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Benjamin Wertz

Date

**EXPLORING THE INFLUENCE OF DIRHODIUM CATALYST STRUCTURE ON THE
REGIO- AND STEREOSELECTIVITY PROPERTIES OF DONOR/ACCEPTOR
CARBENES**

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Abstract

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By Benjamin Wertz

The reactions of donor/acceptor dirhodium carbenes with the C-H bonds of organic compounds are capable of very high regio- and stereoselectivity and have the ability to select preferentially for highly specific C-H bonds in substrate molecules that may contain many of them. Over the past decade, the discovery of novel dirhodium catalysts with a variety of shapes and selectivity profiles has led to many remarkable advances in the field of organic synthesis. These have caused chemists to reevaluate the conventional thinking that non-acidic C-H bonds at sp^3 -hybridized positions are inert and do not represent viable positions for synthetic manipulation.

The first chapter of this thesis presents the development of these novel catalysts in historical context and highlights some of the reactions that they can perform. While there are undoubtedly many other valuable applications for the catalysts described in this section, the work has been presented as a reference for future researchers who may be searching for a simple set of guidelines to better understand how they can apply dirhodium carbene chemistry effectively in their research. Accordingly, the types of reactions described in this chapter are diverse and are intended to call attention to both the strengths and weaknesses of dirhodium carbene strategies for organic synthesis.

The second chapter contains original research which highlights the relationship between the ligand structure and the selectivity properties of the dirhodium cyclopropanecarboxylate complexes. Catalysts of this type are well established for the regio- and stereoselective functionalization of sterically accessible primary or secondary C-H sites. For trisubstituted cyclopropanes, substitution at the C1 aryl group controls the regio- and stereoselectivity of the catalysts. This work reveals how the formal removal of an aryl substituent at the C2-position of the cyclopropane can also significantly impact the shape of the catalysts and the selectivity observed in their reactions.

Section 3 presents a novel contribution to synthetic organic reaction methodology: the application of dirhodium tetracarboxylate catalysts to the functionalization of aryl- or heteroaryl-cyclobutanes. Depending on the catalyst chosen, either the benzylic C1-position of the arylcyclobutane or the distal C3 methylene group reacts with high regio- and stereoselectivity.

The fourth chapter of this work describes the design, synthesis, and applications of dirhodium cyclopropanecarboxylate catalysts with two aryl groups and one other substituent bonded to the cyclopropane. A series of cyclohexyl- and trimethylsilyl- substituted diarylcyclopropane carboxylate complexes were prepared and tested in C-H insertion and asymmetric cyclopropanation reactions. The shapes and selectivity properties of the new catalysts mirrored their triarylcyclopropane counterparts, but with some subtle differences. A trimethylsilyl-substituted catalyst was proficient for asymmetric cyclopropanations at very low loading.

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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
2020

ACKNOWLEDGEMENTS

It is truly a great accomplishment to graduate with a PhD from the Davies Group at Emory University, and I undoubtedly owe a great debt of gratitude to many of my current and former coworkers, family, and friends who have been instrumental to my success over the past years. I would like to dedicate this section to recognizing these individuals for their support during my journey to becoming a Doctor of Philosophy in Chemistry.

I would first like to recognize Prof. Huw M. L. Davies, who has provided invaluable guidance to me on my journey toward becoming a competent scientist and published author. In addition to his assistance in steering my research toward a productive outcome, my time with Prof. Davies has enabled me to grow as an independent thinker and taught me that being a skilled chemist is not merely about coming up with new ways to synthesize compounds, but rather taking strides toward solving the grand challenges of organic chemistry and chemical science. In addition to the support he has personally provided to my research and professional growth, Prof. Davies' involvement with the NSF Center for Selective Functionalization has afforded me with numerous opportunities to benefit from the perspectives of other leading figures in my field. I am deeply indebted to all participants in NSF-CCHF for sharing their research, and for providing useful feedback and suggestions at meetings and poster sessions. I am also very grateful for the advice, training, and support I have received from my other committee members, Prof. Lanny S. Liebeskind and Prof. Frank E. McDonald, who provided me with useful feedback and invaluable training in spectroscopy and organic reactions.

I also owe an incredible debt of gratitude to Dr. John Bacsá and the Emory University X-Ray Crystallography Center. While most PhD theses in organic chemistry feature one or two key X-

ray structure determinations as proof to verify chemical structures assigned by other means, the present work features many of them. This fact reflects the importance of these structures to understanding the structure and selectivity properties of the dirhodium catalysts, and it also speaks to the high level of technical expertise and advanced equipment which was available to myself and to my contemporary PhD students at Emory University.

I am extremely grateful to all current and former members of the Davies research group who have provided support to me during my time at Emory. Among his many virtues, Prof. Davies is skilled at identifying and hiring exceptionally talented postdoctoral researchers, and I have benefitted immensely from my interactions with these highly capable individuals. Specifically, I would like to acknowledge Dr. Zachary Garlets, who helped me learn how to write an effective SI section, and whose pioneering work with small, strained rings ultimately lead to a new method for the regio- and stereoselective functionalization of cyclobutanes. Dr. Zhi Ren also contributed greatly to my success by providing invaluable feedback on the new catalysts I prepared from a computational chemistry perspective. I am also thankful for the opportunity to have worked with Prof. Sidney Wilkerson-Hill, Prof. Jefferey Mighion, Dr. Sandeep Raikar, Prof. Kuangbiao Liao, Prof. Janakiram Vaitla, Dr. Mark Matulenko, Prof. Igor Jurburg, Dr. Ladena Bolton, and Dr. Xun Yang.

I would also like to recognize my contemporary PhD students Dr. Wenbin Liu, Dr. Hyunmin Park, Dr. Jiantao Fu, Dr. Bowen Zhang, Yannick Boni, Robert Kubiak, Bo Wei, Jack Sharland, Aaron Bosse, Sam McKinnon, and Maizie Lee who contributed greatly to my intellectual and professional development through many helpful and productive discussions.

My work at Emory was also aided greatly by love and support from my family and friends. I am very grateful to Dr. Deborah Panitch and Dr. William Wertz (my mother and father) for their

steadfast support and for believing in me. I am also highly indebted to Prof. John T. Welch (SUNY Albany), Prof. Marina Petrukhina (SUNY Albany), and Bruce S. King (Wake Forest University) for introducing me to organic chemistry research, and to all of my former undergraduate instructors for training me to think like a scientist.

Finally, I would also like to recognize my former coworkers at Albany Molecular Research, Inc (AMRI) for contributing greatly to my professional and intellectual growth. My experience working at the Eli Lilly and Company site in Indianapolis helped to greatly improve my lab skills and inspired me to attend graduate school. I would like to recognize Dr. Honglu Zhang, Dr. Kevin McGee, Brian Struss, Dr. Loren Schubert, Jesse Wolfe, Randy and Tara Pryor, Delvis Dore, Chase Buchanan, Jay Afragola, Josiah Miller, Sarah Glancy, Dr. Bruno Chapsal, Nardos Teumelsan, Deanna Nichols, Greg Storer, and Dr. Alan Henderson for being great teammates, for many excellent chemistry discussions, and for helping me to feel at home in Indiana.

Table of Contents

Chapter 1. General Introduction to Donor/Acceptor Carbenes and Dirhodium Catalysts.....	1
1.1 Introduction.....	1
1.2 Structure of Dirhodium Tetracarboxylates.....	3
1.3 Mechanism of Dirhodium Carbene Reactions.....	6
1.4 Strengths and Limitations of Donor/Acceptor Carbenes.....	13
1.5 Stereoselective Cyclopropanation Reactions.....	18
1.6 Established Classes of Dirhodium Tetracarboxylate Catalyst.....	23
1.6.1 Development and Applications of Dirhodium Tetraproline Catalysts.....	25
1.6.2 Dirhodium Complexes with Phthalimido- Protected Amino Acid Ligands.....	29
1.6.3 Introduction to Dirhodium Triarylcyclopropanecarboxylates.....	36
1.7 C-H Functionalization with Dirhodium Carbenes.....	42
1.7.1 Reactions at Innately Favored Sites.....	43
1.7.2 Site- and Stereoselective Functionalization of Unactivated C-H Bonds.....	47
1.8 References.....	62
 Chapter 2. Study of Dirhodium Diarylcyclopropanecarboxylate Catalysts.....	 71
2.1 Background.....	71
2.1.1 Substituent Effects in The Triarylcyclopropanecarboxylates.....	72
2.1.2 Design of Dirhodium Diarylcyclopropanecarboxylates.....	75
2.2 Results and Discussion.....	77
2.2.1 Synthesis of Diarylcyclopropanecarboxylates.....	79
2.2.2 Evaluation of Catalysts.....	87

2.2.3 X-Ray Analysis of Dirhodium Catalysts.....	91
2.2.4 DFT Study of Rh ₂ (DPCP) ₄ Catalysts.....	94
2.2.5 Conclusion.....	98
2.3 References.....	100
 Chapter 3. The Regio- and Stereoselective Functionalization of Arylcyclobutanes.....	103
3.1 Introduction and Related Work.....	103
3.1.1 Selective Functionalization of Silacyclobutanes and Silacyclopentanes.....	105
3.1.2 Selective Functionalization of Cyclohexanes.....	107
3.1.3 Selective Functionalization of Bicyclo[1.1.1]pentanes.....	110
3.1.4 Overcoming Electronic Activation with <i>ortho</i> -TPCP Catalysts.....	113
3.2 Results and Discussion.....	115
3.2.1 Synthesis of Cyclobutane Substrates.....	119
3.2.2 C-H Functionalization of Arylcyclobutanes at C1.....	121
3.2.3 C-H Functionalization of Arylcyclobutanes at C3.....	124
3.2.4 Discovery and Isolation of Stable Pyridinium Ylide Dyes.....	127
3.3 Conclusion.....	131
3.4 References.....	132
 Chapter 4. Rh₂(DPCP)₄ Catalysts With sp³-Hybridized Substituent Groups.....	136
4.1 Introduction.....	136
4.1.1 Design of sp ³ -Functionalized Diarylcyclopropanecarboxylate Catalysts.....	138
4.2 Results and Discussion.....	140

4.2.1 Preparation of Cyclohexyl-DPCP Catalysts.....	140
4.2.2 Evaluation of Cyclohexyl-DPCP Catalysts.....	144
4.2.3 Trimethylsilyl Diarylcyclopropanecarboxylates.....	147
4.2.4 Evaluation of TMS-DPCP Catalysts.....	151
4.2.5 C-H Insertion Reactions with Rh ₂ (2-TMS-DPCP) ₄ Catalysts.....	154
4.2.6 Cyclopropanation Using the Rh ₂ (2-TMS-DPCP) ₄ Catalysts.....	156
4.2.7 Structure of the Trimethylsilyl-DPCP Catalysts.....	159
4.3 Conclusion.....	165
4.4 References.....	166
Experimental Sections.....	168
S.1 General Methods.....	168
S.2 Experimental Section for Chapter 2.....	169
S.2.1 List of Previously Reported Compounds.....	169
S.2.2 Synthesis of Cyclopropanecarboxylate Ligands.....	171
S.2.3 Preparation of Dirhodium Catalysts.....	182
S.2.4 Evaluation of Dirhodium Catalysts, General Procedures.....	190
S.2.5 Characterization Data for Primary Alcohol Derivatives.....	193
S.2.6 Determination of the Relative Configuration for Compounds 2.41 and 2.42	199
S.2.7 ¹ H and ¹³ C NMR Spectra.....	200
S.2.8 Chiral HPLC Traces.....	223
S.2.9 Computational Studies.....	252
S.3.10 References.....	284
S.3 Experimental Section for Chapter 3.....	285

S.3.1 General Considerations.....	285
S.3.2 Catalyst Structures.....	286
S.3.3 Synthesis of Substrates and Reagents.....	287
S.3.4 Catalyst Screening for C-H Functionalization Reactions.....	294
S.3.5 Characterization of C1 Functionalization Products.....	304
S.3.6 Characterization of C3 Functionalization Products.....	316
S.3.7 Competition Study.....	328
S.3.8 Determination of Absolute Configurations.....	333
S.3.9 Synthesis and Characterization of Stable Pyridinium Ylides.....	334
S.3.10 NMR Spectra.....	336
S.3.11 Chiral HPLC Traces.....	369
S.3.12 References.....	395
S.4 Experimental Section for Chapter 4.....	397
S.4.1 General Methods.....	397
S.4.2 List of Previously Prepared Compounds.....	398
S.4.3 Synthesis of Cyclopropanecarboxylate Ligands.....	399
S.4.4 Preparation and Characterization of Dirhodium Catalysts.....	417
S.4.5 Reactions with Other Substrates.....	423
S.4.6 Copies of NMR Spectra.....	430
S.4.7 Chiral HPLC Traces.....	456
S.4.8 Computational Studies.....	494
S.4.9 References.....	539
Appendix: X-Ray Crystallography Section.....	540

A.1 Single Crystal X-Ray Crystallographic Data and Experimental.....	540
A.2 References.....	739

List of Schemes

Scheme 1.1.1: Examples of carbenes participating in traditional organic reactions.....	2
Scheme 1.3.1: Catalytic cycle for carbene transfer reactions.....	7
Scheme 1.3.2: Examples of other types of dirhodium carbene reactions.....	12
Scheme 1.4.1: Selective reactions of carbenes without traditional donor/acceptor groups.....	16
Scheme 1.5.1: Industrial application of Rh ₂ (S-DOSP) ₄ -catalyzed cyclopropanation.....	19
Scheme 1.5.2: Cyclopropanations using Rh ₂ (<i>R-p</i> -PhTPCP) ₄ with trichloroethyl diazoacetates....	20
Scheme 1.5.3: Cyclopropanation reactions at low catalyst loading with Rh ₂ (<i>R-p</i> -PhTPCP) ₄	22
Scheme 1.6.1: The Taber synthesis of pentalenolactone E methyl ester.....	24
Scheme 1.6.2: General preparation of arylsulfonylproline catalysts.....	25
Scheme 1.6.3: Cyclization of 2-(2-benzyloxyphenyl)-2-diazoacetate using Rh ₂ (S-PTTL) ₄	30
Scheme 1.6.4: Carbene C-H insertion reactions of a diazophosphonate ester.....	31
Scheme 1.6.5: Selected applications of phthalimido-amino acid type dirhodium catalysts.....	35
Scheme 1.6.6: Synthesis of Rh ₂ (<i>R</i> -TPCP) ₄	37
Scheme 1.6.7: Comparison of Rh ₂ (<i>R</i> -BTPCP) ₄ and Rh ₂ (<i>R</i> -DOSP) ₄ in methylene chloride.....	39
Scheme 1.6.8: Primary site selectivity in the C-H insertion reactions of Rh ₂ (<i>R-p</i> -PhTPCP) ₄	41

Scheme 1.6.9: Intramolecular C-H insertion reactions to form 4,5, and 6-membered rings.....	44
Scheme 1.6.10: C-H insertion as an alternative to traditional synthetic disconnections.....	46
Scheme 1.6.11: Multifold cross-coupling to prepare Rh ₂ [<i>R</i> -3,5-di(<i>p</i> - ^t BuC ₆ H ₄)TPCP] ₄	50
Scheme 1.6.12: Unactivated primary site functionalization with Rh ₂ [<i>R</i> -tris(<i>p</i> - ^t BuC ₆ H ₄)TPCP] ₄	51
Scheme 1.6.13: C2 functionalization of n-pentane derivatives with a D ₂ -symmetric catalyst.....	54
Scheme 1.6.14: Overcoming benzylic activation with Rh ₂ (S-2-Cl-5-Br-TPCP) ₄	56
Scheme 1.6.15: Examples of tertiary site functionalization with Rh ₂ (S-TCPTAD) ₄	58
Scheme 1.6.16: Selective functionalization of the C3 equatorial C-H bond of cyclohexanes.....	60
Scheme 2.1.1: Synthesis of Rh ₂ [(1 <i>S</i> ,2 <i>R</i>)-DPCP] ₄	75
Scheme 2.1.2: Cyclopropanation reactions with E-DPCP show very low enantioselectivity.....	76
Scheme 2.2.1: Reactions used to evaluate the Rh ₂ (DPCP) ₄ catalysts.....	78
Scheme 2.2.2: Cyclopropanation reactions in the synthesis of Rh ₂ (DPCP) ₄ catalysts.....	79
Scheme 2.2.3: Strategy for Preparing Z-Diarylcyclopropanecarboxylates.....	81
Scheme 2.2.4: The DPCP ligand is too bulky to form a dirhodium tetracarboxylate complex.....	82
Scheme 2.2.5: Conventional Suzuki coupling reactions to prepare DPCP ligands.....	85
Scheme 2.2.6: The direct ligand exchange reaction to prepare the Rh ₂ (DPCP) ₄ catalysts.....	86
Scheme 3.1.1: C-H insertion into the C3/distal C-H bond of silacyclobutanes.....	106
Scheme 3.1.2: Selective C-H insertion with silacyclopentanes using aryldiazoacetates.....	107

Scheme 3.1.3: Previous approaches to the C-H functionalization of cyclohexanes.....	108
Scheme 3.1.4: Rh ₂ (S-TPPTTL) ₄ -catalyzed C-H insertion into substituted cyclohexanes.....	109
Scheme 3.1.5: The C-H functionalization of bicyclo[1.1.1]pentanes.....	112
Scheme 3.1.6: Overcoming electronic activation with Rh ₂ (2-Cl-5-BrTPCP) ₄	114
Scheme 3.2.1: Synthesis of arylcyclobutanes substrates.....	119
Scheme 3.2.2: Synthesis of pyridyl cyclobutanes.....	121
Scheme 3.2.3: Scope of the C-H functionalization reaction at C1 (1/2).....	122
Scheme 3.2.4: Scope of the C-H functionalization reaction at C1 (2/2).....	123
Scheme 3.2.5: Scope of the C-H functionalization reaction at C3 (1/2).....	125
Scheme 3.2.6: Scope of the C-H functionalization reaction at C3 (2/2).....	126
Scheme 3.2.7: Unexpected formation of stable pyridinium ylides from compound 3.72	127
Scheme 3.2.8: Reaction to form a pyridinium ylide from 2,4,6-collidine.....	129
Scheme 4.2.1: Stereoselective cyclopropanation reactions with α-cyclohexylstyrene.....	141
Scheme 4.2.2: Preparation of diastereomeric 2-Cy-DPCP ligands.....	142
Scheme 4.2.3: Ligand exchange reaction to form the cyclohexyl-DPCP catalysts.....	143
Scheme 4.2.4: First generation synthesis of Rh ₂ [(1 <i>R</i> ,2 <i>R</i>)-2-TMS-DPCP] ₄	148
Scheme 4.2.5: Rapid synthesis of 2-TMS-DPCP catalysts from trichloroethyl diazoacetates.....	150
Scheme 4.2.6: Primary site-selective C-H insertion reactions using catalysts 4.11 or 4.8	155

Scheme 4.2.7: Cyclopropanation of styrenes with the novel silyl-DPCP catalysts.....	157
Scheme 4.2.8: Cyclopropanation at very high TON using catalyst 4.57 in dimethyl carbonate....	158

List of Tables

Table 1.4.1: Reactions of dirhodium tetraprolinates with different types of diazo compound.....	14
Table 2.2.1: Ligand screen for the cross-coupling reaction.....	83
Table 2.2.2: Cyclopropanation of styrene with Rh ₂ (DPCP) ₄ catalysts.....	87
Table 2.2.3: C-H insertion reactions of 4-ethyltoluene with DPCP catalysts.....	88
Table 2.2.4: C-H insertion reactions with 4-isopropyltoluene using Rh ₂ (DPCP) ₄ catalysts.....	90
Table 3.2.1: Catalyst screening for regioselectivity with (4- <i>tert</i> -butyl)phenylcyclobutane.....	116
Table 4.2.1: Evaluation of cyclohexyl-DPCP catalysts in asymmetric cyclopropanation.....	145
Table 4.2.2: Evaluation of cyclohexyl-DPCP catalysts in C-H functionalization reactions.....	146
Table 4.2.3: Evaluation of 2-TMS-DPCP catalysts in C-H functionalization reactions.....	152

List of Figures

Figure 1.2.1: The solid state structure of dirhodium tetraacetate dihydrate.....	3
Figure 1.2.2: MO diagram for a dirhodium tetracarboxylate complex of D _{4h} symmetry.....	4
Figure 1.2.3: Lewis structures for a generic dirhodium carbene complex.....	5
Figure 1.2.4: FMO interactions of the dirhodium and carbene fragments.....	6
Figure 1.3.1: Transition states for C-H insertion and cyclopropanation with aryldiazoacetates.....	8

Figure 1.5.1: Cyclopropanation of alkenes versus C-H functionalization.....	18
Figure 1.6.2: Possible ligand orientations of Rh ₂ (DOSP) ₄ with point group classifications.....	25
Figure 1.6.3: Proposed model for asymmetric induction with a D ₂ -symmetric catalyst.....	28
Figure 1.6.4: The crystal structure of Rh ₂ (S-TCPTAD) ₄ shows an (α,α,α,α)-C ₂ conformation.....	32
Figure 1.6.5: The Fox model for asymmetric induction with Rh ₂ (S-PTTL) ₄	36
Figure 1.6.6: Illustration of Hansen's proposal that the 2- <i>cis</i> aryl blocks the reaction site.....	37
Figure 1.6.7: Catalyst-controlled site selectivity in the reactions of 2-methylpentane.....	49
Figure 2.1.1: Illustration of the substituent effect at the C1 aryl group of TPCP catalysts.....	73
Figure 2.2.1: Solid state X-ray structures of the <i>E</i> -DPCP catalysts 2.5 and 2.31	92
Figure 2.2.2: Two polymorphic crystals were observed for catalyst 2.9	93
Figure 2.2.3: Energy-minimized conformations of Rh ₂ [(1 <i>R</i> ,2 <i>S</i>)-DPCP] ₄	95
Figure 2.2.4: Energy-minimized conformations of Rh ₂ [(1 <i>R</i> ,2 <i>R</i>)-DPCP] ₄	97
Figure 3.1.1: Challenges in the C-H functionalization reactions of substituted cyclobutanes.....	113
Figure 3.2.1: Photographs of the pyridinium ylide solution in Et ₂ O/hexanes.....	128
Figure 3.2.2: The solid state structure of compound 3.105 obtained by X-ray diffraction.....	129
Figure 3.2.3: Proposed explanation for the solvatochromism of the pyridinium ylide 3.105	130
Figure 4.1.1: Dirhodium cyclopropanecarboxylate catalyst types relevant to the present study...	137
Figure 4.2.1: The solid state structure of Rh ₂ [(1 <i>R</i> ,2 <i>S</i>)-2-CyDPCP] ₄	144

Figure 4.2.2: Structures of the catalyst 4.11 and 4.8	154
Figure 4.2.3: The solid state structure of catalyst 4.6 observed by X-ray diffraction.....	159
Figure 4.2.4: The crystal structure of Rh ₂ (S-PTPA) ₄	160
Figure 4.2.5: Comparison of the crystal structures of 2-TMS-DPCP and TPCP catalysts.....	161
Figure 4.2.6: Computed minimum energy conformations of catalyst 4.6	163
Figure 4.2.7: Computed minimum energy conformations of catalyst 4.8	164

List of Charts

Chart 1.3.1: Commonly observed byproducts of “failed” dirhodium carbene reactions.....	10
Chart 1.4.1: Classification of diazo compounds based on their substituent groups.....	13
Chart 1.6.1: Highly selective catalysts for unactivated primary, secondary, or tertiary sites.....	48
Chart 1.6.2: 3D structures of some highly selective dirhodium catalysts for C-H insertion.....	59
Chart 2.1.1: Three types of dirhodium cyclopropanecarboxylate catalyst.....	71
Chart 2.2.2: Ligands evaluated for the multifold cross-coupling reaction with 2.31	84
Chart 3.1.1: Examples of cyclobutanes in pharmaceutical agents and natural products.....	104
Chart 3.2.1: Relative rates of functionalization for catalysts 3.33 and 3.43	118
Chart 4.1.1: Selective C-H functionalization of complex molecules using TPCP catalysts.....	136
Chart 4.1.2: Dirhodium cyclopropanecarboxylate catalysts examined in the present study.....	139

List of Abbreviations

Ac	acetyl
APCI	atmospheric pressure chemical ionization
Ar	aryl
Bn	benzyl
Bu	butyl
c	concentration in g/100 mL
cal	calorie
Cy	cyclohexyl
dba	dibenzylideneacetone
DCC	N,N'-dicyclohexylcarbodiimide
DCE	1,2-dichloroethane
DCM	dichloromethane
deg	degree
DIBAL-H	diisobutylaluminum hydride
DMAP	4-dimethylaminopyridine
DMF	N,N-dimethylformamide
DMP	Dess-Martin periodinane

DMSO	dimethyl sulfoxide
dppf	1,1'-bis(diphenylphosphino)ferrocene
dr	diastereomeric ratio
<i>E</i>	entgegen (opposite)
EDG	electron-donating group
ee	enantiomeric excess
FTIR	Fourier transform infrared spectroscopy
Et	ethyl
equiv	equivalent
ESI	electrospray ionization
EWG	electron-withdrawing group
FMO	frontier molecular orbital
g	gram
h	hour
HOMO	highest occupied molecular orbital
HPLC	high pressure liquid chromatography
HRMS	high resolution mass spectrometry
Hz	Hertz

IR	infrared
L	ligand
LUMO	lowest unoccupied molecular orbital
<i>m</i>	<i>meta</i> - substitution
Me	methyl
min	minute
mol	mole (amount of substance)
mp	melting point
MS	mass spectrometry
NMR	nuclear magnetic resonance
<i>o</i>	<i>ortho</i> - substitution
o-NBSA	<i>ortho</i> -nitrobenzenesulfonyl azide
<i>p</i>	<i>para</i> - substitution
p-ABSA	<i>para</i> -acetamidobenzenesulfonyl azide
Ph	phenyl
refl	reflux
rr	regioisomeric ratio
rt	retention time

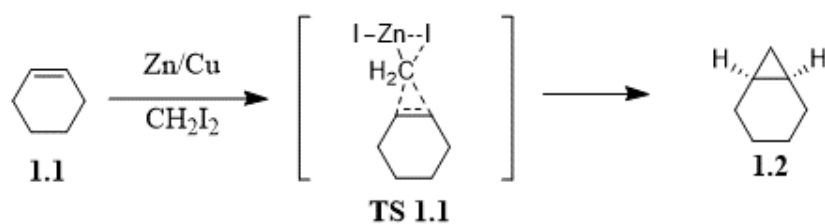
r.t.	room temperature
SiO₂	silicon dioxide (silica gel)
TCE	2,2,2-trichloroethyl
temp	temperature
<i>t</i>	tertiary
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	trimethylsilyl
<i>Z</i>	zusammen (together)
[α]_D^{<i>X</i>}	specific rotation at 589 nm and <i>X</i> degrees Celsius
Δ	heat applied

Chapter 1: General Introduction to Dirhodium Catalysts and Donor/Acceptor Carbenes

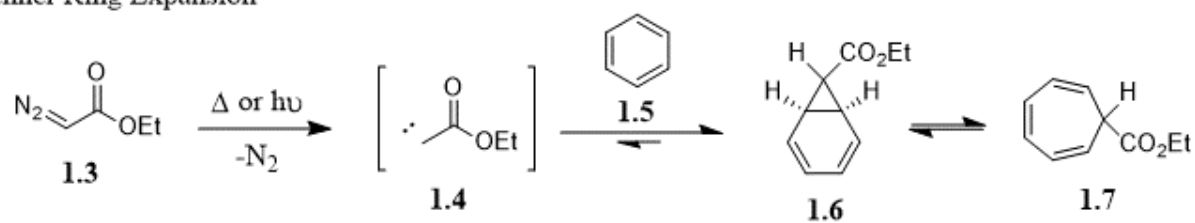
1.1 Introduction

The strategic application of carbene chemistry can often streamline the synthesis of organic compounds.^{1,2,3} Free carbenes lack a complete octet of electrons in their valence shell, and usually react to form products with a more stable electron configuration. While certain types of stabilized carbenes are persistent and can even be isolated,⁴ many others are unstable and can undergo reactions with functional groups such as the π -bonds of benzene rings⁵ or the C-H bonds of alkanes.⁶ Over more than a century, reactive carbenes have been utilized to develop a variety of practical synthetic methods. Some examples are shown in Scheme 1.1.1.⁷ In the Simmons-Smith reaction, alkenes such as cyclohexene **1.1** can form cyclopropanes like **1.2** via the zinc carbenoid shown in transition state **TS 1.1**. In the Buchner reaction, diazo compounds such as **1.3** decompose to free carbenes to react with aromatic rings, forming the equilibrating products **1.6** and **1.7**. Diazo ketones with an *s-trans* geometry such as **1.8** are decomposed to free carbenes which rearrange to make ketenes of the type **1.10** in the Wolff rearrangement. Using the Wulff-Dötz benzannulation reaction, chromium carbenes like compound **1.12** can be used as starting materials to prepare a variety of functionalized naphthoquinones including vitamin K₁ (**1.14**). A key development in this field was the discovery that certain transition metals (such as rhodium⁸, copper⁹, silver¹⁰, and gold¹¹) can decompose diazo groups to form electrophilic metal-stabilized carbenes. This has led to many advancements, including numerous applications in the synthesis of medicines and natural products.^{12,13,14}

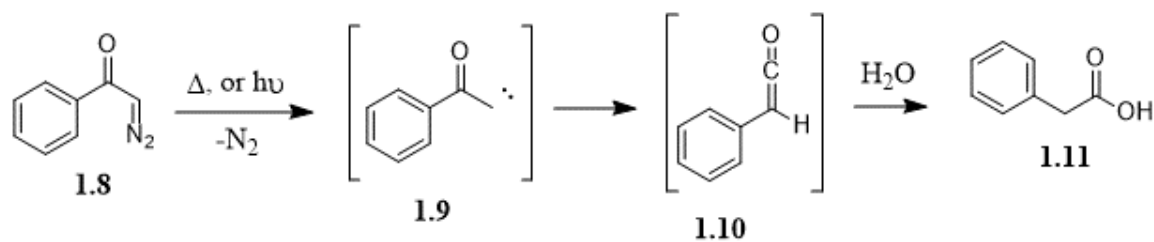
Simmons-Smith Reaction



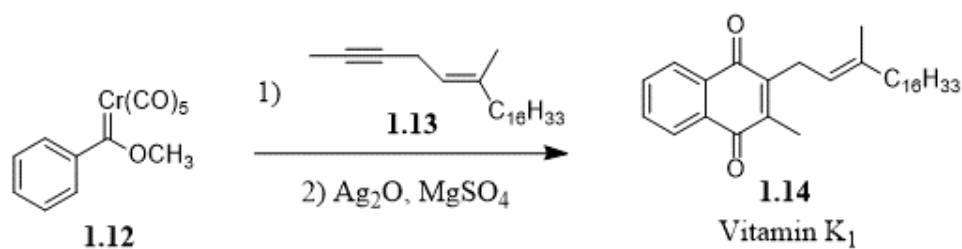
Buchner Ring Expansion



Wolff Rearrangement



Dötz Benzannulation



Scheme 1.1.1: Examples of carbenes participating in traditional organic reactions⁷

1.2 Structure of Dirhodium Tetracarboxylates

The most effective catalysts for decomposing diazo compounds are the rhodium(II) tetracarboxylates,¹⁵ which are the focus of this work. In most cases, these complexes are prepared via an exchange reaction using an excess of the desired ligand and a suitable rhodium(II) precursor.¹⁶ The structure of dirhodium tetraacetate dihydrate was first elucidated by Cotton¹⁷ in 1971 using X-ray crystallography (Figure 1.2.1) and it illustrates several essential

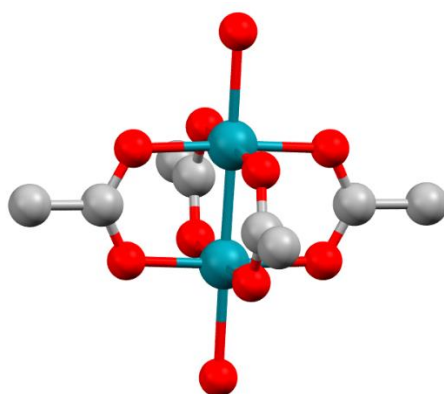


Figure 1.2.1: The solid state structure of dirhodium tetraacetate dihydrate.

features of dirhodium tetracarboxylates that are relevant to catalysis. Each rhodium atom has an electron count of 18 when both two-electron donor ligands (in this example, water molecules) are bound to the complex, or 16 electrons when there are no coordinated axial ligands. Due to the greater stability of the 18-electron complex, dirhodium tetracarboxylates readily coordinate to many solvents and nucleophiles.¹⁸ The oxidation state at each rhodium atom is (II), with rhodium having a d^7 electron configuration. Two sigma-bonded rhodium atoms lie at the center of a planar “disc” or “paddlewheel” formed by four μ_2 -acetato ligands, each bound to the metal atoms via oxygen and arranged at 90 degree angles relative to each other. A molecular orbital diagram for a generic dirhodium tetracarboxylate complex is shown in Figure 1.2.2.

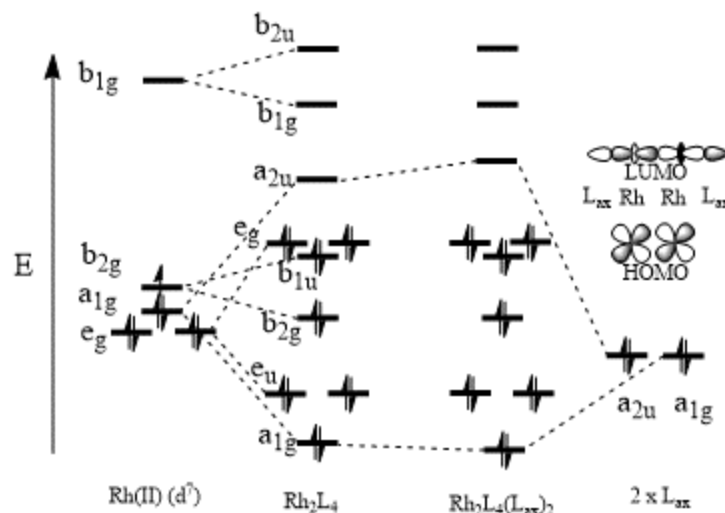


Figure 1.2.2: MO diagram for a dirhodium tetracarboxylate complex of D_{4h} symmetry.¹⁹ (x,y axes are directed toward the equatorial ligands, z axis along the Rh-Rh bond.)

The MO diagram illustrates the irreducible representations of the orbitals in the complex, the spatial orientation of the frontier MOs, and how the addition of axial ligands will result in a more stable 18-electron configuration for Rh.¹⁹ Due to this arrangement, all of the synthetically relevant steps in the catalytic cycle occur at the axial sites.

The symmetry properties of the frontier molecular orbitals of the tetracarboxylate complex and the carbene fragment allow them to form a three-center/four electron bond (Figure 1.2.3). This interaction imparts significant stability to the Rh-C π^* -molecular orbital, which is the LUMO of the carbene complex. By lowering this orbital, the electrophilicity of the carbene is significantly increased relative to many other types of metal carbene complex. The three-center/four electron bond can also be conceptualized using Lewis structures, which illustrate the delocalization of electrons among the three atoms (Figure 1.24). There is partial double bond character for both the Rh-Rh and Rh-C bonds, but the major resonance structures feature single

bonds between all three atoms. Because of the “super-electrophilicity” of the dirhodium carbene, it is capable of reacting with very poor nucleophiles such as unactivated C-H bonds.¹⁹

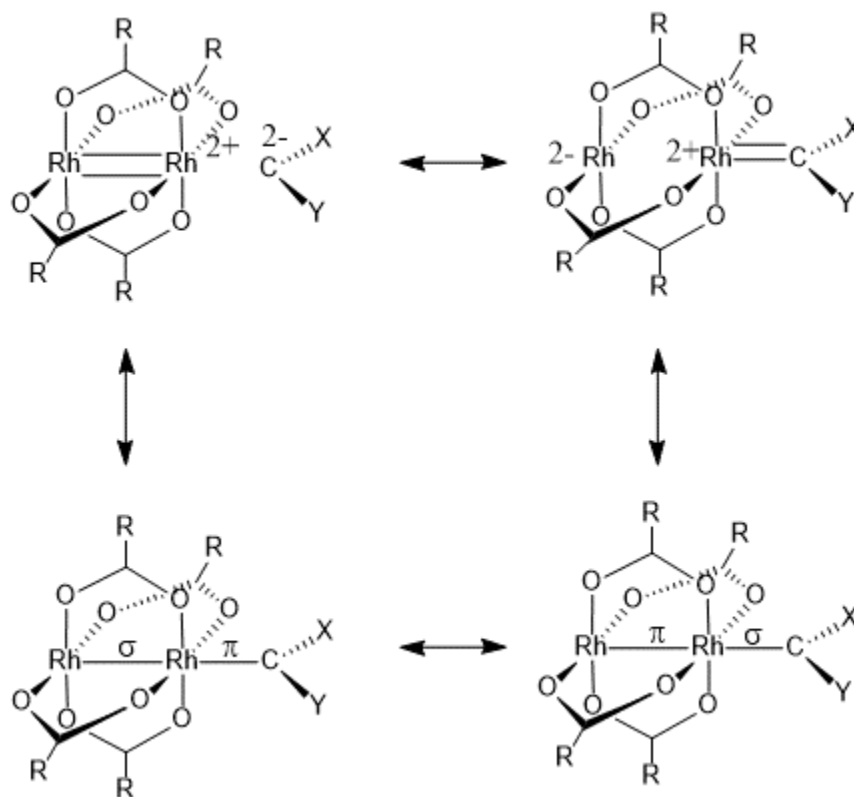


Figure 1.2.3: Lewis structures for a generic dirhodium carbene complex. This depiction illustrates the three-center four electron bond between the two rhodium atoms and the carbene.¹⁹

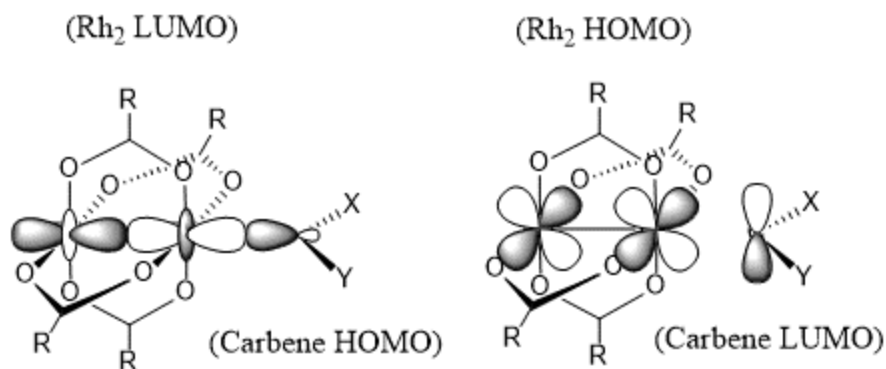
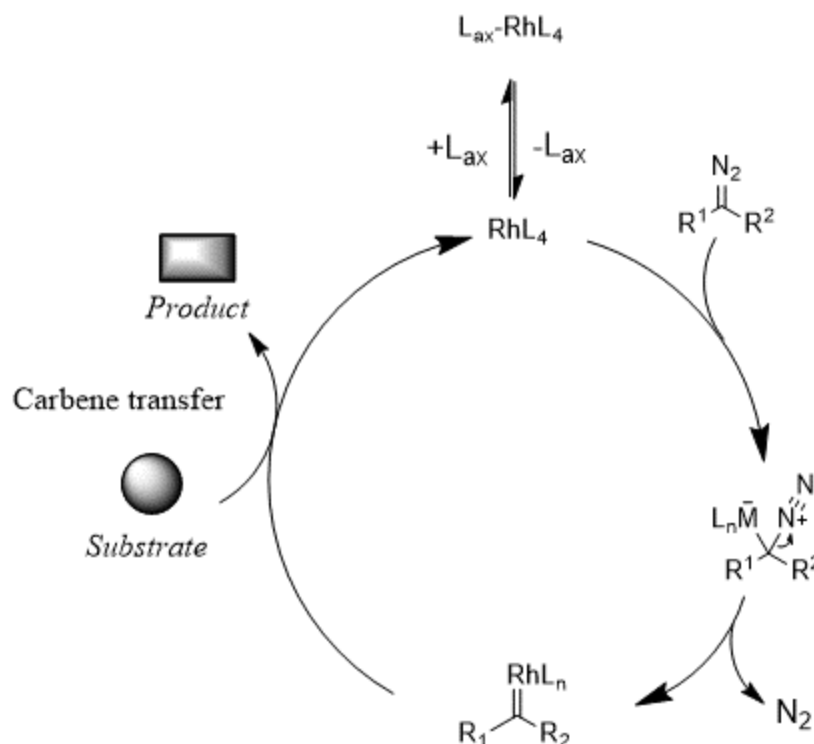


Figure 1.2.4: FMO interactions of the dirhodium and carbene fragments.¹⁹

The fact that the central paddlewheel of dirhodium tetracarboxylate complexes is planar also has significant implications for the design of regio- and enantioselective catalysts. A ligand such as acetate which has its steric bulk pointing entirely toward the periphery of the disc (away from the carbene) cannot block an incoming substrate molecule from the axial carbene ligand. For a catalyst design to be effective, it must limit the conformational space of the ligands to the extent that they cannot all lie flat in the plane of the paddlewheel.²⁰

1.3 Mechanism of Dirhodium Carbene Reactions

The reactions of dirhodium carbenes are challenging to study experimentally due to the short lived and highly reactive nature of these chemical species, but over the past decades some of their mechanistic features have been elucidated.²¹ A generalized catalytic cycle depicting the formation and reaction of a dirhodium carbene is shown in Scheme 1.3.1.



Scheme 1.3.1: Catalytic cycle for carbene transfer reactions.²²

A free axial coordination site must be available on one of both faces of the catalyst to react with the diazo compound. The rate limiting step of the catalytic cycle is the extrusion of dinitrogen to form the carbene intermediate.²² Transfer of the carbene unit onto the substrate may proceed as a concerted reaction or in discrete steps but is necessary to turn over the catalyst.

Reactive conformational models for simplified cyclopropanation and C-H insertion²³⁻²⁴ reactions with aryldiazoacetates are shown in Figure 1.3.1. In both cases, the transition states (**TS 1.2** and **TS 1.3**) are concerted and asynchronous, and there is substantial build-up of a partial positive charge at the reaction site of the substrate.

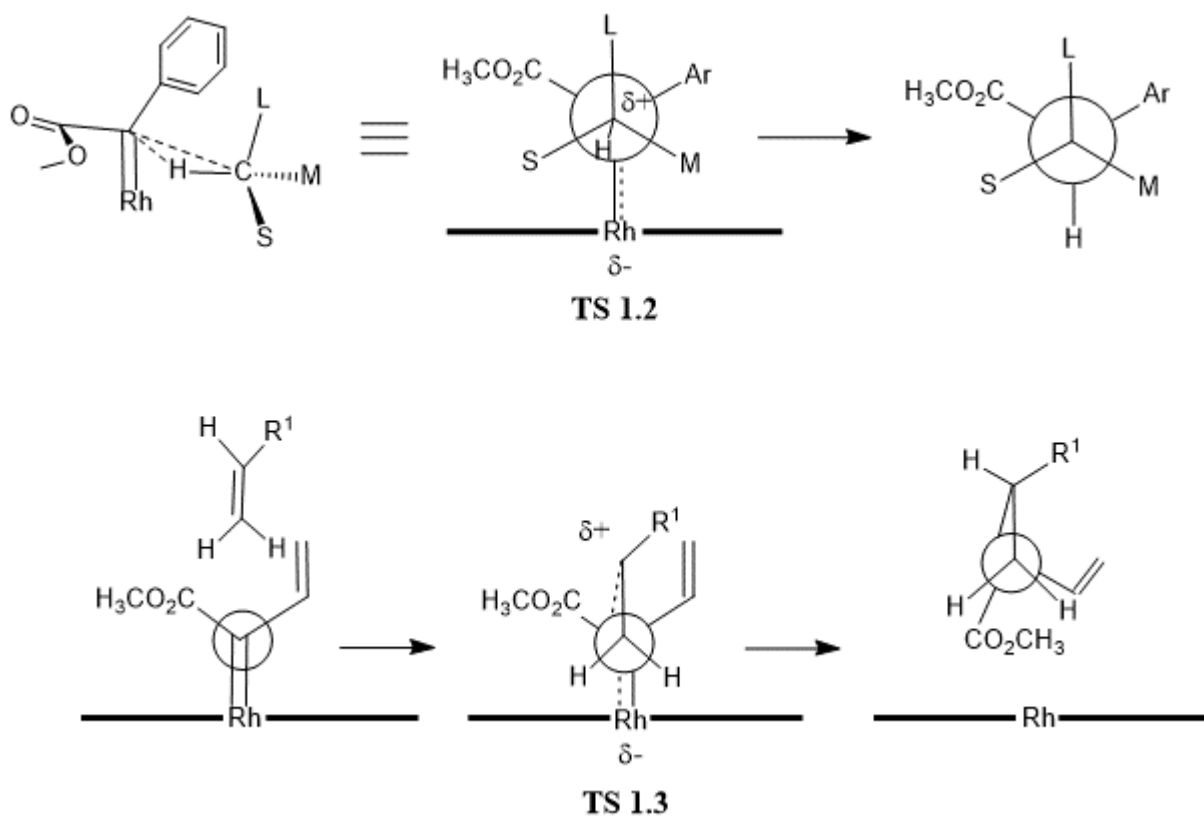


Figure 1.3.1: Transition states for C-H insertion and cyclopropanation with aryldiazoacetates.²³⁻²⁴

In the C-H insertion reaction, neighboring electron donating substituents on the substrate (**S**, **M**, or **L**) can help mitigate this charge buildup, resulting in innate selectivity for more substituted, electronically stabilized C-H sites.^{6,15,23} The placement of both donor and acceptor substituents on the carbene often leads to an increase in stereoselectivity because the transition state is more ordered and sterically congested than in the acceptor-only case²³. As shown, the electron-donating phenyl group of the carbene will preferentially remain in conjugation with the C=Rh π -bond to facilitate charge delocalization, while the plane containing the ester remains roughly orthogonal to the C-Rh bond.

When oriented in this manner, the effective steric demand of the acceptor group is increased, which prevents the substrate molecule from approaching the carbene center from its direction. Because the dirhodium paddlewheel will act as a sterically demanding “surface”, the major diastereomer of C-H insertion reactions can often be predicted using a simple Newman projection analysis. The sterically imposing ester group also has a significant influence on the transition state for cyclopropanation. In this case, an end-on approach of the alkene group to the carbene will minimize steric clash with the ester while still allowing sufficient orbital overlap for the reaction to occur.

The models shown above explain why consistently high diastereoselectivity is observed with donor/acceptor dirhodium carbenes even when the catalyst is sparsely functionalized. They can also be applied to accurately predict the major diastereomer of the reactions^{15,23}. When the catalyst pocket is chiral and has a well-defined shape, high enantioselectivity may be observed and site-selectivity for less electronically activated C-H bonds can be achieved¹⁵. Thus, by changing the structure of the catalyst the reaction can be tuned to give high *ee* and site selectivity at C-H sites in a variety of different chemical environments.

The mechanism of the carbene reaction has implications for the manner in which the reactions should be conducted. The decomposition of the donor/acceptor diazo component usually occurs rapidly at room temperature (20 °C) or below²². This step is very thermodynamically favorable because it results in the extrusion of dinitrogen gas and is exothermic. Because of the high reactivity of dirhodium carbenes, they must be trapped efficiently for a high yielding reaction to occur. The intended substrate must react quickly enough to outcompete side reactions of the rhodium carbene with the free diazo compound and when possible, the solvent. If the concentration of the carbene trap is too low or the concentration of the diazo compound and

rhodium carbene become sufficiently high, a mixture of carbene dimerization products will be often be produced (Chart 1.3.1).²⁵ The reaction of two carbene units can generate an alkene, while the reaction of the carbene with a diazo compound can generate azines⁷. Slow addition of the diazo compound as a dilute solution is often sufficient to avoid these problems. In some cases, ketones can be observed in the mixtures from oxo-transfer to the carbene. In the case of efficient carbene trapping, the reaction often proceeds in good to excellent yield²¹. Because water molecules are very small and nucleophilic, it must be strictly excluded in rhodium carbene reactions to avoid OH-insertion byproducts. Because of the highly reactive and electrophilic nature of the rhodium carbene, they may generate stereoisomeric mixtures of products, particularly when the substituents of the carbene group or the catalyst structure are not well-matched to a specifically desired reaction.

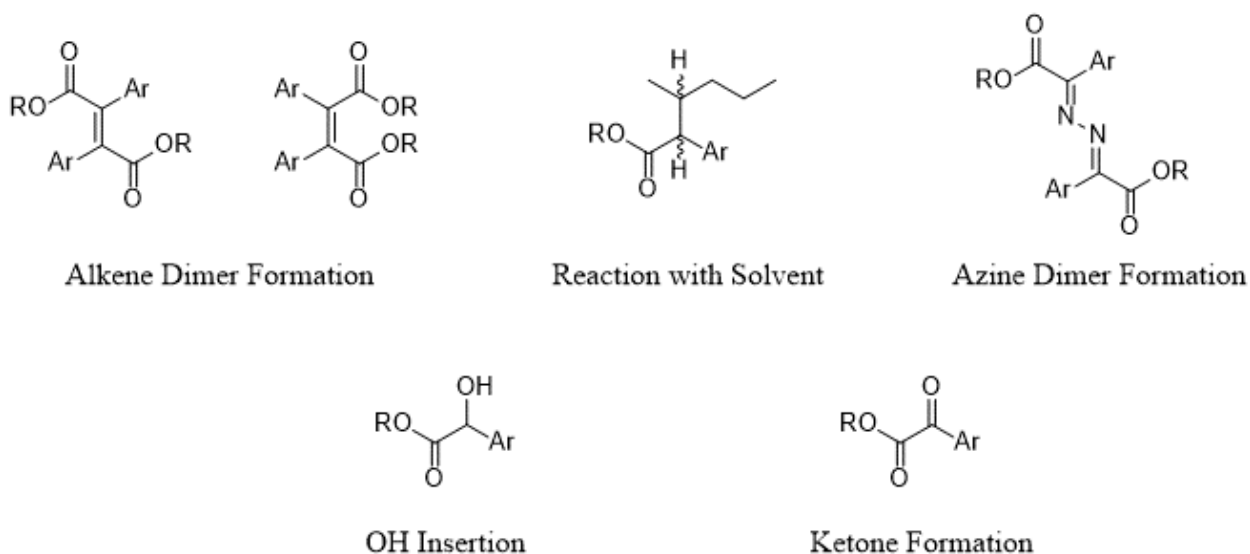
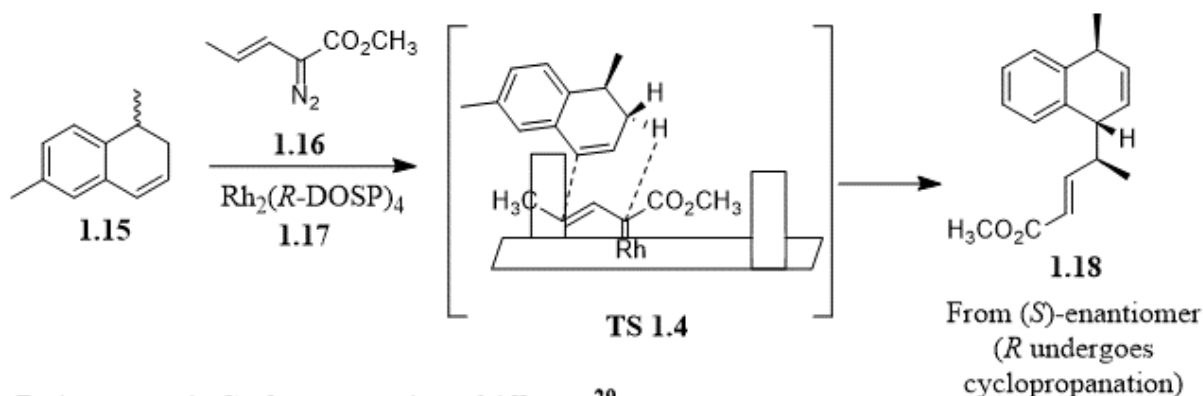


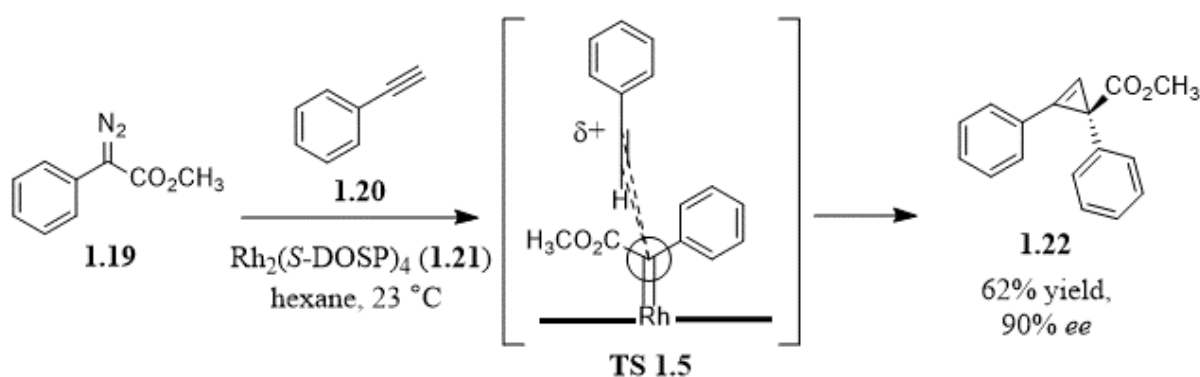
Chart 1.3.1: Commonly observed byproducts of "failed" dirhodium carbene reactions.^{7,21,25}

While the most popular applications for dirhodium carbenes involve the cyclopropanation²⁶ and C-H insertion²⁷ reactions depicted in Figure 1.3.1, many other classes of transformations have been reported for these versatile intermediates. Some examples of these other reactions are illustrated in Scheme 1.3.2.²⁸⁻³³ An enantiodivergent C-H Cope reaction is depicted in **1.3.2A**²⁸. In this entry, only the (*S*)-enantiomer of 1,6-dimethyl-1,2-dihydronaphthalene (**1.15**) will react to form product **1.18** when Rh₂(*R*-DOSP)₄ (**1.17**) is used as the catalyst, and the (*R*)-enantiomer undergoes cyclopropanation at the 1,2-disubstituted alkene group (product not shown). The observed stereochemistry of the C-H Cope product can be rationalized by considering boat-like transition state **1.4**. Entry **1.3.2B**²⁹ illustrates how alkynes can react to generate cyclopropene rings such as **1.22** with high enantioselectivity. The reaction is likely to occur via an end-on approach of the alkyne (**TS 1.5**), because disubstituted alkynes generally do not react with donor/acceptor carbenes. When a carbene is located in proximity to a carbonyl group, as in example **1.3.2C**³⁰, it can form ylide intermediates such as **1.24**. Carbonyl ylides are 1,3-dipoles that can undergo cycloaddition with π -bonds to form products such as **1.25**, and have been widely applied in the synthesis of complex alkaloid natural products.³¹ Entry **1.3.2D** depicts an example of a [4+3] cycloaddition reaction in which a carbene derived from diazo compound **1.27** reacts with the furan **1.26** to furnish the cyclopentyl-fused oxabicyclo[3.2.1]octane **1.29**. As can be seen from these examples as well as others reported in the chemical literature³⁴, dirhodium carbenes show a remarkable diversity of reactivity and can be used to good effect in asymmetric synthesis.

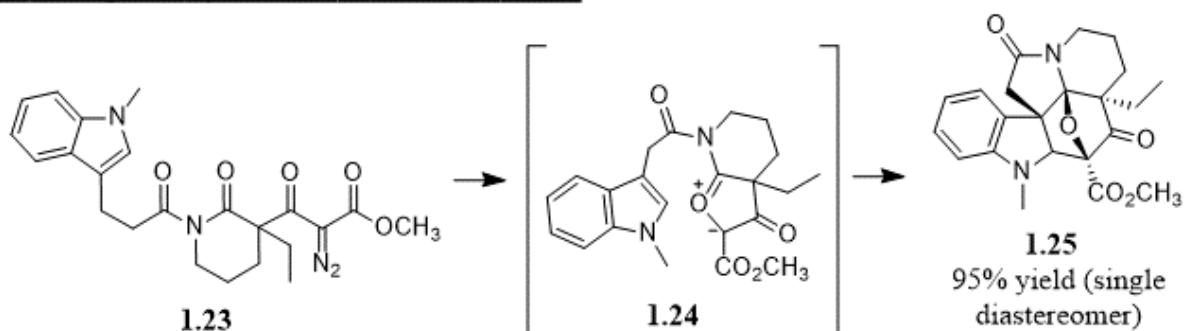
A. The Enantiodivergent C-H Cope Reaction²⁸



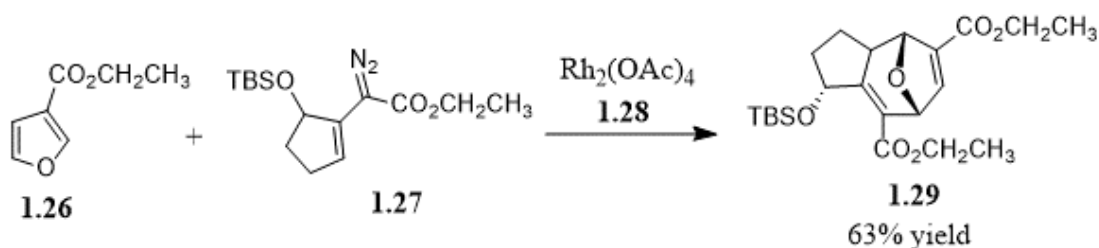
B. Asymmetric Cyclopropanation of Alkynes²⁹



C. 1,3-Dipolar Cyclization of Carbonyl Ylides³⁰



D. Rhodium-Catalyzed [4+3] Cycloaddition³²



Scheme 1.3.2: Examples of other types of dirhodium carbene reactions.²⁸⁻³²

One of the grand challenges of modern organic chemistry is to develop new synthetic methods for site-selective C-H functionalization that are highly selective for a single position within a molecule that can also be directed to a desired site by the catalyst.³⁵ In the case of dirhodium carbenes, extensive work has shown that this is indeed possible,³⁶ but another critical factor controlling the outcome and selectivity of the reaction is the structure of the carbene group.

1.4 Strengths and Limitations of Donor/Acceptor Carbenes

Dirhodium carbenes and the diazo compounds from which they are derived can be divided into classes based on the electronic properties of the two substituents at the carbon atom (Chart 1.4.1). Of these classes, the most electron-deficient types (acceptor/acceptor and acceptor only) generally show poor site- and stereoselectivity for intermolecular reactions due to the fact that acceptor groups tend to not engage in conjugation with the carbene group, leading to less orderly transition states.³⁷ The acceptor groups do not stabilize the electrophilic character of the carbene center, and carbenes of these types are often more reactive than donor-stabilized carbenes.¹⁵

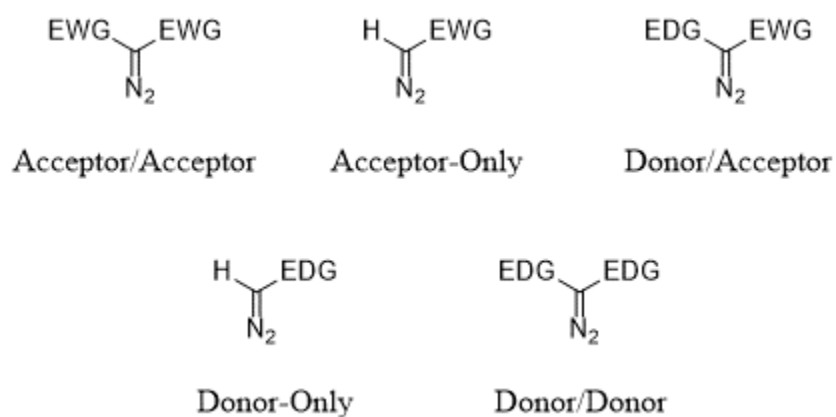
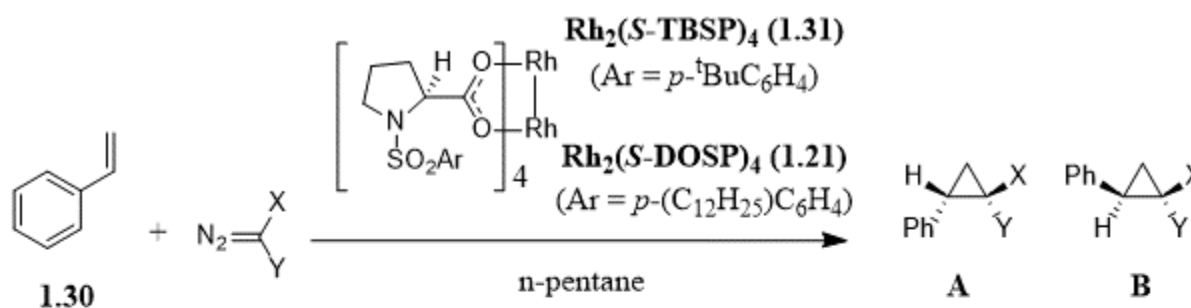


Chart 1.4.1: Classification of diazo compounds based on the electronic properties of the substituent groups.

Due to the reasons described in section 1.3, donor/acceptor dirhodium carbenes such as aryldiazoacetates frequently react with good to excellent site- and stereoselectivity in a variety of carbene transformations, but it is often challenging to achieve similar results with the other types. This effect is illustrated by the cyclopropanation of styrene with $\text{Rh}_2(\text{TBSP})_4$ and $\text{Rh}_2(\text{DOSP})_4$,³⁷ two first generation chiral catalysts commonly employed in the Davies group (Table 1.4.1).



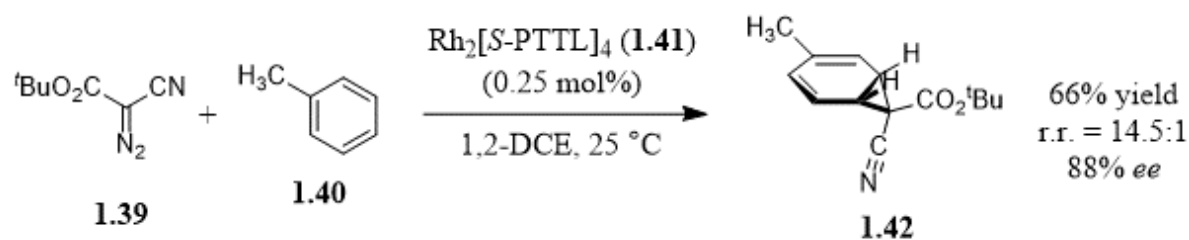
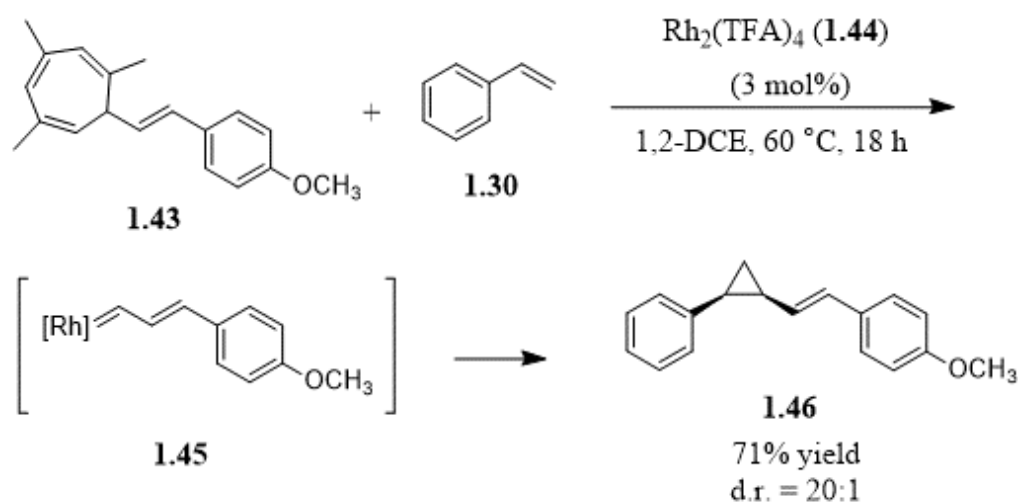
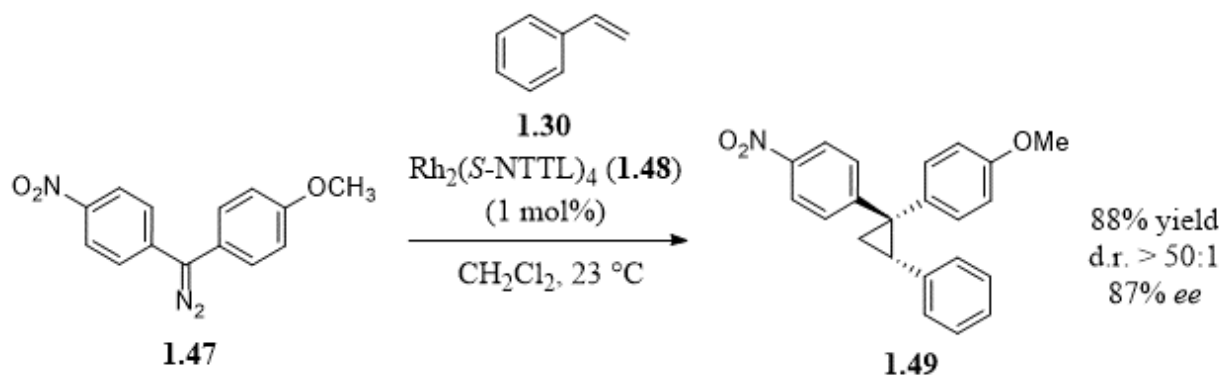
Diazo	X	Y	Catalyst	Yield	A : B	ee of A	ee of B
1.32	CO ₂ CH ₃	CH=CHPh	Rh ₂ (S-TBSP) ₄	91%	98 : 2	90%	n.d.
1.32	CO ₂ CH ₃	CH=CHPh	Rh ₂ (S-DOSP) ₄	91%	98 : 2	94%	n.d.
1.33	CO ₂ CH ₃	H	Rh ₂ (S-TBSP) ₄	80%	55 : 45	6%	30%
1.34	CO ₂ CH ₃	COCH ₃	Rh ₂ (S-TBSP) ₄	57%	75 : 25	5%	8%
1.35	CO ₂ CH ₃	CO ₂ CH ₃	Rh ₂ (S-TBSP) ₄	63%	N/A	7%	N/A
1.36	CO ₂ CH ₃	CH ₃	Rh ₂ (S-DOSP) ₄	45%	80 : 20	12%	58%
1.19	CO ₂ CH ₃	Ph	Rh ₂ (S-TBSP) ₄	90%	98 : 2	87%	n.d.
1.37	H	CH ₂ =CH ₂	Rh ₂ (S-DOSP) ₄	<10%	31 : 69	<5%	17%
1.38	H	Ph	Rh ₂ (S-DOSP) ₄	<10%	35 : 65	<5%	N/A

Table 1.4.1: Reactions of dirhodium tetraprolinates with different types of diazo compound.³⁷

In this study, donor/acceptor carbenes frequently gave enantiomeric excess values over 80% and favored the *E* diastereomer by a ratio of 98:2, while other types struggled to achieve even modest

enantioselectivity and showed inferior d.r. This observation can be rationalized by considering the steric and electronic influence of the substituents on the metal-bound carbene: pulling density away from the carbene will make it more electrophilic and reactive toward nucleophiles, while electron-donating groups such as aryl or vinyl will reduce electrophilic reactivity. Donor groups tend to remain in conjugation with the Rh=C π -bond, while acceptor substituents often do not, and are thus more sterically imposing than donor groups. With only a single acceptor group, lower stereospecificity and stereoselectivity are observed in these intermolecular reactions.³⁸

There are many synthetic applications for conventional donor/acceptor carbenes, but the constraint that the carbene substituents must be restricted to specific groups in order to achieve acceptable regio- and stereoselectivity significantly limits the practical utility of dirhodium carbene methods in synthesis. While the reactions of the other types of diazo compound are often not selective when conventional EDG and EWG are placed on the carbene, there are some notable exceptions to this rule. Some examples³⁹⁻⁴¹ of successful strategies using other types of carbene precursor are shown in Scheme 1.4.1. A recurring feature of all of these strategies is the design of the reaction such that one of the carbene substituents is likely to remain in-plane and conjugated with the Rh=C π - system.

A. Cyclopropanation of Arenes with Cyanodiazooacetates³⁹B. *In situ* formation of Donor Rhodium Carbenes via Retro-Buchner Reactions⁴⁰C. Diarylcarbenes that Behave as Donor/Acceptor Carbenes⁴¹**Scheme 1.4.1:** Selective reactions of carbenes without traditional donor/acceptor groups.³⁹⁻⁴¹

Using an appropriate chiral catalyst, cyanodiazooacetates such as **1.39** can undergo highly regio- and enantioselective cyclopropanation reactions with functionalized arenes³⁹. The fact that reasonably high yield, *rr*, and *ee* are observed is significant because the reaction uses an acceptor/acceptor type carbene. The cyano- group has two pi bonds and is cylindrically symmetric, so it tends to remain in conjugation with the carbene group even though it is electron-withdrawing. As a consequence, the carbene is very electrophilic and reactive but achieving a later, more well-ordered transition state is more feasible than with conventional acceptor/acceptor carbenes.

Donor-only rhodium carbenes tend to be challenging to prepare and are often unstable, but a strategy recently developed by the Echavarren group has enhanced their utility in synthesis.⁴⁰ The Buchner ring expansion (see scheme 1.1.1) is reversible, and in some instances norcaradiene products generated in this reaction are able to act as carbene precursors in the presence of a suitable transition metal catalyst such as a dirhodium complex. When a vinylic cycloheptatriene such as **1.43** is used, the resulting donor-only metal carbene is proficient in a number of reactions such as *cis*-diastereoselective cyclopropanation. While this reaction shows excellent diastereoselectivity, no enantioselective variant has yet been reported. Achieving high *ee* in this transformation would likely be challenging because of the diminished steric demand in the catalyst pocket when only one substituent group is present on the carbene.

The use of two aryl groups with substantially different electron density enables the carbene to behave as though it were a donor/acceptor type even though aryl substituents have traditionally been used as donor groups.⁴¹ In these reactions, the electron-rich aryl rings tend to be more coplanar with the carbene π -system, while the electron-deficient aryls do not. Due to this effect, the reaction of compounds such as **1.47** can form cyclopropanes like compound **1.49** with high

stereoselectivity similar to what might be obtained using a traditional donor/acceptor carbene group.

1.5 Stereoselective Cyclopropanation Reactions

One of the most powerful applications of dirhodium carbene chemistry is the highly diastereoselective and enantioselective [2+1] cyclization reaction with alkene groups to form cyclopropanes.⁴⁵ When donor/acceptor diazo compounds are used as reactants, the reaction is highly diastereoselective for *cis* cyclopropanes.⁴⁶ The order of reactivity for the alkene component is shown in Figure 1.5.1. It is worth noting that while donor/acceptor carbenes do not undergo cyclopropanation with hindered alkenes, even tetrasubstituted alkenes form cyclopropanes when ethyl diazoacetate is used as the carbene precursor.⁴⁷ When possible, alkenes which are less reactive to cyclopropanation will instead undergo C-H insertion at an allylic position.

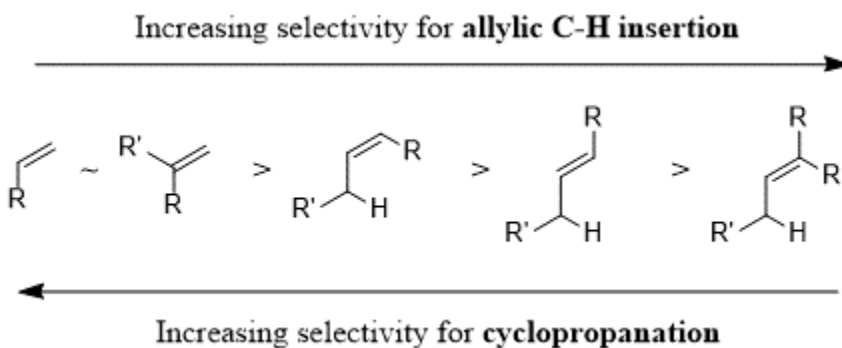
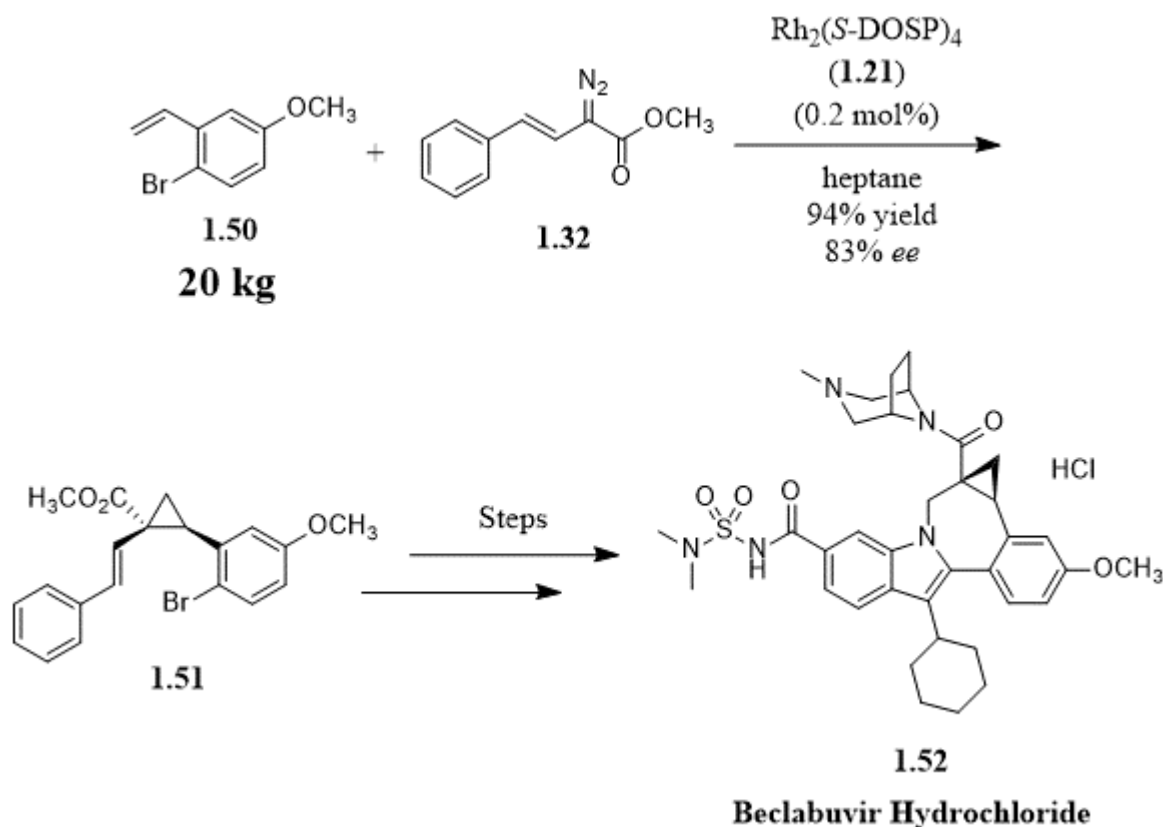


Figure 1.5.1: Cyclopropanation of alkenes versus C-H functionalization.¹⁵

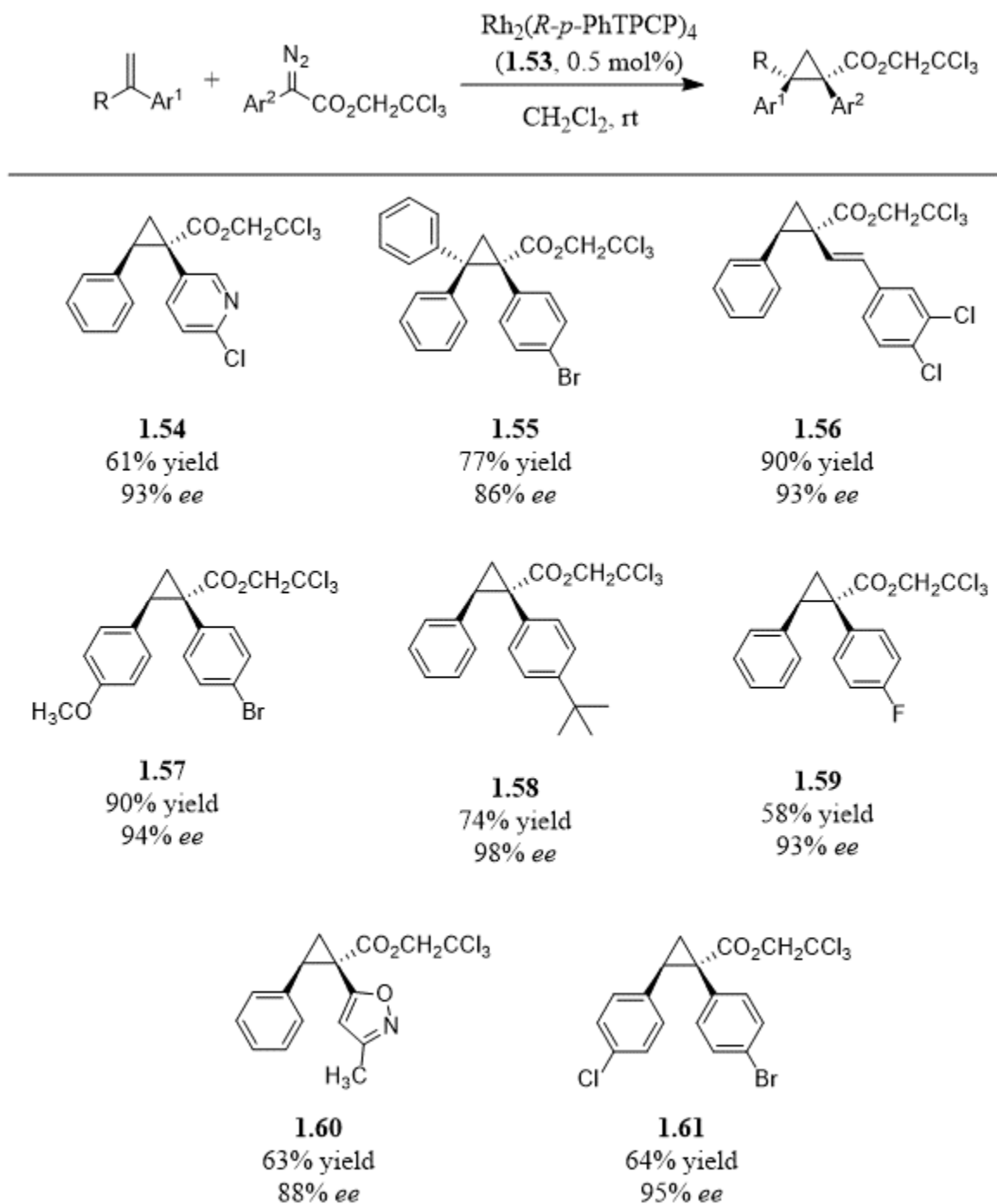
When an appropriately designed chiral dirhodium catalyst is used in conjunction with a donor/acceptor-type diazo compound, cyclopropanation reactions often proceed with good to excellent enantioselectivity. Many of the cyclopropanes synthetically accessible via this method

are pharmaceutically relevant, and dirhodium carbene chemistry is amenable to being performed on scale. When the diazo compound is handled properly, the reactions tend to be safe, robust and high-yielding.⁴⁸ An asymmetric cyclopropanation reaction using a donor/acceptor dirhodium carbene was recently conducted on a multi-kilogram scale by the Bristol-Myers Squibb company in the synthesis of the investigational antiviral drug Beclabuvir (**1.52**, Scheme 1.5.1).⁴⁹

Other classes of chiral dirhodium tetracarboxylate are also highly proficient in cyclopropanation. Using $\text{Rh}_2(R\text{-}p\text{-PhTPCP})_4$ (**1.53**) with 2,2,2-trichloroethyl diazoacetates, a very large number of cyclopropanation reactions can be performed with high enantioselectivity and site selectivity⁵⁰ (Table 1.5.1).



Scheme 1.5.1: Industrial application of $\text{Rh}_2(\text{S-DOSP})_4$ (**1.21**)-catalyzed cyclopropanation.

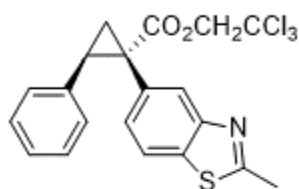
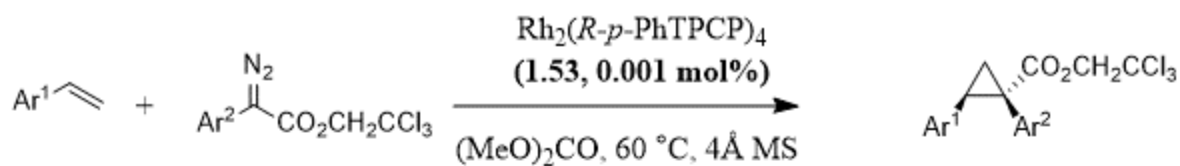
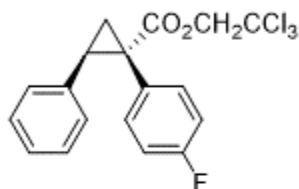
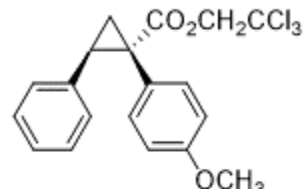
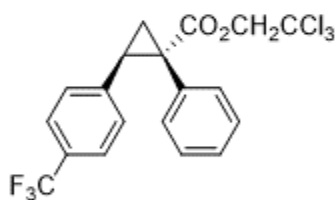
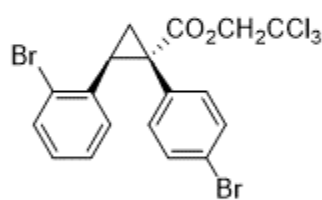
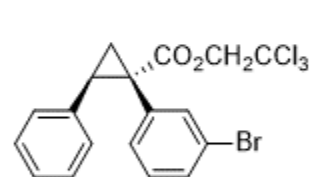
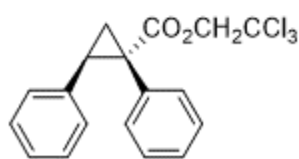
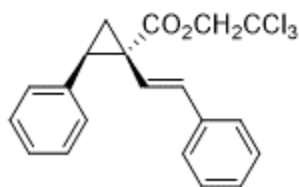
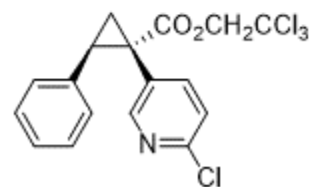


Scheme 1.5.2: Cyclopropanations using $\text{Rh}_2(\text{R-}p\text{-PhTPCP})_4$ with trichloroethyl

diazoacetates.⁵⁰

In these cyclopropanation reactions, the presence of heteroatoms on the diazo compound can occasionally have a detrimental effect on yield, as in the reactions for form compounds **1.54** and **1.60**. However, it is worth noting that in these examples the products are also generated in high enantioselectivity. As shown by the table, the substrates that work best for cyclopropanation with $\text{Rh}_2(R\text{-}p\text{-PhTPCP})_4$ are those that have *para* substitution on the phenyl rings of the styrene component or the diazo. Here, the 2,2,2-trichloroethyl ester group is used as the acceptor group on the diazo compound because an ester which is longer and bulkier⁵¹ occupies more volume in the catalyst pocket close to the carbene group, resulting in an increase to enantioselectivity.

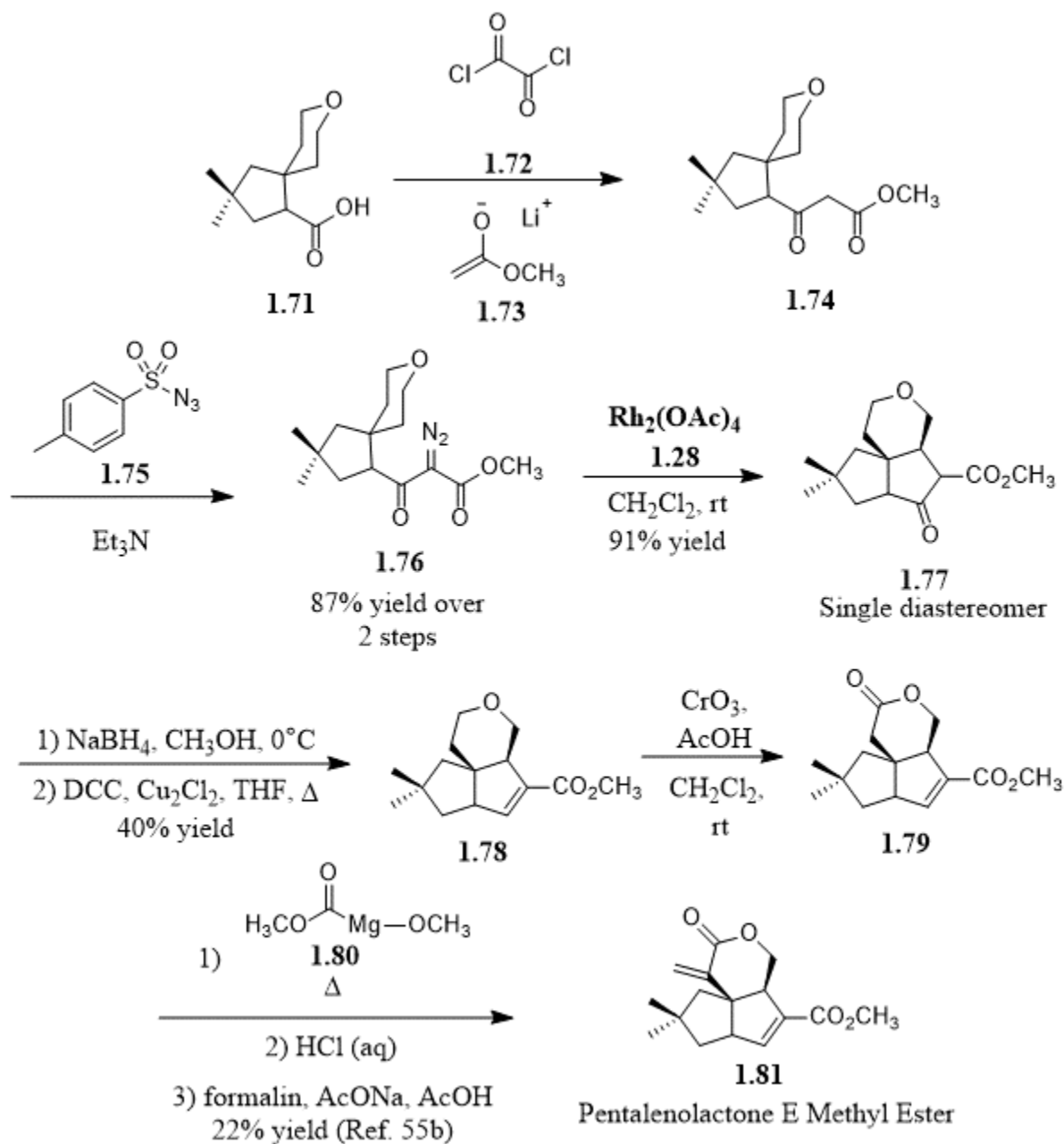
The use of dimethyl carbonate as the solvent in cyclopropanation reactions often has an additional reinforcing effect on enantioselectivity and can significantly improve the reaction yield, *ee*, and catalyst loading (Table 1.5.2)²². In this series, enantioselectivity above 90% *ee* is frequently observed. Examples such as compounds **1.66** and **1.67** show that under these conditions, the catalyst can also show good performance with components that have *ortho* and *meta* substituted aryl groups.

**1.62**87% yield, 86% *ee***1.63**90% yield, 95% *ee***1.64**94% *ee*, 90% yield**1.65**90% yield, 97% *ee***1.66**70% yield, 96% *ee***1.67**90% yield, 92% *ee***1.68**89% yield, 94% *ee***1.69**88% yield, 96% *ee***1.70**65% yield, 94% *ee*

Scheme 1.5.3: Cyclopropanation reactions at low catalyst loading with Rh₂(*R-p*-PhTPCP)₄.²²

1.6 Established Classes of Dirhodium Catalyst

The first dirhodium tetracarboxylates to be widely applied in organic synthesis were typically derived from small, commonly available carboxylic acids such as acetic acid, trifluoroacetic acid, pivalic acid, or other simple alcanoic acids. Despite the relative structural simplicity of these ligands as compared to their modern counterparts, they are highly effective for leveraging the innate reactivity of many substrates and for conducting intramolecular reactions.⁵² Carbene reactions often occur under mild conditions, and C-H insertions with simple achiral catalysts can proceed with retention of stereochemistry and show high diastereoselectivity in substrate-controlled reactions.^{53,54} Early contributors to the field were quick to capitalize on these useful properties, as evidenced by the incorporation of carbene steps in several prominent syntheses of the late 20th century such as Taber's total synthesis of Pentalenolactone E methyl ester (**1.81**, Scheme 1.6.1).^{55a,b} In this synthesis, the key step was a highly diastereoselective, rhodium-catalyzed intramolecular C-H insertion of intermediate **1.76** to form the stereodefined tricyclic core **1.77**.

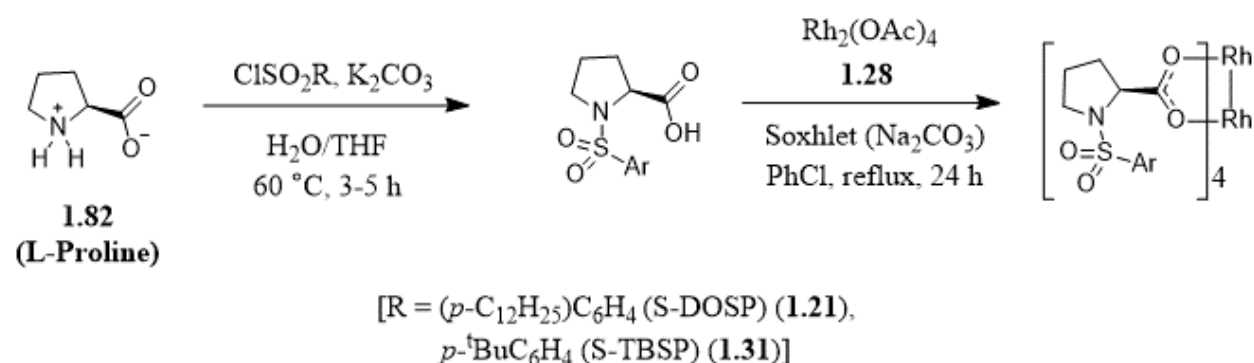


Scheme 1.6.1: The Taber synthesis of pentalenolactone E methyl ester (**1.81**).^{55a,55b}

A key development on the timeline of dirhodium tetracarboxylates was the discovery of more sophisticated chiral catalysts by the pioneering work of researchers such as Davies⁵⁶ and Hashimoto.⁵⁷ The following sections will be dedicated to these more advanced catalysts which are highly effective for asymmetric synthesis and can induce site-selective insertion reactions.

1.6.1 Development and Applications of Dirhodium Tetraproline Catalysts

The first generation of chiral dirhodium catalysts developed in the Davies group were prepared from arylsulfonylproline ligands, which can be easily obtained from the sulfonylation reaction of prolines. Being a proteinogenic amino acid, L-proline (**1.82**) is an inexpensive and abundant chiral pool starting material, and a number of functionalized proline derivatives are commercially available. A general synthesis of dirhodium tetraproline catalysts is shown in Figure 1.6.2.



Scheme 1.6.2: General Preparation of arylsulfonylproline catalysts.⁵⁶

Using an *N*-sulfonyl dodecylphenyl protecting group ($\text{Rh}_2(\text{S-DOSP})_4$, **1.21**) yields a catalyst which has excellent asymmetric induction potential as well as high solubility in aliphatic hydrocarbons. In addition to enantioselective cyclopropanation,⁵⁸⁻⁶⁰ **DOSP** is also highly capable as a catalyst for numerous other asymmetric carbene transformations, including the cyclopropanation of alkynes,⁶¹ C-H insertion,⁶²⁻⁶³ Si-H insertion,⁶⁴ other cycloaddition reactions,⁶⁵ and even the synthesis of functionalized heterocycles such as pyridines⁶⁶ and pyrroles⁶⁷. Dirhodium tetraprolinates generally show the highest selectivity for C-H bonds at sterically accessible secondary positions.

Considerable effort has been made toward developing models for the asymmetric reactions of the arylsulfonylprolinate catalysts that can predict enantioselectivity. A key assumption is that because the ligands are relatively large, they cannot all exist in the periphery of the catalyst and in plane with the rhodium disc.^{20,56} Assuming the ligand is completely crowded out from the periphery, there are four possible orientations for the tetracarboxylate complex (Figure 1.6.2). To explain its remarkably high enantioselectivity, it was proposed that the catalyst $\text{Rh}_2(\text{DOSP})_4$ would assume a conceptually D_2 -symmetric ($\alpha,\beta,\alpha,\beta$) geometry, which can provide effective steric control of the incoming substrate as it approaches the carbene center.

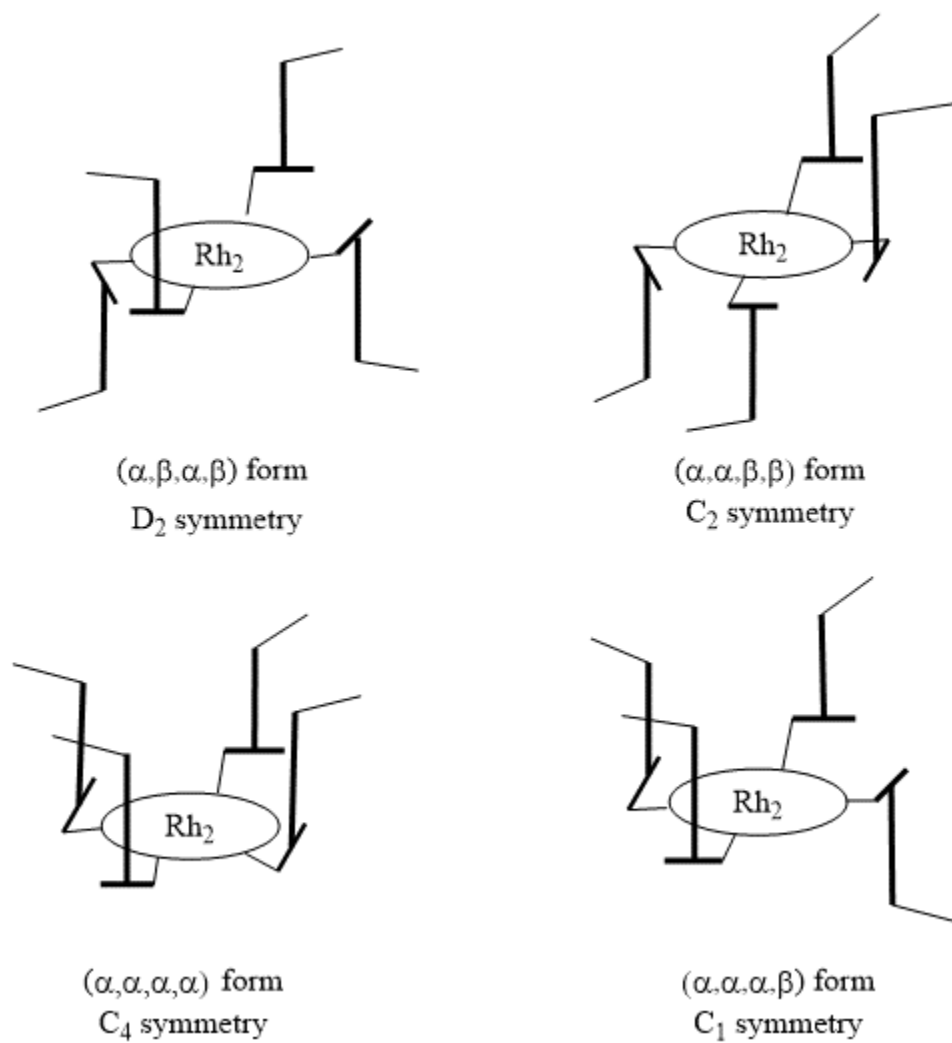


Figure 1.6.2: Possible ligand orientations of $\text{Rh}_2(\text{DOSP})_4$ with point group classifications.^{20,56}

A D_2 -catalyst would also be ideal in this regard because both the top and bottom faces of the dirhodium disc are identical. In the C_4 and C_2 symmetric orientations in which one or both faces of the disc are relatively less crowded, it was initially thought that the resulting catalyst would not show high enantioselectivity. The high asymmetric induction observed for the first generation catalyst $Rh_2(DOSP)_4$ was rationalized on the basis that the carboxylate ligands act as blocking groups, forming “walls” to restrict the approach of the substrate toward the reaction center (Figure 1.6.3)²⁴. The less hindered approach trajectory would then consistently favor one enantiomer of the product, because the “medium” substituent on the C-H substrate or the R-group on an alkene would prefer to be oriented away from the blocking group on the ligand.

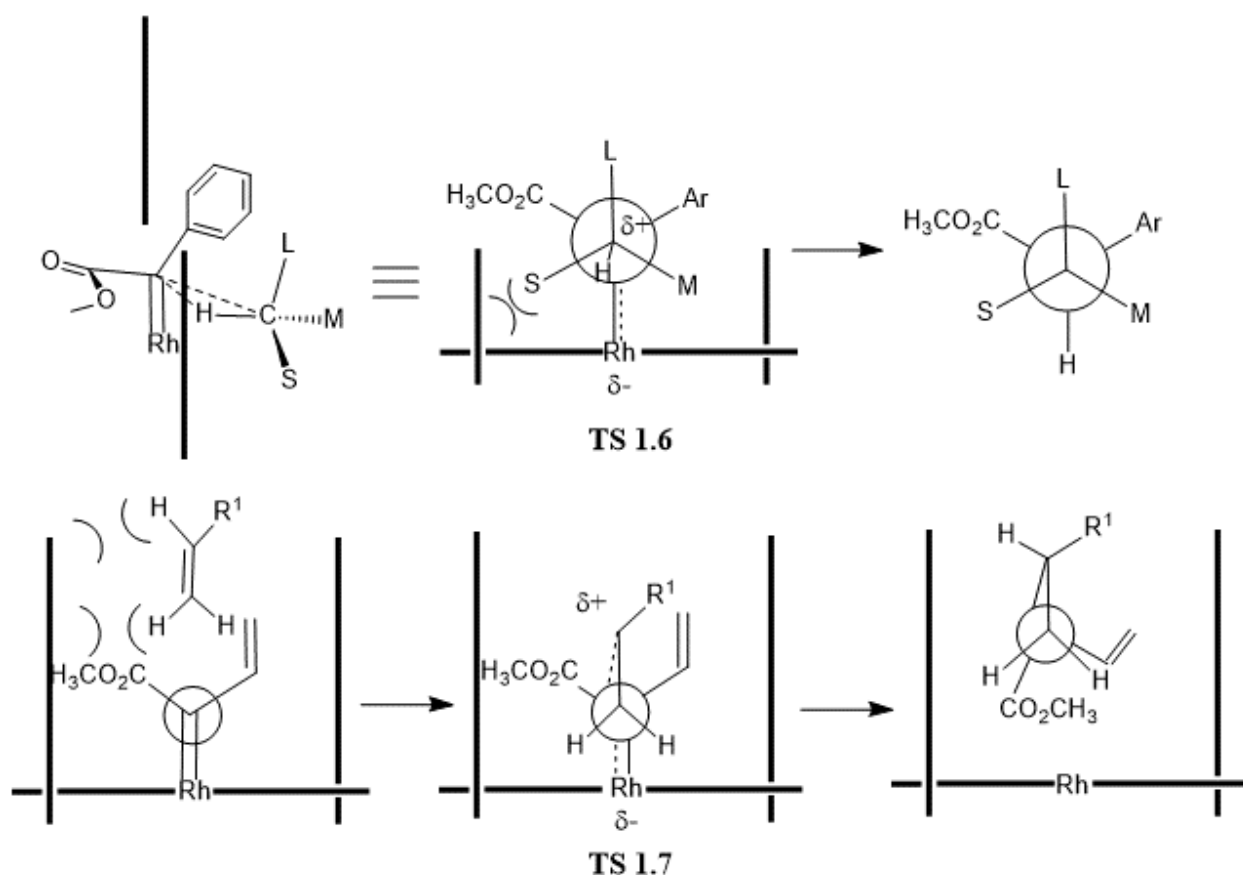


Figure 1.6.3: Proposed model for asymmetric induction with a D_2 -symmetric catalyst^{20,24,56}.

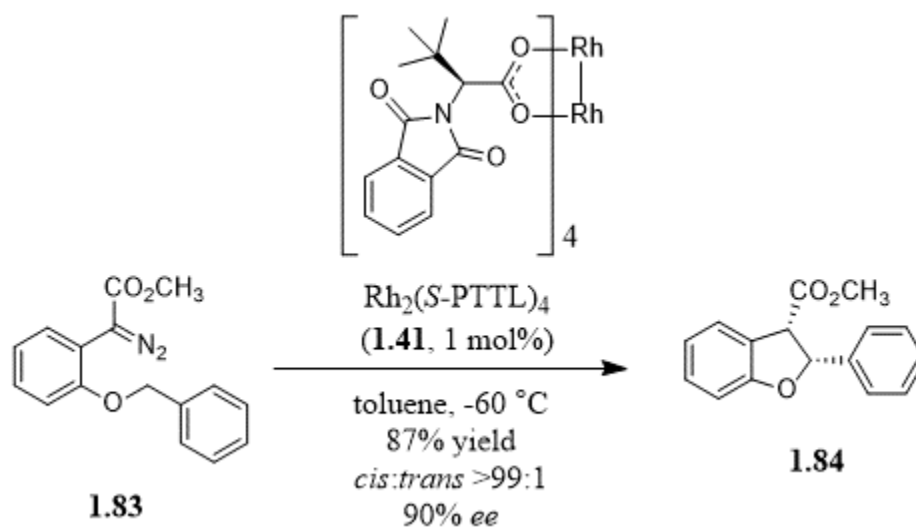
While the D₂ model is successful at predicting the stereochemistry of the products in certain cases, it is not universally applicable to all carbene reactions. Work toward developing more detailed models of the tetraproline catalysts with greater predictive accuracy is ongoing in the Davies group. The development of highly enantioselective new catalyst types, additional X-ray data, and the emergence of new, more powerful computational methods have all contributed greatly to a significantly improved understanding of metal carbene reactions.

Even considering over two decades of major advancements in design, Rh₂(**DOSP**)₄ is still frequently identified as the catalyst of choice for carbene transformations. While widely regarded as the “gold standard” of asymmetric carbene catalysts, the tetraprolinates do suffer from certain limitations. The enantioselectivity of Rh₂(**DOSP**)₄ is usually good to excellent when the structure of the donor group on the carbene is changed, but it tends to show variation with respect to the acceptor substituent.⁶⁸ In most cases, smaller esters (i.e., methyl) give optimal results. The proline-type catalysts may also show reduced enantioselectivity when polar aprotic solvents such as dichloromethane are used instead of aliphatic hydrocarbons.⁶⁹ These shortcomings gave impetus to the development of a second-generation class of catalyst which can overcome the above restrictions.

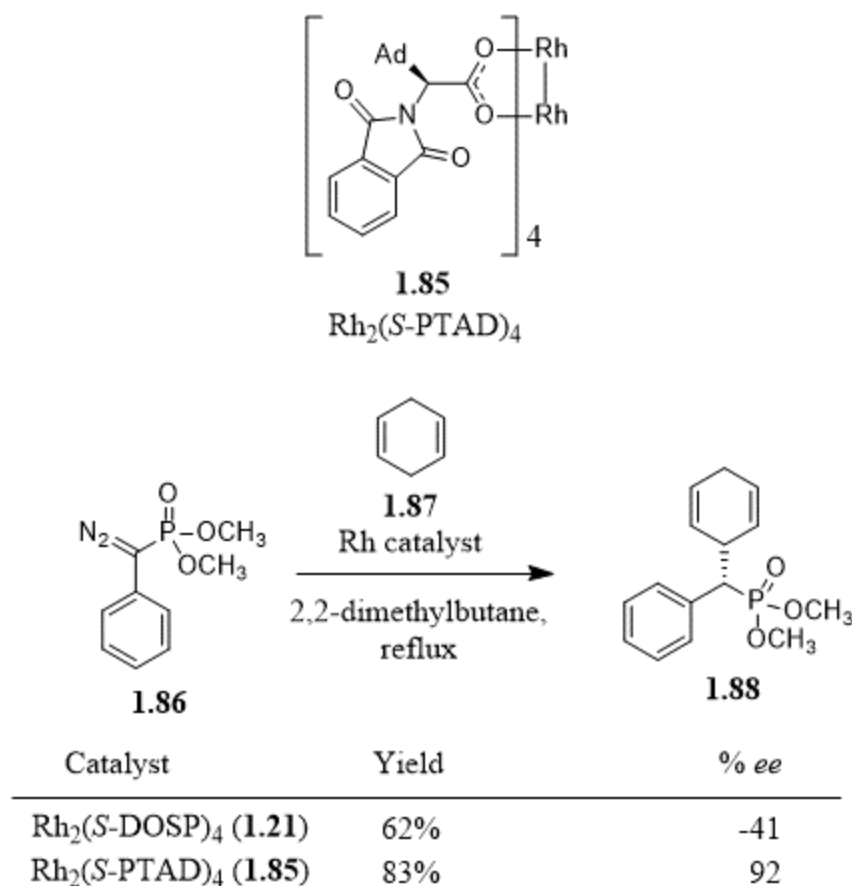
1.6.2 Dirhodium Complexes with Phthalimido-Protected Amino Acid Ligands

The dirhodium phthalimido catalyst Rh₂(**PTTL**)₄ was discovered by Hashimoto, who applied it to the intramolecular cyclization reactions of 2-(2-benzyloxyphenyl)-2-diazoacetates such as compound **1.83** to afford 2-aryl-3-methoxycarbonyl-2,3-dihydrobenzofurans (**1.84**) in very high diastereo- and enantioselectivity⁷⁰ (Scheme 1.6.3). Rh₂(**PTTL**)₄ and other *tert*-leucine based

catalysts often show good to excellent stereoselectivity for many carbene reactions and have the added advantage of performing well in polar aprotic solvents such as methylene chloride,⁷¹ which often are not the best choice for the proline-type dirhodium catalysts. Larger acceptor substituents are also well-tolerated, as illustrated by the reaction of the diazophosphonate **1.86** to form the C-H functionalization product **1.88** in high yield and *ee* (Scheme 1.6.4). There is good complementarity between the proline and phthalimido classes of chiral dirhodium catalyst, with many reactions performing substantially better in one system over the other.



Scheme 1.6.3: Cyclization of 2-(2-benzyloxyphenyl)-2-diazoacetate (**1.83**) using $\text{Rh}_2(\text{S-PTTL})_4$ (**1.41**).⁷⁰



Scheme 1.6.4: Carbene C-H insertion reactions of diazophosphonate ester **1.86**. Higher yield and ee are observed when $\text{Rh}_2(\text{S-PTAD})_4$ (**1.85**) is used as the catalyst instead of $\text{Rh}_2(\text{S-DOSP})_4$ (**1.21**)⁶⁸

Unlike the tetraproline catalysts which were thought to be D_2 -symmetric, pioneering work by Charette⁷² and Fox⁷³ showed that there is strong experimental and computational evidence for a stable “all-up” ($\alpha,\alpha,\alpha,\alpha$)- C_2 conformation of $\text{Rh}_2(\text{PTTL})_4$ and related catalysts when the side chain of the amino acid is large. This conformation is also demonstrated quite clearly in the X-ray structure of the Davies catalyst $\text{Rh}_2(\text{S-TCPTAD})_4$ (**1.89**) (Figure 1.6.4). In the ($\alpha,\alpha,\alpha,\alpha$)- C_2 orientation, all four phthalimido groups of the catalyst are placed on the same face of the catalyst

and the opposite face is blocked by four sterically imposing *tert*-butyl groups. This bowl-shaped geometry is stabilized by steric hinderance from the bulky *tert*-butyl groups, which inhibit ligand rotation. A model for enantioinduction with $\text{Rh}_2(\text{PTTL})_4$ in which the rhodium carbene complex adopts this geometry has been proposed by Fox to explain the high levels of stereoselectivity which can be obtained using catalysts of this type (Figure 1.6.5).

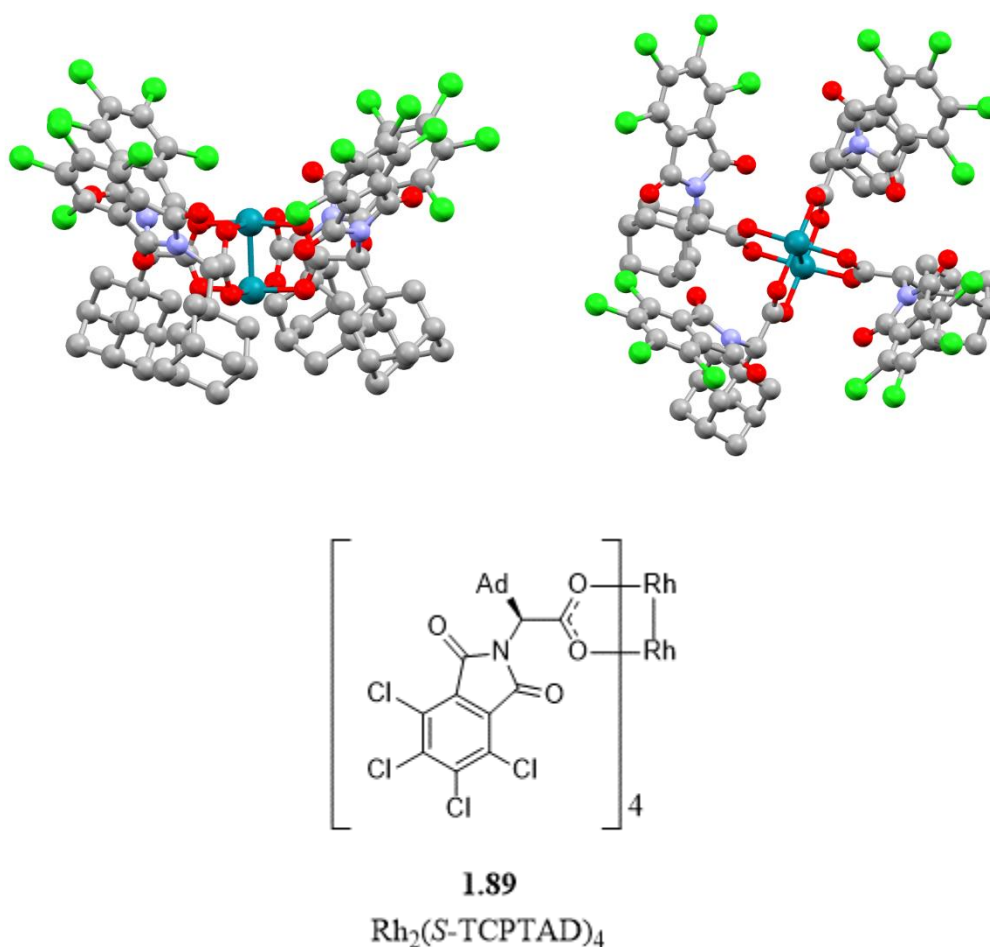


Figure 1.6.4: The crystal structure of $\text{Rh}_2(\text{S-TCPTAD})_4$ (**1.89**) shows an $(\alpha, \alpha, \alpha, \alpha)\text{-C}_2$ conformation

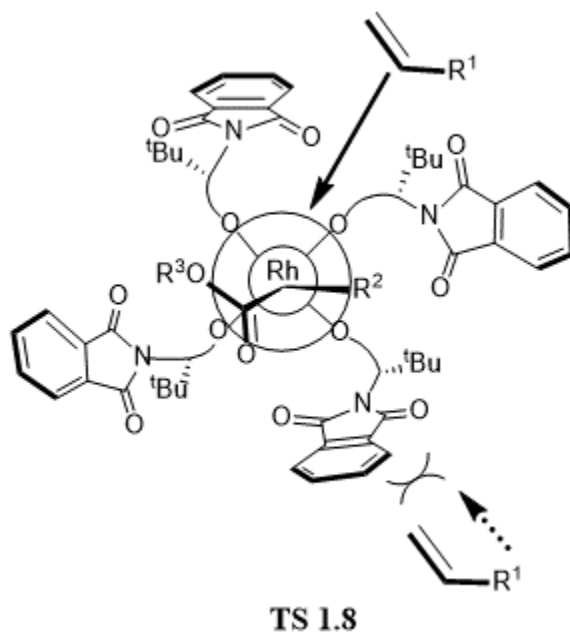
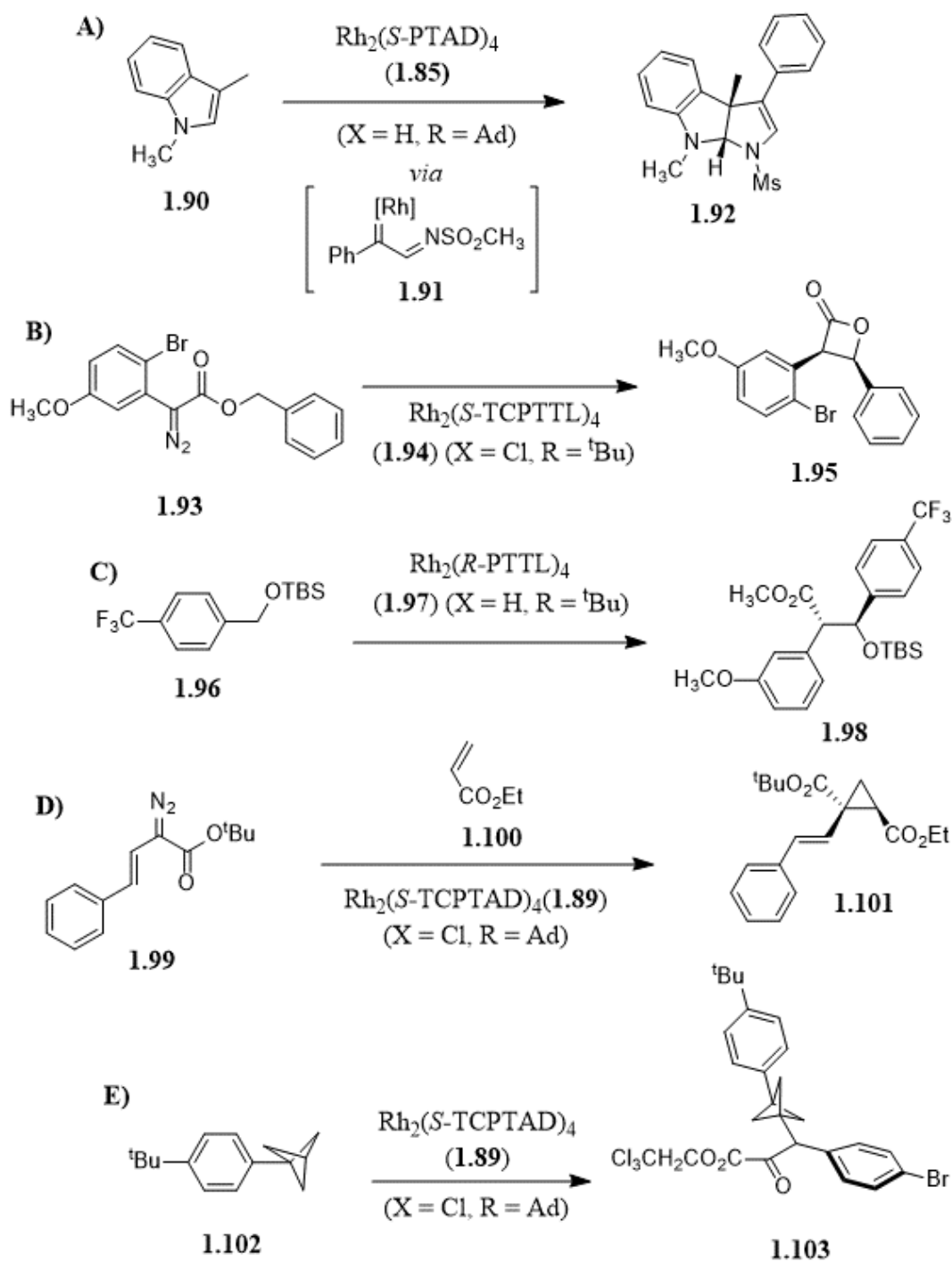


Figure 1.6.5: The Fox model for asymmetric induction with $\text{Rh}_2(\text{S-PTTL})_4$ (**1.41**).⁷⁵

In the Fox model⁷⁵, when the $(\alpha,\alpha,\alpha,\alpha)$ form of the dirhodium carbene reacts with a substrate such as an alkene there are two “channels” for possible substrate approach due to the C_2 symmetry of the bowl. The substrate must approach from the wide channel due to steric hinderance from the walls of the catalyst pocket. The large acceptor group makes attack from one side of the complex improbable, resulting in attack from a single direction with high enantioselectivity. Reactions at the bottom face of the $(\alpha,\alpha,\alpha,\alpha)$ complex do not occur to a significant extent because the *tert* butyl groups are too sterically demanding. When the substituent group on the amino acid is less sterically demanding, the population of other conformations may be more significant. In the case of the phenylalanine derivative $\text{Rh}_2(\text{PTPA})_4$, an $(\alpha,\alpha,\beta,\beta)$ form is observed in the crystal structure⁵⁷. While $\text{Rh}_2(\text{PTTL})_4$ frequently gives high enantioselectivity in carbene transformations,⁷¹ $\text{Rh}_2(\text{PTPA})_4$ is not usually as selective.

A significant development in the phthalimido-protected amino acid class of catalysts was the discovery of $\text{Rh}_2(\text{PTAD})_4$ ⁷⁶ by the Davies group. This catalyst formally replaces the *tert*-butyl side chain on the amino acid ligand with an even more sterically demanding adamantyl group. Replacement of the *tert*-butyl group of $\text{Rh}_2(\text{PTTL})_4$ with the larger adamantyl substituent gives improved regio- and stereoselectivity over the parent catalyst in many cases. Like $\text{Rh}_2(\text{PTTL})_4$, the catalyst $\text{Rh}_2(\text{PTAD})_4$ adopts an ($\alpha,\alpha,\alpha,\alpha$) shape with all four of the phthalimido groups on a single face of the rhodium disc and all four adamantyl groups on the opposite side.⁷⁷

In most reactions with C-H bonds, phthalimido-amino acid type catalysts tend to select more electronically stabilized tertiary⁷⁸ or secondary⁷⁹ sites. In addition to its role as a highly effective catalyst for carbene reactions, the perchloro-variant $\text{Rh}_2(\text{TCPTAD})_4$ is also effective for some C-H amination reactions using rhodium nitrene intermediates⁷⁶. The placement of electron-withdrawing halogen substituents on the catalyst is thought to stabilize a π - π interaction between the carbene unit and an electron-deficient aryl group of a phthalimido substituent, leading to heightened enantioselectivity. Some illustrative examples of these catalysts in asymmetric synthesis are shown in Scheme 1.6.5.⁸⁰⁻⁸⁴



A) 81% yield, 94% *ee*.⁸⁰ B) 72% yield, 97% *ee*, *cis:trans* >19:1.⁸¹ C) 86% yield, >97:3 *dr*, 98% *ee*.⁸²
D) 89% yield, >97:3 *dr*, 97% *ee*.⁸³ E) 99% yield, 90% *ee*.⁸⁴

Scheme 1.6.5: Selected applications of phthalimido-amino acid type dirhodium catalysts.⁸⁰⁻⁸⁴

In example **1.6.5A**, the carbene **1.91** is generated *in situ* via the decomposition of a triazole.

Using $\text{Rh}_2(\text{S-PTAD})_4$ (**1.85**) as the catalyst, the product **1.92** is obtained in 81% yield and 94% *ee*. The mechanism of this reaction has been proposed to proceed via an initial cyclopropanation event followed by ring-opening and subsequent 5-*exo*-trig cyclization to form the product⁸⁰.

Example **1.6.5B** illustrates how phthalimido catalysts are also proficient for the intramolecular cyclization reactions of donor/acceptor diazo compounds, as illustrated by the formation of the β -lactone **1.95** from **1.93** in very high diastereoselectivity and *ee*⁸¹. The catalyst $\text{Rh}_2(\text{R-PTTL})_4$ (**1.97**) can accommodate bulky substrates like compound **1.98** and still achieve excellent yield and *ee*⁸² (**Figure 1.6.5C**). $\text{Rh}_2(\text{S-TCPTAD})_4$ (**1.89**) is capable of very high enantioselectivity in the cyclopropanation reactions of acrylate esters (**Figure 1.6.5D**). In an illustrative example, compound **1.100** reacts to give **1.101** in 89% yield, 97% *ee* and >97:3 d.r.⁸³. $\text{Rh}_2(\text{S-TCPTAD})_4$ (**1.89**) is also remarkable for its ability to functionalize the distal C-H bond of arylbicyclopentanes such as **1.102** with high regio- and stereoselectivity⁸⁴. In **Figure 1.6.5E**, the product **1.103** is generated in near-perfect yield and 90% *ee*.

1.6.3 Introduction to Dirhodium Triarylcyclopropanecarboxylates

The first attempts to use cyclopropanecarboxylates as ligands for dirhodium catalysts were made by Dr. Janelle Thompson in the early 2000's,⁸⁵ however they did not achieve prominence until nearly a decade later with the discovery that triarylcyclopropanecarboxylates were highly effective for enantioselective cyclopropanation reactions.⁸⁶ The use of triaryl-substituted cyclopropanes was first proposed by Dr. Jørn Hansen, who examined the lowest energy conformers of the dirhodium complexes *in silico*.⁸⁷ The model developed by Dr. Hansen (**Figure 1.6.6**) suggested that a substituent with a *syn*-relation to the carboxylate group was necessary in order for the cyclopropane ligand to exert a significant steric influence on the active site space of

the catalyst. To test this prediction, $\text{Rh}_2(\text{R-TPCP})_4$ (**1.106**) was prepared using the well-established catalyst $\text{Rh}_2(\text{R-DOSP})_4$ (**1.17**) by the cyclopropanation reaction of methyl phenyldiazoacetate (**1.19**) with 1,1-diphenylethylene (**1.104**) (Scheme 1.6.6).

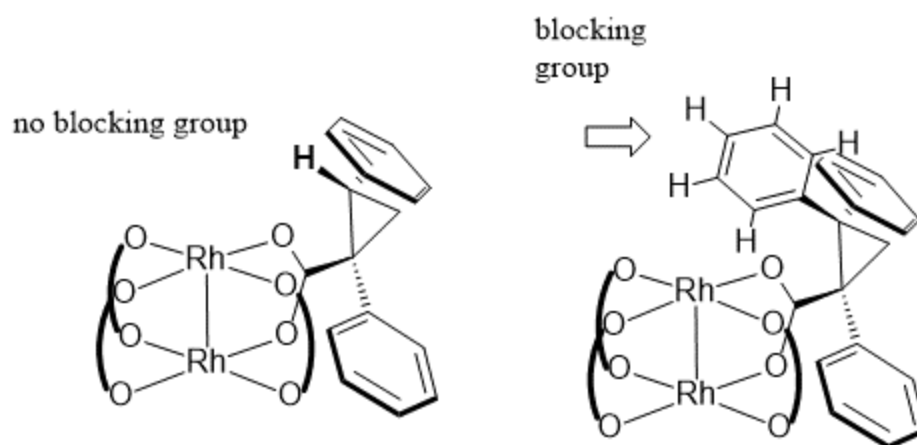
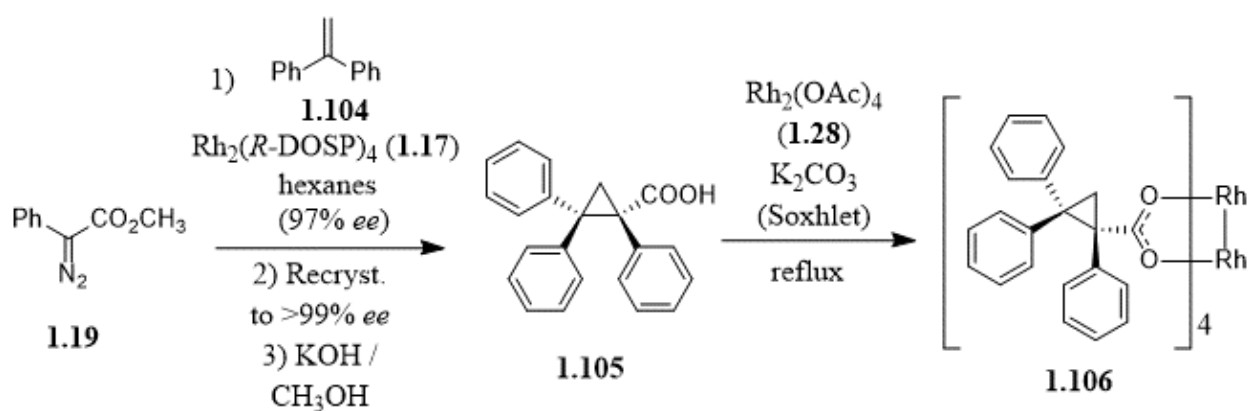


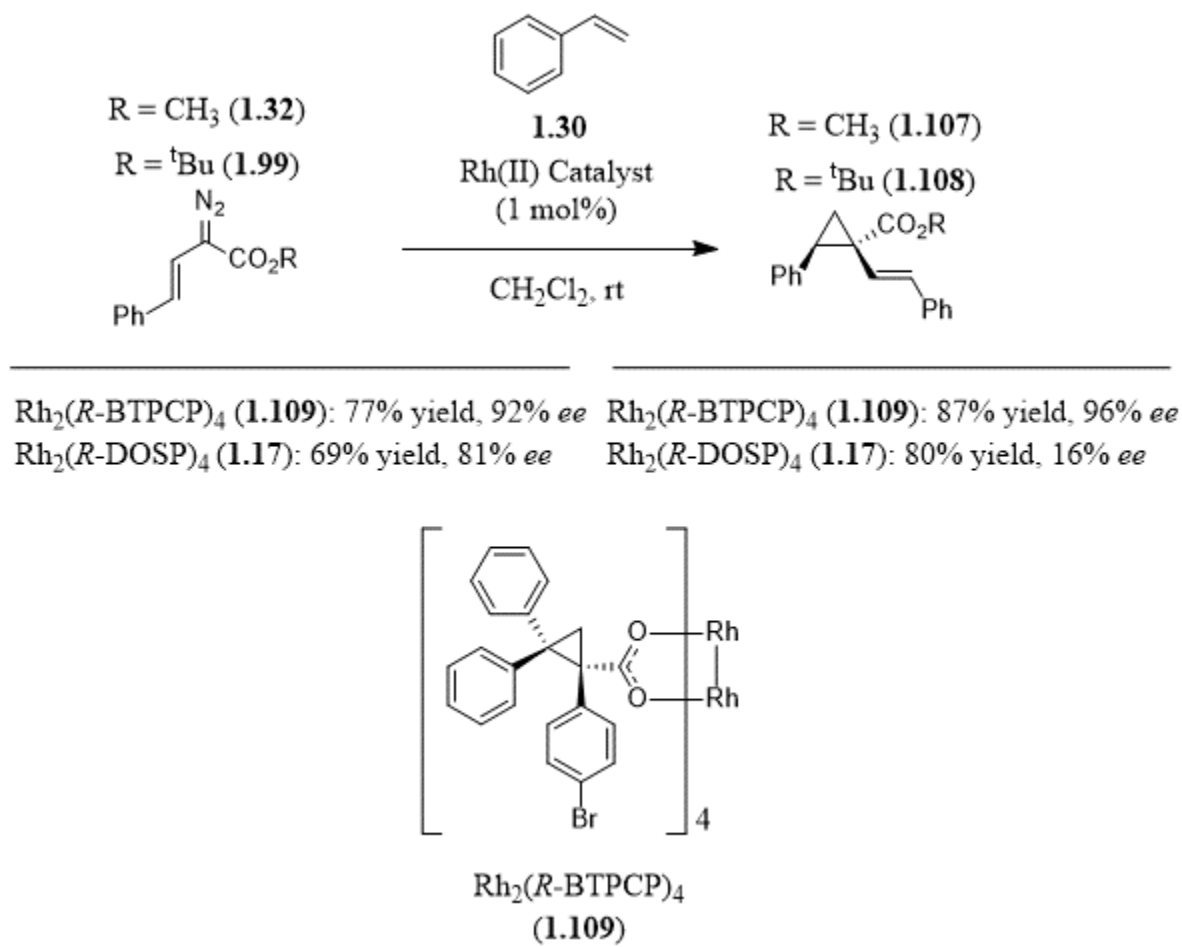
Figure 1.6.6: Illustration of Hansen's proposal that the 2-*cis* aryl blocks the reaction site.⁸⁷



Scheme 1.6.6: Synthesis of $\text{Rh}_2(\text{R-TPCP})_4$ (**1.106**)

This reaction proceeds with very high stereoselectivity (97% ee and >95:5 dr).⁸⁷ The product was recrystallized to enantiopurity and then subjected to hydrolysis conditions with potassium hydroxide to afford the free carboxylic acid. To prepare the dirhodium tetracarboxylate complex, a ligand exchange reaction was conducted with rhodium acetate in toluene. Hansen's sample of the catalyst was not perfectly pure but it did show promising results. Hansen's initial experiments showed that $\text{Rh}_2(\text{R-TPCP})_4$ (**1.106**) was capable of achieving up to 67% ee in the cyclopropanation of styrene (**1.30**) with methyl phenyldiazoacetate (**1.19**).

Inspired by the success of $\text{Rh}_2(\text{R-TPCP})_4$ (**1.106**), further advances in this series of catalyst were made by Dr. Changming Qin, who studied the effect of adding additional substituents to the aryl groups of the triarylcyclopropane. This concept proved to be highly successful, and many useful catalysts were developed based on this premise. The first dirhodium complex studied by Dr. Qin was $\text{Rh}_2(\text{p-BrTPCP})_4$, (also referred to as $\text{Rh}_2(\text{BTPCP})_4$),⁸⁶ which performs better than $\text{Rh}_2(\text{DOSP})_4$ in asymmetric cyclopropanation reactions using chlorinated solvents and in reactions involving carbenes with large ester groups (Scheme 1.6.7).



Scheme 1.6.7: Comparison of $\text{Rh}_2(\text{R-BTPCP})_4$ (**1.109**) and $\text{Rh}_2(\text{R-DOSP})_4$ (**1.17**) in

methylene chloride.⁸⁶

The high enantioselectivity observed using catalyst **1.109** was initially rationalized on the basis that the carbene might react from a D_2 -symmetric conformation, which is displayed in the crystal structure of this catalyst⁸⁶. However, more recent evidence suggests that a D_2 geometry is not actually the most stable orientation for this dirhodium complex.⁸⁸ Like the phthalimido-amino acid type catalysts, the dirhodium triarylcyclopropanecarboxylates uniformly show good enantioselectivity in chlorocarbon solvents such as dichloromethane and 1,2-dichloroethane.

(1.53).^{89,90}

When the *para*-bromine atoms of Rh₂(**BTPCP**)₄ are replaced by phenyl groups, the enantioselectivity of the catalyst in both cyclopropanation and C-H insertion^{89,90} reaction modes increases even further. Rh₂(***p*-PhTPCP**)₄ is one of the most versatile and highly enantioselective catalysts in the “toolbox” of dirhodium tetracarboxylates. Some examples of C-H functionalization reactions with Rh₂(***R-p*-PhTPCP**)₄ (**1.53**) are shown in Scheme 1.6.8. In entry **1.6.8A**, the catalyst guides the rhodium carbene derived from diazo compound **1.111** to a primary allylic site, while in example **1.6.8B**, the activating group is a phenyl ring. The reaction with compound **1.115** illustrates how the carbene reaction can tolerate *trans* alkene groups and oxazolidine functionality while still giving 81% yield and 97% *ee* for the primary site. Even with the relatively electron-poor aryl group of compound **1.118**, the reaction can still occur at primary sites in high yield and *ee* using the Rh₂(***R-p*-PhTPCP**)₄ catalyst (**1.53**).

Even in competition with other allylic or benzylic sites, Rh₂(***p*-PhTPCP**)₄ maintains both high enantioselectivity and high regioselectivity for primary C-H sites. The latter feature is particularly noteworthy because the highly selective functionalization of unactivated primary C-H bonds in the presence of other accessible C-H sites is a largely unsolved problem in organic chemistry.⁹¹ Prolinate catalysts such as Rh₂(**DOSP**)₄ generally perform best when the acceptor group is a methyl group, while triarylcyclopropanecarboxylate catalysts often give superior results with 2,2,2-trihaloethyl esters.

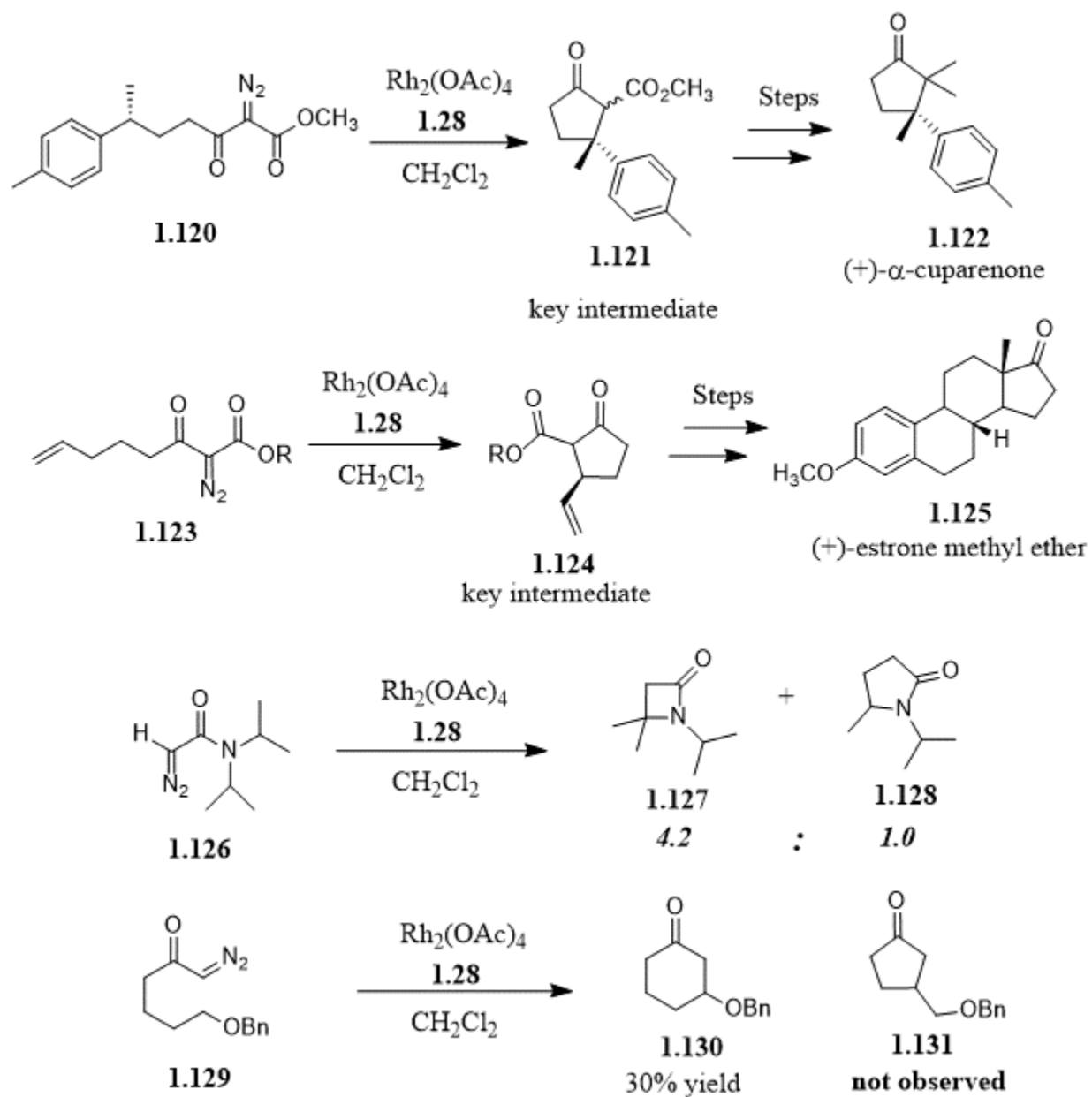
1.7 C-H Functionalization with Dirhodium Carbenes

The C-H insertion reactions of donor/acceptor carbenes with dirhodium tetracarboxylate catalysts is arguably the most revolutionary application of carbene chemistry to organic synthesis. The past decades have witnessed the emergence of a large number of robust and

efficient approaches to C-H bond functionalization⁹²⁻⁹⁷ using non-enzymatic catalysts. However, most strategies rely on substrate control to achieve selectivity for the desired C-H bond with a minority being genuinely controlled by the catalyst. The reactions described in this section will illustrate how dirhodium carbenes can react with high selectivity at inherently favorable sites in the traditional manner - or alternatively, guided to unactivated positions by steric control from the catalyst.

1.7.1 Reactions at Innately Favorable Sites

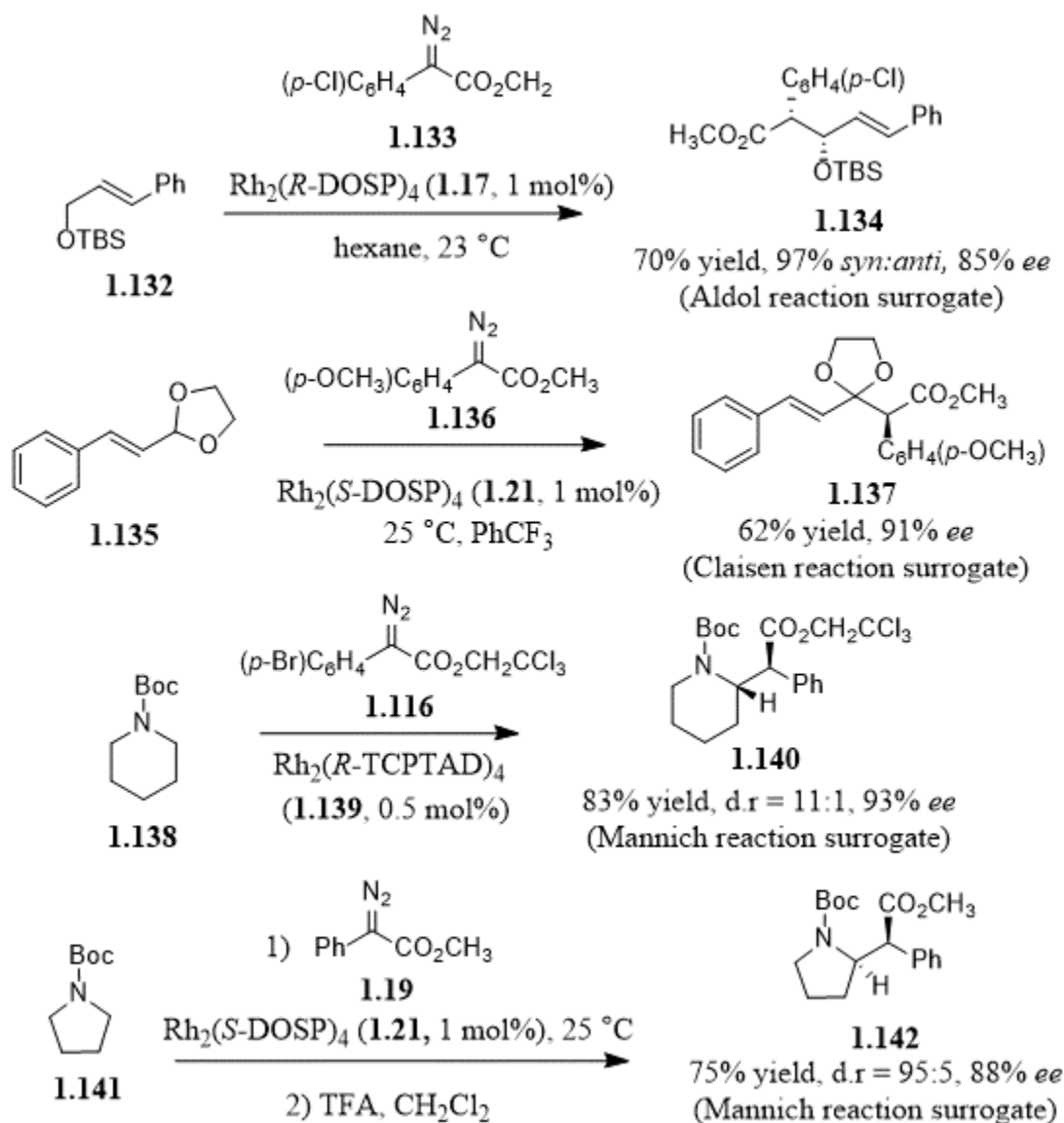
While the use of donor/acceptor carbenes greatly enhances regio- and stereoselectivity for intermolecular reactions, for intramolecular reactions they generally behave in a similar fashion as the other classes of carbene but with higher selectivity (i.e. in scheme 1.6.5B).⁸¹ In the absence of reactive functional groups, the intramolecular C-H insertion reactions of metal carbenes often yield 5-membered rings.⁹⁸ When there are multiple competing sites for these cyclizations, insertion occurs preferentially into C-H bonds at positions with increasing alkyl substitution due to the electronic stabilizing effect. Intramolecular carbene cyclizations to form cyclopentanes have been elegantly applied to many total syntheses such as (+)- α -cuparenone (**1.122**)⁹⁹ and (+)-estrone methyl ether (**1.125**).¹⁰⁰ In the presence of an electron-donating heteroatom, the formation of 4¹⁰¹, 5, or 6¹⁰²-membered rings is commonly observed via C-H insertion at a position α - to the heteroatom, with the reaction to form 5-membered rings being preferred over the other sizes. These effect are illustrated by the reactions of compounds **1.26** and **1.29**. The traditional substrates for intramolecular C-H insertion reactions are acceptor-only type diazo compounds such as diazoketones, diazoesters, and diazomalones.¹⁰³



Scheme 1.6.9: Intramolecular C-H insertion reactions to form 4,5, and 6-membered rings.⁹⁹⁻¹⁰²

Intramolecular cyclization reactions often show high diastereoselectivity, even with acceptor-only and acceptor/acceptor carbenes. As previously mentioned, the use of donor/acceptor carbenes can enhance the stereoselectivity of the reaction, such as in the Fukuyama synthesis of (-)-ephedradine.¹⁰⁴ While there are numerous applications for these reactions, they rely on an innate order of reactivity to achieve regioselectivity and are useful only in specific circumstances. With donor/acceptor carbenes, intermolecular reactions are capable of achieving comparably high site- and stereoselectivity and represent a more direct and universal strategy for organic synthesis¹⁵.

Using donor/acceptor type carbenes, many asymmetric catalysts developed in the Davies lab are ideal for conducting diastereo- and enantioselective C-H insertion reactions α - to heteroatoms (Scheme 1.6.10).¹⁰⁵ In many cases, these reactions can be considered as surrogates for widely utilized classical transformations such as the Aldol, Michael, Claisen, or Mannich reactions, but are often much more time and atom-economical to perform. Proficient substrates for this type of C-H insertion reaction are numerous, and include such compounds as allyl silyl ethers (**1.132**),¹⁰⁶ acetals (**1.135**),¹⁰⁷ piperidines (**1.138**),¹⁰⁸ alkoxy silanes,¹⁰⁹ and pyrrolidines (**1.141**).¹¹⁰ Rh₂(**DOSP**)₄ is often a highly enantioselective catalyst for C-H insertion reactions α -to heteroatoms, even in cases such as the activated tertiary site of the acetal **1.135**.



Scheme 1.6.10: C-H insertion as an alternative to traditional synthetic disconnections.^{106-108,110}

The reactions described in this section have illustrated how the innate reactivity of certain C-H bonds within a substrate can be used to guide C-H functionalization with dirhodium carbenes. Using the latest generation of sterically demanding dirhodium cyclopropanecarboxylate catalysts,¹¹¹⁻¹¹² it is also possible to overcome this inherent selectivity for electronically stabilized positions to react almost exclusively at less activated primary or secondary sites. By increasing the steric demand of the ligands, the more substituted positions can be excluded from the reaction center of the catalyst.

1.7.2 Site- and Stereoselective Functionalization of Unactivated C-H Bonds

The insertion reactions of dirhodium carbenes into unactivated C-H bonds (e.g. alkane substrates such as butane which lack other functional groups) have been known for decades,¹¹³ but until recently were largely considered impractical for use in synthesis. Because hydrocarbon molecules contain many C-H bonds in similar chemical environments, it is challenging to achieve high selectivity for a single position. Due to recent advances in the design of dirhodium catalysts, it is now possible to select the most sterically accessible primary,¹¹⁴ secondary,¹¹⁵ or tertiary¹¹⁶ sites within a substrate molecule with good to excellent regio- and stereoselectivity (Chart 1.6.1, Figure 1.6.7). In these reactions, the major product is highly dependent on the catalyst used - the favored reaction site can be switched by simply using a different catalyst.

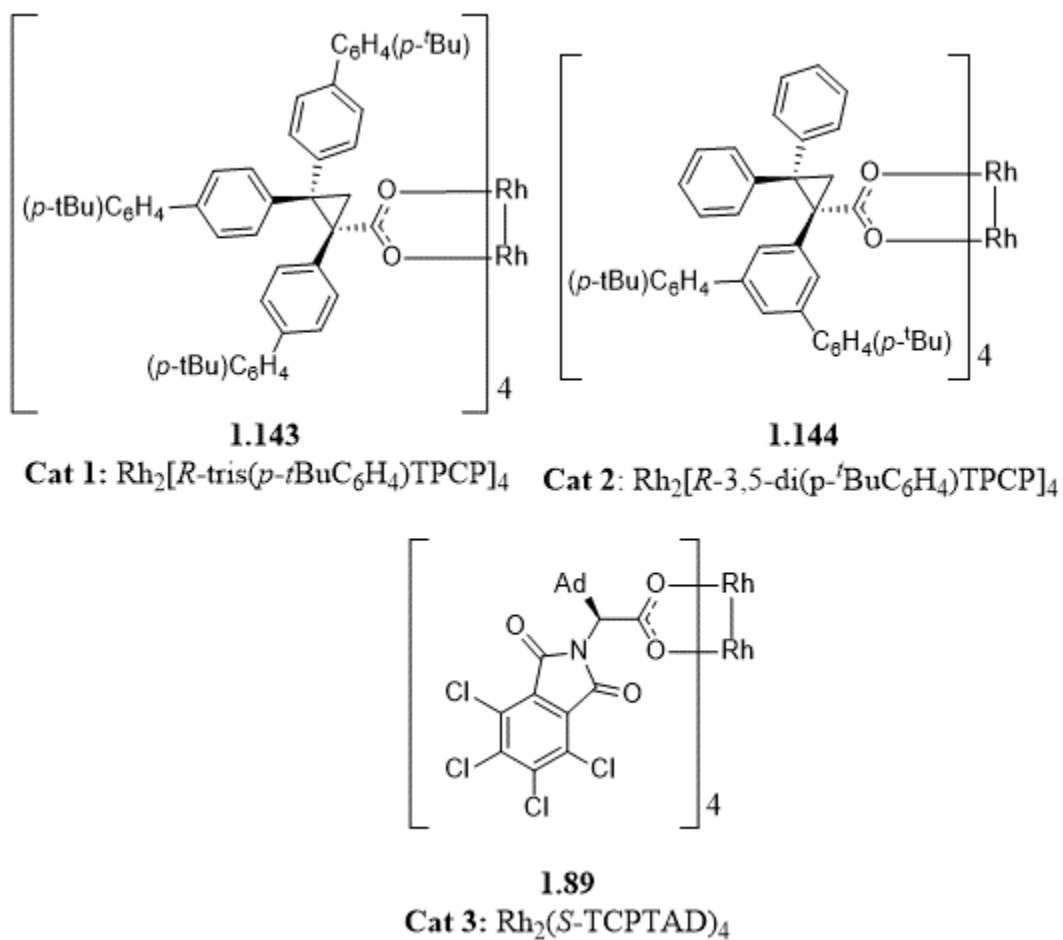


Chart 1.6.1: Highly selective catalysts for unactivated primary (**1.143**), secondary (**1.144**), or tertiary (**1.89**) sites.

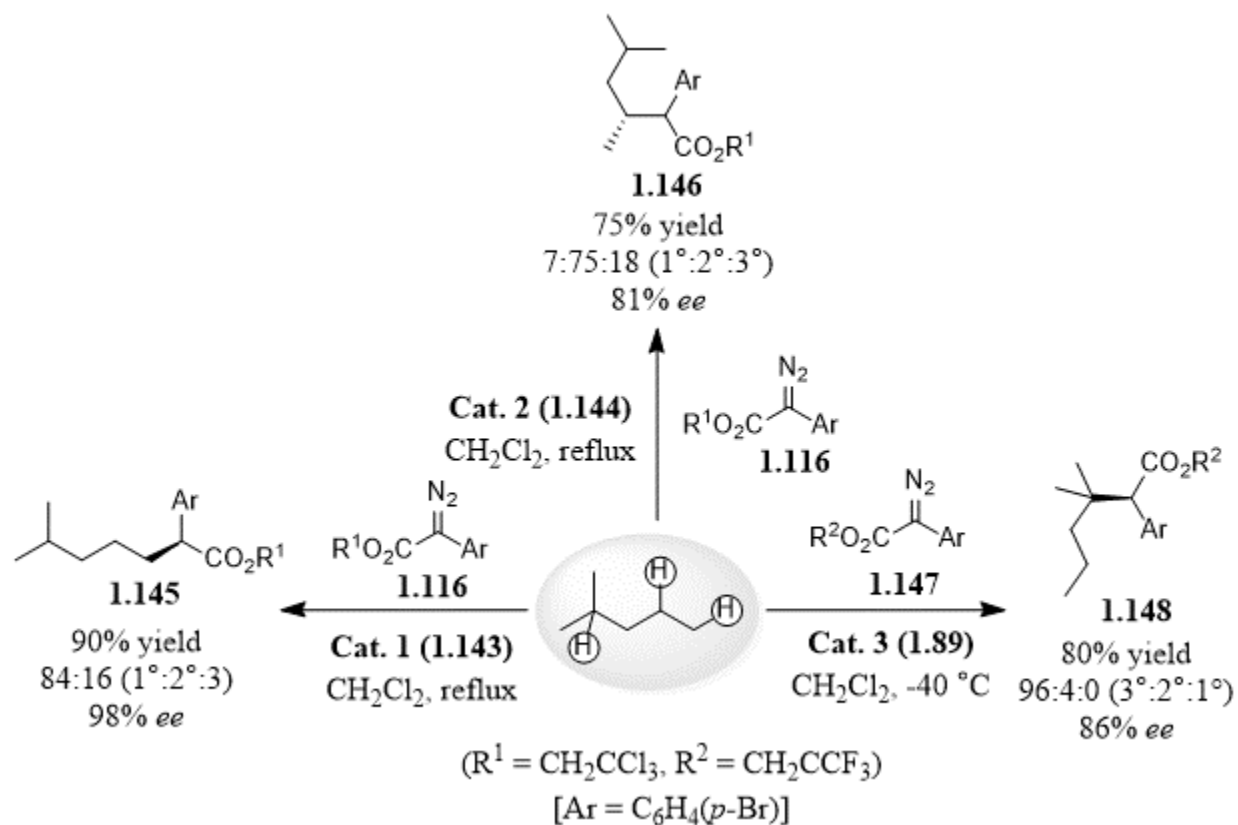
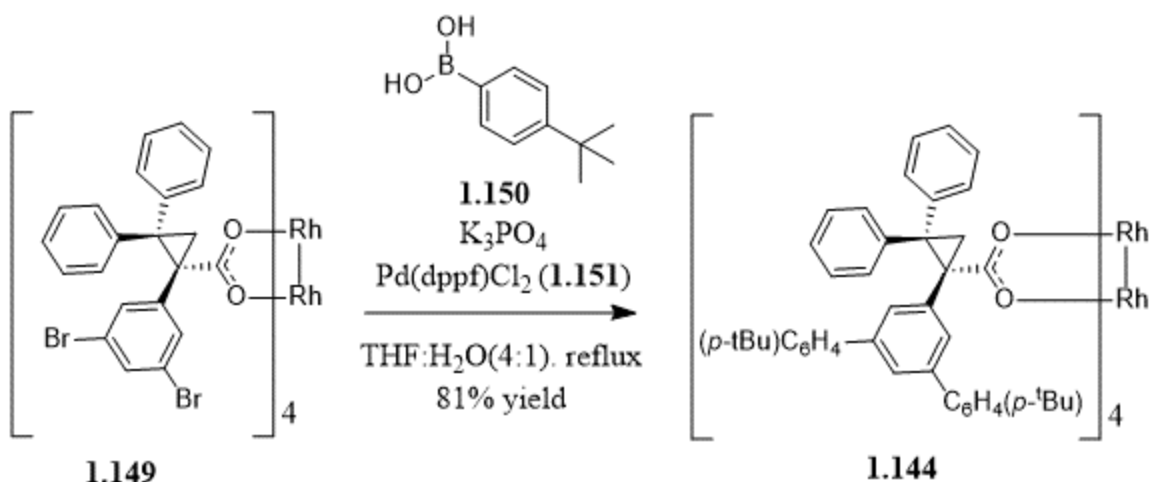


Figure 1.6.7: Catalyst-controlled site selectivity in the reactions of 2-methylpentane.^{112,114,116}

The reactions proceed with good yield and high *ee*.

A key development which enabled the preparation of some of the novel catalysts was the discovery that halogenated dirhodium tetracarboxylate complexes can participate in multifold cross coupling reactions with boronic acids under Suzuki reaction conditions (Scheme 1.6.11). An illustrative example of this reaction is the synthesis of the highly bulky catalyst **1.144** using the brominated dirhodium triarylcyclopropane **1.149**.



Scheme 1.6.11: Multifold cross-coupling to prepare $\text{Rh}_2[\text{R-3,5-di}(p\text{-}^t\text{BuC}_6\text{H}_4)\text{TPCP}]_4$ (**1.144**).

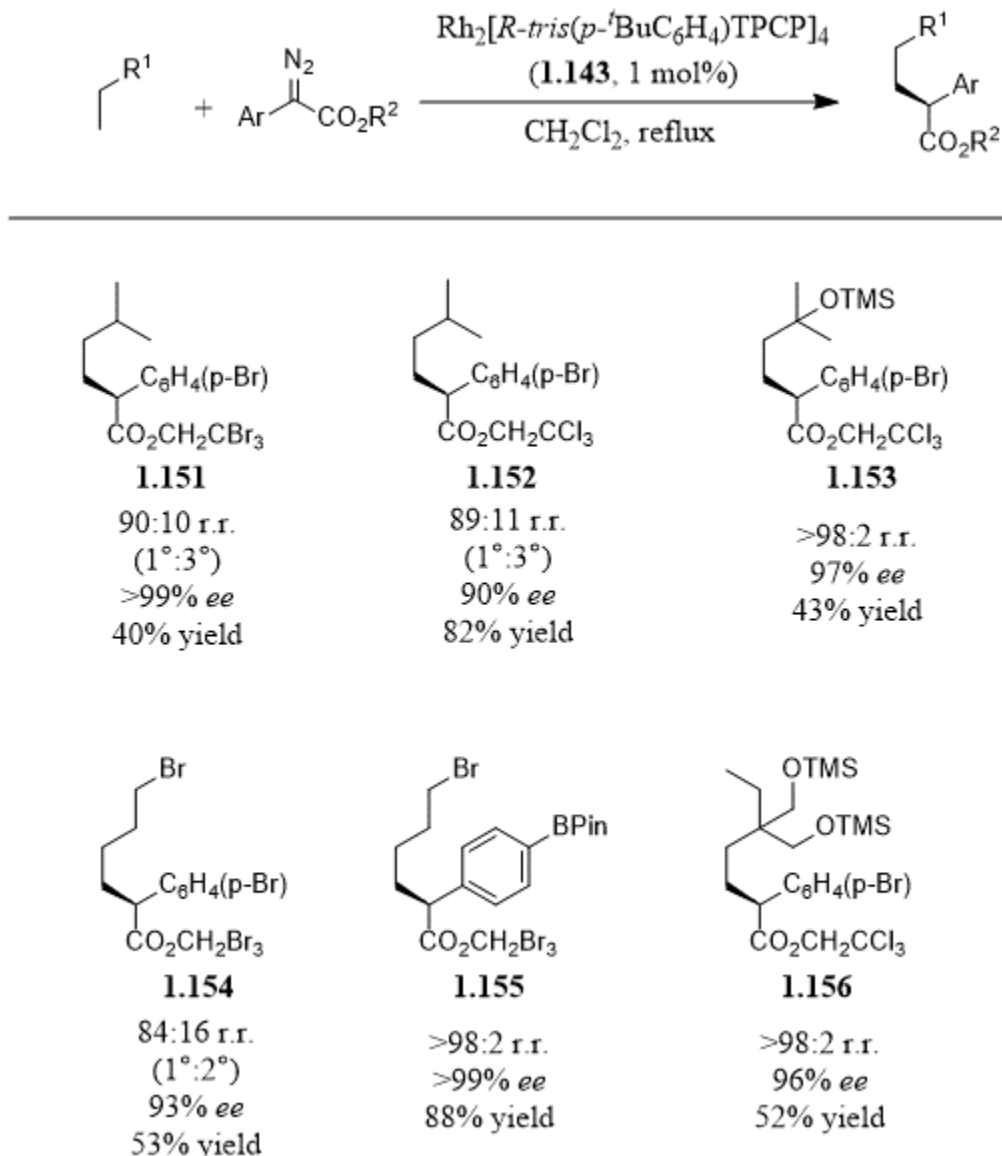
The synthesis of this catalyst requires an “on-rhodium” multifold cross-coupling because the ligand is too bulky for direct exchange with a rhodium(II) precursor.

These reactions can sometimes be challenging to perform due to low coupling efficiency and difficult purifications, but in many instances, they yield a separable and structurally well-defined product. The multifold cross coupling strategy is necessary because when the carboxylate ligands become very large, the ligand substitution reaction may fail to generate a significant yield of the tetra-substituted carboxylate complex. In these cases, a mixture containing partially exchanged products is observed. Even when subjected to rigorous purification, tetracarboxylate complexes with fewer than four chiral ligands often show lower enantioselectivity than those having four chiral ligands.

The design of catalysts which are highly selective for unactivated primary sites in the presence of viable secondary and tertiary positions is considered to be very challenging, and successful implementation of such a catalyst design is largely unprecedented outside of the Davies group. Primary sites are inherently unfavorable for C-H insertion reactions because there

is very little stabilization of the partial positive charge which develops during the transition state.

As such, any strategy for achieving site selectivity at unactivated primary C-H bonds must rely solely on steric control. Despite this, the current “best-in-class” primary-selective catalyst $\text{Rh}_2[\text{tris}(p\text{-}^t\text{BuC}_6\text{H}_4)\text{TPCP}]_4$ can often yield good regio- and stereoselectivity for many substrates (Scheme 1.6.12). All of the examples **1.151**–**1.156** show exceptional *ee* and *rr*.



Scheme 1.6.12: Unactivated primary site functionalization with



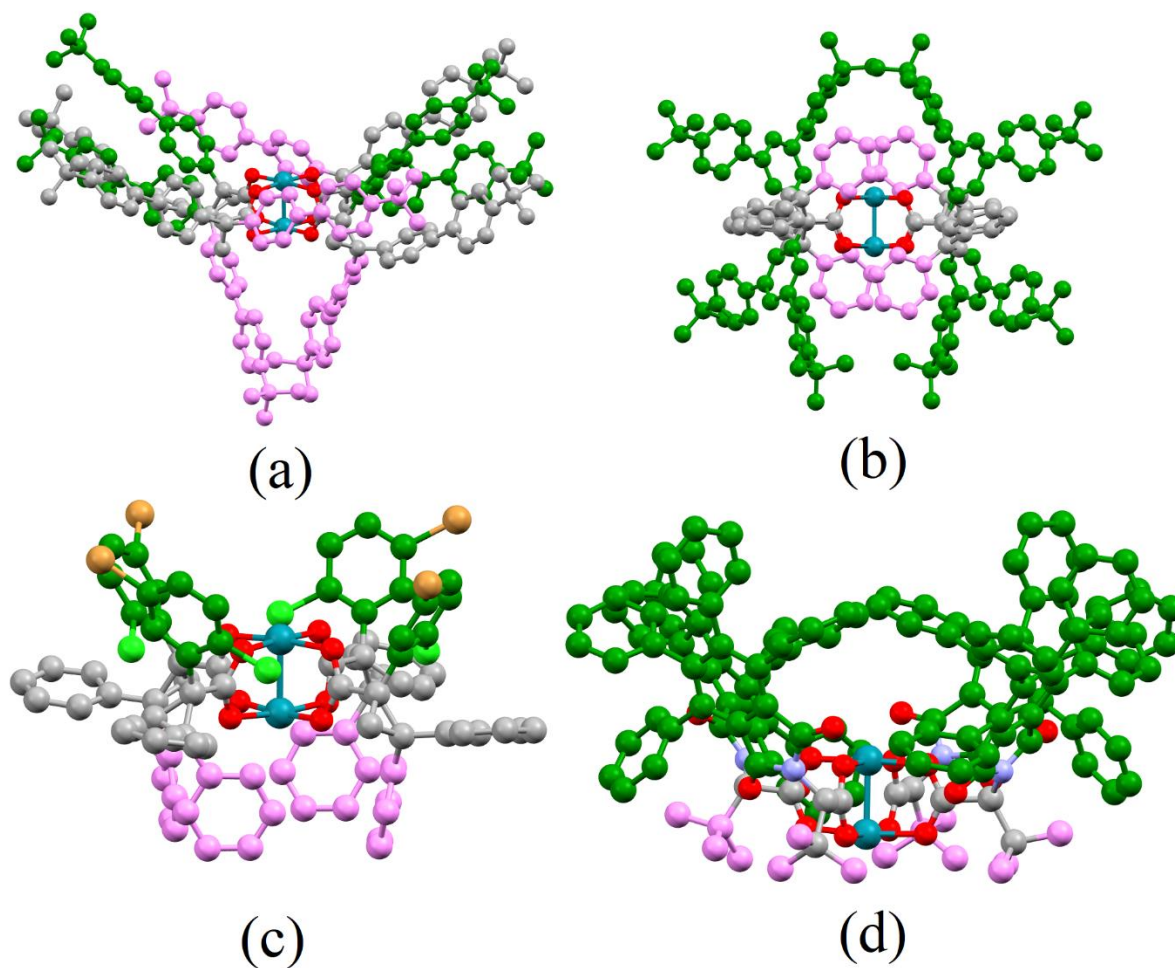
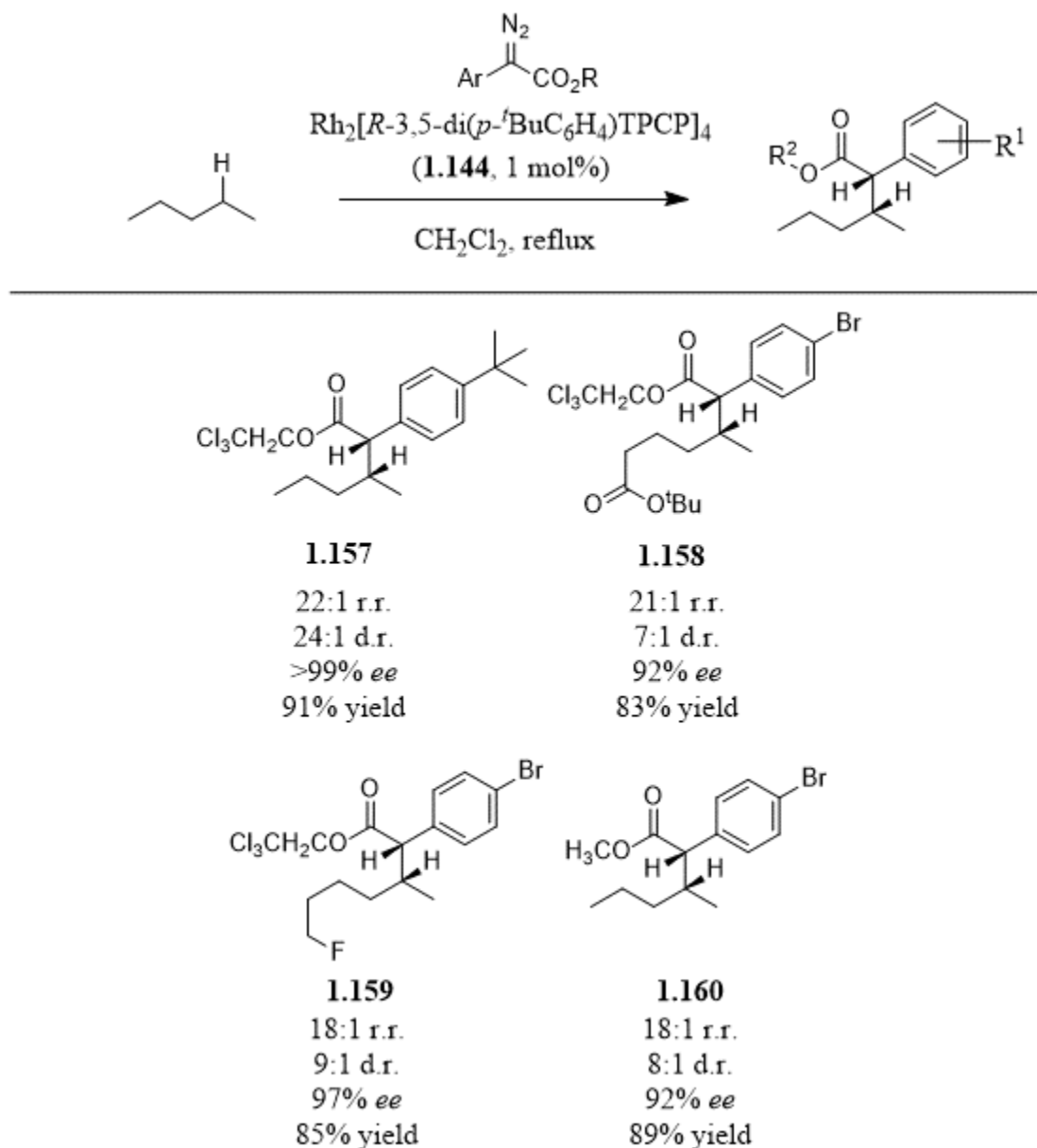


Chart 1.6.2: 3D structures of some highly selective dirhodium catalysts for C-H insertion. (a) Computed structure of $\text{Rh}_2[\text{R-}tris(p\text{-}^t\text{BuC}_6\text{H}_4)\text{TPCCP}]_4$ (**1.143**) [ONIOM (B3LYP:UFF)].¹¹⁴ (b): X-ray structure of $\text{Rh}_2[\text{R-}3,5\text{-di}(p\text{-}^t\text{BuC}_6\text{H}_4)\text{TPCCP}]_4$ (**1.144**).¹¹² (c): X-ray structure of $\text{Rh}_2[\text{S-}2\text{-Cl-}5\text{-BrTPCCP}]_4$ (**1.161**).¹¹⁷ (d) X-ray structure of $\text{Rh}_2(\text{S-TPPTTL})_4$ (**1.174**).¹¹⁹ Solvent molecules have been omitted for clarity.

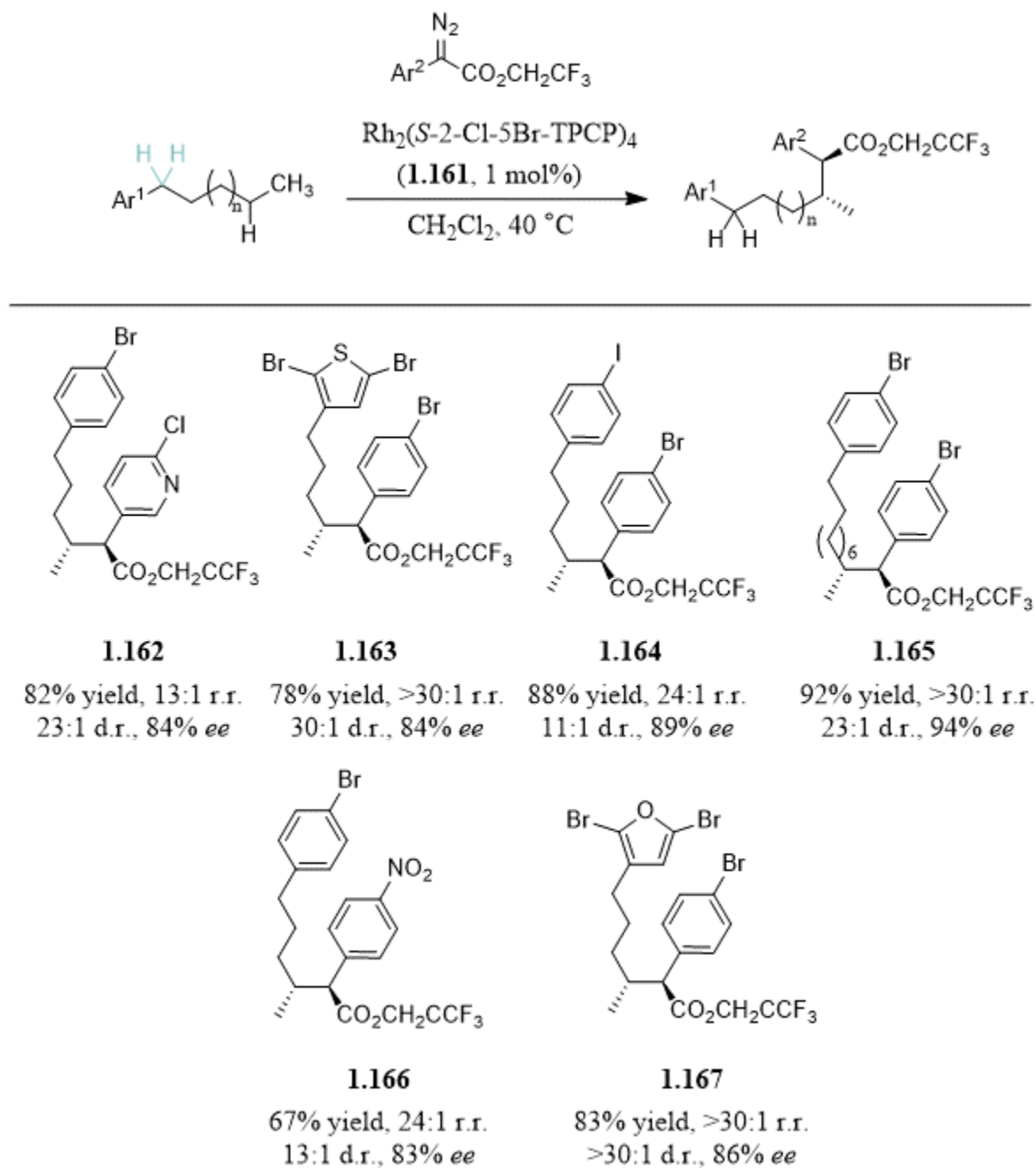
$\text{Rh}_2[\text{tris}(p\text{-}^t\text{BuC}_6\text{H}_4)\text{TPCP}]_4$ is extremely crowded, and ONIOM calculations indicate that it adopts a rigid C_2 -symmetric geometry in solution (Chart 1.6.2a). The $(\alpha, \alpha', \alpha, \alpha')$ ligand orientation adopted by this catalyst is similar to the arrangement displayed by $\text{Rh}_2(p\text{-PhTPCP})_4$, but more of the steric bulk is shifted toward the periphery of the catalyst rather than directly above the rhodium center. One face of the $\text{Rh}_2[R\text{-tris}(p\text{-}^t\text{BuC}_6\text{H}_4)\text{TPCP}]_4$ (**1.143**) catalyst is completely blocked off by two *tert*-butyl biphenyl groups, while the opposing face remains highly shielded by the other long aryl groups. Using 2,2,2-trichloroethyl aryldiazoacetates as carbene precursors, primary sites are favored by a substantial margin - even with challenging substrates such as 2-methylpentane. Examples such as **1.155** illustrate that it is possible to achieve both exceptionally high regioselectivity and enantioselectivity using this catalyst.

The cyclopropanecarboxylate catalyst $\text{Rh}_2[3,5\text{-di}(p\text{-}^t\text{BuC}_6\text{H}_4)\text{TPCP}]_4$ is highly effective for the selective functionalization of sterically accessible, unactivated secondary C-H bonds¹¹². By placing the 4-*tert*-butyl-phenyl substituents at both meta positions of the α -aryl group, the ligands become too wide to fit on the same face of the dirhodium paddlewheel and must alternate between opposite faces of the complex (Chart 1.6.2b). The resulting catalyst shows $(\alpha, \beta, \alpha, \beta)$ D_2 -like symmetry and is less hindered than the primary-selective catalysts $\text{Rh}_2(p\text{-PhTPCP})_4$ or $\text{Rh}_2[\text{tris}(p\text{-}^t\text{BuC}_6\text{H}_4)\text{TPCP}]_4$, but still too sterically crowded to accommodate tertiary sites. Exceptionally high site- and stereoselectivity for the sterically accessible C2 secondary site is observed across a range of unactivated substrates (Scheme 1.6.13). Placement of an electron-withdrawing group on the alkane is well-tolerated, as illustrated by examples **1.158** and **1.159**.



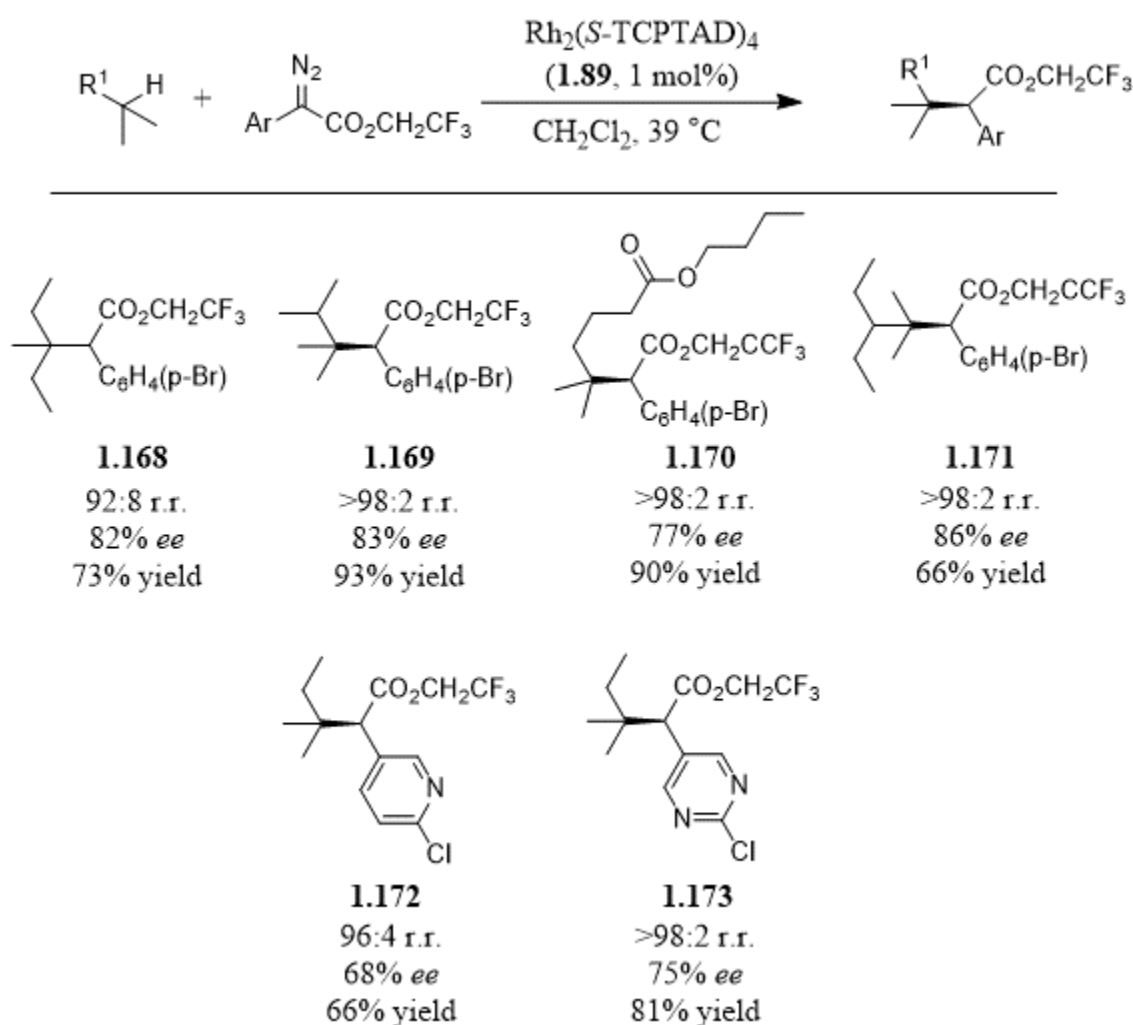
Scheme 1.6.13: C2 functionalization of n-pentane derivatives with a D_2 -symmetric catalyst.¹¹²

Sterically crowded dirhodium triarylcyclopropanecarboxylates are also highly effective for the selective C-H functionalization of unactivated methylene sites in the presence of electronically activated C-H bonds (Scheme 1.6.14).¹¹⁷ The key to success for this type of reaction is to place an *ortho*-chloro substituent on the aryl ring α - to the dirhodium carboxylate, as in catalyst **1.161** (Chart 1.6.2c). The presence of the chlorine atom causes hindered rotation of the α -aryl group with respect to the cyclopropane ring, locking the dirhodium tetracarboxylate complex into a rigid C₄-symmetric ($\alpha,\alpha,\alpha,\alpha$) geometry. The strategic placement of a bromine atom at the 5-position of the C1-aryl group adds an additional element of helical chirality, which often allows catalyst **1.161** to achieve high *ee* as well as high regioselectivity. Because many functional groups such as pi systems and heteroatoms cause electronic activation of neighboring C-H sites, *ortho*-chlorinated TPCP catalysts are highly versatile and can enable many useful retrosynthetic disconnections. Examples **1.162-1.167** all show >20:1 r.r. for the C2 site over the benzylic position as well as over 80% *ee*.



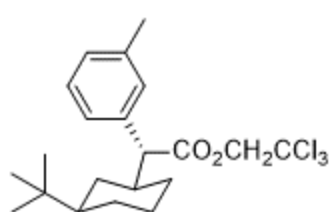
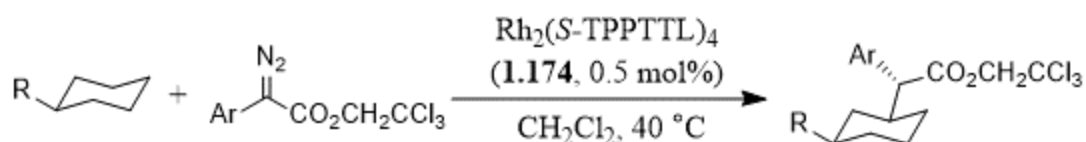
Scheme 1.6.14: Overcoming benzylic activation with $\text{Rh}_2(\text{S-2-Cl-5-Br-TPCP})_4$ (**1.161**).¹¹⁷

The phthalimido-amino acid class of dirhodium tetracarboxylate catalyst has many applications in the C-H functionalization of unactivated C-H bonds. As discussed in section 1.6.2, this type of catalyst adopts a C_2 -symmetric ($\alpha,\alpha,\alpha,\alpha$) “chiral crown” conformation when the amino acid side chain group is sufficiently large.¹¹⁸ The most effective catalyst for the functionalization of unactivated tertiary C-H bonds is $Rh_2(\text{TCPTAD})_4$ (Scheme 1.6.15). In contrast to the triarylcyclopropanecarboxylates, the **TCPTAD** catalyst is not particularly sterically demanding, but presents a well-defined chiral pocket which is rigidified by the presence of the chlorine atoms (see also Figure 1.6.4). Once the carbene is bound to the dirhodium center, a chloro-phthalimido group consistently engages in a π -interaction with the aryl group of the carbene unit. Together, these features enable sterically hindered tertiary C-H bonds to react with high site- and enantioselectivity. The substrate scope of the tertiary selective C-H insertion reactions is quite general, and reactions with the **TCPTAD** catalyst can often show enantiomeric excess values above 80%. While these reactions generally show very high regioselectivity, in the case of compounds **1.168-1.173** the *ee* of the products was not as good as with the triarylcyclopropanecarboxylate catalysts **1.143** and **1.144**.

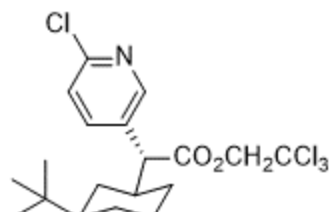


Scheme 1.6.15: Examples of tertiary site functionalization with $\text{Rh}_2(\text{S-TCPTAD})_4$ (**1.189**).¹¹⁶

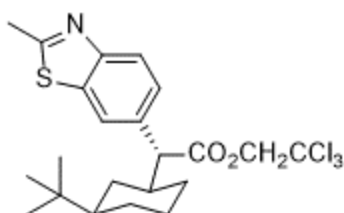
As with $\text{Rh}_2(\text{2-Cl-5-Br-TPCP})_4$, introducing additional elements of steric control at a slight distance from the reaction center can greatly affect the site selectivity of the phthalimido-amino acid type of catalyst. This effect is illustrated by the site-selective reaction of the catalyst $\text{Rh}_2(\text{S-TPPTTL})_4$ (**1.174**) at the C3 equatorial positions of monosubstituted cyclohexane derivatives (Scheme 1.6.16).¹¹⁹ The structure of this large catalyst places 16 phenyl groups at the edges of the phthalimide face of the catalyst, and like the other sterically demanding catalysts in this class, adopts an $(\alpha,\alpha,\alpha,\alpha)$ ligand orientation with one face of the dirhodium paddlewheel blocked by the four *tert*-butyl groups (Chart 1.6.2d). Using $\text{Rh}_2(\text{S-TPPTTL})_4$ (**1.174**), the regioselectivity of C-H insertion is frequently >50:1 favoring the C3 equatorial product, and the catalyst is routinely able to achieve enantiomeric excess values above 90%. When other dirhodium catalysts are used in these reactions, mixtures of C3, C4, and C5 insertion are observed as the major products. The reaction of $\text{Rh}_2(\text{S-TPPTTL})_4$ (**1.174**) with *tert*-butylcyclohexane and 2,2,2-trichloroethyl 4-bromophenyldiazoacetate (**1.116**) has been studied in detail using computational methods, and a model has been developed to explain the high selectivity. On formation of the dirhodium carbene from the diazo compound, the shape of the ligand framework of this catalyst changes, and the phenyl groups rotate to create a well-defined helical carbene pocket. This “induced fit” model rationalizes the site selectivity for the C3-equatorial position on the basis that the *tert*-butyl substituent of the cyclohexane would prefer be pointed away from the “wall” formed by the 16 phenyl groups, placing the enantiotopic C3-equatorial hydrogen in close proximity to the dirhodium carbene.



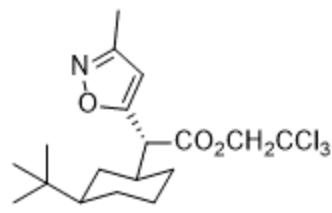
1.175
88% yield, 94% *ee*
>50:1 r.r.
16:1 d.r.



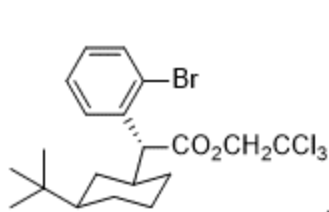
1.176
58% yield, 98% *ee*
>50:1 r.r.
9.8:1 d.r.



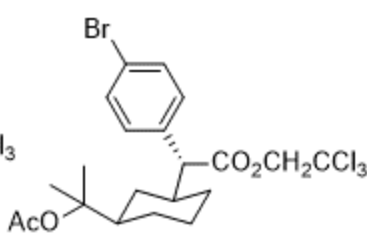
1.177
71% yield, 98% *ee*
>50:1 r.r.
13:1 d.r.



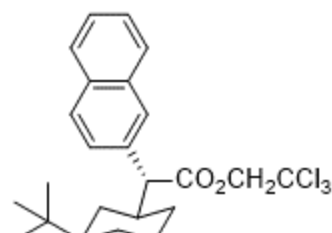
1.178
41% yield, 83% *ee*
>50:1 r.r.
25:1 d.r.



1.179
62% yield, 85% *ee*
40:1 r.r.
19:1 d.r.



1.180
75% yield, 97% *ee*
>50:1 r.r.
12.4:1 d.r.



1.181
81% yield, 98% *ee*
>50:1 r.r.
11:1 d.r.

Scheme 1.6.16: Selective functionalization of the C3 equatorial C-H bond of cyclohexanes.

The examples described in this section have illustrated that very high regio- and stereoselectivity can be achieved for C-H bonds in a variety of different chemical environments in the dirhodium catalyzed reactions of donor/acceptor aryldiazoacetates. Over the past decade, the scope and utility of C-H functionalization reactions has increased dramatically due to the discovery of new catalysts with specialized applications. Despite these advances, there are undoubtedly many useful dirhodium tetracarboxylate catalysts that have yet to be discovered by a future generation of researchers.

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Chapter 2: Study of Dirhodium

Diarylcyclopropanecarboxylate Catalysts

2.1 Background

While the dirhodium triarylcyclopropanes (**TPCP**) have three aryl substituents, the dirhodium diarylcyclopropanecarboxylates (**E-DPCP** and **Z-DPCP**) only have two. The cyclopropane ligands in the triaryl series generally have identical aromatic groups at the C2- position of the cyclopropane, and the formal removal of one of these substituents introduces an additional stereocenter onto the ligand framework. As a consequence, the $\text{Rh}_2(\text{DPCP})_4$ catalysts can be described as either *E* or *Z* diastereomers depending on the placement of the second aryl substituent (Chart 2.1.1).

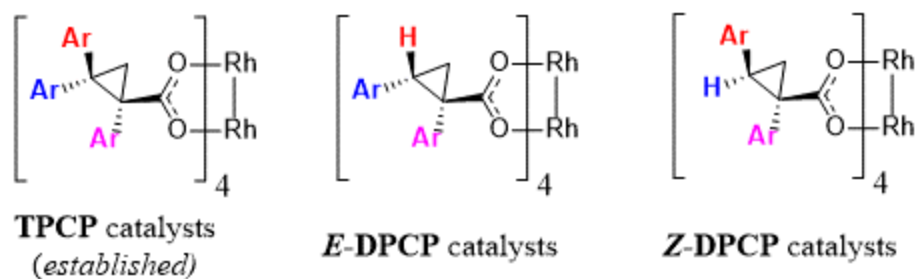


Chart 2.1.1: Three types of dirhodium cyclopropanecarboxylate catalyst.

As previously discussed in Chapter 1.6.3, pioneering work by Dr. Jorn Hansen suggested that **E-DPCP** type catalysts are unlikely to demonstrate high enantioselectivity because they lack the key blocking group *syn* to the rhodium carboxylate group on the cyclopropane.¹ However, this study did not examine how adding additional functionality to the **DPCP** ligand might affect the

complex, or how a diaryl catalyst with Z-geometry might behave in carbene reactions. In this chapter, the site- and enantioselectivity properties of **DPCP** catalysts will be discussed in detail.

2.1.1 Substituent Effects in The Triarylcyclopropanecarboxylates

The placement of substituent groups on the α -aryl ring of the **TPCP** ligands has been shown to have a pronounced effect on the geometry of the catalyst² (Figure 2.1.1). This effect is observed computationally by the minimum energy conformations of the catalysts. Each of these classes of catalyst also selects different types of C-H bonds in reactions at sp^3 -centers.

When a 2-chloro substituent is introduced on this aryl group (Figure 2.1.1A), the triarylcyclopropane catalyst becomes rigidly locked in a $(\alpha,\alpha,\alpha,\alpha)$ -C₄ conformation with the four aryl substituents completely shielding the dirhodium center on one face of the rhodium disc.³ The less crowded face has a relatively narrow bowl shape which is large enough to fit the rhodium carbene but still sufficiently hindered that it can exclude many types of C-H sites from the reaction center.

If substituents are placed in the meta positions of the α -aryl (Figure 2.1.1B), the cyclopropane ligands become wide enough to force the neighboring positions onto the opposite face of the dirhodium paddlewheel, leading to a conceptually D₂/ $(\alpha,\beta,\alpha,\beta)$ arrangement⁴ In this shape, both faces of the dirhodium paddlewheel are effectively identical. Like the *ortho*-chloro triarylcyclopropane catalysts, D₂-symmetric dirhodium carbenes prefer to react at secondary sites. Due to the more spacious catalyst pocket, they often tend to react at activated secondary sites or primary positions than the *ortho*-chloro **TPCP** catalysts, but often show higher yield and *ee* than the *ortho* catalysts.

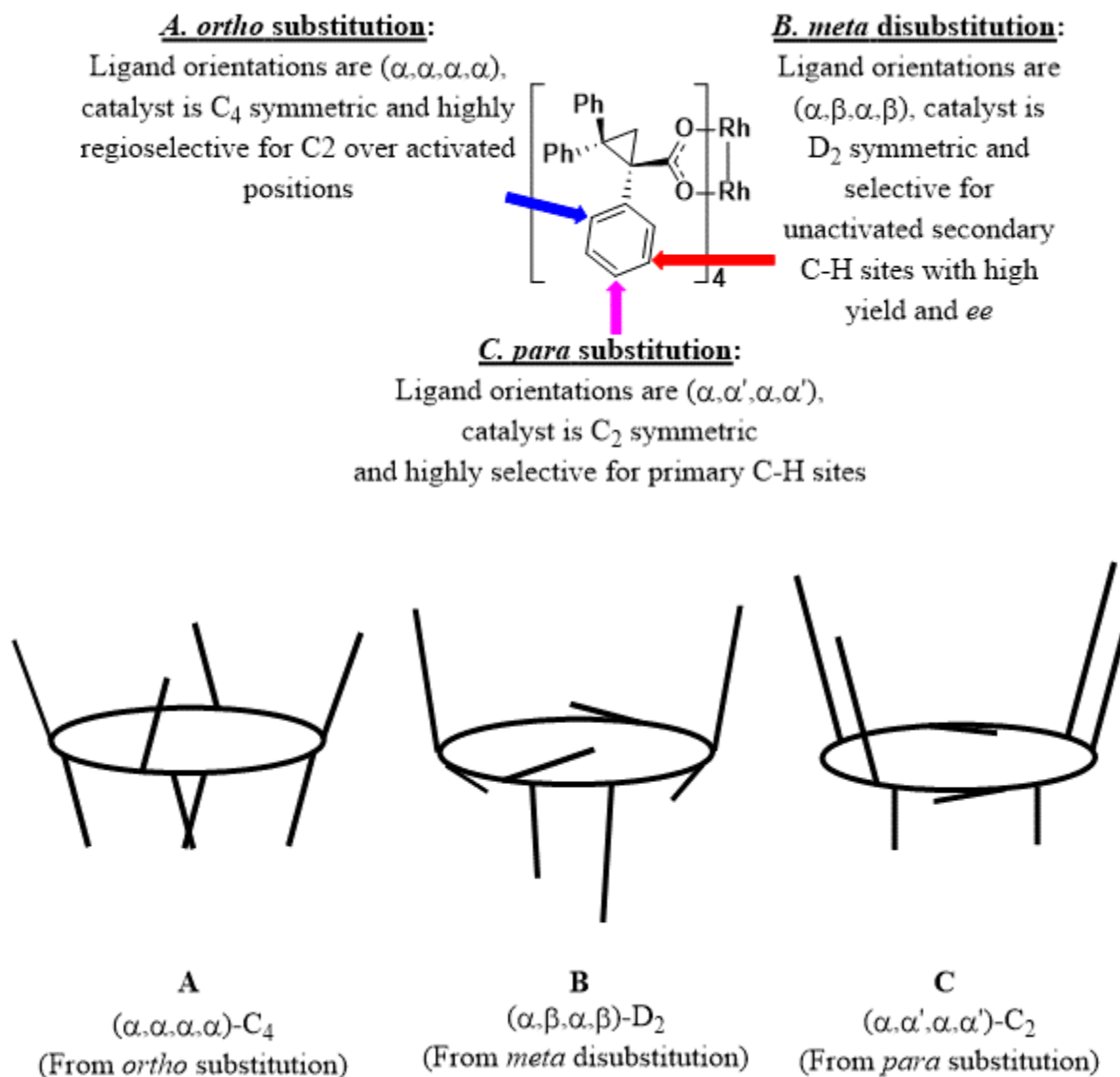


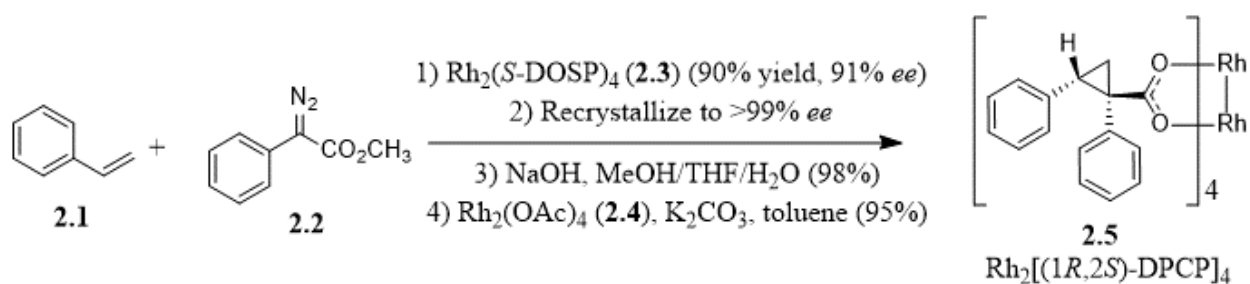
Figure 2.1.1: Illustration of the substituent effect at the C1 aryl group of TPCP catalysts.²

When the substituent is placed at the *para* position of the C1-aryl (Figure 2.1.1C), or if the C1-aryl is unsubstituted, the catalyst prefers to adopt a C₂/($\alpha,\alpha',\alpha,\alpha'$) shape.⁵ Catalysts of this type have an entirely different selectivity profile and react preferentially at primary C-H sites. This is a remarkable fact because primary C-H sites have fewer neighboring C-C bonds with which to stabilize the partial positive charge that develops during the transition state of the carbene C-H insertion event (see Figure 1.3.1). The additional alkyl substituents present at secondary and tertiary sites can stabilize the transition state via donation from the additional electron-rich C-C bonds. The C₂/($\alpha,\alpha',\alpha,\alpha'$) shape is sufficiently hindered at the carbene stage to crowd out the more stabilized C-H sites. An additional feature of the *para*-substituted **TPCP** catalysts is that they often display exceptionally high enantioselectivity.

2.1.2 Design of Dirhodium Diarylcyclopropanecarboxylates

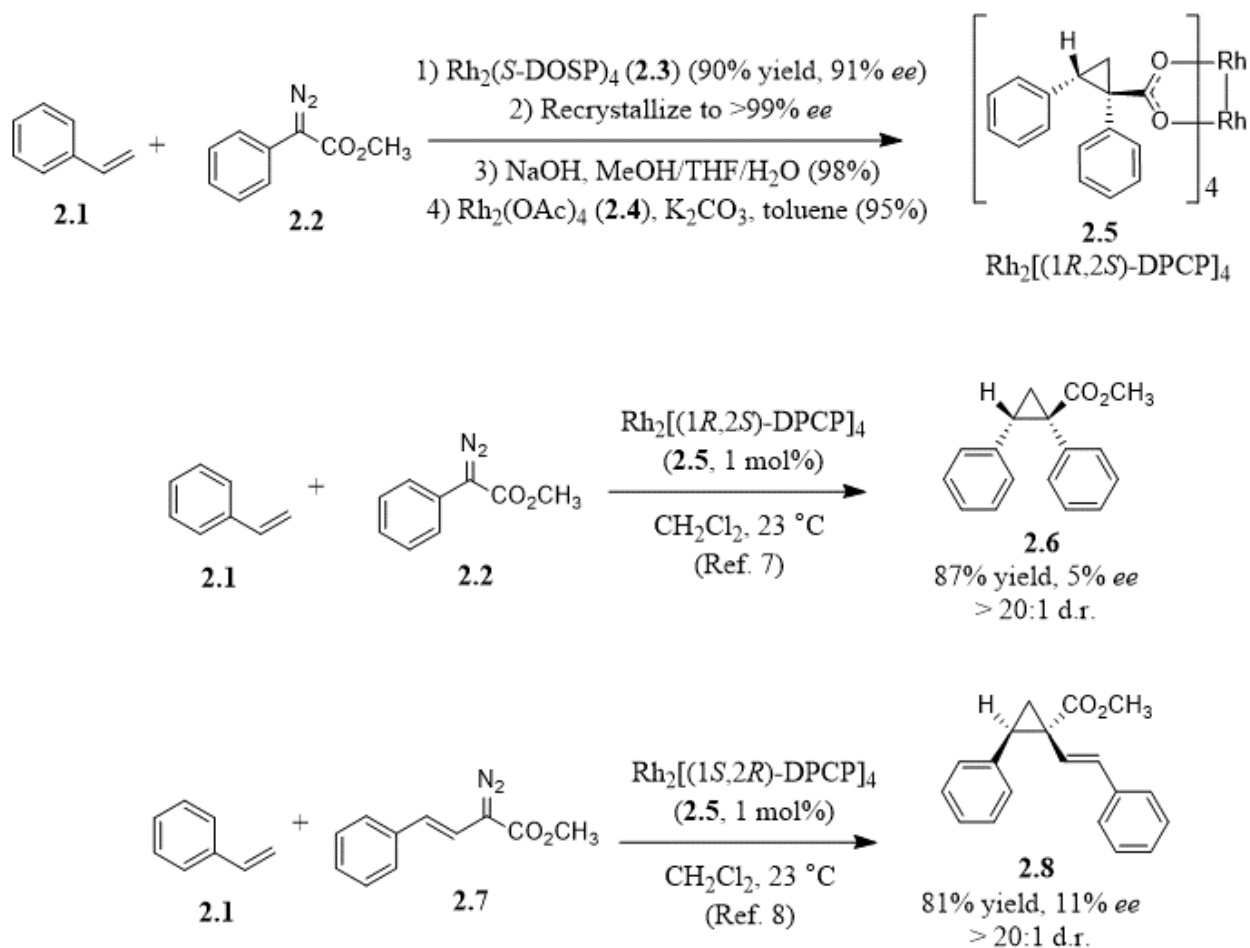
The discovery of these remarkable substituent effects prompted us to investigate whether modifying the C1-aryl group would have a similar effect on diarylcyclopropane catalysts. The **E-DPCP** class of catalysts can be rapidly prepared in high enantiopurity using dirhodium carbene chemistry⁶. The key step in the ligand synthesis is the asymmetric cyclopropanation reaction of a styrene derivative with a donor/acceptor type diazo compound (Scheme 2.2.1). Using functionalized diazo compounds and styrenes, a series of Rh₂(**E-DPCP**)₄ can be generated with *ortho*, *meta*, or *para* substituents on the C1 or C2 aryl rings.

The first **E-DPCP** catalyst Rh₂[(1*R*,2*S*)-DPCP]₄ (**2.5**) was prepared by Dr. Janelle Thompson during her investigation into novel dirhodium catalyst scaffolds in the early 2000's.⁷ In the synthesis of this catalyst, the tetraproline Rh₂(*S*-DOSP)₄ (**2.3**) was used for forming the cyclopropane ring. The cyclopropane ester product was recrystallized to enantiopurity, and subsequently saponified to the free carboxylic acid. Ligand exchange with Rh₂(OAc)₄ (**2.4**) in toluene then afforded Rh₂[(1*S*,2*R*)-DPCP]₄ (**2.5**) in high yield (Scheme 2.1.1).



Scheme 2.1.1: A key step in the synthesis of Rh₂[(1*S*,2*R*)-DPCP]₄ (**2.5**) is the asymmetric cyclopropanation of styrene with a chiral dirhodium catalyst.⁷

While it is fortunate that there is a short route to the **E-DPCP** type catalysts, early experiments suggested they are ineffective as a chiral catalysts. Dr. Thompson and Dr. Changming Qin⁸ found that catalyst **2.5** was incapable of achieving high enantioselectivity in the cyclopropanation reaction of methyl *trans*-styryldiazoacetate with styrene (Scheme 2.1.2):



Scheme 2.1.2: Cyclopropanation reactions with E-DPCP show very low enantioselectivity.^{7,8}

These results are consistent with Hansen's hypothesis that lacking the key substituent *syn* to the dirhodium carboxylate, **E-DPCP** catalysts cannot show high enantioselectivity¹. However, $\text{Rh}_2[(1S,2R)\text{-DPCP}]_4$ (**2.5**) still exhibits low but measurable enantioselectivity in the cyclopropanation reactions that generate compounds **2.6** and **2.8**. This fact would suggest that the

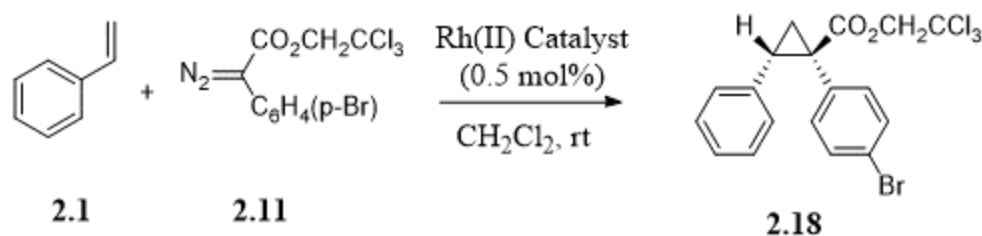
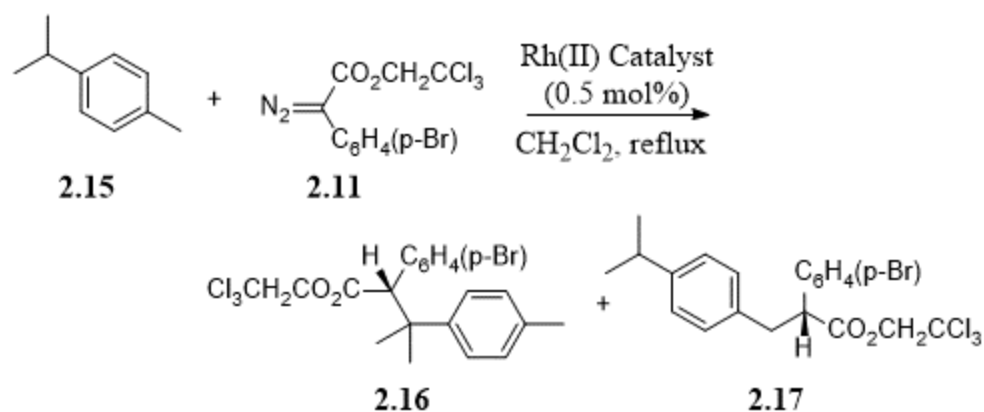
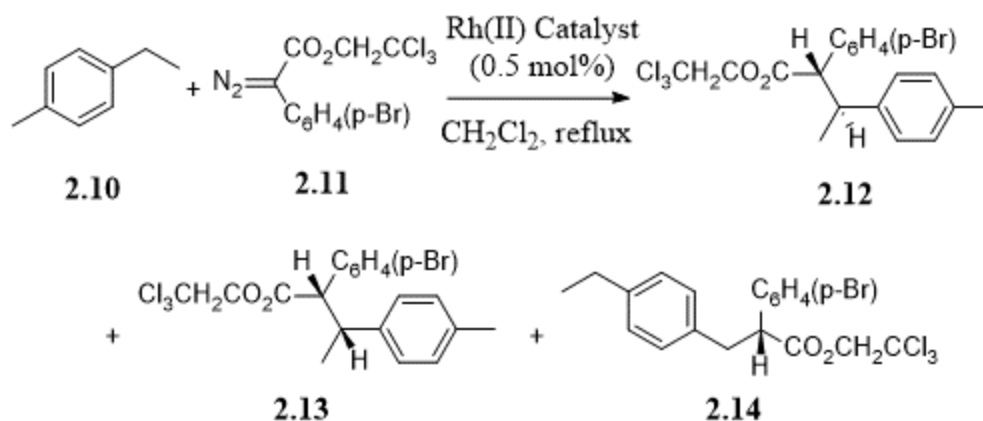
placement of additional structural features on the diarylcyclopropane ligand may enable the catalysts to show higher *ee*.

The present study focused on opportunities to develop the under-investigated diarylcyclopropanecarboxylate catalysts into useful synthetic tools. A logical starting point for this work was to add additional functionality to the C1 aryl group. The range of conformers displayed by the triaryl catalysts varies dramatically depending on the arrangement of substituents at this aryl substituent, so if a similar effect were to occur in the diaryl series then they might be capable of high enantioselectivity. The **Z-DPCP** type catalysts were also seen as promising because they possess a *syn*- aryl substituent, and thus might be expected to show high enantioselectivity comparable to Rh₂(**TPCP**)₄. Another objective was to investigate the selectivity of dirhodium diarylcyclopropanecarboxylates in C-H insertion reactions. As diarylcyclopropanecarboxylate catalysts are more sterically open than triarylcyclopropanes, they should show higher selectivity for tertiary C-H sites than Rh₂(**TPCP**)₄.

2.2 Results and Discussion

As with **TPCP**, the syntheses of functionalized **E-DPCP** ligands use an asymmetric carbene cyclopropanation reaction as the key step. A **Z-DPCP** catalyst Rh₂[(1*R*,2*R*)-DPCP]₄ (**2.9**) was also prepared in this manner, but additional synthetic manipulations were invoked to set the desired functionality and stereochemistry at C2. In order to classify the site selectivity of the new catalysts, they were each tested with the substrates 4-ethyltoluene (**2.10**) and 4-isopropyltoluene (**2.15**) using the diazo compound 2,2,2-trichloroethyl 4-bromophenyldiazoacetate (**2.11**, Scheme 2.2.1). These reactions are effectively a competition between primary, secondary, and tertiary benzylic sites. When performed properly, they are also

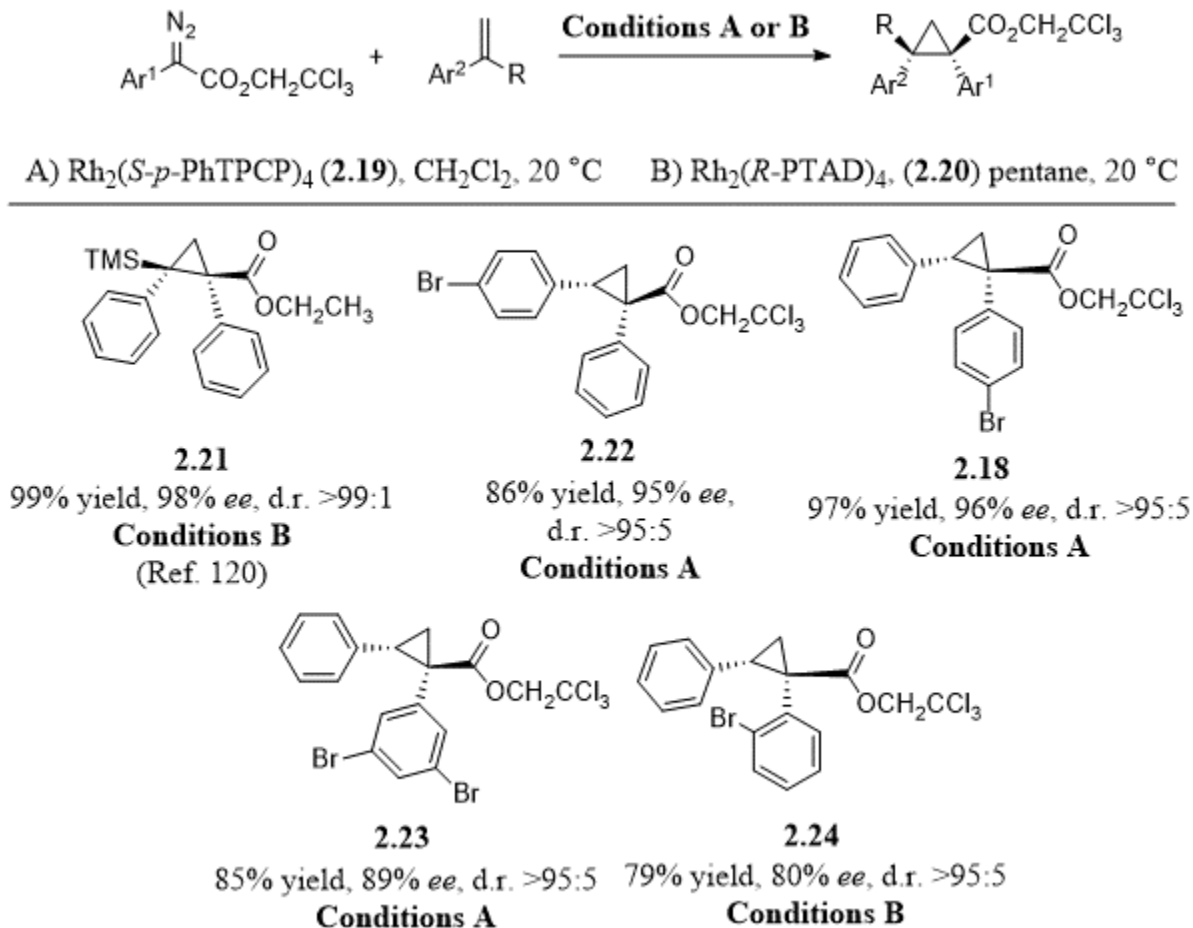
fairly high yielding with most dirhodium catalysts. To examine whether the **DPCP** catalysts could be effective in asymmetric cyclopropanation, their reactions with styrene (**2.1**) were also performed.



Scheme 2.2.1: Reactions used to evaluate the $\text{Rh}_2(\text{DPCP})_4$ catalysts.

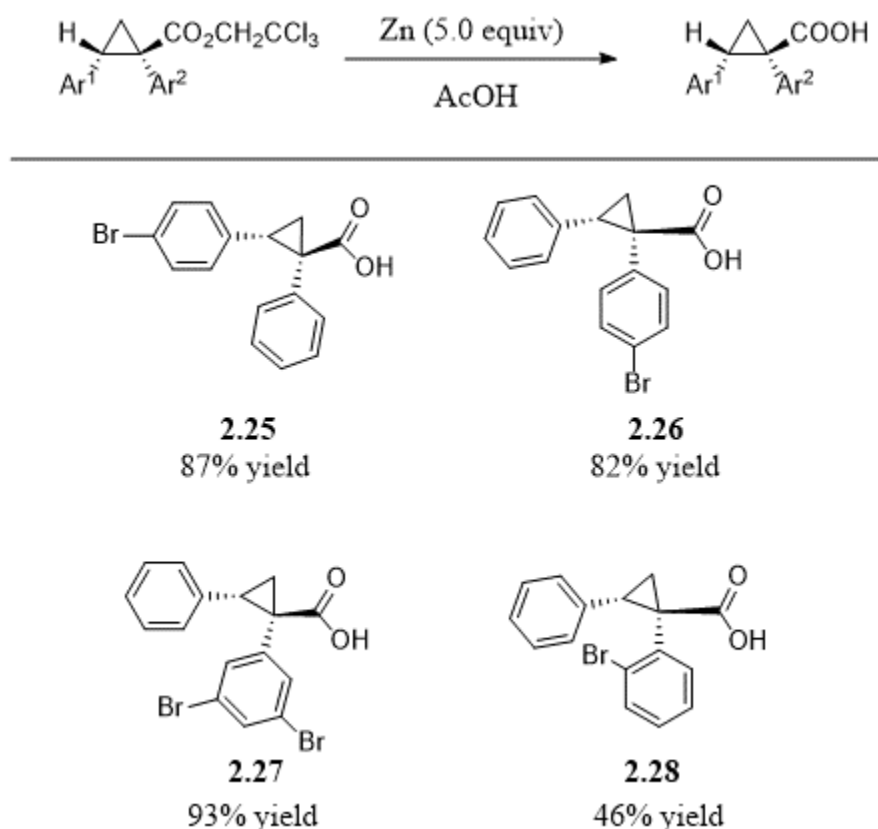
2.2.1 Synthesis of Dirhodium Diarylcyclopropanecarboxylates

A key step in the synthesis of each of the $\text{Rh}_2(\text{DPCP})_4$ complexes is the cyclopropanation reaction of a styrene compound with a chiral dirhodium catalyst (Scheme 2.2.2). Optimal results are obtained using $\text{Rh}_2(S\text{-}p\text{-PhTPCP})_4$ (**2.19**) or $\text{Rh}_2(R\text{-PTAD})_4$ (**2.20**). In the case of compound **2.21**, a 2-trimethylsilyl cyclopropane was prepared as a precursor for the catalyst $\text{Rh}_2[(1R,2R)\text{-Z-DPCP}]_4$ (**2.9**).⁹



Scheme 2.2.2: Cyclopropanation reactions in the synthesis of $\text{Rh}_2(\text{DPCP})_4$ catalysts.

The advantage of using 2,2,2-trichloroethyl esters as the acceptor group on the diazo component of rhodium carbene reactions is twofold. First, the longer and bulkier ester groups occupy space near the reactive site of the dirhodium catalyst pocket, leading to increasing enantioselectivity with the triarylcyclopropanecarboxylate catalysts.¹⁰ The trichloroethyl group is also readily deprotected to the free carboxylic acid in high yield via treatment with zinc powder in acetic acid solvent. (Scheme 2.2.2)¹¹

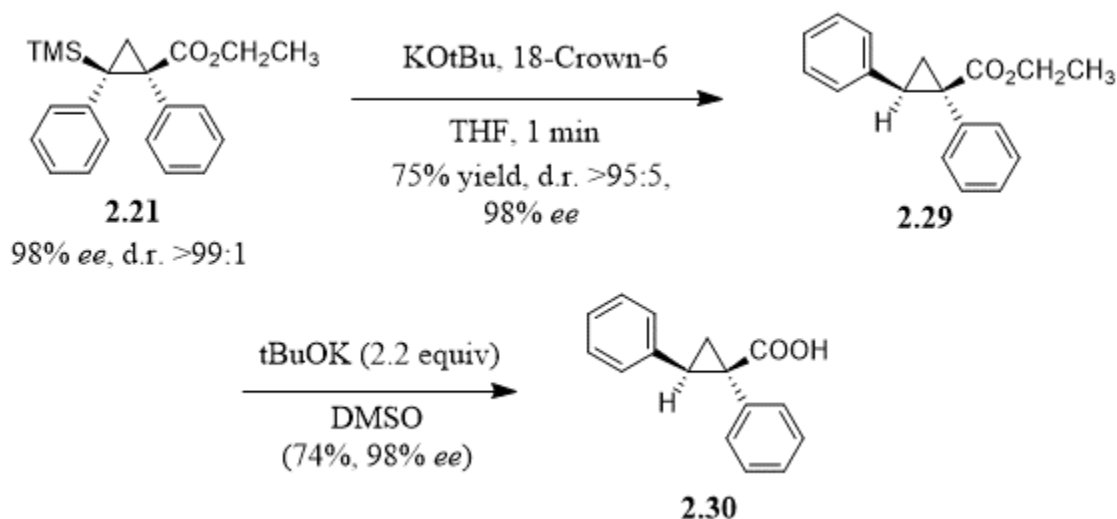


Scheme 2.2.2: Deprotection of 2,2,2-trichloroethyl esters with zinc powder in acetic acid.

The deprotection reactions of the 2,2,2-trichloroethyl esters **2.22**, **2.18**, and **2.23** proceed to completion in high yield using 5.0 equivalents of finely powdered zinc dust in acetic acid. These conditions are very mild and may tolerate a wide range of functionality such as silyl groups (see Chapter 4). Because finely powdered zinc is prone to oxidize under long-term storage in aerobic

environments, it may be necessary to use additional equivalents of the material or obtain a fresh supply to achieve optimal results. Some cyclopropanecarboxylates such as **2.24** are sterically hindered and will react sluggishly even when a large excess of zinc is used.

The trimethylsilylcyclopropane **2.21** can be used to prepare $\text{Rh}_2(\text{Z-DPCP})_4$ ligands in high diastereo- and enantiopurity (Scheme 2.2.3). Brief treatment with potassium *tert*-butoxide and 18-crown-6 causes desilylation of the trimethylsilyl group, inverting the C2 stereocenter with high fidelity to yield the *Z*-cyclopropanecarboxylate **2.29**⁹. The ethyl ester can then be deprotected using potassium *tert* butoxide in DMSO to afford **2.30**. This method represents a useful and general strategy for preparing *Z*-diarylcyclopropanecarboxylates from donor/acceptor dirhodium carbenes.

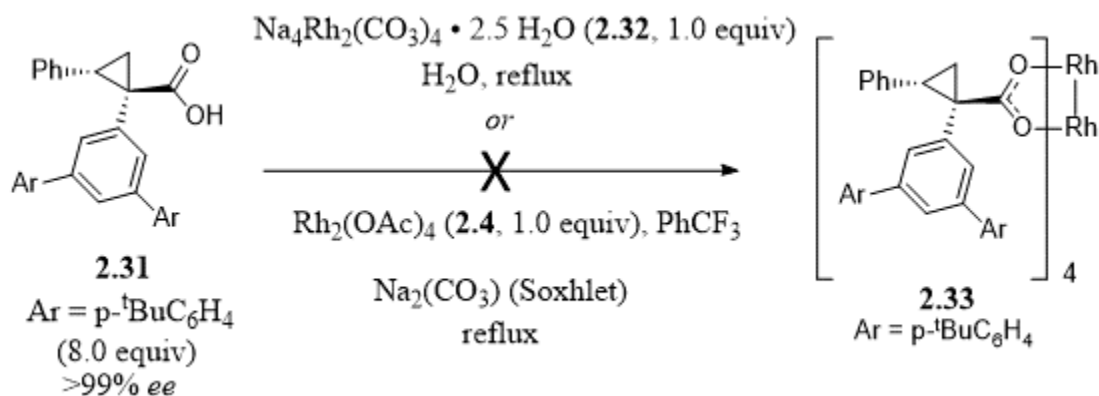


Scheme 2.2.3: Strategy for Preparing *Z*-Diarylcyclopropanecarboxylates.⁹

It is difficult to prepare compounds such as **2.30** directly from *E*-alkenes because they are generally too hindered to react with donor/acceptor dirhodium carbenes (See chapter 1.5). In addition to the desilylation reaction, Su, et al. have shown that the cyclopropanation reactions of α -trimethylsilylstyrenes with donor/acceptor carbenes show very high yield, diastereoselectivity,

and *ee* when a phthalimido-amino acid type catalyst is used as the catalyst in a hydrocarbon solvent⁹. The Davies catalyst $\text{Rh}_2(\text{R-PTAD})_4$ (**2.20**) was found to give the highest yield and stereoselectivity in these reactions and was used to synthesize compound **2.21**.

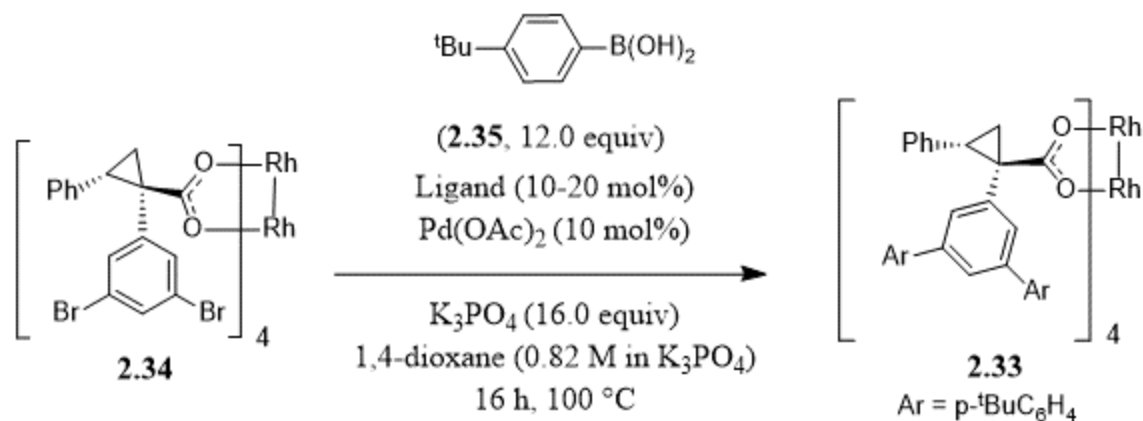
Transition metal catalyzed $\text{sp}^2\text{-sp}^2$ cross-coupling reactions can also be useful for preparing sterically demanding cyclopropanecarboxylate ligands. The Suzuki coupling reactions can either be performed on the free cyclopropanes in the standard fashion or as a sequential, multifold cross-coupling on dirhodium tetracarboxylate complexes with aryl halide functionality. For most cyclopropanecarboxylates, higher yield and purity are observed when the cross-coupling is performed on the free cyclopropane ligand. However, when the cyclopropanecarboxylate ligands are sufficiently bulky, the direct ligand exchange reactions with rhodium acetate or carbonate do not yield a significant quantity of the tetracarboxylate complexes. (Scheme 2.2.4).



Scheme 2.2.4: The DPCP ligand is too bulky to form a dirhodium tetracarboxylate complex.

In these cases, the multifold cross coupling reaction is the preferred strategy for preparing the catalyst. While the ferrocenyl-bisphosphine complex $\text{Pd}(\text{dppf})\text{Cl}_2$ (**2.36**) often performs optimally with $\text{Rh}_2(\text{TPCP})_4$ substrates, in the case of $\text{Rh}_2[(1R,2S)\text{-3,5-diBrDPCP}]_4$ (**2.34**) this complex did not give acceptable results. A screen of commercially available phosphine ligands

was performed to identify the optimal catalyst for performing this reaction (Table 2.2.1, Chart 2.2.2). The sterically congested, electron-rich bisphosphine ligand (R)-(-)-DTBM-SEGPHOS (**2.34**) was found to perform optimally in this experiment.



Run	Ligand	L: Pd Ratio	Isolated Yield
1	None (Control)	N/A	0% ^a
2	dppf (2.36)	1.0 (as Pd(dppf)Cl ₂)	0% ^a
3	(R)-(-)-DTBM-SEGPHOS (2.37)	1.5	90%
4	RuPhos (2.38)	2	56%
5	SPhos (2.39)	2	60%
6	SPhos ^b (2.39)	2	0% ^a
7	CataCXium A (2.40)	2	39%
8	<i>t</i> BuXPhos (2.41)	2	0% ^a

Table 2.2.1: Ligand screen for the cross-coupling reaction. ^aAn inseparable mixture of byproducts was obtained containing apparently none of the desired product. ^bAttempted Negishi Coupling reaction run in THF/NMP (1:1) with Pd₂(dba)₃ as Pd source.

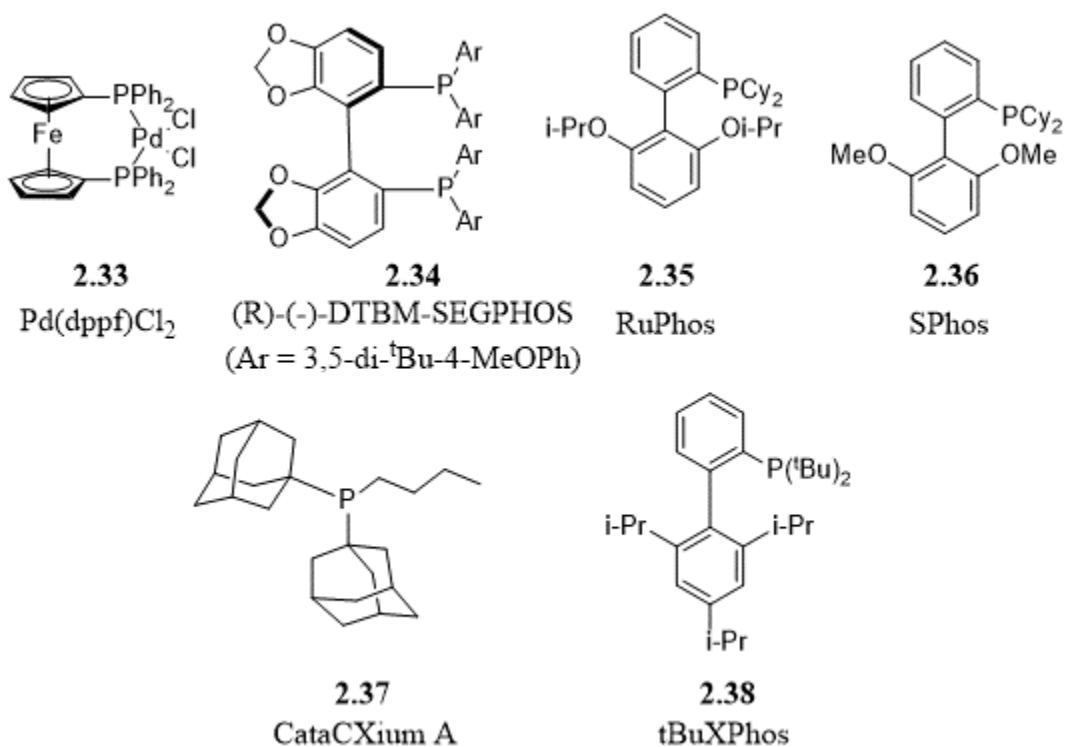
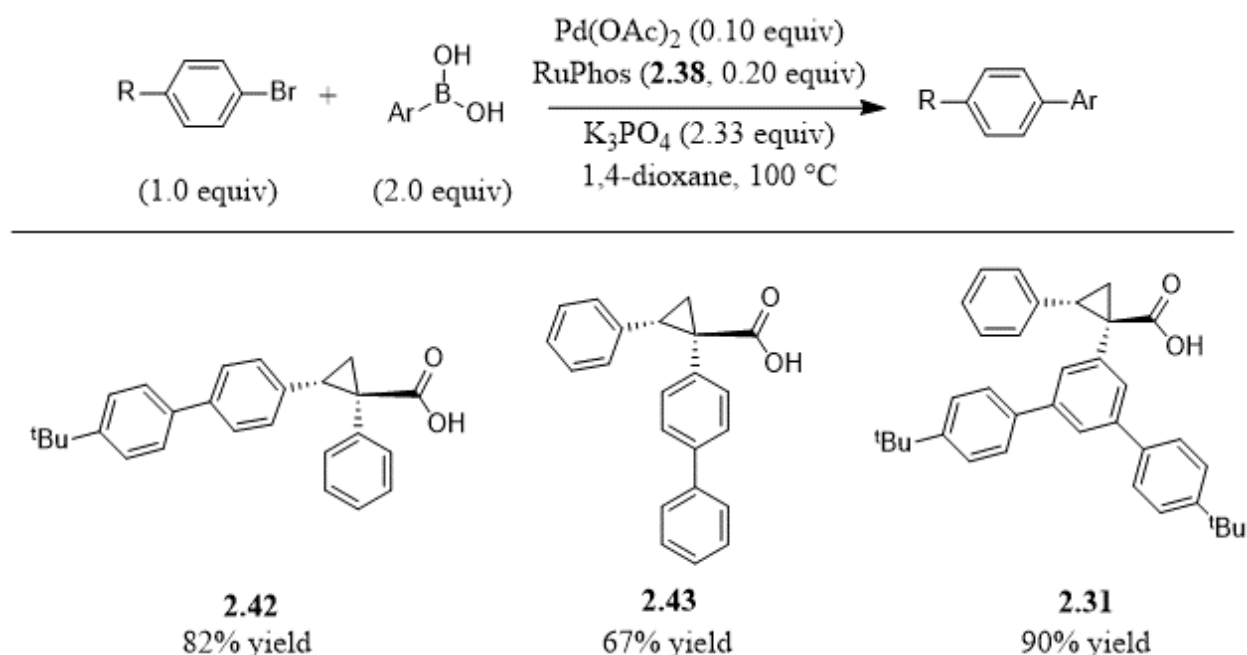


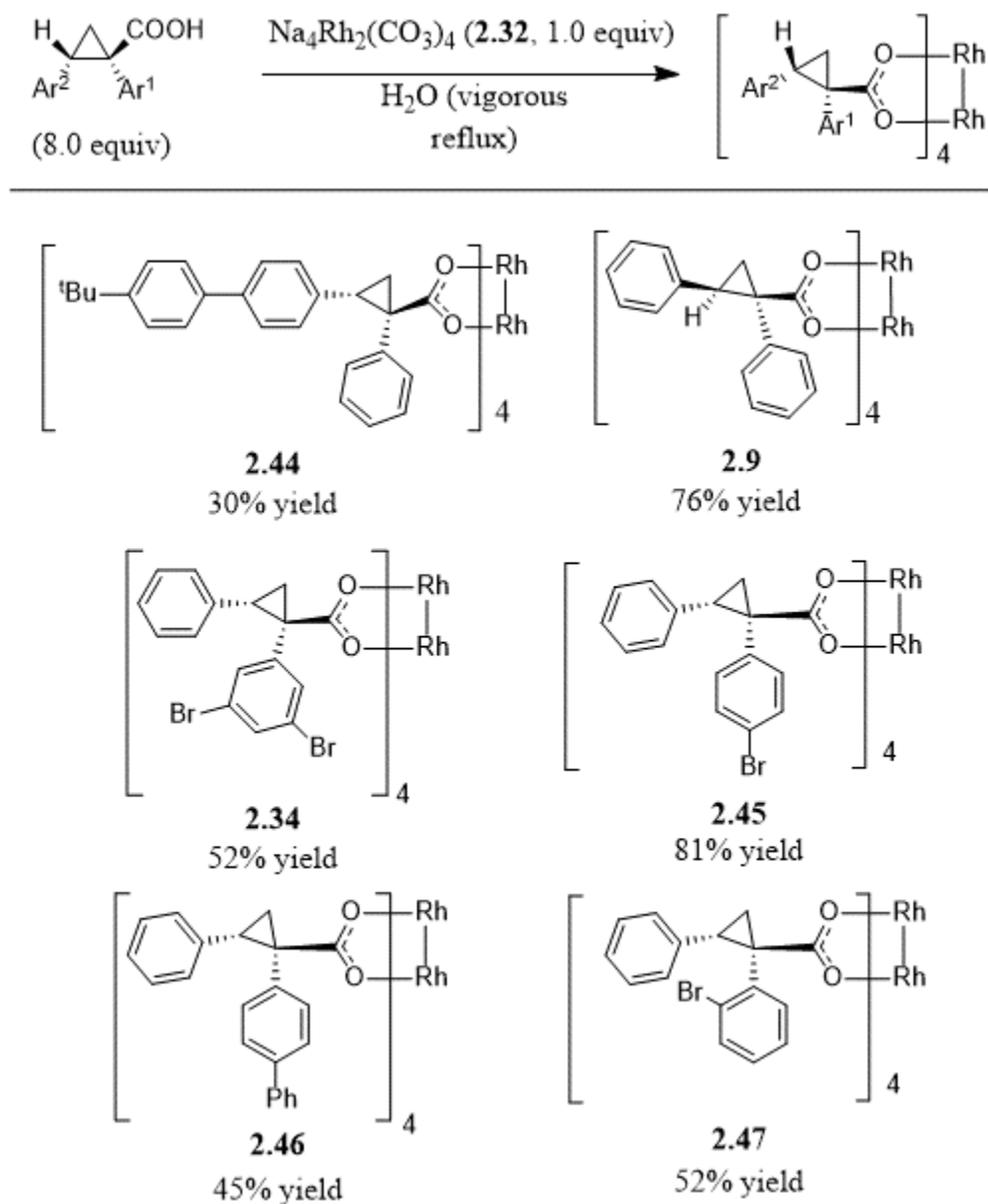
Chart 2.2.2: Ligands evaluated for the multifold cross-coupling reaction with **2.31**.

The Suzuki coupling reactions of the free ligands also proceed with respectable yield. To prepare the cyclopropanecarboxylates **2.42**, **2.43**, and **2.31**, conventional Suzuki couplings were performed using the corresponding arylboronic acids (Scheme 2.2.5). These reactions tend to be more robust than the multifold couplings and are the preferred method for preparing cyclopropanecarboxylate ligands with *para*-substituents at the C1 aryl group.



Scheme 2.2.5: Conventional Suzuki coupling reactions to prepare DPCP ligands

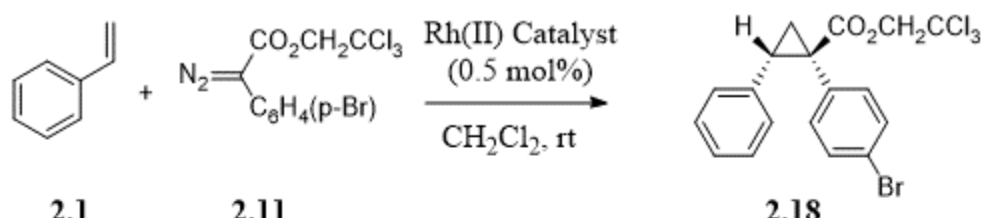
For all of the catalysts studied except the very hindered complex **2.33**, The dirhodium tetracarboxylate complexes were prepared via ligand substitution reactions. The use of a large excess (8.0 equiv) of the free ligands is required to drive the substitution reactions with the rhodium(II) precursor $\text{Na}_4\text{Rh}_2(\text{CO}_3)_4$ (**2.32**) to completion. Following a fractional recrystallization to $\geq 99\%$ *ee*, the diarylcyclopropanecarboxylate ligands were heated with the rhodium precursor $\text{Na}_4\text{Rh}_2(\text{CO}_3)_4$ (**2.32**, Scheme 2.2.6). While the reaction with compound **2.31** did not undergo complete exchange with sodium rhodium carbonate, the substitution reactions to prepare the other catalysts proceeded in reasonable yield. It is easier to isolate the tetracarboxylate complex from the ligand substitution reaction mixtures than the Suzuki coupling mixtures because the tetracarboxylate compound is significantly more nonpolar than the mono-, di-, or tri-substituted complexes.

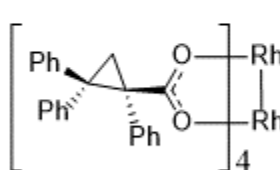


Scheme 2.2.6: The direct ligand exchange reaction to prepare the Rh₂(DPCP)₄ catalysts.

2.2.2 Evaluation of Catalysts

Having a number of structurally diverse diarylcyclopropanecarboxylate catalysts in hand, they were reacted with styrene (**2.1**) to gauge their potential for enantiomeric excess in cyclopropanation reactions (Table 2.2.2).

		
2.1	2.11	2.18
Catalyst	Yield, %	ee, %
Rh₂(S-TPCP)₄ (2.48)	90	91
2.5	92	8
2.33	93	6
2.34	77	12
2.44	70	6
2.45	85	14
2.46	82	26
2.47	72	10
2.9	76	84



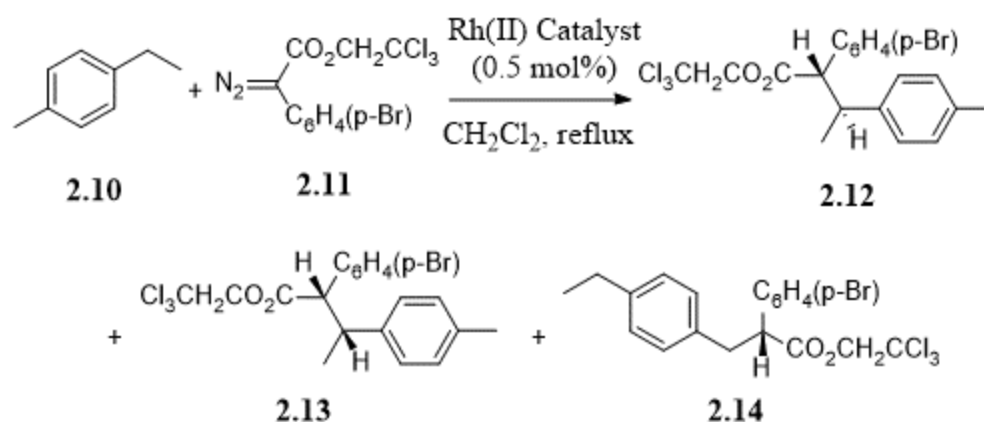
2.48
Rh₂(S-TPCP)₄

Table 2.2.2: Cyclopropanation of styrene with Rh₂(DPCP)₄ catalysts.

Irrespective of the substitution pattern at the α -aryl substituent, all of the **E-DPCP** type catalysts performed quite poorly with respect to enantioselectivity. As would be expected when using donor/acceptor type dirhodium carbenes (see Section 1.3), the diastereoselectivities for the cyclopropanation reactions were uniformly very high. In stark contrast to the **E-DPCP** catalysts, the **Z-DPCP** type catalyst **2.9** performed almost as well as the dirhodium triarylcyclopropanecarboxylate Rh₂(S-TPCP)₄ (**2.48**). This result appeared to be consistent with Dr. Jorn Hansen's hypothesis that the most important structural feature of the dirhodium

cyclopropanecarboxylate catalysts is the aryl substituent *syn* to the dirhodium carboxylate group (Section 1.6).

Due to the variety of shapes accessible to dirhodium tetracarboxylate complexes, some catalysts perform very well for certain C-H insertion reactions but might show only modest yield or enantioselectivity in cyclopropanation reactions. To test the selectivity of the Rh₂(DPCP)₄ catalysts in C-H insertion reactions, they were reacted with 4-ethyltoluene (**2.10**, Table 2.23).



Catalyst	Yield, %	2°:1°	2.41:2.42	ee 2°, %	ee 1°, %
Rh ₂ (S-DOSP) ₄ (2.3)	66	92:8	75:25	-81	82
Rh ₂ (S-TPCP) ₄ (2.48)	91	19:81	76:24	<5	93
2.5	90	95:5	85:15	13	<5
2.33	32	95:5	87:13	<5	55
2.34	68	95:5	88:12	29	-23
2.44	81	95:5	85:15	13	<5
2.45	43	93:7	86:14	<5	<5
2.46	57	96:4	87:13	<5	<5
2.47	62	93:7	82:18	<5	<5
2.9	87	91:9	82:18	-45	66

Table 2.2.3: C-H insertion reactions of 4-ethyltoluene with DPCP catalysts.

Insertion into the secondary C-H bonds of 4-ethyltoluene (**2.10**) is favored for both the *E*-**DPCP** and *Z*-**DPCP** catalysts. By contrast, the triarylcyclopropanecarboxylate catalyst Rh₂(S-TPCP)₄ (**2.48**) afforded the primary insertion product in a 19:81 ratio with 93% primary enantioselectivity. As in the cyclopropanation reactions of styrene (**2.1**), all of the catalysts surveyed showed reasonably good diastereoselectivity due to the use of the donor/acceptor carbene. A small but nontrivial amount of the minor (2*S*,3*R*)/(2*R*,3*S*) diastereomer **2.13** was generated in all of the reactions. For the *Z*-**DPCP** catalyst **2.9**, enantioselectivity was modest but significantly improved over the *E*-**DPCP** catalysts.

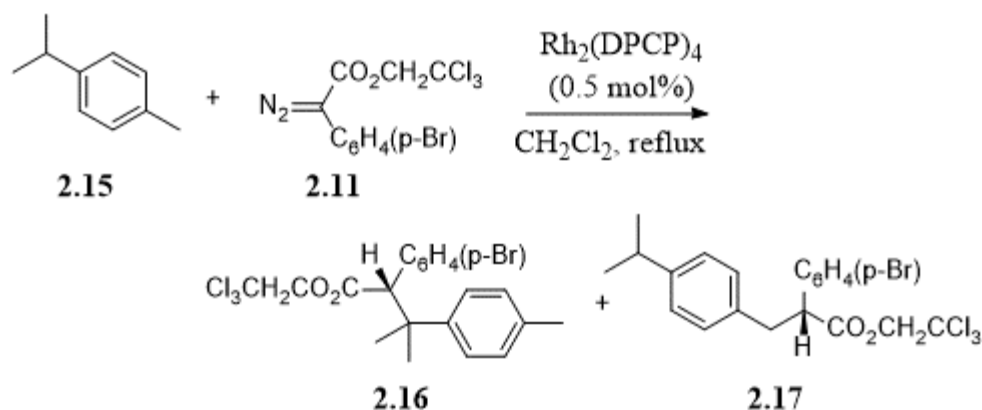
The C-H insertion reactions of 4-ethyltoluene (**2.10**) can be challenging to perform because in most cases they generate mixtures of structurally similar products which are hard to separate. The presence of six major peaks of similar polarity complicates HPLC analysis of the materials due to overlaps. In these reactions the products had to be derivatized to the corresponding primary alcohols with LiAlH₄ and then subjected to flash column chromatography to remove **2.13**. The use of an extended analysis time with a conventional Chiralpak AD-H HPLC column was found to provide baseline resolution of the remaining four peaks.

The **DPCP** catalysts were evaluated against the substrate 4-isopropyltoluene (**2.15**) to examine whether they would show higher selectivity for the primary or the tertiary C-H sites of this molecule (Table 2.2.4). All of the *E*-**DPCP** catalysts which were tested showed a markedly higher propensity to react at the tertiary site relative to either the Rh₂(**TPCP**)₄ catalysts or Rh₂(*Z*-**DPCP**)₄. However, the tertiary site selectivity of these catalysts was not very good, with most of the catalysts preferring the primary site by a small ratio. Interestingly, catalysts **2.33** and **2.34** both showed a slight preference for reaction at the tertiary site with low to modest enantioselectivity. For 4-isopropyltoluene (**2.15**), the optimal diarylcyclopropane catalyst for

both primary site selectivity and enantioselectivity again proved to be **Z-DPCP** catalyst **2.9**.

While this entry showed both moderately good primary site selectivity and enantioselectivity (90:10 1°:3° site selectivity and 72% ee), its performance was not comparable to the triarylcyclopropanecarboxylate $\text{Rh}_2(\text{S-TPCP})_4$ (**2.48**), which showed much greater primary site selectivity (>99:1 1°:3°) and significantly higher ee (93%).

In all of the above cases, the **E-DPCP** catalysts showed significantly diminished enantioselectivity relative to either **Z-DPCP** or **TPCP**. To better understand why this might be the case, the structures of the diaryl catalysts were studied by single crystal X-ray diffraction and density functional theory calculations¹².



Catalyst	Yield, %	3°:1°	ee 3°, %	ee 1°, %
$\text{Rh}_2(\text{S-DOSP})_4$ (2.3)	69	36:64	-67	81
$\text{Rh}_2(\text{S-TPCP})_4$ (2.48)	85	<1:99	---	93
2.5	74	39:61	40	6
2.33	70	57:43	41	<5
2.34	91	56:44	51	14
2.44	96	34:66	47	<5
2.45	87	43:57	38	14
2.46	87	35:65	37	10
2.47	95	24:76	12	6
2.9	87	10:90	<5	72

Table 2.2.4: C-H insertion reactions with 4-isopropyltoluene using $\text{Rh}_2(\text{DPCP})_4$ catalysts.

2.2.3 X-Ray Analysis of Dirhodium Catalysts

Single crystal X-ray diffraction is a valuable method for probing the structure of dirhodium catalysts. Dirhodium tetracarboxylates are bench-stable solids that often form well-defined solvate complexes¹³, and in many cases X-ray quality single crystals can be grown under ambient conditions. However, there are two major limitations to X-ray analysis. First, the key step of the reactions they catalyze occurs through a carbene intermediate. The carbene may adopt a substantially different shape from that of the free catalyst¹⁴. Secondly, the absence of solvent and crystal packing effects may stabilize conformations which are not preferred by the complex in the solution phase¹⁵. Given these limitations, the solid state structures are still very useful for confirming the structure and absolute configuration of dirhodium tetracarboxylates. In many cases, the geometry observed in the solid state is similar to the computed minimum-energy structures of these materials¹⁶.

Single crystals of the ***E*-DPCP** catalysts **2.5** and **2.34** and the ***Z*-DPCP** dirhodium catalyst **2.9** were grown by slow evaporation of solvent or vapor diffusion experiments. In the case of catalyst **2.9**, two polymorphic crystals of the substance were observed. The solid state structures of these compounds were then determined from X-ray diffraction experiments. The structures of the ***E*-DPCP** catalysts **2.5** and **2.34** are shown in Figure 2.2.1.

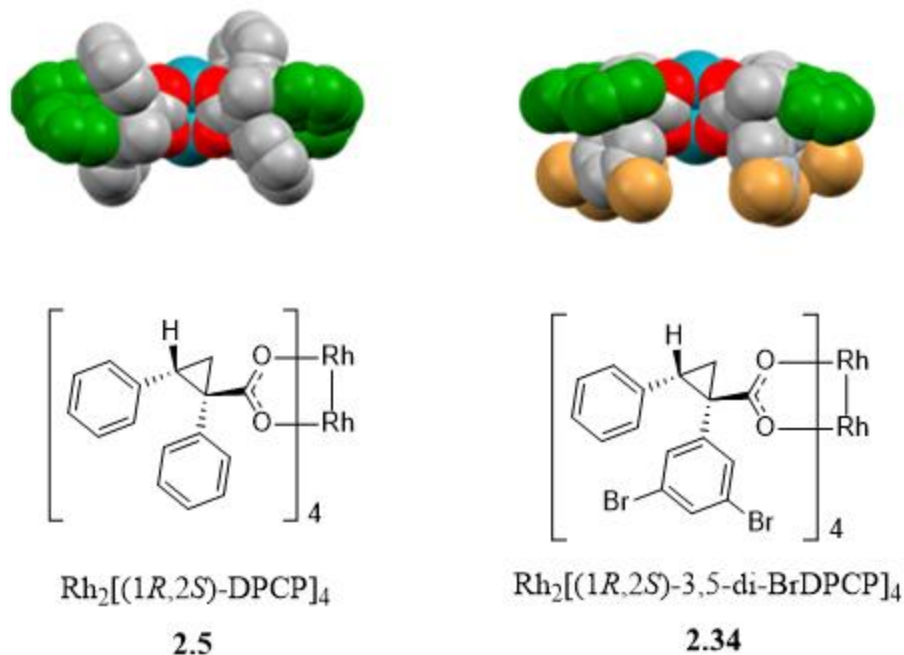


Figure 2.2.1: Solid state X-ray structures of the ***E*-DPCP** catalysts **2.5** and **2.31**. Solvent molecules have been omitted for clarity. Solved by Dr. John Bacsá, Emory University.

The crystal structure of diaryl catalyst **2.5** displays a conceptually D_2 -symmetric ($\alpha,\beta,\alpha,\beta$)-geometry. Many D_2 -symmetric catalysts are capable of high enantioselectivity, which could potentially explain why the ***E*-DPCP** catalysts are capable of achieving low to modest enantioselectivity for cyclopropanation and C-H insertion reactions. For a D_2 -like geometry, asymmetric induction from the catalyst could arise via a model similar to the one described by Figure 1.6.3. However, even in the D_2 geometry the C_2 -aryl group *anti* to the dirhodium carboxylate is directed toward the periphery of the catalyst where it will likely have a minimal influence on the substrate trajectory during the reaction.

Unlike $\text{Rh}_2[(1R,2S)\text{-DPCP}]_4$ (**2.5**), the catalyst $\text{Rh}_2[(1R,2S)\text{-3,5-di-BrDPCP}]_4$ (**2.34**) exhibits an ($\alpha,\alpha,\alpha,\alpha$) shape which is nearly C_2 symmetric. This arrangement illustrates a plausible orientation from which the catalyst could react to give products with extremely low

enantioselectivity despite the chirality and enantiopurity of its framework. Virtually none of the steric bulk from the cyclopropane aryl substituents resides on the top face of the rhodium disc, and the bottom face is quite crowded by comparison due to the presence of the eight aryl bromide substituents. This arrangement contrasts sharply with the triarylcyclopropanecarboxylate catalyst $\text{Rh}_2[R\text{-}3,5\text{-di}(p\text{-}^t\text{BuC}_6\text{H}_4)\text{TPCP}]_4$ (**2.34**), which places neighboring *meta*-disubstituted ligands on alternating faces of the dirhodium paddlewheel in both the solid state structure and the computed minimum energy conformation⁴.

For the catalyst $\text{Rh}_2[(1R,2R)\text{-Z-DPCP}]_4$ (**2.9**), two polymorphic crystals could be grown from acetonitrile solvent. These crystals gave differing X-ray structures (Figure 2.2.2), with the first polymorph showing a C_2 -symmetric ($\alpha,\alpha,\beta,\beta$) shape (**Crystal 1**), and the second displaying an C_1 -symmetric ($\alpha,\alpha,\beta,\gamma$) geometry (**Crystal 2**).

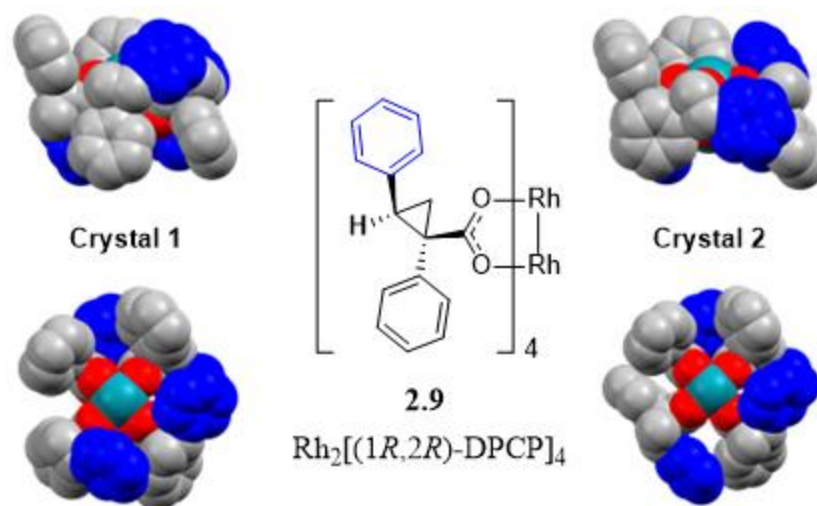


Figure 2.2.2: Two polymorphic crystals were observed for catalyst **2.9**. Solvent molecules have been omitted for clarity. Solved by Dr. John Bacsá, Emory University

Both of these orientations place significantly greater steric bulk adjacent to the rhodium centers as compared to the X-ray structures of the C2-epimer $\text{Rh}_2[(1R,2S)\text{-DPCP}]_4$ (**2.5**), and do not exhibit a conformation with a bare rhodium atom as does catalyst **2.9**. However, the fact that the $(\alpha,\alpha,\beta,\gamma)$ (**Crystal 2**) polymorph is observed with one of the ligands slipping into a γ -orientation suggests that there may be a significant degree of conformational mobility in this complex. It is worth noting that significantly greater uncertainty was observed in the atomic coordinates of the **Crystal 1** structure due to a poorly diffracting sample, however the two polymorphic crystals were clearly distinguishable as having significantly different atomic coordinates.

2.2.4 DFT Study of $\text{Rh}_2(\text{DPCP})_4$ Catalysts

While the X-ray structures of the $\text{Rh}_2(\text{DPCP})_4$ catalysts provided some useful insights as to why they might exhibit the observed selectivity properties, the inherent limitations of X-ray crystallographic analysis inspired us to conduct a computational study to identify possible minimum energy conformations of the new catalysts¹². Due to advances in computer technology and the increasing availability of convenient, user-friendly software packages¹⁷, accurate modeling of complex many-atom systems such as the dirhodium tetracarboxylate complexes under consideration has become more accessible to the practicing synthetic chemist. Refinements to exchange-correlation functionals¹⁸⁻²⁰ over the past several decades have resulted in density functional theory-based computational methods becoming more efficient and widely embraced for modeling chemical reactions and organometallic complexes.

The computational method chosen for studying the $\text{Rh}_2(\text{DPCP})_4$ catalysts¹² was B3LYP-D3BJ/BS1, which uses the B3LYP functional²⁰⁻²² with Grimme dispersion correction at the D3 level²³ and Becke-Johnson (BJ) damping.²⁴⁻²⁶ BS1 was used as the basis set, with Lanl2dz being

applied to rhodium and 6-31G(d,p) for the other atoms. The Hay-Wadt effective core potential²⁷⁻²⁹ was used for rhodium. Frequency analysis was conducted for each minimum with zero imaginary frequency.

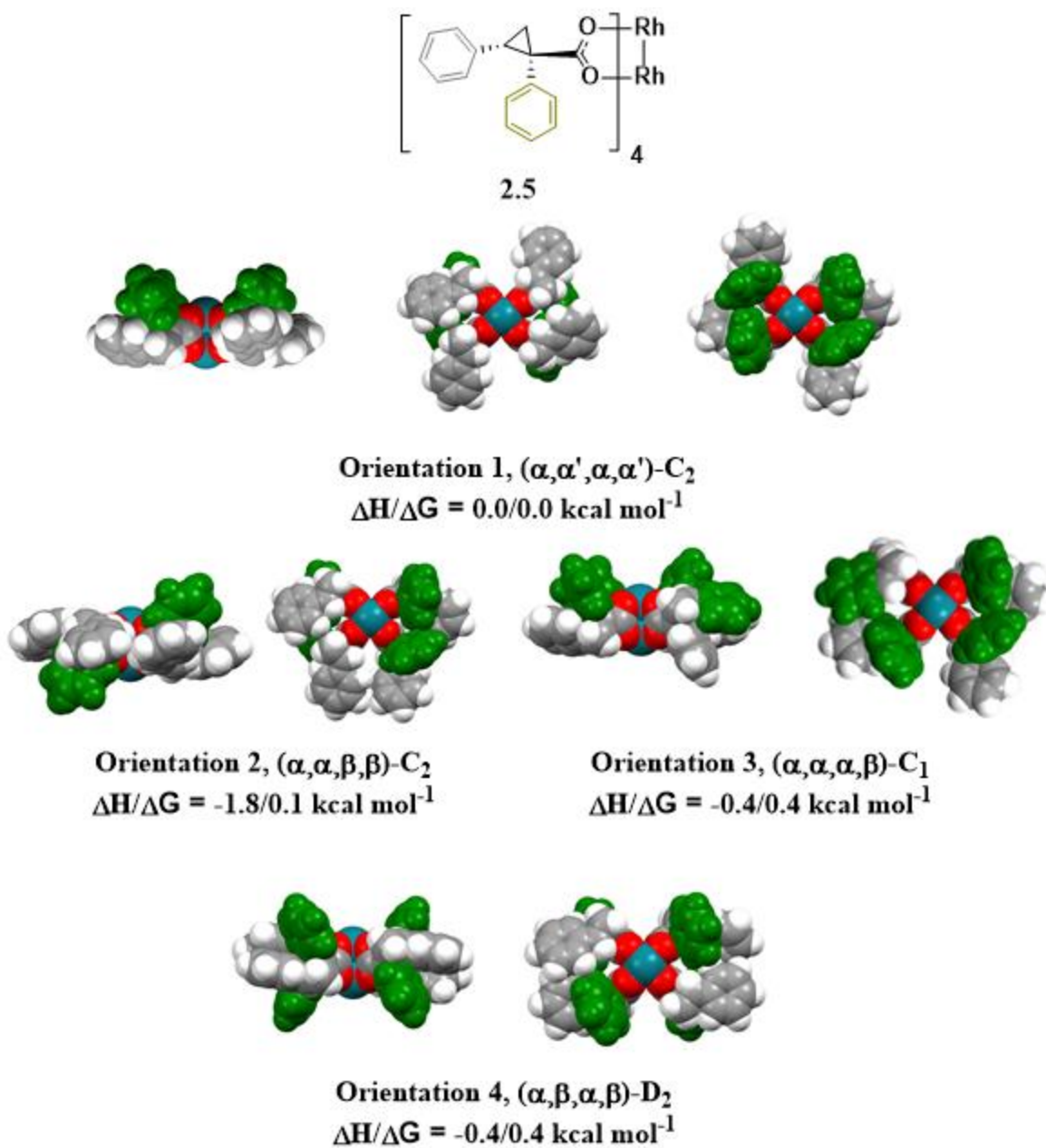


Figure 2.2.3: Energy-minimized conformations of Rh₂[(1R,2S)-DPCP]₄ (2.5). Calculation by Dr.

Zhi Ren and Dr. Djamaladdin G. Musaev, Emory University.¹²

To model the catalyst in solution, bulk solvent effects were incorporated in all calculations using the conductor-like polarizable continuum model (C-PCM)³⁰⁻³¹ and CH₂Cl₂ as the solvent.

The lowest energy conformations of the ***E*-DPCP** catalyst Rh₂[(1*R*,2*S*)-DPCP]₄ (**2.5**) are shown in Figure 2.2.3. The most striking feature of this catalyst from a structural perspective is that it has multiple low lying conformations which are quite different in terms of shape but very close in energy. While catalyst **2.5** exhibits an (α,β,α,β)-D₂ geometry in the X-ray structure, this shape (Orientation 4) was 0.4 kcal/mol higher in Gibbs free energy than the (α, α',α,α')-C₂ shape displayed in Orientation 1. The sterically open Orientation 1 closely resembles the X-ray structure of Rh₂[(1*R*,2*S*)-3,5-di-BrDPCP]₄ (**2.34**), which is also an (α, α',α,α')-C₂ form. Based on these results, it appears likely that the low to modest enantioselectivity and relatively increased tertiary site selectivity of the ***E*-DPCP** type catalysts results from a dirhodium carbene which is neither structurally well-defined nor particularly sterically hindered at the reaction site. Without placing an additional substituent on the cyclopropane ring, is unlikely that further development of the ***E*-DPCP** ligand scaffold will produce catalysts which are capable of high asymmetric induction and site selectivity with a wide variety of substrates. An exception to this rule is the reaction of the ***E*-DPCP** catalysts with the sterically congested tertiary site of 4-isopropyltoluene, which proceeds in moderate *ee*. In this case, it would appear that placing increased steric bulk on the substrate may partially compensate for the sterically open chiral catalyst.

