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RHODIUM CATALYZED ASYMMETRIC TRANSFORMATIONS OF VINYLCARBENOIDS

By

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Doctor of Philosophy

Chemistry

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Dean of the James T. Laney School of Graduate Studies

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RHODIUM CATALYZED ASYMMETRIC TRANSFORMATIONS OF VINYLCARBENOIDS

By

Yajing Lian

M.Sc., College of William & Mary, 2005

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

An abstract of

A dissertation submitted to the Faculty of the

James T. Laney School of Graduate Studies of Emory University

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Abstract

RHODIUM CATALYZED ASYMMETRIC TRANSFORMATIONS OF VINYLCARBENOIDS

By Yajing Lian

Donor-acceptor carbenoids are capable of undergoing many highly asymmetric transformations catalyzed by chiral dirhodium carboxylate catalysts. The use of vinyldiazoacetates as donor-acceptor carbenoid precursors is particularly interesting because vinyl groups in such diazoacetates participate in the reaction, leading to several unusual transformations.

The first chapter is devoted to exploring the cyclopropanation/Cope rearrangement reaction between siloxyvinyldiazoacetate and various acyclic dienes. The combination of siloxyvinyldiazoacetate with enantiomerically pure $Rh_2(PTAD)_4$ is very effective not only in achieving high asymmetric induction, but also in accomplishing an excellent enantiodivergent approaches with racemic dienes. Synthetic applications of this methodology have been demonstrated in the synthesis of 5-*epi*-vibsanin E, (+)-barekoxide and (-)-barekol.

The second chapter describes the reaction between vinylcarbenoids and *N*-heterocycles through rhodium-bound ylide intermediates. A novel Rh_2(*S*-DOSP)$_4$-catalyzed asymmetric cyclopentannulation of indolyl rings through the C2–C3 double bond with vinylcarbenoids was developed in a highly diastereo- and enantioselective fashion. The reactive site of indoles was shown to not be restricted to the C3 position, but also is effective at the C2 site, leading to cycloadducts in either the *exo*- or the *endo*-configuration. The second part describes the novel vinylogous reactivity of substituted vinylcarbenoids. (*Z*)-vinylcarbenoids were discovered to have a greater tendency than (*E*)-vinylcarbenoids for reactions occurring at the vinylogous position. Rh_2(*S*-biTISP)$_2$-catalyzed asymmetric vinylogous alkylations between *N*-heterocycles and *trans*-alkylvinyldiazoacetates was successfully developed in a highly enantioselective fashion.

The third part focuses on the stereocontrol of the combined C-H functionalization/Cope rearrangement (CHCR). Guided by a recent computational analysis of the CHCR reaction, an effective CHCR reaction with cyclopentenyl derivatives proceeding through a boat transition state is developed with high asymmetric induction. The CHCR products generated the opposite series of diastereomers to what had been reported earlier. Vinyl ethers undergo the CHCR reaction effectively. The reaction generated products of defined stereochemistry that might typically be generated through the vinylogous Mukaiyama aldol reaction.

The last chapter covers some miscellaneous reactions of vinylcarbenoids. Most of these reactions proceed through rhodium-bound ylide intermediates. Both carbenoid and vinylogous reactivities are possible and lead to different types of products with high selectivity.

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For my parents and my wife

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Chapter I: General Introduction to Donor-Acceptor Carbenoids

1.1 Introduction

Useful methods for organic synthesis need to be highly selective.[1,2] Free carbenes have been known for decades and are capable of reacting with organic compounds in several ways, but these processes are typically not selective and controllable, making them less useful from a synthetic organic point of view.[3-10] A great improvement in carbene chemistry has been achieved by modulating the reactivity of free carbenes by their association with suitable transition-metal complexes. The resulting metal-carbenoid intermediates are stabilized by π-backbonding to the carbenoid from transition-metals.[3]

Transition-metal-stabilized carbenoids are readily accessible from diazo compounds and the chemistry is amenable to a catalytic cycle.[3] For example, in the metal catalyzed C-H functionalization reaction with diazo compounds (Figure **1.1**), the negatively polarized carbon of the diazo compound attacks the axial site of the metal catalyst, followed by irreversible extrusion of N_2 to form a metal carbenoid intermediate. The extrusion of N_2 is proposed to be the rate-determining step.[11] Once the carbenoid is formed, it inserts into a C-H bond and regenerates the catalyst.

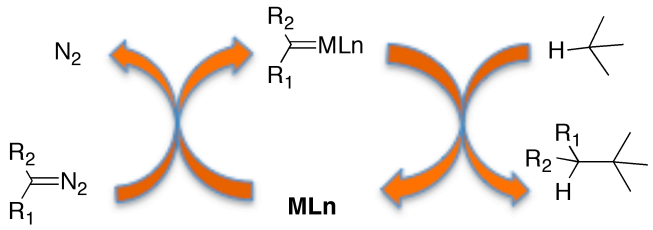
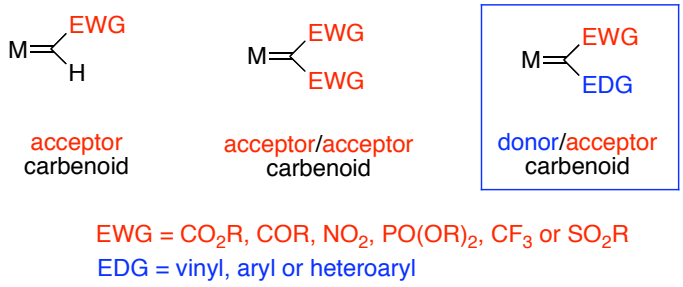


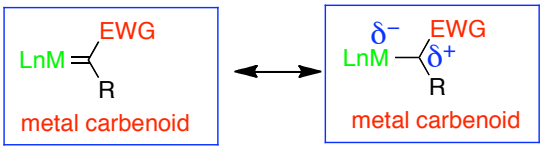
Figure 1.1 Catalytic cycle of C-H functionalization of metal carbenoids

Even though the association with metal complexes strongly stabilizes carbenes and enables them to selectively react with substrates, early examples have been mainly focused on intramolecular reactions.[4] A significant milestone in the carbenoid chemistry is the introduction of donor-acceptor carbenoids developed by the Davies group. Metal-stabilized carbenoids are classified into three major types: acceptor, acceptor-acceptor, and donor-acceptor carbenoids (Scheme **1.1**).[3,12] The conventional metal carbenoids, acceptor or acceptor-acceptor carbenoids, contain one or two electron-withdrawing groups (EWG), respectively. The Davies group has focused on the third type, which contains an electron-donating group (EDG) and an electron-accepting group (EWG).



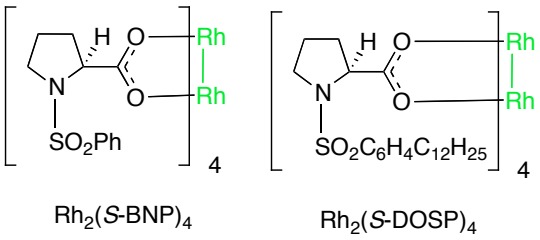
Scheme 1.1 Three types of metal-catalyzed carbenoids

Metal carbenoids with donating groups have advantages over the other two types of carbenoids.[3] According to the resonance structure of metal carbenoids (Scheme **1.2**), the donating group can stabilize the positive charge of the carbenoid carbon, making this type of metal carbenoid more stable and thus more selective in organic reactions. As an added benefit, this subtle structure modification dramatically suppresses carbenoid dimerization,[13] which is a major undesired side-reaction with acceptor and acceptor-acceptor carbenoids.



Scheme 1.2 Resonance structures of carbenoids

Rhodium(II) carboxylates have been established as the most useful catalyst at decomposing diazo compounds and high asymmetric induction has been achieved with some chiral rhodium(II) carboxylate catalysts.[14-17] The McKervey group has developed a variety of *N*-protected *L*-prolines as ligands in the Rh(II)-catalyzed intramolecular asymmetric C-H functionalization reaction with carbenoids.[17-19] One of the most notable examples is Rh_2(*S*-BNP)$_4$ (Scheme **1.3**). The Davies group has discovered that this type of dirhodium complexes is an exceptional chiral catalyst to catalyze intermolecular reactions with donor-acceptor carbenoids in a highly stereoselective fashion.[14]



Scheme 1.3 Two proline based dirhodium catalysts

The nature of the solvent has a dramatic effect on the enantioselectivity in the rhodium carboxylate-catalyzed carbenoid reaction.[13] As prolinate catalysts give enhanced asymmetric induction in non-polar hydrocarbon solvents and Rh_2(*S*-BNP)$_4$ is not very soluble in such solvents, the Davies group developed the Rh_2(*S*-DOSP)$_4$ containing a dodecyl chain in the ligand, which makes it very soluble in hydrocarbon solvents, even at

-78 °C.[20-22] Subsequently, it has quickly become a general catalyst for a range of transformations with donor-acceptor substituted diazo compounds.

The enhancement of enantioselectivity in hydrocarbon solvents has been proposed to be a result of solvent-induced orientation of all the prolinate ligands leading to a complex with D_2 symmetry.[22] The four bulky sulfonyl ligands of Rh_2(*S*-DOSP)$_4$ exist in an "up-down-up-down" configuration, which allows the catalyst to define the approaching face of the substrate to the carbenoid, typically resulting in high asymmetric induction (Figure **1.2**).

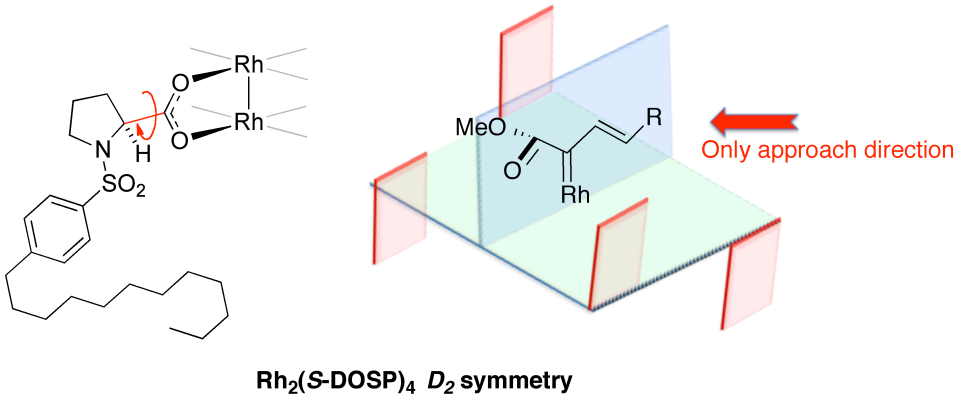
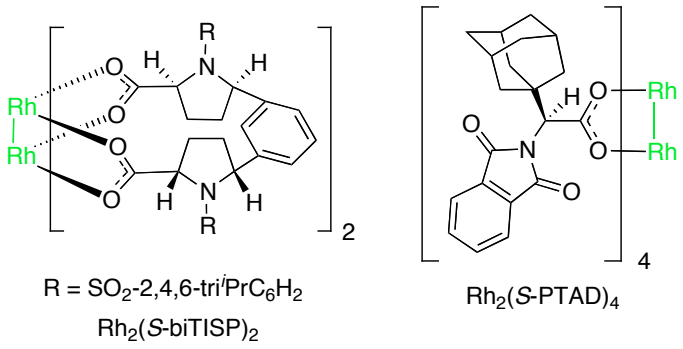


Figure 1.2 D_2 symmetry of Rh_2(*S*-DOSP)$_4$

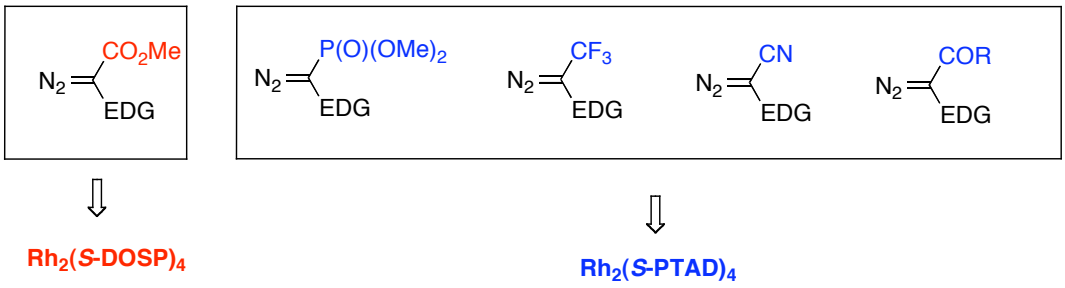
Since the development of Rh_2(*S*-DOSP)$_4$ as an exceptional catalyst for the intermolecular reaction of donor-acceptor carbenoids, other chiral dirhodium catalysts have been developed by the Davies group. Two catalysts that have been extensively used are Rh_2(*S*-biTISP)$_2$ and Rh_2(*S*-PTAD)$_4$.[23] Both of these catalysts are capable of achieving high levels of asymmetric induction when Rh_2(*S*-DOSP)$_4$ produces inferior results (Scheme **1.4**). The chiral ligands on Rh_2(*S*-biTISP)$_2$ are C_2 symmetric, but the catalyst behaves as a D_2 symmetric complex.[24] The complex is locked in a D_2 configuration with

the *N*-arylsulfonyl groups adopting an "up-down-up-down" arrangement. Because of the rigid conformation, similar asymmetric induction has been achieved with Rh_2(*S*-biTISP)$_2$ in both polar and non-polar solvents. In contrast to Rh_2(*S*-DOSP)$_4$ and Rh_2(*S*-biTISP)$_2$ adopting a D_2 symmetry, the phthalimide catalyst, Rh_2(*S*-PTAD)$_4$, which is a simple adamantyl derivative of Hashimoto's catalyst Rh_2(*S*-PTTL)$_4$, has been shown to adopt an essentially C_4 symmetric arrangement with the ligands aligned in an "up-up-up-up" arrangement.[14,25-27]



Scheme 1.4 Two other dirhodium catalysts

An attractive feature of the chemistry developed in the Davies group is the synergy between chiral dirhodium tetracarboxylate catalysts and donor-acceptor carbenoids. Generally, in the reaction with donor-acceptor carbenoids containing a methyl ester as the acceptor group, Rh_2(*S*-DOSP)$_4$ gave high enantioselectivity, while in reactions with other types of donor-acceptor carbenoids, Rh_2(*S*-PTAD)$_4$ would be the optimal catalyst (Scheme **1.5**). These predictable enantioselectivity makes the chemistry even more attractive because very limited optimization studies are necessary in order to achieve the best reaction outcome.



Scheme 1.5 Combinations of dirhodium catalysts and diazoacetates

Having established the optimum combination of catalyst and carbenoid precursor, the Davies group has developed several novel transformations with donor-acceptor carbenoids, including cyclopropanation of olefins,[28,29] direct C-H functionalization,[13,30-35] Si-H insertion[36] and O-H insertion followed by [2,3] sigmatropic rearrangement.[37] In addition to these reactions, the use of vinyldiazoacetates as the donor-acceptor carbenoid precursor can lead to other interesting transformations. These include the cyclopropanation/Cope rearrangement (CPCR) with dienes,[38-41] [3 + 2] cycloaddition with electron rich olefins,[42] vinylogous reactivity,[43-45] and the combined C-H functionalization/Cope rearrangement (CHCR) (Figure **1.3**).[46-48] One unique feature of using a vinyl group as the electron-donating group in the donor-acceptor carbenoid, is that the vinyl group can be selectively involved in the reaction and lead to "*non-classical*" transformations. My projects involve the use of vinylcarbenoids as precursors to achieve highly stereoselective transformations. In this chapter, a concise introduction of the first four "classical" reactions will be covered. A detailed introduction of the "*non-classical*" transformations will be described in later chapters.

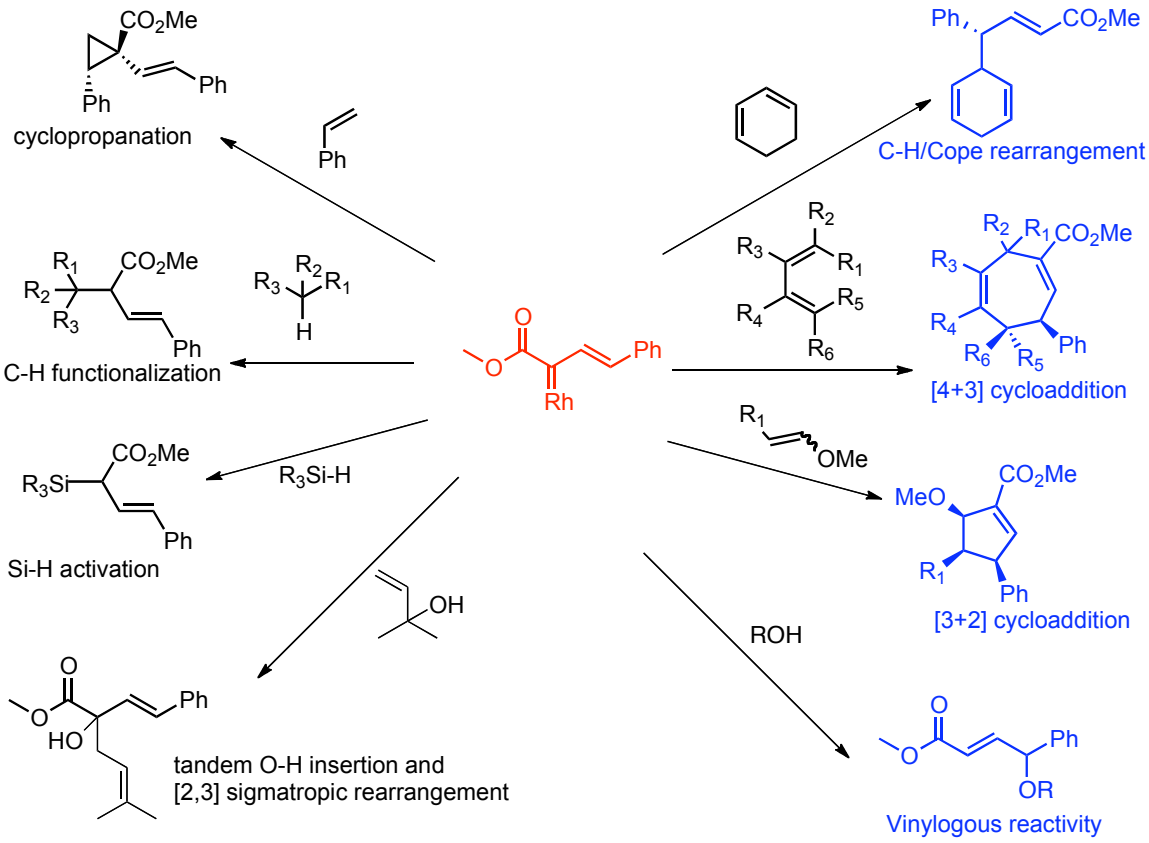
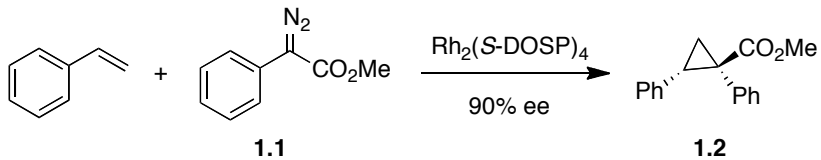


Figure 1.3 Chemistry developed in the Davies group

1.2 Cyclopropanation of olefins

The Rh_2(*S*-DOSP)$_4$ catalyzed cyclopropanation reaction between donor-acceptor carbenoids and olefins is highly diastereoselective and enantioselective.[21,29,49,50] For example, the decomposition of methyl phenyldiazoacetate **1.1** with styrene in the presence of a catalytic amount of Rh_2(*S*-DOSP)$_4$ afforded cyclopropane **1.2** as a single diastereomer with 90% ee (eq. **1.1**).[21]



(1.1)

Very recent computational studies conducted by Dr. Hansen in the Davies lab suggested a concerted but highly asynchronous transition state for the cyclopropanation.[51] In this model, the substrate approaches the rhodium core through an end-on model, in which the dihedral angel of the C=C double bond in styrene and the C=Rh double bond in the carbenoid is about 15° (Figure **1.4**). In the transition state, the bond length of C1-C2 was calculated to be 2.278A, whereas the bond distance of C1-C3 was calculated to be 2.844A. These bond lengths support the concept that the cyclopropanation proceeds through a highly asynchronous mechanism.

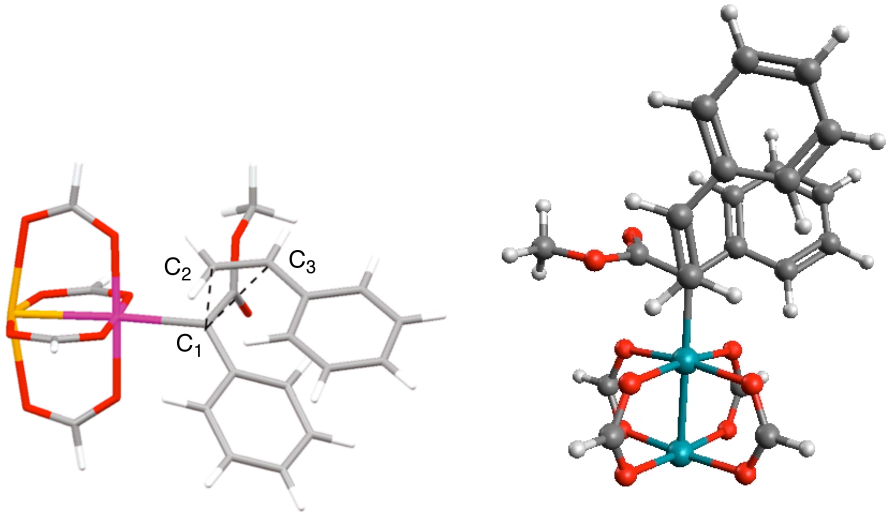


Figure 1.4 Calculated transition state for cyclopropanation

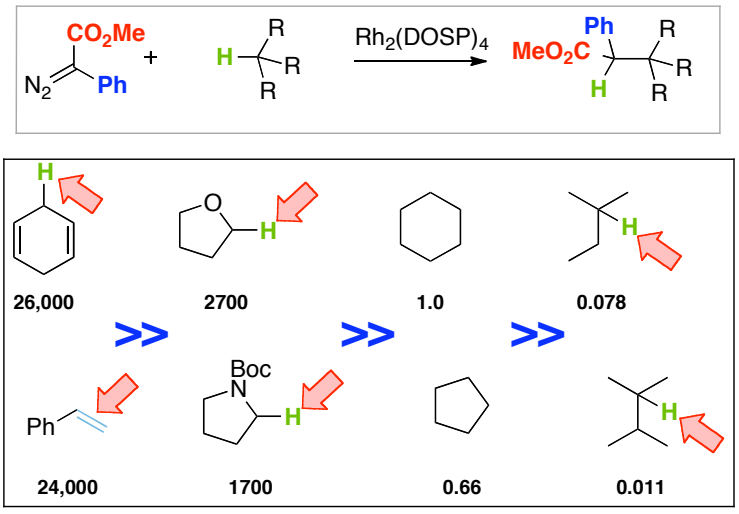
1.3 Direct C-H functionalization

Donor-acceptor carbenoids have been demonstrated to undergo selective intermolecular C-H functionalization by means of carbenoid-induced C-H insertion reaction.[52] Before the discovery of donor-acceptor carbenoids, the metal-catalyzed C-H

functionalization reaction with traditional acceptor[53] or acceptor-acceptor carbenoids was conducted using a large excess of trapping reagents in order to limit the unwanted side reaction of carbenoid dimerization.[54-57] Due to the enhanced stability of donor-acceptor carbenoids, the intermolecular C-H functionalization reaction can be carried out with the trapping agent serving as the limiting reagent.[30,58-60]

Achieving highly selective C-H functionalization reactions is a major challenge.[58,61,62] The introduction of relatively stable donor-acceptor carbenoids has overcome many of the selectivity problems, especially for intermolecular C-H functionalization. The selective C-H functionalization with donor-acceptor carbenoids is governed by the steric and electronic effects of the substrate.[58] A general overview of the competing selectivity trends is given in Table **1.1**.

Table 1.1 Site selectivity in the carbenoid reactivity



Competitive studies have been conducted and reveal that the relative carbons that can stabilize positive charge are more reactive towards C-H functionalization with metal carbenoids.[13] 1,4-Cyclohexadiene undergoes C-H functionalization 26,000 times faster

than cyclohexane. On the other hand, steric effects also play a key role in controlling selectivity. Tertiary C-H bonds are electronically more favorable than secondary C-H bonds, but secondary C-H bonds are sterically more accessible towards C-H insertion reactions. This can be seen in the rate difference between the methylene in cyclohexane and the methylene site in 2-methylbutane.

A computational study has been carried out to understand the possible mechanism and selectivity in the C-H insertion reaction.[63] The carbenoid-induced C-H functionalization is proposed to proceed through a concerted but highly nonsynchronous transition state. Three possible orientations of the carbenoid and the substrate can be concluded: the C-H bond is orientated in a parallel plane to the carbene, either parallel to the Rh-C bond (a), perpendicular to the Rh-C bond (b), or with a C-H-C bond angle close to 180° (Figure **1.5**). The recent computational calculations described a transition state with a C-H-C bond angle in the range of 117-165°, which suggests model **C** in which the C-H bond of the substrate approaches at a vector nearly orthogonal to the carbenoid plane may be the most useful for understanding this chemistry.

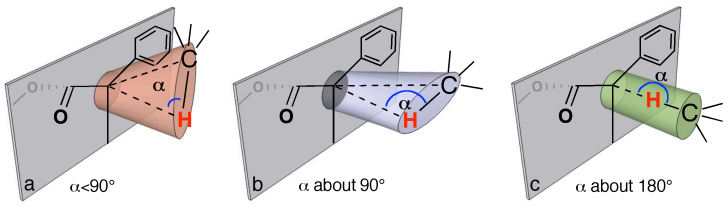


Figure 1.5 Three different C-H insertion models

The calculation suggests a considerable amount of hydride shift character associated with transition state **C**. A partial positive charge on the carbon in the substrate is built up in the transition state, and thus, if the substrate can stabilize the positive charge, it is more

reactive towards C-H functionalization. A possible model has been proposed to explain the diastereoselectivity as shown in Figure **1.6**. The projection is along the C-C bond that is formed in the process. This model provides a simple rationale for the relative orientation of the large (L), medium (M), and small substituent (S) in the substrate during the insertion event and therefore, allows for prediction of the relative stereochemistry in the products. In this model, the ester groups are considered to be more sterically crowded than the aryl (or vinyl) groups, because of the planer property of the aryl groups. The largest of the substituents (L) is orientated in the position furthest from each upward ligands. The second most sterically demanding group (M) is pointed away from the ester group, while the least sterically demanding of the substituents (S), is located close to the ester group.

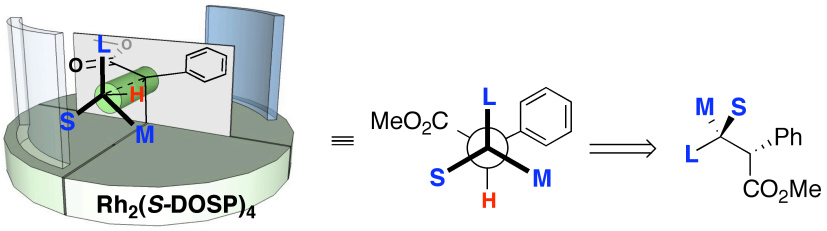
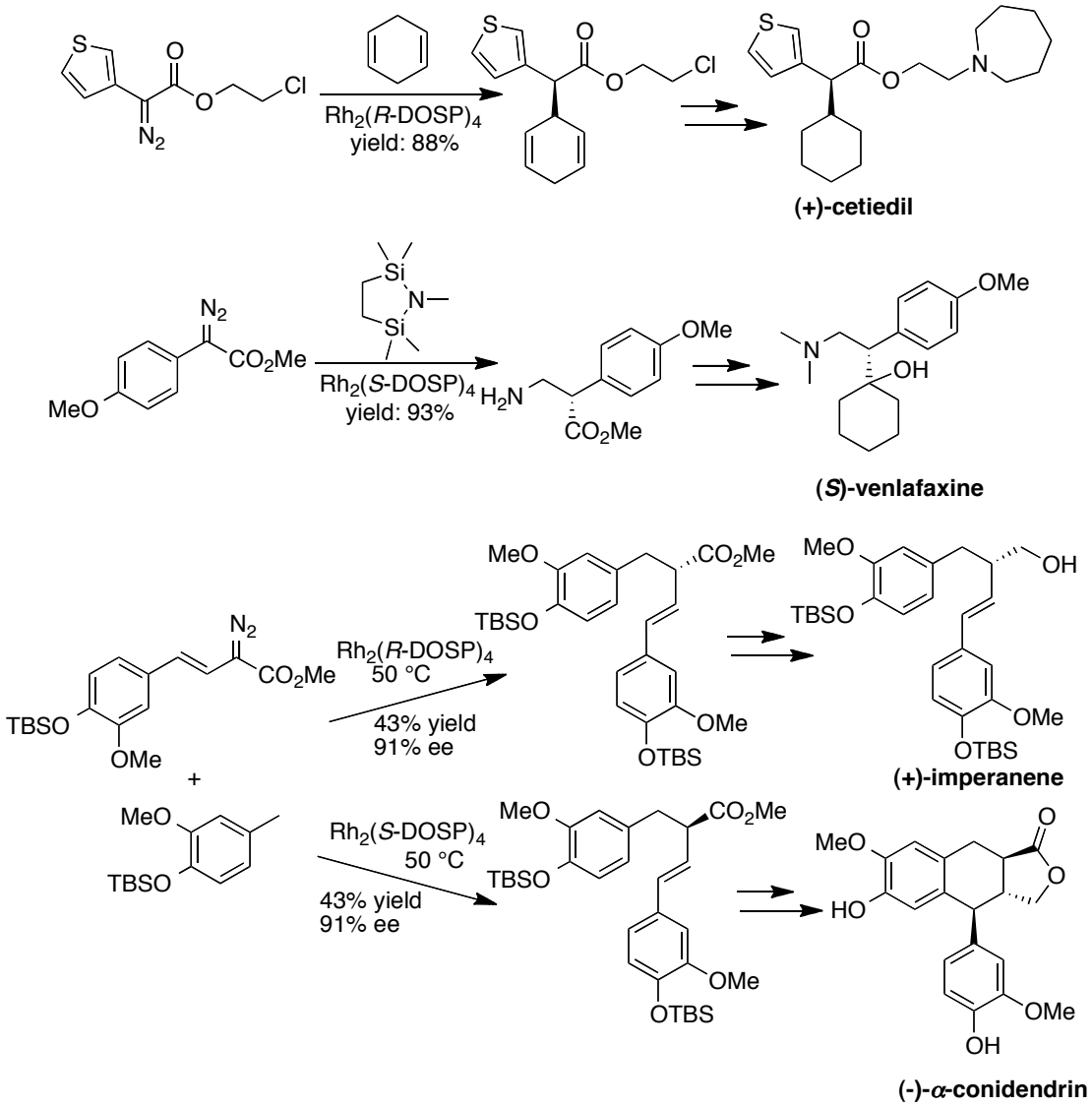


Figure 1.6 Predicted stereochemical outcome in the C-H insertion reaction

C-H functionalization offers alternative strategies to streamline the synthesis of complex organic molecules. The carbenoid induced C-H functionalization reaction has been successfully applied in the total synthesis of many natural products or biologically active compounds. All of the syntheses involve the intermolecular C-H insertion reaction as the key stereo-controlling step (**Scheme 1.6**).[12,32,33,64,65]

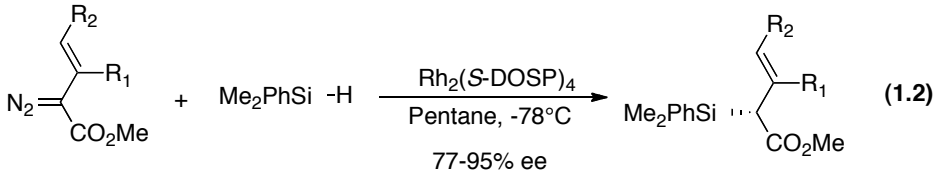


Scheme 1.6 Applications of C-H insertion in synthesis

1.4 Si-H insertion

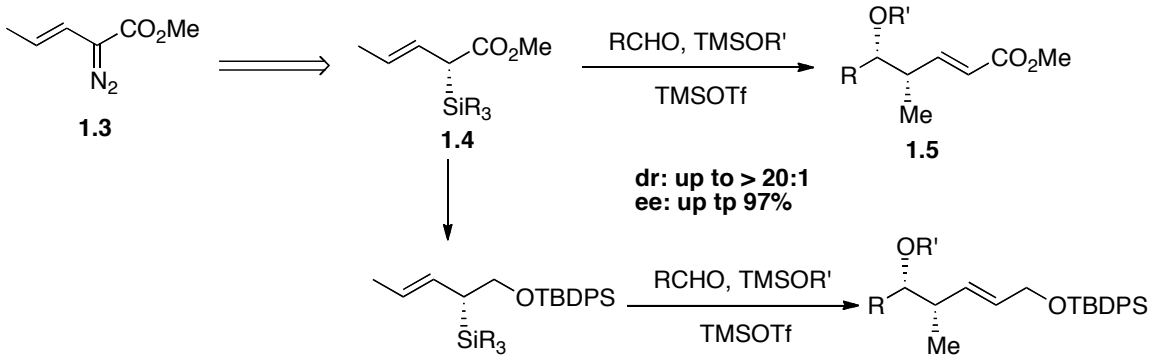
Allylsilanes are versatile intermediates in organic synthesis.[66-68] One of the attractive methods of synthesizing enantioenriched allylsilanes is the reaction between vinylcarbenoids and trialkylsilanes by means of a Si-H insertion. Rh_2(*S*-DOSP)$_4$ has been

demonstrated to be an effective catalyst in the C-H functionalization reactions with donor-acceptor carbenoids. The extension to the Si-H insertion reaction with trialkylsilanes in the presence of Rh_2(*S*-DOSP)$_4$ successfully generated allylsilanes in good yield with high asymmetric induction (eq. **1.2**).[36]



(1.2)

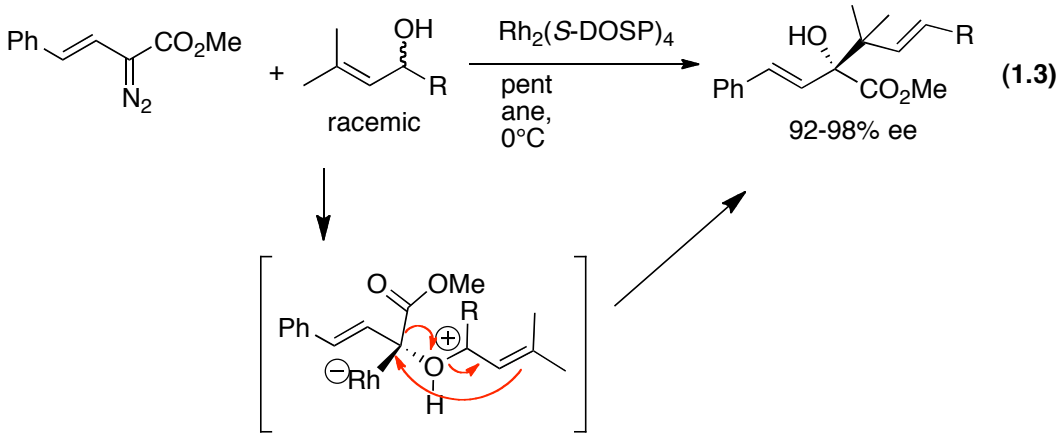
This methodology offers rapid access to enantioenriched allylsilanes, which have been applied in the asymmetric allylation or crotylation reaction of aldehydes (Scheme **1.7**).[43] The Rh_2(*S*-DOSP)$_4$ catalyzed asymmetric Si-H insertion reaction of silanes with vinyldiazoacetate **1.3** afforded the allylsilane **1.4**, which subsequently reacts with aldehydes and generates the vinylogous Mukaiyama aldol product **1.5**. The reaction affords product **1.5** with *syn*- configuration in good yield with moderate to good diastereoselectivity and enantioselectivity.



Scheme 1.7 Application of asymmetric Si-H insertion

1.5 O-H insertion followed by [2,3]-sigmatropic rearrangement

Rh_2(*S*-DOSP)$_4$-catalyzed oxonium ylide/[2,3]-sigmatropic rearrangement reactions of racemic allylic alcohols with donor-acceptor carbenoids are capable of high asymmetric induction (eq. **1.3**).[37] The reaction is proposed to occur via a chiral rhodium-associated oxonium ylide intermediate, which undergoes the [2,3]-sigmatropic rearrangement with effective transfer of chirality. The reaction is capable of generating two adjacent quaternary centers in 92-98% ee. Highly substituted allylic alcohols are crucial for the reaction to undergo the O-H insertion/[2,3]-sigmatropic rearrangement selectively; otherwise the direct O-H insertion would be dominant in the reaction, leading to racemic mixtures of O-H insertion products.

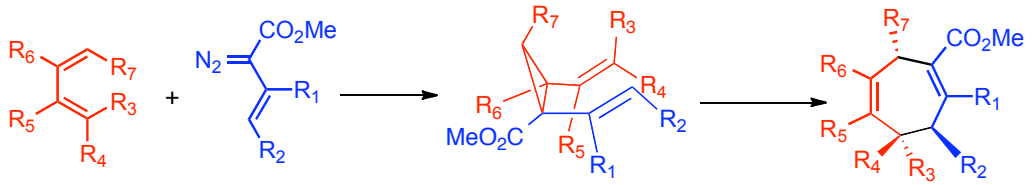


(1.3)

Chapter II: Asymmetric Cyclopropanation/Cope Rearrangement and its Application in Total Syntheses

2.1 Introduction

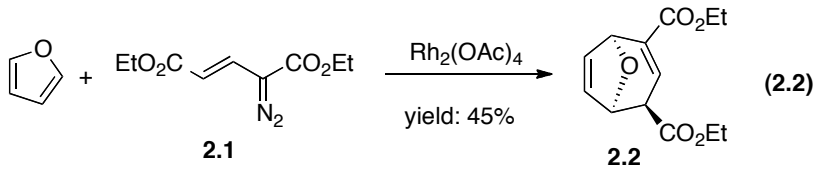
Seven-membered carbocyclic rings are present in a variety of natural products of biological interest.[69-72] Due to the higher enthalpic and entropic barriers as well as the flexibility of the ring skeleton, it is more difficult to stereospecifically generate or functionalize cycloheptanes, compared to five- or six-membered rings. In recent years, cycloaddition processes have been shown to be particularly versatile for the synthesis of seven-membered rings. One of the most effective methods is the cyclopropanation/Cope rearrangement (CPCR) developed by the Davies group.[73,74] The reaction between vinylcarbenoids and dienes proceeds through *cis*-divinylcyclopropane intermediates, which can then undergo a Cope rearrangement *via* a boat transition state to produce cycloheptadienes in high diastereocontrol (eq **2.1**). This methodology is an effective approach to highly functionalized cycloheptyl rings.



(2.1)

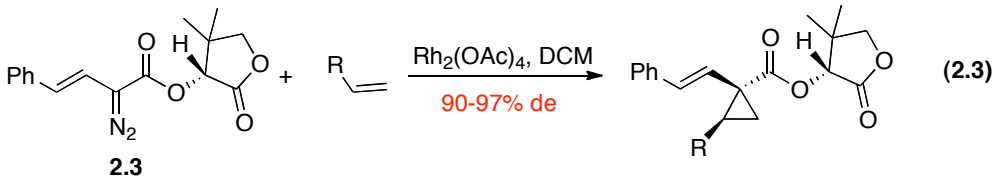
The first CPCR reaction between vinylcarbenoids and dienes has been reported in 1985.[75] The $Rh_2(OAc)_4$-catalyzed decomposition of diazoacetate **2.1** with furan selectively generated product **2.2** exclusively as its *endo* diastereomer (eq **2.2**). Subsequently, this method has been successfully applied to a variety of substrates,

including cyclopentadiene, acyclic dienes, oxygenated dienes, furans and pyrroles.[41,74,76-79] The broad substrate scope indicates that the CPCR reaction is a general strategy in building up seven-membered rings. This strategy is also demonstrated to be very effective in intramolecular reactions.[80,81] In this chapter, focused will be placed on the development of asymmetric versions of the CPCR reaction and its synthetic applications.

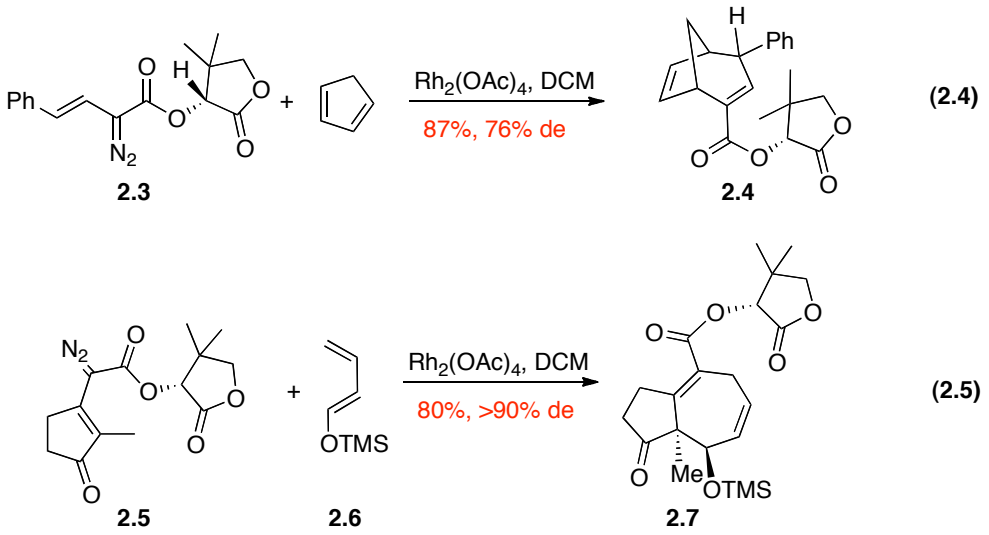


2.1.1 Asymmetric transformation by using chiral auxiliaries

The CPCR reaction between vinylcarbenoids and dienes has been demonstrated to be highly diastereoselective.[73,79,82] The stereochemistry is controlled in the cyclopropanation step. A stereoselective cyclopropanation step would result in the formation of seven-membered rings in a highly stereoselective fashion because the Cope rearrangement proceeds through a well-defined boat transition state. The chiral auxiliary was initially used to achieve the asymmetric synthesis of cycloheptyl rings. Several α-hydroxy esters were screened as chiral auxiliaries for asymmetric cyclopropanation with rhodium(II)-stabilized vinylcarbenoids. Using either (*R*)-pantolactone or (*S*)-lactate resulted in greater than 90% de (eq **2.3**).[83]



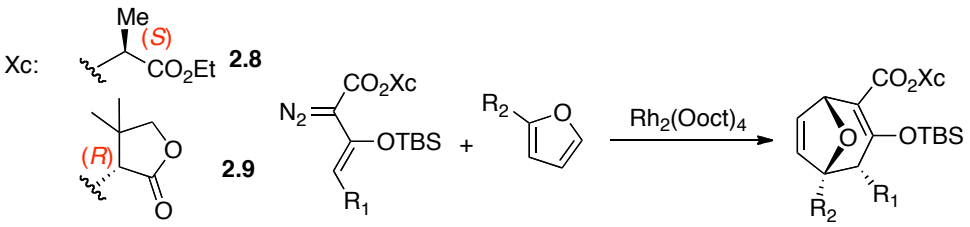
With the discovery of effective auxiliaries in the cyclopropanation reaction, the chemistry was extended to cyclopentadiene. A very facile CPCR reaction was observed and the bicyclo[3.2.1]octadiene **2.4** was isolated in 87% yield with 76% de (eq **2.4**).[83] Another more elaborate example was the reaction of trimethylsiloxybutadiene **2.6** with diazo **2.5**. A valuable building block, hydroazulene **2.7** was effectively produced in 80% yield and in greater than 90% de (eq **2.5**).[83]



The extension of this asymmetric cycloaddition to furans effectively generated enantioenriched 8-oxabicyclo[3.2.1]octene derivatives.[82] 8-Oxabicyclo[3.2.1]octene products are versatile intermediates in organic synthesis and with subsequent ring-opening reactions, a wide range of cyclic and acyclic products containing multiple stereocenters can be obtained.[84,85] The rhodium(II)-catalyzed decomposition of chiral diazoacetates **2.8** and **2.9** with a variety of furans generated 8-oxabicyclo[3.2.1]octene derivatives in good yields with high asymmetric induction, ranging from 75-95% de (Table **2.1**).[82] Higher levels of asymmetric induction have been observed with (*R*)-

pantolactone as the chiral auxiliary compared to (*S*)-lactate. Using these two inexpensive chiral auxiliaries, both enantiomers of the cycloadducts can be generated.

Table 2.1 Diastereoselective synthesis of 3-siloxy-8-oxabicyclo[3.2.1]octa-2,6-diene-2-carboxylates



entry	R_1	R_2	Xc			
			(*S*)-lactate		(*R*)-pantolactone	
			yield, (%)	de, (%)	yield, (%)	de, (%)
1	H	H	72	79 (1*S*)	82	94 (1*R*)
2	Me	H	62	90 (1*S*)	75	95 (1*R*)
3	H	Me	81	75 (1*S*)	91	83 (1*R*)
4	Me	Me	91	84 (1*S*)	69	94 (1*R*)
5	H	COMe	74	79 (1*S*)	65	94 (1*R*)

A model has been proposed to explain the asymmetric induction in this system. It can be readily rationalized by assuming that the carbonyl group of the auxiliary interacts with the carbenoid carbon as shown in Figure **2.1**.[21,82] This interaction allows effective transfer of the chiral influence of the stereogenic center in the chiral auxiliary to the carbenoid carbon. The weak coordination between the carbenoid and the auxiliary still allows the complex to undergo carbenoid reactivity rather than ylide chemistry. The favored interactions with the carbenoid for (*S*)-lactate and (*R*)-pantolactone auxiliary as shown would be expected to minimize steric interaction with the "wall" of the catalyst. The overall effect is to block one of the two faces of the carbenoid. Therefore, the substrate

preferentially attacks the carbenoid carbon from a single unblocked face and high level of asymmetric induction is thus achieved. (*S*)-Lactate and (*R*)-pantolactone auxiliaries have opposite chiral influenece and result in the formation of the opposite enantiomers of the oxabicycles.

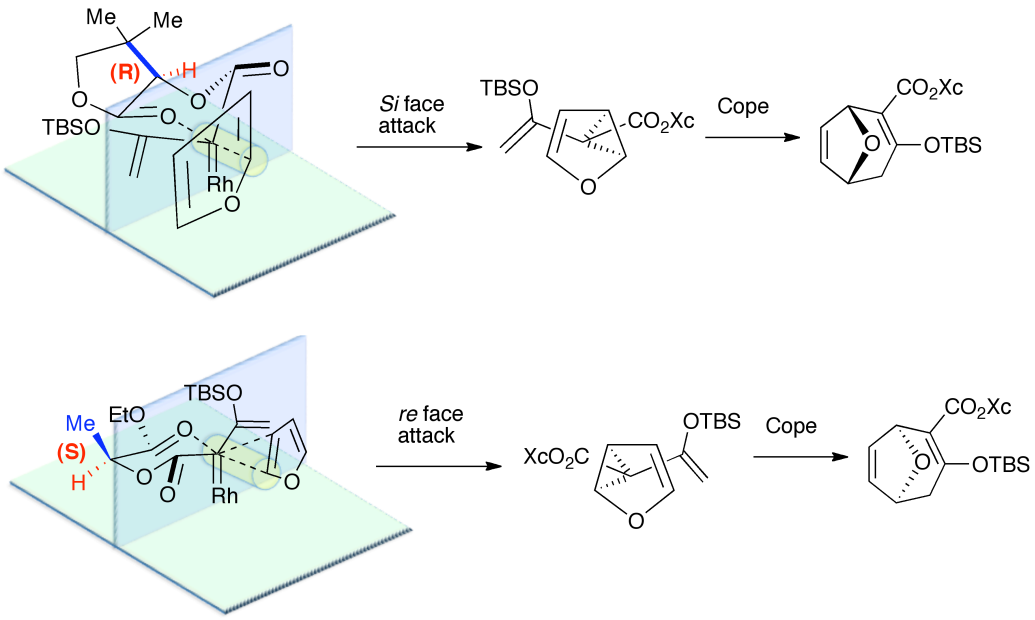
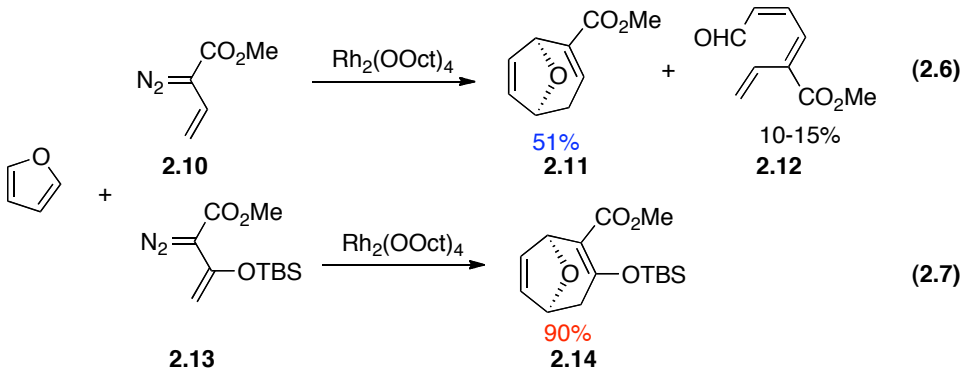
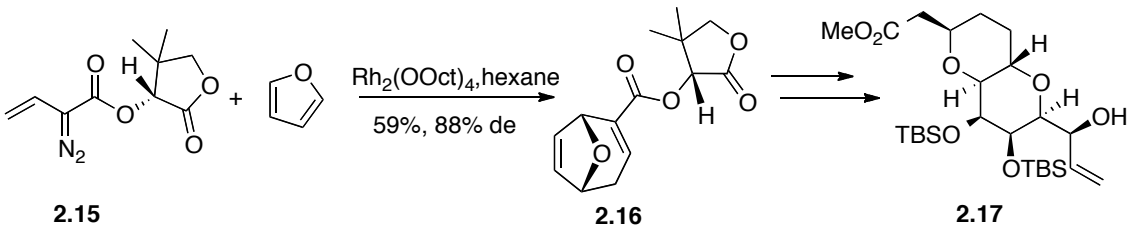


Figure 2.1 Two possible transition states for CPCR with chiral auxiliaries

The use of 2-siloxy-substituent vinyldiazoacetates as carbenoid precursors is very beneficial because it results not only in high asymmetric induction, but also avoids the formation of triene byproducts.[82] These types of products are considered to arise through the intermediacy of zwitterionic species formed by the attack of carbenoids on the 2-position of furans. In a test system, the reaction of siloxyvinyldiazoacetate **2.13** with furan produced compound **2.14** in 90% yield (eq **2.6**). In contrast, the reaction with unsubstituted vinyldiazoacetate **2.10** afforded the cycloadduct **2.11** in only 51% yield with a significant amount of triene side product **2.12** (eq. **2.7**).[82]



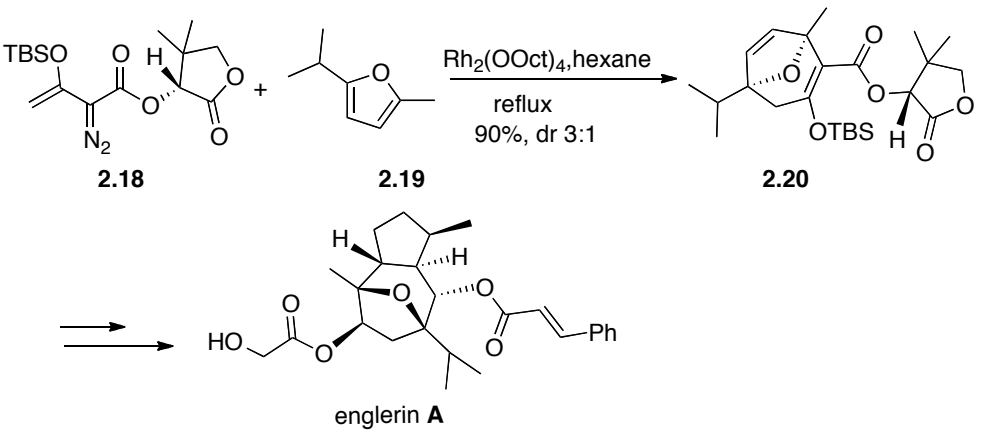
The synthetic utility of the asymmetric CPCR reaction with furans has been illustrated in the synthesis of norhalichondrin B (Scheme **2.1**).[86] The rhodium-catalyzed decomposition of diazoester **2.15** with furan gave oxabicyclo[3.2.1]octene **2.16** in 59% yield with good diastereoselectivity. This cycloadduct **2.16** was further converted to product **2.17**, an advanced intermediate in the synthesis of norhalichondrin B.



Scheme 2.1 Synthesis of a key intermediate in the synthesis of norhalichondrin B

A more recent synthetic application of this method has been demonstrated in the asymmetric synthesis of (-)-englerin **A** (Scheme **2.2**).[87] Theodorakis reported a CPCR reaction between siloxyvinyldiazoacetate **2.18** containing (*R*)-pantolactone as the auxiliary and disubstituted furan **2.19**. The reaction afforded product **2.20** in good yield with moderate diastereoselectivity. Two newly formed quaternary centers are generated in one step with complete diastereocontrol. Furan **2.19** contains two possible double

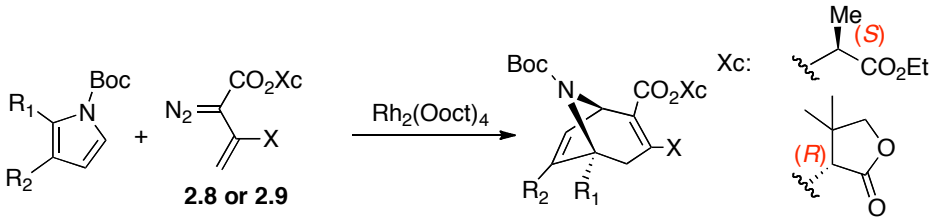
bonds for initial cyclopropanation, yet the reaction selectively undergoes cyclopropanation on the least sterically hindered double bond without any formation of the other possible regioisomer.[87]



Scheme 2.2 The total synthesis of englerin A

An asymmetric [4 + 3] annulation between vinylcarbenoids and pyrroles would be a very useful transformation because it would result in direct access to enantioenriched tropane skeletons.[88] Tropane moieties are found in natural alkaloids, many of which possess potent biological activities.[89,90] They are particularly useful probes to study the neurochemistry of drug addiction.[90-93] The asymmetric [4 + 3] cycloaddition has been shown to be applicable to various *N*-Boc-protected pyrroles and a series of enantioenriched tropanes are generated in moderate to good yields (Table **2.2**). The reaction of vinyldiazoacetate **2.8** or **2.9** with pyrroles generated the corresponding tropanes in decent yields with low to moderate asymmetric induction, ranging from 31-79% ee.[88,94]

Table 2.2 The synthesis of tropanes



entry	R_1	R_2	X	Xc (*S*)-lactate yield, (%)	de, (%)	Xc (*R*)-pantolactone yield, (%)	de, (%)
1	H	H	H	82	66 (1*R*)	64	69 (1*S*)
2	H	H	OTBS	64	66 (1*R*)	66	68 (1*S*)
3	Ph	H	H	64	53 (1*R*)	--	--
4	Ph	H	OTBS	74	52 (1*R*)	56	52 (1*S*)
5	Ac	H	H	30	67 (1*R*)	--	--
6	Ac	H	OTBS	58	79 (1*R*)	69	78 (1*S*)
7	-(CH2)$_4$-		H	48	55 (1*R*)	--	--
8	-(CH2)$_4$-		OTBS	--	--	31	37 (1*S*)

The asymmetric induction in the CPCR reaction with pyrroles has been found to be opposite to what has been observed in the reaction with furans.[82] The use of these types of chiral auxiliaries for carbenoid reactions has been well established in the reaction with furans. Even with one face of the carbenoid fully blocked, it is still possible that the reaction with pyrroles results in the formation of different enantiomers of tropanes, depending on how pyrroles approach the carbenoid carbon (Figure **2.2**). If initial bond formation occurs at the 2-position or 3-position of pyrrole in the nonsynchronous cyclopropanation stage, this would lead to different enantiomers of cycloadducts. The reaction with furan favors bond formation at the 2-position, which is consistent with the electrophilicity of furan; while the observed asymmetric induction with pyrrole would require the cyclopropanation to initially occur at the 3-position of *N*-Boc-pyrrole. The

result can be rationalized based on the interference between the bulky Boc group present on the nitrogen and the rhodium "wall".

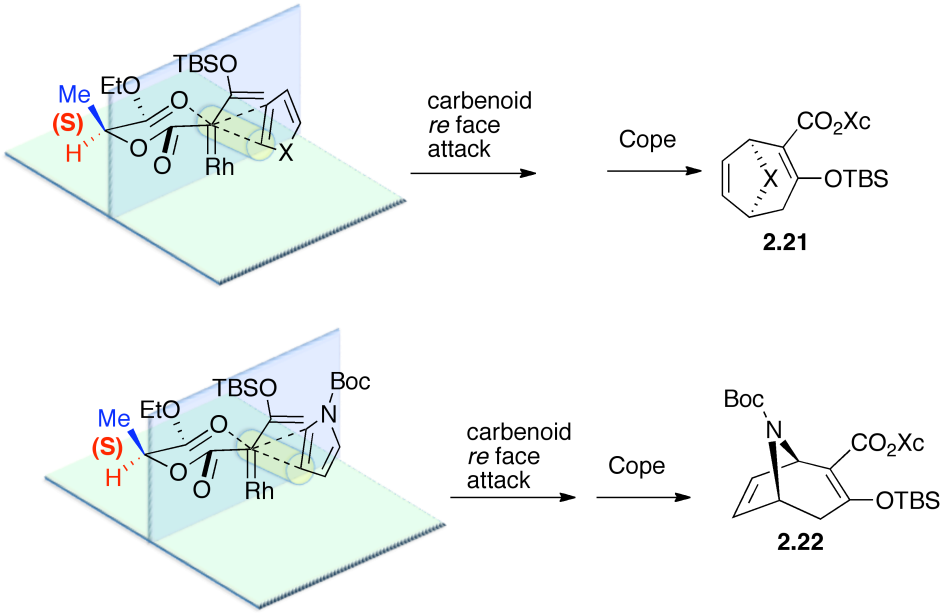


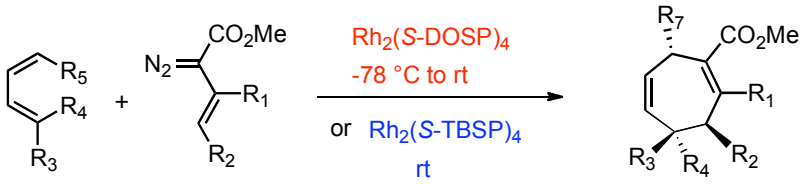
Figure 2.2 The CPCR transition state with pyrroles

2.1.2 Catalytic asymmetric transformation

The most attractive strategy for enantioselective CPCR reactions is to use a catalytic amount of chiral catalysts to achieve highly asymmetric transformations. Even though the chiral auxiliary approach is satisfactory, leading to the cycloadduct with highly asymmetric control, a stoichiometric amount of the auxiliary is still required. The first catalytic asymmetric construction of cycloheptadiene derivatives *via* the CPCR reaction using Rh_2(*S*-TBSP)$_4$ as chiral catalyst has been reported (Table **2.3**).[95] The reaction of vinyldiazoacetates with dienes in hydrocarbon solvents results in a general and

enantioselective entry into seven-membered carbocycles. The asymmetric induction has been further improved to greater than 95% ee with Rh_2(*S*-DOSP)$_4$. Rh_2(*S*-DOSP)$_4$ is generally more soluble in hydrocarbon solvents than Rh_2(*S*-TBSP)$_4$, which allows the reaction to be conducted at temperatures as low as -78 °C.[40]

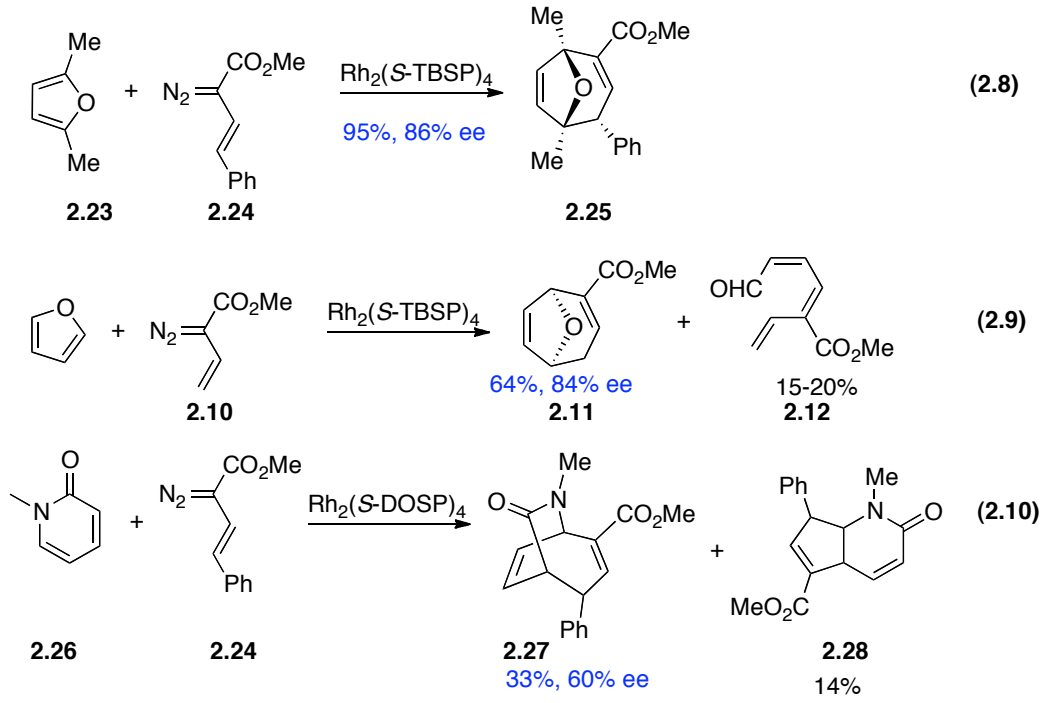
Table 2.3 The Rh_2(*S*-TBSP)$_4$ or Rh_2(*S*-DOSP)$_4$ catalyzed [4 + 3] cycloaddition



entry	R_1	R_2	R_3	R_4	R_5	Rh_2(*S*-TBSP)$_4$ yield, (%)	Rh_2(*S*-TBSP)$_4$ ee, (%)	Rh_2(*S*-DOSP)$_4$ yield, (%)	Rh_2(*S*-DOSP)$_4$ ee, (%)
1	H	Ph	Me	H	H	41	90	51	98
2	H	Ph	H	Me	H	79	90	47	96
3	H	Ph	OTBS	H	H	67	85	47	93
4	H	Ph	H	-CH_2-		92	75	77	93
5	H	Me	H	-CH_2-		75	83	47	91
6	H	$CH=CH_2$	H	-CH_2-		64	91	58	92
7	-$(CH_2)_3$-			-CH_2-		68	68	66	74
8	-$(CH_2)_4$-		H	-CH_2-		70	69	61	73

This reaction has also been effectively extended to electron-rich heterocycles. The Rh_2(*S*-TBSP)$_4$-catalyzed reaction of vinyldiazoacetate **2.24** with 2,5-dimethylfuran **2.23** afforded annulation product **2.25** in good yield with high enantiomeric excess (eq. **2.8**).[95] A similar result was obtained, when diazoacetate **2.10** reacted with furan (eq. **2.9**).[82] However, in addition to cycloadduct **2.11**, a triene byproduct **2.12** was isolated in about 20% yield, arising from a zwitterionic intermediate. Side products arising from the zwitterionic intermediate dominated the reaction, when the reaction was extended to *N*-heterocycles. The reaction between diazoacetate **2.24** and 1-methyl-2-pyridone **2.26**

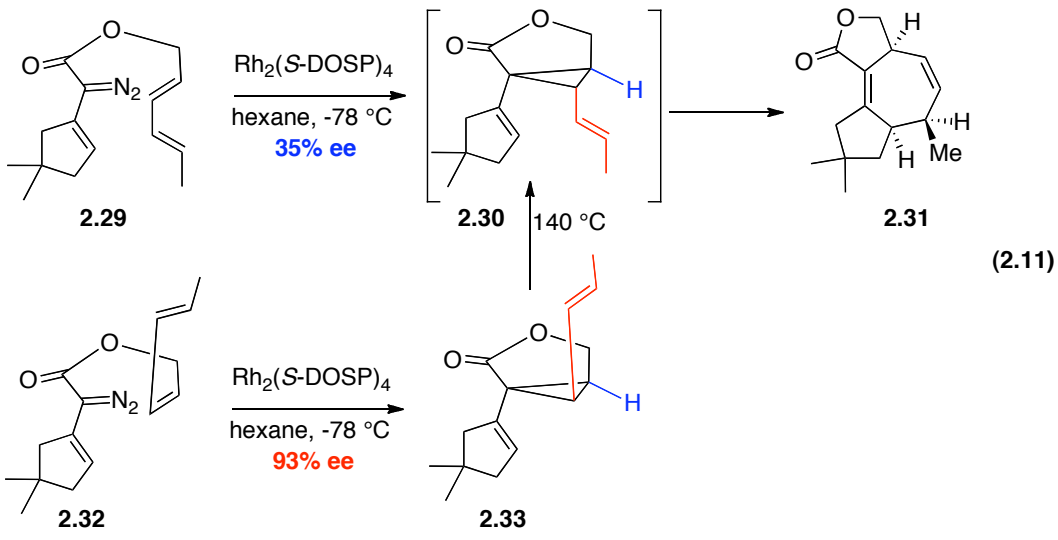
generated the CPCR product **2.27** in only 33% yield with 60% ee (eq. **2.10**). A [3 + 2] annulation byproduct **2.28** was isolated in 14% yield, presumably through a zwitterionic intermediate.[96]



2.1.3 Intramolecular CPCR reaction

The stereochemistry of the cyclopropanation between vinylcarbenoids and dienes is controlled by the diene geometry in the intramolecular CPCR reaction.[80,81] In the case where the double bond nearest the ester tether is *trans*, cyclopropanation would generate *cis*-divinylcyclopropane, which would rearrange into cycloheptadiene. Unlike the ineffective intermolecular cyclopropanation reaction between (*E*)-olefins and donor-acceptor carbenoids, the intramolecular cyclopropanation of *trans*-alkenes is still effective. In the case where the double bond nearest the tether is *cis*, the *trans*-divinylcyclopropane would be generated.

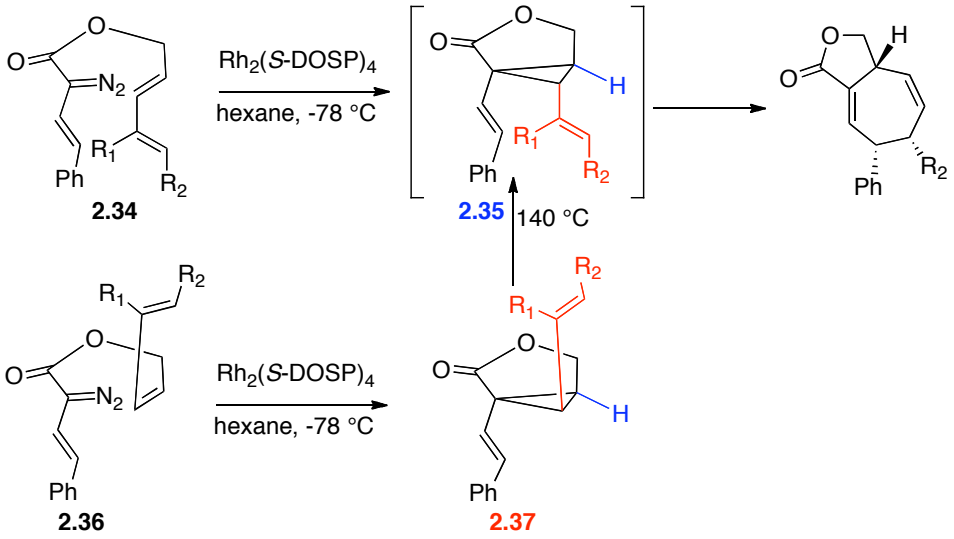
Chiral dirhodium catalysts have been shown to be very effective in catalyzing intermolecular CPCR reaction in a highly stereoselective fashion.[40] Subsequently, the Davies group has explored the possibility of using chiral dirhodium catalysts in the intramolecular CPCR reaction. The Rh_2(*S*-DOSP)$_4$-catalyzed decomposition of **2.29**, containing a *trans*-alkene nearest the tether generated product **2.31** with full relative stereo-control but only in 35% ee (eq. **2.11**).[41,97] The reaction is believed to proceed through *cis*-divinylcyclopropane **2.30** intermediate, which rapidly undergoes the Cope rearrangement to generate product **2.31**. A much more effective route is to use **2.32** containing a *cis*-alkene nearest the tether as the precursor, which results in the formation of *trans*-divinylcyclopropane **2.33** with 93% ee. Upon heating, cyclopropane **2.33** rearranged to the [4 + 3] product **2.31** without any loss of enantioselectivity. Presumably, the rearrangement would occur through an initial isomerization from **2.33** to **2.30** *via* a diradical intermediate. In this process, only two out of three stereochemical centers are broken and the product retains the same level of asymmetric induction.



(2.11)

To evaluate the effect of the diene structure on the asymmetric induction in the intramolecular CPCR reaction with vinylcarbenoids, various diazoacetates containing *trans*-dienyl moieties have been tested with Rh_2(*S*-DOSP)$_4$ (Table **2.4**).[80] The reactions led directly to fused cycloheptadienes through the intermediacy of *cis*-divinylcyclopropane **2.35** and low to moderate levels of asymmetric induction were observed. The reaction with the *cis*-dienylmethyl system **2.36** resulted in the formation of isolable *trans*-divinyl cyclopropane **2.37,** which isomerized and rearranged to generate the cycloheptadiene. Considerable improvement of asymmetric induction is achieved with *cis*-dienyl substrate **2.36**, compared to the *trans*-dienyl substrate **2.34**.

Table 2.4 Intramolecular [4 + 3] cycloaddition

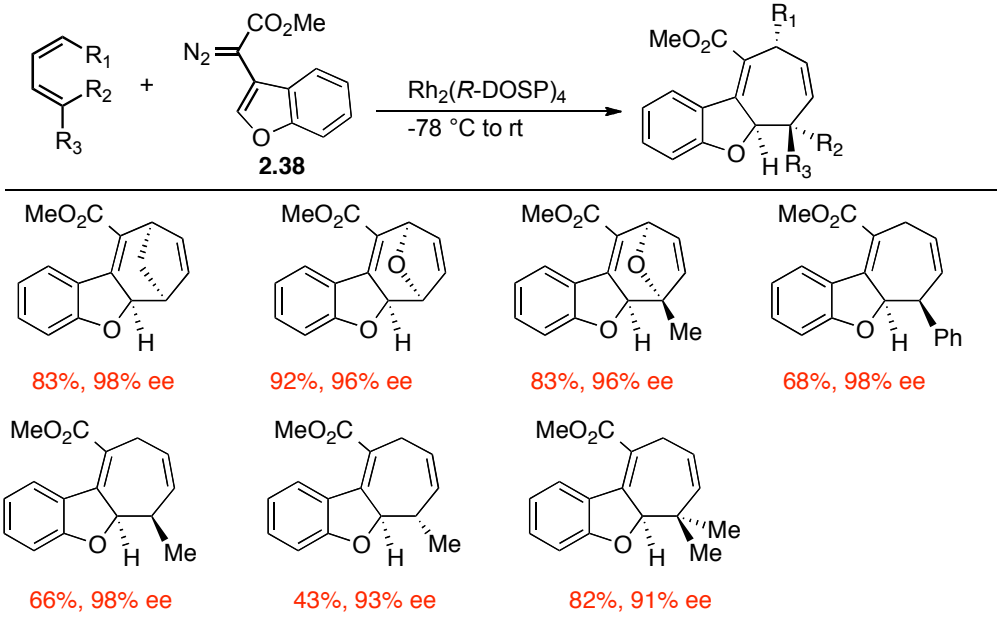


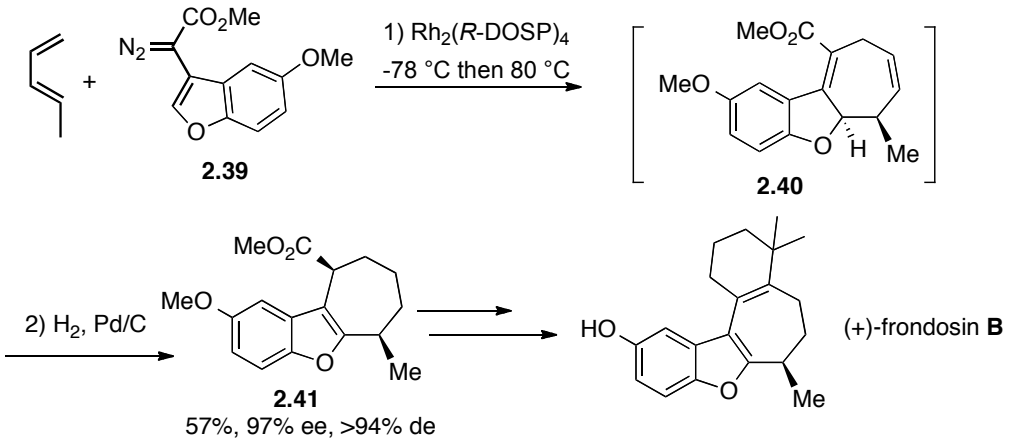
R_1	R_2	2.34 yield, (%)	2.34 ee, (%)	2.36 yield, (%)	2.36 ee, (%)
H	Me	74	24	78	62
H	H	71	50	76	67
Me	H	53	46	63	41

2.1.4 CPCR reaction with benzofuranyldiazoacetates

It has been illustrated that benzofuranyldiazoacetates can selectively undergo the CPCR reaction with dienes, which shows that the benzofuran moiety is a reactive component in the Cope rearrangement.[98] The Rh_2(*S*-DOSP)$_4$-catalyzed decomposition of benzofuranyl diazoacetate **2.38** with a variety of dienes generated the [4 + 3] cycloadducts as single diastereomers in good yields with excellent asymmetric induction (Table **2.5**). A synthetic application of this methodology has been demonstrated in the formal synthesis of (+)-Frondosin B (Scheme **2.3**).[98] The key step is the Rh_2(*R*-DOSP)$_4$-catalyzed CPCR reaction between benzofurandiazoacetate **2.39** and *trans*-piperylene. Because the [4 + 3] cycloadduct **2.40** is not stable, the crude mixture was subjected to hydrogenation rapidly and product **2.41** was isolated in 57% yield over two steps. Tautomerization of the remaining enoate double bond rearomatized the benzofuran ring.

Table 2.5 The [4 + 3] cycloaddition with benzofuranyl diazoacetate

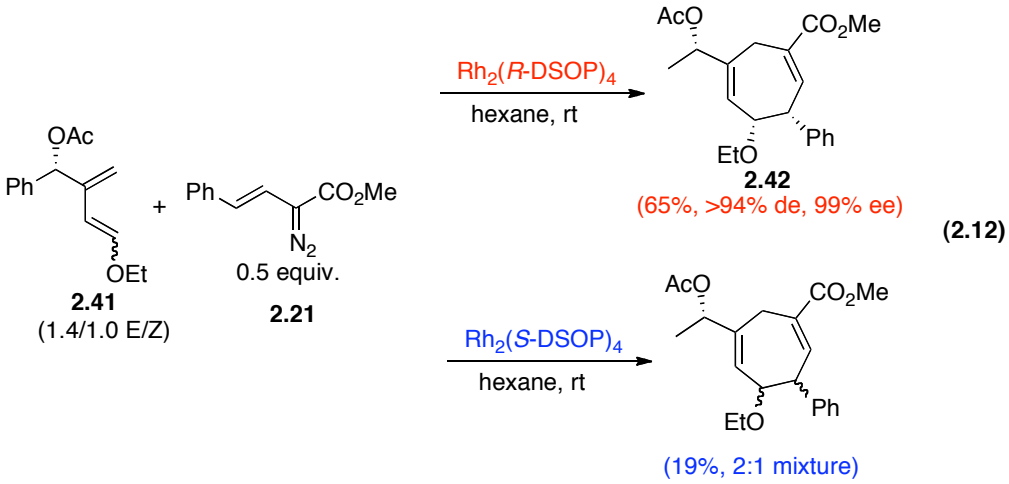




Scheme 2.3 The formal synthesis of frondosin B

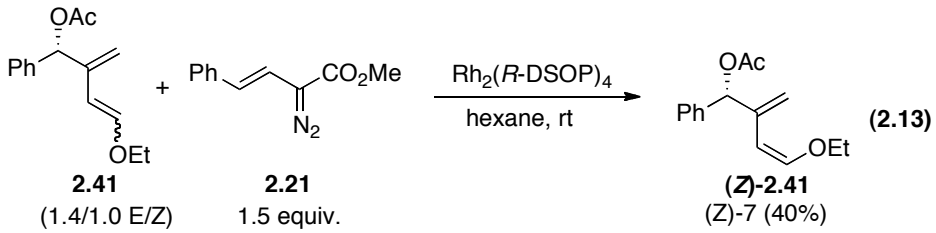
2.1.5 Double stereodifferentiation

Donor-acceptor carbenoids are capable of high discrimination in stereodifferentiation reactions.[99,47] A powerful enantiodifferentiation in the CPCR reaction has been reported in 2005 (eq. **2.12**).[99] The matching of the enantiopure diene **2.41** with the chiral catalyst is very pronounced because good yield and high diastereoselectivity is only obtained when the reaction of vinyldiazoacetate **2.21** is catalyzed by Rh_2(*R*-DOSP)$_4$. Very poor yield and diastereoselectivity is obtained when the reaction is catalyzed by Rh_2(*S*-DOSP)$_4$.



(2.12)

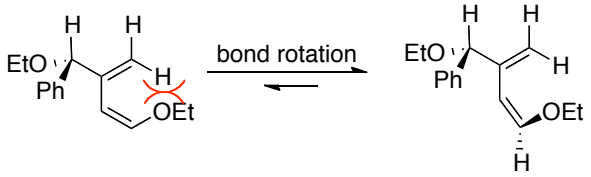
The stereochemistry of product **2.42**, in which the ethoxy group is *cis* to the phenyl group, indicates that only the *E* isomer of the diene reacted, even though a regioisomeric mixture of the starting materials has been used. Under appropriate conditions, the *Z*-diene was recovered cleanly. In the reaction with excess of diazoacetate **2.21** (eq. **2.13**), complete consumption of (*E*)-**2.41** was achieved and (*Z*)-**2.41** was recovered in 40% yield.



(2.13)

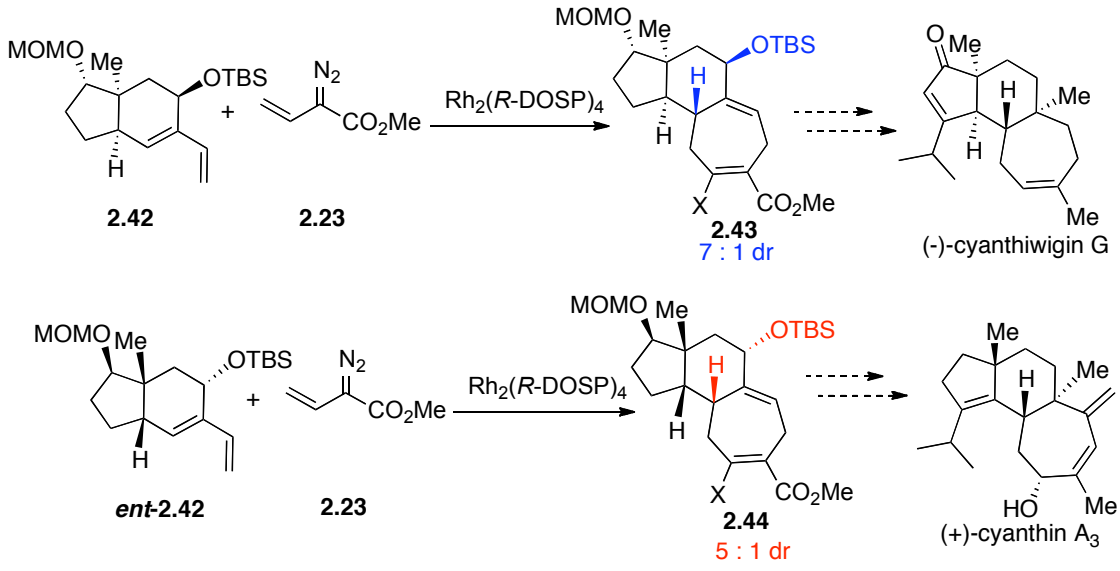
A rationalization has been proposed to explain the different reactivity between the *Z*-isomer and the *E*-isomer of the diene. With a large group at the 3-position, the *E*-diene would exist predominantly in the s-*cis* conformation. In the corresponding *Z*-isomer, the ethoxy group would be twisted from planarity due to the steric repulsion (Scheme **2.4**). The resulting twist out of conjugation would limit the electron-donating ability of the

ethoxy group to the double bond and thus deactivate the substrate towards cyclopropanation.



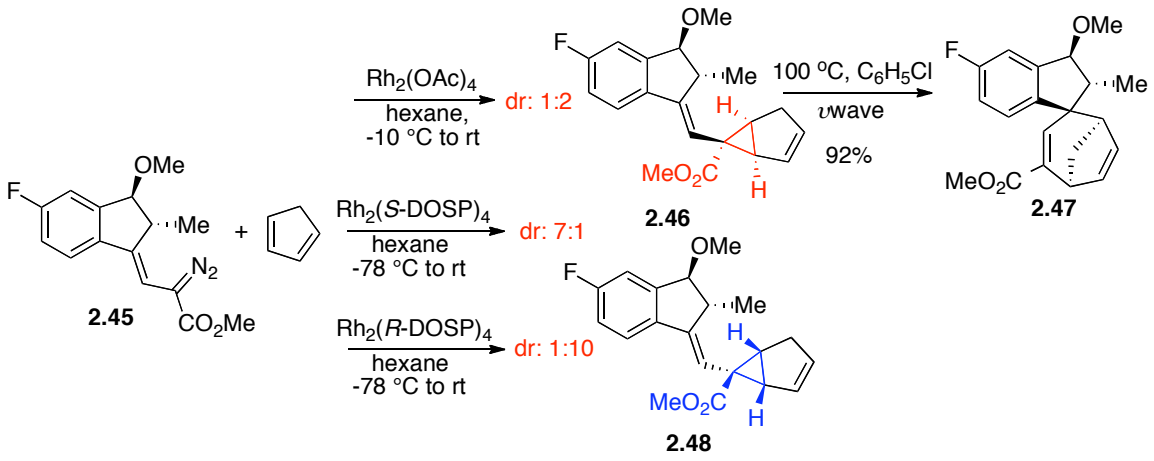
Scheme 2.4 Deactivation of diene (*Z*)-**2.41**

The use of a chiral catalyst in the CPCR reaction can overcome the inherent directing nature of a chiral substrate. An intriguing example has been reported by the Sarpong group and results in a parallel kinetic resolution approach to the cyathane and cyanthiwigin diterpenes (Scheme **2.5**).[100] The Rh_2(*R*-DOSP)$_4$-catalyzed reaction of vinyldiazoacetate **2.23** with (+)-**2.42** preferentially generated tricycle **2.43** with a 7:1 dr, while the reaction with (-)-**2.42** favored the other diastereomer **2.44** with a 5:1 ratio. Product **2.43** is a potential precursor to (-)-cyanthiwigin G, while **2.44** has potential to be applied in the synthesis of (+)-cyanthin A_3.



Scheme 2.5 Kinetic approaches in the total synthesis

Another impressive example of double stereoselectivity in the CPCR reaction has been reported by Panek (Scheme **2.6**).[101] Instead of using enantiopure diene substrates, they began with enantiopure vinyldiazoacetate **2.45**, which contains chiral centers adjacent to vinyl group. The $Rh_2(OAc)_4$-catalyzed reaction of **2.45** with cyclopentadiene resulted in poor selectivity. The diastereoselectivity was improved to 7:1 favoring isomer **2.46** with Rh_2(*S*-DOSP)$_4$. This ratio could be further improved to a 10:1 favoring the other diastereomer **2.48** using Rh_2(*R*-DOSP)$_4$ as catalyst. Upon heating under microwave conditions, the divinylcyclopropane **2.46** undergoes a Cope rearrangement to generate product **2.47** in good yield. In contrast, although product **2.48** is also a *cis*-divinylcyclopropane, the Cope rearrangement is not possible, presumably due to steric effects between the cyclopentene ring and the methyl group.



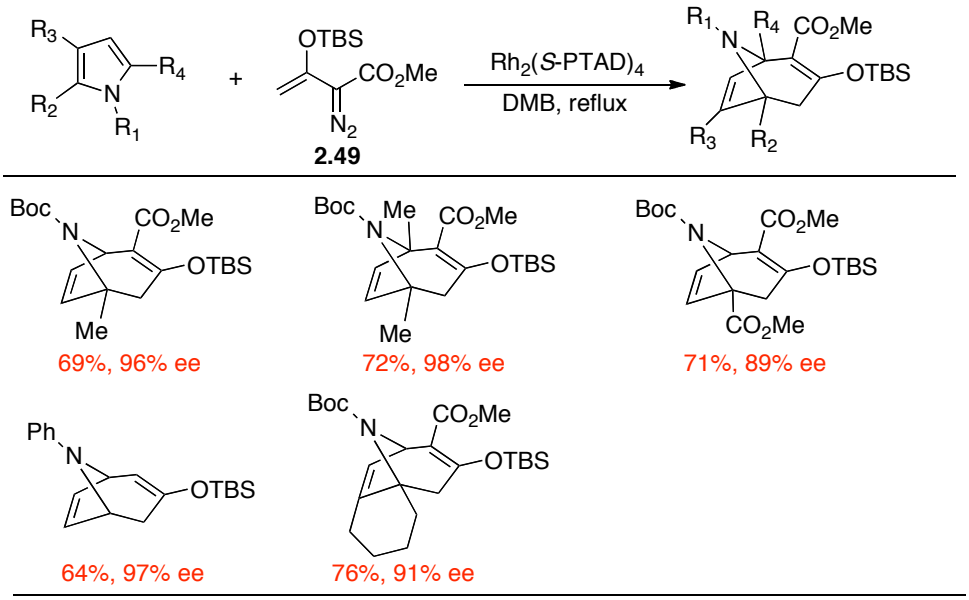
Scheme 2.6 Entiodifferentiation with chiral diazoacetate

2.1.6 Reaction of siloxyvinyldiazoacetate with $Rh_2(PTAD)_4$

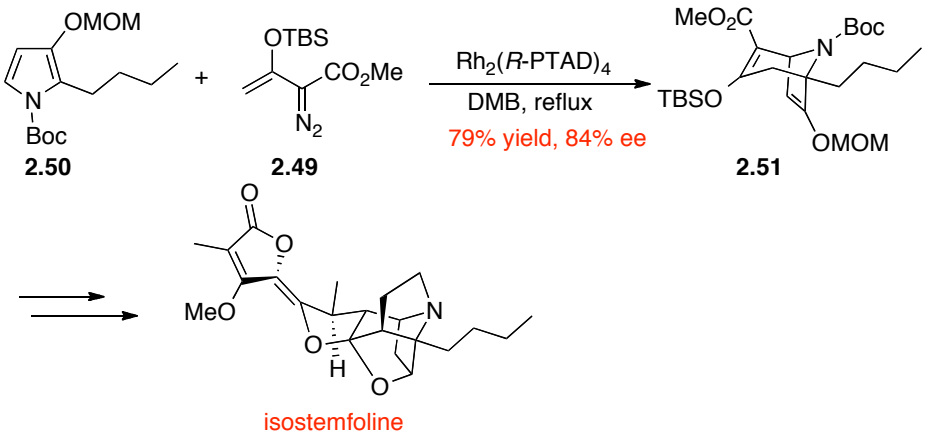
The 8-azabicyclo[3.2.1]octane framework is a constituent of a wide range of natural products and biologically active compounds.[102] As previously mentioned, the CPCR

reaction between vinylcarbenoids and pyrroles is not very effective in the construction of seven-membered rings because many side products are generated presumably through zwitterionic intermediates.[96] One solution to this problem has been the use of siloxyvinyldiazoacetate, which gives much better results. Particularly, high asymmetric induction can be achieved with Rh_2(*S*-PTAD)$_4$.[103] The Rh_2(*S*-PTAD)$_4$-catalyzed decomposition of diazoacetate **2.49** was applicable to a range of pyrroles and the annulation products were isolated in good yields with high asymmetric induction (Table **2.6**).[103]

Table 2.6 The asymmetric synthesis of tropanes



The synthetic illustration of this method has been demonstrated in the total synthesis of isostemofoline.[104] The Rh_2(*R*-PTAD)$_4$-catalyzed reaction of pyrrole and diazoacetate **2.49** afforded the cycloadduct **2.51** in 79% yield with 84% ee (Scheme **2.7**). This cycloadduct has been used as a key precursor in the synthesis of isostemofoline.[104]



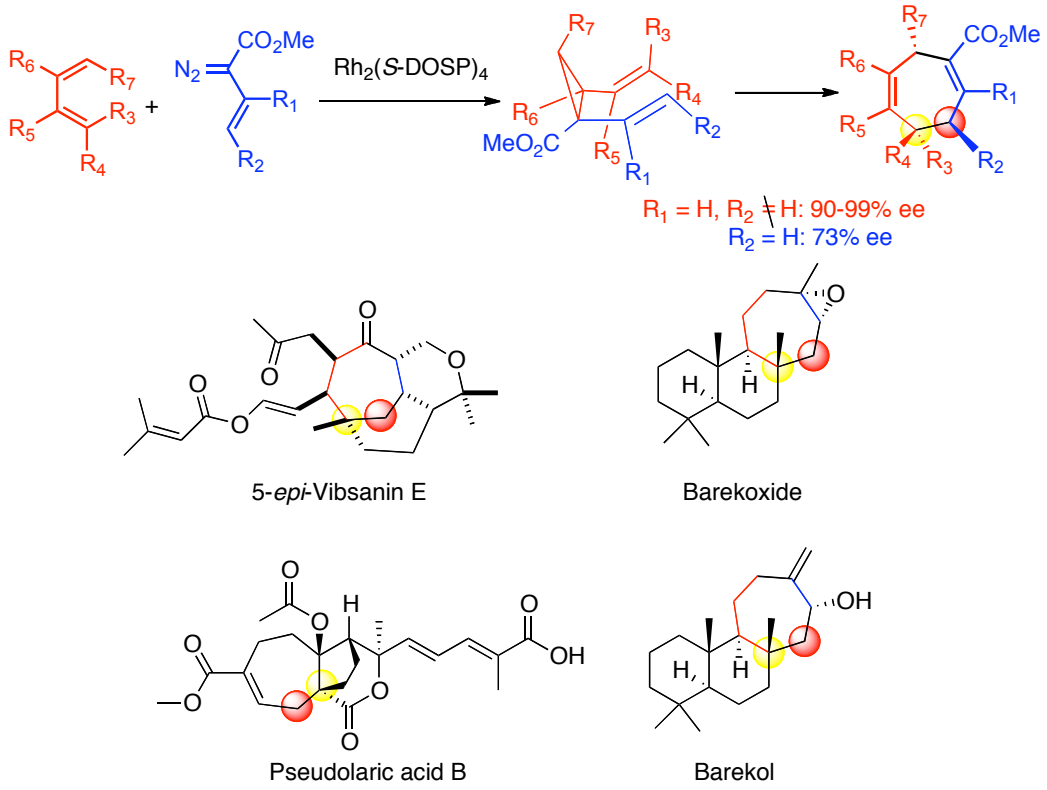
Scheme 2.7 The synthesis of isostemfoline

2.2 Results and discussion

2.2.1 Asymmetric [4 + 3] cycloaddition with acyclic dienes

The Davies group has demonstrated that the dirhodium tetraprolinate catalyst Rh_2(*S*-DOSP)$_4$ gives high asymmetric induction in the [4 + 3] cycloaddition provided that R_2 is alkyl or aryl, and R_1 is unfunctionalized (Scheme **2.8**).[40] A much lower asymmetric induction is observed when R_2 is hydrogen. When R_2 is a substituted group, one more stereocenter can be generated in a controllable fashion. However, from a synthetic point of view, it is valuable to develop a highly asymmetric CPCR reaction in the case when R_2 is hydrogen, because the synthesis of many natural products requires R_2 to be hydrogen. Some representative examples containing R_2 as hydrogen are listed in Scheme **2.8**.[105,106] Intrigued by the fact that the Rh_2(*S*-PTAD)$_4$-catalyzed reaction of siloxydiazoacetate **4.49** with pyrroles generated tropane derivatives in a highly asymmetric fashion,[103] we wanted

to explore whether this combination of siloxyvinyldiazoacetate **4.49** with Rh_2(*S*-PTAD)$_4$ could be applied to other systems, such as acyclic dienes.

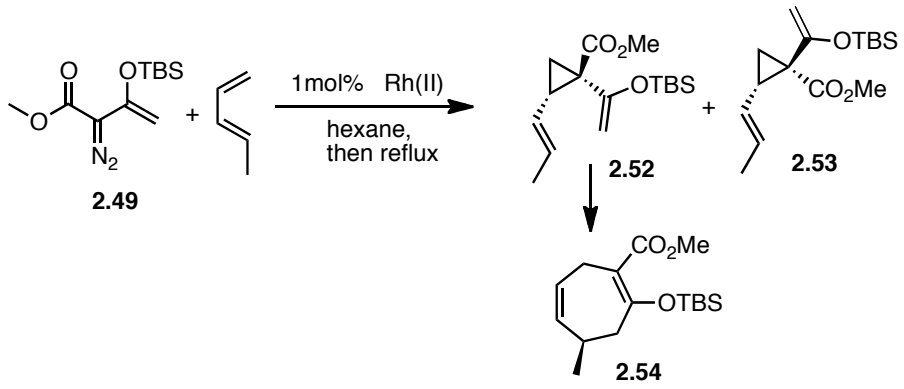


Scheme 2.8 Typical CPCR reaction and some representative natural products

The reaction of 3-siloxy-2-diazobutenoate **2.49** with *trans*-piperylene was used to optimize conditions for the [4 + 3] cycloaddition (Table **2.7**). The reaction generated *cis*-divinylcyclopropane **2.52** and *trans*-divinylcyclopropane **2.53** as a mixture with higher than 10:1 ratio favoring **2.52**. Upon heating, only the cyclopropane **2.52** underwent the Cope rearrangement to afford the product **2.54**. The Rh_2(*S*-DOSP)$_4$-catalyzed reaction at room temperature, generated the desired product **2.54** in high yield but with poor enantioselectivity (38% ee). The enantioselectivity could be improved to 53% ee by conducting the reaction at -26 °C but under these conditions the yield dropped to 35%. In

contrast, the Rh_2(*S*-PTAD)$_4$-catalyzed reaction at room temperature gave **2.54** in 78% yield and 86% ee. At -26 °C, the enantioselectivity improved to 95% ee and the yield was 88%. As previously observed in the Rh_2(*S*-PTAD)$_4$ and Rh_2(*S*-DOSP)$_4$ catalyzed reaction with pyrroles, both catalysts preferentially generated the same enantiomer in this [4 + 3] annulation.[103]

Table 2.7 Optimization of the enantioselective [4 + 3] cycloaddition

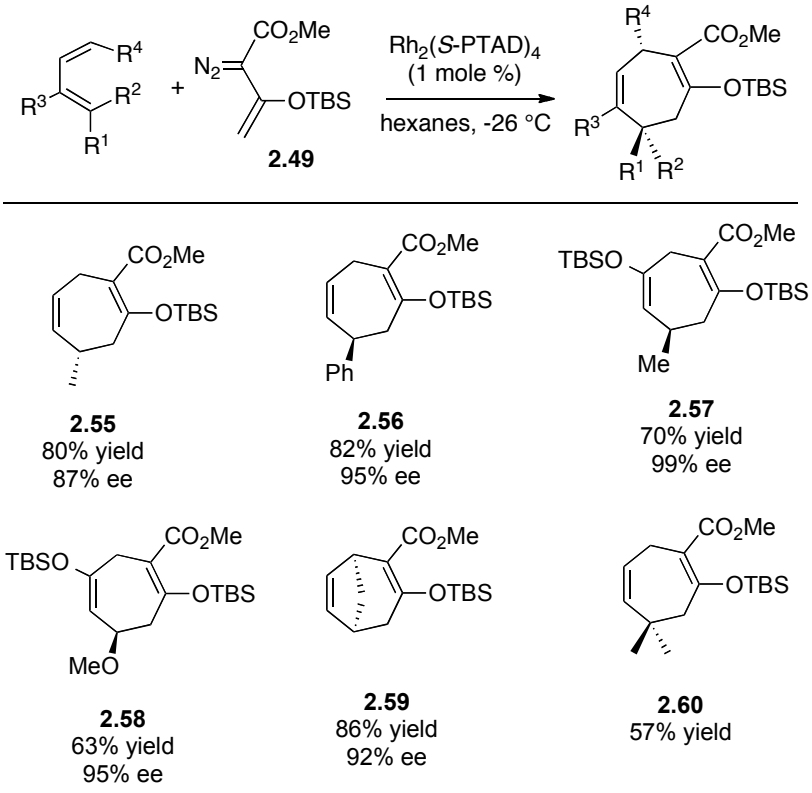


Rh(II)	Temp (°C)	Yield (%)	ee(%)
Rh_2(*S*-DOSP)$_4$	23	85	43
Rh_2(*S*-DOSP)$_4$	-26	35	53
Rh_2(*S*-PTAD)$_4$	23	78	86
Rh_2(*S*-PTAD)$_4$	-26	88	95

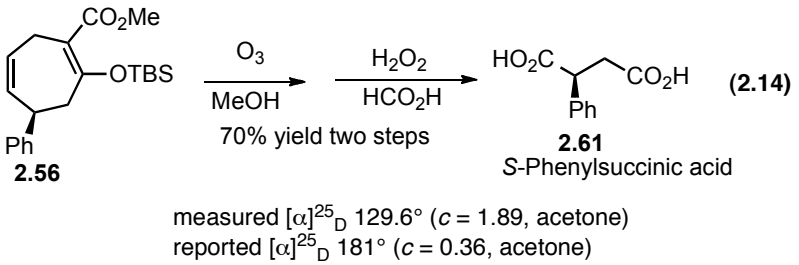
The Rh_2(*S*-PTAD)$_4$-catalyzed reaction of **2.49** could be extended to a variety of dienes and the results are summarized in Table **2.8**. In all the test systems, the cycloadducts are formed in good yields (57-86%) with high asymmetric induction (87-98% ee). The reaction with *cis*-piperylene generated cycloheptadiene **2.55**, the opposite enantiomer to the product generated from *trans*-piperylene. Even though the cycloadduct **2.60**, from the reaction with 4-methyl-1,3-pentadiene, is achiral, a successful reaction with this

substrate is intriguing, because a 4-substituted-1,3-diene is required for the total synthesis of Vibsanin E.[107-109]

Table 2.8 [4 + 3] Cycloaddition between **2.49** and dienes



The absolute configuration of the product **2.56** was confirmed by converting it to (*S*)-phenylsuccinic acid **2.61** through a two-step sequence (eq. **2.14**).[40] Treating **2.56** with ozone in methanol, followed by oxidative cleavage of the two double bonds afforded product **2.61** in good yield. The absolute configuration of **2.56** was confirmed by comparing the optical rotation of compound **2.61** with the reported value.[40] The absolute stereochemistry of other cycloadducts was tentatively assigned based on a similar asymmetric induction model.



measured $[\alpha]^{25}_{D}$ 129.6° (*c* = 1.89, acetone)
reported $[\alpha]^{25}_{D}$ 181° (*c* = 0.36, acetone)

The stereochemical outcome of the reaction is consistent with the predictive model for cyclopropanation of pyrroles with 3-siloxy-2-diazobutenoate **2.49**.[110,111] The vinylcarbenoid in complex **2.62** aligns with the bulky group (OTBS) pointing away from the phthalimido groups (Figure **2.3**). The substrate would only approach from the front face, because the back face is blocked by another phthalimido group. The divinylcyclopropane **2.63** is generated and then undergoes the Cope rearrangement through a boat transition state to form **2.64**.

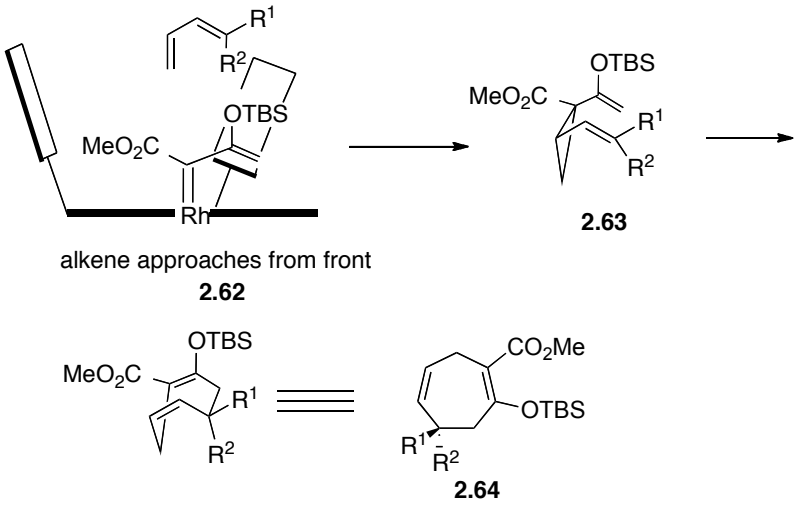
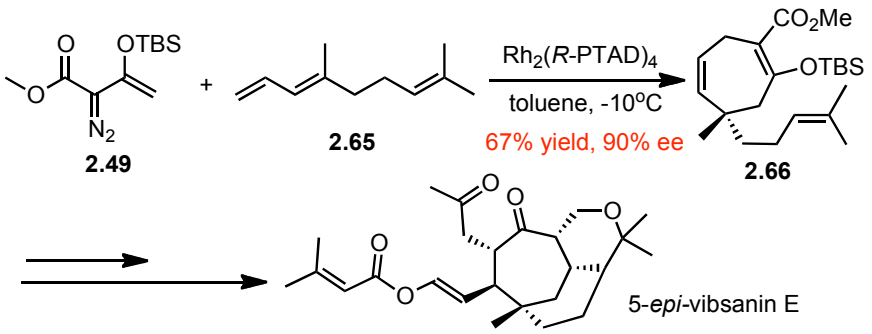


Figure 2.3 Proposed reaction mechanism for the CPCR reaction

Having established the successful CPCR reaction with acyclic dienes, Justin Denton from the Davies Lab and Brett Schwartz from the Williams Lab established a collaboration to complete the total synthesis of the (5)-*epi*-Vibsanin **E** (Scheme **2.9**). The

key step of the synthesis is a CPCR reaction between the siloxydiazoacetate **2.49** with triene **2.65**. The cycloadduct **2.66** was prepared by Denton in 70% yield with 90% ee, which is an advanced precursor in the total synthesis of (5)-*epi*-Vibsanin **E.**



Scheme 2.9 The total synthesis of 5-*epi*-vibsanin E

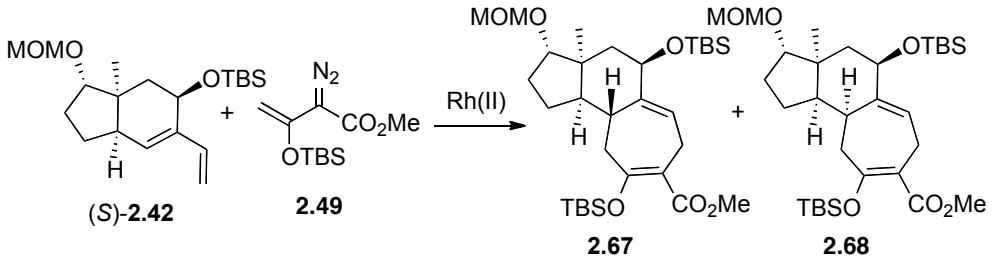
2.2.2 Enantiodifferentiation in the [4 + 3] cycloaddition

The combination of diazoacetate **2.49** and $Rh_2(PTAD)_4$ can be used in a more elaborate fashion in the CPCR reaction. Excellent enantiodifferentiation is possible, when the reaction is conducted with enantiopure dienes. As previously described, the Sarpong group applied the CPCR reaction as a stereodivergent approach to the core of the cyanthane diterpenes (Scheme **2.5**).[100] Moderate diastereoselectivity (5:1) was achieved when the combination of enantiopure $Rh_2(DOSP)_4$ and unsubstituted vinyldiazoacetate **2.23** was used. We rationalized that the use of siloxyvinyldiazoacetate **2.49** with $Rh_2(PTAD)_4$ would result in much improved diastereoselectivity in this chemistry.

The reaction of (*S*)-**2.42** with **2.49** in the presence of various dirhodium catalysts was conducted using toluene as solvent as summerized in Table **2.9**. The reaction catalyzed by Rh_2(*R*-DOSP)$_4$ generated tricycle **2.67** exclusively, while the reaction catalyzed by Rh_2(*S*-DOSP)$_4$ still gave a slight preference of **2.67** over **2.68** (entries **1** and **2** in Table

2.9). These results indicate that the substrate control favors the formation of **2.67**, which is enhanced in the matched reaction using Rh_2(*R*-DOSP)$_4$ as catalyst. The mismatched reaction using Rh_2(*S*-DOSP)$_4$ as catalyst gives a mixture of products. The diastereocontrol of the CPCR cycloaddition is further enhanced when the enantiomers of Rh_2(PTAD)$_4$ are used as catalysts. In the matched reaction with Rh_2(*R*-PTAD)$_4$ as catalyst, **2.67** was formed as a single diastereomer in good yield (entry **3**). In contrast to the result with Rh_2(*S*-DOSP)$_4$, the mismatched reaction using Rh_2(*S*-PTAD)$_4$ as catalyst also generated **2.68** exclusively (entry **4**). These results reveal that the reaction is under strong catalyst control.

Table 2.9 Reaction between enantiopure diene and diazoacetates

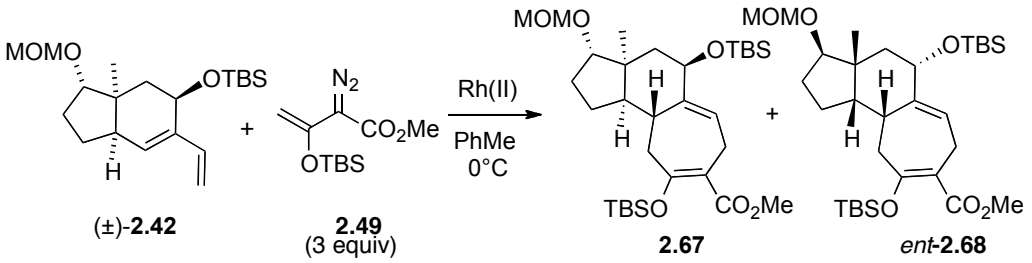


entry	substrate	catalyst	ratio (**2.67**/**2.68**)	yield (**2.67**+**2.68,** %)
1	(*S*)-**2.42**	Rh_2(*R*-DOSP)$_4$	>19:1	76
2	(*S*)-**2.42**	Rh_2(*S*-DOSP)$_4$	2:1	63
3	(*S*)-**2.42**	Rh_2(*R*-PTAD)$_4$	>19:1	81
4	(*S*)-**2.42**	Rh_2(*S*-PTAD)$_4$	<1:19	80

With the discovery that the siloxyvinyldiazoacetate **2.49** gives much better stereodifferentiation with **2.42**, we next explored whether a kinetic resolution would be feasible when using (±)**-2.42** (Table **2.10**). The Rh_2(*R*-DOSP)$_4$-catalyzed reaction of **2.49** with (±)**-2.42** was highly diastereoselective, generating the major diastereomer **2.67** with 10:1 diastereoselectivity, but only in 53% ee. In contrast, the reaction catalyzed by

Rh_2(*R*-PTAD)$_4$ had excellent catalyst control, in which **2.67** and the other diastereomer (*ent*-**2.68)** were produced in nearly 1:1 ratio. Both products **2.67** and *ent*-**2.68** were generated with high asymmetric induction (up to 99% ee).

Table 2.10 Reaction between racemic **2.42** and diazoacetate **2.49**



catalyst	ratio (**2.67**/*ent*-**2.68**)	yield (**2.67**, %)	yield (*ent*-**2.68**, %)	ee (**2.67**, %)	ee (*ent*-**2.68**, %)
Rh_2(*R*-DOSP)$_4$	10:1	48	ND[a]	53	ND[a]
Rh_2(*R*-PTAD)$_4$	1.7:1	39	25	90	99

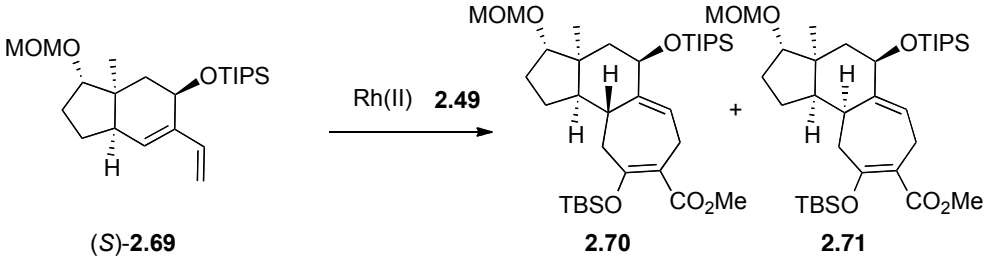
[a] Not determined.

As a collaborative project, Stephen Born and Laura Miller from the Sarpong group synthesized several other enantiopure bicyclic dienes (*S*)-**2.69**, (*S*)-**2.72**, (*S*)-**2.75**, and (*S*)-**2.78** for further testing. These dienes offered an opportunity to explore the effect of protecting group sizes and ring skeletons on the diastereoselective outcome in the CPCR reaction with diazoacetate **2.49**.

The CPCR reaction with enantiopure dienes can also be effectively extended to a more sterically hindered diene (*S*)-**2.69,** using TIPS as the protecting group instead of TBS. The Rh_2(*R*-PTAD)$_4$-catalyzed reaction of (*S*)-**2.69** and diazoacetate **2.49** generated product **2.70** as a single diastereomer (entry 1, Table **2.11**), while the reaction initiated by Rh_2(*S*-PTAD)$_4$ afforded the opposite diastereomer **2.71** exclusively (entry 2, Table **2.11**). Extension of the substrate from a bicyclo[4.3.0]nonane to a bicyclo[4.4.0]decane system

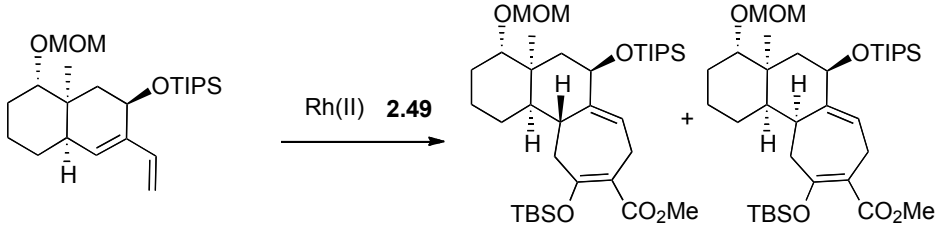
revealed the subtle structural modification on the reaction outcome. The Rh_2(*R*-PTAD)$_4$-catalyzed reaction of diene (*S*)-**2.72** with diazoacetate **2.49** generated two diastereomers of the cycloadducts **2.73** and **2.74** in a 9:1 ratio (entry 3, Table **2.11**). The same reaction catalyzed by Rh_2(*S*-PTAD)$_4$ switched the diastereoselectivity favoring product **2.74** with a 5:1 dr. These results indicate that the catalyst has a controlling influence on the diastereoselectivity but the chiral catalyst influence on the bicyclo[4.4.0]decane substrate could not overwhelm the chiral influence of the substrate. Even though that the structures of dienes (*S*)-**2.72** and (*S*)-**2.69** are similar, they each have distinct reaction profiles.

Table 2.11 Reaction scope between enantiopure diene and diazoacetate **2.49**



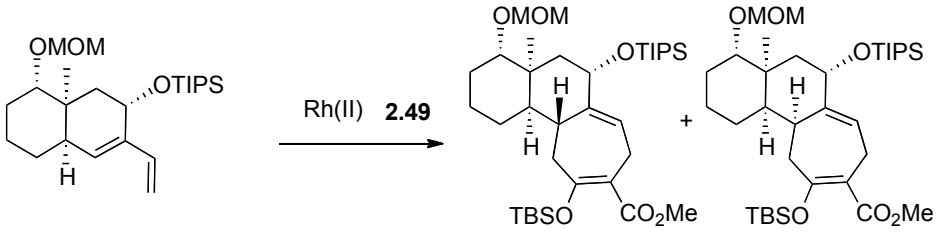
(*S*)-**2.69** **2.70** **2.71**

entry	catalyst	ratio (**2.70**/**2.71**)	yield (major isomer only, %)
1	Rh_2(*R*-PTAD)$_4$	>19:1	82
2	Rh_2(*S*-PTAD)$_4$	<1:19	76



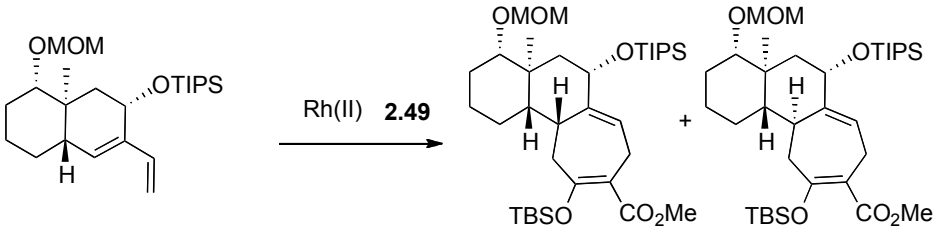
(*S*)-**2.72** **2.73** **2.74**

entry	catalyst	ratio (**2.73**/**2.74**)	yield (major isomer only, %)
3	Rh_2(*R*-PTAD)$_4$	9:1	77
4	Rh_2(*S*-PTAD)$_4$	1:5	66



(*S*)-**2.75** **2.76** **2.77**

entry	catalyst	ratio (**2.76/2.77**)	yield (major isomer only, %)
5	Rh_2(*R*-PTAD)$_4$	4:1	63
6	Rh_2(*S*-PTAD)$_4$	1:7	69



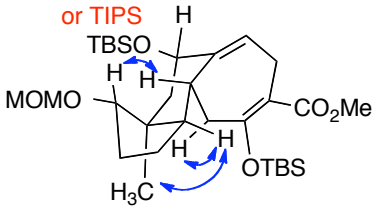
(*S*)-**2.78** **2.79** **2.80**

entry	catalyst	ratio (**2.79/2.80**)	yield (major isomer only, %)
7	Rh_2(*R*-PTAD)$_4$	2:1	55
8	Rh_2(*S*-PTAD)$_4$	1:16	81

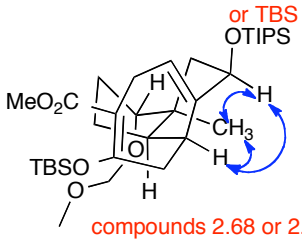
With an access to other bicyclo[4.4.0]decane substrates, studies were conducted to determine if different pairs of diastereomeric products could be achieved. Substrate (*S*)-**2.75**, an epimer of (*S*)-**2.72** at the siloxy carbon, is closely positioned next to the diene. Interestingly, the result is greatly affected by this change. The reaction catalyzed by Rh_2(*R*-PTAD)$_4$ afforded products **2.76** and **2.77** in a ratio of 4:1 (entry 5). The reaction with Rh_2(*S*-PTAD)$_4$ favored **2.77** in a 7:1 dr (entry 6). The double stereoselectivity result is opposite to the result with (*S*)-**2.72**. The Rh_2(*R*-PTAD)$_4$ is a matched catalyst in the reaction of (*S*)-**2.72** and better selectivity is obtained. In contrast, Rh_2(*S*-PTAD)$_4$ affords better diastereoselectivity with (*S*)-**2.75**. The next series of experiments examined the influence of the ring fusion on the selectivity. In all the test systems to date, the bicyclic

systems have *cis*-fused configuration. The diene (*S*)-**2.78**, an epimer of (*S*)-**2.75** has a *trans*-fused ring. The reaction of (*S*)-**2.78** catalyzed by Rh_2(*R*-PTAD)$_4$ showed poor selectivity. Impressively, the diastereoselectivity was enhanced to 16:1 favoring product (*S*)-**2.80** with Rh_2(*S*-PTAD)$_4$ (entries 5 and 6). Even thought the diastereoselective control of these reactions is not as promising as the reaction with bicyclo[4.3.0]nonane derivatives, they are still effective transformations because cycloadducts are isolated in 55-81% yield.

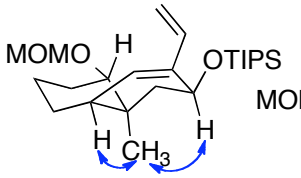
Careful ^{1}H nOe studies were conducted to confirm all the proposed structures of compounds **2.67** to **2.80**. Some key nOe results are summarized in Figure **2.4**.



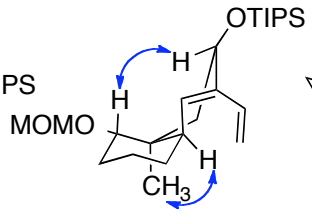
compounds 2.67 or 2.70



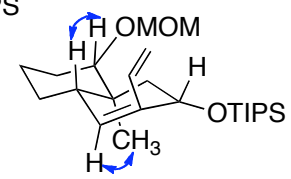
compounds 2.68 or 2.71



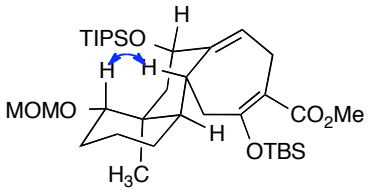
compound 2.72



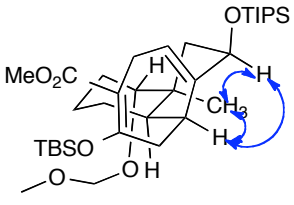
compound 2.75



compound 2.78



compound 2.73



compound 2.74

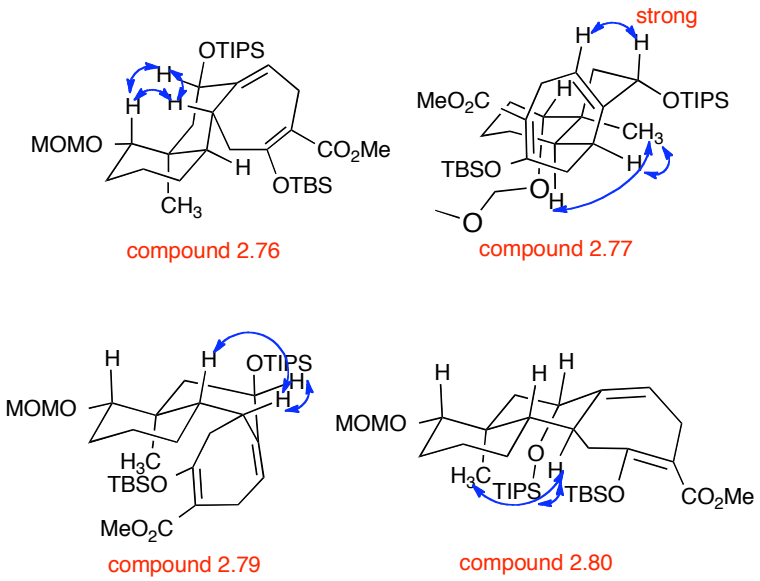


Figure 2.4 nOe assignment of cycloadducts

The detailed mechanism for the double stereodifferentiation is not clearly understood. The stereochemistry of the [4 + 3] cycloaddition is controlled in the initial cyclopropanation step, while the Cope rearrangement of the divinylcyclopropane proceeds through a boat transition state.[40] Theoretical calculations of cyclopropanation have shown that the alkene approaches in approximately an end-on mode.[51] Several studies have demonstrated that the same sense of asymmetry is obtained in the reaction of siloxyvinyldiazoacetate catalyzed by either Rh_2(*R*-DOSP)$_4$ or Rh_2(*R*-PTAD)$_4$.[103] Even though Rh_2(DOSP)$_4$ has been proposed to adopt a D_2-symmetry,[40,112] the model of Rh_2(*R*-PTAD)$_4$ is still under debate.[113] Presumably, these catalysts would force the diene to approach from the front face as illustrated in Figure **2.5**. This approach results in a matched double stereoselection because the siloxy group of the diene (*S*)-**2.42** is pointing away from the carbenoid during the cyclopropanation event. The Cope rearrangement of the divinylcyclopropane would generate **2.67**. The reaction of (*S*)-**2.42** catalyzed by Rh_2(*S*-DOSP)$_4$ or Rh_2(*S*-PTAD)$_4$ is a mismatched reaction, but the stereodirecting

influence of Rh_2(*S*-PTAD)$_4$ is sufficiently strong to overwhelm the inherent stereodirecting influence of (*S*)-**2.42**, leading to the clean formation of **2.68**.

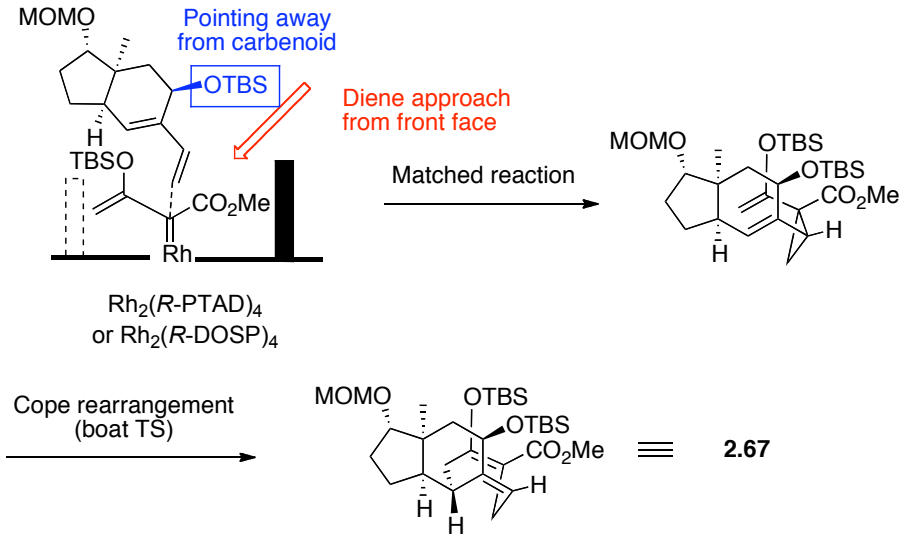
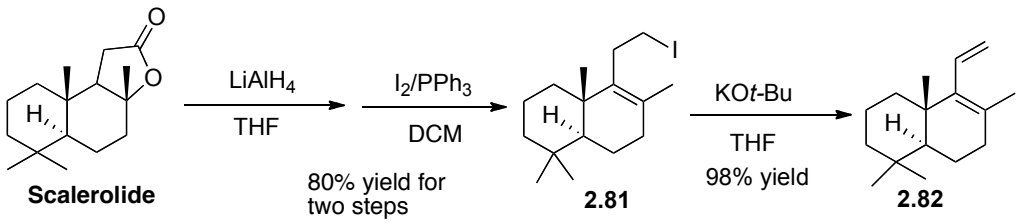


Figure 2.5 Proposed transition state in the enantiodifferentiation

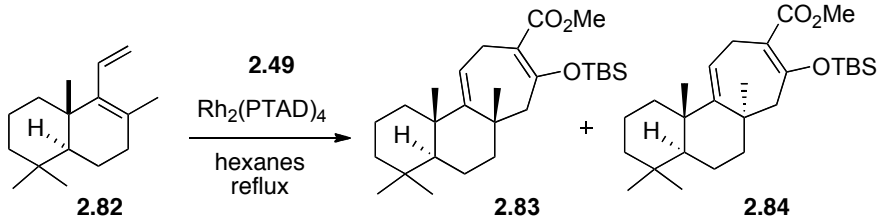
Having established an understanding of the factors controlling stereoselective outcome, we then applied this strategy to the synthesis of (+)-barekoxide and (-)-barekol.[114,115] The requisite diene was prepared in three steps from commercially available (+)-scalerolide (Scheme **2.10**). LAH reduction of scalerolide afforded a diol intermediate, which was then subjected to iodine in the presence of PPh_3 to generate product **2.81** in good yield over two steps. An E_2 elimination afforded diene **2.82** in nearly quantitative yield.



Scheme 2.10 The synthesis of diene **2.82**

The reaction efficiency of the CPCR reaction is dependent on substrate structure. Due to the more sterically crowded nature of the double bond in the diene **2.82**, a higher temperature (70 °C) and 3-5 equivalents of **2.49** were required for complete consumption of the diene (Table **2.12**). The Rh_2(*R*-PTAD)$_4$-catalyzed reaction of **2.49** with **2.82** gave a 6:1 mixture of diastereomers favoring **2.83**, while the Rh_2(*S*-PTAD)$_4$ catalyzed reaction gave a 9:1 mixture of diastereomers favoring **2.84**. In this case, the reaction initiated by Rh_2(*S*-PTAD)$_4$ is a matched reaction, in which not only higher diastereoselectivity was achieved, but also less amount of diazoacetate **2.49** was required for the completion of the reaction. The mixture of **2.83** and **2.84** was only slightly separable by chromatography on silica gel impregnated with 5% $AgNO_3$, but fortunately **2.83** could be selectively crystallized from methanol. In the Rh_2(*R*-PTAD)$_4$-catalyzed reaction, the pure desired diastereomer **2.83** was isolated in 47% yield after a single recrystallization. In this way, the configuration of a demanding quaternary stereocenter at the B-C ring fusion was effectively installed.

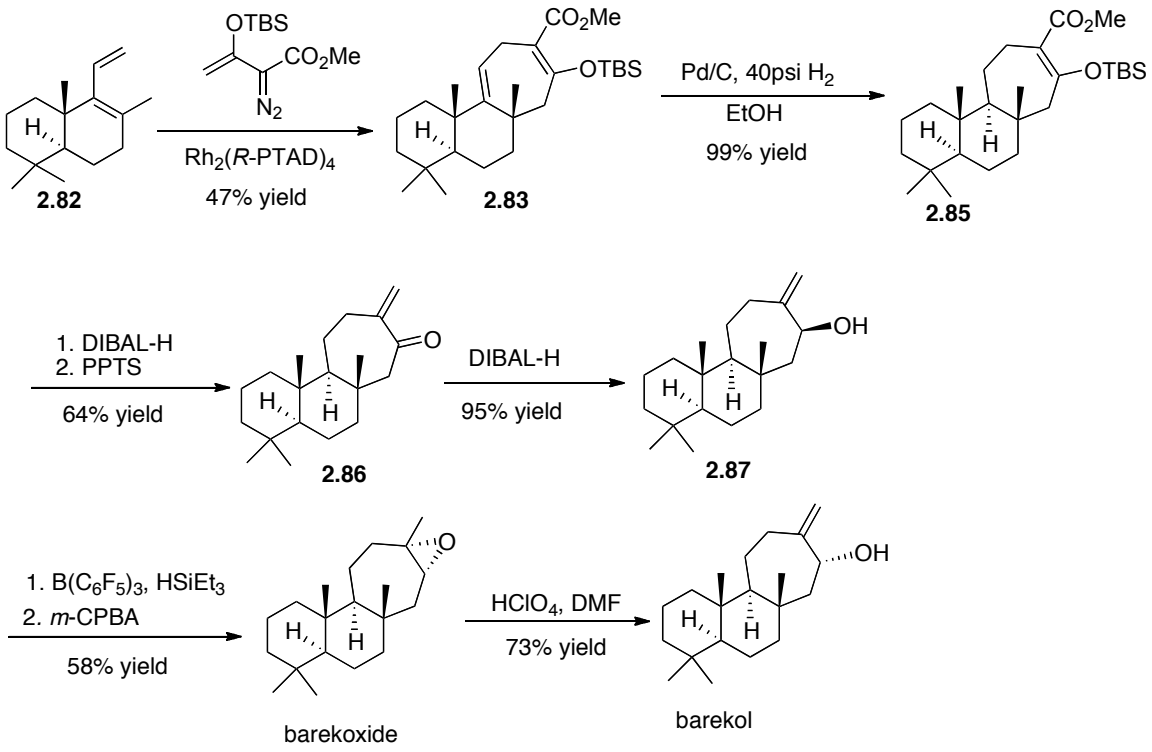
Table 2.12 Stereodivergent [4 + 3] cycloaddition



2.82 **2.83** **2.84**

catalyst	ratio (**2.49**/**2.82**)	dr (**2.83**/**2.84**)	yield (**2.83** + **2.84**, %)
Rh_2(*R*-PTAD)$_4$	5:1	6:1	65 (47[a])
Rh_2(*S*-PTAD)$_4$	3:1	1:9	63

[a] Isolated yield of pure **2.83**.



Scheme 2.11 The synthesis of barekoxide and barekol

The synthesis of (+)-barekoxide and (-)-barekol from the tricycle **2.83** was readily achieved as illustrated in Scheme **2.11**. Palladium-catalyzed hydrogenation of **2.83** selectively generated **2.85** in essentially quantitative yield, without the formation of the other diastereomer. Reduction of the ester group in **2.85** followed by elimination of the formed allylic alcohol under acidic condition generated enone **2.86** in 64% overall yield over two steps. DIBAL-H reduction of the enone **2.86** generated allylic alcohol **2.87**, an epimer of (-)-barekol, in 95% yield. Again, the product **2.87** was generated as a single isomer. An attempt to use an asymmetric CBS reduction of **2.86** to generate barekol directly was unsuccessful and **2.87** was always produced as the major isomer. This result indicates that the reduction step is mainly under substrate control. An alternative approach to barekol was developed in a three-step sequence. Conjugate reduction of **2.87**

with double bond isomerization using the Gevorgyan procedure[116] followed by epoxidation in the presence of *m*-CPBA generated (+)-barekoxide in 58% yield over two steps. Acid-catalyzed isomerization of (+)-barekoxide to (-)-barekol was achieved in 73% yield using the literature procedure.[114] The structure of barekol was unambiguously assigned based on the X-ray crystallography (Figure **2.6**). This crystal contains two conformations in which the seven-membered ring adopts both the pseudo-chair and the pseudo-boat conformations, presumably due to the flexibility of the seven-membered ring skeleton. This result supports the structural analysis by Kashman. [105]

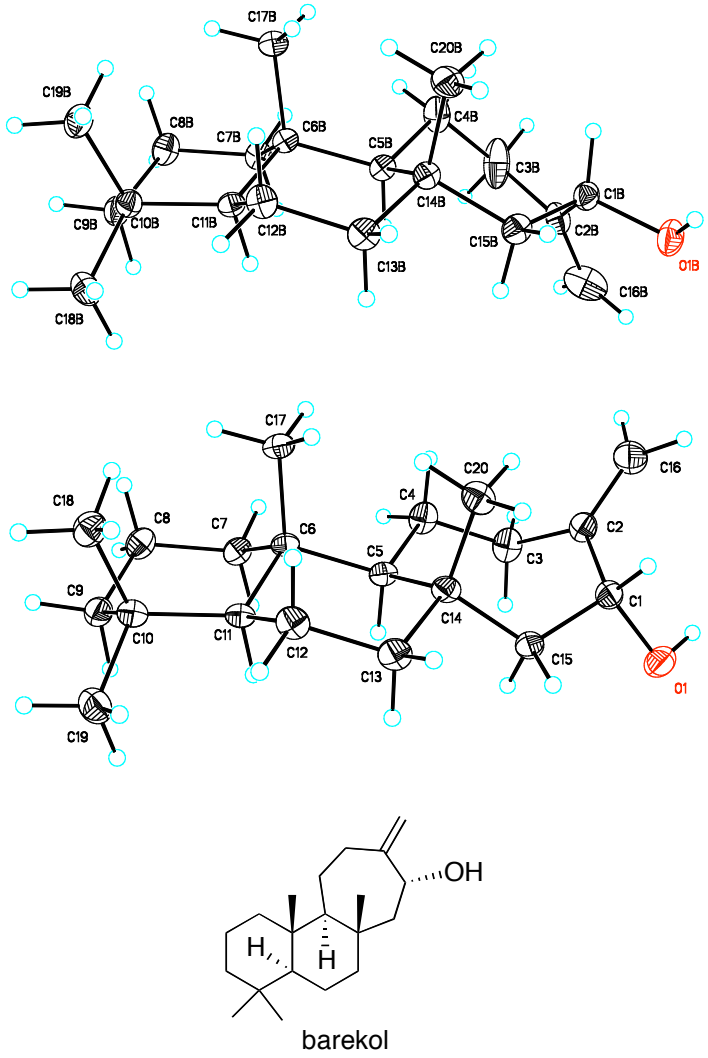


Figure 2.6 X-ray crystallographic structure of barekol

2.3 Conclusion

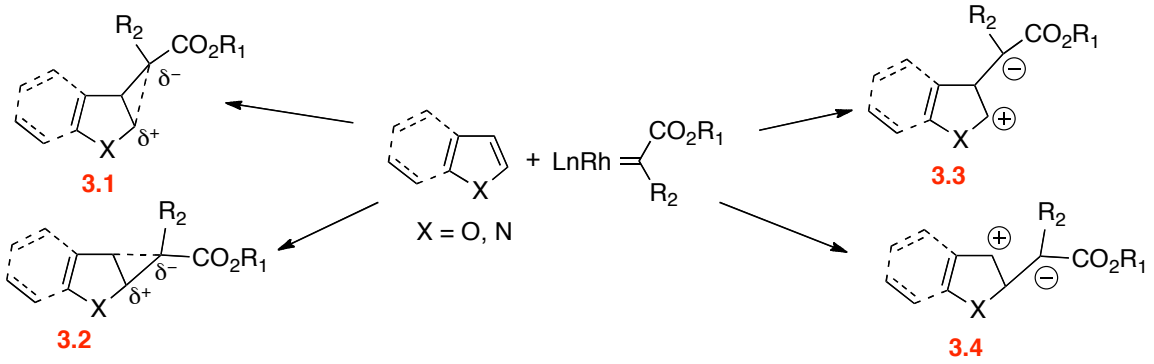
The rhodium-catalyzed CPCR reaction is an effective protocol for the synthesis of seven-membered rings and is particularly useful in generating the rings with an all-carbon quaternary center. The combination of siloxyvinyldiazoacetate **2.49** with enantiopure $Rh_2(PTAD)_4$ is very effective not only in achieving high asymmetric induction, but also is capable of enantiodivergent reaction with racemic substrates. The chiral catalyst controls the diastereoselectivity of the [4 + 3] cycloaddition and in some systems overwhelms the inherent selectivity of the chiral substrate. Even in the system used for the synthesis of (+)-barekoxide and (-)-barekol, which is very sterically crowded and requires elevated temperatures for an effective reaction, good levels of diastereocontrol were feasible. The synthetic application of this methodology has been well demonstrated in the total synthesis of 5-*epi*-vibsanin E, (+)-barekoxide and (-)-barekol.

Chapter III: Intermolecular Reactions of Electron-rich Heterocycles with Rhodium-stabilized Carbenoids

3.1 Introduction

Aromatic heterocycles are ubiquitous in natural products and still remain at the forefront of biological and medicinal chemistry research.[117,118] Considerable interest has been placed in the formation and elaboration of heterocycles.[118-120] The rhodium-catalyzed functionalization of heterocycles with carbenoids can lead to novel transformations.[117] Carbenoids are highly electrophilic species that can react with heterocycles and generate a wide range of products.

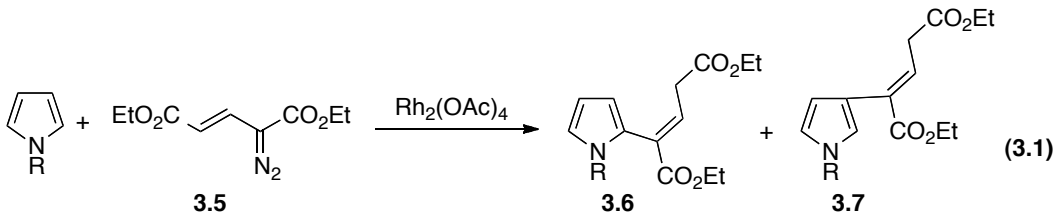
Two main pathways are possible in the reaction between electron rich heterocycles and carbenoids.[117] Either a concerted non-synchronous cyclopropanation or formation of zwitterionic intermediates is possible (Scheme **3.1**). When heterocycles and carbenoids are effective at charge stabilization, zwitterionic intermediates **3.3** or **3.4** can be generated, leading to a variety of products.



Scheme 3.1 Two reaction pathways between heterocycles and carbenoids

3.1.1 Reaction with pyrroles

Pyrrole and *N*-methyl pyrrole have been reported to undergo an efficient alkylation with vinyldiazoacetates.[76] The $Rh_2(OAc)_4$-catalyzed decomposition of **3.5** with pyrrole resulted in the selective formation of a single alkylation product **3.6a** in 71% yield, occurring at the 2-position of pyrrole. The reaction with *N*-methyl pyrrole generated **3.6b** and **3.7b** in a 91:9 ratio (eq. **3.1**).

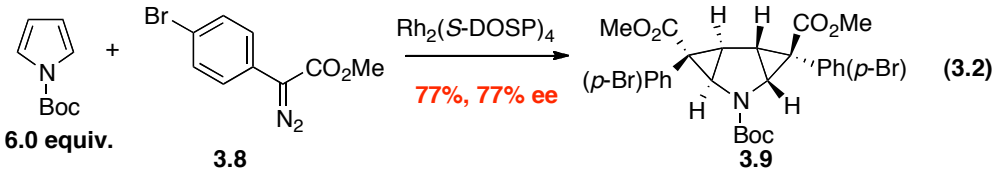


(3.1)

Alkylation products can be considered to be derived from electrophilic attack of the carbenoid on the pyrrole to generate zwitterionic intermediates **3.3** or **3.4**, which then rearrange through a 1,2-proton shift and concurrent aromatization.[121] The preference of alkylation at the 2-position of pyrrole is consistent with the electrophilic substitution reactions of pyrroles. However, the effect of increasing steric bulk at nitrogen makes the reaction to occur at the 3-position more favorable.

The reaction of donor-acceptor carbenoids with *N*-acyl pyrroles is very different from the reaction of more electron rich pyrroles. The Rh_2(*S*-DOSP)$_4$-catalyzed reaction of aryldiazoacetate **3.8** with *N*-Boc pyrrole resulted in the formation of biscyclopropane product **3.9**.[122] The biscyclopropane product **3.9** is still the major product even under conditions when a large excess of pyrrole is used (eq. **3.2**). This result indicates that the monocyclopropanated pyrrole is more effectively cyclopropanated than the *N*-Boc-

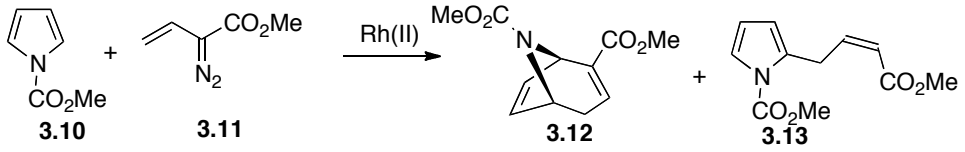
pyrrole itself. The stereochemistry of the monocyclopropanated pyrrole controls which face of the second double bond will be cyclopropanated. Consequently, the resulting bis cyclopropane is favored as a single diastereomer containing six new stereocenters.



6.0 equiv. **3.8** **3.9**

The vinyldiazoacetate **3.11**, which lacks functionality at the vinyl terminus, displays a more complicated reactivity profile (Table **3.1**). It can be attacked at either the carbenoid site to form **3.12** through the cyclopropanation/Cope rearrangement process or the vinylogous position to generate product **3.13**.[123] Electron-deficient catalysts and polar solvents favor the vinylogous reactivity, while electron-rich catalysts and hydrocarbon solvents favor the carbenoid reactivity. Interestingly, the double bond in the product **3.13** is formed with a *Z*-configuration. The detailed reason will be discussed later.

Table 3.1 Reaction between pyrrole and unsubstituted vinylcarbenoid



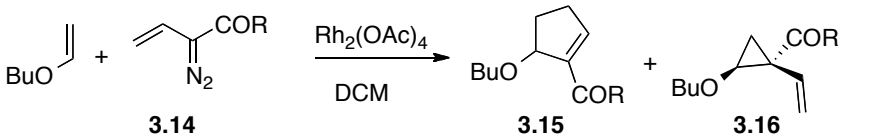
3.10 **3.11** **3.12** **3.13**

Catalyst	Solvent	yield of **3.12** (%)	ratio of **3.12** : **3.13**
$Rh_2(OAc)_4$	DCM	35	55 : 45
$Rh_2(tfa)_4$	DCM	16	15 : 85
$Rh_2(OHex)_4$	Hexane	75	>95 : 5

Another alternative approach to enhance the vinylogous reactivity is by increasing the size of the ester group on the vinylcarbenoid.[124,125] The $Rh_2(OAc)_4$-catalyzed

decomposition of **3.14** with butyl vinyl ether in DCM gave rise to a mixture of cyclopentene **3.15** and vinylcyclopropane **3.16**. Compound **3.15** is presumably generated through the vinylogous reactivity involving a cyclization. Interestingly, increasing the bulk of the ester from methyl to *tert*-butyl resulted in only minor changes in product ratio. However, increasing the size of the ester group to the very bulky 2,6-di-(*tert*-butyl)-4-hydroxytolyl (BHT) derivative resulted in a clean formation of **3.15** in 90% yield (Table **3.2**). The reason for the trend is rationalized by the hypothesis that increasing the size of ester group blocks the carbenoid reactivity and forces the reaction to occur at the vinylogous position.

Table 3.2 Ester size effect on the reactivity

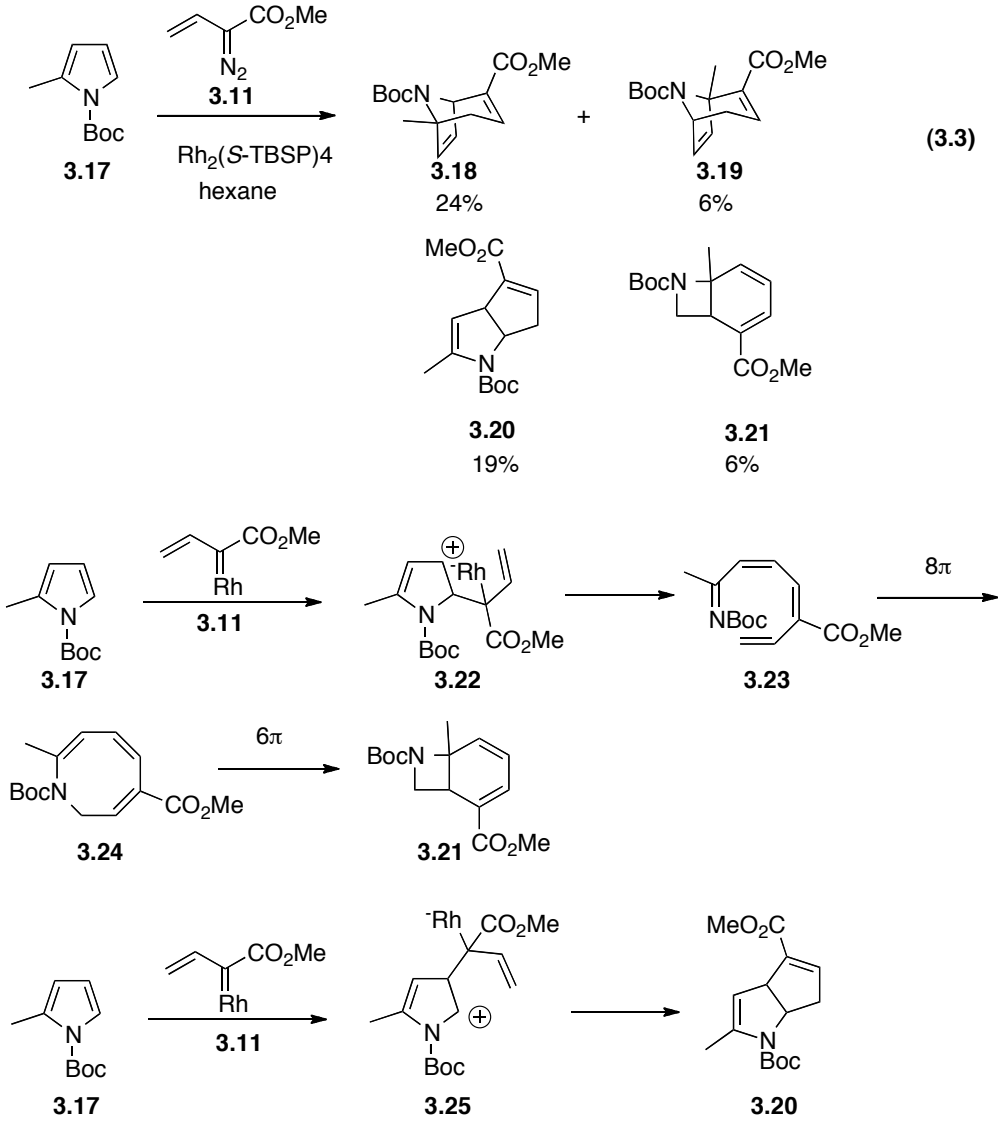


3.14 **3.15** **3.16**

(R = OMe)	(24%)	(37%)
(R = OtBu)	(22%)	(33%)
(R = BHT)	(90%)	(0%)

The formation of zwitterionic intermediates can lead to unexpected products. The Rh_2(*S*-TBSP)$_4$-catalyzed reaction of vinyldiazoacetate **3.11** with 2-methyl-*N*-Boc-pyrrole **3.17** generated a complex mixture (eq. **3.3**).[123] In addition to a regioisomeric mixture of tropanes **3.18** and **3.19**, two other products, the azabicyclo[3.3.0] octane **3.20** and the azabicyclo[4.2.0]octane **3.21** were also formed. The latter two products are proposed to be generated from different zwitterionic intermediates. Attack of the rhodium carbenoid at the 2-position of the pyrrole would generate the zwitterionic intermediate **3.22**, which would then initiate a cascade reaction of ring-opening to the trienamine **3.23** followed by

a successive 8π and 6π electrocyclization to produce **3.21**. Attack at the 3-position of the pyrrole generates the other zwitterionic intermediate, which then cyclizes to generate the [3 + 2] cycloaddition product **3.20** (Scheme **3.2**).

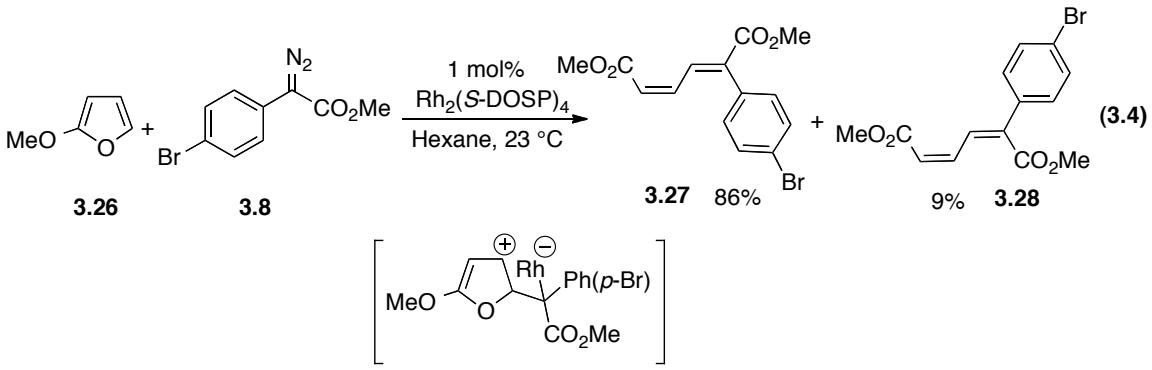


Scheme 3.2 The reaction mechanism of reaction **3.3**

3.1.2 Reaction with furans

An interesting reactivity in the reaction between donor-acceptor carbenoids and furans is the unraveling of the furan ring.[117] When electron-donating groups are incorporated

into furans, the transformation involving zwitterionic intermediates can become the dominant reaction pathway. This is clearly demonstrated in the reaction of aryldiazoacetate **3.8** catalyzed by Rh_2(*S*-DOSP)$_4$ in the presence of 2-methoxyfuran (eq. **3.4**).[126,127] The reaction exclusively afforded the dienes **3.27** and **3.28** in good yields. The reaction is believed to occur through a dipolar intermediate, which preferentially formed due to the electron-donating nature of the methoxy group.



3.1.3 Reaction with benzofurans and indoles

The reaction between donor-acceptor carbenoids with benzofurans and indoles is strongly influenced by the structure of substrates. The reaction of benzofuran or 3-methylbenzofuran with diazoacetate **3.8** catalyzed by Rh_2(*S*-DOSP)$_4$ provided the cyclopropanation product as a single diastereomer with very high asymmetric induction (eq. **3.5**).[122] Cyclopropanation with the initial bond formation at the 2-position would generate the observed enantiomer; however, cyclopropanation with the initial bond formation at the 3-position would involve a steric clash between the rhodium complex and the aryl ring (Figure **3.1**).

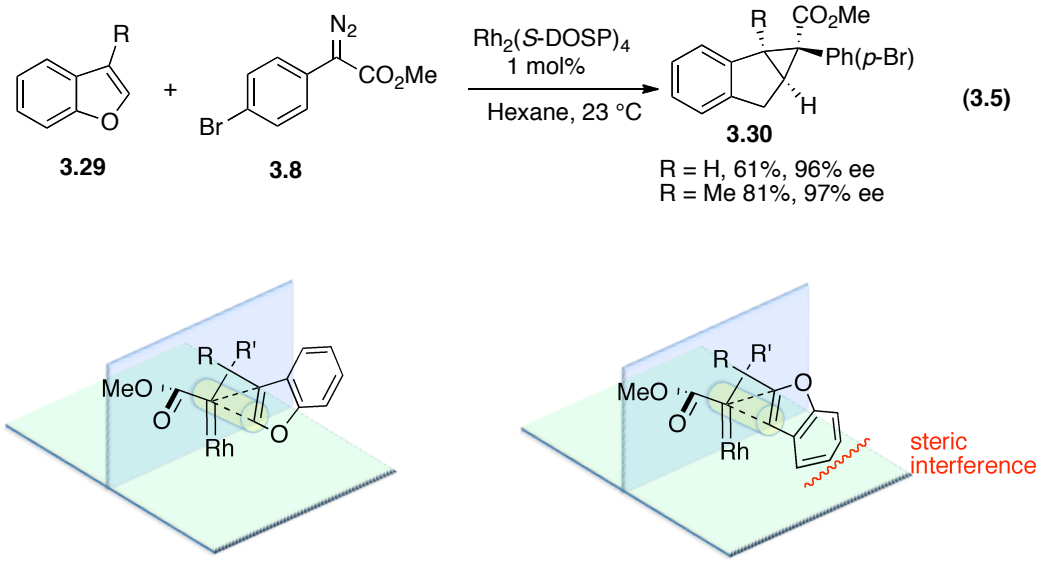
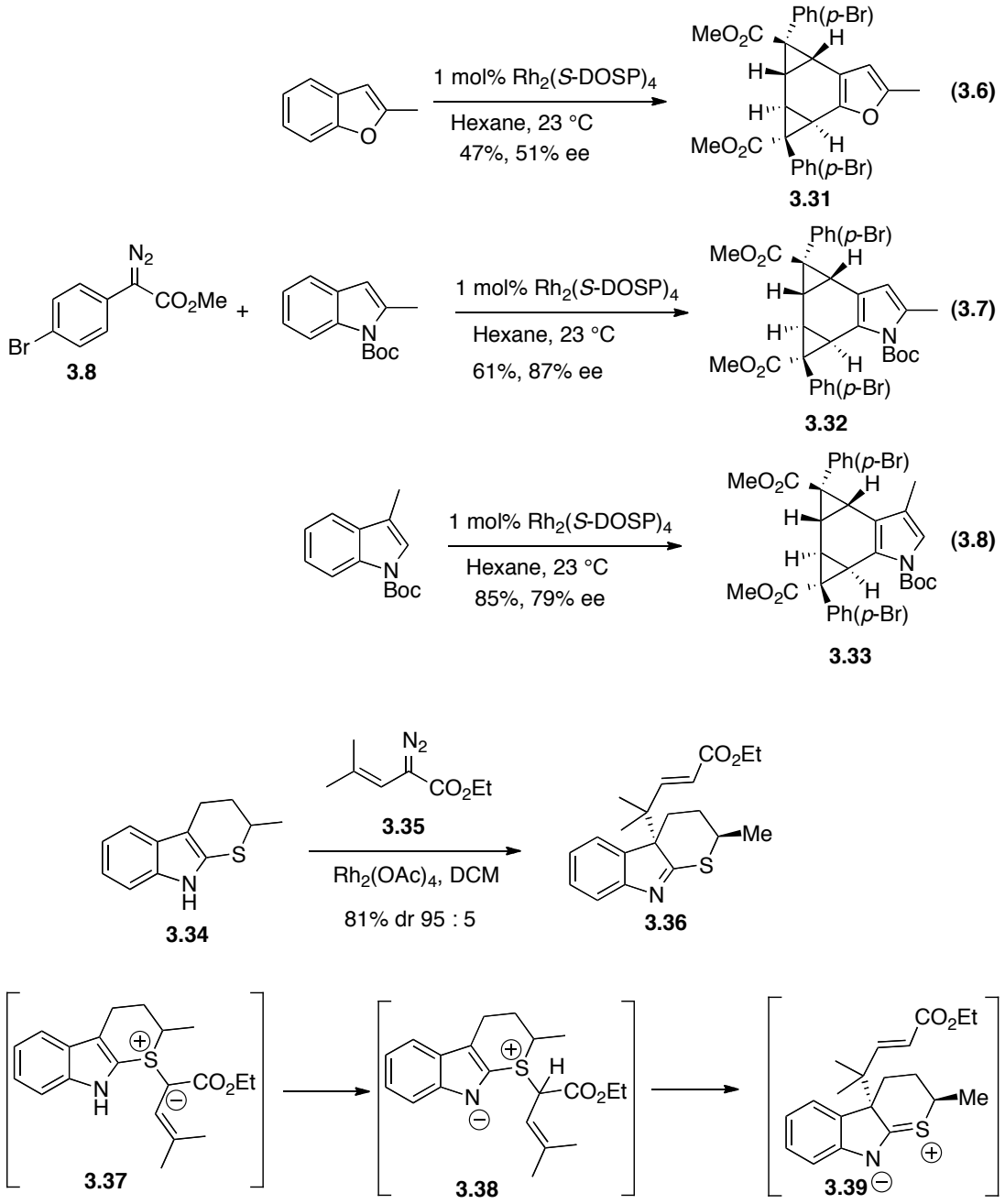


Figure 3.1 Two different transition states for cyclopropanation with benzofuran

Further evidence of the model of cyclopropanation with benzofurans has been provided by the reaction of 2-methylbenzofuran.[122] In this case, rather than the cyclopropanation of the furan double bond, a double cyclopropanation occurred in the benzene ring to give product **3.31** (eq. **3.6**). The *trans*-dicyclopropane pattern is consistent with the reaction with pyrroles (eq. **3.2**). A similar result was observed with the reaction of 2-methyl-*N*-Boc-indole (eq. **3.7**) or 3-methyl-*N*-Boc-indole (eq. **3.8**).

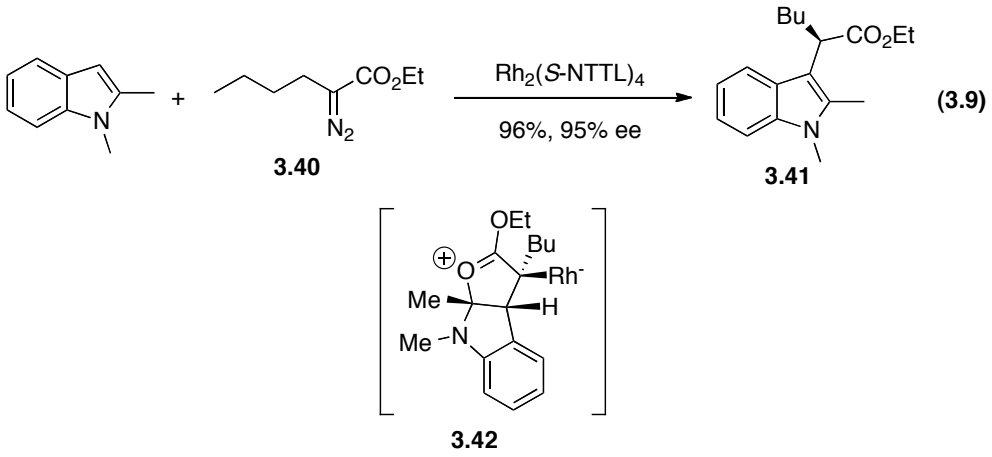
Rainer's group has reported an intriguing transformation between vinyldiazoacetate **3.35** and thioindole **3.34** (Scheme **3.3**).[128] The reaction initially forms a sulfur ylide **2.37** followed by a proton transfer to afford intermediate **2.38**. This intermediate undergoes a [3,3] sigmatropic rearrangement and isomerization to produce compound **2.36** as a single diastereomer. This strategy allows a rapid generation of indolines with a quaternary center at the 3-position. Attempting asymmetric synthesis using chiral catalysts or chiral auxiliaries on the vinyl diazoacetates has been unsuccessful.



Scheme 3.3 Ylide formation followed by [3,3]-sigmatropic rearrangement

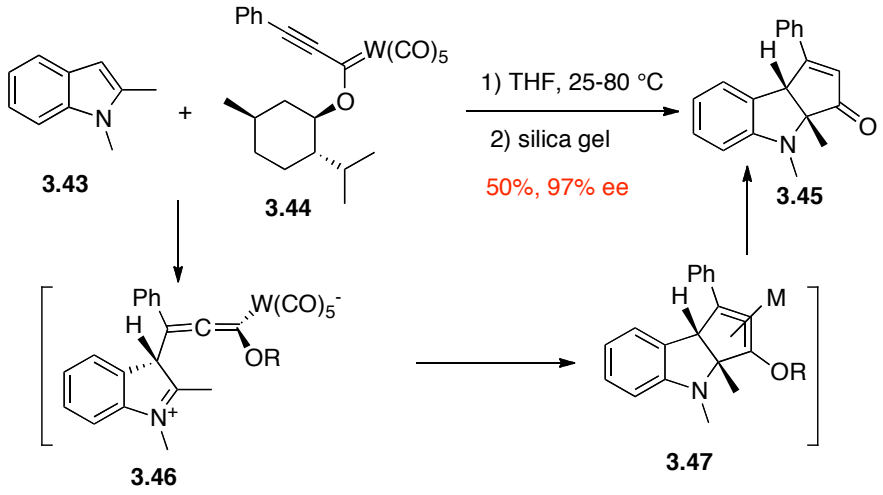
High asymmetric induction has been achieved involving rhodium ylide intermediates recently. Unlike chiral copper or iron catalyzed O-H or N-H insertion reactions of carbenoids, which result in high asymmetric induction,[129,130] rhodium ylide intermediates

generally lead to racemic products. This is possibly due to achiral enolate formation. Recently, Fox reported a remarkable asymmetric functionalization of indoles with alkyldiazoacetates catalyzed by Rh_2(*S*-NTTL)$_4$ (eq. **3.9**).[113] The reaction between 1,2-dimethylindole and diazoacetate **3.40** afforded product **2.41** in good yield with 95% ee. A plausible mechanism has been proposed to explain the reaction outcome based on DFT calculation. This mechanism involves a five-membered ylide transition state **3.42**, in which not only the newly formed C-C bond is formed, but also the ester group is involved.



3.42

Highly asymmetric [3 + 2] annulation between indoles and alkynyl Fischer carbene complexes has been reported by Barluenga (Scheme **3.4**).[131] This reaction involves a vinylogous nucleophilic attack of indole **3.43** to the vinylogous position of alkynyl Fischer carbene **3.44**, which generates zwitterionic intermediate **3.46**. Cyclization of intermediate **3.46** followed by dissociation of the metal complex leads to the annulation product **3.45** in a highly diastereoselective fashion. By using inexpensive menthol as an effective chiral auxiliary, excellent enantioselectivity was achieved (greater than 96% ee).



Scheme 3.4 Vinylogous [3 + 2] annulation

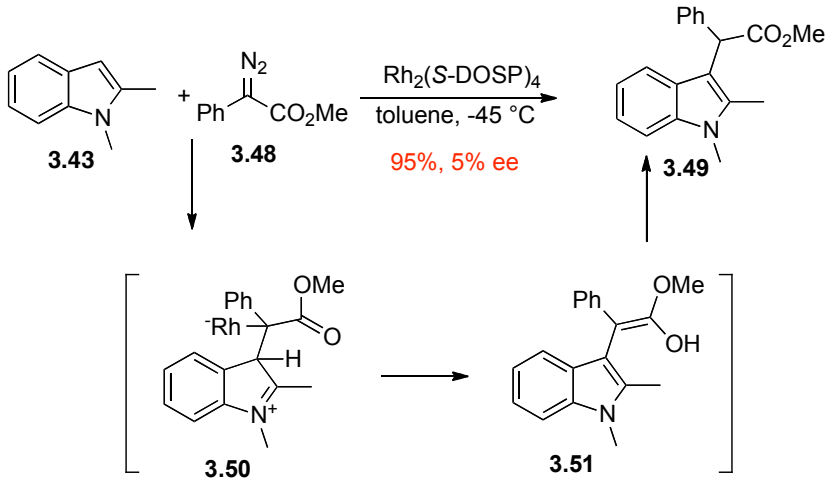
3.2 Results and discussion

3.2.1 Asymmetric [3 + 2] annulation between indoles and vinyldiazoacetates

Fused indolines are ubiquitous in a wide range of natural products of biological interest. Many effective methodologies have been developed for the synthesis of this skeleton.[132-135] Strategies based on the annulation of indoles are particularly useful because indoles are readily accessible.[136,137] However, only a few transformations involving the conversion of indoles into indolines directly have been reported.[138,139] In particular, enantioselective variants are limited.[131] Herein, we describe a catalytic enantioselective [3 + 2] annulation of indoles using rhodium-stabilized vinylcarbenoids as reactive intermediates.

The impetus of this project arose from the reaction between donor-acceptor carbenoids and electron-rich *N*-heterocycles.[117] It has been well established that the reaction of

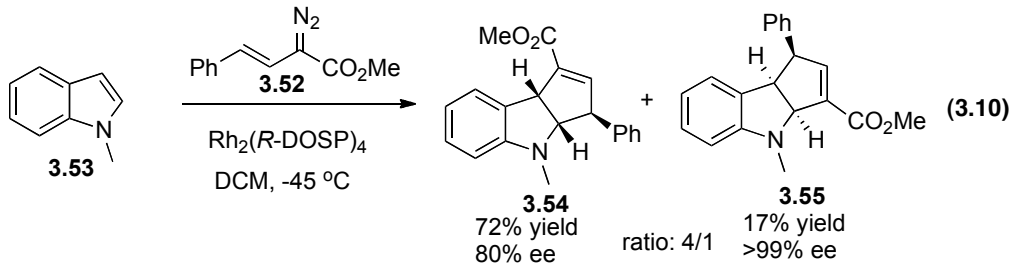
carbenoids with *N*-alkylindoles generates zwitterionic intermediates. The Rh_2(*S*-DOSP)$_4$-catalyzed reaction of diazoacetate **3.48** with 1,2-dimethylindole **3.43** was very efficient, generating alkylation product **3.49** in 95% yield (Scheme **3.5**). However, negligible asymmetric induction was observed (<5% ee). It is generally proposed that zwitterionic intermediate **3.50** is formed, which then undergoes a rapid proton transfer process to generate achiral enol **3.51**. The tautomerization of **3.51** leads to the observed product **3.49**. We rationalized that if other possible reaction pathways involving achiral intermediates were avoided, high asymmetric induction would be possible. For example, a cyclization would occur instead of the proton transfer using vinylcarbenoids. Our explorations of this chemistry led to a highly enantioselective synthesis of cyclopenta[*b*]indoles.



Scheme 3.5 Reaction between dimethylindole and diazoacetate **3.48**

The Rh_2(*R*-DOSP)$_4$-catalyzed reaction of (*E*)-phenylvinyldiazoacetate **3.51** with *N*-methylindole **3.53** in DCM was very effective in the cyclization (eq. **3.10**), but in this case two regioisomeric fused indoline derivatives **3.54** and **3.55** were generated in a 4:1 ratio. Gratefully, these products were produced with high asymmetric induction, 80% ee

for the major isomer **3.54** and >99% ee for the minor isomer **3.55**. The relative configurations of **3.54** and **3.55** were determined by nOe studies (Figure **3.2**). A particularly interesting aspect is that product **3.54** contains an *exo* configuration while **3.55** has an *endo* configuration. It would be reasonable to propose that product **3.54** is generated through the cyclization of an intermediate similar to **3.50**, whereas there are two possible mechanisms for the formation of product **3.55**. Vinylcarbenoids are known to be able to undergo either carbenoid or vinylogous reactivity. In addition, both C2 and C3 of indoles are nucleophilic. At this stage, it was uncertain whether the product **3.55** was generated from competition between the reaction at the carbenoid or the vinylogous site or competition between the initial attack of the carbenoid at the C2 or C3 position of the indole.



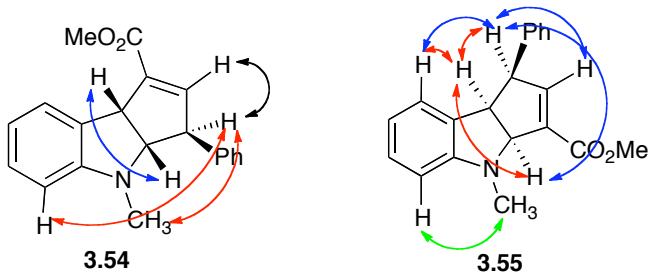
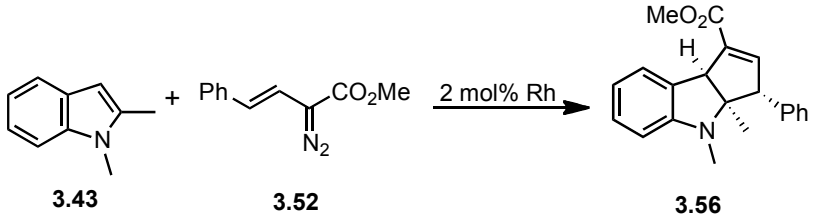


Figure 3.2 nOe studies of two annulation products

In order to determine the cause for the formation of the two regioisomers, a methyl group was introduced to the 2-position of the indole. In this case with 1,2-dimethylindole **3.43**, the reaction would be expected to undergo initial electrophilic attack only at the C3 position. The Rh_2(*S*-DOSP)$_4$-catalyzed [3 + 2] annulation between 1,2-dimethylindole and diazoacetate **3.52** afforded product **3.56** as a single diastereomer. Various reaction conditions were screened (Table **3.3**) and Rh_2(*S*-DOSP)$_4$ proved to be a more effective catalyst than Rh_2(*S*-PTAD)$_4$ in this transformation. The optimal conditions were found to be in the presence of Rh_2(*S*-DOSP)$_4$ with toluene as the solvent at -45 °C and the reaction gave the product **3.56** in 68% yield and with 97% ee.

Table 3.3 Optimized reaction condition between 1,2-dimethylindole and (*E*)-phenylvinyldiazoacetate **3.52**



3.43 **3.52** **3.56**

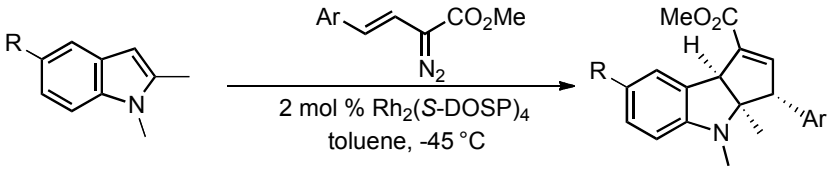
entry	catalyst	solvent	Temp. (°C)	Yield[a] (%)	ee[b] (%)
1	Rh_2(*S*-DOSP)$_4$	Toluene	rt	63	86
2	Rh_2(*S*-DOSP)$_4$	Toluene	-45	68	97
3	Rh_2(*S*-DOSP)$_4$	DCM	-45	51	85
4	Rh_2(*S*-PTAD)$_4$	Toluene	-45	51	80

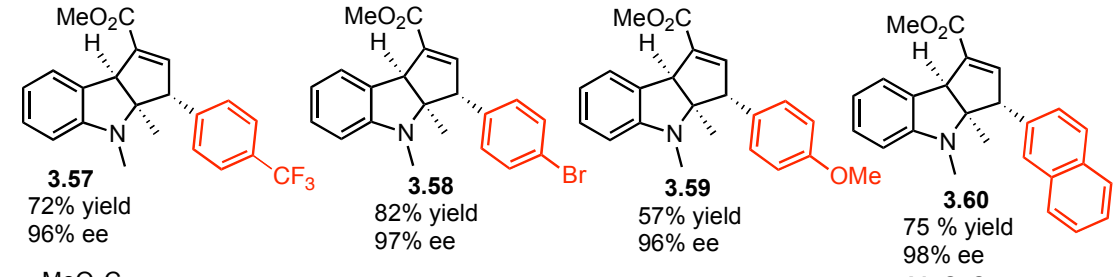
a: Isolated yield. b: enantiomeric excess was determined by chiral OJ column

With the successful annulation reaction of vinyldiazoacetate **3.52** with 1,2-dimethylindole **3.43** in hand, the Rh_2(*S*-DOSP)$_4$-catalyzed [3 + 2] annulation was applicable to a wide range of (*E*)-arylvinyldiazoacetates and 1,2-disubstituted indoles as illustrated in Table **3.4**. In all cases, the fused indolines **3.57-3.66** were produced in good yields with very high asymmetric induction (90-98% ee), exclusively as the *exo*

diastereomers. No other regioisomers were detectable from the NMR of crude mixtures. The absolute configurations of **3.59** and **3.65** were unambiguously assigned by X-ray crystallography (Figures **3.3** and **3.4**), while the relative configurations of **3.57-3.58**, **3.60-3.64**, and **3.66** were assigned by nOe studies. The absolute configurations of other cycloadducts were tentatively assigned, assuming a similar mode of asymmetric induction for all the substrates.

Table 3.4 Annulation of 1,2-disubstituted indoles





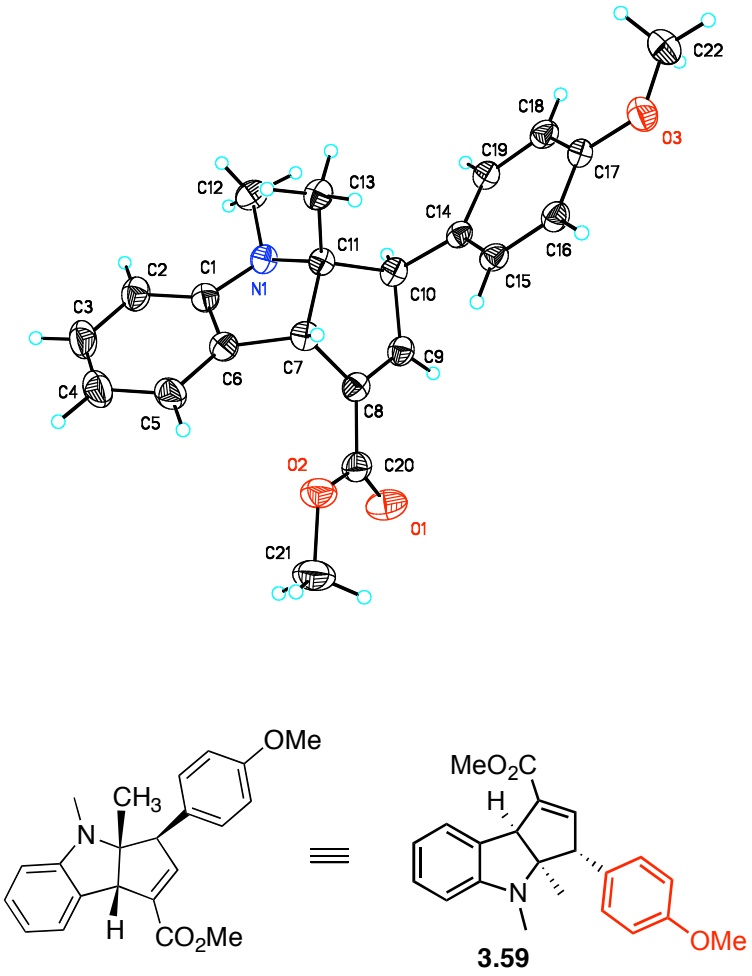


Figure 3.3 X-ray crystallographic structure of product **3.59**

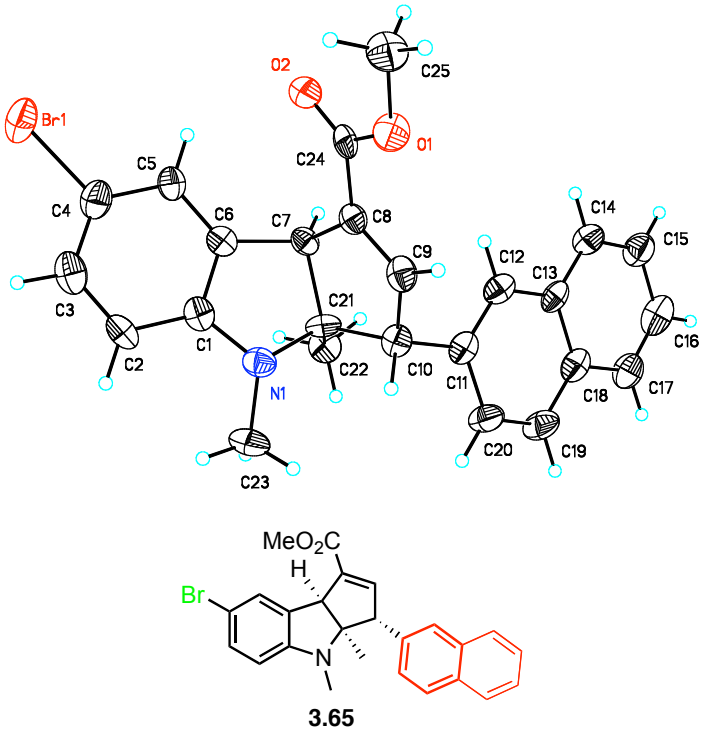
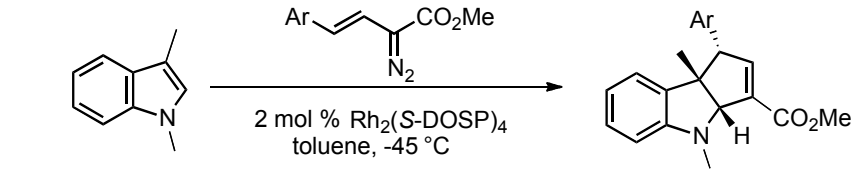
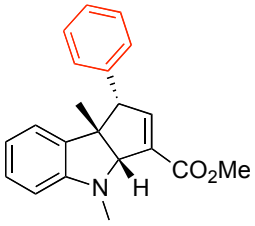
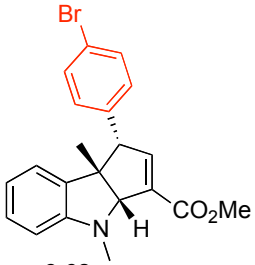
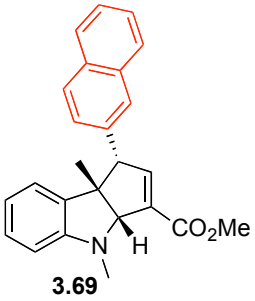


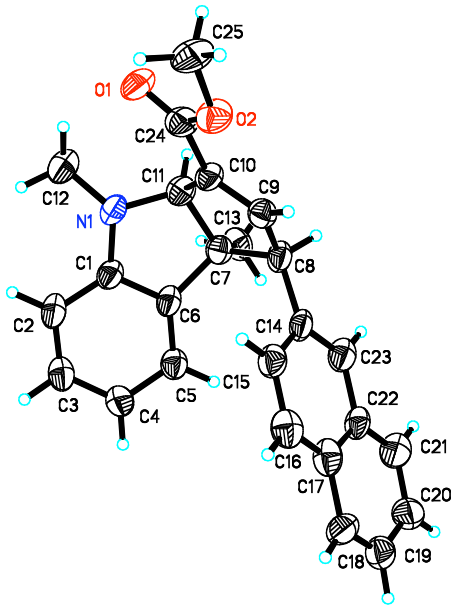
Figure 3.4 X-ray crystallographic structure of product **3.65**

The [3 + 2] annulation was extended to 1,3-disubstituted indolyl derivatives. In this system, the C2 position of indoles becomes accessible to attack. The reaction with 1,3-disubstituted indole derivatives generated the opposite regioisomeric series of fused indolines compared to the reaction with 1,2-disubstituted indoles as seen in Table **3.5**. As observed in the reaction with *N*-methylindole, the asymmetric induction for this series of compounds catalyzed by Rh_2(*S*-DOSP)$_4$ was exceptionally high (99% ee) and only the *endo*- diastereomer was observed. The absolute configuration of **3.69** was unambiguously assigned by X-ray crystallography (Figure **3.5**), while the relative configuration of **3.67** and **3.68** were assigned by nOe experiments. Their absolute configuration was tentatively assigned, assuming an analogous chiral influence by the catalyst in each case.

Table 3.5 Annulation of 1,3-disubstituted indoles



		
3.67 yield: 74% ee: 99%	**3.68** yield: 54% ee: 98%	**3.69** yield: 68% ee: 99%



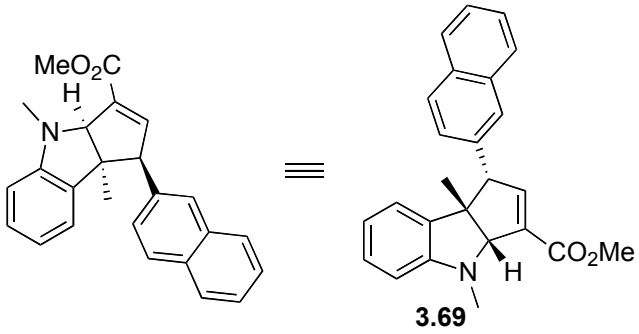
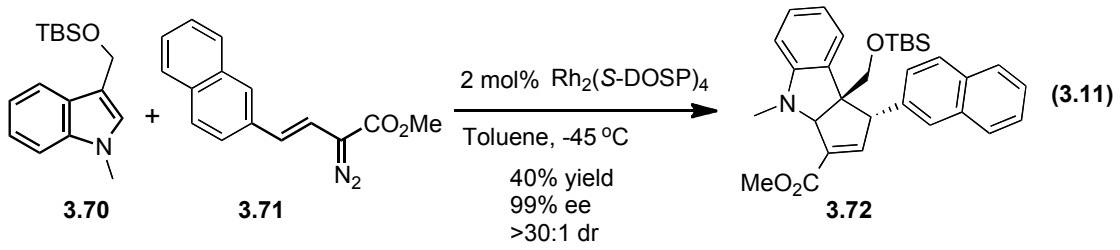
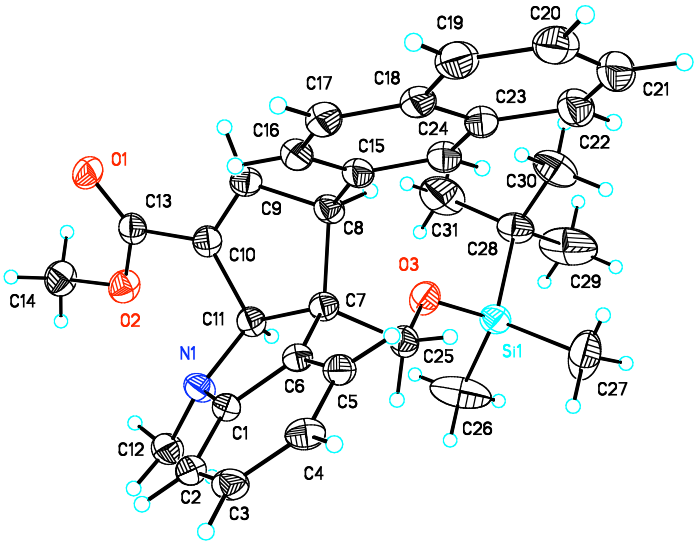


Figure 3.5 X-ray crystallographic structure of product **3.69**

The asymmetric [3 + 2] annulation reaction is also applicable to the more sterically crowded substrate **3.70**. The Rh_2(*S*-DOSP)$_4$-catalyzed reaction between indole **3.70** and vinyldiazoacetate **3.71** generated product **3.72** as a single diastereomer with excellent asymmetric induction (eq. **3.11**). The absolute stereochemistry of the product **3.72** was unambiguously confirmed by X-ray crystallography (Figure **3.6**).





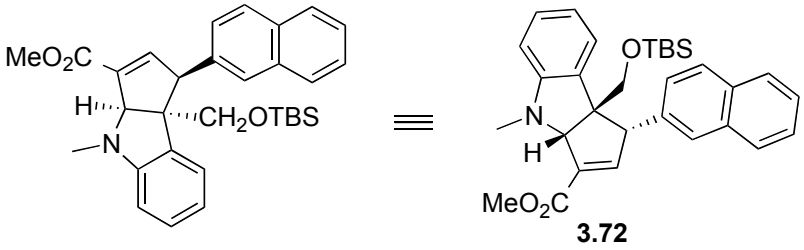


Figure 3.6 X-ray crystallographic structure of product **3.72**

A remarkable feature of the [3 + 2] annulation is that *exo* isomers are produced from 1,2-disubstituted indoles, while *endo* isomers are generated from 1,3-disubstituted indoles. Furthermore, these two types of indoles give opposite absolute configurations at the ring-fusion stereocenters, while the third stereocenter on the vinylogous carbon is the same for both series, which would indicate that both types of indoles approach the carbenoid from the same face of the carbenoid. Although the detailed mechanism of the transformation is not well understood, a plausible mechanism, which rationalizes the observed relative and absolute stereochemistry, is shown in Figure **3.7**. Rh_2(*S*-DOSP)$_4$ has been rationalized to adopt a D_2-symmetric conformation,[21,112] in which a blocking group is in front of the ester and another one is behind the vinyl group. The substrate would attack the carbenoid carbon from the front face. The difference in the ring-fusion stereochemistry can be rationalized by considering whether the initial attack is occurring at the 2 or 3 position of the indole. Similar changes in the absolute configuration of products in the presence of the same chiral catalysts have been observed in the cyclopropanation chemistry of furans, benzofurans, and *N*-Boc-pyrroles.[122] The formation of *exo* or *endo* products would then be controlled by whether the ring closure occurs from an intermediate derived from a carbenoid in either an s-*cis* or s-*trans* configuration as shown in Figure **3.7**. Presumably, the 1,2-disubstituted indoles react with the vinylcarbenoid in a s-*trans* configuration, while the 1,3-disbstituted indoles react with the vinylcarbenoid in a s-*cis* configuration. However, it is also possible that the differentiation occurs by vinyl group orientation of zwitterionic intermediates **T-1** and **T-2** prior to cyclization. The reason why one type of indole favors the s-*trans* conformer rather than the other is not fully understood.

