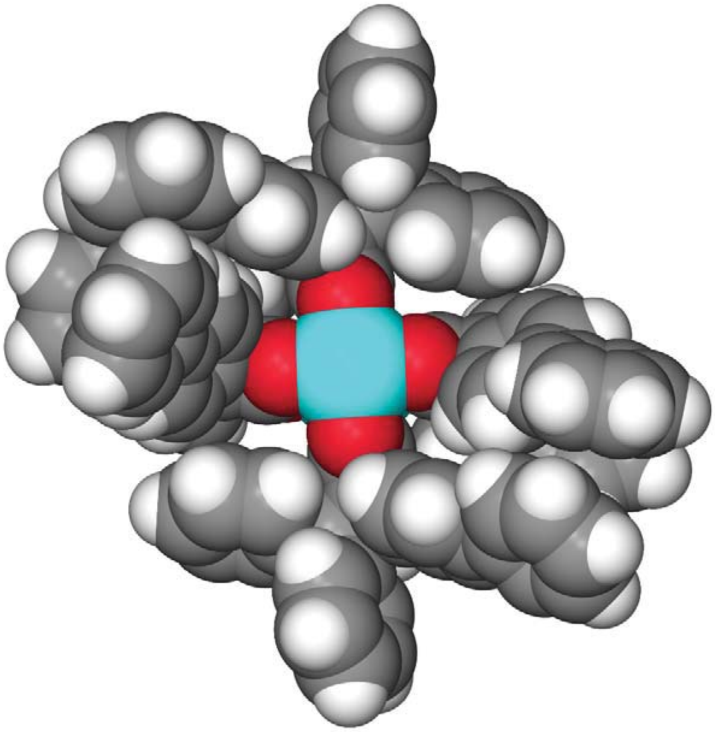
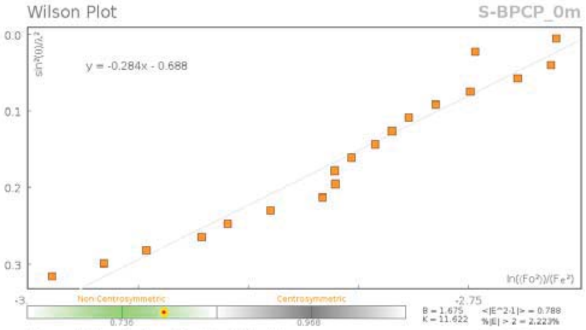
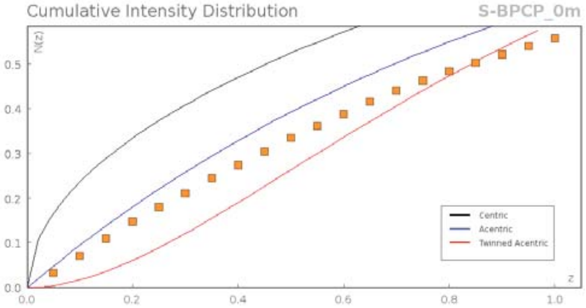


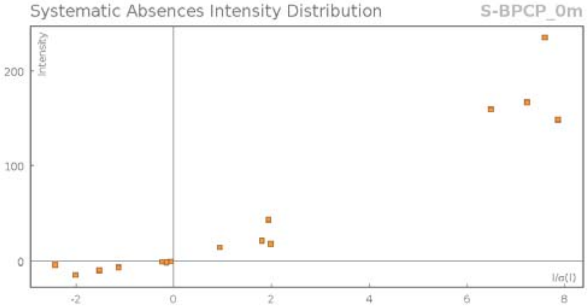
Figure S15

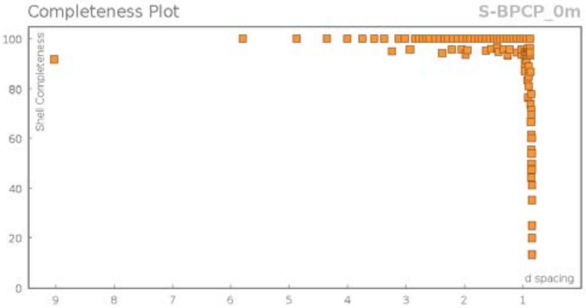
There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

Data Plots: Diffraction Data









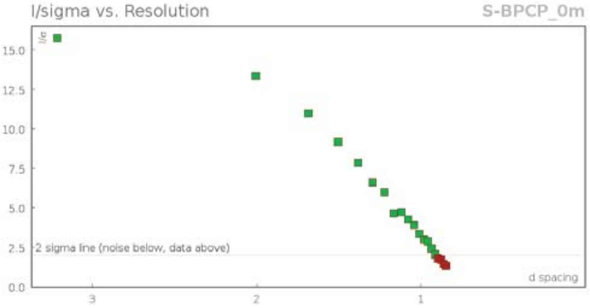


Figure S16

Data Plots: Refinement and Data

Figure S17

Reflection Statistics

Total reflections (after filtering)	19868	Unique reflections	15161
Completeness	0.832	Mean I/	6.51
hkl$_{\text{max}}$ collected	(13, 19, 30)	hkl$_{\text{min}}$ collected	(-13, -20, -15)
hkl$_{\text{max}}$ used	(13, 19, 30)	hkl$_{\text{min}}$ used	(-13, -19, 0)
Lim d$_{\text{max}}$ collected	20.0	Lim d$_{\text{min}}$ collected	0.85
d$_{\text{max}}$ used	17.44	d$_{\text{min}}$ used	0.85
Friedel pairs	2083	Friedel pairs merged	0
Inconsistent equivalents	0	R$_{\text{int}}$	0.0531
R$_{\text{sigma}}$	0.1312	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	52
Multiplicity	(12929, 3544, 14)	Maximum multiplicity	6
Removed systematic absences	15	Filtered off (Shel/OMIT)	191

Table S2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **S-BPCP_0m**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Rh1	-1872.5(12)	-5339(2)	-2345.7(5)	24.5(3)
Rh2	-3534.2(11)	-4589(2)	-2567.9(5)	22.3(3)
O1	-5145(9)	-3813(7)	-2756(4)	23(2)
O2	-3228(8)	-4799(7)	-3338(4)	19(2)
O3	-1673(9)	-5541(7)	-3123(4)	20(2)
O4	-4477(8)	-5597(6)	-2581(4)	16(2)
O5	-2890(9)	-6303(7)	-2354(4)	21(2)
O6	-3787(9)	-4428(7)	-1775(4)	22(2)
O7	-2174(10)	-5129(7)	-1577(4)	28(2)
O8	-2521(9)	-3630(7)	-2567(4)	17.1(19)
O9	-905(8)	-4330(6)	-2365(4)	17(2)
O10	-209(9)	-6051(7)	-2135(4)	18(2)
C1	-6040(16)	-3825(12)	-2362(8)	50(4)
C2	-6754(17)	-4508(14)	-2520(11)	81(8)
C3	-5293(15)	-3598(12)	-3275(7)	43(4)
C4	-4425(16)	-3056(13)	-3490(8)	53(6)
C5	-2384(12)	-5245(11)	-3450(6)	18(2)
C6	-2213(13)	-5484(10)	-4009(6)	20(2)
C7	-3217(13)	-5501(11)	-4416(6)	24(2)
C8	-2354(14)	-4820(10)	-4421(6)	25(3)
C9	-4449(13)	-5362(12)	-4272(6)	23(3)
C10	-5053(13)	-4778(11)	-4560(7)	28(4)
C11	-6206(13)	-4671(12)	-4479(7)	32(4)
C12	-6792(15)	-5115(10)	-4133(7)	35(4)
C13	-6176(14)	-5676(11)	-3853(7)	31(4)
C14	-5041(14)	-5800(11)	-3919(7)	27(4)
C15	-3079(14)	-6120(11)	-4849(7)	30(3)
C16	-3556(16)	-6845(12)	-4791(8)	36(4)
C17	-3455(18)	-7419(14)	-5176(8)	49(5)
C18	-2861(18)	-7292(14)	-5607(9)	49(5)
C19	-2394(17)	-6528(13)	-5691(8)	45(4)
C20	-2490(15)	-5976(12)	-5317(7)	36(4)
C21	-1237(10)	-6078(7)	-4077(6)	22(3)
C22	-1343(10)	-6816(7)	-3858(7)	30(4)
C23	-464(10)	-7354(7)	-3891(6)	28(3)
C24	555(9)	-7196(6)	-4139(6)	28(3)
C25	663(11)	-6464(7)	-4361(7)	40(4)
C26	-210(11)	-5915(7)	-4332(6)	32(4)
C27	1511(9)	-7774(6)	-4154(6)	31(3)
C28	1383(13)	-8526(8)	-3947(10)	74(8)
C29	2280(14)	-9063(9)	-3940(10)	76(8)
C30	3305(12)	-8867(8)	-4170(7)	45(5)
C31	3455(11)	-8133(8)	-4395(8)	46(5)
C32	2561(11)	-7602(8)	-4394(7)	41(4)
C33	-3948(14)	-6231(10)	-2505(6)	16(2)
C34	-4609(14)	-6994(11)	-2598(7)	23(2)
C35	-5467(15)	-7215(11)	-2189(7)	30(2)
C36	-5877(14)	-6916(11)	-2706(6)	27(3)
C37	-5740(14)	-8044(12)	-2057(7)	40(3)
C38	-6838(19)	-8396(14)	-2119(9)	60(6)
C39	-7080(30)	-9119(15)	-1947(11)	85(9)

Atom	x	y	z	U_{eq}
C40	-6270(20)	-9563(17)	-1687(10)	77(7)
C41	-5170(20)	-9277(13)	-1634(8)	56(5)
C42	-4882(19)	-8514(12)	-1812(7)	45(4)
C43	-5707(16)	-6685(11)	-1716(7)	32(3)
C44	-6749(17)	-6337(12)	-1640(7)	39(4)
C45	-6961(19)	-5944(14)	-1182(8)	53(5)
C46	-6175(18)	-5893(13)	-783(8)	46(5)
C47	-5152(19)	-6230(14)	-856(8)	48(5)
C48	-4858(18)	-6623(13)	-1326(8)	47(5)
C49	-3911(11)	-7609(9)	-2888(5)	28(3)
C50	-2892(12)	-7923(9)	-2679(5)	32(4)
C51	-2245(11)	-8439(9)	-2961(5)	29(4)
C52	-2583(10)	-8691(8)	-3453(4)	32(4)
C53	-3610(11)	-8393(9)	-3659(5)	32(4)
C54	-4266(11)	-7866(9)	-3383(5)	29(4)
C55	-1858(11)	-9229(8)	-3759(4)	34(4)
C56	-1810(14)	-9168(9)	-4304(5)	39(4)
C57	-1173(14)	-9683(10)	-4599(5)	49(5)
C58	-529(13)	-10252(9)	-4347(6)	45(4)
C59	-522(14)	-10317(10)	-3804(6)	48(4)
C60	-1178(13)	-9810(9)	-3517(5)	43(4)
C61	-3003(14)	-4679(12)	-1465(6)	27(3)
C62	-3136(15)	-4490(13)	-895(7)	34(3)
C63	-3657(17)	-3694(12)	-718(7)	36(3)
C64	-4306(15)	-4403(11)	-664(7)	36(3)
C65	-3105(17)	-3351(12)	-225(7)	38(3)
C66	-3650(20)	-3332(13)	255(8)	49(5)
C67	-3080(20)	-3025(14)	694(8)	53(5)
C68	-2030(20)	-2733(14)	667(8)	52(6)
C69	-1510(20)	-2695(16)	201(8)	65(8)
C70	-2007(18)	-3008(14)	-251(8)	52(6)
C71	-4100(15)	-3078(11)	-1098(7)	32(3)
C72	-3462(17)	-2745(12)	-1495(7)	40(4)
C73	-3988(17)	-2159(13)	-1803(9)	48(5)
C74	-5038(17)	-1886(14)	-1694(9)	51(5)
C75	-5671(19)	-2179(15)	-1286(9)	63(7)
C76	-5200(20)	-2762(15)	-990(10)	61(7)
C77	-2199(11)	-4775(11)	-529(5)	42(4)
C78	-2428(10)	-5116(12)	-50(6)	55(6)
C79	-1546(10)	-5273(15)	304(5)	62(6)
C80	-397(10)	-5189(12)	182(5)	68(6)
C81	-160(11)	-4891(12)	-306(5)	52(6)
C82	-1039(11)	-4657(14)	-647(5)	49(5)
C83	545(11)	-5337(12)	575(5)	72(5)
C84	492(16)	-5032(16)	1081(6)	92(9)
C85	1392(17)	-5123(16)	1443(6)	95(9)
C86	2357(15)	-5539(14)	1303(7)	81(7)
C87	2439(14)	-5857(15)	804(7)	82(7)
C88	1545(13)	-5753(12)	446(6)	67(6)
C89	-1497(13)	-3729(10)	-2440(6)	15(2)
C90	-792(14)	-2943(11)	-2344(7)	24(2)
C91	-355(14)	-2493(11)	-2821(7)	31(3)
C92	-1406(14)	-2238(11)	-2545(7)	28(3)
C93	714(16)	-2004(13)	-2765(7)	39(4)