In contrast to the ***E*-DPCP** tetracarboxylates, all conformations of Rh₂[(1*R*,2*R*)-*Z*-DPCP]₄ (**2.9**) were relatively hindered at the reaction site space (Figure 2.2.4) This catalyst also appears to adopt multiple conformations, with three of the four preferred conformers having a free energy difference of within 0.6 kcal/mol. Despite its flexibility, all of the orientations observed for this complex displayed multiple aryl groups surrounding the axial binding site.

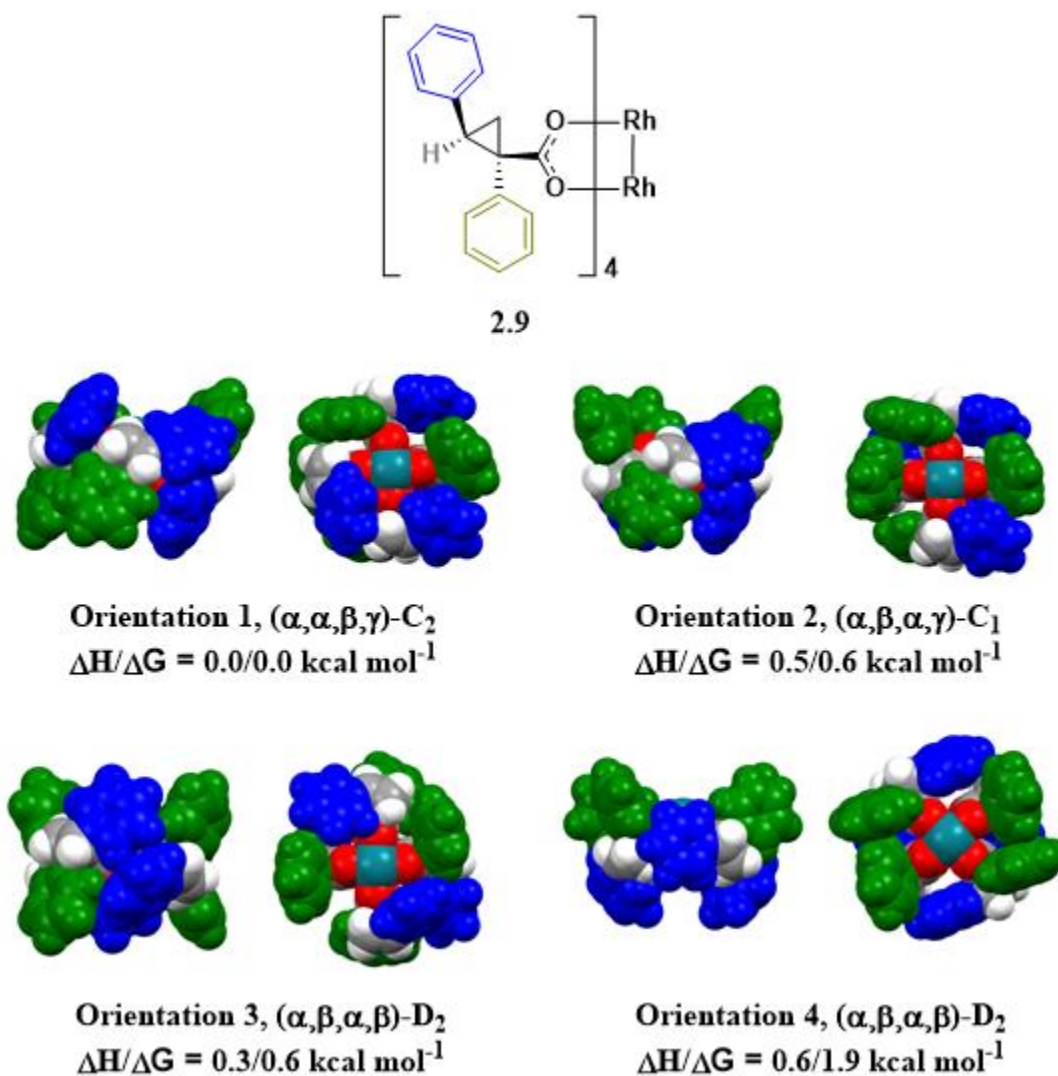


Figure 2.2.4: Energy-minimized conformations of Rh₂[(1R,2R)-DPCP]₄ (**2.9**). Calculation by Dr. Zhi Ren and Dr. Djamaladdin G. Musaev, Emory University.¹²

When supplemented by the X-ray structures and the experimental reaction data (Section 2.2.2), these results are consistent with a reactive conformational model for Rh₂(**Z-DPCP**)₄ (**2.9**) in which the major blocking groups of the carbene, particularly the C2-*cis* aryl substituent, are often in close proximity to the reaction site. Despite not having as great of an effect on enantioselectivity as the C2-*cis* aryl substituent, the C2-*trans* aryl group clearly plays an important role in limiting the conformations of the cyclopropane ligands.

2.2.5 Conclusion

The results of this study suggest that three substituents on the cyclopropane ring are required in order for the dirhodium tetracarboxylate catalysts to maintain their characteristically high enantioselectivity and primary site selectivity. The removal of the C2 aryl substituent *syn*- to the dirhodium carboxylate group causes a significant increase in tertiary site selectivity due to the reduced steric demand and an increase in the number of reasonable ligand conformations, but also a dramatic decrease in enantioselectivity due to the essential role that this group plays in controlling the approach trajectory of the substrate to the carbene.

Placing additional functionality on the C1 aryl group of the ***E*-DPCP** catalysts (as with compounds **2.44**, **2.34**, **2.45**, **2.46**, **2.47**, **2.33**) did have a significant impact on both primary vs. tertiary site selectivity and *ee*. However, it is not evident from this study whether these relatively modest differences actually arise from meaningful changes in the conformational space occupied by the catalysts. Irrespective of the shapes of the ***E*-DPCP**, they all demonstrate site selectivity and enantioselectivity values which suggest they are less sterically hindered at the reactive site relative to the Rh₂(**TPCP**)₄ catalysts.

As illustrated by the *Z*-diarylcyclopropanecarboxylate **2.9**, removal of the C2 aryl substituent *anti*- to the dirhodium carboxylate caused an increase in the number of low-lying conformations. In this case, the steric demand at the rhodium carbene was largely maintained due to the consistent presence of multiple aryl groups at the reaction center, but Rh₂[(1*R*,2*R*)-*Z*-DPCP]₄ (**2.9**) still shows inferior performance relative to Rh₂(**TPCP**)₄ (**2.48**).

While the $\text{Rh}_2(\text{DPCP})_4$ catalysts are not likely to have significant utility from a synthetic perspective, this study has provided further insights into the structural features of the dirhodium cyclopropanecarboxylates that are responsible for the remarkable site selectivity and enantioselectivity observed with this ligand scaffold. Further work on the $\text{Rh}_2(\text{DPCP})_4$ catalysts will be focused on cyclopropane ligands that have a third substituent which is not an aryl group.

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Chapter 3: The Regio- and Stereoselective Functionalization of Cyclobutanes

3.1 Introduction and Related Work

Cyclobutane rings are a structural feature that can be found in many molecules of biological significance, encompassing both natural products¹⁻³ and synthetic pharmaceutical agents.⁴⁻⁶ Due to the angular strain of the C-C bonds in cyclobutane and its derivatives⁷, many cyclobutane compounds are unstable, and they can be challenging to synthesize. General methods for the preparation of functionalized cyclobutane compounds are relatively limited, with the most popular approaches utilizing [2+2] cycloaddition reactions of alkenes to form the ring⁸. Other methods used for forming the cyclobutane ring include intramolecular cyclization^{9,10} and ring contraction or expansion strategies¹¹.

Arylcyclobutanes are found in some synthetic bioactive agents, such as the TRPV3 antagonists¹² **3.1** and **3.2** (Chart 3.1.1). They are also present in many natural products, and a significant number of these can be formed via [2+2] cycloaddition reactions of simpler components¹³. Some notable examples are piperarborenine B¹⁴ (**3.3**) and (+)-Santiaguine¹⁵ (**3.4**). While cycloaddition strategies can be highly effective for forming some of these compounds, they are limited with respect to the scope of products that can be formed, and so the development of completely new synthetic methods for preparing cyclobutane rings is a matter of significance.

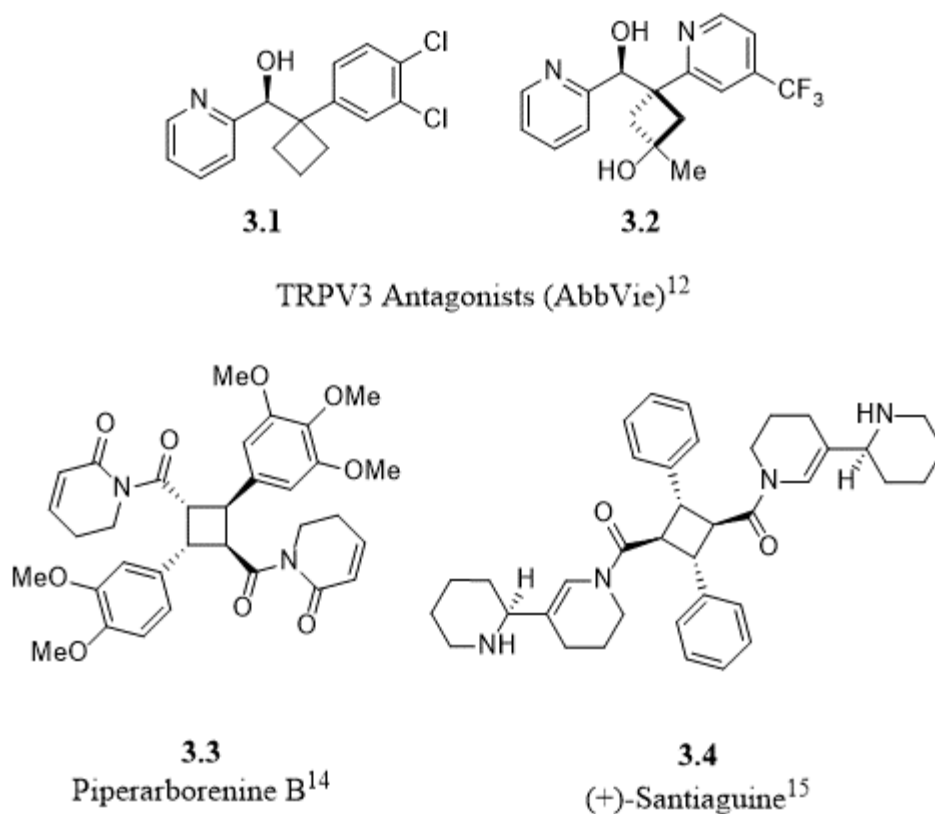
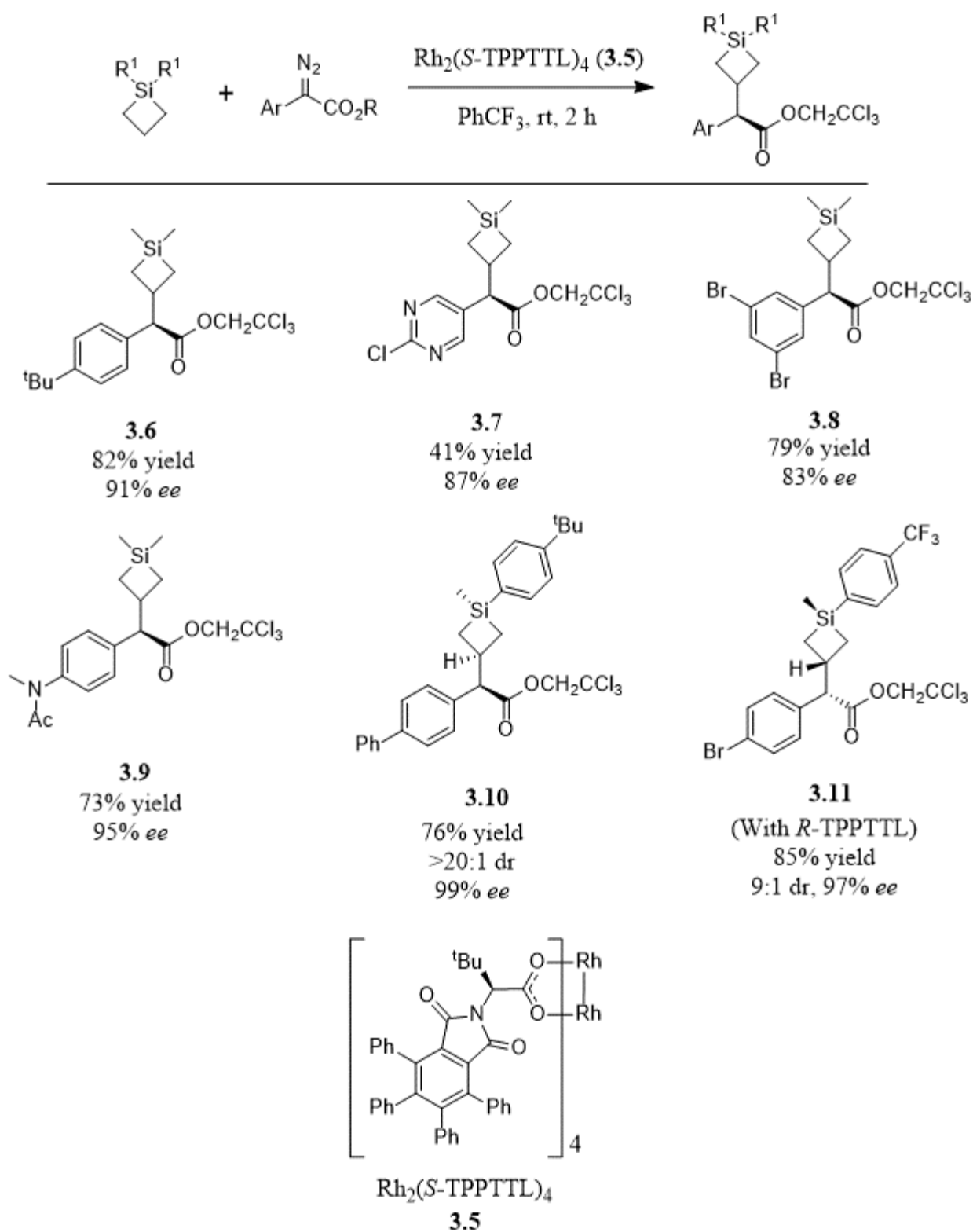


Chart 3.1.1: Examples of cyclobutanes in pharmaceutical agents and natural products¹²⁻¹⁵

A number of powerful strategies for C-H functionalization have been successfully applied to complex cyclobutane targets¹⁶. Nevertheless, site-selective dirhodium catalyzed C-H functionalization reactions of cyclobutanes are largely without precedent in the chemical literature except for the present study. In addition to cyclobutanes, several highly selective carbene insertions into the C-H bonds of other cyclic systems have been reported by the Davies group in recent years. Among the substrates for these reactions are silacyclobutanes¹⁷, silacyclopentanes,¹⁸ functionalized cyclohexane derivatives,¹⁹ and bicyclo[1.1.1]pentanes.²⁰

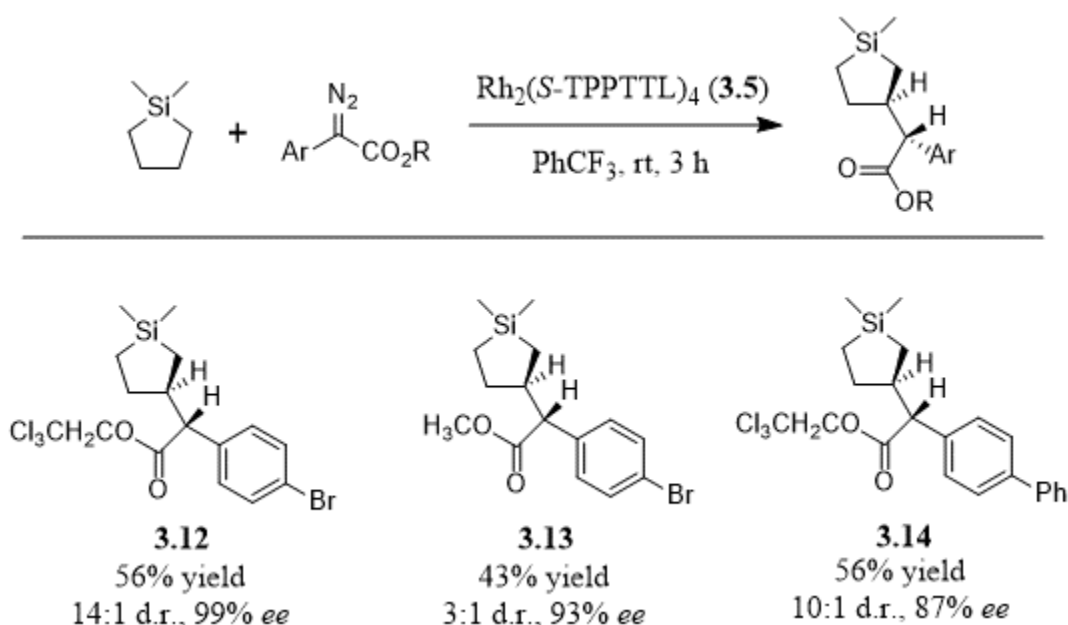
3.1.1 Selective Functionalization of Silacyclobutanes and Silacyclopentanes

The first and most directly analogous of these examples are reactions involving silacyclobutane rings (Scheme 1.1.1)¹⁷⁻¹⁸. Like cyclobutanes, silacyclobutanes are also four-membered rings, but they incorporate a silicon atom in the ring in place of one of the carbon atoms. The silicon atom activates the C3 position of the ring to C-H insertion, and hyperconjugation from the C-Si bond stabilizes the transition states of reactions at that site (the “ β -silicon effect”).²¹ While silicon-containing systems are electronically biased to favor a single C-H site, they are nevertheless capable of very respectable enantioselectivity and yield, as illustrated by examples **3.2-3.7** with aryldiazoacetates as the carbene precursor. Entries **3.6** and **3.7** show that good diastereoselectivity and *ee* can be observed when the substituents on the silicon atom are different groups. A product containing three chiral centers is obtained *via* the desymmetrization of the achiral starting material.



Scheme 3.1.1: C-H Insertion into the C3/distal C-H bond of silacyclobutanes.¹⁸

Five membered rings containing a silicon atom are also effective substrates for the C-H insertion reactions of aryldiazoacetates (Scheme 3.1.2). As with silacyclobutanes, the silicon atom of the silacyclopentane introduces substantial electronic bias for the carbene to react at the position two carbons adjacent to it. Examples **3.12-3.14** react with high selectivity at the β -position of the cyclobutane ring.

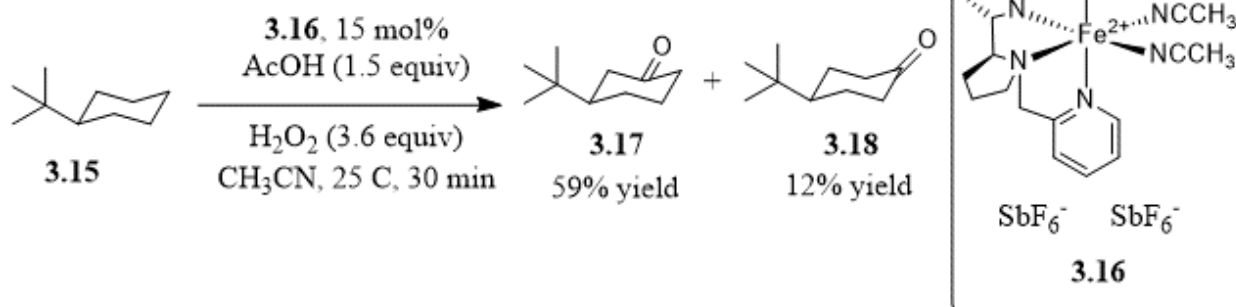


Scheme 3.1.2: Selective C-H insertion with silacyclopentanes using aryldiazoacetates.¹⁸

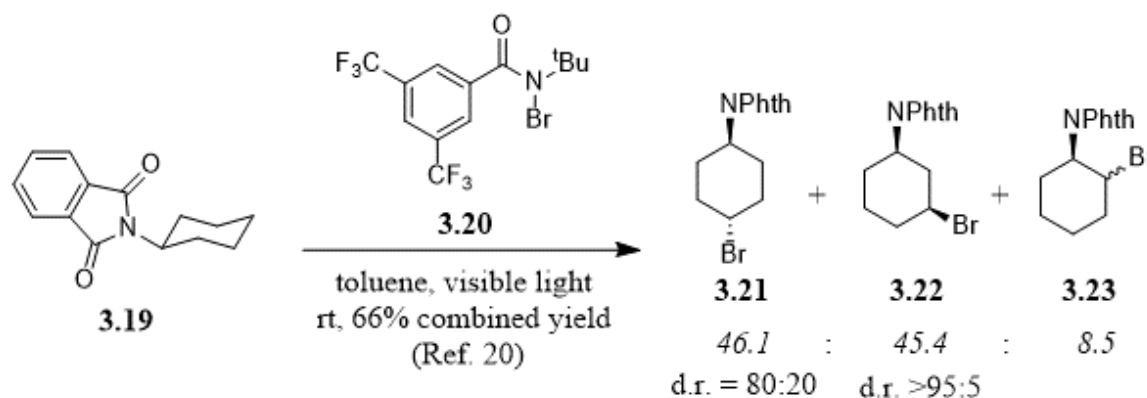
3.1.2 Selective Functionalization of Cyclohexanes

As discussed in Section 1.7, functionalized cyclohexane derivatives are proficient substrates for metal carbene catalyzed C-H insertion reactions with aryldiazoacetates.¹⁹ While 6-membered cyclohexane rings generally possess lower strain energy than cyclobutane rings,²² it can nonetheless be challenging to achieve acceptable levels of site- and stereoselectivity for the C-H functionalization of cyclohexane rings. Two examples which illustrate previous attempts to functionalize monosubstituted cyclohexanes are shown in Scheme 3.1.3.²³⁻²⁴

A. Fe-Catalyzed Methylene Oxidation (Ref. 23)

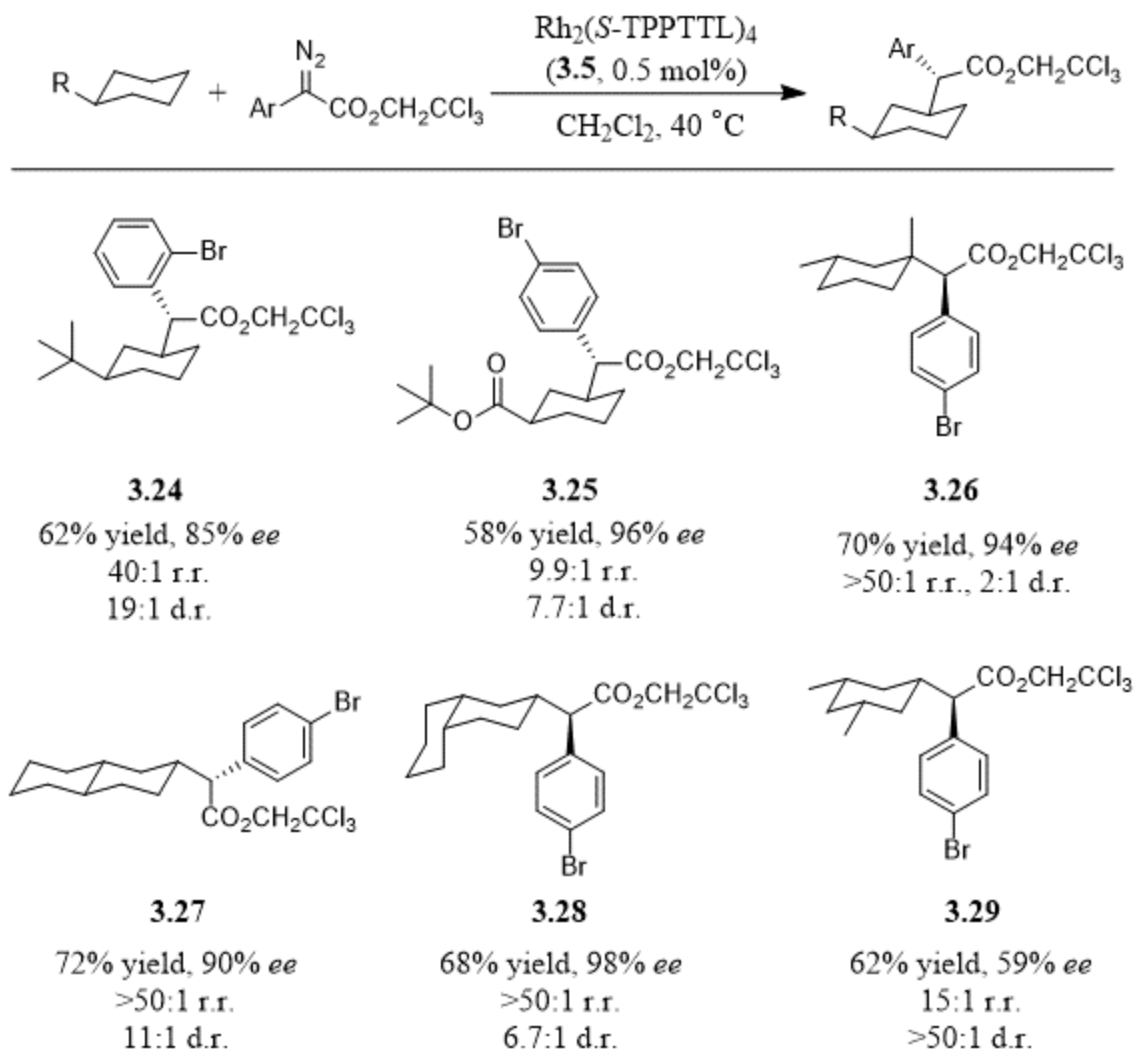


B. C-H Bromination with N-Bromoamides and Visible Light (Ref. 24)

**Scheme 3.1.3:** Previous approaches to the C-H functionalization of cyclohexanes.²³⁻²⁴

In both reactions 3.1.3A and 3.1.3B, regioisomeric mixtures are obtained. In reaction A, the oxidation of *tert*-butyl cyclohexane **3.15** occurs with the highest selectivity for the C3 product **3.17**. This observation was rationalized by White, et al. on the basis of stereoelectronic effects rather than catalyst control from the iron complex **3.16**.²³ In example B, bromination of the phthalimido cyclohexane **3.22** proceeds with very poor regioselectivity, illustrating the challenge of radical halogenation-based approaches.²⁴

Some examples of selective insertion into the C-H bonds of substituted cyclohexanes with donor/acceptor dirhodium carbenes are shown in Scheme 3.1.4.¹⁹



Scheme 3.1.4: Rh₂(S-TPPTTL)₄-catalyzed C-H insertion into substituted cyclohexanes.¹⁹

A great diversity of cyclohexane substrates can be functionalized with high regio- and stereoselectivity using the catalyst Rh₂(TPPTTL)₄. Examples **3.24** and **3.25** illustrate how this catalyst often selects C3-equatorial C-H bonds, which react much faster than axial ones. In the case of disubstituted cyclohexanes, products **3.26-3.29** illustrate how functionalization can still occur preferentially at a single sterically accessible C-H site.

3.1.3 Selective Functionalization of Bicyclo[1.1.1]pentanes

Bicyclo[1.1.1]pentanes (“BCPs”) are a class of compounds which have attracted considerable interest in recent years.²⁰ These molecules are highly strained 5-carbon bicycloalkanes that can be viewed as cyclobutane rings with a bridging methylene unit connecting C1 and C3. While BCP and its derivatives have fascinated academics for many years due to their highly strained molecular framework²⁵, more recently they have become relevant in drug design and medicinal chemistry for their biological properties. In many instances, BCP groups can behave as bioisosteres for alkynes, *tert*-butyl, or phenyl groups, maintaining the desired activity of a prospective drug while improving its pharmacokinetic properties.²⁶⁻²⁸ Some examples of this effect are illustrated by compounds **3.30-3.32** (Chart 3.1.2). Compound **3.30**, an LpPLA2 inhibitor, displayed an identical binding mode with its target protein and improved solubility after replacement of a phenyl group by a BCP group.²⁶ The resveratrol analog **3.31** showed >3 fold higher metabolic stability over the original compound and maintained comparable potency.²⁷ Example **3.32** had significantly greater antibacterial activity than the structurally related drug ciprofloxacin against resistant strains of *staphylococcus aureus*.²⁸

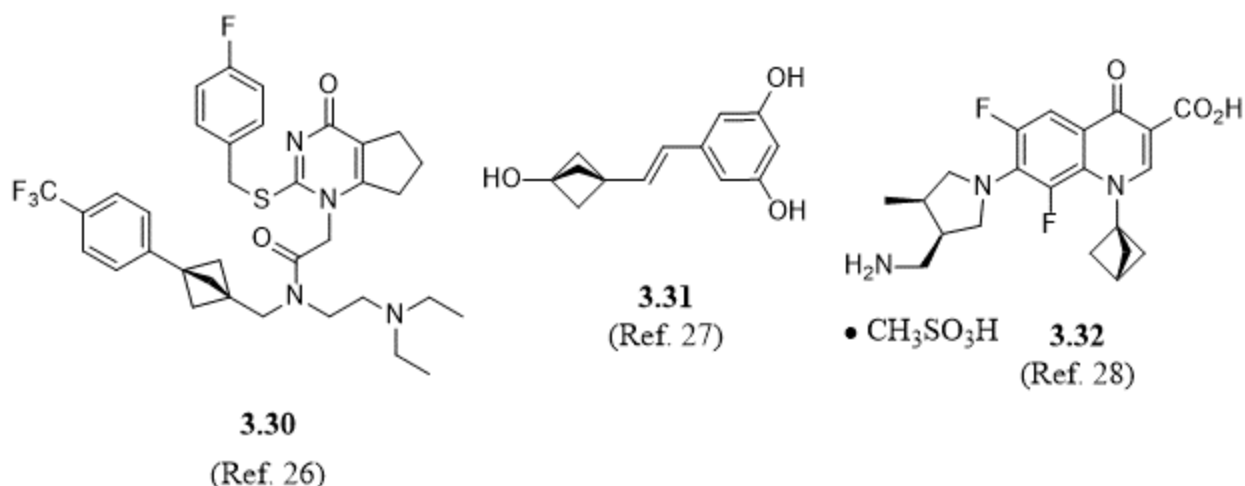
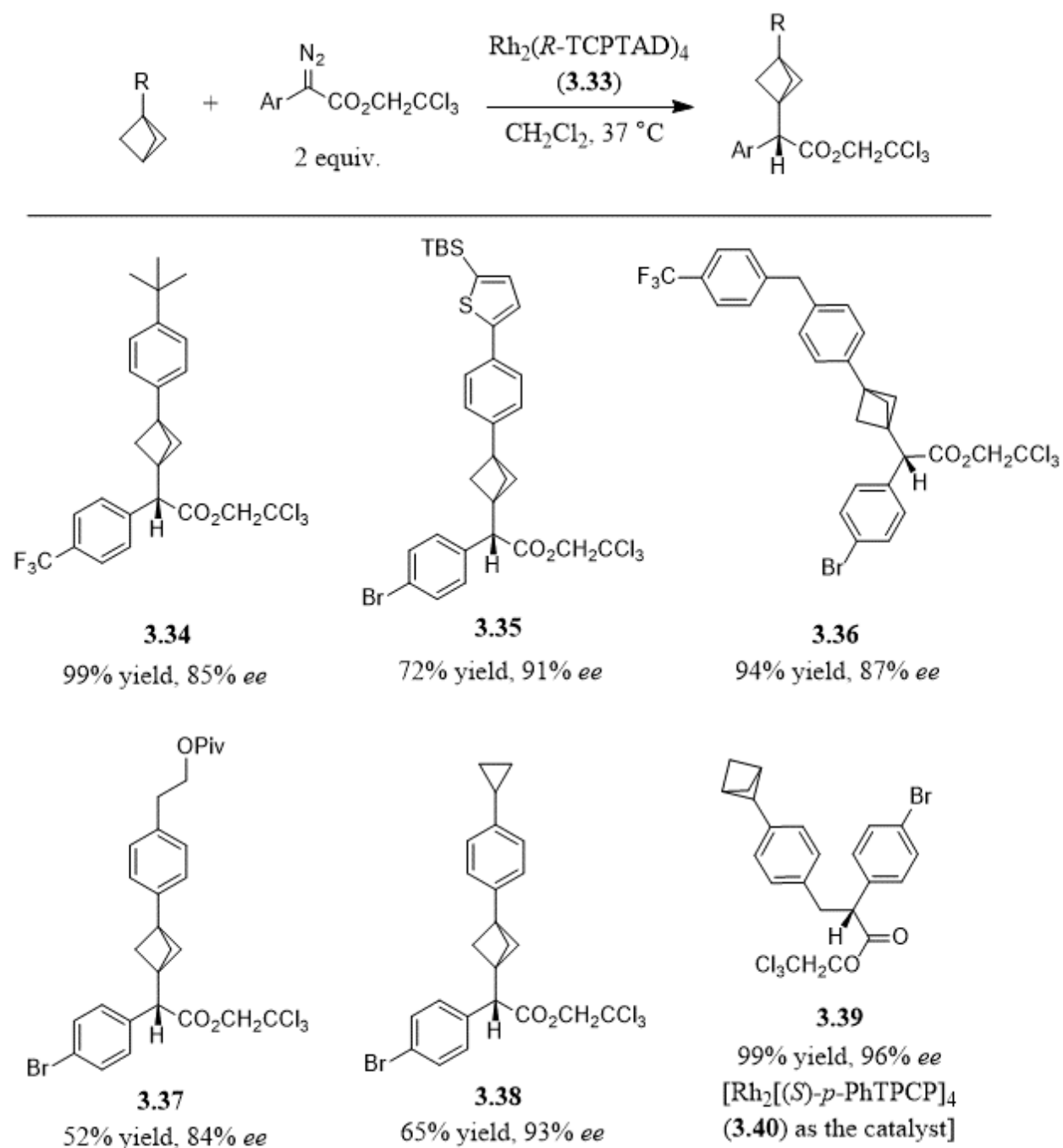


Chart 3.1.2: Bicyclo[1.1.1]pentanes as bioisosteres in medicinal chemistry.²⁶⁻²⁸

An impediment to the more widespread incorporation of BCPs in medicine is the lack of efficient methods for preparing functionalized BCPs. The asymmetric synthesis of functionalized **BCPs** with adjacent chiral centers is also challenging. To solve this problem, a study of the dirhodium-catalyzed C-H insertion reactions of C1-functionalized BCPs was recently conducted by the Davies group²⁰ (Scheme 3.1.5). In this work, the catalyst $\text{Rh}_2(R\text{-TCPTAD})_4$ (**3.33**) exhibited high selectivity for the tertiary C-H bond of the BCP derivative, which is the inherently favored site. Calculations show that the observed preference for tertiary C-H insertion likely arises due to the electronic properties of the BCP ring. Specifically, orbital interactions at the tertiary site enable the system to delocalize significant electric charge onto the neighboring methylene sites.

The reactions of substituted BCPs in this study were also highly asymmetric, with most examples showing enantiomeric excess values of about 90%. The innate preference for reaction to occur at the tertiary C-H site could be overridden to favor a benzylic methyl group (Example **3.39**) when the sterically demanding catalyst $\text{Rh}_2(S\text{-}p\text{-PhTPCP})_4$ (**3.40**) was used.



Scheme 3.1.5: The C-H functionalization of bicyclo[1.1.1]pentanes.²⁰

3.1.4 Overcoming Electronic Activation with *ortho*-TPCP Catalysts

The carbene C-H insertion reactions of cyclobutanes are more challenging than those of silacyclobutanes or bicyclo[1.1.1]pentanes because the latter systems contain a single type of reactive C-H bond, while cyclobutanes show significant competition between the C1-benzylic and C3-methylene sites (Figure 3.1.1). Despite the fact that monosubstituted cyclobutanes also contain four lateral methylene C-H bonds at C2 and C4, these were found to be unreactive toward the dirhodium carbenes utilized in the present study. To develop a method that was capable of giving a clean reaction at the C3 site, it was necessary to use a catalyst which could overcome the inherent bias for reacting at the tertiary C-H bond to yield a single product with high diastereo- and enantioselectivity.

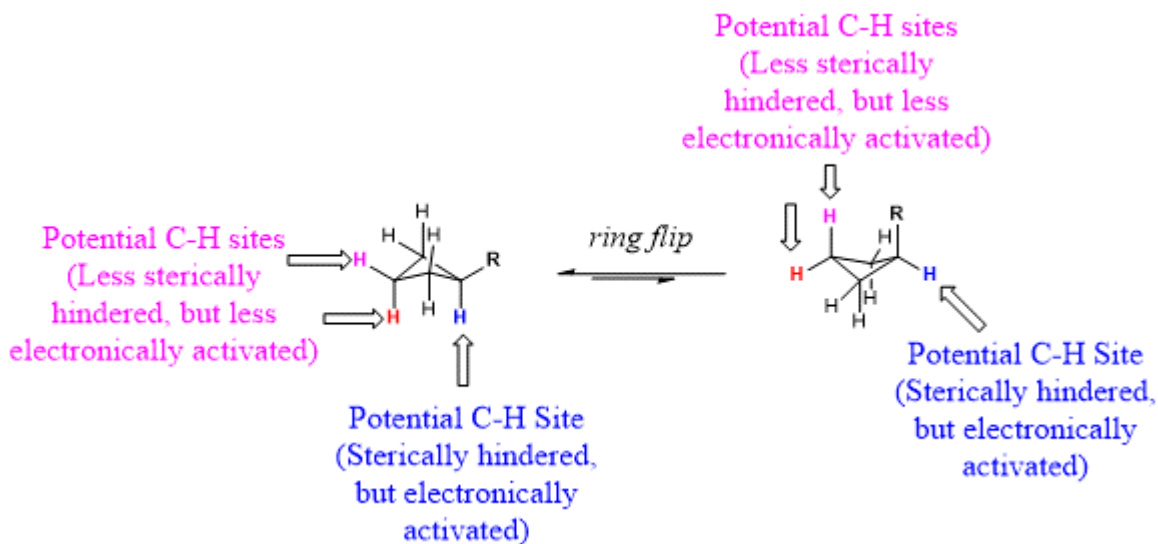
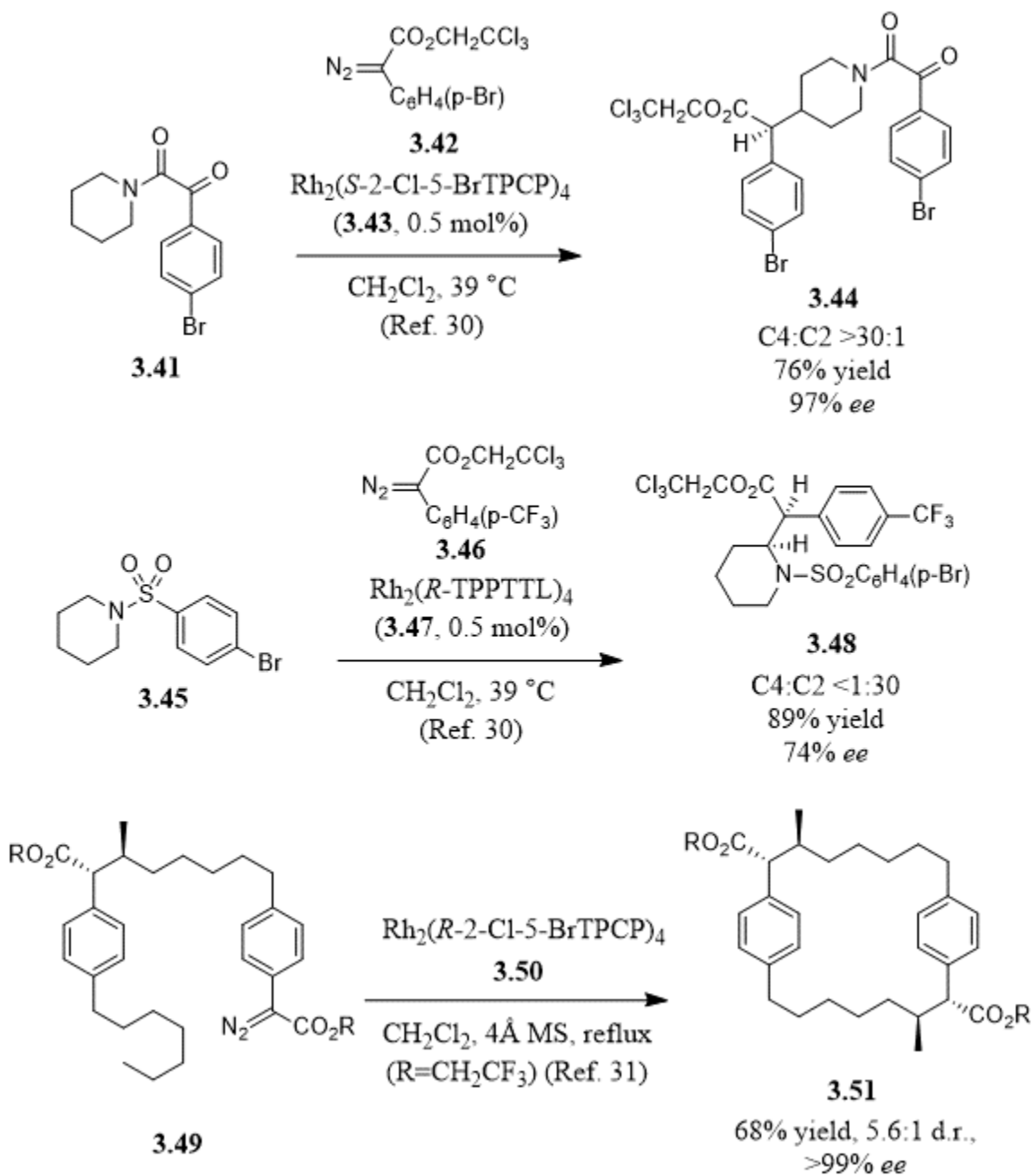


Figure 3.1.1: Challenges in the C-H functionalization reactions of substituted cyclobutanes.

As discussed in section 1.6, the C₄-symmetric *ortho*-chloro **TPCP** catalyst Rh₂(2-Cl-5-Br**TPCP**)₄³⁰⁻³¹ is capable of guiding the carbene to less electronically activated sites via steric exclusion. Some examples which highlight this type of reactivity are shown in Scheme 3.1.6.³⁰

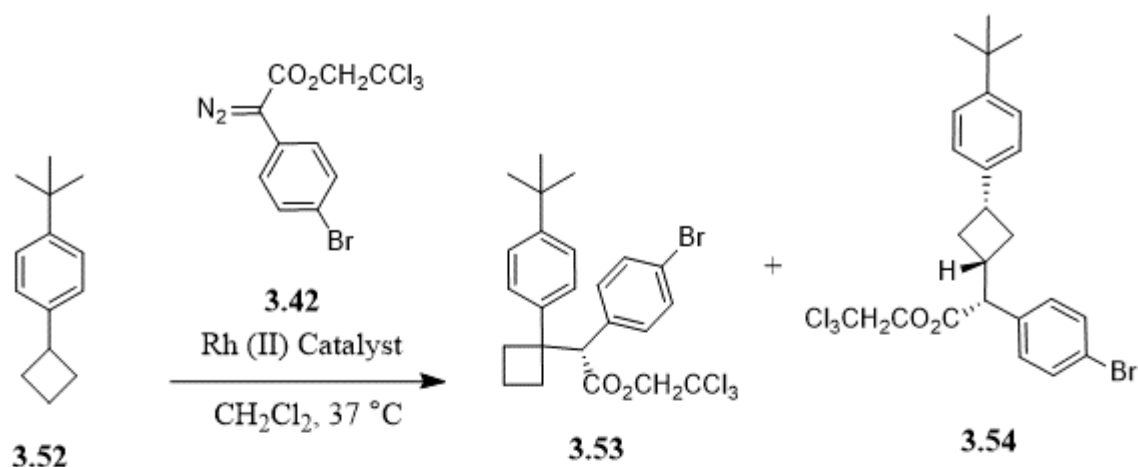


Scheme 3.1.6: Overcoming electronic activation with Rh₂(2-Cl-5-Br**TPCP**)₄³⁰⁻³¹

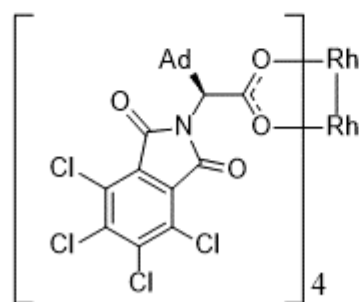
While most sterically open dirhodium catalysts such as Rh₂(**DOSP**)₄ and Rh₂(**TPPTTL**)₄ yield chiefly the C2-insertion product due to the activating effect of the piperidine nitrogen atom (see chapter 1.7.1,) with Rh₂(S-2-Cl-5-BrTPCP)₄ (**3.43**) the C-H insertion reaction of the dicarbonyl-protected piperidine **3.41** produces almost entirely the C4 insertion product **3.44** with 76% yield and 97% *ee*.³⁰ The exceptional regioselectivity for C2 positions with the Rh₂(**2-Cl-5-BrTPCP**)₄ catalyst is also reflected in the cyclization of the linear precursor **3.49** to form the 22-membered macrocycle **3.51**.³¹ The product is obtained in 68% yield and >99% *ee*. Reactions to directly form very large rings such as that of compound **3.51** are considered very challenging because they involve a large decrease in the entropy of the system.³² In the case at hand, it is also possible to imagine a large number of byproducts that could result from the carbene reacting at the other positions of the aliphatic chain. In spite of this, the catalyst **3.50** shows a clear preference for the reaction to occur with a high d.r. at a single methylene position one carbon adjacent to the terminal methyl.

3.2 Results and Discussion

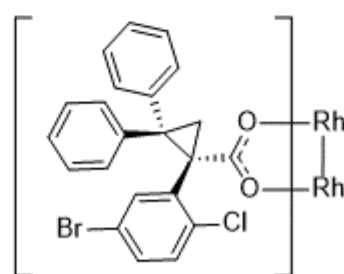
To evaluate the feasibility of achieving site-selective reactions at the C1 and C3 sites of functionalized cyclobutanes using the available toolbox of chiral dirhodium tetracarboxylates, a catalyst screen was conducted.³³ 1-(*tert*-butyl)-4-cyclobutylbenzene (**3.52**) was chosen as a model substrate for the test reactions because it is moderately activated at C1 due to the *tert*-butyl phenyl substituent, and contains no functionality which might poison the dirhodium catalysts. The aryldiazoacetate **3.42** often gives high yield and *ee* for a variety of carbene reactions³⁴. The results of the catalyst screen are shown in Table 3.2.1. (*Work done by Dr. Zachary Garlets*).



Entry	Catalyst	Yield, %	3.53 : 3.54	% ee, 3.53/3.54
1	$\text{Rh}_2(\text{S-DOSP})_4$ (3.55)	94	>95 : 5	32 / n/a
2	$\text{Rh}_2(\text{S-TCPTAD})_4$ (3.56)	65	>95 : 5	98 / na
3	$\text{Rh}_2(\text{S-TPPTTL})_4$ (3.5)	71	>95 : 5	94 / n/a
4	$\text{Rh}_2(\text{R-3,5-di}(p\text{-}^t\text{BuC}_6\text{H}_4)\text{TPCP})_4$ (3.57)	71	33 : 67	3 / 96
5	$\text{Rh}_2(\text{R-tris}(p\text{-}^t\text{BuC}_6\text{H}_4)\text{TPCP})_4$ (3.58)	83	25 : 75	3 / 96
6	$\text{Rh}_2(\text{S-2Cl-5-BrTPCP})_4$ (3.43)	63	17 : 83	34 / 91
7	$\text{Rh}_2(\text{R-PTAD})_4$ (3.59)	74	94 : 6	-54 / -69



3.56
 $\text{Rh}_2(\text{S-TCPTAD})_4$
 (Ref. 4)



3.43
 $\text{Rh}_2(\text{S-2-Cl-5-BrTPCP})_4$
 (Ref. 8)

Table 3.2.1: Catalyst screening for regioselectivity with (4-tert-butyl)phenylcyclobutane.³³

We were pleased to discover that using the catalyst $\text{Rh}_2(\text{S-TCPTAD})_4$ (**3.56**), excellent site selectivity and enantioselectivity are observed for the C1 insertion product **3.53**. Additionally, very respectable regiocontrol was observed for the reaction of the *ortho*-TPCP catalyst $\text{Rh}_2(\text{S-2-Cl-5-BrTPCP})_4$ (**3.43**), with this catalyst favoring the distal functionalization product **3.54** by a ratio of 83:17. While the Davies catalyst $\text{Rh}_2(\text{S-DOSP})_4$ **3.55** showed a very respectable 94% yield for the C1 insertion product in this reaction, it did not show high enantioselectivity (only 32% *ee*).

A competition study was conducted for each of the two catalysts using the diazo compound **3.42**. (Chart 3.2.1). To evaluate the relative rates of reaction at the strained cyclobutane C-H bonds versus those of unstrained systems, a series of experiments were performed on equimolar mixtures of the arylcyclobutane **3.52** and a reference compound (either 4-ethyltoluene (**3.60**) or 4-isopropyltoluene (**3.61**)). These results revealed that there is significant competition between the secondary sites of **3.52** and **3.60**, with the two systems having rates which are close to each other. However, $\text{Rh}_2(\text{R-TCPTAD})_4$ (**3.33**) reacts at the tertiary site of **3.52** much faster than the tertiary site of **3.60**. These results would indicate that the strained geometry of the cyclobutane plays a significant role in accelerating the reaction at C1, but that there is little effect at C3.

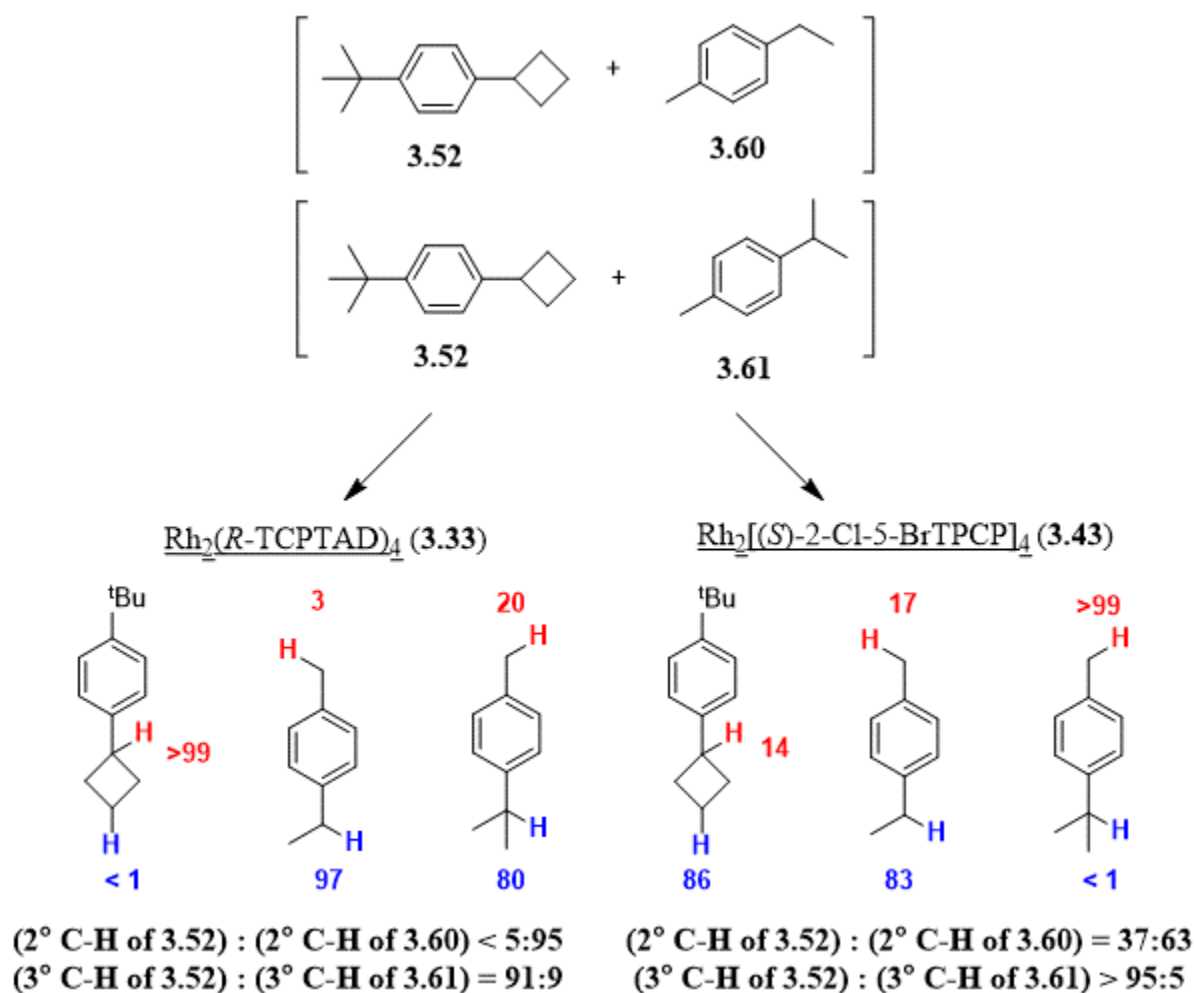
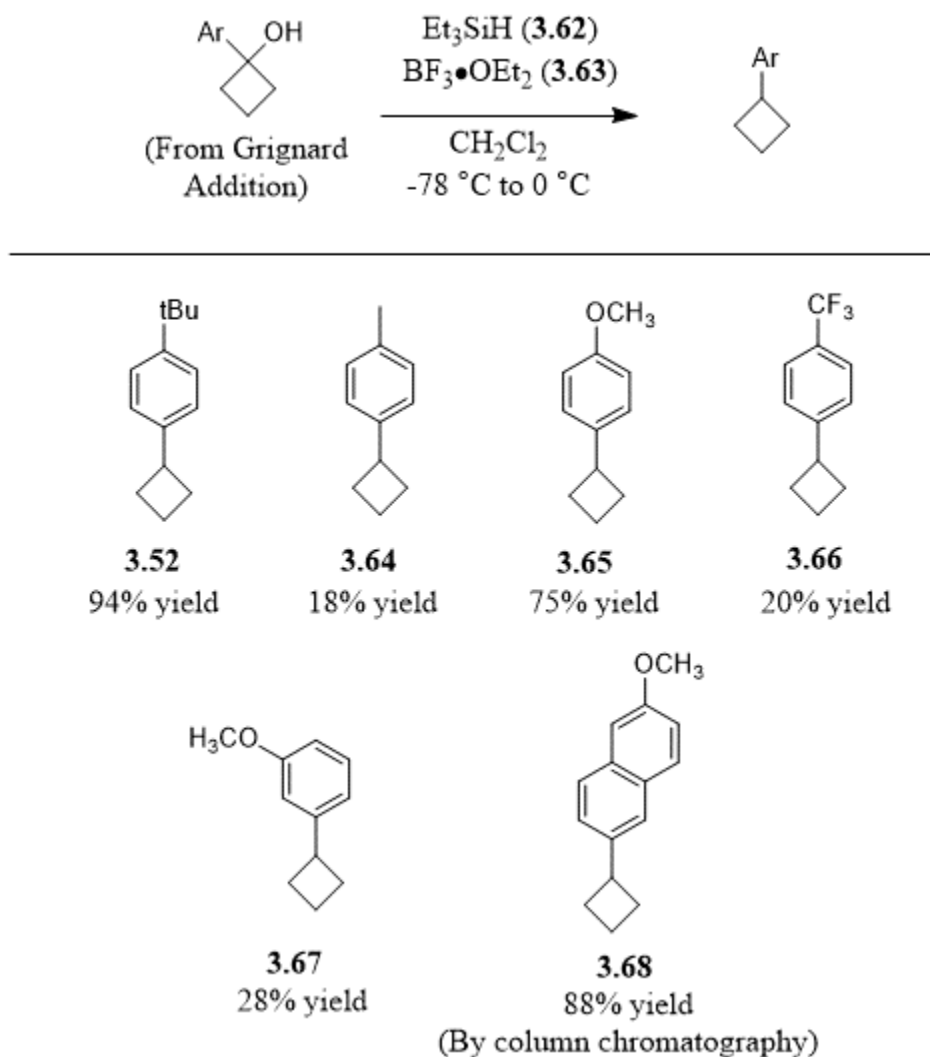


Chart 3.2.1: Relative rates of functionalization for catalysts **3.33** and **3.43**. Equimolar mixtures of the indicated substrates were reacted using each of the two catalysts, and the product distributions were quantified by ^1H NMR.³³ (A total of four reactions were performed for the study.) The ratios in blue and red have been normalized to each substrate.

Having determined that a site-selective reaction was possible for either of the two sterically accessible positions of the cyclobutane, we proceeded to further interrogate the substrate scope of the reaction.

3.2.1 Synthesis of Cyclobutane Substrates

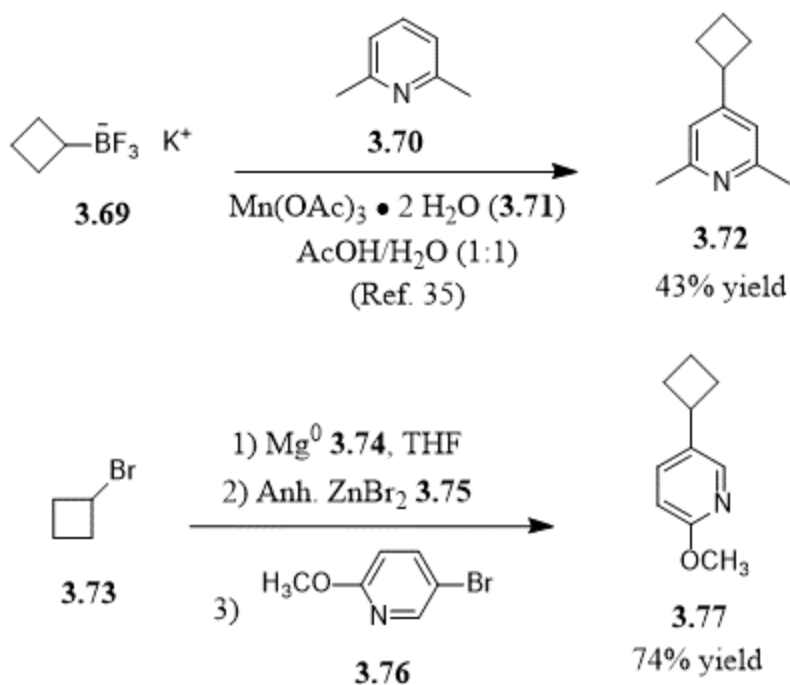
A variety of monoaryl-substituted cyclobutanes were prepared via a two step sequence in which an aryl Grignard reagent is reacted with cyclobutanone to afford a tertiary alcohol, and the resulting cyclobutanol is then reduced to the unfunctionalized cyclobutane using a combination of triethylsilane and boron trifluoride diethyl etherate (Scheme 3.2.1).



Scheme 3.2.1: Synthesis of arylcyclobutane substrates. Compounds **3.52** and **3.64-3.68** were purified by short path (Kugelrohr) distillation, compound **3.68** by column chromatography.³³

With the exception of **3.68**, all of the cyclobutane products were isolated from the crude mixtures by Kugelrohr distillation. While this process provided low recoveries of the lighter, nonpolar cyclobutanes **3.52** and **3.64-3.67** due to their volatility, the purity was much improved compared to using standard flash column chromatography techniques. In the case of entry **3.68**, the product was polar enough such that reasonably good purity could be achieved using flash column chromatography.

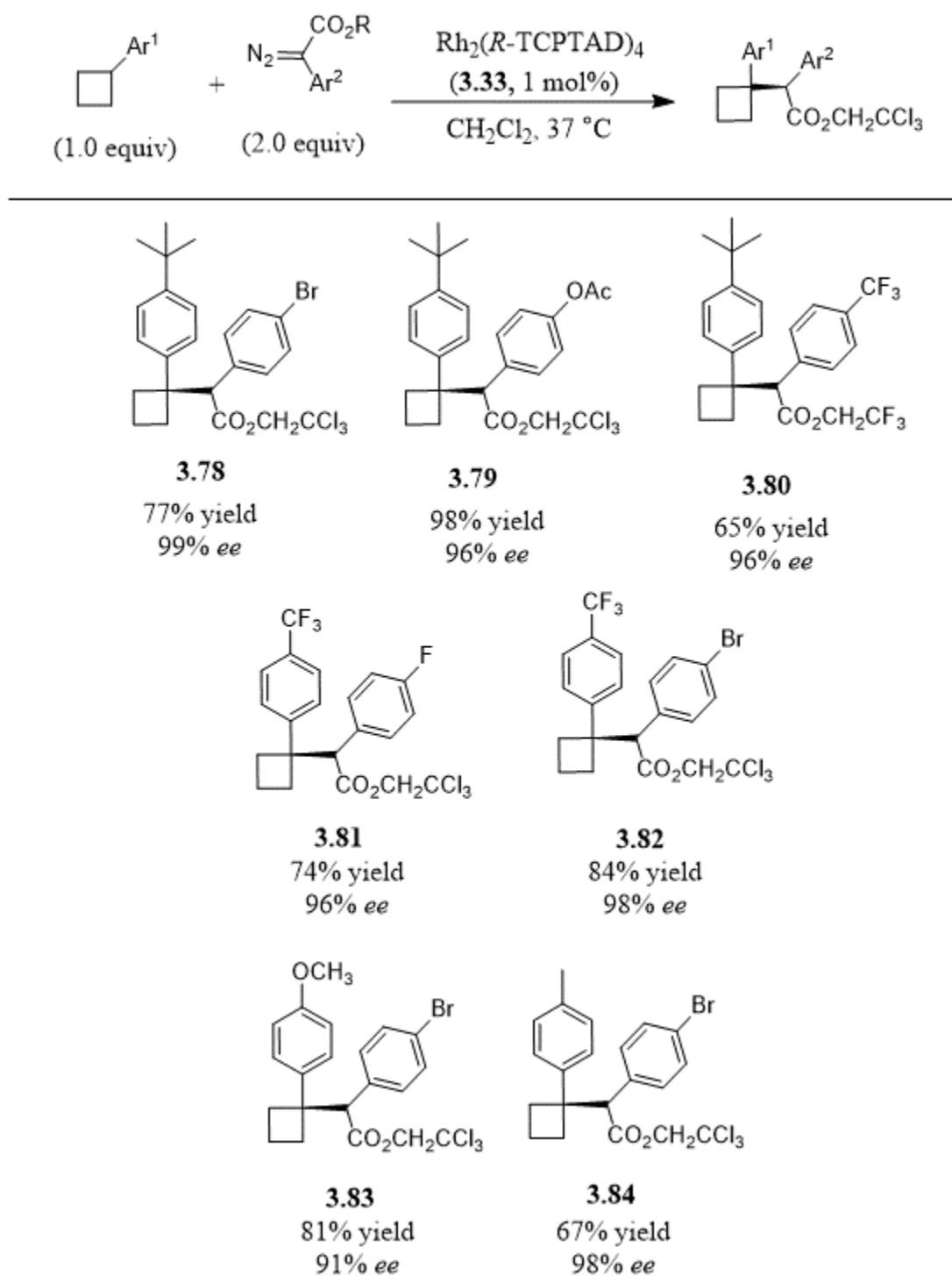
Pyridyl cyclobutanes were also prepared for this study³³, although the two step sequence described above was not effective in these cases. The synthesis of 4-cyclobutyl-2,6-dimethylpyridine (**3.72**) was achieved via an oxidative coupling reaction of potassium cyclobutyltrifluoroborate (**3.69**) with 2,6-lutidine (**3.70**).³⁵ 5-cyclobutyl-2-methoxypyridine (**3.77**) could be made using a Negishi coupling reaction between 5-bromo-2-methoxypyridine (**3.76**) and an organozinc reagent generated *in situ* from a cyclobutyl Grignard reagent and anhydrous ZnBr₂ (**3.75**, Scheme 3.2.2).



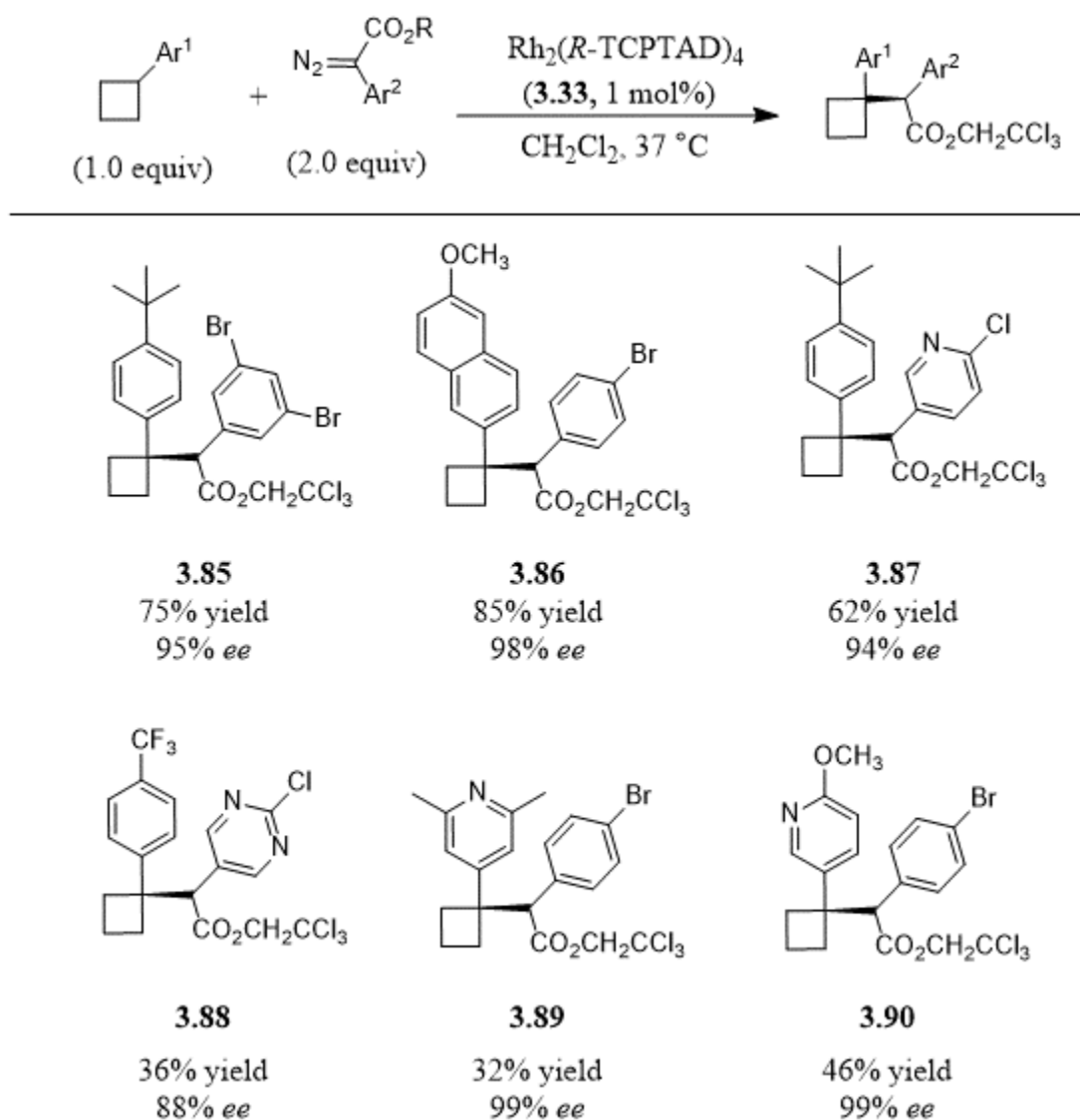
Scheme 3.2.2: Synthesis of pyridyl cyclobutanes.^{33,35}

3.2.2 C-H Functionalization of Arylcyclobutanes at C1

C-H functionalization reactions at the tertiary site of monoaryl cyclobutanes with aryldiazoacetates are interesting because the products can be viewed as analogs of TRPV3 antagonists such as **3.1** and **3.2**.^{12,36} $\text{Rh}_2(\text{TCPTAD})_4$ was identified as the optimum catalyst for forming the C1-functionalized product **3.53**, so it was used for further exploration of the substrate scope at the tertiary site. The reactions of this catalyst with the arylcyclobutanes are shown in Schemes 3.2.3 and 3.2.4.



Scheme 3.2.3: Scope of the C-H functionalization reaction at C1 (1/2)³³



Scheme 3.2.4: Scope of the C-H functionalization reaction at C1 (2/2)³³

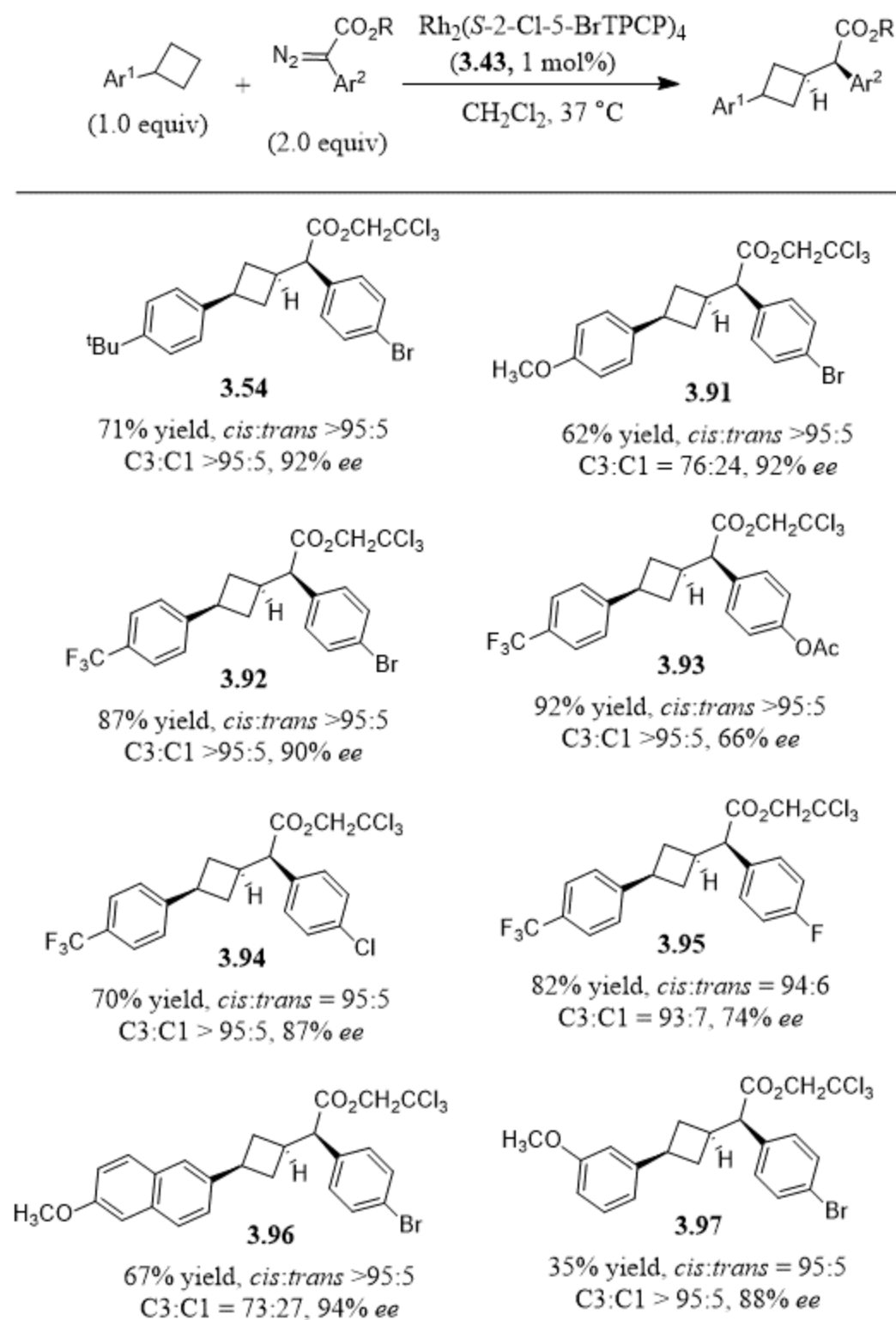
These examples illustrate that a relatively wide range of substrates can undergo the C-H reaction at the tertiary site. Very good to excellent enantioselectivity was observed in every case. The best yields were observed with arylcyclobutanes and diazo compounds which didn't contain strongly coordinating groups such as nitrogen atoms that might poison the catalyst. While heteroaryl-functionalized products such as **3.87** and **3.90** showed very respectable *ee*, their yield

was diminished relative to the other entries. It was also found that heteroatoms on the arylcyclobutane substrate were not tolerated at all when they were adjacent to the cyclobutane ring or were not flanked by a blocking substituent. In the case of compound **3.89**, the reason for the lower yield was due to the generation of a stable pyridinium ylide byproduct (see section 3.4 for further discussion.)

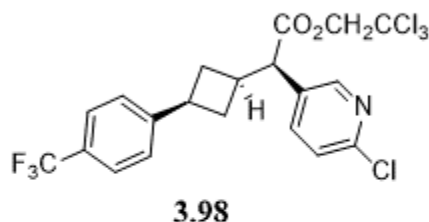
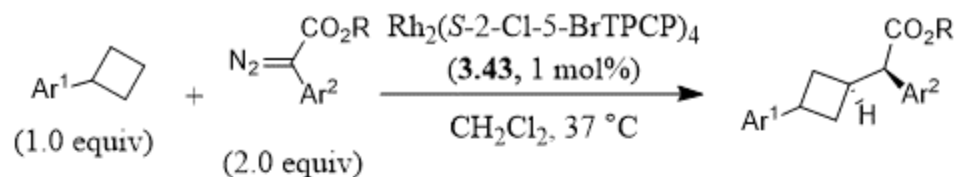
The stoichiometry for the substrate evaluation reactions used 2.0 equivalents of the diazo compound to 1.0 equivalent of the cyclobutane substrate. These conditions were found to provide higher yields for most of the C-H functionalization reactions because the mono-functionalization products did not tend to react a second time. An exception was example **3.84**, in which the methyl C-H site was also found to react to a small extent when an excess of diazo compound was used. Several of the compounds shown in Schemes 3.2.3 and 3.2.4 were supplied to AbbVie for biological evaluation.

3.2.3 C-H Functionalization of Arylcyclobutanes at C3

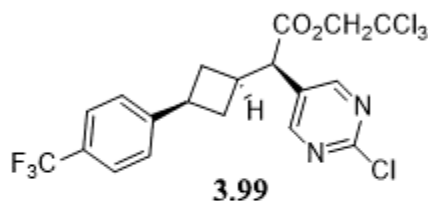
The C₄-symmetric³¹ triarylcyclopropane catalyst Rh₂(S-2-Cl-5-BrTPCP)₄ (**3.43**) gave the highest regioselectivity for functionalization at the C3 position of cyclobutane **3.52**, so this catalyst was chosen for further exploring the substrate scope of the distal functionalization reaction. No change in the temperature, concentration, catalyst loading, or stoichiometry were necessary for these reactions to generate products **3.91-3.101** in high site-selectivity, diastereoselectivity, enantioselectivity, and yield (Schemes 3.2.5 and 3.2.6).



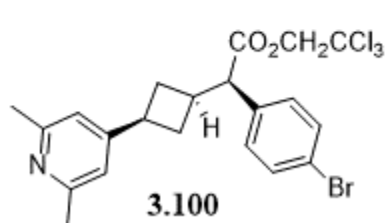
Scheme 3.2.5: Scope of the C-H functionalization reaction at C3 (1/2)³³



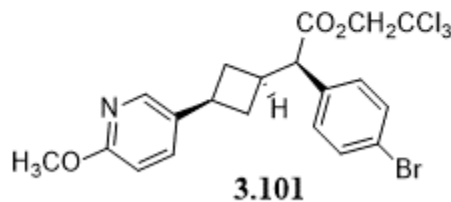
36% yield, *cis:trans* = 93:7
C3:C1 = 87:13, 80% *ee*



29% yield, *cis:trans* = 94:6
C3:C1 = 89:11, 79% *ee*



77% yield, *cis:trans* = 85:15
C3:C1 > 95:5, 93% *ee*



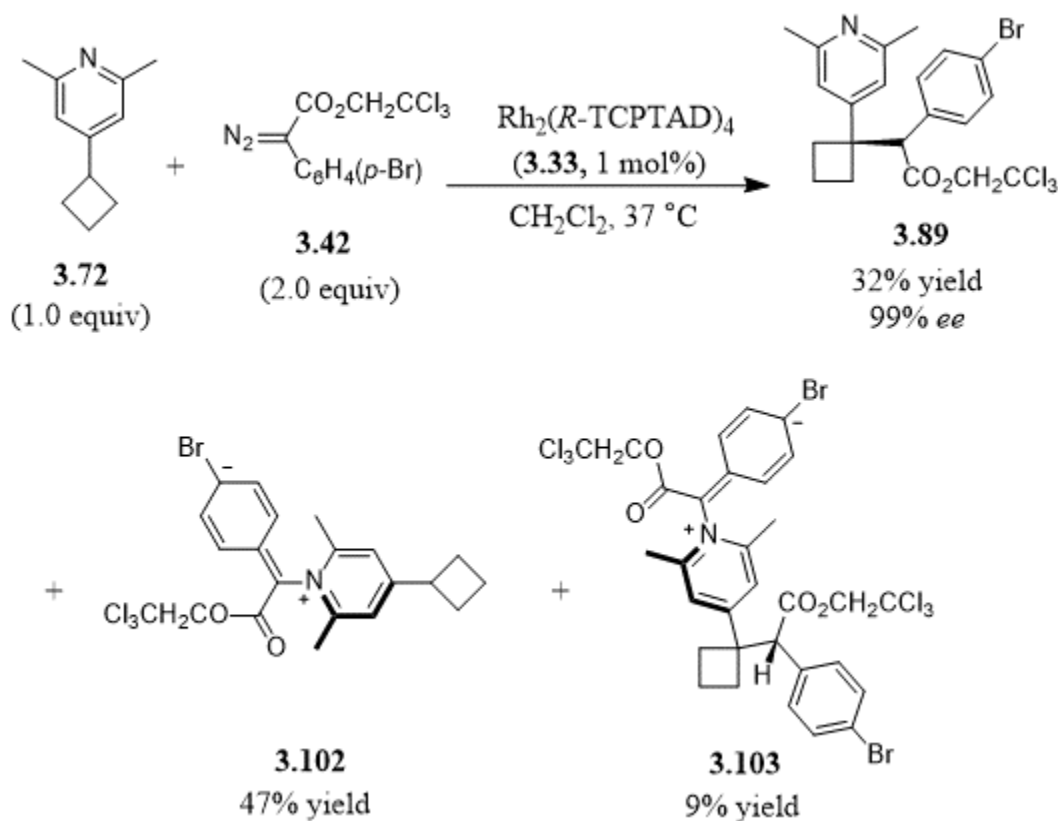
54% yield, *cis:trans* = 92:8
C3:C1 = 78:22, 92% *ee*

Scheme 3.2.6: Scope of the C-H functionalization reaction at C3 (2/2)³³

The C-H insertion reaction at C1 is somewhat more tolerant of functionality on the cyclobutane aryl substituent than the reaction at C3. In the case of methoxy substituted aryl groups, the distal functionalization reactions show somewhat lower r.r. (entries **3.91** and **3.96**) versus trifluoromethyl-substituted aryl groups. It is plausible that this effect could arise from electronic activation of the competing C1 site due the electron-donating -OCH₃ group, although the *tert*-butyl substituted **3.54** also gave a regioisomeric ratio of >95:5 for the C3 site. As in the C1-selective reaction, heteroaryl substituents are tolerated on either the diazo component or the cyclobutane component, but the reaction is likely to fail if the heteroatom is not flanked by a blocking group or is in close proximity to the cyclobutane ring.

3.2.4 Discovery and Isolation of Stable Pyridinium Ylides

While investigating the reaction of 4-cyclobutyl-2,6-lutidine with the $\text{Rh}_2(\text{R-TCPTAD})_4$ catalyst **3.33**, the observation was made that the major byproducts of the reaction were the stable pyridinium ylide compound **3.102** and what was presumed to be a small amount of its C1-functionalization adduct **3.103** (Scheme 3.2.7). Due to the 2,6-disubstitution on the pyridine ring, these substances are sterically hindered at the positions adjacent to nitrogen and are stable enough to purify using flash column chromatography.



Scheme 3.2.7: Unexpected formation of stable pyridinium ylides from compound **3.72**.

These compounds turn a characteristic deep blue color in hexanes/ether (Figure 3.2.1), which changes to reddish purple when the solvent is evaporated and replaced by methylene chloride. Treatment of the solutions with aqueous hydrochloric acid causes immediate decolorization. Sonication of the protonated material with aqueous base (NaOH) restores color to the solution.

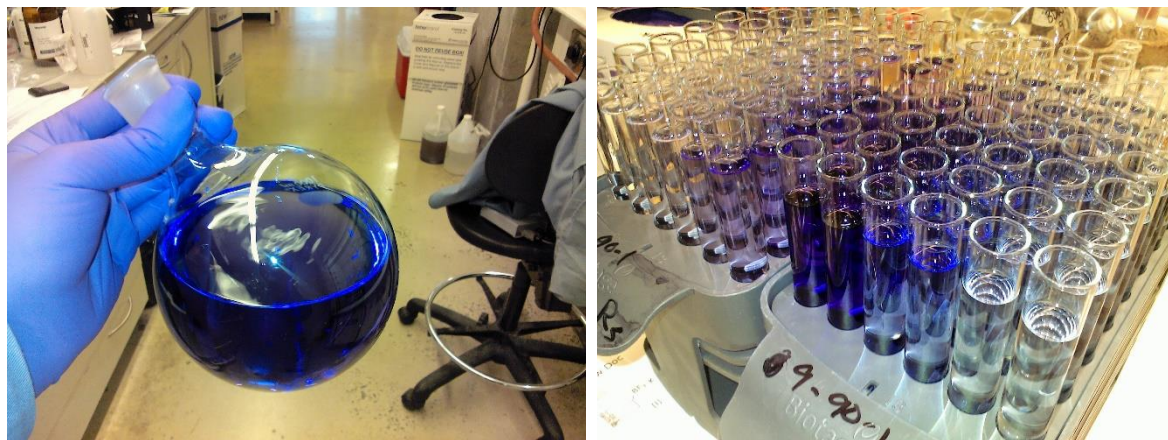
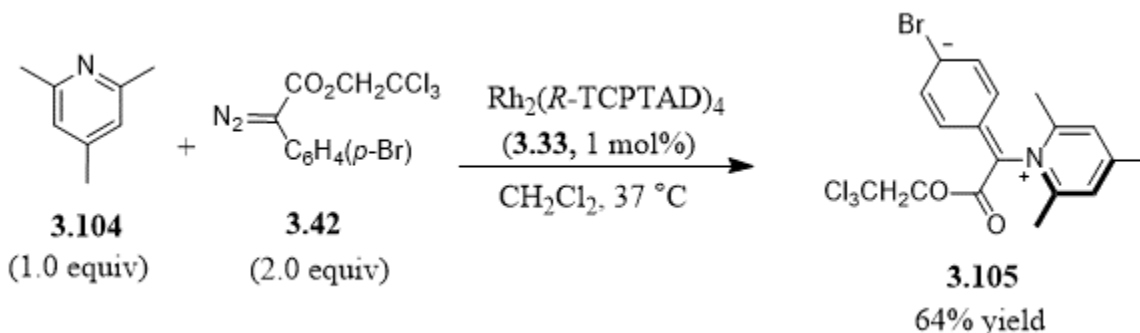


Figure 3.2.1: Photographs of the pyridinium ylide solution in Et₂O/hexanes.

While the compounds **3.102** and **3.103** were interesting due to their bright color, the challenge associated with preparing large quantities of the 4-cyclobutyl-2,6-lutidine starting material (**3.72**) limited possible applications for the new product. The side reaction to produce the C-H functionalization product **3.103** seems to have no significant influence on the ability of the substance to behave as a dye: both compounds produced comparably bright colors which changed depending on the solvent. To improve the yield and reduce the side reaction involving C-H insertion into the tertiary site, the reaction was attempted using 2,4,6-collidine (**3.104**) as the substrate instead of **3.72** (Scheme 3.2.8). The catalyst used for this reaction, Rh₂(*R*-TCPTAD)₄ (**3.33**), is selective for tertiary sites over primary ones. 2,4,6-Collidine does not possess any

tertiary C-H bonds, so it is logical that this reaction might show a higher yield due to a diminished tendency to undergo side reactions at the other sp^3 C-H sites.



Scheme 3.2.8: Reaction to form a pyridinium ylide from 2,4,6-collidine (**3.104**).

An additional benefit to using 2,4,6-collidine (**3.104**) as the starting material is that the product of this reaction is highly crystalline. The structure of compound **3.105** was elucidated by single-crystal X-ray analysis (Figure 3.2.2).

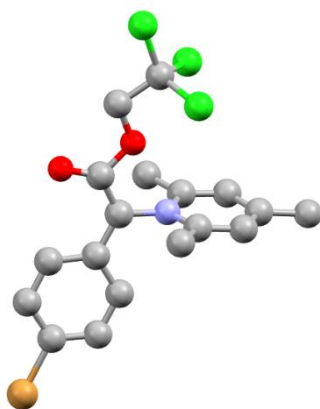


Figure 3.2.2: The solid state structure of compound **3.105** obtained by X-ray diffraction.

(Structure solved by Dr. John Bacsá.)

There are very few reports³⁷⁻³⁹ in the chemical literature describing stable compounds of this general structure, and none which describe their synthesis using dirhodium carbene chemistry or optical properties. A plausible explanation for the solvatochromic behavior of compounds **3.102**

and **3.105** is that they might behave in a manner similar to Reichardt's pyridinium phenolate dyes⁴⁰⁻⁴¹. In these systems, the electronic ground state is much more dipolar than the first photoexcited state, and association of solvents or solute molecules with the dye causes a larger hypsochromic shift in the UV absorption band with increasing polarity of the solvent/solute. An illustration depicting how this phenomenon might affect the energy levels of **3.105** is shown in Figure 3.2.3.

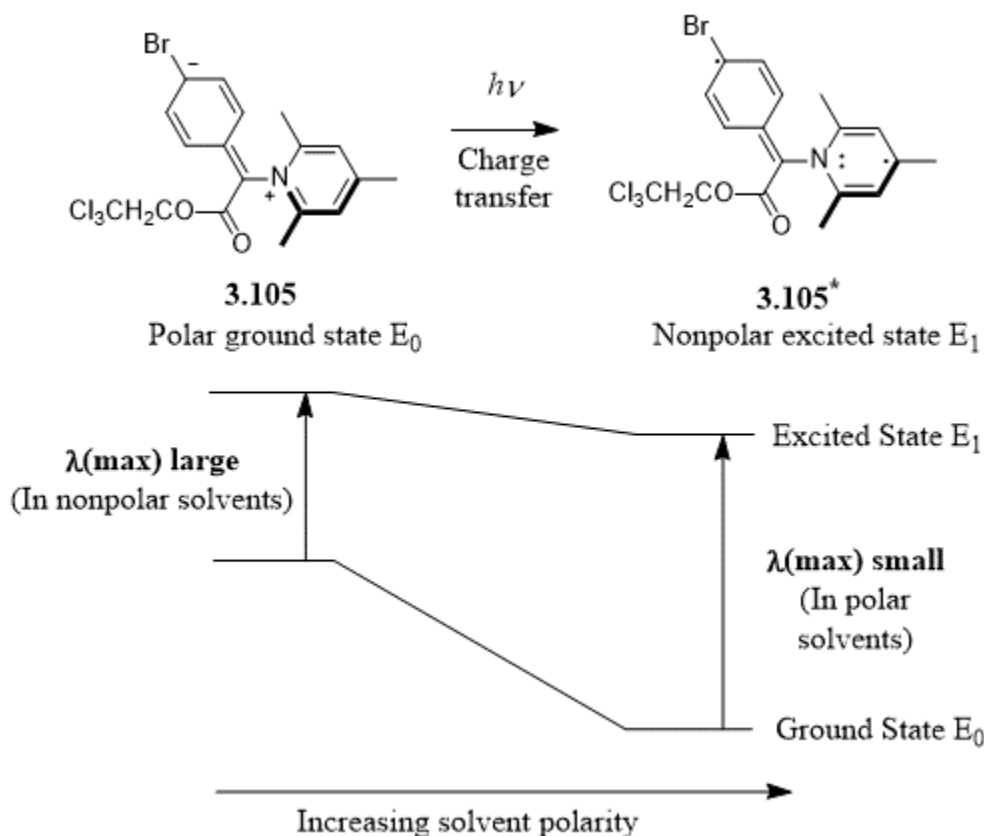


Figure 3.2.3: Proposed explanation for the solvatochromism of the pyridinium ylide **3.105**.

Further studies aimed at exploring the substrate scope of the carbene reactions, the optical properties of these novel pyridinium ylide compounds, and their possible applications are currently being conducted in the Davies lab.

3.3 Conclusion

The dirhodium-catalyzed C-H insertion reactions of donor/acceptor carbenes with arylcyclobutanes are effective for introducing functionality at either the C1 or C3 positions of a variety of substrates with high regio- and stereoselectivity. Historically, most C-H functionalization reactions involving cyclobutanes have utilized directing groups to achieve site selectivity¹⁶, but the current work has demonstrated that catalyst controlled C-H functionalization also represents a feasible strategy for further elaboration of the four membered ring. The reactions described in this chapter occur under very mild conditions and may tolerate heteroatoms on either the cyclobutane or the diazo components. They are also capable of demonstrating exceptionally high stereoselectivity at either the C1 or C3 functionalization sites. Based on the findings of this study, it is anticipated that other catalyst controlled methods for the site-selective C-H functionalization of cyclobutanes are likely to emerge in the coming decades.

3.4 References

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Chapter 4: $\text{Rh}_2(\text{DPCP})_4$ Catalysts With sp^3 -Hybridized Substituent Groups

4.1 Introduction

Dirhodium triarylcyclopropanecarboxylates (**TPCP**) catalysts can demonstrate exceptionally high site- and stereoselectivity for sterically accessible primary or secondary C-H bonds, even with challenging substrates such as **4.1-4.3** that contain many of them (Chart 4.1.1).¹⁻³ The ability of functionalized **TPCP** catalysts to select for primary C-H bonds in preference to secondary or tertiary ones is especially noteworthy because primary sites are electronically deactivated in comparison to more substituted positions.⁴

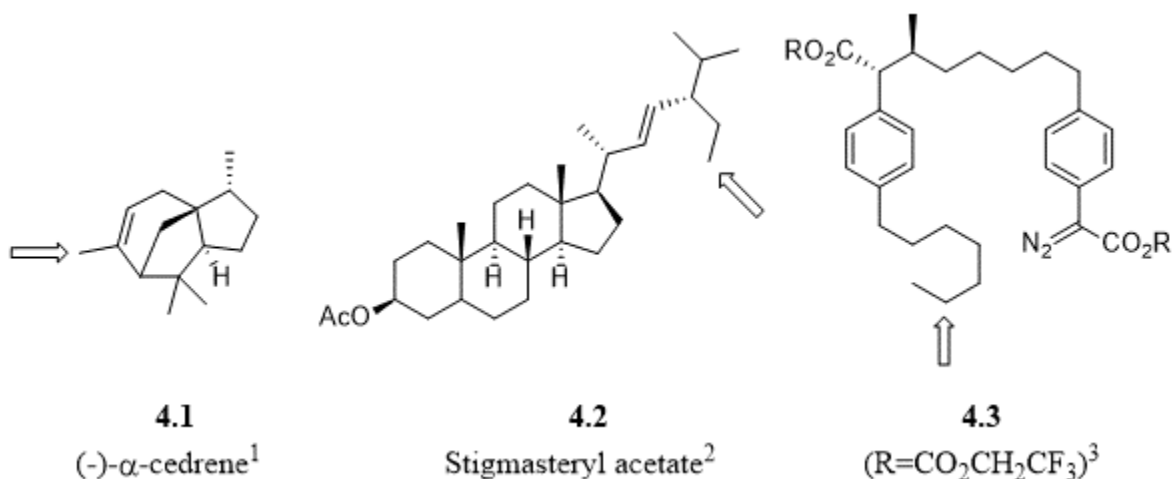
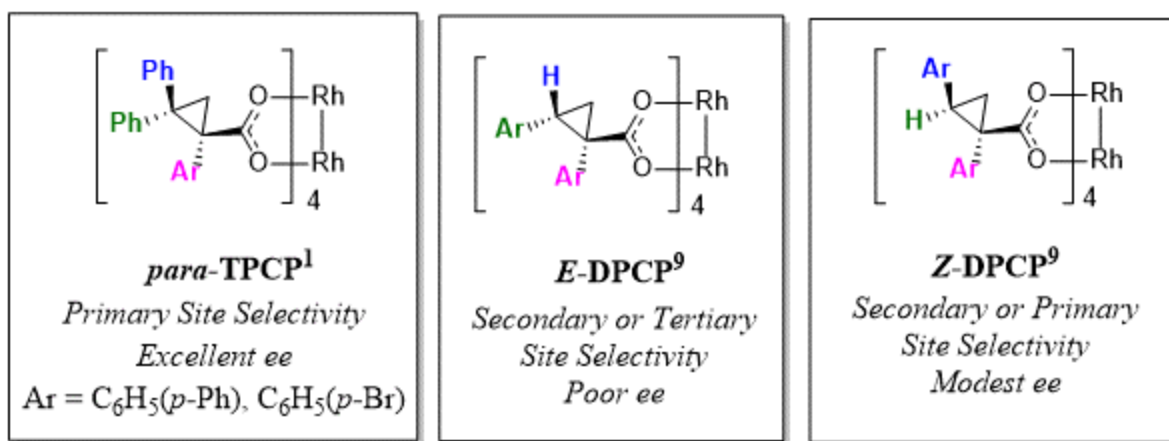


Chart 4.1.1: Selective C-H functionalization of complex molecules using **TPCP** catalysts¹⁻³

Prior work has established that a major determinant of site selectivity with the **TPCP** catalysts is the identity of the C1 aryl substituent, which has a dramatic influence on the overall shape and symmetry of the complex.⁵⁻⁸ When a *para* substituent is placed on this group, primary site selectivity and ee of the catalyst increase substantially.¹ Subsequent studies also revealed that the

C2 phenyl group *syn*- to the dirhodium carboxylate group has a greater impact on the enantioselectivity and primary site selectivity of the catalyst than the C2-aryl *anti* to the carboxylate.⁹

A: Previous Work



B: This Work

Primary selective diarylcyclopropane carboxylates with sp^3 -hybridized substituents

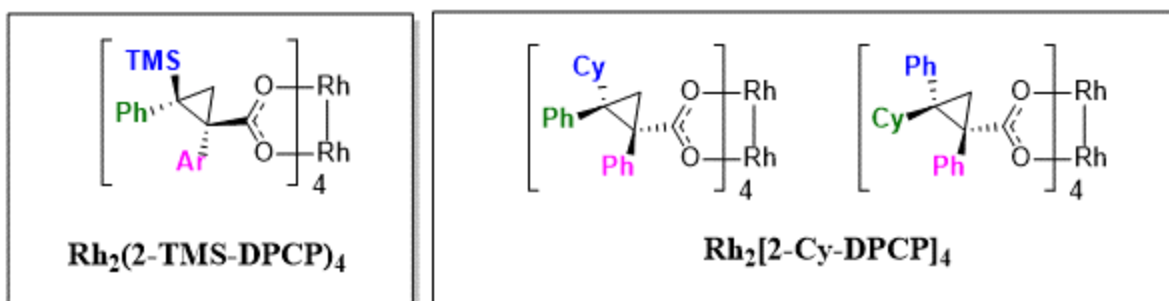


Figure 4.1.1: Dirhodium cyclopropanecarboxylate catalyst types relevant to the present study.^{1,9}

The types of dirhodium catalyst of interest in the present study are illustrated in Figure 4.1.1. Rh₂(DPCP)₄ catalysts of both *E*- and *Z*- geometries display a greater number of stable ligand orientations than Rh₂(TPCP)₄ and show inferior enantioselectivity and regioselectivity⁹ (see chapter 2). While the TPCP catalysts prefer well-defined orientations, formal removal of either aryl group at C2 of the cyclopropane to produce Rh₂(DPCP)₄ produces complexes that exist in a poorly defined conformational space. It is clear from the previous work that three substituents

are required for the cyclopropane catalyst scaffold to achieve optimal performance, but all of the dirhodium cyclopropane catalysts which have been previously explored by the Davies laboratory have used aromatic rings as the substituent groups.

In the present investigation, dirhodium diarylcyclopropanecarboxylate catalysts having two sp^2 -hybridized aryl groups and a third substituent with sp^3 -hybridized atoms were prepared and tested. Each catalyst was evaluated for site selectivity and enantioselectivity in asymmetric C-H insertion reactions using aryldiazoacetates as the carbene precursors. Reactions with styrenes were also performed to identify whether the new catalysts were capable of high enantioselectivity in cyclopropanation reactions.

4.1.1 Design of sp^3 -Functionalized Diarylcyclopropane Catalysts

The first type of sp^3 -functionalized **DPCP** catalyst to be examined were the dirhodium cyclohexyl diarylcyclopropanecarboxylates **4.4** and **4.5**. Work by Grimme¹⁰ has shown that pi-stacking effects are largely dispersive in nature, and that small saturated rings such as cyclohexane should display “stacking” type non-covalent interactions similar to benzene rings. However, the cyclohexyl group also has a substantially greater Van der Waals volume than a phenyl group¹¹⁻¹² and is not constrained to planarity. While both phenyl and cyclohexyl groups are six carbon ring systems, the cyclohexyl group is saturated and often exists as a comparatively wide chair conformer, while the phenyl group is flat and possesses a 6π -aromatic system. Both the *E*- and *Z*- isomers **4.4** and **4.5** were prepared and tested to probe the substitution effect at either C2 position.

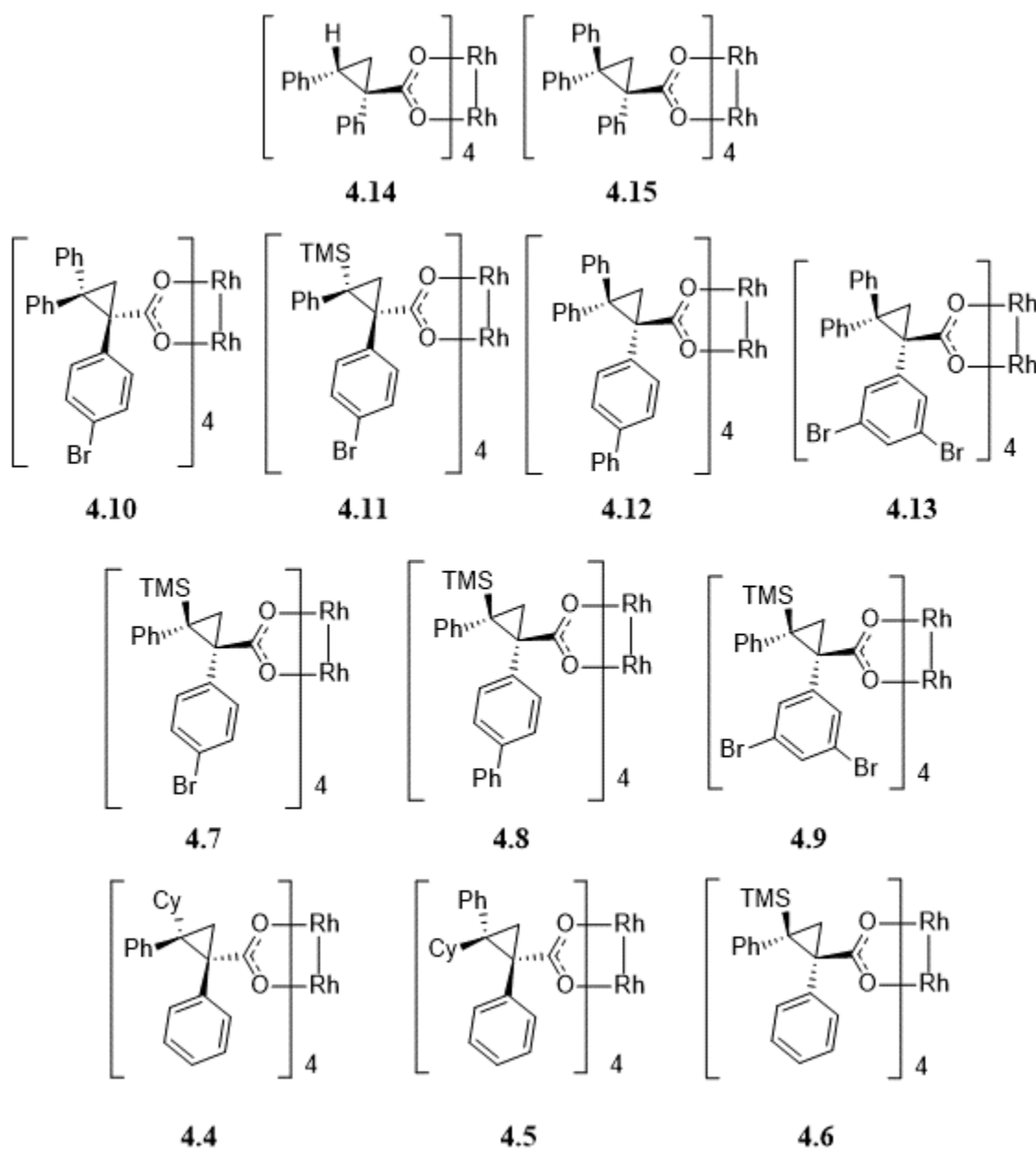


Chart 4.1.2: Dirhodium cyclopropanecarboxylate catalysts examined in the present study.

Trimethylsilyl diarylcyclopropanecarboxylate catalysts were also prepared in the present study (Chart 4.1.2). TMS is a relatively large substituent, and like the cyclohexyl group it has greater width than a phenyl group and occupies a larger Van der Waals volume¹³. For the **TPCP**-type catalysts, the placement of substituents on the C1 aryl group can cause a dramatic change in the shape and symmetry properties of catalysts.⁵⁻⁸ The **E-DPCP** catalysts did not show a similar

substituent effect,⁹ but both **TPCP** and **2-TMS-DPCP** catalysts possess three substituents on the cyclohexanes ring, while **E-DPCP** do not. Based on these facts, it is plausible that geometries favored due to steric crowding effects might be observed for both **TPCP** and **TMS-DPCP**.

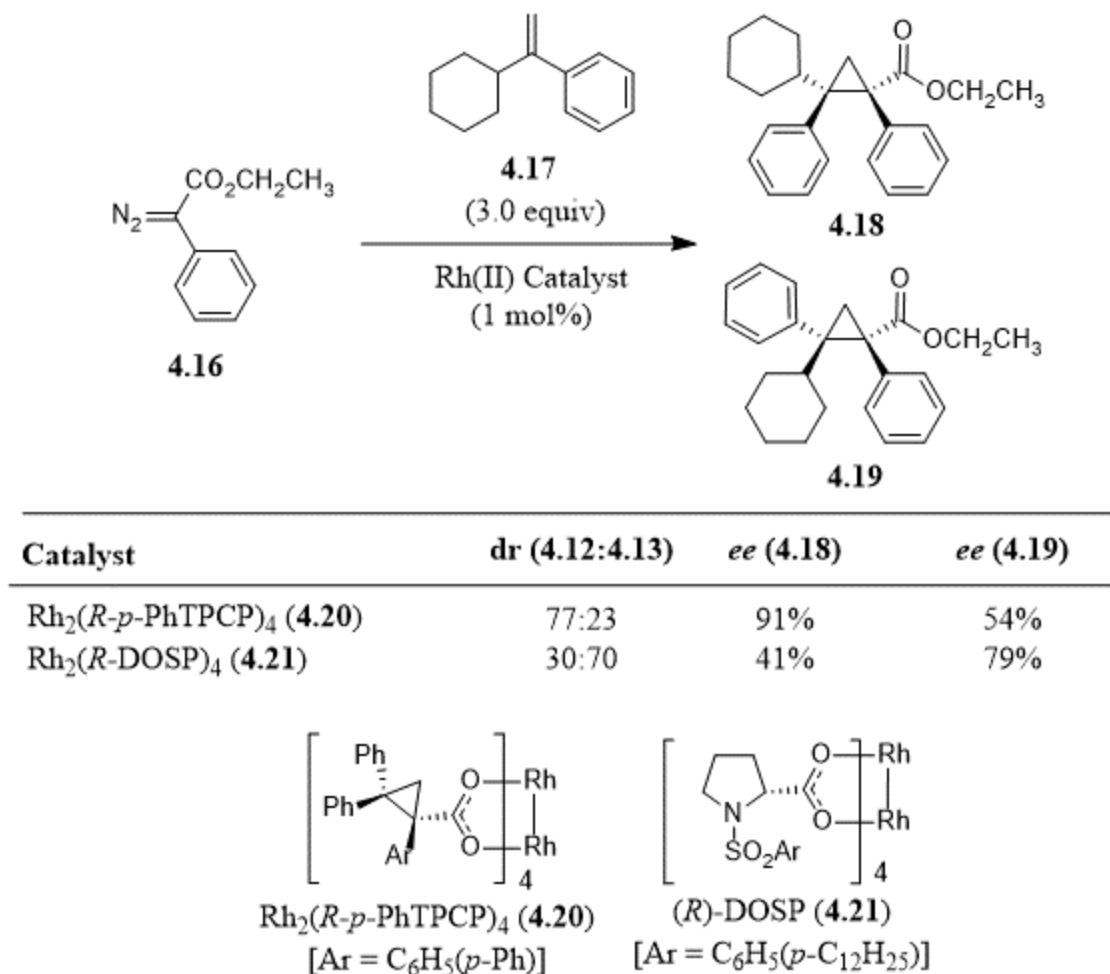
The first **2-TMS-DPCP** catalyst which was studied was $\text{Rh}_2[(1R,2R)\text{-2-TMS-DPCP}]_4$ (**4.6**), a catalyst without any substituents on the C1-aryl group. Compounds **4.11** and **4.8** are analogous to the established **TPCP** complexes $\text{Rh}_2(R\text{-}p\text{-BrTPCP})_4$ (**4.10**)¹⁴ and $\text{Rh}_2(S\text{-}p\text{-PhTPCP})_4$ (**4.12**)¹⁵, which often show high site- and stereoselectivity for sterically accessible primary positions. Entry **4.9** is similar to the **TPCP** catalyst $\text{Rh}_2(S\text{-}3,5\text{-di-BrTPCP})_4$ (**4.13**), which shows substantially higher selectivity for secondary C-H sites⁶ versus *para*-substituted catalysts such as $\text{Rh}_2(S\text{-}p\text{-PhTPCP})_4$ (**4.12**). An attempt was also made to prepare an *ortho*-chloro substituted trimethylsilyl cyclopropane, but the synthesis of this compound was not successful.

4.2 Results and Discussion

4.2.1 Preparation of Cyclohexyl-DPCP Catalysts

To make the cyclohexyl-functionalized diarylcyclopropane catalysts, an asymmetric carbene cyclopropanation reaction was employed as the key step (Scheme 4.2.1). However, this proved challenging because there is little steric or electronic differentiation between the two groups on the alkene **4.17**. While a good number of catalysts and diazo compounds were evaluated for this cyclopropanation reaction,¹⁶ none were highly effective for controlling the diastereoselectivity of the reaction. However, it was found that the catalysts $\text{Rh}_2(R\text{-}p\text{-PhTPCP})_4$ (**4.20**) and $\text{Rh}_2(R\text{-DOSP})_4$ (**4.21**) provided modest but complementary selectivity for the diastereomeric cyclohexyl

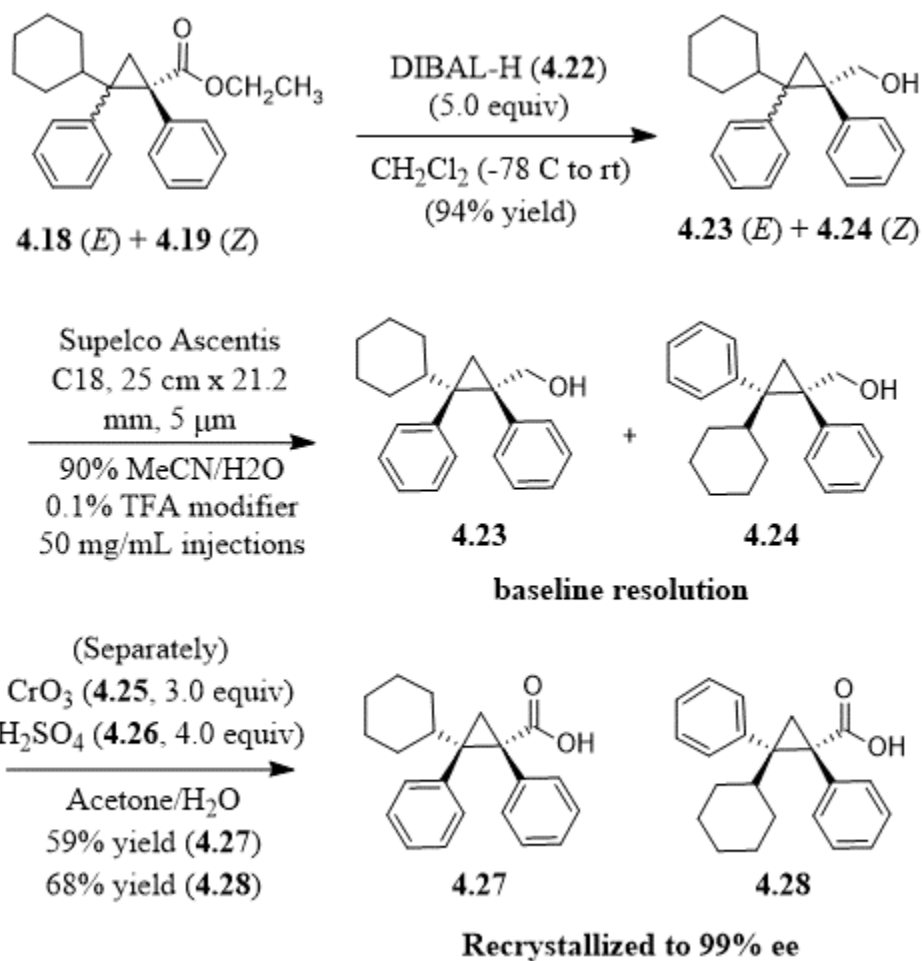
cyclopropanes **4.18** and **4.19** when ethyl phenyldiazoacetate (**4.16**) was used as the carbene precursor (Scheme 4.2.1). In both of these reactions, the major diastereomer was obtained with reasonably good enantioselectivity.



Scheme 4.2.1: Stereoselective cyclopropanation reactions with α -cyclohexylstyrene.

Despite the fact that both diastereomers were desired products, their generation as stereoisomeric mixtures was inefficient because the minor diastereomers generated in either of the two reactions are not produced in high enough enantiomeric excess to be carried forward without performing many recrystallizations on them. Furthermore, the separation of these minor diastereomers proved to be extremely challenging and inefficient using conventional techniques

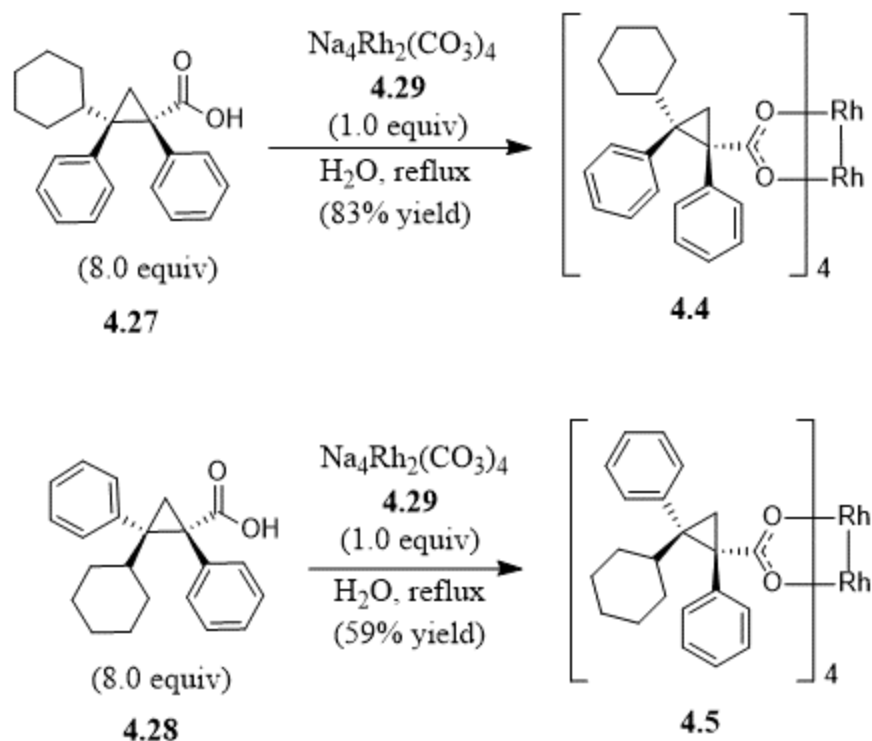
such as flash column chromatography. To efficiently separate the diastereomeric cyclopropanes, it was necessary to derivatize the mixtures as primary alcohols by reducing them with DIBAL-H (4.22, Scheme 4.2.2). The alcohol products could then be separated via reversed phase HPLC on C18-functionalized silica gel. While this process was time consuming and laborious, it provided complete resolution of the structurally similar compounds at a loading sufficient to prepare several hundred milligrams of both **4.23** and **4.24**.



Scheme 4.2.2: Preparation of diastereomeric 2-Cy-DPCP ligands **4.27** and **4.28**.

To oxidize the cyclopropyl methanols **4.23** and **4.24** back to the carboxylic acid oxidation level, they were separately treated with Jones reagent, affording **4.27** and **4.28**. Following

recrystallization to $\geq 99\%$ *ee*, the carboxylic acid products were subjected to ligand exchange with sodium rhodium carbonate (**4.29**) as the rhodium precursor (Scheme 4.2.3). These reactions were both successful, generating catalysts **4.4** and **4.5** in 83% and 59% yield, respectively.



Scheme 4.2.3: Ligand exchange to form the cyclohexyl-DPCP catalysts **4.4** and **4.5**.

The structure of the cyclohexyl catalyst **4.4** was analyzed by X-ray crystallography (Figure 4.2.1). A single crystal diffraction experiment confirmed the expected structure, and the geometry displayed by this catalyst was an $(\alpha, \alpha', \alpha, \alpha')$ - C_2 shape. This ligand orientation is associated with high selectivity for primary C-H sites.^{5,9}

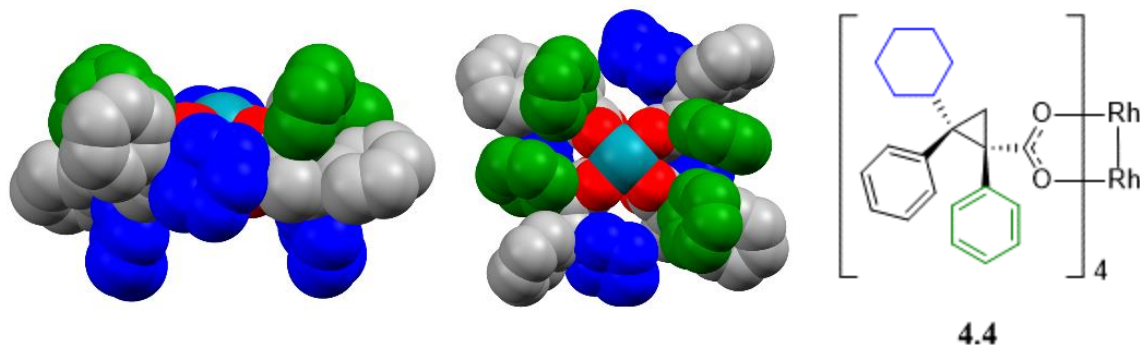
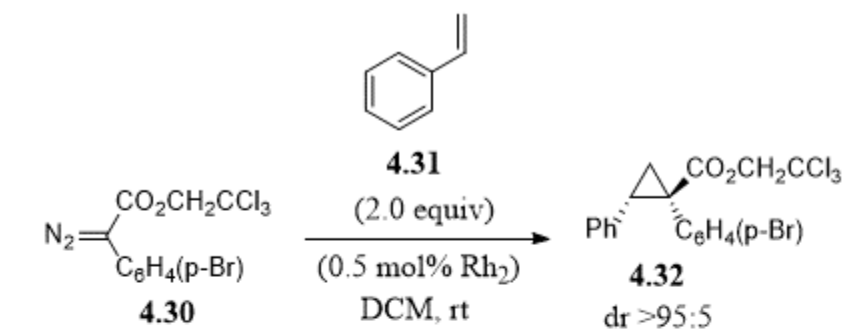


Figure 4.2.1: The solid state structure of $\text{Rh}_2[(1R,2S)\text{-}2\text{-CyDPCP}]_4$ (4.4). Solvent molecules have been omitted for clarity. Solved by Dr. John Bacsá, Emory University.

4.2.2 Evaluation of Cyclohexyl-DPCP Catalysts

To characterize the newly prepared catalysts $\text{Rh}_2[(1R,2S)\text{-}2\text{-CyDPCP}]_4$ (4.4) and $\text{Rh}_2[(1R,2R)\text{-}2\text{-CyDPCP}]_4$ (4.5), they were each reacted with styrene (4.31), 4-ethyltoluene (4.33), and 4-isopropyltoluene (4.36) using 2,2,2-trichloroethyl (4-bromophenyl)diazoacetate (4.30) as the carbene precursor. This series of reactions provides basic information about the site selectivity properties of the catalyst and its capacity for enantioselectivity in cyclopropanation and C-H insertion reactions.⁹ $\text{Rh}_2[(1R,2S)\text{-DPCP}]_4$ (4.27) and $\text{Rh}_2(\text{S-TPCP})_4$ (4.28) were used as reference catalysts for these experiments. A cyclopropanation reaction with styrene is shown in table 4.2.1, and the C-H functionalization reactions are illustrated in table 4.2.2.



Catalyst	Yield, %	ee, %
Rh ₂ [(1 <i>R</i> ,2 <i>S</i>)-DPCP] ₄ (4.14)	92	-8
Rh ₂ [(1 <i>R</i> ,2 <i>S</i>)-2-Cy-DPCP] ₄ (4.4)	71	92
Rh ₂ [(1 <i>R</i> ,2 <i>R</i>)-2-Cy-DPCP] ₄ (4.5)	66	77
Rh ₂ (<i>S</i> -TPCP) ₄ (4.15)	90	-91

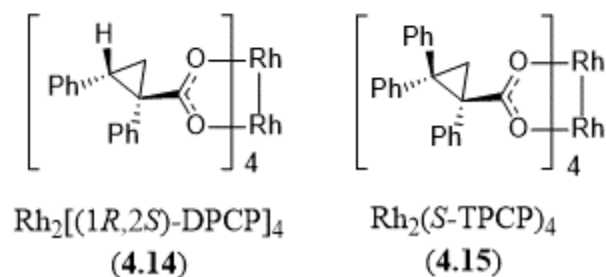
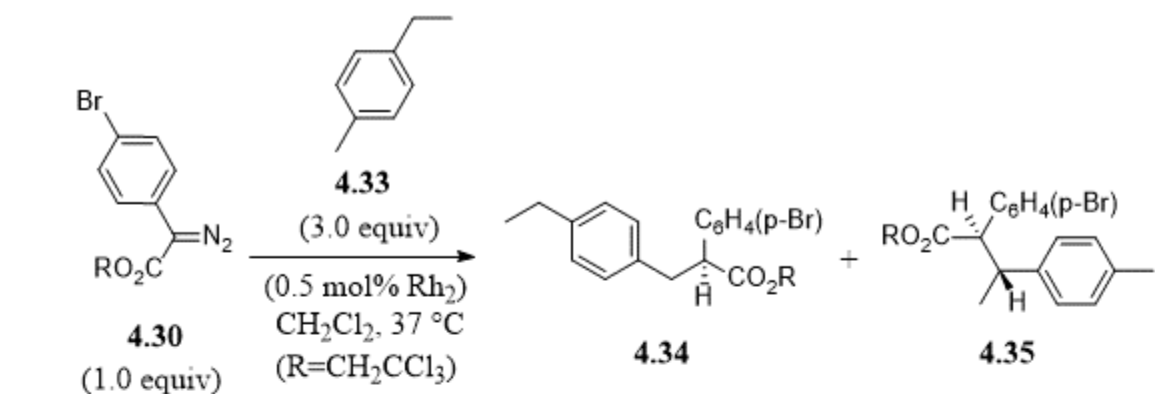
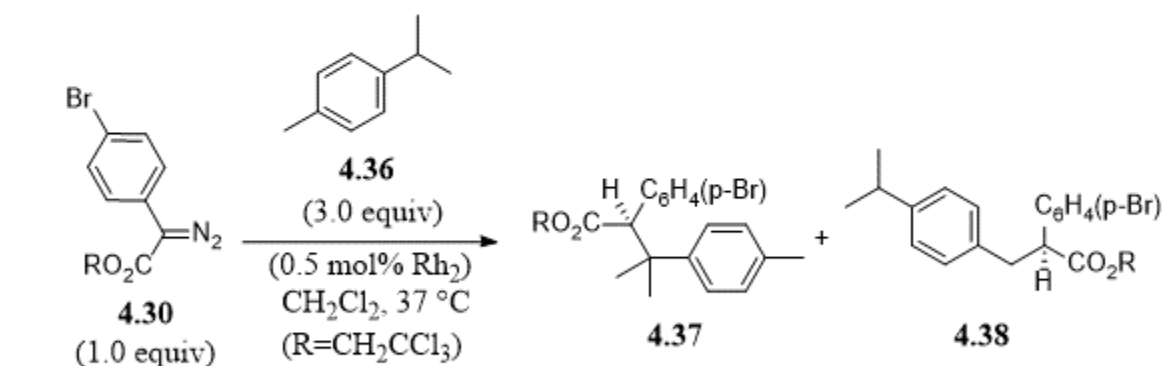


Table 4.2.1: Evaluation of cyclohexyl-DPCP catalysts in asymmetric cyclopropanation.



Catalyst	Yield	1°:2°	dr (2°)	ee (1°)
$\text{Rh}_2[(1R,2S)\text{-DPCP}]_4$ (4.14)	90%	5:95	85:15	<5%
$\text{Rh}_2[(1R,2S)\text{-2-Cy-DPCP}]_4$ (4.4)	76%	67:33	66:33	78%
$\text{Rh}_2[(1R,2R)\text{-2-Cy-DPCP}]_4$ (4.5)	79%	79:21	61:39	89%
$\text{Rh}_2(S\text{-TPCP})_4$ (4.15)	91%	81:19	71:29	-93%



Catalyst	Yield	rr (1°:3°)	ee (1°)	ee (3°)
$\text{Rh}_2[(1R,2S)\text{-DPCP}]_4$ (4.14)	74%	39:61	-6%	-40%
$\text{Rh}_2[(1R,2S)\text{-2-Cy-DPCP}]_4$ (4.4)	88%	89:11	81%	29%
$\text{Rh}_2[(1R,2R)\text{-2-Cy-DPCP}]_4$ (4.5)	81%	>95:5	94%	---
$\text{Rh}_2(S\text{-TPCP})_4$ (4.15)	85%	>95:5	-93%	---

Table 4.2.2: Evaluation of cyclohexyl-DPCP catalysts in C-H functionalization reactions. The (2*R*,3*R*)/(2*S*,3*S*) relative configuration of **4.31** was observed as the major diastereomer in every case.

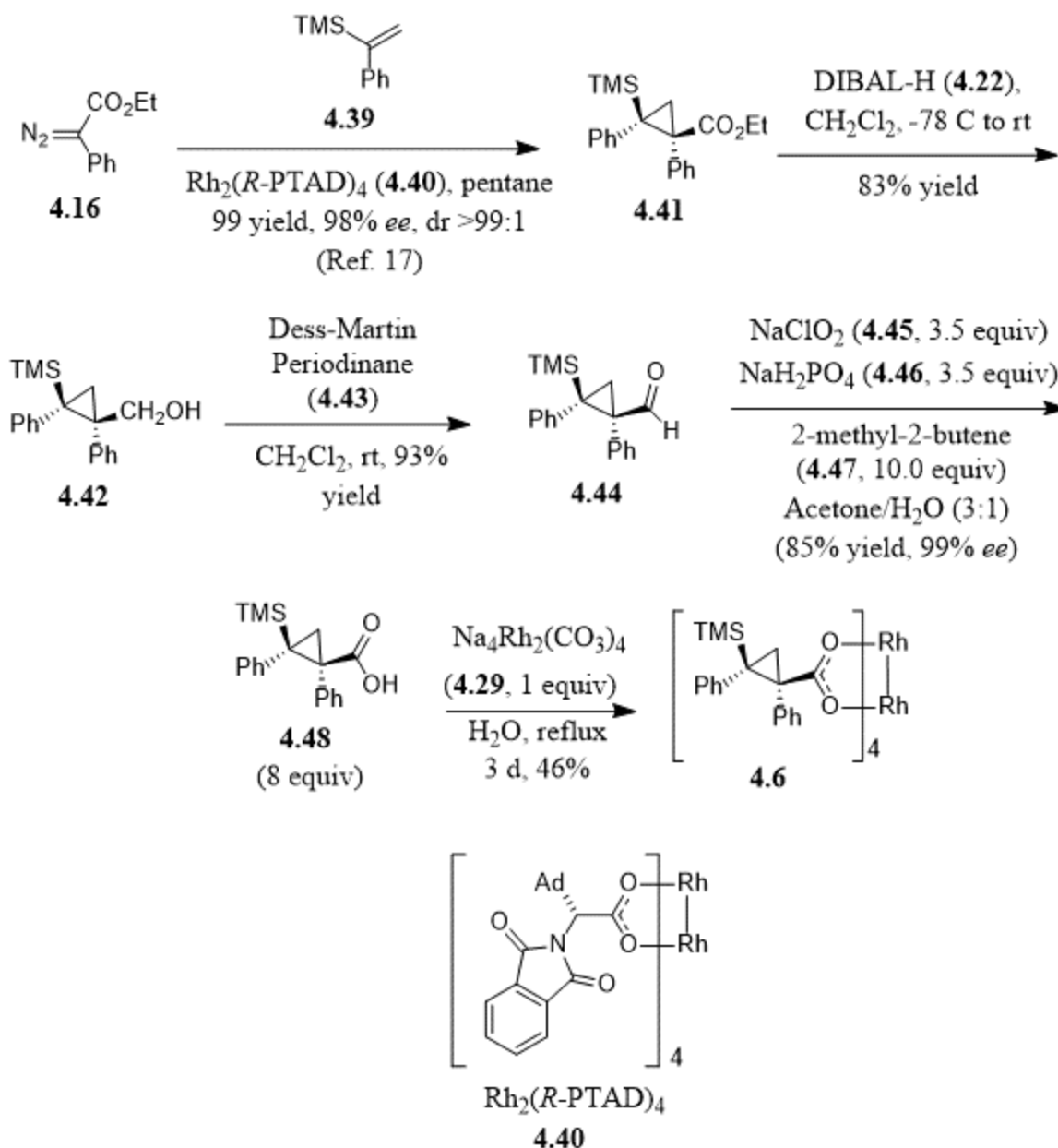
The cyclohexyl catalysts **4.4** and **4.5** both performed much better than the diarylcyclopropane catalyst **4.14** with respect to enantioselectivity and showed a much greater preference for primary sites than **4.14** in the C-H functionalization reactions. The regioselectivity and enantioselectivity of the new catalysts was roughly comparable to that of the triarylcyclopropanecarboxylate catalyst $\text{Rh}_2(\text{S-TPCP})_4$ (**4.15**). Catalysts **4.4** and **4.5** showed higher enantioselectivity than the triaryl catalyst in some cases. However, **4.15** was more consistent in its performance and tended to give higher yields.

The performance of the cyclohexyl-substituted DPCP catalysts **4.4** and **4.5** with these model substrates was encouraging and clearly indicated that three aryl substituents were not strictly required for a dirhodium cyclopropanecarboxylate catalyst to show high site selectivity and enantioselectivity. However, the syntheses of catalysts **4.4** and **4.5** were very inefficient due to the low diastereoselectivity of the asymmetric cyclopropanation step. To continue the study, it was necessary to identify a different class of sp^3 -substituted **DPCP** catalyst which could be prepared on a more reasonable scale.

4.2.3 Trimethylsilyl Diarylcyclopropanecarboxylates

The Van der Waals volume of the trimethylsilyl group is about $10 \text{ \AA}^3$ larger than a phenyl group¹³, so dirhodium cyclopropanecarboxylates with 2-trimethylsilyl substituents might be expected to behave as relatively hindered catalysts. To synthesize these new catalysts, asymmetric cyclopropanation reactions employing α -trimethylsilyl styrene (**4.39**) were conducted. As discussed in chapter 2, work by Su, et al.¹⁷ has shown that when $\text{Rh}_2(\text{R-PTAD})_4$ (**4.40**) is employed as the chiral catalyst, the reactions of aryldiazoacetates with trimethylsilyl styrene (**4.39**) are highly diastereoselective for *Z*-trimethylsilyl cyclopropanecarboxylates and

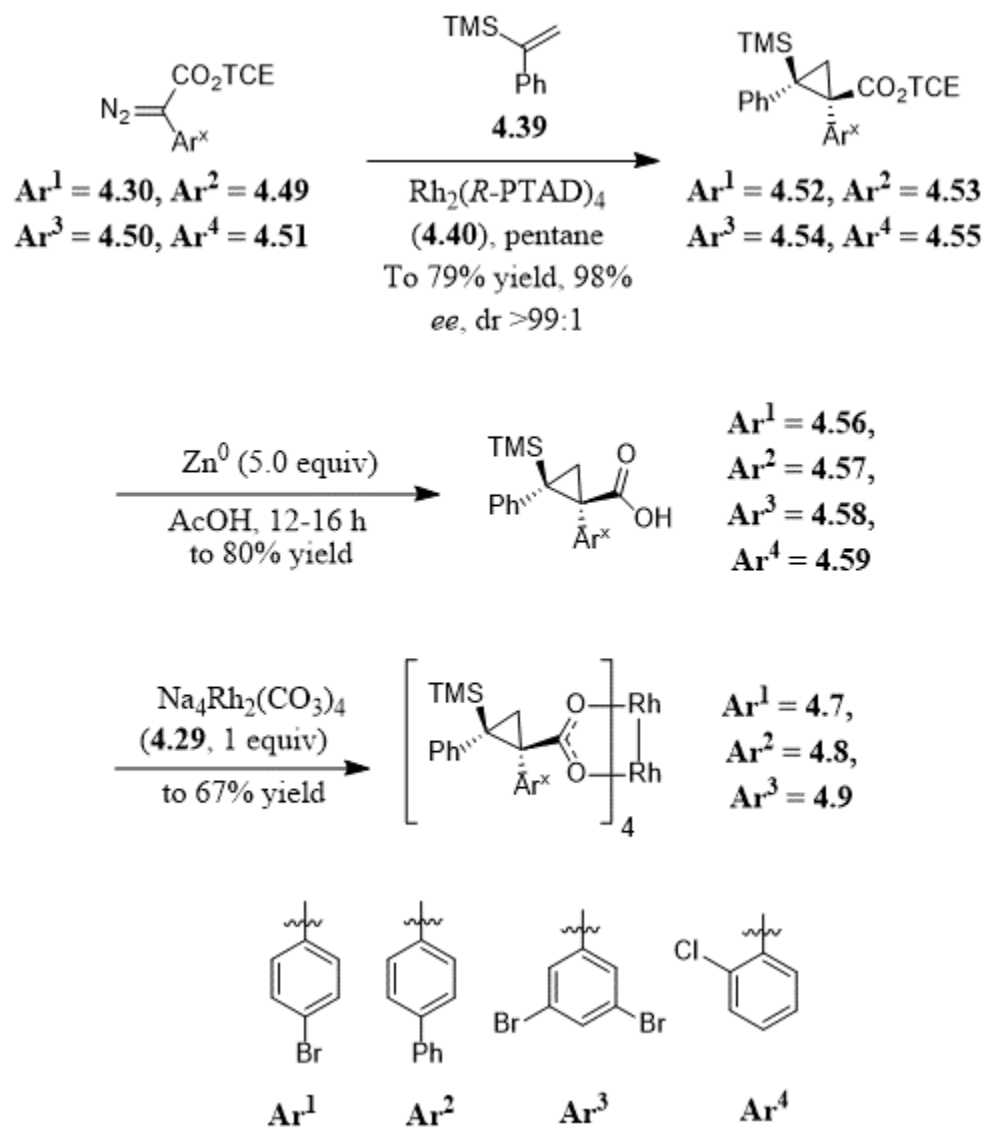
often show very high enantioselectivity (>95% *ee*). To elucidate the effect of adding a trimethylsilyl group to the parent diarylcyclopropane catalyst $\text{Rh}_2[(1R,2S)\text{-DPCP}]_4$ (**4.14**), the unfunctionalized catalyst **4.6** was prepared (Scheme 4.2.4).



Scheme 4.2.4: First generation synthesis of $\text{Rh}_2[(1R,2R)\text{-2-TMS-DPCP}]_4$ (**4.6**).

Due to the acid- and base sensitivity of the trimethylsilyl group, mild and chemoselective conditions were required for deprotecting the ethyl ester **4.41**. In the present synthesis of **4.6**, this problem was solved by reducing with diisobutylaluminum hydride (**4.22**) and then re-oxidizing the resulting cyclopropyl methanol **4.42** to the aldehyde oxidation level using Dess-Martin periodinane (**4.43**). A Pinnick reaction could then be employed to generate the desired carboxylic acid **4.48**.¹⁸ Gratifyingly, the ligand exchange reaction of this acid resulted in a reasonable yield (46%) of the dirhodium tetracarboxylate complex **4.6**. While multiple steps are required in this synthetic strategy, the reduction/oxidation approach to the deprotection of the ethyl ester group tolerates the TMS functionality and proceeds in reasonable overall yield.

To facilitate the rapid preparation of other silyl cyclopropane catalysts, an alternate synthetic route was sought which was shorter and faster than the first generation strategy. 2,2,2-trihaloethyl esters have been extensively utilized in the Davies group to enhance site selectivity and *ee* in the reactions of donor/acceptor carbenes.¹⁹ While the stereoselectivity of the cyclopropanation reactions with trimethylsilylstyrene were previously found to be optimal for methyl, ethyl, and benzyl esters,¹⁷ the 2,2,2-trichloroethyl group is a useful functional handle for preparing dirhodium tetracarboxylates because it can be easily deprotected using zinc dust. In this study, it was found that high stereoselectivity with α -trimethylsilylstyrene (**4.39**) is also observed when 2,2,2-trichloroethyl aryldiazoacetates are used as carbene precursors (Scheme 4.2.5).



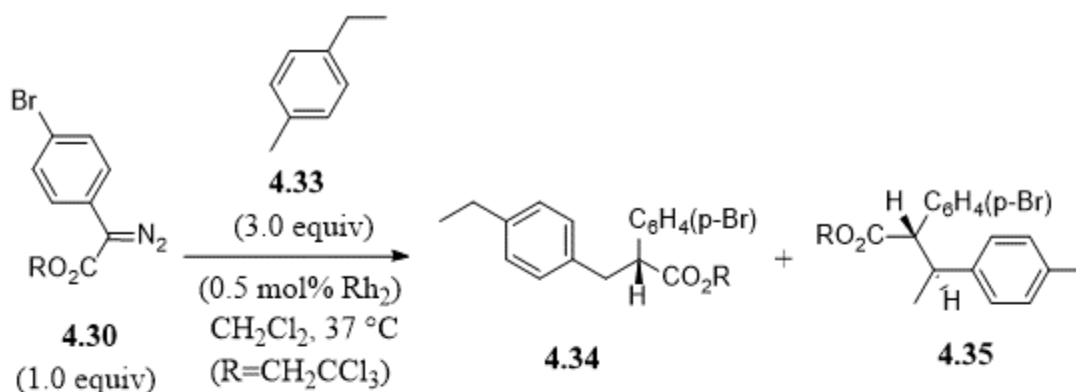
Scheme 4.2.5: Rapid synthesis of 2-TMS-DPCP catalysts from trichloroethyl diazoacetates.

The trimethylsilyl group on the cyclopropane ring is well-tolerated under the conditions for trichloroethyl ester deprotection. Treatment of the 2,2,2-trichloroethyl cyclopropanecarboxylates **4.52-4.55** with zinc dust in acetic acid solvent afforded the carboxylic acids **4.56-4.59** in high yield. The synthesis of the catalysts **4.7-4.9** could then be completed using a conventional ligand exchange reaction with sodium rhodium carbonate (**4.29**). The reactions formed the fully substituted catalysts in reasonable yield despite the prolonged reaction times and relatively high temperature (ca. 100 °C).

The *ortho*-chloro substituted ligand **4.59** did not undergo complete ligand exchange, instead forming an intractable mixture of partially exchanged products. It is likely that this ligand is simply too sterically hindered to give a complete reaction. The employment of alternate conditions at higher temperature (refluxing an excess of the ligand in toluene under a Soxhlet extractor using acetate as the rhodium precursor ligand instead of carbonate) did not solve this problem.

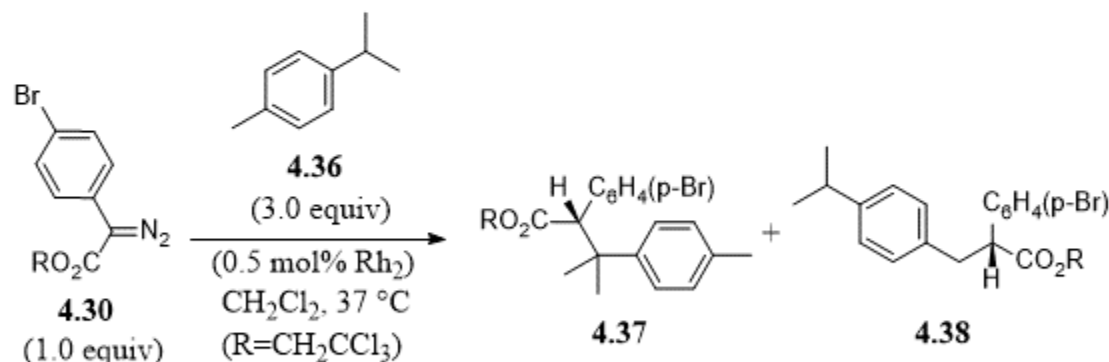
4.2.4 Evaluation of TMS-DPCP Catalysts

The **2-TMS-DPCP** catalysts **4.6-4.9** were evaluated for site- and stereoselectivity in reactions with 4-ethyltoluene (**4.33**) and 4-isopropyltoluene (**4.36**) in the same manner as the cyclohexyl-DPCP catalysts **4.4** and **4.5**. The results of the catalyst screen are shown in Table 4.2.3.



Catalyst	Yield	1°:2°	dr (2°)	ee (1°)
$\text{Rh}_2(\text{S-TPCP})_4$ (4.15)	91%	81:19	71:29	92%
$\text{Rh}_2[(1R,2R)\text{-2-TMS-DPCP}]_4$ (4.6)	77%	74:26	78:22	79%
$\text{Rh}_2[(1R,2R)\text{-2-TMS-}p\text{-Br-DPCP}]_4$ (4.7)	82%	87:13	85:15	94%
$\text{Rh}_2[(1R,2R)\text{-2-TMS-}p\text{-Ph-DPCP}]_4$ (4.8)	62%	83:17	84:16	90%
$\text{Rh}_2[(1R,2R)\text{-2-TMS-3,5-di-Br-DPCP}]_4$ (4.9)	94%	26:74	74:26	55%*

*This catalyst also showed 20% *ee* for the major diastereomer of **4.35**.



Catalyst	Yield	rr (1°:3°)	ee (1°)	ee (3°)
$\text{Rh}_2(\text{S-TPCP})_4$ (4.15)	85%	>95:5	93%	---
$\text{Rh}_2[(1R,2R)\text{-2-TMS-DPCP}]_4$ (4.6)	81%	>95:5	73%	---
$\text{Rh}_2[(1R,2R)\text{-2-TMS-}p\text{-Br-DPCP}]_4$ (4.7)	95%	>95:5	94%	---
$\text{Rh}_2[(1R,2R)\text{-2-TMS-}p\text{-Ph-DPCP}]_4$ (4.8)	95%	>95:5	79%	---
$\text{Rh}_2[(1R,2R)\text{-2-TMS-3,5-di-Br-DPCP}]_4$ (4.9)	89%	71:29	37%	20%

Table 4.2.3: Evaluation of 2-TMS-DPCP catalysts in C-H functionalization reactions. The

(2*S*,3*S*)/(2*R*,3*R*) relative configuration of **4.35** was observed as the major diastereomer in every case.

The unsubstituted TMS-DPCP catalyst **4.6** behaves as though it were less hindered than the triarylcyclopropane catalyst $\text{Rh}_2(\text{S-TPCP})_4$ (**4.15**), demonstrating consistently lower primary site selectivity and *ee*. However, like the cyclohexyl-functionalized catalysts **4.4** and **4.5**, these values were still vastly higher than what was observed for $\text{Rh}_2[(1R,2S)\text{-DPCP}]_4$ (**4.14**), the analogous catalyst without the trimethylsilyl group. It was also observed that placement of a *p*-bromo or *p*-phenyl substituent on the C1 aryl group caused a substantial increase in the primary site selectivity of the catalyst. This effect mirrors the dirhodium triarylcyclopropanecarboxylates, which exhibit a similar effect when substituents are placed at the *para* position (see section 2.1).^{5,8} The most selective catalyst in the series was compound **4.7**, which showed higher *ee* and primary site selectivity than $\text{Rh}_2(\text{S-TPCP})_4$ (**4.15**) for both C-H functionalization reactions.

The *meta*-disubstituted catalyst $\text{Rh}_2[(1R,2R)\text{-2-TMS-3,5-di-Br-DPCP}]_4$ (**4.9**) also mirrors the triarylcyclopropanecarboxylates, showing a substantially greater propensity to react at the secondary C-H site of **4.33** relative to the other catalysts. The triaryl counterpart to this catalyst is $\text{Rh}_2[(S)\text{-3,5-di-Br-TPCP}]_4$ (**4.13**),⁶ which favors the C2 position of *n*-pentane over the primary site by a substantial margin.⁶ Unfortunately, the best triarylcyclopropane catalysts for performing C-H insertion reactions at secondary sites place biphenyl substituents at the *meta* positions of the C1 aryl group, and **2-TMS-DPCP** ligands with such extended functionality are too bulky to form tetracarboxylate complexes via substitution. Multiple attempts were made to perform metal-catalyzed cross-coupling reactions on the aryl bromide groups of catalysts **4.7** and **4.9**, but none were successful. In most cases, loss of the TMS group was observed in these reactions.

Based on the above observations, the trimethylsilyl group appears to be an effective surrogate for the 2-phenyl substituent. Compounds **4.30** and **4.34** can be formed in higher regioselectivity and *ee* with the silyl catalyst **4.7** than with the TPCP catalyst **4.28**. The silyl catalysts also

showed an analogous change in site selectivity when the C1 aryl group was adjusted to match established $\text{Rh}_2(\text{TPCP})_4$ catalysts. The new catalysts were subjected to additional testing to determine whether they were comparably effective for other reactions - or whether they might display a novel type of site selectivity when challenged with more complex substrates.

4.2.5 C-H Insertion Reactions with $\text{Rh}_2(2\text{-TMS-DPCP})_4$ Catalysts

The *para*-functionalized trimethylsilyl cyclopropane catalysts **4.11** and **4.8** (Figure 4.2.2) perform well with simple benzylic substrates such as **4.33** and **4.36**, but to confirm that they are also practically useful in synthesis it was desirable to test them with complex substances having multiple types of C-H sites. The results of these experiments are summarized in Scheme 4.2.6.

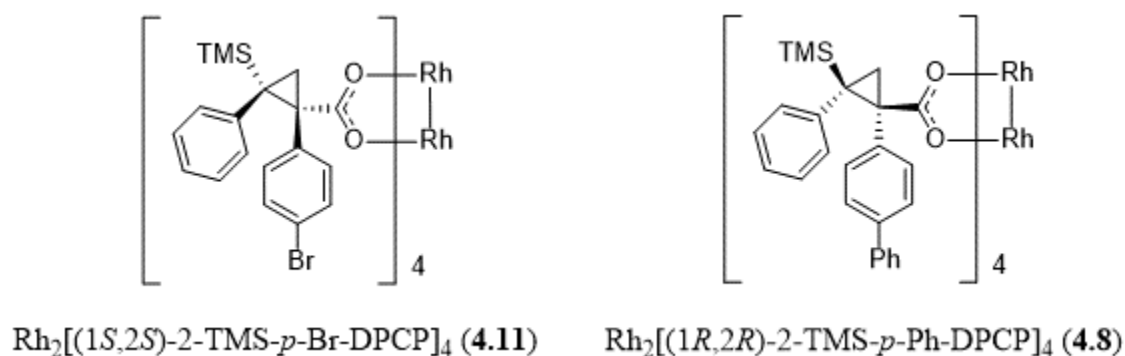
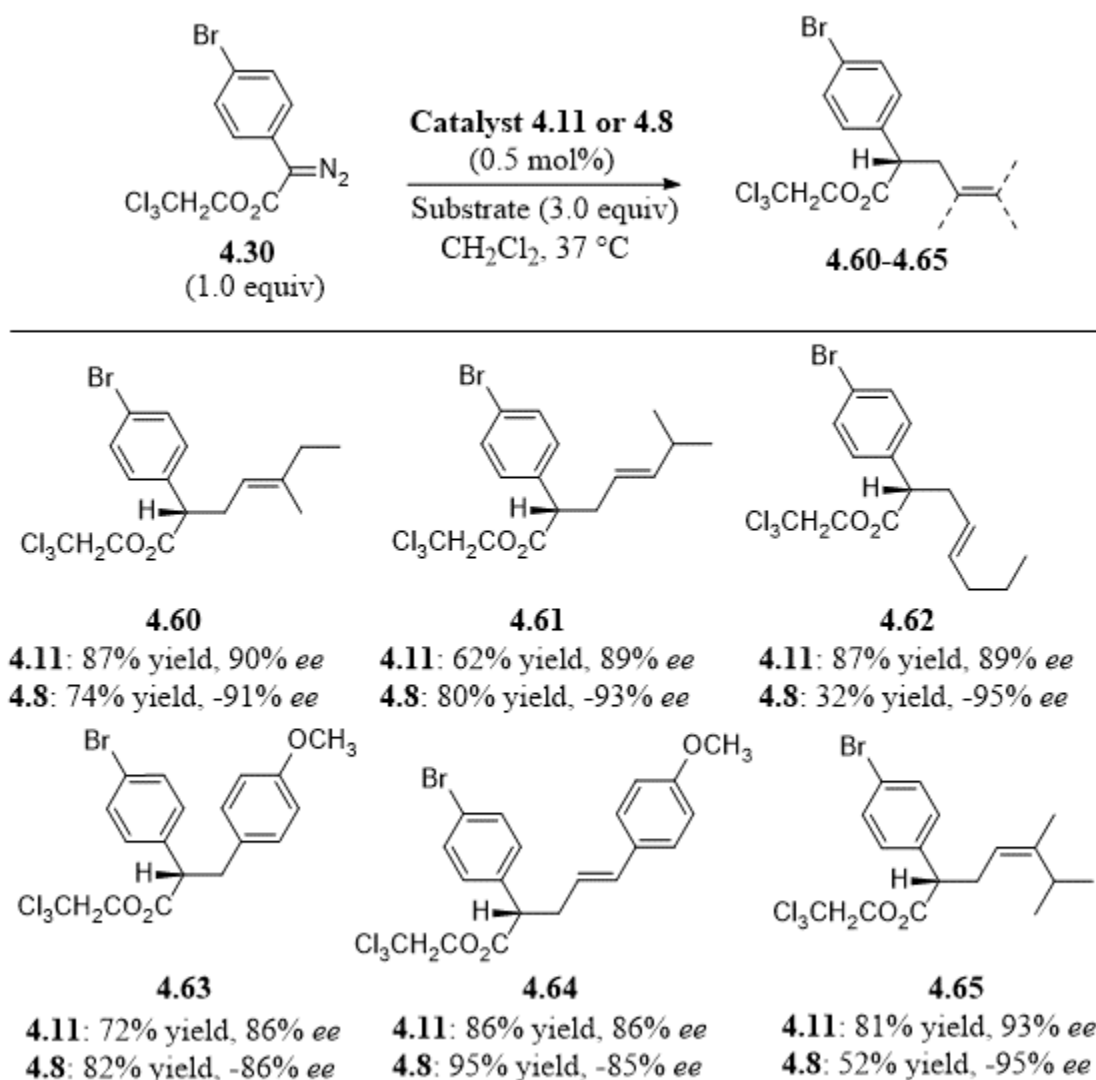


Figure 4.2.2: Catalysts **4.11** and **4.8** were examined in reactions with other C-H substrates.



Scheme 4.2.6: Primary site-selective C-H insertion reactions using catalysts **4.11** and **4.8**. The reaction to form compound **4.62** also generated a small amount of secondary insertion products (Catalyst **4.11**, 11%; Catalyst **4.8**, 20%).

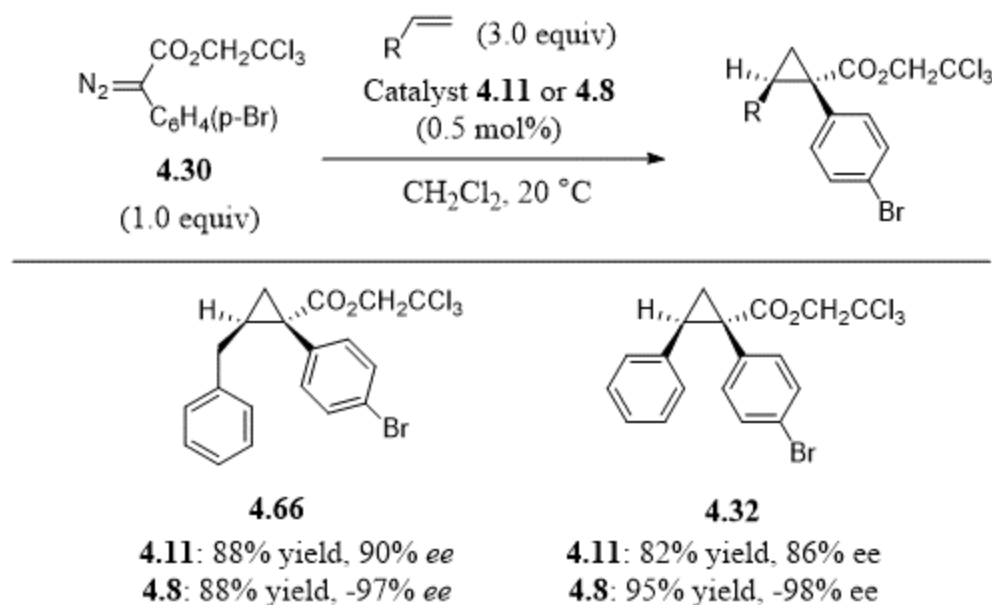
The catalysts **4.11** and **4.8** proved to be highly selective for sterically accessible primary allylic or benzylic sites in these reactions. A regioisomeric ratio of >95:5 was observed for all of the entries except the reaction to form product **4.60**, which also showed a small amount of C-H insertion into the secondary positions of the alkene (11% for catalyst **4.11** and 20% for catalyst **4.8**). Both catalysts showed consistently high enantioselectivity in these reactions, in many cases

over 90% *ee*. The *para*-bromo catalyst **4.11** often outperformed the phenyl-substituted catalyst **4.8**, but for products **4.61** and **4.63**, the phenyl-substituted catalyst proved superior. The low isolated yield observed for compound **4.62** with catalyst **4.8** is likely attributable to impurities in the alkene starting material used in that specific reaction. It is also worth noting that during the course of preparing the racemic standard for compound **4.65**, it was observed the catalyst $\text{Rh}_2[(R/S)\text{-}p\text{-PhTPCP}]_4$ (a 1:1 mixture of **4.12** and **4.20**) fails to generate a significant yield in this reaction.

Currently, there are few established catalysts that are capable of consistently achieving both high primary site selectivity and enantioselectivity in carbene C-H insertion reactions. While the triarylcyclopropanecarboxylates $\text{Rh}_2(\text{S-}p\text{-PhTPCP})_4$ (**4.12**) and $\text{Rh}_2(\text{R-}p\text{-BrTPCP})_4$ (**4.10**) are quite versatile, they do not perform optimally for every reaction. Thus, the addition of $\text{Rh}_2(\text{2-TMS-DPCP})_4$ to the “toolbox” of dirhodium tetracarboxylate catalysts may prove useful for the optimization of reactions at primary C-H sites.

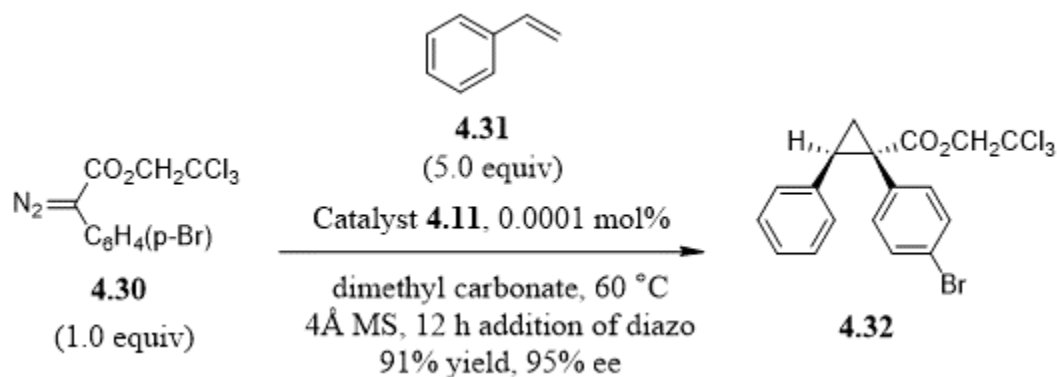
4.2.6 Cyclopropanation Using the $\text{Rh}_2(\text{2-TMS-DPCP})_4$ Catalysts

Sterically demanding dirhodium tetracarboxylate catalysts such as $\text{Rh}_2(\text{S-}p\text{-PhTPCP})_4$ (**4.12**) may show very high enantioselectivity in asymmetric cyclopropanation reactions.²⁰ Having established that the silyl-cyclopropanecarboxylates $\text{Rh}_2[(1S,2S)\text{-2-TMS-}p\text{-BrDPCP}]_4$ (**4.11**) and $\text{Rh}_2[(1R,2R)\text{-2-TMS-}p\text{-PhDPCP}]_4$ (**4.8**) behave as sterically demanding catalysts in the C-H insertion reactions of aryldiazoacetates, it was also of interest to evaluate them as catalysts for asymmetric cyclopropanation. The reactions of the new catalysts with styrenes in DCM at 20 °C are shown in Scheme 4.2.7.



Scheme 4.2.7: Cyclopropanation of styrenes with the novel silyl-DPCP catalysts.

Under standard conditions in DCM, $\text{Rh}_2[(1R,2R)\text{-2-TMS-}p\text{-PhDPCP}]_4$ (**4.8**) performed optimally, showing excellent yield and enantioselectivity for the *E*-cyclopropanes **4.66** and **4.32**. Recent work by Davies, et al.²⁰ has established that reactions using $\text{Rh}_2(\text{S-}p\text{-PhTPCP})_4$ (**4.12**) may demonstrate exceptionally high enantioselectivity when dimethyl carbonate is used as a solvent at elevated temperatures, and that these reactions may occur with high enantioselectivity even at very low loadings of the dirhodium catalyst (to 0.001 mol% loading). To evaluate the performance of the silyl dirhodium catalyst **4.11** under high turnover conditions, a reaction was conducted in dimethyl carbonate at 60°C . To limit thermal decomposition of the diazo compound **4.30**,²¹ it was added to the reaction mixture as a solution over 12 h using a syringe pump (Scheme 4.2.8, work performed with Bo Wei).



Scheme 4.2.8: Cyclopropanation at very high TON using catalyst **4.57** in dimethyl carbonate.

In this reaction, cyclopropane **4.32** is formed in 91% yield and 95% *ee* at a catalyst loading of only 0.0001 mol%. At present time, it is not certain whether the exceptional performance of this catalyst at low loading is simply due to a higher turnover frequency (outcompeting thermal decomposition of the diazo) or a structural feature of $\text{Rh}_2[(1S,2S)\text{-}2\text{-TMS-}p\text{-BrTPCP}]_4$ (**4.11**) which limits catalyst deactivation. Additional work examining the cyclopropanation reactions of catalysts $\text{Rh}_2[(1S,2S)\text{-}2\text{-TMS-}p\text{-BrTPCP}]_4$ (**4.11**) and $\text{Rh}_2[(1R,2R)\text{-}2\text{-TMS-}p\text{-PhDPCP}]_4$ (**4.8**) is currently ongoing in the Davies group.

4.2.7 Structure of Trimethylsilyl-DPCP Catalysts

Single crystals of the trimethylsilyl catalysts **4.6**, **4.7**, and **4.8** were grown from hexanes solvent, and the solid state geometries were determined using X-ray crystallography. The structure of the catalyst $\text{Rh}_2[(1R,2R)\text{-2-TMS-DPCP}]_4$ (**4.6**) is shown in Figure 4.2.3.

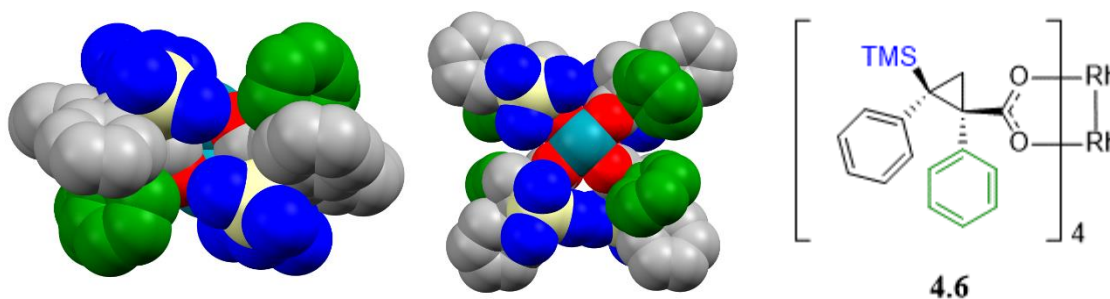


Figure 4.2.3: The solid state structure of catalyst **4.6** observed by X-ray diffraction. Solvent molecules have been omitted for clarity. Solved by Dr. John Bacsá, Emory University.

This compound is intriguing because it represents the first dirhodium cyclopropanecarboxylate to crystallize in the $(\alpha,\alpha,\beta,\beta)\text{-C}_2$ ligand orientation. While low-lying geometries with this shape have been observed computationally for catalysts such as $\text{Rh}_2[(1R,2S)\text{-DPCP}]_4$ (**4.27**)⁹ (see section 2.2), no other dirhodium cyclopropanecarboxylate catalyst prepared in the Davies lab has previously displayed this orientation in the X-ray structure. However, this type of ligand orientation is adopted by other types of dirhodium catalyst such as with the dirhodium phthalimido-amino acid catalyst $\text{Rh}_2(S\text{-PTPA})_4$ (**4.67**) (Figure 4.2.4.).²² Catalyst **4.67** may show high enantioselectivity in some circumstances,²³ but it is not usually as selective as catalysts with larger side chain groups such as $\text{Rh}_2(R\text{-PTAD})_4$ (**4.40**), which crystallizes in a “chiral crown” $(\alpha,\alpha,\alpha,\alpha)\text{-C}_2$ conformation.²⁴

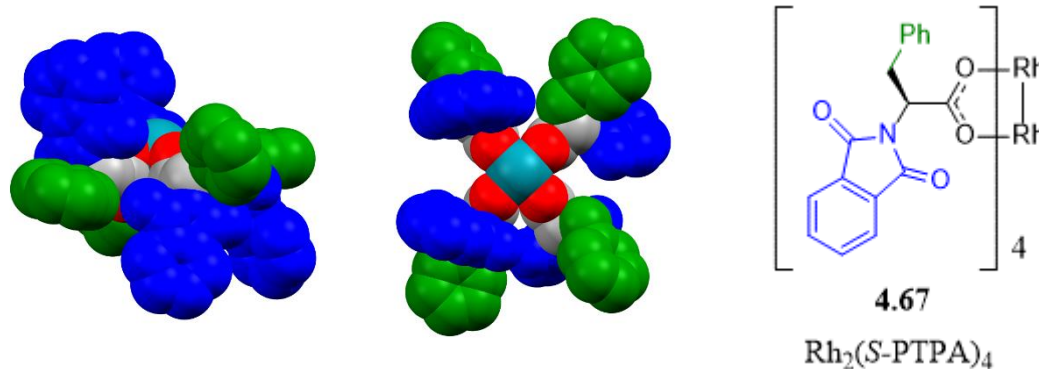


Figure 4.2.4: The crystal structure of $\text{Rh}_2(\text{S-PTPA})_4$ (**4.67**)²². Solvent molecules have been hidden for clarity. This structure also displays an $(\alpha,\alpha,\beta,\beta)$ - C_2 geometry, although the catalyst is less crowded at rhodium than entry **4.6** (X-Ray coordinates obtained from Reference 22).

The silyl-substituted cyclopropanes **4.11** and **4.8** displayed ligand orientations very similar to their triaryl cyclopropane counterparts in the solid state. Both catalyst **4.11** and $\text{Rh}_2(R\text{-}p\text{-BrTPCP})_4$ (**4.10**)¹⁵ exhibit an $(\alpha,\beta,\alpha,\beta)$ - D_2 geometry, while catalyst **4.8** and $\text{Rh}_2(\text{S-}p\text{-PhTPCP})_4$ (**4.12**)⁸ are $(\alpha,\alpha'\alpha,\alpha')$ - C_2 shaped (Figure 4.2.5).

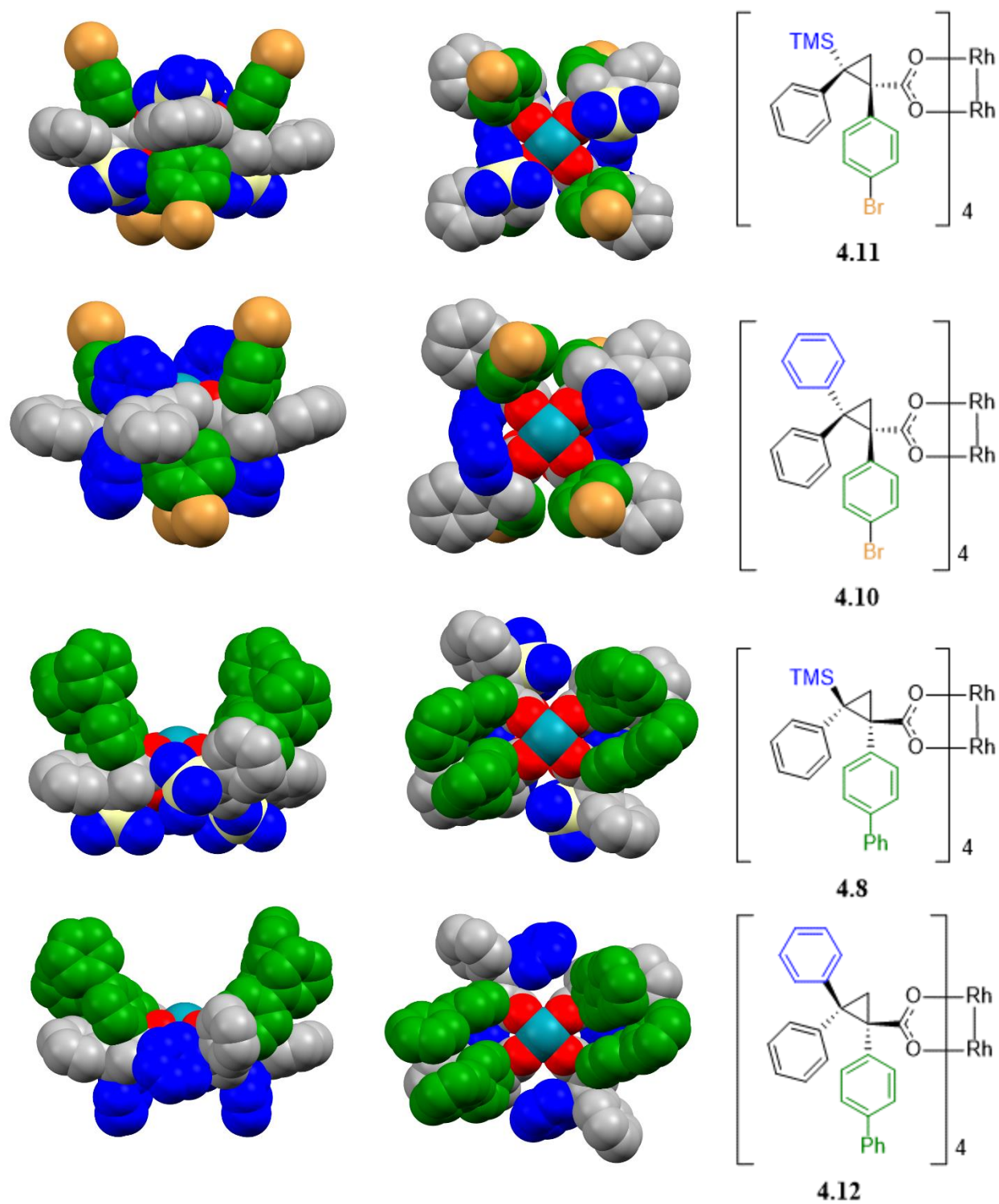


Figure 4.2.5: Comparison of the crystal structures of 2-TMS-DPCP versus TPCP catalysts.

All crystal structures were solved by Dr. John Bacsa.

To determine whether this trend was also relevant to the solution phase geometry of the trimethylsilyl cyclopropane catalysts, they were studied using density functional theory calculations. These were performed by Dr. Zhi Ren and Prof. Djamaladdin G. Musaev at the Cherry L. Emerson Center for Scientific Computation. The results of this study (Figures 4.2.6 and 4.2.7) revealed that like the analogous triarylcyclopropanecarboxylate catalysts **4.15** and **4.12**,⁵ the unsubstituted and *para*-phenyl substituted 2-trimethylsilyl cyclopropanecarboxylate catalysts **4.6** and **4.8** both prefer to adopt an ($\alpha,\alpha'\alpha,\alpha'$)-C₂ geometry.²⁵

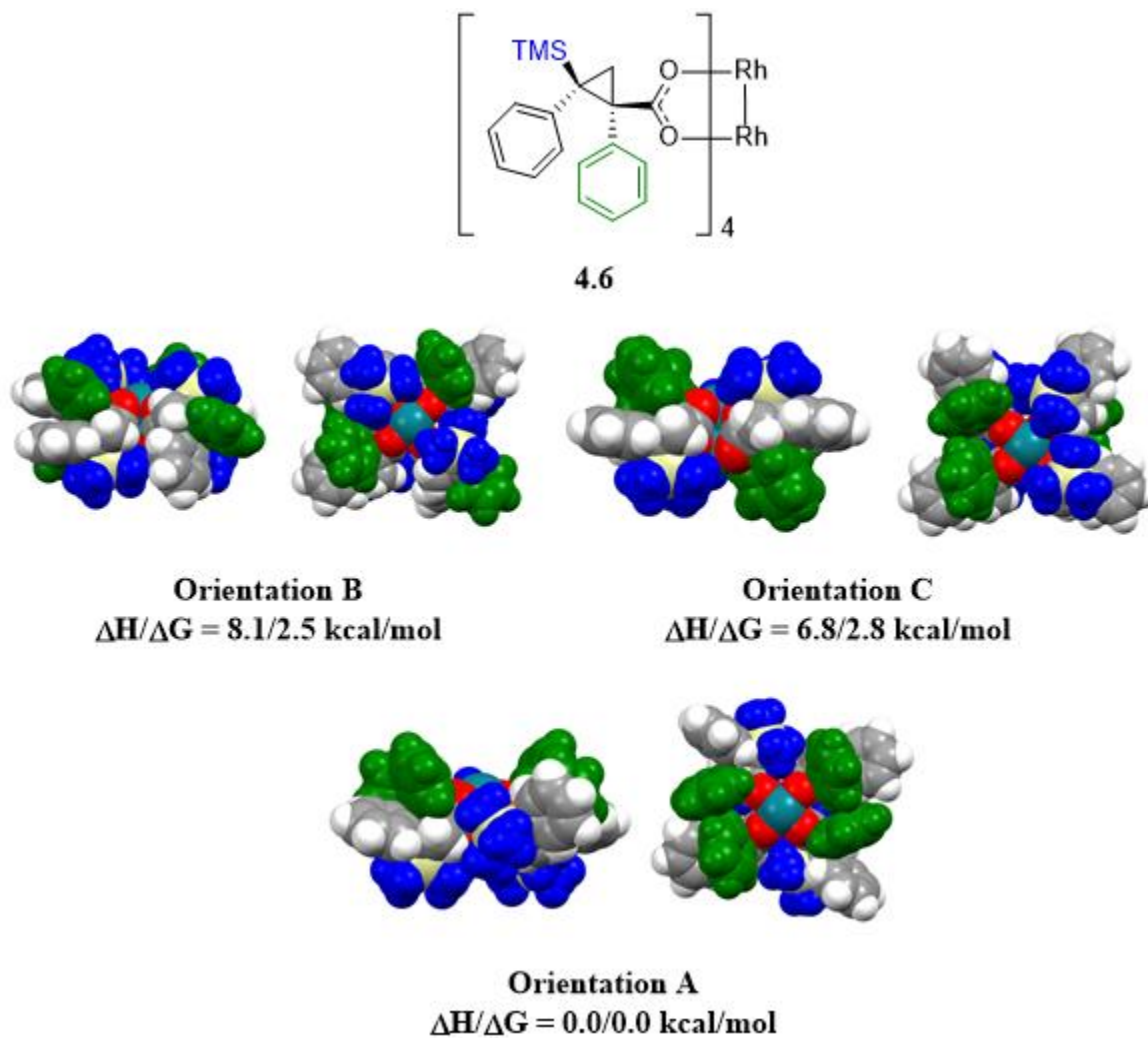


Figure 4.2.6: Computed minimum energy conformations of catalyst **4.6**. Calculation performed

by Dr. Zhi Ren and Dr. Djamaladdin G. Musaev.²⁵

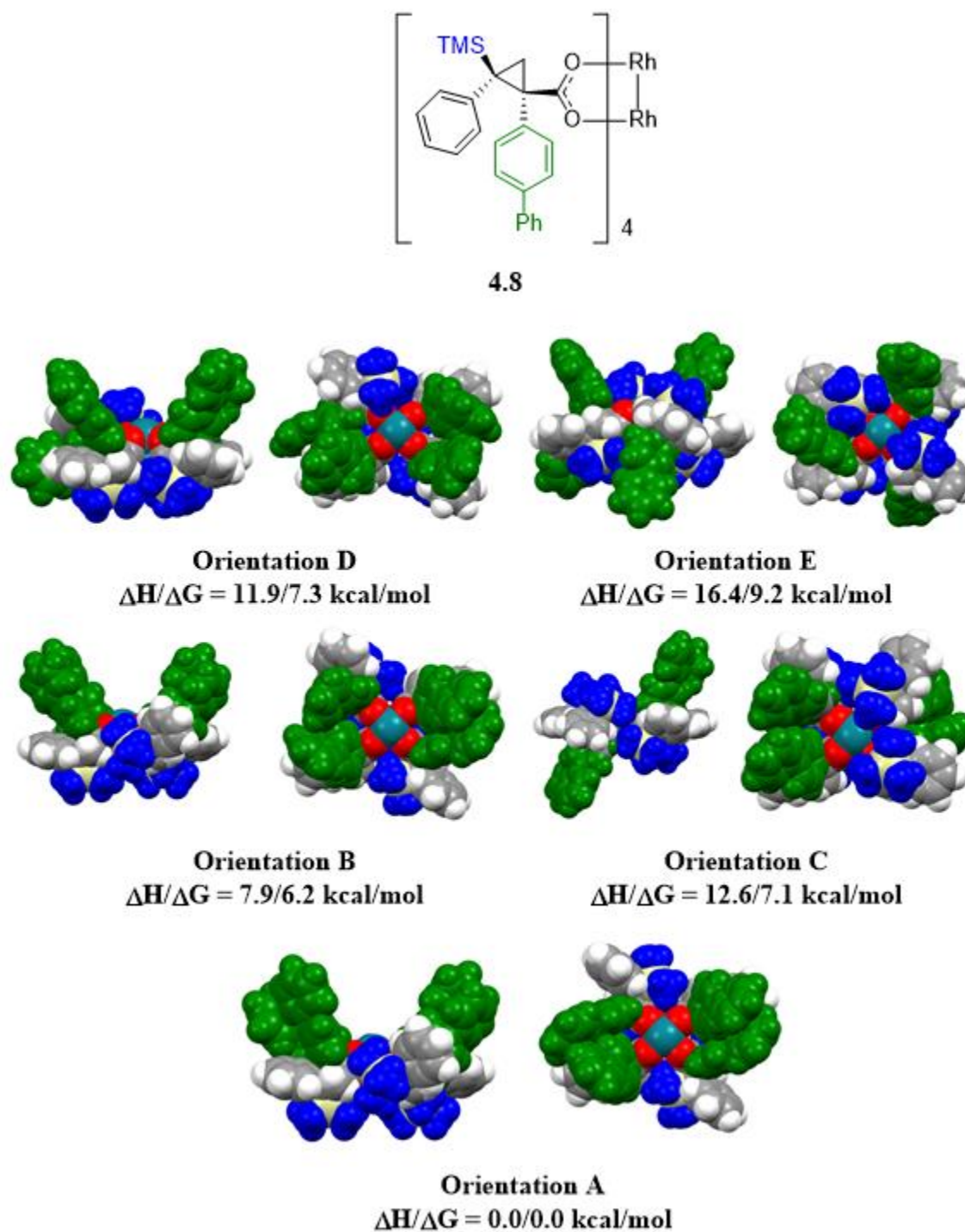


Figure 4.2.7: Computed minimum energy conformations of catalyst **4.8**. Calculation performed

by Dr. Zhi Ren and Dr. Djamaladdin G. Musaev.²⁵

4.3 Conclusion

The work presented in this chapter illustrates that dirhodium cyclopropanecarboxylate catalysts with two aryl substituents and one sp^3 -hybridized substituent may be proficient for the site- and stereoselective functionalization of C-H bonds with donor/acceptor carbenes. While the synthesis of the cyclohexyl-substituted catalysts was challenging due to the low diastereoselectivity of the cyclopropanation reaction used to prepare them, a variety of *Z*-trimethylsilyl cyclopropanecarboxylate ligands can be rapidly synthesized with high yield and *ee*. In most cases, the regio- and stereoselectivity properties of the cyclohexyl and silyl-functionalized catalysts mirrored their triarylcyclopropanecarboxylate counterparts. The structures of the silyl catalysts were also highly similar to their triarylcyclopropanecarboxylate analogs, as evidenced by X-ray diffraction data and minimum-energy orientations in the DFT studies. Based on these results, future investigators of the dirhodium cyclopropanecarboxylate catalyst scaffold would be reasonable to propose designs that place other types of sp^3 -hybridized substituents onto the cyclopropane ring. However, the classification of the catalyst (in terms of its orientation or preferred type of C-H site) is unlikely to change by simply replacing an aryl substituent with a comparably-sized sp^3 group.

4.4 References

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Experimental Sections

S.1 General Methods

Reagents were used as received from commercial suppliers unless otherwise stated. Styrene was filtered through a plug of silica gel before use. All glassware was oven-dried prior to use and all reactions were performed under an inert gas (argon or nitrogen) unless otherwise stated. Dichloromethane, toluene, hexane, pentane, and di-ethyl ether solvents were obtained from drying columns (Grubbs type solvent purifier) immediately prior to use. Preparative flash chromatography was performed on a Biotage MPLC system using SiliCycle SilaFlash P60 silica (normal phase, 60 Å, 40-63 µm.) ^1H NMR spectra were recorded on Varian Nuclear Magnetic Resonance spectrometers at 600, 500, 400 or 300 MHz. ^{13}C NMR spectra were recorded at 150, 100 or 75 MHz and ^{13}C NMR spectra were obtained with complete proton decoupling. High resolution mass spectra were recorded on a Finnigan LTQ FTMS. Melting points were measured on a MEL-TEMP electrothermal apparatus and are uncorrected. FTIR spectra were collected on a Nicolet iS10 from Thermo Scientific. Optical rotations were measured on a PerkinElmer Model 341 Polarimeter. Chiral HPLC analyses using standard pressure columns were performed on Varian Prostar 210, Agilent 1100, or Agilent 1290 Infinity II instruments. UHPLC analyses were performed on the Agilent 1290 Infinity II instrument. A corresponding racemic standard was run sequentially with every chiral analysis to verify the retention times of the major and minor enantiomers. These were prepared using either $\text{Rh}_2(\text{OOct})_4$, $\text{Rh}_2(\text{OAc})_4$, or a 1:1 mixture of both enantiomers of the indicated chiral catalyst. Absolute configurations for the C-H functionalization products are reported by analogy to reference 1.

S.2 Experimental Section for Chapter 2

S.2.1 List of Previously Reported Compounds

2,2,2-trichloroethyl 2-diazo-2-(3,5-dibromophenyl)acetate²

2,2,2-trichloroethyl 2-(2-bromophenyl)-2-diazoacetate²

2,2,2-trichloroethyl 2-diazo-2-phenylacetate³

2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate⁴

2,2,2-trichloroethyl (1*R*,2*S*)-1-(4-bromophenyl)-2-phenylcyclopropane-1-carboxylate⁵

Ethyl (1*R*,2*R*)-1,2-diphenyl-2-(trimethylsilyl)cyclopropane-1-carboxylate (**2.21**)⁶

Ethyl (1*R*,2*R*)-1,2-diphenylcyclopropane-1-carboxylate (**2.29**)⁶

(±)-2,2,2-trichloroethyl 2-(4-bromophenyl)-3-(*p*-tolyl)butanoate⁷

(±)-2,2,2-trichloroethyl 2-(4-bromophenyl)-3-(4-isopropylphenyl)propanoate⁷

(±)-2,2,2-trichloroethyl 2-(4-bromophenyl)-3-(4-ethylphenyl)propanoate⁸

(±) methyl 2-(4-bromophenyl)-3-methyl-3-(*p*-tolyl)butanoate⁸

Dirhodium tetrakis ((*S*)-1-([1,1'-biphenyl]-4-yl)-2,2-diphenylcyclopropane-1-carboxylate)

[Rh₂(*S-p*-PhTPCP)₄] (**2.19**)⁸

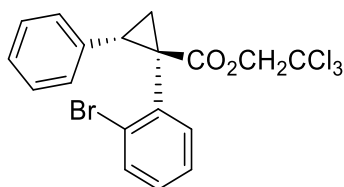
Dirhodium tetrakis[1-[[4-dodecylphenyl]sulfonyl](2*S*)-prolinate] Rh₂(*S*-DOSP)₄(**2.3**)⁹

Dirhodium tetrakis ((*S*)-1,2,2-triphenylcyclopropanecarboxylate) Rh₂(*S*-TPCP)₄ (**2.48**)¹⁰

Dirhodium tetrakis ((1*R*,2*S*)-1,2-diphenylcyclopropane-1-carboxylate) Rh₂(1*R*,2*S*)-DPCP)₄
(2.5)¹¹

Dirhodium tetrakis ((*R*)-2-(adamantanyl)-2-(1,3-dioxoisindolin-2-yl)acetate) Rh₂[(*R*)-PTAD]₄
(2.20)¹²

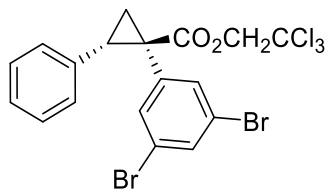
S.2.2 Synthesis of Cyclopropanecarboxylate Ligands



2,2,2-trichloroethyl (1R,2S)-1-(2-bromophenyl)-2-phenylcyclopropane-1-carboxylate (**2.24**)

A round bottom flask was charged with anhydrous pentane (60 mL) styrene (**2.1**, 10.6 g, 101 mmol, 5.0 equiv,) and $\text{Rh}_2(\text{R-PTAD})_4$ (**2.20**, 160 mg, 102 μmol , 0.5 mol%.) The flask was placed under an argon atmosphere, and then the mixture was cooled to 0 °C using an ice bath. 2,2,2-trichloroethyl 2-(2-bromophenyl)-2-diazoacetate (**2.11**, 7.6 g, 20 mmol, 1.0 equiv) dissolved in anhydrous pentane (100 mL) was introduced dropwise with stirring on. After the addition had completed, the mixture was stirred under argon for an additional 2 h 30 min. Then, volatiles were removed on a rotary evaporator, and the crude product was purified by flash column chromatography on normal phase silica gel (0-10% EtOAc / hexanes.) 5.8 g of the desired product **2.24** were obtained as a colorless oil (79% yield.) Chiral HPLC (OD-H, 1.0 mL / min, 0.5% i-PrOH / hexanes, $\lambda = 254 \text{ nm}$. rt 15.0 min (major) 21.0 (minor); 80% ee. $[\alpha]_{\text{D}}^{20} - 36.1^\circ$ (c 1.00, CHCl_3). IR (neat): 3089, 3064, 3034, 2952, 1735, 1238, 1154, 810, 745, 716, 695 cm^{-1} . The ^1H NMR and ^{13}C NMR spectra of this compound showed that this compound exists as a mixture of rotational isomers at room temperature. The signals converged when the spectra were collected at 85 °C. ^1H NMR (500 MHz, Toluene- d_8) δ 7.24 (d, $J = 7.9 \text{ Hz}$, 1H), 7.02 – 6.89 (m, 4H), 6.86 (t, $J = 7.8 \text{ Hz}$, 1H), 6.79 – 6.73 (m, 2H), 6.71 (td, $J = 7.7, 1.7 \text{ Hz}$, 1H), 4.61 (d, $J = 11.9 \text{ Hz}$, 1H), 4.52 (d, $J = 11.9 \text{ Hz}$, 1H), 3.47 (t, $J = 8.6 \text{ Hz}$, 1H), 2.33 – 2.20 (m, 1H), 1.85 (dd, $J = 7.6, 5.3 \text{ Hz}$, 1H). ^{13}C NMR (126 MHz, Toluene- d_8) δ 170.3, 135.6, 134.4, 133.5, 132.7, 128.6,

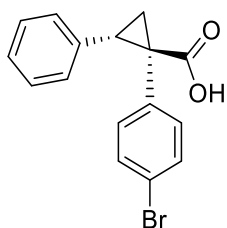
128.2, 128.1, 127.4, 126.5, 126.3, 95.2, 74.6, 38.3, 34.2, 22.4. HRMS (APCI) m/z : $[M+H]^+$ (Pos.) calcd for $C_{18}H_{15}O_2^{79}Br^{35}Cl_3$ 446.9316; found 446.9317. Further chiral purification was performed at the next step of the synthesis.



2,2,2-trichloroethyl (1R,2S)-1-(3,5-dibromophenyl)-2-phenylcyclopropane-1-carboxylate (2.23)

A round-bottom flask was charged with $Rh_2(S\text{-}p\text{-PhTPCP})_4$ (**2.15**, 50.0 mg, 28.3 μ mol, 0.5 mol%,) styrene (**2.1**, 2.95 g, 28.3 mmol, 5.0 equiv,) and anhydrous DCM (57 mL). A dropping funnel was attached to the flask, and the apparatus was purged with argon for 10 minutes. A solution of 2,2,2-trichloroethyl 2-diazo-2-(3,5-dibromophenyl)acetate (**2.11**, 2.55 g, 5.66 mmol, 1.0 equiv) in DCM (45 mL) was introduced dropwise over 2 h with moderate stirring at room temperature. The mixture was then concentrated in vacuo to afford 4.05 g of a thick green oil. The desired product was separated from the crude mixture by flash column chromatography on normal phase silica gel (50 g, 0-5% EtOAc / hexanes.) 2.52 g of 2,2,2-trichloroethyl (1R,2S)-1-(3,5-dibromophenyl)-2-phenyl-cyclopropane-1-carboxylate (**2.23**) were obtained as a colorless solid after drying under high vacuum (85% yield). mp 91.0-93.0 $^{\circ}C$ (from EtOAc). Chiral HPLC: OD-H column, 0.5 mL/min, 0.5 % iPrOH in hexanes, $\lambda = 230$ nm. rt 14.5 min (major) 18.3 min (minor); 89% ee. $[\alpha]_D^{20} +2.8^{\circ}$ ($c = 1.00$, $CHCl_3$). IR (solid): 3069, 3030, 2950, 1721, 1583, 1553, 1254, 1235, 1161, 1116, 721, 697 cm^{-1} ; 1H NMR (600 MHz, Chloroform- d) δ 7.41 (t, $J = 1.8$ Hz, 1H), 7.19 – 7.09 (m, 4H), 6.88 – 6.79 (m, 2H), 4.84 (d, $J = 11.9$ Hz, 1H), 4.61 (d, $J = 11.9$ Hz, 1H), 3.22 (dd, $J = 9.4, 7.5$ Hz, 1H), 2.26 (dd, $J = 9.4, 5.4$ Hz, 1H), 1.98 (dd, $J = 7.5,$

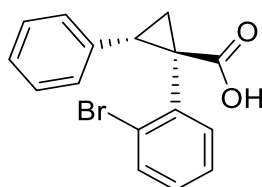
5.4 Hz, 1H). ^{13}C NMR (75 MHz, Chloroform- d) δ 170.9, 137.8, 134.5, 133.9, 133.0, 128.2, 128.1, 127.3, 121.9, 94.8, 74.5, 36.3, 34.3, 19.9. HRMS (APCI) $[\text{M}+\text{H}]^+$ (Pos.) calcd for $\text{C}_{18}\text{H}_{14}\text{O}_2^{79}\text{Br}^{35}\text{Cl}_3$ 524.8421; found 524.8424. Further chiral purification was performed at the next step of the synthesis.



(1R,2S)-1-(4-Bromophenyl)-2-phenylcyclopropane-1-carboxylic acid (2.26)

A 20 mL scintillation vial was charged with 2,2,2-trichloroethyl (1R,2S)-1-(4-bromophenyl)-2-phenylcyclopropane-1-carboxylate (**2.19**, 110 mg, 0.28 mmol, 1.00 equiv, obtained in 96% ee using $\text{Rh}_2(\text{S-}p\text{-PhTPCP})_4$ (**2.19**) as the catalyst), zinc dust (80.2 mg, 1.38 mmol, 5.00 equiv), and acetic acid (2.50 mL). The mixture was stirred at room temperature for 18 h. Then, it was partitioned between EtOAc/ H_2O . The aqueous phase was extracted with an additional portion of EtOAc, and then dried with MgSO_4 . The EtOAc solution was filtered and concentrated under vacuum to afford the crude product as a colorless solid. Further purification was achieved with flash column chromatography (10-50% Et $_2\text{O}$ /hexanes), which yielded 72 mg of the pure product **2.26** as a colorless solid (82% yield). A racemic precipitate crystallized from a hexanes solution of this material. It was filtered off to afford the enantiopure product as a colorless solid (41 mg, 57% recovery.) mp 72.5-75.0 °C. Chiral HPLC: AD-H, 1.0 mL/min, 5.0% i-PrOH / hexanes, $\lambda = 230$ nm. rt 10.0 min (minor) 11.4 min (major); >99% ee. $[\alpha]_D^{20} - 6.7^\circ$ ($c = 1.00$, CHCl_3 .) IR (solid): 3030, 2924, 2852, 2589, 1681, 1488, 1420, 1280, 1264, 1012, 907, 731, 711, 695 cm^{-1} . ^1H NMR (600 MHz, Benzene- d_6) δ 6.99 (d, $J = 8.1$ Hz, 2H), 6.81 – 6.71 (m, 3H), 6.53 (d, $J =$

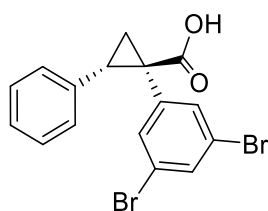
8.0 Hz, 2H), 6.43 (dd, $J = 7.0, 2.6$ Hz, 2H), 3.07 (t, $J = 8.3$ Hz, 1H), 1.92 (dd, $J = 9.3, 5.0$ Hz, 1H), 1.43 (dd, $J = 7.4, 5.0$ Hz, 1H). ^{13}C NMR (126 MHz, DMSO- d_6) δ 174.5, 136.6, 135.5, 134.3, 130.7, 128.5, 128.2, 126.7, 120.2, 37.0, 32.4, 19.0. HRMS (APCI) m/z : $[\text{M}+\text{H}]^+$ (Pos.) calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2^{79}\text{Br}$ 317.0172; found 317.0165.



(1R,2S)-1-(2-bromophenyl)-2-phenylcyclopropane-1-carboxylic acid (2.28)

To a round bottom flask was added: 2,2,2-trichloroethyl (1S,2R)-1-(2-bromophenyl)-2-phenylcyclopropane-1-carboxylate (**2.24**, 5.80 g, 12.9 mmol, 1.0 equiv), glacial acetic acid (100 mL) and zinc dust (4.2 g, 64.5 mmol, 5.0 equiv.) The mixture was stirred at room temperature for 4 days. Then, it was diluted with water (1 L) and extracted with three portions of EtOAc. The pooled organic phase was backwashed with DI water and then dried over MgSO_4 . The resulting filtrate liquid was concentrated in vacuo to afford a colorless solid. The product was purified by flash column chromatography on silica gel (Normal phase, 10-60% EtOAc / hexanes) affording 1.88 g of the desired product **2.28** as a colorless solid (46% yield.) To prepare the enantiopure product from this material (>99% ee,) it was recrystallized from EtOH/hexanes (recrystallization recovery 733 mg, 40%). mp 99-102 °C (from CH_2Cl_2). Chiral HPLC: AD-H, 1.0 mL/min, 1.0% i-PrOH / hexanes, $\lambda = 254$ nm. rt 47.9 min (major) 51.2 min (minor); >99% ee. $[\alpha]_D^{20} +56^\circ$ ($c = 0.29$, EtOH.) IR (solid): 3383, 2971, 2542, 1677, 1426, 1287, 1027, 973, 947, 763, 743, 695 cm^{-1} . The ^1H NMR and ^{13}C NMR spectra of this compound showed that this compound exists as a mixture of rotational isomers at room temperature. The signals converged when the spectra were collected at 85 °C. ^1H NMR (500 MHz, Toluene- d_8) δ 11.81 (s, 1H), 7.19 – 7.08 (m, 1H), 6.87 –

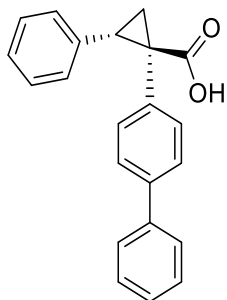
6.77 (m, 4H), 6.74 (s, 1H), 6.64 – 6.49 (m, 3H), 3.31 (s, 1H), 2.07 – 1.87 (m, 1H), 1.71 – 1.59 (m, 1H). ^{13}C NMR (126 MHz, Toluene- d_8) δ 178.32, 135.65, 134.64, 133.45, 132.72, 128.48, 128.18, 127.83, 127.30, 126.38, 126.18, 38.31, 34.27, 22.59. HRMS (APCI) m/z : $[\text{M}+\text{H}]^+$ (Pos.) calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2^{79}\text{Br}$ 317.0172; found 317.0171.



(1R,2S)-1-(3,5-dibromophenyl)-2-phenylcyclopropane-1-carboxylic acid (2.27)

2,2,2-Trichloroethyl (1R,2S)-1-(3,5-dibromophenyl)-2-phenylcyclopropane-1-carboxylate (**2.20**, 2.80 g, 5.3 mmol, 1.0 equiv) was treated with zinc dust (1.74 g, 26.5 mmol, 5.0 equiv) and acetic acid (44 mL). The mixture was stirred at room temperature for 18 h. Then, it was extracted with EtOAc (2x100 mL.) The organic phase was separated and dried over MgSO_4 . Filtration of the mixture and evaporation of solvent in vacuo afforded 1.96 g of (1R,2S)-1-(3,5-dibromophenyl)-2-phenylcyclopropane-1-carboxylic acid (**2.27**, 93% yield.) The product was enantioenriched by crystallization from EtOAc (recrystallization recovery 1.23 g, 70%). mp 218-219 °C (from EtOAc). Chiral HPLC: AD-H, 1.0 mL/min, 1.0% iPrOH in hexanes, $\lambda = 230$ nm. rt 21.4 min (major) 19.0 min (minor), >99% ee. $[\alpha]_D^{20} +12.6^\circ$ ($c = 0.387$, EtOH.) IR (solid): 3069, 3030, 2950, 1720, 1553, 1254, 1235, 811, 721, 697 cm^{-1} . ^1H NMR (600 MHz, DMSO- d_6) δ 12.70 (s, 1H), 7.49 (d, $J = 1.8$ Hz, 1H), 7.16 (d, $J = 1.8$ Hz, 2H), 7.08 (t, $J = 7.4$ Hz, 2H), 7.03 (t, $J = 7.2$ Hz, 1H), 6.93 – 6.86 (m, 2H), 3.02 (dd, $J = 9.1, 7.3$ Hz, 1H), 2.10 (dd, $J = 7.3, 5.3$ Hz, 1H), 1.87 (dd, $J = 9.1, 5.3$ Hz, 1H). ^{13}C NMR (151 MHz, DMSO- d_6) δ 173.8, 140.7, 136.1, 134.1, 132.1,

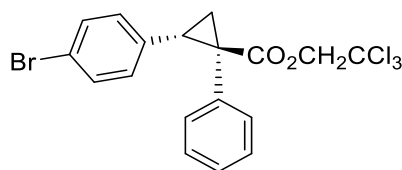
128.6, 128.2, 126.9, 121.6, 36.6, 32.7, 18.8. HRMS (APCI) m/z : $[M+H]^+$ (Pos.) calcd for $C_{16}H_{13}O_2^{79}Br_2$ 394.9277; found 394.9278.



(1R,2S)-1-([1,1'-Biphenyl]-4-yl)-2-phenylcyclopropane-1-carboxylic acid (2.43)

A round bottom flask was charged with phenylboronic acid (1.77 g, 14.5 mmol, 2.0 equiv,) RuPhos (**2.35**, 677 mg, 1.45 mmol, 0.20 equiv,) tribasic potassium phosphate (3.59 g, 16.9 mmol, 2.33 equiv,) and palladium(II) acetate (162.8 mg, 0.73 mmol, 0.10 equiv.) A reflux condenser was attached to the flask, and the apparatus was purged with argon as a solution of (1R,2S)-1-(4-bromophenyl)-2-phenylcyclopropane-1-carboxylic acid (**2.26**, 2.30 g, 7.25 mmol, 1.0 equiv,) in degassed 1,4-dioxane (21 mL) was introduced. The mixture was stirred at 100 °C for 16 h. After cooling to room temperature, the mixture was then passed through a plug of silica gel with 20% MeOH/DCM. The filtrate liquid was concentrated under vacuum, yielding 5.43 g of an orange solid. 1.51 g of the desired product (**2.43**) was obtained from this mixture after flash chromatography on silica (0-38% EtOAc/hexanes) as a colorless solid (67% yield.) An additional recrystallization from toluene was conducted at this stage (recrystallization recovery 1.34 g, 89%). mp 201.5-203.0 °C (from toluene). Chiral HPLC: AD-H, 0.5 mL/min, 5.0% i-PrOH / hexanes, $\lambda = 230$ nm. rt 25.7 min (minor) 29.7 min (major); >99% ee. $[\alpha]_D^{20} + 46^\circ$ (c = 0.287, EtOH.) IR (neat): 3215, 3031, 1680, 1488, 1418, 1286, 1263, 974, 758, 728 cm^{-1} . 1H NMR (500 MHz, DMSO- d_6) δ 12.49 (s, 1H), 7.57 (d, $J = 7.7$ Hz, 2H), 7.52 – 7.36 (m, 5H), 7.31

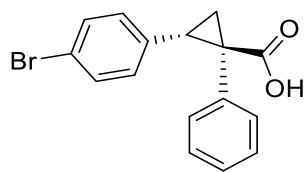
(q, $J = 8.0, 7.4$ Hz, 1H), 7.11 (d, $J = 8.0$ Hz, 2H), 7.04 (dt, $J = 15.5, 7.1$ Hz, 3H), 6.90 (d, $J = 7.5$ Hz, 2H), 3.14 – 3.00 (m, 1H), 2.04 (dd, $J = 7.3, 5.0$ Hz, 1H), 1.96 (dd, $J = 9.2, 4.9$ Hz, 1H). ^{13}C NMR (126 MHz, DMSO- d_6) δ 174.8, 140.1, 138.5, 137.0, 135.1, 132.7, 129.3, 128.6, 128.1, 127.7, 126.9, 126.6, 126.0, 37.2, 32.5, 19.3. HRMS (APCI) m/z : $[\text{M}+\text{H}]^+$ (Pos.) calcd for $\text{C}_{22}\text{H}_{19}\text{O}_2$ 315.1380; found 315.1377.



2,2,2-Trichloroethyl (1R,2S)-2-(4-bromophenyl)-1-phenylcyclopropane-1-carboxylate (2.22)

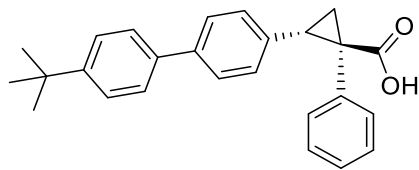
$\text{Rh}_2(\text{S-}p\text{-PhTPCP})_4$ (**2.19**, 53.6 mg, 30.4 μmol , 0.2 mol%) pentane (90 mL,) and 4-bromostyrene (7.79 g, 42.7 mmol, 2.8 equiv) were combined in a round bottom flask. The flask was cooled to 0 $^\circ\text{C}$ using an ice bath, and then a solution of 2,2,2-trichloroethyl 2-diazo-2-phenylacetate (**2.11**, 2.22 g, 15.2 mmol, 1.0 equiv,) in pentane (120 mL) was added dropwise via an addition funnel. After the addition had completed, the mixture was stirred for 1 h and then concentrated to a green oil in vacuo. The oil was subjected to flash column chromatography (2% EtOAc / hexanes,) affording the desired product **2.22** as a colorless solid (2.86 g, 86% yield) mp 68.0–69.0 $^\circ\text{C}$ (from CH_2Cl_2). Chiral HPLC: OD-H, 1.0 mL/min, 1.0% i-PrOH / hexanes, $\lambda = 230$ nm. rt 38.5 min (major) 71.7 min (minor); 95% ee. $[\alpha]_D^{20} - 15.2^\circ$ ($c = 1.00$, CHCl_3 .) IR (solid): 3086, 3031, 2950, 1739, 1492, 1239, 1151, 1050, 830, 808, 709, 701 cm^{-1} . ^1H NMR (600 MHz, Chloroform- d) δ 7.22 – 7.08 (m, 5H), 7.04 (dd, $J = 6.6, 3.0$ Hz, 2H), 6.63 (d, $J = 8.2$ Hz, 2H), 4.81 (d, $J = 11.9$ Hz, 1H), 4.62 (d, $J = 11.8$ Hz, 1H), 3.14 (dd, $J = 9.3, 7.3$ Hz, 1H), 2.26 (dd, $J = 9.3, 5.2$ Hz, 1H), 1.93 (dd, $J = 7.4, 5.2$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform- d) δ 171.8, 134.9, 133.2, 131.9, 130.9, 129.6, 127.9, 127.5, 120.5, 94.9, 74.4, 37.3, 33.1, 20.5. Further chiral

purification was performed during the next step of the synthesis. HRMS (APCI) m/z : $[M+H]^+$ (Pos.) calcd for $C_{18}H_{15}O_2^{79}Br^{35}Cl_3$ 446.9316; found 446.9317.



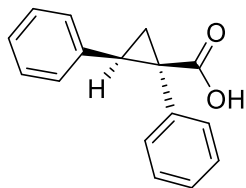
(1R,2S)-2-(4-bromophenyl)-1-phenylcyclopropane-1-carboxylic acid (2.25)

A round bottom flask was charged with 2,2,2-trichloroethyl (1R,2S)-2-(4-bromophenyl)-1-phenylcyclopropane-1-carboxylate (**2.22**, 2.30 g, 5.1 mmol, 1.0 equiv,) acetic acid (45 mL) and zinc dust (1.71 g, 25.5 mmol, 5.0 equiv.) The mixture was stirred at room temperature for 36 h. Then, the mixture was diluted with water (200 mL) and extracted with ethyl acetate (3x150 mL.) The pooled organic phase was backwashed with water (2x150 mL) and then dried with $MgSO_4$. The mixture was gravity filtered, and the filtrate liquid was concentrated under vacuum, affording 1.42 g of the title compound (**2.25**) as a colorless solid (87% yield). To prepare the enantiopure product from this material (>99% ee), it was recrystallized from 100% hexanes (recrystallization recovery 1.11 g, 78%). mp 232.0-232.5 °C (from CH_2Cl_2). Chiral HPLC: AS-H, 1.0 mL/min, 1.0% i-PrOH / hexanes, $\lambda = 230$ nm. rt 9.1 min (major) 19.8 min (minor); >99% ee. $[\alpha]_D^{20} - 43.5^\circ$ ($c = 1.00$, $CHCl_3$.) IR (solid): 3022, 2834, 2548, 1678, 1491, 1435, 1293, 710, 698 cm^{-1} . 1H NMR (600 MHz, Chloroform- d) δ 7.20 – 7.08 (m, 5H), 7.05 – 6.96 (m, 2H), 6.66 – 6.56 (m, 2H), 3.09 (dd, $J = 9.3, 7.4$ Hz, 1H), 2.18 (ddd, $J = 9.4, 5.1, 0.9$ Hz, 1H), 1.88 (dd, $J = 7.3, 5.1$ Hz, 1H). ^{13}C NMR (126 MHz, DMSO- d_6) δ 174.6, 136.7, 135.5, 132.1, 130.9, 130.6, 127.9, 127.1, 119.6, 37.6, 31.7, 19.3. HRMS (APCI) m/z : $[M+H]^+$ (Pos.) calcd for $C_{16}H_{14}O_2^{79}Br$ 317.0172; found 317.0171.



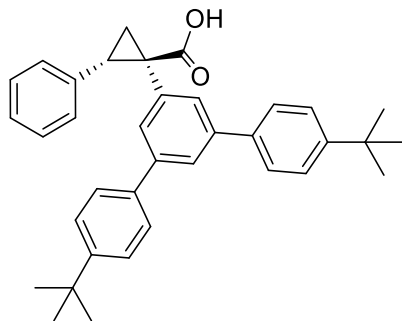
(1R,2S)-2-(4'-(tert-Butyl)-[1,1'-biphenyl]-4-yl)-1-phenylcyclopropane-1-carboxylic acid
(2.42)

To a round-bottom flask was added: (1R,2S)-2-(4-bromophenyl)-1-phenylcyclopropane-1-carboxylic acid (**2.22**, 200 mg, 0.63 mmol, 1.0 equiv,) (4-(tert-butyl)phenyl)boronic acid (**2.25**, 224.5 mg, 1.26 mmol, 2.0 equiv,) RuPhos (**2.38**, 58.8 mg, 0.12 mmol, 0.20 equiv,) palladium(II) acetate (14.2 mg, 63.0 μ mol, 0.10 equiv,) potassium phosphate tribasic (312 mg, 1.47 mmol, 2.33 equiv) and 1,4-dioxane (1.8 mL, pre-degassed with a 15 minute argon sparge.) The mixture was heated at 100 °C for 16 h, and then partitioned between EtOAc (50 mL) and 1 M aqueous HCl. The EtOAc extract was dried over MgSO₄. Filtration and concentration of the filtrate liquid afforded 437.2 mg of a green oil. The components of the oil were separated by flash column (0-5% CH₃OH/CH₂Cl₂), affording 191 mg of the desired product (**2.39**) as a colorless solid (82% yield.) mp 234-235 °C (from CH₂Cl₂). Chiral HPLC: AD-H, 0.5 mL/min, 5.0% i-PrOH / hexanes, λ = 230 nm. rt 21.5 min (minor) 25.8 min (major); >99% ee. $[\alpha]_D^{20} + 10^\circ$ (c = 1.00, EtOH.) IR (solid): 3055, 3031, 2962, 2926, 2866, 2588, 1678, 1280, 972, 817, 698 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ 7.45 – 7.36 (m, 4H), 7.29 (t, J = 7.3 Hz, 2H), 7.15 – 7.09 (m, 3H), 7.05 (dt, J = 7.0, 3.9 Hz, 2H), 6.79 (d, J = 8.0 Hz, 2H), 3.18 (dd, J = 9.3, 7.4 Hz, 1H), 2.21 (dd, J = 9.3, 5.0 Hz, 1H), 1.95 (dd, J = 7.5, 5.0 Hz, 1H), 1.30 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 180.4, 150.2, 139.0, 137.6, 134.8, 134.0, 132.0, 128.4, 128.1, 127.9, 127.4, 126.5, 126.2, 125.7, 37.4, 34.7, 34.5, 33.8, 31.4, 21.0. HRMS (APCI) m/z: [M+H]⁺ (Pos.) calcd for C₂₆H₂₇O₂ 371.2006; found 371.2002.



(1*R*,2*R*)-1,2-diphenylcyclopropane-1-carboxylic acid (**2.30**).

A 25 mL round bottom flask was charged with ethyl (1*R*,2*R*)-1,2-diphenylcyclopropane-1-carboxylate (**2.29**, 208 mg, 0.78 mmol, 1.0 equiv, prepared according to the method of Su, et al⁶) and dimethyl sulfoxide (10 mL). Stirring was turned on, and then solid potassium *t*-butoxide (193 mg, 1.72 mmol, 2.2 equiv) was added, which caused the mixture to turn dark green. After 53 h, the reaction was quenched by pouring into saturated aqueous NH₄Cl (excess.) The mixture was acidified to pH 1 via the addition of 4 M aqueous HCl solution, and then extracted with CH₂Cl₂ (2x100 mL.) The pooled organic phase was dried over Na₂SO₄, and then filtered. Concentration of the liquid phase in vacuo yielded the crude product as a green oil. The material was further purified by flash column chromatography (0-17% EtOAc/hexanes), yielding 136 mg of **2.30** as a colorless solid (73% yield.) Recrystallization from 100% hexanes afforded the enantiopure substance **2.27** (recrystallization recovery 99 mg, 73%). mp 98.0-99.5 °C (from hexanes). Chiral HPLC: AD-H, 1.0 mL/min, 5% i-PrOH / hexanes. rt 15.26 min (minor), 23.1 min (major). *ee* >99%. [α]_D²⁰ + 254.1 ° (c 1.98, EtOH). FTIR: 3027, 2955, 2921, 1689, 1497, 1448, 1418, 1308, 1223, 695 cm⁻¹. ¹H NMR (300 MHz, Methanol-d₄) δ 7.59 – 7.47 (m, 2H), 7.47 – 7.03 (m, 8H), 5.05 (s, 1H), 2.85 (t, *J* = 8.3 Hz, 1H), 2.28 (dd, *J* = 7.6, 4.8 Hz, 1H), 1.55 (dd, *J* = 9.0, 4.8 Hz, 1H). ¹³C NMR (75 MHz, Methanol-d₄) δ 173.0, 140.9, 136.7, 129.9, 128.9, 127.9, 127.7, 126.8, 126.3, 48.5, 48.3, 48.0, 47.7, 47.4, 47.1, 46.8, 38.0, 32.8, 17.6. HRMS (ESI) *m/z*: [M+H]⁺ (Pos.): calcd for C₁₆H₁₅O₂ 239.1067; found 239.1065.

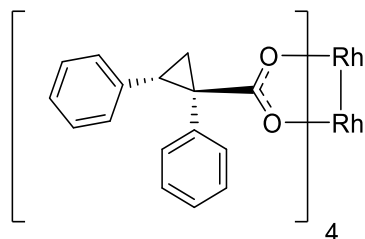


(1R,2S)-1-(4,4''-di-tert-butyl-[1,1':3,1''-terphenyl]-5'-yl)-2-phenylcyclopropane-1-carboxylic acid (2.31)

A 4 mL screw-cap vial was charged with (1R,2S)-1-(3,5-dibromophenyl)-2-phenylcyclopropane-1-carboxylic acid (**2.24**, 50 mg, 0.13 mmol, 1.0 equiv,) (4-(tert-butyl)phenyl)boronic acid (90 mg, 0.50 mmol, 4.0 equiv,) RuPhos (**2.38**, 11.8 mg, 25.2 μ mol, 0.20 equiv,) palladium(II) acetate (2.8 mg, 12.6 μ mol, 0.10 equiv,) and tribasic potassium phosphate (62.4 mg, 0.29 mmol, 2.33 equiv.) Degassed 1,4-dioxane was added (0.26 mL), and the vial was sealed with parafilm. The mixture was stirred vigorously at 100 °C for 16 h. Then, the vial was cooled to room temperature, and its contents were partitioned between 1 M aqueous HCl (50 mL) and EtOAc (50 mL.) The organic phase was separated and dried with Na₂SO₄. The solution was concentrated *in vacuo* after filtration, yielding 128.5 mg of a colorless oil. Chromatographic purification (12 g SiO₂, 0-25% EtOAc/hexanes) afforded 56.9 mg of the desired product **2.31** as a colorless solid (90% yield.) mp 161-164 °C (from CH₂Cl₂). Chiral HPLC: AD-H, 1.0 mL/min, 2.0% iPrOH/hexanes, λ = 230 nm. rt 22.3 min (major) 31.4 min (minor); 99% ee. $[\alpha]^{20}_{\text{D}} +22^{\circ}$ (c = 1.00, EtOH). IR (solid): 3029, 2960, 2902, 2866, 2543, 1682, 1362, 1269, 830, 695 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ 7.53 (s, 1H), 7.39 (d, J = 8.0 Hz, 4H), 7.29 (d, J = 8.0 Hz, 4H), 7.20 – 7.14 (m, 2H), 7.10 (d, J = 6.0 Hz, 3H), 6.89 – 6.81 (m, 2H), 3.21 (t, J = 8.3 Hz, 1H), 2.24 (dd, J = 9.2, 4.9 Hz, 1H), 2.00 (t, J = 6.3 Hz, 1H), 1.33 (s, 18H). ¹³C NMR (75 MHz, CDCl₃) δ 179.9,

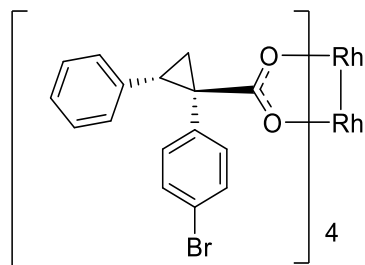
150.2, 140.9, 138.1, 136.1, 135.6, 134.8, 129.7, 128.3, 127.9, 126.8, 126.7, 125.8, 125.6, 124.9, 37.2, 34.5, 34.1, 31.4, 31.2, 20.7. HRMS (APCI) m/z : $[M+H]^+$ (Pos.) calcd for $C_{36}H_{39}O_2$ 503.2945; found 503.2945.

S.2.3 Preparation of Dirhodium Catalysts



Dirhodium tetrakis ((1*R*,2*S*)-1,2-diphenyl-cyclopropanecarboxylate) (2.5)

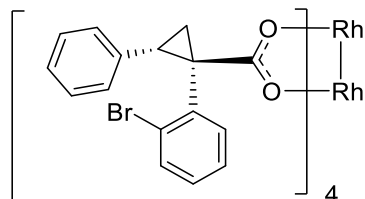
This compound was prepared as described in prior literature. An X-ray quality crystal of the material was grown by vapor diffusion with toluene/hexane. Analytical data for the sample were consistent with the previously reported data.¹² 1H NMR (400 MHz, Chloroform- d) δ 7.13 – 7.01 (m, 6H), 6.96 – 6.89 (m, 2H), 6.76 – 6.68 (m, 2H), 2.96 (dd, J = 9.2, 7.1 Hz, 1H), 2.04 (dd, J = 9.2, 4.8 Hz, 1H), 1.76 (dd, J = 7.2, 4.8 Hz, 1H).



Dirhodium tetrakis((1*R*,2*S*)-1-(4-bromo)phenyl-2-phenyl-cyclopropanecarboxylate) (2.45)

A 100 mL round bottom flask equipped with a magnetic stirbar and reflux condenser was charged with (1*R*,2*S*)-1-(4-bromophenyl)-2-phenylcyclopropane-1-carboxylic acid (**2.26**, 1.60 g,

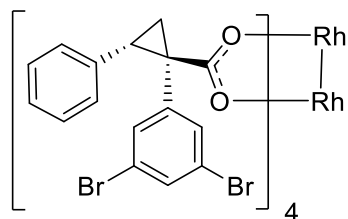
5.0 mmol, 8.0 equiv,) sodium rhodium carbonate 2.5 hydrate (**2.32**, 360 mg, 0.631 mmol, 1.0 equiv,) and water (35 mL.) The flask was purged with argon and heated to reflux. The reaction mixture stirred at reflux for 48 h, and then it was transferred to a separatory funnel and extracted with EtOAc (3x 35mL.) The combined organic layers were washed three times with saturated aqueous NaHCO₃ solution, followed by 10% aqueous NaOH (3x20 mL,) and then brine (20 mL.) The or-ganic extracts were dried with MgSO₄, filtered, and concentrated under vacuum. The resulting material was subjected to chromatographic purification (100:1 toluene/MeCN,) affording the desired product **2.45** as a green solid (755 mg, 81% yield.) mp 180-188 (dec.) ¹H NMR (500 MHz, Chloroform-d) δ 7.24 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 6.2 Hz, 3H), 6.84 – 6.65 (m, 4H), 2.92 (t, J = 8.2 Hz, 1H), 2.01 (dd, J = 9.3, 4.9 Hz, 1H), 1.79 – 1.67 (m, 1H). ¹³C NMR (126 MHz, Chloroform-d) δ 191.4, 136.2, 134.4, 133.3, 130.8, 128.0, 127.8, 126.6, 121.1, 38.9, 33.2, 19.7. IR (Solid): 3086, 3061, 3028, 2979, 1685, 1577, 1491, 1401, 1319, 1011, 774, 763 cm⁻¹. HRMS (ESI) m/z: [M+H]⁺ (Pos.) calcd for C₆₄H₄₈O₈Br₄Rh₂ 1465.8187; found 1465.8196.



Dirhodium tetrakis((1R,2S)-1-(2-bromophenyl)-2-phenylcyclopropanecarboxylate) (2.47**)**

A round bottom flask was charged with (1R,2S)-1-(2-bromophenyl)-2-phenylcyclopropane-1-carboxylic acid (**2.28**, 400 mg, 1.26 mmol, 8.0 equiv,) sodium rhodium carbonate 2.5 hydrate (**2.32**, 91.9 mg, 0.16 mmol, 1.0 equiv,) and degassed, deionized water (10 mL.) A condenser was attached to the flask, and the mixture was heated at reflux under argon for 3 days. Then, the mixture was poured directly into saturated aqueous NaHCO₃ solution (50 mL) and vigorously

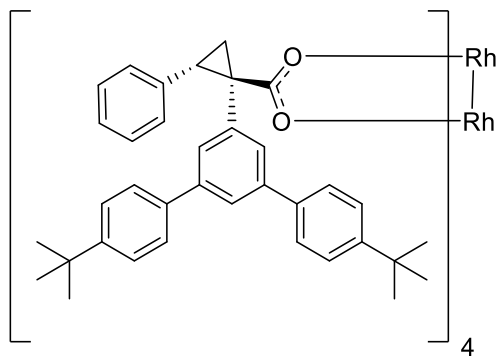
stirred for 30 minutes. After bubbling had ceased, the resulting mixture was frozen and lyophilized to dryness, affording a colorless to green solid. The solid was treated with dichloromethane (100 mL) and sonicated for 5 minutes. The resulting mixture was filtered using a fritted glass funnel, and the solid was extracted two additional times in the same manner. The pooled filtrate liquid afforded 268 mg of a green oil after concentration under vacuum. This material was then subjected to flash column chromatography (0-3% MeCN/toluene) affording 120.4 mg of the desired product **2.47** as a green solid after lyophilization from C₆H₆ (52% yield.) mp 247-250 °C (dec.) The NMR spectra of this compound showed a mixture of rotational isomers at room temperature. The NMR spectra were collected at 85 °C to resolve the signals. ¹H NMR (500 MHz, Toluene-d₈) δ 7.29 (s, 1H), 6.91 (dq, J = 13.8, 7.2 Hz, 4H), 6.80 (d, J = 7.4 Hz, 2H), 6.70 (t, J = 7.8 Hz, 1H), 3.40 (s, 1H), 1.93 (s, 1H), 1.64 (s, 1H). ¹³C NMR (126 MHz, Toluene-d₈) δ 189.5, 136.9, 133.4, 133.0, 129.4, 128.6, 128.5, 128.3, 127.8, 126.6, 126.5, 41.1, 33.7, 30.3, 22.4. IR (solid): 3061, 3030, 2955, 2923, 2853, 1586, 1398, 1321, 1025, 748 cm⁻¹. HRMS (ESI) m/z: [M+H]⁺ (Pos.) calcd for C₆₄H₄₈O₈Br₃⁸¹BrRh₂ 1467.8167; found 1467.8202.



**Dirhodium tetrakis((1*R*,2*S*)-1-(3,5-dibromophenyl)-2-phenylcyclopropanecarboxylate)
(**2.34**)**

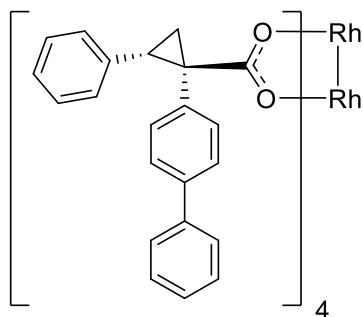
A round bottom flask was charged with (1*R*,2*S*)-1-(3,5-dibromophenyl)-2-phenylcyclopropane-1-carboxylic acid (**2.27**, 1.00 g, 2.52 mmol, 8.0 equiv,) sodium rhodium carbonate 2.5 hydrate (**2.32**, 184 mg, 0.320 mmol, 1.0 equiv,) and degassed, deionized water (20 mL.) The mixture was

heated at a bath temperature of 100 °C under an atmosphere of argon with moderate stirring. After 68 h, the mixture was cooled to room temperature and extracted with ethyl acetate (3x100 mL.) The pooled organic phase was washed with saturated aqueous NaHCO₃ solution (3x100 mL,) followed by 10% aqueous NaOH (3x100 mL,) and then brine (100 mL.) The organic phase was dried over Na₂SO₄, and then gravity filtered. The filtrate liquid was concentrated in vacuo, affording 991 mg of a dark green solid. Purification by flash column chromatography (0-10% EtOAc/hexanes) afforded 296 mg of the desired product **2.34** as a dark green solid (52% yield.) An X-ray quality crystal was grown by vapor diffusion from toluene/hexane containing trace acetonitrile. mp 205-210 (dec., from EtOAc). ¹H NMR (400 MHz, Chloroform-d) δ 7.41 (td, J = 1.8, 0.7 Hz, 1H), 7.17 – 7.07 (m, 3H), 6.98 (dd, J = 1.8, 0.8 Hz, 2H), 6.73 (dd, J = 6.7, 2.9 Hz, 2H), 3.05 – 2.92 (m, 1H), 2.02 (dd, J = 9.2, 5.1 Hz, 1H), 1.80 (dd, J = 7.3, 5.2 Hz, 1H) ¹³C NMR (100 MHz, Chloroform-d) δ 191.0, 139.2, 135.2, 133.4, 132.6, 128.1, 127.9, 126.9, 121.9, 38.5, 33.7, 29.7, 19.6. IR (solid): 3063, 3029, 2923, 2852, 1581, 1552, 1393, 1304, 741 cm⁻¹. HRMS (ESI) m/z: [M+H]⁺ (Pos.) calcd for C₆₄H₄₄O₈Br₆⁸¹Br₂Rh₂ 1781.4567; found 1781.4607.



Dirhodium tetrakis((1R,2S)-1-(3,5-di-(4-tert-butyl)phenyl)-2-phenylcyclopropanecarboxylate) (2.33)

A 4 mL screw-cap vial was charged with dirhodium tetrakis ((1*R*,2*S*)-1-(3,5-dibromophenyl)-2-phenylcyclopropane-carboxylate) (**2.34**, 38.2 mg, 21.4 μ mol, 1.0 equiv,) (4-*tert*-butyl)phenylboronic acid (**2.35**, 45.7 mg, 0.26 mmol, 12.0 equiv,) (R)-(-)-DTBM-SEGPHOS (**2.37**, 3.8 mg, 3.20 μ mol, 0.15 equiv,) palladium(II) acetate (0.5 mg, 2 μ mol, 0.1 equiv,) tribasic potassium phosphate (72.6 mg, 0.34 mmol, 16.0 equiv,) and degassed 1,4-dioxane (0.42 mL.) The vial was purged with argon before and during the addition of the solvent, and immediately sealed thereafter. Parafilm was used as a precaution to seal the mixture from atmospheric gases. The mixture was heated at 100 °C for 16 h. At the end of the heating period, it was dry-loaded onto silica gel and subjected to flash column chromatography (0-6% EtOAc/hex). 43.0 mg of the desired product **2.33** was obtained from the column as a green solid after drying under high vacuum (90% yield). mp 198-200 °C (dec., from EtOAc). ¹H NMR (300 MHz, CDCl₃) δ 7.52 (t, *J* = 1.7 Hz, 1H), 7.41 – 7.23 (m, 8H), 7.13 (d, *J* = 1.7 Hz, 2H), 7.11 – 6.99 (m, 3H), 6.82 – 6.66 (m, 2H), 2.94 (dd, *J* = 9.2, 7.1 Hz, 1H), 2.18 – 2.04 (m, 1H), 1.76 (dd, *J* = 7.1, 4.8 Hz, 1H), 1.32 (s, 15H). ¹³C NMR (75 MHz, CDCl₃) δ 191.6, 150.0, 140.6, 138.3, 137.0, 136.2, 129.6, 128.2, 127.8, 126.8, 126.1, 125.5, 124.3, 39.6, 34.4, 33.4, 31.3, 29.7. IR (Solid): 3087, 3054, 3029, 2960, 2927, 2903, 2866, 1580, 1399, 1362, 1269, 1114, 831 cm⁻¹. HRMS (ESI) *m/z*: [M+H]⁺ (Pos.) calcd for C₁₄₄H₁₄₈O₈Rh₂ 2210.9279; found 2210.9240.

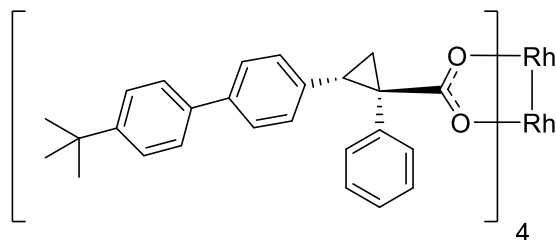


Dirhodium tetrakis((1R,2S)-1-([1,1'-biphenyl]-4-yl)-2-phenylcyclopropane-1-carboxylate)

(2.46)

(1R,2S)-1-([1,1'-biphenyl]-4-yl)-2-phenylcyclopropane-1-carboxylic acid (**2.43**, 1.0 g, 3.18 mmol, 8.0 equiv) and sodium rhodium carbonate 2.5 hydrate (**2.32**, 232 mg, 0.40 mmol, 1.0 equiv) were combined in a round bottom flask with degassed, deionized water (25 mL.) A reflux condenser was attached to the flask, and the mixture was heated at 100 °C for 2 days with moderate stirring. Then the mixture was poured into saturated aqueous NaHCO₃ solution (100 mL) and stirred for 30 minutes. After bubbling had ceased, the mixture was frozen and lyophilized to dryness, affording a faintly green solid. The solid was treated with toluene (120 mL) and sonicated for 5 minutes. The mixture was filtered, and the solid phase was extracted two additional times in the same manner. Concentration of the filtrate under high vacuum afforded 854 mg of dark green solid. The material was purified by flash column chromatography (0-1% MeCN/toluene.) 362 mg of compound **2.46** were obtained after lyophilization from C₆H₆ (45% yield.) mp 145-150 °C (dec.) ¹H NMR (600 MHz, CDCl₃) δ 7.49 – 7.42 (m, 2H), 7.38 – 7.33 (m, 2H), 7.33 – 7.26 (m, 3H), 7.09 – 7.00 (m, 3H), 7.00 – 6.94 (m, 2H), 6.77 (dd, J = 7.4, 2.2 Hz, 2H), 2.97 (dd, J = 9.3, 7.2 Hz, 1H), 2.09 (dd, J = 9.3, 4.8 Hz, 1H), 1.81 (dd, J = 7.2, 4.8 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 191.8, 140.8, 139.3, 137.0, 134.7, 132.2, 128.8, 128.1, 127.9, 127.2, 127.0, 126.4, 126.2, 39.4, 33.3, 20.0. IR (Solid): 3085, 3057, 3028, 2923, 2852, 1578,

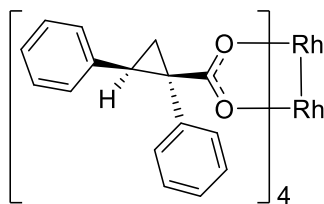
1497, 1487, 1397, 1321, 1094, 975, 761, 736 cm^{-1} . HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ (Pos.) calcd for $\text{C}_{88}\text{H}_{68}\text{O}_8\text{Rh}_2$ 1458.3019; found 1458.3054.



**Dirhodium tetrakis((1R,2S)-1-phenyl-2-(4-tert-butyl)phenyl-cyclopropanecarboxylate)
(2.44)**

A round bottom flask was charged with (1R,2S)-2-(4'-(tert-butyl)-[1,1'-biphenyl]-4-yl)-1-phenylcyclopropane-1-carboxylic acid (**2.42**, 130 mg, 0.35 mmol, 8.0 equiv,) sodium rhodium carbonate 2.5 hydrate (**2.32**, 25.6 mg, 44 μmol , 1.0 equiv,) and de-gassed, deionized water (2.76 mL.) The mixture was stirred at reflux under an argon atmosphere for 41 h. Then, the mixture was treated with saturated aqueous NaHCO_3 solution (100 mL) and the aqueous phase was lyophilized to dryness. The resulting salty green residue was extracted with 5% acetonitrile in toluene (3x50 mL.) The organic phase was filtered and concentrated to dryness in vacuo, affording 101 mg of a dark green oil. The oil was subjected to flash column chromatography (0-3% MeCN/toluene,) affording 34.3 mg of the desired product **2.44** as a green solid. (30% yield.) mp 100-110 $^{\circ}\text{C}$ (dec., from C_6H_6) ^1H NMR (300 MHz, Chloroform- d) δ 7.50 – 7.40 (m, 4H), 7.33 (d, J = 8.2 Hz, 2H), 7.15 – 7.08 (m, 3H), 7.03 – 6.94 (m, 2H), 6.78 (d, J = 8.2 Hz, 2H), 3.09 – 2.93 (m, 1H), 2.13 – 2.07 (m, 1H), 1.81 (dd, J = 7.1, 4.8 Hz, 1H), 1.38 – 1.33 (m, 9H). ^{13}C NMR (75 MHz, Chloroform- d) δ 191.7, 150.1, 138.5, 137.6, 135.9, 135.5, 131.8, 128.3, 127.7, 126.8, 126.4, 126.1, 125.6, 39.7, 34.5, 32.9, 31.4, 20.2. IR (solid): 3056, 3028, 2953, 2923, 2864,

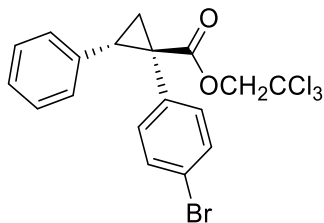
1581, 1499, 1395, 1321, 821 cm^{-1} . HRMS (ESI) m/z : $[M+H]^+$ (Pos.) calcd for $\text{C}_{104}\text{H}_{100}\text{O}_8\text{Rh}_2$ 1682.5523; found 1682.5556.



Dirhodium tetrakis ((1*R*,2*R*)-1,2-diphenylcyclopropane-1-carboxylic acid) (**2.9**)

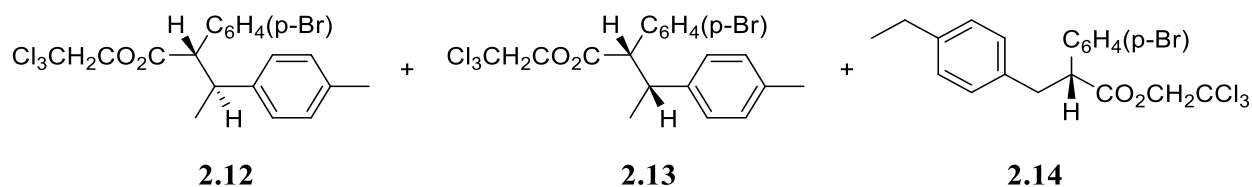
A 10 mL round bottom flask equipped with a reflux condenser was charged with a magnetic stirbar, (1*R*,2*R*)-1,2-diphenylcyclopropane-1-carboxylic acid (**2.30**, 99 mg, 0.42 mmol, 8.0 equiv,) sodium rhodium carbonate (**2.32**, 30.3 mg, 52.0 μmol , 1.0 equiv) and de-gassed, deionized water (3.3 mL.) The mixture was heated at a bath temperature of 100 $^{\circ}\text{C}$ for 4 d with vigorous stirring. At the end of the heating period, the mixture was partitioned between CH_2Cl_2 (100 mL) and saturated aqueous NaHCO_3 solution (100 mL.) The organic phase was separated and washed with 5 additional 25 mL aliquots of saturated NaHCO_3 solution. Then, the CH_2Cl_2 phase was dried over Na_2SO_4 and filtered. Concentration in vacuo afforded 58.3 mg of the crude product as a green residue. The desired product was separated from the mixture by flash column chromatography (24 g SiO_2 , 0-16% EtOAc / hexanes,) which afforded 45.7 mg of the desired product **2.9** as a green solid after lyophilization from C_6H_6 (76% yield.) mp 224.0-225.5 (dec.) ^1H NMR (399 MHz, CDCl_3) δ 7.33 – 7.19 (m, 6H), 7.14 – 7.07 (m, 2H), 7.01 (dd, J = 7.8, 1.7 Hz, 2H), 2.55 (t, J = 8.6 Hz, 1H), 1.72 (dd, J = 8.0, 4.7 Hz, 1H), 1.28 (dd, J = 9.3, 4.6 Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 188.6, 141.7, 136.4, 130.1, 129.2, 127.8, 127.7, 126.7, 126.2, 39.8, 34.1, 20.4. FTIR: 3057, 3026, 1578, 1494, 1401, 1244, 1030, 979, 770, 726, 694 cm^{-1} . HRMS (ESI) m/z : $[M+H]^+$ (Pos.) calcd for $\text{C}_{64}\text{H}_{52}\text{O}_8\text{NaRh}_2$ 1177.1665; found 1177.1685.

S.2.4 Evaluation of Dirhodium Catalysts, General Procedures



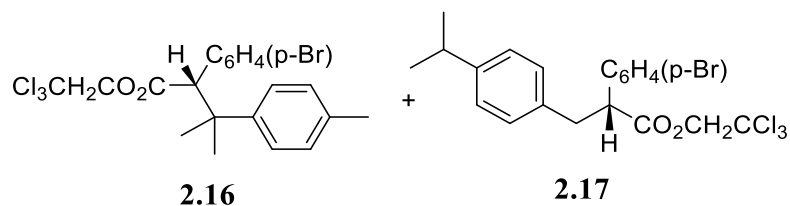
General Procedure 1: Cyclopropanation of Styrene.

A 10 mL vial was charged with styrene (**2.1**, 55.9 mg, 0.54 mmol, 2.0 equiv,) the dirhodium catalyst (1.3 μ mol, 0.5 mol%) and dichloromethane (1.0 mL.) To this mixture was added a solution of 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**2.11**, 100 mg, 0.27 mmol, 1.0 equiv) in DCM (2.5 mL) over 2 h using a syringe pump. After the addition had completed, the mixture was concentrated to dryness under vacuum, and the crude product thus obtained was subjected to column chromatography (12 g SiO₂, 0-5% EtOAc/hexanes,) affording 2,2,2-trichloroethyl (1*R*,2*S*)-1-(4-bromophenyl)-2-phenylcyclopropane-1-carboxylate (**2.18**) as a colorless solid in the indicated yield. The *ee* determination was made directly on the cyclopropanation products using chiral HPLC (OJ-H, 1.0 mL/min, 1.0% i-PrOH / hexanes, λ = 230 nm. rt 7.9 min (major) 12.5 min (minor)).



General Procedure 2: C-H Insertion into 4-Ethyltoluene.

A 10 mL vial equipped with a magnetic stir bar was charged with the dirhodium catalyst (1.0 μ mol, 0.5 mol%), dichloromethane (1.0 mL,) and 4-ethyltoluene (**2.10**, 22, 72 mg, 0.60 mmol, 3.0 equiv.) The vial was held under an argon atmosphere, and the mixture was heated to reflux. Then, a solution of 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**2.11**, 75 mg, 0.20 mmol, 1.0 equiv) in dichloromethane (2.5 mL) was introduced over 1.5 h via syringe pump with stirring on. After 12-16 h at 40 °C, the contents of the vial were concentrated in vacuo, and the crude mixture was analyzed by ^1H NMR. The diastereomeric ratio of the reaction was determined by integration of the methyl doublets at 1.40 ppm and 1.02 ppm. The primary/secondary insertion ratio was determined by integration of the benzylic methine protons at 3.94 ppm (primary insertion) and 3.80 ppm (secondary insertion, including the overlapping signals from both diastereomers.) The enantiomeric excess values were determined via reduction to the corresponding primary alcohols (See General Procedure 4.) All reactions gave predominantly the diastereomer **2.12** for insertion into the secondary site (confirmed by X-ray crystallography experiments – see section 2.3.7).



General Procedure 3: C-H Insertion into 4-Isopropyltoluene.

A 10 mL vial equipped with a magnetic stir bar was charged with the dirhodium catalyst (1.0 μmol , 0.5 mol%), dichloromethane (1.0 mL,) and 4-isopropyltoluene (81 mg, 0.60 mmol, 3.0 equiv.) The vial was held under an argon atmosphere, and the mixture was heated to reflux. Then, a solution of 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**2.11**, 75 mg, 0.20 mmol, 1.0 equiv) in dichloromethane (2.5 mL) was introduced over 1.5 h via syringe pump with stirring on. After 12-16 h at 40 $^{\circ}\text{C}$, the contents of the vial were concentrated in vacuo, and the crude mixture was analyzed by ^1H NMR. The ratio of primary insertion product to tertiary insertion product was determined by the relative integration of the 2,2,2-trichloroethyl methylene doublets at 4.68 ppm (primary) and 4.43 ppm (tertiary.) The enantiomeric excess values were determined via reduction to the corresponding primary alcohols (See General Procedure 4.)

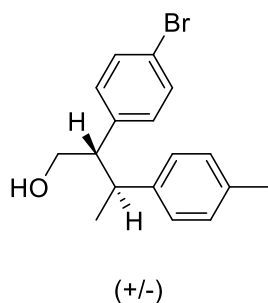
General Procedure 4: Reduction to Primary Alcohols for Enantiomeric Excess

Determinations.

A round bottom flask was charged with the analyte (1.0 equiv) and anhydrous tetrahydrofuran (0.1 molar with respect to the analyte). The mixture was cooled to 0 $^{\circ}\text{C}$ using an ice bath, and then a solution of lithium aluminum hydride (1.0 equiv) in tetrahydrofuran (1.0 M in LiAlH_4) was added dropwise via syringe to the stirring mixture. The mixture warmed to room temperature with the cooling bath over the course of 3-4 h. After stirring for 12-17 h, the reaction mixtures were poured onto sodium sulfate decahydrate (50 g / mmol analyte) and stirred for 10-

30 min. Then, they were filtered through coarse paper, washing with diethyl ether (300 mL / mmol analyte). The filtrate was concentrated under vacuum to afford the crude primary alcohols. The alcohols were purified by flash column chromatography (0-15% EtOAc / hexanes for 4-isopropyltoluene or 0-30% EtOAc/hexanes for 4-ethyltoluene). Following purification, chiral HPLC was used to determine the enantiomeric excess values of these materials. The following methods were used to analyze the mixtures: 4-isopropyltoluene: Chiralpak AD-H, 1.0 mL/min, 3.0% i-PrOH / hexanes, $\lambda = 230$ nm. 4-ethyltoluene: Chiralpak AD-H, 0.80 mL/min, 1.0% i-PrOH / hexanes, $\lambda = 230$ nm. For the mixtures containing the C-H functionalization products of 4-ethyltoluene, flash column purification was effective for removing the minor diastereomer **2.42**, which showed a slight overlap in the HPLC analysis. The enantiomeric excess observed for the alcohol derivatives was assumed to be equal to that of the C-H insertion reactions. Racemic standards for the alcohol products were prepared as described on the following pages. The standards were run concurrently with each analysis to validate the HPLC method.

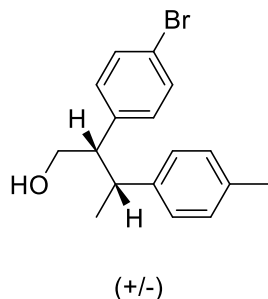
S.2.5 Characterization Data for Primary Alcohol Derivatives



(±)-*anti*-2-(4-bromophenyl)-3-(p-tolyl)butan-1-ol (**2.48**)

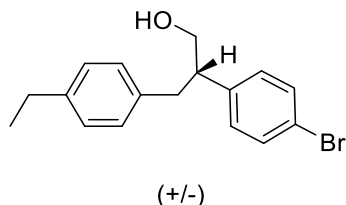
General Procedure 4 was used to reduce a 42:58 diastereo-mixture (**2.12**:**2.13**) of (±)-2,2,2-trichloroethyl 2-(4-bromophenyl)-3-(p-tolyl)butanoate (400 mg, 0.86 mmol) prepared via the method of Bess, et al⁷. Flash column chromatography on silica gel (0-30% EtOAc/hexanes) gave

complete resolution of the *syn* and *anti* diastereomers. 94 mg of compound **2.48** were obtained in 34% yield (82% yield based on the diastereo-purity of the starting material) as a colorless oil. IR (film): 3568, 3339, 3021, 2962, 2921, 2875, 1514, 1487, 1453, 1406, 1375, 1073, 1052, 1010, 817 cm^{-1} . Chiral HPLC: AD-H, 0.80 mL/min, 1.0% i-PrOH / hexanes, $\lambda = 230$ nm, rt 44.6 min and 54.7 min. ^1H NMR (500 MHz, CDCl_3) δ 7.35 – 7.28 (m, 2H), 6.97 (d, $J = 7.7$ Hz, 2H), 6.85 (dd, $J = 11.7, 8.0$ Hz, 4H), 3.96 (dt, $J = 9.7, 4.3$ Hz, 1H), 3.86 (dd, $J = 10.9, 8.2$ Hz, 1H), 3.11 (p, $J = 7.2$ Hz, 1H), 2.99 (td, $J = 8.2, 5.1$ Hz, 1H), 2.26 (s, 3H), 1.32 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 141.1, 139.8, 135.5, 131.2, 130.7, 128.7, 127.7, 120.3, 64.7, 54.2, 41.1, 21.0, 20.0. The relative configuration was confirmed by single crystal X-ray diffraction analysis of the minor diastereomer ($\pm$)-*syn*-2-(4-bromophenyl)-3-(*p*-tolyl)butan-1-ol isolated from the same reaction mixture. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ (Pos.) calcd for $\text{C}_{17}\text{H}_{19}\text{O}^{79}\text{Br}^{23}\text{Na}$ 341.0512; found 341.0507



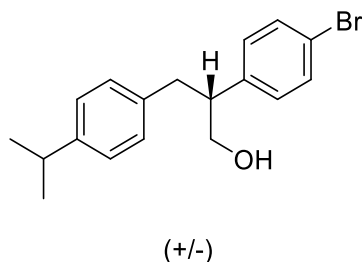
(±)-syn-2-(4-bromophenyl)-3-(p-tolyl)butan-1-ol (2.49)

Isolated from the same reaction mixture as compound **2.48**, using procedure 4 to reduce a 42:58 diastereo-mixture (**2.12:2.13**) of (±)-2,2,2-trichloroethyl 2-(4-bromophenyl)-3-(p-tolyl)butanoate⁷ (400 mg, 0.86 mmol). 128 mg of the (±)-syn stereoisomer was obtained in 47% yield as a colorless crystalline solid (81% yield based on the diastereo-purity of the starting material). mp 98.0-99.0 °C (from CHCl₃). IR (solid): 3463, 3020, 2954, 2927, 2895, 2870, 1514, 1485, 1375, 1072, 1055, 1008, 819, 723 cm⁻¹ Chiral HPLC: AD-H, 0.80 mL/min, 1.0% i-PrOH / hexanes, λ = 230 nm, rt 53.0 min (The enantiomeric pair for the minor diastereomer **2.49** showed no resolution under these conditions, and the retention time is reported for monitoring purposes only. Enantiomeric excess values were not determined for this minor product. It was removed by column chromatography prior to analysis.) ¹H NMR (500 MHz, CDCl₃) δ 7.52 – 7.47 (m, 2H), 7.20 – 7.16 (m, 2H), 7.15 (s, 4H), 3.61 – 3.46 (m, 2H), 2.99 – 2.79 (m, 2H), 2.35 (s, 3H), 1.02 (d, J = 6.6 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 142.1, 140.9, 136.1, 131.7, 130.3, 129.4, 127.1, 120.6, 65.8, 55.1, 42.0, 21.0, 20.9. A single crystal of adequate size was grown from CHCl₃/hexanes to confirm the relative configuration of this compound using X-ray crystallography. HRMS (ESI) m/z: [M+Na]⁺ (Pos.) calcd for C₁₇H₁₉O⁷⁹Br²³Na 341.05115; found 341.0506.



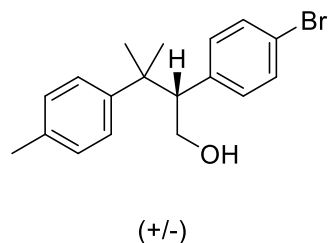
(±)-2-(4-bromophenyl)-3-(4-ethylphenyl)propan-1-ol (2.50)

(±)-2,2,2-trichloroethyl 2-(4-bromophenyl)-3-(4-ethylphenyl)propanoate (**2.14**) prepared via the method of Qin, et al⁸ (60 mg, 0.13 mmol, 1.0 equiv) was dissolved in CH₂Cl₂ (10 mL). The flask was cooled to -78 °C using a bath of dry ice in acetone, and then a solution of diisobutylaluminum hydride (92 mg, 0.65 mmol, 5.0 equiv) in CH₂Cl₂ (0.65 mL, 1.0 M) was introduced dropwise via syringe. The mixture was stirred for 17 h, during which time the flask warmed to room temperature with the cooling bath. Then, the flask was cooled to 0 °C and the reaction was quenched via the addition of methanol (1 mL). The mixture was concentrated to a colorless solid under vacuum. The solid was washed with ethyl acetate (3x10 mL) and then filtered through silica gel (15 g) with 100% ethyl acetate (100 mL). Concentration of the filtrate liquid afforded 34 mg of **2.50** as a colorless oil (82% yield). IR (solid): 3569, 3321, 3020, 2962, 2926, 2870, 1514, 1487, 1406, 1073, 1010, 822, 731 cm⁻¹. Chiral HPLC: AD-H, 0.80 mL/min, 1.0% i-PrOH / hexanes, λ = 230 nm, rt 57.9 min and 69.2 min. ¹H NMR (500 MHz, CDCl₃) δ 7.43 (d, J = 8.1 Hz, 2H), 7.08 (dd, J = 10.1, 8.0 Hz, 4H), 6.99 (d, J = 7.8 Hz, 2H), 3.77 (dd, J = 11.0, 6.3 Hz, 2H), 3.10 – 3.02 (m, 1H), 2.98 (dd, J = 13.6, 7.3 Hz, 1H), 2.84 (dd, J = 13.6, 7.6 Hz, 1H), 2.60 (q, J = 7.6 Hz, 2H), 1.33 (d, J = 6.9 Hz, 1H), 1.21 (t, J = 7.6 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 142.1, 141.2, 136.6, 131.6, 129.8, 128.9, 127.8, 120.5, 66.2, 49.7, 38.1, 28.4, 15.5. HRMS (ESI) m/z: [M+Na]⁺ (Pos.) calcd for C₁₇H₁₉O⁷⁹Br²³Na 341.0512; found 341.0506.



(±)-2-(4-bromophenyl)-3-(4-isopropylphenyl)propan-1-ol (2.51)

(±)-2,2,2-trichloroethyl 2-(4-bromophenyl)-3-(4-isopropylphenyl)propanoate (**2.17**, 63 mg, 0.13 mmol, 1.00 equiv)⁷ was dissolved in CH₂Cl₂ (10 mL) in a 20 mL scintillation vial, and the solution was cooled to -78 °C using a bath of dry ice in acetone. Then, diisobutylaluminum hydride (190 mg, 1.3 mmol, 10.0 equiv) in CH₂Cl₂ (1.3 mL, 1.0 M) was introduced dropwise via syringe. The mixture was stirred for 14 h, during which time the vial gradually warmed to room temperature with the cooling bath. At the end of the stir period, the vial was cooled to 0 °C in an ice bath and the reaction was quenched via the addition of methanol (1 mL). The mixture was concentrated under vacuum to a colorless solid. The solid was washed with diethyl ether (3x10 mL) and filtered through silica gel (10 g), washing with additional diethyl ether (100 mL). Concentration of the filtrate liquid afforded 24 mg of product **2.51** as a colorless oil (55% yield). IR (film): 3568, 3340, 2958, 2923, 2869, 1513, 1488, 1072, 1009, 819 cm⁻¹. Chiral HPLC: AD-H, 1.0 mL/min, 3.0% i-PrOH / hexanes, λ = 230 nm, rt 13.5 min and 15.6 min. ¹H NMR (500 MHz, CDCl₃) δ 7.44 (d, J = 8.3 Hz, 2H), 7.16 – 7.07 (m, 4H), 7.01 (d, J = 7.9 Hz, 2H), 3.76 (qd, J = 10.9, 6.2 Hz, 2H), 3.05 (td, J = 7.3, 5.4 Hz, 1H), 2.98 (dd, J = 13.7, 7.4 Hz, 1H), 2.86 (ddd, J = 13.6, 10.8, 7.2 Hz, 2H), 1.36 (s, J = 6.6 Hz, 1H), 1.23 (d, J = 6.9 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 146.7, 141.3, 136.7, 131.6, 129.8, 128.9, 126.4, 120.5, 66.2, 49.6, 38.1, 33.7, 24.0. HRMS (ESI) m/z: [M+Na]⁺ (Pos.) calcd for C₁₇H₁₉O⁷⁹Br²³Na 355.0668; found 355.0670.



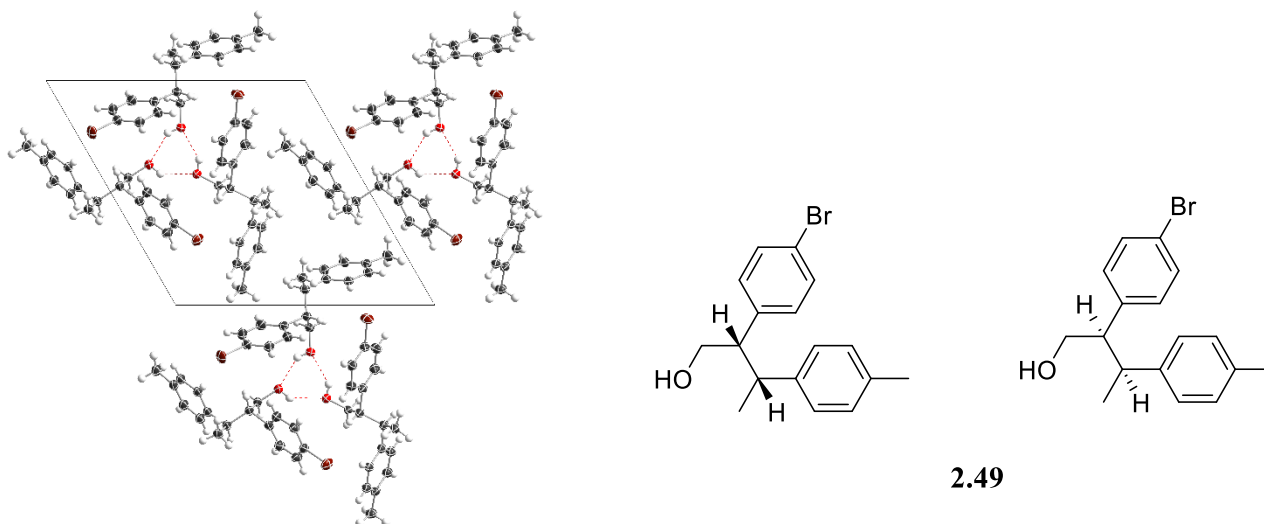
(±)-2-(4-bromophenyl)-3-methyl-3-(p-tolyl)butan-1-ol (2.52)

This compound was prepared according to General Procedure 4 with (±)-methyl 2-(4-bromophenyl)-3-methyl-3-(p-tolyl)butanoate (**2.53**, 99 mg, 1.00 equiv, 0.27 mmol)⁸ as the starting material. 84 mg of the pure product was obtained as a colorless oil (92% yield). IR (film): 3569, 3350, 2967, 2929, 2888, 1513, 1488, 1407, 1386, 1364, 1074, 1026, 1009, 818, 771, 728 cm⁻¹. Chiral HPLC: AD-H, 1.0 mL/min, 3.0% i-PrOH / hexanes, λ = 230 nm, rt 22.3 min and 44.6 min. ¹H NMR (500 MHz, CDCl₃) δ 7.41 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 6.97 (d, J = 8.2 Hz, 2H), 3.83 (t, J = 10.6 Hz, 1H), 3.75 (s, 1H), 3.07 (dd, J = 10.3, 4.6 Hz, 1H), 2.35 (s, 3H), 1.28 (d, J = 8.1 Hz, 3H), 1.21 (s, 3H), 0.98 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 144.5, 138.5, 135.6, 131.7, 131.1, 128.8, 126.2, 120.8, 62.7, 59.0, 39.7, 28.9, 24.4, 20.9. HRMS (ESI) m/z: [M+Na]⁺ (Pos.) calcd for C₁₈H₂₁O⁷⁹Br²³Na 355.0668; found 355.0668.

S.2.6 Determination of the Relative Configuration for Compounds

2.48 and 2.49

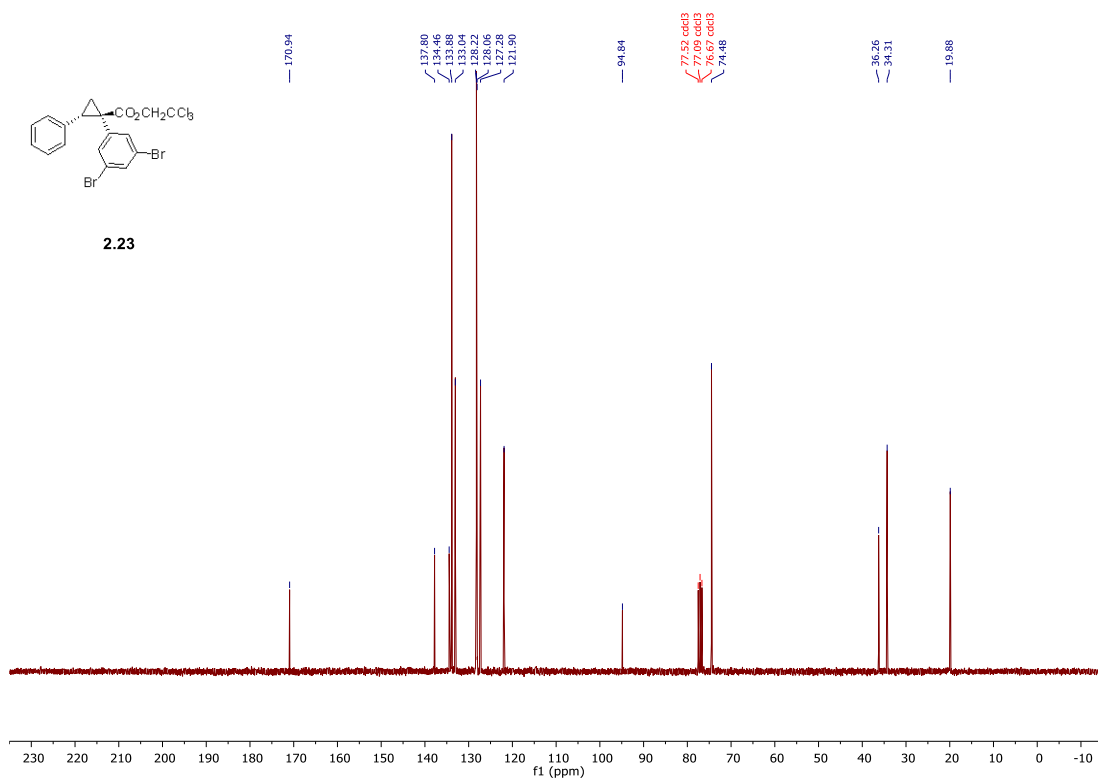
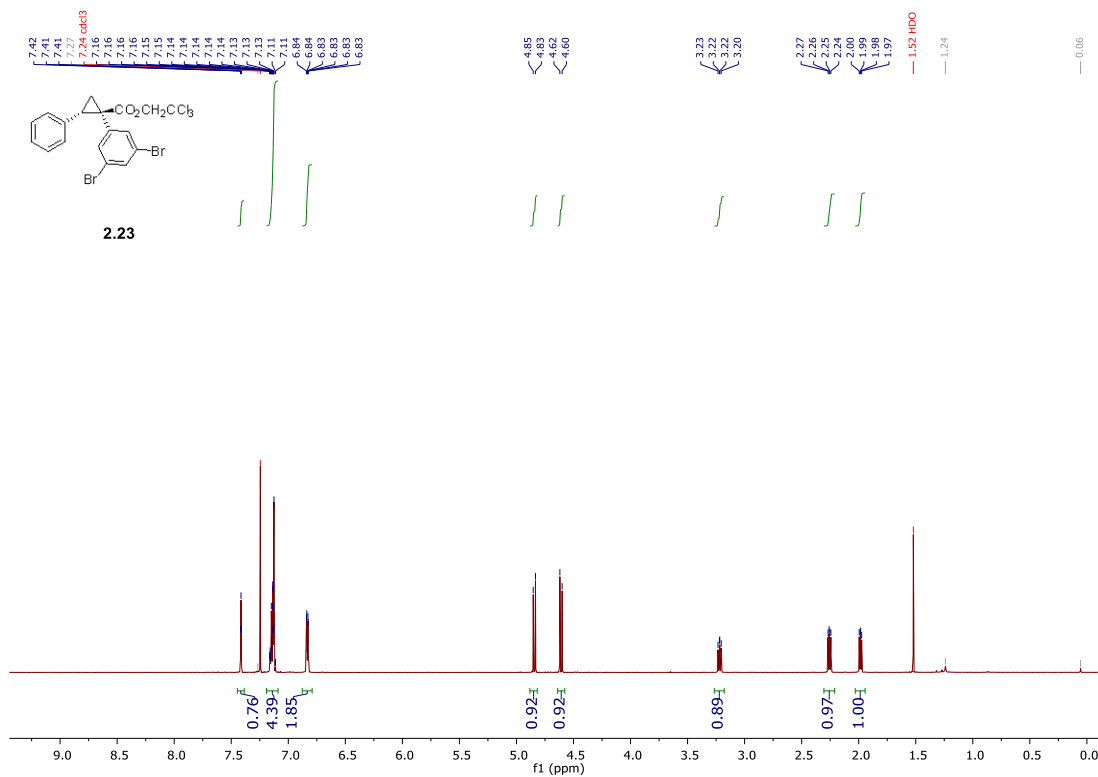
Approximately 40 mg of ($\pm$)-(2*S*,3*R*)/(2*R*,3*S*)-2-(4-bromophenyl)-3-(*p*-tolyl)butan-1-ol (**2.49**) was placed in a 20 mL scintillation vial and dissolved in dimethyl carbonate. The vial was left partially open to allow for evaporation of solvent, yielding colorless single crystals. X-ray crystallographic analysis confirmed racemic co-crystals of (2*S*,3*R*)-2-(4-bromophenyl)-3-(*p*-tolyl)butan-1-ol and (2*R*,3*S*)-2-(4-bromophenyl)-3-(*p*-tolyl)butan-1-ol (**2.49**).