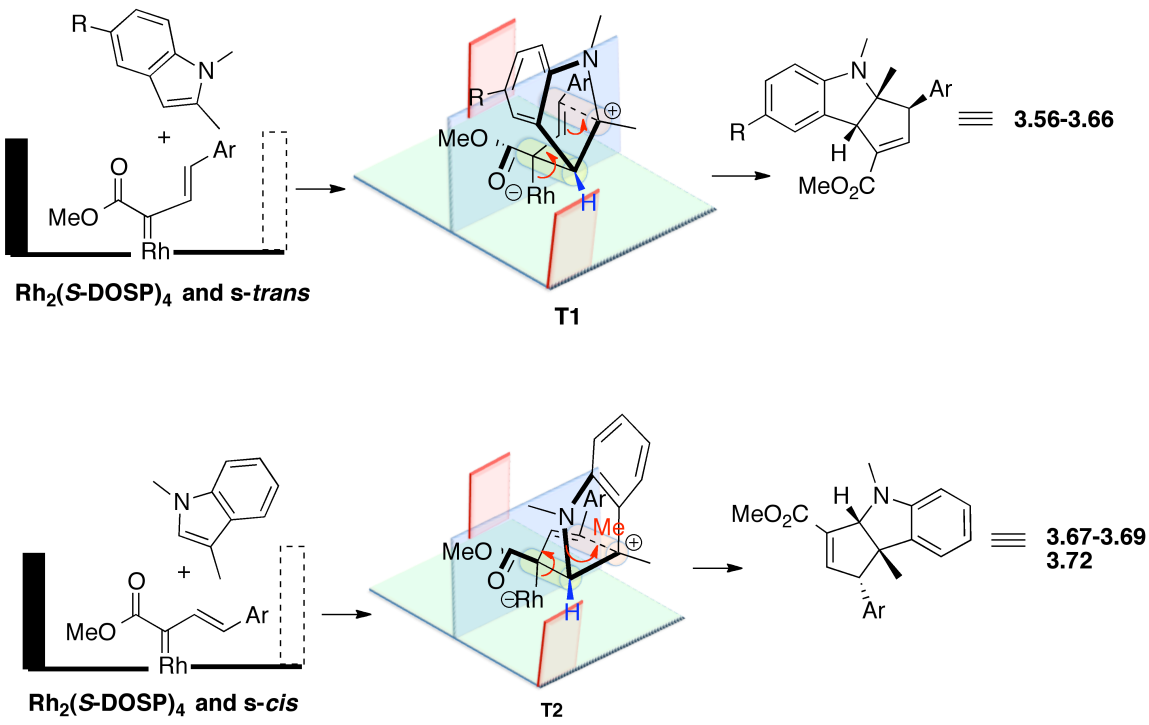


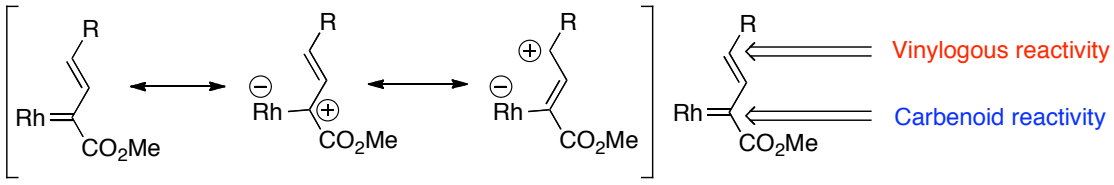
Figure 3.7 Proposed mechanism for the [3 + 2] annulation

In conclusion, a novel Rh_2(*S*-DOSP)$_4$-catalyzed asymmetric cyclopentannulation of indolyl rings across the C2–C3 double bond by reaction with vinylcarbenoids has been developed in a highly diastereo- and enantioselective maner. The reactive site of indoles in the presence of rhodium(II)-stabilized vinylcarbenoids is not restricted to the C3 position, but also can occur at the C2 site, leading to cycloadducts in either the *exo*- or the *endo*- configuration. This transformation possibly proceeds via a zwitterionic intermediate, but all the mechanistic details are still not fully understood.

3.2.2 Introduction of 4-substituted (*Z*)-pent-2-enoates into sterically encumbered pyrroles and indoles

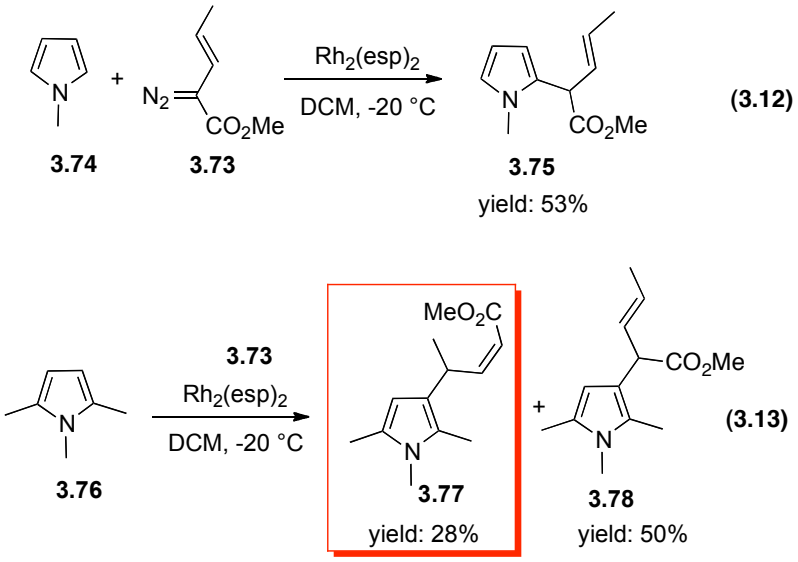
The investigation into the asymmetric [3 + 2] annulation of vinylcarbenoids with indoles led to the discovery of novel vinylogous reactivity with substituted

vinylcarbenoids. One of the unusual features of the vinylcarbenoid chemistry is the occurrence of the vinylogous reactivity when the vinyl group is unsubstituted.[44,45,124] As mentioned previously, the vinylogous reactivity of vinylcarbenoids can be enhanced by using polar solvents, bulky esters on the carbenoid or diruthenium or silver catalysts (Scheme **3.6**).[45]



Scheme 3.6 Two different reactivities in rhodium carbenoids

The impetus for this investigation arose from an unexpected result observed during studies on the reaction of pyrroles with vinyldiazoacetates. The $Rh_2(esp)_2$-catalyzed decomposition of (*E*)-vinyldiazoacetate **3.73** with *N*-methylpyrrole **3.74** (6 equiv) afforded the expected aromatic substitution product **3.75** (eq. **3.12**).[140] When the reaction was repeated with the more bulky substrate 1,2,5-trimethylpyrrole **3.76**, an unexpected product **3.77** was formed in 28% yield, in addition to the expected aromatic substitution product **3.78** (eq. **3.13**). Two interesting features of this reaction are intriguing. First, **3.77** was formed exclusively as the *Z* isomer even though the reaction began with (*E*)-vinylcarbenoid. Second, **3.77** had to be generated from the attack at the vinylogous position of the vinylcarbenoid. This type of reactivity profile has not yet been seen in the previous rhodium-catalyzed reactions of vinylcarbenoids with a substituent at the vinyl terminus. Therefore, we decided to further explore this unusual reactivity.



To enhance this novel vinylogous reactivity, an understanding of the vinylcarbenoid conformations is crucial. Rhodium-stabilized vinylcarbenoids could in principle exist in two possible conformations, *s-cis* (conformer **A**) and *s-trans* (conformer **B**) as shown in Figure **3.8**.[46] Recent computational studies showed that these two conformers of *trans*-vinylcarbenoids were in equilibrium. The formation of **3.77** as the (*Z*)-isomer is indicative that the vinylogous reactivity occurs through conformer **B**. This led us to propose that the highly substituted pyrrole **3.76** is sterically too crowded for an effective reaction at the carbenoid center and leads to competing vinylogous reactivity occurring through conformer **B**. We then became intrigued with the concept that the s-*trans* conformer of vinylcarbenoids would preferentially favor the vinylogous reactivity and the vinylogous reactivity could be enhanced if the (*Z*)-vinylcarbenoid was used as substrate. In this case, the *s-cis* conformation of the carbenoid (conformer **C**) would be expected to interfere with the catalyst "wall", and so, the (*Z*)-vinylcarbenoid would be expected to preferentially exist in the *s-trans* conformation (conformer **D**) and would undergo the vinylogous reactivity.

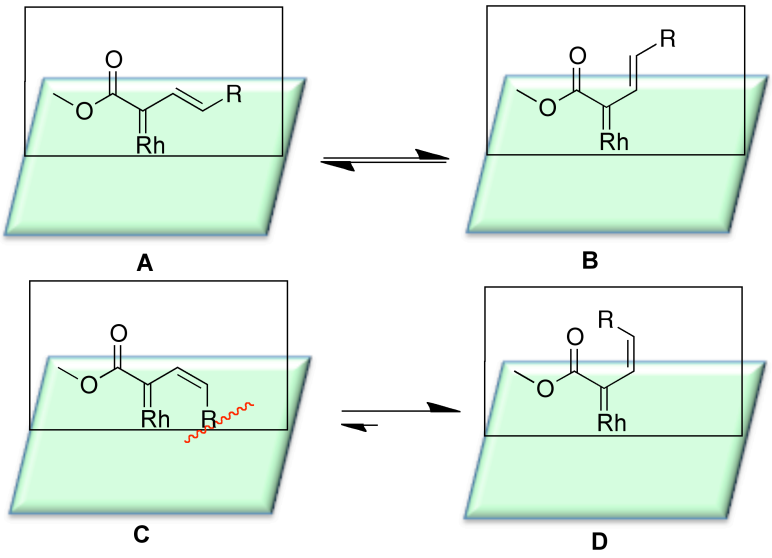
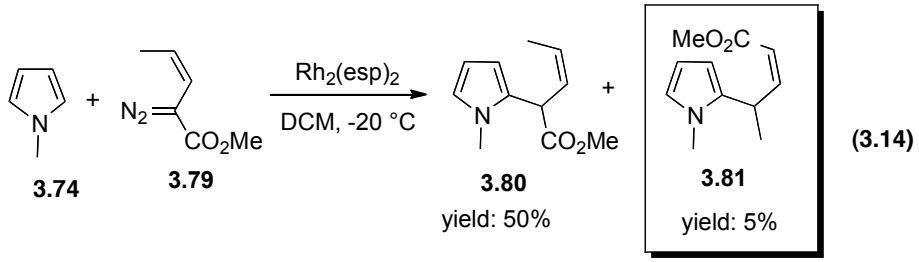
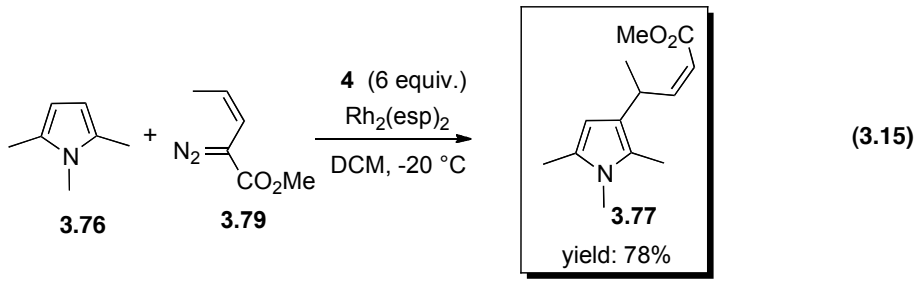


Figure 3.8 Conformations of vinylcarbenoids

To test our hypothesis, the reaction of *N*-methylpyrrole **3.74** and 1,2,5-trimethylpyrrole (**3.76)** was repeated with the (*Z*)-vinyldiazoacetate **3.79** as the carbenoid precursor. Even though the reaction with *N*-methylpyrrole **3.74** still preferentially generated the normal alkylation product **3.80**, a trace amount of the vinylogous product **3.81** was also formed (eq. **3.14**). In contrast, the reaction with 1,2,5-trimethylpyrrole **3.76** led to the formation of the vinylogous substitution product **3.77** cleanly in 78% yield, exclusively as the *Z* isomer (eq. **3.15**). It should be noted that no detectable amount of product derived from reaction occurring at the carbenoid center was observed. The reaction could also be conducted with some of the more standard catalysts such as rhodium acetate and rhodium trifluoroacetate but the highest yield of **3.77** was obtained when Du Bois' $Rh_2(esp)_2$ catalyst was used.[140]

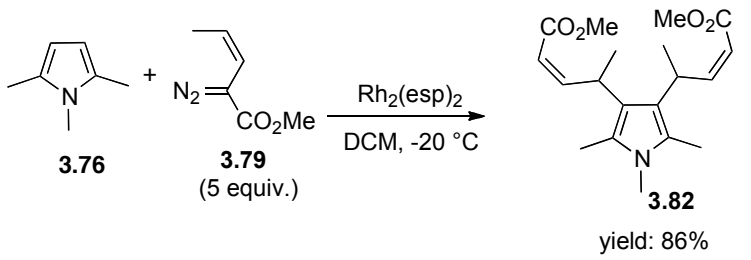


(3.14)



(3.15)

It has also been shown that a sterically crowded substrate favors vinylogous reactivity. Consequently, we set forth to explore if a second alkylation process was feasible with the product **3.77**. The $Rh_2(esp)_2$-catalyzed reaction using 5 equiv of the (*Z*)-vinyldiazoacetate **3.79** with 1,2,5-trimethylpyrrole generated the bis-alkylated product **3.82** in 86% yield (eq **3.16**). As this reaction was conducted with an achiral catalyst, **3.82** was formed as a 1:1 mixture of diastereomers. The diastereoselectivity indicates that the diastereocontrol of the second alkylation is independent of the existing stereocenter installed in the first alkylation step.

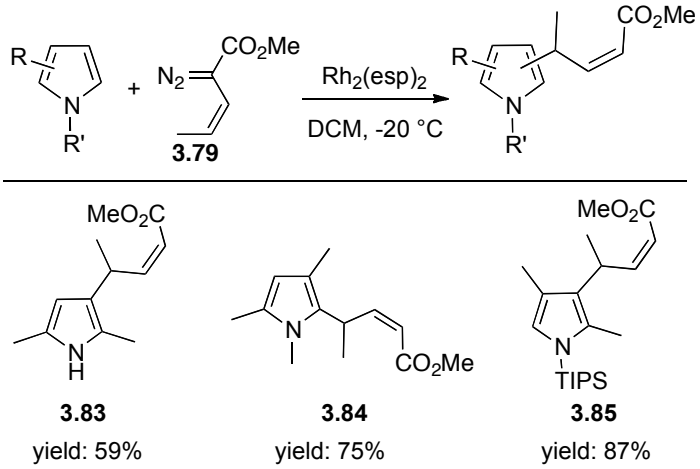


(3.16)

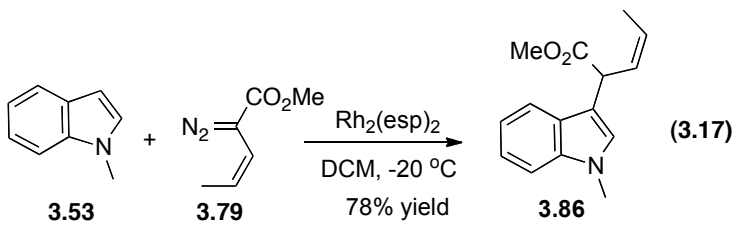
The $Rh_2(esp)_2$-catalyzed vinylogous reaction of diazoacetate **3.79** is applicable to a range of sterically crowded pyrroles, forming the alkylated pyrroles **3.83-3.85** in 59-87%

yields (Table **3.6**). Interestingly, not only could *N*-protected pyrrole undergo the alkylation with vinyldiazoacetate **3.79**, but also, an *N*-unprotected pyrrole was able to furnish the vinylogous product **3.83**. The regioselectivity in the formation of **3.84** and **3.85** reveals that *N*-TIPS is acting as a bulky protecting group,[141] blocking the reactivity at the 2-position of pyrrole and forcing the reaction to occur at the 3-position.

Table 3.6 Vinylogous reaction of **3.79** with pyrroles



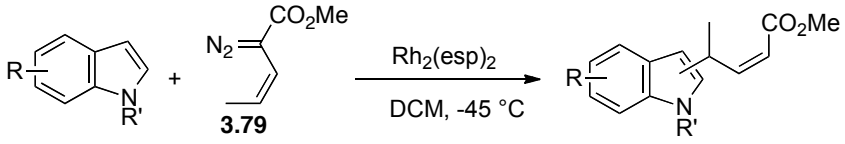
The extension of the reaction to *N*-methylindole **3.53** was not successful and the regular aromatic substitution product **3.80** was isolated in 78% yield (eq **3.17**). This result is consistent with the data obtained from the reaction with pyrrole derivatives that a sterically crowded aromatic system is essential in order to achieve the highly selective vinylogous reactivity. The reaction with a less bulky substrate leads to the carbenoid reactivity product.

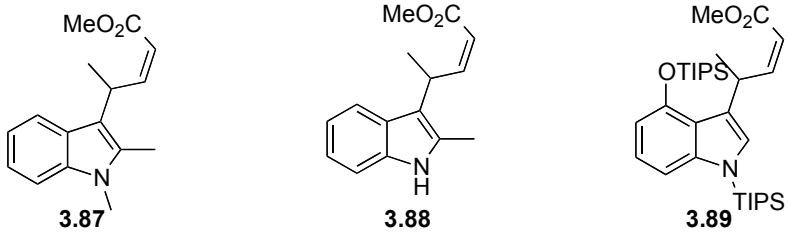


(3.17)

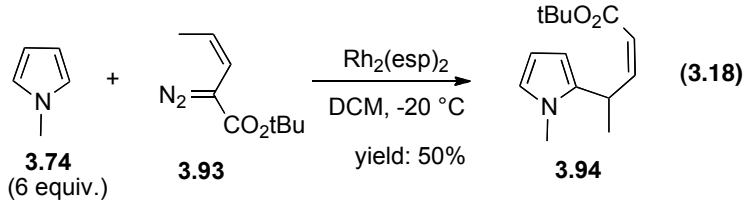
The vinylogous reactivity can also be successfully applied to indoles as long as they are sufficiently sterically crowded. The $Rh_2(esp)_2$-catalyzed decomposition of diazoacetate **3.79** with a variety of indoles afforded the vinylogous alkylation products as shown in Table **3.7**. The transformation still remained effective even at temperature as low as -45 °C, presumably because of the greater nucleophilicity of indoles over pyrroles.[142] In all cases, products were generated exclusively as the *Z*-enoates. Both unprotected and protected (methyl or benzyl) 2-methylindoles afforded the vinylogous products in good yields. Typically, substitution at the 2-position of the indole is necessary for the vinylogous reactivity to occur. However, a similar effect can be achieved when a bulky substituent is introduced to the 4-position of the indole, as illustrated in the formation of product **3.89**.

Table 3.7 Vinylogous reaction of **3.70** with pyrroles



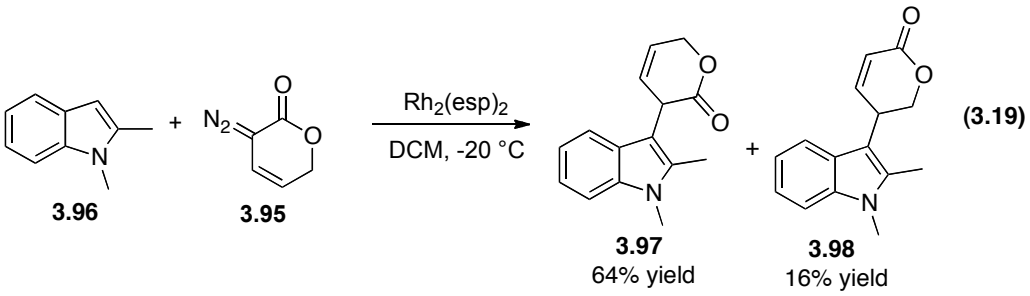


We have demonstrated that the reaction of diazoacetate **3.79** with various sterically encumbered *N*-heterocycles selectively afforded the vinylogous reactivity products. It has been shown that increasing the size of the ester group enhances the vinylogous reactivity.[124] In order to further extend this transformation to less crowded substrates, the use of *tert*-butyl (*Z*)-vinyldiazoacetate **3.93** as the carbenoid precursor instead of the methyl ester diazoacetate **3.79** as a complimentary strategy for enhancing vinylogous reactivity was examined (eq **3.18**). The $Rh_2(esp)_2$-catalyzed reaction of **3.93** with 6.0 equiv of *N*-methylpyrrole caused a major change in the reaction outcome. No evidence of the regular alkylation product was observed and the vinylogous product **3.94** could be isolated in 50% yield.



(3.18)

Having demonstrated the successful vinylogous reaction with *cis*-vinydiazoacetate **3.79**, the next step explored extension of the vinylogous transformation to diazolactone **3.95** (eq. **3.19**). The $Rh_2(esp)_2$-catalyzed reaction between **3.95** and 1,2-dimethylindole **3.96** generated the vinylogous reactivity product **3.98** in only 16% yield, whereas the carbenoid reactivity product **3.97** was generated as the major product in 64% yield. This result reveals that even though **3.95** is a *cis*-vinylcarbenoid, this type of carbenoid still favors carbenoid reactivity over vinylogous reactivity. This is presumably because the carbenoid center is in a rigid ring system and it is less sterically crowded compared to acyclic *cis*-vinylcarbenoids.



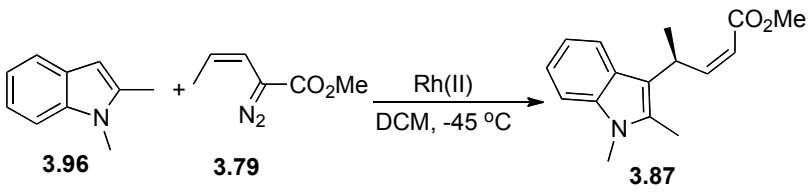
In summary, these studies demonstrate that (*Z*)-vinylcarbenoids have greater tendency than (*E*)-vinylcarbenoids for reaction occurring at the vinylogous position of vinylcarbenoids rather than at the carbenoid center. This type of reactivity leads to an effective method for the functionalization of pyrroles and indoles.

3.2.3 Asymmetric vinylogous alkylation of *N*-heterocycles

Developing an effective asymmetric functionalization of indolyl or pyrrolyl cores has been a high priority in the organic community recently, as they are constituents of natural products and pharmaceutical targets.[119,120,142] The most widely used approach has been the conjugate addition of heterocycles to α,β-unsaturated carbonyl compounds using non-racemic transition-metal catalysts or organocatalysts.[143-146] An alternative approach is a metal-catalyzed carbenoid reaction, which has been successfully applied to various natural product synthesis or protein modifications.[146] However, enantioselective variants are limited. Fox has shown that the electrophilic substitution reaction of methyl 2-diazopropanoate generates 3-substituted indoles with high asymmetric induction.[113] We have demonstrated that enantioenriched 4-substituted indoles can be generated in a cascade sequence involving a combined C-H functionalization/Cope rearrangement followed by an elimination promoted by aromatization.[147] Within this scenario, we herein

describe a highly asymmetric vinylogous alkylation of *N*-heterocycles by *trans*-alkyl vinyldiazoacetates in the presence of a bridged dirhodium catalyst, Rh_2(*S*-biTISP)$_2$.[29,148,149]

Table 3.8 Asymmetric alkylation between indole **3.96** and diazoacetate **3.79**



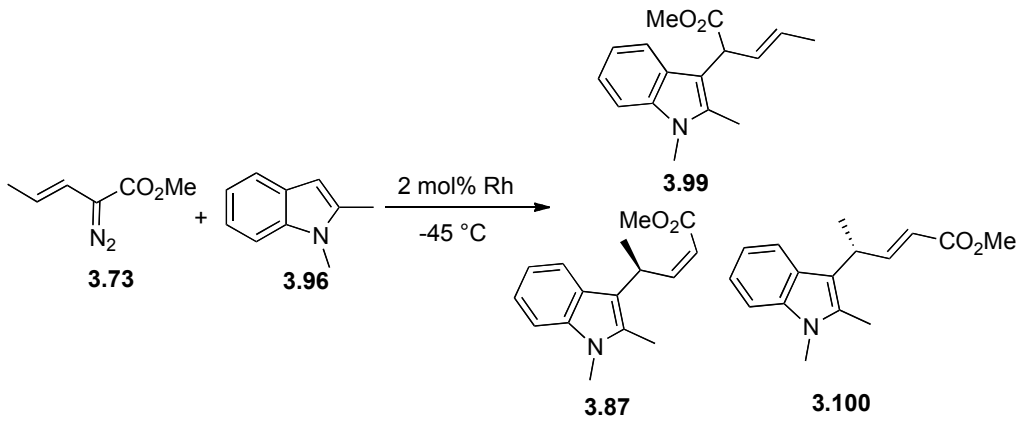
entry	catalyst	yield (%)	ee (%)
1	Rh_2(*S*-PTAD)$_4$	88	48
2	Rh_2(*S*-DOSP)$_4$	93	-10
3	Rh_2(*S*-biTISP)$_2$	90	0
4	Rh_2(*S*-TISP)$_4$	84	-26

We have shown that *cis*-alkylvinyldiazoacetates have a greater tendency over *trans*-alkylvinyldiazoacetates to react at the vinylogous carbon rather than at the carbenoid center.[150] The goal of this study was to achieve an asymmetric version of the novel indole functionalization. The study began by the use of some of the standard chiral dirhodium catalysts that have been developed for the reactions of vinyldiazoacetates. The alkylation of indole **3.96** with *Z*-vinyldiazoacetate **3.79** was used as the standard screening reaction and the results are summarized in Table **3.8**. All four screened catalysts produced the alkylation product **3.87** in excellent yield (up to 93%). The two most widely-used chiral catalysts for the asymmetric transformation of donor-acceptor carbenoids, Rh_2(*S*-PTAD)$_4$ and Rh_2(*S*-DOSP)$_4$, gave low to moderate asymmetric induction in the test reaction. The more bulky catalyst Rh_2(*S*-TISP)$_4$ gave low enantioselectivity, and the bulky and

conformationally constrained catalyst Rh_2(*S*-biTISP)$_2$ gave 0% ee. These studies demonstrate that a highly enantioselective method for the functionalization of indoles with *Z*-vinyldiazoacetate **3.79** was not accessible using the currently available chiral catalysts.

The previous approach with *cis*-alkylvinyldiazoacetates was not successful for the asymmetric induction, which led us to investigate an alternative route. Intrigued by the formation of product **3.77** from the reaction between **3.76** and vinyldiazoacetate **3.73** (eq **3.13**), we decided to re-explore the possibility of using *E*-vinyldiazoacetate as an effective carbenoid precursor for the vinylogous reactivity. Recently, we reported that *trans*-alkylvinyldiazoacetates could exist in either *s-cis* or *s-trans* conformer and the rotational barrier between the two conformers was small. Therefore, we rationalized that we might be able to force the reaction to occur at the vinylogous center by using more bulky catalysts. Seven widely used dirhodium catalysts for the donor-acceptor carbenoid chemistry were screened as summarized in Table **3.9**. The reaction of vinyldiazoacetate **3.73** with 1,2-dimethylindole **3.96** generated three products. Products **3.87** and **3.100** are generated through the vinylogous reactivity, in which **3.87** is formed from the s-*trans* conformer and **3.100** is formed from the s-*cis* conformer of vinylcarbenoids. Compound **3.99** is derived from attack of the heterocycle at the carbenoid center, and could in principle be derived from the reaction occurring either through the s-*trans* or the s-*cis* conformer of the carbenoid.

Table 3.9 Asymmetric alkylation between indole **3.96** and diazoacetate **3.73**



entry	catalyst	solvent	ratio of **3.99/3.87/3.100**	yield of **3.87**(%)	ee of **3.87** and **3.100** (%)
1	$Rh_2(OAc)_4$	DCM	5/62/33	57	--- and ---
2	$Rh_2(TFA)_4$	DCM	7/49/44	43	--- and ---
3	$Rh_2(esp)_4$	DCM	0/74/26	52	--- and ---
4	Rh_2(*S*-PTAD)$_4$	DCM	8/76/16	55	-8 and -59
5	Rh_2(*S*-DOSP)$_4$	DCM	36/26/38	25	17 and 82
6	Rh_2(*S*-DOSP)$_4$	Toluene	43/14/43	13	33 and 92
7	Rh_2(*S*-TISP)$_4$	DCM	5/89/6	67	39 and --
8	Rh_2(*S*-TISP)$_4$	Toluene	18/73/9	58	47 and 7
9	Rh_2(*S*-biTISP)$_2$	DCM	3/89/9	66	89 and --
10	Rh_2(*S*-biTISP)$_2$	Toluene	20/60/20	57	48 and ---

The product distribution of the reaction with the sterically crowded nucleophilic indoles is controlled by the vinylcarbenoid structures. The *cis*-alkylvinylcarbenoid would preferentially exist as the *s-trans* (conformer **A)** conformer and the nucleophile would predominantly attack the vinylcarbenoid from the vinylogous site (Figure **3.9**). In contrast, the rhodium-stabilized *trans*-alkylvinylcarbenoid could, in principle, exist *s-trans* (conformer **C**) or *s-cis* (conformer **D**). On the basis of the reactivity patterns that we have observed to date, we proposed that carbenoids in s-*trans* configurations (conformers

A and **C)** were more likely to display the vinylogous reactivity than carbenoids in s-*cis* configurations (conformers **B** and **D**). Less sterically crowded catalysts give considerable amounts of **3.99** and **3.100**, whereas the bulky catalysts Rh_2(*S*-TISP)$_4$ and Rh_2(*S*-biTISP)$_2$ give a strong preference for the formation of **3.87**. Most notable is the comparison between Rh_2(*S*-DOSP)$_4$, which gives close to equimolar amounts of the three compounds, and Rh_2(*S*-TISP)$_4$, which gives about a 9:1 preference of **3.87** over the other two products. Furthermore, in the Rh_2(*S*-biTISP)$_2$ catalyzed reaction, **3.87** is isolated in 66% yield and in 89% ee. Interestingly, unlike the reported cyclopropanation, in which the asymmetric induction with Rh_2(*S*-biTISP)$_2$ is opposite to the reaction catalyzed by Rh_2(*S*-DOSP)$_4$, The Rh_2(*S*-biTISP)$_2$-catalyzed vinylogous reaction afforded the same asymmetric sense as the reaction with Rh_2(*S*-DOSP)$_4$. Conducting the reaction in DCM at -45 ^{o}C in the presence of 2 mol% Rh_2(*S*-biTISP)$_2$ was chosen as the optimal condition for this transformation.

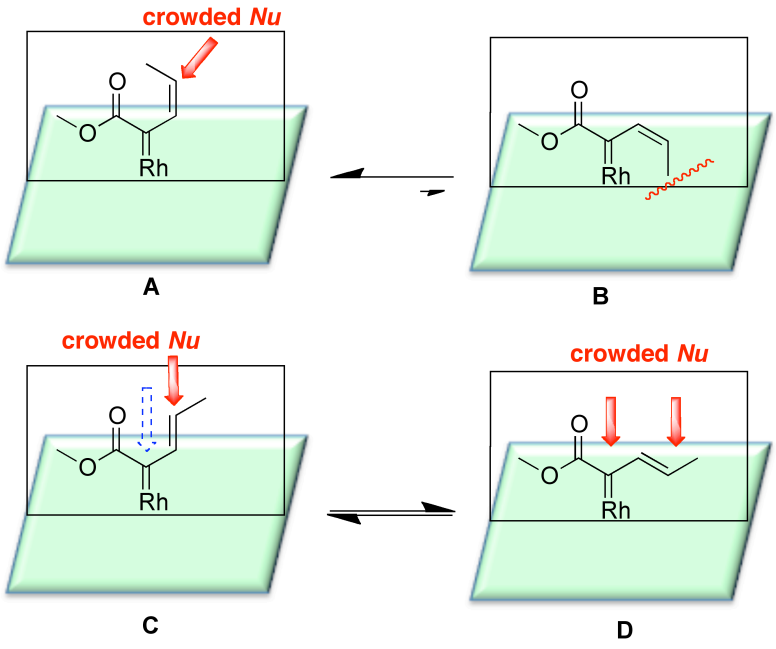
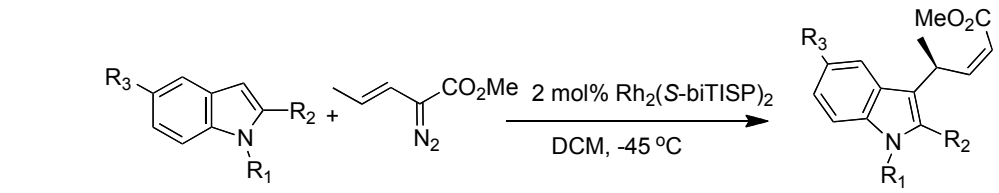
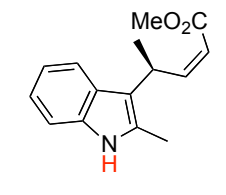


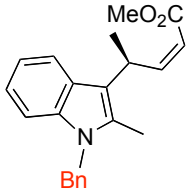
Figure 3.9 Relationship between reactivity and carbenoid structures

Table 3.10 Substrate scope of asymmetric vinylogous reactivity

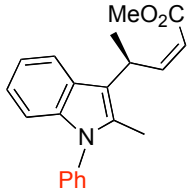




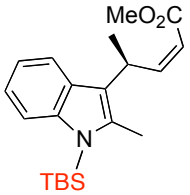
3.88
yield: 67%
ee: 82%



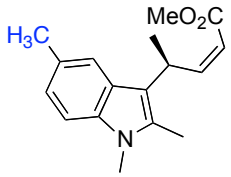
3.91
yield: 74%
ee: 90%



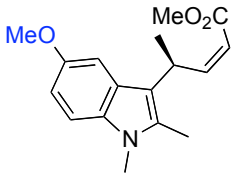
3.101
yield: 81%
ee: 95%



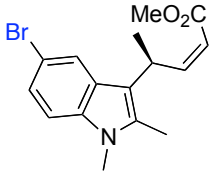
3.102
yield: 83%
ee: 94%



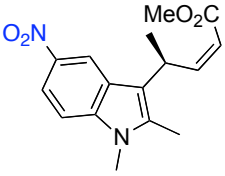
3.103
yield: 70%
ee: 88%



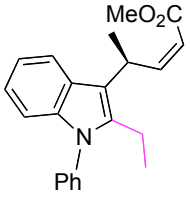
3.90
yield: 72%
ee: 86%



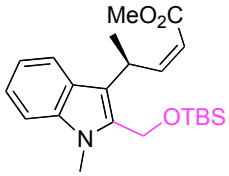
3.104
yield: 81%
ee: 88%



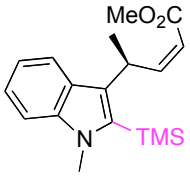
3.105
yield: 48%
ee: 87%



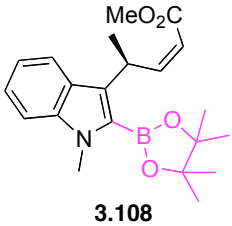
3.106
yield: 86%
ee: 94%



3.92
yield: 64%
ee: 91%



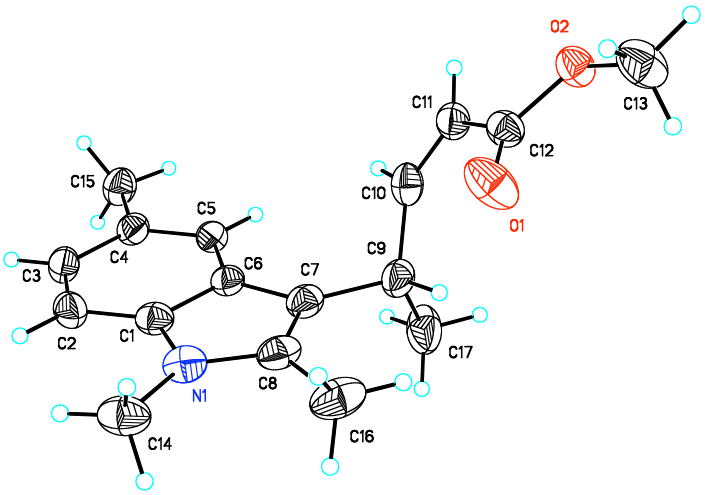
3.107
yield: 74%
ee: 92%

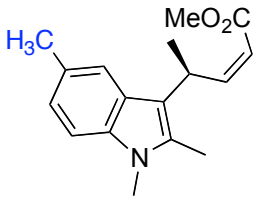


3.108
yield: 82%
ee: 94%

The Rh_2(*S*-biTISP)$_2$-catalyzed asymmetric vinylogous alkylation was applicable to a range of substituted indoles bearing different functionalities as illustrated in Table **3.10**. All transformations were very effective and the (*Z*)-pent-2-enoates were produced in 64-86% yields with high asymmetric induction (82-94% ee). Both the protected and unprotected 2-methylindoles were equally effective in producing the vinylogous alkylation products. Increasing the size of the *N*-protecting group enhanced the asymmetric induction slightly, improving from 82% ee in product **3.88** to 95% ee in

product **3.101**. This transformation was also successfully applied to indoles bearing different functionalities at the 5-position, even with an electron-withdrawing group, such as nitro (**3.99**). Indoles with functional groups at the 2-position were also compatible, such as TMS and pinacol boronate ester at the 2-position (**3.107** and **3.108**). The generation of products **3.107** and **3.108** may offer the opportunity for further functionalization. The absolute configuration of product **3.103** was unambiguously assigned by X-ray crystallography (Figure **3.10**), while others were tentatively assigned, assuming a similar transition state for all the asymmetric reactions.



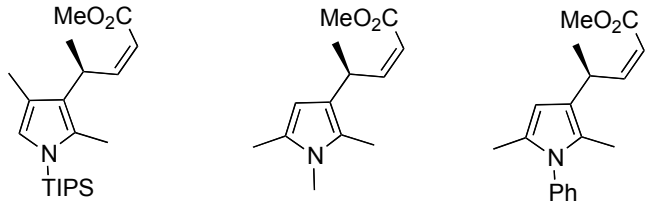


3.103

Figure 3.10 X-ray crystallographic structure of product **3.103**

This reaction can be extended to pyrrolyl derivatives as shown in Table **3.11**. However, due to the low reactivity of pyrroles, the reaction was conducted at -20 ^{o}C instead of -45 ^{o}C. Even so, alkylation products were still generated in good yields with high asymmetric induction (87-91% ee). The absolute configuration of these products was tentatively assigned based on the assumption of similar asymmetric induction observed in compound **3.103**.

Table 3.11 Scope of asymmetric vinylogous reactivity with pyrroles

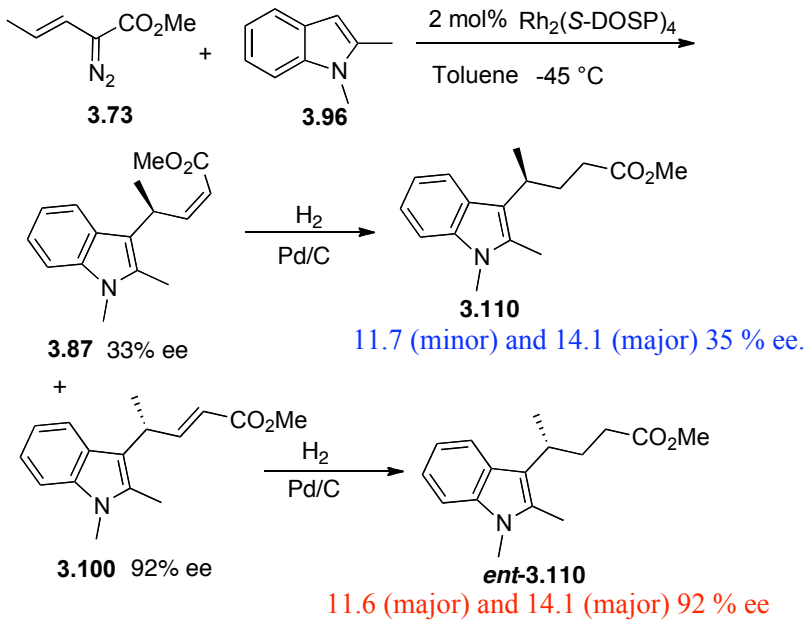


3.85
yield: 65%
ee: 91%

3.77
yield: 46%
ee: 87%

3.109
yield: 72%
ee: 89%

The absolute configuration of product **3.100** was determined by comparison of the chiral HPLC retention time of its hydrogenation product with the hydrogenation product derived from the (*Z*)-product **3.87** (Scheme **3.7**). The Rh_2(*S*-DOSP)$_4$-catalyzed vinylogous reaction of **3.96** with diazoacetate **3.73** generated product **3.87** with 33% ee and product **3.100** with 92% ee. Both of these products were subjected to palladium-catalyzed hydrogenation, leading to opposite enantiomers of product **3.110** in nearly quantitative yield. The observation of the opposite enantiomers was confirmed by HPLC trace.

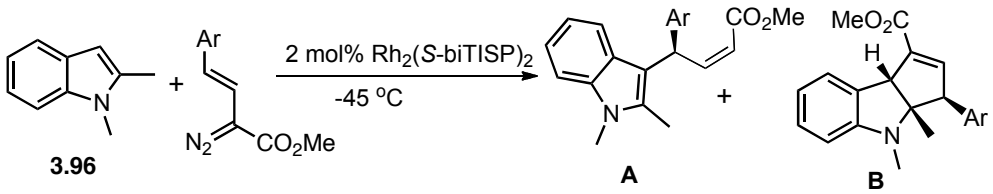


Scheme 3.7 Structural confirmation of two vinylogous reactivity products

With the successful vinylogous alkylation of indoles with *trans*-methylvinyldiazoacetate **3.73** in hand, we next explored whether this reaction could be applied to *trans*-arylvinyldiazoacetates because such diazoacetates represent an important class of donor-acceptor carbenoid precursors. The Rh_2(*S*-biTISP)$_2$-catalyzed decomposition of *trans*-phenylvinyldiazoacetate **3.52** with dimethylindole **3.96** in DCM selectively generated the vinylogous alkylation product **3.111A** in excellent yield, but only 49% ee was achieved (entry **1**, Table **3.12**). Conducting the reaction in toluene improved the enantioselectivity to 79% ee; however, a significant amount of the [3 + 2] annulation product **3.111B** was generated as a byproduct. Product **3.111A** was isolated in only 53% yield. In order to obtain reasonable asymmetric induction and reaction yield, the combination of toluene in the presence of Rh_2(*S*-biTISP)$_2$ was chosen as the optimal condition. This reaction was then applied to other *trans*-arylvinyldiazoacetates as summarized in Table **3.12**. In all cases, alkylation products were generated in moderate

yields (46% to 57%) with moderate to good asymmetric induction (70-79% ee). The absolute configuration of products **3.111-3.114** was tentatively assigned based on the assumption that similar asymmetric induction would occur as was observed for the product **3.103**.

Table 3.12 Vinylogous alkylation with arylvinyldiazoacetate



entry	Ar	solvent	product	ratio of **A**/**B**	yield (**A**, %)	ee of **A** and **B** (%)
1	Ph-	DCM	**3.111**	**A** only	87	49 and --
2	Ph-	TFT	**3.111**	6/1	70	50 and 88
3	Ph-	Toluene	**3.111**	2.2/1	53	79 and 97
4	*p*-CF_3Ph-	Toluene	**3.112**	2.2/1	51	76 and 92
5	*p*-BrPh-	Toluene	**3.113**	2.5/1	57	79 and 96
6	Naph-	Toluene	**3.114**	2.2/1	46	70 and 96

A plausible transition state to rationalize the absolute stereochemistry of the reaction is proposed as shown in Figure **3.11**. Four prolinate groups in Rh_2(*S*-biTISP)$_2$ have been proposed to adopt a D_2-symmetric configuration, in which a blocking group is in front of the ester group and the other blocking group is behind the vinyl group.[148] These four prolinate groups are locked by the bridged ligand. Indoles would attack the vinylogous carbon of vinylcarbenoids as the s-*trans* conformer from the front face. A zwitterionic intermediate containing two newly formed stereocenters would be generated and on deprotonation and proto-demetalation, it would afford the observed product.

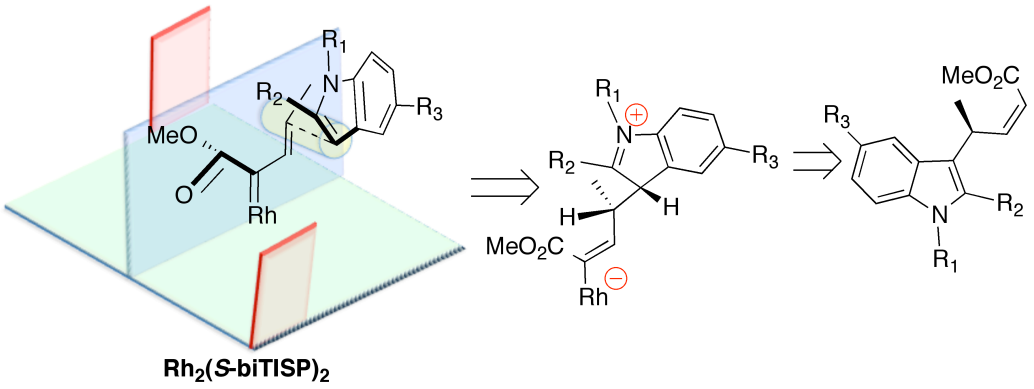


Figure 3.11 Possible reaction mechanism for the asymmetric induction

In conclusion, the Rh_2(*S*-biTISP)$_2$-catalyzed asymmetric vinylogous alkylation between *N*-heterocycles and *trans*-alkylvinyldiazoacetates was successfully developed into a highly enantioselective process. This bridged catalyst not only provides high asymmetric induction, but also, favors attack at the vinylogous position of the vinylcarbenoid.

Chapter IV: Stereocontrol of the Combined C-H Functionalization/Cope Rearrangement

4.1 Introduction

Developing practical methods for C-H functionalization is an intense area of current research in the synthetic community because such methods offer alternative strategies to streamline the synthesis of complex molecules and pharmaceutical targets.[59,62,151-158] One of the key challenges in this field is the development of broadly applicable stereoselective C-H functionalization methods. In the case of "traditional" synthetic strategies, focus is on controlling reactivity at the functional group in the molecule.[157-160] Similar control in the C-H functionalization field is more challenging because C-H bonds are generally strong, and many C-H bonds are present in most organic molecules. Two fundamental directions have evolved for the development of practical methods for stereoselective C-H functionalization (Figure **4**.**1**).[61,151,153-156,161] One approach is the direct C-H activation (path a), involving oxidative addition of the C-H bond onto an active metal center, followed by subsequent reactions. Here, we highlight the other approach using transition-metal-coordinated carbenes or nitrenes to insert into the C-H bond (path b).

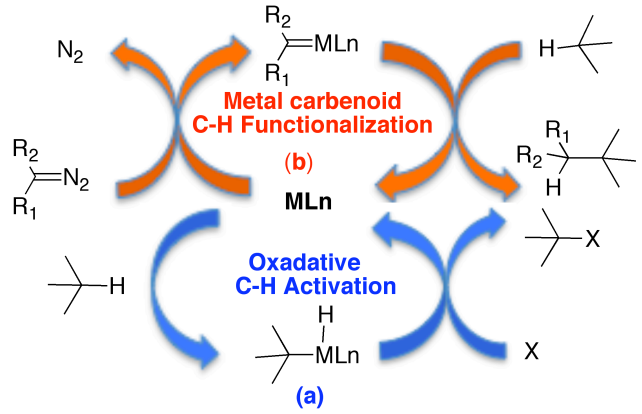
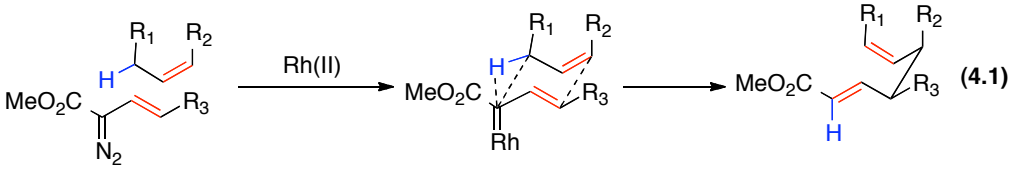


Figure 4.1 Two different strategies developed for C-H functionalization

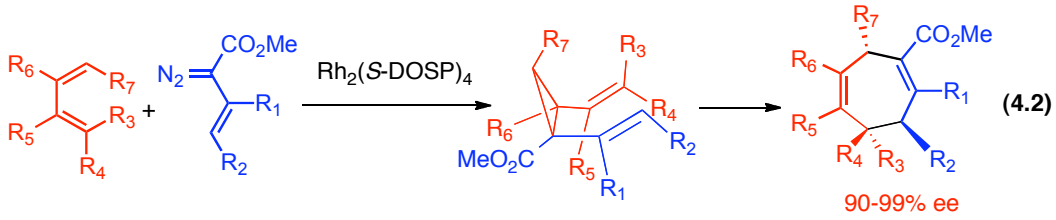
Traditionally, control in the carbenoid approach for C-H functionalization has been achieved by conducting the reaction in an intramolecular fashion. If selectivity in intermolecular reactions could be achieved, the transformation would be even more appealing because it would avoid the sequence steps required to make the substrate for the intramolecular transformation.[117,162] The intermolecular C-H functionalization induced by donor-acceptor carbenoids is an important protocol in the field.[162,163] An attractive feature of such functionalization is the possibility of initiating a cascade sequence. A spectacular transformation is the C-H functionalization reaction of allylic C-H bonds with vinylcarbenoids. In this particular case, the regular C-H insertion did not occur. Instead, two double bonds migrated, involving a Cope rearrangement through a chairlike transition state (eq. **4.1**).[40] This remarkable transformation is named as the combined C-H functionalization/Cope rearrangement (CHCR). This reaction is exceptionally diastereo- and enantioselective, affording products in greater than 95% de and 95% ee.



This chapter describes our endeavors towards expanding the scope of this novel C-H functionalization reaction. The background covers the discovery of the reaction,[164] the general substrate scope, and addresses the major challenges associated with the reaction.[165] Focus will be placed on synthetic applications to complex natural product syntheses. In addition, recent computational modeling studies will be described which provide a detailed understanding of the reaction mechanism, and offer a guide on how to further expand the scope of this synthetically useful methodology.

4.1.1 Discovery

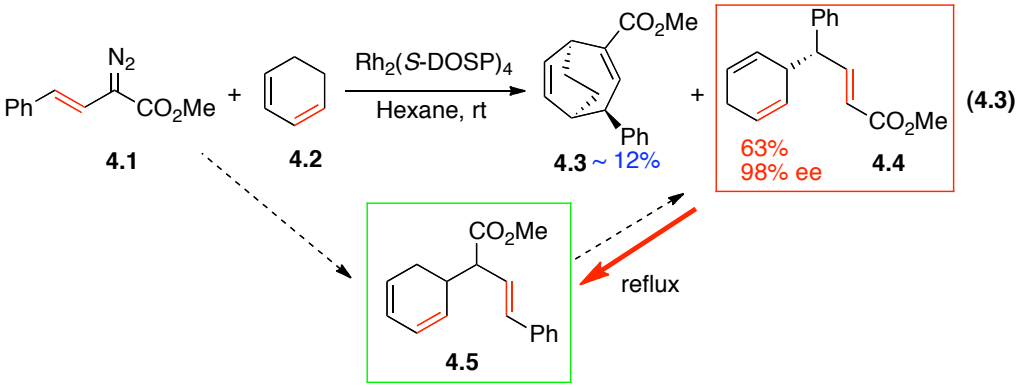
Donor-acceptor carbenoids are versatile intermediates, which selectively undergo a variety of transformations, including the tandem cyclopropanation/Cope rearrangement and the intermolecular C-H functionalization. One of the highlights of the use of vinylcarbenoids is the asymmetric cyclopropanation/Cope rearrangement reaction with dienes in the presence of Rh_2(*S*-DOSP)$_4$ (eq. **4.2**).[40]



(4.2)

A breakthrough in the C-H functionalization chemistry of donor-acceptor carbenoids was achieved during studies to extend the cyclopropanation/Cope rearrangement reaction to 1,3-cyclohexadiene. The reaction of vinyldiazoacetate **4.1** with 1,3-cyclohexadiene **4.2**, generated the 1,4-cyclohexadiene **4.4** in 63% yield with 98% ee as the major product. Only a minor amount of the expected cyclopropanation/Cope rearrangement product **4.3** was formed (eq. **4.3**).[164] The formation of product **4.4** was unexpected, not only because

of the excellent asymmetric induction, but also, because two double bonds underwent migration during the reaction. It seems reasonable to assume that the product **4.4** is generated by means of a Cope rearrangement of the direct C-H insertion product **4.5**. However, this is not the case because compound **4.4** is the kinetic product and slowly rearranged into product **4.5** in refluxing hexane. Therefore, it is proposed that the 1,4-cyclohexadiene **4.4** is a kinetically favored product generated through a concerted mechanism, in which the initial C-H activation is interrupted by a Cope rearrangement. This process is named as "the combined C-H functionalization/Cope rearrangement" (CHCR).

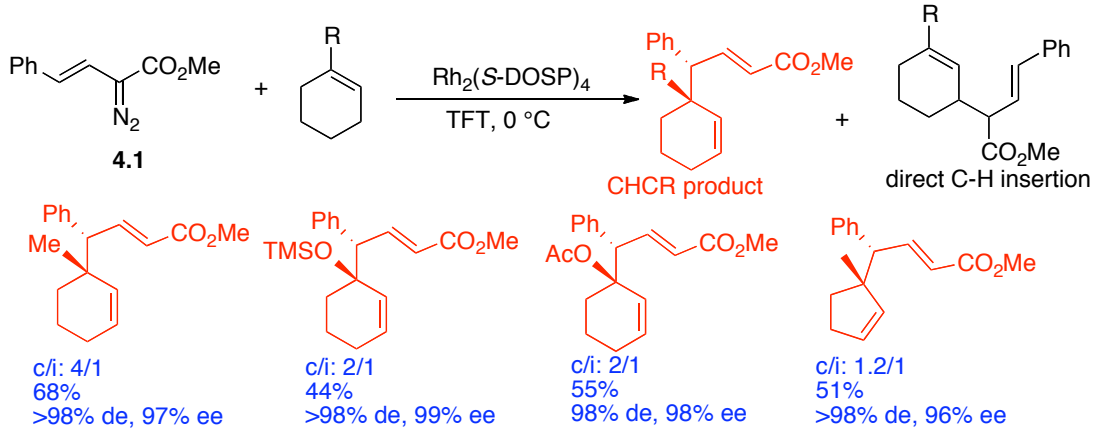


4.1.2 Substrate scope of the CHCR reaction

Cyclic olefins. After the discovery of the CHCR reaction with 1,3-cyclohexadiene, the reaction has been extended to other cyclic olefins, generating products with two new stereogenic centers in a highly stereoselective fashion. The Rh_2(*S*-DOSP)$_4$-catalyzed decomposition of vinyldiazoacetate **4.1** with cyclohexene derivatives afforded a mixture of two C-H functionalization products: the CHCR product (c) and the direct C-H insertion product (i) (Table **4.1**).[165] In all cases, the CHCR products are generated in a highly diastereo- and enantioselective maner. However, unlike the reaction with 1,3-

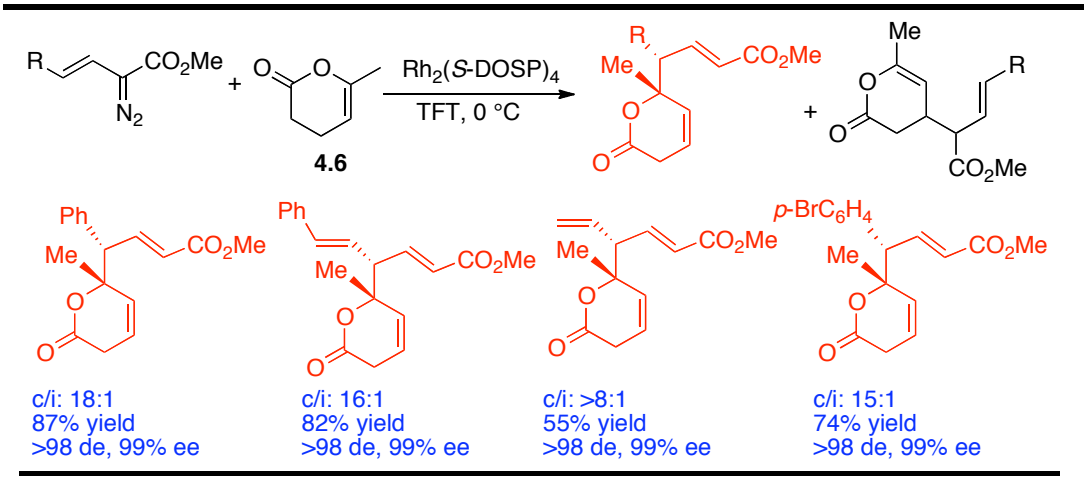
cyclohexadiene, which generates the product **4.4** exclusively, the ratio of the CHCR product to the C-H insertion product (c/i) in these reactions is generally low, ranging from 2/1 to 4/1. The ratio even drops to 1.2/1 with 1-methylcyclopentene.

Table 4.1 CHCR reaction between vinylcarbenoid and cyclohexene derivatives

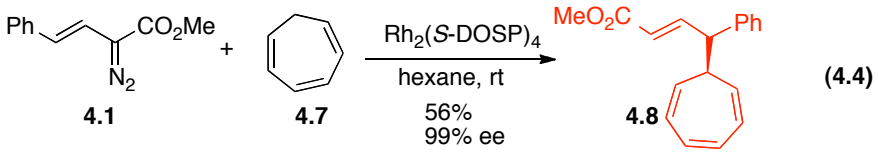


An excellent substrate for the CHCR reaction is dihydropyranone **4.6**. The Rh_2(*S*-DOSP)$_4$ catalyzed reaction of pyranone **4.6** gave a strong preference for the CHCR product, which was generated in good yields and with extremely high asymmetric induction (Table **4.2**).[165]

Table 4.2 CHCR reaction with dihydropyranone **4.6**



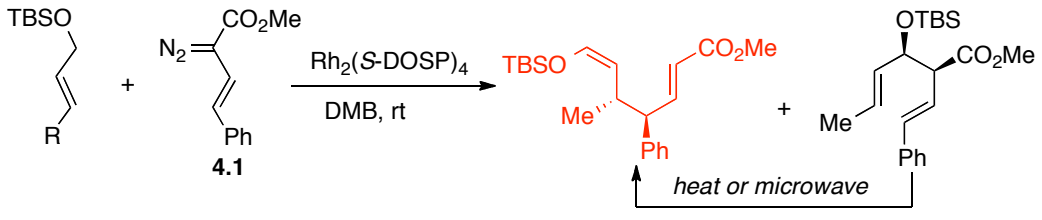
Another good substrate for the CHCR reaction is cycloheptatriene **4.7**. The reaction with vinyldiazoacetate **4.1** generated CHCR product **4.8** in 56% yield and with 99% ee (< 5%) (eq **4.4**).[166] Only trace amount of the direct C-H insertion product was formed



(4.4)

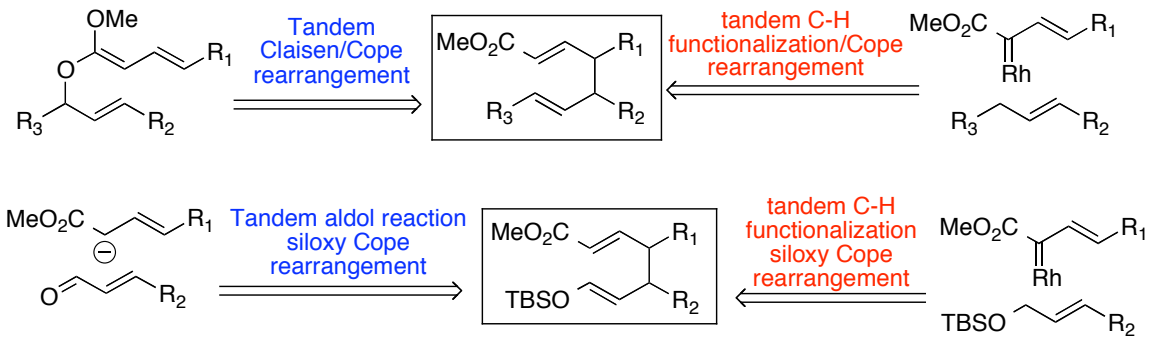
Acyclic olefins. Having established effective CHCR reactions with cyclic olefins, the reaction was then applied to acyclic olefins. The reaction of vinyldiazoacetate **4.1** with various silyl ethers of allylic alcohols catalyzed by Rh_2(*S*-DOSP)$_4$ afforded both the CHCR product and direct C-H insertion product in good diastereo- and enantio-control (Table **4.3**).[167] To improve the selectivity favoring the CHCR reaction, various solvents were screened in the study. Trifluorotoluene (TFT) as solvent was found to enhance the ratio (c/i) to 4:1, but resulted in significantly lower reaction yield. An interesting aspect of this reaction is that the CHCR product is thermodynamically more stable, and in this case, the direct C-H insertion product can undergo a siloxy Cope rearrangement to form the CHCR product under forcing conditions, such as heat or microwave.

Table 4.3 CHCR reaction with acyclic olefins



R:	Me	(*E*)CH_3CH_2=CH-	C_6H_5
	61% (combined) c/i 1:1 >98% de >98% de 89% ee 88% ee	69% (combined) c/i 2.5:1 >98% de >98% de 92% ee 91% ee	94% (combined) c/i 1.4:1 >98% de >98% de 91% ee 91% ee

The CHCR reaction of vinylcarbenoids with allylic C-H bonds can be considered as a surrogate of the tandem Claisen/Cope rearrangement. In addition, products derived from this combined C-H functionalization/siloxy Cope rearrangement can be classically generated from a tandem aldol reaction/siloxy Cope rearrangement (Scheme **4.1**).[167]



Scheme 4.1 The CHCR reaction as a strategic synthetic reaction

4.1.3 Proposed predictive mechanism of the CHCR reaction

The CHCR product is generally produced in a highly diastereo- and enantioselective maner. A predictive model has been proposed to account for the reaction outcome.[168] Rh_2(*S*-DOSP)$_4$ is considered to adopt a D_2-symmetric arrangement and can be simply viewed as a blocking group in front of the ester group, while a blocking group is in the back of the vinyl moiety (Figure **4.2**).[21,112] It should be noted that the perpendicular oritentation of the ester group also blocks attack of the substrate to the ester side of the carbenoid. In the transition state, the metalcarbenoid initiates the C-H insertion, but the process is interrupted by a Cope rearrangement through a chair transition state. Due to the rigid stereo-defined chairlike transition state, the two new stereogenic centers are produced in a highly stereoselective fashion.

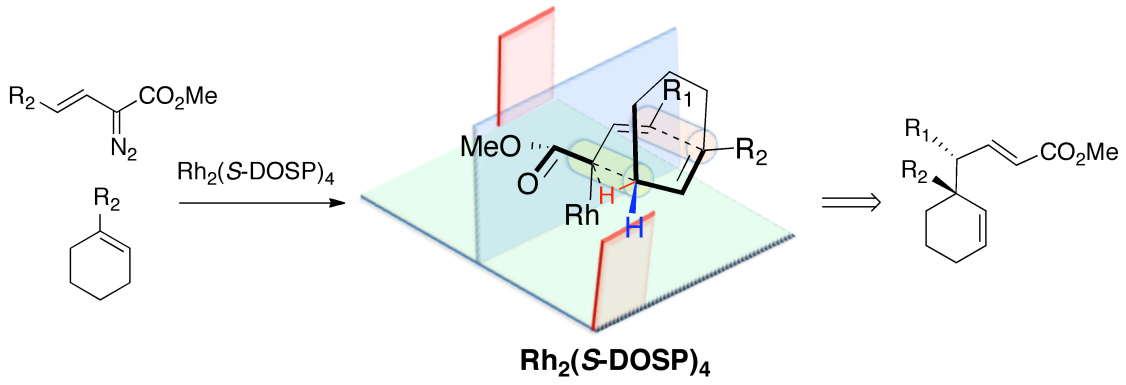


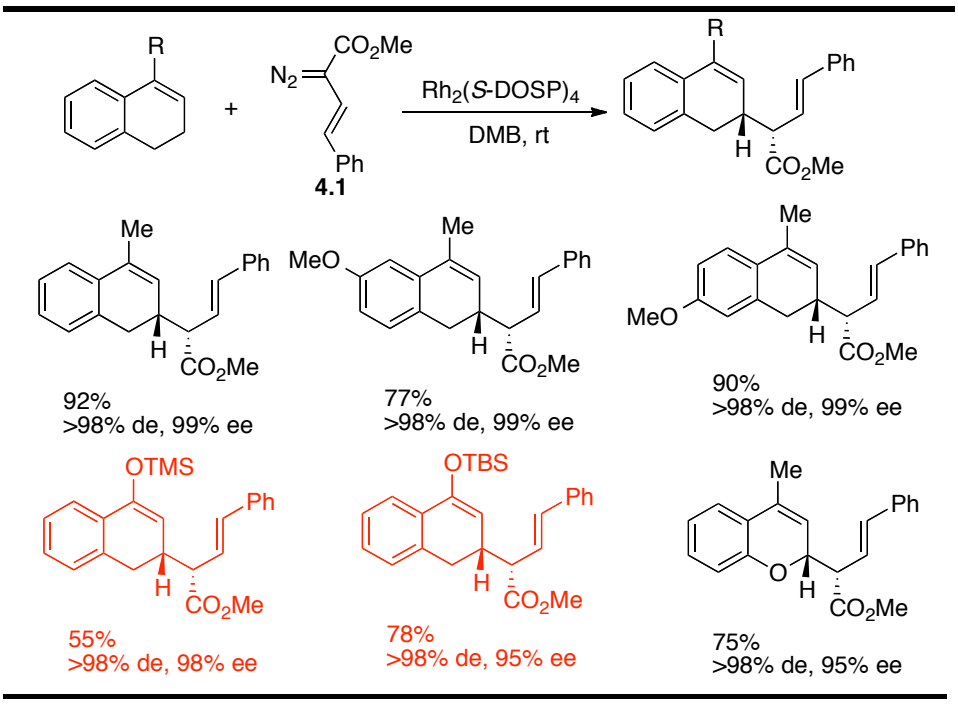
Figure 4.2 Proposed mechanism for the CHCR reaction

4.1.4 CHCR reaction followed by a retro-Cope rearrangement

A long-term goal in the development of the CHCR reaction is to expand substrate scope. Considering the substrate structure favoring the CHCR reaction over the direct C-H insertion, it was hypothesized that substrates with flat three-dimensional structures would give the highest ratio of the CHCR product to the direct C-H insertion product. If this were the case, dihydronaphthalene derivatives would be expected to selectively undergo the CHCR reaction. The Rh_2(*S*-DOSP)$_4$-catalyzed reaction of diazoacetate **4.1** with several dihydronaphthalenes were thus conducted as summarized in Table **4.4**.[48] Surprisingly, the reaction did not afford the CHCR product, but instead generated the C-H insertion product as a single isomer (> 98% de) with exceptionally high enantioselectivity (95-99% ee). The highly diastereoselective nature of this direct C-H insertion reaction is unexpected because earlier studies indicate that the direct C-H insertion reaction between aryldiazoacetates and cycloalkene displays only moderate diastereoselectivity. A more elaborate mechanism was proposed in which the CHCR product was initially formed followed by a retro-Cope rearrangement through a chair

transition state to form the direct C-H insertion product (Figure **4.3**). Owing to the highly diastereoselective nature of the formal C-H insertion product, it is reasonable to conclude that dihydronaphthalene systems can undergo the CHCR reaction selectively over the direct C-H insertion reaction.

Table 4.4 CHCR reaction followed by Cope rearrangement



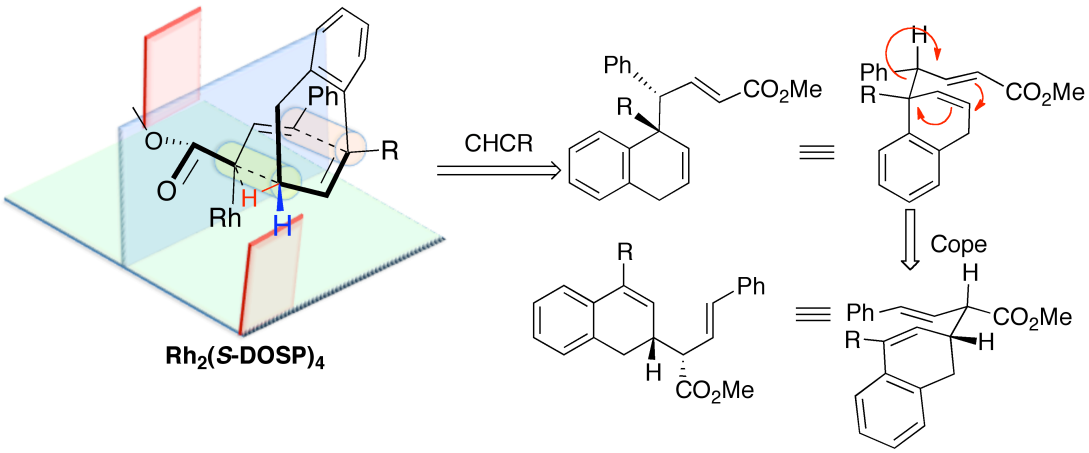
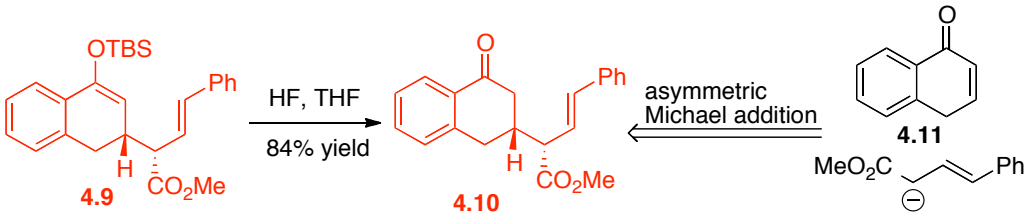


Figure 4.3 Reaction mechanism for the formal C-H insertion reaction

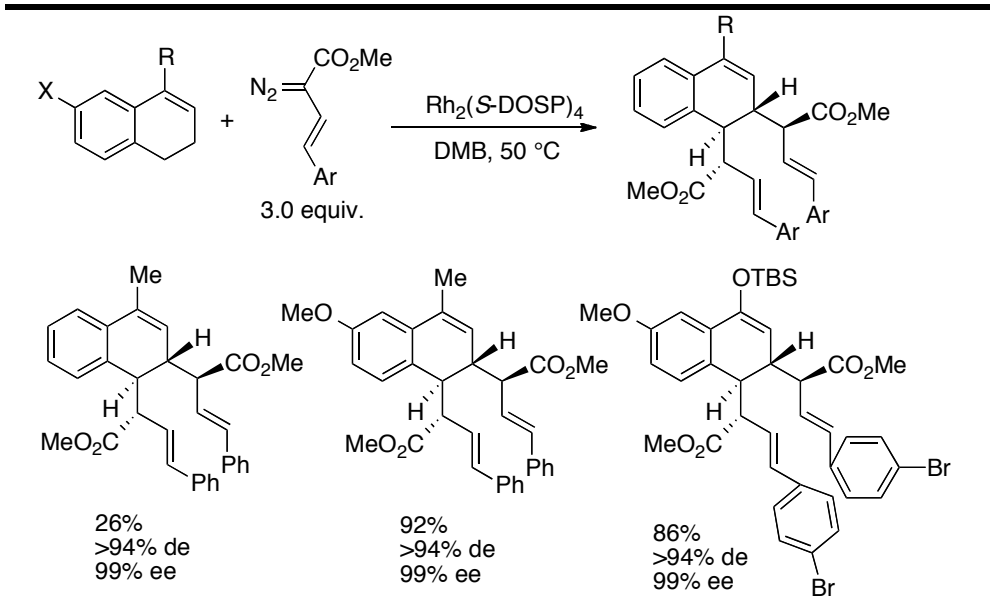
The CHCR reaction with siloxy dihydronaphthalenes is particularly interesting because treating product **4.9** with HF yielded ketone **4.10** in 84% yield. This typical product is classically generated *via* an asymmetric Michael addition to a corresponding unsaturated ketone **4.11**. As a result, this CHCR reaction followed by a retro-Cope rearrangement can be considered as a surrogate of the asymmetric Michael addition (Scheme **4.2**).[48] In this case, the comparison with conventional chemistry is intriguing because substrate **4.11** is not a valid substrate for the Michael addition because it would exist as 1-naphthol.



Scheme 4.2 The CHCR retro-Cope rearrangement as a Michael addition

Double C-H functionalization of dihydronaphthalenes. An attractive feature of vinylcarbenoids is the possibility to undergo a cascade transformation. During the process of optimizing the CHCR reaction with dihydronaphthalene, a significant amount of the double C-H insertion product was formed when excess of the diazoacetate was used. Products containing four new stereogenic centers were generated with >94% de and 99% ee (Table **4.5**).[169] To force the double C-H insertion reaction to completion, a methoxy group was introduced to the 6-position of naphthalene in order to facilitate the benzylic C-H insertion. This is an effective method for functionalizing two adjacent C-H bonds in a highly diastereoselective and enantioselective fashion.

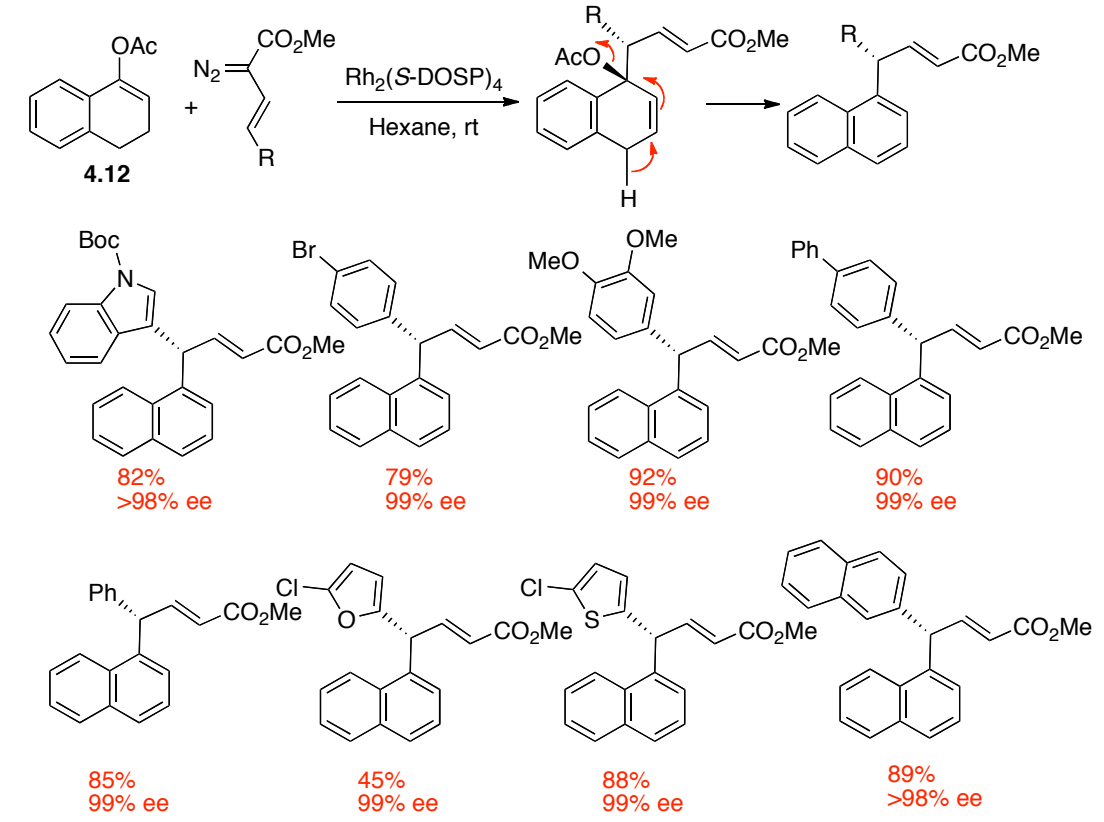
Table 4.5 Double C-H functionalization with dihydronaphthalenes



4.1.5 CHCR reaction followed by elimination

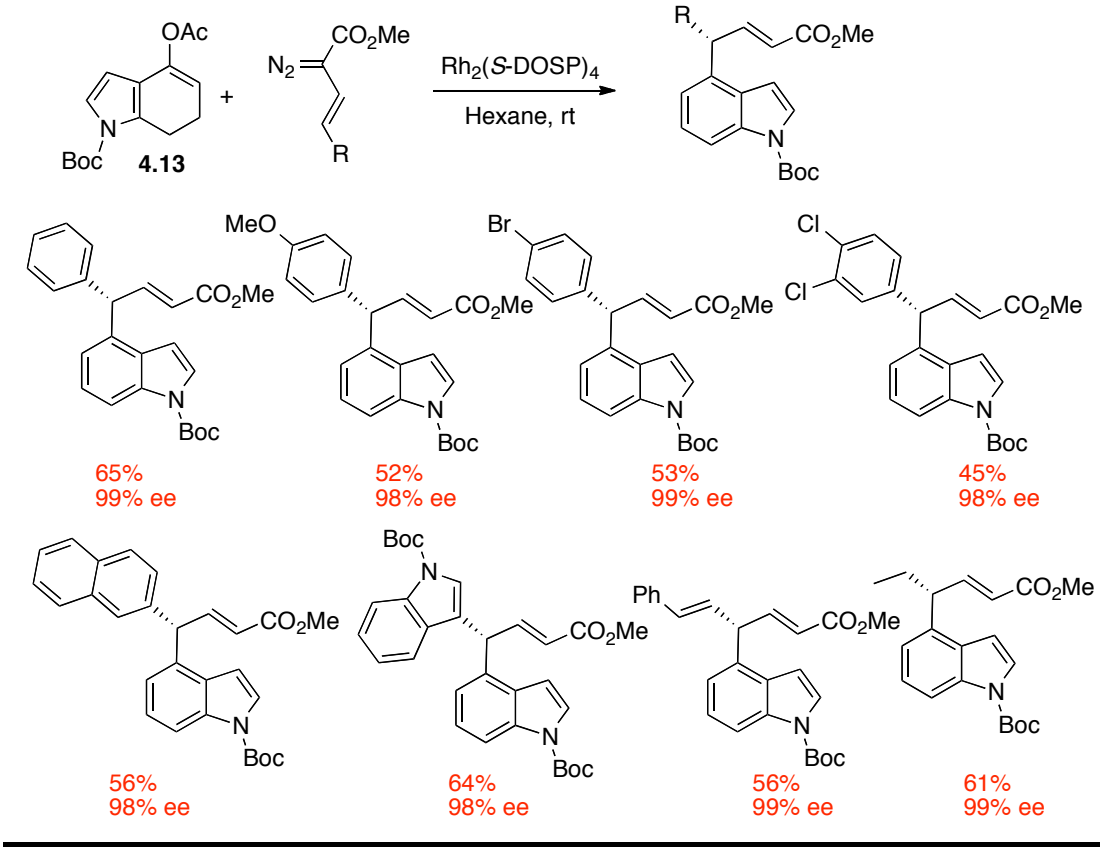
Tandem reactions are of intense interest in the organic chemistry community because they can rapidly generate structural complexity.[158] It was envisioned that performing the CHCR reaction using substrates containing a leaving group at a suitable location could lead to a subsequent elimination. It was proposed that such a process could be promoted by aromatization to generate new substituted aromatic rings. Indeed, the reaction of 4-acetoxy-1,2-dihydronaphthalene **4.12** with a variety of vinyldiazoacetates effectively afforded 1,1-diarylalkyl derivatives in a highly enantioselective maner (Table **4.6**).[170] The mechanism of this transformation is considered to be a CHCR reaction followed by elimination of acetic acid to generate butenoate derivatives. The absolute stereochemistry of the products is consistent with the predicted outcome from a *s-cis*/chair transition state.

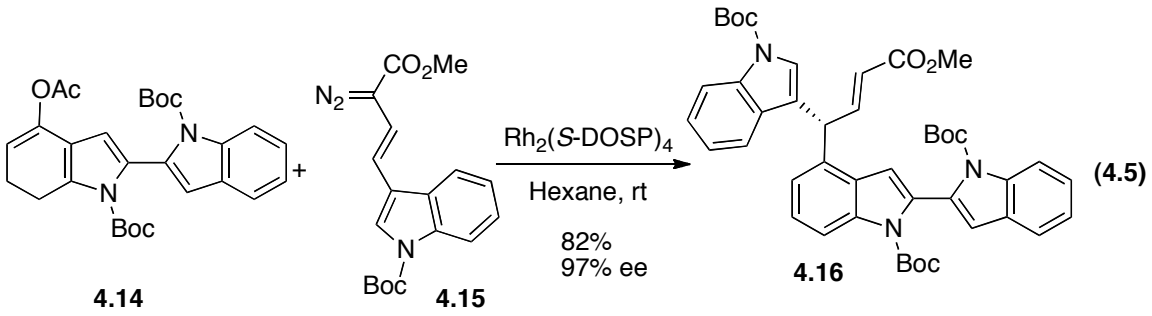
Table 4.6 Asymmetric synthesis of 1,1-diarylalkyl derivatives



A second application of this strategy is the synthesis of 4-substituted indoles from a single 4-acetoxy-6,7-dihydroindole precursor **4.13** (Table **4.7**).[147] These examples are particularly interesting since the 4-position of indoles is difficult to be selectively functionalized by traditional methods. An excellent illustration of this strategy is the reaction between bisindole **4.14** and 3-indolylvinyldiazoacetate **4.15**, which generated the trisindole derivative **4.16** in 82% yield and 97% ee (eq. **4.5**).[147] The successful outcome of this reaction underscores the facility of the CHCR reaction because indole moieties are generally reactive in carbenoid chemistry. These indole derivatives could be further converted into 1-naphthyl and 4-indoyl arylalkylamines, and these compounds are of therapeutic interest because they are selective monoamine reuptake inhibitors.[171]

Table 4.7 Asymmetric synthesis of 4-substituted indoles

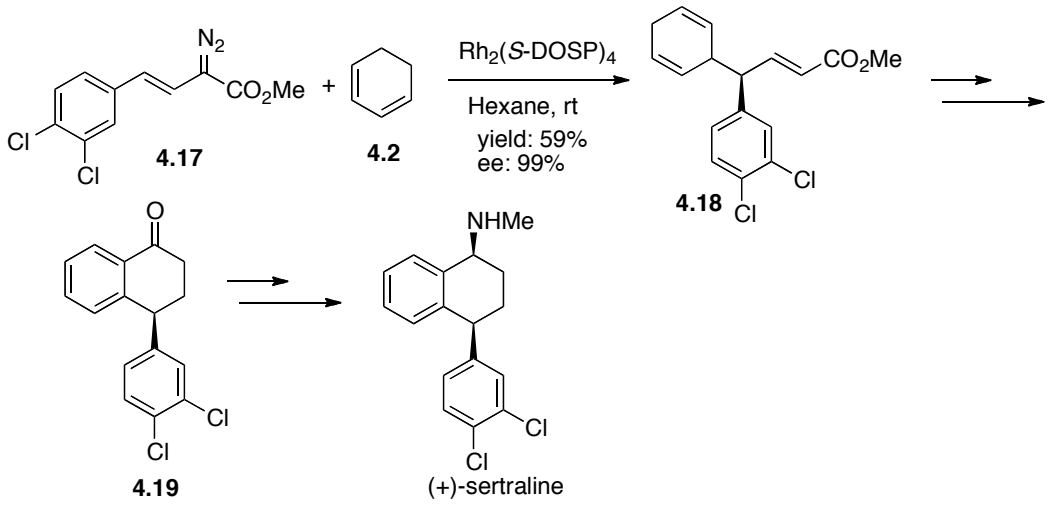




4.1.6 Enantiodifferentiation and application in the syntheses of complex molecules

The CHCR reaction has been demonstrated to be extremely useful in the synthesis of complex natural products and pharmaceutical targets. The first illustration using the

CHCR reaction to generate a significant target was the short formal synthesis of the antidepressant (+)-sertraline (Scheme **4.3**).[164] The Rh_2(*S*-DOSP)$_4$-catalyzed reaction of vinyldiazoacetate **4**.**17** with 1,3-cyclohexadiene **4**.**2** generated 1,4-cyclohexadiene **4**.**18** in 59% yield with 99% ee. Compound **4**.**18** was subsequently converted in a four-step sequence to the 4-aryltetralone **4**.**19**, which is a known precursor for the total synthesis of (+)-sertraline.



Scheme 4.3 The formal synthesis of (+)-sertraline

Dihydronaphthalene derivatives are excellent substrates for the CHCR reaction.[47] The Davies group demonstrated that this type of substrates could be used in a kinetic differentiation reaction. The reaction of racemic dihydronaphthalene **4**.**20** with diazoacetate **4**.**21** in the presence of Rh_2(*S*-DOSP)$_4$ resulted in a kinetic resolution of the starting material, in which the (*R*)-enantiomer of the substrate selectively underwent the CHCR reaction. The (*S*)-enantiomer could not achieve the necessary chair transition state for the CHCR reaction and consequently underwent cyclopropanation of the double bond, as this reaction avoided the steric repulsion of the methyl group with the rhodium complex (Figure **4.4**).[47] The CHCR product **4**.**22** containing three stereogenic centers was

generated in a single step with high asymmetric induction. An equal amount of the cyclopropanation product **4.23** was also isolated with excellent enantioselectivity. This model substrate demonstrates that an excellent enantiodifferentiation can be achieved in the CHCR reaction.

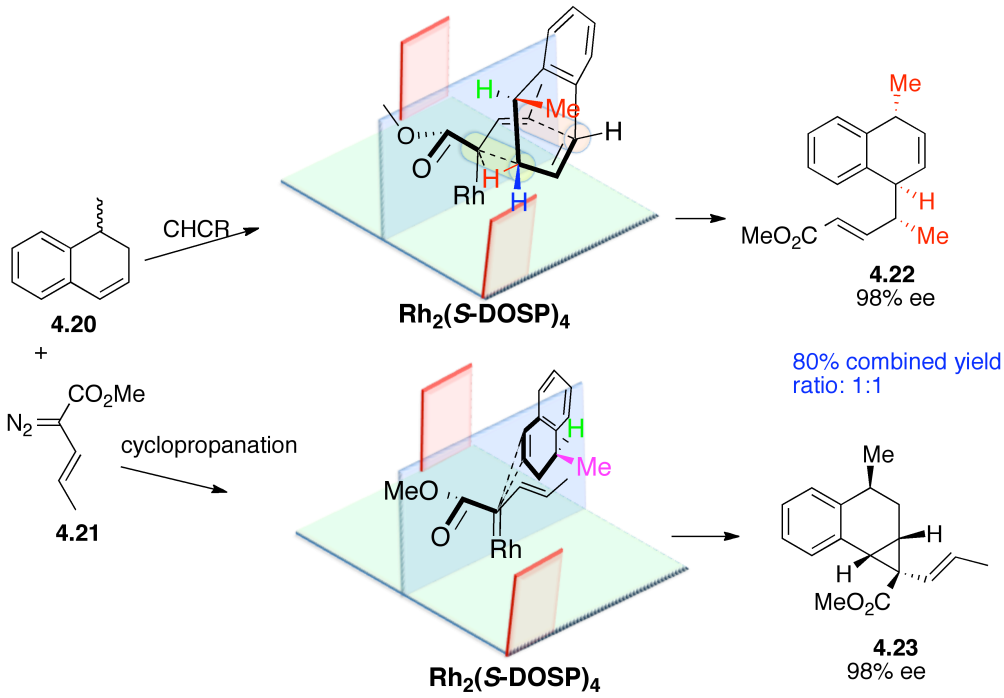
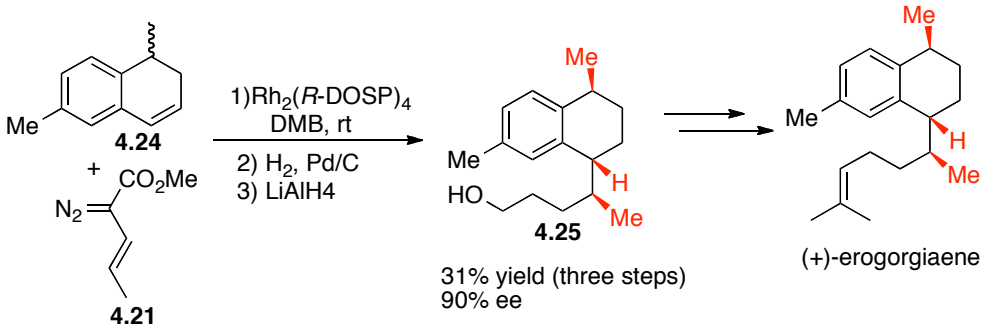


Figure 4.4 Enantiodifferentiation of racemic dihydronaphthalene

Intrigued by the successful enantiodifferentiation of the model substrate in the CHCR reaction, the Davies group then applied this strategy to more elaborate substrates and completed the total syntheses of a family of marine diterpene natural products isolated from *Pseudopterogorgia elisabetha*. The concise synthesis of (+)-erogoigiaene represents a general approach to this class of diterpenes.[47] The Rh_2(*R*-DOSP)$_4$-catalyzed reaction of diazoacetate **4.21** with racemic naphthalene **4.24** generated an inseparable 1:1 mixture of the desired CHCR product and the corresponding cyclopropane (Scheme **4.4**). The mixture was consequently subjected to hydrogenation and reduction to yield the alcohol

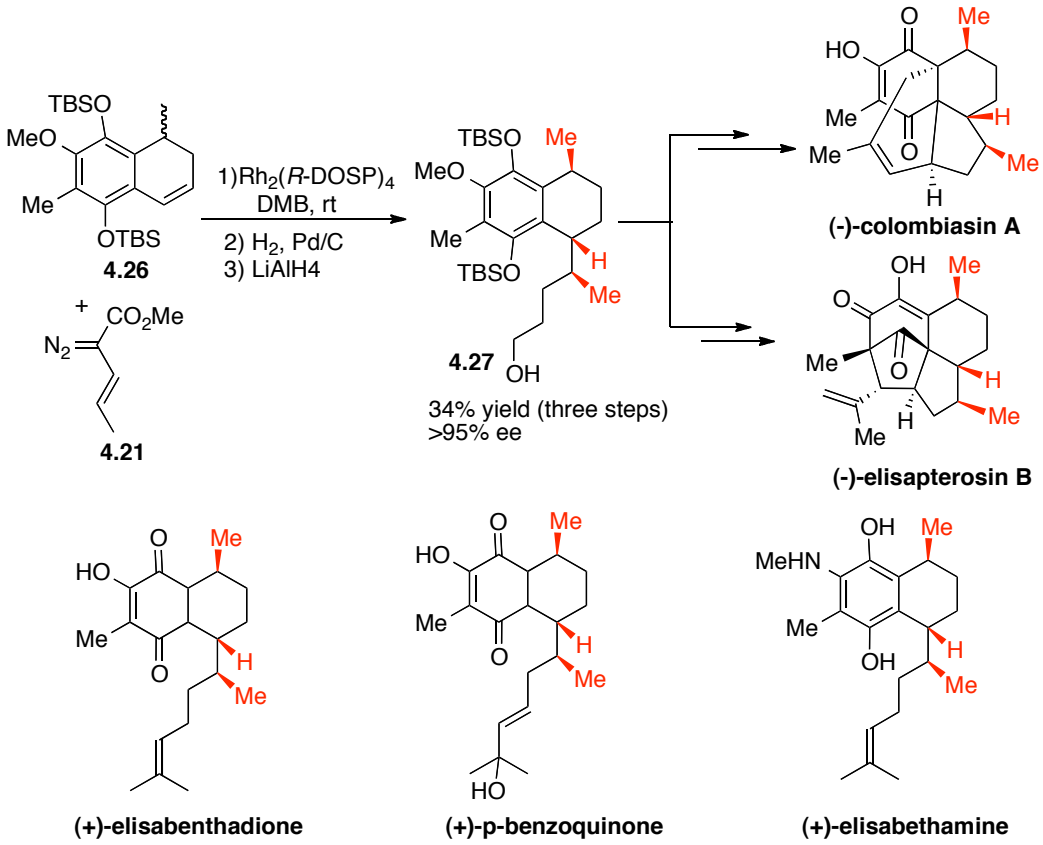
4.25 in 34% yield with good enantioselectivity. The completion of the total synthesis was readily achieved by oxidation of the alcohol to an aldehyde followed by a Wittig reaction. This remarkable total synthesis was accomplished within 10 days and highlights the power of the CHCR reaction in synthesizing complex molecules.[47]



Scheme 4.4 The total synthesis of (+)-erogorgiaene

This enantiodifferentiation reaction has also been extended to more complex systems as demonstrated in the total syntheses of (-)-colombiasin **A** and (-)-elisapterosin **B** (Scheme **4.5**).[168] The CHCR reaction is applicable to highly functionalized dihydronaphthalenes such as compound **4.26**. Once again, excellent enantiodifferentiation has been achieved. The concise synthesis has also offered the opportunity to aid in possible structural reassignments of some diterpenes in the family.[172,173] With compound **4.27** in hand, the synthesis of the assigned structure of (+)-elisabethadione was readily achieved using conventional methods. Interestingly, it was determined that the synthetic product did not match the original reported spectroscopic data isolated from natural source. During the attempt to resolve this discrepancy, another natural product (+)-*p*-benzoquinone was also synthesized and the spectroscopic data was consistent with the reported data. This implied that either the structure of (+)-elisabethadione was misassigned or there were errors in the reported spectral data. The study also raised doubts about the assigned

structure of (+)-elisabethamine because the aminohydroquinone structure is known to be very sensitive to air. Indeed, the synthetic elisabethamine readily converted to a corresponding quinone derivative.

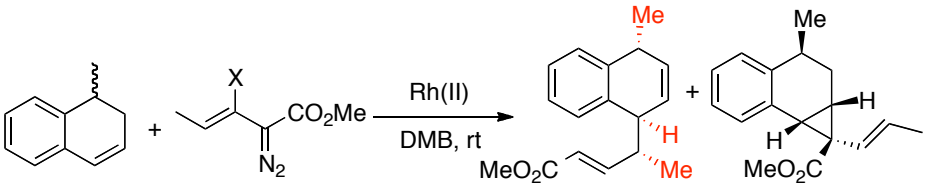


Scheme 4.5 The total synthesis of several diterpene natural products

Having demonstrated the dramatic success of the dihydronaphthalene system in the CHCR reaction and its applications to total synthesis, systematic studies have been focused on understanding the controlling influences on the CHCR reaction. Three parameters have been evaluated, including the catalyst, the vinyldiazoacetate and the dihydronaphthalene (Table **4.8**).[27] The studies demonstrate that diazoacetate **4.21** with Rh_2(*S*-DOSP)$_4$ and siloxyvinyldiazoacetate **4.28** with Rh_2(*S*-PTAD)$_4$ are the best combinations for achieving the most effective enantiodifferentiation reaction between the

cyclopropanation and the CHCR reaction in these systems. The combination of diazoacetate **4.21** with Rh_2(*S*-PTAD)$_4$ favors cyclopropanation with low asymmetric induction, while siloxyvinyldiazoacetate **4.28** with Rh_2(*S*-DOSP)$_4$ favors the CHCR reaction but the reaction does proceed with good enantioselectivity.

Table 4.8 CHCR reaction between dihydronaphthalene and two vinylcarbenoids



entry	X	Rh(II)	ratio	ee(%)		combined yield (%)
				a	**b**	
1	H, **4.21**	Rh_2(*S*-DOSP)$_4$	1:1	94	74	72
2	H, **4.21**	Rh_2(*S*-PTAD)$_4$	1:7	-40	-34	42
3	OTBS, **4.28**	Rh_2(*S*-DOSP)$_4$	3:1	86	53	58
4	OTBS, **4.28**	Rh_2(*S*-PTAD)$_4$	1:1	88	96	90

4.1.7 Computational modeling of the CHCR reaction

Although a chair transition state model has been proposed to rationalize the stereochemical outcome of the CHCR reaction, a detailed understanding of the process was lacked. A combination of experimental results and theoretical calculations has been utilized to gain a deeper understanding of this reaction.[46] Computational studies indicate that the mechanism of the reaction involves a concerted but highly asynchronous, hydride-transfer/C-C bond formation transition state, in which no C-C bond forms and the terminal C-C bond forms before a zwitterionic intermediate is generated (Figure **4.5**).

This transition state is consistent with the earlier calculation on the direct C-H insertion of donor-acceptor carbenoids, where has also been shown to involve the hydride-transfer at the initial stage.[63]

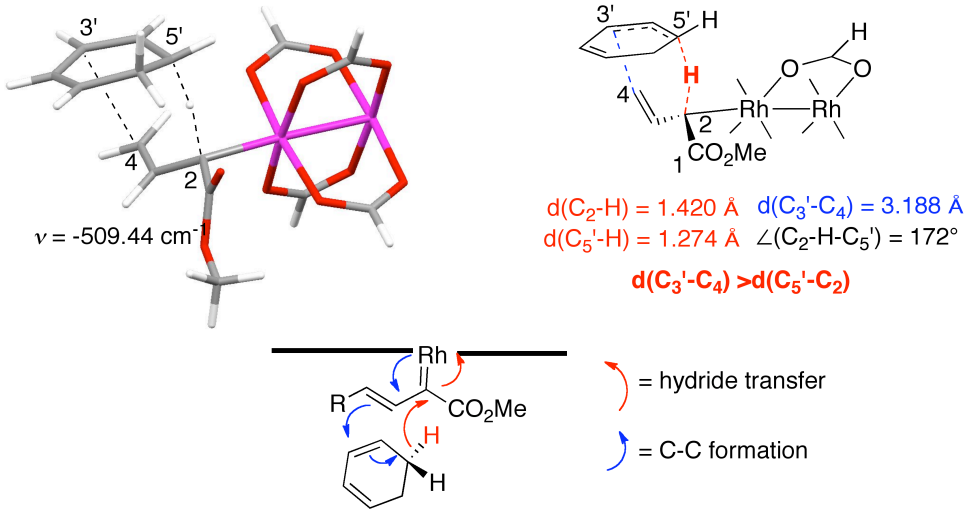
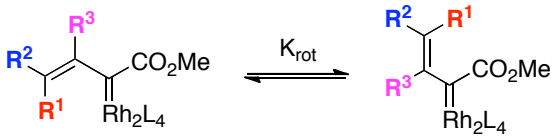


Figure 4.5 Most stable TS structure and geometrical characteristics

Considering the importance of vinylcarbenoid structures on the stereochemical outcome of the CHCR reaction, a computational calculation was conducted to investigate the equilibrium between *s-trans* and *s-cis* conformers of vinylcarbenoids (Table **4.9**).[46] It was found there was a small preference favoring the *s-trans* conformer over the *s-cis* conformer of (*E*)-methylvinylcarbenoid **4.21** (-0.2 kcal/mol) and the rotation energy is only 1.40 kcal/mol. This calculation indicates that a Curtin-Hammett situation is likely to be present in the CHCR reaction of (*E*)-vinylcarbenoids. (*Z*)-vinylcarbenoids prefer to exist in the s-*trans* conformer and internally substituted vinylcarbenoids prefer to exist in the s-*cis* conformer.

Table 4.9 Influence of substitution on conformational preference



s-*cis* s-*trans*

Entry	R^1	R^2	R^3	ΔG_{rot} (kcal/mol)	K_{rot}
1	H	H	H	-0.59	2.74
2	H	Me	H	-0.20	1.40
3	H	H	Me	+1.78	0.049
4	Me	H	H	-3.63	462
5	H	Ph	H	-0.12	1.22

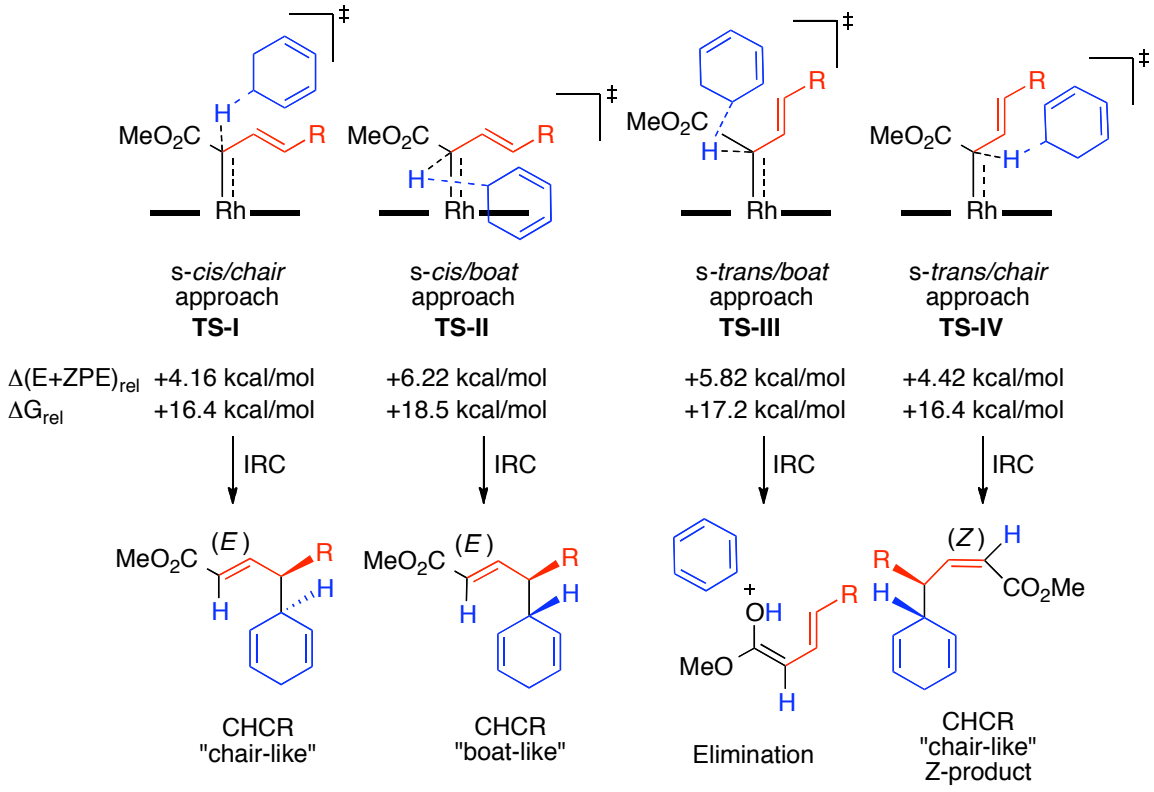


Figure 4.6 Forward intrinsic reaction coordinate analysis

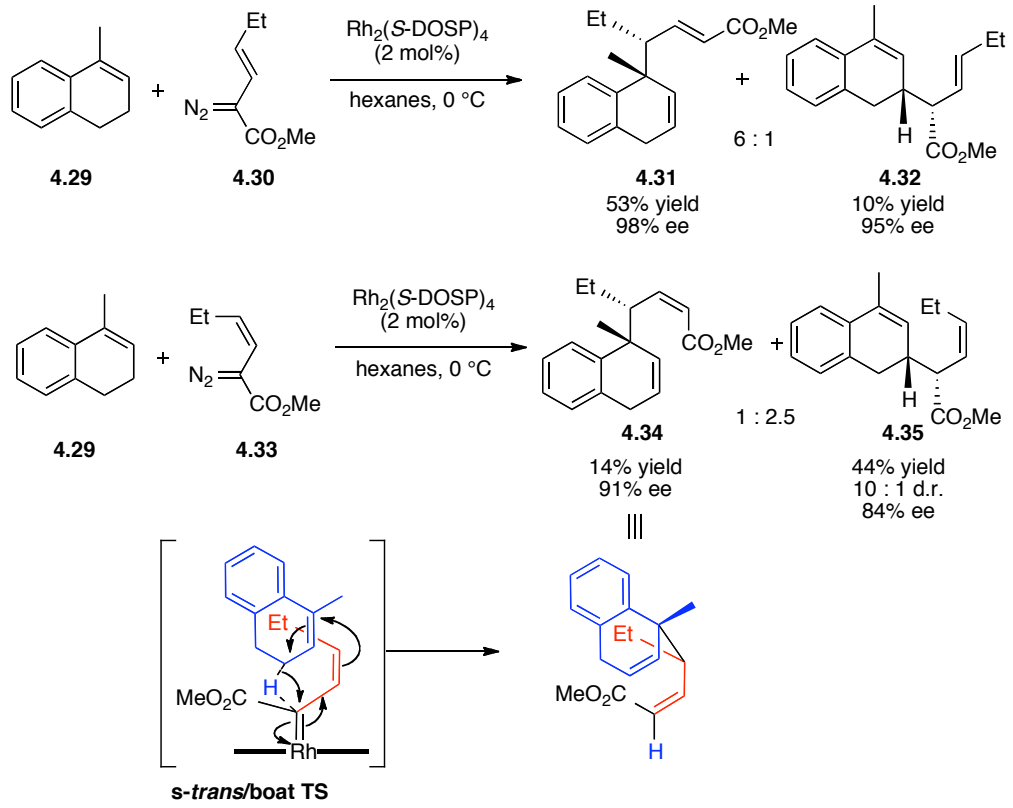
Four combinations of vinylcarbenoid conformations (*s-cis*/*s-trans*) and substrate orientations (boat/chair transition states) gave rise to distinct pathways in the CHCR reaction with 1,3-cyclohexadiene as shown in Figure **4.6**. Their energies (E + ZPE) and Gibbs free energies relative to free carbenoid and substrate were calculated. The *s-cis*/chair approach is the most stable transition state and gives a predicted product consistent with experimental results.[164] However, alternative orientations are also energetically feasible and only slightly less favored, owing to the small energetic difference. The studies indicate that it may be possible to enhance the diastereoselectivity of the CHCR reaction by accessing the other energetically reasonable transition states.

4.2 Results and discussion

4.2.1 Substrate designed to access other transition states

We decided to test the hypothesis that other transition states may be accessible in the CHCR reaction by changing the steric requirements of the substrates. As a test substrate, we decided to use 1-methyldihydronaphthalene **4.29**, known to be effective in the CHCR reaction.[48] The reaction between **4.29** and **4.30** catalyzed by Rh_2(*S*-DOSP)$_4$ in hexane led to two isolated products, the predicted CHCR product **4.31** and the direct C-H insertion product **4.32** in a 6:1 ratio (Scheme **4.6**).[48] The CHCR product **4.31** was formed in 53% yield with 98% ee, and the stereochemistry is consistent with the *s-cis*/chair predictive model. The C-H insertion product **4.32** is likely derived from the direct C-H insertion reaction in this case. No change in the ratio of **4.31/4.32** was observed when the reaction was extended overnight. The reaction with the *Z*-vinyldiazoacetate **4.33** led to a 1:2.5

ratio of the CHCR product **4.34** (14% yield, 91% ee) to the direct C-H insertion product **4.35** (44% yield, 10:1 d.r., 84% ee for the major diastereomer). In this case, the latter product is indeed derived from a direct C-H insertion process, as the attenuated diastereo- and enantioselectivity related to the CHCR product is consistent with previous findings in the C-H insertion chemistry.

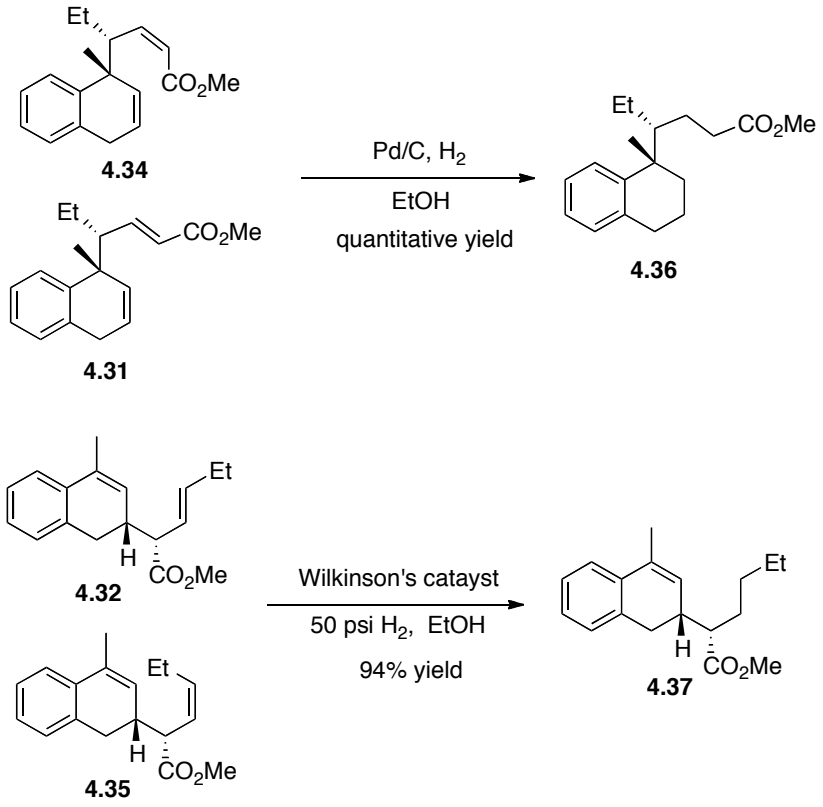


Scheme 4.6 CHCR reactions between dihydronaphthalene and two vinyldiazoacetates

Interestingly, the CHCR product **4.34** contains a *Z*-double bond, but has retained the same stereogenic centers as the product **4.31** derived from *E*-vinyldiazoacetate **4.30**. This result indicates that the formation of **4.34** proceeds through the s-*trans*/boat transition state, and demonstrates that, through appropriate vinylcarbenoid conformational control,

a “non-traditional” transition state for the CHCR reaction can be favored. This is consistent with our original hypothesis.

The absolute configuration of product **4.34** was unambiguously assigned by X-ray crystallography (Figure **4**.**7**), while the absolute stereochemistry of other products **4.31**, **4.32**, **4.34**, **4.35** was confirmed by the products derived from them as shown in Scheme **4.7**. Both CHCR products **4.31** and **4.34** were subjected to a standard hydrogenation and led to the same compound **4.36** in quantitative yield. The structure of products **4.32** and **4.35** was determined by their selective reduction in the presence of Wilkinson’s catalyst to afford the same product **4.37**. The absolute and relative configuration of the (*E*)- C-H insertion product **4.32** was assigned assuming a similar stereochemical outcome to the initiated substrate.



Scheme 4.7 Stereochemistry assignment of products **4.31**, **4.32**, **4.35**

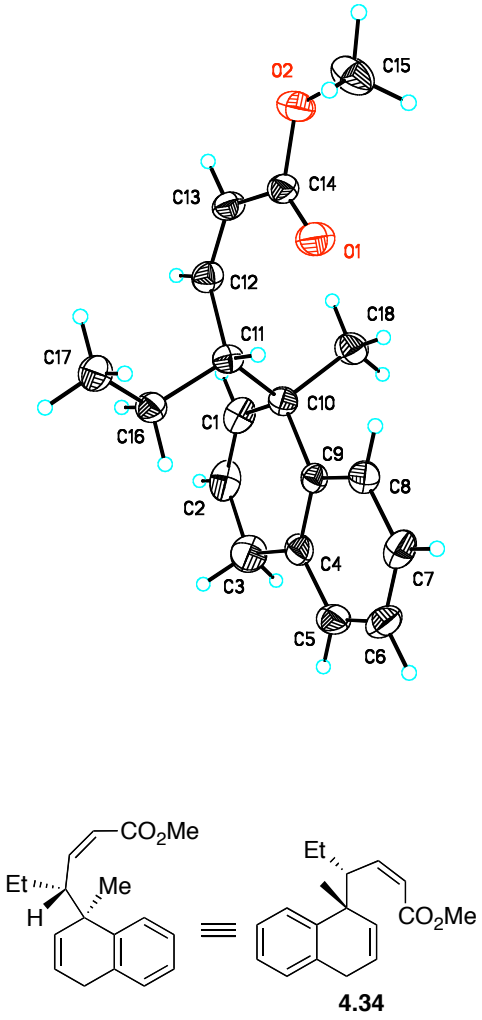


Figure 4.7 X-ray crystallographic structure of product **4.34**

4.2.2 CHCR reaction with cyclopentyl derivatives

The previous set of experiments has demonstrated that other "non-traditional" transition states are possible in the CHCR reaction. However, from a synthetic point of view, the efficiency of the described reaction was limited because the CHCR product was generated as the minor product. In addition, the stereochemistry of the two new

stereocenters is the same as the product derived from *E*-vinyldiazoacetates through a s-*cis*/chair approach. As an ongoing project, we became interested in exploring whether the opposite diastereomeric series of the CHCR products could be generated to what have been reported through the s-*cis*/chair approach.

In order to limit the number of potential transition states available for the CHCR reaction, the study described herein was conducted with *β*-siloxyvinyldiazoacetate **4.38**. Indeed, the computational calculation has shown that the vinyl carbenoid with internal substitution strongly prefers to adopt the *s-cis* configuration. In the *s-trans* configuration, the siloxy group would be pointing towards the "wall" of the catalyst (Figure **4.8**).[46]

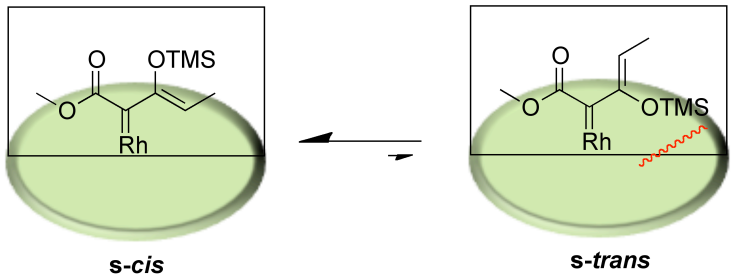
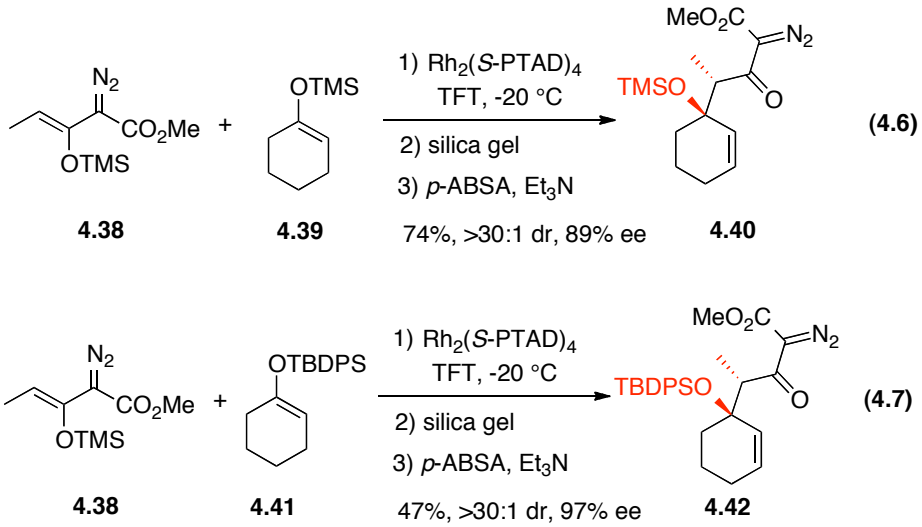


Figure 4.8 The s-*cis* and s-*trans* configurations of the rhodium carbenoid derived from **4.38**

Previous studies have shown that Rh_2(*S*-PTAD)$_4$ is the optimum chiral catalyst for asymmetric reactions with siloxyvinyldiazoacetate **4.38**.[27,103] Consequently, Rh_2(*S*-PTAD)$_4$ was selected to catalyze the reaction of the siloxycyclohexene **4.39** (eq **4.6**). Characterizable material was obtained by hydrolysis of the silyl enol ether of the crude product followed by conversion of the *β*-keto ester to the *β*-keto-*α*-diazoacetate **4.40** in 74% yield through the three-step sequence. The *β*-keto-*α*-diazoacetate **4.40** was formed as a single diastereomer with 89% ee. The extension to a more bulky siloxycyclohexene

4.41 selectively afforded the diazoacetate **4.42** with even higher enantioselectivity (97% ee) (eq. **4.7**). The relative and absolute configuration of product **4.42** was unambiguously determined using X-ray crystallography (The product was derived from Rh_2(*R*-PTAD)$_4$), while the configuration of product **4.40** was tentatively assigned on the assumption that the environment of the formation of **4.40** would be similar to **4.42** (Figure **4.9**).



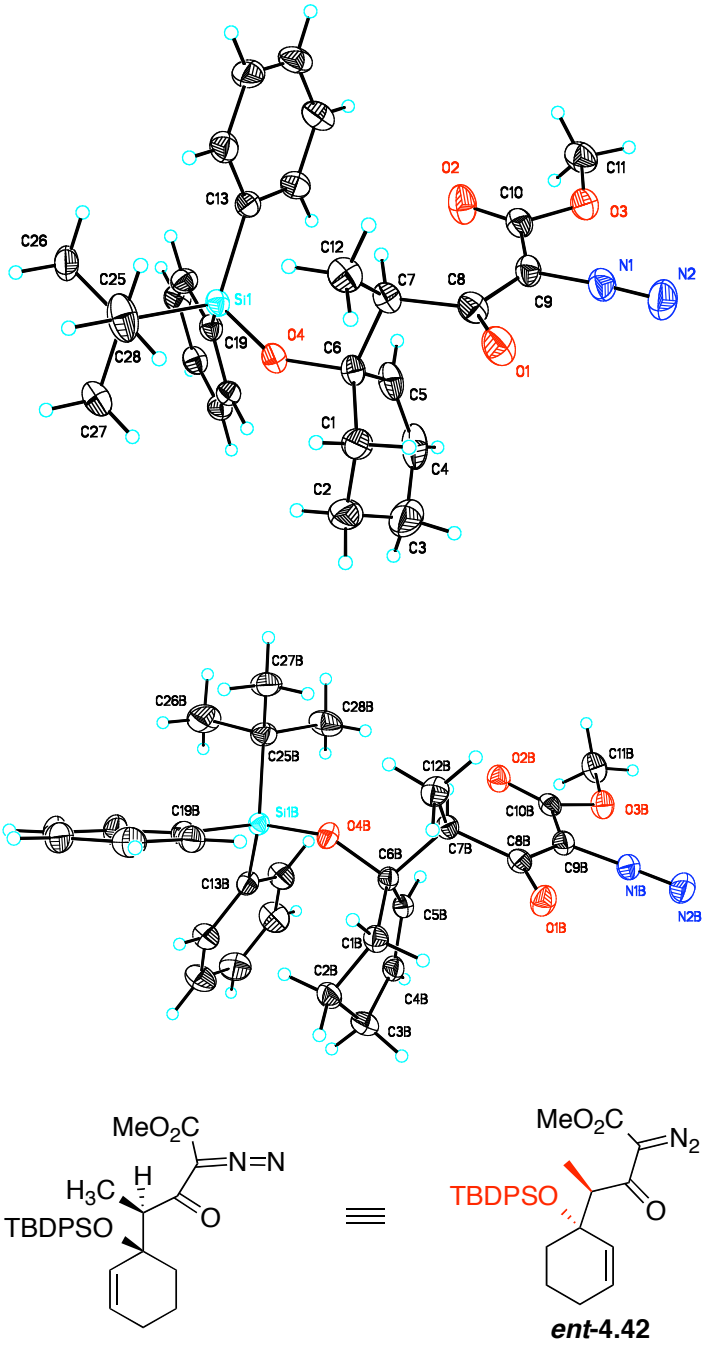


Figure 4.9 X-ray crystallographic structure of product **4.42**

The observed configuration of product **4.42** is consistent with the previously reported examples of the CHCR reaction proceeding through a chair transition state. A careful analysis of both the chair and boat possible transition states reveals that the remainder of

the cyclohexyl ring would be pointing towards the "wall" of the catalyst in the boat transition state (Figure **4.10**). Therefore, it would be reasonable to assume that this arrangement is unfavorable and thus the reaction can only proceed through an s-*cis*/chair transition state, which would generate the product as a single diastereomer.

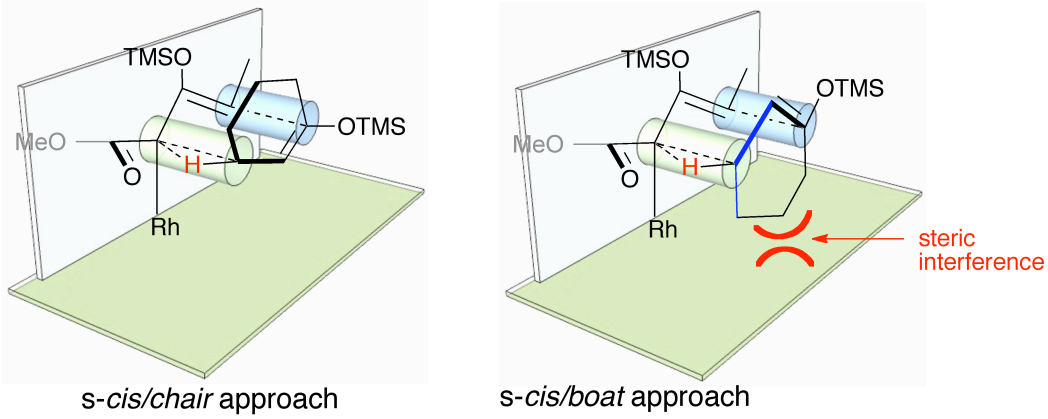
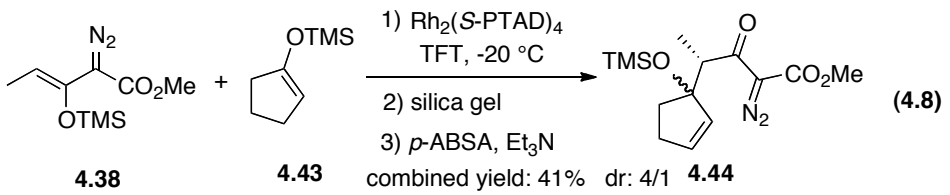


Figure 4.10 Two possible transition states with cyclohexenyl rings

Carefully analyzing the boat transition state, we rationalized that a possible way to limit the steric influence of the ring would be to use a smaller ring size such as a cyclopentenyl ring. Indeed, when the reaction was repeated with the siloxycyclopentene **4.43**, two diastereomers of the CHCR product **4.44** were produced in a 4:1 ratio (eq **4.8**). This is the first example of a CHCR reaction generating a mixture of diastereomeric products. It is reasonable to assume that the CHCR reaction proceeds through both the s-*cis*/chair and s-*cis*/boat transition states, leading to a mixture of diastereomeric products (Figure **4.11**).



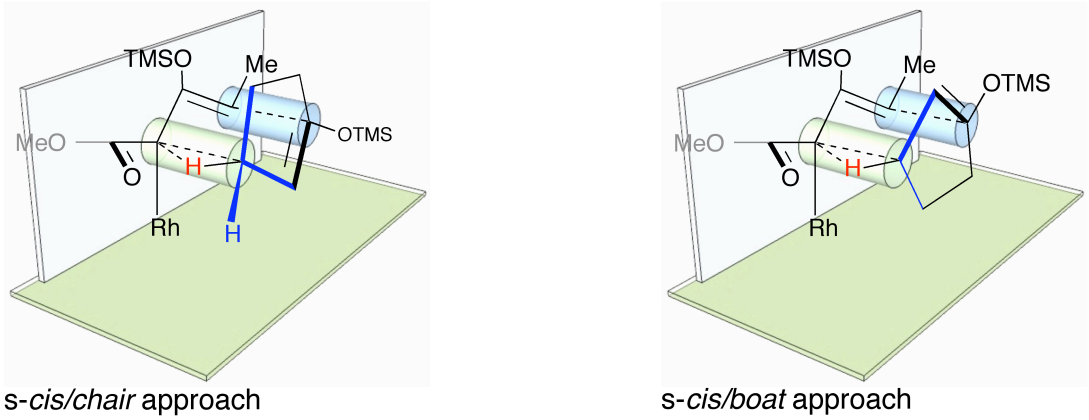


Figure 4.11 Two possible transition states with cyclopentenyl rings

The formation of **4.44** suggested that the cyclopentyl ring is small enough to be incorporated into the boat transition state. With this in mind, the next experiments explored whether a high level of diastereoselectivity can be achieved through a boat transition state *via* simple substrate modification. We further rationalized that a 2-substituent on the cyclopentenyl ring would cause the chair transition state to be destabilized and force the reaction to proceed through the boat transition state (Figure **4.12**). If this were the case, then the opposite diastereomeric series of products would become accessible in a highly diastereoselective fashion.

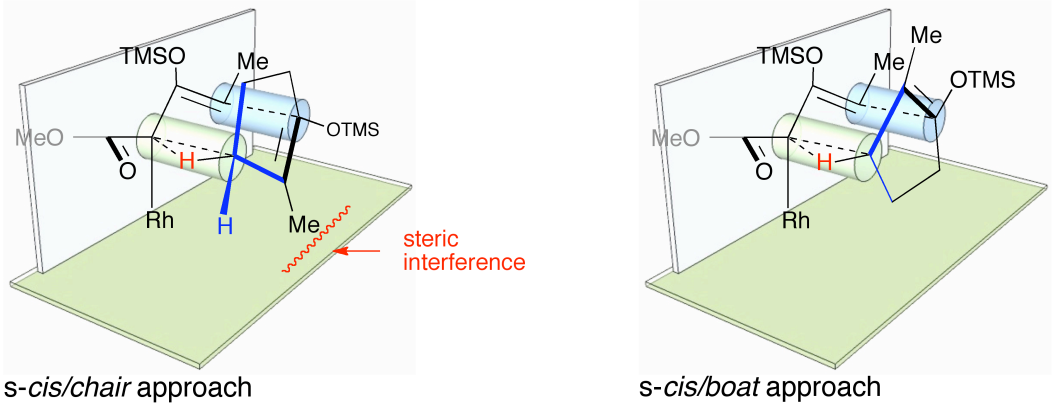
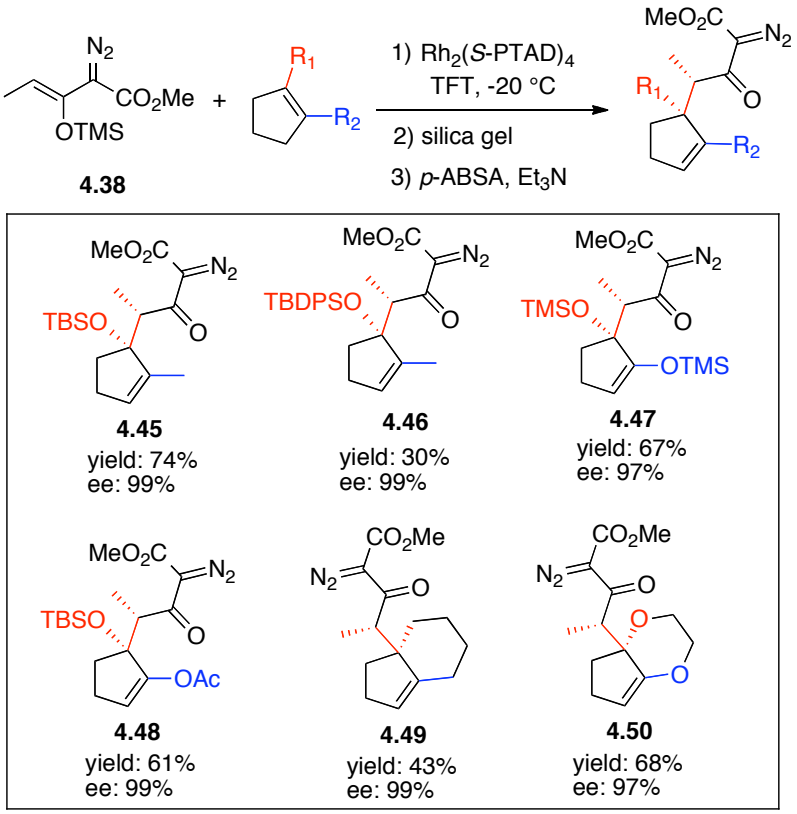


Figure 4.12 Two possible transition states with disubstituted cyclopentenes

Table 4.10 CHCR reaction with cyclopentenyl derivatives



The Rh_2(*S*-PTAD)$_4$-catalyzed decomposition of siloxydiazoacetate **4.38** in the presence of 1,2-disubstituted cyclopentenyl derivatives afforded the *β*-keto-*α*-diazoacetates **4.45**-**4.10** as summarized in Table **4.10**. In all cases, a single CHCR product was produced with excellent diastereoselectivity (dr >30:1) and enantioselectivity (>97% ee). For the reaction with the unsymmetrical cyclopentene substrates, two types of allylic C-H bonds are available. The resulting products **4.45**, **4.46** and **4.48**, are all derived from site selective C-H functionalization initiated at the methylene group allylic to the siloxy group. The result is consistent with the reaction mechanism because the CHCR reactions proceed through a hydride shift event and the siloxy group can strongly stabilize the resulting positive charge. The relative and absolute configuration of **4.46** was

unambiguously assigned by X-ray crystallography (Figure **4.13**). The stereochemical configurations of products **4.48** and **4.49** were also unambiguously confirmed by X-ray crystallography of products derived from them (see infra). In each case, the relative configuration is consistent with a reaction proceeding though a boat transition state, and is opposite to the products **4.40** and **4.42** derived from a cyclohexene derivative. The structures of other products were tentatively assigned by assuming a similar boat transition state model.

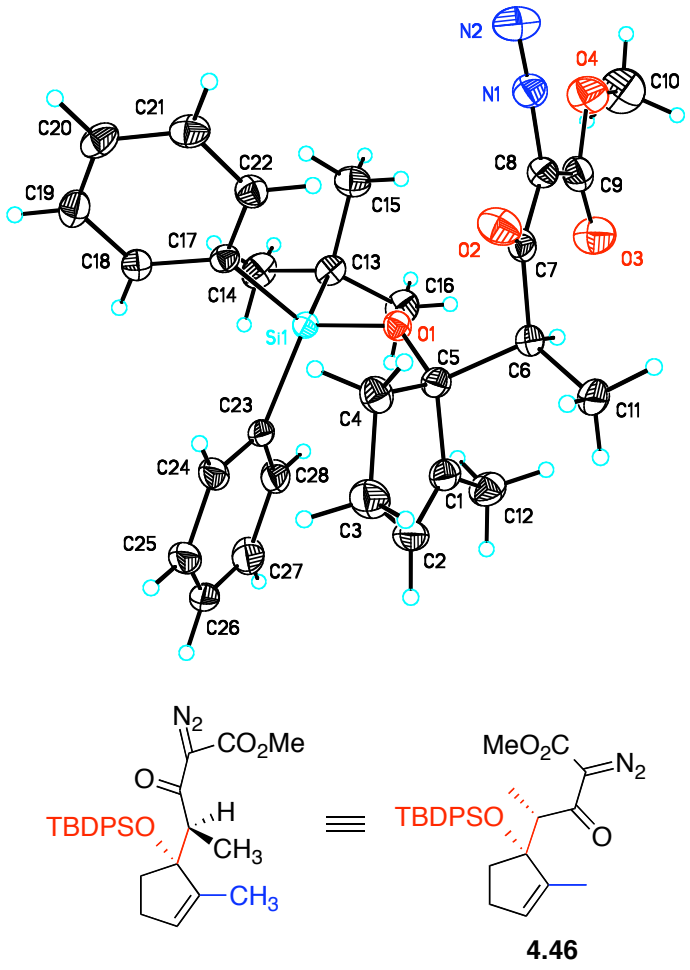


Figure 4.13 X-ray crystallographic structure of product **4.46**

Generally, the CHCR reaction is influenced by other stereogenic centers present in the substrate because of the strict chair or boat transition state and high levels of

enantiodifferentiation have been reported.[47,174] Consequently, we became interested in exploring if a desymmetrization event would be feasible in a CHCR reaction. In order to test this hypothesis, the reaction with cyclopentene **4.51** was conducted. It successfully generated product **4.52** as a single diastereomer with extremely high enantioselectivity (eq. **4.8**). This represents the first example of desymmetrization in the CHCR reaction. The relative configuration of **4.52** inside the ring was assigned by nOe study and was consistent with the outcome predicted by a boat transition state model (Figure **4.14**), while the stereochemistry in the chain was tentatively assigned based on a similar boat transition state.

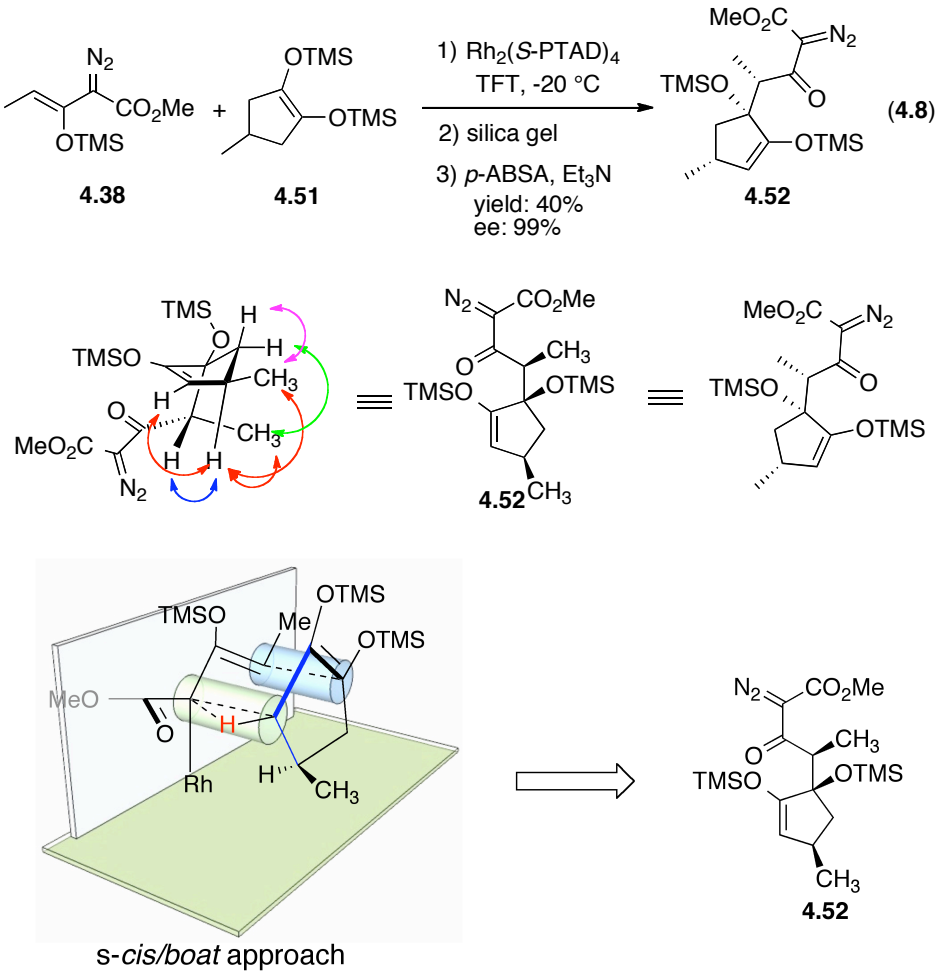
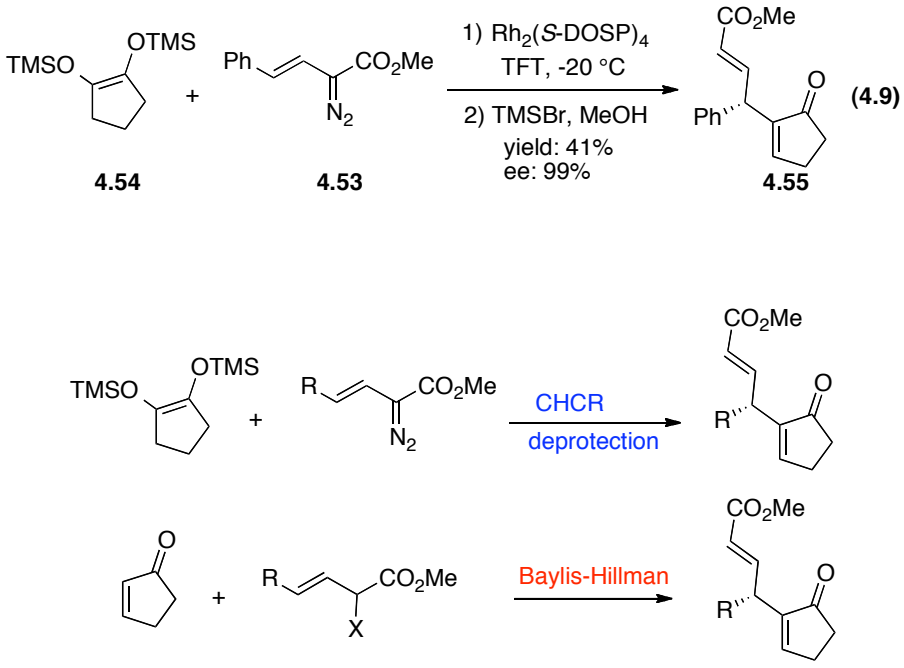


Figure 4.14 Structure and transition state for product **4.52**

The CHCR reaction *via* a boat transition state is not limited to siloxyvinyldiazoacetate **4.38**, but is also applicable to *trans*-phenylvinyldiazoacetate **4.53**. Previous studies have shown that Rh_2(*S*-DOSP)$_4$ is the optimum chiral catalyst for asymmetric reactions with *trans*-vinyldiazoacetates.[40] We decided to choose Rh_2(*S*-DOSP)$_4$ as the optimal catalyst for the reaction of vinyldiazoacetate **4.53**. The reaction with substrate **4.54** afforded the cyclopentenone **4.55** in 41% yield upon deprotection of the TMS protecting group in methanol in the presence of catalytic amount of TMSBr (eq. **4.9**). Again, a high level of asymmetric induction was observed. The absolute configuration of product **4.55** was unambiguously confirmed by X-ray crystallography (Figure **4.15**). This method would offer an alternative complementary approach to the Baylis-Hillman reaction in a highly enantioselective fashion (Scheme **4.8**).[175]



Scheme 4.8 Complementary of the CHCR reaction to the Baylis-Hillman reaction

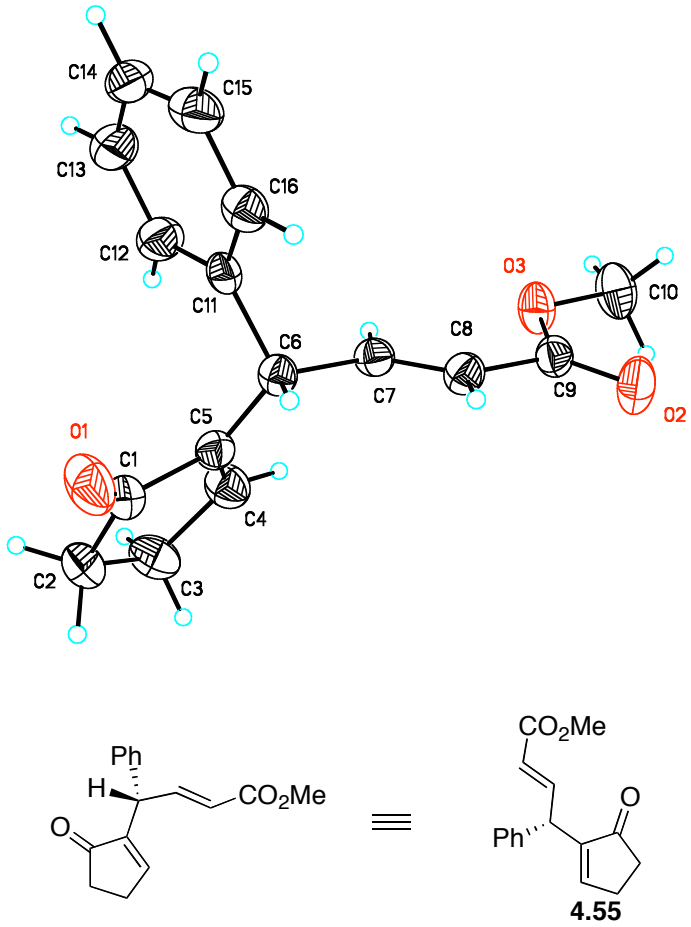
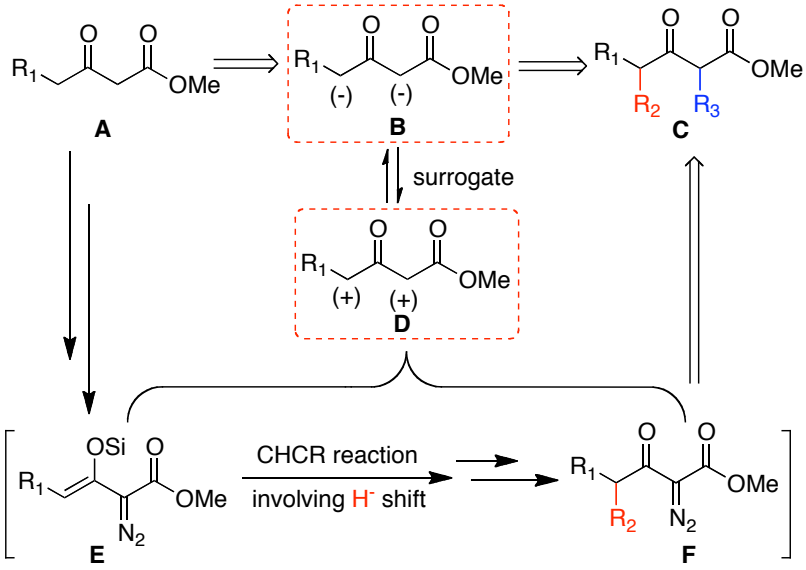


Figure 4.15 X-ray crystallographic structure of product **4.55**

Another attractive feature of this chemistry is the possibility of converting the CHCR products into β-keto-α-diazoacetates, which then could undergo a second carbenoid transformation. In this point, ketocarbenoids offer interesting opportunities in synthesis because they are electrophilic α to the carbonyl, displaying natural *umpolung* reactivity (Scheme **4.9**).[176] Together with the fact that vinylcarbenoids show electrophilicity either α or γ to the carbonyl, the CHCR reaction of siloxyvinyldiazoacetate could be used to complement the classic dianion chemistry of β-ketoester **B**. β-Keto esters are well known as precursors to monoanion and dianions, and thus are capable of reacting as mononucleophilic or dinucleophilic reagents. In contrast, the sequential carbenoid

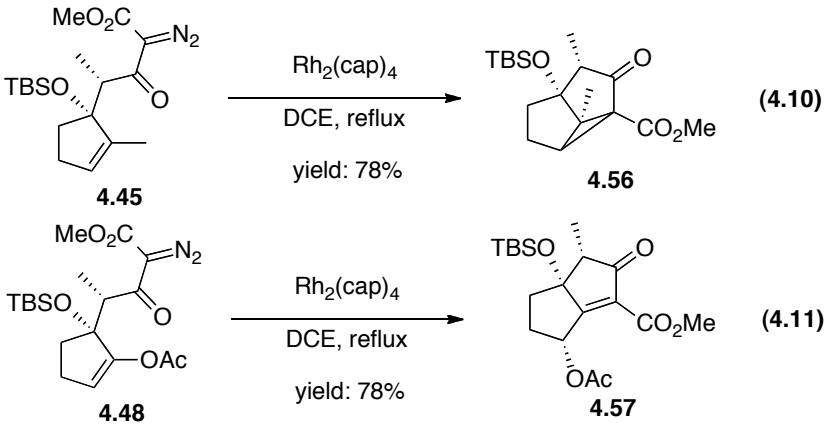
transformations cause compound **E** to behave as a dication intermediate. Therefore, the carbenoid approach enables the reversal of the reactivity profile of *β*-keto esters.

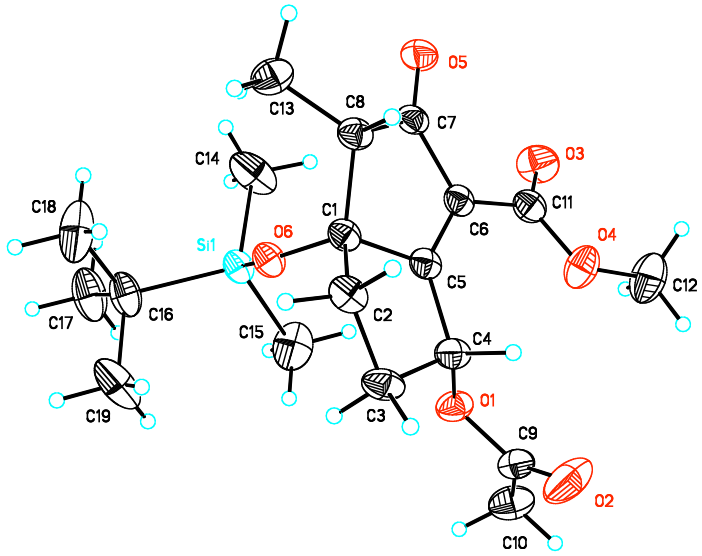


Scheme 4.9 The *β*-keto esters acting as either dianionic or dicationic precursors

To evaluate if two sequential C-H functionalization steps were feasible, a systematic study was conducted on the intramolecular reaction of the *β*-keto-*α*-diazoacetates derived from the intermolecular CHCR reaction. $Rh_2(cap)_4$ is the optimum catalyst for the intramolecular reaction of ketodiazoacetates and was selected to catalyze the second carbenoid transformation.[177] The outcome of the second diazo decomposition was quite variable, illustrating the subtle structural influence on the reactivity. Decomposition of diazoacetate **4.45** in the presence of $Rh_2(cap)_4$ in dichloroethane under reflux selectively afforded the cyclopropanation product **4.56** in good yield (eq **4.10**). However, in the reaction of **4.48** where a methyl group has been replaced by an acetate group, an unexpected product **4.57** was produced, involving a migration of the acetate group (eq

4.11). The structure of **4.57** was unambiguously confirmed by X-ray crystallography (Figure **4.16**).





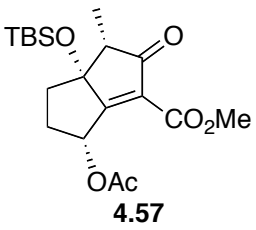
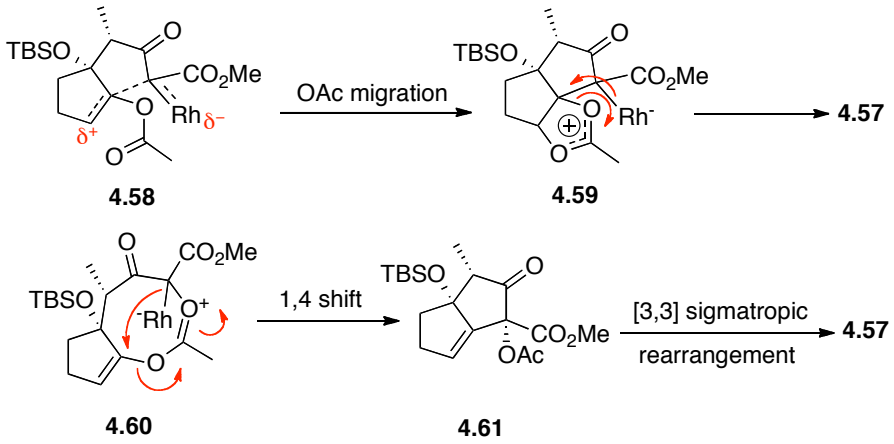


Figure 4.16 X-ray crystallographic structure of product **4.57**

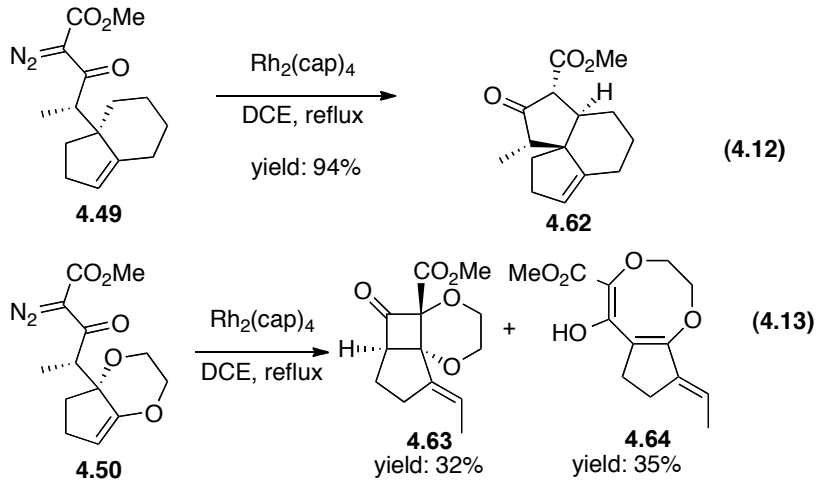
Two plausible mechanisms are proposed to explain this unusual reactivity (Scheme **4.10**). Rhodium-carbenoid-induced cyclopropanation is considered to proceed *via* a concerted non-synchronous process. One mechanistic possibility would be the formation of a zwitterionic-like structure **4.58**. This process is interrupted by an acetate migration to stabilize the positive charge and to form a second zwitterionic intermediate **4.59**. Elimination of the rhodium catalyst from **4.59** followed by acetate migration would generate **4.57** directly. The second possible mechanism would involve the formation of ylide **4.60** at the initial step, which would then undergo a 1,4 shift to generate another intermediate **4.61**. Finally, a [3,3] sigmatropic rearrangement would proceed to afford the more thermodynamically stable product **4.57**.

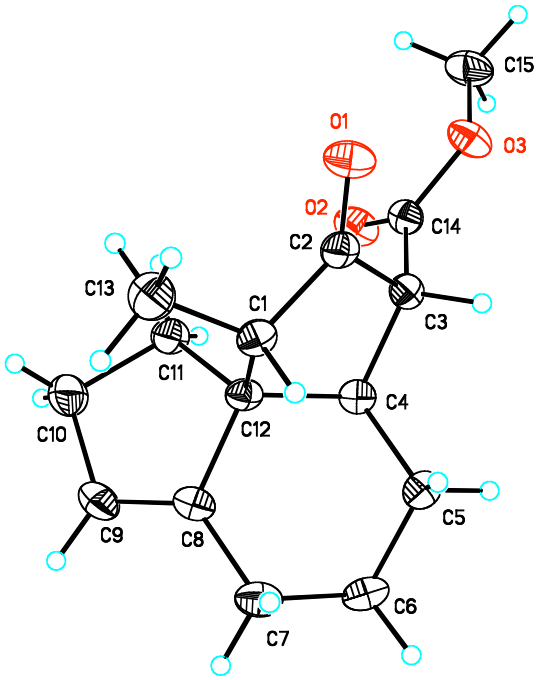


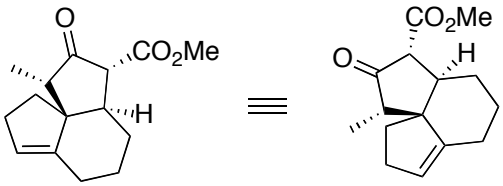
Scheme 4.10 Two possible mechanisms for the formation of compound **4.57**

Conducting the reaction with bicyclic diazo compounds also gave interesting results. The $Rh_2(cap)_4$-catalyzed decomposition of compound **4.49** afforded a fused [5,6,5] ring system **4.62** in excellent yield via the second C-H functionalization of cyclohexyl ring. Interestingly, the product is formed as a single diastereomer exclusively and only the keto tautomer was observed (eq **4.12**). The structure of the product **4.62** was unambiguously

assigned by X-ray crystallography (Figure **4.17**). Of particular interest is the high regioselectivity of this transformation because the C-H bond of cyclohexyl ring is only slightly more reactive than the C-H bond of cyclopentyl ring in the intermolecular carbenoid-induced C-H functionalization reaction.[178] When the active carbon was replaced with an oxygen, the reaction outcome of **4.50** under the same condition was quite different, resulting in the formation of a cyclobutane derivative **4.63** and a fused medium ring product **4.64** in about a 1 : 1 ratio (eq. **4.13**). Even though **4.50** was highly enantioenriched, cyclobutane derivative **4.63** was produced as a racemic mixture. Again, the structure of both of these two products was confirmed by X-ray crystallography (Figure **4.18** and **4.19**).







4.62

Figure 4.17 X-ray crystallographic structure of product **4.62**

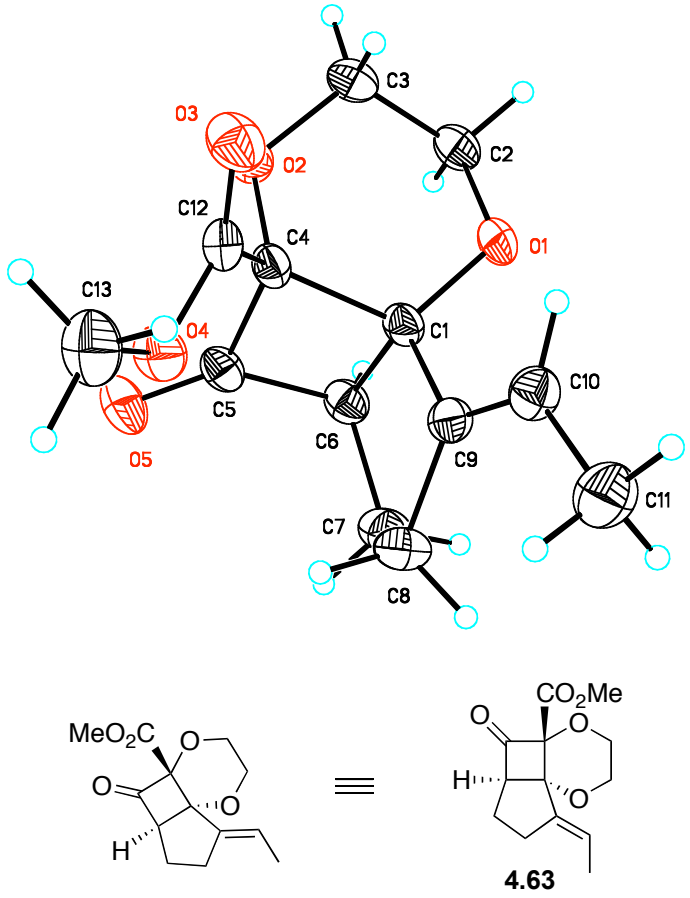


Figure 4.18 X-ray crystallographic structure of product **4.63**

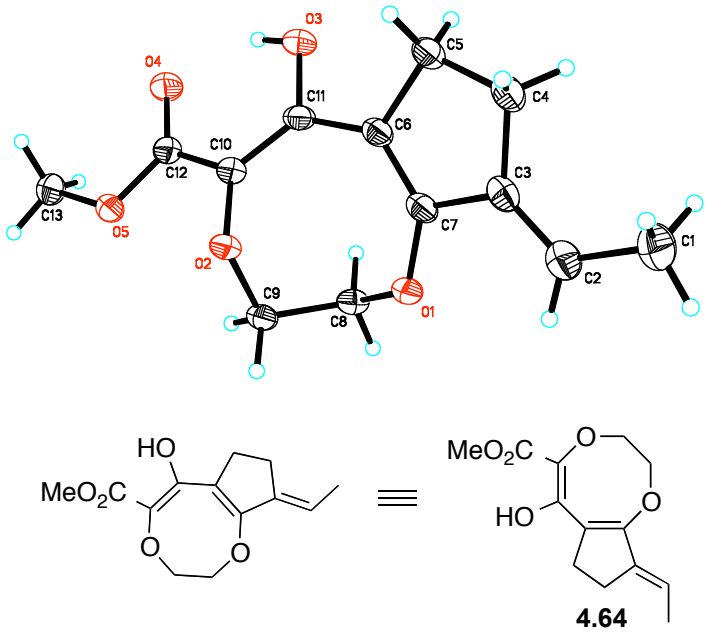
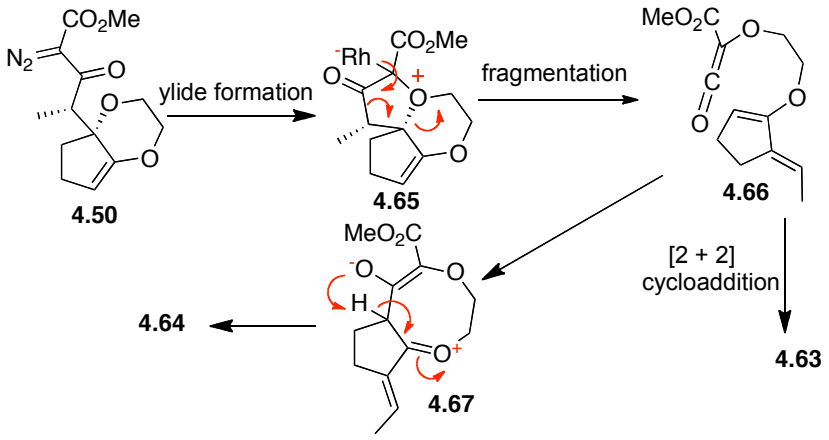


Figure 4.19 X-ray crystallographic structure of product **4.64**

A reasonable mechanism is proposed to explain the formation of products **4.63** and **4.64** as shown in Scheme **4.11**. It is hypothesized that the carbenoid carbon would be readily trapped by the ether group to form ylide **4.65**,[179,180] which would undergo a novel fragmentation reaction as described to produce ketene **4.66**. This ketene would undergo either a [2 + 2] cycloaddition to produce **4.63** as a single diastereomer, or a stepwise reaction to generate compound **4.64**. The formation of achiral ketene intermediate **4.66** is supported by the evidence that compound **4.63** was isolated as a racemic mixture, even though the diazoacetate **4.50** was enantiomerically pure.



Scheme 4.11 Proposed mechanism for decomposition of diazoacetate **4.50**

In conclusion, an effective CHCR reaction proceeding through a boat transition state has been developed. The design of suitable substrates for this study was guided by a recent computational analysis of the CHCR reaction. The products are readily converted to β-keto-α-diazoacetates, which undergo a range of intramolecular transformations. These include cyclopropanation, C–H functionalization, cyclization/acetate transposition, and ylide formation/ ylide fragmentation/[2 + 2] cycloaddition.

4.2.3 CHCR reaction with vinyl ethers

We have successfully demonstrated that careful evaluation of the transition state in the CHCR reaction would enable us to develop the CHCR reaction through a boat transition state with cyclopentenyl derivatives. Further evaluation of the s-*cis*/boat transition state model led us to the hypothesize that acyclic trisubstituted vinyl ethers might be ideal substrates for the CHCR reaction because it was anticipated that steric repulsion with the catalyst "wall" would be avoided in a s-*cis*/boat transition state (Figure **4.20**). If this were indeed the case, the scope of the CHCR reaction would be greatly broadened because vinyl ethers are readily accessible from the corresponding ketones *via* the Wittig reaction.[181]

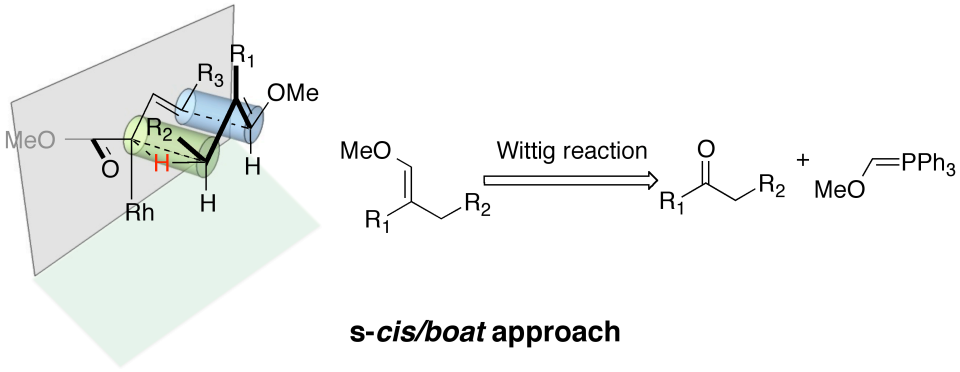
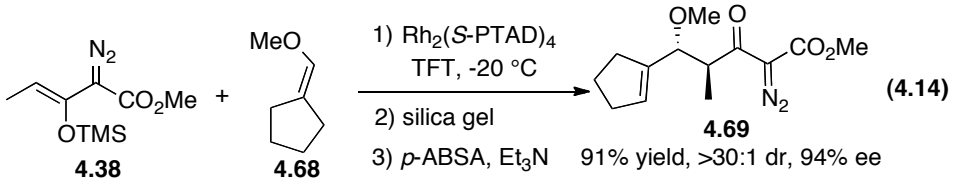


Figure 4.20 Rationalization of substrate design

In order to test the hypothesis presented above, the Rh_2(*S*-PTAD)$_4$-catalyzed decomposition of siloxyvinyldiazoacetate **4.38** with vinyl ether **4.68** was examined (eq. **4.14**). The reaction generated diazoacetate **4.69** in excellent yield with high stereocontrol. Even though the siloxyvinyldiazoacetate **4.38** is one of the best vinylcarbenoid precursors with regard to favoring the CHCR reaction over a direct C-H insertion reaction, the formation of **4.69** in 91% yield is much higher than the yields obtained in the previous

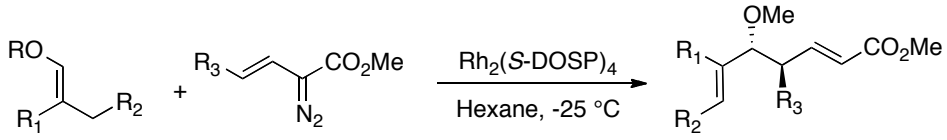
study using cyclopentene substrates. This remarkable reaction outcome indicates that vinyl ethers may be excellent substrates favoring the CHCR reaction over the direct C-H functionalization reaction.

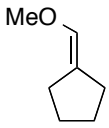
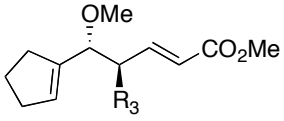
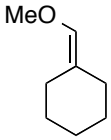
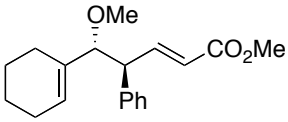
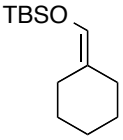
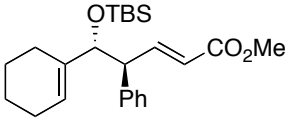
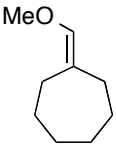
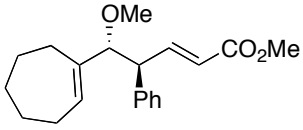
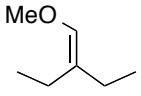
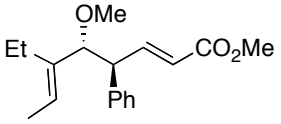


With the success of reaction **4.14** in hand, we then focused on expanding the scope of this reaction to a range of vinyl ethers and vinyldiazoacetates. Previous studies have shown that Rh_2(*S*-DOSP)$_4$ is the optimum chiral catalyst for asymmetric reactions with *trans*-vinyldiazoacetates,[21] and therefore, Rh_2(*S*-DOSP)$_4$ was chosen as the catalyst for this study. The Rh_2(*S*-DOSP)$_4$-catalyzed reaction of *trans*-phenylvinyldiazoacetate **4.53** with vinyl ether **4.68** generated the CHCR product **4.78** as a single diastereomer in good yield with extremely high asymmetric induction (entry **1**, Table **4.11**). This transformation was then successfully applied to a variety of *trans*-vinyldiazoacetates and vinyl ethers as summarized in Table **4.11**. In all cases, a single diastereomer of the CHCR products was produced in good yields (67-89%) and with excellent enantioselectivity, in the majority of cases greater than 98% ee. Traces of the direct C-H insertion products were observed in the crude reaction mixtures in some cases, but the amounts were never more than 10% of the total C-H functionalization products. The absolute configuration of product **4.79** was unambiguously assigned by X-ray crystallography (Figure **4.21**). The stereochemical outcome is consistent with the CHCR reaction proceeding *via* a boat transition state, The stereochemical configuration of the other CHCR products **4.78**, **4.80-**

4.86 were tentatively assigned on the assumption that all the substrates reacted through a similar transition state and trajectory of approach.

Table 4.11 Substrate scope in the CHCR reaction between vinylcarbenoids and ethers



entry	ethers		R_3		product		yield (%)	dr	ee (%)
1		**4.68**	Ph	**4.53**		**4.78**	78	>30:1	99
2			2-Naph	**4.74**		**4.79**	88	>30:1	99
3			*p*-OMePh	**4.75**		**4.80**	77	>30:1	98
4			Et	**4.76**		**4.81**	87	>30:1	98
5			Me	**4.77**		**4.82**	67	>30:1	93
6		**4.70**	Ph	**4.53**		**4.83**	88	>30:1	99
7		**4.71**	Ph	**4.53**		**4.84**	75	>30:1	98
8		**4.72**	Ph	**4.53**		**4.85**	89	>30:1	99
9		**4.73**	Ph	**4.53**		**4.86**	74	>30:1	99

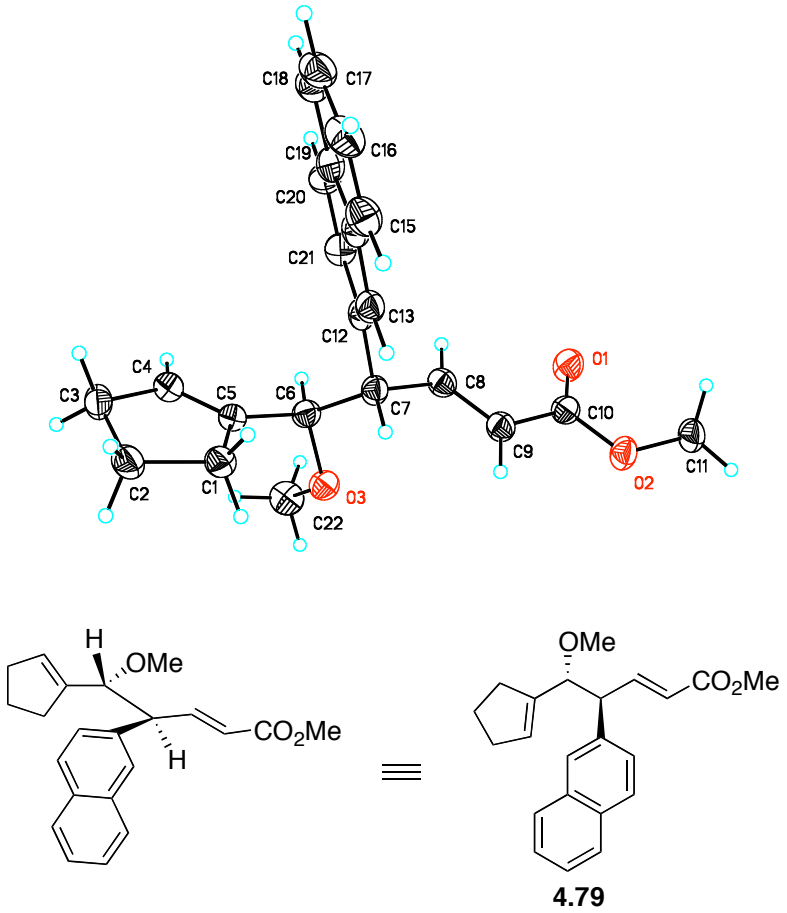


Figure 4.21 X-ray crystallographic structure of product **4.79**

The CHCR reaction with acyclic ether **4.73** is particularly interesting and is worthy of further discussion. As previously mentioned, effective CHCR reactions were limited to cyclic substrates as otherwise a significant amount of competing direct C-H insertion products observed.[167] The ether **4.73** represents the first example of an effective CHCR reaction occurring in acyclic systems. The geometry of the newly formed trisubstituted double bond in **4.86** is consistent with the hypothesis that the reaction proceeds through an *s-cis*/boat transition state because the methyl group is pointing away from the rhodium "wall" in the transition state (Figure **4.22**). The (*E*)- double bond selectivity is opposite to what has been observed in the CHCR reaction proceeding through a chair transition

state,[167] affording the products with (*Z*)- double bonds as shown in Table **4.3**. The resulting geometry of the enoate is indicative that the reaction proceeds through the s-*cis* conformer.

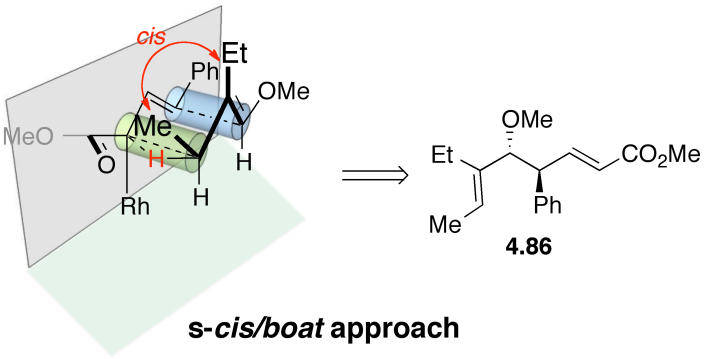
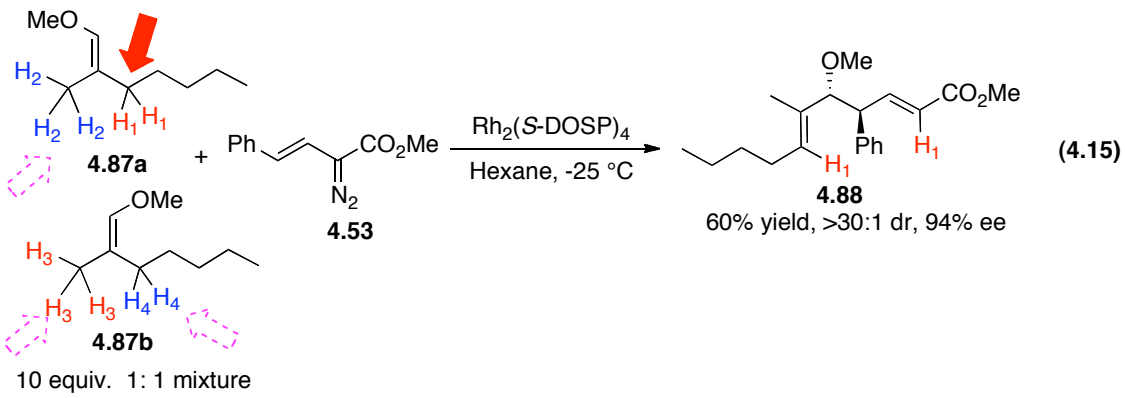


Figure 4.22 Transition state analysis with acyclic substrate

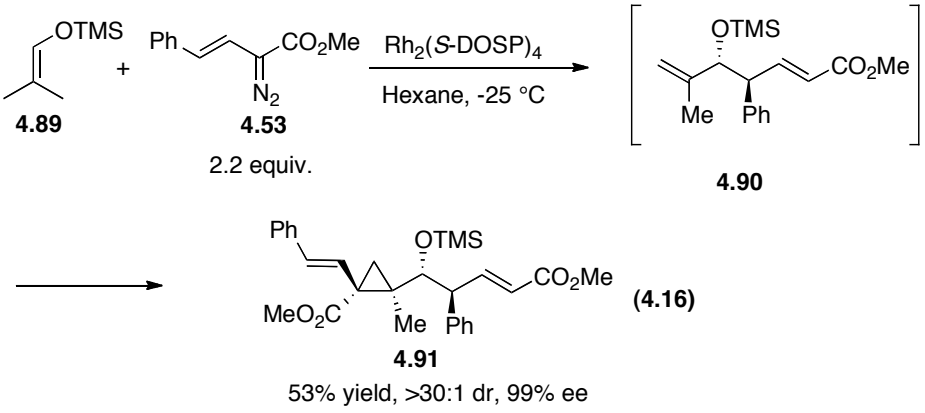
The reaction of donor-acceptor carbenoids is very sensitive to steric and electronic effects of the substrate.[58] Consequently, we wanted to explore the influence of these effects on the CHCR reaction outcome. These influences were readily demonstrated in the reaction of diazo **4.53** with the 1: 1 isomeric mixture of alkene **4.87a** and **4.87b** (eq **4.15**). Each isomer has two possible allylic sites for C-H functionalization. However, it is informative that product **4.88** was formed as the major product in 60% yield. Less than 10% of other CHCR products were observed based on crude NMR. It has been well demonstrated that the methoxy group blocks attacks at the allylic site on the same face,[165] which means that the methyl site (H_2) in **4.87a** and the methylene site (H_4) in **4.87b** are not accessible to C-H functionalization. In addition, the computational studies have shown that the CHCR reaction is initiated by a hydride transfer event. Thus, the methylene site (H_1) in **4.87a** is more reactive than the primary C-H bond of the methyl group (H_3) in **4.87b** because the methylene site would be better at stabilizing positive

charge build-up in the transition state. These steric and electronic effects would explain the high selectivity for the formation of product **4.88**. Once again the C-H functionalization is highly stereoselective as **4.88** was formed with >30:1 dr and 94% ee.



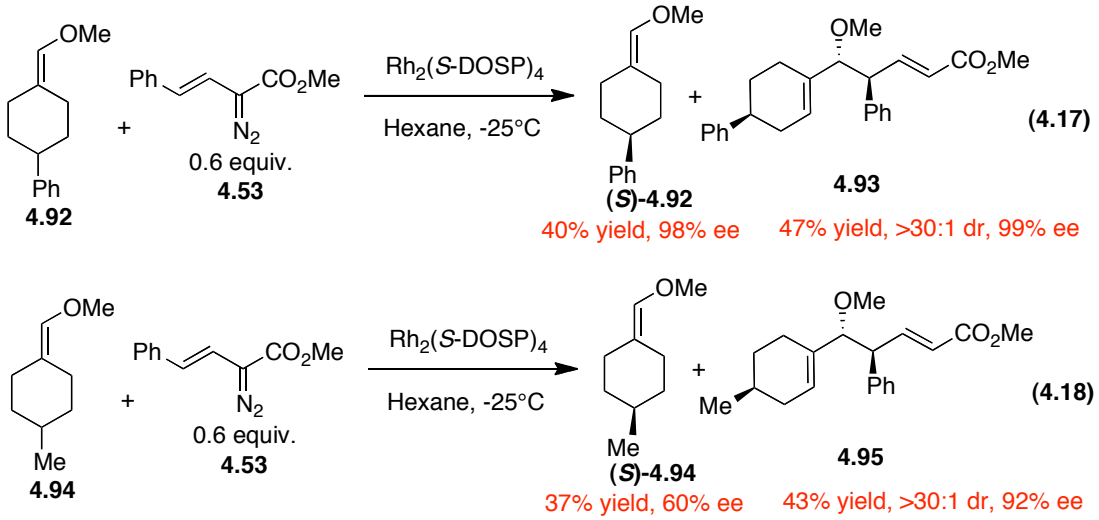
Donor-acceptor carbenoids are versatile intermediates and are capable of initiating consequent reactions.[182] It has been reported that a few systems are capable of undergoing two carbenoid reactions, resulting in the rapid generation of synthetic complexity.[182] It was recognized that if the CHCR reaction was initiated at a primary methyl site of a vinyl ether such as **4.89**, then the resulting 1,2-disubstituted alkene **4.90** would be sterically accessible for a subsequent cyclopropanation (eq **4.16**). In order to test this possibility, the Rh_2(*S*-DOSP)$_4$-catalyzed reaction of ether **4.89** with excess of *trans*-styryldiazoacetate **4.53** was examined (eq. **4.16**). This resulted in the formation of **4.91,** containing four newly formed contiguous stereocenters, two of which are quaternary. **4.91** was formed in 53% yield as a single diastereomer in 99% ee. The relative configuration of the cyclopropane in **4.91** was determined by nOe, while the absolute configuration of **4.91** was tentatively assigned on the basis of the expected s-*cis*/boat transition state model and the predictive transition state model for the cyclopropanation.[21] This reaction indicates that both the CHCR and the cyclopropanation

reactions occurs in a highly stereoselective fashion as only one diastereomer of the product is observed. The reaction represents the first example of the CHCR reaction being initiated by attack at a primary C-H bond. It also represents the first highly diastereoselective cyclopropanation on a 1,1-disubstituted olefin because generally low diastereoselectivity is obtained in such cyclopropanations on 1,1-disubstituted double bonds.[27]



Donor-acceptor carbenoids have been shown to be capable of kinetic resolution, desymmetrization and enantiodifferentiation.[47,99,174] Particularly, the CHCR reaction proceeds strictly through either boat or chair transition states and existing stereocenters on the substrate play a key role in determining reactivity. In order to explore the possibility of a kinetic resolution in the CHCR reaction, the reaction between phenyl-substituted substrate **4.92** and 0.6 equiv of diazo compound **4.53** in the presence of Rh_2(*S*-DOSP)$_4$ was carried out (eq **4.17**). The CHCR product **4.93** was generated as a single diastereomer in 99% ee and in good isolated yield (94% yield based on one enantiomer of ether **4.92**). The unreactive vinyl ether **4.92** was recovered in 40% isolated yield with 98% ee. Therefore, this demonstrates that the Rh_2(*S*-DOSP)$_4$-catalyzed reaction between **4.92** and **4.53** displays a very high level of kinetic resolution. A similar

kinetic resolution was achieved with the methyl-substituted substrate **4.94**, but the stereoselectivity was not as good as the reaction with **4.92** (eq. **4.18**). The CHCR product **4.95** was produced in 92% ee, and the recovered vinyl ether **4.94** was obtained in only 60% ee. This kinetic resolution approach provides a convenient way of making enantioenriched cyclic vinyl ethers with axial chirality. The asymmetric synthesis of this type of compounds is typically challenging and the only successful previous approaches require the use of chiral Wittig reagents as stoichiometric reagents.[183,184] The absolute and relative configuration of products **4.93** and **4.95** were unambiguously assigned by X-ray crystallography and are consistent with the CHCR reaction proceeding though a *s-cis*/boat transition state (Figures **4.23** and **4.24**).



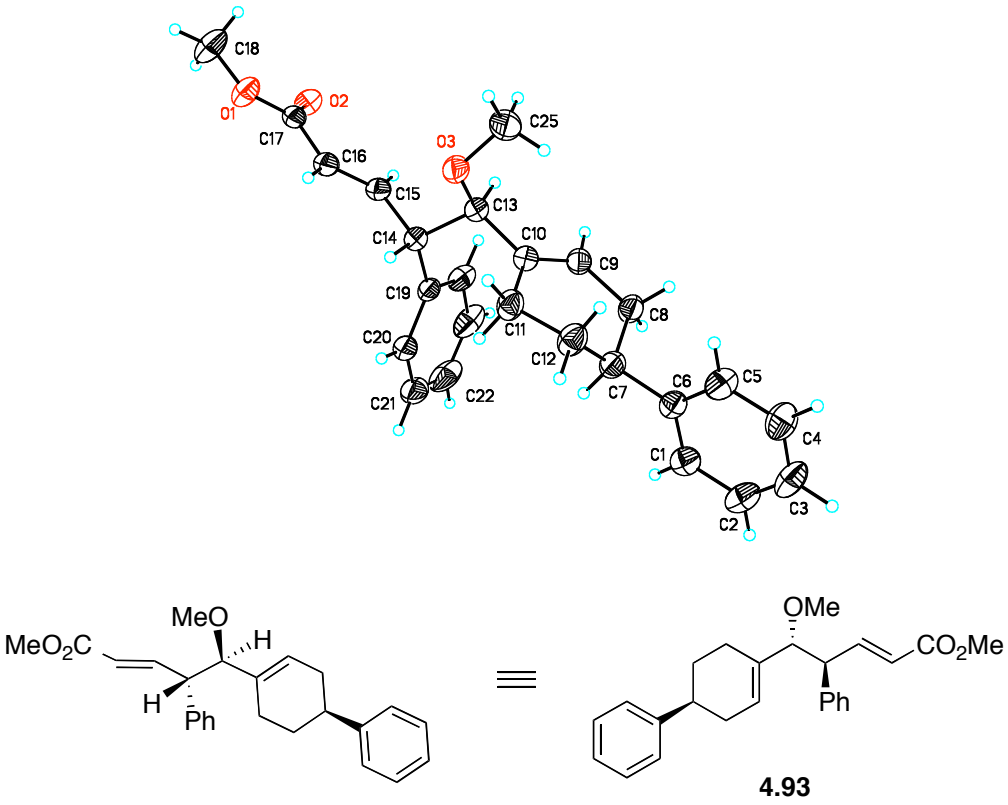


Figure 4.23 X-ray crystallographic structure of product **4.93**

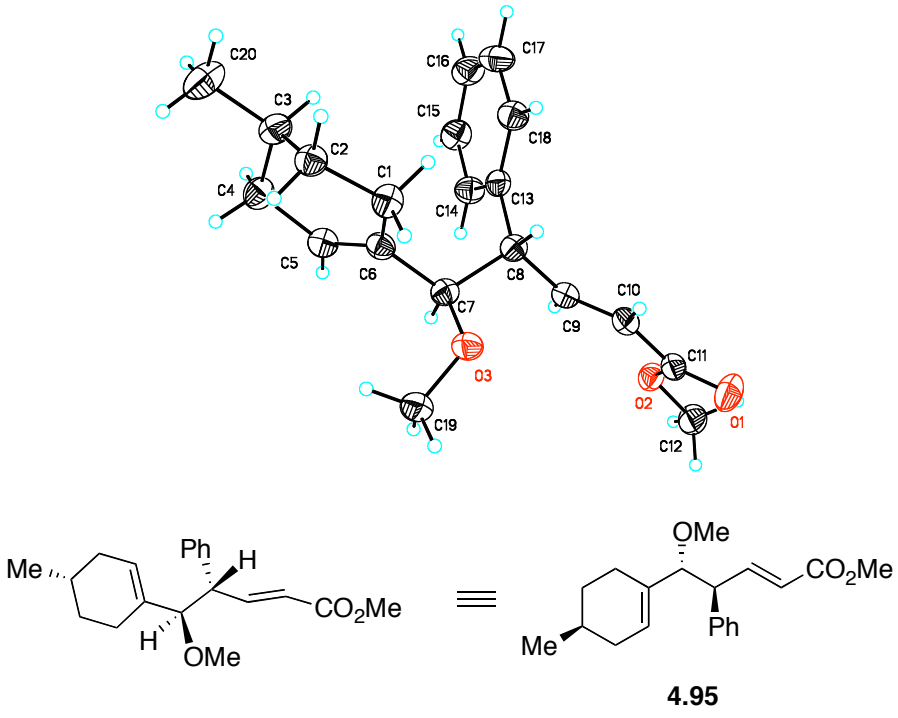


Figure 4.24 X-ray crystallographic structure of product **4.95**

A reasonable mechanism that would be consistent with the kinetic resolution was proposed as shown in Figure **4.25**. Rh_2(*S*-DOSP)$_4$ is proposed to adopt a D_2-symmetry and the substrate would only approach from the front face.[21] The CHCR reaction would be expected to proceed through a boat transition state as shown. The R group in the substrate will need to point away from the carbenoid to avoid steric interference. When R = phenyl, a bulky group, only one enantiomer of the substrate reacts, leading to products with highly stereochemical control and recovery of product **4.92** in high enantiomeric excess. When the R group is methyl, the steric interference is not as dramatic as phenyl and this would account for the moderate kinetic resolution with **4.94**.