Atom	x	y	z	U_{eq}
C94	680(20)	-1229(15)	-2671(12)	86(9)
C95	1570(20)	-746(18)	-2651(13)	97(10)
C96	2660(20)	-1084(16)	-2681(10)	67(6)
C97	2760(20)	-1807(17)	-2805(12)	80(8)
C98	1782(18)	-2281(16)	-2847(10)	70(7)
C99	-451(14)	-2823(11)	-3371(7)	29(3)
C100	114(17)	-3512(13)	-3492(8)	41(4)
C101	134(18)	-3754(13)	-4022(8)	44(5)
C102	-383(17)	-3316(12)	-4415(8)	39(4)
C103	-1004(17)	-2662(12)	-4289(8)	42(5)
C104	-1038(16)	-2440(12)	-3778(7)	37(4)
C105	-56(12)	-2918(9)	-1863(5)	30(3)
C106	840(13)	-3452(10)	-1794(5)	42(5)
C107	1497(13)	-3463(10)	-1339(5)	43(5)
C108	1285(12)	-2970(8)	-927(5)	38(4)
C109	409(13)	-2426(9)	-998(5)	43(5)
C110	-281(12)	-2419(9)	-1447(5)	35(4)
C111	1948(13)	-3025(7)	-425(5)	44(4)
C112	2075(18)	-2375(8)	-95(6)	60(6)
C113	2690(20)	-2416(9)	376(6)	70(7)
C114	3174(18)	-3117(9)	526(6)	61(6)
C115	3031(18)	-3784(9)	219(6)	65(6)
C116	2455(16)	-3729(8)	-256(6)	52(5)
C117	304(16)	-6509(11)	-2532(7)	39(4)
C118	962(15)	-5992(13)	-2882(7)	50(5)
C119	-102(16)	-6300(12)	-1590(8)	47(4)
C120	-889(19)	-6972(14)	-1512(10)	72(7)
O12	-3829(13)	-905(10)	-3699(6)	61(5)
C1A	-4258(19)	-846(15)	-4216(8)	57(7)
C1B	-3588(18)	-1304(14)	-4579(9)	56(7)
C1C	-4460(20)	-504(14)	-3325(9)	60(7)
C9BA	-3920(30)	-538(17)	-2803(9)	90(10)

Table S3 Anisotropic Displacement Parameters (×10^4) **S-BPCP_0m**. The anisotropic displacement factor exponent takes the form: $-2\ \ ^{2}[h^2a^{*2} \times U_{11} + \ldots + 2hka^{*} \times b^{*} \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh1	20.6(7)	21.3(8)	31.3(7)	-3.6(7)	-4.8(6)	5.9(7)
Rh2	13.6(6)	18.7(8)	34.4(8)	-1.5(7)	-5.2(5)	-0.9(6)
O1	15(3)	24(3)	30(3)	2(2)	-1(2)	3(2)
O2	17(3)	18(3)	23(3)	0(2)	-3.1(19)	0(2)
O3	16(4)	18(5)	26(3)	0(3)	-7(3)	-1(3)
O4	11(4)	14(3)	21(5)	2(3)	-6(3)	-1(2)
O5	19(3)	20(4)	22(5)	0(3)	-8(3)	4(3)
O6	20(4)	12(5)	31(3)	0(3)	-7(3)	-2(3)
O7	30(4)	20(5)	32(4)	-2(3)	-8(3)	6(4)
O8	12(2)	18(3)	21(3)	-1(2)	-3.9(19)	2.6(18)
O9	11(3)	14(3)	27(4)	-3(2)	-7(3)	3(2)
O10	14(3)	19(3)	23(3)	1(2)	0(2)	3(2)
C1	36(6)	54(10)	62(7)	22(7)	18(6)	17(6)
C2	40(9)	64(11)	142(18)	-3(12)	34(11)	3(9)
C3	29(7)	60(11)	40(5)	11(5)	-1(4)	6(7)
C4	40(10)	67(13)	54(10)	20(9)	4(8)	0(10)
C5	15(3)	17(3)	21(3)	1(2)	-2.4(18)	-1(2)
C6	17(3)	20(3)	22(3)	-1(2)	-1.3(19)	-2(2)

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
C7	20(3)	24(5)	27(4)	-1(3)	-7(3)	-2(3)
C8	25(5)	24(5)	27(5)	0(4)	-7(4)	-6(4)
C9	19(3)	21(6)	28(6)	-4(5)	-7(3)	-4(3)
C10	20(4)	25(7)	39(7)	1(6)	-10(4)	-4(4)
C11	21(5)	29(8)	44(8)	5(7)	-10(4)	-2(5)
C12	20(5)	30(8)	54(9)	10(7)	-6(5)	2(5)
C13	21(5)	25(7)	46(8)	4(6)	-4(4)	1(4)
C14	20(4)	24(7)	37(7)	4(6)	-4(4)	1(4)
C15	19(6)	33(5)	37(5)	-10(4)	-8(4)	-1(4)
C16	28(8)	34(6)	44(7)	-12(5)	-3(6)	-4(5)
C17	52(11)	43(7)	53(8)	-20(6)	4(7)	-8(6)
C18	43(10)	52(8)	51(8)	-19(6)	0(7)	-8(7)
C19	39(10)	51(8)	46(6)	-19(6)	0(6)	-6(7)
C20	25(8)	44(7)	39(5)	-13(5)	-4(5)	-5(6)
C21	20(4)	22(4)	25(6)	-4(4)	-3(4)	-1(3)
C22	18(5)	24(5)	47(9)	5(5)	1(5)	-1(4)
C23	18(5)	26(6)	40(8)	-3(5)	-6(5)	0(4)
C24	20(5)	25(5)	39(8)	-9(5)	-6(5)	-4(4)
C25	25(5)	30(6)	65(11)	2(6)	10(6)	1(4)
C26	26(5)	27(6)	44(9)	0(6)	8(5)	0(4)
C27	23(5)	28(6)	43(9)	-9(5)	-5(5)	-2(4)
C28	42(7)	41(7)	140(20)	27(9)	33(10)	13(5)
C29	44(7)	44(8)	140(20)	25(10)	31(10)	17(6)
C30	32(7)	40(7)	64(12)	-7(7)	-2(7)	2(5)
C31	29(6)	41(7)	67(12)	-6(7)	-2(6)	0(5)
C32	27(5)	39(7)	56(10)	-3(7)	0(6)	-1(5)
C33	17(3)	17(3)	13(3)	1(2)	-2(2)	1.8(19)
C34	23(4)	18(4)	27(5)	1(3)	-3(3)	1(3)
C35	33(5)	28(5)	30(4)	-3(3)	1(3)	-5(4)
C36	24(4)	29(7)	29(5)	-5(4)	2(4)	1(4)
C37	59(7)	28(5)	34(7)	-3(4)	1(5)	-8(4)
C38	63(7)	41(7)	74(15)	11(8)	-11(7)	-15(5)
C39	85(9)	49(8)	120(20)	29(11)	-21(10)	-22(7)
C40	86(9)	50(8)	94(17)	20(10)	-11(9)	-13(7)
C41	81(9)	35(7)	52(12)	1(7)	-2(8)	-4(6)
C42	63(7)	33(6)	39(10)	-3(6)	-1(6)	0(5)
C43	39(6)	27(7)	31(5)	-3(4)	6(4)	-11(5)
C44	40(6)	38(10)	39(7)	-4(6)	8(5)	-6(6)
C45	53(7)	61(12)	45(7)	-15(8)	9(5)	-2(7)
C46	52(7)	44(11)	42(7)	-6(7)	11(5)	-9(7)
C47	53(7)	51(13)	39(6)	-13(7)	6(5)	-6(7)
C48	45(6)	59(12)	38(6)	-15(7)	1(5)	-3(7)
C49	27(5)	23(6)	35(5)	-2(4)	0(4)	2(4)
C50	28(6)	26(8)	42(6)	1(5)	-2(5)	5(6)
C51	25(6)	19(7)	44(6)	3(5)	1(4)	0(5)
C52	22(5)	29(7)	45(5)	-2(5)	2(4)	-1(5)
C53	24(6)	32(8)	40(6)	-8(6)	1(5)	3(6)
C54	25(6)	27(8)	36(5)	-2(5)	1(4)	4(6)
C55	21(6)	30(7)	53(6)	-6(5)	5(4)	-3(5)
C56	31(8)	35(8)	52(6)	-7(5)	5(5)	-5(7)
C57	41(9)	48(9)	60(6)	-10(6)	7(5)	4(8)
C58	27(8)	42(9)	67(7)	-6(6)	11(6)	-4(7)
C59	33(8)	43(8)	67(7)	-5(6)	10(6)	6(8)
C60	31(8)	38(8)	60(7)	0(5)	8(5)	4(7)
C61	27(5)	19(7)	33(4)	-2(3)	-8(3)	3(5)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C62	39(5)	31(6)	32(4)	-5(3)	-7(3)	4(4)
C63	38(5)	32(5)	38(5)	-4(3)	-3(4)	3(4)
C64	39(5)	29(6)	40(6)	-2(5)	-4(4)	3(4)
C65	41(6)	33(7)	39(5)	-4(4)	-5(4)	3(5)
C66	60(8)	44(13)	45(5)	-10(6)	6(5)	-6(8)
C67	69(9)	48(14)	43(6)	-7(6)	5(5)	-12(9)
C68	69(9)	48(14)	39(7)	-4(7)	3(6)	-12(9)
C69	64(9)	94(18)	38(6)	-12(8)	-1(6)	-34(11)
C70	50(7)	68(14)	37(6)	-9(7)	0(5)	-15(8)
C71	31(6)	29(6)	36(6)	-4(5)	-6(4)	-4(5)
C72	37(6)	40(8)	43(7)	1(6)	-1(5)	0(6)
C73	38(7)	52(10)	55(8)	15(8)	5(6)	4(7)
C74	37(7)	57(10)	58(10)	13(8)	4(6)	4(7)
C75	42(7)	73(12)	74(11)	31(10)	15(7)	19(8)
C76	47(7)	69(12)	69(11)	25(10)	13(7)	19(8)
C77	48(5)	45(9)	31(5)	-9(5)	-10(4)	12(5)
C78	49(6)	75(15)	39(6)	5(8)	-14(5)	4(6)
C79	49(6)	94(17)	43(6)	14(9)	-15(5)	1(7)
C80	48(6)	105(16)	50(6)	18(8)	-15(5)	0(6)
C81	47(6)	64(15)	44(6)	3(8)	-13(5)	6(6)
C82	48(5)	64(13)	35(6)	-4(8)	-11(4)	10(6)
C83	55(6)	96(14)	63(7)	22(7)	-25(5)	-5(8)
C84	76(10)	130(20)	68(7)	9(10)	-31(7)	10(12)
C85	80(11)	120(20)	79(9)	14(10)	-38(8)	4(12)
C86	69(10)	88(19)	85(10)	23(9)	-32(8)	-15(10)
C87	59(8)	99(18)	87(10)	18(10)	-34(8)	-7(10)
C88	47(7)	76(14)	76(9)	21(8)	-22(6)	-17(8)
C89	11(3)	18(3)	16(3)	-1(2)	-2(2)	2.5(18)
C90	15(4)	21(4)	35(4)	-2(3)	-4(3)	-2(3)
C91	25(5)	32(5)	37(4)	0(3)	-6(3)	-9(4)
C92	21(5)	23(5)	40(6)	1(4)	-6(4)	-7(4)
C93	31(5)	51(7)	35(8)	-3(6)	-3(4)	-22(4)
C94	44(7)	56(7)	160(30)	-28(8)	6(8)	-22(5)
C95	50(7)	67(8)	170(30)	-25(9)	3(10)	-30(6)
C96	49(7)	71(9)	79(17)	-12(10)	-4(8)	-27(6)
C97	36(6)	74(10)	130(20)	-22(11)	2(7)	-27(6)
C98	31(5)	65(8)	110(20)	-23(9)	2(6)	-20(5)
C99	19(6)	30(6)	36(4)	1(4)	-5(4)	-11(5)
C100	45(10)	41(7)	37(6)	-2(5)	-10(5)	5(7)
C101	54(11)	40(8)	37(6)	-1(5)	-9(5)	1(8)
C102	43(10)	36(8)	38(6)	0(5)	-11(5)	-7(7)
C103	49(10)	36(8)	39(6)	0(5)	-11(5)	-5(7)
C104	36(8)	35(8)	39(5)	0(5)	-11(5)	-4(7)
C105	19(5)	35(6)	35(5)	-1(4)	-5(4)	-6(5)
C106	29(7)	52(9)	43(6)	-8(6)	-13(5)	8(7)
C107	30(7)	55(9)	44(6)	-2(6)	-13(5)	0(7)
C108	23(7)	49(8)	42(5)	-1(5)	-7(5)	-10(6)
C109	32(7)	53(9)	42(6)	-6(6)	-10(5)	-4(7)
C110	22(7)	44(8)	39(5)	-7(5)	-4(5)	-3(6)
C111	28(8)	62(7)	42(6)	0(5)	-9(5)	-9(6)
C112	65(13)	65(8)	50(8)	-4(6)	-18(8)	-6(7)
C113	80(15)	74(9)	55(8)	-5(7)	-28(9)	-8(8)
C114	61(13)	74(9)	48(8)	0(7)	-14(8)	-12(8)
C115	65(13)	74(9)	54(8)	-1(6)	-28(9)	-3(8)
C116	44(11)	64(8)	49(8)	-2(5)	-17(7)	-3(6)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C117	38(5)	43(5)	36(5)	-4(4)	7(4)	12(4)
C118	25(8)	82(11)	43(8)	17(7)	1(6)	10(8)
C119	38(9)	71(10)	33(5)	14(5)	9(4)	24(7)
C120	53(12)	90(12)	73(12)	41(10)	2(10)	4(11)
O12	55(10)	78(13)	49(10)	6(9)	-10(8)	3(9)
C1A	46(13)	79(19)	45(14)	-12(13)	3(11)	-6(13)
C1B	41(13)	63(17)	64(16)	16(13)	-7(12)	-1(12)
C1C	67(16)	46(17)	67(16)	0(13)	13(13)	-2(13)
C9BA	130(30)	80(20)	61(17)	14(16)	31(17)	-30(20)