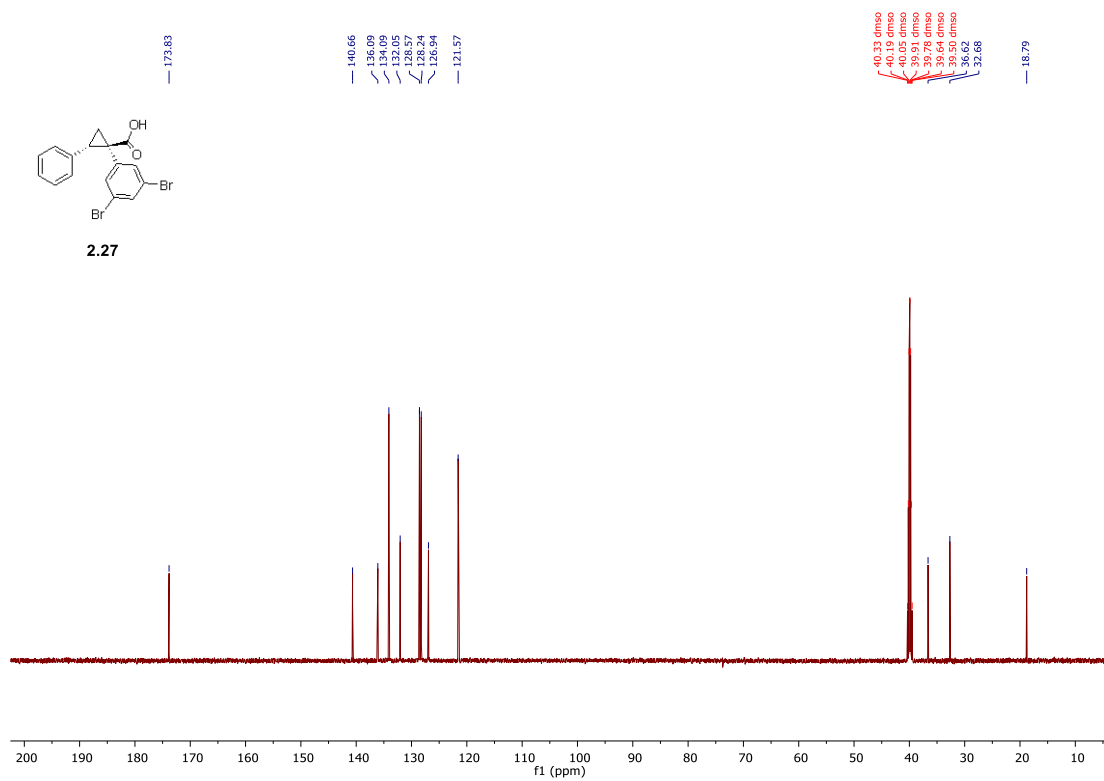
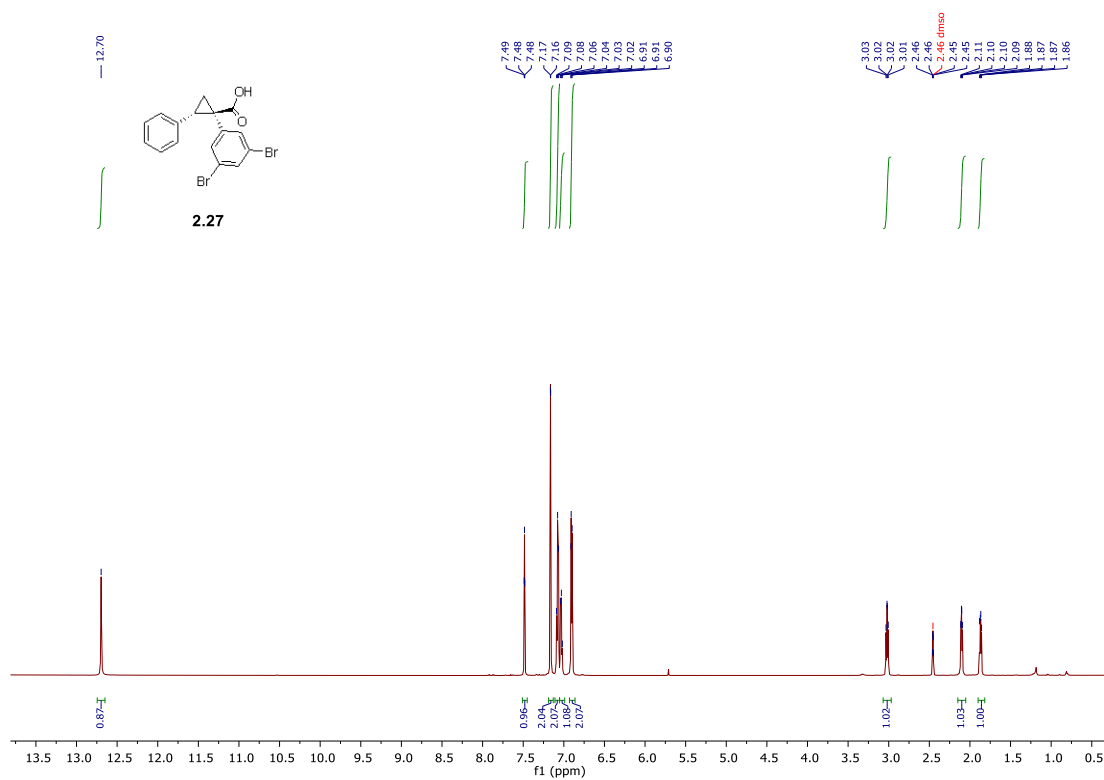


The relative configuration of the other diastereomer ($\pm$)-*anti*-2-(4-bromophenyl)-3-(*p*-tolyl)butan-1-ol (**2.48**) is implied by this result. All of the rhodium carbene reactions conducted in this study generated predominately the *anti* product [(2*S*,3*S*)/(2*R*,3*R*)] for insertion at the secondary site of 4-ethyltoluene (**2.10**).

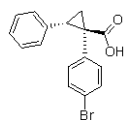
For further crystallographic details, see appendix A.1.

S.2.7 ^1H and ^{13}C NMR Spectra

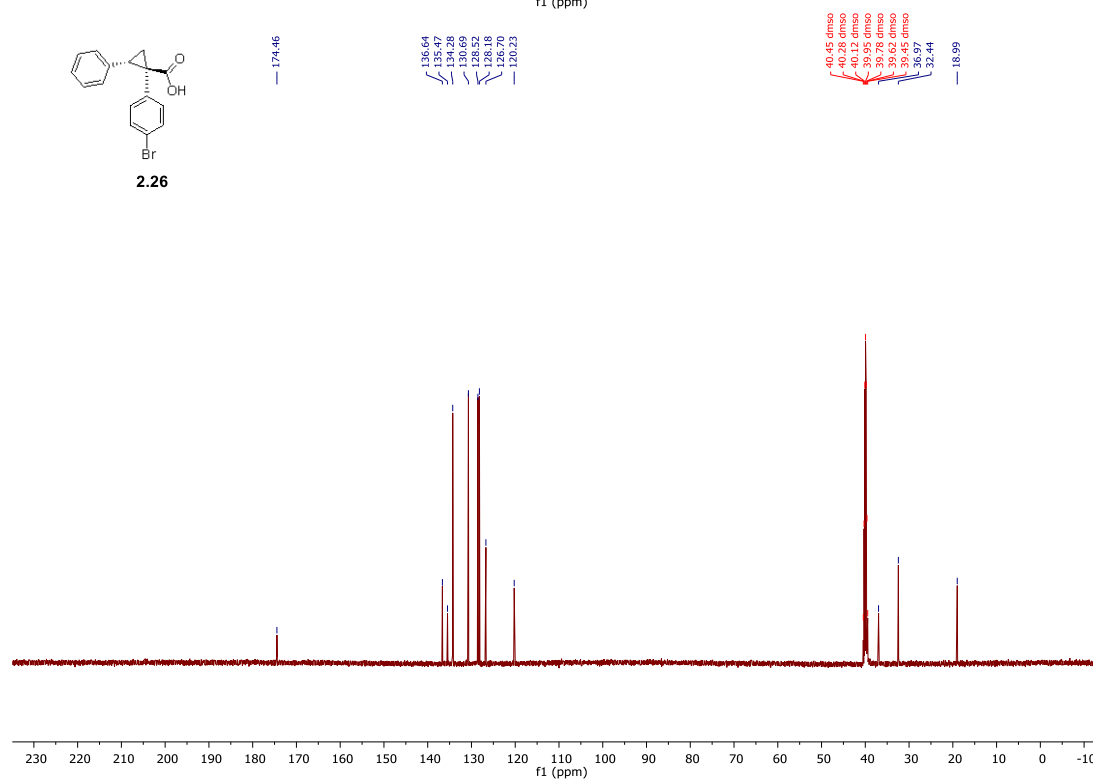


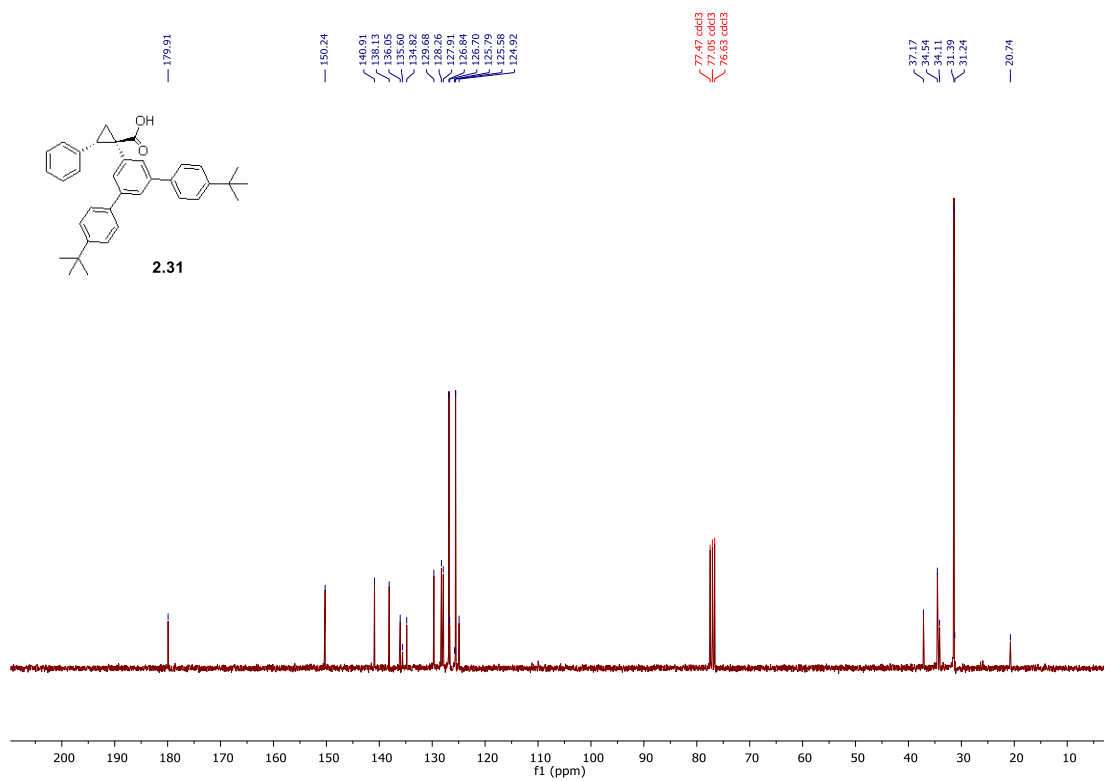
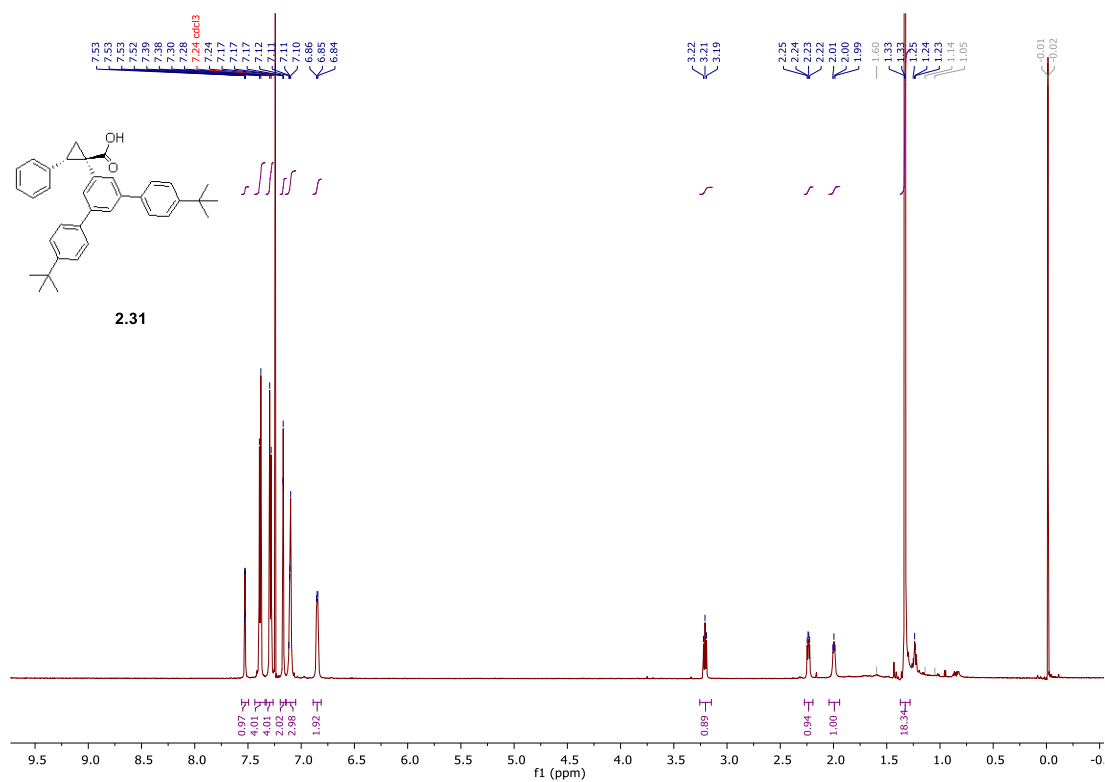


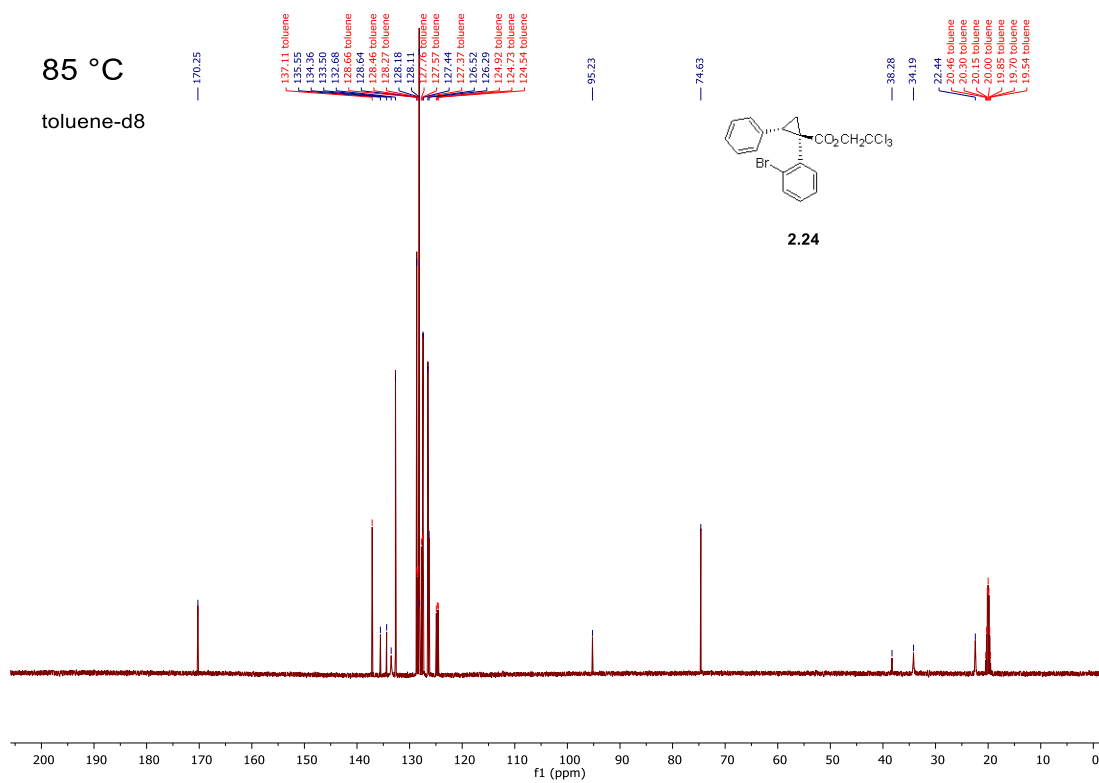
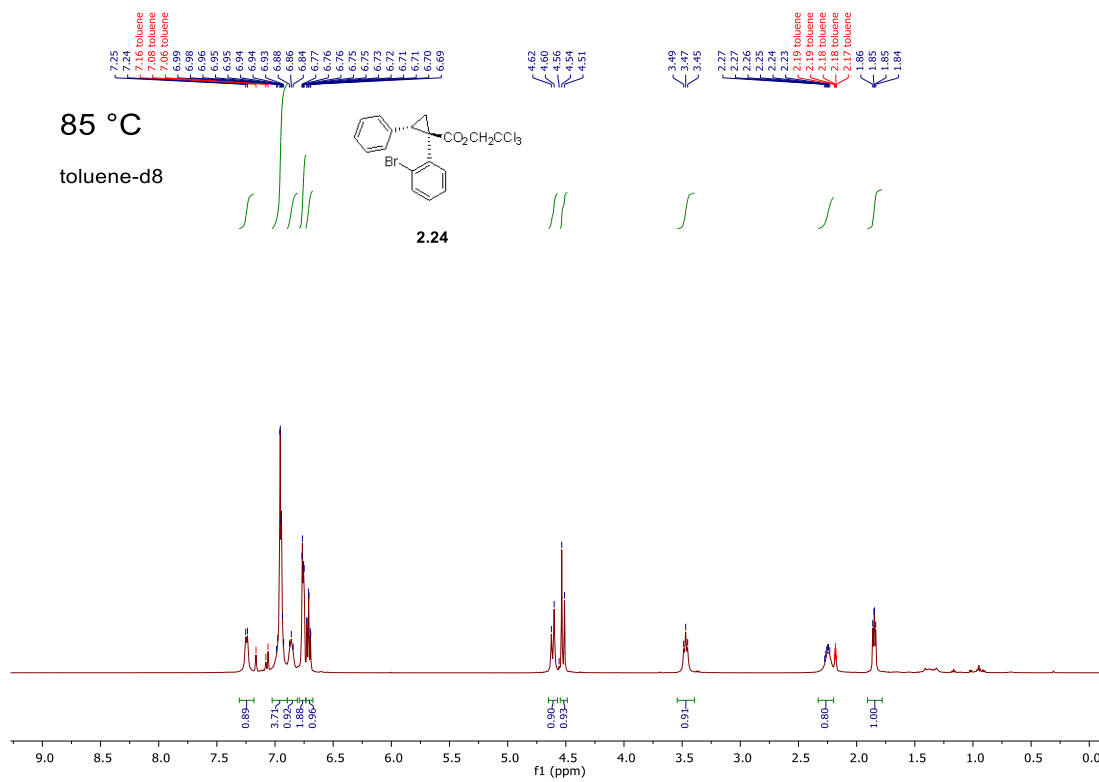
2.26

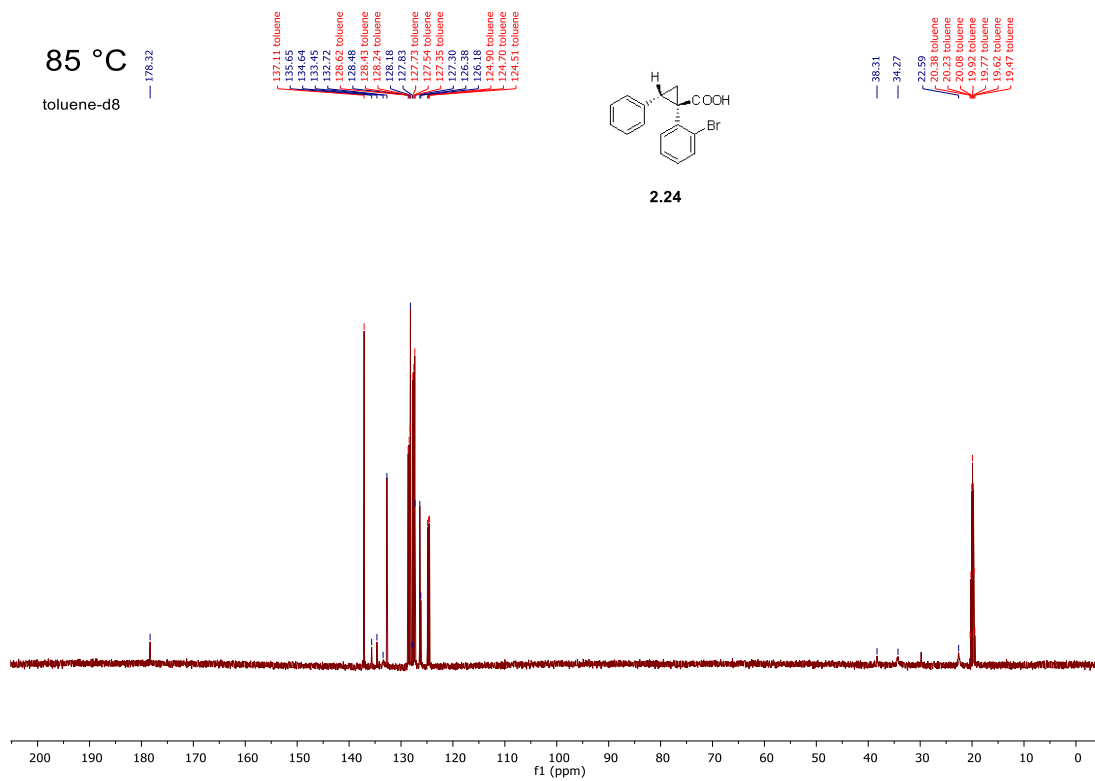
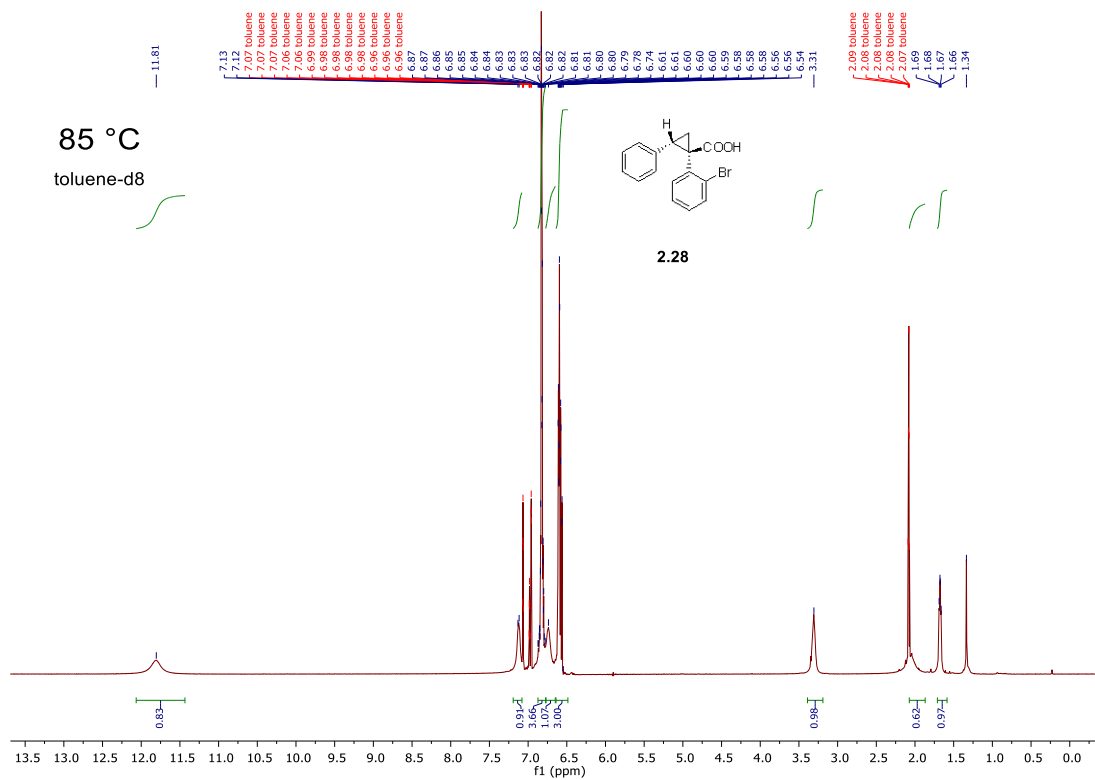


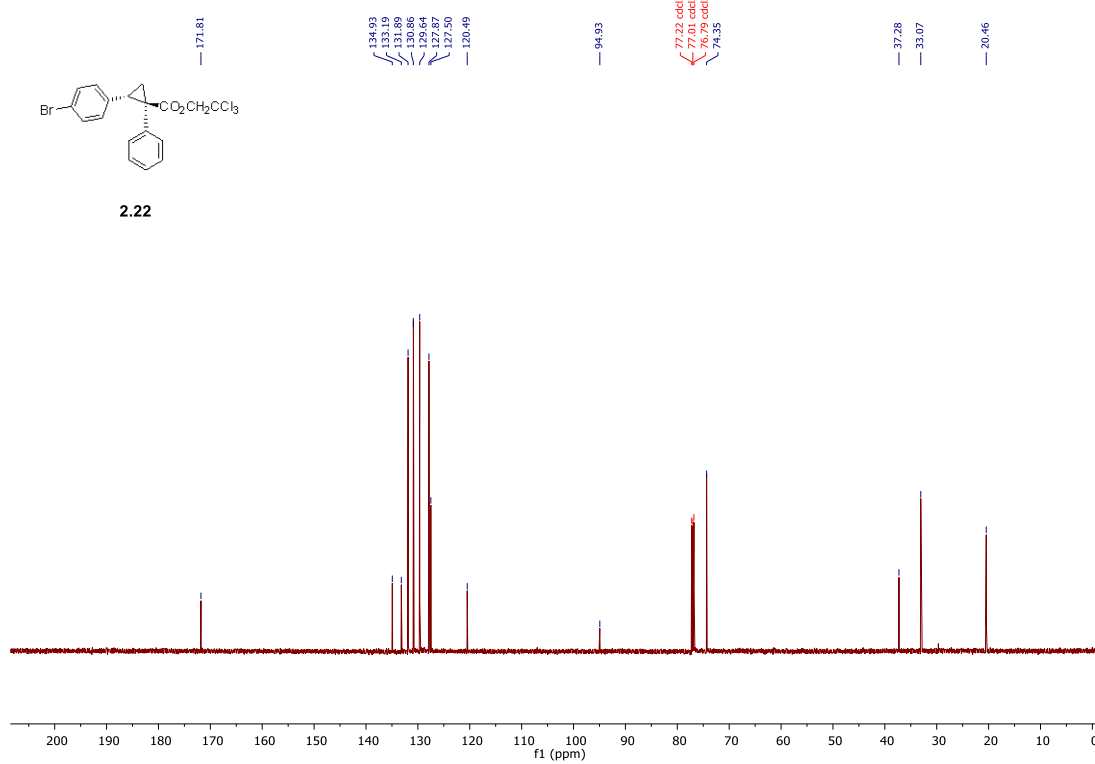
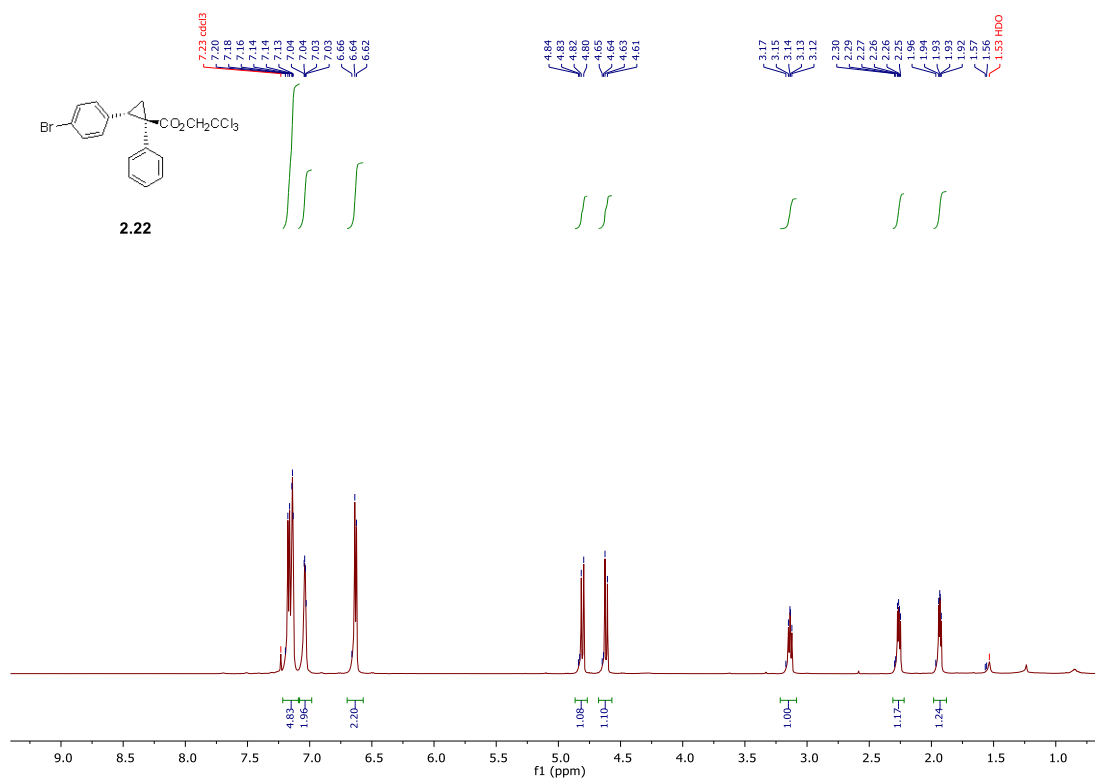
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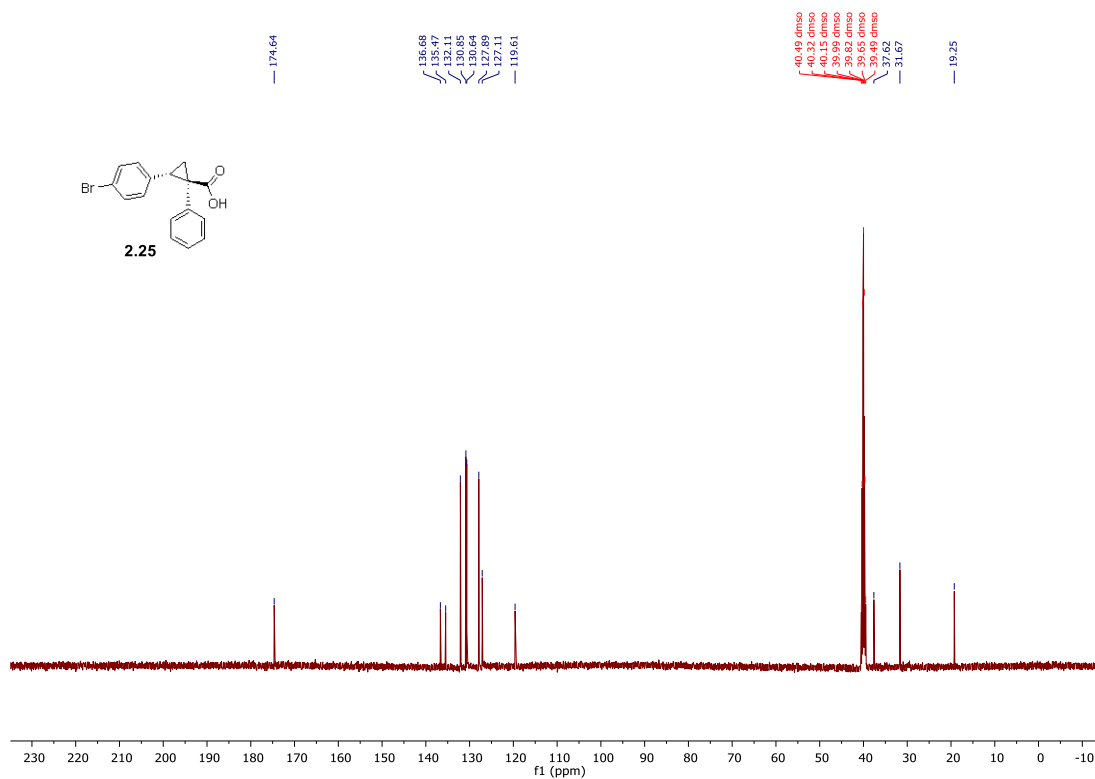
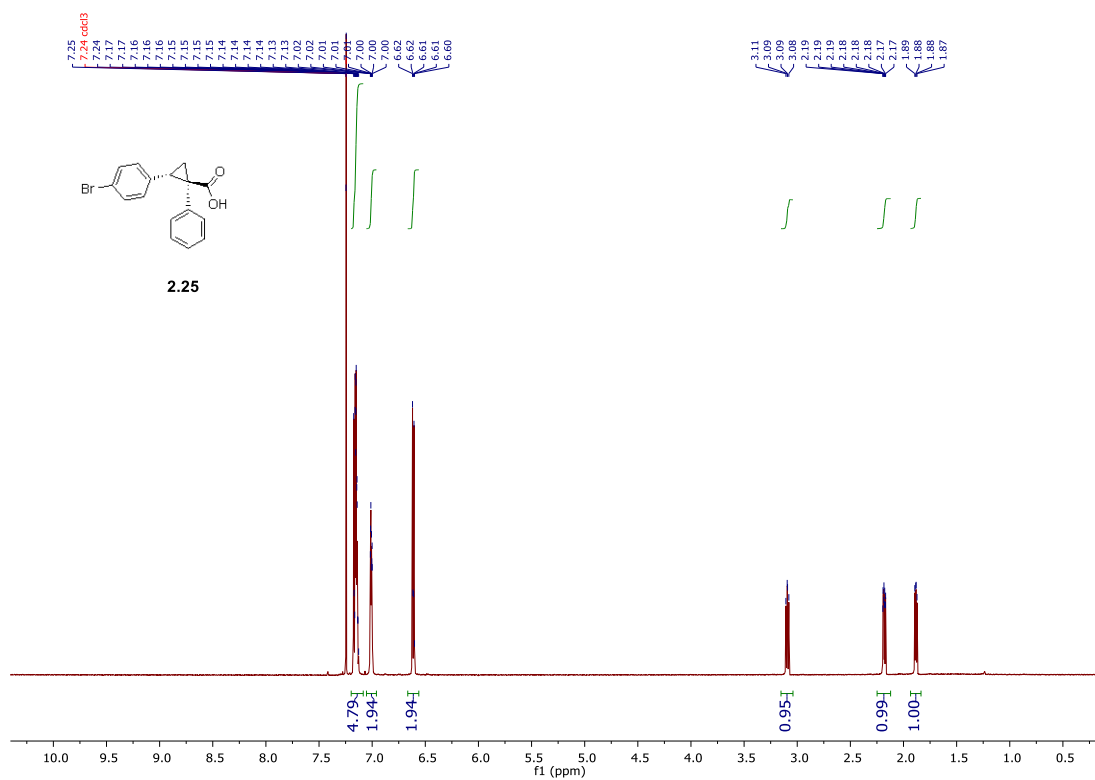


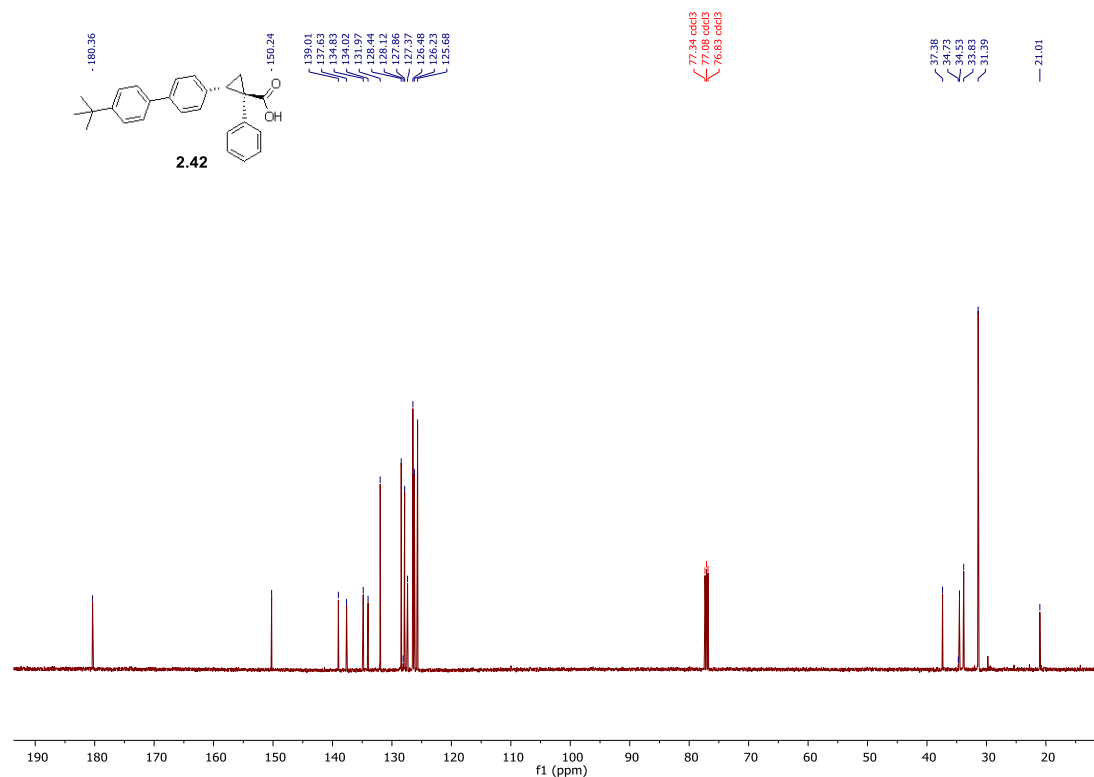
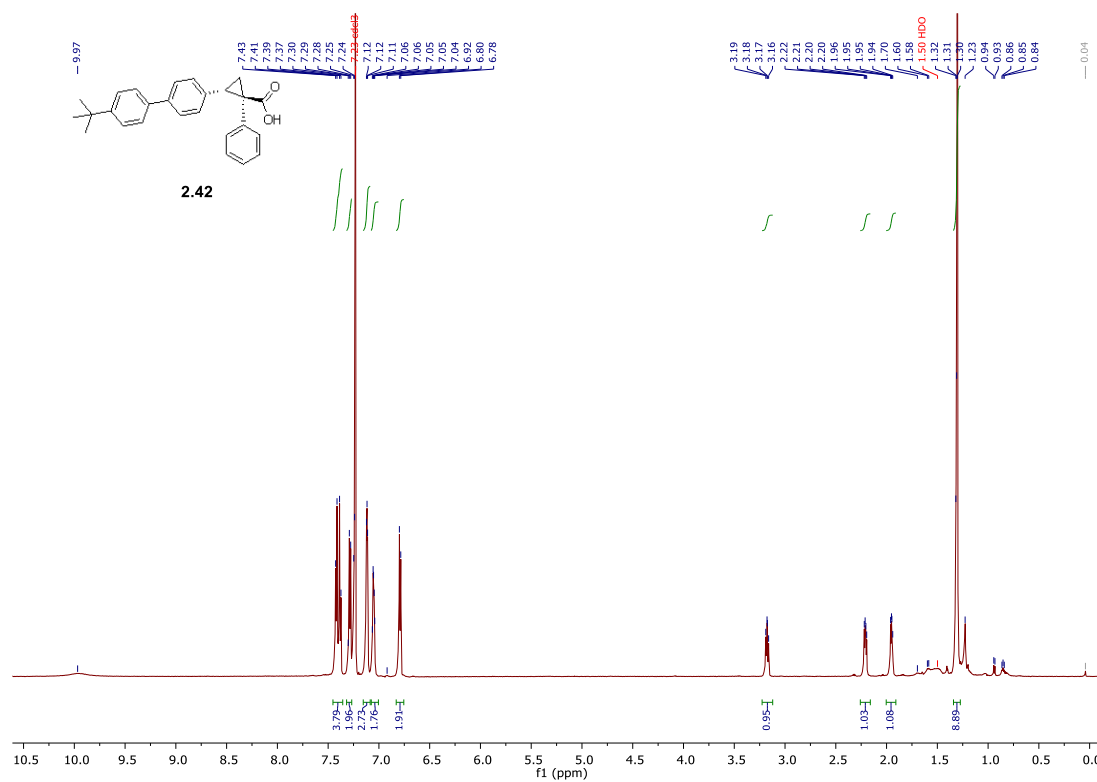


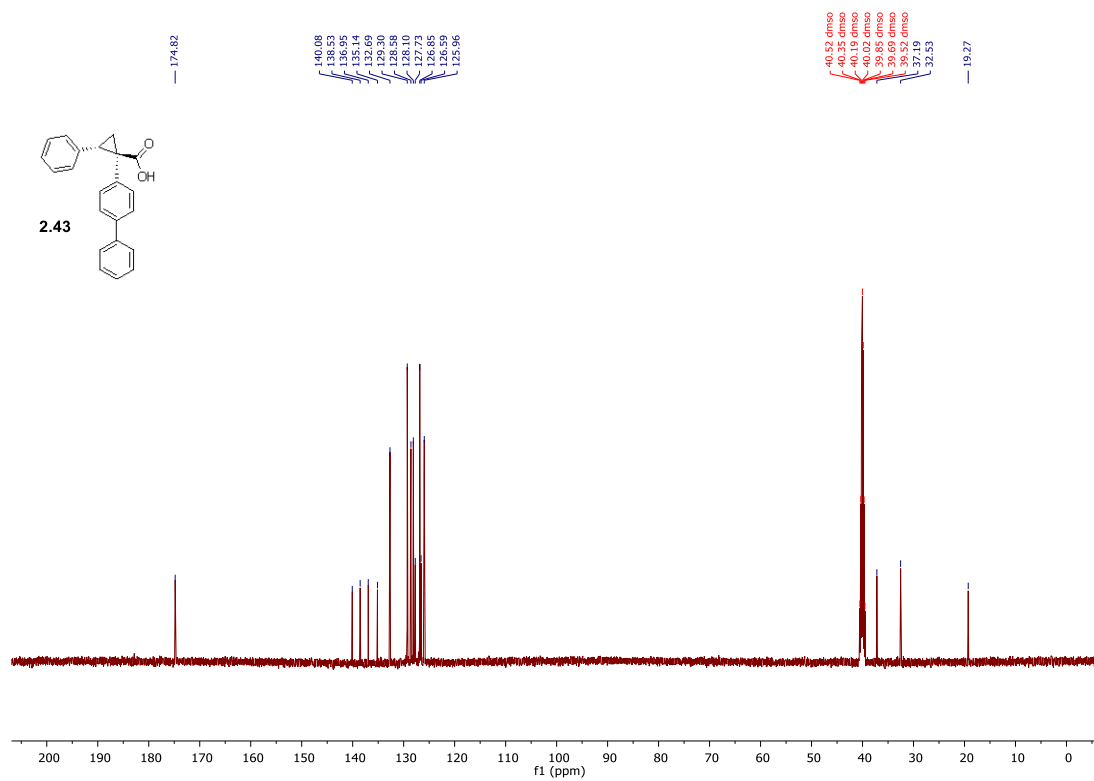
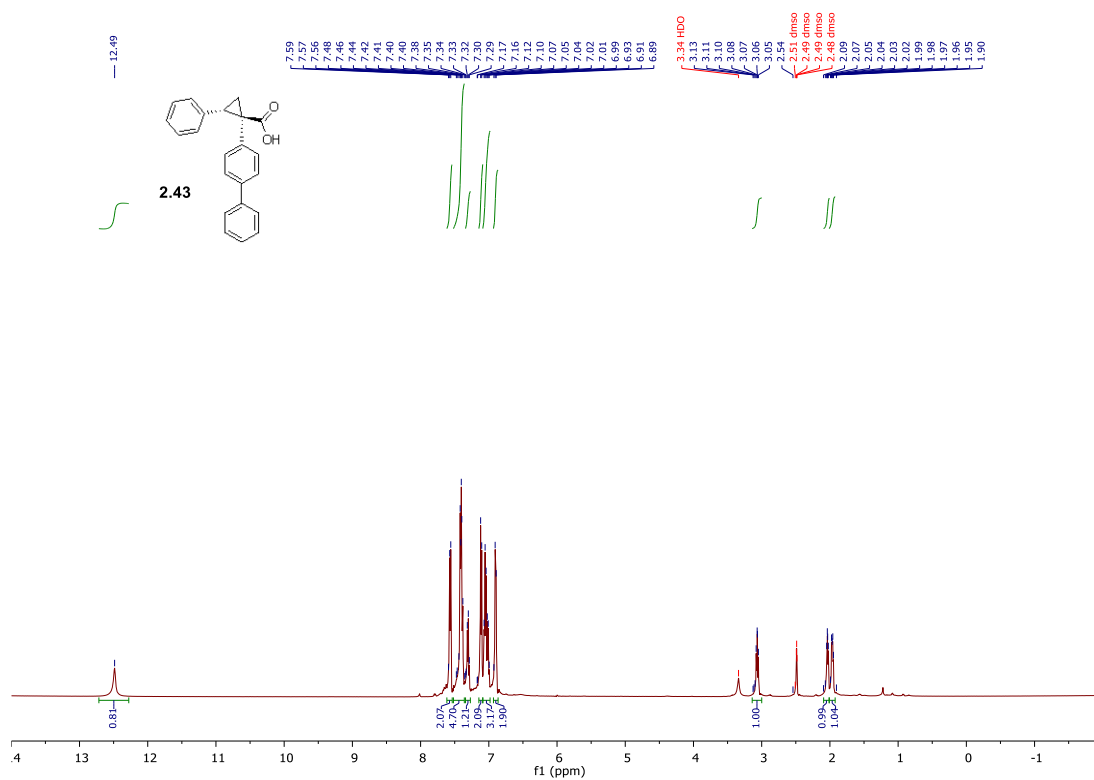


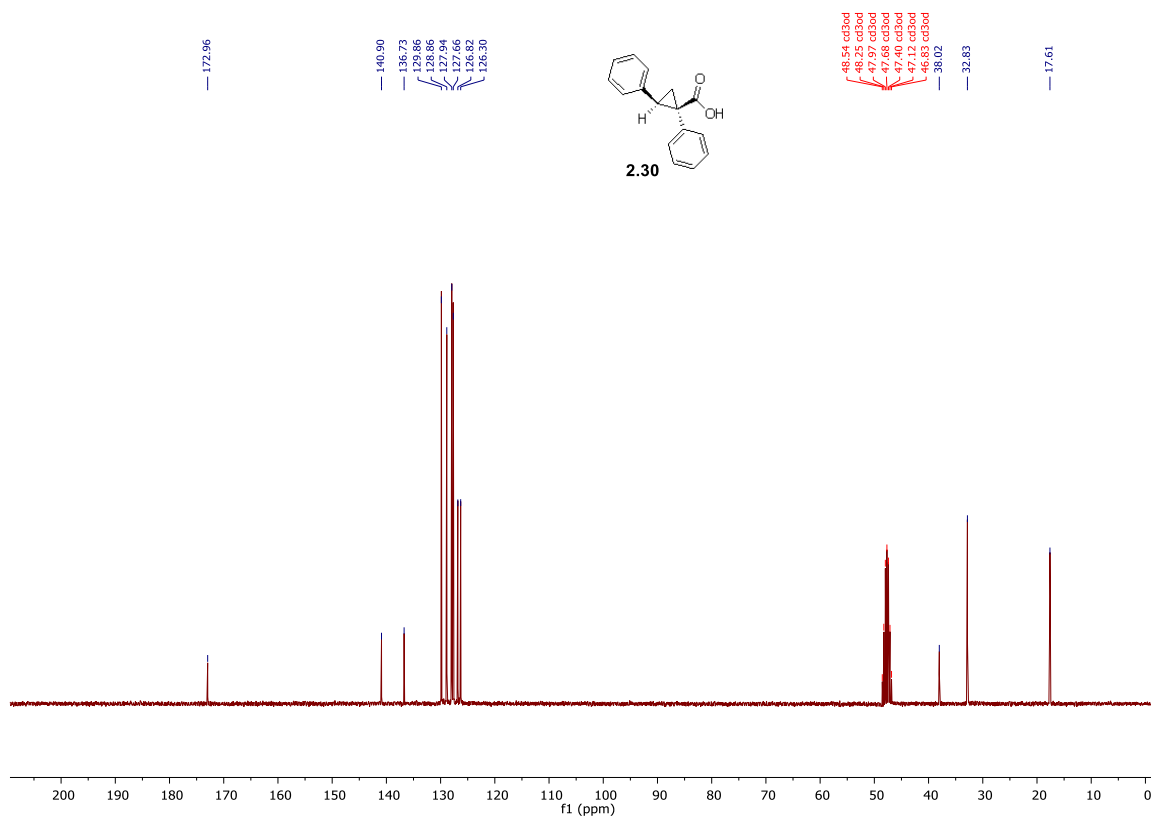
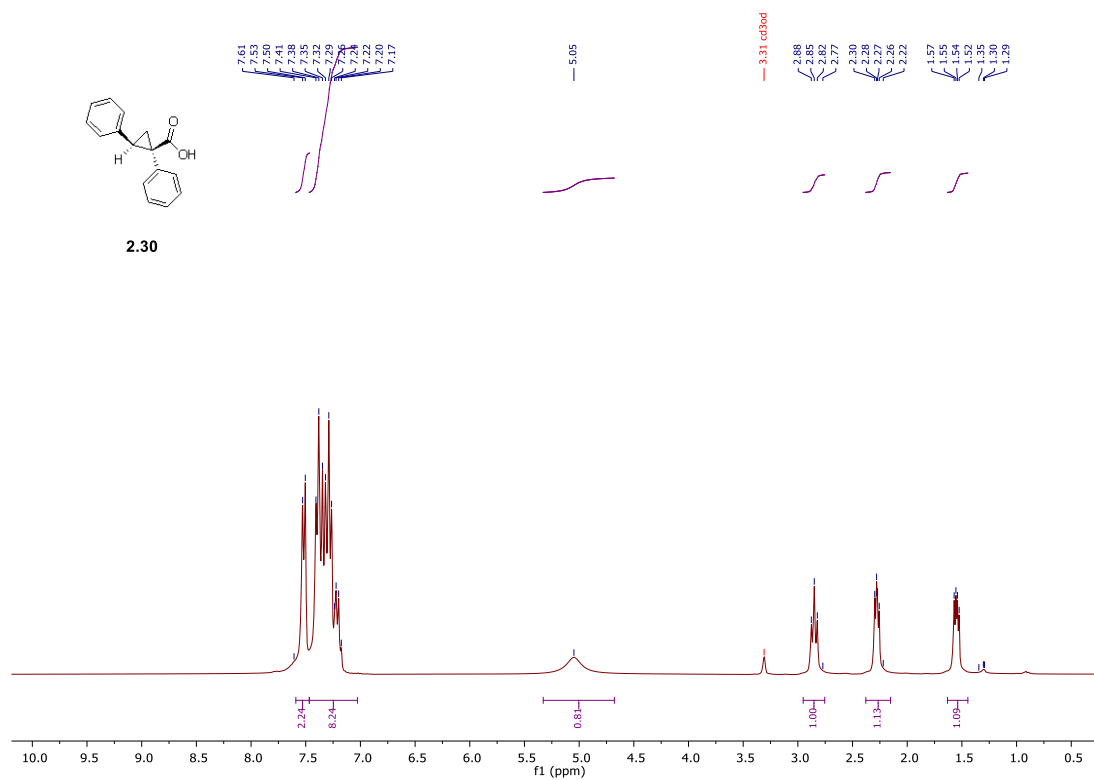


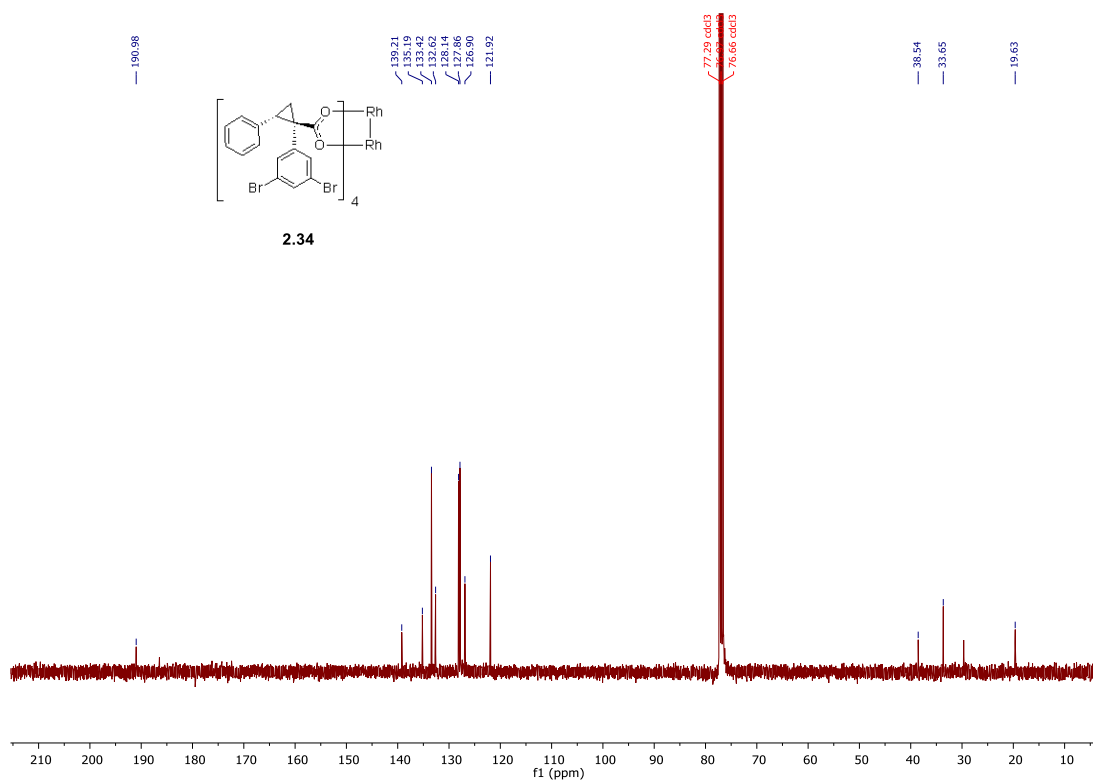


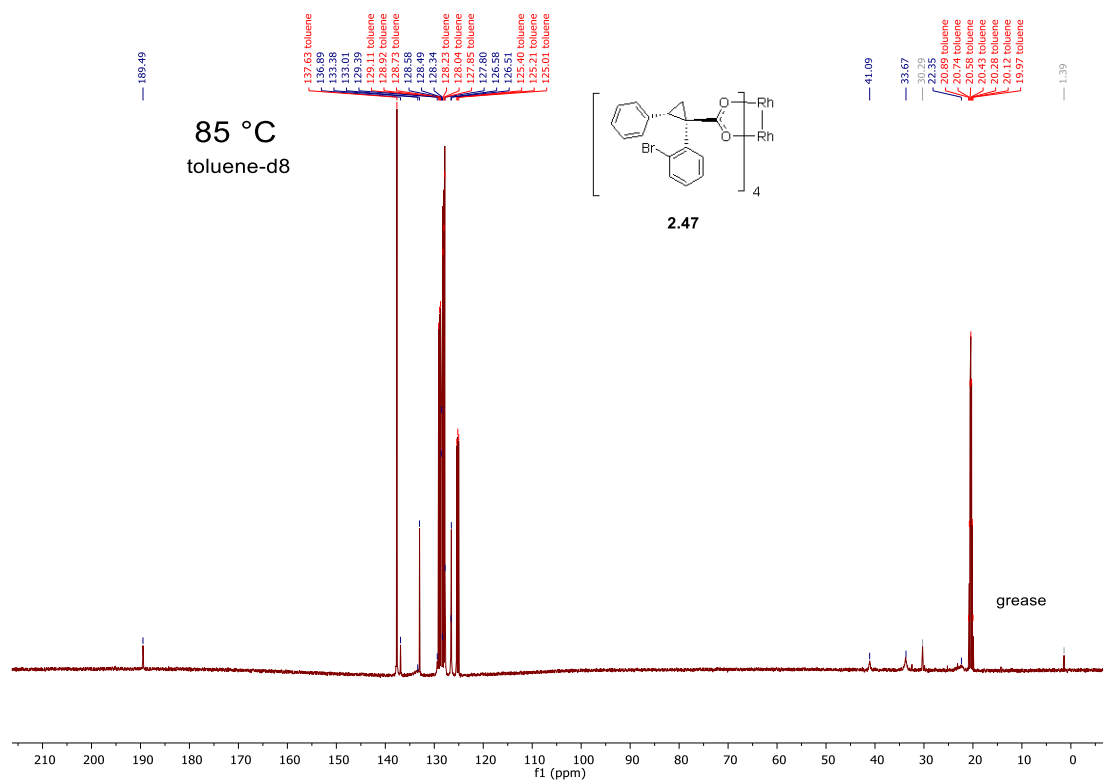
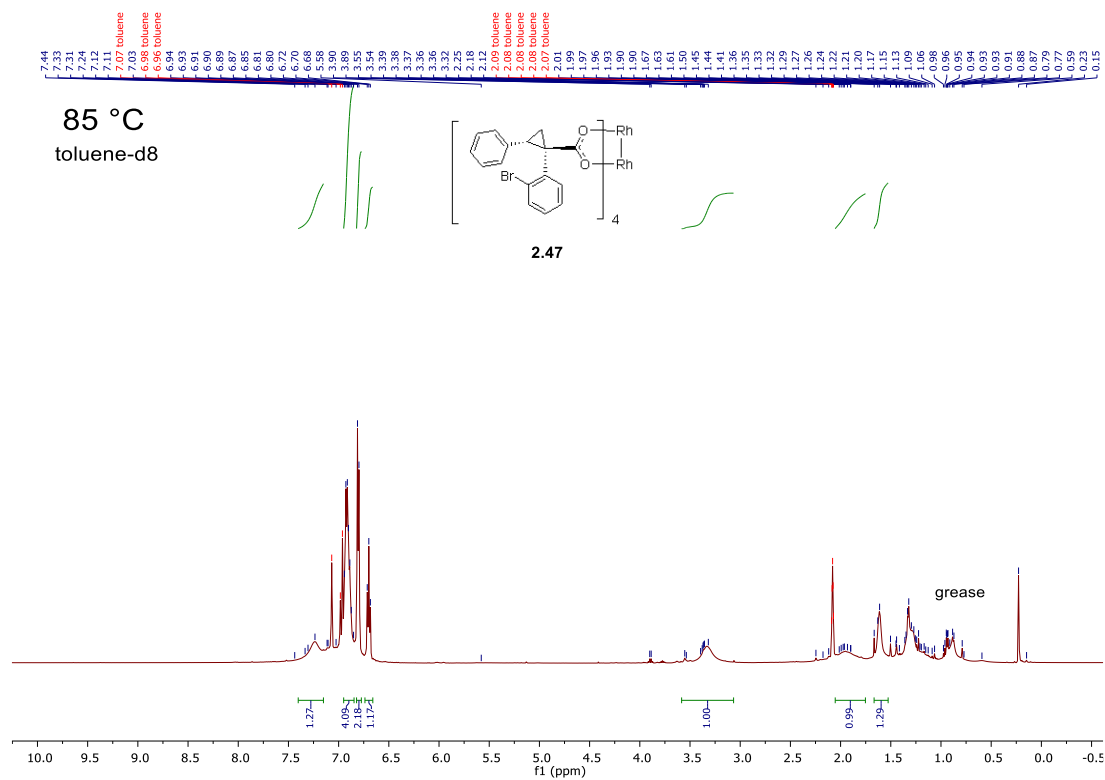


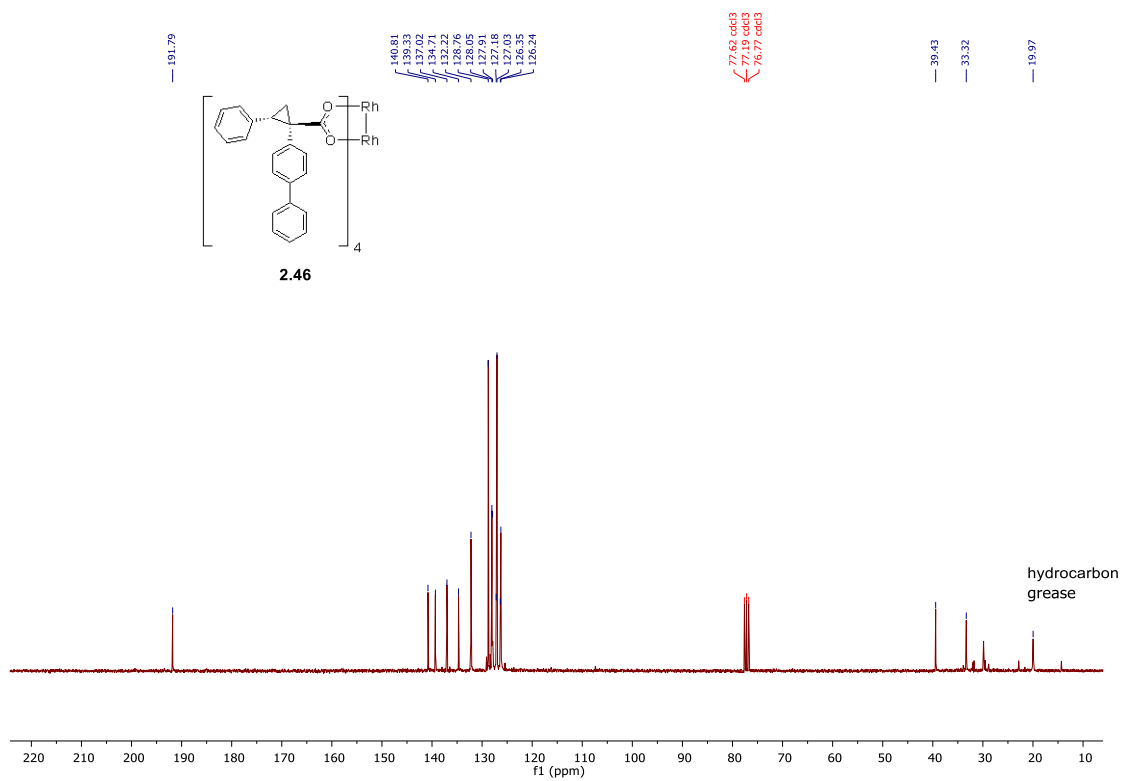
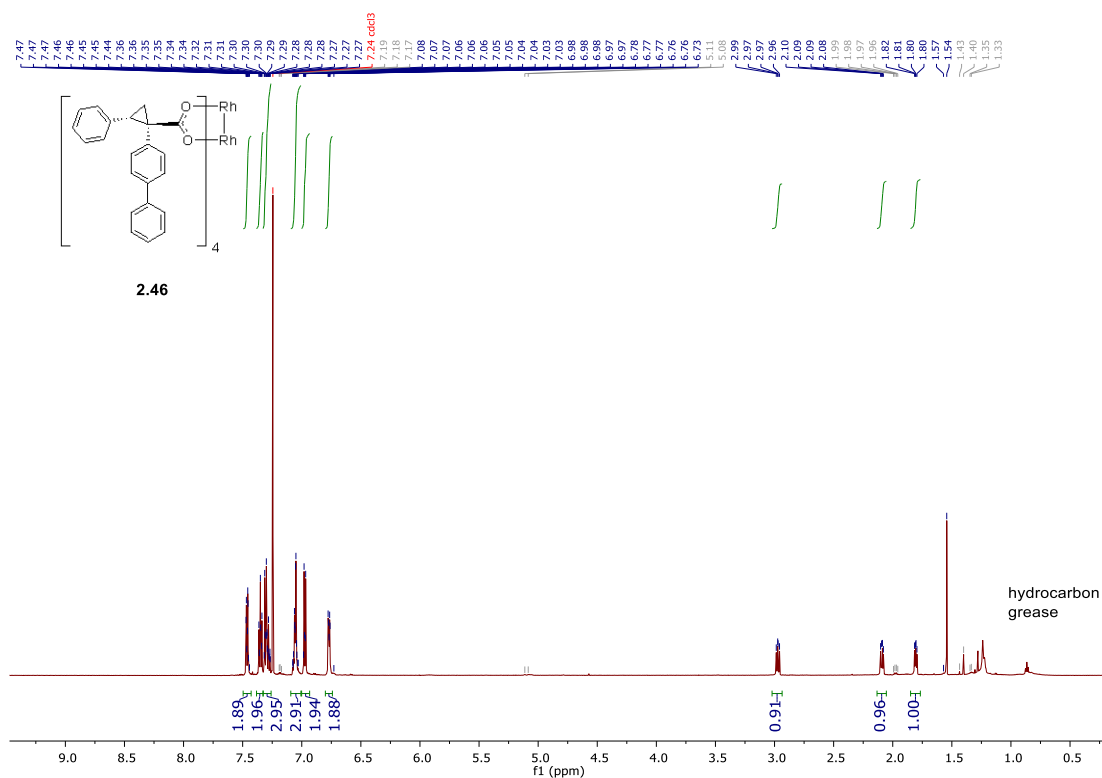


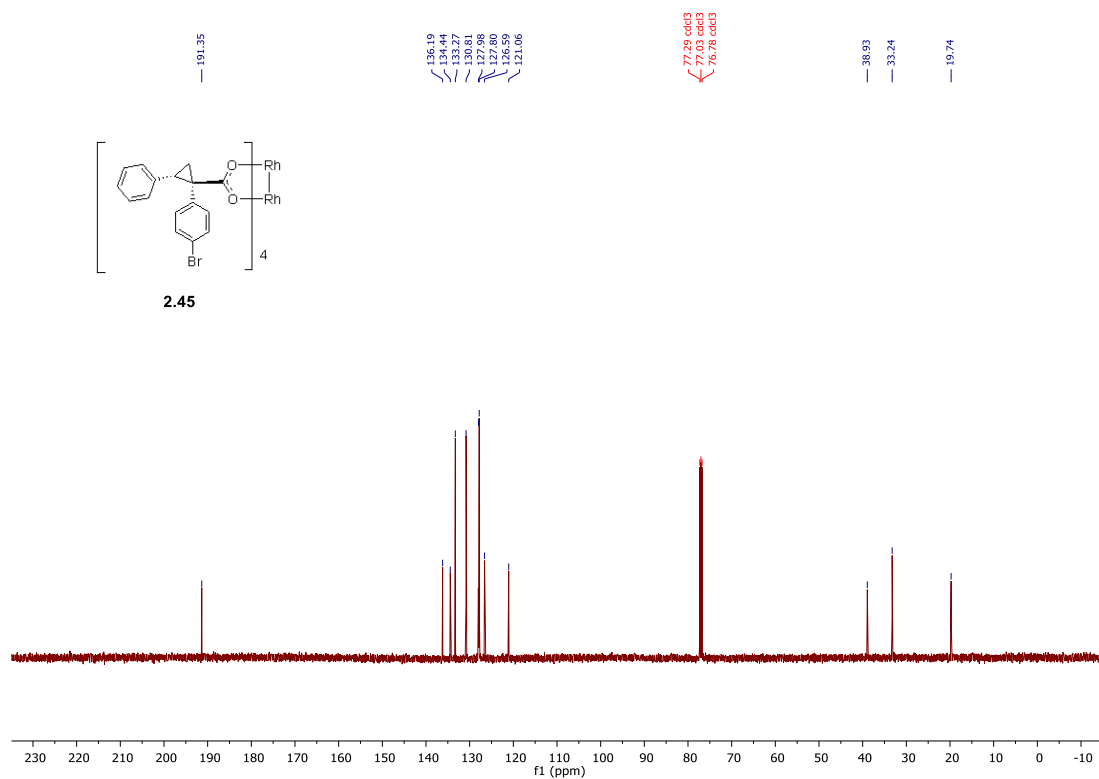
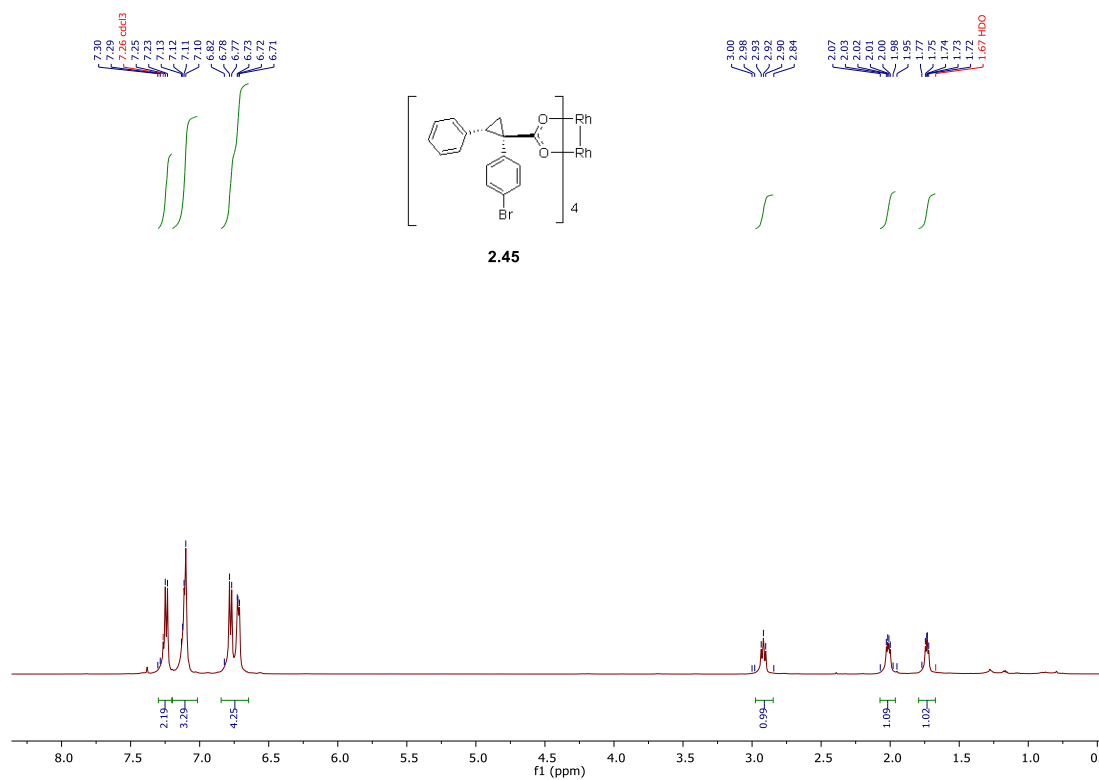


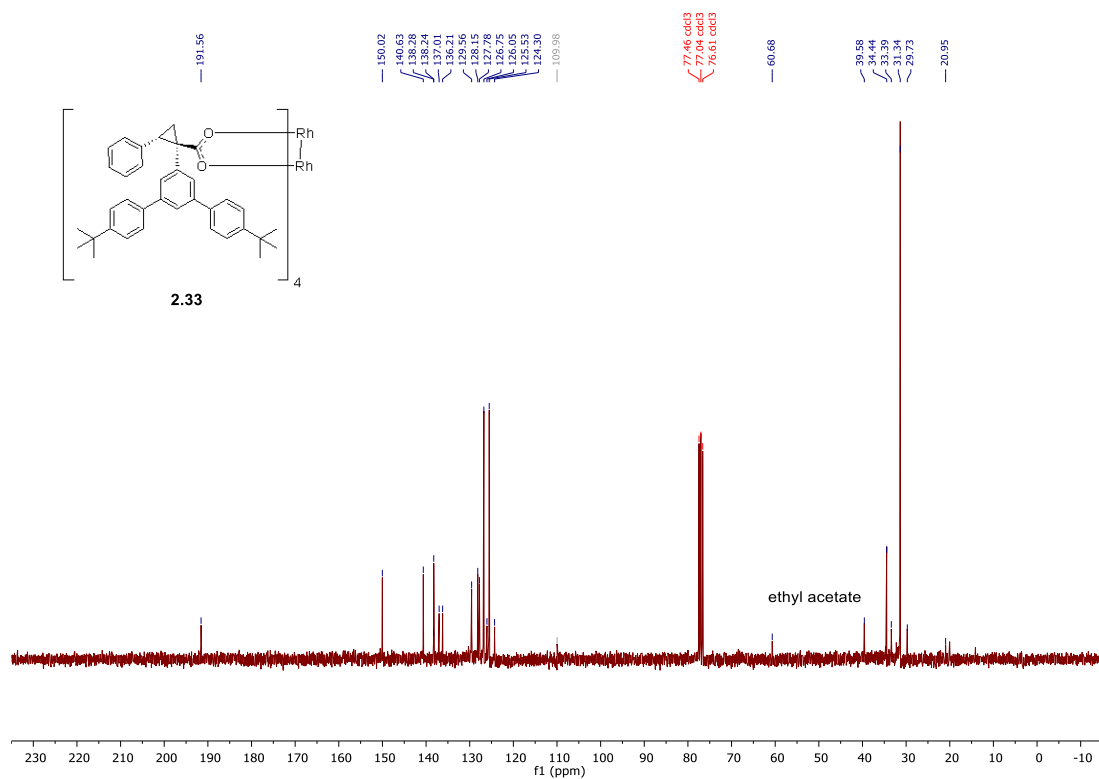
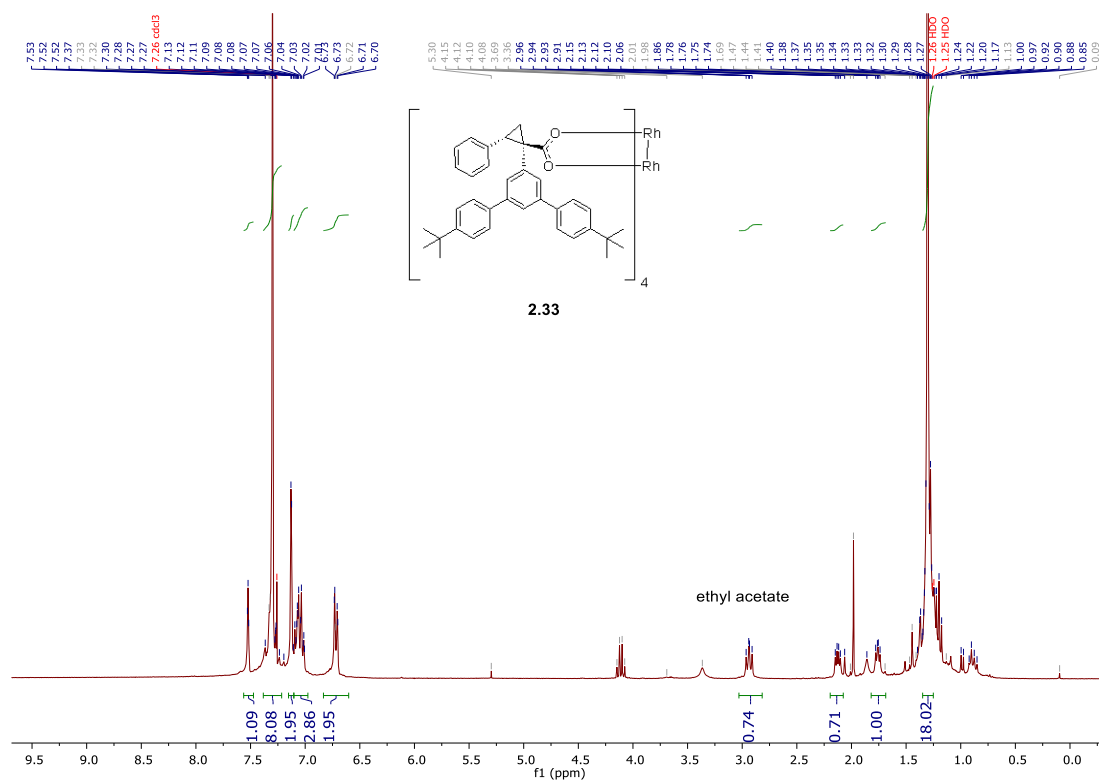


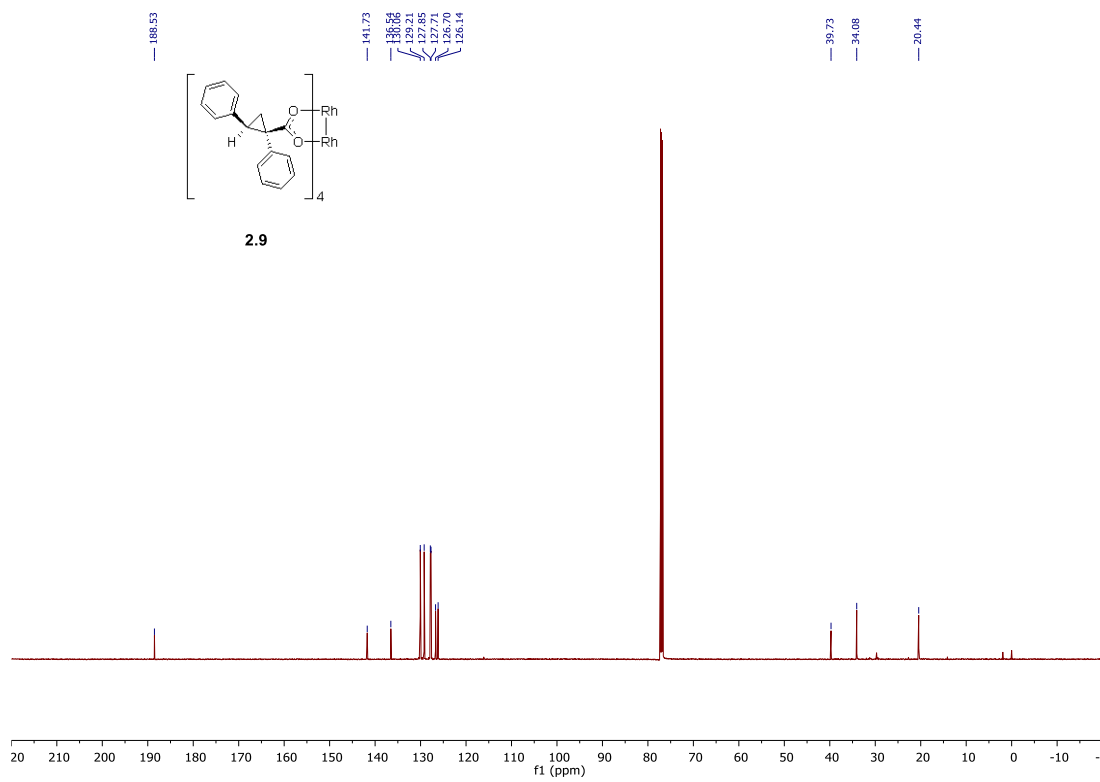
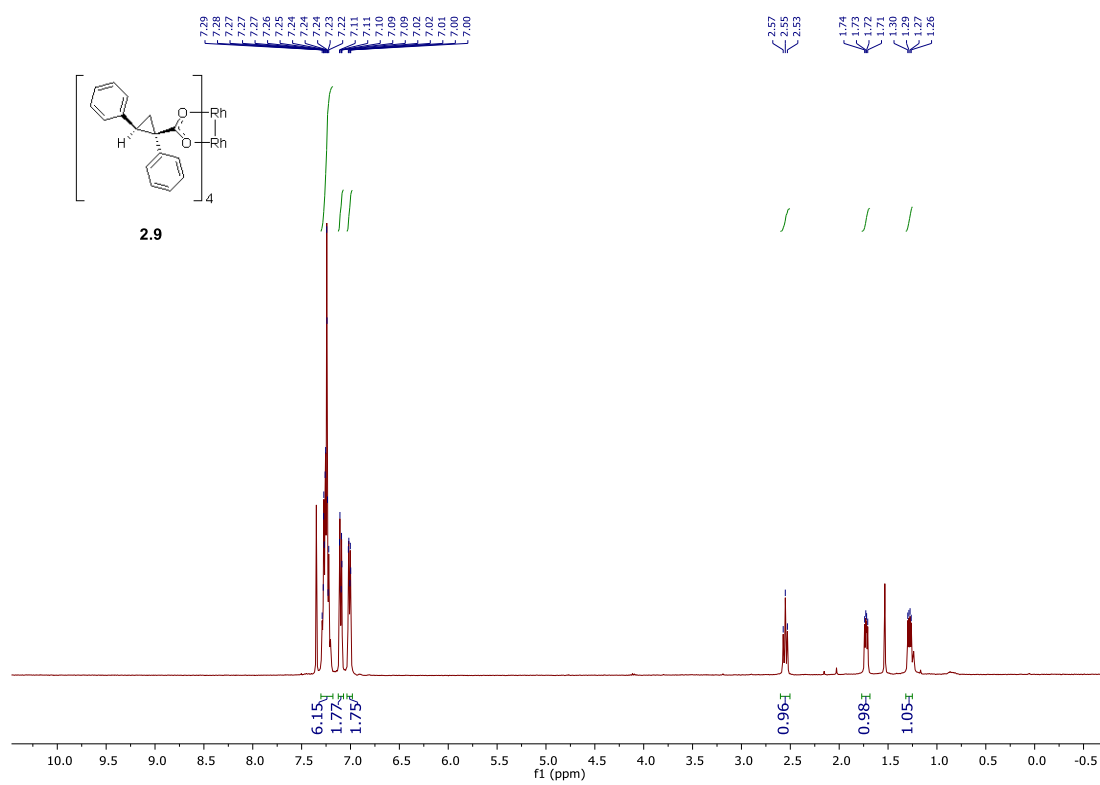


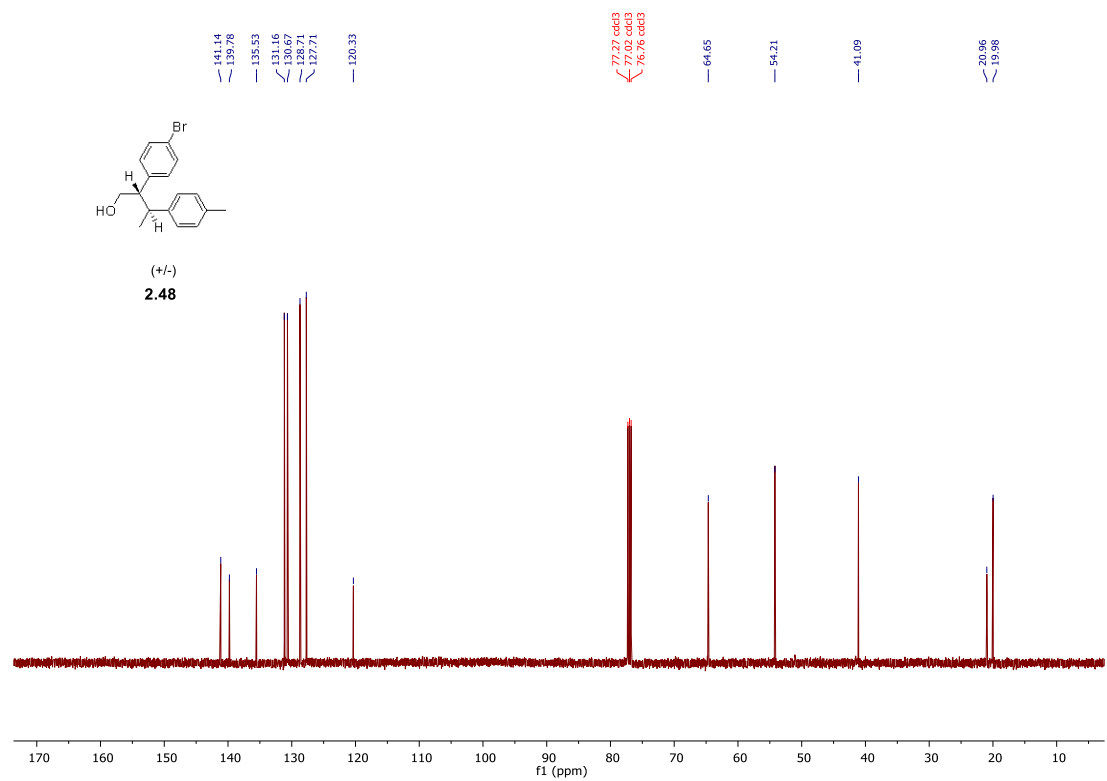
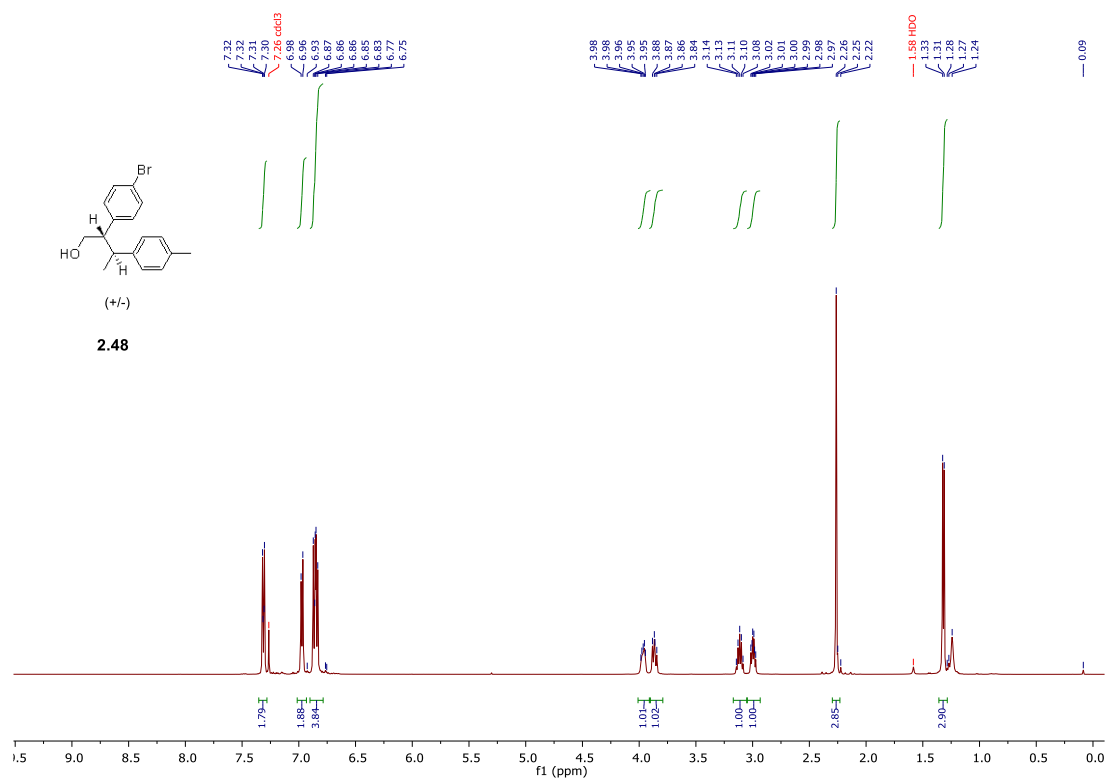


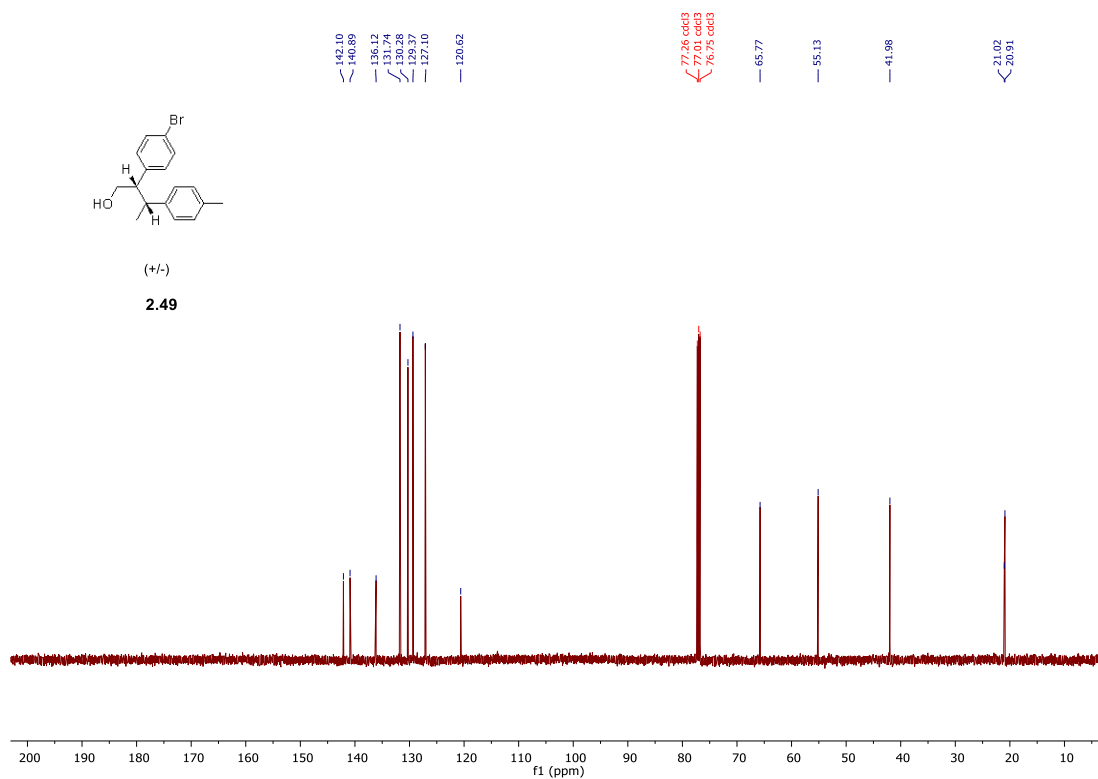
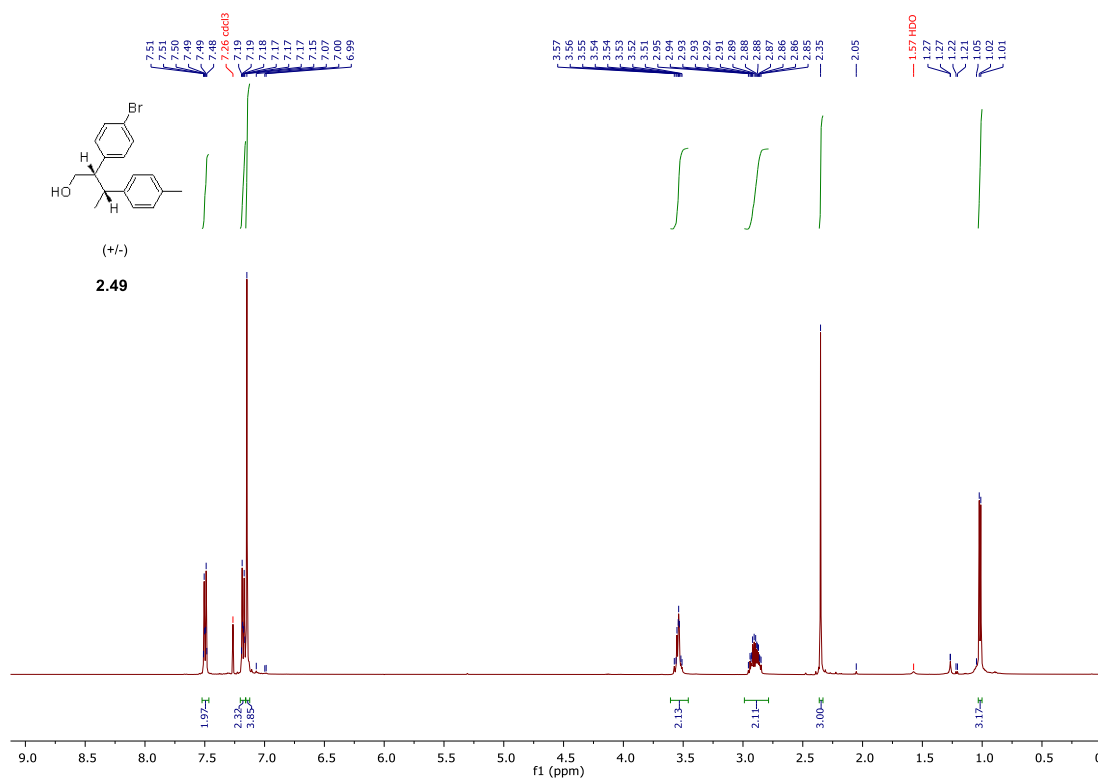


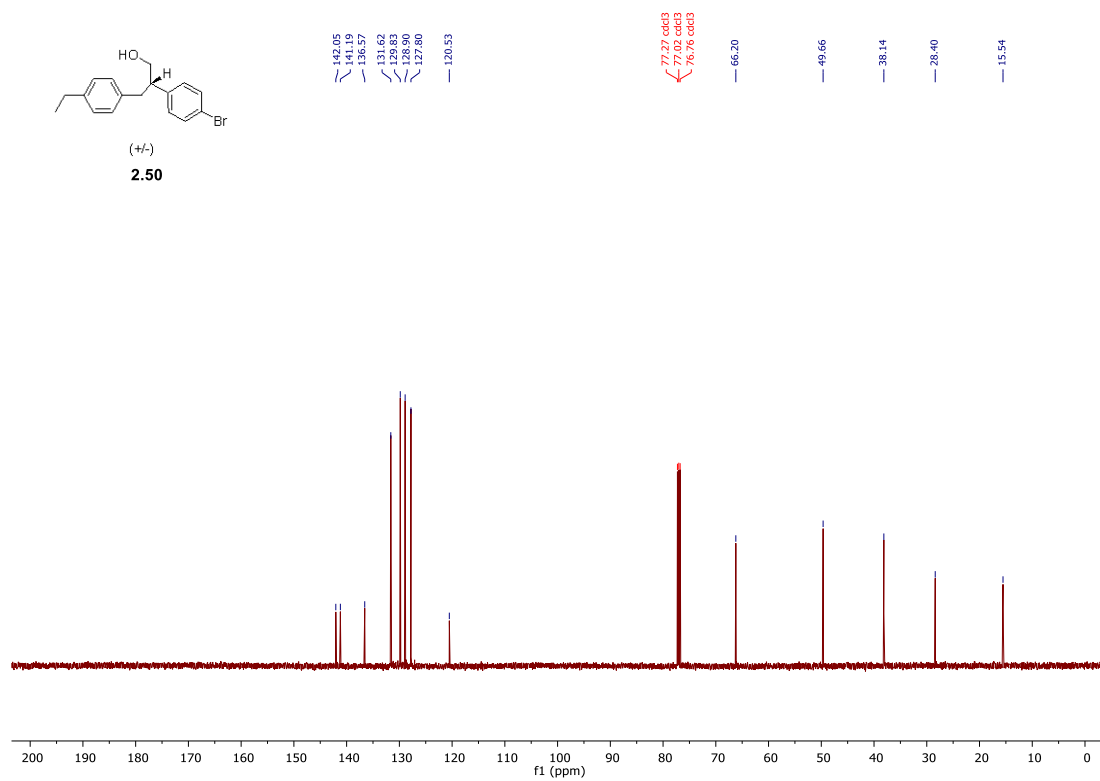
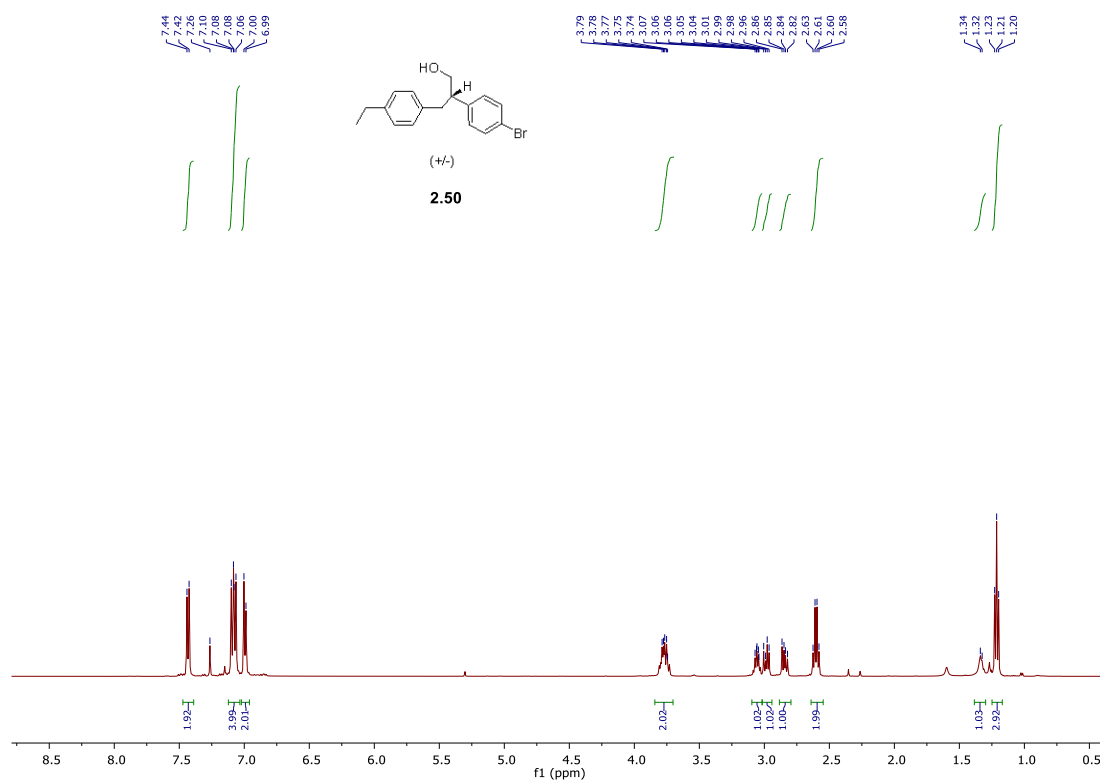


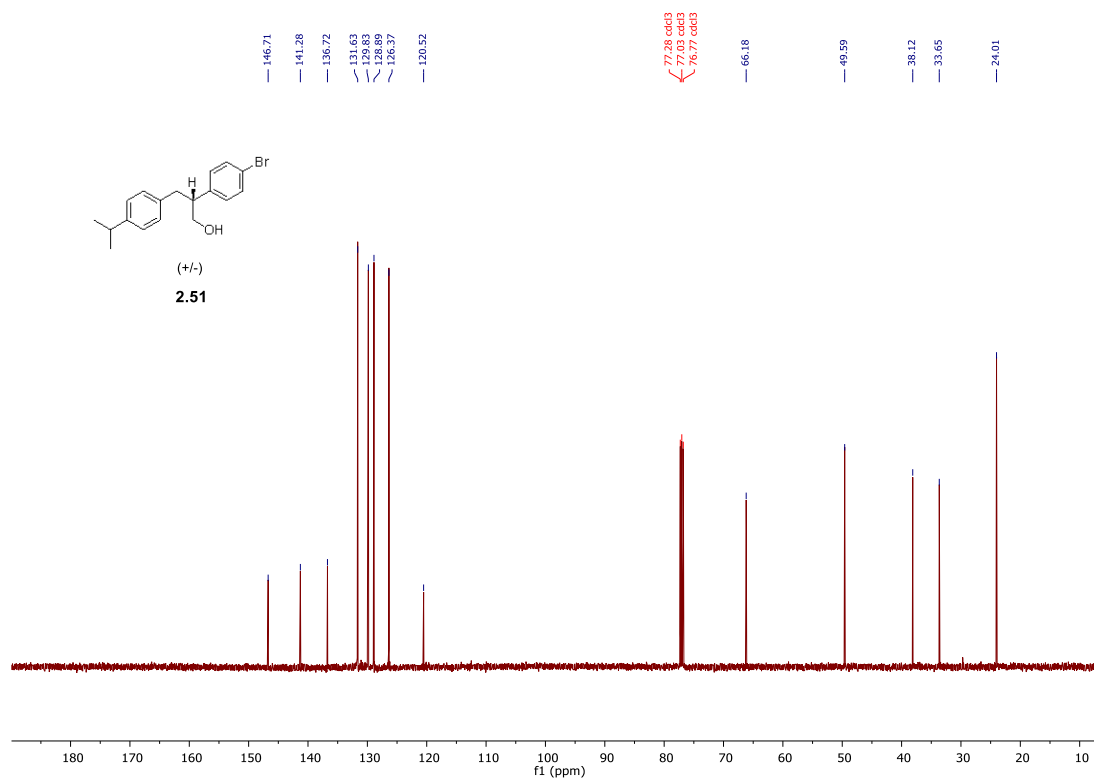
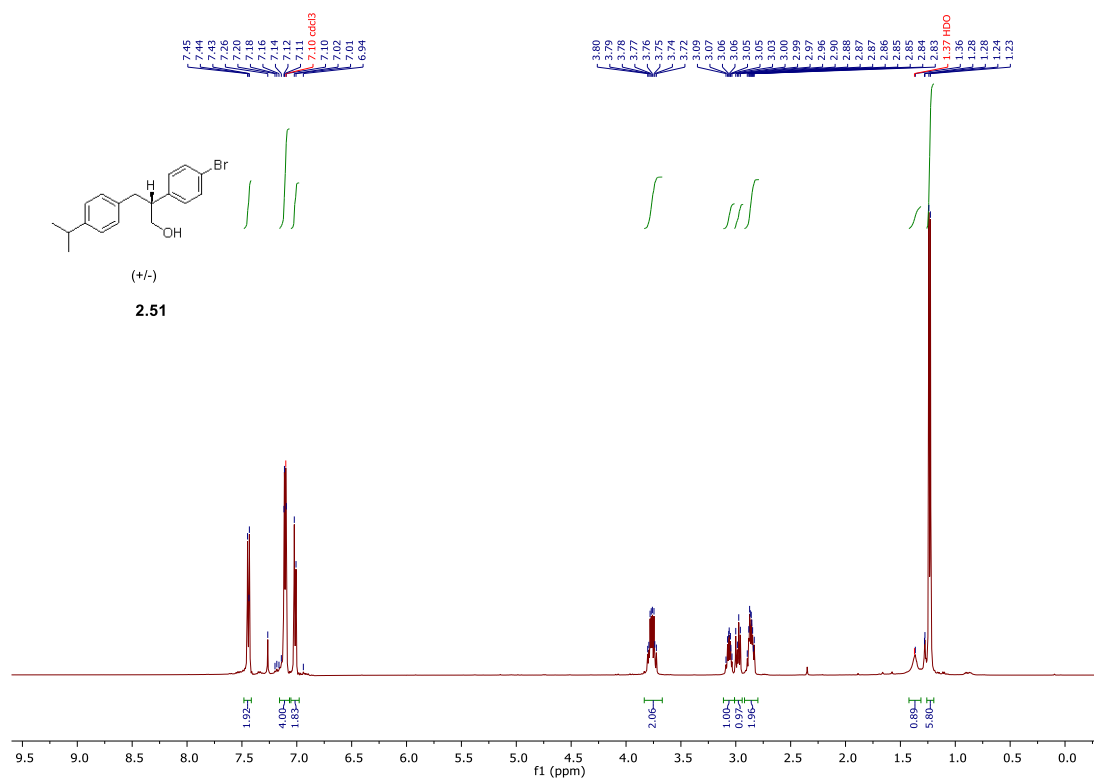


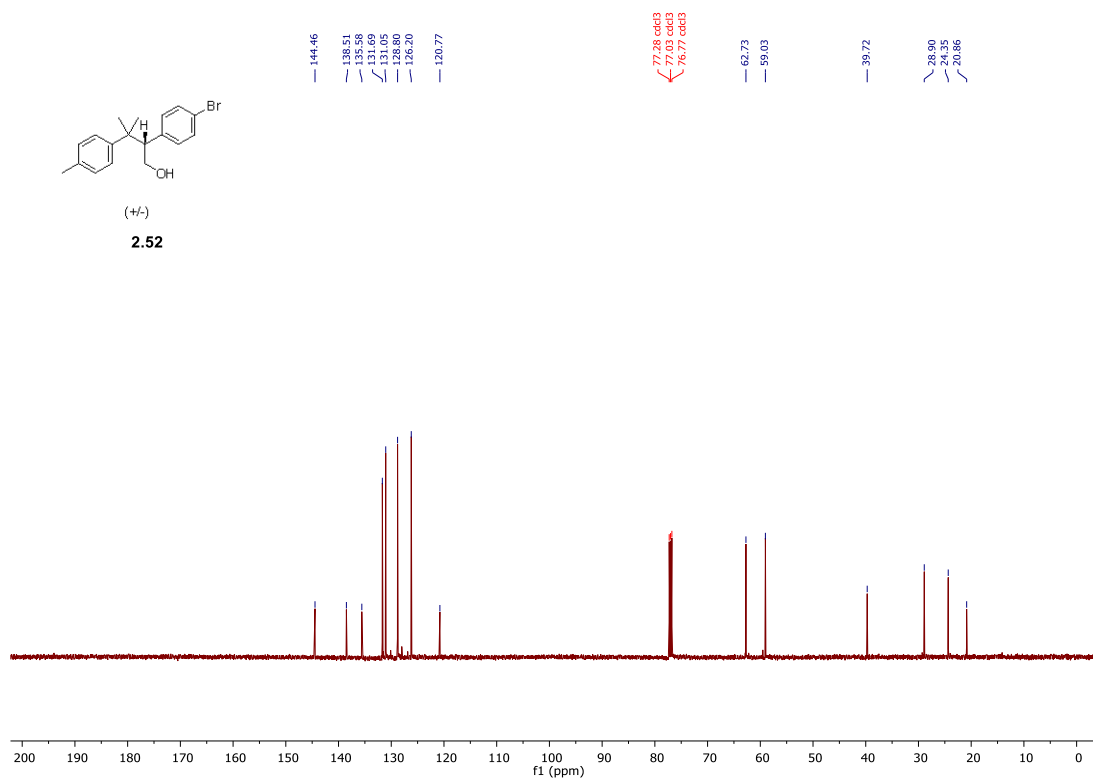
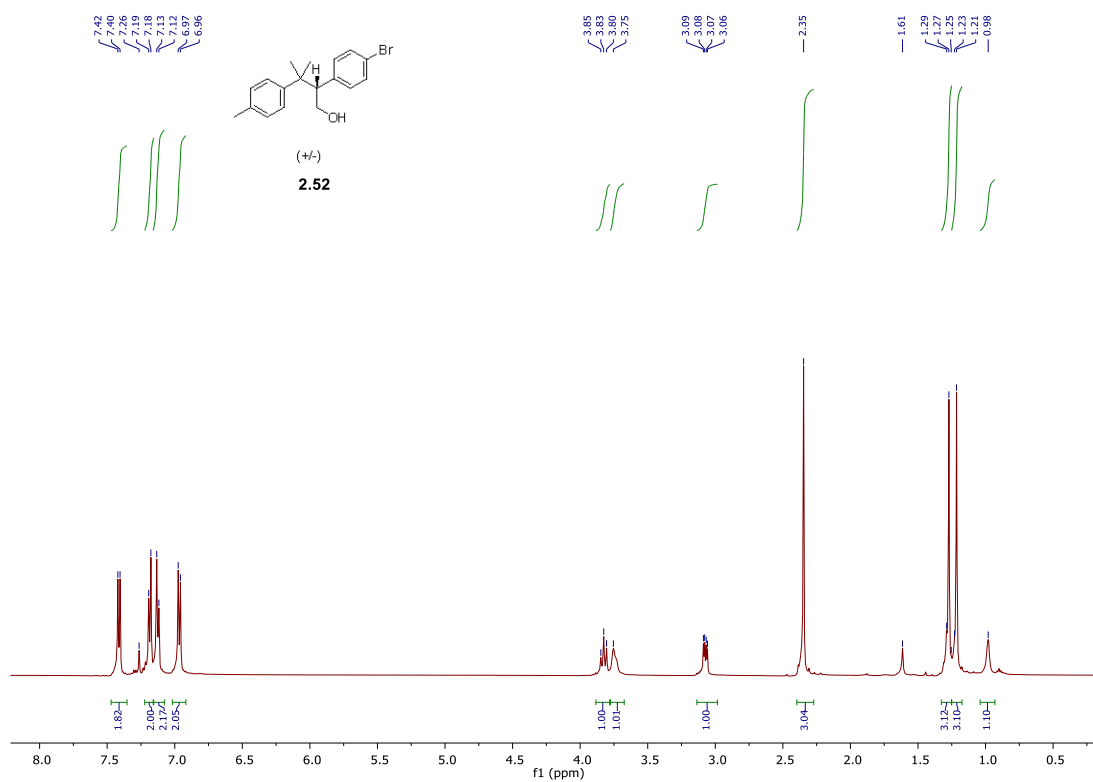




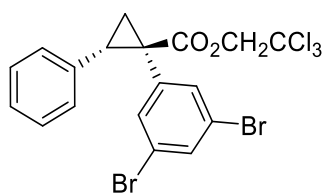




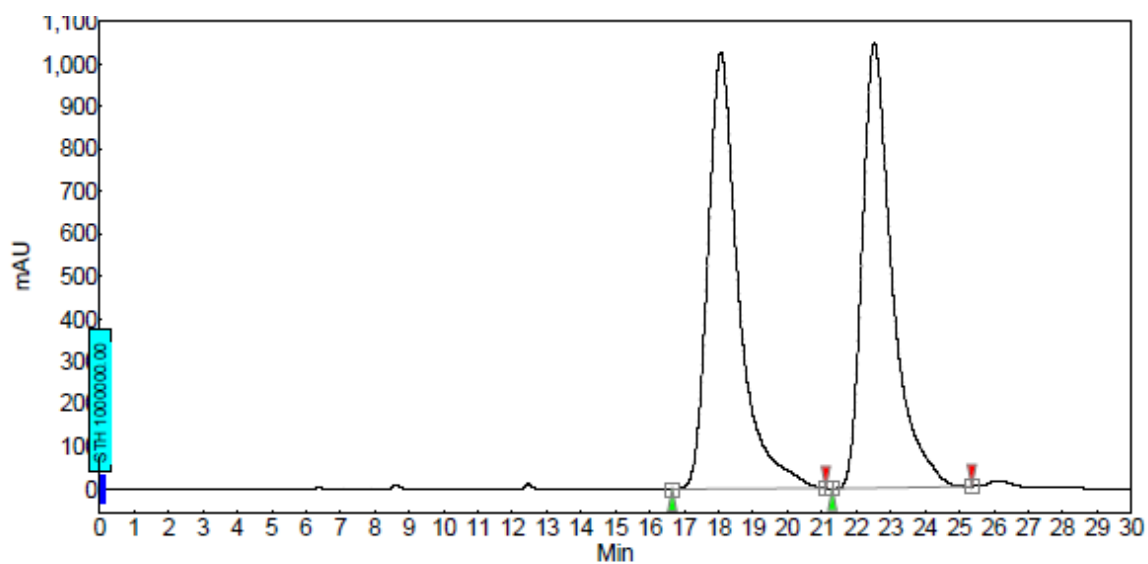




S.2.8 Chiral HPLC Traces

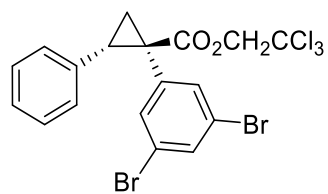


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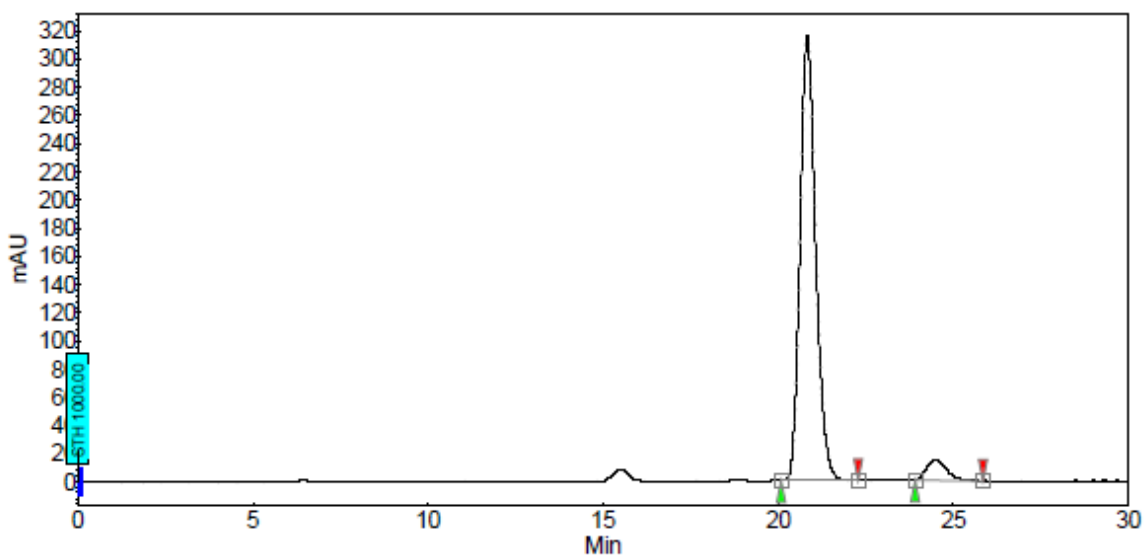
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	18.07	50.22	1026.8	1064.7	50.225
2	UNKNOWN	22.53	49.78	1047.6	1055.1	49.775
Total			100.00	2074.4	2119.8	100.000

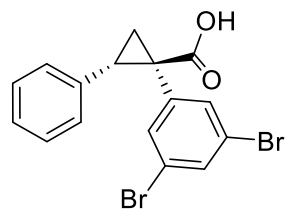


(2.23)

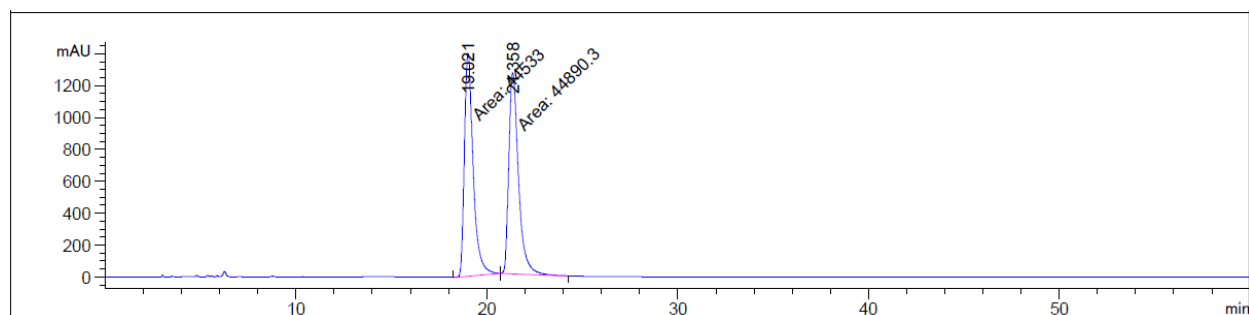
(Reaction ee)

**Peak results :**

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	20.83	94.48	315.7	163.4	94.475
2	UNKNOWN	24.47	5.52	14.5	9.6	5.525
Total			100.00	330.2	173.0	100.000



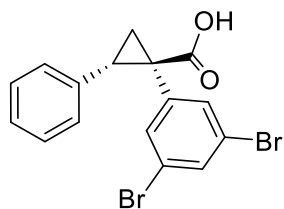
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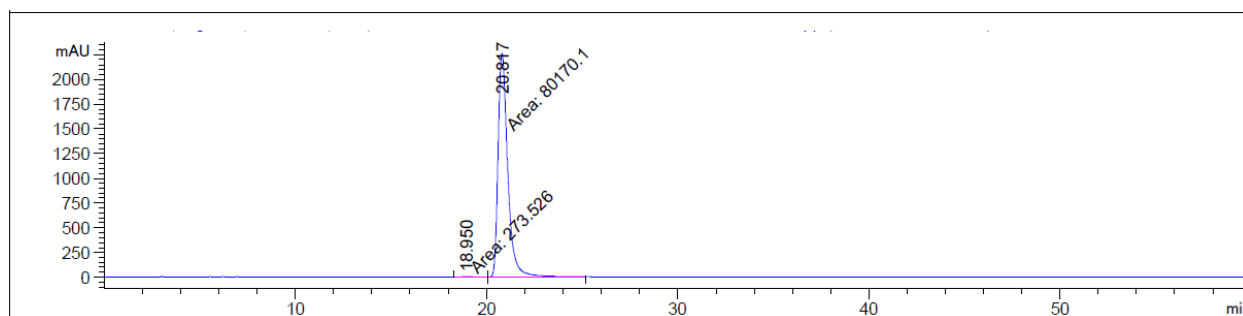
Signal 2: DAD1 B, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.021	MM	0.5307	4.45330e4	1398.56287	49.8002
2	21.358	MM	0.5926	4.48903e4	1262.58093	50.1998

Totals : 8.94234e4 2661.14380

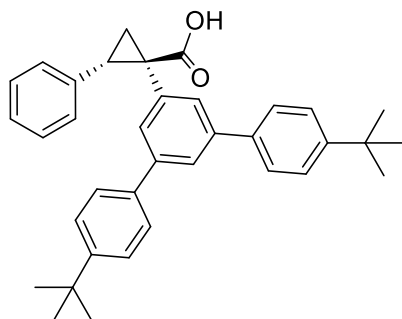
**(2.27)**

(Enantioenriched by fractional crystallization)

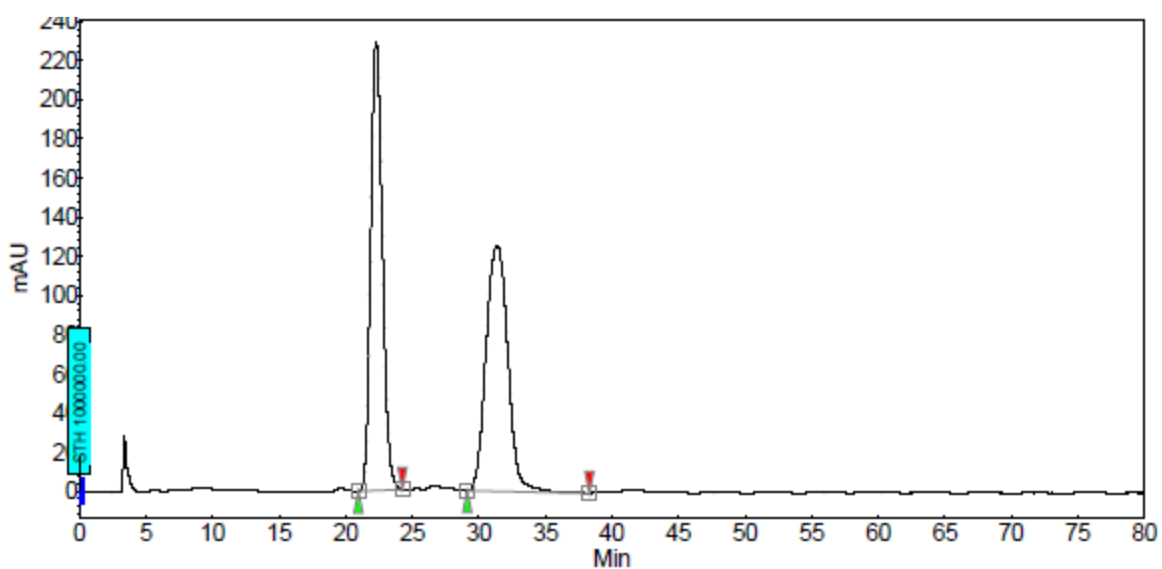


Signal 2: DAD1 B, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.950	MM	0.9231	273.52612	4.93874	0.3400
2	20.817	MM	0.5896	8.01701e4	2266.10400	99.6600

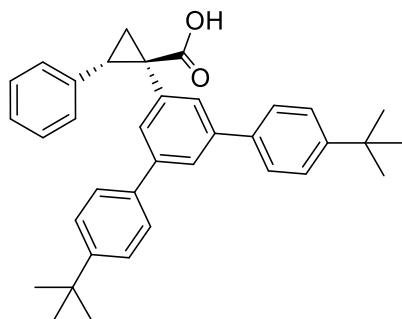


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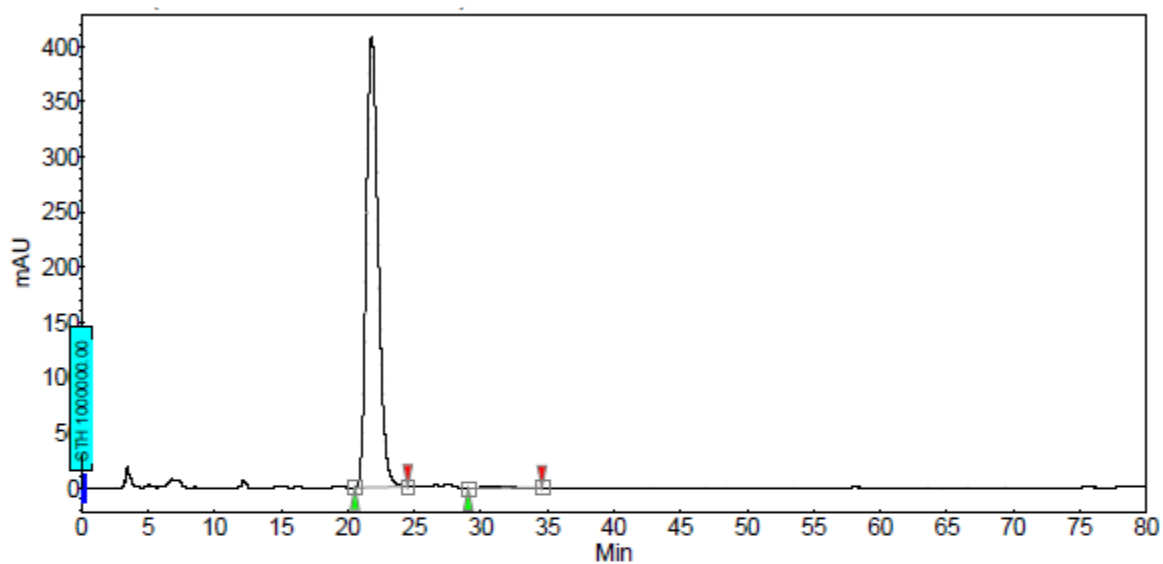
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	22.28	49.42	229.1	234.3	49.415
2	UNKNOWN	31.36	50.58	125.6	239.8	50.585
Total			100.00	354.7	474.1	100.000



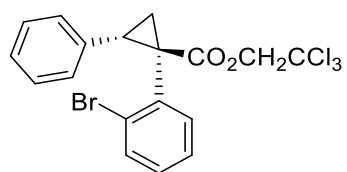
(2.31)

(Enantioenriched by fractional crystallization)

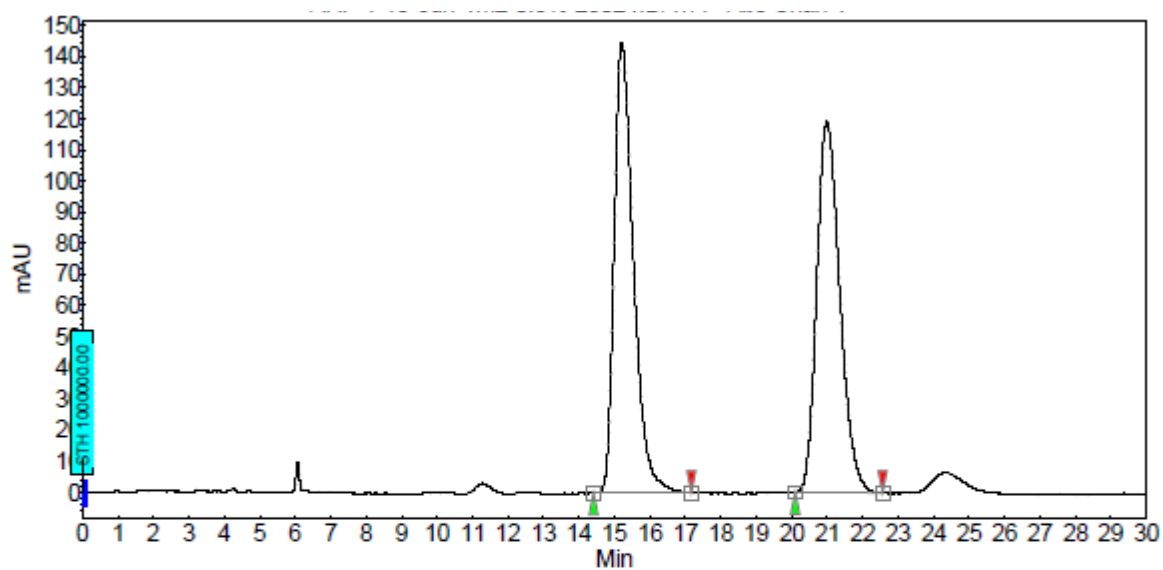


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	21.79	99.28	408.0	422.5	99.279
2	UNKNOWN	30.96	0.72	1.3	3.1	0.721
Total			100.00	409.3	425.5	100.000

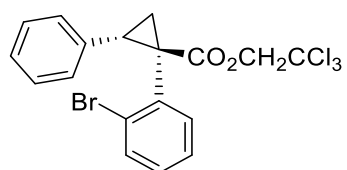


(+/-)

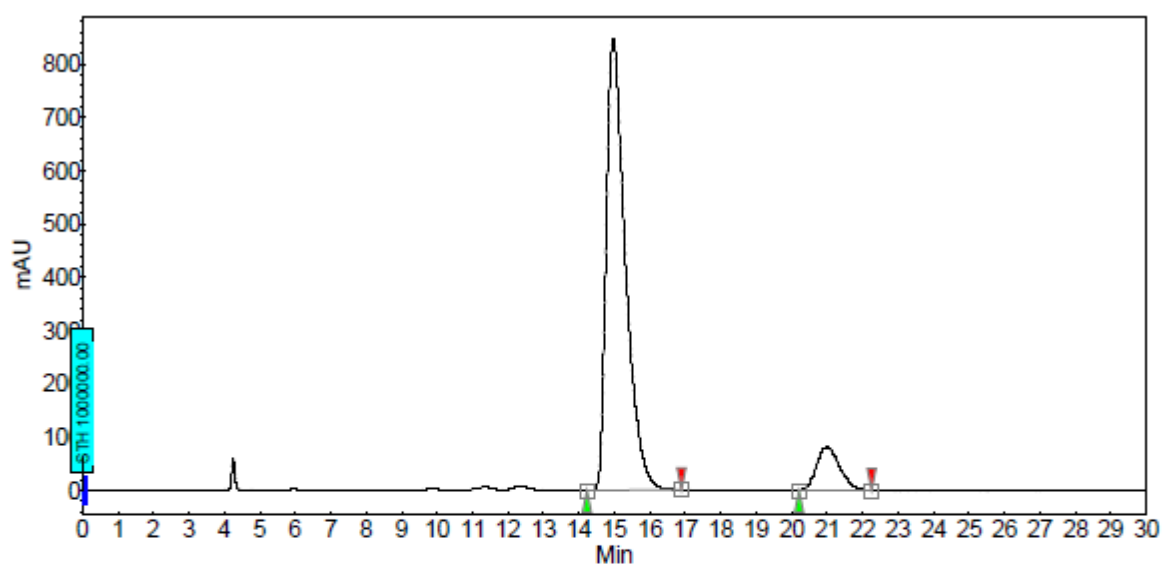


Peak results :

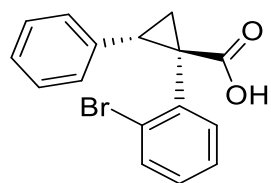
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	15.21	50.30	144.7	91.1	50.304
2	UNKNOWN	20.99	49.70	119.3	90.0	49.696
Total			100.00	264.0	181.0	100.000



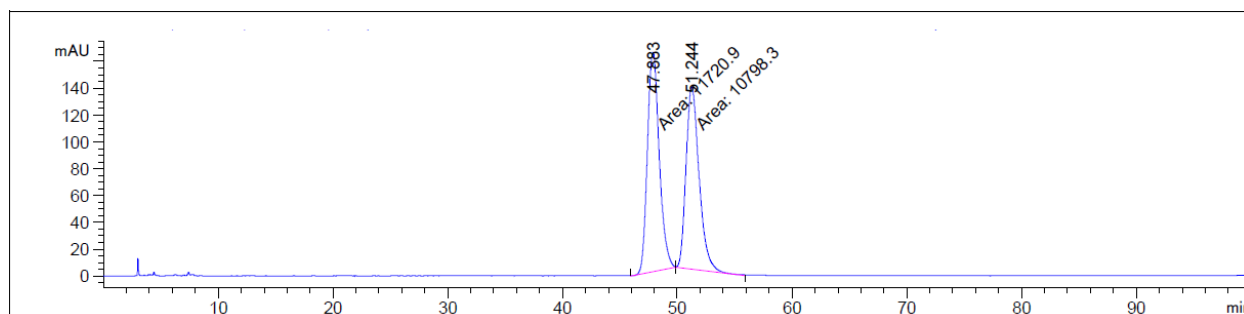
(2.24)

**Peak results :**

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	14.97	89.58	847.2	530.1	89.581
2	UNKNOWN	20.99	10.42	81.8	61.7	10.419
Total			100.00	928.8	591.8	100.000



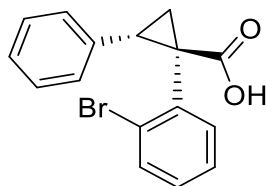
(+/-)



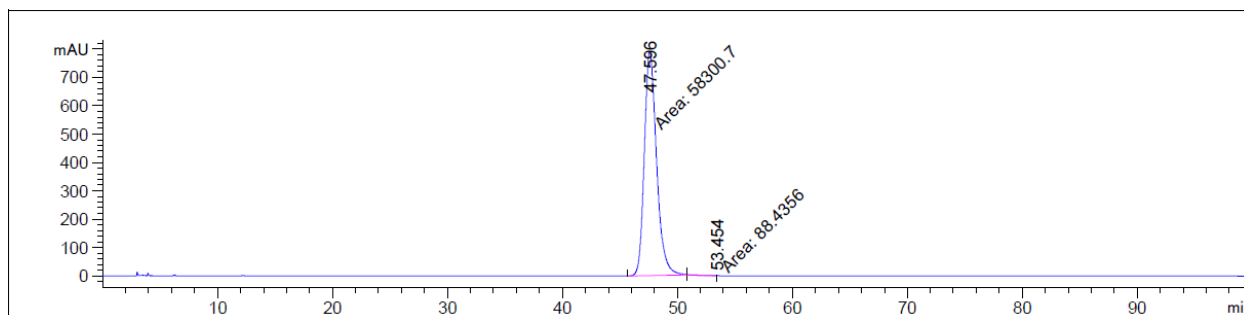
Signal 2: DAD1 B, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	47.883	MM	1.1954	1.17209e4	163.41687	52.0484
2	51.244	MM	1.3232	1.07983e4	136.01695	47.9516

Totals : 2.25192e4 299.43382

**(2.28)**

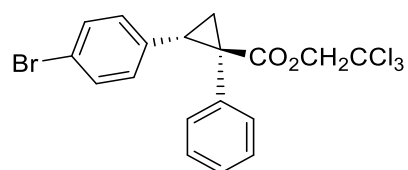
(Enantioenriched by fractional crystallization)



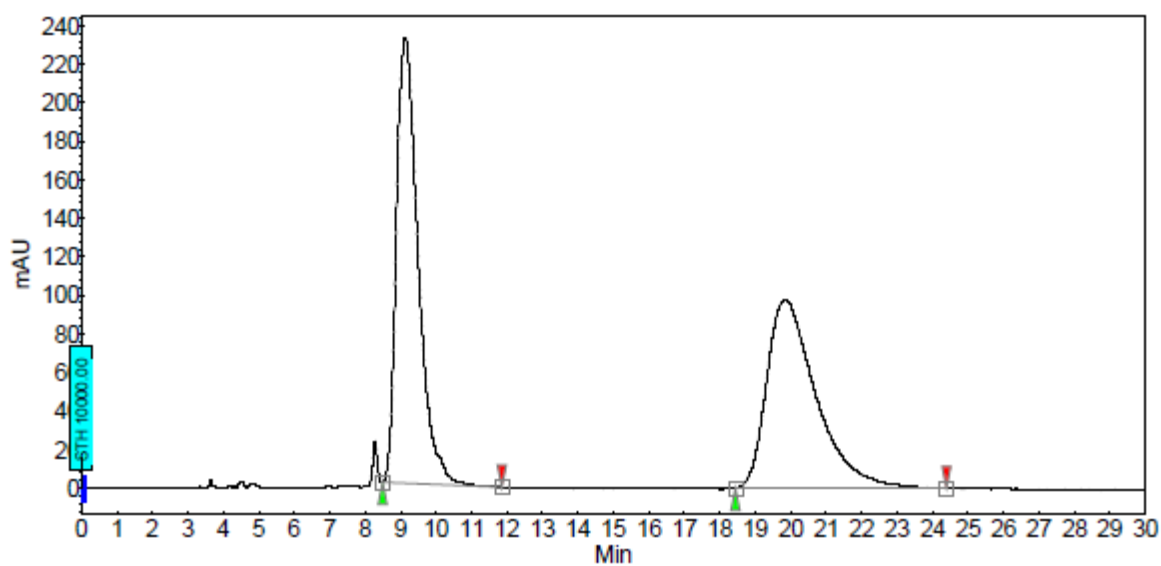
Signal 2: DAD1 B, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	47.596	MM	1.2319	5.83007e4	788.74695	99.8485
2	53.454	MM	0.9387	88.43561	1.57014	0.1515

Totals : 5.83891e4 790.31709

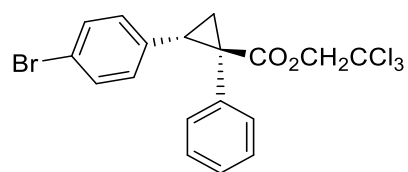


(+/-)



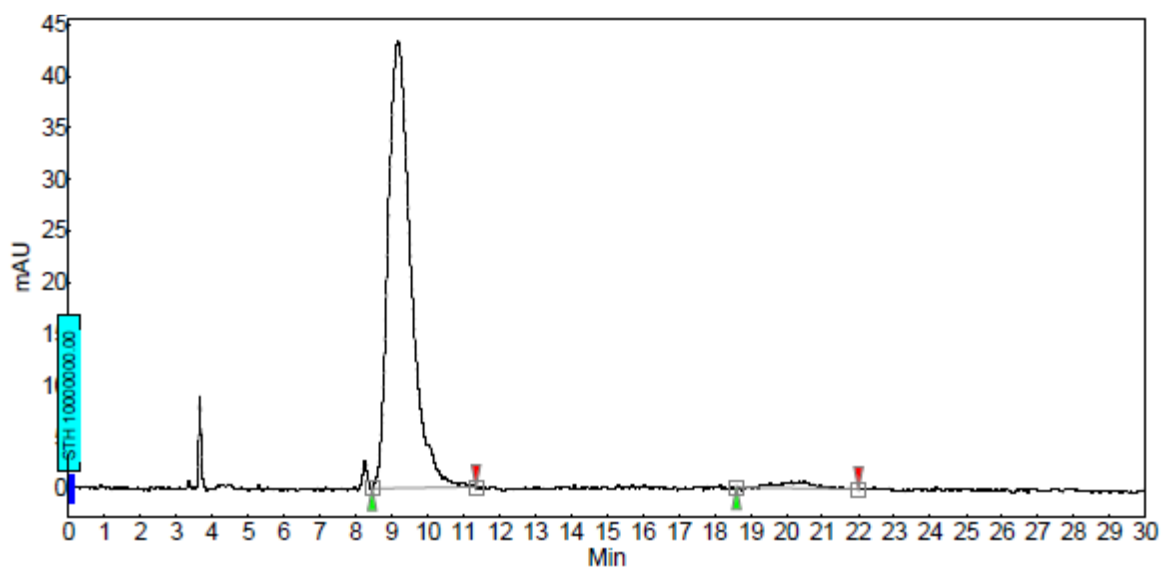
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	9.14	51.01	230.9	163.9	51.008
2	UNKNOWN	19.83	48.99	97.7	157.4	48.992
Total			100.00	328.6	321.3	100.000



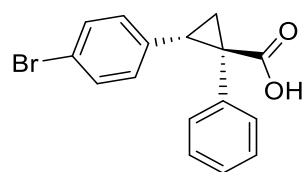
(2.22)

(Reaction ee)

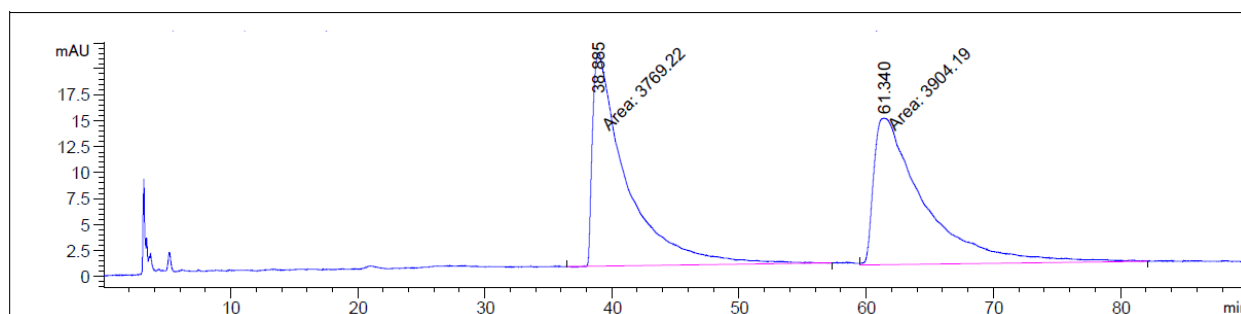


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	9.18	97.51	43.4	31.8	97.513
2	UNKNOWN	20.36	2.49	0.7	0.8	2.487
Total			100.00	44.0	32.6	100.000



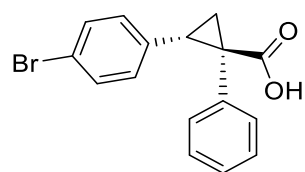
(+/-)



Signal 2: DAD1 B, Sig=230,4 Ref=off

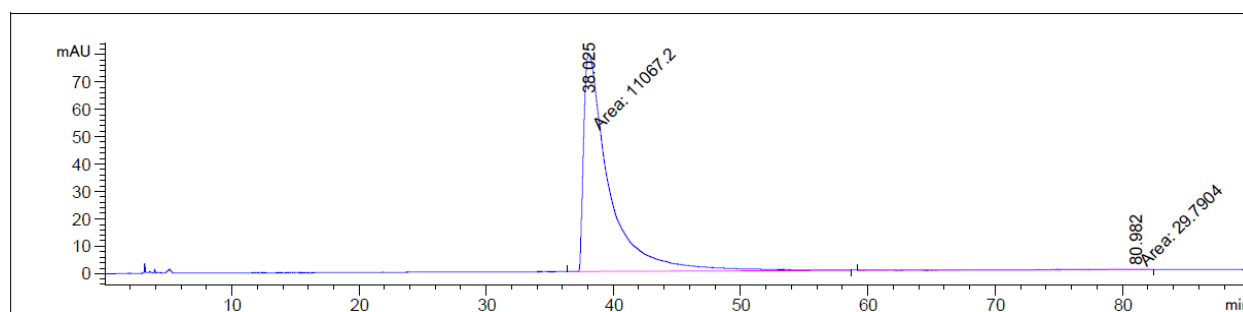
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.885	MM	3.0626	3769.21680	20.51223	49.1205
2	61.340	MM	4.6097	3904.18823	14.11572	50.8795

Totals : 7673.40503 34.62795



(2.25)

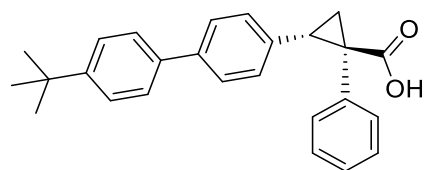
(Enantioenriched by fractional crystallization)



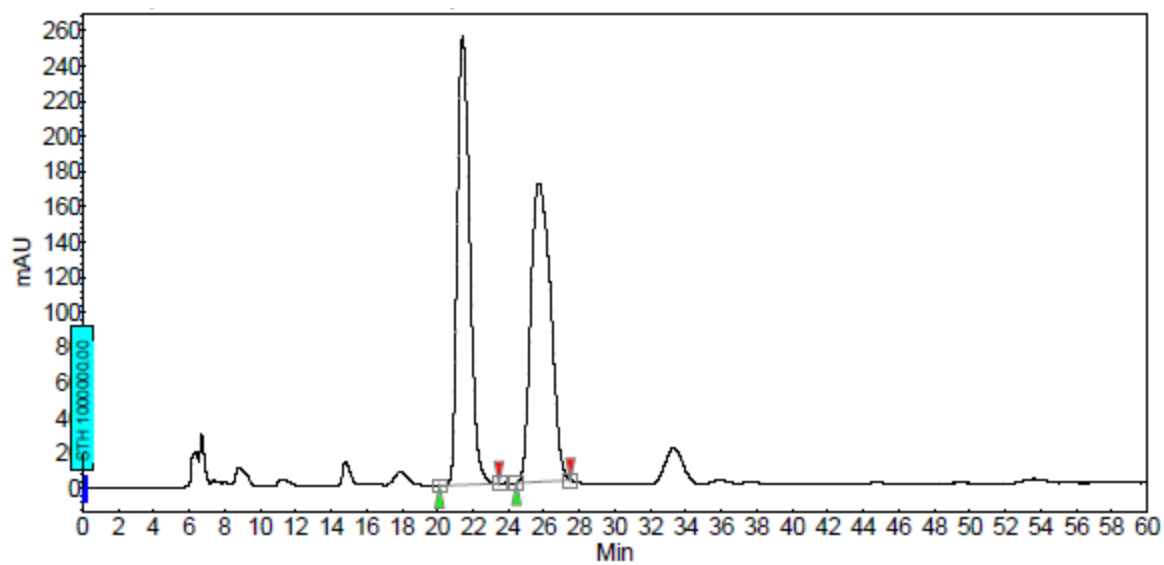
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.025	MM	2.3140	1.10672e4	79.71323	99.7315
2	80.982	MM	8.9129	29.79045	5.57069e-2	0.2685

Totals : 1.10970e4 79.76893

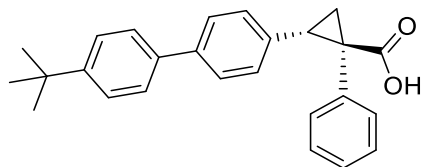


(+/-)



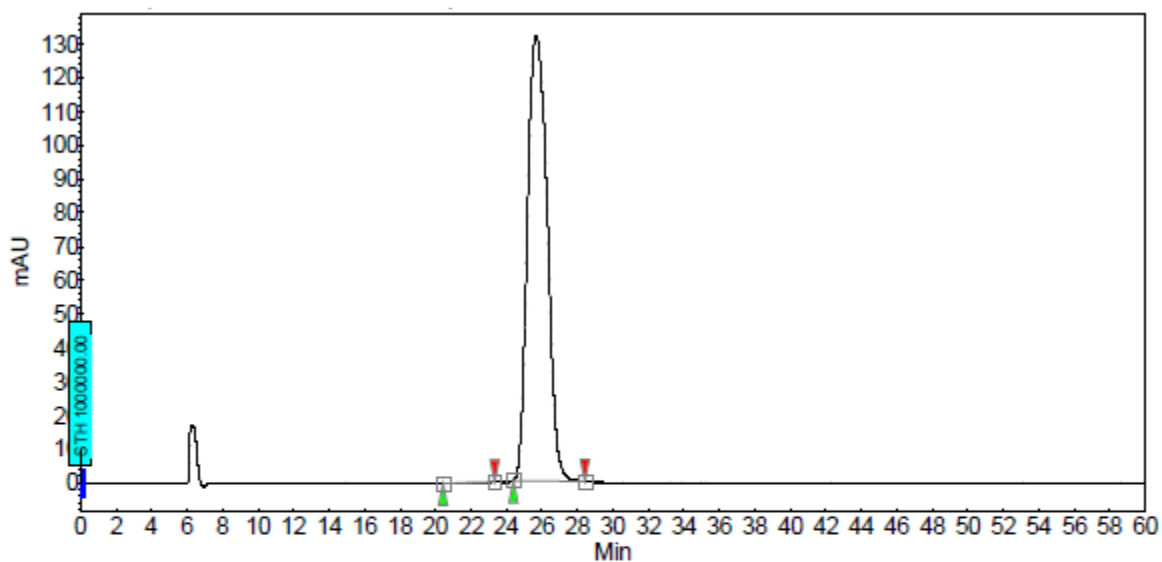
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	21.41	48.89	255.1	207.5	48.890
2	UNKNOWN	25.71	51.31	169.5	218.6	51.310
Total			100.00	424.6	426.1	100.000

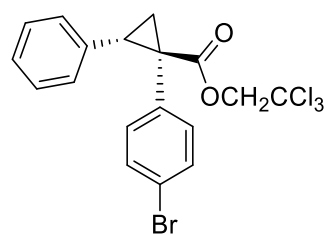


(2.42)

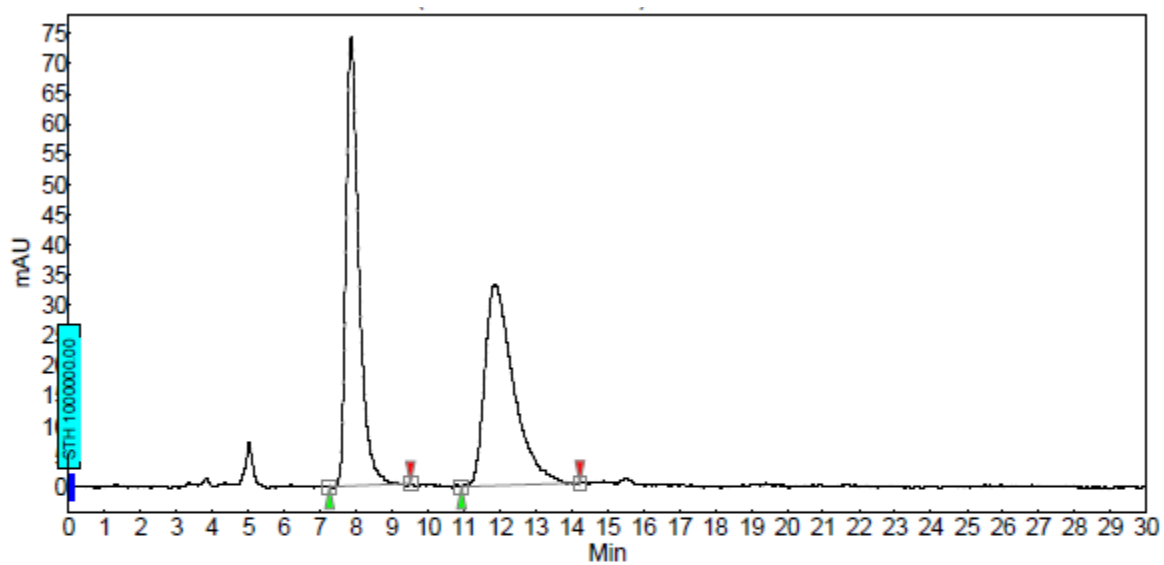
(Enantioenriched by fractional crystallization)

**Peak results :**

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	22.54	0.16	0.3	0.3	0.156
2	UNKNOWN	25.67	99.84	131.9	170.0	99.844
Total			100.00	132.2	170.3	100.000

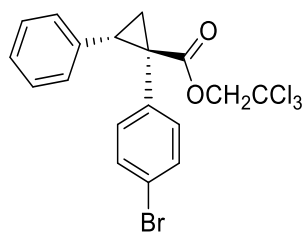


(+/-)



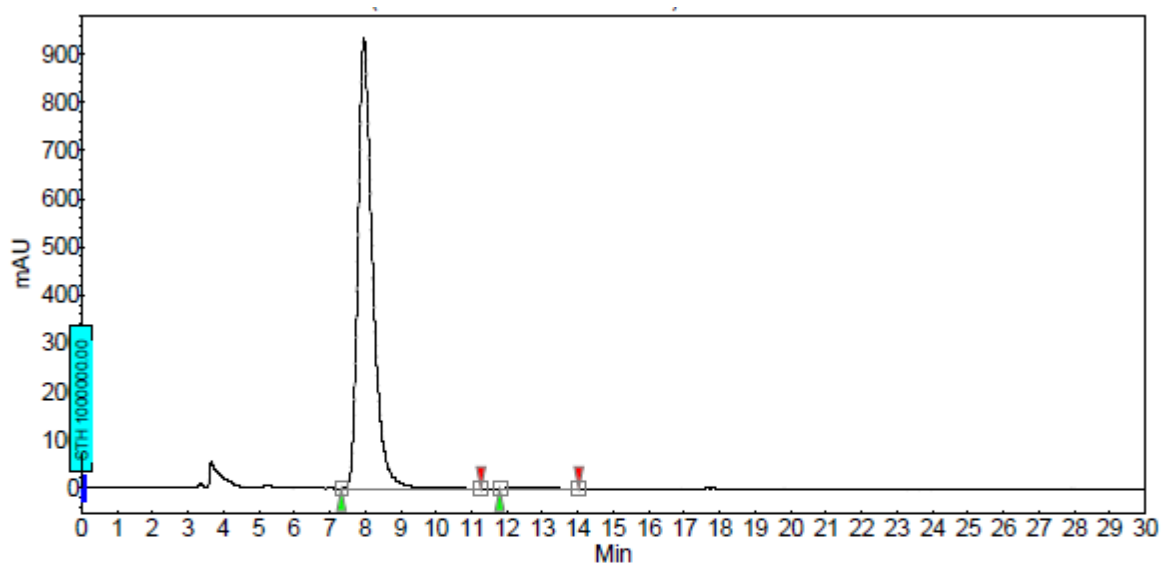
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	7.86	49.99	74.3	30.9	49.991
2	UNKNOWN	11.85	50.01	33.4	30.9	50.009
Total			100.00	107.7	61.8	100.000



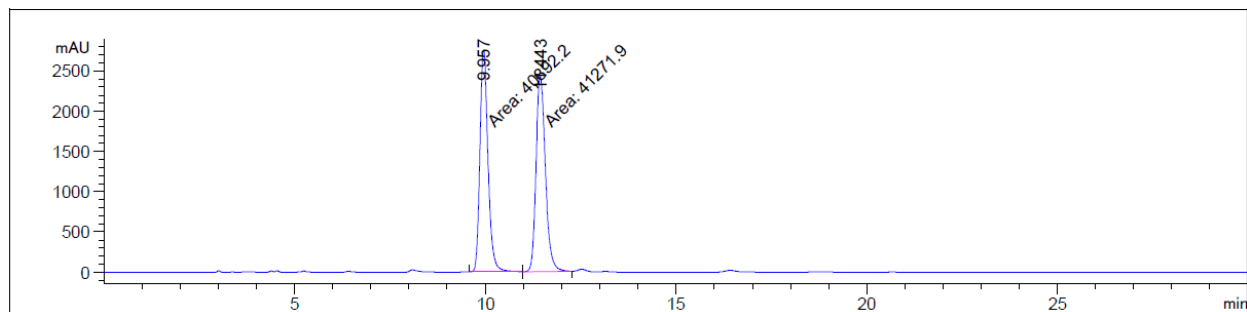
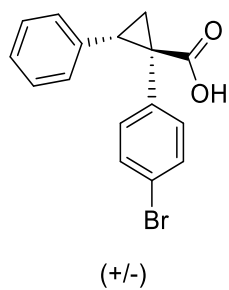
(2.18)

(Enantioenriched by fractional crystallization)



Peak results :

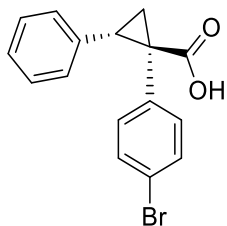
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	7.96	99.39	935.1	448.4	99.387
2	UNKNOWN	12.87	0.61	2.5	2.8	0.613
Total			100.00	937.6	451.2	100.000



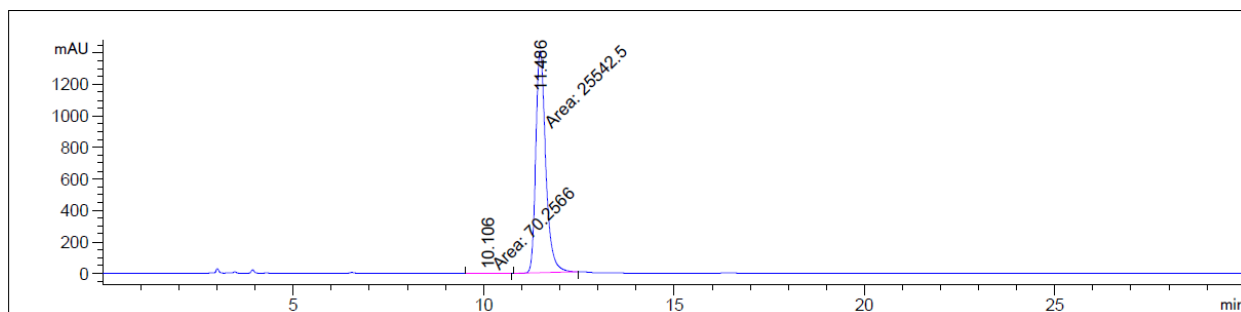
Signal 2: DAD1 B, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.957	MM	0.2470	4.08922e4	2759.04980	49.7689
2	11.443	MM	0.2840	4.12719e4	2422.27197	50.2311

Totals : 8.21641e4 5181.32178

**(2.26)**

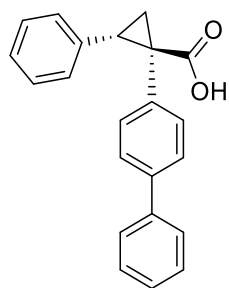
(Enantioenriched by fractional crystallization)



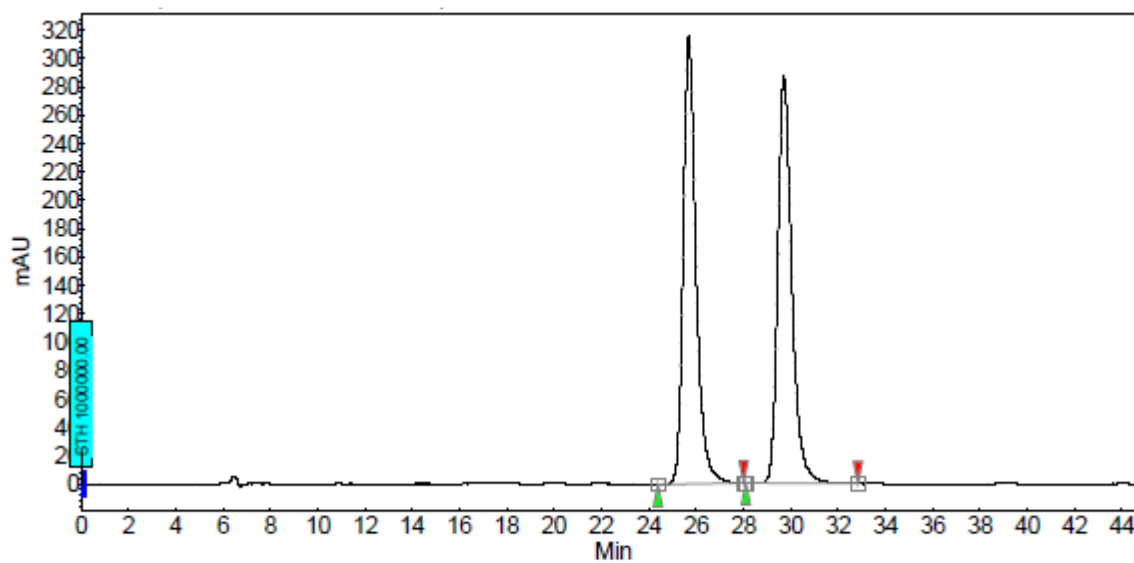
Signal 2: DAD1 B, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.106	MM	0.8629	70.25660	1.35702	0.2743
2	11.486	MM	0.3018	2.55425e4	1410.36853	99.7257

Totals : 2.56127e4 1411.72555

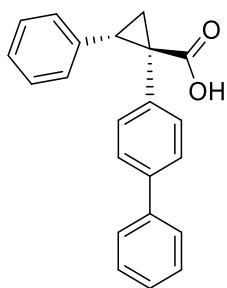


(+/-)



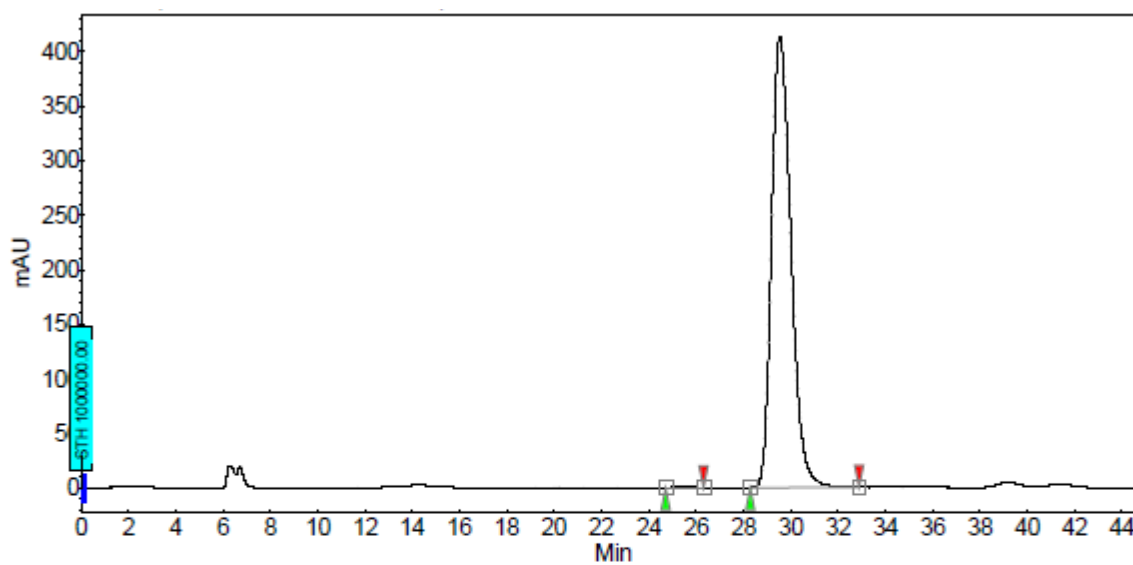
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	25.69	50.01	315.7	197.7	50.008
1	UNKNOWN	29.71	49.99	286.9	197.6	49.992
Total			100.00	602.6	395.3	100.000



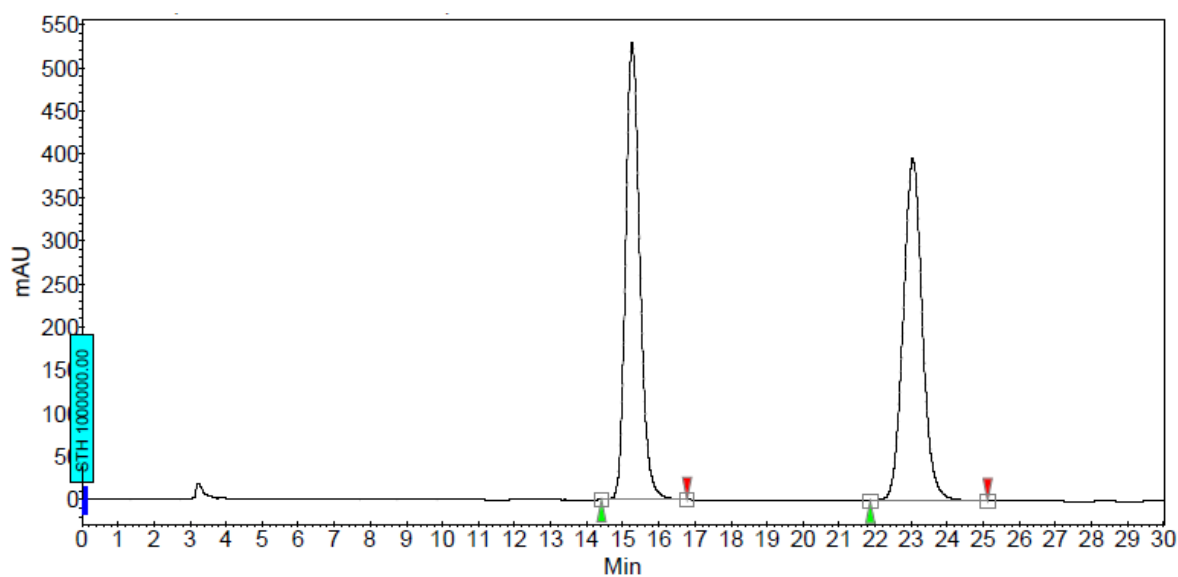
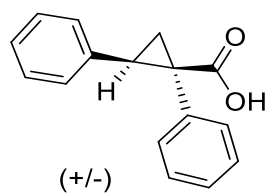
(2.43)

(Enantioenriched by fractional crystallization)



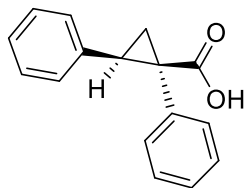
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	25.43	0.18	0.8	0.7	0.175
2	UNKNOWN	29.54	99.82	413.1	394.8	99.825
Total			100.00	413.9	395.5	100.000



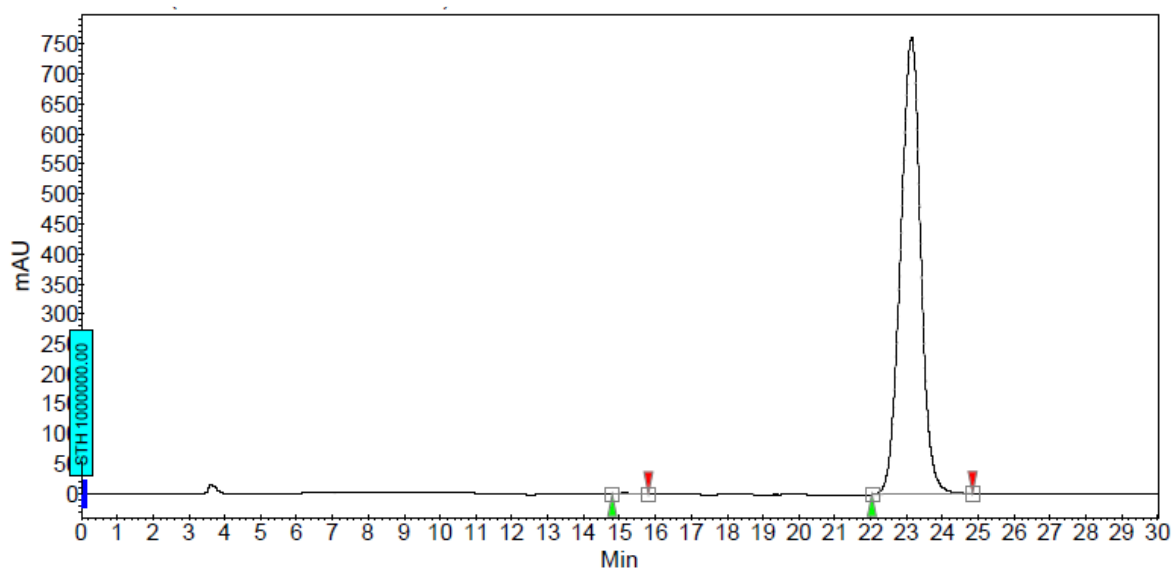
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	15.26	50.00	529.9	242.8	50.002
2	UNKNOWN	23.05	50.00	396.4	242.8	49.998
Total			100.00	926.4	485.5	100.000

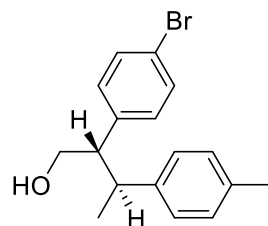


(2.28)

(Enantioenriched by fractional crystallization)

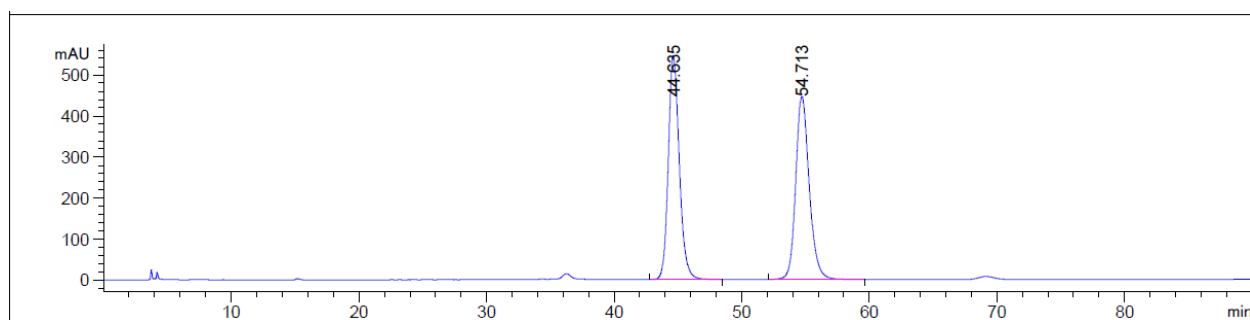
**Peak results :**

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	15.16	0.15	1.6	0.8	0.153
2	UNKNOWN	23.14	99.85	762.4	495.1	99.847
Total			100.00	764.1	495.8	100.000



(+/-)

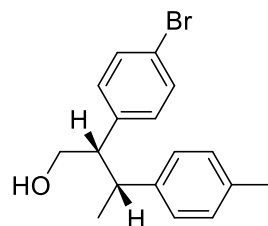
2.48



Signal 2: DAD1 B, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.635	BB	0.9156	3.27277e4	545.79993	49.8233
2	54.713	BB	1.1296	3.29599e4	446.27936	50.1767

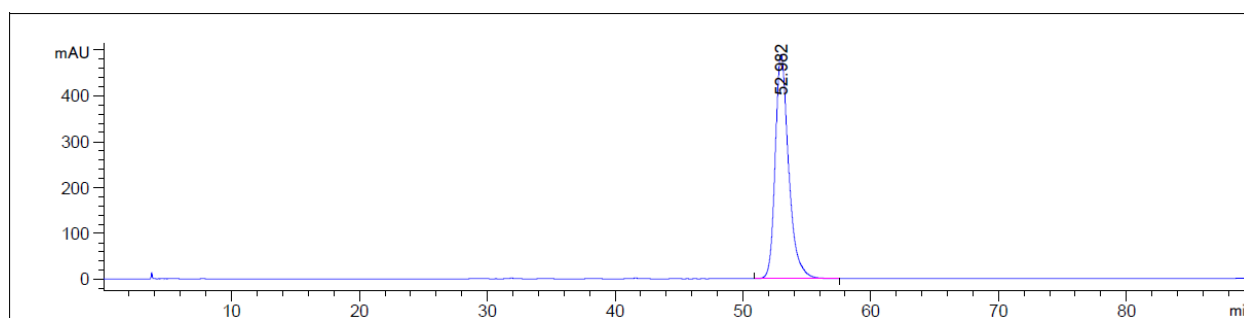
Totals : 6.56876e4 992.07928



(+/-)

2.49

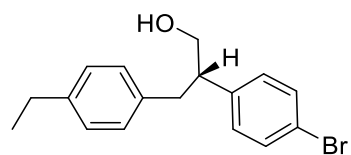
(The enantiomers of minor diastereomer **S2** are not resolved under these conditions. Chromatogram shown for reference)



Signal 2: DAD1 B, Sig=230,4 Ref=360,100

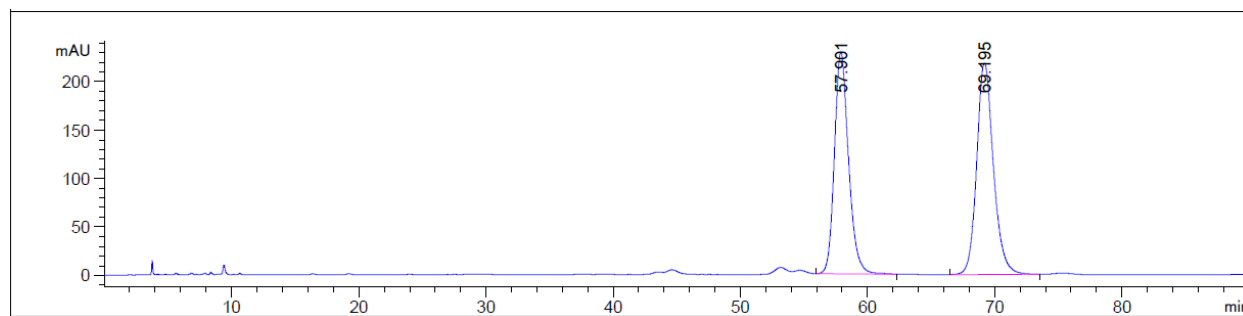
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	52.982	BB	1.1040	3.57025e4	488.89877	100.0000

Totals : 3.57025e4 488.89877



(+/-)

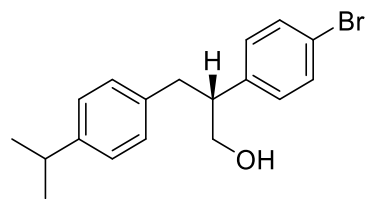
2.50



Signal 2: DAD1 B, Sig=230,4 Ref=360,100

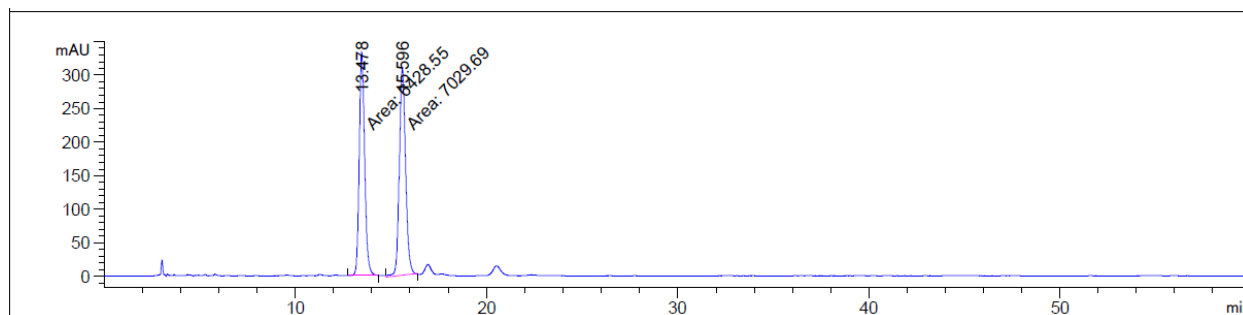
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	57.901	BB	1.1818	1.76933e4	228.89821	46.9846
2	69.195	BB	1.3705	1.99643e4	217.97707	53.0154

Totals : 3.76575e4 446.87527



(+/-)

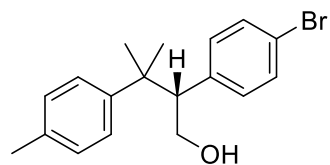
2.51



Signal 2: DAD1 B, Sig=230,4 Ref=360,100

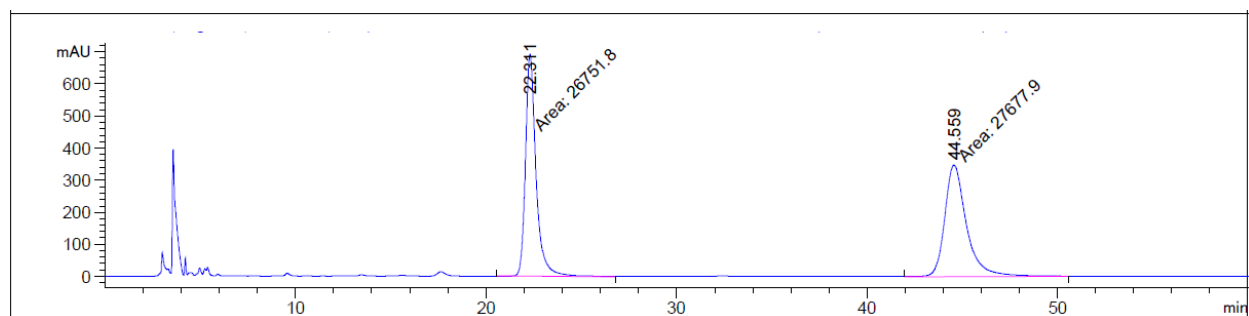
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.478	MM	0.3220	6428.55322	332.78116	47.7667
2	15.596	MM	0.3780	7029.68604	309.97339	52.2333

Totals : 1.34582e4 642.75455



(+/-)

2.52



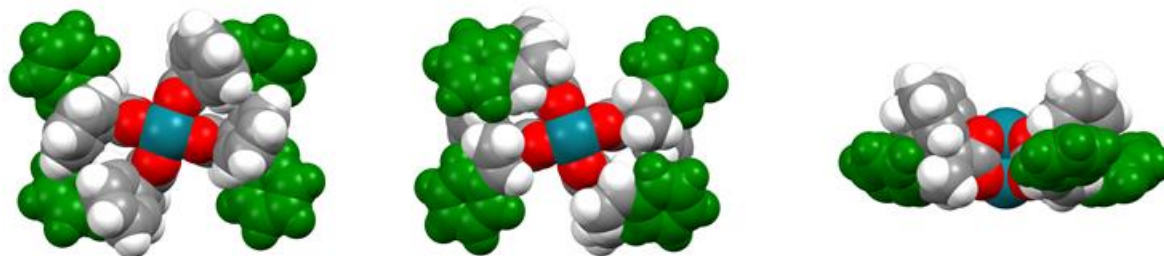
Signal 2: DAD1 B, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.311	MM	0.6437	2.67518e4	692.61169	49.1493
2	44.559	MM	1.3252	2.76779e4	348.09927	50.8507

Totals : 5.44297e4 1040.71097

S.2.9 Computational Studies¹²

Orientation A for Compound 2.5



Orientation A, C_2 , α , α' , α , α' conformation
 $\Delta H/\Delta G = 0.0/0.0$ kcal mol⁻¹

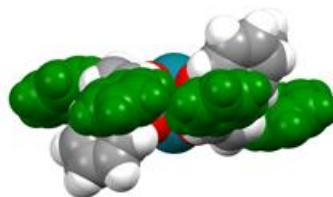
Entry	SCF Energy (a. u.)	Enthalpy (a. u.)	Gibbs Free Energy (a. u.)
Orientation A	-3291.48906467	-3290.424561	-3290.596724
C	17.71798700	4.94735500	6.72877000
C	8.41357200	2.76828200	2.22359800
H	7.89318600	2.02810700	1.62316100
C	18.96993900	5.25928400	7.48288100
O	17.08406400	5.92205800	6.19906800
C	11.77773000	-0.02112700	3.45027000
H	11.43656800	-0.46761900	4.37961700
C	19.76199100	6.45237800	6.85673700
H	19.23690900	6.88355300	6.01187300
C	21.23423800	6.38912300	6.67412700
C	19.06332900	6.60487400	8.16877400
H	19.66645400	6.64334000	9.06973200
H	18.16679400	7.21417100	8.18855600
C	12.58366100	1.92320500	2.24193500
C	23.50106600	5.96821100	7.44172000
H	24.17930000	5.69842700	8.24568500
C	12.26910500	-0.18810800	1.08997000
H	12.31802100	-0.77169300	0.17555400
C	24.00063100	6.22638500	6.16286200
H	25.06633200	6.15815400	5.96761300
O	14.50550900	4.95195900	3.12207300
C	23.11830400	6.58041200	5.14053700
H	23.49197000	6.79189500	4.14309000
C	22.13299000	6.05248300	7.69728900
H	21.76643600	5.83676200	8.69421400
Rh	15.78826800	5.50632300	4.64502400
C	19.72651600	4.07760500	8.00478100

C	7.77134900	3.36114100	3.31341600
H	6.75202700	3.08469800	3.56457400
C	20.36268200	3.21807100	7.09867200
H	20.28963900	3.41688200	6.03549900
C	9.72357300	3.11765400	1.89822700
H	10.20547400	2.63670900	1.05494700
C	21.08966700	2.12118400	7.55183800
H	21.58166400	1.47184600	6.83377500
C	12.15136000	1.31943800	3.43054200
H	12.10512200	1.90736700	4.34008500
C	21.19103400	1.86847600	8.92399800
H	21.76231800	1.01687600	9.28111700
C	11.83279900	-0.77965000	2.27618200
H	11.53637300	-1.82422700	2.28709700
C	20.55648600	2.71636800	9.83268700
H	20.62870700	2.52472500	10.89907300
C	12.64455200	1.15833600	1.07462900
H	12.98283500	1.61671200	0.15006200
C	19.82566300	3.81596000	9.37336600
H	19.33323400	4.47448700	10.08269300
O	17.39558200	3.71970800	6.62042900
C	14.19326700	3.71769100	3.01679000
O	14.82652700	2.75383800	3.55795900
C	12.95643500	3.37325700	2.25190700
C	21.74952200	6.66040600	5.39745700
H	21.06625100	6.93508000	4.59933800
C	11.83411000	4.44868300	2.41351200
H	12.16691200	5.28983300	3.01121600
C	12.55338700	4.28543100	1.11367700
H	13.25383300	5.06270700	0.82969900
H	12.02308800	3.81914400	0.29013700
C	10.42258000	4.06235000	2.66450800
C	9.76116600	4.66272700	3.74678200
H	10.28594600	5.40565900	4.34018100
C	8.44877100	4.31826800	4.07093200
H	7.95998700	4.79481000	4.91546000
C	13.77187000	4.33331700	6.37471100
C	21.94693500	3.40187600	-1.10114700
H	23.02193200	3.24865200	-1.11108100
C	12.47090600	4.28777300	7.11362300
O	14.42567300	3.24394200	6.28283100
C	20.92865700	0.86450200	2.64144300
H	20.72207100	-0.11668800	2.22476200
C	12.34123100	5.36553800	8.23108200
H	13.21163900	6.01154900	8.29302400
C	11.75663500	5.01218900	9.55185800

C	11.55539100	5.48069400	6.96388000
H	10.49148900	5.27520500	6.99993300
H	11.85584300	6.24672300	6.25921700
C	20.33899100	3.20555900	2.87594100
C	9.98323800	4.13303100	10.96194300
H	8.98370800	3.71912400	11.05592400
C	22.30877800	2.32147100	3.98685000
H	23.17196400	2.48228700	4.62565400
C	10.77457000	4.31654800	12.09808100
H	10.39439600	4.04738200	13.07873800
O	17.77924100	3.22841600	3.89676600
C	12.05751300	4.85021900	11.96230900
H	12.68218800	5.00002800	12.83781700
C	10.46818300	4.47841700	9.70132400
H	9.84094700	4.31708200	8.83175100
Rh	16.11369200	3.17580100	5.10488900
C	11.88804800	2.92227400	7.31823000
C	21.16545300	2.94869400	-2.16645400
H	21.62861800	2.44275000	-3.00798800
C	12.42399100	2.04974100	8.27406400
H	13.24834300	2.38439200	8.89511500
C	21.35543100	4.05267500	-0.01940100
H	21.97927700	4.38693600	0.80207900
C	11.89869300	0.76890900	8.43495500
H	12.32070300	0.10250400	9.18120400
C	20.08366500	1.93335600	2.34841600
H	19.22431200	1.78979900	1.70171900
C	10.82705500	0.34390100	7.64268400
H	10.41765200	-0.65365700	7.77007200
C	22.04333300	1.05504500	3.46453500
H	22.70191200	0.22197600	3.69088600
C	10.28306800	1.21020300	6.69376200
H	9.45086400	0.89273800	6.07274300
C	21.45984900	3.39099100	3.69136500
H	21.66635300	4.37225500	4.10443500
C	10.81161900	2.49362100	6.53508800
H	10.38860100	3.16046600	5.79173400
O	14.14211300	5.45710100	5.89486100
C	18.12278200	4.33331500	3.36397500
O	17.45256200	5.41846900	3.42037100
C	19.41093200	4.34960100	2.60160600
C	12.54183900	5.19288300	10.70004800
H	13.54234700	5.60472100	10.59840300
C	19.27804000	4.92039500	1.15863900
H	18.26896600	5.24987100	0.93086300
C	19.97199400	5.70206300	2.22879500

H	19.46070800	6.57372300	2.61934300
H	21.05293100	5.77761400	2.18799800
C	19.96880900	4.26110200	0.01897600
C	19.19433000	3.80231900	-1.05679500
H	18.11886400	3.95725600	-1.03958100
C	19.78457900	3.15284700	-2.14078900
H	19.16602900	2.80724300	-2.96366700

Orientation B for Compound 2.5



Orientation B, C_2 , α , α , β , β conformation
 $\Delta H/\Delta G = -1.8/0.1 \text{ kcal mol}^{-1}$

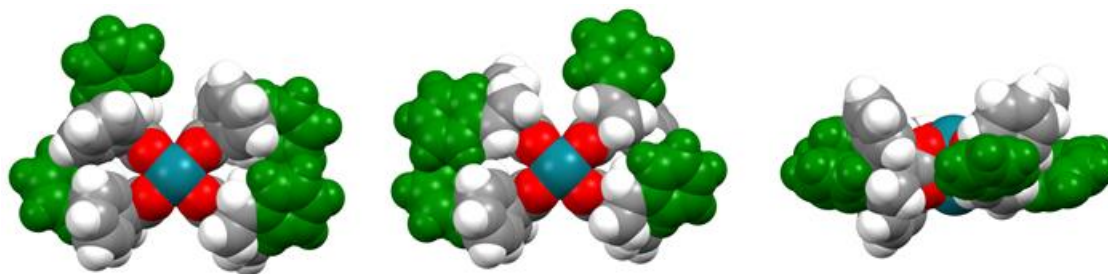
Entry	SCF Energy (a. u.)	Enthalpy (a. u.)	Gibbs Free Energy (a. u.)
Orientation A	-3291.49209082	-3290.427377	-3290.596569
C	17.63229900	4.40528000	5.92837300
C	7.73338100	3.80821000	2.88518800
H	7.00254400	3.30695400	2.25767500
C	18.70152700	4.43693200	6.97344800
O	17.10388500	5.52035700	5.60811700
C	11.00484400	0.69209100	2.84821500
H	10.84567400	0.09317500	3.74007800
C	18.43132600	3.44009700	8.13989800
H	17.53330200	2.85127800	7.98087800
C	18.64609300	3.82872600	9.55765600
C	19.52894100	3.18702800	7.15393800
H	20.55204500	3.33580100	7.48169100
H	19.38070900	2.38501600	6.44069400
C	11.70786600	2.78370700	1.83611300
C	19.98084000	4.74752300	11.36862000
H	20.91599500	5.17797000	11.71409200
C	10.90795200	0.96204000	0.44857800
H	10.67787900	0.56766900	-0.53664600
C	18.92410200	4.56090900	12.26279100
H	19.03291200	4.84398200	13.30518300
O	14.05387400	5.46080800	2.82429800
C	17.72874000	4.00331900	11.80563900
H	16.90443200	3.84172500	12.49310900
C	19.84535600	4.38285900	10.02970400
H	20.67525900	4.54270200	9.35031700
Rh	15.60044700	5.56534300	4.20470000
C	19.30061400	5.78439700	7.23565200
C	7.45197800	4.04597800	4.23251800
H	6.50386800	3.73112300	4.65732900

C	18.61587900	6.73672400	8.00094400
H	17.66308800	6.47223400	8.44796300
C	8.95053300	4.20930300	2.33543200
H	9.15204500	4.00448900	1.29018800
C	19.15502500	8.00739700	8.19427200
H	18.61720600	8.73692100	8.79224800
C	11.50302400	1.98542800	2.97086900
H	11.73267200	2.38465200	3.95260700
C	20.38759400	8.34122800	7.62404100
H	20.80722900	9.33111800	7.77557500
C	10.70262200	0.17640200	1.58305800
H	10.30831200	-0.83056100	1.48455300
C	21.07841600	7.39506200	6.86533900
H	22.03702500	7.64328300	6.41985700
C	11.41001300	2.26085400	0.57616600
H	11.56815300	2.87072700	-0.30834800
C	20.53665900	6.12159000	6.67459700
H	21.07236400	5.39013600	6.07907200
O	17.30290100	3.26877800	5.45227600
C	13.61861900	4.29922500	2.52082100
O	14.26849900	3.21209900	2.66898300
C	12.21830600	4.18074200	2.01294800
C	17.59207600	3.64321500	10.46514500
H	16.65899600	3.20989900	10.11629300
C	11.25698900	5.24790500	2.62947200
H	11.78208200	5.93291000	3.28566600
C	11.65786100	5.32361000	1.19333600
H	12.34716900	6.11142200	0.91099400
H	10.92789700	5.05940200	0.43572900
C	9.91518600	4.84986700	3.12633400
C	9.61613900	5.09446100	4.47499200
H	10.35174300	5.59655100	5.09571400
C	8.39772600	4.69816900	5.02623800
H	8.19022500	4.89741100	6.07342700
C	13.85589900	4.05629400	5.97125000
C	23.62862300	5.06289200	2.81121000
H	24.35336100	5.64977700	2.25490400
C	12.80615400	3.87163800	7.02089000
O	14.37313600	3.00398300	5.47080400
C	20.40631200	8.20928300	3.21165600
H	20.59346100	8.68480500	4.16985200
C	13.07580600	4.71947200	8.30007500
H	13.96383900	5.33655000	8.20644600
C	12.87404400	4.16852200	9.66497600
C	11.96371500	5.07767300	7.36427800
H	10.94766400	4.87444800	7.68496800

H	12.09274900	5.96373000	6.75424200
C	19.64681100	6.27781700	1.95209000
C	11.57270800	3.00755300	11.35765800
H	10.65830100	2.49739900	11.64529400
C	20.45430100	8.25113500	0.79576200
H	20.67412400	8.76617700	-0.13458800
C	12.60878400	3.16077100	12.28186200
H	12.50420000	2.77296600	13.29042600
O	17.29201600	3.50463100	2.59983600
C	13.77695700	3.82210900	11.89925000
H	14.58329100	3.96019100	12.61282900
C	11.70129300	3.50888100	10.06315600
H	10.88709000	3.37463500	9.35996200
Rh	15.81659900	3.18271200	4.01721400
C	12.22471500	2.49516900	7.11572400
C	23.93920700	4.60147200	4.09270600
H	24.90373400	4.82741300	4.53672300
C	12.94186900	1.45540800	7.72047600
H	13.91247900	1.66493300	8.15843900
C	22.39067400	4.77671500	2.23669900
H	22.16710400	5.15478400	1.24564700
C	12.41275500	0.16679300	7.76801600
H	12.97559200	-0.63083300	8.24340500
C	19.88633000	6.91896800	3.17620600
H	19.66759200	6.39832600	4.10210300
C	11.15800300	-0.09783700	7.21011000
H	10.74561400	-1.10147100	7.24892800
C	20.69532700	8.87937600	2.01799800
H	21.10702900	9.88388300	2.04225700
C	10.43610300	0.93435700	6.60868400
H	9.46036500	0.73979900	6.17378100
C	19.93056600	6.95530100	0.76417100
H	19.74643400	6.46833300	-0.18883100
C	10.96777200	2.22532100	6.56388200
H	10.40609000	3.02452200	6.09155100
O	14.17748300	5.25218700	5.66675800
C	17.73107600	4.69722800	2.47194600
O	17.09520800	5.75042700	2.80851600
C	19.12153600	4.87590000	1.95569500
C	13.90796700	4.31758300	10.60195400
H	14.81917800	4.83261700	10.31125100
C	20.07742200	3.72523400	2.41560900
H	19.54949800	2.96869300	2.98505600
C	19.65607100	3.84199600	0.98810700
H	18.95294100	3.10581700	0.61513100
H	20.38189500	4.19217700	0.26212500

C	21.43404300	4.02794800	2.93765600
C	21.76165200	3.56095800	4.21941200
H	21.03195700	2.97475700	4.76927500
C	23.00104500	3.84199900	4.79436700
H	23.23020600	3.47017900	5.78864500

Orientation C for Compound 2.5



Orientation C, C_1 , α , α , α , β conformation

$\Delta H/\Delta G = -0.4/0.4 \text{ kcal mol}^{-1}$

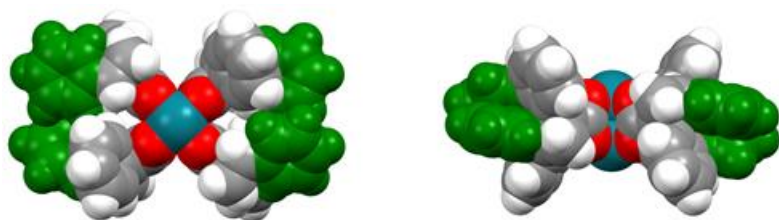
Entry	SCF Energy (a. u.)		Enthalpy (a. u.)	Gibbs Free Energy (a. u.)
Orientation A	-3291.48978458		-3290.425137	-3290.596051
C	17.67254900	4.74493800	6.14799400	
C	7.96781700	3.31330800	2.57271300	
H	7.31548700	2.67553700	1.98376000	
C	18.77975800	4.98038800	7.12574600	
O	17.09414200	5.77200000	5.65734200	
C	11.27217300	0.29777100	3.17038100	
H	11.02852500	-0.18647200	4.11135600	
C	19.68503400	6.20288200	6.78951300	
H	19.36778900	6.71729900	5.88837700	
C	21.16195000	6.12446900	6.95991600	
C	18.71451900	6.26549500	7.92506400	
H	19.10272400	6.22262300	8.93687500	
H	17.83163300	6.87999400	7.79402700	
C	12.03908300	2.26419400	1.97210400	
C	23.16275200	5.68428100	8.26952300	
H	23.61605400	5.40813200	9.21690200	
C	11.43175000	0.25343900	0.75921800	
H	11.31805100	-0.27203400	-0.18422400	
C	23.96775300	5.94469000	7.15756600	
H	25.04827500	5.87215600	7.23498500	
O	14.24357800	5.12555600	2.74833100	
C	23.37038800	6.29820400	5.94723200	
H	23.97949800	6.49421700	5.07099700	
C	21.77525700	5.77480800	8.17277600	
H	21.17055400	5.55458700	9.04520200	
Rh	15.67949100	5.51569600	4.18486800	
C	19.39771500	3.75036200	7.71326400	
C	7.54014700	3.79659500	3.81162800	
H	6.55645000	3.53687900	4.19034600	

C	20.30608200	3.00241800	6.95446900
H	20.56566700	3.34751400	5.95982000
C	9.23119200	3.64198000	2.08298100
H	9.54614300	3.24622500	1.12432100
C	20.88405100	1.84710300	7.47452900
H	21.59196400	1.27970500	6.87762900
C	11.72800300	1.61263600	3.17371600
H	11.83804300	2.14465000	4.11202900
C	20.55879200	1.42574700	8.76768100
H	21.01117300	0.52793700	9.17782200
C	11.11969800	-0.38612900	1.95950900
H	10.75836000	-1.41010900	1.95315800
C	19.65483200	2.16602900	9.53125200
H	19.39921900	1.84425300	10.53631800
C	11.89124200	1.57370800	0.76696300
H	12.13248200	2.06953800	-0.16858600
C	19.07660800	3.32383400	9.00451600
H	18.37294600	3.89986200	9.59832500
O	17.38838900	3.53584800	5.86510000
C	13.84825900	3.91794500	2.61801800
O	14.48938300	2.89097000	3.01662200
C	12.50209000	3.68722400	2.01262300
C	21.98176700	6.38577700	5.85271200
H	21.53006900	6.65340900	4.90359400
C	11.47612900	4.80194700	2.40044900
H	11.93543700	5.58082900	2.99871300
C	11.99788200	4.69694000	1.00461600
H	12.69643700	5.45810000	0.67596800
H	11.33537100	4.31719500	0.23417300
C	10.09737300	4.45503300	2.82879700
C	9.65116900	4.94607700	4.06520800
H	10.30859600	5.58429700	4.64816200
C	8.38561700	4.62248800	4.55480400
H	8.06431900	5.01255500	5.51602100
C	13.83757200	4.26965000	6.05559900
C	23.65739200	4.76606400	1.51623000
H	24.20128700	5.30157300	0.74374100
C	12.67503900	4.20020400	6.99500900
O	14.44008700	3.17543600	5.80363700
C	20.44152600	7.98565700	2.21261700
H	20.79465300	8.61615300	3.02331600
C	12.79722200	5.18026400	8.19997200
H	13.69259200	5.79253200	8.15082200
C	12.45295300	4.72431000	9.57243300
C	11.80200500	5.42690200	7.11065400
H	10.75328000	5.24990400	7.32186200

H	12.00505500	6.24379400	6.42858100
C	19.54048200	5.86319600	1.44926500
C	10.92759900	3.79219600	11.21829100
H	9.93793900	3.42353100	11.47096500
C	19.98420500	7.64418900	-0.13559300
H	19.97709400	8.01038300	-1.15773700
C	11.93562400	3.81000400	12.18482000
H	11.73453400	3.45615200	13.19131200
O	17.46783700	3.24040900	3.00865200
C	13.20339300	4.28743900	11.84658900
H	13.99519800	4.30812000	12.58943700
C	11.18285400	4.24579400	9.92476600
H	10.38917800	4.21392700	9.18659700
Rh	15.96465200	3.14654600	4.42283600
C	12.08481500	2.83726400	7.19479900
C	24.29921100	4.41236300	2.70585000
H	25.34113500	4.67328800	2.86413600
C	12.74021000	1.88329400	7.98407400
H	13.66329200	2.15395700	8.48573400
C	22.31855800	4.43653600	1.30911600
H	21.84027900	4.72841300	0.38148700
C	12.20857600	0.60387200	8.13351600
H	12.72383100	-0.12601200	8.75064300
C	19.99365300	6.69581600	2.48101100
H	19.99022500	6.31391300	3.49598800
C	11.01173400	0.26156700	7.49574900
H	10.59753500	-0.73519300	7.61362500
C	20.44183300	8.46265600	0.89741800
H	20.79598200	9.46608800	0.68191000
C	10.34969600	1.20860800	6.71345500
H	9.41927600	0.95492000	6.21445100
C	19.53242700	6.35029800	0.14052300
H	19.17670800	5.71649100	-0.66612600
C	10.88465900	2.49093600	6.56622900
H	10.37033200	3.22153400	5.95151400
O	14.15990600	5.41272600	5.58894100
C	17.82960700	4.38992300	2.59021700
O	17.21822500	5.48403600	2.82261500
C	19.08787400	4.47669400	1.78548700
C	13.45718200	4.73912200	10.55182800
H	14.44633100	5.10604300	10.29111200
C	20.15140400	3.40206600	2.16480600
H	19.79358200	2.73318200	2.93999100
C	19.40793700	3.31179700	0.87156200
H	18.65633400	2.53586300	0.78015800
H	19.93900900	3.54851600	-0.04414600

C	21.59052900	3.75186200	2.29445900
C	22.25097800	3.39187300	3.47836000
H	21.70641100	2.84287700	4.24014300
C	23.59043400	3.71720800	3.68655900
H	24.07291000	3.43808400	4.61767300

Orientation D for Compound 2.5



Orientation D, D_2 , α , β , α , β conformation
 $\Delta H/\Delta G = -0.2/0.4 \text{ kcal mol}^{-1}$

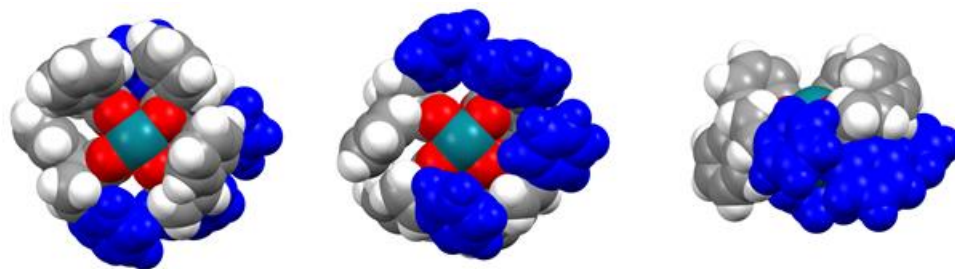
Entry	SCF Energy (a. u.)		Enthalpy (a. u.)	Gibbs Free Energy (a. u.)
Orientation A	-3291.48910508		-3290.424946	-3290.596117
C	17.73788800	4.38431900	6.71170300	
C	8.23475700	4.15928100	0.82977900	
H	7.77642000	4.08292400	-0.15176100	
C	18.99730600	4.51201400	7.51032100	
O	17.08820300	5.45163900	6.45292700	
C	11.16651900	0.47917600	2.32346300	
H	10.60418900	-0.12039200	3.03364500	
C	19.73764700	5.86432200	7.27554900	
H	19.18996800	6.50862300	6.59680500	
C	21.21174900	5.94170200	7.10383100	
C	19.03928500	5.59371700	8.56949200	
H	19.64766100	5.38718600	9.44352300	
H	18.11876400	6.13220100	8.76450900	
C	12.30035400	2.55210300	1.76612800	
C	23.50409400	5.39704500	7.69998700	
H	24.20102000	4.88631900	8.35776300	
C	12.17730900	0.75154300	0.14565800	
H	12.41040000	0.36292400	-0.84112300	
C	23.98193900	6.14713300	6.62249900	
H	25.04916000	6.22128000	6.43743100	
O	14.24514200	5.18760100	3.48068500	
C	23.07498100	6.80585600	5.79062000	
H	23.42892400	7.39481900	4.95029500	
C	22.13461500	5.29797200	7.94269000	
H	21.78901500	4.70692600	8.78222200	
Rh	15.65480000	5.38361300	4.96593200	
C	19.78995100	3.25230700	7.67051300	
C	7.48631100	3.88636300	1.97562600	
H	6.44415800	3.59347500	1.89164600	
C	20.38988800	2.67704500	6.54258100	
H	20.23810600	3.14297500	5.57563300	

C	9.57431800	4.53669000	0.93748700
H	10.13669000	4.75568800	0.03640000
C	21.16104600	1.52391600	6.65319900
H	21.62711800	1.09935900	5.76911800
C	11.58450200	1.76040000	2.67337800
H	11.34590600	2.16707400	3.64914800
C	21.33939900	0.92298700	7.90357900
H	21.94520100	0.02682800	7.99634300
C	11.46276500	-0.02960100	1.05479800
H	11.13460700	-1.02664400	0.77706500
C	20.73369600	1.47921500	9.03070000
H	20.86170600	1.01378500	10.00328000
C	12.59345400	2.03758100	0.50100700
H	13.14808500	2.64392000	-0.20881600
C	19.96006600	2.63757300	8.91337800
H	19.49229300	3.06733400	9.79391900
O	17.41785600	3.21510600	6.31847700
C	13.85679500	4.01748800	3.14636400
O	14.35455000	2.92695300	3.57916500
C	12.72556900	3.92848900	2.17292400
C	21.70603200	6.70224800	6.03308600
H	21.00491000	7.22797400	5.39244000
C	11.62695200	5.01781100	2.34715200
H	11.83768200	5.69023800	3.17327200
C	12.58509100	5.08996900	1.20624700
H	13.35444700	5.85171800	1.24318300
H	12.23364300	4.83771200	0.21265900
C	10.19080900	4.64343100	2.19030500
C	9.42700500	4.36681900	3.33476400
H	9.88539600	4.42568900	4.31597600
C	8.08814100	3.99434800	3.23139700
H	7.52412300	3.77756400	4.13232000
C	13.80646800	3.99485200	6.71276500
C	23.30664600	4.23021300	0.82898400
H	23.76533100	4.30695500	-0.15236200
C	12.54651100	3.86603700	7.51037700
O	14.45613900	2.92804300	6.45175700
C	20.37335000	7.91066100	2.32552700
H	20.93496900	8.50988100	3.03655700
C	11.80664900	2.51375800	7.27414900
H	12.35516700	1.86995100	6.59561300
C	10.33275100	2.43630200	7.10067700
C	12.50373900	2.78376700	8.56891500
H	11.89454700	2.98974500	9.44251400
H	13.42415500	2.24530100	8.76451800
C	19.24025400	5.83792100	1.76599200

C	8.03962800	2.98103700	7.69374200
H	7.34182900	3.49161400	8.35070900
C	19.36444800	7.63947700	0.14669500
H	19.13215500	8.02864600	-0.84005700
C	7.56323100	2.23150200	6.61524000
H	6.49626800	2.15766700	6.42855600
O	17.29563400	3.19999100	3.47691600
C	8.47128200	1.57290800	5.78444200
H	8.11845200	0.98438000	4.94334100
C	9.40877700	3.07979800	7.93848200
H	9.75324400	3.67046600	8.77873700
Rh	15.88798800	3.00008100	4.96330600
C	11.75340300	5.12551100	7.67025600
C	24.05486700	4.50204500	1.97524200
H	25.09719300	4.79446000	1.89177200
C	11.15552700	5.70143800	6.54155700
H	11.30939400	5.23619100	5.57461100
C	21.96688800	3.85333500	0.93604100
H	21.40470600	3.63507700	0.03465800
C	10.38395600	6.85434100	6.65140400
H	9.91948500	7.27934900	5.76669300
C	19.95525800	6.62916200	2.67432100
H	20.19309700	6.22188200	3.65003800
C	10.20316600	7.45447000	7.90183400
H	9.59705600	8.35048000	7.99402000
C	20.07813000	8.42015400	1.05691300
H	20.40641100	9.41739900	0.78005500
C	10.80688600	6.89765300	9.02971900
H	10.67702600	7.36249200	10.00233600
C	18.94814800	6.35319400	0.50093600
H	18.39419100	5.74720600	-0.20971000
C	11.58092400	5.73946400	8.91315400
H	12.04714700	5.30929300	9.79431500
O	14.12682800	5.16493400	6.32243200
C	17.68403000	4.37073200	3.14489400
O	17.18654800	5.46041900	3.58015300
C	18.81509700	4.46114000	2.17140200
C	9.83987700	1.67611600	6.02900900
H	10.54188700	1.15050100	5.38925100
C	19.91380400	3.37170500	2.34488300
H	19.70291700	2.69868700	3.17048200
C	18.95588600	3.30052200	1.20374500
H	18.18655500	2.53871700	1.23982500
H	19.30758900	3.55364300	0.21046800
C	21.34998600	3.74604000	2.18861400
C	22.11353500	4.02164500	3.33346800

H	21.65475200	3.96234000	4.31447900
C	23.45260300	4.39356100	3.23076100
H	24.01646300	4.60947800	4.13199100

Orientation A for Compound 2.9



Orientation A, C_1 , α , α , β , γ conformation

$\Delta H/\Delta G = 0.0/0.0 \text{ kcal mol}^{-1}$

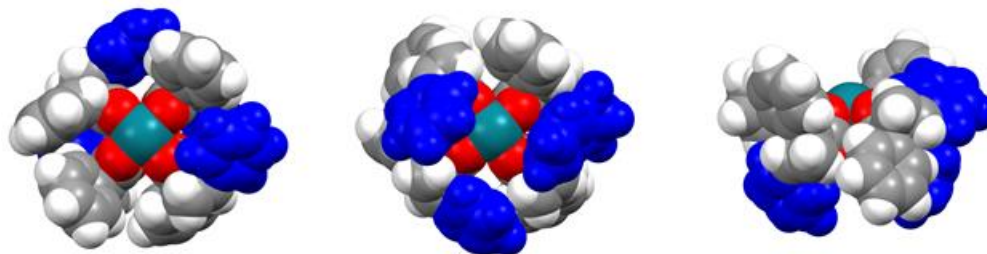
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Orientation A	-3291.49362063		-3290.429106	-3290.597450
Rh	2.23965000	10.67076600	10.83881000	
Rh	-0.14732800	10.50840100	10.82102500	
O	-0.15904000	11.50200500	12.62302300	
O	-0.18145900	12.27512500	9.75967100	
O	0.04919000	8.69068700	11.77698400	
O	2.05471500	11.93927500	12.44878500	
O	0.02160100	9.56018500	8.99559900	
O	2.07273500	12.26353500	9.53033300	
O	2.26937000	9.41047100	9.20674700	
O	2.27194300	9.00197200	12.04383300	
C	0.92330400	12.04475200	13.02490200	
C	1.20484200	8.31754500	12.16014400	
C	0.90478200	12.65587900	9.21567500	
C	1.16913700	9.16752400	8.60648300	
C	5.17544000	10.69468700	14.60185800	
H	6.16385400	10.87356200	14.18867400	
C	-0.70672300	6.72100700	8.22698800	
C	-1.34463800	13.99448700	13.90198500	
H	-0.96831400	14.30735200	12.93507300	
C	0.09500200	12.87941400	6.88802900	
C	1.98798700	13.86336600	14.47949900	
C	0.21806700	7.20531100	7.16400100	
C	-0.52662700	13.22404100	14.74179900	
C	-3.11800900	13.96193800	15.54672000	
H	-4.11763300	14.24858500	15.85914100	
C	1.24421200	8.36239200	7.35047400	
C	0.07203700	8.47423900	6.39486000	
C	0.82273600	6.61727400	14.15725600	
C	4.83293600	9.42604200	15.07494100	
H	5.55155000	8.61327500	15.02759700	

C	1.35549800	6.93962800	12.74359000
C	0.76504800	13.58325100	8.03741000
C	2.62842600	8.13278300	6.82169400
C	0.47405900	15.06055600	8.30739300
C	2.63104600	6.27435800	12.30444700
C	0.11573200	6.10544600	12.93273600
C	0.85426700	12.86105500	14.27701300
C	3.46566700	7.19578100	7.44127600
H	3.09742100	6.63899600	8.29686700
C	2.63875100	10.25497900	15.66965300
H	1.65019000	10.07920100	16.07962800
C	1.97307100	12.63280700	15.31679700
C	2.97510200	11.53041300	15.19825500
C	-2.31338800	13.19209000	16.38658100
H	-2.68507100	12.87054000	17.35504700
C	2.66503200	5.61127900	11.07212400
H	1.75671400	5.54966400	10.48177400
C	-0.91073500	16.26044100	9.99272600
H	-1.68035400	16.34239000	9.23006600
C	1.81729600	14.61625000	7.77417700
C	3.79911700	6.35609800	13.06790300
H	3.77726700	6.87910700	14.01736800
C	3.11125700	8.86217700	5.73145400
H	2.46804300	9.59579800	5.25538800
C	-1.02588600	12.82523200	15.98457000
H	-0.41899000	12.20971900	16.63876100
C	0.87192400	12.31928000	5.86715100
H	1.95139800	12.43292200	5.89526200
C	-2.62772000	14.36236600	14.29957000
H	-3.24198900	14.96594500	13.63773400
C	4.25320900	11.74040900	14.66951100
H	4.52804200	12.72616200	14.30874000
C	-1.90048100	12.02140400	5.80973100
H	-2.98030100	11.90937400	5.78947500
C	0.28874000	15.60111400	9.68426200
C	-0.71199000	8.56548600	14.77004600
H	-1.03396400	8.66397600	13.74196100
C	-2.38008600	5.68827700	10.24238100
H	-3.02510900	5.29348600	11.02131700
C	4.98653200	5.78713100	12.60485000
H	5.88824700	5.85768500	13.20594600
C	3.85093200	5.04184500	10.60612400
H	3.86450200	4.52766800	9.64945100
C	5.01645300	5.13106400	11.37158800
H	5.94031000	4.68869400	11.01151100
C	3.56147300	9.21164000	15.61241100

H	3.28245200	8.23311800	15.98935300
C	-1.88806900	7.38375800	8.58269000
H	-2.16080300	8.30394400	8.08046600
C	-1.29591800	12.72255700	6.85334300
H	-1.89740200	13.15092100	7.64828900
C	4.76346700	6.99044300	6.97802700
H	5.40266500	6.26294800	7.46976400
C	-1.12002100	11.47049400	4.78949100
H	-1.59114400	10.92693500	3.97638400
C	-1.12061100	16.82097200	11.25271200
H	-2.05536800	17.33034500	11.46701000
C	0.23179200	7.58744900	15.12173200
C	-0.39183000	5.51888800	8.87926100
H	0.50543000	4.97900300	8.58822700
C	0.26743000	11.62253300	4.81932000
H	0.87893200	11.19977100	4.02778200
C	-1.21606500	5.00627400	9.88000100
H	-0.95154500	4.07581200	10.37291600
C	-2.71480700	6.87393200	9.58484000
H	-3.62672800	7.40223700	9.84753800
C	4.41110700	8.65601900	5.26217300
H	4.77518100	9.22708400	4.41327400
C	-1.23594800	9.42551000	15.73443400
H	-1.95175600	10.18562500	15.43991700
C	0.61526200	7.48835400	16.46867200
H	1.33450700	6.72789500	16.76060200
C	-0.12750800	16.73628000	12.23021300
H	-0.28420200	17.17385200	13.21087000
C	1.26977900	15.50140400	10.68287900
H	2.20512200	14.98924600	10.48395100
C	5.23946200	7.72023800	5.88390700
H	6.24950800	7.55924400	5.51929200
C	0.08589500	8.34343200	17.43538100
H	0.40013300	8.24592400	18.47015700
C	-0.84129900	9.32123600	17.07024900
H	-1.25534500	9.99167800	17.81715800
C	1.06487600	16.07078700	11.93949900
H	1.84326300	15.99989100	12.69085700
H	1.71411700	14.80381800	14.94464200
H	2.70832200	13.92761000	13.67320500
H	1.60993300	12.77348800	16.33108500
H	2.04264400	14.84355600	6.73780000
H	2.67227100	14.64814400	8.43986100
H	-0.19814900	15.49980200	7.57537800
H	-0.70474500	9.17299600	6.67829200
H	0.30405000	8.45657600	5.33612900

H	0.68487600	6.39276500	6.61309900
H	1.46027200	5.88633700	14.64702500
H	0.19196100	5.04840800	12.70271700
H	-0.82434100	6.56908200	12.65971500

Orientation B for Compound 2.9



Orientation B, C₁, α , β , α , γ conformation
 $\Delta H/\Delta G = 0.5/0.6 \text{ kcal mol}^{-1}$

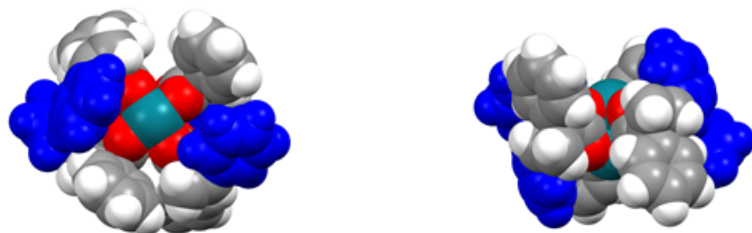
Entry	SCF Energy (a. u.)		Enthalpy (a. u.)	Gibbs Free Energy (a. u.)
Orientation A	-3291.49278181		-3290.428261	-3290.596467
Rh	2.16851600	10.45545200	10.58395500	
Rh	-0.14246800	9.87488400	10.80040600	
O	-0.21534600	11.10348000	12.44754800	
O	-0.59745500	11.53306300	9.65582900	
O	0.44923100	8.25335700	11.92396500	
O	1.88428600	11.86075200	12.08325900	
O	0.02884200	8.79474800	9.05499700	
O	1.59316300	11.86086500	9.19514000	
O	2.26393000	9.12865000	9.00732800	
O	2.59093800	8.98801300	11.96458100	
C	0.73933300	11.92567700	12.63410900	
C	1.67283300	8.16126100	12.27576400	
C	0.35903800	12.15120500	9.07968000	
C	1.17234500	8.71612300	8.49900000	
C	3.32074900	10.01742200	15.75260000	
H	4.34583000	9.73554500	15.53275600	
C	0.81498200	5.61333700	7.87520600	
C	-0.88925300	15.03925000	12.76714900	
H	0.04642800	15.54506200	12.56085100	
C	-1.46645200	13.56538600	8.04887400	
C	1.61436400	13.84475800	14.12066700	
C	1.00850700	6.66138200	6.83341700	
C	-0.86392000	13.75048900	13.31069800	
C	-3.30737800	15.01907100	12.74738900	
H	-4.25226200	15.50868300	12.53201300	
C	1.25173200	8.16211900	7.10277200	
C	-0.02451000	7.68519700	6.45531200	
C	3.31955800	6.20075200	12.67842900	
C	2.52551900	9.19510700	16.55150100	
H	2.92397700	8.26704400	16.94871500	

C	2.05101600	6.97431200	13.10368200
C	0.00189400	13.30360800	8.19938700
C	2.27389400	8.88266900	6.26748800
C	0.94050200	14.54388400	8.21912500
C	0.90267000	6.20979900	13.69509700
C	3.35447400	7.07527200	13.88351600
C	0.45062800	13.06808000	13.57125600
C	3.56064500	8.37181300	6.07788200
H	3.82038700	7.41198800	6.51008100
C	0.70516800	10.77110100	16.32989100
H	-0.31434600	11.06869300	16.55972200
C	0.90956500	12.88438300	15.03443600
C	1.49786700	11.60715300	15.52766100
C	-3.29125800	13.73419400	13.29875300
H	-4.22515200	13.22363800	13.51395800
C	0.14712400	6.79455800	14.72064900
H	0.41641200	7.78224000	15.07999400
C	1.77511100	15.54187100	10.33024800
H	0.79610000	16.00107100	10.43097200
C	0.96700600	13.60273000	7.06328800
C	0.55196800	4.93649100	13.23866100
H	1.11988300	4.47884800	12.43656900
C	1.94647300	10.12992800	5.72025200
H	0.94665700	10.52938400	5.86652200
C	-2.07926800	13.10579400	13.58120500
H	-2.06728300	12.10879600	14.00672600
C	-2.15069800	13.22791400	6.87821800
H	-1.60799800	12.77780500	6.05194600
C	-2.10238100	15.67237000	12.48584000
H	-2.10319400	16.67170800	12.06126300
C	2.81138800	11.21262200	15.24243900
H	3.44707700	11.84548300	14.63365200
C	-3.54457500	14.37043100	9.00876200
H	-4.07859800	14.81220000	9.84446900
C	2.03666100	14.73858300	9.21155700
C	5.20118500	7.31206400	11.40152500
H	5.53988200	7.77450400	12.32272400
C	0.53620000	3.53794500	9.76388000
H	0.42867400	2.74196100	10.49450100
C	-0.53478900	4.25604800	13.79399900
H	-0.79543900	3.26794200	13.42608300
C	-0.93830700	6.11934000	15.27583400
H	-1.51290800	6.58456700	16.07152600
C	-1.28374400	4.84568300	14.81300200
H	-2.12840500	4.31803300	15.24563500
C	1.21246900	9.57696400	16.83929800

H	0.58577700	8.94619300	17.46266400
C	-0.09356000	5.72892200	8.93868500
H	-0.69478900	6.62243400	9.04363900
C	-2.17514400	14.13872100	9.11388200
H	-1.65048000	14.39565000	10.02891600
C	4.51001600	9.09684000	5.35539200
H	5.50694200	8.68974200	5.21507700
C	-4.22353100	14.03355500	7.83317400
H	-5.29053100	14.21639900	7.74818200
C	2.74818200	15.75265900	11.30644300
H	2.52632900	16.37759800	12.16628900
C	4.06772800	6.49196200	11.41842400
C	1.56282400	4.43043500	7.76575500
H	2.25525400	4.31597700	6.93614700
C	-3.52410900	13.46282600	6.76873400
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C	1.42904300	3.40247100	8.69897500
H	2.02185200	2.49897800	8.59333900
C	-0.22504400	4.70382100	9.87491700
H	-0.92314800	4.81877400	10.69771700
C	2.89384500	10.85843300	5.00062700
H	2.62834200	11.82386400	4.58031700
C	5.89952700	7.53838100	10.21417400
H	6.77757800	8.17776100	10.21895200
C	3.64993200	5.89201100	10.22302000
H	2.77075200	5.25563600	10.21889200
C	4.00816200	15.16445100	11.17404000
H	4.76894400	15.32497000	11.93183200
C	3.31093300	14.17518000	9.07546900
H	3.53800400	13.56258700	8.21069700
C	4.18028900	10.34309700	4.81822300
H	4.91875700	10.90763600	4.25716700
C	4.35155200	6.10904200	9.03842700
H	4.01472700	5.62950900	8.12582800
C	5.47767600	6.93527800	9.02747700
H	6.02116800	7.10739200	8.10330400
C	4.28701700	14.38181700	10.05080700
H	5.26927800	13.93417600	9.93029900
H	1.46682500	14.90333200	14.30137500
H	2.59320500	13.58546000	13.73720500
H	0.20695500	13.33408000	15.73128700
H	0.53245200	13.93529000	6.12685800
H	1.80489200	12.92249600	6.96774000
H	0.35605800	15.44548600	8.05366900
H	-0.92330300	7.74295600	7.05810500
H	-0.15473500	7.90891000	5.40173600

H	1.62197100	6.31406000	6.00673000
H	3.21701600	5.13793400	12.88217800
H	3.36263600	6.60847300	14.86194000
H	3.86857200	8.02494800	13.81503200

Orientation C for Compound 2.9



Orientation C, D_2 , α , β , α , β conformation

$\Delta H/\Delta G = 0.3/0.6 \text{ kcal mol}^{-1}$

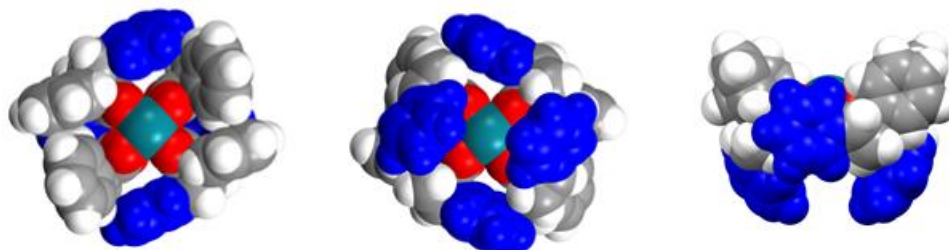
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O	-0.60129400	10.95319000	12.30717200	
O	-0.88599400	11.69799800	9.44697300	
O	0.42316500	8.43397900	11.59467800	
O	1.38961400	12.01204400	12.18180700	
O	0.17463900	9.14130900	8.69607500	
O	1.26755700	12.35403500	9.20433400	
O	2.35515700	9.72387000	8.89011700	
O	2.43346200	9.43150500	11.86612400	
C	0.31712300	11.69488500	12.78851900	
C	1.55977100	8.54926700	12.15452900	
C	0.01754700	12.47906600	8.99707400	
C	1.38533200	9.14176800	8.29935600	
C	-3.75202700	13.37717900	11.83591500	
H	-4.33138400	12.75812200	11.15777500	
C	0.38895600	6.30491400	8.04620200	
C	2.41768700	11.45594500	14.97053000	
H	2.22387500	10.50359200	14.48907200	
C	-1.84713700	13.55515400	7.66943700	
C	-0.98836200	11.56359600	14.98829100	
C	1.11199600	6.97187300	6.92071100	
C	1.45301100	12.47403300	14.90212700	
C	3.91186700	12.90039400	16.20615800	
H	4.85935100	13.06574500	16.70969200	
C	1.70616700	8.38901800	7.04730200	
C	0.53893600	8.09067100	6.11649200	
C	2.96552700	6.54090800	13.13441200	
C	-3.89545800	14.76608400	11.80560700	
H	-4.58802600	15.23015900	11.11003900	

C	1.85359700	7.60420900	13.28634100
C	-0.44259700	13.64881600	8.18668500
C	3.06433100	8.65527600	6.46819000
C	0.09250000	15.02548500	8.63036100
C	0.62494600	7.23816100	14.07066600
C	3.17755900	7.75060600	13.99803200
C	0.15412800	12.18630300	14.19892100
C	4.12606400	7.77115800	6.68053200
H	3.96117300	6.86877400	7.25871900
C	-2.26259000	14.94808500	13.57680800
H	-1.69170200	15.56609000	14.26422800
C	-1.11263500	12.99501400	14.57874900
C	-2.09319500	13.55449600	13.60303100
C	2.96291000	13.91976500	16.14108300
H	3.16845900	14.88641100	16.59097100
C	0.17298800	8.09237200	15.08380200
H	0.74563600	8.98120700	15.32997400
C	0.26587200	15.15574900	11.11954200
H	-0.80863700	15.00818100	11.17054400
C	0.61268100	14.39049200	7.38280800
C	-0.11534300	6.09196200	13.76548500
H	0.22717300	5.43375100	12.97480100
C	3.28954800	9.82351600	5.72917800
H	2.46583300	10.51117200	5.55802100
C	1.74316700	13.70733500	15.49135400
H	1.02398600	14.51731300	15.44250300
C	-2.10983900	12.86708100	6.47896800
H	-1.28341200	12.43573400	5.92076100
C	3.63421400	11.66388600	15.61485100
H	4.36499700	10.86157400	15.65515700
C	-2.86863300	12.77480800	12.73198200
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C	-4.22229500	13.98104000	7.91875200
H	-5.04142400	14.41663000	8.48358000
C	0.90668100	15.18322600	9.87384900
C	4.38149400	7.21797400	11.11998800
H	4.38183200	8.25069900	11.44290000
C	-0.91509200	5.00098200	10.16649700
H	-1.41870700	4.50028600	10.98797300
C	-1.29247600	5.80476800	14.45748000
H	-1.85874200	4.91146400	14.21119200
C	-1.00613500	7.81046400	15.77458400
H	-1.34707600	8.48244100	16.55640500
C	-1.74299500	6.66558600	15.46140400
H	-2.65991400	6.44368600	15.99887400
C	-3.15013200	15.55159000	12.68684700

H	-3.25928600	16.63179800	12.68392600
C	-1.00760400	6.23793500	8.08889700
H	-1.58861600	6.69474000	7.29408500
C	-2.91294700	14.11257400	8.38267600
H	-2.71710400	14.63978800	9.31010800
C	5.39528900	8.04929200	6.16980900
H	6.21104200	7.35380200	6.34426800
C	-4.47827100	13.29047500	6.73191900
H	-5.49636400	13.18886100	6.36843600
C	0.99929300	15.29277900	12.29532200
H	0.48948100	15.25233200	13.25003700
C	3.70368000	6.24736800	11.87339300
C	1.12726900	5.70444400	9.07485200
H	2.21177400	5.75127500	9.05896800
C	-3.41791700	12.73399900	6.01161500
H	-3.60945300	12.19952400	5.08593100
C	0.48008500	5.05564900	10.12501300
H	1.07086100	4.59404200	10.90874100
C	-1.65772100	5.59508400	9.14403000
H	-2.74288000	5.55313500	9.16309400
C	4.55635800	10.10559700	5.21822100
H	4.71824100	11.01388700	4.64549600
C	5.04673700	6.86753900	9.94515800
H	5.55323500	7.63508300	9.36872100
C	3.73779000	4.91620800	11.42842800
H	3.23633500	4.14920100	12.01238200
C	2.38411000	15.46341700	12.24717300
H	2.95250600	15.55185900	13.16799800
C	2.29242300	15.36546400	9.83068400
H	2.79792100	15.39328800	8.87028200
C	5.61399600	9.21849600	5.43894500
H	6.60003300	9.43641600	5.03997900
C	4.40660200	4.56368400	10.25669000
H	4.41572800	3.52745500	9.93277400
C	5.06126300	5.54185000	9.50550900
H	5.58396500	5.27307400	8.59257100
C	3.02903100	15.50292600	11.00964400
H	4.10526600	15.64140300	10.95929900
H	-0.79503700	11.35868400	16.03598700
H	-1.57298700	10.81510700	14.46765900
H	-0.89800900	13.69755900	15.37736700
H	0.29202900	14.79439800	6.42873700
H	1.61090000	13.96957700	7.40330200
H	-0.65142800	15.80529400	8.48178800
H	-0.42046800	8.49595600	6.41530000
H	0.75399200	8.12262400	5.05401100

H	1.78489000	6.31112700	6.37900900
H	2.70750300	5.63867300	13.68201000
H	3.17585900	7.60983600	15.07373500
H	3.83866000	8.52760900	13.63234900

Orientation D for Compound 2.9



Orientation D, C_2 , α , α' , α , α' conformation

$\Delta H/\Delta G = 0.6/1.9 \text{ kcal mol}^{-1}$

Entry	SCF Energy (a. u.)		Enthalpy (a. u.)	Gibbs Free Energy (a. u.)
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O	-0.29050500	11.44379100	12.09908100	
O	-0.40213700	11.90068600	9.34736700	
O	0.42159100	8.54446200	11.60772900	
O	1.87264600	12.09265000	12.00601300	
O	0.26000400	8.99037300	8.85387100	
O	1.81705700	12.26947900	9.11311400	
O	2.48069100	9.40382400	8.91607000	
O	2.56356600	9.23919700	11.80777400	
C	0.68681600	12.17651800	12.45700700	
C	1.63726100	8.37702900	11.95887700	
C	0.59556500	12.60543600	8.97644800	
C	1.45998800	8.78178000	8.48330200	
C	2.74346100	9.76157500	16.01188800	
H	3.76048000	9.54663900	16.32596500	
C	1.50071100	9.66828000	5.66051100	
C	-0.71925600	15.43214900	13.04958300	
H	0.25866800	15.89383400	13.10407700	
C	-1.15632400	14.25202700	8.17955400	
C	1.54296600	13.76269900	14.29632400	
C	1.72889700	8.23051600	5.98877500	
C	-0.83695000	14.05092400	13.24052300	
C	-3.10725400	15.63000700	12.72257400	
H	-3.98403800	16.23835200	12.52263800	
C	1.65783700	7.71491200	7.43850300	
C	2.95864600	7.72180600	6.67837000	
C	3.38711400	6.43350200	12.19645000	
C	1.79245800	8.74102600	15.97429800	
H	2.06854600	7.73289500	16.26560000	

C	2.00152000	7.06293000	12.57163000
C	0.29955100	13.93265400	8.35645000
C	0.92873400	6.42533800	7.69717300
C	1.22078700	15.14369200	8.72341300
C	0.87165400	6.08901500	12.74232400
C	3.17392500	7.05095000	13.53305300
C	0.38168200	13.21019500	13.51102700
C	-0.47335700	6.37749400	7.70001900
H	-1.03454300	7.28561100	7.51463700
C	0.13381100	10.32197900	15.20958300
H	-0.88087800	10.54256200	14.89249800
C	0.64680100	12.75608000	14.95509800
C	1.07619100	11.35962800	15.26448900
C	-3.23708700	14.25240400	12.92109200
H	-4.21732500	13.78710700	12.87850300
C	0.42030500	5.70775600	14.00909300
H	0.89262300	6.12076000	14.89326900
C	2.04659500	15.89546200	10.93268000
H	1.09544600	16.40639700	11.04418900
C	1.32465700	14.49172400	7.38981500
C	0.25495100	5.53850600	11.60837400
H	0.60007700	5.82186000	10.61903100
C	1.64205600	5.24515500	7.93467100
H	2.72480900	5.26979700	7.92798300
C	-2.11298500	13.47031100	13.18104600
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C	-1.74520800	14.27529000	6.91232300
H	-1.13901700	14.06324700	6.03852600
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H	-1.73052400	17.28764300	12.64049700
C	2.38673000	11.06389100	15.65517600
H	3.12336000	11.86033600	15.69641800
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H	-3.89965900	15.03452300	10.03884100
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H	5.07550200	8.64494500	12.21854500
C	0.99236900	12.32911700	4.92220400
H	0.79917400	13.35323500	4.61994500
C	-0.79641800	4.63465200	11.74413600
H	-1.25889100	4.21889100	10.85534400
C	-0.63295400	4.79967900	14.14768200
H	-0.97119700	4.51482200	15.13953400
C	-1.24553700	4.26295700	13.01551100
H	-2.06384200	3.55680400	13.12010800
C	0.48783500	9.02097500	15.56018200

H	-0.25063300	8.22729700	15.50977100
C	2.55717800	10.56252100	5.45609800
H	3.58003600	10.21653000	5.56484700
C	-1.94739800	14.53157400	9.30373600
H	-1.49860700	14.52119700	10.29230000
C	-1.14067000	5.17833800	7.94477300
H	-2.22633500	5.15693600	7.94206800
C	-3.88600800	14.83677900	7.88746200
H	-4.94197800	15.06387100	7.77514000
C	3.00665300	15.98204600	11.94007600
H	2.80087000	16.56058100	12.83578900
C	4.32883400	6.92731000	11.15317900
C	0.18411700	10.13042200	5.51322200
H	-0.64074600	9.44313300	5.67809000
C	-3.10390100	14.56610700	6.76440500
H	-3.54739400	14.58056800	5.77319700
C	-0.07033100	11.45027000	5.14705400
H	-1.09452900	11.79140300	5.03333700
C	2.30512900	11.88528700	5.08598900
H	3.13477700	12.56493900	4.91578000
C	0.97584500	4.04261100	8.17976600
H	1.54758700	3.13850500	8.36573100
C	6.02446000	8.44509200	10.30300600
H	6.64578400	9.32495200	10.44366800
C	4.45346400	6.17565600	9.97616900
H	3.84989900	5.28089800	9.85951200
C	4.23440800	15.33402000	11.79090900
H	4.98684900	15.40006700	12.57087500
C	3.53046500	14.53166900	9.61527700
H	3.74678000	13.97139800	8.71428800
C	-0.41846200	4.00571400	8.18568700
H	-0.93986400	3.07191200	8.37273400
C	5.33617100	6.55797300	8.96679500
H	5.41545400	5.96122800	8.06303300
C	6.12177400	7.70161500	9.12378200
H	6.81292500	8.00265000	8.34237400
C	4.49338100	14.61531700	10.62097300
H	5.45280800	14.12408000	10.48615500
H	1.48406800	14.79159400	14.63074300
H	2.52838500	13.44501300	13.97787300
H	-0.08521900	13.16102800	15.65114800
H	0.94728800	15.02809900	6.52662900
H	2.17809200	13.85545600	7.19442100
H	0.62019800	16.04941800	8.73608200
H	3.70166400	8.43574500	7.01129100
H	3.35991700	6.76765900	6.35769300

H	1.25979400	7.53941000	5.29173900
H	3.28659600	5.35135900	12.18069600
H	3.10259100	6.39431900	14.39218000
H	3.62267200	8.01554400	13.73434000

S.2.10 References

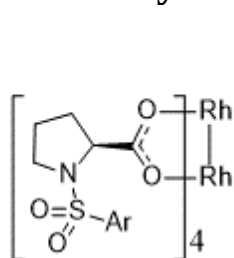
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S.3 Experimental Section for Chapter 3

S.3.1 General Considerations

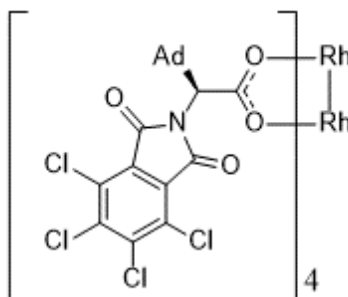
Reactions were carried out under argon in flame-dried or oven-dried glassware unless otherwise specified. Dichloromethane, diethyl ether, tetrahydrofuran, and toluene were purified using a GlassContour solvent system. Chloroform used for C–H functionalization reactions was dried over 4Å molecular sieves and degassed for 1 h with argon and stored under argon for 24 h prior to use. Dichloromethane and 1,2-dichloroethane were distilled under argon from calcium hydride onto molecular sieves and stored under argon for 24 h prior to use. ^1H NMR spectra were recorded at either 300 MHz, 400 MHz, 500 MHz, or 600 MHz on Mercury-300, Varian-400, Varian-500, or Bruker 600 spectrometers. ^{13}C NMR spectra were recorded at either 75 MHz, 100 MHz, 126 MHz, or 151 MHz on Mercury-300, Varian-400, Varian-500, or Bruker 600 spectrometers. ^{19}F NMR spectra were recorded at 282 on Varian-300 spectrometer. NMR spectra were obtained from solutions of deuterated chloroform (CDCl_3) with residual solvent serving as internal standard (7.26 ppm for ^1H and 77.16 ppm for ^{13}C). NMR shifts 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 analysis was performed with glass-backed silica gel plates, visualizing with UV light, and staining with aqueous KMnO_4 or cerium molybdate stain. Racemic standards were generated by performing reactions with $\text{Rh}_2(\text{OAc})_4$ or from $\text{Rh}_2(R/S\text{-DOSP})_4$ or $\text{Rh}_2(R/S\text{-2Cl-TPCP})_4$ which was generated by dissolving an equimolar mixture of the *R* and *S* catalyst in a minimal amount of benzene and lyophilizing.

S.3.2 Catalyst Structures



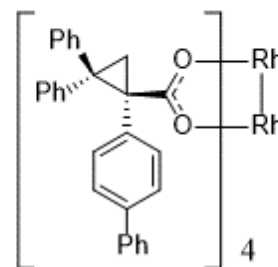
3.55

[R = (*p*-C₁₂H₂₅)C₆H₄]
(*S*-DOSP)
(Ref. 1)



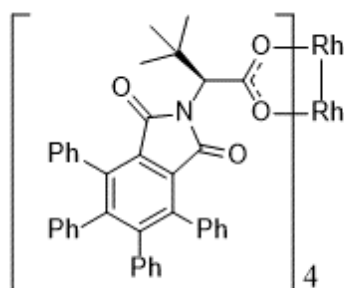
3.56

Rh₂(*S*-TCPTAD)₄
(Ref. 4)



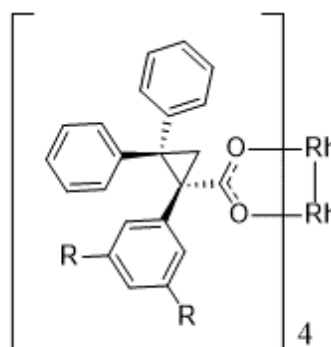
3.40

Rh₂(*S*-*p*-PhTPCP)₄
(Ref. 7)



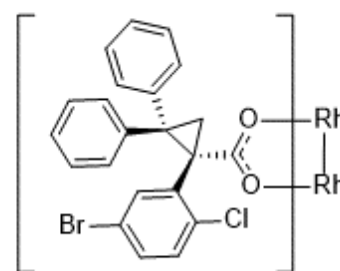
3.5

Rh₂(*S*-TPPTTL)₄
(Ref. 2)



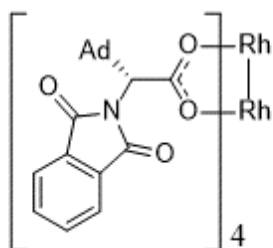
3.57

R = C₆H₄(*p*-*t*Bu)
Rh₂[*R*-3,5-di(*p*-*t*BuC₆H₄)TPCP]₄
(Ref. 5)



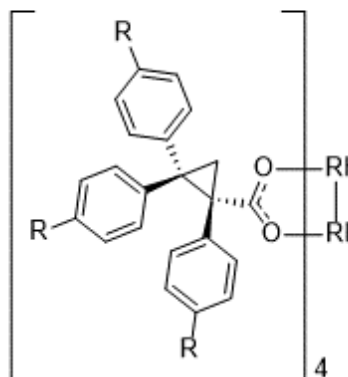
3.43

Rh₂(*S*-2Cl-5Br-TPCP)₄
(Ref. 8)



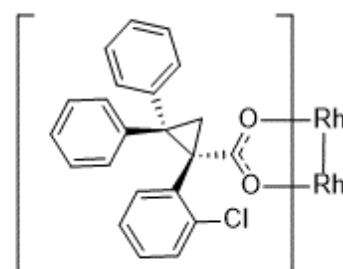
3.59

Rh₂(*R*-PTAD)₄
(Ref. 3)



3.58

R = C₆H₄-*p*-*t*Bu
Rh₂[*R*-tris(*p*-*t*BuC₆H₄)TPCP]₄
(Ref. 6)



3.107

Rh₂(*S*-2Cl-TPCP)₄
(Ref. 9)

The above catalysts were used in this study and have been prepared previously.¹⁻⁹

S.3.3 Synthesis of Substrates and Reagents

Synthesis of Diazo Compounds:

The following diazoacetates were prepared previously:

2,2,2-trichloroethyl 2-diazo-2-(3,5-dibromophenyl)acetate⁵

2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate¹⁰

2,2,2-tribromoethyl 2-(4-bromophenyl)-2-diazoacetate¹⁰

2,2,2-trichloroethyl 2-diazo-2-(4-fluorophenyl)acetate¹⁰

2,2,2-trichloroethyl 2-(4-(tert-butyl)phenyl)-2-diazoacetate¹⁰

2,2,2-trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate¹¹

2,2,2-trichloroethyl 2-(4-acetoxyphenyl)-2-diazoacetate¹¹

2,2,2-trichloroethyl 2-diazo-2-(p-tolyl)acetate¹¹

2,2,2-trichloroethyl 2-diazo-2-(3-methoxyphenyl)acetate¹¹

2,2,2-trichloroethyl 2-(6-chloropyridin-3-yl)-2-diazoacetate¹¹

2,2,2-trichloroethyl 2-(2-chloropyrimidin-5-yl)-2-diazoacetate¹¹

Synthesis of Aryl Cyclobutanes

The synthesis of most aryl-substituted cyclobutanes could be accomplished by utilizing a Grignard reagent addition to cyclobutanone followed by reduction of the tertiary alcohol in one step or two steps (elimination followed by hydrogenation). Heteroaryl-substituted cyclobutanes were synthesized as follows:

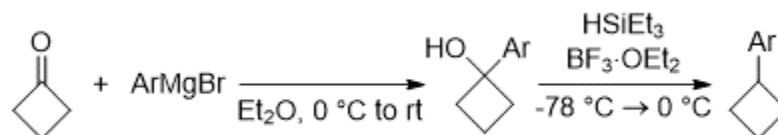
4-cyclobutyl-2,6-dimethylpyridine was prepared according to a literature procedure¹².

Characterization data for this compound were consistent with those reported in the original paper.

5-cyclobutyl-2-methoxypyridine was prepared via the Negishi coupling reaction of 5-bromo-2-methoxypyridine with cyclobutylzinc bromide. Characterization data for the product were consistent with those previously reported in the chemical literature¹³.

General Procedure 1 for the Synthesis of Aryl Substituted Cyclobutanes

The aryl substituted cyclobutanes were generated by a two step sequence.



General Procedure 1, Part A

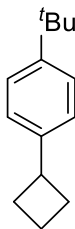
A 3-necked round-bottom flask was equipped with a condenser and addition funnel, and then it was flame-dried under vacuum. After cooling under argon, magnesium (2.5 equiv) was added. The Grignard reagent was formed by the dropwise addition of the corresponding aryl bromide (1.5 equiv) in Et₂O (1 M to the aryl bromide). The Grignard reagent was formed by heating to reflux for 5 h. After formation of the Grignard reagent, the solution was cooled to 0 °C, and then cyclobutanone (1.0 equiv) was added as a solution in ether (0.4 M to cyclobutanone). The reaction mixture was allowed to come to room temperature, and then stirred overnight. The reaction was

quenched by the addition of saturated ammonium chloride at 0 °C. The aqueous layer was extracted 3x50 mL ether. The organics were combined and then washed with brine. The organic layer was dried with magnesium sulfate, filtered, and then residual solvent was removed under reduced pressure. The crude material was purified by silica gel chromatography using hexanes/ethyl acetate as eluent.

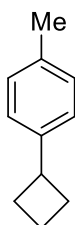
General Procedure 1, Part B

A round-bottom flask was flame-dried and then cooled under argon. The tertiary alcohol was added (1.0 equiv) followed by anhydrous dichloromethane (0.25 M to the tertiary alcohol). Triethylsilane was added (3.2 equiv), and then the reaction mixture was cooled to -78 °C. Once the mixture was cooled, $\text{BF}_3 \cdot \text{OEt}_2$ (3.2 equiv) was added dropwise. The reaction mixture was stirred at -78 °C for 30 minutes, and then was stirred at -40 °C for 30 minutes and then was stirred at 0 °C for 60 minutes. The reaction mixture was slowly quenched by an equal volume of saturated sodium bicarbonate at 0 °C. The layers were separated, and then the aqueous layer was extracted 3 x 50 mL dichloromethane. The organics were combined, dried with magnesium sulfate, filtered, and then the solvent was removed under reduce pressure. The aryl-substituted cyclobutanes were purified by column chromatography on silica gel using pentanes as eluant and/or Kugelrohr distillation.

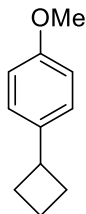
Note: The addition of heteroaromatic-based Grignard reagents was accomplished using methods developed by Senanayake and coworkers.¹⁴



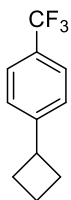
1-(*Tert*-butyl)-4-cyclobutylbenzene (3.52). The title compound was prepared by the reduction of 1-(4-(*tert*-butyl)phenyl)cyclobutan-1-ol¹⁵ (5.24 g, 25.6 mmol) as outlined in General Procedure 1. The cyclobutane was purified by column chromatography using pentanes as eluant. This procedure afforded the title compound (4.5 g, 94%) as a colorless oil. The spectrum was consistent with previously reported ¹H NMR spectra¹⁶: ¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 3.52 (p, *J* = 8.8 Hz, 1H), 2.38–2.26 (m, 2H), 2.22–2.08 (m, 2H), 2.07–1.93 (m, 1H), 1.91–1.77 (m, 1H), 1.32 (s, 9H).



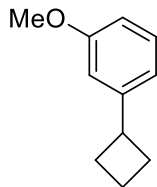
1-Cyclobutyl-4-methylbenzene (3.64). The title compound was prepared by the reduction of 1-(*p*-tolyl)cyclobutan-1-ol¹⁷ (4.1 g, 25 mmol) as outlined in General Procedure 1. The cyclobutane was purified by Kugelrohr distillation (65 °C at 0.5 mmHg). This procedure afforded the title compound (659 mg, 18%) as a colorless oil: ¹H NMR (500 MHz, CDCl₃) δ 7.24–7.17 (m, 4H), 3.60 (p, *J* = 8.7 Hz, 1H), 2.49–2.36 (m, 5H), 2.28–2.17 (m, 2H), 2.14–2.03 (m, 1H), 2.00–1.89 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 143.4, 135.2, 129.0, 126.3, 40.2, 30.1, 21.1, 18.4; IR (neat) 2972, 2937, 2862, 1513, 1444, 1243, 1118. 811, 724 cm⁻¹. MS (APCI+) 147.11736 (147.11683 calcd for C₁₁H₁₅, M + H⁺).



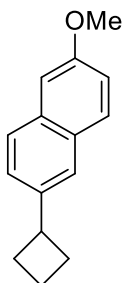
1-cyclobutyl-4-methoxybenzene (3.65). The title compound was prepared by the reduction of 1-(4-methoxyphenyl)cyclobutan-1-ol¹⁷ (4.5 g, 25 mmol) as outlined in General Procedure 1. The cyclobutane was purified by Kugelrohr distillation (82–83 °C at 0.5 mmHg). This procedure afforded the title compound (3.05 g, 75%) as a colorless oil. The spectrum was consistent with previously reported ¹H NMR spectra¹⁸: ¹H NMR (500 MHz, CDCl₃) δ 7.17–7.13 (m, 2H), 6.87–6.82 (m, 2H), 3.79 (s, 3H), 3.54–3.42 (m, 1H), 2.35–2.27 (m, 2H), 2.15–2.04 (m, 2H), 2.04–1.92 (m, 1H), 1.88–1.78 (m, 1H).



1-cyclobutyl-4-(trifluoromethyl)benzene (3.66). The title compound was prepared by the reduction of 1-(4-(trifluoromethyl)phenyl)cyclobutan-1-ol¹⁹ (5.40 g, 25 mmol) as outlined in General Procedure 1. The cyclobutane was purified by Kugelrohr distillation (46 °C at 0.5 mmHg). This procedure afforded the title compound (1.0 g, 20%) as a colorless oil. The spectrum was consistent with previously reported ¹H NMR spectra²⁰: ¹H NMR (500 MHz, CDCl₃) δ 7.54 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 3.60 (p, *J* = 8.7 Hz, 1H), 2.44–2.33 (m, 2H), 2.21–2.11 (m, 2H), 2.11–2.00 (m, 1H), 1.92–1.84 (m, 1H).

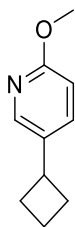


1-Cyclobutyl-3-methoxybenzene (3.67). The title compound was prepared by the reduction of 1-(3-methoxyphenyl)cyclobutan-1-ol²¹ (4.46 g, 25 mmol) as outlined in General Procedure 1. The cyclobutane was purified by Kugelrohr distillation (80 °C at 0.5 mmHg). This procedure afforded the title compound (1.14 g, 28%) as a colorless oil. The spectrum was consistent with previously reported ¹H NMR spectra²²: ¹H NMR (600 MHz, CDCl₃) δ 7.22 (t, *J* = 7.9 Hz, 1H), 6.84–6.80 (m, 1H), 6.78 (t, *J* = 1.9 Hz, 1H), 6.72 (dd, *J* = 7.9, 2.9, 1H), 3.81 (s, 3H), 3.56–3.49 (m, 1H), 2.37–2.30 (m, 2H), 2.19–2.10 (m, 2H), 2.05–1.96 (m, 1H), and 1.88–1.81 (m, 1H).



2-cyclobutyl-6-methoxynaphthalene (3.68). 1-(6-methoxynaphthalen-2-yl)cyclobutan-1-ol (10.0 g, 88% yield, mp 90–91 °C) was prepared by the addition of (6-methoxynaphthalen-2-yl)magnesium bromide to cyclobutanone using General Procedure 1, Part A. ¹H NMR (600 MHz, C₆D₆) δ 7.77 (s, 1H), 7.62 (t, *J* = 9.9 Hz, 2H), 7.54 (d, *J* = 8.9 Hz, 1H), 7.21 (d, *J* = 8.8 Hz, 1H), 6.96 (s, 1H), 3.41 (s, 3H), 2.54–2.45 (m, 2H), 2.39–2.27 (m, 3H), 1.96–1.86 (m, 1H), 1.63–1.53 (m, 1H); ¹³C NMR (151 MHz, C₆D₆) δ 158.2, 142.1, 134.3, 130.1, 129.1, 127.5, 125.1, 123.4, 119.3, 106.0, 77.0, 54.8, 37.2, 13.5; IR (neat) 3365, 2975, 2938, 1629, 1605, 1484, 1501, 1451, 1386, 1264, 1241, 1176, 1147, 1131, 1112, 1024, 955, 923, 907, cm⁻¹. MS (APCI+) 227.10699 (227.10666 calcd for C₁₅H₁₅O₂, M + H⁺ - H₂). The title compound was prepared by the reduction

of 1-(6-methoxynaphthalen-2-yl)cyclobutan-1-ol (5.71 g, 25 mmol) as outlined in General Procedure 1, Part B. The cyclobutane was purified by eluting the crude material through a plug of silica using hexanes. This procedure afforded the title compound (2.1 g, 41%) as a colorless solid, mp 64–65 °C: ^1H NMR (600 MHz, C_6D_6) δ 7.57 (d, J = 8.4 Hz, 1H), 7.50 (d, J = 8.9 Hz, 1H), 7.44 (s, 1H), 7.23 (dd, J = 8.4, 1.7 Hz, 1H), 7.17 (dd, J = 8.9, 2.5 Hz, 1H), 6.92 (d, J = 2.5 Hz, 1H), 3.46 (p, J = 8.8 Hz, 1H), 3.36 (s, 3H), 2.20 (qt, J = 8.2, 2.3 Hz, 2H), 2.09 (pd, J = 9.4, 2.5 Hz, 2H), 1.89–1.79 (m, 1H), 1.76–1.68 (m, 1H); ^{13}C NMR (151 MHz, C_6D_6) δ 157.8, 141.5, 133.8, 129.7, 129.5, 127.2, 126.2, 124.6, 119.2, 106.0, 54.8, 40.8, 30.1, 18.7; IR (neat) 3008, 2961, 2938, 2886, 2861, 1630, 1601, 1483, 1461, 1388, 1352, 1260, 1202, 1162, 1117, 1029, 934, 881, 910, 815 cm^{-1} . ^1MS (APCI+) 211.11202 (211.11174 calcd for $\text{C}_{15}\text{H}_{15}\text{O}$, $\text{M} + \text{H}^+ - \text{H}_2$).



5-cyclobutyl-2-methoxypyridine (3.77). A three-necked round bottom flask was charged with freshly ground magnesium turnings (540 mg, 1.00 equiv, 22.2 mmol), dry THF (62 mL), and a magnetic stirbar. Bromocyclobutane (3.09 g, 1.03 equiv, 22.9 mmol) was added dropwise to the stirring mixture as a neat liquid. The flask was heated at reflux for 16 h, which resulted in the near-complete reaction of magnesium to form a clear emerald green solution. At this stage, the mixture was cooled to -78 °C using a bath of dry ice/acetone, and a solution of anhydrous zinc(II) bromide (5.00 g, 1.00 equiv, 22.2 mmol) in tetrahydrofuran (19.6 mL, 1.13 M) was added by syringe. The flask was removed from the cooling bath and after stirring at room temperature for 18 h, the mixture was diluted with an additional 35.0 mL THF. 5-bromo-2-methoxypyridine (2.09 g, 1.00 equiv, 11.1 mmol) was then added, followed by [1,1'-

bis(diphenylphosphino)ferrocene]dichloropalladium(II) (812 mg, 10.0 mol%, 1.11 mmol). The mixture was heated at reflux for 16 h. Then it was filtered through silica gel (30 g), washing with additional diethyl ether (400 mL). Concentration of the filtrate gave 2.2 g of crude product as a turbid red oil. Kugelrohr distillation (air bath temperature 97 °C at 0.6 mmHg) afforded 1.34 g of pure 5-cyclobutyl-2-methoxypyridine (74% yield). The ^1H NMR spectrum was consistent with previously reported data¹³: ^1H NMR (600 MHz, Chloroform- d) δ 7.95 (s, 1H), 7.44 (dd, 1H), 6.67 (d, 1H), 3.88 (s, 3H), 3.56 – 3.37 (m, 1H), 2.38 – 2.23 (m, 2H), 2.14 – 1.89 (m, 3H), 1.90 – 1.77 (m, 1H).

S.3.4 Catalyst Screening for C-H Functionalization Reactions

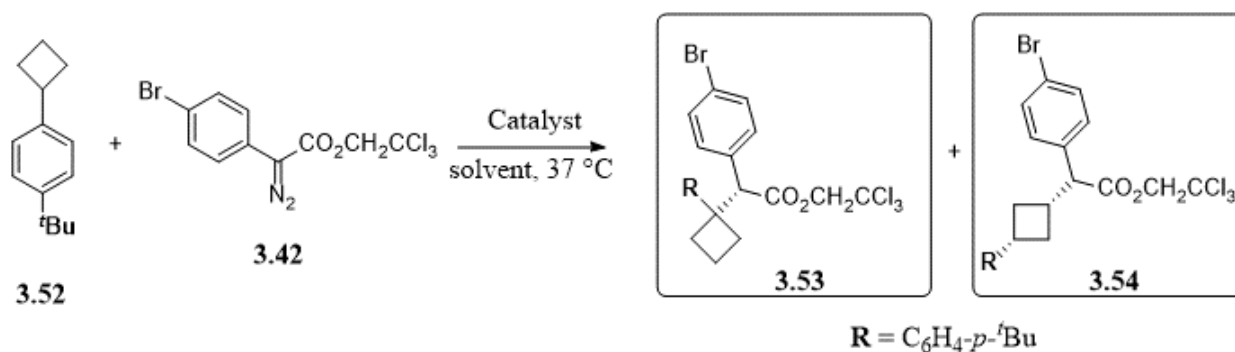
Work done by Dr. Zachary Garlets.

General Procedure 2 for C–H Functionalization Reactions.

An oven-dried vial was equipped with magnetic stir bar and sealed with septa and cap. This was cooled under vacuum, and then flame-dried once. After cooling to room temperature, the vial was loaded with rhodium catalyst (0.5-1 mol%), the indicated quantity of the cyclobutane substrate, and anhydrous solvent (2.0 mL solvent / 1.0 mmol cyclobutane). The mixture was allowed to stir under argon (the mixture was heated if heat was applied) while the diazo compound was prepared. A solution of the diazo compound was prepared by dissolving in the indicated solvent (3 mL solvent / 0.25 mmol diazo compound) and then this mixture was added dropwise by syringe pump over 3 h. Upon completion of the addition, the reaction was stirred an additional 2-4 h. Residual solvent was removed under reduced pressure (if the reaction was heated, it was allowed to come to room temperature before removing residual solvent), and the crude product was purified by silica gel chromatography.

Procedure for Analyzing Reaction Mixtures during Catalyst Screen

Reactions were conducted according to General Procedure 2 using 3 equiv. of the 1-(*tert*-butyl)-4-cyclobutylbenzene. The s at 3.99 ppm is represented by the tertiary functionalization for compound **3.53**. The d at 3.62 ppm is represented by the *cis* secondary distal functionalization for compound **3.54**. The d at 3.89 ppm is represented by the *trans* secondary distal functionalization (a minor product in every case). The enantioselectivity was determined by HPLC analysis of the material after flash chromatography.



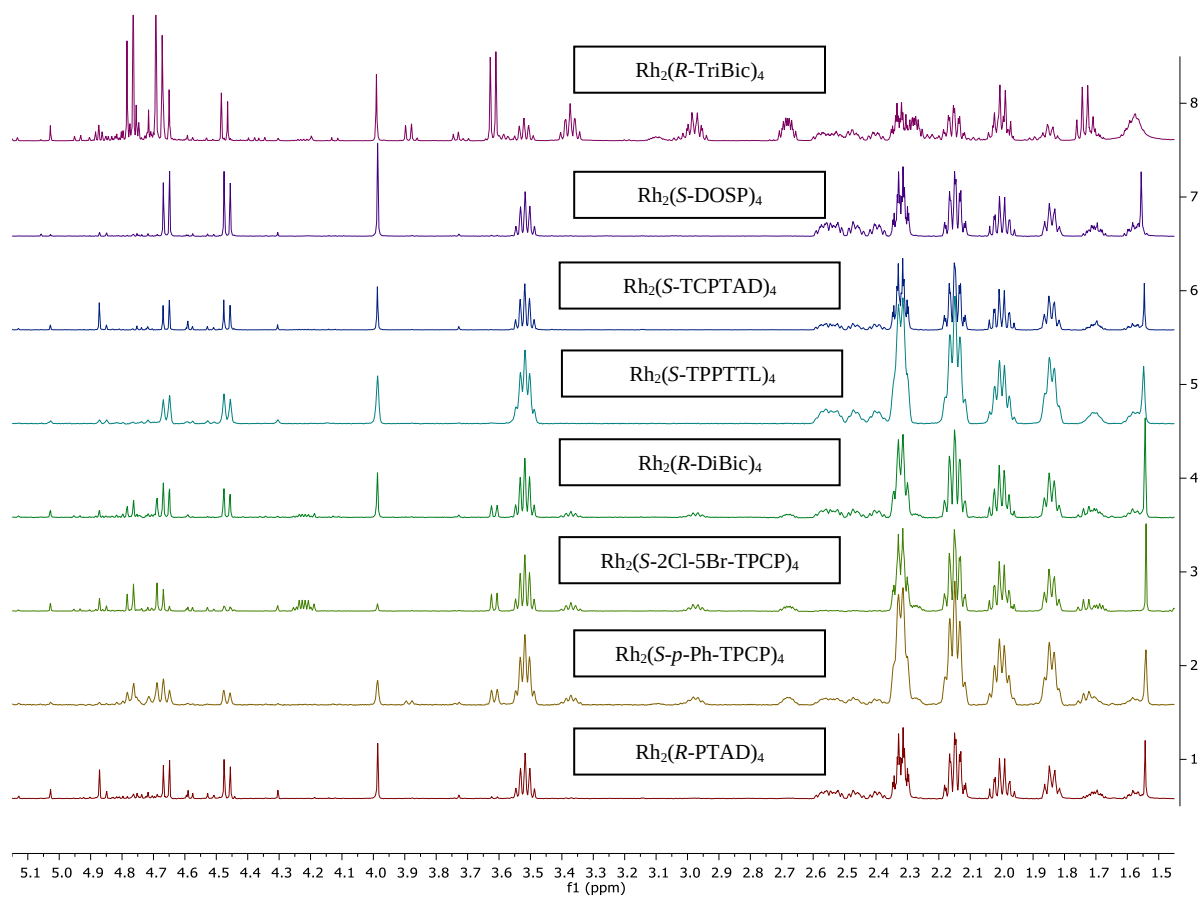
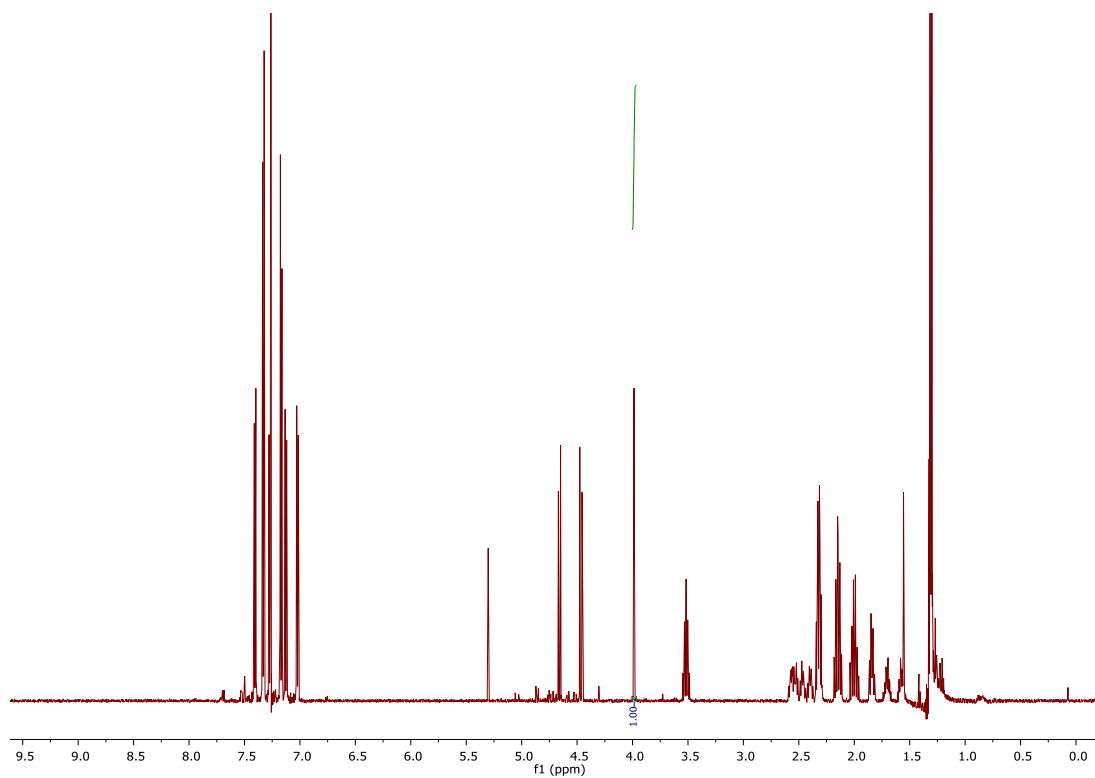
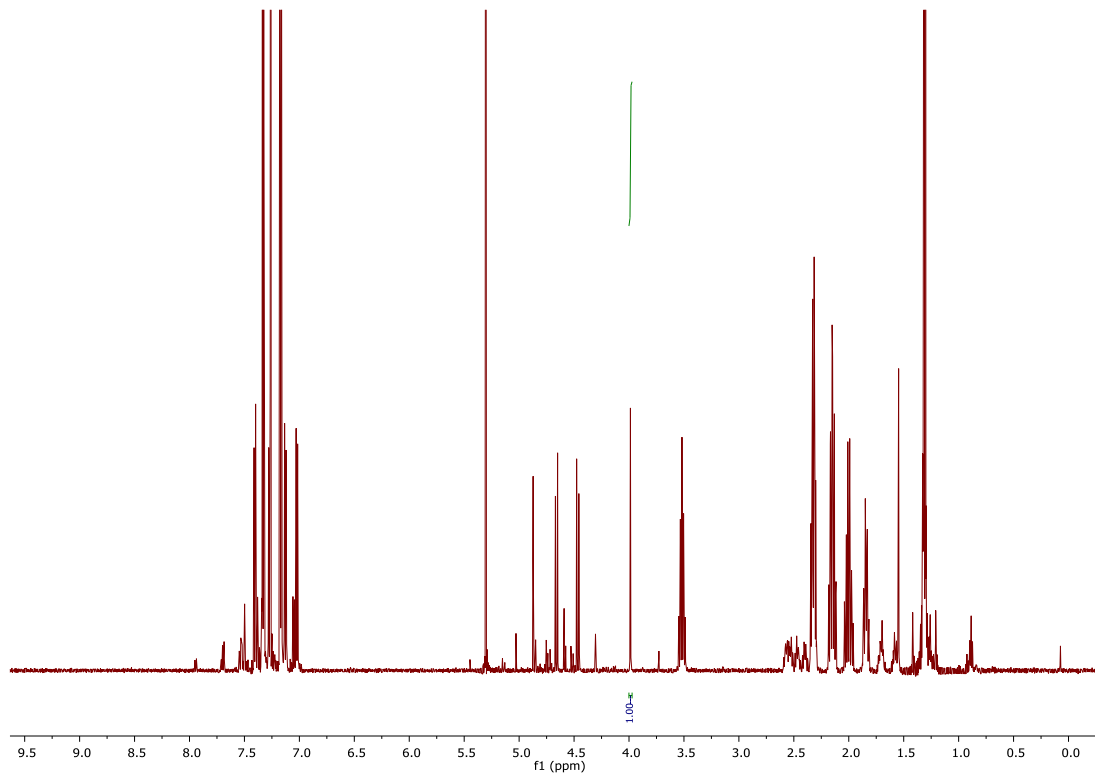


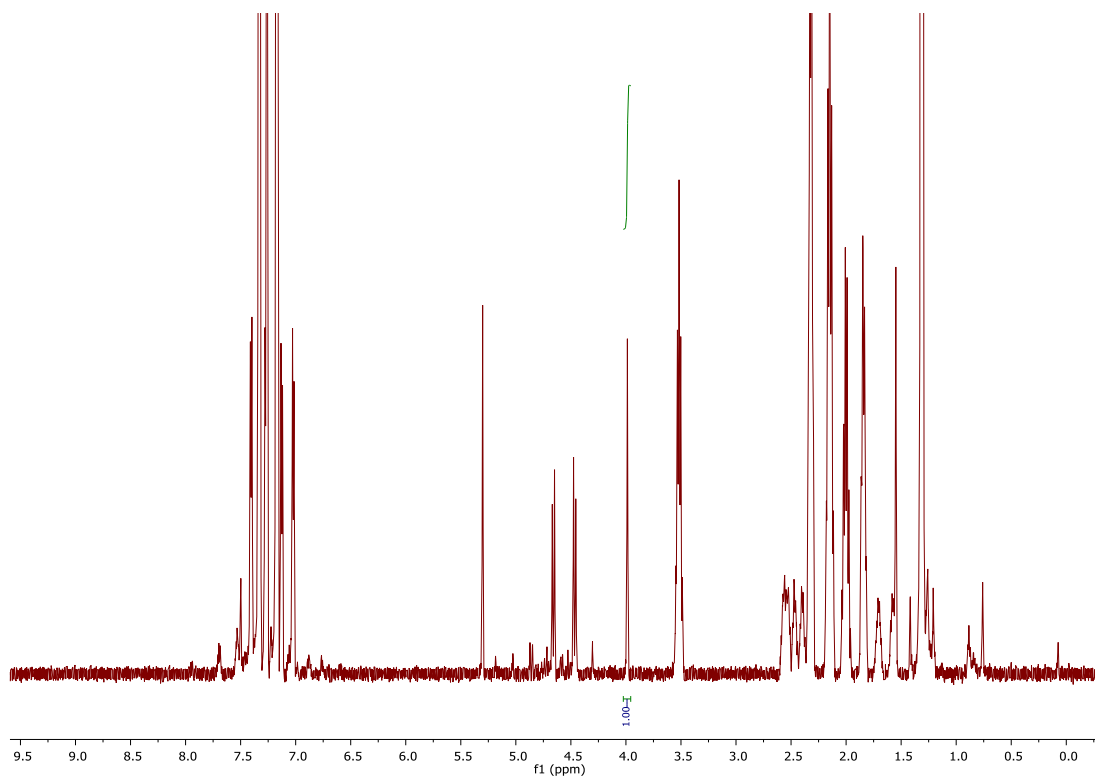
Figure S.3.2: Comparison of crude ¹H NMR spectra for the C-H Functionalization of Cyclobutanes with Different Catalysts. Ratios were determined by comparing s at 3.99 ppm (3° C-H insertion product), d at 3.62 (*cis*-C3 insertion product), and d at 3.89 ppm (*trans*-C3 insertion product).