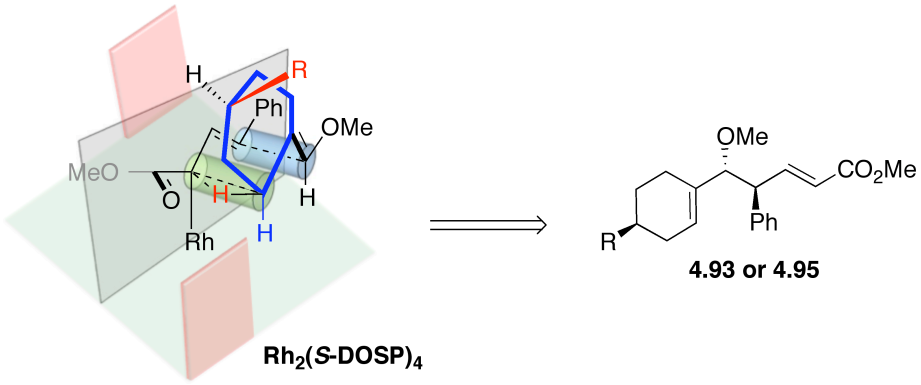
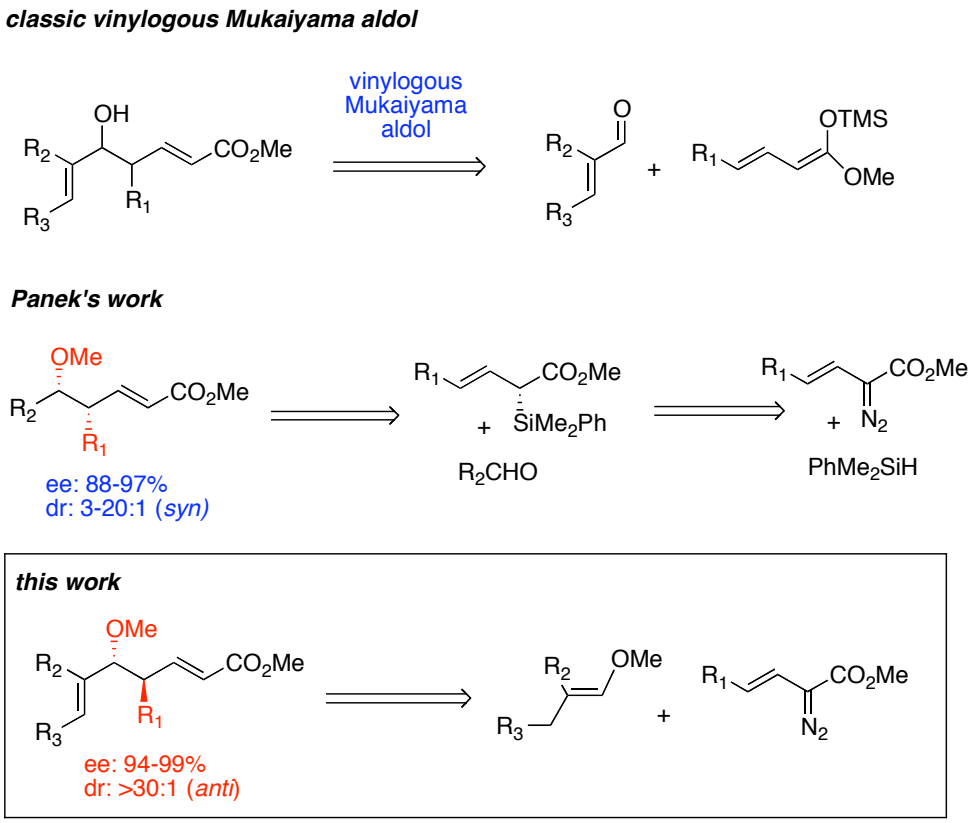


Figure 4.25 Proposed transition state for the kinetic resolution

Intermolecular C-H functionalization by means of carbenoid-induced C-H insertion has been shown to be complementary to many classic reactions, such as aldol reaction, Mannich reaction, Claisen condensation, Michael addition and the Claisen rearrangement.[32,60,185,186] The combined C-H functionalization/Cope rearrangement (CHCR) with vinyl ethers can be applied as a surrogate to the vinylogous Mukaiyama aldol reaction (Scheme **4.12**).[187-189] Recently, Panek reported a carbenoid approach to

generate the typical *syn*-products of a vinylogous Mukaiyama aldol reaction through a two-step sequence: a rhodium-catalyzed asymmetric Si-H insertion between vinyldiazoacetates and silanes followed by a Lewis acid-catalyzed crotylation.[43] The CHCR functionalization complements the Panek approach, leading to a highly stereoselective method for the formation of the typical *anti*-products of the vinylogous Mukaiyama aldol.



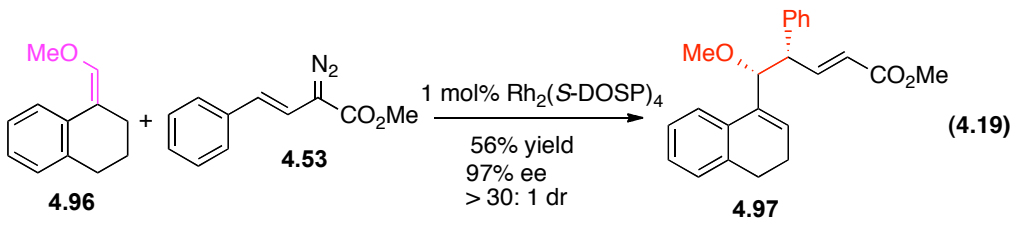
Scheme 4.12 Two vinylcarbenoids approaches to vinylogous Mukaiyama aldol reaction

In conclusion, vinyl ethers have been demonstrated to be excellent substrates for the CHCR reaction. The reaction proceeds through an s-*cis* boat transition state, leading to the formation of products of defined stereochemistry that might typically be generated through the vinylogous Mukaiyama aldol reaction. These studies demonstrate that

asymmetric C-H functionalization by the CHCR reaction can compete with a classic strategic reaction for organic synthesis. Furthermore, the studies underscore the subtle steric and electronic influences that allow the CHCR reaction to be highly regio-, diastereo- and enantioselective. Excellent kinetic resolution is possible, leading to an effective way of making enantiopure vinyl ethers.

4.2.4 Discovery of an elaborate cascade sequence

We have demonstrated that steric and electronic effects play an important role in the CHCR reaction outcome with vinyl ethers. Such investigation led us to discover a novel cascade reaction. The Rh_2(*S*-DOSP)$_4$-catalyzed reaction of diazoacetate **4.53** with ether **4.96** afforded the CHCR product **4.97** as a single diastereomer in 56% yield with high asymmetric induction (eq. **4.19**). The stereochemistry of product **4.97** is consistent with the CHCR reaction proceeding through a boat transition state and the structure was unambiguously assigned by X-ray crystallography (Figure **4.26**, the product was generated in the presence of Rh_2(*R*-DOSP)$_4$). Surprisingly, when the CHCR reaction was attempted on vinyl ether **4.98**, a double bond isomer of vinyl ether **4.96**, no CHCR product was observed. Instead an unexpected product **4.99** containing 10 stereocenters and six-fused rings was isolated as a single diastereomer in 83% yield with 94% ee (eq. **4.20**).



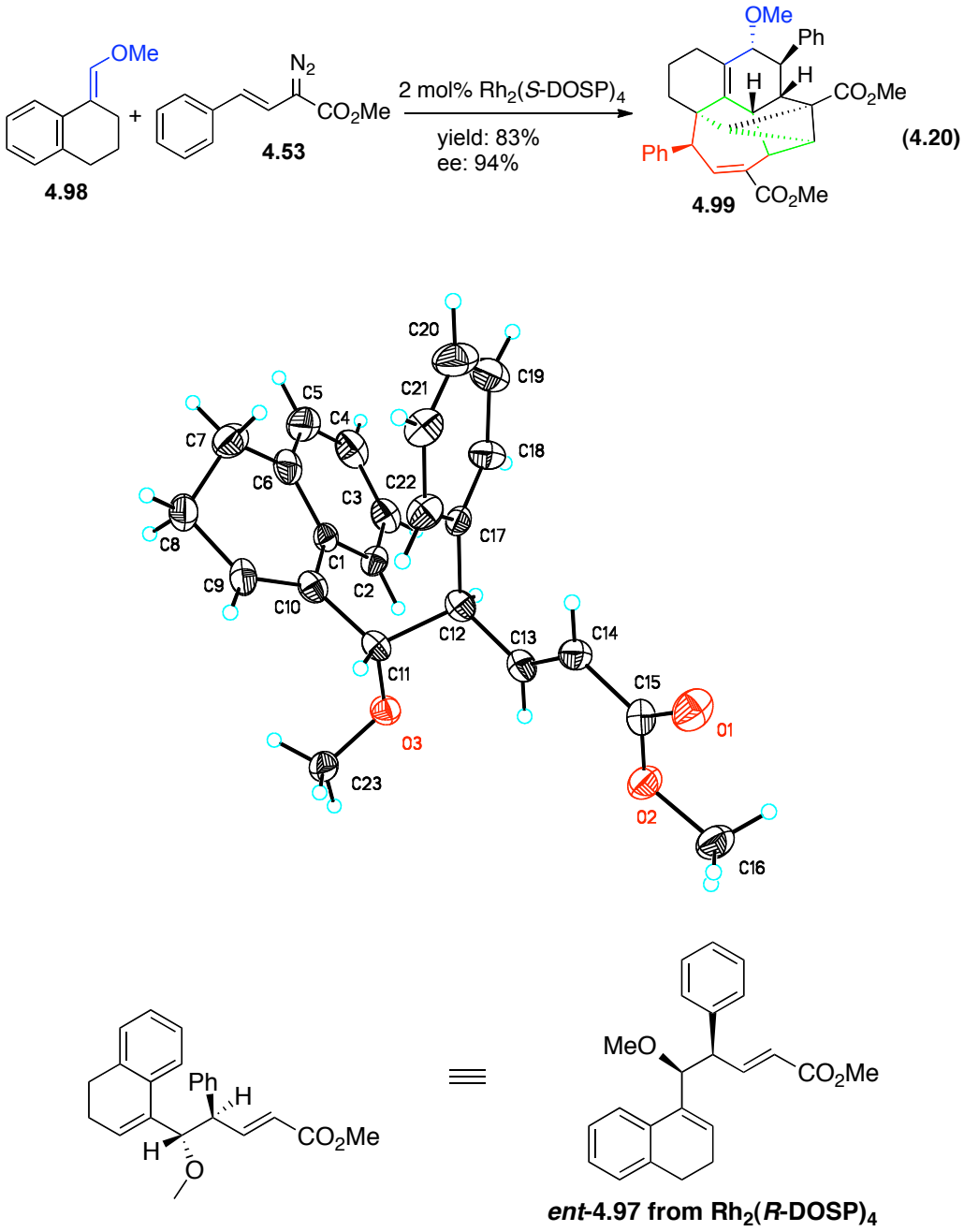
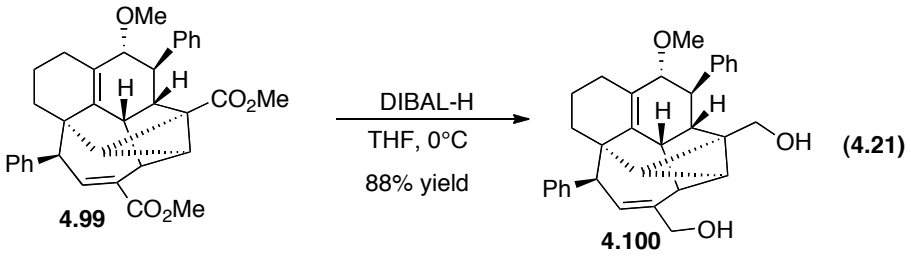
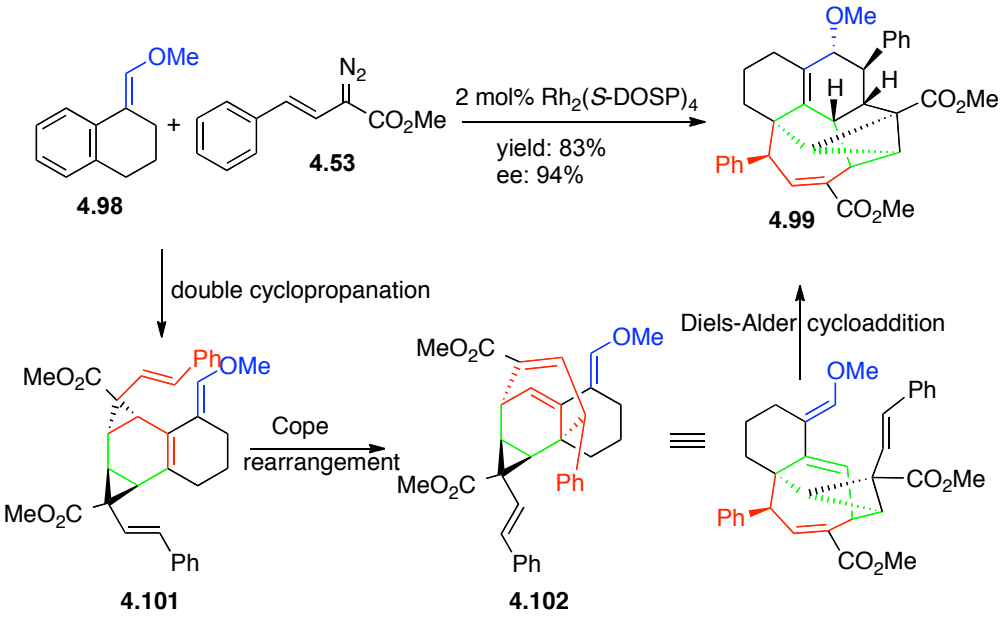


Figure 4.26 X-ray crystallographic structure of product *ent*-**4.97**

The relative stereochemistry of product **4.99** was unambiguously determined by X-ray crystallography of DIBAL-H reduction product **4.100** derived from it (eq. **4.21**, Figure **4.27**). However, the absolute stereochemistry of the product is still uncertain because the product **4.100** was crystallized as a racemic mixture.



A reasonable mechanism is proposed to explain the reaction outcome (Scheme **4.13**). First, a double cyclopropanation would occur on the phenyl ring to generate biscyclopropane **4.101**, which would then undergo a Cope rearrangement through a boat transition state and afford intermediate **4.102**. The intermediate contains diene and dienophile moieties, which are set up for the intramolecular Diels-Alder reaction to generate product **4.99**. All the stereocenters are controlled in the double cyclopropanation process because the Cope rearrangement and the Diels-Alder reaction have been demonstrated to be highly stereoselective.



Scheme 4.13 Mechanism of the formation of product **4.99**

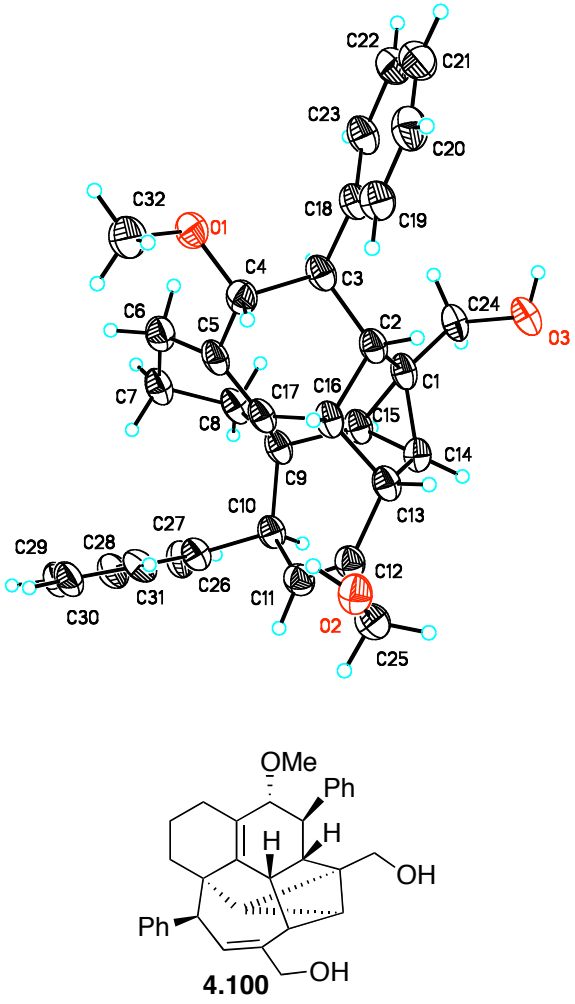
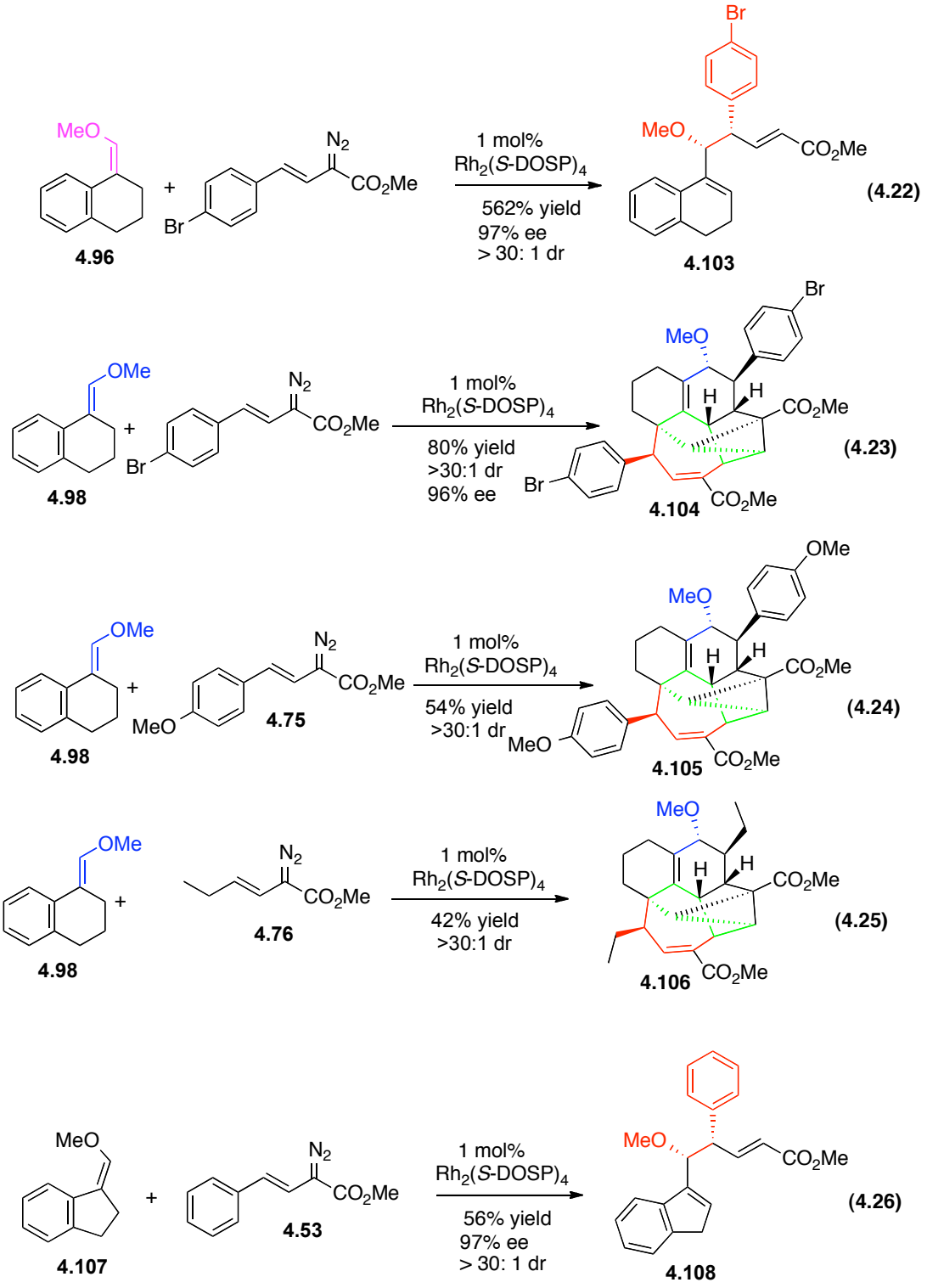


Figure 4.27 X-ray crystallographic structure of product **4.100**

The scope of this reaction can also be extended to other vinylcarbenoids and vinyl ethers (eq. **4.22** to **4.25**). The Rh_2(*S*-DOSP)$_4$-catalyzed reaction of ether **4.98** with various vinylcarbenoids generated only single diastereomers of the cascade reaction products in decent to good yields with excellent asymmetric induction. The reaction between ether **4.96** and **4.102** afforded the CHCR product as a single diastereomer with good enantioselectivity. This reaction can also be extended to indane derivative **4.107** and the CHCR product was generated in 56% yield in a highly stereoselective fashion (eq. **4.26**). This is still an ongoing project and some data needs to be fixed. The relative

configuration of product **4.106** was also unambiguously determined based on X-ray crystallography (Figure **4.28**). Once again, the crystal was formed as a racemic mixture.



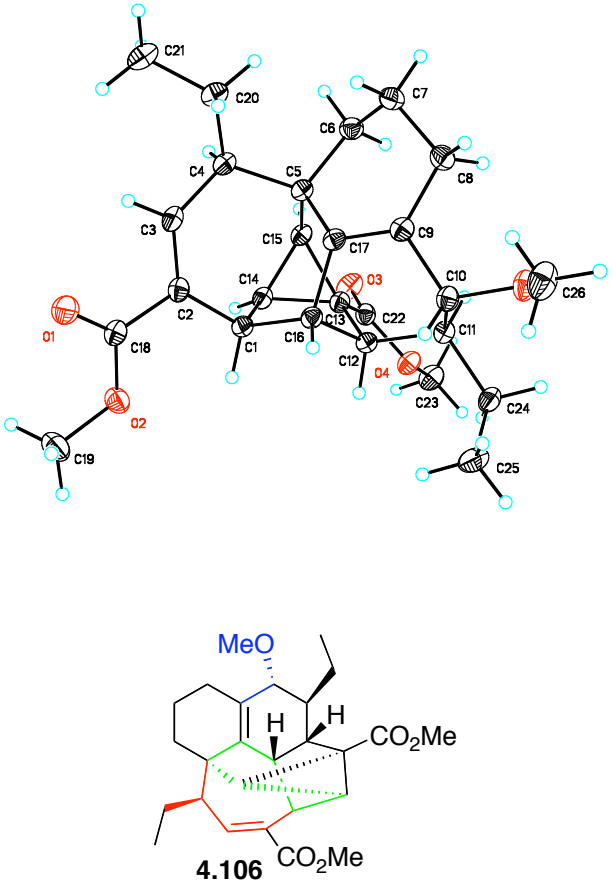


Figure 4.28 X-ray crystallographic structure of product **4.106**

In conclusion, a novel cascade reaction has been successfully developed in a highly diastereo- and enantioselective fashion. This cascade sequence involves double cyclopropanation, Cope rearrangement and intromlecular Diels-Alder reaction. The geometry of vinyl ether plays a crucial role in determining the reaction undergoes CHCR reaction or this novel cascade reaction.

Chapter V: Miscellaneous Reactions with Vinylcarbenoids

5.1 Introduction

We have demonstrated that the reaction between indoles and vinylcarbenoids can selectively undergo either [3 + 2] annulation *via* carbenoid reactivity or vinylogous alkylation *via* vinylogous reactivity under different conditions by modifying the catalyst and solvent.[150,190] The detailed mechanism for these two different reactivity profiles is still not well understood. It is anticipated that by extending these two reactions to other types of electron rich olefins would be helpful in understanding the reaction mechanism. In this miscellaneous chapter, we will mainly focus on transformations involving rhodium-bound ylide intermediates. By modifying steric, electronic or stereoelectronic effects of substrates, some unusual stereoselective transformations were discovered. In has been illustrated that vinylcarbenoids can exist in either the s-*cis* conformer or the s-*trans* conformer and each conformer exhibites different reactivity (Figure **5.1**).[150] This chapter describes preliminary studies to explore other novel reactions of vinylcarbenoids. These projects are incomplete but illustrate new opportunities for further vinylcarbenoid research.

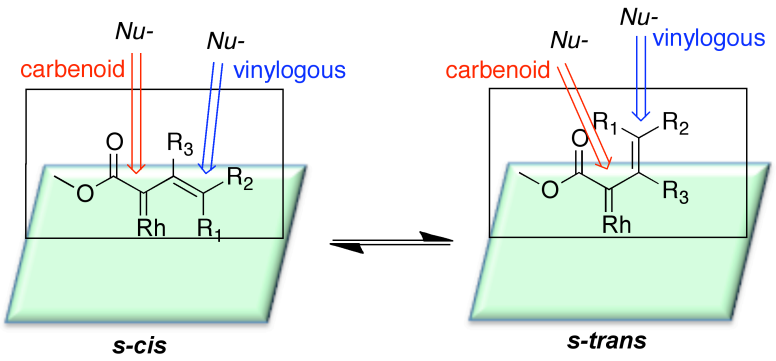
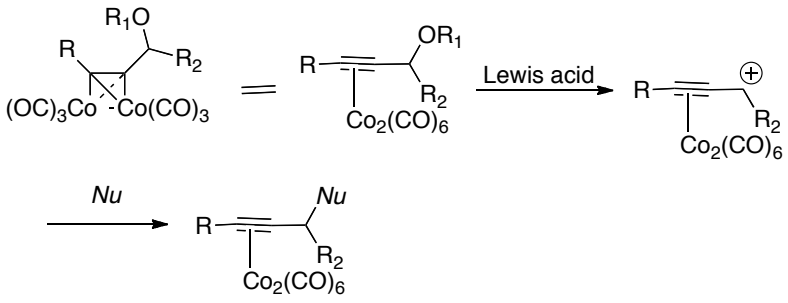


Figure 5.1 Reactivity profiles associated with carbenoid conformers

5.2 Results and discussion

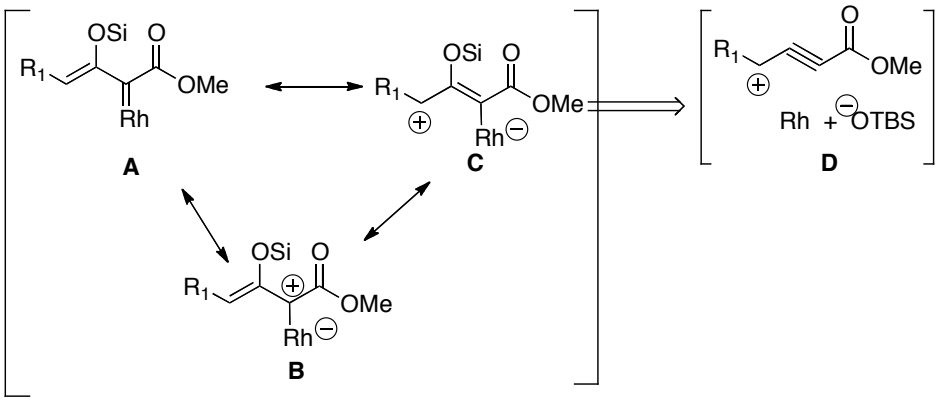
5.2.1 Facial approach to alkynoates by vinylogous reactivity of vinylcarbenoids

The Nicholas reaction, which uses hexacarbonyl(υ-propargylium)cobalt cations as intermediates, has been well known as an effective approach for selectively functionalizing propargylic sites and has been widely used in total synthesis.[191-193] The reaction proceeds through a propargylic cation intermediate, which reacts with a variety of nucleophiles occurring at the propargylic site, exclusively generating the corresponding adducts. Chelation with $Co_2(CO)_6$ plays a crucial role in this chemistry because $Co_2(CO)_6$ not only acts a protecting group for the triple bond, but also ensures the reaction to occur on the propargylic site. An obvious drawback of this chemistry is that stoichiometric amount of $Co_2(CO)_6$ is required and the dicobalt complex needs to be installed before the Nicholas reaction and then removed after the reaction (Scheme **5.1**). In this section, we describe a surrogate approach to the Nicholas reaction products by means of Rh(II)-catalyzed vinylogous transformation of siloxyvinyldiazoacetates with silyl enol ethers.



Scheme 5.1 General approach of the Nicholas reaction

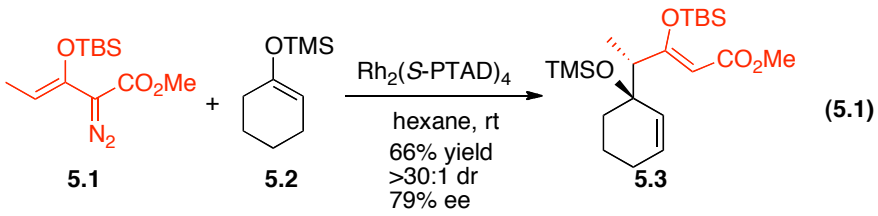
One of the unusual features of the chemistry of vinylcarbenoids is the occurrence of vinylogous reactivity.[45,124] A major theme in this thesis is the reaction of siloxyvinylcarbenoids, which have been shown to be versatile intermediates, capable of initiating the cyclopropanation/Cope rearrangement and the combined C-H functionalization/Cope rearrangement.[27,174] We have demonstrated that vinylcarbenoids with internal substituents favored the vinylogous reactivity.[124] In principle, it is reasonable to rationalize that siloxyvinyldiazoacetate would favor the vinylogous reactivity. The exploration of the vinylogous reactivity with siloxyvinyldiazoacetates led to the discovery of a practical approach to 6-oxo-2-ynoate derivatives. Siloxyvinylcarbenoids offer interesting reactivity profiles in synthesis because they are electrophilic either α or γ to the carbonyl group (Scheme **5.2**), displaying natural *umpolung* reactivity. Particularly, resonance structure **C** would be considered as complementary to a γ propargylic cation, which represents a common intermediate in the Nicholas reaction.



Scheme 5.2 Relationship of siloxyvinylcarbenoid to the Nicholas intermediate

The impetus of this reaction arose from an unexpected result during the exploration of the combined C-H functionalization/Cope rearrangement between

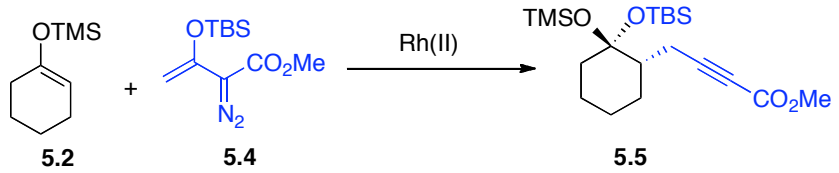
siloxyvinyldiazoacetate and cyclic enol ethers. The Rh_2(*S*-PTAD)$_4$-catalyzed decomposition of diazoacetate **5.1** with cyclohexene **5.2** generated the expected CHCR product **5.3** as a single diastereomer in good yield (eq. **5.1**). When the reaction was repeated with the unsubstituted siloxyvinyldiazoacetate **5.4**, an unexpected product **5.5** was formed as a single diastereomer in 47% yield (eq. **5.2**). The formation of **5.5** is intriguing. Compound **5.5** is the type of product that would be generated from nucleophilic attack at the vinylogous carbon. The OTBS group can migrate from the vinylcarbenoid to the substrate, which is unprecedented in the carbenoid literature. Therefore, we decided to further explore this unusual reactivity. This work was conducted in collaboration effort with undergraduate student, John Haydek.



The reaction of **5.2** was chosen as the model reaction and various dirhodium catalysts and solvents were screened as summarized in Table **5.1**. In all cases, product **5.5** was formed as a single diastereomer. Increasing solvent polarity significantly improved the reaction yield from 47% to 65% (entry **1** and **2**, Table **5.1**), which can be further improved to 80% by choosing $Rh_2(esp)_2$ as the catalyst (entry **4**). $Rh_2(DOSP)_4$ and $Rh_2(TPA)_4$ are not as effective as $Rh_2(esp)_2$, generating the product **5.5** in moderate yield.

The relative configuration of product **5.5** was unambiguously assigned by X-ray crystallography (Figure **5.2**).

Table 5.1 Optimization of vinylogous alkynoate formation



5.2 **5.4** **5.5**

entry	Rh(II)	solvent	Temp. (°C)	yield(%)
1	Rh_2(*S*-PTAD)$_4$	Hexane	r.t.	47%
2	Rh_2(*S*-PTAD)$_4$	DCM	r.t.	65%
3	Rh_2(*S*-DOSP)$_4$	DCM	r.t.	46%
4	Rh_2(esp)$_2$	DCM	r.t.	80%
5	Rh_2(TPA)$_4$	DCM	r.t.	65%

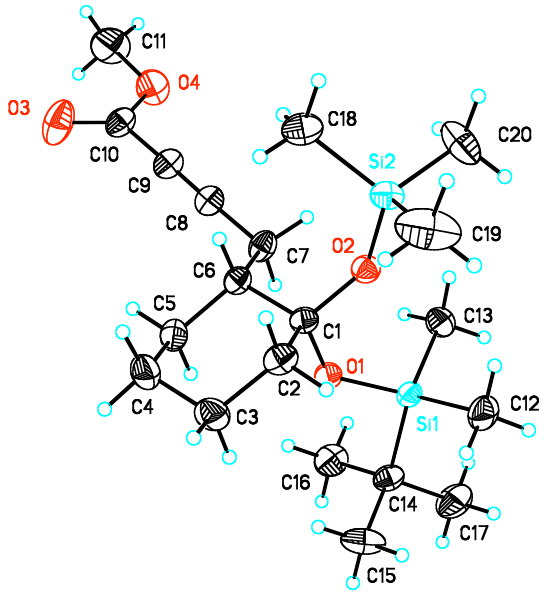
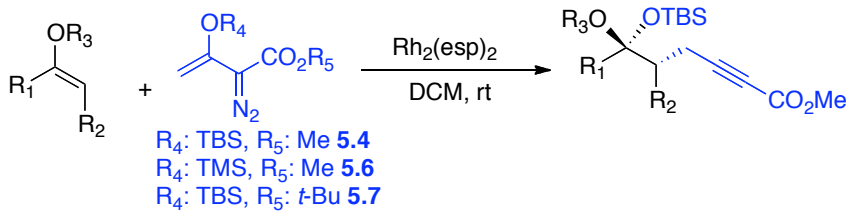
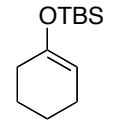
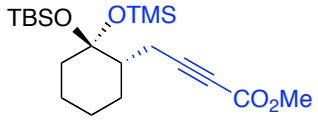
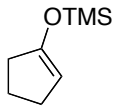
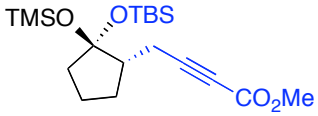
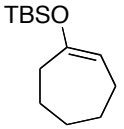
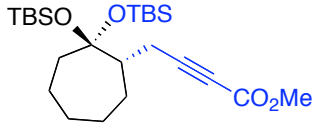
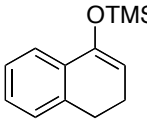
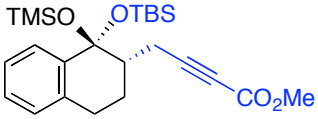
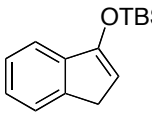
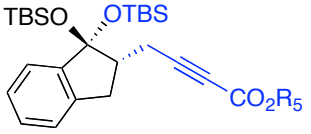
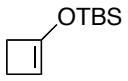
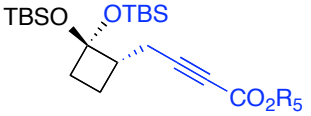
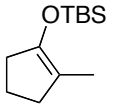
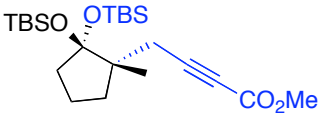
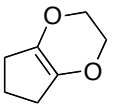
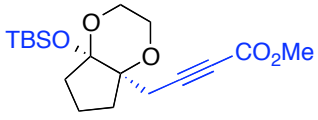


Figure **5.2** X-ray crystallographic structure of compound **5.5**

Table 5.2 Substrate scope with enol ethers

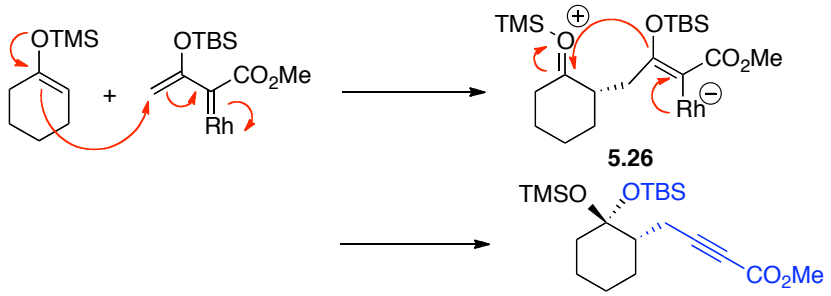


entry	substrate	diazo	product	yield(%)
1	 **5.8**	**5.6**	 **5.16**	49%
2	 **5.9**	**5.4**	 **5.17**	79%
3	 **5.10**	**5.4**	 **5.18**	81%
4	 **5.11**	**5.4**	 **5.19**	69%
5	 **5.12**	**5.4**	 **5.20**	33%
6		**5.7**		**5.21** 84%
7	 **5.13**	**5.4**	 **5.22**	52%
8		**5.7**		**5.23** 98%
9	 **5.14**	**5.4**	 **5.24**	56%
10	 **5.15**	**5.4**	 **5.25**	53%

The $Rh_2(esp)_2$-catalyzed vinylogous reactivity of diazoacetate **5.4** was applicable to a wide range of cyclic substrates as illustrated in Table **5.2**. In all reactions, only single diastereomers of products were generated in good yields. Product **5.16** is the opposite

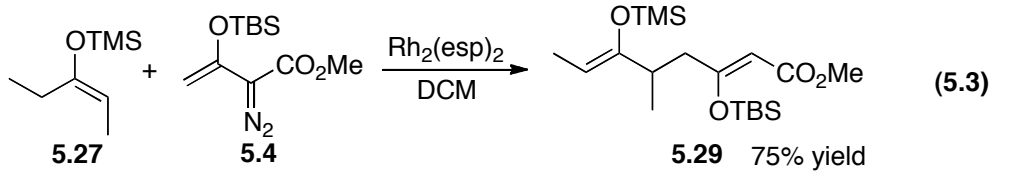
diastereomer to compound **5.5** and shows different ^{1}H and ^{13}C NMR spectrum. This difference rules out the possibility that these two diastereomers have the same NMR spectrum due to the similarity of the structure, and supports the conclusion that only a single diastereomer was generated. This reaction is not limited to trisubstituted enol ethers, but also effective with tetrasubstituted vinyl ethers (entry **9** and **10**). We have demonstrated that increasing the size of the ester group in the vinylcarbenoid enhances the vinylogous reactivity.[124] In cases where the carbenoid reactivity, which is mainly the cyclopropanation reaction, competes with this novel vinylogous reactivity with some substrates resulting in low yields (entry **5** and **7**), diazoacetate **5.7** containing *t*-butyl as the ester group can be used to drive the reaction towards alkynoate formation. The reaction of **5.7** with substrate **5.12** and **5.13** afforded the alkynoate products **5.21** and **5.23** in excellent yield without any formation of carbenoid reactivity products (entry **6** and **8**).

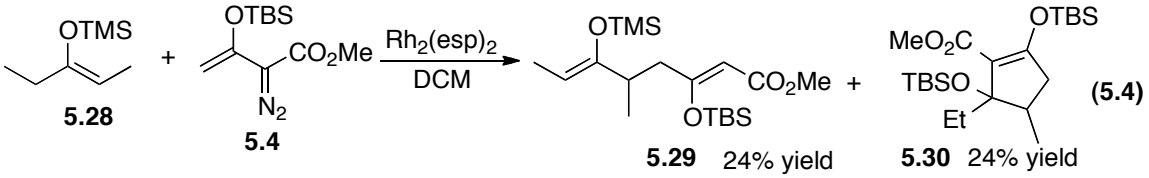
A plausible mechanism is proposed to explain the reaction outcome (Scheme **5.3**). Enol ether as a nucleophile would attack the vinylcarbenoid from the vinylogous position and form zwitterionic intermediate **5.26**, which would undergo OTBS migration to afford product as a single diastereomer. The OTBS migration would be considered as an intramolecular transfer because the product containing the OTBS group on the same face as the alkynoate moiety is formed exclusively.



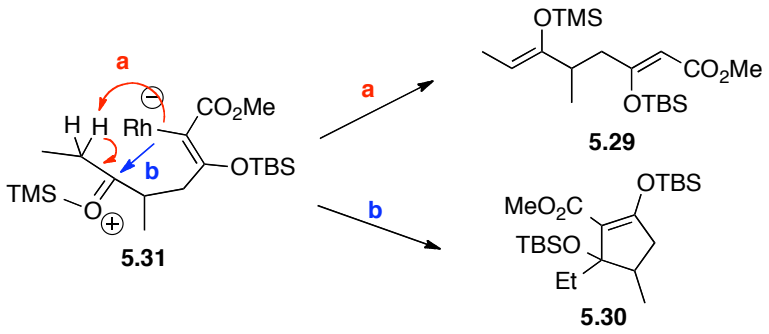
Scheme 5.3 Proposed mechanism for the formation of alkynoates

The extension of the reaction to acyclic enol ethers leads to other interesting transformations. The $Rh_2(esp)_2$-catalyzed reaction of diazoacetate **5.4** with enol ether **5.27** afforded product **5.29** in 75% yield (eq. **5.3**), while the reaction with **5.28**, a regioisomer of **5.27** generated products **5.29** and **5.30** as a 1:1 mixture (eq. **5.4**). The product **5.29** is similar to a compound derived from the combined C-H functionalization/Cope rearrangement on the methylene site, while compound **5.30** was generated from the vinylogous [3 + 2] cycloaddition.





A plausible mechanism was proposed to explain reactions **5.3** and **5.4**. It would be reasonable to assume that both reactions generate the same intermediate **5.31** through vinylogous reactivity (Scheme **5.4**). This intermediate would undergo either direct cyclization to afford the [3 + 2] annulation product **5.30** (Pathway **b**), or proton abstraction on the secondary C-H bond to generate the product **5.29** (Pathway **a**). However, a similar reaction outcome should be obtained if both reactions proceed through the same intermediate **5.31**. Further studies are needed to explain why there is a difference in the product outcome, depending on substrate geometry.



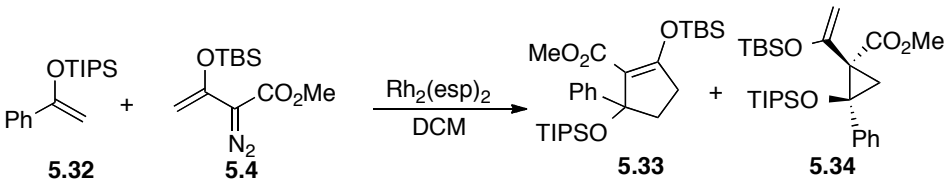
Scheme 5.4 Two different reaction processes

In conclusion, we have developed a general approach to alkynoates by means of vinylogous reactivity exhibited by siloxyvinyldiazoacetate with silyl enol ethers in a highly diastereoselective fashion. When reacted with the trisubstituted or tetrasubstituted vinyl ethers, an unprecedented OTBS migration occurs. This transformation is considered as a surrogate of the Nicholas reaction. The mechanistic details are not fully understood and require further investigation.

Intrigued by the formation of product **5.30**, we then became interested in exploring the vinylogous [3 + 2] cycloaddition. The reaction between substrate **5.32** and diazoacetate **5.4** was then chosen for this study. The reaction generated two products: the vinylogous [3 + 2] cycloaddition product **5.33** and the cyclopropanation product **5.34**. Various dirhodium catalysts and solvents were screened as summarized in Table **5.3**. The reaction catalyzed by Rh_2(*R*-DOSP)$_4$ in hexane generated products **5.33** and **5.34** in a 1:1 ratio. Using more polar solvent, such as DCM, enhanced the ratio to 3.5/1 favoring the product **5.33** (entry **2**). The vinylogous reactivity could be further enhanced by using the electron-deficient catalyst $Rh_2(TFA)_4$ and under these conditions product **5.33** was generated in 80% yield without any formation of cyclopropane **5.34**. A similar selectivity was achieved with Rh_2(*R*-BNP)$_4$, which is an electron-deficient phosphate catalyst, but the

reaction yield was not as good as the reaction with $Rh_2(TFA)_4$. In contrast, the reaction with Rh_2(*S*-PTAD)$_4$ in refluxing DMB generated the cyclopropane **5.34** in 71% yield exclusively. This result is consistent with the proposed mechanism for the vinylogous [3 + 2] cycloaddition because polar solvents and electron-deficient catalysts would be expected to stabilize the zwitterionic intermediate and enhance the vinylogous reactivity.[124]

Table 5.3 Optimization of vinylogous [3 + 2] cycloaddition

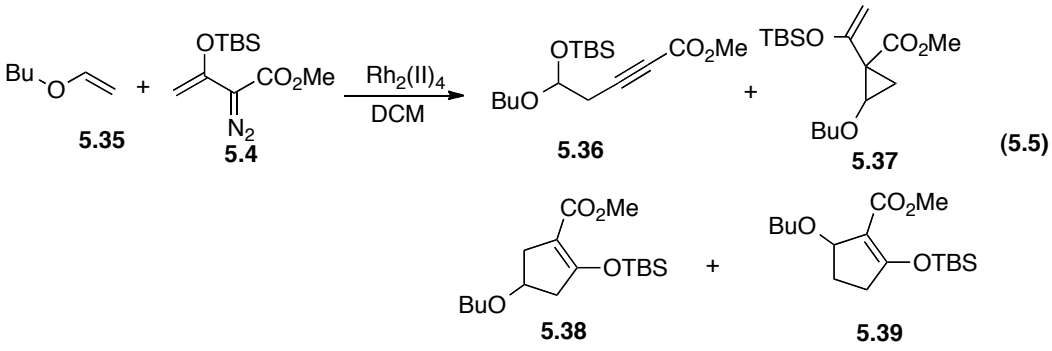


5.32 **5.4** **5.33** **5.34**

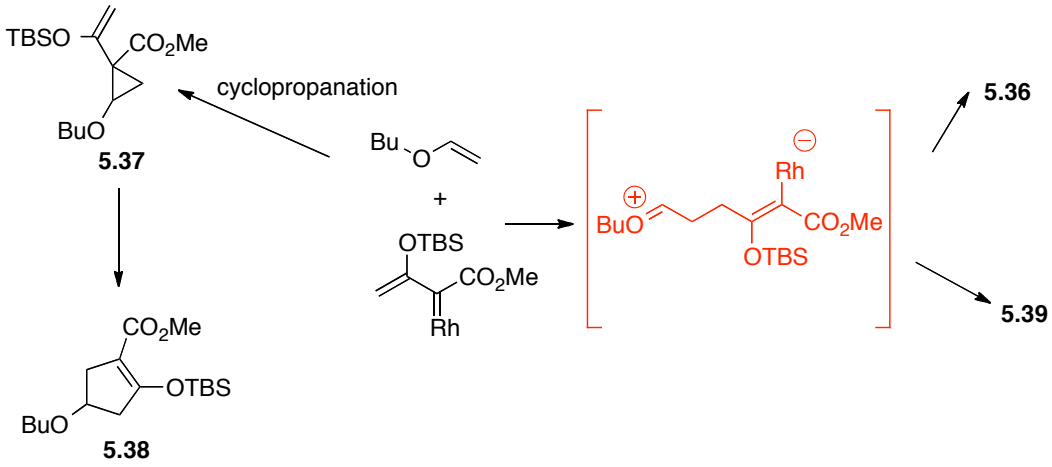
entry	catalyst	solvent	temp (°C)	ratio (**5.33/5.34**)	yield (%) (**5.33 + 5.34**)
1	Rh_2(*R*-DOSP)$_4$	hexane	rt	1/1.1	62
2	Rh_2(*R*-DOSP)$_4$	DCM	rt	3.5/1	47
3	Rh_2(*S*-PTAD)$_4$	DMB	reflux	0/1	71
4	$Rh_2(TFA)_4$	DCM	reflux	1/0	80
5	Rh_2(*R*-BNP)$_4$	DCM	reflux	1/0	60

Attempted extension of the reaction to a less sterically crowded substrate, *n*-butyl vinyl ether **5.35** generated some unexpected results (eq **5.5**). The Rh(II)-catalyzed reaction of diazoacetate **5.4** with **5.35** generated four products: the alkynoate product **5.36**, the cyclopropanation product **5.37**, and two cyclopentenes **5.38** and **5.39**. Presumably, product **5.38** would be generated through a cyclopropanation followed by a ring opening and ring closure process, while the product **5.39** would be generated directly through a vinylogous [3 + 2] cycloaddition mechanism (Scheme **5.5**). Product distribution is consistent with the proposed mechanism because the reaction initiated by $Rh_2(TFA)_4$

afforded the much better combined yield of vinylogous reactivity products **5.36** and **5.39** over the $Rh_2(OAc)_4$-catalyzed reaction.



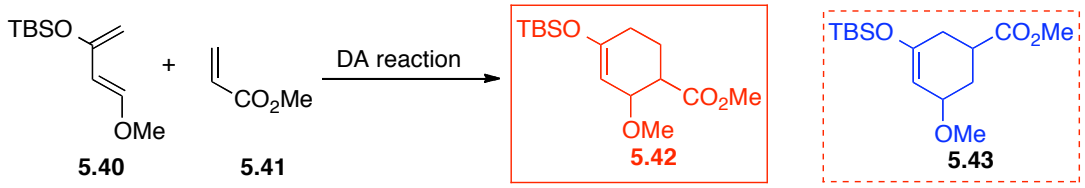
	yield (%)			
	5.36	**5.37**	**5.38**	**5.39**
$Rh_2(TFA)_4$	19	25	11	36
$Rh_2(OAc)_4$	5	62	18	8



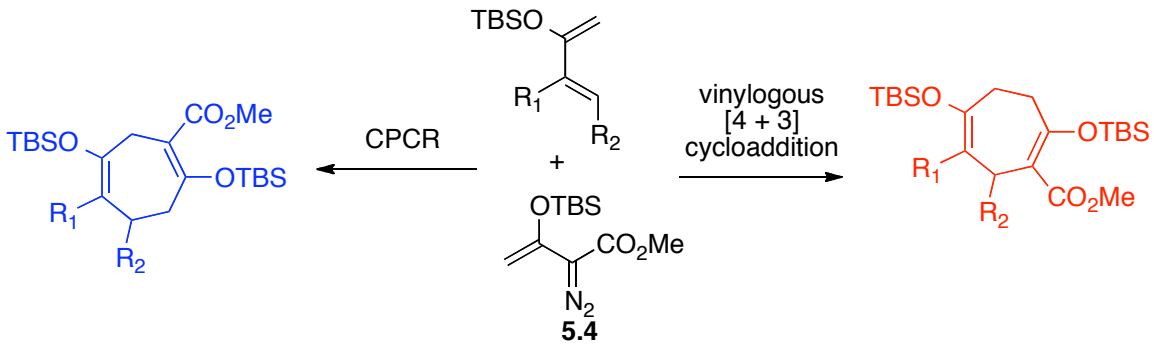
Scheme 5.5 Proposed mechanism of reaction **5.5**

Intrigued by the unexpected vinylogous [3 + 2] annulation with siloxyvinyldiazoacetate, studies were conducted to explore whether this reactivity could be developed into a more synthetic useful transformation. Diels-Alder and hetero-Diels-Alder reactions are powerful methods for the stereoselective construction of six-

membered rings.[194,195] Generally, regioselectivity is controlled by the best overlap coefficient of the HOMO orbital of the diene and the LUMO orbital of the dienophile.[194,195] As an outcome, the regioselectivity in the Diels-Alder reaction is independent of reaction conditions in most cases. For example, the reaction between **5.40** and **5.41** would preferentially form regioisomer **5.41** over the other isomer **5.43** (Scheme **5.6**). The rhodium-catalyzed cyclopropanation/Cope rearrangement of dienes with vinylcarbenoids is an effective protocol for generating seven-membered rings.[174,196] This strategy has been applied to the synthesis of a variety of natural products. We became intrigued about the possibility that a vinylogous [4 + 3] cycloaddition between electron rich dienes and siloxyvinyldiazoacetate **5.4** would generate the opposite regioisomer of the product formed in the standard cyclopropanation/Cope rearrangement reaction (Scheme **5.7**).



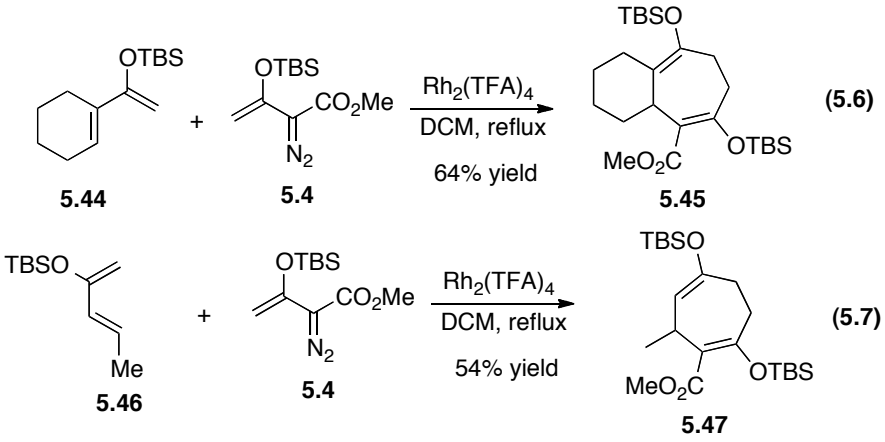
Scheme 5.6 Intermolecular Diels Alder reaction



Scheme 5.7 Two different [4 + 3] cycloadditions with diazoacetate **5.4**

The impetus of this exploration was intrigued by the reaction between **5.35** and **5.4** (eq. **5.5**). Product **5.38** is the opposite regioisomer of product **5.39**. We then rationalized that if dienes are used as substrates rather than mono olefins, an opposite regioisomer to the cyclopropanation/Cope rearrangement product would be generated. This work was conducted in a collaborative effort with undergraduate student, John Haydek.

The $Rh_2(TFA)_4$-catalyzed decomposition of diazoacetate **5.4** with enol ether **5.44** selectively generated the expected vinylogous [4 + 3] cycloaddition product **5.45** in good yield without any formation of the cyclopropanation/Cope rearrangement product (eq. **5.6**). The reaction was also successfully extended to substrate **5.46** and afforded the product **5.47** in good yield (eq. **5.7**). The reaction of **5.4** with **5.46** has been demonstrated to result in a perfect cyclopropanation/Cope rearrangement when catalyzed by Rh_2(*S*-PTAD)$_4$ in hexane. The selective formation of **5.47** indicates that modifying reaction conditions can lead to a complete shift of the reaction from the cyclopropanation/Cope rearrangement to the vinylogous [4 + 3] cycloaddition.



In conclusion, it has been well demonstrated that siloxyvinyldiazoacetate is an excellent carbenoid precursor undergoing vinylogous reactivity with electron rich substrates. Three

different types of products have been discovered, arising from the vinylogous reactivity Further studies need to be conducted to determine the scope and synthetic potential of each of these novel reactions.

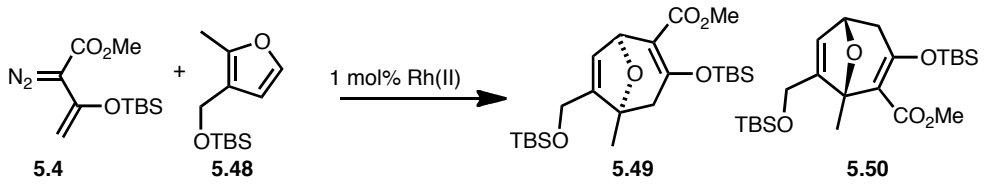
5.2.2 A novel [4 + 3] cycloaddition between siloxyvinyldiazoacetate and furans

The Rh_2(*S*-PTAD)$_4$-catalyzed tandem cyclopropanation/Cope rearrangement reaction between furans and siloxyvinyldiazoacetate effectively generate highly functionalized 8-oxabicyclo[3.2.1]octane derivatives in good yields with moderate to good enantioselectivity. It has also been shown that siloxyvinyldiazoacetate undergoes vinylogous [4 + 3] cycloaddition effectively with electron rich dienes and the reaction generates the opposite regioisomer of the product derived from the cyclopropanation/Cope rearrangement reaction. Herein, we describe another novel [4 + 3] cycloaddition between furans and siloxyvinyldiazoacetate **5.4**, leading to an opposite regioisomer to the cycloadduct derived from the cyclopropanation/Cope rearrangement in a highly stereoselective fashion.

It has been demonstrated that the reaction between 2-substituted or 2,5-disubstituted furans and diazoacetate **5.4** generates the cyclopropanation/Cope rearrangement product as a single isomer in the presence of Rh_2(*S*-PTAD)$_4$. When this reaction was repeated with 2,3-disubstituted furan **5.48**, two regioisomers of [4 + 3] cycloadducts **5.49** and **5.50** were generated in about 1:1 ratio (entry **5**, Table **5.4**). The product **5.49** would be generated through the regular cyclopropanation on the less sterically crowded double bond of furan, followed by a Cope rearrangement, while the mechanism for the formation

of the abnormal product **5.50** was uncertain at this stage. Various conditions were screened as summarized in Table **5.4**. The Rh_2(*S*-DOSP)$_4$-catalyzed reaction in hexane generated products **5.50** and **5.49** in a 0.8:1 ratio (entry **1**). The ratio was slightly enhanced to 1.1/1 when the reaction was carried out at -25 °C (entry **2**). In contrast, the ratio dropped to 0.6/1 in DCM (entry **3**). The reaction catalyzed by Rh_2(*S*-PTAD)$_4$ in hexane at -25°C afforded two products in 1.1/1 ratio. Both products were generated in 88% ee. Surprisingly, the $Rh_2(OAc)_4$-catalyzed reaction in hexane afforded the product **5.49** in 98% yield exclusively.

Table 5.4 Reaction between diazoacetate **5.4** and furan **5.48**



5.4 **5.48** **5.49** **5.50**

entry	catalyst	solvent	Temp (°C)	ratio of **5.50/5.49**	yield (%)	ee (%) **5.49** and **5.50**
1	Rh_2(*S*-DOSP)$_4$	hexane	23	0.8/1	89	
2	Rh_2(*S*-DOSP)$_4$	hexane	-25	1.1/1	86	20 and 61
3	Rh_2(*S*-DOSP)$_4$	CH_2Cl_2	23	0.6/1	85	
4	Rh_2(*S*-PTAD)$_4$	hexane	23	0.6/1	98	82 and 76
5	Rh_2(*S*-PTAD)$_4$	hexane	-25	1.1/1	98	88 and 88
6	$Rh_2(OAc)_4$	hexane	23	0/1	98	
7	$Rh_2(TFA)_4$	hexane	-25	0.7/1	86(NMR)	
8	$Rh_2(TPA)_4$	hexane	23	0.1/1	58(NMR)	

Three possible mechanisms were proposed to explain this novel transformation (Figure **5.3**). The first mechanism involves the vinylogous [4 + 3] cycloaddition occurring at the 5-position of furan (pathway **a**). The second pathway **b** involves a cyclopropanation on the more sterically hindered double bond followed by a Cope rearrangement.[40] The third

mechanism involves a concerted, but not synchronous transition state (pathway **c**). The first mechanism would be less possible because polar solvents and electron-deficient catalysts did not enhance the formation of the product **5.50**. The second pathway would also be less likely based on the fact that donor-acceptor carbenoids are sensitive to steric interaction[3] and decreasing reaction temperature enhanced the formation of the product **5.50**. The third mechanism is unprecedented in literature, but maybe the most likely pathway to occur.

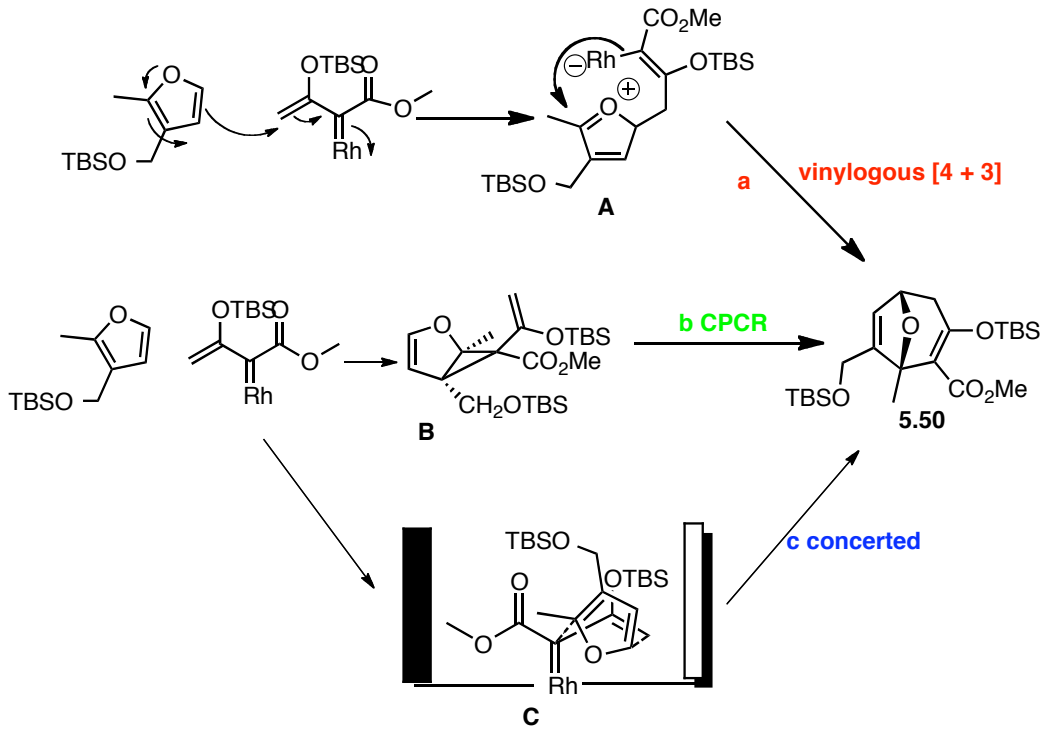
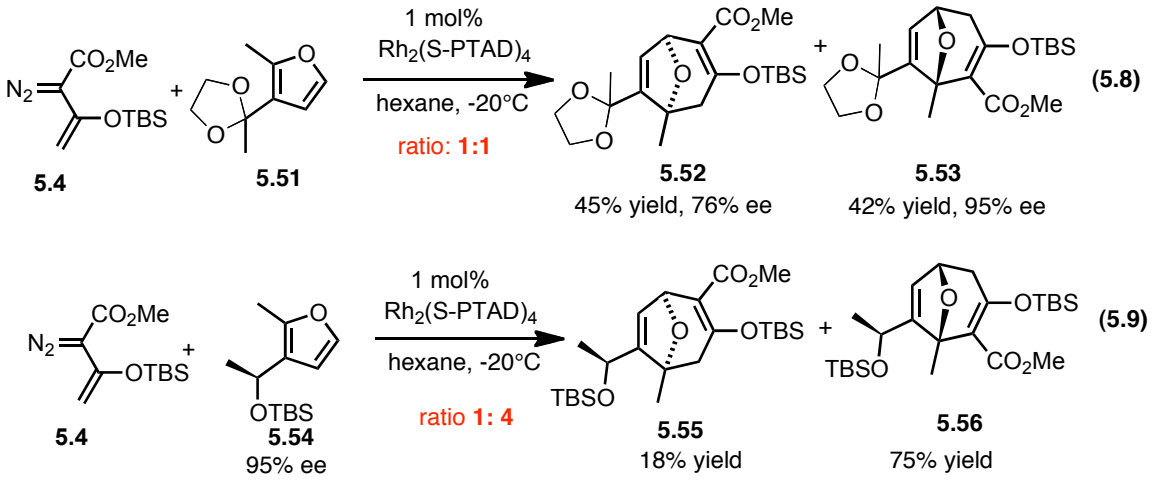


Figure 5.3 Possible mechanisms for the formation of product **5.50**

To understand the detailed mechanism, this reaction was extended to other substrates. The Rh_2(*S*-PTAD)$_4$-catalyzed decomposition of diazoacetate **5.4** in the presence of **5.51** afforded a 1:1 mixture of two products **5.52** and **5.53** (eq. **5.8**). The normal [4 + 3] cycloaddition product **5.52** was isolated in 45% yield with 76% ee, while the abnormal [4

+ 3] cycloadduct **5.43** was produced in 41% yield with remarkably high asymmetric induction (95% ee). This transformation was also applicable to chiral furan **5.54** and good regioselectivity (4:1) was achieved favoring the abnormal [4 + 3] product **5.56** (eq. **5.9**). It is worthwhile to point out that both products are generated as single diastereomers.



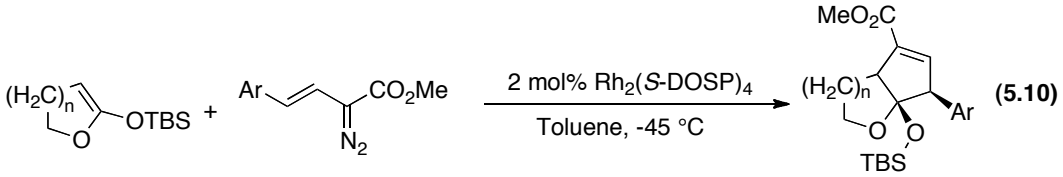
In conclusion, it has been well demonstrated that the reaction between siloxyvinyldiazoacetate and furans generates either the regular cyclopropanation/Cope rearrangement or the abnormal [4 + 3] cycloaddition products. Both types of products are generated with high asymmetric induction. The detailed mechanism for the abnormal [4 + 3] cycloaddition is uncertain and its understanding would be helpful in further improving the regioselectivity favoring the abnormal product formation.

5.2.3 The [3 + 2] cycloaddition between vinylcarbenoids and electron-rich olefins

It has been shown that vinylcarbenoids undergo effective [3 + 2] cycloaddition with either 1,2- or 1,3-disubstituted indoles and excellent stereocontrols are possible.[190]

Presumably, the reaction proceeds through a zwitterionic intermediate and the strong nucleophilicity of indoles would be crucial for the reaction to occur. In principle, silyl ketene acetals of lactones are expected to undergo the effective [3 + 2] annulation with vinylcarbenoids because the nucleophilicity of silyl ketene acetals is comparable to indoles.[142] In this section, we describe a highly asymmetric [3 + 2] annulation between silyl ketene acetals with vinylcarbenoids.

Previous studies have shown that Rh_2(*S*-DOSP)$_4$ is the optimum chiral catalyst for the asymmetric [3 + 2] annulation of vinylcarbenoids with indoles.[197] Rh_2(*S*-DOSP)$_4$ was thus chosen for this study. The Rh_2(*S*-DOSP)$_4$-catalyzed reaction between varied vinyldiazoacetates and silyl ketene acetals underwent effective [3 + 2] annulation (eq. **5.10**). Expected annulation products **5.57**-**5.59** were generated in good yields with excellent asymmetric induction (94-97% ee). Substrates containing either five or six-membered rings were equally effective. The absolute stereochemistry of product **5.59** was unambiguously assigned by X-ray crystallography (Figure **5.4**), while the structures of other two compounds were tentatively determined based on the assumption that all the reactions occur through a similar transition state.



(5.10)

5.57: n = 2, Ar = Ph, yield: 73% ee: 94%

5.58: n = 1, Ar = Ph, yield: 53% ee: 97%

5.59: n = 2, Ar = 2-Naph, yield: 67% ee: 95%

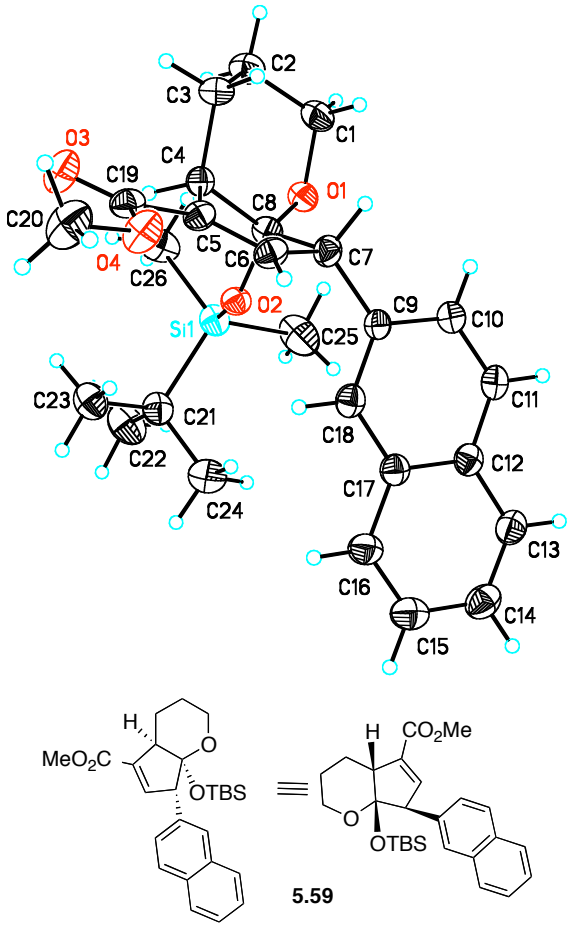
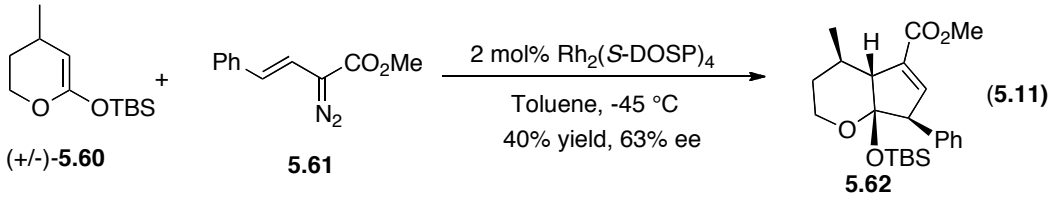


Figure 5.4 X-ray crystallographic structure of product **5.59**

It has been well demonstrated that the reaction of donor-acceptor carbenoids is influenced by the present stereocenters in the substrate.[47,174] We then became interested in exploring if an enantiodifferentiation reaction is possible in this [3 + 2] annulation reaction. The Rh_2(*S*-DOSP)$_4$-catalyzed reaction between racemic **5.60** with diazoacetate **5.61** generated product **5.62** as a single diastereomer in moderate yield with moderate enantioselectivity (eq. **5.11**). The relative stereochemistry of product **5.62** was confirmed based on nOe studies (Figure **5.5**). The formation of **5.62** as a single diastereomer is indicative that this reaction would be under substrate control and substrate **5.60** would

attack the carbenoid carbon from the less hindered face, opposite to the methyl group, leading to the formation of **5.62** exclusively.



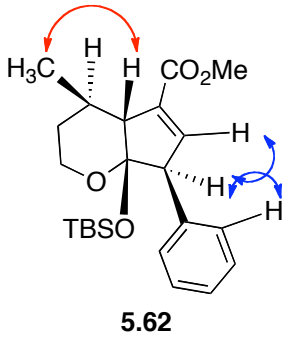
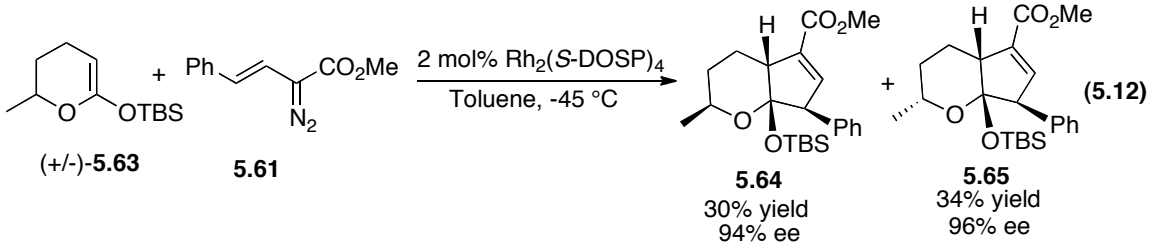


Figure 5.5 ^{1}H nOe studies of **5.62**

The reaction outcome with substrate **5.63** is completely different from the result with **5.60**. The reaction of **5.61** catalyzed by Rh_2(*S*-DOSP)$_4$ is under catalyst control (eq. **5.12**). Two diastereomers **5.64** and **5.65** were produced in a 1:1 ratio and both of them were generated with excellent asymmetric induction. The relative stereo-configuration of these two products was determined based on ^{1}H nOe studies (Figure **5.6**) and the absolute stereochemistry of these two products was tentatively assigned based on a similar asymmetric induction as product **5.59**.



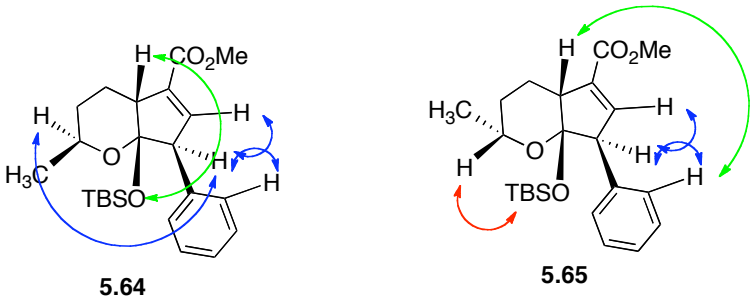
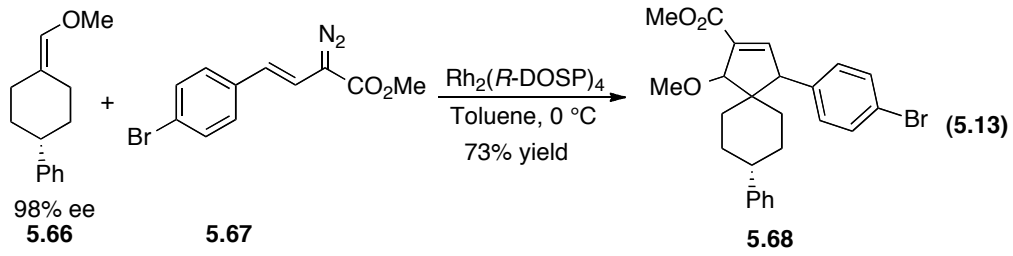


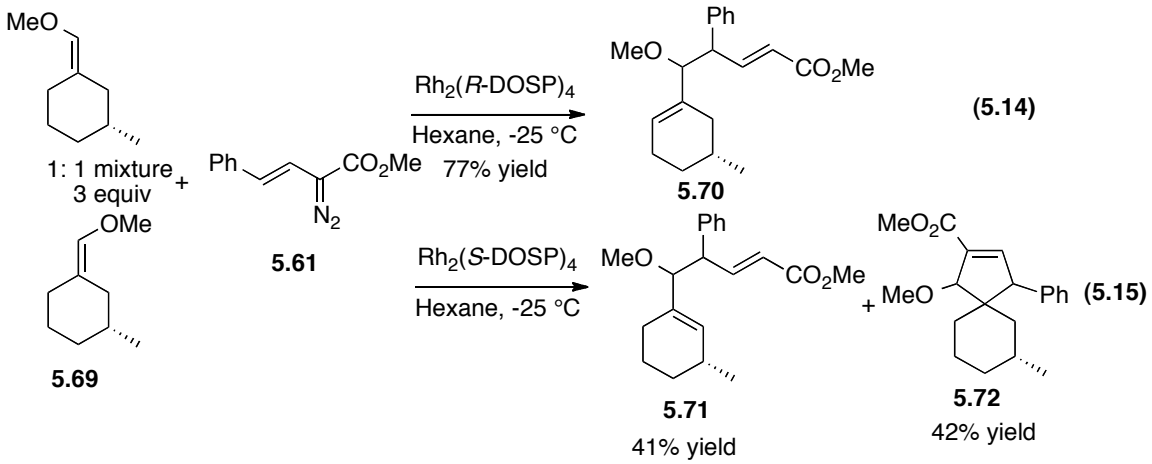
Figure 5.6 ^{1}H nOe studies of products **5.64** and **5.65**

A key feature of cycloaddition between olefins and vinylcarbenoids is the ability of reversing regioselectivity, depending on whether substrates attack the carbenoid carbon or the vinylogous site. We have demonstrated that the reaction between electron rich dienes and siloxyvinyldiazoacetate **5.4** can undergo either the cyclopropanation/Cope rearrangement or the vinylogous [4 + 3] cycloaddition. In this regard, we were also interested in exploring the vinylogous [3 + 2] cycloaddition of vinylcarbenoids, leading to the opposite regioisomer to the product derived from the regular [3 + 2] annulation through the carbenoid reactivity.

The impetus of this project arose from the kinetic resolution of vinyl ethers in the combined C-H functionalization/Cope rearrangement reaction. For example, vinyl ether **5.66** was recovered in 98% ee from such a reaction. The Rh_2(*R*-DOSP)$_4$-catalyzed decomposition of diazoacetate **5.67** with enantiopure ether **5.66** afforded product **5.68** as a single diastereomer in good yield, which represents the first vinylogous [3 + 2] annulation reaction (eq **5.13**). Some of the relative stereocenters need to be defined.



The reaction can also be extended to a more elaborated system. Vinyl ether **5.69** was generated as a 1:1 mixture of two regioisomers, beginning from the enantiopure 3-methylcyclohexanone. The Rh_2(*R*-DOSP)$_4$-catalyzed decomposition of diazoacetate **5.61** with 3.0 equiv of **5.69** generated the CHCR product **5.70** as a single diastereomer (eq **5.14**), while the reaction in the presence of Rh_2(*S*-DOSP)$_4$ afforded two products (eq **5.15**). The CHCR product **5.71** was isolated in 41% yield and the vinylogous [3 + 2] annulation product **5.72** was generated in 42% yield. The structures of these three products need to be confirmed.



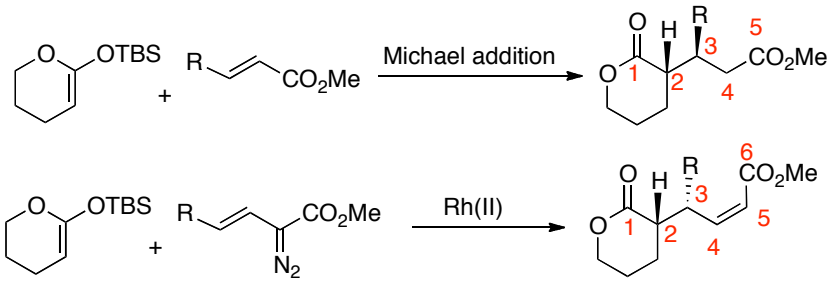
In summary, vinylcarbenoids have been demonstrated to effectively undergo either the regular [3 + 2] annulation or the vinylogous [3 + 2] annulation in a highly stereoselective fashion. The reaction with less sterically crowded olefins undergoes the carbenoid reactivity, while the reaction with crowded substrates favors the vinylogous [3 + 2]

annulation reaction. These studies are sufficiently promising to warrant a thorough evaluation of the scope of these two unusual [3 + 2] cycloadditions.

5.2.4 Vinylogous reactivity of vinylcarbenoids in the formation of 4-substituted (*Z*)-pent-2-enoates

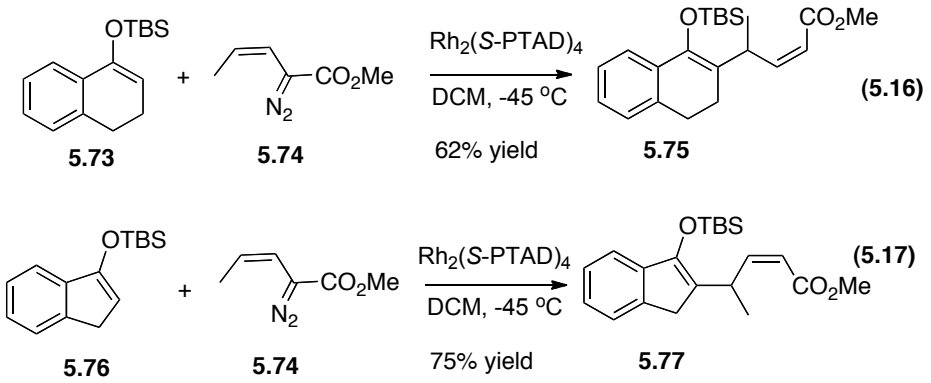
Vinylcarbenoids are capable of undergoing vinylogous reactivity with nucleophiles. We have demonstrated that both (*Z*)- and (*E*)-methylvinyldiazoacetates effectively reacted with *N*-heterocycles and generated 4-substituted (*Z*)-Pent-2-enoates in good yields.[150] In this part, we describe the extension of the reaction scope to other types of nucleophiles, such as silyl enol ethers as well as silyl ketene acetals. This exploration would lead to two different types of products.

A key feature of vinylcarbenoids is that they are electrophilic at the δ carbon to an ester, which makes them different from the traditional conjugate enoates.[198,199] The reaction between silyl ketene acetal and 2-enoates undergoes the Michael addition and generates product containing 1,5-dicarbonyl groups. In contrast, the vinylogous reaction with vinylcarbenoid affords a 1,6-dicarbonyl product (Scheme **5.8**).

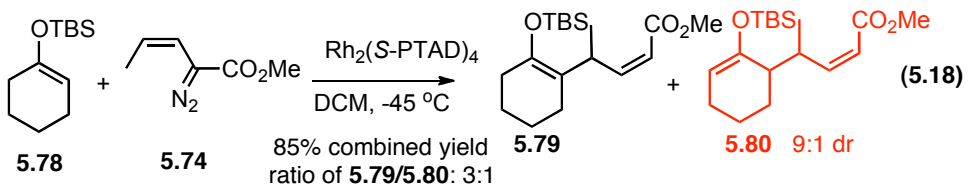


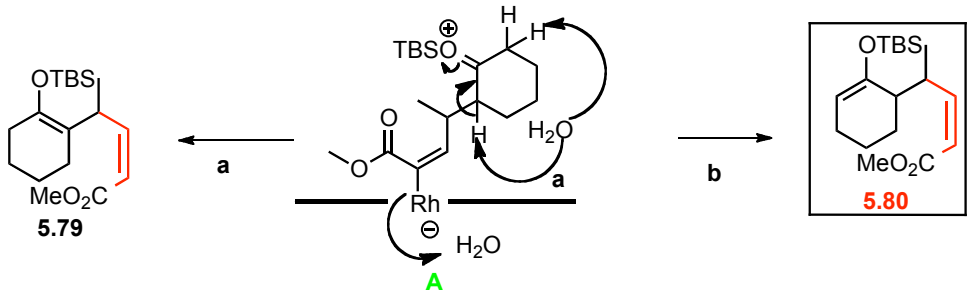
Scheme 5.8 Vinylcarbenoids as synthon of four carbons moiety

It has been shown that *cis*-methylvinylcarbenoids have greater tendency over the *trans*-methylvinylcarbenoids in undergoing the vinylogous reactivity.[150] The study then began with *cis*-methylvinylcarbenoids. The Rh_2(*S*-PTAD)$_4$ catalyzed vinylogous transformation of sterically encumbered silyl enol ether **5.73** with *cis*-methylvinyldiazoacetate **5.74** afforded the expected product **5.75** in good yield (eq. **5.16**). This reaction can also be extended to indene derivative **5.76** and similar results were obtained (eq. **5.17**).



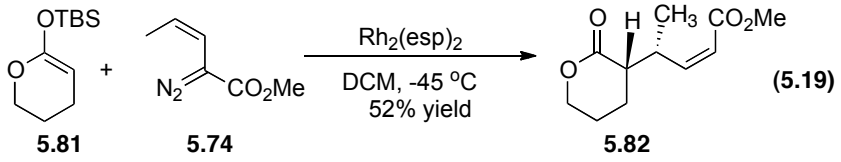
The extension of the reaction to *tert*-butyl(cyclohex-1-en-1-yloxy)dimethylsilane **5.78** led to very interesting results. Two vinylogous products **5.79** and **5.80** were produced in a 3/1 ratio (eq. **5.18**). Both products could be generated from the same zwitterionic intermediate **A**, which contains two different α-protons for elimination (Scheme **5.9**). The elimination with the tertiary proton would afford the product **5.79** (path **a**), while elimination with the methylene proton would generate the product **5.80** (path **b**). The high diastereoselectivity of the product **5.80** is intriguing, indicating that the intermediate **A** is formed in a highly diastereoselective fashion.



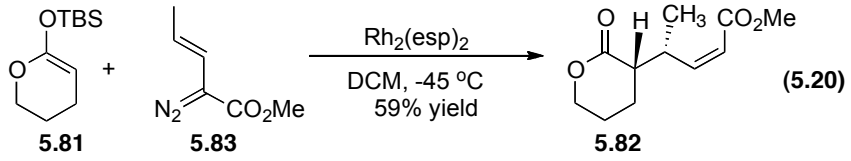


Scheme 5.9 Two reaction pathways of the vinylogous reactivity

Intrigued by the high diastereoselectivity of product **5.80**, we reasoned that if other transformations avoiding elimination could occur, it would be possible to generate *δ*-oxo enoates in a highly diastereoselective fashion. One approach that was considered was the use of silyl ketene acetals instead of silyl enol ethers because the silyl group in silyl ketene acetals is more labile than the one in silyl enol ethers. Consequently, the elimination might be avoided. We then chose ether **5.81** as the model substrate to test our hypothesis. The $Rh_2(esp)_2$-catalyzed decomposition of diazoacetate **5.74** with acetal **5.81** successfully afforded product **5.82** as a single diastereomer in 52% yield (eq. **5.19**).



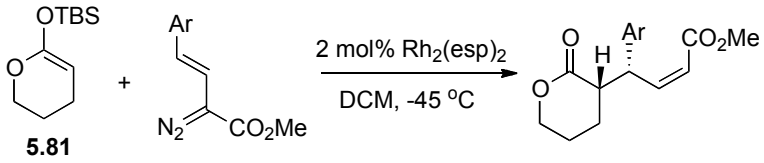
With the highly diastereoselective reaction **5.19** in hand, we next wanted to explore if the opposite diastereomer of product **5.82** would be generated with *trans*-methyl vinyldiazoacetate **5.83** (eq. **5.20**). Surprisingly, the reaction with **5.83** still afforded the same diastereomer **5.82** in 59% yield, slightly better than the reaction beginning from diazoacetate **5.74**. Due to the easy access of (*E*)-vinyldiazoacetates, we then focused on the reaction with (*E*)-vinyldiazoacetates.



5.81 **5.83** **5.82**

This vinylogous transformation could be extended to other *trans*-arylvinyldiazoacetates and products were generated in moderate yields as summarized in Table **5.5**. The moderate yield was because of the occurence of a competing [3 + 2] annulation reaction. The relative configuration of product **5.86** was unambiguously assigned based on X-ray crystallography (Figure **5.7**), while the stereochemistry of other products **5.82**, **5.84**, **5.85**, **5.87** was tentatively assigned based on the assumption of a similar transition state for all the reactions.

Table 5.5 Vinylogous reactions with arylvinyldiazoacetates



5.81

entry	Ar	product	yield (%)
1	Naphthyl	**5.84**	60
2	*p*-OMePh	**5.85**	64
3	*p*-BrPh	**5.86**	61
4	Ph	**5.87**	56

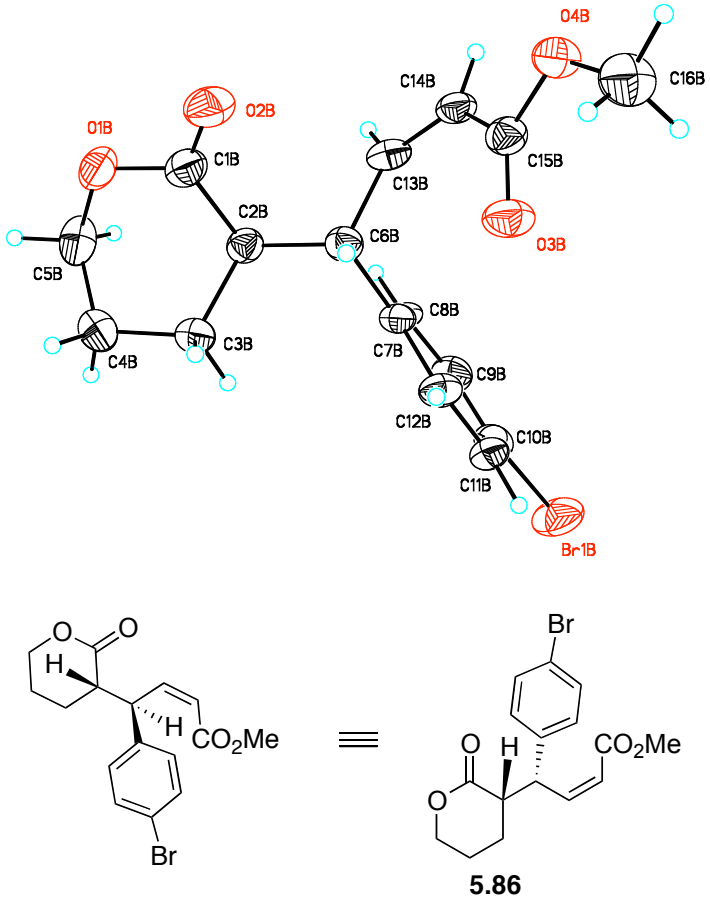
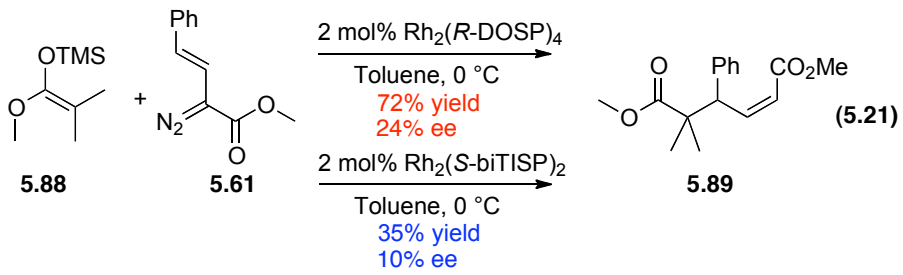
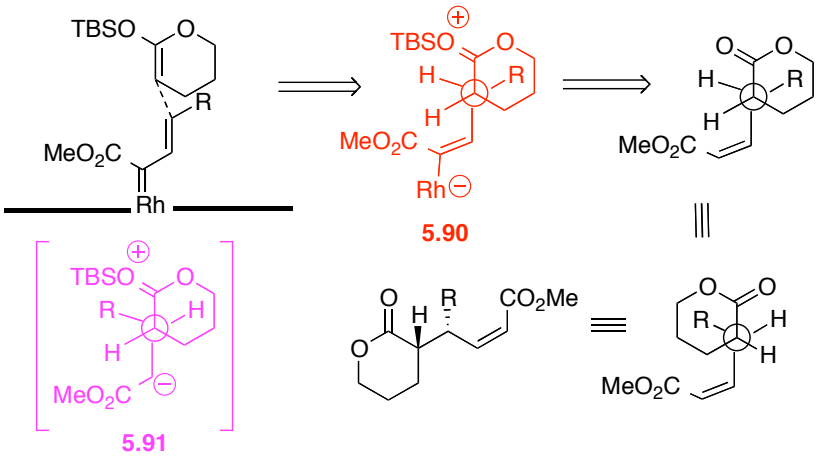


Figure 5.7 X-ray crystallographic structure of product **5.86**

The reaction could also be applied to acyclic ketene acetal **5.88**. The Rh_2(*R*-DOSP)$_4$-catalyzed vinylogous reaction between **5.88** and **5.61** generated product **5.89** in good yield with 24% ee (eq. **5.21**). Even though the reaction was conducted in toluene, no [3 + 2] annulation product was observed. When this reaction was conducted with Rh_2(*S*-biTISP)$_2$, product **5.89** was isolated only in 35% yield with 10% ee.



The high diastereoselectivitve nature of this vinylogous reaction is unprecedented and a possible transition state was proposed to explain the reaction outcome as shown in Scheme **5.10**. Presumably, silyl ketene acetal **5.81** would attack the vinylcarbenoid in the s-*trans* conformation from the vinylogous site and generate intermediate **5.90**, which would lead to the final product after desilylation and proto-demetalation. An interesting feature of this transition state is that the substrate **5.81** attacks the vinylcarbenoid in a fashion that is opposite to the traditional Michael addition,[198,199] which would form intermediate **5.91**. This difference would lead to a different diastereoselective outcome.



Scheme 5.10 Proposed mechanism for the vinylogous reactivity with silyl ketene acetals

In conclusion, vinylcarbenoids have been illustrated to undergo effective vinylogous reactivity with silyl enol ethers and silyl ketene acetals. Products are generated in a highly diastereoselective fashion. The diastereoselective outcome is opposite to the result derived from the Michael addition, and would serve as a complementary strategy to the Michael addition.

This chapter demonstrates that a number of exciting new avenues of research remain in the chemistry of rhodium-catalyzed vinylcarbenoids.

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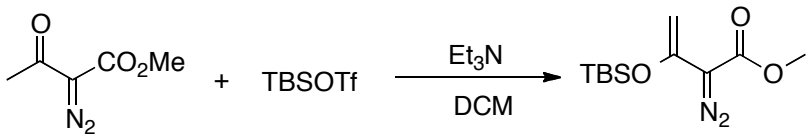
Experimental Section

General methods

All experiments were performed under anhydrous conditions in an atmosphere of argon except where stated, using flame-dried glassware. Toluene and methylenechloride were dried by a solvent purification system (passed through activated alumina columns). Unless otherwise noted, all other reagents were obtained from commercial sources and used as received. ^{1}H Nuclear Magnetic Resonance (NMR) spectra were recorded at 400, 500 or 600 MHz. Data are presented as follows: chemical shift (in ppm on the δ scale relative to δH 7.26 for the residual protons in $CDCl_3$ or δH 7.15 for the residual protons in C_6D_6), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (*J*/Hz), integration. Coupling constants were taken directly from the spectra and are uncorrected. ^{13}C NMR spectra were recorded at 75, 100, 125 or 150 MHz, and all chemical shift values are reported in ppm on the δ scale, with an internal reference of δC 77.0 for $CDCl_3$ or δC 128.39 for C_6D_6. Mass spectral determinations were carried out by using APCI, ESI or EI as ionization source. Melting points are uncorrected. Infrared spectral data are reported in units of cm^{-1}. Analytical TLC was performed on silica gel plates using UV light or potassium permanganate stain if stated. Flash column chromatography was performed on silica gel 60A (230-400 mesh). Optical rotations were measured on Jasco polarimeters. Analytical enantioselective chromatographies were measured on Varian Prostar instrument and used isopropanol/hexane as gradient.

Experiment for Chapter II: Asymmetric Cyclopropanation/ Cope rearrangement and its application in total synthesis



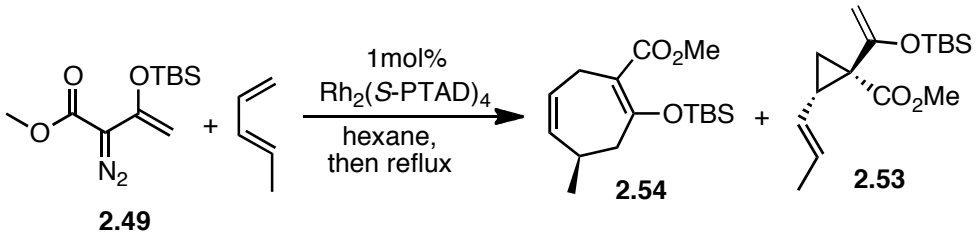
Methyl 3-(*tert*-butyldimethylsilyloxy)-2-diazobut-3-enoate (2.49): The diazo compound was prepared by a modified procedure of Davies. TBSOTf (19.5 mL, 0.085 mol) was added drop-wise to a stirred solution of methyl 2-diazo-3-oxobutanoate (10.0 g, 0.070 mol) and triethylamine (12.3 mL, 0.088 mol) in DCM (200 mL) at 0 °C. The reaction was then aged overnight gradually warming to room temperature. The red solution was then diluted with hexanes (800 mL), washed with dilute $NaHCO_3$ (2 x 500 mL), brine (500 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting orange oil was purified by flash chromatography (1% Et_3N in pure hexane) on silica gel to give the desired compound **2.49** as pink oil (17.8 g) in >98% yield. The physical and spectral data were identical to those previously reported for this compound[1]: ^1H NMR (500 MHz, $CDCl_3$): δ 4.98 (d, J = 2.0 Hz, 1H), 4.23 (d, J = 2.0 Hz, 1H), 3.78 (s, 3H), 0.90 (s, 9H), 0.21 (s, 6H).

General procedure for the enantioselective [4 + 3] cycloaddition

To a flame-dried 25 mL flask containing Rh_2(*S*-PTAD)$_4$ (4.7 mg, 0.01 equiv) and the corresponding dienes (1.50 mmol, 5.0 equiv) in hexane (6 mL) and trifluorotoluene (0.2 mL) under argon atmosphere was added a solution of diazoacetate **2.49** (77 mg, 0.30

[1] Davies, H. M. L.; Ahmed, G.; Churchill, M. R. *J. Am. Chem. Soc.* **1996**, *118*, 10774.

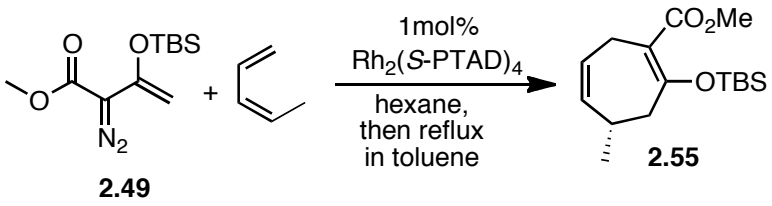
mmol, 1.0 equiv) in hexane (6 mL) by syringe pump over 2 h at -26 °C. The solution was stirred at -26 °C overnight and the heated under reflux for an additional 1 h. The mixture was concentrated under vacuum and purified by flash chromatography in silica gel to provide pure products.



(*R*)-Methyl 2-(*tert*-butyldimethylsilyloxy)-4-methylcyclohepta-1,5-diene carboxylate (2.54): Derived from *trans*-piperylene (103 mg, 1.50 mmol, 5.0 equiv) and purified by flash chromatography (25/1 pentane/Et_2O, R_f: 0.40) in silica gel to provide **2.54** as colorless oil (78.3 mg, 88% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.64-5.69 (m, 1H), 5.38 (dd, *J* = 11.3, 1.2 Hz, 1H), 3.68 (s, 3H), 2.98-3.09 (m, 2H), 2.64 (dd, *J* = 11.0, 13.7 Hz, 1H), 2.44-2.53 (br, 1H), 2.29 (dd, *J* = 2.7, 13.7 Hz, 1H), 1.04 (d, *J* = 7.0 Hz, 3H), 0.95 (s, 9H), 0.18 (s, 3H), 0.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.1, 161.9, 135.1, 126.0, 112.2, 51.1, 41.9, 30.2, 25.7, 25.4, 22.3, 18.3, -3.77, -3.84; IR (neat): 2956, 2930, 2858, 1717, 1692, 1625, 1435, 1372, 1301, 1254, 1219, 1192, 1143, 842, 807, 781 cm^{-1}; HRMS (ESI) calc. for $C_{16}H_{28}O_3SiNa$ $(M+Na)^+$ 319.1700 found 319.1704; HPLC: (AD-H, hexane, 0.3 mL/min) retention times of 25.9 min (major) and 29.3 min (minor), 95 % ee; $[\alpha]^{25}_D$ -20.5 (*c* = 1.36, $CHCl_3$).

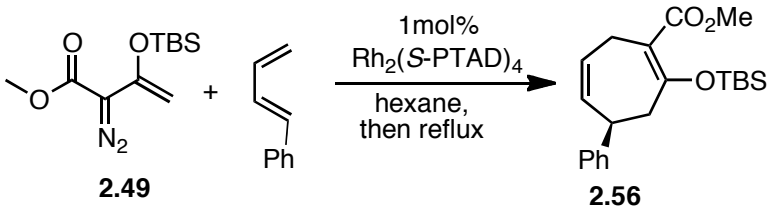
(1S,2R,E)-Methyl 1-(1-(*tert*-butyldimethylsilyloxy)vinyl)-2-(prop-1-enyl) cyclopropanecarboxylate (2.53): ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.64-5.70 (m, 1H),

5.28 (dd, *J* = 8.9, 15.3 Hz, 1H), 4.24 (s, 1H), 4.16 (s, 1H), 3.68 (s, 3H), 2.14 (q, *J* = 8.0 Hz, 1H), 1.66 (d, *J* = 6.4 Hz, 3H), 1.51-1.55 (m, 1H), 1.25 (dd, *J* = 4.3, 8.5 Hz, 1H), 0.90 (s, 9H), 0.17 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.2, 157.0, 128.0, 127.1, 90.9, 51.9, 37.0, 29.8, 25.5, 20.3, 18.0, 13.2, -4.8, -5.1; IR (neat): 2953, 2930, 2858, 1732, 1633, 1338, 1305, 1256, 1205, 1136, 1019, 830, 781 cm^{-1}; HRMS (EI) calc. for $C_{16}H_{29}O_3Si$ $(M+H)^+$ 297.1880 found 297.1874.



2.49 **2.55**

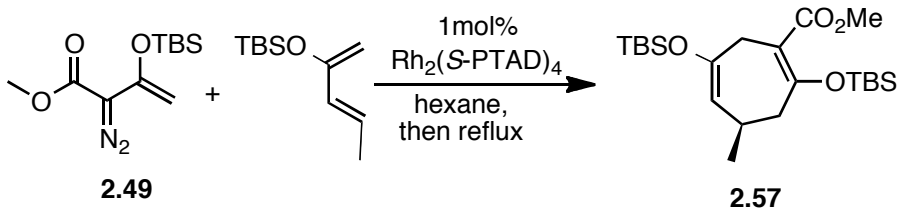
(*S*)-Methyl 2-(*tert*-butyldimethylsilyloxy)-4-methylcyclohepta-1,5-diene carboxylate (2.55): Derived from *cis*-piperylene (103 mg, 1.50 mmol, 5.0 equiv), refluxed in toluene and purified by flash chromatography (25/1 pentane/Et_2O, R_f: 0.40) on silica gel to provide **2.55** as colorless oil (71.2 mg, 80% yield). HPLC: (AD-H, hexane, 0.5 mL/min) retention times of 16.5 min (minor) and 17.7 min (major), 87% ee.



2.49 **2.56**

(*R*)-Methyl 2-(*tert*-butyldimethylsilyloxy)-4-phenylcyclohepta-1,5-diene carboxylate (2.56): Derived from (*E*)-buta-1,3-dienylbenzene (195 mg, 1.50 mmol, 5.0 equiv) and purified by flash chromatography (25/1 pentane/Et_2O, R_f: 0.43) on silica gel to provide

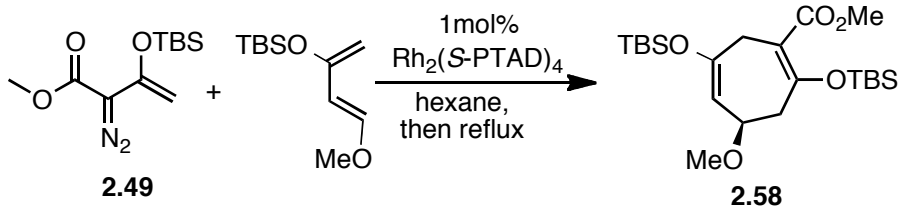
2.56 as colorless oil (88.2 mg, 82% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.34 (m, 2H), 7.22-7.26 (m, 3H), 5.89-5.94 (m, 1H), 5.54 (dm, *J* = 11.3 Hz, 1H), 3.72 (s, 3H), 3.68 (dm, *J* = 11.3 Hz, 1H), 3.15-3.25 (m, 2H), 3.10 (dd, *J* = 11.6, 13.7 Hz, 1H), 2.47 (dd, *J* = 3.1, 13.7 Hz, 1H), 0.92 (s, 9H), 0.16 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.9, 161.4, 144.9, 132.2, 128.6, 127.54, 127.46, 126.6, 112.7, 51.1, 42.8, 41.8, 25.6, 25.3, 18.2, -3.77, -3.82; IR (neat): 2951, 2930, 2858, 1716, 1689, 1624, 1435, 1371, 1252, 1212, 1142, 839, 806, 781, 700 cm^{-1}; HRMS (ESI) calc. for $C_{21}H_{30}O_3SiNa$ $(M+Na)^+$ 381.1856 found 381.1863; HPLC: ((S,S)-Whelk-O1, 0.1% isopropanol in hexane, 0.7 mL/min) retention times of 61.1 min (major) and 79.2 min (minor), 95% ee; $[\alpha]^{25}_D$ -26.3 (*c* = 5.15, $CHCl_3$).



2.49 **2.57**

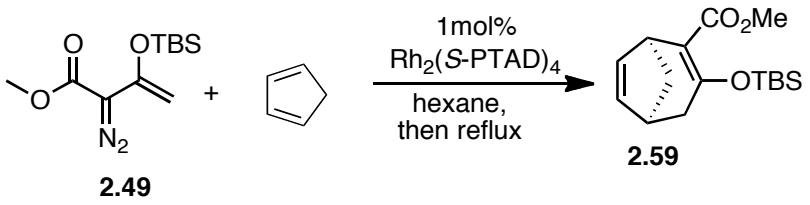
(*R*)-Methyl 2,6-bis(*tert*-butyldimethylsilyloxy)-4-methylcyclohepta-1,5-diene carboxylate (2.57): Derived from (*E*)-*tert*-butyldimethyl(penta-1,3-dien-2-yloxy)silane (298 mg, 1.50 mmol, 5.0 equiv) and purified by flash chromatography (30/1 pentane/Et_2O, R_f: 0.45) in silica gel to provide **2.57** as colorless oil (89.8 mg, 70% yield). ^{1}H NMR (500 MHz, C_6D_6): δ 4.78 (d, *J* = 3.1 Hz, 1H), 3.42 (s, 3H), 3.29-3.44 (m, 2H), 2.45 (br, 1H), 2.31 (dd, *J* = 10.4, 13.7 Hz, 1H), 2.17 (dd, *J* = 3.1, 13.7 Hz, 1H), 0.99 (s, 18H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.20 (s, 3H), 0.174 (s, 3H), 0.166 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6): δ 167.0, 162.3, 150.5, 112.7, 110.0, 50.6, 42.4, 32.5, 29.8, 26.0, 25.9, 23.1, 18.6, 18.2, -3.7, -3.8, -4.3, -4.4; IR (neat): 2956, 2930, 2858, 1719, 1693,

1627, 1332, 1254, 1221, 1142, 913, 839, 780 cm^{-1}; HRMS (APCI) calc. for $C_{22}H_{43}O_4Si_2$ $(M+H)^+$ 427.2694 found 427.2683; HPLC: ((S,S)-DACH DNB 5/100, hexane, 0.7 mL/min) retention times of 21.3 min (minor) and 26.7 min (major), 99% ee; $[\alpha]^{25}_D$ -36.1 (*c* = 1.49, $CHCl_3$).



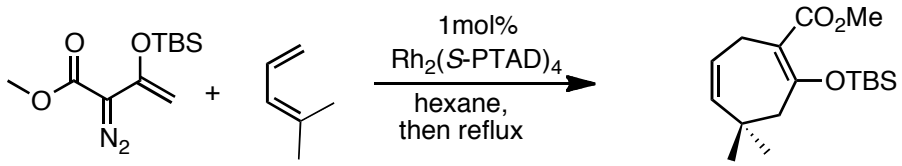
2.49 **2.58**

(*R*)-Methyl 2,6-bis(*tert*-butyldimethylsilyloxy)-4-methoxycyclohepta-1,5-diene carboxylate (2.58): Derived from (*E*)-3-(*tert*-butyldimethylsiloxy)-1-methoxy-1,3-butadiene (322 mg, 1.50 mmol, 5.0 equiv) and purified by flash chromatography (10/1 pentane/Et_2O containing 0.5% Et_3N, R_f: 0.57) in silica gel to provide **2.58** as colorless oil (83.4 mg, 63% yield). ^1H NMR (500 MHz, $CDCl_3$): δ 4.92 (d, *J* = 3.4 Hz, 1H), 4.02-4.04 (m, 1H), 3.68 (s, 3H), 3.33 (s, 3H), 3.24 (d, *J* = 18.0 Hz, 1H), 3.13 (d, *J* = 18.0 Hz, 1H), 2.78 (dd, *J* = 10.1, 13.7 Hz, 1H), 2.54 (dd, *J* = 3.1, 13.7 Hz, 1H), 0.96 (s, 9H), 0.92 (s, 9H), 0.199 (s, 3H), 0.193 (s, 3H), 0.15 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.5, 159.9, 153.6, 110.4, 107.4, 73.8, 55.2, 51.2, 39.9, 32.7, 25.66, 25.61, 18.3, 18.0, -3.8, -4.5, -4.6; IR (neat): 2953, 2930, 2858, 1720, 1693, 1666, 1628, 1329, 1255, 1220, 1142, 1086, 840, 781 cm^{-1}; HRMS (ESI) calc. for $C_{21}H_{39}O_4Si_2$ $(M-CH_3)^+$ 411.2381 found 411.2389; HPLC: (OD-H, hexane, 0.3 mL/min) retention times of 25.9 min (major) and 29.7 min (minor), 95% ee; $[\alpha]^{25}_D$ -34.0 (*c* = 1.70, $CHCl_3$).



2.49 **2.59**

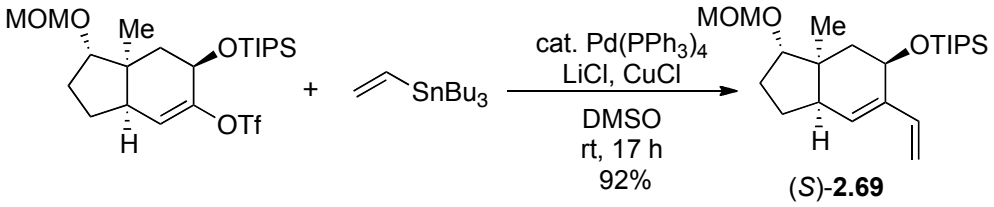
(*1S,5S*)-Methyl 3-(*tert*-butyldimethylsilyloxy)bicyclo[3.2.1]octa-2,6-diene-2-carboxylate (2.59): Derived from cyclopentadiene (99 mg, 1.50 mmol, 5.0 equiv) and purified by flash chromatography (30/1 pentane/Et_2O, R_f: 0.46) in silica gel to provide **2.59** as colorless oil (76.3 mg, 86% yield). The NMR data were consistent with published data. HRMS (APCI) calc for $C_{16}H_{27}O_3Si$ $(M+H)^+$ 295.1724 found 295.1720; HPLC: ((S,S)-Whelk-O1, 0.4 % isopropanol in hexane, 0.3 mL/min) retention times of 27.6 min (minor) and 29.1 min (major), 92% ee; $[\alpha]^{25}_D$ -62.7 (*c* = 1.35, $CHCl_3$).



2.49 **2.60**

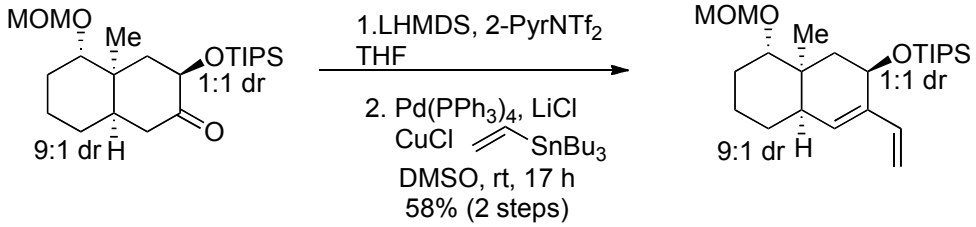
Methyl 2-(*tert*-butyldimethylsilyloxy)-4,4-dimethylcyclohepta-1,5-diene carboxylate (2.60): Derived from 4-methylpenta-1,3-diene (123 mg, 1.50 mmol, 5.0 equiv) and purified by flash chromatography (25/1 pentane/Et_2O, R_f: 0.52) on silica gel to provide **2.60** as colorless oil (52.8 mg, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.56 (dt, *J* = 5.9, 11.3 Hz, 1H), 5.22 (dm, *J* = 11.3 Hz, 1H), 3.68 (s, 3H), 3.01 (dd, *J* = 1.6, 5.9 Hz, 2H), 2.46 (s, 2H), 1.04 (s, 6H), 0.95 (s, 9H), 0.16 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 162.1, 139.5, 123.7, 112.6, 51.0, 47.4, 34.0, 29.9, 25.7, 25.4, 18.3, -3.6; IR (neat):

2954, 1716, 1690, 1363, 1218, 1194, 1143, 1050, 822, 779 cm^{-1}; HRMS (APCI) calc. for $C_{17}H_{31}O_3Si$ $(M+H)^+$ 311.2037 found 311.2037.



Triisopropyl(((3*S*,3a*S*,5*R*,7a*R*)-3-(methoxymethoxy)-3a-methyl-6-vinyl-2,3,3a,4,5,7a-hexahydro-1*H*-inden-5-yl)oxy)silane ((*S*)-2.69): Anhydrous LiCl (1.06 g, 25.08 mmol) was added to a Schlenk flask, which was heated to 120 °C under vacuum for 18 h. After cooling to rt and backfilling with N_2, $Pd(PPh_3)_4$ (0.483 g, 0.418 mmol) and CuCl (2.184 g, 22.07 mmol) were added. The Schlenk flask was evacuated and backfilled with N_2 (4x). A solution of enol triflate (2.16 g, 4.18 mmol) and vinyl tributylstannane (1.99 g, 6.27 mmol) in DMSO (35 mL) was added to the Schlenk flask, and then the mixture was sparged with N_2 for 15 min. The dark red-brown solution was stirred at rt for 17 h, before it was diluted with Et_2O (40 mL) and washed with a 5:1 brine/5% NH_4OH solution (40 mL). The aqueous layer was extracted with Et_2O (40 mL), and the combined organic layers were washed sequentially with H_2O (2 x 40 mL) and brine (2 x 40 mL). After drying over Na_2SO_4 and concentrating, the crude product was purified by flash chromatography (gradient of 20:1 hexanes/EtOAc) to afford diene (*S*)-**2.69** (1.52 g) as clear oil in 92% yield. R_f 0.64 (20:1 hexanes/EtOAc); ^1H NMR (400 MHz, $CDCl_3$): δ 6.46 (dd, *J* = 16.0, 8.0 Hz, 1H), 5.89 (d, *J* = 4.0 Hz, 1H), 5.36 (d, *J* = 16.0 Hz, 1H), 4.97 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 4.0 Hz, 1H), 4.60 (d, *J* = 8.0 Hz, 1H), 4.58-4.55 (m, 1H), 3.70 (t, *J* = 4.0 Hz, 1H), 3.37 (s, 3H), 2.26-2.21 (m, 1H), 2.11-2.04 (m, 2H), 1.73-

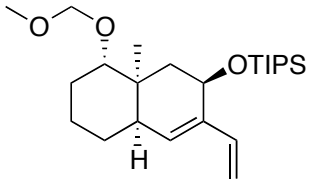
1.60 (m, 3H), 1.54-1.28 (m, 4H), 1.09 (s, 21H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1, 136.2, 128.0, 112.5, 95.5, 86.2, 67.5, 55.3, 44.6, 44.3, 41.7, 30.5, 29.6, 20.3, 18.33, 18.28, 12.9; IR (film) *v*max 2945, 2868, 1641, 1464, 1421, 1383, 1247, 1209, 1147, 1096, 1042 cm^{-1}; HRMS (ESI) calc. for $C_{23}H_{42}NaO_3Si$ $(M+Na)^+$ 417.2801 found 417.2805.



(*S*)-2.72, (*S*)-2.75, (*S*)-2.78: HMDS (2.65 mL, 12.68 mmol) was dissolved in THF (95 mL) and cooled to -78 °C. *n*-BuLi (4.60 mL, 2.5 M in hexanes, 11.50 mmol) was added dropwise. After 40 min. at -78 °C, the ketone (4.18 g, 10.49 mmol) in THF (5 mL) was added dropwise. The reaction was maintained at -78 °C for 1 h, after which 2-pyrNTf$_2$ (4.13 g, 11.53 mmol) in THF (5 mL) was added. After an additional 30 min at -78 °C, the cold bath was removed, and the reaction mixture warmed to rt for 30 min. The reaction mixture was quenched by the addition of sat. aq. NH_4Cl (60 mL). The solution was separated and extracted with EtOAc (3 x 40 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to give golden-orange oil. Upon dilution with 9:1 hexane:EtOAc, the solution was filtered and concentrated. Due to the lability of the enol triflate on silica, the crude material was immediately carried on into the subsequent reaction without purification. R_f :0.35 (9:1 hexanes/EtOAc).

Anhydrous LiCl (2.67 g, 62.91 mmol) was added to an Schlenk flask, which was heated to 120 °C under vacuum for 18 h. After cooling to rt and backfilling with N_2, $Pd(PPh_3)_4$

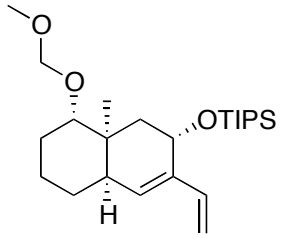
(1.21 g, 1.05 mmol) and CuCl (5.48 g, 55.36 mmol) were added. The Schlenk flask was evacuated and backfilled with N_2 (4x). A solution of enol triflate (5.56 g, 10.49 mmol) and vinyl tributylstannane (4.60 ml, 15.73 mmol) in DMSO (87 mL) was added to the Schlenk flask, and then the mixture was sparged with N_2 for 15 min. The dark red-brown solution was stirred at rt for 17 h, before it was diluted with Et_2O (100 mL) and washed with a 5:1 brine/5% NH_4OH solution (60 mL). The aqueous layer was extracted with Et_2O (40 mL), and the combined organic layers were washed sequentially with H_2O (2 x 60 mL) and brine (2 x 60 mL). In order to remove the organotin impurities, KF/Celite was added and allowed to stir for 1 h, which upon filtering, drying over Na_2SO_4 and concentrating, the crude product was purified by flash chromatography (gradient of 20:1 hexanes/EtOAc) to afford the diene (2.50 g) as a mixture of three isomers in 58% yield (2 steps). R_f: 0.64 (20:1 hexanes/EtOAc). The ratio of (*S*)-**2.72**/(*S*)-**2.75**/(*S*)-**2.78** was 5/4/1. Careful column chromatograpgy on silica gel (20:1 pentane/Et_2O, R_f = 0.54 for (*S*)-**2.75**; R_f = 0.41 for (*S*)-**2.72**; R_f = 0.39 for (*S*)-**2.78**) provided (*S*)-**2.75** as pure colorless oil and a mixture of (*S*)-**2.72** and (*S*)-**2.78**, which were further purified on silica gel (3:1 pentane/methylene chloride, R_f = 0.47 for (*S*)-**2.72**; R_f = 0.43 for (*S*)-**2.78**).



(*S*)-**2.72**

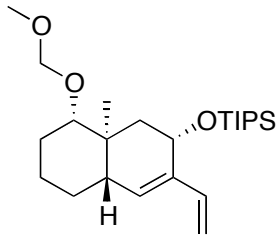
Triisopropyl(((2*R*,4a*R*,8*S*,8a*S*)-8-(methoxymethoxy)-8a-methyl-3-vinyl-1,2,4a,5,6,7,8,8a-octahydronaphthalen-2-yl)oxy)silane ((*S*)-2.72): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.35 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.82 (d, *J* = 5.5 Hz, 1H), 5.36 (dd, *J* = 17.6,

1.8 Hz, 1H), 4.97 (dd, *J* = 11.0, 1.8 Hz, 1H), 4.70 (d, *J* = 7.0 Hz, 1H), 4.61 (d, *J* = 7.0 Hz, 1H), 4.57-4.62 (m, 1H), 3.39 (s, 3H), 3.32-3.35 (m, 1H), 1.92-1.03 (m, 2H), 1.67-1.77 (m, 2H), 1.55-1.66 (m, 2H), 1.41-1.53 (m, 2H), 1.22-1.34 (m, 1H), 1.06-1.12 (m, 21H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.9, 136.8, 130.7, 112.7, 96.0, 80.4, 68.5, 55.7, 39.0, 38.5, 37.5, 29.8, 26.0, 21.7, 19.8, 18.4, 18.3, 13.0; IR (neat): 2939, 2865, 1436, 1097, 1036, 1011, 917, 883, 679 cm^{-1}; HRMS (ESI) calc. for $C_{24}H_{44}O_3NaSi$ $(M+Na)^+$ 431.2952 found 431.2953; $[\alpha]^{25}_D$ 16.3 (*c* = 2.07, $CHCl_3$).



(*S*)-**2.75**

Triisopropyl(((2*S*,4a*R*,8*S*,8a*S*)-8-(methoxymethoxy)-8a-methyl-3-vinyl-1,2,4a,5,6,7,8,8a-octahydronaphthalen-2-yl)oxy)silane ((*S*)-2.75): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.33 (dd, *J* = 17.7, 11.0 Hz, 1H), 5.57 (t, *J* = 0.9 Hz, 1H), 5.35 (dm, *J* = 17.7 Hz, 1H), 4.97 (d, *J* = 11.3 Hz, 1H), 4.64-4.69 (m, 2H), 4.56-4.63 (m, 1H), 3.35 (s, 3H), 3.34-3.39 (m, 1H), 2.39 (dd, *J* = 12.8, 6.4 Hz, 1H), 2.32 (br, 1H), 1.67-1.85 (m, 2H), 1.18-1.58 (m, 5H), 1.07-1.11 (m, 21H), 1.02 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 139.4, 136.5, 131.4, 113.0, 96.9, 77.9, 67.6, 55.3, 43.3, 43.0, 39.2, 28.3, 27.2, 21.2, 20.7, 18.4, 18.3, 13.0; IR (neat): 2941, 2866, 1465, 1105, 1045, 918, 883, 678 cm^{-1}; HRMS (ESI) calc. for $C_{24}H_{44}O_3NaSi$ $(M+Na)^+$ 431.2952 found 431.2953; $[\alpha]^{25}_D$ -5.3 (*c* = 1.51, $CHCl_3$).



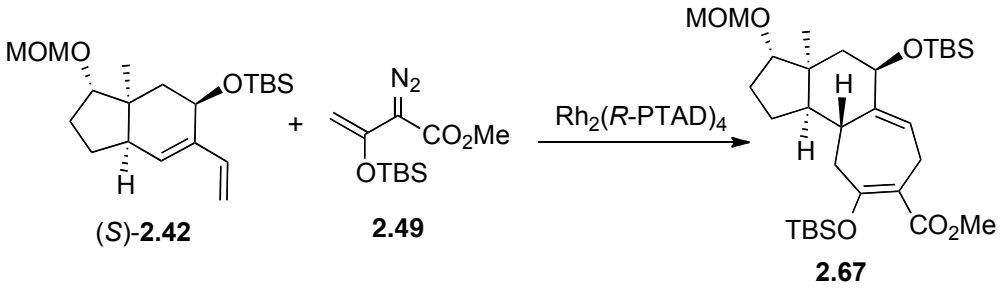
(*S*)-**2.78**

Triisopropyl(((2*S*,4a*S*,8*S*,8a*S*)-8-(methoxymethoxy)-8a-methyl-3-vinyl-1,2,4a,5,6,7,8,8a-octahydronaphthalen-2-yl)oxy)silane ((*S*)-2.78): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.35 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.57 (s, 1H), 5.38 (dm, *J* = 17.7 Hz, 1H), 4.99 (d, *J* = 11.2 Hz, 1H), 4.72 (d, *J* = 7.0 Hz, 1H), 4.59 (d, *J* = 6.7 Hz, 1H), 4.53 (d, *J* = 5.2 Hz, 1H), 3.40 (s, 3H), 3.16 (dd, *J* = 11.0, 4.3 Hz, 1H), 2.35 (d, *J* = 13.7 Hz, 1H), 1.72-1.82 (m, 3H), 1.52-1.62 (m, 1H), 1.30-1.50 (m, 4H), 1.06-1.12 (m, 21H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.65, 137.59, 129.2, 112.4, 95.5, 83.6, 66.2, 55.43, 55.41, 44.4, 43.8, 36.98, 26.9, 26.3, 24.4, 18.3, 13.1, 11.5; IR (neat): 2941, 2865, 1465, 1142, 1038, 931, 882, 771, 675 cm^{-1}; HRMS (ESI) calc. for $C_{24}H_{44}O_3NaSi$ $(M+Na)^+$ 431.2952 found 431.2953; $[\alpha]^{25}_D$ -8.0 (*c* = 2.33, $CHCl_3$).

General procedure for the enantiodivergent [4 + 3] cycloadditions

A solution of methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**2.49**) (46.7 mg, 0.18 mmol, 3.0 equiv) in dried toluene (3 mL) was added dropwise to a stirred solution of diene and $Rh_2(PTAD)_4$ (1.9 mg, 2 mol %) in toluene (3 mL) at 0 °C or room temperature under argon atmosphere over 3 h by syringe pump. The contents were stirred for additional 1 h and then heated to 60 °C for 1 h. The solution was then cooled to room

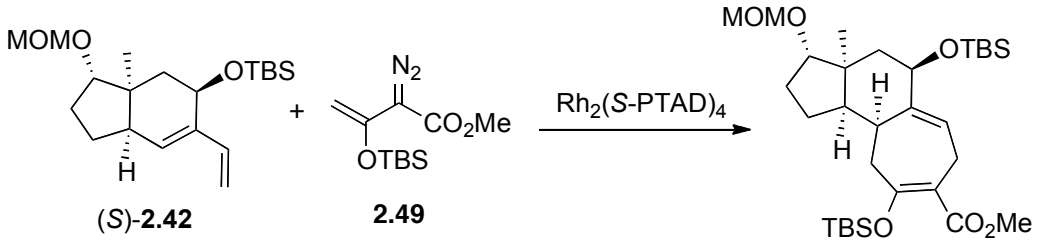
temperature and concentrated *in vacuo*. The residue was then purified by flash chromatography to give product as colorless oil.



(3*S*,3a*S*,5*R*,10a*R*,10b*R*)-Methyl 5,9-bis((*tert*-butyldimethylsilyl)oxy)-3-(methoxy methoxy)-3a-methyl-1,2,3,3a,4,5,7,10,10a,10b-decahydrocyclohepta[*e*]indene-8-carboxylate (2.67): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**2.49**) (46.7 mg, 0.18 mmol, 3.0 equiv) and diene *S*-**2.42**[2] (21.2 mg, 0.06 mmol, 1.0 equiv) with Rh_2(*R*-PTAD)$_4$ (1.9 mg, 2 mol%) at 0 °C, and purified by flash chromatography (10:1 pentane/Et_2O, R_f = 0.38) to give product **(2.67)** (28.3 mg, 81% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.70 (t, *J* = 6.0 Hz, 1H), 4.70 (d, *J* = 6.4 Hz, 1H), 4.64 (d, *J* = 6.4 Hz, 1H), 4.41 (t, *J* = 8.3 Hz, 1H), 4.08 (t, *J* = 4.0 Hz, 1H), 3.67 (s, 3H), 3.34 (s, 3H), 3.00 (dd, *J* = 6.4, 1.6 Hz, 2H), 2.61 (dd, *J* = 13.3, 3.2 Hz, 1H), 2.35-2.48 (m, 2H), 1.94-2.06 (m, 3H), 1.57-1.64 (m, 1H), 1.40-1.52 (m, 3H), 0.95 (s, 9H), 0.87 (s, 3H), 0.85 (s, 9H), 0.17 (s, 3H), 0.16 (s, 3H), 0.01 (s, 3H), -0.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 161.9, 143.4, 122.5, 113.1, 97.0, 83.9, 75.8, 55.2, 51.0, 50.5, 43.5, 41.5, 37.7, 34.8, 28.4, 25.9, 25.7, 25.1 (2C), 23.6, 18.3, 18.1, -3.6, -3.9, -4.6, -4.7; IR (neat): 2951, 2928, 1691, 1201, 1147, 1044, 886, 827, 775 cm^{-1}; HRMS (APCI) calc. for $C_{31}H_{57}O_6Si_2$ $(M+H)^+$ 581.3688 found 581.3696; $[\alpha]^{25}_D$ -15.0 (*c* = 1.34,

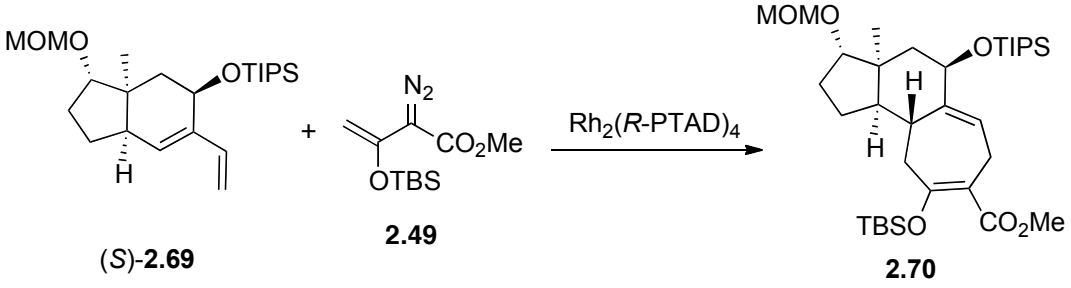
[2] Miller, L. C.; Ndungu, J. M.; Sarpong, R. *Angew. Chem. Int. Ed.* **2009**, *48*, 2398.

$CHCl_3$). For the reaction beginning with racemic diene **2.42** in the presence of Rh_2(*R*-PTAD)$_4$, HPLC of product **2.67**: (AD-H, 0.3% isopropanol in hexane, 0.7 mL/min) retention times of 6.1 min (minor) and 6.9 min (major), 90% ee.



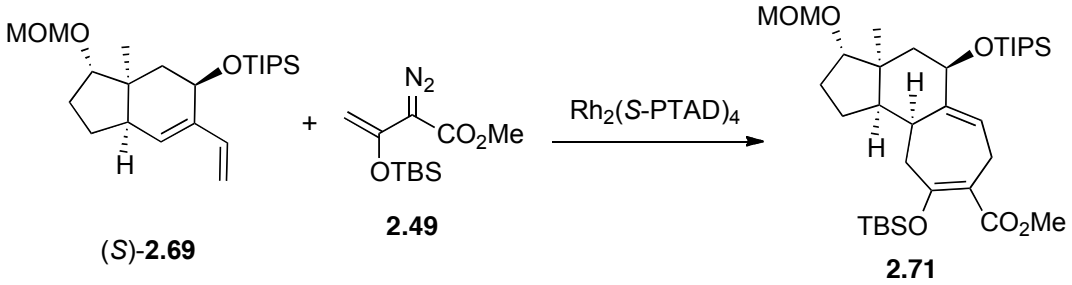
(3*S*,3a*S*,5*R*,10a*S*,10b*R*)-Methyl 5,9-bis((*tert*-butyldimethylsilyl)oxy)-3-(methoxy methoxy)-3a-methyl-1,2,3,3a,4,5,7,10,10a,10b-decahydrocyclohepta[*e*]indene-8-carboxylate (2.68): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**2.49**) (46.7 mg, 0.18 mmol, 3.0 equiv) and diene *S*-**2.42** (21.2 mg, 0.06 mmol, 1.0 equiv) with Rh_2(*S*-PTAD)$_4$ (1.9 mg, 2 mol%) at 0 °C, and purified by flash chromatography (10:1 pentane/Et_2O, R_f = 0.25) to give product (**2.68**) (27.8 mg, 80% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.03–6.07 (m, 1H), 4.66 (d, *J* = 6.7 Hz, 1H), 4.55 (d, *J* = 6.7 Hz, 1H), 3.95-3.99 (m, 1H), 3.69 (s, 3H), 3.56 (d, *J* = 5.4 Hz, 1H), 3.37 (s, 3H), 2.94-3.12 (m, 3H), 2.51-2.55 (m, 1H), 1.99-2.09 (m, 2H), 1.52-1.87 (m, 4H), 1.42-1.46 (m, 1H), 1.16 (s, 3H), 1.08-1.21 (m, 1H), 0.96 (s, 9H), 0.89 (s, 9H), 0.18 (s, 3H), 0.16 (s, 3H), 0.05 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 161.8, 139.9, 120.1, 113.5, 95.1, 85.8, 70.0, 55.5, 51.0, 49.6, 46.0, 42.6, 39.5, 34.8, 28.5, 25.9, 25.7, 24.4, 23.6, 19.0, 18.43, 18.41, -4.0, -4.1, -4.9, -5.0; IR (neat): 2951, 2929, 2857, 1714, 1692, 1361, 1252, 1189, 1148, 1097, 1033, 829, 776 cm^{-1}; HRMS

(APCI) calc. for $C_{31}H_{57}O_6Si_2$ $(M+H)^+$ 581.3688 found 581.3692; $[\alpha]^{25}_D$ 39.8 (*c* = 1.43, $CHCl_3$). For the reaction beginning with racemic diene **2.42** in the presence of Rh_2(*R*-PTAD)$_4$, HPLC of product **2.69**: ((*S*,*S*)-DACH DNB, 0.3% isopropanol in hexane, 0.7 mL/min) retention times of 15.0 min (major) and 16.7 min (minor), 99% ee.

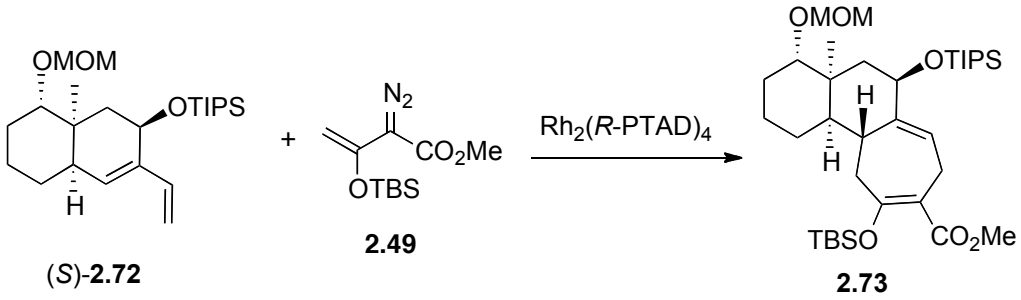


(3*S*,3a*S*,5*R*,10a*R*,10b*R*)-Methyl 9-((*tert*-butyldimethylsilyl)oxy)-3-(methoxymethoxy)-3a-methyl-5-((triisopropylsilyl)oxy)-1,2,3,3a,4,5,7,10,10a,10b-decahydrocyclohepta[*e*]indene-8-carboxylate (2.70): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**2.49**) (46.7 mg, 0.18 mmol, 3.0 equiv) and diene (*S*)-**2.69** (23.7 mg, 0.06 mmol, 1.0 equiv) with Rh_2(*R*-PTAD)$_4$ (1.9 mg, 2 mol %) at 0 °C, and purified by flash chromatography (10:1 pentane/Et_2O, R_f = 0.55) to give product **2.70** (30.6 mg, 82% yield) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.71 (t, *J* = 6.2 Hz, 1H), 4.68 (d, *J* = 6.2 Hz, 1H), 4.64 (d, *J* = 6.24 Hz, 1H), 4.47 (t, *J* = 8.1 Hz, 1H), 4.16 (t, *J* = 3.8 Hz, 1H), 3.67 (s, 3H), 3.34 (s, 3H), 3.00 (d, *J* = 5.7 Hz, 2H), 2.58-2.64 (m, 1H), 2.42-2.50 (m, 2H), 1.96-2.08 (m, 3H), 1.60-1.67 (m, 1H), 1.45-1.54 (m, 2H), 1.42 (dd, *J* = 14.3, 4.3 Hz, 1H), 0.99-1.06 (m, 21H), 0. 95 (s, 9H), 0.87 (s, 3H), 0.17 (s, 3H), 0.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 161.9, 143.4, 122.4, 113.1, 97.2, 84.2, 76.0, 55.3, 50.9, 50.7, 43.6, 41.6, 37.8, 34.6, 28.4, 25.7, 25.0, 24.9, 23.7, 18.3,

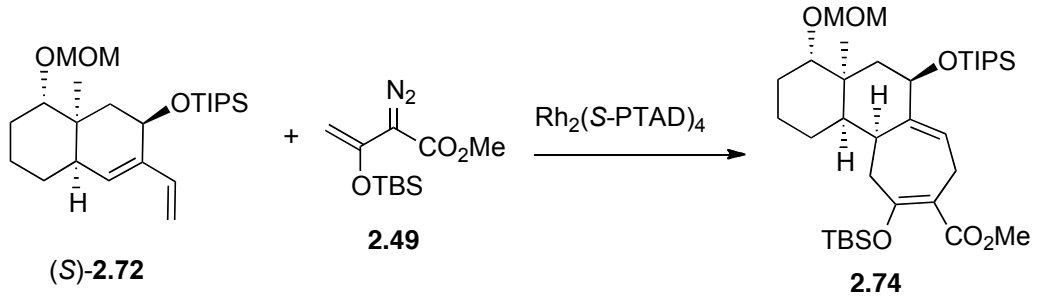
18.2, 18.1, 12.3, -3.6, -3.9; IR (neat): 2944, 2864, 1718, 1691, 1463, 1372, 1202, 1148, 1046, 883, 827 cm^{-1}; HRMS (APCI) calc. for $C_{34}H_{63}O_6Si_2$ $(M+H)^+$ 623.4163 found 623.4164; $[\alpha]^{25}_D$ -17.6 (*c* = 1.83, $CHCl_3$).



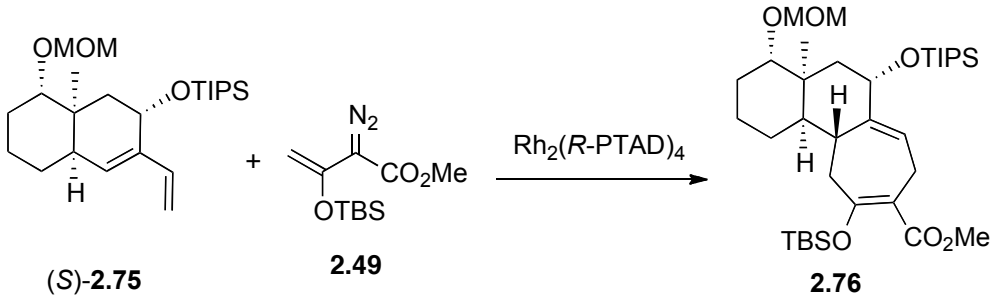
(3*S*,3a*S*,5*R*,10a*S*,10b*R*)-Methyl 9-((*tert*-butyldimethylsilyl)oxy)-3-(methoxymethoxy)-3a-methyl-5-((triisopropylsilyl)oxy)-1,2,3,3a,4,5,7,10,10a,10b-decahydrocyclohepta[*e*]indene-8-carboxylate (2.71): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**2.49**) (46.7 mg, 0.18 mmol, 3.0 equiv) and diene (***S*)-2.69** (23.7 mg, 0.06 mmol, 1.0 equiv) with Rh_2(*S*-PTAD)$_4$ (1.9 mg, 2 mol %) at 0 °C, and purified by flash chromatography (10:1 pentane/Et_2O, R_f = 0.42) to give product **2.71** (28.4 mg, 76% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.13–6.19 (m, 1H), 4.66 (d, *J* = 6.7 Hz, 1H), 4.55 (d, *J* = 6.7 Hz, 1H), 4.03-4.10 (m, 1H), 3.67 (s, 3H), 3.56 (d, *J* = 5.5 Hz, 1H), 3.37 (s, 3H), 2.91-3.12 (m, 3H), 2.47-2.52 (m, 1H), 1.97-2.10 (m, 2H), 1.50-1.88 (m, 5H), 1.16 (s, 3H), 0.98-1.12 (m, 22H), 0.95 (s, 9H), 0.17 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 161.6, 140.1, 120.4, 113.7, 95.1, 85.9, 70.1, 55.5, 50.9, 49.7, 46.1, 42.9, 39.4, 35.0, 28.5, 25.7, 24.3, 23.5, 19.1, 18.5, 18.12, 18.08, 12.4, -4.11, -4.14; IR (neat): 2943, 2865, 1714, 1694, 1463, 1252, 1220, 1189, 1147, 1098, 1034, 881, 830, 781 cm^{-1}; HRMS (APCI) calc. for $C_{34}H_{63}O_6Si_2$ $(M+H)^+$ 623.4163 found 623.4164; $[\alpha]^{25}_D$ 40.3 (*c* = 1.71, $CHCl_3$).



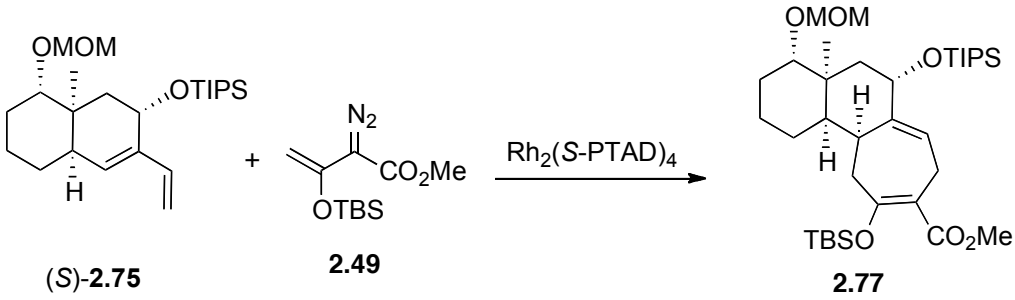
(4*S*,4a*S*,6*R*,11a*R*,11b*R*)-Methyl 10-((*tert*-butyldimethylsilyl)oxy)-4-(methoxymethoxy)-4a-methyl-6-((triisopropylsilyl)oxy)-2,3,4,4a,5,6,8,11,11a,11b-decahydro-1*H*-cyclohepta[*a*]naphthalene-9-carboxylate (2.73): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**2.49**) (46.7 mg, 0.18 mmol, 3.0 equiv) and diene (*S*)-**2.72** (24.5 mg, 0.06 mmol, 1.0 equiv) with Rh_2(*R*-PTAD)$_4$ (1.9 mg, 2 mol %) at room temperature, and purified by flash chromatography (10:1 pentane/Et_2O, R_f = 0.41) to give product **2.73** (29.5 mg, 77% yield) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.68 (t, *J* = 6.2 Hz, 1H), 4.84 (d, *J* = 6.2 Hz, 1H), 4.63 (d, *J* = 6.2 Hz, 1H), 4.27 (dd, *J* = 11.4, 5.2 Hz, 1H), 4.17 (t, *J* = 3.3 Hz, 1H), 3.67 (s, 3H), 3.33 (s, 3H), 2.92-3.02 (m, 3H), 2.63-2.68 (m, 1H), 2.42 (dd, *J* = 13.8, 8.6 Hz, 1H), 2.29 (dd, *J* = 15.2, 3.3 Hz, 1H), 1.93-1.98 (m, 1H), 1.78-1.83 (m, 1H), 1.50-1.62 (m, 4H), 1.36-1.43 (m, 1H), 1.15 (dd, *J* = 14.3, 3.8 Hz, 1H), 1.00-1.10 (m, 21H), 0.952 (s, 3H), 0.949 (s, 9H), 0.15 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.6, 161.6, 144.8, 121.2, 113.4, 97.8, 80.0, 76.9, 55.0, 51.0, 49.4, 43.5, 38.8, 36.8, 30.2, 29.7, 25.7, 25.6, 24.9, 23.0, 22.0, 19.5, 18.3, 18.1, 12.5, -3.8, -4.0; IR (neat): 2934, 2864, 1719, 1691, 1463, 1253, 1212, 1193, 1146, 1045, 828 cm^{-1}; HRMS (ESI) calc. for $C_{35}H_{64}O_6NaSi_2$ $(M+Na)^+$ 659.4134 found 659.4131; $[\alpha]^{25}_D$ -48.1 (*c* = 0.71, $CHCl_3$).



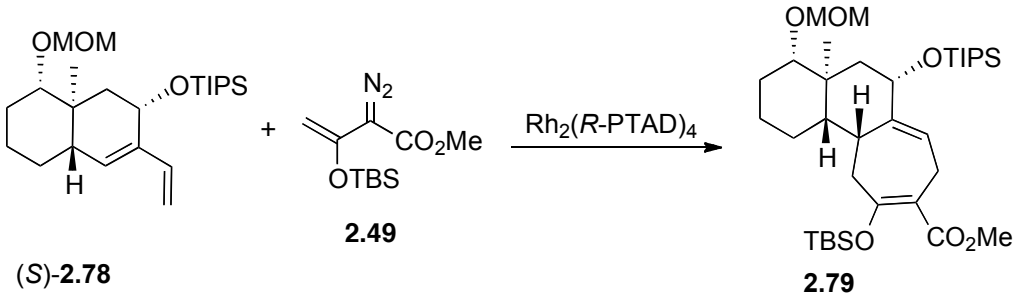
(4*S*,4a*S*,6*R*,11a*S*,11b*R*)-Methyl 10-((*tert*-butyldimethylsilyl)oxy)-4-(methoxymethoxy)-4a-methyl-6-((triisopropylsilyl)oxy)-2,3,4,4a,5,6,8,11,11a,11b-decahydro-1*H*-cyclohepta[*a*]naphthalene-9-carboxylate (2.74): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**2.49**) (46.7 mg, 0.18 mmol, 3.0 equiv) and diene (*S*)-**2.72** (24.5 mg, 0.06 mmol, 1.0 equiv) with Rh_2(*S*-PTAD)$_4$ (1.9 mg, 2 mol %) at room temperature, and purified by flash chromatography (10:1 pentane/Et_2O, R_f = 0.36) to give product **2.74** (25.2 mg, 66% yield) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.14–6.20 (m, 1H), 4.71 (d, *J* = 6.7 Hz, 1H), 4.59 (d, *J* = 6.7 Hz, 1H), 4.18-4.22 (m, 1H), 3.67 (s, 3H), 3.41 (s, 3H), 3.27 (t, *J* = 13.3 Hz, 1H), 3.22 (s, 1H), 3.05 (dd, *J* = 16.7, 9.5 Hz, 1H), 2.91 (dm, *J* = 16.7 Hz, 1H), 2.63 (d, *J* = 11.4 Hz, 1H), 1.80 (dd, *J* = 13.3, 3.8 Hz, 1H), 1.74 (t, *J* = 11.9 Hz, 1H), 1.51-1.68 (m, 6H), 1.40 (dd, *J* = 12.0, 5.2 Hz, 1H), 1.28-1.34 (m, 1H), 1.17 (s, 3H), 1.01-1.11 (m, 21H), 0.95 (s, 9H), 0.18 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.1, 162.2, 140.3, 120.5, 114.0, 95.8, 81.4, 70.3, 55.9, 50.9, 43.7, 41.0, 38.6, 37.9, 35.2, 25.8, 24.9, 24.4, 23.6, 21.7, 19.7, 18.5, 18.2, 18.1, 12.5, -4.05, -4.13; IR (neat): 2934, 2865, 1713, 1694, 1463, 1252, 1202, 1143, 1033, 829 cm^{-1}; HRMS (ESI) calc. for $C_{35}H_{64}O_6NaSi_2$ $(M+Na)^+$ 659.4134 found 659.4132; $[\alpha]^{25}_D$ 9.0 (*c* = 0.40, $CHCl_3$).



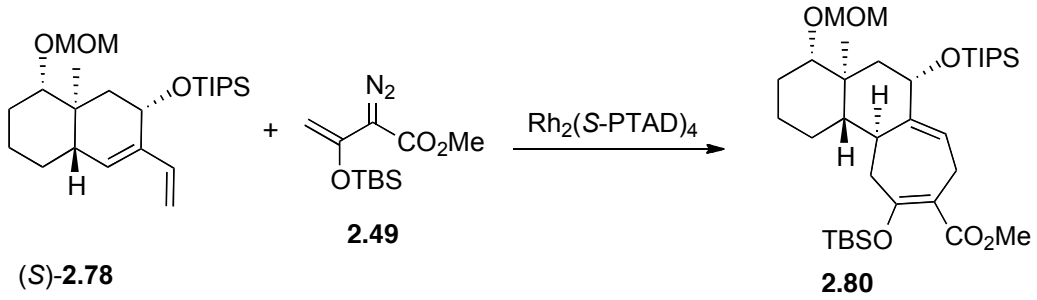
(4*S*,4a*S*,6*S*,11a*R*,11b*R*)-Methyl 10-((*tert*-butyldimethylsilyl)oxy)-4-(methoxymethoxy)-4a-methyl-6-((triisopropylsilyl)oxy)-2,3,4,4a,5,6,8,11,11a,11b-decahydro-1*H*-cyclohepta[*a*]naphthalene-9-carboxylate (2.76): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**2.49**) (46.7 mg, 0.18 mmol, 3.0 equiv) and diene (*S*)-**2.75** (24.5 mg, 0.06 mmol, 1.0 equiv) with Rh_2(*R*-PTAD)$_4$ (1.9 mg, 2 mol %) at room temperature, and purified by flash chromatography (10:1 pentane/Et_2O, R_f = 0.44) to give product **2.76** (24.1 mg, 63% yield) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.95 (t, *J* = 6.2 Hz, 1H), 4.69 (d, *J* = 6.7 Hz, 1H), 4.67 (d, *J* = 6.7 Hz, 1H), 4.09 (dd, *J* = 11.4, 3.2 Hz, 1H), 3.65-3.71 (m, 4H), 3.35 (s, 3H), 3.04 (d, *J* = 6.2 Hz, 2H), 2.68 (d, *J* = 12.4 Hz, 1H), 2.33-2.43 (m, 3H), 1.97-2.01 (m, 1H), 1.75-1.80 (m, 1H), 1.47-1.64 (m, 4H), 1.28-1.38 (m, 1H), 1.01-1.10 (m, 21H), 0.99 (s, 3H), 0.95 (s, 9H), 0.86-0.90 (m, 1H), 0.14 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.5, 161.3, 144.7, 116.5, 114.5, 97.7, 79.1, 70.0, 55.2, 51.0, 49.0, 47.2, 39.5, 37.1, 34.3, 29.2, 25.8, 24.7, 22.5, 21.7, 19.3, 18.4, 18.2, 18.1, 12.5, -3.9, -4.3; IR (neat): 2941, 2864, 1714, 1694, 1626, 1212, 1146, 1043, 880, 827, 679 cm^{-1}; HRMS (ESI) calc. for $C_{35}H_{64}O_6NaSi_2$ $(M+Na)^+$ 659.4134 found 659.4132; $[\alpha]^{25}_D$ -66.6 (*c* = 0.57, $CHCl_3$).



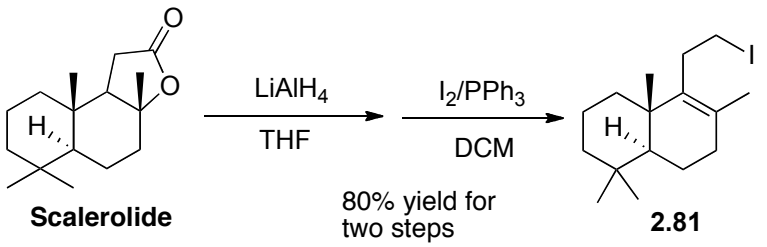
(4*S*,4a*S*,6*S*,11a*S*,11b*R*)-Methyl 10-((*tert*-butyldimethylsilyl)oxy)-4-(methoxy methoxy)-4a-methyl-6-((triisopropylsilyl)oxy)-2,3,4,4a,5,6,8,11,11a,11b-decahydro-1*H*-cyclohepta[*a*]naphthalene-9-carboxylate (2.77): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**2.49**) (46.7 mg, 0.18 mmol, 3.0 equiv) and diene (*S*)-**2.75** (24.5 mg, 0.06 mmol, 1.0 equiv) with Rh_2(*S*-PTAD)$_4$ (1.9 mg, 2 mol %) at room temperature, and purified by flash chromatography (10:1 pentane/Et_2O, R_f = 0.37) to give product **2.77** (26.4 mg, 69% yield) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.85 (dd, *J* = 9.1, 2.9 Hz, 1H), 4.70 (d, *J* = 6.7 Hz, 1H), 4.60 (d, *J* = 6.7 Hz, 1H), 4.17 (d, *J* = 2.4 Hz, 1H), 3.65 (s, 3H), 3.41 (s, 3H), 3.25 (t, *J* = 13.3 Hz, 1H), 3.17 (s, 1H), 3.10 (dm, *J* = 13.3 Hz, 1H), 3.00 (dd, *J* = 17.1, 9.1 Hz, 1H), 2.91 (dt, *J* = 17.1, 3.3 Hz, 1H), 1.87 (dd, *J* = 14.0, 4.2 Hz, 1H), 1.80 (dd, *J* = 14.0, 4.2 Hz, 1H), 1.50-1.68 (m, 6H), 1.39 (s, 3H), 1.33 (d, *J* = 13.8 Hz, 1H), 1.11-1.18 (m, 1H), 0.96-1.05 (m, 21H), 0.96 (s, 9H), 0.20 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.3, 162.7, 140.7, 126.8, 112.1, 96.1, 81.5, 75.8, 55.8, 50.8, 44.3, 38.3, 37.79, 37.76, 32.0, 25.5, 25.3, 25.0, 24.7, 21.6, 19.6, 18.23, 18.15, 12.2, -3.6, -3.7; IR (neat): 2941, 2864, 1716, 1689, 1621, 1462, 1372, 1226, 1202, 1148, 1036, 915, 839, 780 cm^{-1}; HRMS (ESI) calc. for $C_{35}H_{64}O_6NaSi_2$ $(M+Na)^+$ 659.4134 found 659.4137; $[\alpha]^{25}_D$ 20.8 (*c* = 1.32, $CHCl_3$).



(4*S*,4a*S*,6*S*,11a*R*,11b*S*)-Methyl 10-((*tert*-butyldimethylsilyl)oxy)-4-(methoxy methoxy)-4a-methyl-6-((triisopropylsilyl)oxy)-2,3,4,4a,5,6,8,11,11a,11b-decahydro-1*H*-cyclohepta[*a*]naphthalene-9-carboxylate (2.79): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**2.49**) (46.7 mg, 0.18 mmol, 3.0 equiv) and diene (*S*)-**2.78** (24.5 mg, 0.06 mmol, 1.0 equiv) with Rh_2(*R*-PTAD)$_4$ (1.9 mg, 2 mol %) at room temperature, and purified by flash chromatography (10:1 pentane/Et_2O, R_f = 0.36) to give product **2.79** (21.0 mg, 55% yield) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.89-5.91 (m, 1H), 4.72 (d, *J* = 7.1 Hz, 1H), 4.55 (d, *J* = 7.1 Hz, 1H), 4.38 (t, *J* = 8.1 Hz, 1H), 3.68 (s, 3H), 3.37 (s, 3H), 3.20 (dd, *J* = 18.1, 8.1 Hz, 1H), 3.12 (dd, *J* = 11.0, 4.3 Hz, 1H), 3.05 (dm, *J* = 18.1 Hz, 1H), 2.73-2.83 (m, 2H), 2.24 (d, *J* = 12.9 Hz, 1H), 1.98 (dd, *J* = 13.3, 7.1 Hz, 1H), 1.75-1.82 (m, 3H), 1.56 (dd, *J* = 13.2, 7.8 Hz, 1H), 1.18-1.40 (m, 4H), 1.01-1.11 (m, 21H), 0.99 (s, 3H), 0.94 (s, 9H), 0.16 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.5, 162.0, 143.4, 118.7, 111.7, 95.2, 85.8, 69.5, 55.6, 51.1, 48.3, 42.3, 38.8, 37.5, 36.9, 26.9, 25.8, 25.4, 25.1, 24.1, 18.4, 18.15, 18.14, 16.6, 12.3, -3.8, -3.9; IR(neat): 2941, 2864, 1717, 1695, 1630, 1366, 1212, 1042, 878, 839cm^{-1}; HRMS (ESI) calc. for $C_{35}H_{64}O_6NaSi_2$ $(M+Na)^+$ 659.4134 found 659.4137; $[\alpha]^{25}_D$ 36.5 (*c* = 0.66, $CHCl_3$).



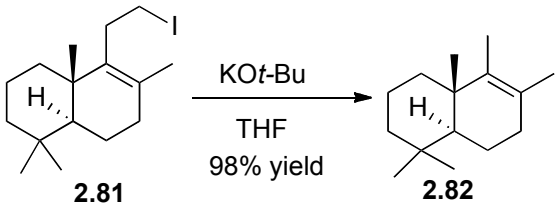
(4*S*,4a*S*,6*S*,11a*S*,11b*S*)-Methyl 10-((*tert*-butyldimethylsilyl)oxy)-4-(methoxymethoxy)-4a-methyl-6-((triisopropylsilyl)oxy)-2,3,4,4a,5,6,8,11,11a,11b-decahydro-1*H*-cyclohepta[*a*]naphthalene-9-carboxylate (2.80): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**2.49**) (46.7 mg, 0.18 mmol, 3.0 equiv) and diene (*S*)-**2.78** (24.5 mg, 0.06 mmol, 1.0 equiv) with Rh_2(*S*-PTAD)$_4$ (1.9 mg, 2 mol %) at room temperature, and purified by flash chromatography (10:1 pentane/Et_2O, R_f = 0.28) to give product **2.80** (31.0 mg, 81% yield) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.71 (t, *J* = 6.2 Hz, 1H), 4.69 (d, *J* = 6.7 Hz, 1H), 4.54 (d, *J* = 6.7 Hz, 1H), 4.21 (t, *J* = 3.8 Hz, 1H), 3.66 (s, 3H), 3.35 (s, 3H), 3.06 (dd, *J* = 11.4, 4.3 Hz, 1H), 2.99 (dd, *J* = 17.1, 7.1 Hz, 1H), 2.93 (ddd, *J* = 17.1, 5.7, 1.4 Hz, 1H), 2.69 (q, *J* = 7.6 H, 1H), 2.50 (d, *J* = 6.7 Hz, 2H), 2.15 (dd, *J* = 13.8, 2.9 Hz, 1H), 1.66-1.80 (m, 3H), 1.45-1.52 (m, 1H), 1.37 (dd, *J* = 13.8, 4.2 Hz, 1H), 1.16-1.27 (m, 2H), 1.15 (s, 3H), 1.12-1.17 (m, 1H), 0.98-1.05 (m, 21H), 0.95 (s, 9H), 0.16 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.7, 161.4, 144.6, 122.1, 113.2, 95.6, 85.8, 75.6, 55.5, 50.9, 49.6, 46.1, 39.4, 36.9, 32.8, 26.3, 25.6, 25.5, 24.7, 23.9, 22.9, 18.21, 18.16, 14.0, 12.2, -3.6, -3.9; IR (neat): 2942, 2864, 1718, 1690, 1626, 1372, 1206, 1141, 1040, 920, 829, 780 cm^{-1}; HRMS (ESI) calc. for $C_{35}H_{64}O_6NaSi_2$ $(M+Na)^+$ 659.4134 found 659.4135; $[\alpha]^{25}_D$ 15.1 (*c* = 0.85, $CHCl_3$).



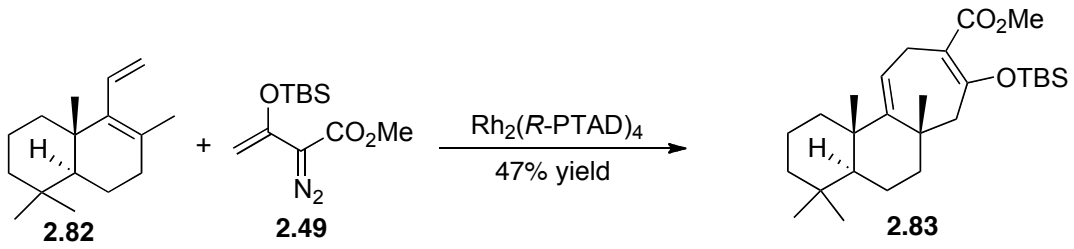
(4a*S*,8a*S*)-8-(2-Iodoethyl)-4,4,7,8a-tetramethyl-1,2,3,4,4a,5,6,8a-octahydro-naphthalene (2.81): Prepared *via* a modified literature procedure.[3] To a solution of (+)-sclareolide (5.0 g, 20 mmol, 1.0 equiv) in dried THF (50 mL) was added $LiAlH_4$ (20 mL of 1M solution in THF, 20 mmol, 1.0 equiv) at 0 °C slowly. The solution was warmed up to room temperature and stirred for additional 3h. The mixture was quenched by saturated NH_4Cl solution and extracted by Et_2O (4 × 200 mL). The organic layers were combined and dried ($MgSO_4$), concentrated under reduced pressure. The residue was then dissolved in 50 mL DCM and added to 50 mL DCM solution containing I_2 (5.6 g, 22.0 mmol, 1.1equiv) and PPh_3 (5.8 g, 22.0 mmol, 1.1 equiv) at 0 °C. The solution was warmed up to room temperature and stirred for additional 4h. Saturated $NaHSO_3$ aqueous solution (50 mL) was added and the mixture was stirred for 30 mins. The mixture was extracted by pentane (4 × 100 mL) and dried ($MgSO_4$), concentrated. The residue was then purified by flash chromatography (pentane, $R_f = 0.76$) on silica gel to give product as colorless solid with trace amount of isomer. The solid was recrystallized from EtOH to afford the pure product **2.81** (5.55 g, 80% yield) as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.03-3.12 (m, 2H), 2.67 (td, *J* = 13.3, 5.1 Hz, 1H), 2.49 (td, *J* = 13.3, 5.1 Hz, 1H), 1.90-2.01 (m, 2H), 1.78-1.81 (m, 1H), 1.59-1.66 (m, 2H), 1.56 (s, 3H), 1.47-1.52 (m, 1H), 1.34-

[3] Alvarez-Manzaneda, E.; Chahboun, R.; Cabrera, E.; Alvarez, E.; Haidour, A.; Ramos, J. M.; Alvarez-Manzaneda, R.; Hmamouchi, M.; Es-Samti, H. *Chem. Commun.*, **2009**, *592*.

1.42 (m, 2H), 1.06-1.16 (m, 3H), 0.92 (s, 3H), 0.88 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.0, 129.1, 51.8, 41.7, 38.6, 37.1, 34.2, 33.6, 33.29, 33.26, 21.6, 20.0, 19.8, 19.0, 18.9, 5.2; IR (neat): 2924, 2865, 1458, 1387, 1162, 907, 733 cm^{-1}; M.p. 75-77 °C; HRMS (APCI) calc. for $C_{16}H_{28}{}^{127}I$ $(M+H)^+$ 347.1230 found 347.1233; $[\alpha]^{25}_D$ 28.3 (*c* = 1.16, $CHCl_3$).

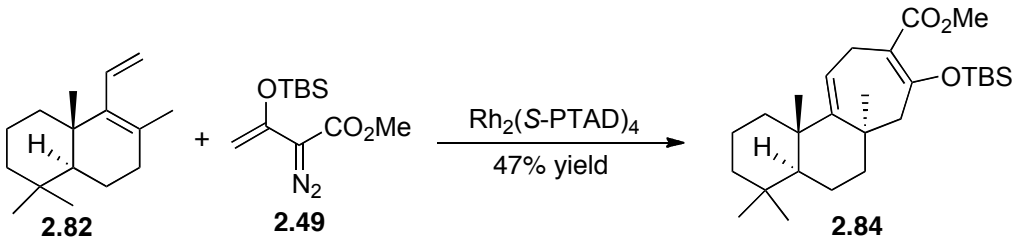


(4a*S*,8a*S*)-4,4,7,8a-Tetramethyl-8-vinyl-1,2,3,4,4a,5,6,6,8a-octahydronaphthalene (2.82): To a solution of iodine **2.81** (2.08g, 6.0 mmol, 1.0 equiv) in THF (5 mL) was added a solution of KO*t*-Bu (1.35g, 12.0 mmol 2.0 equiv) in THF (5 mL) slowly. The mixture was stirred for 6 h at room temperature and then quenched by saturated brine solution. The mixture was extracted by pentane (3 × 100 mL) and dried ($MgSO_4$), concentrated under reduced pressure to afford the diene **2.82** (1.28 g, 98% yield) as colorless oil without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.08-6.16 (m, 1H), 5.23 (dd, *J* = 11.0, 2.7 Hz, 1H), 4.90 (dd, *J* = 17.7, 2.7 Hz, 1H), 2.03-2.10 (m, 2H), 1.63-1.71 (m, 5H), 1.37-1.61 (m, 4H), 1.06-1.19 (m, 3H), 1.00 (s, 3H), 0.89 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0, 135.2, 126.8, 118.3, 51.2, 41.8, 38.1, 37.6, 33.5, 33.3, 33.2, 21.6, 21.1, 20.0, 19.0, 18.9; IR (neat): 2923, 2865, 1457, 1374, 1006, 914 cm^{-1}; HRMS (APCI) calc. for $C_{16}H_{27}$ $(M+H)^+$ 219.2107 found 219.2109; $[\alpha]^{25}_D$ 106.0 (*c* = 1.15, $CHCl_3$).



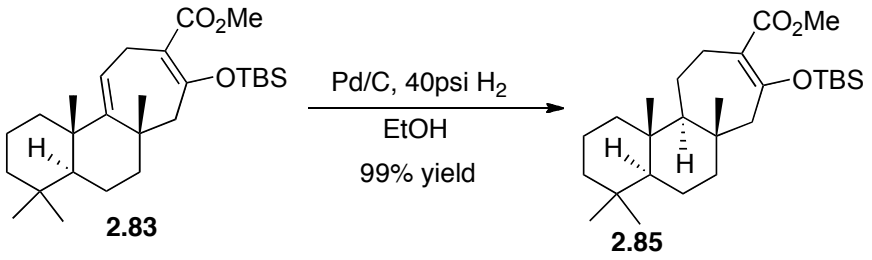
(4a*S*,6a*S*,11b*S*)-Methyl8-((*tert*-butyldimethylsilyl)oxy)-4,4,6a,11b-tetramethyl-2,3,4,4a,5,6,6a,7,10,11b-decahydro-1*H*-cyclohepta[*a*]naphthalene-9-carboxylate (2.83): A solution of methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**2.49**) (2.56 g, 10.0 mmol, 5.0 equiv) in dried hexane (6 mL) was added dropwise to a stirred solution of diene **2.82** (437 mg, 2.0 mmol, 1.0 equiv) and Rh_2(*R*-PTAD)$_4$ (63 mg, 2 mol %) in refluxed hexane (6 mL) over 3 h by syringe pump under argon atmosphere. The solution was cooled to room temperature and concentrated under reduced pressure. The residue was then purified by flash chromatography (20:1 pentane/Et_2O, R_f = 0.60) on silica gel to give products (0.581 g, 65% combined yield) as a mixture of two diastereomers with 6/1 ratio favoring the product **2.83**. The mixture was carefully recrystallized from EtOH and the mother liquid was subsequently purified on silica gel impregnated with 5% $AgNO_3$ and followed by recrystallizing from EtOH again to afford the pure product **2.83** (0.43 g, 47% yield) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.48 (dd, *J* = 8.5, 3.4 Hz, 1H), 3.68 (s, 3H), 3.16 (dd, *J* = 18.3, 8.5 Hz, 1H), 3.05 (dd, *J* = 18.3, 3.4 Hz, 1H), 2.88 (d, *J* = 13.1 Hz, 1H), 1.78 (d, *J* = 13.4 Hz, 1H), 1.32-1.69 (m, 8H), 1.27 (s, 3H), 1.07-1.25 (m, 3H), 1.05 (s, 3H), 0.95 (s, 9H), 0.85 (s, 3H), 0.82 (s, 3H), 0.154 (s, 3H), 0.152 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.9, 162.7, 155.4, 116.5, 110.4, 54.2, 52.4, 51.0, 44.0, 41.9, 41.1, 39.4, 37.2, 34.0, 33.2, 27.3,

27.1, 25.8, 23.4, 21.6, 19.23, 19.19, 18.3, -3.6, -3.7; IR (neat): 2929, 1690, 1377, 1252, 1212, 1139, 1052, 829, 779, 732 cm^{-1}; M.p. 74-76 °C; HRMS (APCI) calc. for $C_{27}H_{47}O_3Si$ $(M+H)^+$ 447.3289 found 447.3284; $[\alpha]^{25}_D$ 24.5 (*c* = 1.64, $CHCl_3$).



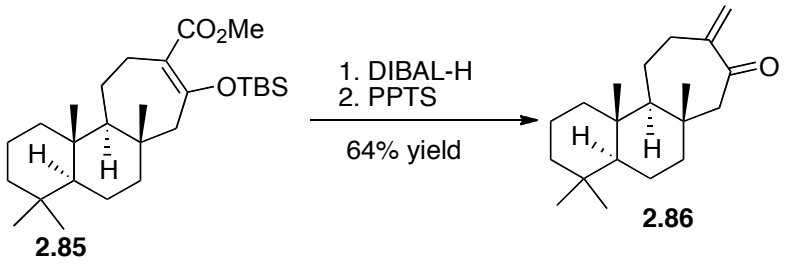
(4a*S*,6a*R*,11b*S*)-Methyl 8-((*tert*-butyldimethylsilyl)oxy)-4,4,6a,11b-tetramethyl-2,3,4,4a, 5,6,6a,7,10,11b-decahydro-1*H*-cyclohepta[*a*]naphthalene-9-carboxylate (2.84): A solution of methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**2.49**) (153 mg, 0.60 mmol, 3.0 equiv) in dried hexane (3 mL) was added dropwise to a stirred solution of diene **2.82** (43.7 mg, 0.2 mmol, 1.0 equiv) and Rh_2(*S*-PTAD)$_4$ (6.3 mg, 2 mol %) in refluxed hexane (3 mL) over 3 h by syringe pump under argon atmosphere. The solution was cooled to room temperature and concentrated under reduced pressure. The residue was then purified by flash chromatography (20:1 pentane/Et_2O, R_f = 0.60) on silica gel to give products (56.3 mg, 63% combined yield) as a mixture of two diastereomers with 9/1 ratio favoring the product **2.84**. The residue was carefully purified on silica gel impregnated with 5% $AgNO_3$ to afford the pure product **2.84** as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.40 (t, *J* = 5.6 Hz, 1H), 3.69 (s, 3H), 3.20 (dd, *J* = 20.8, 5.6 Hz, 1H), 3.06 (ddd, *J* = 20.8, 5.6, 0.8 Hz, 1H), 2.65 (d, *J* = 14.8 Hz, 1H), 1.72-1.90 (m, 4H), 1.35-1.56 (m, 4H), 1.25-1.32 (m, 2H), 1.23 (s, 3H), 1.07-1.22 (m, 2H), 1.05 (s, 3H), 0.93 (s, 9H), 0.90 (s, 3H), 0.83 (s, 3H), 0.14 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (150

MHz, $CDCl_3$): δ 169.3, 158.8, 157.3, 117.5, 109.5, 52.3, 51.2, 43.9, 42.1, 41.0, 40.1, 36.4, 35.1, 34.1, 32.7, 28.4, 25.7, 25.5, 24.9, 21.3, 19.4, 18.3, 17.9, -3.7; IR (neat): 2928, 2858, 1719, 1693, 1434, 1378, 1252, 1199, 1047, 834, 779 cm^{-1}; HRMS (APCI) calc. for $C_{27}H_{47}O_3Si$ $(M+H)^+$ 447.3289 found 447.3284; $[\alpha]^{25}_D$ -2.5 (*c* = 2.66, $CHCl_3$).



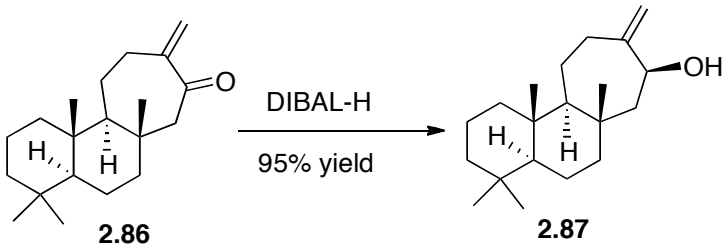
(4a*S*,6a*S*,11a*S*,11b*S*)-Methyl 8-((*tert*-butyldimethylsilyl)oxy)-4,4,6a,11b-tetramethyl-2,3,4,4a,5,6,6a,7,10,11,11a,11b-dodecahydro-1*H*-cyclohepta[*a*]naphthalene-9-carboxylate (2.85): A solution of product **2.83** (0.267 g, 6.0 mmol, 1.0 equiv) in EtOH (15 mL) containing Pd/C (62 mg of 10% palladium on activated carbon, 0.06 mmol, 0.1 equiv) was shaken under H_2 atmosphere (45 psi) over-night. The mixture was filtrated through a celit pad to remove the catalyst and washed with EtOH (2 × 10 mL). The filtrated solution was concentrated to afford the product **2.85** (0.268 g, 99% yield) as colorless viscous oil without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.68 (s, 3H), 2.84 (dd, *J* = 15.3, 7.3 Hz, 1H), 2.49 (d, *J* = 13.7 Hz, 1H), 1.94 (dd, *J* = 14.6, 11.0 Hz, 1H), 1.70-1.80 (m, 3H), 1.47-1.66 (m, 2H), 1.07-1.46 (m, 7H), 0.96-1.01 (m, 1H), 0.98 (s, 3H), 0.93 (s, 9H), 0.84 (s, 3H), 0.79 (s, 3H), 0.77 (s, 3H), 0.72-0.85 (m, 2H), 0.14 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.7, 162.5, 112.3, 64.6, 56.6, 55.2, 51.0, 44.6, 41.9, 39.7, 38.6, 35.4, 33.45, 33.36, 28.3, 25.8, 21.5, 21.2, 19.4, 19.1, 18.7, 18.3, 16.1, -3.6; IR (neat): 2930, 1715, 1688, 1435, 1363, 1249, 1206, 1149, 830,

779, 733 cm^{-1}; HRMS (APCI) calc. for $C_{27}H_{49}O_3Si$ $(M+H)^+$ 449.3446 found 449.3446; $[\alpha]^{25}_D$ -28.2 (*c* = 2.06, $CHCl_3$).



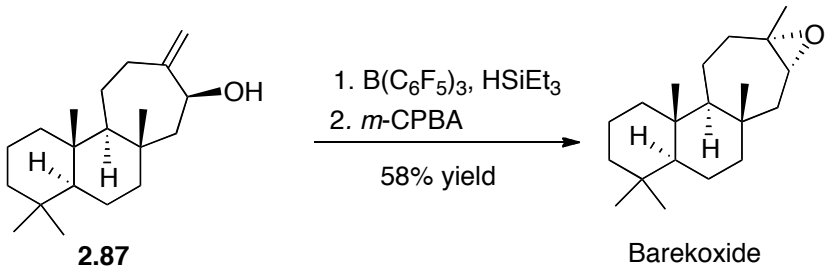
(4a*S*,6a*S*,11a*S*,11b*S*)-4,4,6a,11b-Tetramethyl-9-methylenedodecahydro-1*H*-cyclohepta[*a*] naphthalen-8(11b*H*)-one (2.86): To a solution of ester **2.85** (0.494 g, 1.1 mmol, 1.0 equiv) in THF (5 mL) was added 3.6 mL of DIBAL-H (1.0 M in THF, 3.6 mmol, 3.3 equiv) at 0 °C dropwise. The mixture was stirred for 1h and quenched by 1M of NaOH aqueous solution. The solution was extracted by Et_2O (3 × 20 mL) and dried ($MgSO_4$), concentrated under reduced pressure. The residue was dissolved in dried benzene (30 mL) containing PPTS (27.6 mg, 0.11 mmol, 0.1 equiv) and the solution was heated under reflux with Dean Stark apparatus for 3h. The solution was then concentrated and purified by flash chromatography (85/15 pentane/ Et_2O, R_f = 0.65) on silica gel to give product **2.86** (0.203 g, 64% yield) as a white solid ^1H NMR (600 MHz, $CDCl_3$): 5.95 (d, *J* = 1.1 Hz, 1H), 5.19 (s, 1H), 2.68 (d, *J* = 3.8 Hz, 1H), 2.66 (d, *J* = 4.8 Hz, 1H), 2.34 (t, *J* = 13.1 Hz, 1H), 2.15 (d, *J* = 12.4 Hz, 1H), 2.09 (dd, *J* = 14.3, 7.6 Hz, 1H), 1.80 (dm, *J* = 12.9 Hz, 1H), 1.50-1.64 (m, 3H), 1.30-1.46 (m, 5H), 1.08-1.20 (m, 2H), 0.88 (s, 3H), 0.86 (s, 3H), 0.83-0.90 (m, 2H), 0.81 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 202.1, 147.3, 121.5, 63.5, 60.6, 56.5, 44.6, 41.8, 40.2, 38.8, 37.5, 34.4, 33.44, 33.40, 25.2, 21.5, 19.9, 18.9, 18.8, 16.0; IR (neat): 2934, 2851, 1683, 1611, 1455, 1386, 1288,

1198, 1092, 1037, 942, 899 cm^{-1}; M.p. 94-96 °C; HRMS (APCI) calc. for $C_{22}H_{33}O$ $(M+H)^+$ 289.2526 found 289.2526; $[\alpha]^{25}_D$ 135.3 (*c* = 0.80, $CHCl_3$).



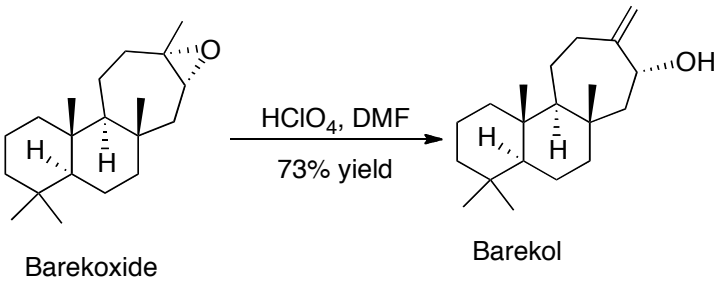
2.86 **2.87**

(4a*S*,6a*S*,8*S*,11a*S*,11b*S*)-4,4,6a,11b-Tetramethyl-9-methylenetetradecahydro-1*H*-cyclohepta[*a*]naphthalen-8-ol (2.87): To a solution of conjugated ketone **2.86** (28.9 mg, 0.1 mmol, 1.0 equiv) in THF (2 mL) was added 0.2 mL of DIBAL-H (1.0 M in THF, 0.2 mmol, 2.0 equiv) at -78 °C dropwise. The mixture was warmed up to -30 °C over 1h and quenched by 1M of HCl aqueous solution. The mixture was extracted by Et_2O (3 × 10 mL), dried ($MgSO_4$), and concentrated under reduced pressure to afford the allylic alcohol **2.87** (27.1 mg, 95% yield) as a white powder without further purification. ^1H NMR (400 MHz, $CDCl_3$): δ 5.01 (t, *J* = 1.5 Hz, 1H), 4.83 (s, 1H), 4.33-4.37 (m, 1H), 2.50 (ddd, *J* = 13.4, 5.5, 3.4 Hz, 1H), 1.92-2.01 (m, 1H), 1.70-1.82 (m, 2H), 1.65 (d, *J* = 5.2 Hz, 2H), 1.31-1.62 (m, 10H), 1.11 (td, *J* = 13.2, 4.4 Hz, 1H), 0.98 (s, 3H), 0.90 (dd, *J* = 10.4, 2.4 Hz, 1H), 0.85 (s, 3H), 0.80 (s, 3H), 0.79 (s, 3H), 0.74-0.82 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.7, 108.2, 71.9, 59.3, 56.7, 53.0, 44.1, 42.0, 40.0, 38.6, 37.1, 34.9, 33.41, 33.38, 24.6, 22.1, 21.5, 18.8, 18.6, 16.2; IR (neat): 3396(br), 2920, 2843, 1462, 1387, 1039, 1012, 899, 757 cm^{-1}; M.p. 63-65 °C; HRMS (APCI) calc. for $C_{20}H_{35}O$ $(M+H)^+$ 291.2682 found 291.2684; $[\alpha]^{25}_D$ 10.5 (*c* = 0.95, $CHCl_3$).



2.87 Barekoxide

Barekoxide: A DCE solution (4 mL) containing alcohol **2.87** (29.0 mg, 0.1 mmol, 1.0 equiv), $B(C_6F_5)_3$ (4.1 mg, 0.008 mmol, 0.08 equiv), $HSiEt_3$ (46.4 mg, 0.4 mmol, 4.0 equiv) was heated under reflux for 14 h. The solution was concentrated and passed through a small pipet column on silica gel with pentane. The solvent was removed under reduced pressure and the residue was dissolved in DCM (5 mL). After cooling down to 0 °C, a DCM solution (5 mL) containing *m*-CPBA (50 mg, 0.2 mmol, 2.0 equiv) was added to the olefin solution and the mixture was stirred for 1h. The solvent was quenched with saturated $Na_2S_2O_3$ aqueous solution. The mixture was extracted with Et_2O (3 × 10 mL) and dried ($MgSO_4$), concentrated under reduced pressure. The residue was purified by flash chromatography (20/1 pentane/Et_2O, R_f = 0.26) on silica gel to afford barekoxide (16.4 mg, 58% yield) as a white powder. ^{1}H NMR (400 MHz, C_6D_6): δ 2.59 (t, *J* = 7.3 Hz, 1H), 1.88 (dd, *J* = 13.7, 7.6 Hz, 1H), 1.70 (dd, *J* = 14.0, 6.4 Hz, 1H), 1.22-1.60 (m, 10H), 1.21 (s, 3H), 0.95-1.19 (m, 3H), 0.85 (s, 3H), 0.83 (s, 3H), 0.80 (s, 3H), 0.72 (s, 3H), 0.47-0.61 (m, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ 64.5, 60.0, 59.9, 56.2, 48.0, 44.2, 42.1, 40.2, 38.9, 37.7, 36.6, 33.6 (2C), 22.7, 21.8, 20.4, 19.8, 19.1, 18.8, 16.2; IR (neat): 2931, 2919, 2845, 1464, 1387, 873 cm^{-1}; M.p. 136-137 °C {lit. M.p. 140 °C}; HRMS (APCI) calc. for $C_{20}H_{35}O$ $(M+H)^+$ 291.2682 found 291.2682; $[\alpha]^{25}_D$ 1.73 (*c* = 0.59, $CHCl_3$) {lit. $[\alpha]^{22}_D$ 5.2 (*c* 0.256, $CHCl_3$)}.