Table S4 Bond Lengths in Å for **S-BPCP_0m**.

Atom	Atom	Length/Å
Rh1	Rh2	2.4106(19)
Rh1	O3	2.076(11)
Rh1	O5	2.063(12)
Rh1	O7	2.076(12)
Rh1	O9	2.096(11)
Rh1	O10	2.371(10)
Rh2	O1	2.369(11)
Rh2	O2	2.082(11)
Rh2	O4	2.078(10)
Rh2	O6	2.114(11)
Rh2	O8	2.054(11)
O1	C1	1.49(2)
O1	C3	1.41(2)
O2	C5	1.300(19)
O3	C5	1.287(17)
O4	C33	1.282(19)
O5	C33	1.304(18)
O6	C61	1.289(18)
O7	C61	1.29(2)
O8	C89	1.254(18)
O9	C89	1.271(19)
O10	C117	1.45(2)
O10	C119	1.49(2)
C1	C2	1.509(11)
C3	C4	1.510(11)
C5	C6	1.54(2)
C6	C7	1.57(2)
C6	C8	1.58(2)
C6	C21	1.559(19)
C7	C8	1.56(2)
C7	C9	1.53(2)
C7	C15	1.57(2)
C9	C10	1.44(2)
C9	C14	1.39(2)
C10	C11	1.39(2)
C11	C12	1.39(3)
C12	C13	1.41(2)
C13	C14	1.37(2)
C15	C16	1.39(3)
C15	C20	1.44(3)

Atom	Atom	Length/Å
C16	C17	1.42(3)
C17	C18	1.36(3)
C18	C19	1.46(3)
C19	C20	1.38(3)
C21	C22	1.415(13)
C21	C26	1.420(12)
C22	C23	1.400(12)
C23	C24	1.403(12)
C24	C25	1.409(12)
C24	C27	1.512(13)
C25	C26	1.408(12)
C27	C28	1.428(13)
C27	C32	1.429(13)
C28	C29	1.410(14)
C29	C30	1.402(16)
C30	C31	1.420(15)
C31	C32	1.401(13)
C33	C34	1.56(2)
C34	C35	1.53(3)
C34	C36	1.52(2)
C34	C49	1.56(2)
C35	C36	1.51(2)
C35	C37	1.52(3)
C35	C43	1.57(3)
C37	C38	1.437(18)
C37	C42	1.437(18)
C38	C39	1.37(3)
C39	C40	1.39(3)
C40	C41	1.39(3)
C41	C42	1.45(3)
C43	C44	1.39(3)
C43	C48	1.41(3)
C44	C45	1.40(3)
C45	C46	1.38(3)
C46	C47	1.36(3)
C47	C48	1.45(3)
C49	C50	1.415(13)
C49	C54	1.421(12)
C50	C51	1.400(12)
C51	C52	1.403(12)
C52	C53	1.409(12)
C52	C55	1.512(13)
C53	C54	1.408(12)
C55	C56	1.428(13)
C55	C60	1.429(13)
C56	C57	1.410(14)
C57	C58	1.402(15)
C58	C59	1.420(15)
C59	C60	1.401(13)
C61	C62	1.53(2)
C62	C63	1.59(3)
C62	C64	1.52(3)
C62	C77	1.523(19)
C63	C64	1.46(3)

Atom	Atom	Length/Å
C63	C65	1.55(3)
C63	C71	1.54(3)
C65	C66	1.42(3)
C65	C70	1.43(3)
C66	C67	1.42(3)
C67	C68	1.34(3)
C68	C69	1.38(3)
C69	C70	1.41(3)
C71	C72	1.42(3)
C71	C76	1.44(3)
C72	C73	1.43(3)
C73	C74	1.36(3)
C74	C75	1.41(3)
C75	C76	1.39(3)
C77	C78	1.415(13)
C77	C82	1.421(12)
C78	C79	1.400(12)
C79	C80	1.403(12)
C80	C81	1.409(12)
C80	C83	1.512(13)
C81	C82	1.408(12)
C83	C84	1.428(13)
C83	C88	1.429(13)
C84	C85	1.410(14)
C85	C86	1.402(15)
C86	C87	1.420(15)
C87	C88	1.401(13)
C89	C90	1.62(2)
C90	C91	1.57(3)
C90	C92	1.51(2)
C90	C105	1.508(19)
C91	C92	1.51(3)
C91	C93	1.52(2)
C91	C99	1.55(2)
C93	C94	1.37(3)
C93	C98	1.37(3)
C94	C95	1.35(3)
C95	C96	1.41(4)
C96	C97	1.31(4)
C97	C98	1.42(3)
C99	C100	1.41(3)
C99	C104	1.42(2)
C100	C101	1.45(3)
C101	C102	1.40(3)
C102	C103	1.40(3)
C103	C104	1.39(3)
C105	C106	1.415(13)
C105	C110	1.420(12)
C106	C107	1.400(12)
C107	C108	1.403(12)
C108	C109	1.409(12)
C108	C111	1.512(13)
C109	C110	1.408(12)
C111	C112	1.428(13)

Atom	Atom	Length/Å
C111	C116	1.429(13)
C112	C113	1.410(14)
C113	C114	1.402(15)
C114	C115	1.420(15)
C115	C116	1.401(13)
C117	C118	1.510(10)
C119	C120	1.510(11)
O12	C1A	1.43(2)
O12	C1C	1.43(3)
C1A	C1B	1.48(3)
C1C	C9BA	1.49(3)

Table S5 Bond Angles in ° for **S-BPCP_0m**.

Atom	Atom	Atom	Angle/°
O3	Rh1	Rh2	88.1(3)
O3	Rh1	O7	176.6(4)
O3	Rh1	O9	92.6(4)
O3	Rh1	O10	91.4(4)
O5	Rh1	Rh2	88.4(3)
O5	Rh1	O3	86.0(4)
O5	Rh1	O7	92.3(5)
O5	Rh1	O9	176.8(4)
O5	Rh1	O10	92.9(4)
O7	Rh1	Rh2	88.9(3)
O7	Rh1	O9	88.9(4)
O7	Rh1	O10	91.6(4)
O9	Rh1	Rh2	88.7(3)
O9	Rh1	O10	90.0(4)
O10	Rh1	Rh2	178.5(3)
O1	Rh2	Rh1	177.4(3)
O2	Rh2	Rh1	88.8(3)
O2	Rh2	O1	93.3(4)
O2	Rh2	O6	176.8(4)
O4	Rh2	Rh1	88.6(3)
O4	Rh2	O1	93.2(4)
O4	Rh2	O2	86.6(4)
O4	Rh2	O6	92.3(4)
O6	Rh2	Rh1	88.2(3)
O6	Rh2	O1	89.8(4)
O8	Rh2	Rh1	88.5(3)
O8	Rh2	O1	89.8(4)
O8	Rh2	O2	91.7(4)
O8	Rh2	O4	176.7(5)
O8	Rh2	O6	89.2(4)
C1	O1	Rh2	115.2(10)
C3	O1	Rh2	115.4(11)
C3	O1	C1	126.3(13)
C5	O2	Rh2	118.1(9)
C5	O3	Rh1	119.5(10)
C33	O4	Rh2	118.0(9)
C33	O5	Rh1	118.3(11)
C61	O6	Rh2	117.0(11)
C61	O7	Rh1	118.3(10)
C89	O8	Rh2	116.2(11)
C89	O9	Rh1	113.6(9)
C117	O10	Rh1	118.6(10)
C117	O10	C119	119.6(14)
C119	O10	Rh1	115.1(10)
O1	C1	C2	102.8(16)
O1	C3	C4	117.0(16)
O2	C5	C6	119.5(13)
O3	C5	O2	125.4(14)
O3	C5	C6	115.0(14)
C5	C6	C7	122.3(13)
C5	C6	C8	115.6(15)
C5	C6	C21	113.7(13)