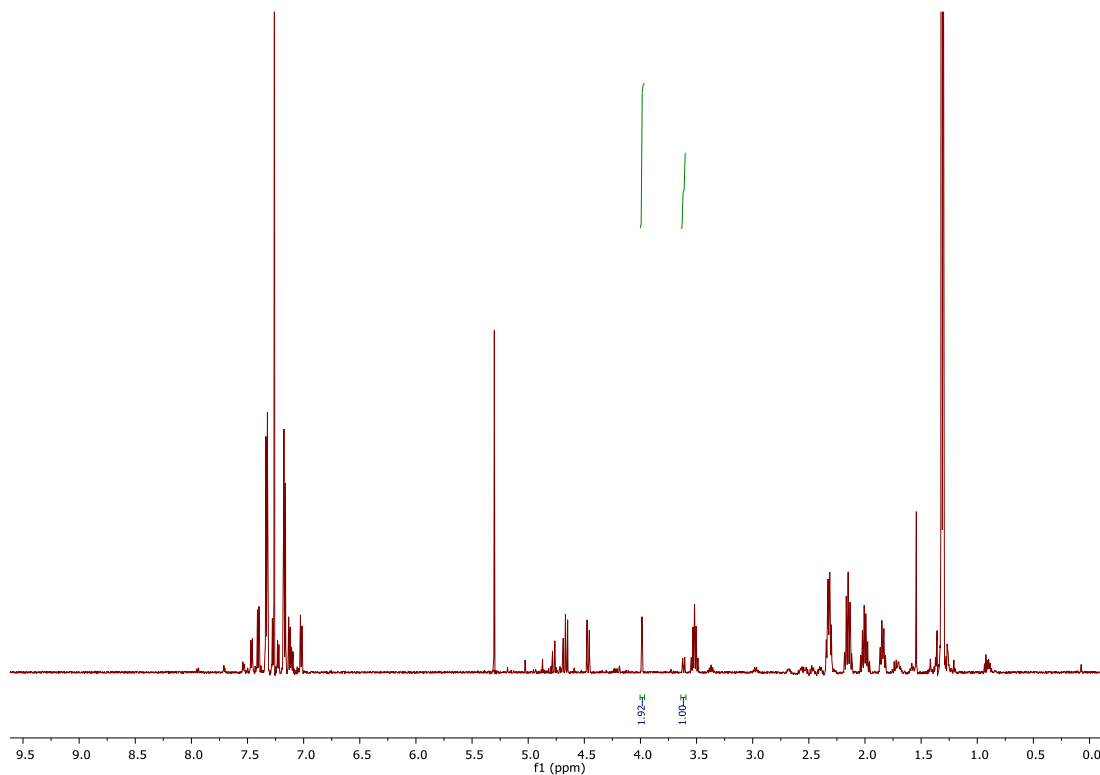
Crude NMR Spectrum using $\text{Rh}_2(\text{S-DOSP})_4$ (**3.55**) as the catalyst.



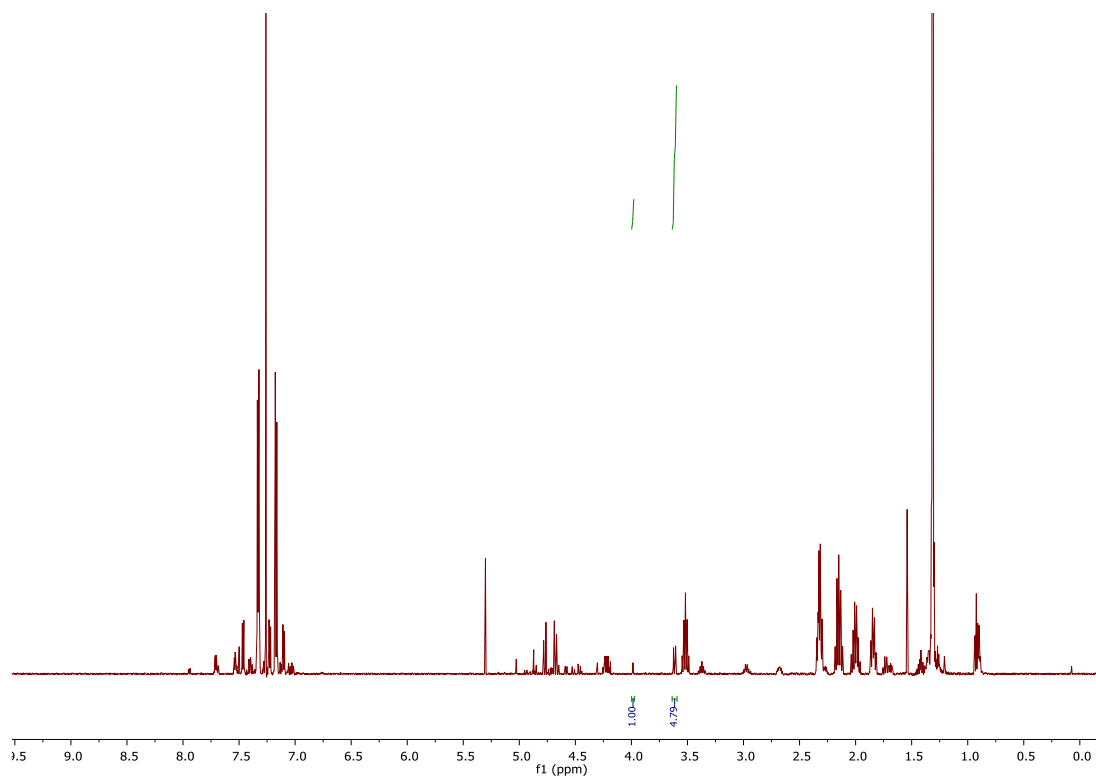
Crude NMR Spectrum using $\text{Rh}_2(\text{S-TCPTAD})_4$ (**3.56**) as the catalyst.



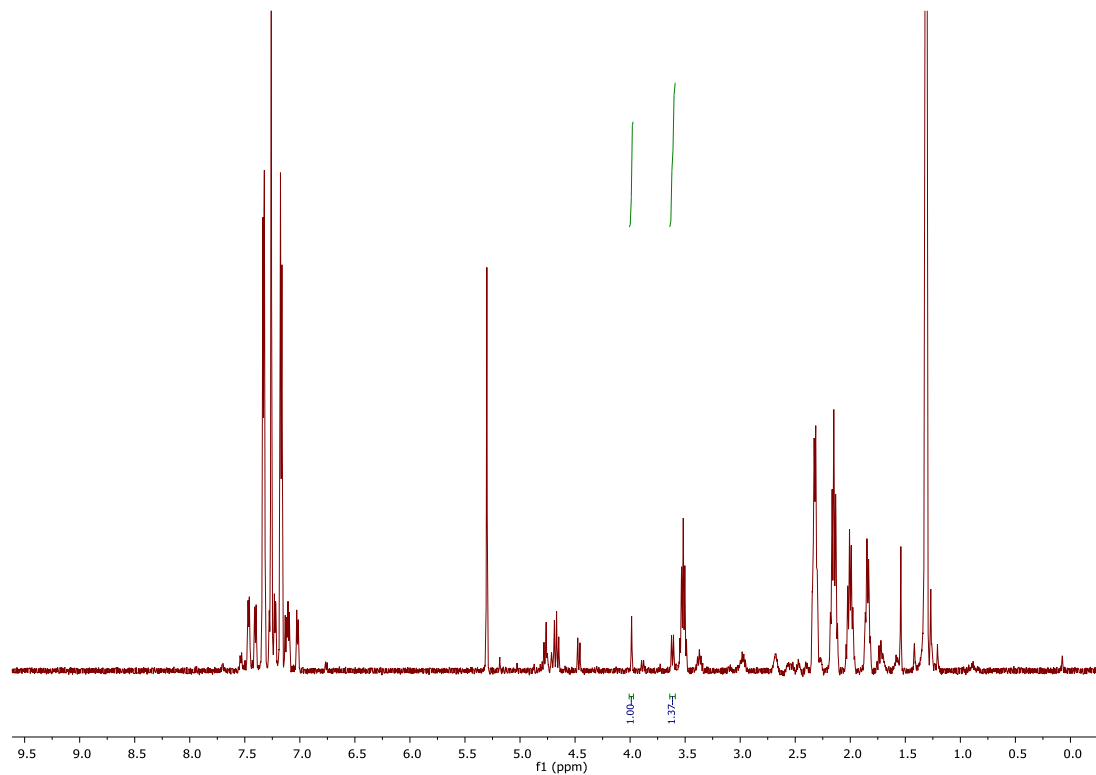
Crude NMR spectrum using $\text{Rh}_2(\text{S-TPPTTL})_4$ (**3.5**) as the catalyst.



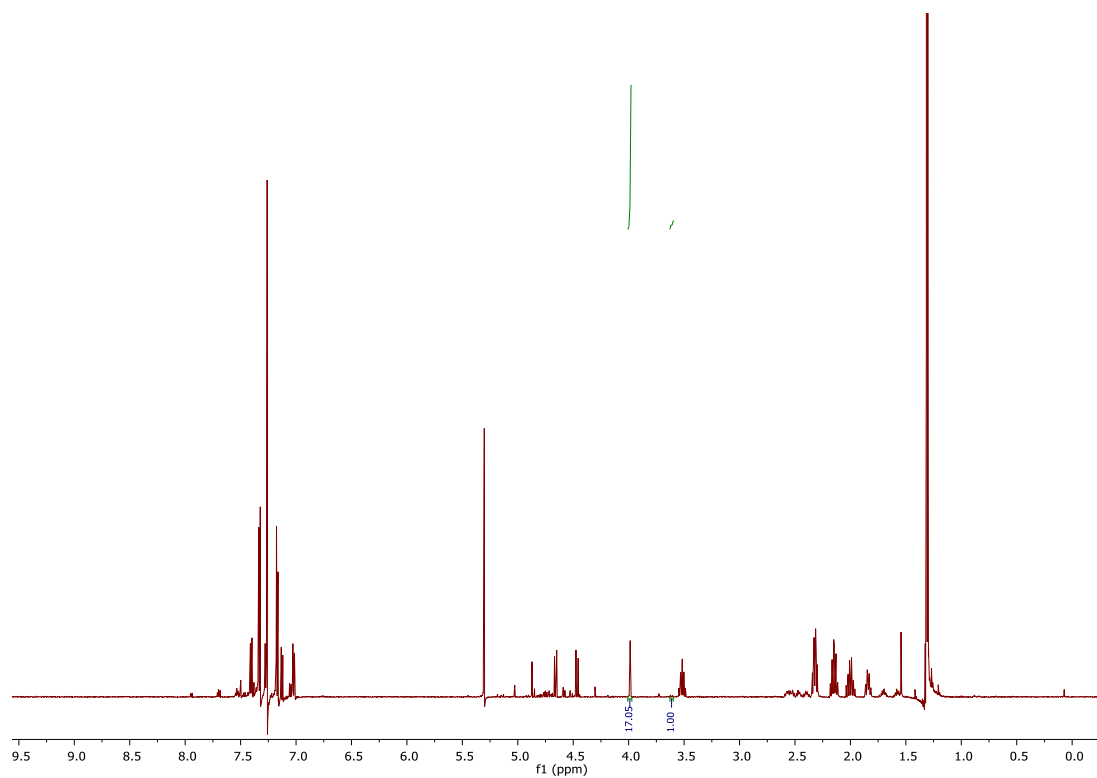
Crude NMR spectrum using $\text{Rh}_2(\text{R-DiBic})_4$ (**3.57**) as the catalyst.



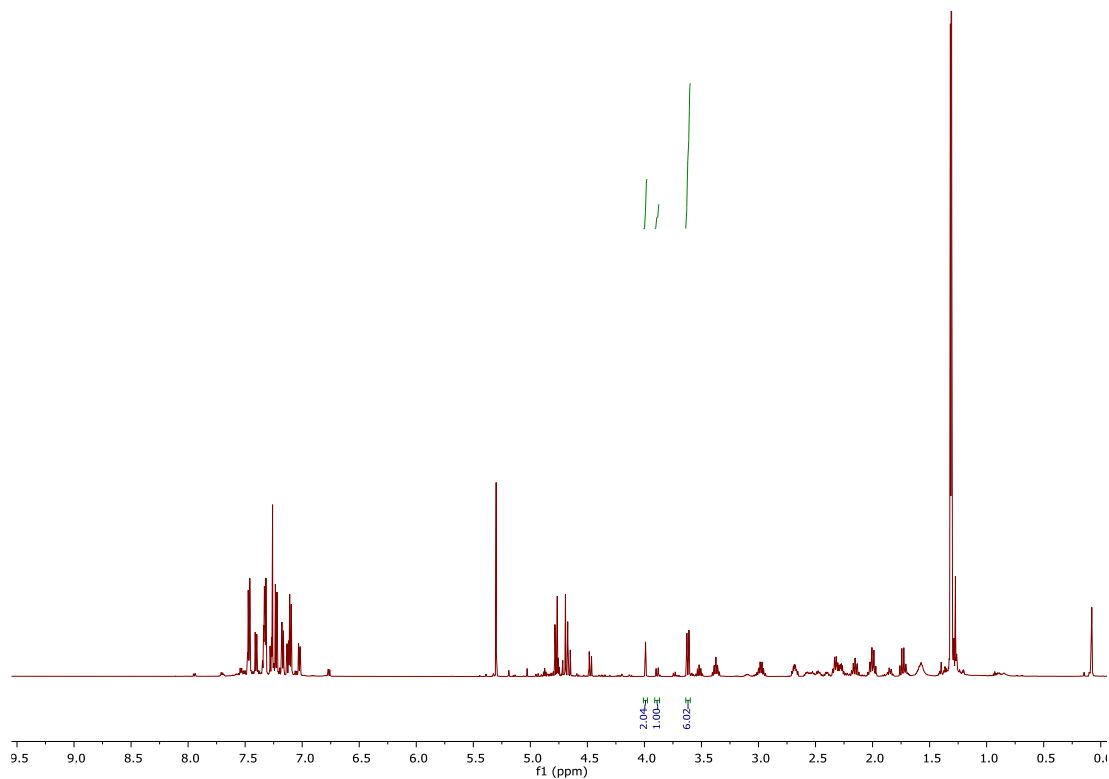
Crude NMR spectrum using $\text{Rh}_2(\text{S-2-Cl-5-BrTPCP})_4$ (**3.43**) as the catalyst.



Crude NMR spectrum using $\text{Rh}_2(\text{S-2-Cl-TPCP})_4$ (**3.107**) as the catalyst.

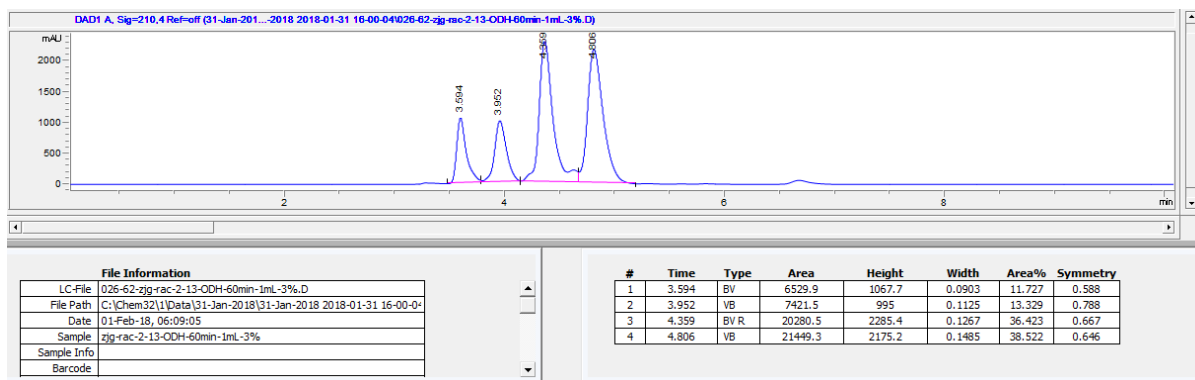


Crude NMR spectrum using $\text{Rh}_2(\text{R-PTAD})_4$ (**3.59**) as the catalyst.

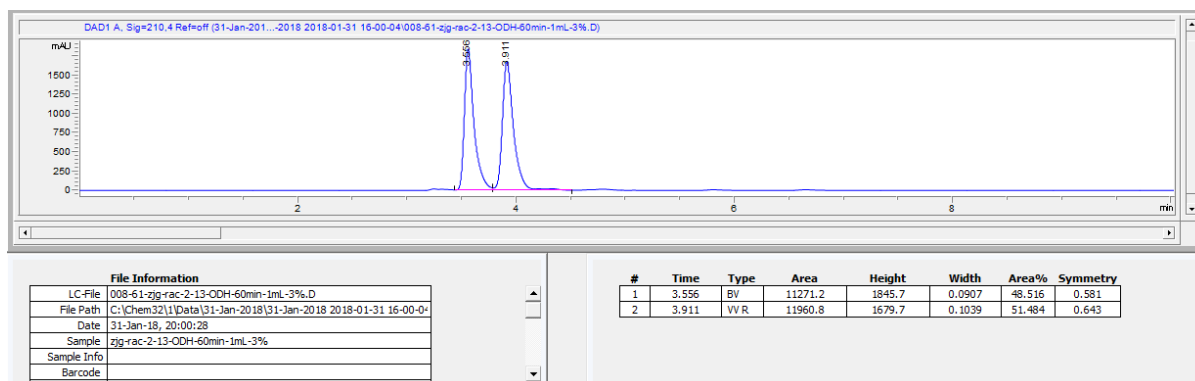


Crude NMR spectrum using $\text{Rh}_2(\text{R-TriBic})_4$ (**3.58**) as the catalyst.

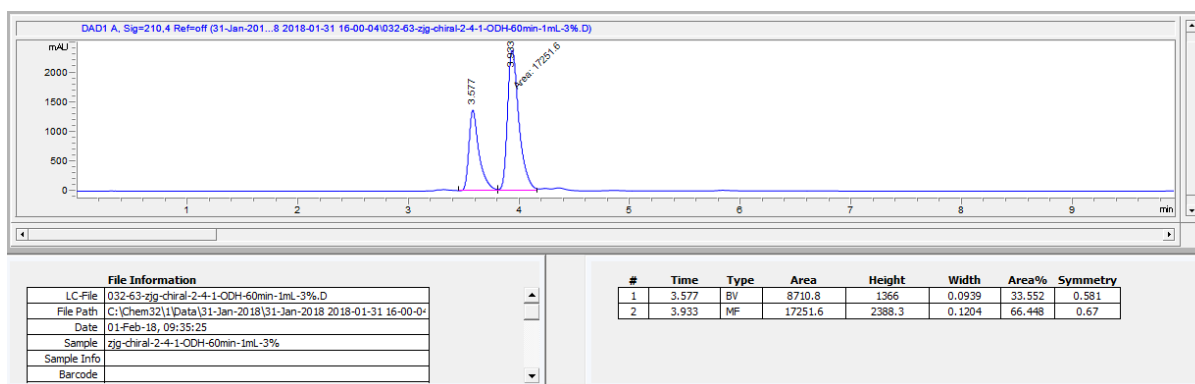
HPLC Traces Generated During Catalyst Screen



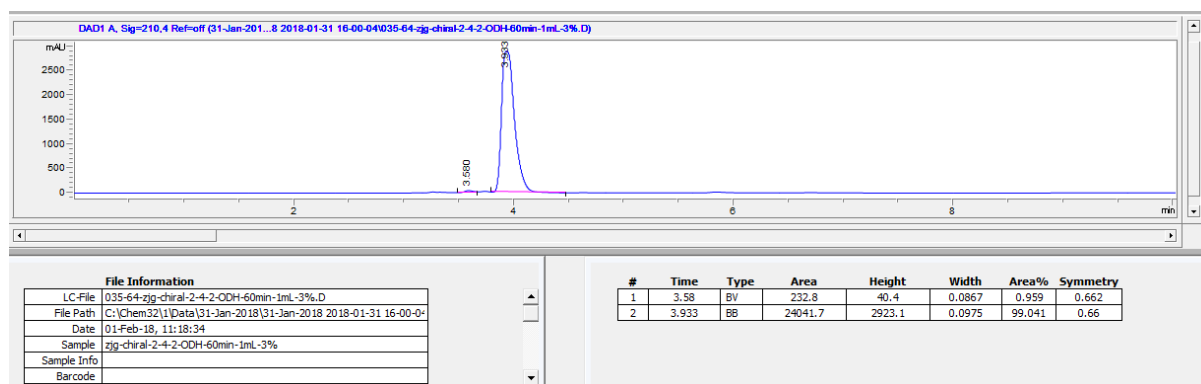
Chiral HPLC trace using $\text{Rh}_2(\text{R/S-2-Cl-TPCP})_4$ (**3.108**) as the catalyst.



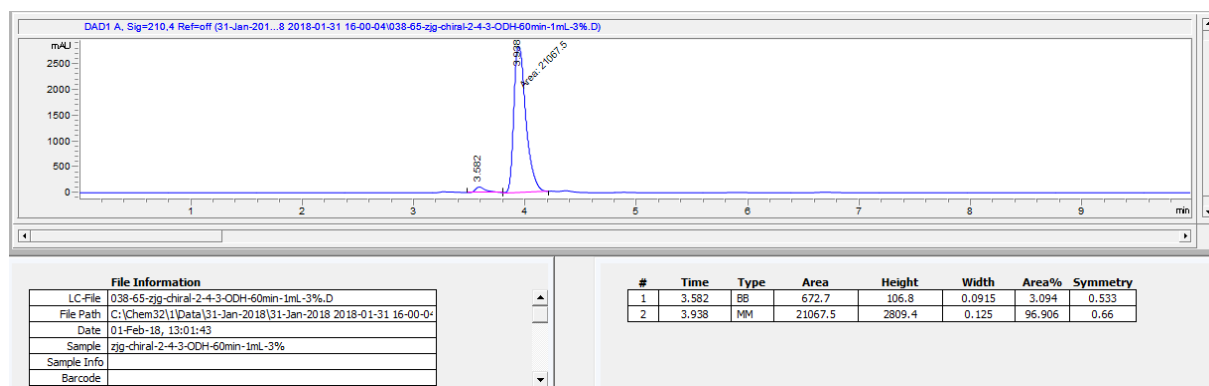
Chiral HPLC trace using $\text{Rh}_2(\text{R/S-TCPTAD})_4$ (**3.109**) as the catalyst.



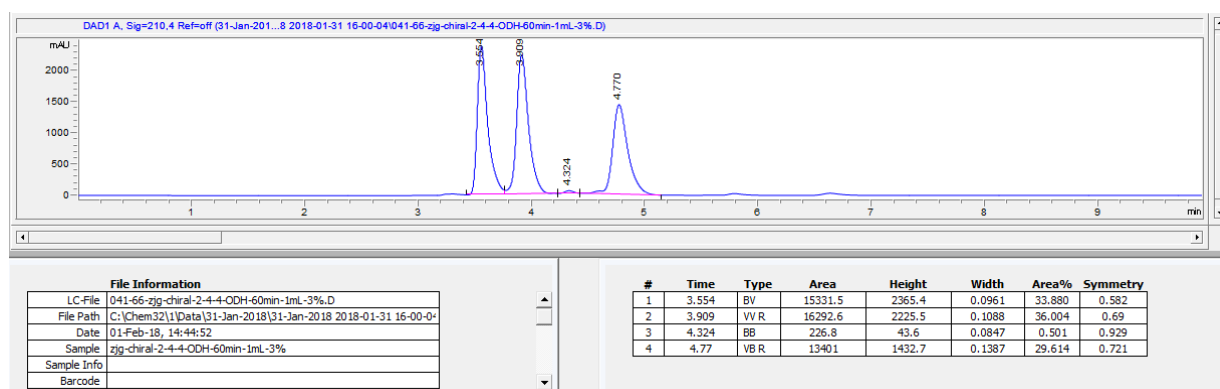
Chiral HPLC trace using $\text{Rh}_2(\text{S-DOSP})_4$ (**3.55**) as the catalyst.



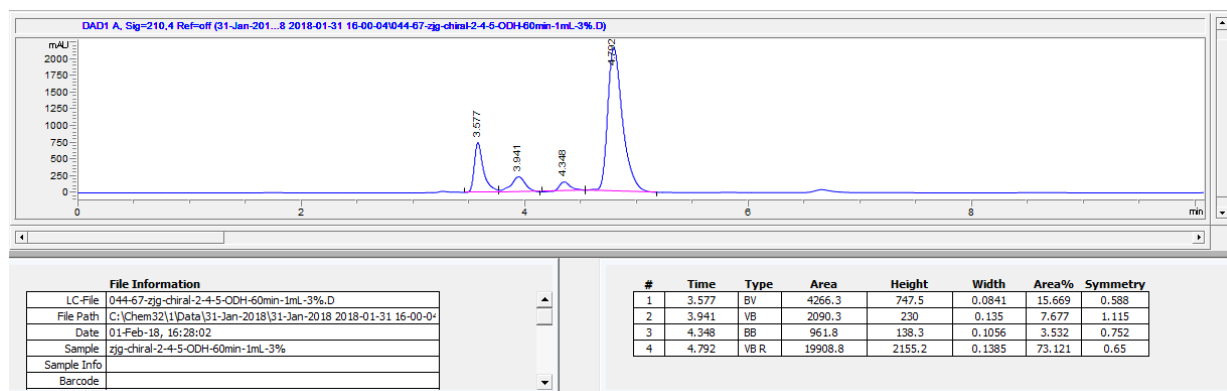
Chiral HPLC trace using $\text{Rh}_2(\text{S-TCPTAD})_4$ (3.56) as the catalyst.



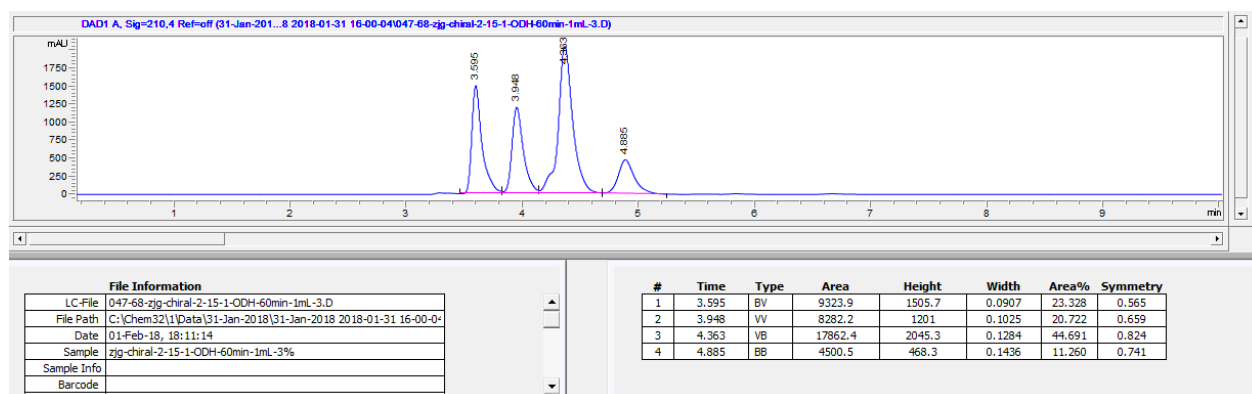
Chiral HPLC trace using $\text{Rh}_2(\text{S-TPPTTL})_4$ (3.5) as the catalyst.



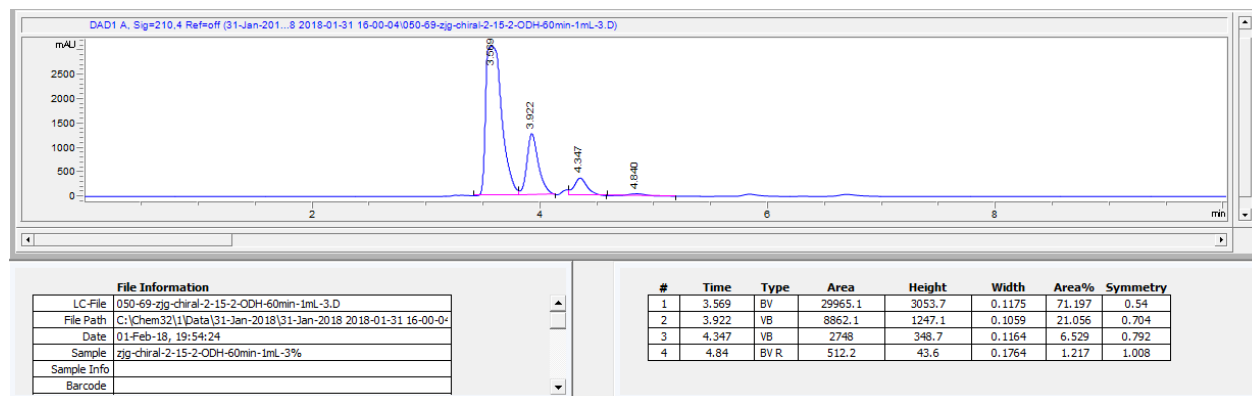
Chiral HPLC trace using $\text{Rh}_2(\text{R-DiBic})_4$ (3.57) as the catalyst.



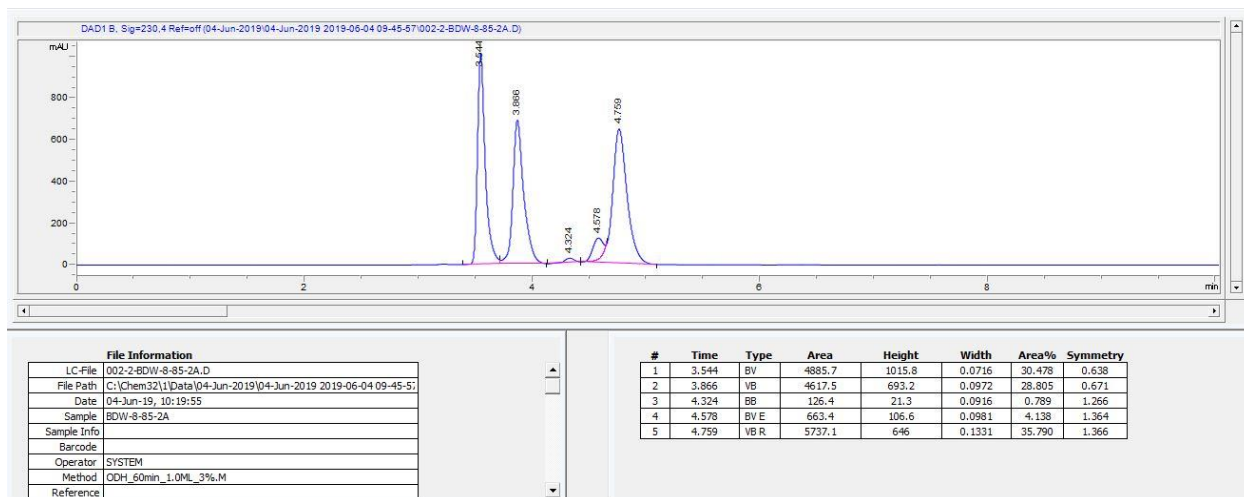
Chiral HPLC trace using $\text{Rh}_2(\text{S-2-Cl-5-BrTPCP})_4$ (**3.43**) as the catalyst.



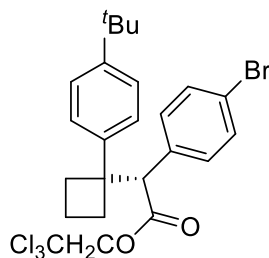
Chiral HPLC trace using $\text{Rh}_2(\text{S-p-PhTPCP})_4$ (**3.40**) as the catalyst.



Chiral HPLC trace using $\text{Rh}_2(\text{R-PTAD})_4$ (**3.59**) as the catalyst.

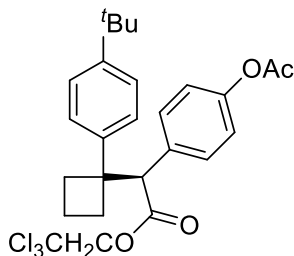


S.3.5 Characterization of C1 Functionalization Products

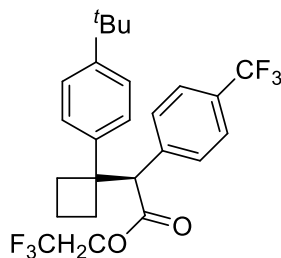


2,2,2-Trichloroethyl (S)-2-(4-bromophenyl)-2-(1-(4-(*tert*-butyl)phenyl)cyclobutyl)acetate (3.53). The general procedure 2 was employed for the C–H functionalization of 1-(*tert*-butyl)-4-cyclobutylbenzene (**3.52**, 141 mg, 0.75 mmol, 3.00 equiv) by reaction of 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**3.42**, 93 mg, 0.25 mmol, 1.00 equiv) using $\text{Rh}_2(\text{S-TCPTAD})_4$ (**3.56**, 5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (87 mg, 65%) as a colorless oil. On evaporation from 100% hexanes, the material crystallized to a colorless solid. mp 84.5–85.5 °C. $[\alpha]_D^{23} + 2.5$ (c 1.00, CHCl_3); ^1H NMR (400 MHz, CHCl_3 -d) δ 7.39 (d, $J = 8.2$ Hz, 2H), 7.26 (d, 2H), 7.11 (d, $J = 8.2$ Hz, 2H), 7.00 (d, $J = 8.1$ Hz, 2H), 4.64 (d, $J = 11.9$ Hz, 1H), 4.44 (d, $J = 12.0$ Hz, 1H), 3.97 (s, 1H), 2.63 – 2.30 (m, 4H), 1.69 (dtt, $J = 12.3, 9.1, 6.3$ Hz, 1H), 1.60 – 1.54 (m, 1H), 1.28 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.5, 149.2, 143.3, 134.2,

131.8, 131.2, 127.2, 124.8, 122.0, 94.7, 74.4, 60.4, 49.4, 34.5, 32.4, 31.6, 30.7, 16.1. IR (neat) 2962, 2867, 1751, 1489, 1135, 1011, 833, 721 cm^{-1} . MS (ESI+) 531.0261 (531.0255 calcd for $\text{C}_{24}\text{H}_{27}\text{O}_2\text{BrCl}_3$, $\text{M} + \text{H}^+$). The enantiopurity was determined to be 98% ee by chiral HPLC analysis (Chiralcel ODH, 15 cm x 4.6 mm, 1% IPA/Hexanes, 1.00 mL/min, λ 230 nm, RT= 3.8 (minor) and 4.6 min (major)).



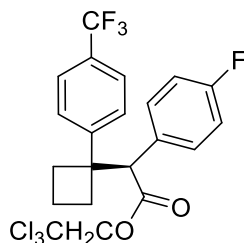
2,2,2-Trichloroethyl (R)-2-(4-acetoxyphe-nyl)-2-(1-(4-(tert-butyl)phenyl)cyclobutyl)acetate (3.79). The general procedure 2 was employed for the C–H functionalization of 1-(tert-butyl)-4-cyclobutylbenzene (**3.52**, 47 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(4-acetoxyphe-nyl)-2-diazoacetate (176 mg, 0.50 mmol) using $\text{Rh}_2(\text{R-TCPTAD})_4$ (**3.33**, 5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (125 mg, 98%) as a colorless solid, mp 70–73 $^{\circ}\text{C}$: $[\alpha]_D^{23} +6.9$ (c 1.0, CH_2Cl_2); ^1H NMR (600 MHz, CDCl_3) δ 7.31–7.29 (m, 2H), 7.29–7.26 (m, 2H), 7.06–7.04 (m, 2H), 7.04–7.01 (m, 2H), 4.67 (d, J = 11.9 Hz, 1H), 4.41 (d, J = 11.9 Hz, 1H), 4.01 (s, 1H), 2.63–2.52 (m, 2H), 2.52–2.44 (m 1H), 2.42–2.34 (m, 1H), 2.30 (s, 3H), 1.73–1.64 (m, 1H), 1.58–1.48 (m, 1H), 1.30 (s, 9H); ^{13}C NMR (151 MHz, CDCl_3) δ 170.7, 169.4, 150.4, 149.1, 143.7, 132.8, 131.1, 127.1, 124.7, 121.1, 94.7, 74.4, 60.4, 49.4, 34.5, 32.3, 31.6, 30.4, 21.3, 16.1; IR (film) 2962, 2868, 1751, 1506, 1368, 1271, 1198, 1169, 1133, 1049, 1018, 910, 830, 756, 722 cm^{-1} . MS (APCI-) 509.1066 (509.1059 calcd for $\text{C}_{26}\text{H}_{28}\text{Cl}_3\text{O}_4$, $\text{M} - \text{H}^+$). The enantiopurity was determined to be 96% ee by chiral HPLC analysis (Chiralcel OD-H, 25 cm x 4.6 mm, 2% IPA/Hexanes, 0.25 mL/min, λ 230 nm, RT= 25.3 and 27.5 min).



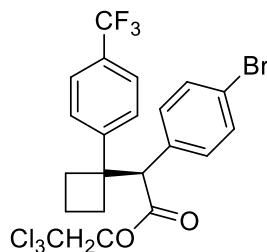
2,2,2-Trifluoroethyl

(R)-2-(1-(4-(*tert*-butyl)phenyl)cyclobutyl)-2-(4-

(trifluoromethyl)phenyl)acetate (3.80). The general procedure 2 was employed for the C–H functionalization of 1-(*tert*-butyl)-4-cyclobutylbenzene (**3.52**, 94 mg, 0.5 mmol) by reaction of 2,2,2-trifluoroethyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate (312 mg, 1.0 mmol) using Rh₂(R-TCPTAD)₄ (**3.33**, 5.3 mg, 0.5 mol%) as catalyst. This procedure afforded the title compound (154 mg, 65%) as a colorless solid, mp 59–62 °C: [α]_D²³ -6.6 (c 1.0, CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.29–7.26 (m, 2H), 6.97–6.94 (m, 2H), 4.37 (dq, *J* = 12.6, 8.5 Hz, 1H), 4.24 (dq, *J* = 12.6, 8.4 Hz, 1H), 4.05 (s, 1H), 2.59–2.53 (m, 1H), 2.53–2.39 (m, 3H), 1.78–1.68 (m, 1H), 1.66–1.56 (m, 1H), 1.31 (s, 9H); ¹³C NMR (151 MHz, CDCl₃) δ 170.4, 149.5, 142.7, 139.1, 130.4, 130.0 (q, *J* = 33 Hz), 127.0, 124.9 (q, *J* = 3.8 Hz), 124.8, 124.3 (q, *J* = 272 Hz), 122.9 (q, *J* = 277 Hz), 60.5, 60.5 (q, *J* = 37 Hz), 49.7, 34.6, 32.0, 31.5, 30.9, 16.0; ¹⁹F NMR (282 MHz, CDCl₃) δ -62.55, -73.57 (t, *J* = 8.5 Hz); IR (film) 2965, 1754, 1619, 1509, 1325, 1275, 1164, 1124, 1070, 1019, 980, 837 cm⁻¹. MS (APCI-) 471.1763 (471.1764 calcd for C₂₅H₂₅O₂F₆, M - H⁺). The enantiopurity was determined to be 96% ee by chiral HPLC analysis (Chiralcel OD-H, 25 cm x 4.6 mm, 2% IPA/Hexanes, 0.25 mL/min, λ 230 nm, RT= 15.3 and 17.8 min).



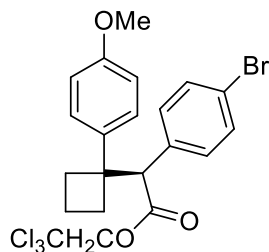
2,2,2-Trichloroethyl **(R)-2-(4-fluorophenyl)-2-(1-(4-(trifluoromethyl)phenyl)-cyclobutyl)acetate (3.81).** The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-(trifluoromethyl)benzene (**3.66**, 50 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-diazo-2-(4-fluorophenyl)acetate (156 mg, 0.50 mmol) using $\text{Rh}_2(\text{R-TCPTAD})_4$ (**3.33**, 5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (90 mg, 74%) as a colorless oil: $[\alpha]^{23}_{\text{D}} +3.5$ (c 1.00, CHCl_3); ^1H NMR (600 MHz, CDCl_3) δ 7.54–7.47 (m, 2H), 7.21–7.12 (m, 4H), 7.03–6.94 (m, 2H), 4.72 (d, $J = 12.0$ Hz, 1H), 4.51 (d, $J = 12.0$ Hz, 1H), 4.06 (s, 1H), 2.73–2.54 (m, 2H), 2.51–2.37 (m, 2H), 1.83–1.64 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 170.4, 164.3 (d, $J = 247$ Hz), 150.6, 131.6 (d, $J = 8.1$ Hz), 130.3 (d, $J = 3.4$ Hz), 128.6 (q, $J = 32.8$ Hz), 128.1, 124.3 (q, $J = 272$ Hz), 124.65 (q, $J = 3.8$ Hz), 115.2 (d, $J = 21.5$ Hz), 94.6, 74.3, 59.5, 49.7, 32.2, 31.4, 16.1; ^{19}F NMR (282 MHz, CDCl_3) δ -62.34, -114.20, -114.33 (m); IR (film) 3046, 2983, 2950, 2869, 1749, 1618, 1606, 1508, 1325, 1228, 1162, 1124, 1114, 1071, 1015, 908, 842, 720 cm^{-1} . MS (ESI-) 516.9926 (516.9924 calcd for $\text{C}_{21}\text{H}_{17}\text{O}_2\text{Cl}_4\text{F}_4$, $\text{M} + \text{Cl}^-$). The enantiopurity was determined to be 96% ee by chiral HPLC (Chiralpak IAU 1.6 μm , 100 mm x 3 mm, 0.5% IPA/Hexanes, 0.5 mL/min, λ 230 nm, RT= 1.93 and 2.14 min).



2,2,2-Trichloroethyl

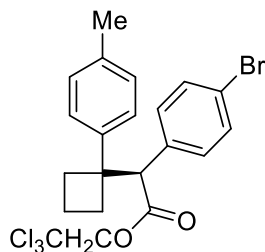
(*R*)-2-(4-bromophenyl)-2-(1-(4-

(trifluoromethyl)phenyl)cyclobutyl)acetate (**3.82**). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-(trifluoromethyl)benzene (**3.66**, 50 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**3.42**, 186 mg, 0.50 mmol) using $\text{Rh}_2(\text{R-TCPTAD})_4$ (**3.33**, 5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (114 mg, 84%) as a colorless oil: $[\alpha]^{23}_{\text{D}} -12.7$ (c 1.0, CH_2Cl_2); ^1H NMR (600 MHz, CDCl_3) δ 7.51 (d, J = 8.1 Hz, 2H), 7.42–7.39 (m, 2H), 7.17 (d, J = 8.1 Hz, 2H), 7.07–7.04 (m, 2H), 4.71 (d, J = 12.0 Hz, 1H), 4.51 (d, J = 12.0 Hz, 1H), 4.05 (s, 1H), 2.69–2.62 (m, 1H), 2.61–2.55 (m, 1H), 2.48–2.40 (m, 2H), 1.80–1.67 (m, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 170.2, 150.4, 133.6, 131.7, 131.4, 128.7 (q, J = 33 Hz), 128.2, 124.7 (q, J = 3.7 Hz), 124.3 (q, J = 272 Hz), 122.4, 94.6, 74.4, 59.8, 49.7, 32.3, 31.5, 16.1; ^{19}F NMR (282 MHz, CDCl_3) δ -62.36; IR (film) 2950, 1750, 1618, 1489, 1410, 1325, 1164, 1124, 1071, 1012, 836, 762, 722 cm^{-1} . MS (APCI-) 540.9355 (540.9357 calcd for $\text{C}_{21}\text{H}_{16}\text{O}_2\text{BrCl}_3\text{F}_3$, $\text{M} - \text{H}^+$). The enantiopurity was determined to be 98% ee by chiral HPLC analysis (Chiralpak AD-H, 25 cm x 4.6 mm, 2% IPA/Hexanes, 0.5 mL/min, λ 210 nm, RT = 9.7 and 10.3 min).

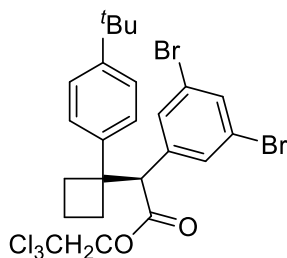


2,2,2-Trichloroethyl (R)-2-(4-bromophenyl)-2-(1-(4-methoxyphenyl)cyclobutyl)acetate

(3.83). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-methoxybenzene (**3.65**, 41 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**3.52**, 186 mg, 0.50 mmol) using $\text{Rh}_2(R\text{-TCPTAD})_4$ (**3.33**, 5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (102 mg, 81%) as a colorless oil: $[\alpha]^{23}_{\text{D}} -15.4$ (c 1.0, CH_2Cl_2); ^1H NMR (600 MHz, CDCl_3) δ 7.40–7.36 (m, 2H), 7.06–7.04 (m, 2H), 6.99–6.95 (m, 2H), 6.80–6.77 (m, 2H), 4.70 (d, $J = 12.0$ Hz, 1H), 4.55 (d, $J = 12.0$ Hz, 1H), 4.00 (s, 1H), 3.79 (s, 3H), 2.66–2.60 (m, 1H), 2.53–2.44 (m, 1H), 2.42–2.35 (m, 2H), 1.79–1.64 (m, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 170.5, 158.1, 137.9, 134.1, 131.8, 131.1, 128.8, 121.9, 113.1, 94.7, 74.4, 60.5, 55.4, 49.3, 32.3, 31.6, 16.0; IR (film) 2948, 2835, 1748, 1610, 1511, 1488, 1464, 1441, 1409, 1372, 1297, 1245, 1178, 1131, 1075, 1032, 1011, 908, 830, 761, 719 cm^{-1} . MS (APCI-) 502.9597 (502.9589 calcd for $\text{C}_{21}\text{H}_{19}\text{O}_3\text{BrCl}_3$, $\text{M} - \text{H}^+$). The enantiopurity was determined to be 91% ee by chiral HPLC analysis (Chiralcel ODH, 25 cm x 4.6 mm, 3% IPA/Hexanes, 1.00 mL/min, λ 210 nm, RT= 4.7 and 6.0 min).

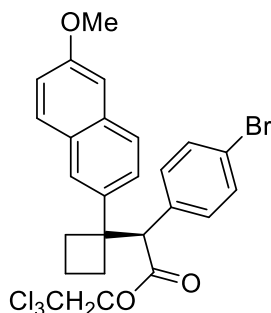


2,2,2-Trichloroethyl (R)-2-(4-bromophenyl)-2-(1-(*p*-tolyl)cyclobutyl)acetate (3.84). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-methylbenzene (**3.64**, 37 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**3.42**, 186 mg, 0.50 mmol) using $\text{Rh}_2(\text{R-TCPTAD})_4$ (**3.33**, 5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (115 mg, 94%) as a colorless oil: $[\alpha]^{23}_{\text{D}} -9.6$ (c 1.0, CH_2Cl_2); ^1H NMR (600 MHz, CDCl_3) δ 7.41–7.38 (m, 2H), 7.11–7.04 (m, 4H), 6.97 (d, J = 8.2 Hz, 2H), 4.69 (d, J = 12.0 Hz, 1H), 4.54 (d, J = 12.0 Hz, 1H), 4.01 (s, 1H), 2.67–2.60 (m, 1H), 2.55–2.49 (m, 1H), 2.46–2.37 (m, 2H), 2.32 (s, 3H), 1.79–1.70 (m, 1H), 1.70–1.63 (m, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 170.5, 143.1, 135.9, 134.1, 131.8, 131.1, 128.5, 127.5, 122.0, 94.7, 74.4, 60.4, 49.5, 32.3, 31.3, 21.1, 16.1; IR (film) 2980, 2946, 2866, 1748, 1514, 1488, 1445, 1409, 1371, 1336, 1130, 1075, 1011, 907, 822, 760, 720 cm^{-1} . MS (APCI-) 486.9645 (486.9640 calcd for $\text{C}_{21}\text{H}_{19}\text{O}_2\text{BrCl}_3$, $\text{M} - \text{H}^+$). The enantiopurity was determined to be 98% ee by chiral HPLC analysis (Chiralcel OJ, 25 cm x 4.6 mm, 2% IPA/Hexanes, 0.5 mL/min, λ 210 nm, RT= 10.9 and 13.9 min).



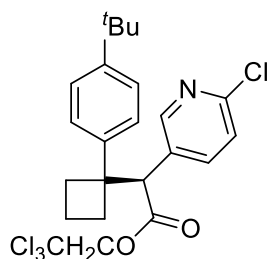
2,2,2-Trichloroethyl (R)-2-(1-(4-(*tert*-butyl)phenyl)cyclobutyl)-2-(3,5-dibromophenyl)acetate (3.85). The general procedure 2 was employed for the C–H

functionalization of 1-(*tert*-butyl)-4-cyclobutylbenzene (**3.52**, 47 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-diazo-2-(3,5-dibromophenyl)acetate (226 mg, 0.50 mmol) using $\text{Rh}_2(\text{R-TCPTAD})_4$ (**3.33**, 5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (115 mg, 75%) as a colorless oil: $[\alpha]^{23}_{\text{D}} -7.3$ (*c* 1.0, CH_2Cl_2); ^1H NMR (600 MHz, CDCl_3) δ 7.57 (t, *J* = 1.7 Hz, 1H), 7.30–7.27 (m, 2H), 7.16 (d, *J* = 1.7 Hz, 2H), 6.95–6.93 (m, 2H), 4.73 (d, *J* = 11.9 Hz, 1H), 4.55 (d, *J* = 11.9 Hz, 1H), 3.96 (s, 1H), 2.69–2.62 (m, 1H), 2.50–2.42 (m, 3H), 1.83–1.72 (m, 2H), 1.32 (s, 9H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.8, 149.7, 142.2, 138.8, 133.2, 131.9, 127.3, 124.7, 122.2, 94.6, 74.6, 60.3, 49.7, 34.6, 31.9, 31.6, 31.5, 16.0; IR (film) 2962, 2867, 1750, 1582, 1554, 1509, 1425, 1364, 1334, 1268, 1194, 1136, 1047, 908, 858, 829, 734 cm^{-1} . MS (APCI-) 606.9220 (606.9214 calcd for $\text{C}_{24}\text{H}_{24}\text{O}_2\text{Br}_2\text{Cl}_3$, $\text{M} - \text{H}^+$). The enantiopurity was determined to be 95% ee by chiral HPLC (Chiralpak AD-H, 25 cm x 4.6 mm, 2% IPA/Hexanes, 0.5 mL/min, λ 230 nm, RT= 6.9 and 8.2 min).



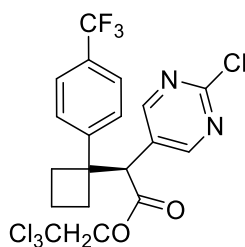
2,2,2-Trichloroethyl (R)-2-(4-bromophenyl)-2-(1-(6-methoxynaphthalen-2-yl)cyclobutyl)acetate (3.86). The general procedure 2 was employed for the C–H functionalization of 2-cyclobutyl-6-methoxynaphthalene (**3.68**, 53 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**3.42**, 186 mg, 0.50 mmol) using $\text{Rh}_2(\text{R-TCPTAD})_4$ (**3.33**, 5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (118 mg, 85%) as a colorless solid, mp 44–49 °C: $[\alpha]^{23}_{\text{D}} -17.1$ (*c* 1.0, CH_2Cl_2); ^1H NMR (600 MHz, CDCl_3) δ 7.64 (dd, *J* = 8.7, 2.1 Hz, 2H), 7.45 (d, *J* = 2.2 Hz, 1H), 7.39–7.36 (m, 2H), 7.17 (dd, *J*

= 8.5, 2.0 Hz, 1H), 7.13 (dd, J = 8.9, 2.5 Hz, 1H), 7.11–7.07 (m, 3H), 4.66 (d, J = 11.9 Hz, 1H), 4.51 (d, J = 12.0 Hz, 1H), 4.10 (s, 1H), 3.92 (s, 3H), 2.73–2.67 (m, 1H), 2.65–2.58 (m, 1H), 2.58–2.47 (m, 2H), 1.82–1.73 (m, 1H), 1.73–1.66 (m, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 170.5, 157.8, 141.1, 134.1, 133.2, 131.8, 131.2, 129.5, 128.5, 126.4, 126.2, 122.0, 119.0, 105.6, 94.7, 74.4, 60.4, 55.5, 49.8, 32.2, 31.3, 16.2, 1 carbon signal is missing due to incidental equivalence; IR (film) 2984, 2948, 1749, 1634, 1605, 1488, 1390, 1372, 1338, 1273, 1217, 1131, 1032, 1011, 925, 852, 908, 813, 761, 723 cm^{-1} . MS (APCI-) 552.9750 (552.9745 calcd for $\text{C}_{25}\text{H}_{21}\text{O}_3\text{BrCl}_3$, $\text{M} - \text{H}^+$). The enantiopurity was determined to be 98% ee by chiral HPLC analysis (Chiralpak AD-H, 25 cm x 4.6 mm, 1% IPA/Hexanes, 0.5 mL/min, λ 230 nm, RT = 18.3 and 20.2 min).

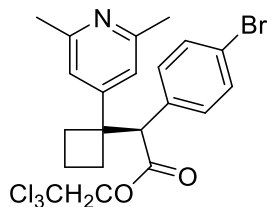


2,2,2-Trichloroethyl (S)-2-(1-(4-(tert-butyl)phenyl)cyclobutyl)-2-(6-chloropyridin-3-yl)acetate (3.87). The general procedure 2 was employed for the C–H functionalization of 1-(tert-butyl)-4-cyclobutylbenzene (**3.52**, 47 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(6-chloropyridin-3-yl)-2-diazoacetate (164 mg, 0.50 mmol) using $\text{Rh}_2(\text{R-TCPTAD})_4$ (**3.33**, 5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (76 mg, 62%) as a viscous oil: $[\alpha]_D^{23}$ -26.7 (c 1.0, CH_2Cl_2); ^1H NMR (600 MHz, CDCl_3) δ 8.18 (d, J = 2.4 Hz, 1H), 7.38 (dd, J = 8.4, 2.5 Hz, 1H), 7.30–7.26 (m, 2H), 7.19 (d, J = 0.7 Hz, 1H), 6.97–6.91 (m, 2H), 4.68 (d, J = 11.9 Hz, 1H), 4.58 (d, J = 11.9 Hz, 1H), 4.09 (s, 1H), 2.74–2.67 (m, 1H), 2.54–2.46 (m, 1H), 2.46–2.37 (m, 2H), 1.82–1.74 (m, 2H), 1.30 (s, 9H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.9, 151.0, 150.8, 149.7, 141.9, 140.3, 129.9, 127.3, 124.9, 123.4, 94.5, 74.7, 57.7, 49.6, 34.6, 32.5, 31.7, 31.5, 16.0;

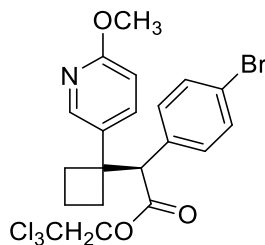
IR (film) 2962, 2868, 1748, 1583, 1562, 1509, 1459, 1395, 1365, 1325, 1141, 1106, 1023, 910, 835, 776, 758, 727 cm^{-1} . MS (APCI-) 486.0572 (486.0567 calcd for $\text{C}_{23}\text{H}_{24}\text{O}_2\text{N}_2\text{Cl}_4$, $\text{M} + \text{H}^+$). The enantiopurity was determined to be 94% ee by chiral HPLC (Chiralpak ADH, 25 cm x 4.6 mm, 2% IPA/Hexanes, 0.5 mL/min, λ 230 nm, RT= 12.3 and 13.8 min).



2,2,2-Trichloroethyl (S)-2-(2-chloropyrimidin-5-yl)-2-(1-(4-(trifluoromethyl)phenyl)-cyclobutyl)acetate (3.88). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-(trifluoromethyl)benzene (**3.66**, 50 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(6-chloropyridin-3-yl)-2-diazoacetate (165 mg, 0.50 mmol) using $\text{Rh}_2(\text{R-TCPTAD})_4$ (**3.33**, 5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (45 mg, 36%) as a colorless film: $[\alpha]_{\text{D}}^{23}$ -14.5 (c 1.00, CHCl_3); ^1H NMR (600 MHz, CHCl_3 -d) δ 8.30 (s, 2H), 7.59 – 7.49 (m, 2H), 7.10 – 7.03 (m, 2H), 4.72 (d, J = 11.9 Hz, 1H), 4.63 (d, J = 11.9 Hz, 1H), 4.13 (s, 1H), 2.85 – 2.76 (m, 1H), 2.60 – 2.50 (m, 1H), 2.46 – 2.33 (m, 2H), 1.95 – 1.84 (m, integration of 2H could not be determined due to overlap with an H_2O peak); ^{13}C NMR (151 MHz, CDCl_3) δ 167.62, 160.01, 159.11, 147.12, 128.44 (q, J = 33.2 Hz), 126.85, 124.22 (q, J = 4.0 Hz), 122.82 (q, J = 271.9 Hz), 92.94, 73.90, 54.29, 48.71, 31.26, 14.78. ^{19}F NMR (282 MHz, CDCl_3) δ -62.53; IR (film) 2987, 2953, 2851, 1750, 1618, 1577, 1546, 1401, 1327, 1158, 1126, 1071, 1015, 838, 775, 723 cm^{-1} . MS (ESI-) 498.9777 (486.9767 calcd for $\text{C}_{19}\text{H}_{14}\text{O}_2\text{N}_2\text{Cl}_4\text{F}_3$, $\text{M} - \text{H}$). The enantiopurity was determined to be 88% ee by chiral HPLC (Chiralpak IHU 1.6 μm , 100 mm x 3 mm, 5.0% IPA/Hexanes, 0.5 mL/min, λ 230 nm, RT= 2.91 and 3.66 min).

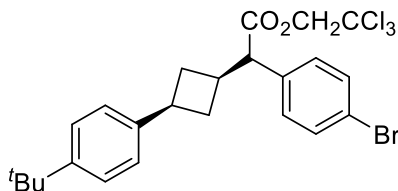


2,2,2-trichloroethyl **(R)-2-(4-bromophenyl)-2-(1-(2,6-dimethylpyridin-4-yl)cyclobutyl)acetate (3.89).** The general procedure 2 was employed for the C-H functionalization of 4-cyclobutyl-2,6-dimethylpyridine (**3.72**, 40.3 mg, 0.25 mmol) by reaction of 2-(4-bromophenyl)-2-diazoacetate (**3.42**, 186 mg, 0.50 mmol) using $\text{Rh}_2(\text{R-TCPTAD})_4$ (**3.33**, 5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (41 mg, 32%) as a colorless oil: $[\alpha]_D^{23} + 4.4$ (c 1.00, CHCl_3); ^1H NMR (600 MHz, CHCl_3 -d) δ 7.42 – 7.36 (m, 2H), 7.10 – 7.04 (m, 2H), 6.63 (s, 2H), 4.67 (d, $J = 12.0$ Hz, 1H), 4.49 (d, $J = 11.9$ Hz, 1H), 3.94 (s, 1H), 2.60 – 2.46 (m, 2H), 2.43 (s, 6H), 2.41 – 2.28 (m, 2H), 1.73 – 1.55 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 169.89, 157.18, 155.75, 133.43, 131.46, 131.20, 122.19, 119.19, 94.42, 74.30, 59.40, 48.99, 31.61, 30.62, 24.51, 16.01. IR (neat) 2949, 2925, 2854, 1749, 1603, 1561, 1489, 1438, 1408, 1372, 1133, 1075, 1011, 826, 761, 719 cm^{-1} . MS (APCI+) 503.9888 (503.9894 calcd for $\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}^{79}\text{Br}^{35}\text{Cl}_3$, $\text{M} + \text{H}^+$) The enantiopurity was determined to be 99% *ee* by chiral HPLC (Chiralpak AD-H, 25 cm x 4.6 mm, 2.0% IPA/Hexanes, 1.0 mL/min, λ 230 nm, RT= 8.9 and 10.0 min). The reaction also unexpectedly yielded pyridinium ylide byproducts, see section S.3.9 for further details.



2,2,2-trichloroethyl (R)-2-(4-bromophenyl)-2-(1-(6-methoxypyridin-3-yl)cyclobutyl)acetate (3.90). The general procedure 2 was employed for the C-H functionalization of 5-cyclobutyl-2-methoxypyridine (**3.77**, 40.8 mg, 0.25 mmol) by reaction of 2-(4-bromophenyl)-2-diazoacetate (**3.42**, 186 mg, 0.50 mmol) using $\text{Rh}_2(\text{R-TCPTAD})_4$ (**3.33**, 5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (59 mg, 46%) as a colorless oil: $[\alpha]_{\text{D}}^{23} - 28.1$ (*c* 1.00, CHCl_3); ^1H NMR (500 MHz, CHloroform-d) δ 7.82 (d, *J* = 2.6 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.28 – 7.21 (m, 1H), 7.05 – 6.98 (m, 2H), 6.63 (d, *J* = 8.6 Hz, 1H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.04 (s, 1H), 3.91 (s, 3H), 2.62 (qd, *J* = 8.2, 4.3 Hz, 1H), 2.54 – 2.37 (m, 2H), 2.33 (tdd, *J* = 10.7, 7.8, 2.2 Hz, 1H), 1.79 (p, *J* = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 170.07, 162.61, 146.27, 138.36, 133.49, 133.23, 131.50, 131.19, 122.09, 109.52, 94.52, 74.19, 59.93, 53.39, 47.41, 32.12, 31.68, 16.20. IR (neat) 2980, 2946, 1748, 1604, 1489, 1374, 1286, 1131, 1023, 1011, 908, 827, 721 cm^{-1} . MS (APCI+) 505.9681 (505.9687 calcd for $\text{C}_{20}\text{H}_{20}\text{O}_3\text{N}^{79}\text{Br}^{35}\text{Cl}_3$, $\text{M} + \text{H}^+$) The enantiopurity was determined to be 99% *ee* by chiral HPLC (Chiralpak AD-H, 25 cm x 4.6 mm, 0.5% IPA/Hexanes, 1.0 mL/min, λ 230 nm, RT= 17.4 and 26.2 min).

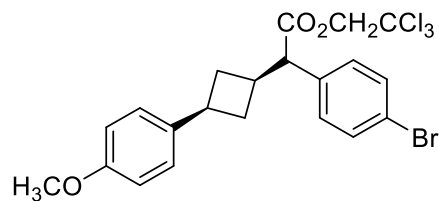
S.3.6 Characterization of C3 Functionalization Products



2,2,2-Trichloroethyl

(S)-2-(4-bromophenyl)-2-((1S,3R)-3-(4-

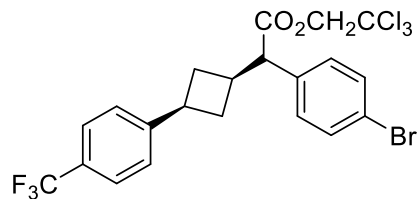
methoxyphenyl)cyclobutyl)acetate (3.54). The general procedure 2 was employed for the C–H functionalization of 1-(*tert*-butyl)-4-cyclobutylbenzene (**3.52**, 50 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**3.42**, 186 mg, 0.50 mmol) using Rh₂(S-2-Cl-5-BrTPCP)₄ (**3.43**, 4.8 mg, 1 mol%) as catalyst. This procedure afforded the title compound (94 mg, 71%) as a colorless oil. The ratio of *cis:trans* cyclobutane diastereomers was >95:5 by ¹HNMR (By relative integration of the doublets at 3.61 and 3.89 ppm, respectively.) The ratio of C3:C1 functionalization products was > 95:5 by ¹HNMR [α]_D²⁰ +71.3 (*c* 1.00, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.49–7.43 (m, 2H), 7.35–7.29 (m, 2H), 7.24–7.20 (m, 2H), 7.12–7.07 (m, 2H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 3.61 (d, *J* = 10.8 Hz, 1H), 3.43–3.28 (m, 1H), 3.08–2.87 (m, 1H), 2.75–2.58 (m, 1H), 2.34–2.21 (m, 1H), 2.00 (q, *J* = 10.3 Hz, 1H), 1.74 (q, *J* = 10.3 Hz, 1H), 1.30 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 171.0, 148.9, 142.0, 135.4, 131.8, 129.9, 125.9, 125.2, 121.6, 94.8, 74.1, 57.7, 35.24, 34.38, 34.17, 34.12, 31.38; IR (film) 3052, 3024, 2961, 2903, 2864, 1749, 1488, 1364, 1132, 1072, 1010, 909, 827, 759, 716, 568 cm⁻¹. MS (APCI+) 530.0175 (530.0176 calcd for C₂₄H₂₆O₂BrCl₃, M⁺). The enantiopurity was determined to be 92% ee by chiral HPLC (Registech (*R,R*)-Whelk, 25 cm x 4.6 mm, 0.5% IPA/Hexanes, 1.0 mL/min, λ 230 nm, RT= 9.4 and 11.6 min).



2,2,2-Trichloroethyl

(S)-2-(4-bromophenyl)-2-((1S,3R)-3-(4-

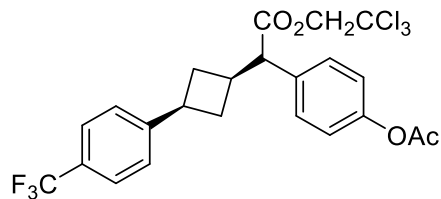
methoxyphenyl)cyclobutyl)acetate (3.91). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-methoxybenzene (**3.65**, 41 mg, 0.25 mmol) by reaction of 2-(4-bromophenyl)-2-diazoacetate (**3.42**, 186 mg, 0.50 mmol) using $\text{Rh}_2(\text{S-2-Cl-5-BrTPCP})_4$ (**3.43**, 4.8 mg, 1 mol%) as catalyst. This procedure afforded the title compound (79 mg, 62%) as a colorless oil. The ratio of *cis:trans* cyclobutane diastereomers was >95:5 by ^1H NMR (By relative integration of the doublets at 3.61 and 3.89 ppm, respectively.) The ratio of C3:C1 functionalization products was 76:24 by ^1H NMR. $[\alpha]^{23}_{\text{D}} +63.1$ (c 1.00, CHCl_3); ^1H NMR (600 MHz, CDCl_3) δ 7.48–7.44 (m, 2H), 7.25–7.21 (m, 2H), 7.08 (d, $J = 8.4$ Hz, 2H), 6.86–6.82 (m, 2H), 4.77 (d, $J = 12.0$ Hz, 1H), 4.68 (d, $J = 12.0$ Hz, 1H), 3.79 (s, 3H), 3.62 (d, $J = 10.7$ Hz, 1H), 3.34 (ddd, $J = 18.0, 9.9, 8.2$ Hz, 1H), 3.01–2.90 (m, 1H), 2.67 (ddt, $J = 10.3, 7.3, 3.8$ Hz, 1H), 2.27 (ddt, $J = 12.6, 7.6, 3.8$ Hz, 1H), 1.95 (q, $J = 10.2$ Hz, 1H), 1.69 (q, $J = 10.3$ Hz, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 171.1, 158.0, 137.3, 135.5, 131.9, 130.1, 127.4, 121.8, 113.9, 94.9, 74.2, 57.8, 55.5, 35.6, 35.2, 34.6, 34.2; IR (neat) 2959, 2932, 1748, 1610, 1513, 1488, 1297, 1246, 1177, 1136, 1073, 1036, 1011, 829, 800, 760, 720 cm^{-1} . MS (APCI-) 502.9594 (502.9589 calcd for $\text{C}_{21}\text{H}_{19}\text{O}_3\text{BrCl}_3$, $\text{M} - \text{H}^+$). The enantiopurity was determined to be 92% *ee* by chiral HPLC (Chiralpak IH-U, 10 cm x 3.0 mm, 1.6 μm particle size, 5% IPA/Hexanes, 0.35 mL/min, λ 230 nm, RT= 3.2 and 3.6 min).



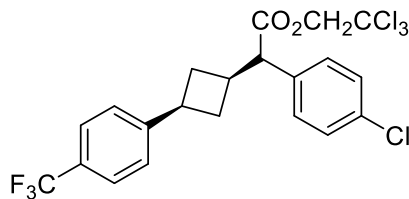
2,2,2-Trichloroethyl

(S)-2-(4-bromophenyl)-2-((1S,3R)-3-(4-

(trifluoromethyl)phenyl)cyclobutyl)acetate (3.92). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-(trifluoromethyl)benzene (**3.66**, 50 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**3.42**, 186 mg, 0.50 mmol) using $\text{Rh}_2(\text{S-2-Cl-5-BrTPCP})_4$ (**3.43**, 4.8 mg, 1 mol%) as catalyst. This procedure afforded the title compound (118 mg, 87%) as a colorless solid. The ratio of *cis:trans* cyclobutane diastereomers was >95:5 by ^1H NMR (By relative integration of the doublets at 3.61 and 3.89 ppm, respectively.) The ratio of C3:C1 functionalization products was >95:5 by ^1H NMR. mp 83.0–83.5 °C: $[\alpha]^{20}_{\text{D}} +71.1$ (c 1.00, CHCl_3); ^1H NMR (600 MHz, CDCl_3) δ 7.53 (d, J = 8.1 Hz, 2H), 7.49–7.44 (m, 2H), 7.27–7.19 (m, 4H), 4.76 (d, J = 12.0, 0.8 Hz, 1H), 4.68 (d, J = 12.0, 0.8 Hz, 1H), 3.61 (d, J = 10.8 Hz, 1H), 3.48–3.39 (m, 1H), 3.07–2.95 (m, 1H), 2.78–2.67 (m, 1H), 2.32 (dtd, J = 11.1, 7.7, 4.8 Hz, 1H), 2.00 (q, J = 10.2 Hz, 1H), 1.73 (q, J = 10.4 Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 170.9, 149.1, 135.2, 132.0, 130.1, 128.4 (q, J = 32.4 Hz), 126.7, 125.4 (q, J = 3.8 Hz), 124.4 (q, J = 27.2 Hz), 121.9, 94.9, 74.2, 57.6, 35.5, 35.1, 34.2, 34.0; ^{19}F NMR (471 MHz, CDCl_3) δ -62.30; IR (film) 3046, 2970, 2939, 2861, 1749, 1618, 1488, 1323, 1162, 1120, 1066, 1012, 834, 758, 718 cm^{-1} . MS (APCI+) 541.9424 (541.9424 calcd for $\text{C}_{21}\text{H}_{17}\text{O}_2\text{BrCl}_3$, M^+). The enantiopurity was determined to be 90% ee by chiral HPLC (Chiralpak OD-H, 25 cm x 4.6 mm, 0.5% IPA/Hexanes, 1.0 mL/min, λ 230 nm, RT= 9.96 and 12.96 min).



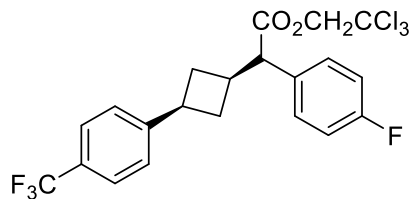
2,2,2-Trichloroethyl (R)-2-(4-acetoxyphenyl)-2-((1S,3S)-3-(4-(trifluoromethyl)phenyl)cyclobutyl)acetate (3.93). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-(trifluoromethyl)benzene (**3.66**, 50 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(4-acetoxyphenyl)-2-diazoacetate (**3.42**, 176 mg, 0.50 mmol) using $\text{Rh}_2(\text{S-2-Cl-5-BrTPCP})_4$ (**3.43**, 4.8 mg, 1 mol%) as catalyst. This procedure afforded the title compound (121 mg, 92%) as a colorless oil. The ratio of *cis:trans* cyclobutane diastereomers was >95:5 by ^1H NMR (By relative integration of the doublets at 3.61 and 3.89 ppm, respectively.) The ratio of C3:C1 functionalization products was >95:5 by ^1H NMR. $[\alpha]^{23}_{\text{D}} +41.8$ (*c* 1.00, CHCl_3); ^1H NMR (600 MHz, CDCl_3) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.36–7.32 (m, 2H), 7.24–7.21 (m, 2H), 7.08–7.03 (m, 2H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 3.64 (d, *J* = 10.7 Hz, 1H), 3.50–3.39 (m, 1H), 3.10–2.98 (m, 1H), 2.75–2.67 (m, 1H), 2.42–2.31 (m, 1H), 2.28 (s, 3H), 1.98 (q, *J* = 10.2 Hz, 1H), 1.75 (q, *J* = 10.3 Hz, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 171.03, 169.33, 150.23, 149.11, 133.60, 129.26, 128.28 (q, *J* = 32.3 Hz), 126.59, 125.24 (q, *J* = 3.3 Hz), 124.31 (q, *J* = 272.1 Hz), 121.83, 94.82, 74.05, 57.48, 35.44, 34.89, 34.20, 34.00, 21.13. ^{19}F NMR (282 MHz, CDCl_3) δ -62.27; IR (neat) 3042, 2968, 2934, 2860, 1749, 1618, 1507, 1421, 1370, 1323, 1196, 1163, 1120, 1066, 1017, 909, 837, 754, 719 cm^{-1} . MS (ESI-) 557.0082 (557.0087 calcd for $\text{C}_{24}\text{H}_{16}\text{N}_4\text{Cl}_4\text{F}_3$, $\text{M} + \text{Cl}^-$). The enantiopurity was determined to be 66% ee by chiral HPLC (Chiralpak IHU 1.6 μm , 100 mm x 3 mm, 5.0% IPA/Hexanes, 0.500 mL/min, λ 230 nm, RT = 3.25 and 3.87 min).



2,2,2-Trichloroethyl

(S)-2-(4-chlorophenyl)-2-((1S,3R)-3-(4-

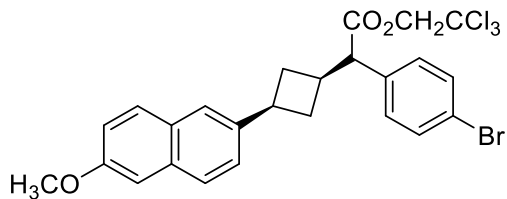
(trifluoromethyl)phenyl)cyclobutyl)acetate (3.94). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-(trifluoromethyl)benzene (**3.66**, 50 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(4-chlorophenyl)-2-diazoacetate (164 mg, 0.50 mmol) using $\text{Rh}_2(\text{S-2-Cl-5-BrTPCP})_4$ (**3.43**, 4.8 mg, 1 mol%) as catalyst. This procedure afforded the title compound (88 mg, 70%) as a colorless oil. The ratio of *cis:trans* cyclobutane diastereomers was equal to 95:5 by ^1H NMR (By relative integration of the doublets at 3.61 and 3.89 ppm, respectively.) The ratio of C3:C1 functionalization products was >95:5 by ^1H NMR. $[\alpha]_D^{23} +62.4$ (c 1.00, CHCl_3); ^1H NMR (600 MHz, CDCl_3) δ 7.53 (d, $J = 8.0$ Hz, 2H), 7.33–7.29 (m, 2H), 7.29–7.26 (m, 2H), 7.25–7.21 (m, 2H), 4.76 (d, $J = 12.0, 1.0$ Hz, 1H), 4.68 (d, $J = 12.0, 1.0$ Hz, 1H), 3.62 (d, $J = 10.6$ Hz, 1H), 3.44 (p, $J = 9.1$ Hz, 1H), 3.08–2.97 (m, 1H), 2.78–2.68 (m, 1H), 2.35–2.29 (m, 1H), 2.00 (q, $J = 10.2$ Hz, 1H), 1.73 (q, $J = 10.3$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 171.0, 149.1, 134.7, 133.8, 129.7, 129.1, 128.4 (q, $J = 32.3$ Hz), 126.7, 125.4 (q, $J = 3.7$ Hz), 122.60 (q, $J = 272$ Hz), 94.9, 74.2, 57.6, 35.5, 35.1, 34.3, 34.0; ^{19}F NMR (282 MHz, CDCl_3) δ -62.30; IR (neat) 3047, 2970, 2939, 2862, 1749, 1618, 1491, 1323, 1162, 1120, 1066, 1015, 834, 765, 715 cm^{-1} . MS (APCI+) 497.9927 (497.9929 calcd for $\text{C}_{21}\text{H}_{17}\text{O}_2\text{Cl}_4\text{F}_3$, M⁺). The enantiomeric excess was determined to be 87% by chiral HPLC (Chiralpak AD-H, 25 cm x 4.6 mm, 1% IPA/Hexanes, 1.0 mL/min, λ 230 nm, RT= 8.96 and 11.74 min).



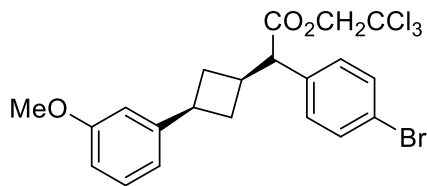
2,2,2-Trichloroethyl

(S)-2-(4-fluorophenyl)-2-((1S,3R)-3-(4-

(trifluoromethyl)phenyl)cyclobutyl)acetate (3.95). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-(trifluoromethyl)benzene (**3.66**, 50 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-diazo-2-(4-fluorophenyl)acetate (156 mg, 0.50 mmol) using $\text{Rh}_2(\text{S-2-Cl-5-BrTPCP})_4$ (**3.43**, 4.8 mg, 1 mol%) as catalyst. Obtained 99 mg of compound **3.95** as a colorless oil (82% yield.) The ratio of *cis:trans* cyclobutane diastereomers was equal to 94:6 by ^1H NMR (By relative integration of the doublets at 3.61 and 3.89 ppm, respectively.) The ratio of C3:C1 functionalization products was equal to 93:7 by ^1H NMR. $[\alpha]^{23}_{\text{D}} +24.9$ (c 1.00, CHCl_3); ^1H NMR (600 MHz, Chloroform- d) δ 7.53 (d, $J = 8.1$ Hz, 2H), 7.36 – 7.29 (m, 2H), 7.24 (s, 2H), 7.03 (t, $J = 8.6$ Hz, 2H), 4.76 (d, $J = 12.0$ Hz, 1H), 4.69 (d, $J = 12.0$ Hz, 1H), 3.63 (d, $J = 10.7$ Hz, 1H), 3.45 (p, $J = 9.1$ Hz, 1H), 3.03 (qt, $J = 10.1, 7.5$ Hz, 1H), 2.78 – 2.68 (m, 1H), 2.37 – 2.28 (m, 1H), 2.00 (q, $J = 10.2$ Hz, 1H), 1.74 (q, $J = 10.3$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.11, 162.33 (d, $J = 246.1$ Hz), 149.05, 131.89 (d, $J = 3.3$ Hz), 129.82 (d, $J = 7.8$ Hz), 128.32 (q, $J = 32.2$ Hz), 126.57, 125.25 (q, $J = 3.3$ Hz), 124.38 (q, $J = 271.8$ Hz), 115.65 (d, $J = 21.7$ Hz), 94.79, 74.05, 57.30, 35.42, 34.93, 34.22, 33.93. ^{19}F NMR (282 MHz, CDCl_3) δ -62.30, -114.59; IR (neat) 3046, 2969, 2940, 2863, 1749, 1618, 1509, 1323, 1225, 1161, 1120, 1066, 1016, 837, 802, 754, 717 cm^{-1} . MS (APCI-) 481.0159 (481.0158 calcd for $\text{C}_{21}\text{H}_{16}\text{O}_2\text{Cl}_3\text{F}_4$, $M - \text{H}^+$). The enantiopurity was determined to be 74% ee by chiral HPLC (Chiralpak AD-H, 25 cm x 4.6 mm, 1.0% IPA/Hexanes, 1.0 mL/min, λ 210 nm, RT= 8.43 and 10.45 min).



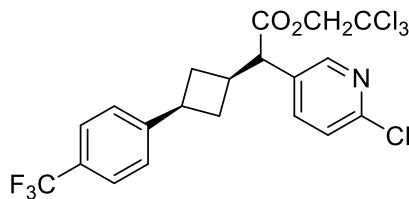
2,2,2-Trichloroethyl (S)-2-(4-bromophenyl)-2-((1S,3R)-3-(6-methoxynaphthalen-2-yl)cyclobutyl)acetate (3.96). The general procedure 2 was employed for the C–H functionalization of 2-cyclobutyl-6-methoxynaphthalene (**3.68**, 53 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**3.42**, 186 mg, 0.50 mmol) using $\text{Rh}_2(\text{S-2-Cl-5-BrTPCP})_4$ (**3.43**, 4.8 mg, 1 mol%) as catalyst. This procedure afforded the title compound (87 mg, 67%) as a colorless solid. Neither the ratio of *cis:trans* cyclobutane diastereomers nor the ratio of C3:C1 functionalization products could be accurately determined by ^1H NMR due to overlaps. For this experiment, the reported values were determined by isolation. mp 84–89 °C: $[\alpha]_D^{23} +80.6$ (*c* 1.00, CH_2Cl_2); ^1H NMR (600 MHz, CDCl_3) δ 7.67 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 3H), 7.29–7.22 (m, 3H), 7.16–7.09 (m, 2H), 4.78 (d, *J* = 11.9 Hz, 1H), 4.70 (d, *J* = 12.0 Hz, 1H), 3.91 (s, 3H), 3.66 (d, *J* = 10.7 Hz, 1H), 3.53 (p, *J* = 9.1 Hz, 1H), 3.04 (dp, *J* = 17.4, 9.7, 8.6 Hz, 1H), 2.76 (dq, *J* = 15.4, 7.6 Hz, 1H), 2.35 (dq, *J* = 12.4, 7.7, 6.2 Hz, 1H), 2.08 (q, *J* = 10.2 Hz, 1H), 1.82 (q, *J* = 10.3 Hz, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 171.1, 157.4, 140.3, 135.5, 133.2, 132.0, 130.1, 129.1, 129.0, 127.0, 125.7, 124.2, 121.8, 119.0, 105.8, 94.9, 74.2, 57.8, 55.4, 35.8, 35.3, 34.3, 34.3; IR (film) 3055, 2961, 2934, 2856, 1750, 1634, 1606, 1487, 1266, 1216, 1135, 1073, 1032, 1011, 852, 830, 810, 761, 718 cm^{-1} . MS (NSI+) 554.9899 (554.9891 calcd for $\text{C}_{25}\text{H}_{23}\text{O}_3\text{BrCl}_3$, $\text{M} + \text{H}^+$). The enantiopurity was determined to be 94% *ee* by chiral HPLC (Chiralpak IH-U, 10 cm x 3.0 mm, 1.6 μm particle size, 5% IPA/Hexanes, 0.35 mL/min, λ 230 nm, RT= 4.4 and 5.7 min).



2,2,2-Trichloroethyl

(S)-2-(4-bromophenyl)-2-((1S,3R)-3-(3-

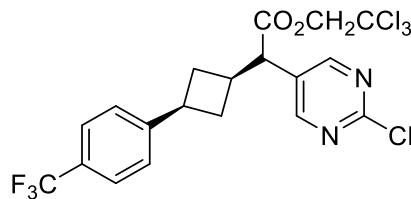
methoxyphenyl)cyclobutyl)acetate (3.97). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-3-methoxybenzene (**3.67**, 41 mg, 0.25 mmol) by reaction of 2-(4-bromophenyl)-2-diazoacetate (**3.42**, 186 mg, 0.50 mmol) using $\text{Rh}_2(\text{S-2-Cl-5-BrTPCP})_4$ (**3.43**, 4.8 mg, 1 mol%) as catalyst. This procedure afforded the title compound (45 mg, 35%) as a colorless oil. The ratio of *cis:trans* cyclobutane diastereomers was equal to 95:5 by ^1H NMR (By relative integration of the doublets at 3.61 and 3.89 ppm, respectively.) The ratio of C3:C1 functionalization products was >95:5 by ^1H NMR. $[\alpha]^{23}_{\text{D}} +63.7$ (*c* 1.00, CHCl_3); ^1H NMR (600 MHz, CDCl_3) δ 7.52–7.43 (m, 2H), 7.24–7.19 (m, 3H), 6.76–6.71 (m, 2H), 6.69 (s, 1H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 11.9 Hz, 1H), 3.79 (s, 3H), 3.61 (d, *J* = 10.8 Hz, 1H), 3.38 (ddd, *J* = 18.1, 10.0, 7.9 Hz, 1H), 2.98 (qt, *J* = 9.9, 7.4 Hz, 1H), 2.69 (dtd, *J* = 10.9, 7.8, 5.0 Hz, 1H), 2.28 (dtd, *J* = 11.1, 7.6, 4.9 Hz, 1H), 1.99 (q, *J* = 10.2 Hz, 1H), 1.73 (q, *J* = 10.3 Hz, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 171.1, 159.8, 146.9, 135.5, 131.9, 130.1, 129.5, 121.8, 118.8, 112.4, 111.2, 94.9, 74.2, 57.8, 55.3, 35.8, 35.2, 34.2, 34.2; IR (neat) 2962, 2934, 2856, 2834, 1748, 1600, 1582, 1488, 1464, 1453, 1433, 1407, 1371, 1332, 1288, 1259, 1194, 1158, 1134, 1073, 1046, 1011, 910, 865, 824, 803, 763, 754, 719, 696 cm^{-1} . MS (APCI-) 502.9595 (502.9589 calcd for $\text{C}_{21}\text{H}_{19}\text{O}_3\text{BrCl}_3$, $\text{M} - \text{H}^+$). The enantiopurity was determined to be 88% *ee* by chiral HPLC (Regis Technologies, Inc. (S,S)-Whelk-01, 25 cm x 4.6 mm, 0.5% IPA/Hexanes, 1.0 mL/min, λ 230 nm, RT = 30.5 and 39.5 min).



2,2,2-Trichloroethyl

(S)-2-(6-chloropyridin-3-yl)-2-((1s,3R)-3-(4-

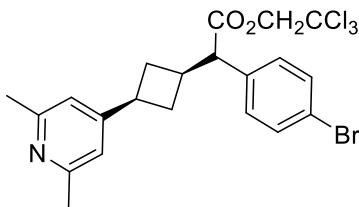
(trifluoromethyl)phenyl)cyclobutyl)acetate (3.98). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-(trifluoromethyl)benzene (**3.66**, 50 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(6-chloropyridin-3-yl)-2-diazoacetate (164 mg, 0.50 mmol) using $\text{Rh}_2(\text{S-2-Cl-5-BrTPCP})_4$ (**3.43**, 4.8 mg, 1 mol%) as catalyst. This procedure afforded the title compound (45 mg, 36%) as a colorless oil. The ratio of *cis:trans* cyclobutane diastereomers was equal to 93:7 by ^1H NMR (By relative integration of the doublets at 3.61 and 3.89 ppm, respectively.) The ratio of C3:C1 functionalization products was 87:13 by ^1H NMR. $[\alpha]^{23}_{\text{D}} +63.1$ (c 1.00, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 8.35 (d, $J = 2.6$ Hz, 1H), 7.70 (dd, $J = 8.3, 2.6$ Hz, 1H), 7.54 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.3$ Hz, 1H), 7.25 (d, $J = 8.2$ Hz, 2H), 4.79 (d, $J = 12.0$ Hz, 1H), 4.71 (d, $J = 12.0$ Hz, 1H), 3.68 (d, $J = 10.7$ Hz, 1H), 3.47 (p, $J = 9.2$ Hz, 1H), 3.01 (qt, $J = 9.9, 7.3$ Hz, 1H), 2.76 (dtd, $J = 15.5, 7.6, 4.9$ Hz, 1H), 2.35 (dtd, $J = 15.6, 7.6, 4.9$ Hz, 1H), 2.06 (q, $J = 10.2$ Hz, 1H), 1.74 (q, $J = 10.3$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 170.3, 151.2, 149.6, 148.7, 138.5, 131.0, 128.6 (q, $J = 32.3$ Hz), 126.7, 125.4 (q, $J = 3.8$ Hz), 124.6, 124.4 (q, $J = 272$ Hz), 94.6, 74.3, 54.8, 35.4, 35.1, 34.3, 34.0; ^{19}F NMR (282 MHz, CDCl_3) δ -62.34; IR (neat) 3048, 2970, 2936, 2862, 1750, 1618, 1585, 1565, 1461, 1323, 1161, 1104, 1065, 1017, 835, 774, 758, 718 cm^{-1} . MS (APCI+) 499.9969 (499.9960 calcd for $\text{C}_{20}\text{H}_{17}\text{O}_2\text{NCl}_4\text{F}_3$, $\text{M} + \text{H}^+$). The enantiopurity was determined to be 80% *ee* by chiral HPLC (Chiralpak OD-H, 25 cm x 4.6 mm, 5% IPA/Hexanes, 1.0 mL/min, λ 230 nm, RT= 11.2 and 19.2 min).



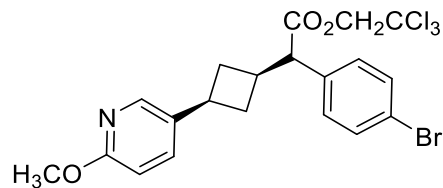
2,2,2-Trichloroethyl

(S)-2-(2-chloropyrimidin-5-yl)-2-((1S,3R)-3-(4-

(trifluoromethyl)phenyl)cyclobutyl)acetate (3.99). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-(trifluoromethyl)benzene (**3.66**, 50 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(2-chloropyrimidin-5-yl)-2-diazoacetate (165 mg, 0.50 mmol) using $\text{Rh}_2(\text{S-2-Cl-5-BrTPCP})_4$ (**3.43**, 4.8 mg, 1 mol%) as catalyst. This procedure afforded the title compound (29 mg, 29%) as a colorless oil. The ratio of *cis:trans* cyclobutane diastereomers was equal to 94:6 by ^1H NMR (By relative integration of the doublets at 3.61 and 3.92 ppm, respectively.) The ratio of C3:C1 functionalization products was 89:11 by ^1H NMR. $[\alpha]_{\text{D}}^{23} +26.0$ (c 1.00, CHCl_3); ^1H NMR (500 MHz, Chloroform- d) δ 8.65 (s, 2H), 7.67 – 7.49 (m, 2H), 7.28 – 7.22 (m, 2H), 4.81 (d, $J = 11.9$ Hz, 1H), 4.75 (d, $J = 11.9$ Hz, 1H), 3.69 (d, $J = 10.6$ Hz, 1H), 3.51 (p, $J = 9.2$ Hz, 1H), 3.02 (dtd, $J = 17.4, 9.9, 7.4$ Hz, 1H), 2.80 (dtd, $J = 12.3, 7.6, 4.8$ Hz, 1H), 2.41 (ddd, $J = 11.5, 7.9, 4.9$ Hz, 1H), 2.12 (q, $J = 10.3$ Hz, 1H), 1.76 (q, $J = 10.3$ Hz, 1H). ; ^{13}C NMR (151 MHz, CDCl_3) δ 169.30, 161.02, 159.20, 148.18, 128.62, 128.61 (q, $J = 32.3$ Hz), 126.49, 125.38 (q, $J = 4.4$ Hz), 124.21 (q, $J = 271.8$ Hz), 94.33, 74.41, 52.62, 35.26, 35.00, 34.16, 34.00. ^{19}F NMR (282 MHz, CDCl_3) δ -62.37; IR (film) 3045, 2974, 2941, 2864, 1750, 1618, 1578, 1547, 1399, 1323, 1155, 1112, 1065, 1016, 908, 837, 774, 729, 714 cm^{-1} . MS (APCI+) 500.9912 (500.9913 calcd for $\text{C}_{19}\text{H}_{16}\text{O}_2\text{N}_2\text{Br}_2\text{Cl}_4\text{F}_3$, $\text{M} + \text{H}^+$). The enantiopurity was determined to be 79% ee by chiral HPLC (Chiralpak OD-H, 25 cm x 4.6 mm, 5% IPA/Hexanes, 1.0 mL/min, λ 210 nm, RT = 19.8 and 23.1 min).



2,2,2-trichloroethyl (S)-2-(4-bromophenyl)-2-((1S,3R)-3-(2,6-dimethylpyridin-4-yl)cyclobutyl)acetate (3.100). The general procedure 2 was employed for the C-H functionalization of 4-cyclobutyl-2,6-dimethylpyridine (**3.72**, 40.3 mg, 0.25 mmol) by reaction of 2-(4-bromophenyl)-2-diazoacetate (**3.42**, 186 mg, 0.50 mmol) using $\text{Rh}_2(\text{S-2-Cl-5-BrTPCP})_4$ (**3.43**, 4.8 mg, 1 mol%) as catalyst. This procedure afforded the title compound (97 mg, 77% yield) as a colorless oil. The ratio of *cis:trans* cyclobutanes was equal to 85:15 by relative integration of the multiplets at 3.11 and 2.98 ppm in the crude ^1H NMR spectrum. The ratio of C3:C1 functionalization products was >95:5 by ^1H NMR. $[\alpha]^{23}_{\text{D}} + 69.4$ (c 1.00, CHCl_3); ^1H NMR (600 MHz, CHCl_3 -d) δ 7.43 (d, $J = 8.0$ Hz, 2H), 7.18 (d, $J = 8.1$ Hz, 2H), 6.68 (s, 2H), 4.73 (d, $J = 11.9$ Hz, 1H), 4.65 (d, $J = 11.9$ Hz, 1H), 3.57 (d, $J = 10.7$ Hz, 1H), 3.27 (p, $J = 9.1$ Hz, 1H), 2.98 (qd, $J = 10.1, 5.0$ Hz, 1H), 2.65 (dtd, $J = 12.1, 7.6, 4.7$ Hz, 1H), 2.45 (s, 6H), 2.23 (dtd, $J = 12.3, 7.6, 4.7$ Hz, 1H), 1.93 (q, $J = 10.2$ Hz, 1H), 1.68 (t, $J = 10.3$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.70, 157.56, 154.16, 135.02, 131.81, 129.88, 121.74, 118.08, 94.68, 74.01, 57.41, 34.68, 34.28, 34.10, 33.19, 24.39. IR (neat) 2965, 2926, 2854, 1749, 1606, 1564, 1488, 1136, 1173, 1101, 826, 763, 718 cm^{-1} . MS (ESI+) 503.9894 (503.9894 calcd for $\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}^{79}\text{Br}^{35}\text{Cl}_3$, $\text{M} + \text{H}^+$) The enantiopurity was determined to be 93% *ee* by chiral HPLC (Chiralpak AD-H, 25 cm x 4.6 mm, 2.0% IPA/Hexanes, 1.0 mL/min, λ 230 nm, $\text{RT} = 18.2$ and 20.8 min)



2,2,2-trichloroethyl (S)-2-(4-bromophenyl)-2-((1S,3R)-3-(6-methoxypyridin-3-yl)cyclobutyl)acetate (3.101). The general procedure 2 was employed for the C-H functionalization of 5-cyclobutyl-2-methoxypyridine (**3.77**, 40.8 mg, 0.25 mmol) by reaction of 2-(4-bromophenyl)-2-diazoacetate (**3.42**, 186 mg, 0.50 mmol) using $\text{Rh}_2(\text{S-2-Cl-5-BrTPCP})_4$ (**3.43**, 4.8 mg, 1 mol%) as catalyst. This procedure afforded the title compound (69 mg, 54% yield) as a colorless oil. The ratio of *cis:trans* cyclobutanes was equal to 92:8 by relative integration of the multiplets at 2.97 and 3.05 ppm in the crude ^1H NMR spectrum. The ratio of C3:C1 functionalization products was equal to 78:22 by relative integration of the multiplets at 2.41 and 3.32 ppm in the crude ^1H NMR spectrum. $[\alpha]_D^{23} + 70.5$ (*c* 1.00, CHCl_3); ^1H NMR (500 MHz, Chloroform-*d*) δ 8.02 – 7.92 (m, 1H), 7.52 – 7.43 (m, 2H), 7.39 (ddd, *J* = 8.5, 2.5, 0.6 Hz, 1H), 7.29 – 7.19 (m, 2H), 6.68 (dd, *J* = 8.4, 0.8 Hz, 1H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 11.9 Hz, 1H), 3.90 (s, 2H), 3.62 (d, *J* = 10.7 Hz, 1H), 3.33 (tt, *J* = 10.1, 8.0 Hz, 1H), 2.99 (dtt, *J* = 10.6, 9.6, 7.4 Hz, 1H), 2.73 – 2.62 (m, 1H), 2.33 – 2.21 (m, 1H), 1.95 (q, *J* = 10.2 Hz, 1H), 1.66 (d, *J* = 10.3 Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 170.78, 162.78, 144.50, 136.85, 135.14, 132.67, 131.82, 129.91, 121.74, 110.46, 94.72, 74.06, 57.50, 53.34, 35.17, 34.21, 32.74. IR (neat) 2966, 2944, 2857, 1748, 1607, 1571, 1493, 1374, 1329, 1284, 1258, 1135, 1028, 1012, 830, 761, 721 cm^{-1} . MS (APCI+) 505.96809 (505.96867 calcd for $\text{C}_{20}\text{H}_{20}\text{O}_3\text{N}^{79}\text{Br}^{35}\text{Cl}_3$, $\text{M} + \text{H}^+$) The enantiopurity was determined to be 92% *ee* by chiral HPLC (Chiralpak AD-H, 25 cm x 4.6 mm, 3.0% IPA/Hexanes, 1.0 mL/min, λ 230 nm, RT= 10.7 and 20.1 min)

S.3.7 Competition Study

Procedure for Determining Relative Rates of C-H Functionalization.

For both $\text{Rh}_2(R\text{-TCPTAD})_4$ (**3.33**) and $\text{Rh}_2[(S)\text{-2-Cl-5-BrTPCP}]_4$ (**3.43**) catalysts, reactions were conducted according to General Procedure 2 using an equimolar mixture of 4-tertbutylphenyl cyclobutane (**3.52**, 1.50 equiv, 70.6 mg, 0.375 mmol) and either 4-ethyltoluene (**3.60**, 1.50 equiv, 45.1 mg, 0.375 mmol) or 4-isopropyltoluene (**3.61**, 1.50 equiv, 50.3 mg, 0.375 mmol) with 2,2,2-trichloroethyl 4-bromophenyldiazoacetate (**3.42**, 1.00 equiv, 93.1 mg, 0.250 mmol) as the diazo component. On completion of the reaction, the mixtures were concentrated under vacuum and the resulting green oils were analyzed by ^1H NMR in CDCl_3 solvent containing 0.3% TMS (v/v) with a relaxation delay of 10 s. The relative rates of C-H functionalization were assumed to correspond to the ratios of the products observed in the crude mixture. The signals at the following chemical shifts were used to determine the ratios:

2,2,2-trichloroethyl 2-(4-bromophenyl)-2-(1-(4-(tert-butyl)phenyl)cyclobutyl)acetate (**3.78**): 4.00 ppm, (s, 1 H) or 2.48 ppm (*m*, 1 H)

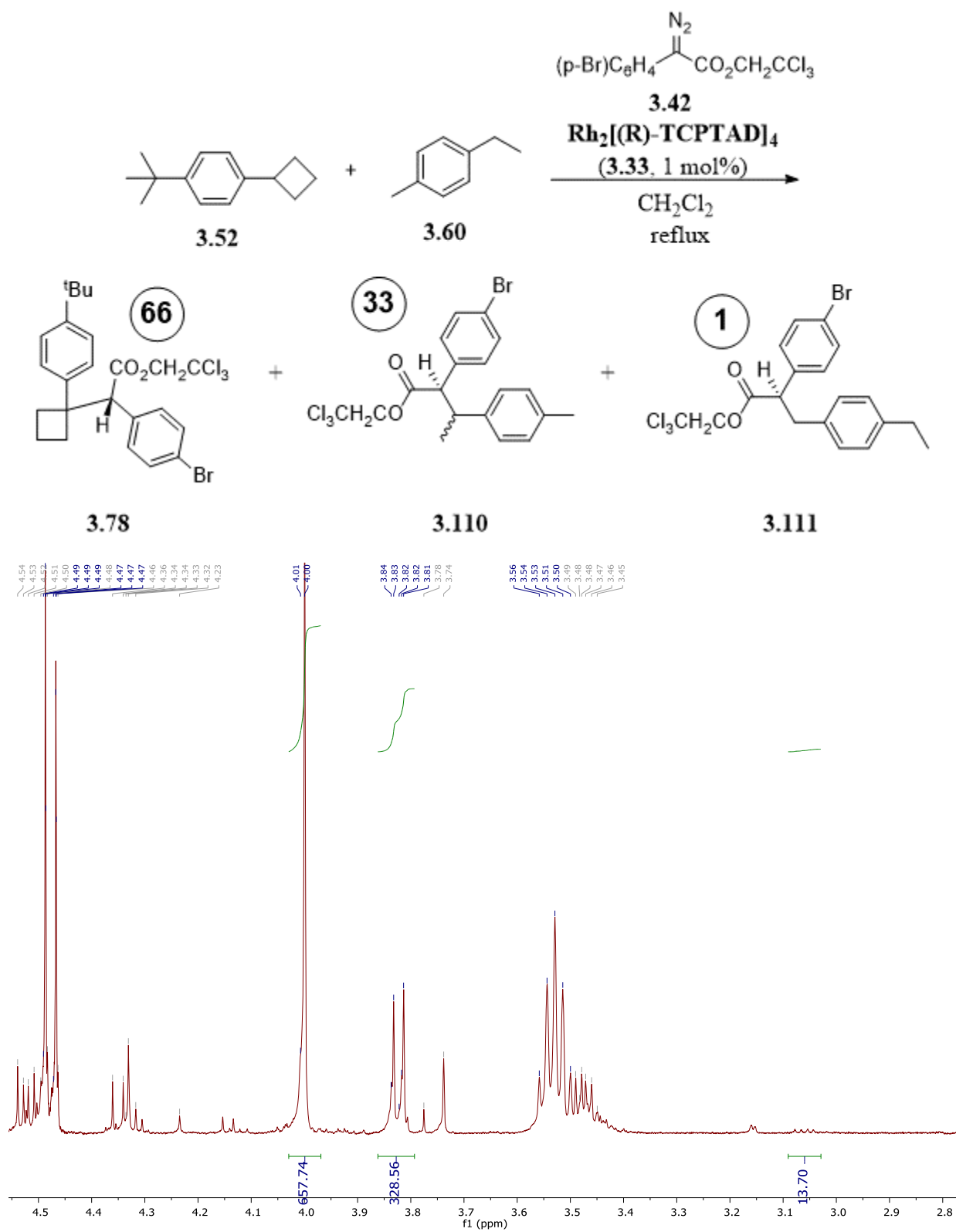
2,2,2-trichloroethyl 2-(4-bromophenyl)-2-(3-(4-(tert-butyl)phenyl)cyclobutyl)acetate (**3.54**): 3.63 ppm (*d*, 1 H)

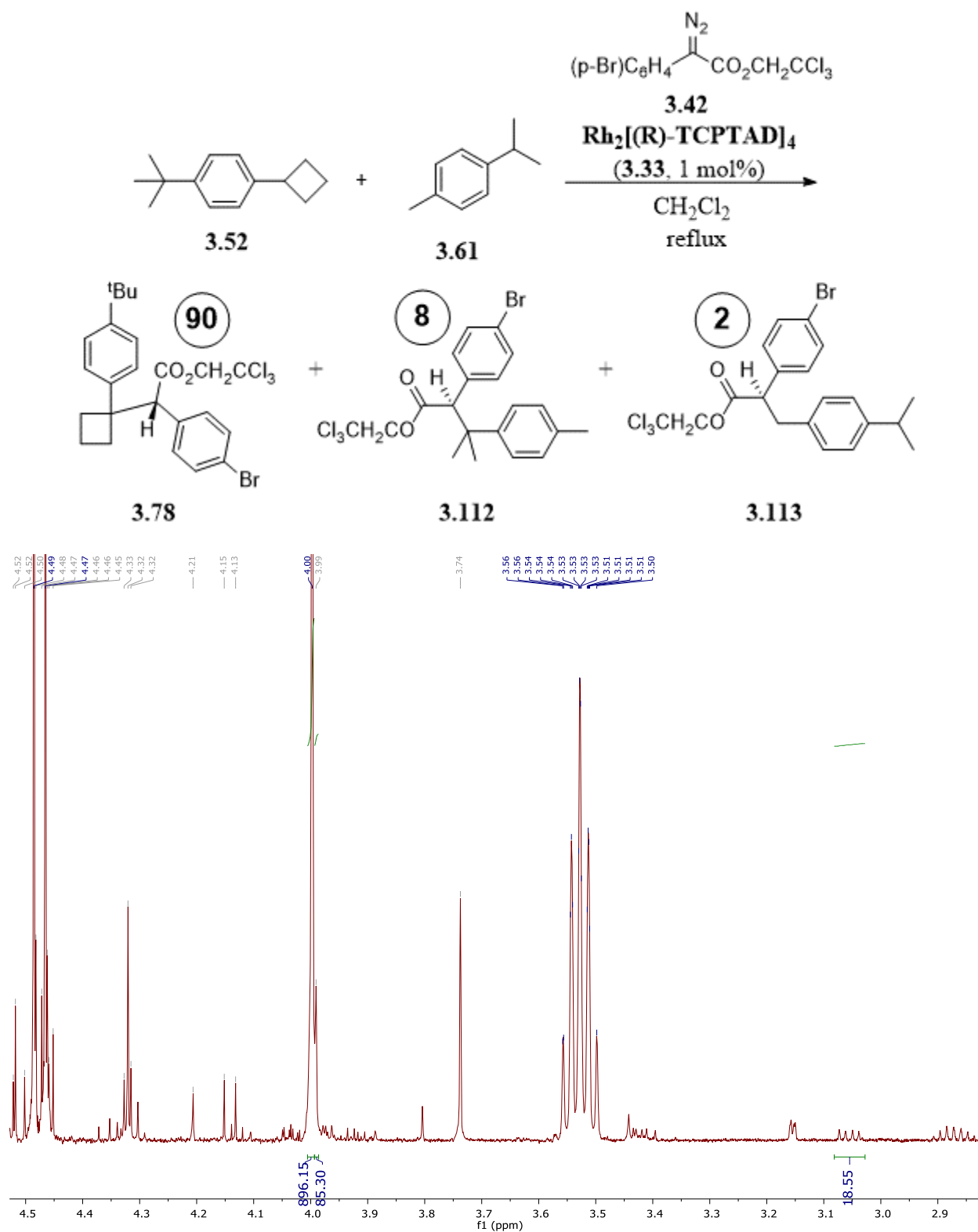
2,2,2-trichloroethyl 2-(4-bromophenyl)-3-(p-tolyl)butanoate (**3.110**): 3.83 ppm (*d*, 1 H, with overlap of both diastereomers)

2,2,2-trichloroethyl 2-(4-bromophenyl)-3-(4-ethylphenyl)propanoate (**3.111**): 3.06 ppm (*dd*, 1 H)

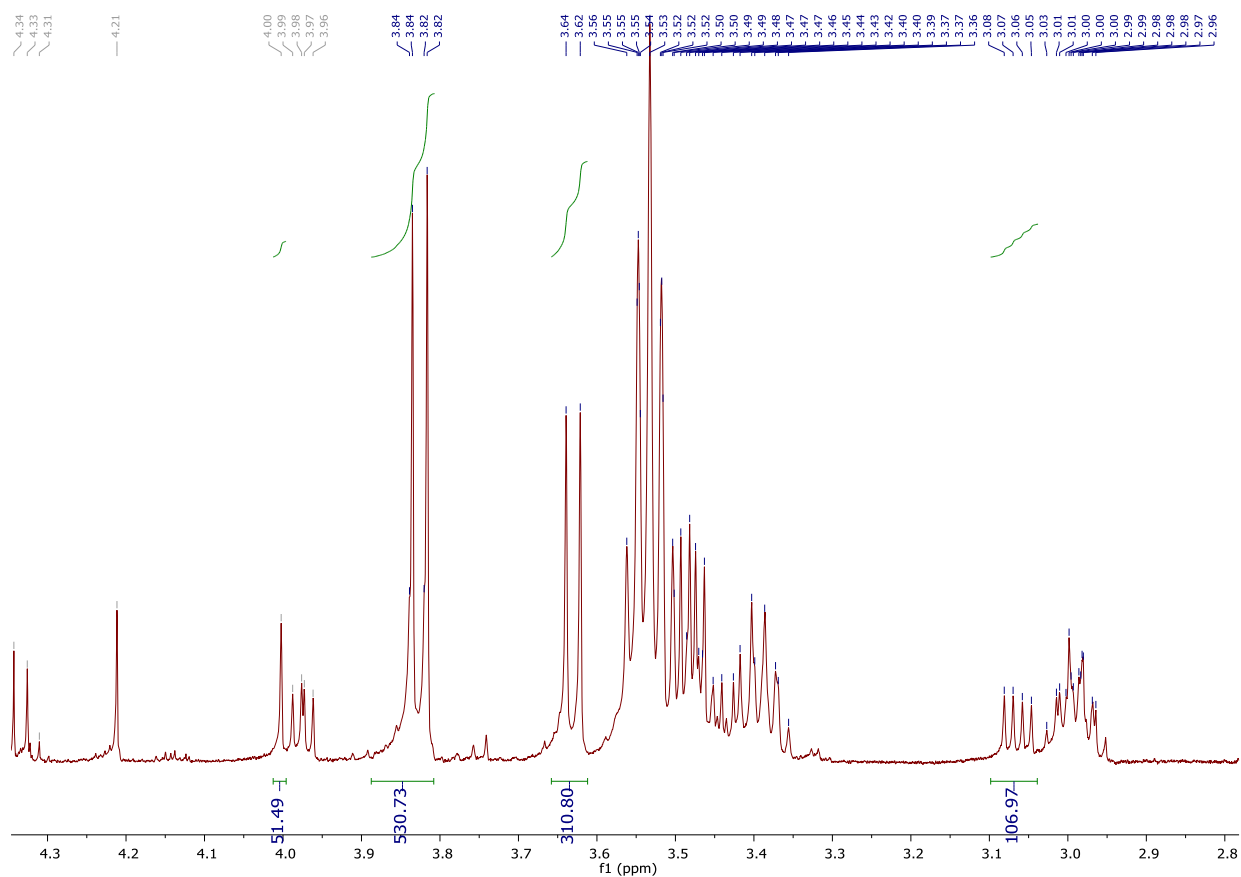
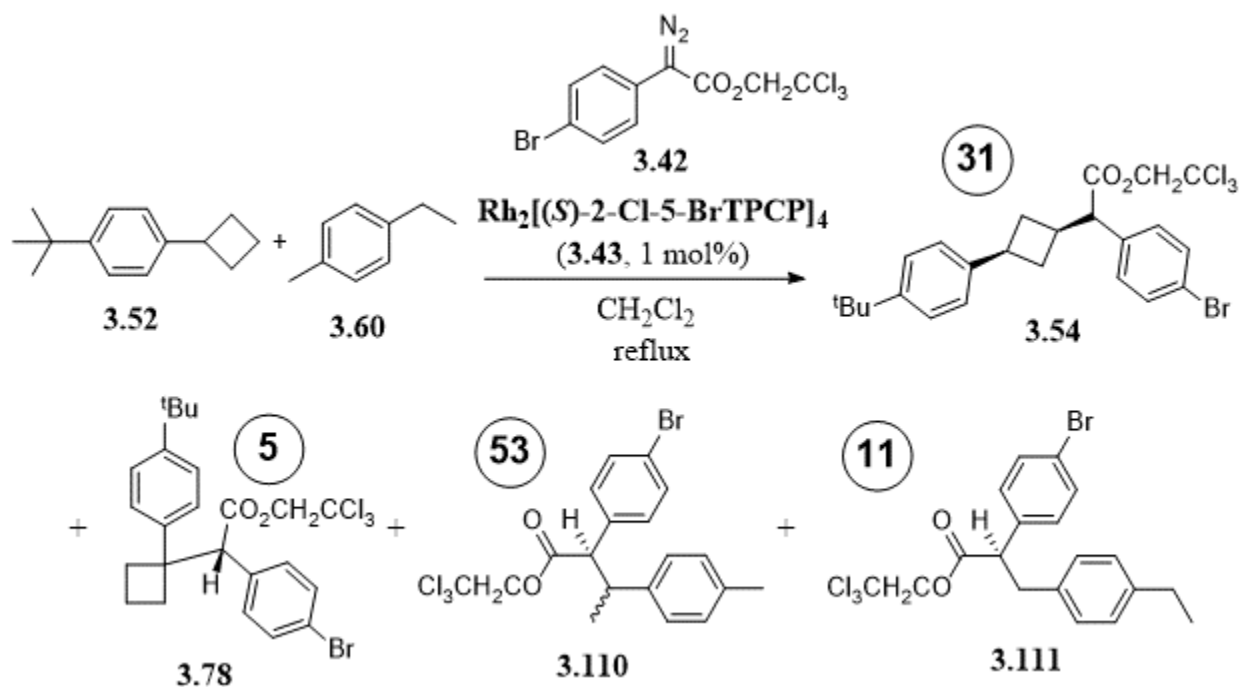
2,2,2-trichloroethyl 2-(4-bromophenyl)-3-methyl-3-(p-tolyl)butanoate (**3.112**): 3.99 ppm (s, 1 H), 4.46 ppm (*d*, 1 H), or 2.30 ppm (s, 3 H)

2,2,2-trichloroethyl 2-(4-bromophenyl)-3-(4-isopropylphenyl)propanoate (**3.113**): 3.06 ppm (*dd*, 1 H)

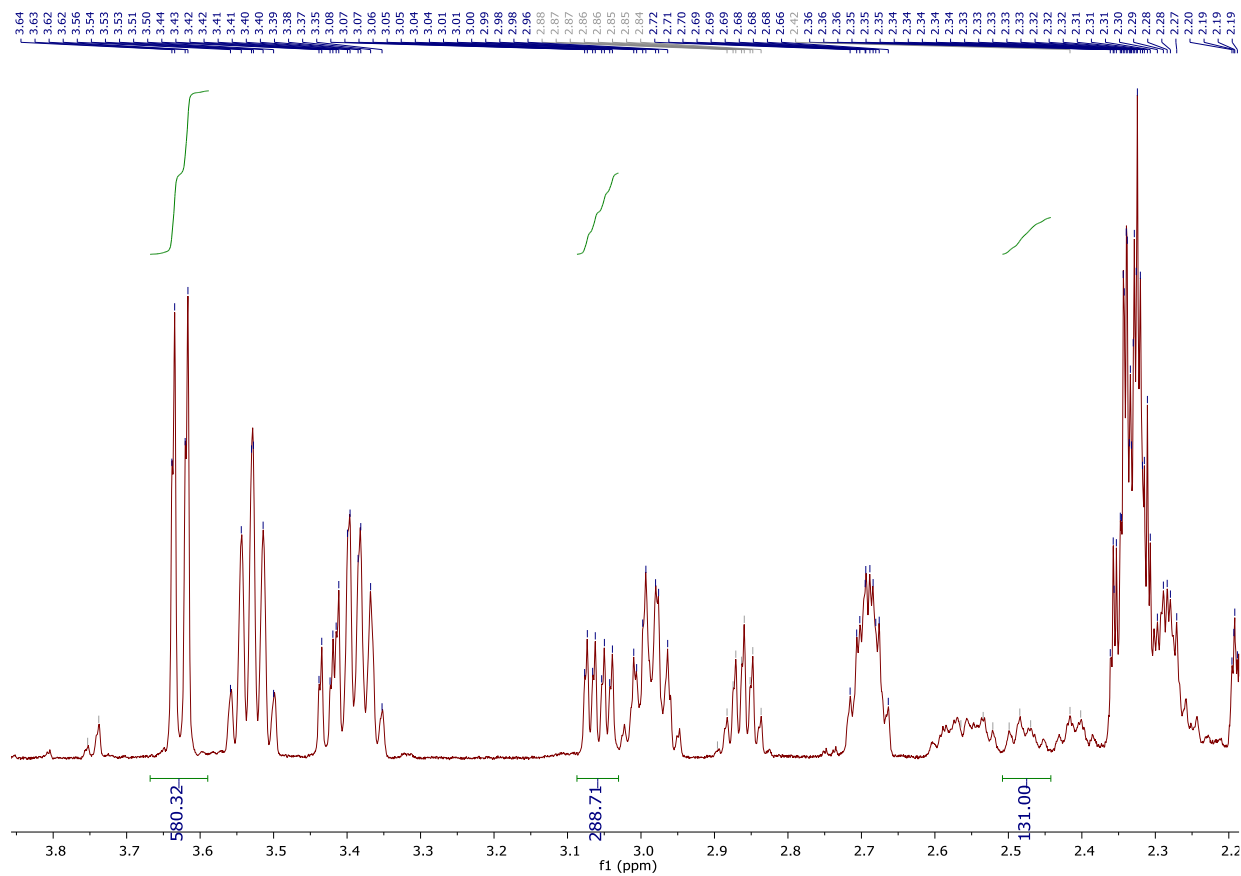
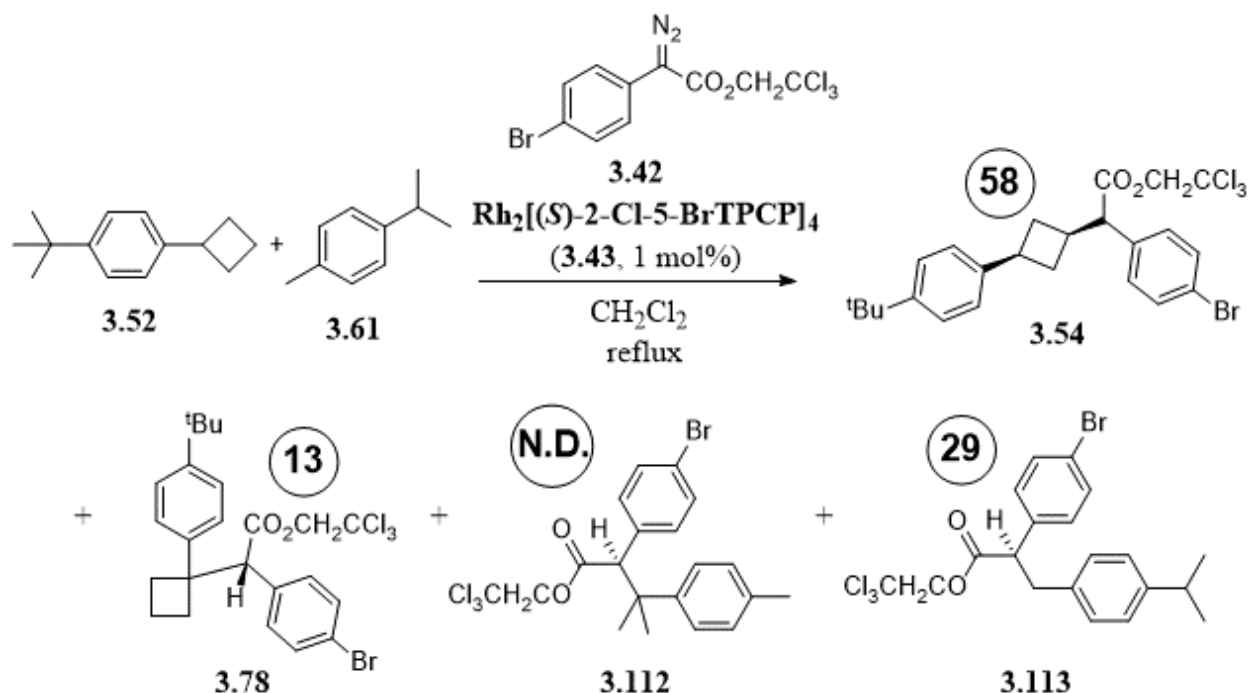




Crude HNMR Spectrum of the above reaction.



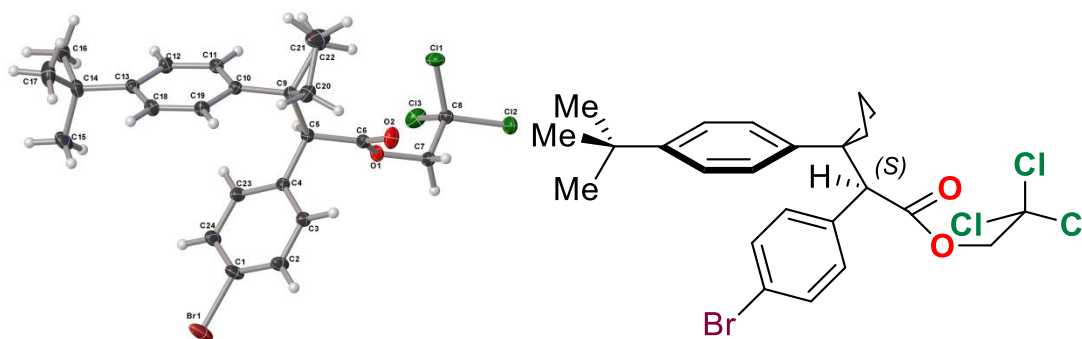
Crude HNMR Spectrum of the above reaction.



Crude HNMR Spectrum of the above reaction.

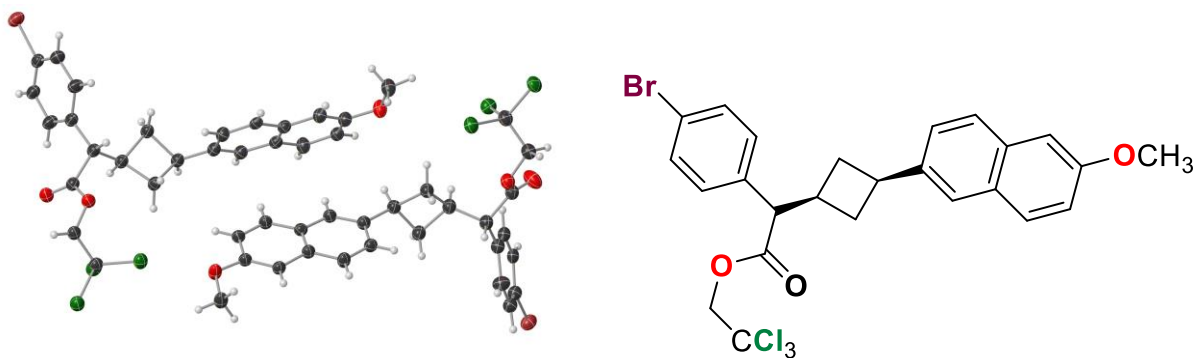
S.3.8 Determination of Absolute Configuration

Approximately 10 mg of **8** which was synthesized with $\text{Rh}_2(\text{S-TCPTAD})_4$ (**3.53**) was placed in a 1 dram vial and was dissolved in hexanes. The solution was capped with a slight crack to allow slow evaporation leaving crystals. X-ray crystallographic analysis unveiled that the configuration was *S*. *This structure obtained by Dr. Zachary Garlets.*



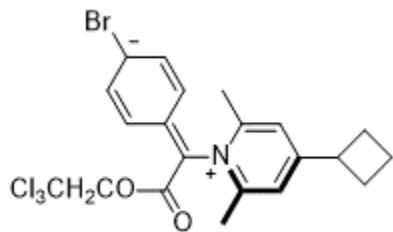
Compound **3.53**.

Approximately 50 mg of (**3.96**) which was synthesized with $\text{Rh}_2(\text{S-2Cl-5Br-TPCP})_4$ (**3.43**) was placed in a 20 ml vial and dissolved in hexanes. Over time, small needles were formed which were sufficient for determining the absolute and relative configuration.

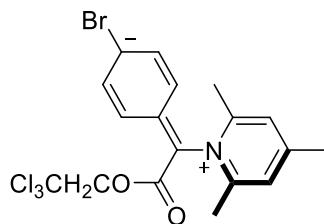


Compound **3.96**.

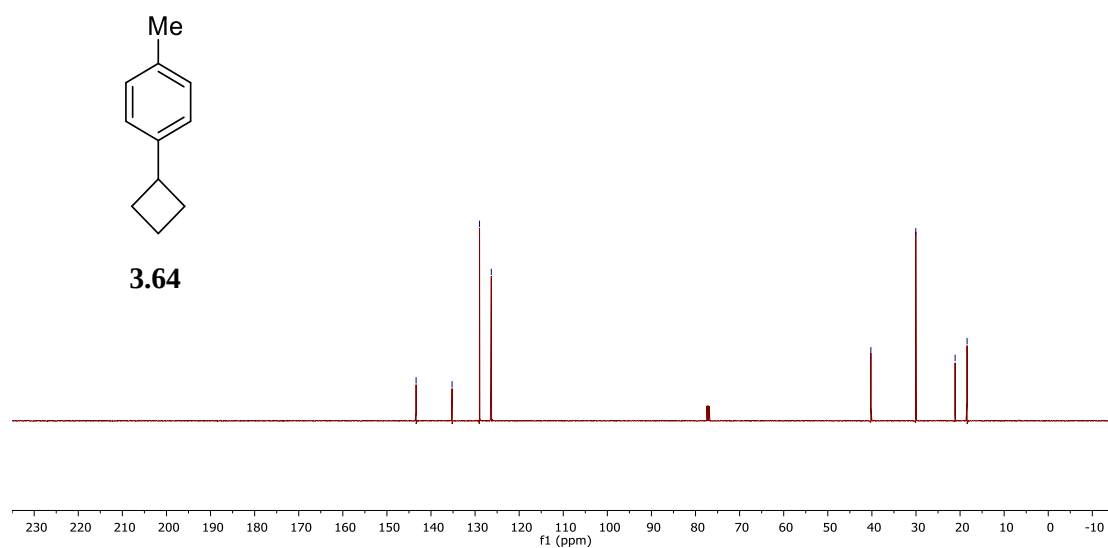
S.3.9 Synthesis and Characterization of Stable Pyridinium Ylides

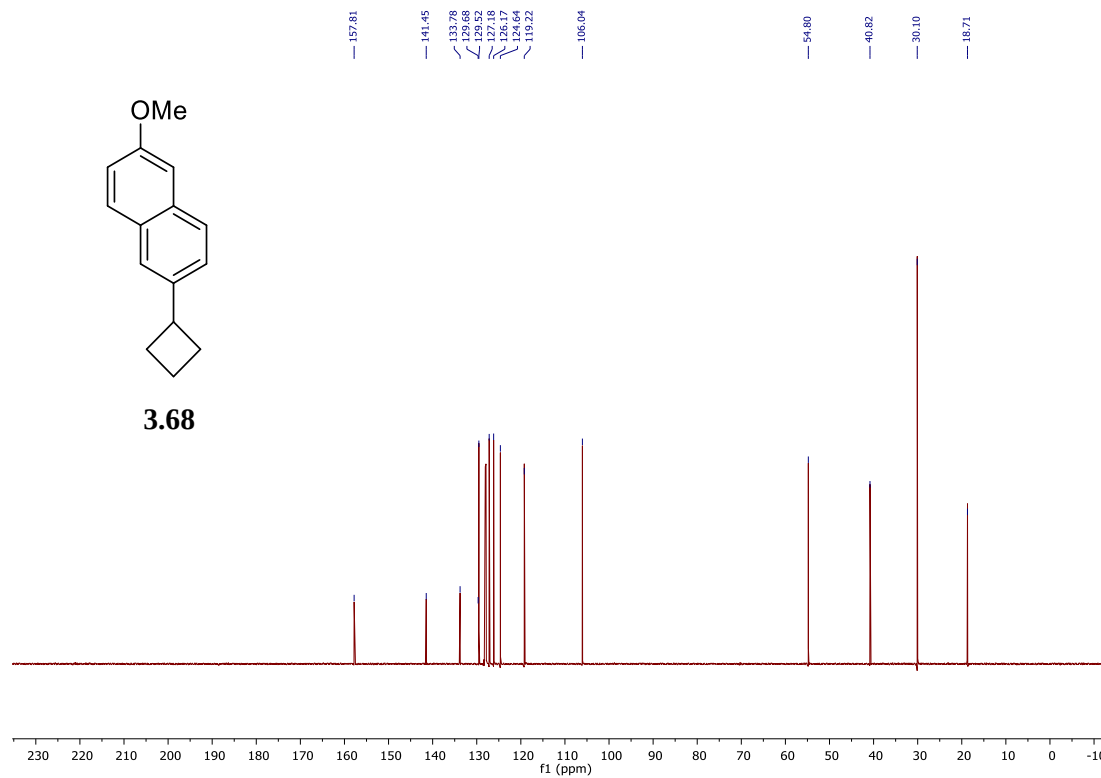
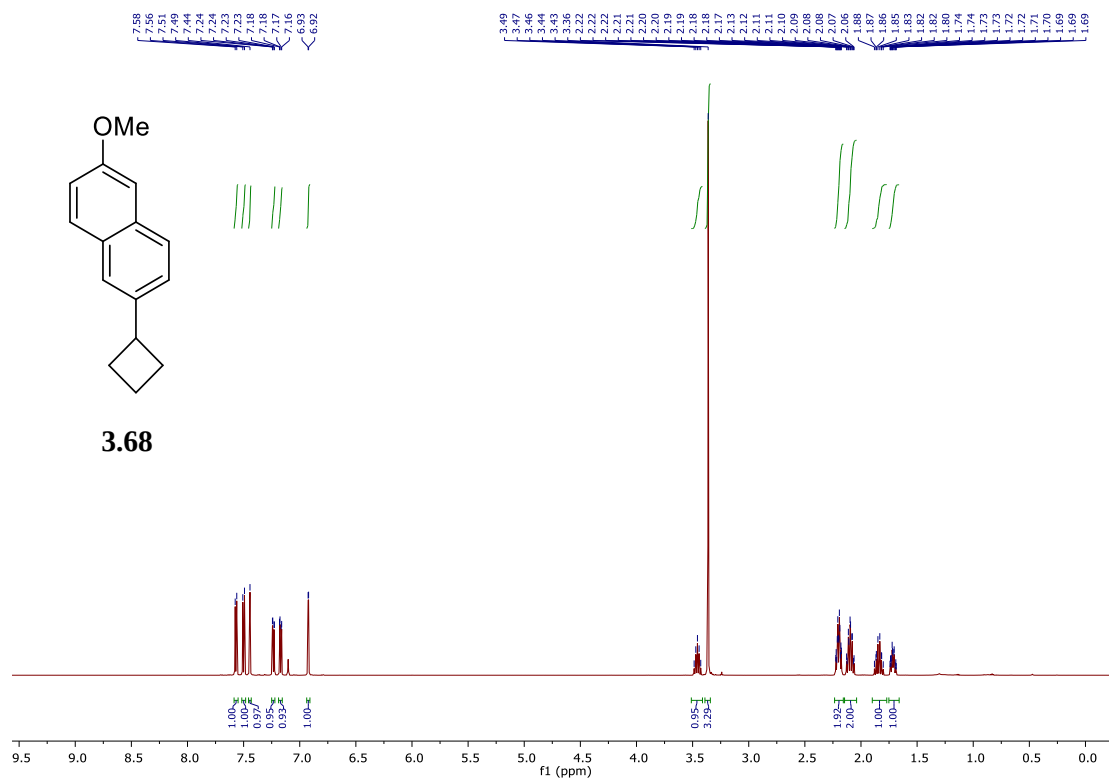


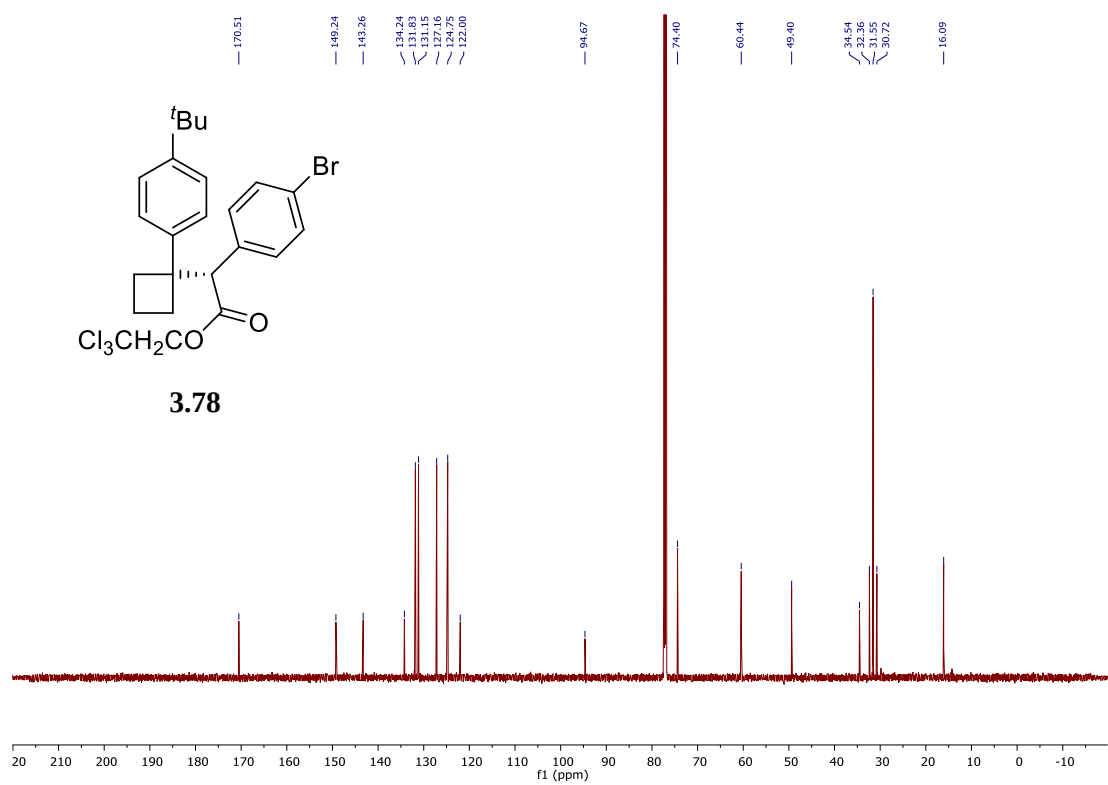
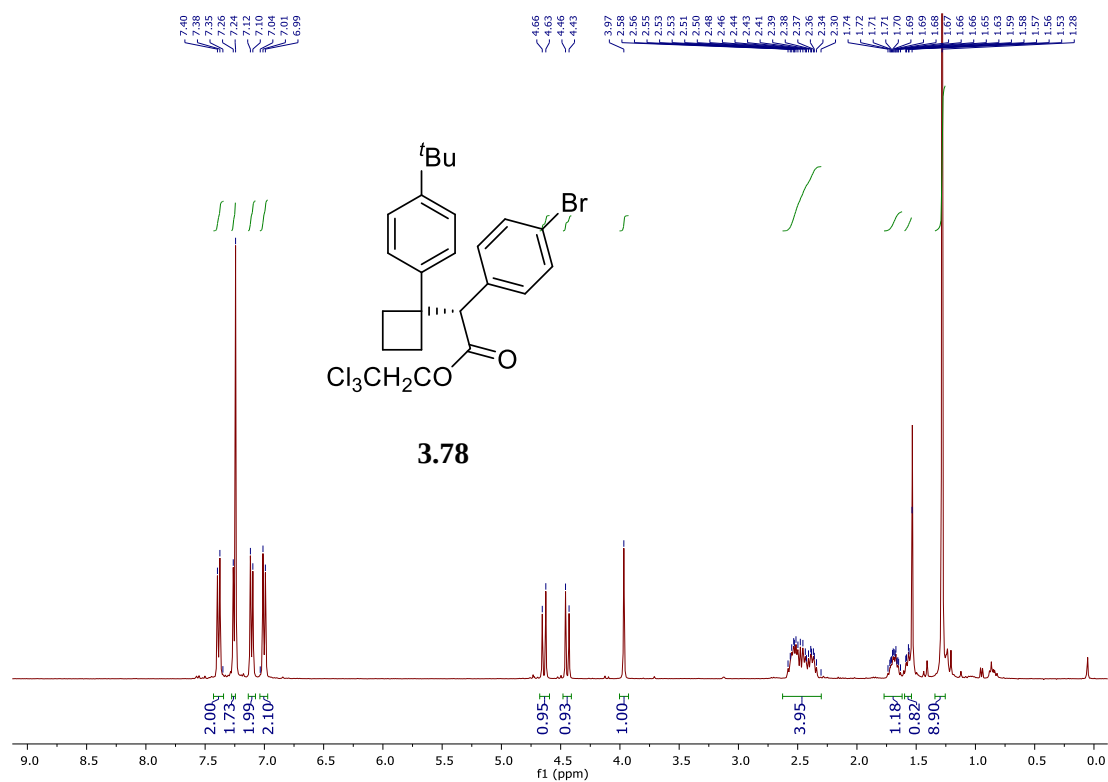
1-bromo-4-(1-(4-cyclobutyl-2,6-dimethylpyridin-1-ium-1-yl)-2-oxo-2-(2,2,2-trichloroethoxy)ethylidene)cyclohexa-2,5-dien-1-ide (3.102). This product was obtained from the same reaction mixture as compound **3.89**, but was isolated using a different purification method. The general procedure 2 was employed for the C-H functionalization of 4-cyclobutyl-2,6-dimethylpyridine (**3.72**, 40.3 mg, 0.25 mmol) by reaction of 2-(4-bromophenyl)-2-diazoacetate (**3.42**, 186 mg, 0.50 mmol) using $\text{Rh}_2(\text{R-TCPTAD})_4$ (**3.33**, 5.3 mg, 1 mol%) as catalyst. After the reaction had completed, the mixture was loaded onto silica gel and the components were separated by column chromatography (30-100% Et_2O /hexanes, then 10% $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$). After evaporation from the chromatography solvent, 60 mg of the title compound were obtained as a purple oil (47% yield). The protons of the 2,6-dimethylpyridyl group did not fully integrate in the ^1H NMR spectrum at room temperature due to broadening, and the trichloroethyl ester group showed two signals at 4.95 and 4.62 ppm. The structure was assigned by high resolution mass spectrometry and by analogy to compound **3.105**. ^1H NMR (500 MHz, Chloroform- d) δ 7.39 (s, 2H), 7.24 – 7.10 (m, 2H), 6.71 (s, 0H), 4.95 (s, 1H), 4.62 (s, 1H), 3.78 – 3.61 (m, 1H), 2.60 (s, 4H), 2.55 – 2.43 (m, 2H), 2.31 – 2.10 (m, 3H), 2.06 – 1.91 (m, 1H). IR (neat) 3056, 2965, 2851, 1634, 1570, 1482, 1406, 1381, 1341, 1259, 1095, 1059, 889, 823, 806, 734, 706 cm^{-1} . HRMS (APCI+) 503.9888 (503.9894 calcd for $\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}^{79}\text{Br}^{35}\text{Cl}_3$, $\text{M} + \text{H}^+$)

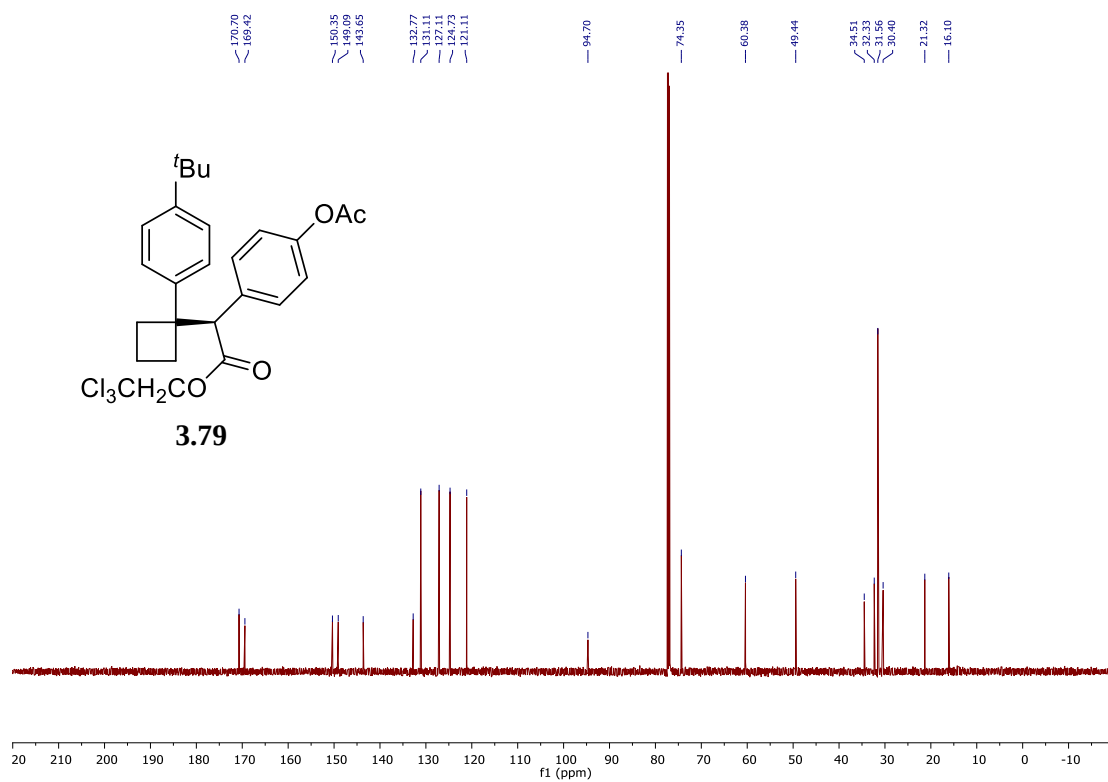
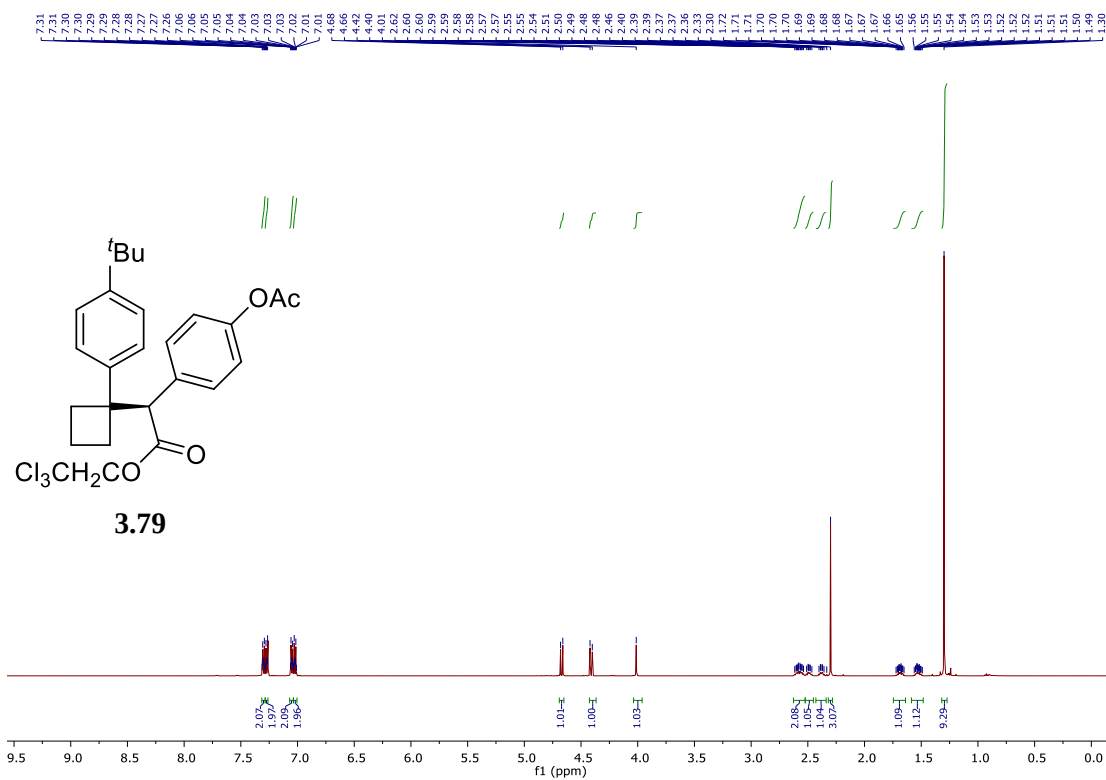


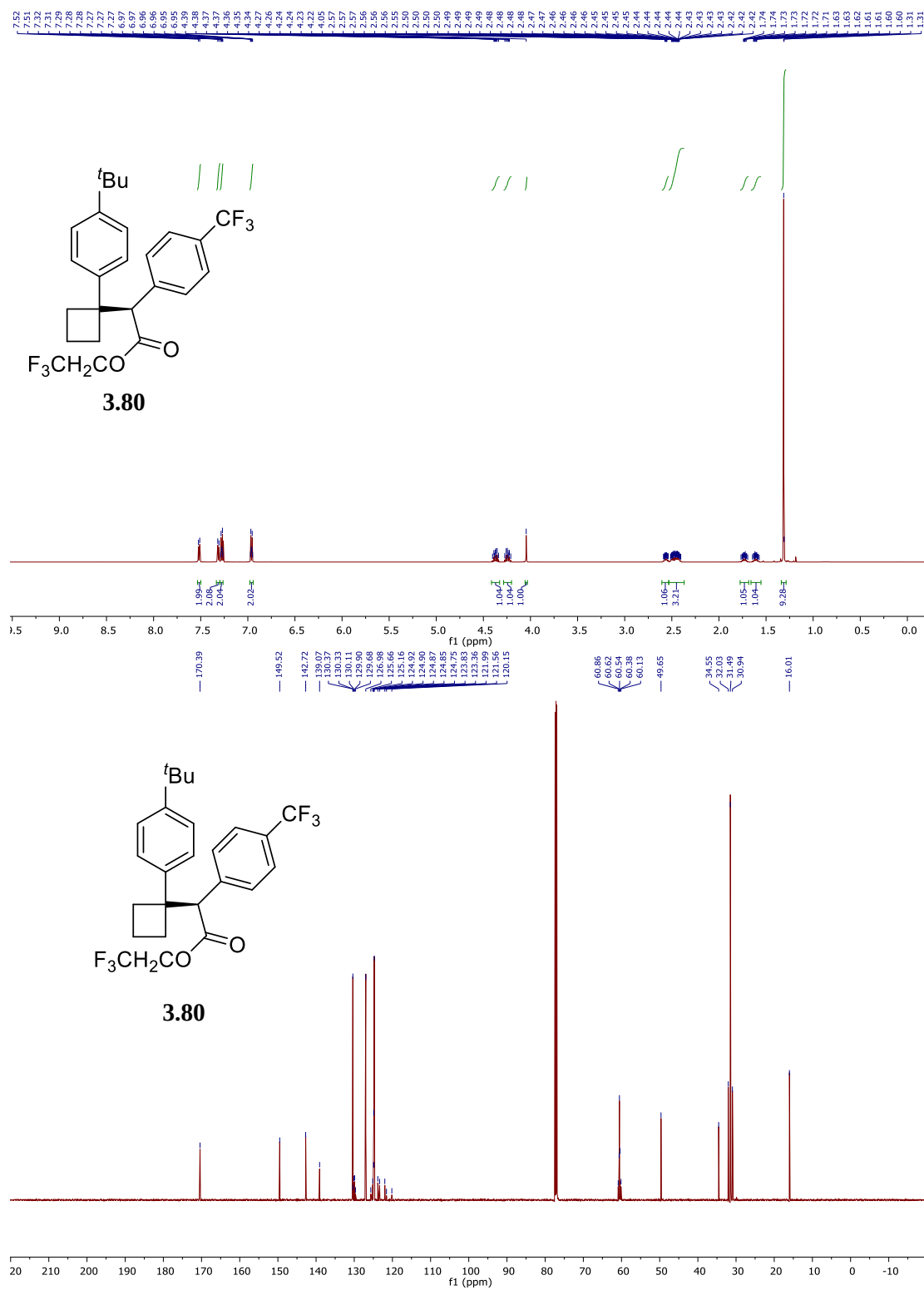
1-bromo-4-(2-oxo-2-(2,2,2-trichloroethoxy)-1-(2,4,6-trimethylpyridin-1-ium-1-yl)ethylidene)cyclohexa-2,5-dien-1-ide (3.105). A scintillation vial was charged with 2,4,6-trimethylpyridine (**3.104**, 90.9 mg, 0.75 mmol, 3.0 equiv), CH₂Cl₂ (2.5 mL), and Rh₂(*R*-TCPTAD)₄ (**3.33**, 5.3 mg, 1 mol%). The mixture was heated to gentle reflux, and then 2-(4-bromophenyl)-2-diazoacetate (**3.42**, 93.1 mg, 0.25 mmol, 1.0 equiv) was added over 3 h using a syringe pump. The mixture was stirred for an additional 3 h, and then it was loaded onto silica gel and the components were separated by column chromatography (0-12% Et₂O/CH₂Cl₂). After evaporation from the chromatography solvent, 74 mg of the title compound were obtained as a reddish purple crystalline solid (64% yield). A well-grown crystal was analyzed by X-ray diffraction, confirming the structure of compound **3.105**. mp 151.0-152.0 °C (dec). As with compound **3.103**, the ¹H NMR signal for the pyridinium aromatic protons at 6.67 ppm was highly broadened and barely observable, and two peaks were observed for the ester group. Several of the carbon NMR signals were too broadened to report. ¹H NMR (600 MHz, Chloroform-d) δ 7.40 (s, 2H), 7.22 – 7.09 (m, 2H), 6.67 (s, 0H), 4.92 (s, 1H), 4.61 (s, 2H), 2.57 (s, 6H), 2.55 (s, 3H). ¹³C NMR (126 MHz, Chloroform-d) δ 160.8, 155.8, 131.3, 127.3, 126.9, 97.8, 72.0, 21.7, 21.1. IR (solid): 3065, 2936, 2923, 2880, 2853, 1637, 1569, 1483, 1409, 1386, 1376, 1340, 1140, 1102, 1063, 975, 947, 857, 831, 807, 760, 735, 702 cm⁻¹. HRMS (APCI+) 463.9579 (463.9581 calcd for C₁₈H₁₈O₂N⁷⁹Br³⁵Cl₃, M + H⁺)

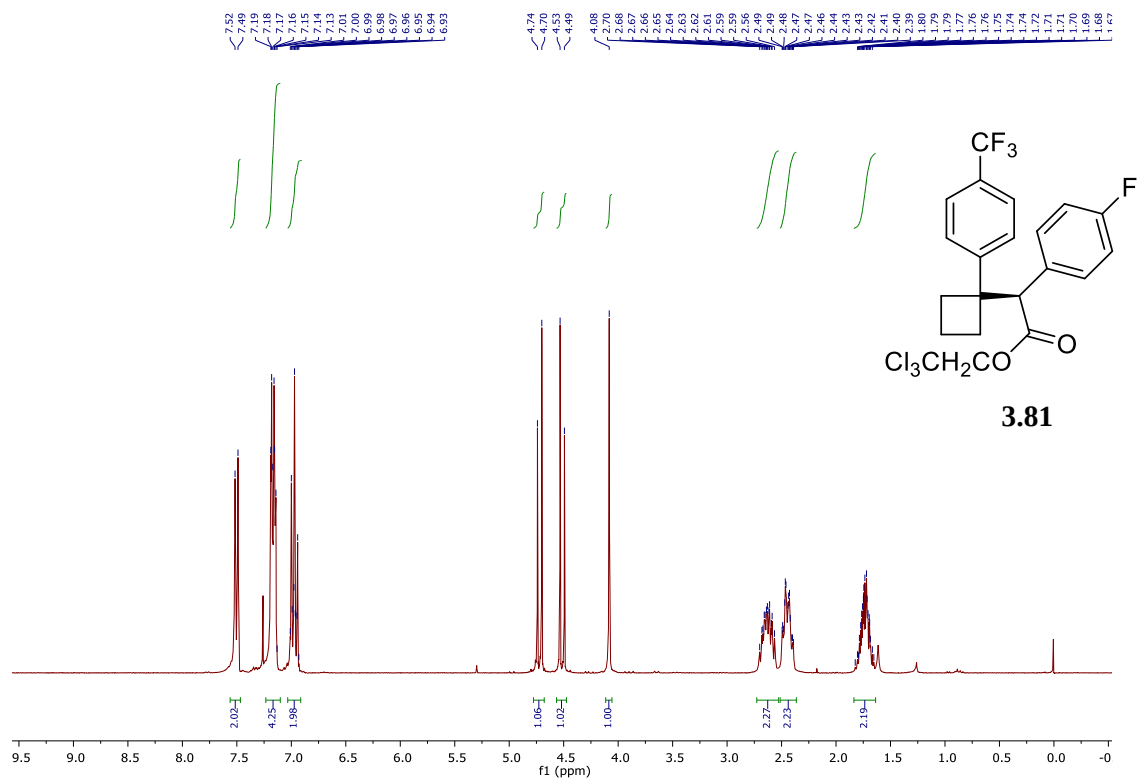
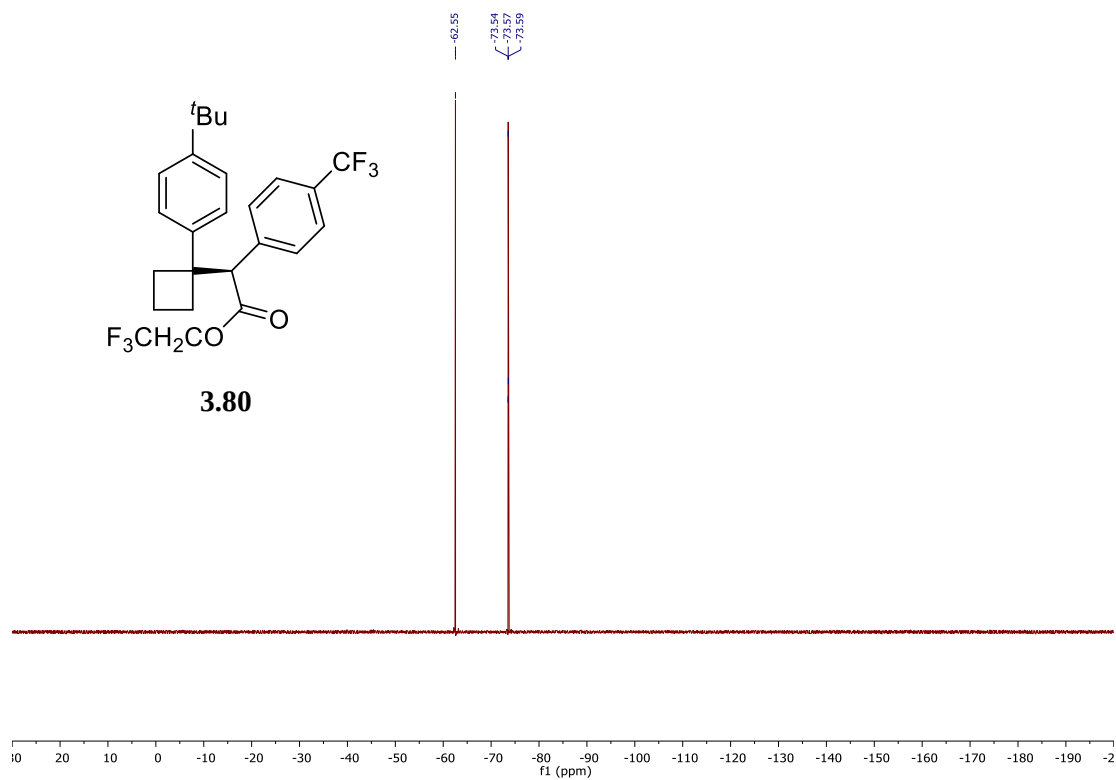


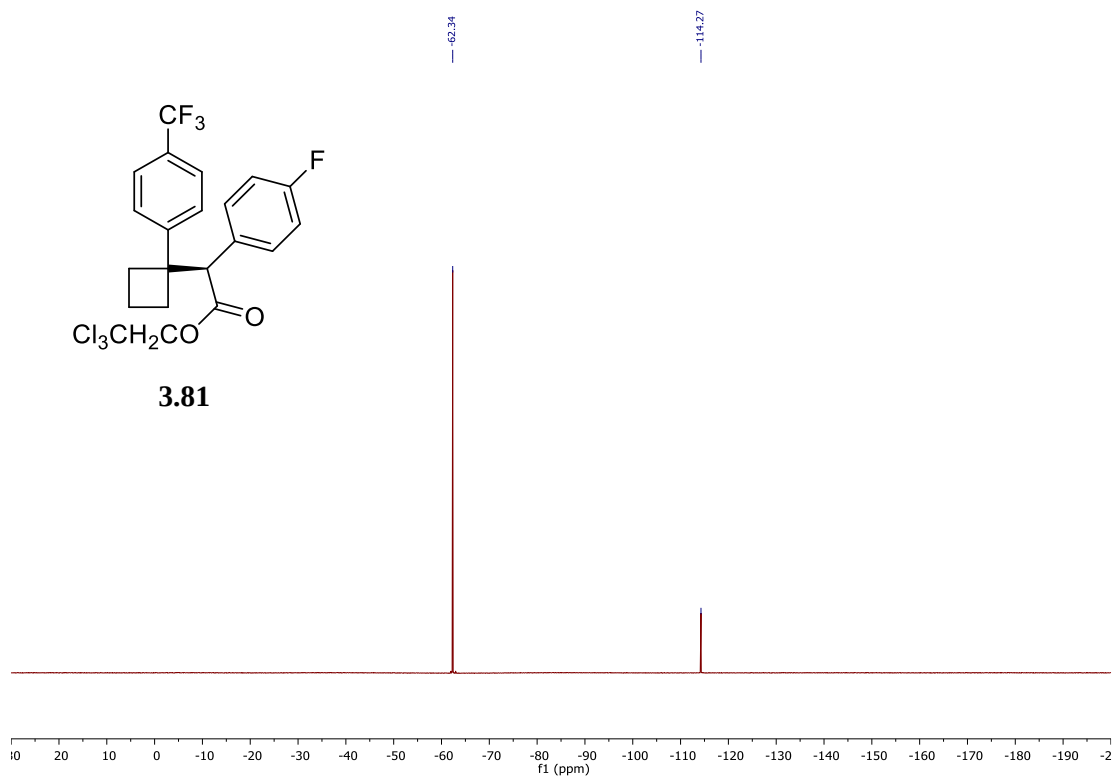
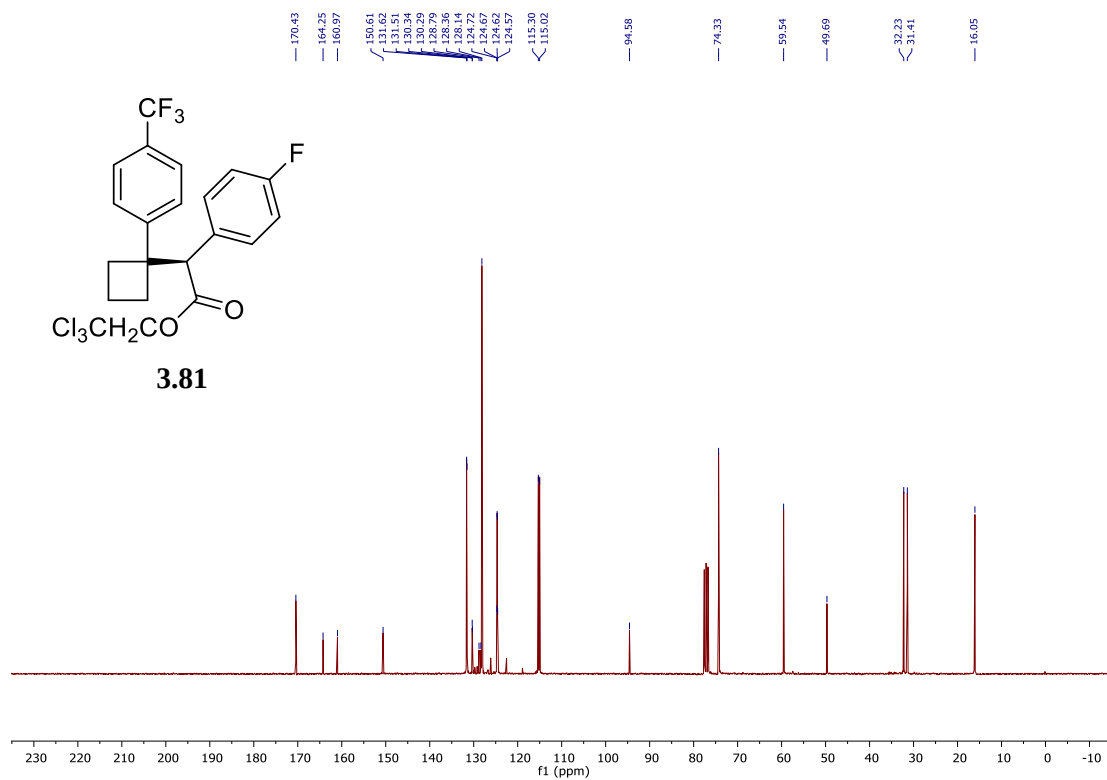


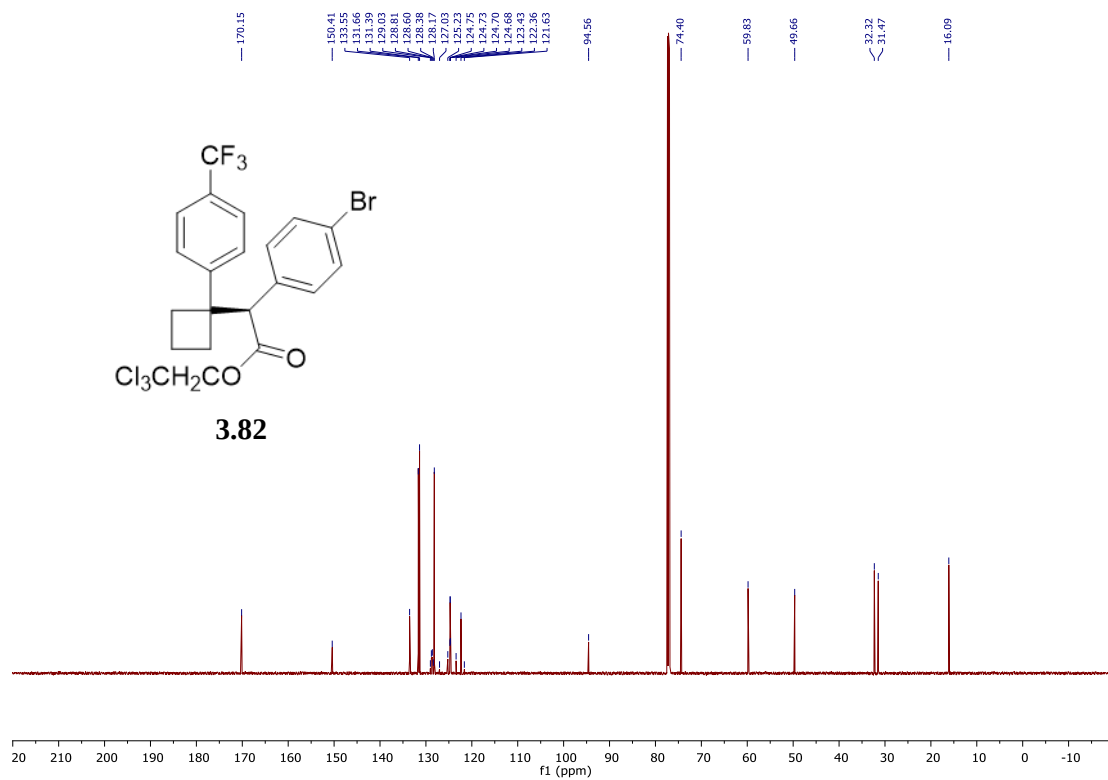
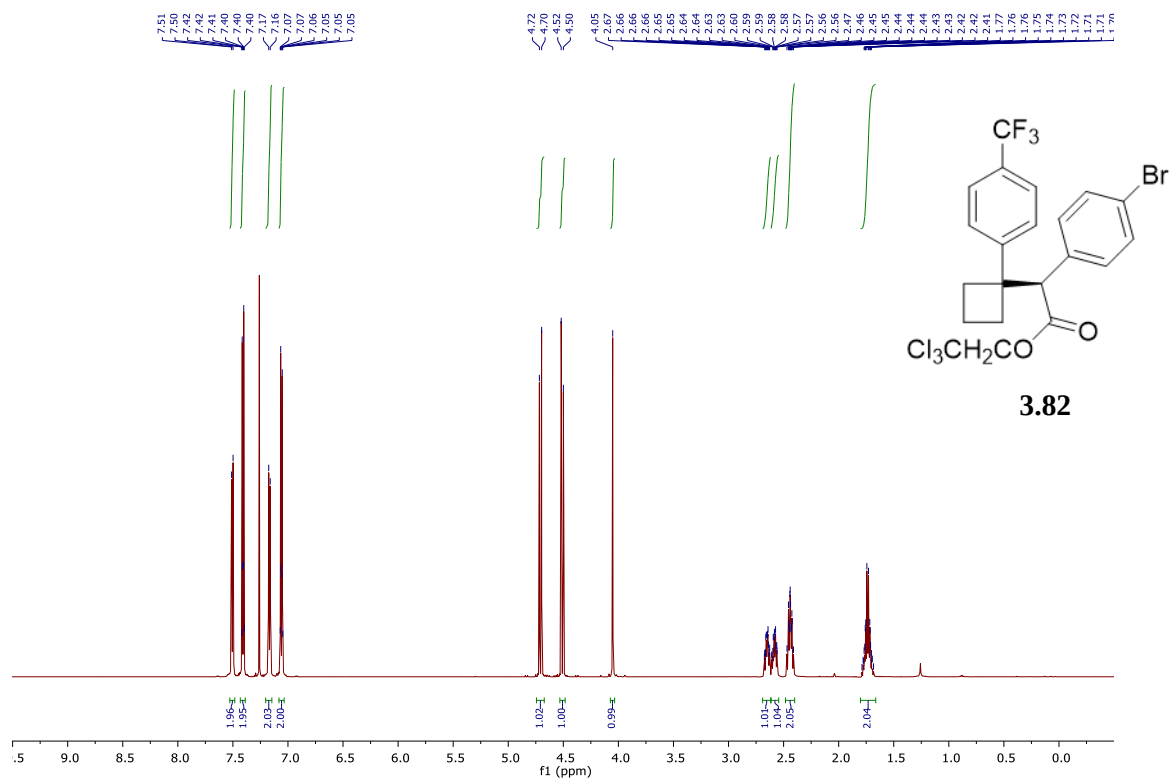


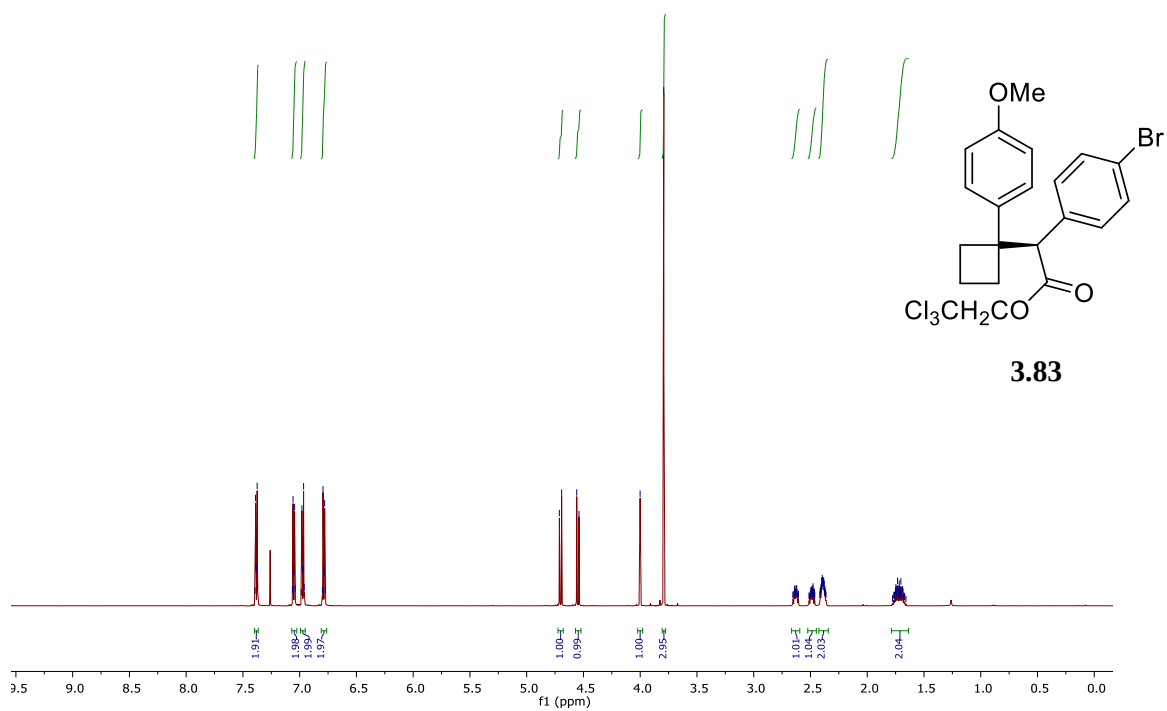
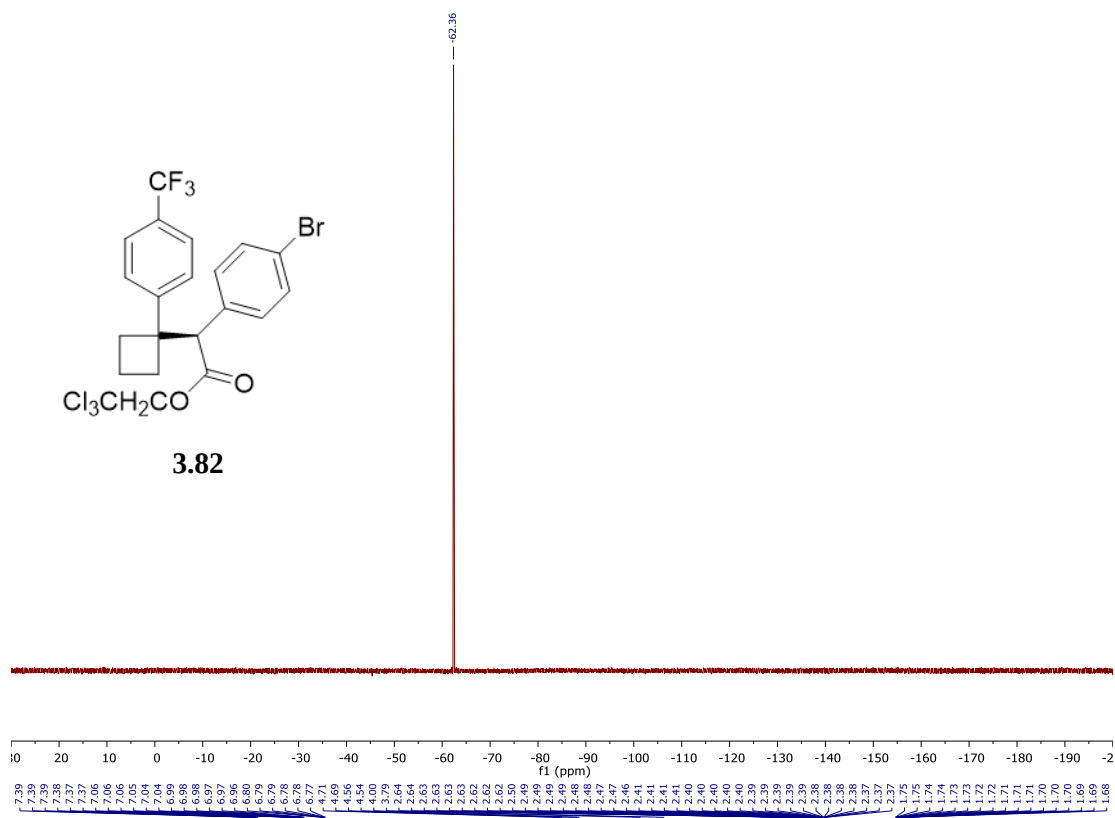


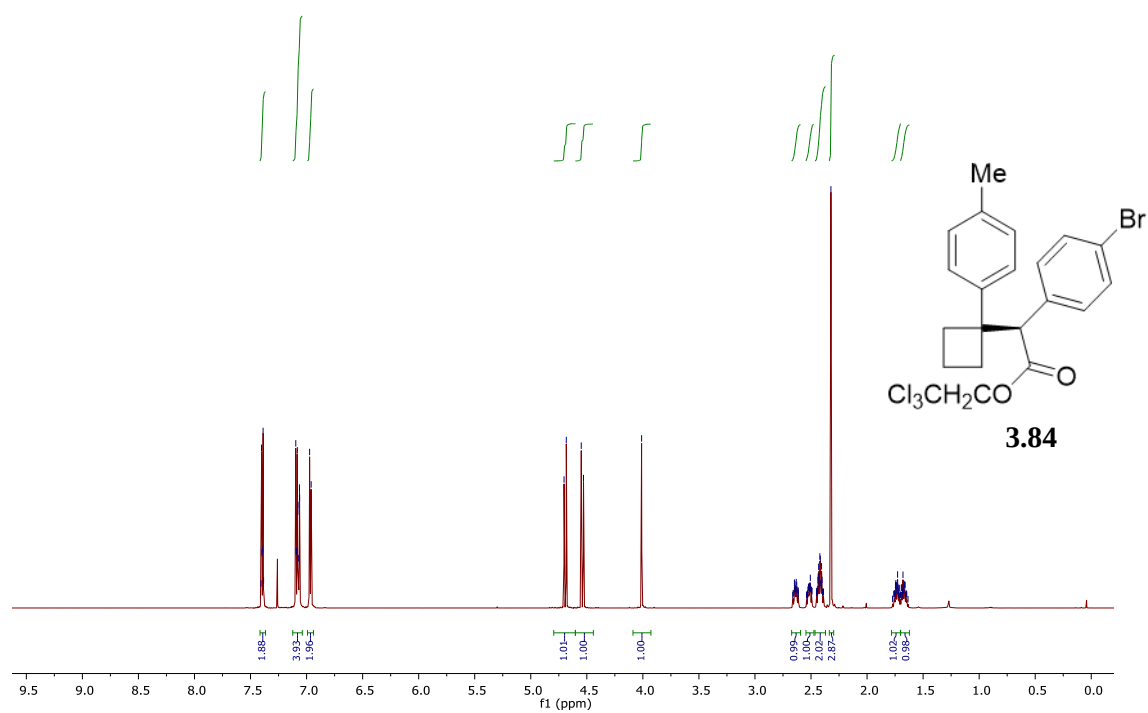
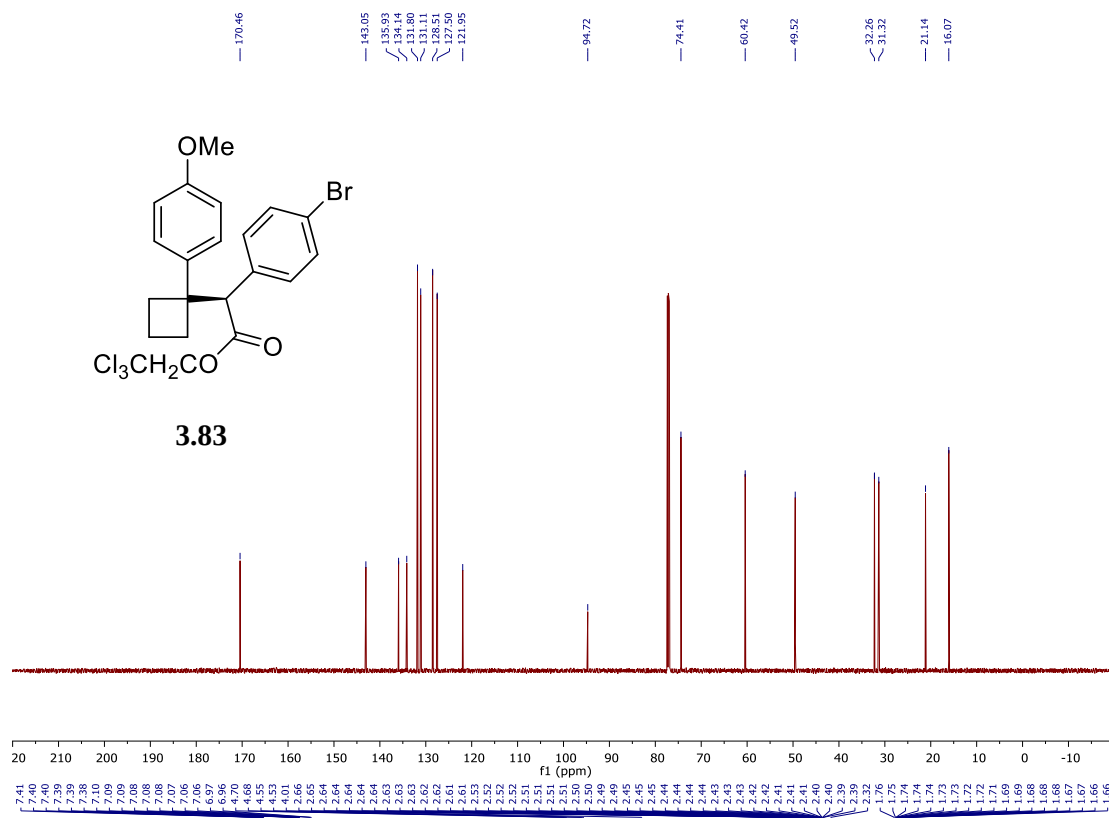


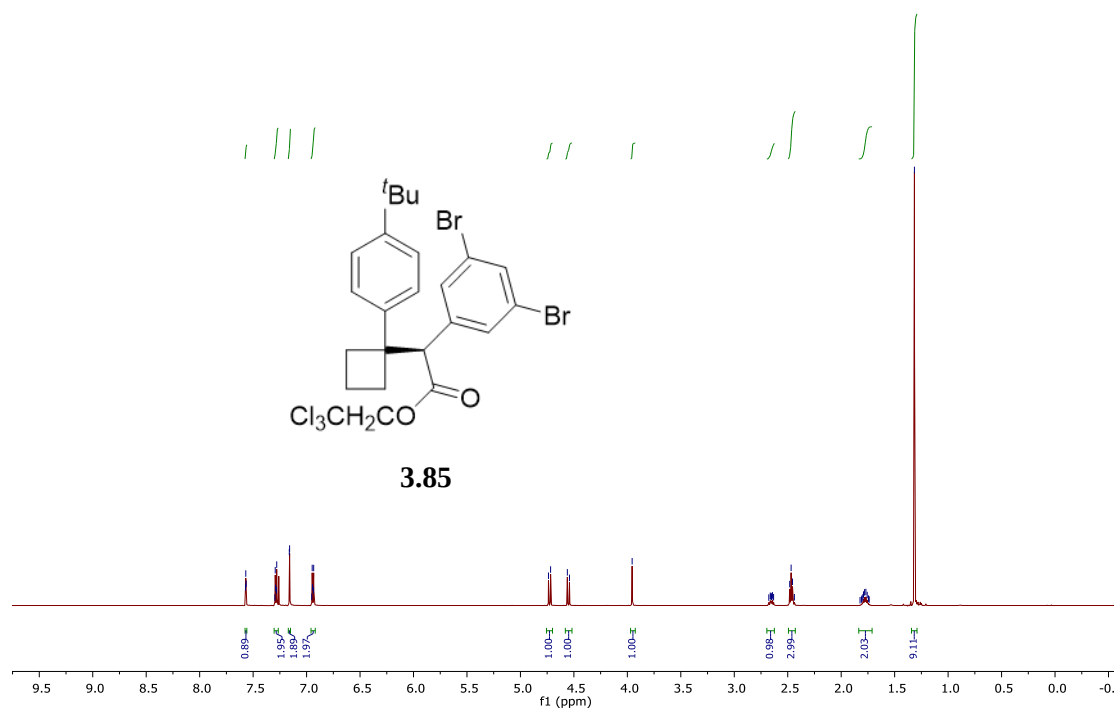
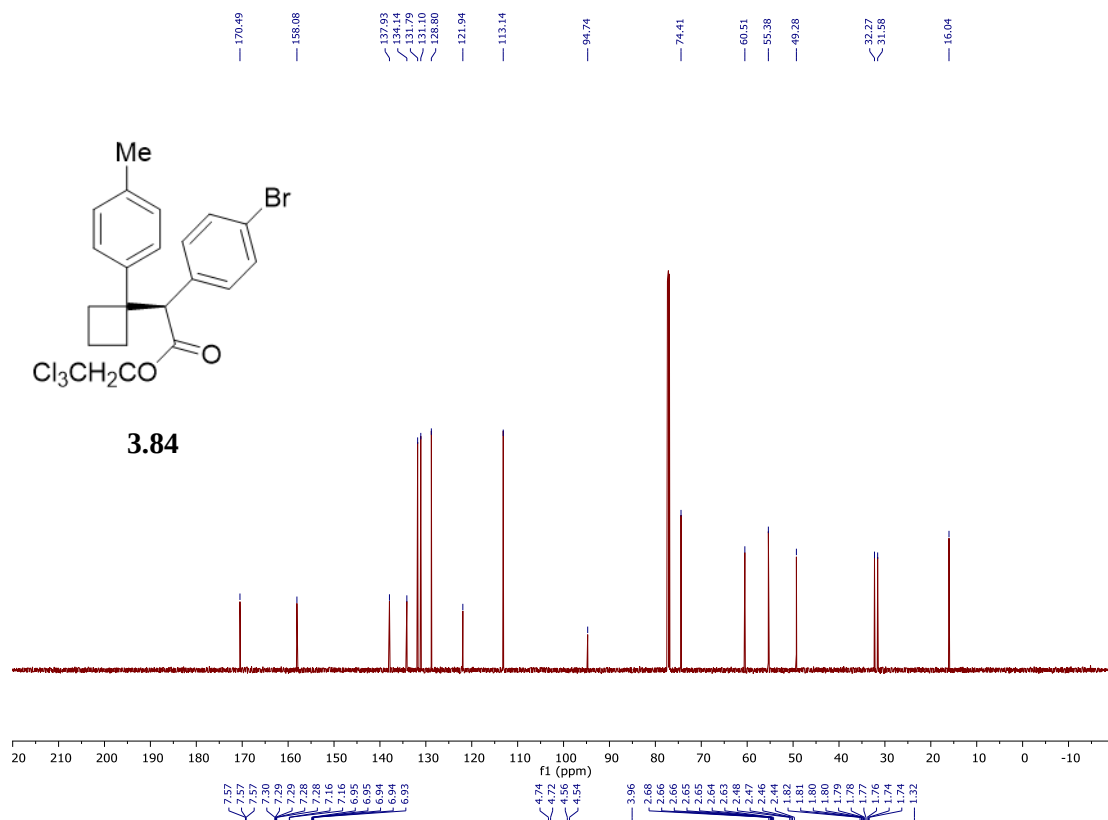


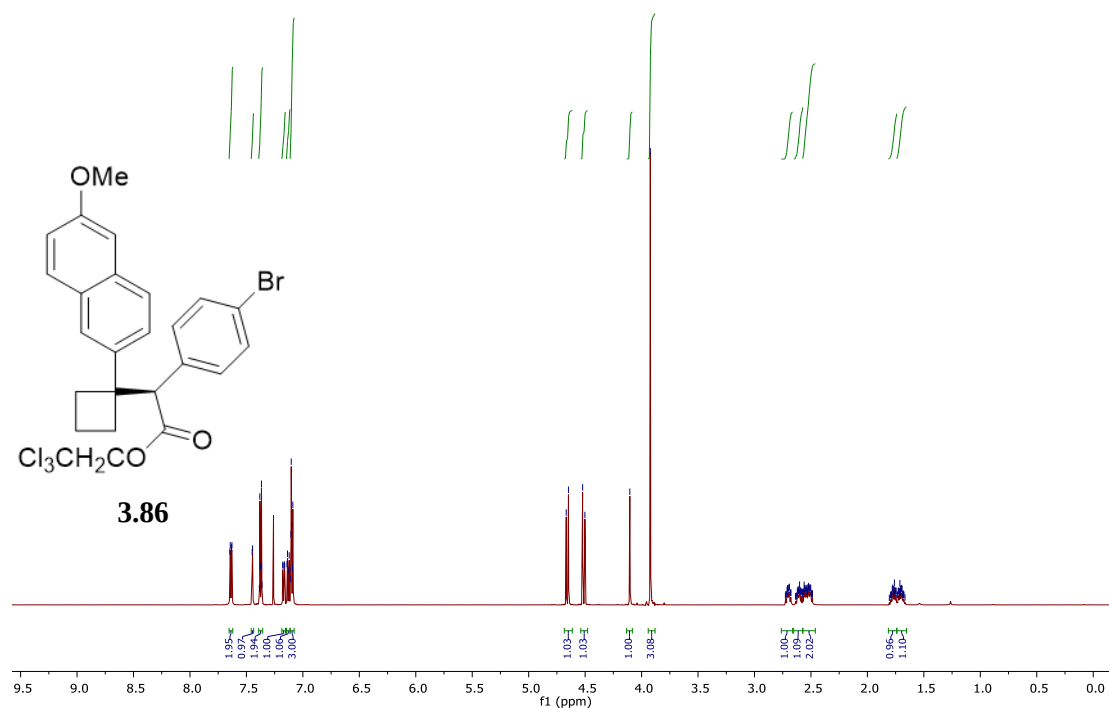
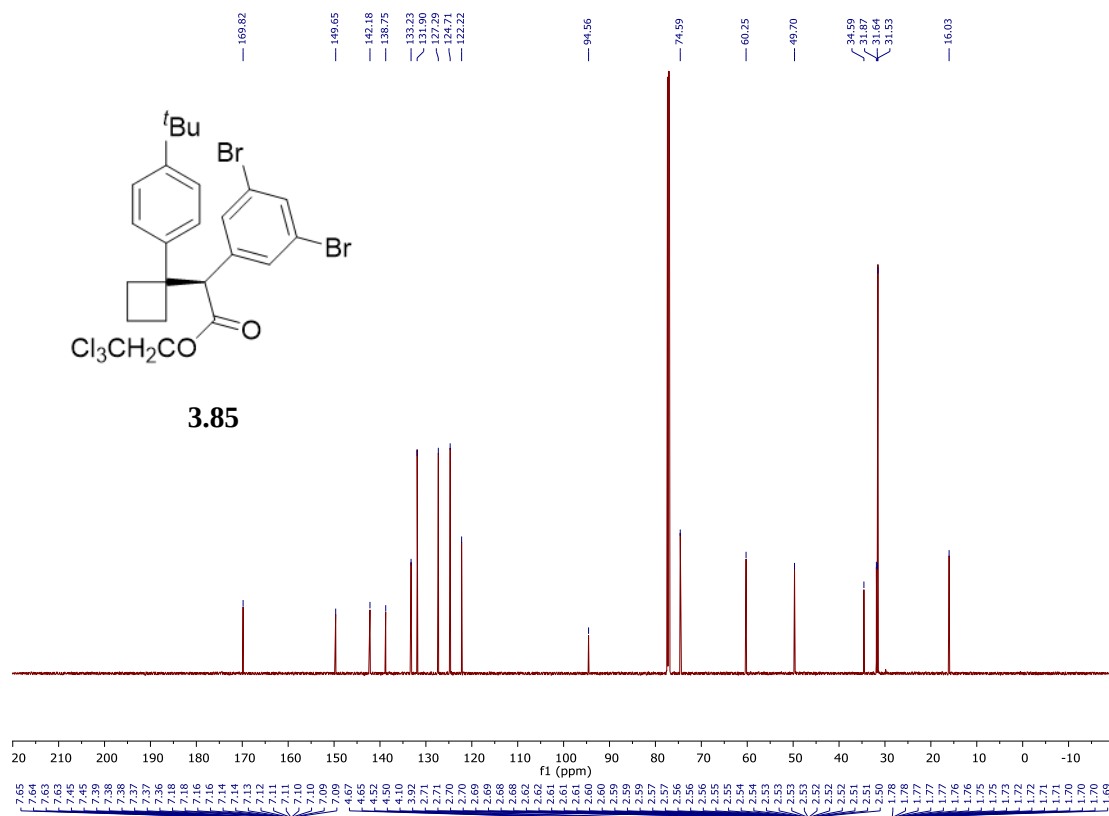


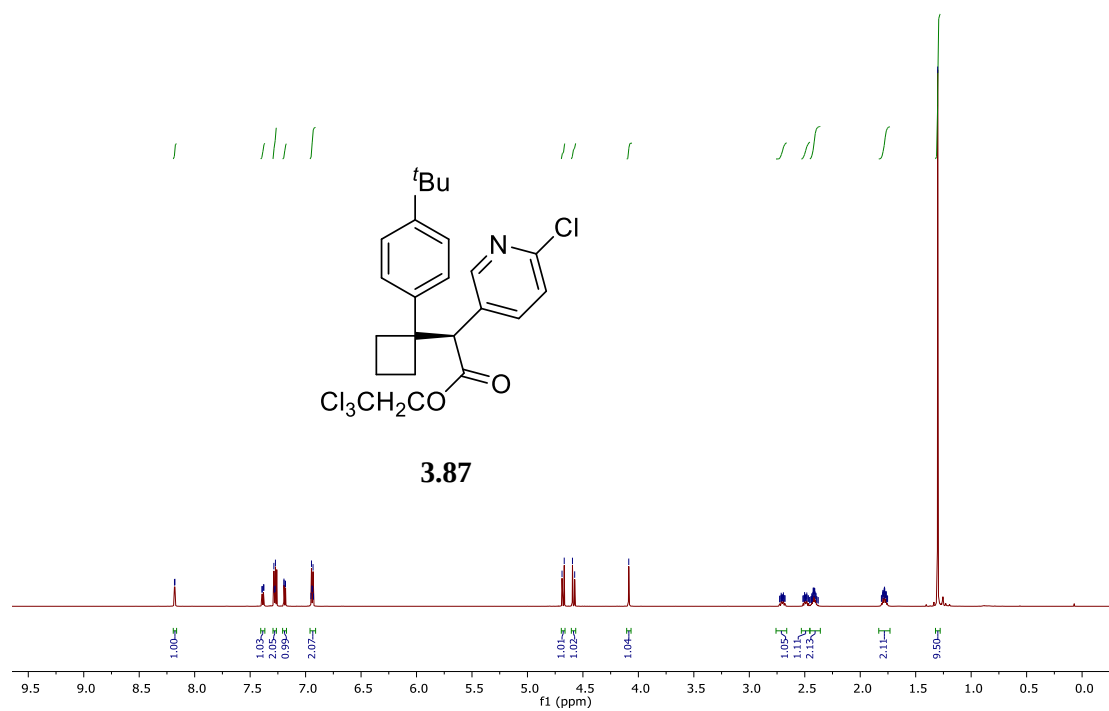
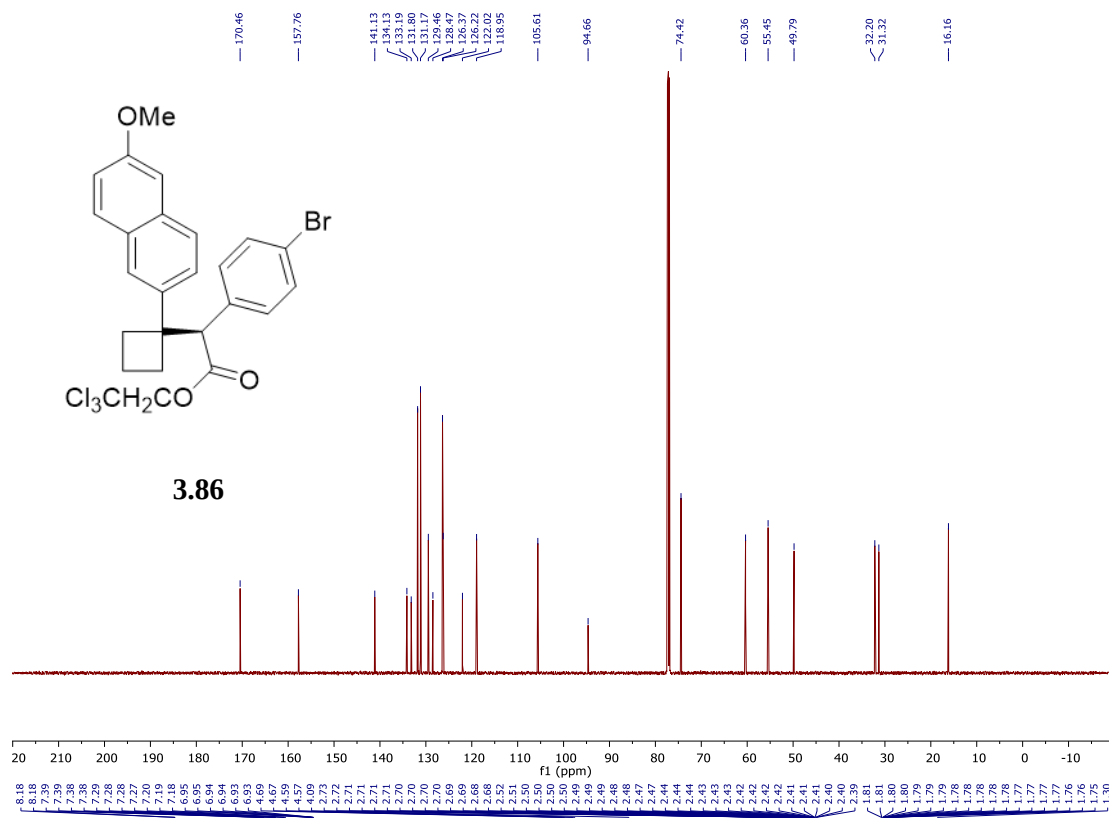


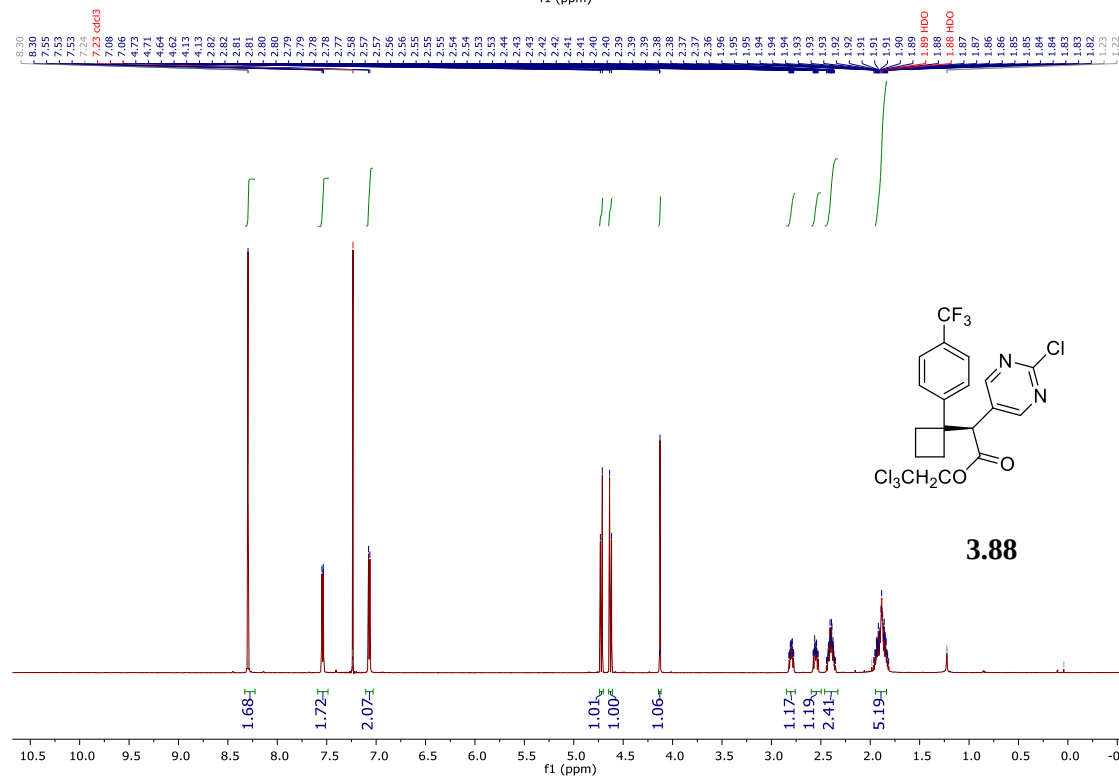
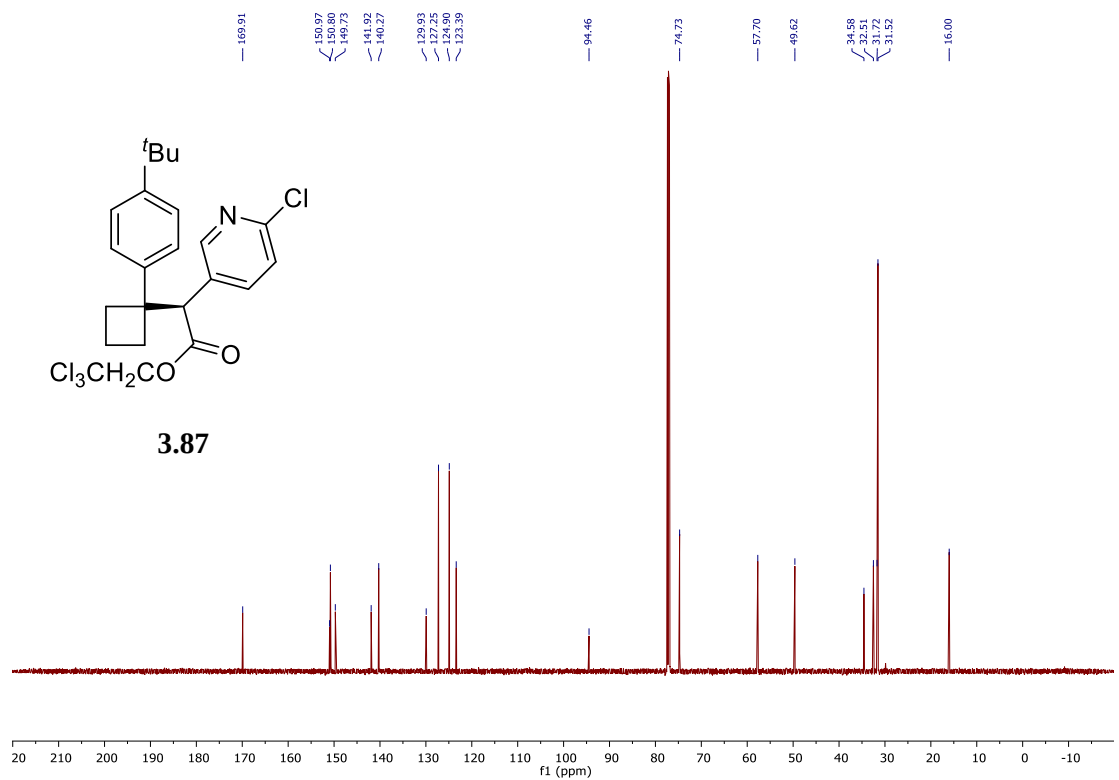


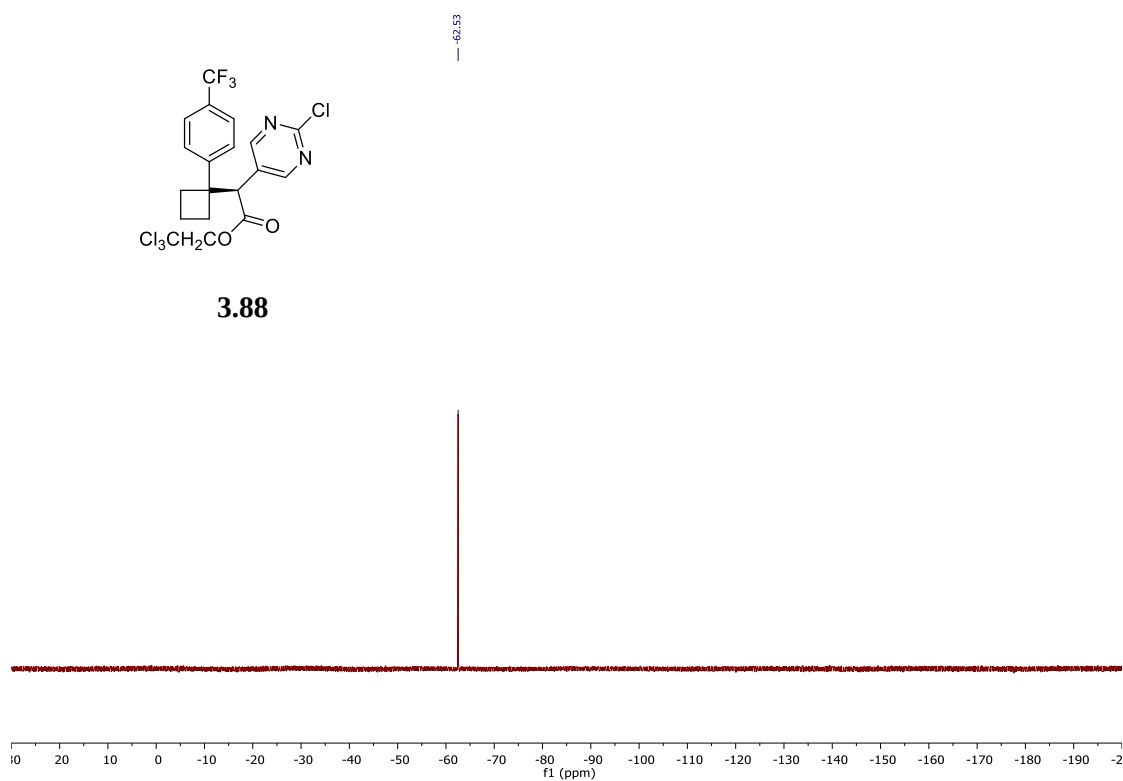
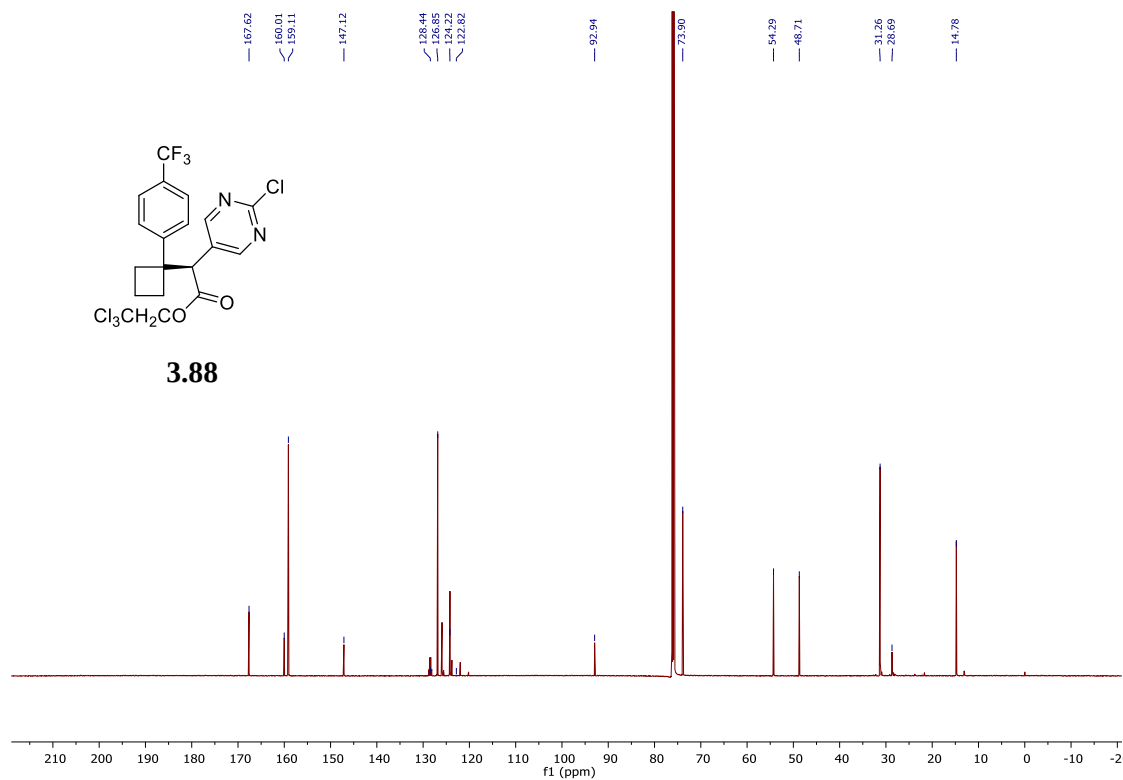


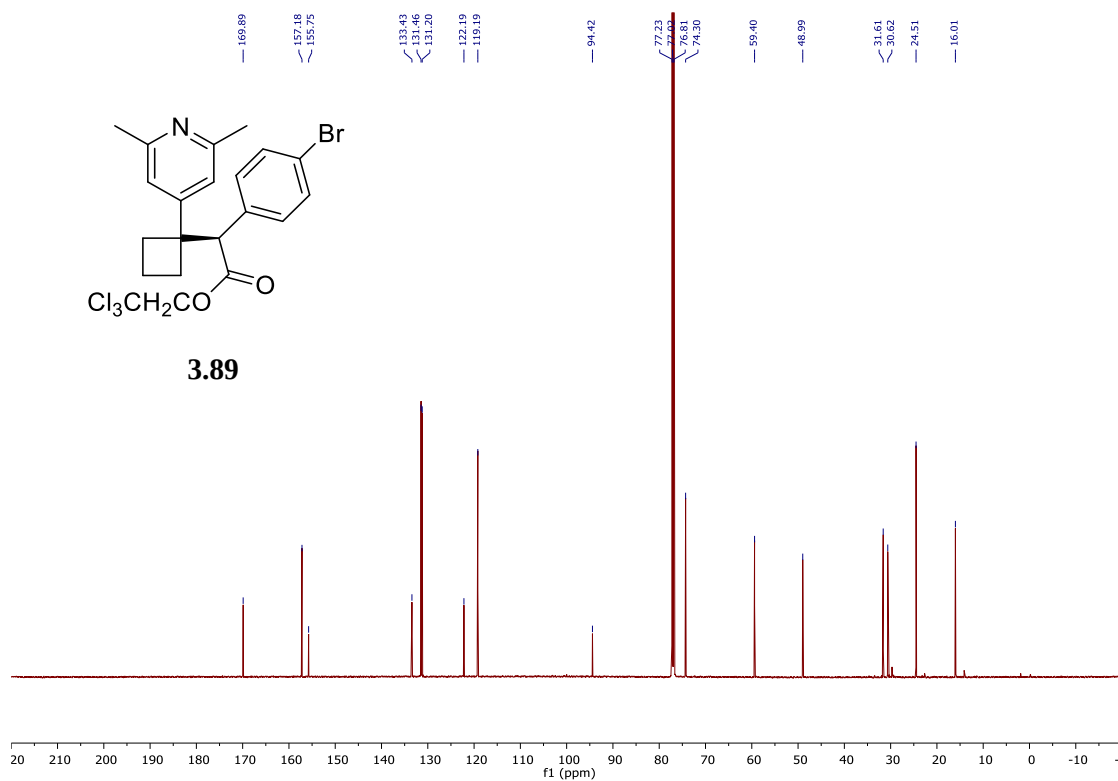
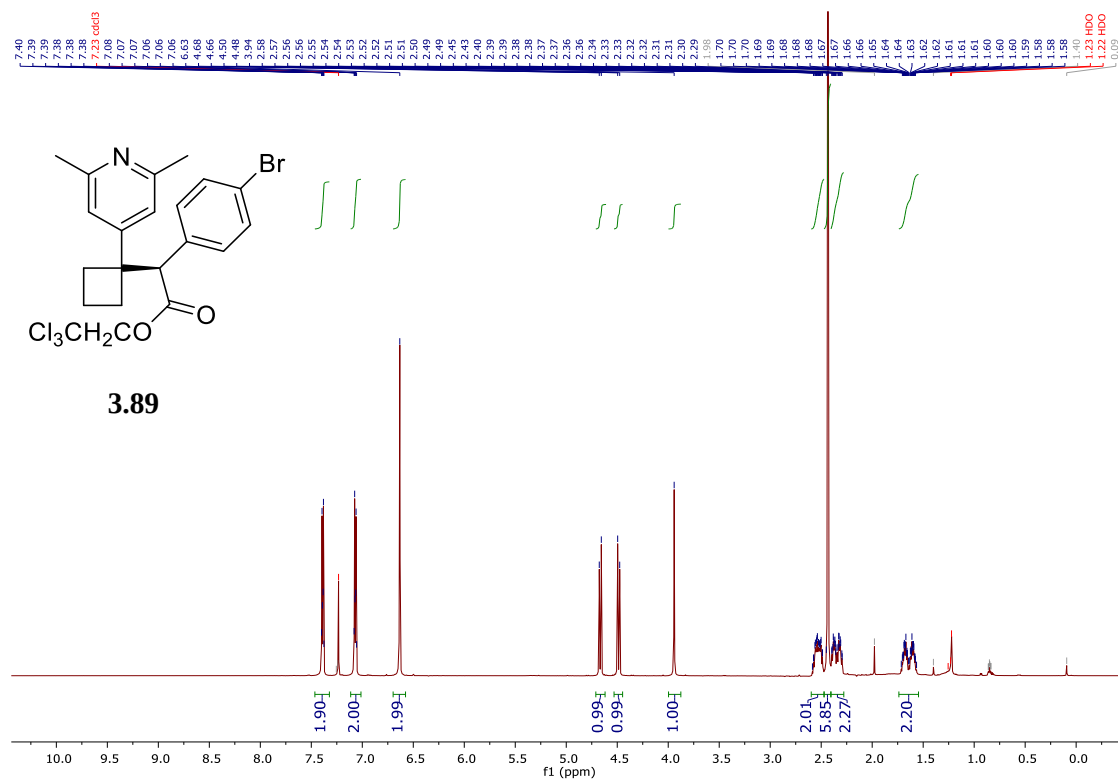


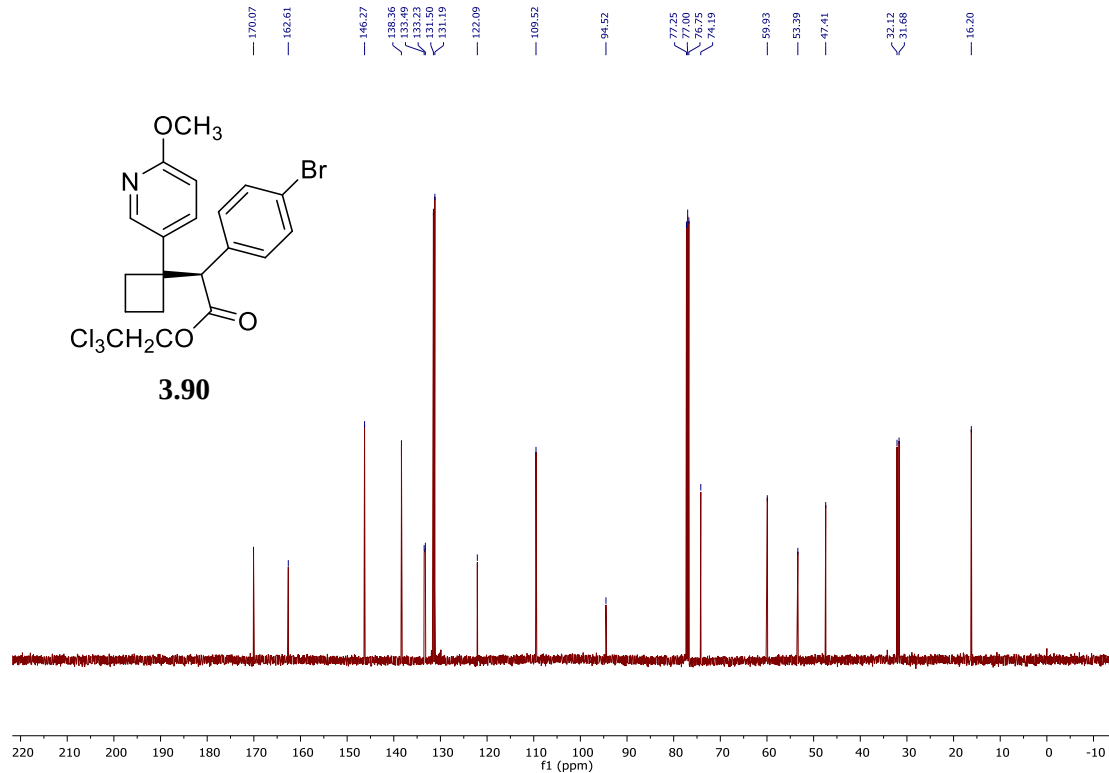
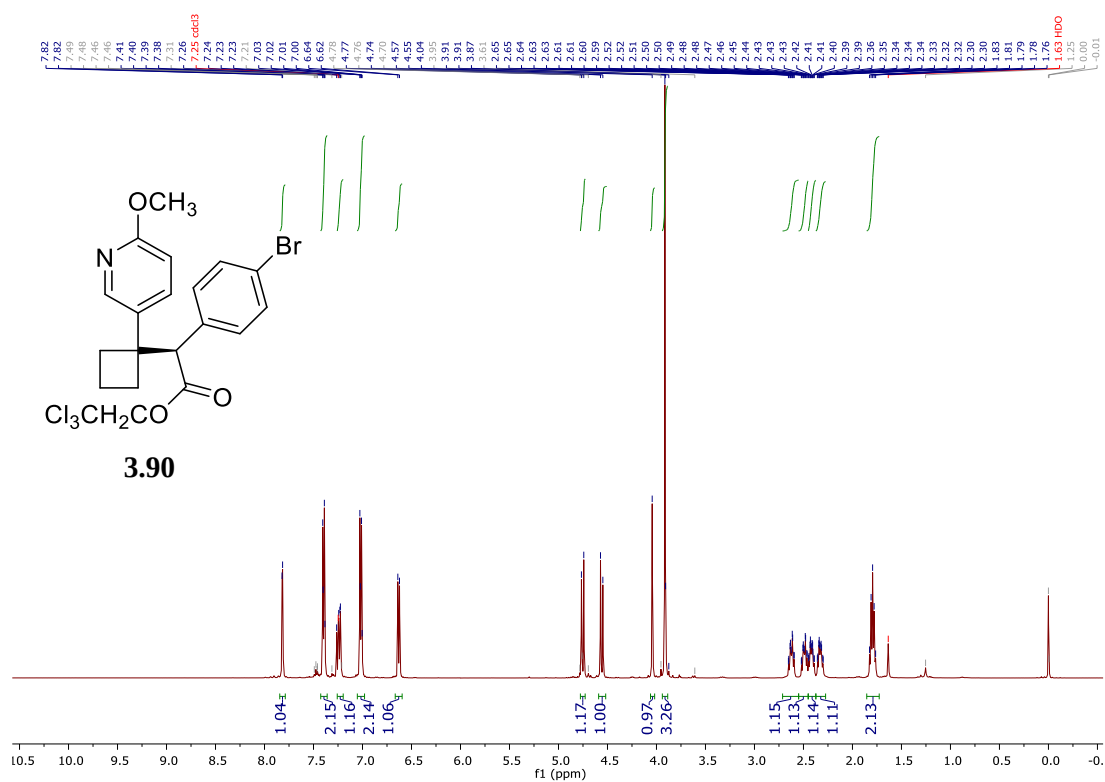


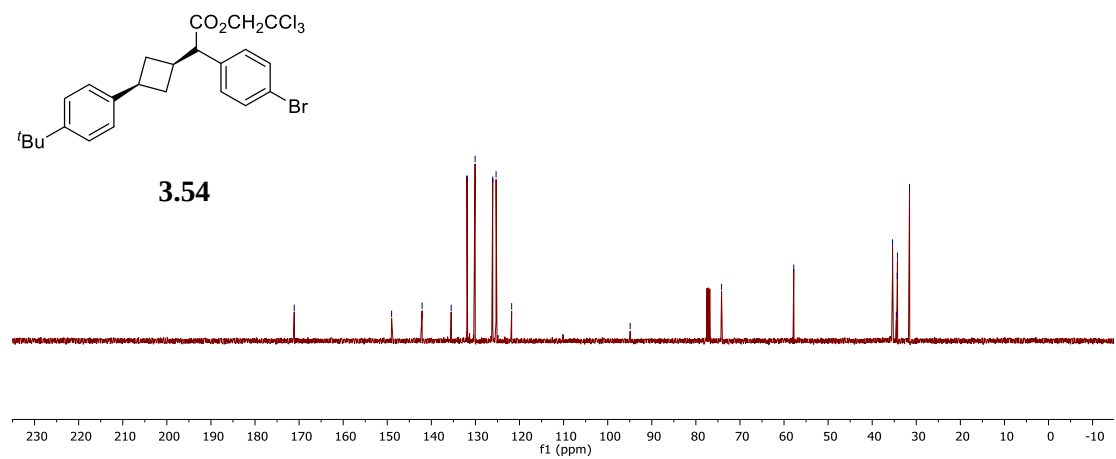
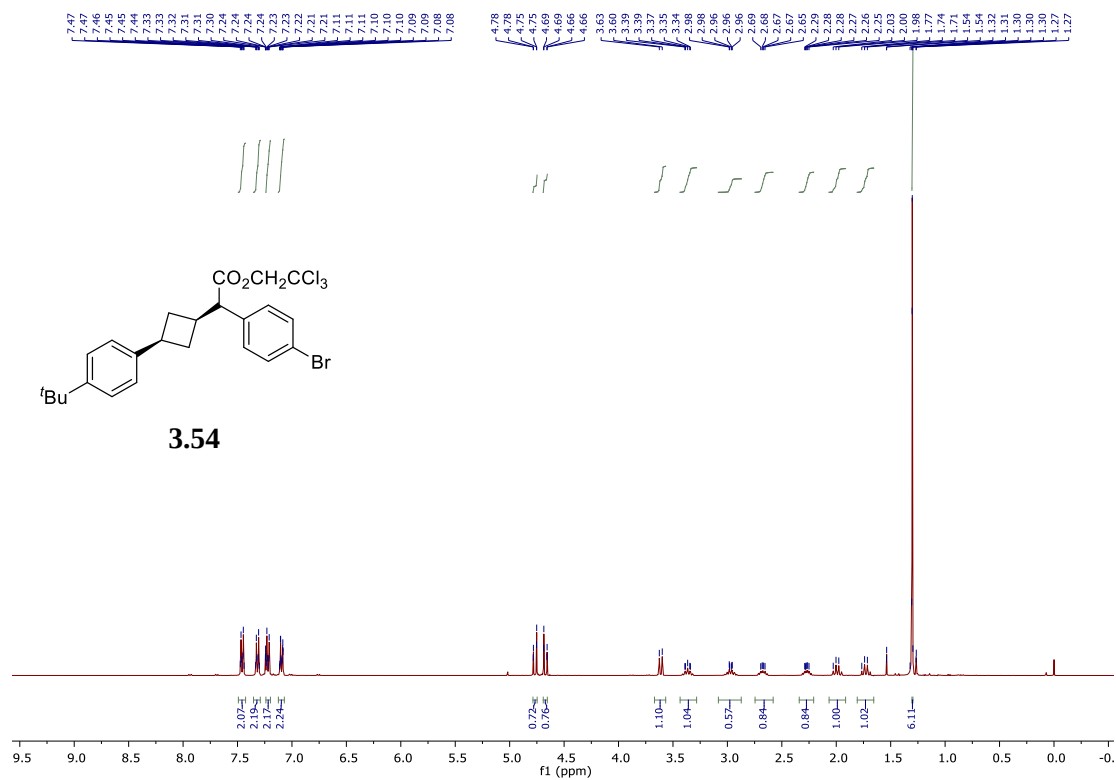


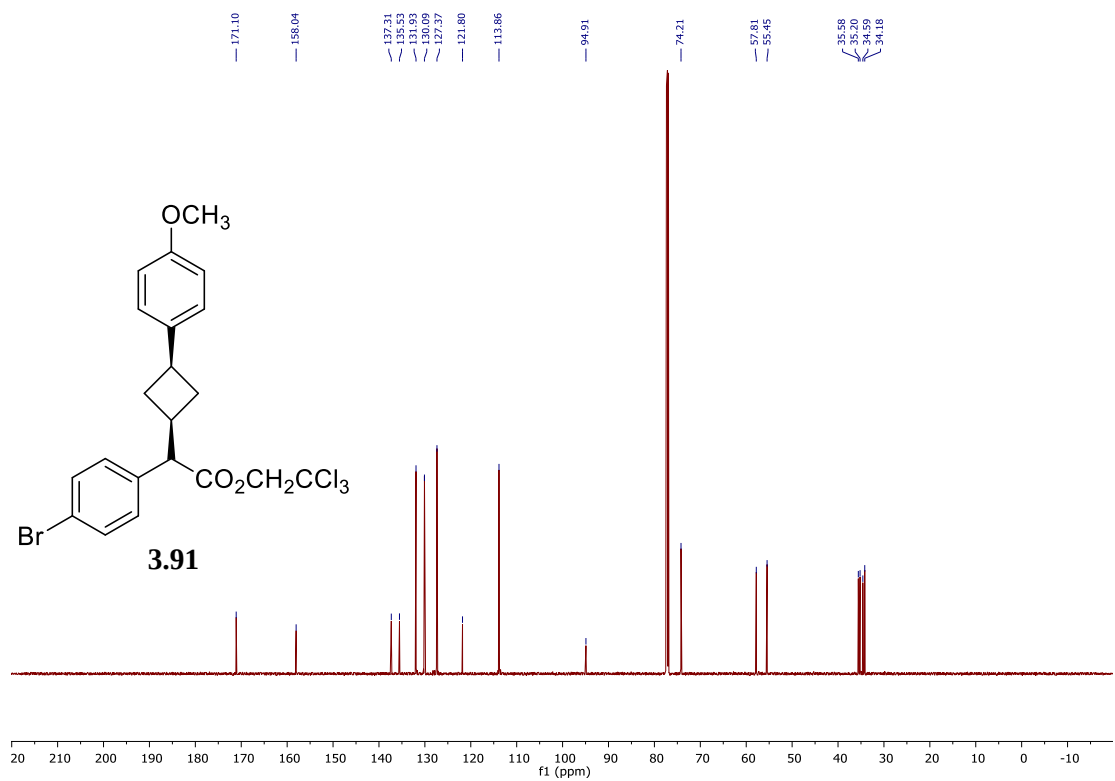
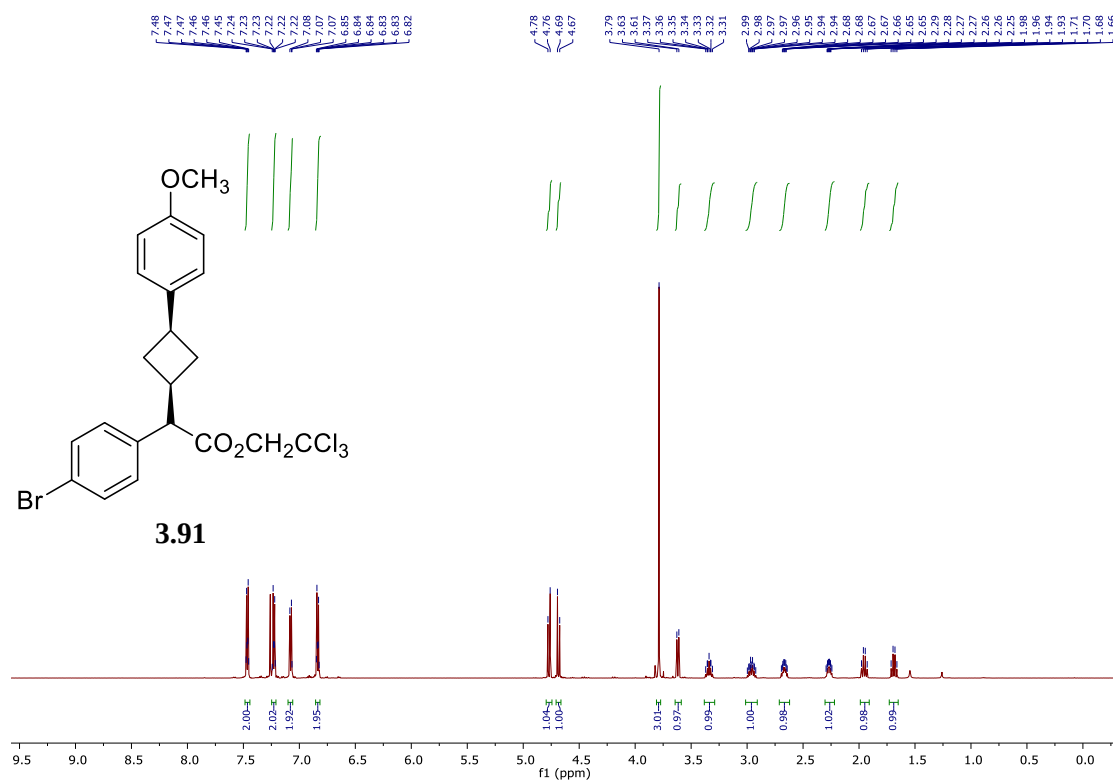


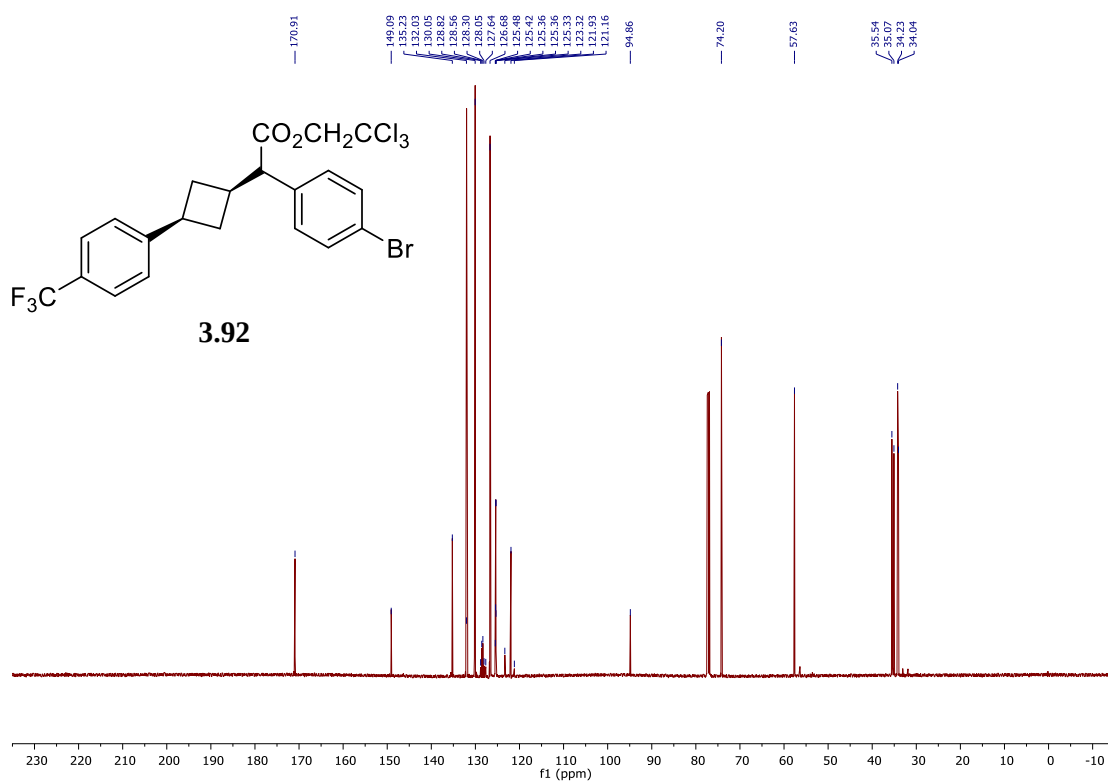


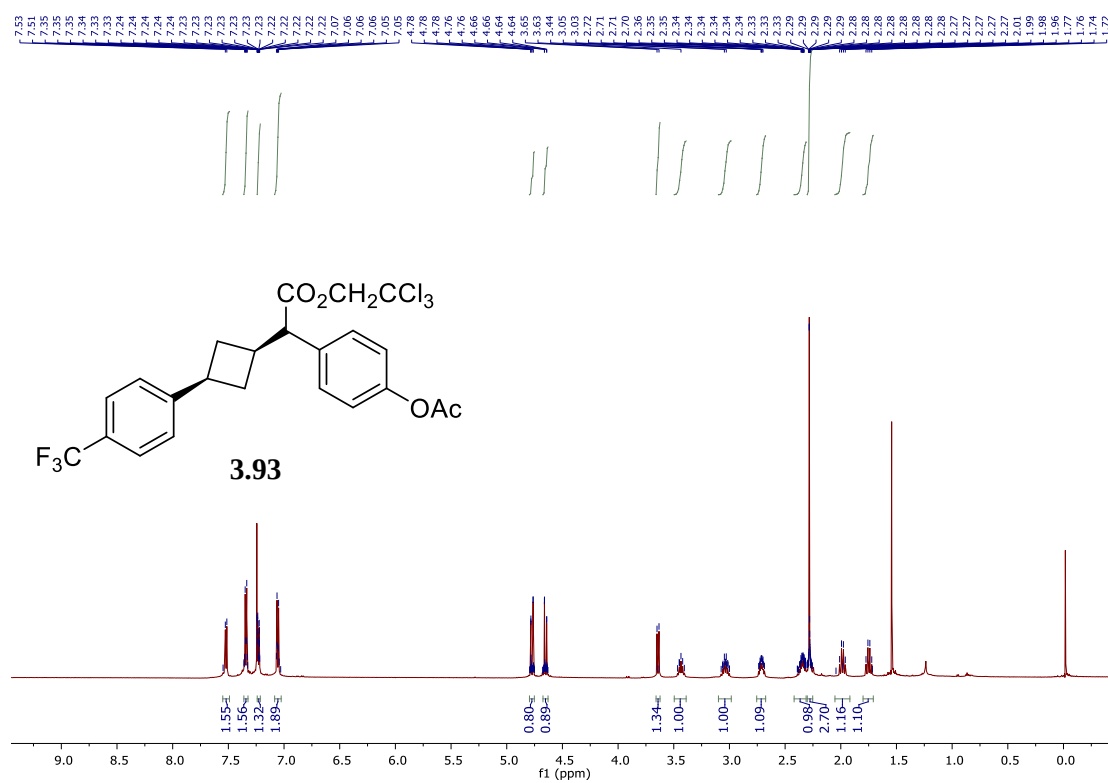
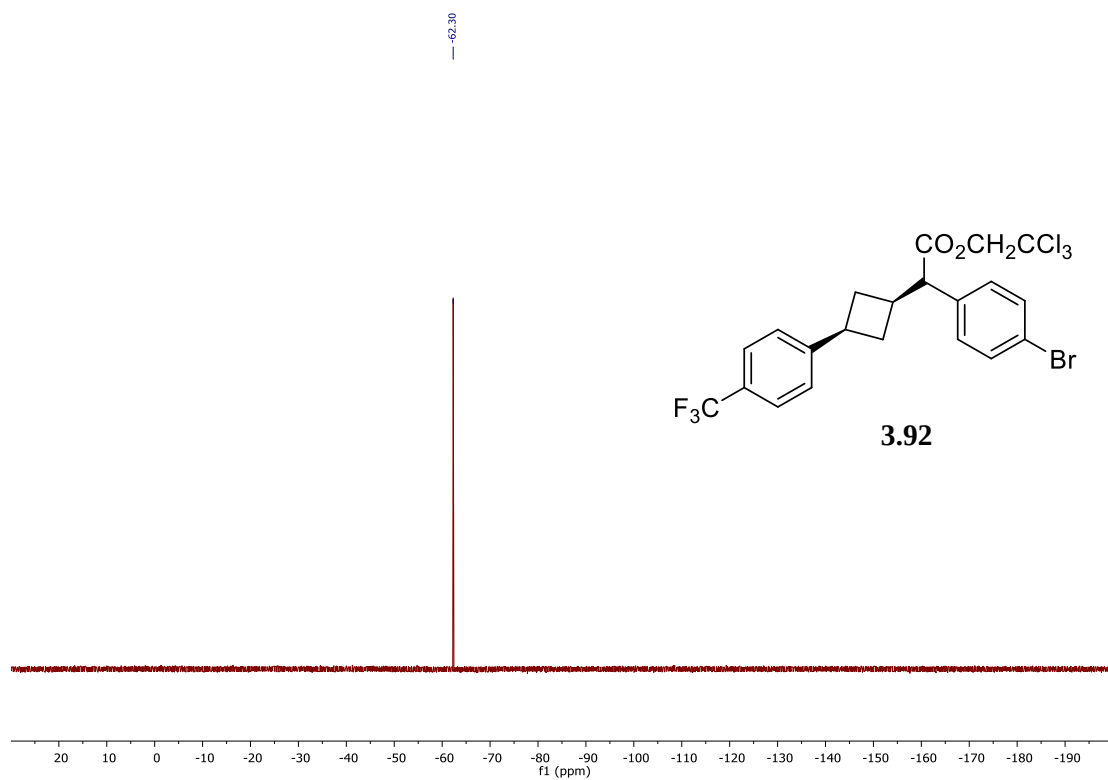


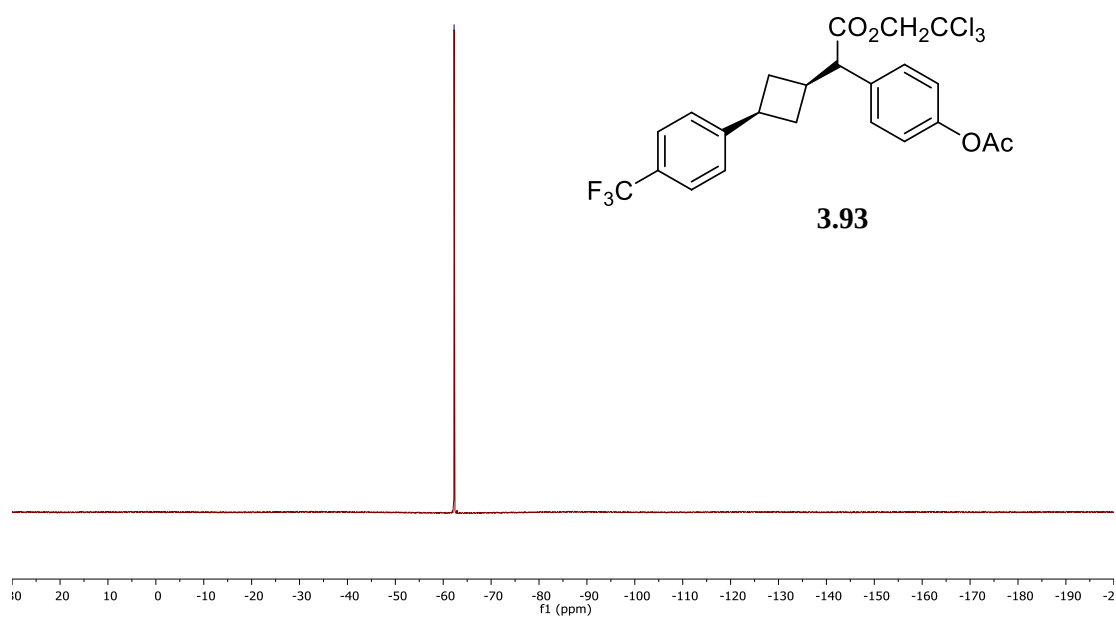
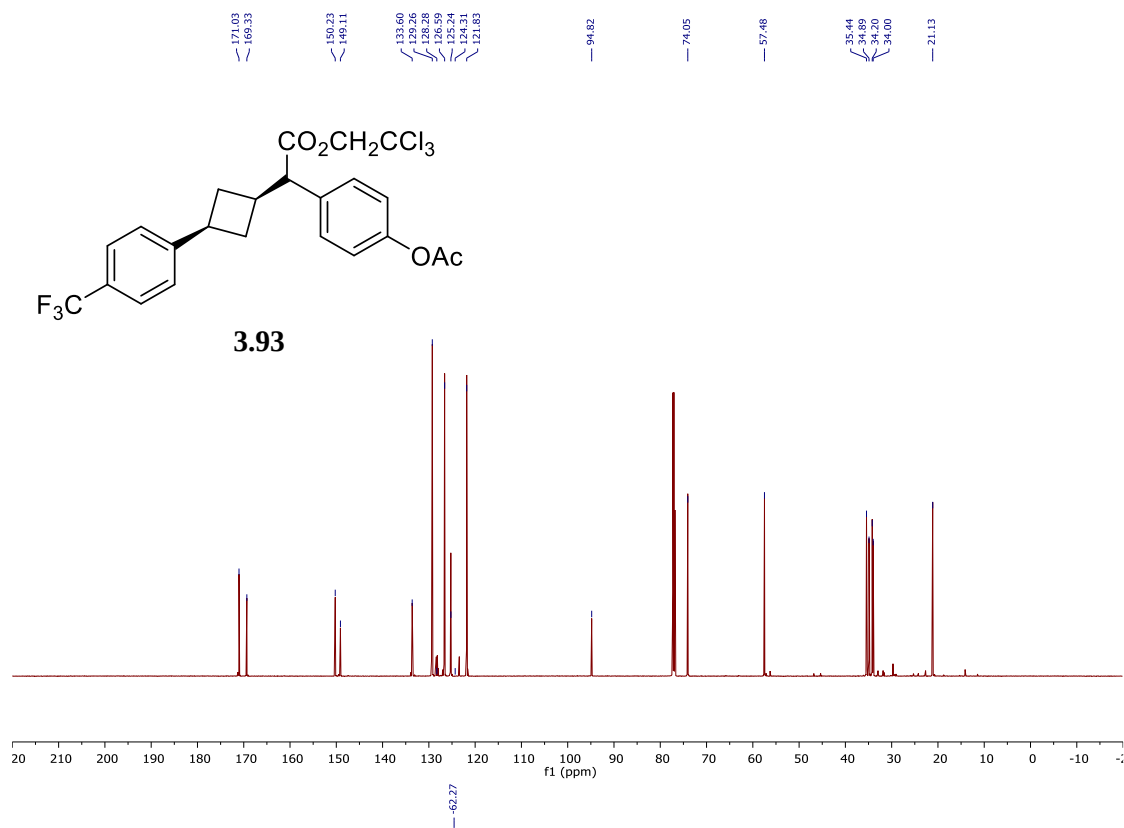


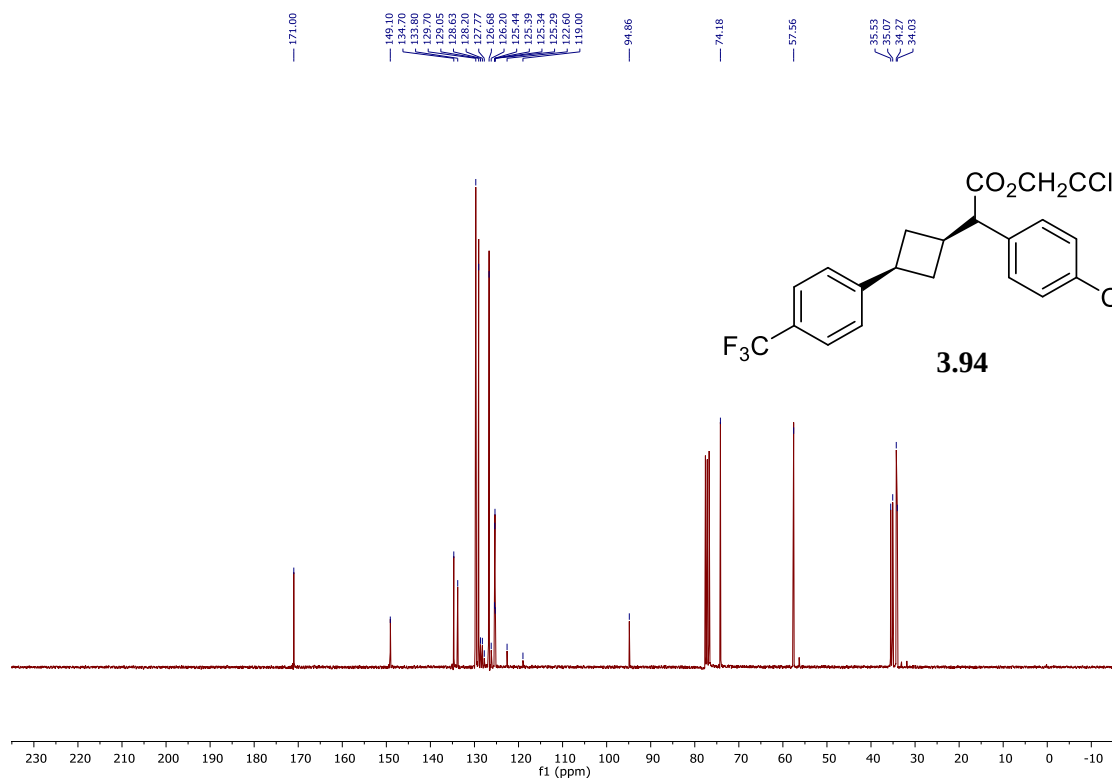


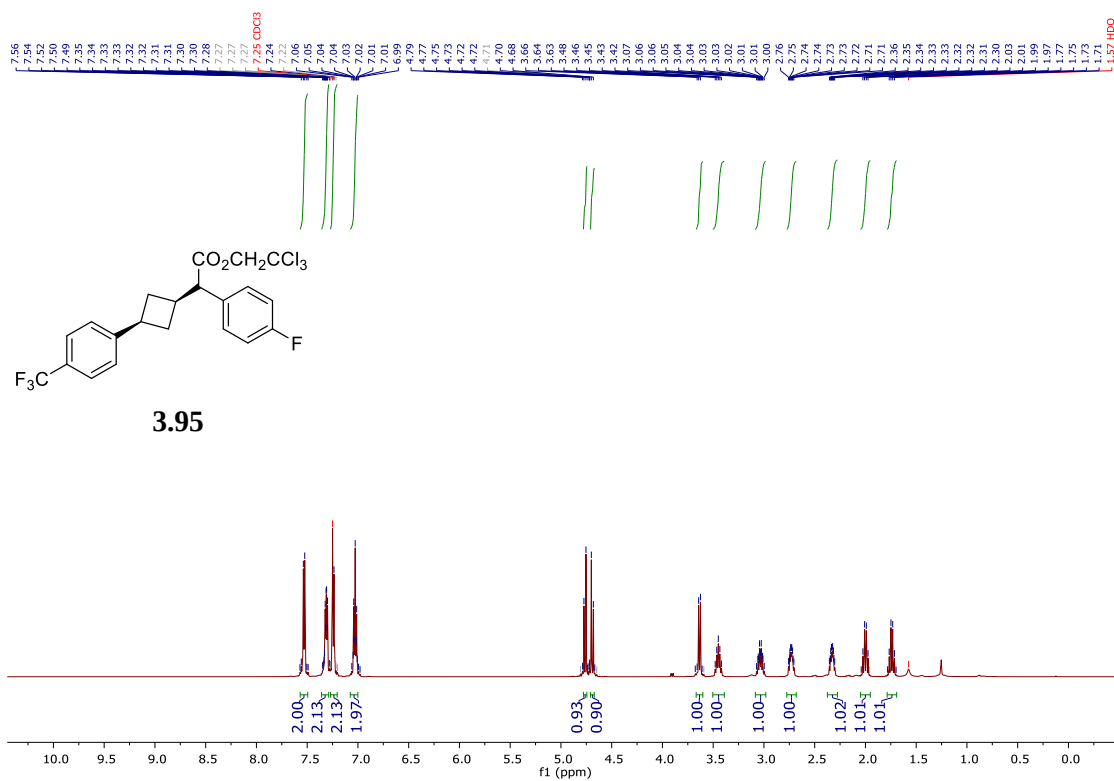
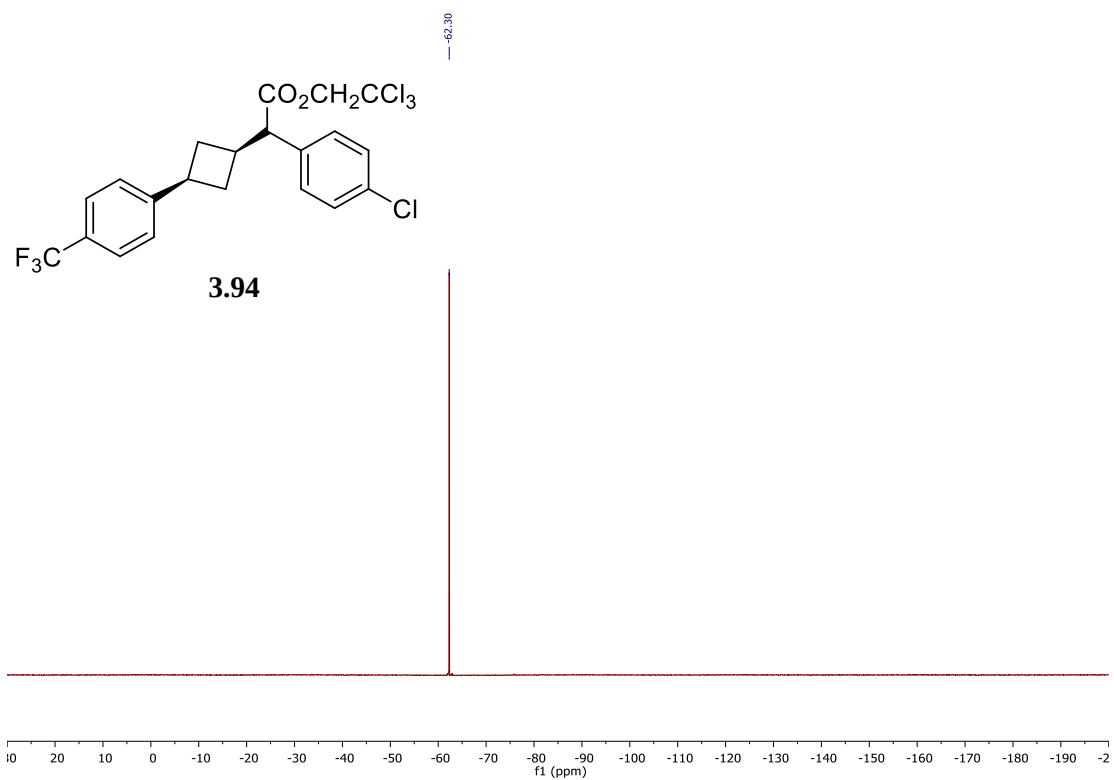


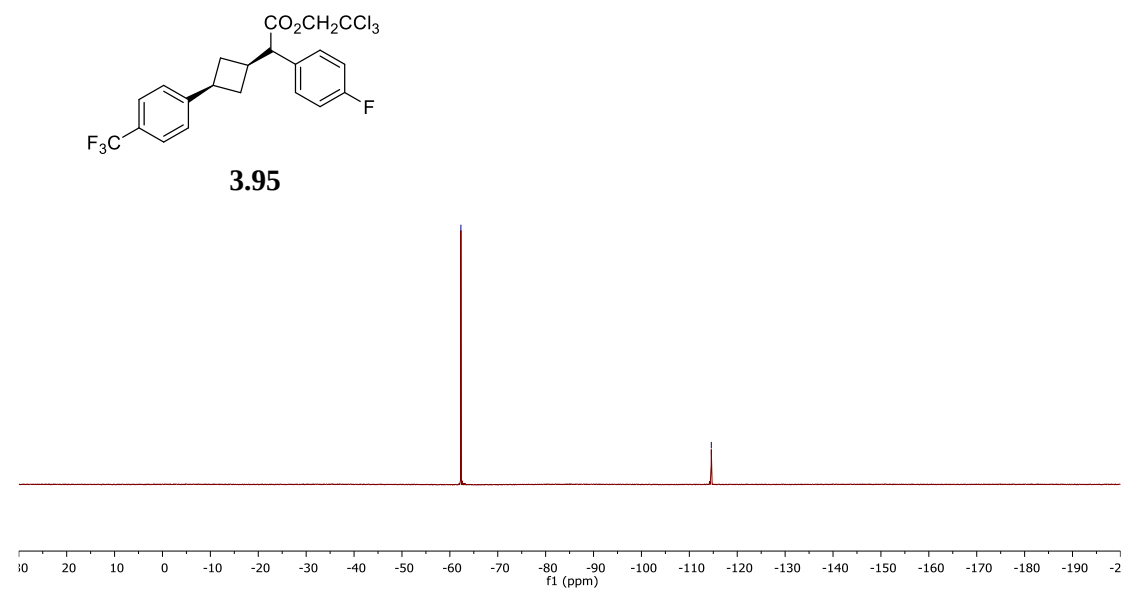
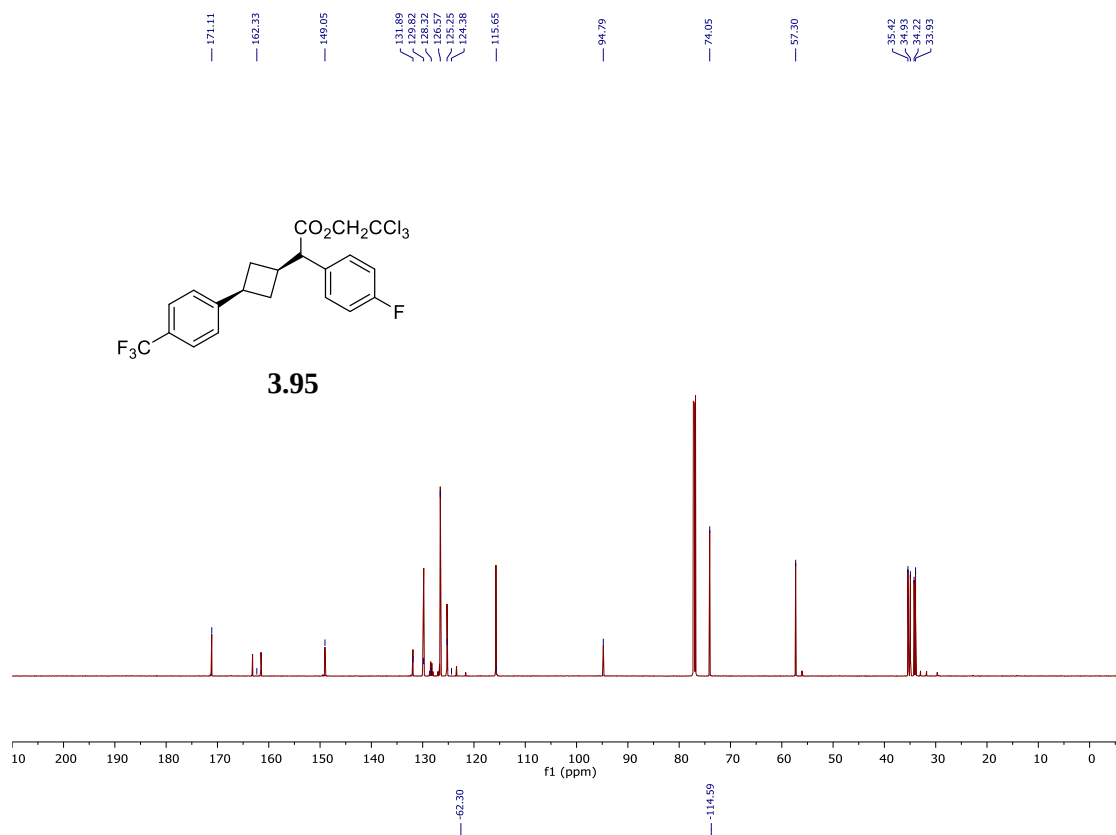