Barekoxide Barekol

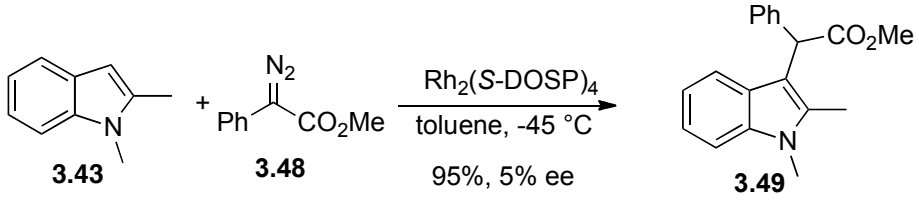
Barekol: To a solution of barekoxide (25 mg, 0.09 mmol, 1.0 equiv) in dried DMF (3 mL) was added 2 drop of $HClO_4$ (70% aqueous solution) and the solution was stirred at room temperature for 16h. The solution was quenched by saturated $NaHCO_3$ solution. The mixture was extracted by Et_2O (3 × 10 mL) and dried ($MgSO_4$), concentrated under reduced pressure. The residue was purified by flash chromatography (85/15 pentane/ Et_2O, R_f = 0.24) on silica gel to afford the the barekol (18.3 mg, 73% yield) as a white powder. Careful recrystallization from pentane afforded some crystals for X-ray crystallographic analysis. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.03 (s, 1H), 4.88 (s, 1H), 4.27 (dd, *J* = 11.0, 3.8 Hz, 1H), 2.42-2.47 (m, 1H), 2.15-2.21 (m, 1H), 1.72-1.83 (m, 2H), 1.67 (dd, *J* = 13.3, 4.3 Hz, 1H), 1.51-1.61 (m, 2H), 1.45-1.50 (m, 1H), 1.32-1.44 (m, 5H), 1.19-1.31(m, 2H), 1.12(td, *J* = 13.3, 4.2 Hz, 1H), 0.95 (s, 3H), 0.84-0.87 (m, 1H), 0.85 (s, 3H), 0.77-0.83 (m, 2H), 0.79 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 155.1, 110.5, 70.8, 60.3, 56.4, 55.4, 45.1, 41.9, 39.9, 38.6, 36.0, 33.4 (2C), 33.2, 24.1, 21.6, 20.3, 18.7, 18.6, 15.8; IR (neat): 3312(br), 2922, 2847, 1462, 1387, 1055, 1009, 897, 734 cm^{-1}; HRMS (APCI) calc. for $C_{20}H_{35}O$ $(M+H)^+$ 291.2682 found 291.2684; $[\alpha]^{25}_D$ -48.7 (*c* = 0.76, $CHCl_3$) {lit. $[\alpha]^{22}_D$ -29 (*c* 1.0, $CHCl_3$)}.

Experiment for Chapter III: Intermolecular reactions of electron-rich heterocycles with rhodium-stabilized carbenoids

1. Asymmetric [3+2] annulation between Indoles and Vinyldiazoacetate

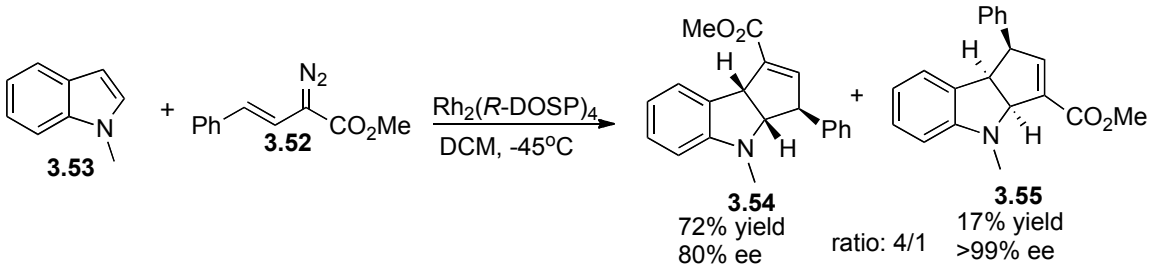
General procedure for annulation with indoles

To a flame-dried 25 mL flask containing Rh_2(*S*-DOSP)$_4$ (5.6 mg, 0.02 equiv) and indoles (0.90 mmol, 6.0 equiv) in 6 mL dried toluene under argon atmosphere was added a solution of (*E*)-aryl vinyldiazoacetate (0.15 mmol, 1.0 equiv) in 6 mL dried toluene by syringe pump over 3 h at -45 °C. The solution was stirred at -45 °C over-night and warmed up to room temperature over 2 h. The mixture was concentrated under reduced pressure and purified by flash chromatography in silica gel (pentane/Et_2O) to provide the corresponding products.



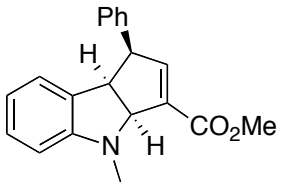
Methyl 2-(1,2-dimethyl-1H-indol-3-yl)-2-phenylacetate (3.49): Derived from 1,2-dimethylindole (**3.43**) (130.6 mg, 0.90 mmol, 6.0 equiv) and methyl 2-diazo-2-phenylacetate (**3.48**) (26.4 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.28) on silica gel to provide **3.49** as colorless foam (41.8 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.9 Hz, 1H), 7.18-7.29 (m, 6H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.03 (m, 1H), 5.31 (s, 1H), 3.72 (s, 3H), 3.67 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 138.8, 136.6, 134.7, 128.2

(3C), 126.8, 126.7, 120.8, 119.3, 108.7, 107.7, 52.2, 48.1, 29.6, 10.7; IR (neat): 1733, 1471, 1367, 1195, 1150, 1008, 738, 697 cm^{-1}; HRMS (APCI) calc. for $C_{19}H_{20}O_2N$ $(M+H)^+$ 294.1489 found 294.1489; HPLC: (OD-H, 1% isopropanol in hexane, 0.7 mL/min) retention times of 32.4 min (major) and 35.1 min (minor), 5% ee.



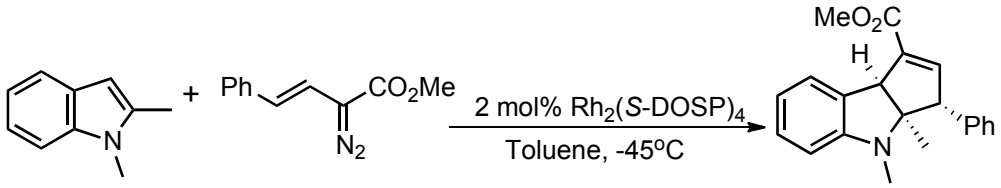
(3*S*,3a*S*,8b*R*)-Methyl 4-methyl-3-phenyl-3,3a,4,8b-tetrahydrocyclopenta[*b*]indole-1-carboxylate (3.54): Derived from *N*-methylindole (**3.53**) (118.1 mg, 0.90 mmol, 6.0 equiv) and (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (**3.52**) (30.4 mg, 0.15 mmol, 1.0 equiv) in the presence of Rh_2(*R*-DOSP)$_4$ (5.6 mg, 0.02 equiv) in CH_2Cl_2, and purified by flash chromatography (DCM, R_f: 0.35 for product **3.54** and 0.20 for product **3.55**) in silica gel to provide **3.54** as colorless oil (32.7 mg, 72% yield) and product **3.55** (7.9 mg, 17% yield) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.3 Hz, 1H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 7.3 Hz, 2H), 7.11-7.16 (m, 1H), 6.84 (s, 1H), 6.70 (td, *J* = 7.6, 0.9 Hz, 1H), 6.45 (d, *J* = 7.6 Hz, 1H), 4.80 (d, *J* = 8.2 Hz, 1H), 4.17 (s, 1H), 4.16 (d, *J* = 8.0 Hz, 1H), 3.82 (s, 3H), 2.88 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.0, 151.5, 144.8, 141.4, 136.7, 129.0, 128.3, 127.7, 127.4, 127.1, 126.1, 117.5, 106.1, 79.0, 57.8, 51.7, 51.5, 33.8; IR (neat): 1714, 1602, 1486, 1435, 1260, 1193, 1097, 1083, 746, 736, 699 cm^{-1}; HRMS (APCI) calc. for $C_{20}H_{20}O_2N$ $(M+H)^+$ 306.1489 found 306.1489; HPLC: (AD-H, 3% isopropanol in hexane, 0.7 mL/min)

retention times of 11.2 min (minor) and 13.0 min (major), 80% ee; $[\alpha]^{25}_{D}$ -25.9 (*c* = 1.05, $CHCl_3$).



3.55

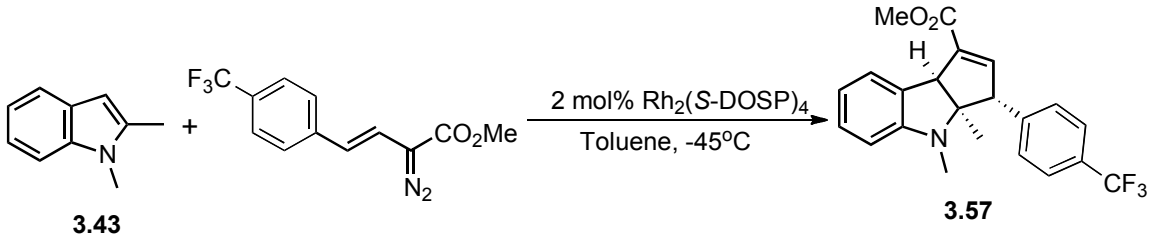
(1*S*,3a*S*,8b*R*)-methyl 4-Methyl-1-phenyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3-carboxylate (3.55): ^{1}H NMR (400 MHz, C_6D_6): δ 6.87-6.97 (m, 4H), 6.79-6.83 (m, 2H), 6.69 (d, *J* = 2.8 Hz, 1H), 6.35 (td, *J* = 7.4, 0.8 Hz, 1H), 6.29 (d, *J* = 8.2 Hz, 1H), 6.14 (d, *J* = 7.4 Hz, 1H), 4.65 (d, *J* = 9.8 Hz, 1H), 4.04 (t, *J* = 9.6 Hz, 1H), 3.92 (dd, *J* = 9.6, 2.6 Hz, 1H), 3.41 (s, 3H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 153.1, 148.1, 139.2, 137.5, 129.2, 128.1, 127.9, 127.7, 126.8, 125.8, 117.1, 107.6, 75.1, 55.6, 51.7, 49.8, 37.2; IR (neat): 1710, 1484, 1455, 1343, 1280, 1205, 1191, 1080, 747, 733, 696 cm^{-1}; HRMS (APCI) calc. for $C_{20}H_{20}O_2N$ $(M+H)^+$ 306.1489 found 306.1489; HPLC: (OD, 3% isopropanol in hexane, 0.7 mL/min) retention times of 9.9 min (minor) and 12.4 min (major), 99% ee; $[\alpha]^{25}_{D}$ 120.4 (*c* = 0.63, $CHCl_3$).



3.43 **3.52** **3.56**

(3*R*,3a*R*,8b*S*)-Methyl 3a,4-dimethyl-3-phenyl-3,3a,4,8b-tetrahydrocyclopenta[*b*]-indole-1-carboxylate (3.56): Derived from 1,2-dimethylindole (**3.43**) (130.6 mg, 0.90 mmol, 6.0 equiv) and (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (**3.52**) (30.4 mg, 0.15

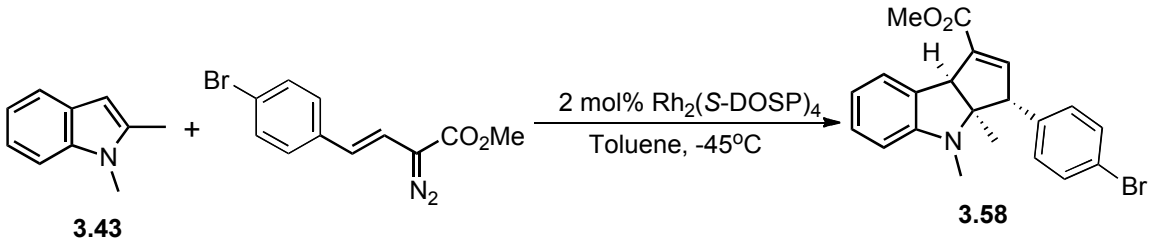
mmol, 1.0 equiv), and purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.52) in silica gel to provide **3.56** as colorless foam (32.4 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.4 Hz, 1H), 7.33-7.37 (m, 2H), 7.24-7.30 (m, 1H), 7.10-7.17 (m, 3H), 6.78 (dd, *J* = 2.4, 1.6 Hz, 1H), 6.66 (td, *J* = 7.4, 0.8 Hz, 1H), 6.38 (d, *J* = 7.4 Hz, 1H), 4.24 (br, 1H), 4.17 (t, *J* = 2.0 Hz, 1H), 3.81 (s, 3H), 2.83 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 150.4, 145.0, 139.0, 136.3, 129.0, 128.5, 128.3, 127.2, 126.6, 126.0, 117.1, 105.6, 79.6, 59.6, 58.8, 51.5, 28.9, 19.7; IR (neat): 2948, 1716, 1602, 1486, 1373, 1273, 1251, 1192, 1125, 1079, 743, 702 cm^{-1}; HRMS (APCI) calc for $C_{21}H_{22}O_2N$ $(M+H)^+$ 320.1645 found 320.1647; HPLC: (OJ, 5% isopropanol in hexane, 0.7 mL/min) retention times of 14.5 min (minor) and 19.8 min (major), 97% ee; $[\alpha]^{25}_D$ 2.69 (*c* = 1.25, $CHCl_3$).



3.43 **3.57**

(3*R*,3a*R*,8b*S*)-Methyl 3a,4-dimethyl-3-(4-(trifluoromethyl)phenyl)-3,3a,4,8b-tetrahydrocyclopenta[*b*]indole-1-carboxylate (3.57): Derived from 1,2-dimethylindole (**3.43**) (130.6 mg, 0.90 mmol, 6.0 equiv) and (*E*)-methyl 2-diazo-4-(4-(trifluoromethyl)phenyl)but-3-enoate (40.5 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.52) in silica gel to provide **3.57** as colorless foam (42.3 mg, 73% yield). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.11-7.15 (m, 1H), 6.73-6.74 (m,

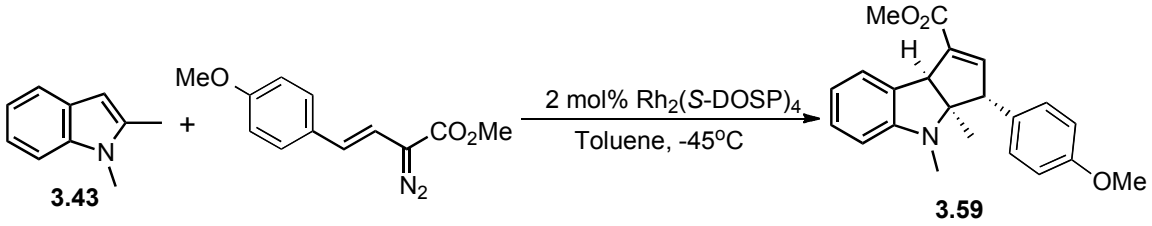
1H), 6.68 (dt, *J* = 0.8, 7.4 Hz, 1H), 6.39 (d, *J* = 7.8 Hz, 1H), 4.25 (br, 1H), 4.23 (t, *J* = 2.0 Hz, 1H), 3.82 (s, 3H), 2.84 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$): δ 164.9, 150.3, 143.9, 143.2, 137.2, 129.3, 128.4, 126.2, 126.0, 125.5 (d, *J* = 2.8 Hz), 117.4, 105.7, 79.5, 59.4, 58.8, 51.7, 29.0, 19.8; IR (neat): 1716, 1603, 1486, 1323, 1272, 1252, 1163, 1121, 1110, 1079, 1066, 1017, 906, 845, 728 cm^{-1}; HRMS (APCI) calc. for $C_{22}H_{21}O_2NF_3$ $(M+H)^+$ 388.1519 found 388.1523; HPLC: (OD, 5% isopropanol in hexane, 0.7 mL/min) retention times of 14.7 min (minor) and 23.3 min (major), 96% ee; $[\alpha]^{25}_D$ 8.28 (*c* = 1.13, $CHCl_3$).



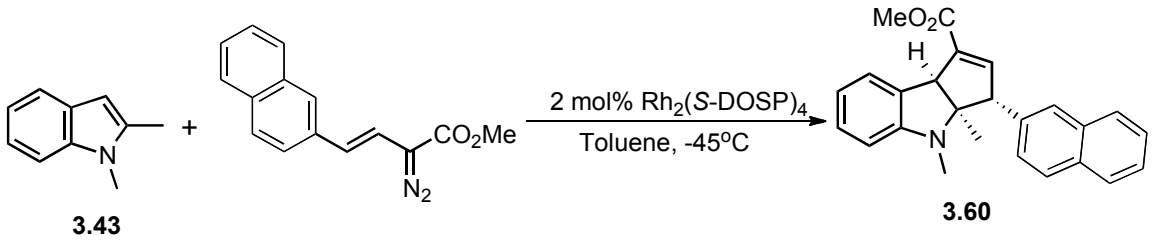
3.43 **3.58**

(3*R*,3a*R*,8b*S*)-Methyl 3-(4-bromophenyl)-3a,4-dimethyl-3,3a,4,8b-tetrahydrocyclopenta[*b*]indole-1-carboxylate (3.58): Derived from 1,2-dimethylindole (**3.43**) (130.6 mg, 0.90 mmol, 6.0 equiv) and (*E*)-methyl 4-(4-bromophenyl)-2-diazobut-3-enoate (42.2 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.41) in silica gel to provide **3.58** as colorless foam (49.2 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.49 (m, 2H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.12 (td, *J* = 7.4, 1.2 Hz, 1H), 7.02-7.05 (m, 2H), 6.72 (dd, *J* = 2.7, 2.0 Hz, 1H), 6.66 (td, *J* = 7.4, 1.2 Hz, 1H), 6.38 (d, *J* = 7.8 Hz, 1H), 4.22 (br, 1H), 4.13 (t, *J* = 1.7 Hz, 1H), 3.81 (s, 3H), 2.81 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 150.3, 144.3, 138.0, 136.8, 131.7, 130.6, 128.3, 126.3, 126.0, 121.1, 117.3, 105.6, 79.4, 59.0, 58.7, 51.6, 29.0, 19.7; IR

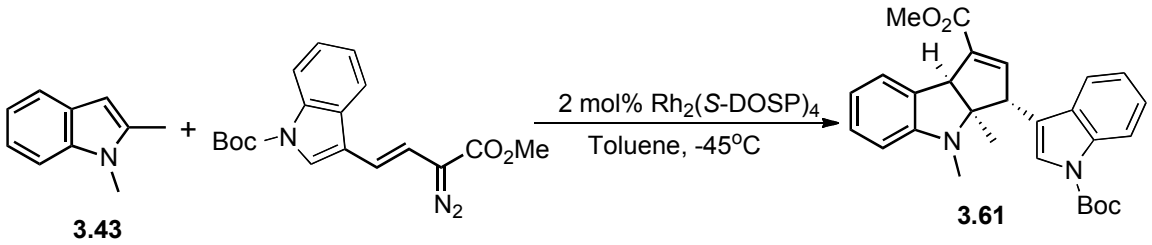
(neat): 1715, 1602, 1272, 1250, 1189, 1107, 1072, 1009, 904, 742, 728 cm^{-1}; HRMS (APCI) calc. for $C_{21}H_{21}O_2N^{79}Br$ $(M+H)^+$ 398.0750 found 398.0752; HPLC: (OD, 5% isopropanol in hexane, 0.7 mL/min) retention times of 16.9 min (minor) and 25.3 min (major), 97% ee; $[\alpha]^{25}_D$ 36.2 (*c* = 1.51, $CHCl_3$).



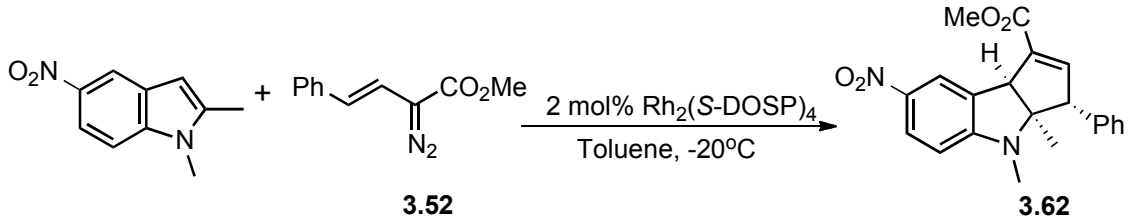
(3*R*,3a*R*,8b*S*)-Methyl 3-(4-methoxyphenyl)-3a,4-dimethyl-3,3a,4,8b-tetrahydrocyclo-penta[*b*]indole-1-carboxylate (3.59): Derived from 1,2-dimethylindole (**3.43**) (130.6 mg, 0.90 mmol, 6.0 equiv) and (*E*)-methyl 2-diazo-4-(4-methoxyphenyl)but-3-enoate (34.9 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.35) in silica gel to provide **3.59** as colorless powder (29.8 mg, 57% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.3 Hz, 1H), 7.13 (td, *J* = 7.6, 1.0 Hz, 1H), 7.04-7.11 (m, 2H), 6.86-6.91 (m, 2H), 6.76 (t, *J* = 2.1 Hz, 1H), 6.66 (td, *J* = 7.3, 1.0 Hz, 1H), 6.37 (d, *J* = 7.9 Hz, 1H), 4.22 (br, 1H), 4.13 (t, *J* = 2.2 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 2.82 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 158.7, 150.5, 145.4, 135.9, 130.9, 130.0, 128.2, 126.6, 126.0, 117.1, 113.9, 105.5, 79.6, 58.8, 58.7, 55.3, 51.5, 28.9, 19.6; IR (neat): 1715, 1633, 1251, 1128, 1030, 814, 732 cm^{-1}; M.p. 99-101 °C; HRMS (APCI) calc. for $C_{22}H_{24}O_3N$ $(M+H)^+$ 350.1751 found 350.1750; HPLC: (OJ, 20% isopropanol in hexane, 0.5 mL/min) retention times of 25.6 min (minor) and 34.7 min (major), 96% ee; $[\alpha]^{25}_D$ 30.7 (*c* = 1.15, $CHCl_3$).



(3*R*,3a*R*,8b*S*)-Methyl 3a,4-dimethyl-3-(naphthalen-2-yl)-3,3a,4,8b-tetrahydrocyclo-penta[*b*]indole-1-carboxylate (3.60): Derived from 1,2-dimethylindole (**3.43**) (130.6 mg, 0.90 mmol, 6.0 equiv) and (*E*)-methyl 2-diazo-4-(naphthalen-2-yl)but-3-enoate (37.9 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.39) in silica gel to provide **3.60** as colorless powder (41.3 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.87 (m, 3H), 7.62 (s, 1H), 7.43-7.55 (m, 3H), 7.27 (d, J = 8.4 Hz, 1H), 7.15 (d, J = 7.6 Hz, 1H), 6.86 (t, J = 1.6 Hz, 1H), 6.70 (t, J = 7.3 Hz, 1H), 6.42 (d, J = 7.9 Hz, 1H), 4.35 (br, 1H), 4.32 (br, 1H), 3.85 (s, 3H), 2.90 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 150.4, 144.9, 136.5, 133.3, 132.6, 128.3, 128.1, 127.6 (4C), 127.1, 126.5, 126.3, 126.1, 125.9, 117.1, 105.6, 79.7, 59.8, 58.9, 51.6, 29.0, 19.7; IR (neat): 1714, 1481, 1273, 1228, 1097, 867, 819, 744, 733 cm^{-1}; M.p. 149-150 °C; HRMS (APCI) calc. for $C_{25}H_{24}O_2N$ $(M+H)^+$ 370.1802 found 370.1799; HPLC: (OD, 5% isopropanol in hexane, 0.7 mL/min) retention times of 18.7 min (minor) and 24.7 min (major), 98% ee; $[\alpha]^{25}_D$ 93.5 (c = 1.31, $CHCl_3$).

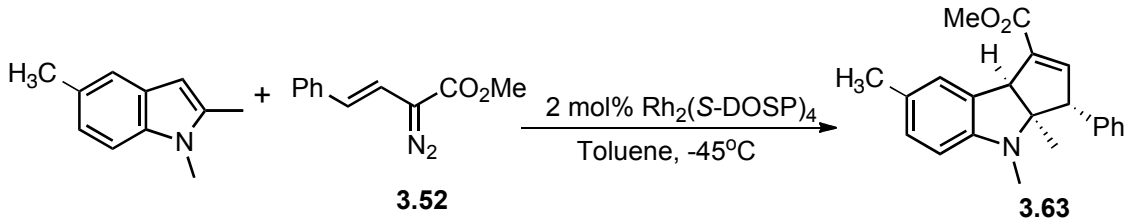


(3*R*,3a*R*,8b*S*)-Methyl 3-(1-(*tert*-butoxycarbonyl)-1H-indol-3-yl)-3a,4-dimethyl-3,3a,4,8b-tetrahydrocyclopenta[*b*]indole-1-carboxylate (3.61): Derived from 1,2-dimethylindole (**3.43**) (130.6 mg, 0.90 mmol, 6.0 equiv) and (*E*)-*tert*-butyl 3-(3-diazo-4-methoxy-4-oxobut-1-enyl)-1H-indole-1-carboxylate (51.2 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.36) in silica gel to provide **3.61** as colorless foam (43.4 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 7.0 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.26-7.38 (m, 3H), 7.14 (td, *J* = 7.4, 1.2 Hz, 1H), 6.81 (dd, *J* = 2.2, 2.0 Hz, 1H), 6.68 (td, *J* = 7.4, 0.8 Hz, 1H), 6.40 (d, *J* = 7.8 Hz, 1H), 4.41 (t, *J* = 2.3 Hz, 1H), 4.32 (br, 1H), 3.81 (s, 3H), 2.91 (s, 3H), 1.70 (s, 9H), 1.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 150.6, 149.7, 144.0, 135.9, 135.6, 130.4, 128.3, 126.4, 126.3, 124.6, 124.4, 122.7, 119.2, 118.7, 117.2, 115.5, 105.7, 84.1, 79.7, 58.7, 51.6, 50.2, 29.2, 28.2, 18.5; IR (neat): 1717, 1486, 1449, 1369, 1253, 1152, 1072, 908, 728 cm^{-1}; HRMS (APCI) calc. for $C_{28}H_{31}O_4N_2$ $(M+H)^+$ 459.2278 found 459.2278; HPLC: (OD, 5% isopropanol in hexane, 0.7 mL/min) retention times of 12.5 min (minor) and 15.3 min (major), 90% ee; $[\alpha]^{25}_D$ 8.9 (*c* = 1.14, $CHCl_3$).



3.52 **3.62**

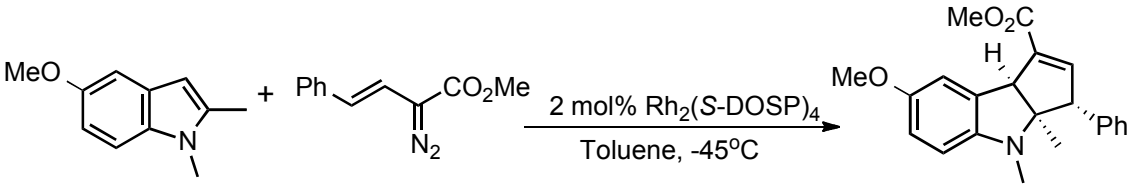
(3*R*,3a*R*,8b*S*)-Methyl 3a,4-dimethyl-7-nitro-3-phenyl-3,3a,4,8b-tetrahydrocyclopenta[*b*]indole-1-carboxylate (3.62): Derived from 1,2-dimethyl-5-nitro-1H-indole (171.2 mg, 0.90 mmol, 6.0 equiv) and (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (**3.52**) (30.4 mg, 0.15 mmol, 1.0 equiv) at -20 °C, and purified by flash chromatography (dichloromethane, R_f: 0.22) in silica gel to provide **3.62** as a yellowish foam (29.8 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (dd, *J* = 2.4, 0.8 Hz, 1H), 8.12 (dd, *J* = 7.6, 2.4 Hz, 1H), 7.29-7.42 (m, 3H), 7.12-7.17 (m, 2H), 6.79 (t, *J* = 2.0 Hz, 1H), 6.28 (d, *J* = 9.0 Hz, 1H), 4.30 (br, 1H), 4.20 (t, *J* = 2.3 Hz, 1H), 3.86 (s, 3H), 2.98 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 154.7, 144.7, 138.2, 137.9, 135.9, 128.82, 128.79, 127.7, 127.2, 126.8, 122.8, 103.3, 80.4, 59.8, 57.9, 51.9, 28.3, 20.8; IR (neat): 1714, 1602, 1492, 1304, 1269, 1100, 1063, 750, 702 cm^{-1}; HRMS (APCI) calc. for $C_{21}H_{21}O_4N_2$ $(M+H)^+$ 365.1496 found 365.1492; HPLC: (AD-H, 20% isopropanol in hexane, 0.7 mL/min) retention times of 13.2 min (major) and 20.5 min (minor), 96% ee; $[\alpha]^{25}_D$ -55.6 (*c* = 0.94, $CHCl_3$).



3.52 **3.63**

(3*R*,3a*R*,8b*S*)-Methyl 3a,4,7-trimethyl-3-phenyl-3,3a,4,8b-tetrahydrocyclopenta-[*b*]indole-1-carboxylate (3.63): Derived from 1,2,5-trimethyl-1H-indole (143.3 mg, 0.90

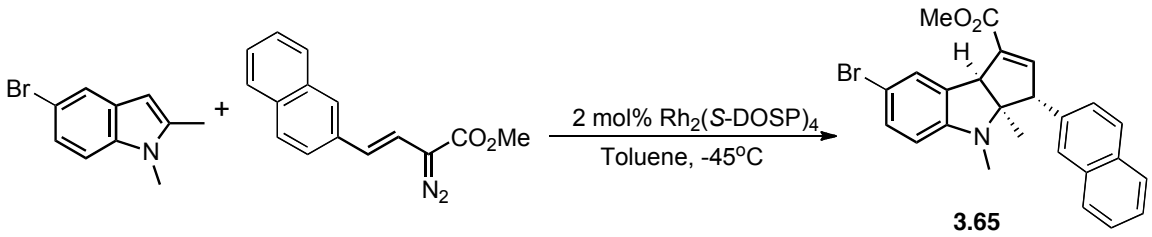
mmol, 6.0 equiv) and (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (**3.52**) (30.4 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography (9/1 pentane/Et_2O, R_f: 0.41) in silica gel to provide **3.63** as colorless foam (37.2 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (t, *J* = 7.8 Hz, 2H), 7.25-7.30 (m, 1H), 7.23 (br, 1H), 7.14-7.17 (m, 2H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.77 (t, *J* = 2.0 Hz, 1H), 6.30 (d, *J* = 7.8 Hz, 1H), 4.20 (br, 1H), 4.16 (t, *J* = 2.3 Hz, 1H), 3.81 (s, 3H), 2.80 (s, 3H), 2.27 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 148.5, 145.1, 139.0, 136.3, 129.1, 128.5 (2C), 127.1, 126.82, 126.77, 126.4, 105.5, 79.8, 59.5, 58.8, 51.5, 29.3, 20.8, 19.5; IR (neat): 2948, 1716, 1495, 1453, 1272, 1251, 1102, 1079, 802, 701 cm^{-1}; HRMS (APCI) calc. for $C_{22}H_{24}O_2N$ $(M+H)^+$ 334.1802 found 334.1798; HPLC: (AD-H, 5% isopropanol in hexane, 0.7 mL/min) retention times of 7.42 min (major) and 9.46 min (minor), 97% ee; $[\alpha]^{25}_D$ 26.6 (*c* = 1.41, $CHCl_3$).



3.52 **3.64**

(3*R*,3a*R*,8b*S*)-Methyl 7-methoxy-3a,4-dimethyl-3-phenyl-3,3a,4,8b-tetrahydrocyclo-penta[*b*]indole-1-carboxylate (3.64): Derived from 5-methoxy-1,2-dimethyl-1H-indole (157.7 mg, 0.90 mmol, 6.0 equiv) and (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (**3.52**) (30.4 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.29) in silica gel to provide **3.64** as colorless foam (40.3 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.37 (m, 2H), 7.25-7.29 (m, 1H), 7.14-7.17 (m, 2H), 7.08-7.10 (m, 1H), 6.79 (dd, *J* = 2.5, 1.6 Hz, 1H), 6.70 (dd, *J* = 8.2, 2.7 Hz, 1H),

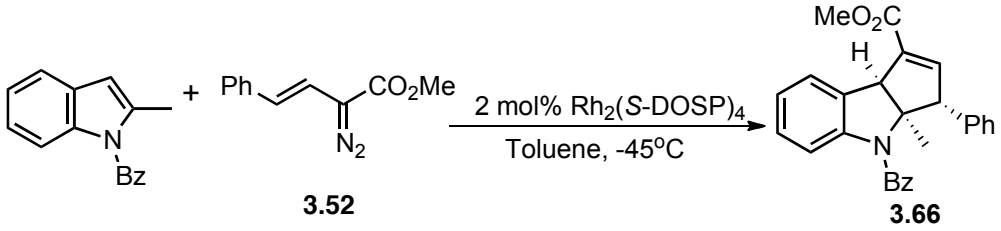
6.30 (d, J = 8.6 Hz, 1H), 4.19 (br, 1H), 4.15 (t, J = 2.3 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 2.78 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 152.4, 145.4, 145.2, 138.9, 136.0, 129.0, 128.5, 127.9, 127.2, 113.6, 112.9, 105.8, 80.0, 59.4, 58.8, 56.1, 51.6, 29.7, 19.3; IR (neat): 1715, 1490, 1453, 1435, 1272, 1144, 1079, 1031, 800, 701 cm^{-1}; HRMS (APCI) calc. for $C_{22}H_{23}O_3N$ $(M)^+$ 349.1673 found 349.1674; HPLC: (AD-H, 5% isopropanol in hexane, 0.7 mL/min) retention times of 12.4 min (major) and 16.2 min (minor), 98% ee; $[\alpha]^{25}_D$ 36.8 (c = 1.03, $CHCl_3$).



3.65

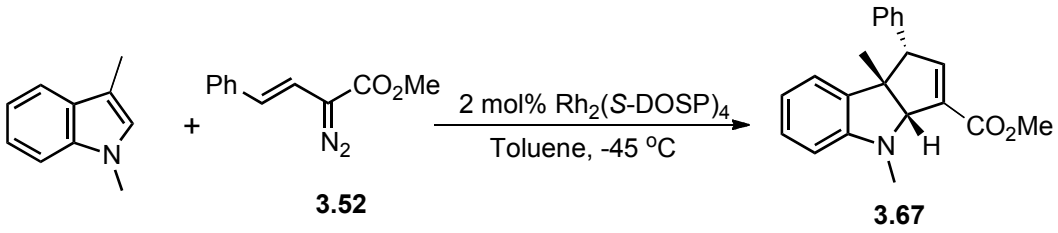
(3*R*,3a*R*,8b*S*)-Methyl 7-bromo-3a,4-dimethyl-3-(naphthalen-2-yl)-3,3a,4,8b-tetrahydrocyclopenta[*b*]indole-1-carboxylate (3.65): Derived from 5-bromo-1,2-dimethyl-1H-indole (202 mg, 0.90 mmol, 6.0 equiv) and (*E*)-methyl 2-diazo-4-(naphthalen-2-yl)but-3-enoate (37.9 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.39) in silica gel to provide **3.65** as colorless powder (52.1 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.87 (m, 3H), 7.59 (s, 1H), 7.46-7.54 (m, 3H), 7.25 (dd, J = 8.6, 2.3 Hz, 1H), 7.21 (dd, J = 8.6, 2.3 Hz, 1H), 6.85 (t, J = 2.3 Hz, 1H), 6.25 (d, J = 8.2 Hz, 1H), 4.32 (t, J = 2.0 Hz, 1H), 4.27 (br, 1H), 3.86 (s, 3H), 2.85 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 149.5, 145.2, 136.1, 136.0, 133.3, 132.6, 130.9, 129.0, 128.7, 128.2, 127.7 (3C), 127.0, 126.4, 126.0, 108.5, 106.9, 80.0, 59.8, 58.6, 51.7, 29.0, 19.7; IR (neat): 1714, 1596, 1482, 1436, 1366, 1272, 1246, 1102, 1084, 907, 730 cm^{-1}; M.p. 150-152 °C; HRMS (APCI) calc. for $C_{25}H_{23}O_2NBr$

$(M+H)^+$ 448.0907 found 448.0907; HPLC: (AD-H, 5% isopropanol in hexane, 0.7 mL/min) retention times of 11.1 min (major) and 17.5 min (minor), 98% ee; $[\alpha]^{25}_D$ 99.3 (*c* = 1.08, $CHCl_3$).



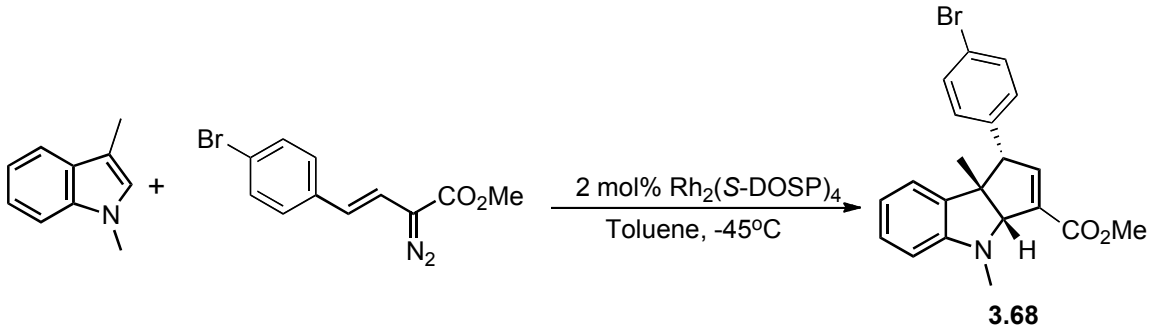
3.52 **3.66**

(3*R*,3a*R*,8b*S*)-Methyl 4-benzyl-3a-methyl-3-phenyl-3,3a,4,8b-tetrahydrocyclopenta [*b*]indole-1-carboxylate (3.66): Derived from 1-benzyl-2-methyl-1*H*-indole (199.2 mg, 0.90 mmol, 6.0 equiv) and (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (**3.52**) (30.4 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography (9/1 pentane/Et_2O, R_f: 0.44) in silica gel to provide **3.66** as colorless foamed powder (35.1 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 7.3 Hz, 1H), 7.23-7.38 (m, 8H), 7.11 (d, *J* = 7.3, 2H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.84 (t, *J* = 2.5 Hz, 1H), 6.66 (t, *J* = 7.3 Hz, 1H), 6.08 (d, *J* = 7.6 Hz, 1H), 4.53 (d, *J* = 16.5 Hz, 1H), 4.35 (d, *J* = 16.5 Hz, 1H), 4.34 (br, 1H), 4.20 (t, *J* = 1.9 Hz, 1H), 3.84 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 149.7, 144.9, 139.1, 138.8, 136.5, 129.0, 128.7, 128.6, 128.1, 127.3, 127.0, 126.4, 126.1, 117.3, 106.5, 80.1, 60.3, 59.0, 51.6, 47.6, 20.5; IR (neat): 1715, 1601, 1483, 1453, 1244, 1102, 908, 727, 699 cm^{-1}; HRMS (APCI) calc. for $C_{27}H_{26}O_2N$ $(M+H)^+$ 396.1958 found 396.1956; HPLC: (AD-H, 5% isopropanol in hexane, 0.7 mL/min) retention times of 8.0 min (minor) and 18.0 min (major), 98% ee; $[\alpha]^{25}_D$ 79.9 (*c* = 0.42, $CHCl_3$).



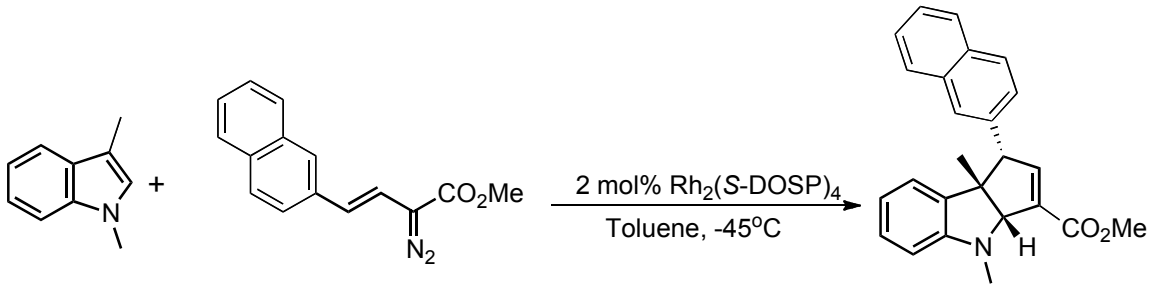
3.52 **3.67**

(1*S*,3a*R*,8b*S*)-Methyl 4,8b-dimethyl-1-phenyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]-indole-3-carboxylate (3.67): Derived from 1,3-dimethylindole (130.6 mg, 0.90 mmol, 6.0 equiv) and (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (**3.52**) (30.4 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.46) in silica gel to provide **3.67** as colorless viscous oil (35.6 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07-7.13 (m, 3H), 6.87-6.93 (m, 4H), 6.36 (d, *J* = 7.6 Hz, 1H), 6.25 (td, *J* = 7.6, 1.0 Hz, 1H), 6.06 (dd, *J* = 7.3, 1.0 Hz, 1H), 4.38 (s, 1H), 3.95 (d, *J* = 2.9 Hz, 1H), 3.84 (s, 3H), 3.06 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 152.2, 147.8, 139.8, 136.5, 132.7, 128.8, 127.8, 127.6, 126.8, 124.5, 117.0, 107.3, 82.3, 64.1, 57.1, 51.7, 36.9, 29.7; IR (neat): 2950, 1714, 1603, 1487, 1245, 1219, 1102, 993, 774, 799 cm^{-1}; HRMS (APCI) calc. for $C_{21}H_{22}O_2N$ $(M+H)^+$ 320.1645 found 320.1649; HPLC: ((R,R)Whelk-01, 1% isopropanol in hexane, 0.7 mL/min) retention times of 9.6 min (minor) and 12.6 min (major), 99% ee; $[\alpha]^{25}_D$ -160.2 (*c* = 0.87, $CHCl_3$).



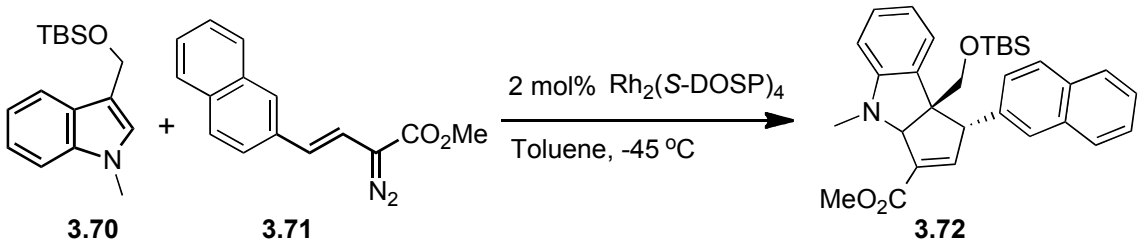
3.68

(1*S*,3a*R*,8b*S*)-Methyl 1-(4-bromophenyl)-4,8b-dimethyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3-carboxylate (3.68): Derived from 1,3-dimethylindole (130.6 mg, 0.90 mmol, 6.0 equiv) and (*E*)-methyl 4-(4-bromophenyl)-2-diazobut-3-enoate (42.2 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.40) in silica gel to provide **3.68** as colorless viscous oil (32.2 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.22 (m, 2H), 6.93 (td, *J* = 7.6, 1.6 Hz, 1H), 6.82 (d, *J* = 2.7 Hz, 1H), 6.74-6.78 (m, 2H), 6.36 (d, *J* = 7.8 Hz, 1H), 6.31 (td, *J* = 7.4, 0.8 Hz, 1H), 6.12 (dd, *J* = 7.4, 0.8 Hz, 1H), 4.35 (s, 1H), 3.89 (d, *J* = 2.7 Hz, 1H), 3.84 (s, 3H), 3.04 (s, 3H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 152.2, 147.3, 138.8, 136.9, 132.2, 130.9, 130.5, 127.9, 124.3, 120.7, 117.4, 107.5, 82.3, 63.6, 57.0, 51.7, 36.9, 29.5; IR (neat): 1715, 1486, 1347, 1264, 1246, 1218, 1192, 1104, 1071, 1010, 795, 739, 677 cm^{-1}; HRMS (APCI) calc. for $C_{21}H_{21}O_2N^{79}Br$ $(M+H)^+$ 398.0750 found 398.0751; HPLC: ((R,R)Whlek-01, 1% isopropanol in hexane, 0.7 mL/min) retention times of 10.7 min (minor) and 13.1 min (major), 98% ee; $[\alpha]^{25}_D$ -118.0 (*c* = 1.14, $CHCl_3$).



3.69

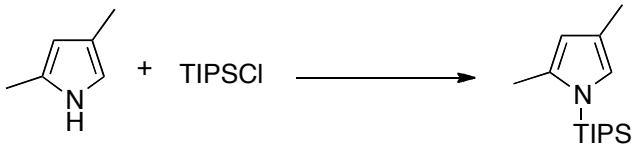
(1*S*,3a*R*,8b*S*)-Methyl 4,8b-dimethyl-1-(naphthalen-2-yl)-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3-carboxylate (3.69): Derived from 1,3-dimethylindole (130.6 mg, 0.90 mmol, 6.0 equiv) and (*E*)-methyl 2-diazo-4-(naphthalen-2-yl)but-3-enoate (37.9 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.37) in silica gel to provide **3.69** as a colourless power (37.6 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68-7.74 (m, 2H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.46 (br, 1H), 7.36-7.44 (m, 2H), 6.91-6.96 (m, 2H), 6.84 (tm, *J* = 7.8 Hz, 1H), 6.38 (d, *J* = 8.2 Hz, 1H), 6.10 (t, *J* = 7.4 Hz, 1H), 6.02 (d, *J* = 7.4 Hz, 1H), 4.43 (s, 1H), 4.13 (d, *J* = 2.4 Hz, 1H), 3.86 (s, 3H), 3.10 (s, 3H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 152.2, 147.8, 137.3, 136.6, 133.0, 132.5, 132.4, 127.65, 127.61, 127.5, 127.4, 127.3, 127.2, 125.7, 125.4, 124.5, 117.2, 107.4, 82.3, 64.2, 57.1, 51.7, 37.1, 29.9; IR (neat): 2950, 1715, 1487, 1247, 1221, 1102, 741 cm^{-1}; M.p. 148-151 °C; HRMS (APCI) calc. for $C_{25}H_{24}O_2N$ $(M+H)^+$ 370.1802 found 370.1801; HPLC: ((R,R)Whlek-01, 1% isopropanol in hexane, 0.7 mL/min) retention times of 15.3 min (minor) and 18.9 min (major), 99% ee; $[\alpha]^{25}_D$ -94.5 (*c* = 0.80, $CHCl_3$).



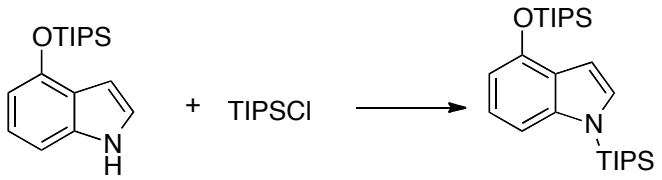
3.70 **3.71** **3.72**

(1*S*,8b*R*)-Methyl 8b-(((*tert*-butyldimethylsilyl)oxy)methyl)-4-methyl-1-(naphthalen-2-yl)-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3-carboxylate (3.72): Derived from 3-((tert-butyldimethylsilyloxy)methyl)-1-methyl-1H-indole (**3.70**) (248 mg, 0.90 mmol, 6.0 equiv)and (*E*)-methyl 2-diazo-4-(naphthalen-2-yl)but-3-enoate (37.9 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography (9/1 pentane/Et_2O, R_f: 0.38) on silica gel to provide **3.72** as colorless power (30.2 mg, 40% yield). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.70-7.77 (m, 2H), 7.57 (d, *J* = 8.6 Hz, 1H), 7.48 (br, 1H), 7.38-7.46 (m, 2H), 6.95 (dd, *J* = 1.0, 8.6 Hz, 1H), 6.91 (d, *J* = 2.7 Hz, 1H), 6.88 (dt, *J* = 1.2, 7.8 Hz, 1H), 6.41 (d, *J* = 7.8 Hz, 1H), 6.05 (dt, *J* = 0.8, 7.4 Hz, 1H), 5.84 (dd, *J* = 0.8, 7.4 Hz, 1H), 4.63 (s, 1H), 4.59 (d, *J* = 2.4 Hz, 1H), 3.87 (d, *J* = 9.8 Hz, 1H), 3.84 (s, 3H), 3.71 (d, *J* = 9.8 Hz, 1H), 3.11 (s, 3H), 0.93 (s, 9H), 0.12 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 165.6, 152.8, 147.9, 137.5, 136.8, 133.0, 132.4, 129.0, 128.1, 127.9, 127.6, 127.56, 127.3, 125.8, 125.6, 125.4, 116.9, 107.6, 77.5, 68.6, 63.2, 570, 51.6, 37.4, 25.8, 18.2, -5.36, -5.43; IR (neat): 2951, 2854, 1717, 1602, 1487, 1436, 1345, 1246, 1219, 1093, 836, 776, 741 cm^{-1}; M.p. 123-125 °C; HRMS (APCI) calc. for $C_{31}H_{38}O_3NSi$ $(M+H)^+$ 500.2616 found 500.2615; HPLC: ((R,R)Whlek-01, 3% isopropanol in hexane, 0.7 mL/min) retention times of 8.6 min (minor) and 10.6 min (major), 99 % ee; $[\alpha]^{25}_D$ -63.8 (*c* = 1.16, $CHCl_3$).

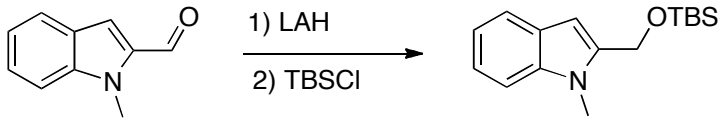
2. Introduction of 4-substituted (*Z*)-pent-2-enoates into sterically encumbered pyrrole and indoles



2,4-Dimethyl-1-(triisopropylsilyl)-1*H*-pyrrole: To a solution containing 2,4-dimethylpyrrole (0.95 g, 10 mmol, 1.0 equiv) in 10 ml dried THF was added 2.5M n-BuLi solution in hexane (4.4 mL, 12 mmol, 1.2 equiv) at -78 °C. After stirring for 30 min, TIPSCl (2.31 g, 12 mmol, 1.2 equiv) was added slowly and the solution was warmed up to room temperature slowly. The mixture was quenched by sodium bicarbonate solution and extracted by pentane (3 × 50 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The crude mixture was purified by flash chromatography in silica gel (pentane/Et_2O, R_f: 0.44) to provide product as colorless oil (1.84 g, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.46 (s, 1H), 5.86 (s, 1H), 2.28 (d, *J* = 0.6 Hz, 3H), 2.06 (d, *J* = 0.6 Hz, 3H), 1.43-1.55 (m, 3H), 1.12 (d, *J* = 7.3 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.4, 122.4, 119.4, 112.9, 18.2, 15.5, 12.8, 11.9; IR (neat): 2946, 2893, 2867, 1704, 1464, 1306, 1138, 1070, 883, 684 cm^{-1}; HRMS (APCI) calc. for $C_{15}H_{28}NSi$ $(M+H)^+$ 250.1986 found 250.1982.



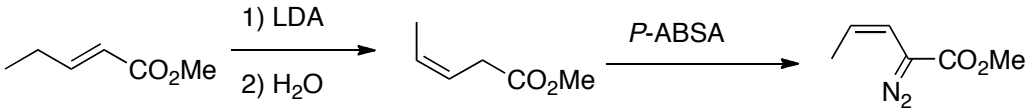
1-(Triisopropylsilyl)-4-((triisopropylsilyl)oxy)-1*H*-indole: To a solution containing 4-((triisopropylsilyl)oxy)-1*H*-indole (2.89 g, 10 mmol, 1.0 equiv) in 10 ml dried THF was added 2.5M n-BuLi solution in hexane (4.4 mL, 12 mmol, 1.2 equiv) at -78 °C. After stirring for 30 min, TIPSCl (2.31 g, 12 mmol, 1.2 equiv) was added slowly and the solution was warmed up to room temperature slowly. The mixture was quenched by sodium bicarbonate solution and extracted by pentane (3 × 50 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The crude mixture was purified by flash chromatography in silica gel (pentane, R_f: 0.41) to provide product as reddish oil (2.27 g, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (d, *J* = 3.4 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.96 (t, *J* = 7.9 Hz, 1H), 6.72 (d, *J* = 3.1 Hz, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 1.62-1.74 (m, 3H), 1.28-1.43 (m, 3H), 1.14 (d, *J* = 7.3 Hz, 36H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 142.7, 129.3, 124.9, 121.7, 108.1, 107.4, 102.3, 18.15, 18.08, 12.9, 12.8; IR (neat): 2944, 2864, 1485, 1259, 1125, 1034, 882, 799, 732 cm^{-1}; HRMS (APCI) calc. for $C_{26}H_{48}NSi_2$ $(M+H)^+$ 446.3269 found 446.3263.



2-(((*tert*-Butyldimethylsilyl)oxy)methyl)-1-methyl-1*H*-indole: To a solution containing 1-methyl-1*H*-indole-2-carbaldehyde (1.59 g, 10 mmol, 1.0 equiv) in 10 mL dried THF was added 1M $LiAlH_4$ (4 mL, 5.0 mmol, 0.5 equiv) at 0 °C. The mixture was stirred for

30 min and was quenched by NH_4Cl solution. 1M HCl solution was added until all precipitate was dissolved and was extracted by Et_2O (3 × 50 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The crude powder was dissolved in 20 mL dried CH_2Cl_2, imidazole (1.36 g, 20 mmol, 2.0 equiv) and TBSCl (2.11 g, 14 mmol, 1.4 equiv) was added in sequence. After stirring at room temperature for 3h, the mixture was quenched by sodium bicarbonate solution, and then was extracted by Et_2O (3 × 50 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The crude mixture was then purified by flash chromatography in silica gel (pentane to 20/1 pentane/Et_2O, R_f: 0.62) to provide the product as colorless powder (2.23 g, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.21 (tm, *J* = 7.6 Hz, 1H), 7.09 (tm, *J* = 7.6 Hz, 1H), 6.38 (s, 1H), 4.84 (s, 2H), 3.79 (s, 3H), 0.91 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 137.9, 127.3, 121.4, 120.6, 119.3, 109.0, 100.7, 58.1, 29.9, 25.8, 18.2, -5.3; IR (neat): 2930, 2855, 1469, 1379, 1245, 1054, 837, 771, 734 cm^{-1}; M.p. 65-67 °C; HRMS (APCI) calc. for $C_{16}H_{26}ONSi$ $(M+H)^+$ 276.1778 found 276.1775.

Procedure of making diazoacetates

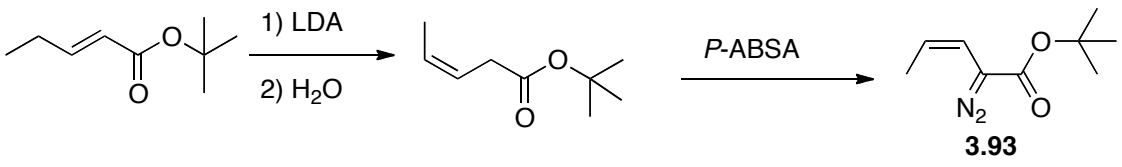


3.79

(*Z*)-Methyl 2-diazopent-3-enoate (3.79): The de-conjugation process was followed by a modified procedure reported by Ukaji and Inomata.[4] To a solution of containing

[4] Guha, S. K.; Shibayama, A.; Abe, D.; Ukaji, Y.; Inomata, K. *Chem. Lett.* **2003**, *32*, 778.

LiHMDS (20.1 g, 120 mmol, 1.5 equiv) and HMPA (83.5 mL, 480 mmol, 6.0 equiv) in 300 mL dried THF was added a solution of methyl pent-2-enoate (9.12 g, 80 mmol, 1.0 equiv) in 20 mL dried THF at -78 °C. After stirring for 30 min, the solution was quenched by methanol. The mixture was poured into saturated NH_4Cl solution and extracted by pentane (3 × 200 mL). The organic layers were combined and washed with H_2O twice and then brine solution. The solvent was removed under reduced pressure and the residue was dissolved in 200 mL dried CH_3CN. After addition of *p*-ABSA (*p*-Acetamidobenzenesulfonyl Azide) (28.8 g, 120 mmol, 1.5 equiv), the solution was cooled down to 0 °C and then DBU (24 mL, 160 mmol, 2.0 equiv) was added quickly. The solution was warmed up to room temperature overnight and quenched by sodium bicarbonate solution and extracted by pentane (2 × 200 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The crude mixture was purified by flash chromatography in silica gel (30/1 pentane/Et_2O, R_f: 0.45) to provide product **7** as reddish oil (7.62 g, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.57-5.67 (m, 2H), 3.80 (s, 3H), 1.63-1.73 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 123.6, 112.0, 52.1, 13.5; IR (neat): 2078, 1694, 1435, 1289, 1220, 1109, 702 cm^{-1}.



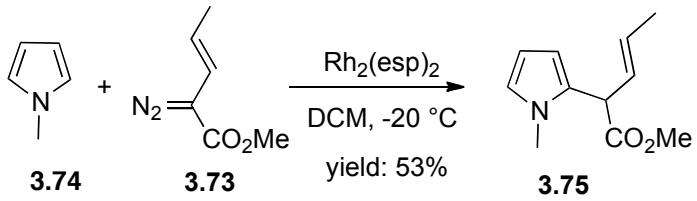
3.93

(*Z*)-*tert*-Butyl 2-diazopent-3-enoate (3.93): Following the general procedure of making the methyl vinyldiazoacetate **3.79**, the product was derived from LiHMDS (4.1 g, 24 mmol, 1.5 equiv), HMPA (17 mL, 96 mmol, 6.0 equiv), *tert*-butyl pent-2-enoate (2.5 g, 16 mmol, 1.0 equiv), *p*-ABSA (*p*-Acetamidobenzenesulfonyl Azide) (5.76 g, 24 mmol,

1.5 equiv) and DBU (4.8 mL, 32 mmol, 2.0 equiv). The crude mixture was purified by flash chromatography in silica gel (40/1 pentane/Et_2O, R_f: 0.51) to provide product **3.93** as reddish oil (1.48 g, 51% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 5.49-5.60 (m, 2H), 1.63-1.70 (m, 3H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 122.7, 112.6, 81.7, 28.2, 13.4; IR (neat): 2978, 2077, 1698, 1368, 1294, 1167, 1106, 701 cm^{-1}.

General procedure for the reactions between pyrroles and methyl vinyldiazoacetate

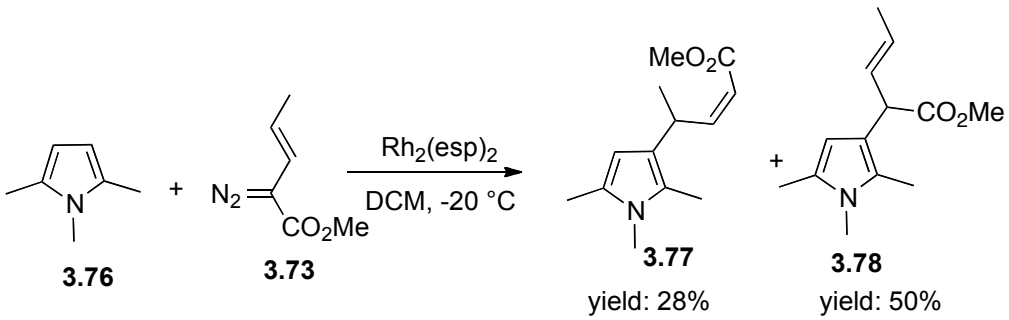
To a flame-dried 25 mL flask containing $Rh_2(esp)_2$ (2.3 mg, 0.02 equiv) and pyrroles (0.90 mmol, 6.0 equiv) in 6 mL dried CH_2Cl_2 under argon atmosphere was added a solution of fresh purified methyl vinyldiazoacetate (21 mg, 0.15 mmol, 1.0 equiv) in 6 mL dried CH_2Cl_2 by syringe pump over 3 h at -20 °C. The solution was warmed up to room temperature over 2 h. The mixture was concentrated under reduced pressure and purified by flash chromatography in silica gel (85/15 pentane/Et_2O, containing 0.5% Et_3N) to provide the corresponding products as colorless oils.



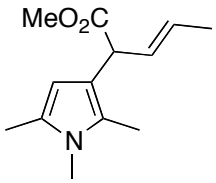
3.74 **3.73** **3.75**

(*E*)-Methyl 2-(1-methyl-1*H*-pyrrol-2-yl)pent-3-enoate (3.75): Derived from *N*-methylpyrrole (**3.74**) (73 mg, 0.90 mmol, 6.0 equiv) and *trans*-methyl vinyldiazoacetate **3.73** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography in silica gel (85/15 pentane/Et_2O, containing 0.5% Et_3N, R_f: 0.46) to provide **3.75** as colorless oil

(15.5 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.57 (dd, *J* = 2.2, 2.0 Hz, 1H), 6.08 (dd, *J* = 3.0, 2.8 Hz, 1H), 6.03-6.06 (m, 1H), 5.75 (ddq, *J* = 15.3, 7.8, 1.6 Hz, 1H), 5.51-5.62 (m, 1H), 4.32 (d, *J* = 7.8 Hz, 1H), 3.71 (s, 3H), 3.54 (s, 3H), 1.72 (ddd, *J* = 6.3, 1.6, 0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 129.0, 128.7, 126.8, 122.5, 107.3, 170.0, 52.3, 47.0, 34.0, 17.8; IR (neat): 2919, 1733, 1434, 1298, 1225, 1192, 1163, 989, 966, 707 cm^{-1}; HRMS (APCI) calc. for $C_{11}H_{16}O_2N$ $(M+H)^+$ 194.1176 found 194.1177.

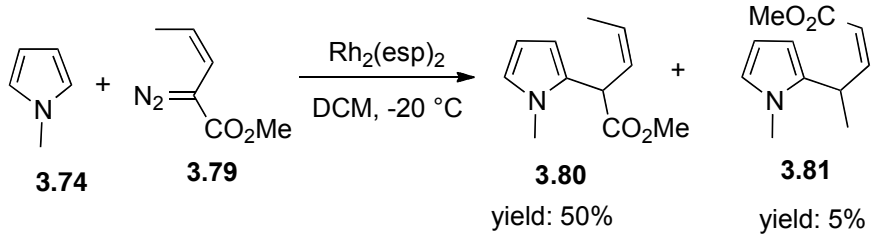


(*Z*)-Methyl 4-(1,2,5-trimethyl-1*H*-pyrrol-3-yl)pent-2-enoate (3.77): Derived from 1,2,5-trimethylpyrrole (**3.76**) (49.1 mg, 0.45 mmol, 3.0 equiv) and *trans*-methyl vinyldiazoacetate **3.73** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography in silica gel (9/1 pentane/Et_2O, containing 0.5% Et_3N, R_f: 0.45) to provide **3.77** as colorless oil (9.2 mg, 28% yield) and **3.78** (16.6 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.21 (dd, *J* = 11.4, 10.8 Hz, 1H), 5.78 (br, 1H), 5.61 (dd, *J* = 11.4, 1.0 Hz, 1H), 4.77-4.86 (m, 1H), 3.73 (s, 3H), 3.35 (s, 3H), 2.20 (s, 3H), 2.15 (s, 3H), 1.29 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 155.6, 127.2, 124.2, 120.9, 114.9, 102.3, 51.0, 30.1, 29.7, 21.3, 12.5, 10.0; IR (neat): 2925, 1719, 1634, 1435, 1397, 1193, 1173, 826 cm^{-1}; HRMS (APCI) calc. for $C_{13}H_{20}O_2N$ $(M+H)^+$ 222.1489 found 222.1488.



3.78

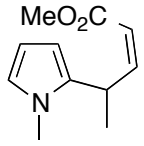
(*E*)-Methyl 2-(1,2,5-trimethyl-1*H*-pyrrol-3-yl)pent-3-enoate (3.78): ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.76-5.84 (m, 2H), 5.50-5.59 (m, 1H), 4.15 (d, *J* = 8.8 Hz, 1H), 3.68 (s, 3H), 3.35 (s, 3H), 2.18 (s, 3H), 2.15 (s, 3H), 1.69 (dd, *J* = 6.0, 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.3, 129.2, 127.4, 126.6, 124.1, 115.2, 104.2, 51.9, 46.9, 30.2, 17.9, 12.4, 10.1; IR (neat): 2917, 1732, 1433, 1238, 1155, 992, 964, 769 cm^{-1}; HRMS (APCI) calc. for $C_{13}H_{20}O_2N$ $(M+H)^+$ 222.1489 found 222.1489.



3.74 **3.79** **3.80** yield: 50% **3.81** yield: 5%

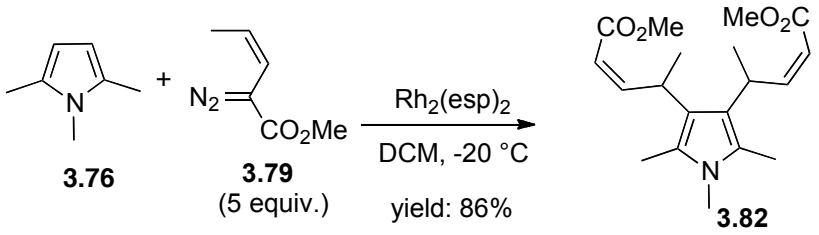
(*Z*)-Methyl 2-(1-methyl-1*H*-pyrrol-2-yl)pent-3-enoate (3.80): Derived from 1-methylpyrrole (**3.74**) (73 mg, 0.90 mmol, 6.0 equiv) and *cis*-methyl vinyldiazoacetate **3.79** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography in silica gel (85/15 pentane/Et_2O, containing 0.5% Et_3N, R_f: 0.39) to provide **3.80** as colorless oil (14.6 mg, 50% yield) and **3.81** as colorless oil (1.4 mg, 5% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.57 (t, *J* = 2.2 Hz, 1H), 6.06-6.09 (m, 2H), 5.77-5.83 (m, 1H), 5.66-5.74 (m, 1H), 4.65 (d, *J* = 9.2 Hz, 1H), 3.71 (s, 3H), 3.58 (s, 3H), 1.70 (dd, *J* = 6.7, 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 129.2, 127.0, 126.1, 122.5, 107.1, 107.0, 52.4,

41.7, 34.0, 13.1; IR (neat): 2920, 1733, 1490, 1434, 1302, 1164, 766, 708 cm^{-1}; HRMS (APCI) calc. for $C_{11}H_{16}O_2N$ $(M+H)^+$ 194.1175 found 194.1174.



3.81

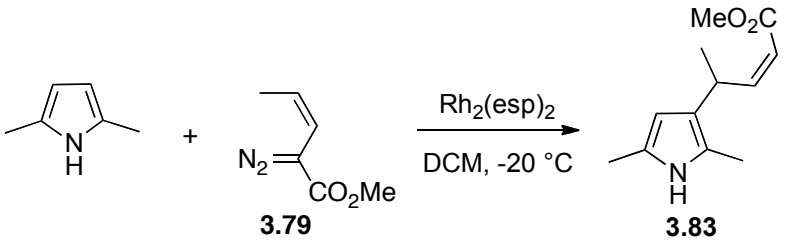
(*Z*)-Methyl 4-(1-methyl-1*H*-pyrrol-2-yl)pent-2-enoate (3.81): ^1H NMR (400MHz, $CDCl_3$): δ 6.55 (t, *J* = 2.4 Hz, 1H), 6.06-6.12 (m, 2H), 5.97-5.99 (m, 1H), 5.74 (dd, *J* = 11.2, 1.0 Hz, 1H), 4.92-5.01 (m, 1H), 3.75 (s, 3H), 3.53 (s, 3H), 1.38 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 166.8, 153.7, 135.5, 121.9, 116.8, 106.8, 104.2, 51.2, 33.7, 30.0, 19.5; IR (neat): 1717, 1637, 1436, 1195, 1176, 826, 705 cm^{-1}; HRMS (APCI) calc. for $C_{11}H_{16}O_2N$ $(M+H)^+$ 194.1176 found 194.1175.



3.76 **3.79** (5 equiv.) **3.82**

(2*Z*,2'*Z*)-Dimethyl 4,4'-(1,2,5-trimethyl-1*H*-pyrrole-3,4-diyl)bis(pent-2-enoate) (3.82): To a flame-dried 25 mL flask containing $Rh_2(esp)_2$ (5.7 mg, 0.05 equiv) and 1,2,5-trimethylpyrrole (**3.76**) (16.4 mg, 0.15 mmol, 1.0 equiv) in 6 mL dried CH_2Cl_2 under argon atmosphere was added a solution of fresh purified *cis*-methyl vinyldiazoacetate **3.79** (105 mg, 0.75 mmol, 5.0 equiv) in 6 mL dried CH_2Cl_2 by syringe pump over 3 h at -20 °C. The solution was stirred at -20 °C over-night and warmed up to room temperature over 2 h. The mixture was concentrated under reduced pressure and purified by flash chromatography in silica gel (85/15 pentane/Et_2O containing 0.5% Et_3N,

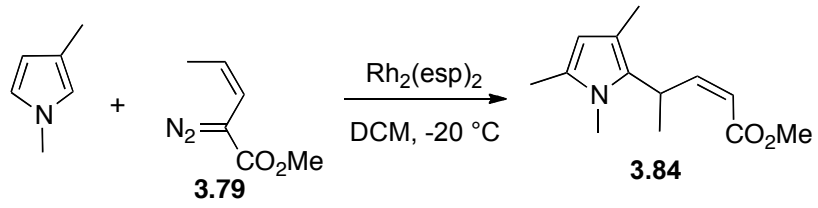
R_f: 0.34) to provide **3.82** as a mixture of two inseparable diastereomers in a ratio of 1/1 (43.2 mg, 86% combined yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.65 (dd, *J* = 11.4, 10.2 Hz, 2H), 6.57 (t, *J* = 10.8 Hz, 2H), 5.70 (dd, *J* = 11.4, 1.0 Hz, 2H), 5.63 (dd, *J* = 11.4, 1.0 Hz, 2H), 4.90-5.05 (m, 4H), 3.73 (s, 6H), 3.72 (s, 6H), 3.35 (s, 3H), 3.34 (s, 3H), 2.26 (s, 6H), 2.25 (s, 6H), 1.42 (d, *J* = 7.3 Hz, 6H), 1.35 (d, *J* = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 166.6, 155.0, 154.7, 123.2, 119.3, 119.2, 116.6, 116.3, 50.99, 50.95, 30.11, 30.05, 30.00, 29.86, 21.6, 21.5, 11.4, 11.2; IR (neat): 2950, 1716, 1634, 1435, 1369, 1192, 1171, 1003, 821 cm^{-1}; HRMS (APCI) calc. for $C_{19}H_{28}O_4N$ $(M+H)^+$ 334.2013 found 334.2010.



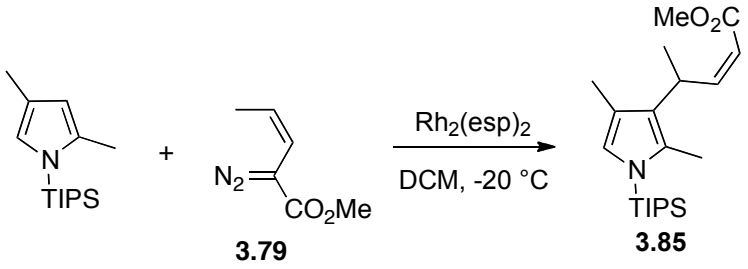
3.79 **3.83**

(*Z*)-Methyl 4-(2,5-dimethyl-1*H*-pyrrol-3-yl)pent-2-enoate (3.83): Derived from 2,5-dimethylpyrrole (85.6 mg, 0.90 mmol, 6.0 equiv) and *cis*-methyl vinyldiazoacetate **3.79** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography in silica gel (7/3 pentane/Et_2O, containing 1% Et_3N, R_f: 0.42) to provide **3.83** as yellowish oil (18.4 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (br, 1H), 6.21 (t, *J* = 11.4 Hz, 1H), 5.75 (d, *J* = 2.8 Hz, 1H), 5.62 (d, *J* = 11.4 Hz, 1H), 4.73-4.81 (m, 1H), 3.72 (s, 3H), 2.22 (s, 3H), 2.17 (s, 3H), 1.29 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 155.5, 125.6, 122.5, 122.0, 115.3, 103.7, 51.2, 29.9, 21.4, 13.2, 11.2; IR (neat): 3380, 2922,

1705, 1634, 1436, 1403, 1195, 1175, 826, 782 cm^{-1}; HRMS (APCI) calc. for $C_{12}H_{18}O_2N$ $(M+H)^+$ 208.1332 found 208.1331.



(*Z*)-Methyl 4-(1,3,5-trimethyl-1*H*-pyrrol-2-yl)pent-2-enoate (3.84): Derived from 1,2,4-trimethylpyrrole (98 mg, 0.90 mmol, 6.0 equiv) and *cis*-methyl vinyldiazoacetate **3.79** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography in silica gel (10/1 pentane/Et_2O, containing 0.5% Et_3N, R_f: 0.49) to provide product **3.84** as colorless oil (24.8 mg, 75% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 6.44 (dd, J = 11.4, 10.2 Hz, 1H), 5.70 (dd, J = 11.4, 1.0 Hz, 1H), 5.65 (s, 1H), 5.01-5.11 (m, 1H), 3.72 (s, 3H), 3.43 (s, 3H), 2.15 (d, J = 0.8 Hz, 3H), 2.13 (s, 3H), 1.43 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 152.8, 129.2, 127.3, 116.7, 113.6, 108.8, 51.3, 30.7, 30.6, 20.1, 12.8, 12.7; IR (neat): 2926, 1717, 1637, 1435, 1396, 1194, 1174, 1010, 824, 773 cm^{-1}; HRMS (APCI) calc. for $C_{13}H_{20}O_2N$ $(M+H)^+$ 222.1489 found 222.1492.

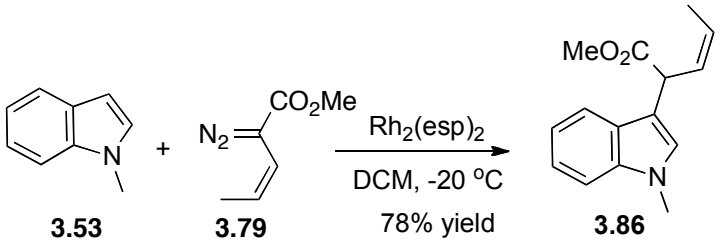


(*Z*)-Methyl 4-(2,4-dimethyl-1-(triisopropylsilyl)-1*H*-pyrrol-3-yl)pent-2-enoate (3.85): Derived from 1-triisopropylsilyl-2,4-dimethylpyrrole (226 mg, 0.90 mmol, 6.0 equiv) and *cis*-methyl vinyldiazoacetate **3.79** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography in silica gel (40/1 pentane/Et_2O, R_f: 0.38) to provide product **3.85** as colorless oil (47.6 mg, 87% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 6.51 (dd, *J* = 11.2, 10.0 Hz, 1H), 6.39 (s, 1H), 5.64 (dd, *J* = 11.2, 1.0 Hz, 1H), 4.80-4.88 (m, 1H), 3.70 (s, 3H), 2.24 (s, 3H), 2.11 (d, *J* = 0.8 Hz, 3H), 1.45 (hept., *J* = 7.6 Hz, 3H), 1.35 (d, *J* = 7.2 Hz, 3H), 1.10 (d, *J* = 7.6 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 154.7, 129.4, 124.1, 122.0, 117.9, 115.8, 50.9, 30.5, 20.6, 18.4, 13.3, 13.1, 12.4; IR (neat): 2948, 2868, 1722, 1463, 1436, 1313, 1192, 1173, 1017, 882, 824, 685 cm^{-1}; HRMS (APCI) calc. for $C_{21}H_{38}O_2NSi$ $(M+H)^+$ 364.2666 found 364.2672.

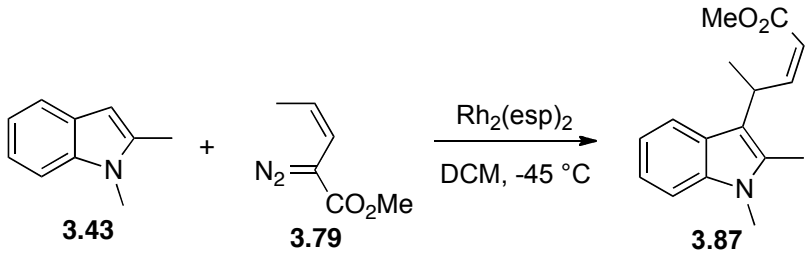
General procedure for the reaction between indoles and methyl vinyldiazoacetate

To a flame-dried 25 mL flask containing $Rh_2(esp)_2$ (2.3 mg, 0.02 equiv) and indoles (0.90 mmol, 6.0 equiv) in 6 mL dried CH_2Cl_2 under argon atmosphere was added a solution of fresh purified methyl vinyldiazoacetate (21.0 mg, 0.15 mmol, 1.0 equiv) in 6 mL dried CH_2Cl_2 by syringe pump over 3 h at -45 °C. The solution was warmed up to room temperature over 2 h. The mixture was concentrated under reduced pressure and purified

by flash chromatography in silica gel (pentane/Et_2O) to provide the corresponding products as colorless oil or powder.

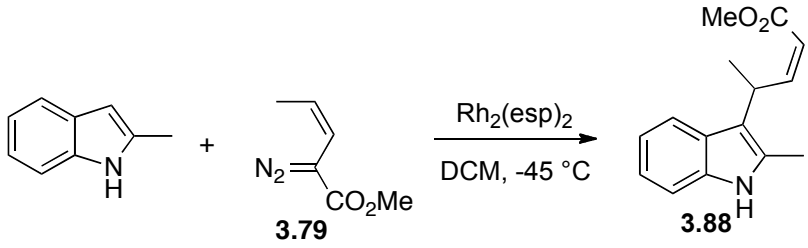


(*Z*)-Methyl 2-(1-methyl-1*H*-indol-3-yl)pent-3-enoate (3.86): Derived from *N*-methylindole (**3.53**) (118.0 mg, 0.90 mmol, 6.0 equiv) and *cis*-methyl vinyldiazoacetate **3.79** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography in silica gel (85/15 pentane/Et_2O, R_f: 0.29) to provide product **3.86** as colorless oil (28.6 mg, 78% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.24 (td, *J* = 8.2, 1.2 Hz, 1H), 7.13 (td, *J* = 7.8, 1.2 Hz, 1H), 7.03 (s, 1H), 5.93-6.00 (m, 1H), 5.66-5.74 (m, 1H), 4.91 (d, *J* = 9.4 Hz, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 1.76 (dd, *J* = 6.7, 1.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.8, 137.0, 127.6, 126.7, 126.6, 126.4, 121.8, 119.2 (2C), 112.0, 109.3, 52.2, 41.0, 32.8, 13.1; IR (neat): 2949, 1732, 1472, 1433, 1330, 1310, 1192, 1152, 1014, 776, 739 cm^{-1}; HRMS (APCI) calc. for $C_{15}H_{18}O_2N$ $(M+H)^+$ 244.1332 found 244.1330.



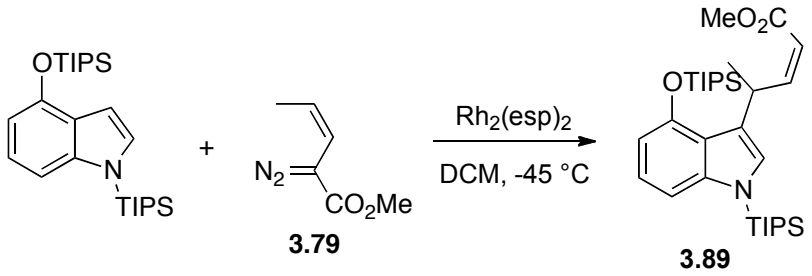
(*Z*)-Methyl 4-(1,2-dimethyl-1*H*-indol-3-yl)pent-2-enoate (3.87): Derived from 1,2-dimethylindole (**3.43**) (65.3 mg, 0.45 mmol, 3.0 equiv) and *cis*-methyl vinyldiazoacetate

3.79 (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography in silica gel (85/15 pentane/Et_2O, R_f: 0.45) to provide product **3.87** as colorless gel powder (34.7 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 7.9 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 1H), 7.16 (td, *J* = 7.9, 1.0 Hz, 1H), 7.07 (td, *J* = 7.6, 1.0 Hz, 1H), 6.79 (t, *J* = 11.4 Hz, 1H), 5.69 (d, *J* = 11.4 Hz, 1H), 5.15-5.22 (m, 1H), 3.74 (s, 3H), 3.65 (s, 3H), 2.45 (s, 3H), 1.56 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 154.1, 136.9, 132.9, 125.8, 120.4, 119.1, 118.6, 116.2, 113.3, 108.9, 51.0, 30.5, 29.5, 20.9, 10.5; IR (neat): 2994, 1716, 1637, 1471, 1435, 1368, 1193, 1173, 824, 737 cm^{-1}; HRMS (APCI) calc. for $C_{16}H_{19}O_2N$ $(M+H)^+$ 258.1489 found 258.1488.

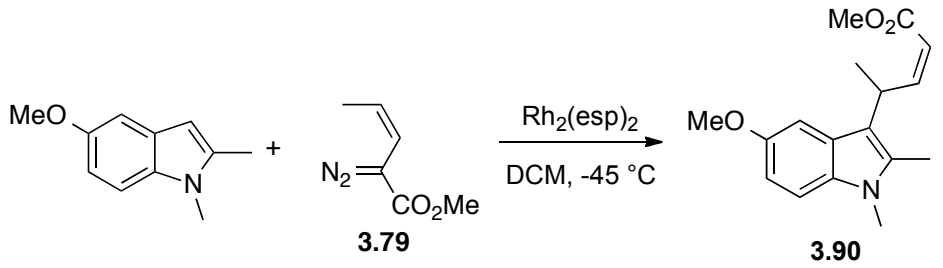


(*Z*)-Methyl 4-(2-methyl-1*H*-indol-3-yl)pent-2-enoate (3.88): Derived from 2-methylindole (118.0 mg, 0.90 mmol, 6.0 equiv) and *cis*-methyl vinyldiazoacetate **3.79** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography in silica gel (7/3 pentane/Et_2O, R_f: 0.41) to provide product **3.88** as colorless powder (26.8 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (br, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.26-7.28 (m, 1H), 7.05-7.13 (m, 2H), 6.76 (t, *J* = 11.2, 10.4 Hz, 1H), 5.71 (dd, *J* = 11.2, 1.0 Hz, 1H), 5.11-5.19 (m, 1H), 3.74 (s, 3H), 2.45 (s, 3H), 1.55 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 153.9, 135.4, 130.9, 126.9, 120.8, 119.06, 119.03, 116.4, 114.0, 110.5, 51.1, 30.2, 20.7, 12.1; IR (neat): 3399(br), 2950, 1717, 1703, 1639, 1460,

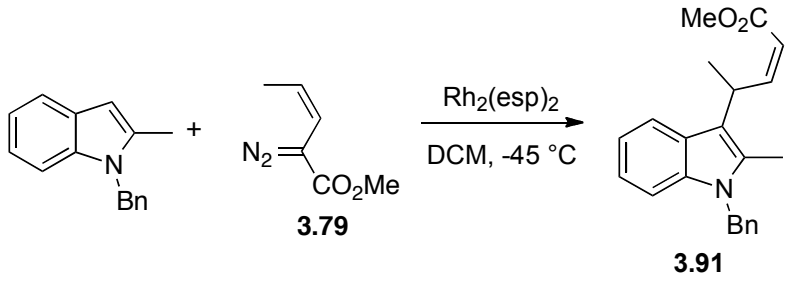
1435, 1301, 1196, 1176, 824, 741 cm^{-1}; M.p. 59-61 °C; HRMS (APCI) calc. for $C_{15}H_{18}O_2N$ $(M+H)^+$ 244.1332 found 244.1330.



(*Z*)-Methyl 4-(1-(triisopropylsilyl)-4-((triisopropylsilyl)oxy)-1*H*-indol-3-yl)pent-2-enoate (3.89): Derived from 1,5-bistriisopropylsilylindole (400.8 mg, 0.90 mmol, 6.0 equiv) and *cis*-methyl vinyldiazoacetate **3.79** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography in silica gel (30/1 pentane/Et_2O, R_f: 0.54) to provide product **3.89** as colorless oil (44.6 mg, 53% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.03 (d, *J* = 8.3 Hz, 1H), 6.90 (t, *J* = 7.9 Hz, 1H), 6.86 (s, 1H), 6.68 (dd, *J* = 11.4, 9.5 Hz, 1H), 6.49 (d, *J* = 7.9 Hz, 1H), 5.76 (dd, *J* = 11.4, 0.6 Hz 1H), 5.06-5.13 (m, 1H), 3.67 (s, 3H), 1.65 (hept., *J* = 7.6 Hz, 3H), 1.49 (d, *J* = 7.0 Hz, 3H), 1.47 (hept., *J* = 7.6 Hz, 3H), 1.17 (dd, *J* = 7.6, 1.6 Hz, 18H), 1.14 (dd, *J* = 7.6, 1.0 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 155.3, 150.2, 144.0, 125.4, 122.7, 121.5, 121.4, 117.2, 107.6, 107.1, 51.0, 31.7, 24.2, 18.3, 18.2, 13.7, 12.9; IR (neat): 2945, 2867, 1730, 1489, 1461, 1264, 1172, 1128, 1098, 882, 782, 687 cm^{-1}; HRMS (APCI) calc. for $C_{32}H_{56}O_3NSi_2$ $(M+H)^+$ 558.3793 found 558.3799.

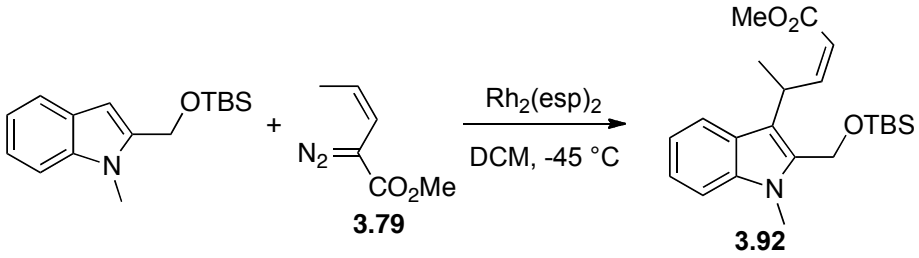


(*Z*)-Methyl 4-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)pent-2-enoate (3.90): Derived from 5-methoxy-1,2-dimethyl-1H-indole (158 mg, 0.90 mmol, 6.0 equiv) and *cis*-methyl vinyldiazoacetate **3.79** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography in silica gel (85/15 pentane/Et_2O, R_f: 0.28) to provide product **3.90** as colorless powder (39.6 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14-7.17 (m, 2H), 6.82 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.75 (dd, *J* = 11.1, 10.5 Hz, 1H), 5.69 (dd, *J* = 11.4, 1.0 Hz, 1H), 5.12-5.20 (m, 1H), 3.88 (s, 3H), 3.74 (s, 3H), 3.61 (s, 3H), 2.42 (s, 3H), 1.55 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 153.9, 153.3, 133.7, 132.4, 126.1, 116.2, 112.8, 109.5, 109.4, 102.2, 56.1, 51.0, 30.4, 29.6, 20.7, 10.6; IR (neat): 2948, 1716, 1486, 1435, 1406, 1227, 1194, 1175, 1033, 824, 793 cm^{-1}; M.p. 91-93 °C; HRMS (APCI) calc. for $C_{17}H_{22}O_3N$ $(M+H)^+$ 288.1594 found 288.1591.



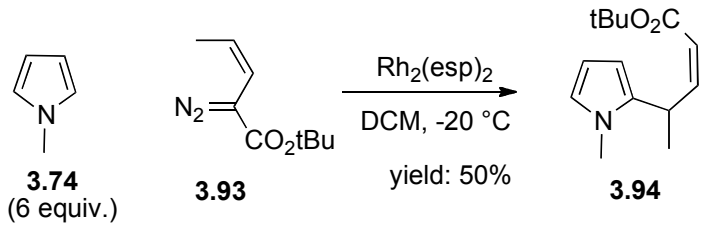
(*Z*)-Methyl 4-(1-benzyl-2-methyl-1*H*-indol-3-yl)pent-2-enoate (3.91): Derived from 1-benzyl-2-methyl-1H-indole (199 mg, 0.90 mmol, 6.0 equiv) and *cis*-methyl vinyldiazoacetate **3.79** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash

chromatography in silica gel (9/1 pentane/Et_2O, R_f: 0.42) to provide product **3.91** as colorless oil (45.5 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.76 (m, 1H), 7.19-7.30 (m, 4H), 7.07-7.13 (m, 2H), 6.97 (d, *J* = 7.3 Hz, 2H), 6.82 (t, *J* = 10.8 Hz, 1H), 5.71 (dm, *J* = 11.2 Hz, 1H), 5.30 (s, 2H), 5.15-5.26 (m, 1H), 3.73 (s, 3H), 2.38 (s, 3H), 1.59 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 154.0, 137.9, 136.8, 132.8, 128.7, 127.2, 126.1, 126.0, 120.6, 119.2, 118.9, 116.3, 114.0, 109.4, 51.0, 46.5, 30.6, 21.0, 10.5; IR (neat): 1716, 1637, 1466, 1452, 1435, 1339, 1194, 1174, 823, 730, 695 cm^{-1}; HRMS (APCI) calc. for $C_{22}H_{24}O_2N$ $(M+H)^+$ 334.1802 found 334.1797.

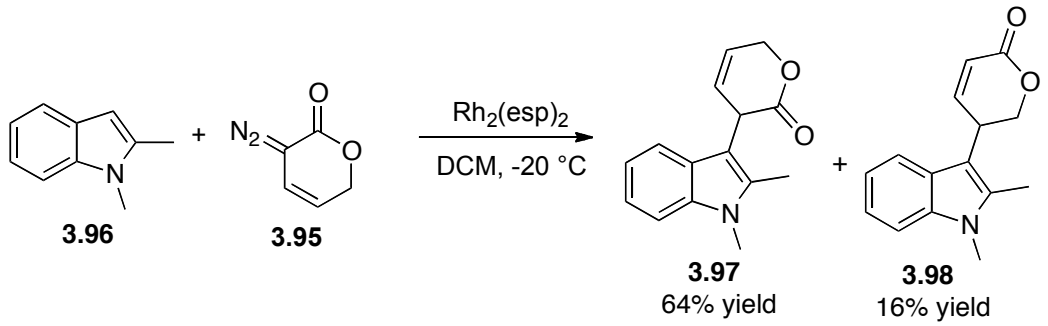


(*Z*)-Methyl 4-(2-(((*tert*-butyldimethylsilyl)oxy)methyl)-1-methyl-1*H*-indol-3-yl)pent-2-enoate (3.92): Derived from 2-((*tert*-butyldimethylsilyloxy)methyl)-1-methyl-1H-indole (248 mg, 0.90 mmol, 6.0 equiv) and *cis*-methyl vinyldiazoacetate **3.79** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography in silica gel (30/1 pentane/Et_2O, R_f: 0.35) to provide product **3.92** as colorless powder (25.6 mg, 44% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.2 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.22 (td, *J* = 7.0, 0.8 Hz, 1H), 7.08 (td, *J* = 7.0, 0.8 Hz, 1H), 6.80 (t, *J* = 11.2 Hz, 1H), 5.68 (d, *J* = 11.2 Hz, 1H), 5.16-5.27 (m, 1H), 4.98 (d, *J* = 12.9 Hz, 1H), 4.85 (d, *J* = 12.9 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 1.59 (d, *J* = 7.0 Hz, 3H), 0.90 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 166.6, 154.1, 137.5, 134.8, 125.2, 121.5,

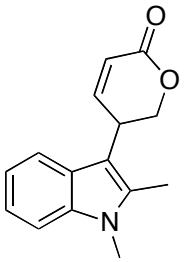
120.2, 118.7, 116.4, 114.8, 109.3, 55.0, 51.0, 30.4, 29.9, 25.8, 21.2, 18.2; IR (neat): 2951, 2929, 1720, 1471, 1436, 1405, 1254, 1195, 1177, 1058, 836, 776, 738 cm^{-1}; M.p. 78-80 °C; HRMS (APCI) calc. for $C_{22}H_{33}O_3NSi$ $(M)^+$ 387.2242 found 387.2241.



(*Z*)-*tert*-Butyl 4-(1-methyl-1*H*-pyrrol-2-yl)pent-2-enoate (3.94): To a flame-dried 25 mL flask containing $Rh_2(esp)_2$ (2.3 mg, 0.02 equiv) and 1-methylpyrrole (**3.74**) (73 mg, 0.90 mmol, 6.0 equiv) in 6 mL dried CH_2Cl_2 under argon atmosphere was added a solution of *tert*-butyl vinyldiazoacetate **3.93** (27.4 mg, 0.15 mmol, 1.0 equiv) in 6 mL dried CH_2Cl_2 by syringe pump over 3 h at -20 ^oC. The solution was stirred at -20 ^oC over-night and warmed up to room temperature over 2 h. The mixture was concentrated under reduced pressure and purified by flash chromatography in silica gel (10/1 pentane/Et_2O, R_f: 0.65) to provide product **3.94** as colorless oil (17.6 mg, 50% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 6.55 (t, *J* = 2.3 Hz, 1H), 6.09 (t, *J* = 3.1 Hz, 1H), 5.93-5.99 (m, 2H), 5.64 (d, *J* = 11.6 Hz, 1H), 4.84-4.93 (m, 1H), 3.52 (s, 3H), 1.51 (s, 9H), 1.38 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 151.4, 135.9, 121.9, 119.2, 106.7, 104.0, 80.4, 33.6, 29.9, 28.2, 19.3; IR (neat): 2976, 1711, 1406, 1367, 1241, 1214, 1151, 828, 705 cm^{-1}; HRMS (APCI) calc. for $C_{14}H_{22}O_2N$ $(M+H)^+$ 236.1645 found 236.1648.



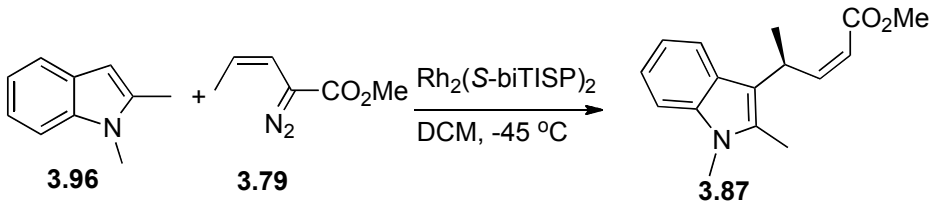
3-(1,2-Dimethyl-1*H*-indol-3-yl)-3,6-dihydro-2*H*-pyran-2-one (3.97): To a flame-dried 25 mL flask containing $Rh_2(esp)_2$ (2.3 mg, 0.02 equiv) and 1,2-dimethylindole (**3.96**) (130.7 mg, 0.90 mmol, 6.0 equiv) in 6 mL dried dichloromethane under argon atmosphere was added a solution of diazolactone **3.95** (18.7 mg, 0.15 mmol, 1.0 equiv) in 6 mL dried dichloromethane by syringe pump over 3 h at -20 ^{o}C. The solution was stirred at -20 ^{o}C over-night and warmed up to room temperature over 2 h. The mixture was concentrated by vacuum and purified by flash chromatography on silica gel (100% Et_2O, R_f: 0.60 for **3.98** and 0.44 for **3.97**) to provide product **3.97** as viscous oil (23.2 mg, 64 % yield) and **3.98** as viscous oil (4.0 mg, 16% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 7.50 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.21 (dt, *J* = 1.3, 7.0 Hz, 1H), 7.08-7.15 (m, 2H), 6.22 (dd, *J* = 2.9, 9.8 Hz, 1H), 4.56 (dd, *J* = 11.1, 12.4 Hz, 1H), 4.38 (ddd, *J* = 1.9, 6.0, 11.1, Hz, 1H), 4.20-4.26 (m, 1H), 3.70 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 164.0, 152.5, 136.9, 134.5, 126.4, 121.5, 121.0, 119.7, 118.4, 109.4, 105.5, 70.7, 32.9, 29.9, 10.8; IR (neat): 2939, 1720, 1472, 1224, 1081, 1038, 821, 738 cm^{-1}; HRMS (APCI) calc. for $C_{15}H_{16}O_2N$ $(M+H)^+$ 242.1176 found 242.1177.



3.98

5-(1,2-Dimethyl-1*H*-indol-3-yl)-5,6-dihydro-2*H*-pyran-2-one (3.98): ^{1}H NMR (400MHz, $CDCl_3$): 7.41 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.21 (dt, *J* = 1.2, 7.0 Hz, 1H), 7.06 (dt, *J* = 0.8, 7.0 Hz, 1H), 6.04 (dq, *J* = 2.7, 10.1 Hz, 1H), 5.94 (dm, *J* = 10.1 Hz, 1H), 5.09-5.21 (m, 2H), 4.51-4.54 (m, 1H), 3.69 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): 170.6, 136.8, 134.7, 127.7, 121.3, 121.2, 119.5, 118.0, 109.2, 107.7, 69.4, 37.8, 29.8, 10.8; IR (neat): 2917, 1727, 1470, 1374, 1215, 1141, 1094, 1018, 891, 735, 679 cm^{-1}; HRMS (APCI) calc. for $C_{15}H_{16}O_2N$ $(M+H)^+$ 242.1176 found 242.1176.

3. Asymmetric vinylogous alkylation of *N*-heterocycles

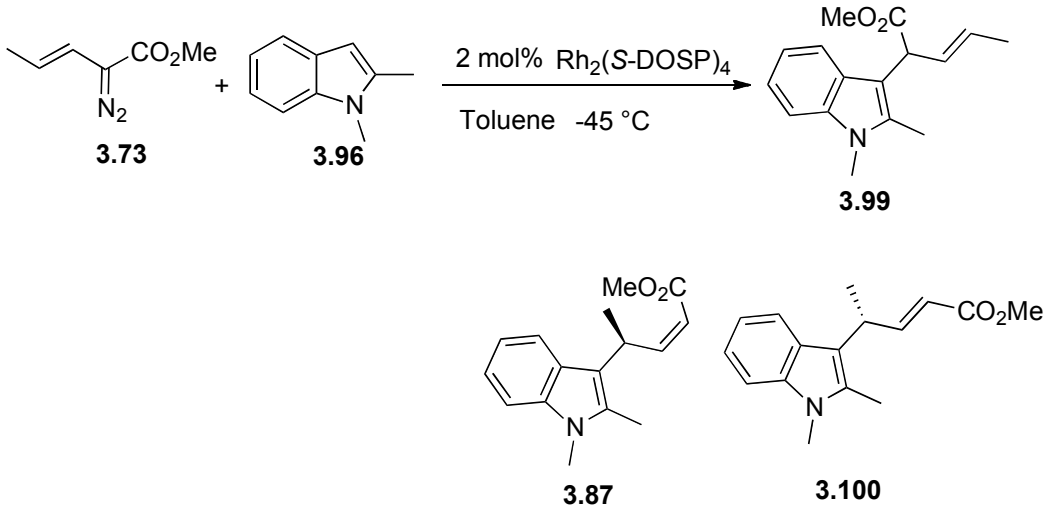


3.96 **3.79** **3.87**

(*S*,*Z*)-Methyl 4-(1,2-dimethyl-1*H*-indol-3-yl)pent-2-enoate (3.87): To a flame-dried 25 mL flask containing Rh_2(*S*-biTISP)$_2$ (5.6 mg, 0.02 equiv) and 1,2-dimethylindole (**3.96**) (130.6 mg, 0.90 mmol, 6.0 equiv) in 6 mL dried CH_2Cl_2 under argon atmosphere was added a solution of fresh purified *cis*-methyl vinyldiazoacetate **3.79** (21.0 mg, 0.15 mmol, 1.0 equiv) in 6 mL dried CH_2Cl_2 by syringe pump over 3 h at -45 °C. The solution was

warmed up to room temperature over night. The mixture was concentrated under reduced pressure and purified by flash chromatography on silica gel (85/15 pentane/Et_2O, R_f: 0.45) to provide the corresponding product **3.87** as colorless gel powder (25.5 mg, 66% yield).

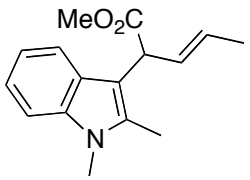
Spectroscopic data on the purified products was consistent with reported value.[5] HPLC: (OD-H, 1% isopropanol in hexane, 0.7 mL/min) retention times of 18.5 (major) and 21.3 (minor), 89% ee; $[\alpha]^{25}_D$ 317.0 (c = 0.89, $CHCl_3$).



Derived from 1,2-dimethylindole (**3.96**) (130.6 mg, 0.90 mmol, 6.0 equiv) and *trans*-methyl vinyldiazoacetate **3.73** (21 mg, 0.15 mmol, 1.0 equiv) in the presence of Rh_2(*S*-DOSP)$_4$ (5.6 mg, 0.02 equiv) and purified by flash chromatography in silica gel (85/15 pentane/Et_2O, R_f: 0.28 for product **3.100** and 0.33 for product **3.99**) to provide product **3.100** as colorless viscous oil (13.1 mg, 34% yield) and product **3.99** as colorless powder (12.3 mg, 32% yield).

[5] Lian, Y.; Davies, H. M. L. *Org. Lett.* **2010**, *12*, 924.

(*E*)-Methyl 4-(1,2-dimethyl-1*H*-indol-3-yl)pent-2-enoate (3.100): ^{1}H NMR (400 MHz, $CDCl_3$): 7.51 (d, *J* = 7.8 Hz, 1H), 7.28 (dd, *J* = 5.5, 15.9 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 7.03 (t, *J* = 7.8 Hz, 1H), 5.84 (dd, *J* = 1.9, 15.9 Hz, 1H), 3.85-3.93 (m, 1H), 3.68 (s, 3H), 3.64 (s, 3H), 2.34 (s, 3H), 1.54 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 167.7, 153.5, 136.9, 132.8, 126.4, 120.8, 119.2, 119.1, 119.0, 112.0, 109.0, 51.6, 33.9, 29.7, 19.6, 10.8; IR (neat): 2921, 1718, 1471, 1408, 1272, 908, 730 cm^{-1}; HRMS (APCI) calc. for $C_{16}H_{20}O_2N$ $(M+H)^+$ 258.1489 found 258.1490; $[\alpha]^{25}_D$ 8.4 (*c* = 1.37, $CHCl_3$); HPLC: (OD-H, 2% isopropanol in hexane, 0.7 mL/min) retention times of 30.1 (major) and 42.9 (minor), 92% ee.

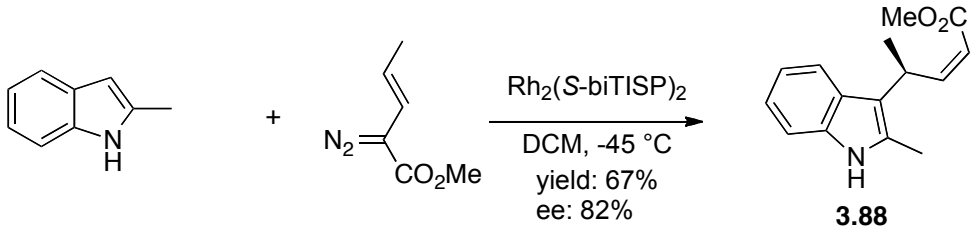


3.99

(*E*)-Methyl 2-(1,2-dimethyl-1*H*-indol-3-yl)pent-3-enoate (3.99): ^{1}H NMR (400 MHz, $CDCl_3$): 7.61 (d, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 7.4 Hz, 1H), 7.14-7.19 (m, 1H), 7.06-7.11 (m, 1H), 6.06 (qq, *J* = 7.4, 1.6 Hz, 1H), 5.47-5.56 (m, 1H), 4.53-4.57 (m, 1H), 3.67 (s, 3H), 3.66 (s, 3H), 2.42 (s, 3H), 1.67-1.70 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 174.3, 136.8, 133.9, 128.0, 127.4, 126.5, 121.0, 119.4, 119.1, 108.9, 108.3, 52.2, 45.9, 29.8, 18.1, 10.8; IR (neat): 2917, 1731, 1471, 1409, 1158, 963, 738 cm^{-1}; HRMS (EI) calc. for $C_{16}H_{20}O_2N$ $(M+H)^+$ 258.1489 found 258.1490; M.p. 70-72 °C.

General procedure for the reaction between indoles and methyl vinyldiazoacetate

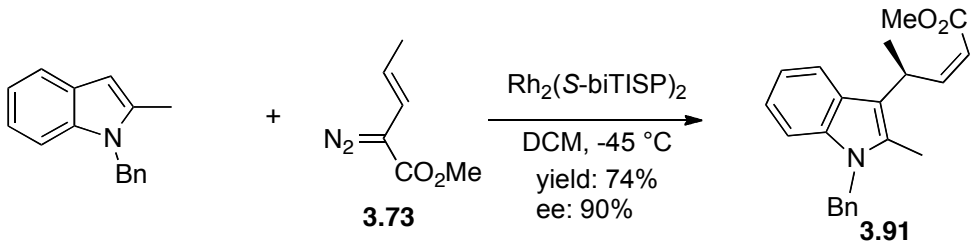
To a flame-dried 25 mL flask containing Rh_2(*S*-biTISP)$_2$ (5.5 mg, 0.02 equiv) and indoles (0.90 mmol, 6.0 equiv) in 6 mL dried CH_2Cl_2 under argon atmosphere was added a solution of fresh purified *trans*-methyl vinyldiazoacetate **3.73** (21.0 mg, 0.15 mmol, 1.0 equiv) in 6 mL dried CH_2Cl_2 by syringe pump over 3 h at -45 °C. The solution was warmed up to room temperature over night. The mixture was concentrated under reduced pressure and purified by flash chromatography on silica gel (pentane/Et_2O) to provide the corresponding products as colorless oil or powder.



3.88

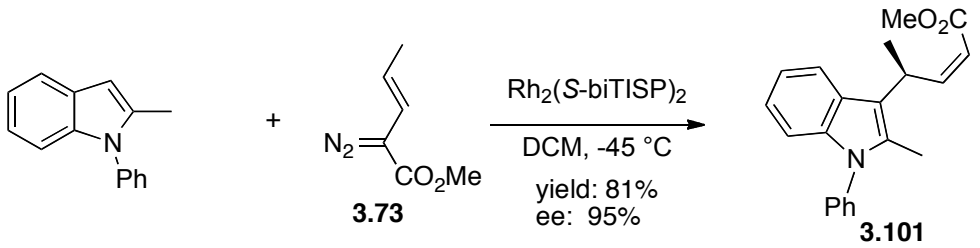
(*S*,*Z*)-Methyl 4-(2-methyl-1*H*-indol-3-yl)pent-2-enoate (3.88): Derived from 2-methylindole (118.0 mg, 0.90 mmol, 6.0 equiv) and *trans*-methyl vinyldiazoacetate **3.73** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography in silica gel (7/3 pentane/Et_2O, R_f: 0.41) to provide product **3.88** as colorless powder (24.6 mg, 67% yield).

Spectroscopic data on the purified products was consistent with reported value.[5] HPLC: (AD-H, 3 % isopropanol in hexane, 0.7 mL/min) retention times of 26.4 (major) and 30.4 (minor), 82% ee; $[\alpha]^{25}_D$ 324.6 (*c* = 0.30, $CHCl_3$).



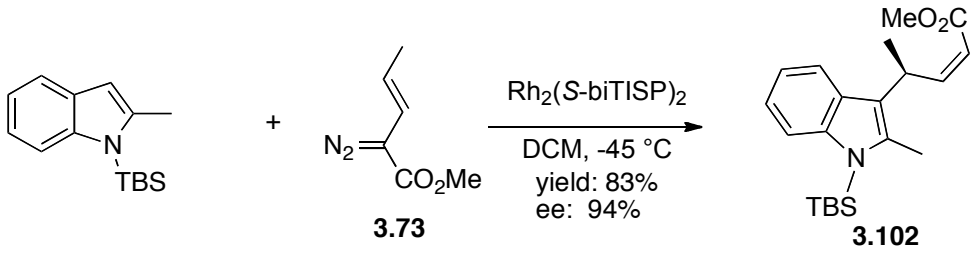
(*S*,*Z*)-Methyl 4-(1-benzyl-2-methyl-1*H*-indol-3-yl)pent-2-enoate (3.91): Derived from 1-benzyl-2-methyl-1H-indole (199 mg, 0.90 mmol, 6.0 equiv) and *trans*-methyl vinyldiazoacetate **3.73** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography on silica gel (9/1 pentane/Et_2O, R_f: 0.42) to provide product **3.91** as colorless oil (37.0 mg, 74% yield).

Spectroscopic data on the purified products was consistent with reported value.[5] HPLC: (AD-H, 1 % isopropanol in hexane, 0.7 mL/min) retention times of 8.9 (major) and 13.1 (minor), 90% ee; $[\alpha]^{25}_D$ 305.5 (*c* = 0.73, $CHCl_3$).



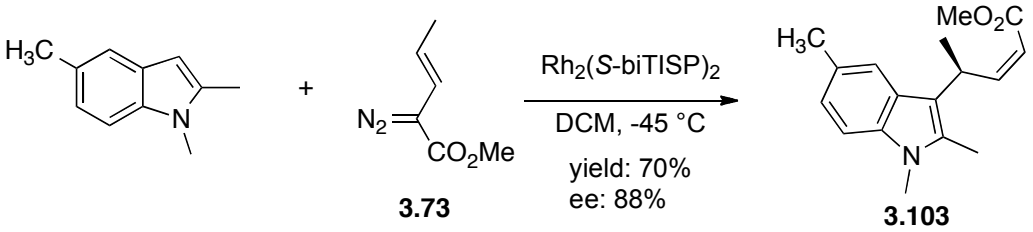
(*S*,*Z*)-Methyl 4-(2-methyl-1-phenyl-1*H*-indol-3-yl)pent-2-enoate (3.101): Derived from 1-phenyl-2-methyl-1H-indole (187 mg, 0.90 mmol, 6.0 equiv) and *trans*-methyl vinyldiazoacetate **3.73** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography on silica gel (10/1 pentane/Et_2O, R_f: 0.44) to provide product **3.101** as colorless oil (38.6 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 7.72-7.76 (m, 1H), 7.49-7.55 (m, 2H), 7.41-7.47 (m, 1H), 7.31-7.34 (m, 1H), 7.05-7.14 (m, 3H), 6.84 (t, *J* = 11.0 Hz, 1H), 5.74 (dm, *J* = 11.0 Hz, 1H), 5.20-5.28 (m, 1H), 3.74 (s, 3H), 2.30 (s, 3H), 1.61

(d, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.8, 153.8, 138.0, 137.8, 133.1, 129.4, 128.3, 127.6, 126.2, 120.9, 119.4, 119.0, 116.5, 114.6, 110.3, 51.1, 30.6, 20.8, 11.3; IR (neat): 1717, 1500, 1368, 1175, 823, 739, 699 cm^{-1}; HRMS (APCI) calc. for $C_{21}H_{22}O_2N$ $(M+H)^+$ 320.1645 found 320.1649; HPLC: (OD-H, 0.5 % isopropanol in hexane, 0.5 mL/min) retention times of 10.2 (major) and 10.9 (minor), 94 % ee; $[\alpha]^{25}_D$ 246.4 (c = 1.22, $CHCl_3$).

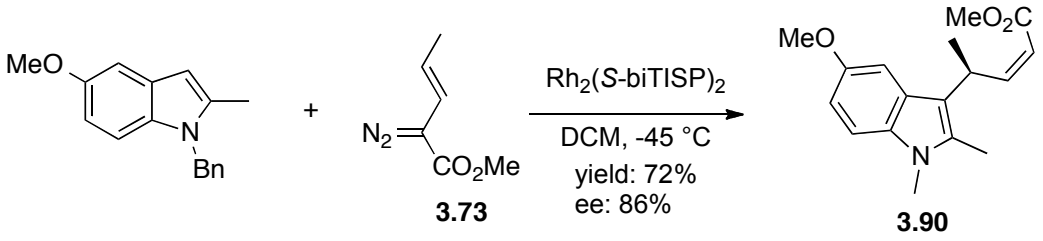


(*S*,*Z*)-Methyl 4-(1-(*tert*-butyldimethylsilyl)-2-methyl-1*H*-indol-3-yl)pent-2-enoate (3.102): Derived from 1-(*tert*-butyldimethylsilyl)-2-methyl-1*H*-indole (221 mg, 0.90 mmol, 6.0 equiv) and *trans*-methyl vinyldiazoacetate **3.73** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography on silica gel (20/1 pentane/Et_2O, R_f: 0.38) to provide product **3.102** as colorless oil (44.6 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65-7.71 (m, 1H), 7.50-7.55 (m, 1H), 7.06-7.10 (m, 2H), 6.83 (dd, J = 11.3, 10.4 Hz, 1H), 5.72 (dd, J = 11.3, 1.2 Hz, 1H), 5.14-5.22 (m, 1H), 3.74 (s, 3H), 2.49 (s, 3H), 1.57 (d, J = 7.0 Hz, 3H), 0.99 (s, 9H), 0.67 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 153.8, 141.9, 137.8, 129.4, 120.0, 119.0, 118.7, 117.8, 116.6, 114.4, 51.0, 30.5, 26.8, 20.6, 20.5, 14.7, 0.0; IR (neat): 2952, 2930, 1720, 1472, 1272, 1193, 1174, 1001, 821, 785, 736 cm^{-1}; HRMS (APCI) calc. for $C_{21}H_{32}O_2NSi$ $(M+H)^+$ 358.2197 found

358.2196. HPLC: (OA-2000, hexane, 0.5 mL/min) retention times of 14.4 (major) and 15.3 (minor), 94 % ee; $[\alpha]^{25}_{D}$ 247.5 (*c* = 0.82, $CHCl_3$).

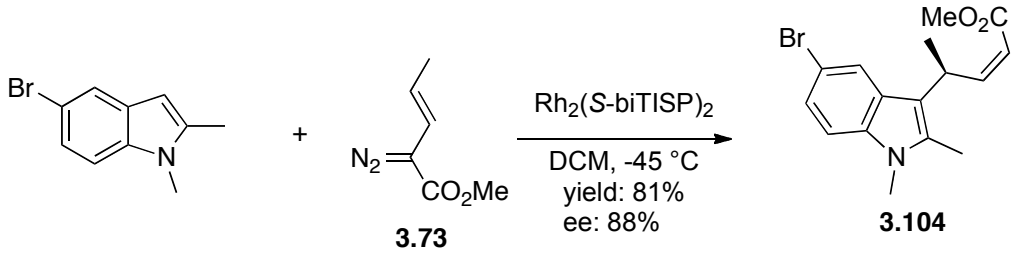


(*S*,*Z*)-Methyl 4-(1,2,5-trimethyl-1*H*-indol-3-yl)pent-2-enoate (3.103): Derived from 1,2,5-trimethyl-1*H*-indole (143 mg, 0.90 mmol, 6.0 equiv) and *trans*-methyl vinyldiazoacetate **3.73** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography on silica gel (85/15 pentane/Et_2O, R_f: 0.49) to provide product **3.103** as colorless oil (28.6 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 7.46 (s, 1H), 7.15 (d, *J* = 8.2 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.80 (t, *J* = 11.4 Hz, 1H), 5.68 (d, *J* = 11.4 Hz, 1H), 5.10-5.18 (m, 1H), 3.74 (s, 3H), 3.61 (s, 3H), 2.46 (s, 3H), 2.42 (s, 3H), 1.55 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 165.8, 154.3, 135.3, 132.9, 127.7, 125.9, 121.8, 116.0, 112.7, 108.6, 51.0, 30.6, 29.5, 21.6, 21.0, 10.5; IR (neat): 1715, 1644, 1436, 1370, 1197, 1181, 1111, 822, 800 cm^{-1}; HRMS (APCI) calc. for $C_{17}H_{22}O_2N$ $(M+H)^+$ 272.1645 found 272.1646; HPLC: (AD-H, 1% isopropanol in hexane, 0.7 mL/min) retention times of 7.9 (major) and 10.5 (minor), 88% ee; $[\alpha]^{25}_{D}$ 354.1 (*c* = 1.13, $CHCl_3$).



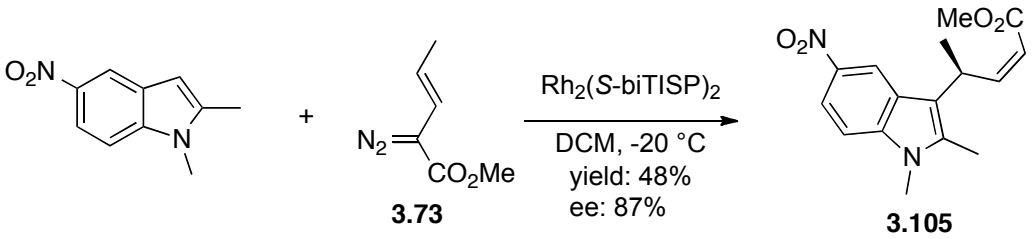
(*S*,*Z*)-Methyl 4-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)pent-2-enoate (3.90): Derived from 5-methoxy-1,2-dimethyl-1H-indole (158 mg, 0.90 mmol, 6.0 equiv) and *trans*-methyl vinyldiazoacetate **3.73** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography on silica gel (85/15 pentane/Et_2O, R_f: 0.28) to provide product **3.90** as colorless powder (31.0 mg, 72% yield).

Spectroscopic data on the purified products was consistent with reported value.[5] HPLC: (AD-H, 1% isopropanol in hexane, 0.7 mL/min) retention times of 15.4 (major) and 22.1 (minor), 86% ee; $[\alpha]^{25}_D$ 377.6 (*c* = 0.52, $CHCl_3$).

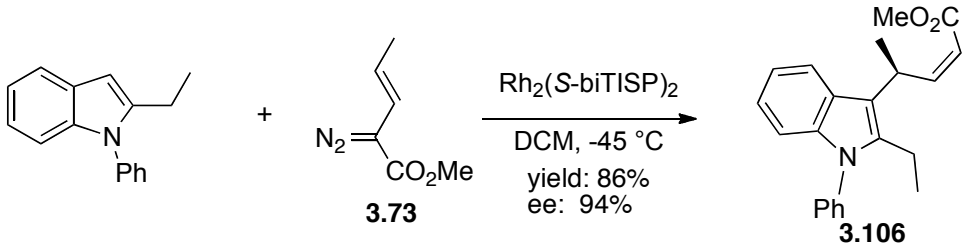


(*S*,*Z*)-Methyl 4-(5-bromo-1,2-dimethyl-1*H*-indol-3-yl)pent-2-enoate (3.104): Derived from 5-bromo-1,2-dimethyl-1H-indole (202 mg, 0.90 mmol, 6.0 equiv) and *trans*-methyl vinyldiazoacetate **3.73** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography on silica gel (85/15 pentane/Et_2O, R_f: 0.34) to provide product **3.104** as colorless powder (40.8 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 7.78 (d, *J* = 1.8 Hz, 1H), 7.21 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.10 (d, *J* = 8.6 Hz, 1H), 6.70 (dd, *J* = 11.6, 10.7 Hz, 1H), 5.70 (dd, *J* = 11.3, 0.9 Hz, 1H), 5.09-5.18 (m, 1H), 3.73 (s, 3H), 3.61 (s, 3H), 2.43

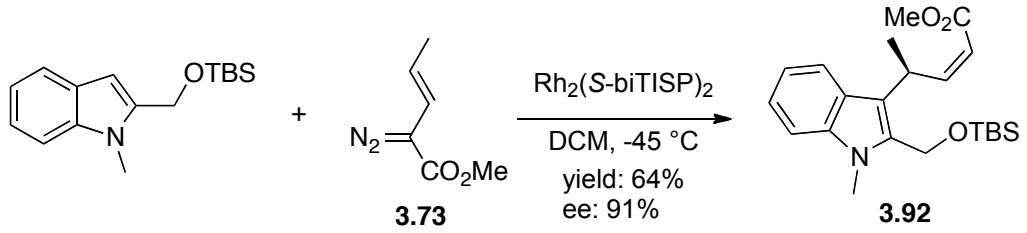
(s, 3H), 1.52 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.7, 153.5, 135.6, 134.3, 127.5, 123.0, 121.5, 116.6, 113.2, 111.9, 110.3, 51.1, 30.3, 29.6, 20.9, 10.6; IR (neat): 2948, 1716, 1473, 1435, 1174, 825, 789 cm^{-1}; HRMS (APCI) calc. for $C_{16}H_{19}O_2NBr$ $(M+H)^+$ 336.0594 found 336.0598; M.p.: 103-105 °C; HPLC: (OJ, 3% isopropanol in hexane, 1.0 mL/min) retention times of 11.9 (major) and 15.8 (minor), 88% ee; $[\alpha]^{25}_D$ 299.3 (c = 0.97, $CHCl_3$).



(*S*,*Z*)-Methyl 4-(1,2-dimethyl-5-nitro-1*H*-indol-3-yl)pent-2-enoate (3.105): Derived from 5-nitro-1,2-dimethyl-1H-indole (171 mg, 0.90 mmol, 6.0 equiv) and *trans*-methyl vinyldiazoacetate **3.73** (21 mg, 0.15 mmol, 1.0 equiv) at -20 °C, and purified by flash chromatography on silica gel (7/3 pentane/Et_2O, R_f: 0.22) to provide product **3.105** as a yellowish powder (21.6 mg, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 8.60 (d, J = 2.1 Hz, 1H), 8.04 (dd, J = 9.2, 2.2 Hz, 1H), 7.24 (d, J = 2.2 Hz, 1H), 6.70 (dd, J = 11.3, 10.7 Hz, 1H), 5.73 (dd, J = 11.3, 0.9 Hz, 1H), 5.14-5.21 (m, 1H), 3.71 (s, 3H), 3.68 (s, 3H), 2.46 (s, 3H), 1.53 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.6, 152.8, 140.8, 139.8, 136.6, 125.1, 117.3, 116.4, 116.3, 116.2, 108.5, 51.2, 30.2, 30.0, 21.1, 10.8; IR (neat): 2950, 1716, 1512, 1485, 1329, 1195, 1176, 825, 740 cm^{-1}; HRMS (APCI) calc. for $C_{16}H_{19}O_4N_2$ $(M+H)^+$ 303.1339 found 303.1339; M.p.: 134-136 °C; HPLC: (AD-H, 10% isopropanol in hexane, 1.0 mL/min) retention times of 14.9 (major) and 15.7 (minor), 87% ee; $[\alpha]^{25}_D$ 287.6 (c = 1.56, $CHCl_3$).



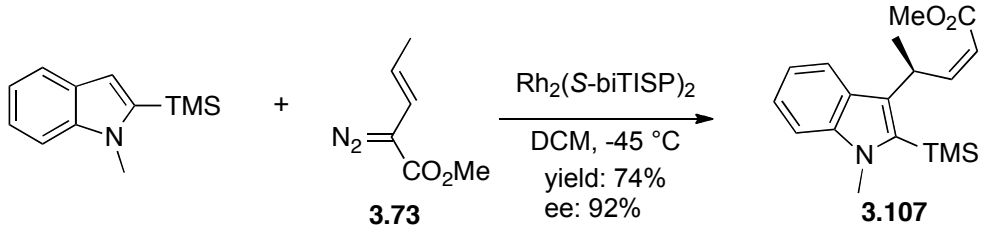
(*S*,*Z*)-Methyl 4-(2-ethyl-1-phenyl-1*H*-indol-3-yl)pent-2-enoate (3.106): Derived from 1-phenyl-2-ethyl-1H-indole (199 mg, 0.90 mmol, 6.0 equiv) and *trans*-methyl vinyldiazoacetate **3.73** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography on silica gel (10/1 pentane/Et_2O, R_f: 0.50) to provide product **3.106** as colorless oil (43.1 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 7.72-7.76 (m, 1H), 7.48-7.54 (m, 2H), 7.41-7.47 (m, 1H), 7.31-7.37 (m, 1H), 7.03-7.13 (m, 2H), 6.99-7.02 (m, 1H), 6.88 (t, *J* = 10.5 Hz, 1H), 5.72 (dd, *J* = 11.3, 0.8 Hz, 1H), 5.19-5.27 (m, 1H), 3.73 (s, 3H), 2.63-2.83 (m, 2H), 1.62 (d, *J* = 7.0 Hz, 3H), 0.94 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.8, 154.0, 139.5, 138.2, 138.0, 129.4, 128.6, 127.9, 126.0, 120.9, 119.3, 119.2, 116.4, 113.9, 110.4, 51.1, 30.6, 21.1, 18.0, 14.9; IR (neat): 2968, 1719, 1597, 1499, 1458, 1370, 1177, 824, 742, 700 cm^{-1}; HRMS (APCI) calc. for $C_{22}H_{24}O_2N$ $(M+H)^+$ 334.1802 found 334.1801; HPLC: (AD-H, hexane, 1.0 mL/min) retention times of 9.0 (major) and 9.7 (minor), 93% ee; $[\alpha]^{25}_D$ 276.2 (*c* = 1.36, $CHCl_3$).



(*S*,*Z*)-Methyl 4-(2-(((*tert*-butyldimethylsilyl)oxy)methyl)-1-methyl-1*H*-indol-3-yl)pent-2-enoate (3.92): Derived from 2-((*tert*-butyldimethylsilyloxy)methyl)-1-methyl-

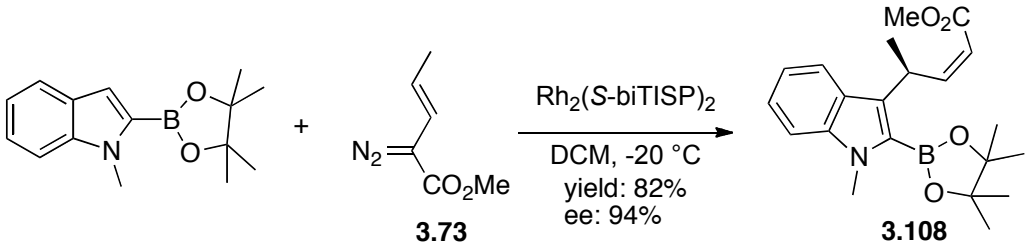
1H-indole (248 mg, 0.90 mmol, 6.0 equiv) and *trans*-methyl vinyldiazoacetate **(3.73)** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography in silica gel (30/1 pentane/Et_2O, R_f: 0.35) to provide product **3.92** as colorless powder (37.2 mg, 64% yield).

Spectroscopic data on the purified products was consistent with reported value.[5] HPLC: (OD, 0.5% isopropanol in hexane, 0.7 mL/min) retention times of 13.9 (minor) and 16.2 (major), 91% ee; $[\alpha]^{25}_D$ 237.3 (*c* = 0.76, $CHCl_3$).



(*S*,*Z*)-Methyl 4-(1-methyl-2-(trimethylsilyl)-1*H*-indol-3-yl)pent-2-enoate (3.107): Derived from 1-methyl-2-(trimethylsilyl)-1*H*-indole (199 mg, 0.90 mmol, 6.0 equiv) and *trans*-methyl vinyldiazoacetate **3.73** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography on silica gel (20/1 pentane/Et_2O, R_f: 0.46) to provide product **3.107** as colorless oil (34.8 mg, 74% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.9 Hz, 1H), 7.00 (dd, *J* = 11.4, 9.8 Hz, 1H), 5.74 (dd, *J* = 11.4, 0.8 Hz, 1H), 5.15-5.24 (m, 1H), 3.82 (s, 3H), 3.76 (s, 3H), 1.61 (d, *J* = 7.0 Hz, 3H), 0.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 154.4, 140.5, 136.1, 127.6, 125.7, 122.0, 120.4, 118.4, 117.1, 109.6, 51.1, 33.3, 32.1, 22.1, 1.6; IR (neat): 2950, 1719, 1405, 1250, 1193, 1174, 839, 738 cm^{-1}; HRMS (APCI) calc. for $C_{18}H_{26}O_2NSi$ $(M+H)^+$ 316.1727 found 316.1728; HPLC: (OD-H,

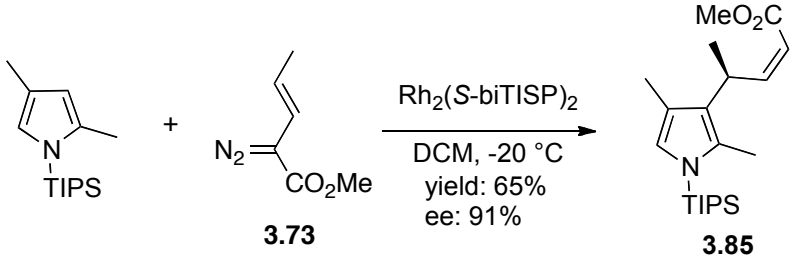
Hexane, 1.0 mL/min) retention times of 4.9 (major) and 6.1 (minor), 92% ee; $[\alpha]^{25}_{D}$ 189.9 (c = 0.91, $CHCl_3$).



(*S*,*Z*)-Methyl 4-(1-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-3-yl)pent-2-enoate (3.108): Derived from 1-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (231 mg, 0.90 mmol, 6.0 equiv) and *trans*-methyl vinyldiazoacetate **3.73** (21 mg, 0.15 mmol, 1.0 equiv) at -20 °C, and purified by flash chromatography on silica gel (10/1 pentane/Et_2O, R_f: 0.39) to provide product **3.108** as colorless oil (45.6 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 8.2 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.26 (t, J = 7.4 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 6.93 (dd, J = 11.4, 10.2 Hz, 1H), 5.69 (d, J = 11.4 Hz, 1H), 5.51-5.61 (m, 1H), 3.93 (s, 3H), 3.75 (s, 3H), 1.61 (d, J = 7.4 Hz, 3H), 1.39 (s, 6H), 1.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 154.7, 140.1, 131.1, 126.1, 123.1, 120.9, 118.6, 116.6, 109.9, 83.5, 50.9, 32.2, 31.2, 24.82, 24.78, 21.8; IR (neat): 2976, 1723, 1525, 1391, 1299, 1260, 1172, 1138, 847, 823, 742 cm^{-1}; HRMS (APCI) calc. for $C_{21}H_{29}O_4NB$ $(M+H)^+$ 370.2184 found 370.2185; HPLC: (AD-H, 3% isopropanol in Hexane, 1.0 mL/min) retention times of 9.3 (major) and 12.4 (minor), 94% ee; $[\alpha]^{25}_{D}$ 172.0 (c = 1.60, $CHCl_3$).

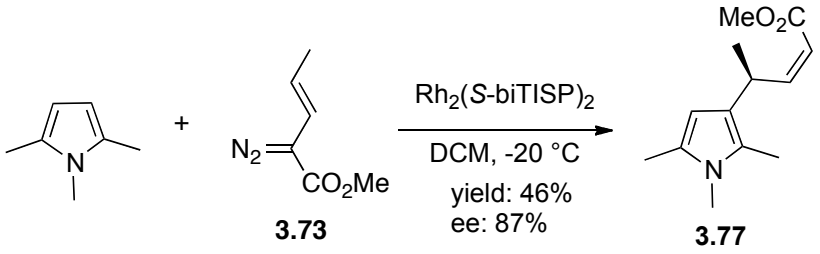
General procedure for the reaction between pyrroles and methyl vinyldiazoacetate

To a flame-dried 25 mL flask containing Rh_2(*S*-biTISP)$_2$ (5.5 mg, 0.02 equiv) and indoles (0.90 mmol, 6.0 equiv) in 6 mL dried CH_2Cl_2 under argon atmosphere was added a solution of fresh purified *trans*-methyl vinyldiazoacetate **3.73** (21.0 mg, 0.15 mmol, 1.0 equiv) in 6 mL dried CH_2Cl_2 by syringe pump over 3 h at -20 °C. The solution was warmed up to room temperature over night. The mixture was concentrated under reduced pressure and purified by flash chromatography on silica gel (pentane/Et_2O with 0.5% Et_3N) to provide the corresponding products as colorless oil or powder.



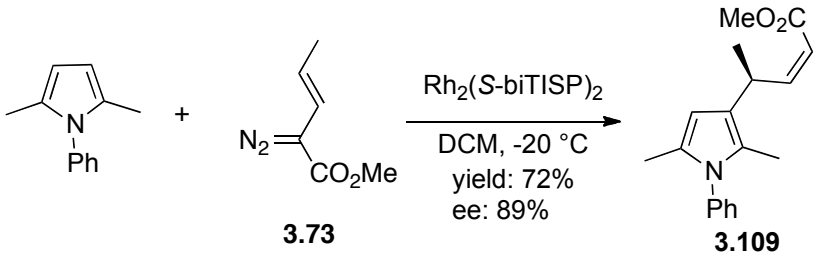
(*S*,*Z*)-Methyl 4-(2,4-dimethyl-1-(triisopropylsilyl)-1*H*-pyrrol-3-yl)pent-2-enoate (3.85): Derived from 1-triisopropylsilyl-2,4-dimethylpyrrole (226 mg, 0.90 mmol, 6.0 equiv) and *trans*-methyl vinyldiazoacetate **3.73** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography on silica gel (40/1 pentane/Et_2O, R_f: 0.38) to provide product **3.85** as colorless oil (35.6 mg, 65% yield).

Spectroscopic data on the purified products was consistent with reported value.[5] HPLC: (OD, 0.2% isopropanol in hexane, 0.7 mL/min) retention times of 16.9 (minor) and 25.3 (major), 91% ee; $[\alpha]^{25}_D$ 194.6 (*c* = 1.63, $CHCl_3$).



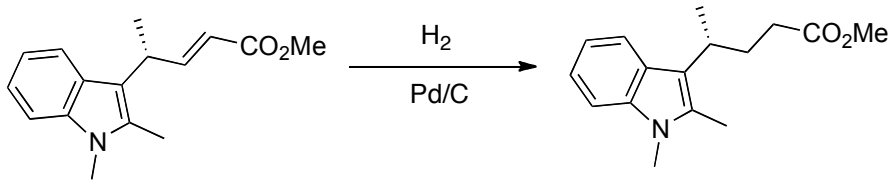
(*S*,*Z*)-Methyl 4-(1,2,5-trimethyl-1*H*-pyrrol-3-yl)pent-2-enoate (3.77): Derived from 1,2,5-trimethylpyrrole (98.2 mg, 0.90 mmol, 6.0 equiv) and *trans*-methyl vinyldiazoacetate **3.73** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography in silica gel (9/1 pentane/Et_2O, containing 0.5% Et_3N, R_f: 0.45) to provide **3.77** as colorless oil (15.3 mg, 46% yield).

Spectroscopic data on the purified products was consistent with reported value.[5] HPLC: (OD-H, 2% isopropanol in hexane, 0.7 mL/min) retention times of 9.8 (minor) and 16.4 (major), 87% ee; $[\alpha]^{25}_D$ 286.1 (*c* = 0.61, $CHCl_3$).



(*S*,*Z*)-Methyl 4-(2,5-dimethyl-1-phenyl-1*H*-pyrrol-3-yl)pent-2-enoate (3.109): Derived from 2,5-dimethyl-1-phenyl-1*H*-pyrrole (154 mg, 0.90 mmol, 6.0 equiv) and *trans*-methyl vinyldiazoacetate **3.73** (21 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography in silica gel (10/1 pentane/Et_2O, containing 0.5% Et_3N, R_f: 0.55) to provide **3.109** as colorless oil (30.8 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.47 (m, 2H), 7.36-7.41 (m, 1H), 7.19-7.23 (m, 2H), 6.30 (t, *J* = 11.0 Hz, 1H), 5.92 (s,

1H), 5.67 (dd, *J* = 11.0, 0.8 Hz, 1H), 4.82-4.91 (m, 1H), 3.73 (s, 3H), 2.04 (s, 3H), 1.97 (s, 3H), 1.37 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 167.0, 155.4, 138.9, 128.9, 128.3, 127.9, 127.5, 125.1, 121.5, 115.1, 103.5, 51.0, 29.8, 21.1, 12.9, 10.7; IR (neat): 2921, 1718, 1499, 1404, 1193, 1174, 1008, 826, 766, 699 cm^{-1}; HRMS (APCI) calc. for $C_{18}H_{22}O_2N$ $(M+H)^+$ 284.1645 found 284.1648; HPLC: (OJ, 1% isopropanol in hexane, 0.7 mL/min) retention times of 16.8 (major) and 18.8 (major), 87% ee; $[\alpha]^{25}_D$ 287.2 (*c* = 1.71, $CHCl_3$).



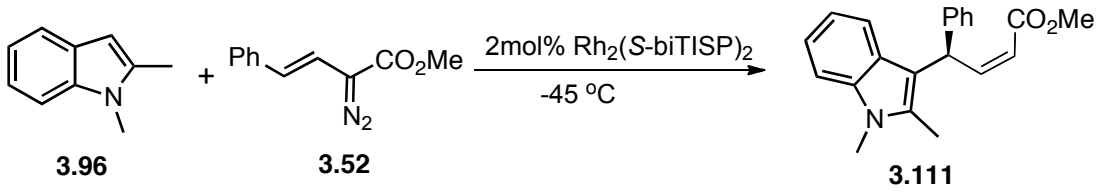
3.100 *ent*-**3.110**

(*R*)-Methyl 4-(1,2-dimethyl-1*H*-indol-3-yl)pentanoate (*ent*-3.110): A solution of product **3.100** (51.4 g, 0.2 mmol, 1.0 equiv) in EtOH (30 mL) containing Pd/C (46 mg of 5% palladium on activated carbon, 0.02 mmol, 0.1 equiv) was shaken under H_2 atmosphere (30 psi) over-night. The mixture was filtrated through a celit pad to remove the catalyst and washed with EtOH (2 × 10 mL). The filtrated solution was concentrated to afford the product *ent*-**3.110** (43.6 g, 84% yield) as colorless viscous oil without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.24 (s, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.03 (m, 1H), 3.64 (s, 3H), 3.57 (s, 3H), 2.97-3.06 (m, 1H), 2.33 (s, 3H), 2.06-2.21 (m, 4H), 1.44 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.4, 136.9, 132.5, 126.1, 120.2, 119.3, 118.3, 114.0, 108.7, 51.3, 32.8, 31.9, 31.1, 29.4, 21.5, 10.4; IR (neat): 2924, 1732, 1470, 1434, 1372, 1335, 1250, 1164, 736 cm^{-1}; HRMS

(APCI) calc. for $C_{16}H_{22}O_2N$ $(M+H)^+$ 260.1645 found 260.1642; $[\alpha]^{25}_D$ -19.6 (*c* = 1.39, $CHCl_3$); HPLC: (OD-H, 3% isopropanol in hexane, 0.7 mL/min) retention times of 11.6 (major) and 14.1 (major), 92% ee; When derived from **3.87**, HPLC: (OD-H, 3% isopropanol in hexane, 0.7 mL/min) retention times of 11.7 (minor) and 14.1 (major), 35% ee.

General procedure for the reaction between 1,2-dimethylindole and *trans*-aryl vinyldiazoacetate

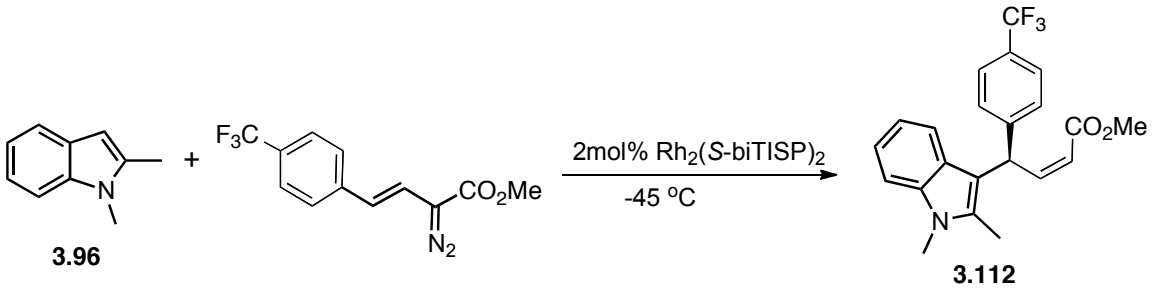
To a flame-dried 25 mL flask containing Rh_2(*S*-biTISP)$_2$ (5.5 mg, 0.02 equiv) and 1,2-dimethylindoles (0.90 mmol, 6.0 equiv) in 6 mL dried toluene under argon atmosphere was added a solution of fresh purified *trans*-methyl vinyldiazoacetate **3.73** (21.0 mg, 0.15 mmol, 1.0 equiv) in 6 mL dried toluene by syringe pump over 3 h at -20 °C. The solution was warmed up to room temperature over night. The mixture was concentrated under reduced pressure and purified by flash chromatography on silica gel (pentane/Et_2O) to provide the corresponding products as colorless oil or powder.



3.96 **3.52** **3.111**

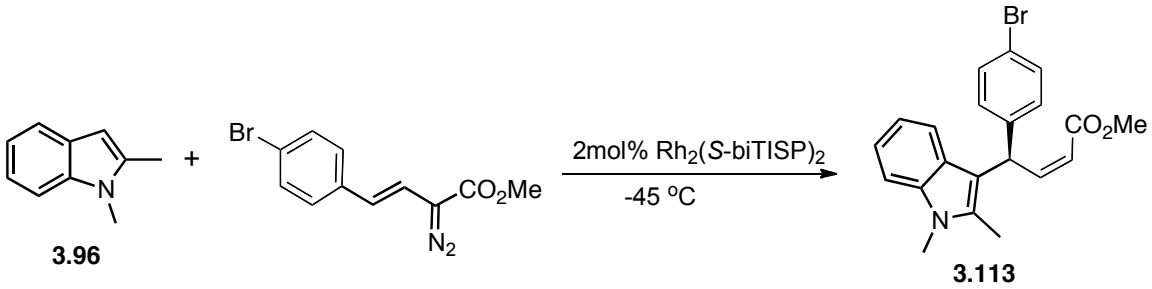
(*R*,*Z*)-Methyl 4-(1,2-dimethyl-1*H*-indol-3-yl)-4-phenylbut-2-enoate (3.111): Derived from 1,2-dimethylindole (**3.96**) (65.4 mg, 0.45 mmol, 3.0 equiv) and *trans*-phenyl vinyldiazoacetate **3.52** (30.4 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography on silica gel (85/15 pentane/Et_2O, R_f: 0.42) to provide **3.111** as colorless powder (25.2 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.31 (m, 7H), 7.12-

7.17 (m, 1H), 6.95-6.98 (m, 1H), 6.92 (t, *J* = 11.3 Hz, 1H), 6.61 (d, *J* = 11.0 Hz, 1H), 5.93 (dd, *J* = 0.8, 11.3 Hz, 1H), 3.76 (s, 3H), 3.70 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (75MHz, d6-benzene): 167.1, 150.2, 142.5, 137.2, 134.9, 128.5, 127.9, 126.5, 126.3, 120.7, 119.7, 119.0, 118.1, 111.0, 109.0, 51.4, 39.9, 29.8, 10.9; IR (neat): 2947, 1716, 1471, 1435, 1229, 1192, 1171, 862, 820, 738, 670 cm^{-1}; HRMS (EI) calc. for $C_{21}H_{22}O_2N$ $(M+H)^+$ 320.1645 found 320.1645; M. p. 100-101 °C; HPLC: (OJ-H, 10 % isopropanol in hexane, 0.7 mL/min) retention times of 24.9 (major) and 31.4 (minor), 79% ee; $[\alpha]^{25}_D$ 162.7 (*c* = 0.52, $CHCl_3$).

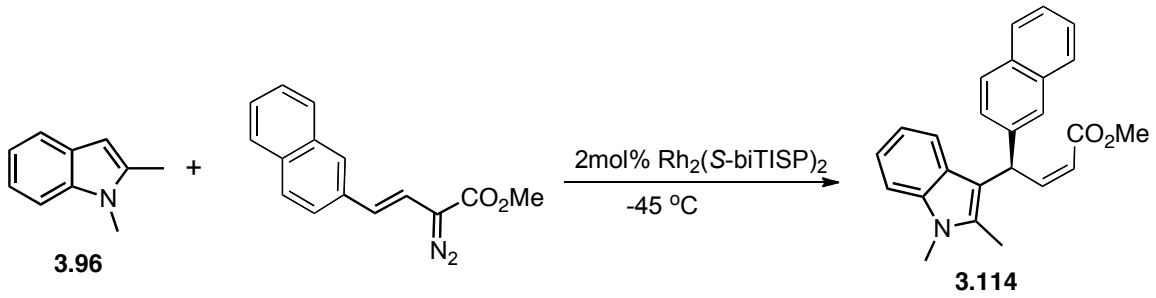


(*R*,*Z*)-Methyl 4-(1,2-dimethyl-1*H*-indol-3-yl)-4-(4-(trifluoromethyl)phenyl)but-2-enoate (3.112): Derived from 1,2-dimethylindole (65.4 mg, 0.45 mmol, 3.0 equiv) and *trans*-trifluorophenyl vinyldiazoacetate (40.5 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography on silica gel (85/15 pentane/Et_2O, R_f: 0.38) to provide **3.112** as colorless oil (29.6 mg, 51% yield). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.29-7.31 (m, 7H), 7.13-7.17 (m, 2H), 6.95-6.99 (m, 1H), 6.86 (t, *J* = 10.6 Hz, 1H), 6.64 (d, *J* = 10.6 Hz, 1H), 5.96 (dd, *J* = 0.8, 11.3 Hz, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$): 167.0, 149.0, 146.7, 137.2, 135.1, 128.1, 126.1, 125.4 (d, *J* = 3.4 Hz), 121.0, 119.4, 119.3, 118.8, 110.3, 109.2, 51.5, 39.8, 29.9, 10.9; IR (neat): 1717, 1615, 1323, 1194, 1162, 1111, 1067, 737

cm^{-1}; HRMS (APCI) calc. for $C_{22}H_{21}O_2NF_3$ $(M+H)^+$ 388.1519 found 388.1523; HPLC: (OD-H, 5 % isopropanol in hexane, 0.7 mL/min) retention times of 14.3 (major) and 15.3 (minor), 77% ee; $[\alpha]^{25}_D$ 156.6 (*c* = 0.26, $CHCl_3$).



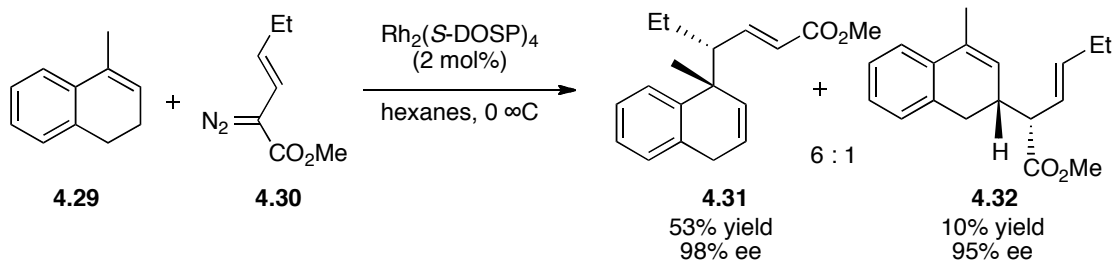
(*R*,*Z*)-Methyl 4-(4-bromophenyl)-4-(1,2-dimethyl-1*H*-indol-3-yl)but-2-enoate (3.113): Derived from 1,2-dimethylindole (65.4 mg, 0.45 mmol, 3.0 equiv) and (*E*)-methyl 4-(4-bromophenyl)-2-diazobut-3-enoate (42.2 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography on silica gel (85/15 pentane/Et_2O, R_f: 0.35) to provide **3.113** as colorless viscous oil (32.6 mg, 55% yield). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.37-7.41 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.11-7.19 (m, 4H), 6.98 (dt, *J* = 0.8, 7.4 Hz, 1H), 6.85 (t, *J* = 10.5 Hz, 1H), 6.54 (d, *J* = 10.5 Hz, 1H), 5.94 (d, *J* = 11.0 Hz, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$): δ 167.0, 149.4, 141.6, 137.2, 135.0, 131.5, 129.6, 126.2, 120.9, 120.2, 119.5, 119.2, 118.5, 110.5, 109.1, 51.5, 39.4, 29.8, 10.9; IR (neat): 1716, 1640, 1484, 1193, 1171, 1009, 906, 864, 730 cm^{-1}; HRMS (APCI) calc. for $C_{21}H_{21}O_2NBr$ $(M+H)^+$ 398.0750 found 398.0751; HPLC: (OD-H, 5 % isopropanol in hexane, 0.7 mL/min) retention times of 13.4 (major) and 14.6 (minor), 79% ee; $[\alpha]^{25}_D$ 111.9 (*c* = 0.65, $CHCl_3$).



3.96 3.114

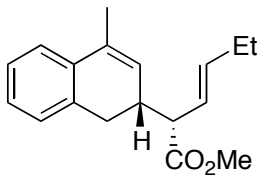
(*R*,*Z*)-Methyl 4-(1,2-dimethyl-1*H*-indol-3-yl)-4-(naphthalen-2-yl)but-2-enoate (3.114): Derived from 1,2-dimethylindole (**3.96**) (65.4 mg, 0.45 mmol, 3.0 equiv) and (*E*)-methyl 2-diazo-4-(naphthalen-2-yl)but-3-enoate (37.9 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography on silica gel (85/15 pentane/Et_2O, R_f: 0.35) to provide **3.114** as colorless powder (22.1 mg, 46% yield). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.75-7.82 (m, 2H), 7.71-7.74 (m, 2H), 7.41-7.47 (m, 2H), 7.37 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.11-7.16 (m, 1H), 6.99 (t, *J* = 10.6 Hz, 1H), 6.92 (td, *J* = 7.1, 0.8 Hz, 1H), 6.01 (dd, *J* = 11.3, 0.8 Hz, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 167.1, 150.0, 140.3, 137.2, 135.0, 133.6, 132.3, 128.1, 128.0, 127.7, 126.9, 126.6, 126.0, 125.6, 120.8, 119.6, 119.1, 118.3, 11.0, 109.0, 51.5, 40.0, 29.9, 11.0; IR (neat): 1715, 1470, 1191, 1173, 856, 735 cm^{-1}; HRMS (APCI) calc. for $C_{25}H_{24}O_2N$ $(M+H)^+$ 370.1802 found 370.1802; M.p. 126-128 °C; HPLC: (OJ-H, 20% isopropanol in hexane, 0.7 mL/min) retention times of 24.0 (major) and 43.9 (minor), 70% ee; $[\alpha]^{25}_D$ 90.6 (*c* = 0.65, $CHCl_3$).

Experiment for Chapter IV: Stereocontrol of the Combined C-H functionalization/Cope rearrangement



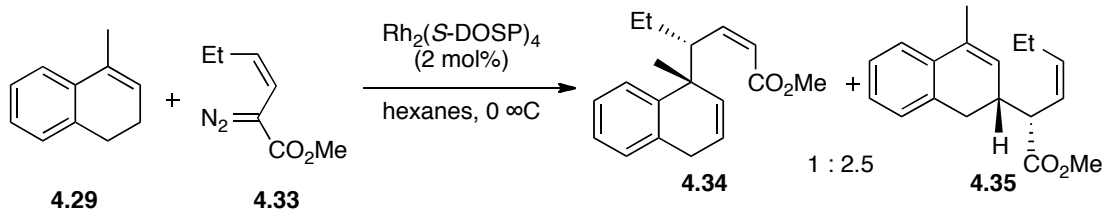
(*R*,*E*)-Methyl 4-((*S*)-1-methyl-1,4-dihydronaphthalen-1-yl)hex-2-enoate (4.31): To a flame dried flask containing anhydrous hexane (25 mL), Rh_2(*S*-DOSP)$_4$ (110.9 mg, 0.060 mmol) and 4-methyl-1,2-dihydronaphthalene (**4.29**) (1.30 g, 9.0 mmol) was added a solution of (*E*)-methyl 2-diazohex-3-enoate (**4.30**) (463 mg, 3.0 mmol) in 25 mL anhydrous hexane via syringe pump over 3h at 0 °C. The mixture was stirred for additional 0.5 h and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (25:1 pentane/Et_2O, R_f = 0.33 for the C-H/Cope product, R_f = 0.41 for the insertion product) to afford the C-H insertion product **4.32** as colorless oil (83.2 mg, 10% yield) and the C-H/Cope product **4.31** as colorless oil (427 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.1 Hz, 1H), 7.15 (t, *J* = 7.1 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.84 (dd, *J* = 15.7, 10.5 Hz, 1H), 5.99 (tt, *J* = 10.0, 3.8 Hz, 1H), 5.92 (d, *J* = 15.7 Hz, 1H), 5.60 (dm, *J* = 10.5 Hz, 1H), 3.77 (s, 3H), 3.32-3.42 (m, 2H), 2.31 (td, *J* = 10.5, 2.9 Hz, 1H), 1.32 (s, 3H), 1.05-1.22 (m, 2H), 0.60 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 150.0, 141.6, 134.5, 131.0, 128.1, 126.4, 125.8, 125.7, 124.6, 123.4, 58.1, 51.4, 42.0, 30.1, 29.5, 22.3, 12.5; IR (neat): 2962, 1720, 1652, 1435, 1264, 1234,1171, 1136, 993, 751 cm^{-1}; HRMS (EI)

calc. for $C_{18}H_{23}O_2$ $(M+H)^+$ 271.2693 found 271.1692; HPLC (OD-H, 0.5% isopropanol in hexane, 0.7 mL/min) retention times of 12.3 min (minor) and 16.7 min (major), 98.2% ee; $[a]^{25}_D$ 27.0 (c = 1.16, $CHCl_3$).



4.32

(*S*,*E*)-Methyl 2-((*R*)-4-methyl-1,2-dihydronaphthalen-2-yl)hex-3-enoate (4.32): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.24 (m, 2H), 7.15 (td, J = 7.1, 1.9 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 5.68 (d, J = 2.9 Hz, 1H), 5.55 (td, J = 15.2, 6.2 Hz, 1H), 5.37 (ddt, J = 15.2, 9.5, 1.4 Hz, 1H), 3.67 (s, 3H), 2.87-2.93 (m, 1H), 2.79-2.86 (m, 1H), 2.64-2.73 (m, 2H), 2.04-2.08 (m, 5H), 0.99 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.3, 136.8, 135.3, 134.5, 133.2, 127.8, 127.0, 126.7, 126.4, 125.0, 122.9, 52.7, 51.7, 35.8, 31.5, 25.5, 19.4, 13.5; IR (neat): 2962, 1732, 1450, 1433, 1248, 1154, 758 cm^{-1}; HRMS (EI) calc. for $C_{18}H_{23}O_2$ $(M+H)^+$ 271.2693 found 271.1693; HPLC (AD-H, 0.5% isopropanol in hexane, 0.7 mL/min) retention times of 11.2 min (minor) and 12.5 min (major), 95% ee; $[a]^{25}_D$ 118.0 (c = 0.69, $CHCl_3$).

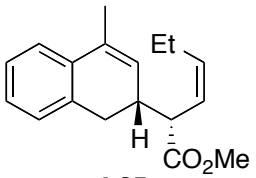


4.29 **4.33** **4.34** **4.35**

To a flame dried flask containing anhydrous hexane (25 mL), Rh_2(*S*-DOSP)$_4$ (110.9 mg, 0.060 mmol) and 4-methyl-1,2-dihydronaphthalene (**4.29**) (1.30 g, 9.0 mmol) was added

a solution of (*Z*)-methyl 2-diazohex-3-enoate (**4.33**) (463 mg, 3.0 mmol) in 25 mL anhydrous hexane via syringe pump over 3h at 0 °C. The mixture was stirred for additional 0.5 h and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (30:1 pentane/Et_2O, R_f = 0.57 for the C-H/Cope product, R_f = 0.43 for the insertion product) to afford the C-H insertion product **4.35** as colorless oil (356 mg, 44% yield) and the C-H/Cope product **4.34** as colorless powder (113 mg, 14% yield).

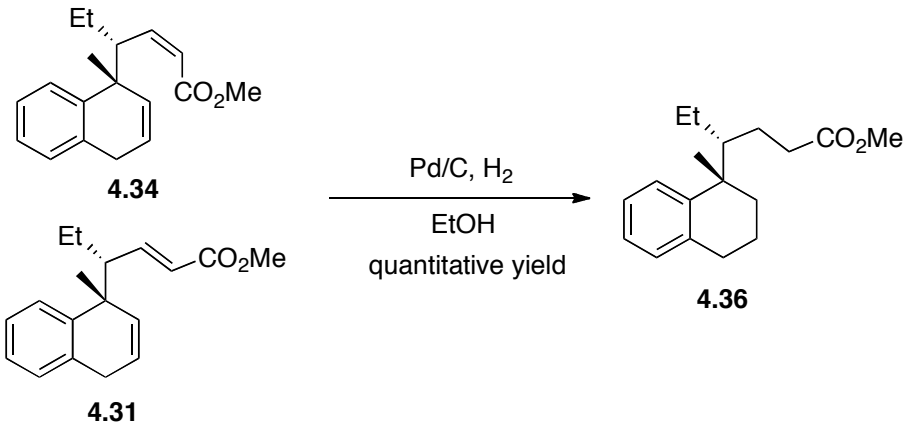
(*R*,*Z*)-Methyl 4-((*S*)-1-methyl-1,4-dihydronaphthalen-1-yl)hex-2-enoate (4.34): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.9 Hz, 1H), 7.24 (td, *J* = 7.4, 1.0 Hz, 1H), 7.15 (td, *J* = 7.4, 1.0 Hz, 1H), 7.10 (d, *J* = 7.3 Hz, 1H), 6.01-6.11 (m, 2H), 5.97 (tt, *J* = 10.2, 3.5 Hz, 1H), 5.60 (tt, *J* = 10.2, 2.2 Hz, 1H), 3.91 (td, *J* = 10.5, 3.2 Hz, 1H), 3.76 (s, 3H), 3.31-3.45 (m, 2H), 1.35 (s, 3H), 1.01-1.18 (m, 2H), 0.61 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 151.6, 142.0, 134.3, 131.0, 127.9, 126.5, 126.4, 125.7, 124.3, 121.9, 51.4, 51.1, 42.4, 30.1, 28.8, 23.3, 12.2; IR (neat): 2957, 1716, 1642, 1435, 1228, 1191, 1170, 999, 908, 759 cm^{-1}; M.p.: 72-78 °C; HRMS (APCI) calc. for $C_{18}H_{23}O_2$ $(M+H)^+$ 271.2693 found 271.1692; HPLC (OD-H, 1% isopropanol in hexane, 0.7 mL/min) retention times of 7.7 min (minor) and 21.3 min (major), 91% ee; $[a]^{25}_D$ 45.0 (*c* = 1.04, $CHCl_3$).



4.35

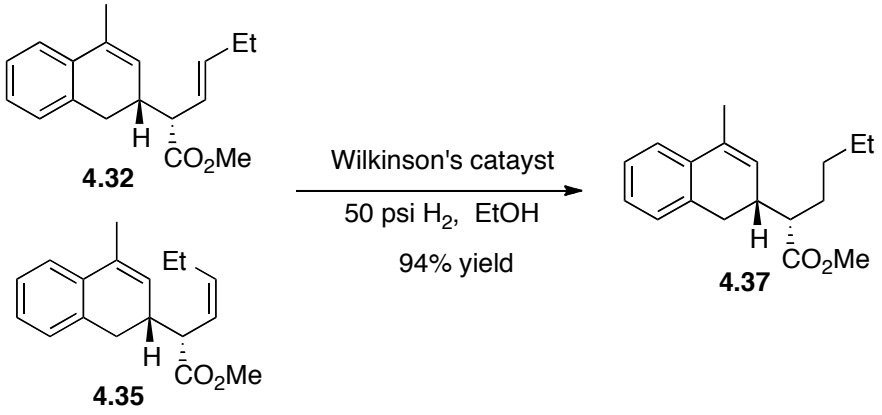
(*S*,*Z*)-Methyl 2-((*R*)-4-methyl-1,2-dihydronaphthalen-2-yl)hex-3-enoate (4.35): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.26 (m, 2H), 7.15 (td, *J* = 7.3, 1.9 Hz, 1H), 7.08 (d, *J* =

7.3 Hz, 1H), 5.72 (d, *J* = 3.2 Hz, 1H), 5.63 (dt, *J* = 10.5, 7.3 Hz, 1H), 5.31 (tt, *J* = 10.5, 1.3 Hz, 1H), 3.67 (s, 3H), 3.26 (t, *J* = 9.8 Hz, 1H), 2.85 (dd, *J* = 14.3, 5.7 Hz, 1H), 2.65-2.74 (m, 1H), 2.65 (t, *J* = 7.3 Hz, 1H), 2.06 (t, *J* = 1.3 Hz, 3H), 1.90-2.00 (m, 2H), 0.92 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0, 136.1, 135.3, 134.5, 133.3, 127.9, 127.0, 126.54, 126.49, 125.3, 122.9, 51.7, 47.4, 35.9, 31.4, 20.9, 19.4, 14.1; IR (neat): 2964, 1733, 1450, 1433, 1334, 1154, 758, 714 cm^{-1}; HRMS (EI) calc. for $C_{18}H_{23}O_2$ $(M+H)^+$ 271.2693 found 271.1693; HPLC (OD-H, 0.5% isopropanol in hexane, 0.7 mL/min) retention times of 9.7 min (minor) and 11.9 min (major), 84% ee; $[a]^{25}_D$ 166.7 (*c* = 0.78, $CHCl_3$).



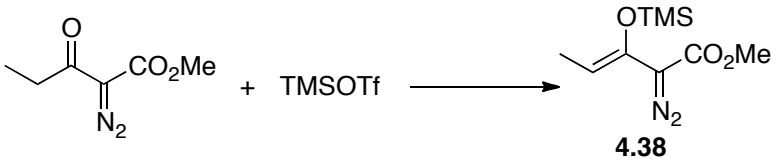
(*R*)-Methyl 4-((*S*)-1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)hexanoate (4.36): To a flame-dried flask containing the C-H/Cope product (either **4.31** or **4.34**) (54 mg, 0.2 mmol, 1.0 equiv) and Pd/C (42.6 mg, 0.020 mmol, 0.10 equiv) in 20 mL dried ethanol was placed and stirred under H_2 atmosphere over-night. The solution was concentrated under reduced pressure. The residue was passed through a short pipet silica gel column (35/1 pentane/ Et_2O, R_f: 0.38) to provide 54.6 mg colorless oil in quantitative yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 8.1 Hz, 1H), 7.12 (td, *J* = 7.5, 1.1Hz, 1H), 7.02-

7.07 (m, 2H), 3.70 (s, 3H), 2.64-2.73 (m, 2H), 2.46 (ddd, *J* = 15.2, 10.8, 6.0 Hz, 1H), 2.35 (ddd, *J* = 15.2, 10.8, 6.0 Hz, 1H), 2.00-2.06 (m, 1H), 1.79-1.85 (m, 1H), 1.48-1.73 (m, 5H), 1.28 (s, 3H), 1.01-1.15 (m, 2H), 0.72 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.4, 145.0, 137.5, 128.9, 126.7, 125.7, 125.0, 51.5, 49.7, 41.4, 34.6, 31.5, 29.9, 29.5, 26.2, 25.1, 19.7, 14.5; IR (neat): 2933, 2872, 1737, 1435, 1254, 1162, 759,733 cm^{-1}; HRMS (EI) calc. for $C_{18}H_{27}O_2$ $(M+H)^+$ 275.2005 found 275.2006; $[a]^{25}_D$ -18.2 (*c* = 1.37, $CHCl_3$) from compound **4.31** and $[a]^{25}_D$ -17.3 (*c* = 1.38, $CHCl_3$) from **4.34**.



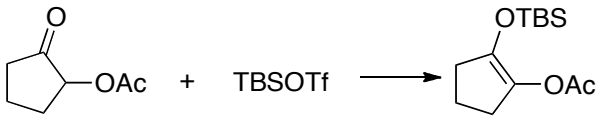
(*S*)-Methyl 2-((*R*)-4-methyl-1,2-dihydronaphthalen-2-yl)hexanoate (4.37): A solution of the direct C-H insertion product (either **4.32** or **4.35**) (0.108 g, 0.4 mmol, 1.0 equiv) in EtOH (15 mL) containing Wikinson's catalyst (37 mg, 0.04 mmol, 0.1 equiv) was shaken under H_2 atmosphere (50 psi) over-night. The mixture was concentrated and passed through a short pipet silica gel column (25/1 pentane/ Et_2O, R_f: 0.41) to afford the product **4.37** (0.103 g, 94% yield) as colorless viscous oil without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11-7.25 (m, 4H), 5.67 (br, 1H), 3.64 (s, 3H), 2.77-2.89 (m, 1H), 2.62-2.75 (m, 2H), 2.38-2.43 (m, 1H), 2.05 (s, 3H), 1.53-1.71 (m, 2H), 1.18-1.39 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.7, 135.3, 135.0,

132.9, 127.6, 127.2, 126.9, 126.5, 122.9, 51.3, 49.0, 36.4, 32.1, 29.7, 29.3, 22.7, 19.4, 13.9; IR (neat): 2951, 1732, 1434, 1190, 1158, 758, 717 cm^{-1}; HRMS (EI) calc. for $C_{18}H_{25}O_2$ $(M+H)^+$ 273.1849 found 273.1845. $[a]^{25}_D$ 129.6 (*c* = 2.01, $CHCl_3$) from compound **4.32** and $[a]^{25}_D$ 114.3 (*c* = 2.01, $CHCl_3$) from **4.35**.



4.38

(*Z*)-Methyl 2-diazo-3-((trimethylsilyl)oxy)pent-3-enoate (4.38): Triethylamine (2.0 mL, 14.3 mmol, 1.4 equiv) was added to a stirring solution of methyl 2-diazo-3-oxopentanoate (1.58 g, 10.1 mmol, 1.0 equiv) in dichloromethane (26 mL) at 0 °C under an inert argon atmosphere. Trimethylsilyl trifluoromethanesulfonate (2.3 mL, 12.2 mmol, 1.2 equiv) was added over 5 min and the mixture was further stirred for 30 min at 0 °C. The reaction mixture was diluted with pentane (100 mL), and the organic phase was subsequently washed with dilute aqueous sodium bicarbonate (100 mL) and brine (100 mL). The organic layer was dried ($MgSO_4$), and the solvent was removed under reduced pressure to yield the title product **4.38** as reddish oil (essentially quantitative yield), which was used without further purification. ^{1}H NMR (400 MHz, C_6D_6): δ 5.71 (q, *J* = 7.0 Hz, 1H), 3.29 (s, 3H), 1.63 (d, *J* = 6.7 Hz, 3H), 0.10 (s, 9H); ^{13}C NMR (150 MHz, C_6D_6): δ 165.0, 133.5, 106.7, 51.7, 12.4, 0.4; IR (neat): 2084, 1709, 1436, 1341, 1253, 1098, 1059, 842, 754 cm^{-1}.

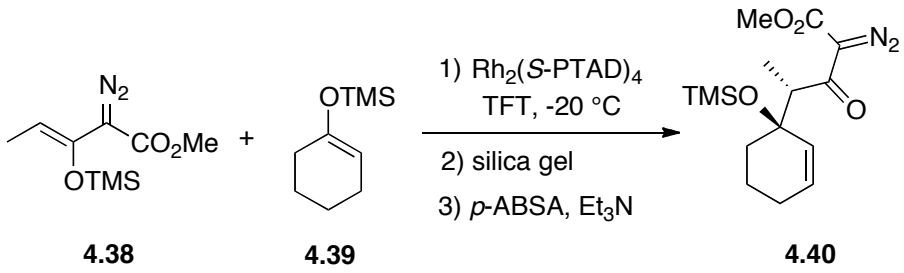


2-((*tert*-Butyldimethylsilyl)oxy)cyclopent-1-en-1-yl acetate: To an oven-dried flask containing 2-oxocyclopentyl acetate (2.13 g, 15.0 mmol, 1.0 equiv) and Et_3N (4.2 mL, 30 mmol, 2.0 equiv) in 20 mL DCM was added slowly with TBSOTf (4.5 mL, 19.5 mmol, 1.3 equiv) at 0 °C. The mixture was stirred for 2 h and was quenched by saturated $NaHCO_3$ solution and extracted by pentane (2 x 50 mL). The organic layers were combined, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography (20/1 pentane/ether, R_f: 0.41) on silica gel to provide product as colorless oil (1.98 g, 52% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 2.46-2.51 (m, 2H), 2.08-2.14 (m, 2H), 1.75 (s, 3H), 1.56-1.64 (m, 2H), 0.98 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6): δ 168.1, 138.8, 128.8, 30.9, 28.3, 26.1, 20.7, 18.6, 17.7, -3.8; IR (neat): 2930, 2857, 1757, 1709, 1340, 1204, 1070, 892, 837, 780 cm^{-1}; HRMS (APCI) calc. for $C_{13}H_{25}O_3Si$ $(M+H)^+$ 257.1568 found 257.1566.

General procedure for making *β*-keto diazoacetates

To an oven-dried 25 mL flask containing Rh_2(*S*-PTAD)$_4$ (16.5 mg, 0.01 equiv) and substrate (1.0 mmol, 1.0 equiv) in 6 mL dried trifluorotoluene under argon atmosphere was added a solution of (*Z*)-methyl 2-diazo-3-((trimethylsilyl)oxy)pent-3-enoate (**4.38**) (365 mg, 1.6 mmol, 1.6 equiv) in 6 mL dried trifluorotoluene by syringe pump over 3 h at -20 °C. The solution was warmed up to room temperature over 2 h. The mixture was concentrated under reduced pressure and then stirred with 5 g silica gel in 15 mL hexane for 30 mins. The mixture was filtrated and washed with several portions of Et_2O. The

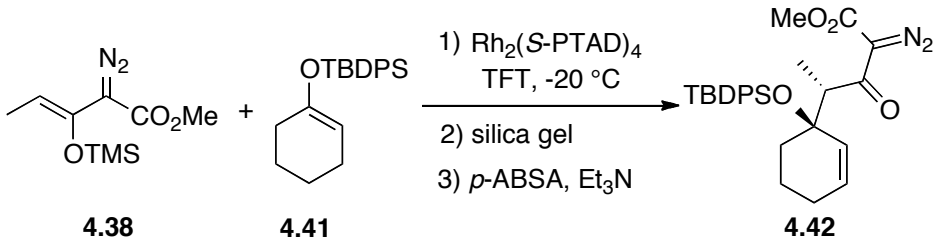
organic layer was concentrated under vacuum and the residue was purified by flash chromatography on silica gel to provide colorless oil, which was dissolved in 5 mL dried CH_3CN containing *p*-ABSA (240 mg, 1.0 mmol, 1.0 equiv), Et_3N (0.30 ml, 2.0 mmol, 2.0 equiv) The mixture was stirred for additional 3h and then concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to provide *β*-keto diazoacetates.



4.38 **4.39** **4.40**

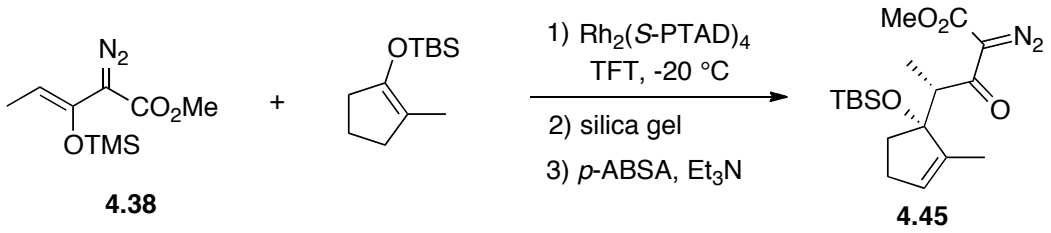
(*S*)-Methyl 2-diazo-3-oxo-4-((*R*)-1-((trimethylsilyl)oxy)cyclohex-2-en-1-yl) pentanoate (4.40): Derived from (cyclohex-1-en-1-yloxy)trimethylsilane (**4.39**) (170.3 mg, 1.0 mmol, 1.0 equiv) and (*Z*)-methyl 2-diazo-3-((trimethylsilyl)oxy)pent-3-enoate (**4.38**) (365 mg, 1.6 mmol, 1.6 equiv), and purified by flash chromatography (20/1 pentane/Et_2O, R_f: 0.25) on silica gel to provide the corresponding *β*-keto ester. The diazo transferred residue was purified by flash chromatography (20/1 pentane/Et_2O, R_f: 0.32) on silica gel to provide **4.40** as yellow oil (240 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82-5.84 (m, 2H), 3.96-4.06 (br, 1H), 3.82 (s, 3H), 1.53-2.02 (m, 6H), 1.05 (d, J = 6.7 Hz, 3H), 0.03 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 194.9, 161.8, 131.9, 129.6, 74.8, 52.0, 50.1, 33.8, 25.0, 18.1, 12.2, 2.3; IR (neat): 2954, 2135, 1722, 1652, 1299, 1200, 1127, 1029, 998, 836 cm^{-1}; HRMS (ESI) calc. for $C_{15}H_{24}O_4N_2NaSi$ $(M+Na)^+$ 347.1398 found 347.1340; $[\alpha]^{25}_D$ 131.9 (c = 1.34, $CHCl_3$); HPLC: (OD-H, 0.2%

isopropanol in hexane, 0.7 mL/min) retention times of 14.4 min (minor) and 16.7 min (major), 90% ee.

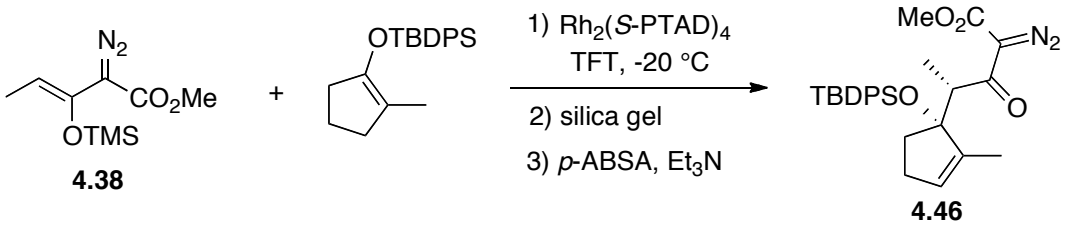


4.38 **4.41** **4.42**

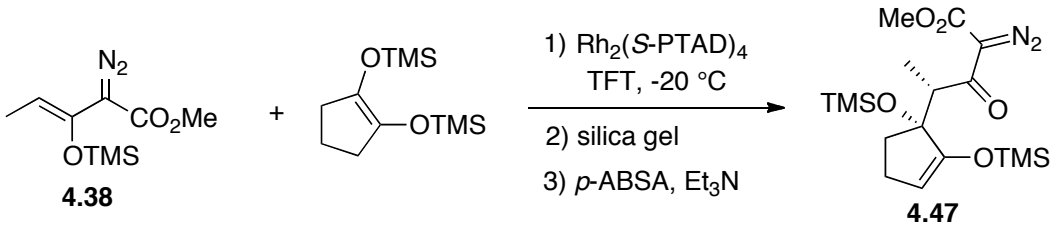
(*S*)-Methyl 4-((*R*)-1-((*tert*-butyldiphenylsilyl)oxy)cyclohex-2-en-1-yl)-2-diazo-3-oxopentanoate (4.42): Derived from *tert*-butyl(cyclohex-1-en-1-yloxy)diphenylsilane (**4.41**) (336.5 mg, 1.0 mmol, 1.0 equiv) and (*Z*)-methyl 2-diazo-3-((trimethylsilyl)oxy)pent-3-enoate (**4.38**) (365 mg, 1.6 mmol, 1.6 equiv), and purified by flash chromatography (10/1 pentane/Et_2O, R_f: 0.42) on silica gel to provide the corresponding *β*-keto ester. The diazo transferred residue was purified by flash chromatography (10/1 pentane/Et_2O, R_f: 0.52) on silica gel to provide **4.42** as a yellow powder (230.1 mg, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68-7.73 (m, 4H), 7.31-7.42 (m, 6H), 5.58-5.66 (m, 1H), 5.35-5.43 (m, 1H), 4.22-4.34 (m, 1H), 3.81 (s, 3H), 1.95-2.07 (m, 1H), 1.74-1.83 (m, 1H), 1.54-1.67 (m, 1H), 1.21-1.38 (m, 3H), 1.25 (d, J = 7.6 Hz, 3H), 1.03 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 194.6, 161.6, 136.5, 136.4, 135.6, 135.5, 131.2, 130.3, 129.1, 127.0, 76.0, 52.0, 51.0 33.6, 27.1, 24.4, 19.5, 18.9, 12.6; IR (neat): 2933, 2136, 1720, 1654, 1427, 1300, 1108, 994, 739, 700 cm^{-1}; HRMS (APCI) calc. for $C_{28}H_{35}O_4Si$ $(M\text{-}N_2+H)^+$ 463.2299 found 463.2296; $[\alpha]^{25}_D$ 107.9 (c = 1.28, $CHCl_3$); HPLC: (AD-H, 100% hexane, 1.0 mL/min) retention times of 12.3 min (minor) and 12.8 min (major), 96% ee.



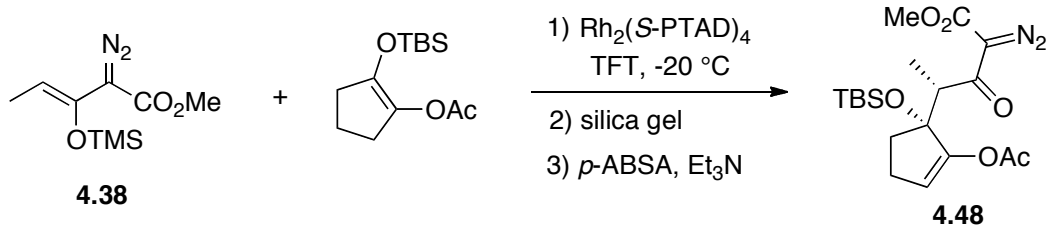
(*S*)-Methyl 4-((*R*)-1-((*tert*-butyldimethylsilyl)oxy)-2-methylcyclopent-2-en-1-yl)-2-diazo-3-oxopentanoate (4.45): Derived from *tert*-butyldimethyl((2-methylcyclopent-1-en-1-yl)oxy)silane (212.4 mg, 1.0 mmol, 1.0 equiv) and (*Z*)-methyl 2-diazo-3-((trimethylsilyl)oxy)pent-3-enoate (**4.38**) (365 mg, 1.6 mmol, 1.6 equiv), and purified by flash chromatography (10/1 pentane/Et_2O, R_f: 0.44) on silica gel to provide the corresponding β-keto ester. The diazo transferred residue was purified by flash chromatography (20/1 pentane/Et_2O, R_f: 0.39) on silica gel to provide **4.45** as yellow oil (226 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.53 (d, J = 1.2 Hz, 1H), 4.27 (br, 1H), 3.81 (s, 3H), 2.76 (ddd, J = 15.3, 9.5, 4.3 Hz, 1H), 2.28-2.38 (m, 1H), 2.11-2.20 (m, 1H), 1.76 (ddd, J = 14.9, 9.2, 4.6 Hz, 1H), 1.70 (q, J = 2.0 Hz, 3H), 0.87 (d, J = 7.6 Hz, 3H), 0.77 (s, 9H), -0.02 (s, 3H), -0.04 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.4, 161.9, 142.0, 129.5, 92.4, 52.0, 45.5, 31.8, 30.0, 25.6, 18.2, 12.3, 11.7, -3.3, -3.7; IR (neat): 2954, 2929, 2856, 2123, 1724, 1655, 1436, 1301, 1211, 1195, 1127, 1066, 773 cm^{-1}; HRMS (ESI) calc. for $C_{18}H_{30}O_4N_2NaSi$ $(M+Na)^+$ 389.1867 found 389.1866; $[\alpha]^{25}_D$ -1.5 (c = 1.39, $CHCl_3$); HPLC: (AD-H, 0.5% isopropanol in hexane, 0.7 mL/min) retention times of 6.8 min (major) and 7.6 min (minor), 99% ee.



(*S*)-Methyl 4-((*R*)-1-((*tert*-butyldiphenylsilyl)oxy)-2-methylcyclopent-2-en-1-yl)-2-diazo-3-oxopentanoate (4.46): Derived from *tert*-butyl((2-methylcyclopent-1-en-1-yl)oxy)diphenylsilane (336.5 mg, 1.0 mmol, 1.0 equiv) and (*Z*)-methyl 2-diazo-3-((trimethylsilyl)oxy)pent-3-enoate (**4.38**) (365 mg, 1.6 mmol, 1.6 equiv), and purified by flash chromatography (20/1 pentane/Et_2O, R_f: 0.27) on silica gel to provide the corresponding β-keto ester. The diazo transferred residue was purified by flash chromatography (10/1 pentane/Et_2O, R_f: 0.42) on silica gel to provide **4.46** as a yellow powder (145 mg, 30% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.59-7.63 (m, 2H), 7.52-7.55 (m, 2H), 7.34-7.39 (m, 2H), 7.29-7.33 (m, 2H), 7.24-7.28 (m, 2H), 4.87 (d, J = 1.4 Hz, 1H), 4.52 (br, 1H), 3.86 (s, 3H), 2.77-2.82 (m, 1H), 1.81-1.88 (m, 1H), 1.73-1.80 (m, 1H), 1.60 (d, J = 1.4 Hz, 3H), 1.38-1.45 (m, 1H), 0.96 (s, 9H), 0.87 (d, J = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.8, 162.0, 140.1, 136.1, 136.0, 135.1, 134.6, 130.2, 129.3, 129.2, 127.1, 126.9, 94.1, 52.0, 45.2, 32.3, 30.0, 27.1, 19.2, 12.2, 11.8; IR (neat): 2930, 2134, 1720, 1647, 1430, 1304, 1189, 1106, 1058, 1011, 736, 700 cm^{-1}; HRMS (ESI) calc. for $C_{28}H_{34}O_4N_2NaSi$ $(M+Na)^+$ 513.2180 found 513.2178; $[\alpha]^{25}_D$ -55.3 (c = 1.27, $CHCl_3$); HPLC: (AD-H, 0.5% isopropanol in hexane, 0.7 mL/min) retention times of 9.2 min (minor) and 11.8 min (major), 99% ee.