Atom	Atom	Atom	Angle/°
C7	C6	C8	59.4(10)
C21	C6	C7	117.0(14)
C21	C6	C8	118.2(13)
C6	C7	C15	114.2(14)
C8	C7	C6	60.8(10)
C8	C7	C15	115.9(14)
C9	C7	C6	122.3(13)
C9	C7	C8	120.2(15)
C9	C7	C15	113.7(13)
C7	C8	C6	59.8(10)
C10	C9	C7	116.2(15)
C14	C9	C7	124.6(16)
C14	C9	C10	118.9(15)
C11	C10	C9	119.0(17)
C12	C11	C10	121.7(17)
C11	C12	C13	117.9(16)
C14	C13	C12	122.4(18)
C13	C14	C9	120.1(17)
C16	C15	C7	119.6(17)
C16	C15	C20	117.1(17)
C20	C15	C7	123.3(17)
C15	C16	C17	121(2)
C18	C17	C16	122(2)
C17	C18	C19	118(2)
C20	C19	C18	120(2)
C19	C20	C15	122(2)
C22	C21	C6	119.0(11)
C22	C21	C26	117.1(8)
C26	C21	C6	123.9(11)
C23	C22	C21	120.8(9)
C22	C23	C24	122.5(9)
C23	C24	C25	117.0(9)
C23	C24	C27	121.8(7)
C25	C24	C27	121.2(7)
C26	C25	C24	121.4(9)
C25	C26	C21	121.3(9)
C28	C27	C24	121.1(7)
C28	C27	C32	117.3(9)
C32	C27	C24	121.6(7)
C29	C28	C27	121.9(11)
C30	C29	C28	118.9(11)
C29	C30	C31	120.9(10)
C32	C31	C30	119.5(11)
C31	C32	C27	121.3(11)
O4	C33	O5	125.9(15)
O4	C33	C34	118.3(13)
O5	C33	C34	115.8(14)
C33	C34	C49	113.4(14)
C35	C34	C33	116.2(15)
C35	C34	C49	121.8(16)
C36	C34	C33	116.0(15)
C36	C34	C35	59.5(11)
C36	C34	C49	119.8(14)
C34	C35	C43	122.0(15)

Atom	Atom	Atom	Angle/°
C36	C35	C34	59.7(11)
C36	C35	C37	117.7(15)
C36	C35	C43	115.9(16)
C37	C35	C34	122.8(16)
C37	C35	C43	109.8(15)
C35	C36	C34	60.8(11)
C38	C37	C35	125.1(17)
C38	C37	C42	115(2)
C42	C37	C35	119.5(16)
C39	C38	C37	123(2)
C38	C39	C40	122(3)
C39	C40	C41	118(3)
C40	C41	C42	121(2)
C37	C42	C41	120(2)
C44	C43	C35	123.0(16)
C44	C43	C48	118.5(18)
C48	C43	C35	118.2(18)
C43	C44	C45	120.6(19)
C46	C45	C44	123(2)
C47	C46	C45	117(2)
C46	C47	C48	123(2)
C43	C48	C47	118(2)
C50	C49	C34	122.0(11)
C50	C49	C54	117.1(8)
C54	C49	C34	120.8(11)
C51	C50	C49	120.8(9)
C50	C51	C52	122.4(9)
C51	C52	C53	117.1(9)
C51	C52	C55	121.8(7)
C53	C52	C55	121.1(7)
C54	C53	C52	121.4(9)
C53	C54	C49	121.2(9)
C56	C55	C52	121.1(7)
C56	C55	C60	117.3(9)
C60	C55	C52	121.6(7)
C57	C56	C55	121.9(11)
C58	C57	C56	118.9(11)
C57	C58	C59	120.9(10)
C60	C59	C58	119.6(11)
C59	C60	C55	121.3(11)
O6	C61	O7	126.6(15)
O6	C61	C62	116.7(15)
O7	C61	C62	116.5(14)
C61	C62	C63	121.1(16)
C64	C62	C61	121.3(14)
C64	C62	C63	55.9(12)
C77	C62	C61	116.6(15)
C77	C62	C63	112.4(15)
C77	C62	C64	115.6(15)
C64	C63	C62	59.7(13)
C64	C63	C65	117.2(17)
C64	C63	C71	118.8(16)
C65	C63	C62	115.0(15)
C71	C63	C62	123.1(16)

Atom	Atom	Atom	Angle/°
C71	C63	C65	113.2(16)
C63	C64	C62	64.4(14)
C66	C65	C63	123.3(18)
C66	C65	C70	117.6(18)
C70	C65	C63	119.1(18)
C67	C66	C65	120(2)
C68	C67	C66	122(2)
C67	C68	C69	120(2)
C68	C69	C70	122(2)
C69	C70	C65	119(2)
C72	C71	C63	125.3(17)
C72	C71	C76	118.7(19)
C76	C71	C63	115.5(18)
C71	C72	C73	118.3(19)
C74	C73	C72	121(2)
C73	C74	C75	122(2)
C76	C75	C74	118(2)
C75	C76	C71	121(2)
C78	C77	C62	122.6(12)
C78	C77	C82	117.1(8)
C82	C77	C62	120.2(12)
C79	C78	C77	120.7(9)
C78	C79	C80	122.2(9)
C79	C80	C81	117.1(9)
C79	C80	C83	121.6(7)
C81	C80	C83	121.1(7)
C82	C81	C80	121.3(9)
C81	C82	C77	121.1(9)
C84	C83	C80	121.0(8)
C84	C83	C88	117.5(9)
C88	C83	C80	121.4(7)
C85	C84	C83	121.9(11)
C86	C85	C84	118.9(11)
C85	C86	C87	121.0(10)
C88	C87	C86	119.5(11)
C87	C88	C83	121.2(11)
O8	C89	O9	132.3(16)
O8	C89	C90	114.2(14)
O9	C89	C90	113.5(13)
C91	C90	C89	118.6(14)
C92	C90	C89	113.3(13)
C92	C90	C91	58.8(12)
C105	C90	C89	115.8(15)
C105	C90	C91	116.9(14)
C105	C90	C92	121.6(15)
C92	C91	C90	58.8(11)
C92	C91	C93	118.3(16)
C92	C91	C99	120.5(14)
C93	C91	C90	119.4(14)
C93	C91	C99	109.7(15)
C99	C91	C90	122.1(15)
C91	C92	C90	62.4(12)
C94	C93	C91	123(2)
C98	C93	C91	123(2)

Atom	Atom	Atom	Angle/°
C98	C93	C94	114(2)
C95	C94	C93	126(3)
C94	C95	C96	116(3)
C97	C96	C95	120(2)
C96	C97	C98	120(3)
C93	C98	C97	122(2)
C100	C99	C91	119.9(16)
C100	C99	C104	117.2(18)
C104	C99	C91	122.8(17)
C99	C100	C101	118.7(18)
C102	C101	C100	122(2)
C103	C102	C101	119(2)
C104	C103	C102	118.8(19)
C103	C104	C99	124(2)
C106	C105	C90	119.9(11)
C106	C105	C110	117.2(8)
C110	C105	C90	122.7(11)
C107	C106	C105	120.8(9)
C106	C107	C108	122.4(9)
C107	C108	C109	117.1(9)
C107	C108	C111	121.8(7)
C109	C108	C111	121.1(7)
C110	C109	C108	121.2(9)
C109	C110	C105	121.1(9)
C112	C111	C108	121.0(7)
C112	C111	C116	117.4(9)
C116	C111	C108	121.6(7)
C113	C112	C111	121.9(11)
C114	C113	C112	119.0(11)
C113	C114	C115	120.9(10)
C116	C115	C114	119.4(11)
C115	C116	C111	121.3(11)
O10	C117	C118	109.3(16)
O10	C119	C120	108.5(16)
C1C	O12	C1A	115.5(17)
O12	C1A	C1B	112.4(19)
O12	C1C	C9BA	113(2)

Table S6 Torsion Angles in ° for **S-BPCP_0m**.

Atom	Atom	Atom	Atom	Angle/°
Rh1	O3	C5	O2	2(2)
Rh1	O3	C5	C6	-175.3(10)
Rh1	O5	C33	O4	-11(2)
Rh1	O5	C33	C34	169.3(11)
Rh1	O7	C61	O6	11(2)
Rh1	O7	C61	C62	-175.4(12)
Rh1	O9	C89	O8	-10(2)
Rh1	O9	C89	C90	168.6(10)
Rh1	O10	C117	C118	77.6(16)
Rh1	O10	C119	C120	76.3(18)
Rh2	O1	C1	C2	-86.7(17)
Rh2	O1	C3	C4	-68(2)
Rh2	O2	C5	O3	-4(2)

Atom	Atom	Atom	Atom	Angle/°
Rh2	O2	C5	C6	173.3(11)
Rh2	O4	C33	O5	10(2)
Rh2	O4	C33	C34	-170.6(11)
Rh2	O6	C61	O7	-12(2)
Rh2	O6	C61	C62	174.2(12)
Rh2	O8	C89	O9	10(2)
Rh2	O8	C89	C90	-169.3(10)
O2	C5	C6	C7	-25(2)
O2	C5	C6	C8	44(2)
O2	C5	C6	C21	-174.7(13)
O3	C5	C6	C7	152.7(15)
O3	C5	C6	C8	-138.8(14)
O3	C5	C6	C21	3(2)
O4	C33	C34	C35	-74.5(19)
O4	C33	C34	C36	-7(2)
O4	C33	C34	C49	137.0(14)
O5	C33	C34	C35	105.2(17)
O5	C33	C34	C36	172.3(15)
O5	C33	C34	C49	-43.3(19)
O6	C61	C62	C63	-36(2)
O6	C61	C62	C64	31(3)
O6	C61	C62	C77	-178.9(16)
O7	C61	C62	C63	150.2(17)
O7	C61	C62	C64	-143.4(18)
O7	C61	C62	C77	7(3)
O8	C89	C90	C91	-79.7(19)
O8	C89	C90	C92	-14(2)
O8	C89	C90	C105	133.6(15)
O9	C89	C90	C91	101.1(18)
O9	C89	C90	C92	167.0(15)
O9	C89	C90	C105	-46(2)
C1	O1	C3	C4	133.2(19)
C3	O1	C1	C2	72(2)
C5	C6	C7	C8	102.7(18)
C5	C6	C7	C9	-6(3)
C5	C6	C7	C15	-150.0(16)
C5	C6	C8	C7	-113.9(15)
C5	C6	C21	C22	64.3(19)
C5	C6	C21	C26	-113.1(18)
C6	C7	C9	C10	126.9(17)
C6	C7	C9	C14	-59(3)
C6	C7	C15	C16	92.8(19)
C6	C7	C15	C20	-88(2)
C6	C21	C22	C23	-177.1(15)
C6	C21	C26	C25	177.1(16)
C7	C6	C21	C22	-87(2)
C7	C6	C21	C26	95.4(19)
C7	C9	C10	C11	174.3(16)
C7	C9	C14	C13	-173.6(16)
C7	C15	C16	C17	179.6(17)
C7	C15	C20	C19	-179.3(17)
C8	C6	C7	C9	-109.1(19)
C8	C6	C7	C15	107.3(17)
C8	C6	C21	C22	-155.3(15)