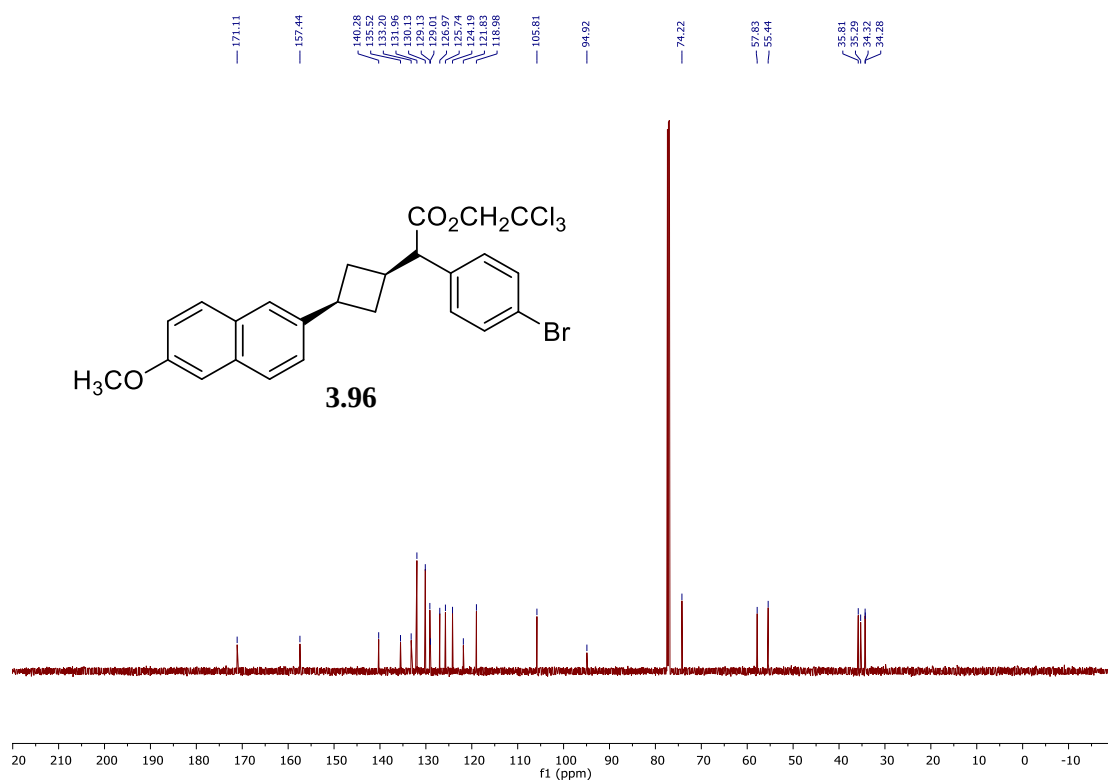
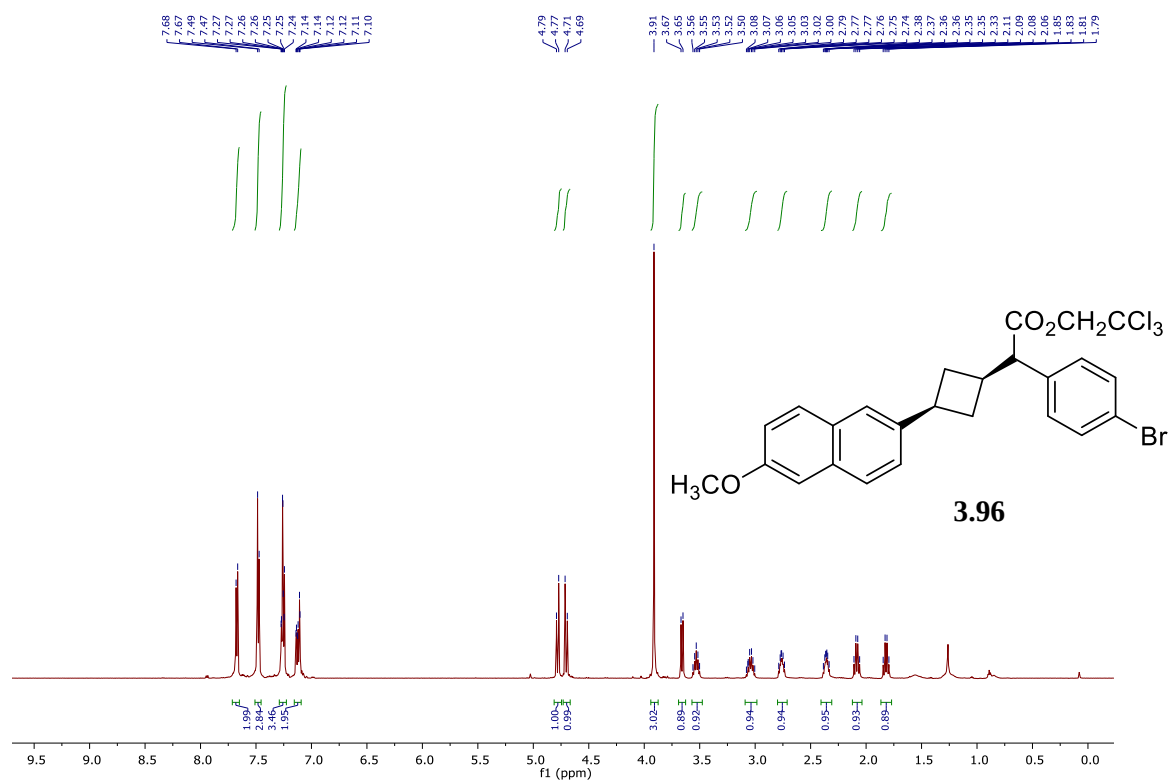


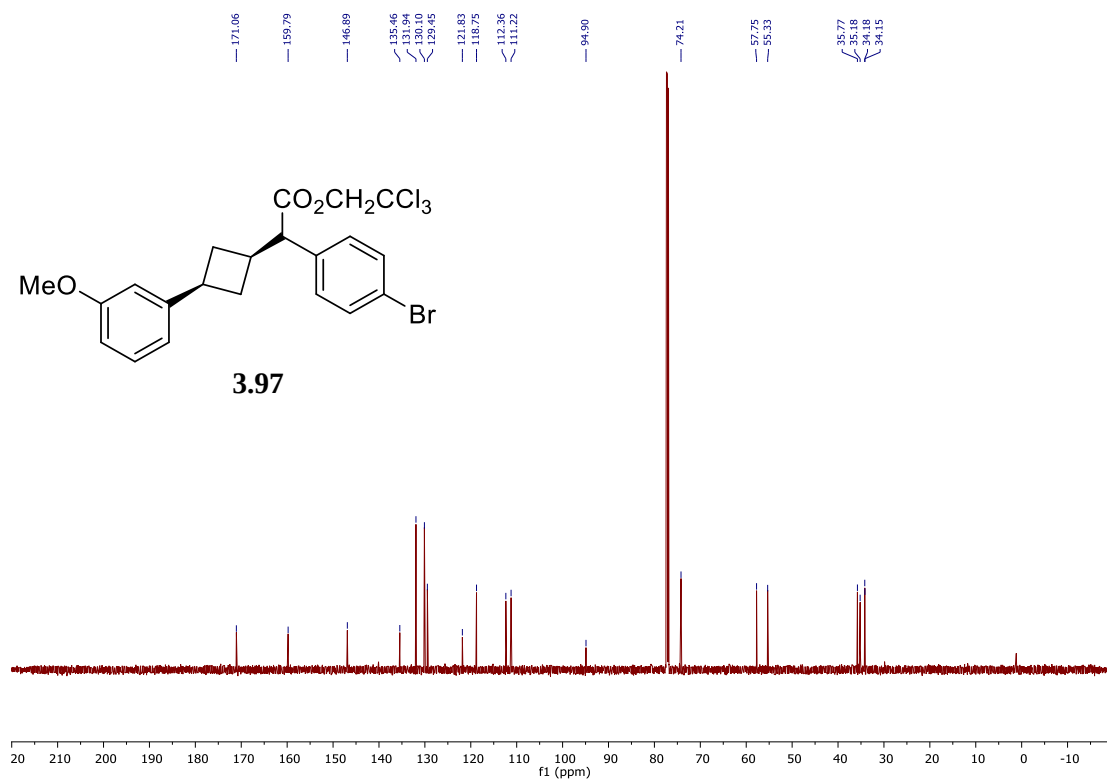
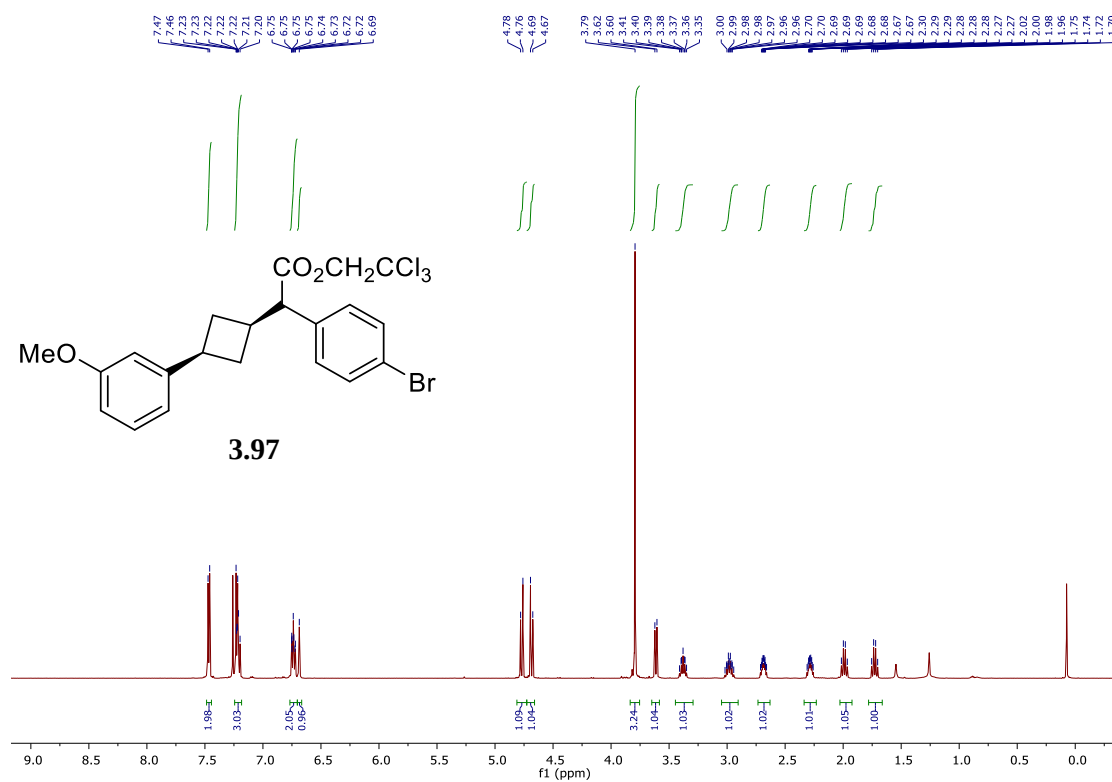


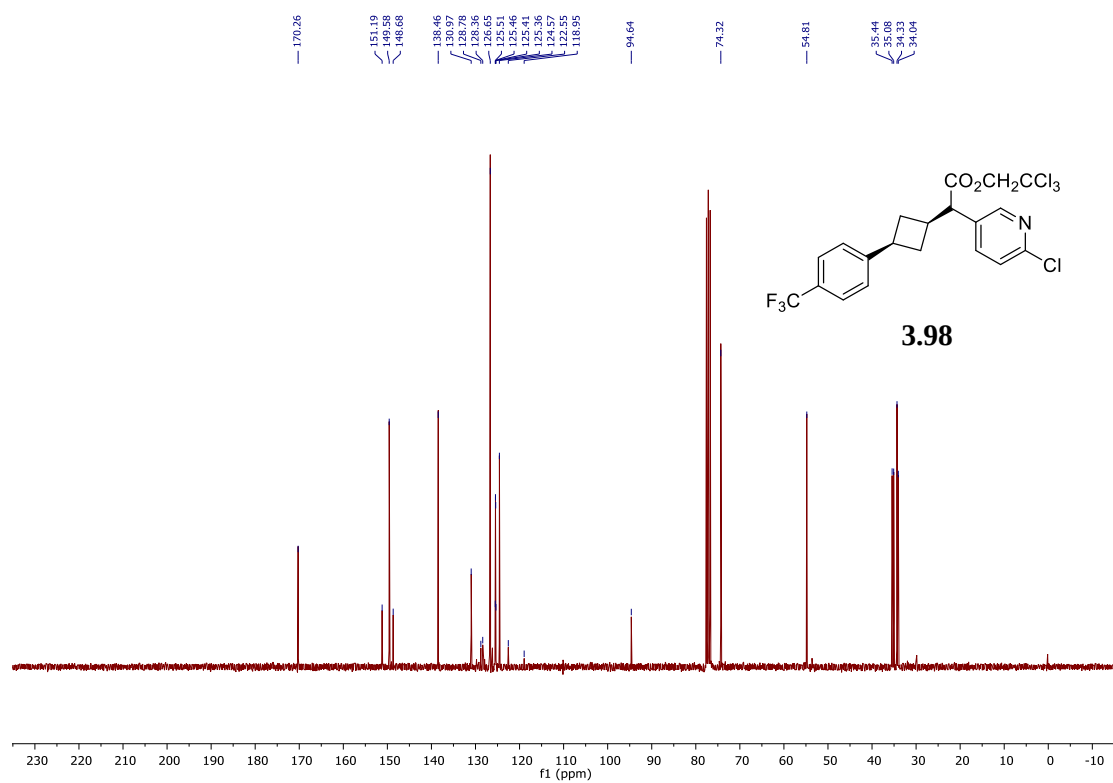
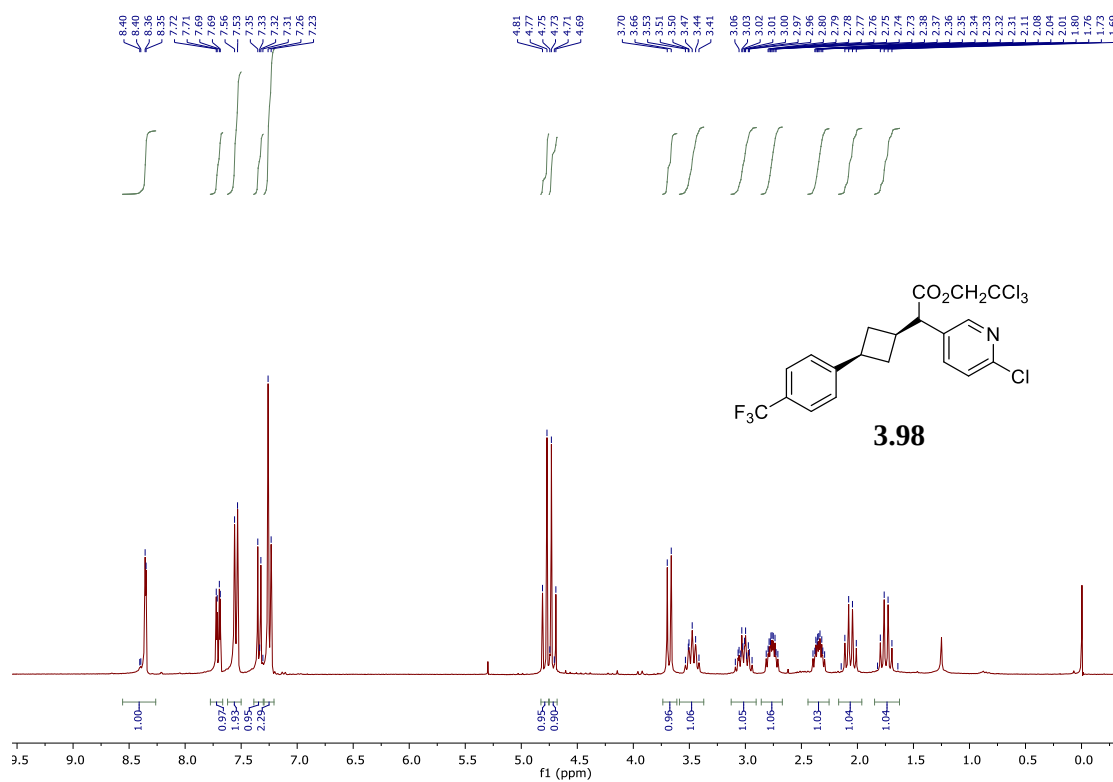


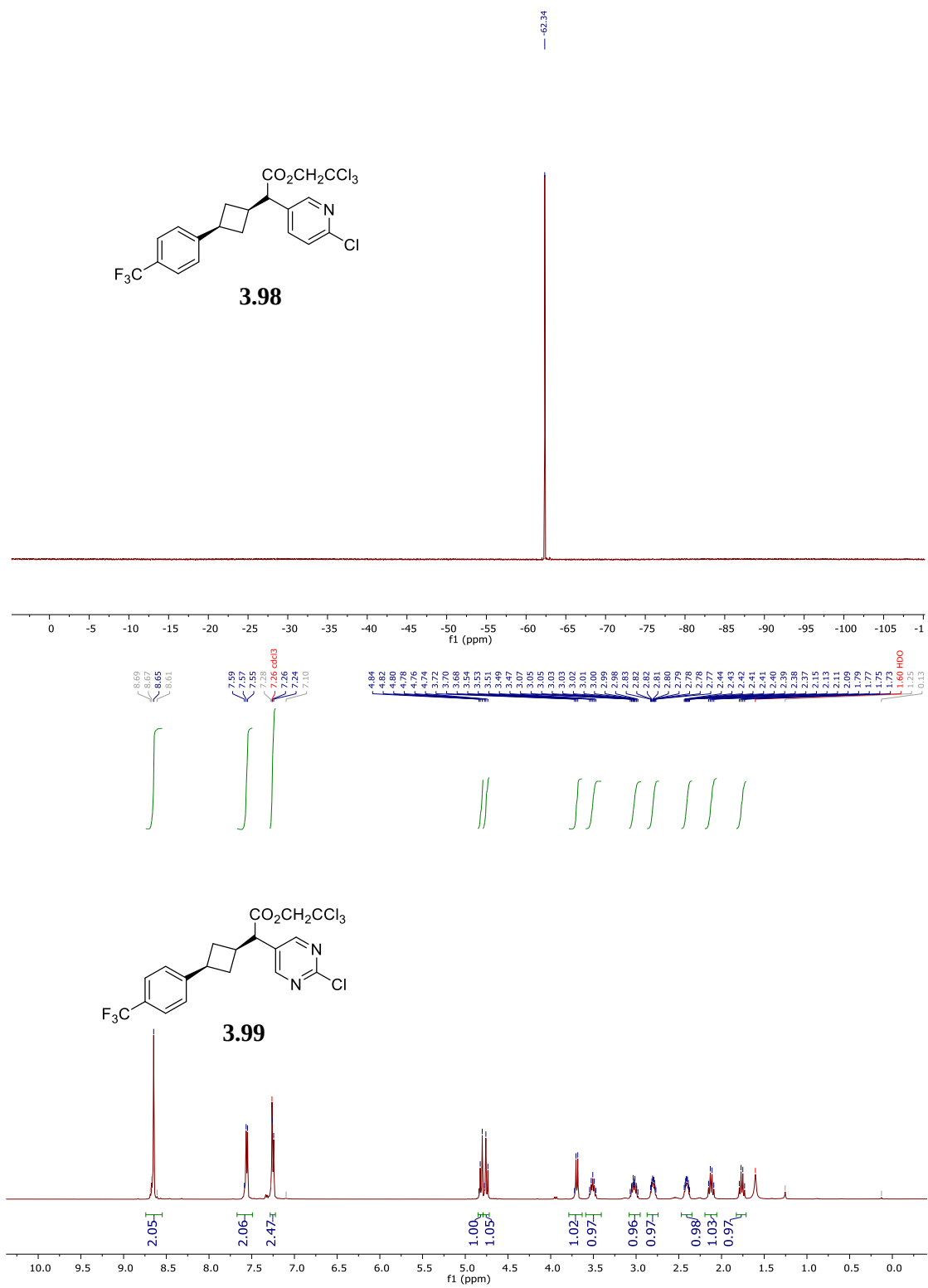


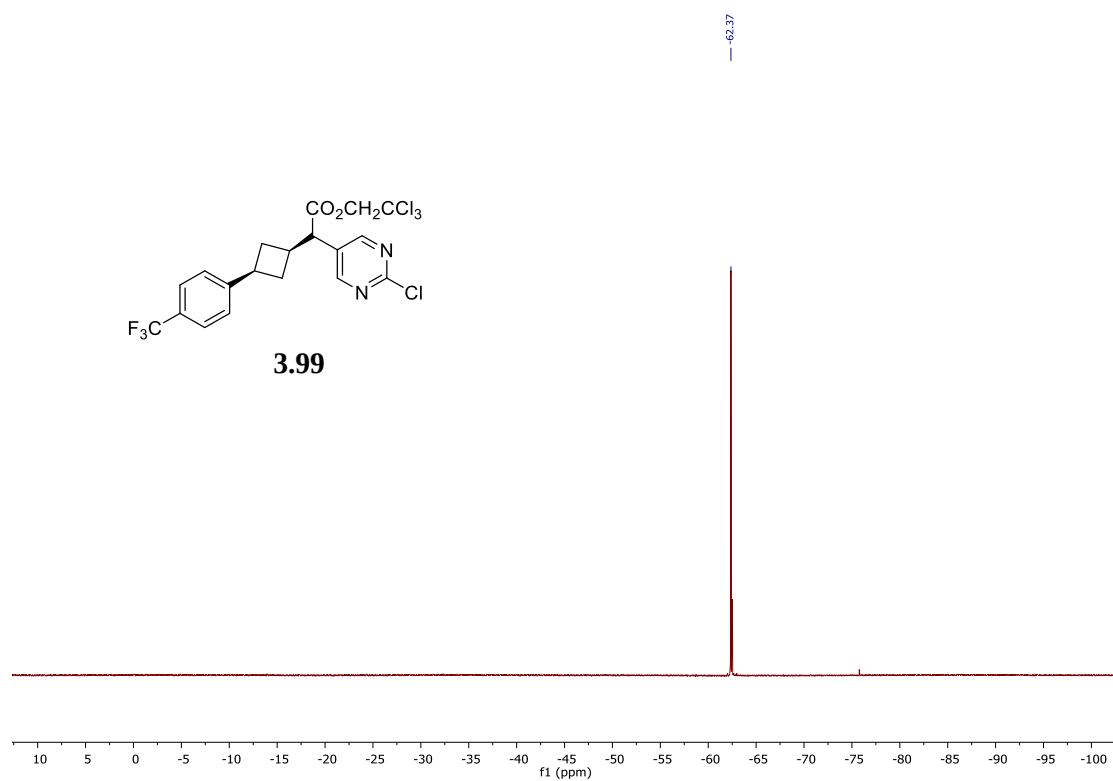
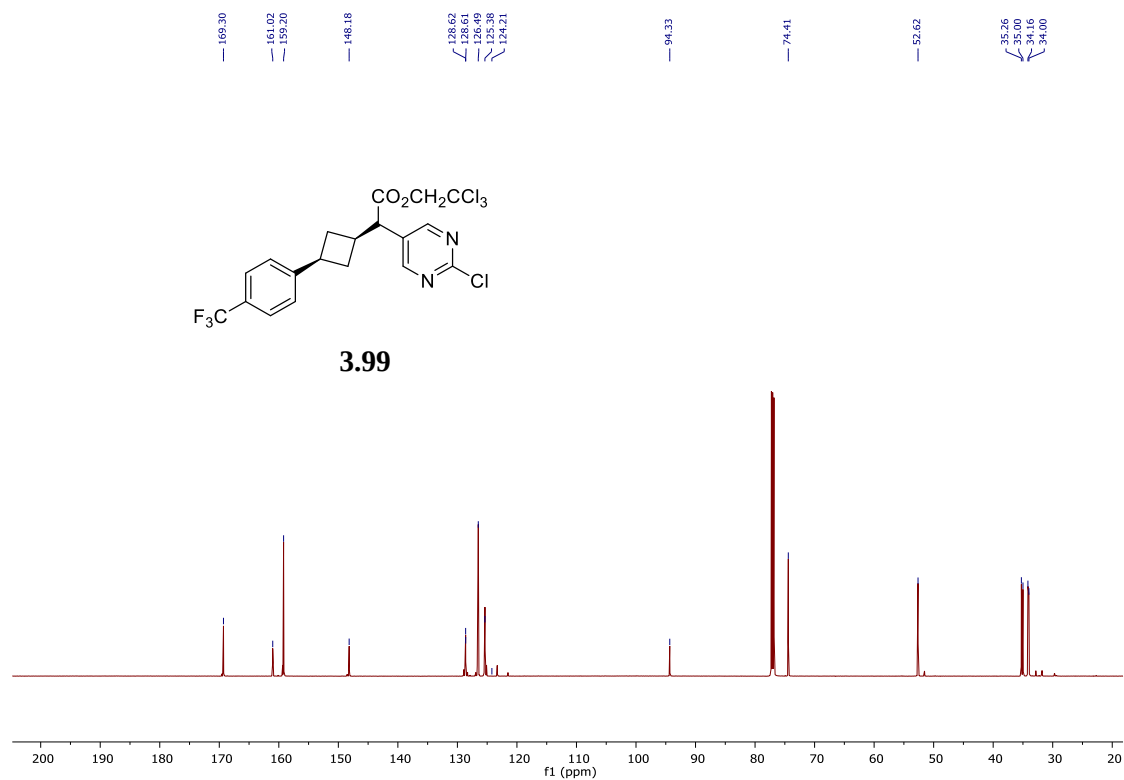


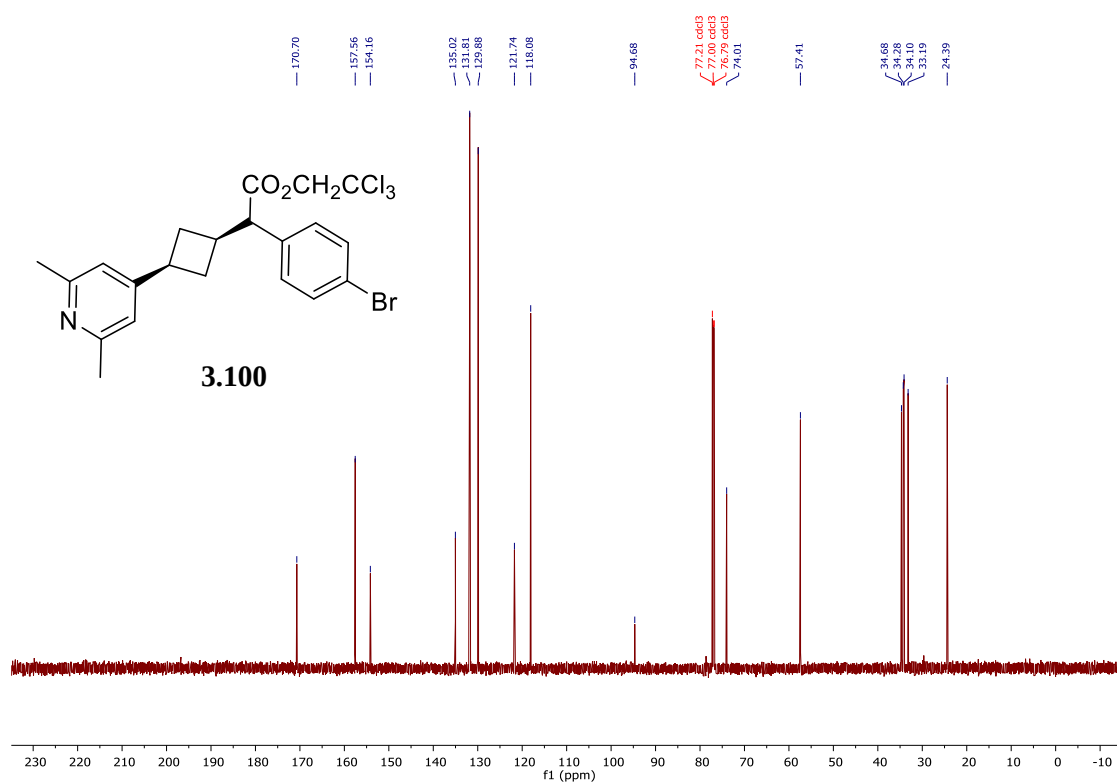
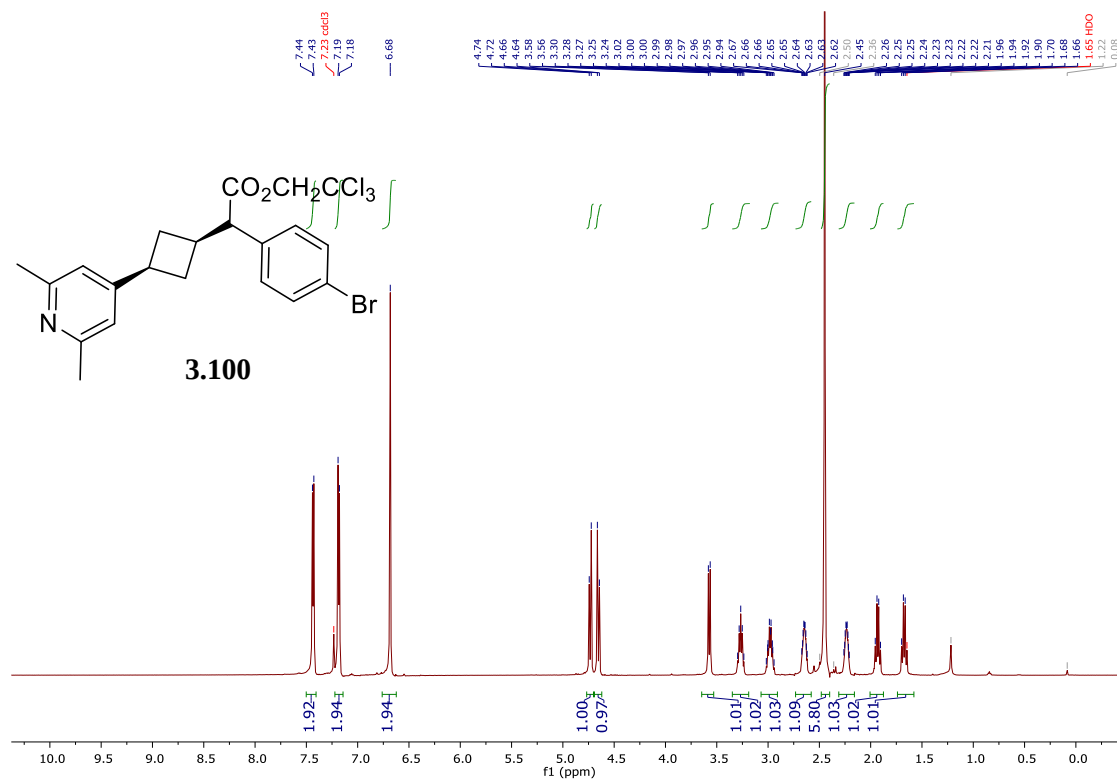


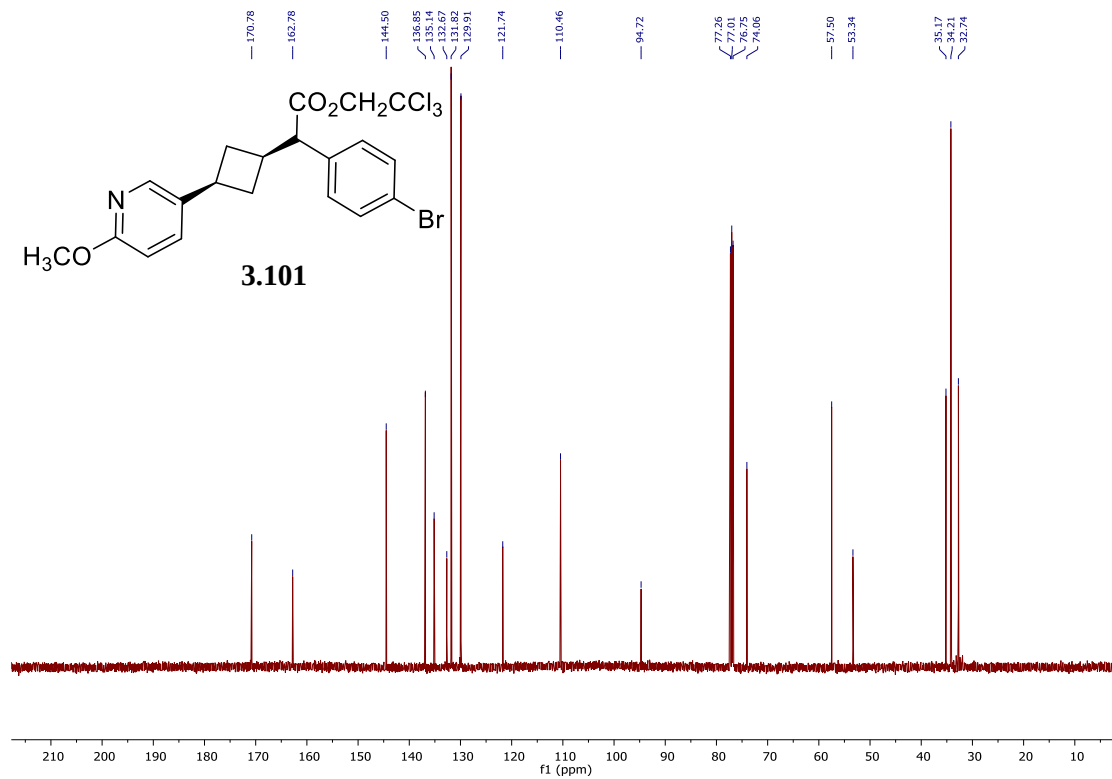
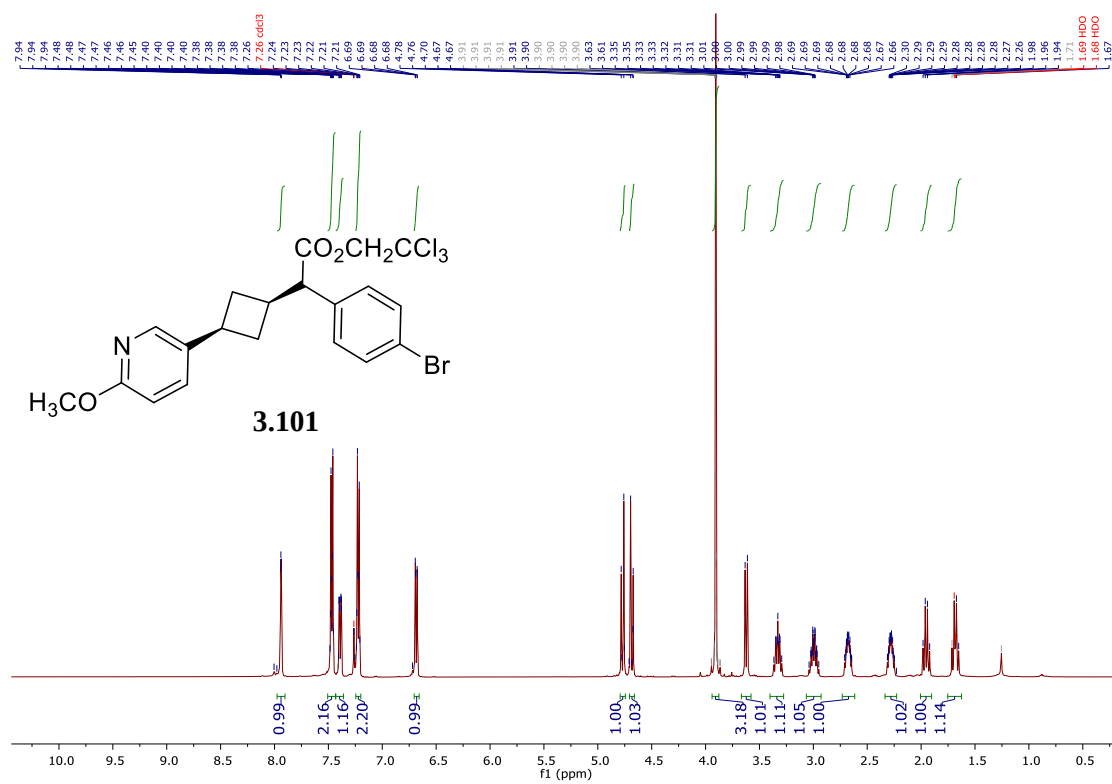


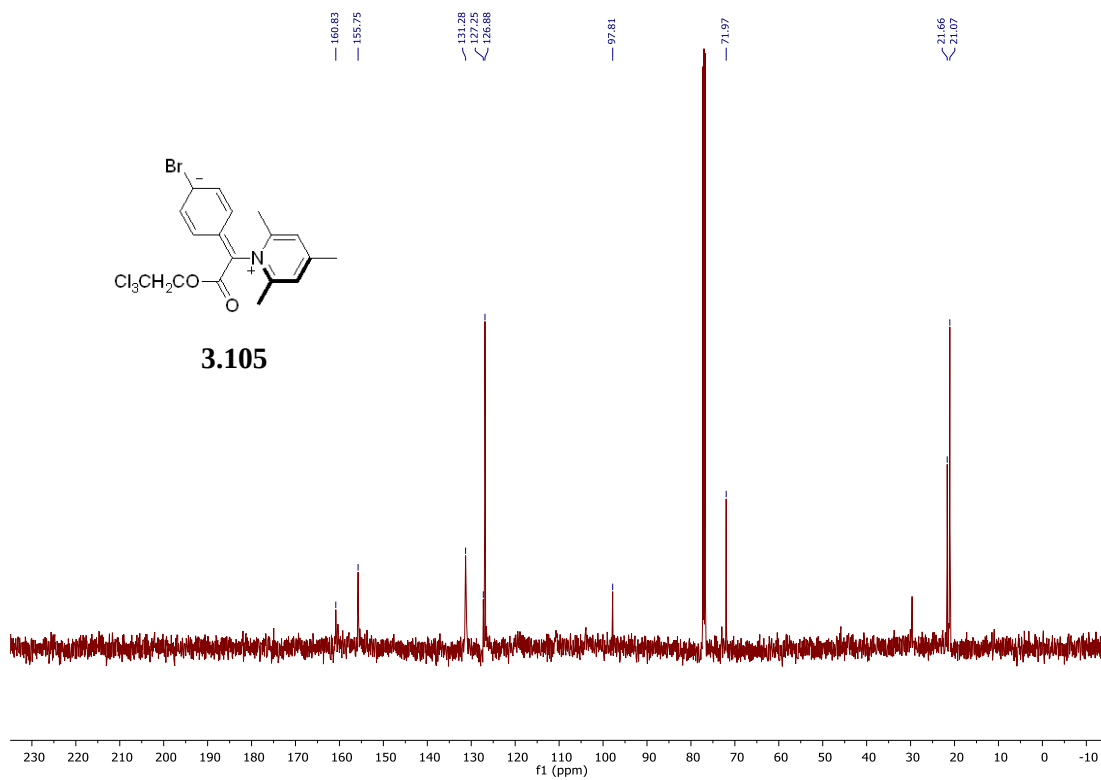
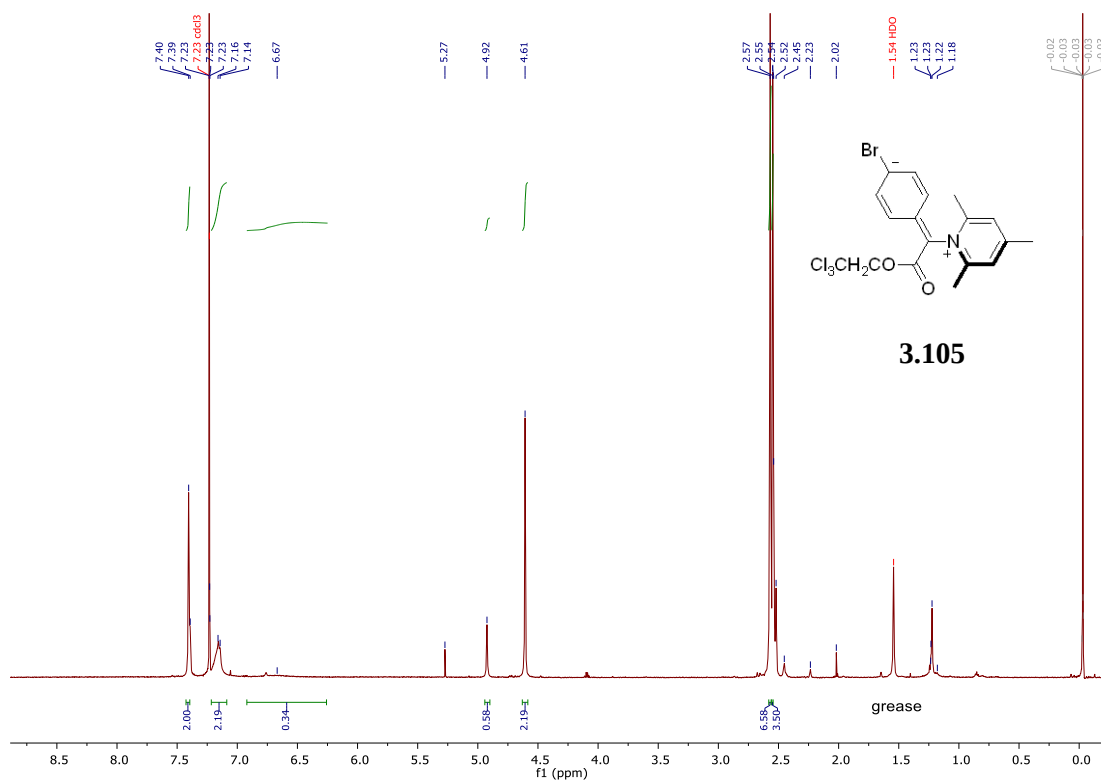




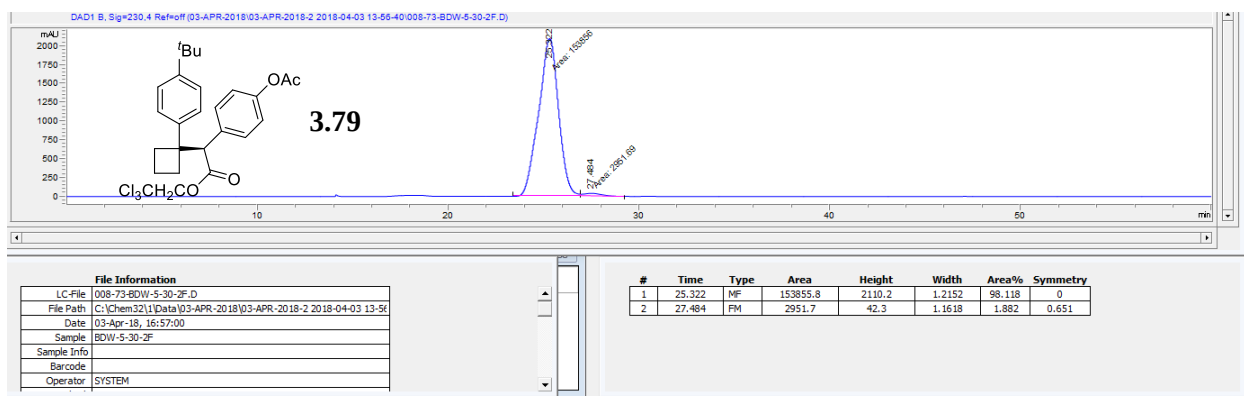
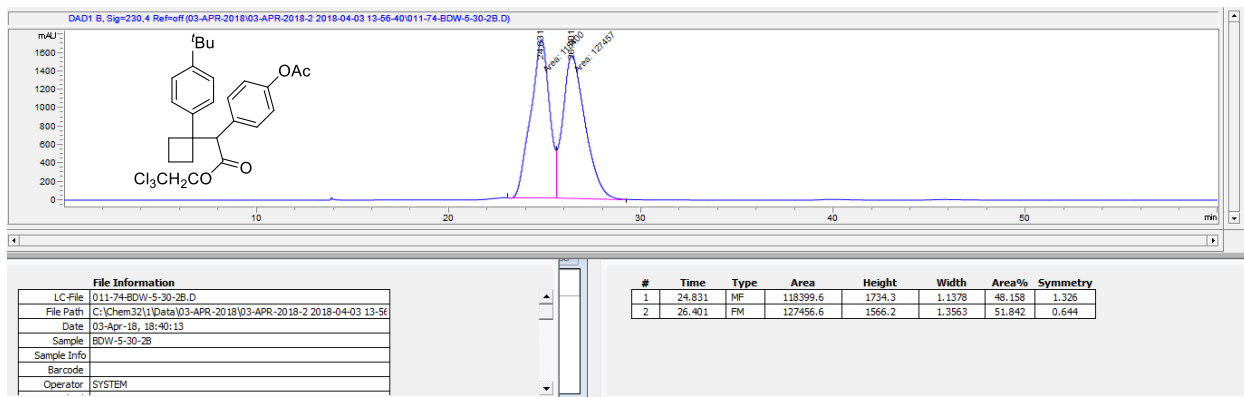


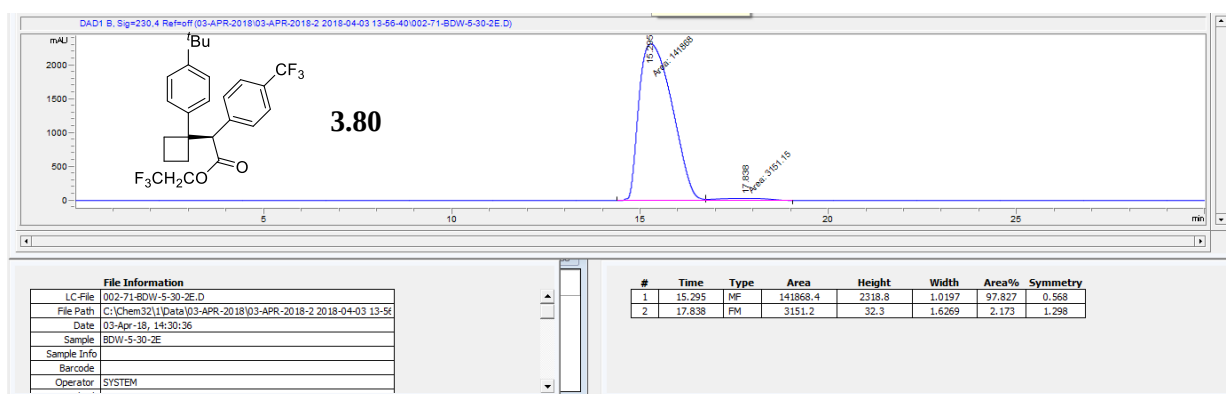
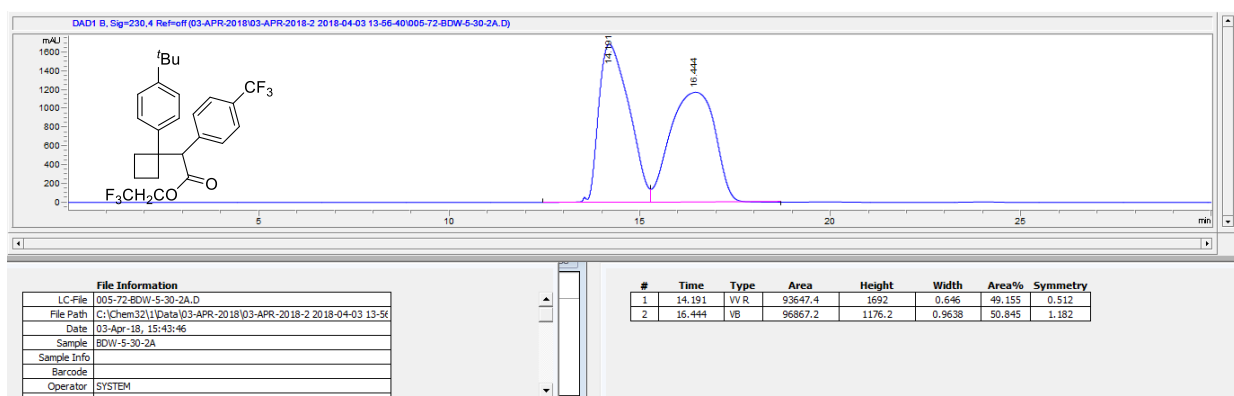


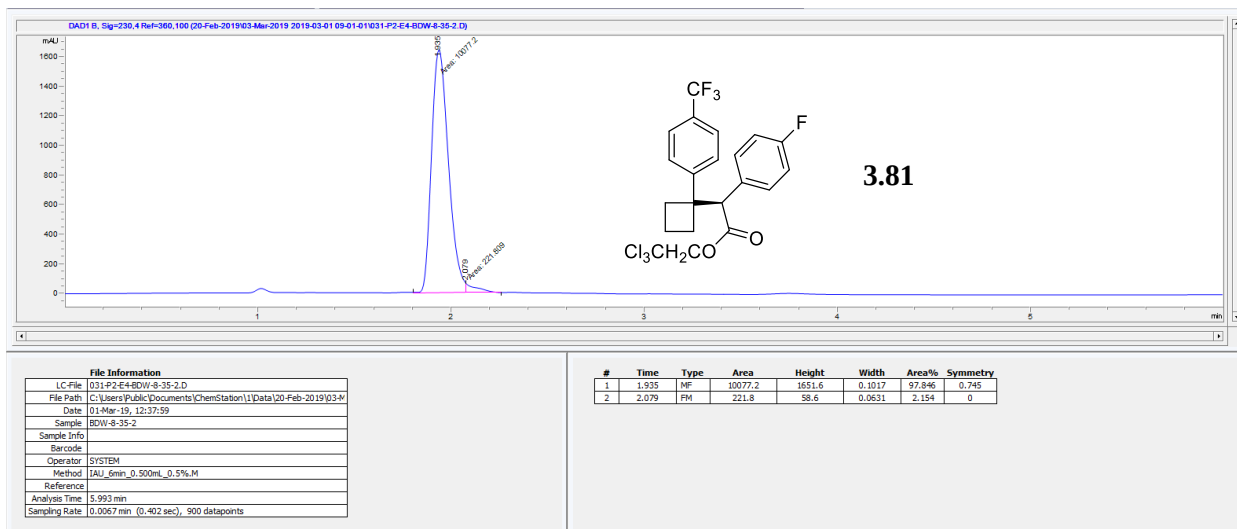
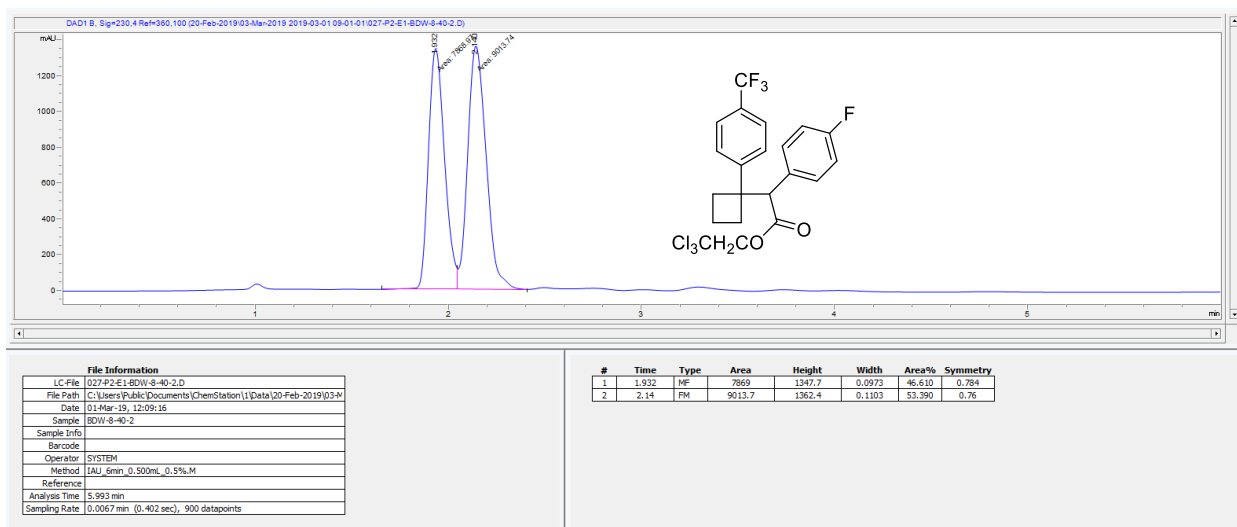


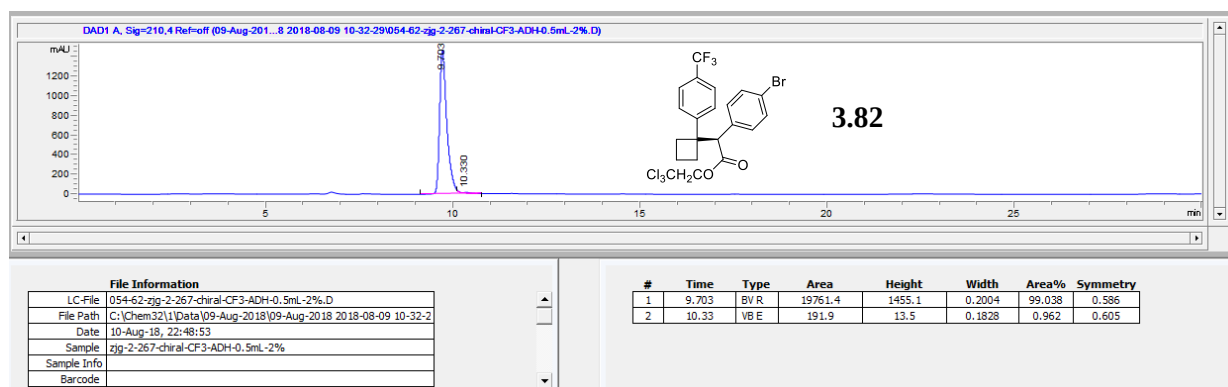
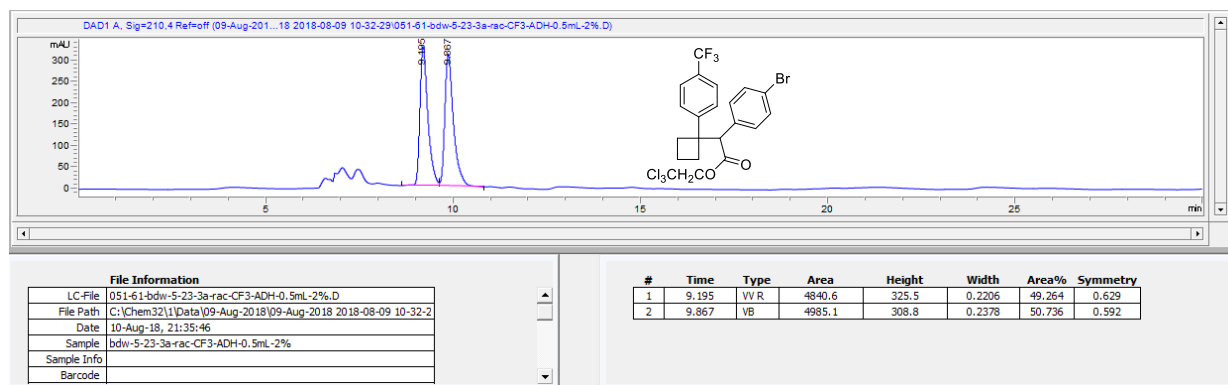


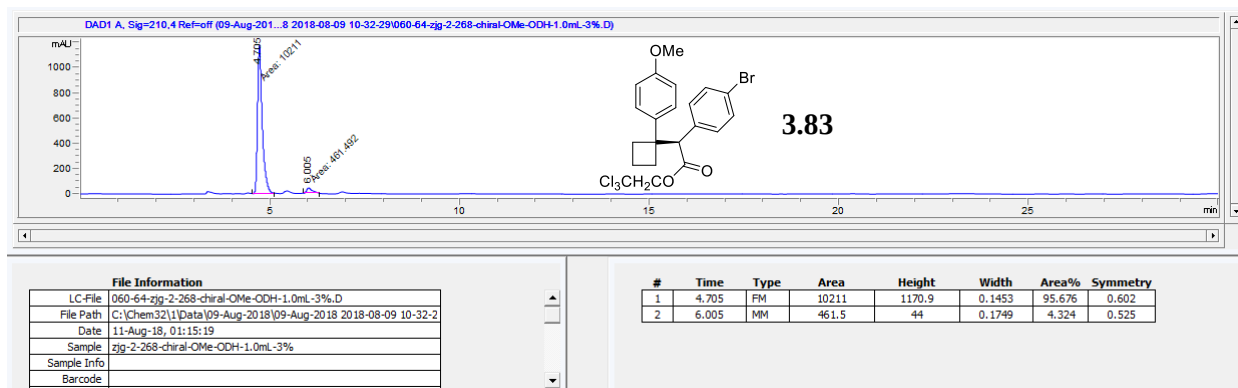
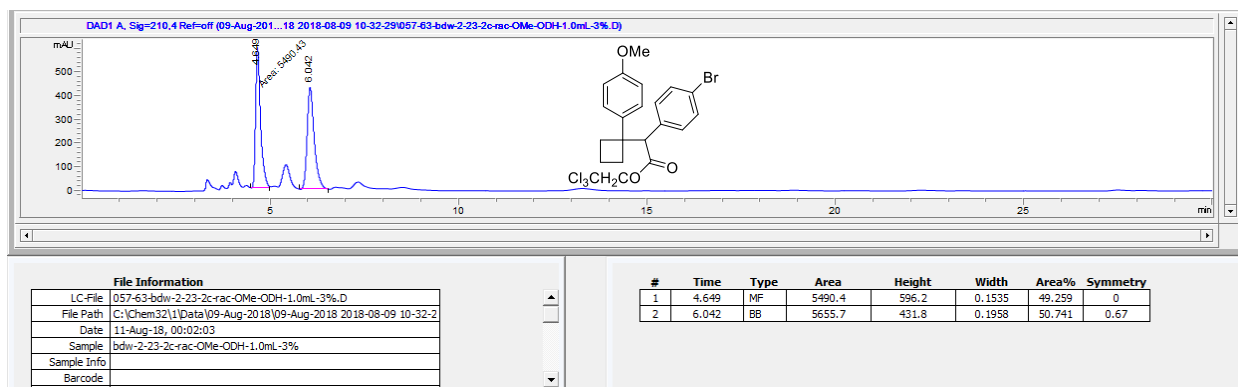
S.3.11 Chiral HPLC Traces

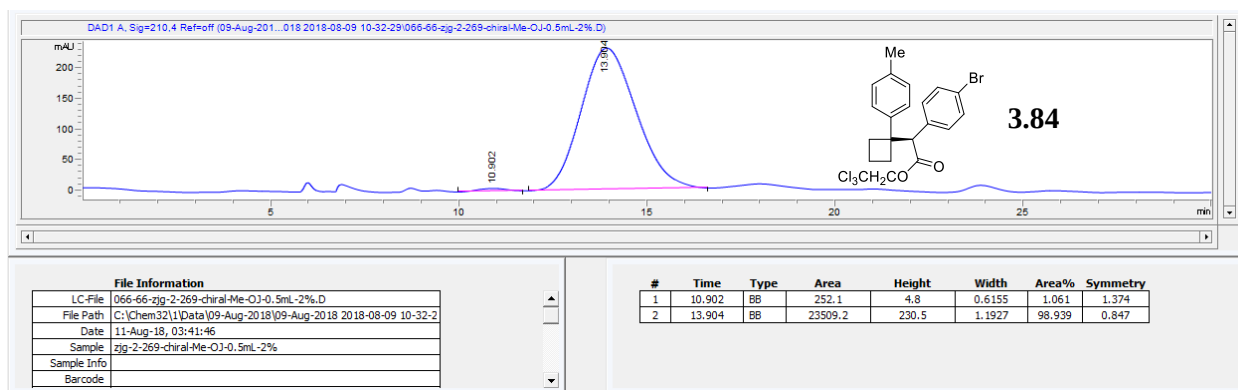
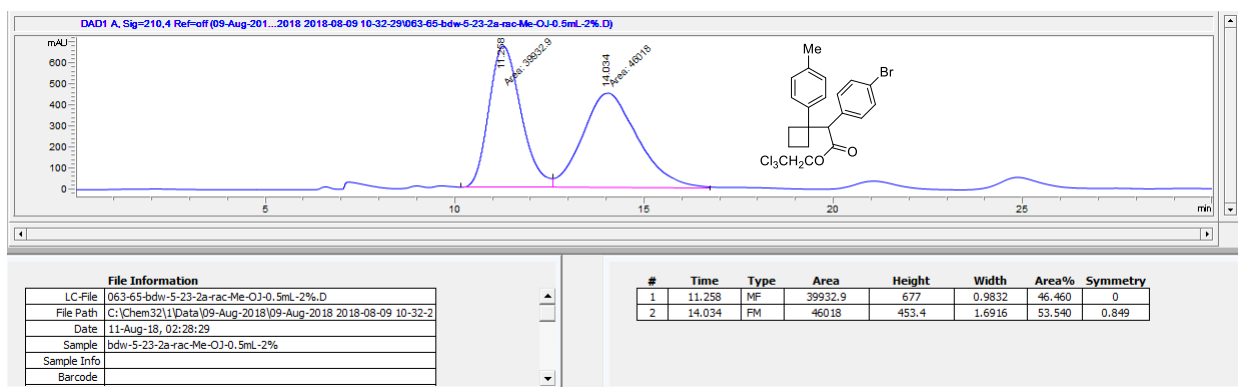


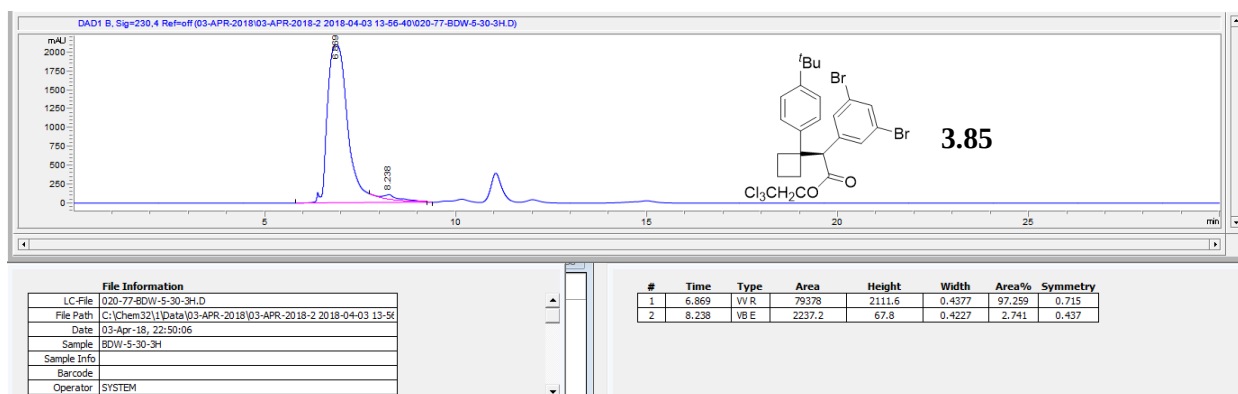
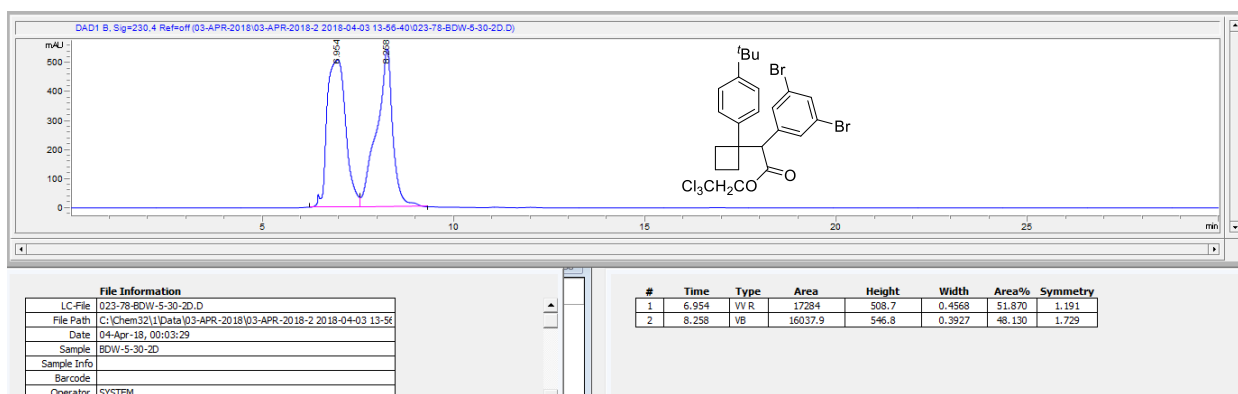


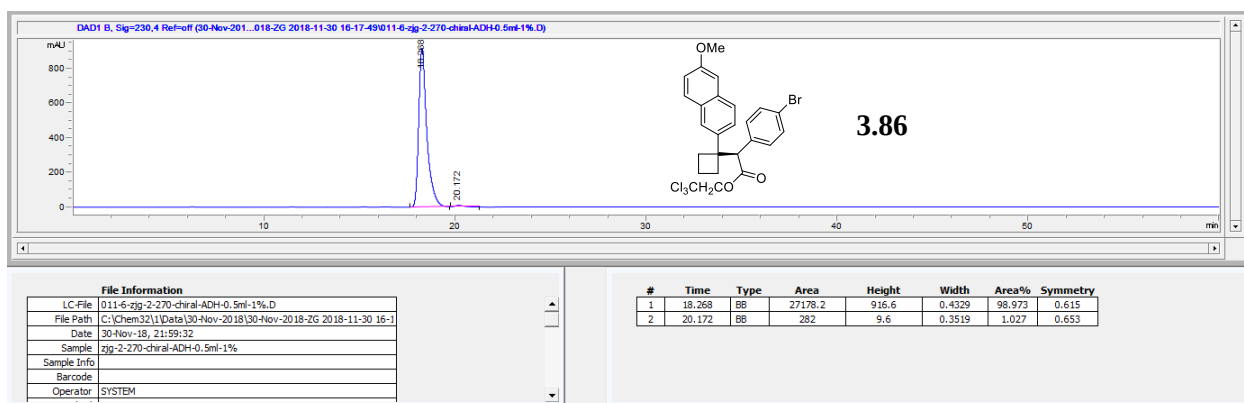
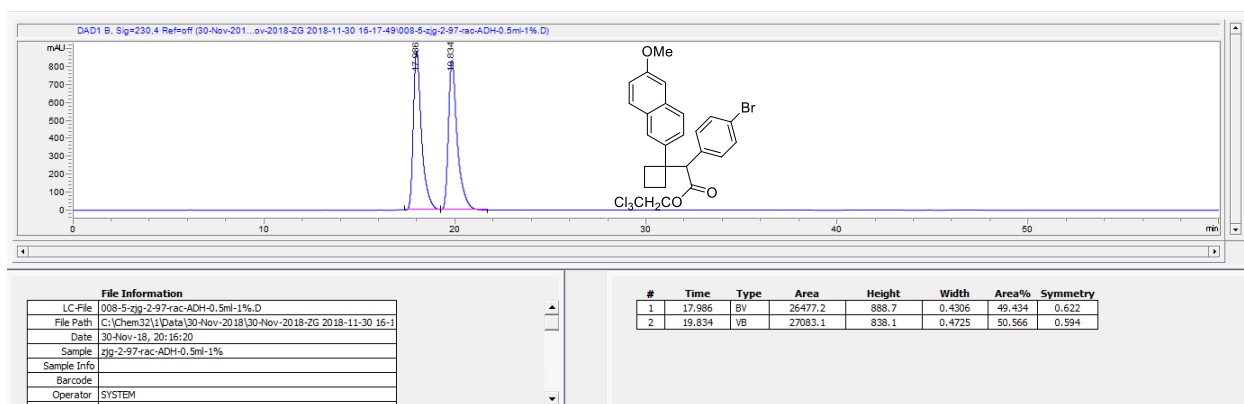


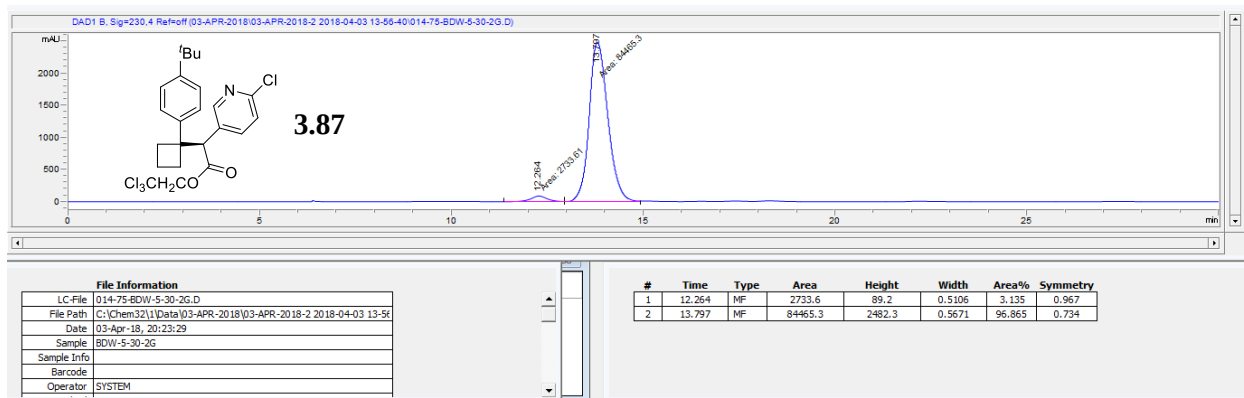
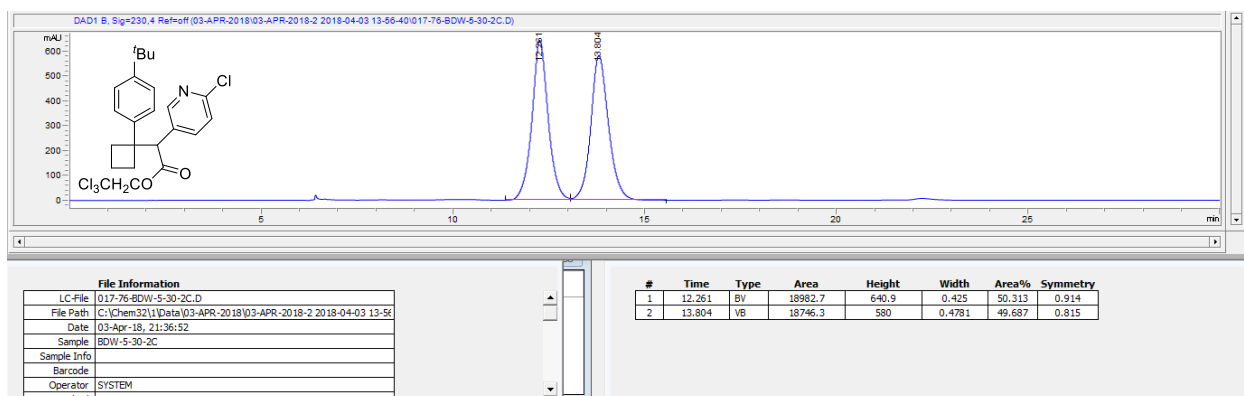


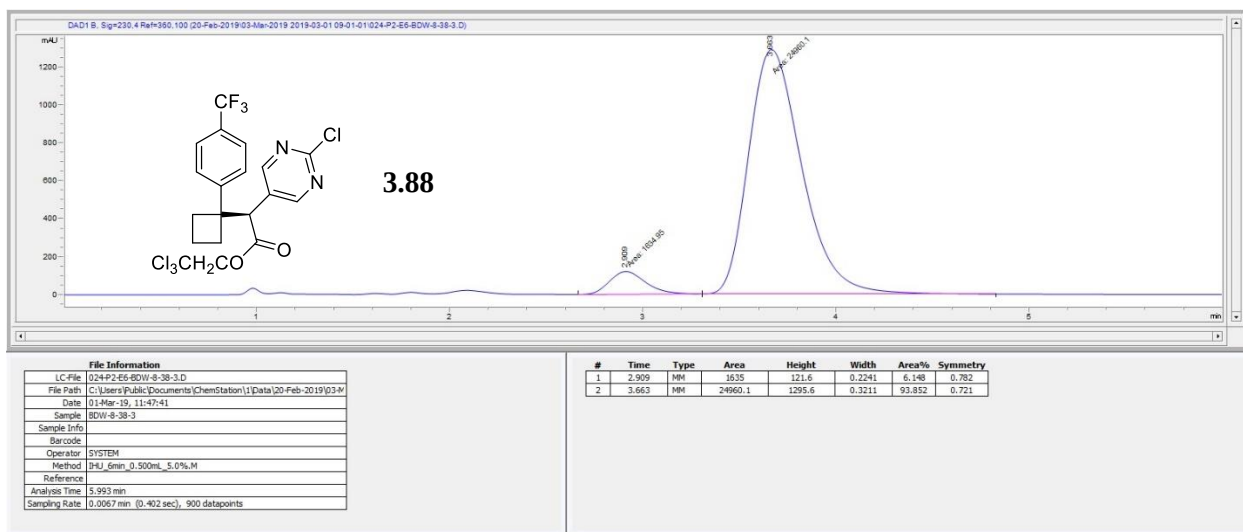
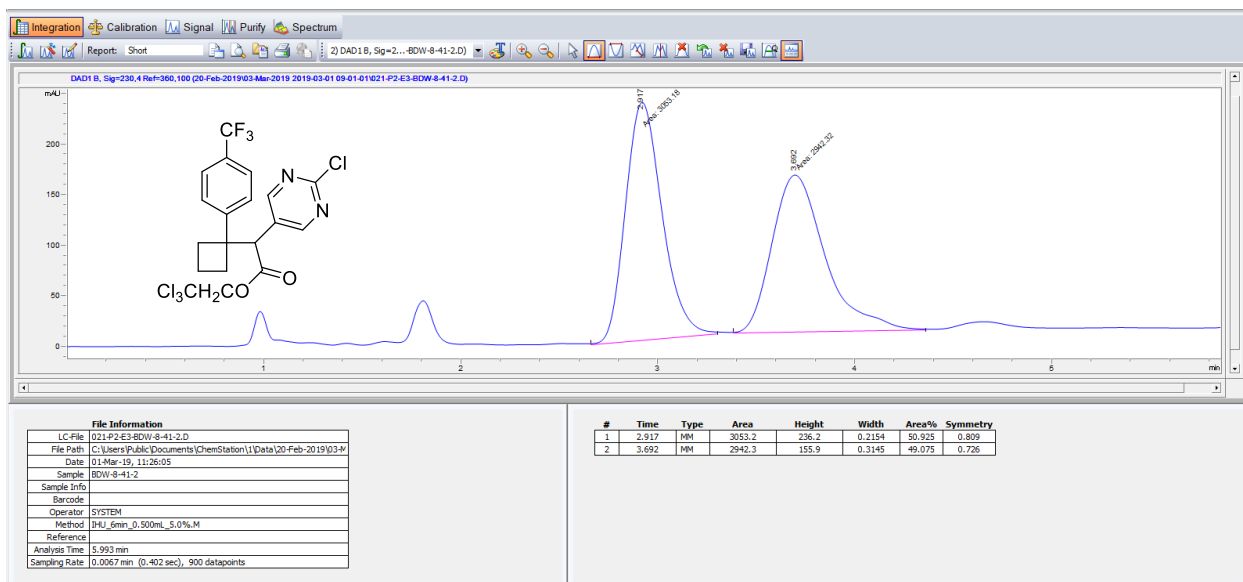


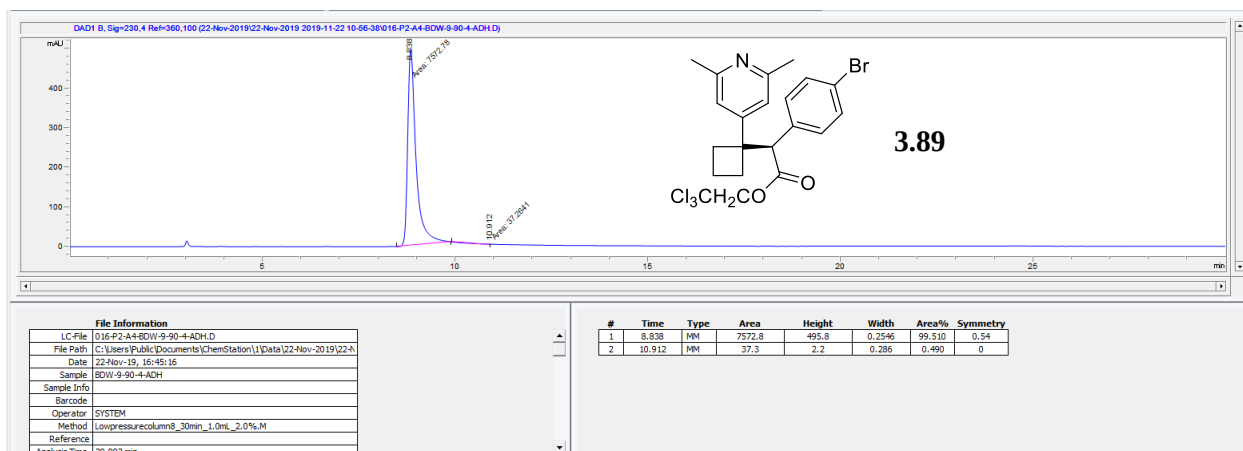
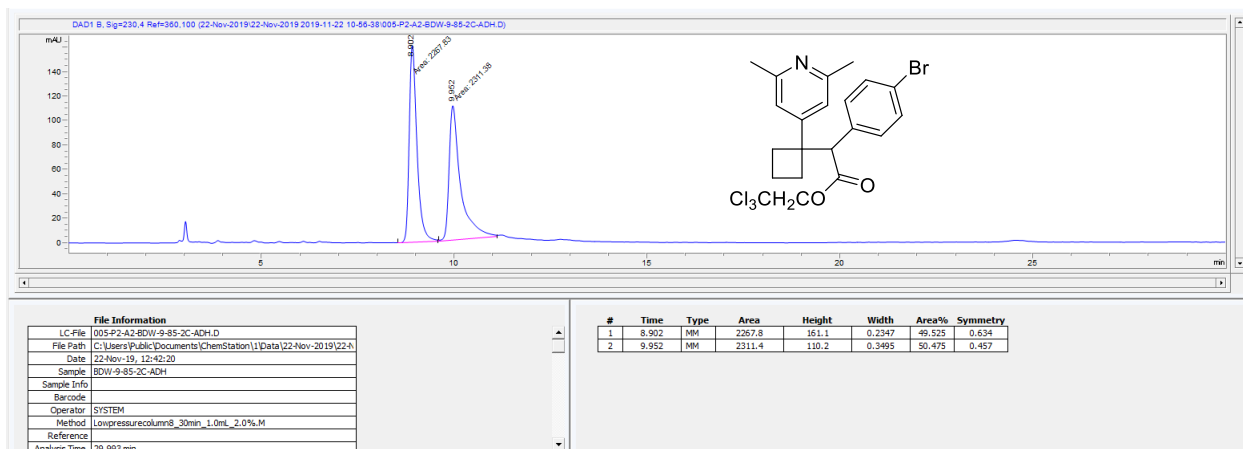


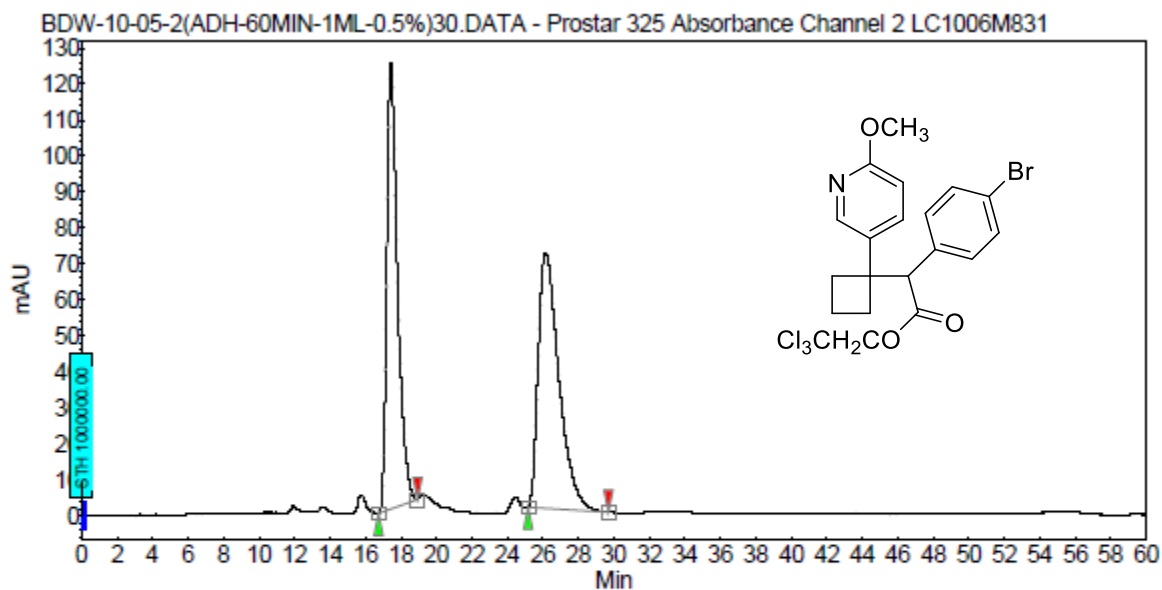






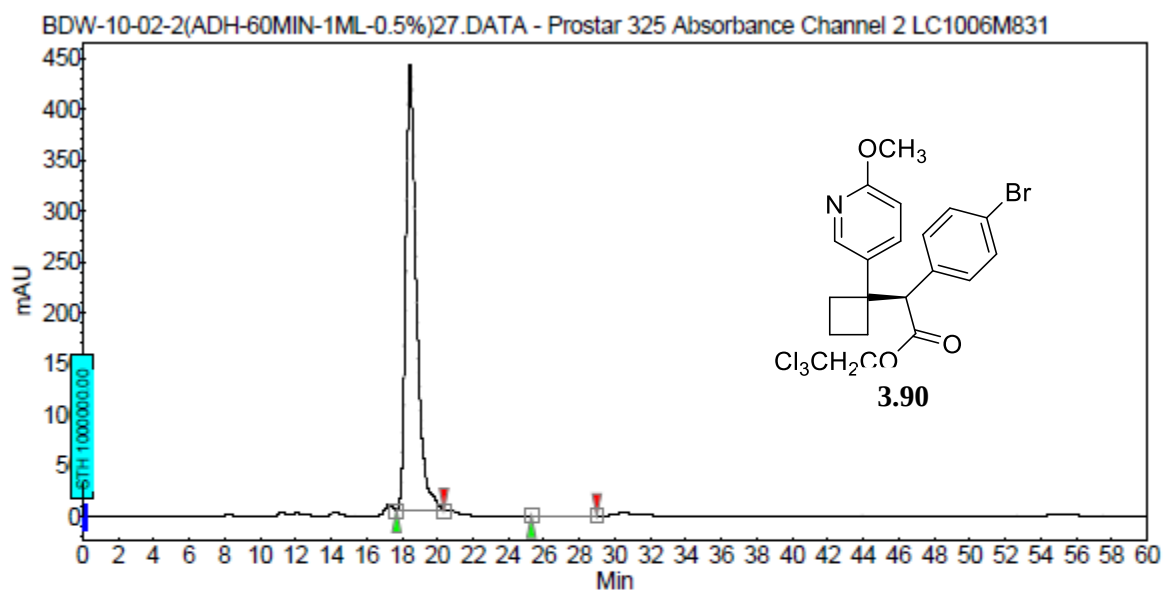






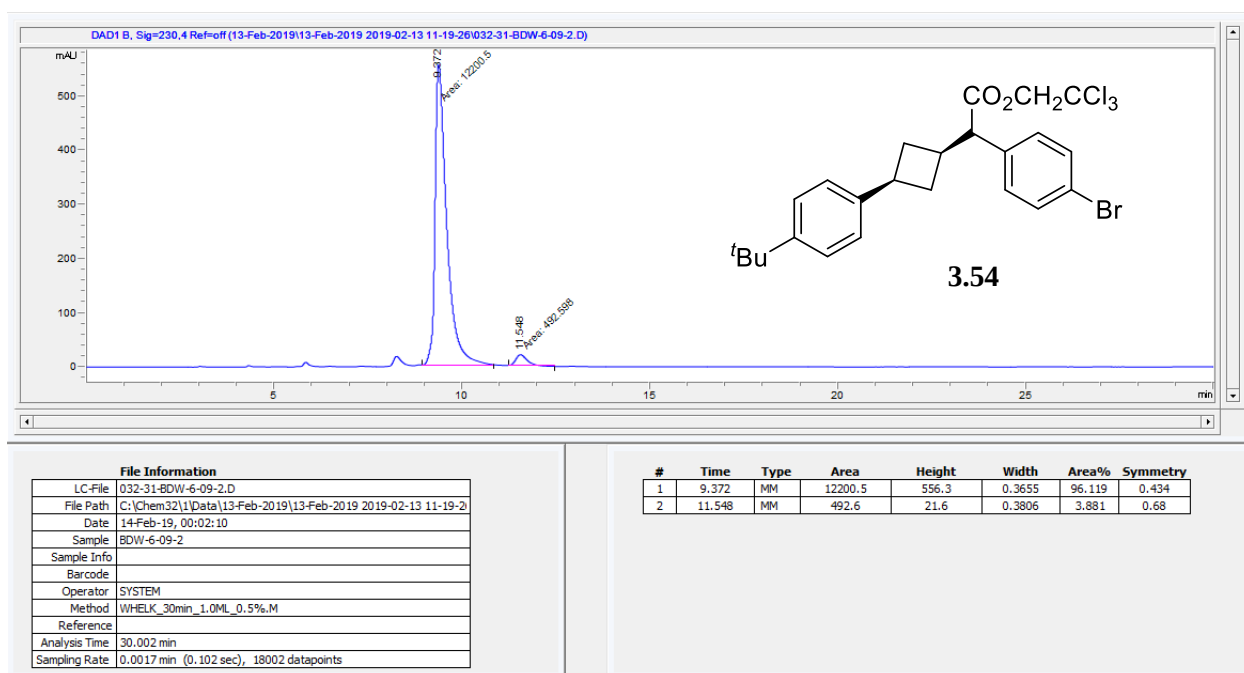
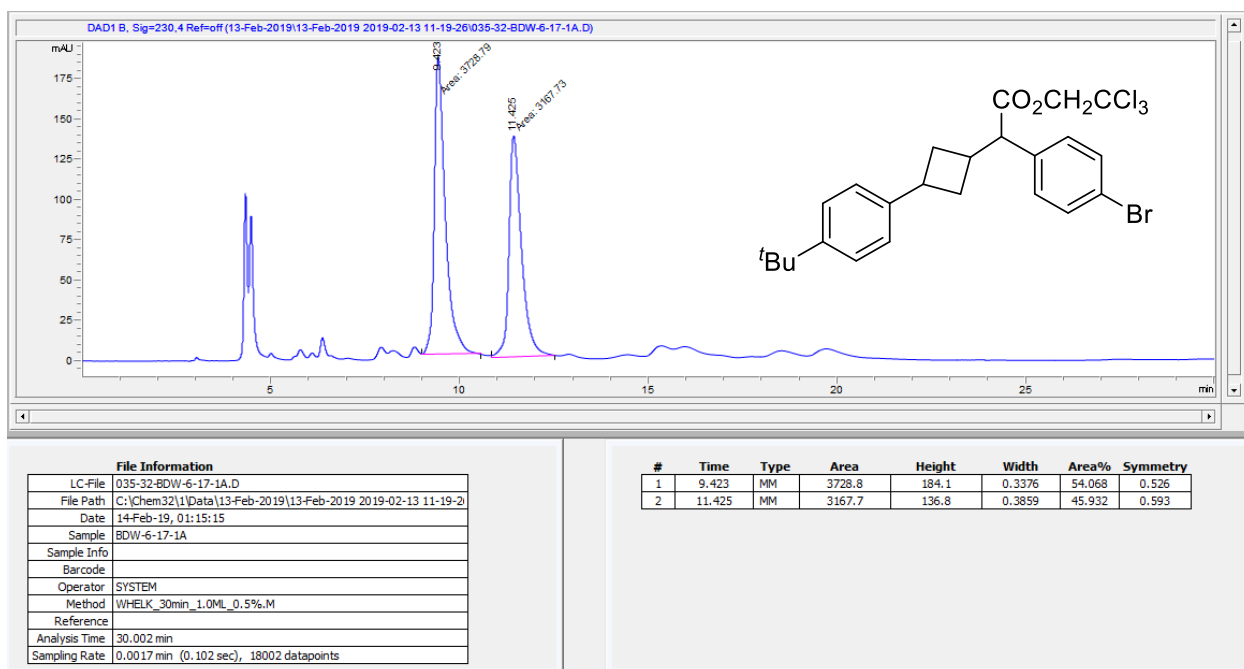
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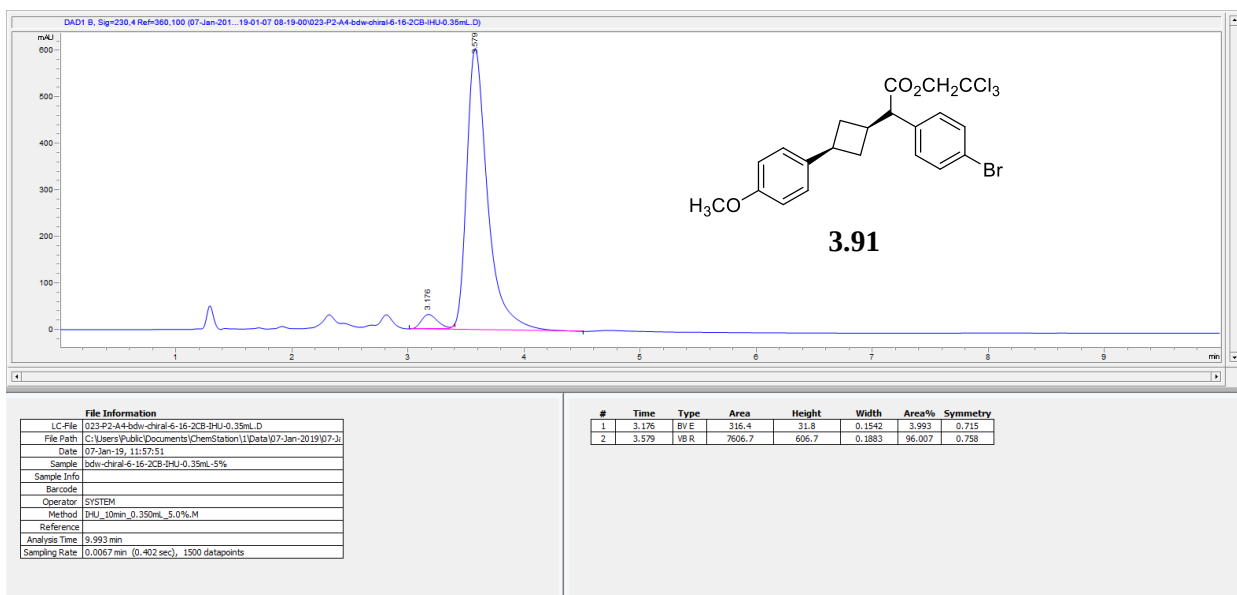
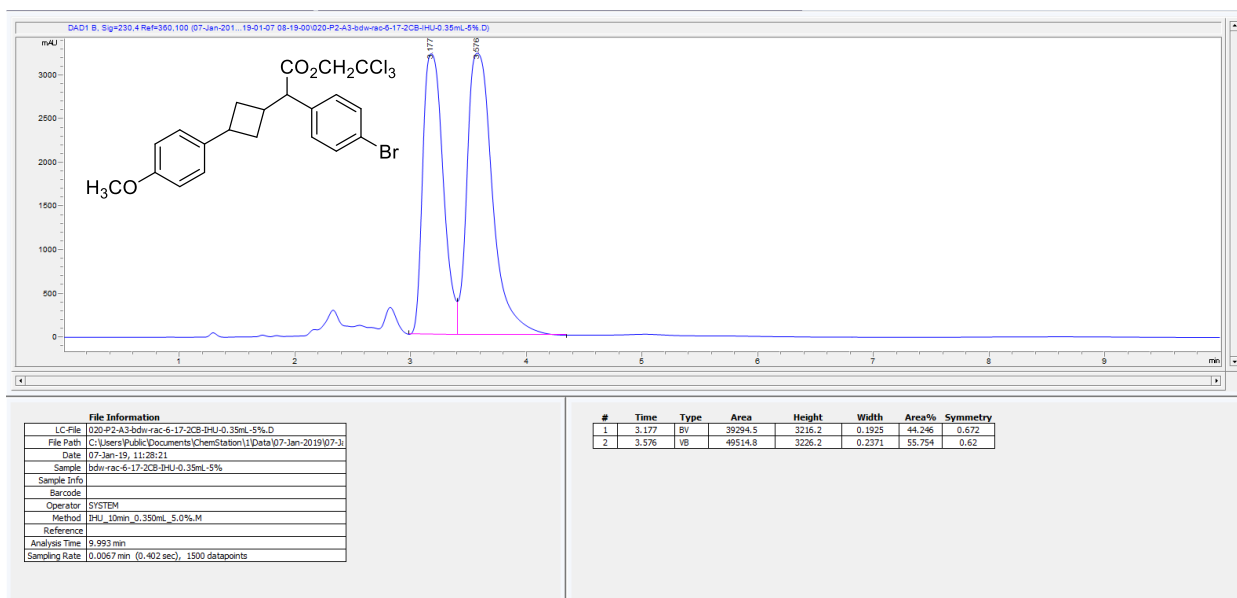
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Total			100.00	194.9	182.4	100.000

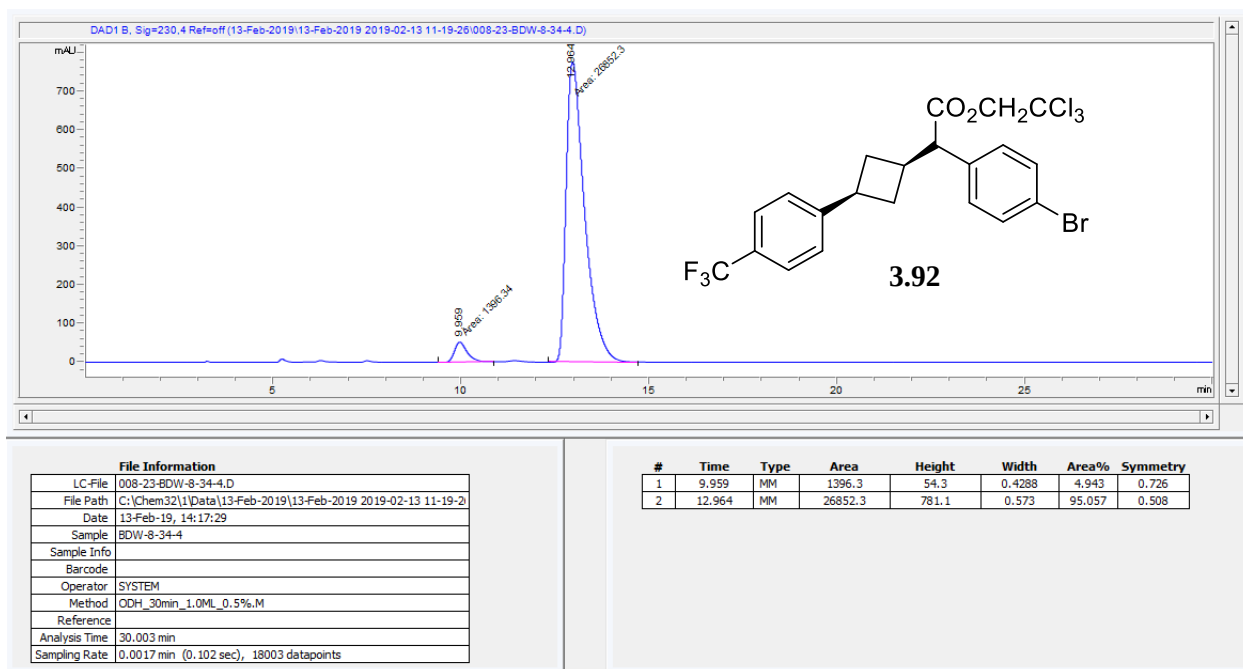
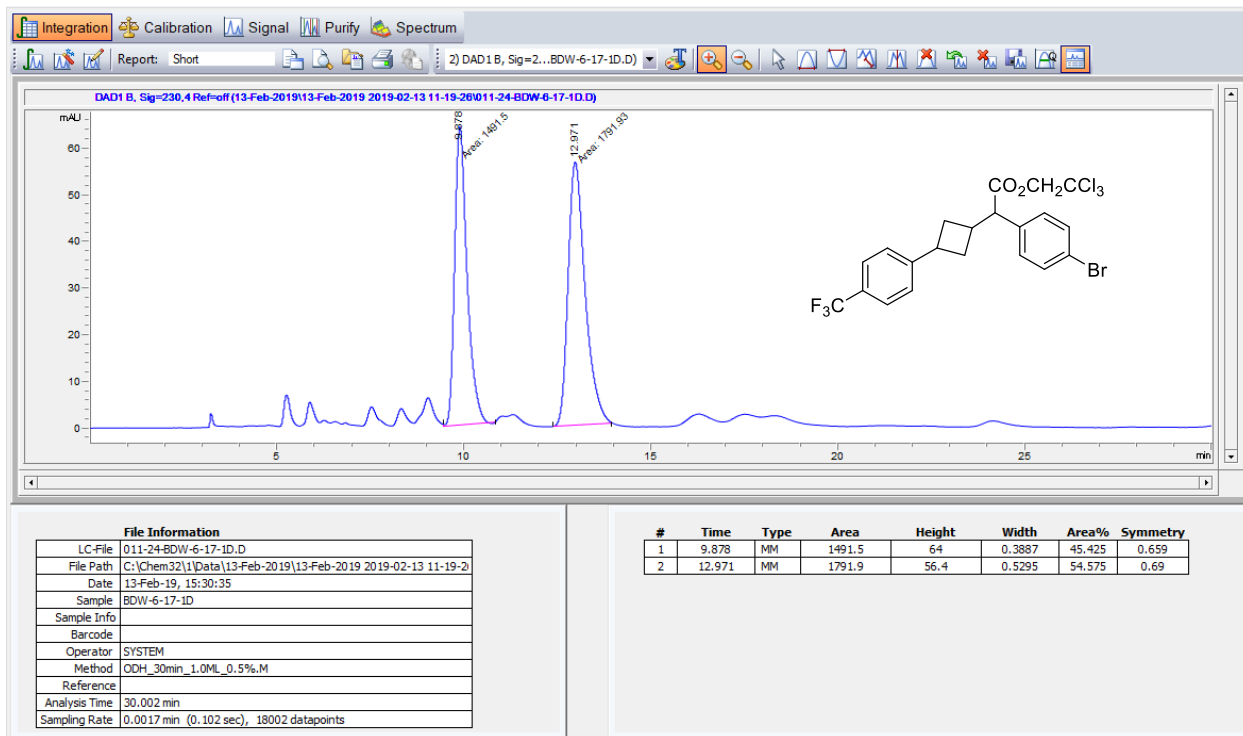


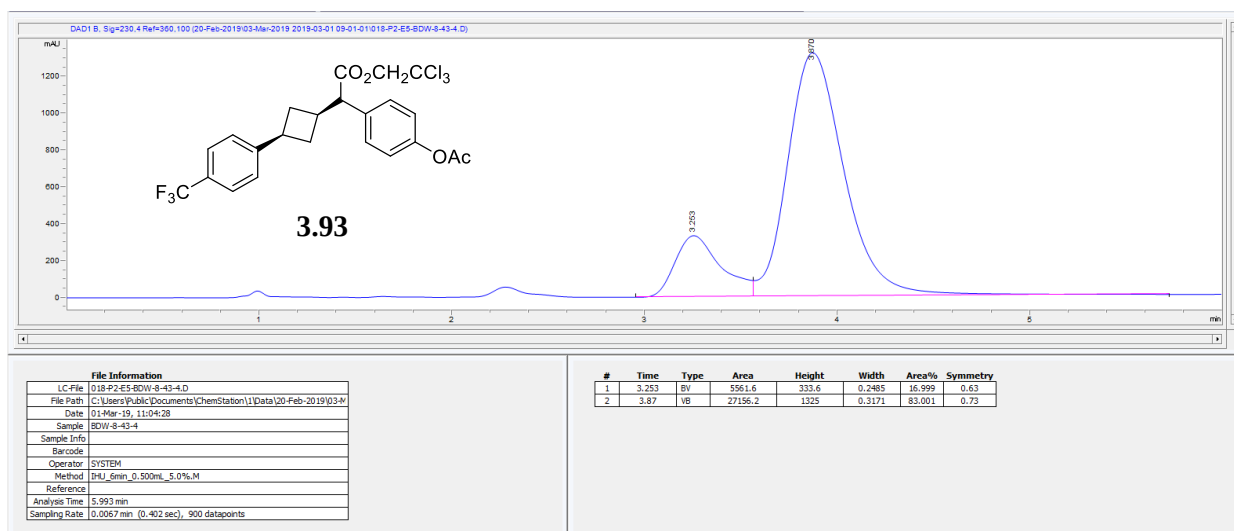
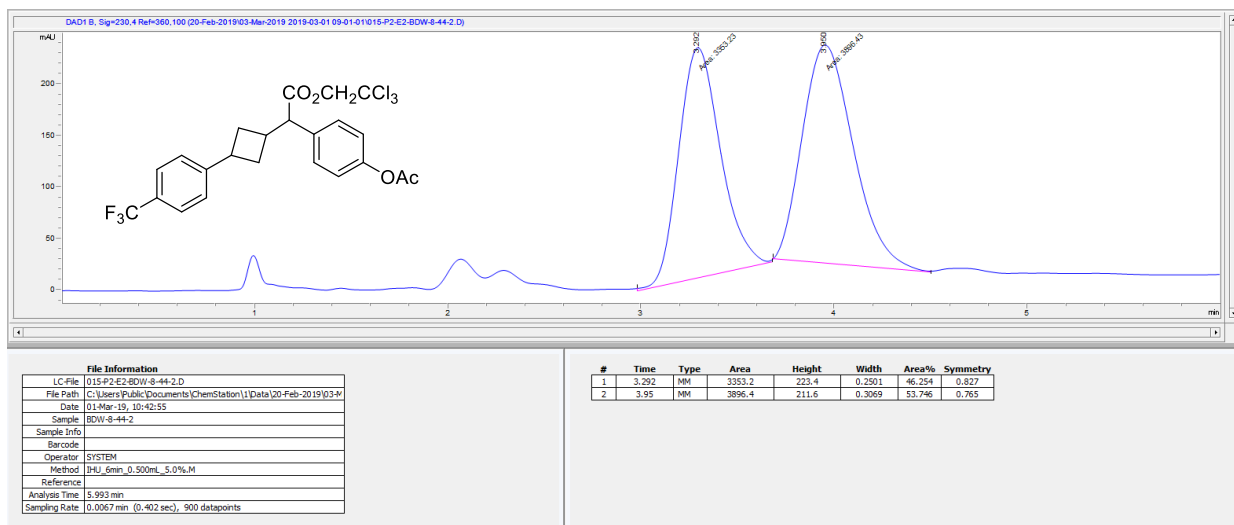
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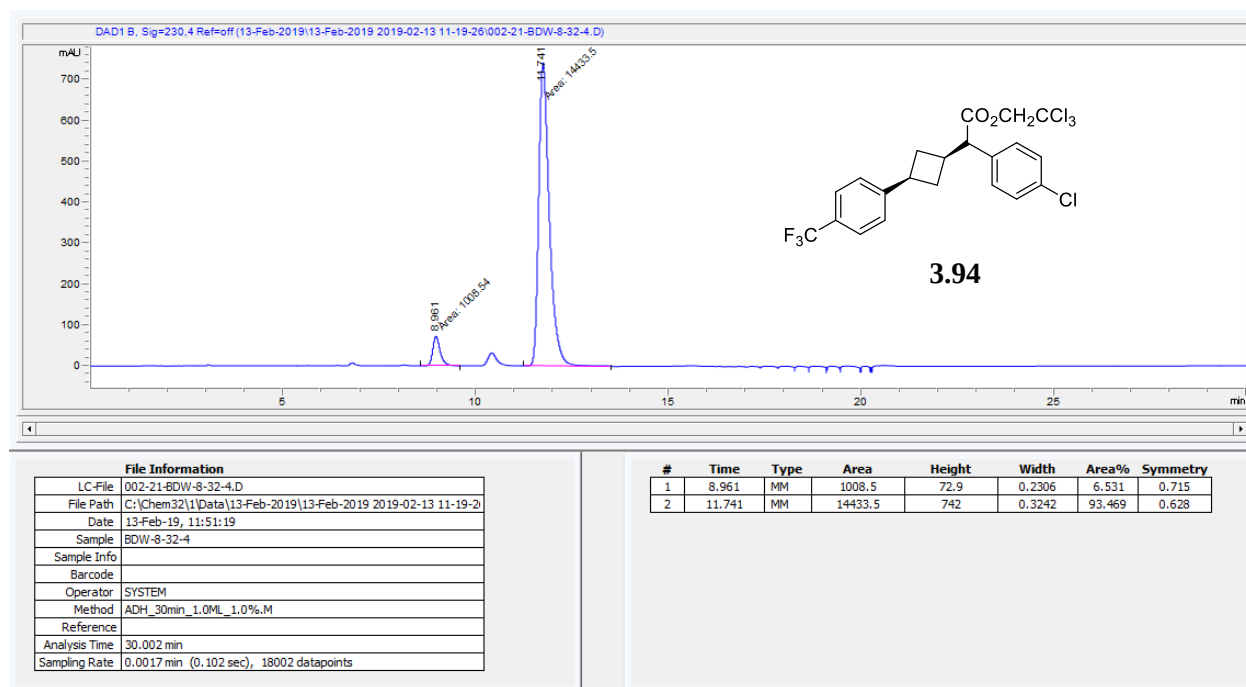
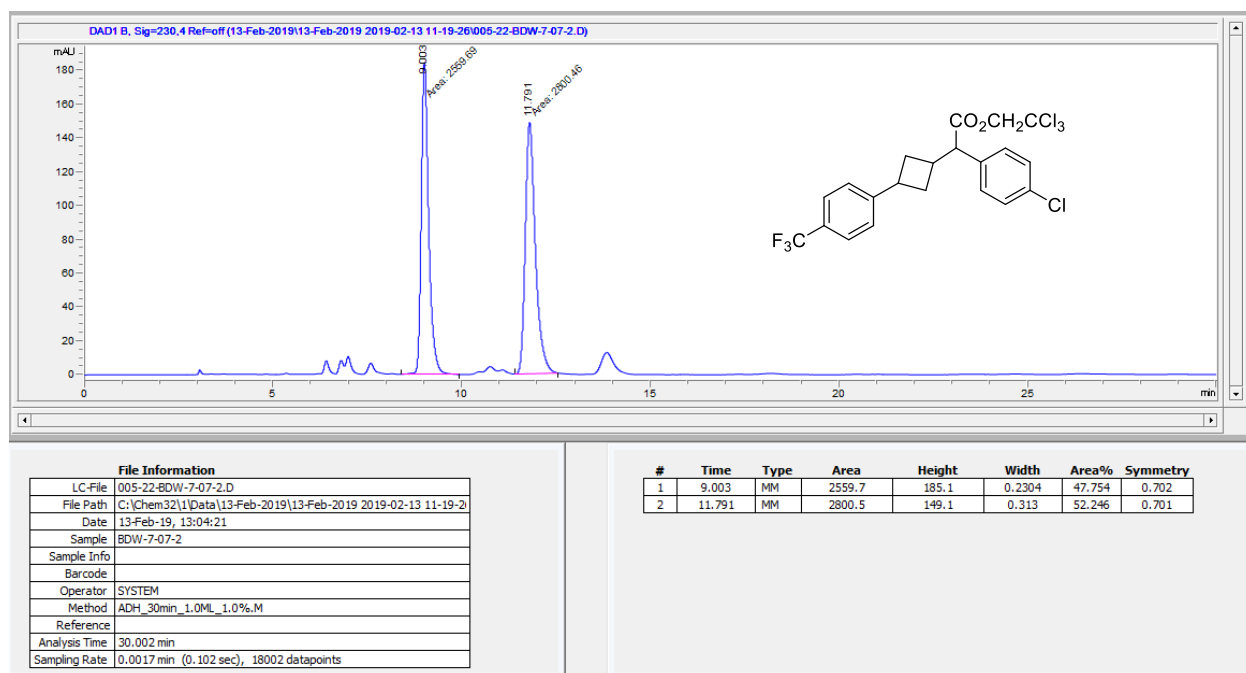
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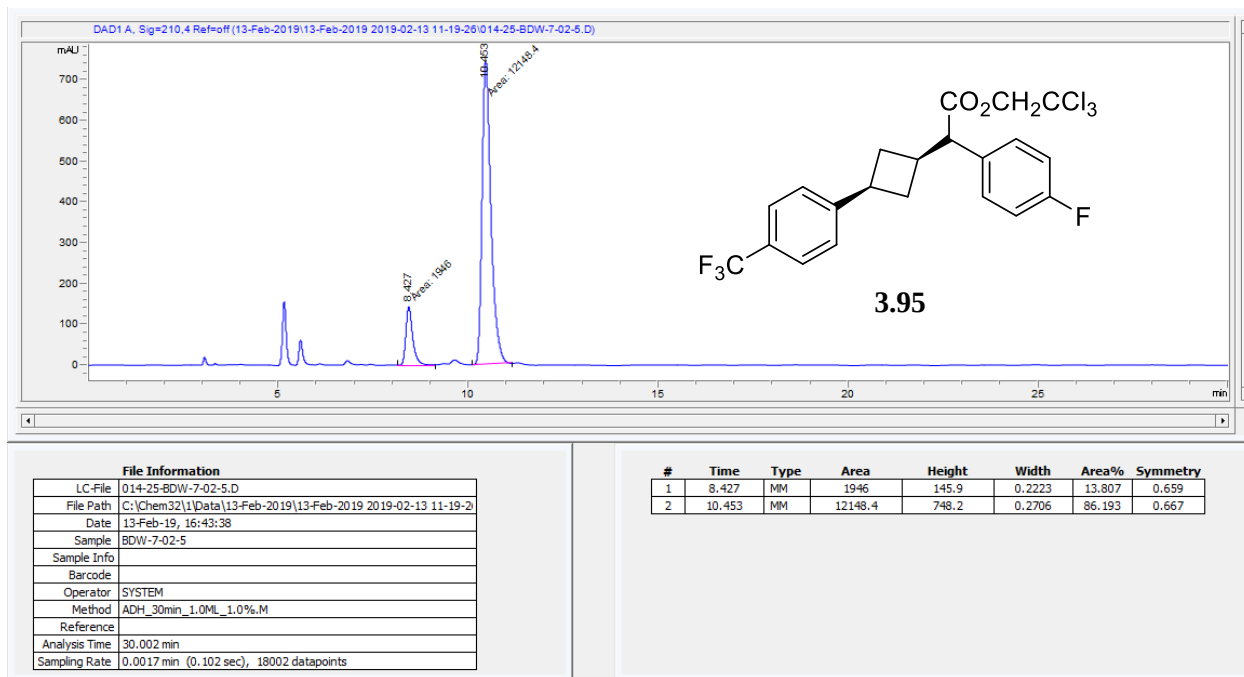
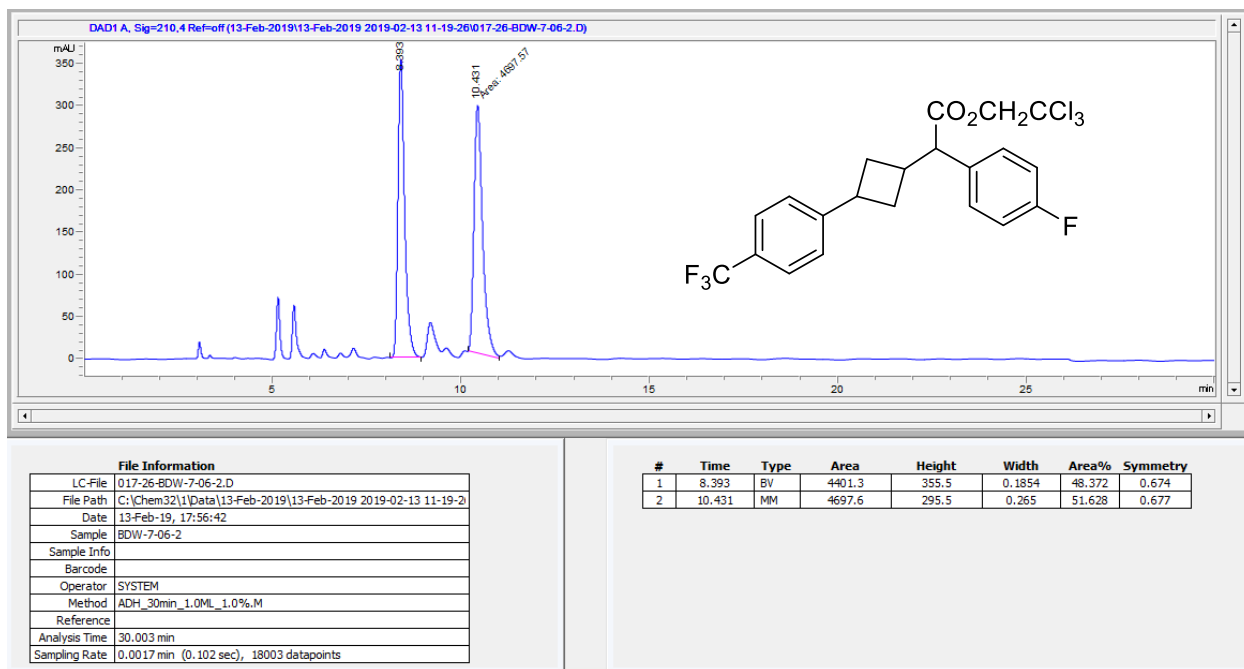


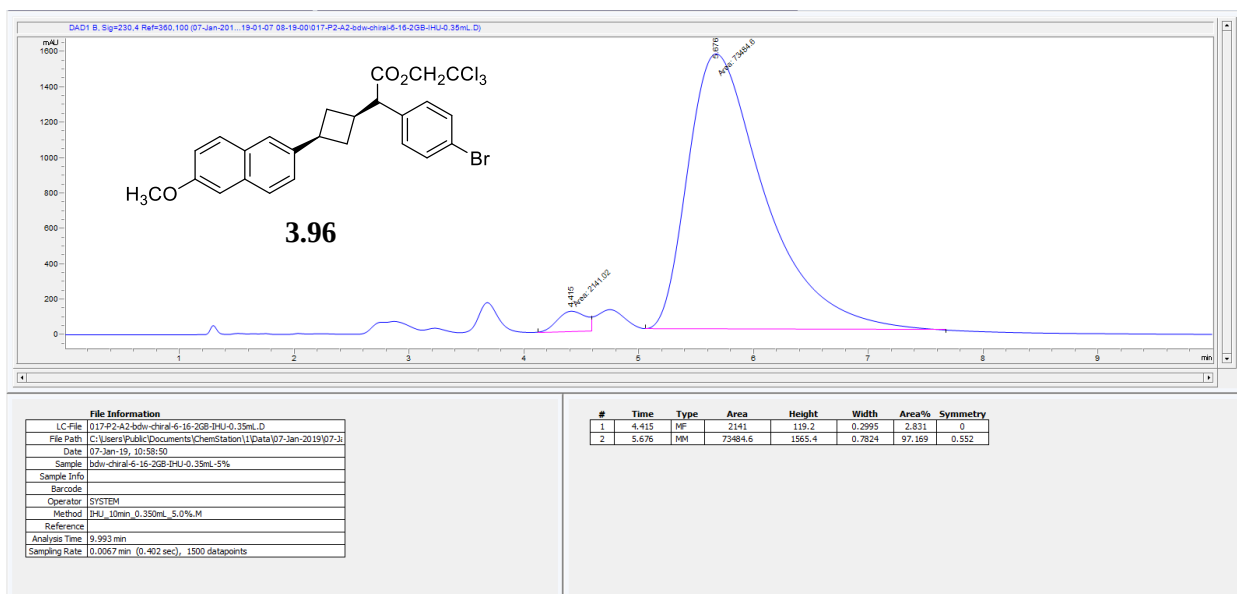
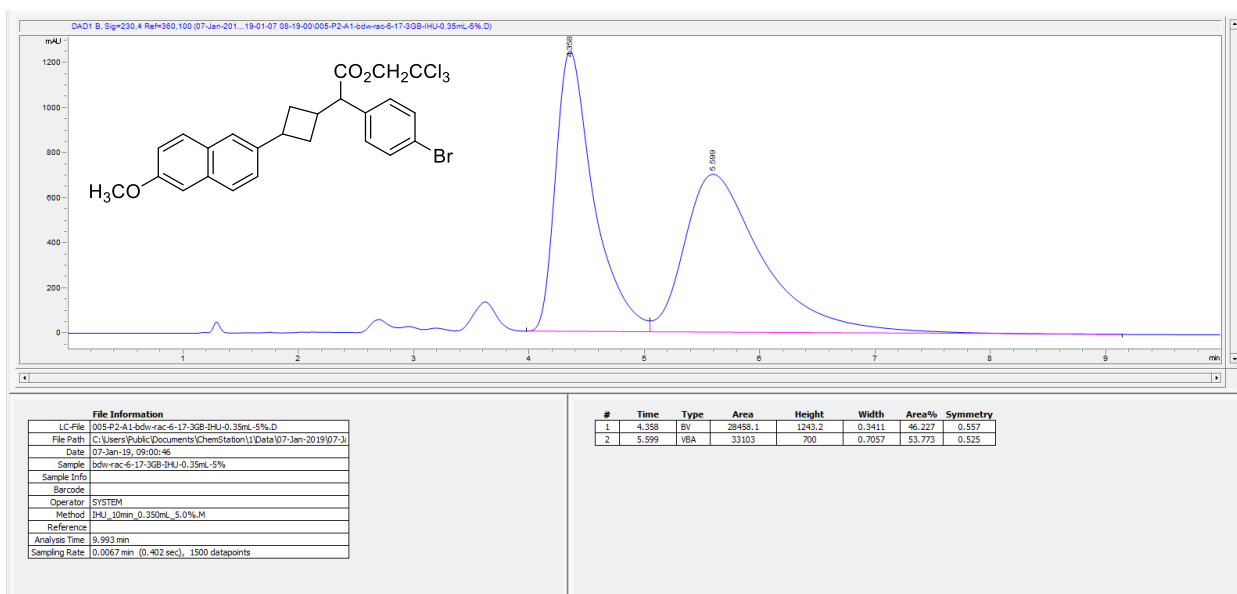










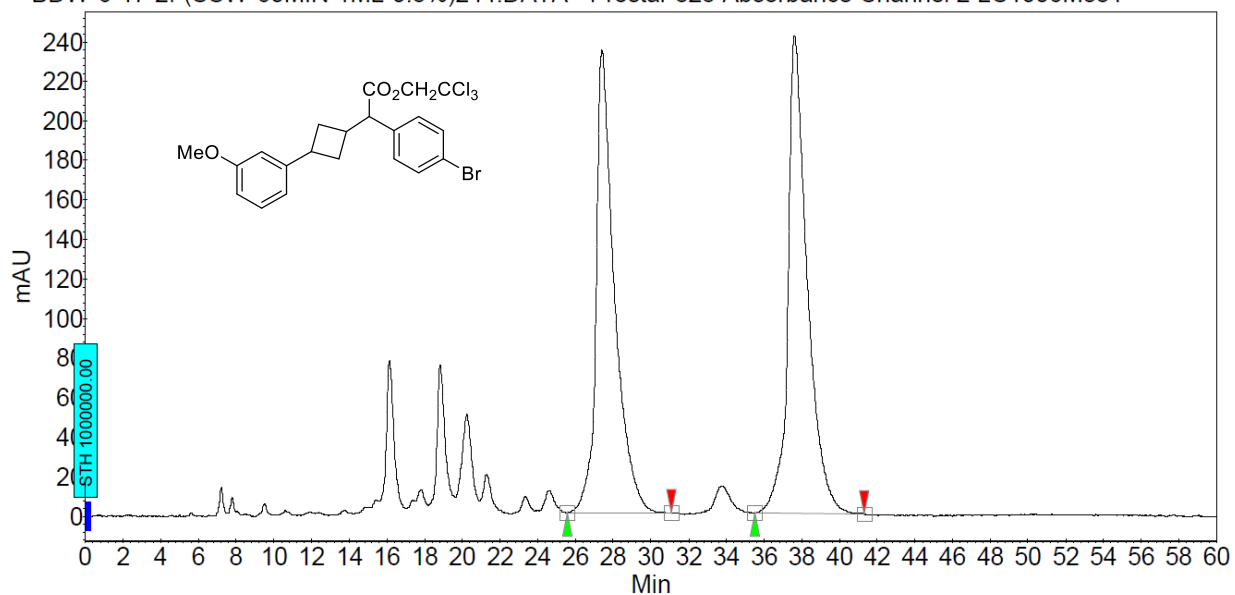


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User : User1

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Printed : 1/7/2019 10:36:26 AM

BDW-6-17-2F(SSW-60MIN-1ML-0.5%)244.DATA - Prostar 325 Absorbance Channel 2 LC1006M831



Peak results :

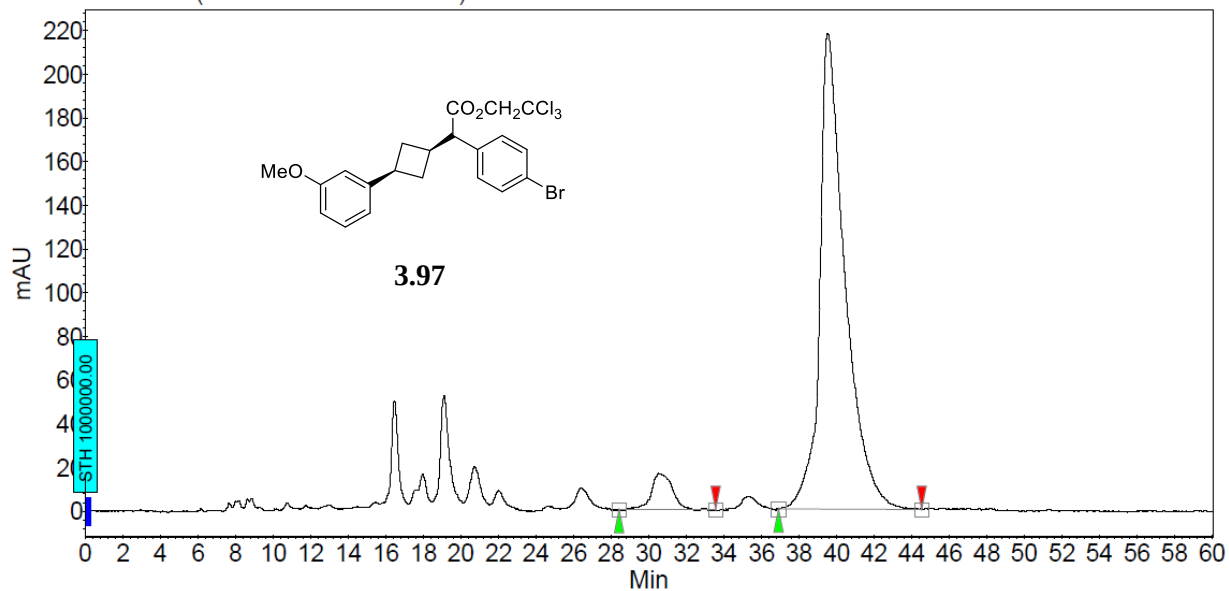
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Total			100.00	475.5	553.4	100.000

Chromatogram : BDW-6-16-2F-B(SSW-60MIN-1ML-0.5%)241_chan

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Method : OD_30min_1mL_0.5%_230nm
User : User1

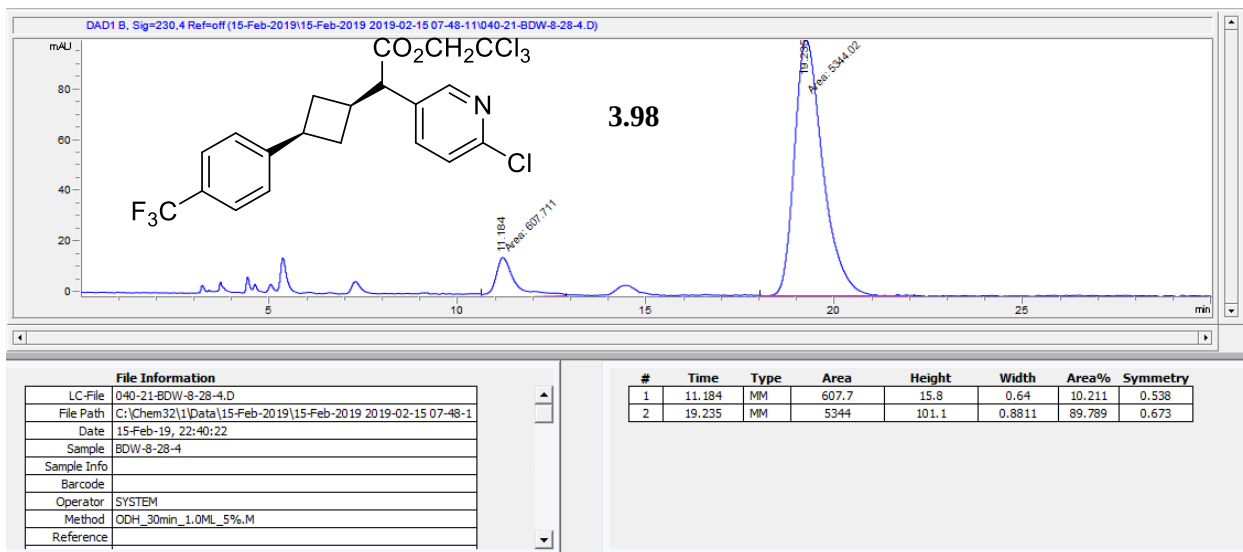
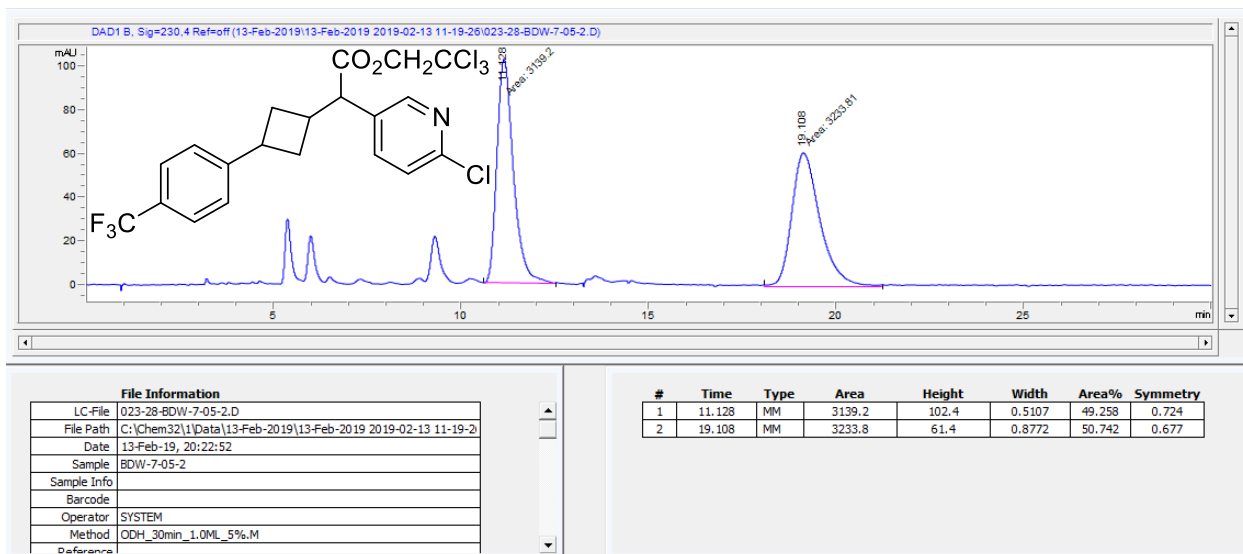
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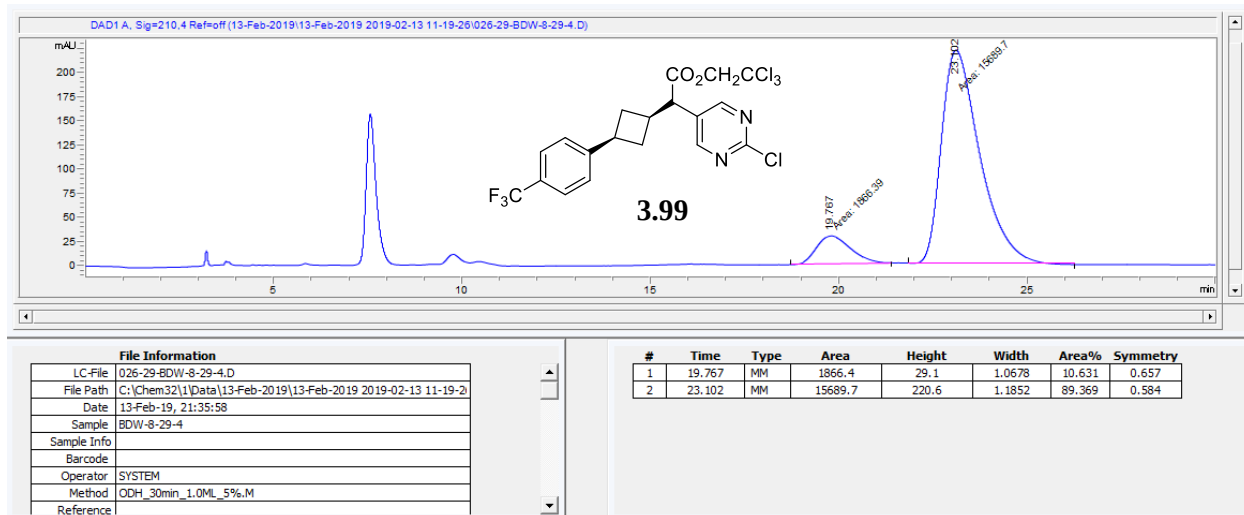
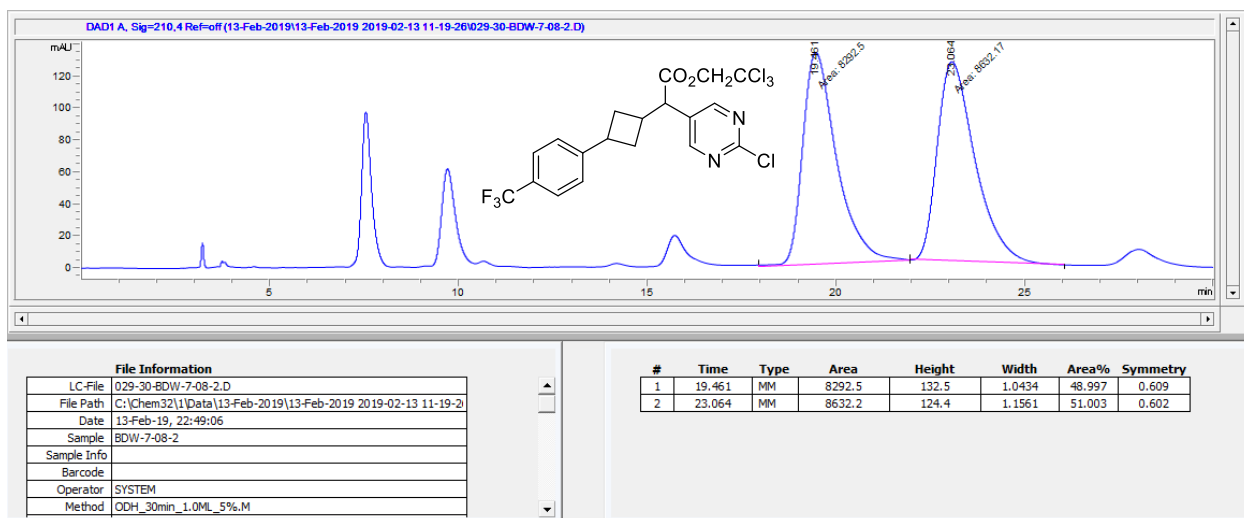
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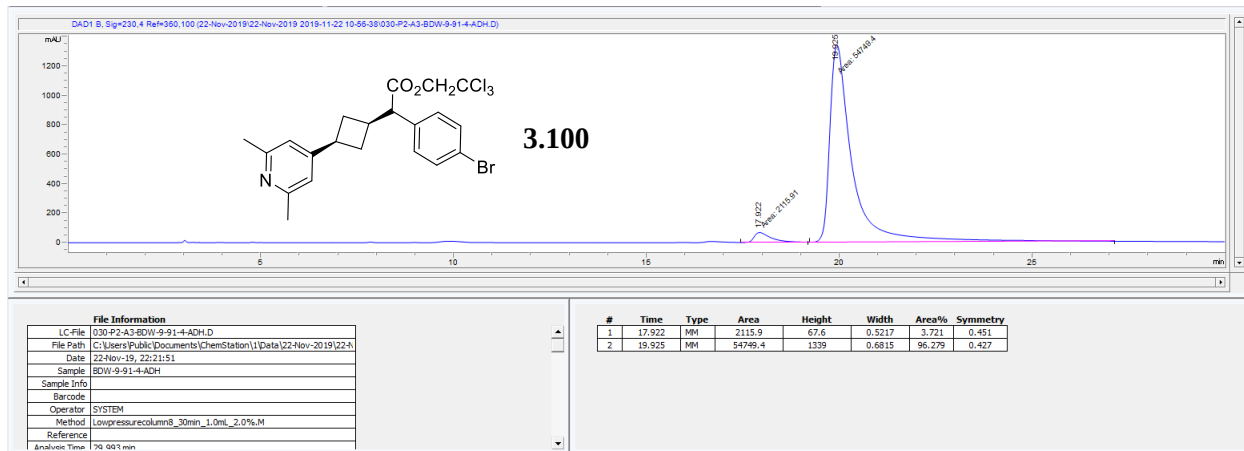
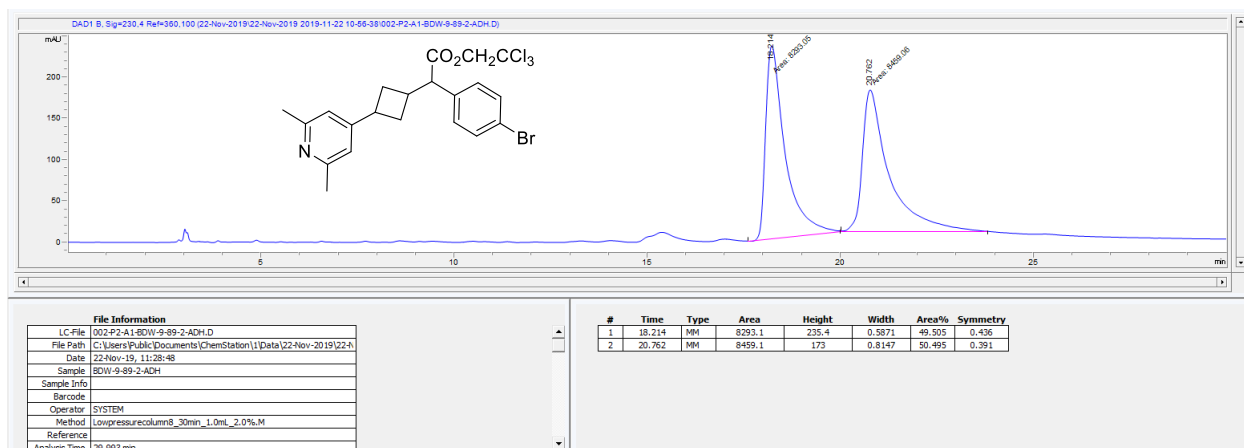


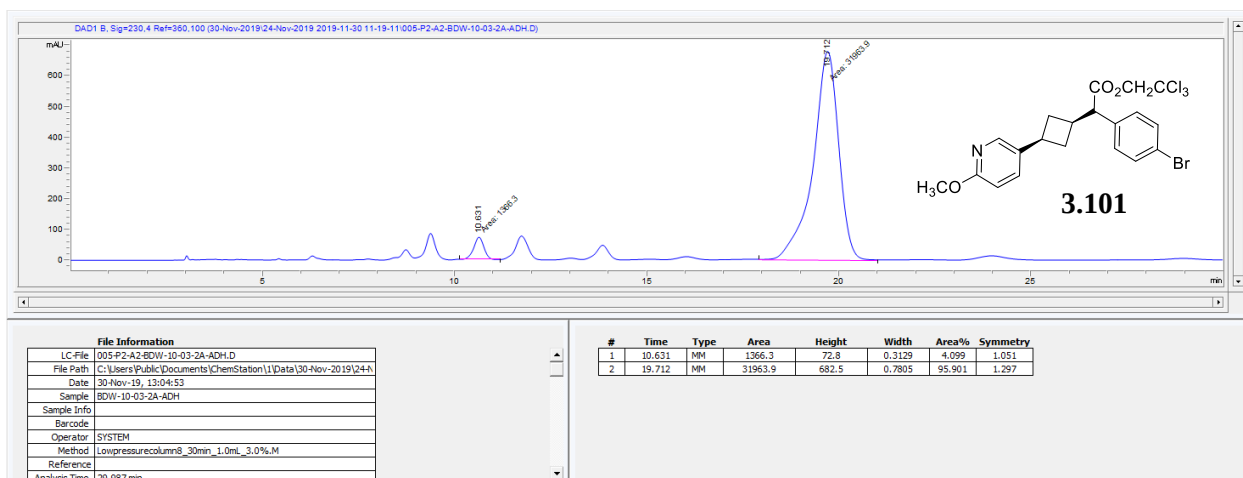
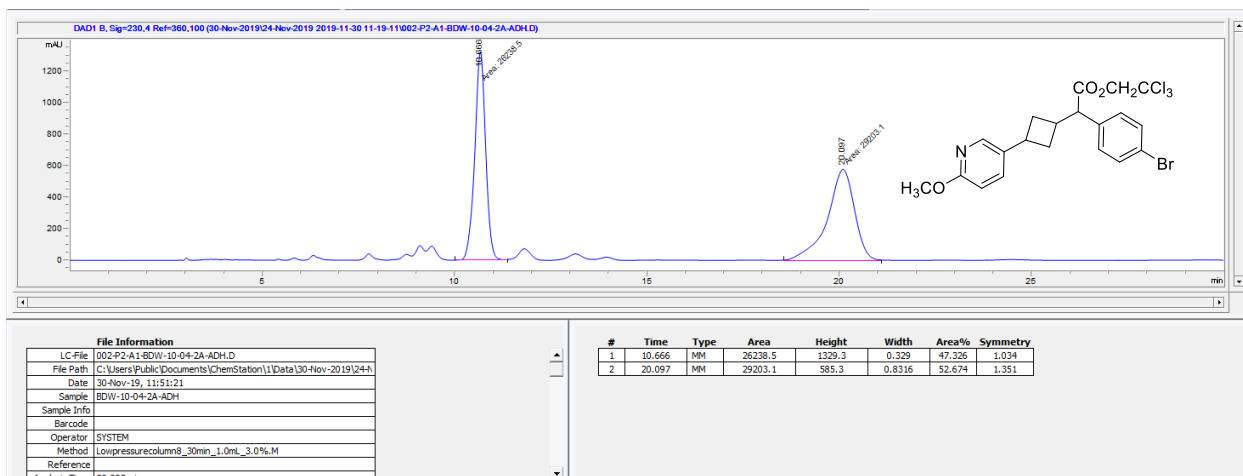
Peak results :

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2	UNKNOWN	30.50	5.85	16.5	21.2	5.847
1	UNKNOWN	39.53	94.15	217.6	341.7	94.153
Total			100.00	234.0	363.0	100.000









S.3.12 References

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S.4 Experimental Section for Chapter 4

S.4.1 General Methods

Reagents were used as received from commercial suppliers unless otherwise stated. Styrene (**4.31**) was filtered through a plug of silica gel before use. All glassware was oven-dried prior to use and all reactions were performed under an inert gas (argon or nitrogen) unless otherwise stated. Dichloromethane, toluene, hexane, pentane, and diethyl ether solvents were obtained from drying columns (Grubbs type solvent purifier) immediately prior to use. Preparative flash chromatography was performed on a Biotage MPLC system using SiliCycle SilaFlash P60 silica (normal phase, 60 Å, 40-63 µm.) ¹H NMR spectra were recorded on Varian Nuclear Magnetic Resonance spectrometers at 600, 500, 400 or 300 MHz. ¹³C NMR spectra were recorded at 150, 100 or 75 MHz and were obtained with complete proton decoupling. High resolution mass spectra were recorded on a Finnigan LTQ FTMS. Melting points were measured on a MEL-TEMP electrothermal apparatus and are uncorrected. FTIR spectra were collected on a Nicolet iS10 from Thermo Scientific. Optical rotations were measured on a PerkinElmer Model 341 Polarimeter. Chiral HPLC analyses using standard pressure columns were performed on Varian Prostar 210, Agilent 1100, or Agilent 1290 Infinity II instruments. All analytical HPLC columns had dimensions of 4.6x250 mm. A corresponding racemic standard was run sequentially with every chiral analysis to verify the retention times of the major and minor enantiomers. These were prepared using either Rh₂(OOct)₄, Rh₂(OAc)₄, or a 1:1 mixture of both enantiomers of the indicated chiral catalyst. Preparative HPLC was conducted using a Supelco Ascentis C18 column (Sigma-Aldrich) having dimensions of 25 cm x 21.2 mm with a particle size of 5 microns. The

procedures for catalyst evaluation with styrene (**4.31**), 4-ethyltoluene (**4.33**), and 4-isopropyltoluene (**4.36**) are described in section S.2.4.

The absolute configurations of the C-H insertion products are assigned based on the precedents established by references 1 and 2. The absolute configurations of cyclopropane products are assigned based on analogy to reference 3.

S.4.2 List of Previously Prepared Compounds

The following compounds were prepared previously:

dirhodium tetrakis[1-[[4-alkyl(C11-C13)phenyl]sulfonyl]-(2*R*)-pyrrolidinecarboxylate] [Rh₂(*R*-DOSP)₄] (**4.21**)³

α -cyclohexyl styrene (**4.17**)⁴

α -trimethylsilyl styrene (**4.39**)⁵

ethyl phenyldiazoacetate (**4.16**)⁶

2,2,2-trichloroethyl (4-bromophenyl)diazoacetate (**4.30**)⁷

2,2,2-trichloroethyl 2-diazo-2-(3,5-dibromophenyl)acetate (**4.50**)⁸

2,2,2-trichloroethyl (2-chlorophenyl)-2-diazoacetate (**4.51**)⁸

2,2,2-trichloroethyl 2-([1,1'-biphenyl]-4-yl)-2-diazoacetate (**4.49**)⁹

ethyl (1*R*,2*R*)-1,2-diphenyl-2-(trimethylsilyl)cyclopropane-1-carboxylate (**4.41**)¹⁰

dirhodium tetrakis[(*R*)-1-([1,1'-biphenyl]-4-yl)-2,2-diphenylcyclopropane-1-carboxylate] [Rh₂(*R*-*p*-PhTPCP)₄] (**4.20**)¹¹

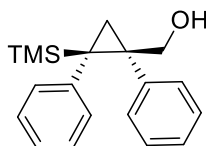
dirhodium tetrakis[(*S*)-1,2,2-triphenylcyclopropane-1-carboxylate] [Rh₂(*S*-TPCP)₄] (**4.15**)¹¹

dirhodium tetrakis[(1*R*,2*S*)-1,2-diphenylcyclopropane-1-carboxylate] [Rh₂[(1*R*,2*S*)-DPCP]₄] (**4.14**)¹²

dirhodium tetrakis[(*R*)-2-(adamantan-1-yl)-2-(1,3-dioxoisindolin-2-yl)acetate] [Rh₂(*R*-PTAD)₄] (**4.40**)¹³

The primary alcohol derivatives of **4.34**, **4.35**, **4.37**, and **4.38** are characterized in section S.2.5 of this thesis.

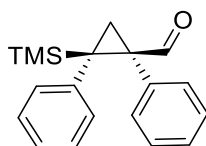
S.4.3 Synthesis of Cyclopropanecarboxylate Ligands



((1*R*,2*R*)-1,2-diphenyl-2-(trimethylsilyl)cyclopropyl)methanol (**4.42**)

To a 250 mL round bottom flask was added ethyl (1*R*,2*R*)-1,2-diphenyl-2-(trimethylsilyl)cyclopropane-1-carboxylate (**4.41**, 334 mg, 0.99 mmol, 1.0 equiv)¹⁰ and CH₂Cl₂ (40 mL.) The solution was cooled to -78 °C using a bath of dry ice/acetone, and then a solution of diisobutylaluminum hydride (**4.22**, 702 mg, 4.93 mmol, 5.0 equiv) in CH₂Cl₂ (4.93 mL, 1.0 M) was added dropwise via syringe. The mixture warmed to room temperature over 4-5 h as the dry ice sublimed. After a total of 17 h, the mixture was cooled to 0 °C using an ice bath, and then the reaction was quenched via the addition of methanol (4.93 mL.) The mixture was concentrated to a colorless solid *in vacuo*, and the material was purified by flash column chromatography on silica gel (24 g, 0-10% EtOAc/hexanes,) affording 243 mg of the title compound **4.42** as a colorless solid (83% yield.) The *ee* of the product was assumed to be identical to that of the

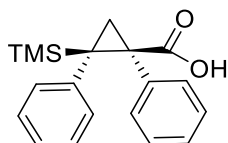
starting material (98% *ee*). mp 114-115 °C, $[\alpha]_D^{20}$ -40.5° (c 1.00, EtOH) ^1H NMR (600 MHz, CDCl_3) δ 7.14 (d, J = 8.0 Hz, 1H), 7.08 (t, J = 7.7 Hz, 2H), 6.99 (t, J = 7.3 Hz, 1H), 6.86 (q, J = 7.1, 6.6 Hz, 5H), 4.49 (ddd, J = 11.3, 4.6, 1.6 Hz, 1H), 3.73 (dd, J = 11.3, 7.8 Hz, 1H), 1.96 (dd, J = 4.9, 1.6 Hz, 1H), 1.42 (d, J = 4.9 Hz, 1H), 1.40 – 1.34 (m, 1H), 0.03 (s, 8H). ^{13}C NMR (151 MHz, CDCl_3) δ 142.2, 139.1, 131.7, 129.4, 127.9, 127.1, 126.2, 124.7, 68.8, 39.3, 29.3, 20.2, 0.23. FTIR: 3353, 3056, 3027, 2947, 2879, 1494, 1445, 1246, 1042, 835, 780, 699 cm^{-1} . HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ (Pos.): calcd for $\text{C}_{19}\text{H}_{24}\text{ONaSi}$ 319.1489; found 319.1485.



(1*R*,2*R*)-1,2-diphenyl-2-(trimethylsilyl)cyclopropane-1-carbaldehyde (4.44)

A 250 mL round bottom flask was loaded with ((1*R*,2*R*)-1,2-diphenyl-2-(trimethylsilyl)cyclopropyl)methanol (**4.42**, 239 mg, 0.81 mmol, 1.0 equiv) and CH_2Cl_2 (121 mL.) Then, solid Dess-Martin periodinane (**4.43**, 514 mg, 1.21 mmol, 1.5 equiv) was added as a single portion with moderate stirring. The reaction was continued for 1 hour at room temperature, and then quenched via the addition of a 1:1 mixture of saturated aqueous NaHCO_3 / saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (100 mL.) After stirring for 30 minutes, the organic phase was separated and then washed with an additional portion of deionized water (100 mL,) and the DCM phase was dried over MgSO_4 and filtered. The filtrate liquid was concentrated under vacuum to afford 233 mg of the title compound **4.44** as a colorless solid (98% yield.) The enantiomeric excess was assumed to be unchanged by the reaction (98% *ee*). mp 77.5-79.5 °C, $[\alpha]_D^{20}$ + 23.6° (c 1.00, CHCl_3) ^1H NMR (600 MHz, CDCl_3) δ 9.73 (s, 1H), 7.12 (dt, J = 16.5, 7.4 Hz, 1H), 7.05 (t, J = 6.9 Hz, 1H), 7.00 (s, 2H), 6.92 (d, J = 6.8 Hz, 3H), 2.49 – 2.42 (m, 1H), 2.16 (d, J = 4.5

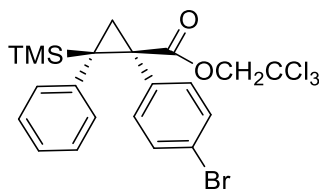
Hz, 1H), 0.10 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 200.7, 140.8, 134.1, 130.3, 127.8, 126.9, 125.5, 48.7, 37.4, 22.8, 0.30. FTIR: 3057, 2953, 2854, 2765, 1697, 1496, 1449, 1246, 840, 696 cm^{-1} . HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ (Pos.): calcd for $\text{C}_{19}\text{H}_{23}\text{OSi}$ 295.1524; found 295.1513.



(1R,2R)-1,2-diphenyl-2-(trimethylsilyl)cyclopropane-1-carboxylic acid (4.48)

To a round bottom flask was added: (1R,2R)-1,2-diphenyl-2-(trimethylsilyl)cyclopropane-1-carbaldehyde (**4.44**, 222 mg, 0.75 mmol, 1.0 equiv,) deionized water (2.7 mL,) acetone (8.0 mL,) sodium phosphate monobasic monohydrate (364 mg, 2.64 mmol, 3.5 equiv,) and 2-methyl-2-butene (**4.47**, 529 mg, 7.54 mmol, 0.80 mL, 10.0 equiv.) Magnetic stirring was turned on, and then solid sodium chlorite (**4.45**, 239 mg, 2.64 mmol, 3.5 equiv) was added over 1 minute. Addition of the sodium chlorite (**4.45**) caused the mixture to turn a green color, which gradually subsided over the course of ca. 1 h. After 2 h 20 min, the mixture was poured into saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution to quench any remaining oxidant. It was stirred for 20 minutes, and then the mixture was partitioned between EtOAc (100 mL) and deionized water (100 mL.) The organic phase was separated, and the aqueous layer was extracted with an additional portion of EtOAc (100 mL). The pooled organics were dried over Na_2SO_4 , and then filtered. Concentration of the filtrate liquid *in vacuo* afforded 305 mg of a colorless solid. The crude material showed 99% *ee*, verifying that the enantiopurity of the major component had not been significantly impacted by the previous steps (S,S-Whelk, 1.0 mL/min, 3.0% i-PrOH/hexanes. rt 5.9 min (major), 7.4 min (minor)). Further purification by flash column chromatography (0-15%

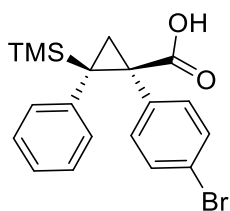
acetone/hexanes), afforded 200 mg of the product **4.48** as a colorless solid (85% yield, 99% *ee*) mp 121.5-122.0 °C (from EtOAc), $[\alpha]_D^{20} - 115.8^\circ$ (c 1.00, CHCl₃) ¹H NMR (600 MHz, CDCl₃) δ 10.46 (s, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.07 (t, *J* = 7.5 Hz, 2H), 7.04 – 6.87 (m, 6H), 2.17 (d, *J* = 4.9 Hz, 1H), 1.99 (d, *J* = 4.9 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 179.8, 140.7, 135.3, 130.4, 130.1, 127.5, 127.4, 126.8, 125.3, 40.1, 33.7, 21.5, -0.7. FTIR: 3080, 3021, 2954, 2898, 2575, 1683, 1495, 1416, 1248, 974, 693 cm⁻¹. HRMS (ESI) *m/z*: [M-H]⁻ (Neg.): calcd for C₁₉H₂₁O₂Si 309.1316; found 309.1320.



2,2,2-trichloroethyl (1*R*,2*R*)-1-(4-bromophenyl)-2-phenyl-2-(trimethylsilyl)cyclopropane-1-carboxylate (4.52)

A round bottom flask was charged with α -trimethylsilylstyrene (**4.39**, 3.00 g, 17.0 mmol, 3.0 equiv,) Rh₂[R-PTAD]₄ (**4.40**, 44.2 mg, 28.4 μ mol, 0.5 mol%) and pentane (34 mL.) Stirring was turned on, and then a solution of 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**4.30**, 2.12 g, 5.67 mmol, 1.0 equiv) in pentane (45 mL) was added dropwise via an addition funnel. After the addition was complete, stirring was continued for 45 min, and then the mixture was concentrated to a thick green oil under vacuum (4.43 g.) The components were separated by flash column chromatography on silica gel (80 g, 0-3% EtOAc / hexanes,) affording 2.54 g of the title compound **4.52** as a faint green oil (86% yield.) >95:5 dr, 97% *ee* (OD-R, 1.0 mL/min, 0.5% i-PrOH/hexanes. rt 4.2 min (minor), 6.8 min (major)) $[\alpha]_D^{20} - 61.1^\circ$ (c 1.00, CHCl₃). The material was carried forward without further enantioenrichment at this stage. ¹H NMR (400 MHz, CDCl₃) δ 7.21 – 7.13 (m, 2H), 7.13 – 7.07 (m, 2H), 7.06 – 6.98 (m, 2H), 6.97 – 6.89 (m,

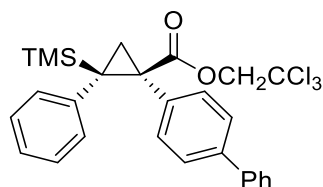
3H), 4.77 (d, $J = 12.0, 0.4$ Hz, 1H), 4.66 (d, $J = 11.9, 0.5$ Hz, 1H), 2.11 (d, $J = 5.0$ Hz, 1H), 1.99 (d, $J = 5.0, 0.4$ Hz, 1H), 0.01 (s, $J = 0.5$ Hz, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 170.9, 140.1, 134.2, 132.3, 130.5, 127.7, 125.6, 121.0, 94.6, 74.9, 39.7, 33.3, 21.3, -1.0. FTIR: 3029, 2952, 2897, 2871, 1739, 1489, 1248, 1217, 1149, 834, 719, 702 cm^{-1} . HRMS (ESI) m/z : $[\text{M}]^+$ (Pos.): calcd for $\text{C}_{21}\text{H}_{22}\text{O}_2\text{BrCl}_3\text{Si}$ 517.9633; found 517.9637.



(1R,2R)-1-(4-bromophenyl)-2-phenyl-2-(trimethylsilyl)cyclopropane-1-carboxylic acid
(4.56)

A mixture of 2,2,2-trichloroethyl (1R,2R)-1-(4-bromophenyl)-2-phenyl-2-(trimethylsilyl)cyclopropane-1-carboxylate (**4.52**, 322 mg, 0.62 mmol, 1.00 equiv), zinc dust (202 mg, 3.09 mmol, 5.00 equiv.), and acetic acid (10 mL) was stirred at room temperature over h. At the end of the stir period, the mixture was concentrated under vacuum to afford 266 mg of crude product as a colorless solid. Further purification was achieved by flash column chromatography on silica gel (0-20% Et₂O/hexanes). Obtained 189 mg of the pure product **4.56** as a colorless solid. The material could be recrystallized to >99% *ee* from hexanes. *ee* >99% (AD-H, 1.0 mL/min, 2.0% i-PrOH/hexanes. rt 18.7 (major,) 20.8 min (minor).) mp 141.0-142.0 °C (from hexanes), $[\alpha]_{\text{D}}^{20} - 97.0^\circ$ (c 1.00, CHCl_3). ^1H NMR (500 MHz, CDCl_3) δ 7.23 – 7.14 (m, 2H), 7.13 – 7.07 (m, 2H), 7.02 (d, $J = 7.5$ Hz, 2H), 6.98 – 6.90 (m, 3H), 2.13 (d, $J = 4.9$ Hz, 1H), 2.05 (d, $J = 4.9$ Hz, 1H), 0.03 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 179.2, 140.4, 134.5, 132.2,

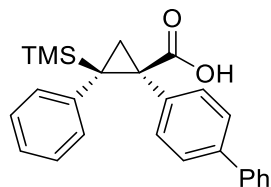
130.6, 127.6, 125.6, 121.0, 39.5, 34.1, 21.9, -0.7. FTIR: 3022, 2954, 2898, 2549, 1686, 1489, 1425, 1295, 1247, 1008, 840, 705 cm^{-1} . HRMS (ESI) m/z : $[M]^+$ (Pos.): calcd for $\text{C}_{19}\text{H}_{21}\text{O}_2\text{BrSi}$ 388.0489; found 388.0492.



2,2,2-trichloroethyl (1R,2R)-1-([1,1'-biphenyl]-4-yl)-2-phenyl-2-(trimethylsilyl)cyclopropane-1-carboxylate (4.53)

A round bottom flask was charged with α -trimethylsilylstyrene (**4.39**, 5.00 g, 28.4 mmol, 3.0 equiv), $\text{Rh}_2[(R)\text{-PTAD}]_4$ (**4.40**, 29.5 mg, 18.9 μmol , 0.2 mol%), and n-pentane (57 mL). Magnetic stirring was engaged, and then a solution of 2,2,2-trichloroethyl 2-([1,1'-biphenyl]-4-yl)-2-diazoacetate (**4.49**, 3.50 g, 9.47 mmol, 1.0 equiv) in CH_2Cl_2 /pentane (1:1 by volume, 76 mL) was added dropwise via an addition funnel over 30 min. After the addition of the diazo compound had completed, stirring was continued for an additional 1.5 h. Then, concentration under vacuum afforded 9.32 g of crude product as a green oil. Further purification was achieved by flash column chromatography (0-2% Et_2O /hexanes), which yielded 3.90 g of 2,2,2-trichloroethyl (1R,2R)-1-([1,1'-biphenyl]-4-yl)-2-phenyl-2-(trimethylsilyl)cyclopropane-1-carboxylate as a colorless solid (**4.53**, 80% yield). mp 83.0-83.5 $^\circ\text{C}$ (from hexanes). 98% ee (AD-H, 1.0 mL/min, 0.5% i-PrOH/hexanes. rt 6.9 min (minor), 8.3 min (major)) $[\alpha]_{\text{D}}^{20} - 78.3^\circ$ (c 1.00, CHCl_3). ^1H NMR (399 MHz, CDCl_3) δ 7.45 (d, $J = 7.4$ Hz, 2H), 7.35 (dd, $J = 8.4, 6.7$ Hz, 2H), 7.29 (s, 5H), 7.10 – 6.81 (m, 5H), 4.79 (d, $J = 11.9$ Hz, 1H), 4.70 (d, $J = 11.9$ Hz, 1H), 2.19 (d, $J = 5.0$ Hz, 1H), 2.00 (d, $J = 4.9$ Hz, 1H), 0.03 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 171.3, 140.5, 140.3, 139.4, 134.1, 130.8, 130.4, 128.6, 127.5, 127.2, 126.9, 126.1, 125.4, 94.7, 74.9,

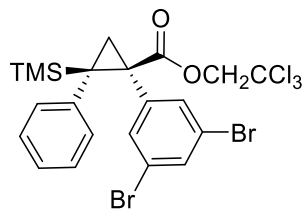
40.0, 33.1, 21.1, -1.0. FTIR: 3083, 3058, 3030, 2997, 2961, 2951, 1743, 1487, 1245, 1215, 1151, 1097, 838, 807, 758, 735, 715 cm^{-1} . HRMS (ESI) m/z : $[M+H]^+$ (Pos.): calcd for $\text{C}_{27}\text{H}_{28}\text{O}_2\text{Cl}_3\text{Si}$ 517.0919; found 517.0930.



(1R,2R)-1-([1,1'-biphenyl]-4-yl)-2-phenyl-2-(trimethylsilyl)cyclopropane-1-carboxylic acid (4.57)

2,2,2-trichloroethyl (1R,2R)-1-([1,1'-biphenyl]-4-yl)-2-phenyl-2-(trimethylsilyl)cyclopropane-1-carboxylate (**4.53**, 3.75 g, 7.24 mmol, 1.00 equiv) was dissolved in acetic acid (110 mL), and then zinc dust (2.37 g, 36.2 mmol, 5.00 equiv) was added. After stirring for 20 h, the mixture was partitioned between ethyl acetate (200 mL) and deionized water (200 mL). The organic phase was separated and washed with an additional 100 mL deionized water. Then, it was dried using MgSO_4 . The mixture was filtered and concentrated to afford 2.7 g of the crude product as a colorless solid. Additional purification by flash column chromatography yielded 2.24 g of pure (1R,2R)-1-([1,1'-biphenyl]-4-yl)-2-phenyl-2-(trimethylsilyl)cyclopropane-1-carboxylic acid as a colorless solid (**4.57**, 80% yield). Observed 97% ee (S,S-Whelk, 1 mL/min, 5% iPrOH/hex). Recrystallization from hot EtOAc/hexanes yielded an enantiopure product having >99% ee (recrystallization recovery 1.59 g, 71%). mp 191.5-192.0 $^{\circ}\text{C}$ (from EtOAc). $[\alpha]_{\text{D}}^{20}$ -125.5 $^{\circ}$ (c 1.00, CHCl_3). ^1H NMR (600 MHz, CDCl_3) δ 10.73 (s, 1H), 7.45 (d, J = 7.6 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.32 – 7.25 (m, 5H), 7.09 – 6.71 (m, 5H), 2.19 (d, J = 4.9 Hz, 1H), 2.02 (d, J = 4.8 Hz, 1H), 0.04 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 179.9, 140.7, 140.6, 139.4, 134.5, 130.8, 130.3, 128.6, 127.5, 127.1, 126.9, 126.1, 125.4, 39.9, 33.9, 21.8, -0.7. FTIR: 3081, 3058, 3030,

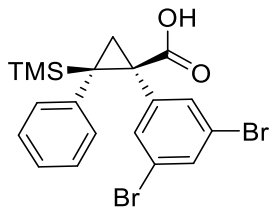
2954, 2898, 2854, 2606, 1685, 1487, 1423, 1298, 1247, 910, 838, 760, 731 cm^{-1} . HRMS (ESI) m/z : $[\text{M}-\text{H}]^-$ (Neg.): calcd for $\text{C}_{25}\text{H}_{25}\text{O}_2\text{Si}$ 385.1629; found 385.1623.



2,2,2-trichloroethyl (1*R*,2*R*)-1-(3,5-dibromophenyl)-2-phenyl-2-(trimethylsilyl)cyclopropane-1-carboxylate (4.54)

A round bottom flask was charged with α -trimethylsilylstyrene (**4.39**, 586 mg, 3.32 mmol, 3.0 equiv,) $\text{Rh}_2[\text{R-PTAD}]_4$ (**4.40**, 8.6 mg, 5.54 μmol , 0.5 mol%) and pentane (5 mL.) The mixture was stirred at a moderate rate as a solution of 2,2,2-trichloroethyl 2-diazo-2-(3,5-dibromophenyl)acetate (**4.50**, 500 mg, 1.11 mmol, 1.0 equiv) in pentane (20 mL) was added dropwise over 1.5 h via a syringe pump. After the addition had completed, the mixture was stirred for an additional 1.5 h, and then concentrated under vacuum to yield 827 mg of a green oil. Purification by flash column chromatography afforded 452 mg of the desired product **4.54** as a colorless solid (68% yield.) The material was carried forward without enantioenrichment at this stage. The diastereomeric ratio was > 95:5 by HNMR. mp 89.0-90.5 $^\circ\text{C}$ (CHCl_3). Observed 87% *ee*. (S,S-Whelk, 1.8 μm , 0.500 mL/min, 2.0% i-PrOH/hexanes. rt 3.144 (major,) 3.333 min (minor.) $[\alpha]_{\text{D}}^{20} - 35.3^\circ$ (c 1.00, CHCl_3) ^1H NMR (600 MHz, CDCl_3) δ 7.32 (d, $J = 1.7$ Hz, 2H), 7.29 (t, $J = 1.8$ Hz, 1H), 7.09 (td, $J = 7.3, 1.3$ Hz, 2H), 7.05 – 6.77 (m, 3H), 4.81 (d, $J = 11.9$ Hz, 1H), 4.69 (d, $J = 11.9$ Hz, 1H), 2.13 (d, $J = 5.1$ Hz, 1H), 2.04 (d, $J = 5.1$ Hz, 1H), 0.04 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 170.3, 139.6, 139.1, 133.8, 132.8, 132.5, 128.2, 127.9, 127.8, 126.0, 121.6, 94.5, 75.0, 39.5, 34.2, 21.8, -0.8. FTIR: 3068, 2953, 1739, 1549, 1247, 1215, 1159,

1116, 843, 785, 716, 701 cm^{-1} . HRMS (ESI) m/z : $[M]^+$ (Pos.): calcd for $\text{C}_{21}\text{H}_{21}\text{O}_2\text{Br}_2\text{Cl}_3\text{Si}$ 595.8738; found 595.8741.

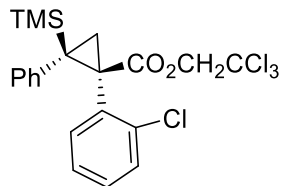


(1*R*,2*R*)-1-(3,5-dibromophenyl)-2-phenyl-2-(trimethylsilyl)cyclopropane-1-carboxylic acid (4.58)

A round bottom flask was charged with 2,2,2-trichloroethyl (1*R*,2*R*)-1-(3,5-dibromophenyl)-2-phenyl-2-(trimethylsilyl)cyclopropane-1-carboxylate (**4.54**, 286 mg, 1.00 equiv, 0.477 mmol), acetic acid (10 mL), and zinc dust (156 mg, 5.00 equiv, 2.38 mmol). The mixture was stirred for 16 h at room temperature. Then, it was partitioned between ethyl acetate (100 mL) and DI water (100 mL.) The organic phase was backwashed with an additional 100 mL portion of DI water. Then, the organic phase was dried using MgSO_4 . Concentration of the filtrate afforded 226 mg of crude product as a colorless oil. Further purification was achieved by flash column chromatography (0-20% Et_2O /hexane). Obtained 177 mg (79% yield) of **4.58** as a colorless solid. Further purification was accomplished by recrystallization from 100% hexanes (recrystallization recovery 119 mg, 67%). mp 175-176 $^\circ\text{C}$ (from 2-propanol). *ee* >99%. Chiral HPLC: AD-H, 1.0 mL/min, 2.0% *i*-PrOH/hexanes. rt 7.3 min (minor,) 8.6 min (major.) $[\alpha]_{\text{D}}^{20} - 66.8^\circ$ (c 1.00, CHCl_3). ^1H NMR (400 MHz, Acetone- d_6) δ 7.43 (d, $J = 1.8$ Hz, 2H), 7.36 (t, $J = 1.8$ Hz, 1H), 7.19 – 6.90 (m, 5H), 2.30 (d, $J = 5.3$ Hz, 1H), 1.97 (d, $J = 5.3$ Hz, 1H), 0.03 (s, 9H). ^{13}C NMR (126 MHz, Acetone- d_6) δ 172.5, 141.6, 140.7, 132.5, 131.6, 128.8, 127.8, 127.2, 125.5, 121.3,

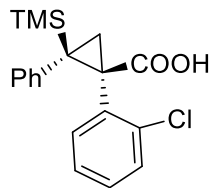
39.5, 33.1, 21.0, -1.4. FTIR: 3059, 2953, 2922, 2898, 1689, 1552, 1249, 838, 740, 694 cm^{-1} .

HRMS (ESI) m/z : $[M-H]^-$ (Neg.): calcd for $\text{C}_{19}\text{H}_{19}\text{O}_2\text{Br}_2\text{Si}$ 464.9516; found 464.9528.



2,2,2-trichloroethyl (1R,2R)-1-(2-chlorophenyl)-2-phenyl-2-(trimethylsilyl)cyclopropane-1-carboxylate (4.55)

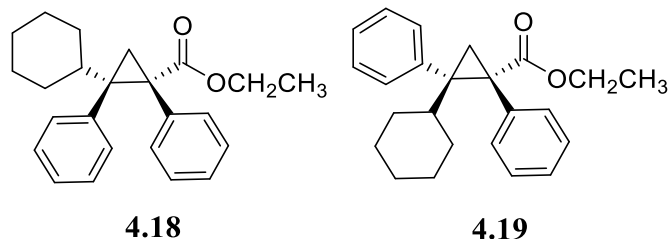
A round bottom flask was charged with α -trimethylsilyl styrene (**4.39**, 3.24 g, 3.00 equiv, 18.4 mmol), n-pentane (37 mL), and $\text{Rh}_2[(R)\text{-PTAD}]_4$ (**4.40**, 19.1 mg, 0.002 equiv, 12.3 μmol). Magnetic stirring was engaged, and then a solution of 2,2,2-trichloroethyl 2-(2-chlorophenyl)-2-diazoacetate (**4.51**, 2.01 g, 1.00 equiv, 6.13 mmol) in n-pentane (49 mL) was added dropwise via an addition funnel. Once the addition had completed, stirring at room temperature was continued for 16 h. Then, the mixture was concentrated to a thick green oil under vacuum, and the crude material was subjected to flash column chromatography (0-5% Et_2O /hexanes). Column purification yielded 2.54 g of the desired product **4.55** as a colorless oil (87% yield). Full characterization was not performed on this material because it could not be used to prepare a dirhodium tetracarboxylate catalyst. An enantiomeric excess determination was performed at the next step of the synthesis. ^1H NMR (500 MHz, CDCl_3) δ 7.55 – 7.32 (m, 1H), 7.18 (d, J = 7.8 Hz, 1H), 7.13 – 6.71 (m, 7H), 4.82 (d, J = 11.9 Hz, 1H), 4.56 (d, J = 11.9 Hz, 1H), 2.40 (d, J = 4.7 Hz, 1H), 1.83 (d, J = 4.7 Hz, 1H), 0.08 (s, 9H).



(1*R*,2*R*)-1-(2-chlorophenyl)-2-phenyl-2-(trimethylsilyl)cyclopropane-1-carboxylic acid

(4.59)

A scintillation vial was charged with 2,2,2-trichloroethyl (1*R*,2*R*)-1-(2-chlorophenyl)-2-phenyl-2-(trimethylsilyl)cyclopropane-1-carboxylate (**4.55**, 2.04 g, 1.00 equiv, 4.28 mmol), zinc dust (1.40 g, 5.00 equiv, 21.4 mmol), and acetic acid (33 mL). The mixture was stirred for 18 h, and then it was diluted with ethyl acetate (200 mL) and the organic phase was washed 3x with DI water. Then, it was dried over MgSO₄ and filtered. Concentration of the filtrate liquid under reduced pressure afforded a crude product as a colorless solid. Further purification was achieved via flash column chromatography (0-5% Et₂O/hexanes). 1.14 g of pure **4.59** were obtained as a colorless solid (77% yield). Observed >99% *ee* (AD-H, 1 mL/min, 2.0% iPrOH/hexanes. rt 13.3 min (major), 15.4 min (minor)). ¹H NMR (600 MHz, CDCl₃) δ 7.38 (s, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.04 – 6.63 (m, 7H), 2.41 (d, *J* = 4.7 Hz, 1H), 1.89 (d, *J* = 4.6 Hz, 1H), 0.04 (s, 9H). This ligand did not react with Na₄Rh₂(CO₃)₄ (**4.29**) or Rh₂(OAc)₄ to form a tetracarboxylate complex.



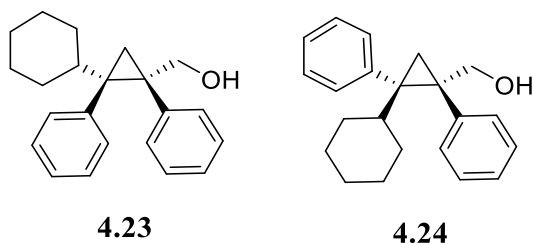
Ethyl 2-cyclohexyl-1,2-diphenylcyclopropane-1-carboxylate (**4.18** and **4.19**)

Procedure A (*E* diastereomer, **4.18):** A round bottom flask was charged with α -cyclohexylstyrene (**4.17**, 1.50 g, 8.05 mmol, 3.0 equiv,) $\text{Rh}_2[\text{R-}p\text{-PhTPCP}]_4$ (**4.20**, 47 mg, 26.8 μmol , 1.0 mol%) and CH_2Cl_2 (16.1 mL.) Stirring was turned on, and then a solution of ethyl phenyldiazoacetate (**4.16**, 510 mg, 2.68 mmol, 1.0 equiv) in CH_2Cl_2 (21.5 mL) was added over 1.5 h using a syringe pump. Once the addition had completed, stirring was continued for 1 h, at which time the mixture was concentrated to a thick green oil *in vacuo* (1.92 g.) This material showed an **4.18**:**4.19** ratio of 77:23 by HNMR. The components of the oil were separated by flash column (105 g SiO_2 , 0-5% EtOAc / hexanes,) affording 685 mg of the desired products as a faint green oil (73% yield.) The d.r. of this material was 74:26 (**4.18**:**4.19**). Further attempts to separate the diastereomers by normal phase column chromatography on a significant scale proved fruitless. The material was carried forward as a mixture of diastereomers (73% yield, 91% *ee* (**4.18**), 54% *ee* (**4.19**). Enantiomeric excess values for the reaction were assumed to be equal to the *ee* observed for the primary alcohol derivative (see next step.) Characterization data for the major product **4.18** were obtained via preparative TLC of a 24 mg sample of the racemic standard (5% EtOAc/hexanes, EMD PLC 60, 5% EtOAc/hexanes, 1 μm thickness, single plate.) ^1H NMR: (600 MHz, Chloroform-*d*) δ 7.42 – 7.30 (m, 2H), 7.11 – 7.05 (m, 4H), 7.01 (dtd, J = 14.2, 7.4, 6.8, 1.4 Hz, 4H), 4.25 (dd, J = 10.8, 7.1 Hz, 1H), 4.17 (dd, J = 10.8, 7.1 Hz, 1H), 2.18 – 2.06 (m, 1H), 1.90 (d, J = 5.3 Hz, 1H), 1.87 (d, J = 5.4 Hz, 1H), 1.78 – 1.69 (m, 2H), 1.69 – 1.63

(m, 1H), 1.53 (s, 1H), 1.32 (t, $J = 7.1$ Hz, 3H), 1.29 – 1.10 (m, 6H), 0.91 (tdd, $J = 12.9, 9.2, 4.2$ Hz, 1H), 0.79 – 0.68 (m, 1H). ^{13}C NMR: (75 MHz, Chloroform- d) δ 171.9, 137.3, 136.2, 132.2, 130.6, 127.3, 126.7, 126.5, 126.2, 77.4, 77.0, 76.6, 61.2, 45.4, 44.7, 41.8, 31.1, 30.8, 29.7, 26.8, 26.7, 26.2, 22.3, 14.3. FTIR: 3057, 2926, 2851, 1717, 1448, 1244, 1188, 1122, 1028, 696 cm^{-1} . HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ (Pos.) calcd for $\text{C}_{24}\text{H}_{29}\text{O}_2$ 349.2162; found 349.2158.

Procedure B (Z Diastereomer, 4.19): A round bottom flask was charged with α -cyclohexylstyrene (**4.17**, 1.18 g, 6.31 mmol, 3.0 equiv,) $\text{Rh}_2[\text{R-DOSP}]_4$ (**4.21**, 39.9 mg, 21.0 μmol , 1.0 mol%) and pentane (12.6 mL.) Stirring was turned on, and then a solution of ethyl phenyldiazoacetate (**4.16**, 400 mg, 2.10 mmol, 1.0 equiv) in pentane (16.8 mL) was added over 1.5 h using a syringe pump. Stirring was continued for 16 h, at which time the mixture was concentrated *in vacuo* to afford 1.62 g of a greenish to orange oil. This material showed an **4.18:4.19** ratio of 30:70 by HNMR. The components of the mixture were separated by flash column (80 g SiO_2 , 0-5% EtOAc / hexanes.) 436 mg of the desired products were obtained from the column as a colorless oil; the d.r. of this material was 40:60 (**4.18:4.19**). Further attempts to separate the diastereomers by normal phase column chromatography on a significant scale proved fruitless. The material was carried forward as a mixture of **4.18** and **4.19**. (59% yield, 41% *ee* (**4.18**), 79% *ee* (**4.19**).) Enantioselectivities for the reaction were assumed to be equal to the *ee* observed for the primary alcohol derivative (see next step.) Characterization data for the major product **4.19** were obtained by preparative TLC using a 24 mg sample of the racemic standard. ^1H NMR (600 MHz, Chloroform- d) δ 7.70 – 7.57 (m, 2H), 7.36 (dd, $J = 8.2, 7.0$ Hz, 2H), 7.34 – 7.25 (m, 5H), 7.23 (dt, $J = 6.9, 1.8$ Hz, 1H), 3.71 (dd, $J = 10.8, 7.1$ Hz, 1H), 3.51 (dd, $J = 10.8, 7.1$ Hz, 1H), 2.26 (d, $J = 4.8$ Hz, 1H), 1.91 (dt, $J = 12.3, 2.7$ Hz, 1H), 1.71 – 1.59 (m, 1H), 1.57 (s, 1H), 1.52 (d, $J = 4.9$ Hz, 1H), 1.50 – 1.44 (m, 1H), 1.40 – 1.35 (m, 1H), 1.04 – 0.88

(m, 2H), 0.86 – 0.71 (m, 5H), 0.68 (tt, $J = 12.8, 3.2$ Hz, 1H), 0.50 (ddd, $J = 11.6, 8.6, 3.0$ Hz, 1H). ^{13}C NMR (75 MHz, Chloroform- d) δ 171.3, 139.0, 136.3, 131.8, 131.1, 127.6, 127.3, 127.1, 126.5, 77.5, 77.0, 76.6, 60.6, 45.7, 43.7, 42.3, 30.8, 30.2, 29.7, 26.6, 26.0, 25.9, 22.6, 13.6. FTIR: 3057, 2926, 2852, 1717, 1446, 1272, 1191, 1067, 1029, 700 cm^{-1} . HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ (Pos.) calcd for $\text{C}_{24}\text{H}_{29}\text{O}_2$ 349.2162; found 349.2156.

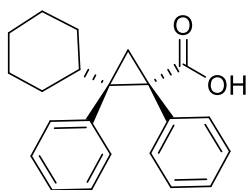


2-cyclohexyl-1,2-diphenylcyclopropylmethanol (**4.23** and **4.24**)

Procedure A: To a round bottom flask was added: the 74:26 mixture of cyclopropyl esters **4.18** and **4.19** (410 mg, 1.18 1.0 equiv) and CH_2Cl_2 (50 mL.) The resulting solution was cooled to -78°C using a bath of dry ice/acetone, and then a solution of diisobutylaluminum hydride (**4.22**, 837 mg, 5.88 mmol, 5.0 equiv) in CH_2Cl_2 (5.88 mL, 1.0 M) was added dropwise via syringe to the stirring mixture. The mixture gradually warmed to room temperature over 5-6 hours as the dry ice sublimed. After a total of 18 h, the flask was cooled to 0°C using an ice bath, and methanol (5.88 mL) was added dropwise via syringe to quench the reaction. The mixture was concentrated under vacuum and passed through a plug of silica gel (30 g, 100% EtOAc as eluent.) The filtrate liquid was concentrated *in vacuo* to afford 341 mg of a mixture of **4.23** and **4.24** as a colorless solid (94% yield.) Complete separation of **4.23** and **4.24** was achieved via preparative HPLC. (Supelco Ascentis C18, 25 cm x 21.2 mm, 5 μm . 15 mL/min. [0.1% TFA in MeCN] = 90%, [0.1% TFA in H_2O] = 10% (v/v.) 500 μL DMSO injections, 50 mg/mL. rt 8.8 min (**4.23**, major), 10.9 min (**4.24**, minor).) Compound **4.23** was carried forward to the next steps without

enantioenrichment. Characterization data for compound **4.23**: 91% *ee* (R,R-Whelk, 1.0 mL/min, 5.0% i-PrOH/hexanes. rt 5.3 min (minor,) 5.8 min (major).) $[\alpha]_D^{20} - 8.2^\circ$ (c 1.00, CHCl₃) ¹H NMR (600 MHz, CDCl₃) δ 7.15 – 7.11 (m, 2H), 7.09 (t, *J* = 7.7 Hz, 2H), 7.03 – 6.91 (m, 6H), 4.60 (dd, *J* = 11.6, 1.3 Hz, 1H), 3.89 (d, *J* = 11.5 Hz, 1H), 1.92 – 1.87 (m, 1H), 1.83 (dd, *J* = 5.2, 1.3 Hz, 1H), 1.80 – 1.64 (m, 5H), 1.60 – 1.52 (m, 1H), 1.41 (ddd, *J* = 11.6, 8.4, 3.0 Hz, 1H), 1.33 – 1.17 (m, 3H), 1.13 (d, *J* = 5.2 Hz, 1H), 0.91 (tdd, *J* = 12.9, 9.1, 3.8 Hz, 1H), 0.65 (tdd, *J* = 12.9, 11.6, 3.6 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 139.8, 138.8, 132.3, 129.1, 127.9, 126.6, 126.0, 125.7, 67.2, 45.0, 44.0, 38.6, 32.0, 31.2, 29.7, 26.9, 26.8, 26.1, 22.2. FTIR: 3239, 3083, 2923, 2850, 1448, 1036, 1020, 907, 706, 695 cm⁻¹. HRMS (ESI) *m/z*: [M+Na]⁺ (Pos.) calcd for C₂₂H₂₆ONa 329.1876; found 329.1873. **Procedure B**: A round bottom flask was charged with the 40:60 mixture of (**4.18:4.19**) (436 mg, 1.25 mmol, 1.0 equiv) and CH₂Cl₂ (50 mL.) The mixture was cooled to -78 °C using a bath of dry ice/acetone, and then a solution of diisobutylaluminum hydride (890 mg, 6.26 mmol, 5.0 equiv) in CH₂Cl₂ (6.26 mL, 1.0 M) was added dropwise to the mixture via syringe with stirring on. The mixture gradually warmed to room temperature over 5-6 hours as the dry ice sublimed. After a total of 17 h, the flask was cooled to 0 °C using an ice bath, and methanol (6.26 mL) was added dropwise to quench the reaction. After stirring for 1 h, the mixture was concentrated to a colorless solid *in vacuo*, and the product was passed through a plug of silica gel (30 g, 100% EtOAc as eluent.) The filtrate liquid was concentrated under vacuum, affording 380 mg of a mixture of **4.23** and **4.24** as colorless solid (98% yield.) Complete separation of **4.23** and **4.24** was achieved via preparative HPLC. (Supelco Ascentis C18, 25 cm x 21.2 mm, 5 μ m. 15 mL/min. [0.1% TFA in MeCN] = 90%, [0.1% TFA in H₂O] = 10% (v/v.) 500 μ L DMSO injections, 50 mg/mL. rt 8.8 min (**4.23**, minor), 10.9 min (**4.24**, major).) Characterization data for compound **4.24**: 81% *ee* (R,R-Whelk,

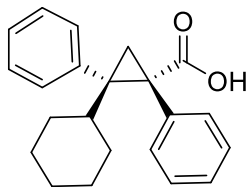
1 mL/min, 5% iPrOH/hexanes. rt 4.0 min (minor,) 5.0 min (major)) $[\alpha]_{\text{D}}^{20} - 61.9^\circ$ (c 1.00, CHCl_3) ^1H NMR (600 MHz, CDCl_3) δ 7.52 (d, $J = 7.4$ Hz, 3H), 7.38 (t, $J = 7.7$ Hz, 3H), 7.34 – 7.21 (m, 5H), 3.83 (dd, $J = 11.6, 1.4$ Hz, 1H), 2.96 (d, $J = 11.6$ Hz, 1H), 1.74 (d, $J = 12.7$ Hz, 1H), 1.64 (d, $J = 12.6$ Hz, 1H), 1.43 (d, $J = 13.4$ Hz, 1H), 1.38 – 1.31 (m, 2H), 1.29 – 1.22 (m, 3H), 1.01 – 0.91 (m, 1H), 0.87 (qd, $J = 12.5, 3.4$ Hz, 1H), 0.82 – 0.72 (m, 2H), 0.63 (qt, $J = 12.9, 3.4$ Hz, 1H), 0.53 – 0.44 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 139.4, 139.3, 131.4, 130.4, 128.2, 128.0, 127.0, 126.8, 126.4, 69.9, 43.8, 42.2, 39.5, 30.5, 30.3, 29.7, 26.6, 26.3, 26.0, 21.3. FTIR: 3279, 3059, 3023, 2923, 2851, 1448, 1020, 999, 783, 704 cm^{-1} . HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ (Pos.) calcd for $\text{C}_{22}\text{H}_{26}\text{ONa}$ 329.1876; found 329.1871.



(1*R*,2*S*)-2-cyclohexyl-1,2-diphenylcyclopropane-1-carboxylic acid (4.27)

To a round bottom flask was added: ((1*R*,2*S*)-2-cyclohexyl-1,2-diphenylcyclopropyl)methanol (188 mg, 0.61 mmol, 1.0 equiv) and acetone (9.8 mL.) Stirring was turned on, and then a solution of Jones reagent composed of chromium (VI) oxide (**4.25**, 280 mg, 1.84 mmol, 3.0 equiv,) water (0.78 mL,) and sulfuric acid (**4.26**, 240 mg, 2.45 mmol, 0.13 mL, 4.0 equiv) was slowly added to the reaction mixture via syringe. The syringe was flushed with the reaction mixture to ensure near-quantitative transfer. Stirring was continued for a 2 h 10 min, and then the reaction was quenched via the addition of 2-propanol (8.5 mL.) Formation of a dark green precipitate was observed. At this stage, the mixture was partitioned between EtOAc (75 mL) and water (75 mL.) The organic phase was separated, and the aqueous phase was extracted with two additional 75 mL portions of EtOAc. The pooled organic phase was dried over Na_2SO_4 and

filtered. Concentration of the filtrate liquid under vacuum afforded 180 mg of a colorless solid. The components of the material were separated by flash column chromatography (24 g SiO₂, 0-20% EtOAc / hexanes,) affording 116 mg of the title compound **4.27** as a colorless solid (59% yield.) The product was purified to a single enantiomer via crystallization from hexanes, affording 73 mg of the material (99% ee. R,R-Whelk, 1.0 mL/min, 5.0% i-PrOH/hexanes. rt 5.3 min (minor,) 5.8 min (major).) $[\alpha]_{\text{D}}^{20}$ - 3.3° (c 0.94, CHCl₃). mp 213.5-215.0 °C. ¹H NMR (600 MHz, CDCl₃) δ 10.43 (s, 1H), 7.37 – 7.31 (m, 2H), 7.12 – 7.06 (m, 4H), 7.02 (dt, J = 14.9, 7.0 Hz, 4H), 2.06 (d, J = 11.8 Hz, 1H), 2.02 (dd, J = 5.3, 1.7 Hz, 1H), 1.97 (dd, J = 5.3, 1.7 Hz, 1H), 1.72 (d, J = 12.9 Hz, 2H), 1.63 (q, J = 12.7, 11.7 Hz, 2H), 1.55 (d, J = 13.5 Hz, 1H), 1.32 – 1.13 (m, 3H), 0.98 – 0.84 (m, 1H), 0.74 – 0.60 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 178.6, 137.2, 135.7, 132.0, 131.0, 127.3, 126.8, 126.7, 126.4, 47.3, 43.8, 40.9, 31.3, 30.9, 26.9, 26.7, 26.2, 23.6. FTIR: 3062, 3023, 2928, 2858, 1690, 1493, 1448, 1390, 1253, 892, 731, 709, 696 cm⁻¹. HRMS (ESI) m/z: [M+H]⁺ (Pos.) calcd for C₂₂H₂₅O₂ 321.1849; found 321.1848.



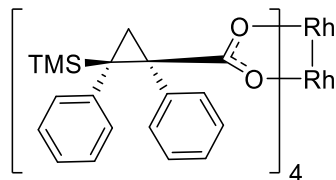
(1R,2S)-2-cyclohexyl-1,2-diphenylcyclopropane-1-carboxylic acid (4.28)

To a round bottom flask was added: ((1R,2R)-2-cyclohexyl-1,2-diphenylcyclopropyl)methanol (**4.24**, 24 mg, 78 μ mol, 1.0 equiv) and acetone (1.25 mL.) Magnetic stirring was turned on, and then a solution of Jones reagent composed of sulfuric acid (**4.26**, 30 mg, 0.31 mmol, 3.9 equiv,) chromium(VI) oxide (**4.25**, 32 mg, 0.21 mmol, 2.7 equiv,) and water (0.10 mL) was added to the mixture via syringe. The syringe was flushed with the reaction mixture to ensure near-quantitative transfer. After the addition was complete, the reaction was continued for 1 h 30 min.

Then, it was quenched via the addition of 2-propanol (1 mL,) causing a color change from bright orange to dark forest green. The mixture was partitioned between H₂O (25 mL) and EtOAc (25 mL.) The organic phase was separated, and the aqueous phase was extracted with two additional portions of EtOAc (25 mL each.) The pooled organic phase was dried with Na₂SO₄ and filtered. Concentration of the filtrate liquid under vacuum afforded 25 mg of a colorless oil. Flash chromatography on silica gel (12 g, 0-25% EtOAc/hexanes) afforded the desired product **4.28** as a colorless solid (17 mg, 68% yield.) Enantioenrichment of this material required derivatization to the sodium salt prior to crystallization: 116 mg of (1*R*,2*S*)-2-cyclohexyl-1,2-diphenylcyclopropane-1-carboxylic acid (**4.28**, obtained from multiple runs) was treated with a solution of sodium hydroxide (80 mg, 2.0 mmol, 5.5 equiv) in 3.1 mL deionized water. The resulting mixture was sonicated for 1 minute, causing a visible change in the appearance of the insoluble material. Then, methanol (1.5 mL) and additional water (3.0 mL) were added. The mixture was heated for 1 minute at just under the reflux temperature, resulting in complete dissolution of the solid phase. The solution was slowly cooled to room temperature, yielding the enantiopure sodium carboxylate salt as a colorless solid. The material thus obtained was filtered and then passed through silica gel (20 g) with 100% EtOAc to neutralize the material. 70 mg of the desired product were obtained after drying under high vacuum (60% recovery.) (99% ee. *R,R*-Whelk, 1.0 mL/min, 5.0% i-PrOH/hexanes. rt 5.4 min (minor,) 8.9 min (major.) $[\alpha]_D^{20} - 84.2^\circ$ (c 1.17, CHCl₃). mp 203.0-205.0 °C. ¹H NMR (399 MHz, CDCl₃) δ 7.55 – 7.50 (m, 2H), 7.36 – 7.26 (m, 3H), 7.25 – 7.13 (m, 5H), 2.10 (d, *J* = 4.8 Hz, 1H), 1.83 (d, *J* = 11.0 Hz, 1H), 1.56 (td, *J* = 9.0, 4.2 Hz, 2H), 1.49 (d, *J* = 4.8 Hz, 1H), 1.48 – 1.39 (m, 1H), 1.34 (d, *J* = 12.1 Hz, 1H), 1.00 – 0.85 (m, 2H), 0.83 – 0.71 (m, 1H), 0.71 – 0.59 (m, 2H), 0.46 (ddd, *J* = 11.3, 8.7, 2.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 177.0, 138.3, 135.8, 131.7, 130.8, 127.6, 127.4, 127.3,

126.6, 46.9, 43.7, 41.9, 30.8, 30.2, 26.6, 26.0, 25.9, 23.6. FTIR: 3240, 3029, 2925, 2852, 1716, 1682, 1454, 1379, 1177, 819, 754, 707, 696 cm^{-1} . HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ (Pos.) calcd for $\text{C}_{22}\text{H}_{25}\text{O}_2$ 321.1849; found 321.1848.

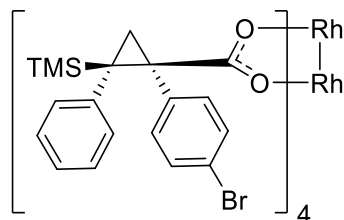
S.4.4 Preparation and Characterization of Dirhodium Catalysts



Dirhodium tetrakis ((1*R*,2*R*)-1,2-diphenyl-2-(trimethylsilyl)cyclopropane-1-carboxylic acid) (4.6)

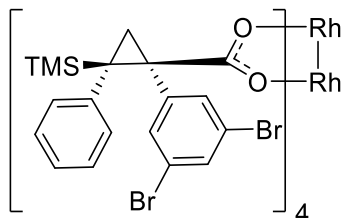
A round bottomed flask was charged with (1*R*,2*R*)-1,2-diphenyl-2-(trimethylsilyl)cyclopropane-1-carboxylic acid (**4.48**, 199.6 mg, 0.64 mmol, 8.0 equiv,) degassed, deionized water (7.2 mL) and the methanol adduct of sodium rhodium carbonate (**4.29**, 49.7 mg, 80.4 μmol , 1.0 equiv.) A reflux condenser was attached to the flask, and the apparatus was purged with argon for 15 minutes. Stirring was turned on (1300 rpm,) and then the mixture was heated to a gentle reflux under an argon atmosphere (bath temperature 103 $^{\circ}\text{C}$.) After 22 h, the mixture was cooled to room temperature, and then water was distilled off at 40 $^{\circ}\text{C}$ using a rotary evaporator, affording a green solid. The components of the material were separated by flash column chromatography on silica gel (40 g, 0-2% MeCN/toluene, then 12 g, 0-12% Et_2O /ligroin.) 46.6 mg of the title compound **4.6** were obtained as a green solid after lyophilization from C_6H_6 (40% yield.) mp 155-165 $^{\circ}\text{C}$ (dec. from C_6H_6) ^1H NMR (600 MHz, CDCl_3) δ 6.99 – 6.93 (m, 5H), 6.90 (dd, J = 8.0, 6.4 Hz, 3H), 6.87 – 6.83 (m, 1H), 6.74 (d, J = 7.7 Hz, 1H), 2.17 (d, J = 4.3 Hz, 1H), 1.63 (d, J = 4.3 Hz, 1H), 0.01 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 193.0, 142.0, 137.3, 131.9, 130.5,

127.9, 127.6, 127.1, 126.9, 126.1, 124.9, 42.2, 33.3, 23.4, 0.7. FTIR: 3057, 3025, 2928, 1573, 1393, 1247, 841, 695 cm^{-1} . HRMS (ESI) m/z : $[M+H]^+$ (Pos.) calcd for $\text{C}_{76}\text{H}_{85}\text{O}_8\text{Rh}_2\text{Si}_4$ 1443.3426; found 1443.3397.



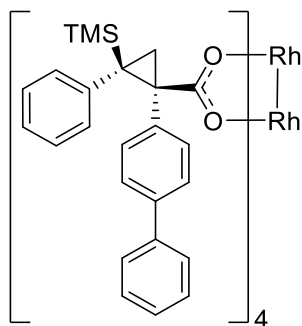
Dirhodium tetrakis ((1*R*,2*R*)-1-(4-bromophenyl)-2-phenyl-2-(trimethylsilyl)cyclopropane-1-carboxylic acid) (4.7**)**

To a round bottomed flask equipped with a reflux condenser was added: (1*R*,2*R*)-1-(4-bromophenyl)-2-phenyl-2-(trimethylsilyl)cyclopropane-1-carboxylic acid (**4.56**, 277 mg, 0.71 mmol, 8.0 equiv,) the methanol adduct of sodium rhodium carbonate (**4.29**, 54.9 mg, 89 μmol , 1.0 equiv,) and degassed, deionized water (8 mL.) The mixture was heated for 3 days at a bath temperature of 103 $^{\circ}\text{C}$ (gentle reflux) and a stir rate of 1000 rpm. Then, water was distilled off at 40 $^{\circ}\text{C}$ using a rotary evaporator, and the resulting green residue was subjected to flash column chromatography (24 g SiO_2 , 0-5% EtOAc/hexanes.) The title compound **4.7** was obtained as a green solid (68 mg, 44% yield) after lyophilization from C_6H_6 . mp 224.0-224.5 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 7.14 – 7.06 (m, 2H), 7.02 – 6.85 (m, 4H), 6.78 – 6.71 (m, 2H), 6.69 (dd, J = 7.3, 1.8 Hz, 1H), 2.05 (d, J = 4.3 Hz, 1H), 1.60 (d, J = 4.2 Hz, 1H), -0.02 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.6, 141.3, 136.4, 132.3, 131.6, 130.4, 128.0, 127.6, 127.3, 125.4, 120.4, 41.6, 33.5, 23.7, 0.6. FTIR: 3059, 3026, 2948, 2896, 1573, 1490, 1400, 1385, 1248, 1010, 843, 701 cm^{-1} . HRMS (ESI) m/z : $[M+H]^+$ (Pos.) calcd for $\text{C}_{76}\text{H}_{85}\text{O}_8\text{Br}_4\text{Rh}_2\text{Si}_4$ 1753.9768; found 1753.9803.



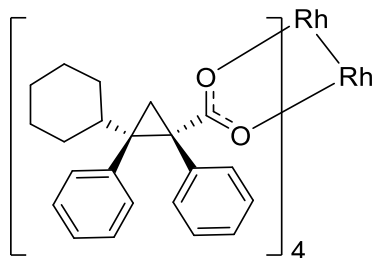
Dirhodium tetrakis ((1*R*,2*R*)-1-(3,5-dibromophenyl)-2-phenyl-2-(trimethylsilyl)cyclopropane-1-carboxylic acid) (4.9**)**

A round bottom flask equipped with a reflux condenser was charged with (1*R*,2*R*)-1-(3,5-dibromophenyl)-2-phenyl-2-(trimethylsilyl)cyclopropane-1-carboxylic acid (**4.58**, 380 mg, 0.81 mmol, 8.0 equiv,) the methanol adduct of sodium rhodium carbonate (**4.29**, 62.7 mg, 0.10 mmol, 1.0 equiv,) and degassed, deionized water (9.1 mL.) The mixture was heated at a block temperature of 105 °C (gentle reflux) and stir rate of 1500 rpm under an argon atmosphere. After 3 d, the mixture was frozen with dry ice and lyophilized. The components of the resulting green solid were separated by column chromatography on silica gel (24 g, 0-4% EtOAc/hexanes) followed by preparative TLC (EMD PLC 60, 50% toluene/pentane, 1 µm thickness, single plate.) 59 mg of the desired product were obtained after lyophilization from C₆H₆ (**4.9**, 28% yield.) mp 185-195 °C (dec.) ¹H NMR (399 MHz, CDCl₃) δ 7.22 (t, *J* = 1.7 Hz, 1H), 7.07 (td, *J* = 7.5, 7.0, 1.3 Hz, 1H), 7.00 (td, *J* = 6.7, 5.8, 2.6 Hz, 4H), 6.95 – 6.88 (m, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 2.09 (d, *J* = 4.4 Hz, 1H), 1.64 – 1.55 (m, 1H), 0.02 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 192.0, 141.3, 140.9, 132.8, 132.0, 131.6, 128.2, 127.3, 127.1, 125.7, 121.6, 41.5, 33.8, 24.1, 0.7. FTIR: 3058, 2952, 1684, 1578, 1551, 1386, 1258, 1249, 843, 740, 703 cm⁻¹. HRMS (ESI) *m/z*: [M+H]⁺ (Pos.) calcd for C₇₆H₇₆O₈Br₇⁸¹BrRh₂Si₄ 2067.6168; found 2067.6150.



**(1*R*,2*R*)-1-([1,1'-biphenyl]-4-yl)-2-phenyl-2-(trimethylsilyl)cyclopropane-1-carboxylic acid
(4.8)**

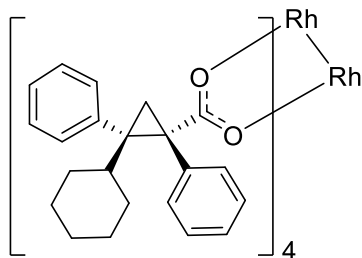
A round bottom flask attached to a reflux condenser was charged with (1*R*,2*R*)-1-([1,1'-biphenyl]-4-yl)-2-phenyl-2-(trimethylsilyl)cyclopropane-1-carboxylic acid (**4.57**, 1.15 g, 2.97 mmol, 8.0 equiv), sodium rhodium carbonate (**4.29**, 230 mg, 0.37 mmol, 1.00 equiv), and degassed deionized water (35 mL). The mixture was stirred at vigorous reflux for 20 h, and then it was concentrated to a solid green residue under high vacuum. The crude material was dry-loaded onto silica gel (10 g) and the desired product was separated by flash column chromatography (0-5% EtOAc/hexanes). 241 mg of a green solid were obtained after lyophilization from C₆H₆ (**4.8**, 37% yield). mp 226-227 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.48 – 7.27 (m, 5H), 7.20 (d, *J* = 7.9 Hz, 2H), 6.98 (p, *J* = 8.0 Hz, 5H), 6.86 (d, *J* = 7.2 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 2.20 (d, *J* = 4.9 Hz, 1H), 1.72 (d, *J* = 4.2 Hz, 1H), 0.06 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 192.9, 141.9, 140.8, 138.6, 136.6, 131.8, 131.0, 128.6, 127.8, 127.0, 126.8, 125.8, 125.0, 41.9, 33.6, 23.6, 0.8. FTIR: 3079, 3056, 3027, 2949, 2895, 1684, 1573, 1486, 1386, 1247, 835, 761 cm⁻¹ HRMS (ESI) *m/z*: [M+H]⁺ (Pos.) calcd for C₁₀₀H₁₀₀O₈Rh₂Si₄ 1746.4600; found 1746.4604.



Dirhodium tetrakis ((1*R*,2*S*)-2-cyclohexyl-1,2-diphenylcyclopropane-1-carboxylic acid)

(4.4)

A round bottom flask equipped with a reflux condenser was loaded with (1*R*,2*S*)-2-cyclohexyl-1,2-diphenylcyclopropane-1-carboxylic acid (**4.27**, 73 mg, 0.23 mmol, 8.0 equiv,) the methanol adduct of sodium rhodium carbonate (**4.29**, 17.6 mg, 28.5 μ mol, 1.0 equiv) and degassed, deionized water (2.5 mL.) The flask was sonicated for ca. 5 minutes under an argon balloon to homogenize the mixture prior to the reaction period. Then, it was heated at a bath temperature of 103 °C (gentle reflux) under an argon atmosphere. Magnetic stirring was maintained at 1090 rpm throughout the reaction period. Heating was continued for 2 days. Then, the mixture was frozen with dry ice and lyophilized. The desired product was purified from the crude solid material by flash column chromatography (24 g SiO₂, 0-8% EtOAc/hexanes,) affording 35 mg of the title compound as a green solid (**4.4**, 83% yield.) mp 224-227 °C. ¹H NMR (399 MHz, CDCl₃) δ 7.08 – 6.30 (m, 10H), 1.92 (d, *J* = 5.0 Hz, 1H), 1.79 (d, *J* = 5.0 Hz, 1H), 1.75 – 1.46 (m, 7H), 1.38 (q, *J* = 13.2, 12.0 Hz, 1H), 1.25 (td, *J* = 8.5, 7.8, 5.4 Hz, 2H), 0.86 (t, *J* = 13.2 Hz, 1H), 0.75 (dd, *J* = 13.1, 10.0 Hz, 1H), 0.60 (td, *J* = 13.2, 9.8 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 191.2, 137.7, 136.5, 130.6, 128.3, 126.7, 126.1, 125.7, 125.5, 48.2, 42.7, 42.4, 31.5, 30.9, 27.0, 26.8, 26.2, 23.9. FTIR: 3055, 2923, 2851, 1568, 1495, 1448, 1387, 697, 676 cm⁻¹. HRMS (ESI) *m/z*: [M]⁺ (Pos.) calcd for C₈₈H₉₂O₈Rh₂ 1482.4897; found 1482.4890.



Dirhodium tetrakis ((1*R*,2*R*)-2-cyclohexyl-1,2-diphenylcyclopropane-1-carboxylic acid)

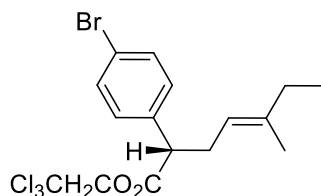
(4.5)

To a 10 mL round-bottomed flask equipped with a reflux condenser was added: (1*R*,2*R*)-2-cyclohexyl-1,2-diphenylcyclopropane-1-carboxylic acid (**4.28**, 70 mg, 0.22 mmol, 8.0 equiv,) the methanol adduct of sodium rhodium carbonate (**4.29**, 16.9 mg, 27.3 μ mol, 1.0 equiv,) and degassed, deionized water (2.5 mL.) Magnetic stirring was engaged, and the mixture was heated at a bath temperature of 103 °C (gentle reflux) for 3 days. Then, the mixture was frozen with dry ice and lyophilized to a green solid. The material was then subjected to flash column purification (12 g, 0-7% EtOAc/hexanes.) 24 mg of the desired product were obtained after drying under high vacuum (**4.5**, 59% yield.) mp 222-225 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.30 – 7.26 (m, 1H), 7.22 (ddt, J = 12.0, 7.0, 3.4 Hz, 5H), 7.14 – 7.02 (m, 2H), 6.98 – 6.88 (m, 2H), 1.50 – 1.39 (m, 2H), 1.36 (p, J = 4.6 Hz, 3H), 1.32 – 1.28 (m, 1H), 1.27 – 1.22 (m, 2H), 0.85 – 0.75 (m, 1H), 0.64 (qt, J = 12.4, 6.5 Hz, 2H), 0.44 – 0.27 (m, 2H), 0.13 (tt, J = 11.4, 2.7 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 188.8, 138.4, 137.0, 131.8, 131.3, 131.0, 127.7, 127.1, 126.6, 126.3, 125.9, 45.5, 43.7, 43.2, 30.4, 29.5, 26.7, 26.0, 25.9, 24.2. FTIR (solid): 3057, 3026, 2926, 2851, 1577, 1493, 1445, 1388, 701, 675 cm^{-1} . HRMS (ESI) m/z : $[\text{M}]^-$ (Neg.) calcd for $\text{C}_{88}\text{H}_{92}\text{O}_8\text{Rh}_2$ 1482.4908; found 1482.4902.

S.4.5 Reactions with Other Substrates

General Procedure A for C-H Insertion into Primary Allylic and Benzylic Sites

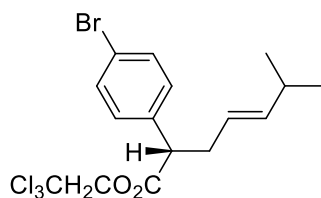
A scintillation vial was charged with the C-H substrate (3.00 equiv, 0.60 mmol), CH_2Cl_2 (1.0 mL), and the indicated dirhodium catalyst (**4.11** or **4.8**, 0.005 Eq, 1.0 μmol). Stirring was turned on, and the mixture was heated to light reflux. Then, a solution of 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**4.30**, 74 mg, 1.00 Eq, 0.20 mmol) in CH_2Cl_2 (2.5 mL) was added dropwise via a syringe pump over 1.5 h. After an additional 1.5 h stir period, the mixture was concentrated under vacuum to a thick green oil. The crude material was wet-loaded onto a silica gel column (normal phase, 12 g) using 100% hexanes and the products were isolated via flash chromatography (0-5% Et_2O /hexanes). Isolated yield, optical rotations and *ee* are reported based on the catalyst and product indicated. The *para* bromo catalyst (**4.11**) used in these experiments was the (1*S*,2*S*) enantiomer, while the *para* phenyl catalyst (**4.8**) was (1*R*,2*R*). Absolute configurations are reported based on the precedent established by reference 2.



2,2,2-trichloroethyl (*S,E*)-2-(4-bromophenyl)-5-methylhept-4-enoate (**4.60**)

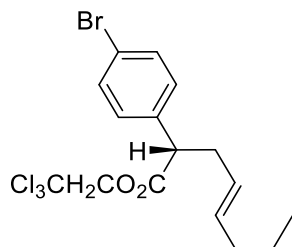
General Procedure A was applied to the functionalization of (*E*)-3-methylpent-2-ene (50 mg, 3.00 Eq, 0.60 mmol). The title compound **4.60** was obtained as a colorless oil. Prepared with catalyst **4.11**: 87% yield, 90% *ee* (AD-H, 1 mL/min, 1.0% *i*PrOH/hex. *rt* = 5.23 min (major), 5.72 min (minor.)) [α]_D²⁰ + 27.1° (*c* = 1.00, CHCl_3). ¹H NMR (300 MHz, CDCl_3) δ 7.49 – 7.41

(m, 2H), 7.28 – 7.17 (m, 2H), 5.03 (tdd, $J = 6.2, 2.9, 1.4$ Hz, 1H), 4.76 (d, $J = 12.0$ Hz, 1H), 4.66 (d, $J = 12.0$ Hz, 1H), 3.67 (t, 1H), 2.94 – 2.73 (m, 1H), 2.58 – 2.40 (m, 1H), 1.93 (q, 2H), 0.92 (t, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 171.7, 140.4, 136.9, 131.7, 129.9, 121.5, 118.5, 94.8, 74.0, 51.2, 32.3, 31.8, 16.1, 12.7. FTIR (film): 2962, 2931, 2874, 2853, 1751, 1488, 1440, 1407, 1372, 1336, 1261, 1134, 1074, 1012, 825, 801, 756, 721 cm^{-1} . HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ (Pos.) calcd for $\text{C}_{16}\text{H}_{19}\text{O}_2\text{BrCl}_3$ 426.9629; found 426.9636.



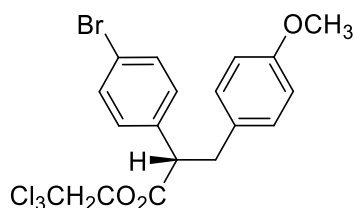
2,2,2-trichloroethyl (S,E)-2-(4-bromophenyl)-6-methylhept-4-enoate (**4.61**)

General Procedure A was applied to the functionalization of (*E*)-4-methylpent-2-ene (50 mg, 3.00 Eq, 0.60 mmol). The title compound **4.61** was obtained as a colorless oil. Prepared with catalyst **4.11**: 62% yield, 89% *ee* (AD-H, 1 mL/min, 1.0% iPrOH/hex. $r_t = 5.12$ min (major), 6.02 min (minor.)) $[\alpha]_D^{20} + 24.5^\circ$ ($c = 1.00$, CHCl_3). ^1H NMR (600 MHz, CDCl_3) δ 7.45 – 7.42 (m, 2H), 7.22 – 7.19 (m, 2H), 5.45 (ddq, $J = 15.3, 6.7, 1.1$ Hz, 1H), 5.28 – 5.21 (m, 1H), 4.72 (d, $J = 11.9, 0.8$ Hz, 1H), 4.65 (d, $J = 12.0, 0.8$ Hz, 1H), 3.68 (dd, $J = 8.5, 7.0$ Hz, 1H), 2.83 – 2.72 (m, 1H), 2.50 – 2.41 (m, 1H), 2.17 (dq, $J = 13.5, 6.7$ Hz, 1H), 0.89 (t, $J = 6.7, 0.7$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 171.4, 141.3, 136.7, 131.7, 129.9, 122.4, 121.5, 94.7, 74.1, 51.4, 36.1, 31.0, 22.4. FTIR (film): 3027, 2956, 2926, 2868, 1751, 1488, 1465, 1438, 1408, 1371, 1260, 1130, 1074, 1012, 971, 824, 807, 755, 721 cm^{-1} . HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ (Pos.) calcd for $\text{C}_{16}\text{H}_{19}\text{O}_2\text{BrCl}_3$ 426.9629; found 426.9633.



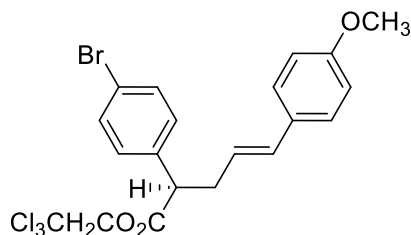
2,2,2-trichloroethyl (S,E)-2-(4-bromophenyl)oct-4-enoate (4.62)

General Procedure A was applied to the functionalization of (*E*)-hex-2-ene (50 mg, 3.00 Eq, 0.60 mmol). The title compound **4.62** was obtained as a colorless oil. A small amount of insertion into the secondary positions was also observed for this substrate (11% for catalyst **4.11**, and 20% for catalyst **4.8**). Prepared with catalyst **4.11**: 87% yield, 89% *ee* (AD-H, 1 mL/min, 1.0% iPrOH/hex. rt = 5.30 min (major), 5.69 min (minor).) $[\alpha]_D^{20} + 26.7^\circ$ ($c = 1.00$, CHCl₃.) ¹H NMR (600 MHz, CDCl₃) δ 7.45 – 7.42 (m, 2H), 7.22 – 7.19 (m, 2H), 5.45 (ddq, $J = 15.3, 6.7, 1.1$ Hz, 1H), 5.28 – 5.21 (m, 1H), 4.72 (d, $J = 11.9, 0.8$ Hz, 1H), 4.65 (d, $J = 12.0, 0.8$ Hz, 1H), 3.68 (dd, $J = 8.5, 7.0$ Hz, 1H), 2.83 – 2.72 (m, 1H), 2.50 – 2.41 (m, 1H), 2.17 (dq, $J = 13.5, 6.7$ Hz, 1H), 0.89 (t, $J = 6.7, 0.7$ Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 171.4, 141.3, 136.7, 131.7, 129.9, 122.4, 121.5, 94.7, 74.1, 51.4, 36.1, 31.0, 22.4. FTIR (film): 3027, 2956, 2926, 2868, 1751, 1488, 1465, 1438, 1408, 1371, 1260, 1130, 1074, 1012, 971, 824, 807, 755, 721 cm⁻¹. HRMS (ESI) m/z : $[M+H]^+$ (Pos.) calcd for C₁₆H₁₉O₂BrCl₃ 426.9629; found 426.9640.



2,2,2-trichloroethyl (S)-2-(4-bromophenyl)-3-(4-methoxyphenyl)propanoate (4.63)

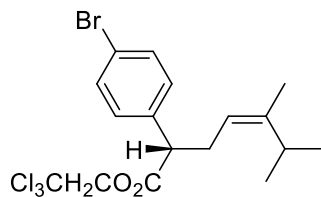
General Procedure A was applied to the functionalization of 1-methoxy-4-methylbenzene (73 mg, 3.00 Eq, 0.60 mmol). The title compound **4.63** was obtained as a colorless oil. Prepared with catalyst **4.11**: 72% yield, 86% *ee* (AS-H, 1 mL/min, 1.0% iPrOH/hex. rt = 10.16 min (major), 12.94 min (minor).) $[\alpha]^{20}_{\text{D}} + 62.4^{\circ}$ (*c* = 1.00, CHCl₃.) ¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.38 (m, 2H), 7.23 – 7.17 (m, 2H), 7.06 – 6.98 (m, 2H), 6.79 – 6.72 (m, 2H), 4.65 (d, 1H), 4.63 (d, 1H), 3.90 (t, 1H), 3.75 (d, *J* = 1.4 Hz, 3H), 3.36 (dd, 1H), 3.00 (dd, *J* = 13.9, 7.1 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 171.3, 158.3, 131.8, 130.0, 129.9, 129.9, 121.7, 113.9, 94.6, 74.1, 55.2, 53.1, 38.5. FTIR (film): 3031, 2998, 2953, 2932, 2910, 2834, 1749, 1611, 1584, 1512, 1488, 1464, 1441, 1407, 1371, 1301, 1247, 1178, 1136, 1074, 1035, 1011, 824, 755, 720 cm⁻¹. HRMS (APCI) *m/z*: [M-H]⁻ (Neg.) calcd for C₁₈H₁₅O₃BrCl₃ 462.9276; found 426.9279.



2,2,2-trichloroethyl (R,E)-2-(4-bromophenyl)-5-(4-methoxyphenyl)pent-4-enoate (4.64)

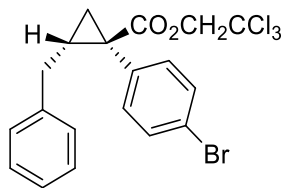
General Procedure A was applied to the functionalization of (*E*)-1-methoxy-4-(prop-1-en-1-yl)benzene (89 mg, 3.00 Eq, 0.60 mmol). The title compound was obtained as a colorless oil.

Prepared with catalyst **4.8**: 95% yield, 85% *ee* (OD-H, 1 mL/min, 1.0% iPrOH/hex. rt = 11.83 min (major), 13.71 min (minor.)) $[\alpha]_{\text{D}}^{20} - 58.1^\circ$ ($c = 1.00$, CHCl_3 .) ^1H NMR (300 MHz, CDCl_3) δ 7.58 – 7.41 (m, 2H), 7.30 – 7.19 (m, 4H), 6.89 – 6.78 (m, 2H), 6.41 (d, $J = 15.8$ Hz, 1H), 5.95 (ddd, $J = 15.7, 7.5, 6.7$ Hz, 1H), 4.76 (d, $J = 12.0$ Hz, 1H), 4.68 (d, $J = 11.9$ Hz, 1H), 3.79 (s, 4H), 3.00 (dddd, $J = 14.3, 8.7, 7.5, 1.3$ Hz, 1H), 2.76 – 2.65 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 171.3, 159.1, 136.5, 132.4, 131.9, 129.9, 129.7, 127.3, 123.4, 121.7, 113.9, 94.7, 74.1, 55.3, 51.3, 36.6. FTIR (film): 3031, 3001, 2953, 2933, 2910, 2835, 1749, 1607, 1510, 1488, 1464, 1440, 1371, 1247, 1174, 1137, 1074, 1035, 1011, 967, 838, 795, 762, 720 cm^{-1} . HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ (Pos.) calcd for $\text{C}_{20}\text{H}_{19}\text{O}_3\text{BrCl}_3$ 490.9578; found 490.9581.



2,2,2-trichloroethyl (*S,Z*)-2-(4-bromophenyl)-5,6-dimethylhept-4-enoate (4.65**)**

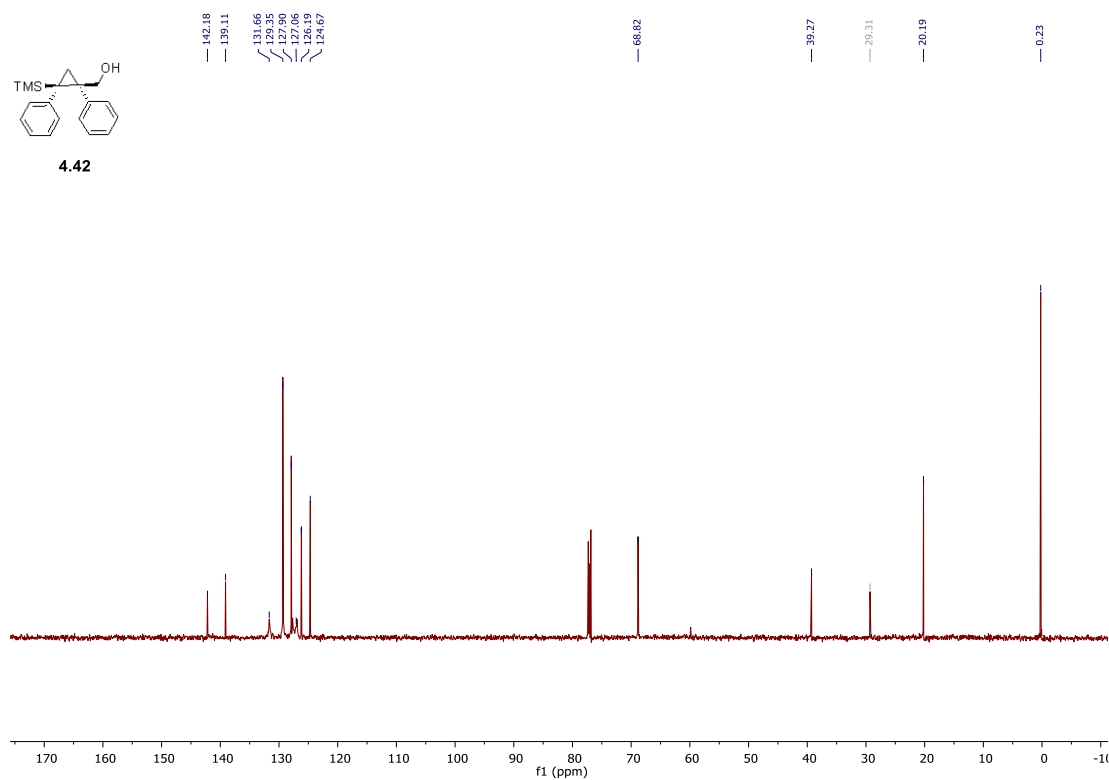
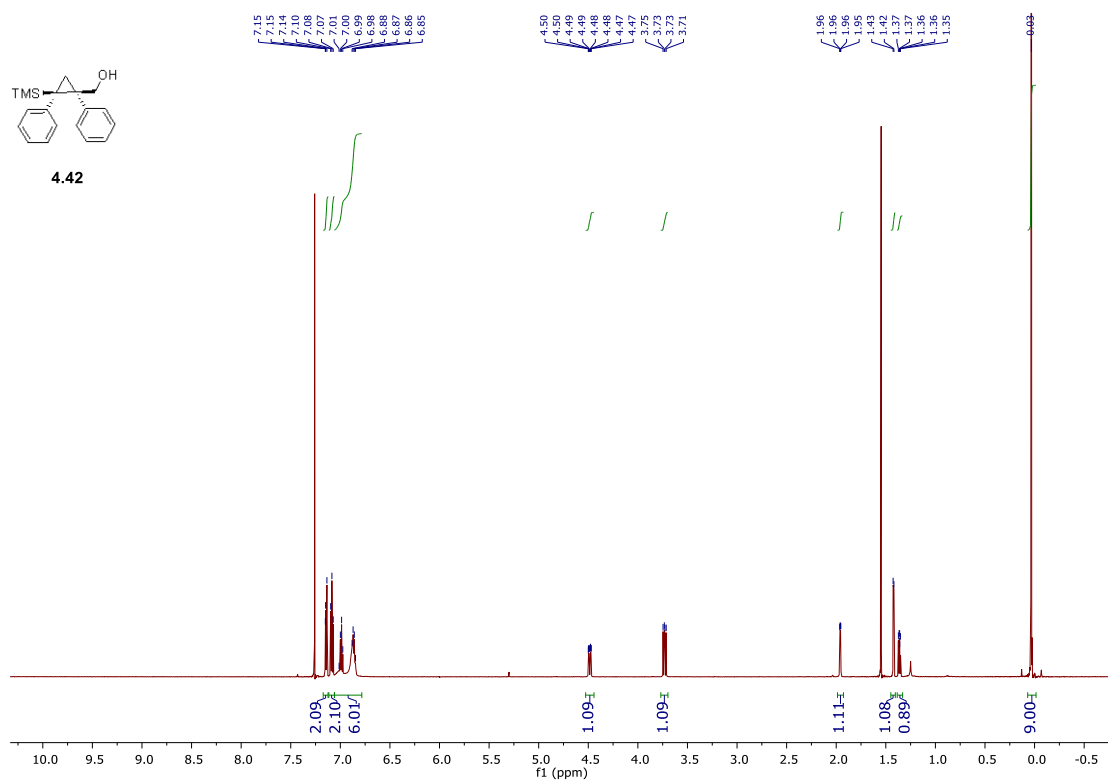
General Procedure A was applied to the functionalization of (*Z*)-3,4-dimethylpent-2-ene (59 mg, 3.00 Eq, 0.60 mmol). The title compound **4.65** was obtained as a colorless oil. Prepared with catalyst **4.11**: 81% yield, 93% *ee* (OD-H, 0.5 mL/min, 0.5% iPrOH/hex. *rt* = 9.23 min (major), 9.96 min (minor.)) $[\alpha]_D^{20} + 23.4^\circ$ (*c* = 1.000, CHCl₃.) ¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.40 (m, 2H), 7.24 – 7.18 (m, 2H), 4.93 (td, *J* = 7.1, 1.6 Hz, 1H), 4.73 (d, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 3.63 (t, *J* = 7.7 Hz, 1H), 2.88 – 2.67 (m, 2H), 2.60 – 2.41 (m, 1H), 1.53 (q, *J* = 1.3 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.88 – 0.81 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 171.7, 144.0, 136.8, 131.7, 129.9, 121.5, 119.0, 94.8, 74.1, 51.5, 31.0, 28.7, 20.7, 20.7, 18.0. FTIR (film): 3031, 3001, 2953, 2933, 2910, 2835, 1749, 1607, 1510, 1488, 1464, 1440, 1371, 1247, 1174, 1137, 1074, 1035, 1011, 967, 838, 795, 762, 720 cm⁻¹. HRMS (ESI) *m/z*: [M+H]⁺ (Pos.) calcd for C₁₇H₂₁O₂BrCl₃ 440.9785; found 440.9788.

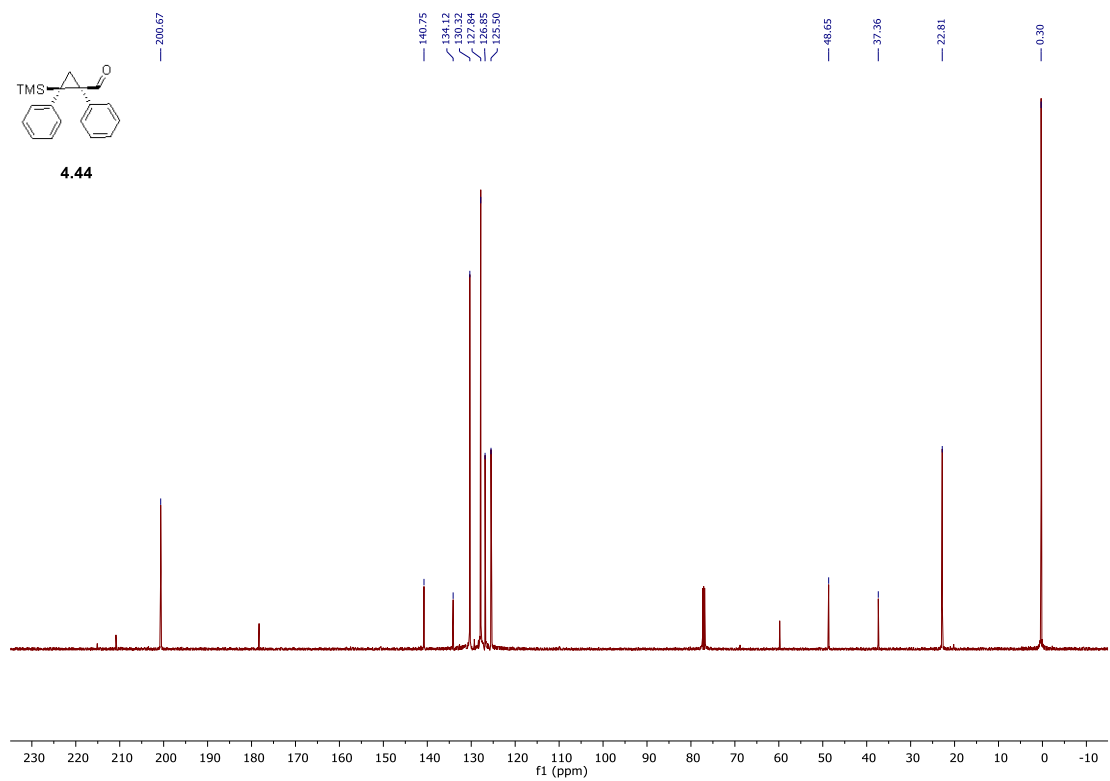
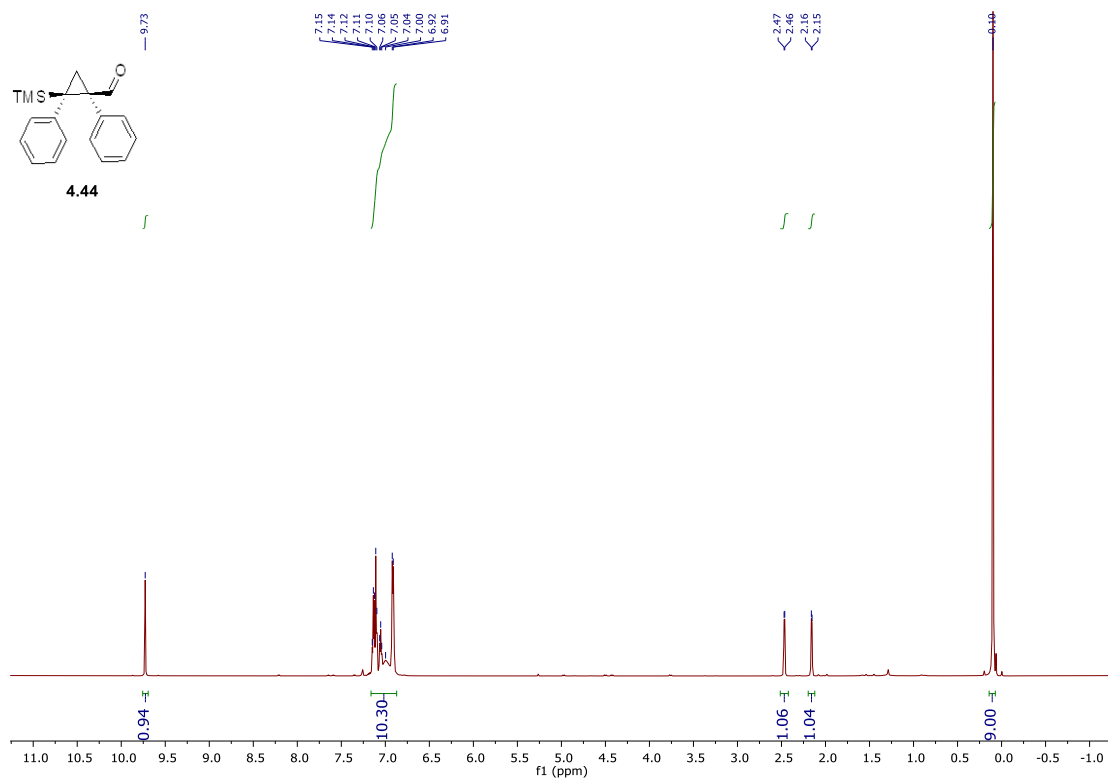


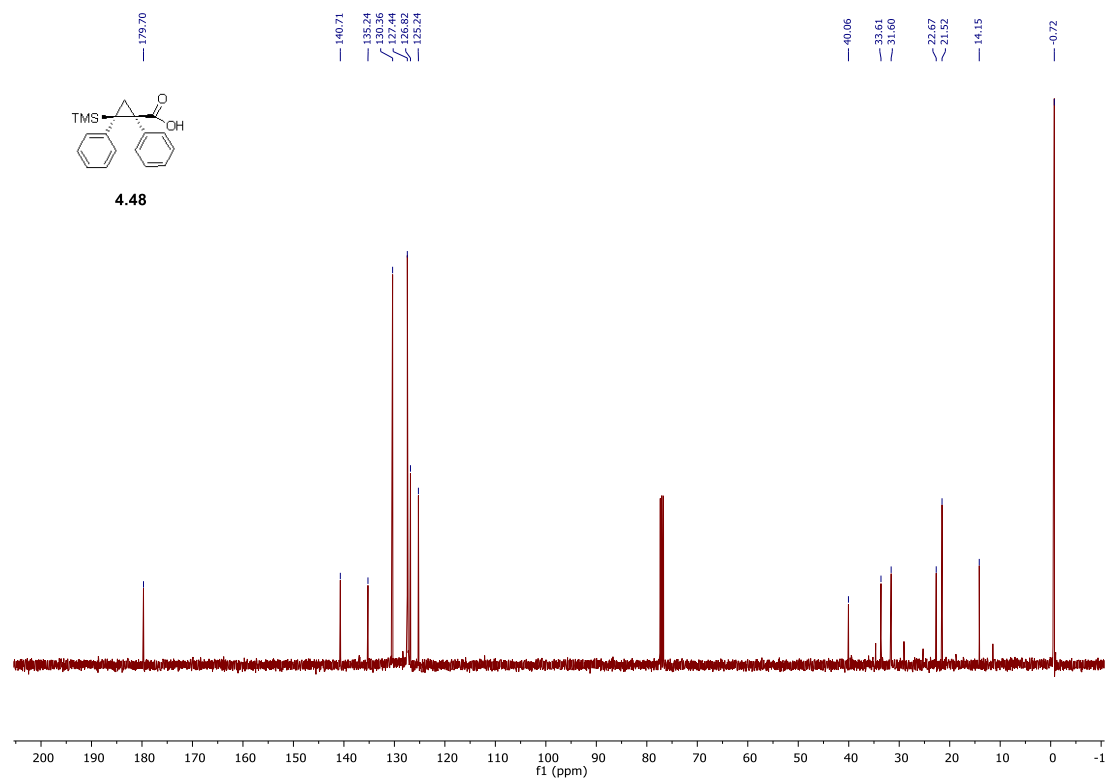
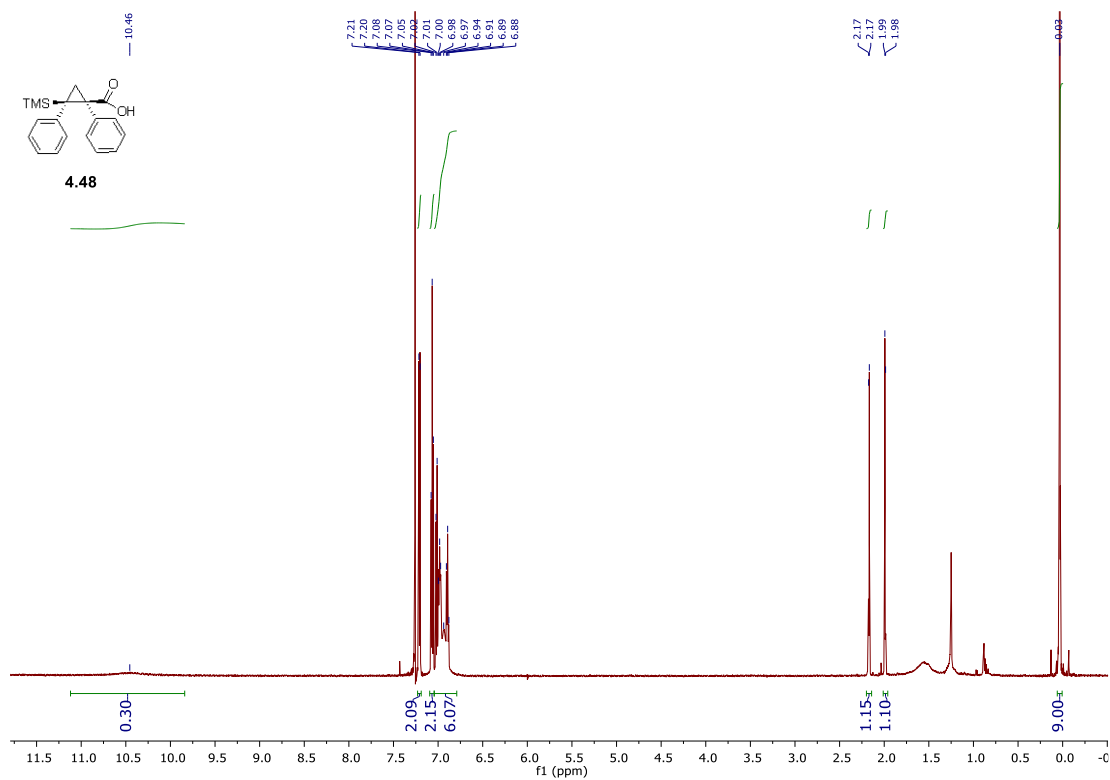
2,2,2-trichloroethyl (1*R*,2*R*)-2-benzyl-1-(4-bromophenyl)cyclopropane-1-carboxylate (4.66)

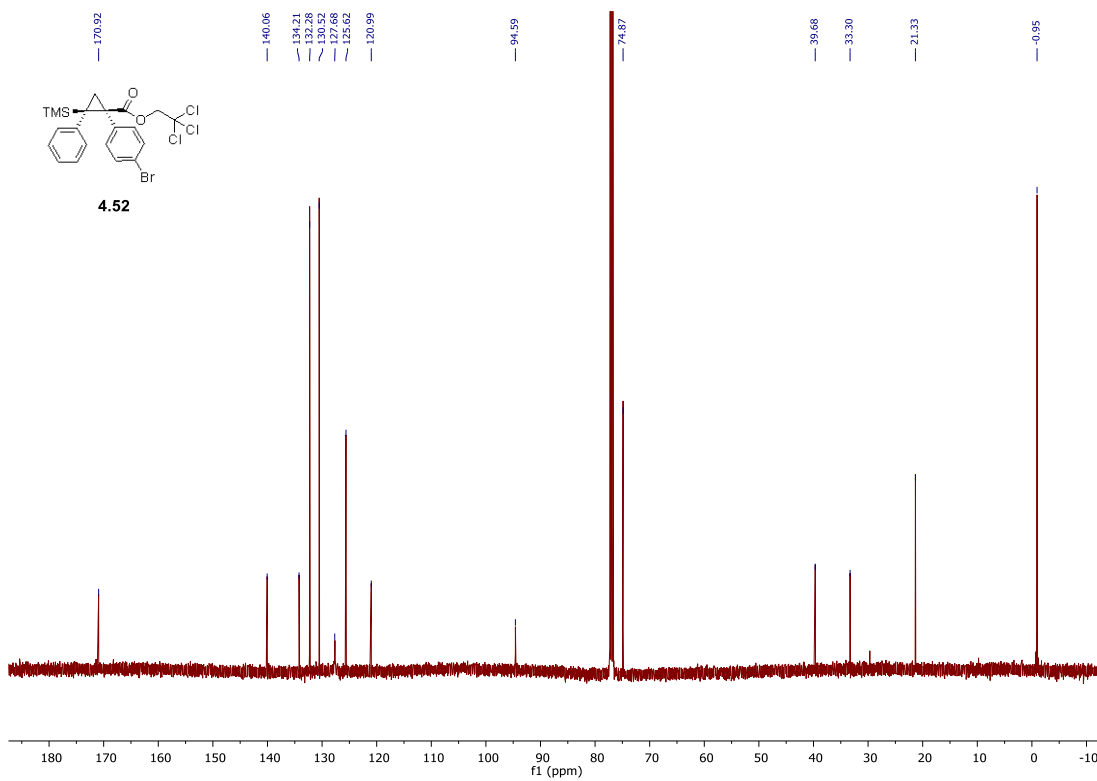
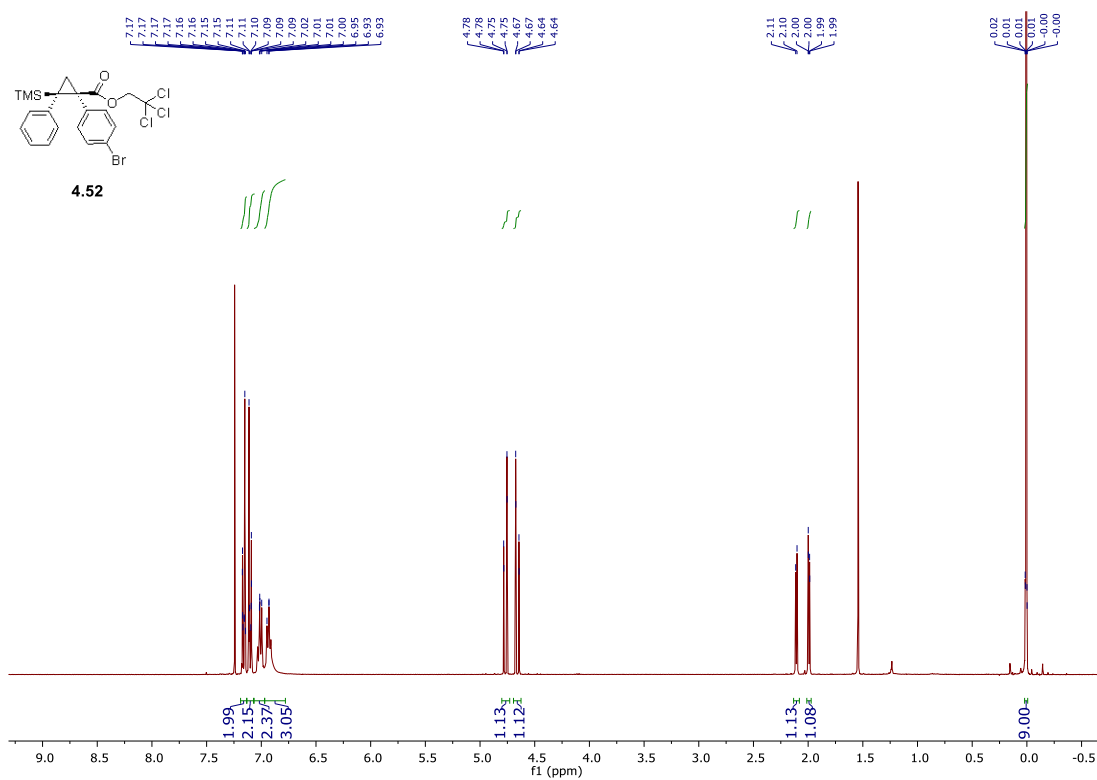
A scintillation vial was charged with allylbenzene (71 mg, 0.60 mmol, 3.0 equiv), CH₂Cl₂ (1.0 mL), and Rh₂[(1*R*, 2*R*)-2-TMS-*p*-PhDPCP]₄ (**4.8**, 1.7 mg, 1.0 μmol, 0.5 mol%). The mixture was heated to light reflux, and then a solution of 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**4.30**, 74 mg, 1.00 Eq, 0.20 mmol) in CH₂Cl₂ (2.5 mL) was added via syringe pump over the course of 1.5 h. After the addition had completed, stirring was continued for 1.5 h at which time the mixture was concentrated to a green oil under reduced pressure. Purification by flash column chromatography (0-10% Et₂O/hexanes) afforded the product **4.66** as a colorless oil (81 mg, 88% yield). Observed 97% *ee* (AD-H, 1.0 mL/min, 1.0% iPrOH/hexanes. rt 8.3 min (major), 10.3 min (minor)). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.48 – 7.43 (m, 2H), 7.26 (dd, *J* = 8.1, 6.8 Hz, 2H), 7.22 – 7.18 (m, 1H), 7.18 – 7.15 (m, 2H), 7.14 – 7.09 (m, 2H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 11.9 Hz, 1H), 2.64 (dd, *J* = 15.2, 5.6 Hz, 1H), 2.30 (tdd, *J* = 9.0, 6.9, 5.6 Hz, 1H), 2.00 (dd, *J* = 15.2, 8.9 Hz, 1H), 1.95 (dd, *J* = 9.1, 4.6 Hz, 1H), 1.38 (dd, *J* = 7.0, 4.6 Hz, 1H). Further work with this reaction is currently ongoing in the Davies lab.