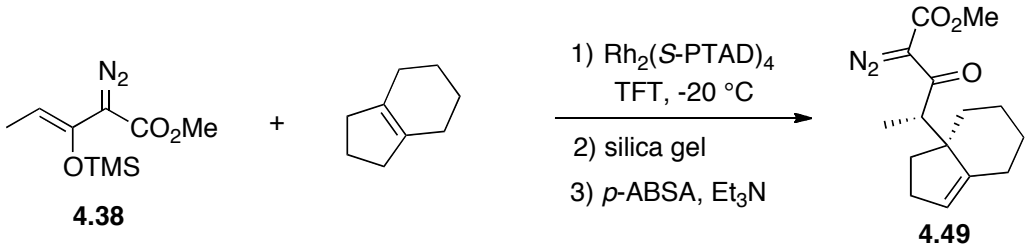


(*S*)-Methyl 4-((*R*)-1,2-bis((trimethylsilyl)oxy)cyclopent-2-en-1-yl)-2-diazo-3-oxopentanoate (4.47): Derived from 1,2-bis((trimethylsilyl)oxy)cyclopent-1-ene (336.5 mg, 1.0 mmol, 1.0 equiv) and (*Z*)-methyl 2-diazo-3-((trimethylsilyl)oxy)pent-3-enoate (**4.38**) (365 mg, 1.6 mmol, 1.6 equiv), and purified by flash chromatography (20/1 pentane/Et_2O, R_f: 0.18) on silica gel to provide the corresponding *β*-keto ester. The diazo transferred residue was purified by flash chromatography (20/1 pentane/Et_2O, R_f: 0.24) on silica gel to provide **4.47** as yellow oil (267 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.74 (t, *J* = 4.2 Hz, 1H), 3.93 (br, 1H), 3.82 (s, 3H), 2.54 (ddd, *J* = 13.7, 9.5, 4.3 Hz, 1H), 2.19-2.31 (m, 1H), 2.04-2.12 (m, 1H), 1.59-1.66 (m, 1H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.25 (s, 9H), 0.02 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 195.2, 162.1, 153.4, 104.5, 88.2, 52.1, 46.0, 30.5, 25.2, 12.0, 1.4, -0.2; HRMS (ESI) calc. for $C_{17}H_{30}O_5N_2NaSi_2$ $(M+Na)^+$ 421.1586 found 421.1586; $[\alpha]^{25}_D$ 26.1 (*c* = 2.06, $CHCl_3$); HPLC: (OD-H, 0.1% isopropanol in hexane, 0.4 mL/min) retention times of 21.9 min (minor) and 25.6 min (major), 97% ee.



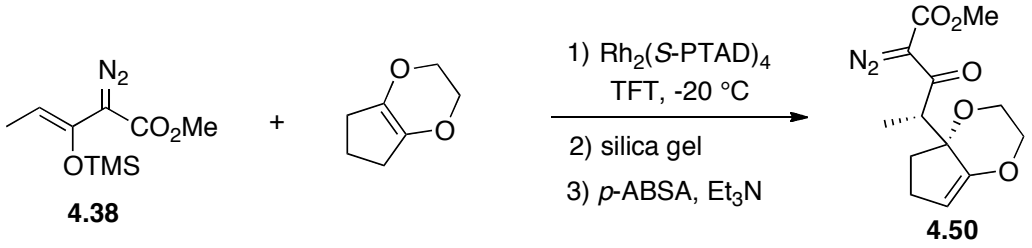
(*S*)-Methyl 4-((*R*)-2-acetoxy-1-((*tert*-butyldimethylsilyl)oxy)cyclopent-2-en-1-yl)-2-diazo-3-oxopentanoate (4.48): Derived from 2-((*tert*-butyldimethylsilyl)oxy)cyclopent-

1-en-1-yl acetate (256.4 mg, 1.0 mmol, 1.0 equiv) and (*Z*)-methyl 2-diazo-3-((trimethylsilyl)oxy)pent-3-enoate (**4.38**) (365 mg, 1.6 mmol, 1.6 equiv), and purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.29) on silica gel to provide the corresponding *β*-keto ester. The diazo transferred residue was purified by flash chromatography (20/1 pentane/Et_2O, R_f: 0.24) on silica gel to provide **4.48** as yellow oil (250 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.89 (t, *J* = 2.4 Hz, 1H), 4.26 (br, 1H), 3.80 (s, 3H), 2.76 (ddd, *J* = 15.0, 9.2, 3.8 Hz, 1H), 2.36-2.46 (m, 1H), 2.22-2.30 (m, 1H), 2.22 (s, 3H), 1.74 (ddd, *J* = 15.0, 9.4, 4.2 Hz, 1H), 0.95 (d, *J* = 7.6 Hz, 3H), 0.77 (s, 9H), -0.01 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 195.4, 168.2, 161.6, 148.5, 116.9, 88.0, 52.0, 45.5, 30.4, 26.5, 25.4, 21.4, 18.1, 12.5, -3.6, -3.8; IR (neat): 2929, 2857, 2137, 1768, 1724, 1653, 1303, 1193, 1072, 835, 775 cm^{-1}; HRMS (ESI) calc. for $C_{19}H_{30}O_6N_2NaSi$ $(M+Na)^+$ 433.1765 found 433.1766; $[\alpha]^{25}_D$ 11.2 (*c* = 1.18, $CHCl_3$); HPLC: (OD-H, 0.5% isopropanol in hexane, 0.7 mL/min) retention times of 8.8 min (minor) and 10.4 min (major), 99% ee.



(*S*)-Methyl 2-diazo-4-((*S*)-2,4,5,6,7,7a-hexahydro-1*H*-inden-7a-yl)-3-oxopentanoate (4.49): Derived from 2,3,4,5,6,7-hexahydro-1*H*-indene (122.2 mg, 1.0 mmol, 1.0 equiv) and (*Z*)-methyl 2-diazo-3-((trimethylsilyl)oxy)pent-3-enoate (**4.38**) (365 mg, 1.6 mmol, 1.6 equiv), and purified by flash chromatography (20/1 pentane/Et_2O, R_f: 0.30) on silica gel to provide the corresponding *β*-keto ester. The diazo transferred residue was purified

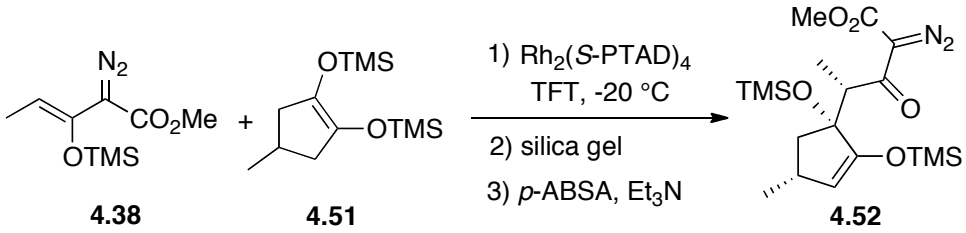
by flash chromatography (20/1 pentane/Et_2O, R_f: 0.41) on silica gel to provide **4.49** as yellow oil (119 mg, 43% yield). ^1H NMR (600 MHz, $CDCl_3$): δ 5.34 (d, *J* = 1.9 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 1H), 3.84 (s, 3H), 2.73 (ddd, *J* = 14.3, 8.6, 3.8 Hz, 1H), 2.29-2.32 (m, 1H), 2.17-2.28 (m, 2H), 1.98-2.03 (m, 1H), 1.87 (d, *J* = 13.8 Hz, 1H), 1.77-1.82 (m, 1H), 1.42-1.61 (m, 3H), 1.18-1.27 (m, 2H), 1.01 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 197.1, 161.6, 146.6, 122.6, 53.1, 52.1, 41.8, 39.9, 33.3, 31.4, 28.1, 26.2, 22.4, 12.8; IR (neat): 2930, 2852, 2135, 1715, 1655, 1436, 1297, 1195, 1128, 988, 731 cm^{-1}; HRMS (ESI) calc. for $C_{15}H_{20}O_3N_2Na$ $(M+Na)^+$ 299.1366 found 299.1367; $[\alpha]^{25}_D$ -31.6 (*c* = 1.85, $CHCl_3$); HPLC: (OD-H, 0.5% isopropanol in hexane, 0.7 mL/min) retention times of 9.1 min (minor) and 10.4 min (major), 99% ee.



(*S*)-Methyl 2-diazo-3-oxo-4-((*R*)-3,4a,5,6-tetrahydro-2*H*-cyclopenta[*b*][1,4]dioxin-4a-yl)pentanoate (4.50): Derived from 3,5,6,7-tetrahydro-2*H*-cyclopenta[*b*][1,4]dioxine[6] (126.1 mg, 1.0 mmol, 1.0 equiv) and (*Z*)-methyl 2-diazo-3-((trimethylsilyl)oxy)pent-3-enoate (**4.38**) (365 mg, 1.6 mmol, 1.6 equiv), and purified by flash chromatography (7/3 pentane/Et_2O, R_f: 0.26) on silica gel to provide the corresponding *β*-keto ester. The diazo transferred residue was purified by flash chromatography (7/3 pentane/Et_2O, R_f: 0.29) on silica gel to provide **4.50** as yellow oil (190 mg, 68% yield). ^1H NMR (400 MHz, C_6D_6): δ 5.10 (t, *J* = 2.4 Hz, 1H), 4.80 (q, *J* = 7.1 Hz, 1H), 4.23-4.28 (m, 1H), 3.72-3.77 (m, 1H),

[6] Fjeldskaar, I. R.; Rongved, P.; Skattebøl, L. *Acta Chem. Scand.* **1987**, 477.

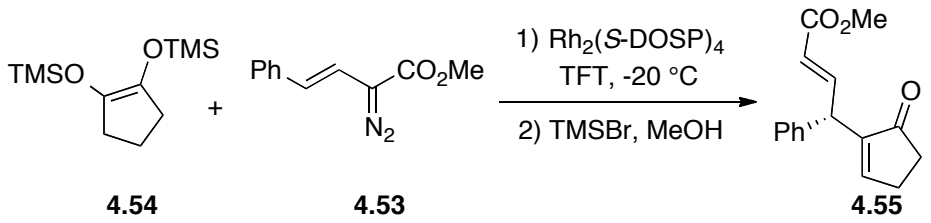
3.56-3.60 (m, 2H), 3.18 (s, 3H), 3.11-3.17 (m, 1H), 1.93-2.05 (m, 3H), 1.20 (d, J = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, C_6D_6): δ 194.7, 162.1, 154.7, 107.3, 87.2, 68.7, 61.9, 51.7, 45.3, 34.5, 26.0, 12.6; IR (neat): 2139, 1716, 1648, 1436, 1302, 1199, 1127, 1001, 899 cm^{-1}; HRMS (APCI) calc. for $C_{13}H_{17}O_5N_2$ $(M+H)^+$ 281.1132 found 281.1133; $[\alpha]^{25}_D$ -17.0 (c = 1.76, CH_3CN); HPLC: (AD-H, 2% isopropanol in hexane, 0.7 mL/min) retention times of 15.3 min (minor) and 18.8 min (major), 97% ee.



4.38 **4.51** **4.52**

(*S*)-Methyl 2-diazo-4-((1*R*,4*R*)-4-methyl-1,2-bis((trimethylsilyl)oxy)cyclopent-2-en-1-yl)-3-oxopentanoate (4.52): Derived from ((4-methylcyclopent-1-ene-1,2-diyl)bis(oxy))bis(trimethylsilane) (**4.51**) (258.5 mg, 1.0 mmol, 1.0 equiv) and (*Z*)-methyl 2-diazo-3-((trimethylsilyl)oxy)pent-3-enoate (**4.38**) (365 mg, 1.6 mmol, 1.6 equiv), and purified by flash chromatography (10/1 pentane/Et_2O, R_f: 0.36) on silica gel to provide the corresponding β-keto ester. The diazo transferred residue was purified by flash chromatography (10/1 pentane/Et_2O, R_f: 0.40) on silica gel to provide **4.52** as yellow oil (166 mg, 40% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 4.60 (d, J = 2.4 Hz, 1H), 4.47 (q, J = 7.1 Hz, 1H), 3.29 (s, 3H), 3.23-3.34 (m, 1H), 2.28-2.38 (m, 1H), 1.45 (dd, J = 14.3, 8.2 Hz, 1H), 1.10 (d, J = 7.0 Hz, 3H), 0.99 (d, J = 6.7 Hz, 3H), 0.22 (s, 9H), 0.21 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 195.3, 162.1, 154.0, 111.0, 89.3, 76.4, 51.7, 42.1, 33.7, 23.1, 12.4, 2.6, 0.2; IR (neat): 2956, 2120, 1728, 1645, 1301, 1248, 1209, 1128, 1044, 837, 751 cm^{-1}; HRMS (ESI) calc. for $C_{18}H_{32}O_5N_2NaSi_2$ $(M+Na)^+$ 435.1742 found 435.1739; $[\alpha]^{25}_D$

46.6 (c = 1.84, $CHCl_3$); HPLC: (OD-H, 0.1% isopropanol in hexane, 0.7 mL/min) retention times of 13.1 min (minor) and 17.2 min (major), 99% ee.



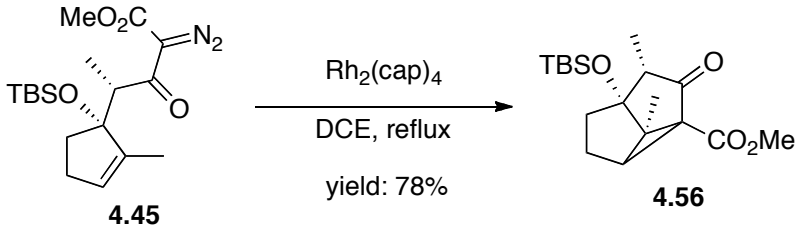
4.54 **4.53** **4.55**

(*S*,*E*)-Methyl 4-(5-oxocyclopent-1-en-1-yl)-4-phenylbut-2-enoate (4.55): To an oven-dried 25 mL flask containing Rh_2(*S*-PTAD)$_4$ (16.5 mg, 0.01 equiv) and 1,2-bis((trimethylsilyl)oxy)cyclopent-1-ene (**4.54**) (336.5 mg, 1.0 mmol, 1.0 equiv) in 6 mL dried trifluorotoluene under argon atmosphere was added a solution of (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (**4.54**) (323.6 mg, 1.6 mmol, 1.6 equiv) in 6 mL dried trifluorotoluene by syringe pump over 3 h at -20 °C. The solution was warmed up to room temperature over 2 h. The mixture was concentrated under reduced pressure and then stirred with TMSBr (7.6 mg, 0.05 mmol, 0.05 equiv) in 25 mL dried methanol for 10 mins. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (1/1 pentane/Et_2O, R_f: 0.42) on silica gel to provide **4.55** as colorless powder (106 mg, 41% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 (t, J = 2.8 Hz, 1H), 7.32 (t, J = 7.3 Hz, 2H), 7.24-7.26 (m, 1H), 7.21 (dd, J = 15.6, 6.9 Hz, 1H), 7.18 (d, J = 7.3 Hz, 2H), 5.73 (dd, J = 15.6, 1.4 Hz, 1H), 4.61 (d, J = 6.9 Hz, 1H), 3.77 (s, 3H), 2.57-2.68 (m, 2H), 2.39-2.50 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 207.6, 166.8, 159.7, 148.1, 146.4, 139.2, 128.9, 128.2, 127.2, 122.2, 51.6, 43.8, 34.5, 26.7; IR (neat): 1701, 1438, 1274, 1193, 1024, 985, 742, 703 cm^{-1}; HRMS (APCI) calc. for $C_{16}H_{17}O_3$ $(M+H)^+$ 257.1172 found 257.1172; $[a]^{25}_D$ -11.0 (c = 0.62, $CHCl_3$); HPLC: (AD-H, 10%

isopropanol in hexane, 0.7 mL/min) retention times of 15.3 min (major) and 24.5 min (minor), 99% ee.

General procedure for the second diazo decomposition

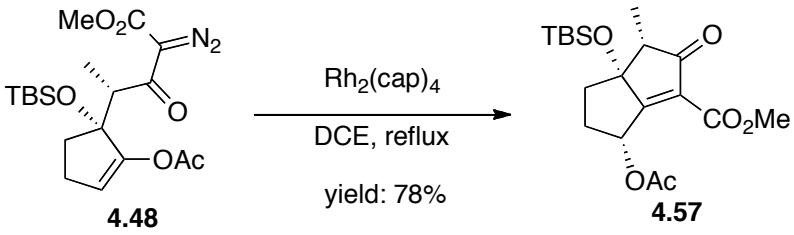
To an oven-dried 10 mL flask containing $Rh_2(cap)_4$ (1.3 mg, 0.02 equiv) and *β*-keto diazoacetate (0.1 mmol, 1.0 equiv) in 5 mL anhydrous Dichloroethane was heated to reflux for 1h under argon atmosphere. The mixture was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel.



4.45 **4.56**

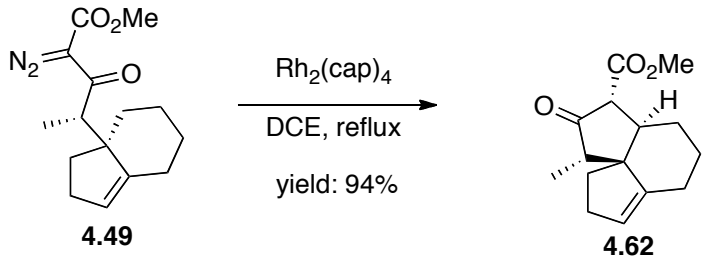
(1*S*,2a^1*R*,4a*R*)-Methyl 4a-((*tert*-butyldimethylsilyl)oxy)-1,2a^1-dimethyl-2-oxooctahydrocyclopropa[*cd*]pentalene-2a-carboxylate (4.56): Derived from Diazoacetate **4.45** (36.6 mg, 0.1 mmol, 1.0 equiv) and was purified by flash chromatography (7/3 pentane/Et_2O, R_f: 0.35) on silica gel to provide **4.56** as colorless powder (26.4 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.73 (s, 3H), 2.58 (d, *J* = 7.8 Hz, 1H), 2.28 (q, *J* = 11.2 Hz, 1H), 2.19 (qd, *J* = 7.8, 1.2 Hz, 1H), 2.05-2.14 (m, 1H), 1.76 (dd, *J* = 11.6, 7.8 Hz, 1H), 1.39-1.46 (m, 1H), 1.36 (s, 3H), 1.23-1.32 (m, 1H), 1.19 (d, *J* = 7.8 Hz, 3H), 0.93 (s, 9H), 0.14 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 208.8, 167.2, 85.5, 59.2, 54.2, 52.4, 50.3, 45.1, 40.5, 26.0, 22.3, 18.5, 13.8, 11.1, -1.6, -3.0; IR (neat):

2957, 2931, 1734, 1251, 1213, 1099, 888, 837, 775 cm^{-1}; M.p. 65-67 °C; HRMS (APCI) calc. for $C_{18}H_{31}O_4Si$ $(M+H)^+$ 339.1991 found 339.1989; $[\alpha]^{25}_D$ 18.0 (*c* = 0.69, $CHCl_3$).



4.48 **4.57**

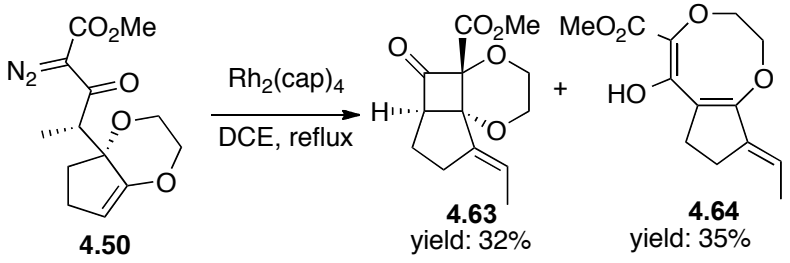
(3*S*,3a*R*,6*R*)-Methyl 6-acetoxy-3a-((*tert*-butyldimethylsilyl)oxy)-3-methyl-2-oxo-2,3,3a,4,5,6-hexahydropentalene-1-carboxylate (4.57): Derived from Diazoacetate **4.48** (41.1 mg, 0.1 mmol, 1.0 equiv) and was purified by flash chromatography (1/1 pentane/Et_2O, R_f: 0.31) on silica gel to provide **4.57** as colorless powder (29.7 mg, 78% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 6.13 (t, *J* = 7.6 Hz, 1H), 3.81 (s, 3H), 2.51 (dt, *J* = 13.3, 7.6 Hz, 1H), 2.34 (q, *J* = 7.2 Hz, 2H), 2.20-2.27 (m, 1H), 2.11 (s, 3H), 1.55-1.61 (m, 1H), 1.21 (d, *J* = 6.6 Hz, 3H), 0.86 (s, 9H), 0.10 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.1, 181.8, 169.8, 161.9, 130.6, 85.6, 68.9, 55.7, 52.2, 36.3, 32.7, 25.9, 20.8, 18.6, 8.6, -2.0, -2.3; IR (neat): 2954, 1746, 1736, 1235, 1114, 1049, 777 cm^{-1}; M.p. 117-120 °C; HRMS (APCI) calc. for $C_{19}H_{31}O_6Si$ $(M+H)^+$ 383.1884 found 383.1883; $[\alpha]^{25}_D$ 48.2 (*c* = 0.70, $CHCl_3$).



4.49 **4.62**

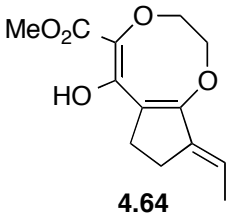
(1*R*,3*S*,3a*R*,9a*R*)-Methyl 3-methyl-2-oxo-2,3,4,5,7,8,9,9a-octahydro-1*H*-cyclopenta[*d*]indene-1-carboxylate (4.62): Derived from Diazoacetate **4.49** (27.7 mg,

0.1 mmol, 1.0 equiv) and was purified by flash chromatography (7/3 pentane/Et_2O, R_f: 0.35) on silica gel to provide **4.62** as colorless powder (23.4 mg, 94% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 5.28-5.30 (m, 1H), 3.37 (s, 3H), 2.83 (s, 1H), 2.28 (ddd, *J* = 12.5, 5.6, 1.8 Hz, 1H), 2.19 (q, *J* = 7.0 Hz, 1H), 2.11 (dm, *J* = 13.4 Hz, 1H), 1.87-2.04 (m, 4H), 1.56 (t, *J* = 13.6 Hz, 1H), 1.33-1.44 (m, 2H), 1.04-1.12 (m, 1H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.72-0.84 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6): δ 209.9, 169.8, 144.0, 124.8, 60.5, 56.1, 52.2, 49.2, 48.2, 36.4, 31.63, 31.58, 26.8, 25.8, 8.0; IR (neat): 2932, 1753, 1725, 1436, 1256, 1151, 990 cm^{-1}; M.p. 74-76 °C; HRMS (APCI) calc. for $C_{15}H_{21}O_3$ $(M+H)^+$ 249.1485 found 249.1482; $[\alpha]^{25}_D$ 170.0 (*c* = 0.98, $CHCl_3$).



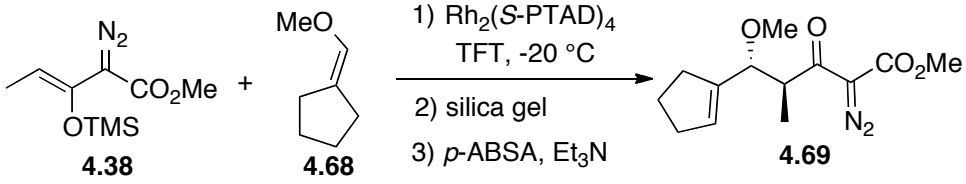
(4a*R*,5a*R*,8a*S*,*E*)-Methyl 8-ethylidene-5-oxooctahydrocyclopenta[1,4]cyclobuta[1,2-*b*][1,4]dioxine-4a-carboxylate (4.63): Derived from Diazoacetate **4.50** (29.0 mg, 0.1 mmol, 1.0 equiv) and was purified by flash chromatography (7/3 pentane/Et_2O, R_f: 0.36 for **4.63**, 0.52 for **4.64**) on silica gel to provide **4.63** as colorless powder (8.1 mg, 32% yield) and **4.64** as a yellowish powder (8.8 mg, 35% yield). ^{1}H NMR (600 MHz, C_6D_6): δ 5.84-5.87 (m, 1H), 4.25 (td, *J* = 11.9, 2.4 Hz, 1H), 3.91 (d, *J* = 8.1 Hz, 1H), 3.48 (td, *J* = 11.9, 2.4 Hz, 1H), 3.34 (dm, *J* = 12.0 Hz, 1H), 3.28 (dm, *J* = 12.0 Hz, 1H), 3.16 (s, 3H), 2.30 (dd, *J* = 16.2, 8.1 Hz, 1H), 2.18-2.26 (m, 1H), 1.98 (dd, *J* = 12.9, 7.9 Hz, 1H), 1.42 (dd, *J* = 6.7, 1.9 Hz, 3H), 1.38-1.42 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6): δ 199.3, 167.0,

143.0, 122.3, 91.8, 80.8, 64.6, 63.2, 62.9, 51.2, 28.5, 27.0, 15.2; IR (neat): 2952, 1796, 1739, 1435, 1276, 1132, 1097, 748 cm^{-1}; M.p. 74-77 °C; HRMS (APCI) calc. for $C_{13}H_{17}O_5$ $(M+H)^+$ 253.1071 found 253.1069; HPLC: (OD-H, 3% isopropanol in hexane, 1.0 mL/min) retention times of 14.9 min (minor) and 17.7 min (major), 2% ee.



4.64

(5*E*,9*E*)-Methyl 9-ethylidene-6-hydroxy-3,7,8,9-tetrahydro-2*H*-cyclopenta[*e*][1,4] dioxocine-5-carboxylate (4.64): ^1H NMR (600 MHz, C_6D_6): δ 11.9 (s, 1H), 5.95-5.98 (m, 1H), 3.82 (br, 2H), 3.50 (t, *J* = 4.3 Hz, 2H), 3.37 (s, 3H), 2.64 (t, *J* = 6.3 Hz, 2H), 2.13 (br, 2H), 1.52 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ 171.2, 165.7, 160.3, 142.4, 119.4, 117.1, 108.9, 66.7, 66.6, 51.6, 28.9, 23.8, 14.7; IR (neat): 1631, 1611, 1447, 1355, 1338, 1267, 1261, 1247, 1085, 816 cm^{-1}; M.p. 119-121 °C; HRMS (APCI) calc. for $C_{13}H_{17}O_5$ $(M+H)^+$ 253.1071 found 253.1069.



4.38 **4.68** **4.69**

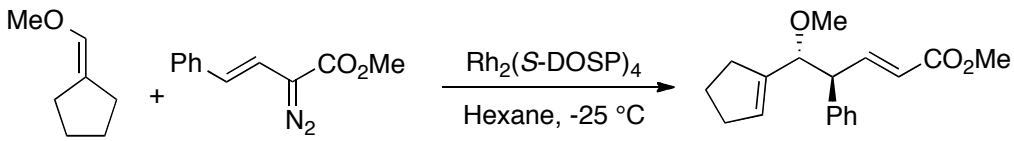
(4*S*,5*R*)-Methyl 5-(cyclopent-1-en-1-yl)-2-diazo-5-methoxy-4-methyl-3-oxopentanoate (4.69): To an oven-dried 25 mL flask containing Rh_2(*S*-PTAD)$_4$ (16.5 mg, 0.01 equiv) and (methoxymethylene)cyclopentane (**4.68**) (112.2 mg, 1.0 mmol, 1.0 equiv) in 6 mL dried trifluorotoluene under argon atmosphere was added a solution of

(*Z*)-methyl 2-diazo-3-((trimethylsilyl)oxy)pent-3-enoate (**4.38**) (365 mg, 1.6 mmol, 1.6 equiv) in 6 mL dried trifluorotoluene by syringe pump over 3 h at -20 °C. The solution was warmed up to room temperature over 2 h. The mixture was concentrated under reduced pressure and then stirred with 5 g silica gel in 15 mL hexane for 30 mins. The mixture was filtrated and washed with several portions of Et_2O. The organic solution was concentrated under vacuum and the residue was purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.31) on silica gel to provide colorless oil, which was dissolved in 5 mL dried CH_3CN containing *p*-ABSA (240 mg, 1.0 mmol, 1.0 equiv), Et_3N (0.30 ml, 2.0 mmol, 2.0 equiv) The mixture was stirred for additional 3h and then concentrated under reduced pressure. The residue was purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.34) on silica gel to provide **4.69** as yellow oil (243 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.71 (t, *J* = 1.8 Hz, 1H), 4.08 (d, *J* = 8.4 Hz, 1H), 3.81-3.88 (m, 1H), 3.80 (s, 3H), 3.10 (s, 3H), 2.14-2.42 (m, 4H), 1.82-1.92 (m, 2H), 0.89 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 195.5, 161.6, 141.3, 131.8, 82.1, 56.3, 52.1, 44.0, 32.1, 29.4, 23.2, 14.1; IR (neat): 2933, 2136, 1721, 1656, 1436, 1375, 1309, 1204, 1122, 1092, 1000, 752 cm^{-1}; HRMS (ESI) calc. for $C_{13}H_{18}O_4N_2Na$ $(M+Na)^+$ 289.1159 found 289.1157; $[\alpha]^{25}_D$ 21.8 (*c* = 1.24, $CHCl_3$); HPLC: (OD-H, 1% isopropanol in hexane, 0.7 mL/min) retention times of 8.2 min (minor) and 13.8 min (major), 94% ee.

General procedure for the reactions with vinyl ethers

To a flame-dried 100 mL flask containing Rh_2(*S*-DOSP)$_4$ (18.7 mg, 0.01 equiv) and vinyl ethers (1.0 mmol, 1.0 equiv) in 20 mL dried hexane under argon atmosphere was added a solution of vinyldiazoacetate (1.2 mmol, 1.2 equiv) in 20 mL dried hexane by syringe

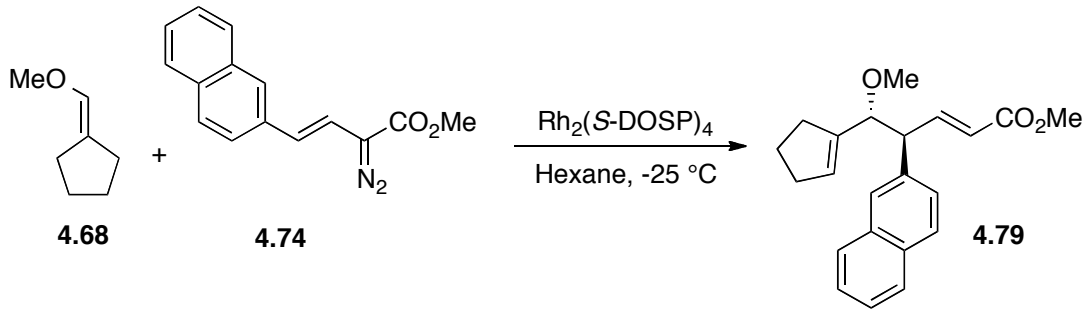
pump over 3 h at -25 °C. The solution was warmed up to room temperature over 2 h. The mixture was concentrated under reduced pressure and purified by flash chromatography (pentane/Et_2O) on silica gel to provide product.



4.68 **4.53** **4.78**

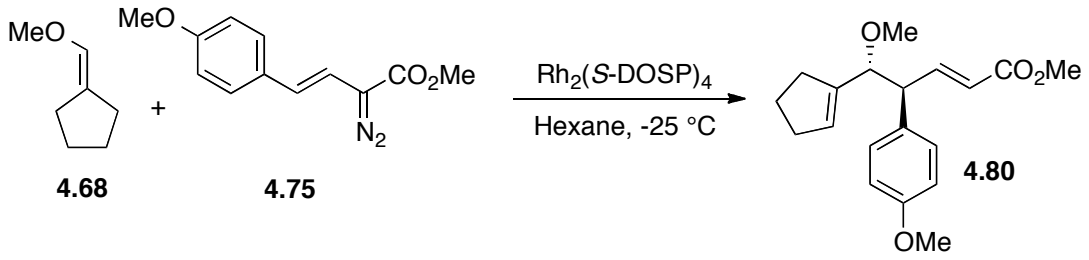
(4*S*,5*R*,*E*)-Methyl 5-(cyclopent-1-en-1-yl)-5-methoxy-4-phenylpent-2-enoate (4.78):

Derived from (methoxymethylene)cyclopentane (**4.68**) (56.1 mg, 0.50 mmol, 1.0 equiv) and (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (**4.53**) (161.8 mg, 0.8 mmol, 1.6 equiv), and was purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.41) on silica gel to provide **4.78** as colorless oil (112 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (dd, *J* = 15.6, 7.6 Hz, 1H), 7.24-7.28 (m, 2H), 7.17-7.22 (m, 1H), 7.11-7.15 (m, 2H), 5.76 (dd, *J* = 15.9, 1.2 Hz, 1H), 5.43 (t, *J* = 2.0 Hz, 1H), 4.07 (d, *J* = 8.5 Hz, 1H), 3.70 (s, 3H), 3.58 (td, *J* = 8.2, 1.0 Hz, 1H), 3.24 (s, 3H), 2.00-2.27 (m, 4H), 1.64-1.81 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.0, 149.8, 141.4, 139.7, 130.9, 128.4 (2C), 126.9, 121.9, 83.2, 56.6, 52.5, 51.4, 31.9, 30.4, 23.3; IR (neat): 2948, 2846, 1720, 1435, 1270, 1234, 1164, 1093, 730, 699 cm^{-1}; HRMS (ESI) calc. for $C_{18}H_{22}O_3Na$ $(M+Na)^+$ 309.1461 found 309.1459; $[\alpha]^{25}_D$ -6.7 (*c* = 1.17, $CHCl_3$); HPLC: (AD-H, 1% isopropanol in hexane, 0.7 mL/min) retention times of 14.7 min (minor) and 17.4 min (major), 99% ee.

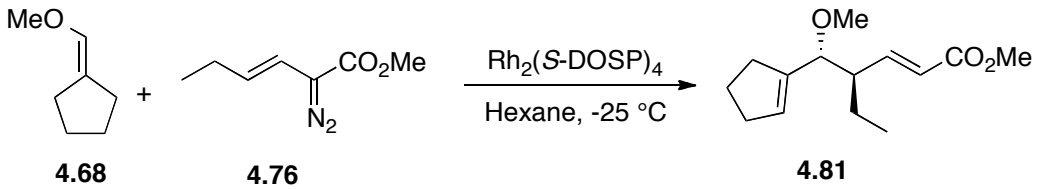


4.68 **4.74** **4.79**

(4*S*,5*R*,*E*)-Methyl 5-(cyclopent-1-en-1-yl)-5-methoxy-4-(naphthalen-2-yl)pent-2-enoate (4.79): Derived from (methoxymethylene)cyclopentane (**4.68**) (56.1 mg, 0.50 mmol, 1.0 equiv) and (*E*)-methyl 2-diazo-4-(naphthalen-2-yl)but-3-enoate (**4.74**) (201.8 mg, 0.8 mmol, 1.6 equiv) in 20 mL dried 1:1 hexane/toluene, and was purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.31) on silica gel to provide **4.79** as colorless powder (148 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.80 (m, 3H), 7.60 (s, 1H), 7.43-7.48 (m, 2H), 7.40 (dd, *J* = 15.7, 7.6 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 5.78 (d, *J* = 15.7 Hz, 1H), 5.46 (s, 1H), 4.20 (d, *J* = 8.6 Hz, 1H), 3.77 (t, *J* = 8. 1Hz, 1H), 3.69 (s, 3H), 3.28 (s, 3H), 2.13-2.24 (m, 3H), 1.95-2.02 (m, 1H), 1.63-1.78 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.0, 149.7, 141.3, 137.2, 133.4, 132.4, 131.1, 128.1, 127.7, 127.6, 127.3, 126.5, 126.0, 125.7, 122.2, 83.1, 56.6, 52.5, 51.4, 31.9, 30.4, 23.3; IR (neat): 2946, 2845, 1720, 1270, 1164, 1093, 747 cm^{-1}; M.p. 63-65 °C; HRMS (ESI) calc. for $C_{22}H_{24}O_3Na$ $(M+Na)^+$ 359.1618 found 359.1615; $[\alpha]^{25}_D$ -32.2 (*c* = 0.89, $CHCl_3$); HPLC: (AS-H, 1% isopropanol in hexane, 0.7 mL/min) retention times of 9.9 min (major) and 13.1 min (minor), 99% ee.

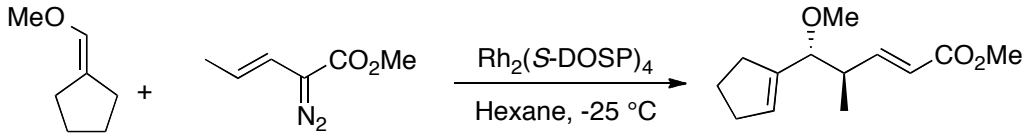


(4*S*,5*R*,*E*)-Methyl 5-(cyclopent-1-en-1-yl)-5-methoxy-4-(4-methoxyphenyl)pent-2-enoate (4.80): Derived from (methoxymethylene)cyclopentane (**4.68**) (112.2 mg, 1.0 mmol, 1.0 equiv) and (*E*)-methyl 2-diazo-4-(4-methoxyphenyl)but-3-enoate (**4.75**) (278.6 mg, 1.2 mmol, 1.2 equiv), and was purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.31) on silica gel to provide **4.80** as colorless oil (243.2 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (dd, *J* = 15.6, 7.6 Hz, 1H), 7.03-7.07 (m, 2H), 6.78-6.82 (m, 2H), 5.73 (dd, *J* = 15.6, 1.3 Hz, 1H), 5.44 (t, *J* = 1.8 Hz, 1H), 4.02 (d, *J* = 8.8 Hz, 1H), 3.77 (s, 3H), 3.69 (s, 3H), 3.51-3.56 (m, 1H), 3.23 (s, 3H), 2.02-2.26 (m, 4H), 1.60-1.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 158.4, 150.2, 141.4, 131.8, 130.8, 129.4, 121.6, 113.8, 83.2, 56.6, 55.2, 51.6, 51.4, 31.9, 30.4, 23.3; IR (neat): 2948, 1720, 1511, 1247, 1164, 1091, 1034, 829 cm^{-1}; HRMS (APCI) calc. for $C_{19}H_{25}O_4$ $(M+H)^+$ 317.1747 found 317.1747; $[\alpha]^{25}_D$ -6.9 (*c* = 3.04, $CHCl_3$); HPLC: (OD-H, 1% isopropanol in hexane, 1.0 mL/min) retention times of 5.7 min (minor) and 11.8 min (major), 98% ee.



(*R*,*E*)-Methyl 4-((*R*)-cyclopent-1-en-1-yl(methoxy)methyl)hex-2-enoate (4.81): Derived from (methoxymethylene)cyclopentane (**4.68**) (112.2 mg, 1.0 mmol, 1.0 equiv)

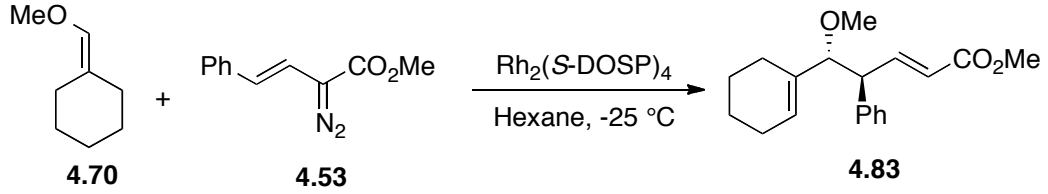
and (*E*)-methyl 2-diazohex-3-enoate (**4.76**) (185.4 mg, 1.2 mmol, 1.2 equiv), and was purified by flash chromatography (10/1 pentane/Et_2O, R_f: 0.30) on silica gel to provide **4.81** as colorless oil (206.3 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81 (dd, *J* = 15.7, 9.4 Hz, 1H), 5.82 (d, *J* = 15.7 Hz, 1H), 5.66 (t, *J* = 2.0 Hz, 1H), 3.72 (s, 3H), 3.68 (d, *J* = 8.2 Hz, 1H), 3.17 (s, 3H), 2.10-2.40 (m, 5H), 1.84-1.92 (m, 2H), 1.38-1.48 (m, 1H), 1.13-1.25 (m, 1H), 0.81 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.0, 150.9, 142.1, 130.7, 122.1, 82.8, 56.5, 51.4, 47.7, 32.0, 30.1, 23.5, 23.3, 11.5; IR (neat): 2933, 1723, 1658, 1267, 1194, 1087, 981 cm^{-1}; HRMS (APCI) calc. for $C_{14}H_{23}O_3$ $(M+H)^+$ 239.1642 found 239.1641; $[\alpha]^{25}_D$ 25.9 (*c* = 1.00, $CHCl_3$); HPLC: (OD-H, 1% isopropanol in hexane, 1.0 mL/min) retention times of 5.2 min (minor) and 16.2 min (major), 99% ee.



4.68 **4.77** **4.82**

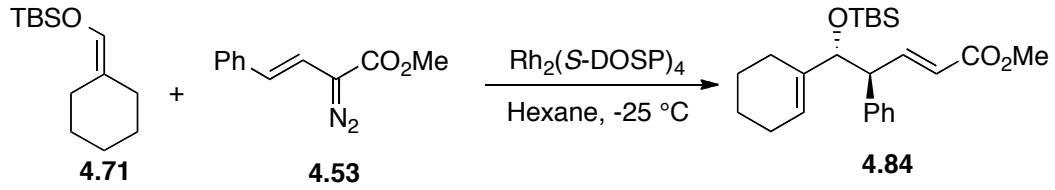
(4*R*,5*R*,*E*)-Methyl 5-(cyclopent-1-en-1-yl)-5-methoxy-4-methylpent-2-enoate (4.82): Derived from (methoxymethylene)cyclopentane (**4.68**) (112.2 mg, 1.0 mmol, 1.0 equiv) and (*E*)-methyl 2-diazopent-3-enoate (**4.77**) (168.2 mg, 1.2 mmol, 1.2 equiv), and was purified by flash chromatography (10/1 pentane/Et_2O, R_f: 0.30) on silica gel to provide **4.82** as colorless oil (149.6 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 (dd, *J* = 15.7, 7.8 Hz, 1H), 5.84 (dd, *J* = 15.7, 1.2 Hz, 1H), 5.66 (t, *J* = 2.2 Hz, 1H), 3.72 (s, 3H), 3.57 (d, *J* = 7.6 Hz, 1H), 3.18 (s, 3H), 2.46-2.55 (m, 1H), 2.11-2.42 (m, 4H), 1.84-1.92 (m, 2H), 0.91 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.2, 152.4, 142.0,

130.9, 120.4, 84.1, 56.5, 51.4, 39.6, 32.0, 29.9, 23.3, 16.2; IR (neat): 2949, 1723, 1656, 1272, 1196, 1088, 980 cm^{-1}; HRMS (ESI) calc. for $C_{13}H_{20}O_3Na$ $(M+Na)^+$ 247.1305 found 247.1308; $[\alpha]^{25}_D$ 23.7 (*c* = 1.63, $CHCl_3$); HPLC: (OD-H, 1% isopropanol in hexane, 1.0 mL/min) retention times of 5.1 min (minor) and 8.8 min (major), 93% ee.



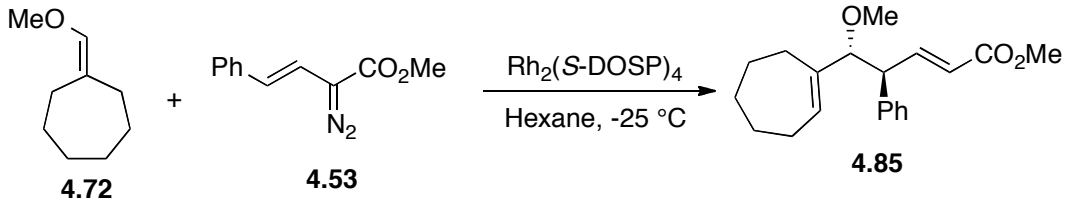
4.70 **4.53** **4.83**

(4*S*,5*R*,*E*)-Methyl 5-(cyclohex-1-en-1-yl)-5-methoxy-4-phenylpent-2-enoate (4.83): Derived from (methoxymethylene)cyclohexane (**4.70**) (63.2 mg, 0.50 mmol, 1.0 equiv) and (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (**4.53**) (161.8 mg, 0.8 mmol, 1.6 equiv), and was purified by flash chromatography (10/1 pentane/Et_2O, R_f: 0.27) on silica gel to provide **4.83** as colorless oil (132 mg, 88% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.32 (dd, *J* = 15.7, 7.4 Hz, 1H), 7.25-7.28 (m, 2H), 7.16-7.21 (m, 1H), 7.09-7.13 (m, 2H), 5.76 (dd, *J* = 15.9, 1.2 Hz, 1H), 5.40 (t, *J* = 2.0 Hz, 1H), 3.71 (d, *J* = 9.4 Hz, 1H), 3.70 (s, 3H), 3.59 (m, 1H), 3.22 (s, 3H), 1.65-1.96 (m, 4H), 1.42-1.51 (m, 3H), 1.22-1.32 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 150.3, 139.7, 133.9, 128.6, 128.3(2C), 126.8, 121.7, 89.0, 56.2, 52.1, 51.4, 24.9, 23.1, 22.4, 22.4; IR (neat): 2926, 1720, 1269, 1197, 1091, 699 cm^{-1}; HRMS (ESI) calc. for $C_{19}H_{24}O_3Na$ $(M+Na)^+$ 323.1618 found 323.1615; $[\alpha]^{25}_D$ -3.4 (*c* = 1.19, $CHCl_3$); HPLC: (AS-H, 1% isopropanol in hexane, 0.7 mL/min) retention times of 7.8 min (major) and 9.1 min (minor), 99% ee.



(4*S*,5*R*,*E*)-Methyl 5-(cyclohex-1-en-1-yl)-5-methoxy-4-phenylpent-2-enoate (4.84):

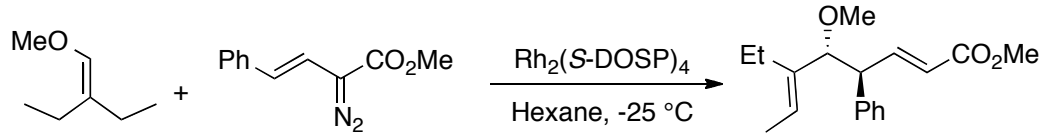
Derived from *tert*-butyl(cyclohexylidenemethoxy)dimethylsilane (**4.71**) (162.3 mg, 1.0 mmol, 1.0 equiv) and (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (**4.53**) (242.5 mg, 1.2 mmol, 1.2 equiv), and was purified by flash chromatography (20/1 pentane/Et_2O, R_f: 0.35) on silica gel to provide **4.84** as colorless oil (300.9 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (dd, *J* = 15.7, 7.8 Hz, 1H), 7.24-7.28 (m, 2H), 7.16-7.21 (m, 1H), 7.09-7.13 (m, 2H), 5.75 (dd, *J* = 15.7, 1.0 Hz, 1H), 5.35 (br, 1H), 4.15 (d, *J* = 7.8 Hz, 1H), 3.70 (s, 3H), 3.56 (t, *J* = 8.2 Hz, 1H), 1.65-2.05 (m, 4H), 1.40-1.53 (m, 3H), 1.22-1.32 (m, 1H), 0.87 (s, 9H), -0.05 (s, 3H), -0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 150.3, 140.1, 137.3, 128.6, 128.2, 126.6, 125.5, 122.1, 80.9, 54.1, 51.4, 25.8, 24.9, 23.5, 22.5(2C), 18.2, -4.6, -5.3; IR (neat): 2923, 2856, 1724, 1656, 1435, 1252, 1163, 1063, 835, 731 cm^{-1}; HRMS (ESI) calc. for $C_{24}H_{36}O_3NaSi$ $(M+Na)^+$ 423.2326 found 423.2334; $[\alpha]^{25}_D$ 5.0 (*c* = 1.39, $CHCl_3$); HPLC: (OD-H, 0.2% isopropanol in hexane, 1.0 mL/min) retention times of 3.7 min (major) and 6.6 min (minor), 98% ee.



(4*S*,5*R*,*E*)-Methyl 5-(cyclohept-1-en-1-yl)-5-methoxy-4-phenylpent-2-enoate (4.85):

Derived from (methoxymethylene)cycloheptane (**4.72**) (140.1 mg, 1.0 mmol, 1.0 equiv) and (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (**4.53**) (242.5 mg, 1.2 mmol, 1.2 equiv),

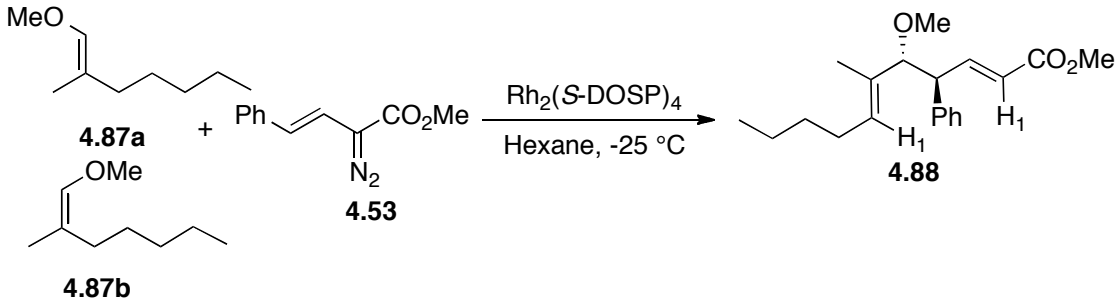
and was purified by flash chromatography (10/1 pentane/Et_2O, R_f: 0.28) on silica gel to provide **4.85** as colorless oil (280.2 mg, 89% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30 (dd, *J* = 15.7, 7.6 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 2H), 5.74 (dd, *J* = 15.7, 1.0 Hz, 1H), 5.55 (t, *J* = 6.2 Hz, 1H), 3.74 (d, *J* = 9.1 Hz, 1H), 3.69 (s, 3H), 3.53 (t, *J* = 8.6 Hz, 1H), 3.22 (s, 3H), 2.05-2.09 (m, 1H), 1.92-2.02 (m, 2H), 1.81-1.86 (m, 1H), 1.63-1.70 (m, 1H), 1.52-1.58 (m, 1H), 1.28-1.40 (m, 3H), 1.18-1.24 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.1, 150.3, 139.9, 133.3, 128.7(2C), 128.3, 126.8, 121.7, 90.3, 56.3, 52.4, 51.4, 32.2, 28.2, 27.2, 26.7, 26.4; IR (neat): 2921, 1721, 1435, 1271, 1233, 1164, 1091, 908, 730, 699 cm^{-1}; HRMS (ESI) calc. for $C_{20}H_{26}O_3Na$ $(M+Na)^+$ 337.1774 found 337.1779; $[\alpha]^{25}_D$ -36.1 (*c* = 0.72, $CHCl_3$); HPLC: (OD-H, 1% isopropanol in hexane, 1.0 mL/min) retention times of 7.6 min (minor) and 9.1 min (major), 99% ee.



4.73 **4.53** **4.86**

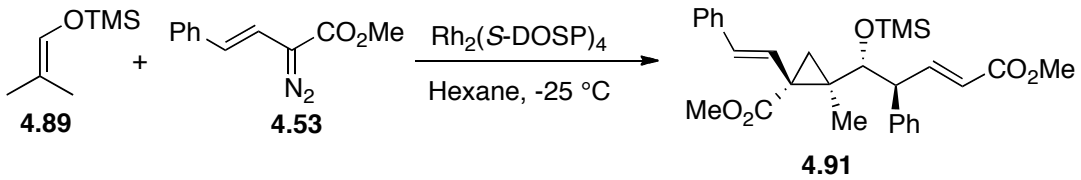
(2*E*,4*S*,5*R*,6*E*)-Methyl 6-ethyl-5-methoxy-4-phenylocta-2,6-dienoate (4.86): Derived from 3-(methoxymethylene)pentane (**4.73**) (60 mg, 0.5 mmol, 1.0 equiv) and (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (**4.53**) (141.7 mg, 0.7 mmol, 1.4 equiv), and was purified by flash chromatography (10/1 pentane/Et_2O, R_f: 0.37) on silica gel to provide **4.86** as colorless oil (107 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (dd, *J* = 15.7, 7.6 Hz, 1H), 7.23-7.27 (m, 2H), 7.17-7.21 (m, 1H), 7.11-7.14 (m, 2H), 5.73 (dd, *J* = 15.7, 1.4 Hz, 1H), 5.30 (q, *J* = 10.2 Hz, 1H), 3.75 (d, *J* = 7.6 Hz, 1H), 3.69 (s, 3H), 3.57 (t, *J* = 7.6 Hz, 1H), 3.22 (s, 3H), 1.97-2.04 (m, 1H), 1.72-1.78 (m, 1H), 1.51 (d, *J* = 6.7 Hz, 3H),

0.93 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 150.0, 140.2, 137.8, 128.7, 128.4, 126.7, 124.8, 121.9, 89.3, 56.4, 52.8, 51.4, 20.0, 13.2, 12.9; IR (neat): 2934, 1722, 1435, 1270, 1164, 1092, 700 cm^{-1}; HRMS (APCI) calc. for $C_{14}H_{19}O$ $(M+H)^+$ 281.1132 found 281.1133; $[\alpha]^{25}_D$ 6.3 (c = 1.36, $CHCl_3$); HPLC: ((R,R)-Whelk O1, 1% isopropanol in hexane, 0.7 mL/min) retention times of 14.6 min (major) and 16.2 min (minor), 99% ee.



(2*E*,4*S*,5*R*,6*E*)-Methyl 5-methoxy-6-methyl-4-phenylundeca-2,6-dienoate (4.88): Derived from 1-methoxy-2-methylhept-1-ene (**4.87**) (1:1 mixture of two regioisomers) (711.2 mg, 5.0 mmol, 10.0 equiv) and (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (**4.53**) (101.1 mg, 0.5 mmol, 1.0 equiv), and was purified by flash chromatography (10/1 pentane/Et_2O, R_f: 0.26) on silica gel to provide **4.88** as colorless oil (94.8 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (dd, J = 15.7, 7.6 Hz, 1H), 7.23-7.26 (m, 2H), 7.16-7.19 (m, 1H), 7.09 (m, 2H), 5.75 (d, J = 15.7 Hz, 1H), 5.13 (t, J = 7.1 Hz, 1H), 3.74 (d, J = 9.5 Hz, 1H), 3.69 (s, 3H), 3.58 (t, J = 8.3 Hz, 1H), 3.20 (s, 3H), 1.76-1.86 (m, 2H), 1.44 (s, 3H), 0.92-1.08 (m, 4H), 0.74 (t, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 150.4, 139.7, 132.2, 130.9, 128.6, 128.4, 126.8, 121.8, 90.2, 56.1, 52.2, 51.4, 31.2, 27.0, 21.8, 13.9, 10.6; IR (neat): 2953, 1723, 1435, 1269, 1164, 1092, 699 cm^{-1}; HRMS (APCI) calc. for $C_{20}H_{29}O_3$ $(M+H)^+$ 317.2111 found 317.2112; $[\alpha]^{25}_D$ -10.3 (c =

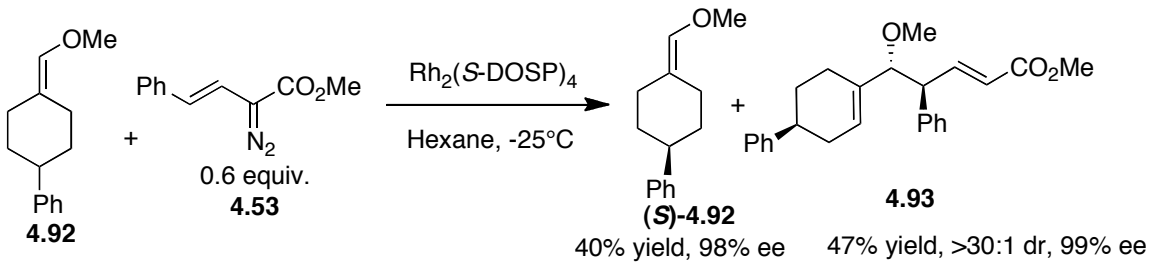
1.03, $CHCl_3$); HPLC: (OD-H, 1% isopropanol in hexane, 1.0 mL/min) retention times of 4.7 min (minor) and 5.6 min (major), 94% ee.



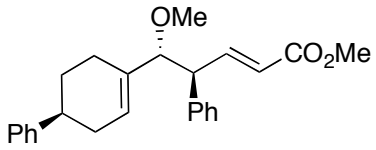
4.89 **4.53** **4.91**

(1*S*,2*R*)-Methyl 2-((1*R*,2*S*,*E*)-5-methoxy-5-oxo-2-phenyl-1-((trimethylsilyl)oxy)pent-3-en-1-yl)-2-methyl-1-((*E*)-styryl)cyclopropanecarboxylate (4.91): To a flame-dried 100 mL flask containing Rh_2(*S*-DOSP)$_4$ (18.7 mg, 0.02 equiv) and vinyl ether **4.89** (73 mg, 0.5 mmol, 1.0 equiv) in 20 mL dried hexane under argon atmosphere was added a solution of vinyldiazoacetate **4.53** (224.4 mg, 1.1 mmol, 2.2 equiv) in 20 mL dried hexane by syringe pump over 3 h at -25 °C. The solution was warmed up to room temperature over 2 h. The mixture was concentrated under reduced pressure and purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.33) on silica gel to provide product **4.91** as colorless gel (129.3 mg, 53% yield). ^{1}H NMR (600 MHz, C_6D_6): δ 7.68 (dd, *J* = 15.6, 9.1 Hz, 1H), 7.24 (d, *J* = 7. 1 Hz, 2H), 7.01-7.17 (m, 8H), 6.78 (d, *J* = 15.6 Hz, 1H), 6.07 (d, *J* = 15.6 Hz, 1H), 6.00 (d, *J* = 15.6 Hz, 1H), 4.51 (d, *J* = 8.0 Hz, 1H), 3.70 (t, *J* = 8.0 Hz, 1H), 3.42 (s, 3H), 3.34 (s, 3H), 1.17 (d, *J* = 5.4 Hz, 1H), 1.16 (s, 3H), 0.72 (d, *J* = 5.4 Hz, 1H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, C_6D_6): δ 172.6, 166.9, 150.4, 141.3, 137.6, 133.3, 129.3, 129.2, 128.6, 128.4, 128.2, 127.5, 127.0, 123.4, 75.7, 55.5, 52.1, 51.4, 37.8, 36.2, 24.6, 15.3, 0.8; IR (neat): 2951, 1717, 1434, 1238, 1165, 1095, 839, 747, 695 cm^{-1}; HRMS (APCI) calc. for $C_{29}H_{37}O_5Si$ $(M+H)^+$ 493.2405 found 493.2420; $[\alpha]^{25}_D$

-58.9 (*c* = 0.47, $CHCl_3$); HPLC: (OD-H, 1% isopropanol in hexane, 1.0 mL/min) retention times of 7.0 min (major) and 12.7 min (minor), 99% ee.



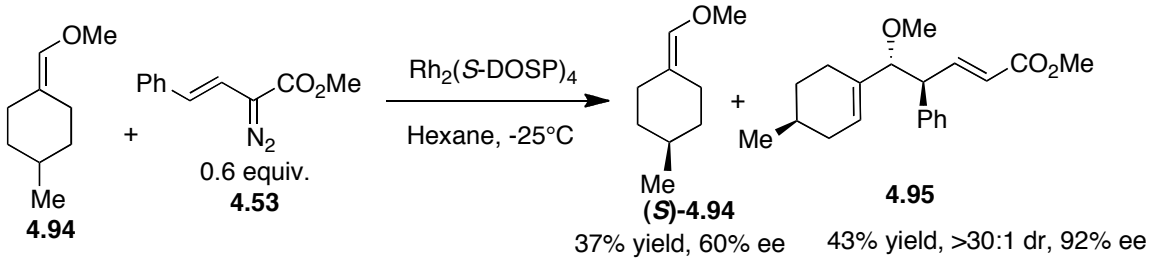
(*S*,*Z*)-(4-(Methoxymethylene)cyclohexyl)benzene (4.92): To a mixture containing (Methoxymethyl)triphenylphosphonium chloride (17.0 g, 48 mmol, 1.2 equiv) in 150 mL dried THF was added KO*t*-Bu (6.5 g, 48 mmol, 1.2 equiv) in one portion at -78 °C. After 30 mins, 4-phenylcyclopentanone (6.98 g, 40 mmol, 1.0 equiv) was added dropwise and the reaction mixture was warmed up to room temperature overnight. The mixture was quenched by H_2O (500 mL) and extracted by pentane (2 x 300 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was distillation by Kuargallor to afford the product **4.92** as colorless oil (8.82 g, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.33 (m, 2H), 7.17-7.23 (m, 3H), 5.83 (s, 1H), 3.58 (s, 3H), 2.92 (d, *J* = 13.7 Hz, 1H), 2.64 (tt, *J* = 12.1, 3.2 Hz, 1H), 2.15-2.23 (m, 1H), 2.03-2.12 (m, 1H), 1.92-2.00 (m, 2H), 1.76-1.85 (m, 1H), 1.47 (qd, *J* = 13.3, 3.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 139.2, 128.3, 126.8, 125.9, 116.9, 59.3, 44.7, 35.6, 34.3, 30.4, 25.3; IR (neat): 2923, 2834, 1687, 1215, 1123, 754, 698 cm^{-1}; HRMS (ESI) calc. for $C_{14}H_{19}O$ $(M+H)^+$ 225.1250 found 225.1254; $[\alpha]^{25}_D$ 2.3 (*c* = 1.07, CH_3CN); HPLC: (OJ, 0.2% isopropanol in hexane, 0.7 mL/min) retention times of 21.6 min (minor) and 25.2 min (major), 98% ee.



4.93

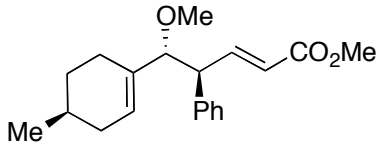
(4*S*,5*R*,*E*)-Methyl 5-methoxy-4-phenyl-5-((*S*)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)pent-2-enoate (4.93): To a flame-dried 100 mL flask containing Rh_2(*S*-DOSP)$_4$ (18.6 mg, 0.01 equiv) and (4-(methoxymethylene)cyclohexyl)benzene (**4.92**) (203 mg, 1.0 mmol, 1.0 equiv) in 20 mL dried hexane under argon atmosphere was added a solution of (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (**4.53**) (121.3 mg, 0.6 mmol, 0.6 equiv) in 20 mL dried hexane by syringe pump over 3 h at -25 °C. The solution was warmed up to room temperature. The mixture was concentrated under reduced pressure and purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.39) on silica gel to provide product **4.93** as colorless powder (178 mg, 47% yield) and recovery **4.92** (120.4 mg, 43% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10-7.36 (m, 11H), 5.76 (d, *J* = 15.9, 1.2 Hz, 1H), 5.53 (s, 1H), 3.80 (d, *J* = 9.2 Hz, 1H), 3.70 (s, 3H), 3.61 (t, *J* = 8.5 Hz, 1H), 3.24 (s, 3H), 2.34-2.43 (m, 1H), 2.02-2.13 (m, 3H), 1.83-1.97 (m, 2H), 1.55-1.66 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 150.2, 146.7, 139.7, 134.2, 128.6, 128.4, 128.3, 127.9, 126.9, 126.7, 126.0, 121.9, 88.4, 56.3, 52.1, 51.4, 40.0, 33.1, 29.6, 23.4; IR (neat): 2911, 1719, 1655, 1434, 1230, 1156, 1083, 703 cm^{-1}; M.p. 83-85 °C; HRMS (APCI) calc. for $C_{24}H_{25}O_2$ (M-MeOH+H)$^+$ 345.1849 found 345.1852; $[\alpha]^{25}_D$ -73.6 (*c* = 1.08, $CHCl_3$); HPLC: (AS-H, 0.5% isopropanol in hexane, 0.7 mL/min) retention times of 12.7 min (major) and 15.6 min (minor), 99% ee.



(*S*,*Z*)-1-(Methoxymethylene)-4-methylcyclohexane (4.94): To a mixture containing (Methoxymethyl)triphenylphosphonium chloride (17.0 g, 48 mmol, 1.2 equiv) in 150 mL dired THF was added KO*t*-Bu (6.5 g, 48 mmol, 1.2 equiv) in one portion at -78 °C. After 30 mins, 4-methylcyclopentanone (4.49 g, 40 mmol, 1.0 equiv) was added dropwise and the reaction mixture was warmed up to room temperature overnight. The mixture was quenched by H_2O (500 mL) and extracted by pentane (2 x 300 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was distillation by Kuargallor to afford the product **4.94** as colorless oil (4.54 g, 81% yield).

Spectroscopy was consistent with the reported value.[7] $[\alpha]^{25}_D$ 1.7 (*c* = 1.02, CH_3CN). HPLC: (AD-H, 100% hexane, 0.3 mL/min) retention times of 14.8 min (minor) and 15.5 min (major), 60% ee.

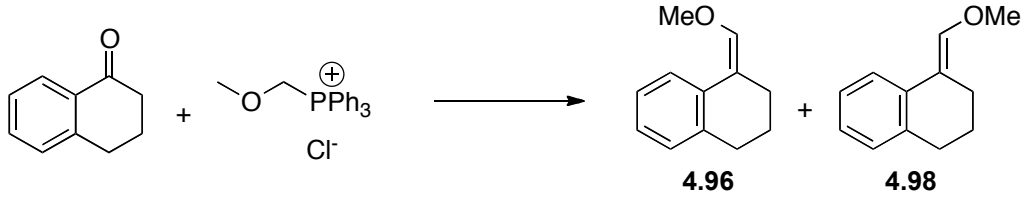


4.95

(4*S*,5*R*,*E*)-Methyl 5-methoxy-5-((*S*)-4-methylcyclohex-1-en-1-yl)-4-phenylpent-2-enoate (4.95): To a flame-dried 100 mL flask containing Rh_2(*S*-DOSP)$_4$ (9.4 mg, 0.01 equiv) and 1-(methoxymethylene)-4-methylcyclohexane (**4.94**) (140.2 mg, 1.0 mmol, 1.0

[7] Fujita, M.; Sakanishi, Y.; Nishii, M.; Yamataka, H.; Okuyama, T. *J. Org. Chem.* **2002**, *67*, 8130.

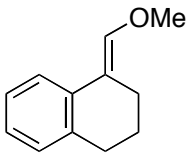
equiv) in 20 mL dried hexane under argon atmosphere was added a solution of (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (**4.53**) (121.3 mg, 0.6 mmol, 0.6 equiv) in 20 mL dried hexane by syringe pump over 3 h at -20 °C. The solution was warmed up to room temperature. The mixture was concentrated under reduced pressure and purified by flash chromatography (10/1 pentane/Et_2O, R_f: 0.31) on silica gel to provide **4.95** as colorless powder (135.2 mg, 43% yield) and recovery **4.94** (51.9 mg, 37% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (dd, *J* = 15.7, 7.6 Hz, 1H), 7.23-7.26 (m, 2H), 7.16-7.20 (m, 1H), 7.09-7.12 (m, 2H), 5.74 (dd, *J* = 15.7, 1.0 Hz, 1H), 5.40 (br, 1H), 3.74 (d, *J* = 9.1 Hz, 1H), 3.69 (s, 3H), 3.57 (t, *J* = 8.1 Hz, 1H), 3.20 (s, 3H), 1.95-2.05 (m, 1H), 1.73-1.84 (m, 2H), 1.49-1.62 (m, 2H), 1.23-1.31 (m, 1H), 1.03-1.10 (m, 1H), 0.84 (d, *J* = 6.7 H, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 150.4, 139.7, 133.8, 128.6, 128.3, 128.1, 126.8, 121.7, 88.5, 56.1, 52.1, 51.4, 33.5, 30.7, 28.5, 23.0, 21.6; IR (neat): 2907, 1722, 1435, 1269, 1161, 1090, 731, 699 cm^{-1}; M.p. 82-84 °C; HRMS (ESI) calc. for $C_{20}H_{26}ONa$ $(M+Na)^+$ 337.1774 found 337.1774; $[\alpha]^{25}_D$ -70.2 (*c* = 0.63, $CHCl_3$); HPLC: (AS-H, 1% isopropanol in hexane, 0.7 mL/min) retention times of 7.7 min (major) and 8.8 min (minor), 92% ee.



To an oven-dried flask containing (methoxymethyl)triphenylphosphonium chloride (17.0 g, 48 mmol, 1.2 equiv) in 150 mL dried THF was added potassium *tert*-butanoate (6.5 g, 48 mmol, 1.2 equiv) in one portion at -78 °C. After 30 mins, α-tetralone (5.85 g, 40 mmol, 1.0 equiv) was injected slowly. The solution was then warmed up to room

temperature over 2 h and was stirred for additional 3 h. The mixture was quenched by H_2O (250 mL) and extracted by pentane (2 x 200 mL). The organic layers were combined, dried ($MgSO_4$) and concentrated under reduced pressure. The crude residue was distillated under high vacuum to afford the product as a mixture of two isomers in 3/1 ratio in essentially quantitative yield. Isomeric pure compound was obtained by careful chromatography on silica gel with 10/1 pentane/DCM.

(*Z*)-1-(Methoxymethylene)-1,2,3,4-tetrahydronaphthalene (4.96): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 7.6 Hz, 1H), 7.12-7.17 (m, 1H), 7.06-7.10 (m, 2H), 6.09 (s, 1H), 3.72 (s, 3H), 2.84 (t, J = 6.1 Hz, 2H), 2.28-2.32 (m, 2H), 1.82-1.89 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.5, 136.4, 133.4, 128.8, 128.6, 125.7, 125.5, 111.6, 60.3, 30.7, 29.6, 24.1; IR (neat): 2928, 1645, 1483, 1452, 1258, 1244, 1203, 1136, 1073, 761 cm^{-1}; HRMS (APCI) calc. for $C_{12}H_{14}O$ $(M)^+$ 174.1039 found 174.1037.

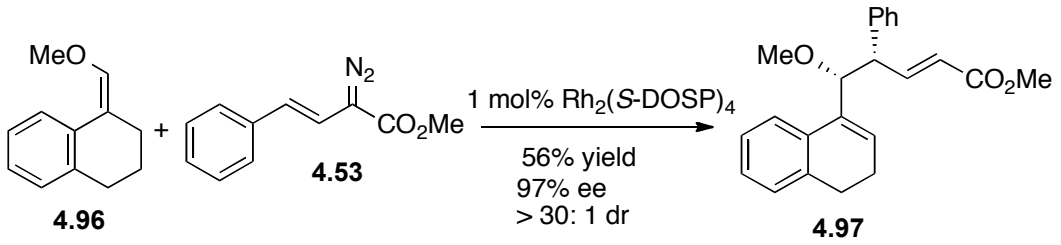


4.98

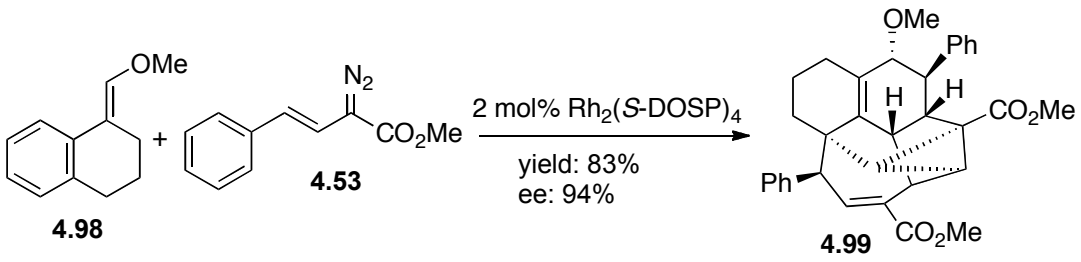
(*E*)-1-(Methoxymethylene)-1,2,3,4-tetrahydronaphthalene (4.98):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 7.2 Hz, 1H), 7.02-7.12 (m, 3H), 6.63 (t, J = 1.8Hz, 1H), 3.55 (s, 3H), 2.73 (t, J = 6.0 Hz, 2H), 2.49-2.54 (m, 2H), 1.76-1.82 (m, 2H). Spectroscopic data on the purified products was consistent with reported value.[8]

[8] Yamazaki, J.; Watanabe, T.; Tanaka, K. *Tetrahedron*: *Asymmetry* **2001**, *19*, 669.

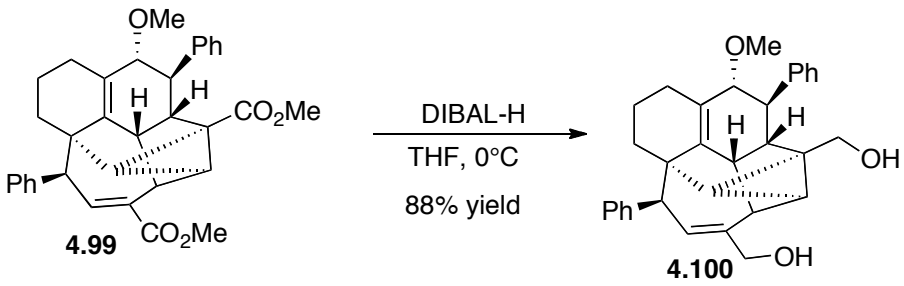


(4*S*,5*R*,*E*)-Methyl 5-(3,4-dihydronaphthalen-1-yl)-5-methoxy-4-phenylpent-2-enoate (4.97): To a flame-dried 25 mL flask containing Rh_2(*S*-DOSP)$_4$ (9.4 mg, 0.01 equiv) and (*Z*)-1-(methoxymethylene)-1,2,3,4-tetrahydronaphthalene (**4.96**) (87.1 mg, 0.50 mmol, 1.0 equiv) in 6 mL dried hexane under argon atmosphere was added a solution of (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (**4.53**) (161.8 mg, 0.8 mmol, 1.6 equiv) in 6 mL dried hexane by syringe pump over 3 h at -25 °C. The solution was warmed up to room temperature over 2 h. The mixture was concentrated under reduced pressure and purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.34) on silica gel to provide **4.97** as colorless powder (98.2 mg, 56% yield). Recrystallization from pentane afforded a nice crystal for X-ray crystallographic analysis. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.43 Hz, 1H), 7.39 (dd, *J* = 15.6, 7.4 Hz, 1H), 7.09-7.23 (m, 6H), 6.98 (d, *J* = 5.9 Hz, 2H), 5.85 (t, *J* = 4.4 Hz, 1H), 5.76 (d, *J* = 15.6 Hz, 1H), 4.28 (d, *J* = 7.43 Hz, 1H), 3.88 (t, *J* = 7.8 Hz, 1H), 3.71 (s, 3H), 3.33 (s, 3H), 2.47-2.56 (m, 1H), 2.10-2.30 (m, 2H), 1.97-2.07 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.0, 149.2, 140.2, 137.3, 133.3, 133.1, 130.0, 128.5, 128.4, 127.6, 126.83, 126.80, 126.3, 123.4, 122.3, 87.5, 56.7, 52.1, 51.4, 28.1, 22.6; IR (neat): 2934, 1720, 1435, 1270, 1197, 1093, 763, 729, 699 cm^{-1}; HRMS (ESI) calc. for $C_{23}H_{24}O_3Na$ $(M+Na)^+$ 371.1618 found 371.1615; HPLC: (OD-H, 1% isopropanol in hexane, 1.0 mL/min) retention times of 8.9 min (minor) and 19.1 min (major), 94% ee; $[\alpha]^{25}_D$ -7.9 (*c* = 0.44, $CHCl_3$).

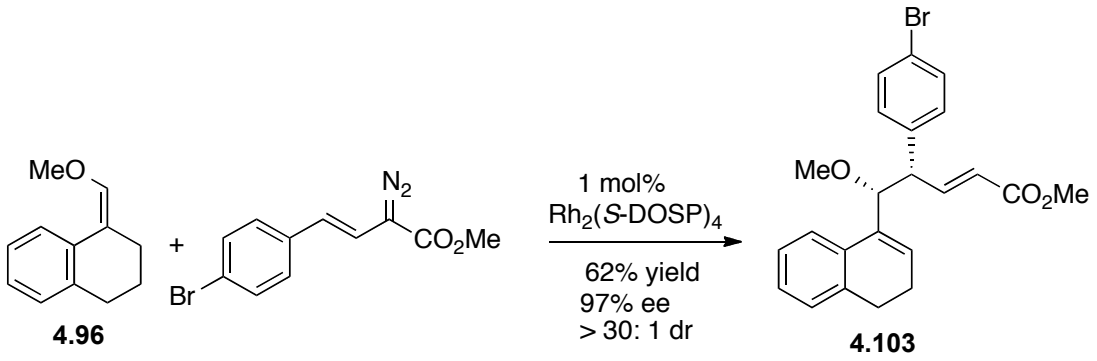


Product 4.99: To a flame-dried 100 mL flask containing Rh_2(*R*-DOSP)$_4$ (18.6 mg, 0.02 equiv) and (*E*)-1-(methoxymethylene)-1,2,3,4-tetrahydronaphthalene (88 mg, 0.5 mmol, 1.0 equiv) in 20 mL dried hexane under argon atmosphere was added a solution of (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (202 mg, 1.0 mmol, 2.0 equiv) in 20 mL dried hexane by syringe pump over 3 h at 0 °C. The solution was warmed up to room temperature and heated under reflux condition for 30 min. The mixture was concentrated under reduced pressure and purified by flash chromatography (7/3 pentane/Et_2O, R_f: 0.38) on silica gel to provide as colorless powder (226 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14-7.36 (m, 10H), 6.84 (s, 1H), 4.18 (d, *J* = 9.5 Hz, 1H), 3.80 (d, *J* = 4.2 Hz, 1H), 3.74 (s, 3H), 3.52 (s, 3H), 3.44 (t, *J* = 1.3 Hz, 1H), 3.00-3.08 (m, 1H), 3.01 (s, 3H), 2.62 (dd, *J* = 9.5, 2.9 Hz, 1H), 2.40 (dd, *J* = 8.1, 4.3 Hz, 1H), 2.13 (d, *J* = 5.6 Hz, 1H), 1.95-2.03 (m, 1H), 1.75-1.84 (m, 2H), 1.19-1.26 (m, 2H), 0.97-1.02 (m, 1H), -0.22--0.13 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 173.6, 168.3, 145.9, 145.5, 143.8. 142.4, 133.1, 131.5, 130.5, 130.0, 128.5, 128.4, 128.3, 128.2, 127.2, 126.1, 87.1, 60.0, 56.8, 55.8, 55.1, 52.3, 51.7, 45.1, 44.0, 41.8, 37.4, 37.1, 36.4, 35.9, 23.8, 17.9; IR (neat): 2927, 1710, 1435, 1237, 1109, 759, 701 cm^{-1}; HRMS (APCI) calc. for $C_{34}H_{35}O_5$ $(M+H)^+$ 523.2479 found 523.2484; $[\alpha]^{25}_D$ -46.3 (*c* = 1.04, $CHCl_3$), HPLC: ((R,R)-Whelk O1, 5%

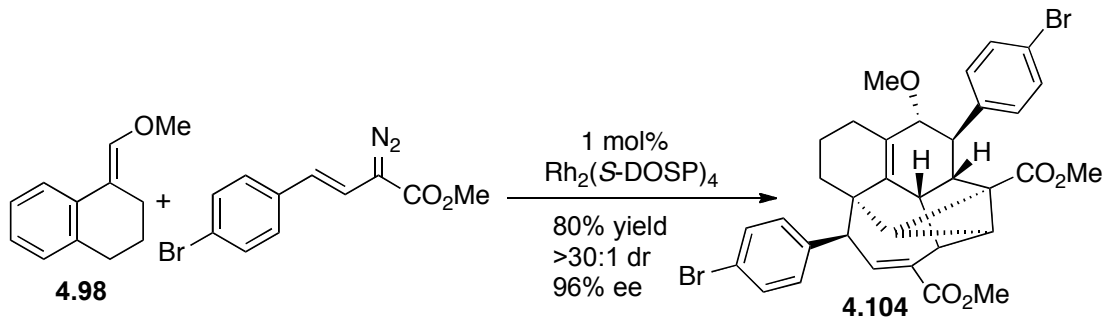
isopropanol in hexane, 0.7 mL/min) retention times of 39.5 min (major) and 55.4 min (minor), 94% ee.



Product 4.100: To a solution of product **4.99** (157 mg, 0.3 mmol, 1.0 equiv) in THF (10 mL) was added 1.8 mL of DIBAL-H (1.0 M in THF, 1.8 mmol, 6.0 equiv) at 0 °C dropwise. The mixture was warmed up to rt and stirred for 30 min. The solution was quenched by 1M of HCl aqueous solution and extracted by Et_2O (4 × 200 mL) and dried ($MgSO_4$), concentrated under reduced pressure to afford the crude alcohol, which was purified by flash column chromatography (100% Et_2O, R_f: 0.42) to provide **4.100** as a white powder (123 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16-7.33 (m, 10H), 5.40 (br, 1H), 4.36 (d, *J* = 9.8 Hz, 1H), 4.06 (s, 2H), 3.70 (d, *J* = 11.7 Hz, 1H), 3.62 (d, *J* = 2.0 Hz, 1H), 3.42 (d, *J* = 11.7 Hz, 1H), 3.11 (s, 3H), 2.97 (t, *J* = 3.8 Hz, 1H), 2.70 (t, *J* = 3.6 Hz, 1H), 2.55-2.62 (m, 2H), 1.92-2.02 (m, 1H), 1.72-1.80 (m, 3H), 1.61 (br, 2H), 1.06-1.22 (m, 2H), 0.93-0.99 (m, 1H), -0.23--0.10 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 144.3, 141.5, 135.5, 130.1, 129.6, 128.6, 127.8, 127.7, 127.6, 126.3, 126.0, 86.2, 68.8, 64.7, 59.6, 56.7, 56.5, 53.3, 45.6, 44.5, 39.6, 37.9, 36.9, 36.6, 29.0, 23.4, 17.8; IR (neat): 3363, 2926, 1452, 1109, 1008, 909, 766, 731, 701 cm^{-1}; HRMS (APCI) calc. for $C_{32}H_{35}O_3$ $(M+H)^+$ 467.2581 found 467.2574; $[\alpha]^{25}_D$ 0.12 (*c* = 1.56, $CHCl_3$).

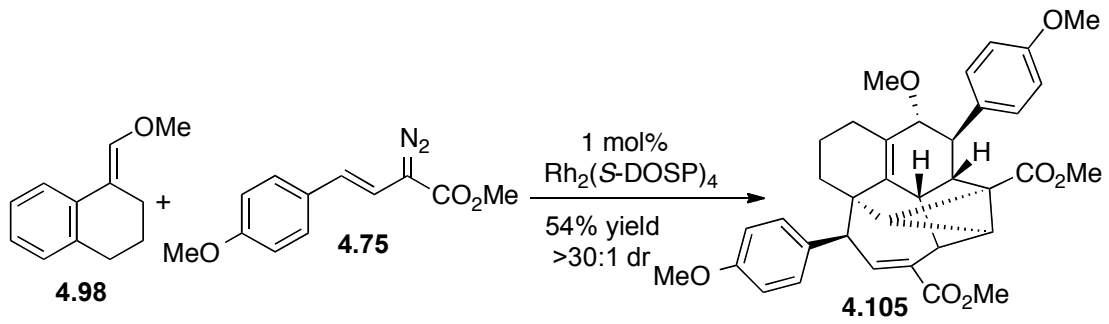


Product 4.103: To a flame-dried 25 mL flask containing Rh_2(*S*-DOSP)$_4$ (9.4 mg, 0.01 equiv) and (*Z*)-1-(methoxymethylene)-1,2,3,4-tetrahydronaphthalene (**4.96**) (87.1 mg, 0.50 mmol, 1.0 equiv) in 6 mL dried hexane under argon atmosphere was added a solution of (*E*)-methyl 4-(4-bromophenyl)-2-diazobut-3-enoate (169 mg, 0.6 mmol, 1.2 equiv) in 6 mL dried hexane by syringe pump over 3 h at -25 $^{\circ}$C. The solution was warmed up to room temperature over 2 h. The mixture was concentrated under reduced pressure and purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.29) on silica gel to provide **4.103** as colorless powder (109.8 mg, 62% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.6 Hz, 1H), 7.34 (dd, *J* = 15.6, 7.6 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 2H), 5.86 (br, 1H), 5.74 (d, *J* = 15.6 Hz, 1H), 4.23 (d, *J* = 7.6 Hz, 1H), 3.85 (t, *J* = 7.6 Hz, 1H), 3.72 (s, 3H), 3.33 (s, 3H), 2.52-2.59 (m, 1H), 2.22-2.30 (m, 1H), 2.14-2.10 (m, 1H), 2.04-2.09 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 148.1, 139.2, 137.2, 133.0, 132.9, 131.4, 130.3, 130.2, 127.7, 127.0, 126.3, 123.3, 122.6, 120.7, 87.2, 56.7, 51.5, 51.4, 28.1, 22.6; IR (neat): 2934, 1720, 1435, 1286, 1197, 1093, 825, 770, 732 cm^{-1}; HRMS (APCI) calc. for $C_{22}H_{20}O_2Br$ $(M\text{-}OCH_3)^+$ 395.0641 found 395.0643. HPLC: (OD-H, 1% isopropanol in hexane, 1.0 mL/min) retention times of 6.7 min (minor) and 8.5 min (major), 97% ee; $[\alpha]^{25}_D$ -32.0 (*c* = 1.07, $CHCl_3$).



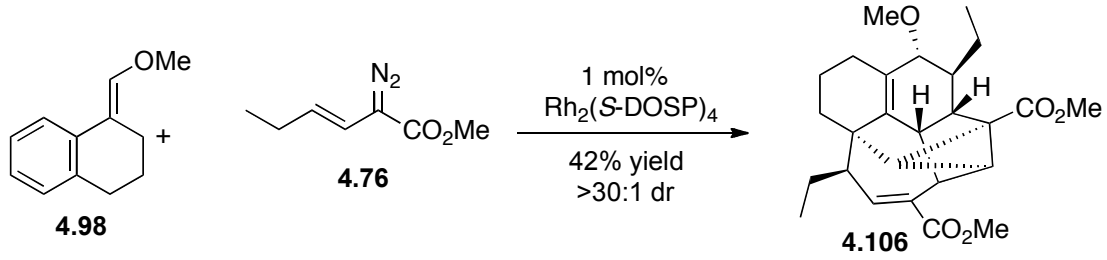
Product 4.104: To a flame-dried 100 mL flask containing Rh_2(*S*-DOSP)$_4$ (18.6 mg, 0.02 equiv) and (*E*)-1-(methoxymethylene)-1,2,3,4-tetrahydronaphthalene (**4.98**) (88 mg, 0.5 mmol, 1.0 equiv) in 20 mL dried hexane under argon atmosphere was added a solution of (*E*)-methyl 4-(4-bromophenyl)-2-diazobut-3-enoate (296 mg, 1.05 mmol, 2.1 equiv) in 20 mL dried hexane by syringe pump over 3 h at 0 $^{\circ}$C. The solution was warmed up to room temperature and heated under reflux condition for 30 min. The mixture was concentrated under reduced pressure and purified by flash chromatography (7/3 pentane/Et_2O, R_f: 0.32) on silica gel to afford product **4.104** as colorless formed powder (250 mg, 80% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40-7.47 (m, 4H), 7.15 (d, *J* = 8.6 Hz, 2H), 7.13 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.03 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.73 (br, 1H), 4.09 (d, *J* = 10.0 Hz, 1H), 3.76 (d, *J* = 2.4 Hz, 1H), 3.74 (s, 3H), 3.52 (s, 3H), 3.43 (t, *J* = 4.3 Hz, 1H), 3.07 (s, 3H), 3.02 (br, 1H), 2.95 (t, *J* = 3.4 Hz, 1H), 2.57 (dd, *J* = 10.0, 2.9 Hz, 1H), 2.39 (dd, *J* = 8.1, 3.8 Hz, 1H), 2.11 (d, *J* = 8.1 Hz, 1H), 1.95-2.03 (m, 1H), 1.75-1.84 (m, 2H), 1.23 (td, *J* = 13.8, 3.3 Hz, 1H), 1.03-1.09 (m, 1H), -0.17--0.04 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 173.1, 167.8, 144.7, 144.2, 143.9, 141.2, 132.8, 131.9, 131.6, 131.3, 131.2, 129.7, 121.0, 119.7, 59.8, 55.9, 55.3, 54.2, 52.2, 51.6, 44.8, 43.7, 41.3, 37.0, 36.8, 36.1, 35.6, 23.4, 17.9; IR (neat): 2930, 1713, 1487, 1436, 1250, 1108, 828, 753 cm^{-1}; HRMS

(APCI) calc. for $C_{34}H_{32}O_5Br_2$ $(M)^+$ 678.0611 found 678.0621; $[\alpha]^{25}_D$ -33.4 (*c* = 1.16, $CHCl_3$); HPLC: ((S,S)-Whelk O1, 9% isopropanol in hexane, 1.0 mL/min) retention times of 38.1 min (minor) and 41.9 min (minor), 96% ee.



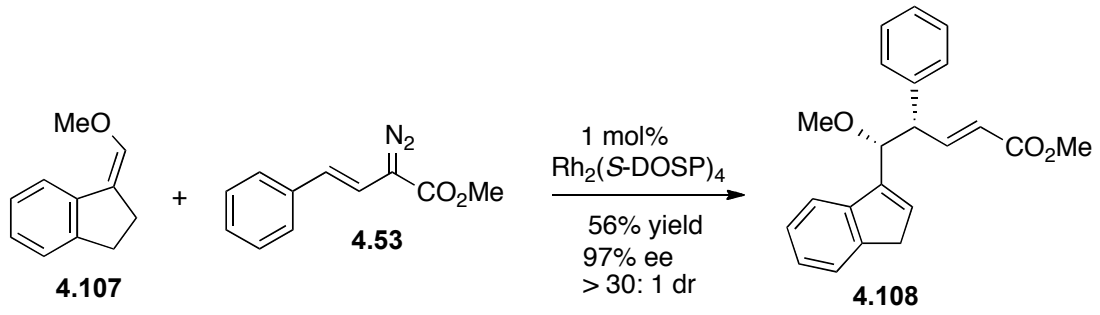
Product 4.105: To a flame-dried 100 mL flask containing Rh_2(*S*-DOSP)$_4$ (18.6 mg, 0.02 equiv) and (*E*)-1-(methoxymethylene)-1,2,3,4-tetrahydronaphthalene (**4.98**) (88 mg, 0.5 mmol, 1.0 equiv) in 20 mL dried hexane under argon atmosphere was added a solution of (*E*)-methyl 2-diazo-4-(4-methoxyphenyl)but-3-enoate (244 mg, 1.05 mmol, 2.1 equiv) in 20 mL dried hexane by syringe pump over 3 h at 0 °C. The solution was warmed up to room temperature and heated under reflux condition for 30 min. The mixture was concentrated under reduced pressure and purified by flash chromatography (1/1 pentane/Et_2O, R_f: 0.29) on silica gel to afford product **4.105** as colorless formed powder (158 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.21 (m, 2H), 7.13-7.16 (m, 1H), 7.03-7.07 (m, 1H), 6.79-6.91 (m, 5H), 4.12 (d, *J* = 10.0 Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 3.74 (s, 4H), 3.41 (t, *J* = 4.3 Hz, 1H), 3.07 (s, 3H), 3.02 (m, 1H), 2.95 (m, 1H), 2.58 (dd, *J* = 10.0, 2.9 Hz, 1H), 2.38 (dd, *J* = 8.1, 3.8 Hz, 1H), 2.10 (d, *J* = 8.1 Hz, 1H), 1.92-2.03 (m, 1H), 1.75-1.83 (m, 2H), 1.18-1.24 (m, 1H), 0.97-1.06 (m, 1H), -0.17--0.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.4, 168.1, 158.5, 57.6, 146.0, 143.5, 137.4,

134.4, 132.9, 131.0, 130.9, 130.5, 128.7, 27.8, 113.9, 113.5, 112.9, 86.7, 59.8, 55.7, 55.6, 55.1, 53.9, 52.0, 51.4, 44.7, 43.7, 41.4, 37.1, 36.8, 36.0, 35.7, 23.5, 17.7; IR (neat): 2949, 1712, 1510, 1246, 1177, 1109, 757 cm^{-1}; HRMS (APCI) calc. for $C_{26}H_{35}O_5$ $(M)^+$ 582.2612 found 582.2618; $[\alpha]^{25}_D$ -51.7 (*c* = 1.22, $CHCl_3$).



Product 4.106: To a flame-dried 100 mL flask containing Rh_2(*S*-DOSP)$_4$ (18.6 mg, 0.02 equiv) and (*E*)-1-(methoxymethylene)-1,2,3,4-tetrahydronaphthalene (**4.98**) (88 mg, 0.5 mmol, 1.0 equiv) in 20 mL dried hexane under argon atmosphere was added a solution of (*E*)-methyl 2-diazohex-3-enoate (170 mg, 1.1 mmol, 2.2 equiv) in 20 mL dried hexane by syringe pump over 3 h at 0 °C. The solution was warmed up to room temperature and heated under reflux condition for 30 min. The mixture was concentrated under reduced pressure and purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.31) on silica gel to afford product **4.106** as colorless formed powder (89.9 mg, 42% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.91 (br, 1H), 3.70-3.76 (m, 4H), 3.60 (s, 3H), 3.38 (s, 3H), 3.26 (t, *J* = 4.3 Hz, 1H), 2.60 (m, 1H), 2.53 (m, 2H), 2.23 (dd, *J* = 8.2, 4.3 Hz, 1H), 2.10 (m, 2H), 1.95 (d, *J* = 8.6 Hz, 1H), 1.80-1.90 (m, 3H), 1.50-1.74 (m, 5H), 1.17-1.25 (m, 1H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 173.9, 168.1, 145.6, 142.9, 134.0, 131.4, 83.5, 59.4, 52.0, 51.4, 50.9, 50.8, 47.8, 44.9, 42.3, 42.2, 37.0, 36.3, 36.1, 35.3, 25.0, 23.9, 23.7, 19.8, 12.1, 9.9; IR (neat): 2933, 1709, 1435, 1228,

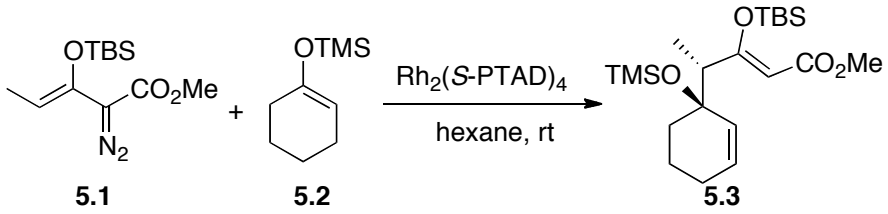
1112, 732 cm^{-1}; HRMS (APCI) calc. for $C_{26}H_{35}O_5$ $(M+H)^+$ 427.2479 found 427.2484; $[\alpha]^{25}_D$ -1.0 (*c* = 0.89, $CHCl_3$).



(4*S*,5*R*,*E*)-Methyl 5-(1*H*-inden-3-yl)-5-methoxy-4-phenylpent-2-enoate (4.108): To a flame-dried 25 mL flask containing Rh_2(*S*-DOSP)$_4$ (18.7 mg, 0.01 equiv) and (*Z*)-1-(methoxymethylene)-2,3-dihydro-1*H*-indene (**4.107**) (160.2 mg, 1.0 mmol, 1.0 equiv) in 20 mL dried hexane under argon atmosphere was added a solution of (*E*)-methyl 4-phenyl-2-diazobut-3-enoate (**4.53**) (283.1 mg, 1.4 mmol, 1.4 equiv) in 20 mL dried hexane by syringe pump over 3 h at -25 °C. The solution was warmed up to room temperature over 2 h. The mixture was concentrated under reduced pressure and purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.28) on silica gel to provide **4.108** as colorless oil (183.4 mg, 56% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.42 (dd, *J* = 15.6, 7.8 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.15-7.24 (m, 4H), 7.08-7.13 (m, 2H), 3.71 (s, 3H), 3.31 (s, 3H), 3.26-3.35 (m, 1H), 3.15 (d, *J* = 23.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 148.7, 144.6, 1428, 141.9, 140.2, 132.6, 128.44, 128.39, 126.9, 126.1, 124.8, 123.9, 122.5, 120.3, 82.8, 57.1, 52.6, 51.4, 37.7; IR (neat): 2947, 1720, 1455, 1165, 1094, 910, 769, 698 cm^{-1}; HRMS (ESI) calc. for $C_{22}H_{22}O_3Na$ $(M+Na)^+$ 357.1461 found 357.1459; HPLC: (OD-H, 1% isopropanol in hexane, 1.0 mL/min) retention times of 13.0 min (major) and 14.4 min (minor), 97% ee; $[\alpha]^{25}_D$ 1.20 (*c* = 1.20, $CHCl_3$).

Experiment for Chapter V: Miscellaneous Reactions with Vinylcarbenoids

Facial Approach to Alkynoates by Vinylogous Reactivity of Vinylcarbenoids

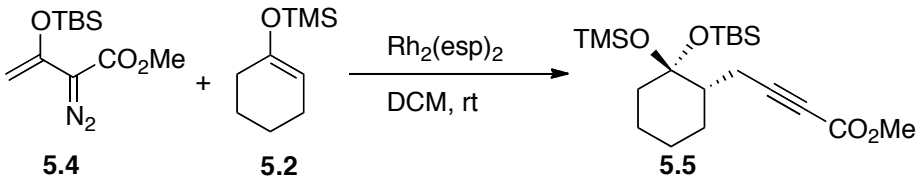


5.1 **5.2** **5.3**

(*R*,*Z*)-Methyl 3-((*tert*-butyldimethylsilyl)oxy)-4-((*R*)-1-((trimethylsilyl)oxy)cyclohex-2-en-1-yl)pent-2-enoate (5.3): In an oven-dried 25 mL flask, Rh_2(S-PTAD)$_4$ (4.8 mg, 0.01 equiv) and trimethylsiloxycyclohexene **5.2** (0.26 mg, 1.50 mmol, 5.0 equiv) were dissolved in 6 mL hexene under argon atmosphere. Diazo **5.1** (78 mg, 0.30 mmol, 1.0 equiv) in 6 mL hexane was injected by syringe pump over 1 h. The solution was concentrated by vacuum and purified by flash chromatography (40/1 pentane/Et_2O, R_f: 0.47) to provide 79.7 mg colorless oil in 66 % yield. ^{1}H NMR (500MHz, $CDCl_3$): δ 5.74-5.79 (m, 1H), 5.25 (s, 1H), 3.63 (s, 3H), 2.24 (q, *J* = 7.0 Hz, 1H), 1.90-2.03 (m, 2H), 1.78-1.84 (m, 1H), 1.58-1.73 (m, 3H), 1.14 (d, *J* = 7.0 Hz, 3H), 0.97 (s, 9H), 0.22 (s, 3H), 0.17 (s, 3H), 0.08 (s, 6H); ^{13}C NMR (100MHz, $CDCl_3$): δ 170.5, 166.3, 131.8, 129.9, 100.1, 74.1, 52.1, 50.4, 34.1, 25.9, 25.0, 19.2, 18.5, 14.5, 2.4, -3.9, -4.0; IR (neat): 2952, 2858, 1723, 1626, 1251, 1198, 1159, 1072, 899, 840, 782 cm^{-1}; HRMS (ESI) calc for $C_{21}H_{40}O_4Si_2Na$ $(M+Na)^+$ 435.2357 found 435.2340; HPLC: (OD-H, 0 % isopropanol in hexane, 0.09 mL/min) retention times of 47.1 (minor) and 50.5 (major), 79 % ee; $[\alpha]^{25}_D$ 77.9 (*c* = 2.02, $CHCl_3$).

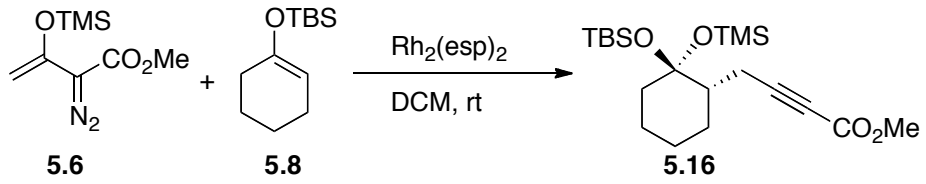
General Procedure for the vinylogous alkylation formation

To a flame-dried 25 mL flask containing $Rh_2(esp)_2$ (7.7 mg, 0.02 equiv) and vinyl ethers (0.5 mmol, 1.0 equiv) in 6 mL dried DCM under argon atmosphere was added a solution of siloxyvinyldiazoacetate (1.0 mmol, 2.0 equiv) in 6 mL dried DCM by syringe pump over 3 h at room temperature. The solution was stirred at room temperature for additional 1h. The mixture was concentrated under reduced pressure and purified by flash chromatography (pentane/Et_2O) on silica gel to provide product.



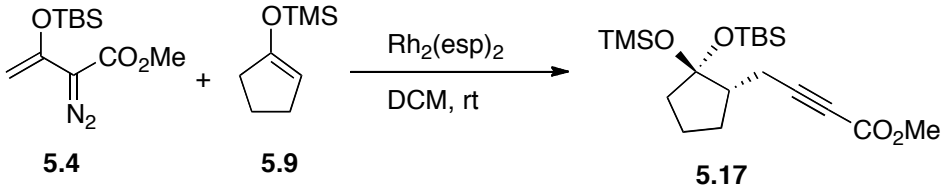
5.4 **5.2** **5.5**

Methyl 4-((1*S*,2*S*)-2-((*tert*-butyldimethylsilyl)oxy)-2-((trimethylsilyl)oxy)cyclohexyl) but-2-ynoate (5.5): Derived from Methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (256 mg , 1.0 mmol, 2.0 equiv) and (cyclohex-1-en-1-yloxy)trimethylsilane (85 mg, 0.5 mmol, 1 equiv), and purified through column chromatography (30/1 pentane/ethyl ether) on silica gel (0.159 g, 80% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.76 (s, 3H), 2.71 (dd, *J* = 17.4, 3.1 Hz, 1H), 2.11 (dd, *J* = 17.4, 10.7 Hz, 1H), 1.90-1.93 (m, 1H), 1.83 (dm, *J* = 11.9 Hz, 1H), 1.68 (dm, *J* = 12.8 Hz, 1H), 1.50-1.61 (m, 3H), 1.42-1.48 (m, 1H), 1.12-1.29 (m, 2H), 0.86 (s, 9H), 0.16 (s, 9H), 0.09 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 154.3, 99.3, 90.6, 73.2, 52.5, 47.7, 41.6, 29.3, 26.0, 25.5, 23.7, 18.8, 2.0, -2.5, -3.0; IR (neat): 2934, 2240, 1709, 1435, 1246, 1049, 806 cm^{-1}; HRMS (ESI) calc. for $C_{20}H_{38}O_4Si_2$ $(M+Na)^+$ 421.2201 found 421.2200; M.p. 50-52°C.



5.6 **5.8** **5.16**

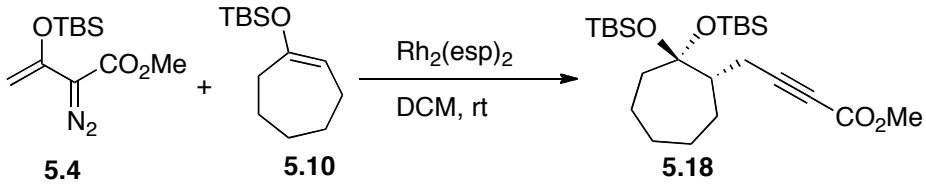
Methyl 4-((1*S*,2*R*)-2-((*tert*-butyldimethylsilyl)oxy)-2-((trimethylsilyl)oxy)cyclohexyl) but-2-ynoate (5.16): Derived from methyl 2-diazo-3-((trimethylsilyl)oxy)but-3-enoate (**5.6**) (214.3 mg, 1.0 mmol, 2.0 equiv) and *tert*-butyl(cyclohex-1-en-1-yloxy)dimethyl silane (**5.8**) (106.2 mg, 0.5 mmol, 1 equiv), and purified through column chromatography (30/1 pentane/ethyl ether) on silica gel to provide **5.16** as colorless oil (97.5 mg, 49% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.75 (s, 3H), 2.76 (dd, *J* = 17.6, 2.9 Hz, 1H), 2.18 (dd, *J* = 17.6, 10.6 Hz, 1H), 1.88-1.93 (m, 1H), 1.81-1.86 (m, 1H), 1.56-1.68 (m, 3H), 1.47-1.53 (m, 2H), 1.25 (qd, *J* = 11.9, 2.9 Hz, 1H), 1.12-1.20 (m, 1H), 0.92 (s, 9H), 0.15 (s, 6H), 0.12 (s, 9H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 154.4, 99.7, 90.6, 73.2, 52.5, 47.2, 41.4, 29.0, 26.1, 25.2, 23.9, 18.6, 18.4, 1.9, -1.8, -2.6; IR (neat): 2934, 2237, 1716, 1246, 1049, 833, 729 cm^{-1}; HRMS (ESI) calc. for $C_{20}H_{38}O_4Si_2$ $(M+Na)^+$ 421.2201 found 421.2200.



5.4 **5.9** **5.17**

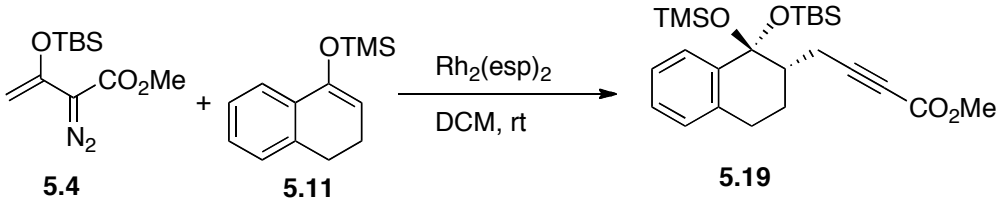
Methyl 4-((1*S*,2*S*)-2-((*tert*-butyldimethylsilyl)oxy)-2-((trimethylsilyl)oxy)cyclopentyl) but-2-ynoate (5.17): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**5.4**) (256 mg, 1.0 mmol, 2.0 equiv) and (cyclopent-1-en-1-yloxy)trimethylsilane (**5.9**) (99.2 mg, 0.5 mmol, 1 equiv), and purified through column chromatography (30/1

pentane/ethyl ether, R_f: 0.42) in silica gel (0.134 g, 63% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.75 (s, 3H), 2.49 (dd, *J* = 17.6, 3.5 Hz, 1H), 2.24 (dd, *J* = 17.6, 9.8 Hz, 1H), 1.92-1.98 (m, 2H), 1.75-1.81 (m, 2H), 1.57-1.71 (m, 2H), 1.35-1.43 (m, 1H), 0.84 (s, 9H), 0.16 (s, 9H), 0.09 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.3, 106.1, 90.3, 72.6, 52.5, 48.3, 40.2, 28.0, 25.8, 19.7, 18.1, 17.9, 1.7, -2.7, -3.2; IR (neat): 2954, 2238, 1717, 1247, 831, 777 cm^{-1}; HRMS (ESI) calc. for $C_{19}H_{36}O_4Si_2Na$ $(M+Na)^+$ 407.2044 found 407.2044.

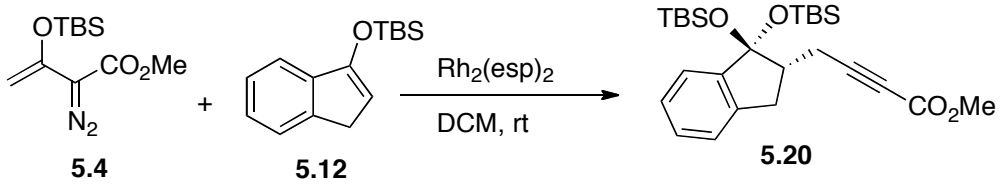


5.4 **5.10** **5.18**

(*S*)-Methyl 4-(2,2-bis((*tert*-butyldimethylsilyl)oxy)cycloheptyl)but-2-ynoate (5.18): Derived from Methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**5.4**) (256 mg, 1.0 mmol, 2.0 equiv) and *tert*-butyl(cyclohept-1-en-1-yloxy)dimethylsilane (**5.10**) (113 mg, 0.5 mmol, 1 equiv) and purified through column chromatography (30/1 pentane/ethyl ether, R_f: 0.56) on silica gel (0.291 g, 81% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.65 (s, 3H), 2.65 (d, *J* = 17.6, 2.4 Hz, 1H), 2.07 (dd, *J* = 17.6, 11.4 Hz, 1H), 1.56-1.80 (m, 6H), 1.35-1.50 (m, 3H), 1.21-1.33 (m, 2H), 0.82 (s, 9H), 0.77 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H), 0.02 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 154.4, 102.6, 91.0, 77.3, 77.0, 76.7, 72.9, 52.5, 52.4, 47.5, 27.3, 26.3, 26.2, 26.0, 25.6, 20.5, 20.1, 18.4, 18.3, -1.8, -2.3, -2.5, -3.0; IR (neat): 2952, 2928, 2857, 2237, 1717, 1471, 1462, 1434, 1248, 1179, 1150, 1114, 1072, 1022, 1004, 980 cm^{-1}; HRMS (ESI) calc. for $C_{24}H_{46}O_4Si_2Na$ $(M+Na)^+$ 477.2827 found 477.2827.

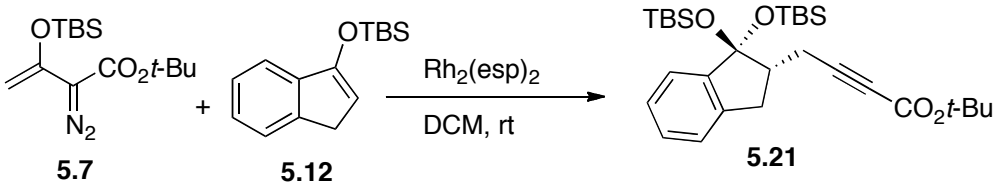


Methyl 4-((1*R*,2*S*)-1-((*tert*-butyldimethylsilyl)oxy)-1-((trimethylsilyl)oxy)-1,2,3,4-tetrahydronaphthalen-2-yl)but-2-ynoate (5.19): Derived from Methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**5.4**) (256 mg, 1.0 mmol, 2.0 equiv) and ((3,4-dihydronaphthalen-1-yl)oxy)trimethylsilane (**5.11**) (109 mg, 0.5 mmol, 1 equiv), and purified through column chromatography (30/1 pentane/ethyl ether, R_f: 0.38) in silica gel (0.154 g, 69% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55-7.58 (m, 1H), 7.15-7.19 (m, 2H), 7.03-7.06 (m, 1H), 3.78 (s, 3H), 2.76-2.89 (m, 3H), 2.31 (dd, *J* = 17.6, 11.4 Hz, 1H), 2.12-2.20 (m, 1H), 2.05 (tm, *J* = 11.0 Hz, 1H), 1.81-1.89 (m, 1H), 0.78 (s, 9H), 0.17 (s, 3H), 0.09 (s, 3H), -0.05 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.2, 140.6, 135.7, 128.5, 127.7, 126.7, 125.6, 97.9, 89.7, 73.4, 52.6, 47.0, 28.3, 25.9, 24.8, 19.1, 18.1, 1.4, -2.1, -2.4; IR (neat): 2953, 2929, 2238, 1717, 1249, 1069, 861, 797 cm^{-1}; HRMS (ESI) calc. for $C_{24}H_{38}O_4Si_2Na$ $(M+Na)^+$ 469.2201 found 469.2199; M.p. 43-46 °C.



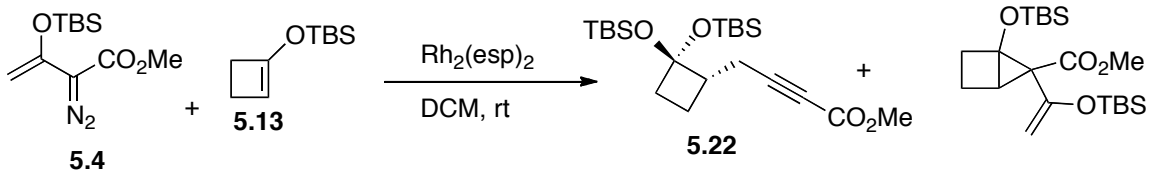
(*R*)-Methyl 4-(1,1-bis((*tert*-butyldimethylsilyl)oxy)-2,3-dihydro-1*H*-inden-2-yl)but-2-ynoate (5.20): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**5.4**) (256 mg, 1.0 mmol, 2.0 equiv) and ((1*H*-inden-3-yl)oxy)(*tert*-butyl)dimethylsilane (**5.12**) (123 mg, 0.5 mmol, 1 equiv) and purified through column chromatography (30/1

pentane/ethyl ether, R_f: 0.42) in silica gel (79.4 mg, 33% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.6 Hz, 1H), 7.25-7.27 (m, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 3.79 (s, 3H), 3.17 (dd, *J* = 15.2, 6.7 Hz, 1H), 2.7-2.62 (q, *J* =15.2, 8.1 Hz, 1H), 2.72-2.76 (m, 1H), 2.67 (dd, *J* = 15.2, 8.1 Hz, 1H), 2.52-2.62 (m, 2H), 0.96 (s, 9H), 0.77 (s, 9H), 0.18 (s, 3H), -0.05 (s, 3H), -0.07 (s, 3H), -0.10 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 154.2, 145.6, 140.4, 128.6, 125.0, 122.9, 105.7, 89.1, 77.3, 77.0, 76.7, 73.2, 52.6, 51.4, 35.0, 25.9, 25.7, 18.5, 18.2, 18.1, -2.5, -3.1, -3.2, -3.3; IR (neat): 2929, 2952, 2856, 2239, 1718, 1472, 1462, 1435, 1247, 1190, 1157, 1141, 1059, 878 cm^{-1}; HRMS (APCI) calc. for $C_{26}H_{43}O_4Si_2$ $(M+H)^+$ 475.2694 found 475.2698.

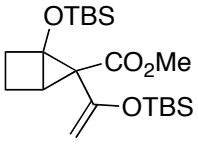


(*R*)-*tert*-Butyl 4-(1,1-bis((*tert*-butyldimethylsilyl)oxy)-2,3-dihydro-1*H*-inden-2-yl)but-2-ynoate (5.21): Derived from *tert*-butyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**5.7**) (298 mg, 1.0 mmol, 2 equiv) and ((1*H*-inden-3-yl)oxy)(*tert*-butyl)dimethylsilane (**5.12**) (123 mg, 0.5 mmol, 1 equiv), and purified through column chromatography (30/1 pentane/ethyl ether, R_f: 0.46) in silica gel to provide **5.21** as colorless oil (0.219 g, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.6 Hz, 1H), 7.30-7.35 (m, 1H), 7.24-7.26 (m, 3H), 3.79 (s, 3H), 3.25 (dd, *J* = 15.2, 6.7 Hz, 1H), 2.60-2.75 (m, 2H), 2.47-2.57 (m, 2H), 1.51 (s, 9H), 0.96 (s, 9H), 0.75 (s, 9H), 0.15 (s, 3H), 0.02 (s, 3H), -0.05 (s, 3H), -0.12 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 152.9, 145.8, 140.3, 128.6, 126.3, 125.0, 123.0, 105.8, 86.2, 83.0, 77.2, 77.0, 76.8, 74.8, 51.4, 35.1,

28.0, 25.9, 25.8, 18.5, 18.2, 18.1, -2.4, -3.06, -3.1, -3.3; IR (neat): 1709, 1374, 1255, 1205, 1170, 1104, 988 cm^{-1}; HRMS (APCI) calc. for $C_{25}H_{39}O_3Si_2$ $(M\text{-}OC(CH_3)_3)^+$ 443.2438 found 443.2433.

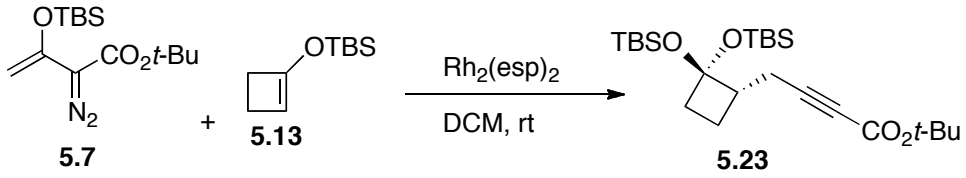


(*S*)-Methyl 4-(2,2-bis((*tert*-butyldimethylsilyl)oxy)cyclobutyl)but-2-ynoate (5.22): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**5.4**) (256 mg, 1.0 mmol, 2.0 equiv) and *tert*-butyl(cyclobut-1-en-1-yloxy)dimethylsilane (**5.13**) (92 mg, 0.5 mmol, 1.0 equiv), and purified through column chromatography (30/1 pentane/ethyl ether, R_f: 0.42) in silica gel (0.0941 g, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.74 (s, 3H), 2.59-2.69 (m, 1H), 2.51 (dd, *J* = 17.2, 5.9 Hz, 1H), 2.44 (dd, *J* = 17.2, 5.9 Hz, 1H), 2.13-2.14 (m, 2H), 1.83-1.93 (m, 1H), 1.29-1.43 (m, 1H), 0.89 (s, 9H), 0.88 (s, 9H), 0.16 (s, 3H), 0.15 (s, 3H), 0.13 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 154.3, 98.2, 89.0, 77.3, 77.0, 76.7, 72.7, 52.5, 48.4, 48.4, 38.3, 25.8, 18.7, 18.5, 18.0, 17.9; IR (neat): 2952, 2929, 2857, 2237, 1717, 1472, 1462, 1434, 1245, 1217, 1193, 1162, 1120, 1071, 1042, 992, 938 cm^{-1}; HRMS (APCI) calc. for $C_{21}H_{41}O_4Si_2$ $(M+H)^+$ 413.2538 found 413.2533.



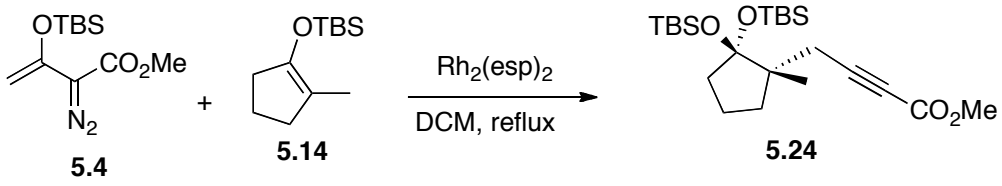
Methyl 1-((*tert*-butyldimethylsilyl)oxy)-5-(1-((*tert*-butyldimethylsilyl)oxy)vinyl) bicyclo[2.1.0]pentane-5-carboxylate: Derived from *tert*-butyl 3-((*tert*-

butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**5.7**) (298 mg, 1.0 mmol, 2 equiv) and *tert*-butyl(cyclobut-1-en-1-yloxy)dimethylsilane (**5.13**) (92 mg, 0.5 mmol, 1.0 equiv), and purified through column chromatography (30/1 pentane/ethyl ether, R_f: 0.50) on silica gel to provide the product as colorless oil (0.1052 g, 49% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.44 (s, 1H), 4.23 (s, 1H), 3.65 (s, 3H), 2.79 (d, *J* = 4.2 1H), 2.34 (td, *J* =10.4, 4.2 Hz, 1H), 2.11-2.17 (m, 1H), 2.96-2.04 (m, 1H), 1.13-1.18 (m, 1H), 0.90 (s, 9H), 0.85 (s, 9H), 0.20 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 170.4, 150.0, 95.2, 77.2, 77.0, 76.8, 68.7, 51.6, 45.0, 37.9, 31.5, 25.6, 17.7, 16.7, 5.0, 4.7, 4.2, 4.0; IR (neat): 2949, 2929, 2857, 1720, 1638, 1472, 1462, 1434, 1359, 1277, 1248, 1221, 1170, 1119, 1083, 1059, 1024, 1005, 959, 939 cm^{-1}; HRMS (APCI) calc. for $C_{21}H_{41}O_4Si_2$ $(M+H)^+$ 413.2538 found 413.2535.

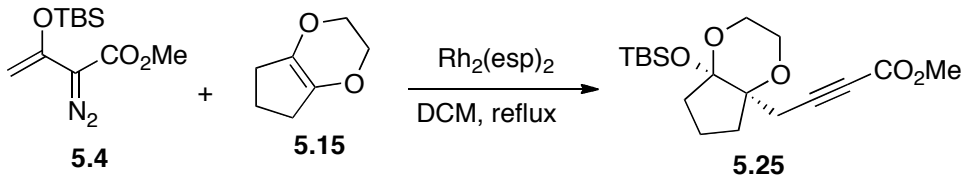


(*S*)-*tert*-Butyl 4-(2,2-bis((*tert*-butyldimethylsilyl)oxy)cyclobutyl)but-2-ynoate (5.23): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**5.4**) (256 mg, 1.0 mmol, 2.0 equiv) and *tert*-butyl(cyclobut-1-en-1-yloxy)dimethylsilane (**5.13**) (92 mg, 0.5 mmol, 1.0 equiv), and purified through column chromatography (30/1 pentane/ethyl ether, R_f: 0.42) on silica gel to provide **5.23** as colorless oil (0.2237 g, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.61-2.67 (m, 1H), 2.48 (dd, *J* = 17.2, 5.9 Hz, 1H), 2.41 (dd, *J* = 17.2, 5.9 Hz, 1H), 2.14-2.21 (m, 2H), 1.84-1.91 (m, 1H), 1.48 (s, 9H), 0.88-0.96 (m, 1H), 0.90 (s, 9H), 0.89 (s, 9H), 0.161 (s, 3H), 0.156 (s, 3H), 0.13 (s, 3H), 0.12 (s, 3H);

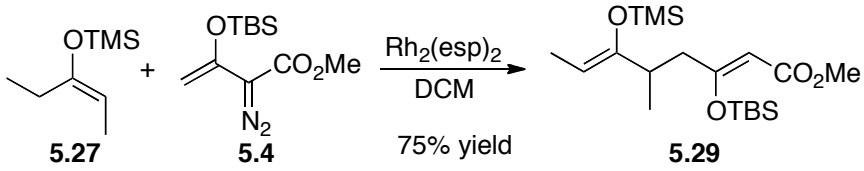
^{13}C NMR (100 Hz, $CDCl_3$): δ 153.2, 98.5, 86.2, 82.9, 77.5, 77.2, 76.9, 74.6, 48.6, 38.5, 28.2, 26.1, 26.0, 18.8, 18.21, 18.15, 3.2, 2.6; IR (neat): 2953, 2930, 2896, 2857, 2237, 1708, 1472, 1463, 1391, 1368, 1250, 1218, 1161, 1120, 1069, 1042, 993, 938, 812 cm^{-1}; HRMS (APCI) calc. for $C_{20}H_{37}O_3Si_2$ $(M\text{-}OC(CH_3)_3)^+$ 381.2281 found 381.2273.



(*S*)-Methyl 4-(2,2-bis((*tert*-butyldimethylsilyl)oxy)-1-methylcyclopentyl)but-2-ynoate (5.24): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**5.4**) (154 mg, 0.6 mmol, 2.0 equiv) and *tert*-butyldimethyl((2-methylcyclopent-1-en-1-yl)oxy)silane (**5.14**) (64 mg, 0.3 mmol, 1.0 equiv) under refluxed DCM, and purified through column chromatography (30/1 pentane/ethyl ether, R_f: 0.42) on silica gel to provide product **5.24** as colorless oil (0.0743 g, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.75 (s, 3H), 2.53 (d, *J* = 17.2 Hz, 1H), 2.29 (d, *J* = 17.2 Hz, 1H), 2.00-2.06 (m, 1H), 1.81-1.90 (m, 1H), 1.50-1.72 (m, 4H), 1.03 (s, 3H), 0.89 (s, 9H), 0.87 (s, 3H), 0.16 (s, 3H), 0.141 (s, 3H), 0.135 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 154.3, 108.1, 90.1, 77.3, 77.0, 76.7, 73.7, 52.5, 49.6, 36.5, 33.8, 26.1, 26.0, 25.5, 21.4, 18.4, 17.9, -1.6, -1.8, -2.1, -2.4; IR (neat): 2953, 2930, 2857, 2235, 1717, 1472, 1463, 1434, 1248, 1159, 1117, 1074, 1046, 1000, 938, 889 cm^{-1}; HRMS (APCI) calc. for $C_{23}H_{44}O_4Si_2$ $(M+H)^+$ 440.2773 found 440.2771.

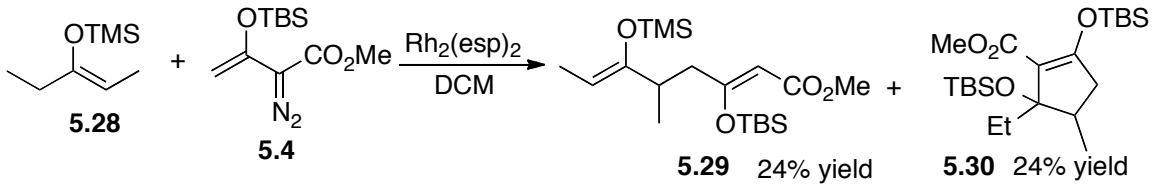


Methyl 4-((4a*R*,7a*S*)-7a-((*tert*-butyldimethylsilyl)oxy)hexahydro-2*H*-cyclopenta[*b*][1,4]dioxin-4a-yl)but-2-ynoate (5.25): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**5.4**) (256 mg, 1.0 mmol, 2.0 equiv) and 3,5,6,7-tetrahydro-2*H*-cyclopenta[*b*][1,4]dioxine (**5.15**) (64.2 mg, 0.5 mmol, 1.0 equiv) under refluxed DCM, and purified through column chromatography (10/1 pentane/ethyl ether, R_f: 0.26) on silica gel to provide product **5.25** as colorless oil (93.6 g, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.89-3.95 (m, 1H), 3.76-3.83 (m, 1H), 3.74 (s, 3H), 3.56 (dt, *J* = 11.3, 3.0 Hz, 1H), 3.49 (dt, *J* = 11.3, 3.0 Hz, 1H), 2.77 (dd, *J* = 17.2, 1.0 Hz, 1H), 2.47 (d, *J* = 17.2 Hz, 1H), 2.14-2.23 (m, 1H), 1.94-2.03 (m, 1H), 1.57-1,86 (m, 4H), 0.89 (s, 9H), 0.13 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 154.0, 102.2, 87.0, 81.9, 74.0, 59.8, 59.4, 52.5, 35.7, 28.1, 26.4, 25.7, 18.1, 17.4, -3.2, -3.3; IR (neat): 2954, 2857, 2239, 1715, 1250, 1108, 1076, 1030, 837 cm^{-1}; HRMS (ESI) calc. for $C_{18}H_{30}O_5SiNa$ $(M+Na)^+$ 377.1755 found 377.1756.



(2*Z*,6*Z*)-Methyl 3-((*tert*-butyldimethylsilyl)oxy)-5-methyl-6-((trimethylsilyl)oxy)octa-2,6-dienoate (5.29): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**5.4**) (256 mg, 1.0 mmol, 2.0 equiv) and (*Z*)-trimethyl(pent-2-en-3-yloxy)silane

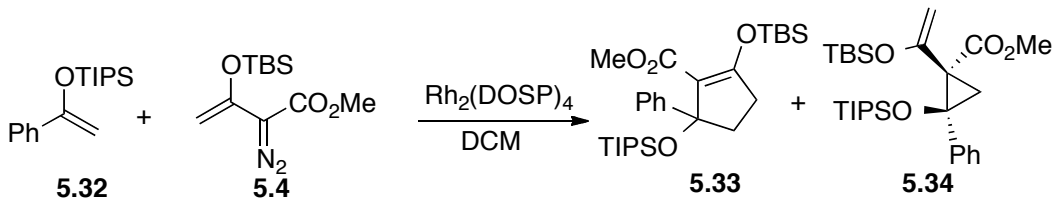
(79 mg, 0.5 mmol, 1 equiv), and purified through column chromatography (30/1 pentane/ethyl ether, R_f: 0.37) on silica gel to provide **5.29** as colorless oil (0.0465 g, 24% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.08 (s, 1H), 4.54 (q, *J* = 6.7 Hz, 1H), 3.64 (s, 3H), 2.34-2.44 (m, 2H), 1.93 (q, *J* = 4.3 Hz, 1H), 1.50 (d, *J* = 6.7 Hz, 3H), 1.03 (d, *J*= 6.7 Hz, 3H), 0.97 (s, 9H), 0.22 (s, 3H), 0.19 (s, 12H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 166.8, 165.8, 154.3, 100.8, 100.2, 77.3, 77.0, 76.7, 50.5, 43.4, 37.7, 25.8, 18.5, 17.8, 11.1; IR (neat): 2953, 2931, 2859, 1703, 1614, 1463, 1437, 1384, 1249, 1219, 1197, 1162, 1127, 1074, 1043, 1013, 1003, 954, 866, 834 cm^{-1}; HRMS (APCI) calc. for $C_{19}H_{39}O_4Si_2$ $(M+H)^+$ 387.2381 found 387.2384.



5.28 **5.4** **5.29** 24% yield **5.30** 24% yield

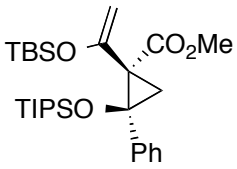
Methyl 2,5-bis((*tert*-butyldimethylsilyl)oxy)-5-ethyl-4-methylcyclopent-1-enecarboxylate (5.30): Derived from *tert*-butyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (298 mg, 1.0 mmol, 2 equiv) and (*Z*)-trimethyl(pent-2-en-3-yloxy)silane (79 mg, 0.5 mmol, 1 equiv), and purified through column chromatography (30/1 pentane/ethyl ether, R_f: 0.39) on silica gel to provide **5.30** as colorless oil (0.0470 g, 24% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 3.44 (s, 1H), 2.22-2.07 (m, 2H), 1.72 (dt, *J* = 6.8, 1.2 Hz, 3H), 1.12 (t, *J* = 7.6 Hz, 3H) 0.26 (s, 9H); ^{13}C NMR (100 Hz, C_6D_6): δ 167.1, 165.8, 155.2, 101.1, 101.0, 50.4, 44.3, 38.6, 26.5 19.3, 18.5, 11.7, 1.3, -3.4, -3.5; IR (neat): 2954, 2930, 2858, 1722, 1672, 1627, 1436, 1382, 1252, 1206, 1154, 1112, 1040,

981, 904, 837, 824 cm^{-1}; HRMS (APCI) calc. for $C_{19}H_{39}O_4Si_2$ $(M+H)^+$ 387.2381 found 387.2380.



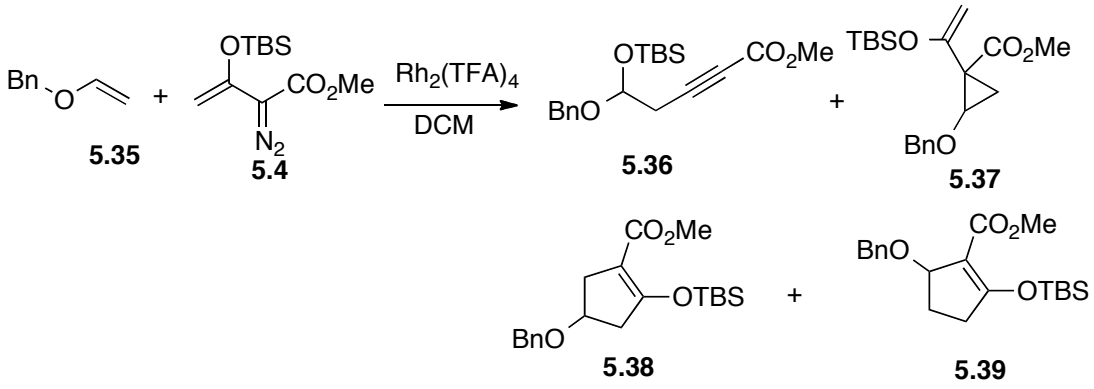
5.32 **5.4** **5.33** **5.34**

Methyl 2-((*tert*-butyldimethylsilyl)oxy)-5-phenyl-5-((triisopropylsilyl)oxy)cyclopent-1-enecarboxylate (5.33): In an oven-dried 25 mL flask, Rh_2(*R*-DOSP)$_4$ (5.6 mg, 0.03 equiv) and triisopropyl(1-phenylvinyloxy)silane (53 mg, 0.019 mmol, 1.0 equiv) were dissolved in 5 mL hexane under argon atmosphere. Diazo (0.115 g, 0.45 mmol, 2.4 equiv) in 5 mL hexane was injected by syringe pump over 1 h. The solution was concentrated by vacuum. Crude NMR showed a ratio of 1.1/1 for cyclopropanation product/terminus product. Separation by chromatography (30/1 hexane/Et_2O, containing 1% Et_3N, R_f: 0.47 for cyclopropanation product and 0.32 for terminus product) provided (32 mg + 27 mg) colorless oil in 62 % combined yield. ^1H NMR (500MHz, $CDCl_3$): δ 7.39-7.42 (m, 2H), 7.27 (t, *J* = 7.3 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 3.45 (s, 3H), 2.50-2.64 (m, 2H), 2.23-2.33 (m, 2H), 1.05-1.13 (m, 19H), 1.01 (s, 9H), 0.27 (s, 6H), 0.26 (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$): δ 166.3, 164.1, 150.0, 127.6, 125.8, 124.4, 116.1, 86.2, 50.0, 40.5, 33.3, 25.4, 18.4, 18.2, 13.6, -3.7; IR (neat): 2946, 2892, 2865, 1713, 1625, 1436, 1380, 1254, 1231, 1105, 1057, 945, 831, 784 cm^{-1}; HRMS (EI) calc. for $C_{28}H_{49}O_4Si_2(M+H)^+$ 505.3164 found 505.3183; HPLC: (whelk (R,R), 0.1% isopropanol in hexane, 0.7 mL/min) retention times of 7.4 (major) and 8.8 (minor), 14% ee.



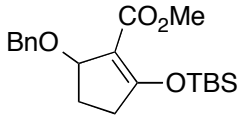
5.34

(1*S*,2*S*)-Methyl 1-(1-((*tert*-butyldimethylsilyl)oxy)vinyl)-2-phenyl-2-((triisopropyl silyl)oxy)cyclopropanecarboxylate (5.34): ^{1}H NMR (500MHz, $CDCl_3$): δ 7.39-7.40 (m, 2H), 7.19-7.26 (m, 3H), 4.19 (d, *J* = 1.4 Hz, 1H), 3.90 (d, *J* = 1.5 Hz, 1H), 3.74 (s, 3H), 2.08 (d, *J* = 6.7 Hz, 1H), 2.01 (d, *J* = 6.7 Hz, 1H), 0.84-0.97 (m, 19H), 0.81 (s, 9H), -0.12(s, 3H), -0.17 (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$): δ 169.3, 152.8, 138.8, 128.7, 127.6, 127.3, 93.6, 66.8, 52.0, 44.0, 25.7, 22.3, 17.9, 12.8, -5.3, -5.4; IR (neat): 2948, 2893, 2867, 1733, 1318, 1251, 1127, 1015, 831, 786, 698 cm^{-1}; HRMS (EI) calc. for $C_{28}H_{49}O_4Si_2$ $(M+H)^+$ 505.3164 found 505.3183.



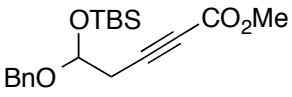
In an oven-dried 50 mL flask, $Rh_2(TFA)_4$ (13.2 mg, 0.01 equiv) and vinyl ether (1.5 mL, 10.0 mmol, 10 equiv) were dissolved in 10 mL CH_2Cl_2 under argon atmosphere and heat to reflux. Diazo (0.256 g, 1.0 mmol, 1.0 equiv) in 10 mL CH_2Cl_2 was injected by syringe pump over 2 h. The solution was concentrated by vacuum. Crude NMR showed a 0.56/0.71/0.35/1.0 ratio of four products in sequence. Careful separation by

chromatography (9/2/0.5 pentane/CH_2Cl_2/Et_2O, R_f: 0.75, 0.71, 0.55, 0.51 respectly) provided colorless oil (78 mg + 58 mg + 47 mg + 90 mg) in 83 % combined yield.



5.39

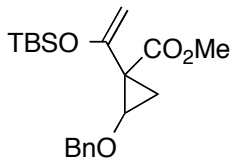
Methyl 5-(benzyloxy)-2-((*tert*-butyldimethylsilyl)oxy)cyclopent-1-enecarboxylate (5.39): ^{1}H NMR (500MHz, $CDCl_3$): δ 4.51 (t, *J* = 5.8 Hz, 1H), 3.69 (s, 3H), 3.99-4.04 (m, 2H), 2.67-2.74 (m, 1H), 2.20-2.26 (m, 1H), 1.99-2.06 (m, 1H), 1.81-1.87 (m, 1H), 1.46-1.55 (m, 2H), 1.32-1.39 (m, 2H), 0.97 (s, 9H), 0.89 (t, *J* = 7.6 Hz, 3H), 0.21 (s, 3H), 0.19 (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$): δ 169.3, 165.3, 110.1, 81.3, 68.6, 50.5, 33.7, 32.1, 27.1, 15.7, 25.3, 19.4, 18.1, 13.9, -3.9, -4.0; IR (neat): 2955, 2932, 2860, 1718, 1698, 1440, 1398, 1232, 1092, 857, 842, 783 cm^{-1}; HRMS (ESI) calc. for $C_{17}H_{32}O_4SiNa$ $(M+Na)^+$ 351.2068 found 351.2138.



5.36

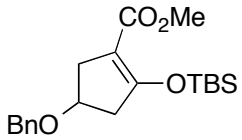
Methyl 5-(benzyloxy)-5-((*tert*-butyldimethylsilyl)oxy)pent-2-ynoate (5.36): ^{1}H NMR (500MHz, $CDCl_3$): δ 4.83 (t, *J* = 4.9 Hz, 1H), 3.75 (s, 3H), 3.61 (dt, *J* = 9.2, 6.7 Hz, 1H), 3.30 (dt, *J* = 9.2, 6.7 Hz, 1H), 2.42 (t, *J* = 7.3 Hz, 2H), 1.81-1.86 (m, 2H), 1.50-1.56 (m, 2H), 1.32-1.40 (m, 2H), 0.90 (t, *J* = 7.6 Hz, 3H), 0.89 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 154.2, 96.3, 89.4, 72.8, 66.6, 52.5, 35.1, 31.7, 25.7, 19.3, 18.0,13.8, 13.7, -4.4, -4.6; IR (neat): 2957, 2933, 2859, 2241, 1720, 1435, 1255, 1134,

1076, 838 cm^{-1}; HRMS (ESI) calc. for $C_{17}H_{32}O_4SiNa$ $(M+Na)^+$ 351.2068 found 351.2138.



5.37

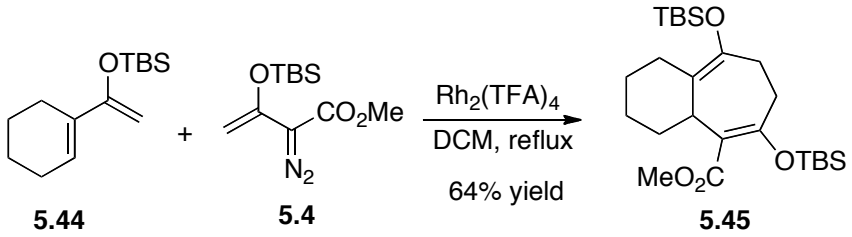
Methyl 2-(benzyloxy)-1-(1-((*tert*-butyldimethylsilyl)oxy)vinyl) cyclopropanecarboxylate (5.37): ^{1}H NMR (500MHz, $CDCl_3$): δ 4.38 (d, *J* = 1.0 Hz, 1H), 4.36 (d, *J* = 1.0 Hz, 1H), 3.91 (dd, *J* = 7.0, 4.9 Hz, 1H), 3.70 (dt, *J* = 9.1, 6.7 Hz, 1H), 3.32-3.37 (m, 1H), 3.33 (s, 3H), 1.42-1.50 (m, 3H), 1.39 (t, *J* = 5.5 Hz, 1H), 1.27-1.34 (m, 2H), 0.98 (s, 9H), 0.82 (t, *J* = 7.6 Hz, 3H), 0.26 (s, 3H), 0.23 (s, 3H); ^{13}C NMR (100MHz, C_6D_6): δ 171.9, 153.4, 94.4, 71.0, 64.3, 51.0, 36.0, 31.8, 25.5, 21.0, 19.3, 17.9, 13.7, -4.6, -5.7; IR (neat): 2958, 2932, 2860, 1724, 1634, 1435, 1332, 1276, 1129, 1095, 832 cm^{-1}; HRMS (ESI) calc. for $C_{17}H_{32}O_4SiNa$ $(M+Na)^+$ 351.2068 found 351.2138.



5.38

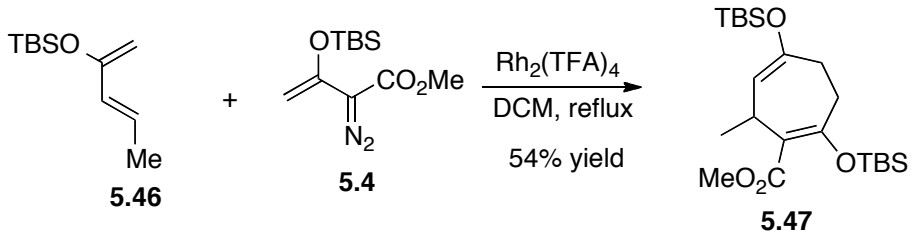
Methyl 4-(benzyloxy)-2-((*tert*-butyldimethylsilyl)oxy)cyclopent-1-enecarboxylate (5.38): ^{1}H NMR (500MHz, $CDCl_3$): δ 4.03 (m, 1H), 3.77 (s, 3H), 3.43 (q, *J* = 7.3 Hz, 1H), 3.35 (q, *J* = 6.4 Hz, 1H), 2.82 (dd, *J* = 7.3, 15.6 Hz, 1H), 2.68 (dd, *J* = 7.3, 15.6 Hz, 1H), 2.52 (m, 2H), 1.53 (m, 2H), 1.36 (m, 2H), 0.96 (s, 9H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.20 (s, 6H); ^{13}C NMR (150MHz, $CDCl_3$): δ 165.3, 161.9, 105.9, 74.3, 68.5, 50.6, 42.9, 36.2, 32.0, 25.4, 19.4, 18.2, 13.9, -4.1; IR (neat): 2955, 2932, 2860, 1718, 1698, 1633, 1440,

1389, 1232, 1092, 857, 842, 783 cm^{-1}; HRMS (ESI) calc. for $C_{17}H_{32}O_4SiNa$ $(M+Na)^+$ 351.2068 found 351.2138.

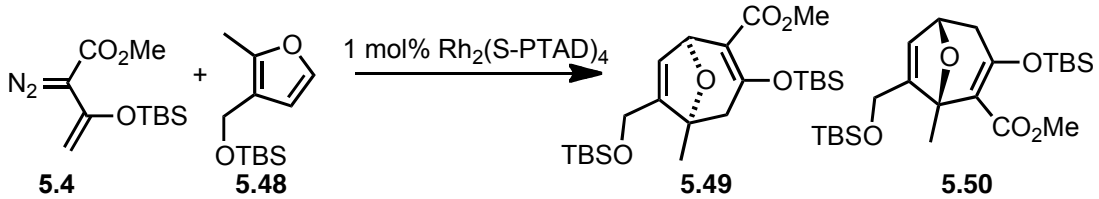


5.44 **5.4** **5.45**

Methyl 6,9-bis((*tert*-butyldimethylsilyl)oxy)-2,3,4,4a,7,8-hexahydro-1*H*-benzo[7]annulene-5-carboxylate (5.45): To an oven-dried 25 mL flask containing $Rh_2(TFA)_4$ (6.7 mg, 0.02 equiv) and *tert*-butyl((1-(cyclohex-1-en-1-yl)vinyl)oxy)dimethylsilane (**5.44**) (119.2 mg, 0.5 mmol, 1.0 equiv) in 5 mL DCM under argon atmosphere was added diazoacetate (**5.4**) (256 mg, 1.0 mmol, 2.0 equiv) in 6 mL DCM over 3 h under refluxed condition. The solution was then concentrated under reduced pressure. The mixture was purified by flash column chromatography on silica gel (30/1 hexane/Et_2O, R_f: 0.47) to provide product **5.45** as colorless oil in 64% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 3.70 (s, 3H), 3.15 (d, *J* = 9.2 Hz, 1H), 2.95 (d, *J* = 12.8 Hz, 1H), 2.83 (m, 1H), 2.53 (m, 1H), 2.05-2.28 (m, 3H), 1.72-1.90 (m, 3H), 1.50-1.58 (m, 3H), 1.19-1.30 (m, 2H), 0.93 (d, *J* = 7.6 Hz, 18H), 0.14 (s, 6H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 161.4, 141.8, 120.9, 115.0, 51.2, 41.8, 35.0, 34.2, 32.7, 31.0, 28.1, 27.8, 25.8, 25.7, 18.3, 18.1, -3.91, -3.98, -4.09, -4.24; IR (neat): 2928, 2856, 1717, 1697, 1633, 1472, 1434, 1362, 1289, 1251, 1201, 1159, 1128, 1009, 904, 837, 778 cm^{-1}; HRMS (APCI) calc. for $C_{25}H_{47}O_4Si_2$ $(M+H)^+$ 467.3007 found 467.3012.

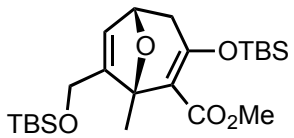


Methyl 2,5-bis((*tert*-butyldimethylsilyl)oxy)-7-methylcyclohepta-1,5-dienecarboxylate (5.47): To an oven-dried 25 mL flask containing $Rh_2(TFA)_4$ (6.7 mg, 0.02 equiv) and (*E*)-*tert*-butyldimethyl(penta-1,3-dien-2-yloxy)silane (**5.46**) (99.2 mg, 0.5 mmol, 1.0 equiv) in 5 mL DCM under argon atmosphere was added diazoacetate (**5.4**) (256 mg, 1.0 mmol, 2.0 equiv) in 6 mL DCM over 3 h under refluxed condition. The solution was then concentrated under reduced pressure. The mixture was purified by flash column chromatography on silica gel (30/1 hexane/Et_2O, R_f: 0.47) to provide product **5.47** as colorless oil in 64% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.07 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.64 (q, *J* = 6.0 Hz, 1H), 3.46 (s, 3H), 2.64-2.69 (m, 1H), 2.32-2.37 (m, 1H), 2.05-2.11 (m, 2H), 1.31 (d, *J* = 6.0 Hz, 3H), 0.98 (s, 9H), 0.97 (s, 9H), 0.17 (s, 3H), 0.14 (s, 3H), 0.11 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 159.3, 150.7, 116.8, 111.9, 51.2, 32.5, 30.0, 25.7, 21.1, 18.2, 17.9, -3.9, -4.0, -4.3, -4.6; IR (neat): 2954, 2929, 2857, 1716, 1694, 836 cm^{-1}; HRMS (APCI) calc. for $C_{22}H_{43}O_4Si_2$ $(M+H)^+$ 427.2689 found 427.2694.



(*S*)-Methyl 2-((*tert*-butyldimethylsilyl)oxy)-5-(((*tert*-butyldimethylsilyl)oxy)methyl)-4-methoxy-4-methylcyclohepta-1,5-dienecarboxylate (5.49): To an oven-dried 50 mL

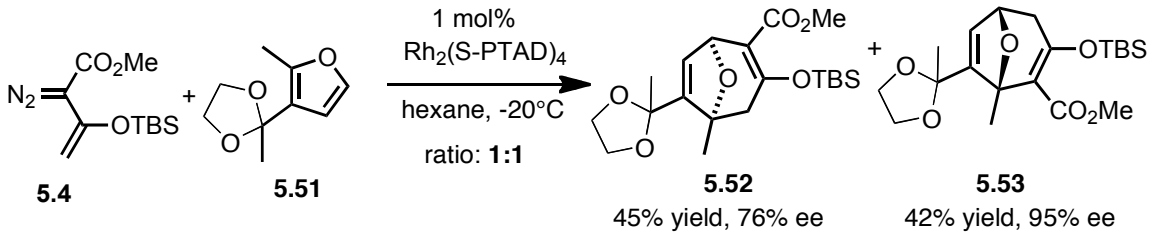
flask containing Rh_2(*S*-PTAD)$_4$ (9.3 mg, 0.01 equiv) and furan derivative (**5.48**) (0.113 g, 0.50 mmol, 1.0 equiv) in 20 mL hexane under argon atmosphere was added a solution of diazoacetate **5.4** (0.128 g, 0.50 mmol, 1.0 equiv) in 10 mL hexane by syringe pump over 2 h. The mixture was stirred for additional 1 h and concentrated by vacuum. The residue was carefully separated by flash chromatography (9/2/1 pentane/CH_2Cl_2/Et_2O, R_f: 0.36 for **5.50** and 0.34 for **5.49**) to provide colorless oil (92 mg + 84 mg + 46 mg) in 98% combination yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.28 (s, 1H), 5.24 (s, 1H), 4.24 (dd, *J* = 13.4, 19.5 Hz, 2H), 3.70 (s, 3H), 2.31 (d, *J* = 17.7 Hz, 1H), 2.16 (d, *J* = 17.7 Hz, 1H), 1.47 (s, 3H), 0.94 (s, 9H), 0.89 (s, 9H), 0.19 (d, *J* = 12.5 Hz, 6H), 0.05 (d, *J* = 4.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.4, 159.5, 142.8, 133.1, 113.3, 83.0, 75.9, 58.4, 50.8, 40.8, 25.9, 25.6, 22.4, 18.3, 18.2, -3.6, -5.4, -5.5; IR (neat): 2954 2930, 2895, 2858, 1721, 1687, 1618, 1373, 1256, 1204, 1059, 883, 839, 781 cm^{-1}; HRMS (ESI) calc. for $C_{23}H_{42}O_5NaSi_2$ $(M+Na)^+$ 477.2467 found 477.2458; HPLC: (OD, 0.5% isopropanol in hexane, 0.7mL/min) retention times of 11.6 (minor) and 15.9 (major), 88% ee.



5.50

(1*S*,5*S*)-Methyl 3-((*tert*-butyldimethylsilyl)oxy)-7-(((*tert*-butyldimethylsilyl)oxy) methyl)-1-methyl-8-oxabicyclo[3.2.1]octa-2,6-diene-2-carboxylate (5.50): ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.69 (q, 1H), 4.86 (d, *J* = 6.1 Hz, 1H), 4.58 (d, 1H), 4.36 (d, 1H), 3.69 (s, 3H), 2.71 (dd, *J* = 17.4, 6.4 hz, 1H), 1.78 (d, *J* = 17.4 Hz, 1H), 1.47 (s, 3H), 0.90 (s, 9H), 0.89 (s, 9H), 0.14 (d, *J* = 14.6 Hz, 6H), 0.06 (d, *J* = 6.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.2, 155.9, 152.8, 119.9, 119.1, 82.3, 75.6, 58.8, 51.0, 33.4, 25.9,

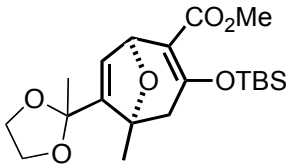
25.5, 18.9, 18.3, 18.0; IR (neat): 2953, 2931, 2898, 2858, 1698, 1615, 1362, 1196, 1121, 1075, 1058, 838 cm^{-1}; HRMS (ESI) calc. for $C_{23}H_{42}O_5NaSi_2$ $(M+Na)^+$ 477.2467 found 477.2463; HPLC: (OD, 0.5% isopropanol in hexane, 0.7mL/min) retention times of 8.2 (minor) and 9.4 (major), 88% ee.



To a flame-dried 25 mL flask containing Rh_2(*S*-PTAD)$_4$ (8.4 mg, 0.01 equiv) and 2-methyl-2-(2-methylfuran-3-yl)-1,3-dioxolane (**5.51**) (84.1 mg, 0.5 mmol, 1.0 equiv) in 6 mL dried hexane under argon atmosphere was added a solution of methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**5.4**) (180 mg, 0.7 mmol, 1.4 equiv) in 6 mL dried hexane by syringe pump over 3 h at -20 °C. The solution was warmed up to room temperature. The mixture was concentrated under reduced pressure and purified by flash chromatography (7/3 pentane/Et_2O, R_f: 0.46 for **5.52**, 0.38 for **5.53**) on silica gel to provide products as colorless oil (94.6 mg, 48% yield for normal product; 86.9 mg, 44% yield for normal product).

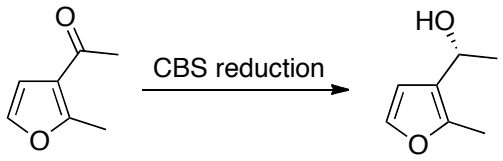
(1*S*,5*S*)-Methyl 3-((*tert*-butyldimethylsilyl)oxy)-1-methyl-7-(2-methyl-1,3-dioxolan-2-yl)-8-oxabicyclo[3.2.1]octa-2,6-diene-2-carboxylate (5.53): ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.92 (d, *J* = 2.0 Hz, 1H), 4.80 (dd, *J* = 6.3, 2.0 Hz, 1H), 3.78-4.01 (m, 4H), 3.69 (s, 3H), 2.68 (dd, *J* = 17.2, 6.3 Hz, 1H), 1.83 (d, *J* = 17.2 Hz, 1H), 1.66 (s, 3H), 1.59 (s, 3H), 0.89 (s, 9H), 0.123 (s, 3H), 0.117 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.7, 155.7, 152.1, 125.1, 119.8, 106.7, 82.9, 74.8, 64.7, 64.5, 51.0, 33.1, 25.6, 25.5, 20.8, 18.0,

-3.8, -3.9; IR (neat): 2950, 1709, 1360, 1302, 1190, 1041, 866, 838 cm^{-1}; HRMS (APCI) calc. for $C_{20}H_{33}O_6Si$ $(M+H)^+$ 397.2041 found 397.2043; $[\alpha]^{25}_D$ -50.7 (*c* = 0.89, $CHCl_3$); HPLC: (AD-H, 2% isopropanol in hexane, 0.7 mL/min) retention times of 14.2 min (major) and 18.4 min (minor), 96% ee.



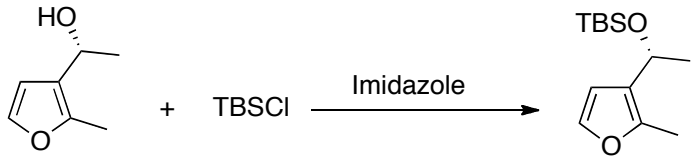
5.52

(*S*)-Methyl 2-((*tert*-butyldimethylsilyl)oxy)-4-methoxy-4-methyl-5-(2-methyl-1,3-dioxolan-2-yl)cyclohepta-1,5-dienecarboxylate (5.52): ^1H NMR (400 MHz, $CDCl_3$): δ 6.48 (d, *J* = 2.0 Hz, 1H), 5.22 (d, *J* = 2.0 Hz, 1H), 3.82-4.01 (m, 4H), 3.70 (s, 3H), 2.33 (d, *J* = 18.0 Hz, 1H), 2.22 (d, *J* = 18.0 Hz, 1H), 1.55 (s, 3H), 1.51 (s, 3H), 0.94 (s, 9H), 0.20 (s, 3H), 0.18 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.3, 159.7, 143.7, 135.5, 112.7, 107.0, 83.2, 75.3, 64.7, 64.4, 50.9, 41.2, 25.6, 25.5, 23.8, 18.3, -3.6, -3.8; IR (neat): 2932, 1718, 1864, 1615, 1371, 1022, 1041, 883, 832, 783 cm^{-1}; HRMS (APCI) calc. for $C_{20}H_{33}O_6Si$ $(M+H)^+$ 397.2041 found 397.2041; $[\alpha]^{25}_D$ 20.5 (*c* = 0.80, $CHCl_3$); HPLC: (AD-H, 2% isopropanol in hexane, 0.7 mL/min) retention times of 14.9 min (minor) and 15.7 min (minor), 76% ee.



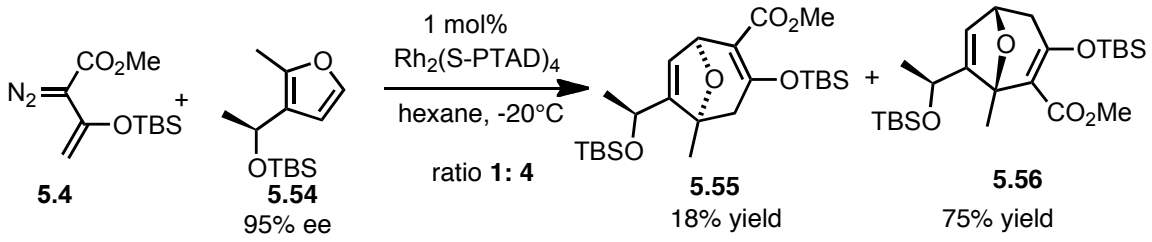
(*R*)-1-(2-Methylfuran-3-yl)ethanol: To a solution containing (*R*)-CBS (0.55g, 2.0 mmol, 0.05 equiv) in dried DCM (50 mL), was added BH_3Me_2S (4.0 mL, 40 mmol, 1.0

equiv) and stirred for 30 mins. The mixture was cooled down to -20 °C and 1-(2-methylfuran-3-yl)ethanone (5.0 g, 40 mmol, 1.0 equiv) in 20 mL DCM was added over 3h by syringe pump. The solution was stirred for additional 1h and warmed up to room temperature. The mixture was quenched with MeOH carefully and then concentrated under reduced pressure. The mixture was purified by flash column chromatography on silica gel (7/3 pentane/Et_2O, R_f = 0.46) to afford the product as colorless oil (4.72g, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 1.4 Hz, 1H), 6.37 (d, *J* = 1.4 Hz, 1H), 4.83 (q, *J* = 6.4 Hz, 1H), 2.28 (s, 3H), 1.65-1.74 (br, 1H), 1.44 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 140.4, 123.4, 108.4, 62.6, 23.8, 11.7; IR (neat): 3351(br), 2974, 1140, 1082, 999, 896, 726 cm^{-1}; $[\alpha]^{25}_D$ -10.4 (*c* = 1.22, $CHCl_3$); GC (Supelco 5°C/min 30°C to 180°C): 14.4 min (minor), 14.5 min (major), 95% ee.



(*R*)-*tert*-Butyldimethyl(1-(2-methylfuran-3-yl)ethoxy)silane (5.54): In an oven-dried flask containing alcohol (0.63 g, 5.0 mmol, 1.0 equiv), and imidazole (0.65 g, 10.0 mmol, 2.0 equiv) in 20 mL DCM was added TBSCl (0.91 g, 6.0 mmol, 1.2 equiv) in one portion. The mixture was stirred at rt for 3 h and quenched with sodium bicarbonate solution. The solution was extracted by Et_2O (3 x 30 mL) and dired ($MgSO_4$), concentrated under reduced pressure to provide an oil, which was purified by flash chromatography (20/1 pentane, R_f: 0.84) to provide product 5.54 as colorless oil (1.15 g, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 1.8 Hz, 1H), 6.32 (d, *J* = 1.8 Hz, 1H), 4.77 (q, *J* = 6.4 Hz, 1H), 2.25 (s, 3H), 1.35 (d, *J* = 6.4 Hz, 3H), 0.87 (s, 9H), 0.03 (s, 3H),

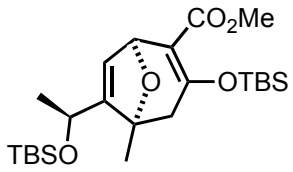
-0.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 139.9, 124.5, 109.4, 109.3, 63.7, 25.9, 25.8, 18.2, 11.9, -4.8, -5.0; IR (neat): 2956, 2928, 2857, 1254, 1085, 1006, 831, 774, 730 cm^{-1}; HRMS (ESI) calc. for $C_{13}H_{24}O_2NaSi$ $(M+Na)^+$ 263.1438 found 263.1436; $[\alpha]^{25}_D$ -18.5 (*c* = 0.69, $CHCl_3$).



To a flame-dried 25 mL flask containing Rh_2(*S*-PTAD)$_4$ (8.4 mg, 0.01 equiv) and (*R*)-*tert*-butyldimethyl(1-(2-methylfuran-3-yl)ethoxy)silane (**5.54**) (120 mg, 0.5 mmol, 1.0 equiv) in 6 mL dried hexane under argon atmosphere was added a solution of methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**5.4**) (180 mg, 0.7 mmol, 1.4 equiv) in 6 mL dried hexane by syringe pump over 3 h at -20 °C. The solution was warmed up to room temperature. The mixture was concentrated under reduced pressure and purified by flash chromatography (10/1 pentane/Et_2O, R_f: 0.41 for abnormal product, 0.33 for normal product) on silica gel to provide as colorless oil (176.1 mg, 75% yield for **5.56**; 41.2 mg, 18% yield for **5.55**).

(1*S*,5*S*)-Methyl 3-((*tert*-butyldimethylsilyl)oxy)-7-((*S*)-1-((*tert*-butyldimethylsilyl)oxy) ethyl)-1-methyl-8-oxabicyclo[3.2.1]octa-2,6-diene-2-carboxylate (5.56): ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.81 (s, 1H), 4.81 (dm, *J* = 5.6 Hz, 1H), 4.57 (q, *J* = 6.0 Hz, 1H), 3.69 (s, 3H), 2.68 (dd, *J* = 17.2, 6.0 Hz, 1H), 1.79 (d, *J* = 17.2 Hz, 1H), 1.55 (s, 3H), 1.32 (d, *J* = 6.3 Hz, 1H), 0.89 (s, 18H), 0.12 (s, 3H), 0.10 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 159.6, 153.4, 121.9, 119.4, 82.7, 75.0, 64.3, 51.1, 33.6, 25.9,

25.6, 25.5, 24.1, 19.8, 18.2, 18.0, -3.7, -4.6, -4.7; IR (neat): 2952, 2858, 1698, 1361, 1253, 1052, 866, 830, 775 cm^{-1}; HRMS (APCI) calc. for $C_{24}H_{45}O_5Si_2$ $(M+H)^+$ 469.2800 found 469.2798; $[a]^{25}_D$ -31.4 (*c* = 0.78, $CHCl_3$).



5.55

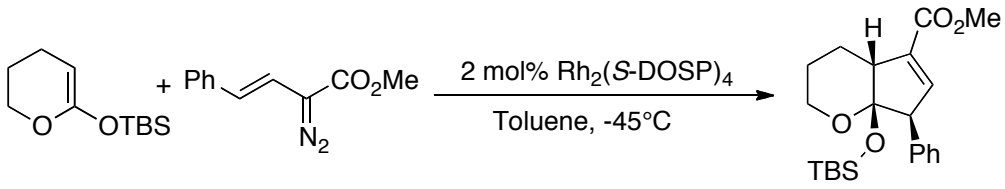
(*S*)-Methyl 2-((*tert*-butyldimethylsilyl)oxy)-5-((*S*)-1-((*tert*-butyldimethylsilyl)oxy) ethyl)-4-methoxy-4-methylcyclohepta-1,5-dienecarboxylate (5.55): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.23 (t, *J* = 1.5 Hz, 1H), 5.22 (d, *J* = 1.1 Hz, 1H), 4.47-4.52 (m, 1H), 3.70 (s, 3H), 2.31 (d, *J* = 1.1 Hz, 2H), 1.51 (s, 3H), 1.31 (d, *J* = 6.3 Hz, 1H), 0.94 (s, 9H), 0.88 (s, 9H), 0.21 (s, 3H), 0.17 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 159.9, 147.0, 132.3, 112.9, 83.4, 75.5, 64.7, 50.8, 41.3, 25.9, 25.6, 23.0, 22.7, 18.3, 18.0, -3.6, -3.7, -4.0, -4.7; IR (neat): 2952, 2930, 2858, 1720, 1686, 1618, 1371, 1253, 1203, 883, 834, 777 cm^{-1}; HRMS (APCI) calc. for $C_{24}H_{45}O_5Si_2$ $(M+H)^+$ 469.2800 found 469.2798; $[a]^{25}_D$ 3.2 (*c* = 0.77, $CHCl_3$).

The [3 + 2] cycloaddition between vinylcarbenoids and electron rich olefins

General procedure for the [3 + 2] cycloaddition between vinylcarbenoids and electron rich olefins

To a flame-dried 25 mL flask containing Rh_2(*S*-DOSP)$_4$ (5.6 mg, 0.02 equiv) and silyl ketene acetals (0.90 mmol, 6.0 equiv) in 6 mL dried toluene under argon atmosphere was

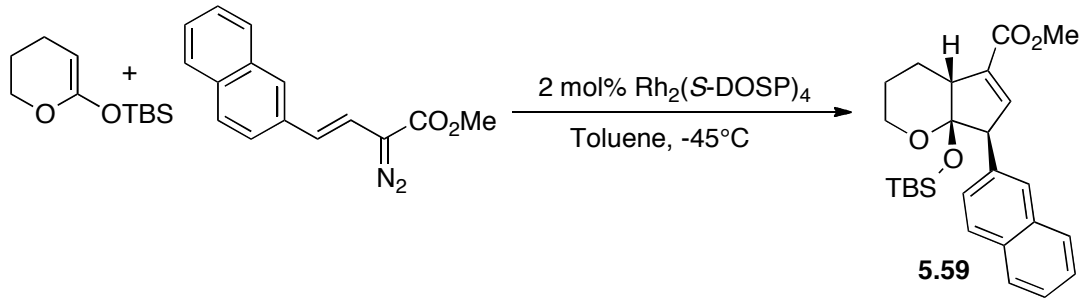
added a solution of (*E*)-aryl vinyldiazoacetate (0.15 mmol, 1.0 equiv) in 6 mL dried toluene by syringe pump over 3 h at -45 °C. The solution was stirred at -45 °C over-night and warmed up to room temperature over 2 h. The mixture was concentrated under reduced pressure and purified by flash chromatography in silica gel (pentane/Et_2O) to provide the corresponding products.



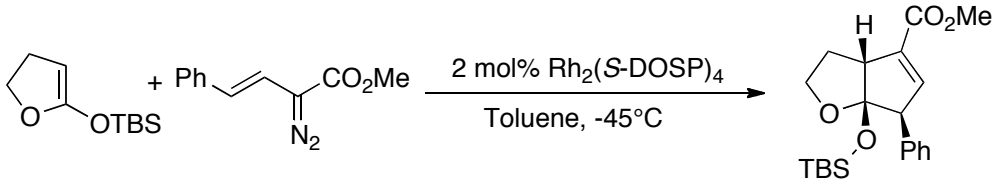
5.57

(4a*R*,7*S*,7a*S*)-Methyl 7a-((*tert*-butyldimethylsilyl)oxy)-7-phenyl-2,3,4,4a,7,7a-hexahydrocyclopenta[*b*]pyran-5-carboxylate (5.57): Derived from *tert*-butyl(3,4-dihydro-2H-pyran-6-yloxy)dimethylsilane (193 mg, 0.90 mmol, 6.0 equiv) and *trans*-phenyl vinyldiazoacetate (30.4 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography in silica gel (20/1 pentane/Et_2O, R_f: 0.29) to provide 42.5 mg colorless gel solid in 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.31 (m, 3H), 7.13-7.17 (m, 2H), 6.93 (d, *J* = 2.0 Hz, 1H), 4.17 (d, *J* = 1.6 Hz, 1H), 4.05-4.12 (m, 1H), 3.80 (dd, *J* = 3.6, 18.0 Hz, 1H), 3.79 (s, 3H), 2.75 (dd, *J* = 6.3, 11.0 Hz, 1H), 2.29-2.38 (m, 1H), 1.51-1.66 (m, 2H), 1.29-1.41 (m, 1H), 0.86-0.98 (m, 1H), 0.63 (s, 9H), -0.05 (s, 3H), -0.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 143.4, 139.0, 136.7, 129.7, 127.6, 126.6, 106.8, 64.4, 53.7, 51.5, 49.1, 27.7, 25.9, 22.3, 17.9, -3.0, -3.6; IR (neat): 2949, 2855, 1717, 1252, 1165, 1086, 940, 835, 778, 697 cm^{-1}; HRMS (APCI) calc. for $C_{22}H_{33}O_4Si$ $(M+H)^+$ 389.2143 found 389.2140; HPLC: (OD, 1% isopropanol in hexane, 0.7 mL/min)

retention times of 8.8 min (minor) and 9.7 min (major), 94% ee; $[\alpha]^{25}_{D}$ -64.2 (*c* = 1.08, $CHCl_3$).

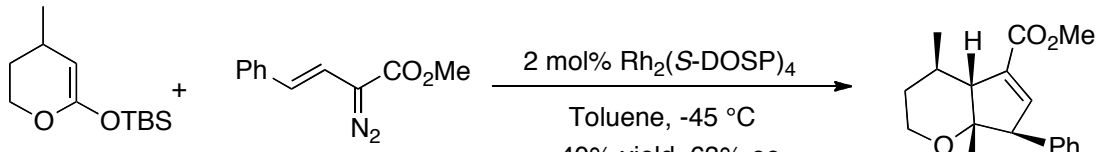


(4a*R*,7*S*,7a*S*)-Methyl 7a-((*tert*-butyldimethylsilyl)oxy)-7-(naphthalen-2-yl)-2,3,4,4a,7,7a-hexahydrocyclopenta[*b*]pyran-5-carboxylate (5.59): Derived from *tert*-butyl(3,4-dihydro-2H-pyran-6-yloxy)dimethylsilane (193 mg, 0.90 mmol, 6.0 equiv) and *trans*-naphthalenyl vinyldiazoacetate (37.9 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography in silica gel (9/1 pentane/Et_2O, R_f: 0.39) to provide 39.6 mg colorless solid in 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.84 (m, 3H), 7.61 (s, 1H), 7.40-7.47 (m, 2H), 7.30 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.02 (d, *J* = 2.0 Hz, 1H), 4.34 (d, *J* = 1.6 Hz, 1H), 4.09-4.18 (m, 1H), 3.81-3.90 (m, 1H), 3.81 (s, 3H), 2.81 (dd, *J* = 6.8, 11.6 Hz, 1H), 2.32-2.43 (m, 1H), 1.55-1.69 (m, 2H), 1.34-1.46 (m, 1H), 0.57 (s, 9H), -0.07 (s, 3H), -0.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 143.7, 139.4, 134.5, 133.3, 132.7, 128.4, 127.8, 127.7, 127.1, 125.9, 125.4, 107.2, 64.7, 54.11, 54.08, 51.8, 49.4, 27.9, 26.0, 22.5, 18.0, -2.8, -3.3; IR (neat): 2949, 2854, 1716, 1253, 1164, 835, 779 cm^{-1}; HRMS (APCI) calc. for $C_{26}H_{35}O_4Si$ $(M+H)^+$ 439.2299 found 439.2305; HPLC: (AD-H, 1% isopropanol in hexane, 0.7 mL/min) retention times of 7.8 min (minor) and 8.3 min (major), 95% ee; $[\alpha]^{25}_{D}$ -103.0 (*c* = 1.12, $CHCl_3$).



5.58

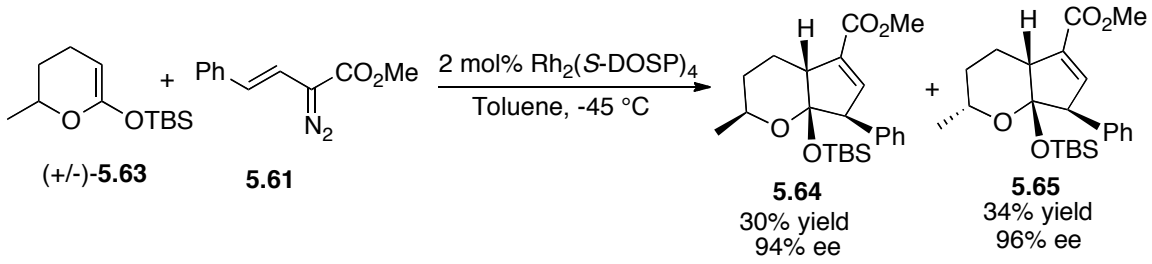
(3a*R*,6*S*,6a*S*)-Methyl 6a-((*tert*-butyldimethylsilyl)oxy)-6-phenyl-3,3a,6,6a-tetrahydro -2*H*-cyclopenta[*b*]furan-4-carboxylate (5.58): Derived from *tert*-butyl(4,5-dihydrofuran-2-yloxy)dimethylsilane (180 mg, 0.90 mmol, 6.0 equiv) and *trans*-phenyl vinyldiazoacetate (30.4 mg, 0.15 mmol, 1.0 equiv), and purified by flash chromatography in silica gel (20/1 pentane/Et_2O, R_f: 0.23) to provide 29.6 mg colorless gel solid in 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.29 (m, 2H), 7.19 (tt, *J* = 1.3, 7.3 Hz, 1H), 7.08-7.11 (m, 2H), 6.75 (dd, *J* = 2.0, 2.4 Hz, 1H), 4.14 (dt, *J* = 2.8, 7.9 Hz, 1H), 4.05 (t, *J* = 2.2 Hz, 1H), 3.77 (s, 3H), 3.72-3.80 (m, 1H), 3.43 (dq, *J* = 1.9, 7.6 Hz, 1H), 2.17-2.31 (m, 2H), 0.48 (s, 9H), 0.01 (s, 3H), -0.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 145.8, 137.9, 134.4, 129.4, 128.1, 126.9, 116.3, 68.1, 62.4, 55.4, 51.6, 28.0, 25.3, 17.4, -3.4, -3.6; IR (neat): 2950, 2855, 1717, 1288, 1256, 1113, 1064, 1048, 897, 836, 776, 698 cm^{-1}; HRMS (APCI) calc. for $C_{21}H_{31}O_4Si$ $(M+H)^+$ 375.1986 found 375.1993; HPLC: (OD, 1% isopropanol in hexane, 0.7 mL/min) retention times of 6.9 min (minor) and 12.3 min (major), 97% ee; $[\alpha]^{25}_D$ -127.5 (*c* = 0.39, $CHCl_3$).



(+/-)-**5.60** **5.61** **5.62**

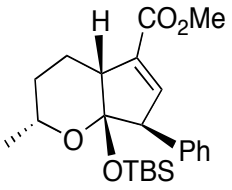
(4*R*,4a*R*,7*S*,7a*R*)-Methyl 7a-((*tert*-butyldimethylsilyl)oxy)-4-methyl-7-phenyl-2,3,4,4a,7,7a-hexahydrocyclopenta[*b*]pyran-5-carboxylate (5.62): A solution of

methyl (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (**5.61**) (30.7 mg, 0.15 mmol, 1.0 equiv) in dried toluene (6 mL) was added dropwise to a stirred solution of *tert*-butyldimethyl((4-methyl-3,4-dihydro-2*H*-pyran-6-yl)oxy)silane (**5.60**) (206 mg, 0.90 mmol, 6.0 equiv) and Rh_2(*S*-DOSP)$_4$ (5.6 mg, 2 mol %) in hexane (6 mL) at -45°C under argon atmosphere over 3 h by syringe pump. The contents was stirred at -45 ^oC over-night and warmed up to room temperature over 2 h. The solution was then cooled to room temperature and concentrated under reduced pressure. The residue was then purified by flash chromatography (10:1 pentane/Et_2O, R_f = 0.52) to give product **5.62** (23.9 mg, 40% yield) as colorless oil. ^1H NMR (600 MHz, $CDCl_3$): δ 7.25-7.27 (m, 2H), 7.21-7.23 (m, 1H), 7.13 (d, *J* = 6.7 Hz, 2H), 6.97 (d, J = 1.4 Hz, 1H), 4.21 (s, 1H), 4.08-4.11 (m, 1H), 3.83-3.87 (m, 1H), 3.78 (s, 3H), 3.40 (d, *J* = 10.5 Hz, 1H), 1.49-1.53 (m, 2H), 1.32-1.39 (m, 1H), 1.06 (d, *J* = 6.2 Hz, 3H), 0.63 (s, 9H), -0.06 (s, 3H), -0.57 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.8, 144.1, 139.8, 136.5, 129.7, 127.5, 126.6, 108.4, 64.0, 56.6, 52.4, 51.5, 35.9, 31.5, 25.8, 21.2, 17.8, -3.1, -3.7; IR (neat): 2952, 2927, 2855, 1718, 1436, 1264, 1245, 1157, 1096, 1084, 1055, 937, 834, 778, 697 cm^{-1}; HRMS (APCI) calc. for $C_{23}H_{35}O_4Si$ $(M+H)^+$ 403.2305 found 403.2307; HPLC: (AD-H, 1% isopropanol in hexane, 0.7 mL/min) retention times of 5.8 min (minor) and 6.6 min (major), 63% ee; $[\alpha]^{25}_D$ -35.5 (*c* = 0.44, $CHCl_3$).



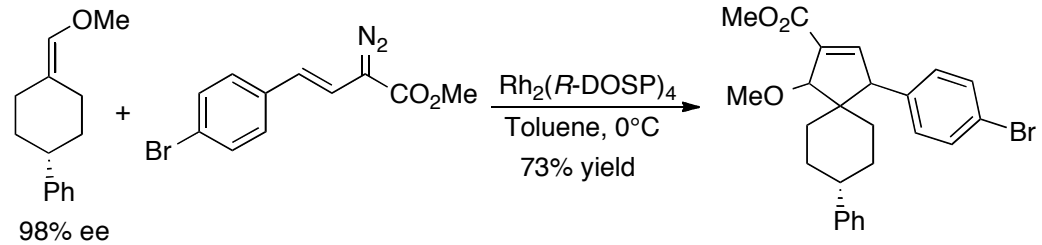
(2*S*,4a*R*,7*S*,7a*S*)-Methyl 7a-((*tert*-butyldimethylsilyl)oxy)-2-methyl-7-phenyl-2,3,4,4a,7,7a-hexahydrocyclopenta[*b*]pyran-5-carboxylate (5.64): A solution of methyl (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (**5.61**) (30.7 mg, 0.15 mmol, 1.0 equiv) in dried toluene (6 mL) was added dropwise to a stirred solution of *tert*-butyldimethyl((2-methyl-3,4-dihydro-2*H*-pyran-6-yl)oxy)silane (**5.63**) (206 mg, 0.90 mmol, 6.0 equiv) and Rh_2(*S*-DOSP)$_4$ (5.6 mg, 2 mol %) in hexane (6 mL) at -45 °C under argon atmosphere over 3 h by syringe pump. The contents was stirred at -45 ^{o}C over-night and warmed up to room temperature over 2 h. The solution was then cooled to room temperature and concentrated under reduced pressure. The residue was then purified by flash chromatography (10:1 pentane/Et_2O, R_f = 0.51 for the first isomer, 0.41 for the second isomer) to give product (18.0 mg, 30% yield for the first isomer and 20.3 mg, 34% yield for the second isomer) as colorless oils. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.29 (m, 3H), 7.12-7.14(m, 2H), 6.93 (d, *J* = 2.0 Hz, 1H), 4.20 (d, *J* = 1.3 Hz, 1H), 3.87-3.93 (m, 1H), 3.79 (s, 3H), 2.61-2.65 (m, 1H), 2.35-2.39 (m, 1H), 1.58-1.61 (m, 1H), 1.23-1.31 (m, 5H), 0.62 (s, 9H), -0.05 (s, 3H), -0.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 142.7, 139.6, 136.7, 129.6, 127.5, 126.5, 107.8, 70.8, 52.9, 51.5, 48.5, 29.6, 28.6, 25.9, 21.6, 17.8, -2.8, -3.5; IR (neat): 1709, 1436, 1245, 1227, 1216, 1085, 939, 893, 834, 778, 753, 697 cm^{-1}; HRMS (APCI) calc. for $C_{23}H_{35}O_4Si$ $(M+H)^+$ 403.2305 found 403.2309;

HPLC: (OD, 1% isopropanol in hexane, 0.7 mL/min) retention times of 7.2 min (minor) and 10.4 min (major), 94% ee; $[\alpha]^{25}_{D}$ -48.5 (*c* = 0.68, $CHCl_3$).



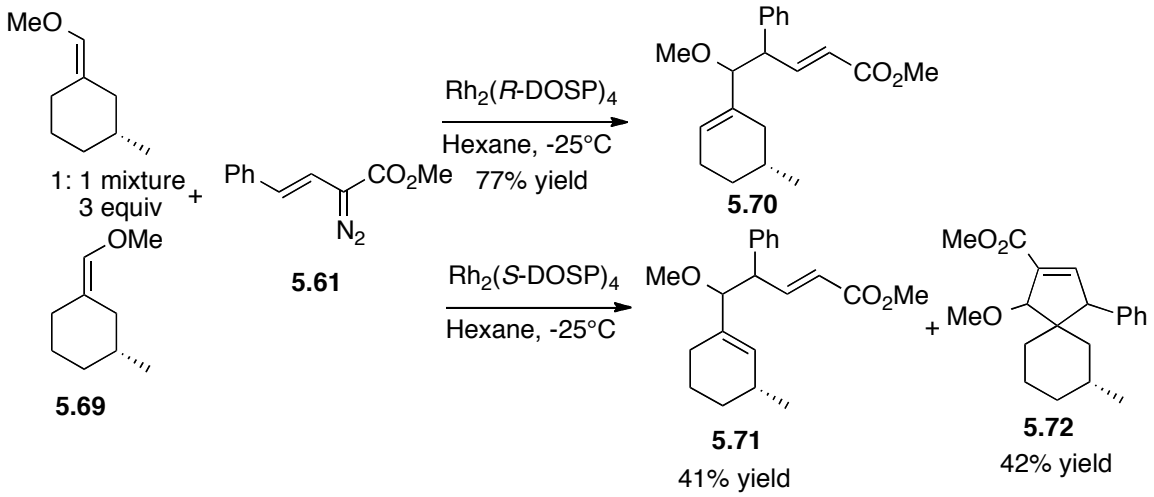
5.63

(2*R*,4a*R*,7*S*,7a*S*)-Methyl 7a-((*tert*-butyldimethylsilyl)oxy)-2-methyl-7-phenyl-2,3,4,4a,7,7a-hexahydrocyclopenta[*b*]pyran-5-carboxylate (5.63): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17-7.25 (m, 5H), 6.88 (t, *J* = 2.4 Hz, 1H), 3.83-3.92 (m, 1H), 3.80-3.81 (m, 1H), 3.74 (s, 3H), 3.62 (s, 1H), 3.22-3.24 (m, 1H), 2.36-2.42 (m, 1H), 1.85-1.94 (m, 1H), 1.43-1.49 (m, 1H), 1.19-1.29 (m, 1H), 1.16 (d, *J* =7.6 Hz, 3H), 0.62 (s, 9H), 0.02 (s, 3H), -0.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 147.6, 137.9, 134.0, 129.6, 128.3, 127.0, 106.6, 67.4, 62.9, 51.3, 48.1, 28.1, 25.8, 21.9, 20.7, 18.1, -2.8, -3.2; IR (neat): 1716, 1281, 1246, 1139, 1093, 1027, 894, 835, 796, 776, 745, 696 cm^{-1}; HRMS (APCI) calc. for $C_{23}H_{35}O_4Si$ $(M+H)^+$ 403.2305 found 403.2311; HPLC: (AD-H, 1% isopropanol in hexane, 0.7 mL/min) retention times of 7.3 min (minor) and 8.0 min (major), 63% ee; $[\alpha]^{25}_{D}$ -163.1 (*c* = 1.06, $CHCl_3$).