Atom	Atom	Atom	Atom	Angle/°
C8	C6	C21	C26	27(2)
C8	C7	C9	C10	54(2)
C8	C7	C9	C14	-131.4(19)
C8	C7	C15	C16	160.7(15)
C8	C7	C15	C20	-20(2)
C9	C7	C8	C6	112.5(16)
C9	C7	C15	C16	-54(2)
C9	C7	C15	C20	125.1(17)
C9	C10	C11	C12	-1(3)
C10	C9	C14	C13	0(3)
C10	C11	C12	C13	1(3)
C11	C12	C13	C14	-1(3)
C12	C13	C14	C9	0(3)
C14	C9	C10	C11	0(3)
C15	C7	C8	C6	-104.5(16)
C15	C7	C9	C10	-89(2)
C15	C7	C9	C14	85(2)
C15	C16	C17	C18	2(3)
C16	C15	C20	C19	0(3)
C16	C17	C18	C19	-5(3)
C17	C18	C19	C20	5(3)
C18	C19	C20	C15	-2(3)
C20	C15	C16	C17	1(3)
C21	C6	C7	C8	-108.4(15)
C21	C6	C7	C9	142.5(16)
C21	C6	C7	C15	-1(2)
C21	C6	C8	C7	106.4(15)
C21	C22	C23	C24	0(3)
C22	C21	C26	C25	0(3)
C22	C23	C24	C25	0(3)
C22	C23	C24	C27	177.8(16)
C23	C24	C25	C26	0(3)
C23	C24	C27	C28	5(3)
C23	C24	C27	C32	-178.1(17)
C24	C25	C26	C21	0(3)
C24	C27	C28	C29	-178(2)
C24	C27	C32	C31	178.3(17)
C25	C24	C27	C28	-177(2)
C25	C24	C27	C32	0(3)
C26	C21	C22	C23	0(3)
C27	C24	C25	C26	-177.7(17)
C27	C28	C29	C30	-4(4)
C28	C27	C32	C31	-4(3)
C28	C29	C30	C31	2(4)
C29	C30	C31	C32	-1(3)
C30	C31	C32	C27	2(3)
C32	C27	C28	C29	5(3)
C33	C34	C35	C36	106.0(17)
C33	C34	C35	C37	-148.8(15)
C33	C34	C35	C43	3(2)
C33	C34	C36	C35	-106.5(17)
C33	C34	C49	C50	63(2)
C33	C34	C49	C54	-115.6(18)
C34	C35	C37	C38	-118(2)

Atom	Atom	Atom	Atom	Angle/°
C34	C35	C37	C42	67(2)
C34	C35	C43	C44	115(2)
C34	C35	C43	C48	-72(2)
C34	C49	C50	C51	-176.0(16)
C34	C49	C54	C53	176.8(17)
C35	C34	C49	C50	-84(2)
C35	C34	C49	C54	98(2)
C35	C37	C38	C39	-173(2)
C35	C37	C42	C41	173.2(18)
C35	C43	C44	C45	172.3(19)
C35	C43	C48	C47	-170.7(18)
C36	C34	C35	C37	105.2(18)
C36	C34	C35	C43	-103.3(19)
C36	C34	C49	C50	-154.3(17)
C36	C34	C49	C54	27(3)
C36	C35	C37	C38	-48(3)
C36	C35	C37	C42	137.5(19)
C36	C35	C43	C44	46(2)
C36	C35	C43	C48	-140.7(18)
C37	C35	C36	C34	-113.8(19)
C37	C35	C43	C44	-91(2)
C37	C35	C43	C48	83(2)
C37	C38	C39	C40	1(5)
C38	C37	C42	C41	-2(3)
C38	C39	C40	C41	-4(5)
C39	C40	C41	C42	4(4)
C40	C41	C42	C37	-1(3)
C42	C37	C38	C39	2(4)
C43	C35	C36	C34	113.5(17)
C43	C35	C37	C38	88(2)
C43	C35	C37	C42	-87(2)
C43	C44	C45	C46	-1(3)
C44	C43	C48	C47	3(3)
C44	C45	C46	C47	2(4)
C45	C46	C47	C48	1(4)
C46	C47	C48	C43	-3(4)
C48	C43	C44	C45	-1(3)
C49	C34	C35	C36	-108.3(17)
C49	C34	C35	C37	-3(2)
C49	C34	C35	C43	148.3(16)
C49	C34	C36	C35	111.5(18)
C49	C50	C51	C52	-2(3)
C50	C49	C54	C53	-2(3)
C50	C51	C52	C53	1(3)
C50	C51	C52	C55	178.1(15)
C51	C52	C53	C54	0(3)
C51	C52	C55	C56	-145.0(17)
C51	C52	C55	C60	34(2)
C52	C53	C54	C49	0(3)
C52	C55	C56	C57	-177.5(16)
C52	C55	C60	C59	178.9(16)
C53	C52	C55	C56	32(2)
C53	C52	C55	C60	-148.9(17)
C54	C49	C50	C51	3(3)

Atom	**Atom**	**Atom**	**Atom**	**Angle/°**
C55	C52	C53	C54	-177.3(15)
C55	C56	C57	C58	-3(3)
C56	C55	C60	C59	-2(3)
C56	C57	C58	C59	1(3)
C57	C58	C59	C60	1(3)
C58	C59	C60	C55	0(3)
C60	C55	C56	C57	4(3)
C61	C62	C63	C64	108.9(18)
C61	C62	C63	C65	-143.0(17)
C61	C62	C63	C71	2(3)
C61	C62	C64	C63	-109(2)
C61	C62	C77	C78	-137(2)
C61	C62	C77	C82	47(3)
C62	C63	C65	C66	-108(2)
C62	C63	C65	C70	75(2)
C62	C63	C71	C72	-56(3)
C62	C63	C71	C76	133(2)
C62	C77	C78	C79	-171(2)
C62	C77	C82	C81	178(2)
C63	C62	C77	C78	77(2)
C63	C62	C77	C82	-99(2)
C63	C65	C66	C67	178.4(19)
C63	C65	C70	C69	-180(2)
C63	C71	C72	C73	-177.8(18)
C63	C71	C76	C75	177(2)
C64	C62	C63	C65	108.2(19)
C64	C62	C63	C71	-107(2)
C64	C62	C77	C78	15(3)
C64	C62	C77	C82	-161(2)
C64	C63	C65	C66	-40(3)
C64	C63	C65	C70	142(2)
C64	C63	C71	C72	-127(2)
C64	C63	C71	C76	62(3)
C65	C63	C64	C62	-104.5(18)
C65	C63	C71	C72	90(2)
C65	C63	C71	C76	-82(2)
C65	C66	C67	C68	1(4)
C66	C65	C70	C69	2(3)
C66	C67	C68	C69	3(4)
C67	C68	C69	C70	-5(4)
C68	C69	C70	C65	2(4)
C70	C65	C66	C67	-4(3)
C71	C63	C64	C62	113.7(19)
C71	C63	C65	C66	104(2)
C71	C63	C65	C70	-74(2)
C71	C72	C73	C74	5(3)
C72	C71	C76	C75	5(4)
C72	C73	C74	C75	-2(4)
C73	C74	C75	C76	0(4)
C74	C75	C76	C71	-1(4)
C76	C71	C72	C73	-6(3)
C77	C62	C63	C64	-106.6(17)
C77	C62	C63	C65	2(2)
C77	C62	C63	C71	146.9(17)

Atom	Atom	Atom	Atom	Angle/°
C77	C62	C64	C63	100.7(19)
C77	C78	C79	C80	-8(4)
C78	C77	C82	C81	2(3)
C78	C79	C80	C81	4(4)
C78	C79	C80	C83	178.0(19)
C79	C80	C81	C82	3(3)
C79	C80	C83	C84	-46(3)
C79	C80	C83	C88	137(2)
C80	C81	C82	C77	-5(3)
C80	C83	C84	C85	-176(2)
C80	C83	C88	C87	177(2)
C81	C80	C83	C84	128(2)
C81	C80	C83	C88	-49(2)
C82	C77	C78	C79	5(3)
C83	C80	C81	C82	-171.5(19)
C83	C84	C85	C86	-1(4)
C84	C83	C88	C87	0(3)
C84	C85	C86	C87	1(4)
C85	C86	C87	C88	0(4)
C86	C87	C88	C83	0(4)
C88	C83	C84	C85	1(4)
C89	C90	C91	C92	101.3(16)
C89	C90	C91	C93	-151.5(16)
C89	C90	C91	C99	-7(2)
C89	C90	C92	C91	-110.4(16)
C89	C90	C105	C106	61(2)
C89	C90	C105	C110	-113.1(19)
C90	C91	C93	C94	-96(3)
C90	C91	C93	C98	90(3)
C90	C91	C99	C100	-62(2)
C90	C91	C99	C104	122.0(19)
C90	C105	C106	C107	-176.8(18)
C90	C105	C110	C109	178.4(18)
C91	C90	C105	C106	-86(2)
C91	C90	C105	C110	100(2)
C91	C93	C94	C95	-175(3)
C91	C93	C98	C97	178(2)
C91	C99	C100	C101	-172.0(17)
C91	C99	C104	C103	170.3(18)
C92	C90	C91	C93	107.1(19)
C92	C90	C91	C99	-108.7(18)
C92	C90	C105	C106	-154.4(17)
C92	C90	C105	C110	31(3)
C92	C91	C93	C94	-28(3)
C92	C91	C93	C98	158(2)
C92	C91	C99	C100	-131.7(19)
C92	C91	C99	C104	52(3)
C93	C91	C92	C90	-109.1(17)
C93	C91	C99	C100	86(2)
C93	C91	C99	C104	-91(2)
C93	C94	C95	C96	-6(5)
C94	C93	C98	C97	4(4)
C94	C95	C96	C97	11(5)
C95	C96	C97	C98	-8(5)

Atom	**Atom**	**Atom**	**Atom**	**Angle/°**
C96	C97	C98	C93	0(5)
C98	C93	C94	C95	0(5)
C99	C91	C92	C90	111.3(19)
C99	C91	C93	C94	116(2)
C99	C91	C93	C98	-58(3)
C99	C100	C101	C102	1(3)
C100	C99	C104	C103	-6(3)
C100	C101	C102	C103	-5(3)
C101	C102	C103	C104	4(3)
C102	C103	C104	C99	2(3)
C104	C99	C100	C101	5(3)
C105	C90	C91	C92	-112.4(17)
C105	C90	C91	C93	-5(2)
C105	C90	C91	C99	138.9(16)
C105	C90	C92	C91	104.3(18)
C105	C106	C107	C108	2(3)
C106	C105	C110	C109	4(3)
C106	C107	C108	C109	-3(3)
C106	C107	C108	C111	175.6(18)
C107	C108	C109	C110	5(3)
C107	C108	C111	C112	155(2)
C107	C108	C111	C116	-26(3)
C108	C109	C110	C105	-6(3)
C108	C111	C112	C113	180(2)
C108	C111	C116	C115	-177.5(19)
C109	C108	C111	C112	-27(3)
C109	C108	C111	C116	152.4(18)
C110	C105	C106	C107	-2(3)
C111	C108	C109	C110	-173.9(17)
C111	C112	C113	C114	-1(4)
C112	C111	C116	C115	2(3)
C112	C113	C114	C115	-2(4)
C113	C114	C115	C116	4(4)
C114	C115	C116	C111	-4(3)
C116	C111	C112	C113	1(3)
C117	O10	C119	C120	-74(2)
C119	O10	C117	C118	-132.6(15)
C1A	O12	C1C	C9BA	-175(2)
C1C	O12	C1A	C1B	-177.5(19)

Table S7: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **S-BPCP_0m**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	**x**	**y**	**z**	U_{eq}
H1A	-6494	-3346	-2372	60
H1B	-5704	-3893	-2014	60
H2A	-7442	-4331	-2704	122
H2B	-6967	-4795	-2214	122
H2C	-6316	-4840	-2745	122
H3A	-6052	-3359	-3317	52
H3B	-5297	-4071	-3485	52
H4A	-4491	-2554	-3324	80