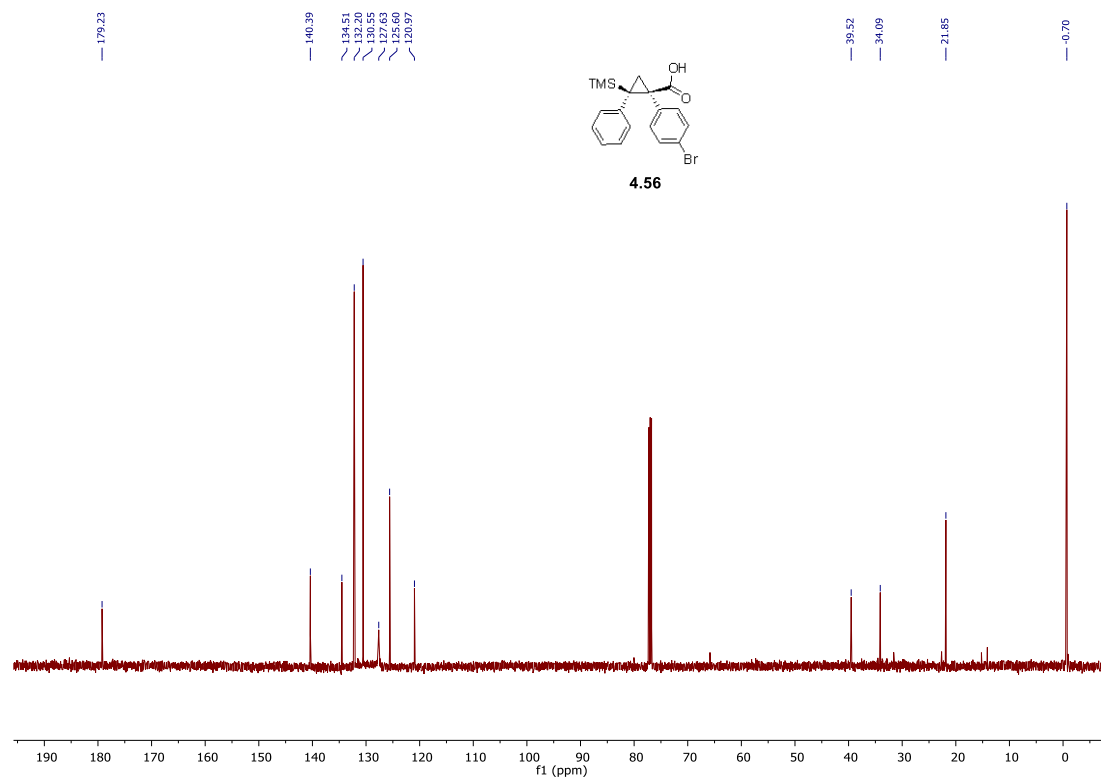
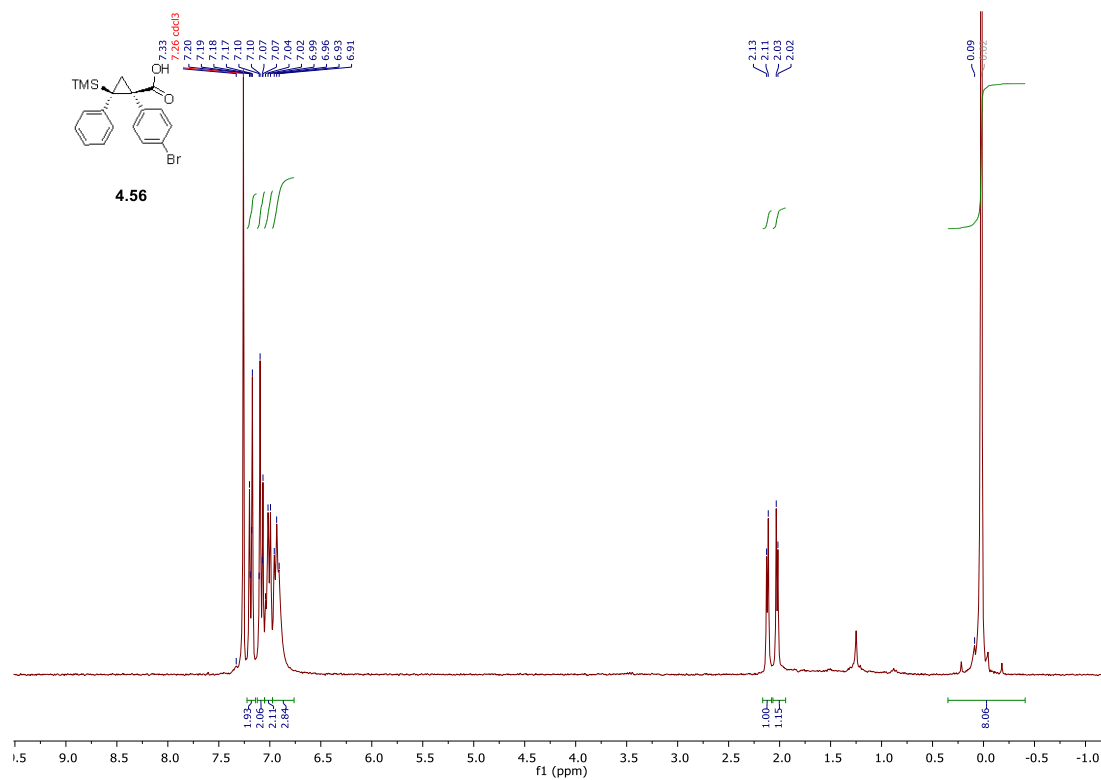
S.4.6 Copies of NMR Spectra

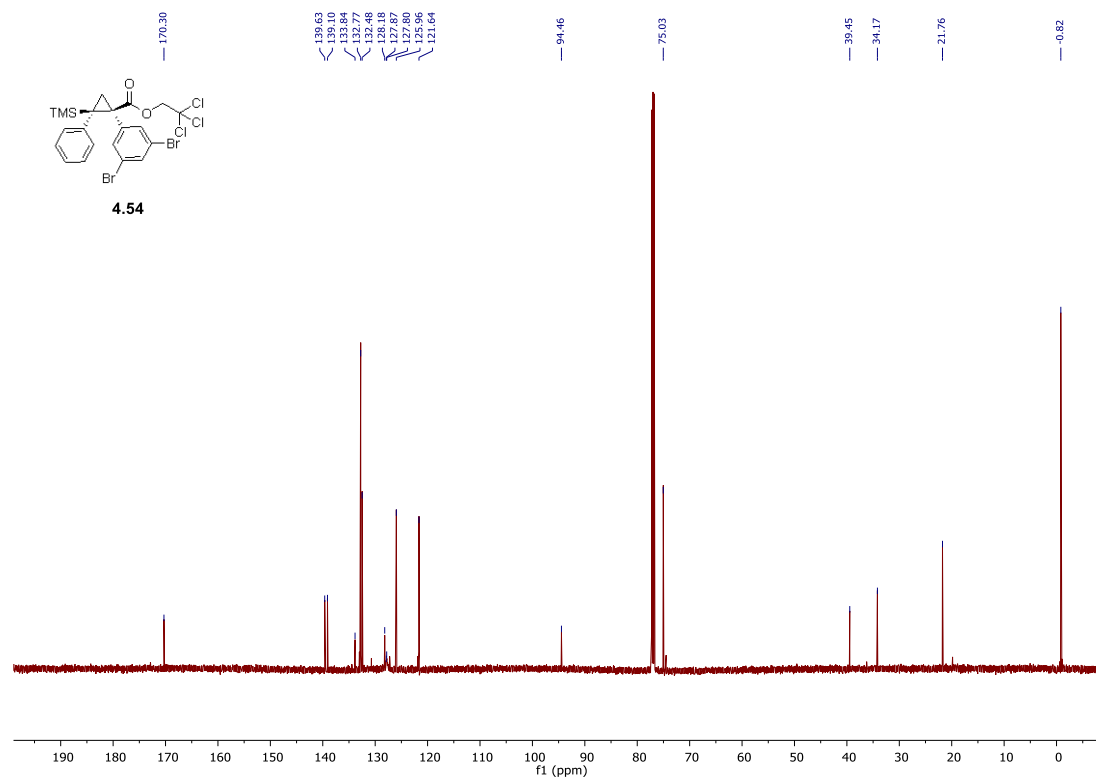
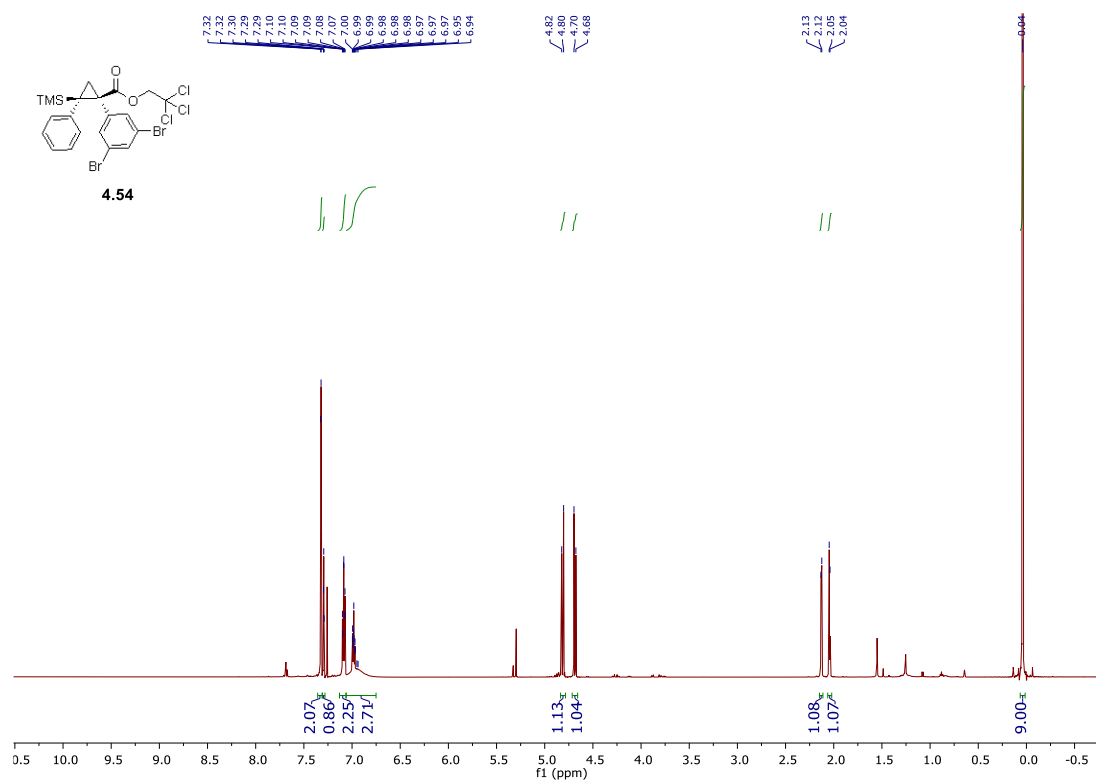


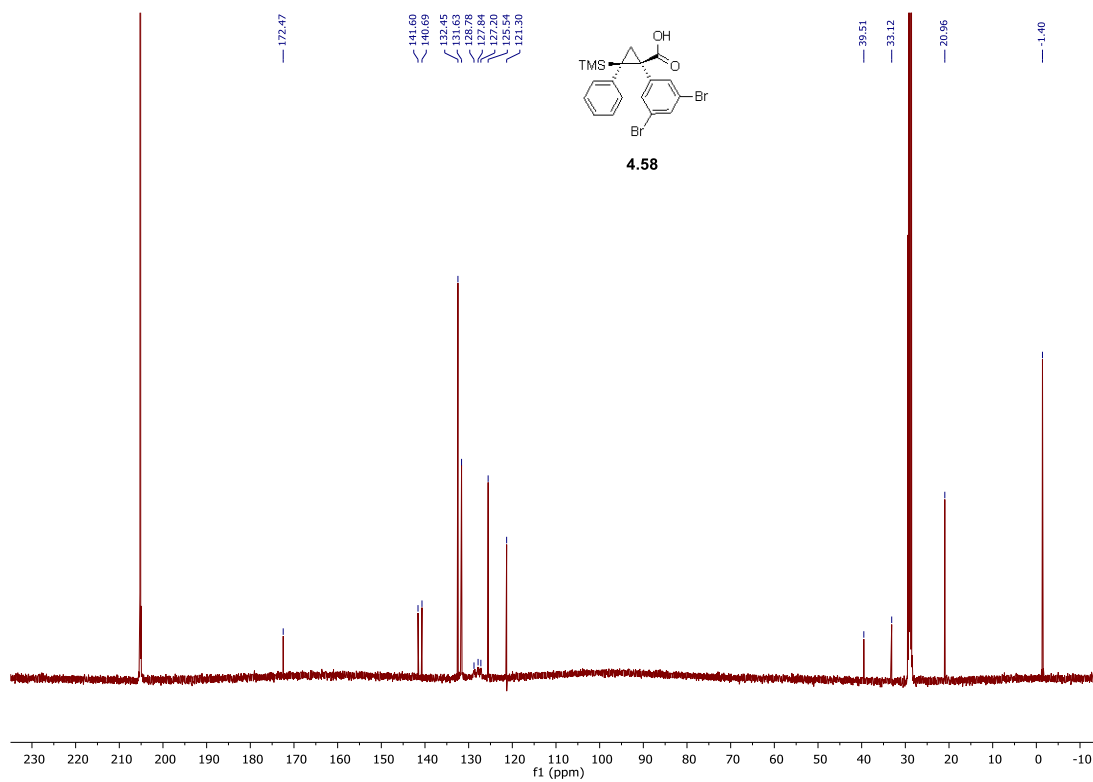
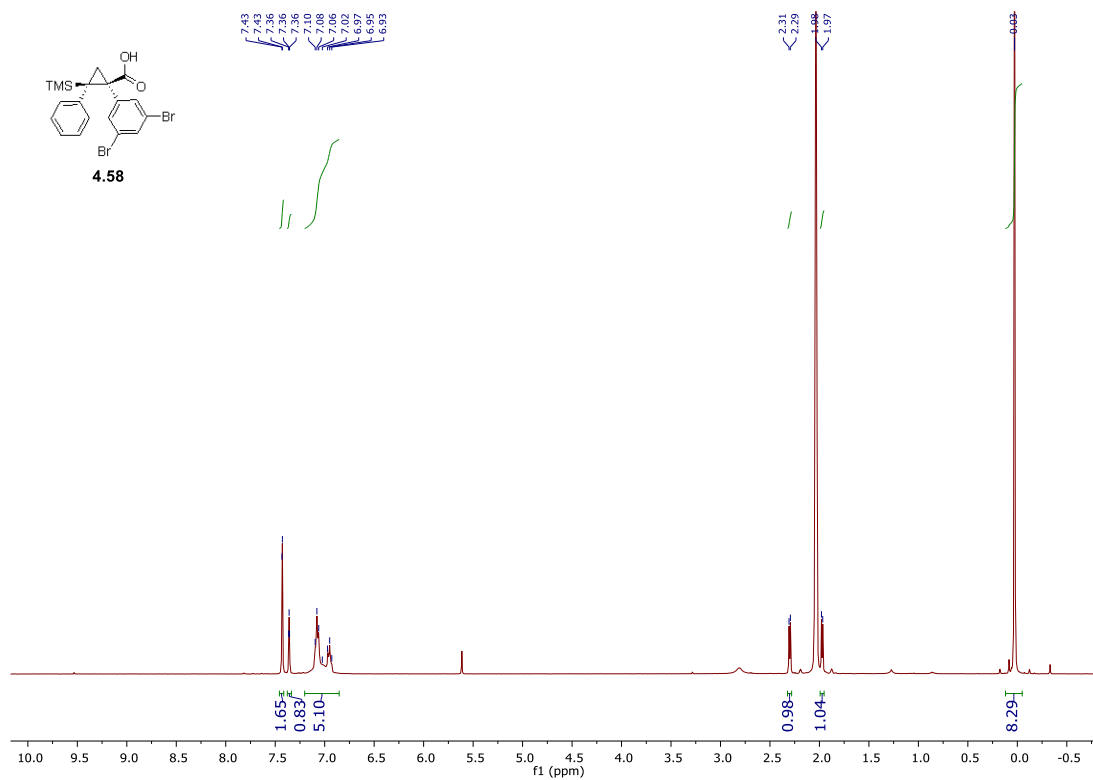


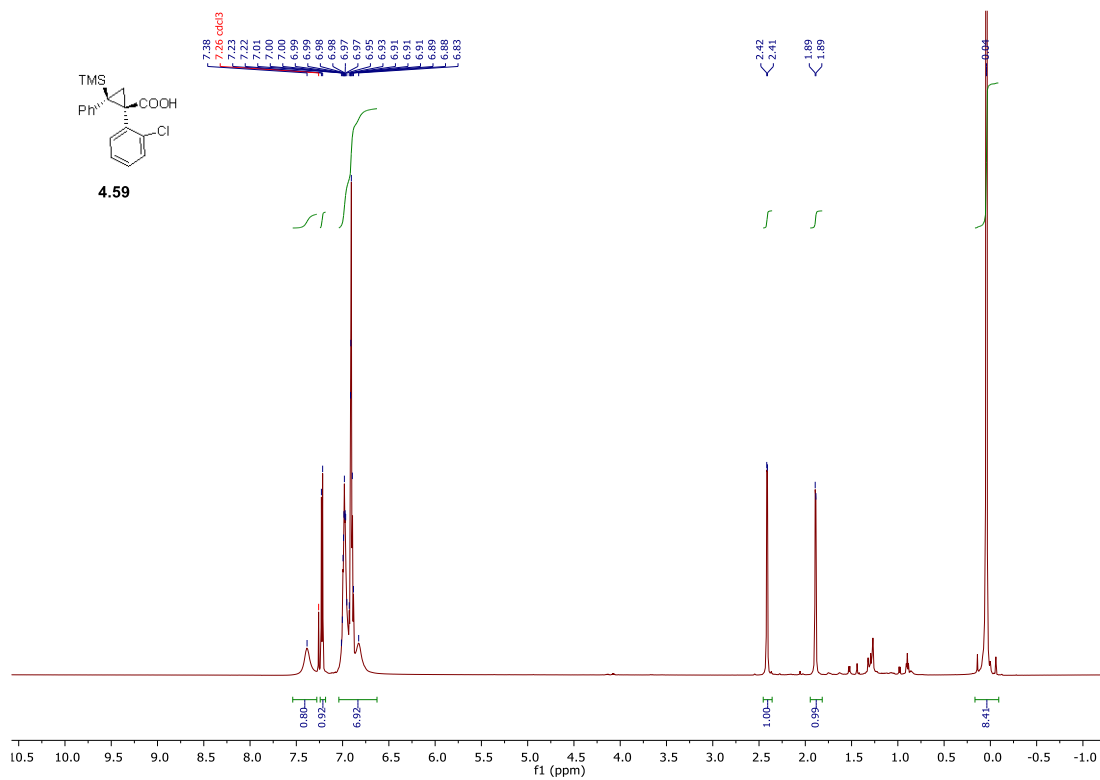
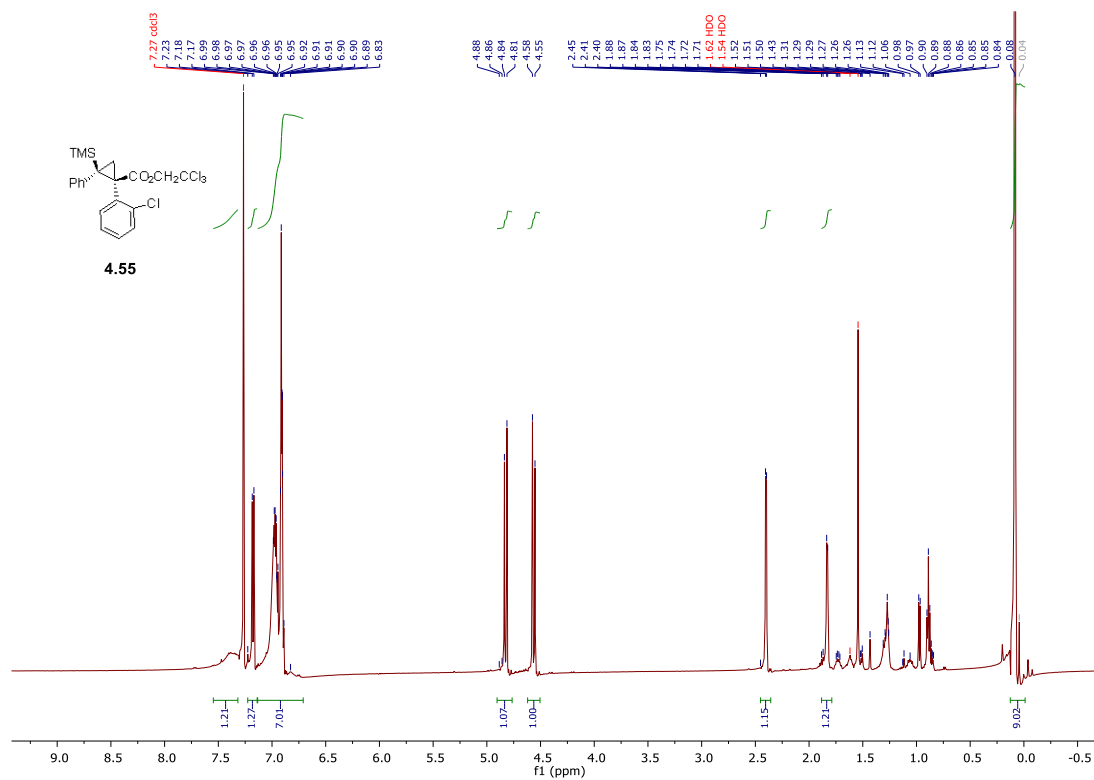


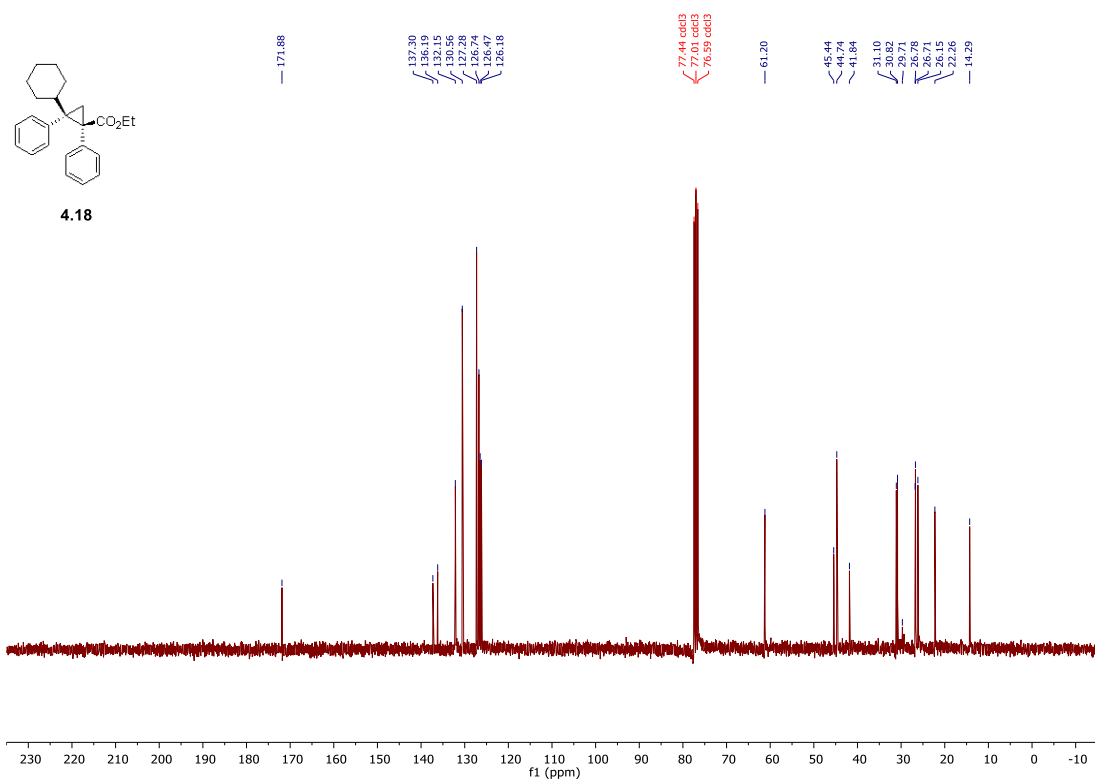


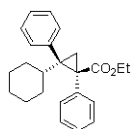
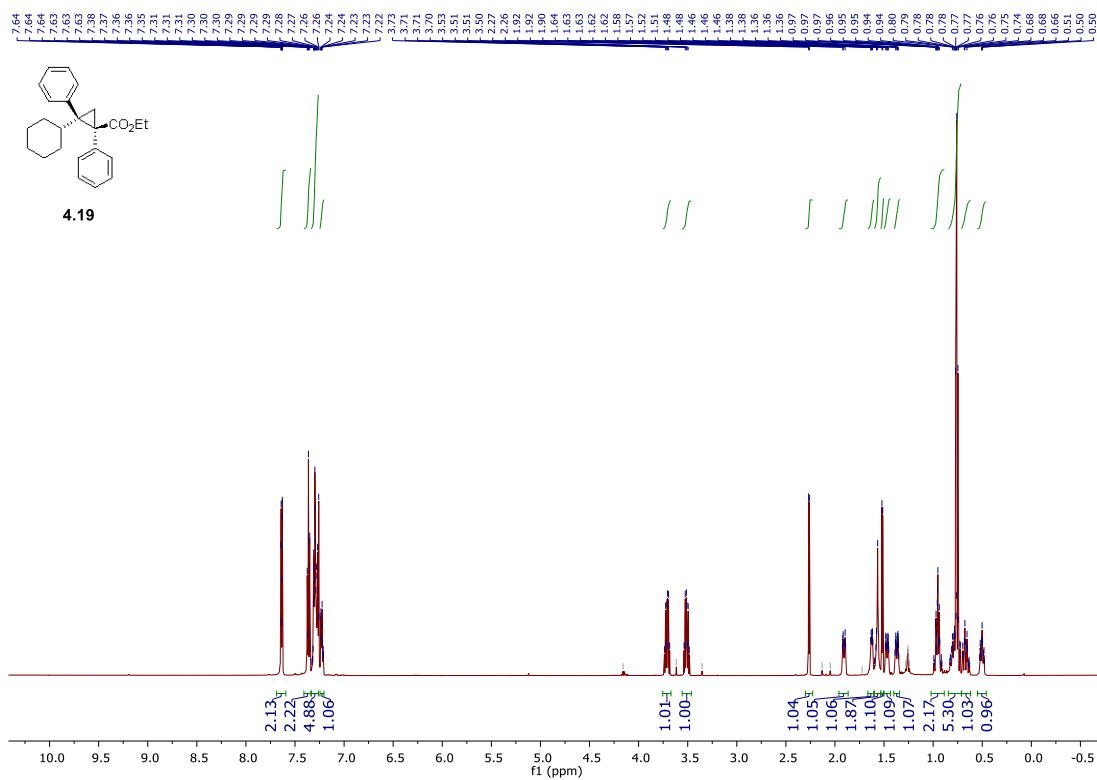




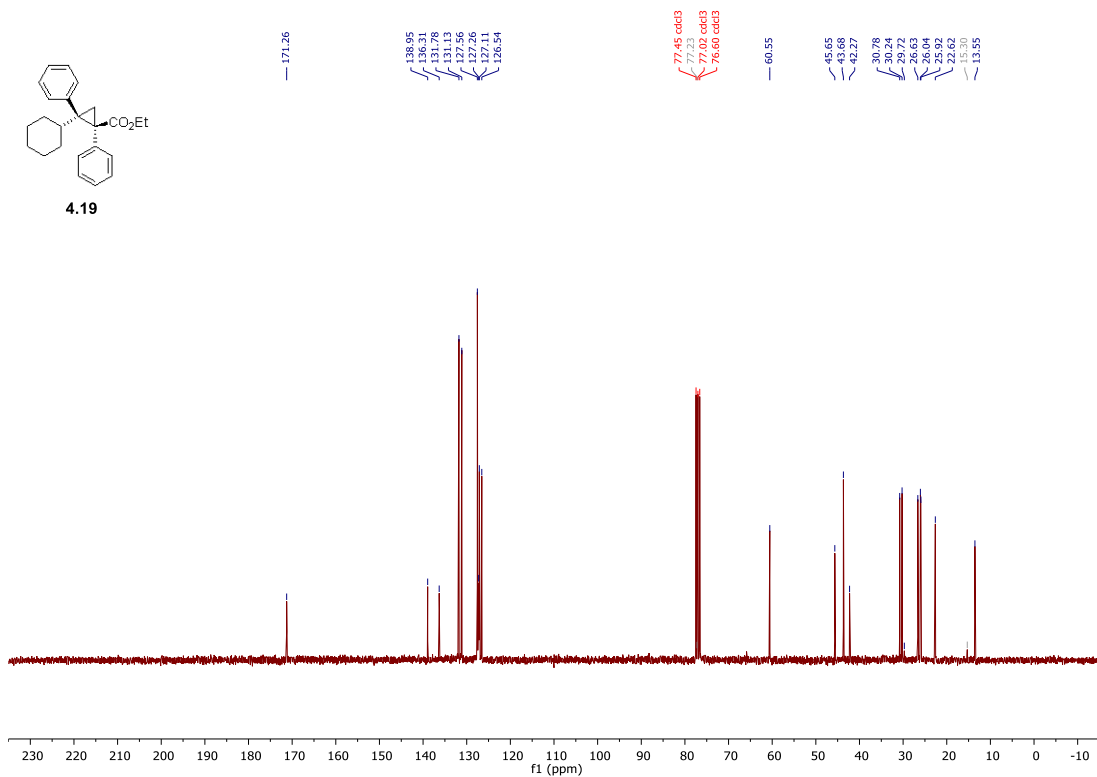


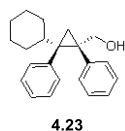
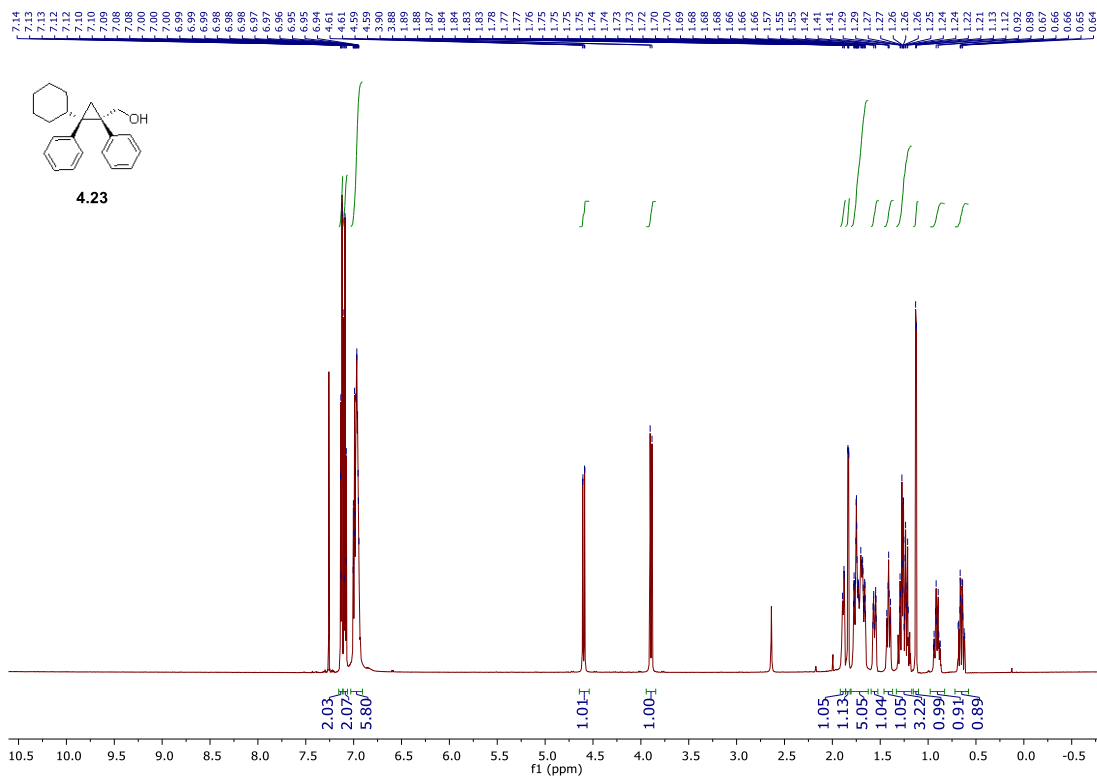




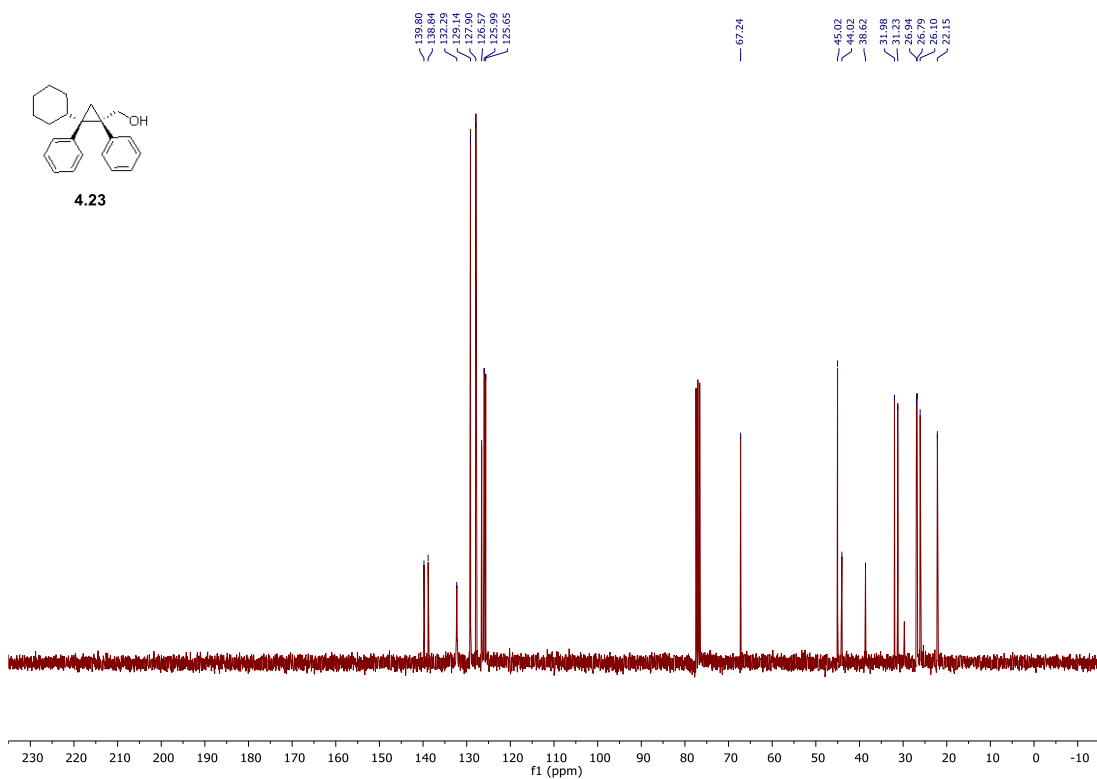


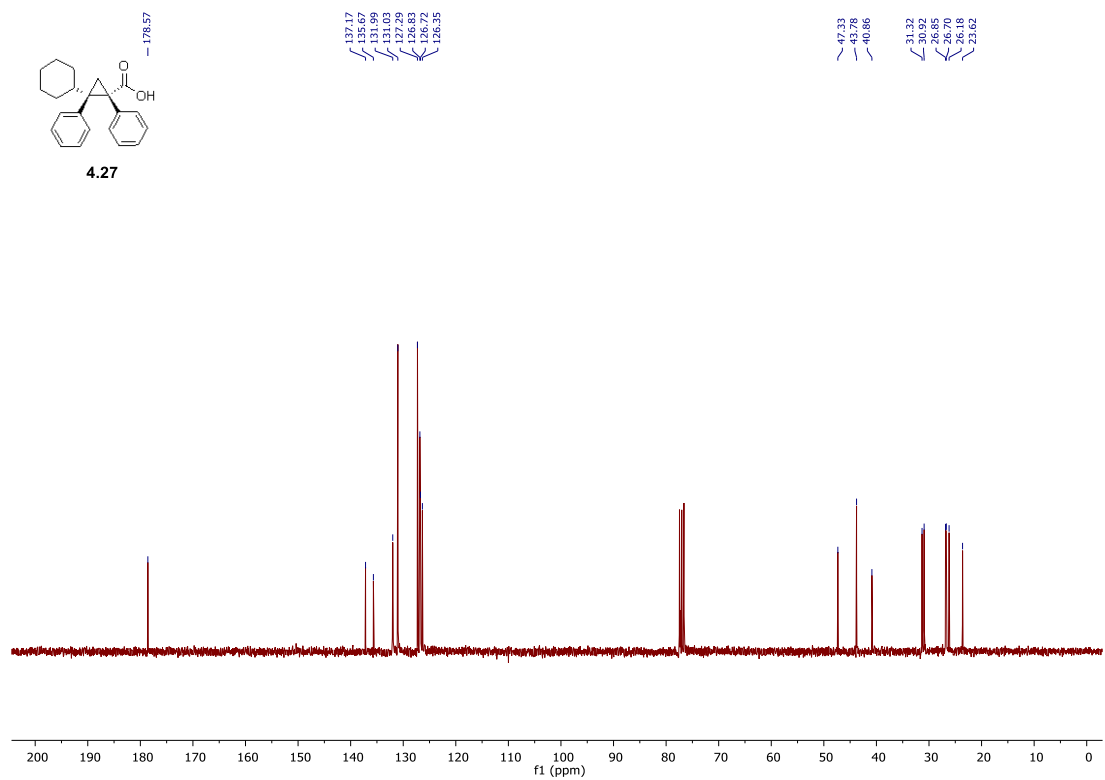
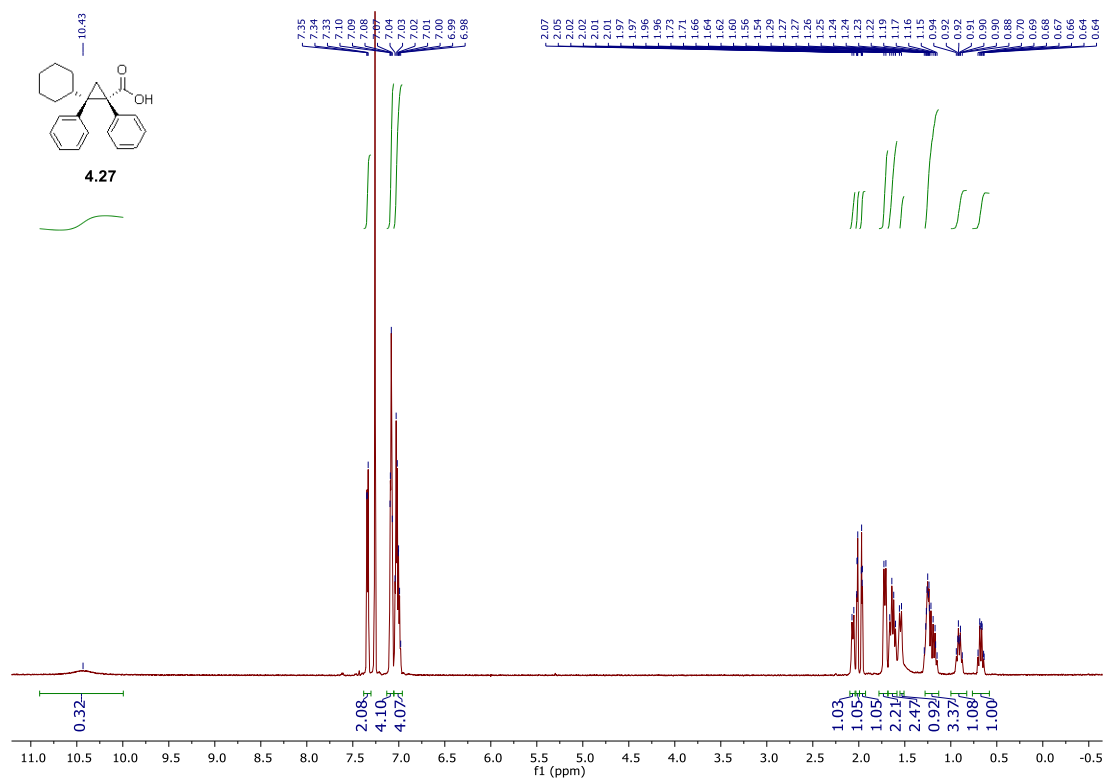
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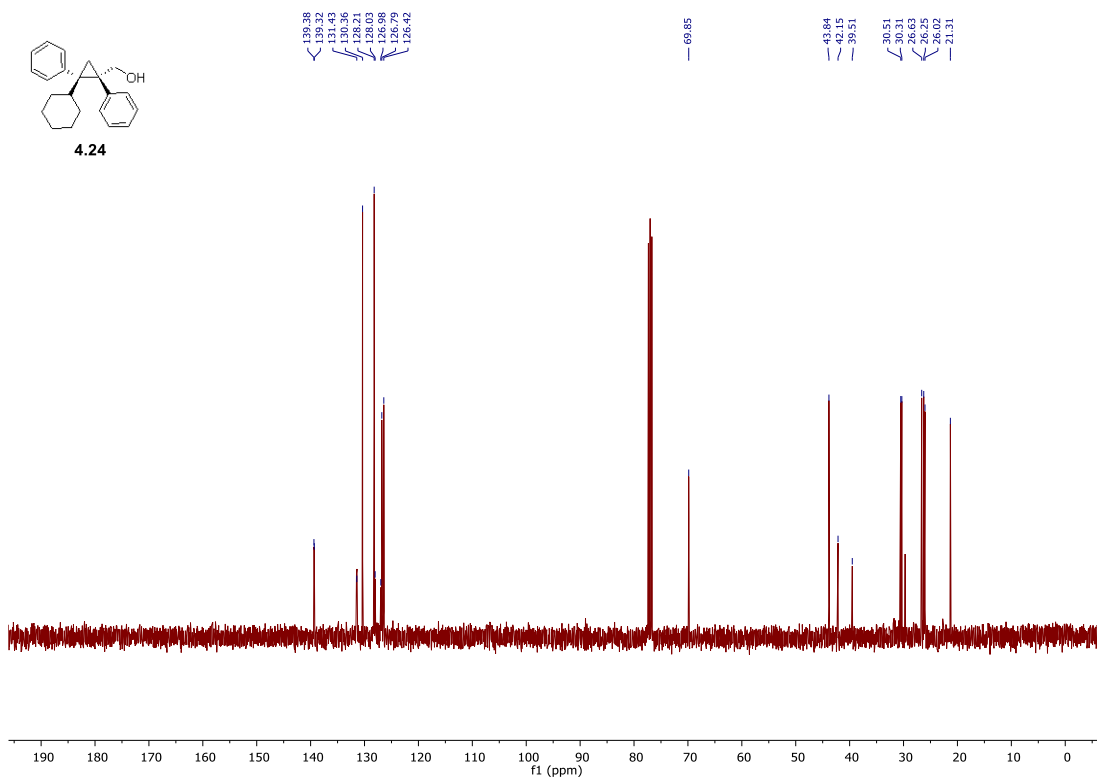


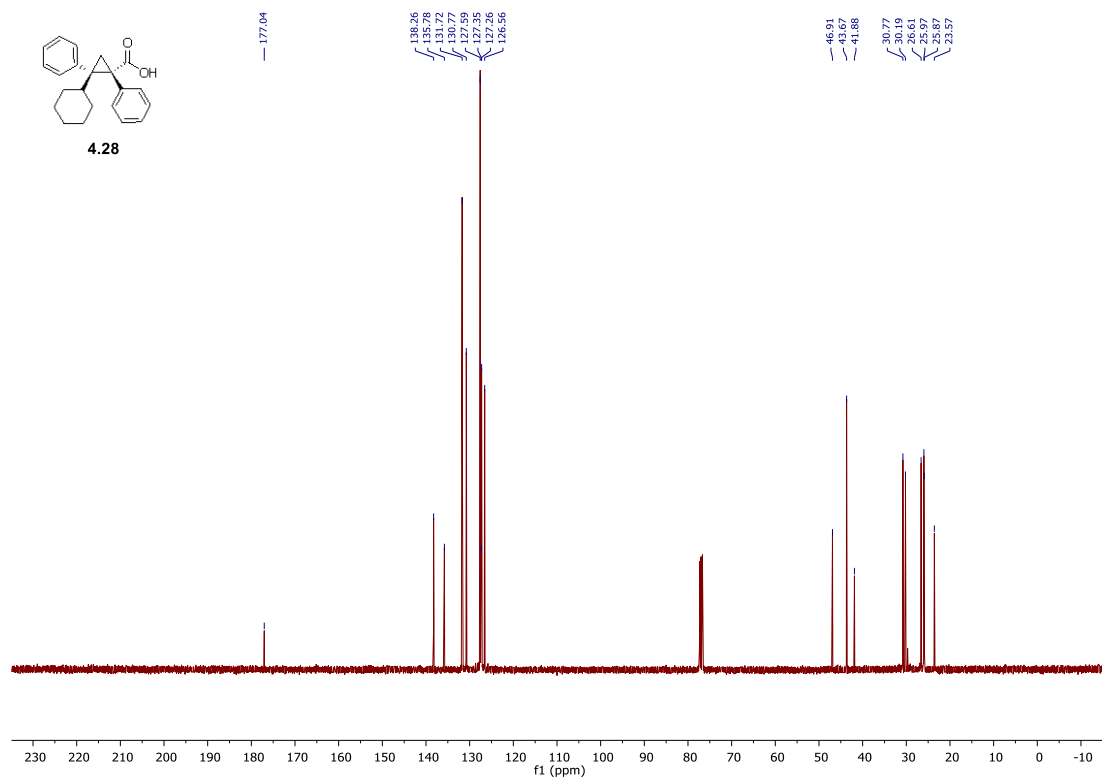
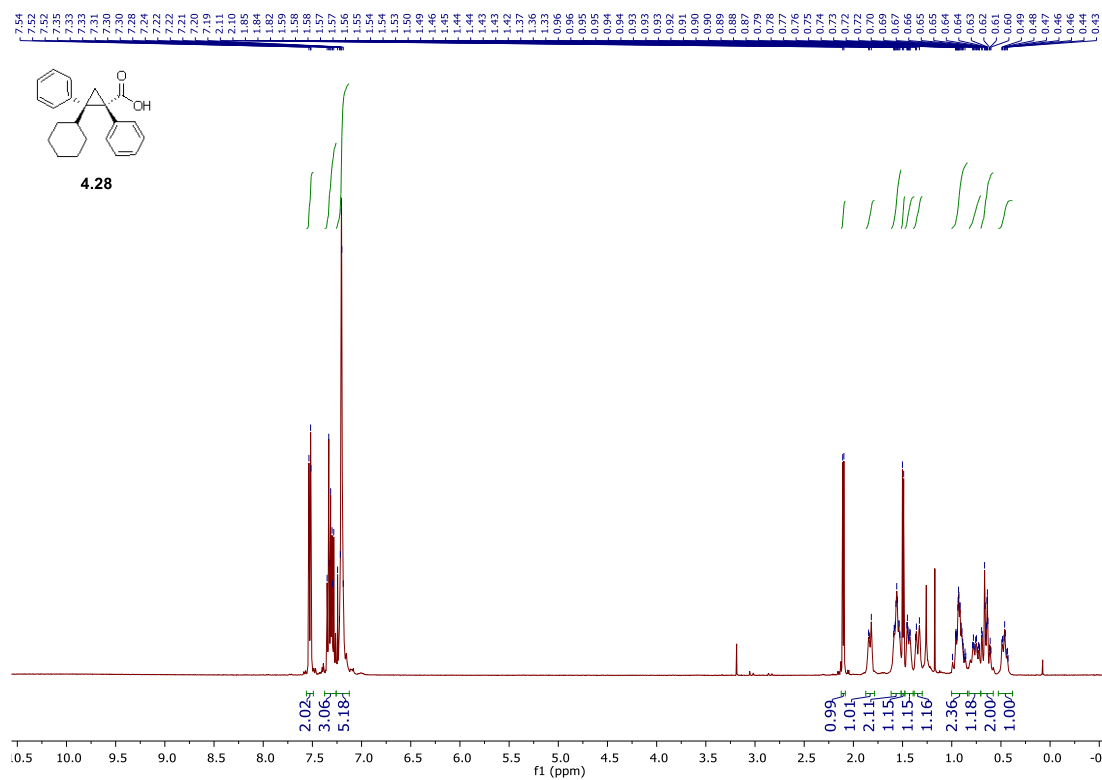


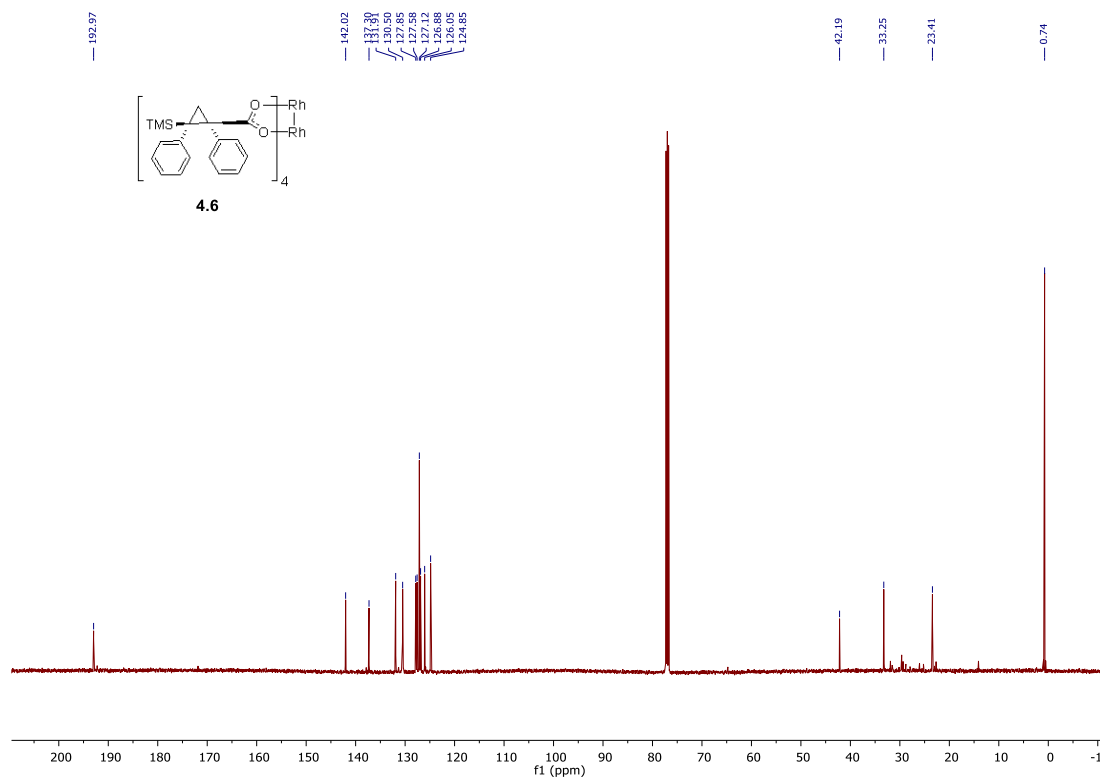
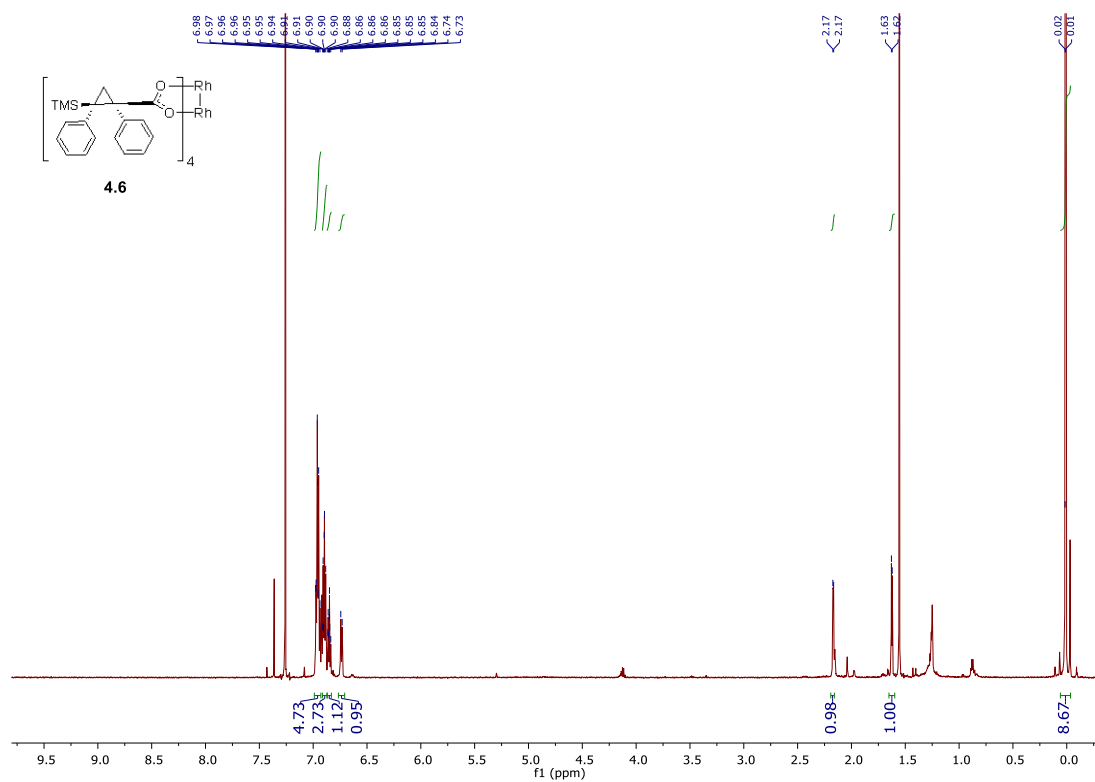
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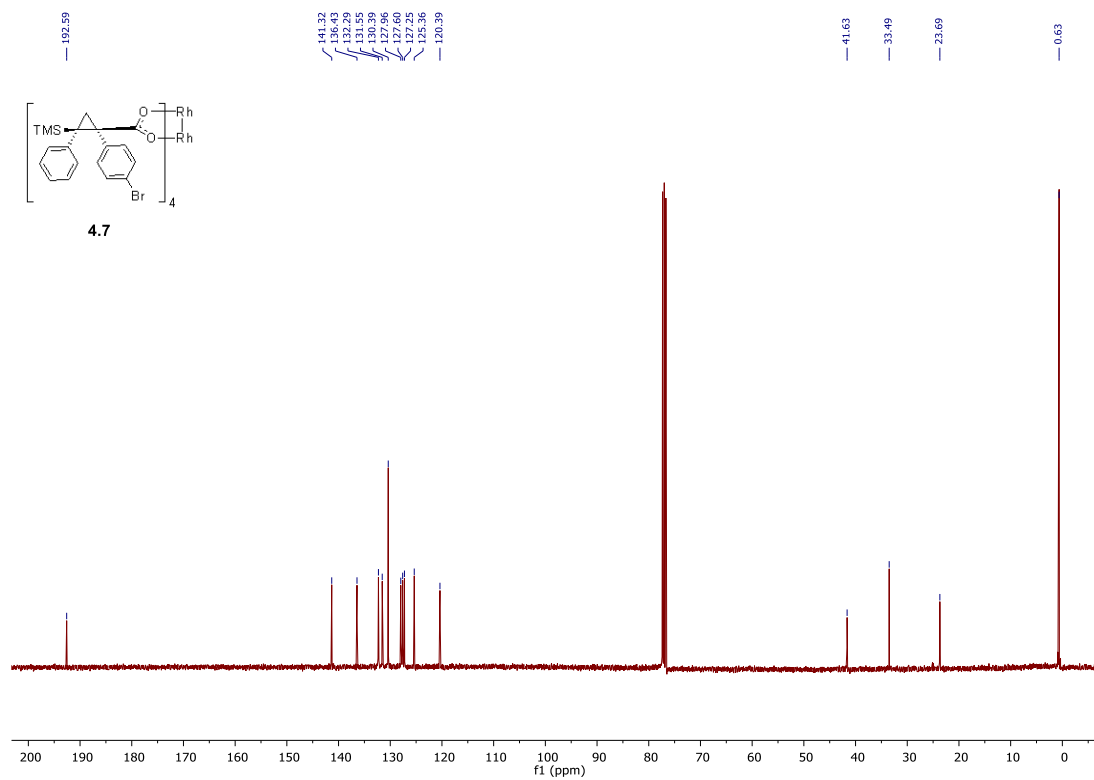
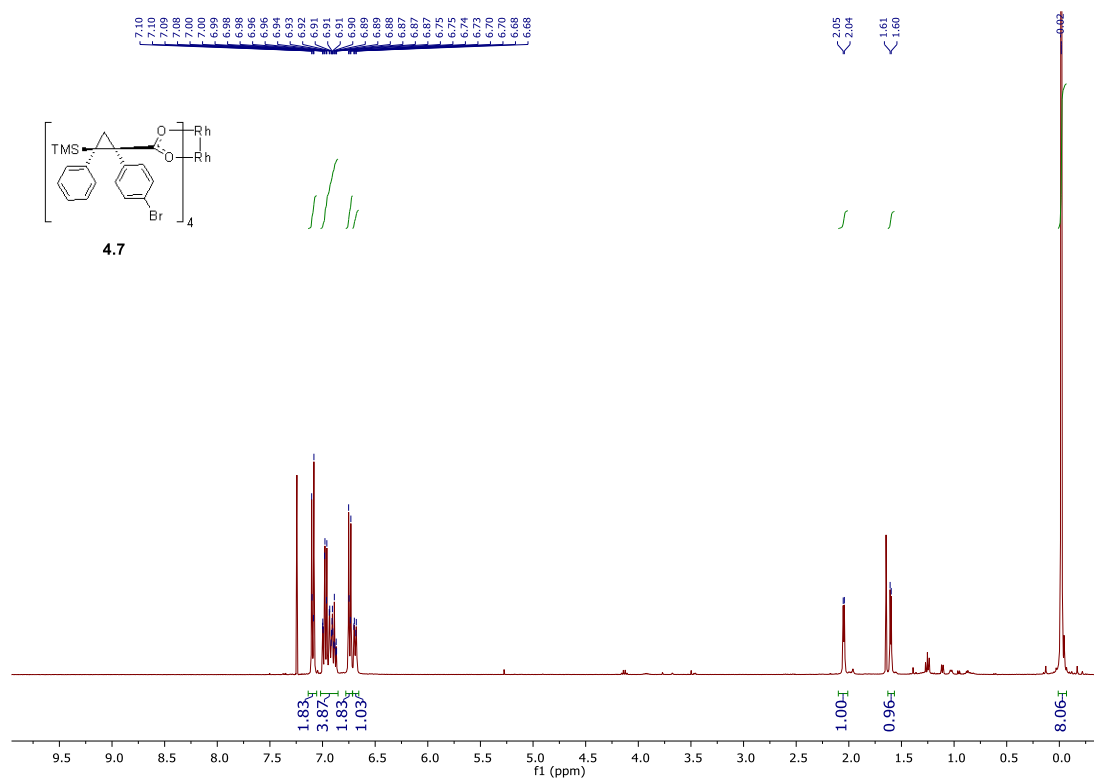


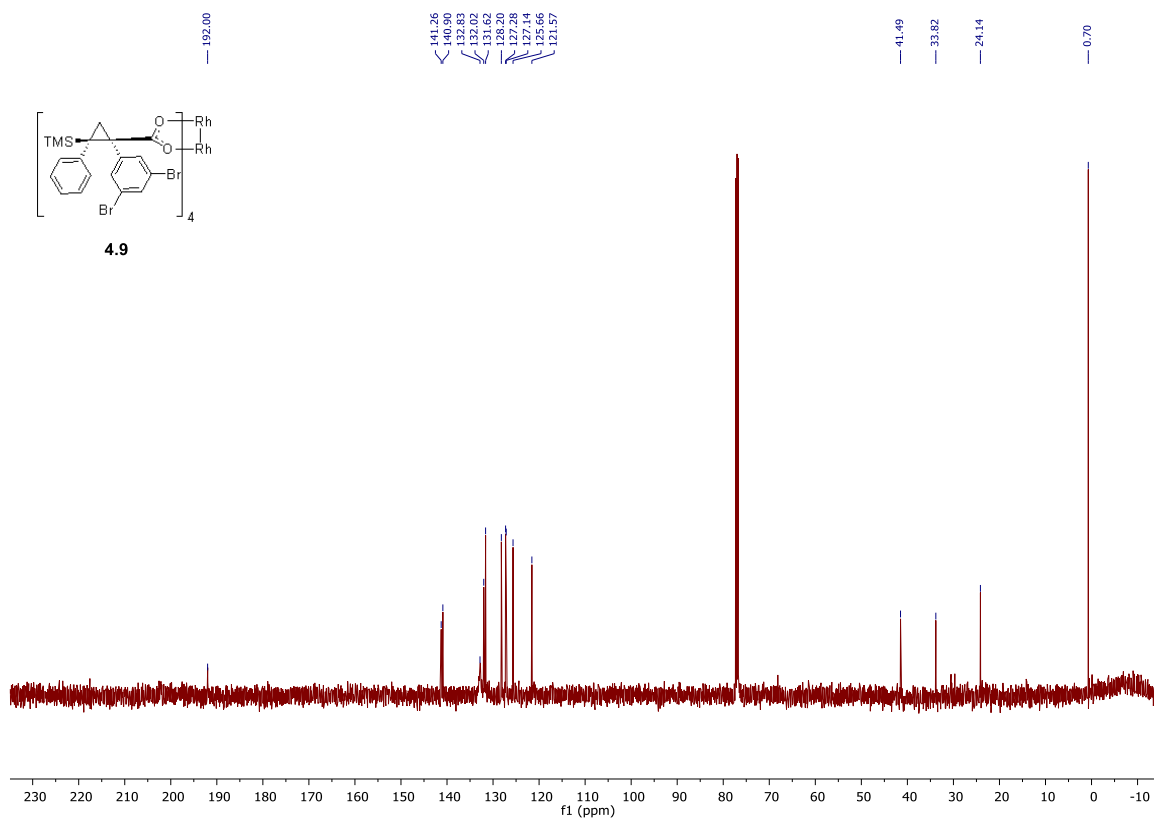
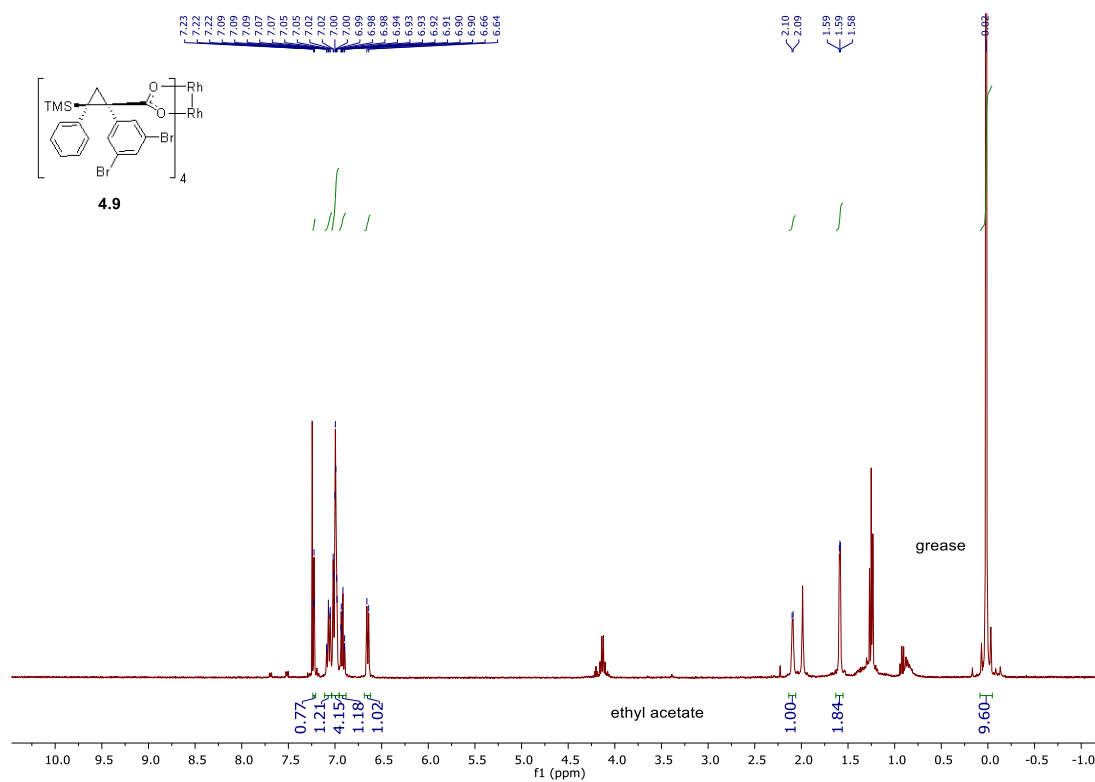


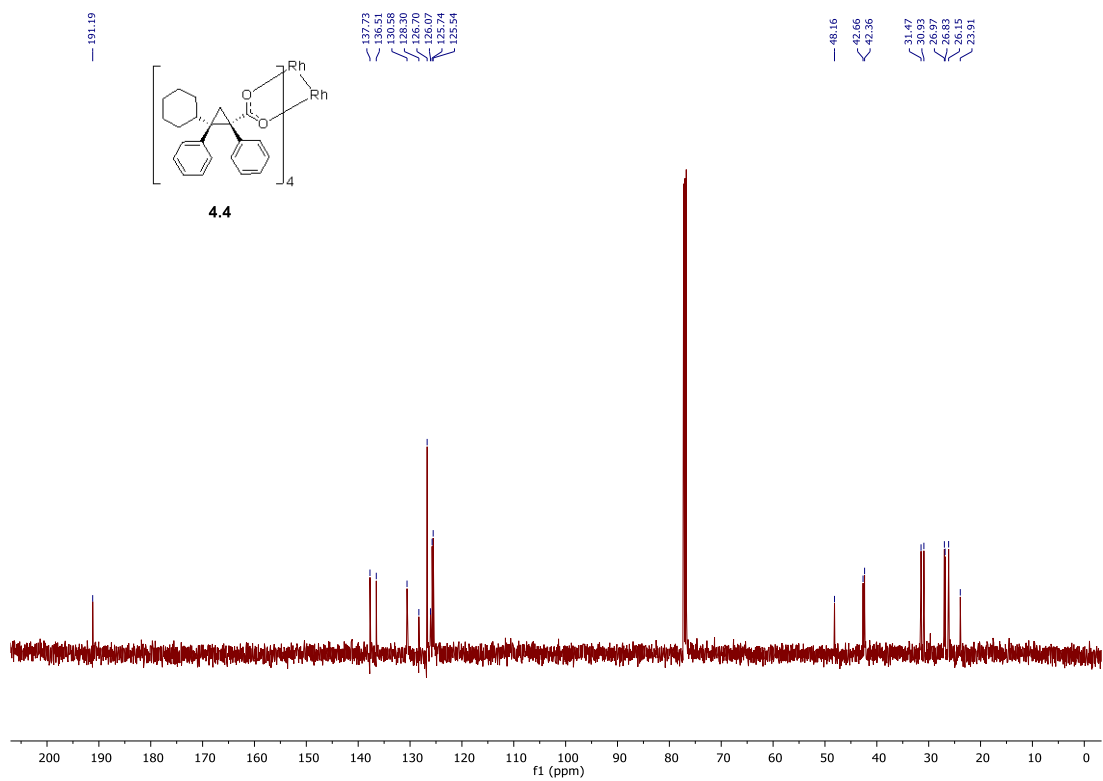
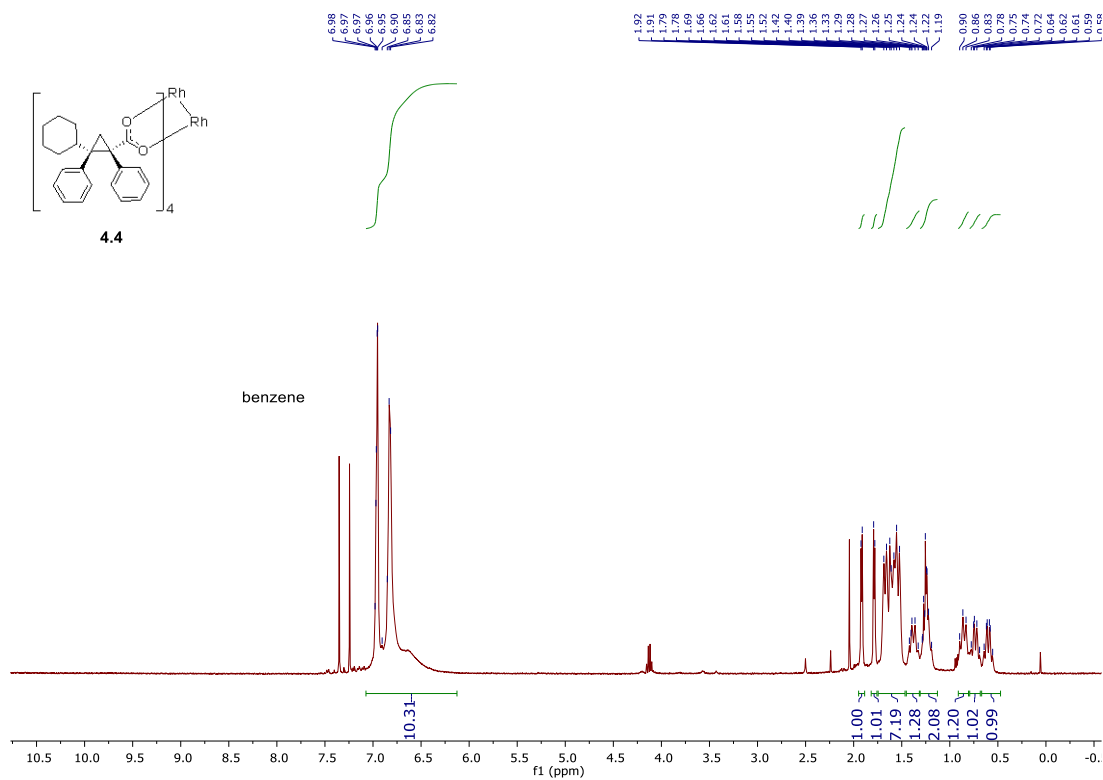


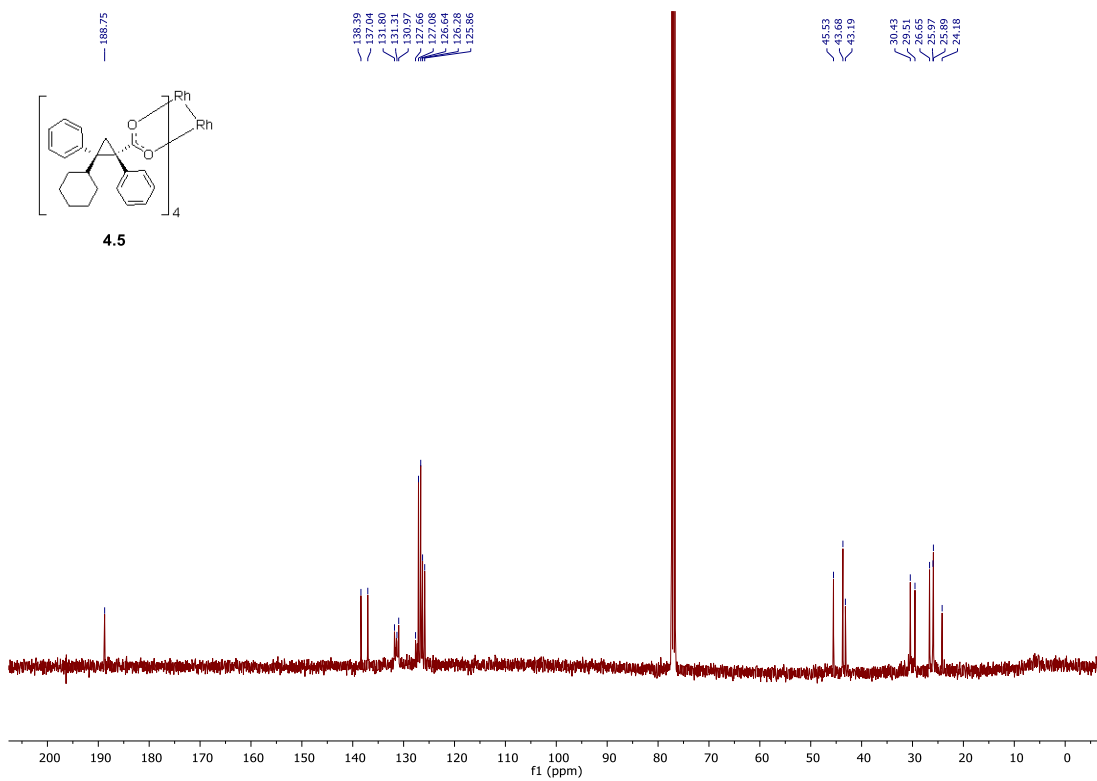
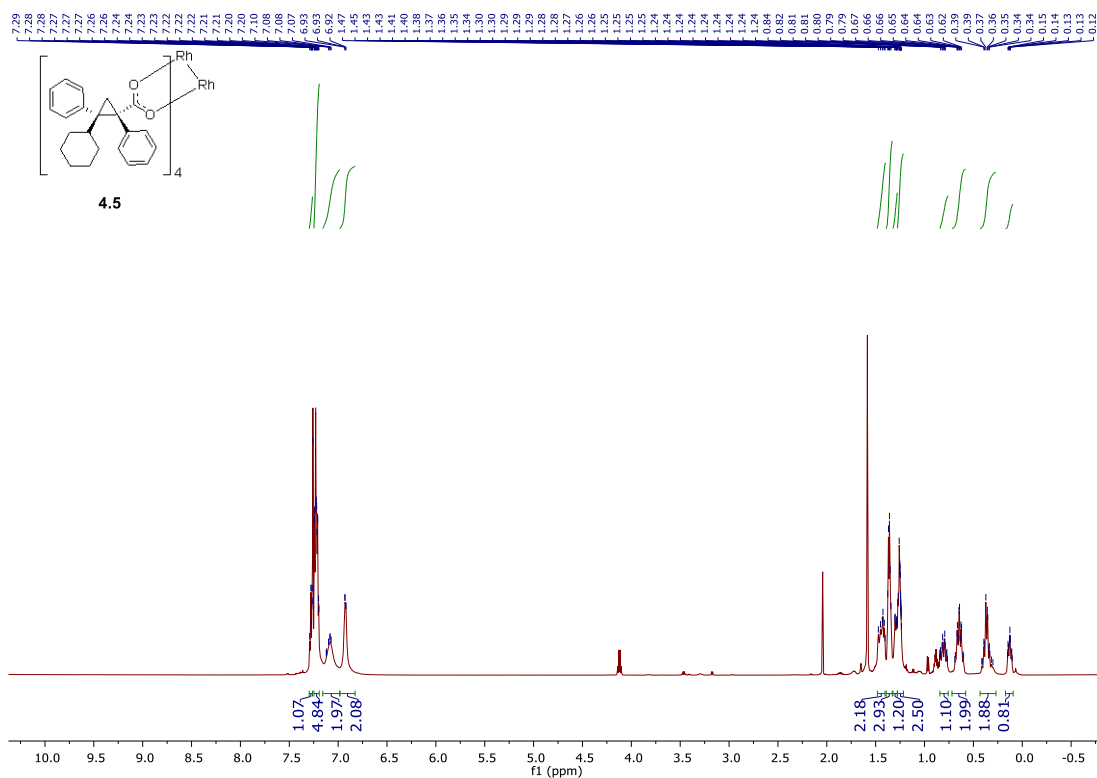


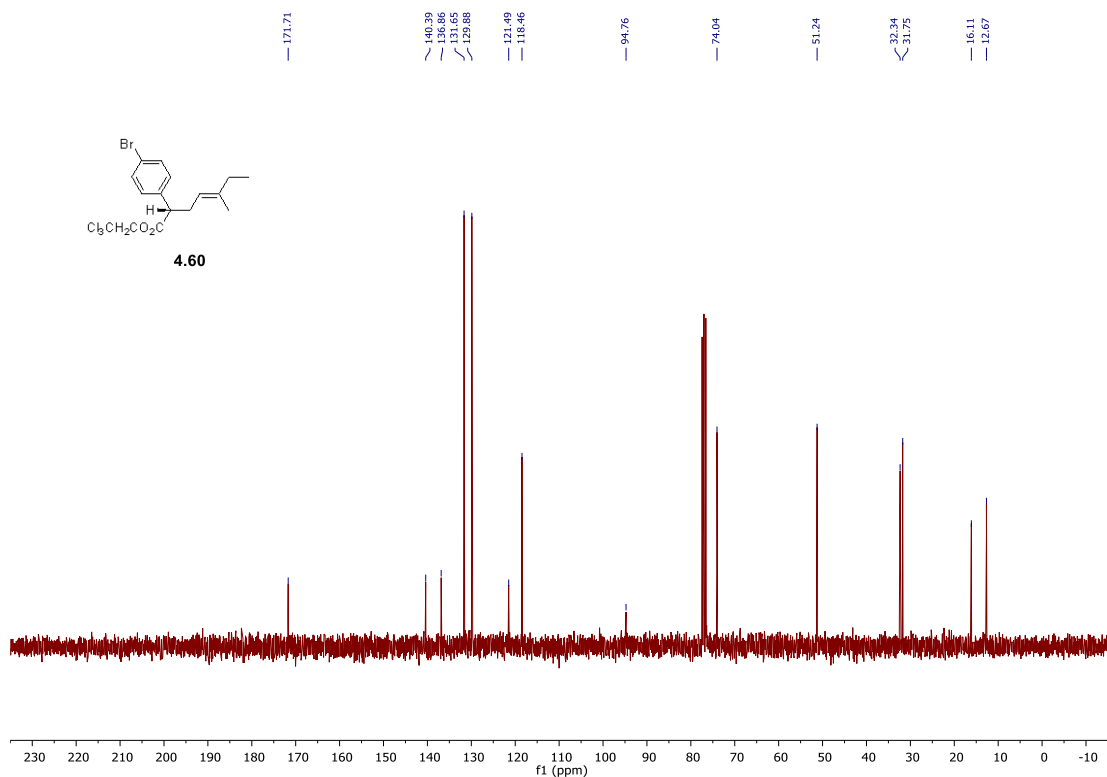
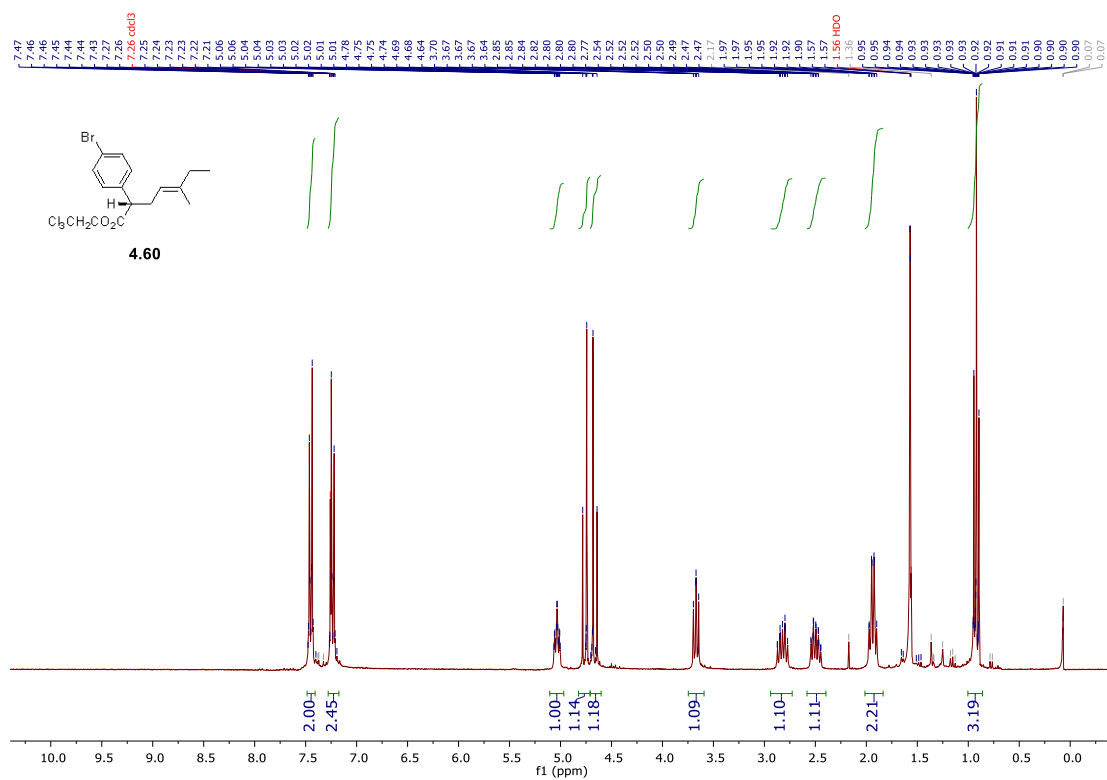


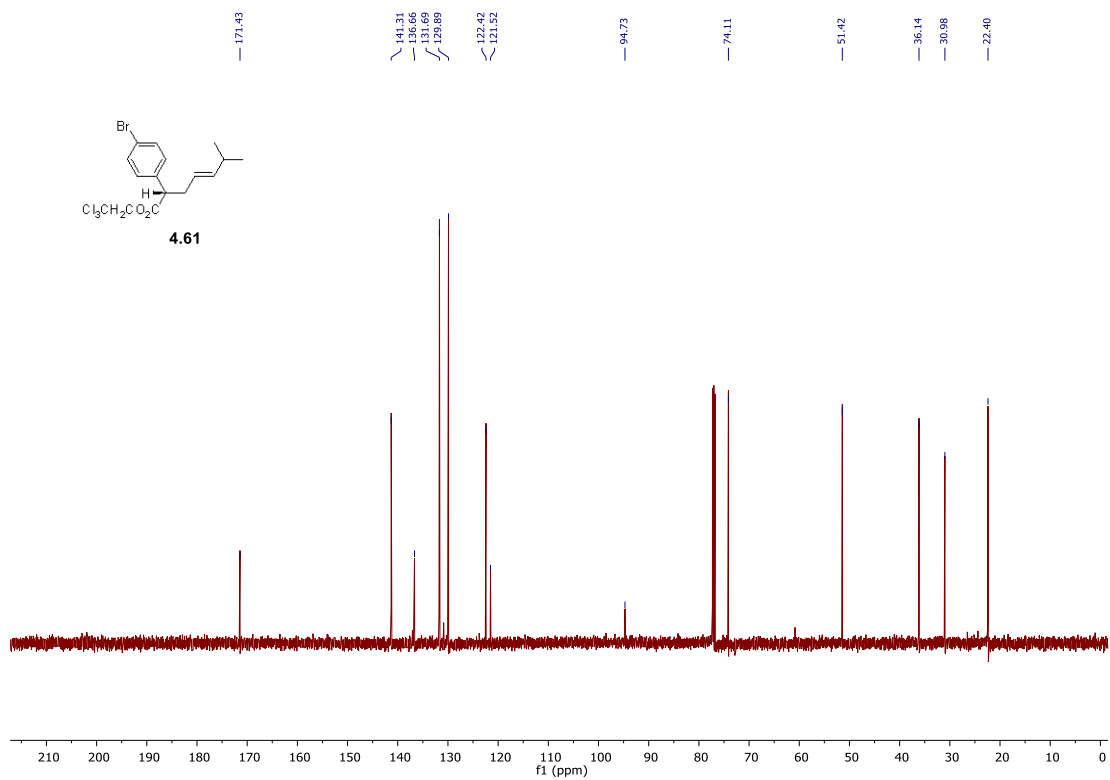
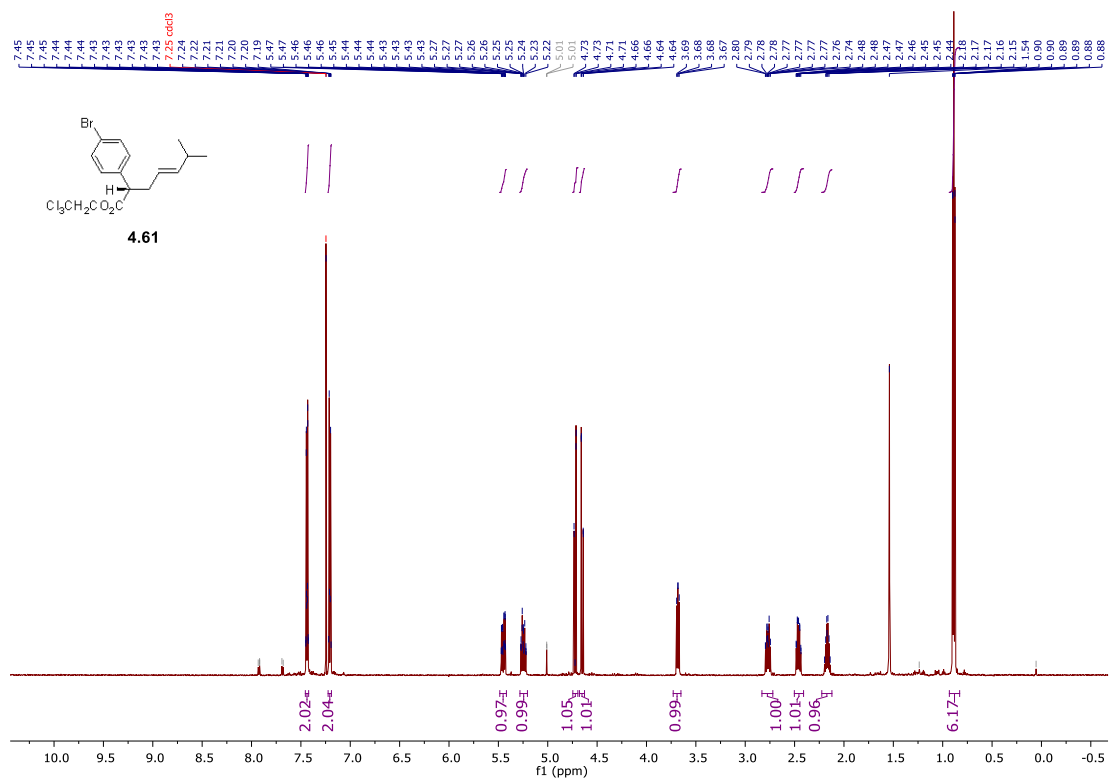


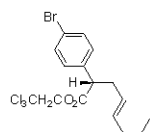
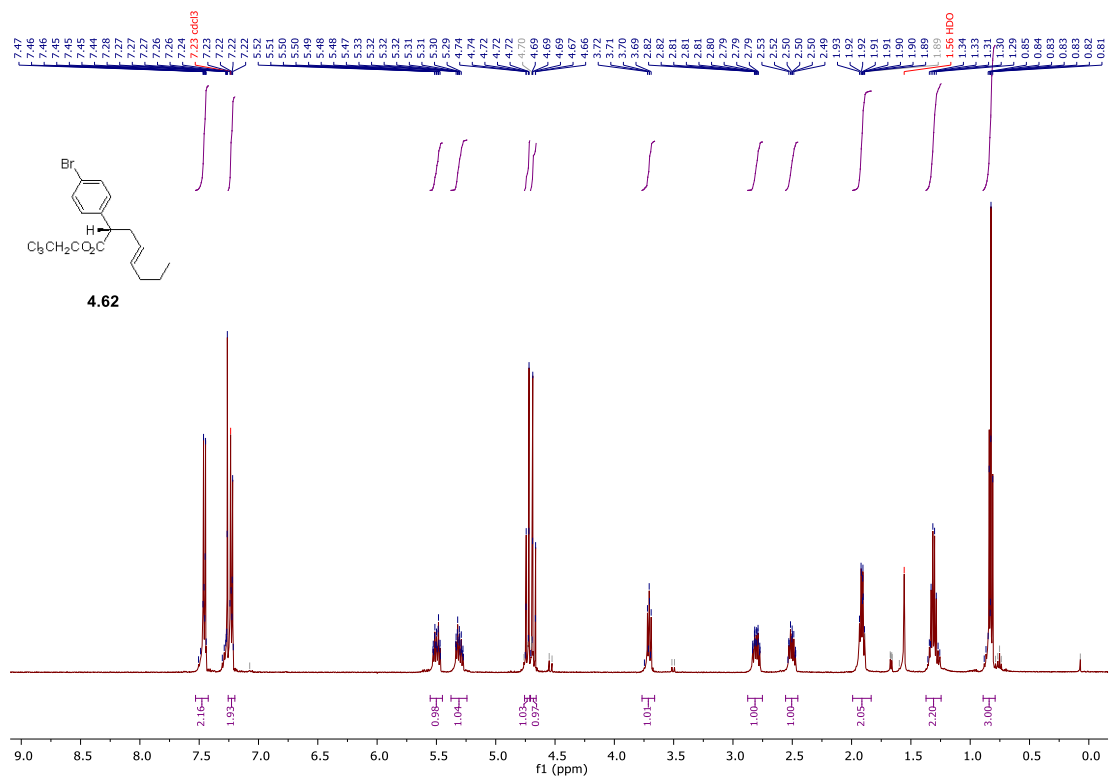




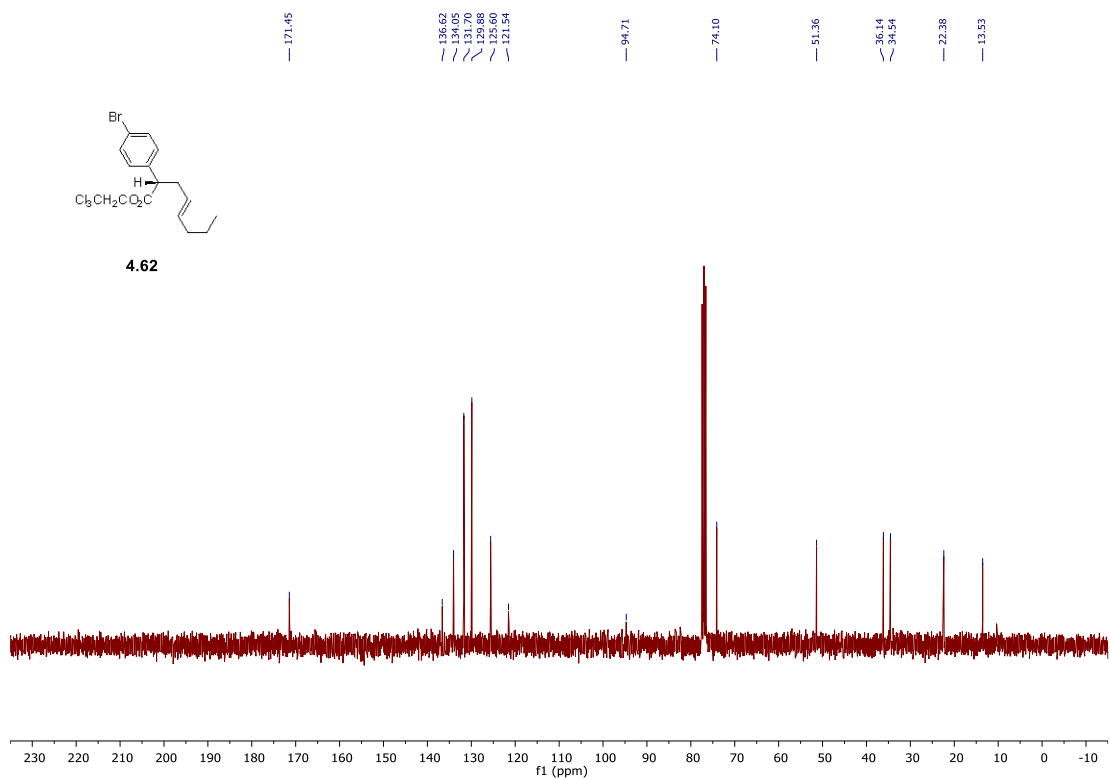


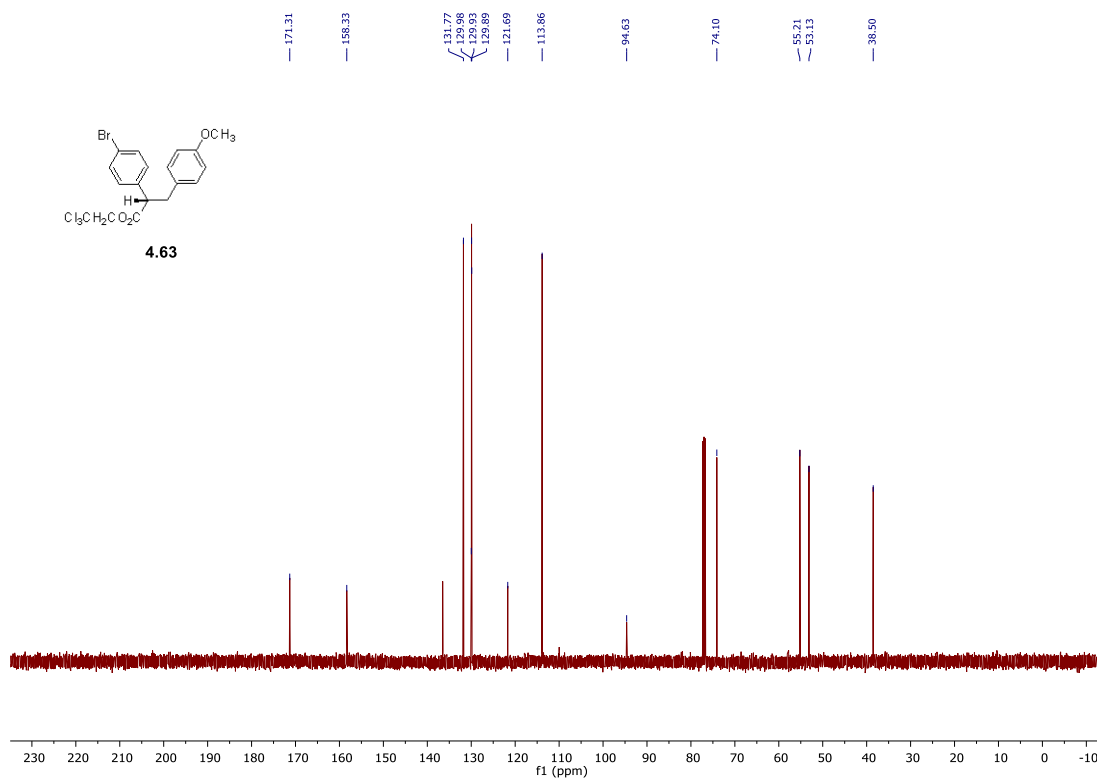
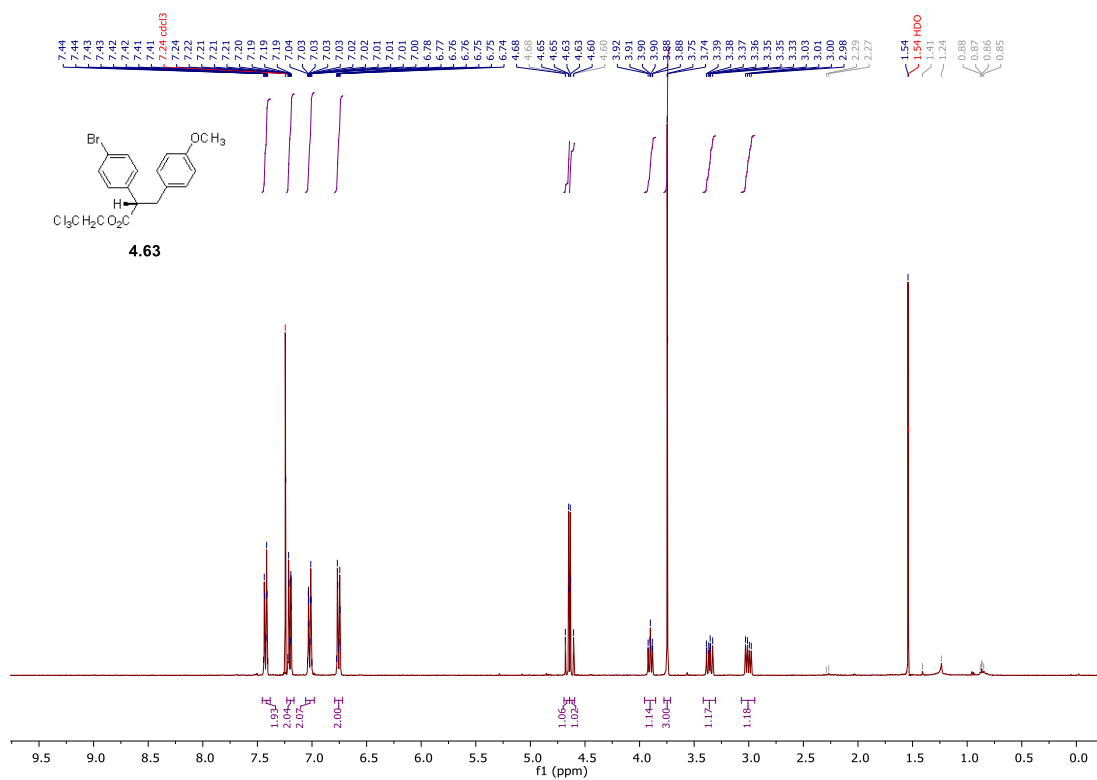


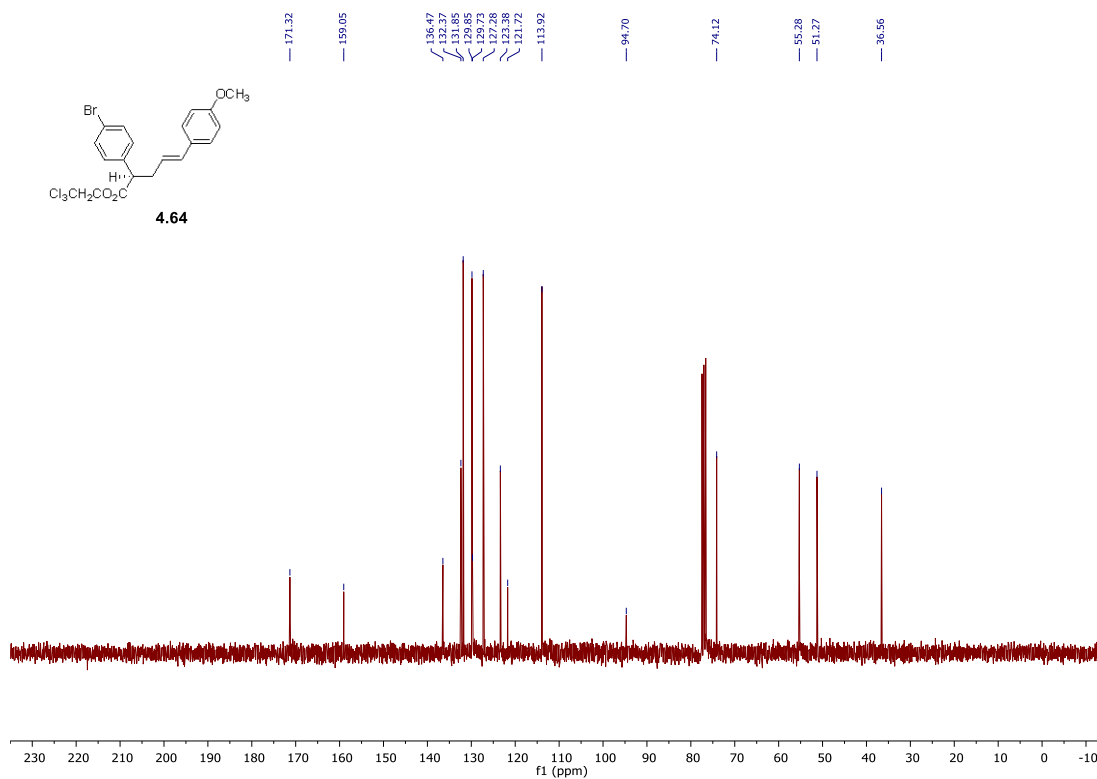
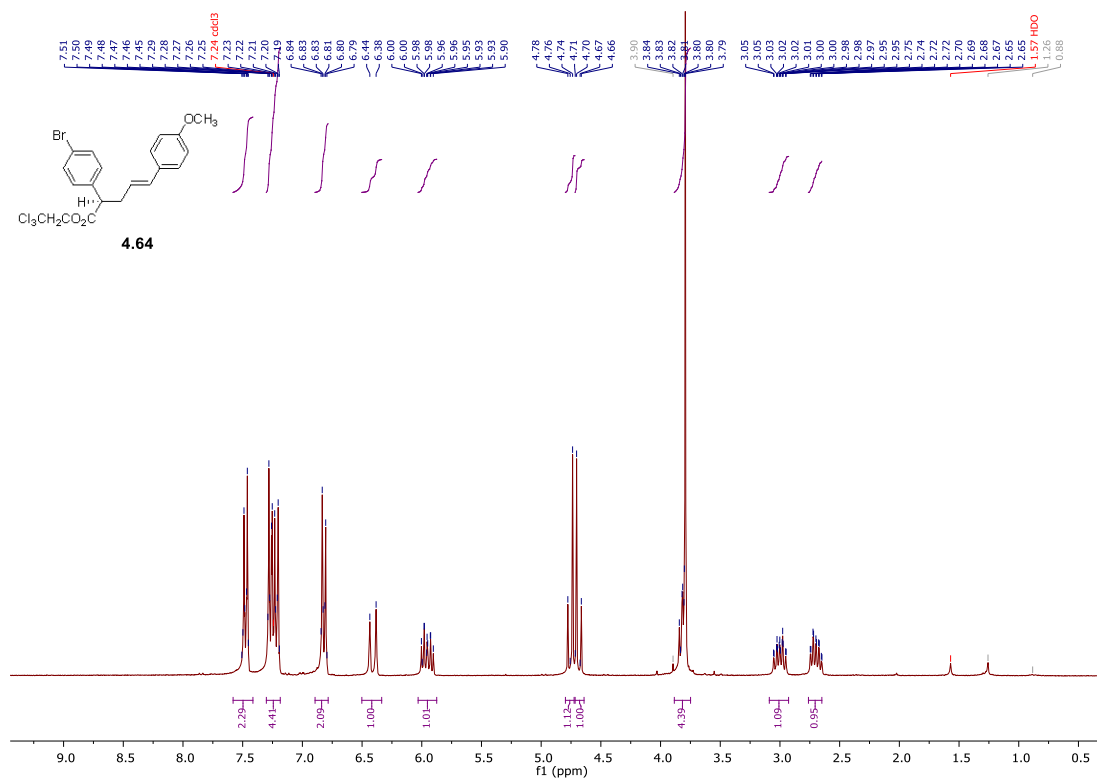


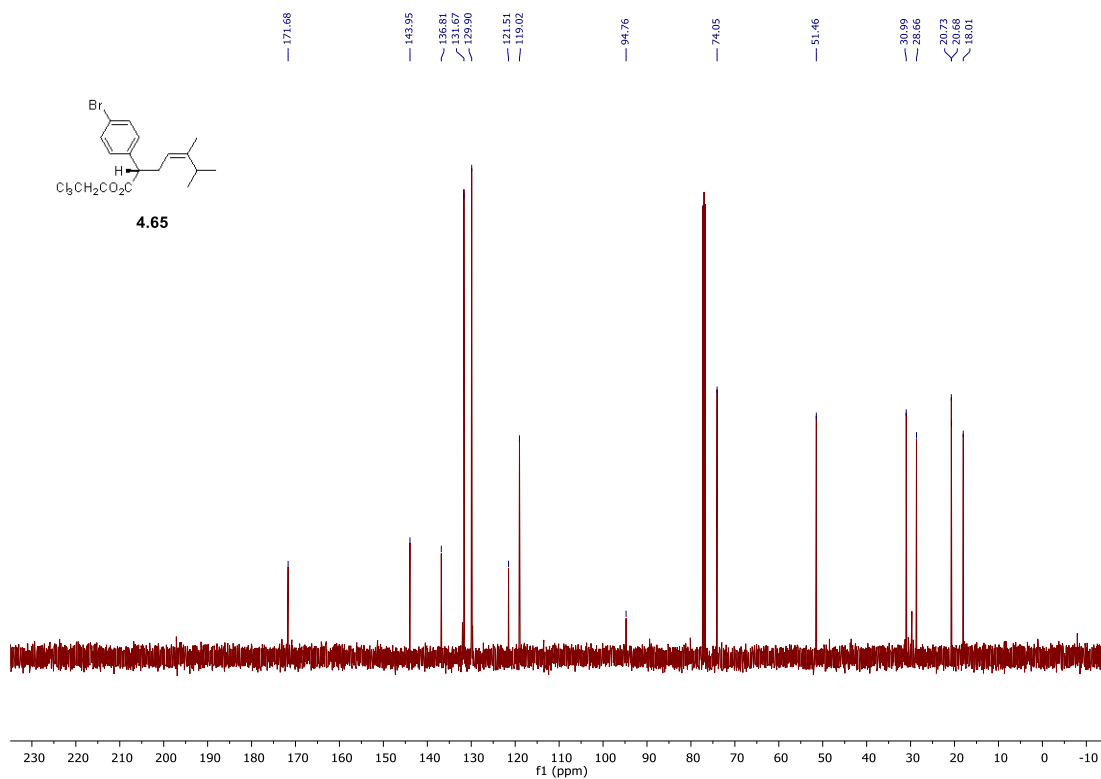
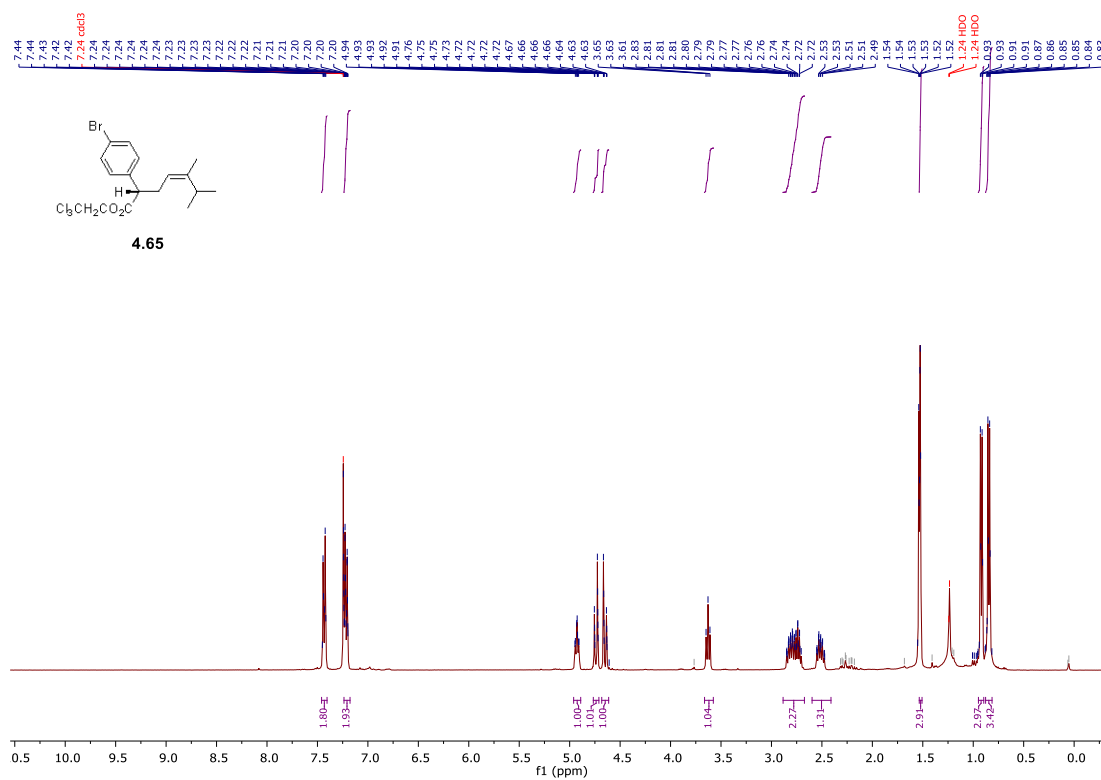


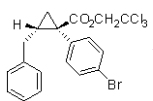
4.62



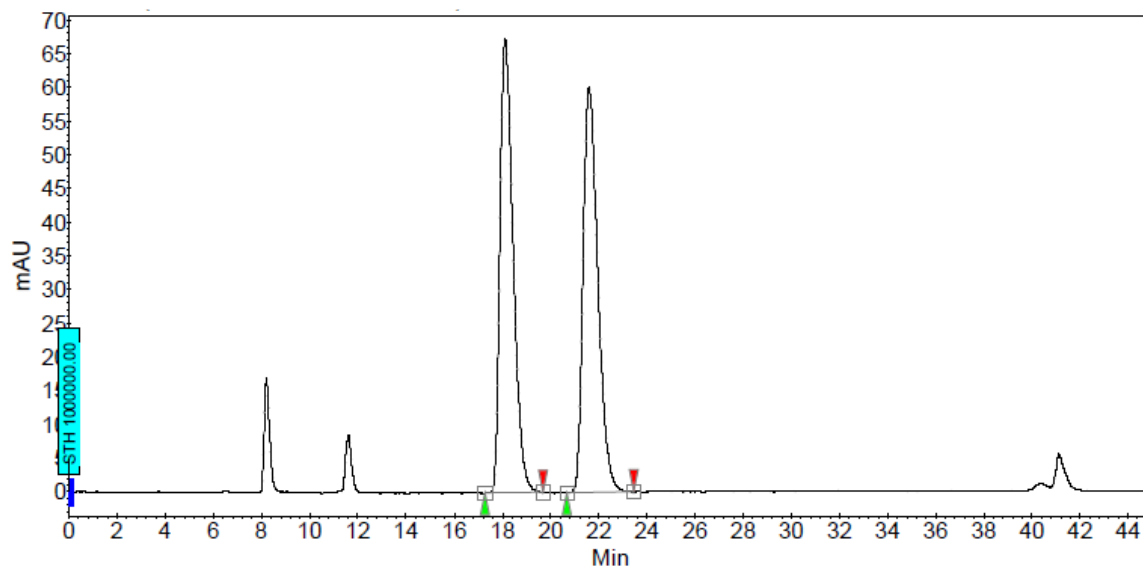
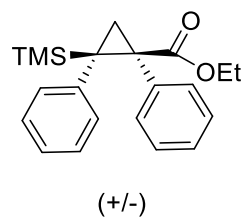






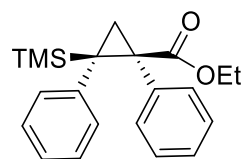


S.4.7 Chiral HPLC Traces

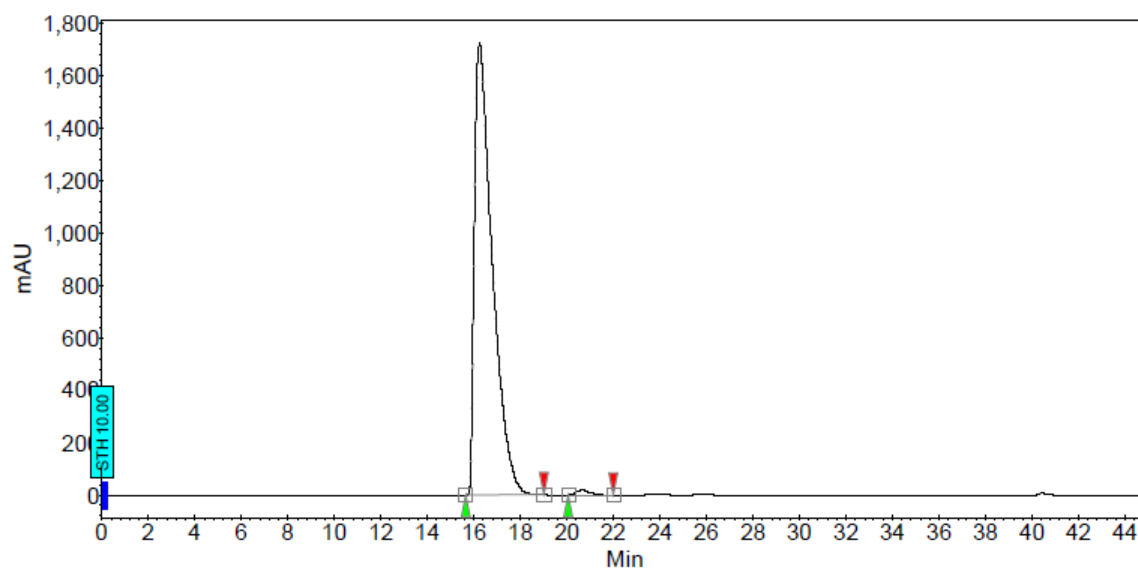


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	18.11	50.01	67.4	42.6	50.014
2	UNKNOWN	21.60	49.99	60.1	42.6	49.986
Total			100.00	127.5	85.2	100.000

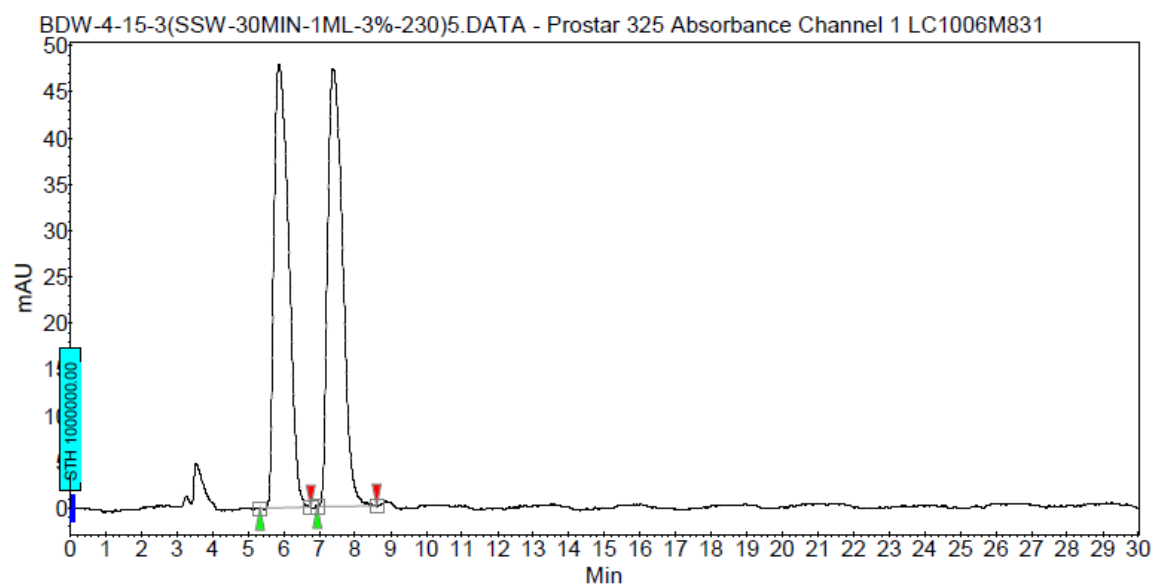
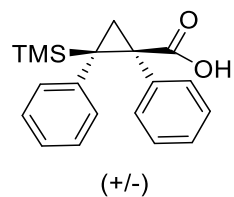


4.16



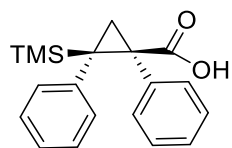
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	16.24	99.24	1727.6	1537.2	99.241
2	UNKNOWN	20.65	0.76	18.5	11.8	0.759
Total			100.00	1746.1	1549.0	100.000

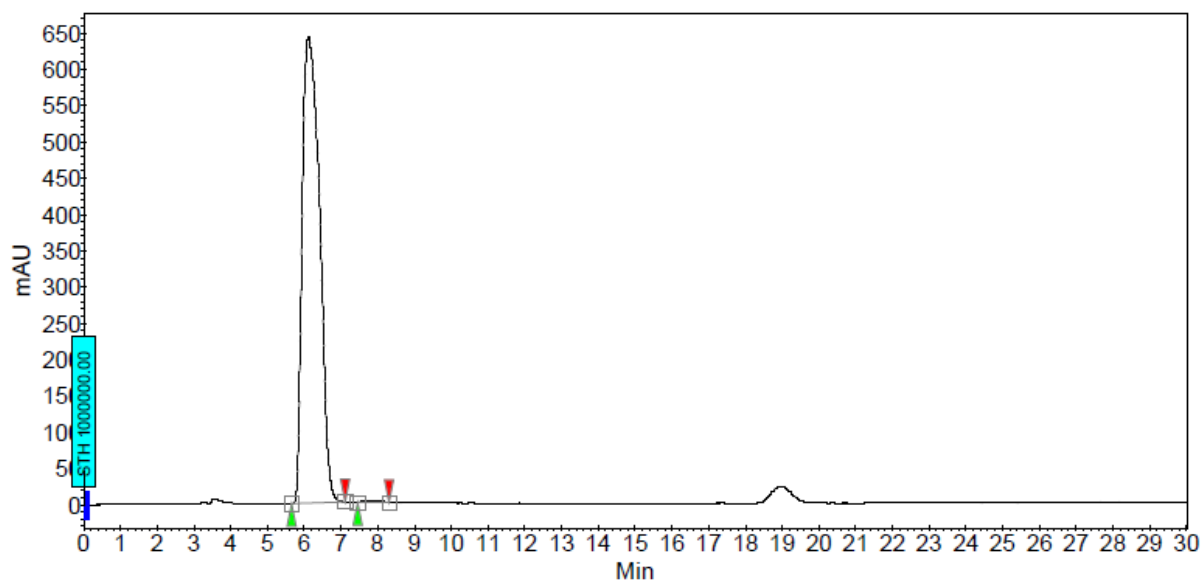


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	5.87	49.68	48.0	22.9	49.681
2	UNKNOWN	7.39	50.32	47.3	23.2	50.319
Total			100.00	95.3	46.1	100.000

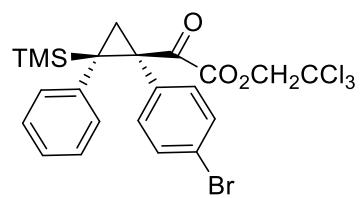


4.48

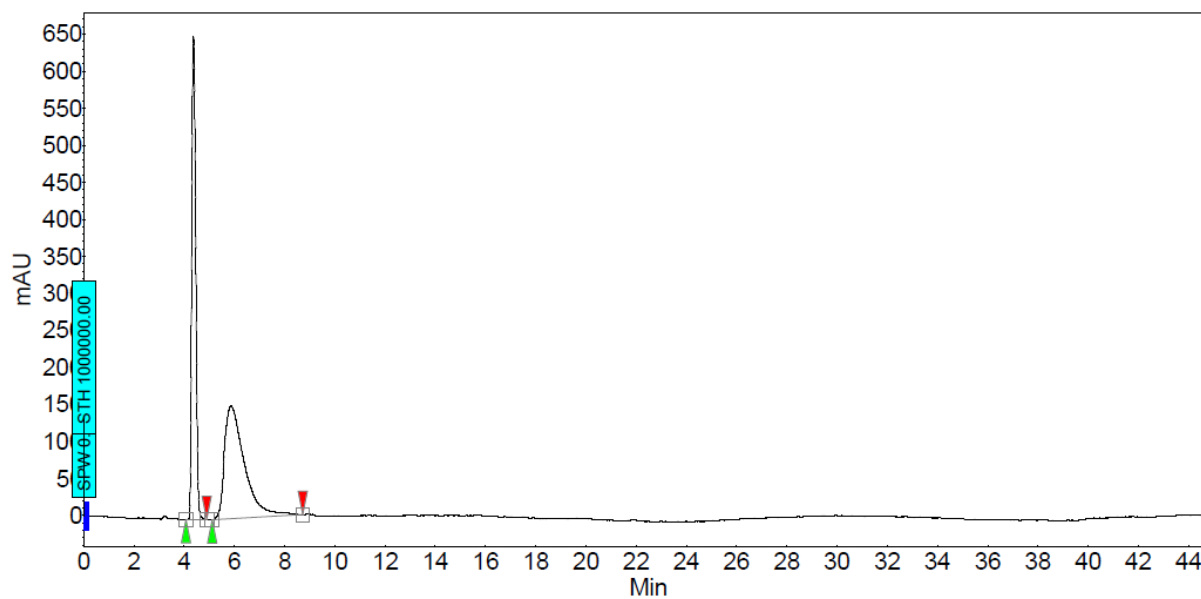


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	6.11	99.52	643.5	351.0	99.517
2	UNKNOWN	7.81	0.48	3.2	1.7	0.483
Total			100.00	646.7	352.7	100.000

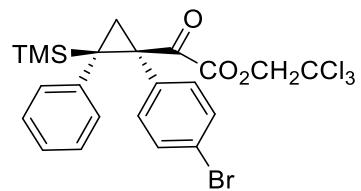


(+/-)

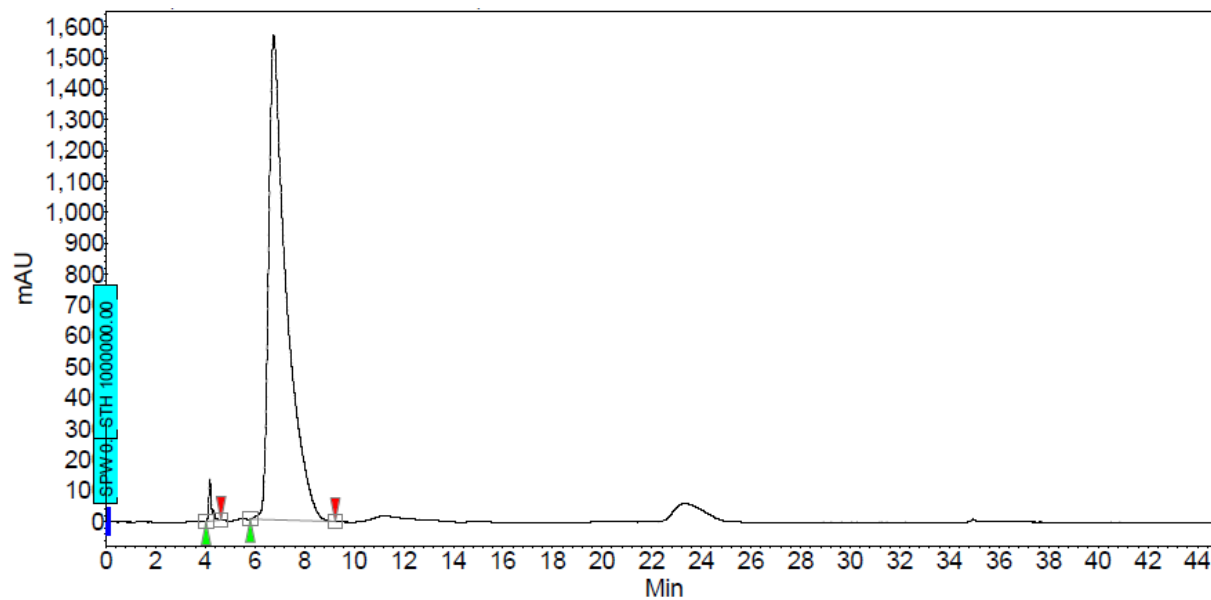


Peak results :

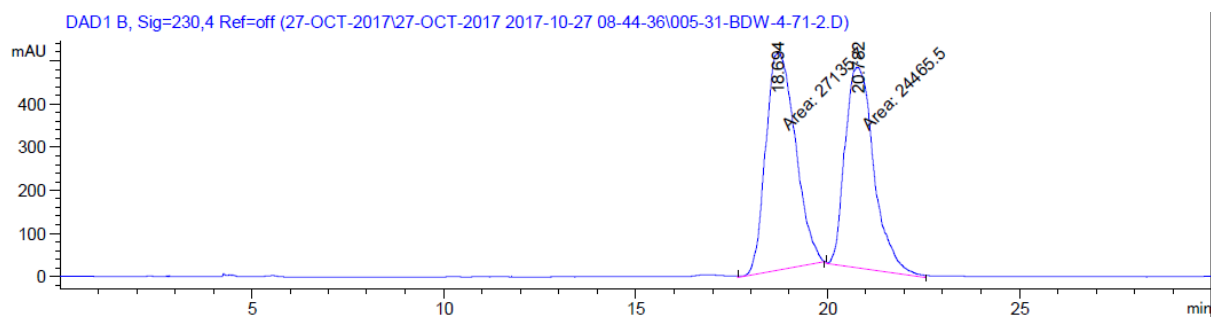
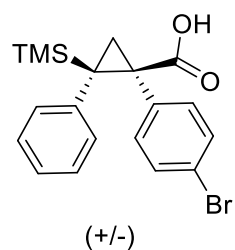
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	4.37	46.05	651.5	119.5	46.048
2	UNKNOWN	5.86	53.95	152.1	140.0	53.952
Total			100.00	803.6	259.5	100.000



4.52

**Peak results :**

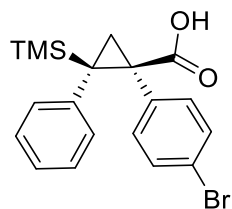
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	4.19	1.38	135.8	18.1	1.381
1	UNKNOWN	6.76	98.62	1567.0	1296.3	98.619
Total			100.00	1702.9	1314.5	100.000



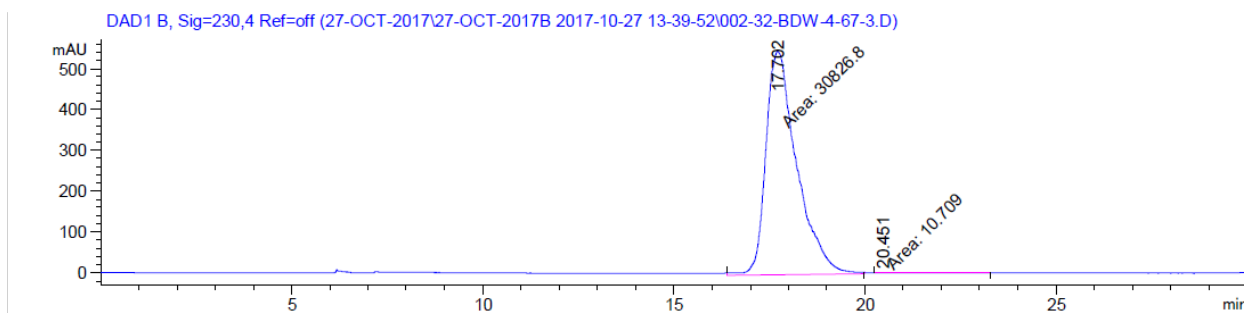
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.694	MM	0.8963	2.71357e4	504.57501	52.5874
2	20.782	MM	0.8771	2.44655e4	464.91687	47.4126

Totals : 5.16011e4 969.49188



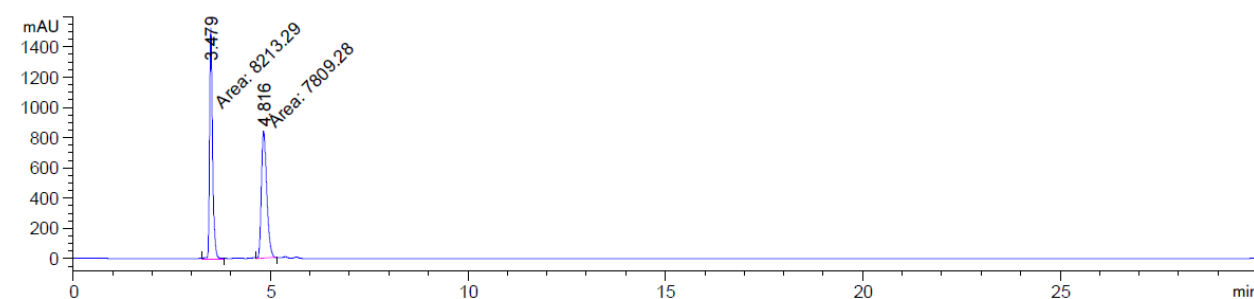
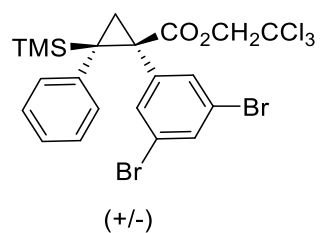
4.56



Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.702	MM	0.9380	3.08268e4	547.76343	99.9653
2	20.451	MM	0.2690	10.70905	6.63510e-1	0.0347

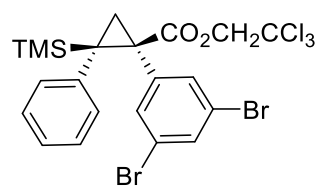
Totals : 3.08375e4 548.42694



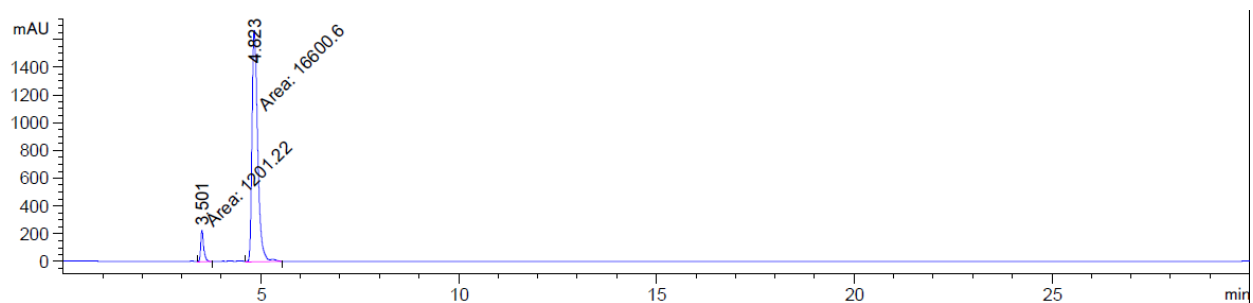
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.479	MM	0.0894	8213.28906	1530.70801	51.2608
2	4.816	MM	0.1554	7809.27734	837.59692	48.7392

Totals : 1.60226e4 2368.30493



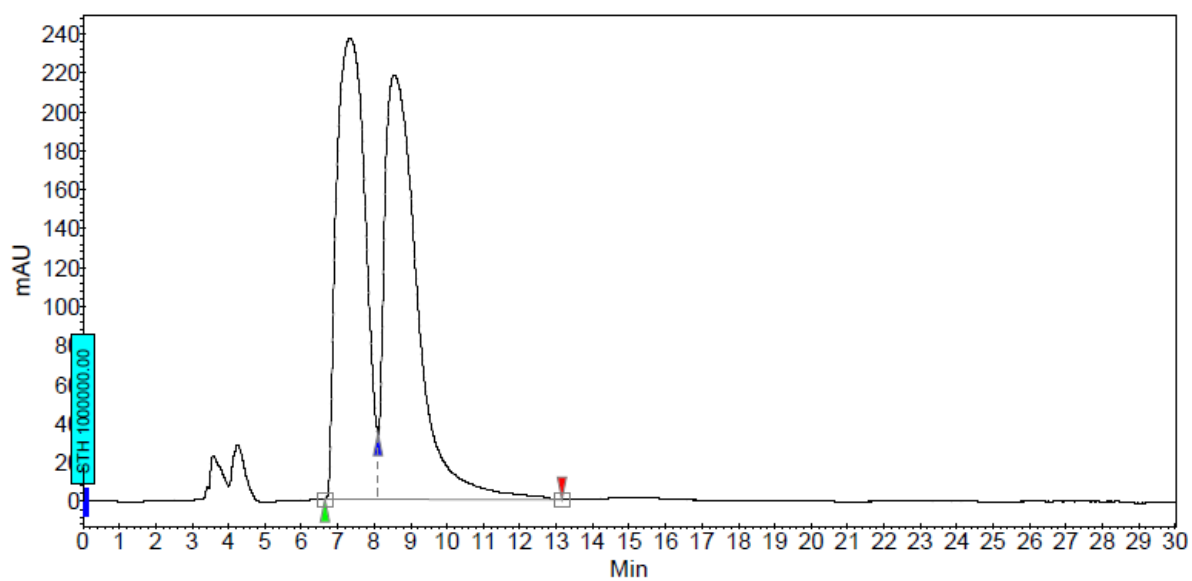
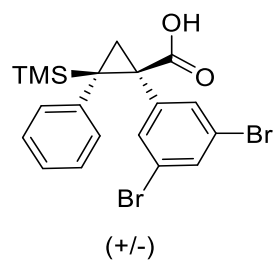
4.54



Signal 2: DAD1 B, Sig=230,4 Ref=off

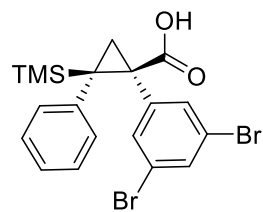
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.501	MM	0.0882	1201.22180	226.94489	6.7477
2	4.823	MM	0.1657	1.66006e4	1669.60767	93.2523

Totals : 1.78018e4 1896.55255

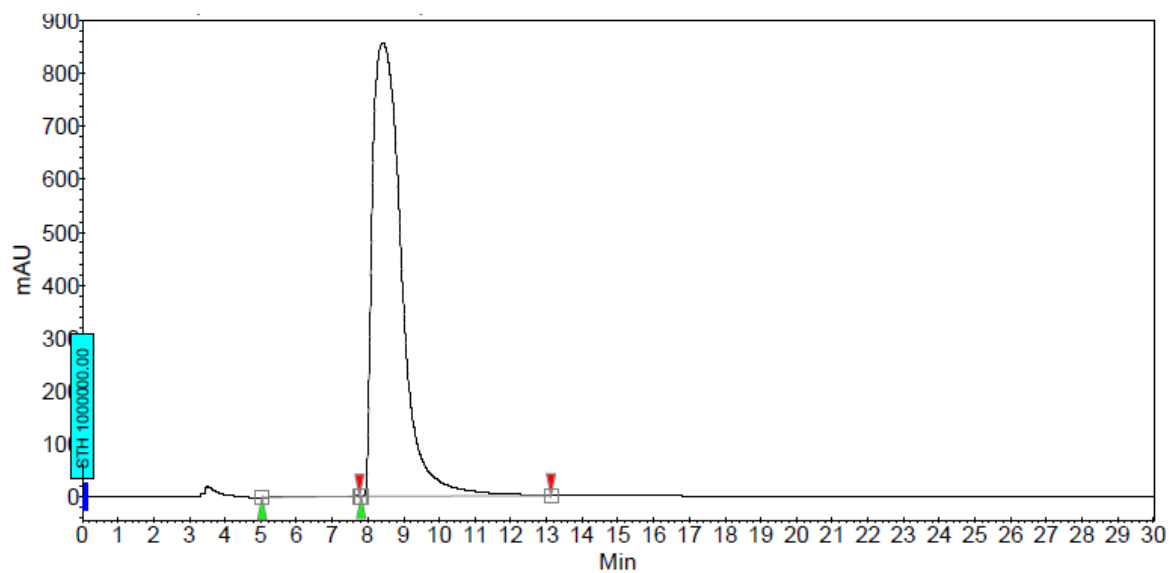


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	7.34	48.25	236.6	213.8	48.248
2	UNKNOWN	8.56	51.75	218.0	229.3	51.752
Total			100.00	454.6	443.1	100.000

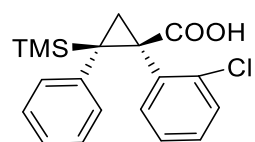


4.58

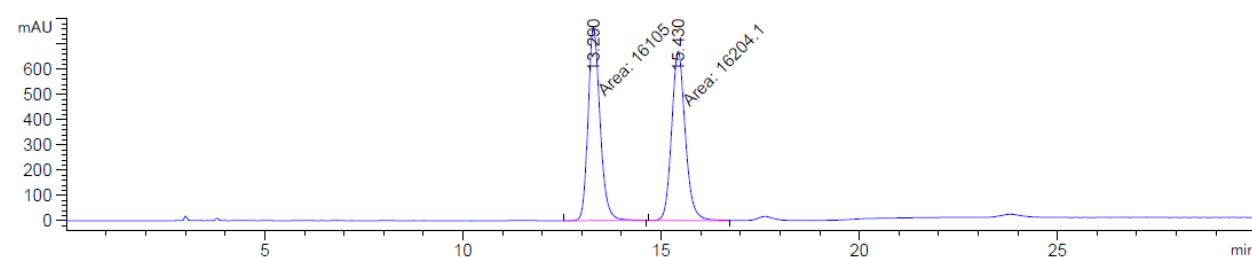


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	7.41	0.02	0.7	0.2	0.021
1	UNKNOWN	8.42	99.98	857.0	806.1	99.979
Total			100.00	857.6	806.3	100.000



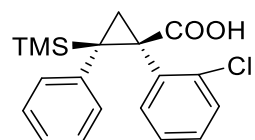
(+/-)



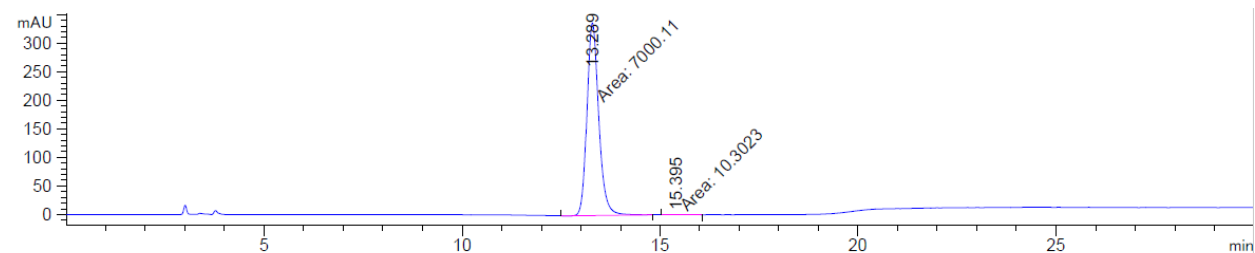
Signal 2: DAD1 B, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.290	MM	0.3505	1.61050e4	765.71149	49.8466
2	15.430	MM	0.4027	1.62041e4	670.56964	50.1534

Totals : 3.23092e4 1436.28113



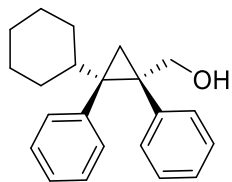
4.59



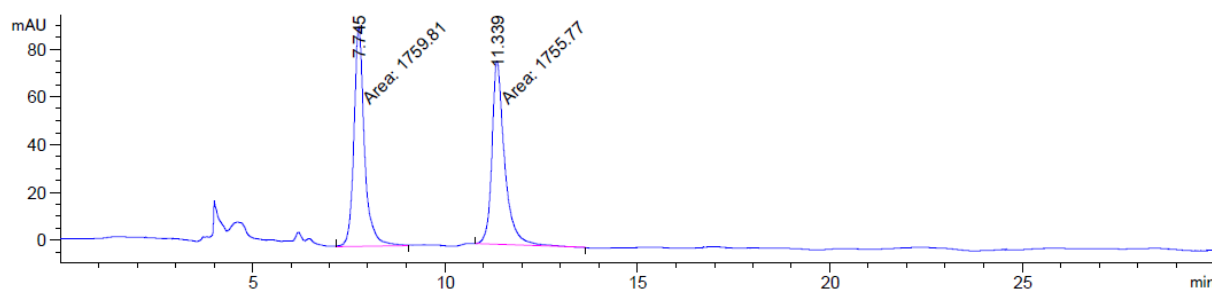
Signal 2: DAD1 B, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.289	MM	0.3461	7000.11230	337.10568	99.8530
2	15.395	MM	0.5864	10.30233	2.92803e-1	0.1470

Totals : 7010.41464 337.39849



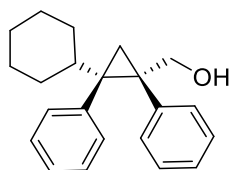
(+/-)



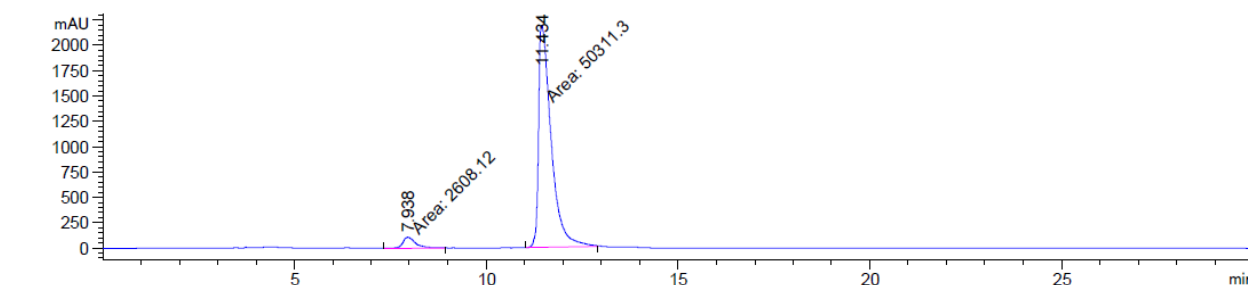
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.745	MM	0.3186	1759.80542	92.07153	50.0574
2	11.339	MM	0.3813	1755.76917	76.75454	49.9426

Totals : 3515.57458 168.82607



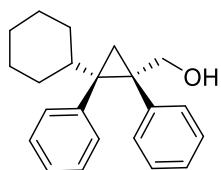
4.23

From $\text{Rh}_2(\text{R-}p\text{-PhTPCP})_4$:

Signal 2: DAD1 B, Sig=230,4 Ref=off

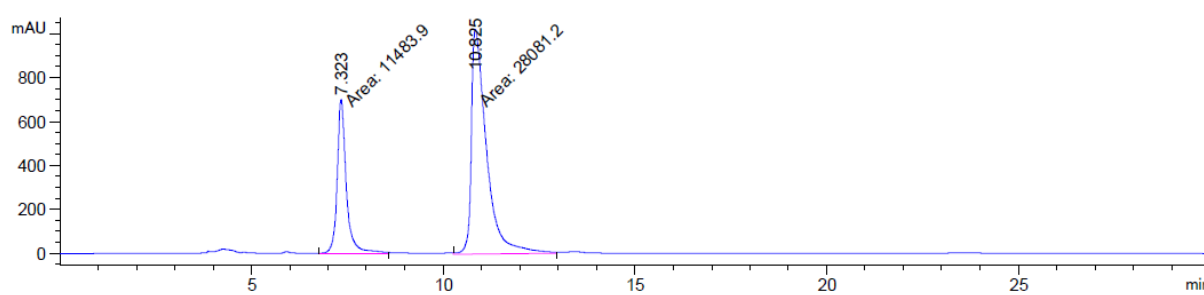
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.938	MM	0.3994	2608.12476	108.84543	4.9285
2	11.434	MM	0.3824	5.03113e4	2192.92822	95.0715

Totals : 5.29194e4 2301.77365



4.23

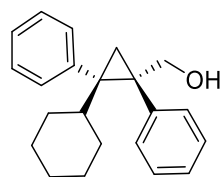
From $\text{Rh}_2(\text{R-DOSP})_4$



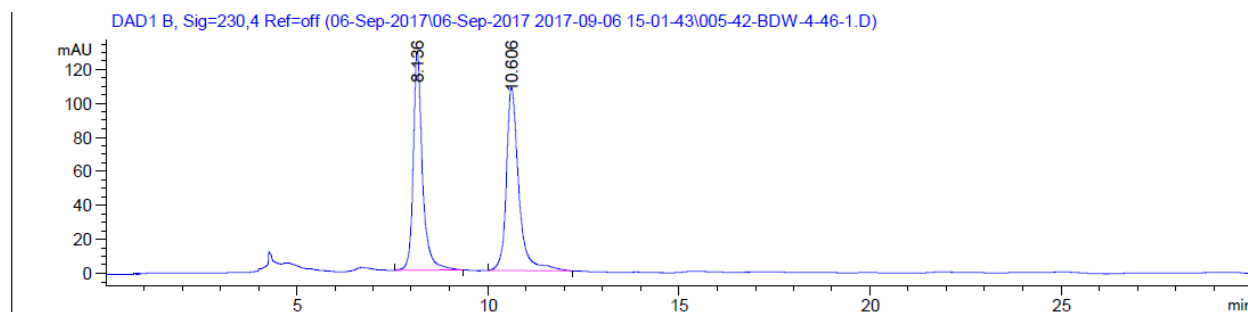
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.323	MM	0.2735	1.14839e4	699.88080	29.0252
2	10.825	MM	0.4571	2.80812e4	1023.93774	70.9748

Totals : 3.95651e4 1723.81854



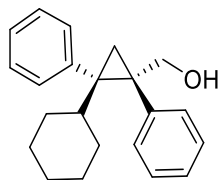
(+/-)



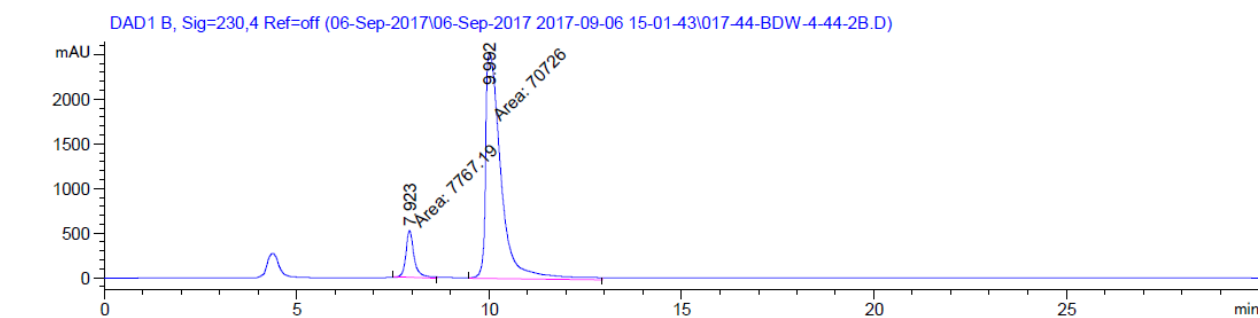
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.136	BB	0.2311	2151.96362	128.69029	46.9845
2	10.606	BB	0.3211	2428.19507	107.68302	53.0155

Totals : 4580.15869 236.37331



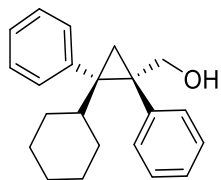
4.24

From Rh₂(R-DOSP)₄

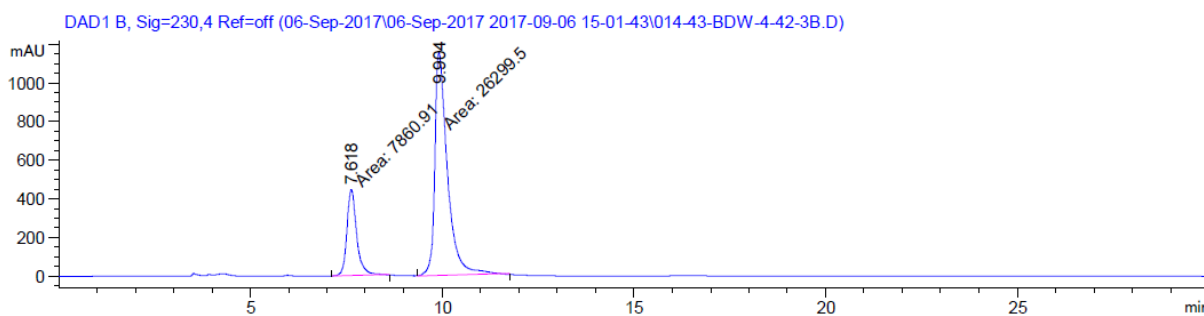
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.923	MM	0.2480	7767.19287	522.04584	9.8954
2	9.992	MM	0.4682	7.07260e4	2517.44678	90.1046

Totals : 7.84932e4 3039.49261



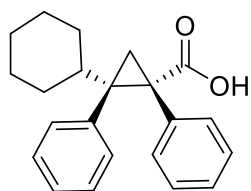
4.24

From $\text{Rh}_2(\text{R-}p\text{-PhTPCP})_4$ 

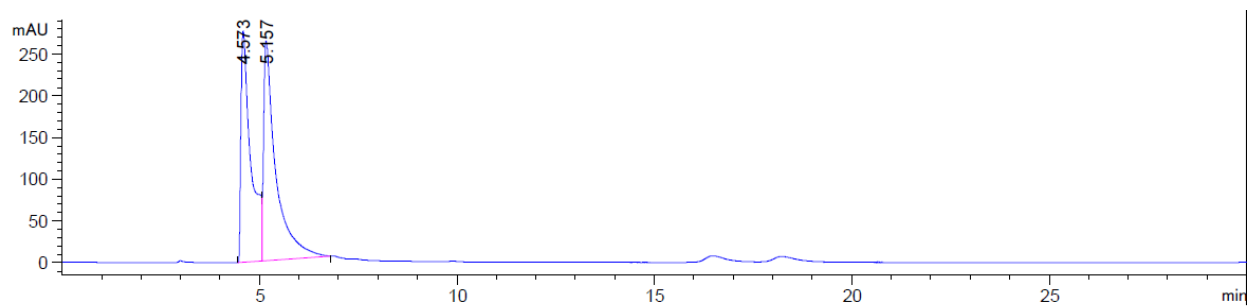
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.618	MM	0.2945	7860.90771	444.87115	23.0118
2	9.904	MM	0.3801	2.62995e4	1153.23914	76.9882

Totals : 3.41604e4 1598.11029



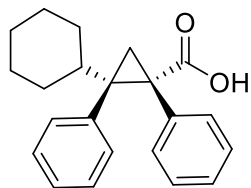
(+/-)



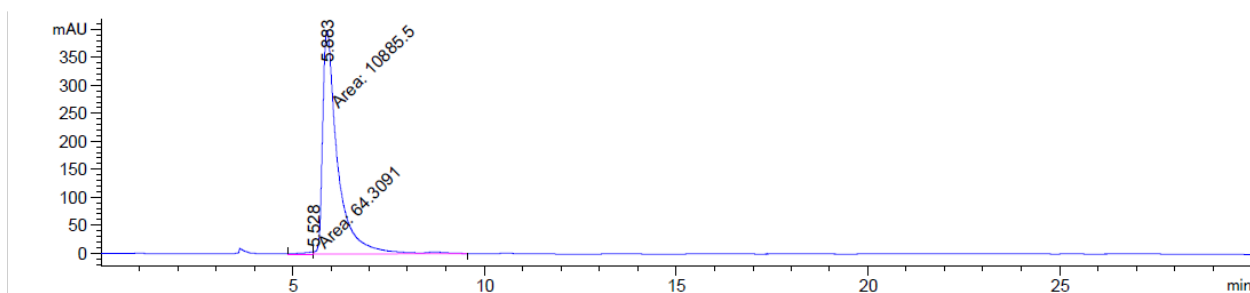
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.573	BV	0.2385	4778.81006	276.72427	45.9880
2	5.157	VB	0.2896	5612.62842	263.35245	54.0120

Totals : 1.03914e4 540.07672



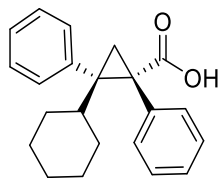
4.27



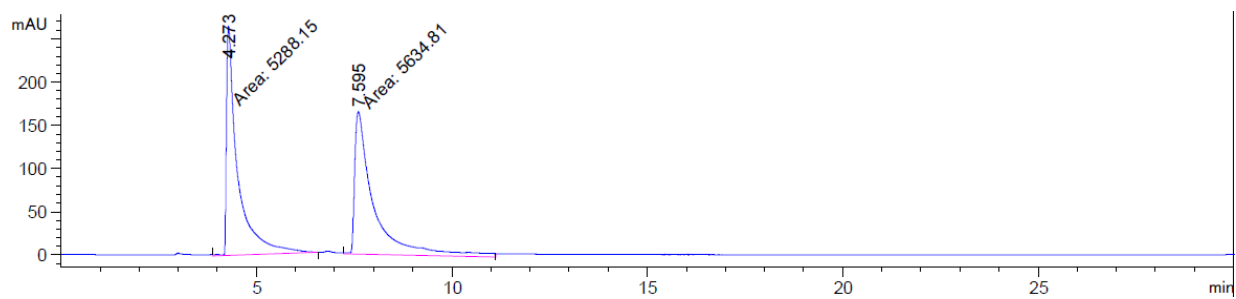
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.528	MF	0.3278	64.30907	3.27008	0.5873
2	5.883	FM	0.4546	1.08855e4	399.11838	99.4127

Totals : 1.09498e4 402.38846



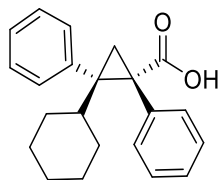
(+/-)



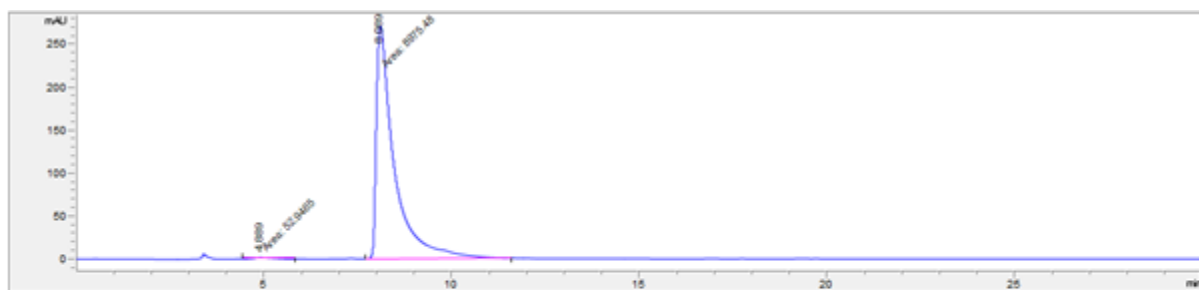
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.273	MM	0.3313	5288.15283	265.99622	48.4132
2	7.595	MM	0.5689	5634.80713	165.07961	51.5868

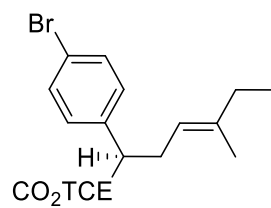
Totals : 1.09230e4 431.07582



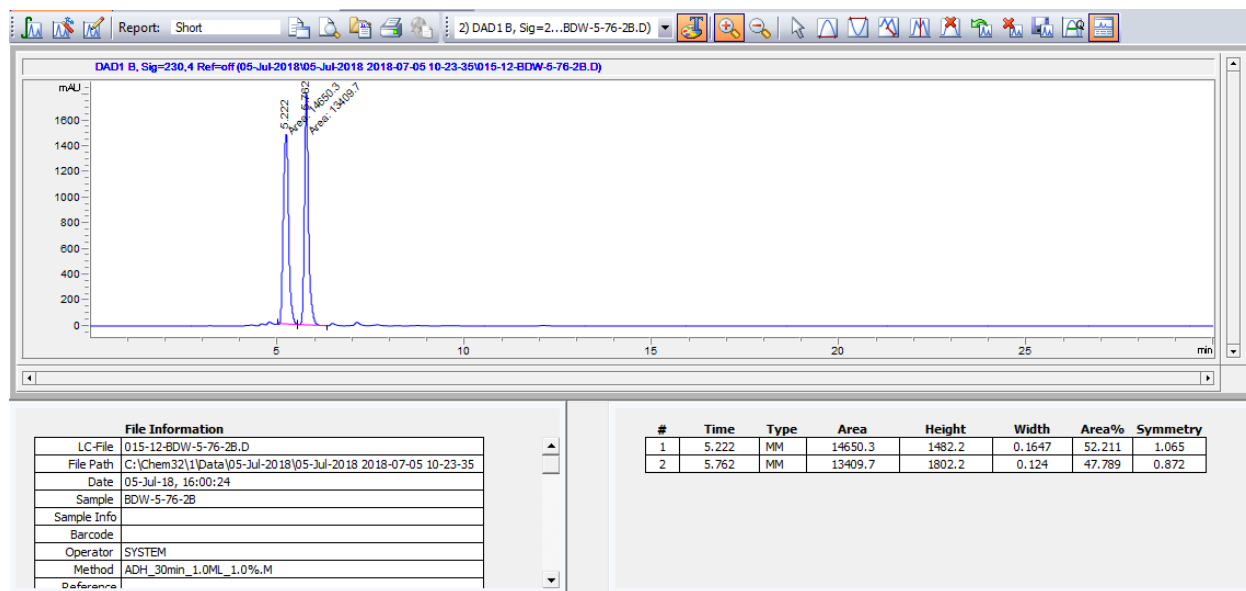
4.28

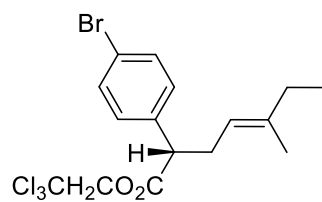


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.889	MM	52.9	1.6	0.5628	0.586	0.53
2	8.089	MM	8975.5	270.4	0.5531	99.414	0.279

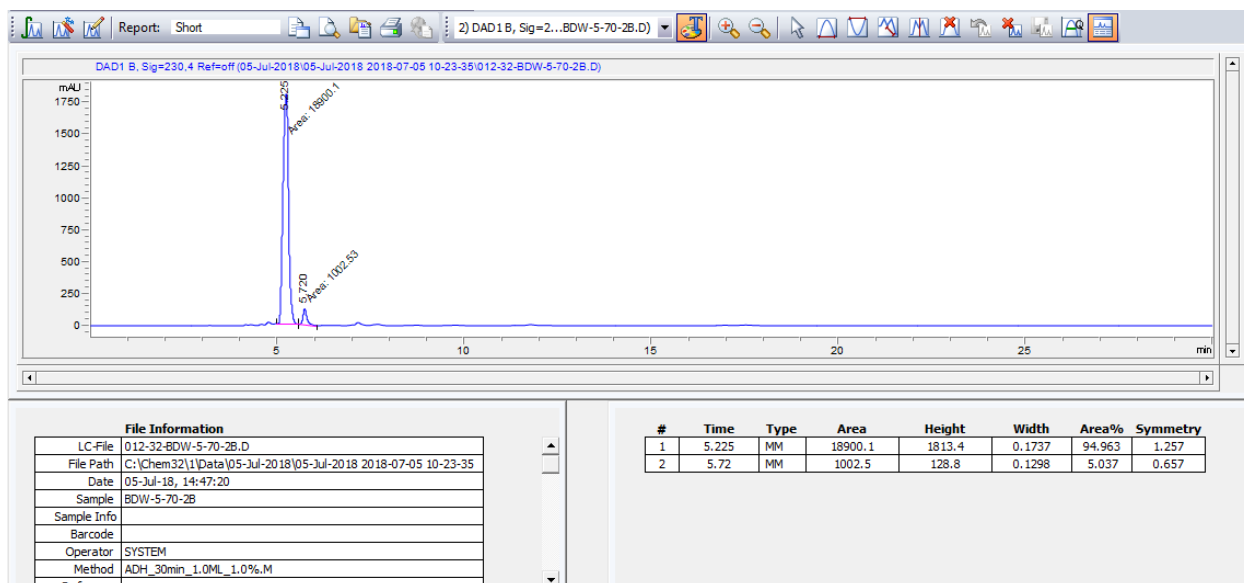


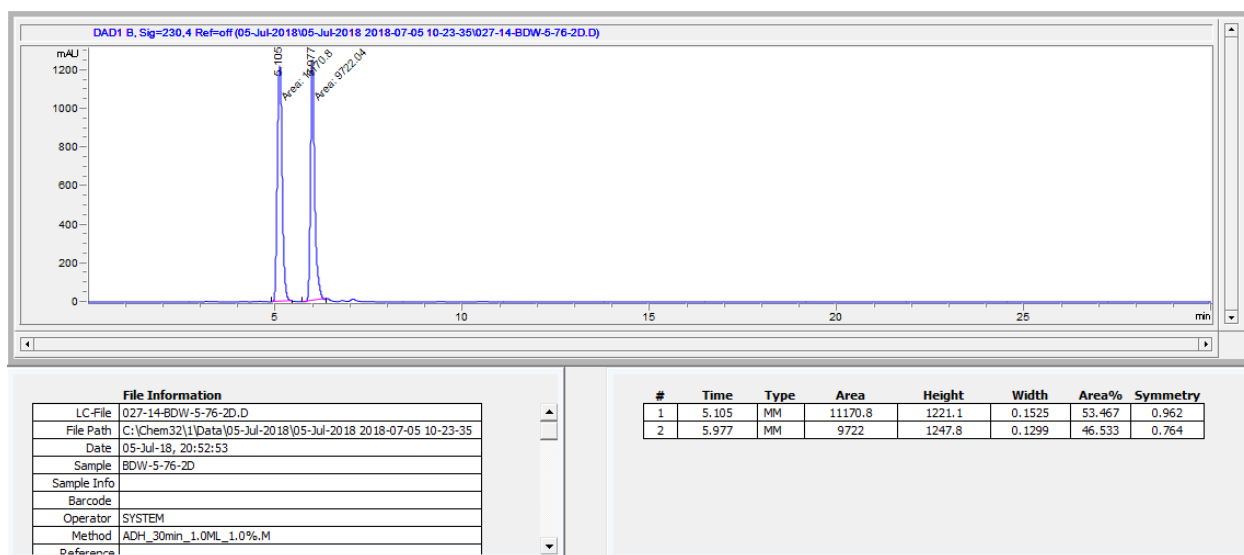
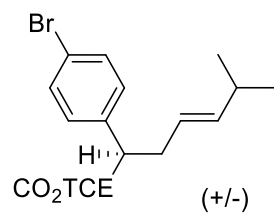
(+/-)

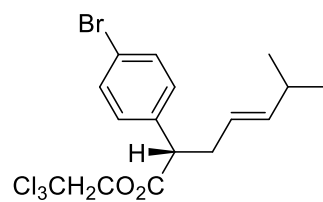




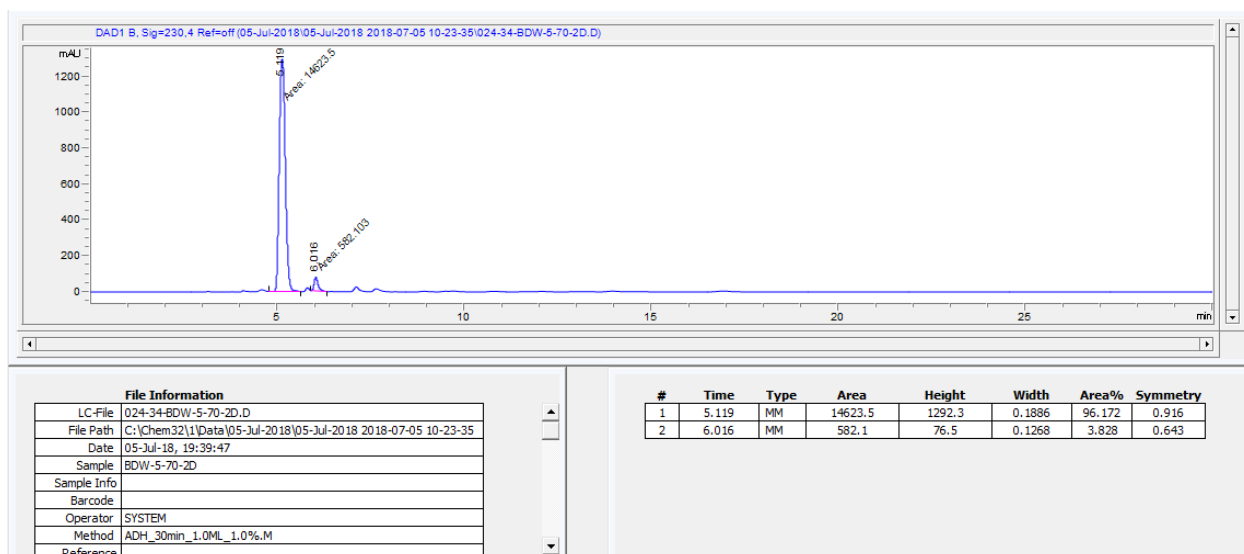
4.60

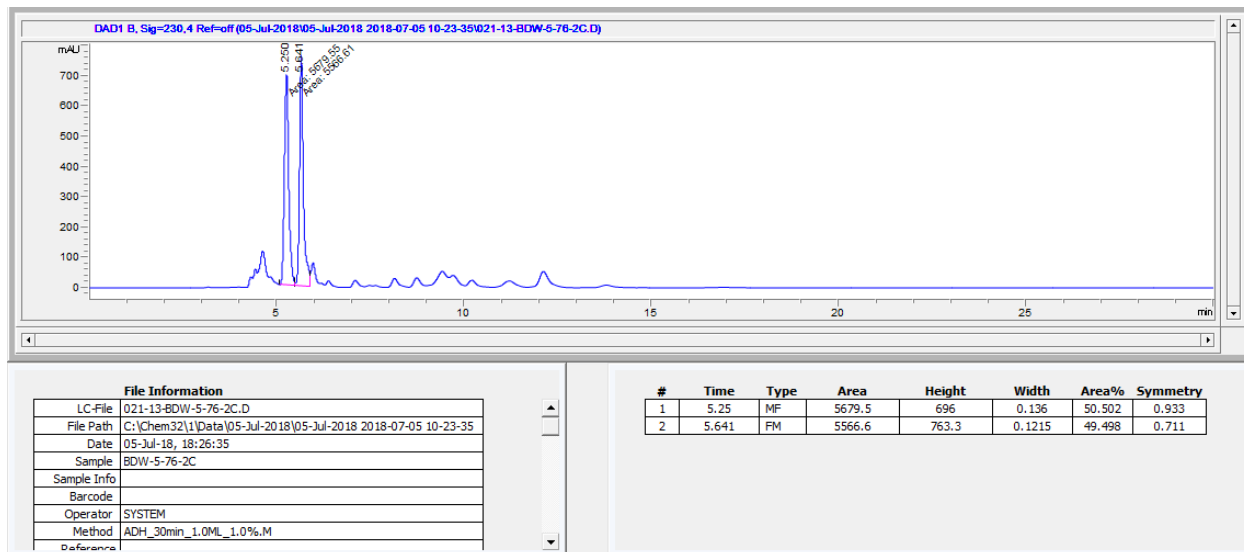
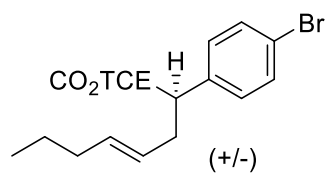


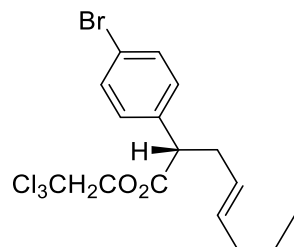




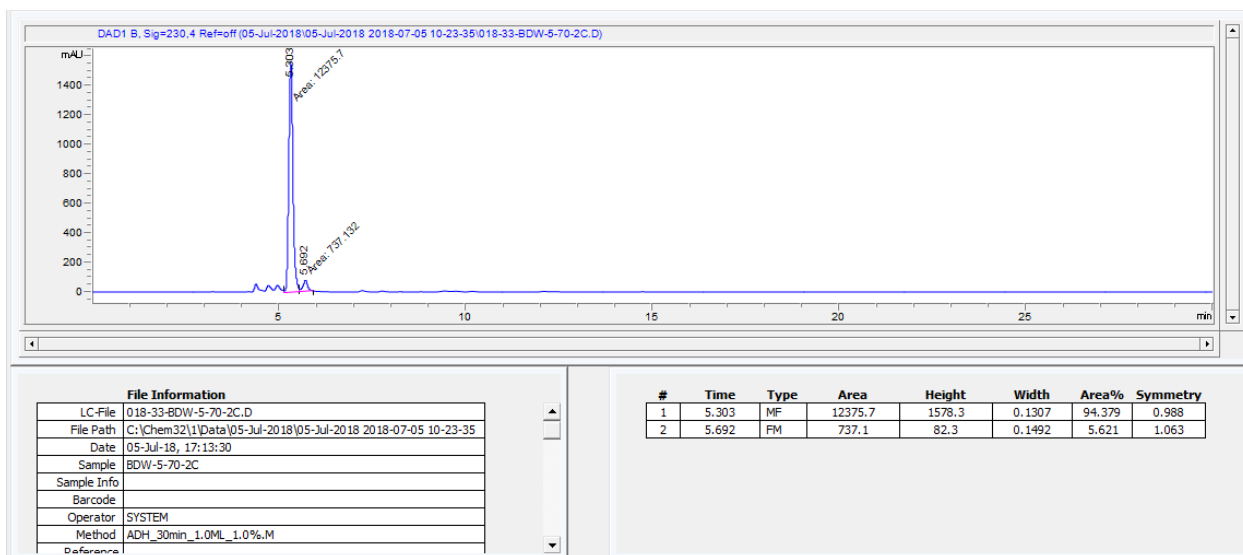
4.61

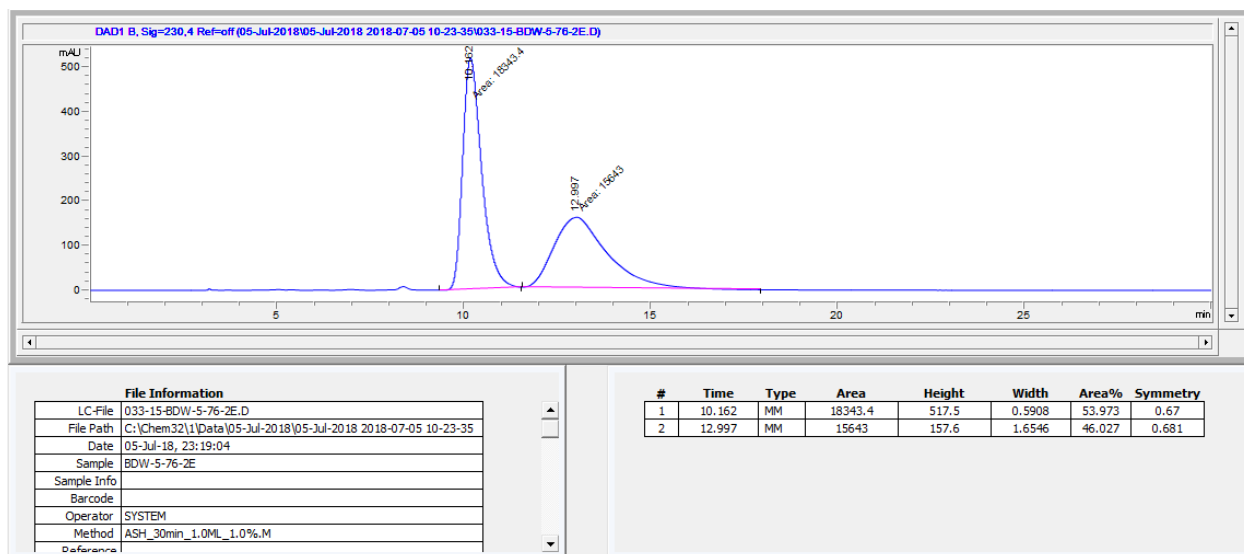
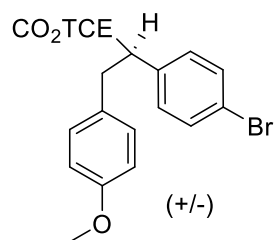


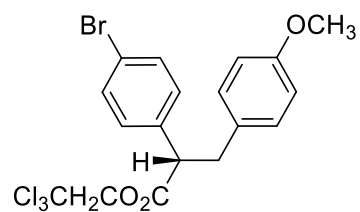




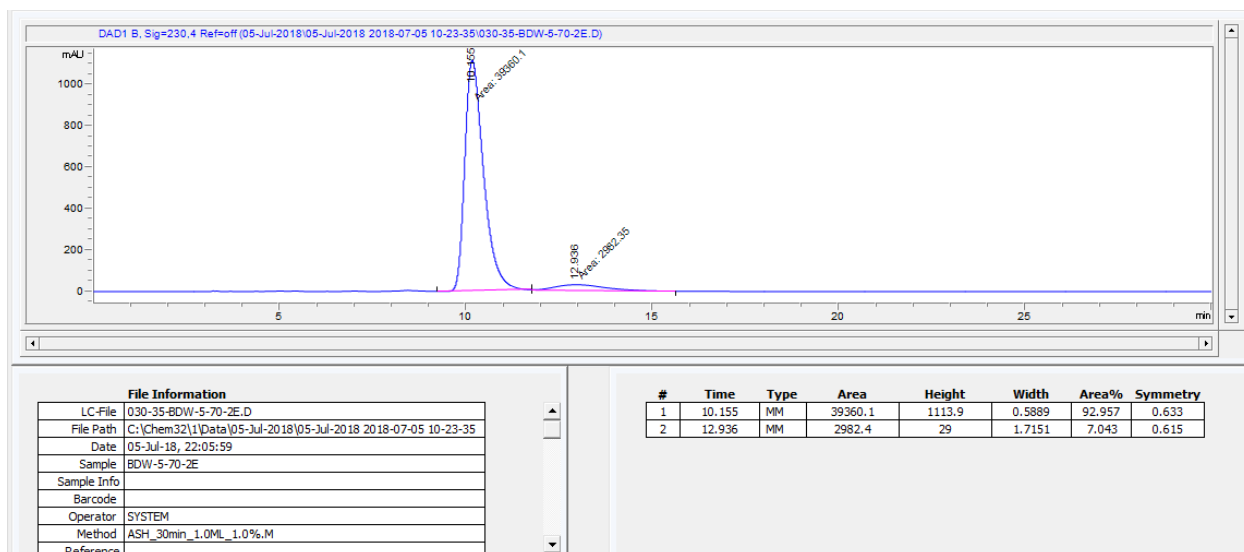
4.62

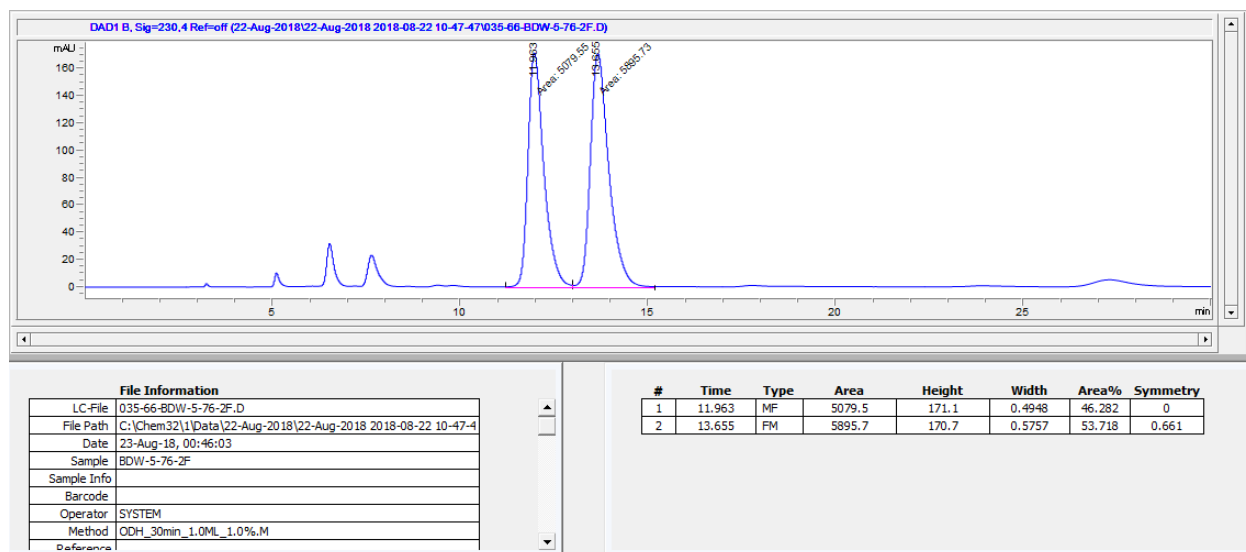
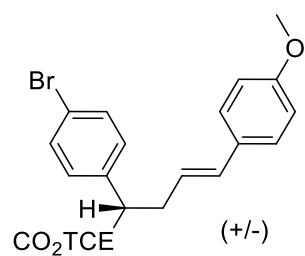


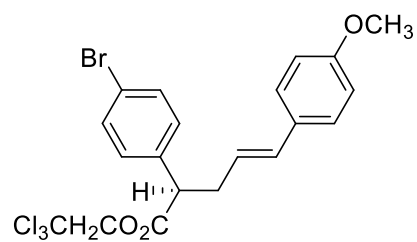




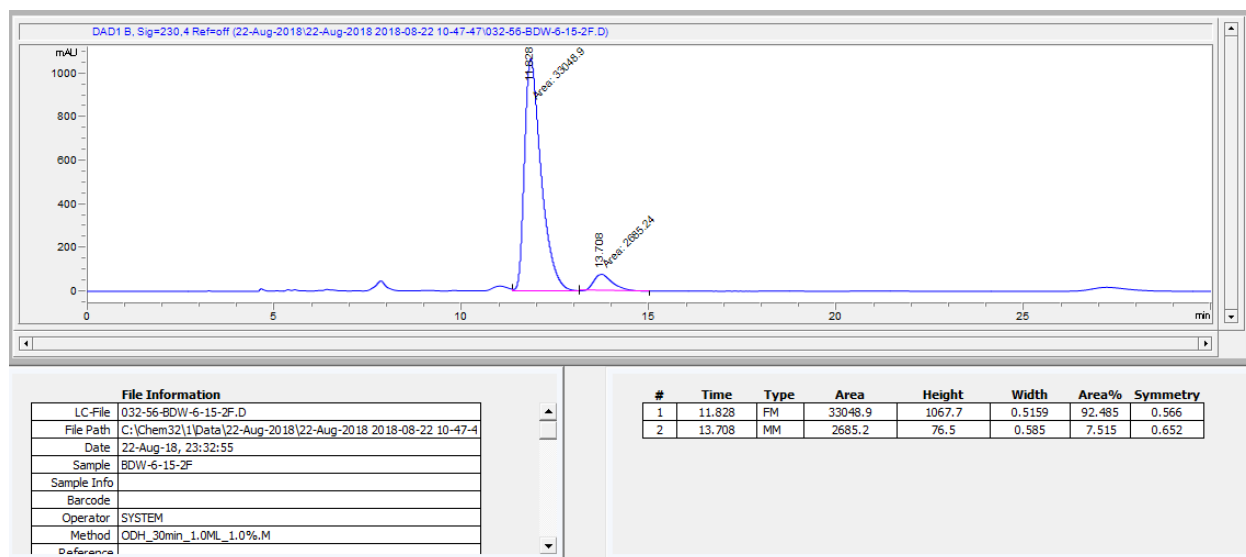
4.63

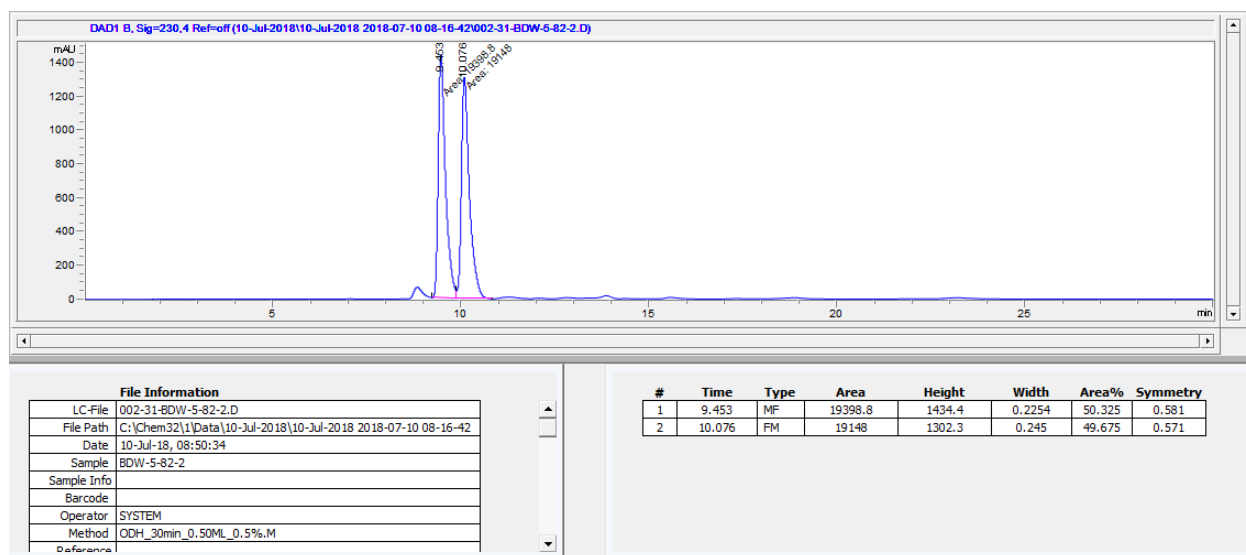
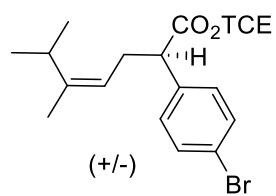


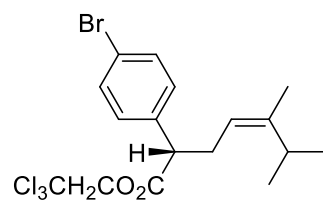




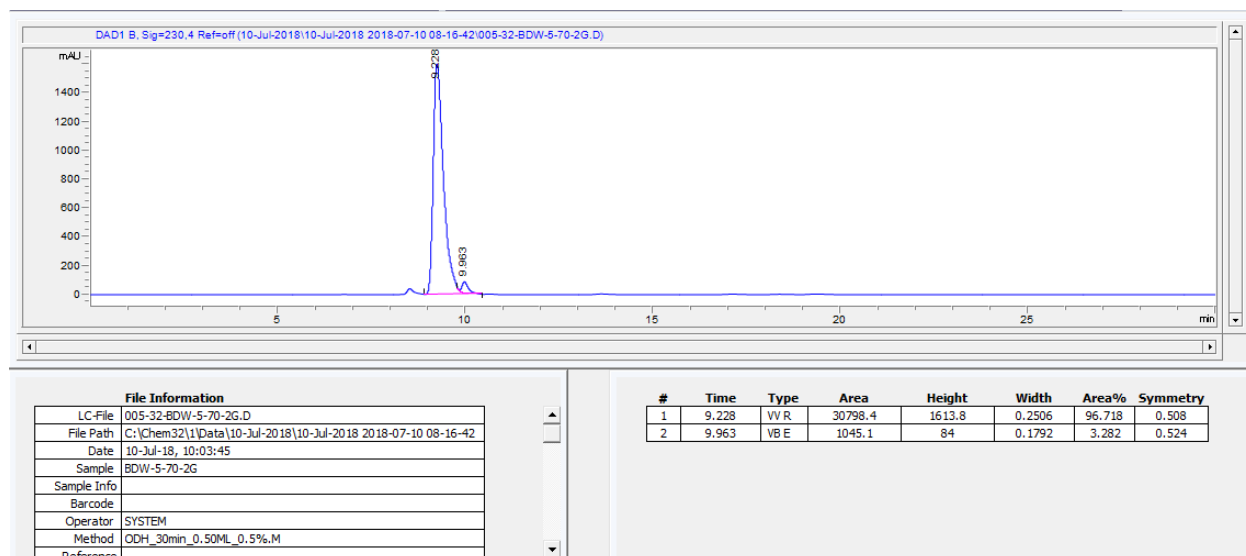
4.64

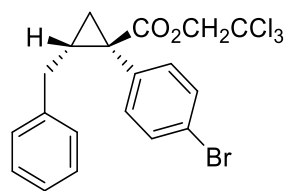




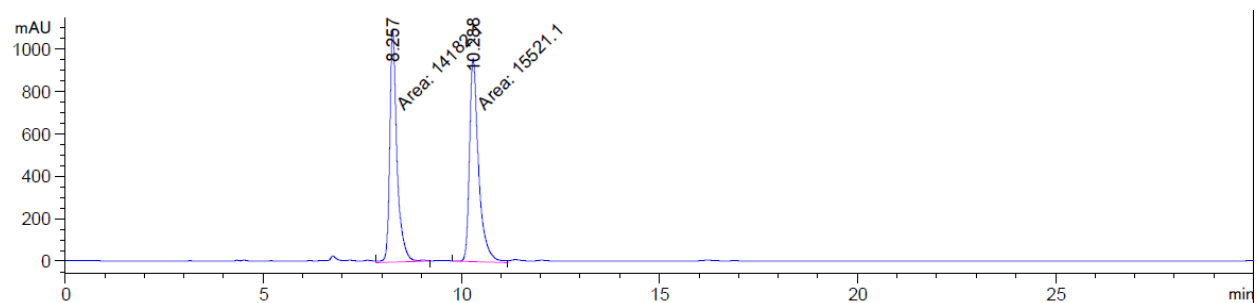


4.65



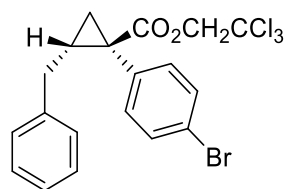


(+/-)

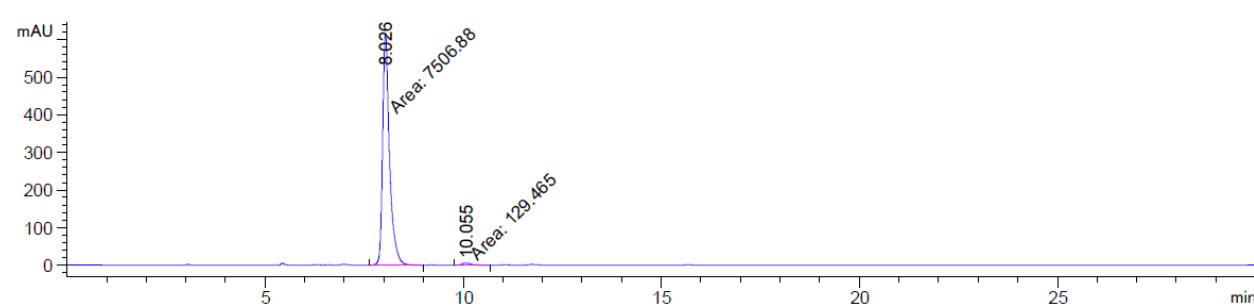


Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.257	MM	0.2149	1.41821e4	1100.02112	47.7460
2	10.288	MM	0.2697	1.55211e4	959.17090	52.2540



4.66



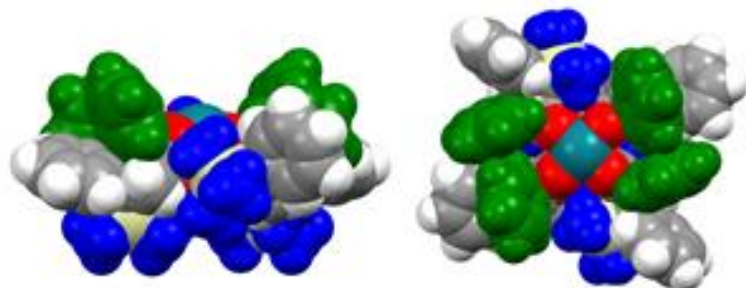
Signal 2: DAD1 B, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.026	MM	0.2029	7506.88086	616.73224	98.3046
2	10.055	MM	0.3126	129.46471	6.90275	1.6954

Totals : 7636.34557 623.63499

S.4.8 Computational Studies¹⁵

Orientation A for Compound 4.6



Orientation A
 $\Delta H/\Delta G = 0.0/0.0$ kcal/mol

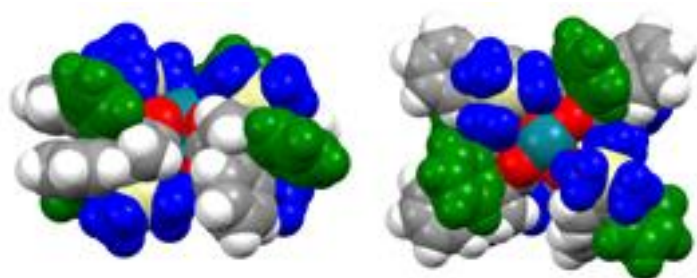
Entry	SCF Energy (a. u.)		Enthalpy (a. u.)	Gibbs Free Energy (a. u.)
Orientation A	-4926.35812615		-4924.855220	-4925.082033
Rh	2.58180000	15.98240000	5.02150000	
Rh	2.83180000	16.92110000	2.84770000	
Si	1.69610000	11.41200000	4.60710000	
Si	-2.02778777	16.54540794	6.06591182	
Si	3.41460000	19.13540000	8.35890000	
Si	5.87260487	14.47711156	6.32493096	
O	1.74560000	15.35600000	2.11600000	
O	1.73860000	14.35230000	4.12750000	
O	4.50160000	15.81780000	2.62080000	
O	0.78510000	16.94790000	5.12700000	
O	4.40620000	15.07920000	4.75310000	
O	1.15700000	18.03240000	3.19170000	
O	3.45500000	17.68600000	5.80590000	
O	3.89650000	18.39250000	3.70890000	
C	2.01820000	13.29720000	0.02240000	
H	2.82460000	13.24860000	0.48300000	
C	4.51670000	19.73650000	5.51350000	
C	4.92020000	15.10770000	3.57480000	
C	-0.77716063	19.86661046	3.53805963	
C	6.05910000	14.15730000	3.26190000	
C	7.44299342	13.58682279	1.22440886	
H	7.29252413	12.68579755	1.39841828	
C	0.51370000	17.84590000	4.28130000	
C	2.04490000	13.39340000	-1.34520000	

H	2.86100000	13.37900000	-1.79080000
C	6.27344085	12.80964670	3.91656580
H	6.96207574	12.23632279	3.54525921
H	5.48881264	12.33956817	4.23961106
C	-1.37420443	19.55947327	2.32566956
H	-1.72046330	18.70662319	2.19259636
C	-1.81293483	18.31560518	5.43277439
C	7.85972338	16.23644457	0.63581560
H	7.97035733	17.13860941	0.43944802
C	6.92147038	14.55616773	2.10872073
C	0.84120000	13.27000000	0.74070000
C	-0.77454796	16.10478104	7.38471657
H	0.11223693	16.20195097	7.02862520
H	-0.90907799	15.19638832	7.66367921
H	-0.88237761	16.69052035	8.13758212
C	-0.57310000	18.81190000	4.56770000
C	8.16565610	13.94214746	0.11554553
H	8.52181763	13.27983068	-0.43143687
C	8.37843090	15.30931238	-0.20994285
C	2.09240000	10.26690000	1.37940000
H	2.85280000	10.79050000	1.48620000
C	-0.72627420	19.22346849	6.05153601
H	-0.11905658	18.82322763	6.69350858
H	-0.96446711	20.14469828	6.23972907
C	-3.11748899	18.93999544	5.11879921
C	4.92790000	22.89270000	2.51930000
C	7.16279552	15.87306759	1.79619697
H	6.85613173	16.53879731	2.36864436
C	4.64100000	20.90600000	4.53400000
C	5.85150000	22.75320000	3.52540000
H	6.57770000	23.33280000	3.55250000
C	1.48920000	14.41970000	2.86590000
C	-0.36020000	12.64020000	2.95270000
H	-0.60930000	13.05000000	3.79570000
H	-1.10720000	12.33840000	2.41240000
C	0.83550000	13.19600000	2.23610000
C	3.90620000	18.55290000	4.98080000
C	-0.26633866	21.14609691	3.69598397
H	0.13765219	21.37215312	4.50263869
C	0.87520000	11.83150000	2.92400000
C	6.72545558	14.03355446	4.69328771
C	5.65290000	19.51540000	6.52670000
H	5.85110000	18.60150000	6.78450000
H	6.42890000	20.09360000	6.46210000
C	-1.46697073	20.49714618	1.30273098
H	-1.89572469	20.27730468	0.50728634

C	8.19458797	14.28605798	4.68790888
C	3.63630000	21.15500000	3.57740000
H	2.85070000	20.65850000	3.61330000
C	-0.89861539	21.80824965	1.47691520
C	3.28580000	22.36690000	7.00000000
H	2.57970000	21.98290000	6.53190000
C	8.65436428	15.60088969	4.83137668
H	8.04974307	16.30324516	4.91922017
C	0.91190000	10.62380000	2.01130000
C	-0.31250000	13.52070000	-1.35520000
H	-1.10810000	13.58900000	-1.83290000
C	4.23970000	17.50930000	8.76460000
H	4.23640000	16.94620000	7.98710000
H	3.76080000	17.07610000	9.47520000
H	5.14490000	17.66970000	9.04000000
C	3.77190000	22.08450000	2.61370000
H	3.08730000	22.19810000	1.99430000
C	4.36760000	21.58660000	7.33860000
C	5.73640000	21.77940000	4.49960000
H	6.39940000	21.70250000	5.14640000
C	-0.33565968	22.08146802	2.71106591
H	0.00618349	22.93125679	2.87225921
C	0.72180000	12.14550000	6.02860000
H	0.69640000	13.10120000	5.94030000
H	1.14180000	11.91190000	6.85940000
H	-0.17420000	11.79960000	6.01500000
C	4.37860000	20.12040000	7.04310000
C	4.45530813	13.31086344	6.67074707
H	3.82048802	13.35633590	5.95090285
H	4.02588181	13.56262857	7.49126036
H	4.78905545	12.41404718	6.74563205
C	9.12973549	13.24309807	4.59474824
H	8.84063470	12.36583066	4.49203740
C	-3.68355003	19.90706006	5.95477044
H	-3.19655037	20.23592294	6.67536625
C	-1.94282508	15.33068204	4.64834291
H	-2.64489769	15.52104060	4.02167378
H	-2.04855947	14.43794636	4.98547511
H	-1.09261050	15.40898152	4.21020126
C	3.51970000	11.79280000	4.70570000
H	3.96740000	11.41610000	3.94430000
H	3.88310000	11.41390000	5.50970000
H	3.64850000	12.74410000	4.71390000
C	3.22000000	23.69270000	7.33260000
H	2.46970000	24.19020000	7.10010000
C	-3.89845279	18.47073417	4.09329477

H	-3.53722894	17.82681996	3.52797985
C	10.02214696	15.84797186	4.84108775
H	10.32694554	16.72250548	4.91717912
C	1.58990000	9.53020000	4.80220000
H	0.67650000	9.25010000	4.71590000
H	1.92190000	9.27910000	5.66770000
H	2.12040000	9.10770000	4.12210000
C	5.27686487	16.22992109	6.32306891
H	6.00580320	16.81550870	6.10536779
H	4.93626171	16.45298785	7.19267904
H	4.57982151	16.33038890	5.67098064
C	1.60630000	18.96410000	7.94080000
H	1.51080000	18.45640000	7.13170000
H	1.22130000	19.83540000	7.81880000
H	1.15300000	18.51230000	8.65700000
C	-0.21380000	9.84650000	1.79250000
H	-1.02170000	10.11130000	2.17080000
C	2.13990000	9.09740000	0.56530000
H	2.93820000	8.86480000	0.14890000
C	4.25060000	24.29300000	8.00390000
H	4.20790000	25.19340000	8.22940000
C	5.37640000	23.51690000	8.34730000
H	6.08960000	23.89460000	8.80820000
C	-0.35450000	13.43550000	0.01100000
H	-1.16950000	13.48560000	0.45650000
C	3.50140000	20.18610000	9.93210000
H	3.05810000	19.72540000	10.64880000
H	3.06980000	21.02900000	9.77820000
H	4.42020000	20.33420000	10.16730000
C	-4.97555759	20.38413294	5.71683014
H	-5.32867034	21.05724783	6.25203309
C	1.06720000	8.33300000	0.38970000
H	1.11750000	7.57230000	-0.14290000
C	-3.75929803	16.40843173	6.84052642
H	-3.83269402	17.02537447	7.57259944
H	-3.89681477	15.51388059	7.16168219
H	-4.42360942	16.61627361	6.17945536
C	10.48752145	13.52547944	4.65719489
H	11.10605853	12.83179829	4.64526744
C	5.39460000	22.21250000	7.99260000
H	6.14960000	21.71170000	8.20470000
C	10.92466995	14.83576051	4.73996628
H	11.83579893	15.02352052	4.72632092
C	-5.19477136	18.89894724	3.84982422
H	-5.68022030	18.54518350	3.13858536
C	-5.74712121	19.84067869	4.66226751

H	-6.62303577	20.12318238	4.52598180
C	-0.18090000	8.69080000	1.03340000
H	-0.93890000	8.16050000	0.93620000
C	7.15178578	14.22548355	7.66642024
H	7.45764430	13.31691080	7.65013051
H	6.75843628	14.41635672	8.52179041
H	7.89248761	14.81709399	7.51629808
C	0.90820000	13.50780000	-2.04810000
H	0.97230822	13.58526410	-3.11336497
H	8.85786368	15.62133195	-1.11420387
H	5.07444587	23.60512260	1.73452083
H	-0.94222054	22.54192675	0.69928000

Orientation B for Compound 4.6

Orientation B
 $\Delta H/\Delta G = 8.1/2.5$ kcal/mol

Entry	SCF Energy (a. u.)		Enthalpy (a. u.)	Gibbs Free Energy (a. u.)
Orientation B	-4926.34371921		-4924.842343	-4925.078093
Rh	2.04713800	16.28091700	5.02403000	
Rh	2.40215300	17.08501200	2.79201200	
Si	-0.57721400	14.78280200	-0.01279000	
Si	-2.67364700	17.06891200	5.77470100	
Si	4.62861500	20.91105900	2.46537300	
Si	5.10544300	13.39296500	6.50832600	
O	1.47964800	15.38149700	2.10226900	
O	1.07218800	14.66069400	4.20554000	
O	4.18148100	16.03980500	2.74285300	
O	0.35592700	17.46138200	5.10867500	
O	3.79512600	15.23421700	4.81754800	
O	0.64518000	18.13656500	2.97219600	
O	3.11069300	17.90410800	5.72930400	
O	3.35770000	18.69243200	3.62713400	
C	-0.80981600	12.28041000	4.25853600	
H	-1.47245300	13.12690200	4.13132400	
C	4.27629900	19.95005200	5.40242900	
C	4.48519700	15.32635200	3.75454400	
C	-1.07650500	20.23245200	3.17013300	
C	5.73503700	14.50600200	3.67834700	
C	7.51136800	14.53613100	1.84704700	
H	7.21041600	13.54569000	1.52304800	
C	0.06772900	18.19569700	4.10788600	
C	-1.07106200	11.33543100	5.24851800	
H	-1.94712000	11.44687400	5.88146300	
C	5.52203600	13.00475200	3.61360200	
H	6.16446400	12.44109800	2.94464800	
H	4.49453700	12.65290300	3.63889500	

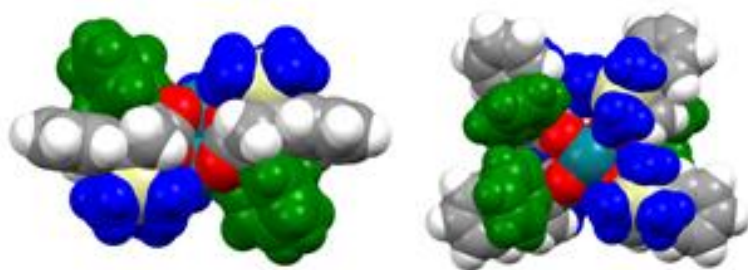
C	-1.50796600	19.86166700	1.88914900
H	-1.81537600	18.83898200	1.70742900
C	-2.32425500	18.80436200	5.02723400
C	8.30200100	17.09170300	2.63428800
H	8.60213200	18.08712600	2.94910200
C	6.84300800	15.16152800	2.90307700
C	0.30963800	12.15628400	3.42561100
C	-1.67375200	16.74798500	7.34386600
H	-0.60388300	16.66721400	7.14196100
H	-2.01592000	15.81140300	7.80207600
H	-1.82969700	17.54931800	8.07619800
C	-1.00870400	19.21972700	4.28052100
C	8.56927200	15.17542700	1.19457500
H	9.07632900	14.67181900	0.37645500
C	8.97108000	16.45240500	1.58678800
C	-2.52772700	12.47067200	1.53008600
H	-2.66896100	13.40443800	2.06662400
C	-1.30091700	19.67884200	5.69295800
H	-0.69760600	19.24740500	6.48382100
H	-1.51821500	20.73499300	5.81526900
C	-3.57457900	19.44389600	4.49174100
C	6.75612100	19.14823700	8.84533200
C	7.25003300	16.44969100	3.28120800
H	6.73320300	16.95286800	4.09203600
C	-0.21175000	10.24621000	5.42391400
C	5.08755300	19.67868100	6.63786100
C	5.88672800	20.23893200	8.86297700
H	5.84791100	20.89138200	9.73064800
C	1.08238900	14.50666300	2.93895200
C	1.24205500	12.74722200	1.08336000
H	2.00480300	13.38718500	0.65382400
H	1.44395700	11.68428400	1.00022300
C	0.61497600	13.20055800	2.38733200
C	3.53506600	18.75840100	4.88373200
C	-0.66165100	21.55089900	3.38161900
H	-0.30430900	21.85097200	4.36193000
C	-0.18224700	13.21873300	1.03834800
C	6.10114000	13.58914300	4.87551300
C	3.58105000	21.28440100	5.19870400
H	2.61731500	21.26053400	4.69765300
H	3.63839700	22.00574600	6.00768600
C	-1.53320900	20.78869700	0.84973600
H	-1.87470900	20.48361500	-0.13558600
C	7.57511800	13.43261400	5.11960600
C	5.95936900	18.57908100	6.63718500
H	5.98408500	17.92155400	5.77453400

C	-1.12438600	22.10734600	1.07361600
C	7.30251300	20.92826000	4.64504600
H	7.26803500	19.89709200	4.30717100
C	8.28802700	14.47186200	5.73769900
H	7.77063300	15.39402300	5.98380600
C	-1.27959100	12.19679800	0.94743200
C	0.91014500	10.11688300	4.60507900
H	1.58997400	9.27994700	4.73714800
C	2.83605900	21.04489300	1.87878900
H	2.19480700	20.22675100	2.21048100
H	2.82534500	21.06964000	0.78093800
H	2.38793200	21.98451400	2.22302500
C	6.78566100	18.31296400	7.72506300
H	7.45467600	17.45770400	7.69671600
C	6.10227000	21.64466100	4.77326300
C	5.05821700	20.50019500	7.76814000
H	4.38933000	21.35296600	7.80464700
C	-0.68676700	22.48529200	2.34275900
H	-0.35850100	23.50423500	2.52739400
C	0.94189000	15.49397900	-0.88432200
H	1.63752000	15.97189700	-0.19194400
H	0.60896100	16.23884000	-1.61839200
H	1.48146000	14.71275200	-1.43341300
C	4.80886600	20.99137000	4.37897100
C	3.39329400	12.63424300	6.24741700
H	2.73617700	13.21701400	5.60009000
H	2.90405700	12.52548000	7.22469200
H	3.48254500	11.62787000	5.82122200
C	8.25828600	12.25332300	4.80181100
H	7.71947000	11.43359400	4.33561100
C	-4.17249400	20.54446900	5.11610400
H	-3.71443500	20.97094000	6.00332700
C	-2.43428300	15.68682700	4.51463400
H	-3.03103800	15.85903900	3.61307100
H	-2.76872900	14.74046000	4.95710300
H	-1.38776900	15.57379800	4.22187600
C	-1.50614000	16.11255100	0.95121200
H	-2.45121400	15.72564600	1.34708700
H	-1.74893400	16.93906000	0.27115100
H	-0.92069200	16.51874400	1.77885800
C	8.52535500	21.51675100	4.96154800
H	9.44212600	20.94187900	4.86299000
C	-4.20381500	18.89782300	3.36114400
H	-3.75901000	18.03819800	2.86881900
C	9.64590800	14.33944800	6.02197400
H	10.18015300	15.15924700	6.49429700

C	-1.71912100	14.17573400	-1.39839100
H	-1.26858700	13.34167700	-1.94937000
H	-1.89653900	14.99163700	-2.11019100
H	-2.68823000	13.83603600	-1.01939500
C	5.09277500	14.95743000	7.56627600
H	6.11395600	15.23943200	7.84688500
H	4.54155500	14.76700700	8.49656500
H	4.63192900	15.80648100	7.05771500
C	5.58157300	19.48087000	1.68208200
H	5.24715600	18.50372900	2.03639600
H	6.65323600	19.57068100	1.89208800
H	5.46147000	19.51534200	0.59113700
C	-1.12158000	10.99281500	0.25204800
H	-0.17119600	10.76936000	-0.22304800
C	-3.57971500	11.56270200	1.43409300
H	-4.53460400	11.79304000	1.89834900
C	8.57115300	22.84040600	5.40939600
H	9.52279800	23.30127900	5.65811600
C	7.38439800	23.56459700	5.53510100
H	7.40876400	24.59485600	5.87959500
C	1.16778000	11.06838900	3.61497000
H	2.05252300	10.96707500	2.99408800
C	5.45815000	22.50541800	1.85089500
H	5.31687900	22.60047300	0.76662600
H	6.53380000	22.51494700	2.05519900
H	5.02321800	23.39425500	2.32345500
C	-5.35601400	21.09601100	4.61821100
H	-5.80224200	21.95088700	5.11883300
C	-3.40622900	10.35867000	0.74450700
H	-4.22450600	9.64845500	0.66862700
C	-4.49386400	17.08356600	6.29406100
H	-4.71201100	17.93124900	6.95409200
H	-4.72830200	16.16153800	6.84046600
H	-5.16722800	17.15212400	5.43403300
C	9.61885400	12.11528900	5.08632100
H	10.13073500	11.19127200	4.83163600
C	6.16073200	22.96975600	5.21850200
H	5.24257300	23.54252500	5.31112200
C	10.31846800	13.15783100	5.69638900
H	11.37691500	13.05215800	5.91638900
C	-5.38283200	19.44491200	2.86018300
H	-5.84714300	19.00977500	1.97960000
C	-5.96415300	20.55133200	3.48676100
H	-6.88256900	20.98116800	3.09751500
C	-2.17436500	10.07949000	0.15176400
H	-2.02968500	9.15087500	-0.39350300

C	6.06933700	12.08903900	7.49741400
H	6.21694400	11.16986800	6.91800400
H	5.50953500	11.82619600	8.40420200
H	7.05698800	12.45082300	7.80167100
H	9.79502400	16.94707400	1.08085100
H	-0.41581100	9.50735900	6.19363100
H	7.40188400	18.94779300	9.69524400
H	-1.14576800	22.83111000	0.26385000

Orientation C for Compound 4.6



Orientation C
 $\Delta H/\Delta G = 6.8/2.8$ kcal/mol

Entry	SCF Energy (a. u.)		Enthalpy (a. u.)	Gibbs Free Energy (a. u.)
Orientation C	-4926.34508200		-4924.844318	-4925.077627
Rh	6.96670000	10.79250000	2.96770000	
Si	9.75220000	15.12190000	5.96860000	
Si	4.64830000	9.36510000	-1.05730000	
O	8.44140000	10.91570000	4.35460000	
O	8.26260000	13.16360000	4.46700000	
O	5.43010000	10.78960000	1.61350000	
O	5.45570000	13.04540000	1.51950000	
C	11.64550000	13.34980000	7.12470000	
C	11.89580000	13.15590000	8.48140000	
H	11.19280000	12.94830000	9.05180000	
C	13.18510000	13.26760000	8.99260000	
H	13.33650000	13.13290000	9.89910000	
C	14.23860000	13.57750000	8.16050000	
H	15.09810000	13.66260000	8.50670000	
C	14.01480000	13.76040000	6.81520000	
H	14.72450000	13.96460000	6.24890000	
C	12.72840000	13.64010000	6.29960000	
H	12.58920000	13.75610000	5.38610000	
C	10.24940000	13.37000000	6.55380000	
C	9.74580000	12.03890000	5.94310000	
C	9.20020000	12.53390000	7.26570000	
H	9.47130000	12.06150000	8.06760000	
H	8.29080000	12.86920000	7.27970000	
C	10.64780000	10.83760000	5.89660000	
C	11.60290000	10.73760000	4.89660000	
H	11.71320000	11.44300000	4.30110000	
C	12.39690000	9.60530000	4.76820000	
H	13.04030000	9.55660000	4.09710000	

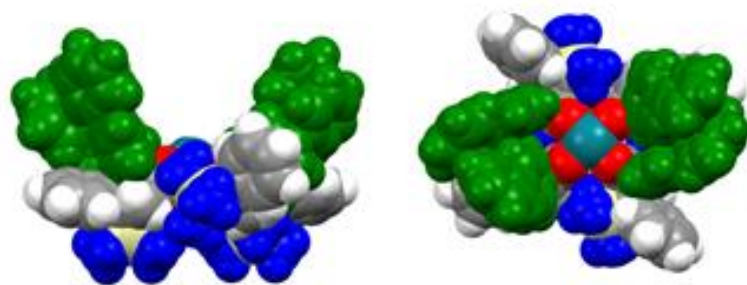
C	12.22710000	8.54940000	5.64390000
H	12.75660000	7.79010000	5.56440000
C	11.28260000	8.62210000	6.62660000
H	11.16510000	7.90990000	7.21250000
C	10.48990000	9.77360000	6.75370000
H	9.85050000	9.81790000	7.42690000
C	10.19970000	15.46610000	4.18620000
H	11.09730000	15.17030000	4.01960000
H	10.13830000	16.40950000	4.01700000
H	9.59440000	14.99770000	3.60880000
C	7.96510000	15.52220000	6.36180000
H	7.38990000	14.95220000	5.84590000
H	7.78710000	16.44070000	6.14300000
H	7.80510000	15.37880000	7.29770000
C	10.76530000	16.29660000	7.03300000
H	10.70430000	16.02840000	7.95130000
H	10.42480000	17.18850000	6.93870000
H	11.68410000	16.27290000	6.75010000
C	8.74740000	12.05500000	4.82240000
C	2.64790000	11.23260000	-1.81530000
C	1.28380000	11.00460000	-1.91960000
H	0.83310000	10.57060000	-1.23220000
C	0.58120000	11.42190000	-3.04800000
H	-0.33210000	11.26570000	-3.10250000
C	1.22160000	12.05830000	-4.07820000
H	0.74180000	12.33950000	-4.82300000
C	2.58020000	12.27980000	-4.00300000
H	3.02240000	12.70860000	-4.70160000
C	3.29200000	11.86060000	-2.88240000
H	4.21110000	12.00150000	-2.84420000
C	3.44700000	10.77670000	-0.62080000
C	2.74240000	10.76350000	0.71840000
H	3.01960000	10.09600000	1.36400000
H	1.79350000	10.96370000	0.72850000
C	3.69700000	11.90540000	0.43760000
C	3.14570000	13.27600000	0.17410000
C	3.79610000	14.13650000	-0.69800000
H	4.56960000	13.84960000	-1.12890000
C	3.31980000	15.40640000	-0.94030000
H	3.76140000	15.96370000	-1.53960000
C	2.18090000	15.85130000	-0.28620000
H	1.85440000	16.70670000	-0.44950000
C	1.53850000	15.02770000	0.60290000
H	0.78740000	15.33330000	1.05660000
C	2.00390000	13.74410000	0.82820000
H	1.55270000	13.18800000	1.42080000

C	6.35300000	10.00030000	-1.46290000
H	6.28420000	10.71200000	-2.10540000
H	6.88200000	9.28820000	-1.82900000
H	6.77130000	10.32850000	-0.66390000
C	3.93980000	8.51900000	-2.56930000
H	3.02650000	8.27670000	-2.40240000
H	4.44920000	7.73020000	-2.76410000
H	3.98000000	9.11800000	-3.31950000
C	4.72760000	8.05710000	0.25940000
H	5.13830000	8.42050000	1.04620000
H	5.24490000	7.31550000	-0.05940000
H	3.83890000	7.76130000	0.47020000
C	4.97300000	11.90730000	1.24380000
Rh	6.87210000	13.17700000	2.96770000
Si	4.08660000	8.84760000	5.96860000
Si	9.19050000	14.60440000	-1.05730000
O	5.39740000	13.05380000	4.35460000
O	5.57620000	10.80590000	4.46700000
O	8.40870000	13.17990000	1.61350000
O	8.38310000	10.92410000	1.51950000
C	2.19330000	10.61970000	7.12470000
C	1.94300000	10.81360000	8.48140000
H	2.64600000	11.02120000	9.05180000
C	0.65370000	10.70190000	8.99260000
H	0.50230000	10.83660000	9.89910000
C	-0.39980000	10.39200000	8.16050000
H	-1.25930000	10.30690000	8.50670000
C	-0.17600000	10.20910000	6.81520000
H	-0.88570000	10.00490000	6.24890000
C	1.11040000	10.32940000	6.29960000
H	1.24960000	10.21340000	5.38610000
C	3.58940000	10.59960000	6.55380000
C	4.09300000	11.93060000	5.94310000
C	4.63860000	11.43560000	7.26570000
H	4.36750000	11.90800000	8.06760000
H	5.54800000	11.10030000	7.27970000
C	3.19100000	13.13190000	5.89660000
C	2.23590000	13.23190000	4.89660000
H	2.12560000	12.52650000	4.30110000
C	1.44190000	14.36420000	4.76820000
H	0.79850000	14.41290000	4.09710000
C	1.61170000	15.42010000	5.64390000
H	1.08220000	16.17940000	5.56440000
C	2.55620000	15.34740000	6.62660000
H	2.67370000	16.05960000	7.21250000
C	3.34890000	14.19590000	6.75370000

H	3.98830000	14.15160000	7.42690000
C	3.63910000	8.50340000	4.18620000
H	2.74150000	8.79920000	4.01960000
H	3.70050000	7.56000000	4.01700000
H	4.24440000	8.97180000	3.60880000
C	5.87370000	8.44730000	6.36180000
H	6.44890000	9.01730000	5.84590000
H	6.05170000	7.52880000	6.14300000
H	6.03370000	8.59070000	7.29770000
C	3.07350000	7.67290000	7.03300000
H	3.13450000	7.94110000	7.95130000
H	3.41400000	6.78100000	6.93870000
H	2.15470000	7.69660000	6.75010000
C	5.09140000	11.91450000	4.82240000
C	11.19090000	12.73690000	-1.81530000
C	12.55500000	12.96490000	-1.91960000
H	13.00570000	13.39900000	-1.23220000
C	13.25760000	12.54760000	-3.04800000
H	14.17090000	12.70380000	-3.10250000
C	12.61720000	11.91120000	-4.07820000
H	13.09700000	11.63000000	-4.82300000
C	11.25860000	11.68970000	-4.00300000
H	10.81640000	11.26090000	-4.70160000
C	10.54680000	12.10890000	-2.88240000
H	9.62770000	11.96800000	-2.84420000
C	10.39180000	13.19280000	-0.62080000
C	11.09640000	13.20600000	0.71840000
H	10.81920000	13.87350000	1.36400000
H	12.04530000	13.00590000	0.72850000
C	10.14180000	12.06410000	0.43760000
C	10.69310000	10.69350000	0.17410000
C	10.04270000	9.83300000	-0.69800000
H	9.26920000	10.11990000	-1.12890000
C	10.51900000	8.56310000	-0.94030000
H	10.07740000	8.00580000	-1.53960000
C	11.65790000	8.11820000	-0.28620000
H	11.98440000	7.26280000	-0.44950000
C	12.30030000	8.94180000	0.60290000
H	13.05140000	8.63620000	1.05660000
C	11.83490000	10.22540000	0.82820000
H	12.28610000	10.78150000	1.42080000
C	7.48580000	13.96920000	-1.46290000
H	7.55460000	13.25750000	-2.10540000
H	6.95680000	14.68130000	-1.82900000
H	7.06750000	13.64100000	-0.66390000
C	9.89900000	15.45050000	-2.56930000

H	10.81230000	15.69280000	-2.40240000
H	9.38960000	16.23930000	-2.76410000
H	9.85880000	14.85150000	-3.31950000
C	9.11120000	15.91240000	0.25940000
H	8.70050000	15.54900000	1.04620000
H	8.59390000	16.65400000	-0.05940000
H	9.99990000	16.20820000	0.47020000
C	8.86580000	12.06220000	1.24380000

Orientation A for Compound 4.8



Orientation A
 $\Delta H/\Delta G = 0.0/0.0$ kcal/mol

Entry	SCF Energy (a. u.)		Enthalpy (a. u.)	Gibbs Free Energy (a. u.)
Orientation A	-5850.72638898		-5848.880030	-5849.147438
Rh	2.58180000	15.98240000	5.02150000	
Rh	2.83180000	16.92110000	2.84770000	
Si	1.69610000	11.41200000	4.60710000	
Si	-2.52990000	16.43110000	4.54610000	
Si	3.41460000	19.13540000	8.35890000	
Si	5.87260487	14.47711156	6.32493096	
O	1.74560000	15.35600000	2.11600000	
O	1.73860000	14.35230000	4.12750000	
O	4.50160000	15.81780000	2.62080000	
O	0.78510000	16.94790000	5.12700000	
O	4.40620000	15.07920000	4.75310000	
O	1.15700000	18.03240000	3.19170000	
O	3.45500000	17.68600000	5.80590000	
O	3.89650000	18.39250000	3.70890000	
C	2.01820000	13.29720000	0.02240000	
H	2.82460000	13.24860000	0.48300000	
C	4.51670000	19.73650000	5.51350000	
C	4.92020000	15.10770000	3.57480000	
C	0.64140000	24.03830000	2.37520000	
C	-0.37280000	20.17960000	4.01680000	
C	6.05910000	14.15730000	3.26190000	
C	7.44299342	13.58682279	1.22440886	
H	7.29252413	12.68579755	1.39841828	
C	0.51370000	17.84590000	4.28130000	
C	2.04490000	13.39340000	-1.34520000	
H	2.86100000	13.37900000	-1.79080000	
C	6.27344085	12.80964670	3.91656580	
H	6.96207574	12.23632279	3.54525921	

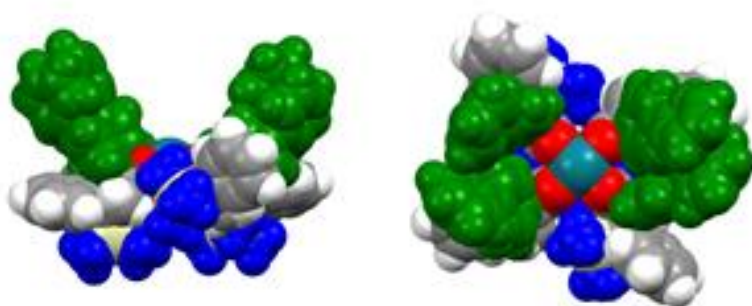
H	5.48881264	12.33956817	4.23961106
C	-0.52140000	20.41980000	2.66000000
H	-0.82730000	19.73650000	2.10820000
C	-2.05150000	18.25100000	4.74540000
C	7.85972338	16.23644457	0.63581560
H	7.97035733	17.13860941	0.43944802
C	6.92147038	14.55616773	2.10872073
C	0.84120000	13.27000000	0.74070000
C	-1.82740000	15.35770000	5.90930000
H	-0.86950000	15.42880000	5.91100000
H	-2.07970000	14.44390000	5.75960000
H	-2.17090000	15.65030000	6.75660000
C	1.69770000	24.76910000	2.88190000
H	2.16760000	24.42590000	3.60750000
C	-0.57310000	18.81190000	4.56770000
C	8.16565610	13.94214746	0.11554553
H	8.52181763	13.27983068	-0.43143687
C	8.37843090	15.30931238	-0.20994285
C	2.09240000	10.26690000	1.37940000
H	2.85280000	10.79050000	1.48620000
C	-1.21850000	18.69410000	5.96920000
H	-0.88520000	18.00080000	6.56020000
H	-1.47730000	19.51580000	6.41490000
C	-3.14500000	19.14860000	4.31080000
C	4.92790000	22.89270000	2.51930000
C	7.16279552	15.87306759	1.79619697
H	6.85613173	16.53879731	2.36864436
C	0.90820000	13.50780000	-2.04810000
C	4.64100000	20.90600000	4.53400000
C	5.85150000	22.75320000	3.52540000
H	6.57770000	23.33280000	3.55250000
C	1.48920000	14.41970000	2.86590000
C	-0.36020000	12.64020000	2.95270000
H	-0.60930000	13.05000000	3.79570000
H	-1.10720000	12.33840000	2.41240000
C	0.83550000	13.19600000	2.23610000
C	-0.04390000	24.55880000	1.29740000
H	-0.74680000	24.07370000	0.92860000
C	3.90620000	18.55290000	4.98080000
C	0.09250000	21.22080000	4.80570000
H	0.19840000	21.07990000	5.71890000
C	0.87520000	11.83150000	2.92400000
C	6.72545558	14.03355446	4.69328771
C	5.65290000	19.51540000	6.52670000
H	5.85110000	18.60150000	6.78450000
H	6.42890000	20.09360000	6.46210000

C	-0.22290000	21.65920000	2.10410000
H	-0.35570000	21.80590000	1.19540000
C	8.19458797	14.28605798	4.68790888
C	3.63630000	21.15500000	3.57740000
H	2.85070000	20.65850000	3.61330000
C	0.29170000	22.71450000	2.93710000
C	3.28580000	22.36690000	7.00000000
H	2.57970000	21.98290000	6.53190000
C	0.93570000	13.65700000	-3.54820000
C	8.65436428	15.60088969	4.83137668
H	8.04974307	16.30324516	4.91922017
C	0.91190000	10.62380000	2.01130000
C	-0.31250000	13.52070000	-1.35520000
H	-1.10810000	13.58900000	-1.83290000
C	4.23970000	17.50930000	8.76460000
H	4.23640000	16.94620000	7.98710000
H	3.76080000	17.07610000	9.47520000
H	5.14490000	17.66970000	9.04000000
C	3.77190000	22.08450000	2.61370000
H	3.08730000	22.19810000	1.99430000
C	0.29970000	25.82420000	0.73420000
H	-0.18780000	26.17830000	0.02580000
C	4.36760000	21.58660000	7.33860000
C	5.73640000	21.77940000	4.49960000
H	6.39940000	21.70250000	5.14640000
C	2.08880000	25.98610000	2.36020000
H	2.80940000	26.44340000	2.72930000
C	5.12780000	23.86450000	1.44880000
C	9.67216776	15.31715560	-3.80795107
H	9.65458796	14.78242530	-4.56845780
C	0.39970000	22.44090000	4.28920000
H	0.69160000	23.11220000	4.86290000
C	0.72180000	12.14550000	6.02860000
H	0.69640000	13.10120000	5.94030000
H	1.14180000	11.91190000	6.85940000
H	-0.17420000	11.79960000	6.01500000
C	4.37860000	20.12040000	7.04310000
C	4.45530813	13.31086344	6.67074707
H	3.82048802	13.35633590	5.95090285
H	4.02588181	13.56262857	7.49126036
H	4.78905545	12.41404718	6.74563205
C	9.12973549	13.24309807	4.59474824
H	8.84063470	12.36583066	4.49203740
C	-3.93450000	19.83780000	5.23610000
H	-3.71760000	19.80850000	6.13980000
C	-1.99740000	15.79620000	2.87110000

H	-2.43170000	16.30600000	2.18310000
H	-2.24240000	14.87170000	2.78690000
H	-1.04590000	15.88470000	2.78290000
C	10.30706142	17.33621097	-2.75234535
H	10.73441575	18.16053375	-2.79809642
C	3.51970000	11.79280000	4.70570000
H	3.96740000	11.41610000	3.94430000
H	3.88310000	11.41390000	5.50970000
H	3.64850000	12.74410000	4.71390000
C	3.22000000	23.69270000	7.33260000
H	2.46970000	24.19020000	7.10010000
C	-3.53610000	19.20340000	2.99710000
H	-3.02210000	18.75010000	2.36860000
C	10.30881573	16.52754138	-3.85205292
H	10.74056145	16.79900067	-4.62963279
C	10.02214696	15.84797186	4.84108775
H	10.32694554	16.72250548	4.91717912
C	4.88660000	23.43120000	0.10230000
H	4.61470000	22.55880000	-0.07120000
C	1.58990000	9.53020000	4.80220000
H	0.67650000	9.25010000	4.71590000
H	1.92190000	9.27910000	5.66770000
H	2.12040000	9.10770000	4.12210000
C	5.27686487	16.22992109	6.32306891
H	6.00580320	16.81550870	6.10536779
H	4.93626171	16.45298785	7.19267904
H	4.57982151	16.33038890	5.67098064
C	1.60630000	18.96410000	7.94080000
H	1.51080000	18.45640000	7.13170000
H	1.22130000	19.83540000	7.81880000
H	1.15300000	18.51230000	8.65700000
C	-0.21380000	9.84650000	1.79250000
H	-1.02170000	10.11130000	2.17080000
C	2.13990000	9.09740000	0.56530000
H	2.93820000	8.86480000	0.14890000
C	4.25060000	24.29300000	8.00390000
H	4.20790000	25.19340000	8.22940000
C	5.37640000	23.51690000	8.34730000
H	6.08960000	23.89460000	8.80820000
C	0.12970000	14.58460000	-4.20800000
H	-0.48410000	15.08970000	-3.72460000
C	9.68393615	16.95921895	-1.56259872
H	9.70052866	17.53203893	-0.82928852
C	-0.35450000	13.43550000	0.01100000
H	-1.16950000	13.48560000	0.45650000
C	1.80920000	12.90720000	-4.31680000

H	2.37350000	12.31330000	-3.87550000
C	9.04133208	14.86308577	-2.62585492
H	8.63638649	14.02708619	-2.58935538
C	3.50140000	20.18610000	9.93210000
H	3.05810000	19.72540000	10.64880000
H	3.06980000	21.02900000	9.77820000
H	4.42020000	20.33420000	10.16730000
C	-5.04740000	20.57080000	4.81460000
H	-5.54240000	21.06030000	5.43070000
C	1.06720000	8.33300000	0.38970000
H	1.11750000	7.57230000	-0.14290000
C	-4.42610000	16.31300000	4.63210000
H	-4.72910000	16.63610000	5.48400000
H	-4.69540000	15.39760000	4.52350000
H	-4.81250000	16.84490000	3.93260000
C	10.48752145	13.52547944	4.65719489
H	11.10605853	12.83179829	4.64526744
C	1.39430000	26.52610000	1.27560000
H	1.65410000	27.34250000	0.91310000
C	5.60660000	25.14750000	1.69870000
H	5.78080000	25.43670000	2.56500000
C	5.06570000	24.33920000	-0.94400000
H	4.91280000	24.09220000	-1.82760000
C	5.39460000	22.21250000	7.99260000
H	6.14960000	21.71170000	8.20470000
C	10.92466995	14.83576051	4.73996628
H	11.83579893	15.02352052	4.72632092
C	9.04561523	15.74352251	-1.46832319
C	5.50610000	25.71220000	-0.59430000
H	5.54640000	26.35950000	-1.26020000
C	5.82410000	26.01410000	0.56270000
H	6.22170000	26.84180000	0.70840000
C	-4.65270000	19.89400000	2.55060000
H	-4.87220000	19.89680000	1.64590000
C	-5.42200000	20.56590000	3.44990000
H	-6.18650000	21.01630000	3.17010000
C	-0.18090000	8.69080000	1.03340000
H	-0.93890000	8.16050000	0.93620000
C	7.15178578	14.22548355	7.66642024
H	7.45764430	13.31691080	7.65013051
H	6.75843628	14.41635672	8.52179041
H	7.89248761	14.81709399	7.51629808
C	1.02700000	13.91020000	-6.30530000
H	0.99540000	13.93870000	-7.23430000
C	1.90050000	12.97780000	-5.66500000
H	2.49700000	12.45030000	-6.14650000

C	0.23760000	14.76230000	-5.58400000
H	-0.22080000	15.45200000	-6.00750000

Orientation B for Compound 4.8

Orientation B
 $\Delta H/\Delta G = 7.9/6.2$ kcal/mol

Entry	SCF Energy (a. u.)		Enthalpy (a. u.)	Gibbs Free Energy (a. u.)
Orientation B	-5850.71323149		-5848.867382	-5849.137508
Rh	2.58914800	16.09306900	5.15541000	
Rh	2.73478500	16.99705400	2.94165400	
Si	1.41156700	11.56572000	5.18964600	
Si	-2.57162900	16.26463700	4.08051200	
Si	3.11815000	19.40484700	8.35442600	
Si	7.28089400	15.03263400	6.12810900	
O	1.76789600	15.31258700	2.26394700	
O	1.68442400	14.42668500	4.34084000	
O	4.49935000	15.97511500	2.69456600	
O	0.75953200	17.05233000	5.34078400	
O	4.41789800	15.16470600	4.79984000	
O	0.95323700	17.97242000	3.28895000	
O	3.47924000	17.83759200	5.83703300	
O	3.70397500	18.62692400	3.73539800	
C	2.68758200	12.97056100	0.66956800	
H	3.44322700	13.20396000	1.41378900	
C	4.29960500	20.05728500	5.52646700	
C	4.93810300	15.23788100	3.63691400	
C	-0.00243900	24.20548000	2.90766800	
C	-0.63502800	20.13925100	4.21745200	
C	6.13076500	14.38138200	3.32435200	
C	6.35462100	13.20874200	1.09404000	
H	5.99140600	12.29423800	1.55186700	
C	0.37582600	17.84172000	4.41506300	
C	3.08062700	12.73363200	-0.63934800	
H	4.13249500	12.79693000	-0.89455700	
C	6.32342900	13.10915800	4.12301500	

H	6.67273700	12.24365900	3.56940700
H	5.58393900	12.88543400	4.87909300
C	-0.50922900	20.45106200	2.85549800
H	-0.53036800	19.65367300	2.12368300
C	-2.25547800	18.09301000	4.54491400
C	7.27030700	15.52990800	-0.12509000
H	7.60486300	16.45002100	-0.59489200
C	6.49987900	14.36530300	1.86578000
C	1.33509600	12.91942600	1.04163100
C	-1.91870300	15.12833100	5.43393400
H	-0.82784700	15.12188800	5.47576800
H	-2.26428700	14.10335400	5.25571200
H	-2.29699700	15.43308600	6.41679700
C	0.88871700	25.02495700	3.62041700
H	1.37923900	24.63591800	4.50664500
C	-0.82582300	18.71684100	4.67211000
C	6.66332700	13.20738600	-0.26654000
H	6.56437500	12.28727500	-0.83476600
C	7.11649800	14.37010700	-0.90545000
C	2.38338000	10.14129800	2.22060200
H	3.21804200	10.79428000	2.45497700
C	-1.65905000	18.43694200	5.88845400
H	-1.33231000	17.62782200	6.53034800
H	-2.05510800	19.29487900	6.42156000
C	-3.31957800	18.99924300	3.99135600
C	4.17135500	23.37126000	2.71966400
C	6.96880300	15.52513500	1.23185900
H	7.07472500	16.43909500	1.80579300
C	2.13425700	12.43487300	-1.63494900
C	4.30082800	21.17363100	4.51788800
C	5.34436000	23.08697800	3.43223000
H	6.22562100	23.70576800	3.29089000
C	1.52322700	14.36328600	3.07981300
C	-0.34688400	12.61626400	3.03502800
H	-0.78356600	13.21224500	3.82719600
H	-1.06772600	12.23515000	2.31865100
C	0.98610000	13.09625500	2.49189700
C	-0.57729200	24.70725300	1.72865700
H	-1.27943600	24.09175600	1.17345700
C	3.78882300	18.74973300	5.00074900
C	-0.58735400	21.19009800	5.13942100
H	-0.68714600	20.98124200	6.19908000
C	0.87252800	11.80304400	3.36053000
C	7.27832700	14.23293800	4.38509900
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H	5.71568700	19.01794400	6.88907300

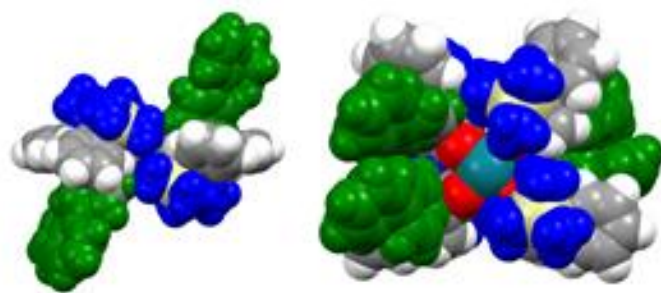
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C	8.66348300	14.14428700	3.80878900
C	3.13063200	21.44824800	3.79265600
H	2.24825800	20.83289000	3.93170100
C	-0.27320100	22.82146400	3.36105300
C	2.56020000	22.48702100	6.88680900
H	1.80817900	21.87163800	6.40539400
C	2.56870800	12.14811800	-3.02172800
C	9.33562200	15.31236900	3.41567600
H	8.82818300	16.26891200	3.49559200
C	1.08541200	10.52823500	2.58905700
C	0.78159900	12.41225300	-1.26874500
H	0.02743900	12.17790300	-2.01429200
C	3.99977100	17.78811800	8.79063800
H	3.92472800	17.03595400	8.00373700
H	3.55628200	17.38397900	9.70976600
H	5.06289300	17.96586200	8.99433600
C	3.07590400	22.51100000	2.90176200
H	2.15311600	22.70837800	2.37549300
C	-0.26961800	25.98965100	1.27632800
H	-0.72547700	26.36159800	0.36296400
C	3.79235700	21.91566200	7.23845000
C	5.40825100	22.00093400	4.30575700
H	6.34119700	21.80799900	4.82337300
C	1.20009900	26.30435400	3.16432100
H	1.91482600	26.91069700	3.71227800
C	4.05982900	24.54933100	1.82941300
C	6.84776100	13.67332100	-4.62170300
H	6.19495700	13.11891000	-5.28990800
C	-0.40840600	22.50836700	4.72003100
H	-0.38512100	23.30403400	5.45797100
C	0.44331200	12.58682400	6.44767600
H	0.72485600	13.64116800	6.43228000
H	0.64989800	12.18428600	7.44782000
H	-0.63747500	12.51817200	6.28400700
C	4.02292900	20.44643800	7.01900700
C	6.04314600	14.21554700	7.29709400
H	5.01376400	14.33872300	6.95499600
H	6.13742700	14.66856800	8.29215300
H	6.24921300	13.14345300	7.40064500
C	9.33999400	12.92315700	3.70685900
H	8.84489300	12.01021100	4.02358400
C	-4.25942600	19.61799900	4.82521400
H	-4.20256600	19.46804400	5.89893400

C	-1.78985100	15.86017700	2.40994300
H	-2.21688100	16.48597700	1.61801200
H	-1.98090900	14.81442200	2.14238800
H	-0.70708200	16.01290500	2.40981500
C	8.74217700	15.12315700	-4.25086200
H	9.58668500	15.68928100	-4.63376500
C	3.26188700	11.82973900	5.39952600
H	3.83573200	11.19763400	4.71285200
H	3.57255100	11.57874400	6.42145400
H	3.51678400	12.87335200	5.20728200
C	2.30434900	23.83622300	7.12613100
H	1.34338900	24.26094900	6.85015600
C	-3.43507100	19.19147100	2.60497000
H	-2.72119900	18.71499800	1.94118500
C	7.92577500	14.40392300	-5.12758100
H	8.12733900	14.41466100	-6.19487700
C	10.63712900	15.25971600	2.92118800
H	11.13502900	16.17587100	2.61608100
C	3.27421800	24.50468200	0.66599700
H	2.77163300	23.58125300	0.39538900
C	1.01574500	9.75382900	5.58266400
H	-0.03701600	9.52008100	5.38480300
H	1.21019600	9.55724200	6.64453900
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C	6.98731400	16.88857400	6.02114800
H	7.65319600	17.37096800	5.29671200
H	7.17141200	17.34768000	6.99979500
H	5.95387000	17.09700300	5.73666500
C	1.29442500	19.15422200	7.95817900
H	1.14229000	18.56712300	7.05167300
H	0.79492800	20.12171100	7.83487400
H	0.80051100	18.63404500	8.78904800
C	0.02141800	9.67658900	2.27053300
H	-0.98804900	9.95210400	2.56137700
C	2.60858400	8.94625600	1.54003300
H	3.62022400	8.67156700	1.25420700
C	3.27932800	24.64344200	7.71970300
H	3.08148500	25.69558500	7.90302000
C	4.50764000	24.08455000	8.07591200
H	5.27260700	24.70050200	8.54071200
C	1.84743500	12.63210900	-4.12537500
H	0.96300400	13.24011600	-3.95883800
C	8.48347300	15.11246100	-2.88029100
H	9.13496300	15.65846600	-2.20418900
C	0.38965100	12.65238000	0.04966300
H	-0.66565500	12.61742200	0.29838600

C	3.72268700	11.38276100	-3.26183500
H	4.27425500	10.97273800	-2.42070800
C	6.59116200	13.66203800	-3.25184100
H	5.73452300	13.11191100	-2.87762100
C	3.21526400	20.46543800	9.92465400
H	2.80077700	19.90672300	10.77331400
H	2.65198500	21.39856900	9.82269900
H	4.25102700	20.72827300	10.17015100
C	-5.27518900	20.41659600	4.29441400
H	-5.99284400	20.88639600	4.96138400
C	1.53676100	8.10754300	1.22065100
H	1.70991400	7.17658900	0.68850500
C	-4.44304100	16.03685100	3.97111300
H	-4.93344500	16.35359300	4.89903300
H	-4.68368100	14.97956400	3.80556400
H	-4.87486600	16.61850200	3.15047700
C	10.64561100	12.86522100	3.21309000
H	11.15153000	11.90624100	3.14276900
C	0.62302100	26.79156100	1.99054800
H	0.87896100	27.78196600	1.62705900
C	4.70987500	25.75365700	2.14686800
H	5.29748000	25.81870700	3.05783100
C	3.13927300	25.62582200	-0.14949500
H	2.52242700	25.56934900	-1.04184500
C	4.75872100	22.73117000	7.83878600
H	5.71411400	22.30277400	8.12735000
C	11.29852600	14.03253600	2.81535500
H	12.31277800	13.98892300	2.42917800
C	7.40434000	14.37976700	-2.35885600
C	3.79234400	26.81645600	0.17641800
H	3.68571700	27.69106400	-0.45892800
C	4.57953600	26.87486100	1.32844100
H	5.08451300	27.79855900	1.59751200
C	-4.44522300	19.98930000	2.07104800
H	-4.50867100	20.12903200	0.99551200
C	-5.37060600	20.60882100	2.91559000
H	-6.15829400	21.23194700	2.50204700
C	0.24263700	8.47624500	1.59162000
H	-0.59784400	7.83015200	1.35335600
C	9.00165600	14.72288400	6.85109700
H	9.25541300	13.65658400	6.83463300
H	9.02759400	15.05979600	7.89490400
H	9.78147000	15.25749800	6.29968600
C	3.42531300	11.61187800	-5.65256500
H	3.75566700	11.40662100	-6.66660000
C	4.14808000	11.11794600	-4.56368000

H	5.04058600	10.52059000	-4.72645800
C	2.27162600	12.36731500	-5.42727700
H	1.70520600	12.75920400	-6.26731000

Orientation C for Compound 4.8



Orientation C
 $\Delta H/\Delta G = 12.6/7.1$ kcal/mol

Entry	SCF Energy (a. u.)		Enthalpy (a. u.)	Gibbs Free Energy (a. u.)
Orientation C	-5850.70537106		-5848.859977	-5849.136161
Rh	2.40971700	16.06920100	4.83411600	
Rh	2.75414300	16.95155400	2.63042000	
Si	-0.64743800	15.11471700	-0.08541800	
Si	-2.10464100	17.06956500	5.91485000	
Si	4.10269800	18.75200400	8.14966000	
Si	6.20808100	14.99993400	0.39188900	
O	1.54116400	15.44103400	1.92490500	
O	1.38151300	14.49451400	3.96875600	
O	4.32928000	15.63601700	2.46964100	
O	0.74995500	17.29259900	4.96848100	
O	4.11256800	14.94939000	4.61094900	
O	1.18042200	18.24762200	2.96739700	
O	3.50876900	17.67155100	5.52809300	
O	3.97808400	18.38172100	3.43564600	
C	-0.59244100	12.32368800	4.05304700	
H	-1.07563800	13.28559300	4.16587100	
C	4.72933500	19.69533100	5.25100000	
C	4.66424400	14.91719200	3.46181100	
C	-1.24559400	23.37023300	0.34121300	
C	-0.61644200	20.30705100	3.33040200	
C	5.79224200	13.94864700	3.28241300	
C	6.51085600	12.09778400	4.89246800	
H	7.44960300	12.60620800	5.08434700	
C	0.55641600	18.18354900	4.07816500	
C	-0.87213600	11.30886700	4.96084600	
H	-1.56249600	11.49932900	5.77735700	
C	7.17833900	14.54565600	3.14358700	
H	7.99105200	14.03662100	3.65200700	

H	7.25252700	15.62892600	3.16897900
C	-1.01010900	19.97641100	2.02576500
H	-1.16693700	18.93761300	1.76558300
C	-1.73320100	18.81440100	5.19705800
C	4.12010100	10.75727100	4.43860400
H	3.16969200	10.26307400	4.27794600
C	5.57201800	12.66157900	4.02526000
C	0.32615900	12.13398200	3.01031200
C	-0.98182500	16.58450100	7.35415500
H	0.02099100	16.30602700	7.02598100
H	-1.43052000	15.73119500	7.87846200
H	-0.89003400	17.40307900	8.07737600
C	-0.49914200	24.56081300	0.34619400
H	0.28466000	24.70125400	1.08254500
C	-0.46219200	19.23707200	4.37525200
C	6.26471100	10.87511600	5.52025300
H	7.02157600	10.44991100	6.17290100
C	5.06800800	10.17951400	5.29986100
C	-2.52980900	12.67869200	1.44261300
H	-2.56568800	13.51250800	2.13745500
C	-0.64258900	19.62277900	5.83202700
H	0.00321100	19.13359500	6.54980500
H	-0.82169700	20.67290400	6.03573600
C	-2.99490900	19.51333400	4.77703300
C	4.20750200	23.18401700	2.72085000
C	4.36783500	11.97182000	3.81534300
H	3.60957000	12.39577700	3.16249600
C	-0.24774600	10.05336500	4.85863400
C	4.59040000	20.90343500	4.36654600
C	5.48236500	22.82787100	3.18244200
H	6.34488600	23.41524400	2.88210900
C	1.22306800	14.48400500	2.70331200
C	1.16716300	12.92014500	0.68008600
H	1.93190700	13.57157100	0.27500200
H	1.31293700	11.86818100	0.45975400
C	0.64850500	13.25856000	2.06673500
C	-2.22891900	23.20807800	-0.65015000
H	-2.83864600	22.30978600	-0.65847300
C	4.02131100	18.49374800	4.70559600
C	-0.40061700	21.65731400	3.62259100
H	-0.07708200	21.95534500	4.61384700
C	-0.23209100	13.44858800	0.78216800
C	6.55088200	13.90489500	1.93199700
C	6.01545200	19.43663800	6.01339000
H	6.32061500	18.39989300	6.12023400
H	6.84026700	20.12137100	5.84459700

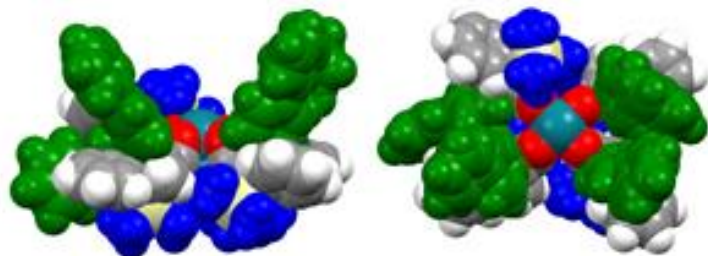
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H	-1.48422500	20.66142400	0.05473200
C	7.03291900	12.53937000	1.52934400
C	3.31107500	21.26621200	3.91470000
H	2.44914700	20.66842400	4.19618300
C	-1.00904200	22.31862500	1.35816300
C	3.53766900	22.03404100	7.17558500
H	2.65654700	21.52996200	6.78994000
C	-0.50227800	8.98150000	5.84889800
C	6.11724100	11.59577300	1.03858900
H	5.06290400	11.85120500	1.00131500
C	-1.37185400	12.47562400	0.67564200
C	0.64634500	9.85506300	3.79746200
H	1.12232500	8.88709800	3.67173500
C	4.87794300	17.02778500	8.13843800
H	4.67637600	16.47552200	7.21823000
H	4.47677400	16.45256600	8.98295600
H	5.96405000	17.09211000	8.27733600
C	3.12158700	22.37708400	3.10333600
H	2.11713500	22.63243800	2.78238200
C	-2.45344600	24.19862600	-1.60553100
H	-3.22272700	24.05329800	-2.35869200
C	4.75916000	21.34364600	7.21648000
C	5.67023400	21.70390800	3.98663200
H	6.67629400	21.45027100	4.30149200
C	-0.72546500	25.55304200	-0.60676200
H	-0.13001200	26.46135400	-0.58466300
C	4.01219900	24.36262500	1.84522700
C	4.86000000	7.42237200	7.89943900
H	5.13842400	7.26292600	8.93725300
C	-0.60072700	22.64592700	2.65933000
H	-0.45980100	23.68636100	2.93504200
C	0.82665500	15.92040200	-0.95239400
H	1.47771100	16.45086100	-0.25483700
H	0.44996900	16.63426100	-1.69575200
H	1.43255200	15.17883200	-1.48571800
C	4.81187000	19.90429100	6.78737300
C	6.47018500	16.84278700	0.72534600
H	5.78594300	17.24581800	1.47485400
H	6.32396200	17.39765600	-0.21053500
H	7.49939300	17.03066900	1.05529500
C	8.38714100	12.18968100	1.58132100
H	9.11079500	12.91265600	1.94631400
C	-3.55411200	20.54829500	5.53476800
H	-3.05153300	20.88059800	6.43826800
C	-2.13560100	15.73403200	4.58503600

H	-2.83728900	15.98848500	3.78469100
H	-2.47112000	14.79008700	5.03179800
H	-1.14852300	15.57505300	4.14477600
C	3.84483100	6.63446600	5.85589600
H	3.34068100	5.85561200	5.29107600
C	-1.51072000	16.33306200	1.06586600
H	-2.41177900	15.89439300	1.50613900
H	-1.81863600	17.21486900	0.49060100
H	-0.85260700	16.66108300	1.87342900
C	3.45029600	23.35851700	7.60079100
H	2.49742400	23.87838100	7.55261700
C	-3.67119900	19.08829600	3.62268300
H	-3.24674800	18.28716200	3.02490800
C	4.20401100	6.41439800	7.18795100
H	3.97786000	5.46555400	7.66559400
C	6.54188900	10.33511300	0.62253900
H	5.81531900	9.61598700	0.25440900
C	3.08084400	24.32980700	0.79366000
H	2.50627700	23.42554400	0.61625100
C	-1.87124600	14.65587700	-1.45756500
H	-1.45364000	13.89491700	-2.12725700
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H	4.48707300	15.14960400	-1.39488300
H	3.70963500	14.95657400	0.19036000
C	2.21790300	18.70320200	8.15761200
H	1.82869200	18.24035500	7.24936700
H	1.80495100	19.71531200	8.23833500
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H	-0.45807900	11.23187800	-0.82391400
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C	5.80466200	23.33904700	8.13089500
H	6.69311700	23.84127900	8.50379800
C	0.54543900	8.14876600	6.27713600
H	1.54871900	8.30656900	5.89612000
C	4.13429400	7.85407500	5.24385900
H	3.86914000	8.01060100	4.20233000
C	0.93222300	10.87945800	2.89528300
H	1.64920800	10.69067700	2.10370200
C	-1.78231400	8.77789600	6.39007700

H	-2.60892600	9.39918800	6.05762300
C	5.15019700	8.64095100	7.28647300
H	5.63799800	9.42794000	7.85412800
C	4.64974300	19.54895500	9.78140700
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H	4.17668600	20.52398700	9.93671100
H	5.73553800	19.69761900	9.81516200
C	-4.75363800	21.15063100	5.14766500
H	-5.17166100	21.95259400	5.74989500
C	-3.57763900	10.74100200	0.44291200
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C	8.81752800	10.92838900	1.16327500
H	9.87335900	10.67648500	1.21231300
C	-1.70300300	25.37667200	-1.58877200
H	-1.87895700	26.14894000	-2.33187100
C	4.75881600	25.53733000	2.03809800
H	5.46584700	25.59073500	2.86077600
C	2.90692900	25.43294800	-0.04206000
H	2.18727100	25.38096900	-0.85302700
C	5.88842300	22.01234300	7.70210900
H	6.83911700	21.48913900	7.74860100
C	7.89640500	9.99522000	0.68416700
H	8.22926500	9.01272800	0.36200300
C	4.78788500	8.87831700	5.95037500
C	3.65596200	26.59428700	0.16050900
H	3.51957800	27.45347400	-0.48977600
C	4.58215500	26.64185200	1.20539100
H	5.16374900	27.54317000	1.37756100
C	-4.86673200	19.68778800	3.23173900
H	-5.37016300	19.34898100	2.33053000
C	-5.41363700	20.72442800	3.99414600
H	-6.34485200	21.19418000	3.69087200
C	-2.43350600	10.53251200	-0.32872800
H	-2.38955800	9.69931100	-1.02471300
C	7.56014200	14.50911200	-0.84492900
H	8.55994500	14.60540600	-0.40525500
H	7.51523400	15.16442600	-1.72397200
H	7.44758800	13.47465100	-1.18580200
C	-0.95766700	6.94563700	7.74171400
H	-1.13468400	6.16096300	8.47169200
C	-2.00763000	7.76904000	7.32672500
H	-3.00651600	7.62142000	7.72768400

C	0.32072500	7.14057200	7.21290800
H	1.15092500	6.51740500	7.53318900

Orientation D for Compound 4.8



Orientation D
 $\Delta H/\Delta G = 11.9/7.3$ kcal/mol

Entry	SCF Energy (a. u.)		Enthalpy (a. u.)	Gibbs Free Energy (a. u.)
Orientation D	-5850.70657184		-5848.861105	-5849.135810
Rh	2.59426000	16.19687500	5.00977800	
Rh	2.87440800	17.34624100	2.92329400	
Si	0.60418600	12.02890100	4.60893400	
Si	-1.78017000	18.40428100	1.65830800	
Si	3.67637200	18.77744300	8.62551000	
Si	6.83116400	14.17017200	6.03316800	
O	1.91258900	15.77124200	2.01928400	
O	1.62596200	14.69491200	3.98263000	
O	4.60968500	16.26225000	2.63311500	
O	0.78876700	17.19614300	5.23062700	
O	4.35108000	15.19078300	4.60209400	
O	1.07392000	18.30397400	3.27880000	
O	3.62449300	17.75397700	5.89519600	
O	3.86017400	18.85167400	3.93648800	
C	2.94010400	13.33172500	0.44428400	
H	3.56411400	13.29485800	1.33283900	
C	4.75149500	19.84391400	5.90320400	
C	4.91173000	15.34746100	3.46706600	
C	-0.00645600	23.02113700	8.42325100	
C	-0.67895100	19.82787800	5.61060700	
C	5.94887200	14.33892700	3.07081300	
C	6.59856600	13.54545900	0.74831500	
H	6.17330200	12.57045900	0.95675400	
C	0.41738100	18.01757300	4.32910000	
C	3.53292600	13.24922600	-0.80715800	
H	4.60939900	13.16362500	-0.88083300	
C	5.67125600	12.92893500	3.57398600	
H	5.87423600	12.10828500	2.89419200	
H	4.77389700	12.80600200	4.16743400	

C	0.16339900	20.90146000	5.29457500
H	0.65661900	20.91667100	4.32809300
C	-1.91473100	18.99258800	3.47079400
C	7.70647800	16.01832100	0.14679900
H	8.11882300	16.99681400	-0.08086100
C	6.56571500	14.55046400	1.71852200
C	1.55356700	13.49494500	0.57764400
C	-1.35716400	16.57185400	1.57102300
H	-0.35316500	16.36870100	1.94395600
H	-1.38836600	16.23786400	0.52633200
H	-2.07462200	15.96213200	2.13101200
C	0.21479600	22.72980400	9.77892300
H	0.19784400	21.69609600	10.11150300
C	-0.88190300	18.74611200	4.58539500
C	7.15831900	13.77289900	-0.50773500
H	7.17098400	12.96942300	-1.23813400
C	7.70107200	15.02040000	-0.84342000
C	2.09795600	10.51003500	1.89681600
H	2.91470000	11.05076200	2.36512400
C	-2.15989000	17.95869000	4.55823100
H	-2.09516300	16.90807100	4.29151600
H	-2.89983600	18.17272100	5.32297700
C	-2.68432700	20.28351600	3.54701900
C	4.85679700	23.64130900	3.81032900
C	7.15510800	15.78451000	1.40161500
H	7.15783900	16.57865800	2.14067100
C	2.76412700	13.32858000	-1.98041200
C	4.83601700	21.13106400	5.13603100
C	6.04788300	23.02730200	4.22420700
H	6.99866200	23.50879000	4.01662100
C	1.54539600	14.76854700	2.71614400
C	-0.48514300	13.27305600	2.19557500
H	-1.02161900	13.87984500	2.91657700
H	-1.07159000	13.00637200	1.32203700
C	0.97344500	13.60929300	1.96013700
C	0.05372000	24.36044200	8.00496800
H	-0.13046800	24.60215200	6.96229600
C	4.01839800	18.74358300	5.19733300
C	-1.30455800	19.81597000	6.85931500
H	-1.95609700	18.99187000	7.13027500
C	0.55707500	12.31816500	2.71195100
C	6.82712800	13.66142500	4.18083000
C	5.90626000	19.41428200	6.79038200
H	6.10511900	18.35296500	6.84943200
H	6.79829900	20.03129000	6.76467400
C	0.36348200	21.94236900	6.19313800

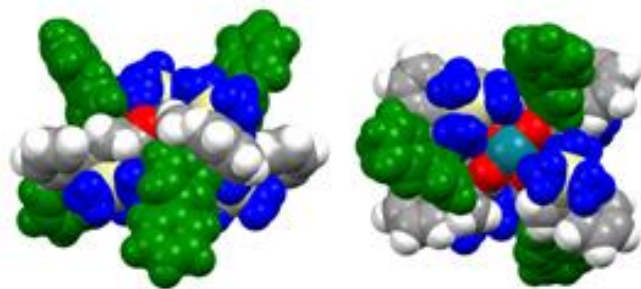
H	1.03059600	22.75829100	5.93328300
C	8.20407900	13.26896100	3.71931200
C	3.64631300	21.73509000	4.70704800
H	2.70716000	21.23674800	4.90959300
C	-0.26098700	21.93344800	7.45144300
C	3.57568200	22.14426800	7.98296900
H	2.67037000	21.75721100	7.52861600
C	3.42567100	13.26254700	-3.30481300
C	9.18847600	14.24752100	3.51321700
H	8.93184300	15.29409500	3.64319000
C	0.80100700	11.04411500	1.95411700
C	1.37844300	13.49465500	-1.84687900
H	0.75460700	13.54875200	-2.73427900
C	4.39678800	17.03154100	8.73169800
H	4.30421800	16.46750800	7.80261900
H	3.87454500	16.48263000	9.52622900
H	5.45833100	17.06589800	9.00595600
C	3.65013500	22.96212000	4.05754700
H	2.70691500	23.41634400	3.76797400
C	0.32908700	25.37963400	8.91675600
H	0.36668200	26.41051800	8.57657100
C	4.72484500	21.34056500	8.00968700
C	6.03781300	21.79227200	4.87329000
H	6.98220000	21.34681000	5.16683200
C	0.49471700	23.74783100	10.68947100
H	0.67801300	23.50214400	11.73150800
C	4.86772400	24.96154700	3.13831600
C	8.02938200	14.98810300	-4.61557100
H	7.49487700	14.57088000	-5.46438800
C	-1.09813000	20.85359800	7.76731800
H	-1.59958300	20.82998000	8.73012600
C	-0.51696700	13.22598200	5.55119000
H	-0.22701600	14.27106200	5.42263300
H	-0.47641700	12.98460900	6.62129400
H	-1.56007000	13.11074300	5.23214600
C	4.67422400	19.93982600	7.46389000
C	5.33134000	13.55160600	6.99844500
H	4.42667300	14.11652100	6.76866300
H	5.53606200	13.64229700	8.07253100
H	5.13597900	12.49405600	6.78594600
C	8.55310100	11.92505900	3.54252500
H	7.80681500	11.15390100	3.71041700
C	-4.01270400	20.32269900	3.98914800
H	-4.49363500	19.40587200	4.31630600
C	-0.53621600	19.40937400	0.65560400
H	-0.80465700	20.47074900	0.62209400

H	-0.51217000	19.04013500	-0.37748100
H	0.46767700	19.31724800	1.07986700
C	9.83038600	16.31496400	-3.70686600
H	10.71949200	16.92293200	-3.84907400
C	2.35017900	11.96802400	5.31805700
H	2.96083000	11.22487700	4.79225200
H	2.31680300	11.67450900	6.37487100
H	2.84630000	12.93739800	5.24761900
C	3.58478600	23.42778800	8.52637200
H	2.68575300	24.03275900	8.49100900
C	-2.09651000	21.48003000	3.10642000
H	-1.07011700	21.46884300	2.75571000
C	9.16763300	15.77430500	-4.81188000
H	9.53420600	15.96629700	-5.81620200
C	10.48019500	13.89331400	3.12864400
H	11.22481600	14.66737800	2.96507400
C	3.94872400	25.25993800	2.11792500
H	3.23859200	24.50212300	1.80062600
C	-0.16200600	10.31050700	4.84334400
H	-1.14622600	10.24213500	4.36507700
H	-0.29295600	10.10453900	5.91314100
H	0.46758700	9.52133000	4.41954700
C	7.04539300	16.03605500	6.16664000
H	7.92031900	16.37971900	5.60294300
H	7.18247300	16.33174900	7.21308600
H	6.16040100	16.54604900	5.78044900
C	1.82838200	18.79891600	8.26589000
H	1.58077700	18.44152900	7.26495600
H	1.42862300	19.81266600	8.36918000
H	1.30206500	18.16860500	8.99494800
C	-0.23849500	10.33611400	1.34011600
H	-1.25077900	10.72659000	1.38658000
C	2.34980300	9.30860700	1.23673300
H	3.36255000	8.91703300	1.19775200
C	4.74861800	23.93032800	9.11497700
H	4.75746800	24.93052500	9.53917300
C	5.89612100	23.13683000	9.15786500
H	6.80448400	23.51436100	9.61976300
C	2.99924700	14.07347000	-4.36970000
H	2.17087400	14.75934000	-4.21865800
C	9.36054200	16.07093300	-2.41633600
H	9.89347400	16.47863000	-1.56211500
C	0.78446100	13.57785100	-0.58558900
H	-0.28916300	13.71886200	-0.51704700
C	4.51773500	12.40324400	-3.51690800
H	4.84677500	11.75046600	-2.71386800

C	7.56017100	14.74394300	-3.32609100
H	6.65925200	14.15483200	-3.18877400
C	3.90345200	19.51351800	10.36045700
H	3.45814300	18.84309200	11.10661200
H	3.42189200	20.49263000	10.45164500
H	4.96293400	19.64005600	10.61182700
C	-4.73007900	21.52089600	4.00469300
H	-5.75953300	21.52639000	4.35230000
C	1.30415200	8.61348100	0.62215900
H	1.49802000	7.67796100	0.10538600
C	-3.50378500	18.64658900	0.91834000
H	-4.26802500	18.13547100	1.51574600
H	-3.53880100	18.23431700	-0.09759200
H	-3.77542700	19.70595500	0.86633900
C	9.84748100	11.56516800	3.16026800
H	10.09731600	10.51604600	3.02804700
C	0.55370100	25.07644400	10.26215400
H	0.77429400	25.86907900	10.97099900
C	5.79568200	25.94977100	3.50886500
H	6.49697600	25.74839300	4.31312600
C	3.95724800	26.50440000	1.48893000
H	3.24273200	26.71142900	0.69721200
C	5.88163300	21.85211900	8.60993000
H	6.77616800	21.23812100	8.65743300
C	10.81553500	12.54800700	2.94906900
H	11.82145400	12.27036200	2.64768100
C	8.21949700	15.27955700	-2.20641800
C	4.88644200	27.47690600	1.86611200
H	4.89375000	28.44609400	1.37590000
C	5.80601000	27.19359700	2.87885300
H	6.52747900	27.94560200	3.18580900
C	-2.80761300	22.67888500	3.12253100
H	-2.32795800	23.59330600	2.78443000
C	-4.12981300	22.70523400	3.57415200
H	-4.68550900	23.63841300	3.58818200
C	0.00920400	9.13141500	0.67793200
H	-0.81188700	8.59775100	0.20713500
C	8.34074200	13.33079000	6.80871600
H	8.30645400	12.24328900	6.67457500
H	8.36216000	13.53690800	7.88616400
H	9.27862200	13.68860400	6.37276100
C	4.73775100	13.17979100	-5.79851400
H	5.24396800	13.14925700	-6.75895800
C	5.16765400	12.36215700	-4.75041300
H	6.00845400	11.68944800	-4.89314100
C	3.64878300	14.03323900	-5.60315500

H	3.31045100	14.67708300	-6.41000300
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Orientation E for Compound 4.8



Orientation E
 $\Delta H/\Delta G = 16.4/9.2$ kcal/mol

Entry	SCF Energy (a. u.)		Enthalpy (a. u.)	Gibbs Free Energy (a. u.)
Orientation E	-5850.69871964		-5848.853832	-5849.132723
Rh	2.01100000	16.32730000	4.95260000	
Rh	2.42760000	17.06390000	2.70950000	
Si	-0.79180000	14.77860000	-0.01790000	
Si	-2.60150000	17.16890000	5.74730000	
Si	4.48840000	21.23760000	2.60840000	
Si	4.99440000	13.46040000	6.60040000	
O	1.29080000	15.47710000	2.05440000	
O	1.05300000	14.68700000	4.15790000	
O	4.05820000	15.79380000	2.65320000	
O	0.31720000	17.49840000	4.95630000	
O	3.75960000	15.27390000	4.82940000	
O	0.79040000	18.30220000	2.89730000	
O	3.07460000	17.96460000	5.62130000	
O	3.63190000	18.53840000	3.50740000	
C	-0.78010000	12.27670000	4.26650000	
H	-1.49240000	13.08570000	4.15950000	
C	4.54730000	19.78980000	5.32800000	
C	4.40970000	15.22820000	3.73980000	
C	-1.28010000	22.98770000	-0.36410000	
C	-1.10460000	20.25710000	2.97640000	
C	5.69440000	14.45630000	3.74070000	
C	7.84920000	14.49180000	2.36520000	
H	7.82830000	13.41300000	2.26320000	
C	0.11240000	18.28880000	3.97830000	
C	-0.94170000	11.35110000	5.29110000	
H	-1.78070000	11.45160000	5.97340000	
C	5.56020000	12.94510000	3.73680000	
H	6.25680000	12.38160000	3.12340000	
H	4.54930000	12.54670000	3.72950000	

C	-1.47780000	19.81290000	1.70080000
H	-1.70150000	18.76480000	1.54760000
C	-2.28480000	18.86340000	4.89480000
C	7.99140000	17.25030000	2.62760000
H	8.02040000	18.33110000	2.70690000
C	6.81270000	15.15950000	3.02660000
C	0.30910000	12.19860000	3.38940000
C	-1.57290000	16.93560000	7.31450000
H	-0.50720000	16.82820000	7.10280000
H	-1.91920000	16.03310000	7.83410000
H	-1.70810000	17.78090000	8.00000000
C	-0.33210000	24.01720000	-0.49260000
H	0.45690000	24.11100000	0.24770000
C	-0.98940000	19.28870000	4.12010000
C	8.95120000	15.18650000	1.86710000
H	9.75720000	14.63200000	1.39580000
C	9.05430000	16.57840000	2.00360000
C	-2.58390000	12.36350000	1.57840000
H	-2.75600000	13.28620000	2.12490000
C	-1.28290000	19.79020000	5.52010000
H	-0.66150000	19.40200000	6.31970000
H	-1.52770000	20.84340000	5.61020000
C	-3.55260000	19.44570000	4.33650000
C	7.01290000	18.14800000	8.49780000
C	6.89910000	16.55680000	3.12940000
H	6.09950000	17.11240000	3.60500000
C	-0.01450000	10.31090000	5.47930000
C	5.43370000	19.28510000	6.43630000
C	5.82080000	18.82960000	8.79090000
H	5.47840000	18.89180000	9.81940000
C	0.98090000	14.56610000	2.88990000
C	1.14920000	12.82630000	1.02110000
H	1.87090000	13.50150000	0.57490000
H	1.39710000	11.77370000	0.93100000
C	0.53440000	13.25110000	2.34130000
C	-2.26960000	22.86530000	-1.35410000
H	-3.02450000	22.09000000	-1.26190000
C	3.68790000	18.68690000	4.76950000
C	-0.80090000	21.61120000	3.13800000
H	-0.49560000	21.98450000	4.11000000
C	-0.29540000	13.23310000	1.01490000
C	6.04680000	13.61200000	4.99750000
C	3.89980000	21.14740000	5.48010000
H	2.87750000	21.26830000	5.13430000
H	4.11980000	21.67910000	6.40120000
C	-1.54030000	20.69030000	0.62510000

H	-1.80790000	20.31210000	-0.35710000
C	7.51220000	13.54500000	5.31590000
C	6.62840000	18.61720000	6.14120000
H	6.96110000	18.53700000	5.11490000
C	-1.23180000	22.05310000	0.78440000
C	7.47300000	20.99630000	4.07370000
H	7.33450000	20.15390000	3.40540000
C	-0.16740000	9.34240000	6.58980000
C	8.16230000	14.68400000	5.81410000
H	7.59860000	15.60470000	5.92260000
C	-1.34380000	12.15830000	0.95230000
C	1.06960000	10.22980000	4.59350000
H	1.79220000	9.42660000	4.70090000
C	2.61580000	21.27520000	2.38570000
H	2.10460000	20.35470000	2.67210000
H	2.38500000	21.46830000	1.32980000
H	2.17650000	22.10030000	2.95770000
C	7.41000000	18.06870000	7.15310000
H	8.35080000	17.59120000	6.89830000
C	-2.31120000	23.74420000	-2.43590000
H	-3.08940000	23.63660000	-3.18630000
C	6.35270000	21.54110000	4.72250000
C	5.04770000	19.39090000	7.77650000
H	4.11910000	19.89510000	8.02610000
C	-0.37410000	24.89700000	-1.57350000
H	0.37300000	25.68130000	-1.65760000
C	7.81450000	17.50980000	9.56760000
C	12.01310000	17.68750000	-0.09960000
H	12.50790000	17.39850000	-1.02250000
C	-0.86580000	22.49630000	2.06300000
H	-0.63840000	23.54580000	2.22310000
C	0.66970000	15.53820000	-0.94400000
H	1.39320000	16.00220000	-0.27070000
H	0.29220000	16.30270000	-1.63480000
H	1.18890000	14.78100000	-1.54410000
C	4.98890000	20.96900000	4.44270000
C	3.29850000	12.68370000	6.29410000
H	2.66510000	13.24160000	5.60230000
H	2.76870000	12.60120000	7.25260000
H	3.41020000	11.66550000	5.90300000
C	8.25040000	12.36650000	5.16270000
H	7.75870000	11.47550000	4.78260000
C	-4.18810000	20.54520000	4.92390000
H	-3.74830000	21.01370000	5.79930000
C	-2.41290000	15.70250000	4.57840000
H	-3.09230000	15.78510000	3.72410000

H	-2.67020000	14.78350000	5.11950000
H	-1.39160000	15.60280000	4.20600000
C	11.83370000	19.14540000	1.81610000
H	12.19740000	19.98570000	2.40090000
C	-1.71740000	16.07300000	0.99510000
H	-2.59570000	15.64000000	1.48460000
H	-2.07030000	16.86670000	0.32480000
H	-1.08130000	16.52560000	1.75910000
C	8.74970000	21.51730000	4.26900000
H	9.59610000	21.07470000	3.75100000
C	-4.15590000	18.84470000	3.21990000
H	-3.67790000	17.98700000	2.75560000
C	12.48250000	18.77990000	0.63390000
H	13.34690000	19.33950000	0.28860000
C	9.51800000	14.65010000	6.13560000
H	10.00960000	15.54580000	6.50600000
C	8.45280000	16.27800000	9.34210000
H	8.34790000	15.78440000	8.38210000
C	-1.97560000	14.13860000	-1.35130000
H	-1.52700000	13.31730000	-1.92260000
H	-2.20980000	14.94830000	-2.05370000
H	-2.91570000	13.77120000	-0.92760000
C	4.93210000	15.05260000	7.61430000
H	5.94130000	15.40220000	7.85580000
H	4.42170000	14.85640000	8.56640000
H	4.40900000	15.86000000	7.09840000
C	5.33530000	20.04710000	1.40640000
H	5.25970000	19.01150000	1.74550000
H	6.39330000	20.29700000	1.27190000
H	4.85470000	20.12150000	0.42210000
C	-1.14750000	10.96790000	0.24310000
H	-0.20350000	10.79670000	-0.26540000
C	-3.58960000	11.40190000	1.51260000
H	-4.53850000	11.57960000	2.01090000
C	8.93550000	22.60850000	5.12280000
H	9.92870000	23.01890000	5.28010000
C	7.83080000	23.17000000	5.76410000
H	7.95990000	24.02520000	6.42170000
C	0.95700000	8.87140000	7.28880000
H	1.94310000	9.24080000	7.02330000
C	10.72450000	18.42600000	2.25760000
H	10.24410000	18.69830000	3.19290000
C	1.22790000	11.16070000	3.56830000
H	2.08770000	11.08170000	2.91020000
C	-1.43610000	8.87940000	6.97670000
H	-2.31520000	9.21590000	6.43500000

C	10.90210000	16.96880000	0.34170000
H	10.52930000	16.13640000	-0.24780000
C	5.09080000	22.98960000	2.20490000
H	4.75220000	23.27900000	1.20200000
H	6.18270000	23.06600000	2.23000000
H	4.68830000	23.72020000	2.91700000
C	-5.38580000	21.04260000	4.40380000
H	-5.86210000	21.89790000	4.87520000
C	-3.37720000	10.21190000	0.80980000
H	-4.15900000	9.45980000	0.75790000
C	-4.40810000	17.22410000	6.31480000
H	-4.60490000	18.10680000	6.93430000
H	-4.63180000	16.33380000	6.91580000
H	-5.10430000	17.25030000	5.47060000
C	9.60760000	12.32600000	5.49140000
H	10.16490000	11.40200000	5.36480000
C	-1.36410000	24.76460000	-2.55030000
H	-1.39650000	25.44930000	-3.39280000
C	7.94420000	18.10630000	10.83270000
H	7.47670000	19.06830000	11.02080000
C	9.19780000	15.66380000	10.34760000
H	9.67620000	14.70830000	10.15140000
C	6.55210000	22.64350000	5.56140000
H	5.70260000	23.10420000	6.05530000
C	10.24730000	13.46790000	5.97650000
H	11.30410000	13.43980000	6.22550000
C	10.23810000	17.32830000	1.52580000
C	9.31920000	16.26760000	11.60130000
H	9.89880000	15.78970000	12.38570000
C	8.68870000	17.49160000	11.83910000
H	8.78250000	17.97330000	12.80830000
C	-5.34940000	19.33810000	2.69720000
H	-5.79430000	18.86210000	1.82780000
C	-5.96970000	20.44360000	3.28710000
H	-6.89930000	20.83130000	2.88050000
C	-2.15390000	10.00120000	0.17270000
H	-1.97970000	9.08420000	-0.38350000
C	5.93260000	12.19730000	7.66420000
H	6.11930000	11.26460000	7.11900000
H	5.33660000	11.95190000	8.55260000
H	6.90000000	12.58360000	8.00220000
C	-0.44990000	7.51060000	8.71220000
H	-0.55900000	6.80460000	9.53040000
C	-1.57620000	7.97280000	8.02710000
H	-2.56570000	7.62120000	8.30550000
C	0.81750000	7.96410000	8.33840000

H	1.69900000	7.61830000	8.87100000
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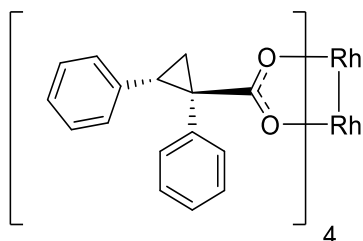
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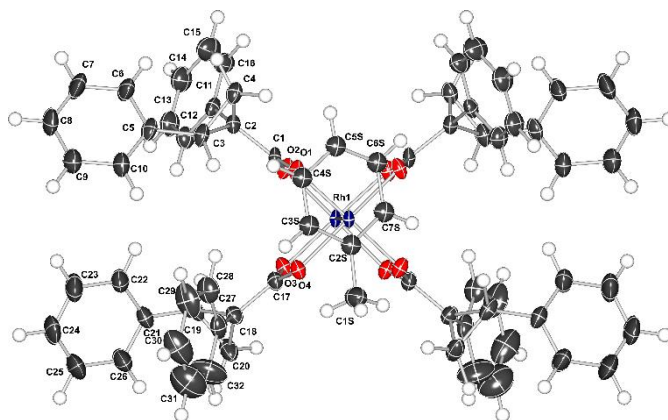
Appendix: X-Ray Crystallography Section

A.1 Single Crystal X-Ray Diffraction Data and Experimental

This contents of this section were prepared by Dr. John Bacsa, Emory University X-Ray Crystallography Center. All structures were submitted by Benjamin Wertz and solved by Dr. John Bacsa.



Dirhodium tetrakis ((1*R*,2*S*)-1,2-diphenyl-cyclopropanecarboxylate) (2.5)



Experimental. Single green prism crystals of **2.5** were used as supplied. A suitable crystal with dimensions $0.19 \times 0.12 \times 0.05$ mm³ was selected and mounted on a Bruker D8 VENTURE diffractometer. The crystal was kept at a steady $T = 100(2)$ K during data collection. The structure was solved with the ShelXT (Sheldrick, 2015) solution program using dual methods and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL-2014 (Sheldrick, 2015) using full matrix least squares minimisation on F^2 .

Crystal Data. $C_{78}H_{68}O_8Rh_2$, $M_r = 1339.215$, orthorhombic, $P2_12_12$ (No. 18), $a = 31.5424(7)$ Å, $b = 8.3838(2)$ Å, $c = 11.9960(3)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 3172.28(13)$ Å³, $T = 100(2)$ K, $Z = 2$, $Z' = 0.5$, $\mu(CuK\alpha) = 4.671$ mm⁻¹, 21187 reflections measured, 6408 unique ($R_{int} = 0.0640$) which were used in all calculations. The final wR_2 was 0.0837 (all data) and R_1 was 0.0373 ($I \geq \sigma(I)$).