To a flame-dried 25 mL flask containing Rh_2(*S*-DOSP)$_4$ (1.9 mg, 0.01 equiv) and ether **5.66** (202.2 mg, 0.10 mmol, 1.0 equiv) in 6 mL dried toluene under argon atmosphere

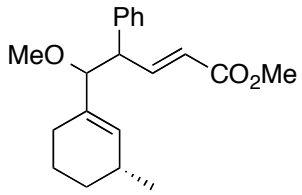
was added a solution of (*E*)-methyl 4-(4-bromophenyl)-2-diazobut-3-enoate (45 mg, 0.16 mmol, 1.6 equiv) in 6 mL dried toluene by syringe pump over 2 h at 0 °C. The mixture was concentrated under reduced pressure and purified by flash chromatography in silica gel (10/1 pentane/Et_2O, R_f: 0.32) to provide **5.68** as colorless oil (33.6 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.42 (m, 2H), 7.27-7.32 (m, 2H), 7.17-7.23 (m, 3H), 7.07-7.10 (m, 2H), 6.89 (d, *J* = 2.8 Hz, 1H), 4.38 (s, 1H), 3.83 (s, 3H), 3.62 (s, 3H), 3.34 (d, *J* = 3.2 Hz, 1H), 2.49 (tt, *J* = 11.6, 3.6 Hz, 1H), 1.66-1.84 (m, 4H), 1.42-1.64 (m, 3H), 0.87 (td, *J* = 13.2, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 147.9, 147.1, 138.0, 137.2, 131.5, 131.0, 128.4, 126.7, 126.0, 120.9, 86.1, 63.6, 60.1, 51.7, 60.1, 51.7, 48.4, 43.7, 38.8, 31.3, 31.1, 30.6; IR (neat): 2923, 2855, 1717, 1485, 1435, 1271, 1248, 1091, 1011, 828, 758, 699 cm^{-1}; HRMS (APCI) calc. for $C_{24}H_{24}O_2Br$ $(M\text{-}OMe)^+$ 423.0954 found 423.0957; $[\alpha]^{25}_D$ 112.5 (*c* = 0.46, $CHCl_3$).



(*E*)-Methyl 5-methoxy-5-((*R*)-5-methylcyclohex-1-en-1-yl)-4-phenylpent-2-enoate (5.70): To a flame-dried 100 mL flask containing Rh_2(*R*-DOSP)$_4$ (8.9 mg, 0.01 equiv) and ether **5.69** (210.3 mg, 1.5 mmol, 3.0 equiv) in 20 mL dried hexene under argon

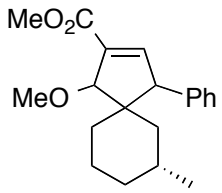
atmosphere was added a solution of (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (101.1 mg, 0.50 mmol, 1.0 equiv) in 20 mL dried hexene by syringe pump over 3 h at -25 °C. The mixture was warmed up to room temperature slowly and concentrated under reduced pressure. The mixture purified by flash chromatography in silica gel (10/1 pentane/Et_2O, R_f: 0.25) to provide **5.70** as colorless oil (121.6 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (dd, *J* = 15.7, 7.6 Hz, 1H), 7.22-7.27 (m, 2H), 7.17-7.21 (m, 1H), 7.10-7.13 (m, 2H), 5.74 (dd, *J* = 15.7, 0.9 Hz, 1H), 5.41 (br, 1H), 3.74 (d, *J* = 9.1 Hz, 1H), 3.69 (s, 3H), 3.55-3.60 (m, 1H), 3.20 (s, 3H), 1.92-2.02 (m, 2H), 1.75-1.81 (m, 1H), 1.48-1.54 (m, 2H), 1.32-1.38 (m, 1H), 0.86 (d, *J* = 6.2 Hz, 3H), 0.78-0.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 150.7, 139.9, 133.9, 128.9, 128.6, 128.4, 127.1, 122.0, 88.8, 56.4, 52.2, 51.6, 31.6, 30.9, 28.7, 25.2, 22.0; IR (neat): 2948.3, 2923, 1722, 1435, 1270, 1163, 1092, 730, 699 cm^{-1}; HRMS (APCI) calc. for $C_{20}H_{27}O_3$ $(M+H)^+$ 315.1955 found 315.1955; $[\alpha]^{25}_D$ 64.0 (*c* = 1.43, $CHCl_3$).

To a flame-dried 100 mL flask containing Rh_2(*S*-DOSP)$_4$ (8.9 mg, 0.01 equiv) and ether **5.69** (210.3 mg, 1.5 mmol, 3.0 equiv) in 20 mL dried hexene under argon atmosphere was added a solution of (*E*)-methyl 2-diazo-4-phenylbut-3-enoate (101.1 mg, 0.50 mmol, 1.0 equiv) in 20 mL dried hexene by syringe pump over 3 h at -25 °C. The mixture was warmed up to room temperature slowly and concentrated under reduced pressure. The mixture purified by flash chromatography in silica gel (10/1 pentane/Et_2O, R_f: 0.25 for **5.71** and 0.44 for **5.72**) to provide **5.71** as colorless oil (64.3 mg, 41% yield) and **5.72** as colorless oil (65.9 mg, 42% yield).



5.71

(*E*)-Methyl 5-methoxy-5-((*R*)-3-methylcyclohex-1-en-1-yl)-4-phenylpent-2-enoate (5.71): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (dd, *J* = 15.7, 7.6 Hz, 1H), 7.23-7.27 (m, 2H), 7.17-7.21 (m, 1H), 7.08-7.12 (m, 2H), 5.77 (dd, *J* = 15.7, 0.9 Hz, 1H), 5.35 (br, 1H), 3.72 (d, *J* = 9.1 Hz, 1H), 3.70 (s, 3H), 3.59-3.63 (m, 1H), 3.23 (s, 3H), 1.88-2.00 (m, 3H), 1.67-1.74 (m, 1H), 1.38-1.53 (m, 4H), 1.04-1.12 (m, 1H), 0.91 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 150.2, 139.8, 133.2, 128.6, 128.3, 127.8, 126.8, 121.8, 89.0, 56.2, 52.1, 51.4, 31.7, 30.4, 28.0, 24.6, 21.5; IR (neat): 2922, 1721, 1434, 1233, 1197, 1090, 699 cm^{-1}; HRMS (ESI) calc. for $C_{20}H_{26}O_3Na$ $(M+Na)^+$ 337.1774 found 337.1781; $[\alpha]^{25}_D$ 16.3 (*c* = 1.14, $CHCl_3$).

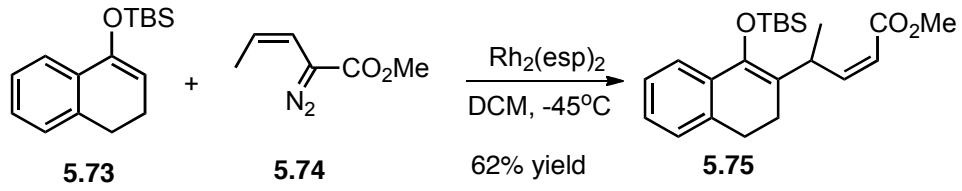


5.72

(7*R*)-Methyl 1-methoxy-7-methyl-4-phenylspiro[4.5]dec-2-ene-2-carboxylate (5.72): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.28 (m, 2H), 7.18-7.24 (m, 1H), 7.14-7.16 (m, 2H), 6.88 (d, *J* = 3.4 Hz, 1H), 4.24 (s, 1H), 3.80 (s, 3H), 3.55 (s, 3H), 3.31 (d, *J* = 3.4 Hz, 1H), 1.55-1.65 (m, 5H), 1.30-1.40 (m, 4H), 0.76-0.83 (m, 1H), 0.72 (d, *J* = 7.6 Hz, 3H), 0.33 (t, *J* = 12.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 148.8, 139.0, 136.7, 129.9, 127.9, 126.7, 86.4, 64.7, 59.9, 51.6, 49.5, 38.7, 38.6, 24.7, 29.6, 23.5, 23.1; IR (neat):

2921, 1716, 1436, 1254, 1095, 1085, 911, 732, 700 cm^{-1}; HRMS (ESI) calc. for $C_{20}H_{26}O_3Na$ $(M+Na)^+$ 337.1774 found 337.1780; $[\alpha]^{25}_D$ -189.3 (*c* = 1.31, $CHCl_3$).

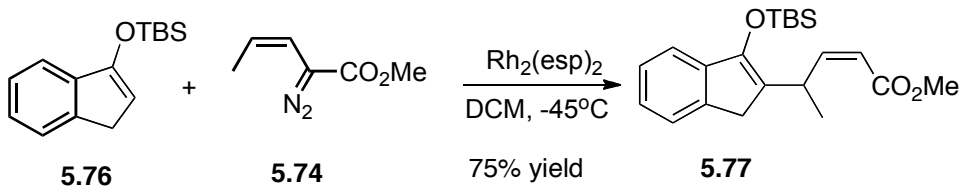
Vinylogous Reactivity of Vinylcarbenoids in the formation of 4-substituted (Z)-Pent-2-enoates



5.73 **5.74** **5.75**

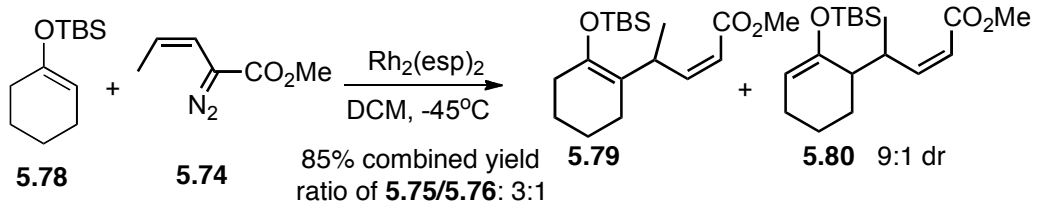
(*E*)-Methyl 2-(1-(*tert*-butyldimethylsilyloxy)-3,4- dihydronaphthalen-2-yl)pent-3-enoate (5.75): To an oven-dried 25 mL flask containing $Rh_2(esp)_2$ (5.0 mg, 0.02 equiv) and dihydronaphthalene **5.73** (0.083 g, 0.32 mmol, 1.0 equiv) in 6 mL DCM under argon atmosphere was added a solution of *cis*-methyl vinyldiazoacetate **5.74** (0.089 g, 0.64 mmol, 2.0 equiv) in 6 mL DCM by syringe pump over 2 h at -45 ^oC using dried ice-acetonitrile bath. The solution was stirred at -45 ^oC for additional 1h and then concentrated by vacuum. The crude mixture was purified by flash chromatography (25/1 pentane/Et_2O, R_f: 0.61) in silica gel to provide 74 mg colorless oil in 62% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.3 Hz, 1H), 7.16 (dt, *J* = 2.4, 7.0 Hz, 1H), 7.08-7.13 (m, 2H), 6.25 (dd, *J* = 9.5, 11.6 Hz, 1H), 5.72 (dd, *J* = 0.9, 11.6 Hz, 1H), 4.86 (m, 1H), 3.72 (s, 3H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.21-2.33 (m, 2H), 1.21 (d, *J* = 7.0 Hz, 3H) 1.03 (s, 9H), 0.08 (s, 3H), -0.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 151.5, 142.7, 136.1, 134.3, 126.5, 126.4, 125.8, 122.7, 122.4, 118.2, 51.1, 32.3, 28.7, 26.0, 22.3, 19.1, 18.4, -3.76, -4.00; IR (neat): 2951, 2930, 2858, 1725, 1634, 1302, 1252, 1194, 1177,

1082, 917, 841, 828, 781, 766 cm^{-1}; HRMS (EI) calc. for $C_{22}H_{33}O_3Si$ $(M+H)^+$ 373.2193 found 373.2197.



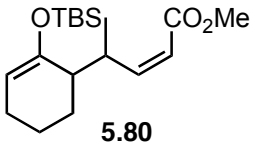
5.76 **5.74** 75% yield **5.77**

(*Z*)-Methyl 4-(3-((*tert*-butyldimethylsilyl)oxy)-1*H*-inden-2-yl)pent-2-enoate (5.77): To an oven-dried 25 mL flask containing $Rh_2(esp)_2$ (2.4 mg, 0.02 equiv) and indene (37 mg, 0.15 mmol, 1.0 equiv) in 6 mL DCM under argon atmosphere was added a solution of *cis*-methyl vinyldiazoacetate (42 mg, 0.30 mmol, 2.0 equiv) in 6 mL DCM by syringe pump over 3 h at -45 °C using dried ice-acetonitrile bath. The solution was warmed up to room temperature over 2 h and then concentrated by vacuum. The crude mixture was purified by flash chromatography (40/1 pentane/Et_2O, R_f: 0.32) in silica gel to provide 40.2 mg colorless oil in 75% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, J = 7.3 Hz, 1H), 7.25-7.28 (m, 2H), 7.14-7.17 (m, 1H), 6.31 (dd, J = 10.1, 11.5 Hz, 1H), 5.74 (d, J = 11.5 Hz, 1H), 4.85-4.90 (m, 1H), 3.74 (s, 3H), 2.29 (m, 2H), 2.21-2.33 (m, 2H), 1.31 (d, J = 6.9 Hz, 3H), 1.07 (s, 9H), 0.24 (s, 3H), 0.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 152.3, 147.8, 142.6, 141.1, 126.3, 125.8, 124.6, 123.8, 118.3, 117.9, 51.4, 32.7, 30.7, 26.1, 20.7, 18.5, -3.6, -3.7; IR (neat): 2952, 2929, 2858, 1722, 1620, 1367, 1251, 1193, 1174, 1137, 1010, 866, 838, 780, 764, 724 cm^{-1}; HRMS (EI) calc. for $C_{21}H_{31}O_3Si$ $(M+H)^+$ 359.2037 found 359.2036.



To an oven-dried 25 mL flask containing $Rh_2(esp)_2$ (4.3 mg, 0.02 equiv) and silyl enol ether (63.7 mg, 0.30 mmol, 1.0 equiv) in 6 mL DCM under argon atmosphere was added a solution of *cis*-methyl vinyldiazoacetate (84.2 mg, 0.60 mmol, 2.0 equiv) in 6 mL DCM by syringe pump over 3 h at -45 ^{o}C using dried ice-acetonitrile bath. The solution was warmed up to room temperature over 2 h and then concentrated by vacuum. The crude mixture was purified by flash chromatography (40/1 pentane/Et_2O, R_f: 0.44 for **5.79** and R_f: 0.42 for **5.80**) in silica gel to provide **5.79** as colorless oil (63.2 mg, 65% yield) and **5.80** as colorless oil (6.2 mg, 7% yield).

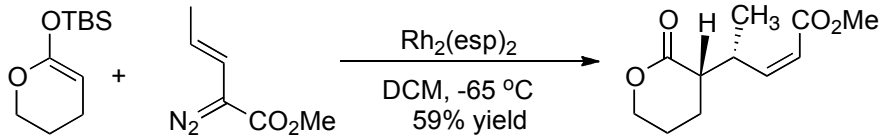
(*Z*)-Methyl 4-(2-((*tert*-butyldimethylsilyl)oxy)cyclohex-1-en-1-yl)pent-2-enoate (5.79): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.25 (dd, *J* = 9.8, 11.7 Hz, 1H), 5.68 (dd, *J* = 1.2, 11.7 Hz, 1H), 4.65-4.73 (m, 1H), 3.70 (s, 3H), 1.94-2.10 (m, 4H), 1.52-1.66 (m, 4H), 1.10 (d, *J* = 7.0 Hz, 3H), 0.94 (s, 9H), 0.15 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7, 152.9, 144.2, 117.7, 116.7, 51.2, 32.3, 30.9, 26.1, 23.61, 23.55, 23.2, 18.7, 18.4, -3.4; IR (neat): 2928, 2857, 1725, 1668, 1253, 1190, 1168, 1014, 931, 830, 776 cm^{-1}; HRMS (EI) calc. for $C_{18}H_{33}O_3Si$ $(M+H)^+$ 325.2194 found 325.2194.



5.80

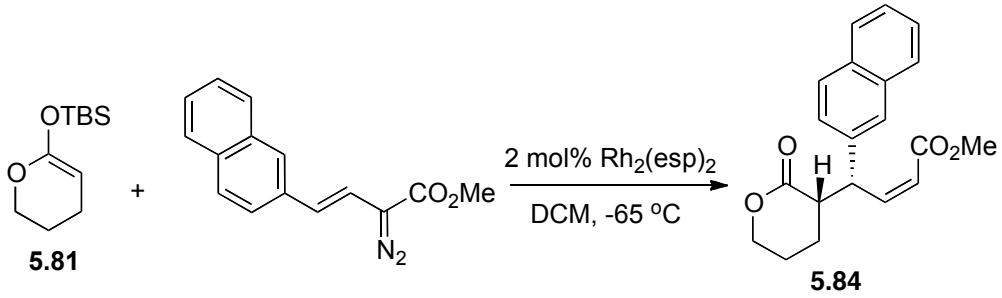
(*Z*)-Methyl 4-(2-((*tert*-butyldimethylsilyl)oxy)cyclohex-2-en-1-yl)pent-2-enoate (5.80): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.30 (dd, *J* = 9.8, 11.6 Hz, 1H), 5.71 (dd, *J* = 0.8,

11.6 Hz, 1H), 4.85-4.87 (m, 1H), 3.84-3.93 (m, 1H), 3.70 (s, 3H), 2.25-2.32 (m, 1H), 1.95-2.03 (m, 2H), 1.62-1.71 (m, 2H), 1.34-1.56 (m, 2H), 0.98 (d, J = 6.7 Hz, 3H), 0.95 (s, 9H), 0.17 (s, 3H), 0.16 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.8, 155.0, 151.6, 118.1, 105.1, 51.3, 43.9, 33.9, 26.0, 25.2, 24.3, 21.4, 16.6, -4.1, -4.4; HRMS (EI) calc. for $C_{18}H_{33}O_3Si$ $(M+H)^+$ 325.2194 found 325.2195.

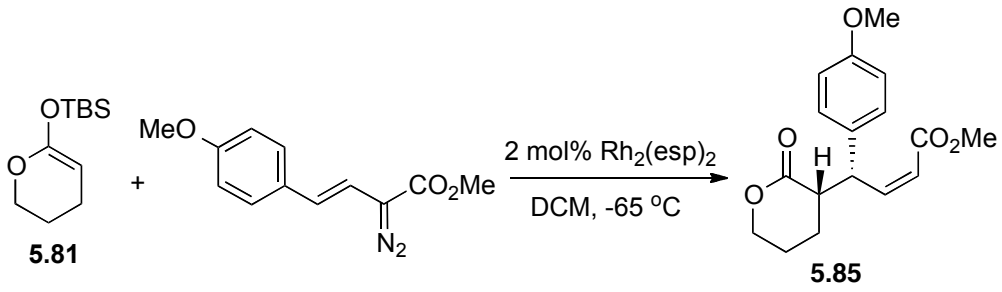


5.81 **5.83** **5.82**

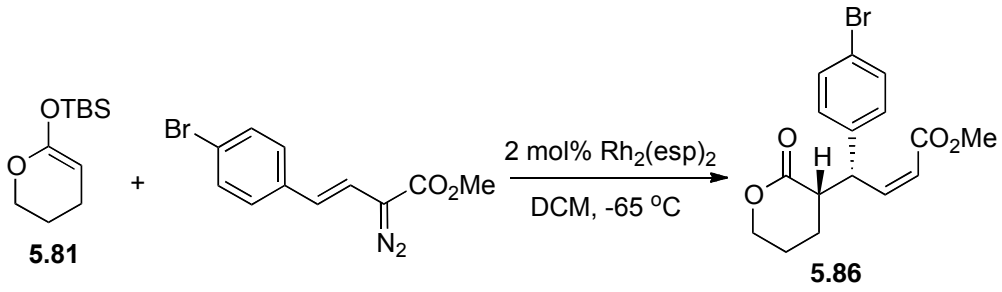
(*R*,*Z*)-Methyl 4-((*S*)-2-oxotetrahydro-2*H*-pyran-3-yl)pent-2-enoate (5.82): To a flame-dried 25 mL flask containing $Rh_2(esp)_2$ (2.3 mg, 0.02 equiv) and *tert*-butyl((3,4-dihydro-2*H*-pyran-6-yl)oxy)dimethylsilane (**5.81**) (193 mg, 0.90 mmol, 6.0 equiv) in 6 mL dried DCM under argon atmosphere was added a solution of (*E*)-methyl 2-diazopent-3-enoate (**5.83**) (21 mg, 0.15 mmol, 1.0 equiv) in 6 mL DCM by syringe pump over 3 h at -65 °C. The solution was stirred at -65 °C over-night and warmed up to room temperature over 2 h. The mixture was concentrated by vacuum and purified by flash chromatography on silica gel (1/1 pentane/Et_2O, R_f: 0.26) to provide 18.9 mg colorless product in 59% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.27 (dd, J = 11.4, 10.2 Hz, 1H), 5.81 (dd, J = 11.8, 1.3 Hz, 1H), 4.24-4.30 (m, 2H), 3.94-4.00 (m, 1H), 3.70 (s, 3H), 2.60-2.66 (m, 1H), 1.98-2.06 (m,1H), 1.82-1.93 (m, 2H), 1.63-1.73 (m, 1H), 1.18 (d, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 166.5, 152.1, 119.5, 68.2, 51.2, 44.8, 33.8, 22.2, 22.0, 17.7; IR (neat): 2952, 1716, 1437, 1196, 1176, 1152, 1083, 1004, 825 cm^{-1}; HRMS (APCI) calc. for $C_{11}H_{17}O_4$ $(M+H)^+$ 213.1127 found 213.1118.



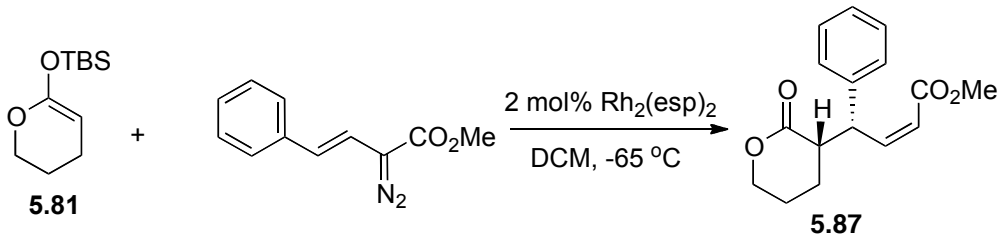
(*R*,*Z*)-Methyl 4-(naphthalen-2-yl)-4-((*S*)-2-oxotetrahydro-2*H*-pyran-3-yl)but-2-enoate (5.84): To a flame-dried 25 mL flask containing $Rh_2(esp)_2$ (2.3 mg, 0.02 equiv) and *tert*-butyl((3,4-dihydro-2*H*-pyran-6-yl)oxy)dimethylsilane (**5.81**) (193 mg, 0.90 mmol, 6.0 equiv) in 6 mL dried DCM under argon atmosphere was added a solution of (*E*)-methyl 2-diazo-4-(naphthalen-2-yl)but-3-enoate (37.9 mg, 0.15 mmol, 1.0 equiv) in 6 mL DCM by syringe pump over 3 h at -65 ^oC. The solution was stirred at -65 ^oC over-night and warmed up to room temperature over 2 h. The mixture was concentrated by vacuum and purified by flash chromatography on silica gel (1/1 pentane/Et_2O, R_f: 0.19) to provide 29.2 mg colorless product in 60% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.78-7.83 (m, 4H), 7.42-7.49 (m, 3H), 6.70 (dd, *J* = 11.4, 10.2 Hz, 1H), 5.86 (dd, *J* = 11.4, 1.0 Hz, 1H), 5.36 (t, *J* = 9.8 Hz, 1H), 4.28-4.37 (m, 3H), 3.69 (s, 3H), 3.03-3.09 (m, 1H), 2.55 (t, *J* = 7.3 Hz, 1H), 1.70-1.95 (m, 6H), 1.56-1.63 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 166.5, 150.0, 137.8, 133.5, 132.4, 128.6, 127.7, 127.6, 127.3, 126.2, 125.9, 125.8, 119.0, 69.4, 68.4, 51.1, 45.2, 44.7, 29.8, 23.1, 22.3, 21.1, 19.1; IR (neat): 2950, 1716, 1436, 1402, 1194, 1173, 1146, 1055, 822, 748 cm^{-1}; HRMS (APCI) calc. for $C_{20}H_{21}O_4$ $(M+H)^+$ 325.1440 found 325.1436.



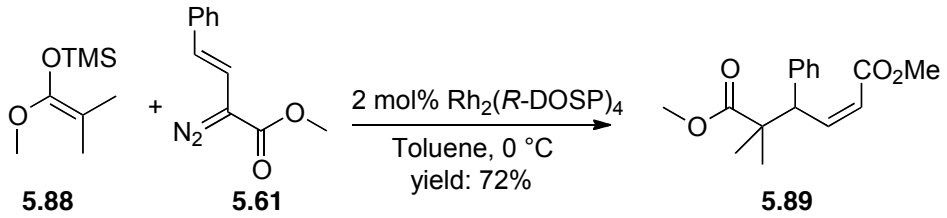
(*R*,*Z*)-Methyl 4-(4-methoxyphenyl)-4-((*S*)-2-oxotetrahydro-2*H*-pyran-3-yl)but-2-enoate (5.85): To a flame-dried 25 mL flask containing $Rh_2(esp)_2$ (2.3 mg, 0.02 equiv) and *tert*-butyl((3,4-dihydro-2*H*-pyran-6-yl)oxy)dimethylsilane (193 mg, 0.90 mmol, 6.0 equiv) in 6 mL dried DCM under argon atmosphere was added a solution of (*E*)-methyl 2-diazo-4-(4-methoxyphenyl)but-3-enoate (37.9 mg, 0.15 mmol, 1.0 equiv) in 6 mL DCM by syringe pump over 3 h at -65 ^{o}C. The solution was stirred at -65 ^{o}C over-night and warmed up to room temperature over 2 h. The mixture was concentrated by vacuum and purified by flash chromatography on silica gel (4/6 pentane/Et_2O, R_f: 0.22) to provide 29.2 mg colorless product in 64% yield.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.25 (m, 2H), 6.83-6.88 (m, 2H), 6.58 (dd, *J* = 11.4, 10.5 Hz, 1H), 5.81 (dd, *J* = 11.4, 1.0 Hz, 1H), 5.13 (t, *J* = 9.8 Hz, 1H), 4.25-4.36 (m, 2H), 3.78 (s, 3H), 3.69 (s, 3H), 2.88-2.94 (m, 1H), 1.72-1.95 (m, 3H), 1.51-1.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 166.6, 158.6, 150.4, 132.3, 129.2, 118.4, 114.2, 68.4, 55.2, 51.1, 45.4, 43.8, 23.0, 21.1; IR (neat): 1717, 1511, 1438, 1248, 1197, 1173, 1149, 1033, 830 cm^{-1}; HRMS (APCI) calc. for $C_{17}H_{21}O_5$ $(M+H)^+$ 305.1389 found 305.1384.



(*R*,*Z*)-Methyl 4-(4-bromophenyl)-4-((*S*)-2-oxotetrahydro-2*H*-pyran-3-yl)but-2-enoate (5.86): To a flame-dried 25 mL flask containing $Rh_2(esp)_2$ (2.3 mg, 0.02 equiv) and *tert*-butyl((3,4-dihydro-2*H*-pyran-6-yl)oxy)dimethylsilane (**5.81**) (193 mg, 0.90 mmol, 6.0 equiv) in 6 mL dried DCM under argon atmosphere was added a solution of (*E*)-methyl 4-(4-bromophenyl)-2-diazobut-3-enoate (41.2 mg, 0.15 mmol, 1.0 equiv) in 6 mL DCM by syringe pump over 3 h at -65 °C. The solution was stirred at -65 °C over-night and warmed up to room temperature over 2 h. The mixture was concentrated by vacuum and purified by flash chromatography on silica gel (1/1 pentane/Et_2O, R_f: 0.18) to provide 32.2 mg colorless product in 61% yield.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.47 (m, 2H), 7.17-7.22 (m, 2H), 6.57 (dd, *J* = 11.4, 10.2 Hz, 1H), 5.86 (dd, *J* = 11.4, 1.0 Hz, 1H), 5.14 (t, *J* = 9.5 Hz, 1H), 4.28-4.32 (m, 2H), 3.69 (s, 3H), 2.88-2.94 (m, 1H), 1.76-1.93 (m, 3H), 1.51-1.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.0, 166.4, 149.3, 139.5, 131.9, 130.0, 121.0, 119.5, 68.4, 51.2, 45.0, 44.0, 23.1, 21.3; IR (neat): 2950, 1720, 1488, 1437, 1402, 1198, 1175, 1151, 1073, 1010, 822 cm^{-1}; HRMS (APCI) calc. for $C_{16}H_{18}BrO_4$ $(M+H)^+$ 353.0388 found 353.0384.



(*R*,*Z*)-Methyl 4-((*S*)-2-oxotetrahydro-2*H*-pyran-3-yl)-4-phenylbut-2-enoate (5.87): To a flame-dried 25 mL flask containing $Rh_2(esp)_2$ (2.3 mg, 0.02 equiv) and *tert*-butyl((3,4-dihydro-2*H*-pyran-6-yl)oxy)dimethylsilane (**5.81**) (193 mg, 0.90 mmol, 6.0 equiv) in 6 mL dried DCM under argon atmosphere was added a solution of (*E*)-methyl 4-phenyl-2-diazobut-3-enoate (30.7 mg, 0.15 mmol, 1.0 equiv) in 6 mL DCM by syringe pump over 3 h at -65 ^{o}C. The solution was stirred at -65 ^{o}C over-night and warmed up to room temperature over 2 h. The mixture was concentrated by vacuum and purified by flash chromatography on silica gel (1/1 pentane/Et_2O, R_f: 0.23) to provide 19.8 mg colorless product in 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.36 (m, 4H), 7.22-7.27 (m, 1H), 6.61 (dd, *J* = 11.3, 10.2 Hz, 1H), 5.84 (dd, *J* = 11.3, 0.8 Hz, 1H), 5.19 (t, *J* = 9.8 Hz, 1H), 4.26-4.38 (m, 2H), 3.68 (s, 3H), 2.93-3.01 (m, 1H), 1.88-1.98 (m, 1H), 1.74-1.86 (m, 2H), 1.51-1.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 166.7, 150.4, 140.6, 129.1, 128.5, 127.3, 119.0, 68.7, 51.4, 45.5, 44.8, 23.3, 21.3; IR (neat): 1717, 1646, 1149, 1173, 1149, 704 cm^{-1}; HRMS (APCI) calc. for $C_{16}H_{19}O_4$ $(M+H)^+$ 275.1278 found 275.1278.

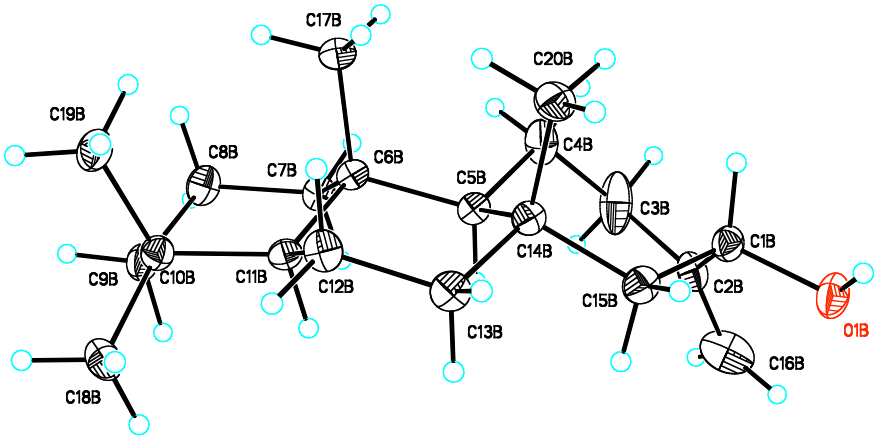


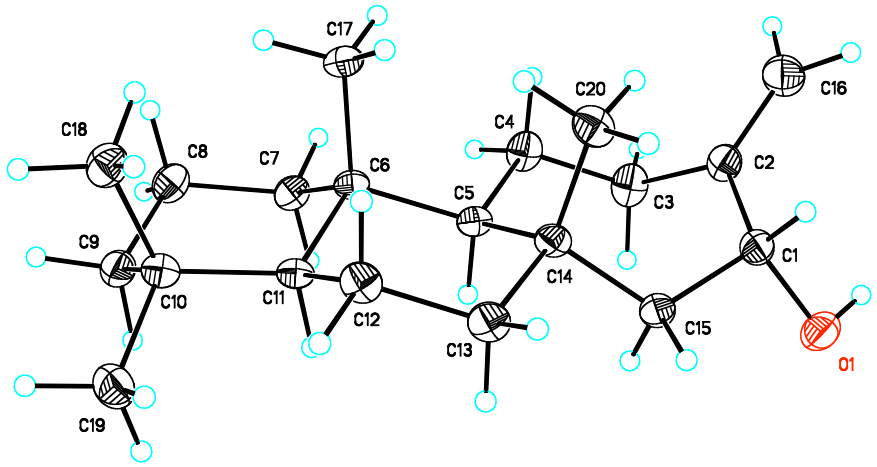
5.88 **5.61** **5.89**

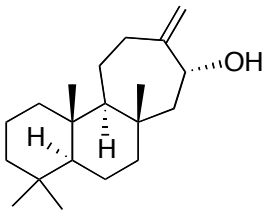
(*Z*)-Dimethyl 5,5-dimethyl-4-phenylhex-2-enedioate (5.89): To a flame-dried 25 mL flask containing Rh_2(*R*-DOSP)$_4$ (5.6 mg, 0.02 equiv) and ((1-methoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane (157 mg, 0.90 mmol, 6.0 equiv) in 6 mL dried toluene under argon atmosphere was added a solution of (*E*)-methyl 4-phenyl-2-diazobut-3-enoate (30.7 mg, 0.15 mmol, 1.0 equiv) in 6 mL toluene by syringe pump over 3 h at room temperature. The solution was concentrated by vacuum and purified by flash chromatography on silica gel (85/15 pentane/Et_2O, R_f: 0.40) to provide 29.8 mg colorless product in 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.31 (m, 2H), 7.22-7.25 (m, 1H), 7.18-7.21 (m, 2H), 6.81 (t, *J* = 11.4 Hz, 1H), 5.91 (dd, *J* = 11.7, 0.8 Hz, 1H), 5.04 (d, *J* = 11.0 Hz, 1H), 3.69 (s, 3H), 3.62 (s, 3H), 1.22 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.0, 166.4, 148.2, 139.8, 129.4, 128.3, 127.2, 120.6, 51.9, 51.3, 50.7, 46.8, 23.6, 23.1; IR (neat): 2950, 1723, 1645, 1436, 1198, 1175, 1131, 996, 814, 704 cm^{-1}; HRMS (APCI) calc. for $C_{16}H_{19}O_4$ $(M-H)^+$ 275.1283 found 275.1278.

Appendix

1. X-ray crystallographic structure of barekol







barekol

Table 1. Crystal data and structure refinement for barekol.

Identification code	barekol	
Empirical formula	C20 H34 O	
Formula weight	290.47	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 6.0927(2) Å	α= 80.027(2)°.
	b = 7.3057(3) Å	β= 86.454(2)°.
	c = 21.0808(8) Å	γ = 67.354(2)°.
Volume	852.89(6) $Å^3$	
Z	2	
Density (calculated)	1.131 Mg/m^3	
Absorption coefficient	0.498 mm^{-1}	
F(000)	324	
Crystal size	0.31 x 0.26 x 0.05 mm^3	
Theta range for data collection	2.13 to 65.87°.	
Index ranges	-6<=h<=7, -8<=k<=7, -24<=l<=24	
Reflections collected	5328	
Independent reflections	3290 [R(int) = 0.0131]	
Completeness to theta = 65.87°	84.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9755 and 0.8609	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3290 / 3 / 379	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.1081	
R indices (all data)	R1 = 0.0390, wR2 = 0.1082	
Absolute structure parameter	0.0(3)	
Largest diff. peak and hole	0.239 and -0.232 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for barekol. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	2486(5)	4224(4)	7135(1)	30(1)
C(2)	4132(5)	2290(3)	6930(1)	30(1)
C(3)	3246(5)	1522(4)	6428(1)	35(1)
C(4)	3619(5)	2463(3)	5737(1)	31(1)
C(5)	1968(4)	4662(3)	5497(1)	23(1)
C(6)	2320(4)	5295(3)	4755(1)	22(1)
C(7)	1808(5)	3857(3)	4377(1)	28(1)
C(8)	1580(5)	4571(4)	3650(1)	32(1)
C(9)	-330(5)	6644(4)	3482(1)	31(1)
C(10)	16(4)	8247(4)	3809(1)	27(1)
C(11)	395(4)	7445(3)	4544(1)	24(1)
C(12)	641(5)	8935(3)	4934(1)	29(1)
C(13)	256(5)	8310(3)	5646(1)	30(1)
C(14)	1968(4)	6195(3)	5939(1)	24(1)
C(15)	863(4)	5743(3)	6601(1)	28(1)
C(16)	6262(6)	1356(4)	7198(1)	43(1)
C(17)	4880(4)	5157(4)	4604(1)	29(1)
C(18)	2034(5)	8838(4)	3481(1)	34(1)
C(19)	-2278(5)	10127(4)	3703(1)	40(1)
C(20)	4433(5)	6231(4)	6037(1)	31(1)
O(1)	882(4)	3798(3)	7627(1)	44(1)
C(1B)	6142(4)	6942(4)	-1645(1)	28(1)
C(2B)	3762(5)	8572(4)	-1543(1)	31(1)
C(3B)	3732(7)	9873(5)	-1072(1)	53(1)
C(4B)	5579(6)	9036(4)	-542(1)	37(1)
C(5B)	5692(4)	7012(3)	-139(1)	23(1)
C(6B)	5963(4)	6939(3)	605(1)	22(1)
C(7B)	3733(4)	8628(3)	825(1)	27(1)
C(8B)	3524(5)	8448(4)	1563(1)	33(1)
C(9B)	3478(4)	6415(4)	1864(1)	31(1)

C(10B)	5645(4)	4618(3)	1700(1)	27(1)
C(11B)	5931(4)	4885(3)	951(1)	23(1)
C(12B)	7962(5)	3144(3)	712(1)	29(1)
C(13B)	7593(5)	3225(3)	-5(1)	29(1)
C(14B)	7509(4)	5184(3)	-430(1)	24(1)
C(15B)	6649(5)	5117(4)	-1101(1)	29(1)
C(16B)	1809(6)	8788(5)	-1840(2)	53(1)
C(17B)	8181(5)	7329(4)	748(1)	31(1)
C(18B)	5080(5)	2714(4)	1921(1)	37(1)
C(19B)	7847(5)	4367(4)	2071(1)	35(1)
C(20B)	10058(5)	5147(4)	-502(1)	33(1)
O(1B)	6087(3)	6318(3)	-2247(1)	37(1)

Table 3. Bond lengths [Å] and angles [°] for barekol.

C(1)-O(1)	1.457(3)	C(12)-H(12B)	0.9900
C(1)-C(2)	1.502(3)	C(13)-C(14)	1.538(3)
C(1)-C(15)	1.529(3)	C(13)-H(13A)	0.9900
C(1)-H(1A)	1.0000	C(13)-H(13B)	0.9900
C(2)-C(16)	1.320(4)	C(14)-C(20)	1.539(3)
C(2)-C(3)	1.497(4)	C(14)-C(15)	1.551(3)
C(3)-C(4)	1.542(3)	C(15)-H(15A)	0.9900
C(3)-H(3A)	0.9900	C(15)-H(15B)	0.9900
C(3)-H(3B)	0.9900	C(16)-H(16)	0.9348
C(4)-C(5)	1.544(3)	C(16)-H(16A)	1.0393
C(4)-H(4A)	0.9900	C(17)-H(17A)	0.9800
C(4)-H(4B)	0.9900	C(17)-H(17B)	0.9800
C(5)-C(14)	1.575(3)	C(17)-H(17C)	0.9800
C(5)-C(6)	1.579(3)	C(18)-H(18A)	0.9800
C(5)-H(5A)	1.0000	C(18)-H(18B)	0.9800
C(6)-C(17)	1.540(3)	C(18)-H(18C)	0.9800
C(6)-C(7)	1.551(3)	C(19)-H(19A)	0.9800
C(6)-C(11)	1.563(3)	C(19)-H(19B)	0.9800
C(7)-C(8)	1.529(3)	C(19)-H(19C)	0.9800
C(7)-H(7A)	0.9900	C(20)-H(20A)	0.9800
C(7)-H(7B)	0.9900	C(20)-H(20B)	0.9800
C(8)-C(9)	1.510(4)	C(20)-H(20C)	0.9800
C(8)-H(8A)	0.9900	O(1)-H(1O)	0.8178
C(8)-H(8B)	0.9900	C(1B)-O(1B)	1.427(3)
C(9)-C(10)	1.541(3)	C(1B)-C(2B)	1.512(3)
C(9)-H(9A)	0.9900	C(1B)-C(15B)	1.544(3)
C(9)-H(9B)	0.9900	C(1B)-H(1BA)	1.0000
C(10)-C(19)	1.531(4)	C(2B)-C(16B)	1.320(5)
C(10)-C(18)	1.541(3)	C(2B)-C(3B)	1.485(4)
C(10)-C(11)	1.557(3)	C(3B)-C(4B)	1.509(4)
C(11)-C(12)	1.528(3)	C(3B)-H(3B1)	0.9900
C(11)-H(11A)	1.0000	C(3B)-H(3B2)	0.9900
C(12)-C(13)	1.522(3)	C(4B)-C(5B)	1.552(3)
C(12)-H(12A)	0.9900	C(4B)-H(4BA)	0.9900

C(4B)-H(4BB)	0.9900	C(18B)-H(18D)	0.9800
C(5B)-C(14B)	1.564(3)	C(18B)-H(18E)	0.9800
C(5B)-C(6B)	1.577(3)	C(18B)-H(18F)	0.9800
C(5B)-H(5BA)	1.0000	C(19B)-H(19D)	0.9800
C(6B)-C(17B)	1.540(3)	C(19B)-H(19E)	0.9800
C(6B)-C(7B)	1.553(3)	C(19B)-H(19F)	0.9800
C(6B)-C(11B)	1.557(3)	C(20B)-H(20D)	0.9800
C(7B)-C(8B)	1.540(3)	C(20B)-H(20E)	0.9800
C(7B)-H(7BA)	0.9900	C(20B)-H(20F)	0.9800
C(7B)-H(7BB)	0.9900	O(1B)-H(1BB)	0.8400
C(8B)-C(9B)	1.521(4)		
C(8B)-H(8BA)	0.9900	O(1)-C(1)-C(2)	109.14(19)
C(8B)-H(8BB)	0.9900	O(1)-C(1)-C(15)	105.1(2)
C(9B)-C(10B)	1.533(3)	C(2)-C(1)-C(15)	114.6(2)
C(9B)-H(9BA)	0.9900	O(1)-C(1)-H(1A)	109.3
C(9B)-H(9BB)	0.9900	C(2)-C(1)-H(1A)	109.3
C(10B)-C(19B)	1.528(4)	C(15)-C(1)-H(1A)	109.3
C(10B)-C(18B)	1.547(3)	C(16)-C(2)-C(3)	123.4(2)
C(10B)-C(11B)	1.564(3)	C(16)-C(2)-C(1)	119.2(2)
C(11B)-C(12B)	1.529(3)	C(3)-C(2)-C(1)	117.4(2)
C(11B)-H(11B)	1.0000	C(2)-C(3)-C(4)	112.70(19)
C(12B)-C(13B)	1.528(3)	C(2)-C(3)-H(3A)	109.1
C(12B)-H(12C)	0.9900	C(4)-C(3)-H(3A)	109.1
C(12B)-H(12D)	0.9900	C(2)-C(3)-H(3B)	109.1
C(13B)-C(14B)	1.536(3)	C(4)-C(3)-H(3B)	109.1
C(13B)-H(13C)	0.9900	H(3A)-C(3)-H(3B)	107.8
C(13B)-H(13D)	0.9900	C(3)-C(4)-C(5)	117.6(2)
C(14B)-C(20B)	1.541(3)	C(3)-C(4)-H(4A)	107.9
C(14B)-C(15B)	1.554(3)	C(5)-C(4)-H(4A)	107.9
C(15B)-H(15C)	0.9900	C(3)-C(4)-H(4B)	107.9
C(15B)-H(15D)	0.9900	C(5)-C(4)-H(4B)	107.9
C(16B)-H(16B)	0.8774	H(4A)-C(4)-H(4B)	107.2
C(16B)-H(16C)	0.9830	C(4)-C(5)-C(14)	114.24(18)
C(17B)-H(17D)	0.9800	C(4)-C(5)-C(6)	111.28(17)
C(17B)-H(17E)	0.9800	C(14)-C(5)-C(6)	115.33(16)
C(17B)-H(17F)	0.9800	C(4)-C(5)-H(5A)	104.9

C(14)-C(5)-H(5A)	104.9	C(10)-C(11)-H(11A)	104.3
C(6)-C(5)-H(5A)	104.9	C(6)-C(11)-H(11A)	104.3
C(17)-C(6)-C(7)	108.19(17)	C(13)-C(12)-C(11)	110.02(17)
C(17)-C(6)-C(11)	113.40(17)	C(13)-C(12)-H(12A)	109.7
C(7)-C(6)-C(11)	107.15(19)	C(11)-C(12)-H(12A)	109.7
C(17)-C(6)-C(5)	111.74(19)	C(13)-C(12)-H(12B)	109.7
C(7)-C(6)-C(5)	108.83(16)	C(11)-C(12)-H(12B)	109.7
C(11)-C(6)-C(5)	107.35(16)	H(12A)-C(12)-H(12B)	108.2
C(8)-C(7)-C(6)	113.65(18)	C(12)-C(13)-C(14)	114.79(18)
C(8)-C(7)-H(7A)	108.8	C(12)-C(13)-H(13A)	108.6
C(6)-C(7)-H(7A)	108.8	C(14)-C(13)-H(13A)	108.6
C(8)-C(7)-H(7B)	108.8	C(12)-C(13)-H(13B)	108.6
C(6)-C(7)-H(7B)	108.8	C(14)-C(13)-H(13B)	108.6
H(7A)-C(7)-H(7B)	107.7	H(13A)-C(13)-H(13B)	107.5
C(9)-C(8)-C(7)	111.81(19)	C(20)-C(14)-C(13)	109.48(19)
C(9)-C(8)-H(8A)	109.3	C(20)-C(14)-C(15)	109.9(2)
C(7)-C(8)-H(8A)	109.3	C(13)-C(14)-C(15)	104.41(18)
C(9)-C(8)-H(8B)	109.3	C(20)-C(14)-C(5)	114.34(18)
C(7)-C(8)-H(8B)	109.3	C(13)-C(14)-C(5)	108.63(18)
H(8A)-C(8)-H(8B)	107.9	C(15)-C(14)-C(5)	109.56(16)
C(8)-C(9)-C(10)	113.8(2)	C(1)-C(15)-C(14)	118.8(2)
C(8)-C(9)-H(9A)	108.8	C(1)-C(15)-H(15A)	107.6
C(10)-C(9)-H(9A)	108.8	C(14)-C(15)-H(15A)	107.6
C(8)-C(9)-H(9B)	108.8	C(1)-C(15)-H(15B)	107.6
C(10)-C(9)-H(9B)	108.8	C(14)-C(15)-H(15B)	107.6
H(9A)-C(9)-H(9B)	107.7	H(15A)-C(15)-H(15B)	107.1
C(19)-C(10)-C(9)	107.2(2)	C(2)-C(16)-H(16)	125.5
C(19)-C(10)-C(18)	107.0(2)	C(2)-C(16)-H(16A)	124.1
C(9)-C(10)-C(18)	110.54(18)	H(16)-C(16)-H(16A)	110.4
C(19)-C(10)-C(11)	109.13(19)	C(6)-C(17)-H(17A)	109.5
C(9)-C(10)-C(11)	108.47(18)	C(6)-C(17)-H(17B)	109.5
C(18)-C(10)-C(11)	114.2(2)	H(17A)-C(17)-H(17B)	109.5
C(12)-C(11)-C(10)	114.01(18)	C(6)-C(17)-H(17C)	109.5
C(12)-C(11)-C(6)	110.72(19)	H(17A)-C(17)-H(17C)	109.5
C(10)-C(11)-C(6)	117.57(17)	H(17B)-C(17)-H(17C)	109.5
C(12)-C(11)-H(11A)	104.3	C(10)-C(18)-H(18A)	109.5

C(10)-C(18)-H(18B)	109.5	C(3B)-C(4B)-H(4BB)	108.7
H(18A)-C(18)-H(18B)	109.5	C(5B)-C(4B)-H(4BB)	108.7
C(10)-C(18)-H(18C)	109.5	H(4BA)-C(4B)-H(4BB)	107.6
H(18A)-C(18)-H(18C)	109.5	C(4B)-C(5B)-C(14B)	111.28(17)
H(18B)-C(18)-H(18C)	109.5	C(4B)-C(5B)-C(6B)	112.40(17)
C(10)-C(19)-H(19A)	109.5	C(14B)-C(5B)-C(6B)	115.77(18)
C(10)-C(19)-H(19B)	109.5	C(4B)-C(5B)-H(5BA)	105.5
H(19A)-C(19)-H(19B)	109.5	C(14B)-C(5B)-H(5BA)	105.5
C(10)-C(19)-H(19C)	109.5	C(6B)-C(5B)-H(5BA)	105.5
H(19A)-C(19)-H(19C)	109.5	C(17B)-C(6B)-C(7B)	108.32(18)
H(19B)-C(19)-H(19C)	109.5	C(17B)-C(6B)-C(11B)	114.60(19)
C(14)-C(20)-H(20A)	109.5	C(7B)-C(6B)-C(11B)	107.75(17)
C(14)-C(20)-H(20B)	109.5	C(17B)-C(6B)-C(5B)	111.23(18)
H(20A)-C(20)-H(20B)	109.5	C(7B)-C(6B)-C(5B)	107.74(18)
C(14)-C(20)-H(20C)	109.5	C(11B)-C(6B)-C(5B)	106.96(15)
H(20A)-C(20)-H(20C)	109.5	C(8B)-C(7B)-C(6B)	112.79(19)
H(20B)-C(20)-H(20C)	109.5	C(8B)-C(7B)-H(7BA)	109.0
C(1)-O(1)-H(1O)	102.9	C(6B)-C(7B)-H(7BA)	109.0
O(1B)-C(1B)-C(2B)	108.7(2)	C(8B)-C(7B)-H(7BB)	109.0
O(1B)-C(1B)-C(15B)	109.05(19)	C(6B)-C(7B)-H(7BB)	109.0
C(2B)-C(1B)-C(15B)	110.45(18)	H(7BA)-C(7B)-H(7BB)	107.8
O(1B)-C(1B)-H(1BA)	109.5	C(9B)-C(8B)-C(7B)	110.93(18)
C(2B)-C(1B)-H(1BA)	109.5	C(9B)-C(8B)-H(8BA)	109.5
C(15B)-C(1B)-H(1BA)	109.5	C(7B)-C(8B)-H(8BA)	109.5
C(16B)-C(2B)-C(3B)	121.8(3)	C(9B)-C(8B)-H(8BB)	109.5
C(16B)-C(2B)-C(1B)	122.2(2)	C(7B)-C(8B)-H(8BB)	109.5
C(3B)-C(2B)-C(1B)	116.0(3)	H(8BA)-C(8B)-H(8BB)	108.0
C(2B)-C(3B)-C(4B)	118.6(2)	C(8B)-C(9B)-C(10B)	114.08(19)
C(2B)-C(3B)-H(3B1)	107.7	C(8B)-C(9B)-H(9BA)	108.7
C(4B)-C(3B)-H(3B1)	107.7	C(10B)-C(9B)-H(9BA)	108.7
C(2B)-C(3B)-H(3B2)	107.7	C(8B)-C(9B)-H(9BB)	108.7
C(4B)-C(3B)-H(3B2)	107.7	C(10B)-C(9B)-H(9BB)	108.7
H(3B1)-C(3B)-H(3B2)	107.1	H(9BA)-C(9B)-H(9BB)	107.6
C(3B)-C(4B)-C(5B)	114.3(2)	C(19B)-C(10B)-C(9B)	111.0(2)
C(3B)-C(4B)-H(4BA)	108.7	C(19B)-C(10B)-C(18B)	107.7(2)
C(5B)-C(4B)-H(4BA)	108.7	C(9B)-C(10B)-C(18B)	107.21(19)

C(19B)-C(10B)-C(11B)	114.57(18)	C(14B)-C(15B)-H(15D)	107.3
C(9B)-C(10B)-C(11B)	108.05(18)	H(15C)-C(15B)-H(15D)	106.9
C(18B)-C(10B)-C(11B)	108.05(17)	C(2B)-C(16B)-H(16B)	126.2
C(12B)-C(11B)-C(6B)	110.60(17)	C(2B)-C(16B)-H(16C)	112.2
C(12B)-C(11B)-C(10B)	114.12(19)	H(16B)-C(16B)-H(16C)	121.4
C(6B)-C(11B)-C(10B)	116.98(17)	C(6B)-C(17B)-H(17D)	109.5
C(12B)-C(11B)-H(11B)	104.6	C(6B)-C(17B)-H(17E)	109.5
C(6B)-C(11B)-H(11B)	104.6	H(17D)-C(17B)-H(17E)	109.5
C(10B)-C(11B)-H(11B)	104.6	C(6B)-C(17B)-H(17F)	109.5
C(13B)-C(12B)-C(11B)	109.2(2)	H(17D)-C(17B)-H(17F)	109.5
C(13B)-C(12B)-H(12C)	109.8	H(17E)-C(17B)-H(17F)	109.5
C(11B)-C(12B)-H(12C)	109.8	C(10B)-C(18B)-H(18D)	109.5
C(13B)-C(12B)-H(12D)	109.8	C(10B)-C(18B)-H(18E)	109.5
C(11B)-C(12B)-H(12D)	109.8	H(18D)-C(18B)-H(18E)	109.5
H(12C)-C(12B)-H(12D)	108.3	C(10B)-C(18B)-H(18F)	109.5
C(12B)-C(13B)-C(14B)	114.10(18)	H(18D)-C(18B)-H(18F)	109.5
C(12B)-C(13B)-H(13C)	108.7	H(18E)-C(18B)-H(18F)	109.5
C(14B)-C(13B)-H(13C)	108.7	C(10B)-C(19B)-H(19D)	109.5
C(12B)-C(13B)-H(13D)	108.7	C(10B)-C(19B)-H(19E)	109.5
C(14B)-C(13B)-H(13D)	108.7	H(19D)-C(19B)-H(19E)	109.5
H(13C)-C(13B)-H(13D)	107.6	C(10B)-C(19B)-H(19F)	109.5
C(13B)-C(14B)-C(20B)	108.6(2)	H(19D)-C(19B)-H(19F)	109.5
C(13B)-C(14B)-C(15B)	105.24(17)	H(19E)-C(19B)-H(19F)	109.5
C(20B)-C(14B)-C(15B)	108.08(18)	C(14B)-C(20B)-H(20D)	109.5
C(13B)-C(14B)-C(5B)	109.09(17)	C(14B)-C(20B)-H(20E)	109.5
C(20B)-C(14B)-C(5B)	114.71(17)	H(20D)-C(20B)-H(20E)	109.5
C(15B)-C(14B)-C(5B)	110.64(19)	C(14B)-C(20B)-H(20F)	109.5
C(1B)-C(15B)-C(14B)	120.10(18)	H(20D)-C(20B)-H(20F)	109.5
C(1B)-C(15B)-H(15C)	107.3	H(20E)-C(20B)-H(20F)	109.5
C(14B)-C(15B)-H(15C)	107.3	C(1B)-O(1B)-H(1BB)	109.5
C(1B)-C(15B)-H(15D)	107.3		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for barekol. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ..\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	29(1)	31(1)	27(1)	-9(1)	-1(1)	-6(1)
C(2)	33(2)	24(1)	27(1)	-2(1)	1(1)	-8(1)
C(3)	48(2)	22(1)	34(1)	-6(1)	1(1)	-12(1)
C(4)	41(2)	19(1)	31(1)	-8(1)	2(1)	-8(1)
C(5)	21(1)	23(1)	29(1)	-9(1)	3(1)	-10(1)
C(6)	19(1)	19(1)	28(1)	-7(1)	3(1)	-6(1)
C(7)	30(1)	25(1)	29(1)	-8(1)	4(1)	-11(1)
C(8)	39(2)	31(1)	30(1)	-13(1)	6(1)	-15(1)
C(9)	30(1)	36(1)	27(1)	-6(1)	1(1)	-14(1)
C(10)	23(1)	27(1)	31(1)	-5(1)	0(1)	-8(1)
C(11)	19(1)	22(1)	29(1)	-6(1)	1(1)	-6(1)
C(12)	32(1)	18(1)	34(1)	-6(1)	-2(1)	-6(1)
C(13)	33(1)	19(1)	35(1)	-11(1)	0(1)	-3(1)
C(14)	22(1)	20(1)	29(1)	-10(1)	-1(1)	-4(1)
C(15)	26(1)	26(1)	28(1)	-9(1)	0(1)	-3(1)
C(16)	38(2)	36(1)	44(1)	-9(1)	-3(1)	0(1)
C(17)	22(1)	30(1)	33(1)	-6(1)	6(1)	-9(1)
C(18)	38(2)	32(1)	34(1)	-2(1)	3(1)	-16(1)
C(19)	40(2)	37(1)	35(1)	-3(1)	-5(1)	-5(1)
C(20)	31(1)	29(1)	37(1)	-9(1)	-4(1)	-14(1)
O(1)	38(1)	46(1)	30(1)	0(1)	5(1)	0(1)
C(1B)	24(1)	37(1)	25(1)	-10(1)	3(1)	-11(1)
C(2B)	33(2)	31(1)	24(1)	1(1)	4(1)	-9(1)
C(3B)	57(2)	44(2)	27(1)	0(1)	-1(1)	13(2)
C(4B)	56(2)	22(1)	28(1)	-5(1)	5(1)	-11(1)
C(5B)	23(1)	20(1)	25(1)	-4(1)	-2(1)	-6(1)
C(6B)	22(1)	22(1)	24(1)	-5(1)	-2(1)	-8(1)
C(7B)	29(1)	21(1)	27(1)	-5(1)	-3(1)	-5(1)
C(8B)	35(2)	30(1)	29(1)	-12(1)	2(1)	-5(1)
C(9B)	29(1)	39(1)	24(1)	-7(1)	2(1)	-12(1)
C(10B)	27(1)	28(1)	25(1)	-3(1)	-1(1)	-10(1)

C(11B)	21(1)	24(1)	26(1)	-5(1)	-2(1)	-8(1)
C(12B)	29(1)	21(1)	31(1)	-2(1)	-1(1)	-4(1)
C(13B)	30(1)	20(1)	34(1)	-9(1)	3(1)	-6(1)
C(14B)	22(1)	23(1)	25(1)	-7(1)	2(1)	-6(1)
C(15B)	26(1)	28(1)	31(1)	-10(1)	2(1)	-7(1)
C(16B)	34(2)	38(2)	77(2)	0(1)	3(2)	-8(1)
C(17B)	36(2)	34(1)	32(1)	-7(1)	-1(1)	-21(1)
C(18B)	43(2)	38(1)	31(1)	0(1)	5(1)	-20(1)
C(19B)	34(2)	38(1)	28(1)	-1(1)	-8(1)	-11(1)
C(20B)	25(1)	38(1)	36(1)	-11(1)	6(1)	-11(1)
O(1B)	34(1)	48(1)	26(1)	-14(1)	3(1)	-10(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for barekol.

	x	y	z	U(eq)
H(1A)	3441	4857	7318	36
H(3A)	1529	1816	6496	42
H(3B)	4085	44	6477	42
H(4A)	3444	1621	5437	37
H(4B)	5281	2383	5703	37
H(5A)	324	4662	5533	27
H(7A)	3108	2514	4464	33
H(7B)	314	3711	4540	33
H(8A)	3122	4590	3478	39
H(8B)	1198	3612	3443	39
H(9A)	-1892	6579	3610	37
H(9B)	-359	7065	3009	37
H(11A)	-1140	7320	4693	29
H(12A)	2246	8976	4871	34
H(12B)	-545	10298	4782	34
H(13A)	-1395	8372	5704	36
H(13B)	422	9296	5888	36
H(15A)	79	7030	6766	34
H(15B)	-401	5267	6526	34
H(16)	7369	109	7123	52
H(16A)	6956	1937	7516	52
H(17A)	5033	5555	4140	43
H(17B)	5995	3772	4737	43
H(17C)	5240	6056	4838	43
H(18A)	1669	9328	3022	52
H(18B)	3533	7661	3532	52
H(18C)	2182	9899	3682	52
H(19A)	-2524	10640	3241	61
H(19B)	-2152	11160	3923	61
H(19C)	-3626	9786	3877	61

H(20A)	4286	7219	6314	46
H(20B)	5077	6599	5618	46
H(20C)	5506	4897	6240	46
H(1O)	1774	2822	7866	53
H(1BA)	7425	7480	-1651	34
H(3B1)	2147	10291	-866	64
H(3B2)	3884	11104	-1316	64
H(4BA)	5239	10036	-249	44
H(4BB)	7158	8844	-736	44
H(5BA)	4097	6964	-192	28
H(7BA)	3803	9949	645	32
H(7BB)	2292	8576	649	32
H(8BA)	4890	8620	1739	39
H(8BB)	2049	9529	1676	39
H(9BA)	2023	6314	1717	37
H(9BB)	3383	6340	2337	37
H(11B)	4455	4830	788	28
H(12C)	9502	3245	779	34
H(12D)	7992	1849	956	34
H(13C)	6085	3054	-61	34
H(13D)	8900	2082	-155	34
H(15C)	7858	3942	-1263	34
H(15D)	5172	4847	-1033	34
H(16B)	1727	8140	-2145	63
H(16C)	402	9877	-1708	63
H(17D)	8060	8647	515	47
H(17E)	9607	6283	609	47
H(17F)	8285	7304	1212	47
H(18D)	4882	2522	2389	55
H(18E)	6392	1541	1800	55
H(18F)	3610	2873	1712	55
H(19D)	7514	4231	2534	52
H(19E)	8258	5548	1937	52
H(19F)	9179	3161	1980	52
H(20D)	11073	3968	-691	49
H(20E)	10684	5081	-78	49

H(20F)	10036	6370	-785	49
H(1BB)	7456	5539	-2334	56

Table 6. Torsion angles [°] for barekol.

O(1)-C(1)-C(2)-C(16)	-96.0(3)
C(15)-C(1)-C(2)-C(16)	146.4(2)
O(1)-C(1)-C(2)-C(3)	83.9(2)
C(15)-C(1)-C(2)-C(3)	-33.7(3)
C(16)-C(2)-C(3)-C(4)	-95.5(3)
C(1)-C(2)-C(3)-C(4)	84.7(3)
C(2)-C(3)-C(4)-C(5)	-74.1(3)
C(3)-C(4)-C(5)-C(14)	55.6(3)
C(3)-C(4)-C(5)-C(6)	-171.6(2)
C(4)-C(5)-C(6)-C(17)	-61.1(2)
C(14)-C(5)-C(6)-C(17)	71.1(2)
C(4)-C(5)-C(6)-C(7)	58.3(2)
C(14)-C(5)-C(6)-C(7)	-169.49(19)
C(4)-C(5)-C(6)-C(11)	173.95(17)
C(14)-C(5)-C(6)-C(11)	-53.8(2)
C(17)-C(6)-C(7)-C(8)	-70.5(3)
C(11)-C(6)-C(7)-C(8)	52.1(2)
C(5)-C(6)-C(7)-C(8)	167.9(2)
C(6)-C(7)-C(8)-C(9)	-56.9(3)
C(7)-C(8)-C(9)-C(10)	55.9(3)
C(8)-C(9)-C(10)-C(19)	-168.87(19)
C(8)-C(9)-C(10)-C(18)	74.8(3)
C(8)-C(9)-C(10)-C(11)	-51.2(3)
C(19)-C(10)-C(11)-C(12)	-60.7(3)
C(9)-C(10)-C(11)-C(12)	-177.1(2)
C(18)-C(10)-C(11)-C(12)	59.1(3)
C(19)-C(10)-C(11)-C(6)	167.30(19)
C(9)-C(10)-C(11)-C(6)	50.8(3)
C(18)-C(10)-C(11)-C(6)	-72.9(2)
C(17)-C(6)-C(11)-C(12)	-65.3(2)
C(7)-C(6)-C(11)-C(12)	175.37(16)
C(5)-C(6)-C(11)-C(12)	58.6(2)
C(17)-C(6)-C(11)-C(10)	68.2(2)
C(7)-C(6)-C(11)-C(10)	-51.1(2)

C(5)-C(6)-C(11)-C(10)	-167.90(19)
C(10)-C(11)-C(12)-C(13)	163.0(2)
C(6)-C(11)-C(12)-C(13)	-61.7(2)
C(11)-C(12)-C(13)-C(14)	58.3(3)
C(12)-C(13)-C(14)-C(20)	74.9(2)
C(12)-C(13)-C(14)-C(15)	-167.4(2)
C(12)-C(13)-C(14)-C(5)	-50.6(3)
C(4)-C(5)-C(14)-C(20)	57.5(2)
C(6)-C(5)-C(14)-C(20)	-73.3(3)
C(4)-C(5)-C(14)-C(13)	-179.88(18)
C(6)-C(5)-C(14)-C(13)	49.3(2)
C(4)-C(5)-C(14)-C(15)	-66.4(2)
C(6)-C(5)-C(14)-C(15)	162.8(2)
O(1)-C(1)-C(15)-C(14)	-167.38(18)
C(2)-C(1)-C(15)-C(14)	-47.5(3)
C(20)-C(14)-C(15)-C(1)	-38.2(3)
C(13)-C(14)-C(15)-C(1)	-155.5(2)
C(5)-C(14)-C(15)-C(1)	88.3(2)
O(1B)-C(1B)-C(2B)-C(16B)	22.3(3)
C(15B)-C(1B)-C(2B)-C(16B)	-97.3(3)
O(1B)-C(1B)-C(2B)-C(3B)	-159.8(2)
C(15B)-C(1B)-C(2B)-C(3B)	80.6(3)
C(16B)-C(2B)-C(3B)-C(4B)	151.8(3)
C(1B)-C(2B)-C(3B)-C(4B)	-26.0(4)
C(2B)-C(3B)-C(4B)-C(5B)	-53.7(4)
C(3B)-C(4B)-C(5B)-C(14B)	90.7(3)
C(3B)-C(4B)-C(5B)-C(6B)	-137.6(2)
C(4B)-C(5B)-C(6B)-C(17B)	-56.9(3)
C(14B)-C(5B)-C(6B)-C(17B)	72.6(2)
C(4B)-C(5B)-C(6B)-C(7B)	61.7(2)
C(14B)-C(5B)-C(6B)-C(7B)	-168.87(16)
C(4B)-C(5B)-C(6B)-C(11B)	177.3(2)
C(14B)-C(5B)-C(6B)-C(11B)	-53.3(2)
C(17B)-C(6B)-C(7B)-C(8B)	-71.4(2)
C(11B)-C(6B)-C(7B)-C(8B)	53.1(2)
C(5B)-C(6B)-C(7B)-C(8B)	168.22(18)

C(6B)-C(7B)-C(8B)-C(9B)	-57.2(3)
C(7B)-C(8B)-C(9B)-C(10B)	57.1(3)
C(8B)-C(9B)-C(10B)-C(19B)	74.1(2)
C(8B)-C(9B)-C(10B)-C(18B)	-168.6(2)
C(8B)-C(9B)-C(10B)-C(11B)	-52.4(2)
C(17B)-C(6B)-C(11B)-C(12B)	-64.4(2)
C(7B)-C(6B)-C(11B)-C(12B)	174.94(18)
C(5B)-C(6B)-C(11B)-C(12B)	59.3(2)
C(17B)-C(6B)-C(11B)-C(10B)	68.5(3)
C(7B)-C(6B)-C(11B)-C(10B)	-52.1(3)
C(5B)-C(6B)-C(11B)-C(10B)	-167.72(18)
C(19B)-C(10B)-C(11B)-C(12B)	58.5(3)
C(9B)-C(10B)-C(11B)-C(12B)	-177.16(19)
C(18B)-C(10B)-C(11B)-C(12B)	-61.5(3)
C(19B)-C(10B)-C(11B)-C(6B)	-72.8(3)
C(9B)-C(10B)-C(11B)-C(6B)	51.5(2)
C(18B)-C(10B)-C(11B)-C(6B)	167.2(2)
C(6B)-C(11B)-C(12B)-C(13B)	-63.5(2)
C(10B)-C(11B)-C(12B)-C(13B)	162.15(18)
C(11B)-C(12B)-C(13B)-C(14B)	59.3(3)
C(12B)-C(13B)-C(14B)-C(20B)	75.0(2)
C(12B)-C(13B)-C(14B)-C(15B)	-169.4(2)
C(12B)-C(13B)-C(14B)-C(5B)	-50.7(3)
C(4B)-C(5B)-C(14B)-C(13B)	178.7(2)
C(6B)-C(5B)-C(14B)-C(13B)	48.7(2)
C(4B)-C(5B)-C(14B)-C(20B)	56.6(3)
C(6B)-C(5B)-C(14B)-C(20B)	-73.4(2)
C(4B)-C(5B)-C(14B)-C(15B)	-66.0(2)
C(6B)-C(5B)-C(14B)-C(15B)	164.06(17)
O(1B)-C(1B)-C(15B)-C(14B)	162.7(2)
C(2B)-C(1B)-C(15B)-C(14B)	-77.9(3)
C(13B)-C(14B)-C(15B)-C(1B)	174.8(2)
C(20B)-C(14B)-C(15B)-C(1B)	-69.2(3)
C(5B)-C(14B)-C(15B)-C(1B)	57.1(3)

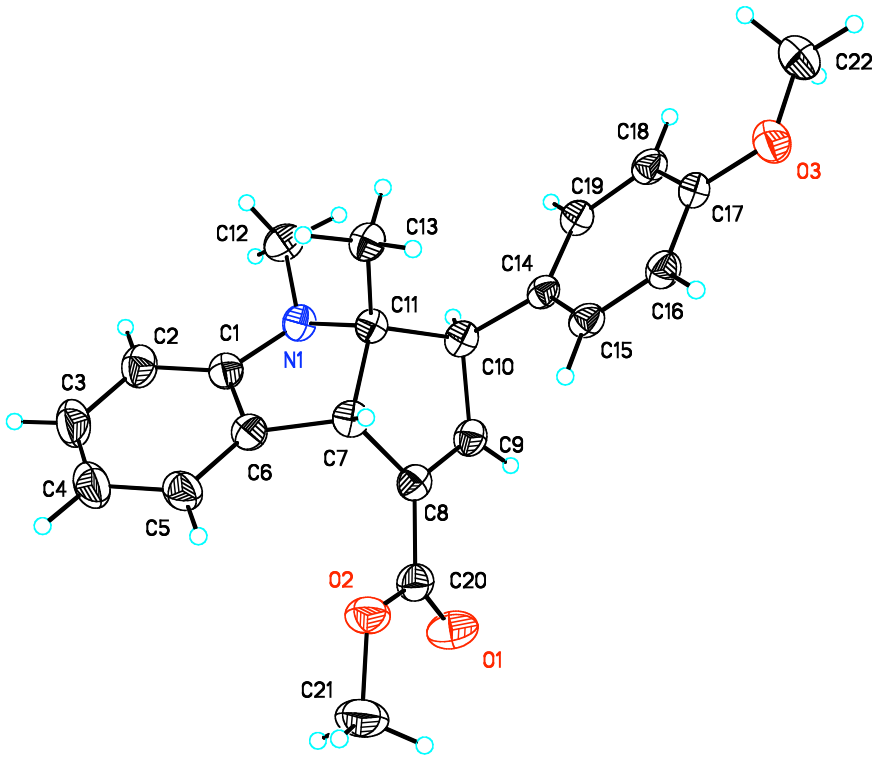
Symmetry transformations used to generate equivalent atoms:

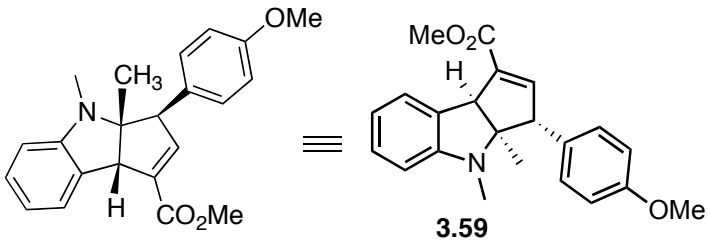
Table 7. Hydrogen bonds for barekol [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1B)-H(1BB)...O(1)#1	0.84	1.99	2.816(3)	168.4

Symmetry transformations used to generate equivalent atoms:
#1 x+1,y,z-1

2. X-ray crystallographic structure of product 3.59





3.59

Table 1. Crystal data and structure refinement for product **3.59**.

Identification code	yl_vii_26s
Empirical formula	C22 H23 N O3
Formula weight	349.41
Temperature	173(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P2(1)
Unit cell dimensions	a = 10.6326(9) Å α= 90°.
	b = 5.7924(5) Å β= 107.396(6)°.
	c = 15.5841(14) Å γ = 90°.
Volume	915.90(14) $Å^3$
Z	2
Density (calculated)	1.267 Mg/m^3
Absorption coefficient	0.672 mm^{-1}
F(000)	372
Crystal size	0.34 x 0.17 x 0.10 mm^3
Theta range for data collection	2.97 to 69.19°.
Index ranges	-12<=h<=11, -6<=k<=5, -16<=l<=18
Reflections collected	6499
Independent reflections	2623 [R(int) = 0.0207]
Completeness to theta = 69.19°	92.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9358 and 0.8037
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2623 / 1 / 240
Goodness-of-fit on F^2	1.085
Final R indices [I>2sigma(I)]	R1 = 0.0313, wR2 = 0.0866
R indices (all data)	R1 = 0.0589, wR2 = 0.1062
Absolute structure parameter	-0.3(3)
Extinction coefficient	0.0082(11)
Largest diff. peak and hole	0.326 and -0.299 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for product **3.59**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-6781(2)	-1971(5)	-2907(2)	35(1)
C(2)	-8107(2)	-1661(5)	-3364(2)	46(1)
C(3)	-8721(3)	-3296(6)	-4013(2)	56(1)
C(4)	-8051(3)	-5181(6)	-4191(2)	54(1)
C(5)	-6720(2)	-5493(5)	-3727(2)	45(1)
C(6)	-6096(2)	-3873(4)	-3093(2)	35(1)
C(7)	-4706(2)	-3766(4)	-2469(2)	33(1)
C(8)	-3680(2)	-2681(4)	-2847(2)	34(1)
C(9)	-3078(2)	-911(4)	-2356(2)	36(1)
C(10)	-3538(2)	-450(4)	-1547(2)	33(1)
C(11)	-4797(2)	-1995(4)	-1741(2)	30(1)
C(12)	-6560(2)	948(4)	-1740(2)	43(1)
C(13)	-5022(2)	-3131(4)	-918(2)	35(1)
C(14)	-2490(2)	-976(4)	-660(2)	30(1)
C(15)	-1765(2)	-3017(4)	-520(2)	33(1)
C(16)	-890(2)	-3543(4)	314(2)	34(1)
C(17)	-715(2)	-1995(5)	1024(2)	35(1)
C(18)	-1403(2)	63(4)	895(2)	38(1)
C(19)	-2277(2)	553(4)	52(2)	34(1)
C(20)	-3326(2)	-3546(5)	-3633(2)	41(1)
C(21)	-3532(3)	-6712(6)	-4633(2)	63(1)
C(22)	283(3)	-1249(6)	2580(2)	57(1)
N(1)	-5961(2)	-594(4)	-2240(1)	35(1)
O(1)	-2678(2)	-2509(4)	-4024(1)	60(1)
O(2)	-3801(2)	-5673(3)	-3860(1)	48(1)
O(3)	155(2)	-2692(3)	1821(1)	50(1)

Table 3. Bond lengths [Å] and angles [°] for product **3.59**.

C(1)-C(2)	1.388(3)	C(15)-H(15)	0.9500
C(1)-N(1)	1.391(3)	C(16)-C(17)	1.393(3)
C(1)-C(6)	1.399(4)	C(16)-H(16)	0.9500
C(2)-C(3)	1.397(4)	C(17)-O(3)	1.369(3)
C(2)-H(2)	0.9500	C(17)-C(18)	1.381(3)
C(3)-C(4)	1.377(5)	C(18)-C(19)	1.393(4)
C(3)-H(3)	0.9500	C(18)-H(18)	0.9500
C(4)-C(5)	1.395(4)	C(19)-H(19)	0.9500
C(4)-H(4)	0.9500	C(20)-O(1)	1.207(3)
C(5)-C(6)	1.380(4)	C(20)-O(2)	1.338(3)
C(5)-H(5)	0.9500	C(21)-O(2)	1.449(3)
C(6)-C(7)	1.508(3)	C(21)-H(21A)	0.9800
C(7)-C(8)	1.522(3)	C(21)-H(21B)	0.9800
C(7)-C(11)	1.554(3)	C(21)-H(21C)	0.9800
C(7)-H(7)	1.0000	C(22)-O(3)	1.421(3)
C(8)-C(9)	1.324(3)	C(22)-H(22A)	0.9800
C(8)-C(20)	1.473(4)	C(22)-H(22B)	0.9800
C(9)-C(10)	1.505(3)	C(22)-H(22C)	0.9800
C(9)-H(9)	0.9500		
C(10)-C(14)	1.525(3)	C(2)-C(1)-N(1)	128.6(3)
C(10)-C(11)	1.563(3)	C(2)-C(1)-C(6)	120.5(3)
C(10)-H(10)	1.0000	N(1)-C(1)-C(6)	110.92(19)
C(11)-N(1)	1.490(3)	C(1)-C(2)-C(3)	117.9(3)
C(11)-C(13)	1.522(3)	C(1)-C(2)-H(2)	121.1
C(12)-N(1)	1.452(3)	C(3)-C(2)-H(2)	121.1
C(12)-H(12A)	0.9800	C(4)-C(3)-C(2)	121.7(2)
C(12)-H(12B)	0.9800	C(4)-C(3)-H(3)	119.2
C(12)-H(12C)	0.9800	C(2)-C(3)-H(3)	119.2
C(13)-H(13A)	0.9800	C(3)-C(4)-C(5)	120.3(3)
C(13)-H(13B)	0.9800	C(3)-C(4)-H(4)	119.8
C(13)-H(13C)	0.9800	C(5)-C(4)-H(4)	119.8
C(14)-C(19)	1.384(3)	C(6)-C(5)-C(4)	118.6(3)
C(14)-C(15)	1.392(3)	C(6)-C(5)-H(5)	120.7
C(15)-C(16)	1.388(3)	C(4)-C(5)-H(5)	120.7

C(5)-C(6)-C(1)	121.0(2)	C(11)-C(13)-H(13C)	109.5
C(5)-C(6)-C(7)	131.2(2)	H(13A)-C(13)-H(13C)	109.5
C(1)-C(6)-C(7)	107.8(2)	H(13B)-C(13)-H(13C)	109.5
C(6)-C(7)-C(8)	116.5(2)	C(19)-C(14)-C(15)	117.9(2)
C(6)-C(7)-C(11)	103.60(19)	C(19)-C(14)-C(10)	119.9(2)
C(8)-C(7)-C(11)	102.6(2)	C(15)-C(14)-C(10)	122.1(2)
C(6)-C(7)-H(7)	111.2	C(16)-C(15)-C(14)	121.2(2)
C(8)-C(7)-H(7)	111.2	C(16)-C(15)-H(15)	119.4
C(11)-C(7)-H(7)	111.2	C(14)-C(15)-H(15)	119.4
C(9)-C(8)-C(20)	123.0(2)	C(15)-C(16)-C(17)	119.7(2)
C(9)-C(8)-C(7)	112.0(2)	C(15)-C(16)-H(16)	120.2
C(20)-C(8)-C(7)	124.9(2)	C(17)-C(16)-H(16)	120.2
C(8)-C(9)-C(10)	113.6(2)	O(3)-C(17)-C(18)	124.9(2)
C(8)-C(9)-H(9)	123.2	O(3)-C(17)-C(16)	115.1(2)
C(10)-C(9)-H(9)	123.2	C(18)-C(17)-C(16)	120.1(2)
C(9)-C(10)-C(14)	113.08(18)	C(17)-C(18)-C(19)	119.2(2)
C(9)-C(10)-C(11)	102.14(19)	C(17)-C(18)-H(18)	120.4
C(14)-C(10)-C(11)	114.32(19)	C(19)-C(18)-H(18)	120.4
C(9)-C(10)-H(10)	109.0	C(14)-C(19)-C(18)	121.9(2)
C(14)-C(10)-H(10)	109.0	C(14)-C(19)-H(19)	119.0
C(11)-C(10)-H(10)	109.0	C(18)-C(19)-H(19)	119.0
N(1)-C(11)-C(13)	111.10(17)	O(1)-C(20)-O(2)	123.5(3)
N(1)-C(11)-C(7)	101.62(18)	O(1)-C(20)-C(8)	125.2(3)
C(13)-C(11)-C(7)	112.9(2)	O(2)-C(20)-C(8)	111.3(2)
N(1)-C(11)-C(10)	108.58(18)	O(2)-C(21)-H(21A)	109.5
C(13)-C(11)-C(10)	115.22(19)	O(2)-C(21)-H(21B)	109.5
C(7)-C(11)-C(10)	106.40(18)	H(21A)-C(21)-H(21B)	109.5
N(1)-C(12)-H(12A)	109.5	O(2)-C(21)-H(21C)	109.5
N(1)-C(12)-H(12B)	109.5	H(21A)-C(21)-H(21C)	109.5
H(12A)-C(12)-H(12B)	109.5	H(21B)-C(21)-H(21C)	109.5
N(1)-C(12)-H(12C)	109.5	O(3)-C(22)-H(22A)	109.5
H(12A)-C(12)-H(12C)	109.5	O(3)-C(22)-H(22B)	109.5
H(12B)-C(12)-H(12C)	109.5	H(22A)-C(22)-H(22B)	109.5
C(11)-C(13)-H(13A)	109.5	O(3)-C(22)-H(22C)	109.5
C(11)-C(13)-H(13B)	109.5	H(22A)-C(22)-H(22C)	109.5
H(13A)-C(13)-H(13B)	109.5	H(22B)-C(22)-H(22C)	109.5

C(1)-N(1)-C(12)	118.42(18)	C(20)-O(2)-C(21)	116.7(2)
C(1)-N(1)-C(11)	108.39(19)	C(17)-O(3)-C(22)	116.9(2)
C(12)-N(1)-C(11)	119.0(2)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for product **3.59**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	36(1)	35(1)	35(1)	5(1)	10(1)	-3(1)
C(2)	37(1)	51(2)	48(2)	9(1)	8(1)	1(1)
C(3)	39(1)	76(2)	44(2)	9(2)	-2(1)	-10(2)
C(4)	52(2)	63(2)	43(2)	-3(2)	7(1)	-25(2)
C(5)	50(2)	46(1)	40(2)	-6(1)	14(1)	-14(1)
C(6)	37(1)	33(1)	36(1)	2(1)	12(1)	-5(1)
C(7)	37(1)	25(1)	36(1)	3(1)	11(1)	3(1)
C(8)	33(1)	32(1)	36(1)	6(1)	10(1)	5(1)
C(9)	33(1)	36(1)	40(2)	4(1)	12(1)	-3(1)
C(10)	33(1)	25(1)	42(2)	0(1)	12(1)	1(1)
C(11)	30(1)	27(1)	32(1)	4(1)	9(1)	2(1)
C(12)	45(1)	36(1)	53(2)	2(1)	21(1)	8(1)
C(13)	35(1)	31(1)	41(1)	5(1)	13(1)	-1(1)
C(14)	29(1)	28(1)	37(1)	-1(1)	14(1)	-6(1)
C(15)	32(1)	29(1)	40(1)	-5(1)	15(1)	-1(1)
C(16)	31(1)	32(1)	41(2)	-3(1)	12(1)	2(1)
C(17)	25(1)	44(1)	34(1)	-1(1)	8(1)	-1(1)
C(18)	34(1)	38(2)	45(2)	-11(1)	16(1)	-4(1)
C(19)	32(1)	29(1)	41(2)	-3(1)	13(1)	-1(1)
C(20)	37(1)	47(2)	38(2)	4(1)	10(1)	9(1)
C(21)	74(2)	67(2)	50(2)	-14(2)	23(2)	11(2)
C(22)	51(2)	73(2)	41(2)	-9(2)	4(1)	-2(2)
N(1)	33(1)	31(1)	39(1)	3(1)	9(1)	5(1)
O(1)	73(1)	62(1)	56(1)	4(1)	38(1)	-1(1)
O(2)	54(1)	45(1)	47(1)	-9(1)	21(1)	2(1)
O(3)	41(1)	62(1)	40(1)	-4(1)	4(1)	9(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for product **3.59**.

	x	y	z	U(eq)
H(2)	-8582	-379	-3240	56
H(3)	-9625	-3102	-4340	67
H(4)	-8497	-6274	-4632	65
H(5)	-6253	-6793	-3846	54
H(7)	-4409	-5310	-2197	39
H(9)	-2420	-17	-2500	43
H(10)	-3802	1208	-1552	40
H(12A)	-7146	65	-1482	65
H(12B)	-7070	2136	-2145	65
H(12C)	-5869	1685	-1256	65
H(13A)	-5865	-3955	-1096	53
H(13B)	-5038	-1944	-473	53
H(13C)	-4307	-4224	-656	53
H(15)	-1871	-4067	-1005	39
H(16)	-412	-4953	401	41
H(18)	-1283	1130	1376	45
H(19)	-2739	1979	-37	40
H(21A)	-2609	-6442	-4600	94
H(21B)	-4108	-6020	-5185	94
H(21C)	-3698	-8376	-4636	94
H(22A)	-584	-1023	2666	85
H(22B)	645	249	2480	85
H(22C)	877	-1978	3116	85

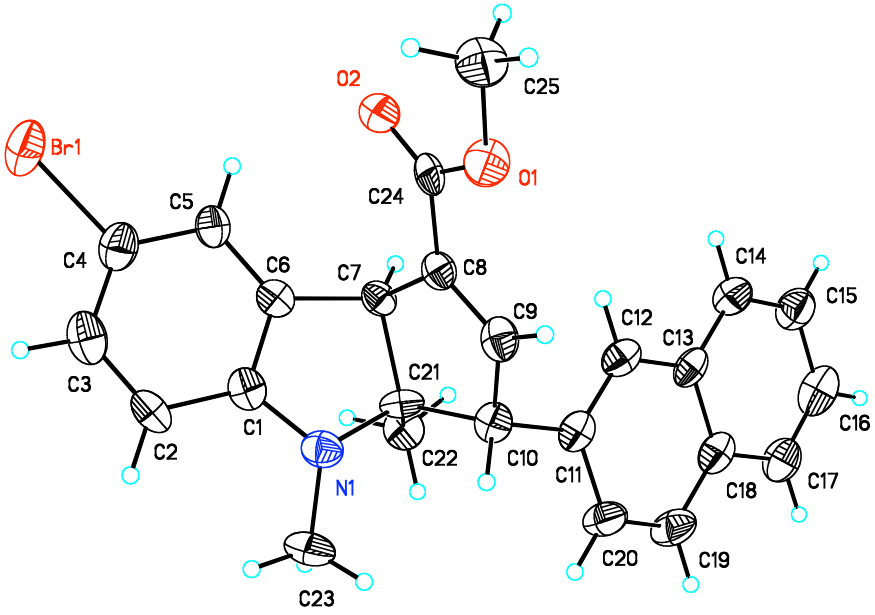
Table 6. Torsion angles [°] for product **3.59**.

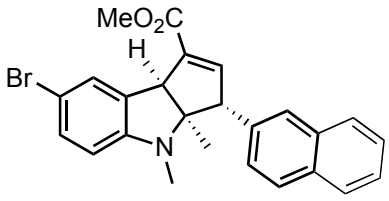
N(1)-C(1)-C(2)-C(3)	179.9(3)
C(6)-C(1)-C(2)-C(3)	-0.4(4)
C(1)-C(2)-C(3)-C(4)	1.0(4)
C(2)-C(3)-C(4)-C(5)	-0.7(5)
C(3)-C(4)-C(5)-C(6)	-0.2(4)
C(4)-C(5)-C(6)-C(1)	0.8(4)
C(4)-C(5)-C(6)-C(7)	177.6(3)
C(2)-C(1)-C(6)-C(5)	-0.5(4)
N(1)-C(1)-C(6)-C(5)	179.2(2)
C(2)-C(1)-C(6)-C(7)	-178.0(2)
N(1)-C(1)-C(6)-C(7)	1.8(3)
C(5)-C(6)-C(7)-C(8)	86.3(3)
C(1)-C(6)-C(7)-C(8)	-96.5(3)
C(5)-C(6)-C(7)-C(11)	-161.9(3)
C(1)-C(6)-C(7)-C(11)	15.3(3)
C(6)-C(7)-C(8)-C(9)	122.7(2)
C(11)-C(7)-C(8)-C(9)	10.3(2)
C(6)-C(7)-C(8)-C(20)	-60.6(3)
C(11)-C(7)-C(8)-C(20)	-172.9(2)
C(20)-C(8)-C(9)-C(10)	-175.7(2)
C(7)-C(8)-C(9)-C(10)	1.1(3)
C(8)-C(9)-C(10)-C(14)	111.4(2)
C(8)-C(9)-C(10)-C(11)	-11.9(3)
C(6)-C(7)-C(11)-N(1)	-25.1(2)
C(8)-C(7)-C(11)-N(1)	96.54(18)
C(6)-C(7)-C(11)-C(13)	94.0(2)
C(8)-C(7)-C(11)-C(13)	-144.37(18)
C(6)-C(7)-C(11)-C(10)	-138.61(19)
C(8)-C(7)-C(11)-C(10)	-17.0(2)
C(9)-C(10)-C(11)-N(1)	-91.2(2)
C(14)-C(10)-C(11)-N(1)	146.3(2)
C(9)-C(10)-C(11)-C(13)	143.5(2)
C(14)-C(10)-C(11)-C(13)	21.0(3)
C(9)-C(10)-C(11)-C(7)	17.5(2)

C(14)-C(10)-C(11)-C(7)	-105.0(2)
C(9)-C(10)-C(14)-C(19)	135.9(2)
C(11)-C(10)-C(14)-C(19)	-107.8(2)
C(9)-C(10)-C(14)-C(15)	-47.0(3)
C(11)-C(10)-C(14)-C(15)	69.3(3)
C(19)-C(14)-C(15)-C(16)	2.2(3)
C(10)-C(14)-C(15)-C(16)	-174.9(2)
C(14)-C(15)-C(16)-C(17)	-0.9(3)
C(15)-C(16)-C(17)-O(3)	179.1(2)
C(15)-C(16)-C(17)-C(18)	-0.5(3)
O(3)-C(17)-C(18)-C(19)	-179.1(2)
C(16)-C(17)-C(18)-C(19)	0.5(3)
C(15)-C(14)-C(19)-C(18)	-2.2(3)
C(10)-C(14)-C(19)-C(18)	175.0(2)
C(17)-C(18)-C(19)-C(14)	0.9(4)
C(9)-C(8)-C(20)-O(1)	-16.2(4)
C(7)-C(8)-C(20)-O(1)	167.4(2)
C(9)-C(8)-C(20)-O(2)	162.8(2)
C(7)-C(8)-C(20)-O(2)	-13.5(3)
C(2)-C(1)-N(1)-C(12)	21.0(4)
C(6)-C(1)-N(1)-C(12)	-158.7(2)
C(2)-C(1)-N(1)-C(11)	160.5(3)
C(6)-C(1)-N(1)-C(11)	-19.2(3)
C(13)-C(11)-N(1)-C(1)	-93.0(2)
C(7)-C(11)-N(1)-C(1)	27.4(2)
C(10)-C(11)-N(1)-C(1)	139.3(2)
C(13)-C(11)-N(1)-C(12)	46.2(3)
C(7)-C(11)-N(1)-C(12)	166.58(19)
C(10)-C(11)-N(1)-C(12)	-81.5(2)
O(1)-C(20)-O(2)-C(21)	-1.6(4)
C(8)-C(20)-O(2)-C(21)	179.3(2)
C(18)-C(17)-O(3)-C(22)	4.5(3)
C(16)-C(17)-O(3)-C(22)	-175.1(2)

Symmetry transformations used to generate equivalent atoms:

3. X-ray crystallographic structure of product 3.65





3.65

Table 1. Crystal data and structure refinement for product **3.65**.

Identification code	YL_VII_59	
Empirical formula	C25 H22 Br N O2	
Formula weight	448.35	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 10.3908(18) Å	α= 90°.
	b = 8.4201(16) Å	β= 105.207(6)°.
	c = 12.468(2) Å	γ = 90°.
Volume	1052.6(3) $Å^3$	
Z	2	
Density (calculated)	1.415 Mg/m^3	
Absorption coefficient	2.820 mm^{-1}	
F(000)	460	
Crystal size	0.21 x 0.19 x 0.13 mm^3	
Theta range for data collection	3.67 to 66.18°.	
Index ranges	-11<=h<=12, -9<=k<=8, -14<=l<=14	
Reflections collected	6414	
Independent reflections	2757 [R(int) = 0.0393]	
Completeness to theta = 66.18°	93.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7107 and 0.5889	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2757 / 1 / 262	
Goodness-of-fit on F^2	1.148	
Final R indices [I>2sigma(I)]	R1 = 0.0422, wR2 = 0.1257	
R indices (all data)	R1 = 0.0545, wR2 = 0.1616	
Absolute structure parameter	0.03(3)	
Largest diff. peak and hole	0.898 and -0.861 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for product **3.65**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	-5187(1)	-3934(1)	-1961(1)	49(1)
C(1)	-7052(5)	-2603(7)	-5662(4)	31(1)
C(2)	-6824(6)	-1402(6)	-4851(5)	34(1)
C(3)	-6268(6)	-1843(8)	-3765(5)	41(1)
C(4)	-5909(6)	-3419(8)	-3498(5)	40(1)
C(5)	-6102(5)	-4598(7)	-4304(4)	29(1)
C(6)	-6672(5)	-4168(7)	-5386(4)	28(1)
C(7)	-7061(5)	-5166(6)	-6436(4)	26(1)
C(8)	-8396(5)	-6008(6)	-6613(4)	26(1)
C(9)	-9265(6)	-5582(7)	-7552(4)	32(1)
C(10)	-8720(5)	-4426(6)	-8228(4)	31(1)
C(11)	-8550(5)	-5147(7)	-9305(4)	32(1)
C(12)	-8187(5)	-6705(7)	-9376(4)	31(1)
C(13)	-7995(5)	-7351(7)	-10360(4)	30(1)
C(14)	-7600(5)	-8941(9)	-10439(4)	37(1)
C(15)	-7405(7)	-9536(9)	-11423(5)	44(1)
C(16)	-7612(6)	-8540(9)	-12353(4)	46(2)
C(17)	-7985(6)	-7001(8)	-12308(5)	41(1)
C(18)	-8183(6)	-6350(8)	-11318(5)	36(1)
C(19)	-8578(7)	-4744(8)	-11235(5)	42(1)
C(20)	-8752(6)	-4160(8)	-10259(4)	38(1)
C(21)	-7394(5)	-3868(8)	-7391(4)	29(1)
C(22)	-6214(6)	-3562(7)	-7887(4)	36(1)
C(23)	-7898(7)	-919(7)	-7314(6)	43(1)
C(24)	-8616(5)	-7174(6)	-5796(4)	28(1)
C(25)	-10207(6)	-8803(9)	-5282(4)	42(1)
N(1)	-7675(5)	-2450(6)	-6780(4)	33(1)
O(1)	-9905(4)	-7665(5)	-6051(3)	39(1)
O(2)	-7779(4)	-7622(5)	-5004(3)	36(1)

Table 3. Bond lengths [Å] and angles [°] for product **3.65**.

Br(1)-C(4)	1.915(6)	C(17)-C(18)	1.413(8)
C(1)-N(1)	1.380(8)	C(17)-H(17A)	0.9500
C(1)-C(6)	1.392(9)	C(18)-C(19)	1.425(10)
C(1)-C(2)	1.406(8)	C(19)-C(20)	1.367(8)
C(2)-C(3)	1.377(9)	C(19)-H(19A)	0.9500
C(2)-H(2A)	0.9500	C(20)-H(20A)	0.9500
C(3)-C(4)	1.395(10)	C(21)-N(1)	1.487(8)
C(3)-H(3A)	0.9500	C(21)-C(22)	1.532(7)
C(4)-C(5)	1.389(8)	C(22)-H(22A)	0.9800
C(5)-C(6)	1.373(8)	C(22)-H(22B)	0.9800
C(5)-H(5A)	0.9500	C(22)-H(22C)	0.9800
C(6)-C(7)	1.518(7)	C(23)-N(1)	1.441(8)
C(7)-C(8)	1.521(7)	C(23)-H(23A)	0.9800
C(7)-C(21)	1.587(7)	C(23)-H(23B)	0.9800
C(7)-H(7A)	1.0000	C(23)-H(23C)	0.9800
C(8)-C(9)	1.327(8)	C(24)-O(2)	1.193(7)
C(8)-C(24)	1.475(7)	C(24)-O(1)	1.357(7)
C(9)-C(10)	1.493(8)	C(25)-O(1)	1.447(7)
C(9)-H(9A)	0.9500	C(25)-H(25A)	0.9800
C(10)-C(11)	1.527(7)	C(25)-H(25B)	0.9800
C(10)-C(21)	1.566(8)	C(25)-H(25C)	0.9800
C(10)-H(10A)	1.0000		
C(11)-C(12)	1.374(9)	N(1)-C(1)-C(6)	111.5(5)
C(11)-C(20)	1.421(8)	N(1)-C(1)-C(2)	127.2(5)
C(12)-C(13)	1.403(8)	C(6)-C(1)-C(2)	121.3(5)
C(12)-H(12A)	0.9500	C(3)-C(2)-C(1)	117.5(5)
C(13)-C(14)	1.411(10)	C(3)-C(2)-H(2A)	121.3
C(13)-C(18)	1.433(8)	C(1)-C(2)-H(2A)	121.3
C(14)-C(15)	1.389(8)	C(2)-C(3)-C(4)	120.6(5)
C(14)-H(14A)	0.9500	C(2)-C(3)-H(3A)	119.7
C(15)-C(16)	1.401(9)	C(4)-C(3)-H(3A)	119.7
C(15)-H(15A)	0.9500	C(5)-C(4)-C(3)	121.9(5)
C(16)-C(17)	1.359(10)	C(5)-C(4)-Br(1)	120.4(5)
C(16)-H(16A)	0.9500	C(3)-C(4)-Br(1)	117.7(4)

C(6)-C(5)-C(4)	117.7(6)	C(14)-C(15)-C(16)	119.3(6)
C(6)-C(5)-H(5A)	121.1	C(14)-C(15)-H(15A)	120.4
C(4)-C(5)-H(5A)	121.1	C(16)-C(15)-H(15A)	120.4
C(5)-C(6)-C(1)	120.9(5)	C(17)-C(16)-C(15)	121.4(6)
C(5)-C(6)-C(7)	130.5(5)	C(17)-C(16)-H(16A)	119.3
C(1)-C(6)-C(7)	108.4(5)	C(15)-C(16)-H(16A)	119.3
C(6)-C(7)-C(8)	114.2(4)	C(16)-C(17)-C(18)	120.9(6)
C(6)-C(7)-C(21)	102.8(4)	C(16)-C(17)-H(17A)	119.5
C(8)-C(7)-C(21)	101.6(4)	C(18)-C(17)-H(17A)	119.5
C(6)-C(7)-H(7A)	112.4	C(17)-C(18)-C(19)	122.8(5)
C(8)-C(7)-H(7A)	112.4	C(17)-C(18)-C(13)	118.7(6)
C(21)-C(7)-H(7A)	112.4	C(19)-C(18)-C(13)	118.4(5)
C(9)-C(8)-C(24)	126.7(5)	C(20)-C(19)-C(18)	121.0(5)
C(9)-C(8)-C(7)	112.7(5)	C(20)-C(19)-H(19A)	119.5
C(24)-C(8)-C(7)	120.7(5)	C(18)-C(19)-H(19A)	119.5
C(8)-C(9)-C(10)	113.8(5)	C(19)-C(20)-C(11)	120.6(6)
C(8)-C(9)-H(9A)	123.1	C(19)-C(20)-H(20A)	119.7
C(10)-C(9)-H(9A)	123.1	C(11)-C(20)-H(20A)	119.7
C(9)-C(10)-C(11)	112.7(5)	N(1)-C(21)-C(22)	110.9(5)
C(9)-C(10)-C(21)	102.6(4)	N(1)-C(21)-C(10)	109.0(4)
C(11)-C(10)-C(21)	114.9(4)	C(22)-C(21)-C(10)	116.1(4)
C(9)-C(10)-H(10A)	108.8	N(1)-C(21)-C(7)	101.6(4)
C(11)-C(10)-H(10A)	108.8	C(22)-C(21)-C(7)	112.3(4)
C(21)-C(10)-H(10A)	108.8	C(10)-C(21)-C(7)	105.9(5)
C(12)-C(11)-C(20)	119.2(5)	C(21)-C(22)-H(22A)	109.5
C(12)-C(11)-C(10)	122.2(5)	C(21)-C(22)-H(22B)	109.5
C(20)-C(11)-C(10)	118.6(5)	H(22A)-C(22)-H(22B)	109.5
C(11)-C(12)-C(13)	122.0(5)	C(21)-C(22)-H(22C)	109.5
C(11)-C(12)-H(12A)	119.0	H(22A)-C(22)-H(22C)	109.5
C(13)-C(12)-H(12A)	119.0	H(22B)-C(22)-H(22C)	109.5
C(12)-C(13)-C(14)	122.6(5)	N(1)-C(23)-H(23A)	109.5
C(12)-C(13)-C(18)	118.8(6)	N(1)-C(23)-H(23B)	109.5
C(14)-C(13)-C(18)	118.6(5)	H(23A)-C(23)-H(23B)	109.5
C(15)-C(14)-C(13)	121.1(6)	N(1)-C(23)-H(23C)	109.5
C(15)-C(14)-H(14A)	119.5	H(23A)-C(23)-H(23C)	109.5
C(13)-C(14)-H(14A)	119.5	H(23B)-C(23)-H(23C)	109.5

O(2)-C(24)-O(1)	123.9(5)	H(25A)-C(25)-H(25C)	109.5
O(2)-C(24)-C(8)	124.8(5)	H(25B)-C(25)-H(25C)	109.5
O(1)-C(24)-C(8)	111.3(4)	C(1)-N(1)-C(23)	121.8(5)
O(1)-C(25)-H(25A)	109.5	C(1)-N(1)-C(21)	109.8(4)
O(1)-C(25)-H(25B)	109.5	C(23)-N(1)-C(21)	120.7(4)
H(25A)-C(25)-H(25B)	109.5	C(24)-O(1)-C(25)	114.8(4)
O(1)-C(25)-H(25C)	109.5		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for product **3.65**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	44(1)	67(1)	33(1)	-10(1)	2(1)	6(1)
C(1)	24(3)	33(3)	37(3)	-5(2)	11(2)	1(2)
C(2)	32(3)	23(3)	48(3)	-7(2)	14(2)	-2(2)
C(3)	31(3)	45(3)	49(3)	-15(3)	15(3)	-1(2)
C(4)	33(3)	49(4)	34(3)	-6(2)	5(2)	1(2)
C(5)	23(3)	33(3)	32(3)	-6(2)	7(2)	-4(2)
C(6)	24(2)	28(3)	34(2)	0(2)	10(2)	-1(2)
C(7)	23(3)	23(2)	32(3)	-1(2)	8(2)	-3(2)
C(8)	28(3)	26(2)	28(2)	-4(2)	11(2)	1(2)
C(9)	34(3)	36(3)	31(2)	-7(2)	15(2)	-3(2)
C(10)	28(3)	35(3)	30(2)	-2(2)	9(2)	2(2)
C(11)	27(3)	41(3)	27(2)	-1(2)	7(2)	0(2)
C(12)	22(3)	42(3)	29(2)	6(2)	7(2)	1(2)
C(13)	16(2)	46(3)	26(2)	1(2)	1(2)	1(2)
C(14)	35(3)	42(3)	32(2)	3(3)	7(2)	6(3)
C(15)	46(4)	49(3)	35(3)	-3(2)	7(2)	8(3)
C(16)	32(3)	75(5)	33(3)	-5(3)	13(2)	1(3)
C(17)	41(3)	54(4)	30(3)	-3(3)	12(2)	1(3)
C(18)	32(3)	50(3)	27(3)	1(2)	7(2)	-2(3)
C(19)	52(4)	48(4)	27(2)	12(2)	14(2)	5(3)
C(20)	45(3)	38(4)	32(2)	9(3)	11(2)	10(3)
C(21)	28(2)	29(2)	32(2)	13(3)	12(2)	9(3)
C(22)	34(3)	40(3)	39(2)	-1(2)	18(2)	-2(2)
C(23)	52(4)	26(3)	53(3)	12(3)	18(3)	3(3)
C(24)	33(3)	24(2)	27(2)	-12(2)	11(2)	-2(2)
C(25)	39(3)	48(3)	46(3)	2(3)	23(2)	-9(3)
N(1)	34(3)	30(2)	36(2)	2(2)	13(2)	4(2)
O(1)	34(2)	46(2)	38(2)	1(2)	14(2)	-8(2)
O(2)	39(2)	30(2)	36(2)	1(2)	6(2)	-3(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for product **3.65**.

	x	y	z	U(eq)
H(2A)	-7046	-326	-5045	41
H(3A)	-6126	-1068	-3193	49
H(5A)	-5848	-5666	-4112	35
H(7A)	-6332	-5902	-6506	31
H(9A)	-10152	-5977	-7774	39
H(10A)	-9341	-3500	-8414	37
H(12A)	-8062	-7366	-8739	37
H(14A)	-7466	-9615	-9808	44
H(15A)	-7134	-10607	-11465	52
H(16A)	-7488	-8950	-13029	55
H(17A)	-8116	-6352	-12951	49
H(19A)	-8723	-4070	-11866	50
H(20A)	-9010	-3084	-10218	46
H(22A)	-6465	-2758	-8473	54
H(22B)	-5973	-4550	-8201	54
H(22C)	-5450	-3180	-7302	54
H(23A)	-8064	-129	-6789	64
H(23B)	-8673	-978	-7961	64
H(23C)	-7109	-610	-7556	64
H(25A)	-11152	-9094	-5527	63
H(25B)	-10015	-8332	-4538	63
H(25C)	-9658	-9755	-5261	63

Table 6. Torsion angles [°] for product **3.65**.

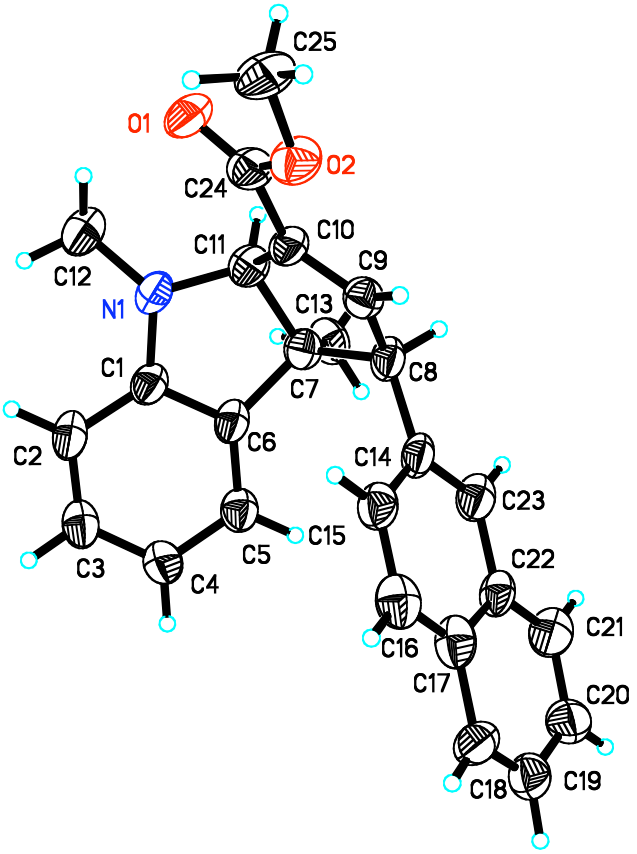
N(1)-C(1)-C(2)-C(3)	175.3(5)
C(6)-C(1)-C(2)-C(3)	-3.0(8)
C(1)-C(2)-C(3)-C(4)	2.0(9)
C(2)-C(3)-C(4)-C(5)	-0.4(9)
C(2)-C(3)-C(4)-Br(1)	-178.3(4)
C(3)-C(4)-C(5)-C(6)	-0.5(8)
Br(1)-C(4)-C(5)-C(6)	177.5(4)
C(4)-C(5)-C(6)-C(1)	-0.5(8)
C(4)-C(5)-C(6)-C(7)	-177.2(5)
N(1)-C(1)-C(6)-C(5)	-176.3(4)
C(2)-C(1)-C(6)-C(5)	2.2(8)
N(1)-C(1)-C(6)-C(7)	1.1(6)
C(2)-C(1)-C(6)-C(7)	179.6(5)
C(5)-C(6)-C(7)-C(8)	81.3(7)
C(1)-C(6)-C(7)-C(8)	-95.8(5)
C(5)-C(6)-C(7)-C(21)	-169.5(5)
C(1)-C(6)-C(7)-C(21)	13.5(5)
C(6)-C(7)-C(8)-C(9)	119.9(5)
C(21)-C(7)-C(8)-C(9)	9.9(6)
C(6)-C(7)-C(8)-C(24)	-60.9(6)
C(21)-C(7)-C(8)-C(24)	-170.9(4)
C(24)-C(8)-C(9)-C(10)	-177.3(4)
C(7)-C(8)-C(9)-C(10)	1.9(6)
C(8)-C(9)-C(10)-C(11)	111.2(5)
C(8)-C(9)-C(10)-C(21)	-12.9(6)
C(9)-C(10)-C(11)-C(12)	-34.8(7)
C(21)-C(10)-C(11)-C(12)	82.2(7)
C(9)-C(10)-C(11)-C(20)	146.4(5)
C(21)-C(10)-C(11)-C(20)	-96.6(6)
C(20)-C(11)-C(12)-C(13)	0.7(8)
C(10)-C(11)-C(12)-C(13)	-178.1(5)
C(11)-C(12)-C(13)-C(14)	178.9(5)
C(11)-C(12)-C(13)-C(18)	0.1(8)
C(12)-C(13)-C(14)-C(15)	-179.3(5)

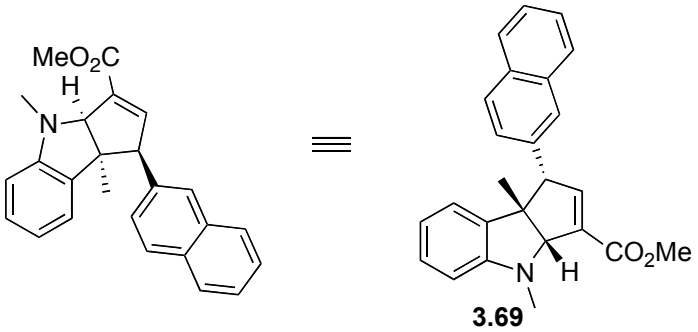
C(18)-C(13)-C(14)-C(15)	-0.5(8)
C(13)-C(14)-C(15)-C(16)	-0.4(9)
C(14)-C(15)-C(16)-C(17)	0.7(10)
C(15)-C(16)-C(17)-C(18)	-0.2(10)
C(16)-C(17)-C(18)-C(19)	-179.8(6)
C(16)-C(17)-C(18)-C(13)	-0.7(9)
C(12)-C(13)-C(18)-C(17)	179.8(5)
C(14)-C(13)-C(18)-C(17)	1.0(8)
C(12)-C(13)-C(18)-C(19)	-1.0(8)
C(14)-C(13)-C(18)-C(19)	-179.8(6)
C(17)-C(18)-C(19)-C(20)	-179.7(6)
C(13)-C(18)-C(19)-C(20)	1.2(9)
C(18)-C(19)-C(20)-C(11)	-0.4(10)
C(12)-C(11)-C(20)-C(19)	-0.5(9)
C(10)-C(11)-C(20)-C(19)	178.4(6)
C(9)-C(10)-C(21)-N(1)	-90.6(5)
C(11)-C(10)-C(21)-N(1)	146.8(4)
C(9)-C(10)-C(21)-C(22)	143.4(5)
C(11)-C(10)-C(21)-C(22)	20.8(8)
C(9)-C(10)-C(21)-C(7)	18.1(5)
C(11)-C(10)-C(21)-C(7)	-104.6(5)
C(6)-C(7)-C(21)-N(1)	-21.6(5)
C(8)-C(7)-C(21)-N(1)	96.8(5)
C(6)-C(7)-C(21)-C(22)	97.0(5)
C(8)-C(7)-C(21)-C(22)	-144.6(5)
C(6)-C(7)-C(21)-C(10)	-135.4(4)
C(8)-C(7)-C(21)-C(10)	-17.0(5)
C(9)-C(8)-C(24)-O(2)	173.7(5)
C(7)-C(8)-C(24)-O(2)	-5.4(7)
C(9)-C(8)-C(24)-O(1)	-7.0(7)
C(7)-C(8)-C(24)-O(1)	173.9(4)
C(6)-C(1)-N(1)-C(23)	-166.2(5)
C(2)-C(1)-N(1)-C(23)	15.3(9)
C(6)-C(1)-N(1)-C(21)	-16.7(6)
C(2)-C(1)-N(1)-C(21)	164.9(5)
C(22)-C(21)-N(1)-C(1)	-95.8(5)

C(10)-C(21)-N(1)-C(1)	135.3(5)
C(7)-C(21)-N(1)-C(1)	23.8(6)
C(22)-C(21)-N(1)-C(23)	54.1(7)
C(10)-C(21)-N(1)-C(23)	-74.9(7)
C(7)-C(21)-N(1)-C(23)	173.7(5)
O(2)-C(24)-O(1)-C(25)	-0.2(7)
C(8)-C(24)-O(1)-C(25)	-179.5(4)

Symmetry transformations used to generate equivalent atoms:

4. X-ray crystallographic structure of product 3.69





3.69

Table 1. Crystal data and structure refinement for product **3.69**.

Identification code	xl_vii_91	
Empirical formula	C25 H23 N O2	
Formula weight	369.44	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.4016(8) Å	α= 90°.
	b = 12.9089(14) Å	β= 90°.
	c = 18.1051(16) Å	γ = 90°.
Volume	1963.6(3) $Å^3$	
Z	4	
Density (calculated)	1.250 Mg/m^3	
Absorption coefficient	0.620 mm^{-1}	
F(000)	784	
Crystal size	0.28 x 0.13 x 0.13 mm^3	
Theta range for data collection	4.21 to 68.67°.	
Index ranges	-9<=h<=7, -13<=k<=15, -21<=l<=21	
Reflections collected	13520	
Independent reflections	3304 [R(int) = 0.0630]	
Completeness to theta = 68.67°	94.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9237 and 0.8455	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3304 / 0 / 254	
Goodness-of-fit on F^2	1.009	
Final R indices [I>2sigma(I)]	R1 = 0.0798, wR2 = 0.2193	
R indices (all data)	R1 = 0.1234, wR2 = 0.2789	
Absolute structure parameter	0.0(8)	
Extinction coefficient	0.0091(17)	
Largest diff. peak and hole	0.350 and -0.289 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for product **3.69**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-9152(7)	-6439(4)	-5930(3)	60(1)
C(2)	-9867(7)	-6257(5)	-5237(3)	70(2)
C(3)	-8999(8)	-5756(5)	-4704(3)	72(2)
C(4)	-7461(8)	-5461(5)	-4828(3)	69(2)
C(5)	-6729(8)	-5674(4)	-5503(3)	61(2)
C(6)	-7583(6)	-6156(4)	-6048(3)	55(1)
C(7)	-7063(7)	-6553(4)	-6803(3)	59(1)
C(8)	-6339(6)	-5717(4)	-7346(3)	57(1)
C(9)	-7765(7)	-5422(5)	-7807(3)	60(1)
C(10)	-8996(7)	-6045(4)	-7722(3)	55(1)
C(11)	-8681(7)	-6870(4)	-7150(3)	61(1)
C(12)	-11094(8)	-7627(5)	-6497(4)	83(2)
C(13)	-5920(8)	-7467(5)	-6694(3)	72(2)
C(14)	-5454(7)	-4833(5)	-6987(3)	60(1)
C(15)	-6294(8)	-3934(5)	-6742(3)	67(2)
C(16)	-5534(8)	-3145(5)	-6367(3)	72(2)
C(17)	-3962(8)	-3233(5)	-6209(3)	68(2)
C(18)	-3141(9)	-2420(5)	-5784(3)	72(2)
C(19)	-1594(10)	-2519(6)	-5635(4)	81(2)
C(20)	-706(9)	-3386(5)	-5904(3)	79(2)
C(21)	-1427(8)	-4147(5)	-6308(3)	75(2)
C(22)	-3042(7)	-4058(5)	-6449(3)	60(1)
C(23)	-3863(8)	-4875(5)	-6870(3)	69(2)
C(24)	-10499(7)	-6020(5)	-8151(3)	63(2)
C(25)	-11948(8)	-5190(6)	-9080(4)	96(2)
N(1)	-9846(6)	-6850(4)	-6549(3)	70(1)
O(1)	-11530(5)	-6670(4)	-8107(2)	82(1)
O(2)	-10557(5)	-5229(3)	-8613(2)	73(1)

Table 3. Bond lengths [Å] and angles [°] for product **3.69**.

C(1)-N(1)	1.371(7)	C(15)-H(15A)	0.9500
C(1)-C(6)	1.385(7)	C(16)-C(17)	1.357(9)
C(1)-C(2)	1.410(8)	C(16)-H(16A)	0.9500
C(2)-C(3)	1.371(9)	C(17)-C(22)	1.385(8)
C(2)-H(2A)	0.9500	C(17)-C(18)	1.474(9)
C(3)-C(4)	1.366(9)	C(18)-C(19)	1.334(10)
C(3)-H(3A)	0.9500	C(18)-H(18A)	0.9500
C(4)-C(5)	1.395(8)	C(19)-C(20)	1.430(10)
C(4)-H(4A)	0.9500	C(19)-H(19A)	0.9500
C(5)-C(6)	1.370(8)	C(20)-C(21)	1.366(9)
C(5)-H(5A)	0.9500	C(20)-H(20A)	0.9500
C(6)-C(7)	1.524(7)	C(21)-C(22)	1.386(9)
C(7)-C(13)	1.534(8)	C(21)-H(21A)	0.9500
C(7)-C(11)	1.553(8)	C(22)-C(23)	1.474(9)
C(7)-C(8)	1.580(7)	C(23)-H(23A)	0.9500
C(8)-C(9)	1.509(8)	C(24)-O(1)	1.209(7)
C(8)-C(14)	1.510(8)	C(24)-O(2)	1.321(7)
C(8)-H(8A)	1.0000	C(25)-O(2)	1.443(7)
C(9)-C(10)	1.320(8)	C(25)-H(25A)	0.9800
C(9)-H(9A)	0.9500	C(25)-H(25B)	0.9800
C(10)-C(24)	1.483(8)	C(25)-H(25C)	0.9800
C(10)-C(11)	1.509(8)		
C(11)-N(1)	1.463(7)	N(1)-C(1)-C(6)	112.3(5)
C(11)-H(11A)	1.0000	N(1)-C(1)-C(2)	127.7(5)
C(12)-N(1)	1.454(8)	C(6)-C(1)-C(2)	120.0(6)
C(12)-H(12A)	0.9800	C(3)-C(2)-C(1)	118.5(5)
C(12)-H(12B)	0.9800	C(3)-C(2)-H(2A)	120.7
C(12)-H(12C)	0.9800	C(1)-C(2)-H(2A)	120.7
C(13)-H(13A)	0.9800	C(4)-C(3)-C(2)	121.3(6)
C(13)-H(13B)	0.9800	C(4)-C(3)-H(3A)	119.4
C(13)-H(13C)	0.9800	C(2)-C(3)-H(3A)	119.4
C(14)-C(23)	1.355(8)	C(3)-C(4)-C(5)	120.4(6)
C(14)-C(15)	1.429(8)	C(3)-C(4)-H(4A)	119.8
C(15)-C(16)	1.381(9)	C(5)-C(4)-H(4A)	119.8

C(6)-C(5)-C(4)	119.4(6)	C(7)-C(13)-H(13A)	109.5
C(6)-C(5)-H(5A)	120.3	C(7)-C(13)-H(13B)	109.5
C(4)-C(5)-H(5A)	120.3	H(13A)-C(13)-H(13B)	109.5
C(5)-C(6)-C(1)	120.4(5)	C(7)-C(13)-H(13C)	109.5
C(5)-C(6)-C(7)	130.5(5)	H(13A)-C(13)-H(13C)	109.5
C(1)-C(6)-C(7)	108.9(5)	H(13B)-C(13)-H(13C)	109.5
C(6)-C(7)-C(13)	108.8(5)	C(23)-C(14)-C(15)	118.1(6)
C(6)-C(7)-C(11)	101.6(4)	C(23)-C(14)-C(8)	121.5(6)
C(13)-C(7)-C(11)	113.5(5)	C(15)-C(14)-C(8)	120.3(5)
C(6)-C(7)-C(8)	116.0(4)	C(16)-C(15)-C(14)	121.6(6)
C(13)-C(7)-C(8)	111.4(4)	C(16)-C(15)-H(15A)	119.2
C(11)-C(7)-C(8)	105.4(4)	C(14)-C(15)-H(15A)	119.2
C(9)-C(8)-C(14)	116.0(5)	C(17)-C(16)-C(15)	119.5(6)
C(9)-C(8)-C(7)	102.2(4)	C(17)-C(16)-H(16A)	120.3
C(14)-C(8)-C(7)	116.0(4)	C(15)-C(16)-H(16A)	120.3
C(9)-C(8)-H(8A)	107.4	C(16)-C(17)-C(22)	122.8(6)
C(14)-C(8)-H(8A)	107.4	C(16)-C(17)-C(18)	120.4(6)
C(7)-C(8)-H(8A)	107.4	C(22)-C(17)-C(18)	116.7(6)
C(10)-C(9)-C(8)	113.8(5)	C(19)-C(18)-C(17)	119.6(7)
C(10)-C(9)-H(9A)	123.1	C(19)-C(18)-H(18A)	120.2
C(8)-C(9)-H(9A)	123.1	C(17)-C(18)-H(18A)	120.2
C(9)-C(10)-C(24)	126.4(5)	C(18)-C(19)-C(20)	121.0(7)
C(9)-C(10)-C(11)	111.9(5)	C(18)-C(19)-H(19A)	119.5
C(24)-C(10)-C(11)	121.6(5)	C(20)-C(19)-H(19A)	119.5
N(1)-C(11)-C(10)	112.4(5)	C(21)-C(20)-C(19)	120.9(7)
N(1)-C(11)-C(7)	106.3(4)	C(21)-C(20)-H(20A)	119.6
C(10)-C(11)-C(7)	104.2(5)	C(19)-C(20)-H(20A)	119.6
N(1)-C(11)-H(11A)	111.2	C(20)-C(21)-C(22)	118.2(7)
C(10)-C(11)-H(11A)	111.2	C(20)-C(21)-H(21A)	120.9
C(7)-C(11)-H(11A)	111.2	C(22)-C(21)-H(21A)	120.9
N(1)-C(12)-H(12A)	109.5	C(21)-C(22)-C(17)	123.5(6)
N(1)-C(12)-H(12B)	109.5	C(21)-C(22)-C(23)	119.6(6)
H(12A)-C(12)-H(12B)	109.5	C(17)-C(22)-C(23)	116.8(5)
N(1)-C(12)-H(12C)	109.5	C(14)-C(23)-C(22)	120.9(6)
H(12A)-C(12)-H(12C)	109.5	C(14)-C(23)-H(23A)	119.5
H(12B)-C(12)-H(12C)	109.5	C(22)-C(23)-H(23A)	119.5

O(1)-C(24)-O(2)	123.5(5)	H(25A)-C(25)-H(25C)	109.5
O(1)-C(24)-C(10)	124.1(6)	H(25B)-C(25)-H(25C)	109.5
O(2)-C(24)-C(10)	112.3(6)	C(1)-N(1)-C(12)	121.4(5)
O(2)-C(25)-H(25A)	109.5	C(1)-N(1)-C(11)	109.3(5)
O(2)-C(25)-H(25B)	109.5	C(12)-N(1)-C(11)	121.2(5)
H(25A)-C(25)-H(25B)	109.5	C(24)-O(2)-C(25)	115.3(5)
O(2)-C(25)-H(25C)	109.5		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for product **3.69**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	45(3)	66(3)	68(3)	10(2)	2(3)	2(3)
C(2)	55(4)	84(4)	71(3)	19(3)	21(3)	1(3)
C(3)	66(4)	81(4)	67(3)	10(3)	13(3)	4(3)
C(4)	76(4)	69(3)	61(3)	2(3)	10(3)	-1(3)
C(5)	54(3)	74(3)	55(3)	4(2)	8(3)	-7(3)
C(6)	50(4)	57(3)	57(3)	3(2)	5(3)	-2(3)
C(7)	56(4)	65(3)	57(3)	-5(2)	2(3)	4(3)
C(8)	41(3)	72(3)	57(3)	-7(2)	-1(3)	4(3)
C(9)	64(4)	70(3)	48(2)	-8(2)	-1(3)	3(3)
C(10)	46(3)	63(3)	57(3)	-10(2)	-6(3)	-4(3)
C(11)	55(4)	62(3)	67(3)	-7(2)	-8(3)	-3(3)
C(12)	70(4)	78(4)	103(5)	22(4)	-6(4)	-19(4)
C(13)	79(4)	80(4)	57(3)	1(3)	4(3)	17(3)
C(14)	46(3)	82(4)	52(3)	11(2)	8(3)	-9(3)
C(15)	69(4)	73(4)	58(3)	6(3)	-1(3)	-10(3)
C(16)	77(5)	77(4)	63(3)	11(3)	14(3)	18(4)
C(17)	63(4)	74(4)	65(3)	19(3)	12(3)	8(3)
C(18)	78(5)	72(4)	66(3)	8(3)	5(3)	-5(4)
C(19)	92(6)	85(4)	67(3)	2(3)	4(4)	-19(4)
C(20)	85(5)	83(4)	70(3)	3(3)	-5(4)	-10(4)
C(21)	75(5)	79(4)	71(4)	7(3)	4(4)	5(4)
C(22)	45(4)	73(4)	63(3)	13(3)	6(3)	7(3)
C(23)	66(4)	77(4)	64(3)	12(3)	6(3)	2(3)
C(24)	59(4)	73(4)	58(3)	-10(3)	-7(3)	-1(3)
C(25)	74(5)	109(5)	105(5)	21(4)	-50(4)	-3(4)
N(1)	57(3)	86(3)	65(3)	5(2)	5(3)	-22(3)
O(1)	62(3)	93(3)	91(3)	1(2)	-15(2)	-18(3)
O(2)	58(3)	85(3)	76(2)	19(2)	-15(2)	-1(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for product **3.69**.

	x	y	z	U(eq)
H(2A)	-10927	-6476	-5142	84
H(3A)	-9477	-5611	-4240	86
H(4A)	-6886	-5109	-4452	82
H(5A)	-5649	-5487	-5583	73
H(8A)	-5572	-6084	-7677	68
H(9A)	-7774	-4841	-8129	72
H(11A)	-8619	-7572	-7381	73
H(12A)	-11768	-7480	-6068	125
H(12B)	-10612	-8314	-6442	125
H(12C)	-11743	-7612	-6947	125
H(13A)	-6394	-7966	-6351	108
H(13B)	-4911	-7213	-6490	108
H(13C)	-5723	-7804	-7170	108
H(15A)	-7402	-3878	-6839	80
H(16A)	-6108	-2544	-6221	87
H(18A)	-3709	-1828	-5617	86
H(19A)	-1073	-2007	-5345	97
H(20A)	400	-3433	-5801	95
H(21A)	-837	-4722	-6487	90
H(23A)	-3268	-5439	-7063	83
H(25A)	-11907	-4566	-9389	144
H(25B)	-12907	-5171	-8772	144
H(25C)	-11976	-5805	-9397	144

Table 6. Torsion angles [°] for product **3.69**.

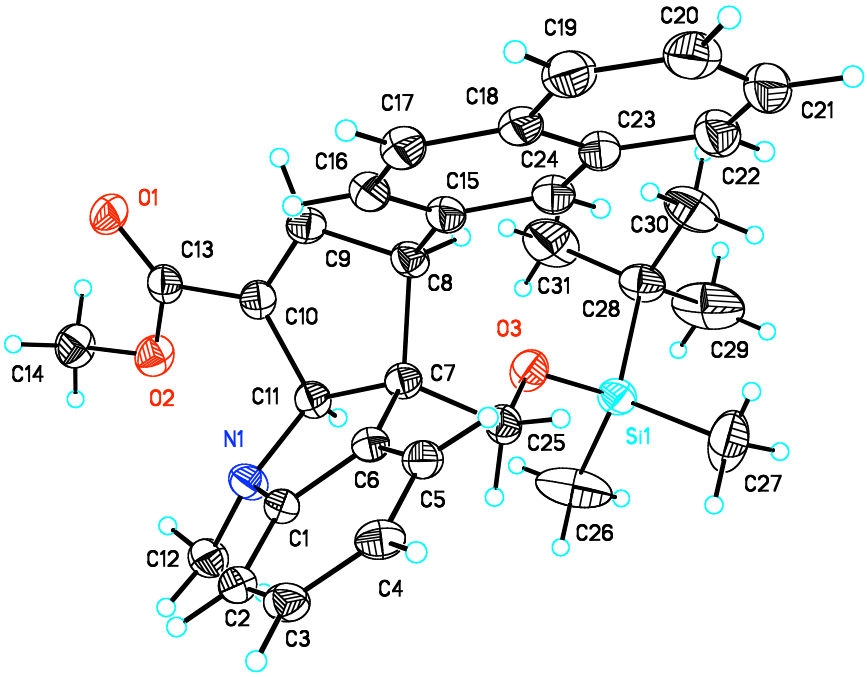
N(1)-C(1)-C(2)-C(3)	-174.6(6)
C(6)-C(1)-C(2)-C(3)	2.9(9)
C(1)-C(2)-C(3)-C(4)	-1.7(9)
C(2)-C(3)-C(4)-C(5)	-0.6(9)
C(3)-C(4)-C(5)-C(6)	1.9(9)
C(4)-C(5)-C(6)-C(1)	-0.7(8)
C(4)-C(5)-C(6)-C(7)	-174.6(5)
N(1)-C(1)-C(6)-C(5)	176.1(5)
C(2)-C(1)-C(6)-C(5)	-1.7(8)
N(1)-C(1)-C(6)-C(7)	-8.8(6)
C(2)-C(1)-C(6)-C(7)	173.4(5)
C(5)-C(6)-C(7)-C(13)	67.0(8)
C(1)-C(6)-C(7)-C(13)	-107.5(5)
C(5)-C(6)-C(7)-C(11)	-173.1(6)
C(1)-C(6)-C(7)-C(11)	12.5(6)
C(5)-C(6)-C(7)-C(8)	-59.5(8)
C(1)-C(6)-C(7)-C(8)	126.1(5)
C(6)-C(7)-C(8)-C(9)	-96.0(5)
C(13)-C(7)-C(8)-C(9)	138.9(5)
C(11)-C(7)-C(8)-C(9)	15.4(5)
C(6)-C(7)-C(8)-C(14)	31.2(7)
C(13)-C(7)-C(8)-C(14)	-94.0(6)
C(11)-C(7)-C(8)-C(14)	142.6(5)
C(14)-C(8)-C(9)-C(10)	-139.0(5)
C(7)-C(8)-C(9)-C(10)	-11.8(6)
C(8)-C(9)-C(10)-C(24)	-173.5(5)
C(8)-C(9)-C(10)-C(11)	2.9(6)
C(9)-C(10)-C(11)-N(1)	122.3(5)
C(24)-C(10)-C(11)-N(1)	-61.1(6)
C(9)-C(10)-C(11)-C(7)	7.6(6)
C(24)-C(10)-C(11)-C(7)	-175.8(4)
C(6)-C(7)-C(11)-N(1)	-11.8(6)
C(13)-C(7)-C(11)-N(1)	104.8(5)
C(8)-C(7)-C(11)-N(1)	-133.1(5)

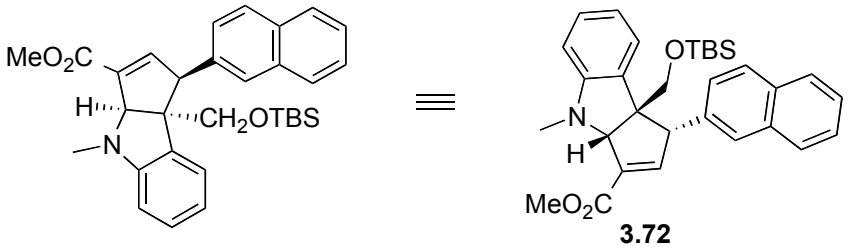
C(6)-C(7)-C(11)-C(10)	107.1(5)
C(13)-C(7)-C(11)-C(10)	-136.3(5)
C(8)-C(7)-C(11)-C(10)	-14.2(5)
C(9)-C(8)-C(14)-C(23)	-148.1(5)
C(7)-C(8)-C(14)-C(23)	91.9(6)
C(9)-C(8)-C(14)-C(15)	33.7(7)
C(7)-C(8)-C(14)-C(15)	-86.3(6)
C(23)-C(14)-C(15)-C(16)	-2.8(8)
C(8)-C(14)-C(15)-C(16)	175.5(5)
C(14)-C(15)-C(16)-C(17)	-1.8(8)
C(15)-C(16)-C(17)-C(22)	4.3(9)
C(15)-C(16)-C(17)-C(18)	-177.6(5)
C(16)-C(17)-C(18)-C(19)	-179.9(6)
C(22)-C(17)-C(18)-C(19)	-1.6(8)
C(17)-C(18)-C(19)-C(20)	2.3(9)
C(18)-C(19)-C(20)-C(21)	-1.5(10)
C(19)-C(20)-C(21)-C(22)	-0.1(9)
C(20)-C(21)-C(22)-C(17)	0.7(9)
C(20)-C(21)-C(22)-C(23)	-178.9(5)
C(16)-C(17)-C(22)-C(21)	178.3(6)
C(18)-C(17)-C(22)-C(21)	0.1(8)
C(16)-C(17)-C(22)-C(23)	-2.1(8)
C(18)-C(17)-C(22)-C(23)	179.7(5)
C(15)-C(14)-C(23)-C(22)	4.9(8)
C(8)-C(14)-C(23)-C(22)	-173.3(4)
C(21)-C(22)-C(23)-C(14)	176.9(5)
C(17)-C(22)-C(23)-C(14)	-2.7(8)
C(9)-C(10)-C(24)-O(1)	172.1(5)
C(11)-C(10)-C(24)-O(1)	-4.0(8)
C(9)-C(10)-C(24)-O(2)	-5.1(8)
C(11)-C(10)-C(24)-O(2)	178.8(5)
C(6)-C(1)-N(1)-C(12)	149.5(5)
C(2)-C(1)-N(1)-C(12)	-32.9(9)
C(6)-C(1)-N(1)-C(11)	0.6(7)
C(2)-C(1)-N(1)-C(11)	178.2(5)
C(10)-C(11)-N(1)-C(1)	-105.8(5)

C(7)-C(11)-N(1)-C(1)	7.6(6)
C(10)-C(11)-N(1)-C(12)	105.2(6)
C(7)-C(11)-N(1)-C(12)	-141.4(5)
O(1)-C(24)-O(2)-C(25)	-0.7(8)
C(10)-C(24)-O(2)-C(25)	176.5(5)

Symmetry transformations used to generate equivalent atoms:

5. X-ray crystallographic structure of product 3.72





3.72

Table 1. Crystal data and structure refinement for product **3.72**.

Identification code	yl_vii_105s	
Empirical formula	C31 H37 N O3 Si	
Formula weight	499.71	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 7.6329(6) Å	α= 90°.
	b = 11.8947(9) Å	β= 99.938(4)°.
	c = 15.9109(11) Å	γ = 90°.
Volume	1422.89(18) $Å^3$	
Z	2	
Density (calculated)	1.166 Mg/m^3	
Absorption coefficient	0.965 mm^{-1}	
F(000)	536	
Crystal size	0.24 x 0.19 x 0.10 mm^3	
Theta range for data collection	2.82 to 66.50°.	
Index ranges	-8<=h<=8, -14<=k<=13, -17<=l<=18	
Reflections collected	9882	
Independent reflections	3934 [R(int) = 0.0463]	
Completeness to theta = 66.50°	89.0 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3934 / 1 / 326	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0561, wR2 = 0.1449	
R indices (all data)	R1 = 0.0701, wR2 = 0.1543	
Absolute structure parameter	0.16(5)	
Extinction coefficient	0.0002(6)	
Largest diff. peak and hole	0.258 and -0.309 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for product **3.72**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-1486(4)	-4624(3)	-5810(2)	43(1)
C(2)	-1694(5)	-4587(3)	-4960(2)	51(1)
C(3)	-1124(5)	-5507(3)	-4452(2)	53(1)
C(4)	-369(5)	-6432(3)	-4763(2)	53(1)
C(5)	-186(5)	-6468(3)	-5618(2)	48(1)
C(6)	-718(5)	-5556(3)	-6137(2)	44(1)
C(7)	-847(5)	-5422(3)	-7095(2)	45(1)
C(8)	942(5)	-5488(3)	-7453(2)	47(1)
C(9)	1474(5)	-4276(3)	-7494(2)	51(1)
C(10)	153(5)	-3580(3)	-7417(2)	49(1)
C(11)	-1484(5)	-4186(3)	-7235(2)	46(1)
C(12)	-3540(5)	-3122(3)	-6421(3)	60(1)
C(13)	251(6)	-2339(3)	-7532(2)	52(1)
C(14)	-1491(7)	-691(3)	-7864(3)	69(1)
C(15)	2332(6)	-6269(3)	-6989(3)	52(1)
C(16)	3567(5)	-5909(3)	-6266(3)	53(1)
C(17)	4798(5)	-6623(3)	-5837(3)	57(1)
C(18)	4863(6)	-7731(3)	-6097(3)	57(1)
C(19)	6162(6)	-8527(4)	-5650(3)	70(1)
C(20)	6154(7)	-9609(4)	-5914(3)	74(1)
C(21)	4891(7)	-9998(4)	-6618(3)	72(1)
C(22)	3690(6)	-9266(4)	-7049(3)	66(1)
C(23)	3660(6)	-8139(3)	-6810(3)	56(1)
C(24)	2407(6)	-7353(3)	-7245(3)	55(1)
C(25)	-2197(6)	-6266(3)	-7538(2)	52(1)
C(26)	-5940(8)	-6019(8)	-9300(4)	134(3)
C(27)	-4106(12)	-8243(5)	-8817(4)	124(3)
C(28)	-2788(5)	-6758(4)	-10154(2)	66(1)
C(29)	-4187(9)	-7201(8)	-10911(4)	140(3)
C(30)	-1187(7)	-7514(5)	-10067(3)	94(2)

C(31)	-2244(10)	-5558(5)	-10335(4)	113(2)
N(1)	-1985(4)	-3802(3)	-6426(2)	51(1)
O(1)	1599(4)	-1805(2)	-7504(2)	63(1)
O(2)	-1387(4)	-1892(2)	-7691(2)	60(1)
O(3)	-2374(4)	-6137(2)	-8440(2)	62(1)
Si(1)	-3800(1)	-6785(1)	-9160(1)	56(1)

Table 3. Bond lengths [Å] and angles [°] for product **3.72**.

C(1)-N(1)	1.390(5)	C(15)-C(24)	1.356(5)
C(1)-C(2)	1.390(5)	C(15)-C(16)	1.421(6)
C(1)-C(6)	1.396(5)	C(16)-C(17)	1.360(6)
C(2)-C(3)	1.384(6)	C(16)-H(16A)	0.9500
C(2)-H(2A)	0.9500	C(17)-C(18)	1.386(6)
C(3)-C(4)	1.373(6)	C(17)-H(17A)	0.9500
C(3)-H(3A)	0.9500	C(18)-C(23)	1.416(6)
C(4)-C(5)	1.392(5)	C(18)-C(19)	1.463(6)
C(4)-H(4A)	0.9500	C(19)-C(20)	1.353(7)
C(5)-C(6)	1.381(5)	C(19)-H(19A)	0.9500
C(5)-H(5A)	0.9500	C(20)-C(21)	1.423(7)
C(6)-C(7)	1.520(5)	C(20)-H(20A)	0.9500
C(7)-C(25)	1.522(5)	C(21)-C(22)	1.361(6)
C(7)-C(11)	1.552(5)	C(21)-H(21A)	0.9500
C(7)-C(8)	1.570(5)	C(22)-C(23)	1.395(6)
C(8)-C(9)	1.502(5)	C(22)-H(22A)	0.9500
C(8)-C(15)	1.505(6)	C(23)-C(24)	1.427(6)
C(8)-H(8A)	1.0000	C(24)-H(24A)	0.9500
C(9)-C(10)	1.326(5)	C(25)-O(3)	1.427(4)
C(9)-H(9A)	0.9500	C(25)-H(25A)	0.9900
C(10)-C(13)	1.492(5)	C(25)-H(25B)	0.9900
C(10)-C(11)	1.513(5)	C(26)-Si(1)	1.850(6)
C(11)-N(1)	1.477(4)	C(26)-H(26A)	0.9800
C(11)-H(11A)	1.0000	C(26)-H(26B)	0.9800
C(12)-N(1)	1.438(5)	C(26)-H(26C)	0.9800
C(12)-H(12A)	0.9800	C(27)-Si(1)	1.844(5)
C(12)-H(12B)	0.9800	C(27)-H(27A)	0.9800
C(12)-H(12C)	0.9800	C(27)-H(27B)	0.9800
C(13)-O(1)	1.203(5)	C(27)-H(27C)	0.9800
C(13)-O(2)	1.341(5)	C(28)-C(30)	1.505(7)
C(14)-O(2)	1.454(5)	C(28)-C(31)	1.528(7)
C(14)-H(14A)	0.9800	C(28)-C(29)	1.557(7)
C(14)-H(14B)	0.9800	C(28)-Si(1)	1.877(4)
C(14)-H(14C)	0.9800	C(29)-H(29A)	0.9800

C(29)-H(29B)	0.9800	C(15)-C(8)-C(7)	115.8(3)
C(29)-H(29C)	0.9800	C(9)-C(8)-H(8A)	107.0
C(30)-H(30A)	0.9800	C(15)-C(8)-H(8A)	107.0
C(30)-H(30B)	0.9800	C(7)-C(8)-H(8A)	107.0
C(30)-H(30C)	0.9800	C(10)-C(9)-C(8)	112.3(3)
C(31)-H(31A)	0.9800	C(10)-C(9)-H(9A)	123.9
C(31)-H(31B)	0.9800	C(8)-C(9)-H(9A)	123.9
C(31)-H(31C)	0.9800	C(9)-C(10)-C(13)	123.5(4)
O(3)-Si(1)	1.631(3)	C(9)-C(10)-C(11)	112.8(3)
		C(13)-C(10)-C(11)	123.7(4)
N(1)-C(1)-C(2)	126.9(3)	N(1)-C(11)-C(10)	111.5(3)
N(1)-C(1)-C(6)	112.2(3)	N(1)-C(11)-C(7)	106.8(3)
C(2)-C(1)-C(6)	120.9(3)	C(10)-C(11)-C(7)	103.3(3)
C(3)-C(2)-C(1)	117.7(3)	N(1)-C(11)-H(11A)	111.6
C(3)-C(2)-H(2A)	121.1	C(10)-C(11)-H(11A)	111.6
C(1)-C(2)-H(2A)	121.1	C(7)-C(11)-H(11A)	111.6
C(4)-C(3)-C(2)	122.2(3)	N(1)-C(12)-H(12A)	109.5
C(4)-C(3)-H(3A)	118.9	N(1)-C(12)-H(12B)	109.5
C(2)-C(3)-H(3A)	118.9	H(12A)-C(12)-H(12B)	109.5
C(3)-C(4)-C(5)	119.7(3)	N(1)-C(12)-H(12C)	109.5
C(3)-C(4)-H(4A)	120.2	H(12A)-C(12)-H(12C)	109.5
C(5)-C(4)-H(4A)	120.2	H(12B)-C(12)-H(12C)	109.5
C(6)-C(5)-C(4)	119.4(3)	O(1)-C(13)-O(2)	124.1(3)
C(6)-C(5)-H(5A)	120.3	O(1)-C(13)-C(10)	125.3(4)
C(4)-C(5)-H(5A)	120.3	O(2)-C(13)-C(10)	110.5(4)
C(5)-C(6)-C(1)	120.1(3)	O(2)-C(14)-H(14A)	109.5
C(5)-C(6)-C(7)	130.1(3)	O(2)-C(14)-H(14B)	109.5
C(1)-C(6)-C(7)	109.3(3)	H(14A)-C(14)-H(14B)	109.5
C(6)-C(7)-C(25)	108.5(3)	O(2)-C(14)-H(14C)	109.5
C(6)-C(7)-C(11)	102.0(3)	H(14A)-C(14)-H(14C)	109.5
C(25)-C(7)-C(11)	112.8(3)	H(14B)-C(14)-H(14C)	109.5
C(6)-C(7)-C(8)	116.7(3)	C(24)-C(15)-C(16)	118.2(4)
C(25)-C(7)-C(8)	111.2(3)	C(24)-C(15)-C(8)	120.2(4)
C(11)-C(7)-C(8)	105.4(3)	C(16)-C(15)-C(8)	121.6(3)
C(9)-C(8)-C(15)	116.2(3)	C(17)-C(16)-C(15)	121.6(4)
C(9)-C(8)-C(7)	103.1(3)	C(17)-C(16)-H(16A)	119.2

C(15)-C(16)-H(16A)	119.2	H(26B)-C(26)-H(26C)	109.5
C(16)-C(17)-C(18)	120.1(4)	Si(1)-C(27)-H(27A)	109.5
C(16)-C(17)-H(17A)	120.0	Si(1)-C(27)-H(27B)	109.5
C(18)-C(17)-H(17A)	120.0	H(27A)-C(27)-H(27B)	109.5
C(17)-C(18)-C(23)	120.9(4)	Si(1)-C(27)-H(27C)	109.5
C(17)-C(18)-C(19)	121.7(4)	H(27A)-C(27)-H(27C)	109.5
C(23)-C(18)-C(19)	117.4(4)	H(27B)-C(27)-H(27C)	109.5
C(20)-C(19)-C(18)	119.8(5)	C(30)-C(28)-C(31)	109.5(5)
C(20)-C(19)-H(19A)	120.1	C(30)-C(28)-C(29)	107.9(5)
C(18)-C(19)-H(19A)	120.1	C(31)-C(28)-C(29)	110.1(5)
C(19)-C(20)-C(21)	121.3(5)	C(30)-C(28)-Si(1)	110.9(3)
C(19)-C(20)-H(20A)	119.3	C(31)-C(28)-Si(1)	109.9(3)
C(21)-C(20)-H(20A)	119.3	C(29)-C(28)-Si(1)	108.6(3)
C(22)-C(21)-C(20)	119.7(4)	C(28)-C(29)-H(29A)	109.5
C(22)-C(21)-H(21A)	120.2	C(28)-C(29)-H(29B)	109.5
C(20)-C(21)-H(21A)	120.2	H(29A)-C(29)-H(29B)	109.5
C(21)-C(22)-C(23)	121.2(5)	C(28)-C(29)-H(29C)	109.5
C(21)-C(22)-H(22A)	119.4	H(29A)-C(29)-H(29C)	109.5
C(23)-C(22)-H(22A)	119.4	H(29B)-C(29)-H(29C)	109.5
C(22)-C(23)-C(18)	120.5(4)	C(28)-C(30)-H(30A)	109.5
C(22)-C(23)-C(24)	122.6(4)	C(28)-C(30)-H(30B)	109.5
C(18)-C(23)-C(24)	116.9(4)	H(30A)-C(30)-H(30B)	109.5
C(15)-C(24)-C(23)	122.4(4)	C(28)-C(30)-H(30C)	109.5
C(15)-C(24)-H(24A)	118.8	H(30A)-C(30)-H(30C)	109.5
C(23)-C(24)-H(24A)	118.8	H(30B)-C(30)-H(30C)	109.5
O(3)-C(25)-C(7)	109.5(3)	C(28)-C(31)-H(31A)	109.5
O(3)-C(25)-H(25A)	109.8	C(28)-C(31)-H(31B)	109.5
C(7)-C(25)-H(25A)	109.8	H(31A)-C(31)-H(31B)	109.5
O(3)-C(25)-H(25B)	109.8	C(28)-C(31)-H(31C)	109.5
C(7)-C(25)-H(25B)	109.8	H(31A)-C(31)-H(31C)	109.5
H(25A)-C(25)-H(25B)	108.2	H(31B)-C(31)-H(31C)	109.5
Si(1)-C(26)-H(26A)	109.5	C(1)-N(1)-C(12)	121.2(3)
Si(1)-C(26)-H(26B)	109.5	C(1)-N(1)-C(11)	108.4(3)
H(26A)-C(26)-H(26B)	109.5	C(12)-N(1)-C(11)	121.1(3)
Si(1)-C(26)-H(26C)	109.5	C(13)-O(2)-C(14)	116.3(3)
H(26A)-C(26)-H(26C)	109.5	C(25)-O(3)-Si(1)	126.3(2)

O(3)-Si(1)-C(27)	109.9(3)	O(3)-Si(1)-C(28)	105.17(18)
O(3)-Si(1)-C(26)	108.7(3)	C(27)-Si(1)-C(28)	110.9(3)
C(27)-Si(1)-C(26)	110.2(5)	C(26)-Si(1)-C(28)	111.9(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for product **3.72**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	40(2)	41(2)	49(2)	-4(1)	12(2)	-1(2)
C(2)	51(2)	54(2)	52(2)	-9(2)	17(2)	-11(2)
C(3)	52(2)	70(2)	39(2)	-2(2)	12(2)	-7(2)
C(4)	48(2)	64(2)	50(2)	12(2)	12(2)	2(2)
C(5)	46(2)	46(2)	53(2)	3(2)	13(2)	2(2)
C(6)	45(2)	44(2)	43(2)	1(1)	14(1)	-3(2)
C(7)	49(2)	45(2)	41(2)	2(2)	11(1)	-1(2)
C(8)	56(2)	46(2)	41(2)	3(2)	18(2)	3(2)
C(9)	57(2)	55(2)	45(2)	2(2)	18(2)	-6(2)
C(10)	61(2)	45(2)	41(2)	3(1)	11(2)	-3(2)
C(11)	54(2)	44(2)	42(2)	2(2)	10(2)	2(2)
C(12)	57(2)	48(2)	78(3)	1(2)	21(2)	11(2)
C(13)	74(3)	46(2)	38(2)	0(2)	19(2)	-7(2)
C(14)	85(3)	47(2)	76(3)	11(2)	17(2)	1(2)
C(15)	59(2)	47(2)	55(2)	-2(2)	27(2)	-3(2)
C(16)	56(2)	47(2)	61(3)	-3(2)	21(2)	0(2)
C(17)	56(2)	54(2)	63(3)	2(2)	17(2)	-3(2)
C(18)	57(2)	49(2)	71(3)	3(2)	30(2)	-5(2)
C(19)	59(3)	63(3)	91(3)	11(2)	25(2)	1(3)
C(20)	68(3)	62(3)	99(4)	26(3)	35(3)	13(3)
C(21)	80(3)	51(2)	91(4)	6(2)	33(3)	5(3)
C(22)	78(3)	55(2)	71(3)	3(2)	28(2)	5(3)
C(23)	64(3)	51(2)	60(3)	-5(2)	30(2)	-9(2)
C(24)	59(2)	56(2)	52(2)	0(2)	21(2)	-3(2)
C(25)	68(2)	48(2)	43(2)	-2(2)	15(2)	-5(2)
C(26)	91(4)	233(9)	87(5)	26(5)	40(3)	46(5)
C(27)	226(9)	79(3)	81(4)	-19(3)	63(4)	-61(5)
C(28)	67(2)	90(3)	42(2)	0(2)	12(2)	3(3)
C(29)	107(4)	268(11)	45(3)	-32(5)	12(3)	-11(6)
C(30)	103(4)	117(4)	66(3)	1(3)	29(3)	30(4)

C(31)	160(6)	102(4)	93(4)	37(4)	69(4)	26(5)
N(1)	58(2)	47(2)	53(2)	1(1)	21(1)	9(2)
O(1)	74(2)	52(2)	67(2)	0(1)	24(1)	-17(2)
O(2)	68(2)	47(1)	66(2)	11(1)	12(1)	0(2)
O(3)	81(2)	66(2)	41(2)	-7(1)	14(1)	-21(2)
Si(1)	62(1)	63(1)	45(1)	-4(1)	15(1)	-4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for product **3.72**.

	x	y	z	U(eq)
H(2A)	-2211	-3952	-4734	62
H(3A)	-1259	-5497	-3870	64
H(4A)	25	-7045	-4396	64
H(5A)	302	-7115	-5842	58
H(8A)	641	-5764	-8055	56
H(9A)	2625	-4035	-7567	62
H(11A)	-2499	-4119	-7722	56
H(12A)	-3654	-2948	-5831	90
H(12B)	-4597	-3533	-6698	90
H(12C)	-3430	-2421	-6732	90
H(14A)	-2739	-454	-7967	104
H(14B)	-961	-527	-8370	104
H(14C)	-842	-281	-7372	104
H(16A)	3532	-5153	-6079	64
H(17A)	5614	-6361	-5358	68
H(19A)	7009	-8285	-5175	84
H(20A)	7009	-10118	-5624	88
H(21A)	4886	-10764	-6786	86
H(22A)	2857	-9528	-7522	79
H(24A)	1595	-7599	-7731	66
H(25A)	-1800	-7040	-7373	63
H(25B)	-3362	-6141	-7360	63
H(26A)	-6423	-6050	-8768	201
H(26B)	-6782	-6368	-9761	201
H(26C)	-5748	-5233	-9445	201
H(27A)	-4631	-8236	-8297	186
H(27B)	-2950	-8623	-8703	186
H(27C)	-4899	-8643	-9270	186
H(29A)	-3675	-7192	-11435	210
H(29B)	-5243	-6718	-10984	210

H(29C)	-4523	-7972	-10791	210
H(30A)	-685	-7489	-10593	140
H(30B)	-1541	-8287	-9963	140
H(30C)	-293	-7260	-9587	140
H(31A)	-1720	-5549	-10856	169
H(31B)	-1369	-5285	-9855	169
H(31C)	-3294	-5070	-10412	169

Table 6. Torsion angles [°] for product **3.72**.

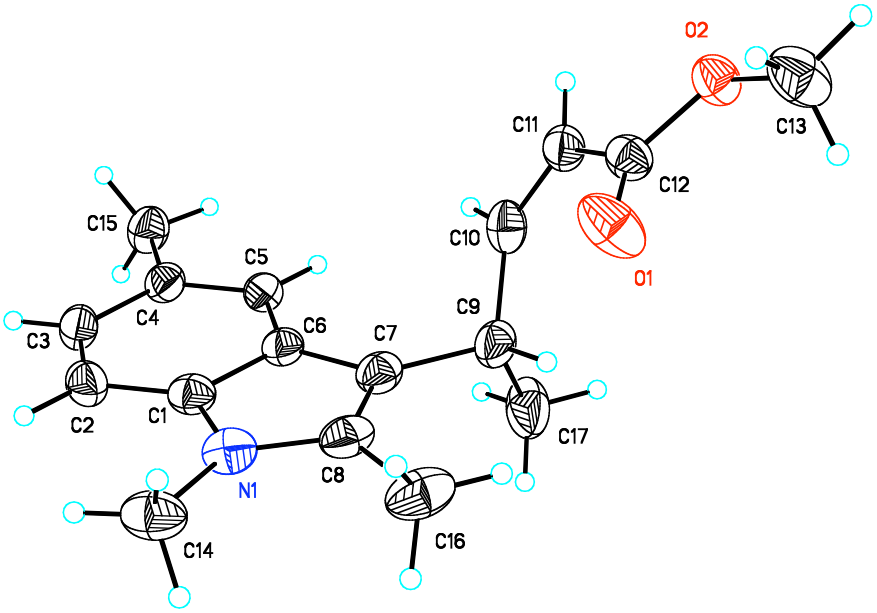
N(1)-C(1)-C(2)-C(3)	179.2(3)
C(6)-C(1)-C(2)-C(3)	-0.3(5)
C(1)-C(2)-C(3)-C(4)	0.2(5)
C(2)-C(3)-C(4)-C(5)	-1.0(6)
C(3)-C(4)-C(5)-C(6)	1.9(5)
C(4)-C(5)-C(6)-C(1)	-2.1(5)
C(4)-C(5)-C(6)-C(7)	-172.8(4)
N(1)-C(1)-C(6)-C(5)	-178.3(3)
C(2)-C(1)-C(6)-C(5)	1.3(5)
N(1)-C(1)-C(6)-C(7)	-5.8(4)
C(2)-C(1)-C(6)-C(7)	173.8(3)
C(5)-C(6)-C(7)-C(25)	62.1(5)
C(1)-C(6)-C(7)-C(25)	-109.4(3)
C(5)-C(6)-C(7)-C(11)	-178.6(4)
C(1)-C(6)-C(7)-C(11)	9.9(4)
C(5)-C(6)-C(7)-C(8)	-64.4(5)
C(1)-C(6)-C(7)-C(8)	124.2(3)
C(6)-C(7)-C(8)-C(9)	-94.7(3)
C(25)-C(7)-C(8)-C(9)	140.2(3)
C(11)-C(7)-C(8)-C(9)	17.6(4)
C(6)-C(7)-C(8)-C(15)	33.3(4)
C(25)-C(7)-C(8)-C(15)	-91.8(4)
C(11)-C(7)-C(8)-C(15)	145.7(3)
C(15)-C(8)-C(9)-C(10)	-142.1(3)
C(7)-C(8)-C(9)-C(10)	-14.3(4)
C(8)-C(9)-C(10)-C(13)	-172.9(3)
C(8)-C(9)-C(10)-C(11)	4.8(4)
C(9)-C(10)-C(11)-N(1)	121.4(3)
C(13)-C(10)-C(11)-N(1)	-60.9(4)
C(9)-C(10)-C(11)-C(7)	7.0(4)
C(13)-C(10)-C(11)-C(7)	-175.2(3)
C(6)-C(7)-C(11)-N(1)	-10.5(4)
C(25)-C(7)-C(11)-N(1)	105.7(3)
C(8)-C(7)-C(11)-N(1)	-132.8(3)

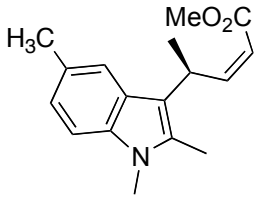
C(6)-C(7)-C(11)-C(10)	107.2(3)
C(25)-C(7)-C(11)-C(10)	-136.6(3)
C(8)-C(7)-C(11)-C(10)	-15.1(3)
C(9)-C(10)-C(13)-O(1)	-18.5(6)
C(11)-C(10)-C(13)-O(1)	164.0(3)
C(9)-C(10)-C(13)-O(2)	160.2(3)
C(11)-C(10)-C(13)-O(2)	-17.3(5)
C(9)-C(8)-C(15)-C(24)	-147.2(4)
C(7)-C(8)-C(15)-C(24)	91.6(4)
C(9)-C(8)-C(15)-C(16)	34.2(5)
C(7)-C(8)-C(15)-C(16)	-87.0(4)
C(24)-C(15)-C(16)-C(17)	0.0(6)
C(8)-C(15)-C(16)-C(17)	178.7(3)
C(15)-C(16)-C(17)-C(18)	-0.4(6)
C(16)-C(17)-C(18)-C(23)	0.1(6)
C(16)-C(17)-C(18)-C(19)	-179.7(4)
C(17)-C(18)-C(19)-C(20)	178.6(4)
C(23)-C(18)-C(19)-C(20)	-1.2(6)
C(18)-C(19)-C(20)-C(21)	-0.6(7)
C(19)-C(20)-C(21)-C(22)	1.6(7)
C(20)-C(21)-C(22)-C(23)	-0.6(7)
C(21)-C(22)-C(23)-C(18)	-1.3(6)
C(21)-C(22)-C(23)-C(24)	-179.4(4)
C(17)-C(18)-C(23)-C(22)	-177.6(4)
C(19)-C(18)-C(23)-C(22)	2.2(6)
C(17)-C(18)-C(23)-C(24)	0.6(5)
C(19)-C(18)-C(23)-C(24)	-179.6(4)
C(16)-C(15)-C(24)-C(23)	0.7(6)
C(8)-C(15)-C(24)-C(23)	-178.0(3)
C(22)-C(23)-C(24)-C(15)	177.1(4)
C(18)-C(23)-C(24)-C(15)	-1.0(6)
C(6)-C(7)-C(25)-O(3)	178.6(3)
C(11)-C(7)-C(25)-O(3)	66.3(4)
C(8)-C(7)-C(25)-O(3)	-51.8(4)
C(2)-C(1)-N(1)-C(12)	-33.9(5)
C(6)-C(1)-N(1)-C(12)	145.6(3)

C(2)-C(1)-N(1)-C(11)	179.0(3)
C(6)-C(1)-N(1)-C(11)	-1.4(4)
C(10)-C(11)-N(1)-C(1)	-104.3(3)
C(7)-C(11)-N(1)-C(1)	7.8(4)
C(10)-C(11)-N(1)-C(12)	108.6(4)
C(7)-C(11)-N(1)-C(12)	-139.3(3)
O(1)-C(13)-O(2)-C(14)	2.0(5)
C(10)-C(13)-O(2)-C(14)	-176.7(3)
C(7)-C(25)-O(3)-Si(1)	-174.0(3)
C(25)-O(3)-Si(1)-C(27)	-37.2(4)
C(25)-O(3)-Si(1)-C(26)	83.5(4)
C(25)-O(3)-Si(1)-C(28)	-156.6(3)
C(30)-C(28)-Si(1)-O(3)	69.9(4)
C(31)-C(28)-Si(1)-O(3)	-51.2(4)
C(29)-C(28)-Si(1)-O(3)	-171.7(5)
C(30)-C(28)-Si(1)-C(27)	-48.8(5)
C(31)-C(28)-Si(1)-C(27)	-170.0(5)
C(29)-C(28)-Si(1)-C(27)	69.6(6)
C(30)-C(28)-Si(1)-C(26)	-172.2(5)
C(31)-C(28)-Si(1)-C(26)	66.6(5)
C(29)-C(28)-Si(1)-C(26)	-53.9(6)

Symmetry transformations used to generate equivalent atoms:

6. X-ray crystallographic structure of product 3.103





3.103

Table 1. Crystal data and structure refinement for product **3.103**.

Identification code	yl_106s	
Empirical formula	C17 H21 N O2	
Formula weight	271.35	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 7.1902(3) Å	α= 90°.
	B = 11.3975(4) Å	β= 90°.
	C = 18.3499(6) Å	γ = 90°.
Volume	1503.78(10) $Å^3$	
Z	4	
Density (calculated)	1.199 Mg/m^3	
Absorption coefficient	0.618 mm^{-1}	
F(000)	584	
Crystal size	0.43 x 0.18 x 0.12 mm^3	
Theta range for data collection	4.57 to 65.95°.	
Index ranges	-8<=h<=7, -13<=k<=11, -21<=l<=21	
Reflections collected	8918	
Independent reflections	2474 [R(int) = 0.0214]	
Completeness to theta = 65.95°	96.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9295 and 0.7770	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2474 / 0 / 181	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0353, wR2 = 0.1136	
R indices (all data)	R1 = 0.0377, wR2 = 0.1172	
Absolute structure parameter	0.0(3)	
Largest diff. peak and hole	0.155 and -0.137 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for product **3.103**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-10383(2)	-3781(2)	-4934(1)	38(1)
C(2)	-10439(3)	-4584(2)	-5509(1)	43(1)
C(3)	-10413(3)	-5758(2)	-5342(1)	42(1)
C(4)	-10331(2)	-6169(2)	-4616(1)	39(1)
C(5)	-10286(2)	-5362(2)	-4052(1)	37(1)
C(6)	-10299(2)	-4148(2)	-4197(1)	35(1)
C(7)	-10243(2)	-3099(2)	-3763(1)	40(1)
C(8)	-10305(2)	-2169(2)	-4238(1)	44(1)
C(9)	-10202(2)	-3004(2)	-2939(1)	45(1)
C(10)	-8701(3)	-3754(2)	-2611(1)	44(1)
C(11)	-7153(3)	-3417(2)	-2273(1)	41(1)
C(12)	-6538(2)	-2198(2)	-2193(1)	39(1)
C(13)	-4731(3)	-936(2)	-1455(1)	61(1)
C(14)	-10415(3)	-1862(2)	-5600(1)	54(1)
C(15)	-10307(3)	-7469(2)	-4471(1)	49(1)
C(16)	-10299(3)	-878(2)	-4084(2)	59(1)
C(17)	-12085(3)	-3361(3)	-2606(1)	71(1)
N(1)	-10402(2)	-2575(2)	-4943(1)	44(1)
O(1)	-6926(2)	-1393(1)	-2585(1)	65(1)
O(2)	-5435(2)	-2090(1)	-1605(1)	44(1)

Table 3. Bond lengths [Å] and angles [°] for product **3.103**.

C(1)-N(1)	1.376(2)	C(2)-C(3)-C(4)	122.34(15)
C(1)-C(2)	1.397(2)	C(5)-C(4)-C(3)	118.97(16)
C(1)-C(6)	1.417(2)	C(5)-C(4)-C(15)	121.49(15)
C(2)-C(3)	1.372(3)	C(3)-C(4)-C(15)	119.54(15)
C(3)-C(4)	1.414(2)	C(4)-C(5)-C(6)	120.77(15)
C(4)-C(5)	1.385(2)	C(5)-C(6)-C(1)	117.99(15)
C(4)-C(15)	1.505(3)	C(5)-C(6)-C(7)	135.42(15)
C(5)-C(6)	1.410(2)	C(1)-C(6)-C(7)	106.58(16)
C(6)-C(7)	1.437(2)	C(8)-C(7)-C(6)	106.83(15)
C(7)-C(8)	1.373(3)	C(8)-C(7)-C(9)	125.35(17)
C(7)-C(9)	1.516(2)	C(6)-C(7)-C(9)	127.77(17)
C(8)-N(1)	1.376(2)	C(7)-C(8)-N(1)	109.83(16)
C(8)-C(16)	1.499(3)	C(7)-C(8)-C(16)	129.68(18)
C(9)-C(10)	1.502(3)	N(1)-C(8)-C(16)	120.48(18)
C(9)-C(17)	1.540(3)	C(10)-C(9)-C(7)	111.88(15)
C(10)-C(11)	1.331(3)	C(10)-C(9)-C(17)	108.81(18)
C(11)-C(12)	1.465(3)	C(7)-C(9)-C(17)	111.05(15)
C(12)-O(1)	1.199(2)	C(11)-C(10)-C(9)	128.49(17)
C(12)-O(2)	1.344(2)	C(10)-C(11)-C(12)	124.99(16)
C(13)-O(2)	1.435(2)	O(1)-C(12)-O(2)	123.26(17)
C(14)-N(1)	1.454(2)	O(1)-C(12)-C(11)	126.54(15)
		O(2)-C(12)-C(11)	110.20(14)
N(1)-C(1)-C(2)	130.23(16)	C(1)-N(1)-C(8)	108.94(15)
N(1)-C(1)-C(6)	107.81(16)	C(1)-N(1)-C(14)	124.63(17)
C(2)-C(1)-C(6)	121.96(17)	C(8)-N(1)-C(14)	126.35(17)
C(3)-C(2)-C(1)	117.97(15)	C(12)-O(2)-C(13)	116.48(15)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for product **3.103**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	29(1)	42(1)	43(1)	4(1)	2(1)	0(1)
C(2)	41(1)	56(1)	33(1)	3(1)	1(1)	1(1)
C(3)	42(1)	49(1)	36(1)	-8(1)	3(1)	1(1)
C(4)	34(1)	42(1)	39(1)	-4(1)	3(1)	1(1)
C(5)	33(1)	44(1)	34(1)	0(1)	1(1)	2(1)
C(6)	27(1)	40(1)	38(1)	-3(1)	1(1)	2(1)
C(7)	31(1)	40(1)	49(1)	-6(1)	1(1)	0(1)
C(8)	31(1)	40(1)	61(1)	-4(1)	0(1)	3(1)
C(9)	38(1)	48(1)	48(1)	-17(1)	0(1)	-2(1)
C(10)	58(1)	37(1)	37(1)	-5(1)	2(1)	-6(1)
C(11)	50(1)	37(1)	36(1)	-3(1)	-3(1)	5(1)
C(12)	37(1)	43(1)	35(1)	4(1)	-1(1)	-2(1)
C(13)	60(1)	46(1)	75(1)	3(1)	-22(1)	-14(1)
C(14)	45(1)	53(1)	65(1)	20(1)	2(1)	3(1)
C(15)	57(1)	41(1)	48(1)	-6(1)	3(1)	2(1)
C(16)	46(1)	38(1)	94(2)	-2(1)	3(1)	4(1)
C(17)	48(1)	115(2)	50(1)	-27(1)	10(1)	-12(1)
N(1)	38(1)	41(1)	52(1)	7(1)	4(1)	0(1)
O(1)	81(1)	49(1)	65(1)	19(1)	-29(1)	-16(1)
O(2)	49(1)	39(1)	43(1)	1(1)	-8(1)	-4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for product **3.103**.

	x	y	z	U(eq)
H(2A)	-10494	-4326	-6001	52
H(3A)	-10453	-6313	-5728	51
H(5A)	-10245	-5630	-3562	44
H(9A)	-9950	-2168	-2806	54
H(10A)	-8881	-4578	-2650	53
H(11A)	-6389	-4011	-2068	49
H(13A)	-3945	-961	-1019	91
H(13B)	-5772	-398	-1373	91
H(13C)	-3994	-662	-1871	91
H(14A)	-10503	-2373	-6028	82
H(14B)	-9266	-1402	-5626	82
H(14C)	-11487	-1330	-5589	82
H(15A)	-10249	-7608	-3945	73
H(15B)	-9216	-7820	-4706	73
H(15C)	-11439	-7826	-4669	73
H(16A)	-10215	-749	-3557	89
H(16B)	-11449	-526	-4269	89
H(16C)	-9228	-513	-4324	89
H(17A)	-12026	-3285	-2074	106
H(17B)	-12362	-4177	-2735	106
H(17C)	-13065	-2849	-2796	106

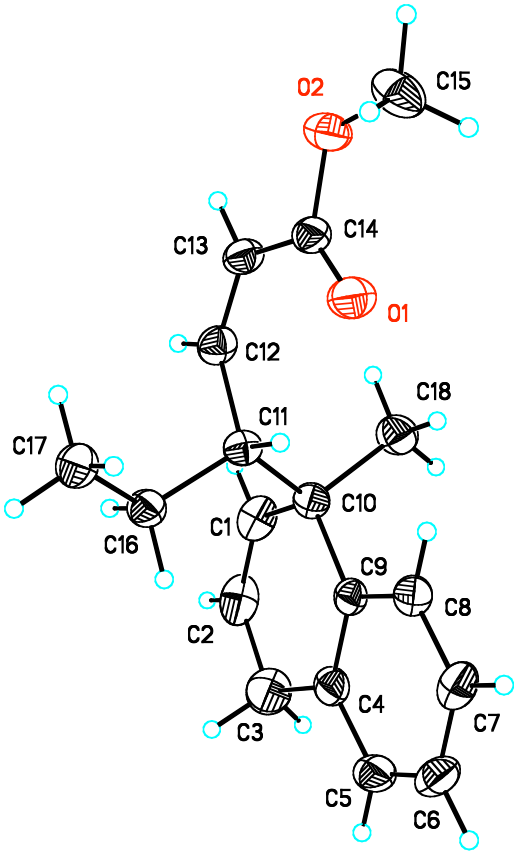
Table 6. Torsion angles [°] for product **3.103**.

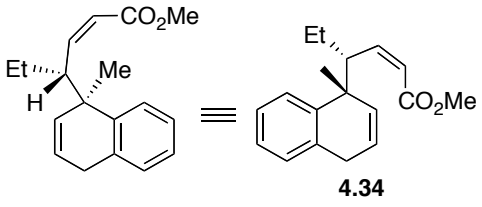
N(1)-C(1)-C(2)-C(3)	-179.62(19)
C(6)-C(1)-C(2)-C(3)	0.1(3)
C(1)-C(2)-C(3)-C(4)	-0.1(3)
C(2)-C(3)-C(4)-C(5)	0.4(3)
C(2)-C(3)-C(4)-C(15)	-179.99(18)
C(3)-C(4)-C(5)-C(6)	-0.8(3)
C(15)-C(4)-C(5)-C(6)	179.66(16)
C(4)-C(5)-C(6)-C(1)	0.8(2)
C(4)-C(5)-C(6)-C(7)	-179.12(18)
N(1)-C(1)-C(6)-C(5)	179.35(14)
C(2)-C(1)-C(6)-C(5)	-0.4(2)
N(1)-C(1)-C(6)-C(7)	-0.75(19)
C(2)-C(1)-C(6)-C(7)	179.49(15)
C(5)-C(6)-C(7)-C(8)	-179.78(18)
C(1)-C(6)-C(7)-C(8)	0.34(17)
C(5)-C(6)-C(7)-C(9)	-2.0(3)
C(1)-C(6)-C(7)-C(9)	178.12(15)
C(6)-C(7)-C(8)-N(1)	0.20(18)
C(9)-C(7)-C(8)-N(1)	-177.65(15)
C(6)-C(7)-C(8)-C(16)	179.50(18)
C(9)-C(7)-C(8)-C(16)	1.7(3)
C(8)-C(7)-C(9)-C(10)	-131.44(18)
C(6)-C(7)-C(9)-C(10)	51.2(2)
C(8)-C(7)-C(9)-C(17)	106.8(2)
C(6)-C(7)-C(9)-C(17)	-70.6(3)
C(7)-C(9)-C(10)-C(11)	111.8(2)
C(17)-C(9)-C(10)-C(11)	-125.1(2)
C(9)-C(10)-C(11)-C(12)	-4.2(3)
C(10)-C(11)-C(12)-O(1)	-25.5(3)
C(10)-C(11)-C(12)-O(2)	154.77(16)
C(2)-C(1)-N(1)-C(8)	-179.37(17)
C(6)-C(1)-N(1)-C(8)	0.9(2)
C(2)-C(1)-N(1)-C(14)	-2.6(3)
C(6)-C(1)-N(1)-C(14)	177.70(15)

C(7)-C(8)-N(1)-C(1)	-0.7(2)
C(16)-C(8)-N(1)-C(1)	179.94(16)
C(7)-C(8)-N(1)-C(14)	-177.43(16)
C(16)-C(8)-N(1)-C(14)	3.2(3)
O(1)-C(12)-O(2)-C(13)	0.6(3)
C(11)-C(12)-O(2)-C(13)	-179.69(16)

Symmetry transformations used to generate equivalent atoms:

7. X-ray crystallographic structure of product 4.34





4.34

Table 1. Crystal data and structure refinement for product **4.34**.

Identification code	yl_v_84cope	
Empirical formula	C18 H22 O2	
Formula weight	270.36	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 9.2525(4) Å	α= 90°.
	b = 7.5766(3) Å	β= 103.735(2)°.
	c = 11.1876(4) Å	γ = 90°.
Volume	761.85(5) $Å^3$	
Z	2	
Density (calculated)	1.179 Mg/m^3	
Absorption coefficient	0.588 mm^{-1}	
F(000)	292	
Crystal size	0.29 x 0.23 x 0.13 mm^3	
Theta range for data collection	4.07 to 68.02°.	
Index ranges	-10<=h<=10, -8<=k<=8, -13<=l<=12	
Reflections collected	5184	
Independent reflections	2380 [R(int) = 0.0169]	
Completeness to theta = 68.02°	95.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9275 and 0.8479	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2380 / 1 / 181	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0292, wR2 = 0.0761	
R indices (all data)	R1 = 0.0294, wR2 = 0.0762	
Absolute structure parameter	0.1(2)	
Largest diff. peak and hole	0.137 and -0.148 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for product **4.34**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	1883(2)	3424(2)	4455(1)	42(1)
C(2)	764(2)	2504(2)	4675(2)	49(1)
C(3)	-538(2)	1952(3)	3700(2)	57(1)
C(4)	-554(2)	2667(2)	2441(1)	38(1)
C(5)	-1805(2)	2377(2)	1481(2)	45(1)
C(6)	-1883(2)	2968(2)	314(2)	47(1)
C(7)	-688(2)	3860(2)	64(1)	44(1)
C(8)	560(2)	4172(2)	1004(1)	37(1)
C(9)	646(1)	3601(2)	2206(1)	31(1)
C(10)	2026(2)	4063(2)	3212(1)	33(1)
C(11)	3428(1)	3188(2)	2874(1)	32(1)
C(12)	4857(2)	3847(2)	3688(1)	37(1)
C(13)	5903(2)	4851(2)	3397(1)	37(1)
C(14)	5871(1)	5618(2)	2177(1)	35(1)
C(15)	7189(2)	7494(2)	1126(2)	53(1)
C(16)	3369(2)	1168(2)	2939(1)	37(1)
C(17)	4595(2)	270(2)	2460(2)	45(1)
C(18)	2210(2)	6087(2)	3260(2)	43(1)
O(1)	4938(1)	5405(2)	1234(1)	46(1)
O(2)	7067(1)	6652(2)	2256(1)	44(1)

Table 3. Bond lengths [Å] and angles [°] for product **4.34**.