Atom	x	y	z	U_{eq}
H4B	-4560	-2999	-3860	80
H4C	-3659	-3261	-3425	80
H8A	-2619	-4314	-4301	31
H8B	-1805	-4802	-4702	31
H10	-4668	-4471	-4802	34
H11	-6603	-4283	-4666	38
H12	-7583	-5044	-4086	42
H13	-6563	-5979	-3610	37
H14	-4655	-6185	-3725	33
H16	-3957	-6960	-4488	43
H17	-3811	-7902	-5130	59
H18	-2752	-7691	-5849	58
H19	-2026	-6412	-6002	54
H20	-2159	-5486	-5369	43
H22	-2019	-6948	-3687	36
H23	-562	-7844	-3739	34
H25	1339	-6339	-4535	48
H26	-111	-5426	-4485	39
H28	672	-8670	-3810	89
H29	2191	-9549	-3782	92
H30	3907	-9230	-4176	54
H31	4157	-8002	-4545	55
H32	2653	-7119	-4555	49
H36A	-6201	-6392	-2720	33
H36B	-6238	-7286	-2948	33
H38	-7427	-8114	-2289	72
H39	-7820	-9322	-2007	101
H40	-6469	-10048	-1549	92
H41	-4598	-9588	-1478	67
H42	-4128	-8326	-1767	54
H44	-7326	-6364	-1901	47
H45	-7678	-5703	-1146	64
H46	-6342	-5636	-473	55
H47	-4598	-6208	-585	57
H48	-4120	-6831	-1369	57
H50	-2643	-7781	-2343	38
H51	-1551	-8626	-2815	35
H53	-3866	-8552	-3990	39
H54	-4957	-7678	-3531	35
H56	-2219	-8767	-4473	47
H57	-1180	-9646	-4963	59
H58	-90	-10599	-4542	54
H59	-77	-10701	-3637	57
H60	-1170	-9854	-3154	51
H64A	-4976	-4476	-896	43
H64B	-4405	-4602	-312	43
H66	-4405	-3525	281	59
H67	-3450	-3026	1013	64
H68	-1645	-2552	969	62
H69	-785	-2452	182	78
H70	-1620	-2990	-566	62
H72	-2705	-2906	-1554	48
H73	-3598	-1959	-2089	58
H74	-5355	-1486	-1899	61

Atom	x	y	z	U_{eq}
H75	-6404	-1981	-1216	75
H76	-5607	-2957	-708	74
H78	-3189	-5240	31	66
H79	-1731	-5442	638	75
H81	608	-4847	-407	63
H82	-853	-4418	-961	59
H84	-169	-4759	1178	111
H85	1346	-4907	1776	114
H86	2964	-5608	1545	97
H87	3096	-6139	714	99
H88	1604	-5963	112	80
H92A	-2150	-2315	-2723	34
H92B	-1351	-1765	-2337	34
H94	-50	-1012	-2614	104
H95	1479	-207	-2618	116
H96	3320	-785	-2611	80
H97	3489	-2016	-2867	96
H98	1871	-2806	-2936	84
H100	474	-3811	-3230	50
H101	505	-4220	-4106	52
H102	-312	-3464	-4764	47
H103	-1394	-2375	-4547	50
H104	-1483	-2004	-3696	44
H106	998	-3807	-2059	50
H107	2109	-3817	-1308	52
H109	282	-2056	-738	51
H110	-907	-2076	-1471	42
H112	1738	-1902	-196	72
H113	2768	-1975	587	84
H114	3606	-3146	838	73
H115	3323	-4263	334	78
H116	2401	-4168	-471	63
H11A	-296	-6783	-2732	47
H11B	821	-6895	-2374	47
H11C	464	-5580	-3011	75
H11D	1239	-6291	-3172	75
H11E	1609	-5769	-2692	75
H11F	-308	-5873	-1360	57
H11G	693	-6452	-1508	57
H12A	-1677	-6809	-1575	108
H12B	-801	-7158	-1158	108
H12C	-699	-7384	-1750	108
H1AA	-4248	-301	-4323	68
H1AB	-5058	-1023	-4231	68
H1BA	-3978	-1311	-4915	84
H1BB	-3510	-1830	-4450	84
H1BC	-2833	-1075	-4611	84
H1CA	-5235	-727	-3312	72
H1CB	-4540	39	-3431	72
H9BA	-3103	-432	-2826	135
H9BB	-4027	-1051	-2657	135
H9BC	-4268	-155	-2581	135

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L. Palatinus and G. Chapuis, Superflip - a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions, *J. Appl. Cryst.*, (2007), **40**, 786-790.

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```
#==============================================================================
# PLATON/CHECK-( 70414) versus check.def version of 310314   for Entry: s-bpcp_0
# Data: S-BPCP_0m.cif - Type: CIF              Bond Precision   C-C = 0.0254 A
# Refl: S-BPCP_0m.fcf - Type: LIST4                            Temp = 100 K
#                                X-Ray        Nref/Npar =   7.4
# Cell   11.764(3)   17.436(4)   26.079(7)         90    91.389(6)         90
# Wavelength 0.71073    Volume Reported       5347(2)   Calculated       5348(2)
# SpaceGroup from Symmetry P 21       Hall: P 2yb              monoclinic
#                Reported P 1 21 1        P 2yb              monoclinic
# MoietyFormula C120 H104 O10 Rh2, C4 H10 O
#      Reported C120 H104 O10 Rh2, C4 H10 O
#    SumFormula C124 H114 O11 Rh2
#      Reported C124 H114 O11 Rh2
# Mr        =   1985.98[Calc],   1985.97[Rep]
# Dx,gcm-3  =     1.233[Calc],     1.233[Rep]
# Z         =         2[Calc],         2[Rep]
# Mu (mm-1) =     0.368[Calc],     0.368[Rep]
# F000      =    2072.0[Calc],    2072.0[Rep]  or F000' =   2068.35[Calc]
# Reported   T Limits: Tmin=0.601             Tmax=0.745  AbsCorr=MULTI-SCAN
# Calculated T Limits: Tmin=0.817 Tmin'=0.817  Tmax=0.929
# Reported   Hmax= 13, Kmax= 19, Lmax= 30, Nref=  15161        , Th(max)= 24.713
# Obs in FCF Hmax= 13, Kmax= 19, Lmax= 30, Nref=  15161[  9127], Th(max)= 24.712
# Calculated Hmax= 13, Kmax= 20, Lmax= 30, Nref=  18219[  9441], Ratio=1.61/0.83
# Reported   Rho(min) = -1.43, Rho(max) =  1.40 e/Ang**3 (From CIF)
# Calculated Rho(min) = -1.48, Rho(max) =  1.69 e/Ang**3 (From CIF+FCF data)
# w=1/[sigma**2(Fo**2)+(0.0002P)**2+ 61.2351P], P=(Fo**2+2*Fc**2)/3
# R= 0.0987( 10889), wR2= 0.2180( 15161), S = 1.104      (From CIF+FCF data)
# R= 0.0987( 10889), wR2= 0.2181( 15161), S = 1.104      (From FCF data only)
# R= 0.0987( 10889), wR2= 0.2181( 15161), S = 1.104, Npar= 1240, Flack   0.11(3)
#==============================================================================
For Documentation: http://http://www.platonsoft.nl/CIF-VALIDATION.pdf
#==============================================================================

#==============================================================================
>>> The Following Improvement and Query ALERTS were generated - (Acta-Mode) <<<
#==============================================================================
Format: alert-number_ALERT_alert-type_alert-level text

220_ALERT_2_B Large Non-Solvent  C     Ueq(max)/Ueq(min) Range        6.4 Ratio
342_ALERT_3_B Low Bond Precision on  C-C Bonds ...............     0.0254 Ang.
#==============================================================================
029_ALERT_3_C _diffrn_measured_fraction_theta_full Low .......      0.967 Note
090_ALERT_3_C Poor Data / Parameter Ratio (Zmax > 18) ........      7.36 Note
241_ALERT_2_C High     Ueq as Compared to Neighbors for .....       C28 Check
241_ALERT_2_C High     Ueq as Compared to Neighbors for .....       C29 Check
241_ALERT_2_C High     Ueq as Compared to Neighbors for .....       C39 Check
241_ALERT_2_C High     Ueq as Compared to Neighbors for .....       C94 Check
241_ALERT_2_C High     Ueq as Compared to Neighbors for .....       C95 Check
242_ALERT_2_C Low      Ueq as Compared to Neighbors for .....       O10 Check
242_ALERT_2_C Low      Ueq as Compared to Neighbors for .....       C27 Check
242_ALERT_2_C Low      Ueq as Compared to Neighbors for .....       C30 Check
242_ALERT_2_C Low      Ueq as Compared to Neighbors for .....       C93 Check
242_ALERT_2_C Low      Ueq as Compared to Neighbors for .....       C96 Check
244_ALERT_4_C Low   'Solvent' Ueq as Compared to Neighbors of        C1C Check
330_ALERT_2_C Large Average Phenyl  C-C Dist.  C27    -C32          1.42 Ang.
330_ALERT_2_C Large Average Phenyl  C-C Dist.  C37    -C42          1.42 Ang.
330_ALERT_2_C Large Average Phenyl  C-C Dist.  C55    -C60          1.42 Ang.
330_ALERT_2_C Large Average Phenyl  C-C Dist.  C83    -C88          1.42 Ang.
330_ALERT_2_C Large Average Phenyl  C-C Dist.  C99    -C104         1.41 Ang.
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330_ALERT_2_C Large Average Phenyl  C-C Dist.  C111   -C116         1.42 Ang.
601_ALERT_2_C Structure Contains Solvent Accessible VOIDS of .         47 Ang3
790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd.  #         1 Note
C120 H104 O10 Rh2
906_ALERT_3_C Large K value in the Analysis of Variance ......      2.131 Check
911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L=  0.588       278 Why ?
915_ALERT_3_C Low Friedel Pair Coverage ......................         69 %
971_ALERT_2_C Check Calcd Residual Density  0.97A From     Rh2       1.69 eA-3
971_ALERT_2_C Check Calcd Residual Density  1.01A From      O3       1.67 eA-3
976_ALERT_2_C Check Calcd Residual Density  0.92A From      O9      -1.12 eA-3
976_ALERT_2_C Check Calcd Residual Density  0.97A From      O4      -0.91 eA-3
976_ALERT_2_C Check Calcd Residual Density  0.93A From      O4      -0.85 eA-3
#==============================================================================
002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         59 Note
003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...        132 Why ?
033_ALERT_4_G Flack x Value Deviates > 2*sigma from Zero .....      0.110
083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large.      61.24 Why ?
720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........         11 Note
790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #         2 Note
C4 H10 O
791_ALERT_4_G The Model has Chirality at C6      .............          S Verify
791_ALERT_4_G The Model has Chirality at C34     .............          S Verify
791_ALERT_4_G The Model has Chirality at C62     .............          S Verify
791_ALERT_4_G The Model has Chirality at C90     .............          S Verify
860_ALERT_3_G Number of Least-Squares Restraints .............       1416 Note
909_ALERT_3_G Percentage of Observed Data at Theta(Max) still          33 %
910_ALERT_3_G Missing # of FCF Reflections Below Th(Min) .....          2 Why ?
#==============================================================================

ALERT_Level and ALERT_Type Summary
==================================
2 ALERT_Level_B = A Potentially Serious Problem - Consider Carefully
29 ALERT_Level_C = Check. Ensure it is Not caused by an Omission or Oversight
13 ALERT_Level_G = General Info/Check that it is not Something Unexpected

26 ALERT_Type_2 Indicator that the Structure Model may be Wrong or Deficient.
9 ALERT_Type_3 Indicator that the Structure Quality may be Low.
9 ALERT_Type_4 Improvement, Methodology, Query or Suggestion.
#==============================================================================

0 Missing  Experimental  Info Issue(s) (Out of  54 Tests) -  100 % Satisfied
2 Experimental  Data  Related Issue(s) (Out of  28 Tests) -   93 % Satisfied
29 Structural  Model   Related Issue(s) (Out of 117 Tests) -   75 % Satisfied
12 Unresolved or to be Checked Issue(s) (Out of 223 Tests) -   95 % Satisfied

#==============================================================================
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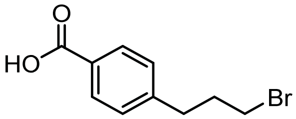
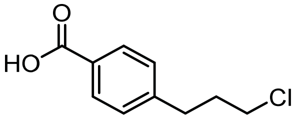
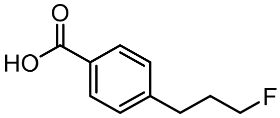
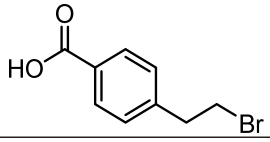
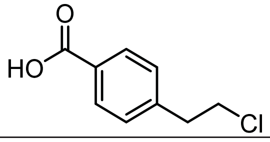
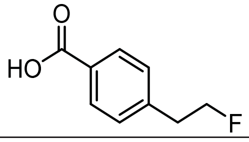
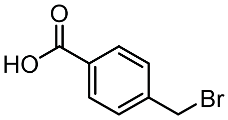
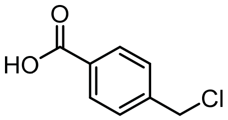
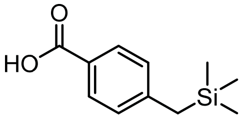
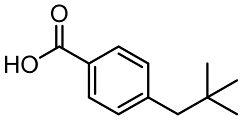
8. Predictive Model: Carboxylic Acid Surrogate Calculation

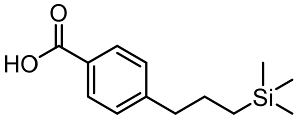
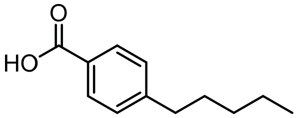
Carboxylic acid surrogate structures, as described in the manuscript, were calculated using Gaussian 09 with the def2-TZVP basis set and M06-2x functional. Charges were calculated with NBO. The following table includes the substrates, the structures calculated, the regioisomeric ratio converted to energetic preference, the NBO charge used in the correlations, and the prediction values.