$R_1=3.73\%$

Compound	2.5
Formula	C ₇₈ H ₆₈ O ₈ Rh ₂
$D_{calc.}/\text{g cm}^{-3}$	1.402
μ/mm^{-1}	4.671
Formula Weight	1339.215
Colour	green
Shape	prism
Size/mm ³	0.19×0.12×0.05
T/K	100(2)
Crystal System	orthorhombic
Flack Parameter	0.022(11)
Hooft Parameter	0.050(8)
Space Group	$P2_12_12$
$a/\text{\AA}$	31.5424(7)
$b/\text{\AA}$	8.3838(2)
$c/\text{\AA}$	11.9960(3)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
$V/\text{\AA}^3$	3172.28(13)
Z	2
Z'	0.5
Wavelength/ $\text{\AA}$	1.54178
Radiation type	CuK α
$\theta_{min}/^\circ$	2.80
$\theta_{max}/^\circ$	74.50
Measured Refl's.	21187
Ind't Refl's	6408
Refl's with $I \geq \sigma(I)$	5736
R_{int}	0.0640
Parameters	476
Restraints	225
Largest Peak	0.9606
Deepest Hole	-0.6170
GooF	1.0615
wR_2 (all data)	0.0837
wR_2	0.0770
R_1 (all data)	0.0462
R_1	0.0373

Structure Quality Indicators

Reflections:

d min (Cu)	0.80	I/ σ	16.2	R _{int}	6.40%	complete	99%
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Refinement:

Shift	0.001	Max Peak	1.0	Min Peak	-0.6	Goof	1.062	Flack	0.022(11)
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A green prism-shaped crystal with dimensions $0.19 \times 0.12 \times 0.05 \text{ mm}^3$ was mounted. Data were collected using a Bruker D8 VENTURE diffractometer equipped with an Oxford Cryosystems low-temperature device operating at $T = 100(2) \text{ K}$.

Data were measured using ϕ and ω scans with a narrow frame width using $\text{CuK}\alpha$ radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program **APEX2** (Bruker, V2 v2016.5-1). The maximum resolution that was achieved was $\Theta = 74.50^\circ$ ($0.80 \text{ \AA}$).

The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program **APEX2** (Bruker, V2 v2016.5-1). The unit cell was refined using **SAINT** (Bruker, V8.37A, after 2013) on 2008 reflections, 9% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using **SAINT** (Bruker, V8.37A, after 2013). The final completeness is 99.60 % out to 74.50° in Θ . A multi-scan absorption correction was performed using **SADABS-2016/2** (Bruker, 2016/2). The $wR_2(\text{int})$ was 0.1334 before and 0.0845 after correction. The ratio of minimum to maximum transmission is 0.7786. The $\lambda/2$ correction factor is Not present. The absorption coefficient μ of this material is 4.671 mm^{-1} at this wavelength ($\lambda = 1.54178 \text{ \AA}$) and the minimum and maximum transmissions are 0.587 and 0.754.

The structure was solved and the space group $P2_12_12$ (# 18) determined by the **ShelXT** (Sheldrick, 2015) structure solution program using using dual methods and refined by full matrix least squares minimisation on F^2 using version of ShelXL-2014 (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

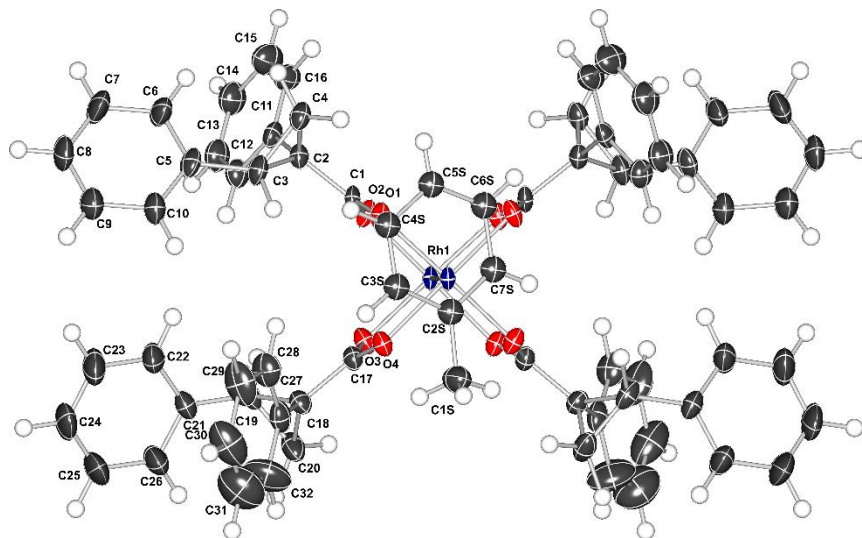
_refine_special_details: Refinement using NoSpherA2, an implementation of NON-SPHERICAL Atom-form-factors in **Olex2**. Please cite: F. Kleemiss, H. Puschmann, O. Dolomanov, S. Grabowsky - to be published - 2020 NoSpherA2 implementation of HAR makes use of tailor-made aspherical atomic form factors calculated on-the-fly from a Hirshfeld-partitioned electron density (ED) - not from spherical-atom form factors. The ED is calculated from a gaussian basis set single determinant SCF wavefunction - either Hartree-Fock or DFT using selected functionals - for a fragment of the crystal. This fragment can be embedded in an electrostatic crystal field by employing cluster charges. The following options were used: SOFTWARE: ORCA PARTITIONING: NoSpherA2 INT ACCURACY: Normal METHOD: PBE BASIS SET: x2c-SVP CHARGE: 0 MULTIPLICITY: 1 RELATIVISTIC: DKH2 DATE: 2020-05-04_14-18-13

The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with

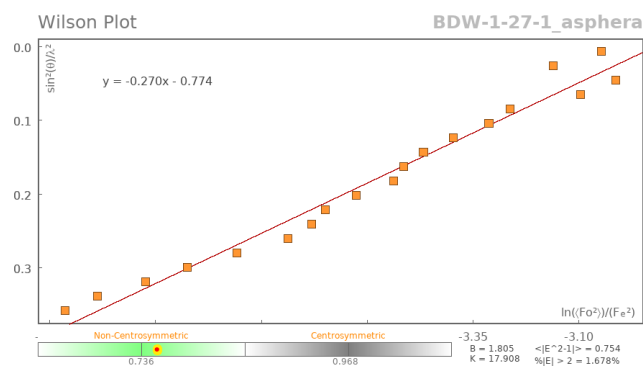
the other half consisting of symmetry equivalent atoms.

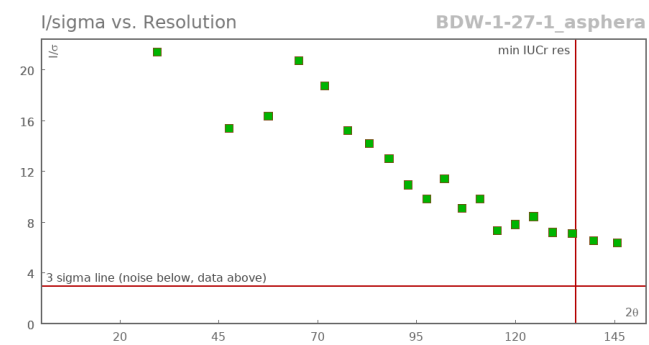
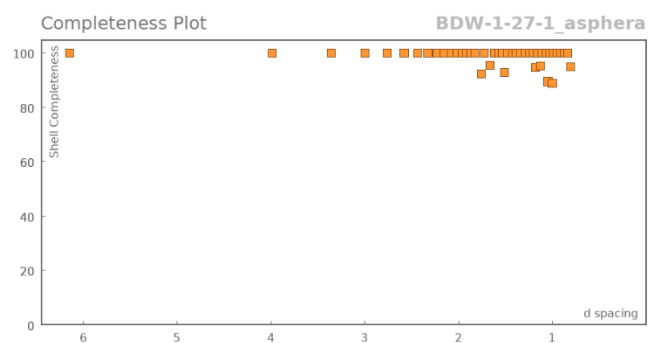
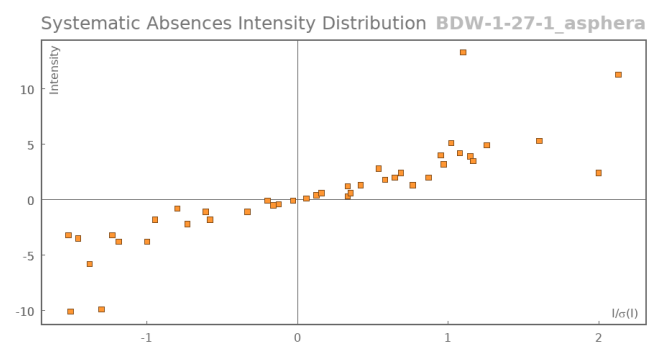
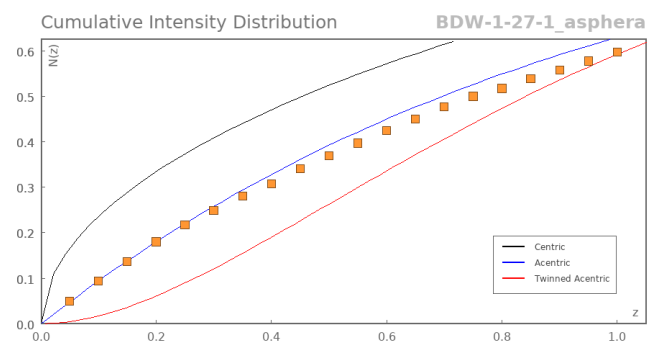
The Flack parameter was refined to 0.022(11). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the **Olex2** results in 0.050(8). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that 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 S1:

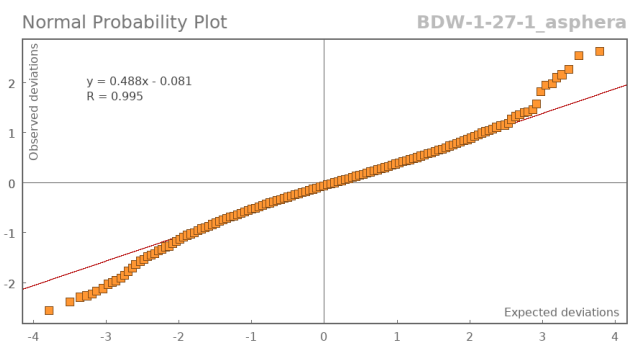
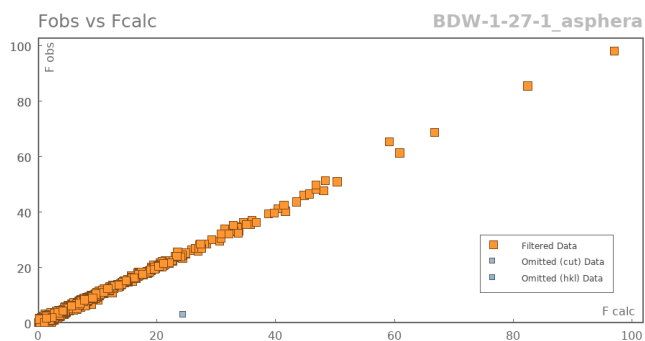


Data Plots: Diffraction Data





Data Plots: Refinement and Data



Reflection Statistics

Total reflections (after filtering)	21232
Completeness	0.985
hkl _{max} collected	(31, 10, 14)
hkl _{max} used	(39, 10, 14)
Lim d _{max} collected	100.0
d _{max} used	15.77
Friedel pairs	3571
Inconsistent equivalents	2
R _{sigma}	0.0619
Omitted reflections	0
Multiplicity	(11043, 3233, 903, 251, 2)
Removed systematic absences	45
Unique reflections	6408
Mean I/ σ	11.83
hkl _{min} collected	(-39, -10, -13)
hkl _{min} used	(-39, 0, 0)
Lim d _{min} collected	0.77
d _{min} used	0.8
Friedel pairs merged	0
R _{int}	0.064
Intensity transformed	0
Omitted by user (OMIT hkl)	1
Maximum multiplicity	10
Filtered off (Shel/OMIT)	0

Images of the Crystal on the Diffractometer

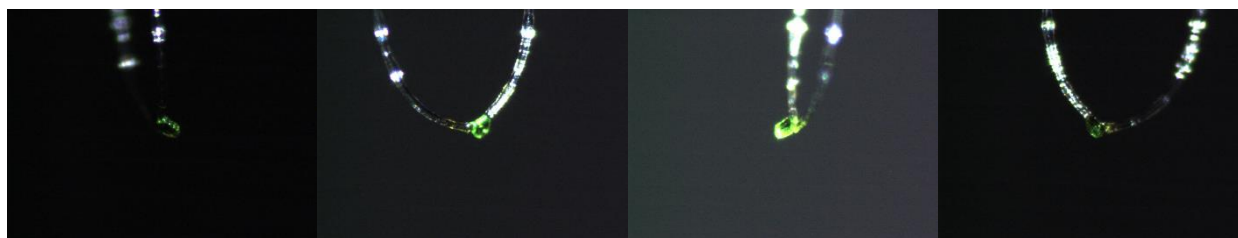


Table S1: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$). U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
Rh1	4939.67(18)	6405.6(8)	3885.1(6)	17.9(2)
O1	5411.5(8)	6665(4)	5018(3)	25.7(7)
O2	5511.8(9)	4003(4)	5065(3)	26.5(8)
O3	4480.2(9)	6049(4)	2740(3)	28.1(8)
O4	4605.2(8)	3409(4)	2690(2)	25.7(7)
C1	5602.4(12)	5429(5)	5329(4)	23.4(9)
C2	5975.0(11)	5626(5)	6105(5)	24.8(8)
C3	6263.6(13)	7090(6)	5854(4)	32.3(11)
C4	5967.8(13)	7083(6)	6838(4)	31.2(10)
C5	6731.9(12)	7034(5)	5986(5)	33.1(10)
C6	6937.7(13)	6413(8)	6916(4)	44.7(12)
C7	7376.8(14)	6415(9)	7003(5)	55.9(15)
C8	7618.4(13)	7103(7)	6166(6)	51.2(13)
C9	7421.8(15)	7758(7)	5244(5)	46.4(14)
C10	6982.6(13)	7694(6)	5155(5)	38.9(12)
C11	6159.2(12)	4087(5)	6497(4)	28.2(9)
C12	6406.3(13)	3170(6)	5794(4)	33.1(10)
C13	6547.0(12)	1663(6)	6121(5)	40.39
C14	6441.5(15)	1086(7)	7162(5)	45.0(11)
C15	6196.4(17)	1988(7)	7873(5)	50.2(13)
C16	6058.9(13)	3507(7)	7544(4)	38.5(10)
C17	4399.6(13)	4642(5)	2422(4)	26.0(10)
C18	4034.3(13)	4461(6)	1624(4)	28.1(10)
C19	3682.1(14)	5736(6)	1751(4)	33.0(10)
C20	3982.9(15)	5823(7)	811(4)	41.3(13)
C21	3233.2(14)	5249(6)	1573(4)	33.1(10)
C22	3007.7(15)	4554(7)	2431(5)	44.7(14)
C23	2595.0(16)	4033(8)	2270(6)	60.2(18)
C24	2399.7(15)	4245(8)	1270(6)	62.7(18)
C25	2611.6(18)	4992(11)	412(5)	68.0(18)
C26	3028.2(16)	5486(8)	566(5)	51.7(16)
C27	3893.7(9)	2822(5)	1362(5)	35.0(11)
C28	3798.9(9)	1748(6)	2217(5)	45.5(12)
C29	3617.8(10)	272(7)	1973(6)	63.8(15)

Atom	x	y	z	U_{eq}
C30	3530.9(12)	-137(8)	882(6)	74.4(15)
C31	3621.5(13)	887(10)	74(8)	93(2)
C32	3799.5(12)	2345(9)	292(6)	78(2)
C1S	5125(3)	238(15)	2045(7)	44(3)
C2S	5080(3)	142(13)	3275(6)	31.4(8)
C3S	4703(3)	-538(12)	3731(9)	31.4(8)
C4S	4641(4)	-638(13)	4854(9)	31.4(8)
C5S	4944(3)	-94(16)	5595(6)	31.4(8)
C6S	5312(4)	541(13)	5212(9)	31.4(8)
C7S	5377(3)	699(13)	4048(9)	31.4(8)
C8S	4968(5)	1812(12)	-1088(11)	70(3)
C9S	4981(4)	3653(12)	-1145(8)	47.2(19)
C10S	4988(5)	4525(11)	-158(8)	48(2)
C11S	5019(5)	6174(12)	-181(8)	56(3)
C12S	5013(3)	6943(12)	-1180(7)	42.3(18)
C13S	4997(4)	6103(10)	-2159(8)	48(2)
C14S	4993(4)	4447(10)	-2154(8)	39.1(17)

Table S2: Anisotropic Displacement Parameters ($\times 10^4$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh1	11.2(3)	15.5(4)	27.1(4)	-0.2(3)	0.7(3)	2.4(4)
O1	19.4(13)	20(2)	37.6(18)	0.4(12)	-3.8(12)	-3.1(14)
O2	21.0(13)	20(2)	38.5(18)	-0.0(11)	-10.0(12)	-3.6(13)
O3	24.5(14)	24(2)	35.9(18)	-1.7(12)	-9.3(12)	2.2(13)
O4	21.4(12)	23.5(19)	32.1(16)	-0.2(13)	-5.9(11)	-1.0(14)
C1	12.7(19)	22(2)	35(2)	1.0(15)	-0.7(16)	-4.4(17)
C2	18.2(16)	24.6(19)	32(2)	0.3(14)	1(2)	-3(2)
C3	21.6(19)	30(2)	45(3)	-4.5(16)	-6.9(18)	-3(2)
C4	23(2)	30(2)	40(3)	-1.6(17)	-5.9(19)	-6(2)
C5	23.0(18)	33(2)	44(3)	-5.9(15)	-9(2)	-8(2)
C6	26(2)	65(3)	43(3)	-11(3)	-9.1(18)	9(3)
C7	29(2)	80(4)	58(3)	-9(3)	-18(2)	8(4)
C8	22(2)	67(3)	64(4)	-9(2)	-2(3)	-2(3)
C9	30(2)	58(4)	52(4)	-7(2)	1(2)	-1(3)
C10	24(2)	42(3)	51(3)	-3.4(19)	0(2)	-1(2)
C11	19.5(17)	30(2)	35(2)	5.2(11)	-6.9(11)	-3.9(11)
C12	29.1(19)	29(2)	41(2)	4.6(10)	0.9(12)	-3.9(10)
C13	32.44	35.03	53.7	9.06	-2.62	-0.15
C14	39(2)	41(3)	55(2)	9.2(14)	-3.7(12)	3.4(12)
C15	52(3)	49(3)	49(3)	16.2(15)	-3.0(14)	7.9(13)
C16	38(2)	44(2)	34(2)	11.6(15)	-2.3(12)	2.2(13)
C17	20(2)	28(3)	30(2)	-1.8(17)	-2.6(17)	1.8(18)

C18	26(2)	30(2)	29(2)	-0.4(17)	-5.1(19)	3.2(19)
C19	31(2)	26(2)	42(3)	2.1(18)	-15(2)	1(2)
C20	30(2)	50(3)	44(3)	-8(2)	-9(2)	20(2)
C21	25(2)	33(3)	41(2)	1.6(17)	-10.1(19)	-2(2)
C22	26(2)	61(4)	47(3)	1(2)	-2(2)	9(3)
C23	26(2)	84(5)	70(4)	-5(3)	-2(2)	16(4)
C24	25(2)	92(5)	71(4)	-13(2)	-8(3)	-12(4)
C25	35(3)	112(6)	56(4)	-13(3)	-17(3)	-8(5)
C26	33(3)	77(5)	45(3)	-9(3)	-12(2)	10(3)
C27	23.8(19)	32(2)	50(3)	4.5(13)	-2.8(14)	-9.8(13)
C28	44(2)	33(3)	60(3)	-8.0(16)	-4.4(16)	-7.0(14)
C29	55(3)	33(3)	103(3)	-12.0(17)	-19.5(19)	-10.1(16)
C30	76(4)	43(3)	104(3)	7.1(18)	-32.0(19)	-20.3(16)
C31	115(4)	68(3)	97(3)	-4.6(15)	-23.6(15)	-17.2(13)
C32	121(5)	58(3)	55(3)	-4(2)	-22.3(18)	-15.6(15)
C1S	43(2)	54(6)	34.9(15)	-11.1(18)	0.0(8)	-0.7(8)
C2S	35.1(16)	24.2(13)	34.9(15)	3.1(8)	0.1(8)	-0.9(8)
C3S	35.1(16)	24.2(13)	34.9(15)	3.1(8)	0.1(8)	-0.9(8)
C4S	35.1(16)	24.2(13)	34.9(15)	3.1(8)	0.1(8)	-0.9(8)
C5S	35.1(16)	24.2(13)	34.9(15)	3.1(8)	0.1(8)	-0.9(8)
C6S	35.1(16)	24.2(13)	34.9(15)	3.1(8)	0.1(8)	-0.9(8)
C7S	35.1(16)	24.2(13)	34.9(15)	3.1(8)	0.1(8)	-0.9(8)
C8S	103(9)	52(3)	55(4)	-2.4(11)	-6(3)	0.7(10)
C9S	45(3)	51(2)	45.7(19)	-0.7(8)	-2.5(9)	0.1(7)
C10S	46(6)	53(3)	45(2)	-4.0(18)	-0.5(12)	-0.7(10)
C11S	66(7)	54(3)	48(2)	-5.5(18)	0.2(14)	-1.2(10)
C12S	25(4)	53(3)	49(2)	-2.0(15)	3.4(15)	-1.3(10)
C13S	45(3)	50(2)	48(2)	1.0(9)	-0.5(9)	0.1(8)
C14S	23(4)	50(3)	45(2)	1.8(10)	-0.9(11)	-0.3(8)

Table S3: Bond Lengths in Å

Atom	Atom	Length/Å
Rh1	Rh1 ¹	2.3874(14)
Rh1	O1	2.027(3)
Rh1	O2 ¹	2.037(3)
Rh1	O3	2.020(3)
Rh1	O4 ¹	2.035(3)
O1	C1	1.255(5)
O2	C1	1.269(5)

O3	C17	1.265(6)
O4	C17	1.262(5)
C1	C2	1.508(6)
C2	C3	1.557(6)
C2	C4	1.505(6)
C2	C11	1.490(6)
C3	C4	1.504(7)
C3	C5	1.486(5)
C5	C6	1.392(7)
C5	C10	1.387(7)
C6	C7	1.389(6)
C7	C8	1.386(8)
C8	C9	1.383(9)
C9	C10	1.390(7)
C11	C12	1.382(6)
C11	C16	1.383(7)
C12	C13	1.395(6)
C13	C14	1.380(8)
C14	C15	1.378(8)
C15	C16	1.402(8)
C17	C18	1.506(6)
C18	C19	1.549(6)
C18	C20	1.510(6)
C18	C27	1.478(6)
C19	C20	1.476(7)
C19	C21	1.489(6)
C21	C22	1.380(7)
C21	C26	1.385(7)
C22	C23	1.387(7)
C23	C24	1.360(9)
C24	C25	1.378(9)
C25	C26	1.390(7)
C27	C28	1.397(8)
C27	C32	1.378(9)
C28	C29	1.394(7)
C29	C30	1.381(10)
C30	C31	1.326(11)
C31	C32	1.370(11)
C1S	C2S	1.484(11)
C2S	C3S	1.428(13)
C2S	C7S	1.397(12)
C3S	C4S	1.363(15)
C4S	C5S	1.383(13)

C5S	C6S	1.358(15)
C6S	C7S	1.417(15)
C8S	C9S	1.545(11)
C9S	C10S	1.391(11)
C9S	C14S	1.381(11)
C10S	C11S	1.386(13)
C11S	C12S	1.360(4)
C12S	C13S	1.371(4)
C13S	C14S	1.389(4)

¹1-x,1-y,+z

Table S4: Bond Angles in °

Atom	Atom	Atom	Angle/°
O2 ¹	Rh1	O1	93.74(13)
O3	Rh1	O1	177.41(14)
O3	Rh1	O2 ¹	86.93(11)
O4 ¹	Rh1	O1	86.93(11)
O4 ¹	Rh1	O2 ¹	174.71(14)
O4 ¹	Rh1	O3	92.17(12)
C1	O1	Rh1	117.6(3)
C1	O2	Rh1 ¹	119.3(3)
C17	O3	Rh1	119.2(3)
C17	O4	Rh1 ¹	118.6(3)
O2	C1	O1	126.5(4)
C2	C1	O1	117.8(4)
C2	C1	O2	115.6(4)
C3	C2	C1	115.0(4)
C4	C2	C1	115.9(3)
C4	C2	C3	58.8(3)
C11	C2	C1	113.8(3)
C11	C2	C3	121.0(3)
C11	C2	C4	121.6(4)
C4	C3	C2	58.9(3)
C5	C3	C2	122.4(4)
C5	C3	C4	122.2(4)
C3	C4	C2	62.3(3)
C6	C5	C3	124.1(5)
C10	C5	C3	118.5(5)
C10	C5	C6	117.3(4)
C7	C6	C5	121.6(5)
C8	C7	C6	119.7(5)
C9	C8	C7	119.9(4)
C10	C9	C8	119.5(5)
C9	C10	C5	121.9(5)
C12	C11	C2	120.6(5)
C16	C11	C2	120.1(4)
C16	C11	C12	119.1(5)
C13	C12	C11	120.8(5)
C14	C13	C12	119.7(5)
C15	C14	C13	120.2(5)
C16	C15	C14	119.8(5)
C15	C16	C11	120.3(5)
O4	C17	O3	125.7(4)
C18	C17	O3	116.0(4)
C18	C17	O4	118.2(4)
C19	C18	C17	114.7(4)
C20	C18	C17	114.6(4)
C20	C18	C19	57.7(3)
C27	C18	C17	117.3(4)
C27	C18	C19	116.6(3)
C27	C18	C20	122.2(4)
C20	C19	C18	59.9(3)
C21	C19	C18	118.6(4)

Atom	Atom	Atom	Angle/°
C21	C19	C20	121.0(4)
C19	C20	C18	62.5(3)
C22	C21	C19	119.9(4)
C26	C21	C19	122.0(5)
C26	C21	C22	118.1(4)
C23	C22	C21	120.8(5)
C24	C23	C22	120.5(6)
C25	C24	C23	119.9(5)
C26	C25	C24	119.7(6)
C25	C26	C21	121.0(6)
C28	C27	C18	120.5(5)
C32	C27	C18	122.2(6)
C32	C27	C28	116.8(5)
C29	C28	C27	120.3(6)
C30	C29	C28	120.1(7)
C31	C30	C29	119.3(7)
C32	C31	C30	121.8(9)
C31	C32	C27	121.7(8)
C3S	C2S	C1S	118.7(8)
C7S	C2S	C1S	125.3(8)
C7S	C2S	C3S	115.9(7)
C4S	C3S	C2S	121.5(10)
C5S	C4S	C3S	121.1(10)
C6S	C5S	C4S	120.1(8)
C7S	C6S	C5S	119.6(10)
C6S	C7S	C2S	121.8(10)
C10S	C9S	C8S	119.2(9)
C14S	C9S	C8S	121.4(9)
C14S	C9S	C10S	119.4(8)
C11S	C10S	C9S	120.6(9)
C12S	C11S	C10S	119.3(10)
C13S	C12S	C11S	120.7(9)
C14S	C13S	C12S	120.7(10)
C13S	C14S	C9S	119.1(10)

¹1-x,1-y,+z

Table S5: Torsion Angles in °

Atom	Atom	Atom	Atom	Angle/°
Rh1	O1	C1	O2	-5.3(3)
Rh1	O1	C1	C2	175.5(3)
Rh1 ¹	O2	C1	O1	7.8(3)
Rh1 ¹	O2	C1	C2	-173.0(3)
Rh1	O3	C17	O4	-6.1(3)
Rh1	O3	C17	C18	176.1(3)
Rh1 ¹	O4	C17	O3	8.4(3)
Rh1 ¹	O4	C17	C18	-173.8(3)
O1	C1	C2	C3	-38.8(4)
O1	C1	C2	C4	27.1(5)
O1	C1	C2	C11	175.5(4)
O2	C1	C2	C3	141.9(4)
O2	C1	C2	C4	-152.3(4)
O2	C1	C2	C11	-3.8(5)
O3	C17	C18	C19	-29.4(5)
O3	C17	C18	C20	34.7(5)
O3	C17	C18	C27	-171.6(4)
O4	C17	C18	C19	152.7(4)
O4	C17	C18	C20	-143.2(4)
O4	C17	C18	C27	10.5(5)
C1	C2	C3	C4	106.4(5)
C1	C2	C3	C5	-142.9(4)
C1	C2	C4	C3	-104.7(5)
C1	C2	C11	C12	75.0(4)
C1	C2	C11	C16	-100.3(5)
C2	C3	C5	C6	-47.0(6)
C2	C3	C5	C10	135.6(5)
C2	C4	C3	C5	-111.1(3)
C2	C11	C12	C13	-174.1(4)
C2	C11	C16	C15	173.6(4)
C3	C5	C6	C7	-178.9(6)
C3	C5	C10	C9	176.8(5)
C5	C6	C7	C8	2.4(7)
C5	C10	C9	C8	2.1(6)
C6	C7	C8	C9	-1.1(8)
C7	C8	C9	C10	-1.1(7)
C11	C12	C13	C14	-0.6(5)
C11	C16	C15	C14	1.6(5)
C12	C13	C14	C15	0.4(5)

C13	C14	C15	C16	-0.9(6)
C17	C18	C19	C20	104.6(5)
C17	C18	C19	C21	-144.2(4)
C17	C18	C20	C19	-104.6(6)
C17	C18	C27	C28	52.1(4)
C17	C18	C27	C32	-136.2(3)
C18	C19	C21	C22	83.4(5)
C18	C19	C21	C26	-97.3(5)
C18	C20	C19	C21	-107.3(3)
C18	C27	C28	C29	172.2(2)
C18	C27	C32	C31	-172.0(2)
C19	C21	C22	C23	-177.3(5)
C19	C21	C26	C25	178.7(6)
C21	C22	C23	C24	-2.2(7)
C21	C26	C25	C24	-0.5(7)
C22	C23	C24	C25	-0.4(8)
C23	C24	C25	C26	1.7(8)
C27	C28	C29	C30	0.00(4)
C27	C32	C31	C30	-0.00(4)
C28	C29	C30	C31	0.00(4)
C29	C30	C31	C32	0.00(3)
C1S	C2S	C3S	C4S	-
C1S	C2S	C7S	C6S	179.1(10)
C2S	C3S	C4S	C5S	-
C2S	C7S	C6S	C5S	179.1(11)
C3S	C4S	C5S	C6S	-0.4(13)
C4S	C5S	C6S	C7S	-3.5(13)
C8S	C9S	C10S	C11S	-0.6(10)
C8S	C9S	C14S	C13S	2.5(16)
C9S	C10S	C11S	C12S	177.0(10)
C9S	C14S	C13S	C12S	179.0(10)
C10S	C11S	C12S	C13S	4.9(17)
C11S	C12S	C13S	C14S	3.3(15)
				-3.4(15)
				-0.6(13)

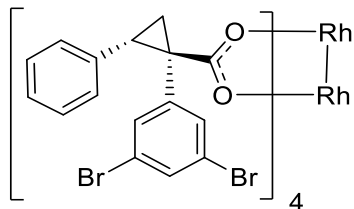
¹1-x,1-y,+z

Table S6: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$). U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
H3	6156(17)	7840(70)	5150(50)	48.4(17)
H4A	5687(17)	7870(70)	6780(50)	46.7(15)
H4B	6122(17)	6990(70)	7630(50)	46.7(15)
H6	6765.1(13)	5954(8)	7537(4)	67.0(18)
H7	7517.8(14)	5923(9)	7665(5)	84(2)
H8	7934.5(13)	7126(7)	6230(6)	77(2)
H9	7594.2(15)	8274(7)	4644(5)	70(2)
H10	6843.4(13)	8137(6)	4473(5)	58.4(18)
H12	6485.2(13)	3591(6)	5042(4)	49.7(15)
H13	6723.5(12)	1005(6)	5604(5)	60.585
H14	6543.3(15)	9(7)	7401(5)	67.6(17)
H15	6116.7(17)	1562(7)	8623(5)	75.2(19)
H16	5887.5(13)	4174(7)	8068(4)	57.7(14)
H19	3731(16)	6610(80)	2440(50)	49.5(15)
H20A	4230(17)	6640(80)	860(50)	61.9(19)
H20B	3860(20)	5620(80)	-100(60)	61.9(19)
H22	3143.6(15)	4425(7)	3179(5)	120(30)
H23	2439.9(16)	3497(8)	2893(6)	130(40)
H24	2102.7(15)	3860(8)	1158(6)	100(20)
H25	2466.5(18)	5178(11)	-317(5)	140(40)
H26	3182.2(16)	6019(8)	-61(5)	100(30)
H28	3861.4(9)	2039(6)	3009(5)	68.3(18)
H29	3550.8(10)	-492(7)	2588(6)	96(2)
H30	3401.0(12)	-1195(8)	702(6)	112(2)
H31	3558.2(13)	588(10)	-716(8)	140(3)
H32	3862.7(12)	3081(9)	-343(6)	117(3)
H1SA	5170(20)	-833(19)	1742(9)	66(4)
H1SB	4865(10)	690(80)	1724(8)	66(4)
H1SC	5366(15)	920(70)	1858(7)	66(4)
H3S	4490(3)	-928(12)	3241(9)	37.7(10)
H4S	4386(4)	-1090(13)	5131(9)	37.7(10)
H5S	4894(3)	-164(16)	6375(6)	37.7(10)
H6S	5525(4)	876(13)	5720(9)	37.7(10)
H7S	5628(3)	1198(13)	3786(9)	37.7(10)
H8SA	5288(5)	1333(12)	-1223(11)	105(4)
H8SB	4852(5)	1439(12)	-263(11)	105(4)
H8SC	4753(5)	1355(12)	-1736(11)	105(4)
H10S	5000(40)	3944(16)	568(14)	72(4)
H11S	5047(5)	6791(12)	528(8)	84(4)
H12S	5019(3)	8136(12)	-1199(7)	51(2)
H13S	4989(4)	6689(10)	-2885(8)	72(3)
H14S	4997(4)	3837(10)	-2870(8)	59(3)

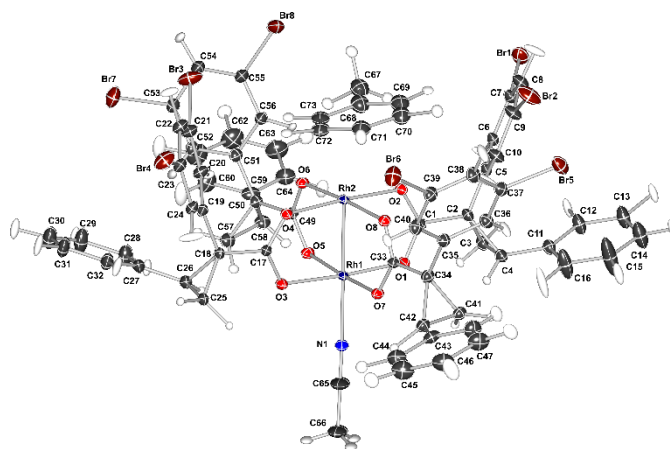
Table S7: Atomic Occupancies for all atoms that are not fully occupied.

Atom	Occupancy
C1S	0.5
H1SA	0.5
H1SB	0.5
H1SC	0.5
C2S	0.5
C3S	0.5
H3S	0.5
C4S	0.5
H4S	0.5
C5S	0.5
H5S	0.5
C6S	0.5
H6S	0.5
C7S	0.5
H7S	0.5
C8S	0.5
H8SA	0.5
H8SB	0.5
H8SC	0.5
C9S	0.5
C10S	0.5
H10S	0.5
C11S	0.5
H11S	0.5
C12S	0.5
H12S	0.5
C13S	0.5
H13S	0.5
C14S	0.5
H14S	0.5



Dirhodium tetrakis ((1*R*,2*S*)-1-(3,5-dibromophenyl)-2-phenylcyclopropanecarboxylate)

(2.34)



Experimental. Single dark blue prism crystals of **2.34** were used as supplied. A suitable crystal with dimensions $0.68 \times 0.49 \times 0.46 \text{ mm}^3$ was selected and mounted on a Bruker D8 diffractometer with APEX2 detector. The crystal was kept at a steady $T = 100(2) \text{ K}$ during data collection. The structure was solved with the **XT** (Sheldrick, 2015) solution program using dual methods and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with **olex2.refine** 1.3-alpha (Bourhis et al., 2015) using full matrix least squares minimisation on F^2 .

Crystal Data. $\text{C}_{87}\text{H}_{71}\text{Br}_8\text{NO}_8\text{Rh}_2$, $M_r = 2103.574$, orthorhombic, $P2_12_12_1$ (No. 19), $a = 16.2100(4) \text{ \AA}$, $b = 19.2876(4) \text{ \AA}$, $c = 25.6190(6) \text{ \AA}$, $\alpha = 90.0^\circ$, $\beta = 90.0^\circ$, $\gamma = 90.0^\circ$, $V = 8009.8(3) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $Z' = 1$, $\mu(\text{Mo K}\alpha) = 4.459 \text{ mm}^{-1}$, 49609 reflections measured, 23988 unique ($R_{\text{int}} = 0.0360$) which were used in all calculations. The final wR_2 was 0.0890 (all data) and R_1 was 0.0418 ($I \geq \sigma(I)$).

$R_1 = 4.18\%$

Compound	2.34
Formula	C ₈₇ H ₇₁ Br ₈ NO ₈ Rh ₂
$D_{calc.}/\text{g cm}^{-3}$	1.744
μ/mm^{-1}	4.459
Formula Weight	2103.574
Colour	dark blue
Shape	prism
Size/mm ³	0.68×0.49×0.46
T/K	100(2)
Crystal System	orthorhombic
Flack Parameter	0.012(5)
Hooft Parameter	-0.011(2)
Space Group	$P2_12_12_1$
$a/\text{\AA}$	16.2100(4)
$b/\text{\AA}$	19.2876(4)
$c/\text{\AA}$	25.6190(6)
$\alpha/^\circ$	90.0
$\beta/^\circ$	90.0
$\gamma/^\circ$	90.0
$V/\text{\AA}^3$	8009.8(3)
Z	4
Z'	1
Wavelength/ $\text{\AA}$	0.71073
Radiation type	Mo K α
$\theta_{min}/^\circ$	1.64
$\theta_{max}/^\circ$	30.51
Measured Refl's.	49609
Ind't Refl's	23988
Refl's with $I \geq \sigma(I)$	20171
R_{int}	0.0360
Parameters	1771
Restraints	2355
Largest Peak	1.2283
Deepest Hole	-1.2136
GooF	1.0386
wR_2 (all data)	0.0890
wR_2	0.0829
R_1 (all data)	0.0582
R_1	0.0418

Structure Quality Indicators

Reflections:	d min (Mo)	0.70	I/σ	17.4	Rint	3.60%	complete	100% (IUCr)	100%	
	CIF		CIF		CIF					
Refinement:	Shift	0.000	Max Peak	1.2	Min Peak	-1.2	Goof	1.039	Flack	.012(5)
	CIF		CIF		CIF		CIF		CIF	

A dark blue prism-shaped crystal with dimensions $0.68 \times 0.49 \times 0.46 \text{ mm}^3$ was mounted. Data were collected using a Bruker D8 diffractometer with APEX2 detector operating equipped with an Oxford Cryosystems low-temperature device operating at $T = 100(2) \text{ K}$.

Data were measured using ω scans using Mo K_α radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program APEX2 (Bruker, V2 v2014.11). The maximum resolution that was achieved was $\theta = 30.51^\circ$ ($0.81 \text{ \AA}$).

The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program **APEX2** (Bruker, V2 v2014.11). The unit cell was refined using **CrysAlisPro** (Rigaku, V1.171.38.41, 2015) on 35319 reflections, 71% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using **CrysAlisPro** (Rigaku, V1.171.38.41, 2015). The final completeness is 99.88 % out to 30.51° in θ . A multi-scan absorption correction was performed using **CrysAlisPro** 1.171.38.41 (Rigaku Oxford Diffraction, 2015). The absorption coefficient μ of this material is 4.459 mm^{-1} at this wavelength ($\lambda = 0.71073 \text{ \AA}$) and the minimum and maximum transmissions are 0.185 and 0.209.

The structure was solved and the space group $P2_12_12_1$ (# 19) determined by the XT (Sheldrick, 2015) structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version of **olex2.refine** 1.3-alpha (Bourhis et al., 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Most hydrogen atom positions were calculated geometrically and refined using the riding model, but some hydrogen atoms were refined freely.

Refinement using NoSpherA2, an implementation of Non-SPHERical Atom-form-factors in Olex2. Please cite: F. Kleemiss, H. Puschmann, O. Dolomanov, S. Grabowsky - to be published - 2020 NoSpherA2 implementation of HAR makes use of tailor-made aspherical atomic form factors calculated on-the-fly from a Hirshfeld-partitioned electron density (ED) - not from spherical-atom form factors. The ED is calculated from a Gaussian basis set single determinant SCF wavefunction - either Hartree-Fock or DFT using selected functionals - for a fragment of the crystal. This fragment can be embedded in an electrostatic crystal field by employing cluster charges. The following options were used: SOFTWARE: ORCA PARTITIONING: NoSpherA2 INT ACCURACY: Normal METHOD: PBE BASIS SET: x2c-TZVP CHARGE: 0 MULTIPLICITY: 1 DATE: 2020-05-01_20-15-21

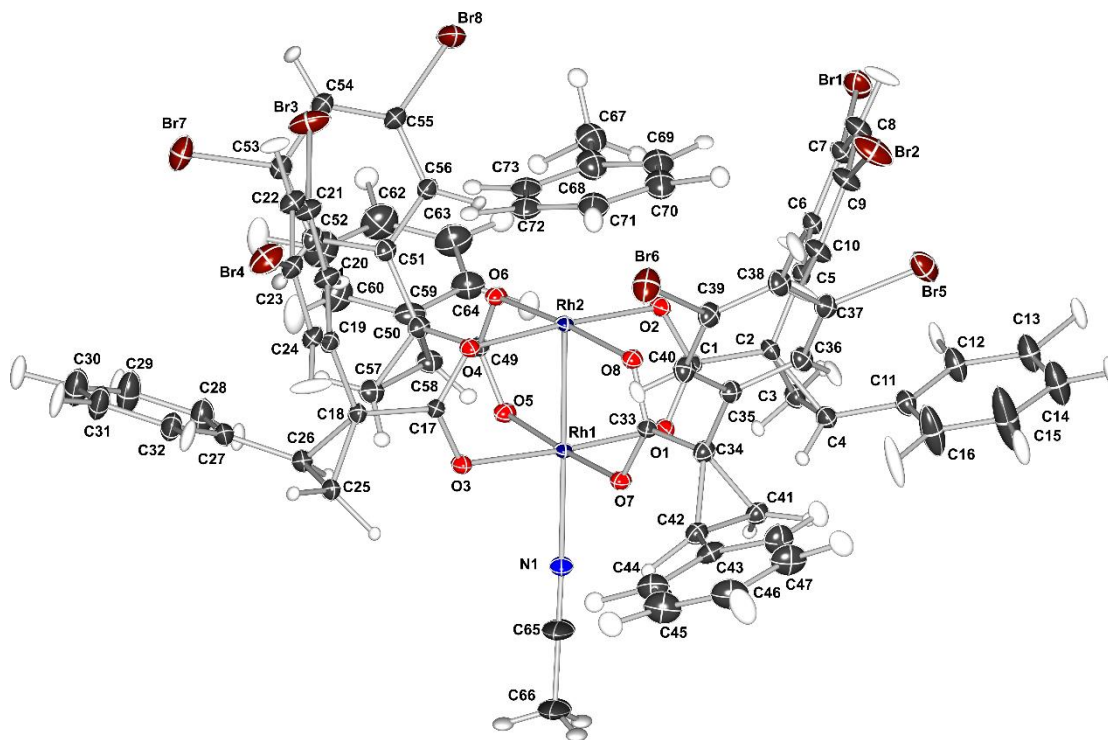


Figure S2: Thermal ellipsoid plot of the molecular structure and the asymmetric unit ($Z'=1$). There are three toluene molecules (two are hidden for clarity) in the asymmetric unit. The toluene molecule shown here is located along the dirhodium axis and within a distance of 2.684(3) Å to Rh2.

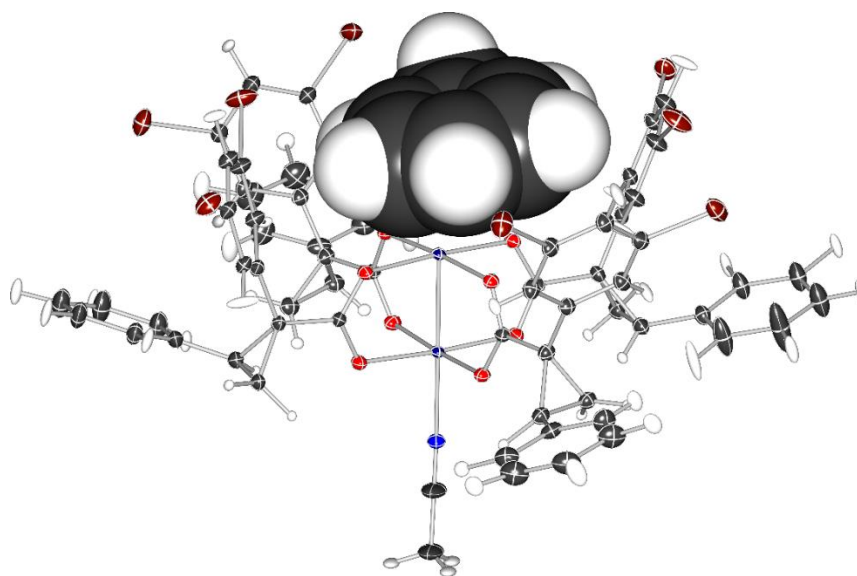


Figure S3: Thermal ellipsoid plot of the molecular structure and the toluene molecule that associates with the Rh-Rh linkage. The toluene is staggered with respect to the carboxylate groups and is within a distance of 2.684(3) Å to Rh2 along the dirhodium axis.

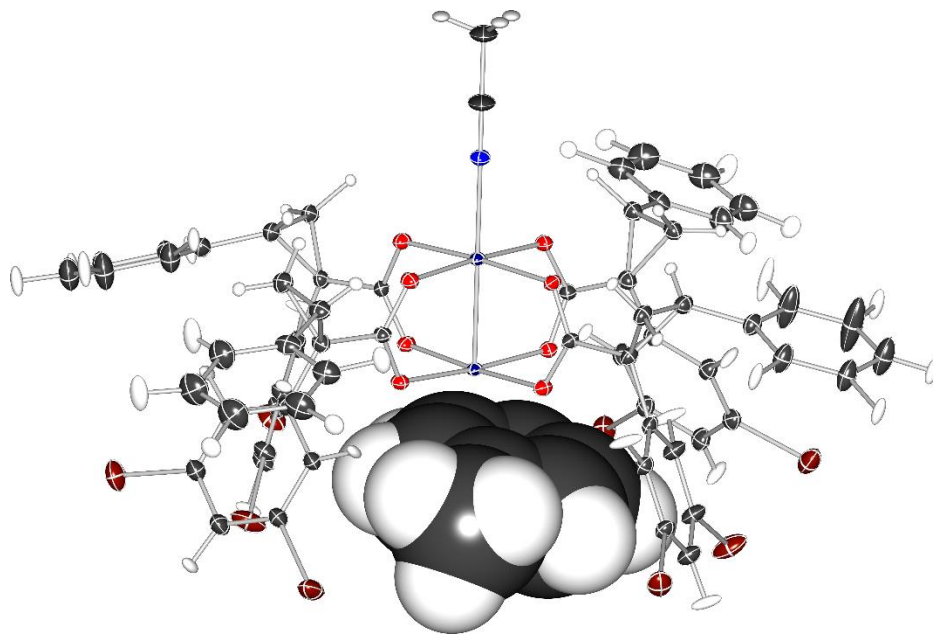
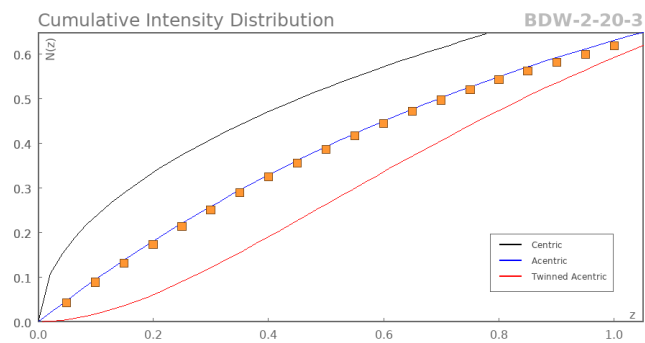
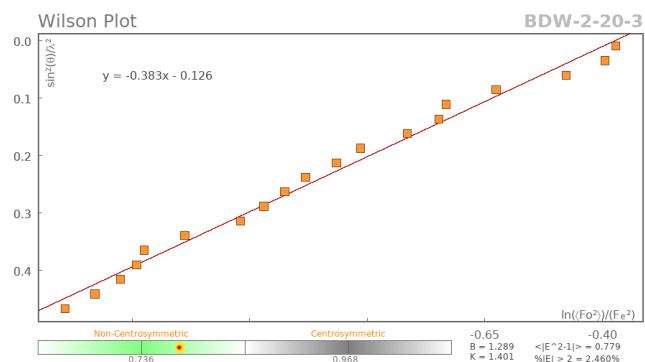
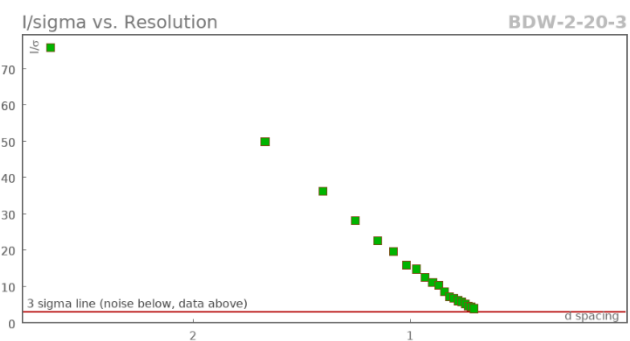
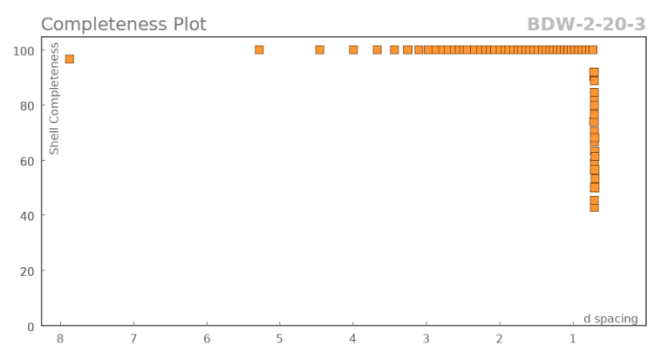
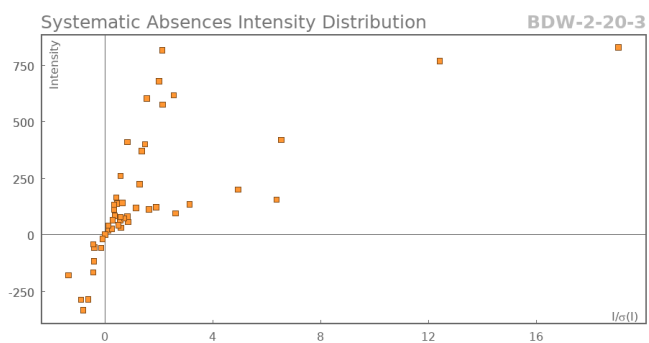


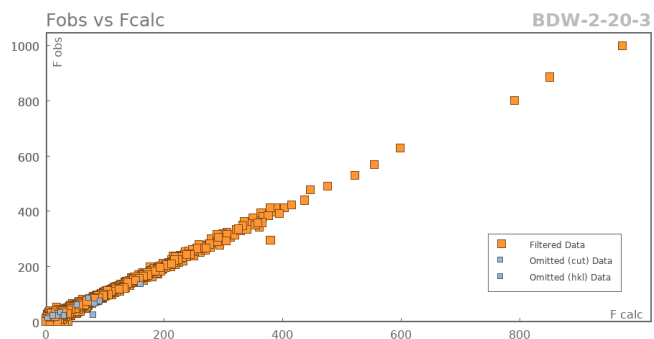
Figure S4: Thermal ellipsoid plot of the molecular structure and the toluene molecule that associates with the Rh-Rh linkage. The toluene is staggered with respect to the carboxylate groups and is within a distance of 2.684(3) Å to Rh2 along the dirhodium axis.

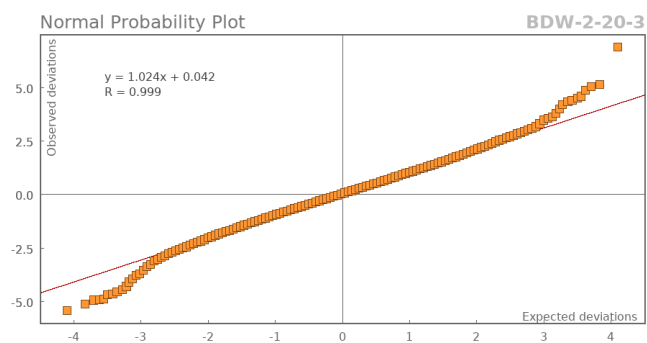
Data Plots: Diffraction Data





Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	49670	Unique reflections	23988
Completeness	0.981	Mean I/σ	17.68
$hkl_{\max}$ collected	(23, 27, 24)	$hkl_{\min}$ collected	(-17, -27, -36)
$hkl_{\max}$ used	(23, 27, 36)	$hkl_{\min}$ used	(-23, 0, 0)
Lim $d_{\max}$ collected	20	Lim $d_{\min}$ collected	0.7
$d_{\max}$ used	13.7	$d_{\min}$ used	0.7
Friedel pairs	7961	Friedel pairs merged	0
Inconsistent equivalents	54	R_{int}	0.036
R_{sigma}	0.0574	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	29
Multiplicity	(45642, 2014)	Maximum multiplicity	6
Removed systematic absences	61	Filtered off (Shel/OMIT)	0

Images of the Crystal on the Diffractometer



Table S8: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$)

for **3d**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
Rh2	5303.6(4)	5112.5(3)	5054.3(3)	10.58(18))
Rh1	6776.5(4)	5045.2(3)	5055.4(3)	10.76(18))
Br1	3819.9(6)	7821.9(5)	7172.7(4)	27.9(3)
Br5	3653.5(6)	3134.3(5)	7481.8(4)	29.4(3)
Br8	3497.1(6)	8358.8(6)	4352.9(4)	31.0(3)
Br4	3337.5(6)	2746.2(5)	2883.5(5)	30.3(3)
Br2	3170.4(6)	4940.0(5)	7180.3(5)	35.9(3)
Br7	4198.0(7)	7009.4(5)	2431.9(4)	30.3(3)
Br6	3238.9(6)	1875.9(5)	5501.9(4)	29.9(3)
Br3	3157.8(7)	5637.4(5)	3275.1(5)	34.6(4)
O2	5371.3(16)	5644.6(12)	5738.0(11)	14.4(5)
O3	6711.0(16)	4586.7(13)	4330.2(11)	15.3(5)
O1	6749.8(16)	5501.8(13)	5779.6(10)	14.5(5)
O7	6672.7(15)	4111.8(12)	5425.1(10)	14.5(5)
O5	6796.2(16)	5985.0(12)	4679.0(11)	15.2(5)
O4	5320.2(15)	4578.5(13)	4374.8(11)	14.1(5)
O8	5287.3(15)	4230.8(12)	5496.9(11)	13.6(5)
O6	5410.0(15)	5989.2(13)	4605.8(11)	14.2(5)
C1	6059(2)	5674.4(17)	5968.5(15)	13.4(6)
N1	8108.9(18)	4946.7(15)	5050.3(13)	16.2(6)
C18	5930(2)	4233.8(18)	3585.4(15)	14.1(5)
C52	5173(2)	6905.1(19)	3353.4(16)	17.1(7)
C8	3611(3)	6357(2)	7126.9(18)	21.4(8)
C34	5947(2)	3337.4(18)	5975.2(16)	16.4(4)
C50	6178(2)	6795.7(18)	4099.7(16)	15.9(5)
C17	5994(2)	4482.0(17)	4141.8(14)	12.1(5)
C11	6433(2)	5447.9(19)	7454.0(16)	17.7(7)
C71	3372(3)	4051(2)	5204(2)	28.1(7)
C49	6123(2)	6212.5(17)	4497.6(15)	13.5(6)
C70	3298(3)	4411(2)	5680(2)	29.8(8)
C3S	5526(3)	7465(2)	5609.1(14)	26.8(9)
C36	4804(2)	3235.9(19)	6642.6(16)	18.4(7)
C40	4645(2)	2678.8(18)	5802.9(17)	18.0(7)
C27	6411(2)	4717(2)	2676.7(16)	19.7(7)
C6	4951(2)	6785.9(19)	6829.5(15)	15.9(7)
C39	3871(3)	2438.7(19)	5960.8(16)	18.7(7)
C12	6233(3)	5957(2)	7813.1(18)	25.8(9)
C41	6672(2)	3309.6(19)	6348.5(16)	16.8(4)

C37	4041(2)	2971.5(18)	6792.9(16)	18.1(6)
C35	5111(2)	3087.1(18)	6143.4(16)	15.9(6)
C57	6954(2)	6812(2)	3777.4(18)	19.4(7)
C7	4165(2)	6900.9(19)	7029.5(16)	17.7(7)
C23	3857(2)	3590.3(19)	3094.2(16)	17.4(7)
C54	3934(3)	7615(2)	3431.8(17)	21.7(7)
C51	5383(2)	7043.8(18)	3867.0(16)	16.0(6)
C58	6861(2)	7345.4(19)	4198.1(17)	19.1(6)
C42	6658(2)	2805.1(19)	5911.4(16)	17.0(4)
C21	3778(2)	4802.7(19)	3243.1(17)	19.5(7)
C9	3883(3)	5691(2)	7025.4(17)	21.6(8)
C28	6539(3)	5419(2)	2548.3(19)	29.9(9)
C26	6617(2)	4489.4(19)	3214.6(16)	16.9(6)
C4S	6373(3)	7419(2)	5678.3(15)	27.0(9)
C56	4866(2)	7473.1(19)	4171.1(17)	16.6(7)
C5S	6780(3)	7958(2)	5928.1(17)	39.9(12)
C20	4601(2)	4821.8(19)	3382.0(16)	17.8(7)
C22	3374(3)	4187(2)	3108.2(17)	20.3(8)
C14	6032(4)	5111(2)	8494(2)	39.0(12)
C32	6095(3)	4276(2)	2291.4(17)	24.5(8)
C2	6043(2)	5939.9(18)	6520.9(15)	14.8(5)
C65	8804(3)	4823(3)	5032(2)	44.9(10)
C5	5211(2)	6104.8(18)	6734.0(15)	14.8(6)
C24	4686(2)	3579.9(18)	3242.6(15)	15.9(7)
C3	6792(3)	6336.7(19)	6711.4(16)	17.3(6)
C59	6670(2)	8089(2)	4083.2(18)	22.4(7)
C19	5057(2)	4202.5(19)	3385.3(15)	14.5(6)
C10S	5677(3)	2624(2)	4369.9(19)	30.5(8)
C72	3570(3)	4418(2)	4749(2)	25.9(7)
C43	6505(2)	2043.4(19)	5980.1(17)	19.7(7)
C61	6358(3)	9044(2)	3489(2)	39.1(11)
C25	6592(2)	3749.8(19)	3389.1(16)	15.9(6)
C60	6566(3)	8355(2)	3582(2)	32.7(9)
C14S	5035(3)	1663(2)	3924(2)	32.2(9)
C68	3605(3)	5503(2)	5238(2)	30.8(6)
C4	6678(2)	5607.7(19)	6905.5(16)	17.0(6)
C44	6692(3)	1596(2)	5567.1(19)	25.8(8)
C38	3561(3)	2575.5(19)	6455.0(17)	20.1(7)
C69	3408(3)	5130(2)	5689(2)	28.9(7)
C16	6420(4)	4764(2)	7614(2)	46.5(15)
C13	6014(3)	5786(2)	8321.1(18)	29.1(9)
C13S	4247(3)	1951(3)	4037(2)	35.3(10)
C33	5966(2)	3935.8(17)	5598.5(15)	13.0(6)

C11S	4899(3)	2909(2)	4464.3(19)	30.1(8)
C55	4164(2)	7748(2)	3947.9(17)	18.9(7)
C10	4667(3)	5553.0(19)	6830.3(17)	19.5(8)
C31	5923(3)	4509(2)	1793.5(18)	30.6(10)
C8S	6562(3)	1677(3)	3997(2)	38.6(8)
C2S	5082(3)	8041(2)	5785.4(15)	31.3(9)
C6S	6340(4)	8537(2)	6105.6(18)	49.0(14)
C53	4458(3)	7192(2)	3138.8(17)	19.8(7)
C64	6551(3)	8546(2)	4502(2)	28.8(8)
C1S	4151(3)	8077(3)	5725(2)	38.6(11)
C73	3701(2)	5138(2)	4772.5(19)	25.1(6)
C46	6281(3)	603(2)	6068(2)	33.4(9)
C9S	5742(3)	1997(3)	4096(2)	37.9(8)
C67	3681(3)	6285(2)	5261(2)	31.4(6)
C63	6364(3)	9239(2)	4421(2)	36.9(10)
C7S	5493(3)	8578(2)	6034.3(17)	41.2(12)
C12S	4187(3)	2575(2)	4300(2)	32.3(8)
C47	6090(3)	1034(2)	6488(2)	32.1(9)
C30	6084(3)	5206(2)	1660.4(19)	35.2(10)
C1D	6207(3)	1753(2)	6443(2)	27.2(9)
C45	6579(3)	881(2)	5611(2)	33.8(10)
C29	6369(4)	5658(3)	2042(2)	39.5(12)
C62	6264(3)	9491(2)	3912(2)	40.8(11)
C15	6199(6)	4599(3)	8126(2)	70(2)
C66	9664(3)	4647(3)	5007(2)	46.2(10)

Table S9: Anisotropic Displacement Parameters ($\times 10^4$) for **2.34**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh2	7.4(3)	12.9(3)	11.4(4)	-0.2(2)	1.1(3)	-0.3(3)
Rh1	7.5(3)	13.8(3)	11.1(4)	-0.4(2)	0.6(3)	-0.5(3)
Br1	36.3(7)	22.3(5)	25.2(7)	9.1(4)	3.1(5)	-3.0(5)
Br5	35.1(7)	26.6(6)	26.4(7)	4.3(5)	12.4(5)	4.0(5)
Br8	25.6(6)	39.8(7)	27.4(7)	14.7(5)	-2.9(5)	-4.5(5)
Br4	27.4(6)	25.3(6)	38.3(8)	-7.5(4)	-12.2(6)	1.1(5)
Br2	28.7(6)	27.7(6)	51.2(9)	-6.3(5)	20.6(6)	-2.2(6)
Br7	40.5(7)	31.2(6)	19.4(6)	-1.9(5)	-8.7(5)	0.7(5)
Br6	29.6(6)	34.7(6)	25.4(6)	-14.9(5)	-2.9(5)	2.5(5)
Br3	24.8(6)	23.7(6)	55.4(10)	6.7(4)	-11.3(6)	-2.6(5)
O2	11.5(9)	16.7(10)	15.1(10)	0.3(5)	0.8(5)	-2.8(5)
O3	11.5(9)	20.4(10)	14.0(10)	0.7(5)	-0.1(5)	-2.8(5)
O1	11.1(9)	20.4(10)	12.0(9)	0.4(5)	1.0(5)	-2.5(5)
O7	10.7(9)	17.3(9)	15.4(11)	0.2(5)	0.5(5)	2.6(5)
O5	11.8(9)	16.7(9)	17.1(11)	-0.7(5)	0.5(5)	2.8(5)
O4	10.6(9)	18.2(10)	13.4(10)	-0.5(5)	-0.4(5)	-2.7(5)
O8	10.8(9)	15.4(9)	14.7(11)	-1.2(5)	0.4(5)	1.1(5)
O6	10.2(9)	16.1(9)	16.3(12)	-0.0(5)	0.1(5)	2.2(6)
C1	11.4(9)	15.6(13)	13.1(9)	-0.4(6)	1.8(4)	-2.3(5)
N1	10.0(8)	21.1(12)	17.6(14)	-1.8(5)	-0.4(5)	0.1(9)
C18	15.5(9)	15.5(11)	11.2(9)	1.9(5)	-1.6(4)	-1.5(5)
C52	19.0(13)	15.7(14)	16.6(11)	-1.9(8)	-0.8(6)	2.8(7)
H52	36(9)	70(30)	20(5)	27(8)	-8(3)	-11(4)
C8	19.6(13)	20.7(10)	24(2)	0.9(6)	7.9(9)	-2.6(7)
H8	31(8)	21(6)	100(50)	-1.8(17)	37(10)	-9(3)
C34	16.3(8)	16.3(8)	16.6(9)	-0.6(4)	-0.8(5)	2.8(5)
C50	15.0(10)	15.5(10)	17.2(12)	-1.4(5)	0.2(5)	3.4(5)
C17	12.0(9)	13.3(13)	10.9(9)	0.7(5)	-0.4(4)	0.2(5)
C11	19.4(17)	18.4(11)	15.2(10)	-2.9(8)	1.6(7)	-2.7(6)
C71	20(2)	33.4(9)	30.7(10)	-3.9(6)	-0.9(8)	0.2(6)
H71	47(19)	34.6(12)	31.4(14)	-10(2)	3(2)	-0.8(7)
C49	11.3(9)	14.0(10)	15.3(13)	-0.7(5)	0.4(5)	0.8(6)
C70	24(2)	34.1(9)	31.0(10)	-5.4(7)	0.3(7)	-0.3(6)
H70	31(13)	34.7(12)	31.4(14)	-7.3(15)	1.7(19)	-0.7(7)
C3S	32.7(15)	25.9(15)	22(2)	-0.8(9)	-3.9(11)	1.0(11)
H3S	47(19)	44(18)	160(40)	-12(15)	20(20)	-60(20)
C36	20.5(11)	16.8(14)	18.0(11)	-0.5(7)	3.3(5)	2.8(6)
H36	32(8)	60(30)	26(5)	-23(8)	14(3)	-16(6)

C40	19.7(12)	18.0(14)	16.2(13)	-3.4(7)	1.0(6)	2.4(7)
H40	27(8)	30(20)	21(5)	-15(6)	7(3)	-6(5)
C27	20.8(17)	24.9(12)	13.4(10)	6.3(8)	1.2(7)	0.5(6)
C6	17.2(12)	16.7(11)	13.8(17)	0.8(5)	2.8(8)	-1.5(7)
H6	32(9)	17(4)	120(50)	-1.7(18)	42(10)	-8(3)
C39	18.9(12)	19.4(14)	17.6(12)	-3.4(7)	0.7(6)	4.6(7)
C12	40(2)	19.6(12)	18.4(13)	-4.0(9)	8.8(9)	-3.2(7)
H12	90(30)	22(2)	23(4)	2(2)	24(5)	-0.8(12)
C41	16.7(9)	16.5(8)	17.1(9)	-0.3(4)	-1.3(5)	2.5(5)
H41A	16.6(10)	16.5(9)	17.2(11)	-0.3(5)	-1.3(5)	2.5(5)
H41B	16.9(12)	16.4(10)	17.1(9)	-0.3(5)	-1.2(5)	2.4(5)
C37	19.7(11)	16.1(13)	18.5(9)	0.4(7)	2.3(5)	5.1(5)
C35	16.0(10)	15.0(12)	16.5(11)	-0.3(5)	0.5(5)	2.9(6)
C57	18.3(12)	18.3(12)	21.6(14)	-1.6(6)	2.6(7)	4.2(7)
H57A	20(4)	21(5)	24(5)	1(2)	2.8(17)	4.7(18)
H57B	22(6)	19(6)	22(2)	0(2)	2.4(11)	3.9(12)
C7	18.5(12)	18.0(10)	16.5(18)	1.9(5)	4.4(8)	-1.8(6)
C23	17.9(12)	18.8(10)	15.6(18)	-1.3(5)	-4.8(7)	3.1(7)
C54	21.7(14)	25.2(16)	18.3(12)	3.7(8)	-4.4(7)	0.8(7)
H54	37(13)	50(20)	23(6)	23(9)	-12(4)	-8(5)
C51	15.9(10)	15.8(12)	16.4(11)	-1.1(6)	0.2(5)	2.8(6)
C58	15.7(13)	18.4(9)	23.1(14)	-2.7(5)	1.2(7)	2.3(6)
H58	19(5)	21(4)	25(4)	-1.3(16)	-0.7(19)	1.7(14)
C42	16.5(9)	16.9(7)	17.5(10)	-0.2(4)	-1.3(5)	2.1(5)
H42	16.5(10)	17.6(12)	17.4(11)	-0.5(5)	-1.2(5)	1.9(5)
C21	16.0(11)	18.7(10)	24(2)	0.7(5)	-4.9(8)	1.7(7)
C9	18.5(12)	20.0(11)	26(2)	-0.6(5)	9.6(8)	-2.5(7)
C28	45(3)	25.6(12)	19.1(14)	2.1(9)	-1.7(10)	2.4(7)
H28	60(20)	32(6)	19(8)	-8(5)	-4(6)	6(3)
C26	16.9(13)	19.8(12)	13.9(10)	1.9(6)	0.1(6)	-0.5(6)
H26	23(5)	22(4)	16(4)	-1.3(19)	-1.7(16)	0.2(14)
C4S	32.6(15)	20.5(14)	28(2)	-1.6(9)	-4.2(11)	4.2(11)
H4S	47(19)	44(18)	160(40)	-12(15)	20(20)	-60(20)
C56	16.1(12)	18.6(14)	15.0(13)	0.9(7)	-1.6(6)	2.1(7)
H56	31(12)	50(30)	18(3)	24(9)	-8(3)	-8(4)
C5S	38.8(17)	23.4(16)	57(3)	2.1(9)	-17.2(12)	-4.7(13)
H5S	47(19)	44(18)	160(40)	-12(15)	20(20)	-60(20)
C20	16.2(11)	15.8(11)	21.4(19)	1.2(5)	-4.4(7)	0.4(7)
H20	17(5)	17(3)	30(30)	1.2(15)	-6(5)	-2(3)
C22	18.0(13)	20.1(10)	23(2)	-0.7(6)	-5.6(8)	2.6(7)
H22	22(4)	22(6)	70(40)	1.8(18)	-20(6)	-6(5)
C14	71(3)	23.3(13)	22.8(15)	-2.8(12)	16.7(12)	-1.5(8)
H14	90(40)	22(6)	23(5)	2(3)	24(6)	-0.8(17)

C32	31(2)	26.8(13)	15.5(12)	5.0(9)	-3.4(9)	0.3(7)
H32	80(40)	32(4)	22(6)	-10(6)	-20(6)	6(2)
C2	15.7(9)	15.7(11)	13.1(9)	-0.3(5)	2.5(5)	-2.5(5)
C65	13.2(8)	85(3)	36(2)	12.4(6)	3.1(7)	13(2)
C5	16.1(10)	17.1(10)	11.3(14)	0.4(5)	2.8(6)	-0.8(6)
C24	17.3(11)	15.8(11)	14.6(18)	0.1(5)	-4.1(7)	0.6(7)
H24	26(5)	23(4)	140(50)	8(2)	-35(7)	-28(6)
C3	18.0(12)	19.8(11)	14.1(14)	-1.8(6)	1.7(7)	-3.3(6)
H3A	19(4)	20(5)	15(4)	-1.7(17)	2.6(19)	-3.1(17)
H3B	20(5)	20(3)	15(5)	-1.7(14)	3(2)	-3.2(17)
C59	16.1(17)	17.4(9)	33.6(14)	-3.5(6)	0.1(9)	3.3(6)
C19	16.0(9)	16.1(10)	11.5(15)	1.0(5)	-2.1(5)	0.6(7)
C10S	39.4(11)	29.8(11)	22.4(19)	-3.5(8)	-1.4(9)	2.9(9)
H10S	39.4(11)	28.9(14)	18(5)	-3.7(8)	-1.0(9)	4.9(14)
C72	14.1(17)	32.9(9)	30.6(10)	-2.2(6)	-1.5(7)	0.3(6)
H72	13(9)	32.7(12)	30.6(10)	-1.9(13)	-1.5(8)	0.4(6)
C43	16.1(16)	16.8(9)	26.2(14)	-0.1(6)	-6.4(8)	2.8(6)
C61	50(3)	22.5(13)	44.7(17)	0.8(10)	-3.2(11)	6.4(8)
H61	170(40)	34(5)	40(2)	36(6)	-1.4(12)	4.8(10)
C25	16.6(13)	18.6(11)	12.4(14)	2.9(6)	-1.0(7)	-2.0(6)
H25A	17(5)	17(5)	13(5)	2(2)	-1(2)	-1.8(17)
H25B	20(7)	20(3)	15(5)	3.7(17)	-3(2)	-3.6(17)
C60	41(3)	21.8(13)	35.4(15)	-1.3(9)	-2.4(9)	5.4(7)
H60	170(40)	34(5)	40(2)	36(6)	-1.4(12)	4.8(10)
C14S	39.4(11)	31.0(11)	26(2)	-3.1(8)	-2.0(9)	0.7(9)
H14S	39.4(13)	32(3)	28(11)	-2.7(8)	-2.7(10)	0(3)
C68	26.9(13)	33.6(8)	31.8(9)	-4.6(6)	2.6(6)	-0.6(6)
C4	16.3(13)	19.5(11)	15.2(10)	0.3(6)	1.4(6)	-2.1(6)
H4	20(5)	21(4)	16(4)	2.2(19)	2.0(17)	-2.3(14)
C44	22.5(19)	21.7(11)	33.1(15)	-2.2(8)	-2.5(10)	-3.0(7)
H44	30(30)	23(6)	32(6)	-6(3)	-3(6)	-4.6(19)
C38	22.0(11)	19.5(14)	18.8(10)	-2.5(7)	2.5(5)	4.7(6)
H38	38(9)	80(30)	29(6)	-34(9)	15(4)	-20(7)
C69	21.2(18)	34.1(9)	31.4(9)	-5.0(6)	0.9(6)	-0.5(6)
H69	10(20)	34.1(10)	31.0(14)	-4.4(13)	-1(2)	-0.4(7)
C16	96(4)	19.3(12)	23.8(15)	1.4(9)	21.5(12)	-1.0(7)
H16	260(90)	21(4)	36(9)	18(5)	66(14)	4(2)
C13	46(3)	23.3(13)	18.2(13)	-5.6(11)	9.6(10)	-3.2(7)
H13	90(30)	22(2)	23(4)	2(2)	24(5)	-0.8(12)
C13S	39.3(11)	32.9(12)	34(2)	-3.1(8)	-2.1(9)	-3.1(10)
H13S	39.6(12)	37(3)	44(8)	-2.0(9)	-3.8(10)	-10(3)
C33	11.4(9)	14.5(10)	13.0(13)	-0.4(5)	0.2(5)	0.3(6)
C11S	39.4(11)	29.3(11)	21.6(18)	-3.6(8)	-1.2(9)	3.6(9)

H11S	39.4(11)	28.9(14)	18(5)	-3.7(8)	-1.0(9)	4.9(14)
C55	17.9(13)	21.3(15)	17.4(12)	2.8(7)	-2.8(6)	1.8(7)
C10	18.5(11)	17.6(11)	23(2)	-0.4(6)	7.8(8)	-1.7(7)
H10	42(10)	23(3)	130(40)	-10(2)	55(10)	-25(5)
C31	46(3)	30.6(14)	15.4(13)	7.8(11)	-5.8(9)	1.0(8)
H31	110(50)	33(5)	20(5)	-4(6)	-23(6)	4(2)
C8S	39.7(11)	36.4(12)	39.6(19)	-2.4(8)	-2.7(9)	-6.9(9)
H8SA	39.8(12)	36.4(12)	39.6(19)	-2.3(8)	-2.7(9)	-6.9(9)
H8SB	39.7(12)	36.5(13)	39.5(19)	-2.4(8)	-2.6(9)	-6.9(9)
H8SC	39.7(12)	36.5(13)	40(2)	-2.4(8)	-2.6(9)	-6.9(9)
C2S	38.8(15)	31.0(16)	24(2)	5.3(9)	-7.9(11)	-2.3(12)
C6S	46.4(18)	30.3(17)	70(4)	8.9(10)	-23.7(13)	-14.2(14)
H6S	47(19)	44(18)	160(40)	-12(15)	20(20)	-60(20)
C53	21.1(13)	20.7(15)	17.7(11)	0.9(8)	-2.8(6)	1.5(6)
C64	28(2)	21.6(12)	36.9(16)	-0.3(8)	-1.1(10)	-0.3(7)
H64	90(40)	26(7)	37(3)	16(6)	-7(3)	-2.2(16)
C1S	38.7(16)	48(3)	29(3)	7.5(10)	-8.1(11)	-7.8(19)
H1SA	39(2)	48(3)	29(3)	7.5(11)	-8.1(12)	-7.8(19)
H1SB	39(2)	48(3)	29(3)	7.5(11)	-8.1(12)	-7.7(19)
H1SC	39(2)	48(3)	29(3)	7.5(10)	-8.1(12)	-7.8(19)
C73	11.5(15)	32.8(9)	30.9(9)	-1.9(6)	-1.0(6)	0.2(6)
H73	16(13)	32.6(10)	31.2(10)	-1.6(11)	0.3(12)	0.2(6)
C46	30(2)	22.6(13)	47.5(18)	-1.0(9)	0.6(13)	0.2(8)
H46	110(50)	23(2)	62(9)	-9(3)	31(10)	-2.6(17)
C9S	39.4(11)	35.4(11)	38.9(18)	-2.8(8)	-2.6(9)	-6.7(9)
C67	27.5(14)	33.6(8)	33.0(11)	-4.6(6)	3.3(7)	-0.7(6)
H67A	27.5(14)	33.7(10)	33.1(12)	-4.6(6)	3.4(7)	-0.5(6)
H67B	27.5(15)	33.8(10)	33.0(11)	-4.7(6)	3.3(7)	-0.7(6)
H67C	27.5(15)	33.7(10)	33.0(11)	-4.6(6)	3.3(7)	-0.6(6)
C63	40(3)	22.7(13)	47.6(18)	2.2(9)	-3.1(12)	1.2(8)
H63	50(20)	25(3)	47(3)	4(4)	-3.8(19)	1.3(11)
C7S	45.1(17)	31.2(17)	47(3)	9.1(10)	-19.9(13)	-8.6(13)
H7S	47(19)	44(18)	160(40)	-12(15)	20(20)	-60(20)
C12S	39.4(11)	30.6(11)	27(2)	-3.3(8)	-1.6(9)	0.9(9)
H12S	39.5(12)	31(4)	31(9)	-3.8(8)	-0.8(9)	-1(3)
C47	34(2)	18.8(12)	43.0(18)	0.2(9)	0.6(12)	5.3(7)
H47	60(40)	19(5)	49(7)	0(4)	15(8)	5.5(19)
C30	55(3)	30.6(14)	19.4(14)	6.8(12)	-3.9(11)	1.9(8)
H30	100(50)	34(7)	21(4)	-3(7)	-13(5)	5(2)
C1D	33(2)	18.8(12)	29.5(15)	0.2(8)	-0.1(9)	4.6(7)
H1D	60(30)	19(4)	34(6)	-2(3)	12(7)	4.3(17)
C45	33(2)	21.8(12)	46.4(18)	-3.2(8)	1.3(12)	-2.3(7)
H45	50(30)	24(5)	48(4)	-8(4)	6(4)	-4.7(17)

C29	69(3)	29.4(14)	20.0(15)	2.8(11)	-6.6(11)	3.7(7)
H29	130(40)	38(6)	24(7)	-20(7)	-19(6)	9(3)
C62	49(3)	25.5(14)	48.1(17)	2.2(10)	-3.9(13)	2.9(8)
H62	50(20)	25(3)	47(3)	4(4)	-3.8(19)	1.3(11)
C15	160(7)	22.4(14)	29.0(16)	1.3(11)	38.5(15)	-0.0(7)
H15	110(40)	22(3)	27(7)	-4(3)	25(6)	-1.1(16)
C66	13.5(8)	87(3)	38(2)	13.0(6)	3.2(7)	13(2)
H66A	13.5(10)	87(3)	38(2)	12.9(7)	3.3(7)	13(2)
H66B	13.5(9)	87(3)	38(2)	12.8(7)	3.2(7)	13(2)
H66C	13.5(10)	87(3)	38(2)	13.0(6)	3.2(7)	13(2)

Table S10: Bond Lengths in Å for **2.34**.

Atom	Atom	Length/Å
Rh2	Rh1	2.3911(9)
Rh2	O2	2.033(3)
Rh2	O4	2.023(3)
Rh2	O8	2.044(3)
Rh2	O6	2.052(3)
Rh1	O3	2.060(3)
Rh1	O1	2.054(3)
Rh1	O7	2.041(2)
Rh1	O5	2.053(2)
Rh1	N1	2.168(3)
Br1	C7	1.898(4)
Br5	C37	1.900(4)
Br8	C55	1.906(4)
Br4	C23	1.910(4)
Br2	C9	1.895(4)
Br7	C53	1.893(4)
Br6	C39	1.900(4)
Br3	C21	1.900(4)
O2	C1	1.263(4)
O3	C17	1.275(4)
O1	C1	1.265(4)
O7	C33	1.275(4)
O5	C49	1.264(4)
O4	C17	1.258(4)
O8	C33	1.265(4)
O6	C49	1.264(4)
C1	C2	1.505(5)

N1	C65	1.152(5)
C18	C17	1.507(5)
C18	C26	1.544(5)
C18	C19	1.508(5)
C18	C25	1.508(5)
C52	C51	1.385(6)
C52	C53	1.396(5)
C8	C7	1.404(5)
C8	C9	1.383(5)
C34	C41	1.516(5)
C34	C35	1.502(5)
C34	C42	1.552(5)
C34	C33	1.505(5)
C50	C49	1.521(5)
C50	C57	1.506(6)
C50	C51	1.498(5)
C50	C58	1.554(5)
C11	C12	1.384(5)
C11	C4	1.492(6)
C11	C16	1.382(6)
C71	C70	1.409(7)
C71	C72	1.402(7)
C70	C69	1.397(6)
C3S	C4S	1.388(6)
C3S	C2S	1.398(6)
C36	C37	1.391(5)
C36	C35	1.402(5)
C40	C39	1.399(5)
C40	C35	1.397(5)
C27	C28	1.409(6)
C27	C26	1.484(6)
C27	C32	1.400(6)
C6	C7	1.390(5)
C6	C5	1.401(5)
C39	C38	1.387(6)
C12	C13	1.389(6)
C41	C42	1.484(5)
C37	C38	1.392(6)
C57	C58	1.497(6)
C23	C22	1.393(5)
C23	C24	1.397(5)
C54	C55	1.398(6)
C54	C53	1.398(6)

C51	C56	1.413(5)
C58	C59	1.497(5)
C42	C43	1.500(5)
C21	C20	1.380(5)
C21	C22	1.399(5)
C9	C10	1.392(6)
C28	C29	1.403(7)
C26	C25	1.495(5)
C4S	C5S	1.388(6)
C56	C55	1.379(5)
C5S	C6S	1.400(7)
C20	C19	1.405(5)
C14	C13	1.376(6)
C14	C15	1.391(7)
C32	C31	1.381(6)
C2	C5	1.490(5)
C2	C3	1.516(5)
C2	C4	1.562(5)
C65	C66	1.436(6)
C5	C10	1.403(5)
C24	C19	1.392(5)
C3	C4	1.503(5)
C59	C60	1.392(7)
C59	C64	1.400(6)
C10S	C11S	1.395(7)
C10S	C9S	1.403(7)
C72	C73	1.405(6)
C43	C44	1.398(6)
C43	C1D	1.398(6)
C61	C60	1.392(6)
C61	C62	1.392(8)
C14S	C13S	1.422(7)
C14S	C9S	1.387(7)
C68	C69	1.398(7)
C68	C73	1.394(7)
C68	C67	1.514(6)
C44	C45	1.397(6)
C16	C15	1.396(7)
C13S	C12S	1.382(7)
C11S	C12S	1.388(7)
C31	C30	1.412(7)
C8S	C9S	1.487(7)
C2S	C1S	1.520(7)

C2S	C7S	1.386(7)
C6S	C7S	1.388(8)
C64	C63	1.387(6)
C46	C47	1.394(7)
C46	C45	1.375(7)
C63	C62	1.402(8)
C47	C1D	1.404(6)
C30	C29	1.389(7)

Table S11: Bond Angles in ° for **2.34**.

Atom	Atom	Atom	Angle/°
O2	Rh2	Rh1	88.42(8)
O4	Rh2	Rh1	87.72(8)
O4	Rh2	O2	176.14(11)
O8	Rh2	Rh1	88.11(7)
O8	Rh2	O2	86.71(11)
O8	Rh2	O4	93.10(11)
O6	Rh2	Rh1	87.79(7)
O6	Rh2	O2	93.55(11)
O6	Rh2	O4	86.37(11)
O6	Rh2	O8	175.89(10)
O3	Rh1	Rh2	88.32(8)
O1	Rh1	Rh2	87.52(8)
O1	Rh1	O3	175.83(11)
O7	Rh1	Rh2	88.06(7)
O7	Rh1	O3	92.04(11)
O7	Rh1	O1	87.56(11)
O5	Rh1	Rh2	88.11(8)
O5	Rh1	O3	87.49(11)
O5	Rh1	O1	92.64(10)
O5	Rh1	O7	176.15(11)
N1	Rh1	Rh2	178.03(8)
N1	Rh1	O3	90.48(11)
N1	Rh1	O1	93.67(11)
N1	Rh1	O7	90.44(11)
N1	Rh1	O5	93.39(11)
C1	O2	Rh2	118.3(2)
C17	O3	Rh1	117.2(2)
C1	O1	Rh1	118.5(2)
C33	O7	Rh1	118.1(2)

C49	O5	Rh1	117.7(2)
C17	O4	Rh2	119.7(2)
C33	O8	Rh2	118.5(2)
C49	O6	Rh2	118.7(2)
O1	C1	O2	126.2(3)
C2	C1	O2	116.1(3)
C2	C1	O1	117.7(3)
C65	N1	Rh1	172.8(4)
C26	C18	C17	115.5(3)
C19	C18	C17	113.5(3)
C19	C18	C26	118.7(3)
C25	C18	C17	117.6(3)
C25	C18	C26	58.7(2)
C25	C18	C19	122.0(3)
C53	C52	C51	120.1(4)
C9	C8	C7	117.1(4)
C35	C34	C41	120.5(3)
C42	C34	C41	57.8(2)
C42	C34	C35	119.2(3)
C33	C34	C41	114.6(3)
C33	C34	C35	116.6(3)
C33	C34	C42	115.2(3)
C57	C50	C49	115.6(3)
C51	C50	C49	116.9(3)
C51	C50	C57	119.6(3)
C58	C50	C49	115.9(3)
C58	C50	C57	58.6(3)
C58	C50	C51	117.4(3)
O4	C17	O3	126.0(3)
C18	C17	O3	118.1(3)
C18	C17	O4	115.9(3)
C4	C11	C12	122.8(4)
C16	C11	C12	118.5(4)
C16	C11	C4	118.8(4)
C72	C71	C70	119.4(4)
O6	C49	O5	126.2(3)
C50	C49	O5	116.9(3)
C50	C49	O6	116.9(3)
C69	C70	C71	119.4(5)
C2S	C3S	C4S	121.2(4)
C35	C36	C37	119.5(4)
C35	C40	C39	119.4(4)
C26	C27	C28	117.9(4)

C32	C27	C28	118.2(4)
C32	C27	C26	123.9(4)
C5	C6	C7	119.3(3)
C40	C39	Br6	119.6(3)
C38	C39	Br6	118.6(3)
C38	C39	C40	121.7(4)
C13	C12	C11	120.9(4)
C42	C41	C34	62.3(3)
C36	C37	Br5	119.4(3)
C38	C37	Br5	118.9(3)
C38	C37	C36	121.7(4)
C36	C35	C34	121.1(4)
C40	C35	C34	119.3(4)
C40	C35	C36	119.5(4)
C58	C57	C50	62.3(3)
C8	C7	Br1	118.4(3)
C6	C7	Br1	119.4(3)
C6	C7	C8	122.2(4)
C22	C23	Br4	117.7(3)
C24	C23	Br4	119.2(3)
C24	C23	C22	123.1(3)
C53	C54	C55	116.9(4)
C50	C51	C52	121.9(4)
C56	C51	C52	119.4(4)
C56	C51	C50	118.6(4)
C57	C58	C50	59.1(3)
C59	C58	C50	118.3(3)
C59	C58	C57	122.5(4)
C41	C42	C34	59.9(3)
C43	C42	C34	120.8(3)
C43	C42	C41	123.8(4)
C20	C21	Br3	118.5(3)
C22	C21	Br3	118.8(3)
C22	C21	C20	122.6(4)
C8	C9	Br2	118.5(3)
C10	C9	Br2	119.0(3)
C10	C9	C8	122.5(4)
C29	C28	C27	120.2(5)
C27	C26	C18	120.3(3)
C25	C26	C18	59.5(2)
C25	C26	C27	123.6(4)
C5S	C4S	C3S	118.7(4)
C55	C56	C51	119.1(4)

C6S	C5S	C4S	120.3(5)
C19	C20	C21	119.1(3)
C21	C22	C23	116.4(4)
C15	C14	C13	117.3(5)
C31	C32	C27	121.8(4)
C5	C2	C1	115.6(3)
C3	C2	C1	117.4(3)
C3	C2	C5	120.0(3)
C4	C2	C1	116.2(3)
C4	C2	C5	116.9(3)
C4	C2	C3	58.4(2)
C66	C65	N1	178.2(6)
C2	C5	C6	122.4(3)
C10	C5	C6	119.5(4)
C10	C5	C2	118.1(3)
C19	C24	C23	118.3(3)
C4	C3	C2	62.3(2)
C60	C59	C58	124.0(4)
C64	C59	C58	118.7(4)
C64	C59	C60	117.2(4)
C20	C19	C18	117.5(3)
C24	C19	C18	122.0(3)
C24	C19	C20	120.3(3)
C9S	C10S	C11S	119.6(5)
C73	C72	C71	119.8(4)
C44	C43	C42	118.6(4)
C1D	C43	C42	123.3(4)
C1D	C43	C44	118.0(4)
C62	C61	C60	119.0(5)
C26	C25	C18	61.8(2)
C61	C60	C59	122.6(5)
C9S	C14S	C13S	119.8(5)
C73	C68	C69	118.1(4)
C67	C68	C69	120.0(5)
C67	C68	C73	121.8(4)
C2	C4	C11	120.2(3)
C3	C4	C11	122.5(3)
C3	C4	C2	59.3(2)
C45	C44	C43	121.4(5)
C37	C38	C39	118.0(4)
C68	C69	C70	121.8(5)
C15	C16	C11	120.0(5)
C14	C13	C12	121.4(4)

C12S	C13S	C14S	120.1(5)
O8	C33	O7	126.1(3)
C34	C33	O7	116.4(3)
C34	C33	O8	117.4(3)
C12S	C11S	C10S	121.1(5)
C54	C55	Br8	118.5(3)
C56	C55	Br8	118.7(3)
C56	C55	C54	122.8(4)
C5	C10	C9	119.4(3)
C30	C31	C32	119.7(5)
C1S	C2S	C3S	120.9(4)
C7S	C2S	C3S	119.7(5)
C7S	C2S	C1S	119.3(4)
C7S	C6S	C5S	120.5(5)
C52	C53	Br7	119.2(3)
C54	C53	Br7	119.1(3)
C54	C53	C52	121.6(4)
C63	C64	C59	121.5(5)
C68	C73	C72	121.3(4)
C45	C46	C47	120.2(4)
C14S	C9S	C10S	119.8(5)
C8S	C9S	C10S	120.7(5)
C8S	C9S	C14S	119.5(4)
C62	C63	C64	119.8(5)
C6S	C7S	C2S	119.5(5)
C11S	C12S	C13S	119.6(5)
C1D	C47	C46	119.8(5)
C29	C30	C31	119.2(5)
C47	C1D	C43	120.7(5)
C46	C45	C44	119.9(5)
C30	C29	C28	120.7(5)
C63	C62	C61	119.8(5)
C16	C15	C14	121.6(5)

Table S12: Torsion Angles in ° for **2.34**.

Atom	Atom	Atom	Atom	Angle/°
Rh2	O2	C1	O1	12.2(3)
Rh2	O2	C1	C2	-167.6(2)
Rh2	O4	C17	O3	12.6(3)
Rh2	O4	C17	C18	-166.0(2)

Rh2	O8	C33	O7	-4.4(3)
Rh2	O8	C33	C34	173.1(2)
Rh2	O6	C49	O5	-7.0(3)
Rh2	O6	C49	C50	171.1(2)
Rh1	O3	C17	O4	-6.4(3)
Rh1	O3	C17	C18	172.2(2)
Rh1	O1	C1	O2	-6.0(3)
Rh1	O1	C1	C2	173.8(2)
Rh1	O7	C33	O8	11.6(3)
Rh1	O7	C33	C34	-165.9(2)
Rh1	O5	C49	O6	14.2(3)
Rh1	O5	C49	C50	-163.8(2)
Br1	C7	C8	C9	-179.2(3)
Br1	C7	C6	C5	178.7(3)
Br5	C37	C36	C35	176.8(3)
Br5	C37	C38	C39	-177.4(3)
Br8	C55	C54	C53	177.0(3)
Br8	C55	C56	C51	-177.3(3)
Br4	C23	C22	C21	-177.5(3)
Br4	C23	C24	C19	178.8(3)
Br2	C9	C8	C7	177.3(3)
Br2	C9	C10	C5	-177.5(3)
Br7	C53	C52	C51	178.7(3)
Br7	C53	C54	C55	-178.4(3)
Br6	C39	C40	C35	-179.4(3)
Br6	C39	C38	C37	178.1(3)
Br3	C21	C20	C19	176.8(3)
Br3	C21	C22	C23	-179.6(3)
O2	C1	C2	C5	2.6(4)
O2	C1	C2	C3	-148.3(3)
O2	C1	C2	C4	145.4(3)
O3	C17	C18	C26	-31.6(4)
O3	C17	C18	C19	-173.7(3)
O3	C17	C18	C25	34.8(4)
O1	C1	C2	C5	-177.2(3)
O1	C1	C2	C3	31.9(4)
O1	C1	C2	C4	-34.4(4)
O7	C33	C34	C41	36.7(4)
O7	C33	C34	C35	-174.7(3)
O7	C33	C34	C42	-27.7(4)
O5	C49	C50	C57	28.3(4)
O5	C49	C50	C51	177.4(3)
O5	C49	C50	C58	-37.5(4)

O4	C17	C18	C26	147.1(3)
O4	C17	C18	C19	5.1(3)
O4	C17	C18	C25	-146.5(3)
O8	C33	C34	C41	-141.1(3)
O8	C33	C34	C35	7.6(4)
O8	C33	C34	C42	154.5(3)
O6	C49	C50	C57	-150.0(3)
O6	C49	C50	C51	-0.9(4)
O6	C49	C50	C58	144.2(3)
C1	C2	C5	C6	-109.7(3)
C1	C2	C5	C10	69.0(4)
C1	C2	C3	C4	-105.4(4)
C1	C2	C4	C11	-140.4(3)
C1	C2	C4	C3	107.4(5)
C18	C26	C27	C28	114.8(4)
C18	C26	C27	C32	-64.8(4)
C18	C19	C20	C21	-174.6(4)
C18	C19	C24	C23	175.8(4)
C18	C25	C26	C27	-108.1(3)
C52	C51	C50	C49	-108.5(4)
C52	C51	C50	C57	39.3(4)
C52	C51	C50	C58	106.9(4)
C52	C51	C56	C55	-0.4(4)
C52	C53	C54	C55	1.0(4)
C8	C7	C6	C5	-1.8(5)
C8	C9	C10	C5	0.4(5)
C34	C41	C42	C43	-108.9(3)
C34	C35	C36	C37	-177.3(3)
C34	C35	C40	C39	179.3(3)
C34	C42	C43	C44	122.3(4)
C34	C42	C43	C1D	-59.7(4)
C50	C57	C58	C59	-105.9(3)
C50	C51	C56	C55	175.1(3)
C50	C58	C59	C60	-69.9(4)
C50	C58	C59	C64	107.1(4)
C11	C12	C13	C14	3.6(6)
C11	C4	C2	C5	2.0(4)
C11	C4	C2	C3	112.2(5)
C11	C4	C3	C2	-108.4(5)
C11	C16	C15	C14	-3.5(7)
C71	C70	C69	C68	-1.1(5)
C71	C72	C73	C68	-2.7(5)
C70	C69	C68	C73	-0.8(5)

C70	C69	C68	C67	177.3(4)
C3S	C4S	C5S	C6S	-0.0(3)
C3S	C2S	C7S	C6S	-0.0(3)
C36	C37	C38	C39	1.1(4)
C36	C35	C40	C39	1.5(4)
C40	C39	C38	C37	0.9(4)
C27	C28	C29	C30	-0.9(6)
C27	C32	C31	C30	1.4(5)
C6	C5	C2	C3	40.4(4)
C6	C5	C2	C4	107.7(4)
C6	C5	C10	C9	-0.8(5)
C12	C13	C14	C15	-6.2(7)
C41	C42	C43	C44	-165.4(4)
C41	C42	C43	C1D	12.6(5)
C57	C58	C59	C60	-0.2(5)
C57	C58	C59	C64	176.7(4)
C23	C22	C21	C20	-3.2(5)
C23	C24	C19	C20	0.4(5)
C54	C55	C56	C51	0.6(5)
C58	C59	C60	C61	177.5(4)
C58	C59	C64	C63	-179.3(4)
C42	C43	C44	C45	178.6(4)
C42	C43	C1D	C47	-178.8(4)
C21	C20	C19	C24	1.0(5)
C9	C10	C5	C2	-179.5(4)
C28	C29	C30	C31	3.5(7)
C4S	C5S	C6S	C7S	0.0(3)
C5S	C6S	C7S	C2S	0.0(3)
C32	C31	C30	C29	-3.7(6)
C59	C60	C61	C62	1.1(6)
C59	C64	C63	C62	2.1(5)
C10S	C11S	C12S	C13S	-0.0(6)
C10S	C9S	C14S	C13S	-1.7(6)
C72	C73	C68	C69	2.7(5)
C72	C73	C68	C67	-175.3(4)
C43	C44	C45	C46	-0.1(5)
C43	C1D	C47	C46	0.8(5)
C61	C62	C63	C64	-0.4(6)
C14S	C13S	C12S	C11S	-1.9(6)
C44	C45	C46	C47	-0.1(6)

Table S13: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement

Parameters ($\text{\AA}^2 \times 10^3$) for **3d**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
H52	5560(30)	6660(30)	3120(20)	42(13)
H8	3030(30)	6440(20)	7290(30)	50(18)
H71	3210(40)	3396(9)	5180(20)	38(7)
H70	3050(30)	4090(20)	6084(13)	32(5)
H3S	5254(16)	7014(7)	5408(2)	84(13)
H36	5107(2)	3509.5(19)	6871.6(16)	39(14)
H40	4849(2)	2567.6(18)	5473.9(17)	27(11)
H6	5410(30)	7150(20)	6740(30)	60(20)
H12	6200(11)	6532(8)	7702(19)	45(12)
H41A	7120(30)	3770(20)	6316(19)	16.8(6)
H41B	6630(30)	3080(20)	6703(18)	16.8(5)
H57A	7358(18)	6485(16)	3842(18)	22(3)
H57B	6860(30)	6940(20)	3434(5)	21(3)
H54	3440(30)	7840(30)	3230(20)	37(13)
H58	7200(20)	7190(20)	4466(11)	21(3)
H42	7130(30)	2870(20)	5581(19)	17.2(7)
H28	6950(40)	5740(30)	2810(20)	37(11)
H26	6950(20)	4780(20)	3406(16)	20(3)
H4S	6620(16)	6932(4)	5516(4)	84(13)
H56	5060(30)	7510(30)	4530(20)	34(13)
H5S	7452(4)	7941(12)	5990(5)	84(13)
H20	4890(30)	5290(20)	3490(20)	22(11)
H22	2690(30)	4170(30)	2980(20)	39(16)
H14	5820(40)	4930(20)	8865(11)	45(13)
H32	5960(40)	3790(30)	2390(20)	44(14)
H24	5050(30)	3140(30)	3220(30)	60(20)
H3A	7194(19)	6380(20)	6458(12)	18(3)
H3B	6650(20)	6718(13)	6910(14)	18(3)
H10S	6250(30)	2820(20)	4471(19)	29(2)
H72	3510(30)	4160(20)	4345(9)	25(3)
H61	6300(50)	9210(30)	3060(30)	80(14)
H25A	7040(30)	3600(20)	3694(19)	16(3)
H25B	6450(30)	3380(20)	3115(18)	18(3)
H60	6670(50)	8100(30)	3280(20)	80(14)
H14S	5200(30)	1160(30)	3740(20)	33(5)
H4	7010(20)	5293(16)	6731(14)	19(3)
H44	6990(30)	1840(20)	5170(20)	27(11)
H38	3049(3)	2407.7(19)	6557.6(17)	50(16)
H69	3330(30)	5480(20)	6021(12)	25(7)

H16	6590(60)	4360(20)	7340(20)	100(30)
H13	5772(10)	6250(20)	8680(15)	45(12)
H13S	3680(30)	1760(30)	3880(20)	40(4)
H11S	4760(30)	3430(30)	4608(19)	29(2)
H10	4900(30)	5070(30)	6680(30)	66(18)
H31	5720(40)	4180(30)	1490(20)	54(17)
H8SA	6612(8)	1258(9)	4197(10)	38.6(8)
H8SB	6613(8)	1570(15)	3632(3)	38.6(8)
H8SC	6989(3)	1995(7)	4097(12)	38.6(8)
H6S	6546(16)	9010(5)	6309(3)	84(13)
H64	6700(40)	8340(30)	4920(20)	49(15)
H1SA	3870(30)	7880(20)	5412(15)	38.6(12)
H1SB	3920(30)	7930(20)	6078(15)	38.7(12)
H1SC	3970(30)	8667(17)	5713(18)	38.7(13)
H73	3820(30)	5410(20)	4410(10)	27(5)
H46	6170(40)	80(30)	6140(20)	64(19)
H67A	3091(13)	6550(20)	5173(17)	31.4(7)
H67B	3970(20)	6450(30)	5594(13)	31.4(7)
H67C	4110(20)	6530(20)	4904(14)	31.4(7)
H63	6290(40)	9560(30)	4770(20)	42(9)
H7S	5180(16)	9045(6)	6182(5)	84(13)
H12S	3570(30)	2830(30)	4460(20)	34(4)
H47	5820(40)	870(30)	6850(20)	44(15)
H30	6000(40)	5400(30)	1260(20)	50(17)
H1D	6060(30)	2060(20)	6730(20)	39(13)
H45	6650(30)	630(30)	5240(20)	40(12)
H29	6590(40)	6170(30)	1980(20)	64(16)
H62	6030(30)	10060(30)	3840(20)	42(9)
H15	6260(40)	4032(9)	8210(20)	52(16)
H66A	9844(6)	4658(19)	4650(3)	46.2(10)
H66B	9977(3)	4975(11)	5207(12)	46.2(10)
H66C	9745(4)	4190(8)	5146(13)	46.2(10)

Crystal Data. $\text{C}_{68}\text{H}_{58}\text{N}_2\text{O}_8\text{Rh}_2$, $M_r = 1236.981$, monoclinic, $P2_1$ (No. 4), $a = 9.8716(8)$ Å, $b = 18.221(3)$ Å, $c = 18.301(2)$ Å, $\beta = 91.066(10)^\circ$, $\alpha = \gamma = 90^\circ$, $V = 3291.2(7)$ Å³, $T = 100.01(10)$ K, $Z = 2$, $Z' = 1$, $\mu(\text{Cu K}\alpha) = 4.468$ mm⁻¹, 9572 reflections measured, 5823 unique ($R_{\text{int}} = 0.0761$) which were used in all calculations. The final wR_2 was 0.1889 (all data) and R_1 was 0.0688 ($I \geq \sigma(I)$).

$R_1 = 6.88\%$

Structure Quality Indicators

Reflections:	d min (Cu)	0.91	I/ σ	7.8	R _{int}	7.41%	complete	64%
							84% (U _{Cr})	
Refinement:	Shift	0.001	Max Peak	0.9	Min Peak	-0.8	Goof	1.032
							Flack	.08(3)

A violet needle-shaped crystal with dimensions $0.11 \times 0.07 \times 0.05 \text{ mm}^3$ was mounted on a nylon loop with paratone. Data were collected using a XtaLAB Synergy, Dualflex, HyPix diffractometer equipped with an Oxford Cryosystems low-temperature device operating at $T = 100.01(10) \text{ K}$.

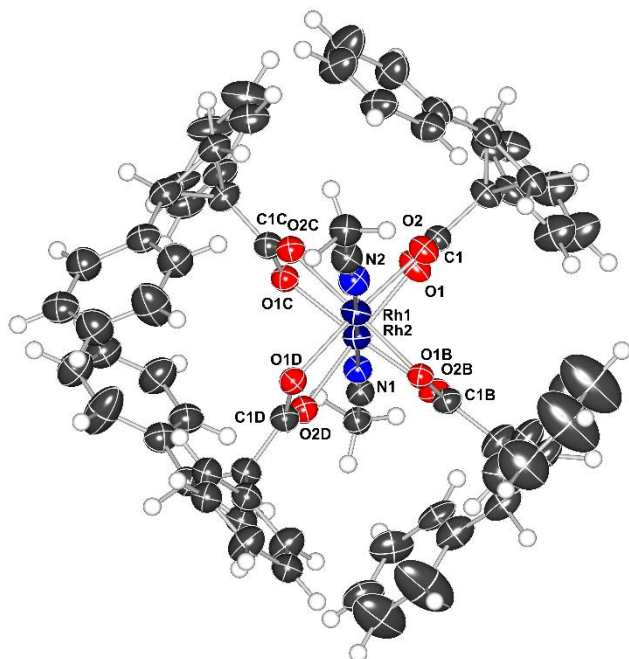
Data were measured using ω scans using Cu K_α radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program **CrysAlisPro** (Rigaku, V1.171.39.20a, 2015). The maximum resolution that was achieved was $\Theta = 57.90^\circ$ ($0.91 \text{ \AA}$).

The unit cell was refined using **CrysAlisPro** (Rigaku, V1.171.39.20a, 2015) on 2289 reflections, 24% of the observed reflections.

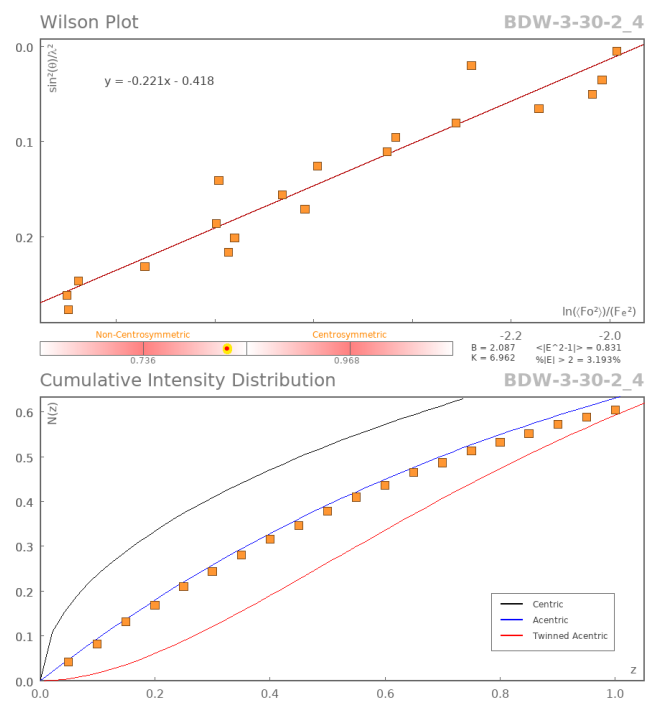
Data reduction, scaling and absorption corrections were performed using **CrysAlisPro** (Rigaku, V1.171.39.20a, 2015). The final completeness is 84.30 % out to 57.90° in Θ . A numerical absorption correction based on Gaussian integration over a multifaceted crystal model was performed using **CrysAlisPro** 1.171.40.76a (Rigaku Oxford Diffraction, 2020). An empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm was also performed. The absorption coefficient μ of this material is 4.468 mm^{-1} at this wavelength ($\lambda = 1.54184 \text{ \AA}$) and the minimum and maximum transmissions are 0.703 and 1.000.

The structure was solved and the space group $P2_1$ (# 4) determined by the **ShelXT** (Sheldrick, 2015) structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version of **olex2.refine** 1.3-dev (Bourhis et al., 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Most hydrogen atom positions were calculated geometrically and refined using the riding model, but some hydrogen atoms were refined freely.

Figure S5:

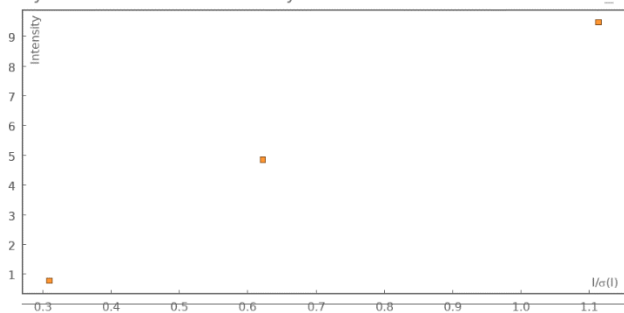


Data Plots: Diffraction Data



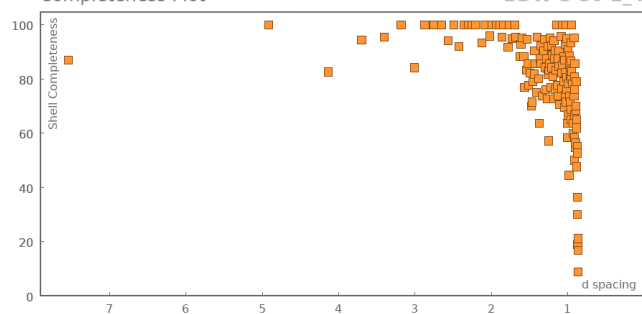
Systematic Absences Intensity Distribution

BDW-3-30-2_4



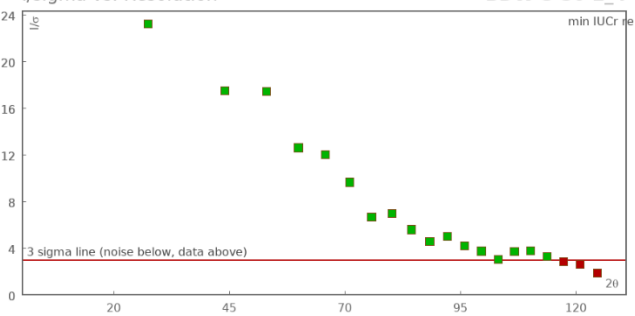
Completeness Plot

BDW-3-30-2_4



I/σ vs. Resolution

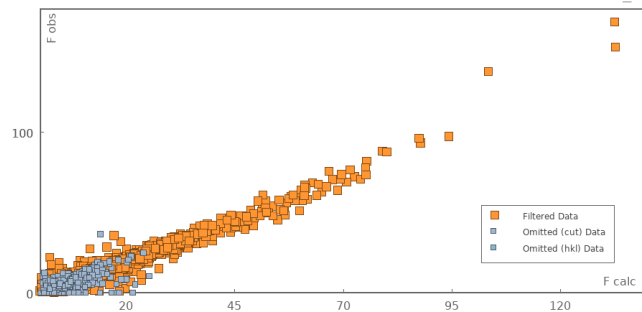
BDW-3-30-2_4

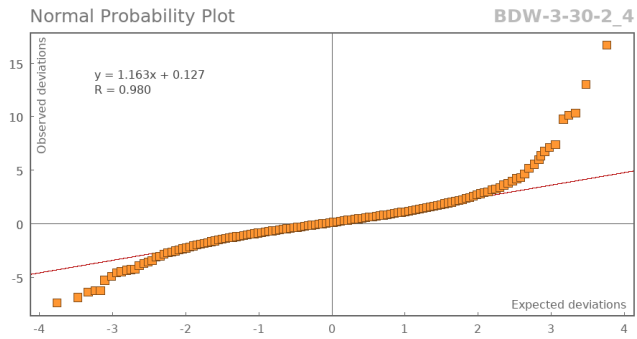


Data Plots: Refinement and Data

Fobs vs Fcalc

BDW-3-30-2_4





Reflection Statistics

Total reflections (after filtering)	8841	Unique reflections	5830
Completeness	0.639	Mean I/σ	9.11
$hkl_{\max}$ collected	(11, 18, 15)	$hkl_{\min}$ collected	(-11, -16, -21)
$hkl_{\max}$ used	(10, 17, 20)	$hkl_{\min}$ used	(-10, -16, 0)
Lim $d_{\max}$ collected	20	Lim $d_{\min}$ collected	0.91
$d_{\max}$ used	18.22	$d_{\min}$ used	0.91
Friedel pairs	954	Friedel pairs merged	0
Inconsistent equivalents	66	R_{int}	0.0741
R_{sigma}	0.1283	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	7
Multiplicity	(5984, 1335, 207, 47, 20, 2)	Maximum multiplicity	7
Removed systematic absences	3	Filtered off (Shel/OMIT)	734

Images of the Crystal on the Diffractometer



Table S14: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **2.9 (Crystal 1)**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
Rh1	5078(2)	6219.2(16)	7517.3(12)	36.8(11)
Rh2	7418(2)	5930.9(15)	7533.0(12)	36.3(12)
O1	7755(6)	6770(5)	8216(4)	44(3)
O2	5521(5)	6964(5)	8320(4)	39(3)
C1	6718(5)	7102(5)	8487(5)	34.0(18)
C2	7018(4)	7637(3)	9058(3)	42.2(17)
C3	6218(6)	8359(3)	9065(3)	42.8(18)
C4	5886(6)	7790(5)	9602(3)	42.1(19)
C5	5328(6)	8620(4)	8480(4)	45(2)
C6	5831(7)	9109(6)	7947(5)	62(5)
C7	5033(9)	9370(7)	7376(5)	88(7)
C8	3719(9)	9164(7)	7305(5)	68(5)
C9	3182(7)	8702(6)	7792(5)	58(5)
C10	3987(6)	8434(5)	8375(5)	51(4)
C11	8474(4)	7672(4)	9359(4)	45(2)
C12	9337(6)	8197(6)	9098(6)	49(3)
C13	10706(6)	8203(6)	9343(6)	55(4)
C14	11103(6)	7697(6)	9854(6)	68(5)
C15	10266(7)	7178(7)	10134(6)	84(6)
C16	8913(7)	7167(5)	9878(5)	68(5)
O1B	4786(5)	5460(5)	8281(4)	31.4(18)
O2B	7023(5)	5285(5)	8440(4)	36(3)
C1B	5829(5)	5160(4)	8600(4)	36.2(17)
C2B	5540(4)	4677(3)	9211(3)	50.5(18)
C3B	6238(6)	3928(3)	9260(4)	52.1(19)
C4B	6718(5)	4517(5)	9749(3)	51(2)
C5B	7023(6)	3585(4)	8691(5)	55(3)
C6B	6508(8)	2958(5)	8321(6)	132(9)
C7B	7230(10)	2595(6)	7791(7)	102(7)
C8B	8478(9)	2829(6)	7604(5)	63(5)
C9B	9023(7)	3421(6)	7935(5)	64(5)
C10B	8295(6)	3793(5)	8474(5)	49(4)
C11B	4127(4)	4728(4)	9543(4)	54(2)
C12B	3108(6)	4290(7)	9268(8)	74(5)
C13B	1766(6)	4396(9)	9507(10)	94(7)
C14B	1551(8)	4912(12)	10035(13)	143(10)
C15B	2533(9)	5368(11)	10304(12)	140(10)
C16B	3859(7)	5268(7)	10054(7)	74(5)

O1C	7662(6)	6624(5)	6673(4)	37.7(18)
O2C	5485(5)	6968(5)	6740(4)	38.8(18)
C1C	6629(5)	7019(5)	6474(4)	38.4(16)
C2C	6896(4)	7599(3)	5950(3)	44.8(15)
C3C	6027(6)	7648(4)	5251(3)	46.3(17)
C4C	5779(6)	8180(3)	5839(4)	44.3(18)
C5C	5056(5)	7104(3)	4990(3)	48(2)
C6C	5184(7)	6797(5)	4284(3)	59(2)
C7C	4288(9)	6278(5)	4009(4)	56(4)
C8C	3239(8)	6041(5)	4413(5)	68(5)
C9C	3062(8)	6312(6)	5087(5)	85(6)
C10C	3968(8)	6839(5)	5370(4)	59(5)
C11C	8356(4)	7881(4)	5903(4)	47.6(19)
C12C	9267(7)	7502(6)	5492(7)	52(4)
C13C	10602(7)	7776(6)	5425(7)	50(4)
C14C	10934(7)	8409(7)	5786(9)	62(5)
C15C	10063(8)	8788(7)	6214(9)	74(6)
C16C	8722(7)	8530(6)	6250(8)	56(4)
O1D	4776(6)	5401(4)	6766(4)	37.3(17)
O2D	6952(5)	5058(5)	6892(4)	38.9(17)
C1D	5773(5)	4952(4)	6669(5)	40.1(16)
C2D	5477(4)	4315(3)	6212(3)	43.4(14)
C3D	6280(6)	4200(4)	5515(3)	46.6(17)
C4D	6610(6)	3738(3)	6154(4)	45.0(18)
C5D	7209(6)	4725(3)	5195(3)	50(3)
C6D	6891(8)	5049(6)	4511(4)	91(7)
C7D	7739(9)	5551(6)	4182(5)	64(5)
C8D	8923(8)	5751(5)	4510(5)	57(4)
C9D	9282(7)	5462(5)	5160(5)	65(5)
C10D	8426(7)	4952(5)	5498(4)	50(4)
C11D	4028(5)	4013(4)	6215(4)	44.5(17)
C12D	3065(6)	4306(6)	5752(6)	47(2)
C13D	1736(6)	4012(7)	5744(6)	47(2)
C14D	1456(7)	3455(7)	6218(7)	60(5)
C15D	2379(7)	3167(6)	6701(6)	44(3)
C16D	3705(7)	3451(7)	6693(7)	56(4)
N1	9561(12)	5538(8)	7535(6)	40(2)
N2	2978(13)	6605(9)	7491(7)	52(3)
C67	10657(15)	5262(10)	7568(8)	39(3)
C68	11959(15)	4924(10)	7531(9)	38(3)
C69	1808(17)	6875(11)	7403(9)	52(3)
C70	577(17)	7199(11)	7392(10)	53(3)

Table S15: Anisotropic Displacement Parameters ($\times 10^4$) for **2.9 (Crystal 1)**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh1	30.1(15)	34.3(18)	45.9(14)	0.8(8)	-1.2(7)	-2.3(8)
Rh2	32.8(16)	34.1(18)	41.9(14)	-0.5(8)	-3.3(7)	0.1(8)
O1	28(2)	53(6)	52(5)	5.9(14)	-2.1(14)	-16(3)
O2	29(2)	42(6)	46(4)	5.1(11)	-0.4(11)	-7(3)
C1	29.8(18)	35(2)	37(2)	3.8(8)	0.5(8)	-0.1(9)
C2	32(2)	46(3)	48(3)	7.3(12)	-2.6(11)	-11.1(14)
C3	36(3)	47(3)	45(3)	9.8(13)	-2.7(14)	-11.2(14)
C4	31(3)	49(4)	46(3)	9.7(15)	-4.4(14)	-9.5(15)
C5	42(3)	44(5)	48(4)	10.2(17)	-7.4(16)	-13(2)
C6	54(4)	72(9)	59(6)	-6(3)	-17(2)	5(4)
C7	66(5)	111(14)	87(8)	-25(4)	-35(3)	37(5)
C8	61(4)	66(12)	76(6)	-10(3)	-27(3)	13(4)
C9	52(3)	48(10)	72(7)	2(3)	-21(2)	4(4)
C10	43(3)	46(9)	62(5)	8(2)	-12(2)	-3(3)
C11	33(2)	47(4)	55(4)	9.1(12)	-5.0(13)	-15.6(17)
C12	32(3)	48(6)	66(6)	10.2(18)	-4.2(18)	-11(3)
C13	33(3)	50(8)	83(8)	9.3(19)	-9.7(18)	-7(4)
C14	41(3)	61(9)	101(10)	1(2)	-21(2)	7(4)
C15	47(3)	82(10)	121(11)	-10(2)	-33(3)	29(5)
C16	43(3)	70(7)	90(8)	-4(2)	-23(2)	13(4)
O1B	30.1(18)	31(2)	34(2)	1.5(7)	0.4(7)	-0.3(8)
O2B	31.2(19)	29(6)	48(4)	2.6(9)	-1.3(9)	7(3)
C1B	32.1(17)	35(2)	41(2)	0.7(7)	-2.1(7)	3.8(8)
C2B	32(2)	60(3)	59(3)	0.5(12)	-2.9(10)	25.3(14)
C3B	29(3)	56(3)	70(3)	-1.7(13)	-5.7(13)	24.1(14)
C4B	34(3)	56(4)	64(3)	-2.8(15)	-5.4(13)	26.9(16)
C5B	31(3)	60(4)	74(5)	-3.9(17)	-3.3(17)	20(2)
C6B	77(6)	139(10)	182(14)	-63(4)	64(5)	-72(6)
C7B	66(6)	102(8)	139(11)	-43(4)	42(4)	-32(5)
C8B	46(5)	55(8)	89(8)	-12(3)	10(3)	17(4)
C9B	41(4)	56(8)	97(8)	-11(3)	11(3)	12(4)
C10B	29(3)	47(6)	72(7)	2(2)	-6(2)	28(3)
C11B	33(2)	69(5)	59(4)	2.4(13)	-2.1(13)	28.1(17)
C12B	36(3)	96(9)	90(9)	-6(2)	4.9(19)	2(5)
C13B	38(3)	120(13)	123(13)	-11(2)	13(2)	-23(6)
C14B	47(3)	187(16)	196(17)	-29(3)	33(3)	-92(8)
C15B	44(4)	181(15)	195(17)	-24(3)	31(3)	-90(8)
C16B	38(3)	94(8)	90(8)	-3(2)	5(2)	0(4)

O1C	36.5(18)	37(2)	40(2)	0.7(7)	-0.5(7)	-0.1(8)
O2C	36.6(17)	38(2)	42(2)	0.8(6)	0.0(7)	0.8(8)
C1C	36.7(17)	37(2)	41(2)	0.9(6)	-0.4(6)	0.3(7)
C2C	36(2)	46(2)	53(2)	1.7(9)	0.1(8)	10.2(10)
C3C	39(3)	46(3)	54(2)	4.7(11)	-1.8(10)	7.8(10)
C4C	35(3)	44(3)	54(3)	1.5(11)	-0.4(12)	9.0(11)
C5C	39(3)	44(4)	60(3)	6.5(16)	-6.3(11)	8.1(13)
C6C	56(3)	59(3)	62(3)	-2.4(8)	-0.6(8)	0.5(8)
C7C	49(4)	51(7)	68(4)	4(3)	-6.0(19)	3(2)
C8C	60(5)	70(8)	74(4)	-10(4)	1(2)	-5(3)
C9C	74(7)	99(11)	83(5)	-36(4)	14(3)	-21(3)
C10C	50(5)	62(8)	65(3)	-7(3)	1(2)	1(2)
C11C	35(2)	45(3)	63(4)	2.2(10)	-1.4(10)	14.4(15)
C12C	41(3)	40(5)	76(8)	-1.8(15)	9.2(19)	13(3)
C13C	39(3)	28(6)	84(8)	2.9(16)	7(2)	22(3)
C14C	38(3)	36(7)	111(10)	3(2)	6(2)	7(4)
C15C	36(3)	56(6)	130(12)	0(2)	6(3)	-14(4)
C16C	34(3)	49(5)	84(9)	4.1(16)	-4(2)	5(3)
O1D	36.2(18)	38(2)	38(2)	-0.2(7)	0.8(7)	1.6(8)
O2D	37.6(17)	39(2)	41(2)	0.9(6)	1.1(6)	0.7(8)
C1D	37.9(16)	39.9(19)	42(2)	1.0(5)	0.6(6)	0.4(7)
C2D	42.0(16)	42.0(18)	46.1(19)	0.4(6)	0.4(6)	-2.4(6)
C3D	45(3)	45(3)	50(2)	1.0(11)	2.8(10)	-3.2(10)
C4D	42(2)	42(3)	51(3)	0.0(10)	1.2(11)	-3.9(11)
C5D	45(3)	47(5)	57(3)	1.3(16)	4.4(14)	0.4(17)
C6D	72(6)	117(12)	84(5)	-39(4)	-21(3)	43(4)
C7D	54(5)	70(9)	68(5)	-10(3)	-2(2)	15(3)
C8D	49(5)	56(8)	66(6)	-1(3)	1(2)	7(3)
C9D	55(4)	70(9)	72(6)	-12(3)	-5(2)	17(3)
C10D	46(3)	46(8)	60(4)	1(3)	3.1(19)	0(3)
C11D	42.5(17)	44(3)	48(3)	-0.3(7)	0.6(7)	-2.2(11)
C12D	45.0(19)	47(3)	48(3)	0.2(6)	-0.2(6)	-0.5(8)
C13D	45(2)	47(3)	49(3)	0.1(7)	-0.0(7)	-0.6(8)
C14D	46(3)	66(7)	69(7)	-7.0(16)	-8.1(17)	19(3)
C15D	41(3)	43(5)	47(5)	0.2(14)	0.8(14)	-2(3)
C16D	43(3)	61(6)	65(6)	-6.1(15)	-5.9(16)	15(3)
N1	39(2)	41(3)	41(3)	0.7(7)	0.7(7)	-0.3(9)
N2	52(3)	53(3)	52(3)	0.1(7)	1.4(7)	-0.4(9)
C67	38(2)	40(3)	40(3)	0.4(7)	0.7(7)	-0.2(9)
C68	37(3)	38(3)	39(3)	-0.6(8)	0.8(7)	0.3(9)
C69	51(3)	52(3)	53(3)	-0.1(7)	1.2(7)	-0.1(9)
C70	52(3)	53(3)	55(4)	0.4(8)	1.2(7)	-0.1(9)

Table S16: Bond Lengths in Å for **2.9 (Crystal 1)**.

Atom	Atom	Length/Å
Rh1	Rh2	2.369(3)
Rh1	O2	2.042(7)
Rh1	O1B	1.990(7)
Rh1	O2C	2.017(7)
Rh1	O1D	2.046(8)
Rh1	N2	2.188(13)
Rh2	O1	1.998(7)
Rh2	O2B	2.077(6)
Rh2	O1C	2.036(7)
Rh2	O2D	2.025(7)
Rh2	N1	2.233(12)
O1	C1	1.296(3)
O2	C1	1.241(3)
C1	C2	1.456(3)
C2	C3	1.533(2)
C2	C4	1.536(2)
C2	C11	1.531(2)
C3	C4	1.469(2)
C3	C5	1.453(3)
C5	C6	1.417(3)
C5	C10	1.377(3)
C6	C7	1.382(3)
C7	C8	1.354(3)
C8	C9	1.342(3)
C9	C10	1.406(3)
C11	C12	1.372(3)
C11	C16	1.386(3)
C12	C13	1.416(3)
C13	C14	1.365(3)
C14	C15	1.361(3)
C15	C16	1.407(3)
O1B	C1B	1.2965(18)
O2B	C1B	1.2412(18)
C1B	C2B	1.4544(15)
C2B	C3B	1.5303(14)
C2B	C4B	1.5374(14)
C2B	C11B	1.5345(15)
C3B	C4B	1.4697(14)
C3B	C5B	1.4517(15)

C5B	C6B	1.4172(17)
C5B	C10B	1.3774(17)
C6B	C7B	1.3823(17)
C7B	C8B	1.3540(18)
C8B	C9B	1.3433(18)
C9B	C10B	1.4055(17)
C11B	C12B	1.3718(17)
C11B	C16B	1.3866(17)
C12B	C13B	1.4165(18)
C13B	C14B	1.3667(18)
C14B	C15B	1.3618(18)
C15B	C16B	1.4072(17)
O1C	C1C	1.295(3)
O2C	C1C	1.242(3)
C1C	C2C	1.455(3)
C2C	C3C	1.529(2)
C2C	C4C	1.539(2)
C2C	C11C	1.534(2)
C3C	C4C	1.472(2)
C3C	C5C	1.453(3)
C5C	C6C	1.416(3)
C5C	C10C	1.377(3)
C6C	C7C	1.383(3)
C7C	C8C	1.354(3)
C8C	C9C	1.343(3)
C9C	C10C	1.406(3)
C11C	C12C	1.370(3)
C11C	C16C	1.386(3)
C12C	C13C	1.417(3)
C13C	C14C	1.366(3)
C14C	C15C	1.362(3)
C15C	C16C	1.407(3)
O1D	C1D	1.295(3)
O2D	C1D	1.241(3)
C1D	C2D	1.456(3)
C2D	C3D	1.528(2)
C2D	C4D	1.540(2)
C2D	C11D	1.533(2)
C3D	C4D	1.472(2)
C3D	C5D	1.456(3)
C5D	C6D	1.414(3)
C5D	C10D	1.378(3)
C6D	C7D	1.384(3)

C7D	C8D	1.354(3)
C8D	C9D	1.344(3)
C9D	C10D	1.406(3)
C11D	C12D	1.370(3)
C11D	C16D	1.387(3)
C12D	C13D	1.417(3)
C13D	C14D	1.367(3)
C14D	C15D	1.362(3)
C15D	C16D	1.407(3)
N1	C67	1.194(19)
N2	C69	1.26(2)
C67	C68	1.43(2)
C69	C70	1.35(2)

Table S17: Bond Angles in ° for **2.9 (Crystal 1)**.

Atom	Atom	Atom	Angle/°
O2	Rh1	Rh2	86.73(19)
O1B	Rh1	Rh2	89.51(19)
O1B	Rh1	O2	89.4(4)
O2C	Rh1	Rh2	87.25(19)
O2C	Rh1	O2	90.8(4)
O2C	Rh1	O1B	176.7(3)
O1D	Rh1	Rh2	88.67(19)
O1D	Rh1	O2	174.0(4)
O1D	Rh1	O1B	86.8(4)
O1D	Rh1	O2C	92.7(4)
N2	Rh1	Rh2	174.1(5)
N2	Rh1	O2	89.6(4)
N2	Rh1	O1B	95.1(4)
N2	Rh1	O2C	88.2(4)
N2	Rh1	O1D	95.3(4)
O1	Rh2	Rh1	89.37(19)
O2B	Rh2	Rh1	86.44(18)
O2B	Rh2	O1	88.0(4)
O1C	Rh2	Rh1	89.00(19)
O1C	Rh2	O1	89.3(4)
O1C	Rh2	O2B	174.7(3)
O2D	Rh2	Rh1	87.5(2)
O2D	Rh2	O1	175.4(3)
O2D	Rh2	O2B	88.5(4)

O2D	Rh2	O1C	93.9(4)
N1	Rh2	Rh1	174.1(4)
N1	Rh2	O1	95.6(4)
N1	Rh2	O2B	90.5(4)
N1	Rh2	O1C	94.3(4)
N1	Rh2	O2D	87.4(4)
C1	O1	Rh2	118.2(4)
C1	O2	Rh1	120.1(4)
O2	C1	O1	124.5(3)
C2	C1	O1	115.9(3)
C2	C1	O2	119.5(3)
C3	C2	C1	118.9(3)
C4	C2	C1	116.5(3)
C4	C2	C3	57.18(12)
C11	C2	C1	117.6(2)
C11	C2	C3	116.2(2)
C11	C2	C4	116.6(3)
C4	C3	C2	61.52(13)
C5	C3	C2	125.4(3)
C5	C3	C4	125.8(3)
C3	C4	C2	61.30(13)
C6	C5	C3	119.9(3)
C10	C5	C3	126.1(3)
C10	C5	C6	114.0(2)
C7	C6	C5	122.3(3)
C8	C7	C6	120.6(3)
C9	C8	C7	120.0(3)
C10	C9	C8	119.8(3)
C9	C10	C5	123.3(3)
C12	C11	C2	119.3(3)
C16	C11	C2	119.9(3)
C16	C11	C12	120.8(2)
C13	C12	C11	119.3(3)
C14	C13	C12	118.2(3)
C15	C14	C13	123.9(3)
C16	C15	C14	117.6(3)
C15	C16	C11	120.1(3)
C1B	O1B	Rh1	119.1(3)
C1B	O2B	Rh2	119.1(3)
O2B	C1B	O1B	124.44(19)
C2B	C1B	O1B	115.87(18)
C2B	C1B	O2B	119.60(18)
C3B	C2B	C1B	119.27(17)

C4B	C2B	C1B	116.71(17)
C4B	C2B	C3B	57.25(7)
C11B	C2B	C1B	117.46(13)
C11B	C2B	C3B	116.23(16)
C11B	C2B	C4B	116.13(16)
C4B	C3B	C2B	61.62(8)
C5B	C3B	C2B	126.1(2)
C5B	C3B	C4B	125.5(2)
C3B	C4B	C2B	61.13(8)
C6B	C5B	C3B	119.90(17)
C10B	C5B	C3B	126.13(17)
C10B	C5B	C6B	113.93(13)
C7B	C6B	C5B	122.35(15)
C8B	C7B	C6B	120.66(16)
C9B	C8B	C7B	119.85(15)
C10B	C9B	C8B	119.85(15)
C9B	C10B	C5B	123.34(15)
C12B	C11B	C2B	119.06(17)
C16B	C11B	C2B	119.70(17)
C16B	C11B	C12B	120.83(14)
C13B	C12B	C11B	119.36(15)
C14B	C13B	C12B	118.10(17)
C15B	C14B	C13B	123.83(19)
C16B	C15B	C14B	117.57(16)
C15B	C16B	C11B	120.14(15)
C1C	O1C	Rh2	117.3(4)
C1C	O2C	Rh1	121.4(4)
O2C	C1C	O1C	124.5(3)
C2C	C1C	O1C	115.9(3)
C2C	C1C	O2C	119.3(3)
C3C	C2C	C1C	119.2(3)
C4C	C2C	C1C	116.6(3)
C4C	C2C	C3C	57.34(12)
C11C	C2C	C1C	117.5(2)
C11C	C2C	C3C	116.6(3)
C11C	C2C	C4C	115.7(2)
C4C	C3C	C2C	61.67(13)
C5C	C3C	C2C	126.3(3)
C5C	C3C	C4C	124.8(3)
C3C	C4C	C2C	60.98(12)
C6C	C5C	C3C	120.0(3)
C10C	C5C	C3C	126.1(3)
C10C	C5C	C6C	113.9(2)

C7C	C6C	C5C	122.3(3)
C8C	C7C	C6C	120.7(3)
C9C	C8C	C7C	119.8(3)
C10C	C9C	C8C	119.8(3)
C9C	C10C	C5C	123.4(3)
C12C	C11C	C2C	119.2(3)
C16C	C11C	C2C	119.8(3)
C16C	C11C	C12C	120.9(2)
C13C	C12C	C11C	119.4(3)
C14C	C13C	C12C	118.1(3)
C15C	C14C	C13C	123.9(3)
C16C	C15C	C14C	117.5(3)
C15C	C16C	C11C	120.0(3)
C1D	O1D	Rh1	116.8(4)
C1D	O2D	Rh2	121.0(4)
O2D	C1D	O1D	124.5(3)
C2D	C1D	O1D	116.0(3)
C2D	C1D	O2D	119.3(3)
C3D	C2D	C1D	119.1(3)
C4D	C2D	C1D	116.4(3)
C4D	C2D	C3D	57.35(12)
C11D	C2D	C1D	117.5(2)
C11D	C2D	C3D	116.9(3)
C11D	C2D	C4D	115.7(3)
C4D	C3D	C2D	61.72(13)
C5D	C3D	C2D	126.0(3)
C5D	C3D	C4D	124.3(3)
C3D	C4D	C2D	60.93(12)
C6D	C5D	C3D	120.0(3)
C10D	C5D	C3D	125.8(3)
C10D	C5D	C6D	114.1(2)
C7D	C6D	C5D	122.3(3)
C8D	C7D	C6D	120.6(3)
C9D	C8D	C7D	119.9(3)
C10D	C9D	C8D	119.9(3)
C9D	C10D	C5D	123.2(3)
C12D	C11D	C2D	119.6(3)
C16D	C11D	C2D	119.5(3)
C16D	C11D	C12D	120.9(2)
C13D	C12D	C11D	119.4(3)
C14D	C13D	C12D	118.1(3)
C15D	C14D	C13D	123.9(3)
C16D	C15D	C14D	117.5(3)

C15D	C16D	C11D	120.2(3)
C67	N1	Rh2	173.2(13)
C69	N2	Rh1	172.5(13)
C68	C67	N1	174.5(17)
C70	C69	N2	173.0(19)

Table S18: Torsion Angles in ° for **2.9 (Crystal 1)**.

Atom	Atom	Atom	Atom	Angle/°
Rh1	O2	C1	O1	-4.4(10)
Rh1	O2	C1	C2	179.7(6)
Rh1	O1B	C1B	O2B	-3.7(9)
Rh1	O1B	C1B	C2B	172.8(5)
Rh1	O2C	C1C	O1C	-1.9(10)
Rh1	O2C	C1C	C2C	-176.0(6)
Rh1	O1D	C1D	O2D	-13.8(8)
Rh1	O1D	C1D	C2D	171.6(5)
Rh2	O1	C1	O2	-4.5(10)
Rh2	O1	C1	C2	171.6(6)
Rh2	O2B	C1B	O1B	-6.7(10)
Rh2	O2B	C1B	C2B	176.8(5)
Rh2	O1C	C1C	O2C	-4.9(9)
Rh2	O1C	C1C	C2C	169.4(6)
Rh2	O2D	C1D	O1D	5.9(9)
Rh2	O2D	C1D	C2D	-179.6(5)
O1	C1	C2	C3	140.0(7)
O1	C1	C2	C4	-154.6(7)
O1	C1	C2	C11	-9.0(10)
O2	C1	C2	C3	-43.7(12)
O2	C1	C2	C4	21.7(11)
O2	C1	C2	C11	167.3(8)
C1	C2	C3	C4	104.5(7)
C1	C2	C3	C5	-11.0(5)
C1	C2	C4	C3	-108.7(7)
C1	C2	C11	C12	98.2(8)
C1	C2	C11	C16	-80.4(7)
C2	C3	C5	C6	-94.6(6)
C2	C3	C5	C10	84.8(6)
C2	C4	C3	C5	114.9(5)
C2	C11	C12	C13	-176.2(10)
C2	C11	C16	C15	177.4(4)
C3	C5	C6	C7	179.5(4)
C3	C5	C10	C9	-179.4(4)
C5	C6	C7	C8	-0.0(9)
C5	C10	C9	C8	0.0(10)
C6	C7	C8	C9	0.0(10)
C7	C8	C9	C10	-0.0(8)
C11	C12	C13	C14	-2.4(14)
C11	C16	C15	C14	-0.0(10)
C12	C13	C14	C15	1.2(17)
C13	C14	C15	C16	0.0(8)

Atom	Atom	Atom	Atom	Angle/°
O1B	C1B	C2B	C3B	133.8(7)
O1B	C1B	C2B	C4B	-160.6(6)
O1B	C1B	C2B	C11B	-15.8(9)
O2B	C1B	C2B	C3B	-49.5(11)
O2B	C1B	C2B	C4B	16.1(11)
O2B	C1B	C2B	C11B	160.9(8)
C1B	C2B	C3B	C4B	104.6(5)
C1B	C2B	C3B	C5B	-10.5(4)
C1B	C2B	C4B	C3B	-109.1(5)
C1B	C2B	C11B	C12B	89.9(10)
C1B	C2B	C11B	C16B	-82.8(9)
C2B	C3B	C5B	C6B	-110.0(6)
C2B	C3B	C5B	C10B	72.4(7)
C2B	C4B	C3B	C5B	115.9(5)
C2B	C11B	C12B	C13B	-172.2(13)
C2B	C11B	C16B	C15B	173.4(17)
C3B	C5B	C6B	C7B	-177.9(4)
C3B	C5B	C10B	C9B	177.7(4)
C5B	C6B	C7B	C8B	-0.0(11)
C5B	C10B	C9B	C8B	0.0(11)
C6B	C7B	C8B	C9B	0.0(11)
C7B	C8B	C9B	C10B	-0.0(8)
C11B	C12B	C13B	C14B	-3(2)
C11B	C16B	C15B	C14B	1(2)
C12B	C13B	C14B	C15B	5(3)
C13B	C14B	C15B	C16B	-4(3)
O1C	C1C	C2C	C3C	127.7(8)
O1C	C1C	C2C	C4C	-166.5(7)
O1C	C1C	C2C	C11C	-22.5(10)
O2C	C1C	C2C	C3C	-57.7(11)
O2C	C1C	C2C	C4C	8.1(11)
O2C	C1C	C2C	C11C	152.0(8)
C1C	C2C	C3C	C4C	104.6(6)
C1C	C2C	C3C	C5C	-9.6(5)
C1C	C2C	C4C	C3C	-109.1(7)
C1C	C2C	C11C	C12C	82.5(9)
C1C	C2C	C11C	C16C	-100.3(9)
C2C	C3C	C5C	C6C	-123.6(6)
C2C	C3C	C5C	C10C	56.4(7)
C2C	C4C	C3C	C5C	116.3(3)
C2C	C11C	C12C	C13C	177.6(11)
C2C	C11C	C16C	C15C	179.5(13)
C3C	C5C	C6C	C7C	180.0(4)
C3C	C5C	C10C	C9C	180.0(4)
C5C	C6C	C7C	C8C	-0.0(9)
C5C	C10C	C9C	C8C	0.1(9)
C6C	C7C	C8C	C9C	0.0(9)
C7C	C8C	C9C	C10C	-0.1(4)
C11C	C12C	C13C	C14C	0.8(17)
C11C	C16C	C15C	C14C	5.0(18)
C12C	C13C	C14C	C15C	1.0(19)
C13C	C14C	C15C	C16C	-4(2)
O1D	C1D	C2D	C3D	120.2(7)

Atom	Atom	Atom	Atom	Angle/°
O1D	C1D	C2D	C4D	-174.2(6)
O1D	C1D	C2D	C11D	-30.6(9)
O2D	C1D	C2D	C3D	-54.7(10)
O2D	C1D	C2D	C4D	10.9(11)
O2D	C1D	C2D	C11D	154.5(7)
C1D	C2D	C3D	C4D	104.4(6)
C1D	C2D	C3D	C5D	-9.2(5)
C1D	C2D	C4D	C3D	-109.1(7)
C1D	C2D	C11D	C12D	86.0(9)
C1D	C2D	C11D	C16D	-93.3(9)
C2D	C3D	C5D	C6D	-113.3(6)
C2D	C3D	C5D	C10D	66.7(7)
C2D	C4D	C3D	C5D	116.1(3)
C2D	C11D	C12D	C13D	178.4(10)
C2D	C11D	C16D	C15D	-179.9(10)
C3D	C5D	C6D	C7D	-180.0(4)
C3D	C5D	C10D	C9D	-180.0(4)
C5D	C6D	C7D	C8D	0.0(9)
C5D	C10D	C9D	C8D	-0.0(9)
C6D	C7D	C8D	C9D	-0.0(9)
C7D	C8D	C9D	C10D	0.0(4)
C11D	C12D	C13D	C14D	1.8(16)
C11D	C16D	C15D	C14D	1.2(17)
C12D	C13D	C14D	C15D	0.2(16)
C13D	C14D	C15D	C16D	-1.7(19)

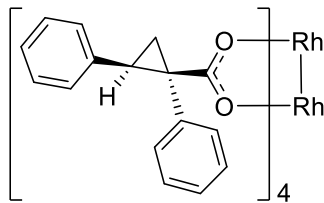
Table S19: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **2.9 (Crystal 1)**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
H3	6811(6)	8808(3)	9314(3)	51(2)
H4a	4924(6)	7493(5)	9525(3)	51(2)
H4b	6184(6)	7889(5)	10176(3)	51(2)
H6	6808(7)	9272(6)	7987(5)	74(6)
H7	5432(9)	9718(7)	7008(5)	106(9)
H8	3143(9)	9358(7)	6886(5)	82(7)
H9	2202(7)	8548(6)	7741(5)	69(6)
H10	3561(6)	8087(5)	8735(5)	61(5)
H12	8999(6)	8575(6)	8735(6)	59(4)
H13	11371(6)	8570(6)	9145(6)	67(5)
H14	12075(6)	7708(6)	10036(6)	82(6)
H15	10603(7)	6815(7)	10512(6)	101(8)
H16	8261(7)	6791(5)	10073(5)	82(6)
H3B	5617(6)	3525(3)	9550(4)	63(2)
H4Ba	7707(5)	4767(5)	9635(3)	62(2)
H4Bb	6482(5)	4472(5)	10332(3)	62(2)
H6B	5579(8)	2770(5)	8449(6)	158(11)
H7B	6823(10)	2150(6)	7542(7)	122(8)
H8B	8998(9)	2560(6)	7217(5)	75(6)
H9B	9953(7)	3597(6)	7796(5)	77(6)
H10B	8727(6)	4236(5)	8714(5)	59(4)

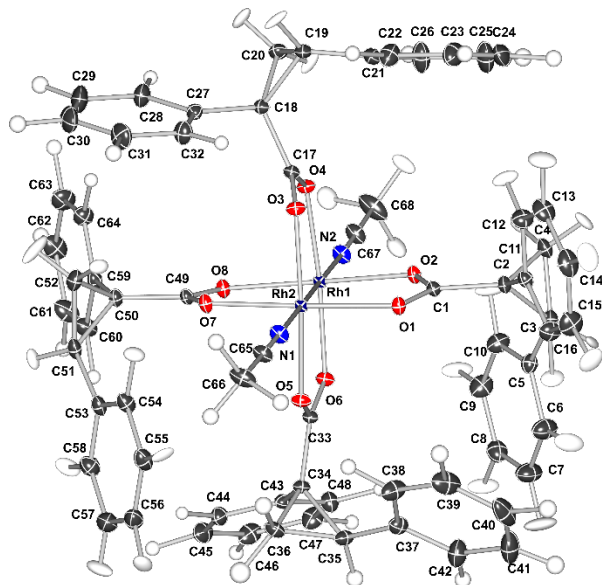
Atom	x	y	z	U_{eq}
H12B	3313(6)	3895(7)	8899(8)	89(6)
H13B	990(6)	4100(9)	9294(10)	113(8)
H14B	609(8)	4959(12)	10236(13)	171(12)
H15B	2317(9)	5763(11)	10671(12)	168(12)
H16B	4618(7)	5590(7)	10246(7)	89(6)
H3C	6587(6)	7896(4)	4799(3)	56(2)
H4Ca	4846(6)	8117(3)	6152(4)	53(2)
H4Cb	6097(6)	8751(3)	5751(4)	53(2)
H6C	5957(7)	6962(5)	3970(3)	70(3)
H7C	4419(9)	6073(5)	3503(4)	67(5)
H8C	2590(8)	5662(5)	4207(5)	81(6)
H9C	2279(8)	6137(6)	5389(5)	102(8)
H10C	3814(8)	7034(5)	5879(4)	71(6)
H12C	8989(7)	7031(6)	5239(7)	63(5)
H13C	11289(7)	7510(6)	5120(7)	60(5)
H14C	11881(7)	8609(7)	5731(9)	74(6)
H15C	10368(8)	9237(7)	6495(9)	89(7)
H16C	8026(7)	8818(6)	6528(8)	67(5)
H3D	5691(6)	3899(4)	5096(3)	56(2)
H4Da	7570(6)	3846(3)	6450(4)	54(2)
H4Db	6310(6)	3157(3)	6131(4)	54(2)
H6D	6014(8)	4911(6)	4253(4)	109(8)
H7D	7472(9)	5769(6)	3693(5)	77(6)
H8D	9535(8)	6117(5)	4266(5)	68(5)
H9D	10164(7)	5610(5)	5406(5)	79(6)
H10D	8719(7)	4742(5)	5987(4)	61(4)
H12D	3301(6)	4728(6)	5419(6)	56(2)
H13D	1015(6)	4208(7)	5397(6)	56(3)
H14D	510(7)	3244(7)	6210(7)	72(6)
H15D	2121(7)	2765(6)	7052(6)	53(4)
H16D	4423(7)	3244(7)	7035(7)	68(5)
H68a	12586(15)	5204(10)	7073(9)	57(4)
H68b	12430(130)	4980(80)	7990(80)	57(4)
H68c	11850(140)	4410(90)	7420(70)	57(4)
H70a	-154(17)	6873(11)	6999(10)	80(5)
H70b	220(150)	7200(90)	7880(90)	80(5)
H70c	660(150)	7690(100)	7220(90)	80(5)

Table S20: Solvent masking (PLATON/SQUEEZE) information for **2.9 (Crystal 1)**:

No	x	y	z	V	e	Content
1	-0.363	-0.360	-0.732	1360.8	137.2	?
2	0.489	0.800	0.033	0.0	0.0	?
3	0.511	0.300	0.967	0.0	0.0	?



Dirhodium tetrakis ((1R,2R)-1,2-diphenylcyclopropane-1-carboxylic acid) (2.9)
(Crystal 2)



Experimental. Single violet crystals of **2.9 (Crystal 2)** were chosen from the sample as supplied. A suitable crystal with dimensions $0.52 \times 0.48 \times 0.23 \text{ mm}^3$ was selected and mounted on a loop with paratone on a XtaLAB Synergy-S diffractometer. The crystal was kept at a steady $T = 100(2) \text{ K}$ during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) solution program using dual methods and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with **olex2.refine** 1.3-dev (Bourhis et al., 2015) using full matrix least squares minimisation on F^2 .

Crystal Data. $\text{C}_{72}\text{H}_{64}\text{N}_4\text{O}_8\text{Rh}_2$, $M_r = 1319.089$, monoclinic, $P2_1$ (No. 4), $a = 9.8960(2) \text{ \AA}$, $b = 21.1720(4) \text{ \AA}$, $c = 14.8082(3) \text{ \AA}$, $\beta = 100.901(2)^\circ$, $\alpha = \gamma = 90^\circ$, $V = 3046.60(11) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 2$, $Z' = 1$, $\mu(\text{MoK}\alpha) = 0.603 \text{ mm}^{-1}$, 67506 reflections measured, 24055 unique ($R_{\text{int}} = 0.0245$) which were used in all calculations. The final wR_2 was 0.0387 (all data) and R_1 was 0.0163 ($I \geq \sigma(I)$).

$R_1 = 1.63\%$

Compound 2.9 (Crystal 2)

Formula	C ₇₂ H ₆₄ N ₄ O ₈ Rh ₂
$D_{calc.}/\text{g cm}^{-3}$	1.438
μ/mm^{-1}	0.603
Formula Weight	1319.089
Colour	violet
Shape	prism
Size/mm ³	0.52×0.48×0.23
T/K	100(2)
Crystal System	monoclinic
Flack Parameter	0.008(7)
Hooft Parameter	-0.023(4)
Space Group	$P2_1$
$a/\text{\AA}$	9.8960(2)
$b/\text{\AA}$	21.1720(4)
$c/\text{\AA}$	14.8082(3)
$\alpha/^\circ$	90
$\beta/^\circ$	100.901(2)
$\gamma/^\circ$	90
$V/\text{\AA}^3$	3046.60(11)
Z	2
Z'	1
Wavelength/ $\text{\AA}$	0.71073
Radiation type	MoK α
$\theta_{min}/^\circ$	2.10
$\theta_{max}/^\circ$	34.34
Measured Refl's.	67506
Ind't Refl's	24055
Refl's with $I \geq \sigma(I)$	23685
R_{int}	0.0245
Parameters	1144
Restraints	97
Largest Peak	0.2434
Deepest Hole	-0.3668
GooF	1.0684
wR_2 (all data)	0.0387
wR_2	0.0386
R_1 (all data)	0.0168
R_1	0.0163

Structure Quality Indicators

Reflections:	d min (Mo)	0.63	I/σ	38.8	Rint	2.43%	complete	95%
	100% (IUCr)							
Refinement:	Shift	0.001	Max Peak	0.2	Min Peak	-0.4	GooF	1.068
	Flack .008(7)							

A violet prism-shaped crystal with dimensions $0.52 \times 0.48 \times 0.23 \text{ mm}^3$ was mounted on a loop with paratone oil. Data were collected using a XtaLAB Synergy, Dualflex, HyPix diffractometer equipped with an Oxford Cryosystems low-temperature device operating at $T = 100(2) \text{ K}$.

Data were measured using ω scans using $\text{MoK}\alpha$ radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program **CrysAlisPro** (Rigaku, V1.171.39.9g, 2015). The maximum resolution that was achieved was $\Theta = 34.34^\circ$ ($0.63 \text{ \AA}$).

The unit cell was refined using **CrysAlisPro** (Rigaku, V1.171.39.9g, 2015) on 56447 reflections, 84% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using **CrysAlisPro** (Rigaku, V1.171.39.9g, 2015). The final completeness is 99.61 % out to 34.34° in Θ . A numerical absorption correction based on Gaussian integration over a multifaceted crystal model was performed using **CrysAlisPro** 1.171.40.76a (Rigaku Oxford Diffraction, 2020). An empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm was also performed. The absorption coefficient μ of this material is 0.603 mm^{-1} at this wavelength ($\lambda = 0.71073 \text{ \AA}$) and the minimum and maximum transmissions are 0.404 and 1.000.

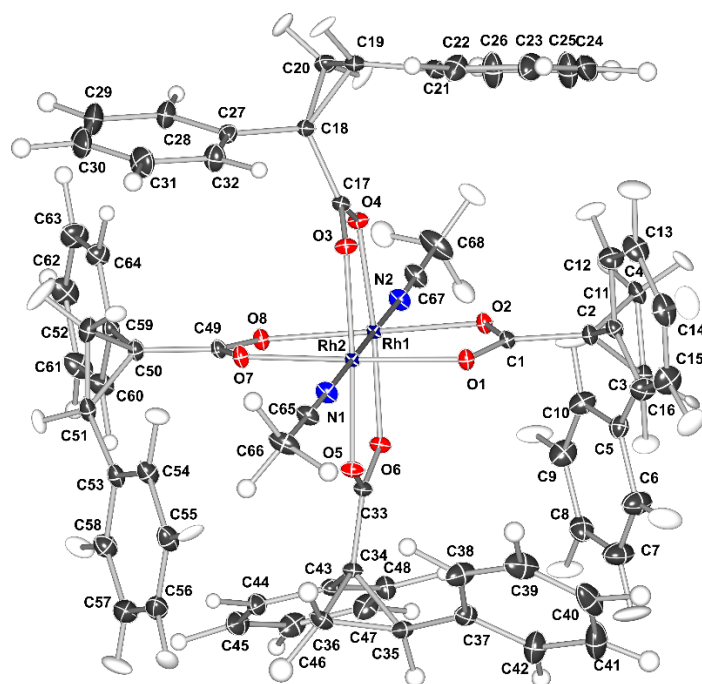
The structure was solved and the space group $P2_1$ (# 4) determined by the ShelXT (Sheldrick, 2015) structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version of **olex2.refine** 1.3-dev (Bourhis et al., 2015). All non-hydrogen atoms were refined anisotropically. Some hydrogen atom positions were calculated geometrically and refined using the riding model, but most hydrogen atoms were refined freely.

_refine_special_details: Refinement using NoSpherA2, an implementation of NOn-SPHERical Atom-form-factors in **Olex2**. Please cite: F. Kleemiss, H. Puschmann, O. Dolomanov, S. Grabowsky - to be published - 2020 NoSpherA2 implementation of HAR makes use of tailor-made aspherical atomic form factors calculated on-the-fly from a Hirshfeld-partitioned electron density (ED) - not from spherical-atom form factors. The ED is calculated from a gaussian basis set single determinant SCF wavefunction - either Hartree-Fock or DFT using selected functionals - for a fragment of the crystal. This fragment can be embedded in an electrostatic crystal field by employing cluster charges. The following options were used: SOFTWARE: ORCA PARTITIONING: NoSpherA2 INT ACCURACY: Normal METHOD: B3LYP BASIS SET: x2c-TZVP CHARGE: 0 MULTIPLICITY: 1 RELATIVISTIC: DKH2 DATE: 2020-05-04_18-38-53

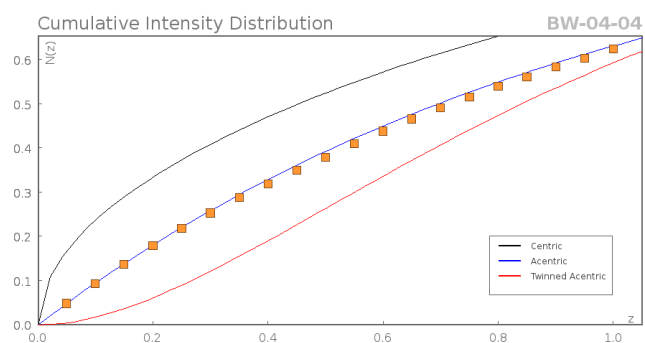
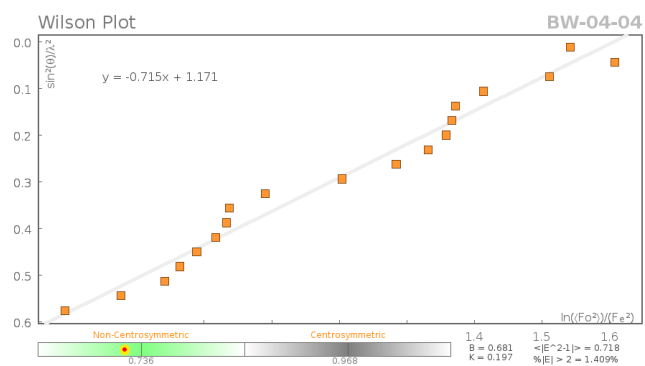
There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

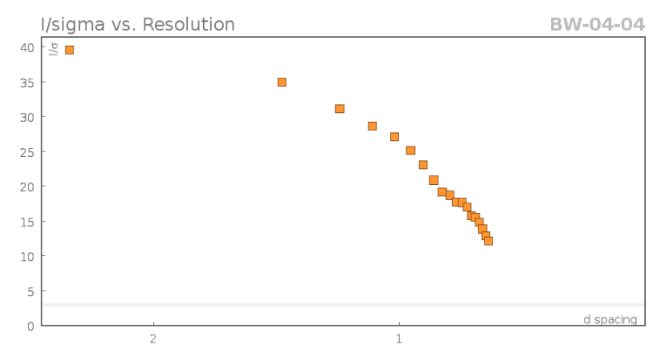
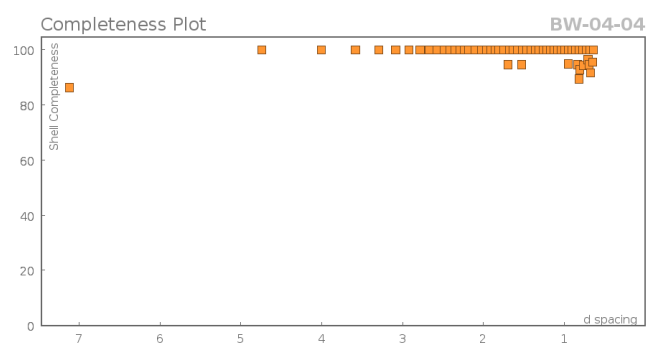
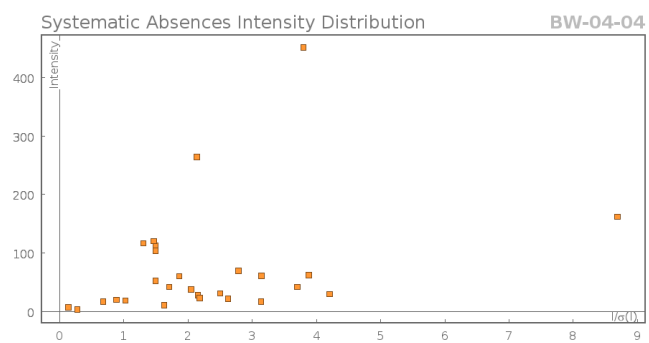
The Flack parameter was refined to $-0.015(5)$. Determination of absolute structure using Bayesian statistics on Bijvoet differences using the **Olex2** results in $-0.019(4)$. Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means 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 S6:

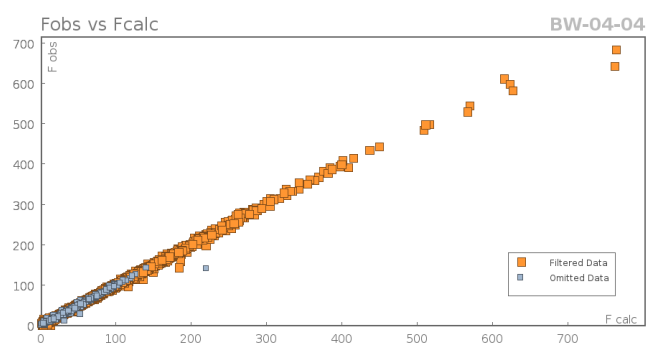


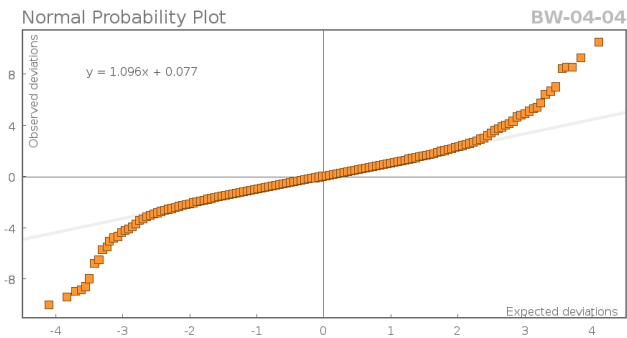
Data Plots: Diffraction Data





Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	65272	Unique reflections	24055
Completeness	0.943	Mean I/σ	32.53
$hkl_{\max}$ collected	(15, 34, 20)	$hkl_{\min}$ collected	(-15, -33, -23)
$hkl_{\max}$ used	(15, 33, 23)	$hkl_{\min}$ used	(-15, -32, 0)
Lim $d_{\max}$ collected	15	Lim $d_{\min}$ collected	0.63
$d_{\max}$ used	9.72	$d_{\min}$ used	0.63
Friedel pairs	10019	Friedel pairs merged	0
Inconsistent equivalents	30	R_{int}	0.0243
R_{sigma}	0.0258	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	83
Multiplicity	(16403, 10958, 5014, 2299, 776, 170, 11)	Maximum multiplicity	12
Removed systematic absences	28	Filtered off (Shel/OMIT)	2262

Images of the Crystal on the Diffractometer

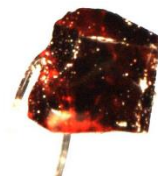
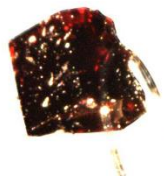


Table S21: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **2.9 (Crystal 2)**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
Rh1	4173.34(6)	5098.72(3)	7491.90(4)	6.801(12)
Rh2	1804.51(6)	4837.16(3)	7410.60(4)	6.910(12)
O1	1856.5(7)	5333.8(3)	8601.8(5)	11.05(11)
O3	1323.0(7)	5630.8(3)	6630.9(5)	11.39(11)
O5	2424.1(7)	4038.0(3)	8106.8(5)	12.00(11)
O2	4027.3(7)	5643.8(3)	8595.2(5)	10.90(11)
O7	1887.9(7)	4372.3(3)	6227.9(5)	11.53(11)
O4	3549.1(7)	5836.4(3)	6624.7(5)	11.00(11)
O8	4157.0(6)	4549.3(3)	6358.0(4)	11.09(11)
O6	4653.8(7)	4304.1(3)	8274.4(5)	10.91(11)
N2	6375.3(8)	5407.5(4)	7589.8(6)	13.30(13)
N1	-361.6(8)	4521.7(4)	7321.0(6)	13.59(14)
C1	2937.4(9)	5640.6(4)	8923.3(6)	9.42(13)
C33	3692.5(9)	3928.6(4)	8354.8(6)	9.51(13)
C66	-2777.5(10)	4009.5(5)	7164.0(9)	20.30(19)
C17	2275.8(9)	5902.1(4)	6322.2(6)	9.48(13)
C49	3014.4(9)	4314.1(4)	5962.3(6)	9.59(13)
C9	7260.5(10)	4998.8(5)	10274.5(8)	21.4(2)
C53	1603.8(10)	2973.9(5)	5658.4(7)	13.97(15)
C68	8769.7(11)	5925.9(6)	7663.2(11)	26.8(2)
C65	-1425.9(9)	4290.5(4)	7251.5(7)	13.27(15)
C12	832.9(11)	6706.0(5)	9471.6(8)	18.17(17)
C27	1065.5(9)	5930.3(4)	4681.0(6)	12.40(14)
C4	4060.7(10)	6526.0(4)	9998.1(7)	14.60(16)
C51	2203.2(10)	3319.5(5)	4952.2(7)	14.50(16)
C11	1552.9(9)	6208.3(4)	9957.1(6)	12.30(15)
C14	-987.4(11)	6593.5(6)	10325.0(9)	23.0(2)
C50	3014.8(9)	3945.3(4)	5102.0(6)	11.56(14)
C52	1641.4(10)	3899.9(5)	4447.3(7)	15.99(16)
C35	3586.2(10)	3082.5(5)	9646.1(7)	14.22(16)
C8	7277.8(11)	4535.4(5)	10940.2(8)	20.32(18)
C34	4084.2(9)	3289.0(4)	8759.8(6)	10.67(13)
C18	1837.5(9)	6302.7(4)	5475.4(6)	10.99(14)
C59	4313.2(9)	3966.3(4)	4728.4(6)	12.92(15)
C19	1396.9(10)	6988.1(4)	5571.5(6)	13.21(15)
C43	5470.1(9)	3051.4(4)	8660.8(6)	11.67(14)
C36	2958.7(10)	2807.6(4)	8731.4(7)	15.42(16)
C2	2934.3(9)	6036.6(4)	9759.9(6)	10.66(14)

C60	5326.1(11)	3509.7(5)	4978.2(8)	18.26(18)
C67	7437.7(10)	5634.1(5)	7625.3(7)	15.09(16)
C6	5245.4(12)	4992.9(5)	11331.1(8)	23.7(2)
C3	4126.1(9)	5954.4(5)	10594.3(6)	13.74(15)
C5	5215.4(9)	5464.1(5)	10668.7(6)	14.26(15)
C15	-282.8(12)	6094.1(6)	10809.0(8)	23.8(2)
C44	5598.7(11)	2602.4(5)	7994.0(7)	15.43(16)
C22	-13.7(12)	7412.2(6)	6643.3(8)	21.3(2)
C20	2742.6(10)	6836.6(5)	5288.9(7)	14.57(16)
C48	6653.5(10)	3264.4(5)	9251.0(7)	15.60(16)
C64	4529.0(11)	4441.8(5)	4122.3(7)	17.47(17)
C16	978.9(11)	5901.7(5)	10623.2(7)	18.25(17)
C28	1664.5(11)	5791.4(5)	3927.5(7)	19.19(18)
C13	-425.5(11)	6899.7(5)	9655.1(8)	21.86(19)
C10	6248.1(10)	5460.5(5)	10148.5(7)	18.43(17)
C31	-985.0(12)	5384.2(6)	3935.2(9)	25.1(2)
C21	1294.0(11)	7297.1(4)	6455.6(7)	14.73(16)
C38	1558.2(12)	3762.5(6)	9877.8(8)	22.5(2)
C56	524.0(12)	2216.3(5)	6900.0(7)	20.19(19)
C47	7933.2(10)	3024.1(5)	9180.0(7)	19.76(18)
C45	6884.3(12)	2361.2(5)	7926.7(7)	19.81(18)
C46	8050.4(11)	2568.9(5)	8523.8(8)	21.11(19)
C7	6266.4(13)	4532.6(6)	11468.8(9)	25.8(2)
C54	411.6(10)	3154.0(5)	5956.7(7)	16.18(16)
C32	-266.2(11)	5719.2(5)	4679.0(7)	18.95(17)
C61	6536.4(11)	3527.6(5)	4637.5(9)	22.9(2)
C30	-385.5(13)	5250.9(6)	3185.0(9)	26.9(2)
C23	-186.2(13)	7749.8(6)	7416.7(8)	24.4(2)
C37	2823.3(10)	3475.2(5)	10213.7(7)	15.53(16)
C58	2251.5(11)	2413.0(5)	5998.8(7)	18.24(17)
C29	939.4(14)	5452.3(6)	3182.0(8)	26.9(2)
C57	1717.8(12)	2036.7(5)	6612.5(8)	20.74(18)
C55	-120.6(11)	2774.3(5)	6574.8(8)	19.17(18)
C63	5734.1(12)	4459.4(5)	3773.2(8)	22.7(2)
C39	885.8(14)	4101.4(6)	10459.2(10)	29.0(3)
C42	3367.2(12)	3537.8(6)	11148.9(8)	24.5(2)
C24	954.6(14)	7970.3(5)	8029.4(8)	25.2(2)
C26	2417.4(12)	7521.9(6)	7072.4(8)	26.0(2)
C62	6744.0(12)	4001.3(6)	4031.9(9)	23.9(2)
C41	2677.6(14)	3865.9(7)	11736.5(9)	31.1(3)
C40	1432.7(14)	4149.5(6)	11391.3(10)	30.1(3)
C25	2249.4(14)	7853.0(6)	7856.2(9)	29.5(2)
N3	6438.4(14)	7234.5(7)	6547.9(10)	41.9(3)

C70	5722.1(15)	6921.9(7)	8089.9(10)	30.4(2)
C69	6118.0(13)	7102.1(6)	7232.5(10)	28.6(2)
C72	5990.1(15)	5824.6(8)	5283.1(10)	34.9(3)
N4	5129.6(14)	6197.2(7)	3602.4(11)	43.4(3)
C71	5515.7(13)	6033.6(6)	4343.8(10)	30.0(3)

Table S22: Anisotropic Displacement Parameters ($\times 10^4$) for **2.9 (Crystal 2)**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh1	5.28(2)	6.88(2)	8.34(2)	-0.326(19)	1.529(18)	-0.187(19)
Rh2	5.31(2)	7.12(2)	8.46(2)	-0.413(19)	1.680(18)	-0.193(19)
O1	9.1(3)	13.1(3)	11.4(3)	-1.8(2)	3.3(2)	-3.0(2)
O3	7.9(2)	12.1(3)	14.2(3)	0.9(2)	2.1(2)	3.8(2)
O5	8.7(2)	10.8(3)	16.5(3)	-0.2(2)	2.3(2)	3.8(2)
O2	8.7(2)	12.2(3)	12.1(3)	-1.7(2)	2.9(2)	-3.2(2)
O7	8.9(3)	13.1(3)	13.0(3)	-1.6(2)	3.0(2)	-4.2(2)
O4	8.2(2)	11.5(3)	12.8(3)	-0.5(2)	0.9(2)	3.3(2)
O8	8.6(2)	12.9(3)	12.3(3)	-1.3(2)	3.3(2)	-3.3(2)
O6	7.8(2)	10.2(3)	14.4(3)	-0.1(2)	1.4(2)	2.0(2)
N2	7.6(3)	13.9(4)	18.3(4)	-1.0(3)	2.3(3)	-1.0(3)
N1	8.2(3)	14.2(4)	18.8(4)	-1.6(3)	3.8(3)	-0.9(3)
C1	8.9(3)	9.4(3)	10.1(3)	-0.4(3)	2.2(3)	-1.1(3)
C33	8.8(3)	8.6(3)	11.0(3)	0.2(3)	1.6(3)	1.2(2)
C66	10.3(4)	14.5(4)	36.3(6)	-1.6(3)	5.0(4)	2.1(4)
C17	9.0(3)	8.4(3)	11.0(3)	0.0(3)	2.0(3)	0.9(2)
C49	9.2(3)	9.4(3)	10.6(3)	-0.7(3)	3.1(3)	-2.0(3)
C9	14.1(4)	27.8(6)	22.7(4)	5.0(3)	4.7(3)	2.2(3)
H9	50(4)	50(5)	83(6)	34(2)	48(3)	38(3)
C53	13.6(4)	13.0(4)	16.1(4)	-3.3(3)	4.8(3)	-5.0(3)
C68	10.5(4)	18.0(5)	52.0(8)	-3.1(4)	6.1(4)	-5.4(5)
H68a	38(9)	47(7)	58(3)	14(4)	11(2)	-7.6(18)
H68b	22(7)	22(2)	75(6)	-1.1(13)	16(4)	-4.8(14)
H68c	48(8)	31(6)	57(3)	13(3)	1(2)	-8.2(18)
C65	8.5(3)	11.9(4)	19.8(4)	-1.2(3)	3.6(3)	0.0(3)
C12	15.9(4)	18.2(4)	20.9(4)	4.1(3)	4.8(4)	2.2(3)
H12	25(8)	57(11)	43(10)	10(6)	14(4)	29(5)
C27	12.6(3)	12.5(4)	11.3(3)	0.8(3)	0.3(3)	-0.0(3)
C4	14.9(4)	11.9(4)	17.4(4)	-2.5(3)	4.2(3)	-4.8(3)
C51	14.7(4)	14.7(4)	15.0(4)	-4.4(3)	5.2(3)	-6.2(3)

C11	12.2(3)	11.5(4)	13.8(4)	-0.5(3)	4.3(3)	-2.3(3)
C14	14.2(4)	27.8(5)	28.7(5)	1.8(4)	8.4(4)	-8.9(4)
H14	23(6)	68(14)	73(14)	9(5)	24(4)	-23(10)
C50	11.9(3)	12.2(4)	11.2(4)	-1.3(3)	3.8(3)	-2.9(3)
C52	15.0(4)	20.8(4)	11.9(4)	-2.1(3)	1.9(3)	-3.1(3)
C35	15.4(4)	13.3(4)	15.1(4)	3.1(3)	5.7(3)	4.2(3)
C8	18.5(4)	19.7(5)	21.8(5)	5.2(4)	1.3(4)	-2.1(4)
H8	50(4)	50(5)	83(6)	34(2)	48(3)	38(3)
C34	11.0(3)	8.8(3)	12.4(3)	0.8(3)	2.7(3)	2.1(2)
C18	11.4(3)	9.9(3)	11.6(3)	0.1(3)	1.8(3)	1.2(3)
C59	13.8(4)	12.6(4)	13.6(4)	-1.9(3)	6.0(3)	-2.9(3)
C19	16.4(4)	10.2(4)	12.7(4)	1.6(3)	1.9(3)	2.4(3)
C43	12.7(3)	10.1(3)	12.5(3)	2.2(3)	3.3(3)	1.5(3)
C36	15.4(4)	10.7(4)	20.9(4)	-1.7(3)	5.6(3)	0.6(3)
C2	10.1(3)	11.3(4)	10.8(3)	-0.8(3)	2.6(3)	-2.6(3)
C60	16.4(4)	15.5(4)	25.2(5)	1.2(3)	9.9(4)	1.0(3)
C67	8.3(3)	13.8(4)	23.3(4)	-1.4(3)	3.4(3)	-3.0(3)
C6	25.1(5)	24.4(6)	24.4(5)	6.4(4)	11.5(4)	6.1(4)
H6	68(8)	43(13)	90(11)	18(9)	65(5)	19(10)
C3	13.5(4)	15.5(4)	12.1(4)	-0.2(3)	2.0(3)	-3.4(3)
C5	12.8(3)	16.5(4)	13.2(4)	0.6(3)	1.7(3)	-1.5(3)
C15	19.1(4)	29.4(6)	26.8(5)	-1.0(4)	13.9(4)	-1.1(4)
H15	42(11)	82(15)	40(10)	-20(9)	22(5)	11(6)
C44	17.5(4)	15.0(4)	14.3(4)	2.5(3)	4.2(3)	-1.0(3)
C22	19.3(5)	26.2(5)	18.1(5)	7.6(4)	3.0(4)	-0.4(4)
C20	16.7(4)	12.8(4)	14.9(4)	-1.6(3)	4.8(3)	2.8(3)
C48	12.5(4)	17.0(4)	17.0(4)	1.6(3)	2.1(3)	-2.5(3)
C64	17.1(4)	18.0(4)	18.9(4)	-1.2(3)	7.3(3)	1.1(3)
C16	17.1(4)	19.1(4)	20.7(4)	0.2(3)	9.2(4)	2.2(3)
H16	40(10)	41(12)	49(12)	28(9)	21(9)	15(9)
C28	19.7(4)	23.6(5)	14.6(4)	-0.4(4)	4.0(3)	-4.0(3)
C13	15.2(4)	20.8(5)	29.3(5)	5.7(3)	3.8(4)	-3.2(4)
H13	45(11)	40(8)	80(14)	14(5)	1(9)	24(5)
C10	13.2(4)	23.2(5)	19.4(4)	3.4(3)	4.0(3)	4.4(3)
H10	48(11)	48(7)	69(11)	27(7)	38(9)	40(4)
C31	20.3(5)	27.3(5)	24.8(5)	-8.0(4)	-3.1(4)	-5.7(4)
C21	18.0(4)	10.8(4)	15.5(4)	0.9(3)	3.3(3)	0.1(3)
C38	21.0(5)	26.6(5)	22.9(5)	9.5(4)	12.1(4)	7.1(4)
C56	26.3(5)	17.8(4)	17.7(4)	-5.5(4)	7.3(4)	-1.9(3)
H56	75(13)	26(9)	45(11)	-13(6)	39(6)	1(4)
C47	12.6(4)	26.6(5)	19.5(4)	5.0(3)	1.6(3)	1.1(3)
C45	24.2(5)	18.1(4)	19.4(4)	7.5(4)	9.9(4)	-0.1(3)
C46	17.2(4)	26.7(5)	21.1(5)	11.1(4)	7.7(4)	4.4(4)

C7	29.2(5)	22.0(5)	27.9(5)	7.2(4)	9.3(4)	7.7(4)
H7	90(17)	61(10)	78(13)	29(11)	42(11)	52(5)
C54	15.4(4)	14.0(4)	21.0(4)	-2.5(3)	8.0(3)	-3.5(3)
H54	37(9)	26(5)	48(10)	10(3)	18(7)	9(4)
C32	15.2(4)	22.7(5)	18.7(4)	-4.3(3)	2.5(3)	-3.6(3)
C61	17.5(4)	18.9(5)	35.7(6)	2.7(4)	13.8(4)	-1.2(4)
C30	30.0(6)	26.9(6)	19.6(5)	-3.5(4)	-5.9(4)	-7.4(4)
C23	27.1(5)	26.0(5)	21.4(5)	9.6(4)	7.8(4)	-0.5(4)
C37	16.1(4)	15.6(4)	16.8(4)	0.4(3)	7.9(3)	1.6(3)
C58	17.6(4)	16.0(4)	22.0(4)	0.4(3)	5.9(4)	-1.4(3)
H58	36(6)	29(10)	77(13)	8(5)	37(4)	4(8)
C29	32.6(6)	31.6(6)	15.9(4)	-1.4(5)	3.0(4)	-8.1(4)
C57	24.0(5)	17.3(4)	20.9(4)	-0.6(4)	4.3(4)	0.3(3)
H57	49(11)	21(5)	82(15)	2(4)	-16(9)	12(4)
C55	20.8(4)	17.2(4)	22.4(5)	-3.8(3)	11.3(4)	-4.7(3)
H55	33(5)	48(10)	29(8)	19(4)	25(3)	24(7)
C63	22.2(5)	23.4(5)	26.0(5)	-3.4(4)	13.6(4)	2.3(4)
C39	28.4(6)	25.3(6)	39.6(7)	9.5(4)	22.6(5)	5.6(5)
C42	21.8(5)	32.6(6)	19.8(5)	-2.2(4)	5.3(4)	-6.5(4)
C24	37.6(6)	17.5(5)	22.4(5)	0.7(4)	10.6(5)	-4.2(3)
C26	20.5(5)	34.2(6)	24.2(5)	-9.1(4)	6.3(4)	-12.8(4)
C62	20.3(5)	23.5(5)	32.7(6)	-2.1(4)	17.2(4)	-2.9(4)
C41	31.2(6)	39.7(7)	25.0(6)	-9.6(5)	12.0(5)	-14.5(5)
C40	35.6(6)	22.7(5)	39.8(7)	-5.8(4)	26.7(6)	-10.8(4)
C25	29.9(6)	33.6(6)	25.8(5)	-11.5(5)	7.5(5)	-14.6(4)
N3	37.2(6)	49.9(8)	41.1(7)	-2.3(6)	14.1(6)	12.8(6)
C70	34.3(6)	26.5(6)	31.7(6)	-1.2(5)	9.7(5)	-0.1(5)
C69	27.2(5)	28.2(6)	31.0(6)	-2.3(4)	6.8(5)	4.6(4)
C72	30.6(6)	43.4(8)	33.3(7)	-3.3(6)	12.5(5)	-9.3(6)
H72a	92(18)	79(18)	49(15)	53(16)	2(14)	19(13)
H72b	180(30)	65(18)	54(17)	-70(20)	-20(19)	7(14)
H72c	140(30)	110(20)	77(19)	20(20)	80(20)	47(17)
N4	35.5(6)	45.9(7)	49.5(8)	-2.1(6)	9.5(6)	17.3(6)
C71	22.7(5)	29.6(6)	40.0(7)	-4.0(4)	11.6(5)	0.4(5)
H4a	50(10)	13(4)	55(10)	-5(3)	37(5)	-10(2)
H4b	42(7)	13(7)	47(7)	-3(4)	31(4)	-4(4)
H3	79(12)	9(8)	26(4)	-1(8)	32(3)	-3(4)
H20a	46(8)	65(13)	15(2)	-18(7)	6.6(15)	8(2)
H20b	20(4)	72(13)	15(4)	-13(4)	6.8(18)	5(5)
H19	16(5)	69(13)	19(6)	5(5)	4(2)	24(5)
H52a	31(6)	30(8)	33(7)	7(3)	19(3)	8(4)
H52b	55(10)	125(19)	21(3)	55(7)	18(2)	22(3)
H51	31(9)	32(9)	35(10)	-1(5)	17(5)	-17(4)

Table S23: Bond Lengths in Å for **2.9 (Crystal 2)**.

Atom	Atom	Length/Å
Rh1	Rh2	2.38949(9)
Rh1	O2	2.0276(7)
Rh1	O4	2.0420(7)
Rh1	O8	2.0402(6)
Rh1	O6	2.0472(7)
Rh1	N2	2.2533(8)
Rh2	O1	2.0459(7)
Rh2	O3	2.0434(7)
Rh2	O5	2.0155(7)
Rh2	O7	2.0242(7)
Rh2	N1	2.2251(8)
O1	C1	1.2649(10)
O3	C17	1.2613(10)
O5	C33	1.2609(10)
O2	C1	1.2640(10)
O7	C49	1.2564(10)
O4	C17	1.2627(10)
O8	C49	1.2724(10)
O6	C33	1.2626(10)
N2	C67	1.1478(12)
N1	C65	1.1482(12)
C1	C2	1.4964(12)
C33	C34	1.5018(12)
C66	C65	1.4471(13)
C17	C18	1.5080(12)
C49	C50	1.4943(12)
C9	C8	1.3886(16)
C9	C10	1.3870(14)
C53	C51	1.4886(14)
C53	C54	1.3891(13)
C53	C58	1.3973(14)
C68	C67	1.4471(14)
C12	C11	1.3932(14)
C12	C13	1.3859(14)
C27	C18	1.4997(13)
C27	C28	1.3904(13)
C27	C32	1.3910(13)
C4	C2	1.5138(13)
C4	C3	1.4922(14)
C51	C50	1.5434(13)
C51	C52	1.4903(15)
C11	C2	1.4957(12)
C11	C16	1.3887(13)
C14	C15	1.3888(18)
C14	C13	1.3864(17)
C50	C52	1.5159(13)
C50	C59	1.4926(12)
C35	C34	1.5496(12)
C35	C36	1.4969(15)
C35	C37	1.4860(13)

Atom	Atom	Length/Å
C8	C7	1.3823(16)
C34	C43	1.4939(12)
C34	C36	1.5044(13)
C18	C19	1.5295(13)
C18	C20	1.4998(13)
C59	C60	1.3914(14)
C59	C64	1.3918(13)
C19	C20	1.5041(13)
C19	C21	1.4842(14)
C43	C44	1.3936(13)
C43	C48	1.3970(13)
C2	C3	1.5482(13)
C60	C61	1.3854(14)
C6	C5	1.3954(14)
C6	C7	1.3909(16)
C3	C5	1.4855(13)
C5	C10	1.3912(13)
C15	C16	1.3894(14)
C44	C45	1.3919(14)
C22	C21	1.3954(15)
C22	C23	1.3877(16)
C48	C47	1.3871(13)
C64	C63	1.3871(14)
C28	C29	1.3963(15)
C31	C32	1.3879(15)
C31	C30	1.3837(18)
C21	C26	1.3830(15)
C38	C37	1.3961(15)
C38	C39	1.3840(16)
C56	C57	1.3826(16)
C56	C55	1.3851(16)
C47	C46	1.3890(16)
C45	C46	1.3860(17)
C54	C55	1.3942(14)
C61	C62	1.3864(17)
C30	C29	1.3795(18)
C23	C24	1.3886(18)
C37	C42	1.3939(15)
C58	C57	1.3861(15)
C63	C62	1.3933(17)
C39	C40	1.388(2)
C42	C41	1.3892(16)
C24	C25	1.3761(18)
C26	C25	1.3926(16)
C41	C40	1.379(2)
N3	C69	1.1526(18)
C70	C69	1.4488(19)
C72	C71	1.450(2)
N4	C71	1.146(2)

Table S24: Bond Angles in ° for **2.9 (Crystal 2)**.

Atom	Atom	Atom	Angle/°
O2	Rh1	Rh2	87.350(18)
O4	Rh1	Rh2	88.186(18)
O4	Rh1	O2	90.70(3)
O8	Rh1	Rh2	88.360(18)
O8	Rh1	O2	175.54(3)
O8	Rh1	O4	87.94(3)
O6	Rh1	Rh2	87.632(18)
O6	Rh1	O2	93.21(3)
O6	Rh1	O4	174.13(3)
O6	Rh1	O8	87.83(3)
N2	Rh1	Rh2	176.43(2)
N2	Rh1	O2	89.91(3)
N2	Rh1	O4	89.57(3)
N2	Rh1	O8	94.33(3)
N2	Rh1	O6	94.81(3)
O1	Rh2	Rh1	88.453(18)
O3	Rh2	Rh1	87.686(18)
O3	Rh2	O1	91.70(3)
O5	Rh2	Rh1	88.174(18)
O5	Rh2	O1	91.99(3)
O5	Rh2	O3	174.37(3)
O7	Rh2	Rh1	87.487(18)
O7	Rh2	O1	175.87(3)
O7	Rh2	O3	87.38(3)
O7	Rh2	O5	88.63(3)
N1	Rh2	Rh1	175.89(2)
N1	Rh2	O1	94.16(3)
N1	Rh2	O3	95.40(3)
N1	Rh2	O5	88.56(3)
N1	Rh2	O7	89.94(3)
C1	O1	Rh2	118.03(5)
C17	O3	Rh2	117.96(6)
C33	O5	Rh2	119.54(6)
C1	O2	Rh1	120.18(6)
C49	O7	Rh2	120.15(6)
C17	O4	Rh1	118.06(6)
C49	O8	Rh1	118.04(5)
C33	O6	Rh1	118.19(6)
C67	N2	Rh1	172.11(8)

C65	N1	Rh2	172.00(8)
O2	C1	O1	125.48(8)
C2	C1	O1	117.73(7)
C2	C1	O2	116.78(8)
O6	C33	O5	125.67(8)
C34	C33	O5	116.72(7)
C34	C33	O6	117.59(7)
O4	C17	O3	125.84(8)
C18	C17	O3	116.12(7)
C18	C17	O4	117.89(7)
O8	C49	O7	125.54(8)
C50	C49	O7	117.48(8)
C50	C49	O8	116.98(7)
C10	C9	C8	120.34(10)
C54	C53	C51	124.31(9)
C58	C53	C51	117.04(8)
C58	C53	C54	118.54(9)
C66	C65	N1	179.04(10)
C13	C12	C11	120.89(10)
C28	C27	C18	120.63(8)
C32	C27	C18	120.83(8)
C32	C27	C28	118.54(9)
C3	C4	C2	61.99(6)
C50	C51	C53	125.92(8)
C52	C51	C53	126.69(8)
C52	C51	C50	59.93(6)
C2	C11	C12	118.69(8)
C16	C11	C12	118.81(9)
C16	C11	C2	122.47(9)
C13	C14	C15	119.67(10)
C51	C50	C49	119.15(7)
C52	C50	C49	115.69(7)
C52	C50	C51	58.30(6)
C59	C50	C49	116.06(8)
C59	C50	C51	115.69(7)
C59	C50	C52	119.70(8)
C50	C52	C51	61.77(6)
C36	C35	C34	59.15(6)
C37	C35	C34	126.74(8)
C37	C35	C36	124.14(9)
C7	C8	C9	119.48(10)
C35	C34	C33	119.55(7)
C43	C34	C33	115.90(7)

C43	C34	C35	115.66(7)
C36	C34	C33	117.76(7)
C36	C34	C35	58.68(6)
C36	C34	C43	117.24(7)
C27	C18	C17	112.35(7)
C19	C18	C17	119.91(8)
C19	C18	C27	117.37(8)
C20	C18	C17	119.28(8)
C20	C18	C27	119.02(8)
C20	C18	C19	59.53(6)
C60	C59	C50	120.53(8)
C64	C59	C50	120.56(9)
C64	C59	C60	118.91(9)
C20	C19	C18	59.25(6)
C21	C19	C18	124.64(8)
C21	C19	C20	123.47(9)
C44	C43	C34	120.51(8)
C48	C43	C34	120.43(8)
C48	C43	C44	119.04(8)
C34	C36	C35	62.17(6)
C4	C2	C1	117.37(7)
C11	C2	C1	116.28(7)
C11	C2	C4	116.62(8)
C3	C2	C1	118.50(7)
C3	C2	C4	58.32(6)
C3	C2	C11	117.25(7)
C61	C60	C59	120.87(10)
C68	C67	N2	179.32(11)
C7	C6	C5	121.48(10)
C2	C3	C4	59.69(6)
C5	C3	C4	124.08(8)
C5	C3	C2	124.78(8)
C3	C5	C6	118.05(9)
C10	C5	C6	117.72(9)
C10	C5	C3	124.15(9)
C16	C15	C14	120.21(10)
C45	C44	C43	120.54(10)
C23	C22	C21	121.19(11)
C19	C20	C18	61.22(6)
C47	C48	C43	120.23(9)
C63	C64	C59	120.48(10)
C15	C16	C11	120.48(10)
C29	C28	C27	120.66(10)

C14	C13	C12	119.92(11)
C5	C10	C9	121.13(10)
C30	C31	C32	120.54(11)
C22	C21	C19	118.27(9)
C26	C21	C19	123.61(9)
C26	C21	C22	117.92(10)
C39	C38	C37	120.56(12)
C55	C56	C57	119.45(10)
C46	C47	C48	120.39(10)
C46	C45	C44	120.00(9)
C45	C46	C47	119.79(9)
C6	C7	C8	119.84(11)
C55	C54	C53	119.96(10)
C31	C32	C27	120.61(10)
C62	C61	C60	119.96(10)
C29	C30	C31	119.45(11)
C24	C23	C22	120.05(11)
C38	C37	C35	124.02(10)
C42	C37	C35	118.24(9)
C42	C37	C38	117.67(10)
C57	C58	C53	121.29(9)
C30	C29	C28	120.20(11)
C58	C57	C56	119.83(10)
C54	C55	C56	120.91(9)
C62	C63	C64	120.09(10)
C40	C39	C38	120.92(12)
C41	C42	C37	121.78(12)
C25	C24	C23	119.22(10)
C25	C26	C21	121.06(11)
C63	C62	C61	119.68(10)
C40	C41	C42	119.71(12)
C41	C40	C39	119.33(11)
C26	C25	C24	120.55(12)
C70	C69	N3	178.80(16)
N4	C71	C72	179.41(14)

Table S25: Torsion Angles in ° for **2.9 (Crystal 2)**.

Atom	Atom	Atom	Atom	Angle/°
Rh1	O2	C1	O1	-2.60(7)
Rh1	O2	C1	C2	177.67(6)
Rh1	O4	C17	O3	14.20(7)
Rh1	O4	C17	C18	-161.19(6)
Rh1	O8	C49	O7	-2.62(7)
Rh1	O8	C49	C50	176.49(6)
Rh1	O6	C33	O5	-10.83(7)
Rh1	O6	C33	C34	167.62(6)
Rh2	O1	C1	O2	-3.67(7)
Rh2	O1	C1	C2	176.06(6)
Rh2	O3	C17	O4	-19.26(7)
Rh2	O3	C17	C18	156.20(6)
Rh2	O5	C33	O6	6.20(7)
Rh2	O5	C33	C34	-172.25(6)
Rh2	O7	C49	O8	-3.10(7)
Rh2	O7	C49	C50	177.79(6)
O1	C1	C2	C4	-164.70(8)
O1	C1	C2	C11	-19.76(9)
O1	C1	C2	C3	128.37(8)
O3	C17	C18	C27	-59.03(9)
O3	C17	C18	C19	85.06(9)
O3	C17	C18	C20	154.68(8)
O5	C33	C34	C35	-60.58(9)
O5	C33	C34	C43	153.45(8)
O5	C33	C34	C36	7.28(9)
O2	C1	C2	C4	15.05(9)
O2	C1	C2	C11	159.99(8)
O2	C1	C2	C3	-51.88(9)
O7	C49	C50	C51	-43.28(10)
O7	C49	C50	C52	23.18(10)
O7	C49	C50	C59	171.10(8)
O4	C17	C18	C27	116.81(8)
O4	C17	C18	C19	-99.10(9)
O4	C17	C18	C20	-29.48(10)
O8	C49	C50	C51	137.53(8)
O8	C49	C50	C52	-156.01(8)
O8	C49	C50	C59	-8.09(9)
O6	C33	C34	C35	120.84(8)
O6	C33	C34	C43	-25.14(9)

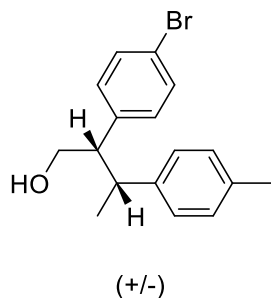
O6	C33	C34	C36	-171.31(8)
C1	C2	C4	C3	-108.17(11)
C1	C2	C11	C12	-80.12(9)
C1	C2	C11	C16	101.71(9)
C1	C2	C3	C4	106.24(11)
C1	C2	C3	C5	-6.35(10)
C33	C34	C35	C36	106.37(11)
C33	C34	C35	C37	-5.34(10)
C33	C34	C43	C44	-102.04(9)
C33	C34	C43	C48	79.61(9)
C33	C34	C36	C35	-109.39(11)
C17	C18	C27	C28	-108.71(8)
C17	C18	C27	C32	71.62(9)
C17	C18	C19	C20	108.44(11)
C17	C18	C19	C21	-3.21(10)
C17	C18	C20	C19	-109.47(11)
C49	C50	C51	C53	-11.83(10)
C49	C50	C51	C52	103.83(11)
C49	C50	C52	C51	-109.76(11)
C49	C50	C59	C60	92.19(9)
C49	C50	C59	C64	-88.01(9)
C9	C8	C7	C6	-0.13(13)
C9	C10	C5	C6	0.96(13)
C9	C10	C5	C3	177.88(9)
C53	C51	C50	C52	-115.66(13)
C53	C51	C50	C59	133.91(10)
C53	C51	C52	C50	114.46(12)
C53	C54	C55	C56	0.05(11)
C53	C58	C57	C56	-0.19(12)
C12	C11	C2	C4	65.09(10)
C12	C11	C2	C3	131.34(9)
C12	C11	C16	C15	-0.81(12)
C12	C13	C14	C15	0.06(13)
C27	C18	C19	C20	-109.22(11)
C27	C18	C19	C21	139.13(8)
C27	C18	C20	C19	106.48(11)
C27	C28	C29	C30	0.04(13)
C27	C32	C31	C30	0.41(13)
C4	C2	C11	C16	-113.09(10)
C4	C2	C3	C5	-112.59(7)
C4	C3	C2	C11	-105.93(7)
C4	C3	C5	C6	172.64(10)
C4	C3	C5	C10	-4.26(11)

C51	C50	C59	C60	-54.63(10)
C51	C50	C59	C64	125.17(9)
C51	C52	C50	C59	103.55(7)
C11	C2	C3	C5	141.48(8)
C11	C16	C15	C14	0.41(13)
C50	C59	C60	C61	-179.72(10)
C50	C59	C64	C63	-179.77(10)
C35	C34	C43	C44	110.65(9)
C35	C34	C43	C48	-67.70(9)
C35	C36	C34	C43	104.89(7)
C35	C37	C38	C39	177.47(11)
C35	C37	C42	C41	-176.18(10)
C8	C7	C6	C5	-0.20(15)
C34	C43	C44	C45	-177.28(9)
C34	C43	C48	C47	177.46(9)
C18	C19	C21	C22	-106.55(10)
C18	C19	C21	C26	78.68(12)
C18	C20	C19	C21	113.55(7)
C59	C60	C61	C62	-0.67(13)
C59	C64	C63	C62	-0.35(13)
C19	C21	C22	C23	-174.10(10)
C19	C21	C26	C25	174.76(12)
C43	C44	C45	C46	-0.21(12)
C43	C48	C47	C46	-0.16(12)
C2	C3	C5	C6	-113.14(10)
C2	C3	C5	C10	69.95(11)
C60	C61	C62	C63	0.34(14)
C44	C45	C46	C47	-0.88(12)
C22	C21	C26	C25	-0.02(13)
C22	C23	C24	C25	0.39(15)
C48	C47	C46	C45	1.07(12)
C64	C63	C62	C61	0.17(14)
C28	C29	C30	C31	-0.43(15)
C21	C26	C25	C24	-0.74(16)
C38	C37	C42	C41	0.85(12)
C38	C39	C40	C41	1.35(15)
C23	C24	C25	C26	0.55(14)
C37	C42	C41	C40	-1.23(14)
C39	C40	C41	C42	0.12(14)

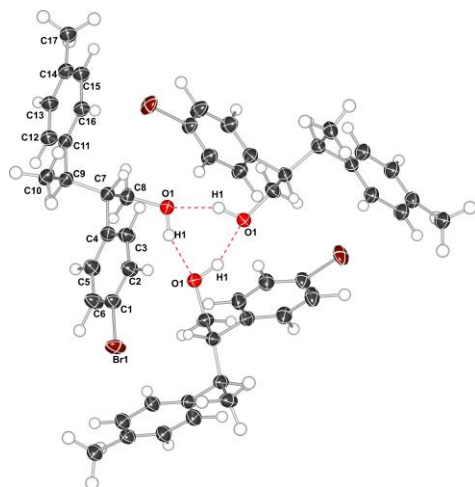
Table S26: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **2.9 (Crystal 2)**.. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
H66a	-3388(17)	4178(8)	6566(12)	30.5(3)
H66b	-2667(17)	3514(8)	7051(12)	30.5(3)
H66c	-3162(17)	3997(8)	7798(12)	30.5(3)
H9	8076(19)	5003(9)	9867(15)	56(4)
H68a	9110(20)	5765(10)	7037(15)	47(4)
H68b	8699(17)	6446(8)	7720(14)	39(3)
H68c	9400(20)	5702(9)	8246(14)	46(4)
H12	1357(17)	6951(9)	8972(13)	41(5)
H14	-1923(17)	6760(10)	10512(15)	53(6)
H8	8100(20)	4161(10)	11033(15)	56(4)
H60	5154(15)	3134(7)	5431(11)	21.9(2)
H6	4470(20)	5016(9)	11717(15)	61(6)
H15	-727(19)	5896(11)	11318(13)	53(6)
H44	4625(15)	2452(7)	7501(10)	18.5(2)
H22	-940(16)	7254(7)	6162(11)	25.5(2)
H48	6585(14)	3629(7)	9772(10)	18.72(19)
H64	3765(14)	4791(7)	3947(10)	21.0(2)
H16	1542(18)	5512(9)	11009(13)	42(5)
H28	2759(15)	5968(7)	3915(10)	23.0(2)
H13	-870(20)	7326(9)	9264(15)	56(6)
H10	6267(19)	5868(9)	9654(14)	51(5)
H31	-2011(16)	5217(8)	3952(11)	30.1(3)
H38	1109(16)	3738(8)	9153(11)	27.0(2)
H56	40(20)	1896(8)	7329(13)	45(5)
H47	8872(15)	3176(7)	9696(11)	23.7(2)
H45	7002(14)	1971(7)	7427(10)	23.8(2)
H46	8994(16)	2332(7)	8507(11)	25.3(2)
H7	6260(20)	4161(11)	11987(16)	73(7)
H54	-137(17)	3608(8)	5698(12)	36(4)
H32	-793(15)	5834(7)	5212(10)	22.7(2)
H61	7383(16)	3183(8)	4886(11)	27.5(2)
H30	-907(15)	4957(8)	2581(11)	32.2(3)
H23	-1233(17)	7827(8)	7536(11)	29.3(3)
H58	3166(18)	2277(8)	5748(14)	44(5)
H29	1456(17)	5365(8)	2600(11)	32.3(3)
H57	2160(20)	1606(8)	6864(16)	54(6)
H55	-1100(16)	2927(8)	6768(11)	34(4)
H63	5875(15)	4846(8)	3284(10)	27.3(2)

H39	-122(17)	4330(8)	10160(12)	34.8(3)
H42	4403(16)	3328(8)	11416(11)	29.5(3)
H24	816(16)	8210(8)	8683(12)	30.2(3)
H26	3483(17)	7467(8)	6911(11)	31.2(3)
H62	7693(16)	4012(8)	3789(11)	28.7(3)
H41	3075(16)	3940(9)	12424(12)	37.3(3)
H40	887(17)	4405(8)	11894(12)	36.2(3)
H25	3198(18)	8027(8)	8329(12)	35.4(3)
H70a	5000(20)	6458(10)	7913(14)	45.6(4)
H70b	6740(20)	6776(10)	8602(14)	45.6(4)
H70c	4970(20)	7311(10)	8315(14)	45.6(4)
H72a	6600(30)	5392(13)	5286(16)	75(8)
H72b	6500(40)	6250(13)	5686(17)	104(12)
H72c	5210(30)	5677(15)	5652(18)	98(11)
H4a	3761(19)	6959(7)	10280(13)	36(4)
H4b	4788(18)	6573(7)	9535(12)	31(4)
H3	3820(20)	5983(7)	11261(11)	35(4)
H20a	2810(19)	6929(10)	4596(12)	42(5)
H20b	3664(16)	6891(10)	5766(11)	35(5)
H19	559(16)	7123(9)	4998(11)	35(4)
H52a	766(17)	4150(8)	4634(11)	30(4)
H52b	1690(20)	3953(13)	3742(13)	66(7)
H51	2730(17)	3013(8)	4530(12)	31(4)
H35	4330(17)	2788(8)	10087(12)	32(4)
H36a	3140(20)	2272(9)	8626(14)	48(5)
H36b	1922(18)	2968(9)	8407(12)	34(4)



2-(4-bromophenyl)-3-(p-tolyl)butan-1-ol (2.49)



Experimental. Single colorless prism crystals of **2.49** were chosen from the sample as supplied. A suitable crystal with dimensions $0.17 \times 0.13 \times 0.09 \text{ mm}^3$ was selected and mounted on a loop with paratone on a XtaLAB Synergy-S diffractometer. The crystal was kept at a constant $T = 100.02(10) \text{ K}$ during data collection. The structure was solved with the **ShelXT 2014/5** (Sheldrick, 2014) solution program using dual-space methods. The model was refined with **olex2.refine** 1.3-dev (Bourhis et al., 2015) using full matrix least squares minimisation on F^2 .

Crystal Data. $\text{C}_{17}\text{H}_{19}\text{BrO}$, $M_r = 319.243$, trigonal, $P3$ (No. 143), $a = 14.76017(8) \text{ \AA}$, $b = 14.76017(8) \text{ \AA}$, $c = 6.46125(4) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$, $V = 1219.074(12) \text{ \AA}^3$, $T = 100.02(10) \text{ K}$, $Z = 3$, $Z' = 1$, $\mu(\text{Cu K}\alpha) = 3.358 \text{ mm}^{-1}$, 33509 reflections measured, 3211 unique ($R_{\text{int}} = 0.0360$) which were used in all calculations. The final wR_2 was 0.0645 (all data) and R_1 was 0.0250 ($I \geq \sigma(I)$).

$R_1 = 2.50\%$

Compound	2.49
Formula	C ₁₇ H ₁₉ BrO
$D_{calc.}/\text{g cm}^{-3}$	1.305
μ/mm^{-1}	3.358
Formula Weight	319.243
Color	colorless
Shape	prism
Size/mm ³	0.17×0.13×0.09
T/K	100.02(10)
Crystal System	trigonal
Flack Parameter	0.19(3)
Space Group	<i>P</i> 3
$a/\text{\AA}$	14.76017(8)
$b/\text{\AA}$	14.76017(8)
$c/\text{\AA}$	6.46125(4)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	120
$V/\text{\AA}^3$	1219.074(12)
<i>Z</i>	3
<i>Z'</i>	1
Wavelength/ $\text{\AA}$	1.54184
Radiation type	Cu K α
$\theta_{min}/^\circ$	3.46
$\theta_{max}/^\circ$	77.80
Measured Refl's.	33509
Ind't Refl's	3211
Refl's with $I \geq \sigma(I)$	3188
R_{int}	0.0360
Parameters	288
Restraints	326
Largest Peak	0.1564
Deepest Hole	-0.1500
GooF	1.0514
wR_2 (all data)	0.0645
wR_2	0.0642
R_1 (all data)	0.0255
R_1	0.0250

Structure Quality Indicators

Reflections:	d min (Cu)	0.79	I/σ	71.9	Rint	3.60%	complete	100%		
	CIF		CIF		CIF					
Refinement:	Shift	0.006	Max Peak	0.2	Min Peak	-0.1	GooF	1.051	Flack	.19(3)
	CIF		CIF		CIF		CIF		CIF	

A colorless prism-shaped crystal with dimensions $0.17 \times 0.13 \times 0.09 \text{ mm}^3$ was mounted on a loop with paratone oil. Data were collected using a XtaLAB Synergy, Dualflex, HyPix diffractometer equipped with an Oxford Cryosystems low-temperature device operating at $T = 100.02(10) \text{ K}$.

Data were measured using ω scans using Cu $K\alpha$ radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program **CrysAlisPro** (Rigaku, V1.171.40.71a, 2020). The maximum resolution that was achieved was $\Theta = 77.80^\circ$ ($0.83 \text{ \AA}$).

The unit cell was refined using **CrysAlisPro** (Rigaku, V1.171.40.71a, 2020) on 25100 reflections, 75% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using **CrysAlisPro** (Rigaku, V1.171.40.71a, 2020). The final completeness is 100.00 % out to 77.80° in Θ . A numerical absorption correction based on Gaussian integration over a multifaceted crystal model was performed using **CrysAlisPro 1.171.40.71a** (Rigaku Oxford Diffraction, 2020). An empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm was also used. The absorption coefficient μ of this material is 3.358 mm^{-1} at this wavelength ($\lambda = 1.54184 \text{ \AA}$) and the minimum and maximum transmissions are 0.689 and 0.902.

The structure was solved and the space group $P3$ (# 143) determined by the **ShelXT 2014/5** (Sheldrick, 2014) solution program using dual-space methods and refined by full matrix least squares minimisation on F^2 using version of **olex2.refine** 1.3-dev (Bourhis et al., 2015). All non-hydrogen atoms were refined anisotropically. Most hydrogen atom positions were calculated geometrically and refined using the riding model, but some hydrogen atoms were refined freely. [The crystals are twinned and a disordered mixture of the two enantiomers \(the R,S and S,R forms\). There is a slight excess of the RS form. Quantum calculations were done on the disordered crystal fragment. We did a quantum calculation for each disorder component \(one for the R,S form and one for the S,R form\). The program ASPHERA2 calculated scattering factors for both enantiomers and both were used for the refinements. The Flack parameter of 0.19\(3\) indicates racemic twinning. A twin law was not used because twinning and NON-SPHERical atom-form-factors are not currently supported](#)

refine_special_details: Refinement using NoSpherA2, an implementation of NON-SPHERical Atom-form-factors in **Olex2**. Please cite: F. Kleemiss, H. Puschmann, O. Dolomanov, S. Grabowsky - to be published - 2020 NoSpherA2 implementation of HAR makes use of tailor-made aspherical atomic form factors calculated on-the-fly from a Hirshfeld-partitioned electron density (ED) - not from spherical-atom form factors. The ED is calculated from a gaussian basis set single determinant SCF wavefunction - either Hartree-Fock or DFT using selected functionals - for a fragment of the crystal. This fragment can be embedded in an electrostatic crystal field by employing cluster charges. The following options were used: SOFTWARE: ORCA PARTITIONING: NoSpherA2 INT ACCURACY: Normal METHOD: PBE BASIS SET: STO-3G CHARGE: 0 MULTIPLICITY: 1 DATE: 2020-05-07_04-34-04 The crystal is an inversion twin.

Figure S7: Thermal ellipsoid plot of the molecular structure of the R,S enantiomer.

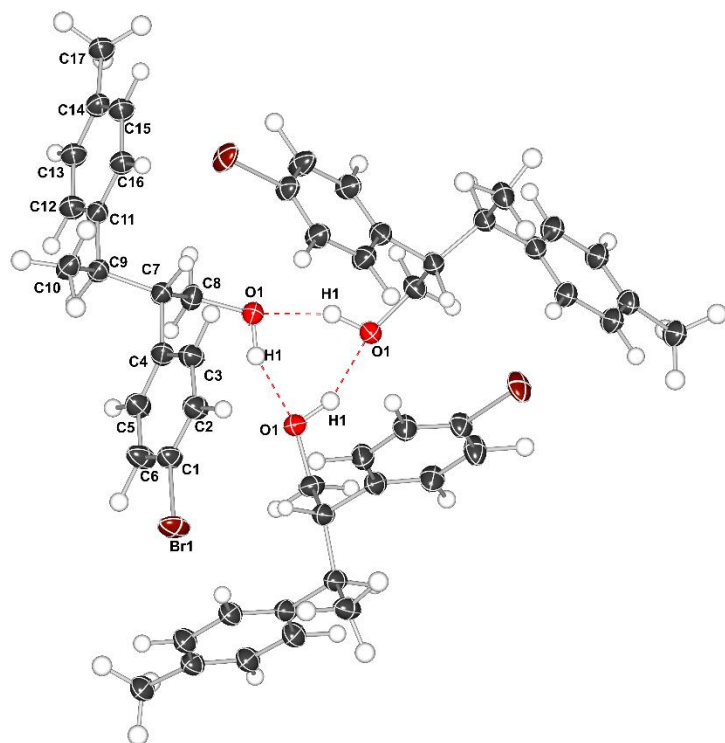
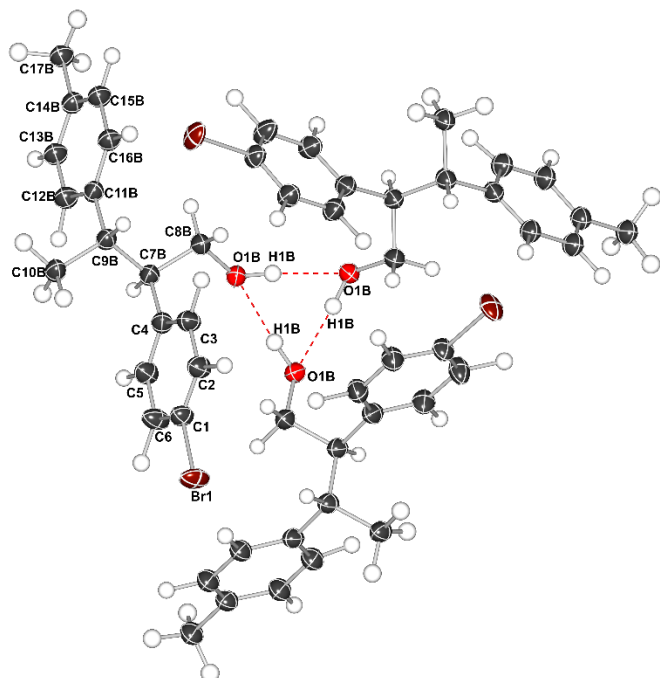


Figure S8: Thermal ellipsoid plot of the molecular structure of the S,R enantiomer.



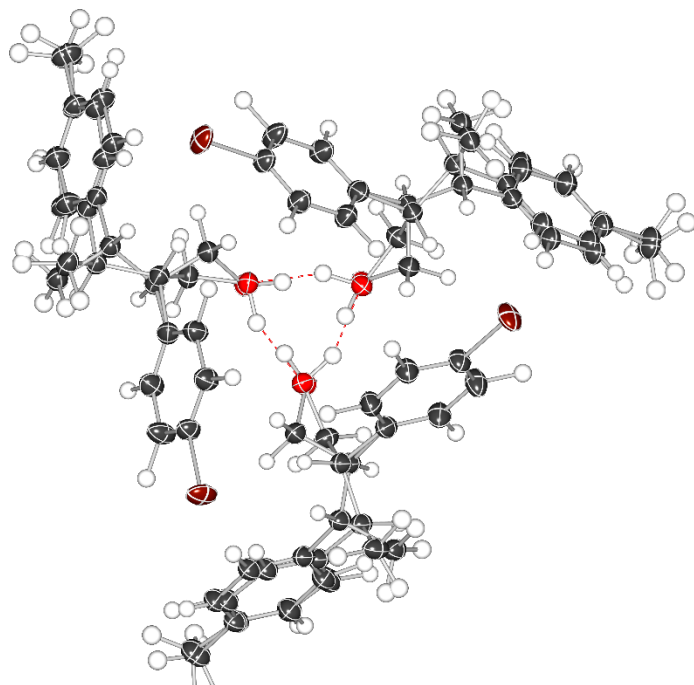
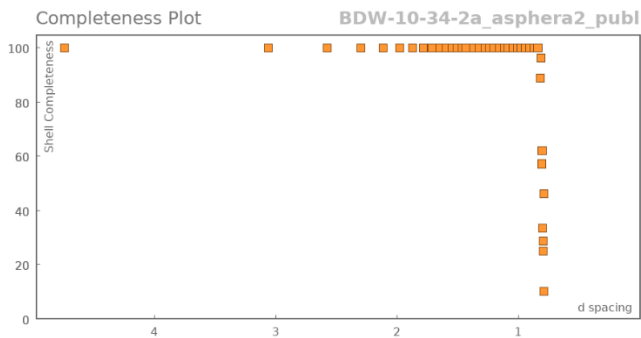
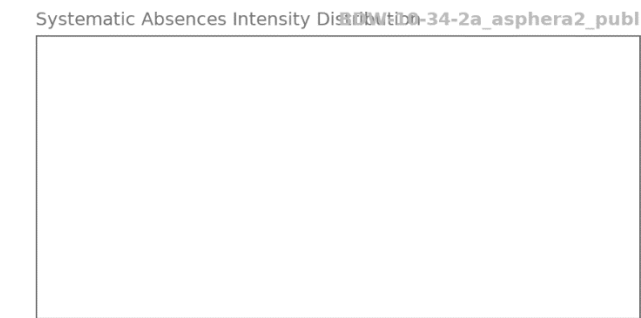
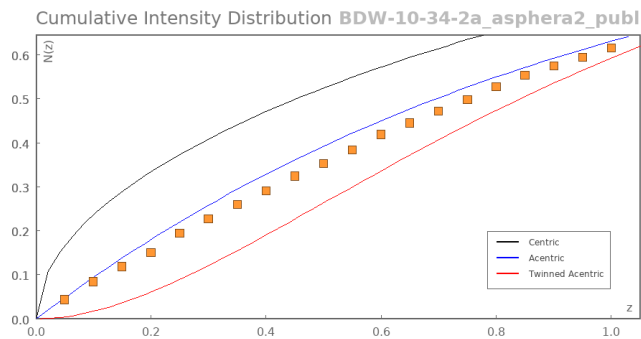
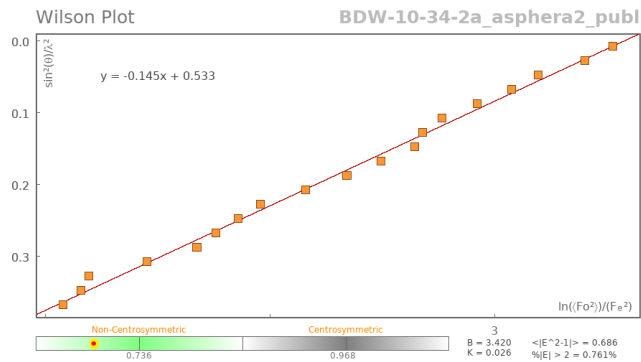


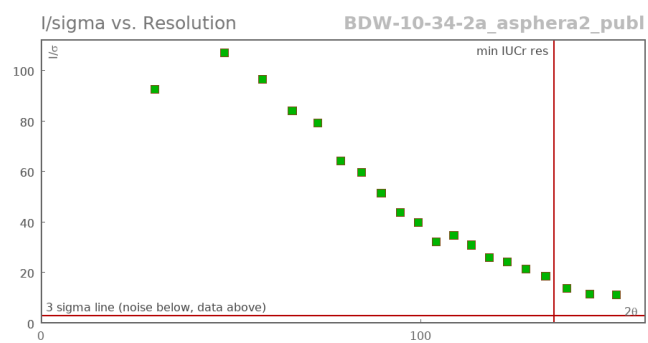
Figure S9: Thermal ellipsoid plot of the asymmetric unit (a mixture of the S,R and of the R,S enantiomers). The OH groups switch positions giving a disorder model that retains the 3-fold symmetry of the crystal.

_refine_special_details: Refinement using NoSpherA2, an implementation of Non-SPHERical Atom-form-factors in **Olex2**. Please cite: F. Kleemiss, H. Puschmann, O. Dolomanov, S. Grabowsky - to be published - 2020 NoSpherA2 implementation of HAR makes use of tailor-made aspherical atomic form factors calculated on-the-fly from a Hirshfeld-partitioned electron density (ED) - not from spherical-atom form factors. The ED is calculated from a gaussian basis set single determinant SCF wavefunction - either Hartree-Fock or DFT using selected functionals - for a fragment of the crystal. This fragment can be embedded in an electrostatic crystal field by employing cluster charges. The following options were used: SOFTWARE: ORCA PARTITIONING: NoSpherA2 INT ACCURACY: Normal METHOD: PBE BASIS SET: STO-3G CHARGE: 0 MULTIPLICITY: 1 DATE: 2020-05-07_04-34-04 The crystal is an inversion twin.

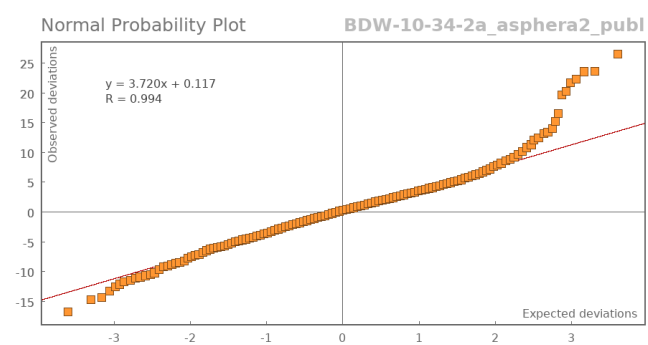
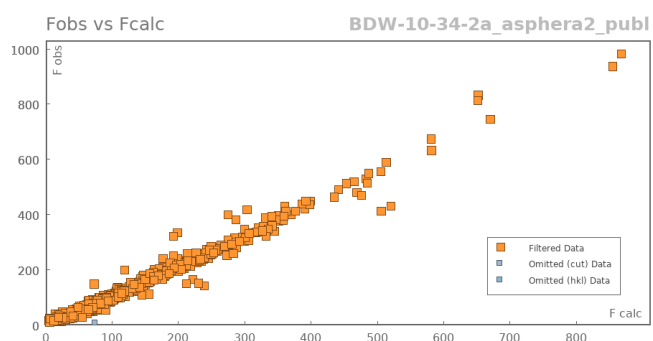
_exptl_absorpt_process_details: **CrysAlisPro** 1.171.40.71a (Rigaku Oxford Diffraction, 2020) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK.

Data Plots: Diffraction Data





Data Plots: Refinement and Data



Reflection Statistics

Total reflections (after filtering)	33509	Unique reflections	3211
Completeness	0.922	Mean I/σ	50.08
$hkl_{\max}$ collected	(18, 18, 8)	$hkl_{\min}$ collected	(-18, -17, -7)
$hkl_{\max}$ used	(9, 18, 8)	$hkl_{\min}$ used	(-18, 0, -7)
Lim $d_{\max}$ collected	100.0	Lim $d_{\min}$ collected	0.77
$d_{\max}$ used	12.78	$d_{\min}$ used	0.79
Friedel pairs	4152	Friedel pairs merged	0
Inconsistent equivalents	21	R_{int}	0.036
R_{sigma}	0.0139	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	1
Multiplicity	(1247, 1679, 1688, 1386, 1040, 751, 544, 293, 138, 76, 23, 13, 1, 1)	Maximum multiplicity	29
Removed systematic absences	0	Filtered off (Shel/OMIT)	0

Table S27: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **2.49**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
Br1	7077.2(4)	9391.8(4)	9727.2(13)	41.0(3)
C1	6379.7(16)	8141.8(16)	8159(4)	33.3(4)
C2	5464.9(17)	7312.0(16)	8934(4)	36.5(4)
C3	4968.0(17)	6390.2(17)	7805(4)	37.7(4)
C4	5359.4(16)	6284.6(16)	5909(4)	34.1(4)
C5	6268.8(16)	7146.3(17)	5168(4)	37.5(5)
C6	6786.1(17)	8070.5(17)	6286(4)	40.8(5)
O1	3626(5)	5771(5)	3282(10)	31.7(5)
C7	4710(5)	5201(5)	4969(8)	30.2(10)
C8	4320(4)	5339(5)	2890(7)	33.5(11)
C9	5368(4)	4654(3)	4752(7)	31.9(6)
C10	5754(6)	4514(5)	6865(8)	37.2(11)
C11	4755(4)	3616(3)	3636(7)	31.1(4)
C12	5053(4)	3466(4)	1645(8)	36.0(5)
C13	4461(5)	2536(5)	581(9)	36.2(5)
C14	3574(12)	1699(9)	1456(18)	33.8(4)
C15	3285(6)	1842(5)	3436(11)	35.7(5)
C16	3855(4)	2785(4)	4486(9)	34.1(5)
C17	2908(11)	712(8)	234(19)	37.3(8)
O1B	3694(3)	5787(3)	2806(5)	31.7(5)
C7B	4870(2)	5318(2)	4533(6)	30.6(6)
C8B	3741(2)	5000(2)	4116(5)	32.4(6)
C9B	4967(2)	4422.6(19)	5573(5)	31.6(5)
C10B	6103(2)	4751(3)	6094(6)	35.6(7)
C11B	4478(2)	3453.4(19)	4217(5)	31.1(4)
C12B	4943(3)	3429(2)	2329(5)	36.0(5)
C13B	4482(3)	2555(3)	1061(6)	36.2(5)
C14B	3536(6)	1673(5)	1594(11)	33.8(4)
C15B	3080(3)	1693(3)	3475(7)	35.7(5)
C16B	3548(2)	2561(2)	4770(6)	34.1(5)

Atom	x	y	z	U_{eq}
C17B	3034(6)	735(5)	179(11)	37.3(8)

Table S28: Anisotropic Displacement Parameters ($\times 10^4$) for **2.49**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	42.4(4)	27.8(4)	40.7(4)	8.5(3)	2.9(3)	-15.4(3)
C1	32.3(10)	28.7(10)	34.8(10)	12.3(8)	-0.8(8)	-9.5(8)
C2	33.6(10)	33.8(10)	38.2(10)	13.9(8)	4.0(8)	-5.5(8)
C3	31.8(10)	30.8(9)	44.9(11)	11.5(8)	1.4(8)	-5.1(8)
C4	30.1(9)	30.4(10)	42.2(11)	15.5(8)	-8.6(8)	-11.0(8)
C5	33.8(10)	36.7(10)	38.9(11)	15.3(8)	2.6(8)	-12.3(8)
C6	34.6(10)	34.2(10)	42.1(12)	8.5(8)	6.6(8)	-11.0(8)
O1	29.8(6)	30.4(6)	37.6(12)	17.2(4)	-2.4(5)	-1.8(6)
C7	29.7(14)	27.8(12)	35.2(11)	16.0(6)	-3.5(5)	-3.0(5)
C8	34.5(15)	37(2)	35.5(12)	22.7(9)	-3.7(5)	-3.0(5)
C9	30.9(9)	29.7(6)	38.2(11)	17.6(4)	-6.8(5)	-6.5(4)
C10	44(2)	34.8(16)	40.1(12)	25.0(8)	-11.5(7)	-8.7(6)
C11	31.0(7)	29.0(5)	36.4(8)	17.4(3)	-6.1(4)	-5.4(4)
C12	35.5(7)	31.6(5)	39.2(9)	15.4(4)	-2.8(5)	-7.6(4)
C13	36.0(7)	31.6(6)	39.3(9)	15.8(4)	-3.3(5)	-7.6(4)
C14	34.2(6)	30.2(5)	38.7(7)	17.4(4)	-4.4(5)	-6.7(4)
C15	35.2(8)	30.7(6)	39.9(7)	15.4(4)	-3.1(5)	-7.9(4)
C16	33.7(8)	29.9(6)	38.6(7)	15.9(4)	-3.6(5)	-6.9(4)
C17	36.8(13)	32.1(6)	41.5(8)	16.0(5)	-3.0(6)	-9.0(4)
O1B	29.8(6)	30.4(6)	37.6(12)	17.2(4)	-2.4(5)	-1.8(6)
C7B	28.5(8)	28.4(7)	36.8(14)	15.6(4)	-4.9(5)	-5.1(5)
C8B	28.3(8)	29.3(8)	40.3(14)	15.1(4)	-4.5(5)	-1.5(6)
C9B	31.6(8)	29.2(6)	36.7(9)	17.2(4)	-6.0(4)	-5.7(4)
C10B	32.4(8)	33.4(10)	44.0(16)	18.8(4)	-8.2(5)	-7.5(7)
C11B	31.0(7)	29.0(5)	36.4(8)	17.4(3)	-6.1(4)	-5.4(4)
C12B	35.5(7)	31.6(5)	39.2(9)	15.4(4)	-2.8(5)	-7.6(4)
C13B	36.0(7)	31.6(6)	39.3(9)	15.8(4)	-3.3(5)	-7.6(4)
C14B	34.2(6)	30.2(5)	38.7(7)	17.4(4)	-4.4(5)	-6.7(4)
C15B	35.2(8)	30.7(6)	39.9(7)	15.4(4)	-3.1(5)	-7.9(4)
C16B	33.7(8)	29.9(6)	38.6(7)	15.9(4)	-3.6(5)	-6.9(4)
C17B	36.8(13)	32.1(6)	41.5(8)	16.0(5)	-3.0(6)	-9.0(4)

Table S29: Bond Lengths in Å for **2.49**.

Atom	Atom	Length/Å
Br1	C1	1.895(2)
C1	C2	1.386(3)
C1	C6	1.378(3)
C2	C3	1.387(3)
C3	C4	1.396(3)
C4	C5	1.393(3)

Atom	Atom	Length/Å
C4	C7	1.521(6)
C4	C7B	1.522(4)
C5	C6	1.387(3)
O1	C8	1.473(3)
C7	C8	1.516(3)
C7	C9	1.549(3)
C9	C10	1.532(3)
C9	C11	1.516(3)
C11	C12	1.412(3)
C11	C16	1.393(3)
C12	C13	1.387(3)
C13	C14	1.394(3)
C14	C15	1.397(3)
C14	C17	1.510(3)
C15	C16	1.391(3)
O1B	C8B	1.467(3)
C7B	C8B	1.512(3)
C7B	C9B	1.552(3)
C9B	C10B	1.532(3)
C9B	C11B	1.517(3)
C11B	C12B	1.409(3)
C11B	C16B	1.392(3)
C12B	C13B	1.386(3)
C13B	C14B	1.395(3)
C14B	C15B	1.397(3)
C14B	C17B	1.509(3)
C15B	C16B	1.391(3)

Table S30: Bond Angles in ° for **2.49**.

Atom	Atom	Atom	Angle/°
C2	C1	Br1	118.82(16)
C6	C1	Br1	119.91(16)
C6	C1	C2	121.26(19)
C3	C2	C1	118.72(19)
C4	C3	C2	121.7(2)
C5	C4	C3	117.60(19)
C7	C4	C3	112.9(3)
C7	C4	C5	129.5(3)
C7B	C4	C3	126.0(2)
C7B	C4	C5	116.4(2)
C7B	C4	C7	13.3(3)
C6	C5	C4	121.6(2)
C5	C6	C1	119.1(2)
C8	C7	C4	107.1(4)
C9	C7	C4	110.8(4)
C9	C7	C8	111.7(4)
C7	C8	O1	107.4(4)
C10	C9	C7	111.2(4)
C11	C9	C7	110.9(3)
C11	C9	C10	111.2(3)
C12	C11	C9	121.0(3)

Atom	Atom	Atom	Angle/°
C16	C11	C9	121.8(3)
C16	C11	C12	117.1(3)
C13	C12	C11	121.0(3)
C14	C13	C12	121.6(4)
C15	C14	C13	117.4(3)
C17	C14	C13	120.8(4)
C17	C14	C15	121.6(4)
C16	C15	C14	121.4(4)
C15	C16	C11	121.4(4)
C8B	C7B	C4	109.1(2)
C9B	C7B	C4	110.0(2)
C9B	C7B	C8B	111.7(2)
C7B	C8B	O1B	109.8(2)
C10B	C9B	C7B	112.2(2)
C11B	C9B	C7B	110.5(2)
C11B	C9B	C10B	110.8(2)
C12B	C11B	C9B	121.0(2)
C16B	C11B	C9B	121.6(2)
C16B	C11B	C12B	117.4(2)
C13B	C12B	C11B	121.1(2)
C14B	C13B	C12B	121.3(3)
C15B	C14B	C13B	117.6(2)
C17B	C14B	C13B	120.7(3)
C17B	C14B	C15B	121.7(3)
C16B	C15B	C14B	121.3(3)
C15B	C16B	C11B	121.2(3)

Table S31: Torsion Angles in ° for **2.49**.

Atom	Atom	Atom	Atom	Angle/°
Br1	C1	C2	C3	-
				178.62(17)
Br1	C1	C6	C5	179.51(19)
C1	C2	C3	C4	-0.7(3)
C1	C6	C5	C4	-1.1(3)
C2	C3	C4	C5	-0.6(3)
C2	C3	C4	C7	178.3(3)
C2	C3	C4	C7B	-179.0(2)
C3	C4	C5	C6	1.6(2)
C3	C4	C7	C8	120.1(3)
C3	C4	C7	C9	-117.8(3)
C3	C4	C7B	C8B	53.4(2)
C3	C4	C7B	C9B	-69.4(3)
C4	C7	C8	O1	-63.8(5)
C4	C7	C9	C10	60.9(5)
C4	C7	C9	C11	-174.8(3)
C4	C7B	C8B	O1B	68.4(3)
C4	C7B	C9B	C10B	-56.1(3)
C4	C7B	C9B	C11B	179.8(2)
O1	C8	C7	C9	174.7(5)
C7	C9	C11	C12	112.5(5)
C7	C9	C11	C16	-65.1(5)

Atom	Atom	Atom	Atom	Angle/°
C9	C11	C12	C13	-176.7(6)
C9	C11	C16	C15	178.8(7)
C11	C12	C13	C14	-2.4(14)
C11	C16	C15	C14	-2.0(15)
C12	C13	C14	C15	1.6(11)
C12	C13	C14	C17	176.9(18)
C13	C14	C15	C16	1(2)
O1B	C8B	C7B	C9B	-169.7(3)
C7B	C9B	C11B	C12B	69.6(3)
C7B	C9B	C11B	C16B	-109.5(3)
C9B	C11B	C12B	C13B	-178.2(3)
C9B	C11B	C16B	C15B	177.1(4)
C11B	C12B	C13B	C14B	0.8(8)
C11B	C16B	C15B	C14B	1.6(8)
C12B	C13B	C14B	C15B	-1.4(6)
C12B	C13B	C14B	C17B	178.9(9)
C13B	C14B	C15B	C16B	0.2(13)

Table S32: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **2.49**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
H2	5090(20)	7410(20)	10380(40)	43.8(5)
H3	4222(13)	5677(14)	8490(40)	45.3(5)
H5	6654(19)	7130(20)	3600(20)	45.0(6)
H6	7590(20)	8820(20)	5750(40)	49.0(6)
H1	4039(10)	6533(6)	3320(140)	47.5(7)
H7	4035(5)	4727(5)	5978(8)	36.2(12)
H8a	3888(4)	4582(5)	2089(7)	40.3(14)
H8b	4982(4)	5878(5)	1911(7)	40.3(14)
H9	6060(4)	5160(3)	3807(7)	38.3(7)
H10a	6090(40)	5253(12)	7730(30)	55.8(17)
H10b	5093(9)	3900(30)	7740(30)	55.8(17)
H10c	6360(30)	4290(40)	6642(8)	55.8(17)
H12	5766(4)	4098(4)	928(8)	43.2(6)
H13	4698(5)	2455(5)	-992(9)	43.4(6)
H15	2593(6)	1196(5)	4179(11)	42.8(6)
H16	3589(4)	2877(4)	6021(9)	40.9(6)
H17a	3000(30)	895(10)	-1429(19)	56.0(12)
H17b	3160(30)	139(16)	570(60)	56.0(12)
H17c	2082(12)	380(20)	680(60)	56.0(12)
H1B	3150(30)	5920(30)	3320(50)	47.5(7)
H7B	5294(2)	5515(2)	3052(6)	36.7(8)
H8Ba	3336(2)	4928(2)	5588(5)	38.8(8)
H8Bb	3345(2)	4235(2)	3337(5)	38.8(8)
H9B	4526(2)	4223.6(19)	7034(5)	37.9(6)
H10d	6599(4)	5117(19)	4729(14)	53.4(10)
H10e	6375(7)	5313(16)	7380(30)	53.4(10)
H10f	6151(4)	4057(4)	6540(40)	53.4(10)
H17d	2850(20)	963(7)	-1315(18)	56.0(12)

Atom	x	y	z	U_{eq}
H17e	3576(10)	437(14)	-70(40)	56.0(12)
H17f	2309(13)	119(9)	890(20)	56.0(12)
H12B	5620(20)	4169(16)	1810(60)	44.8(9)
H13B	4830(30)	2540(30)	-430(30)	44.8(9)
H15B	2338(16)	986(18)	3870(60)	44.8(9)
H16B	3180(30)	2550(30)	6250(30)	44.8(9)

Table S33: Hydrogen Bond information for **2.49**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
O1	H1	O1 ¹	0.9750	1.8284	2.742(10)	155(2)
O1B	H1B	O1B ²	0.9750	1.9394	2.825(5)	150(2)

¹1-y,1+x-y,+z; ²+y-x,1-x,+z

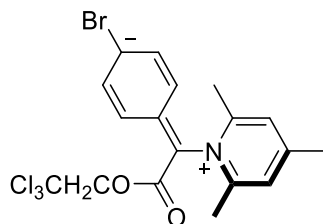
Table S34: Atomic Occupancies for all atoms that are not fully occupied in **2.49**.

Atom	Occupancy
O1	0.351(3)
H1	0.351(3)
C7	0.351(3)
H7	0.351(3)
C8	0.351(3)
H8a	0.351(3)
H8b	0.351(3)
C9	0.351(3)
H9	0.351(3)
C10	0.351(3)
H10a	0.351(3)
H10b	0.351(3)
H10c	0.351(3)
C11	0.351(3)
C12	0.351(3)
H12	0.351(3)
C13	0.351(3)
H13	0.351(3)
C14	0.351(3)
C15	0.351(3)
H15	0.351(3)
C16	0.351(3)
H16	0.351(3)
C17	0.351(3)
H17a	0.351(3)
H17b	0.351(3)
H17c	0.351(3)
O1B	0.649(3)

Atom	Occupancy
H1B	0.649(3)
C7B	0.649(3)
H7B	0.649(3)
C8B	0.649(3)
H8Ba	0.649(3)
H8Bb	0.649(3)
C9B	0.649(3)
H9B	0.649(3)
C10B	0.649(3)
H10d	0.649(3)
H10e	0.649(3)
H10f	0.649(3)
C11B	0.649(3)
C12B	0.649(3)
C13B	0.649(3)
C14B	0.649(3)
C15B	0.649(3)
C16B	0.649(3)
C17B	0.649(3)
H17d	0.649(3)
H17e	0.649(3)
H17f	0.649(3)
H12B	0.649(3)
H13B	0.649(3)
H15B	0.649(3)
H16B	0.649(3)

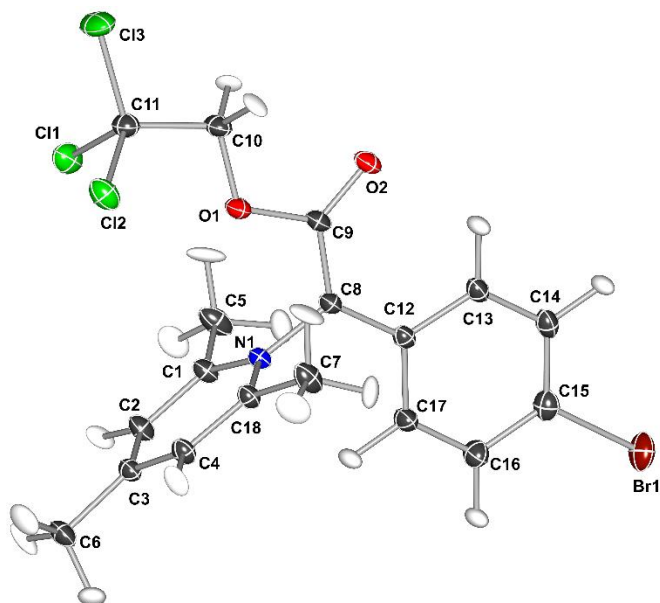
Table S35: Solvent masking (PLATON/SQUEEZE) information for **2.49**.

No	x	y	z	V	e	Content
1	0.000	0.000	-0.175	197.8	15.7	?
2	-0.005	0.506	-0.012	12.9	0.0	?
3	0.040	0.640	0.083	0.0	0.0	?
4	0.173	0.627	0.694	0.0	0.0	?
5	0.333	0.667	-0.198	28.1	2.4	?
6	0.240	0.200	0.167	0.0	0.0	?
7	0.494	0.489	0.988	12.9	0.0	?
8	0.511	0.005	-0.012	12.9	0.0	?
9	0.667	0.333	-0.018	40.9	0.0	?
10	0.667	0.560	0.028	0.0	0.0	?
11	0.747	0.733	0.333	0.0	0.0	?



1-bromo-4-(2-oxo-2-(2,2,2-trichloroethoxy)-1-(2,4,6-trimethylpyridin-1-ium-1-yl)ethylidene)cyclohexa-2,5-dien-1-ide (3.105)

$R_1=1.97\%$



Experimental. Single reddish orange needle crystals of **3.105** recrystallised from ethanol by slow evaporation. A suitable crystal with dimensions $0.68 \times 0.41 \times 0.32 \text{ mm}^3$ was selected and mounted on a loop with paratone on a XtaLAB Synergy-S diffractometer. The crystal was kept at a steady $T = 100.0(1) \text{ K}$ during data collection. The structure was solved with the ShelXT 2018/2 (Sheldrick, 2018) solution program using dual methods and by using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with olex2.refine 1.3-dev (Bourhis et al., 2015) using full matrix least squares minimisation on F^2 .

Crystal Data. $\text{C}_{18}\text{H}_{17}\text{BrCl}_3\text{NO}_2$, $M_r = 465.602$, orthorhombic, $P2_12_12_1$ (No. 19), $a = 11.4016(2) \text{ \AA}$, $b = 11.4410(1) \text{ \AA}$, $c = 14.9264(2) \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 1947.08(5) \text{ \AA}^3$, $T = 100.01(10) \text{ K}$, $Z = 4$, $Z' = 1$, $\mu(\text{Mo K}\alpha) = 2.534 \text{ mm}^{-1}$, 64444 reflections measured, 10151 unique ($R_{\text{int}} = 0.0336$) which were used in all calculations. The final wR_2 was 0.0320 (all data) and R_1 was 0.0197 ($I \geq 2 \sigma(I)$).

Compound	3.105
Formula	C ₁₈ H ₁₇ BrCl ₃ NO ₂
$D_{\text{calc.}}/\text{g cm}^{-3}$	1.588
μ/mm^{-1}	2.534
Formula Weight	465.602
Color	reddish orange
Shape	needle
Size/mm ³	0.68×0.41×0.32
T/K	100.01(10)
Crystal System	orthorhombic
Flack Parameter	0.016(3)
Hooft Parameter	-0.0002(12)
Space Group	$P2_12_12_1$
$a/\text{\AA}$	11.4016(2)
$b/\text{\AA}$	11.4410(1)
$c/\text{\AA}$	14.9264(2)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
$V/\text{\AA}^3$	1947.08(5)
Z	4
Z'	1
Wavelength/ $\text{\AA}$	0.71073
Radiation type	Mo K α
$\theta_{\text{min}}/^\circ$	2.24
$\theta_{\text{max}}/^\circ$	38.14
Measured Refl's.	64444
Indep't Refl's	10151
Refl's $I \geq 2 \sigma(I)$	9068
R_{int}	0.0336
Parameters	511
Restraints	9
Largest Peak	0.3944
Deepest Hole	-0.3923
GooF	1.0476
wR_2 (all data)	0.0320
wR_2	0.0309
R_1 (all data)	0.0270
R_1	0.0197

Structure Quality Indicators

Reflections:	d min (Mo)	0.58	I/σ(I)	43.0	Rint	3.37%	complete 100% (IUCr)	100%		
Refinement:	Shift	0.009	Max Peak	0.4	Min Peak	-0.4	GooF	1.048	Flack	.016(3)

A reddish orange needle-shaped crystal with dimensions $0.68 \times 0.41 \times 0.32 \text{ mm}^3$ was mounted on a loop with paratone. Data were collected using a XtaLAB Synergy, Dualflex, HyPix diffractometer equipped with an Oxford Cryosystems low-temperature device operating at $T = 100.01(10) \text{ K}$.

Data were measured using ω scans using Mo K_{α} radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.40.67a, 2019). The maximum resolution that was achieved was $\Theta = 38.14^{\circ}$ (0.58 Å).

The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.40.67a, 2019). The unit cell was refined using CrysAlisPro (Rigaku, V1.171.40.67a, 2019) on 32333 reflections, 50% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro (Rigaku, V1.171.40.67a, 2019). The final completeness is 99.95 % out to 38.14° in Θ . A numerical absorption correction based on a Gaussian integration over a multifaceted crystal model absorption correction was performed using CrysAlisPro 1.171.39.33a (Rigaku Oxford Diffraction, 2020). An empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm was also applied. The absorption coefficient μ of this material is 2.534 mm^{-1} at this wavelength ($\lambda = 0.71073 \text{ Å}$) and the minimum and maximum transmissions are 0.222 and 1.000.

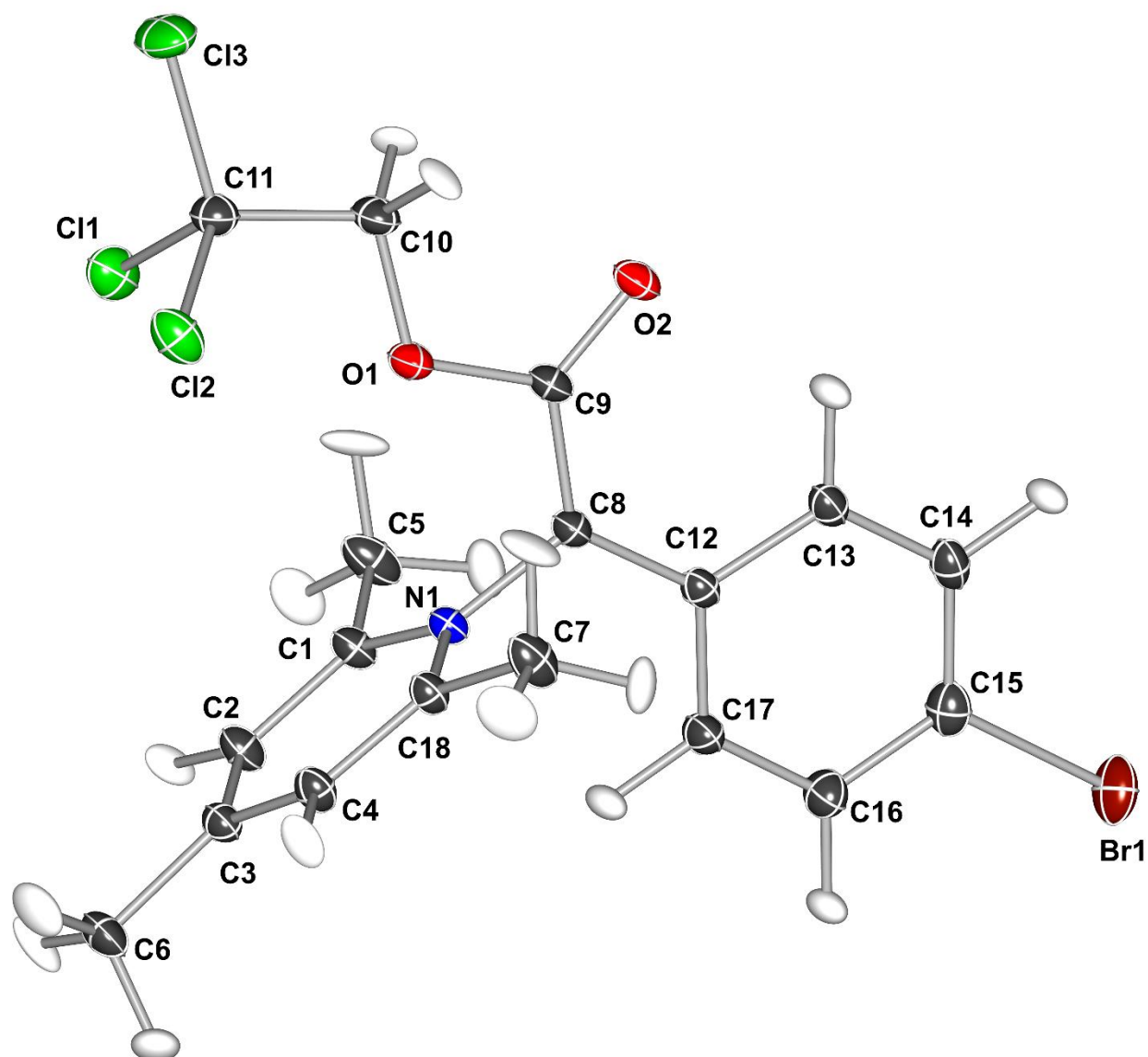
The structure was solved and the space group $P2_12_12_1$ (# 19) determined by the ShelXT 2018/2 (Sheldrick, 2018) structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version of olex2.refine 1.3-dev (Bourhis et al., 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_refine_special_details: Refinement using NoSpherA2, an implementation of NOn-SPHERical Atom-form-factors in Olex2. Please cite: F. Kleemiss, H. Puschmann, O. Dolomanov, S. Grabowsky - to be published - 2020. NoSpherA2 implementation of HAR makes use of tailor-made aspherical atomic form factors calculated on-the-fly from a Hirshfeld-partitioned electron density (ED) - not from spherical-atom form factors. The ED is calculated from a gaussian basis set single determinant SCF wavefunction - either Hartree-Fock or DFT using selected functionals - for a fragment of the crystal. This fragment can be embedded in an electrostatic crystal field by employing cluster charges. The following options were used: SOFTWARE: ORCA PARTITIONING: NoSpherA2 INT ACCURACY: Normal METHOD: PBE BASIS SET: def2-TZVP CHARGE: 0 MULTIPLICITY: 1 DATE: 2020-06-20_22-27-17

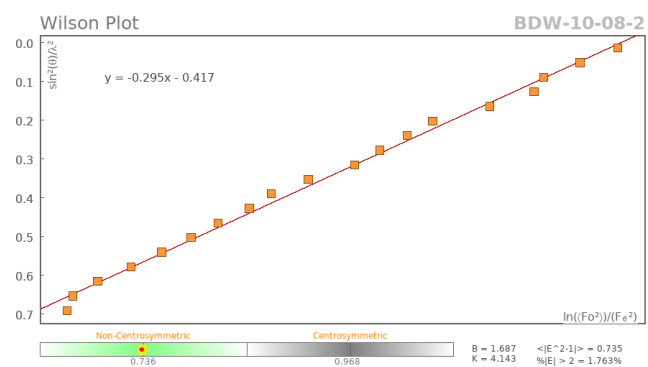
There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

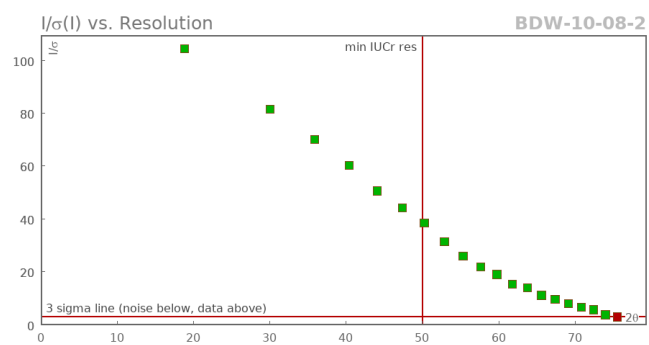
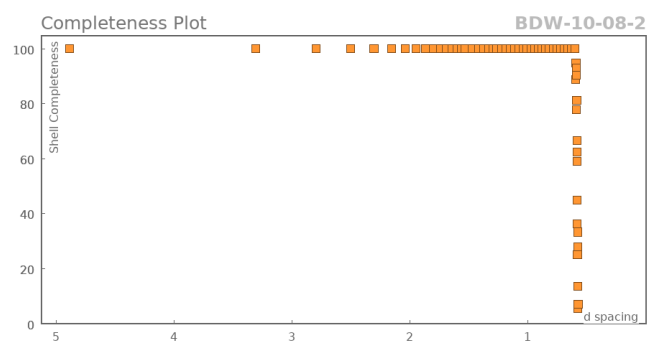
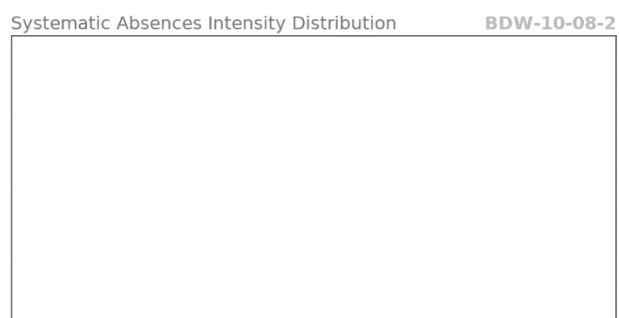
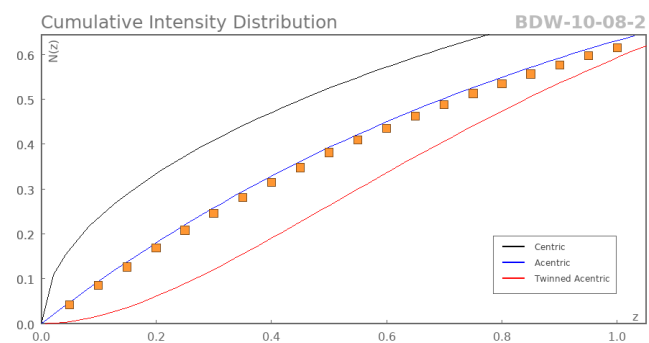
The Flack parameter was refined to 0.016(3). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in -0.0002(12). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that 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 2:

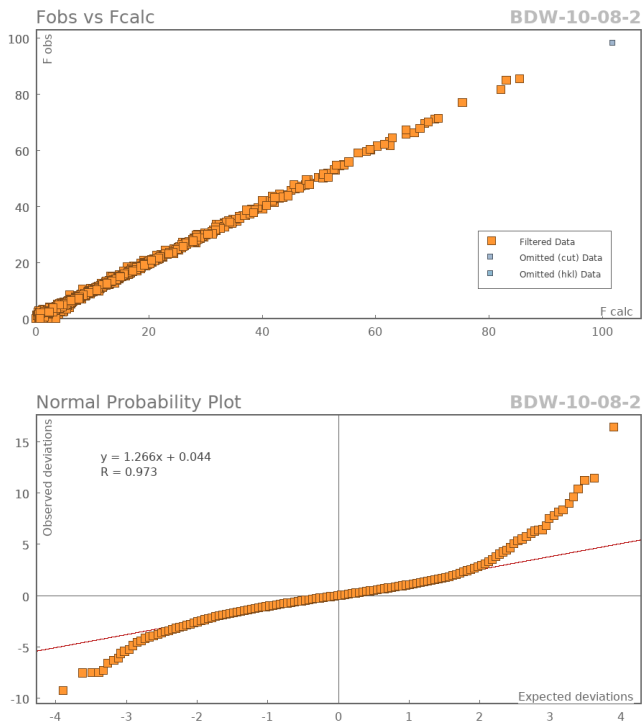


Data Plots: Diffraction Data





Data Plots: Refinement and Data



Reflection Statistics

Total reflections (after filtering)	64444	Unique reflections	10151
Completeness	0.949	Mean I/σ	32.7
$hkl_{\max}$ collected	(19, 19, 25)	$hkl_{\min}$ collected	(-18, -19, -25)
$hkl_{\max}$ used	(19, 19, 25)	$hkl_{\min}$ used	(-19, 0, 0)
Lim $d_{\max}$ collected	100.0	Lim $d_{\min}$ collected	0.36
$d_{\max}$ used	9.08	$d_{\min}$ used	0.58
Friedel pairs	14467	Friedel pairs merged	0
Inconsistent equivalents	0	R_{int}	0.0337
R_{sigma}	0.0232	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	9
Multiplicity	(14624, 10949, 5667, 1459, 668, 194, 75, 7)	Maximum multiplicity	23
Removed systematic absences	0	Filtered off (Shel/OMIT)	0

Images of the Crystal on the Diffractometer



Table 8: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **3.105**. U_{eq} is defined as $1/3$ of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
Br1	4340.22(19)	8308.29(14)	4507.44(11)	26.35(6)
Cl1	2526.4(4)	-602.3(4)	6265.6(3)	24.76(10)
Cl2	2816.0(4)	11.7(4)	8119.7(3)	24.21(10)
Cl3	544.7(4)	-734.1(4)	7491.4(3)	31.20(12)
O2	1409.5(4)	3461.1(5)	6438.3(4)	20.19(10)
O1	2525.9(5)	1886.4(4)	6795.9(4)	20.41(10)
N1	4497.7(5)	2769.1(5)	6389.6(4)	13.34(10)
C2	5920.8(6)	1451.2(6)	5812.5(5)	17.25(13)
C16	4992.1(7)	6069.7(7)	5176.8(5)	20.07(14)
C13	2742.4(6)	5447.6(6)	5716.9(5)	16.93(12)
C4	6033.0(6)	2089.8(6)	7330.2(5)	16.31(12)
C3	6514.8(6)	1447.9(6)	6626.6(5)	15.24(12)
C18	5036.3(6)	2757.3(6)	7206.8(4)	14.66(12)
C8	3477.0(6)	3507.0(6)	6254.5(5)	14.75(11)
C14	2939.1(7)	6520.6(6)	5310.6(5)	18.93(13)
C9	2396.2(6)	3021.5(6)	6483.6(4)	15.28(12)
C12	3664.4(6)	4637.7(6)	5856.7(4)	14.39(12)
C17	4789.7(6)	4986.6(6)	5569.0(5)	17.88(12)
C10	1476.8(6)	1293.7(7)	6990.4(5)	18.52(13)
C15	4063.9(15)	6833.4(13)	5047.2(10)	20.2(4)
C5	4206.1(7)	2048.9(8)	4855.5(5)	23.52(15)
C1	4899.3(6)	2093.9(6)	5702.1(4)	15.45(12)
C7	4529.5(7)	3476.7(7)	7942.7(5)	22.57(15)
C6	7638.9(7)	787.8(7)	6756.9(5)	20.86(14)
C11	1822.3(14)	43.7(14)	7205.1(10)	18.5(3)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	40.01(13)	19.23(9)	19.81(9)	3.87(9)	0.86(8)	6.62(7)
Cl1	24.6(2)	26.8(2)	22.9(2)	1.33(19)	-1.35(19)	-7.16(18)
Cl2	23.3(2)	30.2(2)	19.2(2)	6.9(2)	-3.36(17)	0.06(18)
Cl3	19.6(2)	30.7(2)	43.3(3)	-7.0(2)	2.4(2)	13.8(2)
O2	11.8(2)	23.1(3)	25.7(2)	3.59(19)	1.36(18)	1.1(2)
O1	11.5(2)	19.8(2)	30.0(3)	0.60(18)	1.7(2)	4.7(2)
N1	11.1(2)	14.9(2)	14.0(2)	1.45(19)	-0.47(18)	0.36(18)
C2	15.0(3)	21.1(3)	15.6(3)	5.0(2)	0.4(2)	-1.0(2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C16	20.1(4)	18.7(3)	21.3(3)	1.0(3)	1.9(3)	4.9(3)
C13	14.7(3)	16.6(3)	19.5(3)	3.4(2)	-3.2(2)	-1.9(2)
C4	15.6(3)	18.0(3)	15.4(3)	3.1(2)	-3.2(2)	0.1(2)
C3	12.7(3)	15.9(3)	17.2(3)	2.2(2)	0.1(2)	2.4(2)
C18	13.8(3)	15.9(3)	14.3(3)	2.4(2)	-1.5(2)	-0.7(2)
C8	11.5(3)	15.5(3)	17.2(3)	1.4(2)	-0.3(2)	0.5(2)
C14	20.4(3)	16.8(3)	19.6(3)	5.1(2)	-4.6(2)	-0.5(2)
C9	10.6(3)	18.5(3)	16.7(3)	1.9(2)	0.5(2)	-0.2(2)
C12	12.8(3)	15.6(3)	14.7(3)	1.8(2)	-2.1(2)	-0.5(2)
C17	14.2(3)	17.6(3)	21.9(3)	1.7(2)	-0.3(2)	3.9(3)
C10	12.0(3)	22.1(3)	21.5(3)	0.3(2)	1.7(2)	3.6(3)
C15	25.3(9)	18.8(9)	16.4(8)	2.0(7)	-3.4(7)	1.8(6)
C5	18.6(4)	35.9(4)	16.1(3)	7.5(3)	-3.6(3)	-5.7(3)
C1	12.9(3)	19.9(3)	13.5(3)	3.2(2)	-0.6(2)	-0.9(2)
C7	22.0(4)	27.3(4)	18.5(3)	7.1(3)	-2.8(3)	-7.1(3)
C6	15.5(3)	23.7(3)	23.4(3)	6.7(3)	0.6(3)	3.7(3)
C11	15.0(8)	20.7(8)	19.8(8)	-1.1(7)	0.3(7)	2.6(7)
H13	22(3)	41(4)	74(5)	5(3)	3(3)	20(3)
H16	22(3)	41(4)	74(5)	5(3)	3(3)	20(3)
H17	22(3)	41(4)	74(5)	5(3)	3(3)	20(3)
H14	22(3)	41(4)	74(5)	5(3)	3(3)	20(3)
H10a	25(7)	50(7)	44(7)	16(6)	22(6)	16(7)
H5a	59(10)	77(10)	36(8)	19(8)	-17(7)	-28(8)
H10b	19(6)	46(7)	42(7)	-4(5)	-19(6)	8(6)
H7a	19(7)	88(11)	58(9)	10(8)	10(6)	-20(9)
H4	48(8)	53(8)	20(6)	23(7)	-18(6)	-3(6)
H5b	16(7)	103(13)	47(9)	-13(8)	-3(7)	-22(9)
H2	28(7)	62(8)	35(6)	11(5)	4(4)	-26(3)
H7b	69(11)	21(6)	45(8)	8(7)	1(8)	-2(6)
H6a	45(9)	71(9)	29(7)	38(7)	-5(6)	-20(7)
H7c	58(10)	88(11)	36(8)	11(9)	-30(7)	-17(8)
H6b	25(8)	50(9)	90(12)	-6(7)	-13(8)	3(8)
H5c	66(11)	42(8)	59(10)	19(8)	-11(9)	-1(8)
H6c	48(10)	68(10)	65(11)	23(8)	0(9)	38(9)

Table 9: Bond Lengths in Å for **3.105**.