C(1)-C(2)	1.319(2)	C(16)-C(17)	1.525(2)
C(1)-C(10)	1.5079(19)	C(16)-H(16A)	0.9900
C(1)-H(1A)	0.9500	C(16)-H(16B)	0.9900
C(2)-C(3)	1.480(3)	C(17)-H(17A)	0.9800
C(2)-H(2A)	0.9500	C(17)-H(17B)	0.9800
C(3)-C(4)	1.506(2)	C(17)-H(17C)	0.9800
C(3)-H(3A)	0.9900	C(18)-H(18A)	0.9800
C(3)-H(3B)	0.9900	C(18)-H(18B)	0.9800
C(4)-C(9)	1.394(2)	C(18)-H(18C)	0.9800
C(4)-C(5)	1.397(2)		
C(5)-C(6)	1.366(2)	C(2)-C(1)-C(10)	125.87(14)
C(5)-H(5A)	0.9500	C(2)-C(1)-H(1A)	117.1
C(6)-C(7)	1.380(2)	C(10)-C(1)-H(1A)	117.1
C(6)-H(6A)	0.9500	C(1)-C(2)-C(3)	123.36(14)
C(7)-C(8)	1.385(2)	C(1)-C(2)-H(2A)	118.3
C(7)-H(7A)	0.9500	C(3)-C(2)-H(2A)	118.3
C(8)-C(9)	1.3966(19)	C(2)-C(3)-C(4)	114.38(14)
C(8)-H(8A)	0.9500	C(2)-C(3)-H(3A)	108.7
C(9)-C(10)	1.5282(18)	C(4)-C(3)-H(3A)	108.7
C(10)-C(18)	1.542(2)	C(2)-C(3)-H(3B)	108.7
C(10)-C(11)	1.5804(18)	C(4)-C(3)-H(3B)	108.7
C(11)-C(12)	1.5015(19)	H(3A)-C(3)-H(3B)	107.6
C(11)-C(16)	1.534(2)	C(9)-C(4)-C(5)	119.13(14)
C(11)-H(11A)	1.0000	C(9)-C(4)-C(3)	121.85(13)
C(12)-C(13)	1.331(2)	C(5)-C(4)-C(3)	119.02(14)
C(12)-H(12A)	0.9500	C(6)-C(5)-C(4)	121.97(14)
C(13)-C(14)	1.478(2)	C(6)-C(5)-H(5A)	119.0
C(13)-H(13A)	0.9500	C(4)-C(5)-H(5A)	119.0
C(14)-O(1)	1.2044(17)	C(5)-C(6)-C(7)	119.41(13)
C(14)-O(2)	1.3411(17)	C(5)-C(6)-H(6A)	120.3
C(15)-O(2)	1.444(2)	C(7)-C(6)-H(6A)	120.3
C(15)-H(15A)	0.9800	C(6)-C(7)-C(8)	119.58(15)
C(15)-H(15B)	0.9800	C(6)-C(7)-H(7A)	120.2
C(15)-H(15C)	0.9800	C(8)-C(7)-H(7A)	120.2

C(7)-C(8)-C(9)	121.67(14)	O(2)-C(14)-C(13)	109.48(11)
C(7)-C(8)-H(8A)	119.2	O(2)-C(15)-H(15A)	109.5
C(9)-C(8)-H(8A)	119.2	O(2)-C(15)-H(15B)	109.5
C(4)-C(9)-C(8)	118.22(13)	H(15A)-C(15)-H(15B)	109.5
C(4)-C(9)-C(10)	122.73(12)	O(2)-C(15)-H(15C)	109.5
C(8)-C(9)-C(10)	119.03(12)	H(15A)-C(15)-H(15C)	109.5
C(1)-C(10)-C(9)	111.44(12)	H(15B)-C(15)-H(15C)	109.5
C(1)-C(10)-C(18)	108.64(13)	C(17)-C(16)-C(11)	112.99(12)
C(9)-C(10)-C(18)	108.62(12)	C(17)-C(16)-H(16A)	109.0
C(1)-C(10)-C(11)	110.03(11)	C(11)-C(16)-H(16A)	109.0
C(9)-C(10)-C(11)	108.50(10)	C(17)-C(16)-H(16B)	109.0
C(18)-C(10)-C(11)	109.59(12)	C(11)-C(16)-H(16B)	109.0
C(12)-C(11)-C(16)	109.79(12)	H(16A)-C(16)-H(16B)	107.8
C(12)-C(11)-C(10)	111.73(11)	C(16)-C(17)-H(17A)	109.5
C(16)-C(11)-C(10)	111.52(11)	C(16)-C(17)-H(17B)	109.5
C(12)-C(11)-H(11A)	107.9	H(17A)-C(17)-H(17B)	109.5
C(16)-C(11)-H(11A)	107.9	C(16)-C(17)-H(17C)	109.5
C(10)-C(11)-H(11A)	107.9	H(17A)-C(17)-H(17C)	109.5
C(13)-C(12)-C(11)	128.95(12)	H(17B)-C(17)-H(17C)	109.5
C(13)-C(12)-H(12A)	115.5	C(10)-C(18)-H(18A)	109.5
C(11)-C(12)-H(12A)	115.5	C(10)-C(18)-H(18B)	109.5
C(12)-C(13)-C(14)	126.48(12)	H(18A)-C(18)-H(18B)	109.5
C(12)-C(13)-H(13A)	116.8	C(10)-C(18)-H(18C)	109.5
C(14)-C(13)-H(13A)	116.8	H(18A)-C(18)-H(18C)	109.5
O(1)-C(14)-O(2)	122.99(13)	H(18B)-C(18)-H(18C)	109.5
O(1)-C(14)-C(13)	127.53(13)	C(14)-O(2)-C(15)	115.79(12)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for product **4.34**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	44(1)	52(1)	32(1)	-1(1)	11(1)	10(1)
C(2)	53(1)	60(1)	42(1)	15(1)	25(1)	17(1)
C(3)	46(1)	65(1)	64(1)	20(1)	25(1)	-1(1)
C(4)	33(1)	32(1)	51(1)	3(1)	15(1)	4(1)
C(5)	29(1)	37(1)	71(1)	-7(1)	15(1)	0(1)
C(6)	32(1)	47(1)	56(1)	-16(1)	-3(1)	8(1)
C(7)	43(1)	48(1)	38(1)	-1(1)	2(1)	11(1)
C(8)	37(1)	36(1)	38(1)	2(1)	8(1)	2(1)
C(9)	29(1)	28(1)	37(1)	0(1)	10(1)	4(1)
C(10)	34(1)	32(1)	32(1)	-2(1)	8(1)	-1(1)
C(11)	31(1)	36(1)	29(1)	0(1)	8(1)	-3(1)
C(12)	36(1)	42(1)	30(1)	1(1)	4(1)	-1(1)
C(13)	29(1)	40(1)	40(1)	-4(1)	2(1)	-3(1)
C(14)	29(1)	31(1)	46(1)	-4(1)	9(1)	0(1)
C(15)	61(1)	44(1)	63(1)	-2(1)	33(1)	-8(1)
C(16)	33(1)	35(1)	44(1)	-2(1)	12(1)	0(1)
C(17)	39(1)	42(1)	56(1)	-4(1)	15(1)	5(1)
C(18)	44(1)	37(1)	49(1)	-9(1)	10(1)	-2(1)
O(1)	40(1)	55(1)	42(1)	6(1)	5(1)	-8(1)
O(2)	39(1)	41(1)	54(1)	-4(1)	17(1)	-9(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for product **4.34**.

	x	y	z	U(eq)
H(1A)	2670	3710	5142	51
H(2A)	795	2179	5501	59
H(3A)	-1455	2342	3933	68
H(3B)	-559	646	3659	68
H(5A)	-2627	1751	1645	54
H(6A)	-2752	2766	-320	57
H(7A)	-721	4258	-747	53
H(8A)	1377	4791	827	45
H(11A)	3419	3523	2008	38
H(12A)	5039	3498	4526	44
H(13A)	6755	5100	4038	45
H(15A)	8089	8224	1282	79
H(15B)	6314	8239	817	79
H(15C)	7247	6591	512	79
H(16A)	3458	808	3805	44
H(16B)	2390	757	2451	44
H(17A)	4506	-1013	2525	67
H(17B)	5569	651	2950	67
H(17C)	4499	595	1597	67
H(18A)	1340	6627	3471	65
H(18B)	2298	6520	2456	65
H(18C)	3108	6399	3886	65

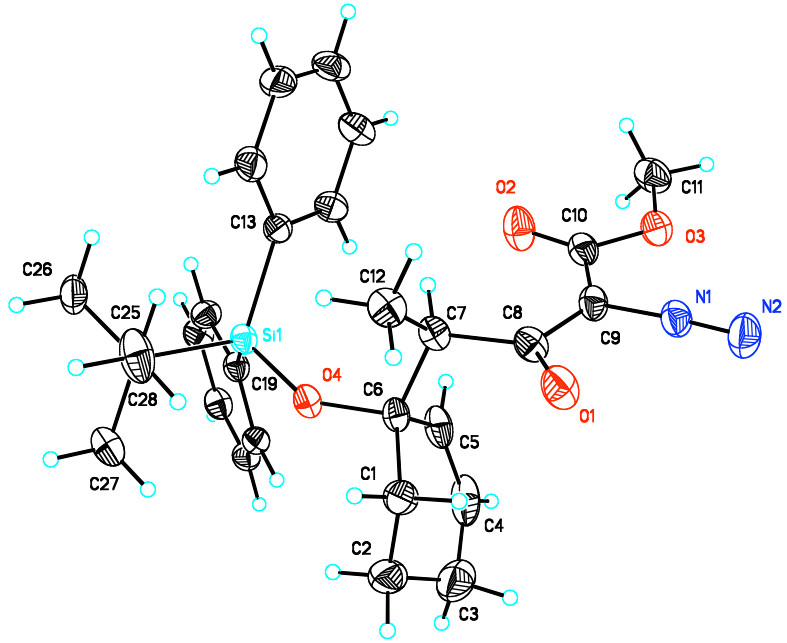
Table 6. Torsion angles [°] for product **4.34**.

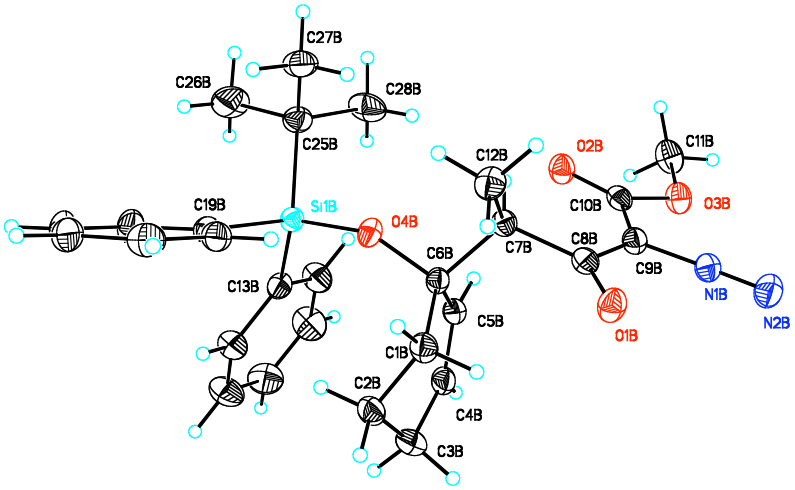
C(10)-C(1)-C(2)-C(3)	0.3(3)
C(1)-C(2)-C(3)-C(4)	-5.3(3)
C(2)-C(3)-C(4)-C(9)	6.8(2)
C(2)-C(3)-C(4)-C(5)	-173.49(15)
C(9)-C(4)-C(5)-C(6)	0.6(2)
C(3)-C(4)-C(5)-C(6)	-179.05(16)
C(4)-C(5)-C(6)-C(7)	0.8(2)
C(5)-C(6)-C(7)-C(8)	-1.2(2)
C(6)-C(7)-C(8)-C(9)	0.2(2)
C(5)-C(4)-C(9)-C(8)	-1.6(2)
C(3)-C(4)-C(9)-C(8)	178.07(15)
C(5)-C(4)-C(9)-C(10)	176.76(13)
C(3)-C(4)-C(9)-C(10)	-3.6(2)
C(7)-C(8)-C(9)-C(4)	1.2(2)
C(7)-C(8)-C(9)-C(10)	-177.22(14)
C(2)-C(1)-C(10)-C(9)	3.2(2)
C(2)-C(1)-C(10)-C(18)	122.88(18)
C(2)-C(1)-C(10)-C(11)	-117.16(17)
C(4)-C(9)-C(10)-C(1)	-1.48(19)
C(8)-C(9)-C(10)-C(1)	176.89(13)
C(4)-C(9)-C(10)-C(18)	-121.12(15)
C(8)-C(9)-C(10)-C(18)	57.25(17)
C(4)-C(9)-C(10)-C(11)	119.81(14)
C(8)-C(9)-C(10)-C(11)	-61.82(16)
C(1)-C(10)-C(11)-C(12)	-68.32(15)
C(9)-C(10)-C(11)-C(12)	169.53(12)
C(18)-C(10)-C(11)-C(12)	51.08(15)
C(1)-C(10)-C(11)-C(16)	54.98(15)
C(9)-C(10)-C(11)-C(16)	-67.18(14)
C(18)-C(10)-C(11)-C(16)	174.37(11)
C(16)-C(11)-C(12)-C(13)	123.64(17)
C(10)-C(11)-C(12)-C(13)	-112.10(17)
C(11)-C(12)-C(13)-C(14)	2.2(3)
C(12)-C(13)-C(14)-O(1)	-3.6(3)

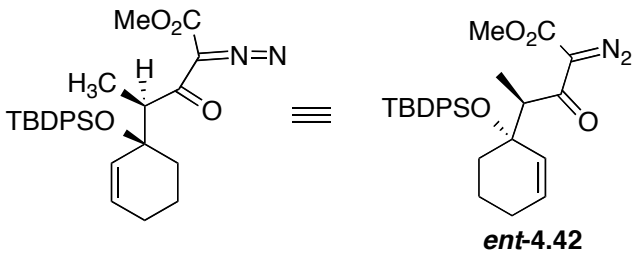
C(12)-C(13)-C(14)-O(2)	175.72(14)
C(12)-C(11)-C(16)-C(17)	-63.07(15)
C(10)-C(11)-C(16)-C(17)	172.54(11)
O(1)-C(14)-O(2)-C(15)	-0.8(2)
C(13)-C(14)-O(2)-C(15)	179.87(12)

Symmetry transformations used to generate equivalent atoms:

8. X-ray crystallographic structure of product *ent*-4.42







***ent*-4.42**

Table 1. Crystal data and structure refinement for product ***ent*-4.42**.

Identification code	yl_9_107rptad	
Empirical formula	C28 H34 N2 O4 Si	
Formula weight	490.66	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 10.0953(7) Å	α= 86.851(3)°.
	b = 10.4877(7) Å	β= 72.453(2)°.
	c = 14.7630(11) Å	γ = 65.333(2)°.
Volume	1349.79(16) $Å^3$	
Z	2	
Density (calculated)	1.207 Mg/m^3	
Absorption coefficient	1.048 mm^{-1}	
F(000)	524	
Crystal size	0.28 x 0.23 x 0.13 mm^3	
Theta range for data collection	3.15 to 69.22°.	
Index ranges	-11<=h<=12, -12<=k<=12, -17<=l<=17	
Reflections collected	12600	
Independent reflections	6887 [R(int) = 0.0161]	
Completeness to theta = 69.22°	90.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8758 and 0.7580	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6887 / 3 / 631	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0272, wR2 = 0.0778	
R indices (all data)	R1 = 0.0275, wR2 = 0.0786	
Absolute structure parameter	0.058(15)	
Largest diff. peak and hole	0.206 and -0.168 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for product ***ent*-4.42**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-1768(3)	5412(3)	5649(2)	46(1)
C(2)	-1897(4)	5268(4)	4665(2)	62(1)
C(3)	-1194(4)	3738(4)	4314(2)	74(1)
C(4)	356(4)	3000(3)	4426(2)	66(1)
C(5)	886(3)	3481(2)	5006(2)	47(1)
C(6)	-93(2)	4826(2)	5643(1)	34(1)
C(7)	80(2)	4574(2)	6662(1)	36(1)
C(8)	-491(2)	3490(2)	7123(1)	39(1)
C(9)	591(2)	2054(2)	7187(1)	39(1)
C(10)	2261(3)	1354(2)	6913(1)	39(1)
C(11)	4363(3)	-763(3)	6957(2)	55(1)
C(12)	-791(3)	5922(3)	7334(2)	46(1)
C(13)	3045(2)	5631(2)	5844(1)	34(1)
C(14)	2869(3)	6408(3)	6646(2)	46(1)
C(15)	3818(3)	5834(3)	7214(2)	54(1)
C(16)	4955(3)	4484(3)	6998(2)	52(1)
C(17)	5133(3)	3692(3)	6223(2)	49(1)
C(18)	4184(3)	4262(3)	5658(2)	41(1)
C(19)	3250(2)	5527(2)	3785(1)	33(1)
C(20)	2815(2)	5102(2)	3083(1)	35(1)
C(21)	3834(3)	4597(2)	2173(2)	39(1)
C(22)	5308(3)	4503(2)	1944(1)	40(1)
C(23)	5766(3)	4928(3)	2624(2)	42(1)
C(24)	4736(2)	5443(2)	3531(1)	39(1)
C(25)	978(3)	8299(2)	4985(2)	43(1)
C(26)	2168(3)	8879(3)	4914(2)	54(1)
C(27)	418(3)	8667(3)	4108(2)	53(1)
C(28)	-412(4)	9013(3)	5868(2)	64(1)
N(1)	-130(2)	1260(2)	7632(1)	43(1)
N(2)	-809(3)	676(3)	7996(2)	61(1)

O(1)	-1858(2)	3793(2)	7477(1)	54(1)
O(2)	3103(2)	1891(2)	6533(1)	57(1)
O(3)	2734(2)	13(2)	7144(1)	47(1)
O(4)	412(2)	5902(2)	5263(1)	37(1)
Si(1)	1870(1)	6307(1)	5004(1)	31(1)
C(1B)	4751(2)	8872(2)	649(2)	36(1)
C(2B)	4250(3)	8635(2)	1705(2)	40(1)
C(3B)	3206(3)	10034(3)	2291(2)	49(1)
C(4B)	3830(2)	11119(2)	2000(2)	37(1)
C(5B)	4922(2)	10994(2)	1197(1)	30(1)
C(6B)	5665(2)	9758(2)	465(1)	28(1)
C(7B)	5910(2)	10270(2)	-559(1)	29(1)
C(8B)	4434(2)	11318(2)	-717(1)	31(1)
C(9B)	4173(2)	12802(2)	-752(1)	32(1)
C(10B)	5011(2)	13553(2)	-570(1)	32(1)
C(11B)	5106(3)	15761(2)	-565(2)	46(1)
C(12B)	6691(2)	9040(2)	-1336(2)	40(1)
C(13B)	7343(2)	9218(2)	2428(1)	34(1)
C(14B)	6832(3)	8483(3)	3159(2)	42(1)
C(15B)	6076(3)	9084(3)	4087(2)	56(1)
C(16B)	5834(3)	10448(3)	4306(2)	57(1)
C(17B)	6329(3)	11197(3)	3599(2)	58(1)
C(18B)	7080(3)	10589(2)	2673(2)	45(1)
C(19B)	8965(2)	6434(2)	1175(1)	33(1)
C(20B)	9866(3)	5656(3)	1738(2)	45(1)
C(21B)	10442(3)	4199(3)	1695(2)	54(1)
C(22B)	10136(3)	3481(3)	1089(2)	54(1)
C(23B)	9228(3)	4219(2)	537(2)	48(1)
C(24B)	8653(2)	5692(2)	575(2)	38(1)
C(25B)	9988(2)	8807(2)	516(2)	38(1)
C(26B)	11149(3)	8367(4)	1076(2)	64(1)
C(27B)	10762(3)	7974(3)	-466(2)	47(1)
C(28B)	9493(3)	10375(3)	343(2)	53(1)
N(1B)	2948(2)	13584(2)	-1041(1)	36(1)
N(2B)	1942(2)	14141(2)	-1302(2)	52(1)
O(1B)	3508(2)	10955(2)	-869(1)	41(1)

O(2B)	6171(2)	13026(2)	-345(1)	39(1)
O(3B)	4309(2)	14933(2)	-675(1)	39(1)
O(4B)	7192(2)	8891(2)	482(1)	33(1)
Si(1B)	8294(1)	8403(1)	1163(1)	27(1)

Table 3. Bond lengths [Å] and angles [°] for product ***ent*-4.42**.

C(1)-C(2)	1.519(3)	C(13)-Si(1)	1.880(2)
C(1)-C(6)	1.536(3)	C(14)-C(15)	1.390(4)
C(1)-H(1A)	0.9900	C(14)-H(14A)	0.9500
C(1)-H(1B)	0.9900	C(15)-C(16)	1.377(4)
C(2)-C(3)	1.505(5)	C(15)-H(15A)	0.9500
C(2)-H(2A)	0.9900	C(16)-C(17)	1.373(4)
C(2)-H(2B)	0.9900	C(16)-H(16A)	0.9500
C(3)-C(4)	1.485(5)	C(17)-C(18)	1.386(3)
C(3)-H(3A)	0.9900	C(17)-H(17A)	0.9500
C(3)-H(3B)	0.9900	C(18)-H(18A)	0.9500
C(4)-C(5)	1.351(4)	C(19)-C(20)	1.397(3)
C(4)-H(4A)	0.9500	C(19)-C(24)	1.398(3)
C(5)-C(6)	1.508(3)	C(19)-Si(1)	1.8831(19)
C(5)-H(5A)	0.9500	C(20)-C(21)	1.391(3)
C(6)-O(4)	1.444(2)	C(20)-H(20A)	0.9500
C(6)-C(7)	1.563(3)	C(21)-C(22)	1.384(3)
C(7)-C(8)	1.521(3)	C(21)-H(21A)	0.9500
C(7)-C(12)	1.532(3)	C(22)-C(23)	1.386(3)
C(7)-H(7A)	1.0000	C(22)-H(22A)	0.9500
C(8)-O(1)	1.223(3)	C(23)-C(24)	1.392(3)
C(8)-C(9)	1.465(3)	C(23)-H(23A)	0.9500
C(9)-N(1)	1.346(3)	C(24)-H(24A)	0.9500
C(9)-C(10)	1.461(3)	C(25)-C(26)	1.532(3)
C(10)-O(2)	1.196(3)	C(25)-C(27)	1.533(3)
C(10)-O(3)	1.344(3)	C(25)-C(28)	1.535(3)
C(11)-O(3)	1.441(3)	C(25)-Si(1)	1.902(2)
C(11)-H(11A)	0.9800	C(26)-H(26A)	0.9800
C(11)-H(11B)	0.9800	C(26)-H(26B)	0.9800
C(11)-H(11C)	0.9800	C(26)-H(26C)	0.9800
C(12)-H(12A)	0.9800	C(27)-H(27A)	0.9800
C(12)-H(12B)	0.9800	C(27)-H(27B)	0.9800
C(12)-H(12C)	0.9800	C(27)-H(27C)	0.9800
C(13)-C(18)	1.391(3)	C(28)-H(28A)	0.9800
C(13)-C(14)	1.399(3)	C(28)-H(28B)	0.9800

C(28)-H(28C)	0.9800	C(13B)-C(18B)	1.395(3)
N(1)-N(2)	1.107(3)	C(13B)-Si(1B)	1.8841(19)
O(4)-Si(1)	1.6306(15)	C(14B)-C(15B)	1.385(3)
C(1B)-C(6B)	1.525(2)	C(14B)-H(14B)	0.9500
C(1B)-C(2B)	1.527(3)	C(15B)-C(16B)	1.387(4)
C(1B)-H(1BA)	0.9900	C(15B)-H(15B)	0.9500
C(1B)-H(1BB)	0.9900	C(16B)-C(17B)	1.370(4)
C(2B)-C(3B)	1.520(3)	C(16B)-H(16B)	0.9500
C(2B)-H(2BA)	0.9900	C(17B)-C(18B)	1.386(3)
C(2B)-H(2BB)	0.9900	C(17B)-H(17B)	0.9500
C(3B)-C(4B)	1.502(3)	C(18B)-H(18B)	0.9500
C(3B)-H(3BA)	0.9900	C(19B)-C(24B)	1.391(3)
C(3B)-H(3BB)	0.9900	C(19B)-C(20B)	1.396(3)
C(4B)-C(5B)	1.322(3)	C(19B)-Si(1B)	1.887(2)
C(4B)-H(4BA)	0.9500	C(20B)-C(21B)	1.387(4)
C(5B)-C(6B)	1.504(3)	C(20B)-H(20B)	0.9500
C(5B)-H(5BA)	0.9500	C(21B)-C(22B)	1.378(4)
C(6B)-O(4B)	1.433(2)	C(21B)-H(21B)	0.9500
C(6B)-C(7B)	1.559(3)	C(22B)-C(23B)	1.376(4)
C(7B)-C(8B)	1.516(3)	C(22B)-H(22B)	0.9500
C(7B)-C(12B)	1.541(3)	C(23B)-C(24B)	1.403(3)
C(7B)-H(7BA)	1.0000	C(23B)-H(23B)	0.9500
C(8B)-O(1B)	1.225(2)	C(24B)-H(24B)	0.9500
C(8B)-C(9B)	1.467(3)	C(25B)-C(27B)	1.537(3)
C(9B)-N(1B)	1.348(3)	C(25B)-C(26B)	1.537(3)
C(9B)-C(10B)	1.457(3)	C(25B)-C(28B)	1.538(3)
C(10B)-O(2B)	1.209(2)	C(25B)-Si(1B)	1.895(2)
C(10B)-O(3B)	1.344(3)	C(26B)-H(26D)	0.9800
C(11B)-O(3B)	1.451(3)	C(26B)-H(26E)	0.9800
C(11B)-H(11D)	0.9800	C(26B)-H(26F)	0.9800
C(11B)-H(11E)	0.9800	C(27B)-H(27D)	0.9800
C(11B)-H(11F)	0.9800	C(27B)-H(27E)	0.9800
C(12B)-H(12D)	0.9800	C(27B)-H(27F)	0.9800
C(12B)-H(12E)	0.9800	C(28B)-H(28D)	0.9800
C(12B)-H(12F)	0.9800	C(28B)-H(28E)	0.9800
C(13B)-C(14B)	1.390(3)	C(28B)-H(28F)	0.9800

N(1B)-N(2B)	1.112(3)	C(8)-C(7)-H(7A)	108.3
O(4B)-Si(1B)	1.6288(15)	C(12)-C(7)-H(7A)	108.3
		C(6)-C(7)-H(7A)	108.3
C(2)-C(1)-C(6)	112.1(2)	O(1)-C(8)-C(9)	117.7(2)
C(2)-C(1)-H(1A)	109.2	O(1)-C(8)-C(7)	121.6(2)
C(6)-C(1)-H(1A)	109.2	C(9)-C(8)-C(7)	120.64(18)
C(2)-C(1)-H(1B)	109.2	N(1)-C(9)-C(10)	115.0(2)
C(6)-C(1)-H(1B)	109.2	N(1)-C(9)-C(8)	111.91(19)
H(1A)-C(1)-H(1B)	107.9	C(10)-C(9)-C(8)	133.05(19)
C(3)-C(2)-C(1)	110.1(2)	O(2)-C(10)-O(3)	124.2(2)
C(3)-C(2)-H(2A)	109.6	O(2)-C(10)-C(9)	125.0(2)
C(1)-C(2)-H(2A)	109.6	O(3)-C(10)-C(9)	110.77(18)
C(3)-C(2)-H(2B)	109.6	O(3)-C(11)-H(11A)	109.5
C(1)-C(2)-H(2B)	109.6	O(3)-C(11)-H(11B)	109.5
H(2A)-C(2)-H(2B)	108.2	H(11A)-C(11)-H(11B)	109.5
C(4)-C(3)-C(2)	110.6(2)	O(3)-C(11)-H(11C)	109.5
C(4)-C(3)-H(3A)	109.5	H(11A)-C(11)-H(11C)	109.5
C(2)-C(3)-H(3A)	109.5	H(11B)-C(11)-H(11C)	109.5
C(4)-C(3)-H(3B)	109.5	C(7)-C(12)-H(12A)	109.5
C(2)-C(3)-H(3B)	109.5	C(7)-C(12)-H(12B)	109.5
H(3A)-C(3)-H(3B)	108.1	H(12A)-C(12)-H(12B)	109.5
C(5)-C(4)-C(3)	124.8(3)	C(7)-C(12)-H(12C)	109.5
C(5)-C(4)-H(4A)	117.6	H(12A)-C(12)-H(12C)	109.5
C(3)-C(4)-H(4A)	117.6	H(12B)-C(12)-H(12C)	109.5
C(4)-C(5)-C(6)	122.1(3)	C(18)-C(13)-C(14)	116.9(2)
C(4)-C(5)-H(5A)	119.0	C(18)-C(13)-Si(1)	118.20(15)
C(6)-C(5)-H(5A)	119.0	C(14)-C(13)-Si(1)	124.85(18)
O(4)-C(6)-C(5)	109.35(15)	C(15)-C(14)-C(13)	120.9(2)
O(4)-C(6)-C(1)	104.92(18)	C(15)-C(14)-H(14A)	119.5
C(5)-C(6)-C(1)	111.51(19)	C(13)-C(14)-H(14A)	119.5
O(4)-C(6)-C(7)	108.73(16)	C(16)-C(15)-C(14)	120.6(2)
C(5)-C(6)-C(7)	109.40(18)	C(16)-C(15)-H(15A)	119.7
C(1)-C(6)-C(7)	112.78(16)	C(14)-C(15)-H(15A)	119.7
C(8)-C(7)-C(12)	107.73(17)	C(17)-C(16)-C(15)	119.6(2)
C(8)-C(7)-C(6)	111.59(17)	C(17)-C(16)-H(16A)	120.2
C(12)-C(7)-C(6)	112.63(19)	C(15)-C(16)-H(16A)	120.2

C(16)-C(17)-C(18)	119.9(2)	C(25)-C(27)-H(27A)	109.5
C(16)-C(17)-H(17A)	120.1	C(25)-C(27)-H(27B)	109.5
C(18)-C(17)-H(17A)	120.1	H(27A)-C(27)-H(27B)	109.5
C(17)-C(18)-C(13)	122.1(2)	C(25)-C(27)-H(27C)	109.5
C(17)-C(18)-H(18A)	119.0	H(27A)-C(27)-H(27C)	109.5
C(13)-C(18)-H(18A)	119.0	H(27B)-C(27)-H(27C)	109.5
C(20)-C(19)-C(24)	117.34(18)	C(25)-C(28)-H(28A)	109.5
C(20)-C(19)-Si(1)	122.22(15)	C(25)-C(28)-H(28B)	109.5
C(24)-C(19)-Si(1)	120.30(15)	H(28A)-C(28)-H(28B)	109.5
C(21)-C(20)-C(19)	121.08(19)	C(25)-C(28)-H(28C)	109.5
C(21)-C(20)-H(20A)	119.5	H(28A)-C(28)-H(28C)	109.5
C(19)-C(20)-H(20A)	119.5	H(28B)-C(28)-H(28C)	109.5
C(22)-C(21)-C(20)	120.45(18)	N(2)-N(1)-C(9)	175.5(3)
C(22)-C(21)-H(21A)	119.8	C(10)-O(3)-C(11)	115.83(19)
C(20)-C(21)-H(21A)	119.8	C(6)-O(4)-Si(1)	143.13(14)
C(21)-C(22)-C(23)	119.69(18)	O(4)-Si(1)-C(13)	113.12(8)
C(21)-C(22)-H(22A)	120.2	O(4)-Si(1)-C(19)	111.99(8)
C(23)-C(22)-H(22A)	120.2	C(13)-Si(1)-C(19)	105.14(9)
C(22)-C(23)-C(24)	119.5(2)	O(4)-Si(1)-C(25)	103.88(10)
C(22)-C(23)-H(23A)	120.2	C(13)-Si(1)-C(25)	114.56(10)
C(24)-C(23)-H(23A)	120.2	C(19)-Si(1)-C(25)	108.24(10)
C(23)-C(24)-C(19)	121.89(19)	C(6B)-C(1B)-C(2B)	111.53(16)
C(23)-C(24)-H(24A)	119.1	C(6B)-C(1B)-H(1BA)	109.3
C(19)-C(24)-H(24A)	119.1	C(2B)-C(1B)-H(1BA)	109.3
C(26)-C(25)-C(27)	108.7(2)	C(6B)-C(1B)-H(1BB)	109.3
C(26)-C(25)-C(28)	109.7(2)	C(2B)-C(1B)-H(1BB)	109.3
C(27)-C(25)-C(28)	107.5(2)	H(1BA)-C(1B)-H(1BB)	108.0
C(26)-C(25)-Si(1)	110.39(17)	C(3B)-C(2B)-C(1B)	110.24(19)
C(27)-C(25)-Si(1)	108.40(16)	C(3B)-C(2B)-H(2BA)	109.6
C(28)-C(25)-Si(1)	111.98(16)	C(1B)-C(2B)-H(2BA)	109.6
C(25)-C(26)-H(26A)	109.5	C(3B)-C(2B)-H(2BB)	109.6
C(25)-C(26)-H(26B)	109.5	C(1B)-C(2B)-H(2BB)	109.6
H(26A)-C(26)-H(26B)	109.5	H(2BA)-C(2B)-H(2BB)	108.1
C(25)-C(26)-H(26C)	109.5	C(4B)-C(3B)-C(2B)	111.57(17)
H(26A)-C(26)-H(26C)	109.5	C(4B)-C(3B)-H(3BA)	109.3
H(26B)-C(26)-H(26C)	109.5	C(2B)-C(3B)-H(3BA)	109.3

C(4B)-C(3B)-H(3BB)	109.3	C(7B)-C(12B)-H(12D)	109.5
C(2B)-C(3B)-H(3BB)	109.3	C(7B)-C(12B)-H(12E)	109.5
H(3BA)-C(3B)-H(3BB)	108.0	H(12D)-C(12B)-H(12E)	109.5
C(5B)-C(4B)-C(3B)	123.8(2)	C(7B)-C(12B)-H(12F)	109.5
C(5B)-C(4B)-H(4BA)	118.1	H(12D)-C(12B)-H(12F)	109.5
C(3B)-C(4B)-H(4BA)	118.1	H(12E)-C(12B)-H(12F)	109.5
C(4B)-C(5B)-C(6B)	123.75(19)	C(14B)-C(13B)-C(18B)	116.93(19)
C(4B)-C(5B)-H(5BA)	118.1	C(14B)-C(13B)-Si(1B)	120.94(16)
C(6B)-C(5B)-H(5BA)	118.1	C(18B)-C(13B)-Si(1B)	122.11(17)
O(4B)-C(6B)-C(5B)	110.29(15)	C(15B)-C(14B)-C(13B)	121.8(2)
O(4B)-C(6B)-C(1B)	109.04(16)	C(15B)-C(14B)-H(14B)	119.1
C(5B)-C(6B)-C(1B)	111.09(15)	C(13B)-C(14B)-H(14B)	119.1
O(4B)-C(6B)-C(7B)	103.37(14)	C(14B)-C(15B)-C(16B)	119.8(2)
C(5B)-C(6B)-C(7B)	110.21(16)	C(14B)-C(15B)-H(15B)	120.1
C(1B)-C(6B)-C(7B)	112.58(15)	C(16B)-C(15B)-H(15B)	120.1
C(8B)-C(7B)-C(12B)	108.82(16)	C(17B)-C(16B)-C(15B)	119.7(2)
C(8B)-C(7B)-C(6B)	112.86(15)	C(17B)-C(16B)-H(16B)	120.2
C(12B)-C(7B)-C(6B)	112.27(17)	C(15B)-C(16B)-H(16B)	120.2
C(8B)-C(7B)-H(7BA)	107.5	C(16B)-C(17B)-C(18B)	120.1(2)
C(12B)-C(7B)-H(7BA)	107.5	C(16B)-C(17B)-H(17B)	119.9
C(6B)-C(7B)-H(7BA)	107.5	C(18B)-C(17B)-H(17B)	119.9
O(1B)-C(8B)-C(9B)	119.54(19)	C(17B)-C(18B)-C(13B)	121.7(2)
O(1B)-C(8B)-C(7B)	122.28(18)	C(17B)-C(18B)-H(18B)	119.2
C(9B)-C(8B)-C(7B)	118.04(16)	C(13B)-C(18B)-H(18B)	119.2
N(1B)-C(9B)-C(10B)	115.60(18)	C(24B)-C(19B)-C(20B)	117.5(2)
N(1B)-C(9B)-C(8B)	112.12(16)	C(24B)-C(19B)-Si(1B)	120.83(17)
C(10B)-C(9B)-C(8B)	132.23(18)	C(20B)-C(19B)-Si(1B)	121.60(16)
O(2B)-C(10B)-O(3B)	123.84(18)	C(21B)-C(20B)-C(19B)	121.3(2)
O(2B)-C(10B)-C(9B)	125.44(19)	C(21B)-C(20B)-H(20B)	119.4
O(3B)-C(10B)-C(9B)	110.72(17)	C(19B)-C(20B)-H(20B)	119.4
O(3B)-C(11B)-H(11D)	109.5	C(22B)-C(21B)-C(20B)	120.5(3)
O(3B)-C(11B)-H(11E)	109.5	C(22B)-C(21B)-H(21B)	119.7
H(11D)-C(11B)-H(11E)	109.5	C(20B)-C(21B)-H(21B)	119.7
O(3B)-C(11B)-H(11F)	109.5	C(23B)-C(22B)-C(21B)	119.6(2)
H(11D)-C(11B)-H(11F)	109.5	C(23B)-C(22B)-H(22B)	120.2
H(11E)-C(11B)-H(11F)	109.5	C(21B)-C(22B)-H(22B)	120.2

C(22B)-C(23B)-C(24B)	120.0(2)	H(27D)-C(27B)-H(27E)	109.5
C(22B)-C(23B)-H(23B)	120.0	C(25B)-C(27B)-H(27F)	109.5
C(24B)-C(23B)-H(23B)	120.0	H(27D)-C(27B)-H(27F)	109.5
C(19B)-C(24B)-C(23B)	121.2(2)	H(27E)-C(27B)-H(27F)	109.5
C(19B)-C(24B)-H(24B)	119.4	C(25B)-C(28B)-H(28D)	109.5
C(23B)-C(24B)-H(24B)	119.4	C(25B)-C(28B)-H(28E)	109.5
C(27B)-C(25B)-C(26B)	109.2(2)	H(28D)-C(28B)-H(28E)	109.5
C(27B)-C(25B)-C(28B)	107.21(19)	C(25B)-C(28B)-H(28F)	109.5
C(26B)-C(25B)-C(28B)	109.5(2)	H(28D)-C(28B)-H(28F)	109.5
C(27B)-C(25B)-Si(1B)	108.09(14)	H(28E)-C(28B)-H(28F)	109.5
C(26B)-C(25B)-Si(1B)	110.69(16)	N(2B)-N(1B)-C(9B)	175.0(2)
C(28B)-C(25B)-Si(1B)	112.01(15)	C(10B)-O(3B)-C(11B)	114.98(17)
C(25B)-C(26B)-H(26D)	109.5	C(6B)-O(4B)-Si(1B)	143.53(12)
C(25B)-C(26B)-H(26E)	109.5	O(4B)-Si(1B)-C(13B)	115.15(8)
H(26D)-C(26B)-H(26E)	109.5	O(4B)-Si(1B)-C(19B)	105.47(8)
C(25B)-C(26B)-H(26F)	109.5	C(13B)-Si(1B)-C(19B)	108.82(9)
H(26D)-C(26B)-H(26F)	109.5	O(4B)-Si(1B)-C(25B)	105.15(9)
H(26E)-C(26B)-H(26F)	109.5	C(13B)-Si(1B)-C(25B)	112.84(9)
C(25B)-C(27B)-H(27D)	109.5	C(19B)-Si(1B)-C(25B)	109.03(9)
C(25B)-C(27B)-H(27E)	109.5		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for product ***ent*-4.42**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	40(1)	57(2)	45(1)	14(1)	-13(1)	-26(1)
C(2)	71(2)	89(2)	54(1)	30(1)	-33(1)	-52(2)
C(3)	113(3)	97(3)	50(2)	17(2)	-33(2)	-75(2)
C(4)	112(2)	47(2)	36(1)	2(1)	-4(1)	-45(2)
C(5)	61(1)	35(1)	33(1)	6(1)	-1(1)	-19(1)
C(6)	35(1)	31(1)	33(1)	6(1)	-5(1)	-14(1)
C(7)	30(1)	35(1)	35(1)	5(1)	-5(1)	-9(1)
C(8)	35(1)	44(1)	30(1)	5(1)	-4(1)	-14(1)
C(9)	43(1)	41(1)	33(1)	8(1)	-7(1)	-22(1)
C(10)	44(1)	36(1)	33(1)	5(1)	-10(1)	-16(1)
C(11)	54(1)	42(2)	60(1)	7(1)	-25(1)	-8(1)
C(12)	47(1)	46(1)	36(1)	-1(1)	-6(1)	-14(1)
C(13)	39(1)	41(1)	26(1)	6(1)	-9(1)	-22(1)
C(14)	67(2)	45(1)	33(1)	6(1)	-16(1)	-28(1)
C(15)	79(2)	70(2)	34(1)	12(1)	-25(1)	-46(2)
C(16)	50(1)	83(2)	36(1)	23(1)	-19(1)	-39(2)
C(17)	39(1)	62(2)	42(1)	15(1)	-13(1)	-17(1)
C(18)	42(1)	46(1)	33(1)	2(1)	-10(1)	-17(1)
C(19)	38(1)	31(1)	27(1)	4(1)	-7(1)	-15(1)
C(20)	37(1)	35(1)	33(1)	5(1)	-12(1)	-16(1)
C(21)	52(1)	38(1)	32(1)	4(1)	-17(1)	-20(1)
C(22)	45(1)	39(1)	28(1)	3(1)	-4(1)	-15(1)
C(23)	38(1)	49(1)	37(1)	7(1)	-7(1)	-19(1)
C(24)	43(1)	49(1)	32(1)	5(1)	-11(1)	-25(1)
C(25)	55(1)	29(1)	39(1)	7(1)	-11(1)	-15(1)
C(26)	85(2)	40(1)	52(1)	15(1)	-28(1)	-36(1)
C(27)	59(2)	42(1)	53(1)	15(1)	-21(1)	-15(1)
C(28)	76(2)	31(1)	55(1)	-1(1)	-1(1)	-8(1)
N(1)	50(1)	44(1)	37(1)	9(1)	-11(1)	-24(1)
N(2)	71(1)	63(2)	60(1)	17(1)	-15(1)	-43(1)

O(1)	35(1)	63(1)	53(1)	21(1)	-4(1)	-19(1)
O(2)	39(1)	44(1)	72(1)	17(1)	-6(1)	-13(1)
O(3)	52(1)	36(1)	54(1)	9(1)	-21(1)	-17(1)
O(4)	37(1)	32(1)	39(1)	9(1)	-11(1)	-13(1)
Si(1)	37(1)	29(1)	26(1)	3(1)	-7(1)	-14(1)
C(1B)	39(1)	33(1)	44(1)	9(1)	-18(1)	-20(1)
C(2B)	43(1)	41(1)	48(1)	18(1)	-20(1)	-26(1)
C(3B)	44(1)	54(2)	41(1)	15(1)	-4(1)	-21(1)
C(4B)	35(1)	32(1)	34(1)	5(1)	-9(1)	-5(1)
C(5B)	31(1)	26(1)	32(1)	5(1)	-11(1)	-11(1)
C(6B)	28(1)	25(1)	32(1)	5(1)	-12(1)	-10(1)
C(7B)	31(1)	25(1)	31(1)	2(1)	-10(1)	-11(1)
C(8B)	35(1)	32(1)	27(1)	3(1)	-9(1)	-15(1)
C(9B)	33(1)	30(1)	32(1)	5(1)	-11(1)	-12(1)
C(10B)	37(1)	29(1)	25(1)	3(1)	-6(1)	-12(1)
C(11B)	65(2)	33(1)	50(1)	7(1)	-25(1)	-25(1)
C(12B)	40(1)	36(1)	35(1)	-5(1)	-11(1)	-8(1)
C(13B)	30(1)	34(1)	33(1)	1(1)	-11(1)	-10(1)
C(14B)	49(1)	41(1)	38(1)	4(1)	-11(1)	-21(1)
C(15B)	66(2)	63(2)	36(1)	5(1)	-5(1)	-32(1)
C(16B)	61(2)	62(2)	37(1)	-11(1)	-3(1)	-22(1)
C(17B)	74(2)	41(1)	47(1)	-10(1)	-7(1)	-20(1)
C(18B)	56(1)	34(1)	39(1)	-1(1)	-8(1)	-17(1)
C(19B)	29(1)	27(1)	38(1)	2(1)	-6(1)	-9(1)
C(20B)	43(1)	34(1)	58(1)	9(1)	-21(1)	-12(1)
C(21B)	43(1)	37(1)	77(2)	19(1)	-23(1)	-11(1)
C(22B)	44(1)	24(1)	77(2)	8(1)	-3(1)	-9(1)
C(23B)	49(1)	32(1)	55(1)	-7(1)	-2(1)	-19(1)
C(24B)	38(1)	31(1)	40(1)	3(1)	-7(1)	-13(1)
C(25B)	34(1)	41(1)	42(1)	5(1)	-10(1)	-20(1)
C(26B)	49(1)	96(2)	66(2)	17(2)	-26(1)	-45(2)
C(27B)	39(1)	46(1)	47(1)	0(1)	2(1)	-18(1)
C(28B)	62(2)	43(1)	57(1)	2(1)	-2(1)	-35(1)
N(1B)	36(1)	31(1)	40(1)	8(1)	-13(1)	-13(1)
N(2B)	43(1)	48(1)	64(1)	17(1)	-23(1)	-16(1)
O(1B)	41(1)	39(1)	54(1)	8(1)	-25(1)	-19(1)

O(2B)	43(1)	33(1)	46(1)	9(1)	-20(1)	-18(1)
O(3B)	49(1)	28(1)	45(1)	6(1)	-20(1)	-16(1)
O(4B)	30(1)	29(1)	34(1)	0(1)	-12(1)	-5(1)
Si(1B)	27(1)	24(1)	31(1)	2(1)	-9(1)	-10(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for product ***ent*-4.42**.

	x	y	z	U(eq)
H(1A)	-2291	4903	6091	55
H(1B)	-2294	6418	5887	55
H(2A)	-2989	5705	4692	75
H(2B)	-1366	5766	4216	75
H(3A)	-1857	3287	4679	89
H(3B)	-1120	3657	3634	89
H(4A)	1023	2126	4063	79
H(5A)	1910	2954	5014	57
H(7A)	1192	4209	6603	43
H(11A)	4586	-1719	7157	82
H(11B)	4728	-288	7313	82
H(11C)	4882	-812	6273	82
H(12A)	-625	5713	7957	69
H(12B)	-1887	6286	7411	69
H(12C)	-417	6628	7066	69
H(14A)	2090	7341	6805	56
H(15A)	3682	6378	7756	65
H(16A)	5612	4102	7382	62
H(17A)	5906	2755	6074	59
H(18A)	4315	3700	5127	50
H(20A)	1808	5159	3230	41
H(21A)	3516	4315	1706	47
H(22A)	6003	4149	1323	48
H(23A)	6775	4868	2472	51
H(24A)	5053	5746	3990	47
H(26A)	1693	9905	4904	81
H(26B)	3022	8468	4328	81
H(26C)	2548	8634	5466	81
H(27A)	-48	9692	4088	80
H(27B)	-342	8300	4145	80

H(27C)	1288	8245	3530	80
H(28A)	-841	10035	5830	95
H(28B)	-93	8787	6443	95
H(28C)	-1191	8672	5895	95
H(1BA)	5387	7951	273	43
H(1BB)	3835	9353	435	43
H(2BA)	3701	8022	1796	48
H(2BB)	5163	8154	1923	48
H(3BA)	2179	10378	2208	58
H(3BB)	3093	9894	2974	58
H(4BA)	3415	11942	2418	44
H(5BA)	5257	11727	1075	36
H(7BA)	6603	10754	-644	35
H(11D)	4519	16747	-655	69
H(11E)	6122	15402	-1041	69
H(11F)	5215	15692	76	69
H(12D)	6819	9409	-1966	59
H(12E)	6055	8522	-1257	59
H(12F)	7697	8406	-1281	59
H(14B)	7006	7542	3019	51
H(15B)	5725	8563	4572	67
H(16B)	5328	10861	4942	68
H(17B)	6158	12135	3745	69
H(18B)	7424	11118	2191	54
H(20B)	10091	6134	2159	54
H(21B)	11051	3692	2087	65
H(22B)	10549	2482	1053	65
H(23B)	8991	3732	130	57
H(24B)	8040	6193	184	46
H(26D)	12017	8582	730	95
H(26E)	11517	7354	1149	95
H(26F)	10655	8885	1707	95
H(27D)	11648	8162	-812	71
H(27E)	10030	8263	-830	71
H(27F)	11102	6965	-383	71
H(28D)	10400	10541	11	80

H(28E)	8963	10943	955	80
H(28F)	8802	10641	-48	80

Table 6. Torsion angles [°] for product ***ent*-4.42**.

C(6)-C(1)-C(2)-C(3)	62.5(3)
C(1)-C(2)-C(3)-C(4)	-49.4(3)
C(2)-C(3)-C(4)-C(5)	18.6(4)
C(3)-C(4)-C(5)-C(6)	2.4(4)
C(4)-C(5)-C(6)-O(4)	-107.0(2)
C(4)-C(5)-C(6)-C(1)	8.6(3)
C(4)-C(5)-C(6)-C(7)	134.0(2)
C(2)-C(1)-C(6)-O(4)	77.9(2)
C(2)-C(1)-C(6)-C(5)	-40.3(3)
C(2)-C(1)-C(6)-C(7)	-163.9(2)
O(4)-C(6)-C(7)-C(8)	177.79(16)
C(5)-C(6)-C(7)-C(8)	-62.9(2)
C(1)-C(6)-C(7)-C(8)	61.9(2)
O(4)-C(6)-C(7)-C(12)	56.5(2)
C(5)-C(6)-C(7)-C(12)	175.83(19)
C(1)-C(6)-C(7)-C(12)	-59.5(2)
C(12)-C(7)-C(8)-O(1)	46.0(3)
C(6)-C(7)-C(8)-O(1)	-78.2(3)
C(12)-C(7)-C(8)-C(9)	-131.7(2)
C(6)-C(7)-C(8)-C(9)	104.2(2)
O(1)-C(8)-C(9)-N(1)	1.1(3)
C(7)-C(8)-C(9)-N(1)	178.86(18)
O(1)-C(8)-C(9)-C(10)	-175.2(2)
C(7)-C(8)-C(9)-C(10)	2.5(3)
N(1)-C(9)-C(10)-O(2)	-178.1(2)
C(8)-C(9)-C(10)-O(2)	-1.8(4)
N(1)-C(9)-C(10)-O(3)	2.0(3)
C(8)-C(9)-C(10)-O(3)	178.3(2)
C(18)-C(13)-C(14)-C(15)	1.3(3)
Si(1)-C(13)-C(14)-C(15)	-178.27(18)
C(13)-C(14)-C(15)-C(16)	0.0(4)
C(14)-C(15)-C(16)-C(17)	-1.1(4)
C(15)-C(16)-C(17)-C(18)	0.9(4)
C(16)-C(17)-C(18)-C(13)	0.5(3)

C(14)-C(13)-C(18)-C(17)	-1.5(3)
Si(1)-C(13)-C(18)-C(17)	178.07(17)
C(24)-C(19)-C(20)-C(21)	0.9(3)
Si(1)-C(19)-C(20)-C(21)	176.62(17)
C(19)-C(20)-C(21)-C(22)	0.1(3)
C(20)-C(21)-C(22)-C(23)	-0.6(4)
C(21)-C(22)-C(23)-C(24)	0.1(4)
C(22)-C(23)-C(24)-C(19)	1.0(4)
C(20)-C(19)-C(24)-C(23)	-1.5(3)
Si(1)-C(19)-C(24)-C(23)	-177.25(18)
C(10)-C(9)-N(1)-N(2)	-174(3)
C(8)-C(9)-N(1)-N(2)	8(3)
O(2)-C(10)-O(3)-C(11)	3.5(3)
C(9)-C(10)-O(3)-C(11)	-176.59(19)
C(5)-C(6)-O(4)-Si(1)	-62.1(3)
C(1)-C(6)-O(4)-Si(1)	178.19(17)
C(7)-C(6)-O(4)-Si(1)	57.3(3)
C(6)-O(4)-Si(1)-C(13)	-33.7(2)
C(6)-O(4)-Si(1)-C(19)	84.9(2)
C(6)-O(4)-Si(1)-C(25)	-158.5(2)
C(18)-C(13)-Si(1)-O(4)	85.57(17)
C(14)-C(13)-Si(1)-O(4)	-94.90(19)
C(18)-C(13)-Si(1)-C(19)	-36.93(18)
C(14)-C(13)-Si(1)-C(19)	142.60(18)
C(18)-C(13)-Si(1)-C(25)	-155.62(16)
C(14)-C(13)-Si(1)-C(25)	23.9(2)
C(20)-C(19)-Si(1)-O(4)	20.9(2)
C(24)-C(19)-Si(1)-O(4)	-163.53(17)
C(20)-C(19)-Si(1)-C(13)	144.13(18)
C(24)-C(19)-Si(1)-C(13)	-40.3(2)
C(20)-C(19)-Si(1)-C(25)	-93.0(2)
C(24)-C(19)-Si(1)-C(25)	82.5(2)
C(26)-C(25)-Si(1)-O(4)	170.65(15)
C(27)-C(25)-Si(1)-O(4)	-70.36(18)
C(28)-C(25)-Si(1)-O(4)	48.1(2)
C(26)-C(25)-Si(1)-C(13)	46.75(18)

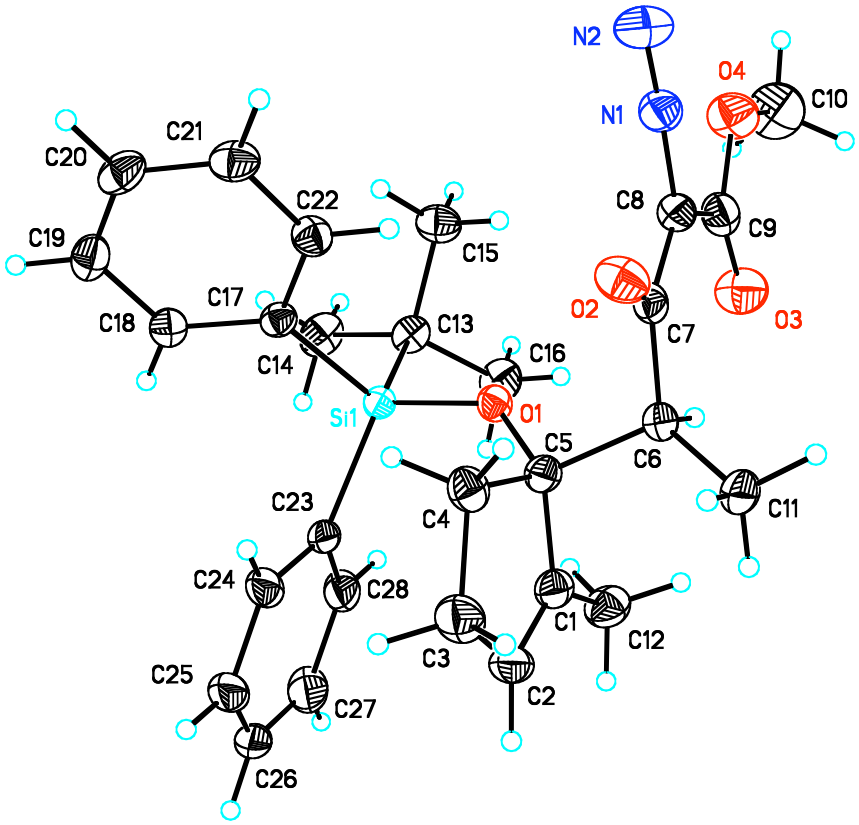
C(27)-C(25)-Si(1)-C(13)	165.75(16)
C(28)-C(25)-Si(1)-C(13)	-75.8(2)
C(26)-C(25)-Si(1)-C(19)	-70.17(18)
C(27)-C(25)-Si(1)-C(19)	48.82(19)
C(28)-C(25)-Si(1)-C(19)	167.3(2)
C(6B)-C(1B)-C(2B)-C(3B)	61.8(2)
C(1B)-C(2B)-C(3B)-C(4B)	-45.5(3)
C(2B)-C(3B)-C(4B)-C(5B)	15.5(3)
C(3B)-C(4B)-C(5B)-C(6B)	0.9(3)
C(4B)-C(5B)-C(6B)-O(4B)	-107.3(2)
C(4B)-C(5B)-C(6B)-C(1B)	13.8(3)
C(4B)-C(5B)-C(6B)-C(7B)	139.2(2)
C(2B)-C(1B)-C(6B)-O(4B)	77.4(2)
C(2B)-C(1B)-C(6B)-C(5B)	-44.4(2)
C(2B)-C(1B)-C(6B)-C(7B)	-168.50(17)
O(4B)-C(6B)-C(7B)-C(8B)	-175.26(14)
C(5B)-C(6B)-C(7B)-C(8B)	-57.4(2)
C(1B)-C(6B)-C(7B)-C(8B)	67.2(2)
O(4B)-C(6B)-C(7B)-C(12B)	61.30(19)
C(5B)-C(6B)-C(7B)-C(12B)	179.17(16)
C(1B)-C(6B)-C(7B)-C(12B)	-56.2(2)
C(12B)-C(7B)-C(8B)-O(1B)	47.2(2)
C(6B)-C(7B)-C(8B)-O(1B)	-78.1(2)
C(12B)-C(7B)-C(8B)-C(9B)	-128.50(18)
C(6B)-C(7B)-C(8B)-C(9B)	106.17(18)
O(1B)-C(8B)-C(9B)-N(1B)	-5.4(3)
C(7B)-C(8B)-C(9B)-N(1B)	170.40(16)
O(1B)-C(8B)-C(9B)-C(10B)	177.14(19)
C(7B)-C(8B)-C(9B)-C(10B)	-7.0(3)
N(1B)-C(9B)-C(10B)-O(2B)	-176.83(18)
C(8B)-C(9B)-C(10B)-O(2B)	0.5(3)
N(1B)-C(9B)-C(10B)-O(3B)	3.9(2)
C(8B)-C(9B)-C(10B)-O(3B)	-178.72(18)
C(18B)-C(13B)-C(14B)-C(15B)	0.9(3)
Si(1B)-C(13B)-C(14B)-C(15B)	-177.4(2)
C(13B)-C(14B)-C(15B)-C(16B)	-1.0(4)

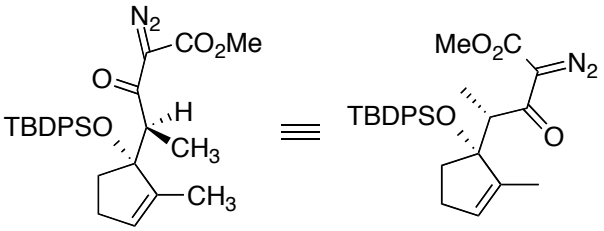
C(14B)-C(15B)-C(16B)-C(17B)	0.8(4)
C(15B)-C(16B)-C(17B)-C(18B)	-0.6(5)
C(16B)-C(17B)-C(18B)-C(13B)	0.5(4)
C(14B)-C(13B)-C(18B)-C(17B)	-0.6(4)
Si(1B)-C(13B)-C(18B)-C(17B)	177.6(2)
C(24B)-C(19B)-C(20B)-C(21B)	0.6(3)
Si(1B)-C(19B)-C(20B)-C(21B)	-175.57(19)
C(19B)-C(20B)-C(21B)-C(22B)	0.1(4)
C(20B)-C(21B)-C(22B)-C(23B)	-1.3(4)
C(21B)-C(22B)-C(23B)-C(24B)	1.7(4)
C(20B)-C(19B)-C(24B)-C(23B)	-0.2(3)
Si(1B)-C(19B)-C(24B)-C(23B)	176.00(16)
C(22B)-C(23B)-C(24B)-C(19B)	-0.9(3)
C(10B)-C(9B)-N(1B)-N(2B)	162(2)
C(8B)-C(9B)-N(1B)-N(2B)	-16(2)
O(2B)-C(10B)-O(3B)-C(11B)	4.3(3)
C(9B)-C(10B)-O(3B)-C(11B)	-176.42(17)
C(5B)-C(6B)-O(4B)-Si(1B)	27.7(3)
C(1B)-C(6B)-O(4B)-Si(1B)	-94.5(2)
C(7B)-C(6B)-O(4B)-Si(1B)	145.50(18)
C(6B)-O(4B)-Si(1B)-C(13B)	-0.3(2)
C(6B)-O(4B)-Si(1B)-C(19B)	119.7(2)
C(6B)-O(4B)-Si(1B)-C(25B)	-125.1(2)
C(14B)-C(13B)-Si(1B)-O(4B)	99.67(19)
C(18B)-C(13B)-Si(1B)-O(4B)	-78.5(2)
C(14B)-C(13B)-Si(1B)-C(19B)	-18.5(2)
C(18B)-C(13B)-Si(1B)-C(19B)	163.36(18)
C(14B)-C(13B)-Si(1B)-C(25B)	-139.61(18)
C(18B)-C(13B)-Si(1B)-C(25B)	42.2(2)
C(24B)-C(19B)-Si(1B)-O(4B)	7.93(18)
C(20B)-C(19B)-Si(1B)-O(4B)	-176.04(17)
C(24B)-C(19B)-Si(1B)-C(13B)	132.00(16)
C(20B)-C(19B)-Si(1B)-C(13B)	-51.97(19)
C(24B)-C(19B)-Si(1B)-C(25B)	-104.54(17)
C(20B)-C(19B)-Si(1B)-C(25B)	71.49(19)
C(27B)-C(25B)-Si(1B)-O(4B)	-59.27(18)

C(26B)-C(25B)-Si(1B)-O(4B)	-178.86(17)
C(28B)-C(25B)-Si(1B)-O(4B)	58.62(17)
C(27B)-C(25B)-Si(1B)-C(13B)	174.45(16)
C(26B)-C(25B)-Si(1B)-C(13B)	54.9(2)
C(28B)-C(25B)-Si(1B)-C(13B)	-67.66(19)
C(27B)-C(25B)-Si(1B)-C(19B)	53.41(19)
C(26B)-C(25B)-Si(1B)-C(19B)	-66.18(19)
C(28B)-C(25B)-Si(1B)-C(19B)	171.31(16)

Symmetry transformations used to generate equivalent atoms:

9. X-ray crystallographic structure of product 4.46





4.46

Table 1. Crystal data and structure refinement for product **4.46**.

Identification code	95s	
Empirical formula	C28 H34 N2 O4 Si	
Formula weight	490.66	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 9.8111(7) Å	α= 90°.
	b = 8.9577(6) Å	β= 107.705(3)°.
	c = 15.8916(12) Å	γ = 90°.
Volume	1330.48(16) $Å^3$	
Z	2	
Density (calculated)	1.225 Mg/m^3	
Absorption coefficient	1.063 mm^{-1}	
F(000)	524	
Crystal size	0.23 x 0.21 x 0.14 mm^3	
Theta range for data collection	2.92 to 69.28°.	
Index ranges	-10<=h<=11, -10<=k<=10, -19<=l<=18	
Reflections collected	8469	
Independent reflections	4271 [R(int) = 0.0176]	
Completeness to theta = 69.28°	96.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8654 and 0.7921	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4271 / 1 / 316	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0285, wR2 = 0.0771	
R indices (all data)	R1 = 0.0292, wR2 = 0.0776	
Absolute structure parameter	0.051(19)	
Largest diff. peak and hole	0.264 and -0.196 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for product **4.46**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	3238(2)	-1915(2)	2417(1)	32(1)
C(2)	3279(2)	-2933(2)	3024(1)	38(1)
C(3)	3774(2)	-2354(2)	3950(1)	43(1)
C(4)	3883(2)	-669(2)	3824(1)	34(1)
C(5)	3713(2)	-401(2)	2830(1)	28(1)
C(6)	5088(2)	117(2)	2619(1)	28(1)
C(7)	5590(2)	1606(2)	3059(1)	28(1)
C(8)	5459(2)	2948(2)	2509(1)	31(1)
C(9)	5040(2)	3158(2)	1553(1)	36(1)
C(10)	4816(3)	4942(3)	431(2)	66(1)
C(11)	6307(2)	-1018(2)	2903(1)	37(1)
C(12)	2829(2)	-2132(2)	1439(1)	42(1)
C(13)	290(2)	2252(2)	1379(1)	29(1)
C(14)	-1323(2)	2538(2)	1187(1)	41(1)
C(15)	1078(2)	3763(2)	1567(1)	37(1)
C(16)	588(2)	1575(3)	563(1)	40(1)
C(17)	936(2)	2140(2)	3381(1)	25(1)
C(18)	-291(2)	2206(2)	3654(1)	29(1)
C(19)	-369(2)	3122(2)	4340(1)	37(1)
C(20)	797(2)	4007(2)	4770(1)	38(1)
C(21)	2024(2)	3970(2)	4515(1)	37(1)
C(22)	2103(2)	3040(2)	3838(1)	32(1)
C(23)	-6(2)	-759(2)	2364(1)	28(1)
C(24)	125(2)	-1503(2)	3158(1)	35(1)
C(25)	-490(2)	-2897(2)	3181(2)	45(1)
C(26)	-1260(3)	-3564(2)	2401(2)	56(1)
C(27)	-1434(3)	-2851(3)	1612(2)	58(1)
C(28)	-816(2)	-1452(2)	1591(1)	42(1)
N(1)	5906(2)	4169(2)	3001(1)	36(1)
N(2)	6297(2)	5116(2)	3470(1)	51(1)

O(1)	2689(1)	757(1)	2441(1)	26(1)
O(2)	6131(1)	1720(2)	3858(1)	41(1)
O(3)	4657(2)	2192(2)	1010(1)	50(1)
O(4)	5151(2)	4603(2)	1360(1)	48(1)
Si(1)	1004(1)	1037(1)	2392(1)	22(1)

Table 3. Bond lengths [Å] and angles [°] for product **4.46**.

C(1)-C(2)	1.319(3)	C(13)-C(15)	1.543(3)
C(1)-C(12)	1.495(3)	C(13)-Si(1)	1.8919(17)
C(1)-C(5)	1.516(2)	C(14)-H(14A)	0.9800
C(2)-C(3)	1.496(3)	C(14)-H(14B)	0.9800
C(2)-H(2A)	0.9500	C(14)-H(14C)	0.9800
C(3)-C(4)	1.531(3)	C(15)-H(15A)	0.9800
C(3)-H(3A)	0.9900	C(15)-H(15B)	0.9800
C(3)-H(3B)	0.9900	C(15)-H(15C)	0.9800
C(4)-C(5)	1.556(2)	C(16)-H(16A)	0.9800
C(4)-H(4A)	0.9900	C(16)-H(16B)	0.9800
C(4)-H(4B)	0.9900	C(16)-H(16C)	0.9800
C(5)-O(1)	1.4453(19)	C(17)-C(18)	1.399(2)
C(5)-C(6)	1.557(2)	C(17)-C(22)	1.408(2)
C(6)-C(7)	1.517(2)	C(17)-Si(1)	1.8749(16)
C(6)-C(11)	1.529(2)	C(18)-C(19)	1.385(3)
C(6)-H(6A)	1.0000	C(18)-H(18A)	0.9500
C(7)-O(2)	1.223(2)	C(19)-C(20)	1.389(3)
C(7)-C(8)	1.468(3)	C(19)-H(19A)	0.9500
C(8)-N(1)	1.339(2)	C(20)-C(21)	1.382(3)
C(8)-C(9)	1.462(2)	C(20)-H(20A)	0.9500
C(9)-O(3)	1.199(3)	C(21)-C(22)	1.382(3)
C(9)-O(4)	1.342(3)	C(21)-H(21A)	0.9500
C(10)-O(4)	1.444(3)	C(22)-H(22A)	0.9500
C(10)-H(10A)	0.9800	C(23)-C(28)	1.391(3)
C(10)-H(10B)	0.9800	C(23)-C(24)	1.398(3)
C(10)-H(10C)	0.9800	C(23)-Si(1)	1.8826(17)
C(11)-H(11A)	0.9800	C(24)-C(25)	1.392(3)
C(11)-H(11B)	0.9800	C(24)-H(24A)	0.9500
C(11)-H(11C)	0.9800	C(25)-C(26)	1.377(3)
C(12)-H(12A)	0.9800	C(25)-H(25A)	0.9500
C(12)-H(12B)	0.9800	C(26)-C(27)	1.370(4)
C(12)-H(12C)	0.9800	C(26)-H(26A)	0.9500
C(13)-C(14)	1.539(2)	C(27)-C(28)	1.397(3)
C(13)-C(16)	1.538(2)	C(27)-H(27A)	0.9500

C(28)-H(28A)	0.9500	C(8)-C(7)-C(6)	119.22(14)
N(1)-N(2)	1.117(2)	N(1)-C(8)-C(9)	116.15(17)
O(1)-Si(1)	1.6496(11)	N(1)-C(8)-C(7)	111.56(15)
		C(9)-C(8)-C(7)	132.11(16)
C(2)-C(1)-C(12)	127.49(18)	O(3)-C(9)-O(4)	124.16(18)
C(2)-C(1)-C(5)	111.40(16)	O(3)-C(9)-C(8)	125.64(18)
C(12)-C(1)-C(5)	121.09(16)	O(4)-C(9)-C(8)	110.20(17)
C(1)-C(2)-C(3)	114.07(17)	O(4)-C(10)-H(10A)	109.5
C(1)-C(2)-H(2A)	123.0	O(4)-C(10)-H(10B)	109.5
C(3)-C(2)-H(2A)	123.0	H(10A)-C(10)-H(10B)	109.5
C(2)-C(3)-C(4)	103.19(15)	O(4)-C(10)-H(10C)	109.5
C(2)-C(3)-H(3A)	111.1	H(10A)-C(10)-H(10C)	109.5
C(4)-C(3)-H(3A)	111.1	H(10B)-C(10)-H(10C)	109.5
C(2)-C(3)-H(3B)	111.1	C(6)-C(11)-H(11A)	109.5
C(4)-C(3)-H(3B)	111.1	C(6)-C(11)-H(11B)	109.5
H(3A)-C(3)-H(3B)	109.1	H(11A)-C(11)-H(11B)	109.5
C(3)-C(4)-C(5)	107.11(15)	C(6)-C(11)-H(11C)	109.5
C(3)-C(4)-H(4A)	110.3	H(11A)-C(11)-H(11C)	109.5
C(5)-C(4)-H(4A)	110.3	H(11B)-C(11)-H(11C)	109.5
C(3)-C(4)-H(4B)	110.3	C(1)-C(12)-H(12A)	109.5
C(5)-C(4)-H(4B)	110.3	C(1)-C(12)-H(12B)	109.5
H(4A)-C(4)-H(4B)	108.5	H(12A)-C(12)-H(12B)	109.5
O(1)-C(5)-C(1)	111.99(12)	C(1)-C(12)-H(12C)	109.5
O(1)-C(5)-C(4)	112.98(13)	H(12A)-C(12)-H(12C)	109.5
C(1)-C(5)-C(4)	103.07(14)	H(12B)-C(12)-H(12C)	109.5
O(1)-C(5)-C(6)	103.24(12)	C(14)-C(13)-C(16)	110.21(14)
C(1)-C(5)-C(6)	110.22(13)	C(14)-C(13)-C(15)	108.45(15)
C(4)-C(5)-C(6)	115.59(13)	C(16)-C(13)-C(15)	107.22(15)
C(7)-C(6)-C(11)	109.49(13)	C(14)-C(13)-Si(1)	110.97(13)
C(7)-C(6)-C(5)	110.15(13)	C(16)-C(13)-Si(1)	111.99(13)
C(11)-C(6)-C(5)	112.91(14)	C(15)-C(13)-Si(1)	107.84(11)
C(7)-C(6)-H(6A)	108.0	C(13)-C(14)-H(14A)	109.5
C(11)-C(6)-H(6A)	108.0	C(13)-C(14)-H(14B)	109.5
C(5)-C(6)-H(6A)	108.0	H(14A)-C(14)-H(14B)	109.5
O(2)-C(7)-C(8)	118.80(16)	C(13)-C(14)-H(14C)	109.5
O(2)-C(7)-C(6)	121.97(16)	H(14A)-C(14)-H(14C)	109.5

H(14B)-C(14)-H(14C)	109.5	C(21)-C(22)-H(22A)	119.4
C(13)-C(15)-H(15A)	109.5	C(17)-C(22)-H(22A)	119.4
C(13)-C(15)-H(15B)	109.5	C(28)-C(23)-C(24)	117.09(17)
H(15A)-C(15)-H(15B)	109.5	C(28)-C(23)-Si(1)	123.89(14)
C(13)-C(15)-H(15C)	109.5	C(24)-C(23)-Si(1)	118.90(13)
H(15A)-C(15)-H(15C)	109.5	C(25)-C(24)-C(23)	121.98(19)
H(15B)-C(15)-H(15C)	109.5	C(25)-C(24)-H(24A)	119.0
C(13)-C(16)-H(16A)	109.5	C(23)-C(24)-H(24A)	119.0
C(13)-C(16)-H(16B)	109.5	C(26)-C(25)-C(24)	119.3(2)
H(16A)-C(16)-H(16B)	109.5	C(26)-C(25)-H(25A)	120.3
C(13)-C(16)-H(16C)	109.5	C(24)-C(25)-H(25A)	120.3
H(16A)-C(16)-H(16C)	109.5	C(27)-C(26)-C(25)	120.18(19)
H(16B)-C(16)-H(16C)	109.5	C(27)-C(26)-H(26A)	119.9
C(18)-C(17)-C(22)	117.22(15)	C(25)-C(26)-H(26A)	119.9
C(18)-C(17)-Si(1)	122.34(12)	C(26)-C(27)-C(28)	120.4(2)
C(22)-C(17)-Si(1)	120.24(12)	C(26)-C(27)-H(27A)	119.8
C(19)-C(18)-C(17)	121.79(16)	C(28)-C(27)-H(27A)	119.8
C(19)-C(18)-H(18A)	119.1	C(23)-C(28)-C(27)	121.0(2)
C(17)-C(18)-H(18A)	119.1	C(23)-C(28)-H(28A)	119.5
C(18)-C(19)-C(20)	119.45(17)	C(27)-C(28)-H(28A)	119.5
C(18)-C(19)-H(19A)	120.3	N(2)-N(1)-C(8)	174.38(19)
C(20)-C(19)-H(19A)	120.3	C(5)-O(1)-Si(1)	133.28(10)
C(21)-C(20)-C(19)	120.17(17)	C(9)-O(4)-C(10)	115.29(19)
C(21)-C(20)-H(20A)	119.9	O(1)-Si(1)-C(17)	109.32(6)
C(19)-C(20)-H(20A)	119.9	O(1)-Si(1)-C(23)	112.56(6)
C(22)-C(21)-C(20)	120.18(17)	C(17)-Si(1)-C(23)	108.49(7)
C(22)-C(21)-H(21A)	119.9	O(1)-Si(1)-C(13)	103.58(7)
C(20)-C(21)-H(21A)	119.9	C(17)-Si(1)-C(13)	108.16(7)
C(21)-C(22)-C(17)	121.17(16)	C(23)-Si(1)-C(13)	114.54(8)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for product **4.46**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	24(1)	31(1)	40(1)	-3(1)	8(1)	1(1)
C(2)	34(1)	26(1)	54(1)	3(1)	14(1)	0(1)
C(3)	45(1)	41(1)	45(1)	13(1)	15(1)	6(1)
C(4)	29(1)	38(1)	34(1)	4(1)	9(1)	0(1)
C(5)	23(1)	26(1)	33(1)	1(1)	8(1)	3(1)
C(6)	25(1)	28(1)	31(1)	-1(1)	10(1)	0(1)
C(7)	22(1)	32(1)	32(1)	-1(1)	9(1)	-1(1)
C(8)	28(1)	29(1)	36(1)	-2(1)	10(1)	-1(1)
C(9)	34(1)	38(1)	39(1)	6(1)	15(1)	2(1)
C(10)	87(2)	61(2)	51(1)	24(1)	25(1)	13(1)
C(11)	27(1)	35(1)	51(1)	-2(1)	14(1)	4(1)
C(12)	42(1)	38(1)	44(1)	-9(1)	10(1)	-1(1)
C(13)	29(1)	31(1)	24(1)	1(1)	3(1)	4(1)
C(14)	31(1)	46(1)	40(1)	-1(1)	0(1)	10(1)
C(15)	45(1)	31(1)	34(1)	8(1)	9(1)	1(1)
C(16)	48(1)	45(1)	24(1)	2(1)	9(1)	5(1)
C(17)	29(1)	24(1)	23(1)	0(1)	7(1)	1(1)
C(18)	28(1)	31(1)	29(1)	2(1)	8(1)	2(1)
C(19)	41(1)	40(1)	33(1)	3(1)	16(1)	8(1)
C(20)	54(1)	35(1)	26(1)	-5(1)	11(1)	6(1)
C(21)	43(1)	34(1)	29(1)	-5(1)	4(1)	-5(1)
C(22)	30(1)	34(1)	30(1)	-1(1)	8(1)	-3(1)
C(23)	23(1)	24(1)	40(1)	-6(1)	14(1)	-2(1)
C(24)	26(1)	32(1)	49(1)	7(1)	15(1)	2(1)
C(25)	40(1)	31(1)	74(1)	12(1)	31(1)	6(1)
C(26)	61(1)	28(1)	101(2)	-19(1)	57(1)	-15(1)
C(27)	63(1)	54(1)	71(2)	-37(1)	41(1)	-29(1)
C(28)	43(1)	44(1)	46(1)	-17(1)	24(1)	-13(1)
N(1)	34(1)	31(1)	42(1)	3(1)	12(1)	2(1)
N(2)	58(1)	34(1)	56(1)	-6(1)	12(1)	-4(1)

O(1)	22(1)	27(1)	30(1)	2(1)	8(1)	2(1)
O(2)	45(1)	41(1)	33(1)	0(1)	6(1)	-9(1)
O(3)	69(1)	47(1)	33(1)	-2(1)	16(1)	-3(1)
O(4)	62(1)	40(1)	42(1)	12(1)	17(1)	3(1)
Si(1)	21(1)	23(1)	22(1)	-2(1)	6(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for product **4.46**.

	x	y	z	U(eq)
H(2A)	3016	-3945	2884	46
H(3A)	4714	-2782	4281	52
H(3B)	3074	-2586	4267	52
H(4A)	4822	-292	4196	40
H(4B)	3120	-141	3994	40
H(6A)	4842	258	1966	33
H(10A)	4916	6018	354	98
H(10B)	3831	4637	124	98
H(10C)	5475	4401	183	98
H(11A)	7142	-637	2755	56
H(11B)	5999	-1964	2594	56
H(11C)	6560	-1181	3542	56
H(12A)	2548	-3173	1295	63
H(12B)	3646	-1889	1231	63
H(12C)	2024	-1474	1149	63
H(14A)	-1668	3168	660	62
H(14B)	-1491	3045	1693	62
H(14C)	-1836	1585	1084	62
H(15A)	727	4414	1050	56
H(15B)	2108	3600	1689	56
H(15C)	899	4235	2079	56
H(16A)	203	2236	55	59
H(16B)	127	595	436	59
H(16C)	1622	1463	679	59
H(18A)	-1093	1606	3360	35
H(19A)	-1212	3144	4514	44
H(20A)	750	4640	5240	46
H(21A)	2815	4585	4807	44
H(22A)	2959	3009	3677	38
H(24A)	648	-1043	3698	42

H(25A)	-379	-3383	3729	54
H(26A)	-1671	-4522	2409	67
H(27A)	-1979	-3311	1077	69
H(28A)	-951	-967	1040	50

Table 6. Torsion angles [°] for product **4.46**.

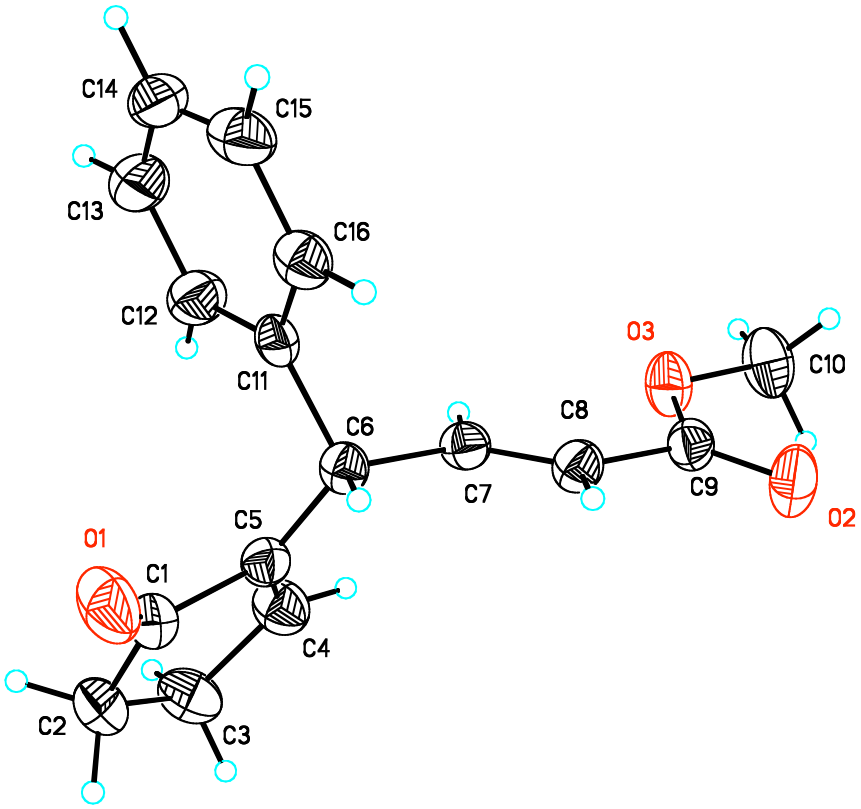
C(12)-C(1)-C(2)-C(3)	178.43(16)
C(5)-C(1)-C(2)-C(3)	0.0(2)
C(1)-C(2)-C(3)-C(4)	6.7(2)
C(2)-C(3)-C(4)-C(5)	-10.29(18)
C(2)-C(1)-C(5)-O(1)	-128.27(15)
C(12)-C(1)-C(5)-O(1)	53.1(2)
C(2)-C(1)-C(5)-C(4)	-6.53(18)
C(12)-C(1)-C(5)-C(4)	174.89(15)
C(2)-C(1)-C(5)-C(6)	117.40(16)
C(12)-C(1)-C(5)-C(6)	-61.18(19)
C(3)-C(4)-C(5)-O(1)	131.37(15)
C(3)-C(4)-C(5)-C(1)	10.31(17)
C(3)-C(4)-C(5)-C(6)	-110.00(16)
O(1)-C(5)-C(6)-C(7)	62.16(16)
C(1)-C(5)-C(6)-C(7)	-178.07(13)
C(4)-C(5)-C(6)-C(7)	-61.73(18)
O(1)-C(5)-C(6)-C(11)	-175.10(14)
C(1)-C(5)-C(6)-C(11)	-55.33(18)
C(4)-C(5)-C(6)-C(11)	61.01(19)
C(11)-C(6)-C(7)-O(2)	-53.0(2)
C(5)-C(6)-C(7)-O(2)	71.69(19)
C(11)-C(6)-C(7)-C(8)	125.34(16)
C(5)-C(6)-C(7)-C(8)	-109.93(16)
O(2)-C(7)-C(8)-N(1)	-3.6(2)
C(6)-C(7)-C(8)-N(1)	177.99(14)
O(2)-C(7)-C(8)-C(9)	171.32(17)
C(6)-C(7)-C(8)-C(9)	-7.1(3)
N(1)-C(8)-C(9)-O(3)	177.52(19)
C(7)-C(8)-C(9)-O(3)	2.8(3)
N(1)-C(8)-C(9)-O(4)	-2.2(2)
C(7)-C(8)-C(9)-O(4)	-176.92(17)
C(22)-C(17)-C(18)-C(19)	0.4(3)
Si(1)-C(17)-C(18)-C(19)	-174.50(14)
C(17)-C(18)-C(19)-C(20)	0.3(3)

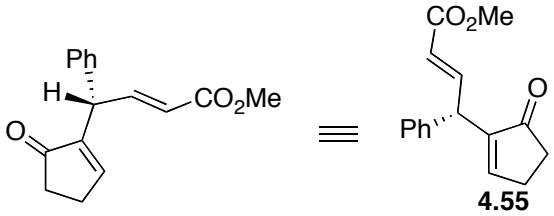
C(18)-C(19)-C(20)-C(21)	-0.2(3)
C(19)-C(20)-C(21)-C(22)	-0.6(3)
C(20)-C(21)-C(22)-C(17)	1.3(3)
C(18)-C(17)-C(22)-C(21)	-1.2(3)
Si(1)-C(17)-C(22)-C(21)	173.80(14)
C(28)-C(23)-C(24)-C(25)	1.8(2)
Si(1)-C(23)-C(24)-C(25)	-174.32(13)
C(23)-C(24)-C(25)-C(26)	-0.5(3)
C(24)-C(25)-C(26)-C(27)	-0.9(3)
C(25)-C(26)-C(27)-C(28)	0.9(3)
C(24)-C(23)-C(28)-C(27)	-1.8(3)
Si(1)-C(23)-C(28)-C(27)	174.18(16)
C(26)-C(27)-C(28)-C(23)	0.4(3)
C(9)-C(8)-N(1)-N(2)	-179(100)
C(7)-C(8)-N(1)-N(2)	-3(2)
C(1)-C(5)-O(1)-Si(1)	62.42(19)
C(4)-C(5)-O(1)-Si(1)	-53.44(19)
C(6)-C(5)-O(1)-Si(1)	-179.02(11)
O(3)-C(9)-O(4)-C(10)	-2.0(3)
C(8)-C(9)-O(4)-C(10)	177.74(17)
C(5)-O(1)-Si(1)-C(17)	89.19(15)
C(5)-O(1)-Si(1)-C(23)	-31.44(16)
C(5)-O(1)-Si(1)-C(13)	-155.70(14)
C(18)-C(17)-Si(1)-O(1)	-162.09(13)
C(22)-C(17)-Si(1)-O(1)	23.20(15)
C(18)-C(17)-Si(1)-C(23)	-39.01(16)
C(22)-C(17)-Si(1)-C(23)	146.28(14)
C(18)-C(17)-Si(1)-C(13)	85.77(15)
C(22)-C(17)-Si(1)-C(13)	-88.94(15)
C(28)-C(23)-Si(1)-O(1)	-94.13(16)
C(24)-C(23)-Si(1)-O(1)	81.73(14)
C(28)-C(23)-Si(1)-C(17)	144.76(15)
C(24)-C(23)-Si(1)-C(17)	-39.38(14)
C(28)-C(23)-Si(1)-C(13)	23.84(18)
C(24)-C(23)-Si(1)-C(13)	-160.30(12)
C(14)-C(13)-Si(1)-O(1)	175.84(12)

C(16)-C(13)-Si(1)-O(1)	52.22(14)
C(15)-C(13)-Si(1)-O(1)	-65.51(13)
C(14)-C(13)-Si(1)-C(17)	-68.22(14)
C(16)-C(13)-Si(1)-C(17)	168.16(12)
C(15)-C(13)-Si(1)-C(17)	50.43(14)
C(14)-C(13)-Si(1)-C(23)	52.88(15)
C(16)-C(13)-Si(1)-C(23)	-70.74(14)
C(15)-C(13)-Si(1)-C(23)	171.52(11)

Symmetry transformations used to generate equivalent atoms:

10. X-ray crystallographic structure of product 4.55





4.55

Table 1. Crystal data and structure refinement for product **4.55**.

Identification code	yl_9_69ph	
Empirical formula	C16 H16 O3	
Formula weight	256.29	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 9.3325(7) Å	α= 90°.
	b = 9.7788(8) Å	β= 90°.
	c = 15.0435(12) Å	γ = 90°.
Volume	1372.88(19) $Å^3$	
Z	4	
Density (calculated)	1.240 Mg/m^3	
Absorption coefficient	0.688 mm^{-1}	
F(000)	544	
Crystal size	0.26 x 0.22 x 0.15 mm^3	
Theta range for data collection	5.40 to 68.01°.	
Index ranges	-11<=h<=10, -9<=k<=11, -14<=l<=18	
Reflections collected	10064	
Independent reflections	2298 [R(int) = 0.0240]	
Completeness to theta = 68.01°	98.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9038 and 0.8414	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2298 / 0 / 237	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0269, wR2 = 0.0696	
R indices (all data)	R1 = 0.0279, wR2 = 0.0704	
Absolute structure parameter	0.0(2)	
Extinction coefficient	0.0040(4)	
Largest diff. peak and hole	0.126 and -0.111 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for product **4.55**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5504(2)	4565(2)	8450(1)	38(1)
C(2)	3880(2)	4636(2)	8379(1)	47(1)
C(3)	3500(2)	6129(2)	8544(1)	48(1)
C(4)	4911(2)	6791(2)	8740(1)	41(1)
C(5)	6020(2)	5943(1)	8696(1)	31(1)
C(6)	7602(2)	6205(1)	8813(1)	29(1)
C(7)	7958(2)	7704(1)	8835(1)	29(1)
C(8)	8809(2)	8314(2)	8256(1)	32(1)
C(9)	9169(2)	9782(1)	8273(1)	32(1)
C(10)	9110(2)	11846(2)	9078(1)	48(1)
C(11)	8222(2)	5525(1)	9644(1)	29(1)
C(12)	7440(2)	5379(2)	10420(1)	42(1)
C(13)	8044(2)	4770(2)	11164(1)	51(1)
C(14)	9438(2)	4308(2)	11138(1)	47(1)
C(15)	10236(2)	4471(2)	10376(1)	43(1)
C(16)	9637(2)	5078(1)	9633(1)	35(1)
O(1)	6242(1)	3570(1)	8311(1)	55(1)
O(2)	9760(1)	10366(1)	7671(1)	49(1)
O(3)	8772(1)	10405(1)	9023(1)	40(1)

Table 3. Bond lengths [Å] and angles [°] for product **4.55**.

C(1)-O(1)	1.210(2)	C(15)-H(11)	0.93(2)
C(1)-C(5)	1.478(2)	C(16)-H(6)	0.948(18)
C(1)-C(2)	1.521(2)		
C(2)-C(3)	1.523(3)	O(1)-C(1)-C(5)	126.22(14)
C(2)-H(9)	0.98(2)	O(1)-C(1)-C(2)	126.29(16)
C(2)-H(16)	1.00(2)	C(5)-C(1)-C(2)	107.48(14)
C(3)-C(4)	1.496(2)	C(1)-C(2)-C(3)	105.35(14)
C(3)-H(12)	0.999(19)	C(1)-C(2)-H(9)	108.5(13)
C(3)-H(13)	0.98(2)	C(3)-C(2)-H(9)	112.8(12)
C(4)-C(5)	1.328(2)	C(1)-C(2)-H(16)	109.4(12)
C(4)-H(8)	0.977(18)	C(3)-C(2)-H(16)	114.3(11)
C(5)-C(6)	1.5092(19)	H(9)-C(2)-H(16)	106.3(16)
C(6)-C(7)	1.5031(19)	C(4)-C(3)-C(2)	104.00(14)
C(6)-C(11)	1.5289(19)	C(4)-C(3)-H(12)	110.9(11)
C(6)-H(5)	0.935(15)	C(2)-C(3)-H(12)	112.9(12)
C(7)-C(8)	1.322(2)	C(4)-C(3)-H(13)	111.2(12)
C(7)-H(1)	0.979(15)	C(2)-C(3)-H(13)	111.8(12)
C(8)-C(9)	1.474(2)	H(12)-C(3)-H(13)	106.2(15)
C(8)-H(2)	0.958(16)	C(5)-C(4)-C(3)	113.95(14)
C(9)-O(2)	1.2037(17)	C(5)-C(4)-H(8)	125.0(11)
C(9)-O(3)	1.3348(17)	C(3)-C(4)-H(8)	120.9(11)
C(10)-O(3)	1.4464(19)	C(4)-C(5)-C(1)	109.14(13)
C(10)-H(3)	0.96(2)	C(4)-C(5)-C(6)	130.64(13)
C(10)-H(10)	0.97(2)	C(1)-C(5)-C(6)	120.16(12)
C(10)-H(14)	1.05(2)	C(7)-C(6)-C(5)	112.56(12)
C(11)-C(12)	1.384(2)	C(7)-C(6)-C(11)	108.78(11)
C(11)-C(16)	1.391(2)	C(5)-C(6)-C(11)	113.06(11)
C(12)-C(13)	1.387(2)	C(7)-C(6)-H(5)	109.3(9)
C(12)-H(4)	0.93(2)	C(5)-C(6)-H(5)	107.3(9)
C(13)-C(14)	1.378(3)	C(11)-C(6)-H(5)	105.6(8)
C(13)-H(15)	0.99(2)	C(8)-C(7)-C(6)	123.98(13)
C(14)-C(15)	1.377(3)	C(8)-C(7)-H(1)	119.3(9)
C(14)-H(7)	0.954(19)	C(6)-C(7)-H(1)	116.6(9)
C(15)-C(16)	1.383(2)	C(7)-C(8)-C(9)	124.49(13)

C(7)-C(8)-H(2)	121.9(10)	C(11)-C(12)-H(4)	117.2(12)
C(9)-C(8)-H(2)	113.6(10)	C(13)-C(12)-H(4)	122.1(12)
O(2)-C(9)-O(3)	123.10(13)	C(14)-C(13)-C(12)	120.09(16)
O(2)-C(9)-C(8)	123.62(14)	C(14)-C(13)-H(15)	118.5(12)
O(3)-C(9)-C(8)	113.28(12)	C(12)-C(13)-H(15)	121.4(13)
O(3)-C(10)-H(3)	106.5(12)	C(15)-C(14)-C(13)	119.71(15)
O(3)-C(10)-H(10)	111.1(11)	C(15)-C(14)-H(7)	118.8(12)
H(3)-C(10)-H(10)	115.1(17)	C(13)-C(14)-H(7)	121.4(12)
O(3)-C(10)-H(14)	109.9(13)	C(14)-C(15)-C(16)	120.29(16)
H(3)-C(10)-H(14)	107.2(17)	C(14)-C(15)-H(11)	120.0(12)
H(10)-C(10)-H(14)	106.9(17)	C(16)-C(15)-H(11)	119.6(12)
C(12)-C(11)-C(16)	118.52(13)	C(15)-C(16)-C(11)	120.62(15)
C(12)-C(11)-C(6)	122.35(13)	C(15)-C(16)-H(6)	122.6(11)
C(16)-C(11)-C(6)	119.09(12)	C(11)-C(16)-H(6)	116.8(11)
C(11)-C(12)-C(13)	120.74(16)	C(9)-O(3)-C(10)	115.65(12)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for product **4.55**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	43(1)	32(1)	40(1)	4(1)	-6(1)	-6(1)
C(2)	42(1)	46(1)	53(1)	3(1)	-9(1)	-13(1)
C(3)	35(1)	56(1)	52(1)	-7(1)	-6(1)	-2(1)
C(4)	41(1)	36(1)	46(1)	-6(1)	-3(1)	1(1)
C(5)	37(1)	30(1)	27(1)	0(1)	-1(1)	-3(1)
C(6)	32(1)	26(1)	29(1)	-2(1)	2(1)	0(1)
C(7)	31(1)	28(1)	29(1)	-1(1)	-2(1)	1(1)
C(8)	35(1)	31(1)	30(1)	1(1)	1(1)	0(1)
C(9)	27(1)	32(1)	35(1)	4(1)	1(1)	-2(1)
C(10)	52(1)	27(1)	66(1)	-5(1)	9(1)	-5(1)
C(11)	32(1)	21(1)	34(1)	-2(1)	-3(1)	-6(1)
C(12)	38(1)	52(1)	37(1)	6(1)	-1(1)	-1(1)
C(13)	50(1)	65(1)	38(1)	13(1)	-3(1)	-12(1)
C(14)	62(1)	35(1)	45(1)	5(1)	-21(1)	-5(1)
C(15)	42(1)	33(1)	54(1)	-8(1)	-15(1)	5(1)
C(16)	36(1)	30(1)	40(1)	-6(1)	-2(1)	1(1)
O(1)	55(1)	29(1)	82(1)	-6(1)	-11(1)	-2(1)
O(2)	60(1)	41(1)	47(1)	7(1)	13(1)	-13(1)
O(3)	46(1)	27(1)	47(1)	-2(1)	9(1)	-6(1)

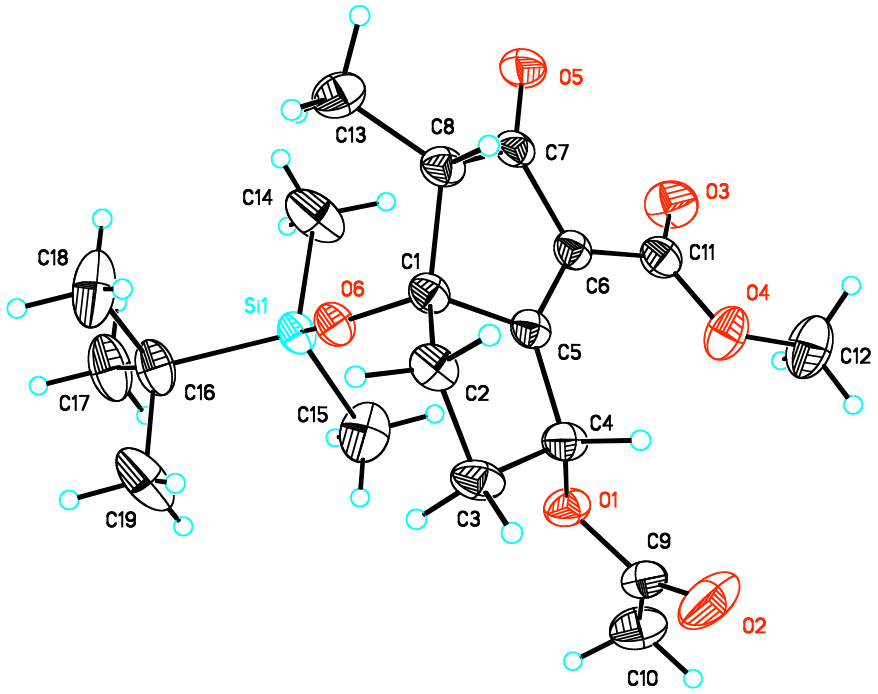
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for product **4.55**.

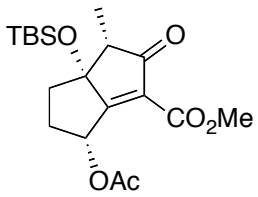
	x	y	z	U(eq)
H(1)	7553(15)	8234(15)	9326(9)	27(4)
H(2)	9256(17)	7824(16)	7780(11)	34(4)
H(3)	8690(20)	12170(20)	9624(14)	61(6)
H(4)	6510(20)	5725(19)	10422(12)	54(5)
H(5)	8073(15)	5796(15)	8333(9)	24(3)
H(6)	10148(19)	5191(17)	9094(12)	41(4)
H(7)	9870(20)	3870(20)	11639(12)	54(5)
H(8)	4976(19)	7773(18)	8852(11)	45(5)
H(9)	3600(20)	4320(20)	7786(14)	67(6)
H(10)	10130(20)	11999(19)	9018(12)	54(5)
H(11)	11170(20)	4140(20)	10350(12)	55(5)
H(12)	2820(20)	6250(20)	9050(12)	56(5)
H(13)	3040(20)	6550(20)	8024(13)	61(6)
H(14)	8610(30)	12380(20)	8553(14)	76(7)
H(15)	7490(20)	4650(20)	11718(14)	68(6)
H(16)	3440(20)	3980(20)	8810(13)	59(5)

Table 6. Torsion angles [°] for product **4.55**.

O(1)-C(1)-C(2)-C(3)	-175.42(16)
C(5)-C(1)-C(2)-C(3)	3.03(18)
C(1)-C(2)-C(3)-C(4)	-2.59(19)
C(2)-C(3)-C(4)-C(5)	1.3(2)
C(3)-C(4)-C(5)-C(1)	0.61(19)
C(3)-C(4)-C(5)-C(6)	177.57(15)
O(1)-C(1)-C(5)-C(4)	176.13(16)
C(2)-C(1)-C(5)-C(4)	-2.32(17)
O(1)-C(1)-C(5)-C(6)	-1.2(2)
C(2)-C(1)-C(5)-C(6)	-179.65(13)
C(4)-C(5)-C(6)-C(7)	-11.0(2)
C(1)-C(5)-C(6)-C(7)	165.70(12)
C(4)-C(5)-C(6)-C(11)	112.79(17)
C(1)-C(5)-C(6)-C(11)	-70.54(16)
C(5)-C(6)-C(7)-C(8)	-119.23(15)
C(11)-C(6)-C(7)-C(8)	114.66(15)
C(6)-C(7)-C(8)-C(9)	-179.79(13)
C(7)-C(8)-C(9)-O(2)	-168.10(15)
C(7)-C(8)-C(9)-O(3)	11.7(2)
C(7)-C(6)-C(11)-C(12)	91.88(16)
C(5)-C(6)-C(11)-C(12)	-33.94(18)
C(7)-C(6)-C(11)-C(16)	-85.94(15)
C(5)-C(6)-C(11)-C(16)	148.25(13)
C(16)-C(11)-C(12)-C(13)	-1.5(2)
C(6)-C(11)-C(12)-C(13)	-179.28(15)
C(11)-C(12)-C(13)-C(14)	0.2(3)
C(12)-C(13)-C(14)-C(15)	1.0(3)
C(13)-C(14)-C(15)-C(16)	-0.9(2)
C(14)-C(15)-C(16)-C(11)	-0.3(2)
C(12)-C(11)-C(16)-C(15)	1.5(2)
C(6)-C(11)-C(16)-C(15)	179.38(12)
O(2)-C(9)-O(3)-C(10)	-0.6(2)
C(8)-C(9)-O(3)-C(10)	179.53(14)

11. X-ray crystallographic structure of product 4.57





4.57

Table 1. Crystal data and structure refinement for product **4.57**.

Identification code	yl_10_21oacf	
Empirical formula	C19 H30 O6 Si	
Formula weight	382.52	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 10.8154(5) Å	α= 90°.
	b = 9.0901(4) Å	β= 101.823(3)°.
	c = 11.3095(4) Å	γ = 90°.
Volume	1088.28(8) $Å^3$	
Z	2	
Density (calculated)	1.167 Mg/m^3	
Absorption coefficient	1.199 mm^{-1}	
F(000)	412	
Crystal size	0.24 x 0.23 x 0.17 mm^3	
Theta range for data collection	3.99 to 67.34°.	
Index ranges	-11<=h<=12, -10<=k<=9, -13<=l<=12	
Reflections collected	6369	
Independent reflections	2903 [R(int) = 0.0163]	
Completeness to theta = 67.34°	92.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8222 and 0.7619	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2903 / 1 / 235	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0300, wR2 = 0.0780	
R indices (all data)	R1 = 0.0314, wR2 = 0.0791	
Absolute structure parameter	0.04(3)	
Largest diff. peak and hole	0.159 and -0.158 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for product **4.57**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-8764(2)	-1336(2)	-2703(2)	31(1)
C(2)	-8474(2)	152(3)	-2069(2)	37(1)
C(3)	-7081(2)	403(3)	-2149(2)	40(1)
C(4)	-7021(2)	-103(2)	-3427(2)	35(1)
C(5)	-8071(2)	-1199(2)	-3735(2)	30(1)
C(6)	-8660(2)	-1909(2)	-4731(2)	31(1)
C(7)	-9895(2)	-2474(2)	-4514(2)	32(1)
C(8)	-10112(2)	-1742(2)	-3354(2)	34(1)
C(9)	-5002(2)	113(3)	-3930(2)	45(1)
C(10)	-3850(2)	-733(3)	-4046(3)	58(1)
C(11)	-8241(2)	-2049(3)	-5888(2)	37(1)
C(12)	-7002(3)	-951(3)	-7132(3)	64(1)
C(13)	-10926(2)	-2622(3)	-2668(2)	46(1)
C(14)	-8558(3)	-5428(3)	-2833(3)	65(1)
C(15)	-6010(3)	-4011(3)	-2305(3)	62(1)
C(16)	-7342(3)	-4581(3)	-194(2)	48(1)
C(17)	-6846(3)	-6169(3)	18(3)	67(1)
C(18)	-8586(3)	-4429(4)	230(3)	77(1)
C(19)	-6361(3)	-3525(4)	540(2)	74(1)
O(1)	-5825(1)	-747(2)	-3506(2)	39(1)
O(2)	-5190(2)	1383(2)	-4153(2)	76(1)
O(3)	-8526(2)	-3039(2)	-6595(2)	55(1)
O(4)	-7500(2)	-921(2)	-6044(2)	48(1)
O(5)	-10615(2)	-3295(2)	-5151(1)	45(1)
O(6)	-8217(1)	-2436(2)	-1864(1)	34(1)
Si(1)	-7563(1)	-4079(1)	-1842(1)	33(1)

Table 3. Bond lengths [Å] and angles [°] for product **4.57**.

C(1)-O(6)	1.421(2)	C(13)-H(13C)	0.9800
C(1)-C(5)	1.516(3)	C(14)-Si(1)	1.850(3)
C(1)-C(2)	1.533(3)	C(14)-H(14A)	0.9800
C(1)-C(8)	1.537(3)	C(14)-H(14B)	0.9800
C(2)-C(3)	1.544(3)	C(14)-H(14C)	0.9800
C(2)-H(2A)	0.9900	C(15)-Si(1)	1.860(3)
C(2)-H(2B)	0.9900	C(15)-H(15A)	0.9800
C(3)-C(4)	1.531(3)	C(15)-H(15B)	0.9800
C(3)-H(3A)	0.9900	C(15)-H(15C)	0.9800
C(3)-H(3B)	0.9900	C(16)-C(18)	1.524(4)
C(4)-O(1)	1.439(3)	C(16)-C(19)	1.541(4)
C(4)-C(5)	1.497(3)	C(16)-C(17)	1.541(4)
C(4)-H(4A)	1.0000	C(16)-Si(1)	1.886(2)
C(5)-C(6)	1.341(3)	C(17)-H(17A)	0.9800
C(6)-C(11)	1.475(3)	C(17)-H(17B)	0.9800
C(6)-C(7)	1.497(3)	C(17)-H(17C)	0.9800
C(7)-O(5)	1.206(3)	C(18)-H(18A)	0.9800
C(7)-C(8)	1.530(3)	C(18)-H(18B)	0.9800
C(8)-C(13)	1.516(3)	C(18)-H(18C)	0.9800
C(8)-H(8A)	1.0000	C(19)-H(19A)	0.9800
C(9)-O(2)	1.190(3)	C(19)-H(19B)	0.9800
C(9)-O(1)	1.345(3)	C(19)-H(19C)	0.9800
C(9)-C(10)	1.493(4)	O(6)-Si(1)	1.6504(15)
C(10)-H(10A)	0.9800		
C(10)-H(10B)	0.9800	O(6)-C(1)-C(5)	111.61(16)
C(10)-H(10C)	0.9800	O(6)-C(1)-C(2)	106.92(16)
C(11)-O(3)	1.202(3)	C(5)-C(1)-C(2)	101.62(17)
C(11)-O(4)	1.335(3)	O(6)-C(1)-C(8)	112.03(17)
C(12)-O(4)	1.441(3)	C(5)-C(1)-C(8)	102.76(17)
C(12)-H(12A)	0.9800	C(2)-C(1)-C(8)	121.25(17)
C(12)-H(12B)	0.9800	C(1)-C(2)-C(3)	102.21(17)
C(12)-H(12C)	0.9800	C(1)-C(2)-H(2A)	111.3
C(13)-H(13A)	0.9800	C(3)-C(2)-H(2A)	111.3
C(13)-H(13B)	0.9800	C(1)-C(2)-H(2B)	111.3

C(3)-C(2)-H(2B)	111.3	H(10A)-C(10)-H(10C)	109.5
H(2A)-C(2)-H(2B)	109.2	H(10B)-C(10)-H(10C)	109.5
C(4)-C(3)-C(2)	103.99(17)	O(3)-C(11)-O(4)	124.5(2)
C(4)-C(3)-H(3A)	111.0	O(3)-C(11)-C(6)	124.8(2)
C(2)-C(3)-H(3A)	111.0	O(4)-C(11)-C(6)	110.67(19)
C(4)-C(3)-H(3B)	111.0	O(4)-C(12)-H(12A)	109.5
C(2)-C(3)-H(3B)	111.0	O(4)-C(12)-H(12B)	109.5
H(3A)-C(3)-H(3B)	109.0	H(12A)-C(12)-H(12B)	109.5
O(1)-C(4)-C(5)	111.32(18)	O(4)-C(12)-H(12C)	109.5
O(1)-C(4)-C(3)	113.15(17)	H(12A)-C(12)-H(12C)	109.5
C(5)-C(4)-C(3)	104.04(18)	H(12B)-C(12)-H(12C)	109.5
O(1)-C(4)-H(4A)	109.4	C(8)-C(13)-H(13A)	109.5
C(5)-C(4)-H(4A)	109.4	C(8)-C(13)-H(13B)	109.5
C(3)-C(4)-H(4A)	109.4	H(13A)-C(13)-H(13B)	109.5
C(6)-C(5)-C(4)	136.3(2)	C(8)-C(13)-H(13C)	109.5
C(6)-C(5)-C(1)	112.47(18)	H(13A)-C(13)-H(13C)	109.5
C(4)-C(5)-C(1)	110.30(18)	H(13B)-C(13)-H(13C)	109.5
C(5)-C(6)-C(11)	127.4(2)	Si(1)-C(14)-H(14A)	109.5
C(5)-C(6)-C(7)	108.27(19)	Si(1)-C(14)-H(14B)	109.5
C(11)-C(6)-C(7)	124.25(19)	H(14A)-C(14)-H(14B)	109.5
O(5)-C(7)-C(6)	127.1(2)	Si(1)-C(14)-H(14C)	109.5
O(5)-C(7)-C(8)	126.0(2)	H(14A)-C(14)-H(14C)	109.5
C(6)-C(7)-C(8)	106.86(17)	H(14B)-C(14)-H(14C)	109.5
C(13)-C(8)-C(7)	114.60(19)	Si(1)-C(15)-H(15A)	109.5
C(13)-C(8)-C(1)	118.35(19)	Si(1)-C(15)-H(15B)	109.5
C(7)-C(8)-C(1)	102.59(17)	H(15A)-C(15)-H(15B)	109.5
C(13)-C(8)-H(8A)	106.9	Si(1)-C(15)-H(15C)	109.5
C(7)-C(8)-H(8A)	106.9	H(15A)-C(15)-H(15C)	109.5
C(1)-C(8)-H(8A)	106.9	H(15B)-C(15)-H(15C)	109.5
O(2)-C(9)-O(1)	122.9(2)	C(18)-C(16)-C(19)	109.2(3)
O(2)-C(9)-C(10)	126.2(3)	C(18)-C(16)-C(17)	109.7(2)
O(1)-C(9)-C(10)	110.9(2)	C(19)-C(16)-C(17)	108.7(2)
C(9)-C(10)-H(10A)	109.5	C(18)-C(16)-Si(1)	110.33(18)
C(9)-C(10)-H(10B)	109.5	C(19)-C(16)-Si(1)	108.36(19)
H(10A)-C(10)-H(10B)	109.5	C(17)-C(16)-Si(1)	110.53(18)
C(9)-C(10)-H(10C)	109.5	C(16)-C(17)-H(17A)	109.5

C(16)-C(17)-H(17B)	109.5	H(19A)-C(19)-H(19B)	109.5
H(17A)-C(17)-H(17B)	109.5	C(16)-C(19)-H(19C)	109.5
C(16)-C(17)-H(17C)	109.5	H(19A)-C(19)-H(19C)	109.5
H(17A)-C(17)-H(17C)	109.5	H(19B)-C(19)-H(19C)	109.5
H(17B)-C(17)-H(17C)	109.5	C(9)-O(1)-C(4)	117.01(18)
C(16)-C(18)-H(18A)	109.5	C(11)-O(4)-C(12)	115.9(2)
C(16)-C(18)-H(18B)	109.5	C(1)-O(6)-Si(1)	139.91(13)
H(18A)-C(18)-H(18B)	109.5	O(6)-Si(1)-C(14)	113.35(11)
C(16)-C(18)-H(18C)	109.5	O(6)-Si(1)-C(15)	112.03(11)
H(18A)-C(18)-H(18C)	109.5	C(14)-Si(1)-C(15)	107.36(15)
H(18B)-C(18)-H(18C)	109.5	O(6)-Si(1)-C(16)	101.61(9)
C(16)-C(19)-H(19A)	109.5	C(14)-Si(1)-C(16)	112.19(13)
C(16)-C(19)-H(19B)	109.5	C(15)-Si(1)-C(16)	110.32(13)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for product **4.57**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	31(1)	28(1)	32(1)	1(1)	3(1)	5(1)
C(2)	40(1)	31(1)	36(1)	-4(1)	2(1)	5(1)
C(3)	38(1)	30(1)	46(1)	-9(1)	-4(1)	-2(1)
C(4)	31(1)	27(1)	45(1)	2(1)	-1(1)	1(1)
C(5)	30(1)	23(1)	35(1)	2(1)	1(1)	6(1)
C(6)	33(1)	25(1)	32(1)	3(1)	2(1)	4(1)
C(7)	30(1)	27(1)	35(1)	4(1)	-3(1)	0(1)
C(8)	29(1)	32(1)	39(1)	2(1)	2(1)	5(1)
C(9)	36(1)	46(2)	50(1)	4(1)	1(1)	-11(1)
C(10)	36(1)	63(2)	77(2)	-6(2)	13(1)	-4(1)
C(11)	36(1)	36(1)	38(1)	1(1)	4(1)	6(1)
C(12)	77(2)	60(2)	67(2)	8(2)	44(2)	7(2)
C(13)	36(1)	46(1)	58(1)	-1(1)	14(1)	1(1)
C(14)	83(2)	34(1)	62(2)	-9(1)	-21(2)	9(1)
C(15)	62(2)	55(2)	76(2)	13(2)	30(1)	25(2)
C(16)	65(2)	41(1)	35(1)	8(1)	7(1)	16(1)
C(17)	104(2)	49(2)	46(1)	14(1)	12(2)	25(2)
C(18)	103(2)	76(2)	64(2)	25(2)	47(2)	25(2)
C(19)	98(2)	69(2)	41(1)	-8(1)	-17(2)	16(2)
O(1)	29(1)	33(1)	54(1)	5(1)	4(1)	0(1)
O(2)	52(1)	50(1)	130(2)	29(1)	24(1)	-6(1)
O(3)	60(1)	59(1)	46(1)	-21(1)	13(1)	-8(1)
O(4)	62(1)	39(1)	50(1)	-2(1)	28(1)	-2(1)
O(5)	43(1)	44(1)	43(1)	-2(1)	-3(1)	-13(1)
O(6)	37(1)	31(1)	32(1)	1(1)	4(1)	7(1)
Si(1)	40(1)	29(1)	30(1)	0(1)	4(1)	6(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for product **4.57**.

	x	y	z	U(eq)
H(2A)	-8572	104	-1219	44
H(2B)	-9027	937	-2494	44
H(3A)	-6850	1455	-2033	47
H(3B)	-6507	-187	-1535	47
H(4A)	-7197	752	-3994	42
H(8A)	-10566	-797	-3598	41
H(10A)	-3265	-84	-4354	87
H(10B)	-4091	-1554	-4608	87
H(10C)	-3438	-1116	-3253	87
H(12A)	-6469	-84	-7156	95
H(12B)	-7702	-945	-7836	95
H(12C)	-6498	-1845	-7143	95
H(13A)	-11758	-2788	-3187	69
H(13B)	-11024	-2077	-1946	69
H(13C)	-10521	-3571	-2428	69
H(14A)	-8651	-5123	-3677	97
H(14B)	-9392	-5476	-2623	97
H(14C)	-8158	-6399	-2722	97
H(15A)	-6138	-3746	-3161	94
H(15B)	-5604	-4978	-2179	94
H(15C)	-5470	-3274	-1819	94
H(17A)	-6735	-6412	878	100
H(17B)	-6034	-6255	-232	100
H(17C)	-7455	-6851	-456	100
H(18A)	-8458	-4696	1086	115
H(18B)	-9218	-5083	-246	115
H(18C)	-8881	-3409	122	115
H(19A)	-6231	-3774	1399	111
H(19B)	-6668	-2511	416	111
H(19C)	-5559	-3619	270	111

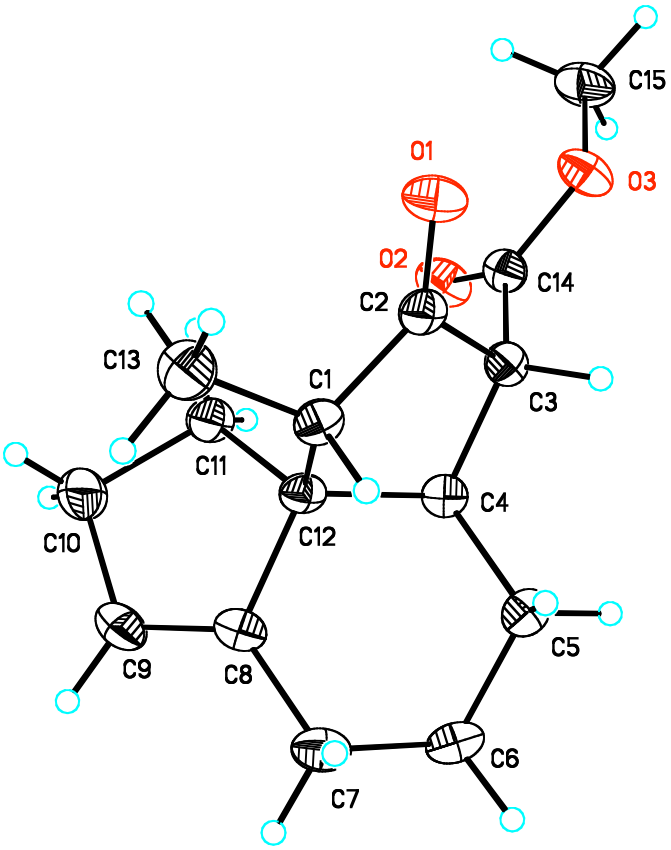
Table 6. Torsion angles [°] for product **4.57**.

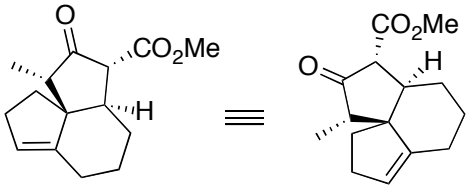
O(6)-C(1)-C(2)-C(3)	77.92(19)
C(5)-C(1)-C(2)-C(3)	-39.18(19)
C(8)-C(1)-C(2)-C(3)	-152.1(2)
C(1)-C(2)-C(3)-C(4)	41.2(2)
C(2)-C(3)-C(4)-O(1)	-146.98(18)
C(2)-C(3)-C(4)-C(5)	-26.0(2)
O(1)-C(4)-C(5)-C(6)	-68.9(3)
C(3)-C(4)-C(5)-C(6)	168.9(2)
O(1)-C(4)-C(5)-C(1)	123.33(19)
C(3)-C(4)-C(5)-C(1)	1.1(2)
O(6)-C(1)-C(5)-C(6)	99.6(2)
C(2)-C(1)-C(5)-C(6)	-146.78(18)
C(8)-C(1)-C(5)-C(6)	-20.6(2)
O(6)-C(1)-C(5)-C(4)	-89.53(19)
C(2)-C(1)-C(5)-C(4)	24.1(2)
C(8)-C(1)-C(5)-C(4)	150.25(17)
C(4)-C(5)-C(6)-C(11)	14.4(4)
C(1)-C(5)-C(6)-C(11)	-177.97(19)
C(4)-C(5)-C(6)-C(7)	-161.8(2)
C(1)-C(5)-C(6)-C(7)	5.8(2)
C(5)-C(6)-C(7)-O(5)	-171.4(2)
C(11)-C(6)-C(7)-O(5)	12.2(3)
C(5)-C(6)-C(7)-C(8)	11.7(2)
C(11)-C(6)-C(7)-C(8)	-164.6(2)
O(5)-C(7)-C(8)-C(13)	30.0(3)
C(6)-C(7)-C(8)-C(13)	-153.07(18)
O(5)-C(7)-C(8)-C(1)	159.6(2)
C(6)-C(7)-C(8)-C(1)	-23.5(2)
O(6)-C(1)-C(8)-C(13)	32.9(3)
C(5)-C(1)-C(8)-C(13)	152.82(19)
C(2)-C(1)-C(8)-C(13)	-94.9(3)
O(6)-C(1)-C(8)-C(7)	-94.4(2)
C(5)-C(1)-C(8)-C(7)	25.6(2)
C(2)-C(1)-C(8)-C(7)	137.9(2)

C(5)-C(6)-C(11)-O(3)	153.9(2)
C(7)-C(6)-C(11)-O(3)	-30.5(3)
C(5)-C(6)-C(11)-O(4)	-26.1(3)
C(7)-C(6)-C(11)-O(4)	149.52(19)
O(2)-C(9)-O(1)-C(4)	5.5(4)
C(10)-C(9)-O(1)-C(4)	-175.7(2)
C(5)-C(4)-O(1)-C(9)	143.2(2)
C(3)-C(4)-O(1)-C(9)	-100.0(2)
O(3)-C(11)-O(4)-C(12)	-1.5(3)
C(6)-C(11)-O(4)-C(12)	178.5(2)
C(5)-C(1)-O(6)-Si(1)	-37.7(3)
C(2)-C(1)-O(6)-Si(1)	-148.04(18)
C(8)-C(1)-O(6)-Si(1)	76.9(2)
C(1)-O(6)-Si(1)-C(14)	-53.5(2)
C(1)-O(6)-Si(1)-C(15)	68.2(2)
C(1)-O(6)-Si(1)-C(16)	-174.0(2)
C(18)-C(16)-Si(1)-O(6)	53.2(2)
C(19)-C(16)-Si(1)-O(6)	-66.3(2)
C(17)-C(16)-Si(1)-O(6)	174.7(2)
C(18)-C(16)-Si(1)-C(14)	-68.2(2)
C(19)-C(16)-Si(1)-C(14)	172.3(2)
C(17)-C(16)-Si(1)-C(14)	53.3(3)
C(18)-C(16)-Si(1)-C(15)	172.1(2)
C(19)-C(16)-Si(1)-C(15)	52.6(2)
C(17)-C(16)-Si(1)-C(15)	-66.4(2)

Symmetry transformations used to generate equivalent atoms:

12. X-ray crystallographic structure of product 4.62





4.62

Table 1. Crystal data and structure refinement for product **4.62**.

Identification code	yl_10_22	
Empirical formula	C15 H20 O3	
Formula weight	248.31	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 14.5359(6) Å	α= 90°.
	b = 6.0722(3) Å	β= 100.992(3)°.
	c = 15.2886(7) Å	γ = 90°.
Volume	1324.69(10) $Å^3$	
Z	4	
Density (calculated)	1.245 Mg/m^3	
Absorption coefficient	0.687 mm^{-1}	
F(000)	536	
Crystal size	0.37 x 0.26 x 0.04 mm^3	
Theta range for data collection	2.94 to 68.48°.	
Index ranges	-17<=h<=17, -7<=k<=6, -18<=l<=17	
Reflections collected	3794	
Independent reflections	1837 [R(int) = 0.0162]	
Completeness to theta = 68.48°	93.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9704 and 0.7853	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1837 / 1 / 163	
Goodness-of-fit on F^2	1.001	
Final R indices [I>2sigma(I)]	R1 = 0.0328, wR2 = 0.0877	
R indices (all data)	R1 = 0.0385, wR2 = 0.0914	
Absolute structure parameter	0.2(3)	
Largest diff. peak and hole	0.181 and -0.141 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for product **4.62**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-9952(1)	753(4)	-2178(1)	26(1)
C(2)	-10601(1)	172(4)	-3045(1)	27(1)
C(3)	-10019(1)	-993(4)	-3662(1)	26(1)
C(4)	-9029(1)	-1188(4)	-3087(1)	26(1)
C(5)	-8385(1)	641(4)	-3316(1)	32(1)
C(6)	-7450(1)	701(4)	-2661(2)	37(1)
C(7)	-7611(2)	1193(4)	-1719(2)	36(1)
C(8)	-8274(1)	-474(4)	-1462(1)	31(1)
C(9)	-8172(2)	-1712(5)	-736(2)	41(1)
C(10)	-8964(2)	-3293(5)	-750(2)	43(1)
C(11)	-9461(1)	-3230(4)	-1734(1)	32(1)
C(12)	-9174(1)	-1021(4)	-2110(1)	25(1)
C(13)	-10438(2)	1078(4)	-1396(2)	40(1)
C(14)	-10445(1)	-3158(4)	-4004(1)	27(1)
C(15)	-11654(2)	-4881(5)	-5020(2)	42(1)
O(1)	-11429(1)	500(3)	-3227(1)	38(1)
O(2)	-10171(1)	-4944(3)	-3729(1)	38(1)
O(3)	-11184(1)	-2869(3)	-4665(1)	37(1)

Table 3. Bond lengths [Å] and angles [°] for product **4.62**.

C(1)-C(13)	1.513(3)	C(14)-O(2)	1.203(3)
C(1)-C(2)	1.514(3)	C(14)-O(3)	1.338(2)
C(1)-C(12)	1.551(3)	C(15)-O(3)	1.454(3)
C(1)-H(1A)	1.0000	C(15)-H(15A)	0.9800
C(2)-O(1)	1.200(2)	C(15)-H(15B)	0.9800
C(2)-C(3)	1.553(3)	C(15)-H(15C)	0.9800
C(3)-C(14)	1.504(3)		
C(3)-C(4)	1.541(3)	C(13)-C(1)-C(2)	114.57(17)
C(3)-H(3A)	1.0000	C(13)-C(1)-C(12)	118.75(19)
C(4)-C(5)	1.535(3)	C(2)-C(1)-C(12)	102.82(16)
C(4)-C(12)	1.552(3)	C(13)-C(1)-H(1A)	106.6
C(4)-H(4A)	1.0000	C(2)-C(1)-H(1A)	106.6
C(5)-C(6)	1.527(3)	C(12)-C(1)-H(1A)	106.6
C(5)-H(5A)	0.9900	O(1)-C(2)-C(1)	126.5(2)
C(5)-H(5B)	0.9900	O(1)-C(2)-C(3)	124.97(19)
C(6)-C(7)	1.531(3)	C(1)-C(2)-C(3)	108.51(16)
C(6)-H(6A)	0.9900	C(14)-C(3)-C(4)	114.15(17)
C(6)-H(6B)	0.9900	C(14)-C(3)-C(2)	111.93(17)
C(7)-C(8)	1.501(3)	C(4)-C(3)-C(2)	104.26(16)
C(7)-H(7A)	0.9900	C(14)-C(3)-H(3A)	108.8
C(7)-H(7B)	0.9900	C(4)-C(3)-H(3A)	108.8
C(8)-C(9)	1.325(3)	C(2)-C(3)-H(3A)	108.8
C(8)-C(12)	1.519(3)	C(5)-C(4)-C(3)	110.99(17)
C(9)-C(10)	1.495(4)	C(5)-C(4)-C(12)	111.93(17)
C(9)-H(9A)	0.9500	C(3)-C(4)-C(12)	105.07(16)
C(10)-C(11)	1.540(3)	C(5)-C(4)-H(4A)	109.6
C(10)-H(10A)	0.9900	C(3)-C(4)-H(4A)	109.6
C(10)-H(10B)	0.9900	C(12)-C(4)-H(4A)	109.6
C(11)-C(12)	1.548(3)	C(6)-C(5)-C(4)	111.85(19)
C(11)-H(11A)	0.9900	C(6)-C(5)-H(5A)	109.2
C(11)-H(11B)	0.9900	C(4)-C(5)-H(5A)	109.2
C(13)-H(13A)	0.9800	C(6)-C(5)-H(5B)	109.2
C(13)-H(13B)	0.9800	C(4)-C(5)-H(5B)	109.2
C(13)-H(13C)	0.9800	H(5A)-C(5)-H(5B)	107.9

C(5)-C(6)-C(7)	110.20(17)	C(12)-C(11)-H(11A)	110.6
C(5)-C(6)-H(6A)	109.6	C(10)-C(11)-H(11B)	110.6
C(7)-C(6)-H(6A)	109.6	C(12)-C(11)-H(11B)	110.6
C(5)-C(6)-H(6B)	109.6	H(11A)-C(11)-H(11B)	108.7
C(7)-C(6)-H(6B)	109.6	C(8)-C(12)-C(11)	101.96(17)
H(6A)-C(6)-H(6B)	108.1	C(8)-C(12)-C(1)	114.74(18)
C(8)-C(7)-C(6)	109.63(19)	C(11)-C(12)-C(1)	112.45(17)
C(8)-C(7)-H(7A)	109.7	C(8)-C(12)-C(4)	112.57(17)
C(6)-C(7)-H(7A)	109.7	C(11)-C(12)-C(4)	113.36(18)
C(8)-C(7)-H(7B)	109.7	C(1)-C(12)-C(4)	102.22(16)
C(6)-C(7)-H(7B)	109.7	C(1)-C(13)-H(13A)	109.5
H(7A)-C(7)-H(7B)	108.2	C(1)-C(13)-H(13B)	109.5
C(9)-C(8)-C(7)	128.9(2)	H(13A)-C(13)-H(13B)	109.5
C(9)-C(8)-C(12)	111.5(2)	C(1)-C(13)-H(13C)	109.5
C(7)-C(8)-C(12)	119.48(19)	H(13A)-C(13)-H(13C)	109.5
C(8)-C(9)-C(10)	112.9(2)	H(13B)-C(13)-H(13C)	109.5
C(8)-C(9)-H(9A)	123.6	O(2)-C(14)-O(3)	123.2(2)
C(10)-C(9)-H(9A)	123.6	O(2)-C(14)-C(3)	125.39(17)
C(9)-C(10)-C(11)	102.45(18)	O(3)-C(14)-C(3)	111.44(19)
C(9)-C(10)-H(10A)	111.3	O(3)-C(15)-H(15A)	109.5
C(11)-C(10)-H(10A)	111.3	O(3)-C(15)-H(15B)	109.5
C(9)-C(10)-H(10B)	111.3	H(15A)-C(15)-H(15B)	109.5
C(11)-C(10)-H(10B)	111.3	O(3)-C(15)-H(15C)	109.5
H(10A)-C(10)-H(10B)	109.2	H(15A)-C(15)-H(15C)	109.5
C(10)-C(11)-C(12)	105.90(18)	H(15B)-C(15)-H(15C)	109.5
C(10)-C(11)-H(11A)	110.6	C(14)-O(3)-C(15)	115.08(19)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for product **4.62**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	28(1)	19(1)	33(1)	-1(1)	7(1)	-1(1)
C(2)	28(1)	19(1)	34(1)	6(1)	4(1)	-2(1)
C(3)	28(1)	22(1)	27(1)	1(1)	3(1)	0(1)
C(4)	26(1)	22(1)	29(1)	-3(1)	5(1)	1(1)
C(5)	31(1)	31(1)	35(1)	2(1)	10(1)	-1(1)
C(6)	27(1)	36(2)	49(1)	-1(1)	10(1)	-8(1)
C(7)	30(1)	31(1)	44(1)	-5(1)	2(1)	-7(1)
C(8)	25(1)	31(1)	34(1)	-4(1)	0(1)	0(1)
C(9)	33(1)	52(2)	33(1)	5(1)	-7(1)	-3(1)
C(10)	42(1)	46(2)	37(1)	14(1)	-1(1)	-5(1)
C(11)	31(1)	26(1)	36(1)	9(1)	1(1)	-3(1)
C(12)	23(1)	19(1)	31(1)	2(1)	3(1)	-2(1)
C(13)	39(1)	44(2)	39(1)	-6(1)	11(1)	6(1)
C(14)	27(1)	28(1)	26(1)	-4(1)	5(1)	1(1)
C(15)	34(1)	43(2)	45(1)	-15(1)	-1(1)	-8(1)
O(1)	25(1)	38(1)	49(1)	-3(1)	2(1)	4(1)
O(2)	40(1)	25(1)	44(1)	-3(1)	-4(1)	-1(1)
O(3)	34(1)	35(1)	36(1)	-6(1)	-7(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for product **4.62**.

	x	y	z	U(eq)
H(1A)	-9655	2193	-2278	32
H(3A)	-9990	-12	-4181	31
H(4A)	-8757	-2659	-3187	31
H(5A)	-8267	398	-3926	38
H(5B)	-8702	2080	-3308	38
H(6A)	-7043	1851	-2844	44
H(6B)	-7129	-736	-2665	44
H(7A)	-7007	1139	-1292	43
H(7B)	-7877	2689	-1700	43
H(9A)	-7651	-1605	-257	49
H(10A)	-9386	-2802	-352	51
H(10B)	-8730	-4790	-573	51
H(11A)	-10150	-3302	-1782	38
H(11B)	-9260	-4486	-2066	38
H(13A)	-10906	2250	-1535	61
H(13B)	-9974	1490	-868	61
H(13C)	-10747	-295	-1278	61
H(15A)	-12180	-4514	-5501	63
H(15B)	-11889	-5656	-4545	63
H(15C)	-11211	-5828	-5253	63

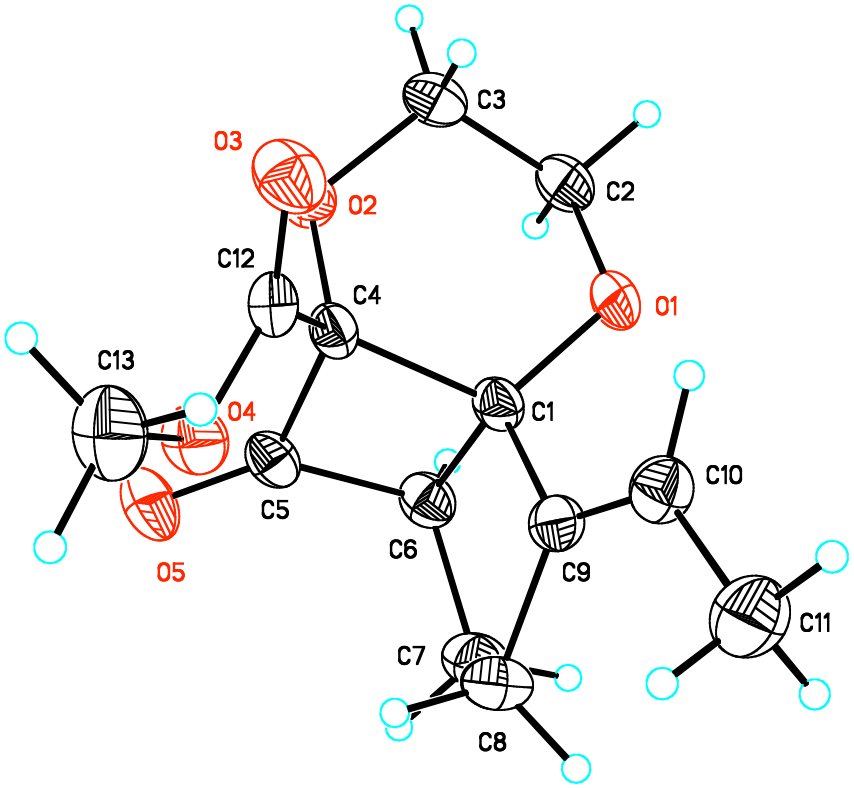
Table 6. Torsion angles [°] for product **4.62**.

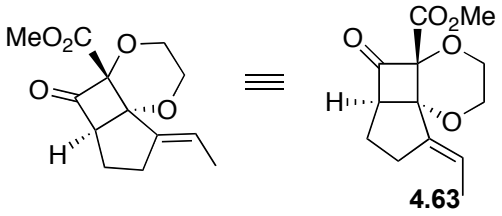
C(13)-C(1)-C(2)-O(1)	20.8(3)
C(12)-C(1)-C(2)-O(1)	151.1(2)
C(13)-C(1)-C(2)-C(3)	-157.7(2)
C(12)-C(1)-C(2)-C(3)	-27.5(2)
O(1)-C(2)-C(3)-C(14)	-51.0(3)
C(1)-C(2)-C(3)-C(14)	127.54(18)
O(1)-C(2)-C(3)-C(4)	-174.9(2)
C(1)-C(2)-C(3)-C(4)	3.7(2)
C(14)-C(3)-C(4)-C(5)	138.19(19)
C(2)-C(3)-C(4)-C(5)	-99.4(2)
C(14)-C(3)-C(4)-C(12)	-100.6(2)
C(2)-C(3)-C(4)-C(12)	21.8(2)
C(3)-C(4)-C(5)-C(6)	171.12(18)
C(12)-C(4)-C(5)-C(6)	54.1(2)
C(4)-C(5)-C(6)-C(7)	-61.8(3)
C(5)-C(6)-C(7)-C(8)	55.9(3)
C(6)-C(7)-C(8)-C(9)	128.2(3)
C(6)-C(7)-C(8)-C(12)	-47.5(3)
C(7)-C(8)-C(9)-C(10)	-176.0(2)
C(12)-C(8)-C(9)-C(10)	-0.1(3)
C(8)-C(9)-C(10)-C(11)	14.1(3)
C(9)-C(10)-C(11)-C(12)	-21.9(3)
C(9)-C(8)-C(12)-C(11)	-13.9(3)
C(7)-C(8)-C(12)-C(11)	162.5(2)
C(9)-C(8)-C(12)-C(1)	108.0(2)
C(7)-C(8)-C(12)-C(1)	-75.7(2)
C(9)-C(8)-C(12)-C(4)	-135.7(2)
C(7)-C(8)-C(12)-C(4)	40.7(3)
C(10)-C(11)-C(12)-C(8)	21.7(2)
C(10)-C(11)-C(12)-C(1)	-101.7(2)
C(10)-C(11)-C(12)-C(4)	143.01(19)
C(13)-C(1)-C(12)-C(8)	-70.0(2)
C(2)-C(1)-C(12)-C(8)	162.32(17)
C(13)-C(1)-C(12)-C(11)	45.9(3)

C(2)-C(1)-C(12)-C(11)	-81.7(2)
C(13)-C(1)-C(12)-C(4)	167.84(19)
C(2)-C(1)-C(12)-C(4)	40.16(19)
C(5)-C(4)-C(12)-C(8)	-41.7(2)
C(3)-C(4)-C(12)-C(8)	-162.30(18)
C(5)-C(4)-C(12)-C(11)	-156.84(17)
C(3)-C(4)-C(12)-C(11)	82.6(2)
C(5)-C(4)-C(12)-C(1)	81.88(19)
C(3)-C(4)-C(12)-C(1)	-38.7(2)
C(4)-C(3)-C(14)-O(2)	15.6(3)
C(2)-C(3)-C(14)-O(2)	-102.6(2)
C(4)-C(3)-C(14)-O(3)	-164.47(16)
C(2)-C(3)-C(14)-O(3)	77.4(2)
O(2)-C(14)-O(3)-C(15)	1.6(3)
C(3)-C(14)-O(3)-C(15)	-178.43(17)

Symmetry transformations used to generate equivalent atoms:

13. X-ray crystallographic structure of product 4.63





4.63

Table 1. Crystal data and structure refinement for product **4.63**.

Identification code	yl_10_25ris	
Empirical formula	C13 H16 O5	
Formula weight	252.26	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	Pna2(1)	
Unit cell dimensions	a = 7.8165(6) Å	α= 90°.
	b = 12.2824(9) Å	β= 90°.
	c = 13.0362(10) Å	γ = 90°.
Volume	1251.55(16) $Å^3$	
Z	4	
Density (calculated)	1.339 Mg/m^3	
Absorption coefficient	0.863 mm^{-1}	
F(000)	536	
Crystal size	0.29 x 0.24 x 0.12 mm^3	
Theta range for data collection	4.95 to 69.21°.	
Index ranges	-9<=h<=9, -12<=k<=13, -15<=l<=13	
Reflections collected	10954	
Independent reflections	2061 [R(int) = 0.0202]	
Completeness to theta = 69.21°	96.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9036 and 0.7880	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2061 / 1 / 163	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0328, wR2 = 0.0915	
R indices (all data)	R1 = 0.0332, wR2 = 0.0921	
Absolute structure parameter	0.08(18)	
Largest diff. peak and hole	0.255 and -0.184 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for product **4.63**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	10206(2)	5367(1)	9763(2)	29(1)
C(2)	12614(2)	4229(2)	10071(2)	40(1)
C(3)	11615(2)	3262(2)	9707(2)	40(1)
C(4)	9044(2)	4314(1)	9679(1)	28(1)
C(5)	8097(2)	4754(2)	10637(1)	31(1)
C(6)	9480(2)	5599(2)	10860(1)	33(1)
C(7)	8880(3)	6776(2)	10869(2)	42(1)
C(8)	8370(2)	6998(2)	9754(2)	42(1)
C(9)	9603(2)	6320(1)	9123(2)	31(1)
C(10)	10210(2)	6541(2)	8202(2)	37(1)
C(11)	9803(3)	7523(2)	7569(2)	53(1)
C(12)	8106(2)	4085(2)	8678(2)	30(1)
C(13)	5529(3)	4380(2)	7773(2)	49(1)
O(1)	11972(1)	5205(1)	9606(1)	36(1)
O(2)	9866(1)	3358(1)	10029(1)	34(1)
O(3)	8656(2)	3525(1)	8009(1)	44(1)
O(4)	6593(2)	4579(1)	8669(1)	38(1)
O(5)	6775(2)	4511(1)	11030(1)	46(1)

Table 3. Bond lengths [Å] and angles [°] for product **4.63**.

C(1)-O(1)	1.4091(19)	C(13)-H(13B)	0.9800
C(1)-C(9)	1.513(3)	C(13)-H(13C)	0.9800
C(1)-C(6)	1.565(3)		
C(1)-C(4)	1.585(2)	O(1)-C(1)-C(9)	109.50(14)
C(2)-O(1)	1.435(2)	O(1)-C(1)-C(6)	120.95(15)
C(2)-C(3)	1.499(3)	C(9)-C(1)-C(6)	104.52(14)
C(2)-H(2A)	0.9900	O(1)-C(1)-C(4)	115.87(13)
C(2)-H(2B)	0.9900	C(9)-C(1)-C(4)	114.45(14)
C(3)-O(2)	1.434(2)	C(6)-C(1)-C(4)	90.24(14)
C(3)-H(3A)	0.9900	O(1)-C(2)-C(3)	110.25(15)
C(3)-H(3B)	0.9900	O(1)-C(2)-H(2A)	109.6
C(4)-O(2)	1.415(2)	C(3)-C(2)-H(2A)	109.6
C(4)-C(12)	1.522(2)	O(1)-C(2)-H(2B)	109.6
C(4)-C(5)	1.549(3)	C(3)-C(2)-H(2B)	109.6
C(5)-O(5)	1.192(2)	H(2A)-C(2)-H(2B)	108.1
C(5)-C(6)	1.526(2)	O(2)-C(3)-C(2)	109.83(15)
C(6)-C(7)	1.521(3)	O(2)-C(3)-H(3A)	109.7
C(6)-H(6A)	1.0000	C(2)-C(3)-H(3A)	109.7
C(7)-C(8)	1.531(3)	O(2)-C(3)-H(3B)	109.7
C(7)-H(7A)	0.9900	C(2)-C(3)-H(3B)	109.7
C(7)-H(7B)	0.9900	H(3A)-C(3)-H(3B)	108.2
C(8)-C(9)	1.517(3)	O(2)-C(4)-C(12)	110.04(14)
C(8)-H(8A)	0.9900	O(2)-C(4)-C(5)	104.25(14)
C(8)-H(8B)	0.9900	C(12)-C(4)-C(5)	121.68(13)
C(9)-C(10)	1.319(3)	O(2)-C(4)-C(1)	113.24(12)
C(10)-C(11)	1.496(3)	C(12)-C(4)-C(1)	119.09(14)
C(10)-H(10A)	0.9500	C(5)-C(4)-C(1)	86.14(13)
C(11)-H(11A)	0.9800	O(5)-C(5)-C(6)	134.54(18)
C(11)-H(11B)	0.9800	O(5)-C(5)-C(4)	132.40(17)
C(11)-H(11C)	0.9800	C(6)-C(5)-C(4)	93.05(13)
C(12)-O(3)	1.191(2)	C(7)-C(6)-C(5)	115.48(15)
C(12)-O(4)	1.330(2)	C(7)-C(6)-C(1)	106.95(15)
C(13)-O(4)	1.455(2)	C(5)-C(6)-C(1)	87.63(13)
C(13)-H(13A)	0.9800	C(7)-C(6)-H(6A)	114.5

C(5)-C(6)-H(6A)	114.5	C(11)-C(10)-H(10A)	116.9
C(1)-C(6)-H(6A)	114.5	C(10)-C(11)-H(11A)	109.5
C(6)-C(7)-C(8)	104.05(15)	C(10)-C(11)-H(11B)	109.5
C(6)-C(7)-H(7A)	110.9	H(11A)-C(11)-H(11B)	109.5
C(8)-C(7)-H(7A)	110.9	C(10)-C(11)-H(11C)	109.5
C(6)-C(7)-H(7B)	110.9	H(11A)-C(11)-H(11C)	109.5
C(8)-C(7)-H(7B)	110.9	H(11B)-C(11)-H(11C)	109.5
H(7A)-C(7)-H(7B)	109.0	O(3)-C(12)-O(4)	125.30(17)
C(9)-C(8)-C(7)	104.59(15)	O(3)-C(12)-C(4)	124.08(15)
C(9)-C(8)-H(8A)	110.8	O(4)-C(12)-C(4)	110.61(15)
C(7)-C(8)-H(8A)	110.8	O(4)-C(13)-H(13A)	109.5
C(9)-C(8)-H(8B)	110.8	O(4)-C(13)-H(13B)	109.5
C(7)-C(8)-H(8B)	110.8	H(13A)-C(13)-H(13B)	109.5
H(8A)-C(8)-H(8B)	108.9	O(4)-C(13)-H(13C)	109.5
C(10)-C(9)-C(1)	123.36(17)	H(13A)-C(13)-H(13C)	109.5
C(10)-C(9)-C(8)	127.52(19)	H(13B)-C(13)-H(13C)	109.5
C(1)-C(9)-C(8)	108.85(16)	C(1)-O(1)-C(2)	113.52(13)
C(9)-C(10)-C(11)	126.29(19)	C(4)-O(2)-C(3)	113.98(14)
C(9)-C(10)-H(10A)	116.9	C(12)-O(4)-C(13)	116.06(16)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for product **4.63**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	20(1)	33(1)	34(1)	-4(1)	-2(1)	-1(1)
C(2)	22(1)	43(1)	54(1)	2(1)	-3(1)	6(1)
C(3)	29(1)	39(1)	52(1)	0(1)	0(1)	10(1)
C(4)	21(1)	32(1)	32(1)	3(1)	0(1)	-1(1)
C(5)	24(1)	40(1)	29(1)	4(1)	-2(1)	3(1)
C(6)	28(1)	39(1)	32(1)	-3(1)	-3(1)	2(1)
C(7)	41(1)	41(1)	44(1)	-9(1)	3(1)	7(1)
C(8)	42(1)	37(1)	47(1)	-3(1)	3(1)	11(1)
C(9)	26(1)	29(1)	39(1)	-3(1)	-4(1)	-1(1)
C(10)	37(1)	37(1)	39(1)	1(1)	-2(1)	-3(1)
C(11)	61(1)	49(1)	50(1)	12(1)	2(1)	2(1)
C(12)	26(1)	33(1)	32(1)	3(1)	2(1)	-6(1)
C(13)	40(1)	64(1)	43(1)	4(1)	-18(1)	-8(1)
O(1)	19(1)	38(1)	51(1)	2(1)	2(1)	-1(1)
O(2)	29(1)	32(1)	43(1)	5(1)	-2(1)	2(1)
O(3)	40(1)	58(1)	35(1)	-9(1)	4(1)	-1(1)
O(4)	29(1)	44(1)	39(1)	-2(1)	-11(1)	1(1)
O(5)	33(1)	66(1)	40(1)	-2(1)	10(1)	-4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10 ^{3}) for product **4.63**.

	x	y	z	U(eq)
H(2A)	12525	4287	10827	48
H(2B)	13836	4135	9892	48
H(3A)	11669	3217	8950	48
H(3B)	12118	2587	9993	48
H(6A)	10270	5401	11434	40
H(7A)	9812	7270	11088	50
H(7B)	7891	6872	11334	50
H(8A)	7173	6772	9627	50
H(8B)	8488	7781	9588	50
H(10A)	10980	6027	7913	45
H(11A)	10420	7482	6916	79
H(11B)	10152	8181	7940	79
H(11C)	8569	7550	7436	79
H(13A)	4447	4776	7844	74
H(13B)	5295	3599	7715	74
H(13C)	6126	4631	7156	74

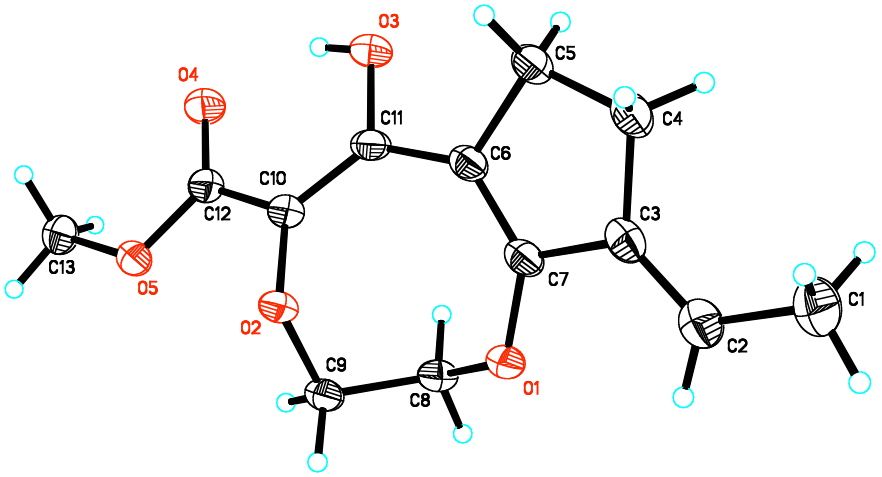
Table 6. Torsion angles [°] for product **4.63**.

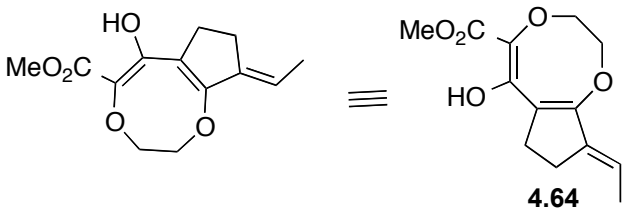
O(1)-C(2)-C(3)-O(2)	-63.3(2)
O(1)-C(1)-C(4)-O(2)	33.8(2)
C(9)-C(1)-C(4)-O(2)	162.71(15)
C(6)-C(1)-C(4)-O(2)	-91.19(15)
O(1)-C(1)-C(4)-C(12)	-97.94(18)
C(9)-C(1)-C(4)-C(12)	31.0(2)
C(6)-C(1)-C(4)-C(12)	137.06(14)
O(1)-C(1)-C(4)-C(5)	137.67(17)
C(9)-C(1)-C(4)-C(5)	-93.42(16)
C(6)-C(1)-C(4)-C(5)	12.67(12)
O(2)-C(4)-C(5)-O(5)	-80.5(2)
C(12)-C(4)-C(5)-O(5)	44.5(3)
C(1)-C(4)-C(5)-O(5)	166.5(2)
O(2)-C(4)-C(5)-C(6)	100.00(13)
C(12)-C(4)-C(5)-C(6)	-135.09(15)
C(1)-C(4)-C(5)-C(6)	-13.02(12)
O(5)-C(5)-C(6)-C(7)	-58.7(3)
C(4)-C(5)-C(6)-C(7)	120.83(16)
O(5)-C(5)-C(6)-C(1)	-166.4(2)
C(4)-C(5)-C(6)-C(1)	13.17(12)
O(1)-C(1)-C(6)-C(7)	110.46(17)
C(9)-C(1)-C(6)-C(7)	-13.40(17)
C(4)-C(1)-C(6)-C(7)	-128.79(14)
O(1)-C(1)-C(6)-C(5)	-133.60(16)
C(9)-C(1)-C(6)-C(5)	102.54(14)
C(4)-C(1)-C(6)-C(5)	-12.85(12)
C(5)-C(6)-C(7)-C(8)	-66.5(2)
C(1)-C(6)-C(7)-C(8)	29.09(18)
C(6)-C(7)-C(8)-C(9)	-33.45(19)
O(1)-C(1)-C(9)-C(10)	35.7(2)
C(6)-C(1)-C(9)-C(10)	166.67(16)
C(4)-C(1)-C(9)-C(10)	-96.3(2)
O(1)-C(1)-C(9)-C(8)	-138.74(15)
C(6)-C(1)-C(9)-C(8)	-7.81(18)

C(4)-C(1)-C(9)-C(8)	89.23(18)
C(7)-C(8)-C(9)-C(10)	-148.32(19)
C(7)-C(8)-C(9)-C(1)	25.9(2)
C(1)-C(9)-C(10)-C(11)	-173.64(19)
C(8)-C(9)-C(10)-C(11)	-0.2(3)
O(2)-C(4)-C(12)-O(3)	-39.7(2)
C(5)-C(4)-C(12)-O(3)	-161.90(17)
C(1)-C(4)-C(12)-O(3)	93.5(2)
O(2)-C(4)-C(12)-O(4)	139.17(15)
C(5)-C(4)-C(12)-O(4)	17.0(2)
C(1)-C(4)-C(12)-O(4)	-87.69(17)
C(9)-C(1)-O(1)-C(2)	-171.91(15)
C(6)-C(1)-O(1)-C(2)	66.6(2)
C(4)-C(1)-O(1)-C(2)	-40.6(2)
C(3)-C(2)-O(1)-C(1)	55.2(2)
C(12)-C(4)-O(2)-C(3)	93.59(16)
C(5)-C(4)-O(2)-C(3)	-134.38(15)
C(1)-C(4)-O(2)-C(3)	-42.5(2)
C(2)-C(3)-O(2)-C(4)	57.9(2)
O(3)-C(12)-O(4)-C(13)	1.8(3)
C(4)-C(12)-O(4)-C(13)	-176.99(15)

Symmetry transformations used to generate equivalent atoms:

14. X-ray crystallographic structure of product 4.64





4.64

Table 1. Crystal data and structure refinement for product **4.64**.

Identification code	yl1026	
Empirical formula	C13 H16 O5	
Formula weight	252.26	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 20.6286(17) Å	α= 90°.
	b = 4.1788(3) Å	β= 95.292(6)°.
	c = 14.3033(9) Å	γ = 90°.
Volume	1227.73(15) $Å^3$	
Z	4	
Density (calculated)	1.365 Mg/m^3	
Absorption coefficient	0.879 mm^{-1}	
F(000)	536	
Crystal size	0.38 x 0.06 x 0.03 mm^3	
Theta range for data collection	2.15 to 67.93°.	
Index ranges	-24<=h<=22, -5<=k<=4, -17<=l<=16	
Reflections collected	7502	
Independent reflections	2112 [R(int) = 0.0375]	
Completeness to theta = 67.93°	95.5 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2112 / 0 / 164	
Goodness-of-fit on F^2	1.007	
Final R indices [I>2sigma(I)]	R1 = 0.0561, wR2 = 0.1588	
R indices (all data)	R1 = 0.0825, wR2 = 0.1769	
Extinction coefficient	0.0030(7)	
Largest diff. peak and hole	0.331 and -0.271 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for product **4.64**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	264(2)	-373(10)	8783(2)	69(1)
C(2)	907(2)	1212(8)	9026(2)	55(1)
C(3)	1353(1)	1745(7)	8421(2)	44(1)
C(4)	1319(1)	830(8)	7401(2)	52(1)
C(5)	1929(1)	2301(8)	7037(2)	48(1)
C(6)	2328(1)	3542(7)	7903(2)	38(1)
C(7)	1974(1)	3327(7)	8654(2)	39(1)
C(8)	2584(1)	6679(7)	9780(2)	40(1)
C(9)	3234(1)	5193(7)	10057(2)	40(1)
C(10)	3491(1)	4809(7)	8483(2)	38(1)
C(11)	2975(1)	4856(7)	7817(2)	39(1)
C(12)	4090(1)	6379(7)	8326(2)	41(1)
C(13)	5147(1)	7948(8)	8926(2)	47(1)
O(1)	2095(1)	4280(5)	9560(1)	41(1)
O(2)	3442(1)	3175(5)	9321(1)	39(1)
O(3)	3041(1)	6086(5)	6956(1)	50(1)
O(4)	4188(1)	7723(5)	7581(1)	51(1)
O(5)	4543(1)	6321(5)	9060(1)	42(1)

Table 3. Bond lengths [Å] and angles [°] for product **4.64**.

C(1)-C(2)	1.495(4)	O(3)-H(3A)	0.8200
C(1)-H(1A)	0.9600		
C(1)-H(1B)	0.9600	C(2)-C(1)-H(1A)	109.5
C(1)-H(1C)	0.9600	C(2)-C(1)-H(1B)	109.5
C(2)-C(3)	1.339(4)	H(1A)-C(1)-H(1B)	109.5
C(2)-H(2A)	0.9300	C(2)-C(1)-H(1C)	109.5
C(3)-C(7)	1.453(4)	H(1A)-C(1)-H(1C)	109.5
C(3)-C(4)	1.504(4)	H(1B)-C(1)-H(1C)	109.5
C(4)-C(5)	1.535(4)	C(3)-C(2)-C(1)	124.9(3)
C(4)-H(4A)	0.9700	C(3)-C(2)-H(2A)	117.6
C(4)-H(4B)	0.9700	C(1)-C(2)-H(2A)	117.6
C(5)-C(6)	1.514(3)	C(2)-C(3)-C(7)	124.9(3)
C(5)-H(5A)	0.9700	C(2)-C(3)-C(4)	127.7(3)
C(5)-H(5B)	0.9700	C(7)-C(3)-C(4)	107.4(2)
C(6)-C(7)	1.355(4)	C(3)-C(4)-C(5)	105.1(2)
C(6)-C(11)	1.460(4)	C(3)-C(4)-H(4A)	110.7
C(7)-O(1)	1.356(3)	C(5)-C(4)-H(4A)	110.7
C(8)-O(1)	1.437(3)	C(3)-C(4)-H(4B)	110.7
C(8)-C(9)	1.497(3)	C(5)-C(4)-H(4B)	110.7
C(8)-H(8A)	0.9700	H(4A)-C(4)-H(4B)	108.8
C(8)-H(8B)	0.9700	C(6)-C(5)-C(4)	105.0(2)
C(9)-O(2)	1.445(3)	C(6)-C(5)-H(5A)	110.7
C(9)-H(9A)	0.9700	C(4)-C(5)-H(5A)	110.7
C(9)-H(9B)	0.9700	C(6)-C(5)-H(5B)	110.7
C(10)-C(11)	1.362(4)	C(4)-C(5)-H(5B)	110.7
C(10)-O(2)	1.391(3)	H(5A)-C(5)-H(5B)	108.8
C(10)-C(12)	1.435(4)	C(7)-C(6)-C(11)	130.9(2)
C(11)-O(3)	1.353(3)	C(7)-C(6)-C(5)	109.6(2)
C(12)-O(4)	1.237(3)	C(11)-C(6)-C(5)	119.4(2)
C(12)-O(5)	1.340(3)	C(6)-C(7)-O(1)	132.3(3)
C(13)-O(5)	1.447(3)	C(6)-C(7)-C(3)	112.0(2)
C(13)-H(13A)	0.9600	O(1)-C(7)-C(3)	115.6(2)
C(13)-H(13B)	0.9600	O(1)-C(8)-C(9)	111.3(2)
C(13)-H(13C)	0.9600	O(1)-C(8)-H(8A)	109.4

C(9)-C(8)-H(8A)	109.4	C(10)-C(11)-C(6)	126.7(2)
O(1)-C(8)-H(8B)	109.4	O(4)-C(12)-O(5)	121.7(3)
C(9)-C(8)-H(8B)	109.4	O(4)-C(12)-C(10)	123.6(3)
H(8A)-C(8)-H(8B)	108.0	O(5)-C(12)-C(10)	114.6(2)
O(2)-C(9)-C(8)	111.6(2)	O(5)-C(13)-H(13A)	109.5
O(2)-C(9)-H(9A)	109.3	O(5)-C(13)-H(13B)	109.5
C(8)-C(9)-H(9A)	109.3	H(13A)-C(13)-H(13B)	109.5
O(2)-C(9)-H(9B)	109.3	O(5)-C(13)-H(13C)	109.5
C(8)-C(9)-H(9B)	109.3	H(13A)-C(13)-H(13C)	109.5
H(9A)-C(9)-H(9B)	108.0	H(13B)-C(13)-H(13C)	109.5
C(11)-C(10)-O(2)	119.7(3)	C(7)-O(1)-C(8)	118.5(2)
C(11)-C(10)-C(12)	120.8(3)	C(10)-O(2)-C(9)	113.0(2)
O(2)-C(10)-C(12)	119.5(2)	C(11)-O(3)-H(3A)	109.5
O(3)-C(11)-C(10)	120.3(3)	C(12)-O(5)-C(13)	115.7(2)
O(3)-C(11)-C(6)	112.9(2)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for product **4.64**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	51(2)	79(3)	76(2)	-5(2)	-2(2)	-12(2)
C(2)	47(2)	62(2)	55(2)	-2(2)	-3(1)	-4(2)
C(3)	41(2)	44(2)	45(2)	1(1)	-8(1)	5(1)
C(4)	45(2)	58(2)	50(2)	-7(2)	-10(1)	7(2)
C(5)	45(2)	59(2)	38(2)	-5(1)	-7(1)	7(2)
C(6)	41(2)	41(2)	32(1)	1(1)	-4(1)	6(1)
C(7)	42(2)	42(2)	33(2)	-1(1)	-6(1)	6(1)
C(8)	47(2)	45(2)	28(1)	-2(1)	3(1)	-1(1)
C(9)	42(2)	49(2)	28(1)	2(1)	0(1)	-2(1)
C(10)	39(2)	46(2)	30(1)	2(1)	3(1)	3(1)
C(11)	48(2)	44(2)	25(1)	0(1)	3(1)	7(1)
C(12)	41(2)	49(2)	34(2)	3(1)	5(1)	8(1)
C(13)	37(2)	55(2)	49(2)	1(2)	6(1)	-3(1)
O(1)	40(1)	54(1)	29(1)	-2(1)	0(1)	-3(1)
O(2)	43(1)	46(1)	26(1)	3(1)	1(1)	3(1)
O(3)	53(1)	69(2)	29(1)	7(1)	3(1)	3(1)
O(4)	50(1)	64(2)	38(1)	11(1)	7(1)	1(1)
O(5)	36(1)	54(1)	35(1)	5(1)	1(1)	-1(1)

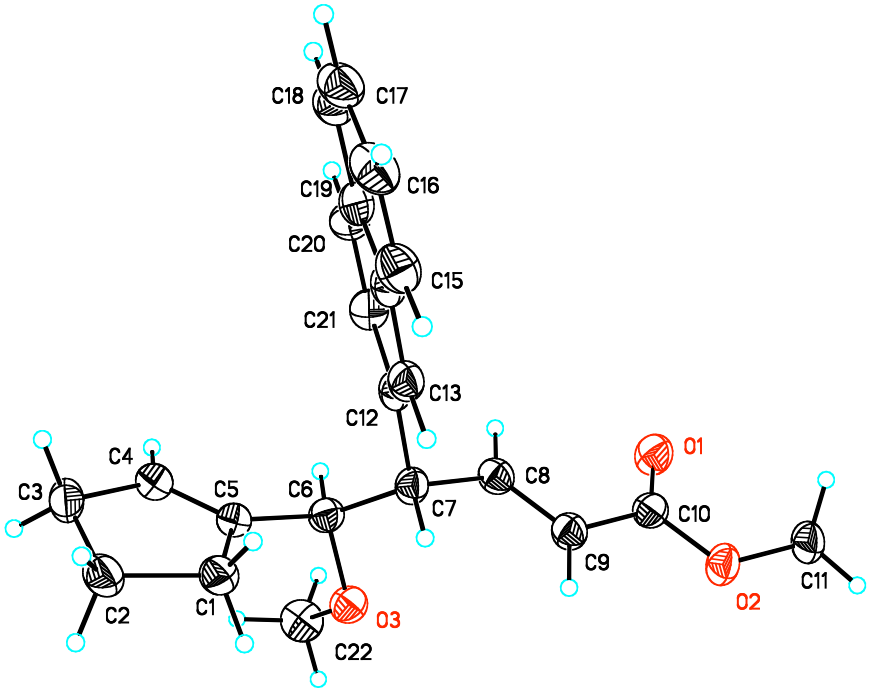
Table 5. Torsion angles [°] for product **4.64**.

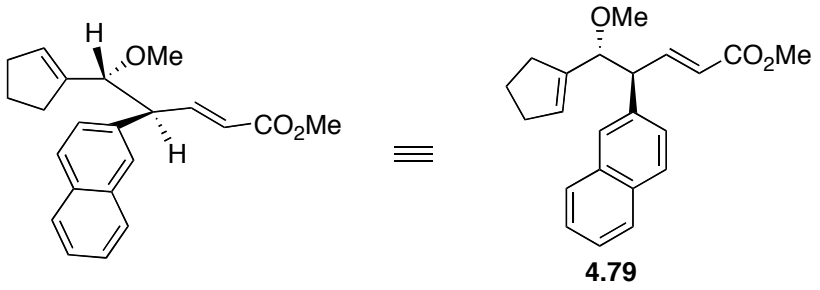
C(1)-C(2)-C(3)-C(7)	179.1(3)
C(1)-C(2)-C(3)-C(4)	-1.7(6)
C(2)-C(3)-C(4)-C(5)	174.9(3)
C(7)-C(3)-C(4)-C(5)	-5.8(3)
C(3)-C(4)-C(5)-C(6)	8.3(3)
C(4)-C(5)-C(6)-C(7)	-8.3(3)
C(4)-C(5)-C(6)-C(11)	174.6(3)
C(11)-C(6)-C(7)-O(1)	1.1(6)
C(5)-C(6)-C(7)-O(1)	-175.5(3)
C(11)-C(6)-C(7)-C(3)	-178.5(3)
C(5)-C(6)-C(7)-C(3)	4.9(3)
C(2)-C(3)-C(7)-C(6)	-179.9(3)
C(4)-C(3)-C(7)-C(6)	0.7(3)
C(2)-C(3)-C(7)-O(1)	0.4(5)
C(4)-C(3)-C(7)-O(1)	-179.0(3)
O(1)-C(8)-C(9)-O(2)	58.7(3)
O(2)-C(10)-C(11)-O(3)	-171.7(2)
C(12)-C(10)-C(11)-O(3)	7.2(4)
O(2)-C(10)-C(11)-C(6)	5.2(5)
C(12)-C(10)-C(11)-C(6)	-175.9(3)
C(7)-C(6)-C(11)-O(3)	-149.3(3)
C(5)-C(6)-C(11)-O(3)	27.2(4)
C(7)-C(6)-C(11)-C(10)	33.7(5)
C(5)-C(6)-C(11)-C(10)	-149.9(3)
C(11)-C(10)-C(12)-O(4)	-3.3(5)
O(2)-C(10)-C(12)-O(4)	175.6(3)
C(11)-C(10)-C(12)-O(5)	175.9(3)
O(2)-C(10)-C(12)-O(5)	-5.1(4)
C(6)-C(7)-O(1)-C(8)	19.6(5)
C(3)-C(7)-O(1)-C(8)	-160.8(2)
C(9)-C(8)-O(1)-C(7)	-92.7(3)
C(11)-C(10)-O(2)-C(9)	-93.0(3)
C(12)-C(10)-O(2)-C(9)	88.0(3)
C(8)-C(9)-O(2)-C(10)	59.0(3)

O(4)-C(12)-O(5)-C(13)	0.5(4)
C(10)-C(12)-O(5)-C(13)	-178.7(2)

Symmetry transformations used to generate equivalent atoms:

15. X-ray crystallographic structure of product 4.79





4.79

Table 1. Crystal data and structure refinement for product **4.79**.

Identification code	90n	
Empirical formula	C22 H24 O3	
Formula weight	336.41	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 8.8529(9) Å	α= 90°.
	b = 6.2316(6) Å	β= 102.238(7)°.
	c = 16.8666(14) Å	γ = 90°.
Volume	909.35(15) $Å^3$	
Z	2	
Density (calculated)	1.229 Mg/m^3	
Absorption coefficient	0.639 mm^{-1}	
F(000)	360	
Crystal size	0.40 x 0.18 x 0.04 mm^3	
Theta range for data collection	2.68 to 69.05°.	
Index ranges	-9<=h<=10, -7<=k<=7, -20<=l<=19	
Reflections collected	5846	
Independent reflections	2672 [R(int) = 0.0246]	
Completeness to theta = 69.05°	91.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9780 and 0.7841	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2672 / 1 / 226	
Goodness-of-fit on F^2	1.111	
Final R indices [I>2sigma(I)]	R1 = 0.0383, wR2 = 0.0970	
R indices (all data)	R1 = 0.0426, wR2 = 0.0996	
Absolute structure parameter	0.0(3)	
Largest diff. peak and hole	0.186 and -0.155 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for product **4.79**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-5652(3)	-6270(4)	-1215(2)	39(1)
C(2)	-6736(3)	-7823(5)	-881(2)	47(1)
C(3)	-6117(3)	-10103(4)	-957(2)	46(1)
C(4)	-4552(3)	-9716(4)	-1143(1)	41(1)
C(5)	-4290(3)	-7668(4)	-1280(1)	35(1)
C(6)	-2823(3)	-6783(4)	-1457(1)	35(1)
C(7)	-3082(3)	-5264(3)	-2193(1)	34(1)
C(8)	-1556(3)	-4573(4)	-2374(1)	35(1)
C(9)	-1007(3)	-2601(4)	-2282(1)	37(1)
C(10)	380(3)	-1946(4)	-2578(1)	36(1)
C(11)	1682(3)	1093(4)	-2957(2)	46(1)
C(12)	-4073(3)	-6287(4)	-2949(1)	34(1)
C(13)	-5390(3)	-5334(4)	-3354(1)	37(1)
C(14)	-6346(3)	-6287(4)	-4060(1)	35(1)
C(15)	-7726(3)	-5334(4)	-4480(2)	44(1)
C(16)	-8623(3)	-6349(5)	-5125(2)	50(1)
C(17)	-8195(3)	-8360(5)	-5389(2)	47(1)
C(18)	-6871(3)	-9328(4)	-5010(2)	42(1)
C(19)	-5888(3)	-8311(4)	-4320(1)	37(1)
C(20)	-4506(3)	-9258(4)	-3910(2)	40(1)
C(21)	-3615(3)	-8259(4)	-3247(2)	40(1)
C(22)	-1155(3)	-6830(5)	-150(2)	49(1)
O(1)	1266(2)	-3112(3)	-2813(1)	48(1)
O(2)	487(2)	215(3)	-2578(1)	43(1)
O(3)	-2029(2)	-5528(3)	-779(1)	39(1)

Table 3. Bond lengths [Å] and angles [°] for product **4.79**.

C(1)-C(5)	1.510(3)	C(14)-C(19)	1.423(3)
C(1)-C(2)	1.551(3)	C(15)-C(16)	1.359(4)
C(1)-H(1A)	0.9900	C(15)-H(15A)	0.9500
C(1)-H(1B)	0.9900	C(16)-C(17)	1.409(4)
C(2)-C(3)	1.538(4)	C(16)-H(16A)	0.9500
C(2)-H(2A)	0.9900	C(17)-C(18)	1.352(4)
C(2)-H(2B)	0.9900	C(17)-H(17A)	0.9500
C(3)-C(4)	1.503(3)	C(18)-C(19)	1.443(3)
C(3)-H(3A)	0.9900	C(18)-H(18A)	0.9500
C(3)-H(3B)	0.9900	C(19)-C(20)	1.402(3)
C(4)-C(5)	1.326(3)	C(20)-C(21)	1.373(3)
C(4)-H(4A)	0.9500	C(20)-H(20A)	0.9500
C(5)-C(6)	1.499(3)	C(21)-H(21A)	0.9500
C(6)-O(3)	1.439(3)	C(22)-O(3)	1.427(3)
C(6)-C(7)	1.538(3)	C(22)-H(22A)	0.9800
C(6)-H(6A)	1.0000	C(22)-H(22B)	0.9800
C(7)-C(8)	1.510(3)	C(22)-H(22C)	0.9800
C(7)-C(12)	1.526(3)		
C(7)-H(7A)	1.0000	C(5)-C(1)-C(2)	103.4(2)
C(8)-C(9)	1.318(3)	C(5)-C(1)-H(1A)	111.1
C(8)-H(8A)	0.9500	C(2)-C(1)-H(1A)	111.1
C(9)-C(10)	1.478(3)	C(5)-C(1)-H(1B)	111.1
C(9)-H(9A)	0.9500	C(2)-C(1)-H(1B)	111.1
C(10)-O(1)	1.196(3)	H(1A)-C(1)-H(1B)	109.0
C(10)-O(2)	1.350(3)	C(3)-C(2)-C(1)	106.67(19)
C(11)-O(2)	1.454(2)	C(3)-C(2)-H(2A)	110.4
C(11)-H(11A)	0.9800	C(1)-C(2)-H(2A)	110.4
C(11)-H(11B)	0.9800	C(3)-C(2)-H(2B)	110.4
C(11)-H(11C)	0.9800	C(1)-C(2)-H(2B)	110.4
C(12)-C(13)	1.356(3)	H(2A)-C(2)-H(2B)	108.6
C(12)-C(21)	1.419(3)	C(4)-C(3)-C(2)	103.28(19)
C(13)-C(14)	1.436(3)	C(4)-C(3)-H(3A)	111.1
C(13)-H(13A)	0.9500	C(2)-C(3)-H(3A)	111.1
C(14)-C(15)	1.408(3)	C(4)-C(3)-H(3B)	111.1

C(2)-C(3)-H(3B)	111.1	C(13)-C(12)-C(7)	121.2(2)
H(3A)-C(3)-H(3B)	109.1	C(21)-C(12)-C(7)	120.1(2)
C(5)-C(4)-C(3)	113.2(2)	C(12)-C(13)-C(14)	121.9(2)
C(5)-C(4)-H(4A)	123.4	C(12)-C(13)-H(13A)	119.0
C(3)-C(4)-H(4A)	123.4	C(14)-C(13)-H(13A)	119.0
C(4)-C(5)-C(6)	125.5(2)	C(15)-C(14)-C(19)	119.5(2)
C(4)-C(5)-C(1)	111.8(2)	C(15)-C(14)-C(13)	122.7(2)
C(6)-C(5)-C(1)	122.8(2)	C(19)-C(14)-C(13)	117.8(2)
O(3)-C(6)-C(5)	109.83(17)	C(16)-C(15)-C(14)	120.3(3)
O(3)-C(6)-C(7)	105.71(17)	C(16)-C(15)-H(15A)	119.9
C(5)-C(6)-C(7)	113.58(19)	C(14)-C(15)-H(15A)	119.9
O(3)-C(6)-H(6A)	109.2	C(15)-C(16)-C(17)	121.1(3)
C(5)-C(6)-H(6A)	109.2	C(15)-C(16)-H(16A)	119.5
C(7)-C(6)-H(6A)	109.2	C(17)-C(16)-H(16A)	119.5
C(8)-C(7)-C(12)	109.28(17)	C(18)-C(17)-C(16)	120.8(3)
C(8)-C(7)-C(6)	110.59(18)	C(18)-C(17)-H(17A)	119.6
C(12)-C(7)-C(6)	112.22(17)	C(16)-C(17)-H(17A)	119.6
C(8)-C(7)-H(7A)	108.2	C(17)-C(18)-C(19)	120.0(2)
C(12)-C(7)-H(7A)	108.2	C(17)-C(18)-H(18A)	120.0
C(6)-C(7)-H(7A)	108.2	C(19)-C(18)-H(18A)	120.0
C(9)-C(8)-C(7)	124.4(2)	C(20)-C(19)-C(14)	119.8(2)
C(9)-C(8)-H(8A)	117.8	C(20)-C(19)-C(18)	121.8(2)
C(7)-C(8)-H(8A)	117.8	C(14)-C(19)-C(18)	118.4(2)
C(8)-C(9)-C(10)	122.0(2)	C(21)-C(20)-C(19)	120.1(2)
C(8)-C(9)-H(9A)	119.0	C(21)-C(20)-H(20A)	120.0
C(10)-C(9)-H(9A)	119.0	C(19)-C(20)-H(20A)	120.0
O(1)-C(10)-O(2)	123.7(2)	C(20)-C(21)-C(12)	121.6(2)
O(1)-C(10)-C(9)	126.4(2)	C(20)-C(21)-H(21A)	119.2
O(2)-C(10)-C(9)	109.81(19)	C(12)-C(21)-H(21A)	119.2
O(2)-C(11)-H(11A)	109.5	O(3)-C(22)-H(22A)	109.5
O(2)-C(11)-H(11B)	109.5	O(3)-C(22)-H(22B)	109.5
H(11A)-C(11)-H(11B)	109.5	H(22A)-C(22)-H(22B)	109.5
O(2)-C(11)-H(11C)	109.5	O(3)-C(22)-H(22C)	109.5
H(11A)-C(11)-H(11C)	109.5	H(22A)-C(22)-H(22C)	109.5
H(11B)-C(11)-H(11C)	109.5	H(22B)-C(22)-H(22C)	109.5
C(13)-C(12)-C(21)	118.7(2)	C(10)-O(2)-C(11)	115.64(19)

C(22)-O(3)-C(6) 112.29(18)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for product **4.79**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	38(2)	42(1)	39(1)	-2(1)	12(1)	-2(1)
C(2)	41(2)	59(2)	42(1)	-5(1)	16(1)	-9(1)
C(3)	47(2)	53(2)	36(1)	5(1)	8(1)	-17(1)
C(4)	46(2)	42(1)	36(1)	-2(1)	11(1)	-5(1)
C(5)	38(1)	36(1)	31(1)	-3(1)	9(1)	-5(1)
C(6)	35(1)	33(1)	37(1)	-4(1)	10(1)	-1(1)
C(7)	33(1)	31(1)	39(1)	1(1)	12(1)	-1(1)
C(8)	33(1)	39(1)	35(1)	0(1)	10(1)	1(1)
C(9)	37(1)	37(1)	40(1)	0(1)	13(1)	0(1)
C(10)	34(1)	40(1)	36(1)	-3(1)	7(1)	-5(1)
C(11)	46(2)	48(1)	48(1)	3(1)	15(1)	-16(1)
C(12)	29(1)	37(1)	38(1)	2(1)	13(1)	-4(1)
C(13)	39(1)	35(1)	42(1)	0(1)	19(1)	-2(1)
C(14)	31(1)	38(1)	41(1)	4(1)	16(1)	-1(1)
C(15)	41(2)	49(1)	45(1)	6(1)	15(1)	6(1)
C(16)	44(2)	67(2)	42(1)	5(1)	13(1)	1(1)
C(17)	38(2)	66(2)	37(1)	-3(1)	11(1)	-7(1)
C(18)	38(2)	53(1)	37(1)	-2(1)	13(1)	-6(1)
C(19)	30(1)	42(1)	41(1)	3(1)	15(1)	-3(1)
C(20)	45(2)	35(1)	43(1)	-3(1)	15(1)	4(1)
C(21)	38(2)	38(1)	44(1)	2(1)	11(1)	3(1)
C(22)	39(2)	58(2)	48(2)	1(1)	4(1)	2(1)
O(1)	41(1)	45(1)	62(1)	-5(1)	22(1)	-5(1)
O(2)	40(1)	37(1)	54(1)	2(1)	17(1)	-7(1)
O(3)	35(1)	41(1)	39(1)	-3(1)	5(1)	-4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for product **4.79**.

	x	y	z	U(eq)
H(1A)	-6164	-5697	-1752	47
H(1B)	-5328	-5058	-838	47
H(2A)	-6729	-7488	-306	56
H(2B)	-7809	-7692	-1198	56
H(3A)	-6032	-10913	-445	55
H(3B)	-6795	-10904	-1402	55
H(4A)	-3825	-10826	-1160	49
H(6A)	-2144	-7997	-1552	42
H(7A)	-3630	-3955	-2056	40
H(8A)	-950	-5631	-2568	42
H(9A)	-1519	-1571	-2018	45
H(11A)	1666	2663	-2927	69
H(11B)	1492	646	-3527	69
H(11C)	2695	563	-2673	69
H(13A)	-5687	-3995	-3164	45
H(15A)	-8032	-3975	-4313	53
H(16A)	-9554	-5691	-5402	60
H(17A)	-8844	-9045	-5839	56
H(18A)	-6588	-10676	-5198	51
H(20A)	-4184	-10592	-4091	48
H(21A)	-2671	-8903	-2982	48
H(22A)	-643	-5913	300	73
H(22B)	-374	-7635	-361	73
H(22C)	-1847	-7835	45	73

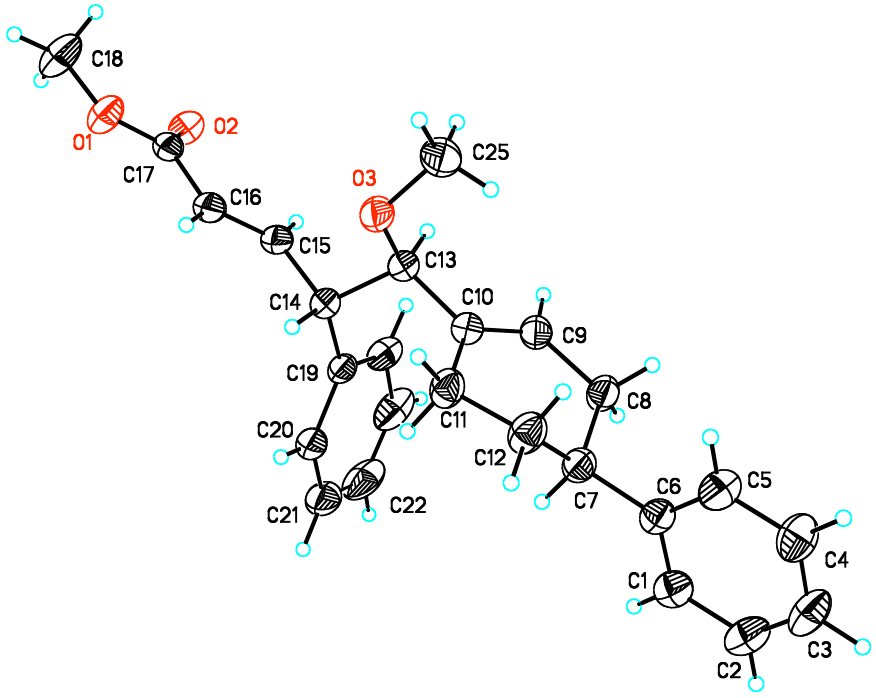
Table 6. Torsion angles [°] for product **4.79**.

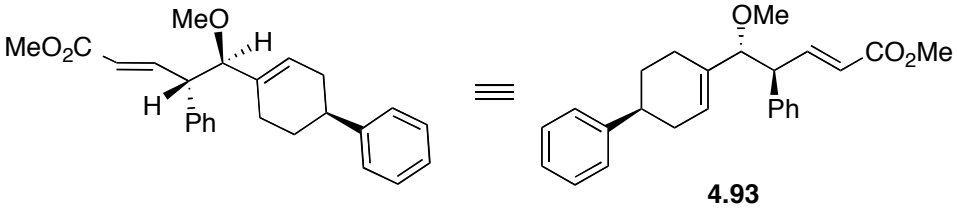
C(5)-C(1)-C(2)-C(3)	-12.6(3)
C(1)-C(2)-C(3)-C(4)	12.4(3)
C(2)-C(3)-C(4)-C(5)	-7.9(3)
C(3)-C(4)-C(5)-C(6)	178.2(2)
C(3)-C(4)-C(5)-C(1)	-0.2(3)
C(2)-C(1)-C(5)-C(4)	8.2(3)
C(2)-C(1)-C(5)-C(6)	-170.3(2)
C(4)-C(5)-C(6)-O(3)	-109.9(3)
C(1)-C(5)-C(6)-O(3)	68.4(3)
C(4)-C(5)-C(6)-C(7)	131.9(3)
C(1)-C(5)-C(6)-C(7)	-49.8(3)
O(3)-C(6)-C(7)-C(8)	63.9(2)
C(5)-C(6)-C(7)-C(8)	-175.60(19)
O(3)-C(6)-C(7)-C(12)	-173.76(17)
C(5)-C(6)-C(7)-C(12)	-53.3(2)
C(12)-C(7)-C(8)-C(9)	123.8(3)
C(6)-C(7)-C(8)-C(9)	-112.2(3)
C(7)-C(8)-C(9)-C(10)	-171.1(2)
C(8)-C(9)-C(10)-O(1)	-11.6(4)
C(8)-C(9)-C(10)-O(2)	166.0(2)
C(8)-C(7)-C(12)-C(13)	-112.8(2)
C(6)-C(7)-C(12)-C(13)	124.2(2)
C(8)-C(7)-C(12)-C(21)	66.5(2)
C(6)-C(7)-C(12)-C(21)	-56.6(2)
C(21)-C(12)-C(13)-C(14)	1.6(3)
C(7)-C(12)-C(13)-C(14)	-179.16(17)
C(12)-C(13)-C(14)-C(15)	179.1(2)
C(12)-C(13)-C(14)-C(19)	1.2(3)
C(19)-C(14)-C(15)-C(16)	0.7(3)
C(13)-C(14)-C(15)-C(16)	-177.2(2)
C(14)-C(15)-C(16)-C(17)	-0.3(4)
C(15)-C(16)-C(17)-C(18)	-0.5(4)
C(16)-C(17)-C(18)-C(19)	0.8(3)
C(15)-C(14)-C(19)-C(20)	179.2(2)

C(13)-C(14)-C(19)-C(20)	-2.8(3)
C(15)-C(14)-C(19)-C(18)	-0.4(3)
C(13)-C(14)-C(19)-C(18)	177.60(19)
C(17)-C(18)-C(19)-C(20)	-179.9(2)
C(17)-C(18)-C(19)-C(14)	-0.3(3)
C(14)-C(19)-C(20)-C(21)	1.6(3)
C(18)-C(19)-C(20)-C(21)	-178.8(2)
C(19)-C(20)-C(21)-C(12)	1.3(3)
C(13)-C(12)-C(21)-C(20)	-2.9(3)
C(7)-C(12)-C(21)-C(20)	177.8(2)
O(1)-C(10)-O(2)-C(11)	5.6(4)
C(9)-C(10)-O(2)-C(11)	-172.1(2)
C(5)-C(6)-O(3)-C(22)	81.4(2)
C(7)-C(6)-O(3)-C(22)	-155.71(17)

Symmetry transformations used to generate equivalent atoms:

16. X-ray crystallographic structure of product 4.93





4.93

Table 1. Crystal data and structure refinement for product **4.93**.