Catalyst 1: $Rh_2[R\text{-}3,5\text{-di}(p\text{-}^tBuC_6H_4)TPCP]_4$

Catalyst 2: $Rh_2(R\text{-}p\text{-}PhTPCP)_4$

Table S15 Calculated results

Substrate	Surrogate Structure	Catalyst 1 $\Delta\Delta G^{\ddagger}$	Catalyst 2 $\Delta\Delta G^{\ddagger}$	Catalyst 3 $\Delta\Delta G^{\ddagger}$	C4 NBO Charge	Catalyst 3 Predictions
1-Br-Hexane		1.709817	0.579292	1.96069	0.01145	
1-Cl-Hexane		1.701512	0.607546	2.018459	0.01067	1.94061
1-F-Hexane		1.705513	0.508436	1.985432	0.0115	1.960094
1-Br-Pentane		1.326782	0.186408	1.62673	0.00015	1.693662
1-Cl-Pentane		1.319812	0.348044	1.6842	-0.00032	
1-F-Pentane		1.260886	0.278301	1.69105	0.00043	1.700235
1-Br-Butane		0.601144	0	1.059959	-0.04601	0.610094
1-Cl-Butane		0.609664	0.199234	1.021151	-0.03811	0.79554
1-TMS-Butane		2.095491	0.51905	2.35603	0.01696	2.088263
1-^{t}Bu-Butane		2.068756	0.495756	2.047321	0.00993	1.923239

1-TMS-Hexane		1.779449	0.467338	2.120907	0.01557	2.055634
Octane		1.943824	0.472225	2.02353	0.01657	2.079108

Catalyst 1:

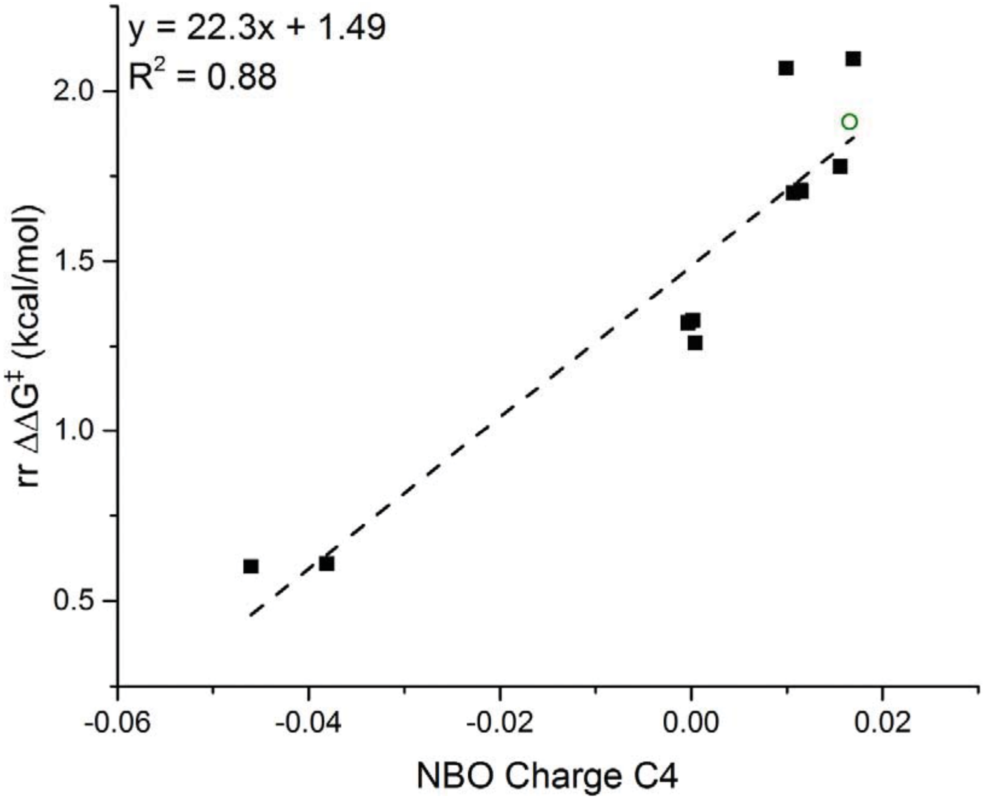


Figure S22

Catalyst 2:

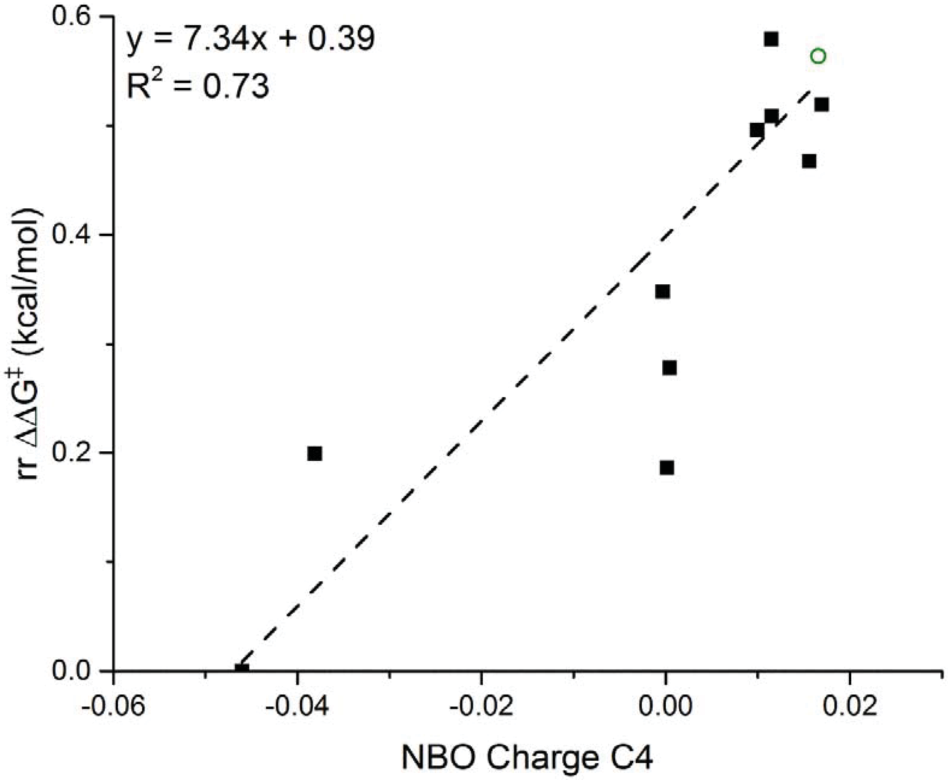


Figure S23

Structure coordinates are below.

1-Bromo Hexane

C	-1.37743000	1.41957500	0.15133400
C	-2.66737100	1.21594800	-0.30441500
C	-3.31229600	0.01096600	-0.04545000
C	-2.65868200	-0.98590100	0.67163300
C	-1.36741600	-0.77231600	1.12440800
C	-0.71132800	0.43007300	0.87190700
H	-0.87764500	2.36037400	-0.04853000
H	-3.19468400	1.98000200	-0.86043700
H	-3.16407400	-1.92018600	0.87349600
H	-0.85968200	-1.54838300	1.68567100
C	-4.69726000	-0.16235200	-0.55138500
O	-5.22425500	-1.36358300	-0.24645400
H	-6.11750100	-1.37707500	-0.61745600
O	-5.30846300	0.66497800	-1.17099900
C	0.70929700	0.63665500	1.32006400
H	0.87976500	0.11166400	2.26328600
H	0.88570400	1.69903000	1.50554000
C	1.70466400	0.13038800	0.26801200
H	1.53731100	-0.93309500	0.08605600
H	1.53259900	0.64556000	-0.67928200
C	3.13013600	0.35528700	0.72344100
H	3.35327500	-0.17899100	1.64375600
H	3.35238900	1.41096500	0.85847000
Br	4.41201100	-0.29517000	-0.59280700

1-Chloro Hexane

C	-0.53769500	1.22456000	0.60490300
C	-1.85489700	1.23359300	0.18332300
C	-2.53195000	0.03280000	-0.00372900
C	-1.88274000	-1.17392300	0.23538500
C	-0.56336300	-1.17260400	0.65698900
C	0.12570700	0.02261600	0.84591600
H	-0.01320500	2.16168700	0.75215700
H	-2.37859700	2.16171400	-0.00471500
H	-2.41242800	-2.10567000	0.09273300
H	-0.05874700	-2.11346700	0.84442500
C	-3.94483400	0.09075000	-0.45560600
O	-4.50277700	-1.12630000	-0.60055900
H	-5.41233500	-0.98102000	-0.89609200
O	-4.55246100	1.10258800	-0.67723100
C	1.57649500	0.01615400	1.24177000
H	1.78676500	-0.85812900	1.86290900
H	1.79934300	0.90123100	1.84299100
C	2.48689000	-0.00400900	0.00819400
H	2.26946000	-0.88741100	-0.59598500
H	2.28063400	0.86779700	-0.61639000
C	3.94687700	-0.00856800	0.40930200
H	4.19677900	-0.88906500	0.99832500

H	4.20725200	0.88132100	0.97926500
Cl	5.01494300	-0.03044100	-1.02329400

1-Fluoro Hexane

C	-0.05843500	1.21418900	0.50067700
C	-1.40310600	1.23075200	0.17701000
C	-2.09507200	0.03347400	0.02573600
C	-1.43282600	-1.17697700	0.20129400
C	-0.08601300	-1.18300700	0.52533800
C	0.61762700	0.00858500	0.67945800
H	0.47784300	2.14857300	0.62045700
H	-1.93660200	2.16207600	0.03895800
H	-1.97397800	-2.10597800	0.08625800
H	0.42815500	-2.12701100	0.66468700
C	-3.53719600	0.09905500	-0.32020000
O	-4.10623800	-1.11541000	-0.44267300
H	-5.03415300	-0.96541100	-0.67144900
O	-4.15771600	1.11445000	-0.48119800
C	2.09142100	-0.00420200	0.97875700
H	2.33718200	-0.88600500	1.57599400
H	2.35095700	0.87260900	1.57764300
C	2.92424700	-0.00928500	-0.30607600
H	2.67541100	-0.88761100	-0.90621800
H	2.68455800	0.87087300	-0.90725600
C	4.40376600	-0.01690900	-0.00028100
H	4.68657000	-0.90605900	0.56899900
H	4.69642700	0.87173700	0.56481700
F	5.13030900	-0.02379500	-1.17691200

1-Bromo Pentane

C	0.79929400	1.21956800	0.43685900
C	2.15529600	1.23220000	0.16298300
C	2.84800900	0.03265500	0.03612100
C	2.17714700	-1.17662300	0.18417200
C	0.81910200	-1.17960600	0.45811400
C	0.11572200	0.01478800	0.59096100
H	0.26162500	2.15497500	0.54129900
H	2.69693000	2.16186300	0.04736100
H	2.72024400	-2.10664500	0.08845200
H	0.29732500	-2.12189400	0.57937500
C	4.30391900	0.09470300	-0.25325700
O	4.87318500	-1.12096600	-0.35353300
H	5.81067400	-0.97529800	-0.54291900
O	4.93124100	1.10919500	-0.38870900
C	-1.36905600	0.00506400	0.84480500
H	-1.65184100	-0.87837500	1.41836800
H	-1.66237500	0.88244400	1.42251200
C	-2.11333600	0.00392700	-0.48146200
H	-1.88039400	-0.87853300	-1.07141100
H	-1.89625500	0.89511400	-1.06436400
Br	-4.04422600	-0.01484400	-0.21018600

1-Chloro Pentane

C	0.00187400	1.21309900	0.39924700
C	1.36343200	1.23044100	0.15472500
C	2.06219700	0.03324300	0.03955700
C	1.39157000	-1.17825500	0.16895800
C	0.02788700	-1.18576000	0.41362200
C	-0.68174600	0.00614600	0.53515800
H	-0.54057700	2.14669500	0.49487100
H	1.90488000	2.16195400	0.05386600
H	1.93921900	-2.10650600	0.08222700
H	-0.49373800	-2.12985200	0.52084400
C	3.52399600	0.10024400	-0.21675900
O	4.09921600	-1.11348200	-0.30721500
H	5.04046100	-0.96415000	-0.47376600
O	4.15141800	1.11688900	-0.33513400
C	-2.17047300	-0.00751000	0.75855800
H	-2.46445900	-0.89250600	1.32453100
H	-2.47854600	0.86879700	1.33067300
C	-2.89627300	-0.00817400	-0.57915200
H	-2.64441800	-0.89067800	-1.16343600
H	-2.65466200	0.88037000	-1.15863100
Cl	-4.66753100	-0.01895400	-0.34799200

1-Fluoro Pentane

C	-0.47400500	1.20938100	0.35999600
C	0.89271500	1.22943600	0.14627300
C	1.59607400	0.03371800	0.04508400
C	0.92456700	-1.17898200	0.15680400
C	-0.44429300	-1.18906400	0.37065800
C	-1.15891400	0.00126700	0.47894800
H	-1.02004100	2.14187900	0.44476500
H	1.43469500	2.16203700	0.05912700
H	1.47546600	-2.10623900	0.08058200
H	-0.96669300	-2.13413300	0.46423600
C	3.06310100	0.10350800	-0.17724900
O	3.64260700	-1.10912600	-0.25588000
H	4.58723400	-0.95739800	-0.39947100
O	3.69170000	1.12127000	-0.27957100
C	-2.65123600	-0.01516000	0.66583200
H	-2.95947300	-0.90353400	1.21948200
H	-2.97656100	0.86105500	1.22917300
C	-3.34939300	-0.01378400	-0.68275400
H	-3.07984800	-0.89819800	-1.26436100
H	-3.09310800	0.88027800	-1.25559100
F	-4.71864700	-0.02498000	-0.49732000

1-Bromo Butane

C	-0.12092700	1.22782400	0.55766000
C	-1.46258600	1.23708300	0.22388200
C	-2.14894200	0.03567400	0.07915200
C	-1.48783800	-1.17360800	0.26825100
C	-0.14438400	-1.17591900	0.60286500
C	0.54821300	0.02184000	0.75293600
H	0.41810100	2.16155100	0.66485800

H	-1.99756000	2.16509200	0.07143400
H	-2.02691400	-2.10369900	0.15425200
H	0.37580200	-2.11551100	0.74577400
C	-3.59064300	0.09579300	-0.27713900
O	-4.15449500	-1.12035400	-0.39550400
H	-5.08162100	-0.97668200	-0.63182900
O	-4.21019400	1.10968000	-0.44700800
C	1.99660000	0.01443200	1.11050900
H	2.27655100	-0.86835500	1.67651000
H	2.29249800	0.91067000	1.64649500
Br	3.11782000	-0.02246800	-0.49988800

1-Chloro Butane

C	0.55382500	1.25935000	0.36330700
C	-0.81000000	1.24929300	0.13003300
C	-1.49145300	0.03911000	0.06271800
C	-0.80543000	-1.16014000	0.22800100
C	0.55880500	-1.14244000	0.46253000
C	1.24716700	0.06472700	0.53402500
H	1.08911200	2.20000100	0.41233800
H	-1.36469600	2.16891800	-0.00146000
H	-1.34251000	-2.09684200	0.17398400
H	1.09879900	-2.07352800	0.58677000
C	-2.95655500	0.07812900	-0.18683000
O	-3.51413300	-1.14549500	-0.23938000
H	-4.45801300	-1.01549500	-0.40732200
O	-3.59817200	1.08232600	-0.32990700
C	2.72400400	0.07474800	0.77491100
H	3.03275300	-0.75556300	1.40455900
H	3.05266300	1.01079400	1.21854100
Cl	3.62753900	-0.10056400	-0.76737000

1-trimethylsilyl Butane

C	0.39546400	1.22443700	-0.71672800
C	1.72026300	1.23532300	-0.32287600
C	2.40326800	0.03692500	-0.13771700
C	1.74501500	-1.17008700	-0.35342500
C	0.41826700	-1.17214100	-0.74751000
C	-0.28068000	0.02153900	-0.93717700
H	-0.13038300	2.16113100	-0.86125300
H	2.24704200	2.16581800	-0.15543400
H	2.27564000	-2.10202500	-0.21426200
H	-0.08960500	-2.11483100	-0.91566100
C	3.82250900	0.09702200	0.28279700
O	4.38473000	-1.12001000	0.42489400
H	5.29953400	-0.96984300	0.70068000
O	4.43839300	1.10881300	0.48569200
C	-1.72888200	0.01277800	-1.30567600
H	-1.96923000	-0.86442200	-1.91198600
H	-1.98386200	0.89816300	-1.89372700
C	-2.47748300	-1.55092700	1.22881000
H	-2.67002100	-2.45806000	0.65199100
H	-1.43340800	-1.56737000	1.54759400

H	-3.10214100	-1.58605800	2.12385200
C	-2.51513600	1.51402500	1.25654500
H	-2.72258800	2.42644300	0.69338600
H	-3.14632800	1.52202600	2.14760200
H	-1.47394900	1.54766200	1.58333300
C	-4.63193300	-0.02952000	-0.34591100
H	-4.84480400	-0.91064000	-0.95427600
H	-5.31153700	-0.04273100	0.50862200
H	-4.86397100	0.85522800	-0.94186700
Si	-2.84924300	-0.01336900	0.22856600

2,2-dimethyl hexane

C	0.10377500	1.22012900	-0.55216900
C	1.45367400	1.23444200	-0.25024500
C	2.14592400	0.03620900	-0.10825000
C	1.47787700	-1.17234600	-0.27580200
C	0.12604700	-1.17459700	-0.57808900
C	-0.58382900	0.01720600	-0.71583200
H	-0.43010600	2.15616600	-0.66798500
H	1.99126400	2.16515900	-0.12419200
H	2.01900800	-2.10290700	-0.17340000
H	-0.39022900	-2.11766400	-0.71458300
C	3.59312200	0.09829400	0.21347800
O	4.16226300	-1.11767700	0.32633000
H	5.09418500	-0.96819800	0.53819400
O	4.21993800	1.11164700	0.36493700
C	-2.05604600	0.00698400	-1.02192500
H	-2.28910900	-0.86804600	-1.63535300
H	-2.30433600	0.89053400	-1.61684800
C	-2.99100800	-0.01477300	0.21117900
C	-2.75262800	-1.27175100	1.04663900
H	-2.89473200	-2.17455200	0.44667500
H	-1.74258000	-1.29174900	1.45910600
H	-3.45648800	-1.30967300	1.88075700
C	-2.76974500	1.22323700	1.07902400
H	-2.92492000	2.13943100	0.50325500
H	-3.47348100	1.22934500	1.91407000
H	-1.75982300	1.24696500	1.49158900
C	-4.43080200	-0.01802700	-0.30361900
H	-4.62225400	-0.89471200	-0.92670800
H	-5.13664800	-0.03573400	0.52927100
H	-4.63552900	0.87382400	-0.90032200

1-trimethylsilyl hexane

C	-1.69500000	-1.24702200	-0.72484300
C	-2.96749500	-1.23966400	-0.18290900
C	-3.62383500	-0.03148700	0.03066500
C	-2.99771800	1.16565500	-0.30176200
C	-1.72314500	1.14698000	-0.84376400
C	-1.05469100	-0.05538800	-1.06409400
H	-1.18644600	-2.18917400	-0.89389800
H	-3.47316000	-2.15969500	0.07932200
H	-3.51202000	2.10245200	-0.13780900

H	-1.23685400	2.07953400	-1.10583300
C	-4.98881900	-0.07064200	0.61017300
O	-5.52981100	1.15280900	0.77223500
H	-6.40950000	1.01751800	1.15117200
O	-5.57801400	-1.07247600	0.91437200
C	0.35000200	-0.06601800	-1.59773500
H	0.50375100	0.79082800	-2.25828300
H	0.51373200	-0.96628100	-2.19523600
C	1.38952000	-0.01998500	-0.47034400
H	1.20900200	0.87560400	0.13226400
H	1.21912700	-0.87276100	0.19415400
C	2.82893000	-0.02968200	-0.98476600
H	2.98750800	0.82368700	-1.65387000
H	2.99701300	-0.92496800	-1.59410400
Si	4.13714800	0.02334900	0.36836300
C	5.83492200	0.00877600	-0.42497400
H	5.97019700	0.87168000	-1.08004200
H	6.62141900	0.03761900	0.33167400
H	5.98102300	-0.89219000	-1.02407400
C	3.92736300	1.58681600	1.38224100
H	3.99082600	2.47656500	0.75232500
H	2.96280400	1.60485300	1.89317400
H	4.70606700	1.66185200	2.14395200
C	3.94748600	-1.47293900	1.48247100
H	2.98247400	-1.47110700	1.99282100
H	4.02443200	-2.40106700	0.91228000
H	4.72601100	-1.48689700	2.24791300

Octane

C	0.64365900	1.22275700	0.58021600
C	1.96631000	1.23276000	0.17637400
C	2.64551100	0.03229000	-0.00672900
C	1.99174800	-1.17458600	0.22050200
C	0.66691000	-1.17332400	0.62422200
C	-0.02617100	0.02108200	0.80759000
H	0.11738700	2.15956800	0.72319200
H	2.49279100	2.16134900	-0.00166200
H	2.52255400	-2.10635300	0.08174500
H	0.15877000	-2.11434300	0.80119100
C	4.06218700	0.09024900	-0.44281200
O	4.62196800	-1.12709400	-0.58547000
H	5.53399300	-0.97947200	-0.87180000
O	4.67461800	1.10139300	-0.65656500
C	-1.48400100	0.01408900	1.17305500
H	-1.70921200	-0.86180300	1.78678600
H	-1.72054800	0.89679800	1.77266500
C	-2.37468200	-0.00145300	-0.07301300
H	-2.12540500	-0.88000600	-0.67639000
H	-2.13666600	0.87069700	-0.69007300
C	-3.86077400	-0.00852000	0.25789800
H	-4.10390700	0.87055000	0.86466400
H	-4.09298300	-0.88161300	0.87750000

C	-4.74473200	-0.02300300	-0.98350100
H	-4.50908700	0.84920300	-1.60025000
H	-4.49857900	-0.90106600	-1.58774400
C	-6.23003700	-0.02967100	-0.64679300
H	-6.50094500	0.85327400	-0.06456300
H	-6.84548300	-0.03835400	-1.54670900
H	-6.49093000	-0.90884200	-0.05433600

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