Atom	Atom	Atom	Angle/°
C10	O1	C9	115.48(6)
C8	N1	C18	119.35(5)
C1	N1	C18	121.03(6)
C1	N1	C8	119.62(5)
C1	C2	C3	120.92(6)
C15	C16	C17	119.61(9)
C12	C13	C14	121.54(7)
C18	C4	C3	120.99(6)
C4	C3	C2	117.69(6)
C6	C3	C2	122.04(6)
C6	C3	C4	120.27(6)
C4	C18	N1	119.63(6)
C7	C18	N1	118.61(6)

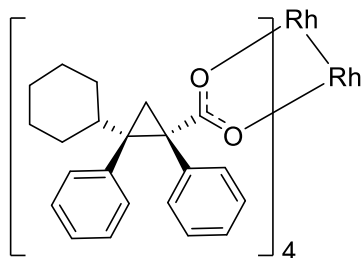
Atom	Atom	Atom	Angle/°
C7	C18	C4	121.77(6)
C9	C8	N1	116.27(6)
C12	C8	N1	117.45(6)
C12	C8	C9	126.19(6)
C15	C14	C13	120.08(9)
O1	C9	O2	119.80(6)
C8	C9	O2	129.04(6)
C8	C9	O1	111.16(6)
C8	C12	C13	122.58(6)
C17	C12	C13	116.42(6)
C17	C12	C8	120.99(6)
C12	C17	C16	122.11(6)
C11	C10	O1	106.10(8)
C16	C15	Br1	119.56(11)
C14	C15	Br1	120.21(10)
C14	C15	C16	120.22(12)
C2	C1	N1	119.53(6)
C5	C1	N1	118.63(6)
C5	C1	C2	121.82(6)
Cl2	C11	Cl1	108.06(9)
Cl3	C11	Cl1	110.81(9)
Cl3	C11	Cl2	109.35(8)
C10	C11	Cl1	110.03(9)
C10	C11	Cl2	110.35(10)
C10	C11	Cl3	108.24(10)

Table 10: Torsion Angles in ° for **3.105**.

Atom	Atom	Atom	Atom	Angle/°
Br1	C15	C16	C17	-179.74(7)
Br1	C15	C14	C13	-179.08(7)
Cl1	C11	C10	O1	-60.69(9)
Cl2	C11	C10	O1	58.47(9)
Cl3	C11	C10	O1	178.09(7)
O2	C9	O1	C10	3.71(8)
O2	C9	C8	N1	179.60(7)
O2	C9	C8	C12	-3.89(10)
O1	C9	C8	N1	-0.65(6)
O1	C9	C8	C12	175.87(5)
N1	C18	C4	C3	1.52(8)
N1	C8	C12	C13	-178.04(6)
N1	C8	C12	C17	3.12(7)
N1	C1	C2	C3	2.67(8)
C2	C3	C4	C18	-3.54(8)
C16	C17	C12	C13	0.59(8)
C16	C17	C12	C8	179.50(7)
C16	C15	C14	C13	0.93(15)
C13	C12	C8	C9	5.48(8)

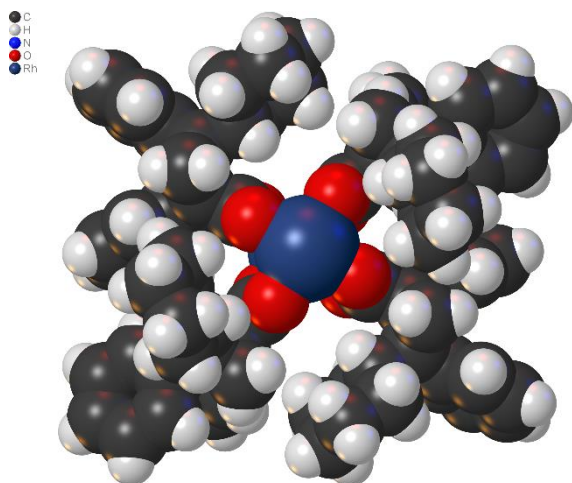
Table 11: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **3.105**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
H13	1854(4)	5210(10)	5936(8)	45.7(17)
H16	5866(5)	6332(10)	4937(8)	45.7(17)
H17	5533(7)	4387(8)	5667(9)	45.7(17)
H14	2203(7)	7124(8)	5200(9)	45.7(17)
H10a	1032(9)	1704(9)	7567(5)	40(3)
H5a	4669(13)	1565(13)	4371(8)	57(4)
H10b	876(8)	1278(10)	6411(5)	36(3)
H7a	3668(11)	3209(14)	8092(9)	55(4)
H4	6440(11)	2095(11)	7982(7)	40(3)
H5b	3339(11)	1659(14)	5009(9)	55(4)
H2	6225(10)	937(12)	5243(8)	42(3)
H7b	4489(13)	4371(10)	7739(9)	45(4)
H6a	7879(11)	292(11)	6195(8)	48(4)
H7c	4980(12)	3386(14)	8538(8)	61(4)
H6b	8373(12)	1422(12)	6915(10)	55(4)
H5c	4028(14)	2952(12)	4601(9)	56(4)
H6c	7577(13)	208(13)	7330(10)	60(5)



Dirhodium tetrakis ((1*R*,2*S*)-2-cyclohexyl-1,2-diphenylcyclopropane-1-carboxylic acid)

(4.4)



Experimental. Single violet irregular-shaped crystals of **4.4** were recrystallized from a mixture of acetonitrile and hexane by vapor diffusion. A suitable crystal $0.17 \times 0.11 \times 0.07$ mm³ was selected and mounted on a loop with paratone oil on an XtaLAB Synergy-S diffractometer with a HyPix detector. The crystal was cooled to $T = 99.98(10)$ K during data collection. The structure was solved with the **ShelXT** (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 2017/1 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. C₁₈₆H₁₉₉N₅O₁₆Rh₄, $M_r = 3172.13$, monoclinic, $P2_1$ (No. 4), $a = 15.39460(15)$ Å, $b = 31.2851(3)$ Å, $c = 16.88533(19)$ Å, $\beta = 90.7110(10)^\circ$, $\alpha = \gamma = 90^\circ$, $V = 8131.71(15)$ Å³, $T = 99.98(10)$ K, $Z = 2$, $Z' = 1$, $\mu(\text{CuK}\alpha) = 3.733$ mm⁻¹, 56521 reflections measured, 24231 unique ($R_{\text{int}} = 0.0689$) which were used in all calculations. The final wR_2 was 0.1841 (all data) and R_1 was 0.0692 ($I > 2\sigma(I)$).

Compound	4.4
Formula	C ₁₈₆ H ₁₉₉ N ₅ O ₁₆ Rh ₄
$D_{calc.}/\text{g cm}^{-3}$	1.296
μ/mm^{-1}	3.733
Formula Weight	3172.13
Color	violet
Shape	irregular
Size/mm ³	0.17×0.11×0.07
T/K	99.98(10)
Crystal System	monoclinic
Flack Parameter	0.018(10)
Hooft Parameter	0.013(4)
Space Group	$P2_1$
$a/\text{\AA}$	15.39460(15)
$b/\text{\AA}$	31.2851(3)
$c/\text{\AA}$	16.88533(19)
$\alpha/^\circ$	90
$\beta/^\circ$	90.7110(10)
$\gamma/^\circ$	90
$V/\text{\AA}^3$	8131.71(15)
Z	2
Z'	1
Wavelength/ $\text{\AA}$	1.54184
Radiation type	CuK α
$\theta_{min}/^\circ$	2.825
$\theta_{max}/^\circ$	65.823
Measured Refl.	56521
Independent Refl.	24231
Reflections with $I > 2\sigma(I)$	22106
R_{int}	0.0689
Parameters	1901
Restraints	3374
Largest Peak	2.132
Deepest Hole	-0.808
GooF	1.040
wR_2 (all data)	0.1841
wR_2	0.1768
R_1 (all data)	0.0748
R_1	0.0692

Structure Quality Indicators

Reflections: $d \min (\text{Cu})$ 0.85 I/σ 10.5 R_{int} 6.89%

Refinement: Shift 0.009 Max Peak 2.1 Min Peak -0.8 GooF 1.040 0.001(11)

A violet irregular-shaped crystal with dimensions 0.17×0.11×0.07 mm³ was mounted on a loop with paratone oil. Data were collected using an XtaLAB Synergy, Dualflex, HyPix diffractometer equipped with an Oxford Cryosystems low-temperature device, operating at $T = 99.98(10)$ K.

Data were measured using ω scans of $1/2^\circ$ per frame for s using $\text{CuK}\alpha$ radiation (micro-focus sealed X-ray tube, 50 kV, 1.0 mA). The total number of runs and images was based on the strategy calculation from the program **CrysAlisPro** (Rigaku, V1.171.39.33a, 2017). The maximum resolution that was achieved was $\theta = 65.823^\circ$.

The diffraction patterns were indexed using **CrysAlisPro** (Rigaku, V1.171.39.33a, 2017) and the unit cells were refined using **CrysAlisPro** (Rigaku, V1.171.39.33a, 2017) on 32809 reflections, 58 % of the observed reflections. Data reduction, scaling and absorption corrections were performed using **CrysAlisPro** (Rigaku, V1.171.39.33a, 2017) and CrysAlisPro 1.171.39.33a (Rigaku Oxford Diffraction, 2017). A numerical absorption correction based on a Gaussian integration over a multifaceted crystal model absorption correction was performed using CrysAlisPro 1.171.39.33a (Rigaku Oxford Diffraction, 2020). An empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm was also applied. The absorption coefficient μ of this material is 3.733 mm^{-1} at this wavelength ($\lambda = 1.54184 \text{ \AA}$) and the minimum and maximum transmissions are 0.639 and 0.986.

The structure was solved and the space group $P2_1$ (# 4) determined by the **ShelXT** (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2017/1 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

There are two Rh_2 molecules in the asymmetric unit and an acetonitrile molecule of crystallization, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

The Flack parameter was refined to 0.018(10). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in 0.013(4). 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 3:

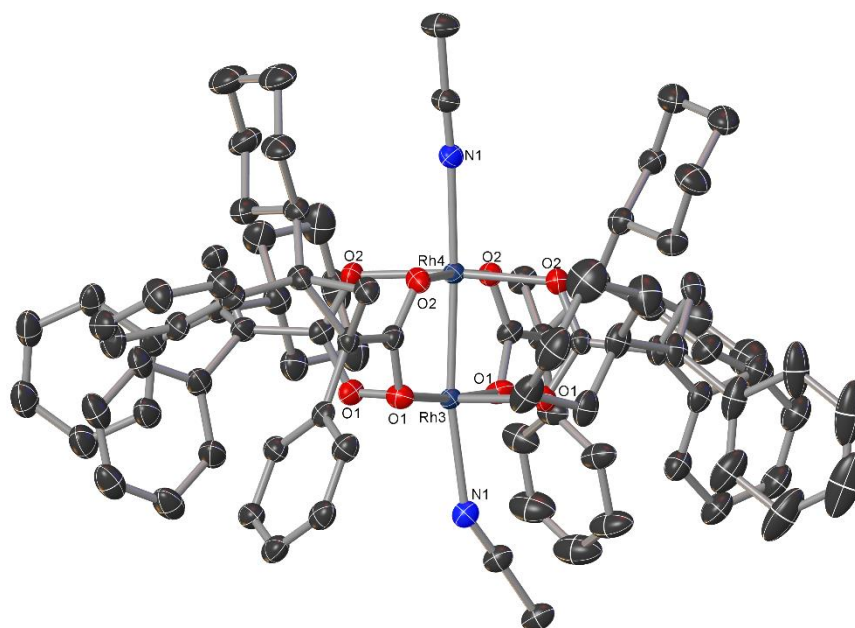


Figure 4:

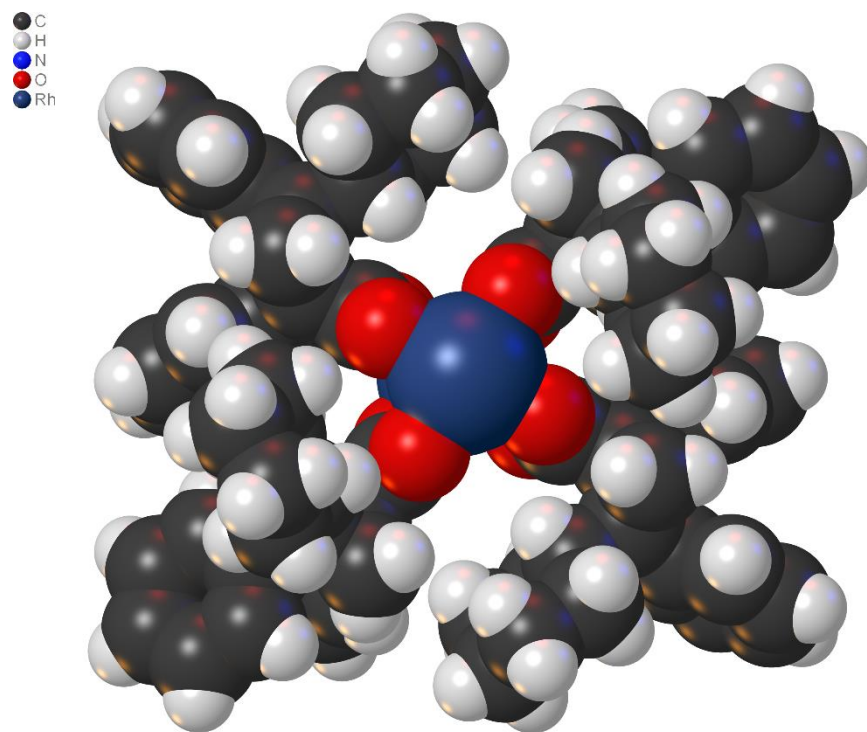


Figure 5:

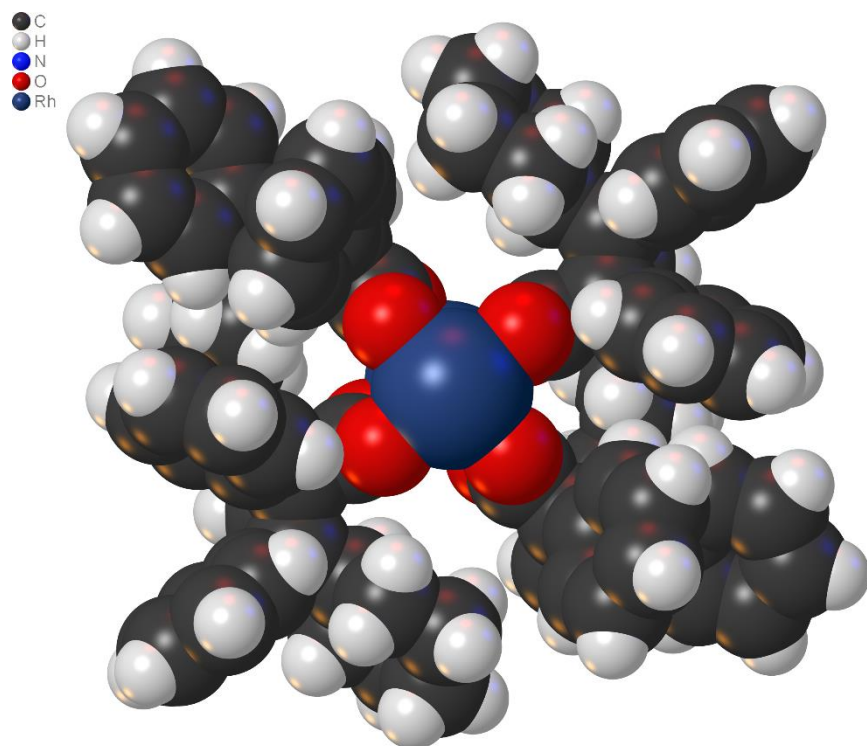


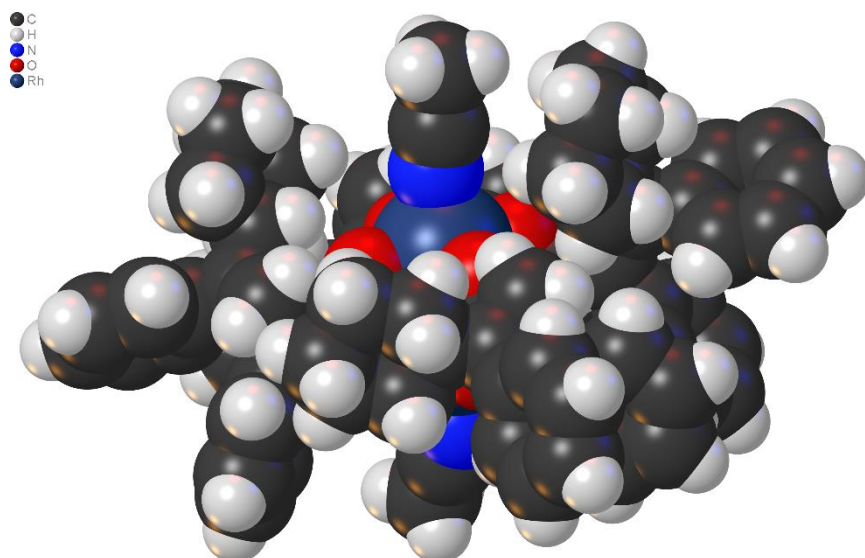
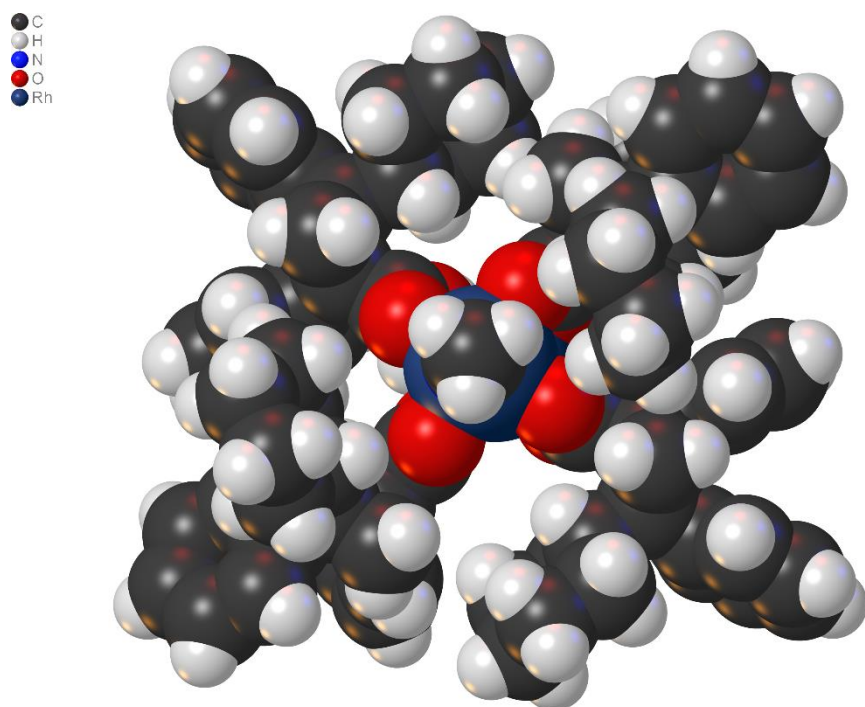
Figure 6:**Figure 7:**

Figure 8:

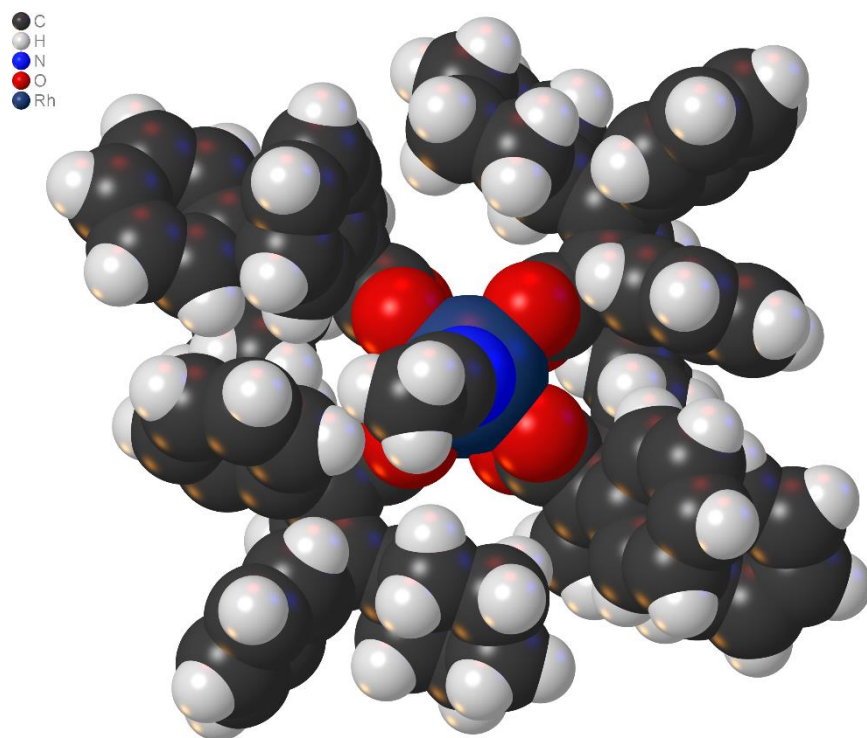


Figure 9:

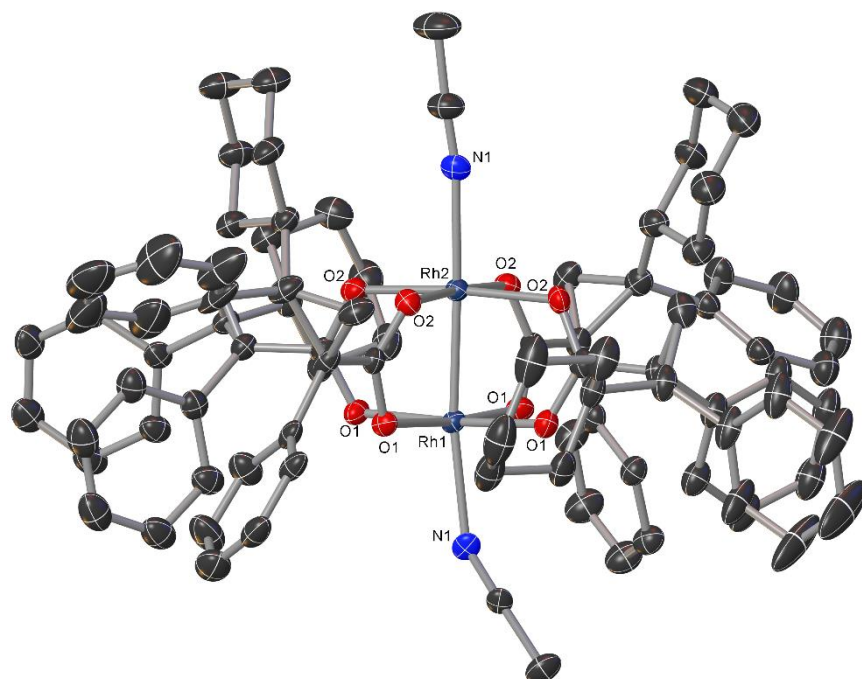


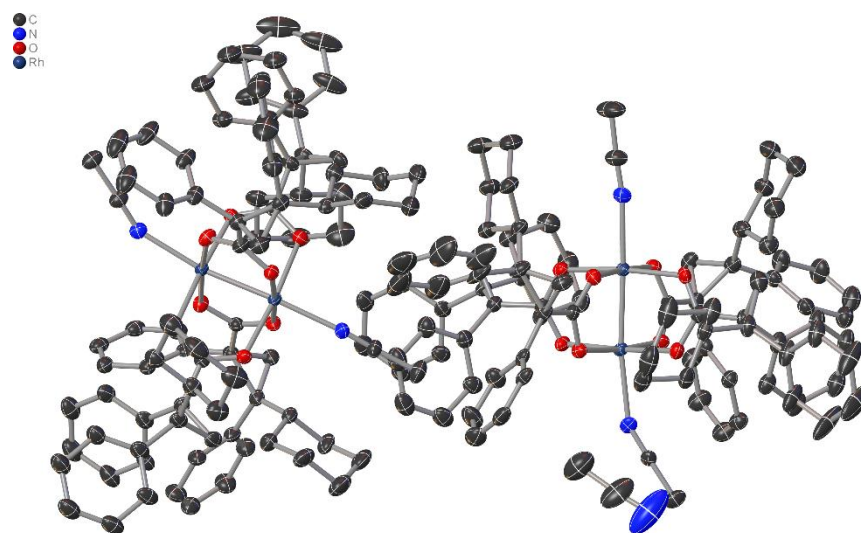
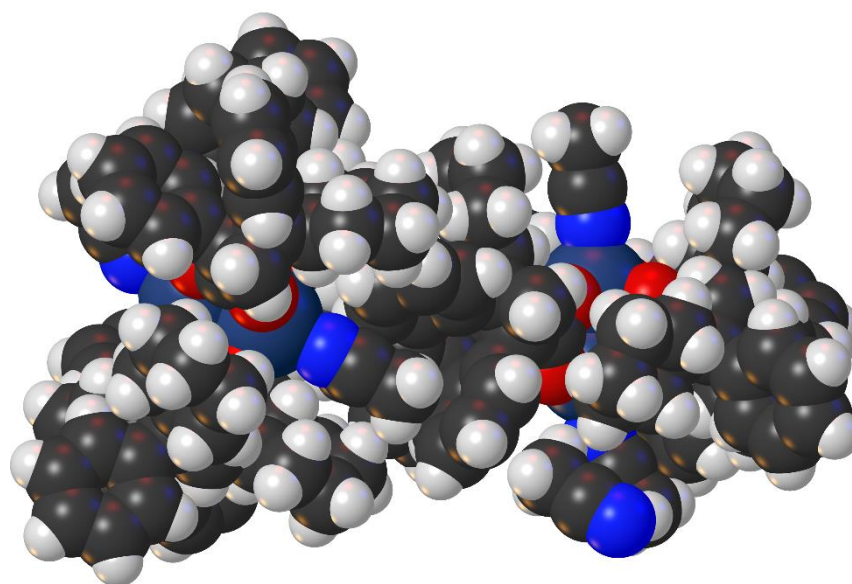
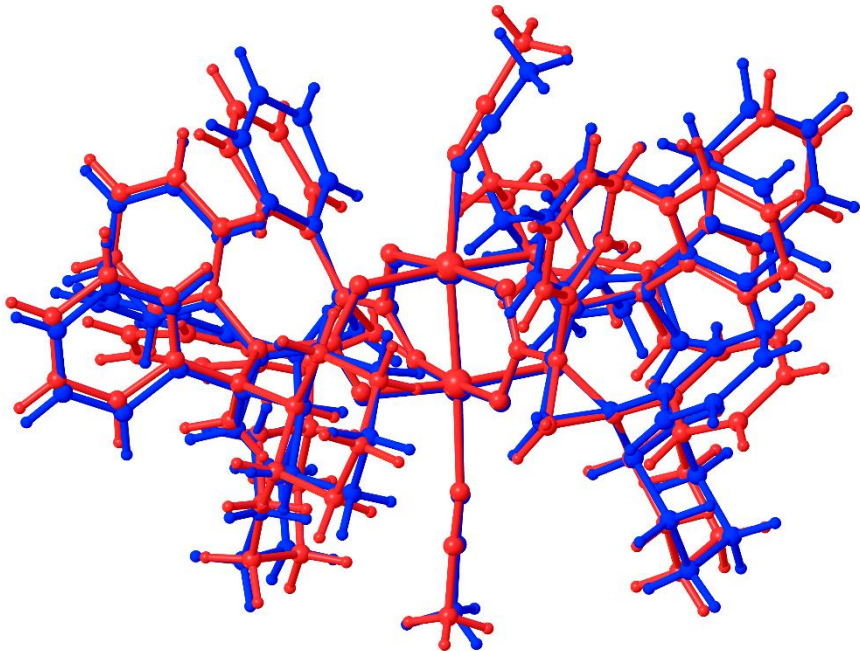
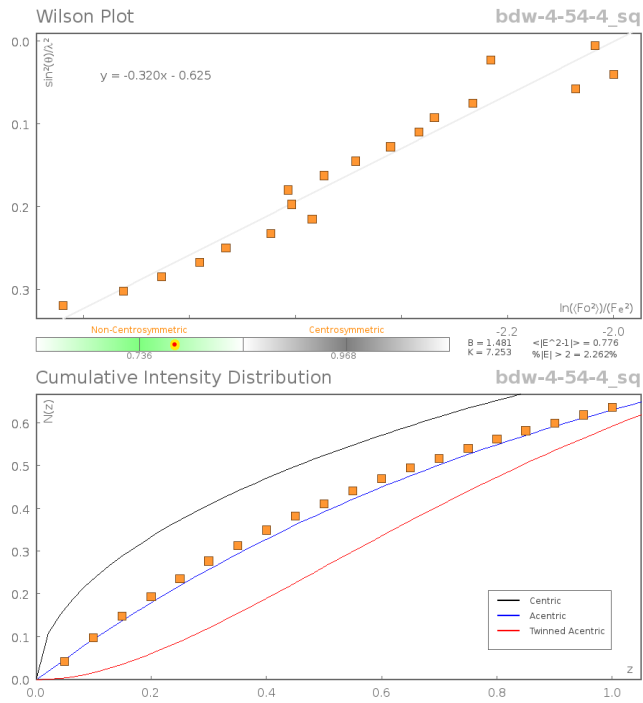
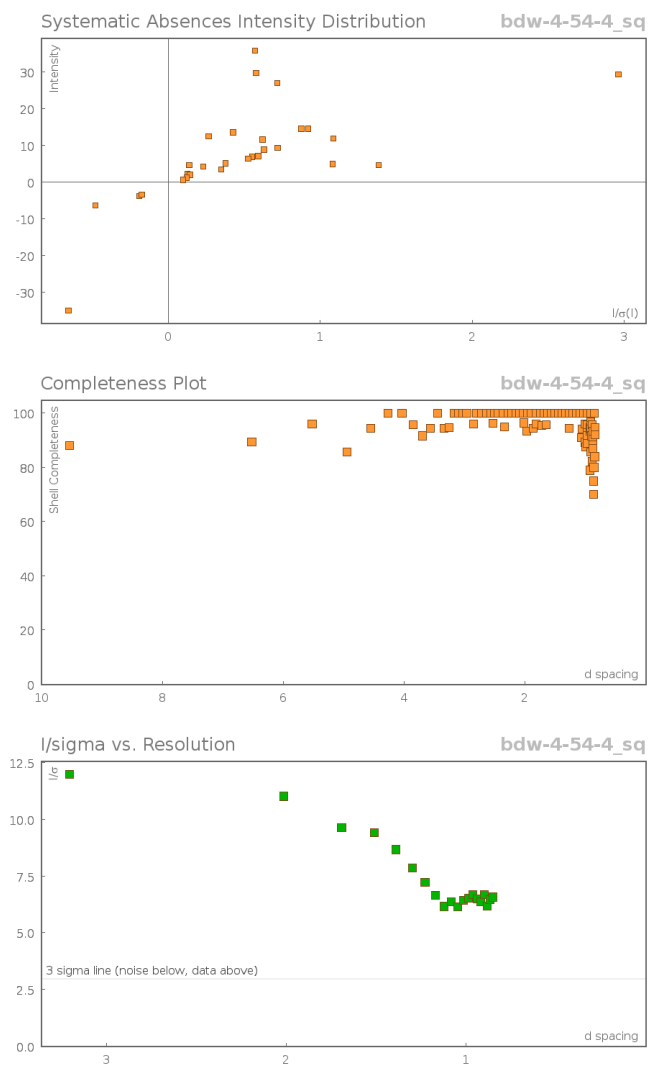
Figure 10:**Figure 11:**

Figure 12:

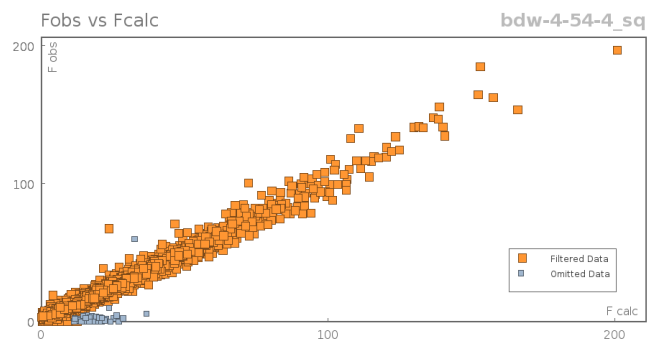


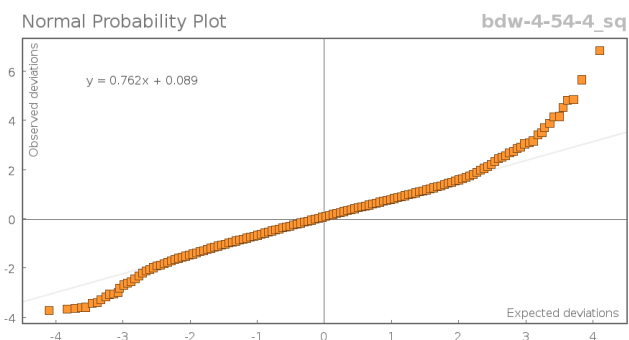
Data Plots: Diffraction Data





Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	56625	Unique reflections	24231
Completeness	0.859	Mean I/σ	10.48
$hkl_{\max}$ collected	(18, 35, 13)	$hkl_{\min}$ collected	(-17, -36, -19)
$hkl_{\max}$ used	(18, 35, 19)	$hkl_{\min}$ used	(-18, -36, 0)
Lim $d_{\max}$ collected	100.0	Lim $d_{\min}$ collected	0.77
$d_{\max}$ used	15.64	$d_{\min}$ used	0.85
Friedel pairs	7959	Friedel pairs merged	0
Inconsistent equivalents	130	R_{int}	0.0689
R_{sigma}	0.0792	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	74
Multiplicity	(16896, 10350, 4494, 1217, 131, 4)	Maximum multiplicity	8
Removed systematic absences	30	Filtered off (Shel/OMIT)	0

Images of the Crystal on the Diffractometer



Table 12: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **4.4** U_{eq} is defined as $1/3$ of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
Rh1	6510.9(4)	3476.5(4)	8283.4(4)	18.45(18)
Rh2	6586.6(5)	4101.3(4)	9090.4(4)	19.84(18)
Rh3	1597.1(4)	6481.6(4)	3249.5(4)	18.24(18)
Rh4	1347.5(5)	5870.4(4)	4059.9(4)	19.50(18)
N5	3907(13)	2127(7)	7324(19)	138(10)
C210	4093(11)	2436(6)	7028(14)	78(6)
C211	4383(12)	2840(6)	6704(14)	78(5)
O1_1	5829(5)	3197.6(19)	9155(3)	24.5(14)
O2_1	6063(4)	3748.9(16)	9987(3)	24.3(14)

Atom	x	y	z	U_{eq}
C1_1	5811(4)	3378.8(18)	9833(3)	22.9(15)
C2_1	5437(3)	3112.6(17)	10499(3)	28.7(16)
C3_1	4434(3)	3072.9(18)	10562(3)	31.5(17)
C4_1	4932(4)	3351(2)	11114(3)	34.4(19)
C5_1	3858(4)	3282(2)	9926(4)	29.4(19)
C6_1	3694(5)	3006(3)	9203(4)	34(2)
C7_1	3150(6)	3241(3)	8580(4)	43(2)
C8_1	2290(5)	3390(4)	8924(5)	57(3)
C9_1	2432(5)	3663(3)	9656(5)	50(3)
C10_1	2993(5)	3432(3)	10279(4)	43(3)
C11_1	4070(4)	2667.0(19)	10904(4)	37(2)
C12_1	3548(7)	2688(2)	11579(5)	43(3)
C13_1	3143(9)	2324(3)	11870(7)	66(4)
C14_1	3251(13)	1938(3)	11502(11)	97(7)
C15_1	3776(11)	1907(2)	10842(9)	85(6)
C16_1	4173(8)	2271(2)	10539(7)	49(3)
C17_1	5988(4)	2728(2)	10722(4)	32(2)
C18_1	6349(6)	2682(3)	11475(4)	36(2)
C19_1	6900(7)	2345(3)	11661(5)	41(2)
C20_1	7127(7)	2055(3)	11091(5)	45(3)
C21_1	6814(6)	2106(3)	10319(5)	36(2)
C22_1	6265(6)	2446(3)	10135(4)	34(2)
O1_2	7637(4)	3288.5(18)	8863(4)	24.2(14)
O2_2	7812(4)	3920.6(15)	9472(4)	24.6(14)
C1_2	8044(4)	3547.3(18)	9322(4)	20.4(16)
C2_2	8887(3)	3382.5(17)	9680(3)	24.9(15)
C3_2	9119(4)	3475.0(18)	10561(3)	29.3(15)
C4_2	9560(4)	3708.2(19)	9915(4)	29.9(18)
C5_2	8515(4)	3733(2)	11092(3)	32.4(19)
C6_2	7735(5)	3494(3)	11396(5)	36(2)
C7_2	7154(5)	3783(3)	11890(5)	44(3)
C8_2	7663(6)	3980(3)	12580(5)	49(3)
C9_2	8459(6)	4217(3)	12294(5)	49(3)
C10_2	9036(5)	3929(3)	11788(4)	42(3)
C11_2	9631(4)	3133(2)	10989(4)	28.2(18)
C12_2	10503(4)	3205(3)	11201(7)	38(3)
C13_2	10966(5)	2905(3)	11642(8)	47(3)
C14_2	10581(6)	2531(3)	11869(7)	45(3)
C15_2	9720(6)	2450(3)	11662(7)	39(2)
C16_2	9248(5)	2752(2)	11229(6)	30(2)
C17_2	9181(4)	2957.4(17)	9339(4)	25.6(17)
C18_2	9978(5)	2911(2)	8973(7)	37(2)
C19_2	10230(6)	2524(2)	8647(7)	42(3)
C20_2	9724(6)	2167(2)	8739(7)	41(3)
C21_2	8934(5)	2200.7(19)	9127(6)	30(2)
C22_2	8668(5)	2592.9(19)	9425(6)	26.4(19)
O1_3	5388(4)	3723.1(16)	7748(4)	21.8(13)
O2_3	5384(4)	4238(2)	8674(3)	24.0(14)
C1_3	5112(4)	4073.2(19)	8043(4)	21.7(16)
C2_3	4271(3)	4249.6(15)	7694(3)	25.1(15)
C3_3	4063(4)	4732.9(16)	7765(4)	35.4(17)
C4_3	3645(4)	4418(2)	8297(4)	33.4(18)
C5_3	4727(4)	5045.7(17)	8116(4)	29.3(18)

Atom	x	y	z	U_{eq}
C6_3	5454(5)	5167(3)	7564(5)	34(2)
C7_3	6105(5)	5467(3)	7965(6)	39(2)
C8_3	5654(6)	5869(2)	8264(6)	45(3)
C9_3	4910(6)	5760(3)	8807(6)	43(3)
C10_3	4265(5)	5453(2)	8409(6)	36(2)
C11_3	3448(5)	4931(2)	7166(4)	56(3)
C12_3	2645(6)	5085(5)	7435(6)	75(4)
C13_3	2125(8)	5343(6)	6956(8)	82(5)
C14_3	2396(9)	5454(5)	6214(8)	83(4)
C15_3	3158(8)	5283(4)	5916(6)	74(4)
C16_3	3695(7)	5034(4)	6400(5)	76(3)
C17_3	3951(4)	4019(2)	6956(3)	26.3(17)
C18_3	3096(4)	3886(3)	6858(4)	31(2)
C19_3	2805(5)	3697(4)	6161(5)	38(2)
C20_3	3354(6)	3651(4)	5531(5)	46(3)
C21_3	4209(6)	3793(5)	5603(4)	49(3)
C22_3	4500(5)	3977(4)	6306(4)	37(2)
O1_4	7183(5)	3803.3(14)	7419(3)	24.5(14)
O2_4	7069(5)	4408.1(17)	8129(3)	23.9(14)
C1_4	7203(4)	4209.3(16)	7500(3)	22.0(16)
C2_4	7459(3)	4466.2(17)	6778(3)	24.6(15)
C3_4	8419(3)	4609.8(19)	6689(3)	24.5(15)
C4_4	7742(4)	4920.3(17)	6926(4)	25.4(16)
C5_4	9094(4)	4478.3(19)	7314(4)	26.5(17)
C6_4	9538(5)	4055(2)	7179(5)	32(2)
C7_4	10144(6)	3941(2)	7870(5)	42(2)
C8_4	10814(5)	4293(3)	8009(6)	45(3)
C9_4	10380(5)	4721(3)	8146(5)	39(2)
C10_4	9763(5)	4836(2)	7458(5)	33(2)
C11_4	8759(4)	4651(2)	5859(3)	27.6(18)
C12_4	8865(7)	5058(2)	5526(4)	30(2)
C13_4	9155(8)	5105(2)	4754(4)	39(2)
C14_4	9306(8)	4753(3)	4294(4)	38(2)
C15_4	9181(9)	4347(3)	4602(4)	41(3)
C16_4	8902(7)	4296(2)	5378(4)	33(2)
C17_4	6943(4)	4361.2(19)	6032(3)	26.7(17)
C18_4	6473(7)	4671(2)	5622(5)	37(2)
C19_4	6065(8)	4583(3)	4905(5)	46(3)
C20_4	6135(8)	4185(3)	4569(5)	47(3)
C21_4	6580(7)	3864(3)	4977(5)	41(2)
C22_4	6977(7)	3952(2)	5703(5)	34(2)
O1_5	2645(4)	6173.1(17)	2809(4)	25.2(15)
O2_5	2545(4)	5645.2(19)	3705(3)	25.0(14)
C1_5	2882(4)	5816.7(18)	3117(4)	22.5(17)
C2_5	3616(3)	5590.6(15)	2701(3)	24.0(15)
C3_5	3637(4)	5096.0(16)	2643(3)	27.2(15)
C4_5	4228(4)	5324.9(19)	3198(4)	29.3(18)
C5_5	2947(4)	4808.5(17)	3012(4)	28.4(18)
C6_5	2147(4)	4732(3)	2504(5)	36(2)
C7_5	1490(5)	4448(3)	2925(6)	43(3)
C8_5	1898(6)	4021(2)	3158(7)	55(3)
C9_5	2711(6)	4086(3)	3660(6)	47(3)
C10_5	3364(5)	4376(2)	3244(6)	40(2)

Atom	x	y	z	U_{eq}
C11_5	4015(4)	4918(2)	1891(3)	29.4(19)
C12_5	4827(5)	4715(4)	1904(4)	36(2)
C13_5	5146(6)	4523(4)	1223(5)	43(3)
C14_5	4683(6)	4541(4)	526(4)	35(2)
C15_5	3881(6)	4744(4)	498(4)	38(3)
C16_5	3553(5)	4934(3)	1177(4)	30(2)
C17_5	3985(4)	5844(2)	2014(3)	23.5(16)
C18_5	4829(4)	6000(3)	2030(4)	31(2)
C19_5	5162(5)	6229(3)	1400(5)	32(2)
C20_5	4661(5)	6304(3)	736(4)	32(2)
C21_5	3814(5)	6148(3)	700(4)	31(2)
C22_5	3480(4)	5922(3)	1337(4)	27.8(19)
O1_6	903(4)	6186.8(14)	2345(3)	24.6(14)
O2_6	830(4)	5589.8(18)	3081(3)	22.6(14)
C1_6	774(4)	5786.6(17)	2438(3)	22.1(15)
C2_6	449(3)	5540.5(18)	1718(3)	26.7(15)
C3_6	-547(3)	5475(2)	1601(3)	28.9(15)
C4_6	14(4)	5119.8(17)	1883(4)	29.8(17)
C5_6	-1164(4)	5689(2)	2181(4)	32.2(19)
C6_6	-1488(5)	6124(2)	1925(5)	37(2)
C7_6	-2059(6)	6328(2)	2555(6)	49(3)
C8_6	-2820(5)	6037(3)	2754(6)	51(3)
C9_6	-2511(6)	5597(3)	3009(6)	50(3)
C10_6	-1927(5)	5393(2)	2384(6)	43(3)
C11_6	-882(5)	5447(2)	760(3)	32.2(19)
C12_6	-1134(7)	5049(2)	448(4)	35(2)
C13_6	-1415(8)	5013(3)	-336(4)	42(2)
C14_6	-1443(9)	5365(3)	-817(4)	46(3)
C15_6	-1184(9)	5761(3)	-525(4)	44(3)
C16_6	-900(8)	5800(2)	258(4)	39(2)
C17_6	991(4)	5598.0(19)	982(3)	30.3(19)
C18_6	1319(7)	5252(2)	565(4)	34(2)
C19_6	1747(7)	5306(3)	-145(5)	41(2)
C20_6	1862(7)	5708(3)	-455(5)	41(2)
C21_6	1543(8)	6061(3)	-50(5)	42(2)
C22_6	1108(7)	6005(2)	659(5)	35(2)
O1_7	2300(4)	6726.8(19)	4151(3)	22.3(14)
O2_7	1905(4)	6206.9(16)	4992(3)	22.9(14)
C1_7	2220(4)	6564.9(18)	4843(3)	20.8(15)
C2_7	2603(3)	6827.8(17)	5515(3)	26.1(15)
C3_7	3588(3)	6778.7(18)	5708(4)	31.1(16)
C4_7	2927(4)	6596(2)	6240(3)	31.4(18)
C5_7	4143(4)	6463(2)	5240(4)	34.1(19)
C6_7	4588(5)	6650(2)	4526(4)	36(2)
C7_7	5097(6)	6311(3)	4077(5)	47(3)
C8_7	5760(6)	6092(4)	4620(6)	55(3)
C9_7	5332(7)	5905(3)	5345(6)	60(3)
C10_7	4810(6)	6243(3)	5791(4)	48(3)
C11_7	4061(4)	7176(2)	5973(4)	41(2)
C12_7	4434(7)	7195(3)	6734(5)	60(3)
C13_7	4902(8)	7553(4)	6977(6)	79(4)
C14_7	4983(7)	7897(3)	6484(7)	80(4)
C15_7	4658(9)	7878(3)	5714(7)	73(4)

Atom	x	y	z	U_{eq}
C16_7	4201(8)	7518(3)	5460(5)	53(3)
C17_7	2186(4)	7264.2(18)	5611(4)	28.4(18)
C18_7	1766(6)	7378(2)	6303(4)	29.4(19)
C19_7	1386(8)	7776(3)	6392(5)	40(2)
C20_7	1381(8)	8063(2)	5776(6)	43(3)
C21_7	1776(8)	7953(2)	5067(5)	43(3)
C22_7	2152(7)	7552(2)	4980(4)	34(2)
O1_8	541(4)	6739.1(19)	3724(4)	25.8(15)
O2_8	160(4)	6141.1(15)	4367(4)	21.5(13)
C1_8	50(4)	6523.7(17)	4183(4)	23.0(17)
C2_8	-768(3)	6752.3(16)	4438(3)	26.0(15)
C3_8	-1132(4)	6695.3(18)	5284(3)	27.7(15)
C4_8	-1553(4)	6482(2)	4595(4)	28.4(17)
C5_8	-677(4)	6414(2)	5903(3)	28.4(18)
C6_8	131(4)	6607(3)	6275(5)	32(2)
C7_8	558(5)	6301(3)	6866(5)	45(3)
C8_8	-77(6)	6173(3)	7510(4)	42(2)
C9_8	-903(6)	5985(3)	7158(5)	46(3)
C10_8	-1324(4)	6289(3)	6554(4)	34(2)
C11_8	-1603(4)	7075(2)	5625(4)	29.6(19)
C12_8	-2514(4)	7080(3)	5627(7)	38(2)
C13_8	-2963(5)	7428(3)	5929(9)	57(3)
C14_8	-2522(6)	7779(3)	6202(9)	57(3)
C15_8	-1620(6)	7784(3)	6200(8)	50(3)
C16_8	-1165(5)	7437(3)	5898(7)	40(3)
C17_8	-869(4)	7193.3(17)	4069(4)	32.5(19)
C18_8	-1574(5)	7302(2)	3590(6)	41(2)
C19_8	-1654(7)	7707(3)	3265(7)	57(3)
C20_8	-1054(7)	8018(3)	3443(8)	60(3)
C21_8	-349(7)	7921(2)	3934(7)	52(3)
C22_8	-257(5)	7511(2)	4241(6)	38(2)
N1_10	6623(6)	4698(3)	9801(5)	25.4(18)
C23_10	6591(8)	5028(4)	10087(8)	39(3)
C24_10	6554(12)	5439(5)	10488(10)	61(4)
N1_9	6395(5)	2837(3)	7668(5)	23.5(18)
C23_9	6325(6)	2468(4)	7651(6)	22(2)
C24_9	6211(8)	2009(4)	7648(8)	37(3)
N1_11	1758(6)	7116(3)	2673(5)	25.1(18)
C23_11	1646(7)	7470(4)	2697(7)	29(2)
C24_11	1508(7)	7932(4)	2705(8)	31(2)
N1_12	1193(6)	5270(3)	4765(5)	23.3(18)
C23_12	1249(7)	4957(4)	5057(6)	27(2)
C24_12	1312(9)	4537(4)	5474(8)	41(3)

Table 13: Anisotropic Displacement Parameters ($\times 10^4$) **4.4.** The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh1	15.9(3)	16.4(4)	23.0(4)	0.0(3)	-0.4(3)	2.3(3)
Rh2	21.0(4)	17.5(4)	20.9(4)	-0.6(3)	-2.1(3)	3.8(3)
Rh3	18.0(3)	16.5(4)	20.2(4)	0.0(3)	-0.3(3)	0.8(3)
Rh4	21.4(3)	16.9(4)	20.3(4)	0.3(3)	0.9(3)	2.0(3)
N5	74(11)	72(8)	270(30)	59(13)	42(14)	24(8)
C210	40(8)	46(6)	148(16)	6(8)	14(9)	20(6)
C211	57(9)	54(7)	125(15)	8(8)	-11(9)	4(6)
O1_1	26(4)	22(3)	25(3)	4(2)	1(3)	2(3)
O2_1	27(3)	27(3)	18(3)	2(2)	-2(3)	4(2)
C1_1	17(4)	26(3)	26(3)	3(2)	-3(3)	7(3)
C2_1	25(3)	32(4)	29(3)	6(3)	3(3)	7(3)
C3_1	25(3)	37(4)	32(4)	12(3)	4(3)	8(3)
C4_1	28(4)	43(5)	32(4)	4(4)	3(3)	13(3)
C5_1	22(3)	30(5)	36(4)	12(3)	2(3)	2(3)
C6_1	32(5)	32(5)	39(4)	11(3)	-2(3)	-7(4)
C7_1	37(5)	40(6)	51(5)	15(4)	-14(4)	-13(4)
C8_1	40(5)	61(8)	70(6)	32(5)	-7(4)	0(5)
C9_1	23(5)	60(7)	68(6)	30(4)	5(4)	9(5)
C10_1	26(4)	46(7)	56(5)	17(5)	8(4)	12(4)
C11_1	22(4)	40(4)	50(5)	23(3)	9(4)	14(3)
C12_1	29(5)	50(5)	51(5)	26(4)	12(4)	17(4)
C13_1	44(7)	52(5)	103(10)	44(5)	42(7)	26(5)
C14_1	100(13)	49(5)	145(13)	39(7)	90(11)	14(7)
C15_1	80(11)	36(4)	140(12)	36(6)	78(11)	16(5)
C16_1	43(7)	36(4)	70(7)	24(4)	31(6)	11(4)
C17_1	24(4)	33(4)	40(4)	12(3)	3(3)	6(3)
C18_1	26(5)	41(5)	40(4)	16(4)	3(3)	5(4)
C19_1	29(5)	44(5)	49(5)	21(4)	2(4)	6(4)
C20_1	34(6)	45(6)	54(5)	20(4)	7(4)	11(4)
C21_1	26(5)	30(5)	53(5)	16(4)	10(4)	5(4)
C22_1	27(5)	30(4)	44(4)	12(3)	7(4)	5(4)
O1_2	23(3)	23(3)	27(3)	-2(3)	-3(2)	0(3)
O2_2	29(4)	23(3)	22(3)	-3(2)	-3(3)	2(2)
C1_2	20(3)	22(3)	20(4)	0(2)	0(3)	0(2)
C2_2	19(3)	26(3)	29(3)	5(3)	-2(2)	-1(2)
C3_2	27(3)	28(4)	32(3)	1(2)	-9(2)	-1(3)
C4_2	21(4)	27(4)	41(5)	7(3)	-10(3)	-1(3)
C5_2	35(4)	29(5)	33(4)	-1(3)	-9(3)	3(3)
C6_2	36(4)	33(5)	40(5)	1(4)	-1(4)	5(4)
C7_2	49(5)	39(6)	43(5)	-1(5)	3(4)	11(4)
C8_2	67(6)	42(7)	39(5)	-2(4)	-2(4)	10(5)
C9_2	70(6)	42(6)	36(6)	-7(4)	-8(5)	1(4)
C10_2	53(5)	39(6)	34(5)	-4(4)	-12(4)	-4(4)
C11_2	27(3)	32(4)	25(4)	1(3)	-4(3)	2(3)
C12_2	28(4)	44(6)	43(6)	10(5)	-10(4)	0(3)
C13_2	36(4)	53(6)	52(7)	13(5)	-14(5)	6(4)
C14_2	38(4)	50(6)	48(7)	14(5)	0(4)	13(4)
C15_2	40(4)	40(5)	37(6)	9(4)	1(4)	9(3)
C16_2	32(4)	31(4)	28(5)	1(3)	-1(4)	2(3)
C17_2	19(3)	28(3)	30(4)	5(3)	-5(3)	3(2)
C18_2	27(4)	31(4)	53(7)	3(4)	8(4)	4(3)
C19_2	30(5)	35(4)	62(8)	-1(4)	6(5)	8(3)
C20_2	35(4)	32(4)	56(7)	-2(5)	5(4)	8(3)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C21_2	25(4)	27(3)	38(5)	0(4)	-7(4)	5(3)
C22_2	22(4)	26(3)	31(5)	4(3)	-3(4)	3(3)
O1_3	20(3)	22(3)	24(3)	2(2)	-5(3)	3(2)
O2_3	22(3)	26(4)	25(3)	1(2)	0(2)	7(3)
C1_3	21(3)	22(3)	22(3)	4(3)	1(2)	3(3)
C2_3	21(3)	19(3)	35(3)	5(3)	-4(2)	1(2)
C3_3	31(4)	21(3)	54(5)	-2(3)	-9(3)	4(2)
C4_3	25(4)	25(4)	50(4)	-5(3)	-2(4)	6(3)
C5_3	32(4)	21(3)	34(5)	2(3)	-6(3)	3(3)
C6_3	37(4)	26(5)	38(5)	-3(4)	-1(3)	-1(3)
C7_3	40(5)	31(5)	44(7)	-7(4)	2(4)	-6(3)
C8_3	47(5)	33(5)	57(7)	-14(4)	2(5)	-7(4)
C9_3	47(5)	30(5)	54(7)	-12(4)	3(4)	1(4)
C10_3	42(5)	20(4)	46(6)	0(4)	2(4)	3(3)
C11_3	64(5)	16(5)	87(6)	5(4)	-44(4)	-3(4)
C12_3	56(6)	46(9)	122(9)	9(7)	-46(5)	5(5)
C13_3	67(8)	65(11)	113(9)	19(8)	-36(6)	15(7)
C14_3	95(9)	49(9)	103(9)	-1(7)	-39(7)	-21(6)
C15_3	93(8)	38(8)	92(8)	15(6)	-37(6)	-23(6)
C16_3	93(8)	51(8)	82(6)	9(6)	-49(5)	-27(6)
C17_3	26(3)	19(4)	33(3)	8(3)	-7(2)	0(3)
C18_3	25(3)	20(5)	46(4)	10(4)	-12(3)	1(3)
C19_3	40(5)	24(5)	50(5)	9(4)	-18(3)	-6(4)
C20_3	52(5)	37(7)	47(5)	1(5)	-16(4)	-8(4)
C21_3	52(5)	63(8)	32(4)	-3(5)	-8(4)	-12(5)
C22_3	33(4)	45(7)	34(4)	-1(4)	-5(3)	-5(4)
O1_4	28(4)	20(2)	26(4)	1(2)	5(3)	2(2)
O2_4	28(4)	17(3)	27(3)	0(2)	-4(3)	5(3)
C1_4	19(4)	20(3)	27(3)	0(2)	-2(3)	0(2)
C2_4	23(3)	22(3)	29(3)	2(2)	1(2)	0(3)
C3_4	26(3)	20(4)	27(3)	-1(3)	0(2)	-3(2)
C4_4	29(4)	22(3)	25(5)	4(3)	2(3)	0(2)
C5_4	24(3)	27(4)	28(4)	4(3)	3(3)	-2(3)
C6_4	39(5)	30(4)	28(5)	5(4)	7(3)	7(3)
C7_4	49(5)	43(5)	34(5)	6(4)	2(4)	18(4)
C8_4	44(5)	53(5)	38(6)	0(4)	-2(4)	17(3)
C9_4	25(5)	49(5)	43(5)	-8(4)	-5(4)	6(4)
C10_4	23(4)	32(4)	45(6)	0(4)	-3(4)	-1(3)
C11_4	26(5)	30(4)	27(3)	-1(2)	1(3)	-7(3)
C12_4	28(5)	32(4)	28(4)	3(3)	-3(3)	-7(4)
C13_4	42(6)	43(4)	32(4)	4(3)	6(4)	-13(5)
C14_4	34(6)	48(4)	33(5)	0(3)	5(4)	-13(4)
C15_4	47(7)	45(4)	31(4)	-6(4)	10(4)	-16(4)
C16_4	34(6)	35(4)	29(4)	-4(3)	4(4)	-6(4)
C17_4	22(4)	31(4)	27(3)	3(3)	3(3)	-5(3)
C18_4	34(5)	41(5)	37(4)	6(3)	-6(4)	1(4)
C19_4	42(6)	59(5)	38(5)	7(4)	-12(4)	-1(5)
C20_4	48(6)	61(5)	32(5)	3(4)	-4(4)	-11(5)
C21_4	43(6)	47(5)	34(4)	-4(3)	-1(4)	-14(4)
C22_4	35(5)	35(4)	33(4)	-4(3)	2(4)	-5(3)
O1_5	23(3)	25(3)	28(4)	3(2)	3(3)	6(2)
O2_5	30(4)	22(3)	24(3)	0(2)	2(2)	11(3)
C1_5	25(4)	21(3)	21(3)	-3(3)	-2(3)	2(3)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C2_5	28(4)	22(3)	22(3)	-5(2)	-1(3)	4(2)
C3_5	33(4)	21(3)	27(3)	1(3)	0(3)	9(2)
C4_5	34(4)	24(4)	29(4)	-2(3)	0(3)	9(3)
C5_5	38(4)	20(3)	28(4)	2(3)	2(3)	8(3)
C6_5	42(4)	30(5)	35(5)	4(4)	-2(4)	-1(4)
C7_5	51(5)	27(5)	53(7)	2(5)	5(5)	-6(4)
C8_5	74(6)	27(5)	64(8)	6(5)	5(6)	-1(4)
C9_5	67(5)	20(5)	56(7)	6(4)	11(4)	9(4)
C10_5	56(5)	23(4)	42(6)	8(4)	5(4)	15(4)
C11_5	37(4)	20(4)	32(3)	-2(3)	4(3)	6(3)
C12_5	38(4)	31(6)	39(4)	-3(4)	5(3)	11(4)
C13_5	44(5)	42(7)	42(4)	-6(4)	6(3)	15(5)
C14_5	37(4)	32(6)	36(4)	-3(4)	13(3)	5(4)
C15_5	38(4)	42(6)	35(4)	-12(4)	5(3)	8(4)
C16_5	36(5)	23(5)	31(3)	-5(3)	5(3)	6(4)
C17_5	27(3)	17(4)	27(3)	-5(3)	4(2)	9(3)
C18_5	28(3)	27(5)	36(4)	-3(4)	3(3)	3(3)
C19_5	32(4)	26(5)	38(4)	-6(3)	8(3)	3(4)
C20_5	39(4)	19(5)	39(4)	-4(4)	5(3)	1(3)
C21_5	38(4)	25(5)	30(4)	0(4)	3(3)	1(4)
C22_5	33(4)	23(5)	27(3)	-2(3)	1(3)	3(4)
O1_6	21(3)	24(3)	29(4)	1(2)	-6(3)	2(2)
O2_6	23(3)	20(3)	24(3)	-2(2)	-3(2)	1(3)
C1_6	16(4)	23(3)	26(3)	1(2)	-3(2)	2(2)
C2_6	26(3)	27(4)	27(3)	0(3)	-1(2)	-6(3)
C3_6	27(3)	29(4)	31(3)	-2(3)	-1(2)	-10(3)
C4_6	31(4)	27(3)	31(5)	-2(3)	2(3)	-8(2)
C5_6	28(4)	40(4)	29(4)	-2(3)	-2(3)	-4(3)
C6_6	35(5)	42(4)	33(5)	-2(4)	-5(4)	1(4)
C7_6	47(6)	56(5)	42(6)	-8(5)	0(5)	10(4)
C8_6	46(6)	71(6)	38(7)	-11(5)	6(5)	8(4)
C9_6	32(6)	62(6)	55(7)	-13(5)	9(5)	-4(4)
C10_6	34(5)	47(5)	47(6)	-4(5)	10(4)	-7(4)
C11_6	28(5)	39(4)	30(3)	-4(3)	0(3)	-10(3)
C12_6	29(5)	43(4)	33(4)	-10(3)	5(4)	-13(4)
C13_6	39(6)	53(5)	34(4)	-12(3)	3(4)	-13(5)
C14_6	47(7)	58(5)	33(5)	-9(3)	-2(4)	-12(4)
C15_6	50(7)	52(5)	31(4)	-3(4)	-5(4)	-9(5)
C16_6	42(6)	43(5)	30(4)	-1(3)	-4(4)	-10(4)
C17_6	27(4)	36(4)	28(3)	-2(3)	0(3)	-11(3)
C18_6	36(5)	43(4)	23(4)	-3(3)	-5(3)	0(4)
C19_6	37(6)	60(5)	27(4)	-4(4)	-1(4)	-5(4)
C20_6	30(6)	62(5)	32(5)	-1(3)	3(4)	-8(4)
C21_6	37(6)	56(5)	33(5)	3(4)	7(4)	-11(5)
C22_6	40(6)	37(4)	29(4)	-2(3)	5(4)	-12(4)
O1_7	21(3)	25(3)	21(3)	-2(2)	-2(2)	0(3)
O2_7	21(3)	24(3)	23(3)	-2(2)	-1(3)	2(2)
C1_7	21(4)	22(3)	20(3)	-3(2)	-2(2)	4(3)
C2_7	25(3)	29(3)	24(3)	-7(2)	-6(3)	3(2)
C3_7	27(3)	38(4)	28(4)	-8(3)	-9(2)	6(2)
C4_7	30(4)	38(5)	25(3)	-6(3)	-9(3)	9(3)
C5_7	24(4)	38(5)	41(4)	-14(3)	-5(3)	2(3)
C6_7	26(5)	41(5)	42(5)	-15(4)	-3(3)	-4(4)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C7_7	33(5)	40(6)	67(6)	-15(5)	15(4)	-6(4)
C8_7	47(6)	46(7)	74(7)	-21(5)	10(4)	10(5)
C9_7	42(7)	61(7)	78(7)	-7(5)	9(5)	24(5)
C10_7	35(5)	54(7)	56(5)	-5(5)	-3(4)	18(5)
C11_7	21(4)	48(4)	54(5)	-28(3)	-2(3)	5(3)
C12_7	24(5)	100(8)	56(5)	-45(5)	-4(4)	2(5)
C13_7	26(6)	111(9)	98(8)	-70(6)	-7(6)	2(6)
C14_7	13(5)	92(8)	134(10)	-70(7)	6(6)	2(6)
C15_7	36(7)	50(5)	134(9)	-40(6)	2(6)	-7(5)
C16_7	29(6)	41(5)	89(7)	-20(4)	0(5)	-3(4)
C17_7	24(4)	27(3)	33(4)	-9(2)	-7(3)	1(3)
C18_7	22(5)	31(4)	35(4)	-10(3)	-6(3)	1(3)
C19_7	38(6)	33(4)	50(5)	-13(3)	-2(4)	6(4)
C20_7	44(7)	29(5)	56(5)	-11(3)	-3(4)	3(4)
C21_7	47(6)	26(4)	56(5)	-7(4)	0(5)	2(4)
C22_7	33(6)	30(4)	38(4)	-4(3)	-6(4)	2(4)
O1_8	21(3)	21(3)	36(4)	3(3)	2(3)	2(3)
O2_8	20(3)	21(3)	23(3)	-1(2)	2(3)	2(2)
C1_8	20(3)	20(3)	28(4)	-2(3)	-2(3)	-1(2)
C2_8	22(3)	25(3)	31(3)	0(3)	0(3)	3(2)
C3_8	24(4)	25(4)	34(3)	0(2)	4(2)	-1(3)
C4_8	23(3)	25(4)	37(4)	-3(3)	3(3)	2(3)
C5_8	33(4)	22(4)	30(3)	-4(3)	5(3)	6(3)
C6_8	31(4)	31(5)	34(5)	3(4)	1(3)	4(3)
C7_8	51(5)	48(7)	37(5)	10(5)	-3(4)	11(5)
C8_8	59(5)	33(6)	34(5)	5(4)	0(4)	8(4)
C9_8	63(5)	37(6)	37(5)	4(4)	2(4)	1(4)
C10_8	41(4)	29(5)	32(4)	-3(4)	6(3)	-3(4)
C11_8	35(4)	24(3)	29(5)	3(3)	4(3)	3(3)
C12_8	35(4)	42(5)	39(6)	0(5)	10(4)	7(3)
C13_8	53(5)	53(6)	65(9)	-8(6)	15(6)	20(4)
C14_8	69(5)	43(6)	58(8)	-2(5)	11(5)	21(4)
C15_8	70(5)	26(4)	52(7)	1(4)	5(5)	13(4)
C16_8	47(5)	26(4)	49(7)	-4(4)	0(5)	2(3)
C17_8	35(4)	27(3)	36(5)	5(3)	15(3)	10(2)
C18_8	40(4)	41(5)	42(6)	10(4)	12(4)	17(3)
C19_8	60(6)	45(5)	66(8)	20(5)	17(5)	24(4)
C20_8	61(6)	44(6)	77(8)	25(6)	27(5)	19(4)
C21_8	57(6)	28(4)	71(8)	14(5)	29(5)	13(4)
C22_8	41(5)	26(4)	48(6)	5(4)	19(4)	6(3)
N1_10	19(4)	29(4)	28(5)	-3(3)	-4(3)	0(3)
C23_10	37(6)	34(4)	45(7)	-12(4)	-7(5)	3(4)
C24_10	71(10)	41(5)	70(10)	-24(6)	-20(8)	14(6)
N1_9	13(4)	24(3)	33(5)	0(3)	-5(3)	-4(3)
C23_9	17(5)	25(3)	25(5)	-1(3)	-4(4)	-5(3)
C24_9	29(6)	24(3)	57(8)	0(4)	1(5)	-5(4)
N1_11	22(4)	24(3)	30(5)	-3(3)	-1(4)	3(3)
C23_11	23(5)	24(3)	41(7)	-2(3)	6(5)	3(3)
C24_11	22(5)	24(3)	49(7)	-1(3)	8(5)	3(3)
N1_12	27(4)	24(3)	19(4)	3(3)	-2(3)	0(3)
C23_12	30(5)	26(4)	26(5)	6(3)	4(4)	3(3)
C24_12	47(7)	30(4)	45(7)	16(4)	5(6)	3(4)

Table 14: Bond Lengths in Å for **4.4**.

Atom	Atom	Length/Å
Rh1	Rh2	2.3849(10)
Rh1	O1_1	2.017(5)
Rh1	O1_2	2.065(5)
Rh1	O1_3	2.089(5)
Rh1	O1_4	2.069(5)
Rh1	N1_9	2.260(9)
Rh2	O2_1	2.047(5)
Rh2	O2_2	2.065(5)
Rh2	O2_3	2.018(5)
Rh2	O2_4	2.034(5)
Rh2	N1_10	2.218(9)
Rh3	Rh4	2.3851(10)
Rh3	O1_5	2.028(5)
Rh3	O1_6	2.071(5)
Rh3	O1_7	2.009(5)
Rh3	O1_8	1.992(5)
Rh3	N1_11	2.226(9)
Rh4	O2_5	2.069(5)
Rh4	O2_6	2.026(5)
Rh4	O2_7	2.071(5)
Rh4	O2_8	2.086(5)
Rh4	N1_12	2.239(9)
N5	C210	1.13(3)
C210	C211	1.45(3)
O1_1	C1_1	1.278(5)
O2_1	C1_1	1.248(5)
C1_1	C2_1	1.519(5)
C2_1	C3_1	1.554(5)
C2_1	C4_1	1.502(6)
C2_1	C17_1	1.516(5)
C3_1	C4_1	1.482(6)
C3_1	C5_1	1.531(6)
C3_1	C11_1	1.506(6)
C5_1	C6_1	1.512(6)
C5_1	C10_1	1.539(6)
C6_1	C7_1	1.526(6)
C7_1	C8_1	1.525(7)
C8_1	C9_1	1.515(8)
C9_1	C10_1	1.533(7)
C11_1	C12_1	1.404(6)
C11_1	C16_1	1.393(7)
C12_1	C13_1	1.390(7)
C13_1	C14_1	1.369(8)
C14_1	C15_1	1.389(8)
C15_1	C16_1	1.392(7)
C17_1	C18_1	1.389(6)
C17_1	C22_1	1.398(6)
C18_1	C19_1	1.386(6)
C19_1	C20_1	1.373(7)
C20_1	C21_1	1.393(7)

Atom	Atom	Length/Å
C21_1	C22_1	1.390(6)
O1_2	C1_2	1.280(5)
O2_2	C1_2	1.248(5)
C1_2	C2_2	1.514(5)
C2_2	C3_2	1.553(5)
C2_2	C4_2	1.504(6)
C2_2	C17_2	1.520(5)
C3_2	C4_2	1.483(6)
C3_2	C5_2	1.529(6)
C3_2	C11_2	1.508(6)
C5_2	C6_2	1.511(6)
C5_2	C10_2	1.542(6)
C6_2	C7_2	1.527(6)
C7_2	C8_2	1.525(7)
C8_2	C9_2	1.515(8)
C9_2	C10_2	1.532(7)
C11_2	C12_2	1.403(6)
C11_2	C16_2	1.394(7)
C12_2	C13_2	1.391(7)
C13_2	C14_2	1.369(8)
C14_2	C15_2	1.389(8)
C15_2	C16_2	1.392(7)
C17_2	C18_2	1.388(6)
C17_2	C22_2	1.396(6)
C18_2	C19_2	1.387(6)
C19_2	C20_2	1.373(7)
C20_2	C21_2	1.393(7)
C21_2	C22_2	1.390(6)
O1_3	C1_3	1.278(5)
O2_3	C1_3	1.251(5)
C1_3	C2_3	1.520(5)
C2_3	C3_3	1.550(5)
C2_3	C4_3	1.505(6)
C2_3	C17_3	1.517(5)
C3_3	C4_3	1.486(6)
C3_3	C5_3	1.530(6)
C3_3	C11_3	1.510(6)
C5_3	C6_3	1.514(6)
C5_3	C10_3	1.543(6)
C6_3	C7_3	1.527(6)
C7_3	C8_3	1.526(7)
C8_3	C9_3	1.515(8)
C9_3	C10_3	1.532(7)
C11_3	C12_3	1.406(6)
C11_3	C16_3	1.390(7)
C12_3	C13_3	1.389(7)
C13_3	C14_3	1.369(8)
C14_3	C15_3	1.389(8)
C15_3	C16_3	1.394(7)
C17_3	C18_3	1.388(6)
C17_3	C22_3	1.398(6)
C18_3	C19_3	1.386(6)
C19_3	C20_3	1.373(7)

Atom	Atom	Length/Å
C20_3	C21_3	1.393(7)
C21_3	C22_3	1.389(6)
O1_4	C1_4	1.278(5)
O2_4	C1_4	1.250(5)
C1_4	C2_4	1.517(5)
C2_4	C3_4	1.554(5)
C2_4	C4_4	1.506(6)
C2_4	C17_4	1.517(5)
C3_4	C4_4	1.484(6)
C3_4	C5_4	1.528(6)
C3_4	C11_4	1.507(6)
C5_4	C6_4	1.509(6)
C5_4	C10_4	1.538(6)
C6_4	C7_4	1.528(6)
C7_4	C8_4	1.526(7)
C8_4	C9_4	1.516(8)
C9_4	C10_4	1.534(7)
C11_4	C12_4	1.404(6)
C11_4	C16_4	1.393(7)
C12_4	C13_4	1.391(7)
C13_4	C14_4	1.369(8)
C14_4	C15_4	1.389(8)
C15_4	C16_4	1.393(7)
C17_4	C18_4	1.389(6)
C17_4	C22_4	1.396(6)
C18_4	C19_4	1.386(6)
C19_4	C20_4	1.373(7)
C20_4	C21_4	1.393(7)
C21_4	C22_4	1.390(6)
O1_5	C1_5	1.281(5)
O2_5	C1_5	1.247(5)
C1_5	C2_5	1.513(5)
C2_5	C3_5	1.551(5)
C2_5	C4_5	1.504(6)
C2_5	C17_5	1.522(5)
C3_5	C4_5	1.482(6)
C3_5	C5_5	1.531(6)
C3_5	C11_5	1.509(6)
C5_5	C6_5	1.512(6)
C5_5	C10_5	1.545(6)
C6_5	C7_5	1.528(6)
C7_5	C8_5	1.526(7)
C8_5	C9_5	1.516(8)
C9_5	C10_5	1.531(7)
C11_5	C12_5	1.402(6)
C11_5	C16_5	1.394(7)
C12_5	C13_5	1.392(7)
C13_5	C14_5	1.369(8)
C14_5	C15_5	1.389(8)
C15_5	C16_5	1.392(7)
C17_5	C18_5	1.388(6)
C17_5	C22_5	1.395(6)
C18_5	C19_5	1.386(6)

Atom	Atom	Length/Å
C19_5	C20_5	1.373(7)
C20_5	C21_5	1.393(7)
C21_5	C22_5	1.390(6)
O1_6	C1_6	1.278(5)
O2_6	C1_6	1.250(5)
C1_6	C2_6	1.518(5)
C2_6	C3_6	1.557(5)
C2_6	C4_6	1.505(6)
C2_6	C17_6	1.516(5)
C3_6	C4_6	1.480(6)
C3_6	C5_6	1.529(6)
C3_6	C11_6	1.507(6)
C5_6	C6_6	1.511(6)
C5_6	C10_6	1.538(6)
C6_6	C7_6	1.526(6)
C7_6	C8_6	1.526(7)
C8_6	C9_6	1.515(8)
C9_6	C10_6	1.533(7)
C11_6	C12_6	1.404(6)
C11_6	C16_6	1.393(7)
C12_6	C13_6	1.390(7)
C13_6	C14_6	1.369(8)
C14_6	C15_6	1.389(8)
C15_6	C16_6	1.392(7)
C17_6	C18_6	1.389(6)
C17_6	C22_6	1.397(6)
C18_6	C19_6	1.386(6)
C19_6	C20_6	1.373(7)
C20_6	C21_6	1.393(7)
C21_6	C22_6	1.390(6)
O1_7	C1_7	1.280(5)
O2_7	C1_7	1.247(5)
C1_7	C2_7	1.516(5)
C2_7	C3_7	1.555(5)
C2_7	C4_7	1.503(6)
C2_7	C17_7	1.518(5)
C3_7	C4_7	1.482(6)
C3_7	C5_7	1.531(6)
C3_7	C11_7	1.505(6)
C5_7	C6_7	1.510(6)
C5_7	C10_7	1.540(6)
C6_7	C7_7	1.527(6)
C7_7	C8_7	1.525(7)
C8_7	C9_7	1.515(8)
C9_7	C10_7	1.533(7)
C11_7	C12_7	1.403(6)
C11_7	C16_7	1.394(7)
C12_7	C13_7	1.391(7)
C13_7	C14_7	1.369(8)
C14_7	C15_7	1.389(8)
C15_7	C16_7	1.392(7)
C17_7	C18_7	1.389(6)
C17_7	C22_7	1.396(6)

Atom	Atom	Length/Å
C18_7	C19_7	1.387(6)
C19_7	C20_7	1.373(7)
C20_7	C21_7	1.393(7)
C21_7	C22_7	1.391(6)
O1_8	C1_8	1.281(5)
O2_8	C1_8	1.247(5)
C1_8	C2_8	1.515(5)
C2_8	C3_8	1.552(5)
C2_8	C4_8	1.502(6)
C2_8	C17_8	1.521(5)
C3_8	C4_8	1.483(6)
C3_8	C5_8	1.529(6)
C3_8	C11_8	1.510(6)
C5_8	C6_8	1.512(6)
C5_8	C10_8	1.543(6)
C6_8	C7_8	1.527(6)
C7_8	C8_8	1.526(7)
C8_8	C9_8	1.515(8)
C9_8	C10_8	1.532(7)
C11_8	C12_8	1.403(6)
C11_8	C16_8	1.393(7)
C12_8	C13_8	1.391(7)
C13_8	C14_8	1.369(8)
C14_8	C15_8	1.389(8)
C15_8	C16_8	1.393(7)
C17_8	C18_8	1.386(6)
C17_8	C22_8	1.397(6)
C18_8	C19_8	1.387(6)
C19_8	C20_8	1.373(7)
C20_8	C21_8	1.393(7)
C21_8	C22_8	1.390(6)
N1_10	C23_10	1.142(16)
C23_10	C24_10	1.45(2)
N1_9	C23_9	1.158(14)
C23_9	C24_9	1.448(16)
N1_11	C23_11	1.121(15)
C23_11	C24_11	1.463(16)
N1_12	C23_12	1.098(14)
C23_12	C24_12	1.494(17)

Table 15: Bond Angles in ° for **4.4**.

Atom	Atom	Atom	Angle/°
O1_1	Rh1	Rh2	87.70(15)
O1_1	Rh1	O1_2	88.4(3)
O1_1	Rh1	O1_3	92.3(3)
O1_1	Rh1	O1_4	176.0(2)
O1_1	Rh1	N1_9	85.0(3)
O1_2	Rh1	Rh2	85.87(14)
O1_2	Rh1	O1_3	174.6(2)
O1_2	Rh1	O1_4	92.9(3)
O1_2	Rh1	N1_9	91.5(3)
O1_3	Rh1	Rh2	88.79(13)
O1_3	Rh1	N1_9	93.9(3)
O1_4	Rh1	Rh2	88.65(14)
O1_4	Rh1	O1_3	86.0(3)
O1_4	Rh1	N1_9	98.7(3)
N1_9	Rh1	Rh2	172.3(2)
O2_1	Rh2	Rh1	87.96(14)
O2_1	Rh2	O2_2	89.3(3)
O2_1	Rh2	N1_10	93.5(3)
O2_2	Rh2	Rh1	89.54(14)
O2_2	Rh2	N1_10	92.6(3)
O2_3	Rh2	Rh1	86.36(15)
O2_3	Rh2	O2_1	90.2(3)
O2_3	Rh2	O2_2	175.9(2)
O2_3	Rh2	O2_4	88.0(3)
O2_3	Rh2	N1_10	91.5(3)
O2_4	Rh2	Rh1	86.93(14)
O2_4	Rh2	O2_1	174.7(2)
O2_4	Rh2	O2_2	92.2(3)
O2_4	Rh2	N1_10	91.6(3)
N1_10	Rh2	Rh1	177.5(2)
O1_5	Rh3	Rh4	87.89(14)
O1_5	Rh3	O1_6	85.6(3)
O1_5	Rh3	N1_11	99.8(3)
O1_6	Rh3	Rh4	88.91(14)
O1_6	Rh3	N1_11	97.7(3)
O1_7	Rh3	Rh4	87.72(15)
O1_7	Rh3	O1_5	92.1(3)
O1_7	Rh3	O1_6	176.0(2)
O1_7	Rh3	N1_11	85.9(3)
O1_8	Rh3	Rh4	87.44(15)
O1_8	Rh3	O1_5	175.3(2)
O1_8	Rh3	O1_6	93.5(3)
O1_8	Rh3	O1_7	88.6(3)
O1_8	Rh3	N1_11	84.9(3)
N1_11	Rh3	Rh4	170.2(2)
O2_5	Rh4	Rh3	87.50(14)
O2_5	Rh4	O2_7	91.8(3)
O2_5	Rh4	O2_8	175.5(2)
O2_5	Rh4	N1_12	88.3(3)
O2_6	Rh4	Rh3	86.76(15)
O2_6	Rh4	O2_5	87.6(3)
O2_6	Rh4	O2_7	174.5(2)
O2_6	Rh4	O2_8	92.4(3)

Atom	Atom	Atom	Angle/°
O2_6	Rh4	N1_12	91.6(3)
O2_7	Rh4	Rh3	87.72(14)
O2_7	Rh4	O2_8	87.8(3)
O2_7	Rh4	N1_12	93.9(3)
O2_8	Rh4	Rh3	87.99(13)
O2_8	Rh4	N1_12	96.3(3)
N1_12	Rh4	Rh3	175.5(2)
N5	C210	C211	175(3)
C1_1	O1_1	Rh1	118.6(4)
C1_1	O2_1	Rh2	118.0(4)
O1_1	C1_1	C2_1	115.7(4)
O2_1	C1_1	O1_1	126.1(4)
O2_1	C1_1	C2_1	118.3(4)
C1_1	C2_1	C3_1	118.7(4)
C4_1	C2_1	C1_1	116.4(4)
C4_1	C2_1	C3_1	58.0(3)
C4_1	C2_1	C17_1	121.0(4)
C17_1	C2_1	C1_1	113.7(4)
C17_1	C2_1	C3_1	118.3(4)
C4_1	C3_1	C2_1	59.3(3)
C4_1	C3_1	C5_1	118.8(4)
C4_1	C3_1	C11_1	116.5(4)
C5_1	C3_1	C2_1	119.0(4)
C11_1	C3_1	C2_1	117.9(4)
C11_1	C3_1	C5_1	114.4(4)
C3_1	C4_1	C2_1	62.8(3)
C3_1	C5_1	C10_1	110.8(4)
C6_1	C5_1	C3_1	114.3(4)
C6_1	C5_1	C10_1	110.5(4)
C5_1	C6_1	C7_1	111.5(4)
C6_1	C7_1	C8_1	110.8(5)
C9_1	C8_1	C7_1	111.4(5)
C8_1	C9_1	C10_1	111.6(5)
C9_1	C10_1	C5_1	111.1(4)
C12_1	C11_1	C3_1	119.4(5)
C16_1	C11_1	C3_1	122.4(4)
C16_1	C11_1	C12_1	118.0(4)
C13_1	C12_1	C11_1	120.8(5)
C14_1	C13_1	C12_1	120.4(5)
C13_1	C14_1	C15_1	120.0(5)
C14_1	C15_1	C16_1	120.1(5)
C15_1	C16_1	C11_1	120.8(5)
C18_1	C17_1	C2_1	121.8(4)
C18_1	C17_1	C22_1	117.4(4)
C22_1	C17_1	C2_1	120.0(4)
C19_1	C18_1	C17_1	121.6(5)
C20_1	C19_1	C18_1	120.4(5)
C19_1	C20_1	C21_1	119.3(5)
C22_1	C21_1	C20_1	120.0(5)
C21_1	C22_1	C17_1	121.0(5)
C1_2	O1_2	Rh1	120.6(4)
C1_2	O2_2	Rh2	117.1(4)
O1_2	C1_2	C2_2	115.9(4)

Atom	Atom	Atom	Angle/°
O2_2	C1_2	O1_2	125.1(4)
O2_2	C1_2	C2_2	118.9(4)
C1_2	C2_2	C3_2	120.3(4)
C1_2	C2_2	C17_2	113.9(3)
C4_2	C2_2	C1_2	117.3(4)
C4_2	C2_2	C3_2	58.0(3)
C4_2	C2_2	C17_2	119.0(4)
C17_2	C2_2	C3_2	117.3(4)
C4_2	C3_2	C2_2	59.3(3)
C4_2	C3_2	C5_2	117.3(4)
C4_2	C3_2	C11_2	117.4(4)
C5_2	C3_2	C2_2	121.7(4)
C11_2	C3_2	C2_2	116.1(4)
C11_2	C3_2	C5_2	114.3(4)
C3_2	C4_2	C2_2	62.6(3)
C3_2	C5_2	C10_2	110.1(4)
C6_2	C5_2	C3_2	115.5(4)
C6_2	C5_2	C10_2	110.2(4)
C5_2	C6_2	C7_2	111.5(4)
C6_2	C7_2	C8_2	110.9(5)
C9_2	C8_2	C7_2	111.4(5)
C8_2	C9_2	C10_2	111.5(5)
C9_2	C10_2	C5_2	111.1(5)
C12_2	C11_2	C3_2	120.0(5)
C16_2	C11_2	C3_2	121.7(4)
C16_2	C11_2	C12_2	118.1(4)
C13_2	C12_2	C11_2	120.7(5)
C14_2	C13_2	C12_2	120.4(5)
C13_2	C14_2	C15_2	120.0(5)
C16_2	C15_2	C14_2	120.0(5)
C15_2	C16_2	C11_2	120.8(5)
C18_2	C17_2	C2_2	121.9(4)
C18_2	C17_2	C22_2	117.7(4)
C22_2	C17_2	C2_2	120.2(4)
C19_2	C18_2	C17_2	121.4(5)
C20_2	C19_2	C18_2	120.3(5)
C19_2	C20_2	C21_2	119.4(5)
C22_2	C21_2	C20_2	120.0(5)
C21_2	C22_2	C17_2	120.9(5)
C1_3	O1_3	Rh1	115.1(3)
C1_3	O2_3	Rh2	120.3(4)
O1_3	C1_3	C2_3	116.4(4)
O2_3	C1_3	O1_3	125.2(4)
O2_3	C1_3	C2_3	117.1(4)
C1_3	C2_3	C3_3	120.0(4)
C4_3	C2_3	C1_3	114.4(4)
C4_3	C2_3	C3_3	58.2(3)
C4_3	C2_3	C17_3	121.2(4)
C17_3	C2_3	C1_3	114.3(3)
C17_3	C2_3	C3_3	117.6(4)
C4_3	C3_3	C2_3	59.4(3)
C4_3	C3_3	C5_3	118.8(4)
C4_3	C3_3	C11_3	113.9(4)

Atom	Atom	Atom	Angle/°
C5_3	C3_3	C2_3	121.1(4)
C11_3	C3_3	C2_3	118.5(4)
C11_3	C3_3	C5_3	114.0(4)
C3_3	C4_3	C2_3	62.4(3)
C3_3	C5_3	C10_3	110.1(4)
C6_3	C5_3	C3_3	114.7(4)
C6_3	C5_3	C10_3	109.7(4)
C5_3	C6_3	C7_3	111.5(4)
C6_3	C7_3	C8_3	110.8(5)
C9_3	C8_3	C7_3	111.4(5)
C8_3	C9_3	C10_3	111.6(5)
C9_3	C10_3	C5_3	111.1(4)
C12_3	C11_3	C3_3	118.1(5)
C16_3	C11_3	C3_3	122.7(5)
C16_3	C11_3	C12_3	118.2(4)
C13_3	C12_3	C11_3	120.9(5)
C14_3	C13_3	C12_3	120.0(5)
C13_3	C14_3	C15_3	120.1(5)
C14_3	C15_3	C16_3	120.1(6)
C11_3	C16_3	C15_3	120.4(5)
C18_3	C17_3	C2_3	122.5(4)
C18_3	C17_3	C22_3	117.3(4)
C22_3	C17_3	C2_3	119.7(4)
C19_3	C18_3	C17_3	121.7(5)
C20_3	C19_3	C18_3	120.4(5)
C19_3	C20_3	C21_3	119.3(5)
C22_3	C21_3	C20_3	120.0(5)
C21_3	C22_3	C17_3	121.2(5)
C1_4	O1_4	Rh1	115.3(4)
C1_4	O2_4	Rh2	120.6(4)
O1_4	C1_4	C2_4	116.5(4)
O2_4	C1_4	O1_4	125.5(4)
O2_4	C1_4	C2_4	117.8(4)
C1_4	C2_4	C3_4	119.2(4)
C4_4	C2_4	C1_4	116.3(4)
C4_4	C2_4	C3_4	58.0(3)
C4_4	C2_4	C17_4	119.3(4)
C17_4	C2_4	C1_4	114.5(4)
C17_4	C2_4	C3_4	118.1(4)
C4_4	C3_4	C2_4	59.4(3)
C4_4	C3_4	C5_4	117.6(4)
C4_4	C3_4	C11_4	116.6(4)
C5_4	C3_4	C2_4	119.6(4)
C11_4	C3_4	C2_4	117.1(4)
C11_4	C3_4	C5_4	115.1(4)
C3_4	C4_4	C2_4	62.6(3)
C3_4	C5_4	C10_4	111.2(4)
C6_4	C5_4	C3_4	115.9(4)
C6_4	C5_4	C10_4	111.0(4)
C5_4	C6_4	C7_4	111.3(4)
C6_4	C7_4	C8_4	110.7(5)
C9_4	C8_4	C7_4	111.3(5)
C8_4	C9_4	C10_4	111.2(5)

Atom	Atom	Atom	Angle/°
C9_4	C10_4	C5_4	110.9(4)
C12_4	C11_4	C3_4	119.5(5)
C16_4	C11_4	C3_4	122.3(4)
C16_4	C11_4	C12_4	117.9(4)
C13_4	C12_4	C11_4	120.8(5)
C14_4	C13_4	C12_4	120.4(5)
C13_4	C14_4	C15_4	119.9(5)
C16_4	C15_4	C14_4	120.1(5)
C15_4	C16_4	C11_4	120.8(5)
C18_4	C17_4	C2_4	121.7(4)
C18_4	C17_4	C22_4	117.7(4)
C22_4	C17_4	C2_4	120.5(4)
C19_4	C18_4	C17_4	121.5(5)
C20_4	C19_4	C18_4	120.3(5)
C19_4	C20_4	C21_4	119.4(5)
C22_4	C21_4	C20_4	120.0(5)
C21_4	C22_4	C17_4	121.0(5)
C1_5	O1_5	Rh3	119.3(4)
C1_5	O2_5	Rh4	117.7(4)
O1_5	C1_5	C2_5	115.4(4)
O2_5	C1_5	O1_5	125.3(4)
O2_5	C1_5	C2_5	119.2(4)
C1_5	C2_5	C3_5	120.8(4)
C1_5	C2_5	C17_5	113.5(3)
C4_5	C2_5	C1_5	117.8(4)
C4_5	C2_5	C3_5	58.0(3)
C4_5	C2_5	C17_5	118.4(4)
C17_5	C2_5	C3_5	117.6(4)
C4_5	C3_5	C2_5	59.4(3)
C4_5	C3_5	C5_5	116.7(4)
C4_5	C3_5	C11_5	118.0(4)
C5_5	C3_5	C2_5	123.0(4)
C11_5	C3_5	C2_5	115.4(4)
C11_5	C3_5	C5_5	113.8(4)
C3_5	C4_5	C2_5	62.6(3)
C3_5	C5_5	C10_5	109.2(4)
C6_5	C5_5	C3_5	115.2(4)
C6_5	C5_5	C10_5	109.8(4)
C5_5	C6_5	C7_5	111.5(4)
C6_5	C7_5	C8_5	110.8(5)
C9_5	C8_5	C7_5	111.1(5)
C8_5	C9_5	C10_5	111.4(5)
C9_5	C10_5	C5_5	111.2(4)
C12_5	C11_5	C3_5	120.5(5)
C16_5	C11_5	C3_5	121.2(4)
C16_5	C11_5	C12_5	118.3(4)
C13_5	C12_5	C11_5	120.4(5)
C14_5	C13_5	C12_5	120.5(5)
C13_5	C14_5	C15_5	120.0(5)
C16_5	C15_5	C14_5	119.9(5)
C15_5	C16_5	C11_5	120.8(5)
C18_5	C17_5	C2_5	121.8(4)
C18_5	C17_5	C22_5	117.8(4)

Atom	Atom	Atom	Angle/°
C22_5	C17_5	C2_5	120.4(4)
C19_5	C18_5	C17_5	121.5(5)
C20_5	C19_5	C18_5	120.4(5)
C19_5	C20_5	C21_5	119.4(5)
C22_5	C21_5	C20_5	120.0(5)
C21_5	C22_5	C17_5	120.9(5)
C1_6	O1_6	Rh3	115.2(4)
C1_6	O2_6	Rh4	121.2(4)
O1_6	C1_6	C2_6	116.7(4)
O2_6	C1_6	O1_6	125.4(4)
O2_6	C1_6	C2_6	117.7(4)
C1_6	C2_6	C3_6	118.9(4)
C4_6	C2_6	C1_6	116.0(4)
C4_6	C2_6	C3_6	57.8(3)
C4_6	C2_6	C17_6	120.4(4)
C17_6	C2_6	C1_6	114.7(4)
C17_6	C2_6	C3_6	117.6(4)
C4_6	C3_6	C2_6	59.3(3)
C4_6	C3_6	C5_6	119.2(4)
C4_6	C3_6	C11_6	116.8(4)
C5_6	C3_6	C2_6	118.6(4)
C11_6	C3_6	C2_6	116.9(4)
C11_6	C3_6	C5_6	114.9(4)
C3_6	C4_6	C2_6	62.9(3)
C3_6	C5_6	C10_6	111.2(4)
C6_6	C5_6	C3_6	114.7(4)
C6_6	C5_6	C10_6	110.8(4)
C5_6	C6_6	C7_6	111.6(4)
C6_6	C7_6	C8_6	110.7(5)
C9_6	C8_6	C7_6	111.4(5)
C8_6	C9_6	C10_6	111.5(5)
C9_6	C10_6	C5_6	111.0(5)
C12_6	C11_6	C3_6	119.7(5)
C16_6	C11_6	C3_6	122.1(4)
C16_6	C11_6	C12_6	118.1(4)
C13_6	C12_6	C11_6	120.7(5)
C14_6	C13_6	C12_6	120.4(5)
C13_6	C14_6	C15_6	120.0(5)
C16_6	C15_6	C14_6	120.0(5)
C15_6	C16_6	C11_6	120.8(5)
C18_6	C17_6	C2_6	122.0(4)
C18_6	C17_6	C22_6	117.5(4)
C22_6	C17_6	C2_6	120.2(4)
C19_6	C18_6	C17_6	121.6(5)
C20_6	C19_6	C18_6	120.4(5)
C19_6	C20_6	C21_6	119.3(5)
C22_6	C21_6	C20_6	120.0(5)
C21_6	C22_6	C17_6	121.2(5)
C1_7	O1_7	Rh3	118.9(4)
C1_7	O2_7	Rh4	117.5(4)
O1_7	C1_7	C2_7	115.3(4)
O2_7	C1_7	O1_7	125.6(4)
O2_7	C1_7	C2_7	119.0(4)

Atom	Atom	Atom	Angle/°
C1_7	C2_7	C3_7	118.2(4)
C1_7	C2_7	C17_7	114.0(4)
C4_7	C2_7	C1_7	118.0(4)
C4_7	C2_7	C3_7	57.9(3)
C4_7	C2_7	C17_7	119.0(4)
C17_7	C2_7	C3_7	118.6(4)
C4_7	C3_7	C2_7	59.3(3)
C4_7	C3_7	C5_7	117.1(4)
C4_7	C3_7	C11_7	118.2(4)
C5_7	C3_7	C2_7	120.3(4)
C11_7	C3_7	C2_7	116.5(4)
C11_7	C3_7	C5_7	114.5(4)
C3_7	C4_7	C2_7	62.8(3)
C3_7	C5_7	C10_7	110.3(4)
C6_7	C5_7	C3_7	115.1(4)
C6_7	C5_7	C10_7	110.5(4)
C5_7	C6_7	C7_7	111.7(4)
C6_7	C7_7	C8_7	110.9(5)
C9_7	C8_7	C7_7	111.4(5)
C8_7	C9_7	C10_7	111.5(5)
C9_7	C10_7	C5_7	111.1(5)
C12_7	C11_7	C3_7	119.9(5)
C16_7	C11_7	C3_7	121.8(4)
C16_7	C11_7	C12_7	118.1(4)
C13_7	C12_7	C11_7	120.6(5)
C14_7	C13_7	C12_7	120.4(5)
C13_7	C14_7	C15_7	120.0(5)
C16_7	C15_7	C14_7	119.9(5)
C15_7	C16_7	C11_7	120.7(5)
C18_7	C17_7	C2_7	121.4(4)
C18_7	C17_7	C22_7	117.6(4)
C22_7	C17_7	C2_7	120.7(4)
C19_7	C18_7	C17_7	121.5(5)
C20_7	C19_7	C18_7	120.3(5)
C19_7	C20_7	C21_7	119.4(5)
C22_7	C21_7	C20_7	120.0(5)
C21_7	C22_7	C17_7	120.9(5)
C1_8	O1_8	Rh3	121.4(4)
C1_8	O2_8	Rh4	116.4(4)
O1_8	C1_8	C2_8	114.9(4)
O2_8	C1_8	O1_8	125.2(4)
O2_8	C1_8	C2_8	119.6(4)
C1_8	C2_8	C3_8	121.1(4)
C1_8	C2_8	C17_8	113.2(3)
C4_8	C2_8	C1_8	117.2(4)
C4_8	C2_8	C3_8	58.1(3)
C4_8	C2_8	C17_8	120.4(4)
C17_8	C2_8	C3_8	116.4(4)
C4_8	C3_8	C2_8	59.3(3)
C4_8	C3_8	C5_8	118.0(4)
C4_8	C3_8	C11_8	116.5(4)
C5_8	C3_8	C2_8	121.9(4)
C11_8	C3_8	C2_8	116.2(4)

Atom	Atom	Atom	Angle/°
C11_8	C3_8	C5_8	114.2(4)
C3_8	C4_8	C2_8	62.6(3)
C3_8	C5_8	C10_8	109.9(4)
C6_8	C5_8	C3_8	114.9(4)
C6_8	C5_8	C10_8	109.9(4)
C5_8	C6_8	C7_8	111.5(5)
C6_8	C7_8	C8_8	110.8(5)
C9_8	C8_8	C7_8	111.4(5)
C8_8	C9_8	C10_8	111.5(5)
C9_8	C10_8	C5_8	111.1(4)
C12_8	C11_8	C3_8	119.6(5)
C16_8	C11_8	C3_8	122.2(4)
C16_8	C11_8	C12_8	118.1(4)
C13_8	C12_8	C11_8	120.7(5)
C14_8	C13_8	C12_8	120.4(5)
C13_8	C14_8	C15_8	120.0(5)
C14_8	C15_8	C16_8	120.0(5)
C15_8	C16_8	C11_8	120.7(5)
C18_8	C17_8	C2_8	122.4(4)
C18_8	C17_8	C22_8	117.9(4)
C22_8	C17_8	C2_8	119.6(4)
C17_8	C18_8	C19_8	121.4(5)
C20_8	C19_8	C18_8	120.3(5)
C19_8	C20_8	C21_8	119.5(5)
C22_8	C21_8	C20_8	119.9(5)
C21_8	C22_8	C17_8	120.9(5)
C23_10	N1_10	Rh2	171.5(10)
N1_10	C23_10	C24_10	177.3(15)
C23_9	N1_9	Rh1	154.1(8)
N1_9	C23_9	C24_9	177.9(12)
C23_11	N1_11	Rh3	147.8(9)
N1_11	C23_11	C24_11	178.4(13)
C23_12	N1_12	Rh4	167.9(9)
N1_12	C23_12	C24_12	178.4(13)

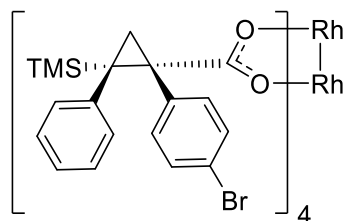
Table 16: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **4.4**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
H21A	4848.04	2787.76	6324.09	118
H21B	4602.57	3022.59	7133.03	118
H21C	3895.55	2982.09	6434.25	118
H4A_1	4993.63	3254.61	11670.68	41
H4B_1	4871.45	3663.77	11047.86	41
H5_1	4169.43	3543.39	9741.71	35
H6A_1	3388.82	2742.16	9362.99	41
H6B_1	4257.28	2922.83	8971.95	41
H7A_1	3034.51	3048.3	8125.19	51
H7B_1	3476.83	3491.29	8383.9	51
H8A_1	1965.05	3556.6	8520.23	68
H8B_1	1935.14	3137.27	9063.35	68
H9A_1	1863.16	3735.09	9886.89	60
H9B_1	2720.29	3932.91	9503.44	60
H10A_1	2671.56	3181.63	10482.84	51
H10B_1	3111.75	3627.16	10728.11	51
H12_1	3470.65	2953.81	11840.52	52
H13_1	2789.88	2343.26	12325.57	79
H14_1	2966.56	1690.78	11699.15	117
H15_1	3864.16	1637.87	10596.18	102
H16_1	4518.06	2249.37	10078.66	59
H18_1	6215.56	2886.09	11871.63	43
H19_1	7122.01	2315.58	12185.27	49
H20_1	7494.99	1820.32	11221.06	53
H21_1	6974.62	1909.44	9918.7	44
H22_1	6076.16	2486.96	9602.95	40
H4A_2	10176.04	3637.15	9816.51	36
H4B_2	9411.16	4013.49	9840.01	36
H5_2	8288.33	3976.44	10766.19	39
H6A_2	7934.16	3249.59	11724.33	43
H6B_2	7395.68	3378.71	10942.73	43
H7A_2	6663.04	3614.2	12098.27	52
H7B_2	6912.43	4013.06	11550.98	52
H8A_2	7283.67	4181.04	12868.1	59
H8B_2	7845.39	3752.13	12952.14	59
H9A_2	8797.97	4322.01	12756.21	59
H9B_2	8273.56	4468.17	11977.13	59
H10A_2	9280.16	3697.32	12121.89	50
H10B_2	9525.38	4098.68	11579.44	50
H12_2	10779.74	3462.23	11041.09	46
H13_2	11553.91	2959.79	11787.46	56
H14_2	10901.91	2326.29	12168.04	54
H15_2	9453.89	2189.95	11815.9	47
H16_2	8657.08	2696.65	11095.48	36
H18_2	10357.81	3149.73	8943.94	44
H19_2	10755.41	2506.75	8359.31	50
H20_2	9911.63	1898.74	8539.38	49
H21_2	8576.38	1955.56	9187.56	36
H22_2	8129.15	2613.17	9690.95	32
H4A_3	3019.87	4357.78	8209.24	40

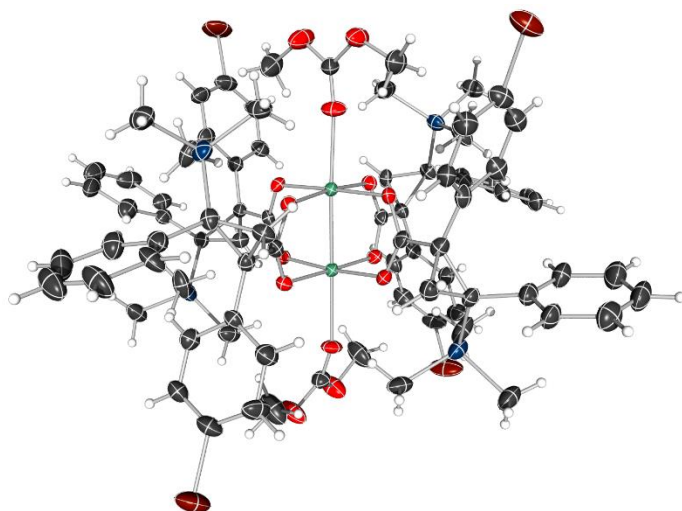
Atom	x	y	z	U_{eq}
H4B_3	3834.89	4414.51	8859.26	40
H5_3	4998.42	4904.47	8589.09	35
H6A_3	5204.87	5308.44	7087.83	41
H6B_3	5757.42	4905.1	7389.66	41
H7A_3	6559.77	5547.88	7583.64	46
H7B_3	6389.9	5318.13	8415.65	46
H8A_3	6080.93	6049.48	8554.15	55
H8B_3	5430.4	6035.95	7806.89	55
H9A_3	4603.28	6026.05	8955.52	52
H9B_3	5143.38	5627.85	9297.47	52
H10A_3	3977.93	5597.38	7954.76	43
H10B_3	3810.59	5372.33	8791.36	43
H12_3	2455.64	5011.36	7950.19	90
H13_3	1582.11	5442.9	7142.8	99
H14_3	2062.22	5648.33	5903	99
H15_3	3312.9	5336.64	5382.61	89
H16_3	4233.52	4933.06	6204.64	91
H18_3	2700.91	3924.93	7279.16	37
H19_3	2222.44	3599.3	6117.84	46
H20_3	3152.16	3524.13	5052.17	55
H21_3	4593.54	3763.69	5170.81	59
H22_3	5081.27	4077.32	6346.69	45
H4A_4	7562.44	5138.55	6531.65	31
H4B_4	7752.63	5021.97	7480.77	31
H5_4	8769.92	4447.25	7821.02	32
H6A_4	9876.14	4069.79	6684.78	39
H6B_4	9093.7	3828.58	7113.38	39
H7A_4	10445.23	3668.56	7753.75	50
H7B_4	9799.18	3899.74	8355.07	50
H8A_4	11179.75	4219.41	8476.2	54
H8B_4	11196.82	4313.25	7543.93	54
H9A_4	10829.38	4945.55	8201.88	47
H9B_4	10048.73	4710.34	8644.33	47
H10A_4	10103.1	4880.93	6970.93	40
H10B_4	9456.82	5105.74	7580.02	40
H12_4	8738.11	5304.79	5831.75	36
H13_4	9248.39	5383.06	4544.9	47
H14_4	9495.55	4787.2	3764.36	46
H15_4	9285.82	4102.29	4283.08	49
H16_4	8809.14	4017.37	5581.82	39
H18_4	6430.79	4950.39	5839.45	45
H19_4	5735.57	4798.47	4643.5	56
H20_4	5882.02	4128.45	4063.95	56
H21_4	6612.86	3584.1	4759.63	49
H22_4	7276.27	3731.09	5978.98	41
H4A_5	4852.67	5334.14	3065.94	35
H4B_5	4107.98	5301.74	3771.02	35
H5_5	2753.4	4949.49	3511.66	34
H6A_5	2318.85	4593.97	2001.9	43
H6B_5	1872.57	5009.66	2372.2	43
H7A_5	983.19	4397.57	2570.88	52
H7B_5	1282.32	4595.96	3405.63	52
H8A_5	1472.97	3850.21	3457.72	66

Atom	x	y	z	U_{eq}
H8B_5	2047.31	3860.17	2673.23	66
H9A_5	2983.85	3805.56	3769.12	57
H9B_5	2550.14	4215.36	4172.82	57
H10A_5	3576.76	4231.99	2762.46	48
H10B_5	3868.01	4427.88	3601.11	48
H12_5	5161.34	4708.1	2380.11	43
H13_5	5688.34	4379.1	1241.6	51
H14_5	4911.21	4414.54	61.02	42
H15_5	3556.93	4753.67	15.47	46
H16_5	3008.11	5076.07	1152.96	36
H18_5	5187.07	5948.11	2481.92	37
H19_5	5739.55	6335.8	1428.14	38
H20_5	4890.68	6460.06	303.54	38
H21_5	3464.43	6195.54	241.38	37
H22_5	2899.91	5818.69	1310.96	33
H4A_6	121.82	4881.96	1509.95	36
H4B_6	-38.8	5032.04	2443.22	36
H5_6	-826.38	5733.51	2684.46	39
H6A_6	-1826.13	6095.56	1425.52	44
H6B_6	-985.77	6312.8	1823.03	44
H7A_6	-2282.47	6605.62	2357.99	58
H7B_6	-1707.67	6382.41	3039.11	58
H8A_6	-3160.45	6166.74	3185.13	62
H8B_6	-3206.28	6008.42	2283.52	62
H9A_6	-3019.75	5410.87	3098.38	60
H9B_6	-2183.91	5621.62	3515.88	60
H10A_6	-2273.9	5334.32	1898.91	51
H10B_6	-1699.25	5117.71	2587.22	51
H12_6	-1113.14	4802.16	774.63	42
H13_6	-1587.75	4742.49	-537.96	50
H14_6	-1639.41	5338.82	-1349.92	55
H15_6	-1200.34	6004.92	-859.56	53
H16_6	-716.62	6070.7	451.75	46
H18_6	1247.71	4972.35	771.16	41
H19_6	1962.69	5064.14	-419.3	49
H20_6	2156.86	5744.27	-941.9	50
H21_6	1622.69	6340.38	-257.25	51
H22_6	885.57	6247.01	928.34	42
H4A_7	2844.81	6736.23	6759.2	38
H4B_7	2864.15	6280.74	6248.79	38
H5_7	3742.28	6235.24	5038.78	41
H6A_7	4988.39	6879.77	4700.58	44
H6B_7	4146.16	6778.11	4167.24	44
H7A_7	5400.87	6446.29	3628.32	56
H7B_7	4690.54	6094.62	3858.38	56
H8A_7	6055.38	5862.06	4325.37	66
H8B_7	6205.38	6302.93	4789.49	66
H9A_7	5783.31	5784.43	5702.87	72
H9B_7	4940.15	5669.27	5180.19	72
H10A_7	5211.31	6460.1	6015.19	58
H10B_7	4502.77	6106	6236.29	58
H12_7	4365.76	6961.34	7087.35	72
H13_7	5166.98	7558.37	7488.22	94

Atom	x	y	z	U_{eq}
H14_7	5262.43	8149.99	6668.02	96
H15_7	4747.45	8109.42	5360.4	88
H16_7	3982.31	7504.94	4932.28	63
H18_7	1737.68	7177.68	6724.98	35
H19_7	1126.94	7851.44	6880.4	48
H20_7	1111.85	8334.42	5833.96	52
H21_7	1788.53	8152.43	4642.38	52
H22_7	2388.06	7472.73	4483.77	41
H4A_8	-2124.22	6592.44	4415.02	34
H4B_8	-1486.44	6167.87	4551.1	34
H5_8	-498.35	6145.07	5631.47	34
H6A_8	-24.18	6875.54	6550.19	39
H6B_8	549.1	6678.37	5854.5	39
H7A_8	1072.77	6439.55	7111.14	55
H7B_8	757.34	6041.67	6583.67	55
H8A_8	201.13	5959.42	7864.57	50
H8B_8	-222.55	6426.78	7831.47	50
H9A_8	-1318.79	5926.73	7587.76	55
H9B_8	-768.04	5710.44	6896.23	55
H10A_8	-1526.02	6549.66	6828.36	41
H10B_8	-1836.79	6148.34	6308.1	41
H12_8	-2827.59	6842.16	5419.71	46
H13_8	-3579.74	7421.6	5946.75	68
H14_8	-2833.02	8019.79	6391.96	68
H15_8	-1313.51	8024.17	6404.45	60
H16_8	-548.45	7447	5877.72	49
H18_8	-2009.91	7094.46	3483.05	49
H19_8	-2127.3	7769.85	2916.95	69
H20_8	-1120	8298.36	3231.79	73
H21_8	69.62	8134.36	4060.15	62
H22_8	228.44	7445.38	4571.4	45
H24A_10	6220.19	5641.06	10162.65	91
H24B_10	7144.38	5548.05	10571.47	91
H24C_10	6271.53	5403.37	11001.16	91
H24A_9	6439.46	1890.73	7154.76	55
H24B_9	5591.95	1940.92	7686.15	55
H24C_9	6525.64	1884.42	8100.17	55
H24A_11	1607.46	8048.39	2174.98	47
H24B_11	1914.3	8064.75	3083.49	47
H24C_11	910.6	7993.74	2863.09	47
H24A_12	1286.56	4305.42	5083.71	61
H24B_12	827.89	4508.49	5841.31	61
H24C_12	1863.06	4522.14	5769.07	61



Dirhodium tetrakis ((1*R*,2*R*)-1-(4-bromophenyl)-2-phenyl-2-(trimethylsilyl)cyclopropane-1-carboxylic acid) (4.11)



Experimental. Single, violet, plate crystals of **4.11** were chosen from the sample as supplied. A suitable crystal with dimensions $0.32 \times 0.26 \times 0.08 \text{ mm}^3$ was selected and mounted on a loop with paratone oil on a XtaLAB Synergy-S diffractometer. The crystal was kept at a steady $T = 106(9) \text{ K}$ during data collection. The structure was solved with the **ShelXT** n/a (Sheldrick, 2015) solution program using dual methods and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL** 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on F^2 .

Crystal Data. $\text{C}_{82}\text{H}_{92}\text{Br}_4\text{O}_{14}\text{Rh}_2\text{Si}_4$, $M_r = 1939.37$, monoclinic, $P2_1$ (No. 4), $a = 14.30555(10) \text{ \AA}$, $b = 23.60506(17) \text{ \AA}$, $c = 14.70686(11) \text{ \AA}$, $\beta = 104.4745(8)^\circ$, $\alpha = \gamma = 90^\circ$, $V = 4808.63(6) \text{ \AA}^3$, $T = 106(9) \text{ K}$, $Z = 2$, $Z' = 1$, $\mu(\text{Cu K}\alpha) = 5.630 \text{ mm}^{-1}$, 65366 reflections measured, 18280 unique ($R_{\text{int}} = 0.0456$) which were used in all calculations. The final wR_2 was 0.1005 (all data) and R_1 was 0.0375 ($I > 2\sigma(I)$).

Compound 4.11

Formula	C ₈₂ H ₉₂ Br ₄ O ₁₄ Rh ₂ Si ₄
$D_{calc.}/\text{g cm}^{-3}$	1.339
μ/mm^{-1}	5.630
Formula Weight	1939.37
Colour	violet
Shape	plate
Size/mm ³	0.32×0.26×0.08
T/K	106(9)
Crystal System	monoclinic
Flack Parameter	-0.001(3)
Hooft Parameter	0.0092(17)
Space Group	$P2_1$
$a/\text{\AA}$	14.30555(10)
$b/\text{\AA}$	23.60506(17)
$c/\text{\AA}$	14.70686(11)
$\alpha/^\circ$	90
$\beta/^\circ$	104.4745(8)
$\gamma/^\circ$	90
$V/\text{\AA}^3$	4808.63(6)
Z	2
Z'	1
Wavelength/ $\text{\AA}$	1.54184
Radiation type	Cu K α
$\theta_{min}/^\circ$	3.103
$\theta_{max}/^\circ$	73.945
Measured Refl's.	65366
Ind't Refl's	18280
Refl's with $I > 2(I)$	17819
R_{int}	0.0456
Parameters	969
Restraints	0
Largest Peak	0.981
Deepest Hole	-0.708
GooF	1.028
wR_2 (all data)	0.1005
wR_2	0.0982
R_1 (all data)	0.0391
R_1	0.0375

Structure Quality Indicators

Reflections:	d min (Cu)	0.80	I/σ	29.1	Rint	4.56%	complete	100% (IUCr)	99%	
Refinement:	Shift	0.001	Max Peak	1.0	Min Peak	-0.7	GooF	1.028	Flack	.001(3)

A violet plate-shaped crystal with dimensions $0.32 \times 0.26 \times 0.08 \text{ mm}^3$ was mounted on a loop with paratone oil. Data were collected using a XtaLAB Synergy, Dualflex, HyPix diffractometer equipped with an Oxford Cryosystems low-temperature device operating at $T = 106(9) \text{ K}$.

Data were measured using ω scans using Cu K α radiation. The diffraction pattern was indexed. The unit cell was refined using **CrysAlisPro** (Rigaku, V1.171.40.53, 2019) on 58890 reflections, 90% of the observed reflections. The total number of runs and images was based on the strategy calculation from the program **CrysAlisPro** (Rigaku, V1.171.40.53, 2019). The maximum resolution that was achieved was $\Theta = 73.945^\circ$ (0.80 Å).

Data reduction, scaling and absorption corrections were performed using **CrysAlisPro** (Rigaku, V1.171.40.53, 2019). The final completeness is 99.70 % out to 73.945° in Θ . A numerical absorption correction based on Gaussian integration over a multifaceted crystal model was performed using CrysAlisPro 1.171.40.53 (Rigaku Oxford Diffraction, 2019). An empirical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK was also performed. The absorption coefficient μ of this material is 5.630 mm $^{-1}$ at this wavelength ($\lambda = 1.54184\text{\AA}$) and the minimum and maximum transmissions are 0.277 and 0.901.

The structure was solved and the space group $P2_1$ (# 4) determined by the ShelXT n/a (Sheldrick, 2015) structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of ShelXL 2018/3 (Sheldrick, 2015). 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

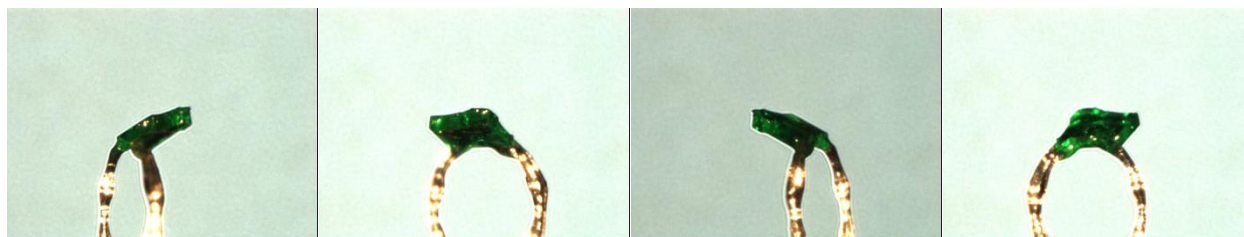


Figure 13: Thermal ellipsoid plot of the molecular structure.

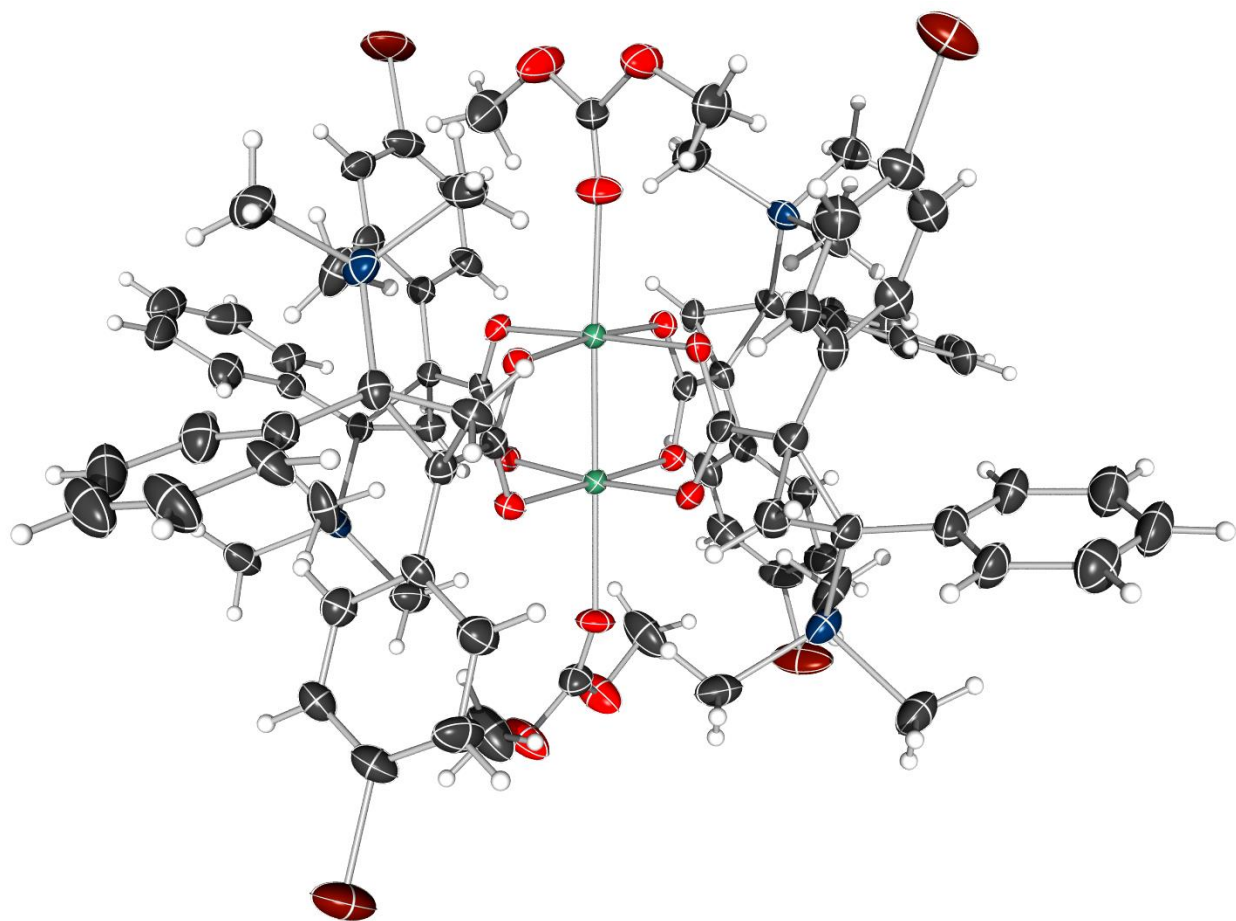


Figure 14: Space filling plot of the molecular structure viewed along the Rh-Rh axis.

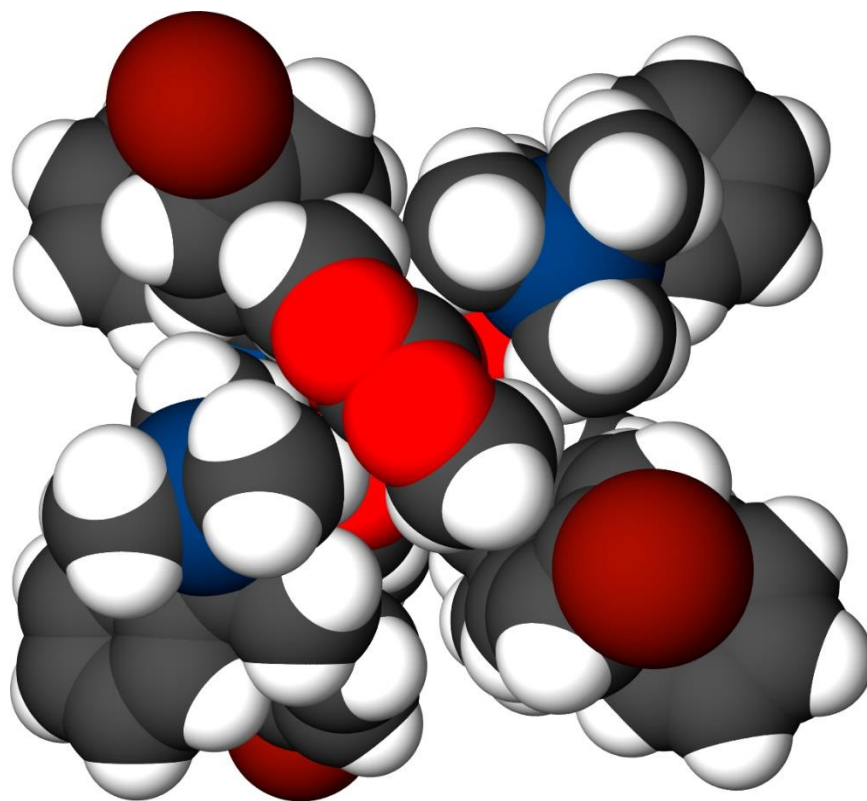
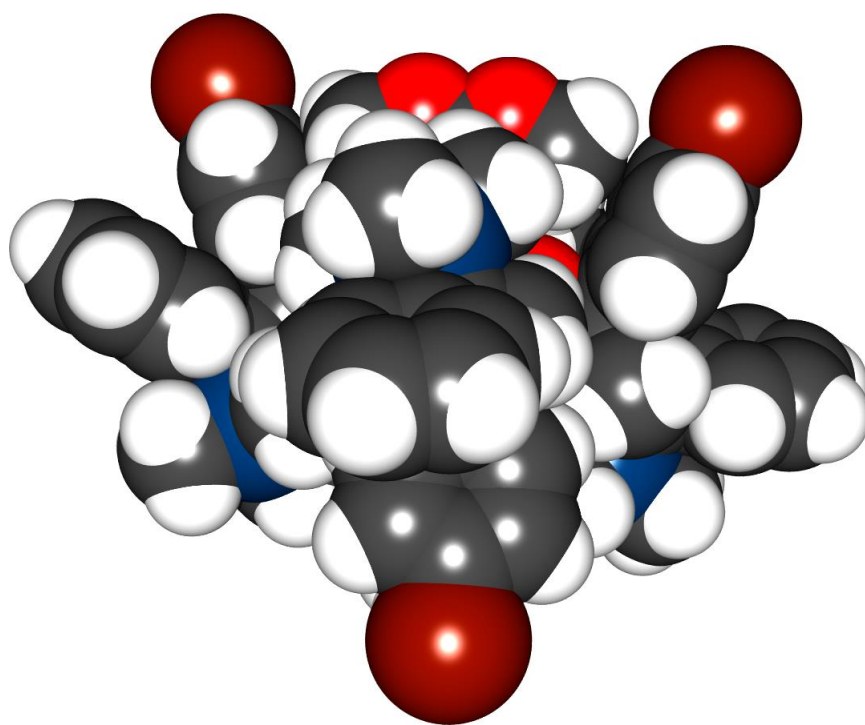
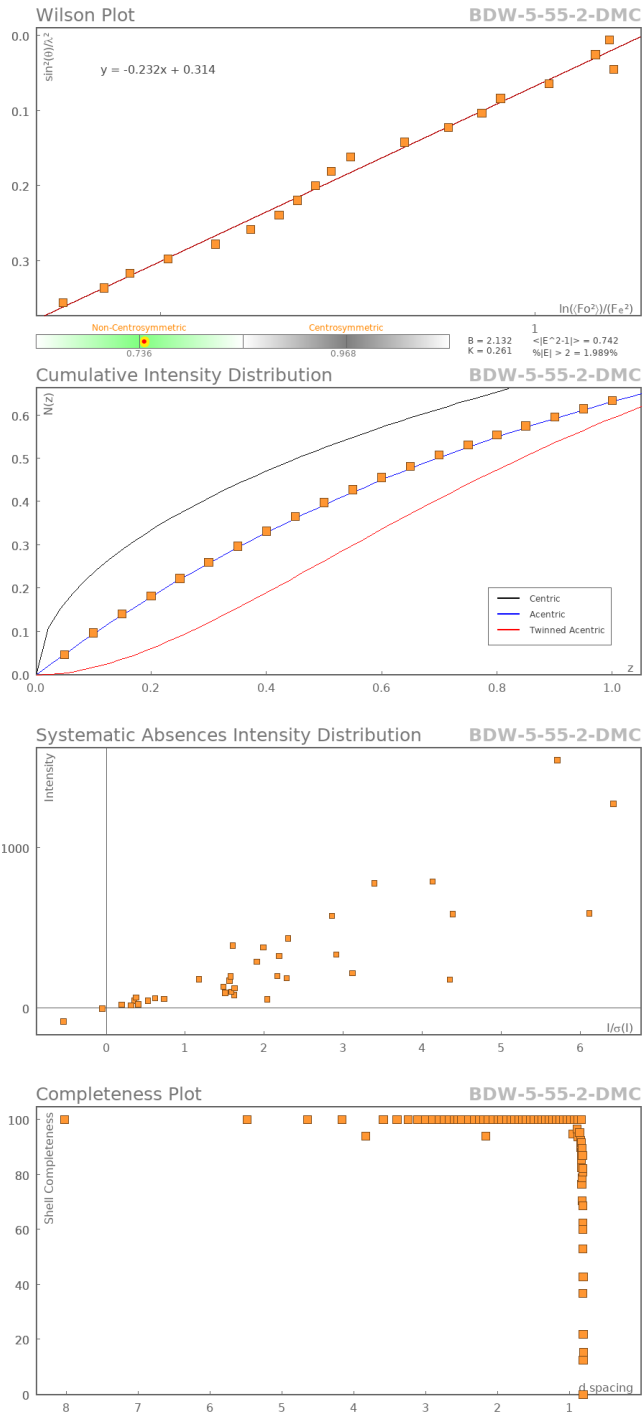
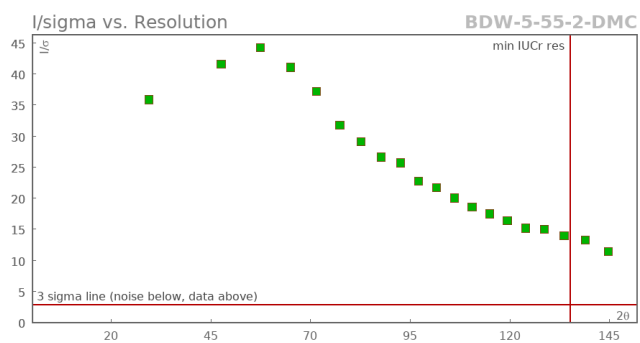


Figure 15: Space filling plot of the molecular structure viewed perpendicular to the Rh-Rh axis.

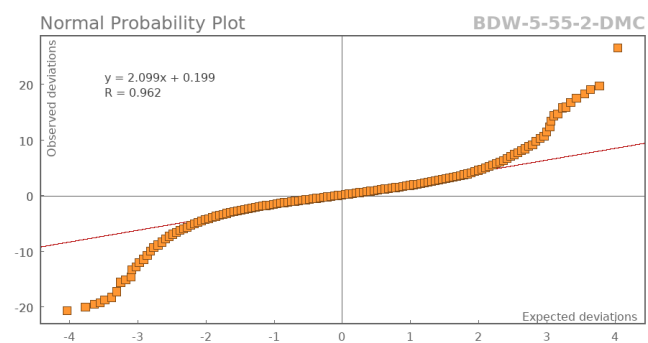
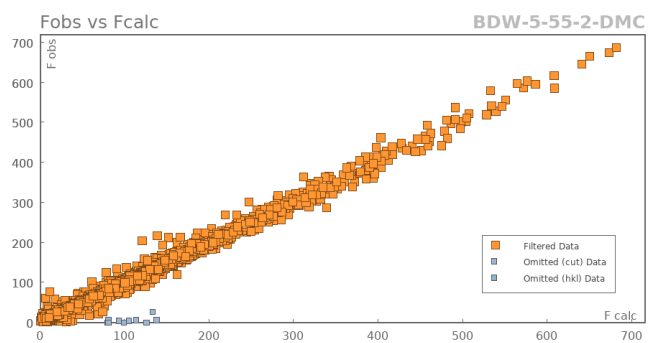


Data Plots: Diffraction Data





Data Plots: Refinement and Data



Reflection Statistics

Total reflections (after filtering)	65418	Unique reflections	18280
Completeness	0.937	Mean I/σ	25.78
$hkl_{\max}$ collected	(12, 29, 18)	$hkl_{\min}$ collected	(-17, -28, -17)
$hkl_{\max}$ used	(17, 29, 18)	$hkl_{\min}$ used	(-17, -28, 0)
Lim $d_{\max}$ collected	100.0	Lim $d_{\min}$ collected	0.77
$d_{\max}$ used	14.24	$d_{\min}$ used	0.8
Friedel pairs	6021	Friedel pairs merged	0
Inconsistent equivalents	187	R_{int}	0.0456
R_{sigma}	0.0344	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	15
Multiplicity	(7971, 6543, 3746, 2267, 1475, 886, 610, 329, 209, 146, 65, 23, 10)	Maximum multiplicity	13
Removed systematic absences	37	Filtered off (Shel/OMIT)	0

Table 17: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **4.11**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
Rh2	7068.09	4689.21	4472.69	18.84(10)
Rh1	5872.7(3)	5237.0(2)	3431.3(3)	18.49(10)
Br2	6768.1(7)	8000.2(4)	755.6(5)	50.7(2)
Br1	9400.5(7)	5375.7(5)	9866.8(6)	62.1(3)
Br4	9707.2(9)	2005.1(5)	3138.5(8)	76.8(4)
Br3	493.6(7)	4198.4(6)	1252.8(8)	76.2(3)
Si3	5217.6(12)	3685.4(8)	6299.0(11)	29.9(3)
Si4	5659.6(12)	4698.5(8)	325.9(11)	29.5(3)
Si1	4504.1(12)	6472.3(8)	5204.5(12)	30.7(3)
Si2	10084.4(11)	5282.0(8)	4537.4(13)	32.3(3)
O4	6935(3)	5177.2(17)	5558(3)	23.5(8)
O11	5944(3)	4662.4(18)	2400(3)	23.6(7)
O10	7181(3)	4202.3(17)	3369(3)	24.5(8)
O6	8043(3)	5270.5(19)	4260(3)	25.7(8)
O9	4856(3)	4715.2(17)	3727(3)	22.6(7)
O8	5994(3)	4137.5(17)	4600(3)	22.8(8)
O7	6918(3)	5734.5(17)	3157(3)	23.0(8)
O5	5913(3)	5756.7(17)	4559(3)	23.9(8)
O1	8246(3)	4189(2)	5517(3)	33.0(10)
O13	3208(4)	5951(3)	1716(5)	59.8(17)
O14	4263(4)	6546(2)	1499(4)	44.5(12)
O12	4763(4)	5782(2)	2391(4)	39.5(11)
O2	8752(5)	3298(2)	5789(4)	52.0(14)
O3	8801(5)	3851(2)	6962(3)	49.2(13)
C1	5706(5)	6469(2)	6125(4)	27.3(12)
C36	7991(5)	6487(3)	1963(5)	33.6(14)
C29	10217(5)	6273(3)	3459(5)	33.6(13)
C43	4295(4)	3555(2)	5132(4)	24.5(11)
C10	5620(5)	6631(3)	7103(4)	32.8(13)
C38	7326(5)	7413(3)	1619(5)	36.5(14)
C82	8577(5)	3816(3)	6044(5)	31.8(13)

Atom	x	y	z	U_{eq}
C70	7793(6)	3144(3)	-920(5)	41.7(16)
C22	7763(4)	5675(3)	3695(4)	26.8(12)
C25	11425(5)	5374(3)	4731(6)	45.5(17)
C17	8214(5)	6038(3)	7232(5)	36.0(14)
C79	4129(5)	6061(3)	1920(4)	30.4(13)
C4	6448(4)	5627(2)	5354(4)	21.0(11)
C40	7813(4)	7102(3)	3207(5)	31.8(13)
C63	5438(6)	4625(3)	-985(4)	39.6(15)
C69	6949(5)	2915(3)	-837(5)	41.5(16)
C81	5246(5)	6721(3)	1610(6)	41.3(16)
C64	4434(5)	4831(4)	528(5)	44.0(17)
C26	9707(5)	4653(3)	3755(6)	45.5(17)
C11	6117(6)	7099(3)	7592(4)	36.9(15)
C20	7588(5)	5415(3)	8542(4)	31.9(13)
C67	6713(5)	3679(3)	191(4)	27.9(12)
C9	6595(4)	6671(2)	5832(4)	26.1(12)
C55	3253(5)	3651(3)	2601(5)	34.0(13)
C39	7428(5)	7525(3)	2561(5)	35.8(14)
C6	3672(6)	6937(3)	5668(6)	46.1(18)
C5	6558(4)	6055(2)	6128(4)	23.9(11)
C52	1708(6)	3027(4)	4820(7)	55(2)
C24	9561(4)	5985(3)	3988(4)	26.8(12)
C48	3274(4)	3483(3)	5216(4)	29.0(12)
C44	6403(5)	3355(3)	6334(5)	41.5(16)
C32	11523(6)	6728(4)	2546(7)	49.7(19)
C13	5415(8)	6934(4)	8885(6)	57(2)
C19	8523(5)	5591(3)	8707(4)	38.2(15)
C14	4905(7)	6463(4)	8405(6)	53(2)
C30	10273(5)	6067(3)	2599(5)	39.2(15)
C45	5376(6)	4455(3)	6558(5)	45.4(18)
C62	6176(4)	3979(2)	801(4)	26.1(12)
C50	1950(6)	3819(4)	5848(6)	53(2)
C12	6007(7)	7241(4)	8483(5)	55(2)
C51	1357(6)	3394(4)	5357(7)	55(2)
C77	7780(6)	2407(3)	2607(5)	44.0(17)
C71	8117(5)	3660(3)	-461(5)	40.3(16)
C49	2898(6)	3861(3)	5762(6)	42.2(16)
C23	8473(4)	6130(3)	3649(4)	27.7(12)
C33	11475(5)	6941(3)	3389(6)	45.8(18)
C65	6501(6)	5298(3)	726(5)	41.4(16)
C57	1710(5)	4096(4)	2127(6)	46.3(18)
C58	1891(5)	4412(3)	2951(5)	40.4(16)
C15	5031(6)	6321(3)	7530(5)	42.5(16)
C80	2959(6)	5438(3)	2159(7)	53(2)
C31	10914(6)	6297(4)	2138(6)	50.1(19)
C3	8647(8)	4394(3)	7355(6)	61(2)
C41	5131(4)	4259(2)	4181(4)	21.1(11)
C42	4361(4)	3830(2)	4183(4)	23.2(11)
C35	8108(4)	6588(3)	2917(4)	27.7(12)
C73	7299(4)	3371(2)	2145(4)	26.0(12)
C54	3435(4)	3944(2)	3454(4)	25.5(11)
C47	4645(4)	3230(2)	4412(4)	26.8(12)
C37	7601(5)	6902(3)	1304(5)	36.8(14)

Atom	x	y	z	U_{eq}
C18	8866(5)	5898(3)	8063(5)	41.8(16)
C68	6400(5)	3171(3)	-277(5)	33.2(13)
C74	8272(5)	3509(3)	2248(4)	32.5(13)
C78	7076(6)	2817(3)	2329(5)	36.6(14)
C72	7576(5)	3915(3)	78(5)	35.1(14)
C53	2660(5)	3060(3)	4759(5)	35.5(14)
C34	10836(5)	6716(3)	3869(5)	37.5(15)
C61	6527(4)	3819(2)	1860(4)	25.4(12)
C21	6953(5)	5566(3)	7712(4)	30.3(13)
C59	2763(4)	4331(3)	3595(5)	34.1(14)
C76	8734(6)	2565(3)	2710(5)	45.0(19)
C66	5554(4)	3632(3)	1288(4)	26.3(12)
C7	3908(5)	5768(3)	4987(6)	41.0(16)
C75	9005(5)	3109(3)	2540(5)	40.3(16)
C56	2390(5)	3727(3)	1929(5)	44.5(17)
C27	9935(5)	5179(3)	5751(5)	40.2(15)
C28	9089(4)	6338(3)	4594(4)	30.6(13)
C46	4757(5)	3319(3)	7231(5)	41.9(17)
C8	4642(5)	6820(3)	4103(5)	36.1(14)
C2	8464(8)	3197(4)	4792(6)	59(2)
C16	7256(4)	5896(2)	7045(4)	24.2(11)
C60	6561(4)	4262(2)	2589(4)	24.3(11)

Table 18: Anisotropic Displacement Parameters ($\times 10^4$) for **4.11**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh2	16.94(18)	21.65(19)	18.46(18)	1.01(15)	5.40(13)	2.26(14)
Rh1	17.27(18)	20.61(18)	18.21(17)	1.43(14)	5.60(13)	1.68(14)
Br2	74.9(6)	32.3(4)	37.9(4)	6.7(3)	0.9(4)	-5.6(3)
Br1	62.0(5)	70.9(6)	38.8(4)	11.7(4)	-14.7(4)	-1.9(4)
Br4	87.6(7)	56.1(5)	67.6(6)	-11.2(5)	-16.2(5)	45.0(5)
Br3	43.3(5)	103.8(8)	63.3(6)	26.8(6)	-20.9(4)	1.0(5)
Si3	33.4(9)	32.6(8)	23.4(8)	1.7(6)	6.9(6)	-8.5(7)
Si4	38.5(8)	28.6(8)	20.9(7)	-1.1(6)	6.6(6)	4.2(7)
Si1	29.3(8)	30.3(8)	33.0(9)	-5.7(7)	8.7(7)	5.9(7)
Si2	21.6(7)	29.3(8)	46.3(9)	0.5(8)	9.2(6)	-0.9(7)
O4	23.2(18)	25(2)	21.5(18)	3.4(16)	3.9(14)	1.7(16)
O11	25.7(19)	25.0(18)	20.7(17)	-0.1(16)	6.9(14)	4.6(16)
O10	21.7(19)	28(2)	23.6(19)	0.7(16)	6.5(15)	4.8(16)
O6	17.4(17)	32(2)	28.2(19)	4.6(18)	7.0(14)	2.7(17)
O9	17.3(17)	22.7(18)	28.5(19)	0.2(17)	7.0(14)	3.0(16)
O8	19.0(18)	24.8(19)	25.0(19)	5.6(15)	5.9(15)	1.0(15)
O7	21.4(19)	28(2)	21.4(18)	3.8(15)	8.0(15)	-2.3(15)
O5	23.0(19)	25(2)	25(2)	3.6(16)	8.1(16)	3.9(15)
O1	28(2)	37(2)	29(2)	10.5(19)	-3.8(17)	6.0(18)
O13	34(3)	51(3)	96(5)	37(3)	17(3)	6(2)
O14	34(2)	42(3)	56(3)	23(2)	9(2)	2(2)
O12	40(3)	32(2)	41(3)	8(2)	0(2)	14(2)
O2	85(4)	35(3)	35(3)	2(2)	15(3)	20(3)
O3	82(4)	35(3)	29(2)	6(2)	11(2)	18(3)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	34(3)	22(3)	29(3)	-2(2)	12(2)	0(2)
C36	36(3)	30(3)	34(3)	-5(3)	6(3)	-12(3)
C29	27(3)	34(3)	42(4)	6(3)	13(3)	-3(3)
C43	23(3)	24(3)	27(3)	3(2)	8(2)	-5(2)
C10	37(3)	34(3)	29(3)	2(3)	11(3)	10(3)
C38	41(4)	29(3)	35(3)	3(3)	3(3)	-8(3)
C82	30(3)	29(3)	36(3)	4(3)	8(3)	5(2)
C70	51(4)	52(4)	22(3)	-5(3)	10(3)	11(3)
C22	20(3)	37(3)	26(3)	-3(2)	10(2)	6(2)
C25	25(3)	44(4)	68(5)	6(3)	13(3)	0(3)
C17	36(3)	39(4)	31(3)	5(3)	6(3)	-4(3)
C79	30(3)	30(3)	32(3)	7(3)	11(3)	7(2)
C4	20(3)	21(3)	22(3)	0(2)	6(2)	-7(2)
C40	30(3)	37(3)	31(3)	1(3)	12(2)	1(3)
C63	53(4)	37(4)	27(3)	-4(3)	6(3)	8(3)
C69	50(4)	37(4)	33(3)	-13(3)	2(3)	1(3)
C81	34(4)	43(4)	48(4)	4(3)	12(3)	-8(3)
C64	36(4)	57(5)	37(4)	-2(3)	4(3)	12(3)
C26	25(3)	36(4)	79(5)	-7(4)	20(3)	-2(3)
C11	62(4)	26(3)	21(3)	4(2)	8(3)	2(3)
C20	41(3)	32(3)	23(3)	1(2)	9(2)	-1(3)
C67	37(3)	26(3)	21(3)	1(2)	8(2)	2(2)
C9	33(3)	20(3)	22(3)	-2(2)	1(2)	-3(2)
C55	40(3)	30(3)	31(3)	7(3)	7(3)	-2(3)
C39	39(4)	30(3)	39(4)	-1(3)	11(3)	0(3)
C6	44(4)	50(4)	45(4)	-5(3)	12(3)	18(3)
C5	22(3)	27(3)	24(3)	-2(2)	7(2)	-4(2)
C52	34(4)	53(5)	69(5)	24(4)	-3(4)	-15(3)
C24	19(3)	31(3)	31(3)	-2(2)	7(2)	-3(2)
C48	29(3)	27(3)	32(3)	11(2)	10(2)	3(2)
C44	33(3)	48(4)	37(4)	9(3)	-3(3)	-6(3)
C32	34(4)	51(4)	72(5)	7(4)	26(4)	-6(3)
C13	92(7)	47(5)	36(4)	-2(3)	24(4)	17(4)
C19	48(4)	37(3)	24(3)	5(3)	1(3)	2(3)
C14	66(5)	53(5)	51(5)	7(4)	35(4)	12(4)
C30	30(3)	41(4)	51(4)	-1(3)	19(3)	-4(3)
C45	65(5)	44(4)	34(4)	-15(3)	26(3)	-20(4)
C62	34(3)	25(3)	19(3)	-5(2)	5(2)	-3(2)
C50	46(4)	63(5)	59(5)	24(4)	30(4)	19(4)
C12	91(7)	45(4)	28(4)	-6(3)	14(4)	7(4)
C51	38(4)	61(5)	70(6)	27(5)	21(4)	3(4)
C77	72(5)	25(3)	36(4)	0(3)	15(3)	9(3)
C71	40(4)	54(4)	32(3)	1(3)	18(3)	3(3)
C49	44(4)	37(4)	51(4)	10(3)	20(3)	2(3)
C23	23(3)	30(3)	30(3)	-7(2)	7(2)	-1(2)
C33	42(4)	35(4)	62(5)	0(3)	16(4)	-10(3)
C65	71(5)	24(3)	32(3)	3(3)	17(3)	-5(3)
C57	31(3)	53(4)	47(4)	21(4)	-4(3)	-7(3)
C58	25(3)	47(4)	49(4)	14(3)	9(3)	5(3)
C15	47(4)	38(4)	47(4)	-2(3)	22(3)	4(3)
C80	46(4)	37(4)	82(6)	18(4)	26(4)	0(3)
C31	40(4)	61(5)	54(5)	-1(4)	21(4)	-4(4)
C3	106(8)	37(4)	43(4)	-1(3)	25(5)	5(4)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C41	29(3)	18(2)	19(2)	-1(2)	11(2)	-2(2)
C42	22(3)	25(3)	24(3)	2(2)	9(2)	2(2)
C35	27(3)	26(3)	32(3)	-2(2)	13(2)	-9(2)
C73	35(3)	21(3)	23(3)	-4(2)	9(2)	4(2)
C54	24(3)	26(3)	26(3)	2(2)	5(2)	-4(2)
C47	28(3)	22(3)	29(3)	-2(2)	5(2)	-1(2)
C37	40(4)	39(4)	29(3)	-3(3)	6(3)	-11(3)
C18	30(3)	46(4)	41(4)	7(3)	-6(3)	-11(3)
C68	35(3)	31(3)	32(3)	-5(3)	7(3)	1(3)
C74	34(3)	36(3)	29(3)	-3(3)	12(3)	4(3)
C78	51(4)	32(3)	31(3)	-1(3)	17(3)	0(3)
C72	44(4)	36(3)	28(3)	0(3)	13(3)	-2(3)
C53	29(3)	29(3)	46(4)	8(3)	6(3)	-3(3)
C34	25(3)	44(4)	45(4)	-1(3)	12(3)	-8(3)
C61	31(3)	25(3)	22(3)	0(2)	10(2)	0(2)
C21	30(3)	28(3)	34(3)	0(2)	9(2)	-4(2)
C59	24(3)	37(3)	43(4)	11(3)	11(3)	-4(2)
C76	59(5)	36(4)	36(4)	-1(3)	2(3)	30(3)
C66	27(3)	28(3)	26(3)	-4(2)	11(2)	-3(2)
C7	29(3)	42(4)	55(4)	-17(3)	18(3)	-8(3)
C75	38(4)	48(4)	34(3)	-2(3)	9(3)	16(3)
C56	45(4)	47(4)	33(4)	8(3)	-7(3)	-6(3)
C27	28(3)	40(4)	45(4)	9(3)	-5(3)	1(3)
C28	30(3)	35(3)	27(3)	-3(2)	8(2)	-4(2)
C46	40(4)	54(4)	28(3)	7(3)	2(3)	-16(3)
C8	39(4)	32(3)	34(3)	0(3)	4(3)	11(3)
C2	100(7)	45(4)	34(4)	-4(3)	23(4)	8(4)
C16	31(3)	23(3)	18(3)	-3(2)	5(2)	-1(2)
C60	25(3)	26(3)	26(3)	-2(2)	12(2)	4(2)

Table 19: Bond Lengths in Å for **4.11**.

Atom	Atom	Length/Å
Rh2	Rh1	2.3733(4)
Rh2	O4	2.016(4)
Rh2	O10	2.027(4)
Rh2	O6	2.036(4)
Rh2	O8	2.058(4)
Rh2	O1	2.302(4)
Rh1	O11	2.056(4)
Rh1	O9	2.034(4)
Rh1	O7	2.019(4)
Rh1	O5	2.052(4)
Rh1	O12	2.302(4)
Br2	C38	1.915(7)
Br1	C19	1.916(7)
Br4	C76	1.909(6)
Br3	C57	1.903(7)
Si3	C43	1.910(6)
Si3	C44	1.856(8)
Si3	C45	1.857(7)

Atom	Atom	Length/Å
Si3	C46	1.875(7)
Si4	C63	1.881(6)
Si4	C64	1.876(7)
Si4	C62	1.914(6)
Si4	C65	1.857(7)
Si1	C1	1.905(7)
Si1	C6	1.867(7)
Si1	C7	1.858(7)
Si1	C8	1.870(7)
Si2	C25	1.880(7)
Si2	C26	1.873(8)
Si2	C24	1.915(7)
Si2	C27	1.865(7)
O4	C4	1.264(7)
O11	C60	1.276(7)
O10	C60	1.270(7)
O6	C22	1.264(8)
O9	C41	1.277(7)
O8	C41	1.267(7)
O7	C22	1.277(7)
O5	C4	1.265(7)
O1	C82	1.190(8)
O13	C79	1.303(9)
O13	C80	1.460(9)
O14	C79	1.339(8)
O14	C81	1.435(8)
O12	C79	1.192(8)
O2	C82	1.322(8)
O2	C2	1.440(9)
O3	C82	1.310(8)
O3	C3	1.447(9)
C1	C10	1.523(8)
C1	C9	1.518(8)
C1	C5	1.560(8)
C36	C35	1.391(9)
C36	C37	1.394(10)
C29	C24	1.520(8)
C29	C30	1.376(10)
C29	C34	1.405(10)
C43	C48	1.505(8)
C43	C42	1.564(8)
C43	C47	1.493(8)
C10	C11	1.410(10)
C10	C15	1.379(10)
C38	C39	1.383(10)
C38	C37	1.383(10)
C70	C69	1.356(11)
C70	C71	1.413(11)
C22	C23	1.491(9)
C17	C18	1.380(9)
C17	C16	1.370(9)
C4	C5	1.501(8)
C40	C39	1.394(10)

Atom	Atom	Length/Å
C40	C35	1.387(9)
C69	C68	1.408(10)
C11	C12	1.400(10)
C20	C19	1.363(10)
C20	C21	1.373(9)
C67	C62	1.496(8)
C67	C68	1.401(9)
C67	C72	1.402(9)
C9	C5	1.521(8)
C55	C54	1.399(9)
C55	C56	1.387(10)
C5	C16	1.512(8)
C52	C51	1.352(14)
C52	C53	1.389(11)
C24	C23	1.549(8)
C24	C28	1.498(8)
C48	C49	1.394(10)
C48	C53	1.389(9)
C32	C33	1.357(12)
C32	C31	1.375(12)
C13	C14	1.417(14)
C13	C12	1.358(13)
C19	C18	1.378(10)
C14	C15	1.384(11)
C30	C31	1.381(10)
C62	C61	1.559(8)
C62	C66	1.514(8)
C50	C51	1.393(14)
C50	C49	1.397(11)
C77	C78	1.383(10)
C77	C76	1.385(12)
C71	C72	1.378(9)
C23	C35	1.523(9)
C23	C28	1.528(8)
C33	C34	1.392(10)
C57	C58	1.390(12)
C57	C56	1.390(12)
C58	C59	1.379(10)
C41	C42	1.497(8)
C42	C54	1.506(8)
C42	C47	1.488(8)
C73	C74	1.400(9)
C73	C78	1.390(9)
C73	C61	1.511(8)
C54	C59	1.378(9)
C74	C75	1.397(10)
C61	C66	1.501(8)
C61	C60	1.490(8)
C21	C16	1.403(8)
C76	C75	1.383(12)

Table 20: Bond Angles in ° for **4.11**.

Atom	Atom	Atom	Angle/°
O4	Rh2	Rh1	90.24(11)
O4	Rh2	O10	179.07(16)
O4	Rh2	O6	86.58(16)
O4	Rh2	O8	93.95(16)
O4	Rh2	O1	87.88(16)
O10	Rh2	Rh1	88.90(11)
O10	Rh2	O6	93.72(16)
O10	Rh2	O8	85.67(16)
O10	Rh2	O1	92.99(16)
O6	Rh2	Rh1	86.83(11)
O6	Rh2	O8	175.06(15)
O6	Rh2	O1	91.86(16)
O8	Rh2	Rh1	88.26(10)
O8	Rh2	O1	93.06(15)
O1	Rh2	Rh1	177.77(12)
O11	Rh1	Rh2	87.48(11)
O11	Rh1	O12	91.82(16)
O9	Rh1	Rh2	88.30(11)
O9	Rh1	O11	85.89(15)
O9	Rh1	O5	93.80(15)
O9	Rh1	O12	93.97(17)
O7	Rh1	Rh2	89.77(11)
O7	Rh1	O11	93.46(16)
O7	Rh1	O9	177.99(16)
O7	Rh1	O5	86.64(16)
O7	Rh1	O12	87.95(17)
O5	Rh1	Rh2	86.22(11)
O5	Rh1	O11	173.70(16)
O5	Rh1	O12	94.48(17)
O12	Rh1	Rh2	177.57(13)
C44	Si3	C43	112.3(3)
C44	Si3	C45	109.9(4)
C44	Si3	C46	105.8(3)
C45	Si3	C43	111.3(3)
C45	Si3	C46	110.4(3)
C46	Si3	C43	107.0(3)
C63	Si4	C62	104.1(3)
C64	Si4	C63	104.6(3)
C64	Si4	C62	112.4(3)
C65	Si4	C63	109.0(3)
C65	Si4	C64	112.3(4)
C65	Si4	C62	113.6(3)
C6	Si1	C1	106.7(3)
C6	Si1	C8	105.8(3)
C7	Si1	C1	114.4(3)
C7	Si1	C6	106.3(4)
C7	Si1	C8	112.8(3)
C8	Si1	C1	110.2(3)
C25	Si2	C24	103.9(3)
C26	Si2	C25	108.1(3)
C26	Si2	C24	113.9(3)

Atom	Atom	Atom	Angle/°
C27	Si2	C25	103.1(3)
C27	Si2	C26	113.6(4)
C27	Si2	C24	113.0(3)
C4	O4	Rh2	116.6(3)
C60	O11	Rh1	119.2(3)
C60	O10	Rh2	118.9(3)
C22	O6	Rh2	119.6(4)
C41	O9	Rh1	118.7(3)
C41	O8	Rh2	118.1(3)
C22	O7	Rh1	116.5(4)
C4	O5	Rh1	119.4(4)
C82	O1	Rh2	156.9(5)
C79	O13	C80	114.1(6)
C79	O14	C81	116.3(5)
C79	O12	Rh1	173.0(5)
C82	O2	C2	114.5(6)
C82	O3	C3	116.4(6)
C10	C1	Si1	113.5(4)
C10	C1	C5	113.7(5)
C9	C1	Si1	117.9(4)
C9	C1	C10	117.4(5)
C9	C1	C5	59.2(4)
C5	C1	Si1	124.8(4)
C35	C36	C37	120.5(6)
C30	C29	C24	119.9(6)
C30	C29	C34	118.8(6)
C34	C29	C24	121.1(6)
C48	C43	Si3	114.3(4)
C48	C43	C42	113.4(5)
C42	C43	Si3	123.6(4)
C47	C43	Si3	116.2(4)
C47	C43	C48	120.3(5)
C47	C43	C42	58.2(4)
C11	C10	C1	121.9(6)
C15	C10	C1	120.0(6)
C15	C10	C11	118.1(6)
C39	C38	Br2	116.6(5)
C37	C38	Br2	121.0(5)
C37	C38	C39	122.4(6)
O1	C82	O2	124.9(6)
O1	C82	O3	125.4(6)
O3	C82	O2	109.6(5)
C69	C70	C71	119.6(6)
O6	C22	O7	125.9(6)
O6	C22	C23	117.8(5)
O7	C22	C23	116.3(5)
C16	C17	C18	122.6(6)
O13	C79	O14	108.5(5)
O12	C79	O13	127.0(6)
O12	C79	O14	124.5(6)
O4	C4	O5	126.3(5)
O4	C4	C5	116.1(5)
O5	C4	C5	117.6(5)

Atom	Atom	Atom	Angle/°
C35	C40	C39	121.1(6)
C70	C69	C68	121.4(6)
C12	C11	C10	120.3(7)
C19	C20	C21	118.7(6)
C68	C67	C62	123.4(6)
C68	C67	C72	117.7(6)
C72	C67	C62	118.9(5)
C1	C9	C5	61.8(4)
C56	C55	C54	120.5(7)
C38	C39	C40	118.0(6)
C4	C5	C1	119.1(5)
C4	C5	C9	115.5(5)
C4	C5	C16	115.4(5)
C9	C5	C1	59.0(4)
C16	C5	C1	120.0(5)
C16	C5	C9	115.5(5)
C51	C52	C53	121.0(8)
C29	C24	Si2	112.1(4)
C29	C24	C23	115.9(5)
C23	C24	Si2	125.6(4)
C28	C24	Si2	114.7(4)
C28	C24	C29	118.9(5)
C28	C24	C23	60.2(4)
C49	C48	C43	119.8(6)
C53	C48	C43	123.4(6)
C53	C48	C49	116.8(6)
C33	C32	C31	120.0(7)
C12	C13	C14	120.1(7)
C20	C19	Br1	118.3(5)
C20	C19	C18	122.7(6)
C18	C19	Br1	119.0(5)
C15	C14	C13	118.8(8)
C29	C30	C31	120.7(7)
C67	C62	Si4	114.2(4)
C67	C62	C61	113.6(5)
C67	C62	C66	118.6(5)
C61	C62	Si4	125.3(4)
C66	C62	Si4	115.7(4)
C66	C62	C61	58.4(4)
C51	C50	C49	118.8(8)
C13	C12	C11	120.5(8)
C52	C51	C50	119.9(7)
C78	C77	C76	118.0(7)
C72	C71	C70	119.2(7)
C48	C49	C50	122.1(8)
C22	C23	C24	117.9(5)
C22	C23	C35	115.2(5)
C22	C23	C28	115.8(5)
C35	C23	C24	121.6(5)
C35	C23	C28	115.7(5)
C28	C23	C24	58.3(4)
C32	C33	C34	120.8(7)
C58	C57	Br3	117.4(6)

Atom	Atom	Atom	Angle/°
C56	C57	Br3	120.5(6)
C56	C57	C58	122.1(6)
C59	C58	C57	117.6(7)
C10	C15	C14	122.1(8)
C32	C31	C30	120.2(8)
O9	C41	C42	116.2(5)
O8	C41	O9	125.5(5)
O8	C41	C42	118.3(5)
C41	C42	C43	119.4(5)
C41	C42	C54	113.2(5)
C54	C42	C43	118.1(5)
C47	C42	C43	58.5(4)
C47	C42	C41	119.0(5)
C47	C42	C54	118.2(5)
C36	C35	C23	121.7(6)
C40	C35	C36	119.4(6)
C40	C35	C23	118.7(5)
C74	C73	C61	120.4(5)
C78	C73	C74	117.9(6)
C78	C73	C61	121.7(6)
C55	C54	C42	118.9(5)
C59	C54	C55	118.8(6)
C59	C54	C42	122.3(6)
C42	C47	C43	63.3(4)
C38	C37	C36	118.5(6)
C19	C18	C17	117.2(6)
C67	C68	C69	119.9(6)
C75	C74	C73	121.7(7)
C77	C78	C73	122.0(7)
C71	C72	C67	122.2(6)
C48	C53	C52	121.4(7)
C33	C34	C29	119.3(7)
C73	C61	C62	118.5(5)
C66	C61	C62	59.3(4)
C66	C61	C73	117.4(5)
C60	C61	C62	119.6(5)
C60	C61	C73	113.7(5)
C60	C61	C66	118.0(5)
C20	C21	C16	120.9(6)
C54	C59	C58	122.3(7)
C77	C76	Br4	117.8(6)
C75	C76	Br4	119.2(6)
C75	C76	C77	122.9(6)
C61	C66	C62	62.3(4)
C76	C75	C74	117.4(7)
C55	C56	C57	118.5(7)
C24	C28	C23	61.6(4)
C17	C16	C5	121.5(5)
C17	C16	C21	117.7(6)
C21	C16	C5	120.7(5)
O11	C60	C61	117.8(5)
O10	C60	O11	124.6(5)
O10	C60	C61	117.6(5)

Table 21: Torsion Angles in ° for **4.11**.

Atom	Atom	Atom	Atom	Angle/°
Rh2	O4	C4	O5	12.1(7)
Rh2	O4	C4	C5	-165.0(3)
Rh2	O10	C60	O11	10.4(8)
Rh2	O10	C60	C61	-166.7(4)
Rh2	O6	C22	O7	-6.9(8)
Rh2	O6	C22	C23	172.5(4)
Rh2	O8	C41	O9	-4.5(7)
Rh2	O8	C41	C42	173.3(4)
Rh2	O1	C82	O2	75.2(14)
Rh2	O1	C82	O3	-103.0(12)
Rh1	O11	C60	O10	-3.4(8)
Rh1	O11	C60	C61	173.7(4)
Rh1	O9	C41	O8	11.8(7)
Rh1	O9	C41	C42	-166.1(3)
Rh1	O7	C22	O6	13.9(8)
Rh1	O7	C22	C23	-165.4(4)
Rh1	O5	C4	O4	-5.1(7)
Rh1	O5	C4	C5	172.0(4)
Br2	C38	C39	C40	178.7(5)
Br2	C38	C37	C36	-179.1(5)
Br1	C19	C18	C17	179.1(6)
Br4	C76	C75	C74	-178.6(5)
Br3	C57	C58	C59	178.7(5)
Br3	C57	C56	C55	-177.8(5)
Si3	C43	C48	C49	46.5(7)
Si3	C43	C48	C53	-134.8(5)
Si3	C43	C42	C41	-5.7(7)
Si3	C43	C42	C54	-150.2(5)
Si3	C43	C42	C47	102.2(5)
Si3	C43	C47	C42	-114.9(5)
Si4	C62	C61	C73	-152.4(5)
Si4	C62	C61	C66	100.9(5)
Si4	C62	C61	C60	-6.0(8)
Si4	C62	C66	C61	-117.2(4)
Si1	C1	C10	C11	-120.9(6)
Si1	C1	C10	C15	58.2(7)
Si1	C1	C9	C5	-115.8(5)
Si1	C1	C5	C4	0.5(7)
Si1	C1	C5	C9	104.5(5)
Si1	C1	C5	C16	-152.0(5)
Si2	C24	C23	C22	-4.1(8)
Si2	C24	C23	C35	-157.0(5)
Si2	C24	C23	C28	100.4(6)
Si2	C24	C28	C23	-118.4(5)
O4	C4	C5	C1	-152.4(5)
O4	C4	C5	C9	140.3(5)
O4	C4	C5	C16	1.3(7)
O6	C22	C23	C24	22.3(8)
O6	C22	C23	C35	176.8(5)
O6	C22	C23	C28	-43.8(8)
O9	C41	C42	C43	-131.8(5)

Atom	Atom	Atom	Atom	Angle/°
O9	C41	C42	C54	14.3(7)
O9	C41	C42	C47	160.1(5)
O8	C41	C42	C43	50.2(7)
O8	C41	C42	C54	-163.7(5)
O8	C41	C42	C47	-17.9(8)
O7	C22	C23	C24	-158.3(5)
O7	C22	C23	C35	-3.8(8)
O7	C22	C23	C28	135.6(6)
O5	C4	C5	C1	30.2(7)
O5	C4	C5	C9	-37.1(7)
O5	C4	C5	C16	-176.1(5)
C1	C10	C11	C12	178.9(7)
C1	C10	C15	C14	-177.9(7)
C1	C9	C5	C4	109.9(5)
C1	C9	C5	C16	-111.1(6)
C1	C5	C16	C17	-116.3(6)
C1	C5	C16	C21	67.6(7)
C29	C24	C23	C22	145.4(6)
C29	C24	C23	C35	-7.4(8)
C29	C24	C23	C28	-110.0(6)
C29	C24	C28	C23	104.9(6)
C29	C30	C31	C32	1.7(12)
C43	C48	C49	C50	178.8(6)
C43	C48	C53	C52	-176.7(6)
C43	C42	C54	C55	-115.2(6)
C43	C42	C54	C59	65.3(7)
C10	C1	C9	C5	102.6(6)
C10	C1	C5	C4	147.1(5)
C10	C1	C5	C9	-108.9(6)
C10	C1	C5	C16	-5.4(8)
C10	C11	C12	C13	-0.6(12)
C70	C69	C68	C67	1.4(11)
C70	C71	C72	C67	0.2(11)
C22	C23	C35	C36	-73.9(7)
C22	C23	C35	C40	100.9(6)
C22	C23	C28	C24	108.2(6)
C4	C5	C16	C17	90.2(7)
C4	C5	C16	C21	-85.9(7)
C69	C70	C71	C72	1.2(11)
C81	O14	C79	O13	-177.1(6)
C81	O14	C79	O12	2.3(10)
C11	C10	C15	C14	1.2(11)
C20	C19	C18	C17	1.4(12)
C20	C21	C16	C17	3.1(9)
C20	C21	C16	C5	179.3(6)
C67	C62	C61	C73	-3.5(8)
C67	C62	C61	C66	-110.2(6)
C67	C62	C61	C60	142.9(5)
C67	C62	C66	C61	101.5(6)
C9	C1	C10	C11	22.3(9)
C9	C1	C10	C15	-158.6(6)
C9	C1	C5	C4	-104.0(6)
C9	C1	C5	C16	103.5(6)

Atom	Atom	Atom	Atom	Angle/°
C9	C5	C16	C17	-48.9(8)
C9	C5	C16	C21	135.1(6)
C55	C54	C59	C58	4.3(9)
C39	C38	C37	C36	0.2(10)
C39	C40	C35	C36	-1.9(9)
C39	C40	C35	C23	-176.8(6)
C5	C1	C10	C11	88.6(7)
C5	C1	C10	C15	-92.3(7)
C24	C29	C30	C31	-175.5(7)
C24	C29	C34	C33	175.4(6)
C24	C23	C35	C36	79.6(7)
C24	C23	C35	C40	-105.6(7)
C48	C43	C42	C41	139.9(5)
C48	C43	C42	C54	-4.7(7)
C48	C43	C42	C47	-112.2(6)
C48	C43	C47	C42	100.3(6)
C32	C33	C34	C29	-1.7(12)
C13	C14	C15	C10	-1.4(13)
C19	C20	C21	C16	-0.2(10)
C14	C13	C12	C11	0.3(14)
C30	C29	C24	Si2	74.7(7)
C30	C29	C24	C23	-78.9(8)
C30	C29	C24	C28	-147.6(6)
C30	C29	C34	C33	1.2(10)
C62	C67	C68	C69	-179.8(6)
C62	C67	C72	C71	179.1(6)
C62	C61	C60	O11	30.9(8)
C62	C61	C60	O10	-151.7(5)
C12	C13	C14	C15	0.6(13)
C51	C52	C53	C48	-2.5(11)
C51	C50	C49	C48	-1.5(11)
C77	C76	C75	C74	-0.3(11)
C71	C70	C69	C68	-2.0(11)
C49	C48	C53	C52	2.0(10)
C49	C50	C51	C52	1.0(12)
C33	C32	C31	C30	-2.2(13)
C57	C58	C59	C54	-1.3(10)
C58	C57	C56	C55	3.7(11)
C15	C10	C11	C12	-0.2(10)
C80	O13	C79	O14	-178.1(7)
C80	O13	C79	O12	2.6(12)
C31	C32	C33	C34	2.2(13)
C3	O3	C82	O1	-1.4(11)
C3	O3	C82	O2	-179.8(7)
C41	C42	C54	C55	98.2(6)
C41	C42	C54	C59	-81.4(7)
C41	C42	C47	C43	108.6(6)
C42	C43	C48	C49	-102.3(7)
C42	C43	C48	C53	76.4(7)
C42	C54	C59	C58	-176.2(6)
C35	C36	C37	C38	-0.6(10)
C35	C40	C39	C38	1.5(10)
C35	C23	C28	C24	-112.7(6)

Atom	Atom	Atom	Atom	Angle/°
C73	C74	C75	C76	1.1(10)
C73	C61	C66	C62	-108.4(6)
C73	C61	C60	O11	178.9(5)
C73	C61	C60	O10	-3.8(7)
C54	C55	C56	C57	-0.6(10)
C54	C42	C47	C43	-107.4(6)
C47	C43	C48	C49	-168.0(6)
C47	C43	C48	C53	10.7(9)
C47	C43	C42	C41	-107.9(6)
C47	C43	C42	C54	107.6(6)
C47	C42	C54	C55	-47.9(8)
C47	C42	C54	C59	132.6(6)
C37	C36	C35	C40	1.4(9)
C37	C36	C35	C23	176.1(6)
C37	C38	C39	C40	-0.7(10)
C18	C17	C16	C5	179.9(6)
C18	C17	C16	C21	-3.9(10)
C68	C67	C62	Si4	-114.0(6)
C68	C67	C62	C61	93.5(7)
C68	C67	C62	C66	27.9(9)
C68	C67	C72	C71	-0.8(10)
C74	C73	C78	C77	0.1(9)
C74	C73	C61	C62	80.4(7)
C74	C73	C61	C66	148.5(5)
C74	C73	C61	C60	-67.9(7)
C78	C77	C76	Br4	177.8(5)
C78	C77	C76	C75	-0.5(11)
C78	C73	C74	C75	-1.0(9)
C78	C73	C61	C62	-100.8(7)
C78	C73	C61	C66	-32.7(8)
C78	C73	C61	C60	110.9(6)
C72	C67	C62	Si4	66.2(7)
C72	C67	C62	C61	-86.3(7)
C72	C67	C62	C66	-151.9(6)
C72	C67	C68	C69	0.0(9)
C53	C52	C51	C50	1.0(12)
C53	C48	C49	C50	0.0(10)
C34	C29	C24	Si2	-99.5(7)
C34	C29	C24	C23	106.9(7)
C34	C29	C24	C28	38.2(9)
C34	C29	C30	C31	-1.1(11)
C61	C73	C74	C75	177.9(6)
C61	C73	C78	C77	-178.7(6)
C21	C20	C19	Br1	-179.9(5)
C21	C20	C19	C18	-2.2(11)
C76	C77	C78	C73	0.6(10)
C66	C62	C61	C73	106.7(6)
C66	C62	C61	C60	-106.9(6)
C66	C61	C60	O11	-37.7(8)
C66	C61	C60	O10	139.6(5)
C56	C55	C54	C42	177.2(6)
C56	C55	C54	C59	-3.2(9)
C56	C57	C58	C59	-2.7(11)

Atom	Atom	Atom	Atom	Angle/°
C28	C24	C23	C22	-104.6(6)
C28	C24	C23	C35	102.6(6)
C28	C23	C35	C36	146.7(6)
C28	C23	C35	C40	-38.5(8)
C2	O2	C82	O1	-3.0(11)
C2	O2	C82	O3	175.5(7)
C16	C17	C18	C19	1.7(11)
C60	C61	C66	C62	109.5(6)

Table 22: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **4.11**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

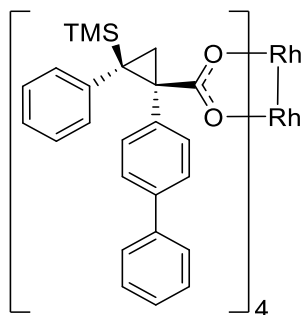
Atom	x	y	z	U_{eq}
H36	8174.18	6139.59	1763.91	40
H70	8155.99	2962.66	-1276.98	50
H25A	11748.58	5035.63	5005.28	68
H25B	11637.15	5688.28	5145.19	68
H25C	11575.01	5445.08	4139.9	68
H17	8433.58	6236.36	6779.2	43
H40	7873.73	7165.54	3843.43	38
H63A	5039.79	4299.13	-1191.31	59
H63B	6042.89	4580.42	-1147.05	59
H63C	5116.67	4958.09	-1283.88	59
H69	6728.59	2581.39	-1156.1	50
H81A	5545.43	6484.57	1233.16	62
H81B	5589.45	6688.05	2257.69	62
H81C	5259.82	7108.2	1412.64	62
H64A	4185.84	5183.86	241.01	66
H64B	4483.3	4848.83	1190.02	66
H64C	4006.19	4529.14	254.85	66
H26A	9766.15	4740.47	3134.31	68
H26B	9048.38	4559.83	3731.26	68
H26C	10114.07	4336.28	3998.64	68
H11	6520.41	7313.92	7320.42	44
H20	7383.19	5197.15	8982.48	38
H9A	7034.56	6922.13	6257.2	31
H9B	6528.15	6747.59	5171.04	31
H55	3714.77	3403.38	2483.12	41
H39	7244.67	7873.17	2758.08	43
H6A	3468.77	6741.85	6157.96	69
H6B	3118.17	7028.02	5169.26	69
H6C	4002.54	7279.07	5913.53	69
H52	1305.93	2747.5	4485.75	66
H44A	6325.83	2952.72	6260.17	62
H44B	6847.21	3437.28	6925.68	62
H44C	6650.86	3505.51	5833.89	62
H32	11968.69	6873.37	2242.48	60
H13	5343.89	7032.14	9475.98	68
H14	4492.91	6252.61	8672.74	63
H30	9875.55	5769.12	2325.6	47
H45A	5654.36	4632.08	6100.61	68

Atom	x	y	z	U_{eq}
H45B	5795.45	4506.36	7173.12	68
H45C	4759.3	4622.76	6535.2	68
H50	1718.85	4070.31	6227.6	63
H12	6342.87	7548.2	8802.65	66
H51	721.2	3363.14	5399.07	66
H77	7619.24	2036.66	2722.23	53
H71	8688.54	3824.93	-523	48
H49	3290.09	4149.47	6077.3	51
H33	11873.15	7240.86	3650.68	55
H65A	7131.38	5199.96	657.98	62
H65B	6536.97	5378.03	1374.36	62
H65C	6271.22	5627.53	354.12	62
H58	1439.45	4669.01	3062.96	48
H15	4707.86	6007.59	7219.63	51
H80A	2396.6	5267.04	1756.67	80
H80B	2827.38	5533.55	2749.47	80
H80C	3488.21	5175.91	2262.54	80
H31	10933.39	6160.82	1549.96	60
H3A	9088.43	4666.78	7213.6	91
H3B	8753.34	4360.15	8023.44	91
H3C	7995.92	4517.05	7088.33	91
H47A	5327.65	3139.69	4551.93	32
H47B	4224.54	2937.62	4068.75	32
H37	7527.07	6837.35	666.01	44
H18	9510.57	6007.2	8183.72	50
H68	5830	3002.13	-218.46	40
H74	8434.26	3876.18	2117.91	39
H78	6432.92	2717.99	2262.96	44
H72	7791.15	4255.28	377.51	42
H53	2890.75	2792.48	4404.24	43
H34	10818.68	6857.37	4454.77	45
H21	6314.08	5447.38	7590.36	36
H59	2902.4	4543.7	4144.34	41
H66A	4990.66	3814.36	1410.9	32
H66B	5470.06	3233.35	1128.71	32
H7A	4238.2	5537.87	4629.22	61
H7B	3247.55	5816.71	4644.09	61
H7C	3929.6	5587.23	5576.69	61
H75	9651.06	3204.84	2616.66	48
H56	2269.49	3536.28	1358.46	53
H27A	10263.61	4839.2	6013.65	60
H27B	9261.29	5146.6	5729.34	60
H27C	10204.53	5497.16	6133.14	60
H28A	9248.18	6737.71	4653.37	37
H28B	8983.22	6163.98	5157.73	37
H46A	4237.7	3534.78	7363.17	63
H46B	5269.49	3285.44	7792.13	63
H46C	4527.77	2947.9	7016.22	63
H8A	4876.54	7199.62	4241.15	54
H8B	4028.17	6830.51	3651.73	54
H8C	5093.3	6609.09	3850.93	54
H2A	8734.15	3484.87	4472.61	88
H2B	7772.44	3207.51	4581.77	88

Atom	x	y	z	<i>U</i>_{eq}
H2C	8692.79	2832.29	4656.58	88

Table 23: Solvent masking (Olex2) information for **4.11**.

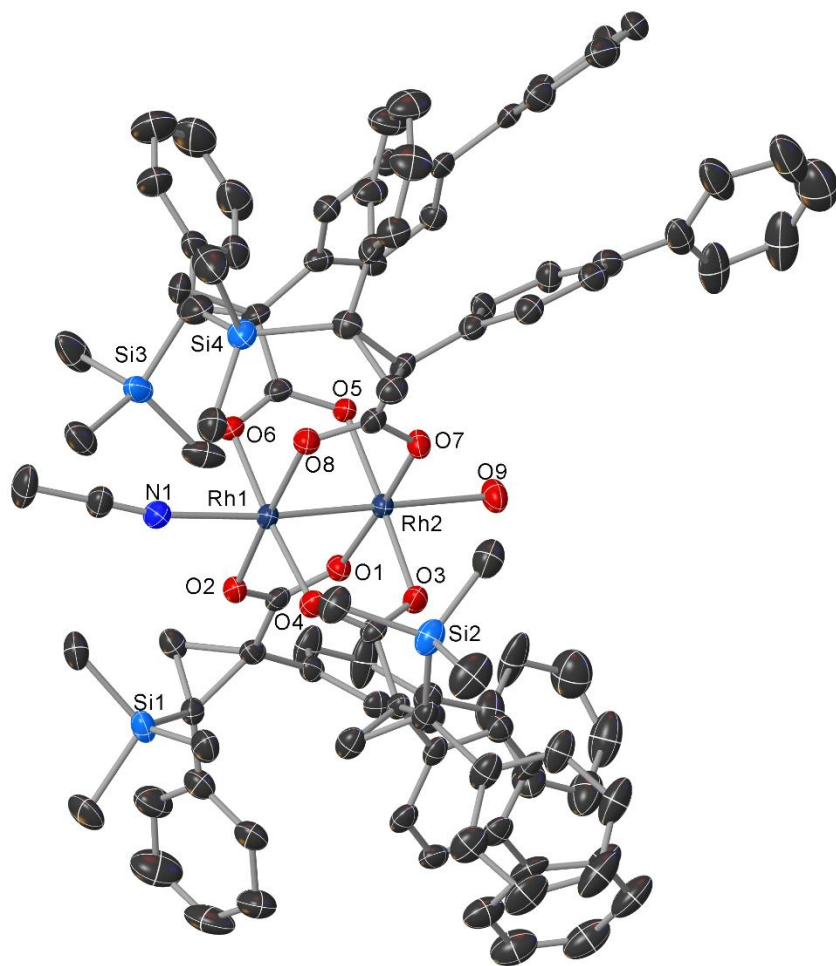
No	x	y	z	V	e	Content
1	0.000	-0.356	0.000	915.1	235.7	?



(1*R*,2*R*)-1-([1,1'-biphenyl]-4-yl)-2-phenyl-2-(trimethylsilyl)cyclopropane-1-carboxylic acid

(4.8)

$R_1=3.28\%$



Compound	4.8
Formula	C ₁₀₉ H ₁₁₃ NO ₉ Rh ₂ Si ₄
$D_{calc.}/\text{g cm}^{-3}$	1.077
μ/mm^{-1}	0.371
Formula Weight	1899.18
Colour	violet
Shape	prism
Size/mm ³	0.30×0.16×0.12
T/K	107(6)
Crystal System	orthorhombic
Flack Parameter	0.012(8)
Hooft Parameter	0.007(7)
Space Group	$P2_12_12_1$
$a/\text{\AA}$	18.2777(3)
$b/\text{\AA}$	24.3504(4)
$c/\text{\AA}$	26.3096(3)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
$V/\text{\AA}^3$	11709.6(3)
Z	4
Z'	1
Wavelength/ $\text{\AA}$	0.71073
Radiation type	MoK α
$\theta_{min}/^\circ$	1.548
$\theta_{max}/^\circ$	27.484
Measured Refl's.	96472
Indep't Refl's	26846
Refl's $I \geq 2 \sigma(I)$	22788
R_{int}	0.0514
Parameters	1141
Restraints	1026
Largest Peak	0.629
Deepest Hole	-0.249
GooF	0.963
wR_2 (all data)	0.0673
wR_2	0.0652
R_1 (all data)	0.0427
R_1	0.0328

Experimental. Single violet crystals of **4.8** were used as supplied. A suitable crystal with dimensions $0.30 \times 0.16 \times 0.12 \text{ mm}^3$ was selected and mounted on a goniometer on a XtaLAB Synergy-Sdiffractometer. The crystal was kept at a steady $T = 107(6) \text{ K}$ during data collection. The structure was solved with the ShelXT (Sheldrick, 2015) solution program using dual methods and by using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on F^2 .

Crystal Data. $\text{C}_{109}\text{H}_{113}\text{NO}_9\text{Rh}_2\text{Si}_4$, $M_r = 1899.18$, orthorhombic, $P2_12_12_1$ (No. 19), $a = 18.2777(3) \text{ \AA}$, $b = 24.3504(4) \text{ \AA}$, $c = 26.3096(3) \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 11709.6(3) \text{ \AA}^3$, $T = 107(6) \text{ K}$, $Z = 4$, $Z' = 1$, $\mu(\text{MoK}\alpha) = 0.371$, 96472 reflections measured, 26846 unique ($R_{\text{int}} = 0.0514$) which were used in all calculations. The final wR_2 was 0.0673 (all data) and R_1 was 0.0328 ($I \geq 2 \sigma(I)$).

Structure Quality Indicators

Reflections:	d min (Mo)	0.77	$I/\sigma(I)$	17.7	R_{int}	5.14%	complete 100% (U _{Cr})	100%		
Refinement:	Shift	-0.004	Max Peak	0.6	Min Peak	-0.2	Goof	0.963	Flack	.012(8)

A violet prism-shaped crystal with dimensions $0.30 \times 0.16 \times 0.12 \text{ mm}^3$ was mounted on a mounted on a loop with paratone. Data were collected using a XtaLAB Synergy, Dualflex, HyPix diffractometer equipped with an Oxford Cryosystems low-temperature device operating at $T = 107(6) \text{ K}$.

Data were measured using ω scans using $\text{MoK}\alpha$ radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.40.24a, 2018). The maximum resolution that was achieved was $\Theta = 27.484^\circ$ ($0.77 \text{ \AA}$).

The unit cell was refined using CrysAlisPro (Rigaku, V1.171.40.24a, 2018) on 40635 reflections, 42% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro (Rigaku, V1.171.40.24a, 2018). The final completeness is 99.90 % out to 27.484° in A numerical absorption correction based on a Gaussian integration over a multifaceted crystal model absorption correction was performed using CrysAlisPro 1.171.39.33a (Rigaku Oxford Diffraction, 2020). An empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm was also applied. The absorption coefficient μ of this material is 0.371 mm^{-1} at this wavelength ($\lambda = 0.71073 \text{ \AA}$) and the minimum and maximum transmissions are 0.648 and 1.000.

The structure was solved and the space group $P2_12_12_1$ (# 19) determined by the ShelXT (Sheldrick, 2015) structure solution program using using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of ShelXL 2018/3 (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

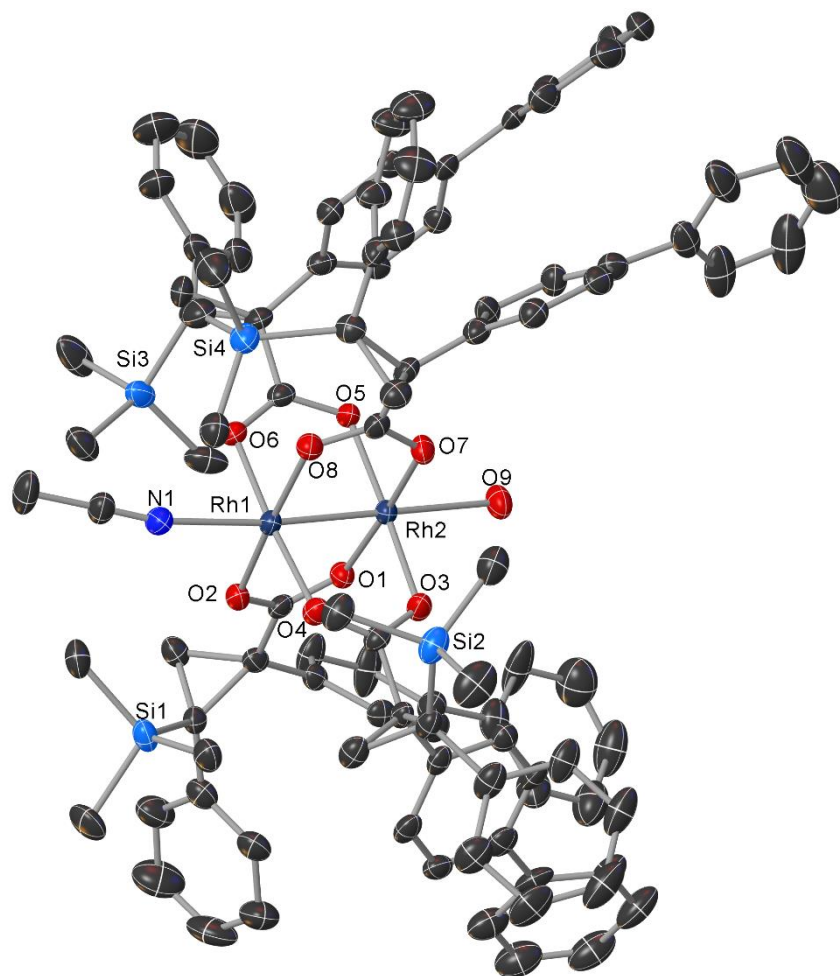
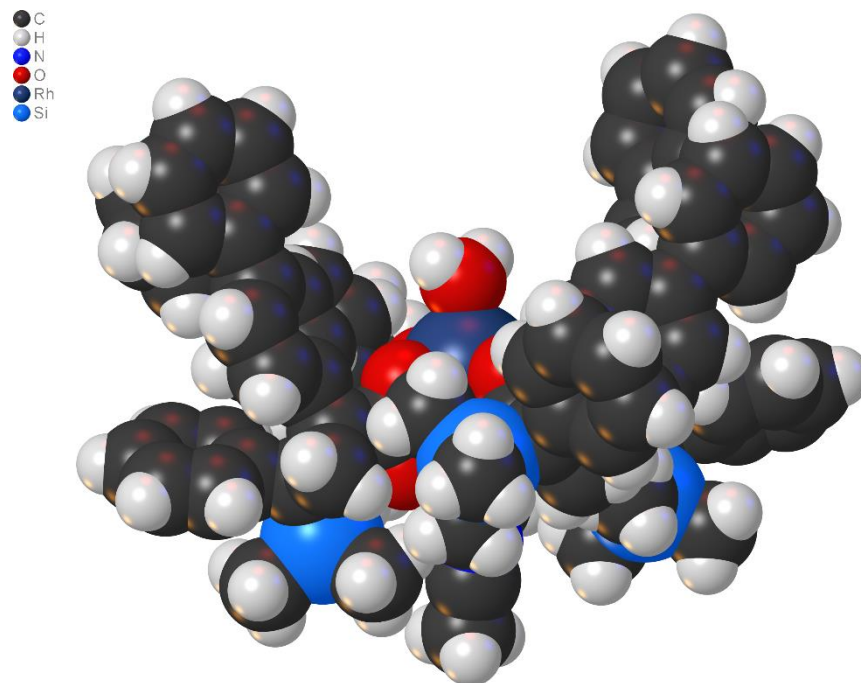
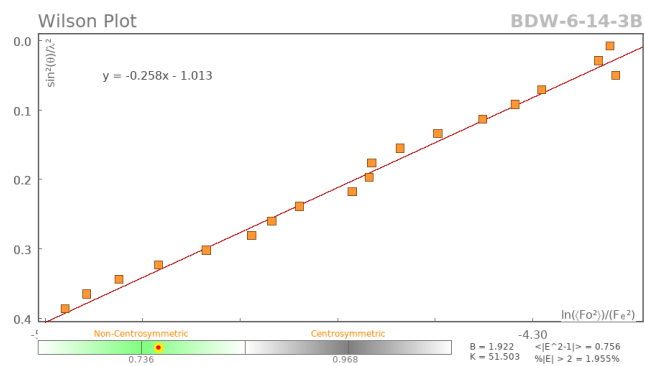
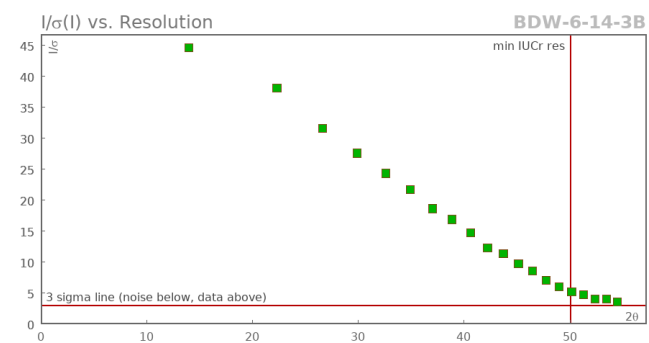
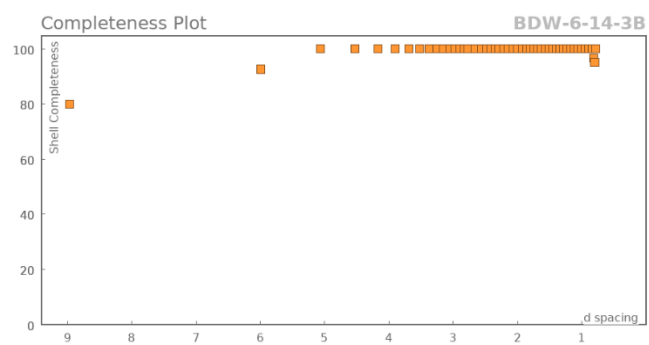
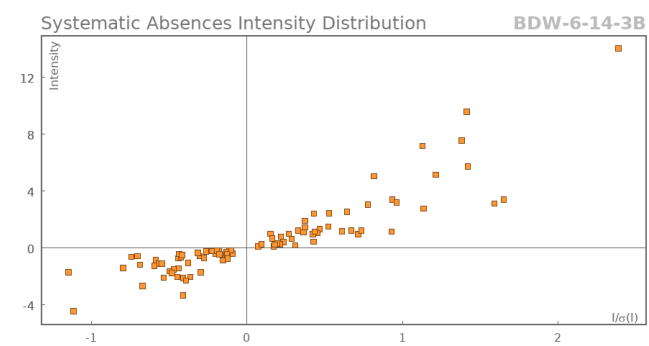
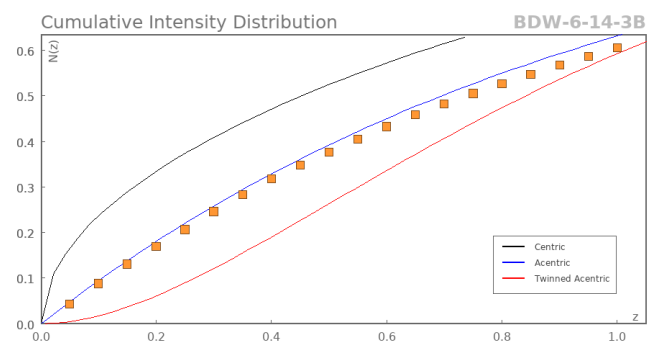
Figure 16:

Figure 17:

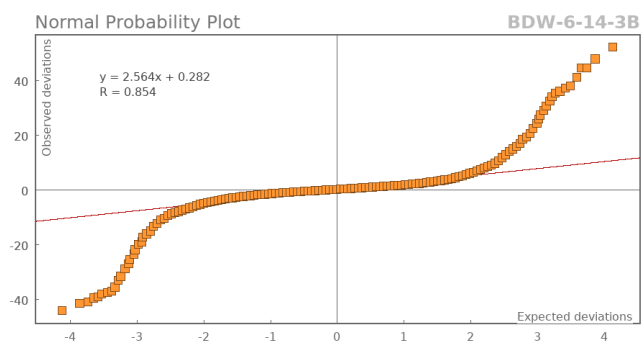
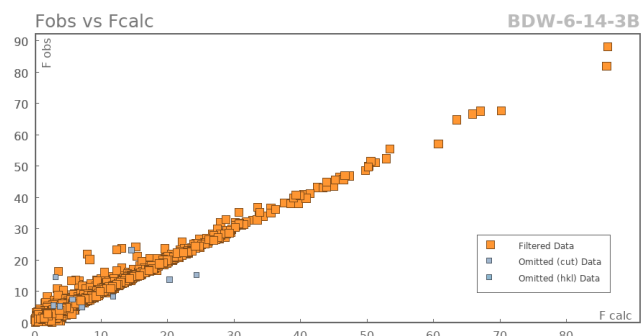
_exptl_absorpt_process_details: CrysAlisPro 1.171.40.24a (Rigaku Oxford Diffraction, 2018) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK.

Data Plots: Diffraction Data





Data Plots: Refinement and Data



Reflection Statistics

Total reflections (after filtering)	96618	Unique reflections	26846
Completeness	0.999	Mean I/σ	15.64
$hkl_{\max}$ collected	(23, 31, 34)	$hkl_{\min}$ collected	(-20, -31, -33)
$hkl_{\max}$ used	(23, 31, 34)	$hkl_{\min}$ used	(-23, 0, 0)
Lim $d_{\max}$ collected	100.0	Lim $d_{\min}$ collected	0.36
$d_{\max}$ used	13.15	$d_{\min}$ used	0.77
Friedel pairs	17607	Friedel pairs merged	0
Inconsistent equivalents	1	R_{int}	0.0514
R_{sigma}	0.0565	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	40
Multiplicity	(41637, 17512, 5214, 1020, 47)	Maximum multiplicity	13
Removed systematic absences	106	Filtered off (Shel/OMIT)	0

Images of the Crystal on the Diffractometer



Table 24: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **4.8**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
Rh1	1413.2(2)	6565.2(2)	1909.3(2)	21.93(6)
Rh2	1549.6(2)	6950.1(2)	1082.6(2)	21.53(6)
Si1	929.8(6)	4688.2(4)	1751.9(3)	31.4(2)
Si3	-1384.7(6)	6748.3(3)	1728.4(4)	34.4(2)
Si4	1865.8(6)	7861.2(4)	3179.9(3)	34.6(2)
Si2	4326.4(5)	6524.9(4)	1914.2(3)	36.1(2)
O9	1646.6(14)	7316.9(8)	250.2(7)	34.9(6)
O1	953.0(12)	6312.8(8)	804.0(7)	23.8(5)
O2	944.0(12)	5894.2(8)	1571.1(7)	25.2(5)
O3	2457.9(12)	6493.9(8)	996.9(7)	28.4(5)
O6	426.3(11)	6963.2(8)	1950.2(7)	24.6(4)
O4	2413.6(12)	6196.6(8)	1806.4(7)	26.2(5)
O5	635.8(12)	7405.2(8)	1213.5(7)	24.5(5)
O8	1887.1(13)	7266.4(8)	2203.7(7)	26.8(5)
O7	2130.6(13)	7563.0(8)	1412.4(7)	26.3(5)
N1	1169.8(16)	6265.1(10)	2683.9(9)	31.2(7)
C15	1111.3(17)	5461.8(12)	8.8(11)	23.6(6)
C77	2475.9(18)	8123.7(13)	2093.9(10)	28.3(7)
C26	2688.0(18)	6201.4(12)	1364.2(10)	24.3(7)
C70	353.1(19)	9879.1(13)	898.6(11)	30.0(7)
C64	-207.3(19)	8292.3(12)	1523.3(11)	28.0(7)
C102	946(2)	6178.8(13)	3069.3(12)	32.8(7)
C27	3317.5(18)	5812.7(12)	1239.5(10)	23.8(7)
C40	3178.7(18)	5009.5(14)	634.4(11)	30.0(7)
C51	281.9(19)	7333.0(12)	1627.1(11)	26.2(7)
C16	1121.5(18)	5503.1(12)	-504.0(11)	27.2(7)
C32	3610(2)	5470.8(13)	1671.8(11)	32.6(7)
C65	-283.0(18)	8393.3(13)	1010.0(11)	29.4(7)
C53	-1125.5(19)	7502.2(13)	1806.5(11)	30.8(7)
C43	3181.7(18)	5698.6(14)	-196.4(11)	29.0(7)
C39	3268.3(18)	5582.9(13)	713.0(10)	26.6(7)
C14	456.5(18)	5457.5(12)	284.8(11)	24.8(7)
C54	-1003(2)	6306.7(14)	2244.5(14)	45.0(9)
C71	928(2)	10174.7(14)	1098.2(14)	36.9(8)
C52	-323(2)	7727.1(12)	1744.0(11)	27.7(7)
C41	3072.8(19)	4797.0(13)	157.4(11)	29.1(7)
C42	3069.0(19)	5137.5(14)	-271.3(12)	32.8(7)
C9	1129(2)	4210.4(14)	522.1(13)	39.9(9)
C57	-664(2)	7678.0(14)	2269.6(11)	33.3(8)
C58	-1719(2)	7863.8(13)	1645.9(13)	34.8(8)
C92	2702(2)	9407.7(13)	964.1(12)	32.7(7)
C44	3286.9(18)	5907.7(13)	286.5(11)	29.8(7)
C17	492(2)	5549.8(14)	-780.6(11)	33.0(8)
C103	642(2)	6055.6(18)	3567.9(13)	49.4(10)
C89	2548.8(19)	8593.1(12)	1721.7(11)	28.4(7)
C93	3199(2)	9343.7(13)	1345.1(12)	32.7(8)
C1	815.8(17)	5919.9(12)	1090.7(11)	24.0(6)
C7	-208.5(19)	5192.0(12)	1121.4(12)	31.5(7)
C2	462.5(18)	5427.6(12)	850.4(11)	25.2(7)

Atom	x	y	z	U_{eq}
C75	-25(2)	10087.7(15)	493.6(13)	38.7(8)
C76	2131.6(18)	7616.7(12)	1891.5(11)	27.3(7)
C69	50.2(19)	8712.6(13)	1832.8(12)	29.1(7)
C3	470.4(18)	4858.0(12)	1111.9(11)	25.4(6)
C28	4086(2)	5931.0(13)	1478.7(11)	29.5(7)
C82	3087.5(19)	8020.1(15)	2478.7(11)	32.8(7)
C66	-122.6(19)	8897.6(13)	803.2(12)	28.9(7)
C33	4720(2)	5768.1(16)	1138.3(12)	39.1(8)
C90	1996.9(18)	8682.0(13)	1365.6(11)	28.3(7)
C67	152.6(18)	9328.8(13)	1116.3(12)	28.7(7)
C84	1793(2)	9186.7(14)	2661.1(13)	38.4(8)
C20	502(2)	5612.3(16)	-1346.6(12)	40.1(9)
C34	4977(2)	6131.4(19)	769.2(12)	42.9(9)
C8	497(2)	4357.5(13)	762.8(12)	32.9(7)
C18	-167(2)	5557(2)	-516.8(13)	53.1(12)
C79	2314(2)	7203.7(14)	3331.6(12)	38.4(9)
C91	2065(2)	9075.1(13)	988.6(11)	31.3(7)
C74	175(3)	10617.6(15)	282.1(14)	47.7(10)
C83	2393(2)	8872.2(13)	2792.3(11)	32.3(7)
C94	3146(2)	8945.5(13)	1710.0(12)	32.3(7)
C72	1145(2)	10673.6(15)	895.9(15)	49.6(10)
C95	2818(2)	9795.6(15)	549.3(14)	43.7(9)
C49	2353(3)	4253.0(19)	-1357.4(14)	55.2(11)
C68	219.0(19)	9220.0(13)	1636.9(12)	28.4(7)
C4	407(2)	4982.5(15)	2292.4(12)	39.3(9)
C78	2393(2)	8271.5(13)	2677.7(11)	29.8(7)
C29	3837(2)	6447.7(15)	2531.7(11)	38.8(9)
C38	5063(2)	5251.8(17)	1186.4(14)	43.5(9)
C59	-2140(3)	8159.1(15)	1981.0(16)	53.8(11)
C55	-1097(2)	6487.9(14)	1090.7(14)	44.2(9)
C47	3007(2)	5006(2)	-1706.9(13)	53.2(11)
C5	1907(2)	4840.7(14)	1781.4(12)	37.9(9)
C85	1766(2)	9732.9(14)	2789.5(15)	47.2(10)
C63	-1941(2)	7892.6(14)	1139.5(13)	40.3(8)
C48	2601(2)	4531.9(19)	-1768.9(14)	55.8(11)
C35	5553(2)	5998(2)	467.4(13)	52.3(11)
C96	2679(2)	9635(2)	38.8(15)	58.2(11)
C6	857(3)	3922.9(13)	1822.2(14)	47.5(10)
C30	4102(2)	7200.3(16)	1611.6(13)	44.0(9)
C80	887(2)	7785.2(15)	3037.1(13)	44.9(10)
C13	-118(2)	4027.1(15)	679.7(15)	47.5(10)
C10	1180(3)	3744.9(15)	219.7(15)	56.4(11)
C86	2327(2)	9976.3(17)	3045.4(15)	53.2(10)
C87	2934(2)	9661.6(15)	3176.4(14)	48.1(10)
C21	72(2)	5974(2)	-1604.7(14)	63.0(14)
C46	3159(2)	5194.2(17)	-1226.1(12)	41.2(9)
C19	-183(2)	5511.7(17)	-0.8(12)	42.4(9)
C25	994(3)	5298.4(16)	-1642.9(13)	48.3(10)
C50	2502(2)	4444.6(16)	-859.0(14)	45.1(9)
C81	1916(3)	8286.6(17)	3769.2(13)	59.8(13)
C60	-2756(3)	8459.0(19)	1818.4(19)	71.6(13)
C11	583(3)	3433.5(16)	161.2(16)	61.6(11)
C56	-2410(2)	6709.2(16)	1771.6(19)	60.4(12)

Atom	x	y	z	U_{eq}
C37	5640(2)	5120(2)	872.4(15)	54.5(11)
C73	756(2)	10892.3(14)	488.7(14)	45.6(9)
C100	3061(3)	10337.6(17)	644(2)	62.6(12)
C97	2770(3)	10016(2)	-350.2(17)	71.5(14)
C88	2964(2)	9126.4(13)	3045.8(11)	33.3(7)
C36	5880(2)	5484(2)	509.0(15)	61.1(12)
C45	2913(2)	4930.3(14)	-798.5(12)	36.0(8)
C98	3025(4)	10538(3)	-234(2)	85.8(16)
C99	3183(3)	10675(2)	201(2)	71.5(13)
C62	-2542(2)	8176.6(16)	977.6(17)	53.7(10)
C61	-2950(3)	8463(2)	1312(2)	75.4(14)
C12	-89(3)	3568.2(18)	396.4(19)	69.0(13)
C31	5314(2)	6491(2)	2045.3(15)	57.1(11)
C23	550(3)	5712(2)	-2396.5(14)	63.6(12)
C24	1029(3)	5341.9(18)	-2153.3(14)	57.4(11)
C22	125(3)	6028(2)	-2115.7(17)	68.5(13)
C109	6318(3)	5528(2)	2929.3(18)	72.0(14)
C104	5709(3)	5600(2)	3209.9(16)	67.8(14)
C106	6145(4)	6428(3)	3550(2)	92.8(19)
C108	6905(3)	5945(2)	2983(2)	86.3(18)
C107	6781(5)	6375(3)	3288(3)	125(3)
C105	5606(3)	6040.9(19)	3532.5(17)	61.1(12)
C110	4916(3)	6085(3)	3836.6(19)	97(2)

Table 25: Anisotropic Displacement Parameters ($\times 10^4$) for **4.8**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh1	24.42(14)	22.91(11)	18.47(10)	1.51(9)	4.46(9)	0.53(10)
Rh2	24.96(14)	20.5(1)	19.13(10)	1.31(8)	3.64(9)	-0.31(10)
Si1	30.9(6)	30.6(5)	32.8(5)	10.9(4)	2.0(4)	-2.5(4)
Si3	28.1(6)	24.9(4)	50.2(5)	3.6(4)	6.6(4)	3.0(4)
Si4	42.7(6)	33.5(5)	27.8(4)	-3.1(4)	5.3(4)	-1.1(4)
Si2	29.7(5)	52.2(6)	26.4(4)	-4.0(4)	0.8(4)	-3.0(5)
O9	50.8(18)	30.9(12)	22.9(10)	2.2(9)	4.0(10)	-10.0(12)
O1	29.4(14)	22.1(10)	19.9(9)	-0.6(8)	3.1(8)	-0.9(9)
O2	27.9(13)	23.6(10)	24.0(10)	4.3(8)	4.5(9)	1.7(10)
O3	26.1(13)	30.6(11)	28.5(10)	7.0(9)	7.0(9)	7.1(10)
O6	27.7(12)	23.2(9)	22.9(9)	-4.3(9)	4.6(8)	1.9(9)
O4	26.6(13)	29.9(11)	22.0(10)	2.7(8)	0.4(8)	4.0(10)
O5	29.4(14)	21.4(10)	22.6(10)	2.7(8)	6.2(8)	3.7(9)
O8	30.2(14)	23.9(10)	26.4(10)	-2.6(8)	1.9(9)	-2.0(10)
O7	32.5(14)	25.5(11)	21.0(9)	-1.5(8)	3.7(9)	-7.5(10)
N1	41.3(19)	27.5(13)	24.9(12)	-1.7(11)	5.0(11)	1.7(13)
C15	13.3(16)	27.7(15)	29.8(14)	-0.9(12)	-2.9(11)	1.0(13)
C77	25.8(19)	33.3(16)	25.9(14)	-3.0(12)	8.9(12)	3.7(14)
C26	24.0(18)	28.0(15)	20.8(13)	-6.2(12)	0.4(12)	-1.2(13)
C70	25.4(19)	30.1(16)	34.5(16)	2.0(13)	16.8(13)	6.7(14)
C64	25.5(19)	25.7(15)	32.8(15)	-6.2(12)	3.2(13)	5.0(14)
C102	32(2)	36.2(17)	30.7(15)	6.1(14)	4.8(14)	3.2(15)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C27	25.2(18)	27.7(15)	18.4(12)	4.3(11)	2.8(11)	6.0(13)
C40	20.6(19)	40.8(17)	28.6(15)	2.8(13)	5.9(12)	10.2(15)
C51	28.4(19)	23.2(15)	27.2(14)	-5.4(12)	2.0(13)	2.0(13)
C16	20.5(18)	32.9(17)	28.3(14)	-0.5(13)	6.3(12)	-0.3(14)
C32	28(2)	41.3(17)	28.3(14)	2.8(13)	-1.9(14)	7.9(16)
C65	29.9(19)	23.1(14)	35.3(15)	2.0(13)	5.4(13)	4.6(14)
C53	28.8(18)	29.4(16)	34.1(16)	-3.2(13)	13.0(13)	5.9(13)
C43	23.3(19)	42.1(17)	21.5(13)	0.6(12)	8.2(12)	12.4(15)
C39	17.3(18)	37.5(16)	25.1(13)	2.6(12)	6.8(12)	3.9(14)
C14	20.1(17)	22.5(15)	31.9(14)	2.2(12)	1.8(12)	-2.6(13)
C54	41(3)	30.0(18)	63(2)	10.1(17)	3.8(19)	-4.6(18)
C71	26(2)	39.0(18)	45.7(18)	0.8(16)	5.0(16)	3.3(15)
C52	31.4(19)	25.6(15)	26.2(14)	-7.2(12)	4.8(13)	4.9(14)
C41	25(2)	24.2(15)	38.5(15)	-4.1(12)	5.7(13)	3.4(14)
C42	18.7(19)	43.2(18)	36.5(15)	-0.6(14)	1.3(13)	11.1(15)
C9	46(2)	26.8(16)	47.1(19)	8.3(14)	0.0(16)	6.7(16)
C57	33(2)	34.7(18)	32.1(15)	4.5(14)	13.2(14)	-3.6(16)
C58	28(2)	28.0(16)	48.0(17)	8.4(14)	8.6(14)	-1.5(14)
C92	32(2)	27.5(16)	38.8(17)	-0.4(13)	3.6(14)	2.8(14)
C44	26(2)	30.3(16)	33.3(15)	2.8(12)	1.3(13)	3.0(14)
C17	32(2)	37.4(19)	29.5(15)	1.7(14)	4.0(13)	5.8(16)
C103	42(3)	69(3)	36.8(18)	18.1(18)	11.6(17)	1(2)
C89	29.7(19)	28.9(16)	26.7(14)	-4.9(12)	3.5(12)	0.3(14)
C93	30(2)	25.5(16)	42.3(17)	-4.3(13)	4.3(14)	-5.6(14)
C1	20.3(17)	26.0(14)	25.8(13)	-4.9(12)	7.0(12)	1.0(12)
C7	32.2(19)	26.9(16)	35.4(16)	6.0(14)	-1.8(15)	-3.5(14)
C2	21.3(18)	23.1(14)	31.3(14)	0.6(12)	3.0(12)	3.1(13)
C75	36(2)	40.3(19)	40.1(18)	0.5(15)	10.6(15)	-0.5(17)
C76	25.5(18)	26.6(14)	30.0(14)	0.5(12)	7.1(14)	5.0(13)
C69	29(2)	30.4(16)	27.5(16)	0.0(13)	5.9(13)	2.4(14)
C3	26.1(18)	24.4(14)	25.6(14)	0.4(12)	6.4(13)	-3.9(13)
C28	29.4(19)	35.9(17)	23.2(14)	3.7(13)	2.8(12)	6.0(15)
C82	32(2)	34.8(17)	31.4(15)	-8.9(14)	-2.1(13)	-2.5(16)
C66	28(2)	29.7(16)	29.2(15)	3.8(12)	1.9(13)	7.3(14)
C33	29(2)	58(2)	30.5(16)	3.6(15)	-1.8(14)	8.4(17)
C90	16.0(18)	28.0(16)	40.9(16)	7.6(13)	4.6(13)	0.2(14)
C67	22.0(18)	30.8(16)	33.3(15)	1.5(13)	14.0(14)	3.1(13)
C84	35(2)	31.4(17)	49(2)	-11.5(15)	4.6(16)	-3.6(15)
C20	32(2)	57(2)	32.1(16)	0.2(15)	-3.7(14)	-19.1(17)
C34	23(2)	75(3)	30.8(17)	0.4(17)	1.7(14)	-3.9(19)
C8	38(2)	28.5(16)	32.5(16)	5.9(13)	-4.8(14)	0.0(15)
C18	17(2)	107(4)	34.4(17)	18(2)	-2.2(14)	-16(2)
C79	41(2)	41.7(19)	32.7(16)	2.0(15)	5.3(15)	-5.5(17)
C91	31(2)	36.2(17)	26.9(15)	6.2(13)	3.9(13)	-0.7(15)
C74	66(3)	40(2)	37.1(19)	8.9(16)	18.2(18)	-0.8(19)
C83	36(2)	34.2(16)	26.5(15)	-6.1(13)	11.5(13)	-4.2(15)
C94	30(2)	33.5(17)	33.6(16)	-3.1(13)	1.8(14)	-1.6(14)
C72	41(3)	36.8(19)	71(2)	-5.4(17)	17.9(18)	0.6(18)
C95	27(2)	44(2)	60(2)	18.8(17)	6.2(17)	3.8(17)
C49	52(3)	66(3)	47(2)	-19.0(18)	-8.9(18)	13(2)
C68	22.9(19)	28.3(16)	34.0(15)	-3.7(13)	4.8(13)	-2.9(14)
C4	43(2)	43(2)	32.4(17)	8.4(15)	2.8(15)	-14.1(18)
C78	35(2)	31.4(16)	22.7(14)	-4.0(12)	-4.1(13)	1.0(14)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C29	34(2)	56(2)	26.3(15)	-3.9(15)	-2.1(14)	-2.7(18)
C38	31(2)	58(2)	41(2)	-3.1(17)	-6.6(15)	8.5(18)
C59	55(3)	42(2)	65(2)	10.3(18)	25(2)	19(2)
C55	42(2)	27.1(17)	63(2)	-4.2(17)	-14.9(19)	10.6(16)
C47	34(3)	90(3)	35.3(17)	-22.6(19)	3.1(16)	7(2)
C5	43(2)	35.2(18)	35.0(17)	10.3(15)	4.8(15)	2.4(17)
C85	48(3)	27.7(17)	66(2)	-7.4(17)	0.0(19)	-0.7(17)
C63	34(2)	36.8(19)	49.9(18)	9.0(16)	8.0(16)	-4.1(15)
C48	41(3)	84(3)	43(2)	-27.9(19)	-5.7(17)	10(2)
C35	29(2)	95(3)	32.4(18)	-6(2)	5.5(15)	-8(2)
C96	21(2)	88(3)	65(2)	32(2)	-3.2(18)	-7(2)
C6	67(3)	30.4(18)	45(2)	17.1(16)	-10.5(19)	3.0(19)
C30	37(2)	56(2)	38.8(19)	-1.3(17)	4.7(16)	-4.1(19)
C80	60(3)	36.7(19)	37.7(18)	-3.2(16)	11.2(18)	9.1(19)
C13	41(3)	31.8(19)	69(3)	-2.4(17)	2.8(19)	-2.3(17)
C10	77(3)	30.9(19)	61(2)	-1.0(17)	16(2)	8.6(19)
C86	54(3)	45(2)	61(2)	-25.5(19)	-2(2)	0.5(19)
C87	50(3)	41.5(19)	53(2)	-13.5(17)	-12.7(19)	-10.5(18)
C21	21(2)	130(4)	38.6(19)	22(2)	8.7(16)	13(2)
C46	27(2)	66(2)	30.9(16)	-12.1(15)	0.9(14)	4.3(18)
C19	20(2)	76(3)	30.3(16)	6.7(17)	3.8(14)	1.2(19)
C25	64(3)	44(2)	36.4(17)	-9.1(16)	3.5(17)	-14(2)
C50	31(2)	51(2)	53(2)	-17.7(18)	-0.2(17)	4.8(18)
C81	89(4)	50(2)	40(2)	-2.2(17)	7(2)	-8(2)
C60	61(3)	60(3)	94(3)	0(3)	17(2)	28(3)
C11	94(3)	26.2(18)	65(2)	-9.9(19)	-21(2)	11(2)
C56	34(3)	43(2)	104(3)	29(2)	-1(2)	-8.0(19)
C37	22(2)	86(3)	57(2)	-14(2)	-4.3(16)	11(2)
C73	57(3)	24.6(17)	55(2)	4.8(16)	26.5(18)	0.3(17)
C100	37(3)	49(2)	102(3)	29(2)	6(2)	-7(2)
C97	39(3)	117(4)	59(2)	40(2)	-3(2)	-8(3)
C88	31(2)	37.6(17)	31.2(15)	-0.2(14)	-6.1(14)	3.9(15)
C36	37(3)	105(3)	41(2)	-22(2)	5.3(18)	1(2)
C45	28(2)	43.4(19)	36.8(16)	-16.1(14)	1.0(14)	15.9(16)
C98	80(3)	88(2)	89(2)	24(2)	0(2)	1(2)
C99	49(3)	57(3)	109(3)	34(2)	5(3)	-7(2)
C62	37(2)	52(2)	72(3)	22(2)	-1.9(19)	1.1(19)
C61	73(4)	61(3)	93(3)	27(3)	9(3)	26(3)
C12	76(3)	43(2)	88(3)	-17(2)	-19(3)	-6(2)
C31	36(2)	85(3)	50(2)	-18(2)	-10.9(17)	-4(2)
C23	49(3)	111(4)	30.8(19)	8(2)	2.0(17)	-16(2)
C24	63(3)	68(3)	41.0(19)	-8.8(18)	8.4(19)	-17(2)
C22	64(2)	84(2)	57.3(18)	12.1(18)	-3.5(17)	2(2)
C109	77(4)	67(3)	72(3)	18(2)	19(3)	4(3)
C104	78(4)	67(3)	58(3)	11(2)	12(2)	1(3)
C106	101(6)	78(4)	100(4)	9(3)	-1(4)	1(4)
C108	67(4)	83(4)	109(4)	39(3)	25(3)	10(3)
C107	109(7)	65(4)	199(8)	30(5)	38(6)	-13(4)
C105	65(4)	55(3)	64(3)	-1(2)	-8(2)	12(3)
C110	85(5)	144(6)	63(3)	-10(3)	2(3)	32(4)

Table 26: Bond Lengths in Å for **4.8**.

Atom	Atom	Length/Å
Rh1	Rh2	2.3815(3)
Rh1	O2	2.049(2)
Rh1	O6	2.051(2)
Rh1	O4	2.055(2)
Rh1	O8	2.065(2)
Rh1	N1	2.210(2)
Rh2	O9	2.3719(19)
Rh2	O1	2.033(2)
Rh2	O3	2.010(2)
Rh2	O5	2.034(2)
Rh2	O7	2.027(2)
Si1	C3	1.926(3)
Si1	C4	1.857(4)
Si1	C5	1.826(4)
Si1	C6	1.877(3)
Si3	C53	1.907(3)
Si3	C54	1.867(4)
Si3	C55	1.869(4)
Si3	C56	1.879(4)
Si4	C79	1.842(4)
Si4	C78	1.916(3)
Si4	C80	1.838(4)
Si4	C81	1.867(4)
Si2	C28	1.896(3)
Si2	C29	1.864(3)
Si2	C30	1.873(4)
Si2	C31	1.839(4)
O1	C1	1.244(3)
O2	C1	1.287(3)
O3	C26	1.272(3)
O6	C51	1.266(4)
O4	C26	1.267(3)
O5	C51	1.278(4)
O8	C76	1.265(3)
O7	C76	1.267(3)
N1	C102	1.114(4)
C15	C16	1.353(4)
C15	C14	1.400(4)
C77	C89	1.511(4)
C77	C76	1.485(4)
C77	C82	1.529(4)
C77	C78	1.585(4)
C26	C27	1.525(4)
C70	C71	1.378(5)
C70	C75	1.368(5)
C70	C67	1.503(4)
C64	C65	1.380(4)
C64	C52	1.509(4)
C64	C69	1.390(4)
C102	C103	1.456(5)

Atom	Atom	Length/Å
C27	C32	1.508(4)
C27	C39	1.497(4)
C27	C28	1.566(5)
C40	C39	1.421(5)
C40	C41	1.371(4)
C51	C52	1.496(4)
C16	C17	1.366(5)
C32	C28	1.507(5)
C65	C66	1.375(4)
C53	C52	1.575(5)
C53	C57	1.542(5)
C53	C58	1.460(5)
C43	C42	1.396(5)
C43	C44	1.382(4)
C39	C44	1.373(4)
C14	C2	1.490(4)
C14	C19	1.396(5)
C71	C72	1.384(5)
C52	C57	1.522(4)
C41	C42	1.400(4)
C42	C45	1.503(4)
C9	C8	1.365(5)
C9	C10	1.388(5)
C58	C59	1.373(5)
C58	C63	1.395(5)
C92	C93	1.361(5)
C92	C91	1.420(5)
C92	C95	1.459(5)
C17	C20	1.497(4)
C17	C18	1.389(5)
C89	C90	1.394(5)
C89	C94	1.388(5)
C93	C94	1.368(4)
C1	C2	1.501(4)
C7	C2	1.530(5)
C7	C3	1.484(5)
C2	C3	1.548(4)
C75	C74	1.452(5)
C69	C68	1.374(4)
C3	C8	1.527(4)
C28	C33	1.517(5)
C82	C78	1.504(5)
C66	C67	1.426(5)
C33	C34	1.395(5)
C33	C38	1.411(5)
C90	C91	1.384(4)
C67	C68	1.400(5)
C84	C83	1.380(5)
C84	C85	1.373(5)
C20	C21	1.363(6)
C20	C25	1.414(6)
C34	C35	1.359(5)
C8	C13	1.400(5)

Atom	Atom	Length/Å
C18	C19	1.362(5)
C74	C73	1.368(6)
C83	C78	1.494(5)
C83	C88	1.385(5)
C72	C73	1.392(6)
C95	C96	1.421(6)
C95	C100	1.415(6)
C49	C48	1.356(6)
C49	C50	1.418(5)
C38	C37	1.378(5)
C59	C60	1.409(6)
C47	C48	1.381(6)
C47	C46	1.374(5)
C85	C86	1.362(6)
C63	C62	1.366(5)
C35	C36	1.391(6)
C96	C97	1.391(6)
C13	C12	1.344(6)
C10	C11	1.338(7)
C86	C87	1.392(6)
C87	C88	1.349(5)
C21	C22	1.354(6)
C46	C45	1.371(5)
C25	C24	1.349(5)
C50	C45	1.410(5)
C60	C61	1.379(7)
C11	C12	1.413(7)
C37	C36	1.375(6)
C100	C99	1.443(6)
C97	C98	1.388(8)
C98	C99	1.227(7)
C62	C61	1.347(6)
C23	C24	1.408(7)
C23	C22	1.321(7)
C109	C104	1.347(7)
C109	C108	1.483(8)
C104	C105	1.381(6)
C106	C107	1.357(9)
C106	C105	1.366(8)
C108	C107	1.340(9)
C105	C110	1.497(7)

Table 27: Bond Angles in ° for **4.8**.

Atom	Atom	Atom	Angle/°
O2	Rh1	Rh2	87.76(5)
O2	Rh1	O6	91.80(8)
O2	Rh1	O4	88.10(8)
O2	Rh1	O8	176.20(8)
O2	Rh1	N1	93.02(9)

Atom	Atom	Atom	Angle/°
O6	Rh1	Rh2	87.36(5)
O6	Rh1	O4	174.97(7)
O6	Rh1	O8	87.62(8)
O6	Rh1	N1	86.04(9)
O4	Rh1	Rh2	87.62(5)
O4	Rh1	O8	92.14(9)
O4	Rh1	N1	98.99(9)
O8	Rh1	Rh2	88.46(5)
O8	Rh1	N1	90.69(9)
N1	Rh1	Rh2	173.37(8)
O9	Rh2	Rh1	177.95(6)
O1	Rh2	Rh1	88.44(5)
O1	Rh2	O9	89.69(7)
O1	Rh2	O5	92.10(9)
O3	Rh2	Rh1	88.36(5)
O3	Rh2	O9	92.45(8)
O3	Rh2	O1	88.90(9)
O3	Rh2	O5	176.68(8)
O3	Rh2	O7	91.27(9)
O5	Rh2	Rh1	88.50(5)
O5	Rh2	O9	90.72(8)
O7	Rh2	Rh1	87.34(5)
O7	Rh2	O9	94.52(7)
O7	Rh2	O1	175.77(7)
O7	Rh2	O5	87.51(9)
C4	Si1	C3	111.24(15)
C4	Si1	C6	105.73(17)
C5	Si1	C3	114.83(14)
C5	Si1	C4	113.09(17)
C5	Si1	C6	105.49(19)
C6	Si1	C3	105.56(15)
C54	Si3	C53	112.52(16)
C54	Si3	C55	110.62(17)
C54	Si3	C56	107.42(19)
C55	Si3	C53	110.69(15)
C55	Si3	C56	108.5(2)
C56	Si3	C53	106.85(17)
C79	Si4	C78	112.27(16)
C79	Si4	C81	106.28(18)
C80	Si4	C79	112.94(17)
C80	Si4	C78	113.63(16)
C80	Si4	C81	105.9(2)
C81	Si4	C78	104.98(16)
C29	Si2	C28	109.81(16)
C29	Si2	C30	110.74(17)
C30	Si2	C28	111.23(15)
C31	Si2	C28	107.82(18)
C31	Si2	C29	107.61(18)
C31	Si2	C30	109.5(2)
C1	O1	Rh2	118.45(18)
C1	O2	Rh1	117.65(18)
C26	O3	Rh2	119.82(18)
C51	O6	Rh1	118.96(19)

Atom	Atom	Atom	Angle/°
C26	O4	Rh1	117.99(19)
C51	O5	Rh2	119.00(19)
C76	O8	Rh1	117.51(18)
C76	O7	Rh2	120.2(2)
C102	N1	Rh1	167.4(3)
C16	C15	C14	122.0(3)
C89	C77	C82	119.3(3)
C89	C77	C78	117.7(3)
C76	C77	C89	115.7(2)
C76	C77	C82	114.2(3)
C76	C77	C78	119.7(3)
C82	C77	C78	57.7(2)
O3	C26	C27	115.7(2)
O4	C26	O3	124.9(3)
O4	C26	C27	119.4(3)
C71	C70	C67	120.4(3)
C75	C70	C71	119.2(3)
C75	C70	C67	120.3(3)
C65	C64	C52	121.7(3)
C65	C64	C69	118.4(3)
C69	C64	C52	119.6(3)
N1	C102	C103	178.6(4)
C26	C27	C28	118.4(2)
C32	C27	C26	116.6(2)
C32	C27	C28	58.7(2)
C39	C27	C26	112.7(2)
C39	C27	C32	120.9(3)
C39	C27	C28	119.6(3)
C41	C40	C39	121.3(3)
O6	C51	O5	124.3(3)
O6	C51	C52	118.2(3)
O5	C51	C52	117.4(3)
C15	C16	C17	121.7(3)
C28	C32	C27	62.6(2)
C66	C65	C64	121.7(3)
C52	C53	Si3	123.7(2)
C57	C53	Si3	119.2(2)
C57	C53	C52	58.4(2)
C58	C53	Si3	111.4(2)
C58	C53	C52	116.9(3)
C58	C53	C57	117.9(3)
C44	C43	C42	120.7(3)
C40	C39	C27	120.6(3)
C44	C39	C27	122.6(3)
C44	C39	C40	116.7(3)
C15	C14	C2	120.8(3)
C19	C14	C15	115.9(3)
C19	C14	C2	123.2(3)
C70	C71	C72	122.1(4)
C64	C52	C53	119.2(3)
C64	C52	C57	118.6(3)
C51	C52	C64	113.8(3)
C51	C52	C53	119.1(3)

Atom	Atom	Atom	Angle/°
C51	C52	C57	116.1(3)
C57	C52	C53	59.7(2)
C40	C41	C42	121.0(3)
C43	C42	C41	117.7(3)
C43	C42	C45	119.1(3)
C41	C42	C45	123.1(3)
C8	C9	C10	122.5(4)
C52	C57	C53	61.8(2)
C59	C58	C53	123.1(3)
C59	C58	C63	115.1(4)
C63	C58	C53	121.6(3)
C93	C92	C91	116.6(3)
C93	C92	C95	121.9(3)
C91	C92	C95	121.5(3)
C39	C44	C43	122.4(3)
C16	C17	C20	121.8(3)
C16	C17	C18	117.7(3)
C18	C17	C20	120.4(3)
C90	C89	C77	119.3(3)
C94	C89	C77	123.4(3)
C94	C89	C90	117.3(3)
C92	C93	C94	123.4(3)
O1	C1	O2	126.6(3)
O1	C1	C2	116.5(3)
O2	C1	C2	116.9(3)
C3	C7	C2	61.8(2)
C14	C2	C1	112.6(3)
C14	C2	C7	118.5(3)
C14	C2	C3	119.2(2)
C1	C2	C7	116.6(3)
C1	C2	C3	121.6(3)
C7	C2	C3	57.6(2)
C70	C75	C74	120.1(4)
O8	C76	O7	125.1(3)
O8	C76	C77	118.5(3)
O7	C76	C77	116.3(3)
C68	C69	C64	121.2(3)
C7	C3	Si1	117.9(2)
C7	C3	C2	60.6(2)
C7	C3	C8	118.3(3)
C2	C3	Si1	125.8(2)
C8	C3	Si1	109.9(2)
C8	C3	C2	116.6(2)
C27	C28	Si2	126.2(2)
C32	C28	Si2	119.8(2)
C32	C28	C27	58.7(2)
C32	C28	C33	116.4(3)
C33	C28	Si2	112.3(3)
C33	C28	C27	113.5(2)
C78	C82	C77	63.0(2)
C65	C66	C67	120.3(3)
C34	C33	C28	120.1(3)
C34	C33	C38	118.5(3)

Atom	Atom	Atom	Angle/°
C38	C33	C28	121.3(3)
C91	C90	C89	121.6(3)
C66	C67	C70	121.5(3)
C68	C67	C70	121.4(3)
C68	C67	C66	117.1(3)
C85	C84	C83	120.3(4)
C21	C20	C17	123.6(4)
C21	C20	C25	116.2(3)
C25	C20	C17	120.1(4)
C35	C34	C33	121.1(4)
C9	C8	C3	121.0(3)
C9	C8	C13	117.2(3)
C13	C8	C3	121.8(3)
C19	C18	C17	121.1(3)
C90	C91	C92	120.1(3)
C73	C74	C75	118.5(4)
C84	C83	C78	119.5(3)
C84	C83	C88	118.1(3)
C88	C83	C78	122.3(3)
C93	C94	C89	120.6(3)
C71	C72	C73	119.0(4)
C96	C95	C92	120.2(4)
C100	C95	C92	121.2(4)
C100	C95	C96	118.6(4)
C48	C49	C50	120.6(4)
C69	C68	C67	121.2(3)
C77	C78	Si4	126.7(2)
C82	C78	Si4	116.9(2)
C82	C78	C77	59.3(2)
C83	C78	Si4	111.8(2)
C83	C78	C77	114.7(3)
C83	C78	C82	118.0(3)
C37	C38	C33	119.6(4)
C58	C59	C60	121.6(4)
C46	C47	C48	119.8(4)
C86	C85	C84	121.0(4)
C62	C63	C58	123.9(4)
C49	C48	C47	120.2(4)
C34	C35	C36	120.1(4)
C97	C96	C95	119.4(5)
C12	C13	C8	122.1(4)
C11	C10	C9	118.3(4)
C85	C86	C87	118.9(4)
C88	C87	C86	120.1(4)
C22	C21	C20	121.0(5)
C45	C46	C47	122.2(4)
C18	C19	C14	121.7(3)
C24	C25	C20	122.4(4)
C45	C50	C49	118.8(4)
C61	C60	C59	120.2(4)
C10	C11	C12	121.8(4)
C36	C37	C38	120.7(4)
C74	C73	C72	121.0(3)

Atom	Atom	Atom	Angle/°
C95	C100	C99	116.0(5)
C98	C97	C96	119.3(5)
C87	C88	C83	121.6(4)
C37	C36	C35	119.9(4)
C46	C45	C42	122.5(3)
C46	C45	C50	118.4(3)
C50	C45	C42	119.1(3)
C99	C98	C97	122.3(5)
C98	C99	C100	124.2(5)
C61	C62	C63	120.2(4)
C62	C61	C60	119.0(5)
C13	C12	C11	118.1(5)
C22	C23	C24	119.0(4)
C25	C24	C23	118.2(4)
C23	C22	C21	122.7(5)
C104	C109	C108	117.2(5)
C109	C104	C105	123.4(6)
C107	C106	C105	122.4(6)
C107	C108	C109	118.0(6)
C108	C107	C106	121.5(7)
C104	C105	C110	120.0(5)
C106	C105	C104	117.3(5)
C106	C105	C110	122.7(5)

Table 28: Torsion Angles in ° for **4.8**.

Atom	Atom	Atom	Atom	Angle/°
Rh1	O2	C1	O1	0.6(4)
Rh1	O2	C1	C2	-179.2(2)
Rh1	O6	C51	O5	14.9(4)
Rh1	O6	C51	C52	-162.5(2)
Rh1	O4	C26	O3	12.6(4)
Rh1	O4	C26	C27	-164.2(2)
Rh1	O8	C76	O7	-2.5(4)
Rh1	O8	C76	C77	-179.9(2)
Rh2	O1	C1	O2	8.1(4)
Rh2	O1	C1	C2	-172.1(2)
Rh2	O3	C26	O4	-4.8(4)
Rh2	O3	C26	C27	172.02(19)
Rh2	O5	C51	O6	-5.8(4)
Rh2	O5	C51	C52	171.6(2)
Rh2	O7	C76	O8	11.6(4)
Rh2	O7	C76	C77	-170.9(2)
Si1	C3	C8	C9	-76.0(3)
Si1	C3	C8	C13	103.3(3)
Si3	C53	C52	C64	145.8(2)
Si3	C53	C52	C51	-1.3(4)
Si3	C53	C52	C57	-106.2(3)
Si3	C53	C57	C52	113.8(3)
Si3	C53	C58	C59	107.5(4)

Atom	Atom	Atom	Atom	Angle/°
Si3	C53	C58	C63	-66.4(4)
Si2	C28	C33	C34	-65.5(4)
Si2	C28	C33	C38	114.3(3)
O1	C1	C2	C14	10.2(4)
O1	C1	C2	C7	-131.7(3)
O1	C1	C2	C3	161.5(3)
O2	C1	C2	C14	-170.0(3)
O2	C1	C2	C7	48.0(4)
O2	C1	C2	C3	-18.7(4)
O3	C26	C27	C32	178.7(3)
O3	C26	C27	C39	-35.0(4)
O3	C26	C27	C28	111.7(3)
O6	C51	C52	C64	148.5(3)
O6	C51	C52	C53	-62.7(4)
O6	C51	C52	C57	5.6(4)
O4	C26	C27	C32	-4.3(4)
O4	C26	C27	C39	142.0(3)
O4	C26	C27	C28	-71.3(4)
O5	C51	C52	C64	-29.1(4)
O5	C51	C52	C53	119.7(3)
O5	C51	C52	C57	-172.0(3)
C15	C16	C17	C20	178.2(3)
C15	C16	C17	C18	0.4(5)
C15	C14	C2	C1	63.6(4)
C15	C14	C2	C7	-155.2(3)
C15	C14	C2	C3	-88.4(4)
C15	C14	C19	C18	1.0(6)
C77	C89	C90	C91	-174.3(3)
C77	C89	C94	C93	176.3(3)
C77	C82	C78	Si4	118.6(3)
C77	C82	C78	C83	-103.6(3)
C26	C27	C32	C28	-108.6(3)
C26	C27	C39	C40	-116.8(3)
C26	C27	C39	C44	61.5(4)
C26	C27	C28	Si2	-0.5(4)
C26	C27	C28	C32	105.5(3)
C26	C27	C28	C33	-146.8(3)
C70	C71	C72	C73	2.1(5)
C70	C75	C74	C73	1.6(5)
C70	C67	C68	C69	-178.6(3)
C64	C65	C66	C67	2.1(5)
C64	C52	C57	C53	109.0(3)
C64	C69	C68	C67	-1.4(5)
C27	C32	C28	Si2	116.6(3)
C27	C32	C28	C33	-102.7(3)
C27	C39	C44	C43	-174.6(3)
C27	C28	C33	C34	85.5(4)
C27	C28	C33	C38	-94.7(4)
C40	C39	C44	C43	3.7(5)
C40	C41	C42	C43	0.4(5)
C40	C41	C42	C45	-176.4(3)
C51	C52	C57	C53	-110.0(3)
C16	C15	C14	C2	-178.2(3)

Atom	Atom	Atom	Atom	Angle/°
C16	C15	C14	C19	-1.5(5)
C16	C17	C20	C21	-136.5(4)
C16	C17	C20	C25	41.4(5)
C16	C17	C18	C19	-0.8(6)
C32	C27	C39	C40	27.9(5)
C32	C27	C39	C44	-153.9(3)
C32	C27	C28	Si2	-106.0(3)
C32	C27	C28	C33	107.7(3)
C32	C28	C33	C34	151.0(3)
C32	C28	C33	C38	-29.2(5)
C65	C64	C52	C51	73.2(4)
C65	C64	C52	C53	-75.5(4)
C65	C64	C52	C57	-144.8(3)
C65	C64	C69	C68	0.7(5)
C65	C66	C67	C70	178.2(3)
C65	C66	C67	C68	-2.6(5)
C53	C58	C59	C60	-173.3(4)
C53	C58	C63	C62	172.6(3)
C43	C42	C45	C46	27.6(5)
C43	C42	C45	C50	-152.8(3)
C39	C27	C32	C28	108.1(3)
C39	C27	C28	Si2	143.8(2)
C39	C27	C28	C32	-110.2(3)
C39	C27	C28	C33	-2.5(4)
C39	C40	C41	C42	1.7(5)
C14	C15	C16	C17	0.8(5)
C14	C2	C3	Si1	148.1(3)
C14	C2	C3	C7	-107.1(3)
C14	C2	C3	C8	2.0(5)
C71	C70	C75	C74	-0.7(5)
C71	C70	C67	C66	-146.0(3)
C71	C70	C67	C68	34.9(5)
C71	C72	C73	C74	-1.2(5)
C52	C64	C65	C66	-174.8(3)
C52	C64	C69	C68	174.6(3)
C52	C53	C58	C59	-102.3(4)
C52	C53	C58	C63	83.7(4)
C41	C40	C39	C27	174.6(3)
C41	C40	C39	C44	-3.7(5)
C41	C42	C45	C46	-155.6(3)
C41	C42	C45	C50	24.0(5)
C42	C43	C44	C39	-1.7(5)
C9	C8	C13	C12	3.2(6)
C9	C10	C11	C12	0.2(6)
C57	C53	C52	C64	-108.0(3)
C57	C53	C52	C51	104.9(3)
C57	C53	C58	C59	-35.6(5)
C57	C53	C58	C63	150.4(3)
C58	C53	C52	C64	-0.3(4)
C58	C53	C52	C51	-147.4(3)
C58	C53	C52	C57	107.7(3)
C58	C53	C57	C52	-106.0(3)
C58	C59	C60	C61	-0.1(7)

Atom	Atom	Atom	Atom	Angle/°
C58	C63	C62	C61	1.7(6)
C92	C93	C94	C89	-2.9(5)
C92	C95	C96	C97	178.0(4)
C92	C95	C100	C99	177.6(4)
C44	C43	C42	C41	-0.5(5)
C44	C43	C42	C45	176.5(3)
C17	C20	C21	C22	177.4(4)
C17	C20	C25	C24	-179.6(4)
C17	C18	C19	C14	0.1(7)
C89	C77	C76	O8	-162.3(3)
C89	C77	C76	O7	20.0(4)
C89	C77	C82	C78	106.0(3)
C89	C77	C78	Si4	148.9(3)
C89	C77	C78	C82	-108.8(3)
C89	C77	C78	C83	0.3(5)
C89	C90	C91	C92	-1.3(5)
C93	C92	C91	C90	-4.5(5)
C93	C92	C95	C96	134.8(4)
C93	C92	C95	C100	-45.8(5)
C1	C2	C3	Si1	-1.3(4)
C1	C2	C3	C7	103.4(3)
C1	C2	C3	C8	-147.5(3)
C7	C2	C3	Si1	-104.8(3)
C7	C2	C3	C8	109.0(3)
C7	C3	C8	C9	144.6(3)
C7	C3	C8	C13	-36.2(4)
C2	C14	C19	C18	177.7(4)
C2	C7	C3	Si1	117.5(2)
C2	C7	C3	C8	-106.3(3)
C2	C3	C8	C9	75.3(4)
C2	C3	C8	C13	-105.4(4)
C75	C70	C71	C72	-1.2(5)
C75	C70	C67	C66	32.8(5)
C75	C70	C67	C68	-146.3(3)
C75	C74	C73	C72	-0.6(5)
C76	C77	C89	C90	36.5(4)
C76	C77	C89	C94	-143.0(3)
C76	C77	C82	C78	-111.0(3)
C76	C77	C78	Si4	-0.9(4)
C76	C77	C78	C82	101.4(3)
C76	C77	C78	C83	-149.5(3)
C69	C64	C65	C66	-1.1(5)
C69	C64	C52	C51	-100.4(3)
C69	C64	C52	C53	110.8(4)
C69	C64	C52	C57	41.5(5)
C3	C7	C2	C14	108.2(3)
C3	C7	C2	C1	-112.1(3)
C3	C8	C13	C12	-176.1(4)
C28	C27	C39	C40	97.0(4)
C28	C27	C39	C44	-84.8(4)
C28	C33	C34	C35	178.6(3)
C28	C33	C38	C37	-179.6(4)
C82	C77	C89	C90	179.0(3)

Atom	Atom	Atom	Atom	Angle/°
C82	C77	C89	C94	-0.5(4)
C82	C77	C76	O8	53.3(4)
C82	C77	C76	O7	-124.3(3)
C82	C77	C78	Si4	-102.3(3)
C82	C77	C78	C83	109.1(4)
C66	C67	C68	C69	2.3(5)
C33	C34	C35	C36	2.6(6)
C33	C38	C37	C36	-0.7(6)
C90	C89	C94	C93	-3.2(5)
C67	C70	C71	C72	177.6(3)
C67	C70	C75	C74	-179.5(3)
C84	C83	C78	Si4	-81.4(3)
C84	C83	C78	C77	71.9(4)
C84	C83	C78	C82	138.7(3)
C84	C83	C88	C87	1.9(5)
C84	C85	C86	C87	0.0(6)
C20	C17	C18	C19	-178.6(4)
C20	C21	C22	C23	5.1(8)
C20	C25	C24	C23	-0.6(6)
C34	C33	C38	C37	0.2(5)
C34	C35	C36	C37	-3.0(6)
C8	C9	C10	C11	0.5(6)
C8	C13	C12	C11	-2.6(6)
C18	C17	C20	C21	41.2(6)
C18	C17	C20	C25	-140.9(4)
C91	C92	C93	C94	6.7(5)
C91	C92	C95	C96	-44.8(5)
C91	C92	C95	C100	134.5(4)
C83	C84	C85	C86	0.3(6)
C94	C89	C90	C91	5.2(5)
C95	C92	C93	C94	-173.0(3)
C95	C92	C91	C90	175.1(3)
C95	C96	C97	C98	2.8(7)
C95	C100	C99	C98	7.0(8)
C49	C50	C45	C42	179.7(3)
C49	C50	C45	C46	-0.7(5)
C78	C77	C89	C90	-114.4(3)
C78	C77	C89	C94	66.1(4)
C78	C77	C76	O8	-12.0(4)
C78	C77	C76	O7	170.4(3)
C78	C83	C88	C87	-175.5(3)
C29	Si2	C28	C27	66.8(3)
C29	Si2	C28	C32	-4.3(3)
C29	Si2	C28	C33	-146.5(2)
C38	C33	C34	C35	-1.2(5)
C38	C37	C36	C35	2.1(6)
C59	C58	C63	C62	-1.8(5)
C59	C60	C61	C62	-0.1(8)
C47	C46	C45	C42	-179.3(3)
C47	C46	C45	C50	1.1(6)
C85	C84	C83	C78	176.3(3)
C85	C84	C83	C88	-1.2(5)
C85	C86	C87	C88	0.7(6)

Atom	Atom	Atom	Atom	Angle/°
C63	C58	C59	C60	1.0(6)
C63	C62	C61	C60	-0.6(7)
C48	C49	C50	C45	-0.1(6)
C48	C47	C46	C45	-0.8(6)
C96	C95	C100	C99	-3.1(6)
C96	C97	C98	C99	0.9(9)
C30	Si2	C28	C27	-56.1(3)
C30	Si2	C28	C32	-127.3(3)
C30	Si2	C28	C33	90.6(3)
C10	C9	C8	C3	177.2(3)
C10	C9	C8	C13	-2.1(5)
C10	C11	C12	C13	0.9(7)
C86	C87	C88	C83	-1.7(6)
C21	C20	C25	C24	-1.5(6)
C46	C47	C48	C49	-0.1(6)
C19	C14	C2	C1	-112.9(4)
C19	C14	C2	C7	28.3(5)
C19	C14	C2	C3	95.1(4)
C25	C20	C21	C22	-0.6(7)
C50	C49	C48	C47	0.5(7)
C100	C95	C96	C97	-1.4(6)
C97	C98	C99	C100	-6.0(10)
C88	C83	C78	Si4	95.9(3)
C88	C83	C78	C77	-110.8(3)
C88	C83	C78	C82	-43.9(4)
C31	Si2	C28	C27	-176.2(3)
C31	Si2	C28	C32	112.6(3)
C31	Si2	C28	C33	-29.5(3)
C24	C23	C22	C21	-7.1(8)
C22	C23	C24	C25	4.8(7)
C109	C104	C105	C106	2.2(7)
C109	C104	C105	C110	-179.1(5)
C109	C108	C107	C106	1.3(10)
C104	C109	C108	C107	-2.8(8)
C108	C109	C104	C105	1.0(7)
C107	C106	C105	C104	-3.9(9)
C107	C106	C105	C110	177.5(6)
C105	C106	C107	C108	2.1(11)

Table 29: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **4.8**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
H9A	1880.1	7612.7	153.1	52
H9B	1454.81	7185.1	-28.9	52
H15	1552.57	5435.53	183.17	28
H40	3192.19	4773.49	912.12	36
H16	1568.73	5499.63	-672.61	33
H32A	3384.46	5517.15	2002.64	39
H32B	3761.47	5098	1595.39	39

Atom	x	y	z	U_{eq}
H65	-446.68	8113.08	798.45	35
H43	3186.03	5934.35	-474.46	35
H54A	-478.92	6300.6	2220.15	67
H54B	-1189.37	5940.1	2209.61	67
H54C	-1144.17	6452.5	2568.98	67
H71	1177.9	10034.79	1377.5	44
H41	3002.46	4421.18	118.03	35
H9	1540.94	4430.41	562.39	48
H57A	-800.74	8015.15	2441.6	40
H57B	-482.13	7390.85	2491.57	40
H44	3373.46	6281.89	323.97	36
H10A	317.58	5746.72	3542.22	74
H10B	376.03	6368.58	3691	74
H10C	1031.61	5970.33	3799.41	74
H93	3595.17	9583.01	1357.94	39
H7A	-349.1	5356.78	1442.55	38
H7B	-614.45	5070.5	912.27	38
H75	-410.31	9889.75	353.37	46
H69	109.3	8649.16	2178.93	35
H82A	3188.76	7641.8	2570.42	39
H82B	3516.4	8253.77	2460.3	39
H66	-193.93	8957.87	457.72	35
H90	1572.42	8472.2	1381.69	34
H84	1406.05	9027.82	2485.02	46
H34	4749.75	6470.48	728.96	51
H18	-603.08	5592.95	-695.38	64
H79A	2313.27	6972.63	3035.95	58
H79B	2053.18	7025.03	3601.67	58
H79C	2809.2	7270.89	3436.12	58
H91	1693.68	9121.42	751.01	38
H74	-86.26	10766.94	12.09	57
H94	3512.9	8910.5	1952.65	39
H72	1545.38	10859.81	1030.1	60
H49	2083.39	3932.91	-1402.44	66
H68	380.21	9496.16	1853.9	34
H4A	390.85	5375.06	2260.54	59
H4B	642.32	4885.75	2606.12	59
H4C	-81.99	4838.87	2289.95	59
H29A	3318.85	6451.53	2473.5	58
H29B	3967.13	6745.86	2752.79	58
H29C	3974.1	6106.02	2686.97	58
H38	4900.92	5001.92	1428.77	52
H59	-2014.86	8161.09	2323.64	65
H55A	-1315.99	6709.33	830.01	66
H55B	-1252.71	6113.8	1052.07	66
H55C	-573.73	6506.99	1062.54	66
H47	3176.96	5196.1	-1989.52	64
H5A	2109.25	4833.56	1444.6	57
H5B	2148.13	4570.58	1987.81	57
H5C	1978.11	5198.19	1927.16	57
H85	1358.01	9939.97	2700.32	57
H63	-1664.21	7707.31	897.75	48
H48	2496.88	4403.86	-2093.96	67

Atom	x	y	z	U_{eq}
H35	5729.96	6250.64	232.57	63
H96	2528.9	9279.15	-34.53	70
H6A	375.14	3805.97	1725.35	71
H6B	946.22	3823	2169.64	71
H6C	1212.37	3748.45	1607.42	71
H30A	4366.66	7235.59	1298.15	66
H30B	4237.96	7493.23	1836.84	66
H30C	3586.18	7218.45	1544.72	66
H80A	829.11	7602.64	2716.2	67
H80B	662.67	8141.31	3021.36	67
H80C	657.14	7571.83	3299.26	67
H13	-561.97	4128.38	825.14	57
H10	1618.53	3651.79	61.89	68
H86	2304.67	10346.5	3131.11	64
H87	3319.3	9820.52	3354.18	58
H21	-264.04	6187.84	-1427.05	76
H46	3437.78	5511.19	-1189.51	49
H19	-632.34	5517.19	165.41	51
H25	1304.97	5052.88	-1479.73	58
H50	2331.48	4253.17	-576.98	54
H81A	1687.62	8093.24	4044.71	90
H81B	1667.82	8628.81	3714.34	90
H81C	2419.4	8356.43	3851.68	90
H60	-3032.33	8655.07	2053.24	86
H11	610.46	3120	-39.81	74
H56A	-2567.97	6864.13	2088.53	91
H56B	-2561.32	6332.32	1752.72	91
H56C	-2622.96	6911.2	1495.49	91
H37	5870.3	4781.11	906.43	65
H73	893.57	11230.47	354.98	55
H100	3137.57	10468.42	971.74	75
H97	2661.49	9922.23	-684.31	86
H88	3378.16	8923.15	3127.88	40
H36	6259.38	5386.72	291.51	73
H98	3078.87	10792.74	-494.9	103
H99	3394.13	11019.09	248.91	86
H62	-2669.88	8172.59	635.43	64
H61	-3356.59	8659.58	1202.91	90
H12	-498.11	3345.79	356.46	83
H31A	5433.43	6135.39	2179.12	86
H31B	5441.83	6768.12	2288.95	86
H31C	5580.66	6551.57	1736.16	86
H23	534.01	5732.12	-2749.26	76
H24	1359.72	5133.32	-2339.84	69
H22	-148.97	6299.95	-2275.58	82
H109	6368.25	5229.93	2711.15	86
H104	5338.65	5339.7	3185	81
H106	6074.59	6739.78	3748.18	111
H108	7346.41	5907.69	2810.35	104
H107	7139.19	6644.55	3320.9	149
H11A	4501.39	6061.75	3613.47	146
H11B	4907.34	6431.17	4011.73	146
H11C	4896.25	5791.62	4079.61	146

Table 30: Solvent masking (PLATON/SQUEEZE) information for **4.8**.

No	x	y	z	V	e	Content
1	-0.343	-0.297	-0.322	5625.4	389.3	?
2	0.000	0.047	0.118	0.0	0.0	?
3	0.000	0.547	0.382	0.0	0.0	?
4	0.010	0.023	0.319	0.0	0.0	?
5	0.010	0.047	0.125	0.0	0.0	?
6	0.010	0.539	0.375	0.0	0.0	?
7	0.021	0.055	0.132	0.0	0.0	?
8	0.031	0.984	0.993	0.0	0.0	?
9	0.052	0.969	0.007	0.0	0.0	?
10	0.094	0.398	0.569	0.0	0.0	?
11	0.125	0.742	0.174	0.0	0.0	?
12	0.167	0.133	0.729	0.0	0.0	?
13	0.177	0.477	0.847	0.0	0.0	?
14	0.177	0.484	0.833	0.0	0.0	?
15	0.177	0.586	0.292	0.0	0.0	?
16	0.188	0.363	0.708	0.0	0.0	?
17	0.208	0.250	0.792	0.0	0.0	?
18	0.208	0.266	0.785	0.0	0.0	?
19	0.226	0.227	0.363	0.0	-0.0	?
20	0.240	0.133	0.847	0.0	0.0	?
21	0.240	0.141	0.840	0.0	0.0	?
22	0.240	0.445	0.979	0.0	0.0	?
23	0.260	0.555	0.479	0.0	0.0	?
24	0.260	0.859	0.340	0.0	0.0	?
25	0.260	0.867	0.347	0.0	0.0	?
26	0.274	0.773	0.863	0.0	0.0	?
27	0.292	0.734	0.285	0.0	0.0	?
28	0.292	0.750	0.292	0.0	0.0	?
29	0.312	0.637	0.208	0.0	0.0	?
30	0.323	0.414	0.792	0.0	0.0	?
31	0.323	0.516	0.333	0.0	0.0	?
32	0.323	0.523	0.347	0.0	0.0	?
33	0.333	0.867	0.229	0.0	0.0	?
34	0.375	0.258	0.674	0.0	0.0	?
35	0.406	0.602	0.069	0.0	0.0	?
36	0.448	0.031	0.507	0.0	0.0	?
37	0.469	0.016	0.493	0.0	0.0	?
38	0.479	0.945	0.632	0.0	0.0	?
39	0.490	0.461	0.875	0.0	0.0	?
40	0.490	0.953	0.625	0.0	0.0	?
41	0.490	0.977	0.819	0.0	0.0	?
42	0.500	0.453	0.882	0.0	0.0	?
43	0.500	0.953	0.618	0.0	0.0	?
44	0.510	0.453	0.875	0.0	0.0	?
45	0.510	0.477	0.681	0.0	0.0	?
46	0.510	0.961	0.625	0.0	0.0	?
47	0.521	0.445	0.868	0.0	0.0	?
48	0.531	0.516	0.007	0.0	0.0	?
49	0.552	0.531	0.993	0.0	0.0	?
50	0.594	0.102	0.431	0.0	0.0	?

No	x	y	z	V	e	Content
51	0.625	0.758	0.826	0.0	0.0	?
52	0.667	0.367	0.271	0.0	0.0	?
53	0.677	0.016	0.167	0.0	0.0	?
54	0.677	0.023	0.153	0.0	0.0	?
55	0.677	0.914	0.708	0.0	0.0	?
56	0.688	0.137	0.292	0.0	0.0	?
57	0.708	0.234	0.215	0.0	0.0	?
58	0.708	0.250	0.208	0.0	0.0	?
59	0.726	0.273	0.637	0.0	0.0	?
60	0.740	0.055	0.021	0.0	0.0	?
61	0.740	0.359	0.160	0.0	0.0	?
62	0.740	0.367	0.153	0.0	0.0	?
63	0.760	0.633	0.653	0.0	0.0	?
64	0.760	0.641	0.660	0.0	0.0	?
65	0.760	0.945	0.521	0.0	0.0	?
66	0.774	0.727	0.137	0.0	0.0	?
67	0.792	0.750	0.708	0.0	0.0	?
68	0.792	0.766	0.715	0.0	0.0	?
69	0.812	0.863	0.792	0.0	0.0	?
70	0.823	0.086	0.208	0.0	0.0	?
71	0.823	0.977	0.653	0.0	0.0	?
72	0.823	0.984	0.667	0.0	0.0	?
73	0.833	0.633	0.771	0.0	0.0	?
74	0.875	0.242	0.326	0.0	0.0	?
75	0.906	0.898	0.931	0.0	0.0	?
76	0.948	0.469	0.493	0.0	0.0	?
77	0.969	0.484	0.507	0.0	0.0	?
78	0.979	0.555	0.368	0.0	0.0	?
79	0.990	0.039	0.125	0.0	0.0	?
80	0.990	0.523	0.181	0.0	0.0	?
81	0.990	0.547	0.375	0.0	0.0	?

A.2 References

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