Identification code	yl_9_128cope	
Empirical formula	C25 H28 O3	
Formula weight	376.47	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 8.46960(10) Å	α= 90°.
	b = 8.2702(2) Å	β= 103.0450(10)°.
	c = 15.7541(3) Å	γ = 90°.
Volume	1075.02(4) $Å^3$	
Z	2	
Density (calculated)	1.163 Mg/m^3	
Absorption coefficient	0.591 mm^{-1}	
F(000)	404	
Crystal size	0.29 x 0.08 x 0.07 mm^3	
Theta range for data collection	2.88 to 69.41°.	
Index ranges	-8<=h<=10, -9<=k<=8, -18<=l<=18	
Reflections collected	5719	
Independent reflections	2970 [R(int) = 0.0143]	
Completeness to theta = 69.41°	93.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9598 and 0.8472	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2970 / 1 / 253	
Goodness-of-fit on F^2	1.017	
Final R indices [I>2sigma(I)]	R1 = 0.0320, wR2 = 0.0834	
R indices (all data)	R1 = 0.0343, wR2 = 0.0855	
Absolute structure parameter	0.0(2)	
Largest diff. peak and hole	0.107 and -0.148 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for product **4.93**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	14043(2)	6046(3)	8600(1)	48(1)
C(2)	14896(3)	7417(3)	8940(2)	58(1)
C(3)	14308(3)	8420(3)	9488(1)	60(1)
C(4)	12841(3)	8073(3)	9689(2)	60(1)
C(5)	11989(2)	6702(3)	9348(1)	54(1)
C(6)	12575(2)	5664(2)	8796(1)	40(1)
C(7)	11624(2)	4209(2)	8382(1)	42(1)
C(8)	10254(2)	4754(2)	7623(1)	46(1)
C(9)	9043(2)	3446(2)	7295(1)	41(1)
C(10)	8969(2)	2055(2)	7689(1)	37(1)
C(11)	10118(2)	1647(3)	8542(1)	46(1)
C(12)	10945(3)	3146(3)	9000(1)	51(1)
C(13)	7720(2)	802(2)	7294(1)	37(1)
C(14)	8457(2)	-781(2)	7035(1)	38(1)
C(15)	7137(2)	-1802(2)	6485(1)	39(1)
C(16)	6514(2)	-3119(2)	6745(1)	40(1)
C(17)	5216(2)	-4044(2)	6167(1)	38(1)
C(18)	3380(3)	-6205(3)	6111(2)	64(1)
C(19)	9789(2)	-482(2)	6548(1)	40(1)
C(20)	11336(2)	-1105(3)	6878(2)	53(1)
C(21)	12542(3)	-907(3)	6431(2)	68(1)
C(22)	12228(3)	-102(4)	5643(2)	78(1)
C(23)	10710(3)	554(3)	5319(2)	67(1)
C(24)	9491(2)	368(3)	5770(1)	50(1)
C(25)	5708(2)	1526(3)	8059(2)	57(1)
O(1)	4651(2)	-5197(2)	6609(1)	50(1)
O(2)	4706(2)	-3815(2)	5390(1)	47(1)
O(3)	6761(1)	302(2)	7885(1)	45(1)

Table 3. Bond lengths [Å] and angles [°] for product **4.93**.

C(1)-C(6)	1.384(3)	C(15)-H(15A)	0.9500
C(1)-C(2)	1.386(3)	C(16)-C(17)	1.474(2)
C(1)-H(1A)	0.9500	C(16)-H(16A)	0.9500
C(2)-C(3)	1.370(3)	C(17)-O(2)	1.217(2)
C(2)-H(2A)	0.9500	C(17)-O(1)	1.332(2)
C(3)-C(4)	1.380(3)	C(18)-O(1)	1.445(2)
C(3)-H(3A)	0.9500	C(18)-H(18A)	0.9800
C(4)-C(5)	1.386(3)	C(18)-H(18B)	0.9800
C(4)-H(4A)	0.9500	C(18)-H(18C)	0.9800
C(5)-C(6)	1.390(3)	C(19)-C(24)	1.386(3)
C(5)-H(5A)	0.9500	C(19)-C(20)	1.395(3)
C(6)-C(7)	1.512(3)	C(20)-C(21)	1.375(3)
C(7)-C(12)	1.518(3)	C(20)-H(20A)	0.9500
C(7)-C(8)	1.534(3)	C(21)-C(22)	1.382(4)
C(7)-H(7A)	1.0000	C(21)-H(21A)	0.9500
C(8)-C(9)	1.501(3)	C(22)-C(23)	1.382(4)
C(8)-H(8A)	0.9900	C(22)-H(22A)	0.9500
C(8)-H(8B)	0.9900	C(23)-C(24)	1.387(3)
C(9)-C(10)	1.315(3)	C(23)-H(23A)	0.9500
C(9)-H(9A)	0.9500	C(24)-H(24A)	0.9500
C(10)-C(11)	1.509(3)	C(25)-O(3)	1.416(2)
C(10)-C(13)	1.511(2)	C(25)-H(25A)	0.9800
C(11)-C(12)	1.523(3)	C(25)-H(25B)	0.9800
C(11)-H(11A)	0.9900	C(25)-H(25C)	0.9800
C(11)-H(11B)	0.9900		
C(12)-H(12A)	0.9900	C(6)-C(1)-C(2)	121.1(2)
C(12)-H(12B)	0.9900	C(6)-C(1)-H(1A)	119.4
C(13)-O(3)	1.429(2)	C(2)-C(1)-H(1A)	119.4
C(13)-C(14)	1.544(2)	C(3)-C(2)-C(1)	120.5(2)
C(13)-H(13A)	1.0000	C(3)-C(2)-H(2A)	119.8
C(14)-C(15)	1.508(2)	C(1)-C(2)-H(2A)	119.8
C(14)-C(19)	1.520(2)	C(2)-C(3)-C(4)	119.5(2)
C(14)-H(14A)	1.0000	C(2)-C(3)-H(3A)	120.2
C(15)-C(16)	1.316(3)	C(4)-C(3)-H(3A)	120.2

C(3)-C(4)-C(5)	119.9(2)	C(7)-C(12)-H(12B)	109.3
C(3)-C(4)-H(4A)	120.0	C(11)-C(12)-H(12B)	109.3
C(5)-C(4)-H(4A)	120.0	H(12A)-C(12)-H(12B)	108.0
C(4)-C(5)-C(6)	121.27(19)	O(3)-C(13)-C(10)	112.26(15)
C(4)-C(5)-H(5A)	119.4	O(3)-C(13)-C(14)	104.49(14)
C(6)-C(5)-H(5A)	119.4	C(10)-C(13)-C(14)	113.74(13)
C(1)-C(6)-C(5)	117.68(19)	O(3)-C(13)-H(13A)	108.7
C(1)-C(6)-C(7)	120.23(17)	C(10)-C(13)-H(13A)	108.7
C(5)-C(6)-C(7)	122.03(17)	C(14)-C(13)-H(13A)	108.7
C(6)-C(7)-C(12)	115.27(16)	C(15)-C(14)-C(19)	109.85(15)
C(6)-C(7)-C(8)	109.70(16)	C(15)-C(14)-C(13)	109.56(13)
C(12)-C(7)-C(8)	109.95(15)	C(19)-C(14)-C(13)	112.68(15)
C(6)-C(7)-H(7A)	107.2	C(15)-C(14)-H(14A)	108.2
C(12)-C(7)-H(7A)	107.2	C(19)-C(14)-H(14A)	108.2
C(8)-C(7)-H(7A)	107.2	C(13)-C(14)-H(14A)	108.2
C(9)-C(8)-C(7)	113.23(16)	C(16)-C(15)-C(14)	125.62(18)
C(9)-C(8)-H(8A)	108.9	C(16)-C(15)-H(15A)	117.2
C(7)-C(8)-H(8A)	108.9	C(14)-C(15)-H(15A)	117.2
C(9)-C(8)-H(8B)	108.9	C(15)-C(16)-C(17)	122.24(18)
C(7)-C(8)-H(8B)	108.9	C(15)-C(16)-H(16A)	118.9
H(8A)-C(8)-H(8B)	107.7	C(17)-C(16)-H(16A)	118.9
C(10)-C(9)-C(8)	124.73(17)	O(2)-C(17)-O(1)	123.36(17)
C(10)-C(9)-H(9A)	117.6	O(2)-C(17)-C(16)	125.91(17)
C(8)-C(9)-H(9A)	117.6	O(1)-C(17)-C(16)	110.73(15)
C(9)-C(10)-C(11)	121.74(18)	O(1)-C(18)-H(18A)	109.5
C(9)-C(10)-C(13)	120.60(17)	O(1)-C(18)-H(18B)	109.5
C(11)-C(10)-C(13)	117.66(16)	H(18A)-C(18)-H(18B)	109.5
C(10)-C(11)-C(12)	112.04(17)	O(1)-C(18)-H(18C)	109.5
C(10)-C(11)-H(11A)	109.2	H(18A)-C(18)-H(18C)	109.5
C(12)-C(11)-H(11A)	109.2	H(18B)-C(18)-H(18C)	109.5
C(10)-C(11)-H(11B)	109.2	C(24)-C(19)-C(20)	119.01(19)
C(12)-C(11)-H(11B)	109.2	C(24)-C(19)-C(14)	121.42(16)
H(11A)-C(11)-H(11B)	107.9	C(20)-C(19)-C(14)	119.55(19)
C(7)-C(12)-C(11)	111.55(17)	C(21)-C(20)-C(19)	120.6(2)
C(7)-C(12)-H(12A)	109.3	C(21)-C(20)-H(20A)	119.7
C(11)-C(12)-H(12A)	109.3	C(19)-C(20)-H(20A)	119.7

C(20)-C(21)-C(22)	120.2(2)	C(19)-C(24)-H(24A)	120.0
C(20)-C(21)-H(21A)	119.9	C(23)-C(24)-H(24A)	120.0
C(22)-C(21)-H(21A)	119.9	O(3)-C(25)-H(25A)	109.5
C(21)-C(22)-C(23)	119.7(2)	O(3)-C(25)-H(25B)	109.5
C(21)-C(22)-H(22A)	120.2	H(25A)-C(25)-H(25B)	109.5
C(23)-C(22)-H(22A)	120.2	O(3)-C(25)-H(25C)	109.5
C(22)-C(23)-C(24)	120.4(3)	H(25A)-C(25)-H(25C)	109.5
C(22)-C(23)-H(23A)	119.8	H(25B)-C(25)-H(25C)	109.5
C(24)-C(23)-H(23A)	119.8	C(17)-O(1)-C(18)	116.10(15)
C(19)-C(24)-C(23)	120.1(2)	C(25)-O(3)-C(13)	113.24(15)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for product **4.93**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	48(1)	52(1)	43(1)	4(1)	8(1)	-2(1)
C(2)	51(1)	68(2)	53(1)	3(1)	7(1)	-19(1)
C(3)	71(1)	58(2)	46(1)	-5(1)	0(1)	-27(1)
C(4)	72(1)	58(2)	48(1)	-14(1)	13(1)	-12(1)
C(5)	51(1)	58(1)	53(1)	-6(1)	14(1)	-11(1)
C(6)	43(1)	41(1)	33(1)	4(1)	1(1)	-4(1)
C(7)	41(1)	39(1)	43(1)	1(1)	5(1)	-4(1)
C(8)	47(1)	36(1)	49(1)	5(1)	0(1)	-6(1)
C(9)	41(1)	36(1)	43(1)	0(1)	-1(1)	1(1)
C(10)	35(1)	35(1)	39(1)	0(1)	8(1)	0(1)
C(11)	53(1)	39(1)	43(1)	8(1)	3(1)	-6(1)
C(12)	57(1)	47(1)	44(1)	6(1)	2(1)	-11(1)
C(13)	34(1)	34(1)	44(1)	1(1)	10(1)	-1(1)
C(14)	34(1)	34(1)	47(1)	1(1)	10(1)	-2(1)
C(15)	31(1)	39(1)	48(1)	-3(1)	13(1)	0(1)
C(16)	33(1)	40(1)	47(1)	-3(1)	9(1)	2(1)
C(17)	31(1)	34(1)	49(1)	-5(1)	9(1)	2(1)
C(18)	65(1)	71(2)	52(1)	4(1)	4(1)	-35(1)
C(19)	33(1)	32(1)	56(1)	-10(1)	14(1)	-6(1)
C(20)	38(1)	37(1)	84(2)	-9(1)	15(1)	-2(1)
C(21)	43(1)	51(1)	120(2)	-21(2)	35(1)	-5(1)
C(22)	64(2)	75(2)	112(2)	-40(2)	59(2)	-29(1)
C(23)	76(2)	69(2)	64(1)	-17(1)	32(1)	-33(1)
C(24)	45(1)	52(1)	53(1)	-9(1)	13(1)	-14(1)
C(25)	54(1)	55(1)	69(1)	-5(1)	31(1)	3(1)
O(1)	51(1)	50(1)	46(1)	1(1)	5(1)	-18(1)
O(2)	45(1)	51(1)	47(1)	-1(1)	13(1)	-10(1)
O(3)	44(1)	39(1)	59(1)	-1(1)	24(1)	-3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for product **4.93**.

	x	y	z	U(eq)
H(1A)	14473	5356	8226	57
H(2A)	15896	7663	8792	69
H(3A)	14906	9349	9728	72
H(4A)	12416	8773	10060	72
H(5A)	10985	6467	9494	64
H(7A)	12378	3525	8131	50
H(8A)	9687	5685	7815	55
H(8B)	10731	5126	7139	55
H(9A)	8273	3636	6764	49
H(11A)	10954	888	8432	56
H(11B)	9511	1098	8927	56
H(12A)	10153	3774	9242	61
H(12B)	11836	2812	9491	61
H(13A)	6988	1273	6764	45
H(14A)	8935	-1394	7579	46
H(15A)	6720	-1464	5901	47
H(16A)	6915	-3487	7325	48
H(18A)	3053	-7006	6497	96
H(18B)	3780	-6762	5652	96
H(18C)	2447	-5532	5847	96
H(20A)	11558	-1672	7416	63
H(21A)	13595	-1325	6666	82
H(22A)	13051	0	5324	93
H(23A)	10501	1136	4785	81
H(24A)	8451	824	5544	60
H(25A)	5089	1115	8469	85
H(25B)	4960	1843	7514	85
H(25C)	6346	2466	8313	85

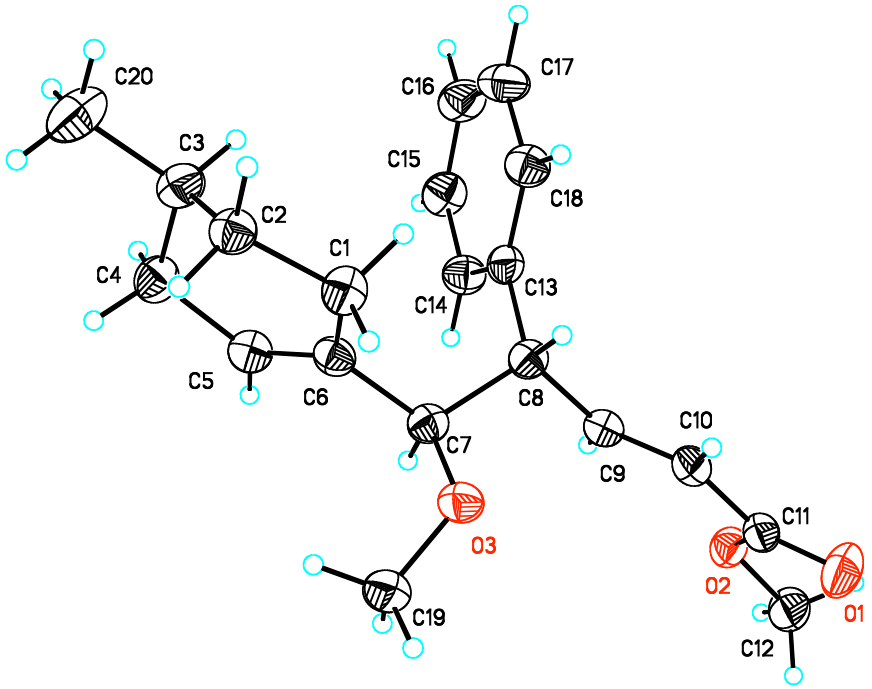
Table 6. Torsion angles [°] for product **4.93**.

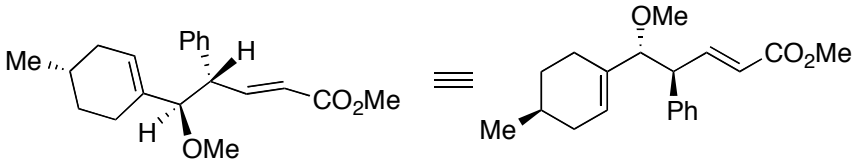
C(6)-C(1)-C(2)-C(3)	0.7(3)
C(1)-C(2)-C(3)-C(4)	-1.2(3)
C(2)-C(3)-C(4)-C(5)	1.1(4)
C(3)-C(4)-C(5)-C(6)	-0.6(4)
C(2)-C(1)-C(6)-C(5)	-0.2(3)
C(2)-C(1)-C(6)-C(7)	176.94(18)
C(4)-C(5)-C(6)-C(1)	0.1(3)
C(4)-C(5)-C(6)-C(7)	-176.93(19)
C(1)-C(6)-C(7)-C(12)	134.73(19)
C(5)-C(6)-C(7)-C(12)	-48.3(3)
C(1)-C(6)-C(7)-C(8)	-100.5(2)
C(5)-C(6)-C(7)-C(8)	76.5(2)
C(6)-C(7)-C(8)-C(9)	-167.97(17)
C(12)-C(7)-C(8)-C(9)	-40.2(2)
C(7)-C(8)-C(9)-C(10)	10.8(3)
C(8)-C(9)-C(10)-C(11)	1.0(3)
C(8)-C(9)-C(10)-C(13)	-178.81(18)
C(9)-C(10)-C(11)-C(12)	17.6(3)
C(13)-C(10)-C(11)-C(12)	-162.56(17)
C(6)-C(7)-C(12)-C(11)	-175.70(16)
C(8)-C(7)-C(12)-C(11)	59.7(2)
C(10)-C(11)-C(12)-C(7)	-48.0(2)
C(9)-C(10)-C(13)-O(3)	-125.49(19)
C(11)-C(10)-C(13)-O(3)	54.7(2)
C(9)-C(10)-C(13)-C(14)	116.1(2)
C(11)-C(10)-C(13)-C(14)	-63.7(2)
O(3)-C(13)-C(14)-C(15)	68.91(18)
C(10)-C(13)-C(14)-C(15)	-168.34(15)
O(3)-C(13)-C(14)-C(19)	-168.48(14)
C(10)-C(13)-C(14)-C(19)	-45.7(2)
C(19)-C(14)-C(15)-C(16)	129.77(19)
C(13)-C(14)-C(15)-C(16)	-106.0(2)
C(14)-C(15)-C(16)-C(17)	179.59(16)
C(15)-C(16)-C(17)-O(2)	8.1(3)

C(15)-C(16)-C(17)-O(1)	-172.00(17)
C(15)-C(14)-C(19)-C(24)	63.0(2)
C(13)-C(14)-C(19)-C(24)	-59.4(2)
C(15)-C(14)-C(19)-C(20)	-115.46(19)
C(13)-C(14)-C(19)-C(20)	122.10(18)
C(24)-C(19)-C(20)-C(21)	-1.2(3)
C(14)-C(19)-C(20)-C(21)	177.33(19)
C(19)-C(20)-C(21)-C(22)	-0.8(3)
C(20)-C(21)-C(22)-C(23)	2.3(4)
C(21)-C(22)-C(23)-C(24)	-1.8(4)
C(20)-C(19)-C(24)-C(23)	1.6(3)
C(14)-C(19)-C(24)-C(23)	-176.9(2)
C(22)-C(23)-C(24)-C(19)	-0.1(3)
O(2)-C(17)-O(1)-C(18)	0.6(3)
C(16)-C(17)-O(1)-C(18)	-179.30(17)
C(10)-C(13)-O(3)-C(25)	68.91(19)
C(14)-C(13)-O(3)-C(25)	-167.38(15)

Symmetry transformations used to generate equivalent atoms:

17. X-ray crystallographic structure of product 4.95





4.95

Table 1. Crystal data and structure refinement for product **4.95**.

Identification code	yl_9_105mch	
Empirical formula	C20 H26 O3	
Formula weight	314.41	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 8.8153(7) Å	α= 90°.
	b = 9.6717(8) Å	β= 99.800(5)°.
	c = 10.6323(9) Å	γ = 90°.
Volume	893.27(13) $Å^3$	
Z	2	
Density (calculated)	1.169 Mg/m^3	
Absorption coefficient	0.611 mm^{-1}	
F(000)	340	
Crystal size	0.22 x 0.21 x 0.12 mm^3	
Theta range for data collection	4.22 to 69.14°.	
Index ranges	-10<=h<=10, -11<=k<=11, -12<=l<=12	
Reflections collected	5892	
Independent reflections	2778 [R(int) = 0.0153]	
Completeness to theta = 69.14°	92.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9303 and 0.8774	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2778 / 1 / 208	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0300, wR2 = 0.0735	
R indices (all data)	R1 = 0.0307, wR2 = 0.0742	
Absolute structure parameter	0.01(17)	
Largest diff. peak and hole	0.110 and -0.200 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for product **4.95**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7533(2)	4120(2)	9598(2)	35(1)
C(2)	6915(2)	4023(2)	10856(2)	34(1)
C(3)	5773(2)	2833(2)	10824(2)	38(1)
C(4)	6612(2)	1476(2)	10673(2)	38(1)
C(5)	7528(2)	1554(2)	9602(2)	34(1)
C(6)	7903(2)	2725(2)	9093(1)	30(1)
C(7)	8698(2)	2705(2)	7941(1)	30(1)
C(8)	7739(2)	3378(2)	6740(1)	29(1)
C(9)	8504(2)	3085(2)	5608(1)	30(1)
C(10)	9274(2)	4016(2)	5053(2)	31(1)
C(11)	10053(2)	3740(2)	3965(2)	32(1)
C(13)	6065(2)	2913(2)	6501(1)	30(1)
C(14)	5666(2)	1532(2)	6265(2)	36(1)
C(15)	4129(2)	1131(2)	6080(2)	41(1)
C(16)	2986(2)	2093(2)	6146(2)	44(1)
C(17)	3367(2)	3463(2)	6363(2)	45(1)
C(18)	4900(2)	3868(2)	6529(2)	37(1)
C(19)	11305(2)	2791(2)	8972(2)	45(1)
C(20)	5000(2)	2811(2)	12004(2)	57(1)
O(2)	9881(1)	2438(1)	3532(1)	35(1)
O(1)	10788(2)	4601(1)	3500(1)	49(1)
O(3)	10112(1)	3473(1)	8150(1)	35(1)
C(12)	10665(2)	2118(2)	2488(2)	45(1)

Table 3. Bond lengths [Å] and angles [°] for product **4.95**.

C(1)-C(6)	1.508(2)	C(16)-C(17)	1.376(3)
C(1)-C(2)	1.531(2)	C(16)-H(16A)	0.9500
C(1)-H(1A)	0.9900	C(17)-C(18)	1.389(2)
C(1)-H(1B)	0.9900	C(17)-H(17A)	0.9500
C(2)-C(3)	1.525(2)	C(18)-H(18A)	0.9500
C(2)-H(2A)	0.9900	C(19)-O(3)	1.411(2)
C(2)-H(2B)	0.9900	C(19)-H(19A)	0.9800
C(3)-C(20)	1.526(2)	C(19)-H(19B)	0.9800
C(3)-C(4)	1.529(2)	C(19)-H(19C)	0.9800
C(3)-H(3A)	1.0000	C(20)-H(20A)	0.9800
C(4)-C(5)	1.505(2)	C(20)-H(20B)	0.9800
C(4)-H(4A)	0.9900	C(20)-H(20C)	0.9800
C(4)-H(4B)	0.9900	O(2)-C(12)	1.4373(17)
C(5)-C(6)	1.322(2)	C(12)-H(12A)	0.9800
C(5)-H(5A)	0.9500	C(12)-H(12B)	0.9800
C(6)-C(7)	1.5122(18)	C(12)-H(12C)	0.9800
C(7)-O(3)	1.4353(18)		
C(7)-C(8)	1.549(2)	C(6)-C(1)-C(2)	112.73(13)
C(7)-H(7A)	1.0000	C(6)-C(1)-H(1A)	109.0
C(8)-C(9)	1.5041(18)	C(2)-C(1)-H(1A)	109.0
C(8)-C(13)	1.522(2)	C(6)-C(1)-H(1B)	109.0
C(8)-H(8A)	1.0000	C(2)-C(1)-H(1B)	109.0
C(9)-C(10)	1.325(2)	H(1A)-C(1)-H(1B)	107.8
C(9)-H(9A)	0.9500	C(3)-C(2)-C(1)	111.07(13)
C(10)-C(11)	1.466(2)	C(3)-C(2)-H(2A)	109.4
C(10)-H(10A)	0.9500	C(1)-C(2)-H(2A)	109.4
C(11)-O(1)	1.2109(19)	C(3)-C(2)-H(2B)	109.4
C(11)-O(2)	1.3405(19)	C(1)-C(2)-H(2B)	109.4
C(13)-C(18)	1.386(2)	H(2A)-C(2)-H(2B)	108.0
C(13)-C(14)	1.393(2)	C(2)-C(3)-C(20)	112.22(14)
C(14)-C(15)	1.391(2)	C(2)-C(3)-C(4)	108.66(12)
C(14)-H(14A)	0.9500	C(20)-C(3)-C(4)	111.48(14)
C(15)-C(16)	1.382(3)	C(2)-C(3)-H(3A)	108.1
C(15)-H(15A)	0.9500	C(20)-C(3)-H(3A)	108.1

C(4)-C(3)-H(3A)	108.1	C(14)-C(13)-C(8)	121.42(14)
C(5)-C(4)-C(3)	111.61(12)	C(15)-C(14)-C(13)	120.19(15)
C(5)-C(4)-H(4A)	109.3	C(15)-C(14)-H(14A)	119.9
C(3)-C(4)-H(4A)	109.3	C(13)-C(14)-H(14A)	119.9
C(5)-C(4)-H(4B)	109.3	C(16)-C(15)-C(14)	120.41(16)
C(3)-C(4)-H(4B)	109.3	C(16)-C(15)-H(15A)	119.8
H(4A)-C(4)-H(4B)	108.0	C(14)-C(15)-H(15A)	119.8
C(6)-C(5)-C(4)	123.79(13)	C(17)-C(16)-C(15)	119.86(16)
C(6)-C(5)-H(5A)	118.1	C(17)-C(16)-H(16A)	120.1
C(4)-C(5)-H(5A)	118.1	C(15)-C(16)-H(16A)	120.1
C(5)-C(6)-C(1)	122.49(12)	C(16)-C(17)-C(18)	119.79(17)
C(5)-C(6)-C(7)	120.25(14)	C(16)-C(17)-H(17A)	120.1
C(1)-C(6)-C(7)	117.24(13)	C(18)-C(17)-H(17A)	120.1
O(3)-C(7)-C(6)	112.19(12)	C(13)-C(18)-C(17)	121.19(16)
O(3)-C(7)-C(8)	104.39(11)	C(13)-C(18)-H(18A)	119.4
C(6)-C(7)-C(8)	113.50(11)	C(17)-C(18)-H(18A)	119.4
O(3)-C(7)-H(7A)	108.9	O(3)-C(19)-H(19A)	109.5
C(6)-C(7)-H(7A)	108.9	O(3)-C(19)-H(19B)	109.5
C(8)-C(7)-H(7A)	108.9	H(19A)-C(19)-H(19B)	109.5
C(9)-C(8)-C(13)	111.39(12)	O(3)-C(19)-H(19C)	109.5
C(9)-C(8)-C(7)	108.90(11)	H(19A)-C(19)-H(19C)	109.5
C(13)-C(8)-C(7)	113.07(11)	H(19B)-C(19)-H(19C)	109.5
C(9)-C(8)-H(8A)	107.8	C(3)-C(20)-H(20A)	109.5
C(13)-C(8)-H(8A)	107.8	C(3)-C(20)-H(20B)	109.5
C(7)-C(8)-H(8A)	107.8	H(20A)-C(20)-H(20B)	109.5
C(10)-C(9)-C(8)	124.23(13)	C(3)-C(20)-H(20C)	109.5
C(10)-C(9)-H(9A)	117.9	H(20A)-C(20)-H(20C)	109.5
C(8)-C(9)-H(9A)	117.9	H(20B)-C(20)-H(20C)	109.5
C(9)-C(10)-C(11)	124.89(14)	C(11)-O(2)-C(12)	115.29(12)
C(9)-C(10)-H(10A)	117.6	C(19)-O(3)-C(7)	112.95(12)
C(11)-C(10)-H(10A)	117.6	O(2)-C(12)-H(12A)	109.5
O(1)-C(11)-O(2)	122.83(14)	O(2)-C(12)-H(12B)	109.5
O(1)-C(11)-C(10)	123.51(15)	H(12A)-C(12)-H(12B)	109.5
O(2)-C(11)-C(10)	113.66(12)	O(2)-C(12)-H(12C)	109.5
C(18)-C(13)-C(14)	118.54(15)	H(12A)-C(12)-H(12C)	109.5
C(18)-C(13)-C(8)	120.04(14)	H(12B)-C(12)-H(12C)	109.5

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for product **4.95**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	41(1)	29(1)	36(1)	-2(1)	9(1)	-2(1)
C(2)	36(1)	33(1)	34(1)	-4(1)	7(1)	1(1)
C(3)	33(1)	43(1)	39(1)	-2(1)	9(1)	-2(1)
C(4)	39(1)	33(1)	42(1)	1(1)	11(1)	-6(1)
C(5)	35(1)	30(1)	36(1)	-3(1)	5(1)	0(1)
C(6)	28(1)	31(1)	29(1)	-2(1)	1(1)	1(1)
C(7)	30(1)	27(1)	33(1)	-2(1)	7(1)	0(1)
C(8)	31(1)	26(1)	31(1)	-1(1)	7(1)	0(1)
C(9)	28(1)	29(1)	31(1)	-1(1)	3(1)	2(1)
C(10)	32(1)	28(1)	32(1)	2(1)	3(1)	2(1)
C(11)	30(1)	30(1)	34(1)	6(1)	4(1)	0(1)
C(13)	30(1)	35(1)	25(1)	1(1)	5(1)	1(1)
C(14)	33(1)	35(1)	40(1)	-2(1)	5(1)	0(1)
C(15)	38(1)	41(1)	44(1)	-3(1)	5(1)	-8(1)
C(16)	30(1)	57(1)	44(1)	-4(1)	3(1)	-6(1)
C(17)	32(1)	54(1)	47(1)	-5(1)	4(1)	9(1)
C(18)	37(1)	36(1)	37(1)	-3(1)	5(1)	2(1)
C(19)	32(1)	63(1)	39(1)	6(1)	3(1)	5(1)
C(20)	58(1)	53(1)	68(1)	-5(1)	36(1)	-6(1)
O(2)	38(1)	35(1)	33(1)	2(1)	12(1)	2(1)
O(1)	59(1)	41(1)	53(1)	7(1)	25(1)	-8(1)
O(3)	28(1)	38(1)	37(1)	1(1)	3(1)	0(1)
C(12)	51(1)	48(1)	39(1)	4(1)	20(1)	12(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for product **4.95**.

	x	y	z	U(eq)
H(1A)	6758	4586	8953	42
H(1B)	8476	4695	9729	42
H(2A)	7783	3879	11567	41
H(2B)	6402	4902	11010	41
H(3A)	4954	2956	10057	46
H(4A)	7313	1261	11480	45
H(4B)	5851	718	10501	45
H(5A)	7855	712	9273	40
H(7A)	8926	1725	7739	36
H(8A)	7753	4401	6876	35
H(9A)	8431	2174	5268	35
H(10A)	9326	4930	5384	37
H(14A)	6446	862	6230	43
H(15A)	3863	190	5907	49
H(16A)	1940	1809	6042	53
H(17A)	2583	4129	6399	53
H(18A)	5154	4817	6664	44
H(19A)	12239	3359	9080	67
H(19B)	11510	1897	8602	67
H(19C)	10995	2644	9804	67
H(20A)	4466	3690	12070	86
H(20B)	5782	2678	12768	86
H(20C)	4256	2051	11932	86
H(12A)	10459	1154	2228	67
H(12B)	11775	2249	2758	67
H(12C)	10295	2731	1767	67

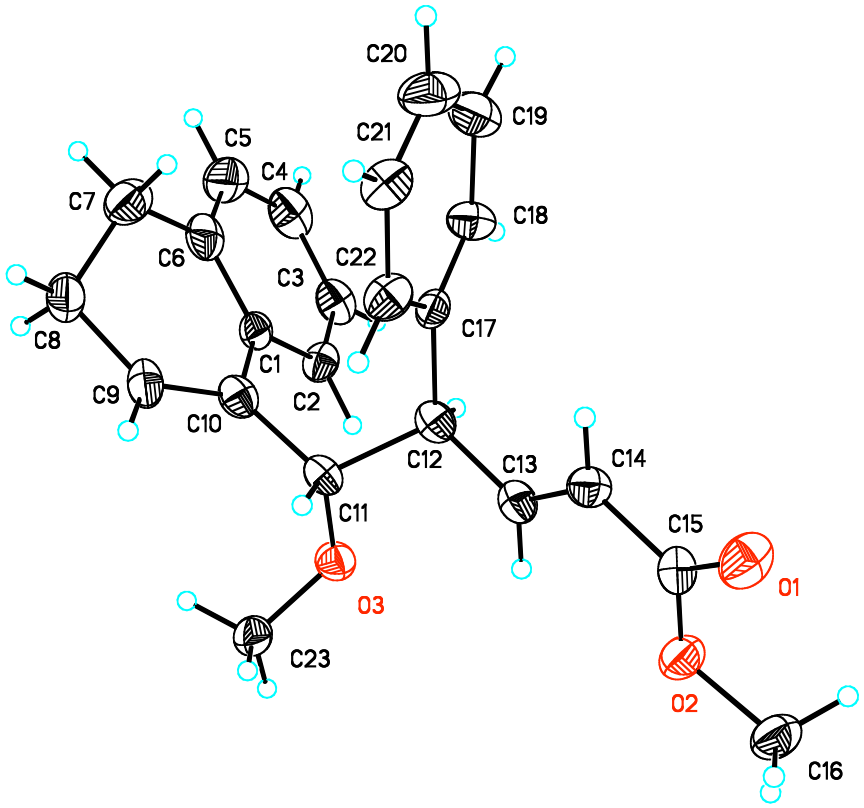
Table 6. Torsion angles [°] for product **4.95**.

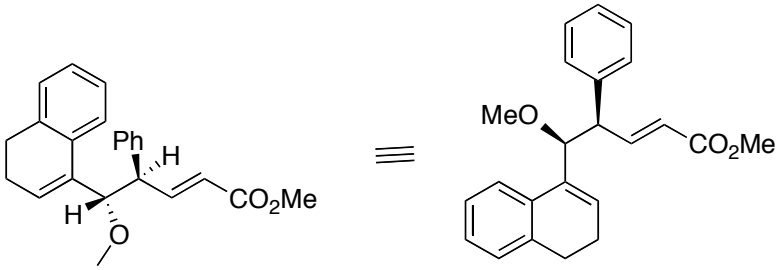
C(6)-C(1)-C(2)-C(3)	-42.02(19)
C(1)-C(2)-C(3)-C(20)	-173.50(15)
C(1)-C(2)-C(3)-C(4)	62.76(18)
C(2)-C(3)-C(4)-C(5)	-49.18(19)
C(20)-C(3)-C(4)-C(5)	-173.36(15)
C(3)-C(4)-C(5)-C(6)	17.1(2)
C(4)-C(5)-C(6)-C(1)	4.1(2)
C(4)-C(5)-C(6)-C(7)	-174.38(15)
C(2)-C(1)-C(6)-C(5)	8.6(2)
C(2)-C(1)-C(6)-C(7)	-172.89(13)
C(5)-C(6)-C(7)-O(3)	-125.19(16)
C(1)-C(6)-C(7)-O(3)	56.28(17)
C(5)-C(6)-C(7)-C(8)	116.77(16)
C(1)-C(6)-C(7)-C(8)	-61.76(17)
O(3)-C(7)-C(8)-C(9)	67.22(13)
C(6)-C(7)-C(8)-C(9)	-170.31(12)
O(3)-C(7)-C(8)-C(13)	-168.39(11)
C(6)-C(7)-C(8)-C(13)	-45.92(17)
C(13)-C(8)-C(9)-C(10)	128.25(15)
C(7)-C(8)-C(9)-C(10)	-106.38(16)
C(8)-C(9)-C(10)-C(11)	178.69(15)
C(9)-C(10)-C(11)-O(1)	-177.74(16)
C(9)-C(10)-C(11)-O(2)	2.1(2)
C(9)-C(8)-C(13)-C(18)	-119.37(15)
C(7)-C(8)-C(13)-C(18)	117.61(15)
C(9)-C(8)-C(13)-C(14)	61.38(19)
C(7)-C(8)-C(13)-C(14)	-61.65(19)
C(18)-C(13)-C(14)-C(15)	-0.8(3)
C(8)-C(13)-C(14)-C(15)	178.43(14)
C(13)-C(14)-C(15)-C(16)	-0.9(3)
C(14)-C(15)-C(16)-C(17)	1.7(3)
C(15)-C(16)-C(17)-C(18)	-0.7(3)
C(14)-C(13)-C(18)-C(17)	1.8(3)
C(8)-C(13)-C(18)-C(17)	-177.46(15)

C(16)-C(17)-C(18)-C(13)	-1.0(3)
O(1)-C(11)-O(2)-C(12)	1.5(2)
C(10)-C(11)-O(2)-C(12)	-178.33(13)
C(6)-C(7)-O(3)-C(19)	73.41(15)
C(8)-C(7)-O(3)-C(19)	-163.27(12)

Symmetry transformations used to generate equivalent atoms:

18. X-ray crystallographic structure of product *ent*-4.97





***ent*-4.97 from Rh_2(*R*-DOSP)$_4$**

Table 1. Crystal data and structure refinement for product ***ent*-4.97**.

Identification code	yl_9_98rs	
Empirical formula	C23 H24 O3	
Formula weight	348.42	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 25.640(7) Å	α= 90°.
	b = 8.757(3) Å	β= 95.636(9)°.
	c = 8.445(2) Å	γ = 90°.
Volume	1887.0(9) $Å^3$	
Z	4	
Density (calculated)	1.226 Mg/m^3	
Absorption coefficient	0.635 mm^{-1}	
F(000)	744	
Crystal size	0.56 x 0.53 x 0.41 mm^3	
Theta range for data collection	5.26 to 69.17°.	
Index ranges	-30<=h<=30, -10<=k<=8, -9<=l<=10	
Reflections collected	5144	
Independent reflections	1908 [R(int) = 0.0223]	
Completeness to theta = 69.17°	85.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7826 and 0.7187	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1908 / 1 / 235	
Goodness-of-fit on F^2	1.523	
Final R indices [I>2sigma(I)]	R1 = 0.0687, wR2 = 0.2118	
R indices (all data)	R1 = 0.0908, wR2 = 0.2898	
Absolute structure parameter	0.1(5)	
Largest diff. peak and hole	0.528 and -0.541 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for product ***ent*-4.97**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	6788(2)	7225(5)	877(5)	30(1)
C(2)	6607(2)	7755(6)	-652(5)	34(1)
C(3)	6679(2)	6872(7)	-1981(5)	39(1)
C(4)	6935(2)	5477(9)	-1821(6)	51(2)
C(5)	7125(2)	4980(8)	-330(7)	50(1)
C(6)	7061(2)	5848(7)	1030(5)	40(1)
C(7)	7258(2)	5341(7)	2690(6)	49(1)
C(8)	7447(2)	6698(8)	3727(6)	46(1)
C(9)	7018(2)	7879(7)	3662(5)	38(1)
C(10)	6696(2)	8114(6)	2334(5)	34(1)
C(11)	6228(2)	9175(6)	2370(4)	31(1)
C(12)	5708(2)	8407(6)	1736(4)	33(1)
C(13)	5258(2)	9451(6)	1959(4)	34(1)
C(14)	4838(2)	9114(6)	2709(5)	34(1)
C(15)	4401(2)	10157(6)	2833(5)	34(1)
C(16)	3972(2)	12453(7)	1948(6)	47(1)
C(17)	5657(2)	6775(6)	2414(4)	29(1)
C(18)	5564(2)	5556(6)	1430(5)	38(1)
C(19)	5496(2)	4076(8)	2011(7)	50(1)
C(20)	5559(3)	3868(8)	3677(8)	56(2)
C(21)	5657(2)	5080(7)	4660(6)	45(1)
C(22)	5708(2)	6576(7)	4067(5)	39(1)
C(23)	6636(2)	11604(7)	2129(6)	39(1)
O(1)	4034(1)	9870(6)	3597(4)	49(1)
O(2)	4427(1)	11460(5)	1987(4)	41(1)
O(3)	6270(1)	10530(4)	1430(3)	35(1)

Table 3. Bond lengths [Å] and angles [°] for product ***ent*-4.97**.

C(1)-C(6)	1.394(7)	C(16)-H(16A)	0.9800
C(1)-C(2)	1.407(6)	C(16)-H(16B)	0.9800
C(1)-C(10)	1.494(6)	C(16)-H(16C)	0.9800
C(2)-C(3)	1.389(7)	C(17)-C(18)	1.360(7)
C(2)-H(2A)	0.9500	C(17)-C(22)	1.400(6)
C(3)-C(4)	1.387(10)	C(18)-C(19)	1.402(8)
C(3)-H(3A)	0.9500	C(18)-H(18A)	0.9500
C(4)-C(5)	1.376(9)	C(19)-C(20)	1.413(9)
C(4)-H(4A)	0.9500	C(19)-H(19A)	0.9500
C(5)-C(6)	1.400(8)	C(20)-C(21)	1.356(10)
C(5)-H(5A)	0.9500	C(20)-H(20A)	0.9500
C(6)-C(7)	1.509(7)	C(21)-C(22)	1.413(8)
C(7)-C(8)	1.526(9)	C(21)-H(21A)	0.9500
C(7)-H(7A)	0.9900	C(22)-H(22A)	0.9500
C(7)-H(7B)	0.9900	C(23)-O(3)	1.415(6)
C(8)-C(9)	1.507(8)	C(23)-H(23A)	0.9800
C(8)-H(8A)	0.9900	C(23)-H(23B)	0.9800
C(8)-H(8B)	0.9900	C(23)-H(23C)	0.9800
C(9)-C(10)	1.342(6)		
C(9)-H(9A)	0.9500	C(6)-C(1)-C(2)	119.2(4)
C(10)-C(11)	1.520(7)	C(6)-C(1)-C(10)	119.5(4)
C(11)-O(3)	1.438(6)	C(2)-C(1)-C(10)	121.3(4)
C(11)-C(12)	1.542(6)	C(3)-C(2)-C(1)	120.0(5)
C(11)-H(11A)	1.0000	C(3)-C(2)-H(2A)	120.0
C(12)-C(13)	1.499(7)	C(1)-C(2)-H(2A)	120.0
C(12)-C(17)	1.550(7)	C(4)-C(3)-C(2)	120.7(5)
C(12)-H(12A)	1.0000	C(4)-C(3)-H(3A)	119.7
C(13)-C(14)	1.334(6)	C(2)-C(3)-H(3A)	119.7
C(13)-H(13A)	0.9500	C(5)-C(4)-C(3)	119.3(5)
C(14)-C(15)	1.458(7)	C(5)-C(4)-H(4A)	120.3
C(14)-H(14A)	0.9500	C(3)-C(4)-H(4A)	120.3
C(15)-O(1)	1.218(6)	C(4)-C(5)-C(6)	121.3(6)
C(15)-O(2)	1.351(6)	C(4)-C(5)-H(5A)	119.3
C(16)-O(2)	1.453(6)	C(6)-C(5)-H(5A)	119.3

C(1)-C(6)-C(5)	119.4(5)	C(13)-C(14)-C(15)	123.9(5)
C(1)-C(6)-C(7)	117.4(5)	C(13)-C(14)-H(14A)	118.1
C(5)-C(6)-C(7)	123.2(6)	C(15)-C(14)-H(14A)	118.1
C(6)-C(7)-C(8)	111.3(5)	O(1)-C(15)-O(2)	122.4(5)
C(6)-C(7)-H(7A)	109.4	O(1)-C(15)-C(14)	123.2(5)
C(8)-C(7)-H(7A)	109.4	O(2)-C(15)-C(14)	114.3(4)
C(6)-C(7)-H(7B)	109.4	O(2)-C(16)-H(16A)	109.5
C(8)-C(7)-H(7B)	109.4	O(2)-C(16)-H(16B)	109.5
H(7A)-C(7)-H(7B)	108.0	H(16A)-C(16)-H(16B)	109.5
C(9)-C(8)-C(7)	108.9(4)	O(2)-C(16)-H(16C)	109.5
C(9)-C(8)-H(8A)	109.9	H(16A)-C(16)-H(16C)	109.5
C(7)-C(8)-H(8A)	109.9	H(16B)-C(16)-H(16C)	109.5
C(9)-C(8)-H(8B)	109.9	C(18)-C(17)-C(22)	120.3(5)
C(7)-C(8)-H(8B)	109.9	C(18)-C(17)-C(12)	121.0(4)
H(8A)-C(8)-H(8B)	108.3	C(22)-C(17)-C(12)	118.7(4)
C(10)-C(9)-C(8)	121.5(5)	C(17)-C(18)-C(19)	122.1(4)
C(10)-C(9)-H(9A)	119.3	C(17)-C(18)-H(18A)	118.9
C(8)-C(9)-H(9A)	119.3	C(19)-C(18)-H(18A)	118.9
C(9)-C(10)-C(1)	118.3(5)	C(18)-C(19)-C(20)	117.5(5)
C(9)-C(10)-C(11)	119.9(4)	C(18)-C(19)-H(19A)	121.2
C(1)-C(10)-C(11)	121.6(4)	C(20)-C(19)-H(19A)	121.2
O(3)-C(11)-C(10)	113.0(3)	C(21)-C(20)-C(19)	120.3(6)
O(3)-C(11)-C(12)	106.1(3)	C(21)-C(20)-H(20A)	119.8
C(10)-C(11)-C(12)	112.5(4)	C(19)-C(20)-H(20A)	119.8
O(3)-C(11)-H(11A)	108.3	C(20)-C(21)-C(22)	121.8(5)
C(10)-C(11)-H(11A)	108.3	C(20)-C(21)-H(21A)	119.1
C(12)-C(11)-H(11A)	108.3	C(22)-C(21)-H(21A)	119.1
C(13)-C(12)-C(11)	109.9(4)	C(17)-C(22)-C(21)	117.8(5)
C(13)-C(12)-C(17)	115.0(3)	C(17)-C(22)-H(22A)	121.1
C(11)-C(12)-C(17)	112.1(4)	C(21)-C(22)-H(22A)	121.1
C(13)-C(12)-H(12A)	106.4	O(3)-C(23)-H(23A)	109.5
C(11)-C(12)-H(12A)	106.4	O(3)-C(23)-H(23B)	109.5
C(17)-C(12)-H(12A)	106.4	H(23A)-C(23)-H(23B)	109.5
C(14)-C(13)-C(12)	126.3(5)	O(3)-C(23)-H(23C)	109.5
C(14)-C(13)-H(13A)	116.9	H(23A)-C(23)-H(23C)	109.5
C(12)-C(13)-H(13A)	116.9	H(23B)-C(23)-H(23C)	109.5

C(15)-O(2)-C(16)	115.9(4)	C(23)-O(3)-C(11)	113.6(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for product ***ent*-4.97**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	21(2)	33(2)	36(2)	0(2)	6(1)	-3(2)
C(2)	30(2)	37(3)	34(2)	11(2)	4(1)	2(2)
C(3)	35(2)	51(3)	33(2)	-2(2)	14(2)	-9(2)
C(4)	37(2)	66(4)	53(2)	-20(3)	20(2)	-7(3)
C(5)	36(2)	52(4)	65(3)	-4(3)	17(2)	5(2)
C(6)	25(2)	48(3)	48(2)	2(2)	10(2)	-8(2)
C(7)	43(3)	44(3)	62(3)	12(3)	10(2)	5(2)
C(8)	38(2)	48(3)	50(2)	8(2)	-9(2)	-5(2)
C(9)	29(2)	47(3)	35(2)	11(2)	-2(1)	-8(2)
C(10)	33(2)	38(3)	31(2)	-1(2)	5(2)	-7(2)
C(11)	32(2)	33(2)	28(2)	-6(2)	2(1)	-7(2)
C(12)	35(2)	36(3)	27(2)	-4(2)	3(2)	-5(2)
C(13)	30(2)	36(2)	34(2)	1(2)	2(1)	-7(2)
C(14)	37(2)	30(2)	35(2)	0(2)	6(1)	-2(2)
C(15)	28(2)	41(3)	33(2)	3(2)	1(2)	-2(2)
C(16)	46(3)	43(3)	53(2)	-6(2)	6(2)	12(3)
C(17)	23(2)	30(2)	32(2)	3(2)	1(1)	4(2)
C(18)	45(2)	30(3)	41(2)	-1(2)	13(2)	-2(2)
C(19)	55(3)	39(3)	57(3)	-4(2)	10(2)	-9(3)
C(20)	60(3)	37(3)	74(3)	12(3)	23(3)	3(3)
C(21)	46(2)	43(3)	46(2)	4(2)	5(2)	7(2)
C(22)	41(2)	40(3)	36(2)	8(2)	7(2)	4(2)
C(23)	30(2)	32(2)	54(2)	5(2)	1(2)	-1(2)
O(1)	43(2)	54(2)	52(2)	11(2)	21(1)	8(2)
O(2)	36(2)	35(2)	54(2)	6(2)	11(1)	5(2)
O(3)	37(2)	31(2)	35(1)	3(1)	1(1)	-3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for product ***ent*-4.97**.

	x	y	z	U(eq)
H(2A)	6437	8716	-776	40
H(3A)	6551	7227	-3009	47
H(4A)	6978	4871	-2731	61
H(5A)	7303	4028	-221	60
H(7A)	7551	4611	2633	59
H(7B)	6974	4809	3179	59
H(8A)	7536	6357	4838	55
H(8B)	7765	7143	3336	55
H(9A)	6975	8471	4583	45
H(11A)	6202	9490	3498	37
H(12A)	5718	8290	562	39
H(13A)	5273	10449	1525	40
H(14A)	4824	8137	3192	40
H(16A)	4029	13358	1304	71
H(16B)	3919	12769	3033	71
H(16C)	3662	11903	1479	71
H(18A)	5543	5712	312	46
H(19A)	5412	3245	1310	60
H(20A)	5531	2873	4111	67
H(21A)	5692	4920	5778	54
H(22A)	5774	7418	4767	47
H(23A)	6646	12494	1430	58
H(23B)	6984	11135	2278	58
H(23C)	6531	11926	3162	58

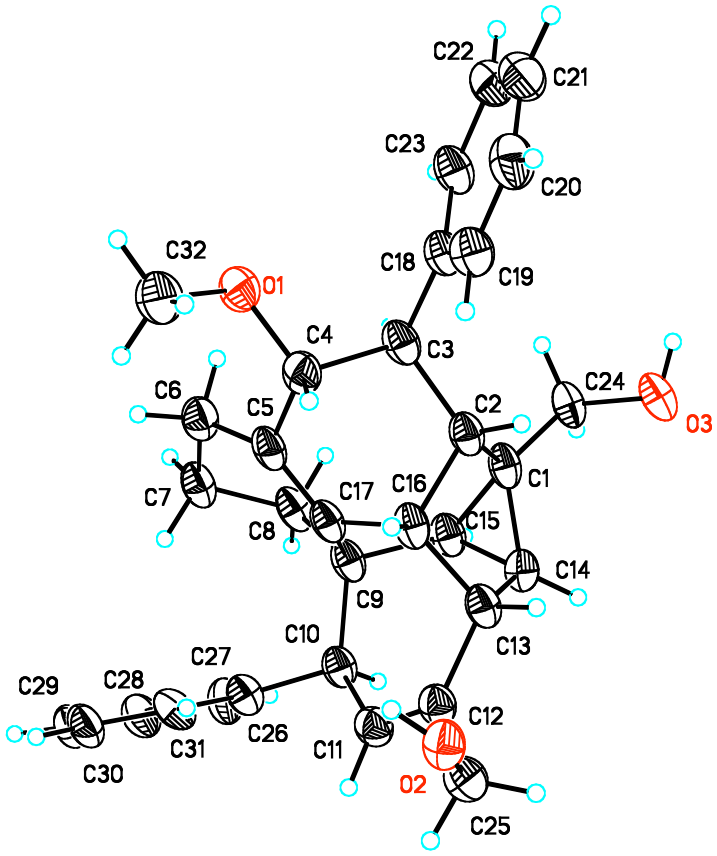
Table 6. Torsion angles [°] for product ***ent*-4.97**.

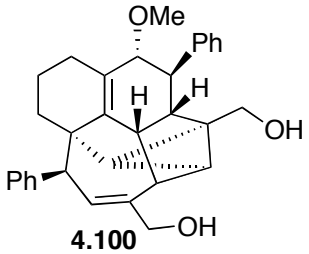
C(6)-C(1)-C(2)-C(3)	3.3(6)
C(10)-C(1)-C(2)-C(3)	-177.2(4)
C(1)-C(2)-C(3)-C(4)	-1.1(7)
C(2)-C(3)-C(4)-C(5)	-0.8(7)
C(3)-C(4)-C(5)-C(6)	0.5(8)
C(2)-C(1)-C(6)-C(5)	-3.6(7)
C(10)-C(1)-C(6)-C(5)	176.9(4)
C(2)-C(1)-C(6)-C(7)	178.6(4)
C(10)-C(1)-C(6)-C(7)	-1.0(6)
C(4)-C(5)-C(6)-C(1)	1.7(8)
C(4)-C(5)-C(6)-C(7)	179.4(5)
C(1)-C(6)-C(7)-C(8)	-37.2(6)
C(5)-C(6)-C(7)-C(8)	145.0(5)
C(6)-C(7)-C(8)-C(9)	53.0(5)
C(7)-C(8)-C(9)-C(10)	-34.5(7)
C(8)-C(9)-C(10)-C(1)	-3.0(7)
C(8)-C(9)-C(10)-C(11)	172.6(4)
C(6)-C(1)-C(10)-C(9)	22.8(6)
C(2)-C(1)-C(10)-C(9)	-156.7(4)
C(6)-C(1)-C(10)-C(11)	-152.8(4)
C(2)-C(1)-C(10)-C(11)	27.7(6)
C(9)-C(10)-C(11)-O(3)	113.6(5)
C(1)-C(10)-C(11)-O(3)	-70.9(5)
C(9)-C(10)-C(11)-C(12)	-126.2(5)
C(1)-C(10)-C(11)-C(12)	49.3(5)
O(3)-C(11)-C(12)-C(13)	-61.7(4)
C(10)-C(11)-C(12)-C(13)	174.2(3)
O(3)-C(11)-C(12)-C(17)	169.1(3)
C(10)-C(11)-C(12)-C(17)	45.0(4)
C(11)-C(12)-C(13)-C(14)	-125.5(5)
C(17)-C(12)-C(13)-C(14)	2.0(6)
C(12)-C(13)-C(14)-C(15)	-177.3(4)
C(13)-C(14)-C(15)-O(1)	-175.6(4)
C(13)-C(14)-C(15)-O(2)	6.1(7)

C(13)-C(12)-C(17)-C(18)	108.5(4)
C(11)-C(12)-C(17)-C(18)	-125.0(4)
C(13)-C(12)-C(17)-C(22)	-71.3(5)
C(11)-C(12)-C(17)-C(22)	55.1(5)
C(22)-C(17)-C(18)-C(19)	2.2(7)
C(12)-C(17)-C(18)-C(19)	-177.6(4)
C(17)-C(18)-C(19)-C(20)	-3.5(8)
C(18)-C(19)-C(20)-C(21)	2.8(9)
C(19)-C(20)-C(21)-C(22)	-1.0(9)
C(18)-C(17)-C(22)-C(21)	-0.2(7)
C(12)-C(17)-C(22)-C(21)	179.6(4)
C(20)-C(21)-C(22)-C(17)	-0.4(8)
O(1)-C(15)-O(2)-C(16)	-4.4(7)
C(14)-C(15)-O(2)-C(16)	173.9(4)
C(10)-C(11)-O(3)-C(23)	-73.9(4)
C(12)-C(11)-O(3)-C(23)	162.3(4)

Symmetry transformations used to generate equivalent atoms:

19. X-ray crystallographic structure of product 4.100





4.100

Table 1. Crystal data and structure refinement for product **4.100**.

Identification code	yl_9_155red	
Empirical formula	C32 H34 O3	
Formula weight	466.59	
Temperature	293(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.3057(8) Å	α= 90°.
	b = 7.6431(5) Å	β= 97.874(4)°.
	c = 28.6755(18) Å	γ = 90°.
Volume	2454.5(3) $Å^3$	
Z	4	
Density (calculated)	1.263 Mg/m^3	
Absorption coefficient	0.621 mm^{-1}	
F(000)	1000	
Crystal size	0.42 x 0.13 x 0.02 mm^3	
Theta range for data collection	3.11 to 69.38°.	
Index ranges	-13<=h<=13, -9<=k<=9, -34<=l<=34	
Reflections collected	15353	
Independent reflections	4209 [R(int) = 0.0699]	
Completeness to theta = 69.38°	91.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9877 and 0.7804	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4209 / 0 / 317	
Goodness-of-fit on F^2	1.038	
Final R indices [I>2sigma(I)]	R1 = 0.0695, wR2 = 0.1455	
R indices (all data)	R1 = 0.1642, wR2 = 0.1777	
Extinction coefficient	0.0033(3)	
Largest diff. peak and hole	0.379 and -0.295 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for product **4.100**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5567(4)	10776(5)	9125(1)	44(1)
C(2)	4631(4)	9402(4)	9201(1)	44(1)
C(3)	3507(4)	9205(5)	8820(1)	47(1)
C(4)	3481(4)	7266(5)	8650(1)	48(1)
C(5)	4636(4)	7097(4)	8437(2)	46(1)
C(6)	4560(4)	7173(5)	7909(1)	53(1)
C(7)	5769(4)	7526(5)	7752(1)	55(1)
C(8)	6393(4)	8976(5)	8060(1)	51(1)
C(9)	6650(4)	8487(5)	8590(1)	45(1)
C(10)	7937(3)	7675(5)	8719(1)	45(1)
C(11)	8126(3)	6774(5)	9198(1)	48(1)
C(12)	7558(3)	7039(5)	9571(1)	45(1)
C(13)	6530(3)	8313(5)	9569(1)	45(1)
C(14)	6748(3)	10136(5)	9391(1)	44(1)
C(15)	6616(3)	10210(5)	8866(1)	47(1)
C(16)	5414(3)	7740(5)	9242(1)	43(1)
C(17)	5616(4)	7455(4)	8735(2)	45(1)
C(18)	2337(4)	9742(5)	8976(1)	46(1)
C(19)	1928(4)	8929(5)	9360(1)	54(1)
C(20)	835(4)	9422(6)	9491(2)	62(1)
C(21)	152(4)	10707(6)	9250(2)	63(1)
C(22)	545(4)	11489(5)	8870(2)	61(1)
C(23)	1636(4)	11010(5)	8736(2)	55(1)
C(24)	5231(3)	12680(5)	9114(1)	49(1)
C(25)	7864(3)	5985(5)	10015(1)	52(1)
C(26)	8262(3)	6448(5)	8343(1)	49(1)
C(27)	8895(3)	7066(5)	7998(1)	55(1)
C(28)	9091(4)	6012(6)	7618(2)	61(1)
C(29)	8665(4)	4320(6)	7586(2)	60(1)
C(30)	8086(4)	3654(5)	7942(2)	58(1)

C(31)	7880(4)	4723(5)	8318(1)	53(1)
C(32)	2099(4)	5218(5)	8277(2)	78(2)
O(1)	2442(3)	7007(3)	8311(1)	56(1)
O(2)	6864(2)	4970(3)	10131(1)	52(1)
O(3)	5007(2)	13263(3)	9571(1)	55(1)

Table 3. Bond lengths [Å] and angles [°] for product **4.100**.

C(1)-C(24)	1.503(4)	C(13)-C(14)	1.515(4)
C(1)-C(14)	1.526(5)	C(13)-C(16)	1.530(5)
C(1)-C(2)	1.528(5)	C(13)-H(13A)	0.9800
C(1)-C(15)	1.545(5)	C(14)-C(15)	1.494(5)
C(2)-C(16)	1.543(4)	C(14)-H(14A)	0.9800
C(2)-C(3)	1.566(5)	C(15)-H(15A)	0.9800
C(2)-H(2A)	0.9800	C(16)-C(17)	1.518(5)
C(3)-C(18)	1.510(5)	C(16)-H(16A)	0.9800
C(3)-C(4)	1.560(4)	C(18)-C(23)	1.376(5)
C(3)-H(3A)	0.9800	C(18)-C(19)	1.397(5)
C(4)-O(1)	1.432(4)	C(19)-C(20)	1.392(5)
C(4)-C(5)	1.520(5)	C(19)-H(19A)	0.9300
C(4)-H(4A)	0.9800	C(20)-C(21)	1.375(5)
C(5)-C(17)	1.331(5)	C(20)-H(20A)	0.9300
C(5)-C(6)	1.508(5)	C(21)-C(22)	1.369(5)
C(6)-C(7)	1.521(5)	C(21)-H(21A)	0.9300
C(6)-H(6A)	0.9700	C(22)-C(23)	1.391(5)
C(6)-H(6B)	0.9700	C(22)-H(22A)	0.9300
C(7)-C(8)	1.528(5)	C(23)-H(23A)	0.9300
C(7)-H(7A)	0.9700	C(24)-O(3)	1.440(4)
C(7)-H(7B)	0.9700	C(24)-H(24A)	0.9700
C(8)-C(9)	1.552(5)	C(24)-H(24B)	0.9700
C(8)-H(8A)	0.9700	C(25)-O(2)	1.448(4)
C(8)-H(8B)	0.9700	C(25)-H(25A)	0.9700
C(9)-C(17)	1.515(5)	C(25)-H(25B)	0.9700
C(9)-C(15)	1.540(4)	C(26)-C(27)	1.382(4)
C(9)-C(10)	1.579(5)	C(26)-C(31)	1.386(5)
C(10)-C(26)	1.511(5)	C(27)-C(28)	1.396(5)
C(10)-C(11)	1.525(5)	C(27)-H(27A)	0.9300
C(10)-H(10A)	0.9800	C(28)-C(29)	1.379(5)
C(11)-C(12)	1.336(4)	C(28)-H(28A)	0.9300
C(11)-H(11A)	0.9300	C(29)-C(30)	1.384(5)
C(12)-C(25)	1.505(5)	C(29)-H(29A)	0.9300
C(12)-C(13)	1.516(5)	C(30)-C(31)	1.398(5)

C(30)-H(30A)	0.9300	C(5)-C(6)-C(7)	112.0(3)
C(31)-H(31A)	0.9300	C(5)-C(6)-H(6A)	109.2
C(32)-O(1)	1.421(4)	C(7)-C(6)-H(6A)	109.2
C(32)-H(32A)	0.9600	C(5)-C(6)-H(6B)	109.2
C(32)-H(32B)	0.9600	C(7)-C(6)-H(6B)	109.2
C(32)-H(32C)	0.9600	H(6A)-C(6)-H(6B)	107.9
O(2)-H(2B)	0.8200	C(6)-C(7)-C(8)	108.7(3)
O(3)-H(3B)	0.8200	C(6)-C(7)-H(7A)	110.0
		C(8)-C(7)-H(7A)	110.0
C(24)-C(1)-C(14)	121.5(3)	C(6)-C(7)-H(7B)	110.0
C(24)-C(1)-C(2)	119.4(3)	C(8)-C(7)-H(7B)	110.0
C(14)-C(1)-C(2)	106.4(3)	H(7A)-C(7)-H(7B)	108.3
C(24)-C(1)-C(15)	118.0(3)	C(7)-C(8)-C(9)	113.6(3)
C(14)-C(1)-C(15)	58.2(2)	C(7)-C(8)-H(8A)	108.8
C(2)-C(1)-C(15)	118.0(3)	C(9)-C(8)-H(8A)	108.8
C(1)-C(2)-C(16)	100.1(3)	C(7)-C(8)-H(8B)	108.8
C(1)-C(2)-C(3)	118.5(3)	C(9)-C(8)-H(8B)	108.8
C(16)-C(2)-C(3)	112.1(3)	H(8A)-C(8)-H(8B)	107.7
C(1)-C(2)-H(2A)	108.5	C(17)-C(9)-C(15)	103.3(3)
C(16)-C(2)-H(2A)	108.5	C(17)-C(9)-C(8)	110.3(3)
C(3)-C(2)-H(2A)	108.5	C(15)-C(9)-C(8)	106.4(3)
C(18)-C(3)-C(4)	111.8(3)	C(17)-C(9)-C(10)	116.9(3)
C(18)-C(3)-C(2)	115.3(3)	C(15)-C(9)-C(10)	107.6(3)
C(4)-C(3)-C(2)	106.8(3)	C(8)-C(9)-C(10)	111.5(3)
C(18)-C(3)-H(3A)	107.6	C(26)-C(10)-C(11)	110.1(3)
C(4)-C(3)-H(3A)	107.6	C(26)-C(10)-C(9)	112.5(3)
C(2)-C(3)-H(3A)	107.6	C(11)-C(10)-C(9)	113.6(3)
O(1)-C(4)-C(5)	112.7(3)	C(26)-C(10)-H(10A)	106.7
O(1)-C(4)-C(3)	108.8(3)	C(11)-C(10)-H(10A)	106.7
C(5)-C(4)-C(3)	103.1(3)	C(9)-C(10)-H(10A)	106.7
O(1)-C(4)-H(4A)	110.7	C(12)-C(11)-C(10)	129.0(4)
C(5)-C(4)-H(4A)	110.7	C(12)-C(11)-H(11A)	115.5
C(3)-C(4)-H(4A)	110.7	C(10)-C(11)-H(11A)	115.5
C(17)-C(5)-C(6)	124.4(4)	C(11)-C(12)-C(25)	121.0(4)
C(17)-C(5)-C(4)	114.3(4)	C(11)-C(12)-C(13)	123.1(4)
C(6)-C(5)-C(4)	117.8(4)	C(25)-C(12)-C(13)	115.8(3)

C(14)-C(13)-C(12)	115.6(3)	C(22)-C(21)-C(20)	119.3(4)
C(14)-C(13)-C(16)	102.5(3)	C(22)-C(21)-H(21A)	120.3
C(12)-C(13)-C(16)	112.7(3)	C(20)-C(21)-H(21A)	120.3
C(14)-C(13)-H(13A)	108.6	C(21)-C(22)-C(23)	120.1(4)
C(12)-C(13)-H(13A)	108.6	C(21)-C(22)-H(22A)	119.9
C(16)-C(13)-H(13A)	108.6	C(23)-C(22)-H(22A)	119.9
C(15)-C(14)-C(13)	112.1(3)	C(18)-C(23)-C(22)	121.3(4)
C(15)-C(14)-C(1)	61.5(2)	C(18)-C(23)-H(23A)	119.3
C(13)-C(14)-C(1)	107.0(3)	C(22)-C(23)-H(23A)	119.3
C(15)-C(14)-H(14A)	120.6	O(3)-C(24)-C(1)	110.9(3)
C(13)-C(14)-H(14A)	120.6	O(3)-C(24)-H(24A)	109.5
C(1)-C(14)-H(14A)	120.6	C(1)-C(24)-H(24A)	109.5
C(14)-C(15)-C(9)	118.7(3)	O(3)-C(24)-H(24B)	109.5
C(14)-C(15)-C(1)	60.3(2)	C(1)-C(24)-H(24B)	109.5
C(9)-C(15)-C(1)	124.1(3)	H(24A)-C(24)-H(24B)	108.0
C(14)-C(15)-H(15A)	114.3	O(2)-C(25)-C(12)	112.7(3)
C(9)-C(15)-H(15A)	114.3	O(2)-C(25)-H(25A)	109.1
C(1)-C(15)-H(15A)	114.3	C(12)-C(25)-H(25A)	109.1
C(17)-C(16)-C(13)	114.1(3)	O(2)-C(25)-H(25B)	109.1
C(17)-C(16)-C(2)	101.9(3)	C(12)-C(25)-H(25B)	109.1
C(13)-C(16)-C(2)	103.1(3)	H(25A)-C(25)-H(25B)	107.8
C(17)-C(16)-H(16A)	112.3	C(27)-C(26)-C(31)	118.4(4)
C(13)-C(16)-H(16A)	112.3	C(27)-C(26)-C(10)	120.0(4)
C(2)-C(16)-H(16A)	112.3	C(31)-C(26)-C(10)	121.5(4)
C(5)-C(17)-C(9)	122.5(4)	C(26)-C(27)-C(28)	121.0(4)
C(5)-C(17)-C(16)	115.0(4)	C(26)-C(27)-H(27A)	119.5
C(9)-C(17)-C(16)	114.3(3)	C(28)-C(27)-H(27A)	119.5
C(23)-C(18)-C(19)	118.5(4)	C(29)-C(28)-C(27)	120.2(4)
C(23)-C(18)-C(3)	120.8(4)	C(29)-C(28)-H(28A)	119.9
C(19)-C(18)-C(3)	120.7(4)	C(27)-C(28)-H(28A)	119.9
C(20)-C(19)-C(18)	119.6(4)	C(28)-C(29)-C(30)	119.4(4)
C(20)-C(19)-H(19A)	120.2	C(28)-C(29)-H(29A)	120.3
C(18)-C(19)-H(19A)	120.2	C(30)-C(29)-H(29A)	120.3
C(21)-C(20)-C(19)	121.1(4)	C(29)-C(30)-C(31)	120.0(4)
C(21)-C(20)-H(20A)	119.4	C(29)-C(30)-H(30A)	120.0
C(19)-C(20)-H(20A)	119.4	C(31)-C(30)-H(30A)	120.0

C(26)-C(31)-C(30)	120.8(4)	O(1)-C(32)-H(32C)	109.5
C(26)-C(31)-H(31A)	119.6	H(32A)-C(32)-H(32C)	109.5
C(30)-C(31)-H(31A)	119.6	H(32B)-C(32)-H(32C)	109.5
O(1)-C(32)-H(32A)	109.5	C(32)-O(1)-C(4)	111.7(3)
O(1)-C(32)-H(32B)	109.5	C(25)-O(2)-H(2B)	109.5
H(32A)-C(32)-H(32B)	109.5	C(24)-O(3)-H(3B)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for product **4.100**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	64(3)	29(2)	42(3)	-3(2)	19(2)	-4(2)
C(2)	61(3)	30(2)	43(3)	-1(2)	12(2)	2(2)
C(3)	65(3)	28(2)	49(3)	4(2)	15(2)	4(2)
C(4)	60(3)	32(2)	52(3)	1(2)	3(2)	1(2)
C(5)	69(3)	22(2)	46(3)	1(2)	12(3)	7(2)
C(6)	70(3)	42(2)	46(3)	-2(2)	7(2)	4(2)
C(7)	79(3)	35(2)	53(3)	-4(2)	16(3)	6(2)
C(8)	74(3)	32(2)	51(3)	2(2)	26(2)	7(2)
C(9)	63(3)	27(2)	47(3)	2(2)	18(2)	1(2)
C(10)	56(3)	34(2)	46(3)	-1(2)	14(2)	-2(2)
C(11)	56(3)	37(2)	50(3)	2(2)	7(2)	3(2)
C(12)	56(3)	36(2)	42(3)	1(2)	8(2)	1(2)
C(13)	59(3)	33(2)	46(3)	-2(2)	14(2)	1(2)
C(14)	54(3)	41(2)	39(3)	-3(2)	11(2)	-4(2)
C(15)	64(3)	31(2)	48(3)	0(2)	15(2)	-1(2)
C(16)	59(3)	32(2)	41(3)	-1(2)	18(2)	-5(2)
C(17)	61(3)	26(2)	49(3)	-1(2)	15(2)	5(2)
C(18)	58(3)	31(2)	51(3)	0(2)	12(2)	-2(2)
C(19)	64(3)	43(3)	56(3)	2(2)	12(3)	-3(2)
C(20)	71(3)	59(3)	61(3)	-8(3)	22(3)	-9(3)
C(21)	59(3)	56(3)	76(4)	-9(3)	18(3)	1(2)
C(22)	66(3)	51(3)	67(3)	-7(2)	8(3)	9(2)
C(23)	72(3)	34(2)	60(3)	-1(2)	17(3)	4(2)
C(24)	66(3)	33(2)	51(3)	-7(2)	23(2)	-3(2)
C(25)	58(3)	43(2)	57(3)	4(2)	13(2)	-1(2)
C(26)	56(3)	40(2)	51(3)	0(2)	14(2)	2(2)
C(27)	63(3)	48(3)	58(3)	-8(2)	21(2)	-11(2)
C(28)	63(3)	60(3)	63(3)	-8(3)	23(3)	6(2)
C(29)	65(3)	52(3)	63(3)	-17(3)	14(3)	7(2)
C(30)	68(3)	34(2)	74(3)	-8(2)	10(3)	5(2)

C(31)	59(3)	38(2)	64(3)	4(2)	17(2)	9(2)
C(32)	80(4)	41(3)	109(4)	-9(3)	-2(3)	-3(2)
O(1)	65(2)	36(2)	66(2)	-2(2)	1(2)	2(1)
O(2)	72(2)	38(2)	46(2)	4(1)	8(2)	-5(1)
O(3)	72(2)	37(2)	61(2)	-6(1)	27(2)	6(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for product **4.100**.

	x	y	z	U(eq)
H(2A)	4361	9620	9507	53
H(3A)	3632	9945	8552	56
H(4A)	3479	6463	8916	58
H(6A)	4007	8091	7789	63
H(6B)	4250	6072	7775	63
H(7A)	5665	7883	7424	66
H(7B)	6250	6471	7783	66
H(8A)	5899	10017	8026	61
H(8B)	7142	9255	7948	61
H(10A)	8503	8651	8736	53
H(11A)	8719	5923	9236	57
H(13A)	6329	8407	9890	54
H(14A)	7284	10946	9582	53
H(15A)	7042	11183	8741	56
H(16A)	5014	6743	9368	52
H(19A)	2384	8064	9527	65
H(20A)	562	8874	9745	75
H(21A)	-569	11042	9345	75
H(22A)	80	12341	8701	74
H(23A)	1897	11559	8479	65
H(24A)	5872	13367	9014	58
H(24B)	4521	12858	8888	58
H(25A)	8518	5200	9976	62
H(25B)	8132	6770	10273	62
H(27A)	9195	8200	8019	66
H(28A)	9509	6453	7386	73
H(29A)	8766	3632	7326	71
H(30A)	7834	2495	7931	70
H(31A)	7482	4272	8555	64
H(32A)	1404	5092	8046	117

H(32B)	1921	4819	8577	117
H(32C)	2741	4534	8184	117
H(2B)	6460	4635	9888	78
H(3B)	4364	13775	9546	82

Table 6. Torsion angles [°] for product **4.100**.

C(24)-C(1)-C(2)-C(16)	-173.8(3)
C(14)-C(1)-C(2)-C(16)	-31.5(4)
C(15)-C(1)-C(2)-C(16)	30.8(4)
C(24)-C(1)-C(2)-C(3)	64.2(5)
C(14)-C(1)-C(2)-C(3)	-153.5(3)
C(15)-C(1)-C(2)-C(3)	-91.3(4)
C(1)-C(2)-C(3)-C(18)	-112.5(4)
C(16)-C(2)-C(3)-C(18)	131.7(3)
C(1)-C(2)-C(3)-C(4)	122.7(3)
C(16)-C(2)-C(3)-C(4)	6.8(4)
C(18)-C(3)-C(4)-O(1)	51.1(4)
C(2)-C(3)-C(4)-O(1)	178.1(3)
C(18)-C(3)-C(4)-C(5)	171.0(3)
C(2)-C(3)-C(4)-C(5)	-62.1(4)
O(1)-C(4)-C(5)-C(17)	175.3(3)
C(3)-C(4)-C(5)-C(17)	58.2(4)
O(1)-C(4)-C(5)-C(6)	15.8(4)
C(3)-C(4)-C(5)-C(6)	-101.3(4)
C(17)-C(5)-C(6)-C(7)	5.9(5)
C(4)-C(5)-C(6)-C(7)	163.2(3)
C(5)-C(6)-C(7)-C(8)	-44.1(4)
C(6)-C(7)-C(8)-C(9)	62.2(4)
C(7)-C(8)-C(9)-C(17)	-38.8(4)
C(7)-C(8)-C(9)-C(15)	-150.1(3)
C(7)-C(8)-C(9)-C(10)	92.8(4)
C(17)-C(9)-C(10)-C(26)	88.1(4)
C(15)-C(9)-C(10)-C(26)	-156.4(3)
C(8)-C(9)-C(10)-C(26)	-40.1(4)
C(17)-C(9)-C(10)-C(11)	-37.9(5)
C(15)-C(9)-C(10)-C(11)	77.6(4)
C(8)-C(9)-C(10)-C(11)	-166.0(3)
C(26)-C(10)-C(11)-C(12)	-151.1(4)
C(9)-C(10)-C(11)-C(12)	-23.8(6)
C(10)-C(11)-C(12)-C(25)	179.0(4)

C(10)-C(11)-C(12)-C(13)	2.8(7)
C(11)-C(12)-C(13)-C(14)	-50.1(5)
C(25)-C(12)-C(13)-C(14)	133.5(4)
C(11)-C(12)-C(13)-C(16)	67.3(5)
C(25)-C(12)-C(13)-C(16)	-109.1(4)
C(12)-C(13)-C(14)-C(15)	78.8(4)
C(16)-C(13)-C(14)-C(15)	-44.2(4)
C(12)-C(13)-C(14)-C(1)	144.3(3)
C(16)-C(13)-C(14)-C(1)	21.3(4)
C(24)-C(1)-C(14)-C(15)	-105.6(4)
C(2)-C(1)-C(14)-C(15)	113.1(3)
C(24)-C(1)-C(14)-C(13)	148.0(3)
C(2)-C(1)-C(14)-C(13)	6.7(4)
C(15)-C(1)-C(14)-C(13)	-106.4(3)
C(13)-C(14)-C(15)-C(9)	-17.1(5)
C(1)-C(14)-C(15)-C(9)	-115.1(4)
C(13)-C(14)-C(15)-C(1)	98.0(3)
C(17)-C(9)-C(15)-C(14)	59.6(4)
C(8)-C(9)-C(15)-C(14)	175.7(3)
C(10)-C(9)-C(15)-C(14)	-64.6(4)
C(17)-C(9)-C(15)-C(1)	-12.2(5)
C(8)-C(9)-C(15)-C(1)	103.9(4)
C(10)-C(9)-C(15)-C(1)	-136.4(4)
C(24)-C(1)-C(15)-C(14)	111.5(4)
C(2)-C(1)-C(15)-C(14)	-92.7(4)
C(24)-C(1)-C(15)-C(9)	-142.3(4)
C(14)-C(1)-C(15)-C(9)	106.3(4)
C(2)-C(1)-C(15)-C(9)	13.5(6)
C(14)-C(13)-C(16)-C(17)	68.2(4)
C(12)-C(13)-C(16)-C(17)	-56.8(4)
C(14)-C(13)-C(16)-C(2)	-41.4(3)
C(12)-C(13)-C(16)-C(2)	-166.4(3)
C(1)-C(2)-C(16)-C(17)	-73.5(4)
C(3)-C(2)-C(16)-C(17)	53.0(4)
C(1)-C(2)-C(16)-C(13)	45.0(3)
C(3)-C(2)-C(16)-C(13)	171.5(3)

C(6)-C(5)-C(17)-C(9)	18.7(5)
C(4)-C(5)-C(17)-C(9)	-139.3(3)
C(6)-C(5)-C(17)-C(16)	165.3(3)
C(4)-C(5)-C(17)-C(16)	7.3(4)
C(15)-C(9)-C(17)-C(5)	111.9(4)
C(8)-C(9)-C(17)-C(5)	-1.5(5)
C(10)-C(9)-C(17)-C(5)	-130.3(4)
C(15)-C(9)-C(17)-C(16)	-34.9(4)
C(8)-C(9)-C(17)-C(16)	-148.3(3)
C(10)-C(9)-C(17)-C(16)	82.9(4)
C(13)-C(16)-C(17)-C(5)	-174.7(3)
C(2)-C(16)-C(17)-C(5)	-64.4(4)
C(13)-C(16)-C(17)-C(9)	-25.4(4)
C(2)-C(16)-C(17)-C(9)	85.0(4)
C(4)-C(3)-C(18)-C(23)	-115.1(4)
C(2)-C(3)-C(18)-C(23)	122.7(4)
C(4)-C(3)-C(18)-C(19)	63.2(5)
C(2)-C(3)-C(18)-C(19)	-58.9(5)
C(23)-C(18)-C(19)-C(20)	-0.3(6)
C(3)-C(18)-C(19)-C(20)	-178.7(4)
C(18)-C(19)-C(20)-C(21)	-0.5(7)
C(19)-C(20)-C(21)-C(22)	1.3(7)
C(20)-C(21)-C(22)-C(23)	-1.4(7)
C(19)-C(18)-C(23)-C(22)	0.2(6)
C(3)-C(18)-C(23)-C(22)	178.6(4)
C(21)-C(22)-C(23)-C(18)	0.7(7)
C(14)-C(1)-C(24)-O(3)	-68.5(4)
C(2)-C(1)-C(24)-O(3)	68.0(5)
C(15)-C(1)-C(24)-O(3)	-136.6(3)
C(11)-C(12)-C(25)-O(2)	-118.8(4)
C(13)-C(12)-C(25)-O(2)	57.6(4)
C(11)-C(10)-C(26)-C(27)	-138.1(4)
C(9)-C(10)-C(26)-C(27)	94.1(4)
C(11)-C(10)-C(26)-C(31)	45.8(5)
C(9)-C(10)-C(26)-C(31)	-82.0(5)
C(31)-C(26)-C(27)-C(28)	3.4(6)

C(10)-C(26)-C(27)-C(28)	-172.8(4)
C(26)-C(27)-C(28)-C(29)	-0.8(7)
C(27)-C(28)-C(29)-C(30)	-2.6(7)
C(28)-C(29)-C(30)-C(31)	3.4(6)
C(27)-C(26)-C(31)-C(30)	-2.6(6)
C(10)-C(26)-C(31)-C(30)	173.5(4)
C(29)-C(30)-C(31)-C(26)	-0.8(6)
C(5)-C(4)-O(1)-C(32)	89.3(4)
C(3)-C(4)-O(1)-C(32)	-157.1(3)

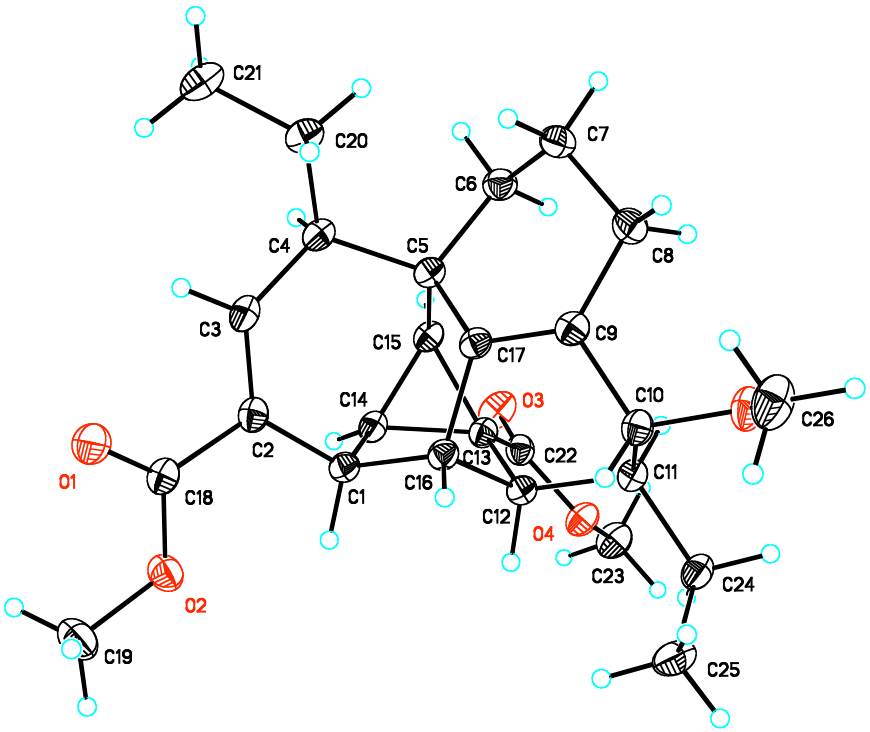
Symmetry transformations used to generate equivalent atoms:

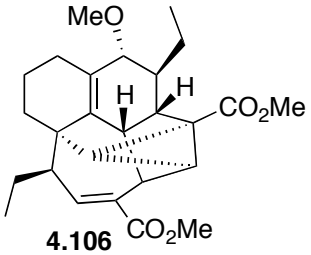
Table 7. Hydrogen bonds for product **4.100** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2B)...O(3)#1	0.82	2.05	2.786(4)	148.7
O(3)-H(3B)...O(2)#2	0.82	2.01	2.743(4)	147.8

Symmetry transformations used to generate equivalent atoms:
#1 x,y-1,z #2 -x+1,-y+2,-z+2

20. X-ray crystallographic structure of product 4.106





4.106

Table 1. Crystal data and structure refinement for product **4.106**.

Identification code	yl_10_75	
Empirical formula	C26 H34 O5	
Formula weight	426.53	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.9705(4) Å	α= 84.822(2)°.
	b = 10.5212(5) Å	β= 78.526(2)°.
	c = 11.7434(5) Å	γ = 66.089(2)°.
Volume	1103.61(8) $Å^3$	
Z	2	
Density (calculated)	1.284 Mg/m^3	
Absorption coefficient	0.703 mm^{-1}	
F(000)	460	
Crystal size	0.28 x 0.23 x 0.18 mm^3	
Theta range for data collection	3.84 to 69.34°.	
Index ranges	-12<=h<=12, -12<=k<=12, -13<=l<=14	
Reflections collected	13119	
Independent reflections	3793 [R(int) = 0.0187]	
Completeness to theta = 69.34°	91.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8839 and 0.8274	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3793 / 0 / 281	
Goodness-of-fit on F^2	1.017	
Final R indices [I>2sigma(I)]	R1 = 0.0391, wR2 = 0.1029	
R indices (all data)	R1 = 0.0405, wR2 = 0.1043	
Extinction coefficient	0.0125(8)	
Largest diff. peak and hole	0.298 and -0.188 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for product **4.106**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	1776(1)	4700(1)	7308(1)	23(1)
C(2)	2134(1)	4899(1)	8452(1)	24(1)
C(3)	3442(2)	4164(1)	8781(1)	26(1)
C(4)	4799(1)	3022(1)	8153(1)	25(1)
C(5)	4505(1)	2310(1)	7162(1)	22(1)
C(6)	5875(1)	979(1)	6739(1)	27(1)
C(7)	5792(2)	-341(1)	7341(1)	29(1)
C(8)	4480(2)	-541(1)	7032(1)	29(1)
C(9)	3109(1)	790(1)	7174(1)	23(1)
C(10)	1791(1)	854(1)	6680(1)	24(1)
C(11)	1776(1)	1778(1)	5571(1)	22(1)
C(12)	1702(1)	3200(1)	5907(1)	21(1)
C(13)	3013(1)	3630(1)	5414(1)	22(1)
C(14)	2959(1)	4691(1)	6266(1)	23(1)
C(15)	4259(1)	3345(1)	6128(1)	23(1)
C(16)	1689(1)	3284(1)	7219(1)	21(1)
C(17)	3095(1)	2026(1)	7398(1)	21(1)
C(18)	994(2)	5958(1)	9291(1)	25(1)
C(19)	-1235(2)	7968(2)	9550(1)	39(1)
C(20)	5604(2)	2020(2)	9077(1)	33(1)
C(21)	6317(2)	2653(2)	9773(2)	45(1)
C(22)	3385(1)	3919(1)	4160(1)	24(1)
C(23)	2631(2)	4158(2)	2344(1)	34(1)
C(24)	532(2)	1897(2)	4922(1)	28(1)
C(25)	-1014(2)	2394(2)	5664(1)	37(1)
C(26)	1372(2)	-1187(2)	7271(2)	42(1)
O(1)	1034(1)	6002(1)	10305(1)	39(1)
O(2)	-107(1)	6899(1)	8790(1)	30(1)
O(3)	4406(1)	4230(1)	3703(1)	35(1)
O(4)	2401(1)	3826(1)	3566(1)	28(1)
O(5)	1920(1)	-464(1)	6348(1)	31(1)

Table 3. Bond lengths [Å] and angles [°] for product **4.106**.

C(1)-C(2)	1.5092(17)	C(13)-C(22)	1.4810(18)
C(1)-C(14)	1.5189(18)	C(13)-C(14)	1.5430(17)
C(1)-C(16)	1.5406(17)	C(13)-C(15)	1.5497(17)
C(1)-H(1A)	1.0000	C(14)-C(15)	1.4768(18)
C(2)-C(3)	1.3334(19)	C(14)-H(14A)	1.0000
C(2)-C(18)	1.4931(18)	C(15)-H(15A)	1.0000
C(3)-C(4)	1.5049(19)	C(16)-C(17)	1.5250(17)
C(3)-H(3A)	0.9500	C(16)-H(16A)	1.0000
C(4)-C(20)	1.545(2)	C(18)-O(1)	1.2053(17)
C(4)-C(5)	1.5723(17)	C(18)-O(2)	1.3426(17)
C(4)-H(4A)	1.0000	C(19)-O(2)	1.4431(17)
C(5)-C(17)	1.5211(17)	C(19)-H(19A)	0.9800
C(5)-C(6)	1.5428(17)	C(19)-H(19B)	0.9800
C(5)-C(15)	1.5434(18)	C(19)-H(19C)	0.9800
C(6)-C(7)	1.5252(19)	C(20)-C(21)	1.527(2)
C(6)-H(6A)	0.9900	C(20)-H(20A)	0.9900
C(6)-H(6B)	0.9900	C(20)-H(20B)	0.9900
C(7)-C(8)	1.5213(19)	C(21)-H(21A)	0.9800
C(7)-H(7A)	0.9900	C(21)-H(21B)	0.9800
C(7)-H(7B)	0.9900	C(21)-H(21C)	0.9800
C(8)-C(9)	1.5026(18)	C(22)-O(3)	1.2046(16)
C(8)-H(8A)	0.9900	C(22)-O(4)	1.3485(16)
C(8)-H(8B)	0.9900	C(23)-O(4)	1.4418(16)
C(9)-C(17)	1.3431(18)	C(23)-H(23A)	0.9800
C(9)-C(10)	1.5136(18)	C(23)-H(23B)	0.9800
C(10)-O(5)	1.4232(15)	C(23)-H(23C)	0.9800
C(10)-C(11)	1.5518(18)	C(24)-C(25)	1.518(2)
C(10)-H(10A)	1.0000	C(24)-H(24A)	0.9900
C(11)-C(24)	1.5392(17)	C(24)-H(24B)	0.9900
C(11)-C(12)	1.5508(17)	C(25)-H(25A)	0.9800
C(11)-H(11A)	1.0000	C(25)-H(25B)	0.9800
C(12)-C(13)	1.5430(17)	C(25)-H(25C)	0.9800
C(12)-C(16)	1.5475(17)	C(26)-O(5)	1.4160(18)
C(12)-H(12A)	1.0000	C(26)-H(26A)	0.9800

C(26)-H(26B)	0.9800	C(8)-C(7)-H(7B)	110.0
C(26)-H(26C)	0.9800	C(6)-C(7)-H(7B)	110.0
		H(7A)-C(7)-H(7B)	108.3
C(2)-C(1)-C(14)	113.72(10)	C(9)-C(8)-C(7)	110.83(11)
C(2)-C(1)-C(16)	113.34(10)	C(9)-C(8)-H(8A)	109.5
C(14)-C(1)-C(16)	102.59(10)	C(7)-C(8)-H(8A)	109.5
C(2)-C(1)-H(1A)	109.0	C(9)-C(8)-H(8B)	109.5
C(14)-C(1)-H(1A)	109.0	C(7)-C(8)-H(8B)	109.5
C(16)-C(1)-H(1A)	109.0	H(8A)-C(8)-H(8B)	108.1
C(3)-C(2)-C(18)	116.22(12)	C(17)-C(9)-C(8)	124.28(12)
C(3)-C(2)-C(1)	123.49(12)	C(17)-C(9)-C(10)	115.43(11)
C(18)-C(2)-C(1)	120.29(11)	C(8)-C(9)-C(10)	117.53(11)
C(2)-C(3)-C(4)	129.34(12)	O(5)-C(10)-C(9)	113.63(11)
C(2)-C(3)-H(3A)	115.3	O(5)-C(10)-C(11)	108.06(10)
C(4)-C(3)-H(3A)	115.3	C(9)-C(10)-C(11)	104.96(10)
C(3)-C(4)-C(20)	107.79(11)	O(5)-C(10)-H(10A)	110.0
C(3)-C(4)-C(5)	115.00(10)	C(9)-C(10)-H(10A)	110.0
C(20)-C(4)-C(5)	115.36(11)	C(11)-C(10)-H(10A)	110.0
C(3)-C(4)-H(4A)	106.0	C(24)-C(11)-C(12)	113.80(10)
C(20)-C(4)-H(4A)	106.0	C(24)-C(11)-C(10)	111.80(10)
C(5)-C(4)-H(4A)	106.0	C(12)-C(11)-C(10)	108.87(10)
C(17)-C(5)-C(6)	110.28(10)	C(24)-C(11)-H(11A)	107.4
C(17)-C(5)-C(15)	102.87(10)	C(12)-C(11)-H(11A)	107.4
C(6)-C(5)-C(15)	107.51(10)	C(10)-C(11)-H(11A)	107.4
C(17)-C(5)-C(4)	117.30(10)	C(13)-C(12)-C(16)	98.77(9)
C(6)-C(5)-C(4)	111.04(10)	C(13)-C(12)-C(11)	119.58(10)
C(15)-C(5)-C(4)	107.06(10)	C(16)-C(12)-C(11)	112.52(10)
C(7)-C(6)-C(5)	113.39(11)	C(13)-C(12)-H(12A)	108.4
C(7)-C(6)-H(6A)	108.9	C(16)-C(12)-H(12A)	108.4
C(5)-C(6)-H(6A)	108.9	C(11)-C(12)-H(12A)	108.4
C(7)-C(6)-H(6B)	108.9	C(22)-C(13)-C(12)	121.77(11)
C(5)-C(6)-H(6B)	108.9	C(22)-C(13)-C(14)	116.69(11)
H(6A)-C(6)-H(6B)	107.7	C(12)-C(13)-C(14)	106.74(10)
C(8)-C(7)-C(6)	108.63(11)	C(22)-C(13)-C(15)	115.74(10)
C(8)-C(7)-H(7A)	110.0	C(12)-C(13)-C(15)	119.99(11)
C(6)-C(7)-H(7A)	110.0	C(14)-C(13)-C(15)	57.04(8)

C(15)-C(14)-C(1)	112.61(11)	C(20)-C(21)-H(21A)	109.5
C(15)-C(14)-C(13)	61.71(8)	C(20)-C(21)-H(21B)	109.5
C(1)-C(14)-C(13)	105.88(10)	H(21A)-C(21)-H(21B)	109.5
C(15)-C(14)-H(14A)	120.7	C(20)-C(21)-H(21C)	109.5
C(1)-C(14)-H(14A)	120.7	H(21A)-C(21)-H(21C)	109.5
C(13)-C(14)-H(14A)	120.7	H(21B)-C(21)-H(21C)	109.5
C(14)-C(15)-C(5)	119.26(11)	O(3)-C(22)-O(4)	122.76(12)
C(14)-C(15)-C(13)	61.25(8)	O(3)-C(22)-C(13)	125.84(12)
C(5)-C(15)-C(13)	122.84(10)	O(4)-C(22)-C(13)	111.38(10)
C(14)-C(15)-H(15A)	114.4	O(4)-C(23)-H(23A)	109.5
C(5)-C(15)-H(15A)	114.4	O(4)-C(23)-H(23B)	109.5
C(13)-C(15)-H(15A)	114.4	H(23A)-C(23)-H(23B)	109.5
C(17)-C(16)-C(1)	114.65(10)	O(4)-C(23)-H(23C)	109.5
C(17)-C(16)-C(12)	102.05(9)	H(23A)-C(23)-H(23C)	109.5
C(1)-C(16)-C(12)	102.68(10)	H(23B)-C(23)-H(23C)	109.5
C(17)-C(16)-H(16A)	112.2	C(25)-C(24)-C(11)	114.36(11)
C(1)-C(16)-H(16A)	112.2	C(25)-C(24)-H(24A)	108.7
C(12)-C(16)-H(16A)	112.2	C(11)-C(24)-H(24A)	108.7
C(9)-C(17)-C(5)	122.06(11)	C(25)-C(24)-H(24B)	108.7
C(9)-C(17)-C(16)	115.23(11)	C(11)-C(24)-H(24B)	108.7
C(5)-C(17)-C(16)	114.21(10)	H(24A)-C(24)-H(24B)	107.6
O(1)-C(18)-O(2)	122.31(12)	C(24)-C(25)-H(25A)	109.5
O(1)-C(18)-C(2)	125.23(12)	C(24)-C(25)-H(25B)	109.5
O(2)-C(18)-C(2)	112.45(11)	H(25A)-C(25)-H(25B)	109.5
O(2)-C(19)-H(19A)	109.5	C(24)-C(25)-H(25C)	109.5
O(2)-C(19)-H(19B)	109.5	H(25A)-C(25)-H(25C)	109.5
H(19A)-C(19)-H(19B)	109.5	H(25B)-C(25)-H(25C)	109.5
O(2)-C(19)-H(19C)	109.5	O(5)-C(26)-H(26A)	109.5
H(19A)-C(19)-H(19C)	109.5	O(5)-C(26)-H(26B)	109.5
H(19B)-C(19)-H(19C)	109.5	H(26A)-C(26)-H(26B)	109.5
C(21)-C(20)-C(4)	113.53(13)	O(5)-C(26)-H(26C)	109.5
C(21)-C(20)-H(20A)	108.9	H(26A)-C(26)-H(26C)	109.5
C(4)-C(20)-H(20A)	108.9	H(26B)-C(26)-H(26C)	109.5
C(21)-C(20)-H(20B)	108.9	C(18)-O(2)-C(19)	115.28(11)
C(4)-C(20)-H(20B)	108.9	C(22)-O(4)-C(23)	115.36(10)
H(20A)-C(20)-H(20B)	107.7	C(26)-O(5)-C(10)	113.09(11)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for product **4.106**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	24(1)	23(1)	22(1)	0(1)	-8(1)	-8(1)
C(2)	29(1)	23(1)	23(1)	0(1)	-5(1)	-13(1)
C(3)	32(1)	28(1)	23(1)	-1(1)	-9(1)	-16(1)
C(4)	26(1)	28(1)	25(1)	1(1)	-9(1)	-13(1)
C(5)	23(1)	24(1)	21(1)	1(1)	-6(1)	-10(1)
C(6)	23(1)	29(1)	27(1)	-1(1)	-5(1)	-9(1)
C(7)	28(1)	25(1)	30(1)	0(1)	-8(1)	-6(1)
C(8)	32(1)	23(1)	31(1)	2(1)	-9(1)	-10(1)
C(9)	27(1)	25(1)	19(1)	3(1)	-5(1)	-12(1)
C(10)	28(1)	24(1)	23(1)	0(1)	-4(1)	-13(1)
C(11)	23(1)	25(1)	21(1)	-1(1)	-4(1)	-11(1)
C(12)	21(1)	23(1)	21(1)	1(1)	-5(1)	-9(1)
C(13)	24(1)	22(1)	22(1)	1(1)	-6(1)	-11(1)
C(14)	28(1)	24(1)	22(1)	2(1)	-8(1)	-13(1)
C(15)	24(1)	27(1)	22(1)	1(1)	-6(1)	-13(1)
C(16)	22(1)	24(1)	19(1)	0(1)	-4(1)	-10(1)
C(17)	23(1)	25(1)	16(1)	2(1)	-5(1)	-10(1)
C(18)	29(1)	27(1)	23(1)	0(1)	-6(1)	-15(1)
C(19)	37(1)	33(1)	35(1)	-6(1)	-1(1)	-4(1)
C(20)	33(1)	34(1)	31(1)	2(1)	-14(1)	-11(1)
C(21)	43(1)	53(1)	42(1)	0(1)	-24(1)	-16(1)
C(22)	27(1)	22(1)	24(1)	1(1)	-5(1)	-11(1)
C(23)	42(1)	43(1)	21(1)	6(1)	-10(1)	-19(1)
C(24)	32(1)	30(1)	28(1)	1(1)	-12(1)	-16(1)
C(25)	29(1)	42(1)	44(1)	5(1)	-14(1)	-17(1)
C(26)	62(1)	41(1)	39(1)	11(1)	-16(1)	-36(1)
O(1)	38(1)	49(1)	24(1)	-8(1)	-8(1)	-8(1)
O(2)	33(1)	27(1)	25(1)	-1(1)	-5(1)	-6(1)
O(3)	39(1)	51(1)	26(1)	6(1)	-5(1)	-29(1)

O(4)	32(1)	35(1)	20(1)	4(1)	-8(1)	-17(1)
O(5)	44(1)	27(1)	30(1)	2(1)	-10(1)	-21(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for product **4.106**.

	x	y	z	U(eq)
H(1A)	802	5459	7200	27
H(3A)	3530	4395	9519	31
H(4A)	5482	3473	7761	30
H(6A)	5970	894	5891	32
H(6B)	6782	1065	6877	32
H(7A)	6729	-1152	7082	34
H(7B)	5659	-260	8193	34
H(8A)	4730	-854	6217	35
H(8B)	4280	-1271	7541	35
H(10A)	848	1298	7250	29
H(11A)	2749	1313	5039	27
H(12A)	766	3946	5711	26
H(14A)	3069	5572	5973	28
H(15A)	5193	3397	5666	27
H(16A)	771	3234	7713	26
H(19A)	-1992	8598	9112	58
H(19B)	-774	8493	9863	58
H(19C)	-1704	7538	10191	58
H(20A)	4879	1733	9619	39
H(20B)	6389	1176	8685	39
H(21A)	6803	1970	10343	67
H(21B)	5545	3480	10178	67
H(21C)	7059	2916	9246	67
H(23A)	1869	4060	1988	51
H(23B)	3622	3523	1970	51
H(23C)	2559	5117	2242	51
H(24A)	521	2549	4257	34
H(24B)	770	975	4603	34
H(25A)	-1740	2438	5193	55
H(25B)	-1277	3320	5964	55

H(25C)	-1024	1745	6316	55
H(26A)	1491	-2083	6993	63
H(26B)	314	-634	7556	63
H(26C)	1933	-1344	7904	63

Table 6. Torsion angles [°] for product **4.106**.

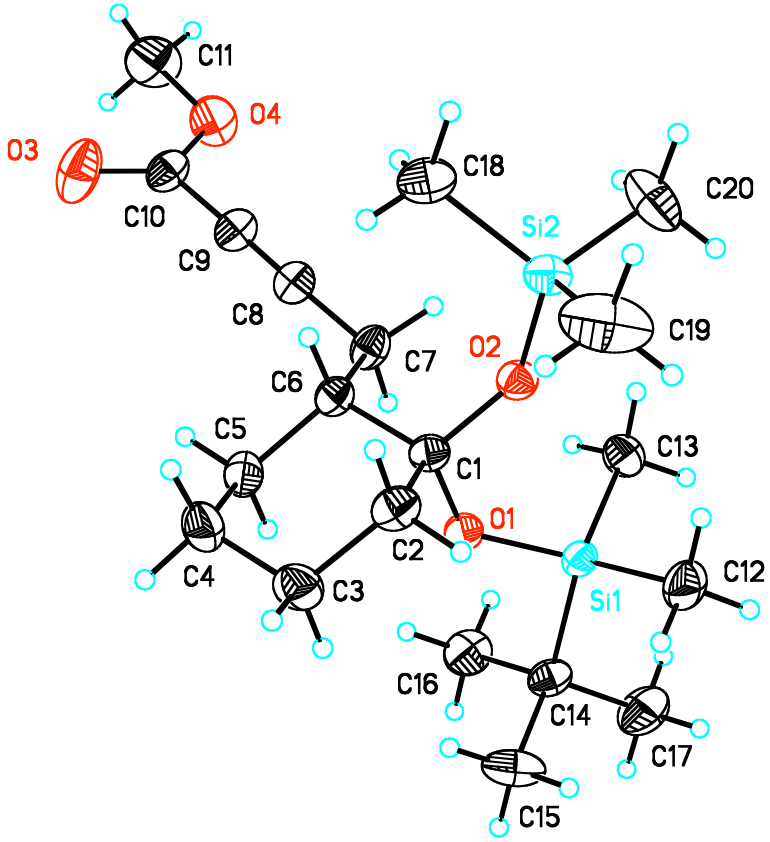
C(14)-C(1)-C(2)-C(3)	-49.41(17)
C(16)-C(1)-C(2)-C(3)	67.25(16)
C(14)-C(1)-C(2)-C(18)	130.96(12)
C(16)-C(1)-C(2)-C(18)	-112.37(13)
C(18)-C(2)-C(3)-C(4)	179.13(12)
C(1)-C(2)-C(3)-C(4)	-0.5(2)
C(2)-C(3)-C(4)-C(20)	-149.36(14)
C(2)-C(3)-C(4)-C(5)	-19.1(2)
C(3)-C(4)-C(5)-C(17)	-40.64(16)
C(20)-C(4)-C(5)-C(17)	85.82(14)
C(3)-C(4)-C(5)-C(6)	-168.69(11)
C(20)-C(4)-C(5)-C(6)	-42.23(15)
C(3)-C(4)-C(5)-C(15)	74.23(13)
C(20)-C(4)-C(5)-C(15)	-159.31(11)
C(17)-C(5)-C(6)-C(7)	-37.13(15)
C(15)-C(5)-C(6)-C(7)	-148.58(11)
C(4)-C(5)-C(6)-C(7)	94.62(13)
C(5)-C(6)-C(7)-C(8)	63.89(14)
C(6)-C(7)-C(8)-C(9)	-47.20(15)
C(7)-C(8)-C(9)-C(17)	7.90(19)
C(7)-C(8)-C(9)-C(10)	168.17(11)
C(17)-C(9)-C(10)-O(5)	174.10(11)
C(8)-C(9)-C(10)-O(5)	12.10(16)
C(17)-C(9)-C(10)-C(11)	56.24(14)
C(8)-C(9)-C(10)-C(11)	-105.76(12)
O(5)-C(10)-C(11)-C(24)	55.74(13)
C(9)-C(10)-C(11)-C(24)	177.32(10)
O(5)-C(10)-C(11)-C(12)	-177.67(10)
C(9)-C(10)-C(11)-C(12)	-56.10(12)
C(24)-C(11)-C(12)-C(13)	-118.57(12)
C(10)-C(11)-C(12)-C(13)	116.00(12)
C(24)-C(11)-C(12)-C(16)	126.27(11)
C(10)-C(11)-C(12)-C(16)	0.84(14)
C(16)-C(12)-C(13)-C(22)	-171.14(11)

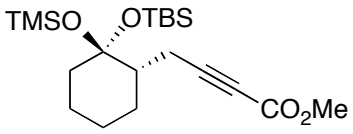
C(11)-C(12)-C(13)-C(22)	66.64(16)
C(16)-C(12)-C(13)-C(14)	-33.59(12)
C(11)-C(12)-C(13)-C(14)	-155.81(11)
C(16)-C(12)-C(13)-C(15)	27.58(13)
C(11)-C(12)-C(13)-C(15)	-94.65(14)
C(2)-C(1)-C(14)-C(15)	79.12(13)
C(16)-C(1)-C(14)-C(15)	-43.66(13)
C(2)-C(1)-C(14)-C(13)	144.58(11)
C(16)-C(1)-C(14)-C(13)	21.80(12)
C(22)-C(13)-C(14)-C(15)	-104.68(12)
C(12)-C(13)-C(14)-C(15)	115.28(11)
C(22)-C(13)-C(14)-C(1)	147.81(11)
C(12)-C(13)-C(14)-C(1)	7.77(13)
C(15)-C(13)-C(14)-C(1)	-107.51(11)
C(1)-C(14)-C(15)-C(5)	-17.23(15)
C(13)-C(14)-C(15)-C(5)	-113.69(12)
C(1)-C(14)-C(15)-C(13)	96.46(11)
C(17)-C(5)-C(15)-C(14)	60.14(13)
C(6)-C(5)-C(15)-C(14)	176.56(10)
C(4)-C(5)-C(15)-C(14)	-64.07(13)
C(17)-C(5)-C(15)-C(13)	-12.73(15)
C(6)-C(5)-C(15)-C(13)	103.69(13)
C(4)-C(5)-C(15)-C(13)	-136.93(11)
C(22)-C(13)-C(15)-C(14)	106.36(12)
C(12)-C(13)-C(15)-C(14)	-91.27(12)
C(22)-C(13)-C(15)-C(5)	-145.62(12)
C(12)-C(13)-C(15)-C(5)	16.75(17)
C(14)-C(13)-C(15)-C(5)	108.02(13)
C(2)-C(1)-C(16)-C(17)	-57.01(14)
C(14)-C(1)-C(16)-C(17)	66.04(13)
C(2)-C(1)-C(16)-C(12)	-166.80(10)
C(14)-C(1)-C(16)-C(12)	-43.75(11)
C(13)-C(12)-C(16)-C(17)	-71.77(11)
C(11)-C(12)-C(16)-C(17)	55.44(12)
C(13)-C(12)-C(16)-C(1)	47.25(11)
C(11)-C(12)-C(16)-C(1)	174.45(10)

C(8)-C(9)-C(17)-C(5)	19.7(2)
C(10)-C(9)-C(17)-C(5)	-140.95(12)
C(8)-C(9)-C(17)-C(16)	165.76(12)
C(10)-C(9)-C(17)-C(16)	5.12(16)
C(6)-C(5)-C(17)-C(9)	-4.23(17)
C(15)-C(5)-C(17)-C(9)	110.19(13)
C(4)-C(5)-C(17)-C(9)	-132.64(13)
C(6)-C(5)-C(17)-C(16)	-150.62(11)
C(15)-C(5)-C(17)-C(16)	-36.20(13)
C(4)-C(5)-C(17)-C(16)	80.97(14)
C(1)-C(16)-C(17)-C(9)	-171.70(11)
C(12)-C(16)-C(17)-C(9)	-61.53(13)
C(1)-C(16)-C(17)-C(5)	-22.93(15)
C(12)-C(16)-C(17)-C(5)	87.24(12)
C(3)-C(2)-C(18)-O(1)	-16.5(2)
C(1)-C(2)-C(18)-O(1)	163.17(13)
C(3)-C(2)-C(18)-O(2)	162.70(11)
C(1)-C(2)-C(18)-O(2)	-17.65(16)
C(3)-C(4)-C(20)-C(21)	-68.91(15)
C(5)-C(4)-C(20)-C(21)	161.04(12)
C(12)-C(13)-C(22)-O(3)	-178.26(13)
C(14)-C(13)-C(22)-O(3)	48.08(19)
C(15)-C(13)-C(22)-O(3)	-16.23(19)
C(12)-C(13)-C(22)-O(4)	3.30(16)
C(14)-C(13)-C(22)-O(4)	-130.37(11)
C(15)-C(13)-C(22)-O(4)	165.33(10)
C(12)-C(11)-C(24)-C(25)	-69.59(15)
C(10)-C(11)-C(24)-C(25)	54.26(15)
O(1)-C(18)-O(2)-C(19)	0.19(19)
C(2)-C(18)-O(2)-C(19)	-179.02(11)
O(3)-C(22)-O(4)-C(23)	-1.42(18)
C(13)-C(22)-O(4)-C(23)	177.09(11)
C(9)-C(10)-O(5)-C(26)	87.37(14)
C(11)-C(10)-O(5)-C(26)	-156.59(12)

Symmetry transformations used to generate equivalent atoms:

21. X-ray crystallographic structure of product 5.5





5.5

Table 1. Crystal data and structure refinement for product **5.5**.

Identification code	yl_9x	
Empirical formula	C20 H38 O4 Si2	
Formula weight	398.68	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.1472(2) Å	α= 90°.
	b = 11.3292(3) Å	β= 90°.
	c = 26.4033(7) Å	γ = 90°.
Volume	2437.06(11) $Å^3$	
Z	4	
Density (calculated)	1.087 Mg/m^3	
Absorption coefficient	1.474 mm^{-1}	
F(000)	872	
Crystal size	0.34 x 0.10 x 0.04 mm^3	
Theta range for data collection	3.35 to 67.95°.	
Index ranges	-9<=h<=8, -13<=k<=10, -29<=l<=27	
Reflections collected	19192	
Independent reflections	4059 [R(int) = 0.0223]	
Completeness to theta = 67.95°	96.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9434 and 0.6342	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4059 / 0 / 236	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0305, wR2 = 0.0835	
R indices (all data)	R1 = 0.0321, wR2 = 0.0848	
Absolute structure parameter	0.45(2)	
Largest diff. peak and hole	0.265 and -0.157 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for product **5.5**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7259(2)	9942(2)	8533(1)	34(1)
C(2)	6046(2)	10284(2)	8121(1)	44(1)
C(3)	4887(2)	9279(2)	7989(1)	52(1)
C(4)	5836(3)	8158(2)	7846(1)	53(1)
C(5)	7016(2)	7821(2)	8267(1)	45(1)
C(6)	8209(2)	8824(2)	8387(1)	36(1)
C(7)	9422(2)	8495(2)	8807(1)	42(1)
C(8)	10558(2)	7554(2)	8667(1)	42(1)
C(9)	11516(2)	6790(2)	8565(1)	43(1)
C(10)	12642(2)	5848(2)	8457(1)	45(1)
C(11)	15092(3)	4932(2)	8691(1)	81(1)
C(12)	5596(3)	11967(2)	9436(1)	55(1)
C(13)	8211(2)	10373(2)	9888(1)	49(1)
C(14)	4618(2)	9516(2)	9866(1)	41(1)
C(15)	3002(2)	9559(2)	9573(1)	63(1)
C(16)	5169(3)	8232(2)	9911(1)	56(1)
C(17)	4345(3)	10009(2)	10403(1)	66(1)
C(18)	10649(3)	10993(3)	7803(1)	73(1)
C(19)	8317(3)	12989(3)	8036(2)	104(1)
C(20)	11030(4)	12347(2)	8776(1)	75(1)
O(1)	6380(2)	9689(1)	8982(1)	36(1)
O(2)	8353(1)	10878(1)	8649(1)	38(1)
O(3)	12458(2)	5137(2)	8124(1)	79(1)
O(4)	13877(2)	5843(1)	8777(1)	66(1)
Si(1)	6247(1)	10403(1)	9526(1)	33(1)
Si(2)	9527(1)	11772(1)	8312(1)	40(1)

Table 3. Bond lengths [Å] and angles [°] for product **5.5**.

C(1)-O(1)	1.415(2)	C(13)-H(13A)	0.9800
C(1)-O(2)	1.418(2)	C(13)-H(13B)	0.9800
C(1)-C(2)	1.520(2)	C(13)-H(13C)	0.9800
C(1)-C(6)	1.534(2)	C(14)-C(16)	1.528(3)
C(2)-C(3)	1.521(3)	C(14)-C(15)	1.528(3)
C(2)-H(2A)	0.9900	C(14)-C(17)	1.539(3)
C(2)-H(2B)	0.9900	C(14)-Si(1)	1.8915(18)
C(3)-C(4)	1.533(3)	C(15)-H(15A)	0.9800
C(3)-H(3A)	0.9900	C(15)-H(15B)	0.9800
C(3)-H(3B)	0.9900	C(15)-H(15C)	0.9800
C(4)-C(5)	1.518(3)	C(16)-H(16A)	0.9800
C(4)-H(4A)	0.9900	C(16)-H(16B)	0.9800
C(4)-H(4B)	0.9900	C(16)-H(16C)	0.9800
C(5)-C(6)	1.529(3)	C(17)-H(17A)	0.9800
C(5)-H(5A)	0.9900	C(17)-H(17B)	0.9800
C(5)-H(5B)	0.9900	C(17)-H(17C)	0.9800
C(6)-C(7)	1.531(2)	C(18)-Si(2)	1.850(2)
C(6)-H(6A)	1.0000	C(18)-H(18A)	0.9800
C(7)-C(8)	1.460(3)	C(18)-H(18B)	0.9800
C(7)-H(7A)	0.9900	C(18)-H(18C)	0.9800
C(7)-H(7B)	0.9900	C(19)-Si(2)	1.845(2)
C(8)-C(9)	1.195(3)	C(19)-H(19A)	0.9800
C(9)-C(10)	1.437(3)	C(19)-H(19B)	0.9800
C(10)-O(3)	1.202(3)	C(19)-H(19C)	0.9800
C(10)-O(4)	1.314(3)	C(20)-Si(2)	1.851(2)
C(11)-O(4)	1.447(3)	C(20)-H(20A)	0.9800
C(11)-H(11A)	0.9800	C(20)-H(20B)	0.9800
C(11)-H(11B)	0.9800	C(20)-H(20C)	0.9800
C(11)-H(11C)	0.9800	O(1)-Si(1)	1.6502(12)
C(12)-Si(1)	1.8650(19)	O(2)-Si(2)	1.6529(12)
C(12)-H(12A)	0.9800		
C(12)-H(12B)	0.9800	O(1)-C(1)-O(2)	106.80(13)
C(12)-H(12C)	0.9800	O(1)-C(1)-C(2)	108.82(14)
C(13)-Si(1)	1.8642(19)	O(2)-C(1)-C(2)	111.84(14)

O(1)-C(1)-C(6)	107.36(14)	C(8)-C(7)-H(7B)	108.8
O(2)-C(1)-C(6)	110.75(13)	C(6)-C(7)-H(7B)	108.8
C(2)-C(1)-C(6)	111.05(14)	H(7A)-C(7)-H(7B)	107.7
C(1)-C(2)-C(3)	112.13(16)	C(9)-C(8)-C(7)	177.9(2)
C(1)-C(2)-H(2A)	109.2	C(8)-C(9)-C(10)	178.0(2)
C(3)-C(2)-H(2A)	109.2	O(3)-C(10)-O(4)	124.29(19)
C(1)-C(2)-H(2B)	109.2	O(3)-C(10)-C(9)	124.4(2)
C(3)-C(2)-H(2B)	109.2	O(4)-C(10)-C(9)	111.33(18)
H(2A)-C(2)-H(2B)	107.9	O(4)-C(11)-H(11A)	109.5
C(2)-C(3)-C(4)	111.32(16)	O(4)-C(11)-H(11B)	109.5
C(2)-C(3)-H(3A)	109.4	H(11A)-C(11)-H(11B)	109.5
C(4)-C(3)-H(3A)	109.4	O(4)-C(11)-H(11C)	109.5
C(2)-C(3)-H(3B)	109.4	H(11A)-C(11)-H(11C)	109.5
C(4)-C(3)-H(3B)	109.4	H(11B)-C(11)-H(11C)	109.5
H(3A)-C(3)-H(3B)	108.0	Si(1)-C(12)-H(12A)	109.5
C(5)-C(4)-C(3)	110.34(17)	Si(1)-C(12)-H(12B)	109.5
C(5)-C(4)-H(4A)	109.6	H(12A)-C(12)-H(12B)	109.5
C(3)-C(4)-H(4A)	109.6	Si(1)-C(12)-H(12C)	109.5
C(5)-C(4)-H(4B)	109.6	H(12A)-C(12)-H(12C)	109.5
C(3)-C(4)-H(4B)	109.6	H(12B)-C(12)-H(12C)	109.5
H(4A)-C(4)-H(4B)	108.1	Si(1)-C(13)-H(13A)	109.5
C(4)-C(5)-C(6)	111.59(16)	Si(1)-C(13)-H(13B)	109.5
C(4)-C(5)-H(5A)	109.3	H(13A)-C(13)-H(13B)	109.5
C(6)-C(5)-H(5A)	109.3	Si(1)-C(13)-H(13C)	109.5
C(4)-C(5)-H(5B)	109.3	H(13A)-C(13)-H(13C)	109.5
C(6)-C(5)-H(5B)	109.3	H(13B)-C(13)-H(13C)	109.5
H(5A)-C(5)-H(5B)	108.0	C(16)-C(14)-C(15)	108.83(19)
C(5)-C(6)-C(7)	112.37(15)	C(16)-C(14)-C(17)	108.46(17)
C(5)-C(6)-C(1)	110.20(14)	C(15)-C(14)-C(17)	109.25(18)
C(7)-C(6)-C(1)	110.19(14)	C(16)-C(14)-Si(1)	109.67(13)
C(5)-C(6)-H(6A)	108.0	C(15)-C(14)-Si(1)	110.28(13)
C(7)-C(6)-H(6A)	108.0	C(17)-C(14)-Si(1)	110.30(15)
C(1)-C(6)-H(6A)	108.0	C(14)-C(15)-H(15A)	109.5
C(8)-C(7)-C(6)	113.79(16)	C(14)-C(15)-H(15B)	109.5
C(8)-C(7)-H(7A)	108.8	H(15A)-C(15)-H(15B)	109.5
C(6)-C(7)-H(7A)	108.8	C(14)-C(15)-H(15C)	109.5

H(15A)-C(15)-H(15C)	109.5	H(19A)-C(19)-H(19C)	109.5
H(15B)-C(15)-H(15C)	109.5	H(19B)-C(19)-H(19C)	109.5
C(14)-C(16)-H(16A)	109.5	Si(2)-C(20)-H(20A)	109.5
C(14)-C(16)-H(16B)	109.5	Si(2)-C(20)-H(20B)	109.5
H(16A)-C(16)-H(16B)	109.5	H(20A)-C(20)-H(20B)	109.5
C(14)-C(16)-H(16C)	109.5	Si(2)-C(20)-H(20C)	109.5
H(16A)-C(16)-H(16C)	109.5	H(20A)-C(20)-H(20C)	109.5
H(16B)-C(16)-H(16C)	109.5	H(20B)-C(20)-H(20C)	109.5
C(14)-C(17)-H(17A)	109.5	C(1)-O(1)-Si(1)	131.50(11)
C(14)-C(17)-H(17B)	109.5	C(1)-O(2)-Si(2)	134.90(11)
H(17A)-C(17)-H(17B)	109.5	C(10)-O(4)-C(11)	115.21(19)
C(14)-C(17)-H(17C)	109.5	O(1)-Si(1)-C(13)	112.35(8)
H(17A)-C(17)-H(17C)	109.5	O(1)-Si(1)-C(12)	111.95(9)
H(17B)-C(17)-H(17C)	109.5	C(13)-Si(1)-C(12)	109.05(11)
Si(2)-C(18)-H(18A)	109.5	O(1)-Si(1)-C(14)	101.50(8)
Si(2)-C(18)-H(18B)	109.5	C(13)-Si(1)-C(14)	110.41(9)
H(18A)-C(18)-H(18B)	109.5	C(12)-Si(1)-C(14)	111.44(9)
Si(2)-C(18)-H(18C)	109.5	O(2)-Si(2)-C(19)	111.20(11)
H(18A)-C(18)-H(18C)	109.5	O(2)-Si(2)-C(18)	112.63(10)
H(18B)-C(18)-H(18C)	109.5	C(19)-Si(2)-C(18)	109.51(16)
Si(2)-C(19)-H(19A)	109.5	O(2)-Si(2)-C(20)	104.01(9)
Si(2)-C(19)-H(19B)	109.5	C(19)-Si(2)-C(20)	110.58(15)
H(19A)-C(19)-H(19B)	109.5	C(18)-Si(2)-C(20)	108.78(14)
Si(2)-C(19)-H(19C)	109.5		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for product **5.5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	33(1)	38(1)	33(1)	2(1)	3(1)	0(1)
C(2)	41(1)	51(1)	39(1)	5(1)	-2(1)	9(1)
C(3)	42(1)	66(1)	49(1)	-2(1)	-11(1)	-1(1)
C(4)	55(1)	58(1)	47(1)	-11(1)	-7(1)	-9(1)
C(5)	51(1)	41(1)	43(1)	-6(1)	2(1)	0(1)
C(6)	38(1)	39(1)	32(1)	-1(1)	2(1)	3(1)
C(7)	46(1)	44(1)	37(1)	-2(1)	-3(1)	13(1)
C(8)	45(1)	43(1)	37(1)	3(1)	0(1)	5(1)
C(9)	47(1)	42(1)	41(1)	6(1)	2(1)	8(1)
C(10)	51(1)	40(1)	45(1)	6(1)	9(1)	10(1)
C(11)	56(1)	60(2)	127(3)	4(2)	-10(2)	23(1)
C(12)	59(1)	33(1)	72(2)	0(1)	9(1)	9(1)
C(13)	43(1)	57(1)	47(1)	-8(1)	-8(1)	-3(1)
C(14)	38(1)	45(1)	40(1)	7(1)	7(1)	4(1)
C(15)	34(1)	80(2)	75(2)	26(1)	4(1)	-6(1)
C(16)	62(1)	45(1)	59(1)	14(1)	13(1)	0(1)
C(17)	71(2)	77(2)	52(1)	2(1)	22(1)	6(1)
C(18)	66(2)	83(2)	69(2)	-5(1)	31(1)	-19(1)
C(19)	62(2)	78(2)	170(3)	78(2)	-3(2)	9(1)
C(20)	89(2)	66(2)	69(2)	8(1)	-17(1)	-39(1)
O(1)	36(1)	38(1)	34(1)	0(1)	4(1)	-3(1)
O(2)	38(1)	36(1)	39(1)	2(1)	4(1)	-1(1)
O(3)	96(1)	74(1)	66(1)	-19(1)	-11(1)	39(1)
O(4)	53(1)	54(1)	90(1)	-6(1)	-18(1)	17(1)
Si(1)	32(1)	31(1)	36(1)	-2(1)	3(1)	3(1)
Si(2)	35(1)	38(1)	46(1)	11(1)	1(1)	1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for product **5.5**.

	x	y	z	U(eq)
H(2A)	6658	10522	7814	52
H(2B)	5397	10972	8236	52
H(3A)	4180	9518	7702	62
H(3B)	4169	9111	8283	62
H(4A)	5054	7504	7786	64
H(4B)	6455	8296	7529	64
H(5A)	7644	7113	8164	54
H(5B)	6384	7620	8575	54
H(6A)	8853	8999	8074	44
H(7A)	10064	9205	8900	51
H(7B)	8797	8246	9110	51
H(11A)	15959	4995	8947	121
H(11B)	15570	5030	8353	121
H(11C)	14570	4155	8715	121
H(12A)	6464	12402	9259	82
H(12B)	5394	12330	9767	82
H(12C)	4587	11990	9234	82
H(13A)	8559	9553	9937	74
H(13B)	8049	10749	10218	74
H(13C)	9057	10802	9698	74
H(15A)	2170	9096	9753	94
H(15B)	3166	9230	9234	94
H(15C)	2633	10380	9545	94
H(16A)	4322	7775	10087	83
H(16B)	6197	8193	10103	83
H(16C)	5340	7903	9572	83
H(17A)	3500	9541	10575	100
H(17B)	3986	10833	10381	100
H(17C)	5373	9965	10594	100
H(18A)	9864	10686	7554	109

H(18B)	11274	10336	7948	109
H(18C)	11404	11543	7636	109
H(19A)	7722	13401	8306	156
H(19B)	7532	12670	7790	156
H(19C)	9056	13544	7865	156
H(20A)	10449	12766	9046	113
H(20B)	11786	12890	8606	113
H(20C)	11652	11688	8921	113

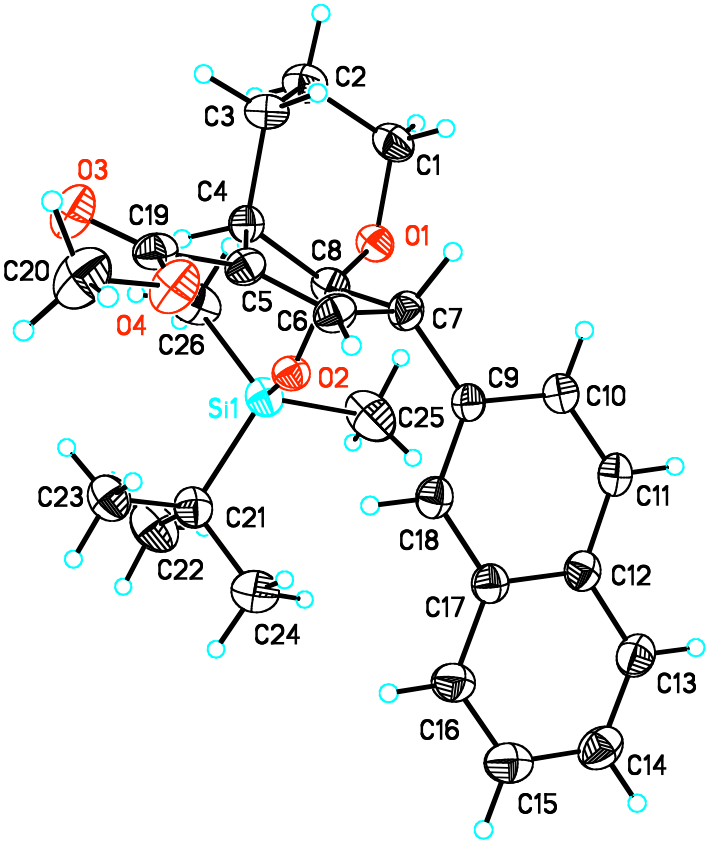
Table 6. Torsion angles [°] for product **5.5**.

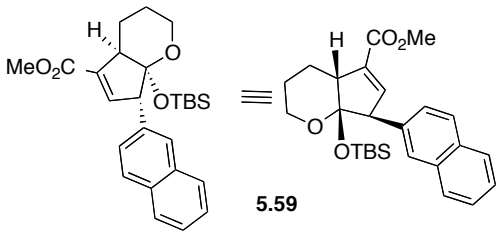
O(1)-C(1)-C(2)-C(3)	-63.2(2)
O(2)-C(1)-C(2)-C(3)	179.07(15)
C(6)-C(1)-C(2)-C(3)	54.8(2)
C(1)-C(2)-C(3)-C(4)	-54.6(2)
C(2)-C(3)-C(4)-C(5)	55.2(2)
C(3)-C(4)-C(5)-C(6)	-57.1(2)
C(4)-C(5)-C(6)-C(7)	-179.36(16)
C(4)-C(5)-C(6)-C(1)	57.3(2)
O(1)-C(1)-C(6)-C(5)	63.41(18)
O(2)-C(1)-C(6)-C(5)	179.66(14)
C(2)-C(1)-C(6)-C(5)	-55.44(19)
O(1)-C(1)-C(6)-C(7)	-61.16(18)
O(2)-C(1)-C(6)-C(7)	55.10(19)
C(2)-C(1)-C(6)-C(7)	179.99(15)
C(5)-C(6)-C(7)-C(8)	65.8(2)
C(1)-C(6)-C(7)-C(8)	-170.86(16)
C(6)-C(7)-C(8)-C(9)	169(6)
C(7)-C(8)-C(9)-C(10)	76(10)
C(8)-C(9)-C(10)-O(3)	96(7)
C(8)-C(9)-C(10)-O(4)	-82(7)
O(2)-C(1)-O(1)-Si(1)	11.1(2)
C(2)-C(1)-O(1)-Si(1)	-109.80(16)
C(6)-C(1)-O(1)-Si(1)	129.92(13)
O(1)-C(1)-O(2)-Si(2)	-168.37(11)
C(2)-C(1)-O(2)-Si(2)	-49.4(2)
C(6)-C(1)-O(2)-Si(2)	75.04(19)
O(3)-C(10)-O(4)-C(11)	2.7(3)
C(9)-C(10)-O(4)-C(11)	-179.03(19)
C(1)-O(1)-Si(1)-C(13)	-68.60(17)
C(1)-O(1)-Si(1)-C(12)	54.51(17)
C(1)-O(1)-Si(1)-C(14)	173.47(15)
C(16)-C(14)-Si(1)-O(1)	58.20(15)
C(15)-C(14)-Si(1)-O(1)	-61.64(17)
C(17)-C(14)-Si(1)-O(1)	177.60(14)

C(16)-C(14)-Si(1)-C(13)	-61.13(17)
C(15)-C(14)-Si(1)-C(13)	179.04(16)
C(17)-C(14)-Si(1)-C(13)	58.27(17)
C(16)-C(14)-Si(1)-C(12)	177.52(15)
C(15)-C(14)-Si(1)-C(12)	57.69(19)
C(17)-C(14)-Si(1)-C(12)	-63.08(17)
C(1)-O(2)-Si(2)-C(19)	79.8(2)
C(1)-O(2)-Si(2)-C(18)	-43.54(19)
C(1)-O(2)-Si(2)-C(20)	-161.16(17)

Symmetry transformations used to generate equivalent atoms:

22. X-ray crystallographic structure of product 5.59





5.59

Table 1. Crystal data and structure refinement for product **5.59**.

Identification code	YL_VII_65N	
Empirical formula	C26 H34 O4 Si	
Formula weight	438.62	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 7.8326(6) Å	α= 90°.
	b = 13.4324(10) Å	β= 90°.
	c = 23.3152(16) Å	γ = 90°.
Volume	2453.0(3) $Å^3$	
Z	4	
Density (calculated)	1.188 Mg/m^3	
Absorption coefficient	1.067 mm^{-1}	
F(000)	944	
Crystal size	0.34 x 0.12 x 0.12 mm^3	
Theta range for data collection	3.79 to 66.58°.	
Index ranges	-9<=h<=8, -15<=k<=13, -23<=l<=27	
Reflections collected	9786	
Independent reflections	3664 [R(int) = 0.0273]	
Completeness to theta = 66.58°	92.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8826 and 0.7129	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3664 / 0 / 287	
Goodness-of-fit on F^2	1.121	
Final R indices [I>2sigma(I)]	R1 = 0.0368, wR2 = 0.0890	
R indices (all data)	R1 = 0.0993, wR2 = 0.1441	
Absolute structure parameter	0.01(5)	
Extinction coefficient	0.0013(3)	
Largest diff. peak and hole	0.540 and -0.847 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for product **5.59**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-4024(5)	4142(3)	1147(2)	42(1)
C(2)	-4028(6)	5258(3)	1207(2)	44(1)
C(3)	-2454(6)	5674(3)	903(2)	37(1)
C(4)	-824(5)	5209(2)	1143(1)	30(1)
C(5)	644(5)	5287(3)	724(1)	32(1)
C(6)	887(5)	4441(2)	442(2)	34(1)
C(7)	-318(5)	3634(2)	628(1)	34(1)
C(8)	-939(5)	4064(3)	1218(1)	31(1)
C(9)	394(5)	2599(2)	653(2)	30(1)
C(10)	-670(6)	1768(3)	556(2)	38(1)
C(11)	-43(6)	818(3)	593(2)	39(1)
C(12)	1687(6)	639(3)	730(2)	34(1)
C(13)	2377(7)	-333(3)	779(2)	41(1)
C(14)	4040(6)	-469(3)	923(2)	46(1)
C(15)	5108(6)	353(3)	1028(2)	47(1)
C(16)	4490(6)	1296(3)	985(2)	42(1)
C(17)	2759(6)	1462(3)	834(1)	33(1)
C(18)	2080(6)	2431(3)	786(2)	36(1)
C(19)	1574(6)	6223(3)	626(2)	36(1)
C(20)	3684(6)	7029(3)	68(2)	58(1)
C(21)	1950(6)	3445(3)	2661(2)	40(1)
C(22)	1764(6)	3327(4)	3316(2)	59(1)
C(23)	2912(6)	4413(3)	2540(2)	47(1)
C(24)	3013(6)	2572(3)	2428(2)	63(2)
C(25)	-1250(7)	2224(3)	2358(2)	68(2)
C(26)	-1584(6)	4428(3)	2663(2)	59(1)
O(1)	-2549(4)	3689(2)	1396(1)	35(1)
O(2)	215(3)	3766(2)	1644(1)	32(1)
O(3)	1376(4)	6972(2)	901(1)	50(1)
O(4)	2673(4)	6157(2)	185(1)	45(1)
Si(1)	-218(2)	3468(1)	2319(1)	37(1)

Table 3. Bond lengths [Å] and angles [°] for product **5.59**.

C(1)-O(1)	1.429(4)	C(15)-C(16)	1.360(5)
C(1)-C(2)	1.505(5)	C(15)-H(15)	0.9500
C(1)-H(1A)	0.9900	C(16)-C(17)	1.419(6)
C(1)-H(1B)	0.9900	C(16)-H(16)	0.9500
C(2)-C(3)	1.528(5)	C(17)-C(18)	1.410(5)
C(2)-H(2A)	0.9900	C(18)-H(18)	0.9500
C(2)-H(2B)	0.9900	C(19)-O(3)	1.205(4)
C(3)-C(4)	1.528(5)	C(19)-O(4)	1.342(4)
C(3)-H(3A)	0.9900	C(20)-O(4)	1.440(4)
C(3)-H(3B)	0.9900	C(20)-H(20A)	0.9800
C(4)-C(5)	1.513(5)	C(20)-H(20B)	0.9800
C(4)-C(8)	1.550(4)	C(20)-H(20C)	0.9800
C(4)-H(4)	1.0000	C(21)-C(23)	1.528(5)
C(5)-C(6)	1.327(5)	C(21)-C(24)	1.537(5)
C(5)-C(19)	1.471(5)	C(21)-C(22)	1.541(5)
C(6)-C(7)	1.502(5)	C(21)-Si(1)	1.877(4)
C(6)-H(6)	0.9500	C(22)-H(22A)	0.9800
C(7)-C(9)	1.499(5)	C(22)-H(22B)	0.9800
C(7)-C(8)	1.569(5)	C(22)-H(22C)	0.9800
C(7)-H(7)	1.0000	C(23)-H(23A)	0.9800
C(8)-O(2)	1.401(4)	C(23)-H(23B)	0.9800
C(8)-O(1)	1.419(4)	C(23)-H(23C)	0.9800
C(9)-C(18)	1.375(5)	C(24)-H(24A)	0.9800
C(9)-C(10)	1.411(5)	C(24)-H(24B)	0.9800
C(10)-C(11)	1.370(5)	C(24)-H(24C)	0.9800
C(10)-H(10)	0.9500	C(25)-Si(1)	1.858(4)
C(11)-C(12)	1.413(5)	C(25)-H(25A)	0.9800
C(11)-H(11)	0.9500	C(25)-H(25B)	0.9800
C(12)-C(17)	1.410(5)	C(25)-H(25C)	0.9800
C(12)-C(13)	1.417(5)	C(26)-Si(1)	1.858(4)
C(13)-C(14)	1.358(6)	C(26)-H(26A)	0.9800
C(13)-H(13)	0.9500	C(26)-H(26B)	0.9800
C(14)-C(15)	1.406(6)	C(26)-H(26C)	0.9800
C(14)-H(14)	0.9500	O(2)-Si(1)	1.658(2)

		C(8)-C(7)-H(7)	108.1
O(1)-C(1)-C(2)	112.8(3)	O(2)-C(8)-O(1)	105.4(3)
O(1)-C(1)-H(1A)	109.0	O(2)-C(8)-C(4)	109.1(3)
C(2)-C(1)-H(1A)	109.0	O(1)-C(8)-C(4)	115.9(3)
O(1)-C(1)-H(1B)	109.0	O(2)-C(8)-C(7)	108.4(3)
C(2)-C(1)-H(1B)	109.0	O(1)-C(8)-C(7)	113.5(3)
H(1A)-C(1)-H(1B)	107.8	C(4)-C(8)-C(7)	104.4(3)
C(1)-C(2)-C(3)	108.7(3)	C(18)-C(9)-C(10)	118.3(3)
C(1)-C(2)-H(2A)	110.0	C(18)-C(9)-C(7)	121.2(3)
C(3)-C(2)-H(2A)	110.0	C(10)-C(9)-C(7)	120.5(4)
C(1)-C(2)-H(2B)	110.0	C(11)-C(10)-C(9)	121.0(4)
C(3)-C(2)-H(2B)	110.0	C(11)-C(10)-H(10)	119.5
H(2A)-C(2)-H(2B)	108.3	C(9)-C(10)-H(10)	119.5
C(4)-C(3)-C(2)	110.7(3)	C(10)-C(11)-C(12)	121.1(4)
C(4)-C(3)-H(3A)	109.5	C(10)-C(11)-H(11)	119.5
C(2)-C(3)-H(3A)	109.5	C(12)-C(11)-H(11)	119.5
C(4)-C(3)-H(3B)	109.5	C(17)-C(12)-C(11)	118.4(4)
C(2)-C(3)-H(3B)	109.5	C(17)-C(12)-C(13)	118.8(4)
H(3A)-C(3)-H(3B)	108.1	C(11)-C(12)-C(13)	122.8(4)
C(5)-C(4)-C(3)	111.7(3)	C(14)-C(13)-C(12)	120.6(4)
C(5)-C(4)-C(8)	100.7(3)	C(14)-C(13)-H(13)	119.7
C(3)-C(4)-C(8)	113.5(3)	C(12)-C(13)-H(13)	119.7
C(5)-C(4)-H(4)	110.2	C(13)-C(14)-C(15)	120.6(4)
C(3)-C(4)-H(4)	110.2	C(13)-C(14)-H(14)	119.7
C(8)-C(4)-H(4)	110.2	C(15)-C(14)-H(14)	119.7
C(6)-C(5)-C(19)	125.7(4)	C(16)-C(15)-C(14)	120.4(4)
C(6)-C(5)-C(4)	111.7(3)	C(16)-C(15)-H(15)	119.8
C(19)-C(5)-C(4)	122.4(3)	C(14)-C(15)-H(15)	119.8
C(5)-C(6)-C(7)	112.6(3)	C(15)-C(16)-C(17)	120.3(4)
C(5)-C(6)-H(6)	123.7	C(15)-C(16)-H(16)	119.8
C(7)-C(6)-H(6)	123.7	C(17)-C(16)-H(16)	119.8
C(9)-C(7)-C(6)	116.5(3)	C(18)-C(17)-C(12)	119.1(4)
C(9)-C(7)-C(8)	115.0(3)	C(18)-C(17)-C(16)	121.7(4)
C(6)-C(7)-C(8)	100.5(3)	C(12)-C(17)-C(16)	119.2(4)
C(9)-C(7)-H(7)	108.1	C(9)-C(18)-C(17)	122.1(4)
C(6)-C(7)-H(7)	108.1	C(9)-C(18)-H(18)	119.0

C(17)-C(18)-H(18)	119.0	C(21)-C(24)-H(24A)	109.5
O(3)-C(19)-O(4)	123.1(4)	C(21)-C(24)-H(24B)	109.5
O(3)-C(19)-C(5)	124.5(4)	H(24A)-C(24)-H(24B)	109.5
O(4)-C(19)-C(5)	112.4(3)	C(21)-C(24)-H(24C)	109.5
O(4)-C(20)-H(20A)	109.5	H(24A)-C(24)-H(24C)	109.5
O(4)-C(20)-H(20B)	109.5	H(24B)-C(24)-H(24C)	109.5
H(20A)-C(20)-H(20B)	109.5	Si(1)-C(25)-H(25A)	109.5
O(4)-C(20)-H(20C)	109.5	Si(1)-C(25)-H(25B)	109.5
H(20A)-C(20)-H(20C)	109.5	H(25A)-C(25)-H(25B)	109.5
H(20B)-C(20)-H(20C)	109.5	Si(1)-C(25)-H(25C)	109.5
C(23)-C(21)-C(24)	108.5(4)	H(25A)-C(25)-H(25C)	109.5
C(23)-C(21)-C(22)	108.5(3)	H(25B)-C(25)-H(25C)	109.5
C(24)-C(21)-C(22)	108.9(4)	Si(1)-C(26)-H(26A)	109.5
C(23)-C(21)-Si(1)	110.7(3)	Si(1)-C(26)-H(26B)	109.5
C(24)-C(21)-Si(1)	110.6(3)	H(26A)-C(26)-H(26B)	109.5
C(22)-C(21)-Si(1)	109.7(3)	Si(1)-C(26)-H(26C)	109.5
C(21)-C(22)-H(22A)	109.5	H(26A)-C(26)-H(26C)	109.5
C(21)-C(22)-H(22B)	109.5	H(26B)-C(26)-H(26C)	109.5
H(22A)-C(22)-H(22B)	109.5	C(8)-O(1)-C(1)	116.7(3)
C(21)-C(22)-H(22C)	109.5	C(8)-O(2)-Si(1)	127.5(2)
H(22A)-C(22)-H(22C)	109.5	C(19)-O(4)-C(20)	116.4(3)
H(22B)-C(22)-H(22C)	109.5	O(2)-Si(1)-C(25)	110.65(18)
C(21)-C(23)-H(23A)	109.5	O(2)-Si(1)-C(26)	111.07(16)
C(21)-C(23)-H(23B)	109.5	C(25)-Si(1)-C(26)	110.6(2)
H(23A)-C(23)-H(23B)	109.5	O(2)-Si(1)-C(21)	102.86(15)
C(21)-C(23)-H(23C)	109.5	C(25)-Si(1)-C(21)	111.0(2)
H(23A)-C(23)-H(23C)	109.5	C(26)-Si(1)-C(21)	110.39(19)
H(23B)-C(23)-H(23C)	109.5		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for product **5.59**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	31(3)	49(2)	47(2)	1(2)	-6(2)	-3(2)
C(2)	36(3)	48(2)	47(2)	5(2)	0(2)	2(2)
C(3)	32(3)	40(2)	39(2)	5(2)	-1(2)	6(2)
C(4)	31(3)	31(2)	28(2)	-1(2)	1(2)	-1(2)
C(5)	35(3)	30(2)	30(2)	5(2)	2(2)	2(2)
C(6)	37(3)	34(2)	32(2)	2(2)	5(2)	5(2)
C(7)	42(3)	31(2)	28(2)	-2(2)	-3(2)	1(2)
C(8)	26(3)	35(2)	31(2)	4(2)	5(2)	-4(2)
C(9)	33(3)	31(2)	27(2)	-4(2)	-1(2)	0(2)
C(10)	39(3)	37(2)	39(2)	-6(2)	-6(2)	0(2)
C(11)	43(3)	33(2)	40(2)	-6(2)	-2(2)	-5(2)
C(12)	40(3)	36(2)	25(2)	-1(2)	2(2)	0(2)
C(13)	52(3)	36(2)	36(2)	-2(2)	-1(2)	2(2)
C(14)	59(4)	41(2)	38(2)	2(2)	2(2)	10(2)
C(15)	42(3)	54(3)	44(2)	2(2)	1(2)	8(2)
C(16)	34(3)	43(2)	49(2)	0(2)	-1(2)	3(2)
C(17)	35(3)	35(2)	30(2)	-1(2)	2(2)	-1(2)
C(18)	37(3)	33(2)	36(2)	-2(2)	3(2)	-4(2)
C(19)	38(3)	36(2)	32(2)	3(2)	-2(2)	9(2)
C(20)	61(4)	39(2)	73(3)	13(2)	25(3)	-10(2)
C(21)	47(3)	40(2)	31(2)	5(2)	-3(2)	-3(2)
C(22)	63(4)	77(3)	37(2)	14(2)	-8(2)	-13(3)
C(23)	44(3)	51(2)	47(2)	6(2)	1(2)	-10(2)
C(24)	58(4)	60(3)	71(3)	-3(2)	-14(3)	10(3)
C(25)	69(4)	64(3)	70(3)	30(3)	-20(3)	-24(3)
C(26)	46(3)	91(3)	39(2)	-3(2)	4(2)	13(3)
O(1)	34(2)	37(1)	35(1)	3(1)	-2(1)	-2(1)
O(2)	36(2)	35(1)	26(1)	1(1)	-2(1)	5(1)
O(3)	59(2)	35(2)	56(2)	-7(1)	15(2)	-2(2)
O(4)	51(2)	37(1)	46(2)	2(1)	19(2)	-3(1)
Si(1)	41(1)	38(1)	31(1)	6(1)	-2(1)	-4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for product **5.59**.

	x	y	z	U(eq)
H(1A)	-5059	3870	1334	51
H(1B)	-4076	3967	735	51
H(2A)	-4005	5444	1617	53
H(2B)	-5077	5537	1033	53
H(3A)	-2533	5534	487	44
H(3B)	-2412	6406	954	44
H(4)	-513	5531	1516	36
H(6)	1729	4355	153	41
H(7)	-1312	3631	359	40
H(10)	-1839	1870	464	46
H(11)	-783	271	524	47
H(13)	1669	-894	710	50
H(14)	4486	-1124	954	55
H(15)	6269	248	1129	56
H(16)	5222	1847	1057	50
H(18)	2811	2985	848	43
H(20A)	2935	7612	38	86
H(20B)	4301	6939	-294	86
H(20C)	4504	7131	380	86
H(22A)	2896	3249	3489	89
H(22B)	1069	2738	3400	89
H(22C)	1208	3920	3475	89
H(23A)	2292	4973	2711	71
H(23B)	3002	4512	2125	71
H(23C)	4058	4374	2707	71
H(24A)	4153	2587	2601	95
H(24B)	3113	2631	2011	95
H(24C)	2449	1943	2524	95
H(25A)	-2431	2274	2222	102
H(25B)	-1243	1989	2756	102

H(25C)	-620	1753	2116	102
H(26A)	-1009	5075	2645	88
H(26B)	-1786	4247	3064	88
H(26C)	-2678	4468	2460	88

Table 6. Torsion angles [°] for product **5.59**.

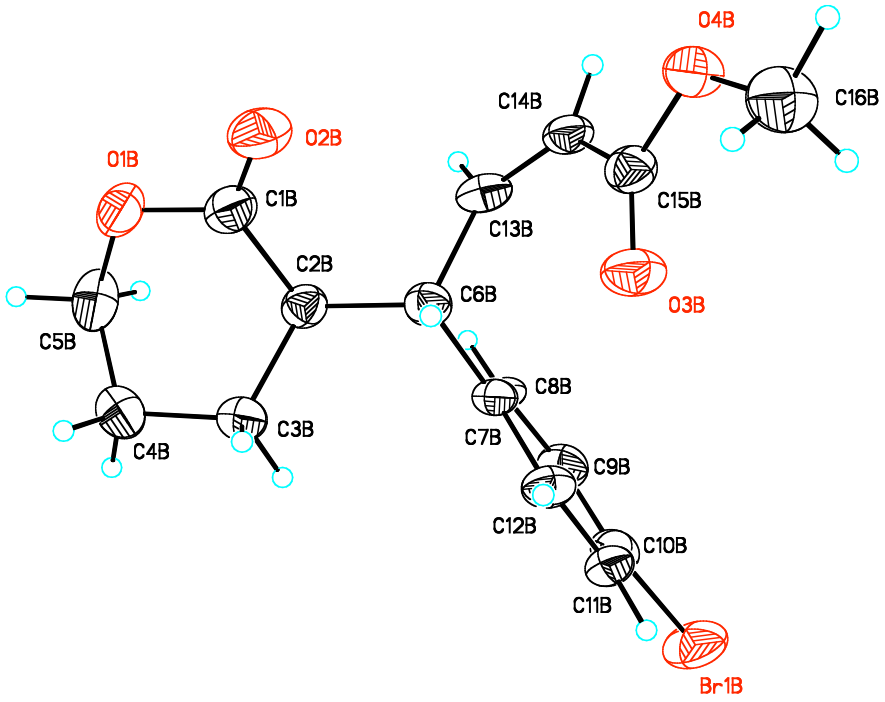
O(1)-C(1)-C(2)-C(3)	60.3(4)
C(1)-C(2)-C(3)-C(4)	-56.5(4)
C(2)-C(3)-C(4)-C(5)	158.3(3)
C(2)-C(3)-C(4)-C(8)	45.3(4)
C(3)-C(4)-C(5)-C(6)	-100.0(4)
C(8)-C(4)-C(5)-C(6)	20.8(4)
C(3)-C(4)-C(5)-C(19)	75.8(4)
C(8)-C(4)-C(5)-C(19)	-163.4(3)
C(19)-C(5)-C(6)-C(7)	-177.6(3)
C(4)-C(5)-C(6)-C(7)	-1.9(5)
C(5)-C(6)-C(7)-C(9)	-142.6(3)
C(5)-C(6)-C(7)-C(8)	-17.6(4)
C(5)-C(4)-C(8)-O(2)	85.4(3)
C(3)-C(4)-C(8)-O(2)	-155.0(3)
C(5)-C(4)-C(8)-O(1)	-155.9(3)
C(3)-C(4)-C(8)-O(1)	-36.4(4)
C(5)-C(4)-C(8)-C(7)	-30.2(4)
C(3)-C(4)-C(8)-C(7)	89.3(4)
C(9)-C(7)-C(8)-O(2)	39.2(4)
C(6)-C(7)-C(8)-O(2)	-86.9(3)
C(9)-C(7)-C(8)-O(1)	-77.6(4)
C(6)-C(7)-C(8)-O(1)	156.4(3)
C(9)-C(7)-C(8)-C(4)	155.3(3)
C(6)-C(7)-C(8)-C(4)	29.3(4)
C(6)-C(7)-C(9)-C(18)	31.7(5)
C(8)-C(7)-C(9)-C(18)	-85.6(5)
C(6)-C(7)-C(9)-C(10)	-150.2(3)
C(8)-C(7)-C(9)-C(10)	92.5(4)
C(18)-C(9)-C(10)-C(11)	-0.1(5)
C(7)-C(9)-C(10)-C(11)	-178.3(3)
C(9)-C(10)-C(11)-C(12)	0.2(5)
C(10)-C(11)-C(12)-C(17)	0.5(5)
C(10)-C(11)-C(12)-C(13)	179.1(3)
C(17)-C(12)-C(13)-C(14)	0.0(5)

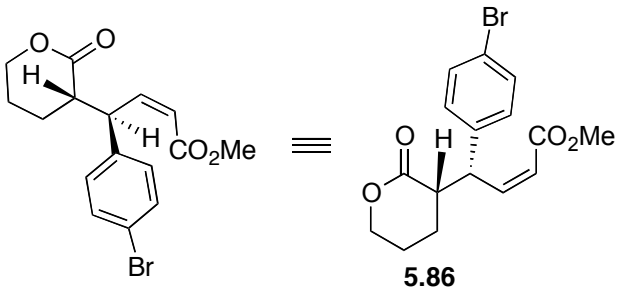
C(11)-C(12)-C(13)-C(14)	-178.6(4)
C(12)-C(13)-C(14)-C(15)	0.1(6)
C(13)-C(14)-C(15)-C(16)	-0.1(6)
C(14)-C(15)-C(16)-C(17)	0.0(6)
C(11)-C(12)-C(17)-C(18)	-1.2(5)
C(13)-C(12)-C(17)-C(18)	-179.9(3)
C(11)-C(12)-C(17)-C(16)	178.5(3)
C(13)-C(12)-C(17)-C(16)	-0.1(5)
C(15)-C(16)-C(17)-C(18)	179.9(3)
C(15)-C(16)-C(17)-C(12)	0.1(6)
C(10)-C(9)-C(18)-C(17)	-0.7(5)
C(7)-C(9)-C(18)-C(17)	177.5(3)
C(12)-C(17)-C(18)-C(9)	1.3(5)
C(16)-C(17)-C(18)-C(9)	-178.4(4)
C(6)-C(5)-C(19)-O(3)	-177.2(4)
C(4)-C(5)-C(19)-O(3)	7.6(6)
C(6)-C(5)-C(19)-O(4)	3.4(6)
C(4)-C(5)-C(19)-O(4)	-171.8(3)
O(2)-C(8)-O(1)-C(1)	160.5(3)
C(4)-C(8)-O(1)-C(1)	39.9(4)
C(7)-C(8)-O(1)-C(1)	-81.0(4)
C(2)-C(1)-O(1)-C(8)	-52.7(4)
O(1)-C(8)-O(2)-Si(1)	-22.7(4)
C(4)-C(8)-O(2)-Si(1)	102.3(3)
C(7)-C(8)-O(2)-Si(1)	-144.6(2)
O(3)-C(19)-O(4)-C(20)	2.6(6)
C(5)-C(19)-O(4)-C(20)	-178.0(3)
C(8)-O(2)-Si(1)-C(25)	74.1(3)
C(8)-O(2)-Si(1)-C(26)	-49.2(3)
C(8)-O(2)-Si(1)-C(21)	-167.3(3)
C(23)-C(21)-Si(1)-O(2)	52.1(3)
C(24)-C(21)-Si(1)-O(2)	-68.1(3)
C(22)-C(21)-Si(1)-O(2)	171.8(3)
C(23)-C(21)-Si(1)-C(25)	170.5(3)
C(24)-C(21)-Si(1)-C(25)	50.2(4)
C(22)-C(21)-Si(1)-C(25)	-69.8(4)

C(23)-C(21)-Si(1)-C(26)	-66.5(3)
C(24)-C(21)-Si(1)-C(26)	173.3(3)
C(22)-C(21)-Si(1)-C(26)	53.2(3)

Symmetry transformations used to generate equivalent atoms:

23. X-ray crystallographic structure of product 5.86





5.86

Table 1. Crystal data and structure refinement for product **5.86**.

Identification code	ylvii_33	
Empirical formula	C16 H17 Br O4	
Formula weight	353.21	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	Pna2(1)	
Unit cell dimensions	a = 15.9648(4) Å	α= 90°.
	b = 8.5979(2) Å	β= 90°.
	c = 22.1885(5) Å	γ = 90°.
Volume	3045.68(12) $Å^3$	
Z	8	
Density (calculated)	1.541 Mg/m^3	
Absorption coefficient	3.800 mm^{-1}	
F(000)	1440	
Crystal size	0.18 x 0.13 x 0.12 mm^3	
Theta range for data collection	3.98 to 66.14°.	
Index ranges	-18<=h<=17, -10<=k<=10, -25<=l<=25	
Reflections collected	19895	
Independent reflections	4794 [R(int) = 0.0432]	
Completeness to theta = 66.14°	96.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6585 and 0.5479	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4794 / 1 / 381	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0468, wR2 = 0.1141	
R indices (all data)	R1 = 0.0526, wR2 = 0.1188	
Absolute structure parameter	0.23(2)	
Largest diff. peak and hole	1.906 and -0.543 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for product **5.86**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	9102(1)	5244(1)	588(1)	58(1)
Br(1B)	3336(1)	4753(1)	10162(1)	59(1)
C(1)	5641(3)	-508(6)	2317(2)	37(1)
C(2)	6307(3)	352(5)	1960(2)	30(1)
C(3)	6500(3)	-533(6)	1379(2)	40(1)
C(4)	6594(3)	-2310(7)	1501(3)	47(1)
C(5)	6575(3)	-2623(6)	2169(3)	42(1)
C(6)	6086(3)	2084(6)	1855(2)	33(1)
C(7)	6818(3)	2888(6)	1542(2)	32(1)
C(8)	6779(3)	3282(6)	932(2)	35(1)
C(9)	7453(3)	3982(6)	647(2)	38(1)
C(10)	8170(3)	4274(6)	980(2)	40(1)
C(11)	8222(3)	3947(6)	1579(2)	42(1)
C(12)	7542(3)	3262(6)	1859(2)	41(1)
C(13)	5889(3)	2866(6)	2436(2)	36(1)
C(14)	5365(3)	4075(6)	2525(2)	36(1)
C(15)	4876(3)	4810(6)	2046(2)	37(1)
C(16)	3829(4)	6669(8)	1861(3)	61(2)
C(1B)	6796(3)	10828(6)	8541(2)	37(1)
C(2B)	6097(3)	9983(5)	8870(2)	29(1)
C(3B)	5901(3)	10876(6)	9450(2)	35(1)
C(4B)	5766(4)	12602(6)	9331(3)	42(1)
C(5B)	5854(3)	12983(7)	8675(3)	45(1)
C(6B)	6302(3)	8262(5)	8973(2)	30(1)
C(7B)	5570(3)	7452(5)	9282(2)	28(1)
C(8B)	4789(3)	7371(5)	8997(2)	29(1)
C(9B)	4122(3)	6579(6)	9251(2)	38(1)
C(10B)	4238(3)	5886(6)	9817(2)	40(1)
C(11B)	4986(3)	5994(5)	10119(2)	38(1)
C(12B)	5654(3)	6769(6)	9847(2)	33(1)

C(13B)	6455(3)	7447(6)	8381(2)	32(1)
C(14B)	6980(3)	6270(5)	8277(2)	31(1)
C(15B)	7507(3)	5505(5)	8730(2)	33(1)
C(16B)	8623(3)	3745(7)	8872(3)	49(1)
O(1)	5797(2)	-2008(4)	2416(2)	44(1)
O(2)	4994(2)	49(4)	2502(2)	45(1)
O(3)	4984(3)	4677(5)	1512(2)	51(1)
O(4)	4282(2)	5736(4)	2281(2)	44(1)
O(1B)	6641(2)	12382(4)	8443(2)	42(1)
O(2B)	7452(2)	10281(4)	8376(2)	49(1)
O(3B)	7409(2)	5551(4)	9272(2)	42(1)
O(4B)	8135(2)	4698(4)	8469(2)	38(1)

Table 3. Bond lengths [Å] and angles [°] for product **5.86**.

Br(1)-C(10)	1.916(5)	C(15)-O(3)	1.203(7)
Br(1B)-C(10B)	1.899(5)	C(15)-O(4)	1.344(6)
C(1)-O(2)	1.210(6)	C(16)-O(4)	1.426(6)
C(1)-O(1)	1.332(6)	C(16)-H(16A)	0.9800
C(1)-C(2)	1.518(6)	C(16)-H(16B)	0.9800
C(2)-C(3)	1.529(7)	C(16)-H(16C)	0.9800
C(2)-C(6)	1.548(7)	C(1B)-O(2B)	1.205(6)
C(2)-H(2A)	1.0000	C(1B)-O(1B)	1.375(6)
C(3)-C(4)	1.559(8)	C(1B)-C(2B)	1.519(6)
C(3)-H(3A)	0.9900	C(2B)-C(3B)	1.531(6)
C(3)-H(3B)	0.9900	C(2B)-C(6B)	1.533(6)
C(4)-C(5)	1.505(9)	C(2B)-H(2BA)	1.0000
C(4)-H(4A)	0.9900	C(3B)-C(4B)	1.523(7)
C(4)-H(4B)	0.9900	C(3B)-H(3BA)	0.9900
C(5)-O(1)	1.457(6)	C(3B)-H(3BB)	0.9900
C(5)-H(5A)	0.9900	C(4B)-C(5B)	1.499(8)
C(5)-H(5B)	0.9900	C(4B)-H(4BA)	0.9900
C(6)-C(13)	1.487(7)	C(4B)-H(4BB)	0.9900
C(6)-C(7)	1.525(6)	C(5B)-O(1B)	1.453(7)
C(6)-H(6A)	1.0000	C(5B)-H(5BA)	0.9900
C(7)-C(12)	1.391(7)	C(5B)-H(5BB)	0.9900
C(7)-C(8)	1.396(7)	C(6B)-C(13B)	1.508(6)
C(8)-C(9)	1.387(7)	C(6B)-C(7B)	1.523(6)
C(8)-H(8A)	0.9500	C(6B)-H(6BA)	1.0000
C(9)-C(10)	1.386(7)	C(7B)-C(12B)	1.391(7)
C(9)-H(9A)	0.9500	C(7B)-C(8B)	1.399(6)
C(10)-C(11)	1.361(7)	C(8B)-C(9B)	1.385(6)
C(11)-C(12)	1.383(7)	C(8B)-H(8BA)	0.9500
C(11)-H(11A)	0.9500	C(9B)-C(10B)	1.402(8)
C(12)-H(12A)	0.9500	C(9B)-H(9BA)	0.9500
C(13)-C(14)	1.349(7)	C(10B)-C(11B)	1.372(7)
C(13)-H(13A)	0.9500	C(11B)-C(12B)	1.394(7)
C(14)-C(15)	1.463(7)	C(11B)-H(11B)	0.9500
C(14)-H(14A)	0.9500	C(12B)-H(12B)	0.9500

C(13B)-C(14B)	1.333(7)	C(4)-C(5)-H(5B)	109.9
C(13B)-H(13B)	0.9500	H(5A)-C(5)-H(5B)	108.3
C(14B)-C(15B)	1.467(6)	C(13)-C(6)-C(7)	110.6(4)
C(14B)-H(14B)	0.9500	C(13)-C(6)-C(2)	110.6(4)
C(15B)-O(3B)	1.213(6)	C(7)-C(6)-C(2)	109.3(4)
C(15B)-O(4B)	1.350(6)	C(13)-C(6)-H(6A)	108.8
C(16B)-O(4B)	1.441(6)	C(7)-C(6)-H(6A)	108.8
C(16B)-H(16D)	0.9800	C(2)-C(6)-H(6A)	108.8
C(16B)-H(16E)	0.9800	C(12)-C(7)-C(8)	118.1(4)
C(16B)-H(16F)	0.9800	C(12)-C(7)-C(6)	120.7(4)
		C(8)-C(7)-C(6)	121.2(4)
O(2)-C(1)-O(1)	119.1(4)	C(9)-C(8)-C(7)	120.9(4)
O(2)-C(1)-C(2)	125.6(4)	C(9)-C(8)-H(8A)	119.5
O(1)-C(1)-C(2)	115.3(4)	C(7)-C(8)-H(8A)	119.5
C(1)-C(2)-C(3)	109.8(4)	C(10)-C(9)-C(8)	118.4(4)
C(1)-C(2)-C(6)	112.8(4)	C(10)-C(9)-H(9A)	120.8
C(3)-C(2)-C(6)	113.4(4)	C(8)-C(9)-H(9A)	120.8
C(1)-C(2)-H(2A)	106.8	C(11)-C(10)-C(9)	122.3(4)
C(3)-C(2)-H(2A)	106.8	C(11)-C(10)-Br(1)	119.1(4)
C(6)-C(2)-H(2A)	106.8	C(9)-C(10)-Br(1)	118.5(4)
C(2)-C(3)-C(4)	111.1(4)	C(10)-C(11)-C(12)	118.6(5)
C(2)-C(3)-H(3A)	109.4	C(10)-C(11)-H(11A)	120.7
C(4)-C(3)-H(3A)	109.4	C(12)-C(11)-H(11A)	120.7
C(2)-C(3)-H(3B)	109.4	C(11)-C(12)-C(7)	121.6(4)
C(4)-C(3)-H(3B)	109.4	C(11)-C(12)-H(12A)	119.2
H(3A)-C(3)-H(3B)	108.0	C(7)-C(12)-H(12A)	119.2
C(5)-C(4)-C(3)	110.1(5)	C(14)-C(13)-C(6)	127.4(5)
C(5)-C(4)-H(4A)	109.6	C(14)-C(13)-H(13A)	116.3
C(3)-C(4)-H(4A)	109.6	C(6)-C(13)-H(13A)	116.3
C(5)-C(4)-H(4B)	109.6	C(13)-C(14)-C(15)	123.8(5)
C(3)-C(4)-H(4B)	109.6	C(13)-C(14)-H(14A)	118.1
H(4A)-C(4)-H(4B)	108.1	C(15)-C(14)-H(14A)	118.1
O(1)-C(5)-C(4)	108.9(4)	O(3)-C(15)-O(4)	122.6(5)
O(1)-C(5)-H(5A)	109.9	O(3)-C(15)-C(14)	126.8(5)
C(4)-C(5)-H(5A)	109.9	O(4)-C(15)-C(14)	110.6(4)
O(1)-C(5)-H(5B)	109.9	O(4)-C(16)-H(16A)	109.5

O(4)-C(16)-H(16B)	109.5	C(7B)-C(6B)-H(6BA)	109.4
H(16A)-C(16)-H(16B)	109.5	C(2B)-C(6B)-H(6BA)	109.4
O(4)-C(16)-H(16C)	109.5	C(12B)-C(7B)-C(8B)	118.2(4)
H(16A)-C(16)-H(16C)	109.5	C(12B)-C(7B)-C(6B)	121.6(4)
H(16B)-C(16)-H(16C)	109.5	C(8B)-C(7B)-C(6B)	120.1(4)
O(2B)-C(1B)-O(1B)	119.2(4)	C(9B)-C(8B)-C(7B)	121.6(4)
O(2B)-C(1B)-C(2B)	126.7(5)	C(9B)-C(8B)-H(8BA)	119.2
O(1B)-C(1B)-C(2B)	114.1(4)	C(7B)-C(8B)-H(8BA)	119.2
C(1B)-C(2B)-C(3B)	108.4(4)	C(8B)-C(9B)-C(10B)	118.2(4)
C(1B)-C(2B)-C(6B)	112.2(4)	C(8B)-C(9B)-H(9BA)	120.9
C(3B)-C(2B)-C(6B)	113.7(4)	C(10B)-C(9B)-H(9BA)	120.9
C(1B)-C(2B)-H(2BA)	107.4	C(11B)-C(10B)-C(9B)	121.6(5)
C(3B)-C(2B)-H(2BA)	107.4	C(11B)-C(10B)-Br(1B)	119.9(4)
C(6B)-C(2B)-H(2BA)	107.4	C(9B)-C(10B)-Br(1B)	118.6(4)
C(4B)-C(3B)-C(2B)	111.8(4)	C(10B)-C(11B)-C(12B)	119.1(5)
C(4B)-C(3B)-H(3BA)	109.3	C(10B)-C(11B)-H(11B)	120.4
C(2B)-C(3B)-H(3BA)	109.3	C(12B)-C(11B)-H(11B)	120.4
C(4B)-C(3B)-H(3BB)	109.3	C(7B)-C(12B)-C(11B)	121.2(4)
C(2B)-C(3B)-H(3BB)	109.3	C(7B)-C(12B)-H(12B)	119.4
H(3BA)-C(3B)-H(3BB)	107.9	C(11B)-C(12B)-H(12B)	119.4
C(5B)-C(4B)-C(3B)	111.6(5)	C(14B)-C(13B)-C(6B)	127.2(4)
C(5B)-C(4B)-H(4BA)	109.3	C(14B)-C(13B)-H(13B)	116.4
C(3B)-C(4B)-H(4BA)	109.3	C(6B)-C(13B)-H(13B)	116.4
C(5B)-C(4B)-H(4BB)	109.3	C(13B)-C(14B)-C(15B)	125.6(4)
C(3B)-C(4B)-H(4BB)	109.3	C(13B)-C(14B)-H(14B)	117.2
H(4BA)-C(4B)-H(4BB)	108.0	C(15B)-C(14B)-H(14B)	117.2
O(1B)-C(5B)-C(4B)	110.3(5)	O(3B)-C(15B)-O(4B)	122.6(4)
O(1B)-C(5B)-H(5BA)	109.6	O(3B)-C(15B)-C(14B)	126.1(4)
C(4B)-C(5B)-H(5BA)	109.6	O(4B)-C(15B)-C(14B)	111.3(4)
O(1B)-C(5B)-H(5BB)	109.6	O(4B)-C(16B)-H(16D)	109.5
C(4B)-C(5B)-H(5BB)	109.6	O(4B)-C(16B)-H(16E)	109.5
H(5BA)-C(5B)-H(5BB)	108.1	H(16D)-C(16B)-H(16E)	109.5
C(13B)-C(6B)-C(7B)	107.7(4)	O(4B)-C(16B)-H(16F)	109.5
C(13B)-C(6B)-C(2B)	110.7(4)	H(16D)-C(16B)-H(16F)	109.5
C(7B)-C(6B)-C(2B)	110.2(4)	H(16E)-C(16B)-H(16F)	109.5
C(13B)-C(6B)-H(6BA)	109.4	C(1)-O(1)-C(5)	116.6(4)

C(15)-O(4)-C(16)	116.0(4)	C(15B)-O(4B)-C(16B)	115.2(4)
C(1B)-O(1B)-C(5B)	116.4(4)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for product **5.86**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ..\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	58(1)	74(1)	43(1)	0(1)	14(1)	-26(1)
Br(1B)	58(1)	72(1)	47(1)	4(1)	16(1)	-26(1)
C(1)	37(3)	43(3)	31(2)	5(2)	2(2)	-6(2)
C(2)	26(2)	39(3)	25(2)	2(2)	1(2)	-1(2)
C(3)	41(3)	48(3)	31(2)	-1(2)	1(2)	4(2)
C(4)	46(3)	42(3)	53(4)	-8(2)	3(2)	-2(2)
C(5)	43(3)	33(3)	51(3)	2(2)	2(2)	1(2)
C(6)	32(2)	45(3)	23(2)	7(2)	3(2)	3(2)
C(7)	35(2)	33(2)	28(2)	2(2)	2(2)	1(2)
C(8)	36(2)	43(3)	25(2)	0(2)	1(2)	1(2)
C(9)	50(3)	44(3)	21(2)	5(2)	4(2)	4(2)
C(10)	50(3)	37(3)	32(3)	0(2)	11(2)	-6(2)
C(11)	41(3)	50(3)	36(3)	2(2)	-5(2)	-6(2)
C(12)	47(3)	49(3)	27(2)	8(2)	-4(2)	-4(2)
C(13)	41(3)	45(3)	23(2)	9(2)	1(2)	5(2)
C(14)	45(3)	42(3)	21(2)	0(2)	6(2)	2(2)
C(15)	37(3)	41(3)	34(3)	8(2)	8(2)	2(2)
C(16)	52(3)	75(4)	55(4)	12(3)	-2(3)	22(3)
C(1B)	39(3)	41(3)	30(2)	1(2)	1(2)	-7(2)
C(2B)	32(2)	31(2)	25(2)	1(2)	-1(2)	-3(2)
C(3B)	41(2)	36(3)	29(2)	-1(2)	4(2)	1(2)
C(4B)	49(3)	36(3)	42(3)	-6(2)	1(2)	0(2)
C(5B)	40(3)	33(3)	62(4)	5(3)	-3(2)	-3(2)
C(6B)	30(2)	32(2)	26(2)	-1(2)	0(2)	-1(2)
C(7B)	30(2)	31(2)	22(2)	-1(2)	5(2)	1(2)
C(8B)	37(2)	34(2)	16(2)	3(2)	3(2)	-1(2)
C(9B)	37(2)	44(3)	34(2)	-4(2)	-1(2)	-2(2)
C(10B)	45(3)	38(3)	36(2)	-8(2)	10(2)	-5(2)
C(11B)	52(3)	36(2)	24(2)	6(2)	6(2)	5(2)
C(12B)	32(2)	42(3)	24(2)	3(2)	0(2)	3(2)

C(13B)	28(2)	46(3)	21(2)	4(2)	1(2)	-4(2)
C(14B)	37(2)	36(2)	20(2)	1(2)	4(2)	-4(2)
C(15B)	30(2)	34(2)	33(3)	0(2)	4(2)	-5(2)
C(16B)	37(3)	59(3)	50(3)	5(3)	-3(2)	13(2)
O(1)	41(2)	43(2)	49(2)	5(2)	5(2)	-3(1)
O(2)	40(2)	53(2)	42(2)	6(2)	11(2)	-2(1)
O(3)	60(2)	65(3)	29(2)	11(2)	4(2)	21(2)
O(4)	38(2)	49(2)	46(2)	4(2)	7(2)	5(2)
O(1B)	48(2)	35(2)	43(2)	7(2)	3(2)	-9(1)
O(2B)	43(2)	57(2)	48(2)	0(2)	14(2)	-6(2)
O(3B)	46(2)	54(2)	26(2)	5(2)	4(1)	9(2)
O(4B)	36(2)	45(2)	32(2)	1(1)	2(1)	6(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for product **5.86**.

	x	y	z	U(eq)
H(2A)	6829	334	2209	36
H(3A)	7026	-128	1201	48
H(3B)	6043	-360	1085	48
H(4A)	6133	-2880	1302	56
H(4B)	7131	-2685	1331	56
H(5A)	6609	-3756	2244	51
H(5B)	7060	-2117	2366	51
H(6A)	5583	2143	1587	40
H(8A)	6284	3068	710	42
H(9A)	7425	4255	232	46
H(11A)	8716	4183	1800	51
H(12A)	7569	3043	2278	49
H(13A)	6164	2469	2783	43
H(14A)	5310	4471	2923	43
H(16A)	4224	7197	1591	91
H(16B)	3498	7446	2080	91
H(16C)	3454	6006	1624	91
H(2BA)	5587	10031	8609	35
H(3BA)	5391	10435	9638	42
H(3BB)	6370	10745	9738	42
H(4BA)	5200	12904	9470	51
H(4BB)	6181	13211	9564	51
H(5BA)	5382	12520	8448	54
H(5BB)	5834	14125	8619	54
H(6BA)	6812	8174	9232	35
H(8BA)	4716	7873	8619	35
H(9BA)	3600	6507	9048	46
H(11B)	5048	5546	10507	45
H(12B)	6176	6831	10052	39
H(13B)	6144	7813	8045	38

H(14B)	7014	5895	7875	37
H(16D)	9063	3211	8644	73
H(16E)	8258	2974	9064	73
H(16F)	8879	4402	9182	73

Table 6. Torsion angles [°] for product **5.86**.

O(2)-C(1)-C(2)-C(3)	-126.8(5)
O(1)-C(1)-C(2)-C(3)	51.9(5)
O(2)-C(1)-C(2)-C(6)	0.7(7)
O(1)-C(1)-C(2)-C(6)	179.4(4)
C(1)-C(2)-C(3)-C(4)	-44.8(5)
C(6)-C(2)-C(3)-C(4)	-172.0(4)
C(2)-C(3)-C(4)-C(5)	-7.1(6)
C(3)-C(4)-C(5)-O(1)	57.0(6)
C(1)-C(2)-C(6)-C(13)	53.3(5)
C(3)-C(2)-C(6)-C(13)	178.9(4)
C(1)-C(2)-C(6)-C(7)	175.3(4)
C(3)-C(2)-C(6)-C(7)	-59.2(5)
C(13)-C(6)-C(7)-C(12)	47.2(6)
C(2)-C(6)-C(7)-C(12)	-74.8(6)
C(13)-C(6)-C(7)-C(8)	-132.3(5)
C(2)-C(6)-C(7)-C(8)	105.8(5)
C(12)-C(7)-C(8)-C(9)	2.0(7)
C(6)-C(7)-C(8)-C(9)	-178.6(4)
C(7)-C(8)-C(9)-C(10)	0.4(7)
C(8)-C(9)-C(10)-C(11)	-2.3(8)
C(8)-C(9)-C(10)-Br(1)	-179.9(4)
C(9)-C(10)-C(11)-C(12)	1.7(8)
Br(1)-C(10)-C(11)-C(12)	179.3(4)
C(10)-C(11)-C(12)-C(7)	0.9(8)
C(8)-C(7)-C(12)-C(11)	-2.7(8)
C(6)-C(7)-C(12)-C(11)	177.9(5)
C(7)-C(6)-C(13)-C(14)	88.4(6)
C(2)-C(6)-C(13)-C(14)	-150.4(5)
C(6)-C(13)-C(14)-C(15)	1.4(9)
C(13)-C(14)-C(15)-O(3)	-15.6(9)
C(13)-C(14)-C(15)-O(4)	166.5(5)
O(2B)-C(1B)-C(2B)-C(3B)	125.3(5)
O(1B)-C(1B)-C(2B)-C(3B)	-53.1(5)
O(2B)-C(1B)-C(2B)-C(6B)	-1.0(7)

O(1B)-C(1B)-C(2B)-C(6B)	-179.5(4)
C(1B)-C(2B)-C(3B)-C(4B)	50.3(5)
C(6B)-C(2B)-C(3B)-C(4B)	175.7(4)
C(2B)-C(3B)-C(4B)-C(5B)	0.4(6)
C(3B)-C(4B)-C(5B)-O(1B)	-52.1(6)
C(1B)-C(2B)-C(6B)-C(13B)	-58.7(5)
C(3B)-C(2B)-C(6B)-C(13B)	177.9(4)
C(1B)-C(2B)-C(6B)-C(7B)	-177.8(4)
C(3B)-C(2B)-C(6B)-C(7B)	58.8(5)
C(13B)-C(6B)-C(7B)-C(12B)	120.6(5)
C(2B)-C(6B)-C(7B)-C(12B)	-118.5(5)
C(13B)-C(6B)-C(7B)-C(8B)	-58.9(5)
C(2B)-C(6B)-C(7B)-C(8B)	61.9(5)
C(12B)-C(7B)-C(8B)-C(9B)	-2.8(7)
C(6B)-C(7B)-C(8B)-C(9B)	176.8(4)
C(7B)-C(8B)-C(9B)-C(10B)	1.8(7)
C(8B)-C(9B)-C(10B)-C(11B)	0.7(7)
C(8B)-C(9B)-C(10B)-Br(1B)	-178.5(4)
C(9B)-C(10B)-C(11B)-C(12B)	-2.1(7)
Br(1B)-C(10B)-C(11B)-C(12B)	177.1(4)
C(8B)-C(7B)-C(12B)-C(11B)	1.4(7)
C(6B)-C(7B)-C(12B)-C(11B)	-178.2(4)
C(10B)-C(11B)-C(12B)-C(7B)	1.0(7)
C(7B)-C(6B)-C(13B)-C(14B)	-92.1(5)
C(2B)-C(6B)-C(13B)-C(14B)	147.4(5)
C(6B)-C(13B)-C(14B)-C(15B)	1.3(8)
C(13B)-C(14B)-C(15B)-O(3B)	18.9(8)
C(13B)-C(14B)-C(15B)-O(4B)	-161.7(4)
O(2)-C(1)-O(1)-C(5)	178.4(5)
C(2)-C(1)-O(1)-C(5)	-0.4(6)
C(4)-C(5)-O(1)-C(1)	-55.7(6)
O(3)-C(15)-O(4)-C(16)	-5.4(8)
C(14)-C(15)-O(4)-C(16)	172.6(5)
O(2B)-C(1B)-O(1B)-C(5B)	-177.5(5)
C(2B)-C(1B)-O(1B)-C(5B)	1.1(6)
C(4B)-C(5B)-O(1B)-C(1B)	53.3(6)

O(3B)-C(15B)-O(4B)-C(16B)	7.1(7)
C(14B)-C(15B)-O(4B)-C(16B)	-172.4(4)

Symmetry transformations used to generate equivalent atoms: