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John Frederick Briones Date

TRANSITION METAL CATALYZED STEREOSELECTIVE TRANSFORMATIONS OF ALKYNES AND DONOR/ACCEPTOR CARBENOIDS

By

John Frederick Briones
Doctor of Philosophy

Chemistry

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An abstract of

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Abstract

TRANSITION METAL CATALYZED STEREOSELECTIVE TRANSFORMATIONS OF ALKYNES AND DONOR/ACCEPTOR CARBENOIDS

By John Frederick Briones

Transition metal-stabilized carbenoids are versatile intermediates in organic synthesis. In particular, donor/acceptor-substituted carbenoids have been demonstrated to undergo highly stereoselective transformations owing to their modulated reactivity and therefore high chemo- and stereoselectivity. These characteristics were crucial to the discovery and development of powerful asymmetric synthetic transformations that are discussed in this thesis.

The first part of this dissertation focuses on the rhodium-catalyzed cyclopropenation of terminal alkynes. By using the prolinate-based catalyst Rh_2(*S*-DOSP)$_4$, highly enantioselective synthesis of vinylcyclopropenes using vinyldiazoacetates was achieved. These vinylcyclopropenes were also found to undergo rhodium-catalyzed ring expansion to the corresponding cyclopentadiene derivatives. Further expanding the scope of donor/acceptor cyclopropenation chemistry, we have developed the Rh_2(*S*-PTAD)$_4$-catalyzed highly enantioselective cyclopropenation of aryl alkynes with siloxyvinyldiazoacetates. This methodology allowed us to synthesize cyclopropene derivatives bearing germinal acceptor groups.

Rhodium catalysts have been shown to be highly effective in cyclopropenating terminal alkynes, however it fails when internal alkynes are used as substrates. This led us to the development of the silver-catalyzed cyclopropenation of internal alkynes which is the focus of the second part of this dissertation. By taking advantage of the highly reactive and sterically less demanding silver carbenoids, highly substituted cyclopropenes have been accessed. Enantioselective variant of this reaction was achieved using gold(I)-BINAP complexes.

The third part of this dissertation focuses on the gold-catalyzed stereoselective cascade reaction of propargyl alcohols and aryldiazoacetates. The reaction involves oxonium ylide formation followed by [2,3]-sigmatropic rearrangement followed by cycloisomerization leading to dihydrofuran derivatives. The reaction can also be extended to homopropargyl alcohols leading to the formation of tetrahydrofuran derivatives. The conventional O-H insertion reaction was minimal in most cases making these reactions very attractive.

The final chapter of this dissertation focuses on the asymmetric Au(I)-catalyzed vinylogous [3+2] cycloaddition reaction of vinyl ethers and styryldiazoacetates. These substrates, under rhodium catalysis, undergo the classical C-H insertion/Cope rearrangement. On the other hand, gold(I)-stabilized carbenoids possess highly electrophilic character at the vinylogous position and therefore undergo vinylogous attack instead of carbenoid attack. Highly functionalized cyclopentene derivatives were accessed using this methodology.

TRANSITION METAL CATALYZED STEREOSELECTIVE TRANSFORMATIONS OF ALKYNES AND DONOR/ACCEPTOR CARBENOIDS

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Obtaining a PhD degree is undoubtedly one of the most hard-earned but deeply rewarding achievements that I have had in my life. I've been fortunate enough to have made it from there to here and I have to express my deepest gratitude to the people that helped me make this possible.

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In memory of Lolo Pinong and Lola Julia

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CHAPTER ONE

Reactions of Donor/Acceptor-Substituted Metallacarbenoids

1.1 Introduction

This chapter broadly discusses the chemistry of metallacarbenoids derived from the decomposition of diazo compounds and transition metal catalysts. The Davies group is well known for the use of chiral dirhodium catalysts to achieve novel and synthetically important transformations involving donor/acceptor-substituted diazo compounds. This strategy has been applied to the development of efficient methods for the asymmetric syntheses of organic synthons as well as in the total synthesis of relevant natural product targets. The development of new transition metal catalysts for carbenoid chemistry is also an active area of research in the Davies group. The use of other transition metal catalysts

for promoting reactions that normally fail under rhodium catalysis will be discussed. Selected types of carbenoid transformations that are a major part of this dissertation will each be briefly discussed in this introduction.

1.2 Metal Carbenoid

The decomposition of diazo compounds using transitional metal catalysts has been an important strategy for organic synthesis.[1] This reaction forms a metal carbenoid species which is utilized in insertion, ylide, and cyclopropanation reactions.[2] Although the chemistry of free carbenes has a long and rich history in organic synthesis, these processes often lack chemoselectivity.[3] By introducing a suitable transition metal complex in the carbene structure capable of π-backbonding, the reactivity is greatly modulated, therefore improving the selectivity of the metal carbenoid species.[4]

Transition metal-catalyzed decomposition of diazo compounds is highly favorable. A very attractive feature of this transformation is its amenability to a catalytic cycle. One of the most common catalytic cycles involving metal carbenoid species is the intermolecular cyclopropanation. This reaction is extremely efficient and as high as 1.8

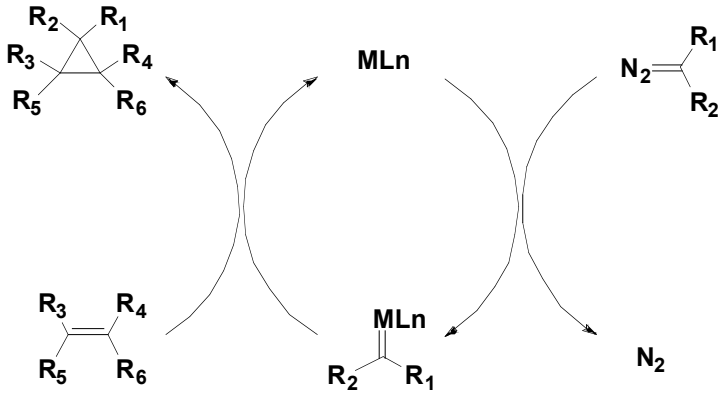
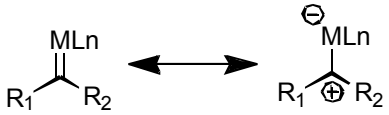


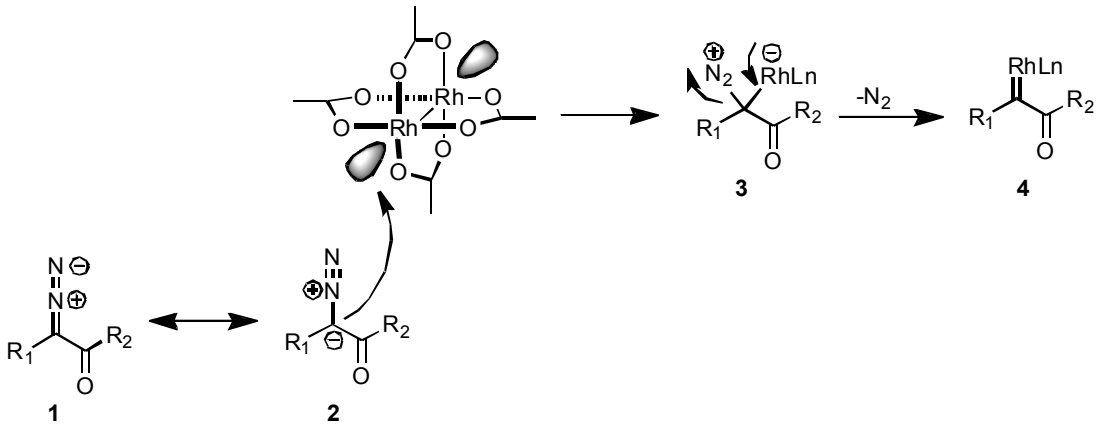
Figure 1.1 Catalytic cycle for metal-catalyzed intermolecular cyclopropanation

million turnover number (TON) has been reported for the intermolecular cyclopropanation of styrene on 0.6 ppm catalyst to substrate ratio.[5] The catalyst cycle begins by the decomposition of the diazo compound which affords the highly reactive metal carbenoid species (Figure 1.1). The nitrogen extrusion is an irreversible step as well as the rate-limiting step.[4,6] This step can occur under very mild conditions and even at temperatures as low as -78 °C.[7] The metal carbenoid species formed is highly electrophilic and can be trapped by an appropriate substrate followed by the regeneration of the metal complex catalyst. The electrophilic nature of the metal carbenoid species can be rationalized though an ylide-like resonance structure (Scheme 1.1).[4]



Scheme 1.1 Resonance structure of a metal-stabilized carbenoid.

In dirhodium catalysis, the first step in the formation of metal-stabilized carbenoid is the attack of a α-diazo carbonyl compound **1**, which can react as a stabilized



Scheme 1.2 $Rh_2(OAc)_4$-catalyzed decomposition of diazo carbonyl compound

ylide **2**, to the vacant axial coordination site on dirhodium complex. Back-donation occurs from the electron density of rhodium to the *p*-orbital of the carbene releasing N_2 affording the rhodium-stabilized carbenoid intermediate **4**.[8] However, the extent of backbonding is relatively limited, which causes the carbenoid to behave as a highly electrophilic species. Electron withdrawing group substituents (EWG) on the carbenoid destabilizes the already δ+ carbenoid carbon making it highly electrophilic and therefore highly reactive. Because of the significant effect of substituents in the reactivity of carbenoids, diazo compounds are classified based on the type of groups attached to the diazo carbon namely; (1) acceptor-, (2) acceptor/acceptor-, and the recently developed (3) donor/acceptor-substituted diazo compounds. The acceptor groups are electron withdrawing in nature while the donor acceptor groups are electron donating. Traditional carbenoids, such as the ones derived from acceptor- and

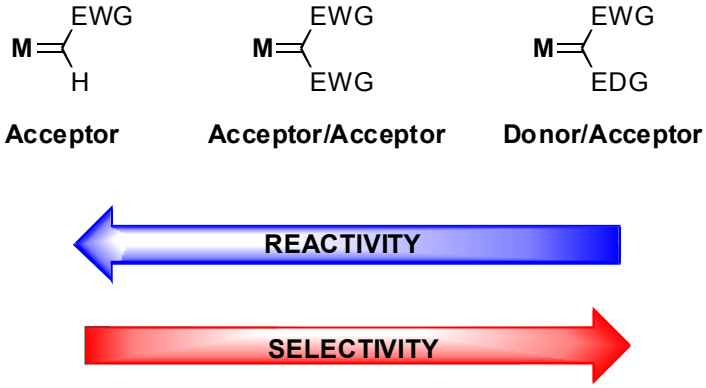


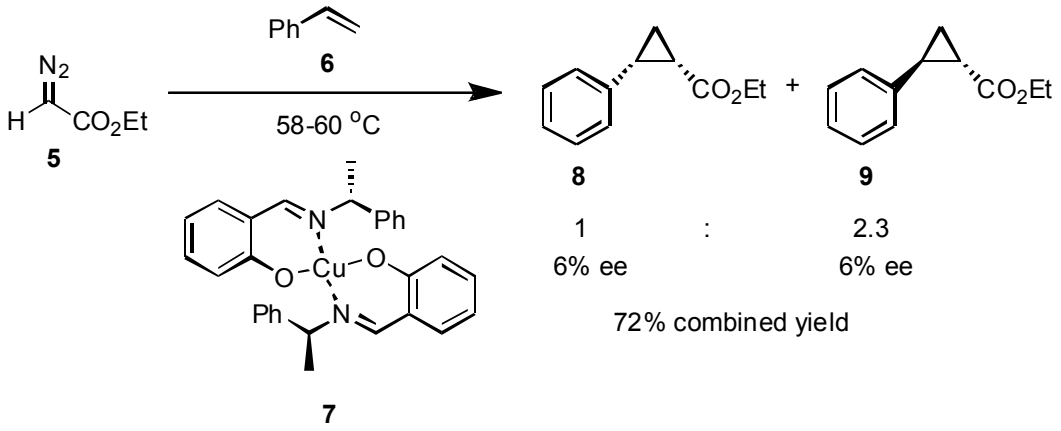
Figure 1.2 Three classes of metal carbenoids

acceptor/acceptor-substituted diazo compounds usually suffers from dimerization reactions before reacting with the desired substrate.[9] Also, these highly reactive carbenoids are often associated with low stereo- and chemoselectivity.[10] To solve these

problems, the Davies group pioneered and explored the broad synthetic potential of donor/acceptor-substituted rhodium carbenoids. These types of metal carbenoids are more stabilized compared to the conventional types of carbenoids which lack the donor group. The electron donating group (EDG) stabilizes the δ+ charge on the carbenoid thereby moderating its reactivity.[11] By taking advantage of the enhanced stability of donor/acceptor-substituted carbenoids, highly chemo-, regio-, and stereoselective transformations were developed in the Davies group including C-H and Si-H insertions, reactions with π-bonds (cyclopropanation and cyclopropenation), and the recently discovered tandem ylide/rearrangement reactions.[4,12] Moreover, these carbenoids are not as prone to homodimerization compared to the traditional carbenoids derived from alkyl diazoacetates.[11]

1.3 Dirhodium Catalysts

Aside from the substituents attached to the carbenoid carbon, the metal and ligands also have a dramatic effect on the efficiency of intermolecular carbenoid reactions by modulating the reactivity of the carbenoid. Copper-based catalysts were the first catalysts used to decompose diazo compounds.[13] However, these types of catalysts generally gave poor stereoselectivity in carbenoid reactions including intermolecular cyclopropanation. The first asymmetric cyclopropanation was reported by Nozaki and coworkers utilizing the copper catalyst **7** for the cyclopropanation of styrene **6** with ethyl diazoacetate (EDA) **5** (Scheme 1.3). The reaction afforded a mixture of diastereomers both with very poor enantiomeric excess.[14] Other transition metal catalysts such as rhodium were later developed and were found to be better alternatives than copper catalysts.



Scheme 1.3 Nozaki's Cu-catalyzed asymmetric cyclopropanation

The use of rhodium as a metal of choice for decomposition of diazo compounds was pioneered by Teyssie and co-workers in 1973 with the discovery that dirhodium (II) tetraacetate $Rh_2(OAc)_4$ was an effective catalyst.[15] Over the past two decades, different classes of dirhodium catalysts have been developed. Among these catalysts, dirhodium tetracarboxylates and tetracarboxamidates have been found to be the most synthetically useful (Figure 1.3).[2, 16-18]

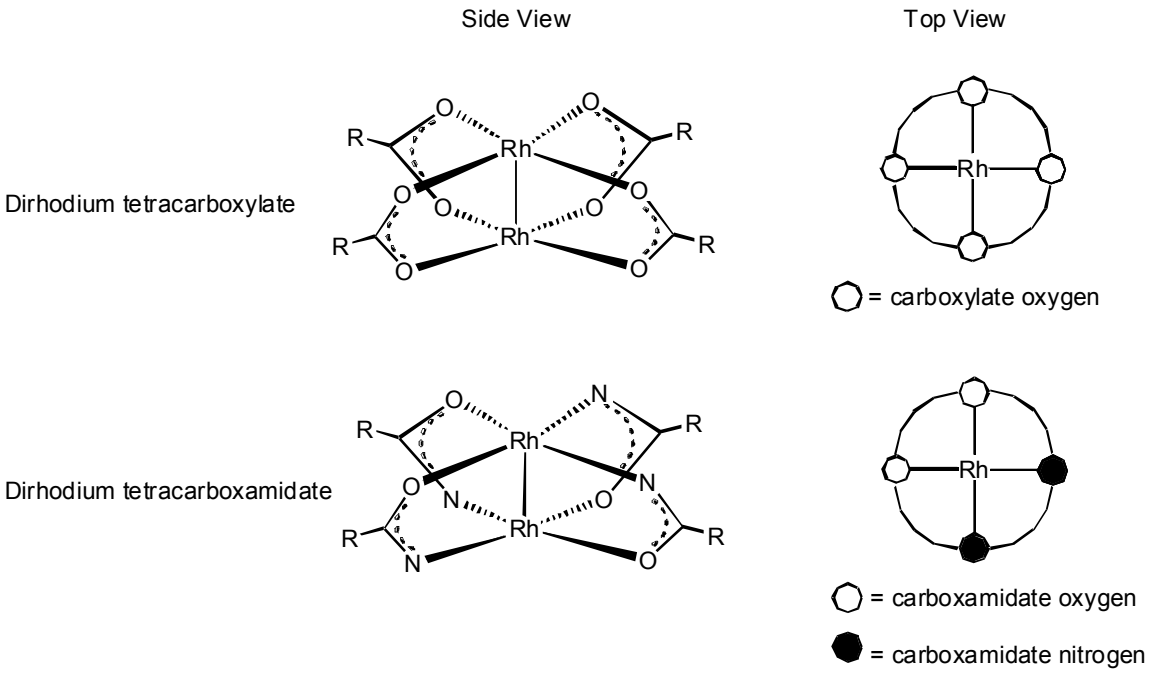


Figure 1.3 General structures of dirhodium tetracarboxylates and tetracarboxamidates

Doyle and coworkers developed the dirhodium carboxamidate catalysts which consist of four ligands based on pyrrolidinone, azetidinone, oxazolidinone, and imidazolidinone frameworks (Figure 1.4).[2] This class of catalysts was found to be effective in intramolecular reactions involving acceptor substituted diazo compounds. The first and most successful catalyst for intramolecular cyclopropanation was $Rh_2(5S\text{-MEPY})_4$ **10** which was found to

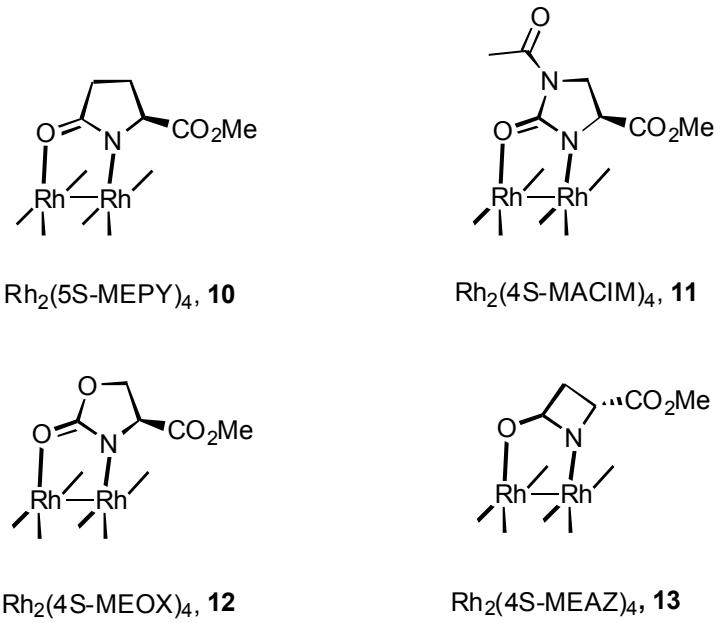
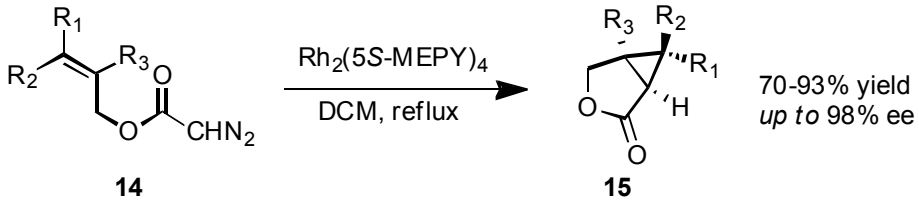


Figure 1.4 Doyle's chiral dirhodium tetracarboxamidates catalysts

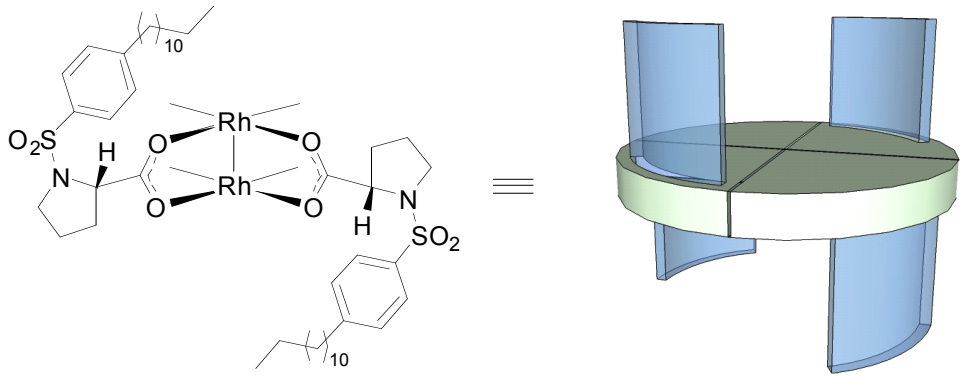
effectively cyclopropanate allyl diazoacetates **14** in good yield and excellent enantioselectivity.[19] In 1993, Davies and co-workers discovered that dirhodium



Scheme 1.4 Doyle's Rh(II)-catalyzed enantioselective cyclopropanation of allyl diazoacetates

tetraprolinate complexes were excellent chiral catalysts when using donor/acceptor-substituted diazo compounds. Based on the early work by McKervey,[21-22] Davies and coworkers developed the variant prolinate catalyst Rh_2(*S*-DOSP)$_4$ **16** which possesses a dodecyl chain in the *para*-position of the aryl group. The dodecyl chain allows the catalyst to be used in hydrocarbon solvents such as pentane and hexane even at low

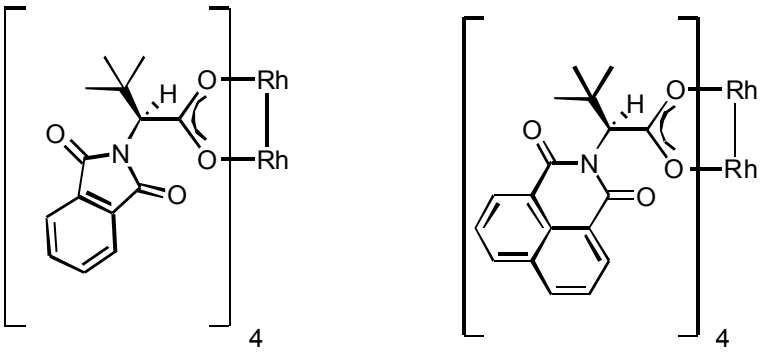
temperatures (i. e. -78 °C) which provides an alternative to the use of dichloromethane at room temperature in standard rhodium carbenoid reactions.[23] High levels of enantioinduction have been achieved in intermolecular cyclopropanation reactions of donor/acceptor-substituted carbenoids in hydrocarbon solvents. The catalyst is believed to adopt a D_2 symmetry in solution with the four arylsulfonyl blocking groups in an up, down, up, down arrangement around the dirhodium core (Figure 1.5). Since the development of this catalyst, it has been used in a variety of stereoselective transformations involving donor/acceptor carbenoids.[24-26]



Rh_2(*S*-DOSP)$_4$, 16 **D_2-symmetric**

Figure 1.5 D_2 symmetry representation of Rh_2(*S*-DOSP)$_4$

Another chiral catalyst that was developed by the Davies group is Rh_2(*S*-PTAD)$_4$ **17** which is based on a family of catalysts synthesized from naturally available amino acids by Hashimoto and coworkers in 1990.[27] Muller and coworkers also developed a related catalyst using an *N*-naphthaloyl-amino acid (Figure 1.6).[28] Hashimoto's phthalamide-based catalysts also showed great selectivity with donor-acceptor diazo

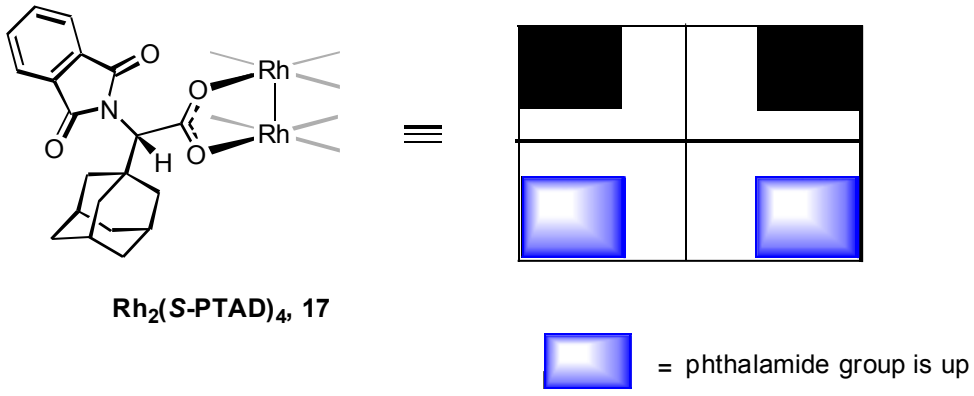


Rh_2(*S*-PTTL)$_4$
Hashimoto

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

Figure 1.6 Structure of Rh_2(*S*-PTTL)$_4$ and Rh_2(*S*-NTTL)$_4$

compounds. Instead of having a *tert*-butyl group, Rh_2(*S*-PTAD)$_4$ possesses an adamantyl group which increases the steric bulk around the dirhodium core and also improves the catalyst's solubility in hydrocarbon solvents at reflux compared to Hashimoto's catalyst.[29] Similar to *N*-phthaloyl-amino acid based dirhodium carboxylate catalysts, the structure of Rh_2(*S*-PTAD)$_4$ have a C_2 symmetric conformation with the phthalamide groups aligned in an "up-up-down-down" arrangement (Figure 1.7).[30-33]



Rh_2(*S*-PTAD)$_4$, 17

Figure 1.7 C_2 symmetry representation of Rh_2(*S*-PTAD)$_4$

1.3.1 Cyclopropanation

Donor/acceptor-substituted rhodium carbenoids have been used extensively by the Davies group in the synthesis of enantioenriched cyclopropanes. The majority of the work in this area of carbenoid chemistry has been done with aryldiazoacetates and vinyldiazoacetates using the dirhodium tetracarboxylate Rh_2(*S*-DOSP)$_4$. Highly stereoselective cyclopropanation of various electron-rich olefins has been achieved using Rh_2(*S*-DOSP)$_4$ in excellent yields using donor/methyl ester carbenoids.

In 2003, Davies and Singleton developed a predictive model for intermolecular cyclopropanation reactions based on the proposed symmetry of Rh_2(*S*-DOSP)$_4$.[34] The two bulky arylsulfone groups on one face of the catalyst are represented by two bold lines (Figure 1.8). In an "end-on" fashion, the alkene approaches the carbenoid to give the expected stereochemistry *via* concerted, asynchronous transition state. The blocking arylsulfonyl groups were also proposed to adopt a highly angled propeller arrangement in different quadrants. This explains the asymmetric induction resulting from the cyclopropanation

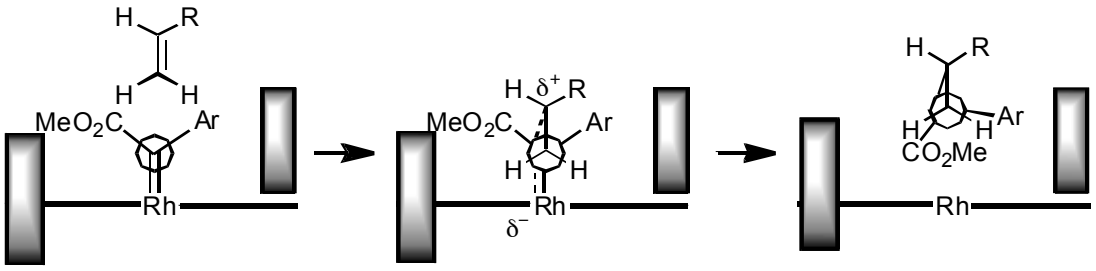
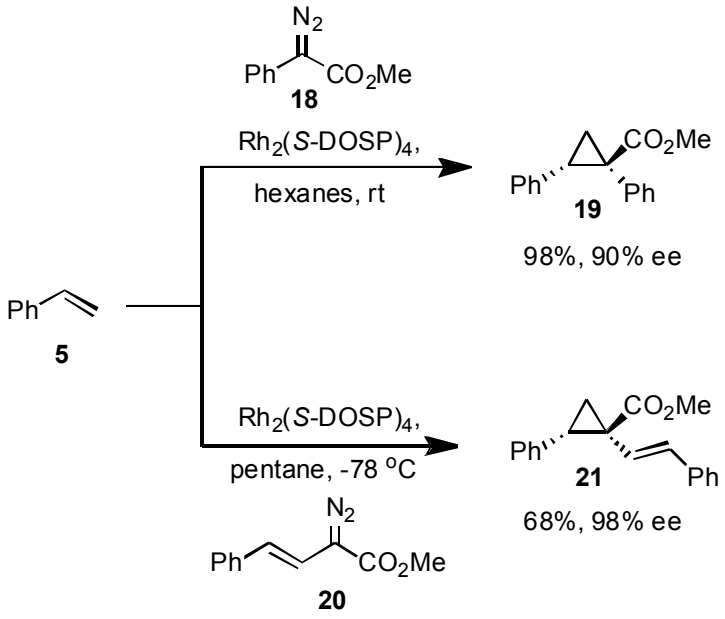


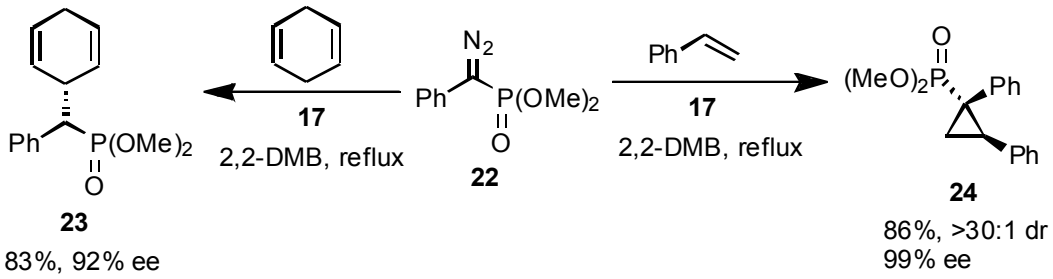
Figure 1.8 Davies and Singleton's model for Rh_2(*S*-DOSP)$_4$-catalyzed cyclopropanation reactions involving donor/acetate carbenoids catalyzed by Rh_2(*S*-DOSP)$_4$ (Scheme 1.5).[5a, 24] Recently, Hansen and Davies reported that based on computational studies, the

cyclopropanation reaction proceeds *via* a concerted but highly asynchronous transition state which supports the earlier predictive model by Davies and Singleton.[35]



Scheme 1.5 Rh_2(*S*-DOSP)$_4$-catalyzed cyclopropenation of styrene with **18** and **20**

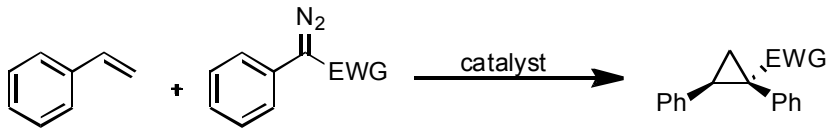
Although Rh_2(*S*-DOSP)$_4$ generally gives high asymmetric induction in a wide range of reactions involving donor/acceptor carbenoids, it is limited to diazo compounds bearing the methyl ester group. Studies have shown that Rh_2(*S*-PTAD)$_4$ is the catalyst of choice when other types of donor/acceptor carbenoids are used. This trend is clearly illustrated in the Rh_2(*S*-PTAD)$_4$-catalyzed cyclopropanation of olefins with donor/acceptor carbenoids bearing phosphonates[36], trifluoromethyl[37], keto[38] and cyano[39] groups as acceptor. In 2004, Davies and Reddy demonstrated that the adamantylglycine-derived catalyst Rh_2(*S*-PTAD)$_4$ is a very effective catalyst for C-H insertion and cyclopropanation reactions using diazophosphonate **22** as the carbenoid precursor (Scheme 1.6).



Scheme 1.6 Rh_2(*S*-PTAD)$_4$-catalyzed carbenoid reactions of diazophosphonates

Davies and Denton, in three independent studies, reported that Rh_2(*S*-PTAD)$_4$ gave higher levels of enantioinduction over Rh_2(*S*-DOSP)$_4$ in the cyclopropanation of styrene with aryldiazo compounds bearing trifluoromethyl, cyano and keto moiety as the acceptor group (Table 1.1). These results showcased the potential of Rh_2(*S*-PTAD)$_4$ as an effective backup catalyst for reactions in which Rh_2(*S*-DOSP)$_4$ fails to provide high asymmetric induction.

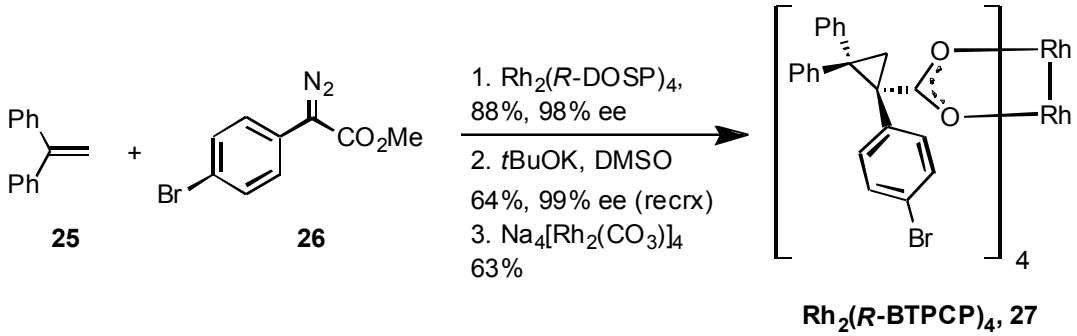
Table 1.1 Comparison between Rh_2(*S*-DOSP)$_4$ and Rh_2(*S*-PTAD)$_4$ on the cyclopropanation of styrene with different aryl diazo compounds.



entry	EWG	Catalyst	de (%)	ee (%)	yield (%)
1	CF_3	Rh_2(*S*-DOSP)$_4$	94	40[a]	80
		Rh_2(*S*-PTAD)$_4$	>94	>98	94
2	CN	Rh_2(*S*-DOSP)$_4$	90	90[a]	85
		Rh_2(*S*-PTAD)$_4$	94	34	86
3	$C(O)CH_3$	Rh_2(*S*-DOSP)$_4$	>94	<5	93
		Rh_2(*S*-PTAD)$_4$	>94	85	90
4	$P(O)(OMe)_2$	Rh_2(*S*-DOSP)$_4$	>94	34[a]	69
		Rh_2(*S*-PTAD)$_4$	>94	99	86

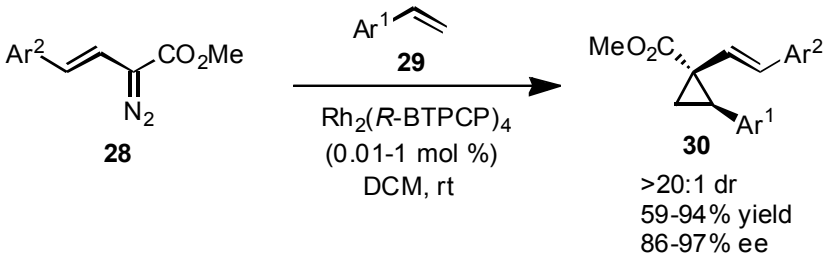
[a] Opposite enantiomer preferrentially formed

A recently developed dirhodium catalyst, Rh_2(*R*-BTPCP)$_4$ **27**, was reported by Davies and coworkers.[40] Interestingly, the cyclopropane-based ligand of Rh_2(*R*-BTPCP)$_4$



Scheme 1.7 Synthesis of Rh_2(*R*-BTPCP)$_4$

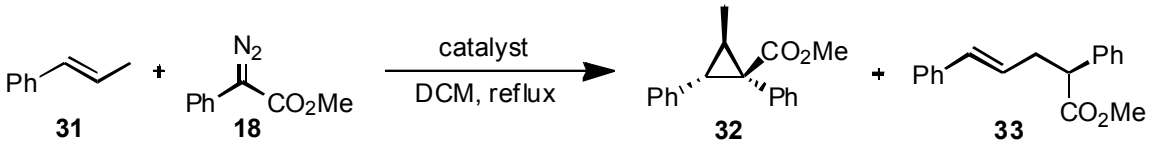
was readily accessed using the donor/acceptor carbenoid strategy developed in the Davies group (Scheme 1.7). This catalyst was found to be effective in highly enantioselective cyclopropenation (Scheme 1.8), C-H/Cope rearrangement and cyclopropanation/Cope rearrangement reactions with donor/acceptor carbenoids. A great advantage of Rh_2(*R*-BTPCP)$_4$ over Rh_2(*S*-DOSP)$_4$ is its tolerance to the size of the ester group in the styryldiazoacetates and also its compatibility with polar solvents such as dichloromethane.[40]



Scheme 1.8 Rh_2(*R*-BTPCP)$_4$-catalyzed cyclopropanation of styrene

Although the cyclopropanation with donor/acceptor carbenoids has been dominated by rhodium catalysis, the exploration of the use of other transition metal catalysts for this type of transformation is still an active area of research in the Davies group. A major breakthrough in donor/acceptor carbenoid chemistry was reported by Davies and Thompson in 2007 when they found that common silver salts such as $AgSbF_6$

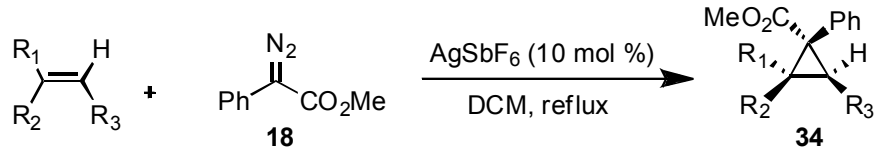
Table 1.2 Catalyst effect in the cyclopropanation of *trans*-beta-methylstyrene

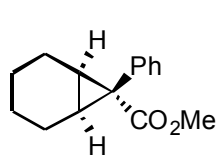


catalyst	yield, %	ratio **32**:**33**	de, %
$AgSbF_6$	80	>20:1	>94
$Rh_2(OAc)_4$	4	1:>20	

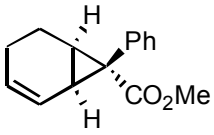
catalyzed the cyclopropanation of highly substituted olefins.[41] It is important to note that these same group of olefins undergoes predominantly C-H insertion, *albeit* in low yields, if $Rh_2(OAc)_4$ is used as catalyst (Table 1.2). Excellent levels of chemoselectivity (cyclopropanation over C-H insertion) as well as diastereoselectivities were achieved for the reactions involving sterically hindered alkenes with **18** and **20** leading to highly substituted cyclopropanes **34** and **35**, respectively (Table 1.3 and Table 1,4). The silver-catalyzed intermolecular cyclopropanation with donor/acceptor-substituted diazoacetates is regarded as one of the most successful silver-catalyzed transformation of diazo compounds because Wolff rearrangement, a reaction typically associated with silver salts[42], was not observed in this study.[41]

Table 1.3 Silver-catalyzed cyclopropanation with **18**

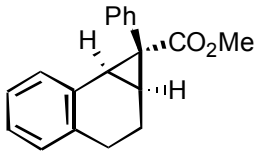




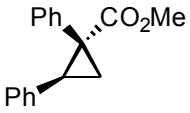
88%



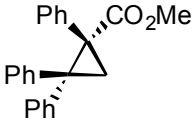
79%



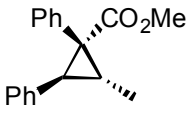
80%



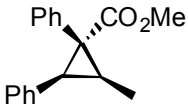
96%



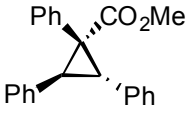
82%



80%



86%



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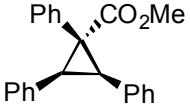
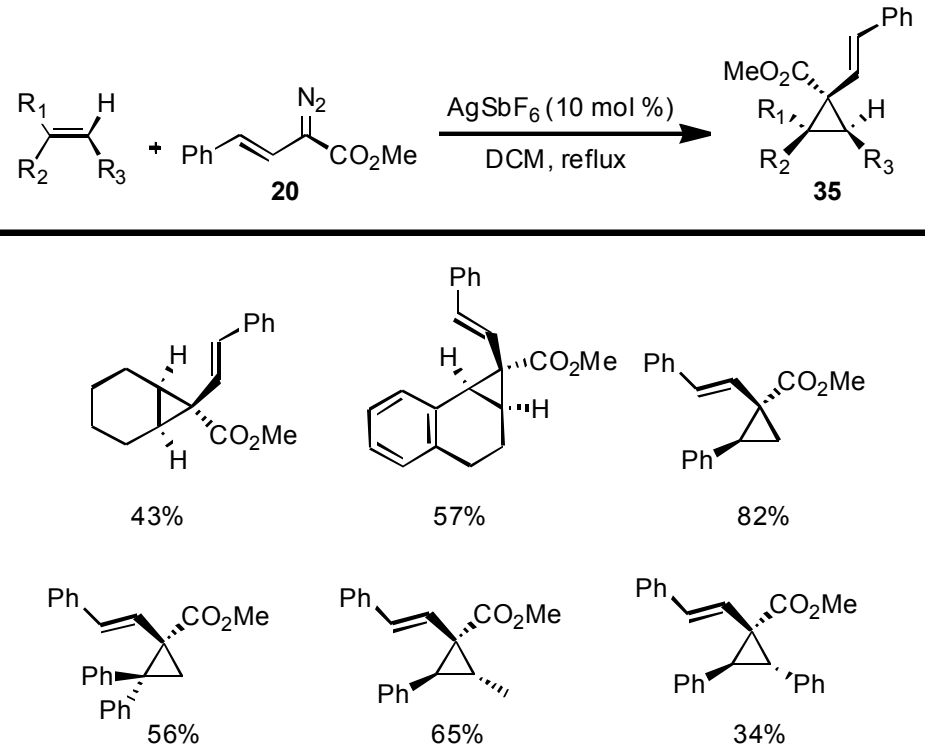


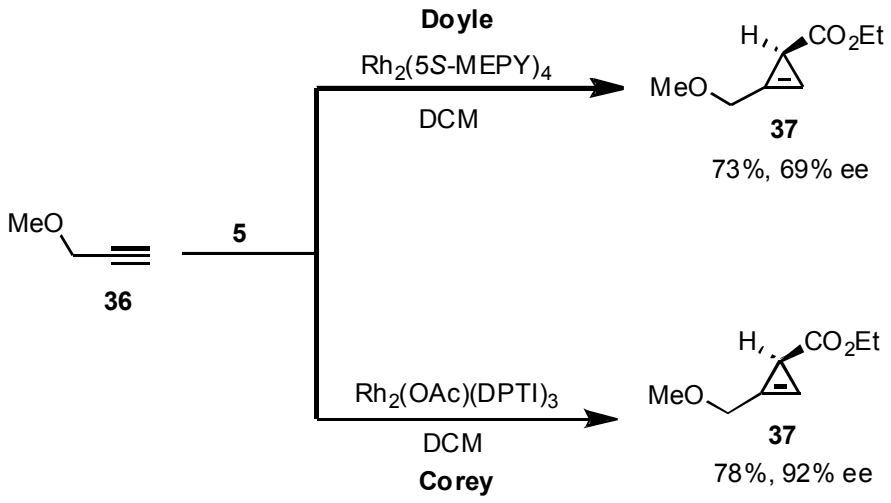
84%

Table 1.4 Silver-catalyzed cyclopropanation with **20**



1.3.2 Cyclopropenation

Prior to the work by Davies and Lee in 2004, only one example of catalytic asymmetric intermolecular cyclopropenation had been reported in the literature. Doyle and co-workers have shown that the carboxamidate catalyst $Rh_2(5S\text{-MEPY})_4$ was an effective catalyst for the enantioselective cyclopropenation of acceptor-substituted diazo compounds (Scheme 1.9).[43] Shortly after this report, Corey and coworkers described the highly enantioselective cyclopropenation of terminal alkynes with ethyl diazoacetate

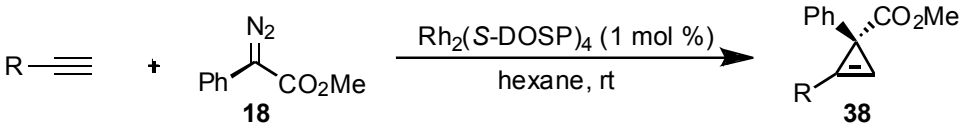


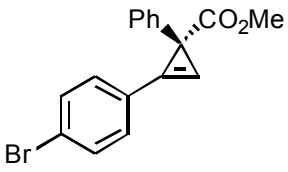
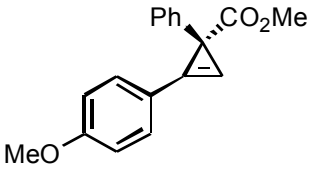
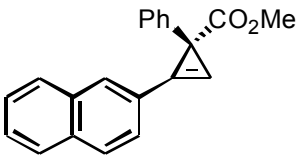
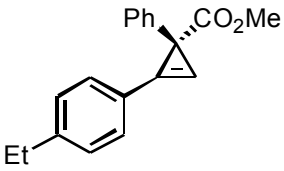
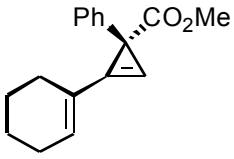
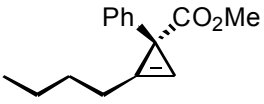
Scheme 1.9 Rh-catalyzed cyclopropenation of terminal alkyne

using a new dirhodium tricarboxamidate catalyst $Rh_2(OAc)(DPTI)_3$ (DPTI = diphenyltriflylimidazolidinone) (Scheme 1.9).[44] Although these reports are great advances in the asymmetric cyclopropenation chemistry, the reactions were limited to the use of acceptor-substituted diazo compounds.

Davies and Lee expanded the cyclopropenation reaction by utilizing the donor/acceptor carbenoid strategy with Rh_2(*S*-DOSP)$_4$ as the optimal catalyst.[45] This study described the first synthesis of enantiomerically enriched cyclopropenes bearing a quaternary stereogenic center. The reaction was applicable to a wide variety of aromatic acetylenes which afford the cyclopropene products in moderate yields (48-74%) and good to excellent enantioselectivity (84-96% ee) (Table 1.5). A variety of aryldiazoacetates were also effective as carbenoid precursor affording the cyclopropene products in 50-65% yields and 86-90% ee (Table 1.6). However, low yield and enantioselectivity (24% yield, 66% ee) were observed when *para*-methoxyphenyl diazoacetate was used presumably reflecting the lower reactivity of the *para*-methoxyphenyl carbenoid.

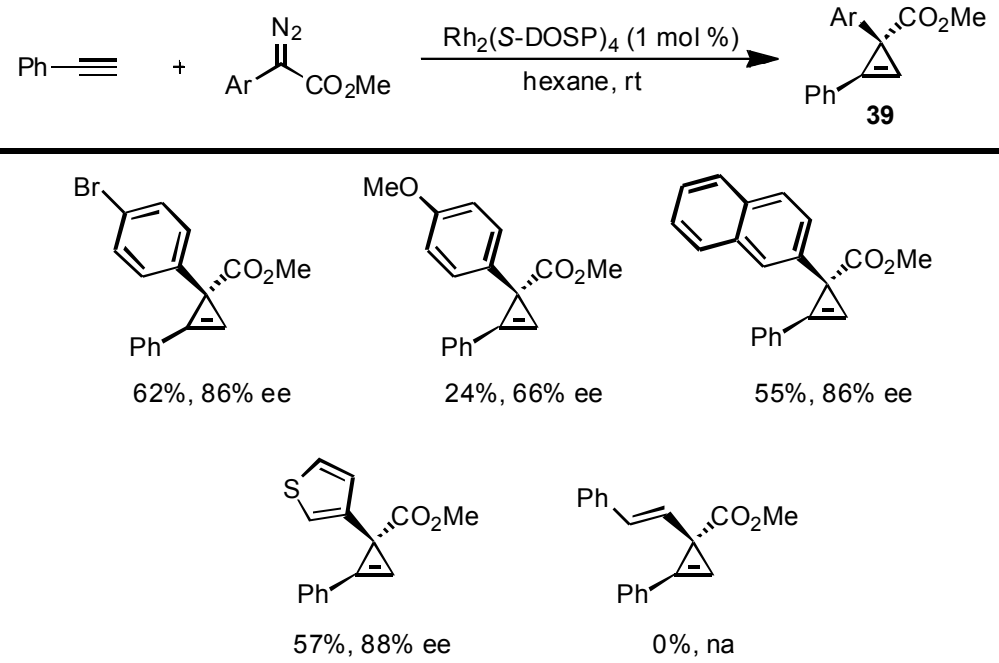
Table 1.5 Rh_2(*S*-DOSP)$_4$-catalyzed cyclopropenation of terminal alkynes with methyl phenyldiazoacetate **18**



 63%, 92% ee	 67%, 86% ee	 60%, 96% ee
 48%, 87% ee	 74%, 92% ee	 51%, 84% ee

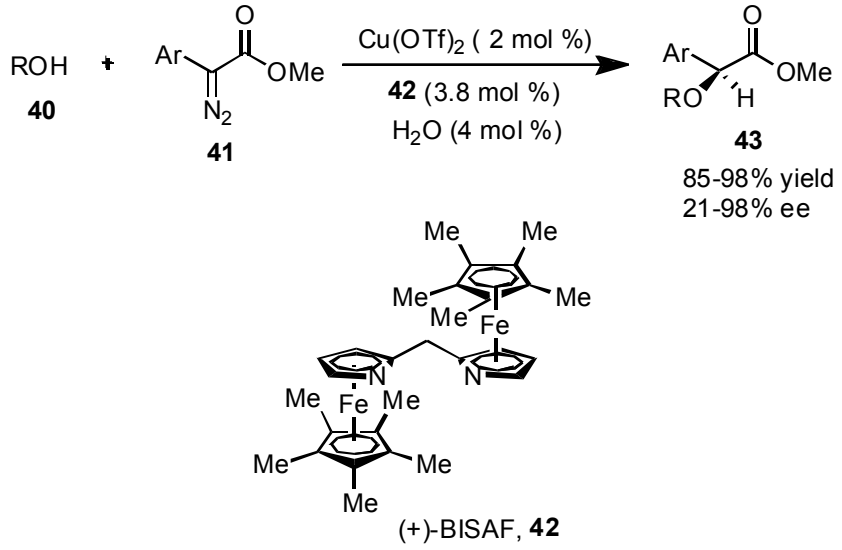
The cyclopropenation reaction reported by Davies and Lee was limited to the use of aryl diazoacetates. In this study, methyl styryldiazoacetate **20** was found to be ineffective in producing the corresponding vinyl cyclopropene product even though this class of diazoacetates has been shown to be an exceptional donor/acceptor carbenoid precursor. It was reasoned that the reaction failed due to product instability rather than an inherent problem with the cyclopropenation reaction itself.[45]

Table 1.6 Rh_2(*S*-DOSP)$_4$-catalyzed cyclopropenation of phenylacetylene with various aryldiazoacetates

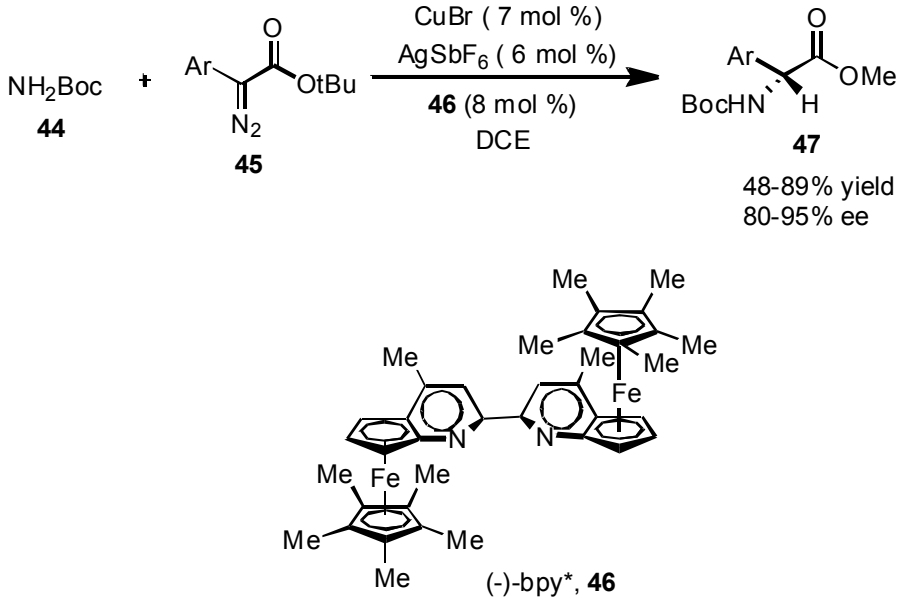


1.3.3 Ylide Chemistry

The Davies group has had a limited success in the ylide chemistry of donor/acceptor carbenoids. The reason for this is primarily because chiral rhodium catalysts usually give no asymmetric induction in O-H and N-H insertion reactions.[46] High asymmetric induction, however, has been achieved in O-H and N-H insertion reactions by the Fu and Zhu groups using chiral copper catalysts.[47-48] The first effective method for catalytic enantioselective O-H insertion reaction was developed by the Fu group using the copper/bisazaferrocene catalyst which coupled alcohols **40** and aryldiazoacetates **41** providing **43** in high yields and generally good ee. The copper/planar-chiral ligand (-)-bpy* catalyst system, also developed by Fu and coworkers accomplished the N–H insertion of a wide range of aryldiazoacetates with carbamate **44**



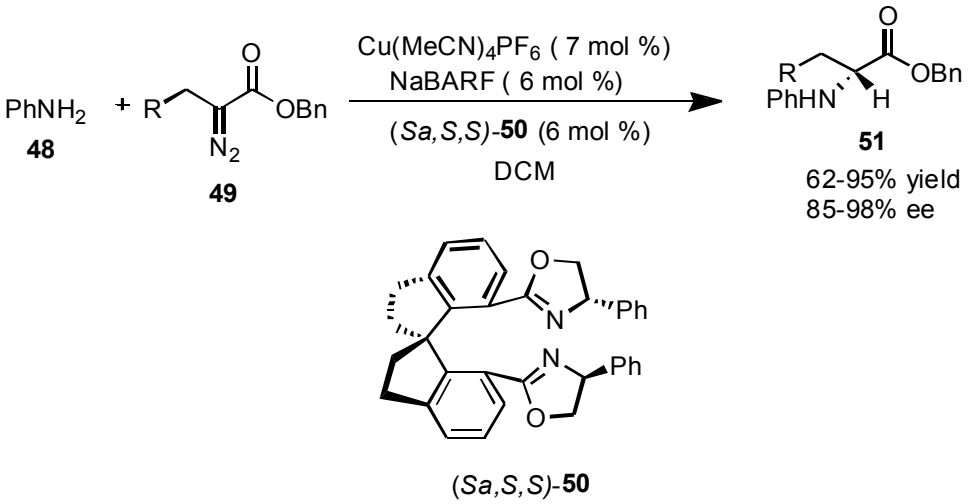
Scheme 1.10 Rh-catalyzed cyclopropenation of terminal alkyne



Scheme 1.11 Rh-catalyzed cyclopropenation of terminal alkyne

in good yield and enantioselectivity (Scheme 1.9).[44] $AgSbF_6$ works as co-catalyst to generate the halide-free copper complex. This method provides an efficient entry for the asymmetric synthesis of α-amino acids. Highly enantioselective N–H insertion of alkyldiazoester **49** with aniline **48** was also achieved with the copper/chiral spirobox **50**

catalyst system by Zhou and co-workers (Scheme 1.12).[46] α-Amino acid derivarives **51** were formed in good yields and excellent enantioselectivity.

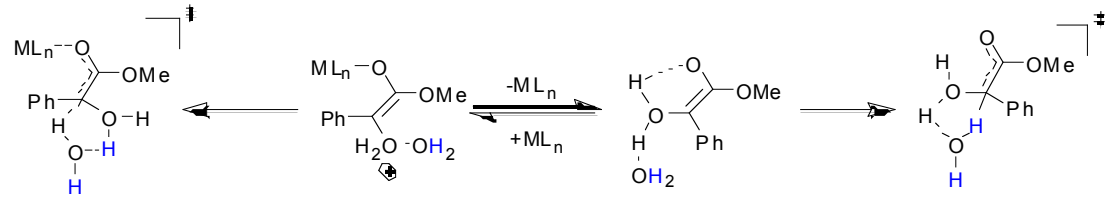


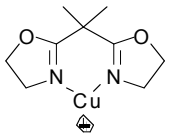
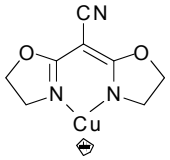
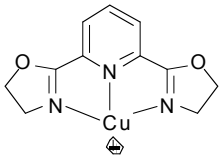
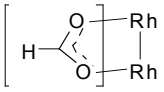
Scheme 1.12 Rh-catalyzed cyclopropenation of terminal alkyne

A computational study was done by Yu and coworkers to explain why copper catalysis is more effective in promoting asymmetric induction than rhodium catalysis.[49] DFT calculations involving carbenoid insertions into O-H bond of water suggests that in the Cu(I)-catalyzed systems, the stereocenter forming step which is the [1,2]-H shift process favors the copper-associated ylide pathway (Table 1.7). On the contrary, initial formation of an enol is favored in Rh(II)catalyzed system leading to racemic insertion products.[49] Cationic complexes also lead to a stronger electrostatic interaction between the metal center and the enolate moiety of the ylide which greatly enhances the stability of the metal-associated ylide (MY). This was clearly seen in entries 1 and 3 wherein MY was more favored for the cationic Cu(I) complex of bisoxazoline (entry 1) than in the neutral Cu(I) complex of semicorrin (entry 3).[49] The donor/acceptor carbenoid strategy

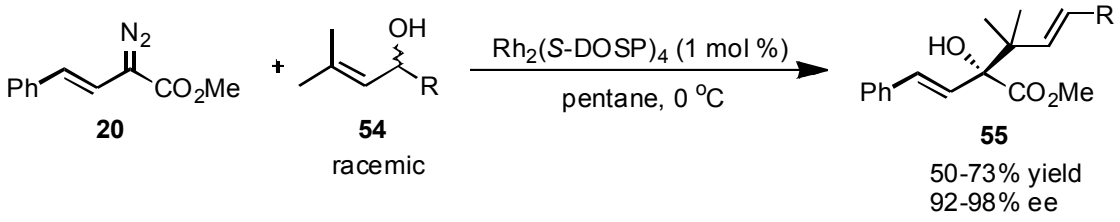
has also been applied to other transformations involving ylide intermediates such as epoxidation and three-component coupling between aryldiazoacetates, alcohols and aldehydes but no asymmetric induction was obtained under rhodium catalysis.[50-51]

Table 1.7 Relative free energies of the two competing pathways for various catalyst systems used in the O-H insertion reaction



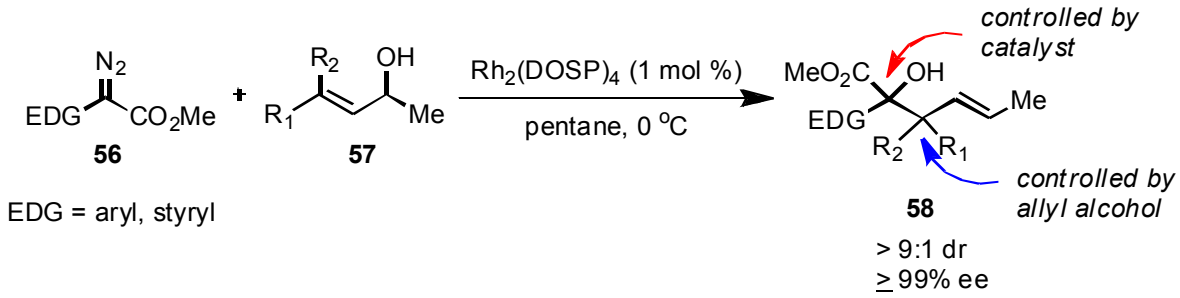
entry	ML_n	$\Delta\Delta G_{sol}$(FY-MY)	entry	ML_n	$\Delta\Delta G_{sol}$(FY-MY)
1		11.5	3		6.0
2		1.8	4		-6.5

A major breakthrough in the ylide chemistry of donor/acceptor carbenoids happened upon the discovery of the novel Rh_2(*S*-DOSP)$_4$-catalyzed tandem ylide formation.[2,3]-sigmatropic rearrangement between donor/acceptor-substituted



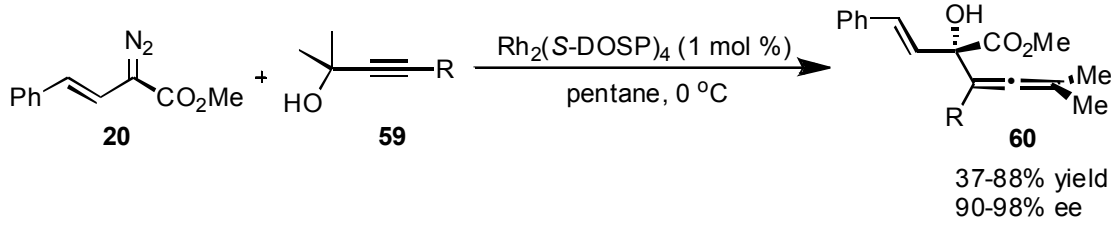
Scheme 1.13 Rh-catalyzed tandem ylide/[2,3]-rearrangement of racemic alcohols

and diazoacetates and allylic alcohols. Davies and Li developed a methodology which involves the reaction of racemic allylic alcohols **54** with methyl styryldiazoacetate **20** affording α-hydroxycarboxylate derivatives **55** in moderate to good yields and excellent enantioselectivity (Scheme 1.13).[52] This reaction proceeds by the formation of an ylide intermediate followed by a [2,3]-sigmatropic rearrangement leading to α-hydroxycarboxylate derivatives possessing two adjacent quaternary centers. Primary alcohols only afforded the O-H insertion product while secondary alcohols gave a mixture of O-H and [2,3]-rearrangement products. This particular reaction works best with tertiary alcohols affording the desired α-hydroxycarboxylate derivatives in exceptionally high enantiomeric excess and moderate to good yields. Later on, the generality of this reaction was investigated to explore possibility of stereoselectively constructing the vicinal stereocenters.[53] Using readily accessible enantioenriched allylic alcohols **57**; it was found that the allylic stereocenter of the homoallylic products is controlled by the chirality of the allylic alcohol and the alkene geometry while the homoallylic quaternary center is set under catalyst control (Scheme 1.14). These general rules allowed the synthesis of any of the four stereoisomers of the α-hydroxycarboxylate products by using the appropriate combination of the chiral catalyst $Rh_2(DOSP)_4$ and the chiral alcohol.[53]



Scheme 1.14 Stereocontrolling elements of the tandem ylide/[2,3]-rearrangement reaction

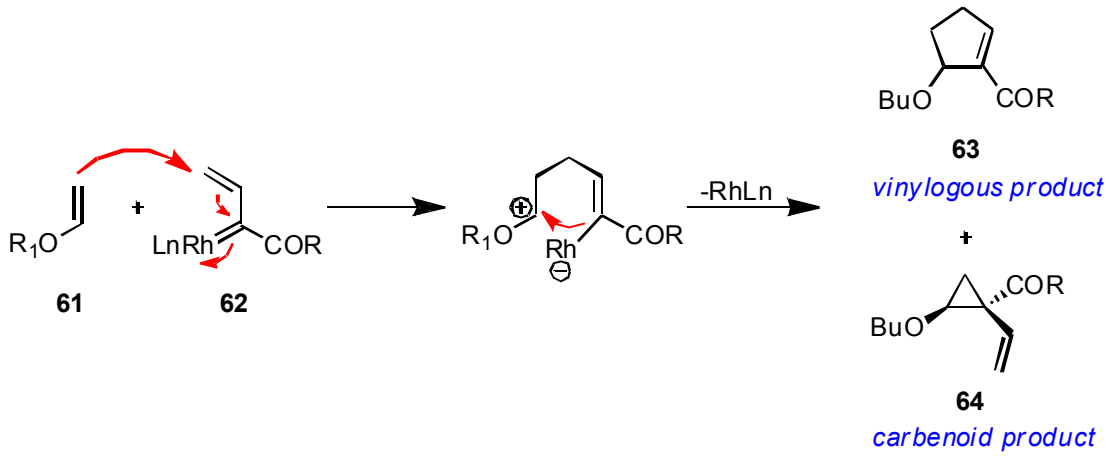
The unexpected development of enantioselective rhodium-catalyzed tandem ylide formation/[2,3]-rearrangement prompted the Davies group to further explore the potential of this novel synthetic methodology. Other substrates that are capable of undergoing the same type of reaction was then explored which lead to the development of the enantioselective synthesis of allenes **60** from donor/acceptor carbenoids and propargyl alcohols **59** (Scheme 1.15).[54]



Scheme 1.15 Rh-catalyzed tandem ylide/[2,3]-rearrangement of propargyl alcohols and **20**

1.3.4 Vinylogous Reactivity

Vinyldiazoacetates are a versatile class of compounds and excellent precursors to vinylcarbenoids which are capable of undergoing a wide range of important synthetic transformations. The Davies group has exploited the use of vinylcarbenoids in asymmetric reactions such as cyclopropanation, formal [3+2] and [4+3] cycloadditions, C-H and Si-H insertion and C-H insertion/Cope rearrangement (CHCR) (Figure1.9). Aside from these useful reactions, the group has a long-standing interest in vinylogous reactivity of vinylcarbenoids. In 1994, Davies and coworkers reported that rhodium-stabilized vinylcarbenoids displayed electrophilic reactivity in both the vinyl terminus and carbenoid site leading to cyclopentene **63** and cyclopropane **64** products, respectively (Scheme 1.16).[55] After systematic studies, it was found that excellent regiocontrol can be achieved by choosing



Scheme 1.16 Vinylogous and carbenoid reactivity of Rh(II)-stabilized vinylcarbenoid

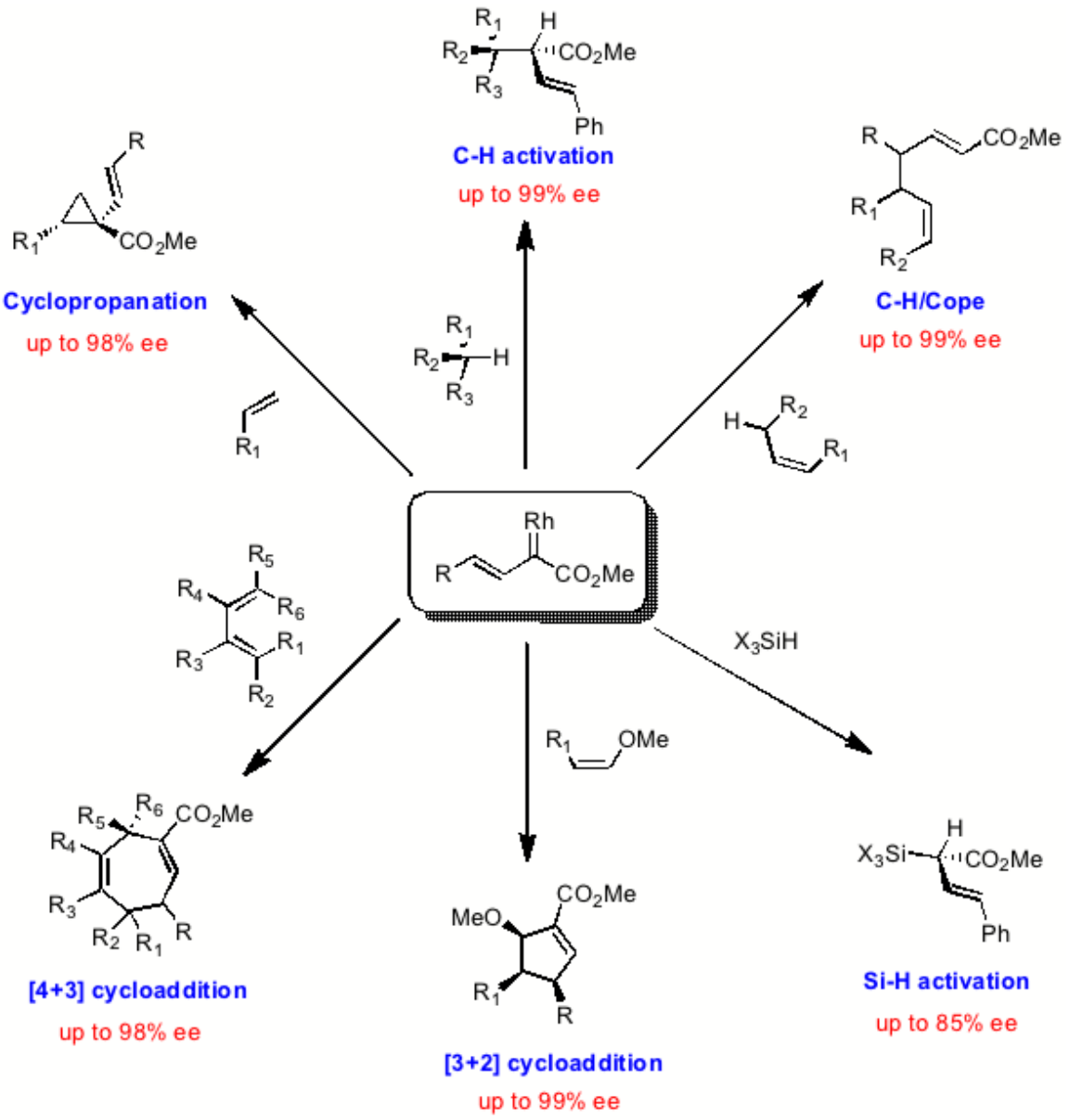
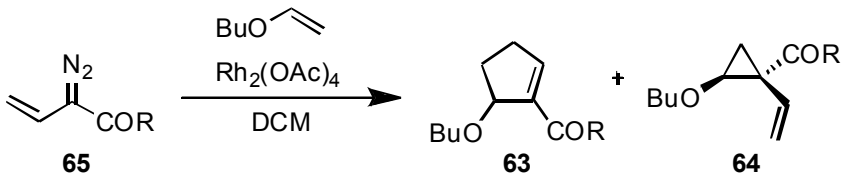


Figure 1.9 Applications of donor/acceptor vinyl carbenoids

the appropriate solvent and vinylcarbenoid. Generally, carbenoids that are less substituted at the vinyl terminus are more likely to enhance vinylogous reactivity. In addition, very bulky ester groups favor vinylogous attack presumably due to the steric encumbrance of the bulky ester group to the carbenoid site (Table 1.8). The mechanism for the formation of the cyclopentene was proposed to proceed through charged intermediates (Scheme

1.16). This was supported by experimental data in which vinylogous reactivity was strongly suppressed when the reaction was carried out in nonpolar solvents instead of dichloromethane.[55]

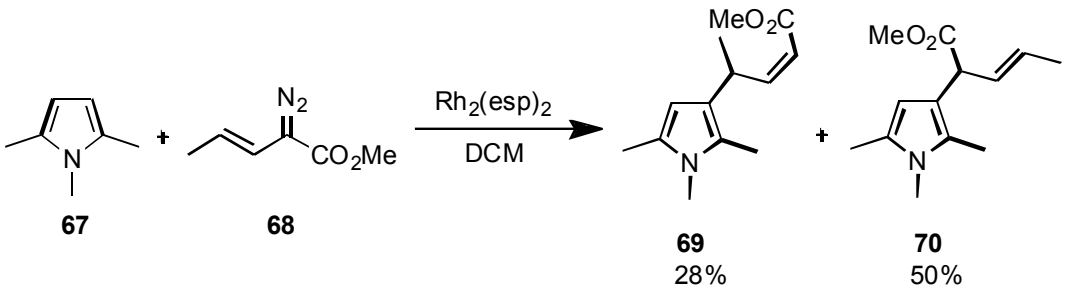
Table 1.8 Effect of the ester group on the Rh-catalyzed reaction with **65**



65 **63** **64**

R	yield (%)	yield (%)
OMe	24	37
OtBu	22	33
BHT	99	0

Recently, a novel approach to enhancing vinylogous reactivity was developed by Davies and Lian in their efforts to functionalize indoles and pyrroles.[56] When a bulky substrate such as 1,2,5-trimethylpyrrole **67** was used, an unexpected product **69** was formed in addition to the expected aromatic product **70**. The formation of this product was believed to occur *via* vinylogous attack of the *s-trans* conformer of the rhodium-stabilized vinylcarbenoids. In principle, rhodium-stabilized vinylcarbenoids could exist in an *s-cis* or an *s-trans* conformation (Figure 1.10). The solid line represents the catalyst face which is projected



Scheme 1.17 Vinylogous reactivity of Rh(II)-stabilized vinylcarbenoid

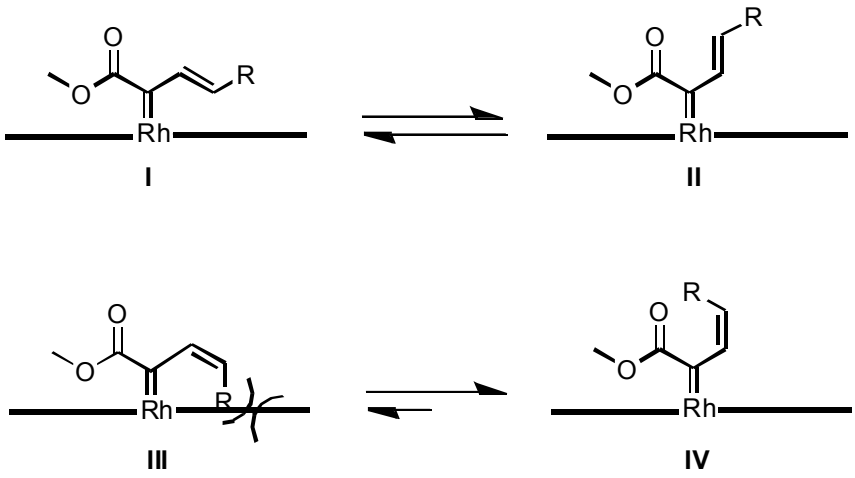
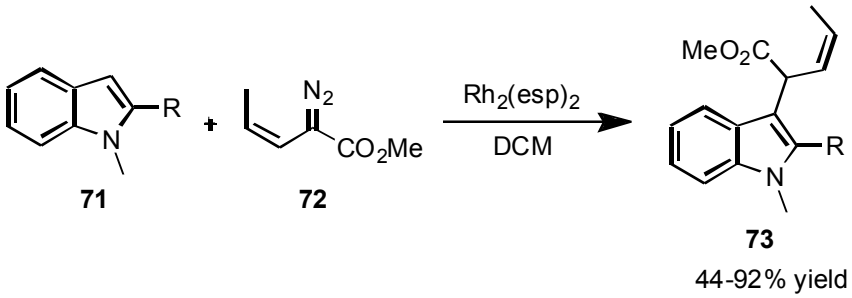


Figure 1.10 Different conformations of Rh(II)-stabilized vinylcarbenoids

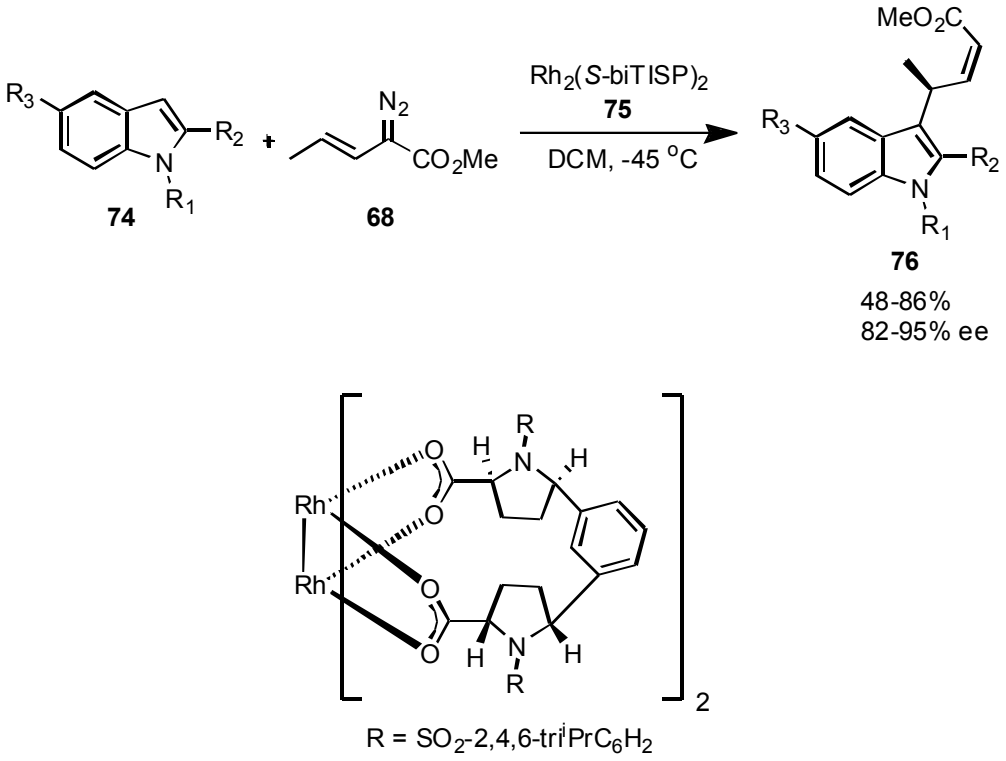
as a steric wall. In the case of *trans* vinyl carbenoid **68**, the corresponding conformers **I** and **II** would both be uninfluenced by the steric wall therefore a mixture of vinylogous products **69** and **70** was obtained. Intrigued by this result, Davies and Lian proposed that by using (*Z*)-vinylcarbenoid as substrate, the vinylogous reactivity would be enhanced since conformer **III** would be greatly disfavored due to steric clash between the vinyl terminus and the rhodium wall. Indeed, when (*Z*)-vinyldiazoacetate **72** was used, the vinylogous product was obtained as the major product. The reaction worked well with

sterically crowded pyrroles and could be extended to sufficiently crowded indoles (Scheme 1.18).



Scheme 1.18 Vinylogous reaction of (*Z*)-vinylcarbenoid **72** with substituted indoles

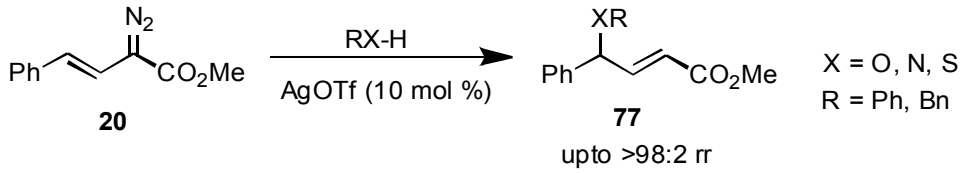
In their efforts to develop the asymmetric version of the vinylogous alkylation strategy, Davies and Lian found that the reaction between *N*-heterocycles and methyl (*Z*)-2-diazo-3-pentenoate **72** using different chiral dirhodium catalysts generally gave poor levels of enantioselectivity.[57] Only up to 48% ee was achieved using Rh_2(*S*-PTAD)$_4$ as catalyst. However, good to excellent levels of enantioselectivity was obtained when (*E*)-2-diazo-3-pentenoate **68** was used as the carbenoid precursor and the bulky Rh_2(*S*-biTISP)$_2$ **75** was used as the catalyst (Scheme 1.19). It was reasoned that by using a very bulky catalyst such as Rh_2(*S*-biTISP)$_2$, the vinylogous reactivity of (*E*)-vinyldiazoacetates was enhanced by re-enforcing the *s-trans* conformation of the carbenoid. The asymmetric vinylogous alkylation was amenable to a wide range of substituted indoles as well as very bulky pyrrole derivatives (Scheme 1.19). These studies by Davies and Lian demonstrated how subtle changes in the structure of the carbenoid as well as changing the steric bulk around the dirhodium core can drastically affect the outcome of donor/acceptor carbenoid reactions.



Rh_2(*S*-BiTISP)$_2$, 75

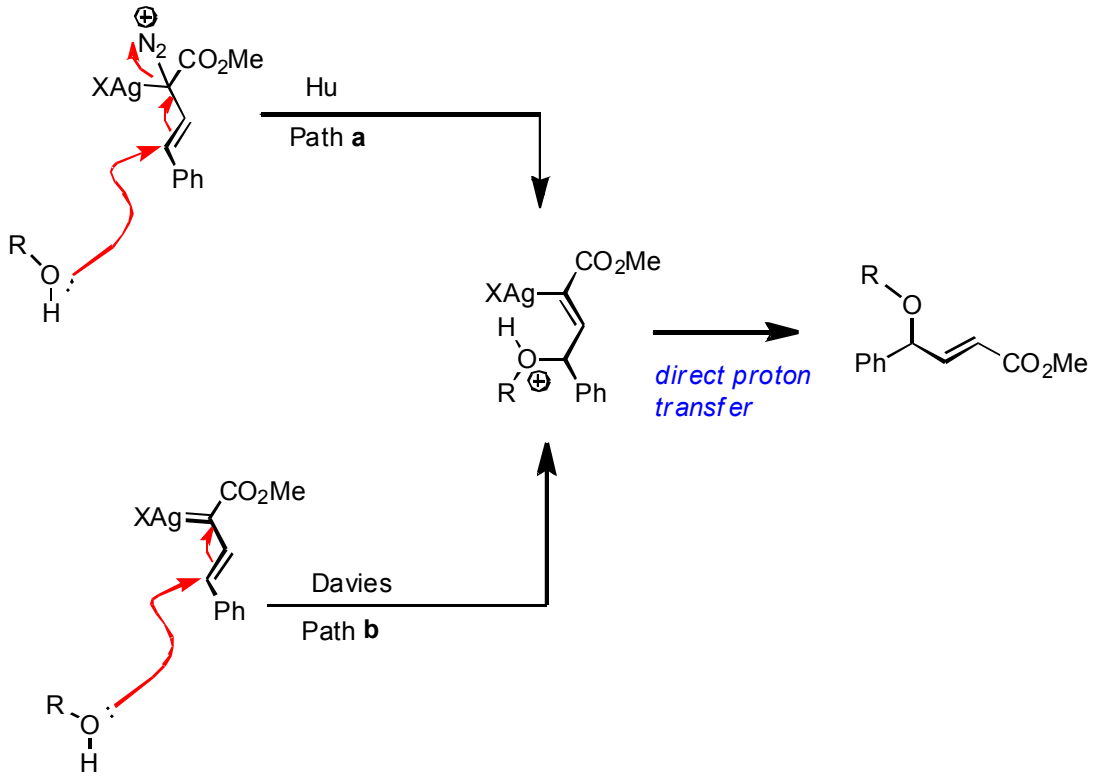
Scheme 1.19 Asymmetric vinylogous reaction of vinylcarbenoid with substituted indoles

Enhancement of vinylogous reactivity of vinylcarbenoids can also be achieved by using electron deficient transition metal catalysts. In 2008, a collaborative work by Davies and Petrukhina described the catalytic activity of highly electrophilic ruthenium(I) mixed carbonyl carboxylate complexes in donor/acceptor carbenoid chemistry.[58] The advantage of these catalysts is their tendency to enhance vinylogous reactivity of vinylcarbenoids. Recently, computational and experimental studies by Davies and Hansen showed that silver vinylcarbenoids displayed a strong preference for electrophilic reactivity at the vinyl terminus in O-H insertion reactions.[59] Hu and coworkers previously demonstrated that silver salts catalyzed insertion of benzyl alcohol, benzyl thiol and aniline occurred at the γ position of methyl styryldiazoacetate **20** (Scheme 1.20).[60]



Scheme 1.20 Hu's silver-catalyzed X-H insertion to styryldiazoacetate

These reactions, however, were believed to proceed *via* Lewis acid-catalyzed processes rather than the intermediacy of silver carbenoid species (Scheme 1.21). Inspired by the previous work in the Davies group suggesting that silver-catalyzed reactions of aryl- and vinyldiazoacetates involve silver carbenoid intermediates, more detailed investigation of this chemistry was done. Experimental data as well as density functional calculations (DFT) demonstrated that the formation of silver(I)-vinylcarbenoids are very facile and highly exothermic which supports the proposed mechanism by Davies and coworkers (Scheme 1.21). Moreover, transition state structures that would correspond to the mechanism proposed by Hu and coworkers were not found in the computation studies.



Scheme 1.21 Mechanistic proposals for vinylogous O-H insertion

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CHAPTER TWO

Rh(II)-Catalyzed Cyclopropenation of Terminal Alkynes with Donor/Acceptor-Substituted Carbenoids

2.1 Introduction

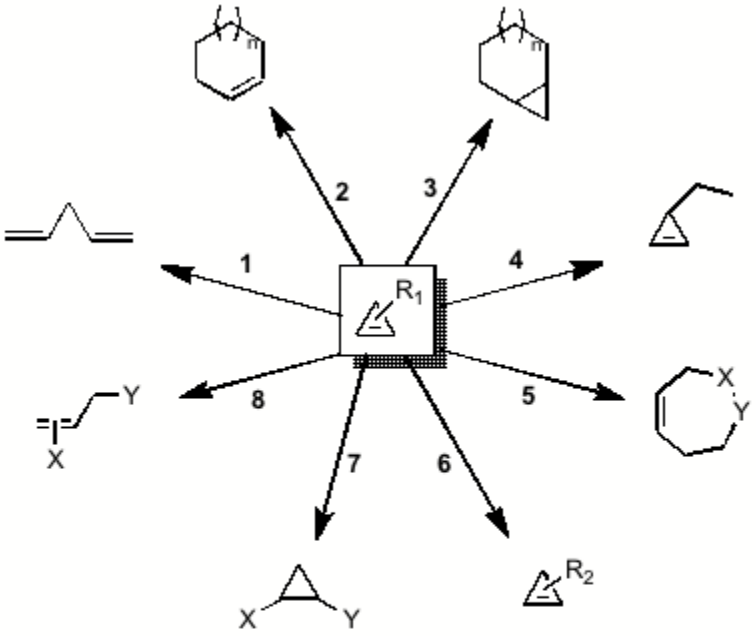
This chapter discusses the development of highly enantioselective and efficient methods for the synthesis of cyclopropenes bearing quaternary stereogenic centers using the donor/acceptor carbenoid strategy. The first part of the chapter will focus on the reinvestigation of the previous cyclopropenation studies done in the Davies group. The explorations lead to the discovery that styryldiazoacetates are excellent carbenoid source for the Rh_2(*S*-DOSP)$_4$-catalyzed cyclopropenation of alkyl alkynes which afforded enantioenriched vinylcyclopropenes. These interesting compounds were also found to undergo a rhodium-catalyzed rearrangement leading to substituted cyclopentadiene derivatives.

The second part of the chapter will focus on the further expansion of the cyclopropenation chemistry using the phthalamide-based catalyst, Rh_2(*S*-PTAD)$_4$ and siloxyvinyldiazoacetates. The development of this method enabled us to indirectly access enantioenriched cyclopropenes bearing germinal acceptor groups. These cyclopropenes undergo rhodium-catalyzed ring expansion to furans.

2.2 Rh_2(*S*-DOSP)$_4$-Catalyzed Cyclopropenation of Alkyl Alkynes with Methyl Styryldiazoacetate

2.2.1 Background

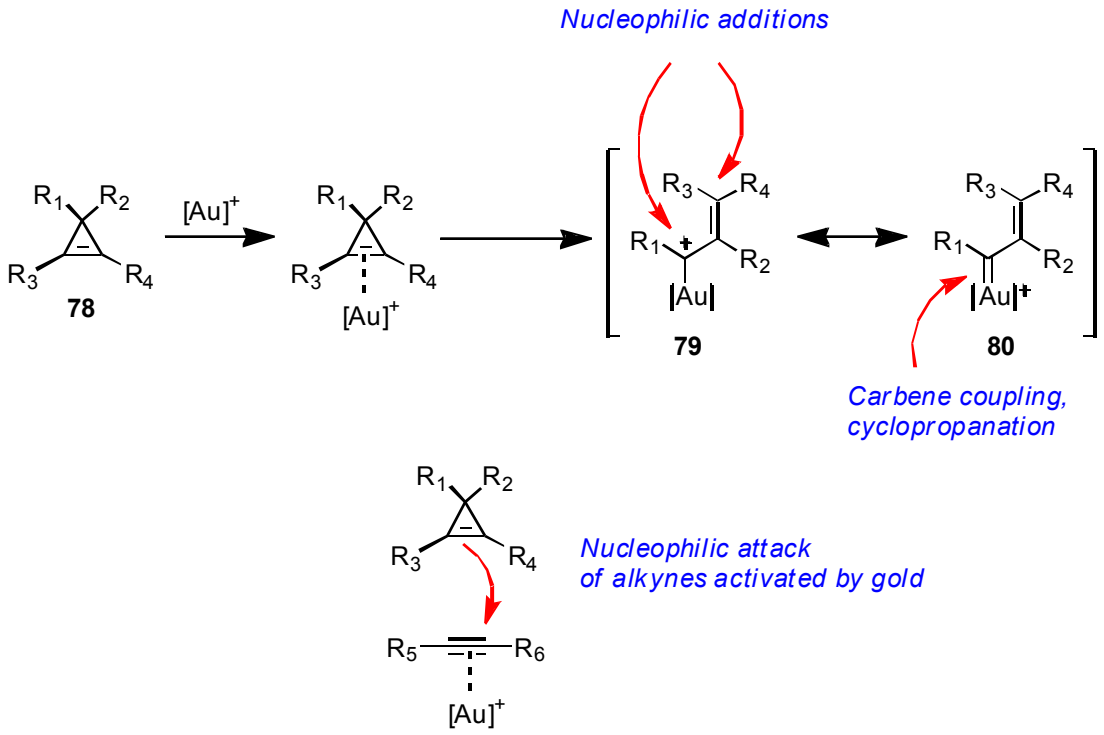
Cyclopropenes, the smallest unsaturated carbocycles, are valuable intermediates due to their versatility in organic synthesis.[1] These compounds possess considerable strain due to the severely distorted sp^2 bond angles which makes these species highly energetic and hence very reactive.[2] Furthermore, an increasing number of biologically active molecules containing the cyclopropene moiety including fatty acids and sterols has been discovered.[3] Cyclopropenes undergo novel transformations that are unknown for normal olefins, allenes, and alkynes. Owing to this reactivity are a variety of significant transformations including transition metal-catalyzed cycloisomerization to heterocycles,[4] cycloaddition reactions with and without ring-opening[5], metathesis[6] and addition to the strained double bond[7] and metalation reactions[8] (Figure 2.1). Methods of utilizing cyclopropenes in enantioselective transformations are also highly desirable. A very efficient method is the use of C_2 symmetric cyclopropenone ketals as chiral building blocks.[9] Catalytic methods for desymmetrization of cyclopropenes have also been developed such as hydrosilation, hydrostannation, hydroacylation and hydroboration.[10]



(1) Ring-opening metathesis; (2) Cycloaddition with ring opening; (3) Cycloaddition with preservation of ring; (4) Ene reactions; (5) Ring expansions; (6) Formal substitution; (7) Addition with preservation of ring; (8) Addition with ring opening

Figure 2.1 Various important synthetic transformations of cyclopropenes

Despite the well-known reactivity of cyclopropenes in transition metal-catalyzed reactions, it was only in 2008 that gold-catalyzed reactions of cyclopropenes have been realized. Since then, various interesting transformations exploiting different aspects of the reactivity of alkenyl organogold carbenoids have been reported.[11] The organogold carbenoid species generated by the ring opening of cyclopropenes have been shown to participate in a variety of reaction types such as nucleophilic addition with alcohols, arenes or carbonyl groups, self- or cross-carbene couplings and cyclopropanation of olefins (Scheme 2.1).[12]

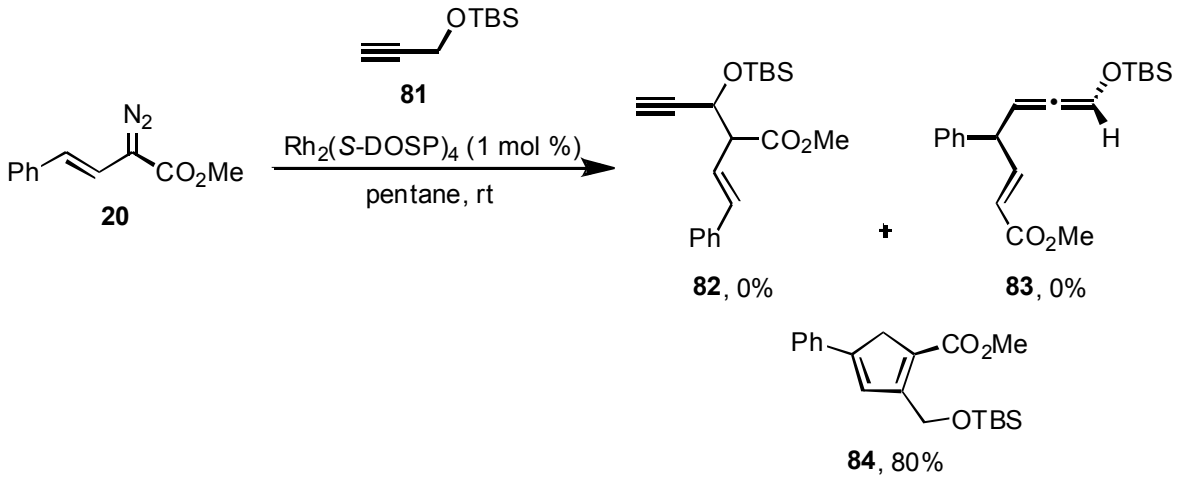


Scheme 2.1 Reactivity profile of gold-activated cyclopropenes

Traditionally, the methods utilized for cyclopropene synthesis were mainly elimination reactions from available cyclopropane precursors. Previously, Baird comprehensively reviewed this type of chemistry.[13] Unfortunately, methods for enantioselective synthesis of cyclopropenes were very rare thus hampering the synthetic potential of this class of compounds. Recently, a number of novel and effective methods for enantioselective cyclopropenation of alkynes have been developed by Doyle, Corey and Davies.[14] Furthermore, Fox and co-workers have reported a convenient approach towards chiral cyclopropenes *via* diastereomeric resolution and parallel kinetic resolution strategies.[15] Altogether, these methods of accessing chiral cyclopropenes have expanded the synthetic utility of these exceptional synthons and opened new directions for exciting chemistry.

2.2.2 Results and Discussion

This project on donor/acceptor cyclopropenation chemistry came about during an exploration on the potential of propargyl systems to undergo C-H activation/Cope rearrangement. To explore the scope of the reaction, a test reaction was carried out with siloxy-protected propargyl alcohol **81** using methyl styryldiazoacetate **20** as the carbenoid precursor. This substrate can undergo, in principle, two competing transformations: (1) C-H insertion on to the methylene site; and (2) C-H insertion followed by Cope rearrangement. It therefore offers an



Scheme 2.2 Rh_2(*S*-DOSP)$_4$-catalyzed reaction of propargyl siloxyether **81** with **20**

opportunity to study the selectivity between the two processes. However, reaction between alkyne **81** and vinyldiazoacetate **20**, in the presence of Rh_2(*S*-DOSP)$_4$ did not give either the C-H insertion product **82** or the C-H/Cope product **83**. Instead cyclopentadiene **84** was formed in 80% yield as a single regioisomer (Scheme 2.2). The regiochemistry of **84** was determined from NOE experiments (Figure 2.2). Intrigued by the reaction

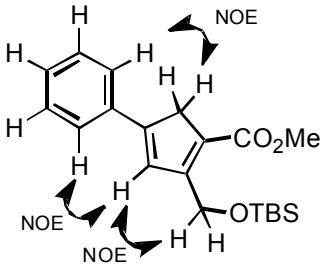
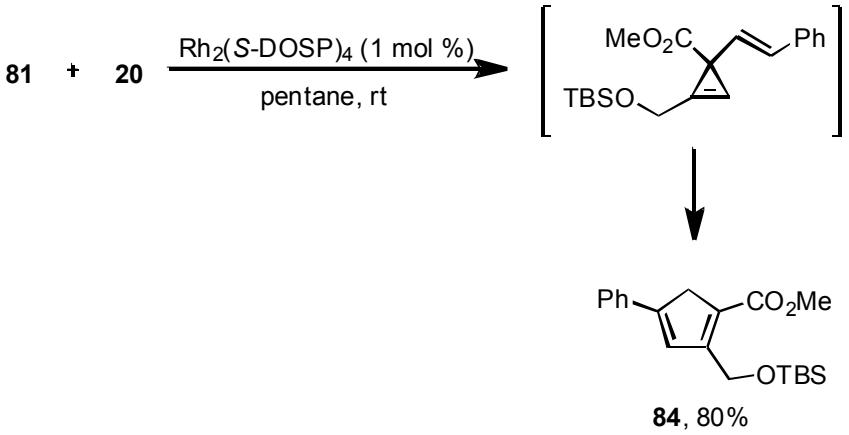


Figure 2.2 nOe Analysis of cyclopentadiene **84**

outcome, we decided to conduct a more detailed study on the formation of the cyclopentadiene derivative as well as the generality of this interesting transformation. At this point, it was proposed that this product was derived from a ring expansion of an *in situ* formed cyclopropenation product of the alkyne (Scheme 2.3). Previously, the Davies



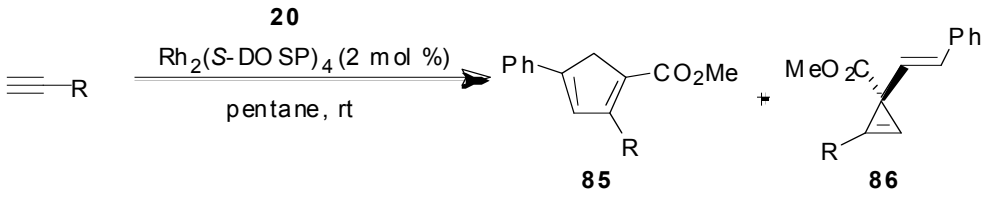
Scheme 2.3 Proposed mechanism for the formation of cyclopentadiene **84**

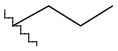
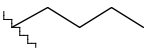
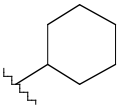
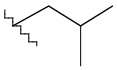
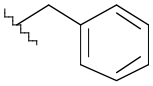
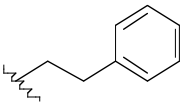
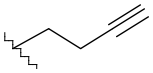
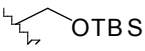
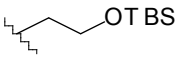
group reported that cyclopropenation of aryl alkynes were not successful using methyl styryldiazoacetate presumably due to product instability.[14] In this study, however, instead of using an aryl alkyne, an alkyl substituted alkyne was used as substrate which could have led to the formation of a relatively more stable cyclopropene product which under the reaction conditions underwent a rearrangement to the cyclopentadiene derivative.

To explore the generality of this reaction, several alkynes were subjected to the same reaction conditions. The reaction appeared to be general based on initial results.

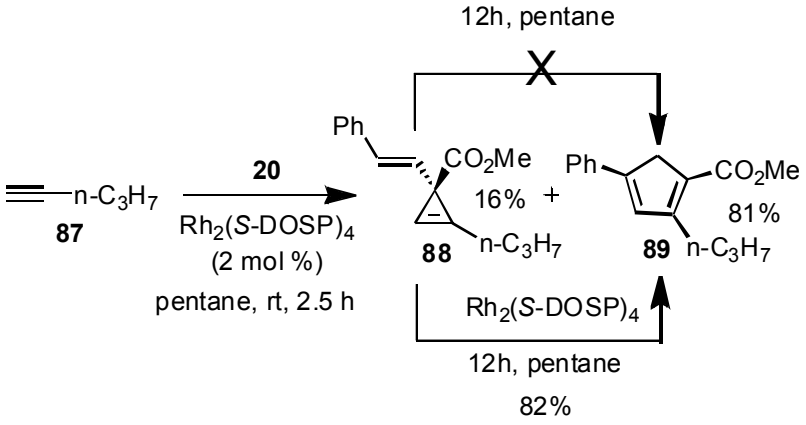
However, when straight chain alkyl alkynes, such as 1-pentyne, 1-hexyne and 1-dodecyne were used as substrate, a mixture of the cyclopentadiene **85** and cyclopropene **86** products was obtained (Table 2.1, entries 1-3). Bulky substituents on the alkyne generally favor the formation of the cyclopropene and in few examples such as entries 4-6 and 12, only the cyclopropene product was isolated in moderate to high yields. On the other hand, other alkynes gave only the cyclopentadiene product (entries 7-8, and 10-11). 1,5-Hexadiyne provided a mixture of the cyclopentadiene and the cyclopropene products in similar yields (entry 9). It is important to note that all the cyclopropenes were formed with very high enantiomeric excess (88-98% ee).

Table 2.1 Rh_2(*S*-DOSP)$_4$-catalyzed reaction alkynes with **20** at room temperature



entry	R	% yield **85**	% yield **86**	% ee **86**
1		81	16	98
2		45	46	96
3		64	18	94
4		14	82	96
5		0	93	88
6		0	37	97
7		88	0	--
8		71	0	--
9		39	33	96
10		80	0	--
11		57	0	--
12		0	51	91

Although these results supported our initial theory that the cyclopentadiene product could be a result of a ring expansion of an *in situ* formed cyclopropene, more in depth mechanistic studies were necessary. To determine whether the rearrangement is metal-catalyzed, we chose the cyclopropene **88** (synthesized from Rh_2(*S*-DOSP)$_4$-catalyzed reaction of 1-pentyne **87** and **20**) as substrate for the test reaction (Scheme 2.4). Cyclopropene **88** proved to be relatively stable as it was left unchanged when left to stir overnight in pentane. However, upon stirring overnight in the presence of Rh_2(*S*-DOSP)$_4$, most of **88** was converted to the corresponding cyclopentadiene **89** which was isolated in 82% isolated yield. ^{1}H NMR monitoring showed the disappearance of the cyclopropenyl proton after 5 minutes of stirring which suggests that the rearrangement of the cyclopropene is very fast at ambient temperature (Figure 2.3). These results confirmed that cyclopentadiene **89** is formed through a rhodium-catalyzed rearrangement of the initially formed cyclopropene **88**.



Scheme 2.4 Rh_2(*S*-DOSP)$_4$-catalyzed rearrangement of **88** to **89**

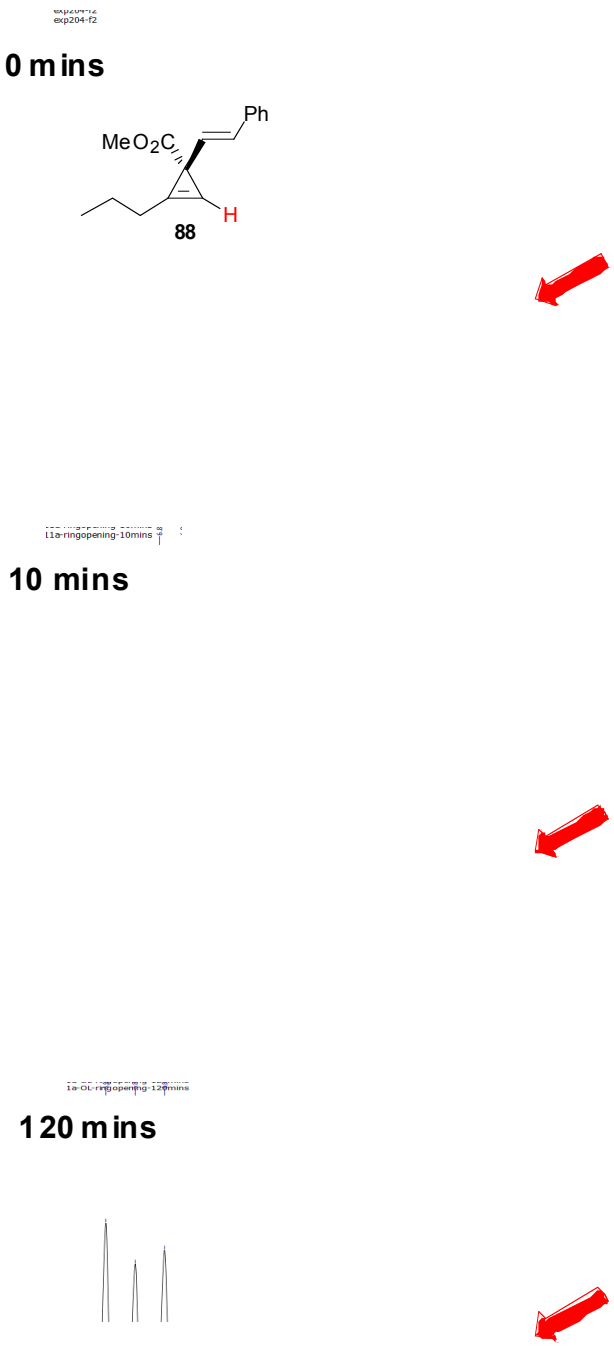
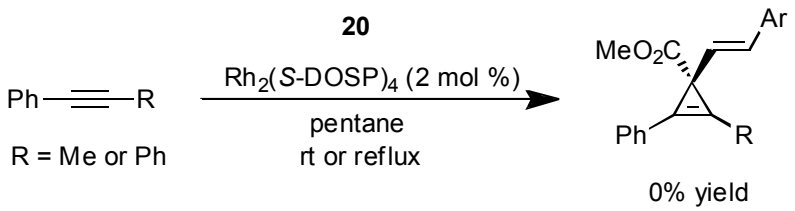


Figure 2.3 ^{1}H NMR monitoring of the Rh-catalyzed rearrangement of **88**

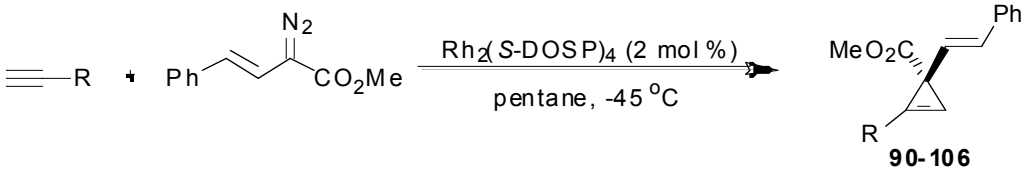
To maximize the utility of the cyclopropenation reaction, conditions were optimized to control the reaction outcome and we began our studies by varying the

temperature. Conducting the reaction at a much lower temperature would likely slow down the cyclopropene ring expansion. Indeed, it was found that by doing the reaction at -45 °C, the cyclopropene product was formed exclusively with improved yields and enantiomeric excess in most cases (Table 2). Cyclopropenes **90-106** were formed in generally good yields (45-89%) and in very high enantiomeric excess (95-99% ee) (Table 2.2). Increasing the length of the alkyl chain or the bulkiness of the alkyne substituent had virtually no effect on the enantioselectivity of the cyclopropenation reaction. Relatively low yield, however, was obtained when 2,2-dimethylbutyne was used (entry 9). Benzylic C-H insertion was not observed in the case of entries 10-12, suggesting that the cyclopropenation is a very favorable reaction. Monocyclopropenation of the diynes used in entries 13 and 14 was a viable process. Clean cyclopropenation and no C—H insertion adjacent to an electron-donating siloxy group was observed in the case of entries 15 and 16. These studies demonstrate that the cyclopropenation reaction can occur in a highly selective manner with a variety of alkyl acetylenes. In contrast to the reaction with mono-substituted alkynes, no cyclopropene product was generated from reactions with disubstituted alkynes, such as 1-phenyl-1-propyne and 1,1-diphenylacetylene (Scheme 2.5).



Scheme 2.5 Rh_2(*S*-DOSP)$_4$-catalyzed reaction of disubstituted alkynes with **20**

Table 2.2 Rh_2(*S*-DOSP)$_4$-catalyzed cyclopropenation alkyl alkynes and at -45 °C



90-106

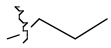
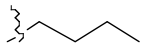
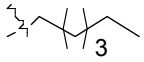
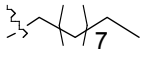
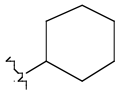
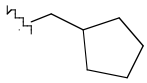
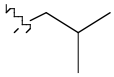
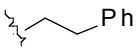
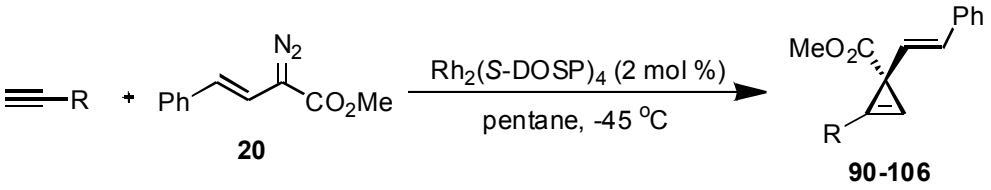
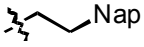
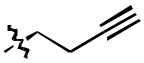
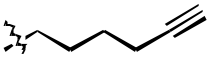
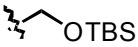
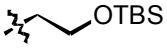
entry	R	product	yield, %	ee, %
1		**90**	81	99
2		**91**	78	98
3		**92**	85	99
4		**93**	87	97
5		**94**	78	97
6[b]		**95**	72	98
7		**96**	82	96
8		**97**	76	98
9		**98**	62	97
10		**99**	89	95
11		**100**	75	98

Table 2.2 Rh_2(*S*-DOSP)$_4$-catalyzed cyclopropenation alkyl alkynes and at -45 °C (*cont.*)

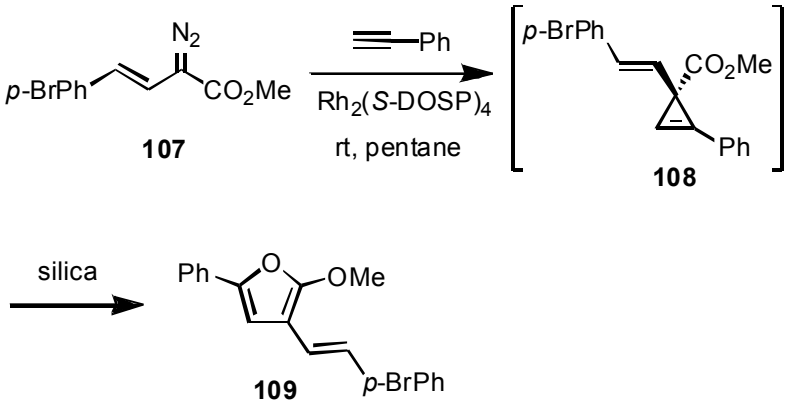


20 **90-106**

entry	R	product	yield, %	ee, %
12[c,d]		**101**	68	99
13		**102**	46	96
14		**103**	89	97
15		**104**	68	98
16		**105**	77	97
17		**106**	85	99

Even though alkyl alkynes have been shown to be very effective systems for highly enantioselective rhodium-catalyzed cyclopropenation with styryldiazoacetates, it would still be interesting to further expand the scope of the reaction to aryl alkynes. As mentioned earlier, the Davies group has previously demonstrated that aryldiazoacetates are excellent carbenoid precursors for Rh_2(*S*-DOSP)$_4$-catalyzed cyclopropenation of aryl

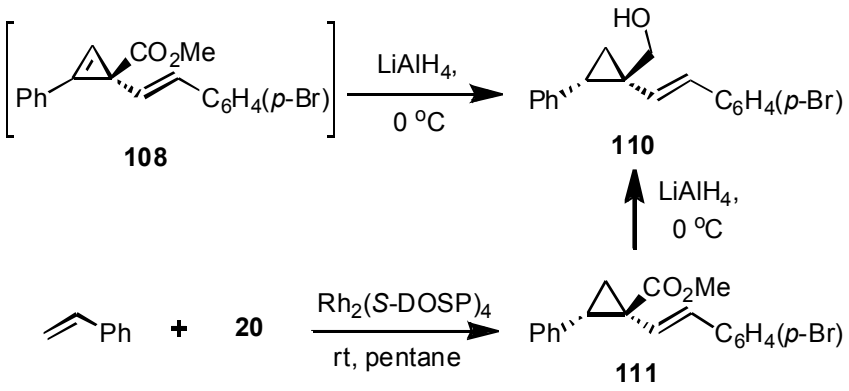
alkynes but styryldiazoacetates failed to produce the desired cyclopropene product.[14d] Intrigued by this, we decided to re-investigate the Rh_2(*S*-DOSP)$_4$-catalyzed reaction of phenylacetylene with methyl *para*-bromophenylvinyldiazoacetate **107** to really understand why the reaction previously failed. ^{1}H NMR analysis of the crude reaction mixture revealed that the cyclopropene **108** was indeed formed (Scheme 2.6). However, **108** was unstable on silica gel and readily rearranged to the furan derivative **109**, which was also unstable and decomposed upon standing at room temperature. The structure of **109** was tentatively assigned on the basis of nOe studies. These observations demonstrated that a cyclopropene could be formed from the reaction of vinyldiazoacetates with aryl alkynes.



Scheme 2.6 Rh_2(*S*-DOSP)$_4$-catalyzed reaction of phenylacetylene and **107**

Since cyclopropene products derived from aryl acetylenes could not be isolated, we decided to trap the product *in situ* to make the reaction useful. Gratifyingly, by performing this we were able to assign the absolute configuration of the cyclopropenes by comparison to the known sense of asymmetric induction observed for the Rh_2(*S*-DOSP)$_4$-catalyzed cyclopropanation of styrene with styryldiazoacetates.[16] The absolute

configuration of the cyclopropenes was assigned in the following manner (Scheme 2.7). The *in situ* formed cyclopropene **108** from the reaction of phenylacetylene and **107** was trapped by addition of $LiAlH_4$ to afford alcohol **110** as a single diastereomer. Chiral HPLC analysis of **110** (92% ee) confirmed that it was the (1*S*, 2*S*)-enantiomer based on comparison of the retention time with cyclopropane **110** obtained from the reduction of cyclopropane ester **111** derived from styrene and **20**. The same absolute configuration was observed with the silyl-substituted cyclopropene **106**, which was determined by X-ray crystallography (Figure 2.4). The absolute configurations of the other cyclopropenes are tentatively assigned by analogy.



Scheme 2.7 Determination of the absolute configuration of the cyclopropenes

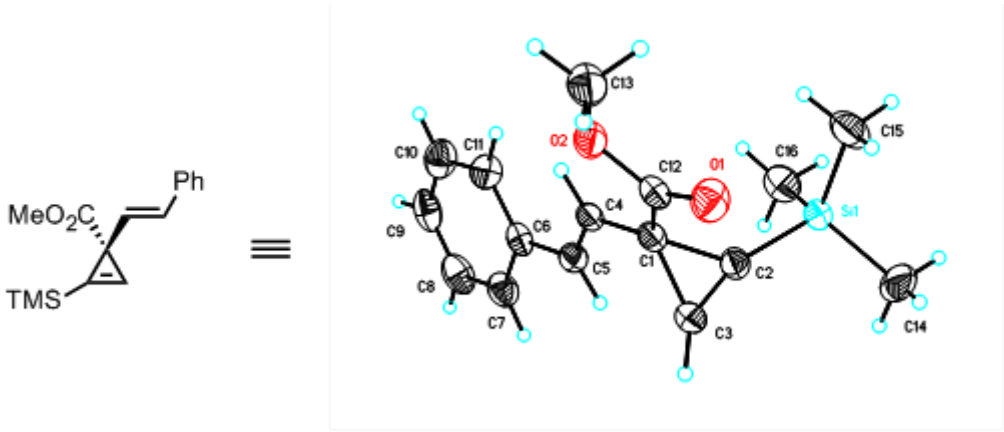
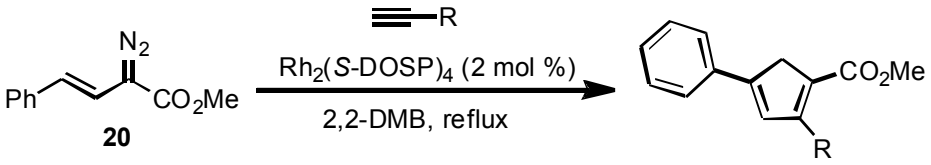


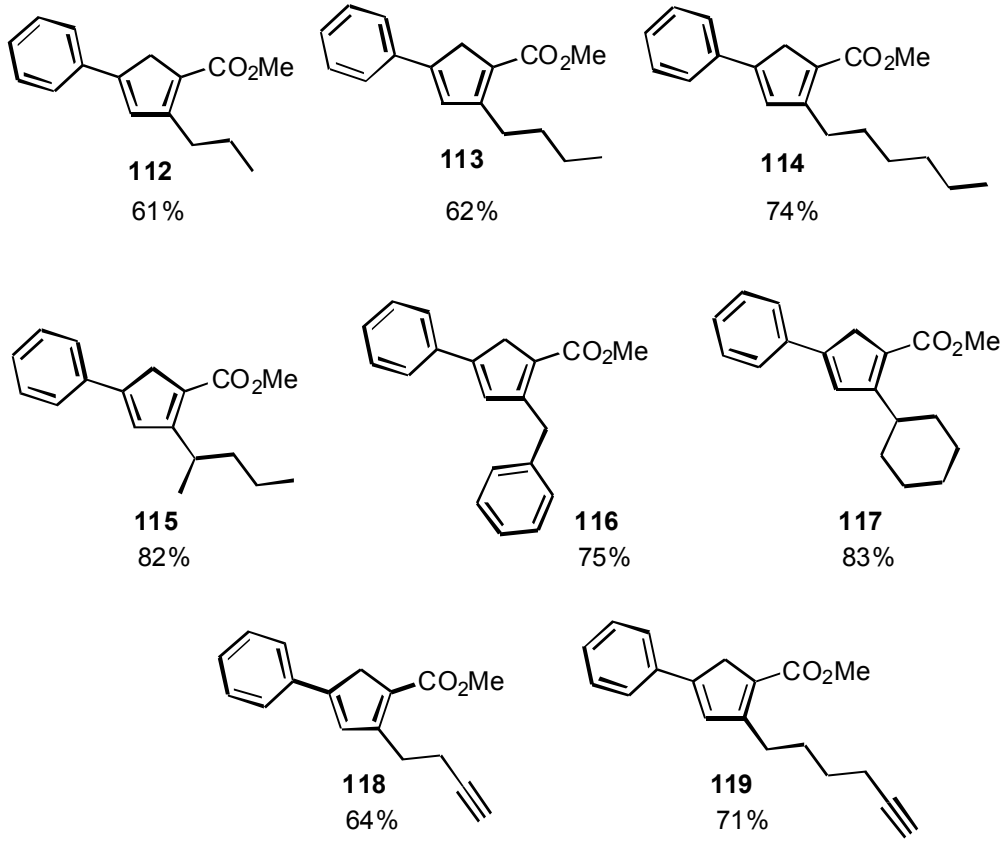
Figure 2.4 X-ray structure of cyclopropene **106**

As cyclopentadienes represent an interesting class of reagents in organic synthesis, efforts were made to optimize their formation. Upon heating the reaction mixture to reflux, using 2,2-dimethylbutane (DMB) as solvent, a range of cyclopentadienes (**112-119**) was formed in moderate to good yields (61-83% yield) (Table 2.3).

Table 2.3 Rh_2(*S*-DOSP)$_4$-catalyzed synthesis of cyclopentadiene derivatives

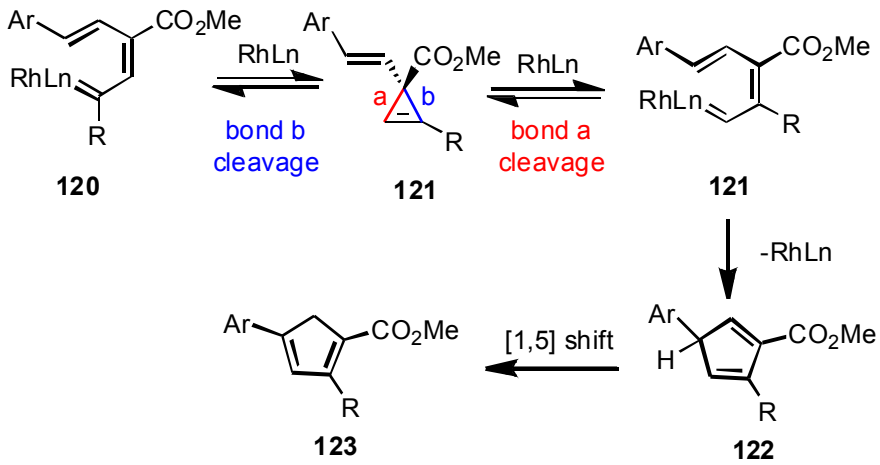


20 **112-119**



The proposed mechanism for the formation of the cyclopentadiene product is based on previous studies by Padwa and co-workers.[4b] The rhodium catalyzed ring–opening of unsymmetrically substituted vinylcyclopropene **121** can potentially lead to two regioisomeric rhodium-carbenoids **120** and **121**, depending on which bond is cleaved (Scheme 2.8). Literature precedence indicates that further reaction occurs preferentially from the least substituted carbenoid **121**.[4b,17] This may be due to preferential cleavage of bond **a** to form **121**, or rapid equilibration between the isomeric vinylcarbenoids, with

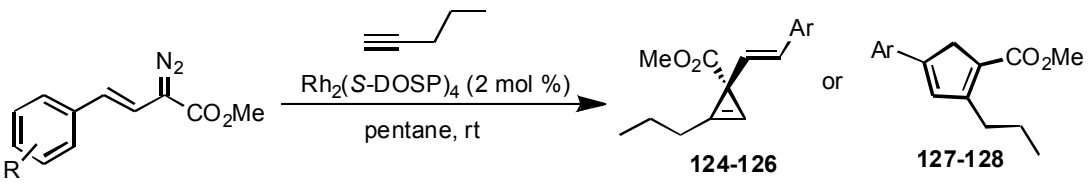
cyclopentadiene formation occurring from **121**. The initially formed cyclopentadiene **122** would then need to undergo a [1,5]-sigmatropic rearrangement to form the observed product **123**.

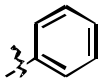
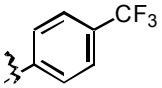
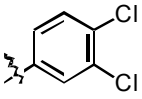
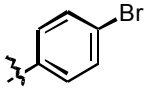
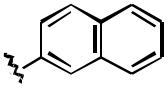
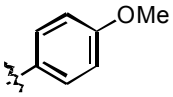


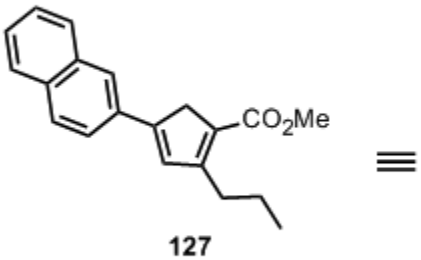
Scheme 2.8 Mechanism for the Rh-catalyzed formation of cyclopentadiene derivative

Other arylvinyldiazoacetates were also tested in the cyclopropenation reaction (Table 2.4). In the case of relatively electron-deficient arylvinyldiazoacetates (entries 2-4), cyclopropenes **124-126** were obtained in good yields (79-88%) and high enantiomeric excess (96-98% ee). In contrast, the reaction of the more electron-rich arylvinyldiazoacetates (entries 5-6), resulted in ring-expansion and consequent formation of cyclopentadienes **127** and **128** in 87% and 78% yields, respectively. The structure of **128** was confirmed by X-ray crystallography (Figure 2.5).

Table 2.4 Rh_2(*S*-DOSP)$_4$-catalyzed reaction of 1-pentyne using various styryldiazoacetates



entry	R	product	yield, %	ee, %
1		**90**	81	99
2		**124**	88	98
3		**125**	79	96
4		**126**	86	97
5		**127**	87	--
6		**128**	78	--



127

≡

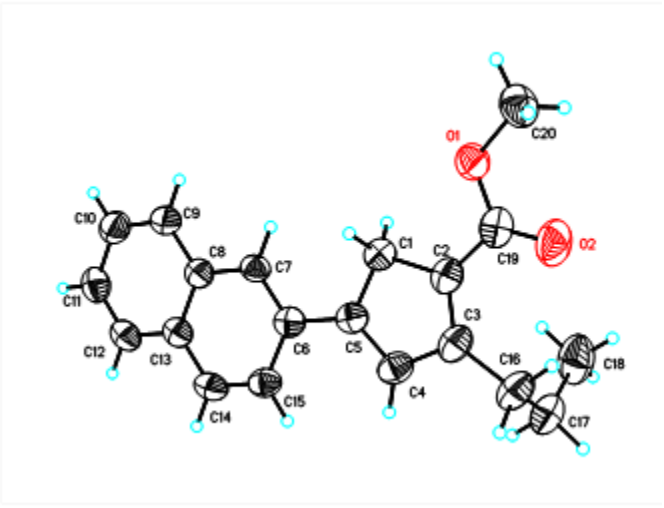


Figure 2.5 X-ray structure of cyclopentadiene **127**

The high enantioselectivity observed in the cyclopropenation reactions suggests that the alkyne approaches the vinylcarbenoid intermediate in a highly organized manner. There are two extreme orientations proposed for the approach of the alkyne during the cyclopropenantion event (Figure 2.6). The first has the alkyne approaching side-on, while the second has the alkyne approaching end-on to the rhodium carbenoid.[16,18] The observation that no cyclopropenantion occurs with disubstituted alkynes, would be evidence to support the end-on approach, as such an approach would be highly unfavorable for disubstituted alkynes since the second substituent will clash with the rhodium catalyst structure.[14d] However, an end-on approach does not give an obvious explanation of why Rh_2(*S*-DOSP)$_4$ gives such high asymmetric induction. The chiral influence of Rh_2(*S*-DOSP)$_4$ has been proposed to be due to steric influence located, not directly in front of the rhodium-carbon bond, but slightly to the side of the carbenoid.[16,18] An end-on approach is unlikely to be influenced by steric groups located to the side of the carbenoid.

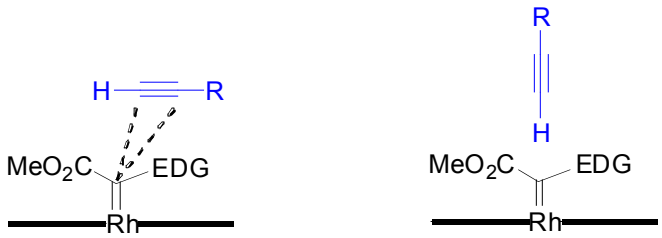


Figure 2.6 Extreme orientations of incoming substrate in cyclopropenation chemistry

With the help of a previous Davies' group member, Dr. Jorn Hansen, Density Functional calculations were conducted in order to obtain a better understanding of the mechanism of the cyclopropenation reaction. The study was conducted using the B3LYP

functional in the reaction between methyl styryldiazoacetate **20** and propyne, catalyzed by dirhodium tetrakisformate, as a model reaction system (Figure 2.7). Only the reaction step involving the rhodium carbenoid complex and propyne was considered, as the pathway leading to the rhodium carbenoid complex has been described in detail in previous works.[18,19] The cyclopropenation step displayed a potential energy activation barrier of +11.6 kcal/mol, and was exothermic by -14.6 kcal/mol. These observations suggest that, a much later transition state occurs in cyclopropenation chemistry in comparison with cyclopropanation reactions of alkenes.[18,19a] Starting from either an end-on or side-on trajectory, the alkyne ultimately obtained approximately the same orientation in all the transition state optimizations. The favored transition structure (**TS-I**) is shown in Figure 2.7 (See Supporting information for more details). A most striking feature of this transition state is the close proximity and directionality of the terminal alkyne hydrogen to a carboxylate ligand (1.956 Å), which indicates a hydrogen bonding interaction. The alkyne is furthermore tilted 18.2° from the ideal end-on approach. These observations imply that a disubstituted alkyne could not have a suitable orientation to undergo the cyclopropenation reaction.

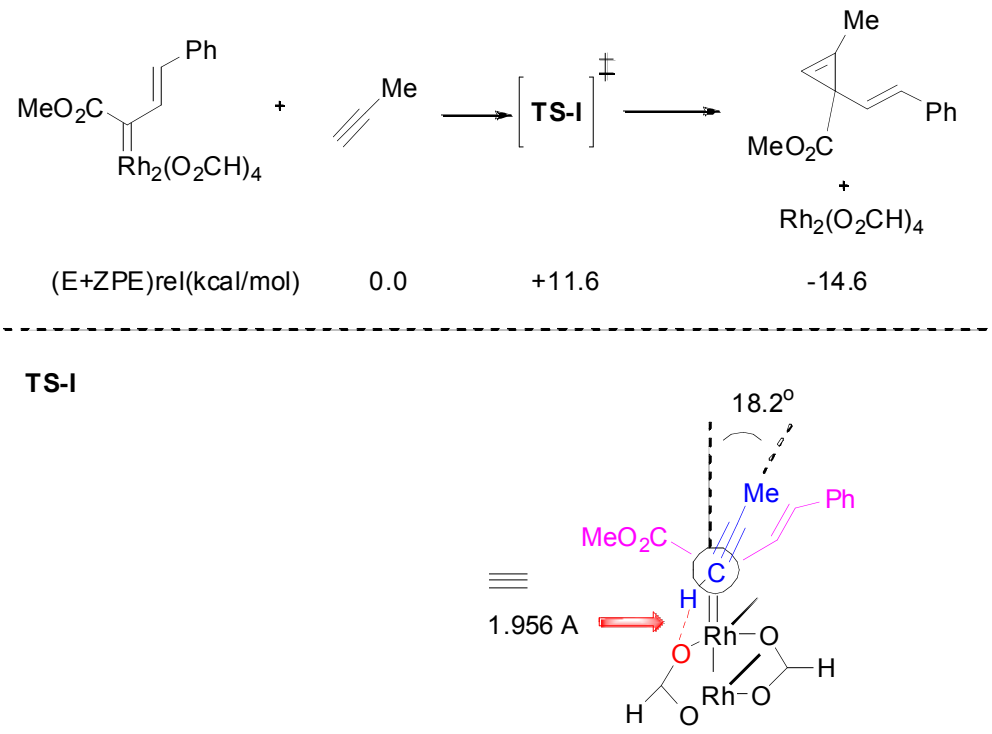


Figure 2.7 Transition state for the cyclopropenation of propyne with **20**

The tilted substrate orientation observed in **TS-I** is of critical importance, as it ensures that the chiral influence of Rh_2(*S*-DOSP)$_4$ would be involved in the asymmetric induction. As this complex is considered to adopt a D_2-symmetric conformation, the chiral carbenoid complex can be represented with blocking groups from the catalyst occupying the front left-hand and the back right-hand quadrants (Figure 2.8).[16,18] The substrate approaches in a tilted orientation so that attack occurs to the front face (*Re*-face) of the carbenoid preferentially. Approach to the *Si*-face is disfavored by the blocking group in the back, as it is on the side of the vinyl group. In the transition state, the terminal alkyne carbon is involved in C–C bond formation with the carbenoid carbon, while positive charge build-up occurs at the internal sp-carbon. The second C–C bond

forms with inversion at the carbenoid center, consistent with previous observations in cyclopropanation and C–H functionalization chemistry.[18,19] This model successfully predicts the sense of asymmetric induction in these reactions.

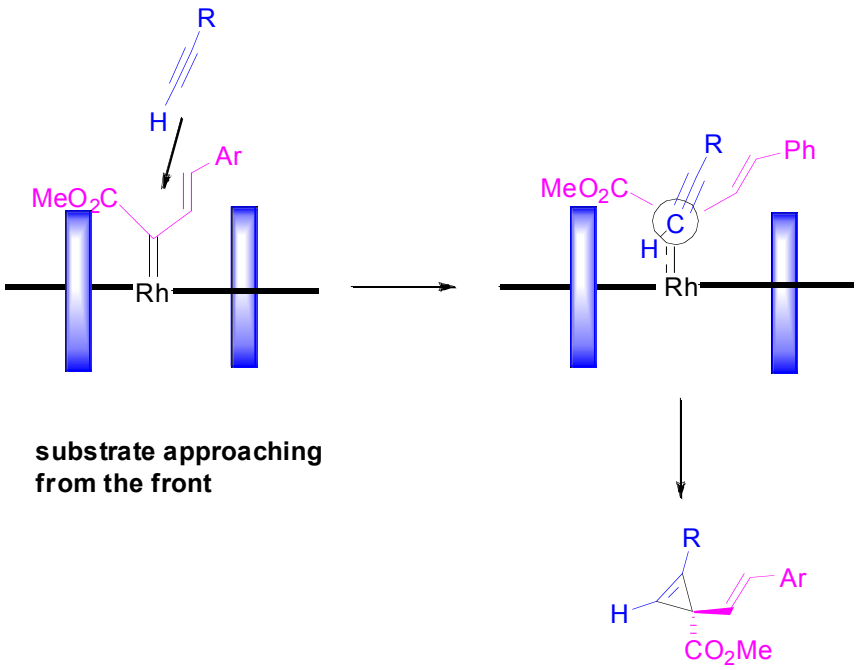


Figure 2.8 Predictive model for the asymmetric induction in Rh_2(*S*-DOSP)$_4$-catalyzed cyclopropenation

2.2.3 Summary

In summary, arylvinyldiazoacetates were found to be effective systems for highly enantioselective Rh_2(*S*-DOSP)$_4$-catalyzed cyclopropenation reactions with terminal

alkynes. The development of this method allowed us to readily access a new class of chiral vinylcyclopropenes with quaternary carbons. Under forcing conditions, the vinylcyclopropenes undergo a rhodium(II)-catalyzed ring expansion to stable cyclopentadienes. Density functional calculations have demonstrated that the exact transition state for the cyclopropenation event involves a tilted end-on approach that also displays a favorable hydrogen-bonding interaction with a carboxylate ligand on the catalyst. These observations provide valuable insights for future catalyst design and expansion of this methodology to more elaborate systems.

2.3 Rh_2(*S*-PTAD)$_4$-Catalyzed Cyclopropenation of Aryl Alkynes and Donor/Acceptor-Carbenoids

2.3.1 Introduction

A very unique and attractive feature of the donor/acceptor carbenoid chemistry developed by the Davies group is the synergy between chiral dirhodium tetracarboxylate catalysts and donor/acceptor diazo compounds. In the past decade or so, the Davies group has established the optimum combination of rhodium catalyst and carbenoid precursor in a variety of synthetically useful transformations. The prolinate-based catalyst, Rh_2(*S*-DOSP)$_4$ generally gives high enantioselectivity when the acceptor group on the carbenoid is a methyl ester (Figure 2.9). This trend was demonstrated in the highly enantioselective cyclopropenation of terminal alkynes with styryldiazoacetates.[20] On the other hand, the phthalimide-based catalyst, Rh_2(*S*-PTAD)$_4$ generally gives high enantioinduction with other types of acceptor groups such as phosphonate, [21] trifluoromethyl, [22] keto, [23] and cyano.[24] In addition, Rh_2(*S*-PTAD)$_4$ has been shown to be a more effective catalyst than

Rh_2(*S*-DOSP)$_4$ in reactions involving siloxyvinyldiazoacetates.[25] The impetus of the following efforts was to further expand the scope of rhodium-catalyzed cyclopropenation of donor/acceptor carbenoids. This work lead us to the development of the highly enantioselective indirect synthesis of cyclopropenes with a quaternary stereogenic center bearing germinal acceptor groups.

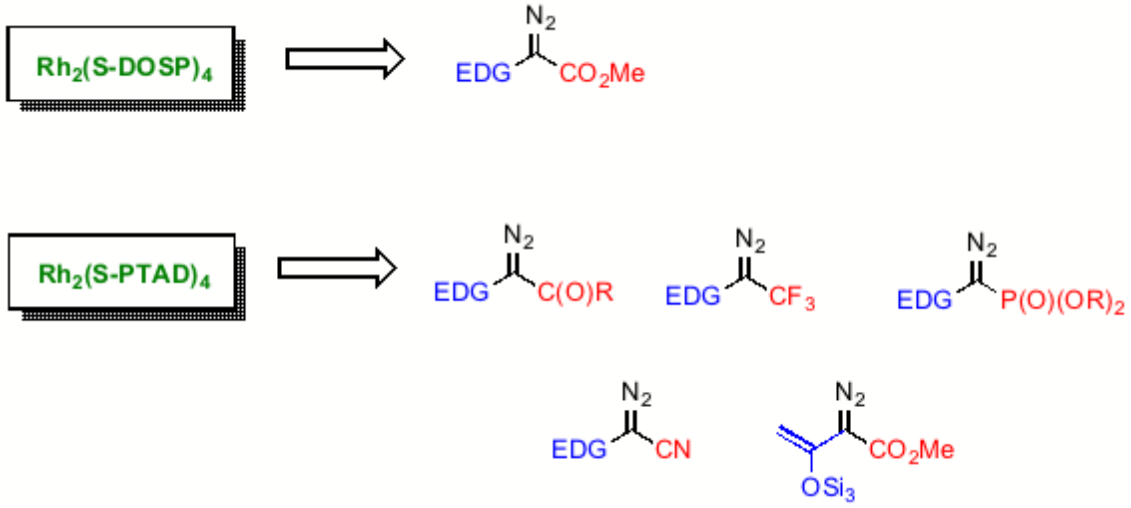
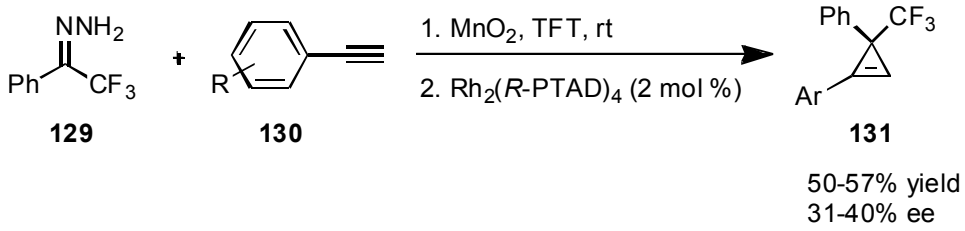


Figure 2.9 Typical catalyst-diazo combination in the Davies carbenoid chemistry

2.3.2 Enantioselective cyclopropenation of alkynes and cyano-, and keto-substituted aryldiazo compounds.

Previously, Dr. Justin Denton studied the intermolecular Rh_2(*R*-PTAD)$_4$-catalyzed cyclopropenation of alkynes utilizing the two-step cyclopropanation sequence. This method proved to be very successful in synthesizing trifluoromethyl-substituted cyclopropanes with very high diastereoselectivity and with high enantioselectivity.[21] Unfortunately, Rh_2(*R*-PTAD)$_4$ was ineffective for the cyclopropenation of alkynes using

1-phenyl-2,2,2-trifluorodiazoethane (formed *in situ* from **129** and MnO_2) providing the cyclopropene products **131** in moderate yields and moderate enantioselectivity (Scheme 2.9).[26] Further exploration using this type of diazo compound for the cyclopropenation of alkynes was not done.



Scheme 2.9 One-pot synthesis of trifluoromethyl-substituted cyclopropenes

My exploration began with exploring the use of various aryldiazo compounds bearing cyano and keto groups as carbenoid precursor for the cyclopropenation chemistry (Table 2.5). Moderate enantioselectivity was obtained when 1-Phenyl-1-diazoacetone was used as the diazo precursor in the cyclopropenation of phenylacetylene providing product in 88% yield and 57% ee (entry 1). Interestingly, a dramatic increase in enantioselectivity was obtained when the aryl group of the diazo compound is electron deficient as in the case of entries 2 and 3. Similar results were obtained when the alkynyldiazoketones were used providing cyclopropenes **135** and **136** in 85 and 91% ee, respectively. The absolute configuration cyclopropene **136** was assigned by X-ray crystallographic analysis (Figure 2.10).

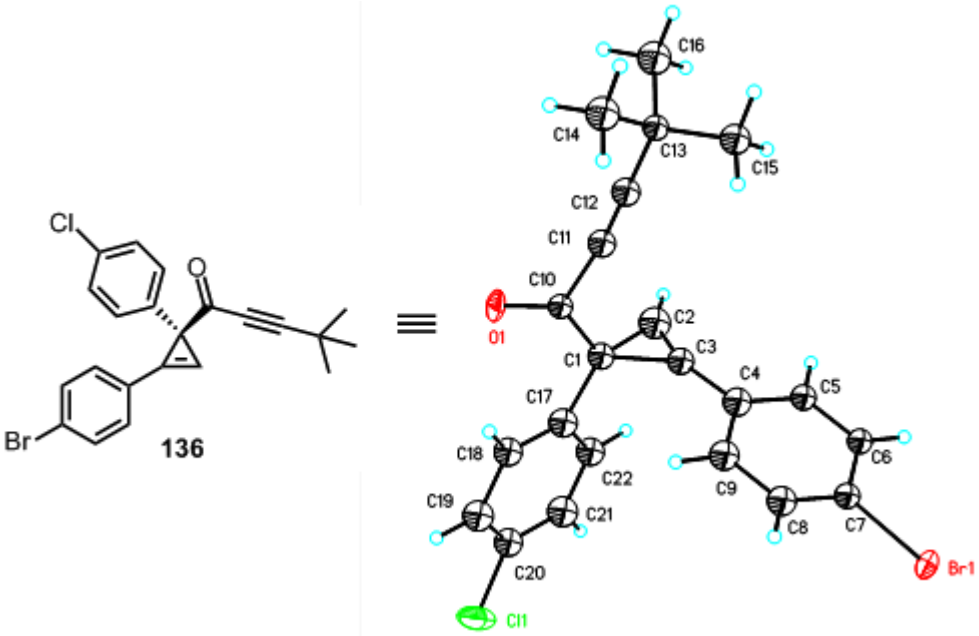
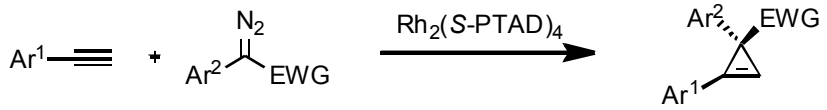
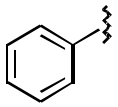
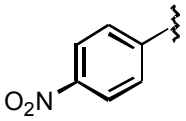
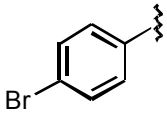
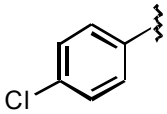
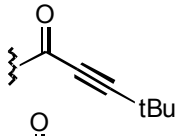
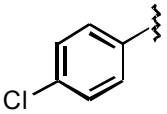
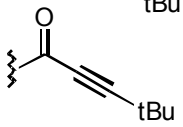


Figure 2.10 X-ray structure of cyclopropene **136**

Table 2.5 Rh_2(*S*-PTAD)$_4$-catalyzed cyclopropenation of aryl alkynes using various aryldiazo compounds



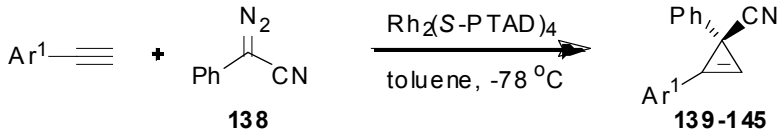
132-137

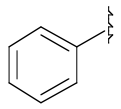
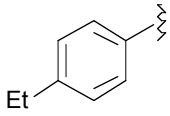
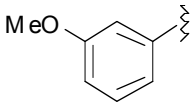
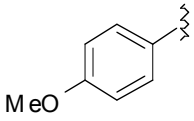
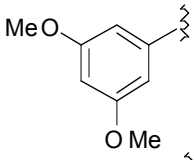
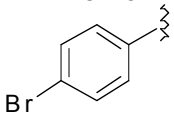
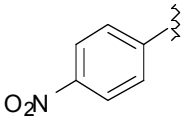
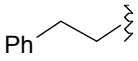
entry	Ar^1	Ar^2	EWG	Product	yield (%)	ee (%)
1	Ph			**132**	88	57
2	Ph			**133**	82	79
3	Ph			**134**	87	89
4	Ph			**135**	84	85
5	*p*BrPh			**136**	95	91

We then focused our attention in the Rh_2(*S*-PTAD)$_4$-catalyzed cyclopropenation of various alkynes using 2-diazo-2-phenyacetonitrile **138** as the carbenoid precursor. Excellent levels of enantioinduction were observed when the less reactive, electron deficient alkynes were used as substrates for the cyclopropenation with **138** (entries 6-7). On the other hand, the use of the more reactive electron rich alkynes as substrates afforded the cyclopropene products in poor to moderate levels of enantioinduction (entries 2-5). Poor enantioselectivity was also observed when alkylalkyne was used as the substrate used for the cyclopropenation reaction (entry 8). The absolute configuration of the cyclopropenylnitriles was tentatively assigned based on the results reported by Davies and Denton.[24] Future work in the Rh_2(*S*-PTAD)$_4$-catalyzed cyclopropenation of alkynes

with diazoketones and diazonitriles includes determining the absolute configuration of the alkynes as well further expanding the scope of these reactions. It would also be necessary to have a model for the Rh_2(*S*-PTAD)$_4$-catalyzed cyclopropenation reaction to determine the approach of the substrate to the carbenoids and also to explain the sense of asymmetric induction. Computational modeling studies involving Rh_2(*S*-PTAD)$_4$-stabilized donor/acceptor carbenoids, particularly in the cyclopropanation chemistry, is an active research in the Davies group. Unfortunately, such working models are not available at this time.

Table 2.6 Rh_2(*S*-PTAD)$_4$-catalyzed cyclopropenation of various aryl alkynes using 2-diazo-2-phenylacetonitrile **138**



entry	Ar^1	Product	yield (%)	ee (%)
1		**137**	86	85
2		**139**	88	52
3		**140**	90	63
4		**141**	92	83
5		**142**	81	37
6		**143**	93	93
7		**144**	88	89
8		**145**	87	44

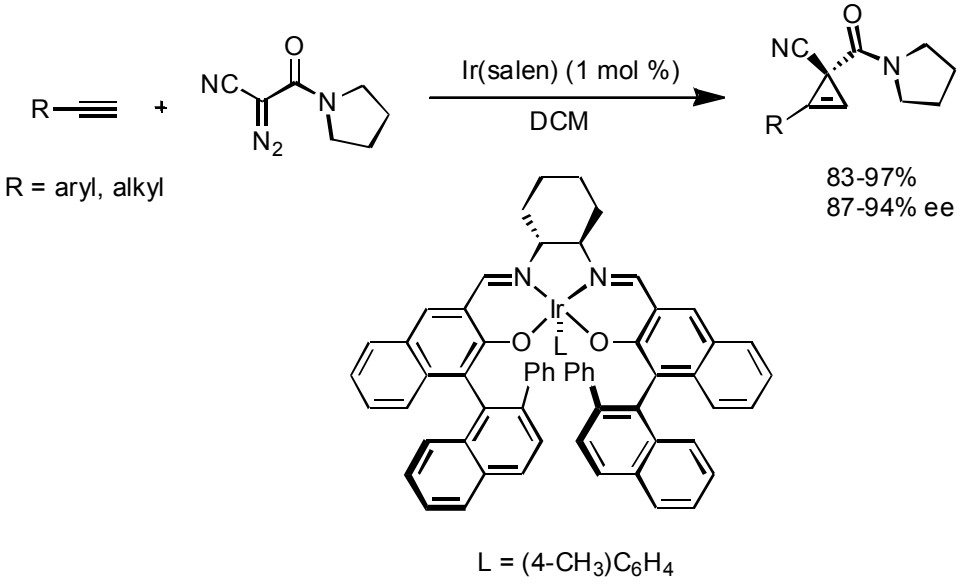
2.3.3 Highly enantioselective cyclopropenation of alkynes and siloxyvinyldiazoacetate.

2.3.3.1 Background

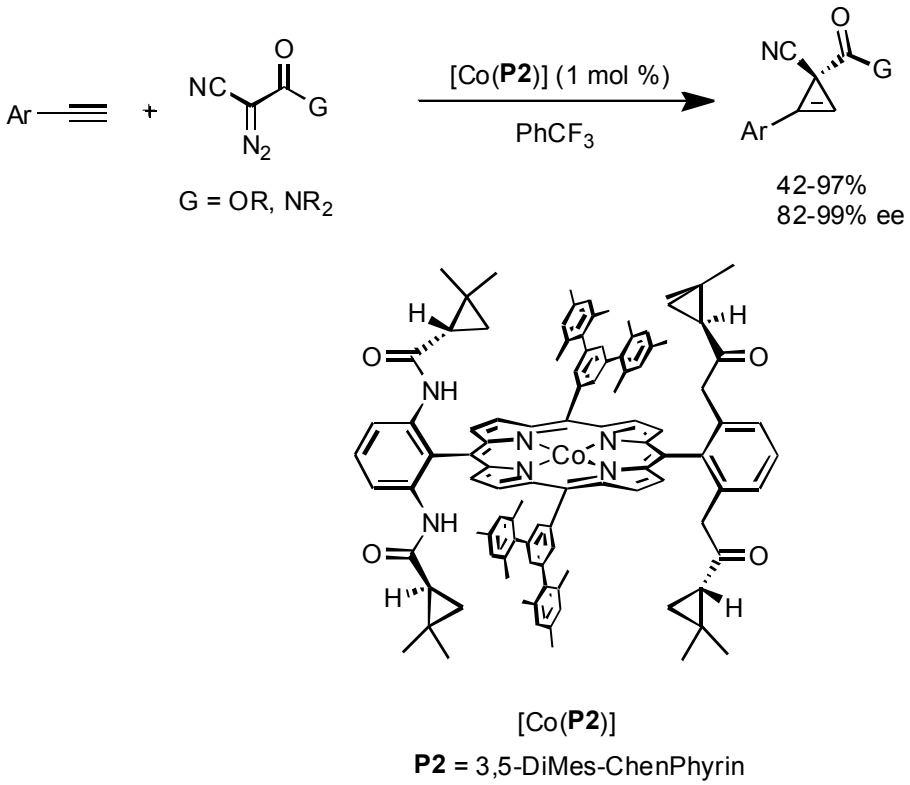
Rhodium-catalyzed asymmetric intermolecular cyclopropenation with acceptor-substituted carbenoids is a well-established process and high levels of asymmetric induction have been achieved.[27] With the recent development of the highly asymmetric cyclopropenation of alkynes with donor/acceptor vinylcarbenoids, the scope of chiral cyclopropenes bearing donor and acceptor groups that could be readily accessed has greatly expanded. Altogether, these great advances in the field of cyclopropene chemistry will potentially pave way to the discovery of interesting and important synthetic transformations utilizing enantioenriched cyclopropenes. On the other hand, the asymmetric synthesis of cyclopropenes containing two acceptor groups *via* dirhodium carbenoid chemistry is far less developed.[28-29] This class of cyclopropenes bearing all-carbon quaternary centers is very interesting and can serve as invaluable chiral synthons for a range of stereoselective synthetic applications. Cyclopropenes bearing geminal acceptor groups such as esters, amides and nitriles are very versatile building blocks for the synthesis of modified chiral cyclopropanes, including biologically active compounds like α-amino acid and β-amino acid cyclopropane derivatives.[30]

Acceptor/acceptor-substituted diazo compounds are very stable thus relatively less reactive with Lewis acidic metal catalysts towards the formation of metal carbenoid intermediates. Forcing conditions are usually required to decompose these types of diazo compounds although the reactions of the corresponding acceptor/acceptor carbenoid often suffer from poor enantioselectivity due to its high electrophilic character. High asymmetric induction has only been achieved in cyclopropenation chemistry when one of the acceptor groups is a cyano group**.** Katsuki and coworkers reported that Ir(salen) complexes catalyzed the enantioselective cyclopropenation of terminal alkynes using α-

cyanodiazoacetamides (Scheme 2.10).[31] Interestingly, these catalysts were also effective when donor/acceptor-substituted diazo compounds were used. Shortly after, Zhang and coworkers demonstrated that the new D_2-symmetric chiral porphyrin, 3,5-diMes-ChenPhyrin is highly effective catalyst for enantioselective cyclopropenation of terminal alkynes with α-cyanodiazoacetamides and α-cyanodiazoacetates (Scheme 2.11).[32]



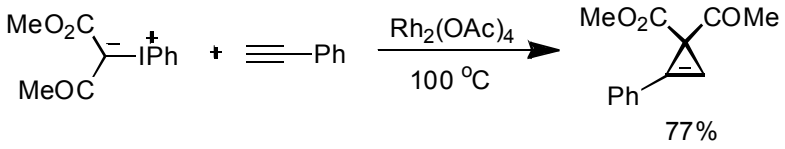
Scheme 2.10 Katsuki's Ir(salen)-catalyzed enantioselective cyclopropenation



Scheme 2.11 Zhang's asymmetric cyclopropenation using chiral cobalt porphyrin

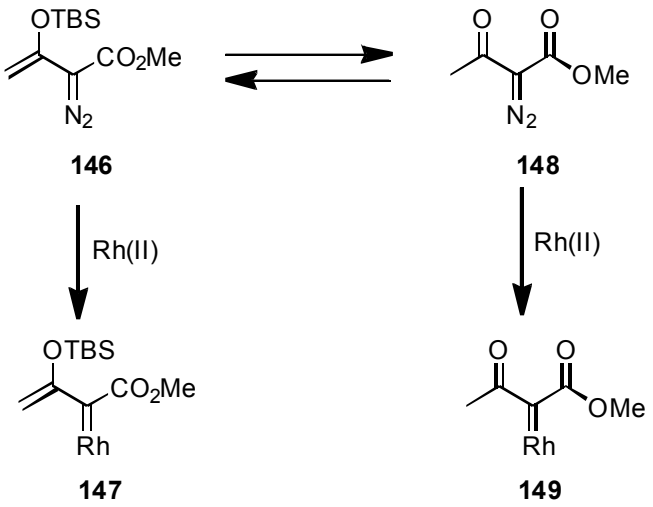
As part of our interest in Rh(II)-catalyzed asymmetric transformations, we wanted to expand the scope of donor/acceptor cyclopropenation chemistry towards the enantioselective synthesis of cyclopropenes bearing geminal acceptor groups. We were especially interested with cyclopropenyl ketones since these compounds are unexplored. In addition, synthesis of enantiomerically pure cyclopropenyl ketones has not been reported in the literature. The earliest reported synthesis of this type of cyclopropene was done via photolysis of pyridazine N-oxides to give 3-acylcyclopropenes.[33] Cho and Liebeskind also reported the synthesis of cyclopropenyl ketones from the corresponding cyclopropenyl esters via Weinreb ketone synthesis.[34] Recently, Hadjiarapoglou and coworkers reported a Rh(II)-catalyzed synthesis of cyclopropenyl ketones from the reaction of acetylenes and carbomethxy iodonium ylides (Scheme 2.12).[35] Although this

methodology nicely showcases the synthetic potential of the iodonium ylide chemistry, the cyclopropenyl ketones were only obtained in moderate to good yields and the reaction has to be conducted in refluxing conditions.



Scheme 2.12 Rh-catalyzed cyclopropenation of phenylacetylene with iodonium ylide

To address the challenge of enantioselective synthesis of cyclopropenes bearing two acceptor groups, we were intrigued by the potential of using the donor/acceptor-substituted diazo compound as an indirect method for the asymmetric synthesis of cyclopropenes bearing two carbonyl acceptor groups. Using siloxyvinyldiazoacetate **146** as carbenoid precursor, we envisioned that highly enantioselective cyclopropenation of alkynes could be achieved and upon removal of the siloxy protecting group could afford the cyclopropene products bearing the keto and ester groups (Scheme 2.13). A further objective of this study is to illustrate the relationship between diazoacetoacetate **148** and siloxyvinyldiazoacetate **146**, which is readily formed from **148**.[36] Diazo decomposition of **148** generates the acceptor/acceptor carbenoid **149**, whereas decomposition of **146** generates the donor/acceptor carbenoid **147**. Acceptor/acceptor carbenoids are highly electrophilic intermediates, whereas the reactivity of donor/acceptor carbenoids is greatly modulated by the influence of the donor group.[37] Hence, it is possible to use **146** as a surrogate for **148** when the high reactivity of the acceptor/acceptor carbenoid **148**, precludes its successful utilization in a particular reaction.

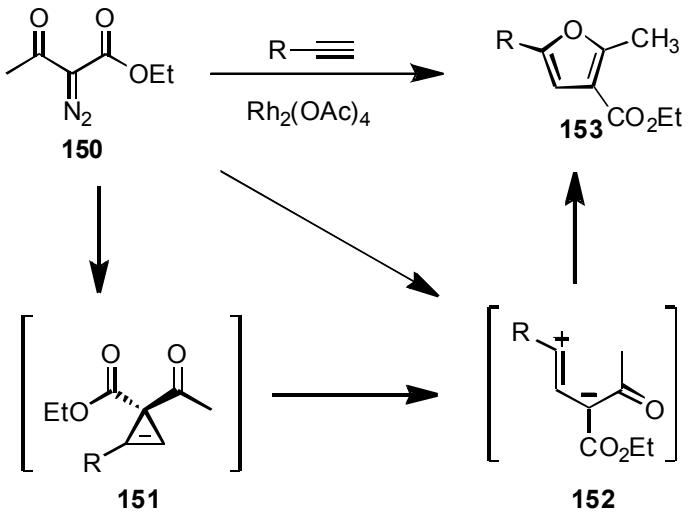


Scheme 2.13 Relationship between siloxyvinyldiazoacetate **146** and diazoacetoacetate **148**

2.3.3.2 Results and Discussion

Our studies began by examining the Rh(II)-catalyzed reaction of methyl diazoacetoacetate **148** in the presence phenylacetylene as trapping agent. One of the challenges of conducting cyclopropenation reactions with the diazoacetoacetate **148** is the tendency of this system to react via zwitterionic intermediates, leading to the formation of different reaction pathways.[38] Early reports by Davies and Romines in an attempt to synthesize racemic cyclopropenes from Rh(II)-catalyzed decomposition of acceptor/acceptor-substituted diazoacetate **150** in the presence of alkynes lead directly to furans although a possible formation of a cyclopropene was suggested (Scheme 2.14).[39] However, before this work, it remained uncertain whether the 2-alkyl furan **153** was formed directly *via* 2+3 cycloaddition or by a rearrangement of an initially formed cyclopropene **151**. The formation of **153** could, in principle, arise from a zwitterionic intermediate **152** formed directly from the reaction of the carbenoid with the alkyne or by

ring-opening of an initially formed cyclopropene **151**. Efforts were then made to address this issue.



Scheme 2.14 Rh-catalyzed reaction of phenylacetylene and **150**

In order to explore whether it would be possible to conduct an asymmetric cyclopropenation of phenylacetylene with diazoacetoacetate **148**, a series of reactions were conducted, varying the catalyst and solvent (Table 2.7). When $Rh_2(Oct)_4$ was used as catalyst, only the furan product **154** was formed as seen in the ^1H NMR of the crude reaction mixture (entry 1). The product was isolated in 97% yield and the structure of **154** was confirmed by X-ray crystallography (Figure 2.11). By conducting the reaction under milder conditions, we envisaged that a cyclopropene product could be isolated and

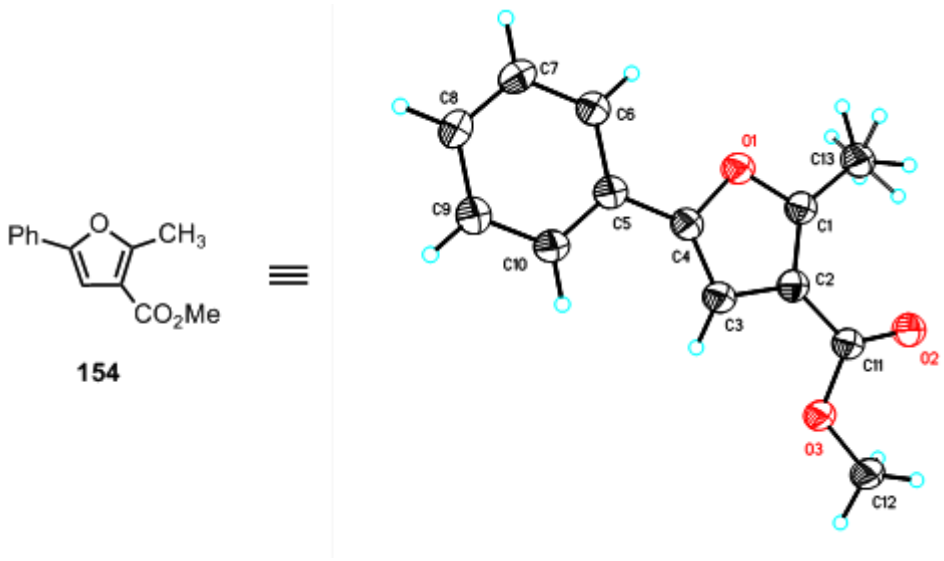
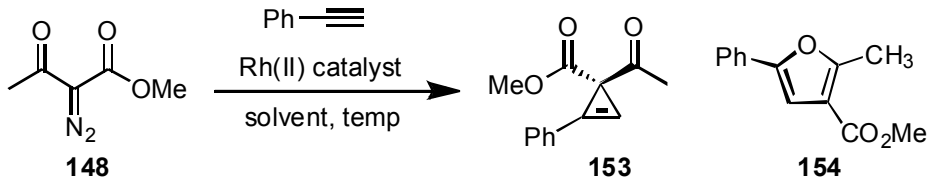


Figure 2.11 X-ray structure of furan **154**

therefore the reaction was conducted at -45 °C. Indeed, ^{1}H NMR analysis of the crude reaction showed a mixture of cyclopropene **153** and the furan **154** (entry 2). It is interesting to note that different reactivity was observed when chiral dirhodium complexes, Rh_2(*S*-DOSP)$_4$ and Rh_2(*S*-PTAD)$_4$, were used as catalysts. In these cases, the cyclopropene product **153** was formed as the major product in 74 and 73% yield, respectively at room temperature (entries 3-4). Not surprisingly, the cyclopropenes were formed in very poor enantiomeric excess for both catalysts even when the reaction was conducted at -45 °C (entries 5-6).

Table 2.7 Rh-catalyzed reaction of phenylacetylene with diazoacetoacetate **148**

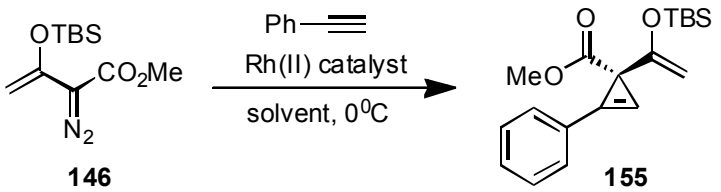


148 **153** **154**

entry	catalyst[c]	solvent	temp (^{o}C)	% yield **153**	% yield **154**	% ee
1	$Rh_2(Oct)_4$	DCM	23	---	97	---
2	$Rh_2(Oct)_4$	DCM	-45	61	24	---
3	Rh_2(*S*-PTAD)$_4$	DCM	23	74	9	<5
4	Rh_2(*S*-PTAD)$_4$	DCM	-45	66	---	<5
5	Rh_2(*S*-DOSP)$_4$	pentane	23	73	17	7
6	Rh_2(S-DOSP)$_4$	pentane	-45	69	---	11

At this point it became apparent that enantiomerically enriched cyclopropenes could not be directly accessed using diazo compound **148** as carbenoid precursor and so we turned our attention to siloxyvinyldiazoacetate **146** because in principle, the cyclopropenyl ketone could be accessed upon deprotection of the silyl protecting group. Several chiral catalysts were also surveyed for this particular reaction to form cyclopropene **155** and the results are shown in Table 2.8. The prolinate-based catalyst Rh_2(*R*-DOSP)$_4$ and the bridged

Table 2.8 Rh-catalyzed cyclopropenation of phenylacetylene with siloxyvinyldiazo-acetate **146**



146 **155**

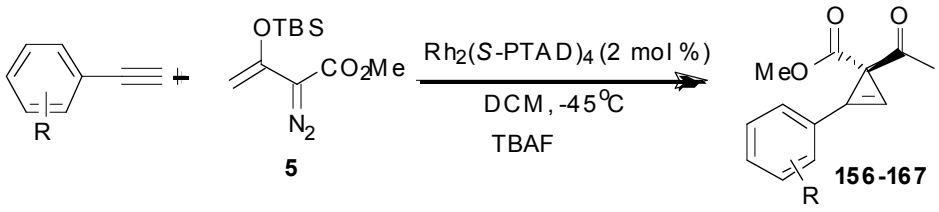
entry	catalyst[c]	solvent	% yield	% ee[d]
1	Rh_2(*R*-DOSP)$_4$	pentane	41	-51
2	Rh_2(*S*-PTAD)$_4$	DCM	93	94
3	Rh_2(*S*-NTTL)$_4$	DCM	93	88
4	Rh_2(*S*-PTTL)$_4$	DCM	91	90
5	Rh_2(*S*-BiTISP)$_2$	pentane	43	58

catalyst Rh_2(*S*-BiTISP)$_2$ both performed poorly in terms of yield and enantioselectivity (entries 1 and 5). Excellent yields and enantioselectivities were obtained using the structurally related catalysts Rh_2(*S*-NTTL)$_4$ and Rh_2(*S*-PTTL)$_4$ (entries 3-4). Davies' Rh_2(S-PTAD)$_4$ gave the optimum result providing the cyclopropene **155** in 93% yield and 94% ee (entry 2). All of the catalysts gave the same sense of enantioinduction as Rh_2(S-PTAD)$_4$. These results are consistent with previous studies on asymmetric reactions with siloxyvinyldiazoacetate **146**. We have reported that Rh_2(*S*-PTAD)$_4$ was a very effective catalyst in asymmetric tandem cyclopropanation/Cope rearrangement reactions with **146.**[25] Muller had observed that Rh_2(*S*-NTTL)$_4$ is better than Rh_2(*S*-DOSP)$_4$ in intermolecular cyclopropanation of olefins with **146**.[39] Again, these results demonstrated

that Rh_2(S-PTAD)$_4$ is a very effective backup catalyst for Rh_2(*S*-DOSP)$_4$ for donor/acceptor carbenoid reactions. Unfortunately, efforts to isolate a single crystal for determining the absolute configuration of the cyclopropene were unsuccessful. The absolute configuration was tentatively assigned based on the results reported by Müller and coworkers[39] and our previous work on rhodium-catalyzed cyclopropenation with alkynes and styryldiazoacetates.[20]

The optimized conditions for the one-pot cyclopropenation/deprotection of arylacetylenes was found to be slow addition of the diazo compound (over 2 h) to a dichloromethane solution of Rh_2(*S*-PTAD)$_4$ (2 mol %) and the alkyne at -45 °C. The silyl protecting group can be removed *in situ* by adding excess amount of TBAF after complete addition of the diazoacetate solution to the reaction mixture. Under the optimized conditions, the substrate scope of the cyclopropenation reaction was investigated. Various aromatic acetylenes were used as trapping agent (Table 2.9) and results showed that the reaction is generally compatible with substituted arylacetylenes affording cyclopropenyl ketones **156-167** in moderate to excellent yields (77-94% yield) and excellent enantioselectivities (93-99% ee). The cyclopropenylketones are relatively stable under the reaction conditions and no rearrangement to the corresponding furans was observed. Clean cyclopropenation and no benzylic C-H insertion were observed using *p*-ethylethynylbenzene (entry 4) and TBS-protected *o*-ethynylbenzylalcohol (entry 12) as substrates, which showed that cyclopropenation can occur in a highly selective manner. Selective monocyclopropenation of diynes in the case of was also possible (entries 9 and 10). Electron rich arylacetylenes, such as *p*-ethynylanisole and 2-

Table 2.9 Rh_2(*S*-PTAD)$_4$-catalyzed cyclopropenation of various aryl alkynes using **5**

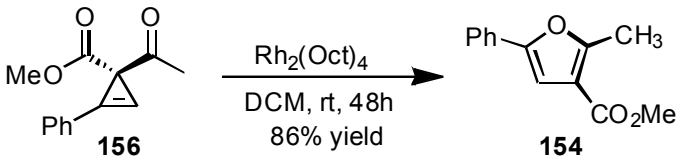


entry	R	product	yield, %	ee, %
1	H	**156**	83	98
2	o-Me	**157**	80	98
3	p-Me	**158**	86	93
4	p-Et	**159**	90	97
5	p-tBu	**160**	87	98
6	p-Br	**161**	92	95
7	p-Ph	**162**	88	98
8	m-CF_3	**163**	94	93
9	p-ethynyl	**164**	85	94
10	m-ethynyl	**165**	88	97
11	p-F, m-Me	**166**	77	97
12	o-CH_2OTBS	**167**	94	99

ethynylnaphthalene also afforded highly enantioenriched cyclopropenes, however, these products were too unstable for full characterization and are not included in the Table. The

absolute configuration of the cyclopropenes **156-167** was tentatively assigned by analogy to **155**.

With the cyclopropenyl ketones in hand, the feasibility of Rh(II)-catalyzed ring expansion of the cyclopropenyl ketones to furans was investigated. Cyclopropene **156** in DCM was stirred in the presence of $Rh_2(Oct)_4$ at 23 °C (Scheme 2.15). ^1H NMR analysis of the crude reaction mixture after two hours showed small amounts of furan product. After 48 h of stirring proton NMR analysis showed near complete conversion of the cyclopropene to the furan product. The product was isolated by flash chromatography and the pure furan product was obtained in 86% yield. In the absence of $Rh_2(Oct)_4$, the cyclopropene did not undergo ring expansion to the corresponding furan. This result demonstrates that indeed the cyclopropene undergoes a Rh(II)-catalyzed rearrangement to the furan product. However, the rearrangement is slower than a typical rhodium-catalyzed cyclopropenation, which means that the reaction between diazoacetoacetate **148** and phenylacetylene is more likely to undergo a mechanism involving zwitterionic intermediates instead of a rearrangement of an initially formed cyclopropene.



Scheme 2.15 Mechanism for the Rh-catalyzed formation of furan derivative

2.3.3.3 Summary

In summary, siloxyvinyldiazoacetates were found to be effective carbenoid precursors for highly enantioselective Rh_2(*S*-PTAD)$_4$-catalyzed cyclopropenation

reactions with aryl acetylenes. A new class of optically active cyclopropenes with quaternary carbon bearing germinal acceptor groups is now readily accessible. Cyclopropenyl ketone was also found to undergo a regioselective Rh(II)-catalyzed ring expansion to furans. This work greatly demonstrated that by simply changing the electronics of the carbenoid (acceptor/acceptor- *versus* donor/acceptor-substituted), a dramatic increase in enantioselectivity in the cyclopropenation chemistry can be achieved. This work also showcased the advantage of the phthalamide-based catalyst, Rh_2(S-PTAD)$_4$, over Rh_2(*S*-DOSP)$_4$ for promoting high asymmetric induction in the cyclopropenation of alkynes using siloxyvinyldiazoacetate as the carbenoid precursor.

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CHAPTER THREE

Silver-Catalyzed Cyclopropenation of Internal Alkynes with Donor/Acceptor-Substituted Carbenoids

3.1 Introduction

This chapter focuses on the development of an efficient method of synthesizing racemic highly-substituted cyclopropene derivatives using donor/acceptor carbenoids and readily available silver(I) salts. This work was inspired by the seminal work of Davies and Thompson on the use of silver salts as catalysts for decomposing donor/acceptor-susbtituted diazo compounds. Using the more reactive and sterically less demanding silver(I)-stabilized donor/acceptor carbenoids, we were able to cyclopropenate internal alkynes; a feat that has not been accomplished in the past. This work also paved the way to the discovery of a variety of novel silver-catalyzed transformations involving donor/acceptor carbenoids which will be discussed in the following chapters.

3.2 Background

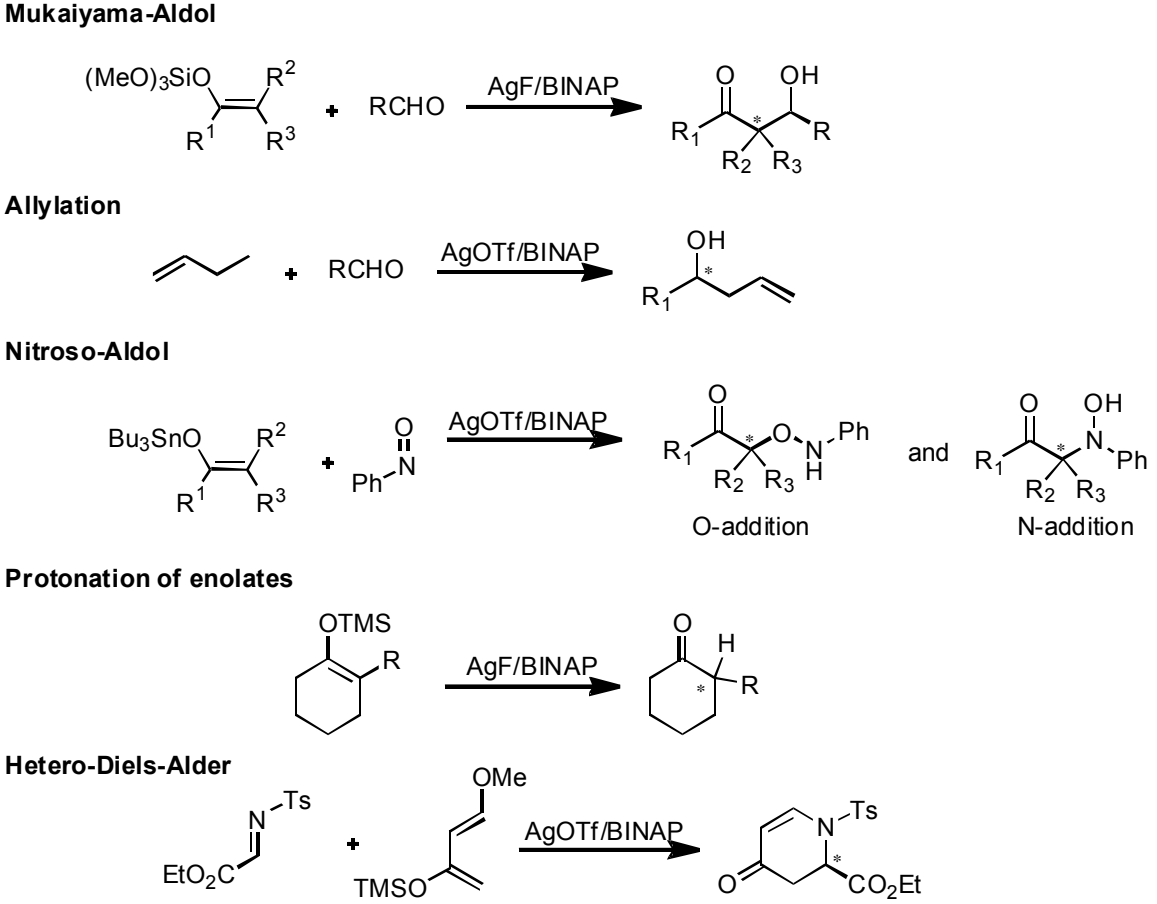
3.2.1 Silver catalysis

3.2.1.1 Silver as Lewis acid

The use of transition metals in organic syntheses has been the focus of research groups in the last few decades**.** A distinct group of late transition metals including copper, silver and gold (also known as the coinage metals) are widely used for significant organic transformations.[1] Silver is a commonly used transition metal for catalysis in industry and has been utilized since ancient time as a precious metal for ornaments and jewelries. Silver-promoted oxidation reactions are one of the earliest examples of the utilization of silver in organic synthesis.[2] Silver (I) is considered to be a mild oxidizing agent (with a reduction potential of 0.8 eV) and is suitable for effective oxidation of primary and secondary alcohols to aldehydes and ketones, respectively. These silver compounds are commonly employed as stoichiometric oxidants in both organic and inorganic synthesis and the reactions proceed *via* radical pathways.[3]

Homogeneous silver-mediated reactions have been known for some time but a significant number of these reports are dated within the past two decades and more elaborate and unique transformations have been only realized within the last 6 years.[4] Copper has been widely studied for decades but both silver and gold were neglected in the area of organic syntheses for a long time. This can be accounted to silver's moderate Lewis acidity. The carbophilic nature of Ag(I) is supported by studies on complexes with pi-donors such as alkenes and aromatic compounds as well as σ-donors such as amines and ethers.[5] In the last decade or so, efforts in studying silver-catalyzed transformations mainly focused on Lewis acid catalysis. In 1996, Yamamoto and co-workers developed a system involving Ag(I) and BINAP (Yamamoto-Yanagisawa system) in the enantioselective Mukaiyama-aldol reactions,[6] allylation reactions,[7] nitroso-aldol type

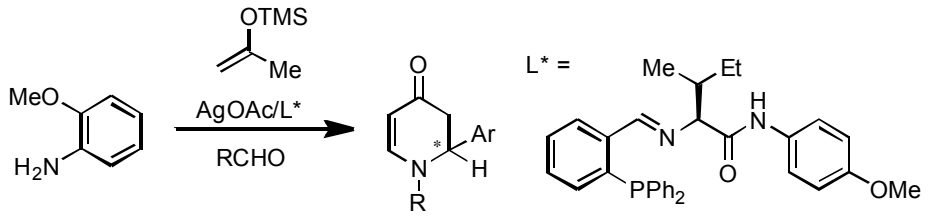
reactions,[8] protonation of enolates[9] and hetero-Diels-Alder reactions (Scheme 3.1).[10] In 2004, Hoveyda and Snapper reported an amino acid derived phosphine-Ag(I) catalyst system for the asymmetric cycloaddition reaction of Danishefsky's diene with arylimines.[11]



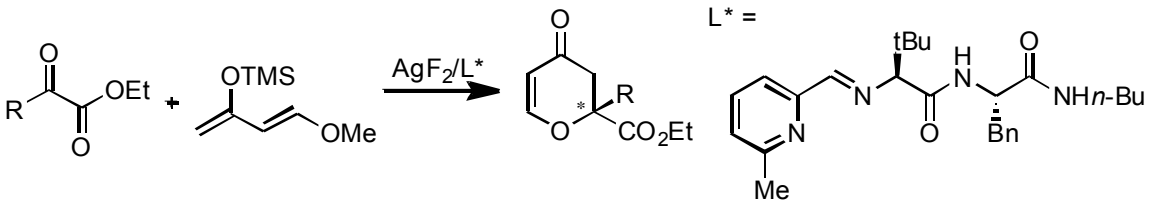
Scheme 3.1 Synthetic applications of Yamamoto's Ag(I)/BINAP catalyst system

Various studies involving asymmetric reactions such as the Mannich reaction (Scheme 3.2)[12] and enantioselective addition of silyl enol ethers to alpha-keto esters using the same catalytic system was reported afterwards (Scheme 3.3).[13] In addition to

these reactions, silver-catalyzed heterocyclizations have made significant progress in the past several years (Scheme 3.4). Silver(I) salts have been used in nucleophilic addition reactions such as cyclization of acetylenic alcohols, amines, acids and imines,[14] cyclization of allenyl ketones or aldehydes,[15] and nucleophilic cyclization of allenes (Scheme 3).[16] Also, there are recent reports on nucleophilic intermolecular addition to alkynes[17] and nucleophilic additions of hydroxyl and carboxyl groups to unactivated olefins (Scheme 3).[18] Numerous natural and unnatural products have been prepared by synthetic routes involving silver-mediated heterocyclization reactions.[14-16]

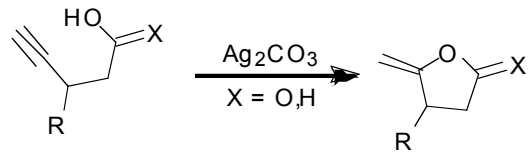


Scheme 3.2 Asymmetric silver-catalyzed Mannich reaction

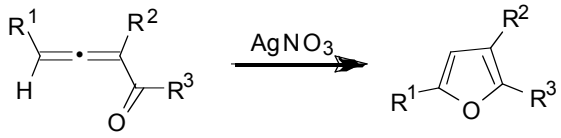


Scheme 3.3 Asymmetric silver-catalyzed addition of silyl enol ether to α-keto esters

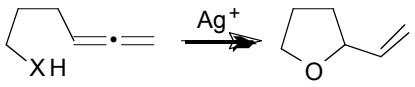
Acetylenic cyclization



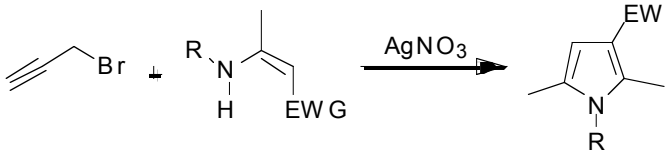
Cyclization of allenic ketone



Allenic cyclization



Intermolecular addition to alkynes

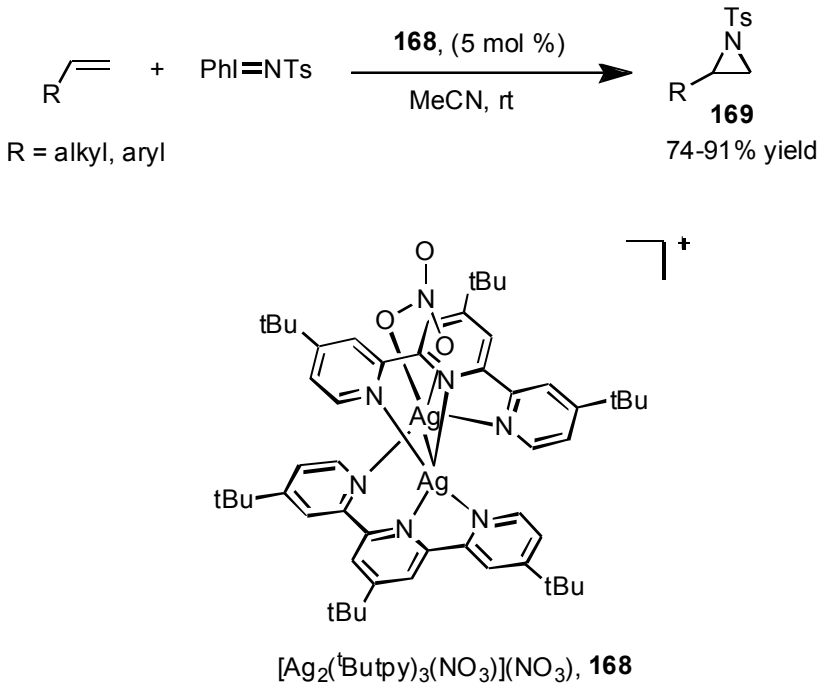


Intramolecular addition to inert olefins

Scheme 3.4 Ag(I)-catalyzed synthesis of heterocycles

3.2.1.2 Silver nitrenes and silylenes

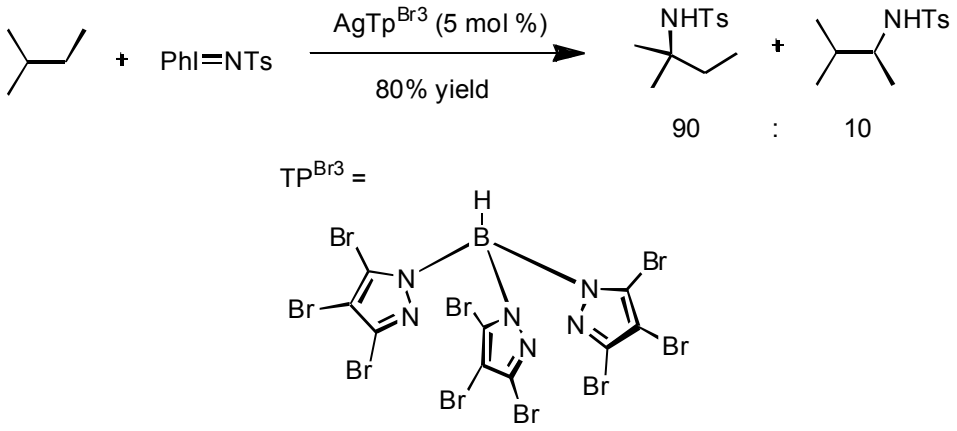
Silver-catalyzed oxidation reactions are very limited. Given the high oxidation potentials associated with silver ions, the development of more silver-based oxidation chemistry to has gained significant progress over the last couple of years. In 2003, He and coworkers discovered a catalytic silver-based system that mediates nitrene-transfer reactions to olefins and inert C-H groups.[19] This work, which utilized a pyridine-supported silver catalyst **168**, constitutes the first silver-catalyzed aziridination of olefins (scheme 3.5). The catalyst structure showed a very unique dinuclear silver(I) $[Ag_2(^tButpy)_3(NO_3)](NO_3)$. This structure possesses a fairly strong Ag-Ag interaction in which the Ag-Ag distance is 2.842 Å. The reaction works for both aliphatic and aromatic olefins affording the



Scheme 3.5 He's silver-catalyzed aziridination of olefins

aziridine products **169** in good yields. Shortly after the seminal work by the He group, the group of Diaz-Requejo and Perez reported that silver-pyrazolylborate complex catalyzed

the amination of hydrocarbons (Scheme 3.6).[20] Linear and branched alkanes were converted into amines



Scheme 3.6 Diaz and Perez's silver-catalyzed C-H amination of hydrocarbons

under mild, catalytic conditions. Tertiary sites are preferred for the functionalization reaction, followed by secondary and, to a lesser extent, primary C-H bonds. Current results indicate that silver probably interacts with iminoiodanes to generate a silver nitrene precursor. Depending on the substrate and reaction conditions, this precursor can lead to reactions *via* either a concerted silver nitrene or a stepwise radical pathway (Figure 3.1).[20]

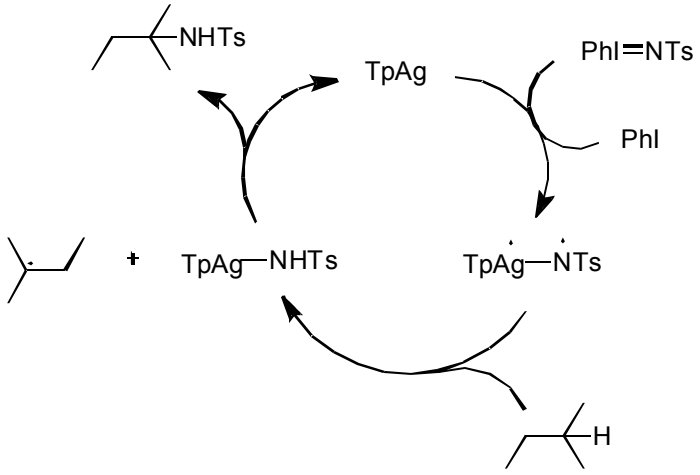
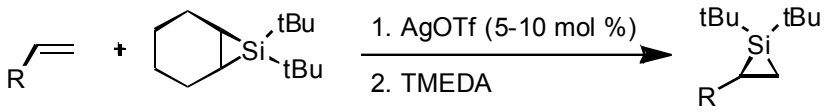
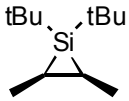
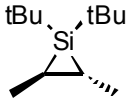
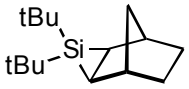
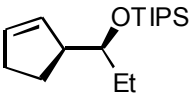
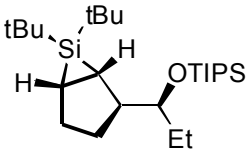


Figure 3.1 Proposed catalytic cycle for AgTp-catalyzed C-H amination

Another recently developed silver-catalyzed method involving group transfer is the silacyclopropanation, pioneered by the Woerpel group.[21] Silacycles are useful synthons that could be transformed into a variety of important intermediates such as polypropionates, allylic ethers, allylic amines, and α-hydroxy acids.[21] This powerful reaction avoids the otherwise harsh conditions generally required for the preparation of silylene intermediates (R_2Si). Stereospecific and diastereoselective di-*tert*- butylsilylene transfer to alkenes have been achieved using a catalytic amount of AgOTf (Table 3.1).[22] The catalytic cycle for the reaction was proposed to begin by coordination of triflate to the electrophilic silicon atom which triggers the heterolysis of the strained C-Si bond of **170** in a transmetallation-like fashion leading to the intermediate **171** (Figure 3.2). β-Silyl elimination extrudes t-Bu_2Si generating the silylsilver complex **172** and cyclohexene. Turnover-limiting cyclization occurs to form the silacyclopropane **174** and generate the coordinatively unsaturated silver catalyst. Since the discovery of Woerpel and coworkers, the silver-catalyzed silylene transfer has led to the development of useful organic transformations. The synthetic utility of this method has also been showcased in several total syntheses of natural products.[23]

Table 3.1. Silver-catalyzed silacyclopropanation of various olefins



substrate	product	yield (%)
		99
		92
		90
		85

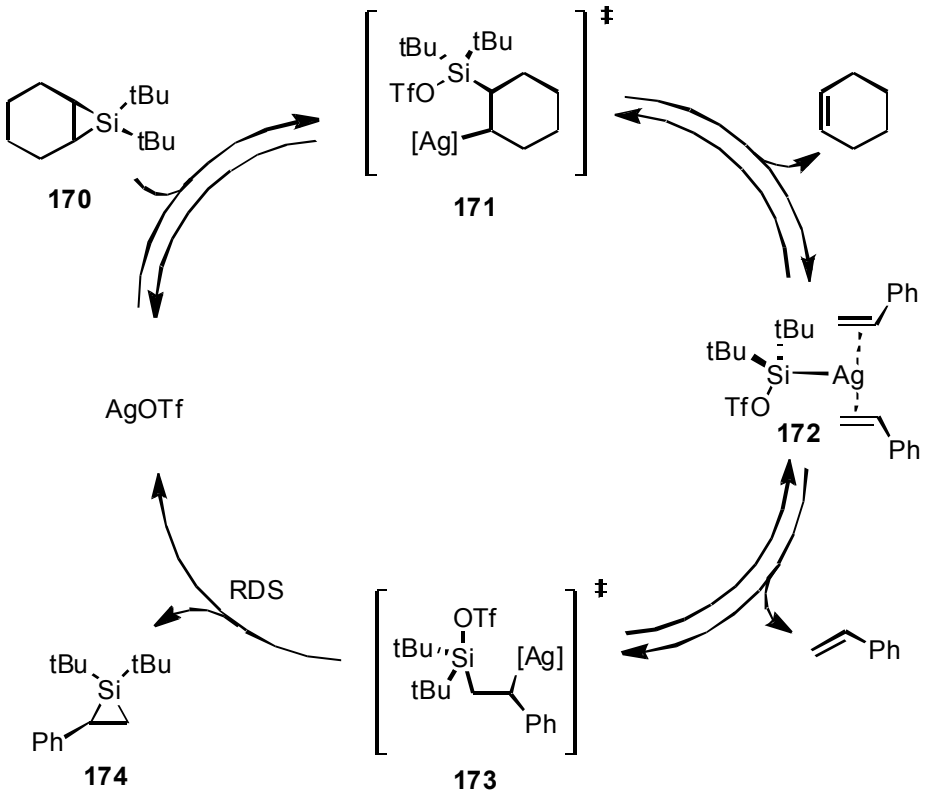
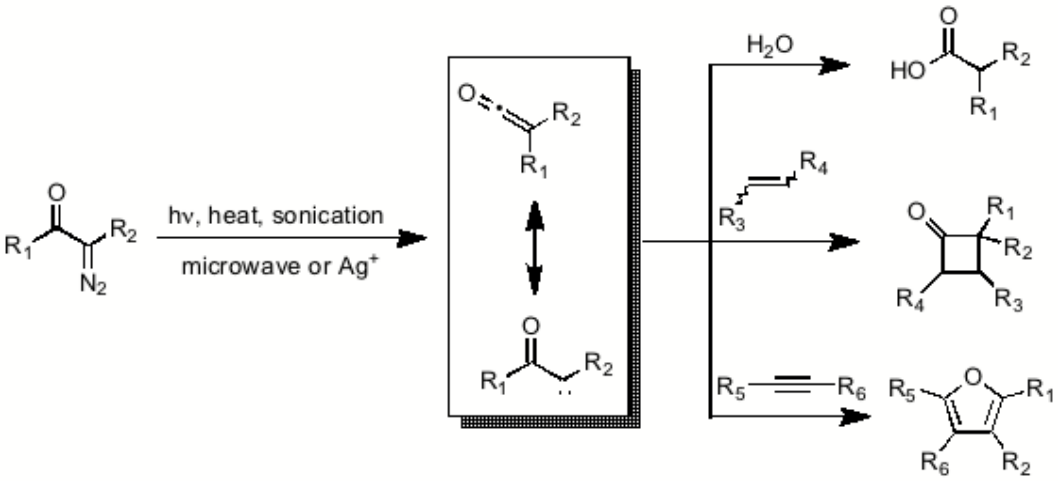


Figure 3.2 Proposed catalytic cycle for Ag-catalyzed silylene transfer to styrene

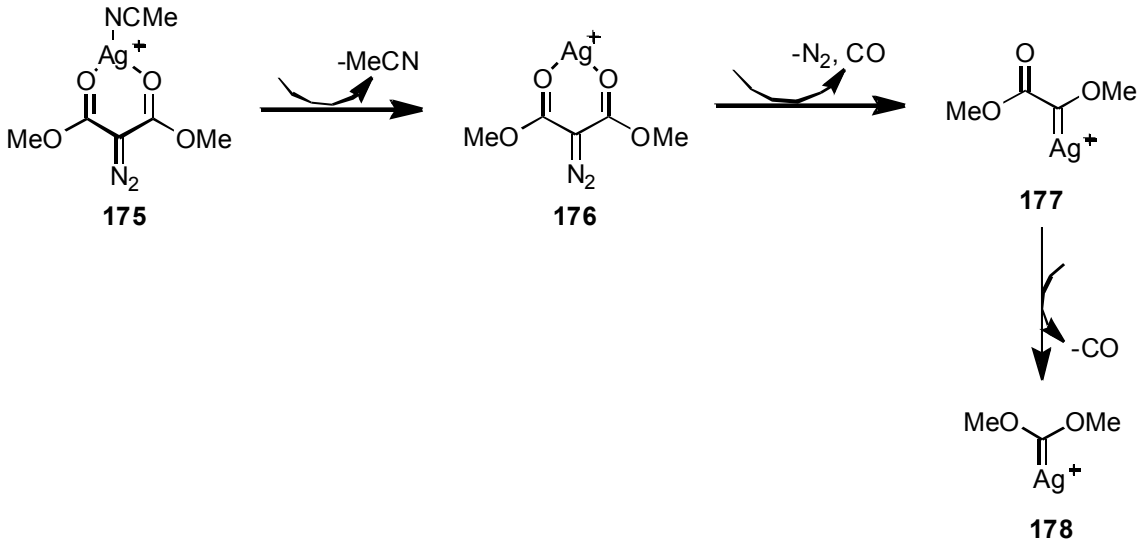
3.2.2 Silver carbenes

Decomposition of diazo compounds by silver has been well-known for a long time. Silver salts have been used to promote the Wolff rearrangement which constitutes the first step of the well-known Arndt-Eisert homologation of carboxylic acids (Scheme 3.7).[24] Although the mechanism of this reaction remains to be fully elucidated, some evidence



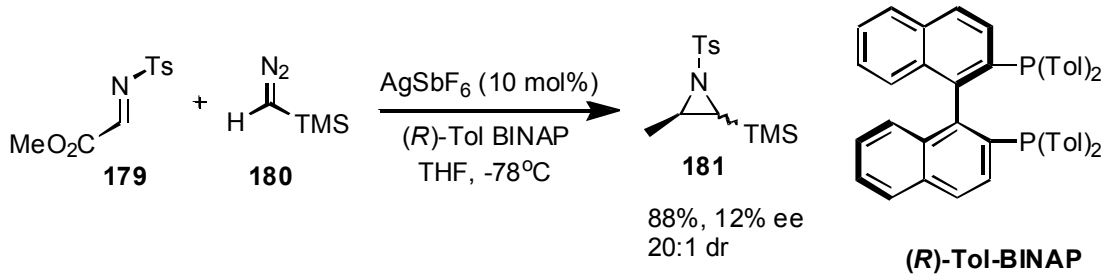
Scheme 3.7 Applications of Wolff rearrangement

supports the intermediacy of silver carbenes in certain circumstances. Beauchamp and Stoltz have shown the formation and rearrangement of a silver carbene species derived from dimethyl diazomalonate using a combined mass spectrometry and computational studies (Scheme 3.8).[25] In this study, they determined that the first stable species was the β-diketo complex **175**. This complex loses the acetonitrile ligand upon activation using low-energy collision-activated dissociation (CAD) to produce the intermediate **176**. Loss of nitrogen and a mole of carbon monoxide occur after further activation leading to the formation of a species with a molecular mass consistent with the silver carbene **177**. After another round of CAD, another expulsion of carbon monoxide occurs leading to the formation of a second carbene species **178**.[25]



Scheme 3.8 Rearrangement of silver carbenes by Mass Spectrometry

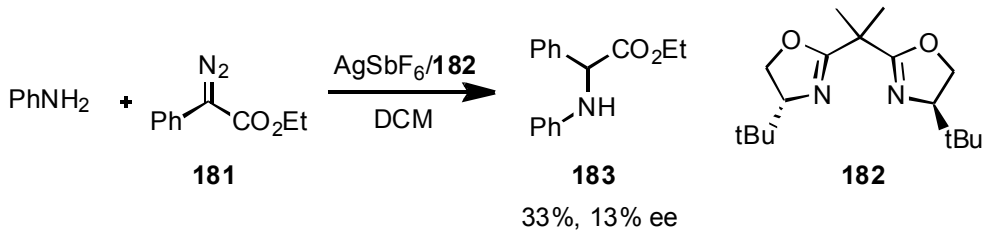
The use of silver as group transfer catalyst is relatively unexplored compared to copper particularly for carbene transfer processes involving diazo precursors.[26] However, in the past decade or so, the potential of silver salts as group transfer catalysts has become an active field of research especially in carbene transfer reactions to π bonds. Jørgensen and co-workers reported in 1999 the addition of trimethylsilyldiazomethane



Scheme 3.9 Jørgensen's asymmetric silver-catalyzed aziridination of iminoesters

180 to *N*-tosyl iminoester **179** which affords the aziridination product **181** in 88% yield and excellent diastereoselectivity (>20:1) (Scheme 3.9). In the presence of a chiral ligand

(*R*)-Tol-BINAP, the product was obtained in 12% ee.[27] In Jørgensen's study, no diethyl fumarate or maleate, common byproducts from reactions involving copper catalysts and EDA, were formed in the presence of silver catalysts. Based on these observation, they proposed that Ag(I)-mediated reactions proceed via Lewis acid activation while Cu(I)-mediated reactions proceed via metallacarbene intermediate. Later in 2004, the same group reported a silver(I)-catalyzed asymmetric carbene N-H insertion to aniline with ethyl phenyldiazoacetate **181** utilizing bisoxazoline ligand **182** affording the amino ester **183** in 33% yield and 13% ee (Scheme 3.10).[28] Again, it was proposed that the reaction proceeded via Lewis acid activation although the mechanism *via* metallacarbene intermediate was not completely excluded (Figure 3.3).



181 **183** **182**

33%, 13% ee

Scheme 3.10 Jørgensen's asymmetric silver-catalyzed N-H insertion with ethyl phenyldiazoacetate **181**

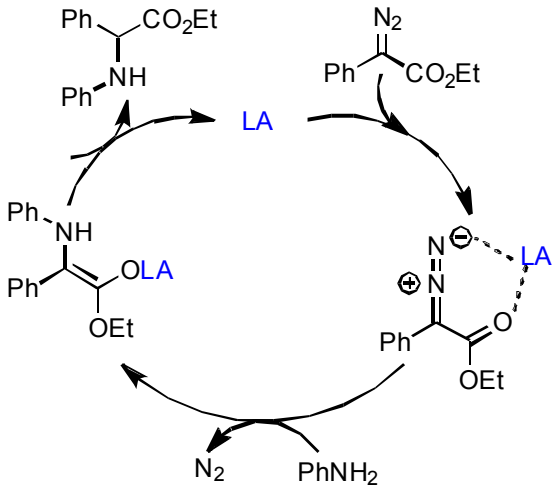
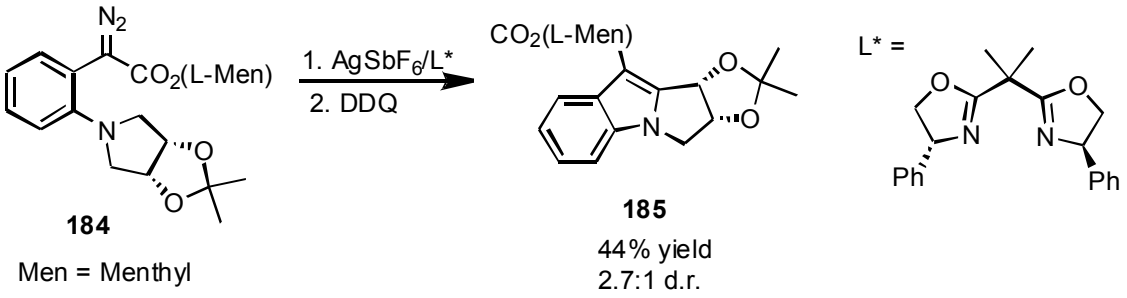


Figure 3.3 Jørgensen's proposed catalytic cycle for Ag(I)-catalyzed N-H insertion

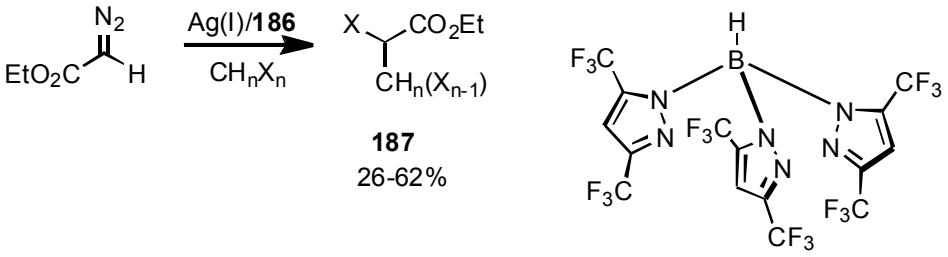
Several silver complexes have been explored in C-H insertion reactions of carbenes. In 1996, Burgess and coworkers described a combinatorial approach to catalyst screening utilizing a combination of ligands, metal and solvents to find the optimum system for an intramolecular C-H insertion reaction of diazoester **184** (Scheme 3.11).[29] Optimum yield and diastereoselectivity were obtained using a silver-based catalyst combination providing the insertion product **185** in moderate yield and diastereoselectivity.



Scheme 3.11 Burgess's Ag(I)-catalyzed intramolecular C-H insertion

In 2003, Dias and Lovely described the activation of carbon-halogen bond *via* a carbene insertion process catalyzed by silver and fluorinated tris(pyrazoyl) borate ligand **186**.[30] Ethyl diazoacetate was employed as the carbenoid precursor while using dichloromethane

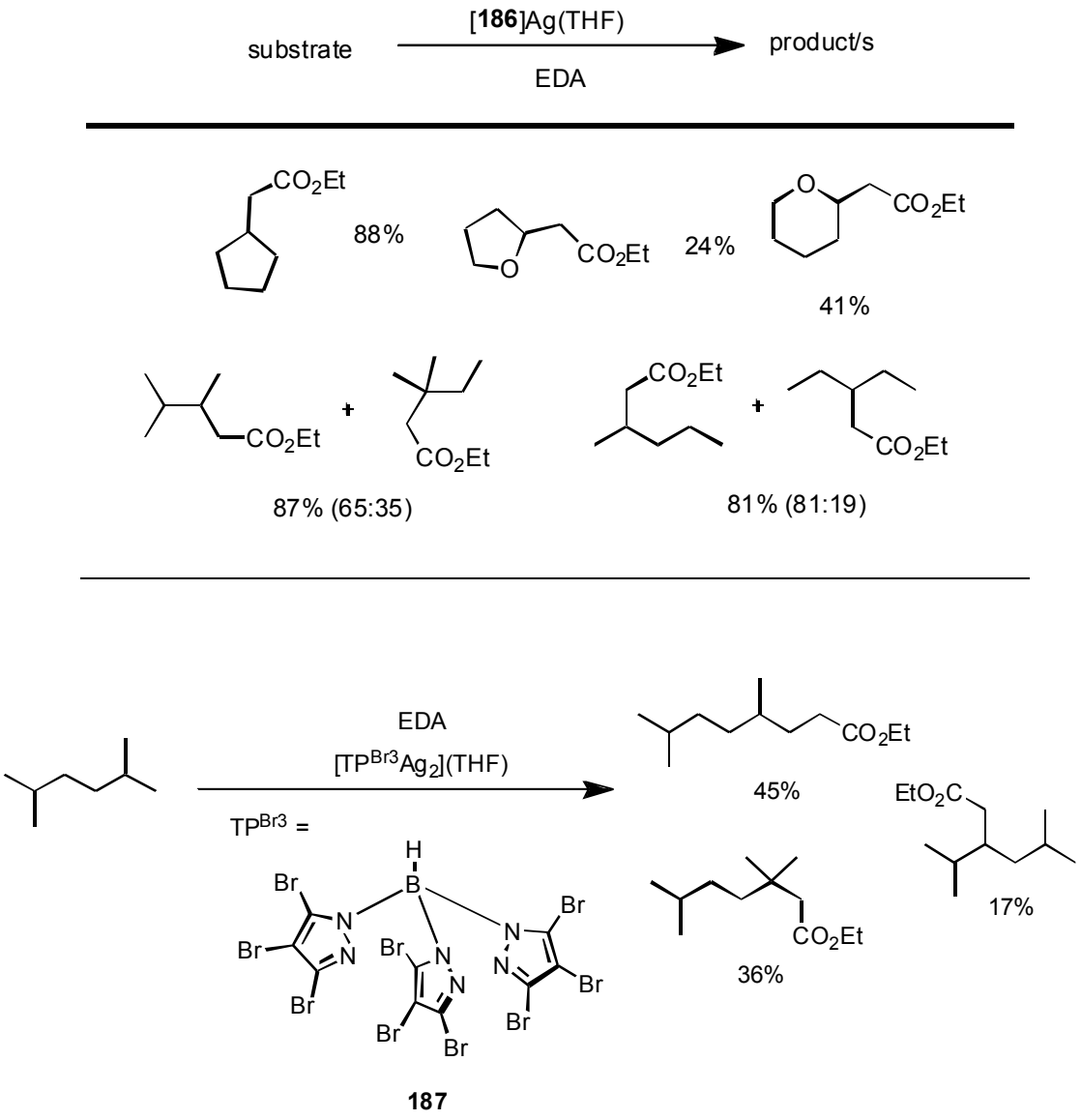
as solvent and benzene as the trapping species. Surprisingly, a 12% byproduct derived from insertion into the C-Cl bond of the solvent was observed. Further studies showed that a variety of alkyl halides could afford the C-X insertion products **187** in low to moderate yields (26-62% yield) (Scheme 3.12). In the same year and using the same



Scheme 3.12 Silver-catalyzed insertion into C-Halogen bonds

catalyst system, Dias and Lovely reported the carbene insertion into saturated C-H bonds.[31] Cyclic and linear hydrocarbons were both generally good substrates for functionalization affording products in 81-88% yield (Table 3.2). Ethers, on the other hand, showed low reactivity due to potential interaction between the silver center and the ether oxygen. Perez and co-workers also examined the silver-catalyzed C-H insertion reaction with EDA using their electron deficient ligand **187**.[32] The modified brominated ligand **187** provided excellent transformations (ca 90% overall yield) with strong preference for primary C-H bond insertion (Scheme 3.13). The silver-catalyzed reaction provided very interesting transformation however; the major challenge is that a mixture of products is always obtained hampering the synthetic utility of this organic transformation.

Table 3.2. Silver-catalyzed C-H insertion to hydrocarbons with ethyl diazoacetate

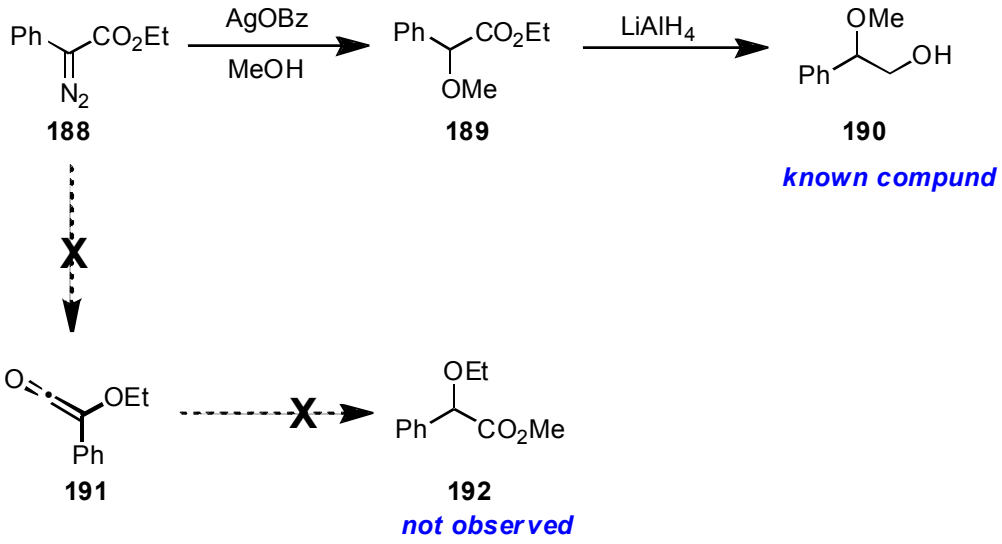


Scheme 3.13 Perez's $AgTp^{Br3}$-catalyzed C-H insertion

3.3 Results and Discussion

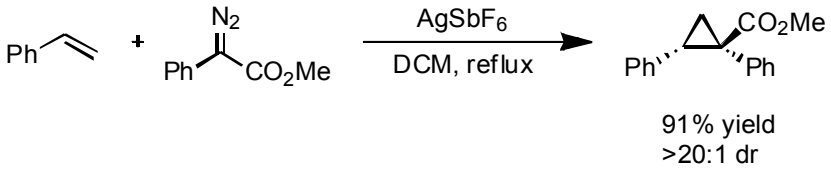
Donor/acceptor-substituted diazo compounds were first shown to react with silver catalysts by Davies and Thompson in 2007.[33] In the past, silver catalysts have been used mainly with highly reactive diazo compounds such as ethyl diazoacetate. These reactions usually suffer from lack of chemo- and stereoselectivity as well as the tendency to undergo diazo dimerizations. In the Davies group, the modulating activity of these

donor/acceptor-stabilized carbenoids is exploited to enhance the selectivity in carbenoid reactions. One of the first reactions that Thompson tested was the silver benzoate catalyzed reaction of ethyl phenyldiazoacetate in the presence of methanol. The reaction afforded the direct O-H insertion product **189** which was then reduced to the known alcohol **190**. In this reaction, the undesired Wolff rearrangement product **191** was not observed.[34] It was reasoned that the stabilizing



Scheme 3.14 Silver-catalyzed decomposition of diazoacetate **188** in methanol.

effect of the donor group of the carbenoid species modulated the reactivity of the silver carbenoid, therefore the Wolff rearrangement pathway was suppressed. The standard cyclopropanation reaction with styrene was then attempted and it was found that among the silver catalysts tested, $AgSbF_6$ gave the highest yield of 91% (Scheme 3.15).[33] It was presumed that since this catalyst has a large and weakly coordinated counter ion, decomposition of the diazo compound was more efficient. As the counter ions became more coordinated with the silver center, the reactivity becomes lower to no decomposition of the diazo compound.



Scheme 3.15 $AgSbF_6$-catalyzed cyclopropanation of styrene.

With the progress made in the Davies group on silver carbenoids, we were interested in utilizing these reactive and sterically less demanding carbenoid in the cyclopropenation of disubstituted alkynes. Although dirhodium catalysts have been shown to effectively catalyze cyclopropenation using donor/acceptor carbenoids, the reaction generally works well with terminal alkynes. We have shown that the sterically demanding dirhodium catalysts are ineffective in cyclopropenating internal alkynes because during the approach of the substrate to the carbenoid, one substituent of the alkyne clashes with the rhodium wall (Figure 3.4).[35] DFT calculations also suggest that H-bonding interactions between the alkyne hydrogen and the oxygen in one the carboxylate ligand of the dirhodium tetracarboxylate catalyst helps direct the approach of the incoming substrate. This interaction would not be possible in the case of internal alkynes.

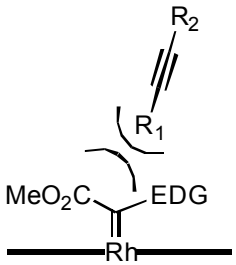
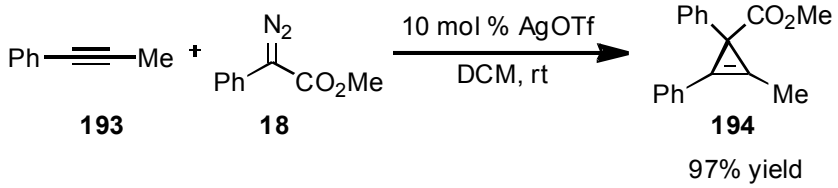


Figure 3.4 Steric clash between rhodium catalyst wall and internal alkyne substrate

With this knowledge in hand, as well as our interest in further expanding the scope of donor/acceptor cyclopropenation chemistry, efforts were made to develop an efficient method for the synthesis of highly substituted cyclopropenes from internal alkynes. The studies began with the cyclopropenation of disubstituted alkyne **193** with methyl phenyldiazoacetate **18** performed in the presence of 10 mol% AgOTf (Scheme 3.16). Gratifyingly, the reaction afforded the cyclopropene product **194** in excellent yield of 97%. Other readily available silver catalysts were screened for the cyclopropenation reaction and the results are summarized in Table 3.3.

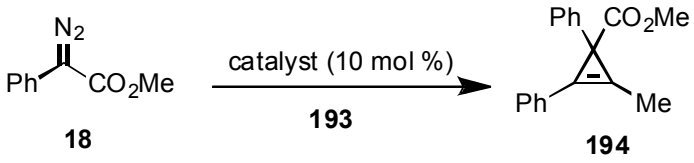


193 **18** **194**

97% yield

Scheme 3.16 AgOTf-catalyzed cyclopropenation of alkyne **193** with diazoacetate **18**

Table 3.3. Cyclopropenation of **193** with **18** using readily available silver(I) salts

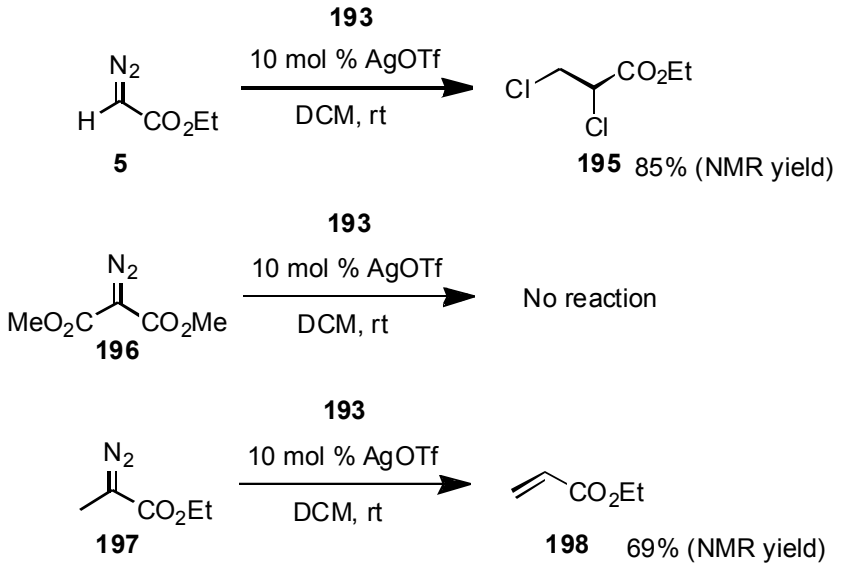


18 **194**

entry	Catalyst	solvent	Yield (%)
1	AgOTf	DCM	97
2	$AgSbF_6$	DCM	95
3	$AgBF_4$	DCM	86
4	$AgNTf_2$	DCM	91
5	$AgNO_3$	DCM	27
6	Ag_3PO_4	DCM	trace
7	AgTFA	DCM	trace
8	Ag_2CO_3	DCM	trace
9	AgOCOPh	DCM	NR
10	Ag_2SO_4	DCM	NR

The results confirm the trend that Thompson observed in the cyclopropanation reaction that the counter ions play the major role on the efficiency of the reaction. Silver catalysts with weakly coordinating counter ions such as triflate, hexafluoroantimonate, tetrafluoroborate and triflimide gave the cyclopropene products in excellent yields with silver triflate and silver hexafluoroantimonate giving the best yields of 97 and 95%, respectively (entries 1-4). Silver nitrate gave only 27% yield of the cyclopropene while the rest afforded only trace amounts of the cyclopropene (entries 5-8). On the other hand, both silver sulfate and silver benzoate failed to decompose the diazo compound (entries 9-10).

Acceptor- and acceptor/acceptor-substituted diazo compounds were also utilized as carbenoid precursors to determine the effect of the carbenoid structure on the silver-catalyzed reactions (Scheme 3.17). Ethyl diazoacetate **5** failed to undergo cyclopropenation with **193**. Instead C-Cl insertion occurred into the solvent dichloromethane to produce the dichloro derivative **195** in 85% yield. Similar reactivity has been reported for silver scorpionate catalysts. Diazomalonate **196** also did not afford the desired cyclopropene products. The ^{1}H NMR analysis of the crude reaction mixture showed that the diazo compounds remained unchanged. Silver complexes are known to be capable of forming thermally stable complexes with diazo compounds containing two electron withdrawing groups, and this may explain the lack of reactivity with these systems.[25,36] Ethyl-2-diazopropanoate **197** was converted to ethyl acrylate **198**, the product of a β-hydride elimination in 69% yield, although under rhodium catalysis, effective cyclopropenation can be achieved with **197**. These results are consistent with the hypothesis that silver carbenoids behave as more reactive intermediates than the rhodium carbenoids, and it is only in the case of donor/acceptor carbenoids that the carbenoid is sufficiently stabilized for effective cyclopropenation to occur.



Scheme 3.17 Ag-catalyzed reaction of acceptor- and acceptor/acceptor-substituted diazo compounds with **193**

We then investigated the generality of the silver-catalyzed cyclopropenation with a range of disubstituted alkynes and the cyclopropene products **199-216** were obtained in good to excellent yields (Table 3.4). The structure of cyclopropene **199** was confirmed by X-ray crystallography (Figure 3.5). 1,2-diaryl alkynes (entries 12-15) were effectively cyclopropenated (64-98%). Cyclopropenation of alkyne with a boronic ester functionality was achieved, as in the case of entry 14. Monocyclopropenation of 1,3-diyne was also a viable process affording the alkynyl cyclopropene **213**. It is also interesting to note that the cyclopropenation reaction is very chemoselective as C-H insertion at the benzylic site (entries 7, 9-11) as well as methylene site next to siloxy groups (entries 8 and 17) was not observed. Terminal alkynes such as phenylacetylene and 1-TMS-phenylacetylene (entries 18 and 19) did not afford the desired cyclopropenes. The reactions with these

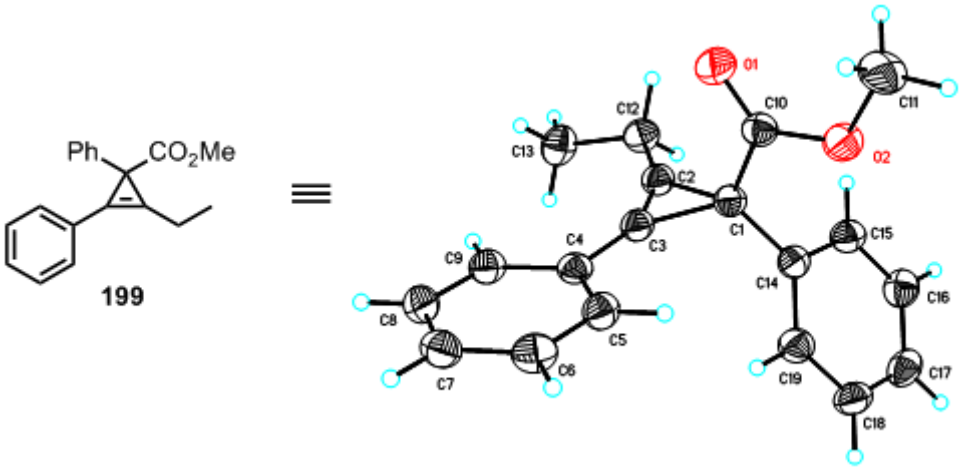
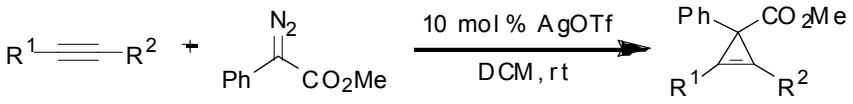


Figure 3.5 X-ray structure of cyclopropene **199**

substrates resulted in the formation of precipitates. It is well-known that terminal alkynes react with silver salts to form insoluble silver acetylides, and this may be the reason for unproductive cyclopropenation of the terminal alkyne.[37]

Several substrates were tested to further determine the chemoselectivity of the AgOTf-catalyzed reaction in more functionalized systems (Table 3.5). Substrates that contain both alkyne and alkene moeities were tested to determine whether cyclopropenation would be more favored over cyclopropanation. In the case of entry 1, the reaction of enyne **217** with **18** only provided the cyclopropanation product **218** in

Table 3.4 AgOTf-catalyzed cyclopropenation of various alkynes with **18**



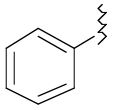
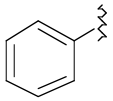
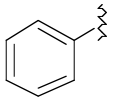
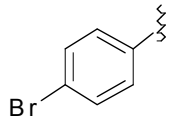
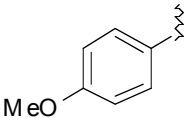
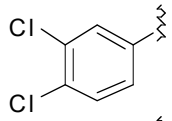
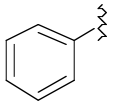
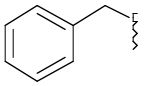
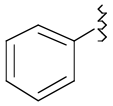
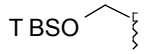
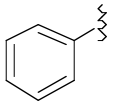
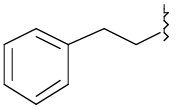
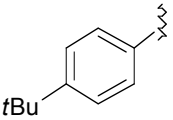
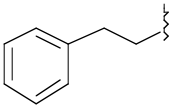
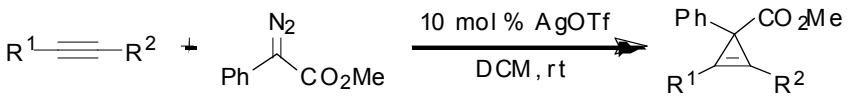
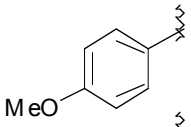
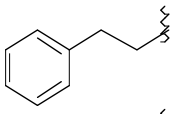
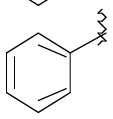
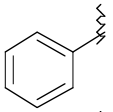
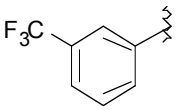
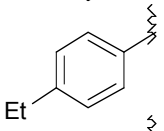
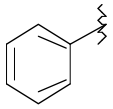
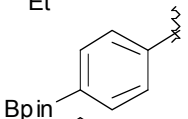
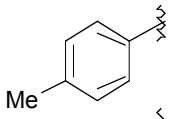
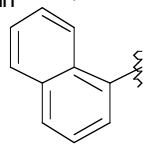
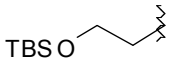
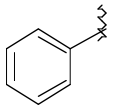
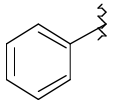
entry	R^1	R^2	product	yield (%)[b]
1			**194**	97
2			**199**	91
3			**200**	93
4			**201**	82
5			**202**	68
6			**203**	81
7			**204**	91
8			**205**	84
9			**206**	87
10			**207**	92

Table 3.4 AgOTf-catalyzed cyclopropenation of various alkynes with **18**



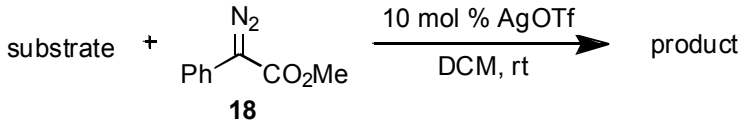
18 199-216

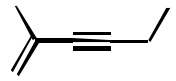
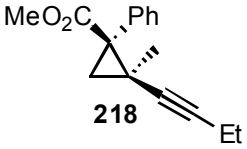
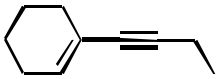
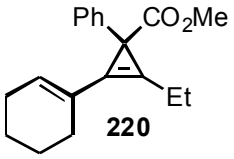
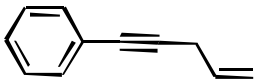
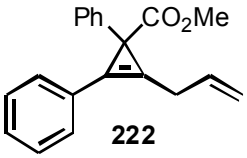
entry	R^1	R^2	product	yield (%)[b]
11			**208**	86
12			**209**	98
13			**210**	88
14			**211**	64
15			**212**	80
16[c]			**213**	92
17			**214**	85
18			**215**	0
19			**216**	0

89% yield as a single diastereomer. The relative configuration of **218** was assigned based on nOe analysis. Interestingly, when the olefin is more highly substituted such as the case of **219**, the reaction favors the formation of the cyclopropene **220** in 85% yield. In the case of entry 3, cyclopropene **222** was isolated in excellent yield (86%). Only a trace

amount of the product from the cyclopropanation of the electronically neutral and unsubstituted olefin moiety of **221** was observed.

Table 3.5. Chemoselectivity studies: cyclopropanation *versus* cyclopropenation



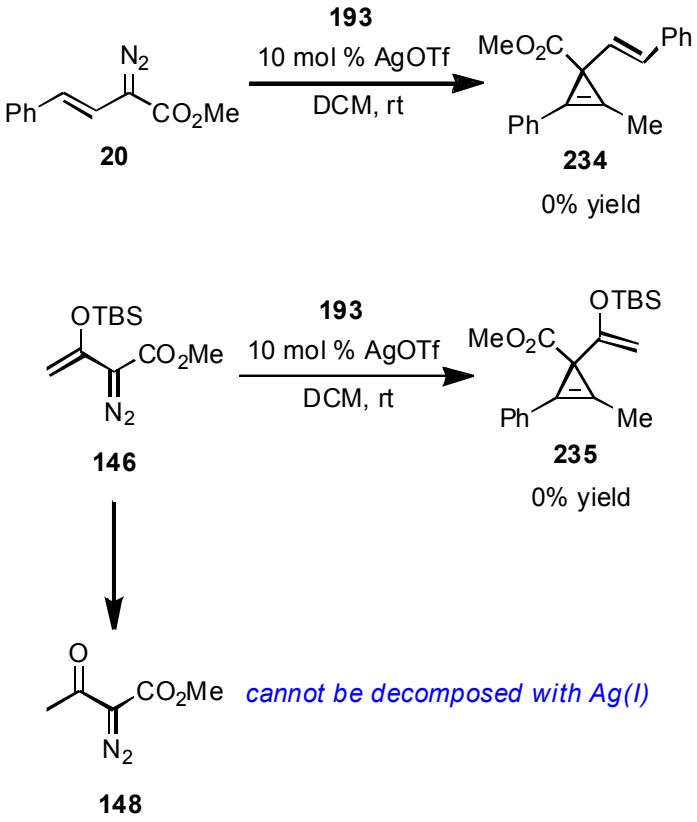
entry	substrate	product	yield (%)[b]
1[c]	 **217**	 **218**	89
2	 **219**	 **220**	85
3	 **221**	 **222**	86

The scope of the AgOTf-catalyzed cyclopropenation was further examined by utilizing various donor/acceptor-substituted diazo compounds with 1-phenyl-1-propyne **193** as the representative alkyne trap (Table 3.6). Excellent yields of the cyclopropene were obtained using both electron poor and relatively electron rich aryldiazoacetates. Reaction with sterically demanding diazo compound such as in the case of entry 4 with the substituted *ortho* positions was also a viable process. Varying the electron withdrawing group on the carbenoid was also possible as the trifluoromethyl-,

phosphonate-, and cyano-substituted cyclopropenes were formed in excellent yields (84-98%, entries 9-11). Although Davies and Thompson have shown that methyl styryldiazoacetate is an effective carbenoid precursor for Ag(I)-catalyzed cyclopropanation reactions, it failed to afford the desired cyclopropene product. This failure is probably due to product instability. Siloxyvinyldiazoacetate **146** also failed to cyclopropenate **193** presumably because under the mildly acidic reaction conditions, deprotection of the siloxy group occurs leading to the corresponding diazoacetoacetate **148** which could not be decomposed by silver.[25,36]

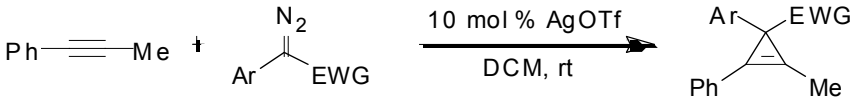
3.4 Summary

In summary, we have demonstrated that silver triflate is an effective catalyst for cyclopropenation of disubstituted alkynes using donor/acceptor-substituted diazo compounds. Using the sterically less demanding silver catalysts, highly substituted cyclopropenes that have not been synthesized before are now readily accessible. These studies demonstrated some advantages of silver catalysis over rhodium catalysis. The cyclopropenation reaction was only successful when donor/acceptor diazo compounds are used which demonstrated the importance of the stabilizing effect of donor groups on the highly electrophilic silver(I)-stabilized carbenoid center.

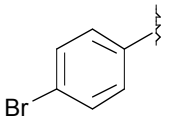
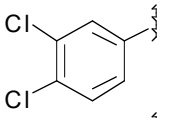
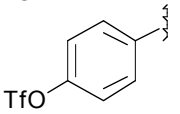
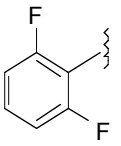
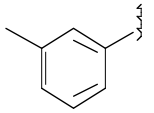
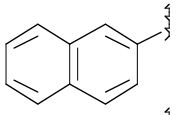
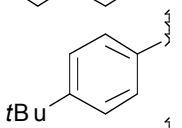
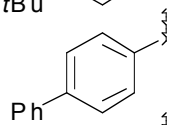
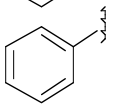
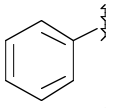
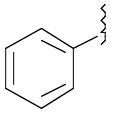


Scheme 3.18 Ag-catalyzed reaction of vinyldiazoacetates with **193**

Table 3.6 AgOTf-catalyzed cyclopropenation of **193** with various aryl diazo compounds



223-233

entry	Ar	EWG	product	yield (%)[b]
1		CO_2Me	**223**	93
2		CO_2Me	**224**	91
3		CO_2Me	**225**	90
4		CO_2Me	**226**	83
5		CO_2Me	**227**	92
6		CO_2Me	**228**	81
7		CO_2Me	**229**	82
8		CO_2Me	**230**	87
9		CF_3	**231**	84
10		CN	**232**	93
11		$P(O)(OiPr)_2$	**233**	98

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CHAPTER FOUR

Highly Enantioselective Gold-Catalyzed Cyclopropenation of Internal Alkynes with Donor/Acceptor-Substituted Carbenoids

4.1 Introduction

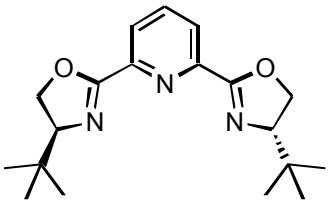
With the development of an efficient method of cyclopropenating internal alkynes using achiral silver catalysts with donor/acceptor carbenoids, we then focused on the development of the enantioselective variant of this reaction. Initial studies were aimed at utilizing the most commonly used silver catalyst systems for asymmetric Lewis acid-mediated transformations. Unfortunately, these systems did not induce high asymmetric induction in the cyclopropenation reaction. We then turned our attention to other transition metal catalysts which are expected to give similar reactivity to silver. This led us to discovering that digold-BINAP catalysts are very effective catalysts in promoting highly enantioselective cyclopropenation of alkynes with donor/acceptor carbenoids. This chapter describes our efforts towards the development of this interesting and useful synthetic transformation. The following chapters will also focus on the use of these

digold-BINAP catalysts in promoting novel asymmetric transformations of donor/acceptor carbenoids.

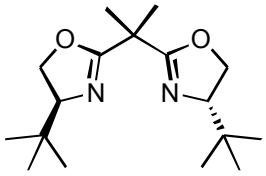
4.2 Asymmetric silver-catalyzed cyclopropenation

Our exploration began by examining the literature on common chiral ligands employed in silver-catalyzed transformations and using these readily available ligands for the cyclopropenation reaction (Figure 4.1).[1] We chose 1-phenyl-1-propyne **193** as the representative alkyne trap and methyl phenyldiazoacetate **18** as carbenoid precursor (Table 4.1). As discussed in Chapter 3.2.1.1, chiral phosphine-silver(I) complexes are frequently used as chiral catalysts for carbon-carbon bond forming reactions (Figure 4.1).[2] The BINAP system has been shown to effectively create a chiral environment around silver. Using 1-phenyl-1-propyne **193** as the test substrate, the silver-catalyzed cyclopropenation with methyl phenyldiazoacetate **18** in the presence of (*S*)- tol-BINAP was conducted. However, the cyclopropene product **234** was only formed in 17% ee (entry 6). Similar result was obtained when the bulkier (*R*)- DTBM-SEGPHOS ligand was used for the reaction affording the cyclopropene product in 70% yield and <5% ee (entry 7). Oxazoline-based ligands were also employed in the cyclopropenation reaction such as tBuBOX and PyBOX. In the case of tBuBOX, the cyclopropene product was obtained in 74% yield and very poor enantioselectivity (entry 1). When PyBOX was used, decomposition of the diazoacetate did not occur presumably due to the high affinity

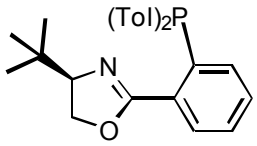
of nitrogen-based ligands to silver (entry 2). Other phosphine-based ligands such as Pfaltz's PHOX ligand (entry 3) and Feringa's MonoPHOS ligand (entry 4) both afforded the desired cyclopropene product **234** *albeit* in very poor enantiomeric excess (18% and <5%, respectively). Lastly, the alkaloid ligand brucine provided **234** in 74% yield and <5% ee (entry 5).



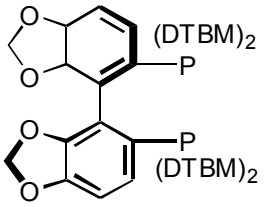
PyBOX



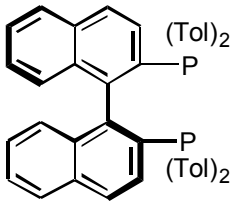
tBuBOX



PHOX

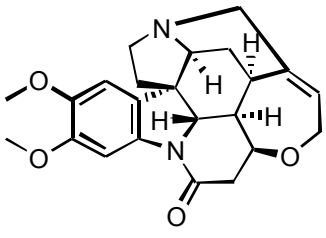


(*R*)-DTBM-SEGPHOS

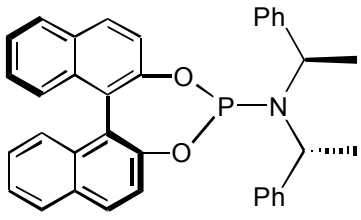


(*S*)-tolylBINAP

DTBM = 3,5-di-tBu,6-OMePh



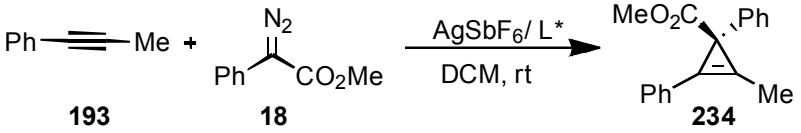
Brucine



MonoPhos

Figure 4.1 Chiral ligands in asymmetric silver catalysis

Table 4.1. Ag(I)-catalyzed cyclopropenation of **193** with **18** using various chiral ligands



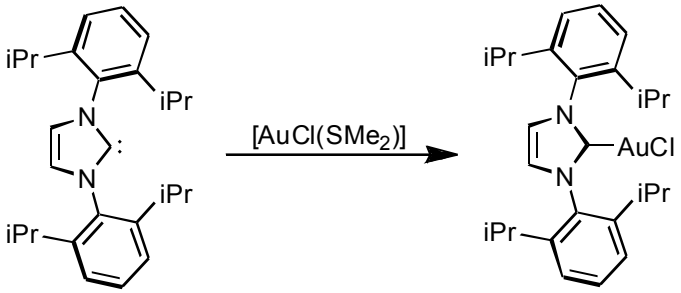
193 **18** **234**

entry	Ligand	mol % Ag	mol % L*	yield (%)	ee (%)
1	tBuBOX	13	14	74	<5
2	pyBOX	13	14	NR	---
3	PHOX	10	12	79	18
4	MonoPhos	10	12	86	7
5	Brucine	5	6	74	<5
6	(*S*)-Tol-BINAP	10	12	81	17
7	(*R*)-DTBM-SEGPHOS	10	12	70	<5

4.3 Asymmetric gold-catalyzed cyclopropenation

Efforts to develop a method for highly asymmetric cyclopropenation of internal alkynes using chiral silver complexes were unsuccessful. Due to the poor enantioselectivity obtained under silver catalysis, we turned our attention to gold(I) catalysts because these complexes are expected to give similar reactivity to silver. The use of gold(I) catalysts for decomposing diazo compounds is very limited. Furthermore, previous reports involving gold-catalyzed reactions of diazo compounds have been limited to the use of achiral gold complexes. In 2005, the first example of a gold-based catalyst for diazo decomposition was reported by Perez and coworkers.[3] The catalyst was synthesized from equimolar amounts of the IPr ligand **235** and gold(I) chloride dimethylsulfide complex (Scheme 4.1). The corresponding gold carbenoid derived from

ethyl diazoacetate was subjected to a wide variety of synthetic transformations which includes cyclopropanation, O-H and N-H insertions (Table 4.2). It is important to note that no diazo coupling side products were observed in any of the reactions. However, poor chemoselectivity was observed when styrene was used as substrate (entry 1). Analysis of the reaction mixture by GC showed that besides the expected *cis*- and *trans*-cyclopropanes, styrylacetate was formed as a mixture of *o*, *m*, and *p* isomers.[3]

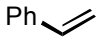
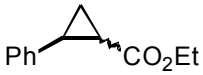
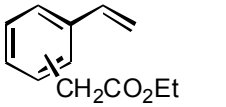
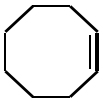
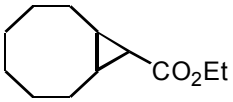
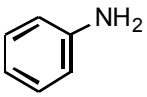
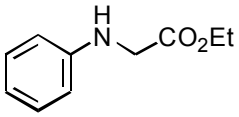
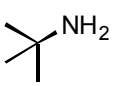
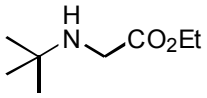


235 **236**

Scheme 4.1 Synthesis of Perez's gold(I) catalyst

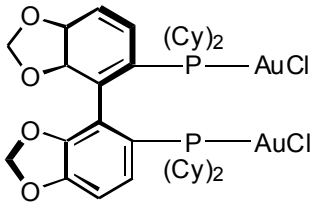
Since 2005, the majority of reports utilizing gold in carbenoid reactions used ethyl diazoacetate as the carbenoid source. However, Perez and Echavarren recently described the use of methyl phenyldiazoacetate and Au(I) catalysts containing phosphine, phosphite or NHC ligands for the cyclopropanation of styrene and cyclohexene.[4,5]

Table 4.2. Reaction of EDA catalyzed by **236** and NaBARF

entry	substrate	product	yield (%)
1		 + 	40 60
2			>99
3			>99
4			>99
5	CH_3OH	$CH_3OCH_2CO_2Et$	>99
6	CH_3CH_2OH	$CH_3CH_2OCH_2CO_2Et$	>99

Due to the lack of reports on asymmetric gold catalysis in carbenoid reactions derived from diazo compounds, we initially focused on the use of Au(I) catalysts, containing various biarylphosphine ligands which have been popularized by Toste and coworkers (Figure 4.2).[6] The Toste group has exploited these digold(I) catalysts and has developed a variety of alkyne and allene transformations, including enantioselective cyclopropanation of olefins *via* cationic gold catalyzed 1,2-rearrangement of propargyl esters[7], the Conia-ene reaction[8], asymmetric hydroamination[9], cycloisomerization[10] and

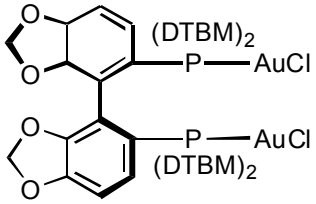
polycyclization reactions[11]. To our knowledge, these types of digold catalysts have not been utilized in any carbenoid reactions involving diazo compounds.



(*R*)-Cy-SEGPHOS(AuCl)$_2$

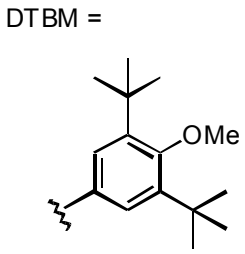
236

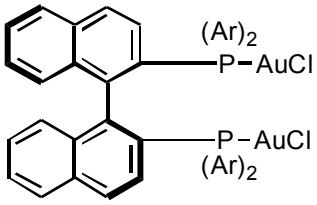
Cy = cyclohexyl



(*S*)-DTBMSEGPHOS(AuCl)$_2$

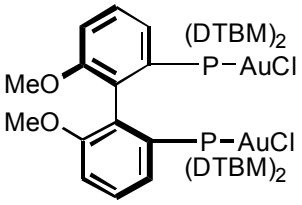
237





(*S*)-ArBINAP(AuCl)$_2$

Ar = phenyl **238**
Ar = tolyl **239**
Ar = xylyl **240**



(*S*)-DTBM-OMe-BIPHEP(AuCl)$_2$

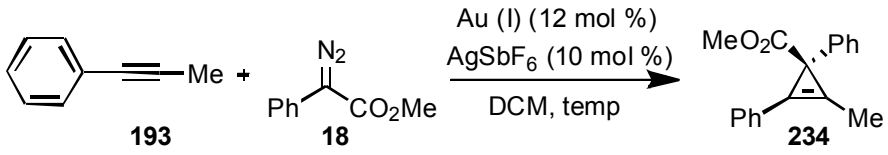
241

Figure 4.2 Chiral digold catalysts used in Toste's alkyne and allene chemistry

We were very pleased when we found that these type of catalysts were highly effective in inducing chiral influence in the cyclopropenation of **193** with methyl phenyldiazoacetate **18** affording the desired cyclopropene product in moderate to good yields and excellent enantioselectivity (Table 4.3). When catalyst **239** was used, the cyclopropene product **234** was obtained in 69% yield and 87% ee (entry 1). The enantiomeric excess was improved to 92% when the reaction was conducted at 0 °C (entry 2). Optimal results were obtained when (*S*)-xylylBINAP(AuCl)$_2$ **240** was used as catalyst providing the cyclopropene **234** in 81% yield and 93% ee (entry 3). Interestingly, when the chiral monogold phosphoramidite catalyst **242** was used, **234** was formed in very low yield and

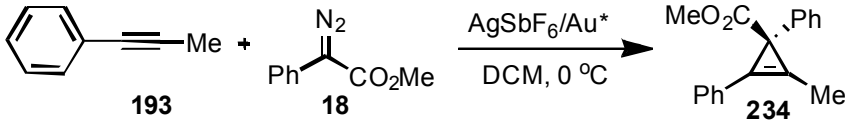
enantiomeric excess (Table 4.4, entry 1). No reaction was observed when **243**, another monodentate gold(I) catalyst, was used (entry 2).

Table 4.3. Gold(I)-catalyzed cyclopropenation of **193** with **18**

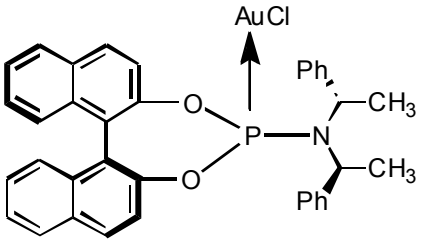


entry	Au(I)	temp (°C)	yield (%)	ee (%)
1	(*S*)-tolBINAP(AuCl)$_2$	23	69	87
2	(*S*)-xylylBINAP(AuCl)$_2$	0	74	92
3	(*S*)-xylylBINAP(AuCl)$_2$	0	81	93
4	(*S*)-DTBM-SegPhos(AuCl)$_2$	0	40	91
5	(*S*)-BINAP(AuCl)$_2$	0	62	92

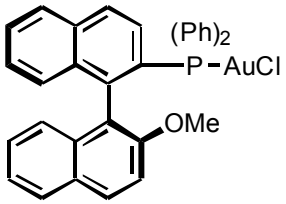
Table 4.4 Cyclopropenation of **193** with **18** catalyzed by monogold catalysts



entry	Au*	yield (%)	ee (%)
1	**242**	16	14
2	**243**	0	0



(*S*)-MONOPHOS(AuCl)
242



243

The scope of the cyclopropenation reaction was explored using various disubstituted alkynes as substrate employing the catalyst (*S*)-xylylBINAP(AuCl)$_2$ **240** (12 mol %) activated by $AgSbF_6$ (10 mol %). The reaction proved to be applicable to a wide range of 1-arylalkynes and the desired cyclopropenes were obtained in moderate to good yields and with excellent levels of enantioselectvitiy (Table 4.5). The absolute configuration of the cyclopropene **234** was assigned unambiguously by X-ray crystallographic analysis (Figure 4.3). The absolute configuration of the other cyclopropene products was assigned by analogy to **234**.

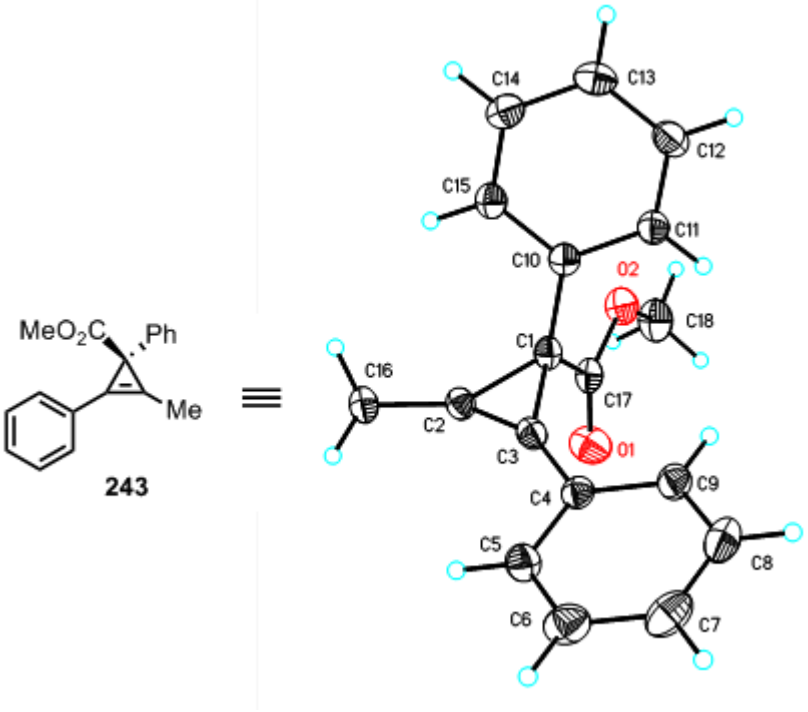
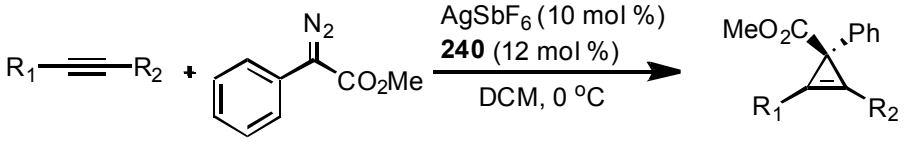


Figure 4.3 X-ray structure of cyclopropene **234**

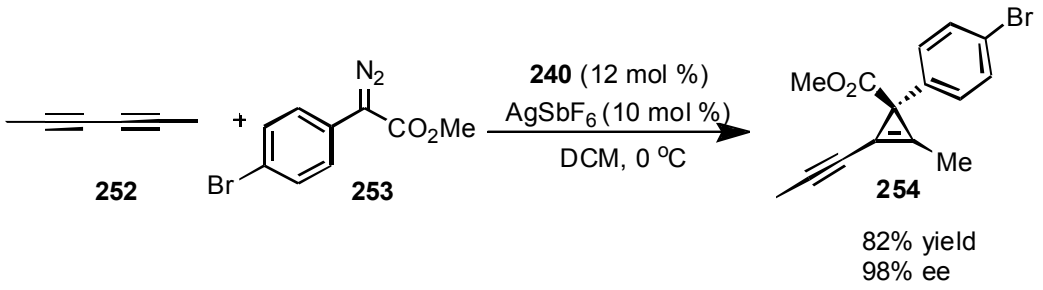
Table 4.5. Enantioselective gold(I)-catalyzed cyclopropenation of various alkynes



18 **243-251**

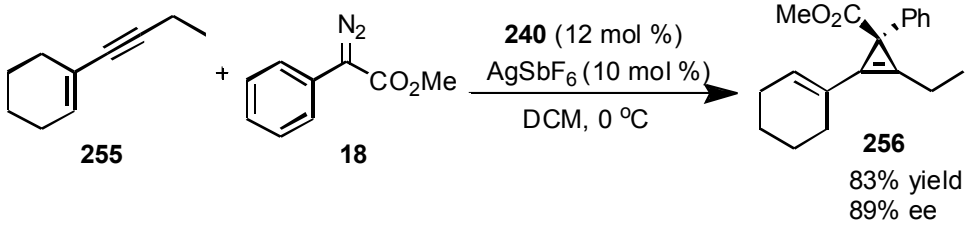
entry	R_1	R_2	product	yield, %[b]	ee, %[c]
1	Ph	Me	**234**	81	93
2	Ph	Et	**243**	68	90
3	Ph	*i*Bu	**244**	70	94
4	Ph	Cy	**245**	83	86
5	Ph	*n*Bu	**246**	72	90
6	Ph	CH_2OTBS	**247**	62	98
7	Ph	CH_2Cy	**248**	78	92
8	Ph	CH_2CHCH_2	**249**	58	96
9	*p*-BrPh	*n*Bu	**250**	76	89
10	*o*-MePh	*n*Bu	**251**	75	93

The less reactive 1,2-dialkyl alkynes generally gave poor yields of the desired cyclopropene products. However, electronically activated systems such as diyne **252** provided the desired cyclopropene product **254** in 82% yield and 98% ee (Scheme 4.2).



Scheme 4.2 Au(I)-catalyzed cyclopropenation of diyne **252** with **253**

In addition, cyclopropenation of enyne **255** provided the cyclopropene **256** in 83% yield and 89% ee (Scheme 4.3). The reaction is highly chemoselective as no cyclopropanation nor C-H insertion product was observed in this reaction.



Scheme 4.3 Au(I)-catalyzed cyclopropenation of enyne **255** with **18**

In general, the chiral gold(I)-complex provided similar types of products to the achiral silver(I)-catalyzed reactions, although a few exceptions were found. An unexpected result was observed in the gold-catalyzed cyclopropenation of 1,2-diaryl alkynes (Scheme 4.4). This type of substrates provide the desired cyclopropene products under silver catalysis.[12] The use of alkyne **257** as substrate in a gold catalyzed reaction gave a complex mixture and the major product isolated was the indene derivative **258**, obtained in 37% yield. When AgOTf was used as catalyst, the reaction of **257** with **18**

provided the cyclopropene product **210** in 88% yield. The structure of indene derivative **258** was confirmed by X-ray crystallographic analysis (Figure 4.4). The proposed mechanism for the formation of **258** is depicted in Scheme 4.5. Initial attack of the alkyne at the gold carbenoid leads to the cationic species **I**. Electrophilic attack of the aryl ring to the vinyl cation **I** and subsequent release of the gold catalyst leads to structure **II**. This intermediate can then undergo 1,5-sigmatropic rearrangements to afford the indene product. Recently, Chang and coworkers reported the formal [3+2] cycloaddtion reaction of aryldiazoacetates and terminal alkynes when achiral Cu(NHC) catalyst was used (Scheme 4.5).[13]

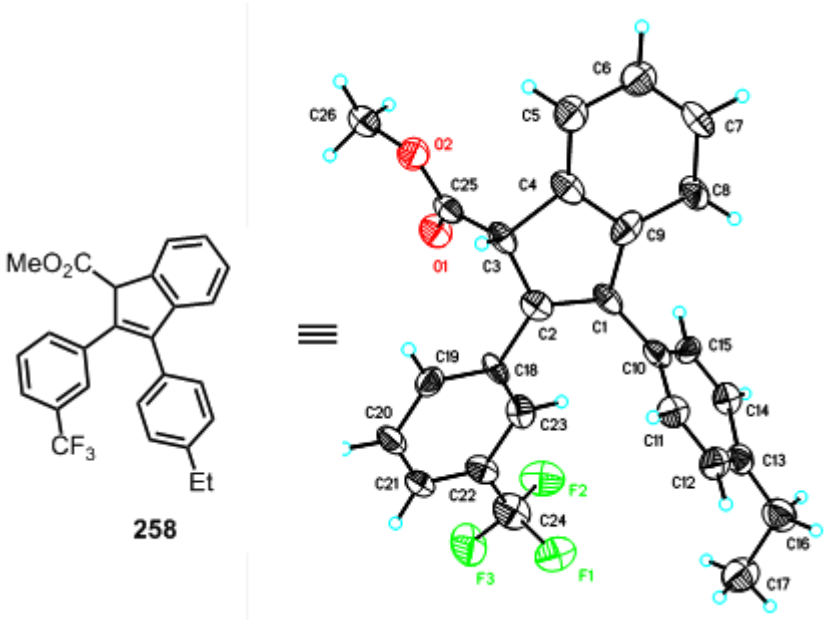
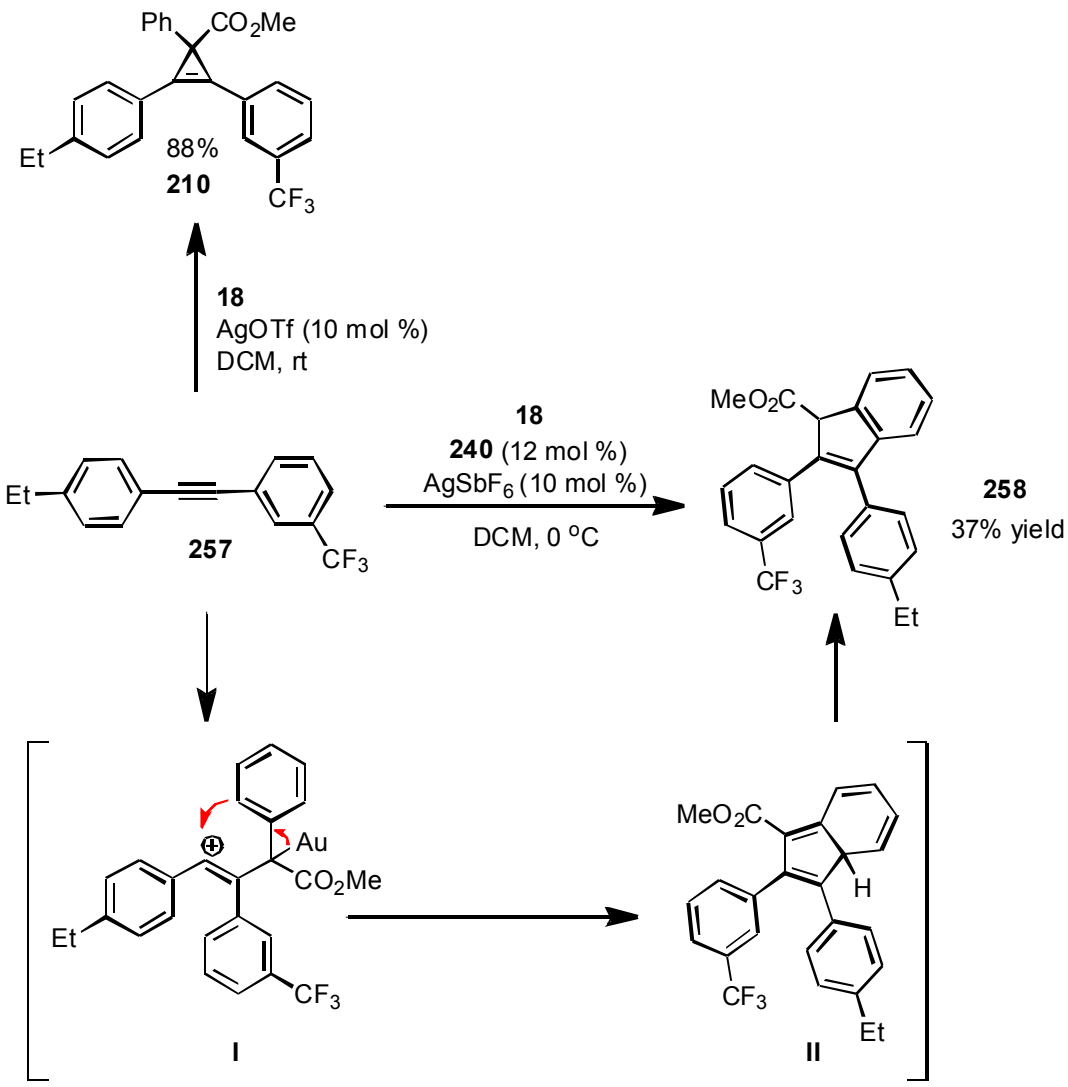
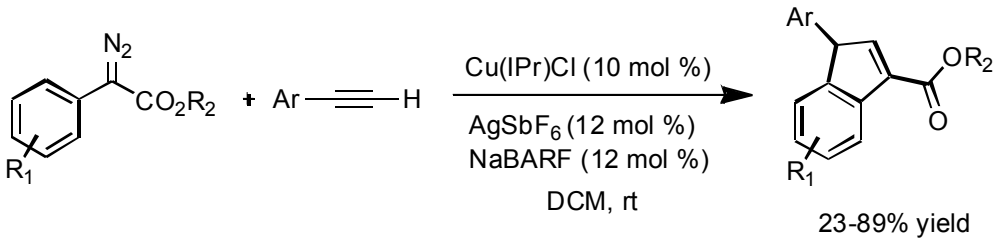


Figure 4.4 X-ray structure of cyclopropene **258**

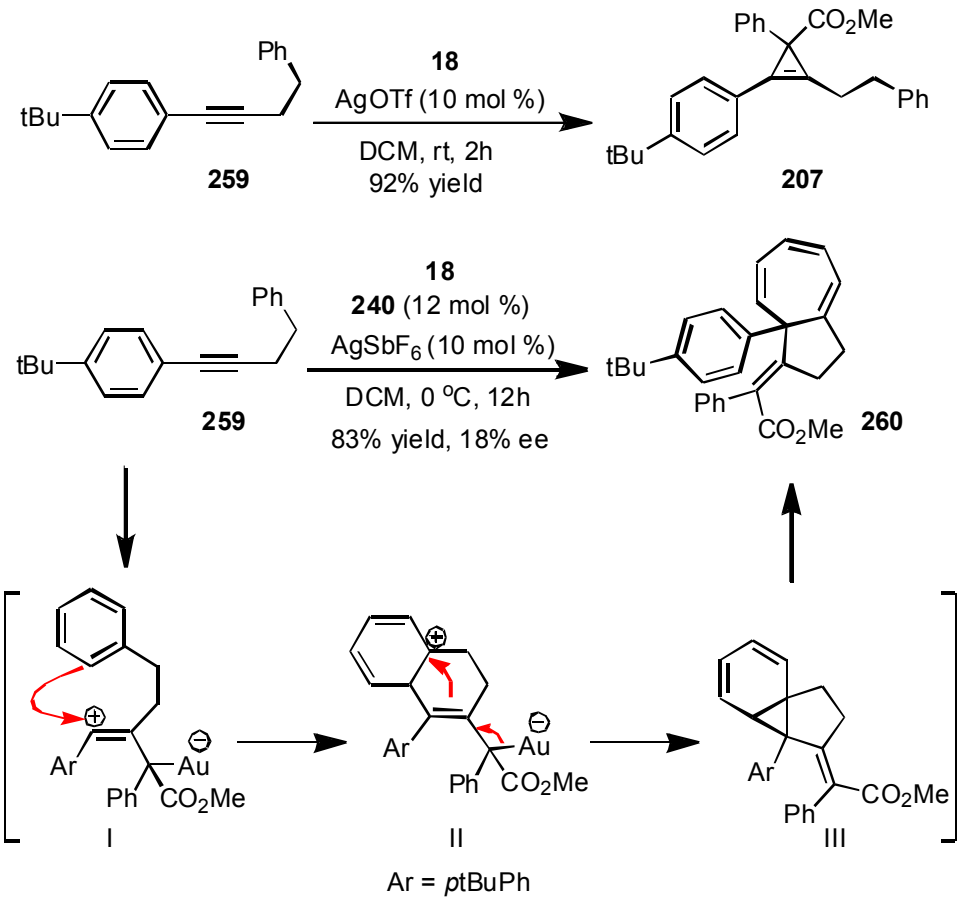


Scheme 4.4 Silver(I) and gold(I)-catalyzed cyclopropenation of diaryl alkyne **257**



Scheme 4.5 Cu(I)-catalyzed formation of indene derivatives from aryl alkynes and aryl diazoacetates

Another interesting transformation showcasing the highly electrophilic character of the Au(I) carbenoid was observed when the aryl alkyne **259** was used as substrate for the cyclopropenation reaction (Scheme 4.6). Instead of formation of the expected cyclopropene product **207** (which was obtained in 92% yield with AgOTf), the bicyclic product **260** was generated in 83% yield. The proposed mechanism for the formation of **260** is depicted in Scheme 4.6. The alkyne is considered to attack the metal carbenoid to form the ionic species **I**. The pendant aromatic ring then attacks the vinyl cation to form the bicyclic intermediate **II** which then rearranges to norcaradiene **III**. The diene undergoes a 6π electrocyclic ring opening to afford the cycloheptatriene derivative **260**. NOE studies were conducted to confirm the regiochemistry of the product. The chiral influence of the catalyst was lost during the transformation affording the product in only 18% ee.



Scheme 4.6 Cu(I)-catalyzed formation of indene derivatives from aryl alkynes and aryl diazoacetates

Various aryldiazoacetates were also screened for the cyclopropenation reaction using 1-phenyl-1-propyne **193** as the representative alkyne trap (Table 4.6). Cyclopropene products **261**-**269** were obtained in moderate to good yields with excellent levels of enantioinduction when (*S*)-xylylBINAP(AuCl)$_2$ (**240**) was used as catalyst. The reaction is amenable to both electron deficient and electron rich aryl diazoacetates. For entries 1-3, the enantioinduction can be improved further by using (*S*)-DTBM-SEGPHOS(AuCl)$_2$ (**237**) as the catalyst. The absolute configuration of cyclopropene **261** was confirmed by X-ray crystallographic analysis (Figure 4.5).

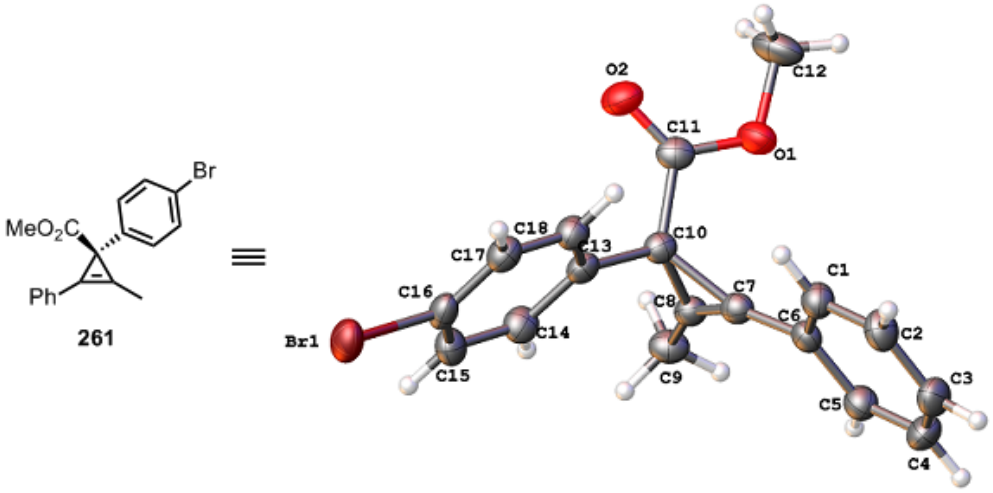
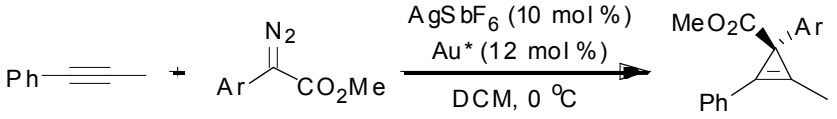
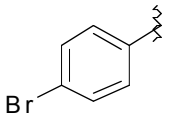
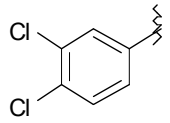
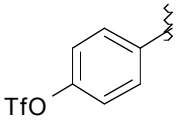
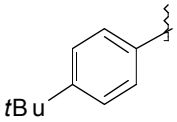
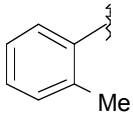
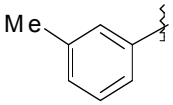
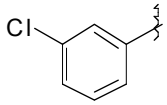
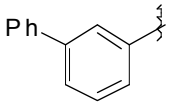
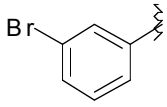


Figure 4.5 X-ray structure of cyclopropene **261**

Table 4.6. Gold(I)-catalyzed cyclopropenation of **193** with various aryl diazoacetates



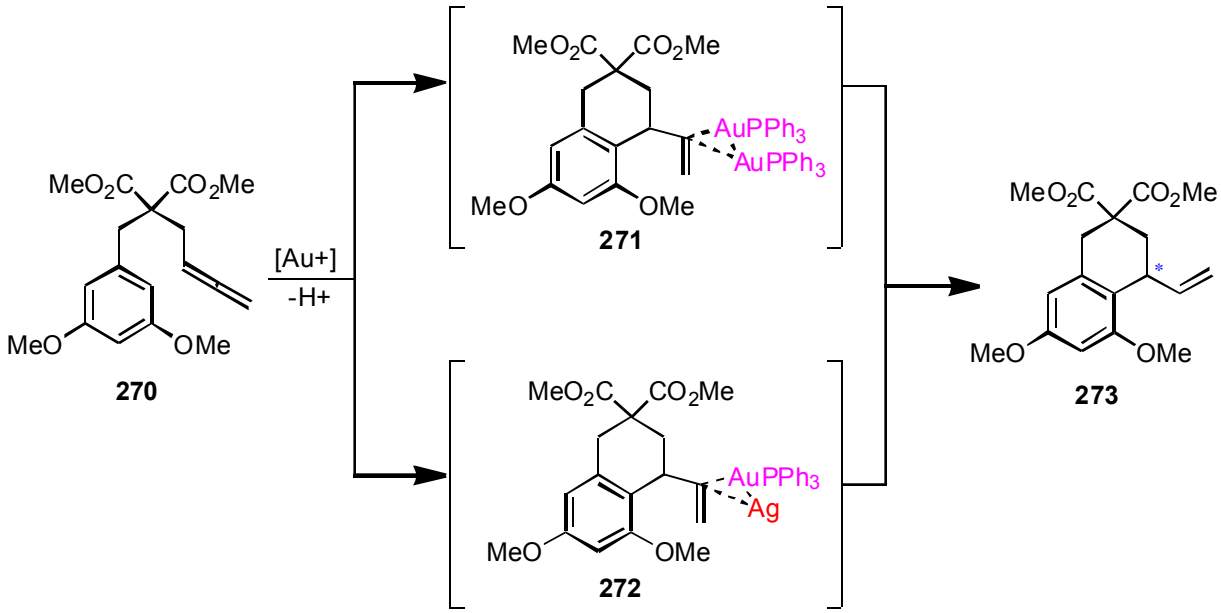
193 **261-269**

entry	Ar	Au*	product	yield, %	ee, %
1		**240**	**261**	88	89
		237	**261**	60	95
2		**240**	**262**	88	87
		237	**262**	79	97
3		**240**	**263**	86	84
		237	**263**	65	95
4		**240**	**264**	62	85
5		**240**	**265**	62	84
6		**240**	**266**	71	92
7		**240**	**267**	77	95
8		**240**	**268**	70	95
9		**240**	**269**	66	97

4.4 Gold *vs* Ag/Au complex-catalyzed cyclopropenation

One interesting aspect of this study is determining the active chiral catalyst in the cyclopropenation reaction. In the last decade, there is a drastic growth of interest in electrophilic gold complexes catalyzed reactions and the number of publications involving Au-mediated enantioselective organic transformations is constantly increasing. Reactions involving gold catalysts normally require silver salts that remove the labile chloride ligands generating a powerful catalytically active species. These silver salts then precipitate out as silver halide in a process more commonly known as silver salt metathesis.[14] Because of our recent success in silver-catalyzed cyclopropanation and cyclopropenation reactions; we were very interested to determine if silver has effect on the cyclopropenation reaction. Moreover, there have been reports suggesting that silver influences reaction outcome in certain gold-catalyzed transformations. For example, Gagné and co-workers, during their study on Au(I)-catalyzed hydroarylation of allene **270** reported that adventitious Ag^+ can intercept key gold intermediates and effect catalysis (Scheme 4.7).[15] The results showed that the resting state of the Au(I)-catalyzed reaction of allene changes in the presence of Ag^+, with silver free catalysts resting at the dinuclear gold structure **271** and Ag^+ containing solutions resting at a heteronuclear species like **272**. Based on ^1H and ^{31}P NMR and mass spectrometric analyses, Gagné proposed a structural model based on existing Au/Ag cluster chemistry literature which may explain the known Ag^+ effects in gold-catalyzed reactions (Figure 4.6).[16] In this proposed structure, Ag^+ is suggested to bind to the vinyl carbon and the Au ion without significantly perturbing the gold-vinyl structure. This means that the 3-center-2-electron

interaction is not equal and the stronger C-Au bond dominates the structure. Only one of the diastereofaces (either **274** or **275**) must be preferentially populated since only a single diastereomer was observed.[15]



Scheme 4.7 "Silver-effect" in gold(I)-catalyzed hydroarylation

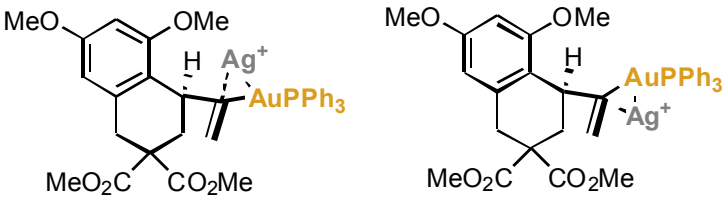


Figure 4.6 Diastereomers of the proposed Ag-Au bimetallic complex

Recently, Shi and coworkers demonstrated that in known gold-catalyzed reactions, silver ions have a drastic effect on the reaction outcome.[17] Similar to Gagne's

observations, Shi found that the combination of Ag^+ and $[L\text{-}Au]^+$ results in the formation of different complexes in solution. ^{31}P NMR analysis of a $(PPh_3)AuCl/AgOTF$ mixture showed a peak at 28.1 ppm (Figure 4.7 C). On the other hand, when the mixture is filtered thru celite, analysis of the filtrate showed a peak at 27.1 ppm (Figure 4.7 D). X-ray photoelectron spectroscopy showed that celite filtration eliminates all the adventitious silver ions making the solution silver-free. Literature-reported gold-catalyzed reactions were then re-evaluated and it was found that in a couple of cases, a significant difference

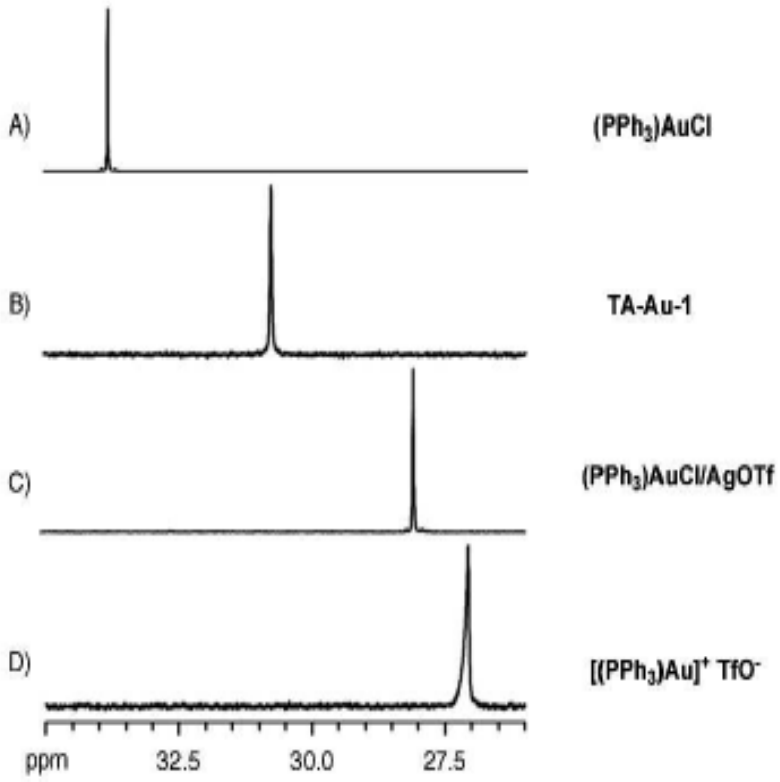
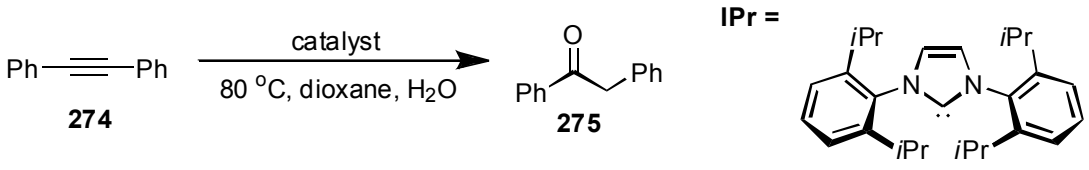


Figure 4.7 ^{31}P NMR of different Au(I) samples

in the reactivities with and without silver was observed. More importantly, there are cases where the conventional $[L\text{-}Au]^+$ catalysts could not promote the reaction without the presence of silver. For example, Nolan and coworkers reported that (IPr)AuCl/AgSbF6 is

the optimal catalyst to promote the hydration of alkyne **274** (Table 4.7).[18] Re-evaluation of this reaction showed that indeed, this catalyst mixture provided ketone **275** in 97% yield (entry 1). However, when the silver-free catalyst was used, **275** was not formed (entry 2). $AgSbF_6$ alone also did not catalyze the hydration reaction. Interestingly, when $AgSbF_6$ was added to the "inactive" silver-free catalyst, the reaction occurred affording **275** in 95% yield (entry 3). These results confirm that for this particular reaction to take place, a mixture of gold and silver is necessary.

Table 4.7. Au/Ag-catalyzed hydration of internal alkyne

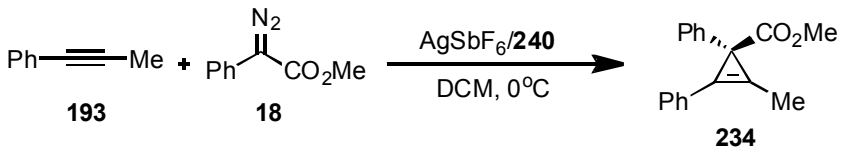


entry	catalyst	time, h	% yield
1	2 mol % (IPr)AuCl/$AgSbF_6$	2	97
2	5 mol % [(IPr)Au]SbF_6 (after celite)	24	0
3	5 mol % $AgSbF_6$	24	0
4	2% [(IPr)Au]SbF_6/ 2 mol % $AgSbF_6$	12	95
5	2% [(IPr)Au]SbF_6/ 1 mol % $AgSbF_6$	24	88
6	2% [(IPr)Au]SbF_6/ 0.5 mol % $AgSbF_6$	24	67

With this knowledge in hand, we began to study the effect of changing the stoichiometry of the silver/gold catalysts. Based on the results shown in Table 4.8, increasing the Au:Ag mole ratio from about 1 to 2.4 did not have significant effect on the level of enantioselectivity. However, when mole ratio is decreased from 1 to 0.3, a steady

drop on the level of enantioinduction was observed. This implies that the achiral silver catalyst might compete with the chiral catalyst complex in the cyclopropenation reaction which would lead to formation of racemic compound.

Table 4.8. Effect of Au:Ag mol ratio on the cyclopropenation of **193**

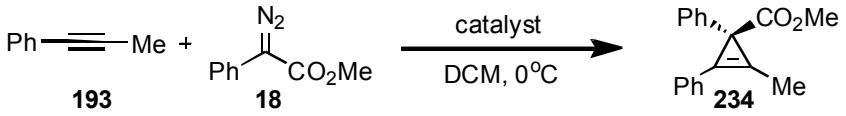


entry	mmol **240**	mmol Ag	ratio Au/Ag	% yield	% ee
1	0.06	0.025	2.4	43	93.4
2	0.06	0.03	2.0	75	94.4
3	0.06	0.04	1.5	80	94.5
4	0.06	0.05	1.2	81	93
5	0.06	0.06	1.0	81	94.3
6	0.06	0.07	0.86	77	94.2
7	0.06	0.10	0.6	70	93
8	0.06	0.12	0.5	68	84
9	0.06	0.20	0.3	68	73

More control experiments were conducted to determine what the active chiral catalyst is (Table 4.9). As seen earlier, poor levels of enantioselectivity were obtained using $AgSbF_6$ in the presence of chiral phosphine ligands, SEGPHOS and BINAP (entries 9-10). These results suggest that the reaction is not catalyzed by a chiral silver-BINAP catalyst. The cyclopropenation was then conducted using Au(I) complexes in the

absence of a silver salt and no diazo decomposition was observed (entries 1-2). As mentioned earlier, these gold(I) complexes

Table 4.9. Control experiments for cyclopropenation of **193**

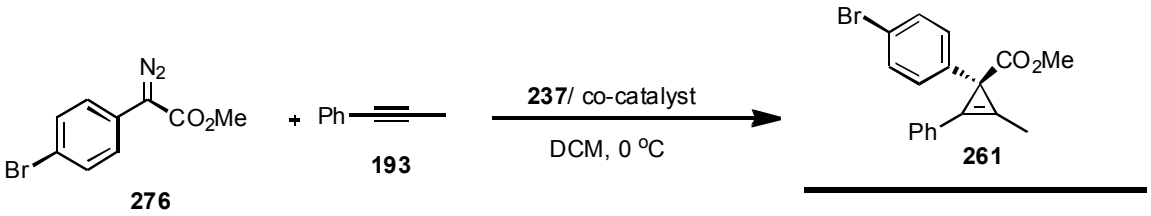


193 **18** **234**

entry	catalyst	co-catalyst	% yield	% ee
1	$Au(PPh_3)Cl$	none	NR	---
2	(*S*)-xylylBINAP$(AuCl)_2$	none	NR	---
3	(*S*)-xylylBINAP$(AuCl)_2$	$NaBF_4$	NR	---
4	(*S*)-xylylBINAP$(AuCl)_2$	NaBARF	NR	---
5	(*S*)-xylylBINAP$(AuCl)_2$	NaOTf	NR	---
6	(*S*)-xylylBINAP$(AuCl)_2$	$NaSbF_6$	NR	---
7	(*S*)-xylylBINAP$(AuCl)_2$	TlOTf	49	91
8	(*R*)-xylylBINAP$(AuCl)_2$	TlOTf	54	-91
9	$AgSbF_6$	(*S*)-TolBINAP	81	17
10	$AgSbF_6$	(*R*)-DTBMSEGPHOS	70	<5

usually require a chloride scavenger to form the active $[L\text{-}Au]^+$ catalyst therefore we next surveyed readily available chloride scavengers for the cyclopropenation reaction. When sodium tetrafluoroborate, sodium triflate and sodium hexafluroantimonate were used as chloride scavengers, no reaction was observed (entries 3-5). When NaBARF was used as additive, the diazo compound was also not decomposed (entry 6). NaBARF is known to effectively activate gold(I) chloride complexes[19] therefore we decided to repeat the reaction using a newly purchased material. Reaction of alkyne **193** and *para*-bromophenyldiazoacetate **276** provided the desired cyclopropene in comparable yields and enantiomeric excess when either $AgSbF_6$ or NaBARF was used as co-catalyst (Scheme 4.8). The use of Tl salt (TlOTf) provided the desired cyclopropene product also

with high levels of enantioinduction (entries 7-8). Thallium salts (i.e. $TlPF_6$) have been commonly utilized as chloride scavengers.[20] This result suggests that the cyclopropenation reaction might be an Au(I)-catalyzed reaction and $AgSbF_6$ only acted as a chloride scavenger; however, more thorough control experiments should still be conducted. In collaboration with Prof. Cora Macbeth, efforts were made to obtain a

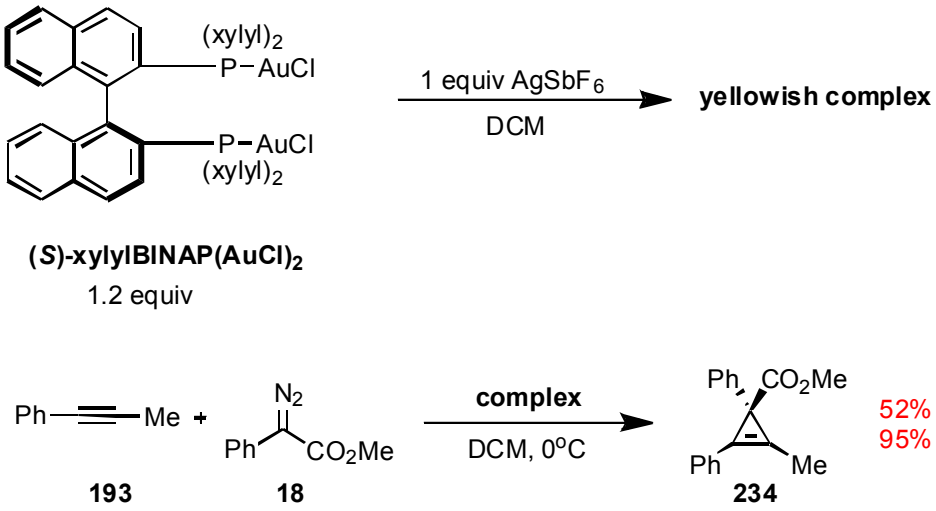


	yield (%)	ee (%)
$AgSbF_6$	60	95
NaBARF	63	93

Scheme 4.8 Cyclopropenation of **193** with **276**

crystal structure of the active catalyst. A solution of Au/Ag catalyst in DCM was prepared containing 1.2 mol ratio of Au:Ag (Scheme 4.9). The mixture usually turns cloudy which presumably is caused by the formation of silver chloride. The solids were then filtered off using an ordinary filter paper to obtain a clear solution of the premade catalyst which was used to prepare crystalline material. However, upon solvent evaporation, a yellowish solid is usually formed and this solid was also tested for catalytic activity (Scheme 4.9). Interestingly, this solid was still catalytically active providing the desired cyclopropene in 52% yield and 95% ee. Moreover, the yellow complex is stable at room temperature for days which is in contrast to the known instability of $[L\text{-}Au]^+$ complexes.[19] After more rigorous efforts in growing crystals from the gold-silver mixture, we were able to isolate crystalline solids from the premade

catalyst solution. Unfortunately, X-ray analysis revealed that it was the starting Au(I) complex with two chloride atoms intact (Figure 4.8).



Scheme 4.9 Cyclopropenation of **193** with isolated gold complex

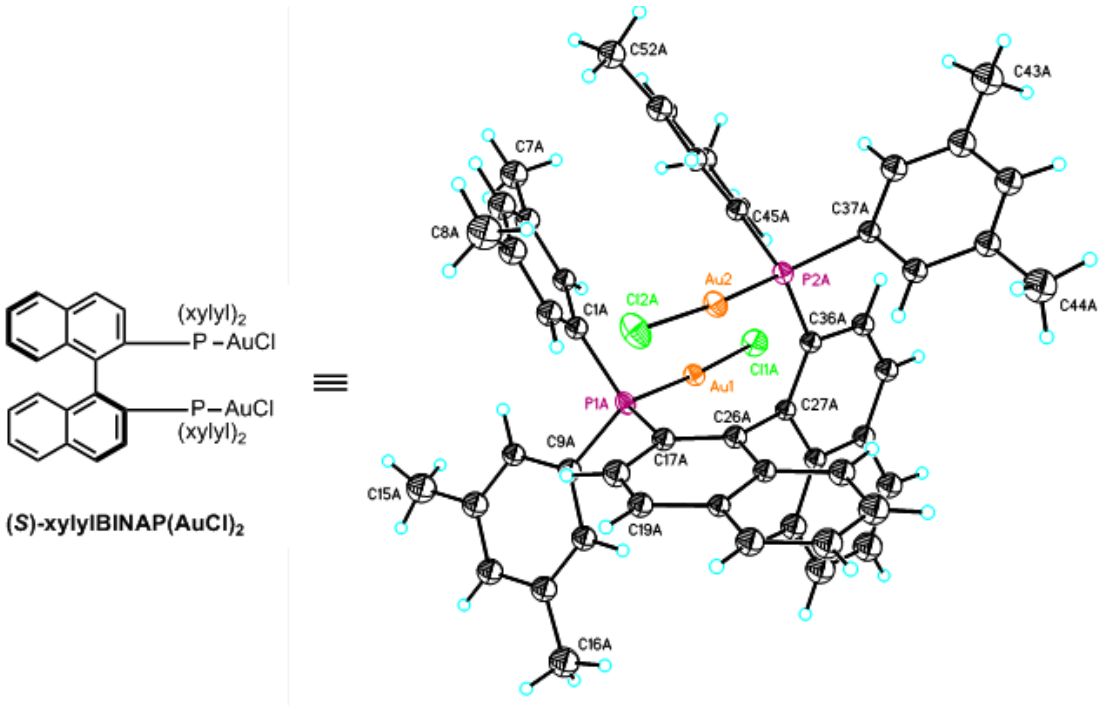
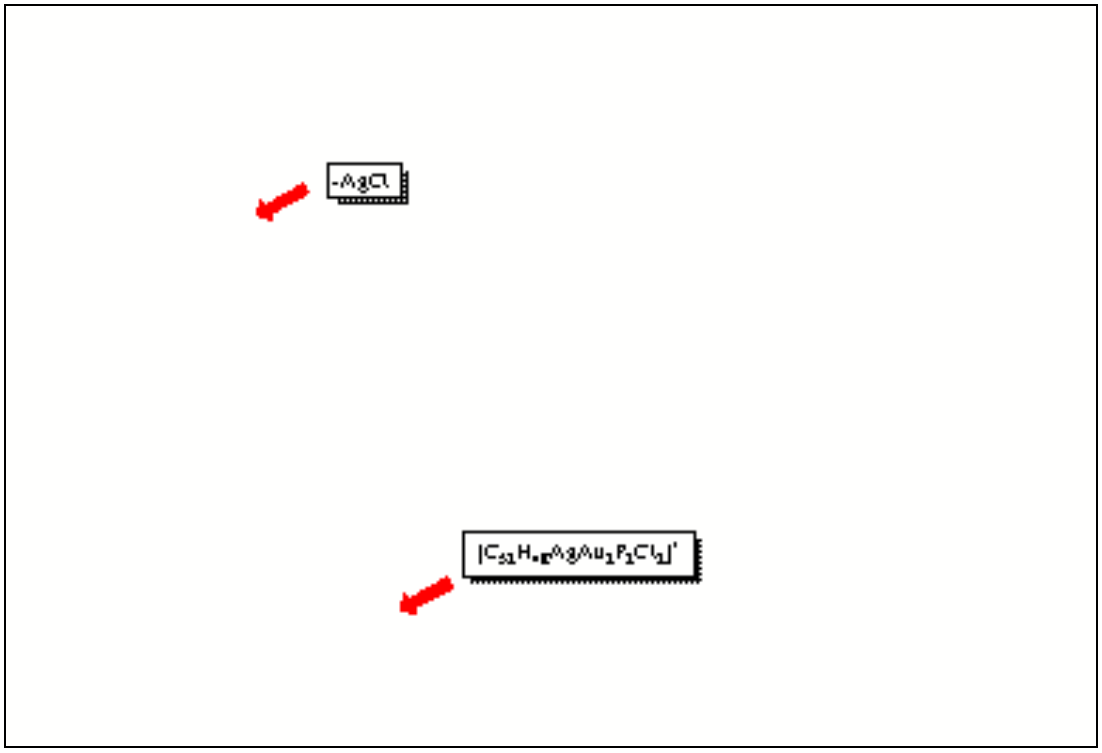


Figure 4.9 X-ray structure of **240**

Mass spectrometric analysis of the isolated catalyst was done and we were delighted to see an interesting *m/z* of 1307.1020 (calcd 1307.0978) which corresponds to molecular formula $[C_{52}H_{48}AgAu_2P_2Cl_2]^+$ (Figure 4.9a). The isotope pattern matched the expected pattern for an Au-Ag containing compound (Figure 4.10). The major *m/z* of 1163.2236 resulted from the loss of AgCl from $[C_{52}H_{48}AgAu_2P_2Cl_2]^+$ as confirmed by MS/MS analysis. The same mass spectrometric results were obtained when the catalyst mixture was filtered thru celite instead of an ordinary filter paper. When catalyst **237** was used for the mass spec analysis (Figure 4.9b), we found a *m/z* of 1751.4464 (calc 1751.4647) which corresponds to molecular formula $[C_{74}H_{100}O_8AgAu_2P_2Cl_2]^+$. The isotope pattern also matched the expected pattern for an Au-Ag containing compound. Similarly, MS/MS analysis confirmed that loss of AgCl from $[C_{74}H_{100}O_8AgAu_2P_2Cl_2]^+$ resulted to the major *m/z* of 1607.5907. If the active chiral catalyst is indeed a Ag-Au cluster, it is noteworthy that the complex is stable enough that it can pass thru celite without losing silver. This is in contrast to what Shi and coworkers observed that by passing thru celite, adventitious silver ions can be completely eliminated as confirmed by X-ray photoelectron spectroscopy.


-AgCl
[C51H48AgAu1P2Cl1]+

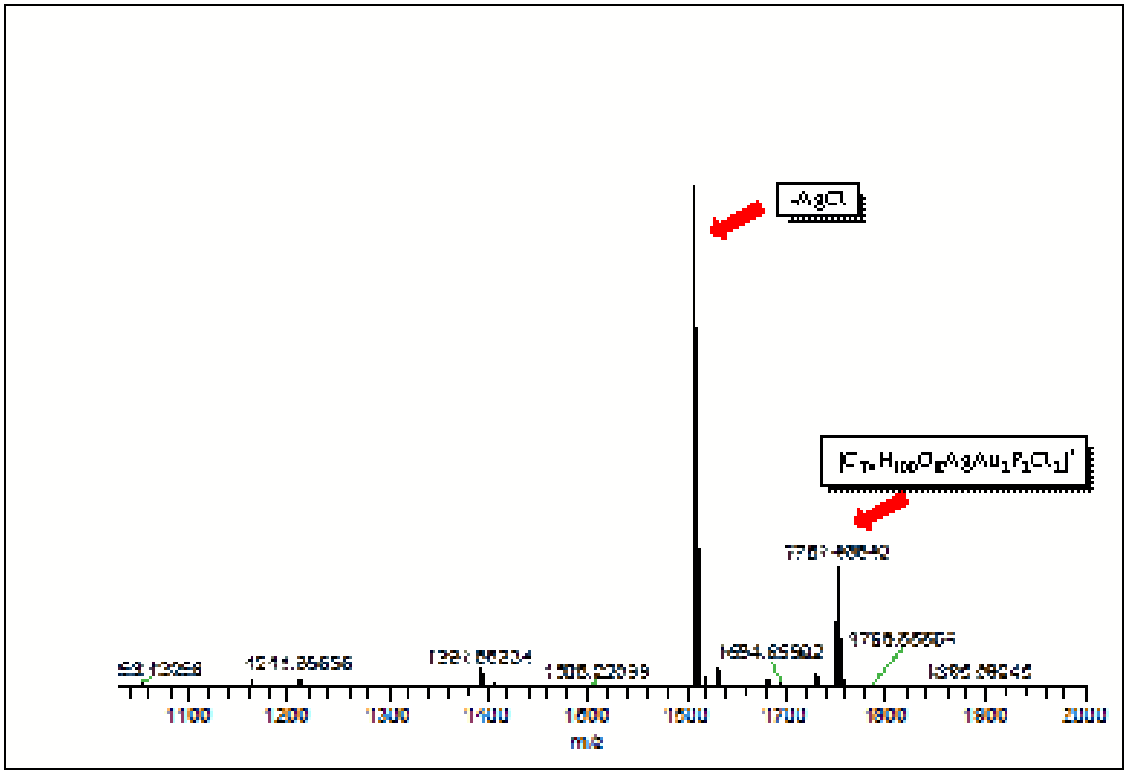
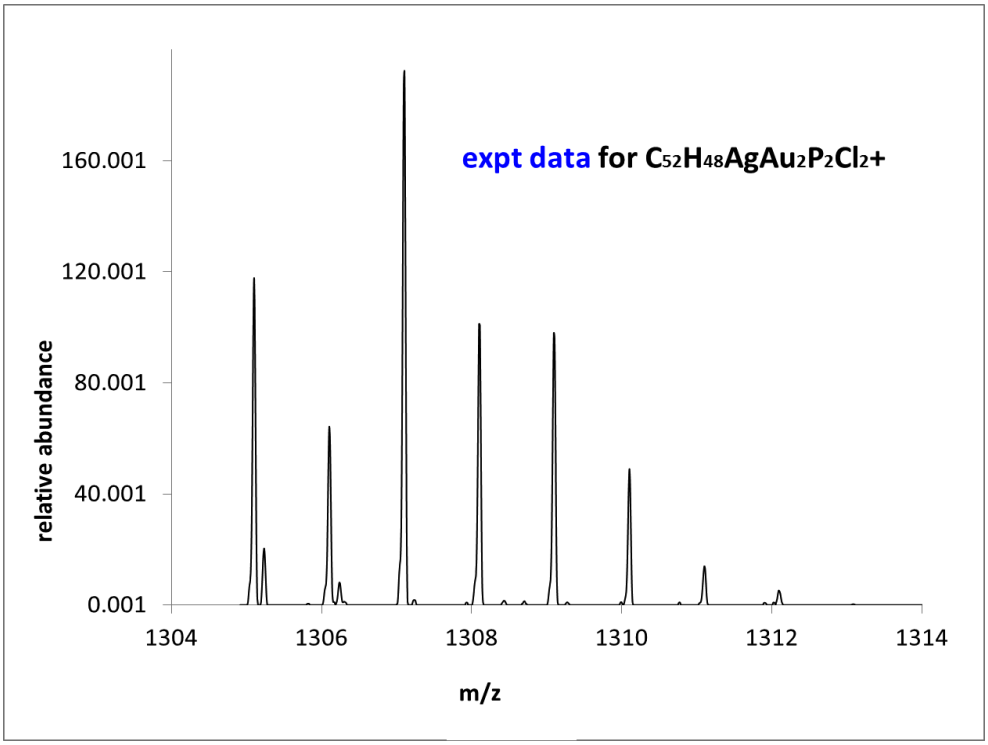

-AgCl
[C72H100O8AgAu1P2Cl1]+
1211.86656
1306.22939
1684.65902
1100
1200
1300
1400
1500
1600
1700
1800
1900
2000
m/z

Figure 4.9 Mass spec analysis for complexes (a) Ag-**240** and (b) Ag-**237**



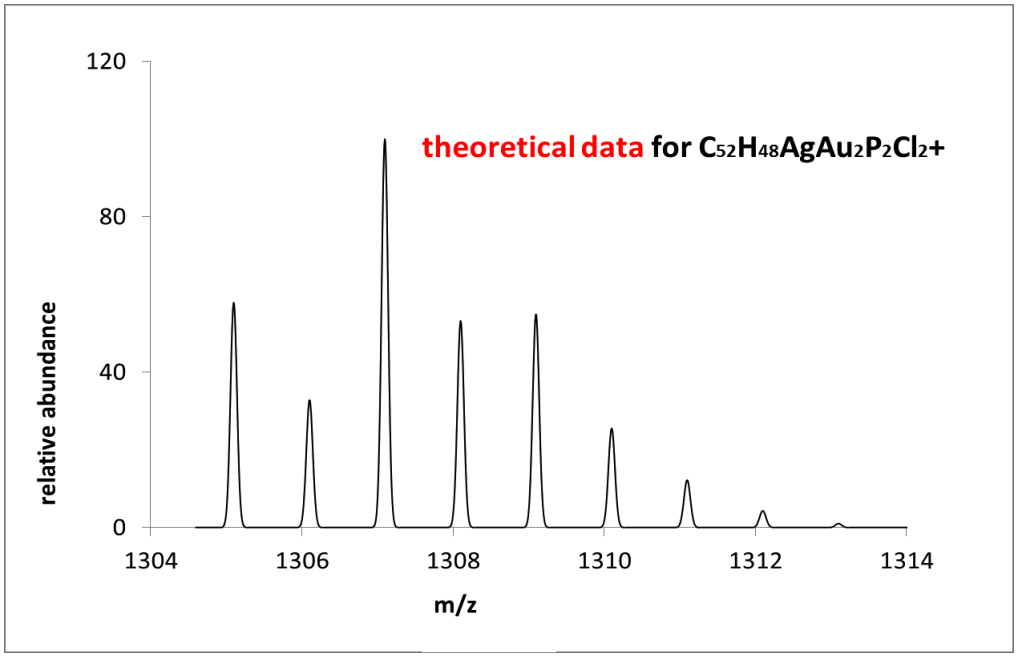


Figure 4.10 Experimental and theoretical isotope patter for Ag-Au containing compound

In collaboration with a former postdoctoral associate Dr. Slava Boyarskikh, computational modeling was conducted to determine if the proposed Au-Ag complex is a plausible structure. Using B3LYP method, geometry optimization showed a completely converged structure of Au-Cl-Ag complex (Figure 411a). We are very pleased that the complex was held together by attractive forces and did not fall apart which means that our hypothetical mixed catalyst structure is energetically reasonable. Although this result is only preliminary, the model shows an interesting argentophilic/aurophilic interaction with a Au-Ag bond of 3.18 Å (Figure 4.11b). This distance is within the usual range of 2.71-3.27 Å for mixed argentophilic/aurophilic reported in the literature.[21] Dr. Boyarskikh's exciting initial results prompted us to further study the system and determine what the structure would look like if the carbenoid is formed. Calculations provided the carbene bound complex showing an interesting π-π stacking interaction between the aryl moiety of the carbenoid and the aryl moiety of one of the phosphine ligands (Figure 4.12a). Because of this interaction one of side of the carbenoid face is totally blocked which may explain the high asymmetric induction. The carbene bound complex where the carbenoid is facing on the other side (i. e. without the π-π stacking interaction) is 5.6 kcal/mol higher energy than the first structure (Figure 4.12b). Lastly, Dr. Boyarskikh calculated the structure of the carbene bound complex in the presence of 1-phenyl-1-propyne **193**. The pre-reaction complex (before TS) is held together by attractive dispersion (pi-pi) interactions involving the carbenoid, the alkyne and phosphine aryl moieties (Figure 4.13). The entire structure was optimized using DFT and took only 48 hours. This means that locating the corresponding transition state using the

same level of theory seems reasonable and therefore would be the focus of future calculations.

Figure 4.11a

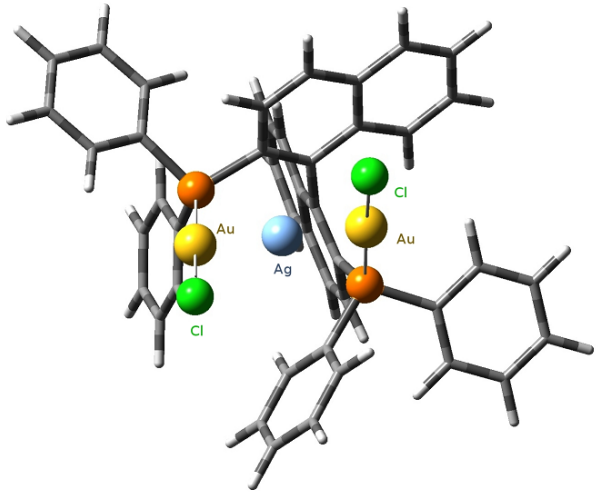


Figure 4.11b

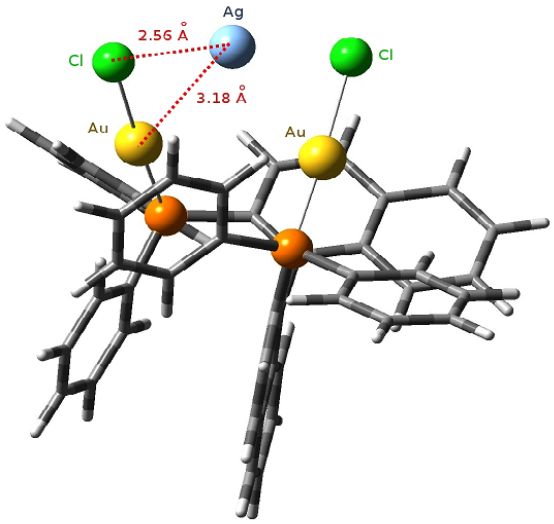


Figure 4.11 Computational model for the Au-Ag complex

Figure 4.12

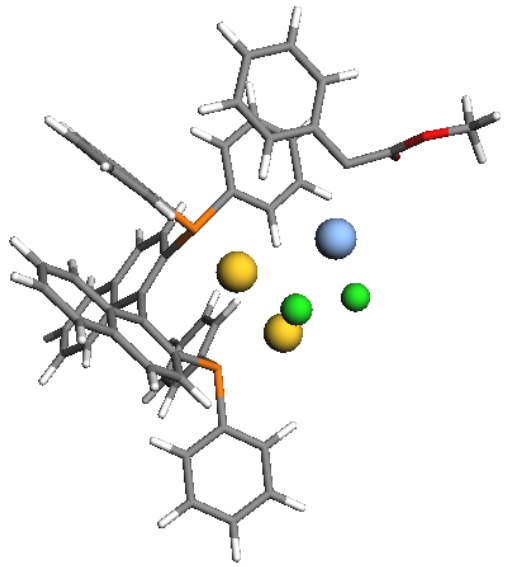


Figure 4.12b

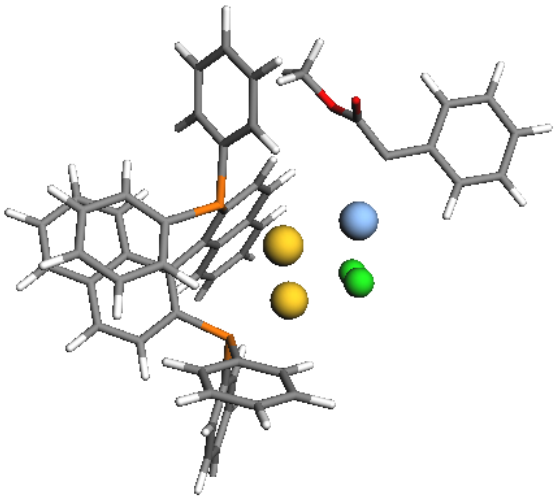


Figure 4.12 Computational models for the carbene bound Ag-Au complex

Figure 4.13

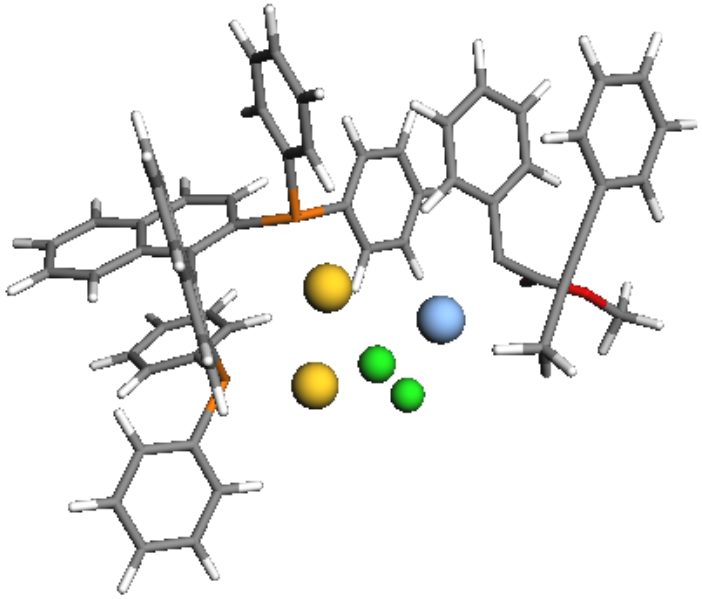


Figure 4.13 Computational model of alkyne coordination with Au-Ag carbenoid

4.5 Gold *vs* Ag/Au complex-catalyzed cyclopropanation of olefins

4.5.1. Toste's cyclopropanation with propargyl esters

We also investigated Toste's cyclopropanation chemistry using the catalyst system that is employed for the cyclopropenation reaction (Table 4.10). The reason for this study is to compare whether the same levels of enantioinduction would be observed if our catalyst system was used for the cyclopropanation reaction. Indeed, different

Table 4.10. Au(I)-catalyzed cyclopropanation of styrene with propargyl ester **276**

276 **277**

entry	Au*	mol % Ag	mol % Au*	% yield	% ee
1	(*S*)-xylylBINAP	5	2.5	83	59
2	(*R*)-xylylBINAP	5	2.5	75	54
3	(*S*)-DTBM Segphos	5	2.5	72	88
4	(*S*)-xylylBINAP	10	12	73	32
5	(*S*)-DTBM Segphos	10	12	76	56
6*	(*S*)-DTBM Segphos	0	2.5	68	31
7	(*S*)-DTBM Segphos	2.5	5	77	61
8	(*S*)-DTBM Segphos	1.25	5	80	85

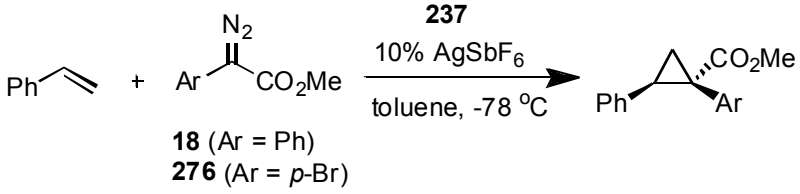
* 3 mol % NaBARF used

results were obtained when the mole ratio of Au:Ag used was changed. Typically, Toste's cyclopropanation[7] is conducted using 5 mol % $AgSbF_6$/2.5 mol % Au while for our cyclopropenation reaction, 10 mol % $AgSbF_6$/12 mol % Au is used. A very pronounced difference is seen in the case of entries 3 and 5 where Toste's system gave 88% ee while our system only gave 56% ee. Moreover, when NaBARF was used as additive the cyclopropane product was only formed in 31% ee. The enantioselectivity also increased from 61% to 85% when the amount silver used is decreased (entryies 7-8). These results clearly suggest that the presence of silver in the reaction system have an influence in the catalysis although the exact mechanism as to how the silver acts in this catalytic system remains unclear.

4.5.2. Cyclopropanation with donor/acceptor carbenoids

With our success in the enantioselective cyclopropenation of internal alkynes, we were interested to see if the digold(I)-BINAP systems are also effective in promoting cyclopropanation of olefins. In addition, we wanted to determine if there is any significant "silver effect" in the cyclopropanation reaction as seen in Toste's cyclopropanation of styrene with propargyl esters. We were especially interested in the cyclopropanation of sterically hindered olefins because dirhodium catalysts are not effective in cyclopropanating these substrates. The Davies group has shown that silver(I) salts are highly efficient catalysts for the cyclopropanating sterically encumbered olefins.[22] We began our studies with the standard test reaction done in our group which involves the use of styrene as substrate for cyclopropanation reaction (Table 4.11). Using diazoacetate **18** and the catalyst **237**, cyclopropane **278** was formed in good yield but the enantioselectivity is moderate (entry 1). The enantioselectivity can be improved when the *para*-bromophenyldiazoacetate **276** was used as substrate providing the cyclopropane **279** in 82% yield and 60% ee (entry 2).

Table 4.11. Au(I)-catalyzed cyclopropanation of styrene



18 (Ar = Ph)
276 (Ar = *p*-Br)

entry	Ar	product	dr	yield (%)	ee (%)
1	Ph	**278**	>20:1	91	35
2	*p*-BrPh	**279**	>20:1	82	60

(entry 2).With these promising results we then extended our studies to the cyclopropanation of β-methylstyrene (*cis* and *trans*) and methyl phenyldiazoacetate **18**

using either **240** and **237** as catalyst (Table 4.12). After optimization of reaction conditions, we found that by conducting the reaction at -78 °C and using toluene as solvent, appreciable levels of enantioselectivity can be achieved using either the *cis* (entry 3) or *trans* (entry 5) isomer of β-methylstyrene. The absolute stereochemistry of cyclopropane **280** was confirmed by X-ray crystallographic analysis (Figure 4.14). In terms of yield and enantioselectivity, *cis*-β-methylstyrene was superior as substrate over the *trans* isomer for the cyclopropanation reaction. With the optimized conditions in hand, we then investigated the scope and generality of the reaction using a variety of highly substituted olefins.

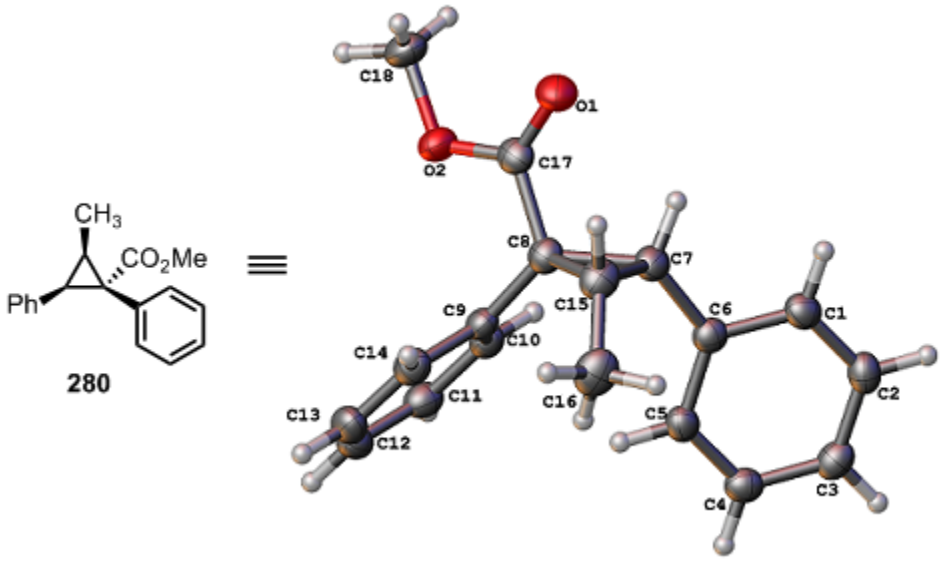
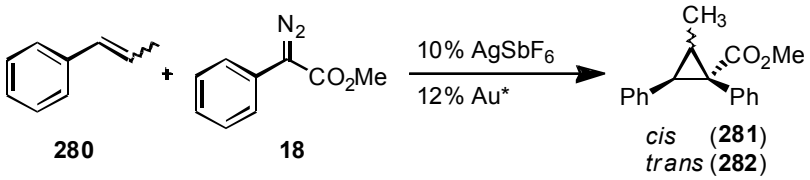


Figure 4.14 X-ray structure of cyclopropane **280**

Table 4.12. Gold(I)-catalyzed cyclopropanation of β-methylstyrene **278** with **18**

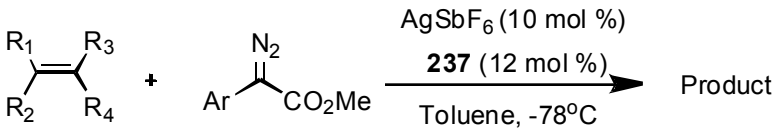


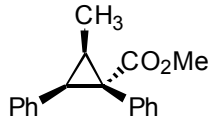
280 **18**

entry	substrate	Au*	Solvent	Temp, °C	Product	yield (%)	ee (%)
1	*cis*	**237**	DCM	0	**281**	91	67
2	*cis*	**237**	DCM	-78	**281**	88	78
3	*cis*	**237**	Toluene	-78	**281**	86	85
4	*trans*	**237**	DCM	0	**282**	68	57
5	*trans*	**237**	Toluene	-78	**282**	64	78
6	*trans*	**240**	Toluene	-78	**282**	59	31

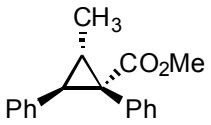
A wide range of highly substituted olefins was used for the cyclopropanation reaction using catalyst **237** (Table 4.13). Good enantioselectivity was obtained for the reaction of 1,2-dihydronaphthalene and **18** which afforded cyclopropane **283** in 88% ee. It is important to note that this substrate gives a mixture of cyclopropanation and C-H insertion products under rhodium catalysis. However, under gold catalysis only the cyclopropane product was obtained in 73% yield. Moderate enantioselectivity was obtained for cyclopropane **286** which reflects the high reactivity of the electron rich (*E*)-1-methoxy-4-(prop-1-en-1-yl)benzene. Similarly, cyclopropane **287** derived from the highly reactive and sterically unhindered 1,3-cyclohexadiene was formed in only 33% ee. On the other hand, *cis*-stilbene and the trisubstituted alkene (2-methylprop-1-en-1-yl)benzene were too sterically hindered for cyclopropanation to occur and therefore did not provide products **284** and **285**, respectively.

Table 4.13. Gold(I)-catalyzed cyclopropanation of various olefins

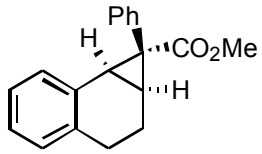




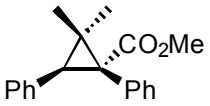
85% ee, 86% yield
281



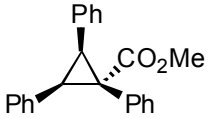
78% ee, 64% yield
282



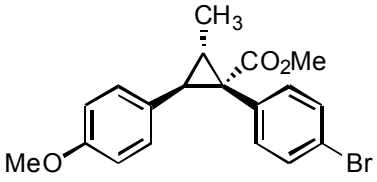
88% ee, 73% yield
283



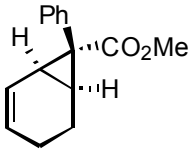
0% yield
284



0% yield
285



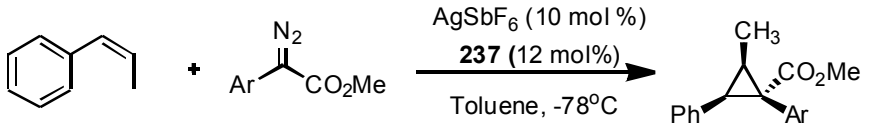
43% ee, 86% yield
286



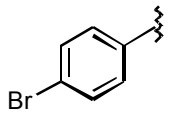
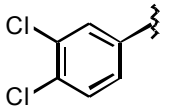
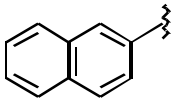
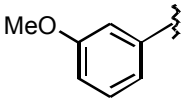
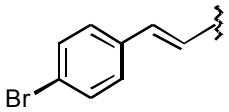
33% ee, 74% yield
287

Excellent levels of enantioselectivity were obtained when other aryl diazoacetates were used for the cyclopropanation of *cis*-**280** (Table 4.14). The reaction is amenable to both electron rich and electron deficient aryl diazoacetates providing the desired cyclopropanes in good yields (76-84%) and good to excellent enatioselectivities (80-94% ee). The reaction can also be expanded to styryldiazoacetates such as the case of entry 5 providing the vinylcyclopropane **292** in 76% yield and 91% ee.

Table 4.14. Gold(I)-catalyzed cyclopropanation of β-methylstyrene **280** with various diazoacetates



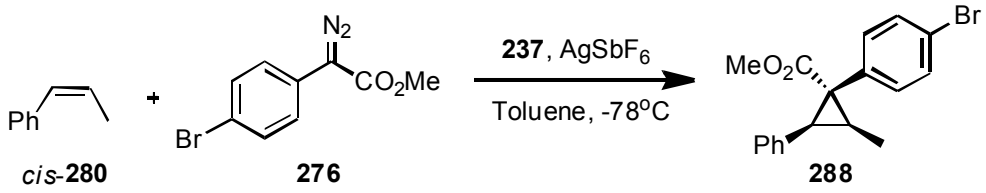
cis-**278** **288-292**

entry	Ar	product	%yield	%ee
1		**288**	83	94
2		**289**	84	80
3		**290**	84	92
4		**291**	81	81
5		**292**	76	91

To determine whether there is a "silver effect" in the gold-catalyzed cyclopropanation, we decided to perform control reactions using the substrate *cis*-**280** and *p*-bromophenyldiazoacetate **276** as the carbenoid precursor. Employing the gold catalyst **237**, varying amounts of the co-catalyst $AgSbF_6$ was used to determine if changing the ratio of the gold catalyst to silver would have influence on the overall cyclopropanation reaction (Table 4.15). Using 3 mol % of the digold catalyst **237** and 1.5 to 9 mol % of $AgSbF_6$, the cyclopropane **288** was formed in good yields and excellent enantioselectivity. The mole ratio of Au:Ag did not significantly affect the enantioselectivity of the reaction, however as the amount of silver is increased, a constant

drop in enantioselectivity was observed. **288** was only formed in 87% ee when a ratio of 1:3 digold:Ag was used as the catalyst system. Similar trend was also observed in the cyclopropenation chemistry. It is interesting to note that when less silver is used, such as in entry 1, **288** was only formed in 88% ee (entry 1). Lower catalyst loading can also be employed without any significant drop in yield and enantioselectivity (entries 4-5).

Table 4.15. Gold(I)-catalyzed cyclopropanation of β-methylstyrene **280** with



cis-**280** **276** **288**

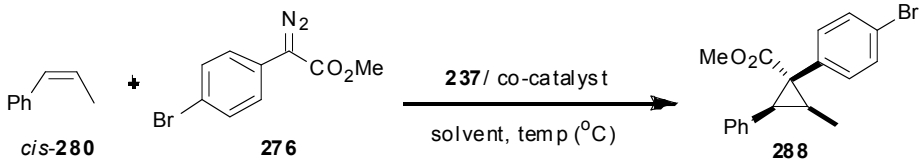
entry	mmol **237**	mmol $AgSbF_6$	ratio (Au:Ag)	% yield	% ee
1	0.03	0.015	1:0.5	74	88
2	0.03	0.03	1:1	82	94
3	0.03	0.045	1:1.5	80	94
4	0.01	0.015	1:1.5	67	94
5	0.015	0.0225	1:1.5	72	92
6	0.03	0.06	1:2	78	92
7	0.03	0.09	1:3	81	87

18

We also conducted the cyclopropanation reaction in the presence and absence of silver to determine whether the reaction only requires gold for it to proceed (Table 4.16). We have already established that these digold catalysts require chloride scavenger activator for the diazo decomposition to proceed. This was again confirmed by the result in entry 1 wherein no reaction was observed when only **237** was used as catalyst. However, when NaBARF was used as co-catalyst (entry 3) the reaction occurred providing the

cyclopropane **288** in 75% yield and a slightly lower enantiomeric excess (88%) compared to the when silver was used as co-catalyst (94%).

Table 4.16. Silver-free *vs* Au/Ag-catalyzed cyclopropanation of **278** with **276**



entry	co-catalyst	solvent	temp	%yield	%ee
1	none	DCM	0	--	--
2	$AgSbF_6$	toluene	-78	83	94
3	NaBARF	toluene	-78	75	88

4.6 Summary

We have developed for the first time, an enantioselective method for the synthesis of cyclopropenes from internal alkynes using digold binap complexes popularized by Toste and co-workers. This work constitutes the first gold(I)-catalyzed asymmetric reaction of carbenoids derived from donor/acceptor-substituted diazo compounds. This also lead us to a very intriguing question of what really is the structure of the chiral catalyst and if silver is involved in the reaction rather than just a chloride scavenger. We have some evidence that support our provocative hypothesis that an Au-Ag-Au cluster is the active catalyst. These include mass spec data that confirmed the presence of a species with a chemical formula $[C_{52}H_{48}AgAu_2P_2Cl_2]^+$ and also computational modeling data that a Au-Ag-Au cluster is energetically reasonable. In terms of experimental data, we have not yet illustrated a major difference between a "silver-free" gold(I)-catalyzed carbenoid

reaction *versus* a silver-activated gold(I) catalyzed reaction. Nevertheless, this work opens new opportunities for the donor/acceptor carbenoid chemistry and we expect that novel and useful synthetic transformations will be developed in the near future.

4.7 Future directions

The development of the enantioselective cyclopropenation of internal alkynes led us to the discovery of an effective chiral gold catalyst system for donor/acceptor carbenoid chemistry. Like silver carbenoids, we found that gold carbenoids are also highly electrophilic which promoted other interesting transformations with internal alkynes rather than the expected cyclopropenation. We envision that with a better understanding of these transformations, powerful and novel synthetic transformations can be developed using the donor/acceptor diazo compounds.

A crucial part of this chemistry is the determination of the structure of the chiral catalyst. Therefore, we expect that this would be a very active field of research in the Davies group in the next few years. At this point, we only have limited and inconclusive experimental data to support the "silver effect" in both the cyclopropenation and cyclopropanation reactions. Therefore, more key control experiments should be done in order to determine if silver is necessary for the reaction to occur with high asymmetric induction. Recently, computational studies have become an integral part of the Davies group and collaboration with a former postdoc in the group Dr. Vyacheslav Boyarskikh provided us with preliminary data that the Au-Ag-Au catalyst is energetically reasonable. These exciting results will definitely prompt the Davies group to further collect computational data and modeling for better understanding of the catalyst structure as well as the corresponding carbenoid structure. With other techniques such as React-IR and X-

ray crystallographic analysis of the mixed metal complexes, we may be able to discover more asymmetric transformations as well as develop a new class of mixed metal chiral catalysts.

The Au(I)-catalyzed cyclopropanation chemistry of highly substituted olefins discussed herein is in its infancy. The scope and limitations of the reaction have not been fully understood; however, promising results demonstrated that very high levels of enantioselectivity can be achieved with sterically hindered olefins. In addition, the Au(I)-catalyzed reaction is highly chemoselective and this has been demonstrated when substrates containing C-H insertion sites were used. This makes the gold catalysts attractive because rhodium catalysts usually give a mixture of cyclopropanation and C-H insertion products when these types of substrates are used for carbenoid reactions. Further understanding of the catalyst and carbenoid structure will be necessary to maximize the potential of this useful reaction.

4.8 References

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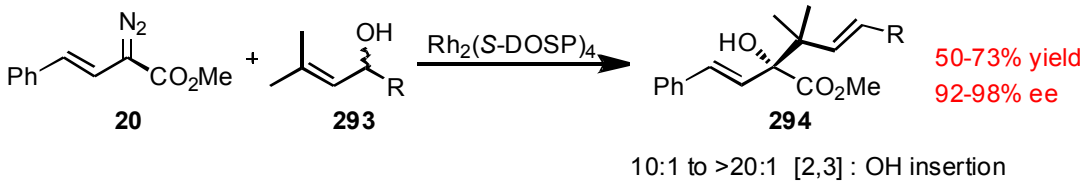
CHAPTER FIVE

Stereoselective Transformations of Propargyl Alcohols with Donor/Acceptor-Substituted Carbenoids

5.1 Introduction

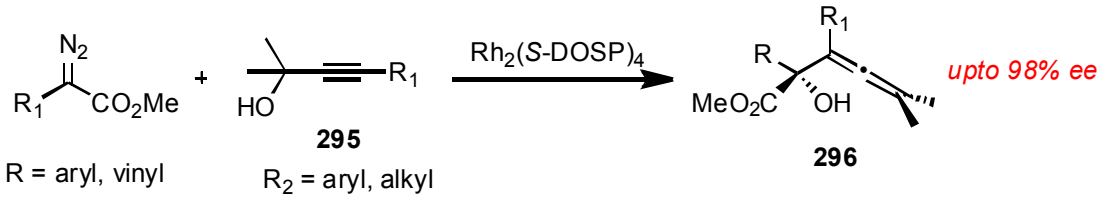
Metallacarbenoids derived from diazo compounds are highly electrophilic in nature and therefore susceptible to nucleophilic attack. This reactivity profile has been exploited *via* formation of ylides which provide intermediates that can undergo further transformations such as cycloaddition[1] and rearrangement reactions[2]. Recently Davies and Li reported a novel highly enantioselective C-C bond formation involving donor/acceptor carbenoids and allylic alcohols **293** *via* tandem ylide formation/[2,3]-sigmatropic rearrangement catalyzed by Rh_2(*S*-DOSP)$_4$ (Scheme 5.1).[3] The reaction

provided the α-hydroxycarboxylate derivatives **294** in moderate to good yields and excellent enantioselectivity.



Scheme 5.1 Rh-catalyzed tandem ylide formation/[2,3]-rearrangement of allylic alcohols

The reaction was later expanded to propargylic alcohols **295** affording enantioenriched α-allenic alcohols **296** which are versatile and useful intermediates in organic syntheses.[4,5] In Dr. Zhanjie Li's study, he found that the reaction works well with tertiary alcohols however primary and secondary alcohols as well terminal alkynols are less effective as substrates.

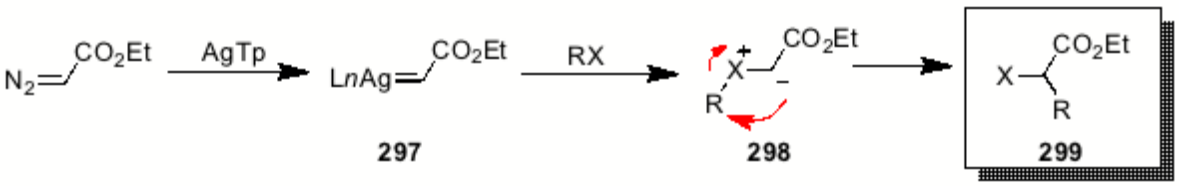


Scheme 5.2 Rh-catalyzed tandem ylide formation/[2,3]-rearrangement of propargylic alcohols

This is because the use of these alcohols often gives a mixture of the allene and the undesired O-H insertion product, the latter being the major product in most cases. DFT calculations show that although a lack of two methyl groups for primary alcohols did not introduce a significant change in the free energy barrier of the O-H insertion, it significantly increased the energy barrier for the C-O bond cleavage step of [2,3]-sigmatropic rearrangement.[6] These calculations rationalize the observed favored formation of O-H insertion product over the [2,3]-rearrangement product in the case of

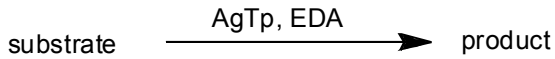
primary propargylic alcohols compared to tertiary propargylic alcohols. With this knowledge in hand, and with our interest in further expanding the scope of silver-catalyzed carbenoid reactions we began to explore the possibility of achieving similar types of reactions using silver(I) catalysts.

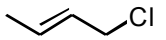
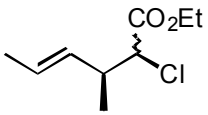
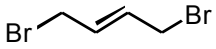
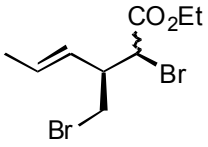
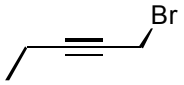
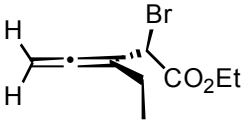
The use of silver-derived carbenes in the ylide chemistry has only recently begun to attract attention and therefore only limited examples are reported in the literature.[7] One of the earlier reports was done by Lovely and coworkers during the course of their investigation in silver-catalyzed cyclopropanation of olefins.[8] When the reaction was done in dichloromethane, formation of a product resulting from the net insertion of the carbene derived from EDA fragment into the C-Cl bond was observed. The mechanism for the formation of this product is depicted in Scheme 5.3. Formation of halonium ylide **298** followed by a 1,2 shift affords the insertion product **299**. This transformation was later on applied to allylic and propargylic halides. The AgTp-catalyzed (Tp = tris(pyrazolyl)borato) reaction provided the rearrangement products in good yields but poor diastereoselectivity (Table 5.1).[9]



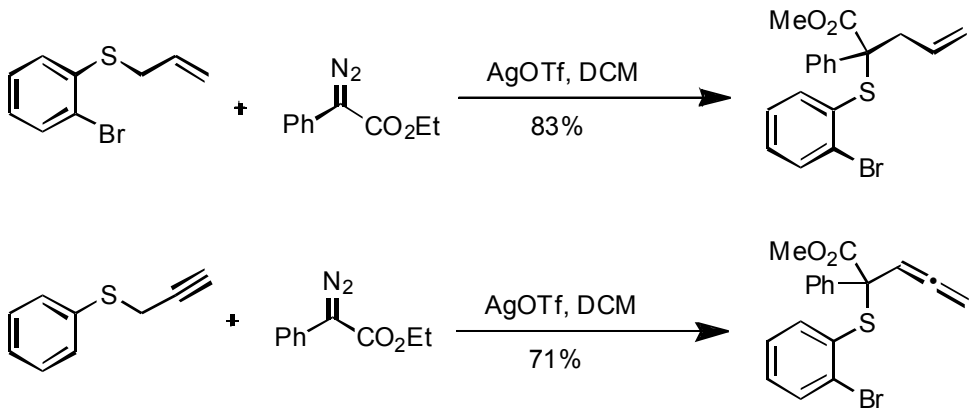
Scheme 5.3 Proposed mechanism for the silver carbenoid C-Cl insertion

Table 5.1. Ag(I)-catalyzed ylide/rearrangement of allylic and propargylic halides with EDA



entry	substrate	product	*syn/anti ratio*	yield (%)
1			1:1	86
2			1:1	70
3			--	71

Recently, Davies and coworkers reported a Ag(I)-catalyzed Doyle-Kirmse reaction of allylic and propargylic sulfides with ethyl phenyldiazoacetate (Scheme 5.4).[10] The reaction provided the rearrangement products, either homoallylic thioethers or allenyl thioethers in good yields and good overall scope. To our knowledge, the rearrangement reactions of allylic and propargylic alcohols with silver carbenoids have not been reported yet.

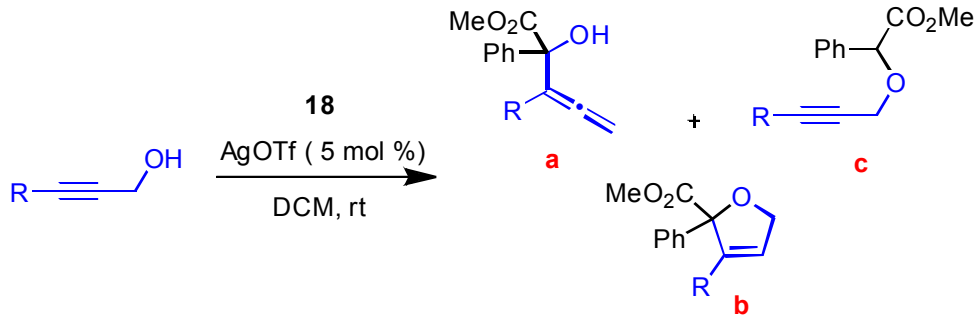


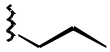
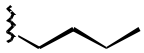
Scheme 5.4 Ag(I)-catalyzed rearrangement of allylic and propargyl sulfides

5.2 Results and Discussion

We began our studies by surveying various primary propargylic alcohols for the AgOTf-catalyzed reaction with methyl phenyldiazoacetate **18** as the carbenoid precursor (Table 5.2). We were very pleased that the formation of the traditional O-H insertion product was minimized. Interestingly, the reaction did not only afford the desired allenol product but also provided the unexpected dihydrofuran derivatives as the major product in most cases. In entries 1 and 7, only the dihydrofuran products **300** and **310** were formed in 84 and 85% yield, respectively. On the other hand, the reaction with the *tert*-butyl substituted alkynol (entry 6), only the O-H insertion product **309** was formed in 92% yield.

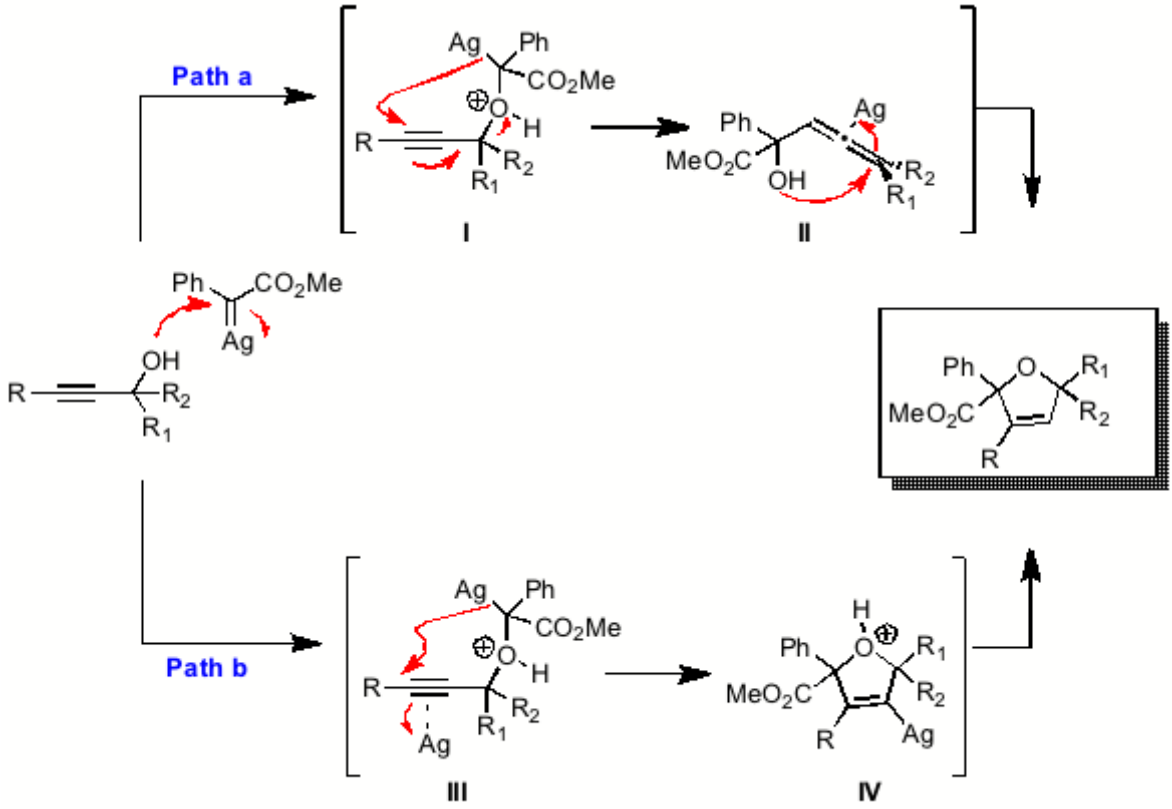
Table 5.2. Ag(I)-catalyzed reaction of primary propargylic alcohols and **18**



entry	R	yield **a** (%)	product	yield **b** (%)	product	yield **c** (%)	product
1	H	--	--	84	**300**	0	--
2		18	**301**	74	**302**	0	--
3		16	**303**	69	**304**	0	--
4		15	**305**	75	**306**	0	--
5		13	**307**	80	**308**	0	--
6		0	--	0	--	92	**309**
7	Ph	0	--	85	**310**	0	--

These results are interesting because they opened up a new opportunity for silver catalysts as backup for rhodium catalysts. In addition, it is intriguing that these primary alcohols only provided the tandem ylide formation/rearrangement product which is in stark contrast with the reaction outcome when dirhodium catalyst was used. The more impressive feature of this reaction is that instead of the expected allenol derivatives, the reaction favored the formation of the dihydrofuran products which we envisioned to have been the result of a silver-catalyzed cycloisomerization of the allenol product. The silver catalyst in this reaction not only catalyzed the decomposition of the diazo compound but

also promoted the cycloisomerization of allenol to the corresponding dihydrofuran product. With this knowledge in hand, we propose two pathways for the formation of the dihydrofuran product (Scheme 5.5). In Path **a**, the reaction begins by the attack of the alcohol substrate to the electrophilic silver carbenoid. The resulting ylide **I** undergoes a [2,3]-sigmatropic rearrangement to afford the allenol product **II**. Coordination of the allenic moiety to the Lewis acidic silver activates it for subsequent nucleophilic attack by the alcohol which results in cycloisomerization to form the dihydrofuran product. In path **b**, the reaction begins by nucleophilic attack of the alcohol to the silver carbenoid which results in the formation of ylide **III**. This intermediate can also be activated by silver which can directly undergo ring closure to form the metalated species **IV**. Protodemetallation and loss of proton of **IV** affords the dihydrofuran product. Although the isolation of the allenol product suggests that the reaction more likely goes though the mechanism described in path **a**, we cannot completely rule out the possibility that the reaction operates through path **b**. Therefore control experiments would be necessary and this would be discussed later on.

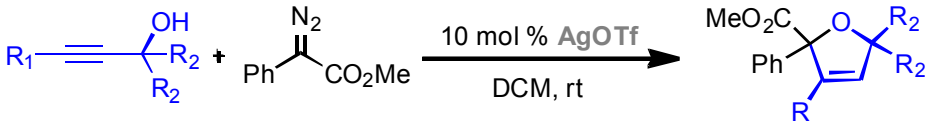


Scheme 5.5 Proposed mechanisms for the formation of dihydrofuran derivatives

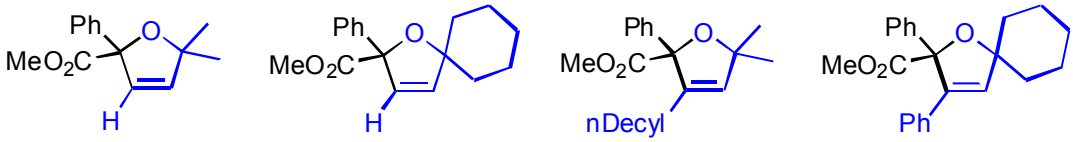
Having established that AgOTf is an effective catalyst for promoting the tandem ylide formation/[2,3]-rearrangement reaction of primary propargyl alcohols and donor/acceptor carbenoids, efforts were then made to determine the scope and generality of this reaction. We then turned our attention to the use of tertiary propargylic alcohols. Various tertiary propargylic alcohols were synthesized *via* lithiation of the corresponding terminal alkynes using *n*BuLi followed by quenching with acetone. These alcohols were then made to react with methyl phenyldiazoacetate **18** in the presence of catalytic amount of AgOTf (Table 5.3). The reaction is highly efficient, providing only the dihydrofuran products in excellent yields (81-97% yield). Both terminal and internal alkynols are

excellent substrate for this reaction. It is important to note that the formation of the O-H insertion product was minimal in all cases.

Table 5.3. Ag(I)-catalyzed reaction of 3° propargylic alcohols and **18**



18 **311-323**

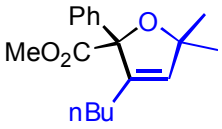


93% yield
311

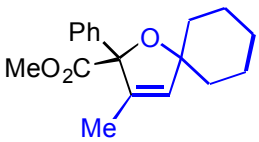
88% yield
312

92% yield
313

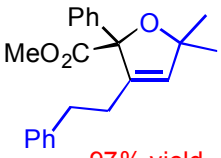
93% yield
314



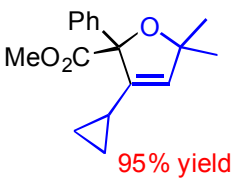
87% yield
315



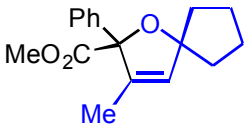
96% yield
316



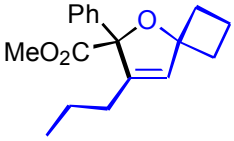
97% yield
317



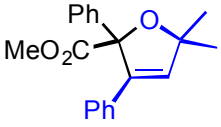
95% yield
318



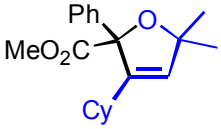
97% yield
319



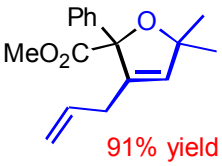
94% yield
320



90% yield
321



93% yield
322

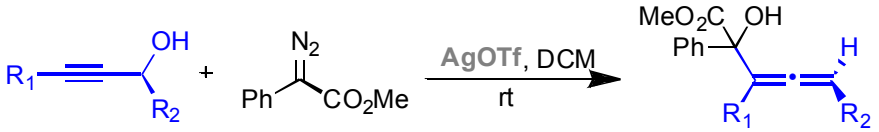


91% yield
323

A different reaction outcome was observed when secondary propargylic alcohols were used as substrates for the reaction (Table 5.4). Depending on the size of the substituent α

to the alcohol (R_2), either the allenol or a mixture of the allenol and the dihydrofuran derivative can be obtained. In cases where R_2 is larger than a methyl group, the

Table 5.4. Ag(I)-catalyzed reaction of 2° propargylic alcohols and **18**



18 **324-332**

entry	R_1	R_2	product	dr	% yield
1	Ph	*i*Pr	**324**	7:1	81
2	$PhCH_2CH_2$	Cy	**325**	4:1	75
3	Ph	Cy	**326**	7:1	77
4	Ph	*t*Bu	**327**	10:1	91
5	*i*Bu	*t*Bu	**328**	10:1	84

reaction led exclusively to the formation of the allenol product (entries 1-5). The products were formed in good yields and moderate diastereoselectivity. The structure of the allenol **327-Br**, the bromo derivative of allenol **327** (synthesized using *p*-bromophenyldiazoacetate as the carbenoid precursor) was confirmed by X-ray crystallographic analysis (Figure 5.1). On the contrary, when R_2 is only a methyl (Scheme 5.6), a diastereomeric mixture of both the allene and the dihydrofuran products was formed. Similar results were obtained when chiral racemic tertiary alcohols bearing bulky groups were used as substrates. Instead of the formation of dihydrofuran products, the reaction provided the allenol derivatives in moderate to good yields and good

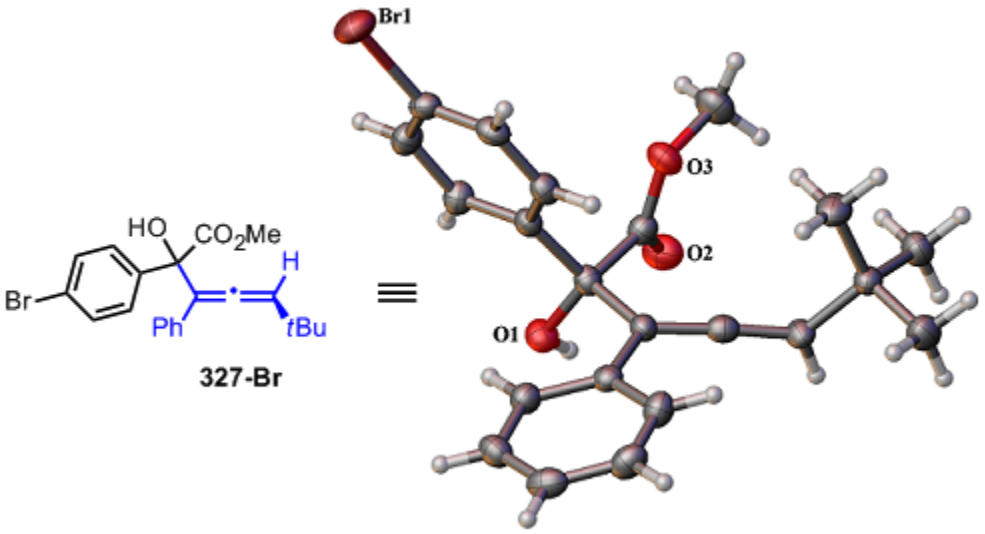
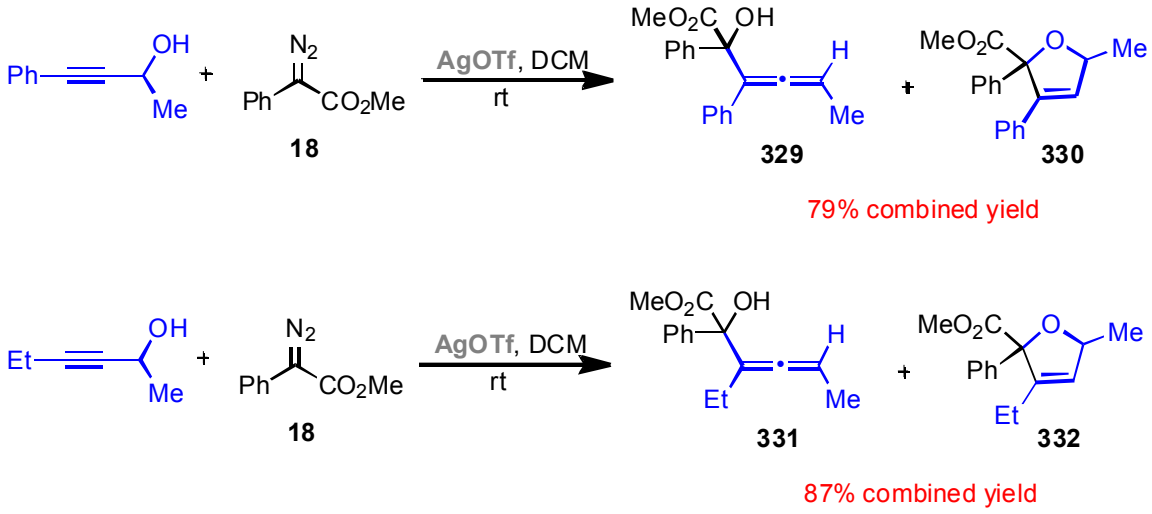


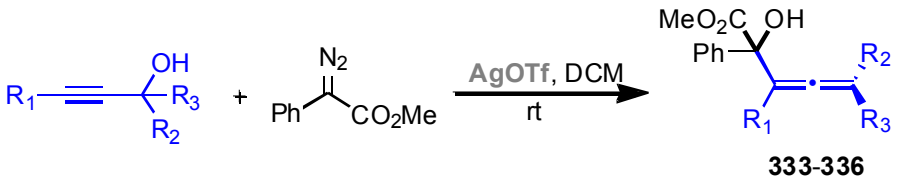
Figure 5.1 X-ray structure of allenol **327-Br**

diastereoselectivity. The structure and relative stereochemistry of the allenol was confirmed by X-ray crystallographic analysis (Figure 5.2). We reasoned that the bulky groups might hinder the coordination of the allenic moiety with the Lewis acidic AgOTf therefore disfavoring the cycloisomerization to occur.



Scheme 5.6 Ag(I)-catalyzed reaction of 2° alcohols and **18**

Table 5.5. Ag(I)-catalyzed reaction of 3° chiral propargylic alcohols and **18**



333-336

entry	R_1	R_2	R_3	product	dr	yield (%)
1	Ph	Me	*t*Bu	**333**	10:1	71
2	H	Me	*t*Bu	**334**	14:1	66
3	Me	Me	*t*Bu	**335**	10:1	61
4	Me	Ph	*t*Bu	**336**	3:1	69

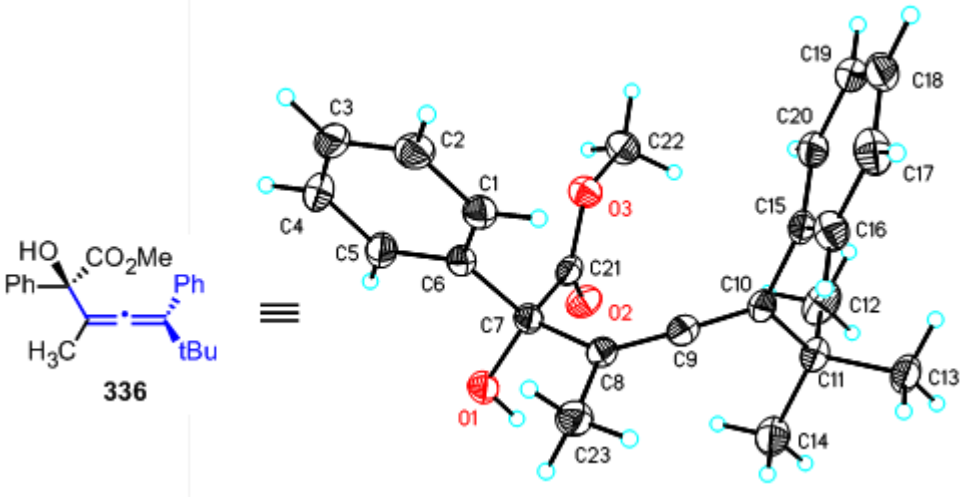
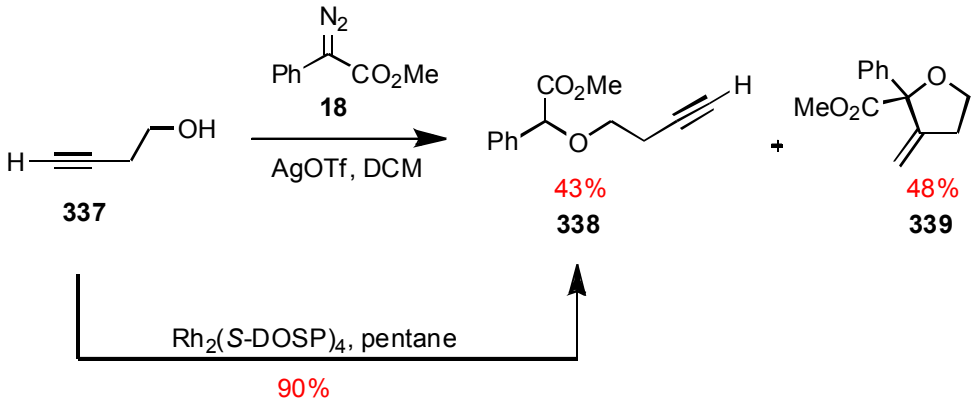


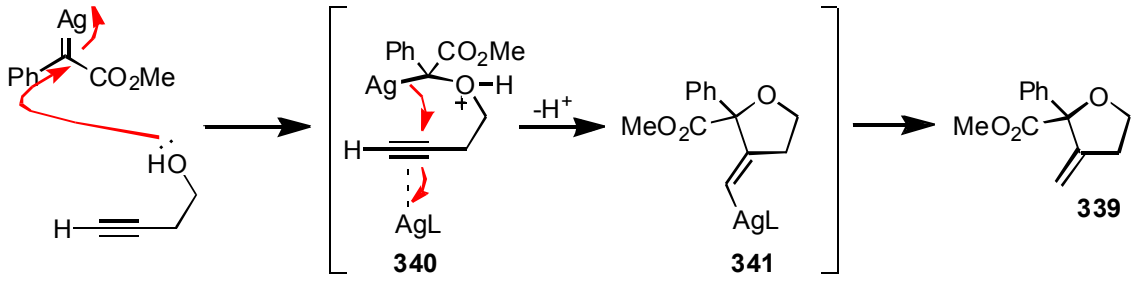
Figure 5.2 X-ray structure of allenol **336**

During the course of our study with the Ag(I)-catalyzed reactions of propargylic alcohols and aryl diazoacetates, we discovered another interesting reaction which involves the use of homopropargylic alcohols. These substrates provide the expected O-H insertion products under rhodium catalysis. However, when AgOTf was used as catalyst, the reaction of diazoacetate **18** and 3-butyn-1-ol **337** gave a mixture of the expected O-H insertion product **338** and a tetrahydrofuran derivative **339** (Scheme 5.7). A plausible mechanism for the formation of the tetrahydrofuran products is depicted in Scheme 5.8.



Scheme 5.7 Ag(I)-catalyzed reaction of 3-butyn-1-ol with **18**

The alcohol attacks the silver carbenoid to afford the ylide species **340.** Complexation of the alkyne moiety to the Lewis acidic Ag^{+} activates the alkyne for a subsequent nucleophilic attack and induces a 5-exo-dig ring closing to afford the carbocycle **341**. The tetrahydrofuran product **339** is formed upon protodemetallation of the metalated species **341**. This type of mechanism involving dinuclear intermediate has been proposed by Fokin and coworkers for the Copper-catalyzed Azide-Alkyne Cycloaddition (CuAAC) reaction (Figure 5.3). DFT calculations showed that the introduction of a



Scheme 5.8 Plausible mechanism for the formation

second copper(I) atom favorably influences the energetic profile of the reaction.[11] The reaction can be extended to various homopropargylic alcohol providing tetrahydrofuran derivatives in moderate to good yields and moderate diastereoselectivity (Table 5.6). The homopropargylic alcohols were synthesized *via* two-step procedure; (1) ring opening of the corresponding substituted epoxide by lithium trimethylsilylacetylide affording the homopropargylic alcohol followed by (2) removal of the TMS group by treatment of the resulting alcohol with potassium carbonate in MeOH.

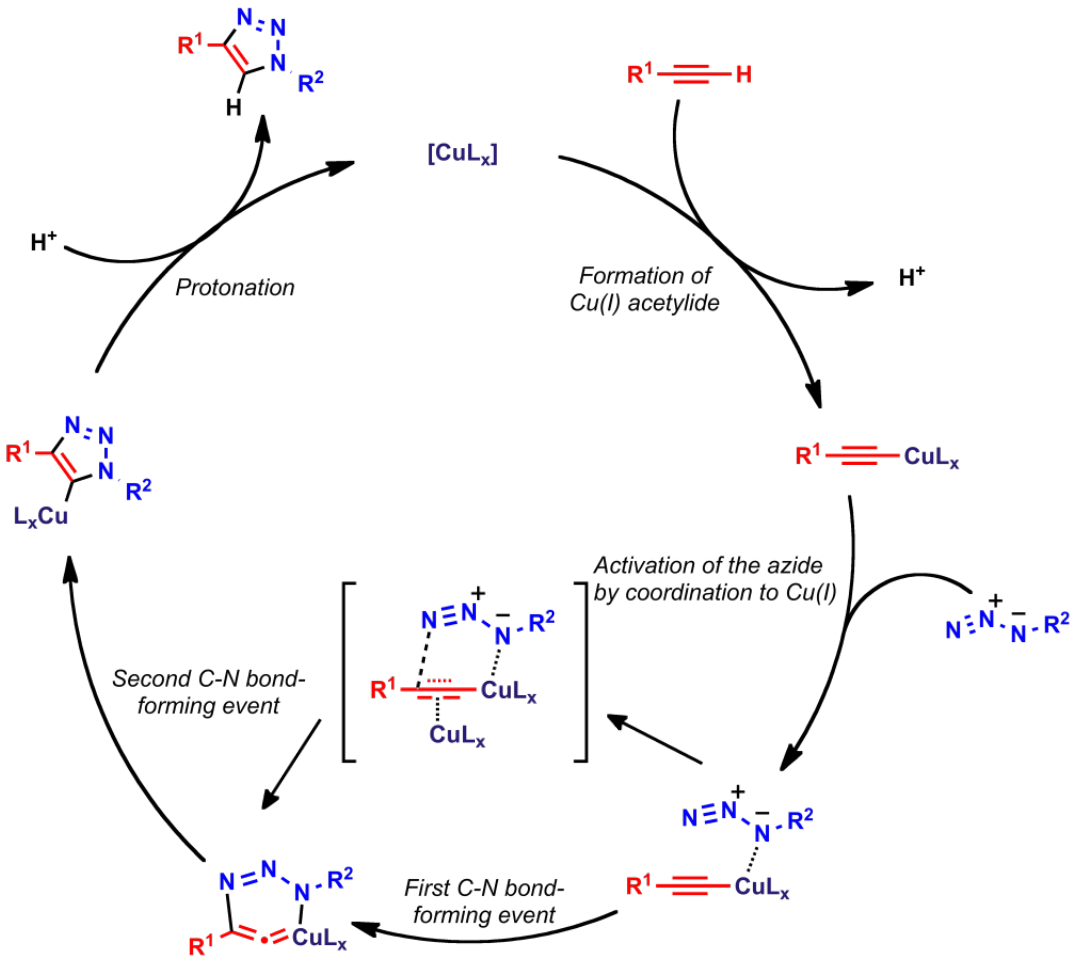
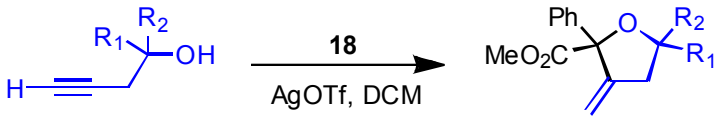
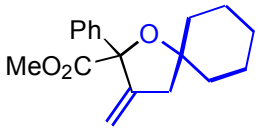


Figure 5.3. Proposed catalytic cycle for the CuAAC reaction based on DFT calculations

Table 5.6. Ag(I)-catalyzed reaction of homopropargylic alcohols and **18**

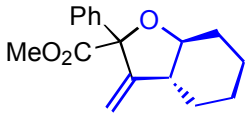


342-348



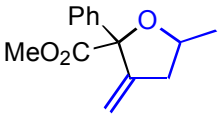
75% yield

342



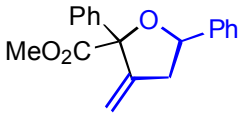
87% yield
>20:1 dr

343



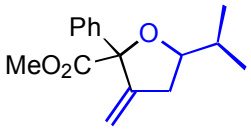
60% yield
5:1 dr

344



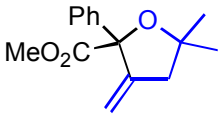
56% yield
3:1 dr

345



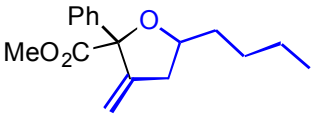
65% yield
10:1 dr

346



62% yield

347



65% yield
10:1 dr

348

We have already established that AgOTf effectively catalyzes the tandem ylide/[2,3]-rearrangement/cycloisomerization of propargylic alcohols with donor/acceptor carbenoids. Depending on the structure of the alcohol, either the allenol or the dihydrofuran product can be obtained. Because chiral allenes and dihydrofuran derivatives are useful intermediates in organic synthesis, we decided to focus our attention to the development of an enantioselective variant of the Ag(I)-catalyzed cascade reaction. The cyclization of chiral allenic alcohols to 2,5-dihydrofuran is an important synthetic transformation and has been applied to the total synthesis of important natural

products (Figure 5.3).[12,13] The attractive feature of our method is that potentially, enantioenriched 2,5-dihydrofuran

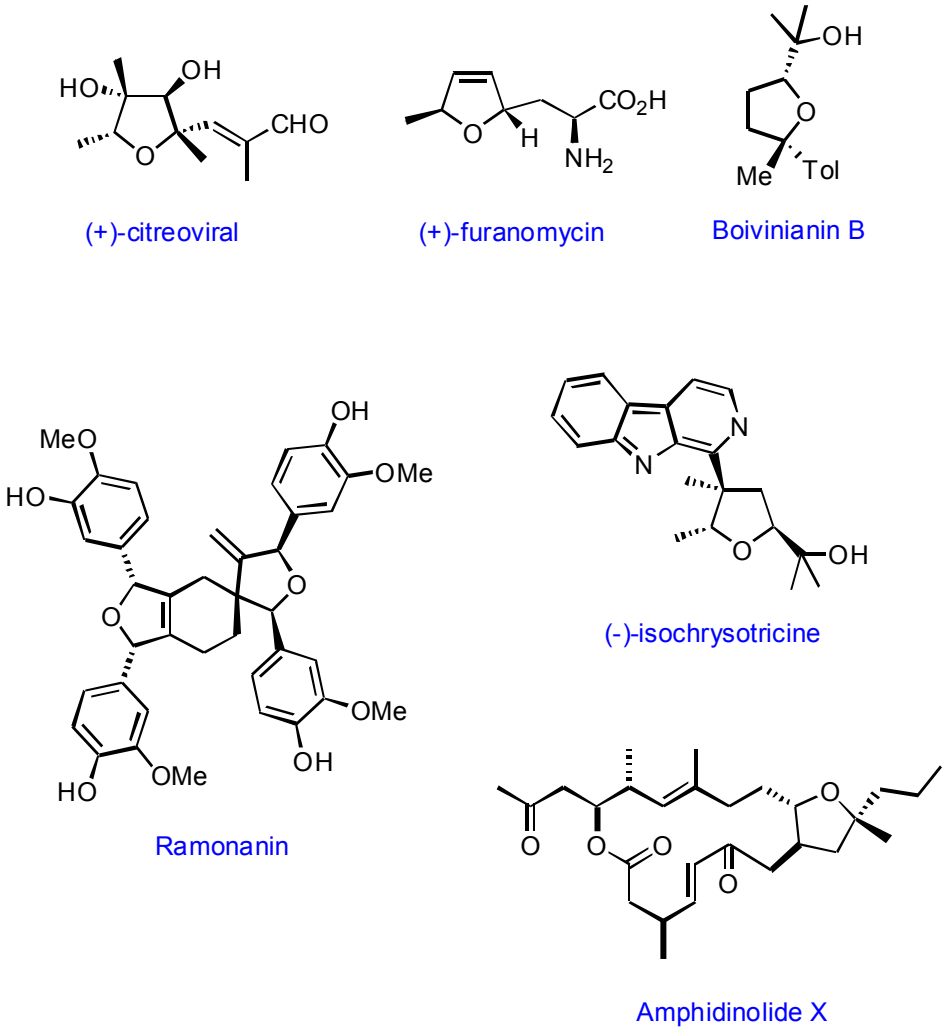


Figure 5.4. Dihydrofuran and tetrahydrofuran structures in natural products

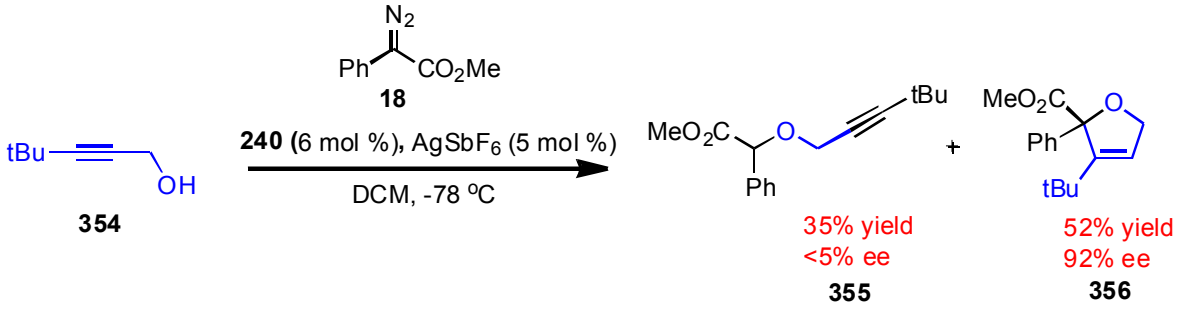
derivativess can be synthesized in one pot. Having recently developed the asymmetric cyclopropenation using gold(I) catalysts, we began our studies by using the digold(I)-BINAP catalyst **240** for the reaction of methyl phenyldiazoacetate **18** and primary propargylic alcohols (Table 5.7). We were pleased to find that the reaction conducted at -78 °C in dichloromethane provided the desired dihydrofuran products in moderate to good yields and moderate enantioselectivity. The O-H insertion product (<5% ee) is

formed as the minor product in all cases. Efforts in improving the enantioselectivity for the reaction with primary alcohols is still undergoing in the Davies group.

Table 5.7. Au(I)-catalyzed reaction of 1° propargylic alcohols and **18**

entry	R	product	yield (%)	ee (%)
1	Ph	**349**	57	51
2	ethyl	**350**	53	48
3	propyl	**351**	67	50
4	butyl	**352**	68	50
5	heptyl	**353**	80	51

Gratifyingly, we found that by adding a bulky group on the alkyne, such as the case of 4,4-dimethylpent-2-yn-1-ol **354**, the dihydrofuran product **356** was formed in 52% yield and 92% ee. The O-H insertion product was isolated in 35% yield and <5% ee (Scheme 5.9). It is important to note that when AgOTf was used as catalyst,

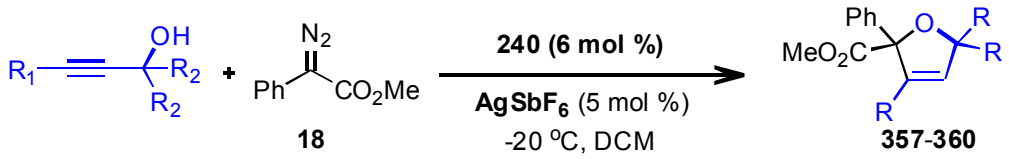


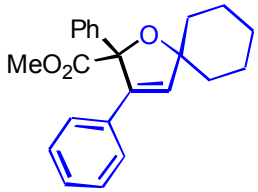
Scheme 5.9 Au(I)-catalyzed reaction of **18** and propargyl alcohol **354**

only the O-H insertion product was formed. At this point, we are still not certain of the gold carbenoid structure; however the dramatic increase in enantioinduction is very interesting because this group should point away from the ylide intermediate. One would expect that the chiral influence of the catalyst would be close to the ylide intermediate; however this seems not to be the case in this particular reaction. Determination of the active catalyst and carbenoid structures as well as development of a model for asymmetric induction to further understand this reaction is undergoing in our lab.

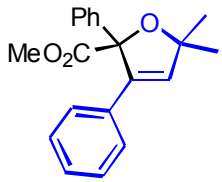
Good to excellent levels of enantioselectivity were also obtained when tertiary propargylic alcohols were used as substrate for the reaction (Table 5.8). The reaction provided the desired dihydrofuran products in good yields while the formation of the O-H insertion products was minimal in all cases. Both disubstituted and terminal alkynols work well for this reaction.

Table 5.8. Au(I)-catalyzed reaction of 3^{o} propargylic alcohols and **18**

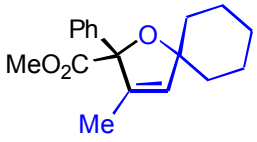




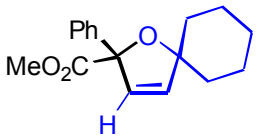
85% yield
92% ee
357



73% yield
90% ee
358

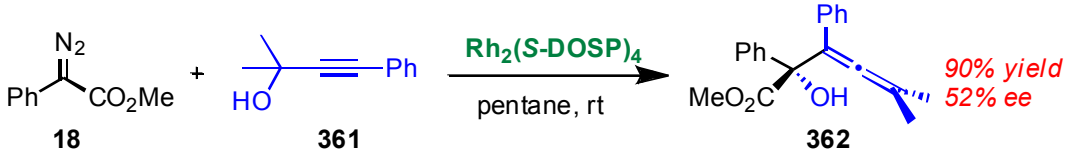


69% yield
91% ee
359

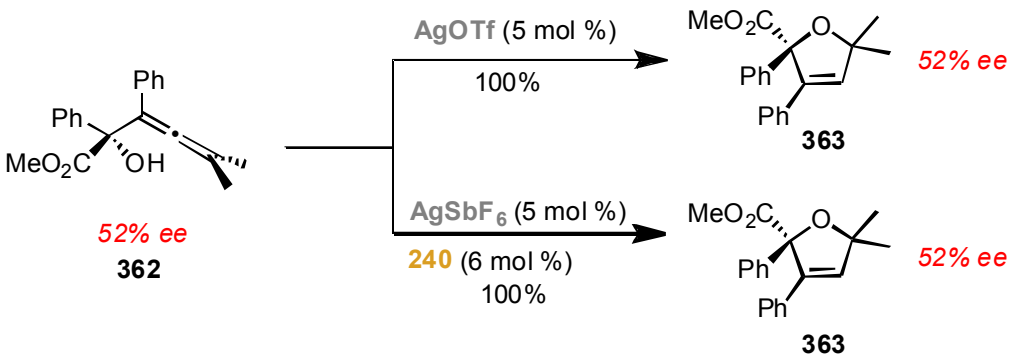


71% yield
83% ee
360

Control experiments were done to determine if the dihydrofuran derivatives resulted from the silver-catalyzed cycloisomerization of the corresponding allenol product. The enantioenriched allenol substrate **362** was synthesized from the reaction of propargyl alcohol **361** and **18** employing Rh_2(*S*-DOSP)$_4$ as catalyst (Scheme 5.10). This substrate was then treated with 5 mol % of AgOTf in $CDCl_3$ and was found to completely convert to the corresponding dihydrofuran product **363** after overnight stirring (Scheme 5.11). The same result was observed when was stirred in the presence of the **240** and $AgSbF_6$. Complete transfer of chirality was observed in both cases.

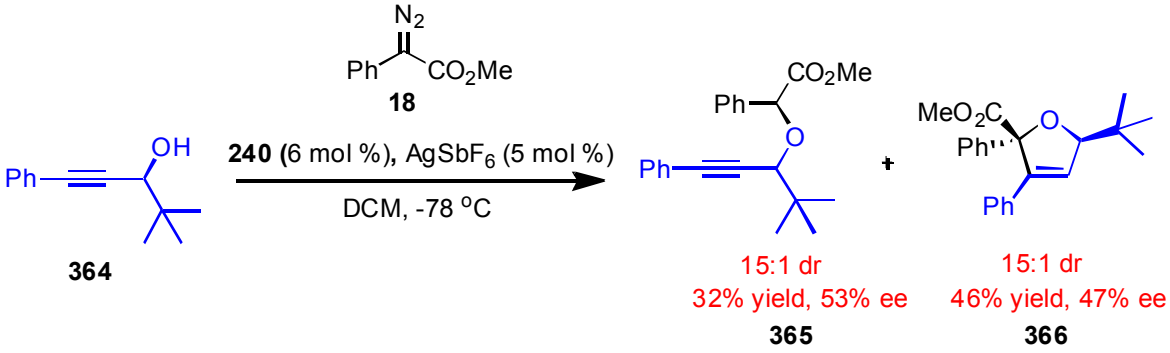


Scheme 5.10 Synthesis of allenol derivative **362**



Scheme 5.11 Ag(I)- and Au(I)-catalyzed cycloisomerization of allenol

Compared to primary and tertiary propargylic alcohols, reaction with secondary propargyl alcohols gave a slightly different reaction outcome. Preliminary results showed that when the propargyl alcohol **364** was used, ca 1:1 mixture of O-H insertion **365** and dihydrofuran product **366** was obtained (Scheme 5.11). The relative stereochemistry of furan **366** was tentatively assigned by nOe analysis. Interestingly, the major diastereomer of the O-H insertion product was formed in 53% ee. We are very intrigued by these results because these suggest that there could be an enantiodifferentiantion taking place. Future work includes reaction optimization as well as conducting the reaction using enantioenriched alcohols to confirm if there is in fact enantiodifferentiation occurring in this particular reaction.



Scheme 5.12 Au(I)-catalyzed reaction of **364** and **18**

5.3 Summary

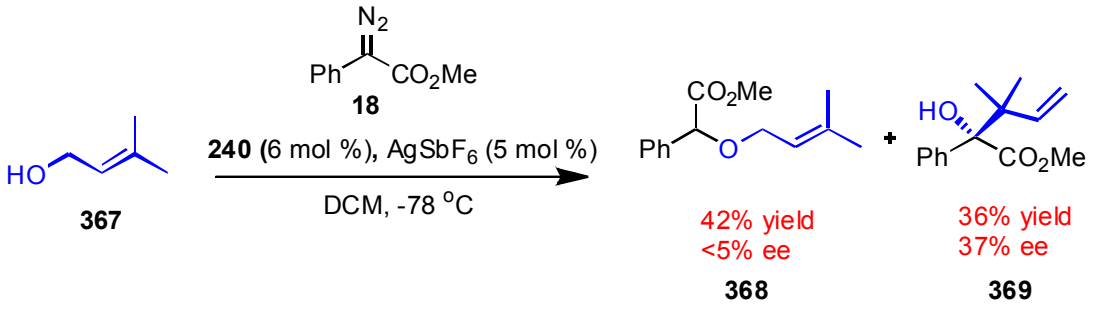
We have developed an efficient method of synthesizing racemic 2,5-dihydrofuran derivatives from the reaction of aryl diazoacetates and propargylic alcohols employing AgOTf as catalyst. Depending on the structure of the propargylic substrate, either the allenic or dihydrofuran product can be obtained. More importantly, the formation of traditional O-H insertion product was significantly suppressed in this reaction. These results provide new opportunities for developing novel transformations with silver(I)-stabilized donor/acceptor carbenoids and offers a backup solution for reactions that fail under rhodium catalysis. Moreover, preliminary results suggest that highly asymmetric tandem oxonium ylide formation/[2,3]-rearrangement/cycloisomerization reaction is possible when the chiral digold-BINAP complexes are employed as catalysts.

5.4 Future Directions

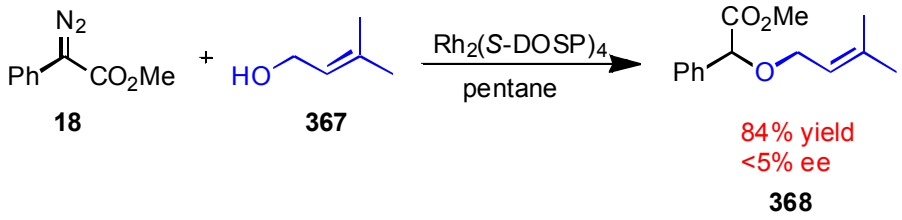
Although the Ag(I)-catalyzed cascade reaction is already well-established, the asymmetric Au(I)-catalyzed reaction of propargylic alcohols with donor/acceptor carbenoids is still in its infancy. A more extensive substrate scope should be surveyed for the reaction. Optimization of reaction conditions, including solvent, temperature and gold(I)-BINAP catalysts is undergoing in the Davies lab. The use of other types of donor/acceptor carbenoids, specifically vinyldiazo compounds, would also be explored in the future. Although the Davies group has reported that AgOTf promotes vinylogous addition of propargyl alcohols with styryldiazoacetates, it would be interesting to see if an entirely different reaction outcome would be observed when the digold-BINAP complexes are used instead.[14] A particularly interesting aspect of this reaction is the

dramatic effect of steric bulk of the substituent on the alkyne and therefore this would also be the focus of research in the future. Efforts to determine the absolute configuration of the allenic and dihydrofuran products are underway in our lab. The development of an enantioselective variant of the reaction of aryldiazoacetates and homopropargylic alcohols would also be extensively explored in the future. In addition, the use of disubstituted homopropargylic alcohols as substrate for the reaction would be explored.

The tandem ylide formation/[2,3]-rearrangement involving allylic alcohols was not explored in this study. However, preliminary results show that the reaction of primary alcohol **367** and methyl phenyldiazoacetate **18** gave about 1:1 mixture of O-H insertion **368** and the rearrangement product **369** (Scheme 5.12). The desired product was isolated in 36% yield and 37% ee. Although only moderate yield and enantioselectivity were obtained in this reaction, this result provides a potential solution for the reaction with primary allylic alcohols. Again, it is important to note that when Rh_2(*S*-DOSP)$_4$ was used as the catalyst, the reaction provided only the O-H insertion product in 84% yield and <5% ee (Scheme 5.13).[3] Future work in this area includes optimizing the reaction conditions (solvent, catalyst and temperature) as well as expanding the scope to other types of allylic alcohols.



Scheme 5.13 Au(I)-catalyzed reaction of **18** and primary allylic alcohol



Scheme 5.13 Rh_2(*S*-DOSP)$_4$-catalyzed reaction of **18** and primary allylic alcohol

5.5 References

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CHAPTER SIX

Highly Enantioselective Gold(I)-Catalyzed Vinylogous [3+2] Cycloaddition of Enol Ethers and Vinylcarbenoids

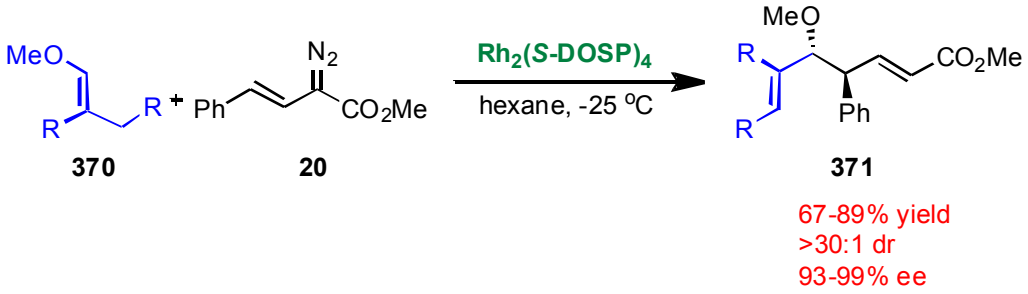
6.1 Introduction

The application of gold(I) catalysts for the decomposition of diazo compounds is a relatively unexplored area of research.[1] Moreover, the majority of these reports used achiral gold catalysts.[2] Recently, we found that using digold(I)-BINAP complexes popularized by Toste and coworkers[3], highly enantioselective cyclopropenation of internal alkynes can be achieved with donor/acceptor carbenoids.[4] This work led us to extensively explore new opportunities for Au(I)-stabilized donor/acceptor carbenoid especially for reactions that fail under rhodium catalysis. As part of our long standing interest in vinylogous reactivity of vinyl carbenoids[5], we began to investigate the possibility of using chiral Au(I)-BINAP complexes in promoting this type of reaction. We envisioned that gold catalysts will have the same reactivity as silver(I) salts in

displaying enhanced electrophilic character in the vinylogous position of vinyl carbenoids.[6] In this chapter we report the highly enantioselective Au(I)-catalyzed vinylogous [3+2] cycloaddition reaction involving vinyl ethers and styryldiazoacetates.

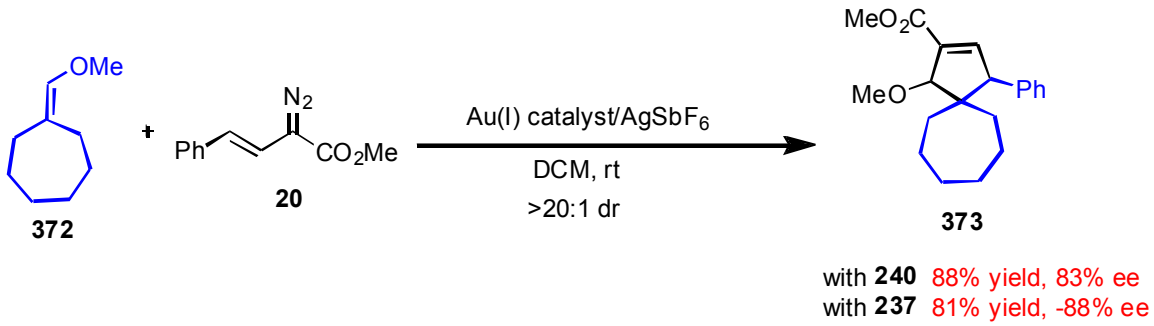
6.2 Results and Discussion

Recently, Lian and Davies reported that vinyl ethers undergo C-H insertion/Cope rearrangement (CHCR) leading to vinylogous Mukaiyama Aldol-type products in a highly diastereo- and enantioselective fashion (Scheme 6.1).[7] We decided to use these enol ethers as substrates



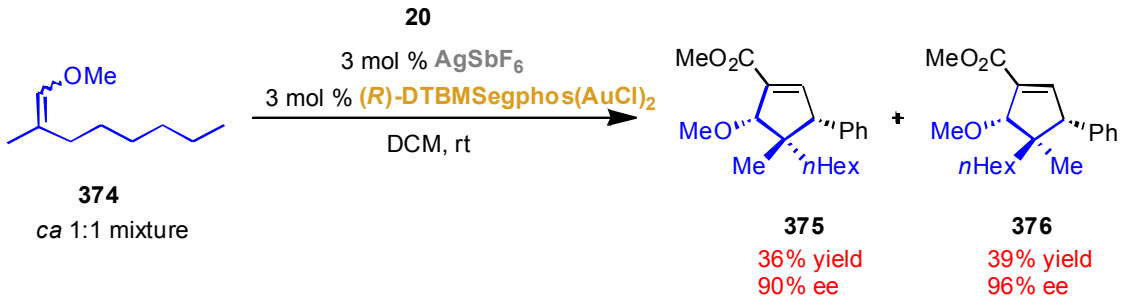
Scheme 6.1 Rh_2(*S*-DOSP)$_4$-catalyzed CHCR reaction of vinyl ethers and **20**

for the Au(I)-catalyzed reaction with vinyl carbenoids. In theory, theses type of substrates can undergo cyclopropanation, C-H insertion, CHCR or [3+2] cycloaddition reaction. We envisaged that Au(I) vinylcarbenoids have enhanced vinylogous reactivity like silver(I) salts therefore the cycloaddition reaction *via* vinylogous attack will be favored. Indeed, reaction of cyclic vinyl ether **372** with phenylvinyldiazoacetate **20** catalyzed by (*S*)-xylylBINAP(AuCl)$_2$ **240** afforded the formal [3+2] cycloaddition product **373** in 88% yield (Scheme 6.2). More importantly, the product was formed as a single diastereomer and in good enantioselectivity (83% ee). The enantioselectivity can be further improved when (*R*)-DTBMSegphos(AuCl)$_2$ **237** was used as the catalyst affording **373** in 81% yield and 88% ee. With



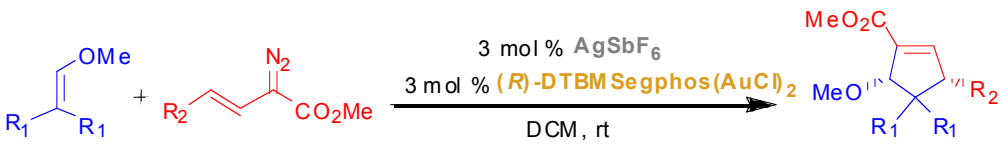
Scheme 6.2 Au(I)-catalyzed reaction of vinyl ethers and **20**

the optimized catalyst in hand, we then explored the scope and generality of this reaction. Various cyclic and acyclic vinyl ethers were synthesized and subjected to the standard reaction conditions (Table 6.1). Indeed, the reaction works well with both cyclic and acyclic substrates providing the desired cyclopentene derivatives **377**-**380** in good yields (68-81%) and excellent enantioselectivity (88-92%). The reaction is highly chemoselective as no cyclopropanation or C-H insertion product was observed. The reaction can also be expanded to different aryl and alkylvinyldiazoacetates using vinyl ether **372** as the representative substrate (entries 5-11). The cyclopentene derivatives **381**-**387** were obtained in good yields (70-90%) and excellent enantioselectivity (91-95%). The utility of this transformation can also be demonstrated in the reaction with an inseperable regioisomeric mixture of enol ether (*ca* 1:1 ratio of isomers). The reaction provided a 1:1 mixture of diastereomers derived from each regioisomer in good yields and excellent enantioselectivity (Scheme 6.3). The relative configuration of each diastereomer was tentatively assigned by nOe analyses.

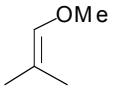
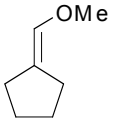
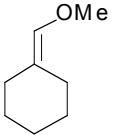
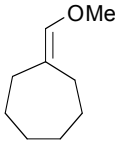
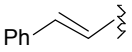


Scheme 6.3 Au(I)-catalyzed reaction of mixed vinyl ether **374** and **20**

Table 6.1 Au(I)-catalyzed vinylogous [3+2] reaction of enol ethers and **20**



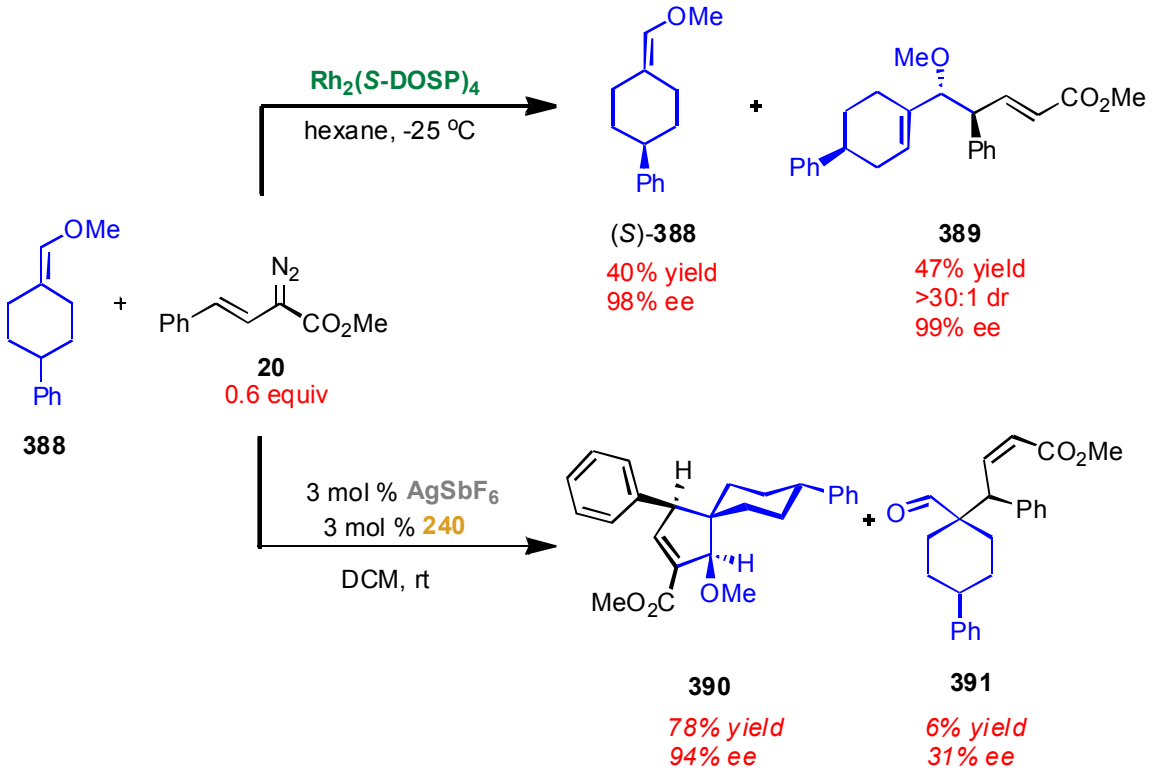
377-387

entry	ethers	R_2	product[a]	yield (%)	ee (%)
1		Ph	**377**	73	92
2		Ph	**378**	68	90
3		Ph	**379**	71	90
4		Ph	**380**	81	88
5		2-Naph	**381**	77	94
6		*p*-OMePh	**382**	79	91
7		*m*,*p*-diClPh	**383**	76	95
8		*p*-BrPh	**384**	84	93
9		Me	**385**	90	91
10		Et	**386**	84	95
11			**387**	70	91

[a] The diastereoselectivity was >20:1 in all cases

We have demonstrated in the past that donor/acceptor carbenoids are capable of kinetic resolution[8], desymmetrization[9] and enantiomer differentiation[10]. This was also recently demonstrated by Lian and Davies in the CHCR reaction with vinyl ethers.[7]

Kinetic resolution was achieved by the reaction of **388** and 0.6 equiv of **20** catalyzed by Rh_2(*S*-DOSP) which afforded the CHCR product **389** as a single diastereomer with 99% ee (Scheme 6.4). The enantioenriched vinyl ether (*S*)-**388** was recovered in 40% yield and 98% ee.



Scheme 6.4 Dynamic kinetic resolution in the Au(I)-catalyzed vinylogous [3+2] reaction

To explore the possibility of kinetic resolution in the Au(I)-catalyzed vinylogous [3+2] cycloaddition reaction, we conducted the reaction of enol ether **388** in the presence of 0.6 equiv of vinyldiazoacetate **20** and using **240** as the catalyst (Scheme 6.4). We were very intrigued by the reaction outcome because the desired spirocyclic product **390** was isolated in slightly more than 50% yield and 94% ee. The absolute stereochemistry of the spirocyclic product was confirmed by X-ray crystallographic analysis (Figure 6.1). The

absolute configuration of the remaining cyclopentene derivatives was assigned by analogy to **390**. Another product, the aldehyde **391**, was also formed in the reaction which was isolated in 6% yield and 31% ee. The relative stereochemistry of **391** has not yet been established. In addition, the recovered starting material was obtained as racemate in isolated yield. These results suggest that instead of kinetic resolution, we achieved a dynamic kinetic resolution. We reason that in the presence of the Lewis acidic gold(I) catalyst, equilibration of the enantiomers of vinyl ether **388** occurs.[11] One of the enantiomer then reacts with the vinyl carbenoid to form the desired

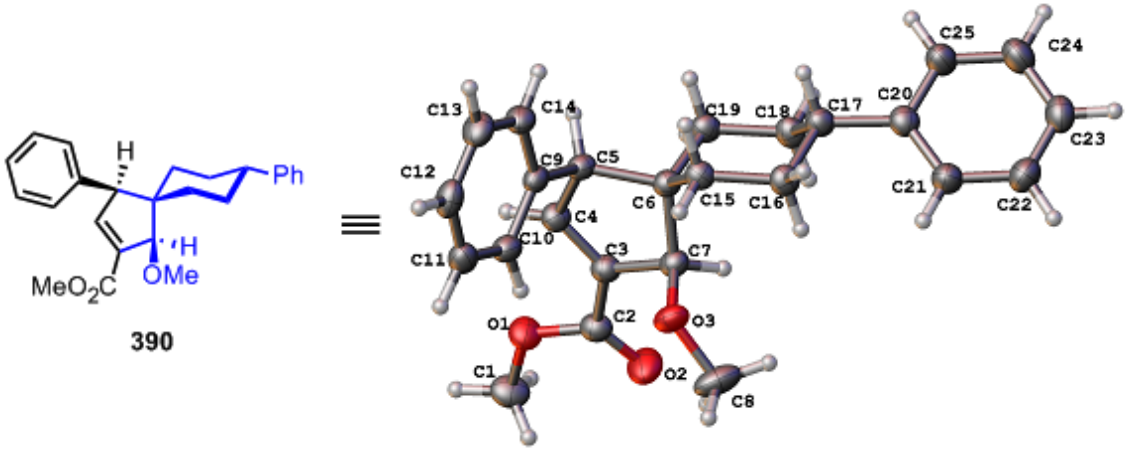


Figure 6.1 X-ray structure of **390**

spirocyclic product. To test our hypothesis, we subjected the enantioenriched cyclic ether (*S*)-**388** to the standard reaction conditions in the absence of the diazo compound. Indeed, after stirring for 12 hours, GC analysis showed that enantioerosion occurred from 98% ee to 43% ee. This confirms our hypothesis that under the reaction conditions, equilibration of the two enantiomers of the cyclic enol ether happens which led to dynamic kinetic resolution. With this knowledge in hand, we investigated the generality of the reaction

with cyclic enol ethers bearing different axial substituents and using **237** as catalyst (Table 6.2). Using 1.2 equiv of the diazo compound, the reaction provided the spirocyclic products **392-394** in good yields (62-70%) and excellent enantioselectivity (93-97%). The absolute configurations of both enantiomers of spirocyclic product **394** were confirmed by X-ray crystallographic analysis (Figure 6.3). Formation of the aldehyde product was minimal in all cases.

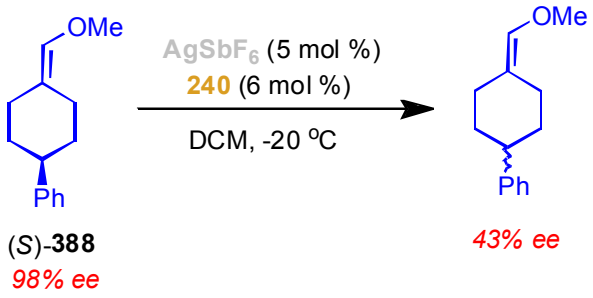
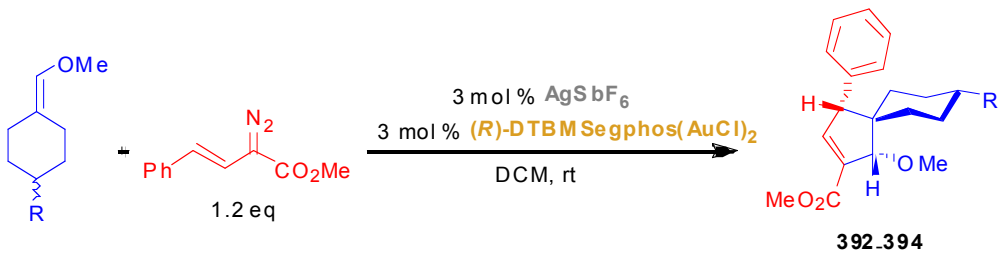


Figure 6.2 Enantioerosion of enol ether (*S*)-**388**

Table 6.2 Dynamic kinetic resolution in the Au(I)-catalyzed vinylogous [3+2] reaction



392-394

entry	R	product	dr	yield (%)	ee (%)
1	Me	**392**	>20:1	65	93
2	Ph	**393**	>20:1	62	93
3	*t*Bu	**394**	>20:1	70	97

The mechanism for the formation of spirocyclic product **390** and aldehyde **391** is depicted in Scheme 6.5. The major difference between the two pathways is the configuration of the vinyl carbenoid. Davies and Hansen recently reported that based on

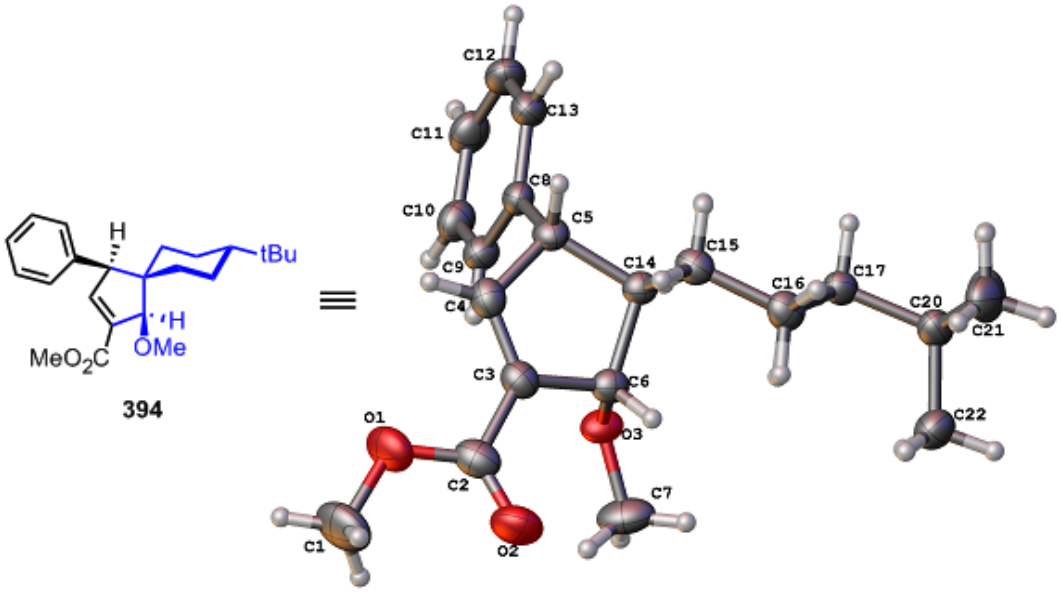
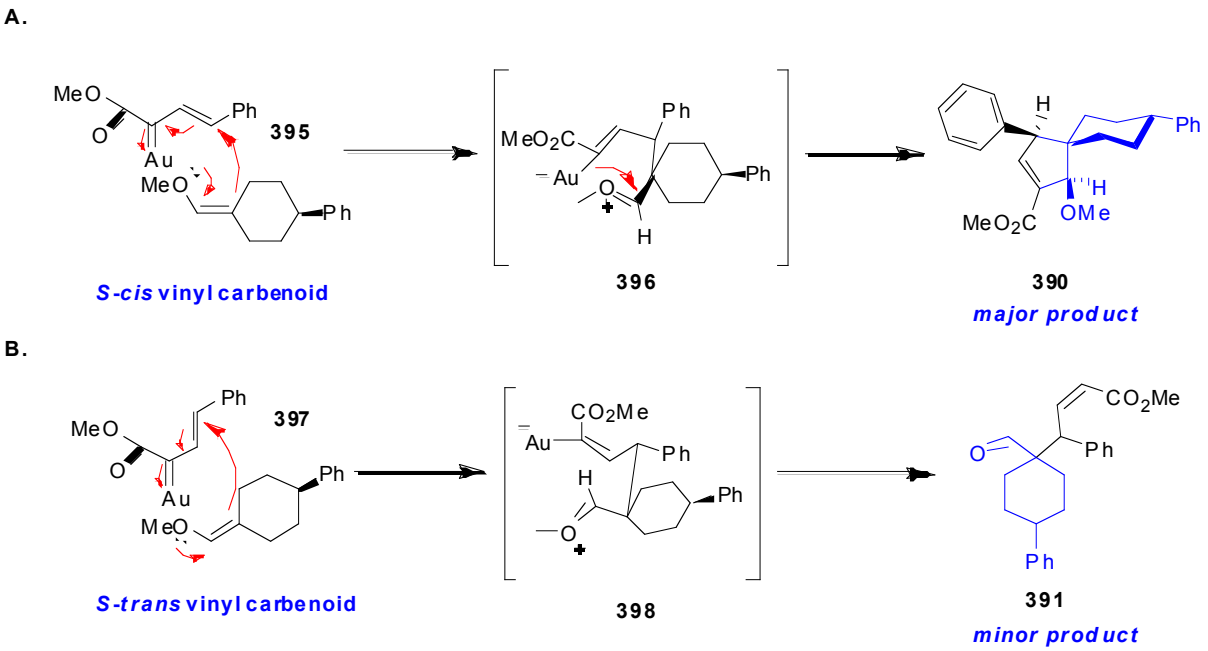


Figure 6.3 X-ray structure of **394**

DFT calculations, the *s-cis* configuration of vinylcarbenoid derived from silver triflate and phenylvinyldiazoacetate **20** is strongly favored over the *s-trans* orientation by about 5.4 kcal/mol.[6b] Based on the product distribution, this seems to also be the case for the

gold(I)-stabilized vinylcarbenoid wherein the *s-cis* orientation is more favored over the *s-trans*. The major product **390** is formed from the frontal attack of the vinyl ether nucleophile to the *s-cis* vinyl carbenoid **395** which affords the zwitterionic intermediate **396**. The Ph group is shown to be sticking out of the plane, as well as the methoxy group pointing up to prevent steric repulsion with the catalyst "wall". This intermediate then undergoes a ring closing to form the desired spirocyclic product **390**. On the other hand, the aldehyde **391** is formed from the frontal attack of the nucleophile to the *s-trans* vinyl

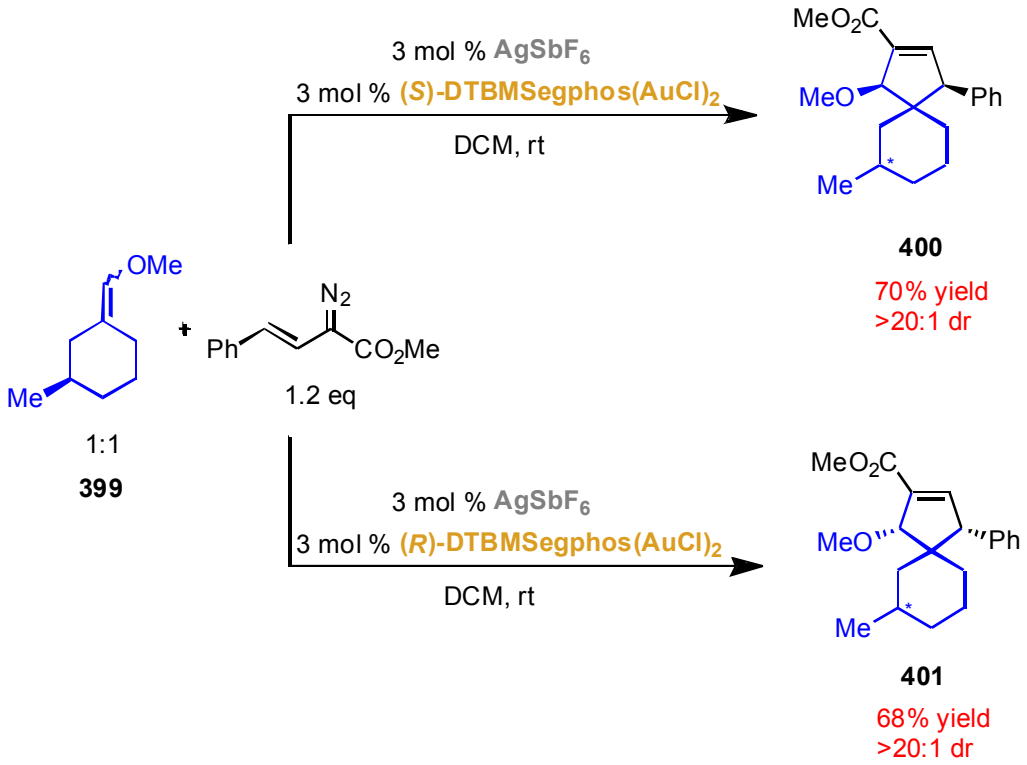


Scheme 6.5 Proposed mechanism for the formation of **390** and **391**

carbenoid **397** which affords the zwitterionic intermediate **398**. This intermediate is not properly set up to undergo ring closing and therefore undergoes demethylation and protodemetallation to afford the aldehyde product. This mechanism explains the *cis* geometry of the double bond in product **391**. Also, the moderate enantioselectivity observed for aldehyde **391** is consistent with a nucleophilic attack *via* the *s-trans* orientation as this position is located away from the chiral influence of the catalyst. At

this point, we are not certain about the exact nature of the demethylation step as well as the relative configuration of the aldehyde product.

The reaction can also be extended to more elaborate systems such as the vinyl ether **399** which was generated as a 1:1 mixture of regioisomers from the enantiopure 3-methylcyclohexanone (Scheme 6.6). Opposite diastereomers **400** and **401** can be synthesized depending on the enantiomer of the catalyst DTBMSegphos$(AuCl)_2$ used. In this reaction, equilibration of the two isomers of **399** occurs while one of the diastereomers reacts with the vinylcarbenoid to form the spirocyclic product. The formation of a single diastereomer in both cases showcases complete catalyst control. The absolute and relative configuration of products **400** and **401** has not been confirmed yet.



Scheme 6.6 Au(I)-catalyzed reaction of **399** and **20**

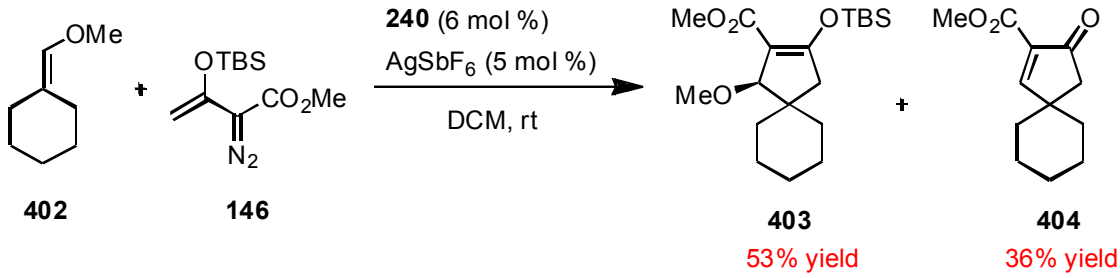
6.3 Summary

We have developed the highly enantioselective Au(I)-catalyzed vinylogous [3+2] cycloaddtion of vinyl ethers and vinyldiazoacetates. This reaction allowed us to access highly functionalized cyclopentene derivatives with 3 stereocenters constructed in a single step. Moreover, dynamic kinetic resolution was achieved when cyclic enol ethers bearing axial substituent was used as substrate. This report constitutes the first example of dynamic kinetic resolution in metal carbenoid chemistry. Moreover, this work is a great advance to the growing field of asymmetric gold(I)-catalyzed carbenoid trnasformations.

6.4 Future Directions

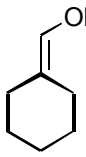
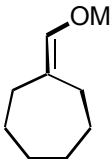
The reaction can also be extended to siloxyvinyldiazoacetates. Preliminary results show that the Au(I)-catalyzed reaction of enol ether **402** with siloxyvinyldiazoacetate **146** provided not only the expected cyclopentene product **403** but also the cyclopentenone derivative **404** (Scheme 6.7). This product arose from the deprotection of the siloxy group of cyclopentene under the Lewis acidic conditions. The enantiomeric excess of spirocyclic product **403** has yet to be determined. When substituted siloxyvinyldiazoacetates were used, the reaction only provided the cylcopentenone products in good yields (79-80%) and moderate enantioselectivity (79% ee for cyclopentenone **406**) (Table 6.3). The enantiomeric excess of product **405** has not been determined yet as well as the absolute stereochemistry of the cyclopentenone products. Since cyclopentenones are key intermediates in organic syntheses, future work will be devoted to the optimization of conditions (solvent, temperature etc.) for this reaction. Preliminary results also showed promising level of enantioselectivity therefore various

Au(I)-BINAP complexes will be screened to achieve better levels of enantioinduction. Lastly, application in synthesis of natural product targets will also be explored in the future.



Scheme 6.7 Au(I)-catalyzed reaction of **399** with **146**

Table 6.3 Au(I)-catalyzed vinylogous [3+2] with enol ethers and siloxyvinyldiazoacetates

entry	enol ether	R	product	yield (%)	ee (%)
1		Ph	**405**	80	TBD
2		Me	**406**	79	79

6.5 References

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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. All solvents were dried by a solvent purification system (passed through activated alumina columns). All other reagents were obtained from commercial sources and used as received unless otherwise stated. ^{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 δ H 0.00 for TMS in $CDCl_3$ 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 $CDCl_3$. 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} and were obtained using Nicolet iS10 FT-IR spectrometer. 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.

Experimental section for Chapter II: Rh(II)-Catalyzed Cyclopropenation of Terminal Alkynes

I. General procedure for Rh_2(*S*-DOSP)$_4$-Catalyzed cyclopropenation of alkyl alkynes

A mixture of alkyne (0.5 mmol) and Rh(II) catalyst (0.01 mmol) was dissolved in 1 mL pentane and stirred at -45°C under an atmosphere of argon. Vinyldiazoacetate (1.0 mmol) in 10 mL pentane was then added to former solution *via* syringe pump over 2 h. After addition, the mixture was stirred for additional 20 min then concentrated *in vacuo*. The residue was purified on silica using hexane/ether as solvent system in the ratio specified in parenthesis.

II. General procedure for Rh_2(*S*-DOSP)$_4$-Catalyzed synthesis of cyclopentadiene derivatives

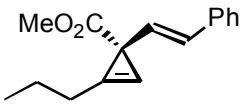
In a two-neck round bottom flask equipped with condenser was added alkyne (0.5 mmol), Rh(II) catalyst (0.01 mmol) and 1 mL 2,2-dimethylbutane (DMB). The solution was stirred under an atmosphere of argon then heated to reflux. Vinyldiazoacetate (1.0 mmol) in 10 mL DMB was then added to former solution *via* syringe pump over 2 h.

After addition, the mixture was allowed to warm to room temperature. After stirring for additional 20 min the crude reaction mixture was concentrated *in vacuo*. The residue was purified on silica using hexane/ether as solvent system in the ratio specified in parenthesis.

III. Procedure for the Synthesis of Alcohol 110.

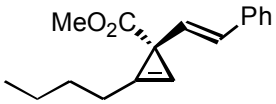
A mixture of phenylacetylene (0.5 mmol) and Rh_2(*S*-DOSP)$_4$ (0.01 mmol) was dissolved in 1 mL pentane and stirred at -45°C under an atmosphere of argon. Vinyldiazoacetate (1.0 mmol) in 10 mL pentane was then added to former solution *via* syringe pump over 2 h. After addition, the mixture was stirred for additional 20 min then the solution was cooled to 0°C by using an ice bath. 1 ml of Lithium aluminum hydride solution (2.4M in THF) was then added dropwise to the crude reaction mixture and stirring was continued at 0°C for 1 hour. The reaction mixture was warmed to room temperature and quenched with saturated aqueous ammonium chloride solution and the layers were separated. The aqueous layer was extracted with diethyl ether and the combined organic layers was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified on silica using 4:1 hexane/EtOAc as solvent system to provide the corresponding alcohol.

IV. Spectral data and full characterization of all compounds



90

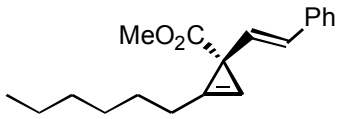
***(R,E)*-methyl 2-propyl-1-styrylcycloprop-2-enecarboxylate (90)**. Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **90** in 81% yield (99 mg) as yellow oil. 99% ee (determined by HPLC: (R,R)-Whelk, 5% i-PrOH in hexanes t_R=8.37 (major) t_R=9.82 (minor)). IR (neat) 1716, 1245, 743 cm^{-1}; ^1H NMR (400 MHz) δ 7.15-7.38 (m, 6H), 6.33 (app t, 1H, *J* = 1.5 Hz), 6.04 (d, 1H, *J* = 15.9 Hz), 3.72 (s,1H), 2.49 (td, 2H, *J* = 7.5, 1.5 Hz), 1.62 (s, 2H, *J* = 7.5 Hz), 0.98 (t, 3H, *J* = 7.5 Hz); ^{13}C-NMR (100 MHz) δ 176.2 (C=O), 137.7 (C), 131.7 (CH), 128.7 (CH), 127.9 (CH), 127.1 (CH), 126.3 (CH), 116.7 (C), 93.3 (CH), 52.2 (CH_3), 30.6 (C), 25.7 (CH_2), 20.6 (CH_2), 13.9 (CH_3). HRMS (ESI) *m/z* calcd for $C_{16}H_{18}O_2$, 242.1307, found 242.13014.



91

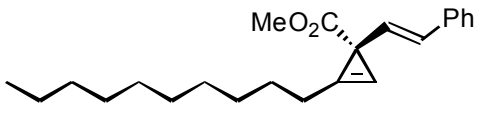
***(R,E)*-methyl 2-butyl-1-styrylcycloprop-2-enecarboxylate (91)**. Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **91** in 78% yield (100 mg) as yellow oil. 98% ee (determined by HPLC: (R,R)-Whelk, 5% i-PrOH in hexanes t_R=8.59 (major) t_R=10.10 (minor)). $[\alpha]^{25}_D$ +1.01° (c 1.24, $CHCl_3$); IR (neat) 1716, 1241, 748 cm^{-1};

^{1}H NMR (400 MHz) δ 7.17-7.38 (m, 6H), 6.33 (s, 1H), 6.01 (d, 1H, *J* = 16 Hz), 3.73 (s, 1H), 2.52 (t, 2H, *J* = 7.2 Hz), 1.59 (s, 2H, *J* = 7.2 Hz), 1.42 (dq, 2H, *J* = 7.2, 2.4 Hz), 0.92 (t, 3H, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz) δ 176.3 (C=O), 137.7 (C), 131.7 (CH), 128.7 (CH), 127.9 (CH), 127.1 (CH), 126.3 (CH), 116.9 (C), 93.2 (CH), 52.2 (CH_3), 30.6 (C), 29.2 (CH_2), 23.4 (CH_2), 22.4 (CH_2), 13.9 (CH_3). HRMS (ESI) *m/z* calcd for $C_{16}H_{21}O_2$, 257.1497, found 257.15363 $[M+H]^+$.



92

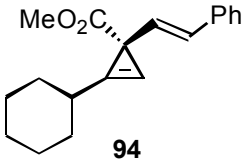
***(R,E)*-methyl 2-hexyl-1-styrylcycloprop-2-enecarboxylate (92)**. Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **92** in 85% yield (120 mg) as yellow oil. 99% ee (determined by HPLC: (R,R)-Whelk, 5% i-PrOH in hexanes t_R=7.90 (major) t_R=9.16 (minor)). IR (neat) 1716, 1239, 746 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.14-7.36 (m, 6H), 6.30 (app t, 1H, *J* = 1.6 Hz), 6.01 (d, 1H, *J* = 16.4 Hz), 3.70 (s, 1H), 2.48 (td, 2H, *J* = 7.6, 1.6 Hz), 1.57 (q, 2H, *J* = 7.6 Hz), 1.19-1.37 (m, 6H), 0.86 (t, 3H, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz) δ 176.2, 137.7, 131.8, 128.7, 127.9, 127.1, 126.3, 116.9, 93.3, 52.2, 31.7, 30.6, 29.0, 27.1, 23.7, 22.8, 14.2. HRMS (ESI) *m/z* calcd for $C_{19}H_{25}O_2$, 285.1810, found 285.18504 $[M+H]^+$.



93

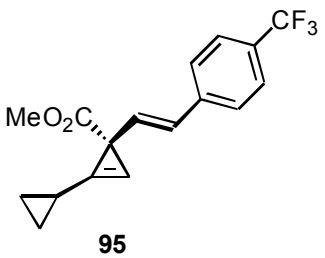
***(R,E)*-methyl 2-decyl-1-styrylcycloprop-2-enecarboxylate (93)**. Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **93** in 87% yield (147 mg) as

yellow oil. 97% ee (determined by HPLC: (R,R)-Whelk, 5% i-PrOH in hexanes t_R=7.59 (major) t_R=9.06 (minor)). $[\alpha]^{25}_D$ +11.36° (c 1.00, $CHCl_3$); IR (neat) 1717, 1240, 752 cm^{-1}; ^1H NMR (400 MHz) δ 7.15-7.35 (m, 6H), 6.30 (s, 1H), 6.00 (d, 1H, *J* = 16 Hz), 3.69 (s, 1H), 2.47 (td, 2H, *J* = 7.6, 1.6 Hz), 1.54 (q, 2H, *J* = 7.6 Hz), 1.22-1.40 (m, 14H), 0.85 (t, 3H, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz) δ 176.2, 137.7, 131.7, 128.7, 127.9, 127.1, 126.3, 116.9, 93.2, 52.2, 32.1, 30.6, 29.8, 29.7, 29.5, 29.4, 29.3, 27.1, 23.7, 22.8, 14.3. HRMS (ESI) *m/z* calcd for $C_{23}H_{33}O_2$, 341.2436, found 341.24722 $[M+H]^+$.



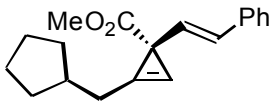
94

***(R,E)*-methyl 2-cyclohexyl-1-styrylcycloprop-2-enecarboxylate (94)**. Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **94** in 78% yield (111 mg) as yellow oil. 97% ee (determined by HPLC: (R,R)-Whelk, 5% i-PrOH in hexanes t_R=7.91 (major) t_R=10.18 (minor)). $[\alpha]^{25}_D$ +3.47° (c 1.00, $CHCl_3$); IR (neat) 2927, 1713, 1242, 747 cm^{-1}; ^1H NMR (400 MHz) δ 7.16-7.38 (m, 6H), 6.30 (d, 1H, 1.2 Hz), 6.04 (d, 1H, *J* = 16 Hz), 3.72 (s, 1H), 2.62 (m, 1H), 1.23-1.90 (m, 10H); ^{13}C-NMR (100 MHz) δ 176.4 (C=O), 137.8 (CH), 132.2 (C), 128.7 (CH), 127.8 (CH), 127.1 (CH), 126.3(CH), 120.6 (C), 91.5 (CH), 52.2 (CH_3), 34.2 (CH_2), 31.0 (CH_2), 30.9 (CH_2), 30.5 (C), 26.1 (CH_2), 25.5 (CH_2). HRMS (ESI) *m/z* calcd for $C_{19}H_{23}O_2$, 282.1620, found 282.16144 $[M+H]^+$.



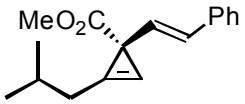
95

***(R,E)*-methyl 2-cyclopropyl-1-(4-(trifluoromethyl)styryl)cycloprop-2-enecarboxylate (95)** Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **95** in 72% yield (121 mg) as yellow oil. 98% ee (determined by HPLC: (R,R)-Whelk, 5% i-PrOH in hexanes t_R=7.27 (major) t_R=8.74 (minor)). IR (neat) 1716, 1322, 1108 cm^{-1}; ^1H NMR (400 MHz) δ 7.50 (d, 2H, *J* = 8 Hz), 7.41 (d, 2H, *J* = 8 Hz), 7.27 (d, 1H, *J* = 16 Hz), 6.20 (s, 1H), 6.10 (d, 1H, *J* = 16 Hz), 3.69 (s, 1H), 1.84 (m, 1H), 0.93 (m, 2H), 0.66 (m, 2H); ^{13}C-NMR (100 MHz) δ 175.6 (C=O), 141.1 (C), 134.3 (CH), 126.8 (CH), 126.4 (CH), 125.6 (C), 125.6 (CH), 118.3 (C), 90.8 (CH), 52.3 (CH_3), 30.1 (C), 8.3 (CH), 7.6 (CH_2), 5.1 (CH_2). HRMS (ESI) *m/z* calcd for $C_{17}H_{16}F_3O_2$, 309.1058, found 309.10976 $[M+H]^+$.



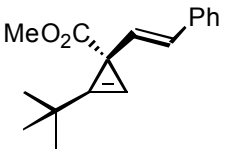
96

***(R,E)*-methyl 2-(cyclopentylmethyl)-1-styrylcycloprop-2-enecarboxylate (96)**. Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **96** in 82% yield (105 mg) as yellow oil. 96% ee (determined by HPLC: (R,R)-Whelk, 5% i-PrOH in hexanes t_R=8.04 (major) t_R=9.79 (minor)). $[\alpha]^{25}_D$ +1.26° (c 0.84, $CHCl_3$); IR (neat) 1716, 1434, 964, 693 cm^{-1} ; ^1H NMR (400 MHz) δ 7.13-7.35 (m, 6H), 6.30 (app t, 1H, *J* = 1.2 Hz), 6.01 (d, 1H, *J* = 16.4 Hz), 3.69 (s, 1H), 2.47 (dd, 1H, *J* = 6, 1.2 Hz), 2.01 (septet, 1H, 7.6 Hz), 1.17-1.83 (m, 8H); ^{13}C-NMR (100 MHz) δ 176.2 (C=O), 137.7 (C), 131.8 (CH), 128.7 (CH), 127.9 (CH), 127.1 (C), 126.3 (CH), 116.7 (C), 93.4 (CH), 52.1 (CH_3), 37.9 (CH), 32.7 (CH_2), 32.6 (CH_2), 30.7 (C), 29.8 (CH_2), 25.5 (CH_2), 25.4 (CH_2). HRMS (ESI) *m/z* calcd for $C_{19}H_{23}O_2$, 282.1653, found 283.16927 $[M+H]^+$.



97

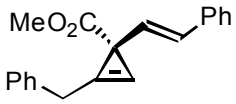
***(R,E)*-methyl 2-isobutyl-1-styrylcycloprop-2-enecarboxylate (97).** Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **97** in 76% yield (97 mg) as yellow oil. 98% ee (determined by HPLC: (R,R)-Whelk, 5% i-PrOH in hexanes t_R=7.80 (major) t_R=9.20 (minor)). IR (neat) 2956, 1718, 1282, 749 cm^{-1}; ^1H NMR (400 MHz) δ 7.17-7.39 (m, 6H), 6.38 (app t, 1H, *J* = 1.6 Hz), 6.05 (d, 1H, *J* = 16.4 Hz), 3.73 (s, 1H), 2.40 (m, 1H), 1.96 (m, 1H), 1.05 (dd, 6H, *J* = 6.8, 2.4 Hz); ^{13}C-NMR (100 MHz) δ 176.2 (C=O), 137.7 (C), 131.7 (CH), 128.7 (CH), 127.9 (CH), 127.1 (C), 126.3 (CH), 116.2 (C), 93.8 (CH), 52.2 (CH_3), 32.7 (CH_2), 30.5 (C), 27.2 (CH), 22.6 (CH_3), 22.5 (CH_3). HRMS (ESI) *m/z* calcd for $C_{17}H_{21}O_2$, 257.1497, found 257.15363 $[M+H]^+$.



98

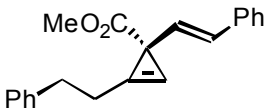
***(R,E)*-methyl 2-tert-butyl-1-styrylcycloprop-2-enecarboxylate (98)**. Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **98** in 62% yield (80 mg) as yellow oil. 95% ee (determined by HPLC: (R,R)-Whelk, 5% i-PrOH in hexanes t_R=6.73 (major) t_R=8.98 (minor)). $[\alpha]^{25}_D$ +4.70° (c 1.24, $CHCl_3$); IR (neat) 2966, 1716, 1243, 745 cm^{-1}; ^1H NMR (600 MHz) δ 7.15-7.40 (m, 6H), 6.21 (s, 1H), 6.07 (d, 1H, *J* = 15.6 Hz), 3.73 (s, 1H), 1.15 (s, 9H); ^{13}C-NMR (125 MHz) δ 176.1 (C=O), 137.8 (C), 131.9 (CH), 128.7 (CH), 127.8 (CH), 127.0 (C), 126.3 (CH), 125.1 (C), 89.9 (CH), 52.1

(CH_3), 32.7 (CH_2), 30.5 (C), 27.2 (CH), 22.6 (CH_3), 22.5 (CH_3). HRMS (ESI) *m/z* calcd for $C_{17}H_{21}O_2$, 257.1497, found 257.15363 $[M+H]^+$.



99

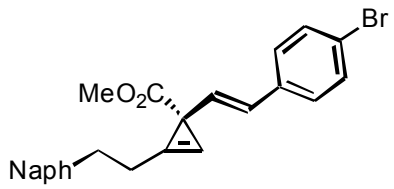
***(R,E)*-methyl 2-benzyl-1-styrylcycloprop-2-enecarboxylate (99)**. Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **99** in 89% yield (129 mg) as yellow oil. 95% ee (determined by HPLC: (R,R)-Whelk, 5% i-PrOH in hexanes t_R=13.27 (major) t_R=15.38 (minor)). $[\alpha]^{25}_D$ -2.96° (c 1.80, $CHCl_3$); IR (neat) 1714, 1244, 747 cm^{-1}; ^1H NMR (400 MHz) δ 7.15-7.33 (m, 6H), 6.44 (app t, 1H, *J* = 1.2 Hz), 6.02 (d, 1H, *J* = 16.4 Hz), 3.81 (d, 2H, J = 1.2 Hz), 3.62 (s, 3H); ^{13}C-NMR (100 MHz) δ 175.7 (C=O), 137.5 (C), 136.4 (C), 131.2 (CH), 128.9 (CH), 128.8 (CH), 128.7 (CH), 128.4 (CH), 127.2 (CH), 127.1 (CH), 126.3 (CH), 115.9 (C), 95.1 (CH), 52.2 (CH_3), 31.3 (CH_2), 30.1 (C). HRMS (ESI) *m/z* calcd for $C_{20}H_{19}O_2$, 291.1340, found 291.13795 $[M+H]^+$.



100

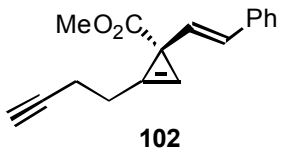
***(R,E)*-methyl 2-phenethyl-1-styrylcycloprop-2-enecarboxylate (100)**. Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **100** in 75% yield (114 mg) as yellow oil. 98% ee (determined by HPLC: (R,R)-Whelk, 5% i-PrOH in hexanes t_R=12.33 (major) t_R=14.85 (minor)). IR (neat) 1714, 1243, 696 cm^{-1}; ^1H NMR (400 MHz) δ 7.15-7.33 (m, 6H), 6.32 (s, 1H), 5.87 (d, 1H, *J* = 16 Hz), 3.68 (s, 3H), 2.90 (m,

2H), 2.83 (m, 2H); ^{13}C-NMR (100 MHz) δ 176.1 (C=O), 140.6 (C), 137.6 (C), 131.4 (CH), 128.7 (CH), 128.6 (CH), 128.0 (CH), 127.1 (CH), 126.5 (CH), 126.3 (CH), 115.9 (C), 94.2 (CH), 52.3 (CH_3), 33.2 (CH_2), 30.7 (C), 25.3 (CH_2). HRMS (ESI) *m/z* calcd for $C_{21}H_{21}O_2$, 305.1497, found 305.15361 $[M+H]^+$.



101

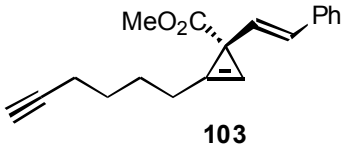
***(R,E)*-methyl 1-(4-bromostyryl)-2-(2-(naphthalen-2-yl)ethyl)cycloprop-2-enecarboxylate (101).** Alkyne was synthesized based on published procedure.[1] Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **101** in 68% yield (104 mg) as yellow oil. 98% ee (determined by HPLC: (R,R)-Whelk, 5% i-PrOH in hexanes t_R=20.11 (major)). IR (neat) 1714, 1243, 696 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.15-7.33 (m, 6H), 6.32 (s, 1H), 5.87 (d, 1H, *J* = 16 Hz), 3.68 (s, 3H), 2.90 (m, 2H), 2.83 (m, 2H); ^{13}C-NMR (100 MHz) δ 176.1 (C=O), 140.6 (C), 137.6 (C), 131.4 (CH), 128.7 (CH), 128.6 (CH), 128.0 (CH), 127.1 (CH), 126.5 (CH), 126.3 (CH), 115.9 (C), 94.2 (CH), 52.3 (CH_3), 33.2 (CH_2), 30.7 (C), 25.3 (CH_2). HRMS (ESI) *m/z* calcd for $C_{25}H_{22}BrO_2$, 432.0725, found 433.08008 $[M+H]^+$.



102

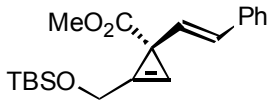
***(R,E)*-methyl 2-(but-3-ynyl)-1-styrylcycloprop-2-enecarboxylate (102)**. Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **102** in 46% yield (58 mg) as yellow oil. 96% ee (determined by HPLC: (R,R)-Whelk, 5% i-PrOH in hexanes

t_R=13.63 (major) t_R=16.37 (minor)). $[\alpha]^{25}_D$ -3.50° (c 0.50, $CHCl_3$); IR (neat) 3292, 1714, 1243, 749 cm^{-1}; ^1H NMR (400 MHz) δ 7.18-7.39 (m, 6H), 6.47 (app t, 1H, *J* = 1.2 Hz), 6.09 (d, 1H, *J* = 16 Hz), 3.72 (s, 3H), 2.78 (m, 2H), 2.50 (m, 2H), 2.02 (t, 1H, *J* = 2.4 Hz); ^{13}C-NMR (100 MHz) δ 175.9 (C=O), 137.5 (C), 131.3 (CH), 128.7 (CH), 128.3 (CH), 127.2 (CH), 126.3 (CH), 115.1 (C), 95.1 (CH), 82.7 (C), 69.6 (CH) 52.3 (CH_3), 30.7 (C), 23.4 (CH_2), 16.9 (CH_2). HRMS (ESI) *m/z* calcd for $C_{17}H_{16}O_2$, 252.1150, found 252.11450.



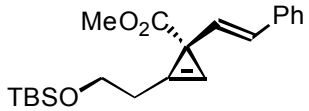
103

***(R,E)*-methyl 2-(hex-5-ynyl)-1-styrylcycloprop-2-enecarboxylate (103)**. Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **103** in 89% yield (58 mg) as yellow oil. 97% ee (determined by HPLC: (R,R)-Whelk, 5% i-PrOH in hexanes t_R=10.76 (major) t_R=12.88 (minor)). IR (neat) 3294, 1713, 1226, 748 cm^{-1}; ^1H NMR (400 MHz) δ 7.18-7.39 (m, 6H), 6.37 (app t, 1H, *J* = 1.2 Hz), 6.04 (d, 1H, *J* = 16.4 Hz), 3.73 (s, 3H), 2.55 (td, 2H, *J* = 6.8, 1.2 Hz), 2.22 (td, 2H, *J* = 7.2, 2.8 Hz), 2.02 (t, 1H, *J* = 2.8 Hz), 1.62-1.76 (m, 2H); ^{13}C-NMR (100 MHz) δ 176.1 (C=O), 137.6 (C), 131.6 (CH), 128.7 (CH), 128.0 (CH), 127.2 (CH), 126.3 (CH), 116.5 (C), 93.8 (CH), 84.1 (C), 69.9 (CH), 52.2 (CH_3), 30.6 (C), 27.9 (CH_2), 26.1 (CH_2), 23.2 (CH_2), 18.3 (CH_2). HRMS (ESI) *m/z* calcd for $C_{19}H_{22}O_2$, 281.1497, found 281.15375 $[M+H]^+$.



104

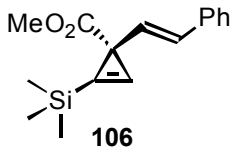
***(R,E)*-methyl 2-((tert-butyldimethylsilyloxy)methyl)-1-styrylcycloprop-2-enecarboxylate (104)**. Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **104** in 68% yield (115 mg) as yellow oil. 98% ee (determined by HPLC: (R,R)-Whelk, 5% i-PrOH in hexanes t_R=7.40 (major) t_R=8.33 (minor)). $[\alpha]^{25}_D$ +7.30° (c 1.00, $CHCl_3$); IR (neat) 1721, 1247, 835 cm^{-1}; ^1H NMR (300 MHz) δ 7.17-7.38 (m, 6H), 6.57 (app t, 1H, *J* = 1.8 Hz), 6.12 (d, 1H, *J* = 16.2 Hz), 4.66 (d, 2H, *J* = 1.8 Hz), 3.72 (s, 3H),0.90 (s, 9H), 0.01 (s, 6H); ^{13}C-NMR (100 MHz) δ 175.5 (C=O), 137.4 (C), 130.8 (CH), 128.7 (CH), 127.3 (CH), 126.3 (CH), 115.8 (C), 95.9 (CH), 56.8 (CH_2), 52.2 (CH_3), 31.8 (C), 31.7 (C), 25.9 (CH_3), 18.5 (C), -5.1 (CH_3),-5.2 (CH_3). HRMS (ESI) *m/z* calcd for $C_{20}H_{28}O_3Si$, 344.1808, found 344.18026.



105

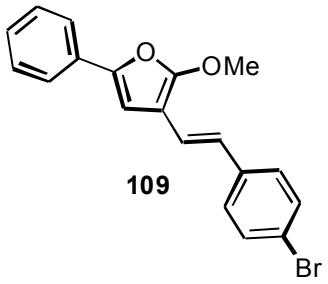
***(R,E)*-methyl 2-(2-(tert-butyldimethylsilyloxy)ethyl)-1-styrylcycloprop-2-enecarboxylate (105)**. Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **105** in 77% yield (137 mg) as yellow oil. 97% ee (determined by HPLC: (R,R)-Whelk, 5% i-PrOH in hexanes t_R=8.44 (major) t_R=9.32 (minor)). $[\alpha]^{25}_D$ +4.73° (c 1.00, $CHCl_3$); IR (neat) 1720, 1247, 836 cm^{-1}; ^1H NMR (400 MHz) δ 7.19-7.38 (m, 6H), 6.40 (app t, 1H, *J* = 1.2 Hz), 6.05 (d, 1H, *J* = 16 Hz), 3.85 (t, 2H, *J* = 6.8 Hz), 3.73 (s, 3H), 2.74 (t, 2H, *J* = 6.8 Hz), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C-NMR (100 MHz) δ 176.1

(C=O), 137.6 (C), 131.6 (CH), 128.7 (CH), 128.1 (CH), 127.1 (CH), 126.3 (CH), 113.9 (C), 94.7 (CH), 60.5 (CH_2), 52.2 (CH_3), 30.2 (C), 27.7 (CH_2), 26.0 (CH_2), 18.4 (C), -5.1 (CH_3),-5.2 (CH_3). HRMS (ESI) *m/z* calcd for $C_{21}H_{30}O_3Si$, 359.1998, found 359.20401 $[M+H]^+$.



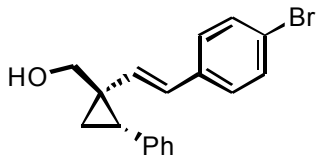
106

***(S,E)*-methyl 1-styryl-2-(trimethylsilyl)cycloprop-2-enecarboxylate (106)**. Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **106** in 85% yield (151 mg) as white needles. Melting point 62-63ºC. 99% ee (determined by HPLC: (R,R)-Whelk, 5% i-PrOH in hexanes t_R=7.06 (major) t_R=8.05 (minor)). IR (neat) 1731, 1702, 1247, 845 cm^{-1}; ^1H NMR (400 MHz) δ 7.40 (d, 2H, *J* = 16 Hz), 7.15-7.33 (m, 5H), 6.95 (s, 1H), 5.87 (d, 1H, *J* = 16 Hz), 3.67 (s, 3H), 0.20 (s, 9H); ^{13}C-NMR (100 MHz) δ 176.5 (C=O), 137.8 (C), 133.3 (CH), 128.7 (CH), 127.8 (CH), 126.9 (CH), 126.2 (CH), 115.2 (C), 110.5 (CH), 52.1 (CH_3), 28.7 (C), -1.0 (CH_3). HRMS (ESI) *m/z* calcd for $C_{16}H_{21}O_2Si$, 273.1266, found 273.13064 $[M+H]^+$.



109

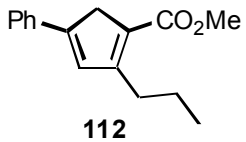
(E)-5-(4-bromostyryl)-2-methoxy-3-phenylfuran (109). Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **109** in 77% yield (136 mg) as yellow oil. IR (neat) 3291, 1322, 1068, 756 cm^{-1}; ^1H NMR (300 MHz) δ 7.57-7.59 (d, 2H, *J* = 8 Hz), 7.44 (d, 2H, *J* = 8 Hz), 7.35-7.39 (m, 2H), 7.29-7.31 (m, 2H), 7.21-7.25 (m, 1H), 6.89 (d, 1H, *J* = 16Hz), 6.77 (s, 1H), 6.61 (d, 1H, *J* = 16Hz), 4.09 (s, 3H); ^{13}C-NMR (100 MHz) δ 157.3 (C), 144.9 (C), 137.2 (C), 131.9 (C), 130.6 (CH), 128.9 (CH), 127.5 (CH), 127.0 (CH), 124.3 (CH), 123.0 (CH), 120.4 (C), 118.6 (CH), 104.2 (CH), 100.7 (C), 59.9 (CH_3). Further characterizations were not done due to instability of the product.



110

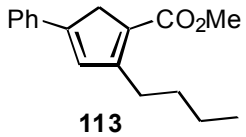
((*1S,2S*)-1-((E)-4-bromostyryl)-2-phenylcyclopropyl)methanol (110)[2]. Purification by silica gel chromatography (hexane/EtOAc, 4:1) gave compound **110** in 91% yield (149 mg) as light yellow oil. 92% ee (determined by HPLC: OD-H, 5% i-PrOH in hexanes t_R=14.11 (major) t_R=8.90 (minor)). IR (neat) 3353, 2924, 1487, 1009 cm^{-1}; ^1H NMR (400 MHz) δ 7.18-7.32 (m, 8H), 6.97 (d, 2H, *J* = 8 Hz), 6.49 (d, 1H, *J* = 16 Hz), 5.65 (d, 1H, *J* = 16 Hz), 3.88 (d, 1H, *J* = 8 Hz), 3.80 (d, 1H, *J* = 12 Hz), 2.44 (m, 1H), 1.85 (br s, 1H), 1.36 (m, 2H); ^{13}C-NMR (100 MHz) δ 137.8 (C), 136.6 (C), 131.7 (CH), 130.9 (CH), 129.3 (CH), 129.1 (CH), 128.4 (CH), 127.6 (CH), 120.8 (C), 68.8 (CH_2), 32.5 (C), 29.8

(CH), 17.3 (CH_2). HRMS (ESI) *m/z* calcd for $C_{18}H_{17}BrO$, 329.2310, found 311.0423 [M-H_2O]$^+$.



112

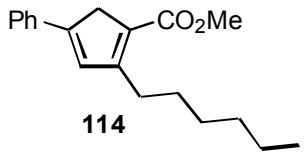
Methyl 4-phenyl-2-propylcyclopenta-1,3-dienecarboxylate (112). Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **112** in 61% yield (75 mg) as yellow oil. IR (neat) 1696, 1205, 717 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.57 (d, 2H, *J* = 7.2 Hz), 7.25-7.37 (m, 3H), 6.84 (s, 1H), 3.78 (s,1H), 3.74 (d, 2H, *J* = 1.2 Hz), 2.84 (t, 2H, 7.6 Hz), 1.64 (s, 2H, *J* = 7.6 Hz), 0.98 (t, 3H, *J* = 7.6 Hz; ^{13}C-NMR (100 Hz) δ 165.5 (C=O), 161.0 (C), 150.9 (C), 135.1 (C), 130.7 (CH), 128.9 (CH), 128.3 (CH), 127.4 (C), 125.8 (CH), 51.0 (CH_3), 42.3 (CH_2), 31.4 (CH_2), 29.1 (CH_2), 22.9 (CH_2), 14.2 (CH_3). HRMS (ESI) *m/z* calcd for $C_{16}H_{18}O_2$, 242.1307, found 242.13004.



113

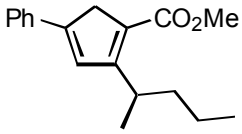
Methyl 2-butyl-4-phenylcyclopenta-1,3-dienecarboxylate (113). Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **113** in 62% yield (80 mg) as yellow. IR (neat) 1698, 1200, 751 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.57 (d, 2H, *J* = 8 Hz), 7.27-7.38 (m, 3H), 6.86 (s, 1H), 3.79 (s, 1H), 3.74 (s, 2H), 2.87 (t, 2H, *J* = 7.6 Hz), 1.60 (m, 2H), 1.41 (s, 2H, *J* = 7.6 Hz), 0.96 (t, 3H, 7.6 Hz); ^{13}C-NMR (100 MHz) δ 165.5

(C=O), 161.3 (C), 150.9 (C), 135.1 (C), 130.7 (CH), 128.9 (CH), 128.3 (CH), 127.2 (C), 125.8 (CH), 51.1 (CH_3), 42.3 (CH_2), 31.4 (CH_2), 29.1 (CH_2), 22.9 (CH_2), 14.2 (CH_3). HRMS (ESI) *m/z* calcd for $C_{17}H_{20}O_2$, 257.1497, found 257.15364 $[M+H]^+$.



114

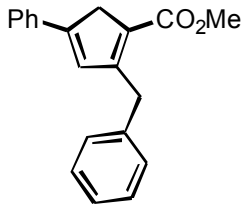
Methyl 2-hexyl-4-phenylcyclopenta-1,3-dienecarboxylate (114). Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **114** in 74% yield (220 mg) as yellow oil. IR (neat) 2925, 1698, 1190, 748 cm^{-1}; ^1H NMR (400 MHz) δ 7.58 (d, 2H, *J* = 8.4 Hz), 7.26-7.38 (m, 3H), 6.85 (s, 1H), 3.79 (s, 3H), 3.74 (s, 2H), 2.86 (t, 2H, *J* = 7.6 Hz), 1.30-1.40 (m, 8H), 0.90 (t, 3H, 6.8 Hz); ^{13}C-NMR (100 MHz) δ 165.5 (C=O), 161.3 (C), 150.9 (C) , 135.1 (C), 130.7 (CH), 128.9 (CH), 128.2 (CH), 127.2 (C), 125.8 (CH), 51.1 (CH_3), 42.3 (CH_2), 31.9 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 22.8 (CH_2), 14.3 (CH_3). HRMS (ESI) *m/z* calcd for $C_{19}H_{25}O_2$, 285.1810, found 285.18462 $[M+H]^+$.



115

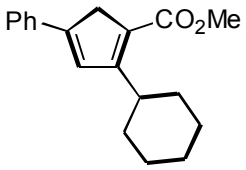
Methyl 2-(pentan-2-yl)-4-phenylcyclopenta-1,3-dienecarboxylate (115). Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **115** in 82% yield (222mg) as yellow oil. IR (neat) 2956, 1701, 1209, 751 cm^{-1}; ^1H NMR (400 MHz) δ 7.56 (dd, 2H, *J* = 7.2, 1.2 Hz), 7.24-7.35 (m, 3H), 6.92 (s, 1H), 3.76 (s, 3H), 3.71 (s, 2H), 1.48

(m, 2H), 1.26 (m, 3H), 1.14 (d, 3H, J = 6.8 Hz), 0.86 (t, 3H, 7.6 Hz); ^{13}C-NMR (100 MHz) δ 165.9 (C=O), 165.6 (C), 151.1 (C), 135.2 (C), 128.9 (CH), 128.3 (CH), 127.4 (CH), 126.6 (C), 125.8 (CH), 51.0 (CH_3), 42.3 (CH_2), 38.8 (CH_2), 32.1 (CH), 20.9 (CH_3), 20.3 (CH_3), 14.3 (CH_3). HRMS (ESI) *m/z* calcd for $C_{18}H_{23}O_2$, 271.1653, found 271.16364 $[M+H]^+$.



116

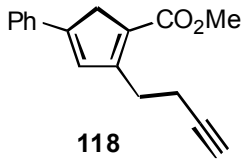
Methyl 2-benzyl-4-phenylcyclopenta-1,3-dienecarboxylate (116). Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **116** in 75% yield (109 mg) as yellow oil. IR (neat) 1692, 1190, 756, 688 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.48 (d, 2H, J = 7.2 Hz), 7.20-7.31 (m, 8H), 6.69 (s, 1H), 4.24 (s, 2H), 3.81 (s, 3H), 3.77 (s, 2H); ^{13}C-NMR (100 MHz) δ 165.5 (C=O), 158.4 (C), 151.1 (C), 139.4 (C), 134.9 (C) , 130.5 (CH), 129.2 (CH), 128.9 (CH), 128.8 (CH), 128.4 (CH), 127.8 (C), 126.5 (CH), 125.9 (CH), 51.3 (CH_3), 42.4 (CH_2), 35.3 (CH_2). HRMS (ESI) *m/z* calcd for $C_{20}H_{19}O_2$, 291.1340, found 291.13790 $[M+H]^+$.



117

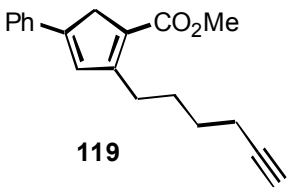
Methyl 2-cyclohexyl-4-phenylcyclopenta-1,3-dienecarboxylate (117). Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **117** in 83% yield (118

mg) as yellow oil. IR (neat) 2923, 1698, 1207, 750 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.57 (d, 2H, *J* = 8.4 Hz), 7.26-7.37 (m, 3H), 6.98 (s, 1H), 3.79 (s, 1H), 3.72 (s, 2H), 3.53 (m, 1H), 1.20-1.80 (m, 10H), 1.41 (s, 2H, *J* = 7.6 Hz), 0.96 (t, 3H, 7.6 Hz); ^{13}C-NMR (100 MHz) δ 166.0 (C=O), 165.5 (C), 151.1 (C), 135.2 (C), 131.0 (CH), 128.9 (CH), 128.2 (CH), 128.0 (C), 125.8 (CH), 51.0 (CH_3), 42.2 (CH_2), 37.6 (CH), 32.3 (CH_2), 26.5 (CH_2), 26.4 (CH_2). HRMS (ESI) *m/z* calcd for $C_{19}H_{23}O_2$, 282.1620, found 282.16144 $[M+H]^+$.



118

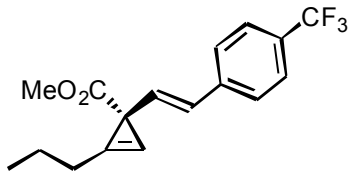
Methyl 2-(but-3-ynyl)-4-phenylcyclopenta-1,3-dienecarboxylate (118). Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **118** in 64% yield (82 mg) as yellow oil. IR (neat) 3293, 1694, 1195 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.55 (dd, 2H, *J* = 8.7, 1.5 Hz), 7.21-7.39 (m, 8H), 6.79 (s, 1H), 3.80 (s, 3H), 3.75 (d, 2H, *J* = 1.5 Hz), 3.18 (m, 2H), 2.93 (m, 2H); ^{13}C-NMR (100 MHz) δ 165.4 (C=O), 159.9 (C), 151.1 (C), 141.8 (C), 135.1 (C) , 130.7 (CH), 129.0 (CH), 128.9 (CH), 128.8 (CH), 128.7 (CH), 128.6 (C), 128.4 (CH), 127.9 (C), 126.2 (CH), 125.9 (CH) 51.2 (CH_3), 42.4 (CH_2), 35.6 (CH_2), 31.5 (CH_2). HRMS (ESI) *m/z* calcd for $C_{17}H_{17}O_2$, 253.1184, found 253.12246 $[M+H]^+$.



119

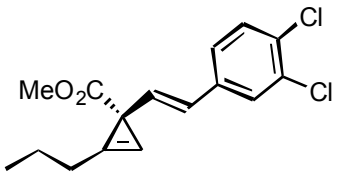
Methyl 2-(hex-5-ynyl)-4-phenylcyclopenta-1,3-dienecarboxylate (119). Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **119** in 71% yield (198

mg) as yellow oil. IR (neat) 3297, 1694, 1189, 749 cm^{-1}; ^1H NMR (400 MHz) δ 7.55 (dd, 2H, *J* = 8.8, 1.6 Hz), 7.24-7.35 (m, 3H), 6.92 (s, 1H), 3.76 (s, 3H), 3.71 (s, 2H), 2.86 (t, 2H, 8 Hz), 2.22 (m, 2H), 1.92 (t, 1H, 2.4 Hz), 1.54-1.75 (m, 4H); ^{13}C-NMR (100 MHz) δ 165.4 (C=O), 160.5 (C), 151.1 (C), 135.0 (C), 130.5 (CH) , 128.9 (CH), 128.3 (CH), 127.6 (C), 125.8 (CH), 84.6 (C), 68.5 (CH), 51.1 (CH_3), 42.4 (CH_2), 28.7 (CH_2), 28.4 (CH_2), 28.2 (CH_2), 18.5 (CH_2) . HRMS (ESI) *m/z* calcd for $C_{19}H_{22}O_2$, 281.1497, found 281.15098 $[M+H]^+$.



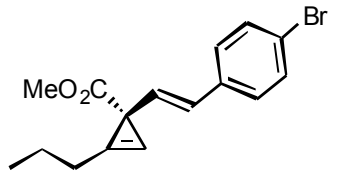
124

***(R,E)*-methyl 2-propyl-1-(4-(trifluoromethyl)styryl)cycloprop-2-enecarboxylate (124)**. Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **124** in 88% yield (137 mg) as yellow oil. 99% ee (determined by HPLC: (S,S)-Whelk, 5% i-PrOH in hexanes t_R=11.82 (major) t_R=13.88 (minor)). IR (neat) 1716, 1614, 1321, 720 cm^{-1}; ^1H NMR (400 MHz) δ 7.50 (d, 2H, *J* = 8 Hz), 7.14 (d, 2H, *J* = 8Hz), 7.36 (d, 1H, *J* = 15.6 Hz), 6.30 (app t, 1H, *J* = 1.2 Hz), 6.03 (d, 1H, *J* = 16.4 Hz), 3.70 (s, 3H), 2.46 (td, 2H, *J* = 7.6, 1.2 Hz), 1.59 (s, 2H, *J* = 7.2 Hz), 0.97 (t, 3H, *J* = 7.6 Hz); ^{13}C-NMR (100 MHz) δ 175.9 (C=O), 141.2 (C), 134.9 (CH), 126.5 (CH), 116.5 (CF_3), 93.1 (CH), 52.2 (CH_3), 30.6 (C), 25.7 (CH_2), 20.6 (CH_2), 13.9 (CH_3). HRMS (ESI) *m/z* calcd for $C_{17}H_{18}F_3O_2$, 311.1214, found 311.12557 $[M+H]^+$.



125

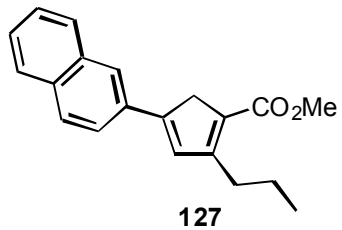
***(R,E)*-methyl 1-(3,4-dichlorostyryl)-2-propylcycloprop-2-enecarboxylate (125)**. Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **125** in 79% yield (122 mg) as yellow oil. 96% ee (determined by HPLC: (R,R)-Whelk, 5% i-PrOH in hexanes t_R=7.91 (major) t_R=9.16 (minor)). IR (neat) 1716, 1472, 1240, 798 cm^{-1}; ^1H NMR (400 MHz) δ 7.39 (d, 1H, *J* = 2 Hz), 7.30 (d, 1H, *J* = 8Hz), 7.24 (d, 1H, *J* = 16 Hz), 7.14 (dd, 1H, *J* = 8, 2 Hz), 6.28 (app t, 1H, *J* = 1.6 Hz), 5.90 (d, 1H, *J* = 16 Hz), 3.69 (s, 3H), 2.45 (td, 2H, *J* = 7.6, 1.2 Hz), 1.59 (s, 2H, *J* = 7.2 Hz), 0.97 (t, 3H, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz) δ 175.8 (C=O), 137.9 (C), 134.2 (CH), 132.7 (C), 130.5 (CH), 127.9 (CH), 125.6 (CH), 125.4 (CH), 116.5 (C) 93.1 (CH), 52.3 (CH_3), 30.5 (C), 25.7 (CH_2), 20.6 (CH_2), 13.9 (CH_3). HRMS (ESI) *m/z* calcd for $C_{16}H_{17}Cl_2O_2$, 311.0561, found 311.06023 $[M+H]^+$.



126

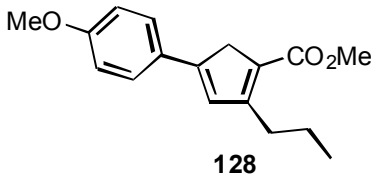
***(R,E)*-methyl 1-(4-bromostyryl)-2-propylcycloprop-2-enecarboxylate (126)**. Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **126** in 86% yield (134 mg) as yellow oil. 97% ee (determined by HPLC: (S,S)-Whelk, 5% i-PrOH in hexanes t_R=8.53 (major) t_R=7.35 (minor)). IR (neat) 1715, 1486, 1242, 794 cm^{-1}; ^1H NMR (400 MHz) δ 7.37 (m, 2H), 7.18-7.38 (m, 3H), 6.29 (app t, 1H, *J* = 1.6 Hz), 5.93 (d, 1H, *J* = 16 Hz), 3.69 (s, 3H), 2.45 (td, 2H, *J* = 7.2, 1.2 Hz), 1.59 (s, 2H, *J* = 7.2

Hz), 0.97 (t, 3H, J = 7.2 Hz) ; ^{13}C-NMR (100 MHz) δ 176.0 (C=O), 136.6 (C), 132.8 (CH), 131.7 (CH), 127.8 (CH), 126.7 (CH), 120.7 (C), 116.6 (C), 93.2 (CH), 52.2 (CH_3), 30.5 (C), 25.7 (CH_2), 20.6 (CH_2), 13.9 (CH_3). HRMS (ESI) *m/z* calcd for $C_{16}H_{18}BrO_2$, 321.0455, found 311.04868 $[M+H]^+$.



127

Methyl 4-(naphthalen-2-yl)-2-propylcyclopenta-1,3-dienecarboxylate (17d). Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **17d** in 87% yield (127 mg) as yellow solid. Melting Point 75-76°C; IR (neat) 1694, 1202, 811 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.95 (br s, 1H), 7.76-7.81 (m, 3H), 7.68 (dd, 1H, J = 11.2, 1.6 Hz), 7.44 (m, 1H), 6.94 (s, 1H), 3.85 (br s, 2H), 3.79 (s, 3H), 2.85 (m, 2H), 1.65 (s, 2H, J = 7.6 Hz), 0.99 (t, 3H, J = 7.6 Hz). HRMS (ESI) *m/z* calcd for $C_{20}H_{21}O_2$, 293.1497, found 293.15375 $[M+H]^+$.



128

Methyl 4-(4-methoxyphenyl)-2-propylcyclopenta-1,3-dienecarboxylate (128). Purification by silica gel chromatography (hexane/Et_2O, 15:1) gave compound **128** in 78% yield (107 mg) as yellow oil. IR (neat) 1693, 1605, 1499, 822 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.47 (d, 2H, J = 8.8 Hz), 6.85 (d, 2H, J = 8.8 Hz), 6.68 (s, 1H), 3.80 (s, 3H), 3.75 (s, 3H), 3.67 (d, 2H, J = 0.8 Hz), 2.80 (m, 2H), 1.61 (s, 2H, J = 7.2 Hz), 0.96 (t, 3H,

J = 7.6 Hz); ^{13}C-NMR (100 MHz) δ 165.6 (C=O), 161.5 (C), 159.8 (C), 150.8 (C), 128.9 (CH), 128.1 (CH), 127.2 (CH), 126.3 (CH), 114.3 (CH), 55.5 (CH_3), 50.9 (CH_3), 42.3 (CH_2), 31.3 (CH2), 22.4 (CH_2), 14.3 (CH_3). HRMS (ESI) *m/z* calcd for $C_{17}H_{21}O_3$, 273.1446, found 273.14859 $[M+H]^+$.

V. Computational Studies

Complete Gaussian'09 Reference: Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

Computational Details: All calculations were performed with the Gaussian '09 software package (See reference above). Density Functional Theory was employed with the 3-parameter hybrid functional B3LYP[1] to locate stationary points on the potential energy surface (PES). The structures were subjected to full geometry optimization with a basis

set consisting of the 1997 Stuttgart relativistic small-core effective core-potential [Stuttgart RSC 1997 ECP][2] for Rh, augmented with a 4f-function (ζ_f(Rh) = 1.350).[3] This basis has been demonstrated to give good accuracy for such catalyst systems described in this paper.[3a] The split valence basis set 6-31G* was used in the optimization and frequency calculations for all other atoms (C, H and O). This composite basis set is abbreviated 6-31G*[Rh-RSC+4f].[3a] Single-point energies were calculated at the B3LYP/6-311+G(2d,2p)[Rh-RSC+4f]//B3LYP/6-31G*[Rh-RSC+4f] level of theory and are reported with added zero-point energies from B3LYP/6-31G*[Rh-RSC+4f] calculations. Heavy atom basis set definitions and corresponding pseudopotential parameters were obtained from the EMSL basis set exchange library.[4] All stationary points were characterized by normal coordinate analysis at the B3LYP/6-31G*[Rh-RSC+4f] level of theory.[5] Transition states were confirmed to have only one imaginary vibrational mode corresponding to movement along the reaction coordinate.[5] Equilibrium structures were confirmed to have zero imaginary vibrational modes.[5] The most stable transition state **TS-I** was further characterized by intrinsic reaction coordinate (IRC) analysis (maxpoints=50) to confirm that the stationary points were smoothly connected to each other.[5] The calculated harmonic zero-point vibrational energies (ZPVE) are reported unscaled. Calculated structures have been visualized using WebMO[6] and Mercury.[7]

Calculated Structures:

Propene

Displayed zero negative eigenfrequencies

Route= #N B3LYP/6-31G(d) 5d OPT FREQ

RB3LYP Energy=-116.650683194 Hartree

ZPE=0.055732 Hartree

Conditions=298K, 1.00000 atm

Internal Energy=-116.590956 Hartree

Enthalpy=-116.590012 Hartree

Free Energy=-116.619179 Hartree

Entropy=61.388 cal/mol-K

Dipole Moment=0.6857 Debye

C	0.00000000	0.00000000	0.00000000
C	1.46047400	-0.00103200	0.00083300
C	2.66775600	0.00008900	-0.00001000
H	3.73367500	0.00031400	-0.00048600
H	-0.39589200	1.01518700	-0.12351500
H	-0.39666800	-0.61396200	-0.81750700
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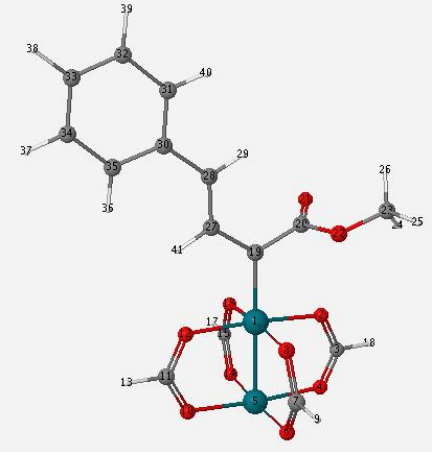
Methyl phenylvinylcarbenoid s-trans conformer M-I



Displayed zero negative eigenfrequencies

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RB3LYP Energy=-1553.56991114 Hartree

ZPE=0.285402 Hartree

Conditions=298K, 1.00000 atm
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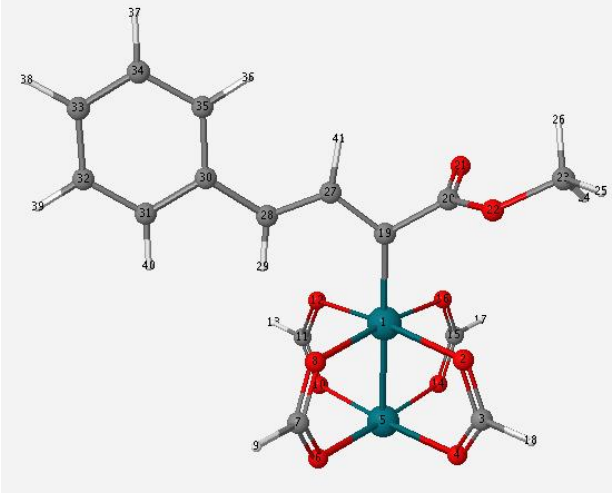
Enthalpy=-1553.255962 Hartree
Free Energy=-1553.344576 Hartree
Entropy=186.503 cal/mol-K
Dipole Moment=9.4786 Debye

Rh	0.00000000	0.00000000	0.00000000
O	-0.83884900	1.80067600	0.55236500
C	-2.10480400	1.86360500	0.67365000
O	-2.95789300	0.95425700	0.49351200
Rh	-2.29573900	-0.92218100	-0.06864400
O	-2.39662200	-0.35780300	-2.05068000
C	-1.38422000	0.20403200	-2.54865400
O	-0.27592100	0.48135100	-1.98944200
H	-1.45525200	0.49734200	-3.60552200
O	-1.45629200	-2.72788300	-0.62263800
C	-0.20522000	-2.80062000	-0.73494600
O	0.66307400	-1.88512000	-0.55377800
H	0.20413800	-3.77825700	-1.02726500
O	-2.07357000	-1.43191100	1.91418100
C	-0.97821600	-1.16020200	2.47572900
O	0.04662700	-0.59370500	1.97827800
H	-0.88339700	-1.44485300	3.53287300
H	-2.49285300	2.84669500	0.97538600
C	1.85560100	0.73642600	0.03584200
C	2.02003400	2.19949600	0.24599800
O	2.35439200	2.67567400	1.31528800
O	1.72037000	2.91171900	-0.85001100
C	1.71850300	4.34118600	-0.68075100
H	0.97175700	4.62839200	0.06325900
H	1.46317200	4.74605900	-1.65974000
H	2.70265300	4.69490900	-0.36186100

C 2.99575200 -0.08897100 -0.06920300
C 4.28596200 0.37442700 0.06239900
H 4.42370800 1.43423200 0.26972400
C 5.50371800 -0.40118300 -0.01053000
C 6.73698200 0.26802600 0.15411900
C 7.94082900 -0.42425000 0.08144200
C 7.93608700 -1.80165200 -0.15491300
C 6.72311300 -2.48339400 -0.31786200
C 5.51934800 -1.79554400 -0.24681700
H 4.58592200 -2.33412300 -0.37210800
H 6.72285600 -3.55415300 -0.49942600
H 8.87460000 -2.34598600 -0.21117200
H 8.88046500 0.10487500 0.20941500
H 6.73550900 1.33900800 0.33982800
H 2.80899400 -1.14473500 -0.24249700

Methyl phenylvinylcarbenoid s-cis conformer M-II



Displayed zero negative eigenfrequencies

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RB3LYP Energy=-1553.56930325 Hartree

ZPE=0.285237 Hartree

Conditions=298K, 1.00000 atm

Internal Energy=-1553.256429 Hartree

Enthalpy=-1553.255484 Hartree

Free Energy=-1553.344386 Hartree

Entropy=187.109 cal/mol-K

Dipole Moment=8.4074 Debye

Rh	0.00000000	0.00000000	0.00000000
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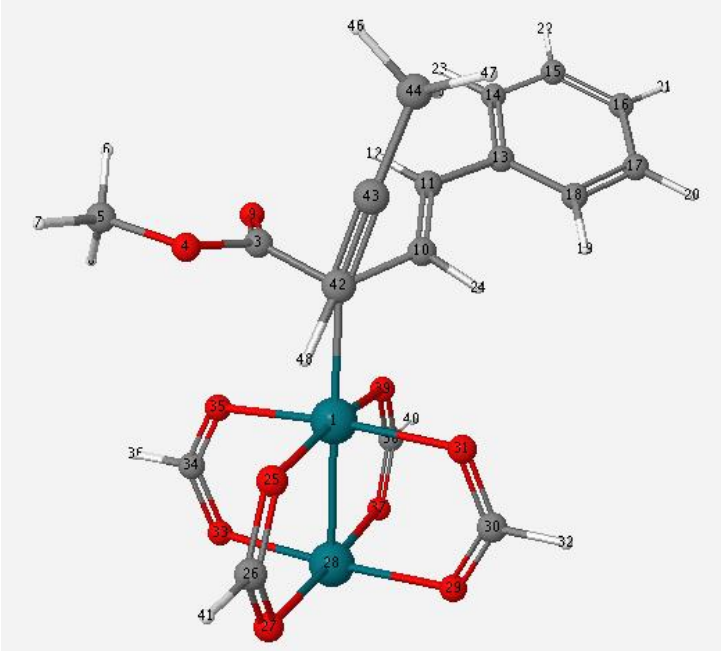
C	-2.22671000	0.65401800	-1.74114800
O	-2.82589500	-0.39218800	-1.37054300
Rh	-1.88751500	-1.60513200	0.00217600
O	-0.94322300	-2.59651800	-1.54753600
C	0.15625100	-2.14570500	-1.95996600
O	0.80672300	-1.13341100	-1.53868400
H	0.62897600	-2.68820900	-2.79134800
O	-0.83182600	-2.71722400	1.38865700
C	0.29367400	-2.29319800	1.75977300
O	0.91065400	-1.24531100	1.37910900
H	0.82492600	-2.89880400	2.50784000
O	-2.71629500	-0.51205000	1.53680400
C	-2.09943200	0.51404900	1.93281400
O	-0.99250200	0.98276900	1.51659600
H	-2.56879300	1.08703000	2.74444700
H	-2.75087100	1.28284700	-2.47473400
C	1.54365700	1.30492100	0.05953400
C	1.21711500	2.74408400	0.25603600
O	1.30965600	3.26971800	1.34928200
O	0.82053900	3.36271100	-0.86360200
C	0.44007500	4.74279500	-0.70872400
H	-0.42266700	4.82351700	-0.04283300
H	0.18523900	5.08527700	-1.71130400
H	1.26831600	5.32715300	-0.29917900
C	2.92434300	1.01774600	0.11206400
C	3.42313400	-0.25196400	-0.08616600

H 2.70096700 -1.03267900 -0.29394600
C 4.80898200 -0.66182100 -0.07163100
C 5.09884400 -2.02340000 -0.31424900
C 6.40884000 -2.48954200 -0.30127300
C 7.45763900 -1.60222600 -0.04530400
C 7.19117600 -0.24835100 0.19701500
C 5.88417700 0.22014300 0.18386400
H 5.69098200 1.27082600 0.37400400
H 8.00909500 0.43781600 0.39615200
H 8.48260800 -1.96231100 -0.03381400
H 6.61430200 -3.53925400 -0.48892900
H 4.27829100 -2.70822200 -0.51140200
H 3.61505200 1.83817000 0.31036400

Cyclopropenation TS-I (right-tilted/s-trans conformer)



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Route= #N b3lyp/gen pseudo=read gfprint OPT=(TS,CalcFC,NoEigenTest) freq

RB3LYP Energy=-1670.20993064 Hartree

ZPE=0.342298 Hartree

Conditions=298K, 1.00000 atm

Internal Energy=-1669.835776 Hartree

Enthalpy=-1669.834831 Hartree

Free Energy=-1669.932174 Hartree

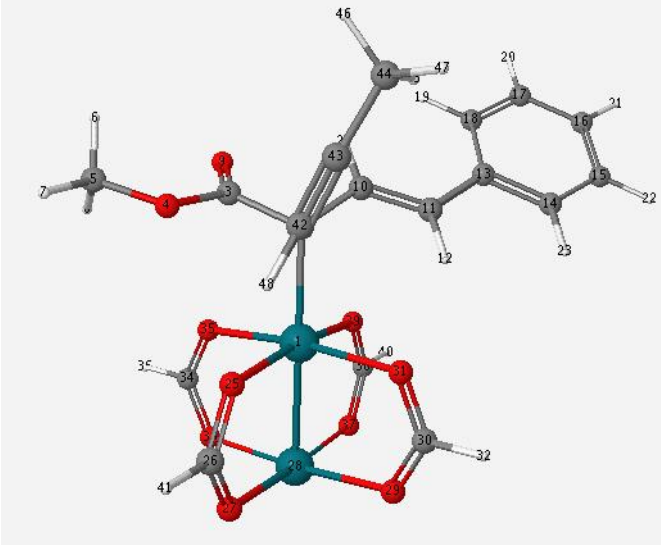
Entropy=204.874 cal/mol-K

Dipole Moment=8.3677 Debye

Rh	0.00000000	0.00000000	0.00000000
C	1.85412200	1.02423400	0.05862800
C	1.91944400	2.15023700	-0.93088900
O	1.27609000	3.26230200	-0.53446000
C	1.11852100	4.27054300	-1.54605500
H	2.09108700	4.59832100	-1.92279900
H	0.60001200	5.09360700	-1.05384700
H	0.52297400	3.87834500	-2.37368300
O	2.41384300	2.02511600	-2.03788900
C	2.98119000	0.14220100	0.23562200
C	4.13739100	0.15832600	-0.48627900
H	4.25562800	0.93006100	-1.24176300
C	5.22388100	-0.81505700	-0.40886900
C	6.37238600	-0.59654800	-1.19616800
C	7.45598400	-1.47004600	-1.14782600
C	7.41249700	-2.58906000	-0.31382600
C	6.27589700	-2.82823400	0.46699900
C	5.19401600	-1.95577400	0.42079300
H	4.31494100	-2.16517200	1.02240100
H	6.23360000	-3.70318600	1.10993900
H	8.25403600	-3.27523800	-0.27568500
H	8.33150900	-1.28025700	-1.76259300
H	6.40607800	0.27218400	-1.84917700
H	2.81731800	-0.63995300	0.97309400
O	-1.06996700	1.22963600	1.28177800
C	-2.30026800	0.97837700	1.50514300
O	-2.99371100	0.03789200	1.04147000

Rh -2.08171500 -1.30836800 -0.23365500
O -1.44532700 -2.41898600 1.39089800
C -0.33776700 -2.13655400 1.92202300
O 0.48823700 -1.22329500 1.59664000
H -0.03675300 -2.75476200 2.78001700
O -2.56886300 -0.10928900 -1.83855300
C -1.76616100 0.81176600 -2.15385800
O -0.66185700 1.12257300 -1.60613900
H -2.05368400 1.43373500 -3.01342200
O -1.07050800 -2.57412300 -1.49764400
C 0.14258400 -2.32127700 -1.73719500
O 0.85488100 -1.36926900 -1.28937000
H 0.65921800 -3.01013700 -2.42004200
H -2.80557900 1.67584100 2.18769100
C 1.61738500 2.04532900 1.92837600
C 2.78503300 2.33412500 2.17659200
C 4.21695400 2.51942200 2.25998500
H 4.69038300 1.85823200 1.51201000
H 4.51400000 3.55258500 2.04848700
H 4.60465000 2.23125100 3.24400000
H 0.54853200 2.02240500 2.04176200

Cyclopropenation TS-II (right-tilted/ s-cis conformer)



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Route= #N b3lyp/gen pseudo=read gfprint OPT=(TS,CalcFC,NoEigenTest) freq

RB3LYP Energy=-1670.20754808 Hartree

ZPE=0.342266 Hartree

Conditions=298K, 1.00000 atm

Internal Energy=-1669.833433 Hartree

Enthalpy=-1669.832489 Hartree

Free Energy=-1669.929265 Hartree

Entropy=203.682 cal/mol-K

Dipole Moment=8.1004 Debye

Rh	0.00000000	0.00000000	0.00000000
C	1.65797200	1.34991700	-0.07497600
C	1.35673300	2.58172400	-0.89228300
O	0.48385900	3.43009700	-0.32353000
C	0.04994300	4.51417700	-1.15956800
H	0.90217100	5.11714500	-1.48476800
H	-0.62474800	5.10534500	-0.53997200
H	-0.47243900	4.12524800	-2.03688600
O	1.81058200	2.73675300	-2.01167900
C	2.97617700	0.81799700	-0.36086000
C	3.46582200	-0.33328300	0.17188100

H 2.84062500 -0.85860900 0.88930000
C 4.75263000 -0.95813200 -0.11744600
C 5.08676000 -2.14511400 0.56539300
C 6.28997200 -2.80294300 0.32125900
C 7.18826800 -2.28716000 -0.61486100
C 6.87325000 -1.11005400 -1.30404900
C 5.67354200 -0.45153400 -1.05918200
H 5.44309100 0.45691700 -1.60741700
H 7.56781200 -0.70787700 -2.03649800
H 8.12724000 -2.79783600 -0.80993200
H 6.52539300 -3.71766400 0.85824200
H 4.38516400 -2.54954900 1.29095700
H 3.56438000 1.37529400 -1.08904100
O -1.17034600 1.11345900 1.30536500
C -2.34309300 0.70247700 1.58950700
O -2.92103100 -0.33819800 1.18170500
Rh -1.88794300 -1.59495800 -0.08971100
O -1.04642100 -2.54680500 1.54162300
C 0.02872700 -2.09235700 2.01375600
O 0.70542700 -1.08852900 1.61891300
H 0.44476900 -2.62544000 2.88094600
O -2.61027300 -0.54780100 -1.70707100
C -1.96569700 0.46803000 -2.08769800
O -0.89502100 0.95314400 -1.60478600
H -2.37868900 1.01180800 -2.94909800
O -0.76027400 -2.75999300 -1.35562600
C 0.38689300 -2.34083300 -1.67409300
O 0.97361900 -1.27820000 -1.29798900
H 0.96232600 -2.97311100 -2.36483100
H -2.91179100 1.34450400 2.27685700
C 1.49990300 2.11273400 1.84920300
C 2.64706300 2.47183000 2.11583800
C 4.07197300 2.70222700 2.20993600

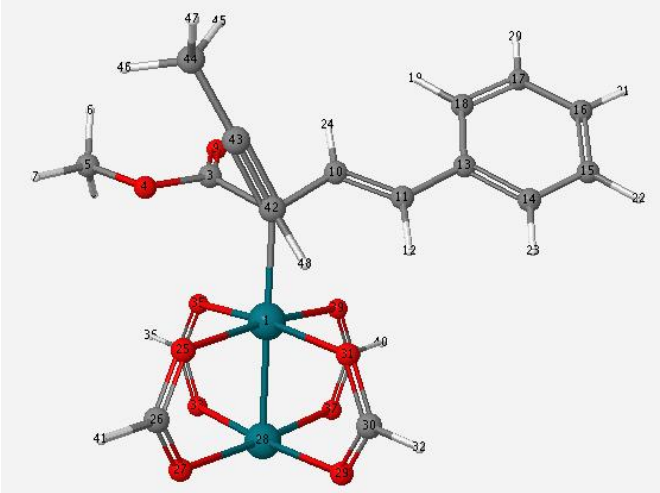
H 4.57511500 2.03823200 1.48697800

H 4.34675200 3.73955600 1.99000900

H 4.44807800 2.43921600 3.20598600

H 0.44398100 2.02150600 2.03119700

Cyclopropenation TS-III (left-tilted/s-cis conformer)



Displayed one negative eigenfrequency

Route= #N b3lyp/gen pseudo=read gfprint OPT=(TS,CalcFC,NoEigenTest) freq

RB3LYP Energy=-1670.20707359 Hartree

ZPE=0.342163 Hartree

Conditions=298K, 1.00000 atm

Internal Energy=-1669.832874 Hartree

Enthalpy=-1669.831930 Hartree

Free Energy=-1669.929534 Hartree

Entropy=205.425 cal/mol-K

Dipole Moment=8.1012 Debye

Rh 0.00000000 0.00000000 0.00000000

C 1.67089400 1.32253700 -0.06915000

C 1.35824300 2.54306100 -0.89238800

O 0.44692400 3.38341500 -0.36990400

C -0.03565800 4.39047600 -1.27396900

H 0.78197400 5.02782100 -1.62256400

H -0.75856000 4.97065300 -0.69962200
H -0.51671200 3.92065700 -2.13491800
O 1.83532400 2.68568400 -2.00481100
C 3.01275800 0.83169700 -0.29690400
C 3.47385200 -0.35154300 0.19137000
H 2.79722000 -0.93940700 0.80524300
C 4.79342100 -0.93342100 -0.01363400
C 5.07718700 -2.17424100 0.59317200
C 6.31437500 -2.79100500 0.42751300
C 7.29817900 -2.17910500 -0.35209200
C 7.03485500 -0.94761900 -0.96345300
C 5.80057500 -0.33012100 -0.79681000
H 5.61172300 0.62317200 -1.28054800
H 7.79747900 -0.47054200 -1.57279300
H 8.26472500 -2.65727200 -0.48513300
H 6.51091200 -3.74758500 0.90365800
H 4.30973400 -2.65174100 1.19749400
H 3.65507100 1.44937300 -0.92329500
O -1.17960100 1.18658800 1.21876500
C -2.35303400 0.78860800 1.50051500
O -2.93123000 -0.27508800 1.14271300
Rh -1.89372600 -1.58713100 -0.06189000
O -1.07961300 -2.48415400 1.61909900
C -0.03157400 -2.00070000 2.11420100
O 0.65074700 -1.00386100 1.69901300
H 0.35772600 -2.48978600 3.01870000
O -2.58225000 -0.59425300 -1.72559200
C -1.91699200 0.39356800 -2.14178900
O -0.84456000 0.88355800 -1.66703900
H -2.31012200 0.90462000 -3.03201600
O -0.75605900 -2.80675200 -1.27017500
C 0.40527200 -2.41475400 -1.57097600
O 0.99768400 -1.34895200 -1.21317900

H 0.98908100 -3.07787500 -2.22510600

H -2.93498500 1.46535200 2.14276800

C 1.71349800 1.81916300 1.94984300

C 2.14079600 2.97153400 1.95054900

C 2.63747300 4.32479000 1.78433300

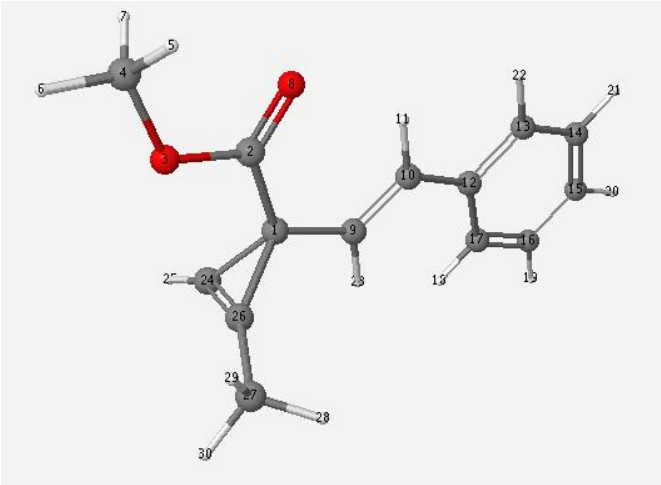
H 3.46541200 4.35578900 1.06407500

H 1.84152700 4.99210700 1.43739700

H 3.01982300 4.70850300 2.73916900

H 1.38735000 0.89603000 2.38825100

Cyclopropene product M-III



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Route= #N B3LYP/6-31G(d) 5d OPT FREQ

RB3LYP Energy=-692.265420067 Hartree

ZPE=0.242562 Hartree

Conditions=298K, 1.00000 atm

Internal Energy=-692.006910 Hartree

Enthalpy=-692.005966 Hartree

Free Energy=-692.068658 Hartree

Entropy=131.946 cal/mol-K

Dipole Moment=3.2977 Debye

C 0.00000000 0.00000000 0.00000000

C	0.66785600	-1.33558700	0.20658400
O	2.02226100	-1.22708000	0.18355500
C	2.73207700	-2.45801000	0.37343600
H	2.49257900	-2.89796700	1.34574200
H	3.78984900	-2.19650700	0.32143400
H	2.47575500	-3.17748200	-0.40918200
O	0.11100400	-2.40140500	0.38373200
C	-1.49033800	0.08473800	0.04826200
C	-2.39621100	-0.88235000	0.27937000
H	-2.04063900	-1.88980900	0.46639800
C	-3.85719300	-0.70988300	0.31261300
C	-4.65177800	-1.80752600	0.69264200
C	-6.04164800	-1.71309200	0.75212000
C	-6.67650100	-0.51350100	0.42770700
C	-5.90437800	0.58679700	0.04141900
C	-4.51691500	0.49029900	-0.01717000
H	-3.94069100	1.35607900	-0.33122900
H	-6.38840300	1.52461700	-0.21999300
H	-7.75955000	-0.43524100	0.47046400
H	-6.62831600	-2.57809700	1.05103200
H	-4.16338000	-2.74550700	0.94646100
H	-1.83581100	1.10286100	-0.13170900
C	0.74222500	1.03474300	-0.84465900
H	0.97158600	1.28772700	-1.86863600
C	0.79609600	1.24765900	0.42328000
C	1.20077300	1.98412400	1.63844700
H	0.32396800	2.24560200	2.24259900
H	1.85053700	1.35550600	2.25954800
H	1.74152500	2.90181100	1.38489300

Dirhodium tetrakis formate

Structure previously reported in ref (5a).

B3LYP Energy=-977.981873264 Hartree

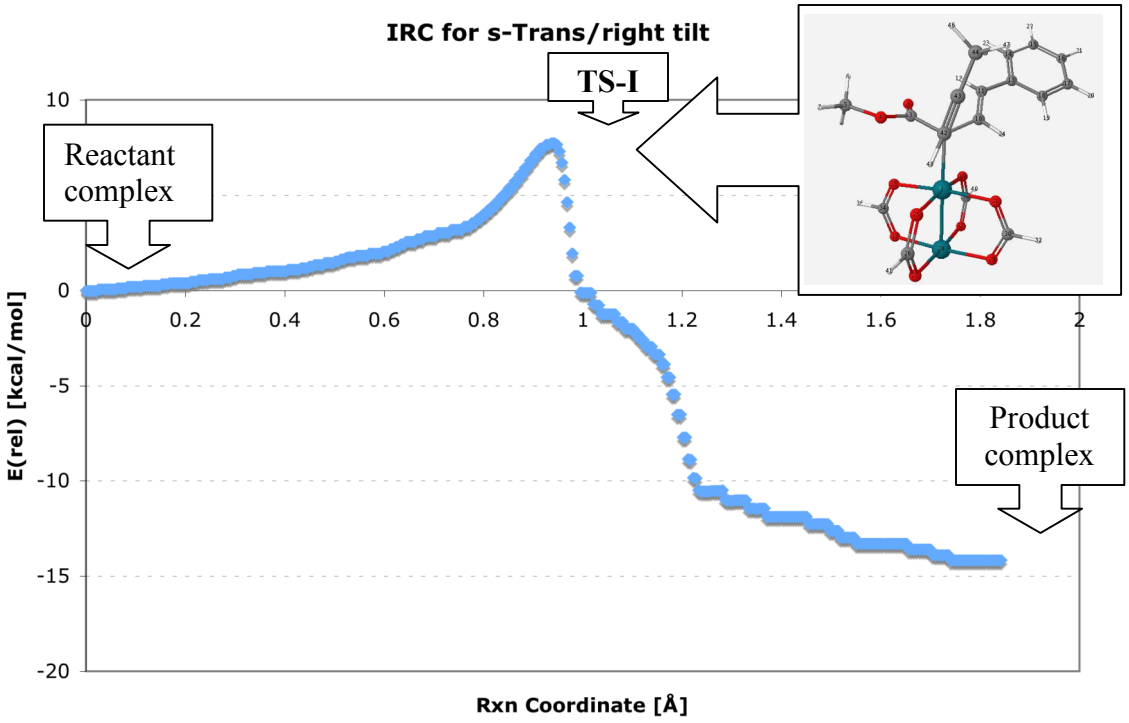
ZPE=0.101954 Hartree

Enthalpy=-977.865223 Hartree

Free Energy=-977.920161 Hartree

Entropy=115.627 cal/mol-K

Intrinsic Reaction Coordinate Analysis: The figure below shows the IRC profile generated for the most stable transition state structure **TS-I**. Maxpoints was set to 50.



Single Point Energy Calculations: Calculated single point energies and zero-point corrected single points are summarized in the table below.

Structure	*Single Point Energy 6-311+G(2d,2p) on C, H, O [A.U.]*	*ZPE 6-31G* on C, H, O [A.U.]*	*E+ZPE [A.U.]*
Propene	-116.6972307	0.055732	-116.6414987
M-I	-1554.002772	0.285402	-1553.71737
TS-I	-1670.682739	0.342298	-1670.340441
M-III	-692.4937939	0.242517	-692.2512769
$Rh_2(O_2CH)_4$	-978.2327362	0.101954	-978.1307822

VI. General procedure for Rhodium(II)-catalyzed cyclopropenation of phenylacetylene with methyl diazoacetoaceate

A mixture of alkyne (0.5 mmol) and Rh(II) catalyst (0.01 mmol) was dissolved in 1 mL solvent (pentane for DOSP, dichloromethane for PTAD and octanoate) and stirred at either room temperature or -45^{o}C (CH_3CN/dry ice bath) under an atmosphere of argon. Methyl diazoacetoacetate (1.0 mmol) in 10 mL solvent was then added to former solution *via* syringe pump over 2 h. After addition, the mixture was stirred for additional 20 min then concentrated *in vacuo*. ^{1}H NMR analysis of the crude reaction mixture was done to determine the presence of cyclopropenes and furan products. The residue was purified on silica using 10: 1 hexane/ether as solvent system to afford the cyclopropene and/or furan product/s.

VII. General procedure for Rh(II)-Catalyzed cyclopropenation phenylacetylene with siloxyvinyldiazoacetate

A mixture of alkyne (0.5 mmol) and Rh(II) catalyst (0.01 mmol) was dissolved in 1 mL solvent (pentane for DOSP and Bi-TISP, dichloromethane for PTAD, PTTL and NTTL) and stirred at -0°C under an atmosphere of argon. Siloxyvinyldiazoacetate[8] (1.0 mmol) in 10 mL solvent was then added to former solution *via* syringe pump over 2 h. After addition, the mixture was stirred for additional 20 min then concentrated *in vacuo*. The residue was purified on silica using 10: 1 hexane/ether as solvent system to afford the cyclopropene product as yellowish oil. HPLC analysis was done using ADH chiral column, using the following solvent system: 1ml/min 1% isopropanol/hexanes.

VIII. Procedure for the synthesis of t-Butyl(2-ethynylbenzyloxy)-dimethylsilane.

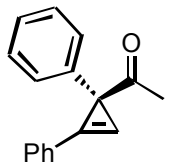
A mixture of 2-ethynylbenzyl alcohol (1.0 equiv), DMAP (0.01 equiv) and Imidazole (1.1 equiv) in DCM was cooled to 0°C using ice-water bath. TBSCl (1.1 equiv) was then added to the solution and the resulting suspension was warmed to room temperature and left stirring overnight. The reaction was diluted with hexanes and quenched with saturated aqueous NH_4Cl solution. The layers were separated and the organic layer was washed with brine, dried over $MgSO_4$ and filtered. The filtrate was concentrated *in vacuo* and the residue was passed through a short silica plug to afford the silyl-protected alkyne (quantitative yield) as colorless oil which was used without further purification. The spectral data of the product is consistent with published results.[9]

IX. General procedure for Rh_2(S-PTAD)$_4$-catalyzed cyclopropenation of aryl alkynes with siloxyvinyldiazoacetate

A mixture of alkyne (0.5 mmol) and Rh_2(*S*-PTAD)$_4$ catalyst (0.01 mmol) was dissolved in 1 mL dichloromethane and stirred at -45°C (CH_3CN/dry ice bath) under an atmosphere of argon. Siloxyvinyldiazoacetate (1.0 mmol) in 10 mL solvent was then added to former solution *via* syringe pump over 2 h. After addition was completed, the mixture was stirred for additional 20 min followed by addition of TBAF (1.0 mmol). The reaction mixture was further stirred at room temperature followed by aqueous work-up. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography using 10:1 hexane/ether then 1:1 hexane/EtOAc to afford the cyclopropenyl ketone product as colorless to yellowish oil. HPLC analyses were done

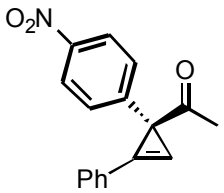
using either ADH, ODH or ASH chiral column with the following parameters: 1ml/min flow rate, 10% isopropanol/hexanes solvent system and UV 254 nm.

IV. Spectral data and full characterization of all compounds



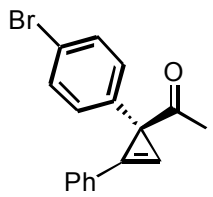
132

(*R*)-1-(1,2-Diphenylcycloprop-2-en-1-yl)ethanone (132). Purification by silica gel chromatography (10:1 pentane/Et_2O) gave compound **132** in 88% yield (94 mg) as yellowish oil. IR (neat) 2921, 1717, 1232, 697 cm^{-1}; ^1H NMR (400 MHz) δ 7.61 (dd, 2H, J = 8.0 Hz, 1.6 Hz), 7.19-7.45 (m, 9H), 2.08 (s, 3H); ^{13}C-NMR (100 MHz) δ 210.1 (C), 140.9 (C), 130.5 (CH), 130.1 (CH), 129.3 (CH), 128.8 (CH), 128.4 (CH), 126.8 (CH), 125.6 (C), 120.1 (C), 102.3 (CH), 42.8 (C), 27.7 (CH_3). HRMS (ESI) *m/z* calcd for $C_{24}H_{20}O_2$, 340.1463, found 341.1533 $[M+H]^+$. HPLC: ODH, 2% iPrOH/hexane, 0.7 $mlmin^{-1}$, UV 254 nm, t_R: 20.3 min (major), 29.1 min (minor), 57% ee.



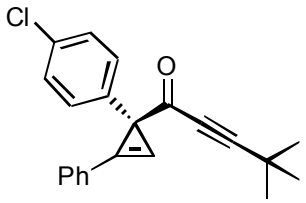
133

(*R*)-1-(1-(4-Nitrophenyl)-2-phenylcycloprop-2-en-1-yl)ethanone (133). Purification by silica gel chromatography (10:1 pentane/Et_2O) gave compound **133** in 82% yield (114 mg) as yellowish oil. IR (neat) 3028, 1717, 1206, 692 cm^{-1}; ^1H NMR (400 MHz) δ 7.61 (dd, 2H, *J* = 8.0 Hz, 1.6 Hz), 7.19-7.45 (m, 9H), 2.08 (s, 3H); ^{13}C-NMR (100 MHz) δ 208.8 (C), 148.5 (C), 146.6 (C), 131.2 (CH), 130.1 (CH), 129.7 (CH), 129.6 (CH), 124.5 (C), 123.4 (CH), 119.2 (C), 101.1 (CH), 42.2 (C), 27.3 (CH_3). HRMS (ESI) *m/z* calcd for $C_{24}H_{20}O_2$, 340.1463, found 341.1533 $[M+H]^+$. HPLC: ODH, 15% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 21.8 min (major), 19.6 min (minor), 80% ee.



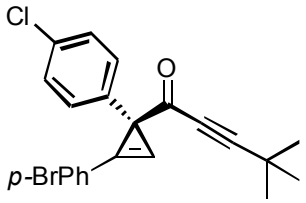
134

(*R*)-1-(1-(4-Bromophenyl)-2-phenylcycloprop-2-en-1-yl)ethanone (134). Purification by silica gel chromatography (10:1 pentane/Et_2O) gave compound **134** in 87% yield (136 mg) as colorless oil. IR (neat) 3028, 1717, 1206, 692 cm^{-1}; ^1H NMR (400 MHz) δ 7.61 (dd, 2H, *J* = 8.0 Hz, 1.6 Hz), 7.19-7.45 (m, 9H), 2.08 (s, 3H); ^{13}C-NMR (100 MHz) δ 209.5 (C), 139.9 (C), 131.4 (CH), 130.8 (CH), 130.6 (CH), 130.1 (CH), 129.4 (CH), 125.1 (C), 120.7 (C), 119.9 (C), 101.7 (CH), 42.2 (C), 27.5 (CH_3). HRMS (ESI) *m/z* calcd for $C_{24}H_{20}O_2$, 340.1463, found 341.1533 $[M+H]^+$. HPLC: ODH, 1% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 27.8 min (major), 34.5 min (minor), 89% ee.



135

(*R*)-1-(1-(4-Chlorophenyl)-2-phenylcycloprop-2-en-1-yl)-4,4-dimethylpent-2-yn-1-one (135). Purification by silica gel chromatography (10:1 pentane/Et_2O) gave compound **135** in 84 % yield (141 mg) as white solid. IR (neat) 2969, 2198, 1649, 1090, 729 cm^{-1}; ^1H NMR (400 MHz) δ 7.60 (m, 2H), 7.42 (m, 2H), 7.32 (d, 2H, J = 8.4 Hz), 7.25 (m, 1H), 7.23 (d, 2H, J = 8.4 Hz), 1.02 (s, 9H); ^{13}C-NMR (100 MHz) δ 189.3 (C), 138.4 (C), 132.7 (C), 130.6 (CH), 130.3 (CH), 130.2 (CH), 129.1 (CH), 128.4 (CH), 125.4 (C), 118.9 (C), 105.6 (C), 100.2 (CH), 79.4 (C), 43.6 (C), 29.9 (CH_3), 27.8 (C). HRMS (ESI) *m/z* calcd for $C_{22}H_{20}ClO$, 335.1158, found 335.1193 $[M+H]^+$. HPLC: ODH, 1% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 7.1 min (major), 8.9 min (minor), 85% ee.



136

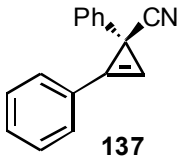
(*R*)-1-(2-(4-Bromophenyl)-1-(4-chlorophenyl)cycloprop-2-en-1-yl)-4,4-dimethylpent-2-yn-1-one (136). Purification by silica gel chromatography (10:1 pentane/Et_2O) gave compound **136** in 95% yield (196 mg) as yellow solid. IR (neat) 3028, 1717, 1206, 692

cm^{-1}; ^{1}H NMR (400 MHz) δ 7.56 (d, 2H, J = 6.8 Hz), 7.44 (d, 2H, J = 6.8 Hz), 7.22-7.29 (m, 5H), 1.03 (s, 9H); ^{13}C-NMR (100 MHz) δ 188.9 (C), 138.0 (C), 132.9 (C), 132.5 (CH), 131.4 (CH), 130.2 (CH), 128.5 (CH), 125.0 (C), 124.3 (C), 118.0 (C), 105.9 (C), 101.3 (CH), 79.3 (C), 43.5 (C), 30.0 (CH_3), 27.9 (C). HRMS (ESI) *m/z* calcd for $C_{24}H_{20}O_2$, 340.1463, found 341.1533 $[M+H]^+$. HPLC: ODH, 1% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 8.2 min (major), 9.7 min (minor), 91% ee.

V. General procedure for the cyclopropenation with phenyldiazonitrile

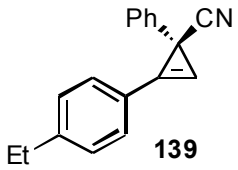
A mixture of alkyne and the Rh (II) catalyst (2 mol %) was placed in an oven-dried round bottom flask and dissolved with 2 mL degassed toluene. The green solution was stirred under an atmosphere of argon and was then cooled to -78 ºC and the diazo compound in 8 mL toluene was then added drop wise over 15 min. The orange solution was then allowed to gradually warm to rt over 6 h. After which, the resulting green solution was then concentrated *in vacuo*. The crude reaction mixture was then further purified by column chromatography and the ee was determined by chiral HPLC.[10]

VI. Spectral data and full characterization of cyclopropenenitriles



137

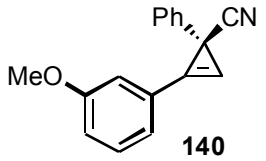
(*R*)-1,2-Diphenylcycloprop-2-enecarbonitrile (137). Purification by silica gel chromatography (10:1 pentane/Et_2O) gave compound **137** in 85% yield (186 mg) as yellow oil. IR (neat) 3057, 2207, 1447, 1265, 764, 695 cm^{-1}; ^1H NMR (400 MHz) δ 7.61 (m, 2H), 7.26-7.45 (m, 8H), 7.10 (s, 1H); ^{13}C-NMR (100 MHz) δ 138.4 (C), 131.4 (CH), 130.5 (CH), 129.9 (CH), 129.5 (CH), 128.9 (CH), 127.6 (CH), 125.7 (CH), 123.4 (C), 122.4 (C), 114.4 (C), 97.5 (CH), 20.1 (C). HRMS (ESI) *m/z* calcd for $C_{16}H_{12}N$, 217.0891, found 218.0925 $[M+H]^+$. HPLC: ODH, 2% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 13.8 min (major), 21.2 min (minor), 85% ee.



139

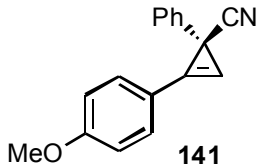
(*R*)-2-(4-Ethylphenyl)-1-phenylcycloprop-2-enecarbonitrile (139). Purification by silica gel chromatography (10:1 pentane/Et_2O) gave compound **139** in 88% yield (216 mg) as yellow oil. IR (neat) 3133, 2961, 2929, 2872, 2224, 1239, 695 cm^{-1}; ^1H NMR (400 MHz) δ 7.50 (d, 2H, J = 8.0 Hz), 7.24-7.39 (m, 7H), 7.02 (s, 1H), 2.66 (q, 2H, J = 7.6 Hz), 1.22 (t, 3H, J = 7.6 Hz); ^{13}C-NMR (100 MHz) δ 148.2 (C), 138.6 (C), 131.9 (C), 130.6 (CH), 129.0 (CH), 128.9 (CH), 127.5 (CH), 125.7 (CH), 122.5 (C), 120.9 (C), 114.2 (C), 96.3 (CH), 29.2 (CH_2), 20.0 (C), 15.6 (CH_3). HRMS (ESI) *m/z* calcd for

$C_{18}H_{16}N$, 245.1204, found 246.1277 $[M+H]^+$. HPLC: ADH, 2% iPrOH/hexane, 0.7 $mlmin^{-1}$, UV 254 nm, t_R: 19.7 min (minor), 22.9 min (major), 52% ee.



140

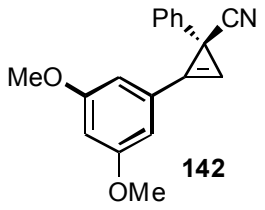
(*R*)-2-(3-methoxyphenyl)-1-phenylcycloprop-2-enecarbonitrile (140). Purification by silica gel chromatography (10:1 pentane/Et_2O) gave compound **140** in 90% yield (223 mg) as yellow oil. IR (neat) 3136, 2224, 1596, 1260, 905, 727, 692 cm^{-1}; ^1H NMR (400 MHz) δ 7.23-7.38 (m, 7H), 7.17 (d, 1H, J = 7.6 Hz), 7.08 (s, 1H), 6.96 (m, 1H), 3.78 (s, 3H); ^{13}C-NMR (100 MHz) δ 160.2 (C), 138.3 (C), 131.5 (C), 130.5 (CH), 129.6 (CH), 129.5 (CH), 128.9 (CH), 127.6 (CH), 125.7 (CH), 124.6 (C), 122.9 (CH), 122.3 (C), 117.4 (CH), 115.2 (CH), 97.9 (CH), 55.7 (CH_3), 20.3 (C). HRMS (ESI) *m/z* calcd for $C_{17}H_{14}NO$, 247.0997, found 248.1069 $[M+H]^+$. HPLC: ADH, 2% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 33.8 min (minor), 38.2 min (major), 63% ee.



141

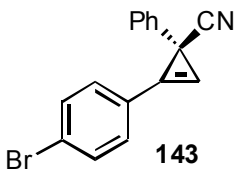
(*R*)-2-(4-Methoxyphenyl)-1-phenylcycloprop-2-enecarbonitrile (141). Purification by silica gel chromatography (10:1 pentane/Et_2O) gave compound **141** in 92% yield (227 mg) as yellow oil. IR (neat) 3135, 2838, 2223, 1774, 1602, 1504, 1253, 1167, 833 cm^{-1}; ^1H NMR (400 MHz) δ 7.52 (d, 2H, J = 8.8 Hz), 7.38 (d, 2H, J = 8.0 Hz), 7.33 (t, 2H, J =

8 Hz), 7.25 (m, 1H), 6.93-6.96 (m, 3H), 3.81 (s, 3H); ^{13}C-NMR (100 MHz) δ 162.0 (C), 138.7 (C), 132.3 (CH), 128.8 (CH), 127.4 (CH), 125.6 (CH), 122.6 (C), 115.7 (C), 115.0 (CH), 113.7 (C), 94.6 (CH), 55.7 (CH_3), 19.9 (C). HRMS (ESI) *m/z* calcd for $C_{17}H_{14}NO$, 247.0997, found 248.1067 $[M+H]^+$. HPLC: ODH, 2% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 23.4 min (major), 27.7 min (minor), 83% ee.



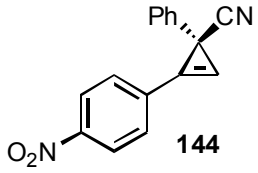
142

(*R*)-2-(3,5-Dimethoxyphenyl)-1-phenylcycloprop-2-enecarbonitrile (142). Purification by silica gel chromatography (10:1 pentane/Et_2O) gave compound **142** in 81% yield (112 mg) as yellowish oil. IR (neat) 3058, 2209, 1465, 1264, 735, 695 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.22-7.38 (m, 5H), 7.09 (s, 1H), 6.72 (d, 2H, *J* = 2.0 Hz), 6.53 (t, 1H, *J* = 3.6 Hz), 3.75 (s, 6H); ^{13}C-NMR (100 MHz) δ 161.4 (C), 138.3 (C), 128.9 (CH), 127.6 (CH), 125.6 (CH), 124.9 (C), 122.2 (C), 114.6 (C), 108.2 (CH), 103.7 (CH), 98.2 (CH), 55.7 (CH_3), 20.4 (C). HRMS (ESI) *m/z* calcd for $C_{18}H_{16}NO_2$, 277.1103, found 278.1174 $[M+H]^+$. HPLC: ODH, 2% iPrOH/hexane, 0.7 mlmin^{-1}, UV 254 nm, t_R: 23.0 min (major), 32.3 min (minor), 37% ee.



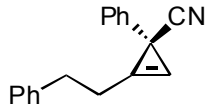
143

(*R*)-2-(4-Bromophenyl)-1-phenylcycloprop-2-enecarbonitrile (143). Purification by silica gel chromatography (10:1 pentane/Et_2O) gave compound **143** in 93% yield (275 mg) as yellow oil. IR (neat) 3134, 2225, 1776, 1479, 1067, 694 cm^{-1}; ^1H NMR (400 MHz) δ 7.54 (d, 2H, *J* = 8 Hz), 7.43 (d, 2H, *J* = 8 Hz), 7.27-7.35 (m, 5H), 7.16 (s, 1H); ^{13}C-NMR (100 MHz) δ 137.9 (C), 132.8 (CH), 131.8 (CH), 128.9 (CH), 127.8 (CH), 126.0 (C), 125.6 (CH), 122.4 (C), 122.0 (C), 113.6 (C), 98.5 (C), 20.2 (C). HRMS (ESI) *m/z* calcd for $C_{16}H_{11}BrN$, 294.9997, found 296.0070 $[M+H]^+$. HPLC: ODH, 2% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 16.2 min (major), 27.1 min (minor), 93% ee.



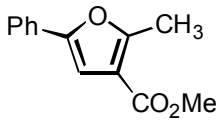
144

(*R*)-2-(4-Nitrophenyl)-1-phenylcycloprop-2-enecarbonitrile (144). Purification by silica gel chromatography (10:1 pentane/Et_2O) gave compound **144** in 88% yield (115 mg) as yellow oil. IR (neat) 3059, 2916, 2209, 1519, 853, 766, 696 cm^{-1}; ^1H NMR (400 MHz) δ 8.30 (d, 2H, *J* = 8.4 Hz), 7.78 (d, 2H, *J* = 8.4 Hz), 7.46 (s, 1H), 7.35-7.37 (m, 5H); ^{13}C-NMR (100 MHz) δ 149.2 (C), 137.2 (C), 131.2 (CH), 129.1 (CH), 128.1 (CH), 125.6 (CH), 124.7 (CH), 121.4 (C), 113.2 (C), 102.7 (CH), 20.6 (C). HRMS (ESI) *m/z* calcd for $C_{16}H_{11}N_2O_2$, 263.0825, found 263.0776 $[M+H]^+$. HPLC: ODH, 15% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 21.7 min (major), 33.5 min (minor), 89% ee.



145

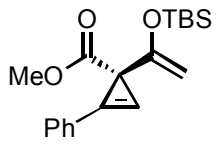
(*S*)-2-Phenethyl-1-phenylcycloprop-2-enecarbonitrile (145). Purification by silica gel chromatography (10:1 pentane/Et_2O) gave compound **145** in 87% yield (214 mg) as colorless oil. IR (neat) 3028, 2223, 1794, 1601, 1494, 906, 727, 695 cm^{-1}; ^1H NMR (400 MHz) δ 7.15-7.30 (m, 10H), 6.55 (br s, 1H), 2.82-2.95 (m, 4H); ^{13}C-NMR (100 MHz) δ 139.9 (C), 139.0 (C), 128.9 (CH), 128.9 (CH), 128.6 (CH), 127.2 (CH), 126.8 (CH), 125.4 (CH), 122.9 (C), 116.9 (C), 96.6 (CH), 32.7 (CH_2), 25.5 (CH_2), 19.9 (C). HRMS (ESI) *m/z* calcd for $C_{18}H_{16}N$, 245.1204, found 246.1276 $[M+H]^+$. HPLC: ODH, 1% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 13.6 min (major), 17.5 min (minor), 44% ee.



154

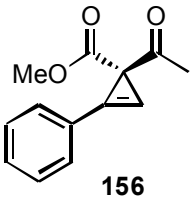
Methyl 2-methyl-5-phenylfuran-3-carboxylate (154) Purification by silica gel chromatography eluting with hexane/Et_2O (10:1) afforded **154** in 97% yield (105 mg) as white solid. MP 55-57°C; R_f 0.72 (hexane/EtOAc 8:2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 6.84 (s, 3H), 3.80 (s. 3H), 2.60 (s. 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 164.6 (C), 158.9 (C), 151.9 (C), 130.2 (C), 128.9 (CH), 127.8 (CH), 123.8 (CH), 115.3 (C), 105.6 (CH), 51.5 (CH_3), 14.0

(CH_3); IR (neat) 2951, 1715, 1614, 1440, 1230, 1096, 907, 729, 690 cm^{-1}; ESI-HRMS: (M+H) m/z, found: 217.0820; calcd ($C_{13}H_{13}O_3$): 217.0858.



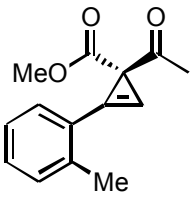
155

Methyl (*R*)-1-(1-((tert-butyldimethylsilyl)oxy)vinyl)-2-phenylcycloprop-2-enecarboxylate (155) Purification by silica gel chromatography eluting with hexane/Et_2O (10:1) afforded **155** in 93% yield (154 mg) as yellowish oil. R_f 0.74 (hexane/EtOAc 8:2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (m, 2H), 7.38 (m, 3H), 6.95 (s, 1H), 4.29 (d, J = 0.4 Hz, 1H), 4.17 (d, J = 0.4 Hz, 1H), 3.67 (s. 3H), 0.88 (s. 9H), 0.16 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 174.3 (C), 158.9 (C), 130.4 (CH), 130.1 (CH), 128.9 (CH), 125.6 (C), 117.3 (C), 99.4 (CH), 90.6 (CH), 52.2 (CH_3), 25.7 (CH_3), -4.6 (CH_3) (CH_3); IR (neat) 2951, 2929, 2857, 1725, 1623, 1297, 1242, 1056, 1013, 832, 696 cm^{-1}; ESI-HRMS: (M+H) m/z, found: 330.1610; calcd ($C_{19}H_{26}O_3Si$): 330.1651; HPLC: ADH, 1% iPrOH/hexane, 1mlmin^{-1}, UV 254 nm, t_R: 21.1 min (minor), 26.3 min (major), 94% ee with Rh_2(*S*-PTAD)$_4$



156

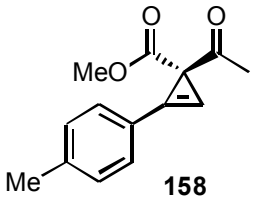
Methyl (*R*)-1-acetyl-2-phenylcycloprop-2-enecarboxylate (156) Purification by silica gel chromatography eluting with hexane/Et_2O (10:1) then hexane/EtOAc (1:1) afforded **156** in 83% yield (90 mg) as yellow oil. R_f 0.30 (hexane/EtOAc 8:2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (m, 2H), 7.42 (m, 3H), 6.98 (s, 1H), 3.69 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 206.1 (C), 172.0 (C), 130.9 (CH), 130.4 (CH), 129.2 (CH). 124.1 (C), 113.3 (C), 96.5 (CH), 52.3 (CH_3), 40.7 (C), 28.1 (CH_3); IR (neat) 3139, 2952, 1721, 1693, 1274, 1229, 697 cm^{-1}; ESI-HRMS: (M+H) m/z, found: 217.0820; calcd ($C_{13}H_{13}O_3$): 217.0858; HPLC: ADH, 10% iPrOH/hexane, 1mlmin^{-1}, UV 254 nm, t_R: 10.6 min (major), 11.3 min (minor), 98% ee with Rh_2(*S*-PTAD)$_4$; $[\alpha]^{23}_D$ +10.9 (*c* 1.0, $CHCl_3$)



157

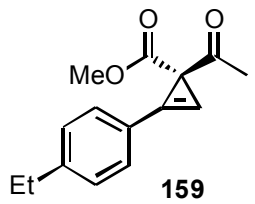
Methyl (*R*)-1-acetyl-2-(o-tolyl)cycloprop-2-enecarboxylate (157) Purification by silica gel chromatography eluting with hexane/Et_2O (10:1) then hexane/EtOAc (1:1) afforded **157** in 80% yield (92 mg) a**s** yellow oil. R_f 0.33 (hexane/EtOAc 8:2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.6 Hz, 1H), 7.30 (m, 3H), 6.99 (s, 1H), 3.71 (s, 3H), 2.52 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 206.2 (C), 172.0 (C), 140.5 (CH), 131.2 (CH), 130.9 (CH), 130.6 (CH), 126.5 (CH), 123.0 (C), 112.4 (C), 98.1 (CH), 52.3 (CH_3), 39.8 (C), 28.1 (CH_3), 20.2 (CH_3); IR (neat) 3138, 2953, 2853, 1720, 1694, 1273, 1208, 723 cm^{-1}; ESI-HRMS: (M+H) m/z, found: 231.0976; calcd ($C_{14}H_{15}O_3$): 231.1016;

HPLC: ADH, 10% iPrOH/hexane, 1mlmin^{-1}, UV 254 nm, t_R: 8.6 min (major), 9.8 min (minor), 98% ee with Rh_2(*S*-PTAD)$_4$; $[\alpha]^{23}_D$ +6.8 (*c* 1.0, $CHCl_3$)



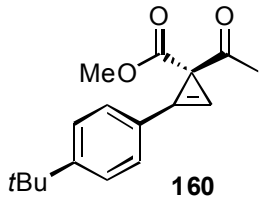
158

Methyl (*R*)-1-acetyl-2-(p-tolyl)cycloprop-2-enecarboxylate (158) Purification by silica gel chromatography eluting with hexane/Et_2O (10:1) then hexane/EtOAc (1:1) afforded **158** in 86% yield (99 mg) as yellow oil. R_f 0.36 (hexane/EtOAc 8:2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.82 (s, 1H), 3.68 (s, 3H), 2.36 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 206.4 (C), 172.1 (C), 141.5 (CH), 130.5 (CH), 129.9 (CH), 121.3 (C), 113.3 (C), 95.1 (CH), 52.3 (CH_3), 40.7 (C), 28.1 (CH_3), 21.8 (CH_3); IR (neat) 3139, 2952, 1720, 1693, 1275, 1229, 820 cm^{-1}; ESI-HRMS: (M+H) m/z, found: 231.0976; calcd ($C_{14}H_{15}O_3$): 231.1016; HPLC: ODH, 10% iPrOH/hexane, 1mlmin^{-1}, UV 254 nm, t_R: 10.6 min (major), 11.3 min (minor), 98% ee with Rh_2(*S*-PTAD)$_4$; $[\alpha]^{23}_D$ +11.8 (*c* 1.0, $CHCl_3$)



159

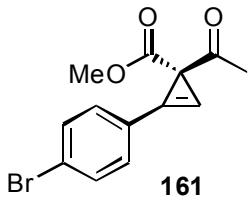
Methyl (*R*)-1-acetyl-2-(4-ethylphenyl)cycloprop-2-enecarboxylate (159) Purification by silica gel chromatography eluting with hexane/Et_2O (10:1) then hexane/EtOAc (1:1) afforded **159** in 90% yield (109 mg) as yellow oil. R_f 0.42 (hexane/EtOAc 8:2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 6.8 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 6.85 (s, 1H), 3.71 (s, 3H), 2.68 (q, *J* = 7.2 Hz, 2H), 2.22 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 206.4 (C), 172.1 (C), 147.7 (CH), 130.6 (CH), 128.8 (CH), 121.5 (C), 113.3 (C), 95.1 (CH), 52.4 (CH_3), 40.7 (C), 29.1 (CH_2), 28.1 (CH_3), 15.5 (CH_3); IR (neat) 3140, 2966, 1723, 1694, 1276, 1230, 837 cm^{-1}; ESI-HRMS: (M+H) m/z, found: 245.1133; calcd ($C_{15}H_{17}O_3$): 245.1172; HPLC: ADH, 2% iPrOH/hexane, 1mlmin^{-1}, UV 254 nm, t_R: 37.4 min (major), 40.2 min (minor), 97% ee with Rh_2(*S*-PTAD)$_4$; $[\alpha]^{23}_D$ +7.8 (*c* 1.0, $CHCl_3$)



160

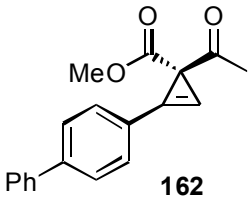
Methyl (*R*)-1-acetyl-2-(4-(tert-butyl)phenyl)cycloprop-2-enecarboxylate (160) Purification by silica gel chromatography eluting with hexane/Et_2O (10:1) then hexane/EtOAc (1:1) afforded **160** in 87% yield (118 mg) as yellow oil. R_f 0.45 (hexane/EtOAc 8:2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 6.83 (s, 1H), 3.71 (s, 3H), 2.22 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 206.4 (C), 172.1 (C), 154.5 (CH), 130.3 (CH), 126.3 (CH), 121.3 (C), 113.2 (C), 95.2 (CH), 52.4 (CH_3), 40.7 (C), 35.2 (C), 31.3 (CH_3), 28.1 (CH_3); IR (neat) 3139, 2957,

1721, 1696, 1270, 1229, 838 cm^{-1}; ESI-HRMS: (M+H) m/z, found: 273.1446; calcd ($C_{17}H_{21}O_3$): 273.1484; HPLC: ADH, 10% iPrOH/hexane, 1mlmin^{-1}, UV 254 nm, t_R: 10.8 min (major), 13.1 min (minor), 98% ee with Rh_2(*S*-PTAD)$_4$; $[\alpha]^{23}_D$ +4.8 (*c* 1.0, $CHCl_3$)



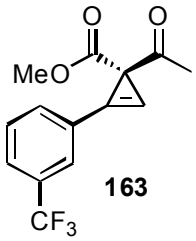
161

Methyl (*R*)-1-acetyl-2-(4-bromophenyl)cycloprop-2-enecarboxylate (161) Purification by silica gel chromatography eluting with hexane/Et_2O (10:1) then hexane/EtOAc (1:1) afforded **161** in 92% yield (137 mg) as yellow oil. R_f 0.38 (hexane/EtOAc 8:2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 6.93 (s, 1H), 3.69 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 205.9 (C), 171.8 (C), 132.6 (CH), 131.8 (CH), 125.5 (C), 123.1 (C), 112.5 (C), 97.2 (CH), 52.5 (CH_3), 40.6 (C), 28.3 (CH_3); IR (neat) 3141, 2951, 1721, 1694, 1273, 1227, 827 cm^{-1}; ESI-HRMS: (M+H) m/z, found: 294.9925; calcd ($C_{13}H_{12}BrO_3$): 294.9964; HPLC: ADH, 10% iPrOH/hexane, 1mlmin^{-1}, UV 254 nm, t_R: 18.3 min (major), 20.9 min (minor), 95% ee with Rh_2(*S*-PTAD)$_4$; $[\alpha]^{23}_D$ +16.9 (*c* 1.0, $CHCl_3$)



162

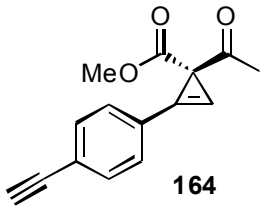
Methyl (*R*)-2-([1,1'-biphenyl]-4-yl)-1-acetylcycloprop-2-enecarboxylate (162) Purification by silica gel chromatography eluting with hexane/Et_2O (10:1) then hexane/EtOAc (1:1) afforded **162** in 88% yield (129 mg) as yellow oil. R_f 0.33 (hexane/EtOAc 8:2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.64 (m, 4H), 7.57 (m, 2H), 7.42 (m, 2H), 7.37 (m, 1H), 6.93 (s, 1H), 3.72 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 206.2 (C), 172.0 (C), 143.8 (CH), 140.2 (CH), 130.9 (CH), 129.2 (CH), 128.3 (CH), 127.9 (CH), 127.4 (CH), 122.9 (C), 113.1 (C), 96.3 (CH), 52.4 (CH_3), 40.8 (C), 28.2 (CH_3); IR (neat) 3139, 3030, 2951, 1721, 1693, 1274, 1229, 843, 696 cm^{-1}; ESI-HRMS: (M+H) m/z, found: 293.1133; calcd ($C_{19}H_{17}O_3$): 293.1172; HPLC: ADH, 10% iPrOH/hexane, 1mlmin^{-1}, UV 254 nm, t_R: 23.2 min (major), 27.5 min (minor), 98% ee with Rh_2(*S*-PTAD)$_4$; $[\alpha]^{23}_D$ +1.6 (*c* 1.0, $CHCl_3$)



163

Methyl (*R*)-1-acetyl-2-(3-(trifluoromethyl)phenyl)cycloprop-2-enecarboxylate (163) Purification by silica gel chromatography eluting with hexane/Et_2O (10:1) then hexane/EtOAc (1:1) afforded **163** in 94% yield (138 mg) as yellow oil. R_f 0.42 (hexane/EtOAc 8:2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 2H), 7.08 (s, 1H), 3.74 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 205.7 (C), 171.6 (C), 133.5 (CH), 132.0 (C, q, *J* = 130.4 Hz)), 129.9 (CH), 127.4 (CH), 127.0 (CH), 125.1 (C), 112.1 (C), 98.6 (CH), 52.5

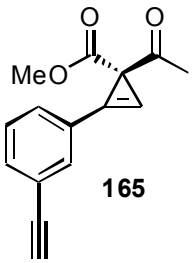
(CH_3), 40.7 (C), 28.4 (CH_3); IR (neat) 3139, 2952, 1721, 1693, 1274, 1229, 697 cm^{-1}; ESI-HRMS: (M+H) m/z, found: 285.0694; calcd ($C_{14}H_{11}F_3O_3$): 285.0733; HPLC: ADH, 10% iPrOH/hexane, 1mlmin^{-1}, UV 254 nm, t_R: 4.5 min (major), 7.1 min (minor), 98% ee with Rh_2(*S*-PTAD)$_4$; $[\alpha]^{23}_D$ +1.7 (*c* 1.0, $CHCl_3$)



164

Methyl (*R*)-1-acetyl-2-(4-ethynylphenyl)cycloprop-2-enecarboxylate (164)

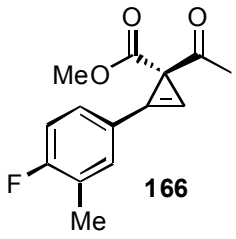
Purification by silica gel chromatography eluting with hexane/Et_2O (10:1) then hexane/EtOAc (1:1) afforded **164** in 85% yield (102 mg) a**s** yellow oil. R_f 0.45 (hexane/EtOAc 8:2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (app t, *J* = 8.8 Hz, 4H), 7.00 (s, 1H), 3.72 (s, 3H), 3.23 (s, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 205.9 (C), 171.8 (C), 132.9 (CH), 130.3 (CH), 124.7 (C), 124.3 (C), 112.7 (C), 97.6 (CH), 83.0 (C), 79.9 (CH), 52.5 (CH_3), 40.7 (C), 28.3 (CH_3), 21.8 (CH_3); IR (neat) 3293, 3142, 2953, 1723, 1694, 1274, 1230, 907, 727 cm^{-1}; ESI-HRMS: (M+H) m/z, found: 241.0820; calcd ($C_{15}H_{13}O_3$): 241.0859; HPLC: ADH, 10% iPrOH/hexane, 1mlmin^{-1}, UV 254 nm, t_R: 17.9 min (major), 19.3 min (minor), 93% ee with Rh_2(*S*-PTAD)$_4$; $[\alpha]^{23}_D$ +2.1 (*c* 1.0, $CHCl_3$)



165

Methyl (*R*)-1-acetyl-2-(3-ethynylphenyl)cycloprop-2-enecarbo-xylate (165)

Purification by silica gel chromatography eluting with hexane/Et_2O (10:1) then hexane/EtOAc (1:1) afforded **165** in 88% yield (106 mg) as yellow oil. R_f 0.41 (hexane/EtOAc 8:2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.69 (t, J = 1.6 Hz, 1H), 7.55 (m, 2H), 7.41 (t, J = 7.6 Hz, 1H), 6.98 (s, 1H), 3.73 (s, 3H), 3.15 (s, 1H), 2.27 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 205.9 (C), 171.8 (C), 134.3 (CH), 133.8 (CH), 130.6 (CH), 129.3 (CH), 124.5 (C), 123.5 (C), 112.5 (C), 97.5 (CH), 82.5 (C), 78.8 (CH), 52.5 (CH_3), 40.7 (C), 28.4 (CH_3); IR (neat) 3284, 3142, 2952, 1721, 1694, 1274, 1224, 1045, 799 cm^{-1}; ESI-HRMS: (M+H) m/z, found: 217.0820; calcd ($C_{13}H_{13}O_3$): 217.0858; HPLC: ADH, 10% iPrOH/hexane, 1mlmin^{-1}, UV 254 nm, t_R: 10.6 min (major), 11.3 min (minor), 98% ee with Rh_2(*S*-PTAD)$_4$; $[\alpha]^{23}_D$ +6.8 (*c* 1.0, $CHCl_3$)

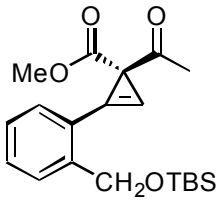


166

Methyl (*R*)-1-acetyl-2-(4-fluoro-3-methylphenyl)cycloprop-2-enecarboxylate (166)

Purification by silica gel chromatography eluting with hexane/Et_2O (10:1) then hexane/EtOAc (1:1) afforded **166** in 77% yield (96 mg) as yellow oil. R_f 0.39 (hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 6.82 (s, 1H), 3.68 (s, 3H), 2.36 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$) 206.1 (C), 171.9 (C), 164.1 (C), 161.6 (C), 133.7 (CH), 129.9 (CH, J = 35.2 Hz), 126.3 (C, J = 72.8 Hz), 120.1 (C), 116.1 (CH, 94.4 Hz), 112.5 (C), 95.5 (CH), 52.4 (CH_3), 40.8 (C), 28.2 (CH_3), 14.6 (CH_3); IR (neat) 3139, 2955, 1719, 1693, 1274, 1229, 697 cm^{-1}; ESI-HRMS: (M+H) m/z, found: 249.0882; calcd ($C_{14}H_{13}FO_3$): 249.0921; HPLC: ADH, 10% iPrOH/hexane, 1mlmin^{-1}, UV 254 nm, t_R: 17.8 min (major), 20.2 min (minor), 97% ee with Rh_2(*S*-PTAD)$_4$; $[\alpha]^{23}_D$ +7.9 (*c* 1.0, $CHCl_3$)



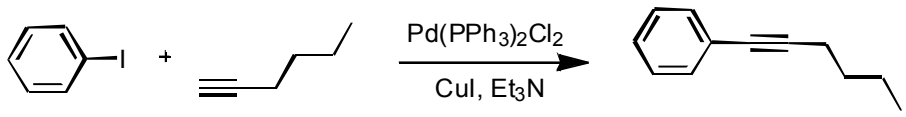
167

Methyl (*R*)-1-acetyl-2-(2-(((tert-butyldimethylsilyl)oxy-methyl)-phenyl)cycloprop-2-enecarbo-xylate (167) Purification by silica gel chromatography eluting with hexane/Et_2O (10:1) then hexane/EtOAc (1:1) afforded **167** in 94% yield (169 mg) as yellow oil. R_f 0.69 (hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J =7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.31-7.43 (m, 2H), 6.95 (s, 1H), 4.98 (s, 2H), 3.72 (s, 3H), 2.25 (s, 3H), 0.98 (s, 9H), 0.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 206.0 (C), 171.9 (C), 143.4 (CH), 131.1 (CH), 130.9 (CH), 127.4 (CH), 126.5 (CH), 120.5 (C), 111.1 (C), 98.6 (CH), 62.7 (CH_2), 52.4 (CH_3), 39.9 (C), 28.2 (CH_3), 26.1 (CH_3), 18.6 (C), -5.1 (CH_3); IR (neat) 3139, 2954, 2885, 2856, 1724, 1693, 1254, 1122, 1079, 837, 757 cm^{-1}; ESI-HRMS: (M+H) m/z, found: 217.0820; calcd ($C_{13}H_{13}O_3$): 217.0858; HPLC: ASH,

10% iPrOH/hexane, 0.7 mlmin^{-1}, UV 254 nm, t_R: 8.4 min (major), 10.3 min (minor), 99% ee with Rh_2(*S*-PTAD)$_4$; $[\alpha]^{23}_D$ +7.2 (*c* 1.0, $CHCl_3$)

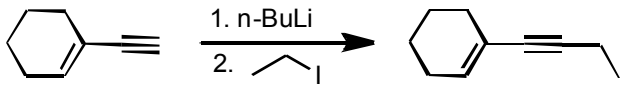
Experimental section for Chapter III: Silver-Catalyzed Cyclopropenation of Internal Alkynes

I. Representative procedure for the synthesis of disubstituted alkynes via Sonogashira coupling.



A mixture of 1-hexyne, $PdCl_2(PPh_3)_2$, iodobenzene in 100 mL triethylamine was stirred for 5 mins under an atmosphere of Argon at room temperature. CuI was added and the reaction was sealed and stirred overnight. The reaction mixture was filtered and the filtrate was washed with water and extracted with diethyl ether. The combined organic layers was washed with brine and dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel chromatography using 20:1 hexane/Et_2O to afford the **1-phenyl-1-hexyne** in 88% yield as colorless oil. ^{1}H NMR (600 MHz) δ 7.37-7.39 (m, 2H), 7.22-7.27 (m, 3H), 2.39 (t, 2H, *J* = 7.2 Hz), 1.57 (q, 2H, *J* = 7.2 Hz), 1.48 (s, 2H, *J* = 6.6 Hz), 0.93 (t, 3H, *J* = 7.2 Hz); ^{13}C-NMR (150 MHz) δ 131.8 (CH), 128.4 (CH), 127.7 (CH), 124.4 (C), 90.6 (C), 80.9 (C), 31.1 (CH_2), 22.3 (CH_2), 19.4 (CH_2), 13.9 (CH_3). The NMR spectral data is consistent with reported literature.[11]

II. Procedure for the synthesis of 1-(but-1-yn-1-yl)cyclohexene



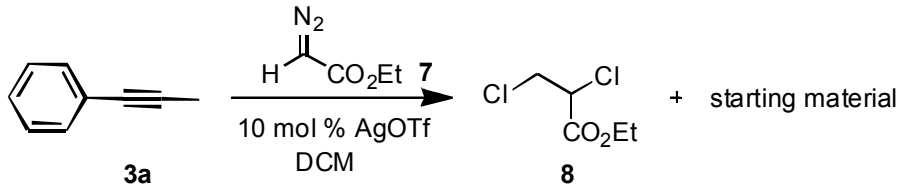
To a cold (-78 ^{o}C) solution of 1-ethynylcyclohexene (1 equiv) in THF under an atmosphere of argon was added slowly *via* syringe *n*-BuLi (2.5M in hexanes). The yellow solution was stirred for 15 mins at -78 ^{o}C then the reaction was warmed to room temperature and stirred for additional 5 mins. Ethyl iodide was then added in one portion *via* syringe and the suspension was stirred vigorously for 12 h. The reaction was quenched with saturated ammonium chloride solution and the layers were separated. The aqueous layer was washed twice with diethyl ether and the combined organic layer was washed with brine, dried over $MgSO_4$, filtered then concentrated *in vacuo*. The residue was loaded to a short silica plug and eluted using hexanes as solvent, then concentrated to afford **1-(but-1-yn-1-yl)cyclohexene** in quantitative yield as light yellow oil. ^{1}H NMR (600 MHz) δ 6.01 (br s, 1H), 2.30 (q, 2H, J = 7.8 Hz), 2.06-2.09 (m, 6H), 1.55-1.64 (m, 6H), 1.15 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (150 MHz) δ 133.4 (CH), 121.2 (C), 88.9 (C), 81.8 (C), 28.8 (CH_2), 25.7 (CH_2), 22.6 (CH_2), 21.8 (CH_2), 14.3 (CH_2), 13.2 (CH_3). The NMR spectral data is consistent with reported literature.[12]

III. General procedure for Ag(I)-catalyzed cyclopropenation of 1-phenyl-1-propyne with methyl phenyldiazoacetate

A mixture of 1-phenyl-1-propyne (1.0 mmol) and Ag(I) catalyst (0.05 mmol) was weighed in a 25-ml one-necked round bottom flask covered with aluminum foil to

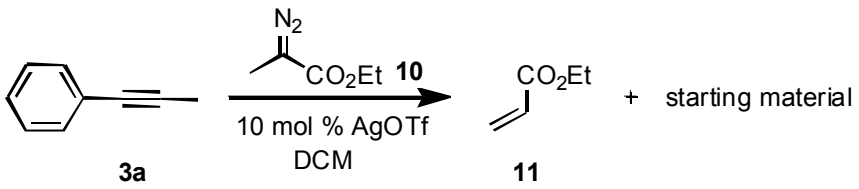
exclude light. The mixture was dissolved with 2 mL dichloromethane and stirred at room temperature under an atmosphere of argon. Methyl phenyldiazoacetate (0.5 mmol) in 8 mL dichloromethane was then added to former solution *via* syringe pump over 1 h. After addition, the mixture was stirred for additional 1 hour then concentrated *in vacuo*. The residue was purified on silica using 10: 1 hexane/ether as solvent system to afford the cyclopropene product.

IV. General procedure for AgOTf-catalyzed cyclopropenation of 3a with ethyl diazoacetate



A mixture of **3a** (0.5 mmol) and AgOTf (0.05 mmol) was weighed in a 25-ml one-necked round bottom flask covered with aluminum foil to exclude light. The mixture was dissolved with 2 mL dichloromethane and stirred at room temperature under an atmosphere of argon. Ethyl diazoacetate **7** (1.0 mmol) in 8 mL dichloromethane was then added to former solution *via* syringe pump over 1 h. After addition, the mixture was stirred for additional 1 hour then concentrated *in vacuo*. ^{1}H NMR analysis of the residue was performed using 4-dimethylaminopyridine (DMAP) as internal standard. The C-Cl bond insertion product **8** was formed in 85% NMR yield. ^{1}H NMR (600 MHz) δ 4.41 (dd, 1H, J = 9.0 Hz, 5.4 Hz), 4.30 (q, 2H, J = 7.2 Hz), 3.96 (dd, 1H, J = 11.4 Hz, 8.4 Hz), 3.8 (dd, 1H, J = 11.4 Hz, 5.4 Hz), 1.32 (t, 3H, J = 7.2 Hz). The NMR spectral data is consistent with published literature.[13]

V. General procedure for AgOTf-catalyzed cyclopropenation of 3a with ethyl-2-diazopropanoate



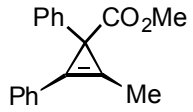
A mixture of **3a** (0.5 mmol) and AgOTf (0.05 mmol) was weighed in a 25-ml one-necked round bottom flask covered with aluminum foil to exclude light. The mixture was dissolved with 2 mL dichloromethane and stirred at room temperature under an atmosphere of argon. Ethyl-2-diazopropanoate **10** (1.0 mmol) in 8 mL dichloromethane was then added to former solution *via* syringe pump over 1 h. After addition, the mixture was stirred for additional 1 hour then concentrated *in vacuo*. ^{1}H NMR analysis of the residue was performed using 4-dimethylaminopyridine (DMAP) as internal standard. Ethyl acrylate was formed in 69% NMR yield. ^{1}H NMR (600 MHz) δ 6.39 (dd, 1H, J = 16.8 Hz, 1.2 Hz), 6.11 (dd, 1H, J = 16.8 Hz, 10.8 Hz), 5.80 (dd, 1H, J = 10.8 Hz, 1.2 Hz).

7. General procedure for AgOTf-catalyzed cyclopropenation of internal alkynes with methyl phenyldiazoacetate

A mixture of alkyne (1.0 mmol) and AgOTf (0.05 mmol) was weighed in a 25-ml one-necked round bottom flask covered with aluminum foil to exclude light. The mixture was dissolved with 2 mL dichloromethane and stirred at room temperature under an atmosphere of argon. Methyl phenyldiazoacetate (0.5 mmol) in 8 mL dichloromethane was then added to former solution *via* syringe pump over 1 h. After addition, the mixture

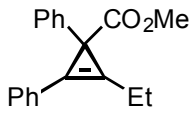
was stirred for additional 1 hour then concentrated *in vacuo*. The residue was purified on silica using 10: 1 hexane/ether as solvent system.

10. Spectral data and full characterization of all cyclopropenes



194

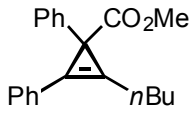
Methyl 2-methyl-1,3-diphenylcycloprop-2-enecarboxylate (194). Purification by silica gel chromatography (R_f = 0.42 in 7:3 hexane/Et_2O) gave compound **194** in 97% yield (128 mg) as white crystals. MP 52-55 ^oC. IR (neat) 3024, 2949, 1716, 1202, 692 cm^{-1}; ^1H NMR (400 MHz) δ 7.64 (dd, 2H, J = 7.2 Hz, 1.2 Hz), 7.24-7.47 (m, 8H), 3.76 (s, 3H), 2.79 (s, 3H); ^{13}C-NMR (100 MHz) δ 175.4 (C), 141.5 (C), 129.6 (CH), 129.2 (CH), 129.1 (CH), 128.8 (CH), 128.5 (CH), 126.9 (C), 126.6 (CH), 111.6 (C), 108.8 (C), 52.2 (CH_3), 35.6 (C), 9.9 (CH_3). HRMS (ESI) *m/z* calcd for $C_{18}H_{15}O_2$, 263.1150, found 263.1076 $[M-H]^+$.



199

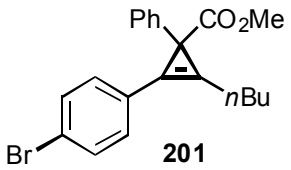
Methyl 2-ethyl-1,3-diphenylcycloprop-2-enecarboxylate (199). Purification by silica gel chromatography (R_f = 0.37 in 10:1 hexane/Et_2O) gave compound **199** in 91% yield (138 mg) as yellow crystals. MP 78-80 ^oC. IR (neat) 2973, 1715, 1202, 692 cm^{-1}; ^1H NMR (400 MHz) δ 7.65 (dd, 2H, J = 8.8 Hz, 1.6 Hz), 7.19-7.43 (m, 8H), 3.70 (s, 3H), 2.79 (q, 2H, *J* = 7.6Hz), 1.36 (t, 3H, *J* = 7.6 Hz); ^{13}C-NMR (100 MHz) δ 175.5 (C), 141.5

(C), 129.6 (CH), 129.1 (CH), 129.0 (CH), 128.4 (CH), 128.3 (CH), 126.8 (C), 126.4 (CH), 111.6 (C), 107.9 (C), 52.2 (CH_3), 35.6 (C), 18.7 (CH_2), 12.4 (CH_3). HRMS (ESI) *m/z* calcd for $C_{19}H_{18}O_2$, 278.1307, found 279.1379 $[M+H]^+$.



200

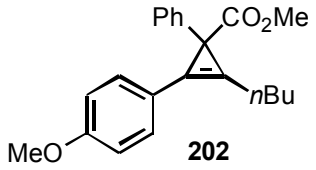
Methyl 2-butyl-1,3-diphenylcycloprop-2-enecarboxylate (200). Purification by silica gel chromatography (R_f = 0.43 in 10:1 hexane/Et_2O) gave compound **200** in 93% yield (143 mg) as yellow oil. IR (neat) 3024, 2954, 2871, 1716, 1200, 690 cm^{-1}; ^1H NMR (400 MHz) δ 7.54 (d, 2H, J = 7.2 Hz), 7.14-7.39 (m, 8H), 3.67 (s, 3H), 2.73 (t, 2H, *J* = 7.2 Hz), 1.73 (q, 2H, *J* = 7.6 Hz), 1.41 (m, 2H), 0.92 (t, 3H, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz) δ 175.5 (C), 141.6 (C), 129.6 (CH), 129.1 (CH), 129.0 (CH), 128.4 (CH), 128.3 (CH), 126.9 (C), 126.4 (CH), 115.8 (C), 108.2 (C), 52.1 (CH_3), 35.6 (C), 29.9 (CH_2), 24.9 (CH_2), 22.8 (CH_2), 14.0 (CH_3). HRMS (ESI) *m/z* calcd for $C_{21}H_{23}O_2$, 307.1653, found 307.1694 $[M+H]^+$.



201

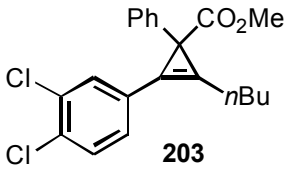
Methyl 2-(4-bromophenyl)-3-butyl-1-phenylcycloprop-2-enecarboxylate (201). Purification by silica gel chromatography (R_f = 0.41 in 10:1 hexane/Et_2O) gave compound **201** in 82% yield (158 mg) as yellow oil. IR (neat) 2954, 1715, 1203, 906, 727, 697 cm^{-1}; ^1H NMR (400 MHz) δ 7.52 (dt, 2H, *J* = 6.4 Hz, 2.0 Hz), 7.15-7.40 (m,

7H), 3.68 (s, 3H), 2.72 (t, 2H, J = 7.6 Hz), 1.71 (app q, 2H, J = 7.6 Hz), 1.40 (m, 2H), 0.92 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (100 MHz) δ 175.2 (C), 141.1 (C), 132.4 (CH), 130.9 (CH), 128.3 (CH), 126.6 (CH), 125.9 (C), 123.2 (C), 116.9 (C), 107.3 (C), 52.2 (CH_3), 35.6 (C), 29.8 (CH_2), 24.9 (CH_2), 22.7 (CH_2), 13.9 (CH_3). HRMS (ESI) *m/z* calcd for $C_{21}H_{22}BrO_2$, 385.0758, found 385.0801 $[M+H]^+$.



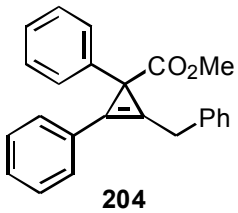
202

Methyl 2-butyl-3-(4-methoxyphenyl)-1-phenylcycloprop-2-enecarboxylate (202). Purification by silica gel chromatography (R_f = 0.17 in 10:1 hexane/Et_2O) gave compound **202** in 68% yield (114 mg) as yellow crystals. MP 55-56 ^oC. IR (neat) 2954, 2931, 2837, 1715, 1603, 1507, 1247, 1200, 1020, 831, 763, 698 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.47 (d, 2H, J = 8.8 Hz), 7.36 (d, 2H, J = 8.0 Hz), 7.25 (t, 2H, J = 7.2 Hz), 7.16 (m, 1H), 6.92 (d, 2H, J = 8.8 Hz), 3.79 (s, 3H), 3.68 (s, 3H), 2.70 (t, 2H, J = 7.2 Hz), 1.71 (app q, 2H, J = 7.6 Hz), 1.41 (m, 2H), 0.92 (t, 3H, J = 7.6 Hz); ^{13}C-NMR (100 MHz) δ 175.7 (C), 160.3 (C), 141.8 (C), 131.0 (CH), 128.4 (CH), 128.2 (CH), 126.3 (CH), 119.4 (C), 114.7 (CH), 112.9 (C), 107.4 (C), 55.6 (CH_3), 52.1 (CH_3), 35.5 (C), 29.9 (CH_2), 24.7 (CH_2), 22.8 (CH_2), 14.0 (CH_3). HRMS (ESI) *m/z* calcd for $C_{22}H_{25}O_3$, 337.1759, found 337.1799 $[M+H]^+$.



203

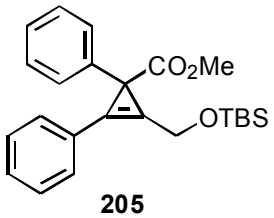
Methyl 2-butyl-3-(3,4-dichlorophenyl)-1-phenylcycloprop-2-enecarboxylate (203). Purification by silica gel chromatography (R_f = 0.76 in 8:2 hexane/EtOAc) gave compound **203** in 94% yield (176 mg) as white amorphous solid. IR (neat) 2954, 2871, 1718, 1465, 1201, 729, 696 cm^{-1}; ^1H NMR (400 MHz) δ 7.60 (d, 1H, J = 2.0 Hz), 7.46 (d, 1H, 8.4 Hz), 7.18-7.36 (m, 6H), 3.70 (s, 3H), 2.74 (t, 2H, *J* = 7.6 Hz), 1.71 (app q, 2H, *J* = 7.6 Hz), 1.41 (m, 2H), 0.93 (t, 3H, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz) δ 174.9 (C), 140.7 (C), 133.4 (C), 133.1 (C), 131.2 (CH), 130.96 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 127.0 (C), 126.7 (CH), 118.4 (C), 106.5 (C), 52.3 (CH_3), 35.8 (C), 29.7 (CH_2), 24.9 (CH_2), 22.7 (CH_2), 13.9 (CH_3). HRMS (ESI) *m/z* calcd for $C_{21}H_{21}Cl_2O_2$, 375.0874, found 375.0915 $[M+H]^+$.



204

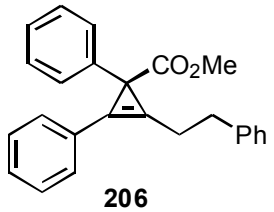
Methyl 2-benzyl-1,3-diphenylcycloprop-2-enecarboxylate (204). Purification by silica gel chromatography (R_f = 0.22 in 10:1 hexane/Et_2O) gave compound **204** in 91% yield (155 mg) as white solid. IR (neat) 3028, 1717, 1206, 692 cm^{-1}; ^1H NMR (400 MHz) δ 7.23-7.44 (m, 15H), 4.07 (AB q, 2H, *J* = 18Hz), 3.69 (s, 3H); ^{13}C-NMR (100 MHz) δ 175.2 (C), 141.2 (C), 137.4 (C), 129.9 (CH), 129.3 (CH), 129.2 (CH), 129.1 (CH), 128.9

(CH), 128.5 (CH), 128.4 (CH), 127.3 (CH), 126.6 (CH), 126.4 (C), 114.8 (C), 109.4 (C), 52.2 (CH_3), 36.3 (C), 31.8 (CH_2). HRMS (ESI) *m/z* calcd for $C_{24}H_{20}O_2$, 340.1463, found 341.1533 $[M+H]^+$.



205

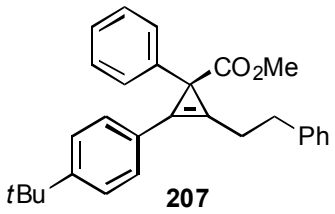
Methyl 2-(((tert-butyldimethylsilyl)oxy)methyl)-1,3-diphenylcycloprop-2-enecarboxylate (205). Purification by silica gel chromatography (R_f = 0.34 in 10:1 hexane/Et_2O) gave compound **205** in 68% yield (134 mg) as yellow oil. IR (neat) 2951, 2928, 2855, 1720, 1204, 1092, 834, 758, 691 cm^{-1}; ^1H NMR (400 MHz) δ 7.62 (dd, 2H, J = 8.8 Hz, 1.6 Hz), 7.19-7.43 (m, 8H), 4.94 (d, 1H, *J* = 16.4 Hz), 4.82 (d, 1H, *J* = 21 Hz), 3.69 (s, 3H), 0.95 (s, 9H), 0.10 (s, 6H); ^{13}C-NMR (100 MHz) δ 174.9 (C), 140.8 (C), 130.0 (CH), 129.4 (CH), 128.9 (CH), 128.6 (CH), 128.3 (CH), 126.6 (CH), 126.2 (CH), 113.9 (C), 110.5 (C), 58.1 (CH_2), 52.2 (CH_3), 37.0 (C), 26.1 (CH_3), 18.6 (C), -5.1 (CH_3). HRMS (ESI) *m/z* calcd for $C_{24}H_{30}O_3Si$, 394.1964, found 394.1954 $[M]^+$.



206

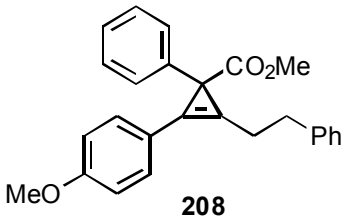
Methyl 2-phenethyl-1,3-diphenylcycloprop-2-enecarboxylate (206). Purification by silica gel chromatography (R_f = 0.50 in 7:3 hexane/Et_2O) gave compound **4i** in 87% yield

(154 mg) as yellow oil. IR (neat) 3025, 2947, 1716, 1494, 1201, 735, 691 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.44 (dd, 2H, J = 6.8 Hz, 1.6 Hz), 7.16-7.38 (m, 13H), 3.68 (s, 3H), 3.06 (m, 4H); ^{13}C-NMR (100 MHz) δ 175.4 (C), 141.4 (C), 140.9 (C), 129.7 (CH), 129.2 (CH), 129.1 (CH), 128.8 (CH), 128.6 (CH), 128.5 (CH), 128.3 (CH), 126.7 (C), 126.4 (CH), 126.5 (CH) 114.8 (C), 108.7 (C), 52.2 (CH_3), 35.7 (C), 33.8 (CH_2), 26.8 (CH_2). HRMS (ESI) *m/z* calcd for $C_{25}H_{23}O_2$, 355.1653, found 355.1690 $[M+H]^+$.



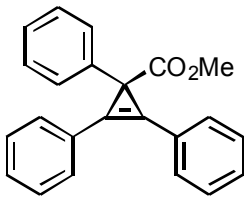
207

Methyl 2-(4-(tert-butyl)phenyl)-3-phenethyl-1-phenylcycloprop-2-enecarboxylate (207). Purification by silica gel chromatography (R_f = 0.72 in 8:2 hexane/EtOAc) gave compound **207** in 92% yield (189 mg) as off-white amorphous solid. IR (neat) 3027, 2951, 1716, 1201, 908, 836, 692 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.39 (s, 4H), 7.33 (d, 2H, *J* = 6.8 Hz), *7*.16-7.27 (m, 8H), 3.66 (s, 3H), 3.04 (s, 4H), 1.30 (s, 9H); ^{13}C-NMR (100 MHz) δ 175.6 (C), 152.5 (C), 141.6 (C), 141.0 (C), 129.5 (CH), 128.8 (CH), 128.6 (CH), 128.5 (CH), 128.3 (CH), 126.6 (CH), 126.5 (CH), 126.1 (CH), 123.8 (C), 113.7 (C), 108.6 (C), 52.2 (CH_3), 35.7 (C), 35.1 (C), 33.9 (CH_2), 31.5 (CH_3), 26.9 (CH_2). HRMS (ESI) *m/z* calcd for $C_{29}H_{31}O_2$, 410.5473, found 411.2319 $[M+H]^+$.



208

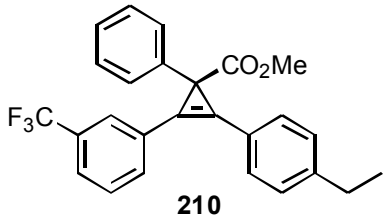
Methyl 2-(4-methoxyphenyl)-3-phenethyl-1-phenylcycloprop-2-enecarboxylate (208). Purification by silica gel chromatography (R_f = 0.56 in 8:2 Hexane/EtOAc) gave compound **208** in 86% yield (165 mg) as yellow oil. IR (neat) 3026, 2947, 2837, 1715, 1603, 1507, 1248, 1206, 1023, 833, 699 cm^{-1}; ^1H NMR (400 MHz) δ 7.36 (dt, 2H, J = 6.8 Hz, 2.0 Hz), 7.18-7.33 (m, 11 H), 6.89 (dt, 2H, *J* = 8.8 Hz, 2.4 Hz), 3.81 (s, 3H), 3.68 (s, 3H), 3.04 (s, 4H); ^{13}C-NMR (100 MHz) δ 175.6 (C), 160.4 (C), 141.6 (C), 140.9 (C), 131.1 (CH), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 126.5 (C), 126.4 (CH), 119.1 (C), 114.6 (CH), 111.9 (C), 108.0 (C), 55.6 (CH_3), 52.1 (CH_3), 35.6 (C), 33.8 (CH_2), 26.7 (CH_2). HRMS (ESI) *m/z* calcd for $C_{26}H_{24}O_3$, 385.1759, found 385.1799 $[M+H]^+$.



209

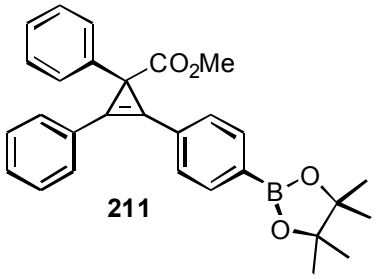
Methyl 1,2,3-triphenylcycloprop-2-enecarboxylate (209). Purification by silica gel chromatography (R_f = 0.33 in 7:3 hexane/Et_2O) gave compound **209** in 98% yield (172 mg) as white crystals. MP 138-139 ^oC. IR (neat) 3025, 2949 1717, 1205, 687 cm^{-1}; ^1H NMR (400 MHz) δ 7.81 (d, 4H, *J* = 6.8Hz), 7.22-7.57 (m, 11H), 3.76 (s, 3H); ^{13}C-NMR (100 MHz) δ 174.7 (C), 140.4 (C), 130.2 (CH), 129.8 (CH), 129.3 (CH), 128.5 (CH),

128.4 (CH), 128.3 (CH), 126.9 (C), 126.8 (CH), 111.6 (C), 52.4 (CH_3), 35.7 (C). HRMS (ESI) *m/z* calcd for $C_{23}H_{19}O_2$, 326.1307, found 325.1232 $[M-H]^+$.



210

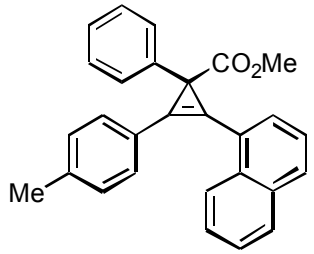
Methyl 2-(4-ethylphenyl)-1-phenyl-3-(3-(trifluoromethyl)phenyl)cycloprop-2-enecarboxylate (210). Purification by silica gel chromatography (R_f = 0.48 in 8:2 Hexane/EtOAc) gave compound **210** in 88% yield (187 mg) as yellow crystals. MP 89-90 ^oC. IR (neat) 3026, 2966, 1719, 1337, 1124, 896, 693 cm^{-1}; ^1H NMR (400 MHz) δ 7.96 (br s, 1 H), 7.85 (d, 1H, *J* = 7.6 Hz), 7.67 (m, 2H), 7.17-7.61 (m, 9H), 3.72 (s, 3H), 2.69 (q, 2H, *J* = 7.6Hz), 1.25 (t, 3H, *J* = 7.6 Hz); ^{13}C-NMR (100 MHz) δ 174.3 (C), 147.1 (C), 139.9 (C),132.9 (CH), 130.5 (CH), 129.8 (CH), 129.0 (CH), 128.5 (CH), 128.3 (CH), 128.0 (CH), 126.9 (CH), 126.4 (C), 125.9 (C), 125.8 (C), 123.6 (C), 113.6 (C), 109.3 (C), 52.4 (CH_3), 35.7 (C), 29.2 (CH_2), 15.6 (CH_3). HRMS (ESI) *m/z* calcd for $C_{26}H_{22}F_3O_2$, 423.1527, found 423.1566 $[M+H]^+$.



211

Methyl 1,2-diphenyl-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)cycloprop-2-enecarboxylate (211). Purification by silica gel chromatography

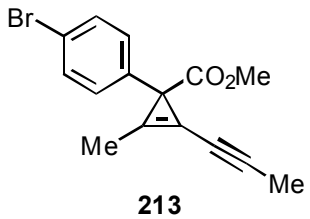
(R_f = 0.15 in 10:1 Hexane/Et_2O) gave compound **211** in 64% yield (145 mg) as white amorphous solid. IR (neat) 2978, 1719, 1604, 1356, 1209, 1141, 760 cm^{-1}; ^1H NMR (400 MHz) δ 7.91 (d, 2H, J = 8.0 Hz), 7.73 (m, 4H), 7.36-7.49 (m, 5H), 7.17-7.27 (m, 3H), 3.69 (s, 3H), 1.35 (s, 12H); ^{13}C-NMR (100 MHz) δ 174.6 (C), 140.1 (C), 135.5 (CH), 130.3 (CH), 129.9 (C), 129.8 (CH), 129.3 (CH), 128.7 (CH), 128.4 (CH), 128.3 (CH), 126.7 (C), 113.0 (C), 111.1 (C), 84.3 (C), 52.3 (CH_3), 35.6 (C), 25.1 (CH_3). HRMS (ESI) *m/z* calcd for $C_{29}H_{30}BO_4$, 453.2262, found 453.2223 $[M+H]^+$.



212

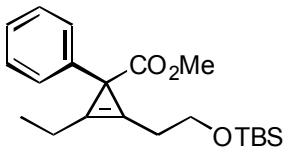
Methyl 2-(naphthalen-1-yl)-1-phenyl-3-(p-tolyl)cycloprop-2-enecarboxylate (212). Purification by silica gel chromatography (R_f = 0.20 in 10:1 Hexane/Et_2O) gave compound **212** in 80% yield (156 mg) as white crystals. MP 149 ^oC. IR (neat) 3026, 2948, 1716, 1203, 906, 773, 728, 698 cm^{-1}; ^1H NMR (400 MHz) δ 8.44 (d, 1H, *J* = 8.8 Hz), 7.90 (t, 2H, *J* = 8.4 Hz), 7.81 (dd, 1H, *J* = 7.2 Hz, 0.8 Hz), 7.70 (d, 2H, *J* = 8.0 Hz), 7.49-7.62 (m, 5H), 7.30 (d, 2H, *J* = 7.6 Hz), 7.15-7.27 (m, 3H), 3.71 (s, 3H), 2.41 (s, 3H); ^{13}C-NMR (100 MHz) δ 174.9 (C), 140.4 (C), 140.1 (C), 133.9 (C), 131.9 (C), 130.4 (CH), 130.2 (CH), 130.1 (CH), 129.2 (CH), 128.9 (CH), 128.4 (CH), 128.3 (CH), 127.2 (CH), 126.7 (CH), 126.5 (CH), 125.9 (CH), 125.7 (CH), 124.6 (C), 124.3 (C), 112.2 (C),

108.1 (C), 52.3 (CH_3), 35.5 (C), 21.8 (CH_3). HRMS (ESI) *m/z* calcd for $C_{28}H_{22}O_2$, 390.1620, found 390.1611 $[M]^+$.



213

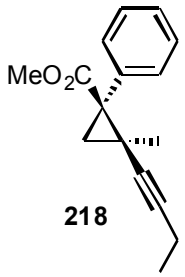
Methyl 1-(4-bromophenyl)-2-methyl-3-(prop-1-yn-1-yl)cycloprop-2-enecarboxylate (213). Purification by silica gel chromatography (R_f = 0.28 in 10:1 hexane/Et_2O) gave compound **213** in 92% yield (140 mg) as yellow oil. IR (neat) 2950, 2914, 1718, 1206, 1008 cm^{-1}; ^1H NMR (400 MHz) δ 7.41 (d, 2H, *J* = 8 Hz), 7.21 (d, 2H, *J* = 8.4 Hz), 3.69 (s, 3H), 2.19 (s, 3H), 2.09 (s, 3H); ^{13}C-NMR (100 MHz) δ 173.9 (C), 139.7 (C), 131.4 (CH), 130.2 (CH), 120.7 (C), 114.0 (C), 98.3 (C), 95.3 (C), 66.3 (C), 52.5 (CH_3), 36.4 (C), 10.3 (CH_2), 5.3 (CH_3). HRMS (ESI) *m/z* calcd for $C_{15}H_{14}B_rO_2$, 304.0099, found 305.0004$[M+H]^+$.



214

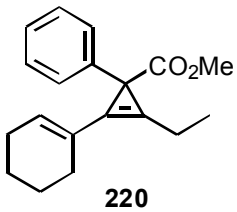
Methyl 2-(2-((tert-butyldimethylsilyl)oxy)ethyl)-3-ethyl-1-phenylcycloprop-2-enecarboxylate (214). Purification by silica gel chromatography (R_f = 0.41 in 10:1 hexane/Et_2O) gave compound **214** in 85% yield (153 mg) as yellow oil. IR (neat) 2951, 2856, 1717, 1099, 833, 697 cm^{-1}; ^1H NMR (400 MHz) δ 7.28 (m, 4H), 7.17 (m, 1H), 3.81

(t, 2H, J = 6.8 Hz), 3.65 (s, 3H), 2.74 (m, 2H), 2.54 (m, 2H), 1.17 (t, 3H, J = 7.2 Hz), 1.17 (d, 3H, J = 4.8 Hz); ^{13}C-NMR (100 MHz) δ 176.3 (C), 142.7 (C), 128.4 (CH), 128.2 (CH), 126.1 (CH), 112.8 (C), 107.2 (C), 60.9 (CH_2), 51.9 (CH_3), 35.0 (C), 28.4 (CH_2), 26.1 (CH_3), 18.4 (C), 18.0 (CH_2), 11.8 (CH_3), -5.1 (CH_3). HRMS (ESI) *m/z* calcd for $C_{21}H_{32}O_3Si$, 360.2121, found 359.2046$[M-H]^+$.



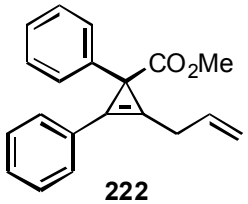
218

(1S,2R)-methyl 2-(but-1-yn-1-yl)-2-methyl-1-phenylcyclopropanecarboxylate (218). Purification by silica gel chromatography (R_f = 0.51 in 10:1 hexane/Et_2O) gave compound **218** in 64% yield (73 mg) as yellow oil. IR (neat) 2974, 1723, 1250, 1210, 697 cm^{-1}; ^{1}H NMR (600 MHz) δ 7.45 (m, 2H), 7.23-7.31 (m, 3H), 3.63 (s, 3H), 1.88 (m, 3H), 1.55 (dd, 1H, J = 4.8 Hz, 1.2 Hz), 1.48 (s, 3H), 0.78 (m, 3H); ^{13}C-NMR (125 MHz) δ 171.5 (C), 137.8 (C), 131.7 (CH), 127.7 (CH), 127.3 (C), 84.5 (C), 81.9 (C), 52.6 (CH_3), 40.9 (C), 27.3 (CH_2), 22.5 (CH_3), 20.5 (C), 13.9 (CH_3), 12.4 (CH_2). HRMS (ESI) *m/z* calcd for $C_{16}H_{19}O_2$, 243.1340, found 243.1380 $[M+H]^+$.



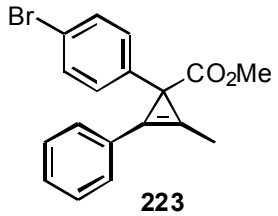
220

Methyl 2-(cyclohex-1-en-1-yl)-3-ethyl-1-phenylcycloprop-2-enecarboxylate (220). Purification by silica gel chromatography (R_f = 0.26 in 10:1 hexane/Et_2O) gave compound **220** in 85% yield (121 mg) as yellow oil. IR (neat) 3022, 2931, 1716, 1433, 1198, 1020, 697 cm^{-1}; ^1H NMR (400 MHz) δ 7.16-7.33 (m, 5H), 6.09 (t, 1H, *J* = 4.0 Hz), 3.68 (s, 3H), 2.61 (q, 2H, *J* = 7.6 Hz), 2.26-2.42 (m, 2H), 2.17 (m, 2H), 1.60-1.75 (m, 4H), 1.22 (t, 3H, *J* = 8.0 Hz); ^{13}C-NMR (100 MHz) δ 175.9 (C), 142.1 (C), 132.9 (CH), 128.6 (CH), 128.1 (CH), 126.1 (CH), 124.7 (C), 113.9 (C), 109.6 (C), 52.0 (CH_3), 35.6 (C), 27.9 (CH_2), 27.8 (CH_2), 25.8 (CH2), 22.6 (CH2), 22.0 (CH2), 18.5 (CH_2), 12.6 (CH_3). HRMS (ESI) *m/z* calcd for $C_{19}H_{23}O_2$, 283.1653, found 283.1692 $[M+H]^+$.



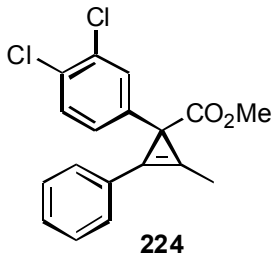
222

Methyl 2-allyl-1,3-diphenylcycloprop-2-enecarboxylate (222). Purification by silica gel chromatography (R_f = 0.41 in 10:1 hexane/Et_2O) gave compound **222** in 86% yield (125 mg) as yellow oil. IR (neat) 3058, 2951, 1716, 1265, 1208, 733, 696 cm^{-1}; ^1H NMR (400 MHz) δ 7.56 (m, 2H), 7.17-7.42 (m, 8H), 6.05 (ddt, 1H, *J* = 17.2 Hz, 10.4 Hz, 6.4 Hz), 5.28 (ddq, 1H, *J* = 17.2 Hz, 3.2 Hz, 1.6 Hz), 5.23 (ddq, 1H, *J* = 8.8 Hz, 1.6 Hz, 1.2 Hz), 3.69 (s, 3H), 3.49 (m, 2H); ^{13}C-NMR (100 MHz) δ 175.3 (C), 141.2 (C), 132.9, 129.8 (CH), 129.2 (CH), 129.1 (CH), 128.5 (CH), 128.3 (CH), 126.6 (CH), 126.6 (CH), 118.2 (CH_2), 113.4 (C), 109.5 (C), 52.2 (CH_3), 35.8 (C), 29.5 (CH_2). HRMS (ESI) *m/z* calcd for $C_{20}H_{19}O_2$, 291.1340, found 291.1378 $[M+H]^+$.



223

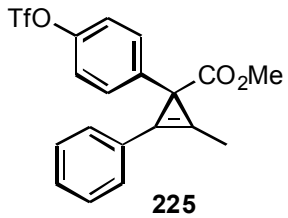
Methyl 1-(4-bromophenyl)-2-methyl-3-phenylcycloprop-2-enecarboxylate (223). Purification by silica gel chromatography (R_f = 0.24 in 10:1 hexane/Et_2O) gave compound **223** in 93% yield (159 mg) as yellow crystals. MP 58-60 ^oC. IR (neat) 2949, 1716, 1487, 1205, 761, 691 cm^{-1}; ^1H NMR (400 MHz) δ 7.56 (dd, 2H, *J* = 8.4 Hz, 1.2 Hz), 7.30-7.44 (m, 7H), 3.72 (s, 3H), 2.40 (s, 3H); ^{13}C-NMR (100 MHz) δ 174.9 (C), 140.5 (C), 131.4 (CH), 130.3 (CH), 129.5 (CH), 129.3 (CH), 129.2 (CH), 126.5 (C), 120.4 (CH), 111.1 (C), 108.3 (C), 52.3 (CH_3), 35.0 (C), 9.84 (CH_3). HRMS (ESI) *m/z* calcd for $C_{19}H_{16}BrO_2$, 343.0289, found 343.0163 $[M+H]^+$**.**



224

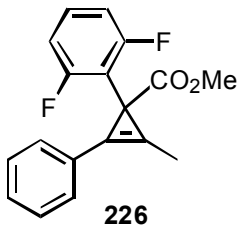
Methyl 1-(3,4-dichlorophenyl)-2-methyl-3-phenylcycloprop-2-enecarboxylate (224). Purification by silica gel chromatography (R_f = 0.34 in 10:1 hexane/Et_2O) gave compound **224** in 91% yield (151 mg) as yellow oil. IR (neat) 2950, 1717, 1201, 761, 690 cm^{-1}; ^1H NMR (400 MHz) δ 7.50-7.54 (m, 3H), 7.35-7.46 (m, 3H), 7.33 (s, 1H), 7.23 (dd, 1H, *J* = 8.4 Hz, 2.0 Hz), 3.72 (s, 3H), 2.40 (s, 3H); ^{13}C-NMR (100 MHz) δ 174.4 (C), 141.7 (C), 132.2 (C), 130.4 (CH), 130.2 (CH), 129.5 (CH), 129.2 (CH), 127.9 (CH),

126.0 (C), 110.6 (C), 108.0 (C), 52.3 (CH_3), 34.7 (C), 9.70 (CH_3). HRMS (ESI) *m/z* calcd for $C_{19}H_{15}Cl_2O_2$, 333.0404, found 333.0443 $[M+H]^+$.



225

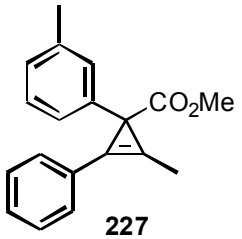
Methyl 2-methyl-3-phenyl-1-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)cycloprop-2-enecar-boxylate (225). Purification by silica gel chromatography (R_f = 0.19 in 10:1 hexane/Et_2O) gave compound **225** in 90% yield (185 mg) as yellow oil. IR (neat) 2953, 1718, 1420, 1203, 1137, 883 cm^{-1}; ^1H NMR (400 MHz) δ 7.54 (m, 2H), 7.37-7.49 (m, 5H), 7.19 (m, 2H), 3.72 (s, 3H), 2.40 (s, 3H); ^{13}C-NMR (100 MHz) δ 174.7 (C), 148.1 (C), 141.9 (C), 130.2 (CH), 129.5 (CH), 129.4 (CH), 129.2 (CH), 126.1 (C), 121.0 (CH), 110.9 (C), 107.9 (C), 52.3 (CH_3), 34.8 (C), 9.68 (CH_3). HRMS (ESI) *m/z* calcd for $C_{19}H_{16}F_3O_5S$, 412.0626, found 413.0662 $[M+H]^+$.



226

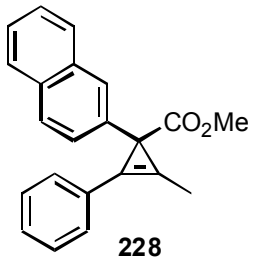
Methyl 1-(2,6-difluorophenyl)-2-methyl-3-phenylcycloprop-2-enecarboxylate (226). Purification by silica gel chromatography (R_f = 0.24 in 10:1 hexane/Et_2O) gave compound **226** in 83% yield (125 mg) as white crystals. MP 112-113 ^oC. IR (neat) 2952,

1720, 1462, 1207, 997, 790 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.62 (d, 2H, *J* = 7.6 Hz), 7.32-7.44 (m, 3H), 7.15 (m, 1H), 6.85 (t, 2H, *J* = 8.4 Hz), 3.70 (s, 3H), 2.46 (s, 3H), 1.34 (s, 9H); ^{13}C-NMR (100 MHz) δ 174.4 (C), 163.9 (d, 149.2 (C), 138.3 (C), 129.5 (CH), 129.1 (CH), 128.9 (CH), 128.1 (CH), 127.0 (C), 125.3 (CH), 111.7 (C), 108.9 (C), 52.2 (CH_3), 35.2 (C), 34.6 (C), 31.6 (CH_3), 9.97 (CH_3). HRMS (ESI) *m/z* calcd for $C_{19}H_{15}F_2O_2$, 301.0995, found 301.1031 $[M+H]^+$**.**



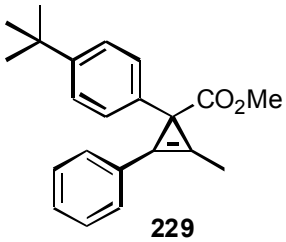
227

Methyl 2-methyl-3-phenyl-1-(m-tolyl)cycloprop-2-enecarboxylate (227). Purification by silica gel chromatography (R_f = 0.41 in 7:3 hexane/Et_2O) gave compound **227** in 92% yield (128 mg) as colorless oil. IR (neat) 2949, 1716, 1221, 1037, 759, 691 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.55 (d, 2H, *J* = 7.2 Hz), 7.39 (t, 2H, *J* = 7.6 Hz), 7.32(m, 1H), 7.16 (m, 3H), 7.00 (m, 1H), 3.69 (s, 3H), 2.38 (s, 3H), 2.30 (s, 3H); ^{13}C-NMR (100 MHz) δ 175.5 (C), 141.4 (C), 137.9 (C), 129.5 (CH), 129.2 (CH), 129.1 (CH), 129.0 (CH), 128.3 (CH), 127.4 (CH), 127.0 (C), 125.6 (CH), 111.7 (C), 108.9 (C), 52.2 (CH_3), 35.6 (C), 21.9 (CH_3), 9.9 (CH_3). HRMS (ESI) *m/z* calcd for $C_{19}H_{18}O_2Na$, 301.1307, found 301.1201 $[M+Na]^+$.



228

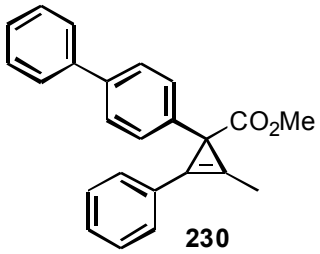
Methyl 2-methyl-1-(naphthalen-2-yl)-3-phenylcycloprop-2-enecarboxylate (228). Purification by silica gel chromatography (R_f = 0.25 in 10:1 hexane/Et_2O) gave compound **228** in 81% yield (128 mg) as yellow oil. IR (neat) 3055, 2949, 2914, 1716, 733, 691 cm^{-1}; ^1H NMR (400 MHz) δ 7.87 (d, 1H, *J* = 1.2 Hz), 7.78 (m, 3H), 7.63 (m, 2H), 7.55 (dd, 1H, *J* = 8.4 Hz, 2.0 Hz), 7.36-7.46 (m, 4H, *J* = 8 Hz), 7.37 (m, 1H), 3.76 (s, 3H), 2.46 (s, 3H); ^{13}C-NMR (100 MHz) δ 175.4 (C), 139.1, 133.3, 132.4, 129.6, 129.3, 129.1, 128.0, 127.8, 127.0, 126.9, 126.8, 126.1, 125.7, 111.6 (C), 108.8 (C), 68.2 (C), 52.3 (CH_3), 35.8 (C), 25.9, 9.98 (CH_3). HRMS (ESI) *m/z* calcd for $C_{22}H_{17}O_2$, 314.1307, found 313.1234 $[M-H]^+$.



229

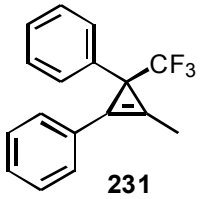
Methyl 1-(4-(*tert*-butyl)phenyl)-2-methyl-3-phenylcycloprop-2-enecarboxylate (229). Purification by silica gel chromatography (R_f = 0.16 in 10:1 hexane/Et_2O) gave compound **229** in 82% yield (131 mg) as light yellow crystals. MP 100-105 ^oC. IR (neat) 2958, 1717, 1209, 760, 691 cm^{-1}; ^1H NMR (400 MHz) δ 7.60 (dd, 2H, *J* = 8.4 Hz, 1.6

Hz), 7.32-7.45 (m, 7H), 3.74 (s, 3H), 2.43 (s, 3H), 1.34 (s, 9H); ^{13}C-NMR (100 MHz) δ 175.6 (C), 149.2 (C), 138.3 (C), 129.5 (CH), 129.1 (CH), 128.9 (CH), 128.1 (CH), 127.0 (C), 125.3 (CH), 111.7 (C), 108.9 (C), 52.2 (CH_3), 35.2 (C), 34.6 (C), 31.6 (CH_3), 9.97 (CH_3). HRMS (ESI) *m/z* calcd for $C_{22}H_{25}O_2$, 321.1810, found 321.1848 $[M+H]^+$**.**



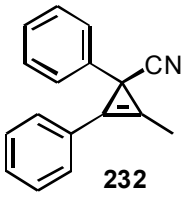
230

Methyl 1-([1,1'-biphenyl]-4-yl)-2-methyl-3-phenylcycloprop-2-enecarboxylate (230). Purification by silica gel chromatography (R_f = 0.18 in 10:1 hexane/Et_2O) gave compound **230** in 87% yield (148 mg) as white amorphous solid. IR (neat) 3027, 2949, 1716, 1209, 907, 727, 691 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.55 (dd, 2H, *J* = 6.4 Hz, 1.2 Hz), 7.27-7.50 (m, 10H), 3.71 (s, 3H), 2.39 (s, 3H); ^{13}C-NMR (100 MHz) δ 175.4 (C), 141.3 (C), 140.5 (C), 139.4 (C), 129.6 (CH), 129.1 (CH), 128.9 (CH), 128.8 (CH), 127.3 (CH), 127.1 (CH), 126.8 (C), 111.5 (C), 108.6 (C), 52.3 (CH_3), 35.3 (C), 9.93 (CH_3). HRMS (ESI) *m/z* calcd for $C_{24}H_{21}O_2$, 341.1497, found 341.1532 $[M+H]^+$.



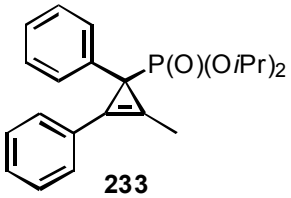
231

(3-methyl-1-(trifluoromethyl)cycloprop-2-ene-1,2-diyl)dibenzene (231). Purification by silica gel chromatography (R_f = 0.53 in 10:1 hexane/Et_2O) gave compound **231** in 84% yield (115 mg) as yellow oil. IR (neat) 3029, 1491, 1447, 1297, 1153, 1118, 690 cm^{-1}; ^1H NMR (400 MHz) δ 7.57 (d, 2H, *J* = 7.2 Hz), 7.21-7.43 (m, 8H), 2.37 (s, 3H); ^{13}C-NMR (100 MHz) δ 138.6 (C), 129.6 (CH), 129.4 (CH), 129.1 (CH), 128.6 (CH), 127.9 (CH), 127.1 (CH), 126.5 (C), 125.9 (C), 109.7 (C), 108.9 (C), 33.6 (C), 9.5 (CH_3). HRMS (ESI) *m/z* calcd for $C_{17}H_{13}F_3$, 274.0969, found 274.0963 $[M]^+$.



232

2-Methyl-1,3-diphenylcycloprop-2-enecarbonitrile (232). Purification by silica gel chromatography (R_f = 0.29 in 10:1 hexane/Et_2O) gave compound **232** in 93% yield (108 mg) as yellow oil. IR (neat) 3028, 2220, 1490, 1447, 907, 728, 689 cm^{-1}; ^1H NMR (400 MHz) δ 7.49 (dd, 2H, *J* = 8.0 Hz, 1.6 Hz), 7.19-7.40 (m, 8H), 2.35 (s, 3H); ^{13}C-NMR (100 MHz) δ 138.1 (C), 130.2 (CH), 129.8 (CH), 129.4 (CH), 128.9 (CH), 127.2 (CH), 125.5 (C), 124.5 (C), 122.2 (C), 107.8 (C), 106.6 (C), 22.2 (C), 8.9 (CH_3). HRMS (ESI) *m/z* calcd for $C_{17}H_{14}N$, 232.1082, found 232.1120 $[M+H]^+$.



233

Diisopropyl (2-methyl-1,3-diphenylcycloprop-2-en-1-yl)phosphonate (233). Purification by silica gel chromatography (R_f = 0.38 in 7:3 hexane/EtOAc) gave compound **233** in 98% yield (181 mg) as yellow oil. IR (neat) 2973, 1715, 1202, 692 cm^{-1}; ^1H NMR (400 MHz) δ 7.62 (d, 2H, J = 6.8 Hz), 7.50 (d, 2H, *J* = 8.0 Hz), 7.35 (app t, 2H, *J* = 7.6 Hz), 7.13-7.30 (m, 4H), 4.60 (m, 2H), 2.44 (s, 3H), 1.27 (d, 3H, 6.0 Hz), 1.25 (d, 3H, 6.0 Hz) 1.17 (d, 3H, 6.0 Hz) 1.05 (d, 3H, 6.4 Hz); ^{13}C-NMR (100 MHz) δ 175.5 (C), 141.8 (C), 141.5 (C), 129.7 (CH), 128.9 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 127.3 (C), 126.3 (CH), 110.8 (C), 109.7 (C), 70.3 (d, *J*p = 26 Hz), 70.10 (d, *J*p = 29 Hz), 31.2 (C), 29.2 (C), 24.6 (CH_3), 24.4 (CH_3), 24.1 (CH_3), 23.8 (CH_3), 10.5 (CH_3). HRMS (ESI) *m/z* calcd for $C_{22}H_{28}O_3P$, 371.1731, found 371.1766 $[M+H]^+$.

Experimental section for Chapter IV: Enantioselective Au(I)-Catalyzed Cyclopropenation of Disubstituted Alkynes

I. General procedure for Ag(I)-catalyzed cyclopropenation of 1-phenyl-1-propyne with methyl phenyldiazoacetate using chiral ligands

A mixture of Ag(I) catalyst and chiral ligand was weighed in a 25-ml one-necked round bottom flask covered with aluminum foil to exclude light. The mixture was dissolved with 2 mL degassed dichloromethane and stirred at room temperature under an atmosphere of argon for *ca* 20 mins. DCM was degassed either by freeze-pump-thaw method or atmosphere exchange under sonication to exclude oxygen in the reaction mixture. The alkyne was added via syringe, followed by dropwise addition of methyl

phenyldiazoacetate (0.5 mmol) in 8 mL degassed dichloromethane *via* syringe pump over 3 h. After addition, the mixture was stirred for additional 12 hour then concentrated *in vacuo*. The residue was purified on silica using 20: 1 pentane/ether as solvent system to afford the cyclopropene product.

II. General procedure for Au(I)-catalyzed cyclopropenation of disubsituted alkynes with donor/acceptor-carbenoids.

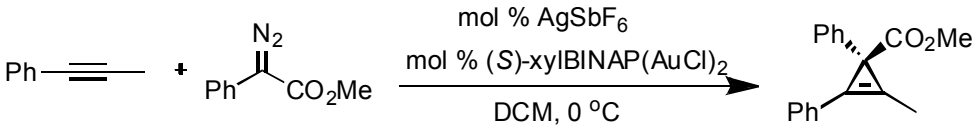
A mixture of $AgSbF_6$ (0.05 mmol) and chiral Au catalyst[14] was weighed in a 25-ml one-necked round bottom flask covered with aluminum foil to exclude light. The mixture was dissolved with 2 mL degassed dichloromethane and stirred at specified temperature under an atmosphere of argon for *ca* 20 mins. DCM was degassed either by freeze-pump-thaw method or atmosphere exchange under sonication to exclude oxygen in the reaction mixture. The alkyne (2.5 mmol) was added via syringe, followed by dropwise addition of aryl diazoacetate (0.5 mmol) in 8 mL degassed dichloromethane *via* syringe pump over 3 h. After addition, the mixture was stirred for additional 12 hour then concentrated *in vacuo*. The residue was purified on silica using 20:1 pentane/ether as solvent system to afford the cyclopropene product.

III. Catalyst loading study for Au(I)-catalyzed cyclopropenation of 1 with methyl phenyldiazoacetate

A mixture of $AgSbF_6$ and chiral Au catalyst (mol % shown in Table 1) was weighed in a 25-ml one-necked round bottom flask covered with aluminum foil to exclude light. The

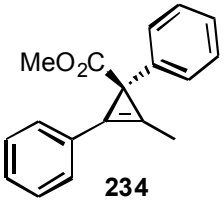
mixture was dissolved with 2 mL degassed dichloromethane and stirred at specified temperature under an atmosphere of argon for *ca* 20 mins. The alkyne (2.5 mmol) was added via syringe, followed by dropwise addition of methyl phenyldiazoacetate (0.5 mmol) in 8 mL degassed dichloromethane *via* syringe pump over 3 h. After addition, the mixture was stirred for additional 12 hour then concentrated *in vacuo*. The residue was purified on silica using 20:1 pentane/ether as solvent system to afford the cyclopropene product.

Table 1. Effect of catalyst loading on the cyclopropenation reaction



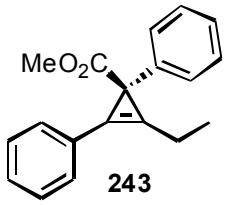
entry	mol % Ag	mol % Au	% yield	% ee
1	10	12	81	93
2	5	6	75	94
3	2.5	3	67	94
4	1.25	1.5	64	94

IV. Spectral data and full characterization of all cyclopropenes



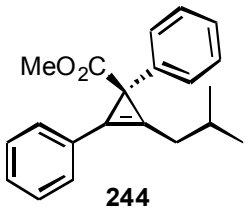
234

(*S*)-Methyl 2-methyl-1,3-diphenylcycloprop-2-enecarboxylate (234). Purification by silica gel chromatography gave compound **234** in 81% yield (107 mg) as white crystals; ^{1}H NMR (400 MHz) δ 7.64 (dd, 2H, J = 7.2 Hz, 1.2 Hz), 7.24-7.47 (m, 8H), 3.76 (s, 3H), 2.79 (s, 3H); ^{13}C-NMR (100 MHz) δ 175.4 (C), 141.5 (C), 129.6 (CH), 129.2 (CH), 129.1 (CH), 128.8 (CH), 128.5 (CH), 126.9 (C), 126.6 (CH), 111.6 (C), 108.8 (C), 52.2 (CH_3), 35.6 (C), 9.9 (CH_3). The spectral data are consistent with the literature.[15] HPLC: SS-WHELK, 1% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 17.8 min (major), 21.5 min (minor), 93% ee with (*S*)-xylylBINAP($AuCl)_2$; $[\alpha]^{23}_D$ -66.5 (*c* 1.0, $CHCl_3$)



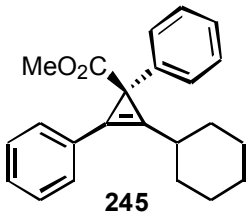
243

(*S*)-Methyl 2-ethyl-1,3-diphenylcycloprop-2-enecarboxylate (243). Purification by silica gel chromatography gave compound **243** in 68% yield (95 mg) as white crystals; ^{1}H NMR (400 MHz) δ 7.65 (dd, 2H, J = 8.8 Hz, 1.6 Hz), 7.19-7.43 (m, 8H), 3.70 (s, 3H), 2.79 (q, 2H, *J* = 7.6Hz), 1.36 (t, 3H, *J* = 7.6 Hz); ^{13}C-NMR (100 MHz) δ 175.5 (C), 141.5 (C), 129.6 (CH), 129.1 (CH), 129.0 (CH), 128.4 (CH), 128.3 (CH), 126.8 (C), 126.4 (CH), 111.6 (C), 107.9 (C), 52.2 (CH_3), 35.6 (C), 18.7 (CH_2), 12.4 (CH_3). The spectral data are consistent with the literature.[3] HPLC: SS-WHELK, 1% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 17.6 min (major), 19.5 min (minor), 90% ee with (*S*)-xylylBINAP($AuCl)_2$; $[\alpha]^{23}_D$ -67.8 (*c* 1.0, $CHCl_3$)



244

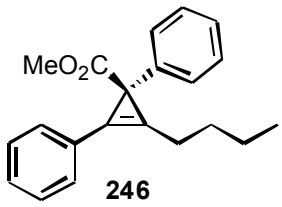
(*S*)-Methyl 2-isobutyl-1,3-diphenylcycloprop-2-enecarboxylate (244). Purification by silica gel chromatography (R_f = 0.58 in 8:2 pentane/Et_2O) gave compound **244** in 70% yield (107 mg) as yellow oil. IR (neat) 2952, 2870, 1716, 1199, 691 cm^{-1}; ^1H NMR (400 MHz) δ 7.55 (dd, 2H, *J* = 8.4 Hz, 1.2 Hz), 7.29-7.40 (m, 5H), 7.23-7.26 (dt, 2H, *J* = 6.8 Hz, 1.6 Hz), 7.17 (m, 1H), 3.68 (s, 3H), 2.62 (dd, 2H, *J* = 16.4, 6.8 Hz), 2.09 (septet, 1H, *J* = 6.8 Hz), 1.02 (d, 3H, *J* = 6.4 Hz), 0.99 (d, 3H, 6.4 Hz); ^{13}C-NMR (100 MHz) δ 175.5 (C), 141.5 (C), 129.6 (CH), 129.1 (CH), 129.0 (CH), 128.4 (CH), 128.2 (CH), 126.9 (C), 126.4 (CH), 115.6 (C), 108.2 (C), 52.1 (CH_3), 35.6 (C), 34.5 (CH_2), 27.9 (CH), 22.9 (CH_3), 22.9 (CH_3). HRMS (ESI) *m/z* calcd for $C_{21}H_{22}O_2$, 307.1653, found 307.1694 $[M+H]^+$. HPLC: AD-H, 3% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 15.1 min (major), 16.2 min (minor), 94% ee with (*S*)-xylylBINAP($AuCl)_2$; $[\alpha]^{23}_D$ -264.7 (*c* 1.0, $CHCl_3$)



245

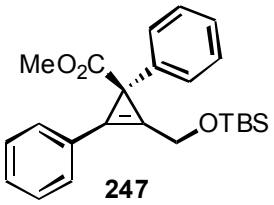
(*S*)-Methyl 2-cyclohexyl-1,3-diphenylcycloprop-2-enecarboxylate (245). Purification by silica gel chromatography (R_f = 0.50 in 8:2 pentane/Et_2O) gave compound **245** in 83% yield (138 mg) as yellow oil. IR (neat) 3023, 2923, 2853, 1716, 1202, 691 cm^{-1}; ^1H NMR

(600 MHz) δ 7.56 (d, 2H, J = 7.2 Hz), 7.32-7.41 (m, 5H), (7.25 (t, 2H, J = 7.2 Hz), 7.17 (t, 1H, J = 6.6 Hz), 3.69 (s, 3H), 2.8 (m, 1H), 2.03 (m, 2H), 1.26-1.77 (m, 6H); ^{13}C-NMR (100 MHz) δ 175.7 (C), 141.8 (C), 129.7 (CH), 129.1 (CH), 128.9 (CH), 128.4 (CH), 128.2 (CH), 126.9 (C), 126.3 (CH), 119.5 (C), 106.6 (C), 52.1 (CH_3), 35.5 (C), 35.3 (CH), 31.6 (CH_2), 31.2 (CH_2), 26.2 (CH_2), 25.8 (CH_2). HRMS (ESI) *m/z* calcd for $C_{23}H_{25}O_2$, 333.1810, found 333.1850 $[M+H]^+$. HPLC: SS-WHELK, 1% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 21.1 min (major), 14.0 min (minor), 86% ee with (*S*)-xylylBINAP$(AuCl)_2$; $[\alpha]^{23}_D$ -146.9 (*c* 1.0, $CHCl_3$)



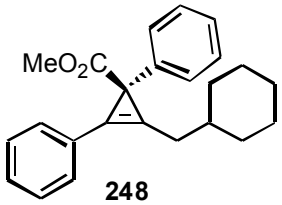
246

(*S*)-Methyl 2-butyl-1,3-diphenylcycloprop-2-enecarboxylate (246). Purification by silica gel chromatography gave compound **246** in 72% yield (110 mg) as yellow oil. IR (neat) 3024, 2954, 2871, 1716, 1200, 690 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.54 (d, 2H, J = 7.2 Hz), 7.14-7.39 (m, 8H), 3.67 (s, 3H), 2.73 (t, 2H, J = 7.2 Hz), 1.73 (q, 2H, J = 7.6 Hz), 1.41 (m, 2H), 0.92 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (100 MHz) δ 175.5 (C), 141.6 (C), 129.6 (CH), 129.1 (CH), 129.0 (CH), 128.4 (CH), 128.3 (CH), 126.9 (C), 126.4 (CH), 115.8 (C), 108.2 (C), 52.1 (CH_3), 35.6 (C), 29.9 (CH_2), 24.9 (CH_2), 22.8 (CH_2), 14.0 (CH_3). The spectral data are consistent with the literature.[15] HPLC: AD-H, 3% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 15.0 min (major), 14.3 min (minor), 90% ee with (*S*)-xylylBINAP$(AuCl)_2$; $[\alpha]^{23}_D$ -120.1 (*c* 1.0, $CHCl_3$)



247

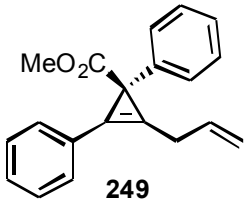
(*R*)-Methyl 2-(((tert-butyldimethylsilyl)oxy)methyl)-1,3-diphenylcycloprop-2-enecarbo-xylate (247). Purification by silica gel chromatography gave compound **247** in 62% yield (122 mg) as yellow oil. IR (neat) 2951, 2928, 2855, 1720, 1204, 1092, 834, 758, 691 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.62 (dd, 2H, J = 8.8 Hz, 1.6 Hz), 7.19-7.43 (m, 8H), 4.94 (d, 1H, *J* = 16.4 Hz), 4.82 (d, 1H, *J* = 21 Hz), 3.69 (s, 3H), 0.95 (s, 9H), 0.10 (s, 6H); ^{13}C-NMR (100 MHz) δ 174.9 (C), 140.8 (C), 130.0 (CH), 129.4 (CH), 128.9 (CH), 128.6 (CH), 128.3 (CH), 126.6 (CH), 126.2 (CH), 113.9 (C), 110.5 (C), 58.1 (CH_2), 52.2 (CH_3), 37.0 (C), 26.1 (CH_3), 18.6 (C), -5.1 (CH_3). The spectral data are consistent with the literature.[3] HPLC: SS-WHELK, 1% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 21.1 min (major), 14.0 min (minor), 86% ee with (*S*)-xylylBINAP$(AuCl)_2$ $[\alpha]^{23}_D$; -7.3 (*c* 1.0, $CHCl_3$)



248

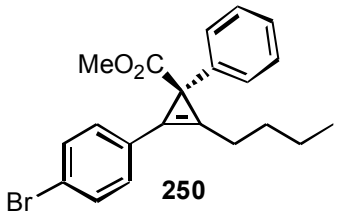
(*S*)-Methyl 2-(cyclohexylmethyl)-1,3-diphenylcycloprop-2-enecarboxylate (248). Purification by silica gel chromatography (R_f = 0.54 in 8:2 pentane/Et_2O) gave compound **248** in 78% yield (135 mg) as yellow oil. IR (neat) 3022, 2922, 2850, 1716, 1213, 756,

691 cm^{-1}; ^1H NMR (400 MHz) δ 7.53 (m, 2H), 7.13-7.40 (m, 8H), 3.67 (s, 3H), 2.61 (dd, 2H, *J* = 16.4, 6.8 Hz), 1.63-1.86 (m, 6H), 0.95-1.32 (m, 5H); ^{13}C-NMR (100 MHz) δ 175.5 (C), 141.5 (C), 129.5 (CH), 129.2 (CH), 129.0 (CH), 128.4 (CH), 128.2 (CH), 127.0 (C), 126.4 (CH), 115.1 (C), 108.2 (C), 52.1 (CH_3), 37.3 (CH_2), 35.6 (C), 33.6 (CH_2), 32.9 (CH), 26.6 (CH_2), 26.4 (CH_2), 26.3 (CH_2). HRMS (ESI) *m/z* calcd for $C_{24}H_{27}O_2$, 347.1966, found 347.2001 $[M+H]^+$. HPLC: AD-H, 1% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 27.4 min (major), 22.5 min (minor), 92% ee with (*S*)-xylylBINAP$(AuCl)_2$ $[\alpha]^{23}_D$; -114.5 (*c* 1.0, $CHCl_3$)



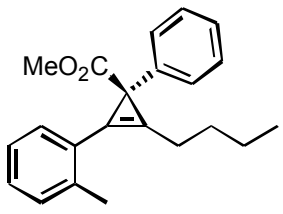
249

(*S*)-Methyl 2-allyl-1,3-diphenylcycloprop-2-enecarboxylate (249). Purification by silica gel chromatography gave compound **249** in 58% yield (84 mg) as yellow oil. IR (neat) 3058, 2951, 1716, 1265, 1208, 733, 696 cm^{-1}; ^1H NMR (400 MHz) δ 7.56 (m, 2H), 7.17-7.42 (m, 8H), 6.05 (ddt, 1H, *J* = 17.2 Hz, 10.4 Hz, 6.4 Hz), 5.28 (ddq, 1H, *J* = 17.2 Hz, 3.2 Hz, 1.6 Hz), 5.23 (ddq, 1H, *J* = 8.8 Hz, 1.6 Hz, 1.2 Hz), 3.69 (s, 3H), 3.49 (m, 2H); ^{13}C-NMR (100 MHz) δ 175.3 (C), 141.2 (C), 132.9, 129.8 (CH), 129.2 (CH), 129.1 (CH), 128.5 (CH), 128.3 (CH), 126.6 (CH), 126.6 (CH), 118.2 (CH_2), 113.4 (C), 109.5 (C), 52.2 (CH_3), 35.8 (C), 29.5 (CH_2). The spectral data are consistent with the literature.[15] HPLC: SS-WHELK, 1% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 11.7 min (major), 13.5 min (minor), 96% ee with (*S*)-xylylBINAP$(AuCl)_2$; $[\alpha]^{23}_D$ -15.2 (*c* 1.0, $CHCl_3$)



250

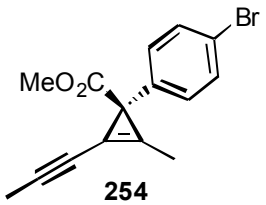
(*S*)-Methyl 2-(4-bromophenyl)-3-butyl-1-phenylcycloprop-2-enecarboxylate (250). Purification by silica gel chromatography gave compound **250** in 76% yield (147 mg) as yellow oil. IR (neat) 2954, 1715, 1203, 906, 727, 697 cm^{-1}; ^1H NMR (400 MHz) δ 7.52 (dt, 2H, *J* = 6.4 Hz, 2.0 Hz), 7.15-7.40 (m, 7H), 3.68 (s, 3H), 2.72 (t, 2H, *J* = 7.6 Hz), 1.71 (app q, 2H, *J* = 7.6 Hz), 1.40 (m, 2H), 0.92 (t, 3H, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz) δ 175.2 (C), 141.1 (C), 132.4 (CH), 130.9 (CH), 128.3 (CH), 126.6 (CH), 125.9 (C), 123.2 (C), 116.9 (C), 107.3 (C), 52.2 (CH_3), 35.6 (C), 29.8 (CH_2), 24.9 (CH_2), 22.7 (CH_2), 13.9 (CH_3). The spectral data are consistent with the literature.[15] HPLC: AD-H, 3% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 14.3 min (major), 16.9 min (minor), 89% ee with (*S*)-xylylBINAP($AuCl)_2$; $[\alpha]^{23}_D$ -84.3 (*c* 1.0, $CHCl_3$)



251

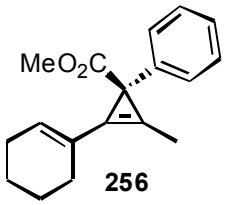
(*S*)-Methyl 2-butyl-1-phenyl-3-(o-tolyl)cycloprop-2-enecarboxylate (251). Purification by silica gel chromatography (R_f = 0.63 in 8:2 hexane/Et_2O) gave compound **251** in 75% yield (120 mg) as yellow oil. IR (neat) 3022, 2954, 2872, 1716, 1198, 729, 697 cm^{-1}; ^1H NMR (400 MHz) δ 7.40 (dd, 1H, *J* = 6.8 Hz, 1.2 Hz), 7.34-7.37 (m, 2H), 7.14-7.24 (m,

6H), 3.69 (s, 3H), 2.85 (dt, 1H, J = 15.6 Hz, 7.6 Hz), 2.76 (dt, 1H, J = 15.6 Hz, 7.6 Hz) 2.50 (s, 3H), 1.59 (m, 2H), 1.35 (m, 2H), 0.85 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (100 MHz) δ 175.8 (C), 141.7 (C), 138.5 (C), 130.5 (CH), 130.3 (CH), 129.3 (CH), 128.4 (CH), 128.2 (CH), 126.4 (CH), 126.3 (CH), 126.2 (C), 116.4 (C), 106.3 (C), 52.1 (CH_3), 34.6 (C), 29.3 (CH_2), 25.3 (CH_2), 22.8 (CH_3), 21.2 (CH_2), 14.0 (CH_3). HRMS (ESI) *m/z* calcd for $C_{22}H_{25}O_2$, 321.1810, found 321.1851 $[M+H]^+$. HPLC: SS-WHELK, 1% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 12.8 min (major), 15.2 min (minor), 93% ee with (*S*)-xylylBINAP(AuCl)$_2$; $[\alpha]^{23}_D$ -1.9 (*c* 1.0, $CHCl_3$)



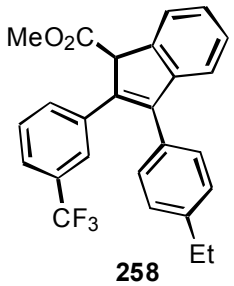
254

(*S*)-Methyl 1-(4-bromophenyl)-2-methyl-3-(prop-1-yn-1-yl)cycloprop-2-enecarboxylate (254). Purification by silica gel chromatography gave compound **254** in 82% yield (125 mg) as yellow oil. IR (neat) 2950, 2914, 1718, 1206, 1008 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.41 (d, 2H, J = 8 Hz), 7.21 (d, 2H, J = 8.4 Hz), 3.69 (s, 3H), 2.19 (s, 3H), 2.09 (s, 3H); ^{13}C-NMR (100 MHz) δ 173.9 (C), 139.7 (C), 131.4 (CH), 130.2 (CH), 120.7 (C), 114.0 (C), 98.3 (C), 95.3 (C), 66.3 (C), 52.5 (CH_3), 36.4 (C), 10.3 (CH_2), 5.3 (CH_3). The spectral data are consistent with the literature.[15] HPLC: AD-H, 1% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 15.5 min (major), 24.5 min (minor), 98% ee with (*S*)-xylylBINAP(AuCl)$_2$; $[\alpha]^{23}_D$ -52.9 (*c* 1.0, $CHCl_3$)



256

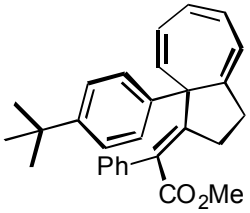
(*S*)-Methyl 2-(cyclohex-1-en-1-yl)-3-ethyl-1-phenylcycloprop-2-enecarboxylate (256). Purification by silica gel chromatography gave compound **256** in 83% yield (117 mg) as yellow oil. IR (neat) 3022, 2931, 1716, 1433, 1198, 1020, 697 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.16-7.33 (m, 5H), 6.09 (t, 1H, J = 4.0 Hz), 3.68 (s, 3H), 2.61 (q, 2H, J = 7.6 Hz), 2.26-2.42 (m, 2H), 2.17 (m, 2H), 1.60-1.75 (m, 4H), 1.22 (t, 3H, J = 8.0 Hz); ^{13}C-NMR (100 MHz) δ 175.9 (C), 142.1 (C), 132.9 (CH), 128.6 (CH), 128.1 (CH), 126.1 (CH), 124.7 (C), 113.9 (C), 109.6 (C), 52.0 (CH_3), 35.6 (C), 27.9 (CH_2), 27.8 (CH_2), 25.8 (CH2), 22.6 (CH2), 22.0 (CH2), 18.5 (CH_2), 12.6 (CH_3). The spectral data are consistent with the literature.[15] HPLC: SS-WHELK, 1% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 9.6 min (major), 11.5 min (minor), 89% ee with (*S*)-xylylBINAP($AuCl)_2$; $[\alpha]^{23}_D$ +7.2 (*c* 1.0, $CHCl_3$)



258

Methyl 3-(4-ethylphenyl)-2-(3-(trifluoromethyl)phenyl)-1H-indene-1-carboxylate (258). Purification by silica gel chromatography (R_f = 0.67 in 8:2 hexane/Et_2O) gave compound **258** in 38% yield (78 mg) as yellowish oil; IR (neat) 3030, 2954, 1738, 1165,

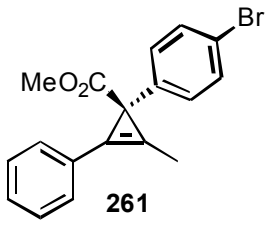
1127, 1017, 698 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.95 (br s, 1H), 7.85 (d, 1H, 7.2 Hz), 7.66 (d, 2H, *J* = 7.8 Hz), 7.62 (d, 1H, *J* = 7.8 Hz), 7.58 (t, 1H, *J* = 7.2 Hz), 7.44 (d, 2H, *J* = 7.8 Hz), 7.31-7.34 (m, 2H), 7.27 (m, 2H), 7.20 (t, 1H, *J* = 7.2 Hz), 7.16 (d, 1H, *J* = 8.4 Hz), 3.72 (s, 3H), 3.52 (s, 1H), 2.71 (q, 2H, *J* = 7.8 Hz), 1.27 (t, 3H, *J* = 7.8 Hz); ^{13}C-NMR (100 MHz) δ 174.2 (C), 147.1 (C), 146.1 (C), 139.8 (C), 130.4 (CH), 129.7 (C), 129.6 (CH), 128.9 (CH), 128.8 (CH), 128.4 (CH), 128.3 (CH), 127.9 (C), 126.8 (CH), 126.5 (CH), 123.6 (C), 113.5 (C), 109.2 (C), 52.4 (CH_3), 35.7 (CH), 29.2 (CH_2), 15.6 (CH_3). HRMS (ESI) *m/z* calcd for $C_{26}H_{21}F_3O_2Na$, 445.1494, found 445.1386 $[M+Na]^+$.



260

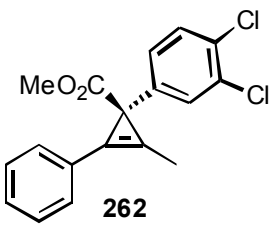
(*E*)-Methyl 2-(8a-(4-(tert-butyl)phenyl)-2,3-dihydroazulen-1(8aH)-ylidene)-2-phenylacetate (260). Purification by silica gel chromatography (R_f = 0.54 in 8:2 hexane/Et_2O) gave compound **260** in 83% yield (170 mg) as yellow oil; IR (neat) 3019, 2951, 2866, 1710, 1222, 732, 696 cm^{-1}; ^{1}H NMR (400 MHz) δ 6.99-7.02 (m, 1H), 6.90 (t, 2H, *J* = 7.2 Hz), 6.79 (d, 2H, *J* = 9.0 Hz), 6.59 (dd, 2H, *J* = 7.8 Hz, 1.2 Hz), 6.33 (m, 1H), 6.31 (d, 2H, *J* = 9.0 Hz), 6.17 (dd, 1H, *J* = 10.2 Hz, 9.6 Hz), 6.12 (d, 1H, *J* = 7.2 Hz), 6.32 (dd, 1H, *J* = 10.2 Hz, 9.6 Hz), 4.89 (d, 1H, *J* = 9.0 Hz), 3.59 (s, 3H), 3.57 (m, 1H), 3.06 (m, 1H), 2.83-2.93 (m, 2H), 1.18 (s, 9H); ^{13}C-NMR (100 MHz) δ 169.1 (C), 166.7 (C), 147.6 (C), 136.8 (C), 136.7 (C), 131.2 (C), 129.9 (CH), 128.8 (C), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.3 (CH), 126.3 (CH), 126.1 (CH), 123.3 (CH), 119.8 (CH), 109.8 (CH), 54.1 (C), 51.9 (CH_3), 34.3 (CH_2), 34.2 (C), 33.4 (CH_2), 31.6 (CH_3). HRMS (ESI)

m/z calcd for $C_{29}H_{31}O_2$, 411.2279, found 411.2322 $[M+H]^+$. HPLC: ODH, 2.5% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 4.5 min (minor), 4.8 min (major), 18% ee with (*S*)-xylylBINAP$(AuCl)_2$.



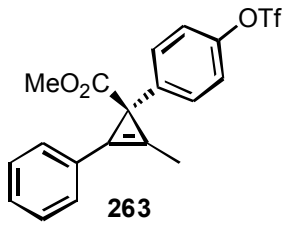
261

(*S*)-Methyl 1-(4-bromophenyl)-2-methyl-3-phenylcycloprop-2-enecarboxylate (261). Purification by silica gel chromatography gave compound **261** in 60% yield (103 mg) as yellow crystals. MP 58-60 ^oC. IR (neat) 2949, 1716, 1487, 1205, 761, 691 cm^{-1}; ^1H NMR (400 MHz) δ 7.56 (dd, 2H, *J* = 8.4 Hz, 1.2 Hz), 7.30-7.44 (m, 7H), 3.72 (s, 3H), 2.40 (s, 3H); ^{13}C-NMR (100 MHz) δ 174.9 (C), 140.5 (C), 131.4 (CH), 130.3 (CH), 129.5 (CH), 129.3 (CH), 129.2 (CH), 126.5 (C), 120.4 (CH), 111.1 (C), 108.3 (C), 52.3 (CH_3), 35.0 (C), 9.84 (CH_3). The spectral data are consistent with the literature.[15] HPLC: SS-WHELK, 4% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 12.1 min (major), 17.3 min (minor), 95% ee with (*S*)-DTBMSEGPHOS$(AuCl)_2$; $[\alpha]^{23}_D$ -98.9 (*c* 1.0, $CHCl_3$)



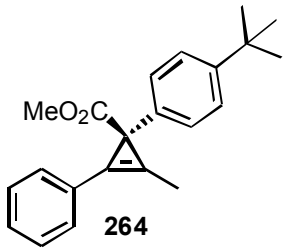
262

(*S*)-Methyl 1-(3,4-dichlorophenyl)-2-methyl-3-phenylcycloprop-2-enecarboxylate (262). Purification by silica gel chromatography gave compound **262** in 79% yield (132 mg) as yellow oil. IR (neat) 2950, 1717, 1201, 761, 690 cm^{-1}; ^1H NMR (400 MHz) δ 7.50-7.54 (m, 3H), 7.35-7.46 (m, 3H), 7.33 (s, 1H), 7.23 (dd, 1H, J = 8.4 Hz, 2.0 Hz), 3.72 (s, 3H), 2.40 (s, 3H); ^{13}C-NMR (100 MHz) δ 174.4 (C), 141.7 (C), 132.2 (C), 130.4 (CH), 130.2 (CH), 129.5 (CH), 129.2 (CH), 127.9 (CH), 126.0 (C), 110.6 (C), 108.0 (C), 52.3 (CH_3), 34.7 (C), 9.70 (CH_3). The spectral data are consistent with the literature.[15] HPLC: SS-WHELK, 1% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 15.6 min (major), 20.0 min (minor), 97% ee with (*S*)-DTBMSEGPHOS($AuCl)_2$; $[\alpha]^{23}_D$ -131.9 (*c* 1.0, $CHCl_3$)



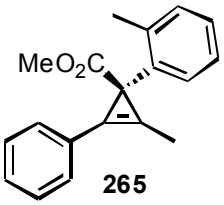
263

(*S*)-Methyl 2-methyl-3-phenyl-1-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)cyclo-prop-2-enecarboxylate (263). Purification by silica gel chromatography gave compound **263** in 65% yield (134 mg) as yellow oil. IR (neat) 2953, 1718, 1420, 1203, 1137, 883 cm^{-1}; ^1H NMR (400 MHz) δ 7.54 (m, 2H), 7.37-7.49 (m, 5H), 7.19 (m, 2H), 3.72 (s, 3H), 2.40 (s, 3H); ^{13}C-NMR (100 MHz) δ 174.7 (C), 148.1 (C), 141.9 (C), 130.2 (CH), 129.5 (CH), 129.4 (CH), 129.2 (CH), 126.1 (C), 121.0 (CH), 110.9 (C), 107.9 (C), 52.3 (CH_3), 34.8 (C), 9.68 (CH_3). The spectral data are consistent with the literature.[15] HPLC: SS-WHELK, 4% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 13.2 min (major), 17.1 min (minor), 95% ee with (*S*)-DTBMSEGPHOS($AuCl)_2$; $[\alpha]^{23}_D$ -81.7 (*c* 1.0, $CHCl_3$)



264

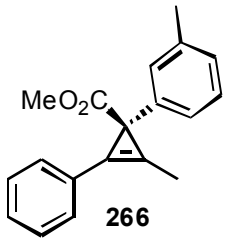
(*S*)-Methyl 1-(4-(tert-butyl)phenyl)-2-methyl-3-phenylcycloprop-2-enecarboxylate (264). Purification by silica gel chromatography gave compound **264** in 62% yield (99 mg) as yellow oil; ^{1}H NMR (400 MHz) δ 7.60 (dd, 2H, *J* = 8.4 Hz, 1.6 Hz), 7.32-7.45 (m, 7H), 3.74 (s, 3H), 2.43 (s, 3H), 1.34 (s, 9H); ^{13}C-NMR (100 MHz) δ 175.6 (C), 149.2 (C), 138.3 (C), 129.5 (CH), 129.1 (CH), 128.9 (CH), 128.1 (CH), 127.0 (C), 125.3 (CH), 111.7 (C), 108.9 (C), 52.2 (CH_3), 35.2 (C), 34.6 (C), 31.6 (CH_3), 9.97 (CH_3). The spectral data are consistent with the literature.[15] HPLC: SS-WHELK, 4% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 12.1 min (major), 17.1 min (minor), 95% ee with (*S*)-xylylBINAP$(AuCl)_2$; $[\alpha]^{23}_D$ -6.7 (*c* 0.8, $CHCl_3$)



265

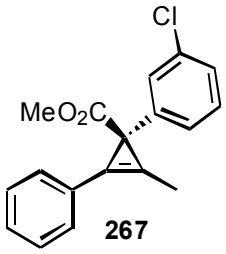
(*R*)-Methyl 2-methyl-3-phenyl-1-(o-tolyl)cycloprop-2-enecarboxylate (265). Purification by silica gel chromatography (R_f = 0.38 in 8:2 pentane/Et_2O) gave compound **265** in 62% yield (86 mg) as colorless oil. IR (neat) 3020, 2984, 1716, 1211, 740, 693 cm^{-1}; ^{1}H NMR (600 MHz) δ 7.59 (d, 2H, *J* = 7.8 Hz), 7.43 (t, 2H, *J* = 7.2 Hz), 7.35 (t,

1H, J = 7.2 Hz), 7.20 (d, 1H, J = 7.8 Hz), 7.12-7.16 (m, 2H), 7.02 (t, 1H, J = 7.2 Hz), 3.69 (s, 3H), 2.41 (s, 3H), 2.38 (s, 3H); ^{13}C-NMR (100 MHz) δ 175.9 (C), 141.2 (C), 137.8 (C), 130.3 (CH), 129.3 (CH), 129.1 (CH), 128.9 (CH), 128.6 (CH), 127.7 (C), 127.3 (CH), 126.3 (CH), 114.4 (C), 109.9 (C), 52.4 (CH_3), 35.2 (C), 19.9 (CH_3), 10.2 (CH_3). HRMS (ESI) *m/z* calcd for $C_{19}H_{19}O_2$, 279.1340, found 279.1378 $[M+H]^+$. HPLC: SS-WHELK, 1% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 12.7 min (major), 17.3 min (minor), 95% ee with (*S*)-xylylBINAP(AuCl)$_2$; $[\alpha]^{23}_D$ -123.9 (*c* 1.0, $CHCl_3$)



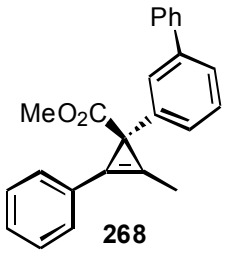
266

(*S*)-Methyl 2-methyl-3-phenyl-1-(m-tolyl)cycloprop-2-enecarboxylate (266). Purification by silica gel chromatography gave compound **266** in 71% yield (99 mg) as colorless oil. IR (neat) 2949, 1716, 1221, 1037, 759, 691 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.55 (d, 2H, J = 7.2 Hz), 7.39 (t, 2H, J = 7.6 Hz), 7.32(m, 1H), 7.16 (m, 3H), 7.00 (m, 1H), 3.69 (s, 3H), 2.38 (s, 3H), 2.30 (s, 3H); ^{13}C-NMR (100 MHz) δ 175.5 (C), 141.4 (C), 137.9 (C), 129.5 (CH), 129.2 (CH), 129.1 (CH), 129.0 (CH), 128.3 (CH), 127.4 (CH), 127.0 (C), 125.6 (CH), 111.7 (C), 108.9 (C), 52.2 (CH_3), 35.6 (C), 21.9 (CH_3), 9.9 (CH_3). The spectral data are consistent with the literature.[15] HPLC: SS-WHELK, 1% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 16.9 min (major), 20.8 min (minor), 92% ee with (*S*)-xylylBINAP(AuCl)$_2$; $[\alpha]^{23}_D$ -62.8 (*c* 1.0, $CHCl_3$)



267

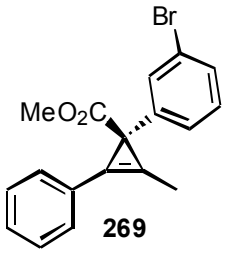
(*S*)-Methyl 1-(3-chlorophenyl)-2-methyl-3-phenylcycloprop-2-enecarboxylate (267). Purification by silica gel chromatography (R_f = 0.42 in 8:2 pentane/Et_2O) gave compound **267** in 77% yield (114 mg) as colorless oil. IR (neat) 3057, 2950, 1722, 1209, 907, 727, 690 cm^{-1}; ^1H NMR (400 MHz) δ 7.52 (d, 2H, *J* = 6.6 Hz), 7.40 (t, 2H, *J* = 7.2 Hz), 7.35 (m, 2H), 7.23 (m, 1H), 7.15-7.20 (m, 2H), 3.69 (s, 3H), 2.38 (s, 3H); ^{13}C-NMR (100 MHz) δ 174.8 (C), 143.5 (C), 134.1 (C), 129.6 (CH), 129.5 (CH), 129.3 (CH), 129.2 (CH), 128.5 (CH), 126.7 (CH), 126.6 (CH), 126.4 (C), 110.9 (C), 108.9 (C), 52.3 (CH_3), 35.2 (C), 9.8 (CH_3). HRMS (ESI) *m/z* calcd for $C_{18}H_{16}ClO_2$, 299.0794, found 299.0832 $[M+H]^+$. HPLC: SS-WHELK, 1% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 14.1 min (major), 17.0 min (minor), 95% ee with (*S*)-xylylBINAP($AuCl)_2$; $[\alpha]^{23}_D$ -232.1 (*c* 1.0, $CHCl_3$)



268

(*S*)-Methyl 1-([1,1'-biphenyl]-3-yl)-2-methyl-3-phenylcycloprop-2-enecarboxylate (268). Purification by silica gel chromatography (R_f = 0.38 in 8:2 pentane/Et_2O) gave

compound **268** in 70% yield (70 mg) as yellow oil. IR (neat) 3026, 2949, 1710, 1225, 755, 697 cm^{-1}; ^1H NMR (600 MHz) δ 7.53-7.60 (m, 5H), 7.39-7.43 (m, 5H), 7.31-7.39 (m, 4H), 3.71 (s, 3H), 2.41 (s, 3H); ^{13}C-NMR (100 MHz) δ 175.4 (C), 141.9 (C), 141.7 (C), 141.3 (C), 129.6 (CH), 129.2 (CH), 128.9 (CH), 128.8 (CH), 127.5 (CH), 127.4 (CH), 126.8 (C), 125.6 (CH), 111.4 (C), 108.9 (C), 52.3 (CH_3), 35.7 (C), 10.0 (CH_3). HRMS (ESI) *m/z* calcd for $C_{24}H_{20}O_2Na$, 363.1463, found 363.1362 $[M+Na]^+$. HPLC: AD-H, 1% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 18.1 min (major), 14.8 min (minor), 95% ee with (*S*)-xylylBINAP$(AuCl)_2$; $[\alpha]^{23}_D$ -70.9 (*c* 1.0, $CHCl_3$)

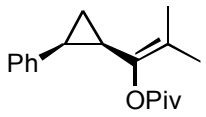


269

(*S*)-Methyl 1-(3-bromophenyl)-2-methyl-3-phenylcycloprop-2-enecarboxylate (269). Purification by silica gel chromatography (R_f = 0.42 in 8:2 pentane/Et_2O) gave compound **269** in 66% yield (115 mg) as colorless oil. IR (neat) 3023, 2949, 1716, 1202, 760, 690 cm^{-1}; ^1H NMR (600 MHz) δ 7.52 (m, 2H), 7.40 (t, 2H, *J* = 8.4 Hz), 7.32 (m, 1H), 7.28-7.36 (m, 3H), 7.12 (t, 1H, *J* = 8.4 Hz), 3.69 (s, 3H), 2.38 (s, 3H); ^{13}C-NMR (100 MHz) δ 174.8 (C), 143.8 (C), 131.4 (C), 129.9 (CH), 129.6 (CH), 129.4 (CH), 129.3 (CH), 129.2 (CH), 127.1 (CH), 126.3 (C), 122.4 (CH), 110.9 (C), 108.3 (C), 52.3 (CH_3), 35.1 (C), 9.8 (CH_3). HRMS (ESI) *m/z* calcd for $C_{18}H_{16}BrO_2$, 343.0289, found 343.0327 $[M+H]^+$. HPLC: AD-H, 1% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 10.8 min (major), 10.0 min (minor), 97% ee with (*S*)-xylylBINAP$(AuCl)_2$; $[\alpha]^{23}_D$ -153.1 (*c* 1.0, $CHCl_3$).

V. Procedure for Au(I)-catalyzed cyclopropanation of olefins with propargyl esters

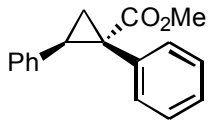
$AgSbF_6$ and (*S*)-DTBM-Segphos$(AuCl)_2$ were placed in a 25 mL round bottom flask. The mixture was dissolved with 5 mL $MeNO_2$ and stirred at room temperature for 20 mins under an atmosphere of argon. Styrene was added *via* syringe followed by the propargyl ester in 5 mL $MeNO_2$. The reaction mixture was stirred for 1.5 hrs then concentrated *in vacuo*. The crude reaction mixture was purified by silica gel chromatography using 20:1 hexane/Et2O as solvent system to afford the cyclopropane product as colorless oil.[16]



277

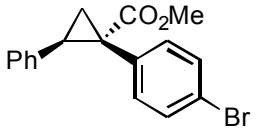
2-Methyl-1-((1*R*,2*S*)-2-phenylcyclopropyl)prop-1-en-1-yl pivalate (277). Purification by silica gel chromatography (using 20:1 hexane/Et_2O solvent system) gave compound **277** in 72% yield (97 mg) as colorless oil. ^{1}H NMR (400 MHz) δ 7.19-7.23 (m, 2H), 7.15 (m, 1H), 7.03 (d, 2H, *J* = 8.0 Hz), 2.26 (dt, 1H, *J* = 7.6, 6.8 Hz), 1.47 (s, 3H), 1.41 (s, 3H), 1.24 (m, 2H), 1.21 (s, 9H), 0.99 (m, 1H). Spectral data is consistent with published results. HPLC: ODH, 0.5% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 3.9 min (major), 4.2 min (minor), 88% ee with (*S*)-DTBM-Segphos$(AuCl)_2$.

VI. General Procedure for Au(I)-catalyzed cyclopropanation of olefins



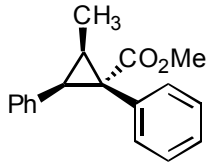
278

(1*S*,2*R*)-Methyl 1,2-diphenylcyclopropanecarboxylate (278). Purification by silica gel chromatography (using 20:1 hexane/Et_2O solvent system) gave compound **278** in 91% yield (114 mg) as colorless oil. ^{1}H NMR (400 MHz) δ 7.52 (d, 2H, J = 6.6 Hz), 7.40 (t, 2H, J = 7.2 Hz), 7.35 (m, 2H), 7.23 (m, 1H), 7.15-7.20 (m, 2H), 3.69 (s, 3H), 2.38 (s, 3H). The spectral data is consistent with published results.[17] HPLC: SS-WHELK, 1.5% iPrOH/hexane, 0.7 mlmin^{-1}, UV 254 nm, t_R: 12.3 min (minor), 14.6 min (major), 35% ee with (*S*)-DTBM-Segphos$(AuCl)_2$.



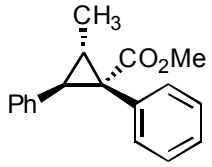
279

(1*S*,2*R*)-Methyl 1-(4-bromophenyl)-2-phenylcyclopropanecarboxylate (279). Purification by silica gel chromatography (using 20:1 hexane/Et_2O solvent system) gave compound **279** in 82% yield (136 mg) as yellowish oil. ^{1}H NMR (400 MHz) δ 7.52 (d, 2H, J = 6.6 Hz), 7.40 (t, 2H, J = 7.2 Hz), 7.35 (m, 2H), 7.23 (m, 1H), 7.15-7.20 (m, 2H), 3.69 (s, 3H), 2.38 (s, 3H). Spectral data is consistent with published results.[18] HPLC: OJH, 2% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 7.6 min (major), 10.7 min (minor), 60% ee with (*S*)-DTBM-Segphos$(AuCl)_2$.



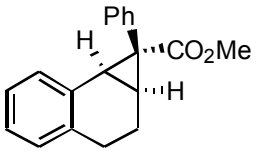
281

(1*S*,2*R*,3*R*)-Methyl 2-methyl-1,3-diphenylcyclopropanecarboxylate (281). Purification by silica gel chromatography (using 20:1 hexane/Et_2O solvent system) gave compound **281** in 86% yield (115 mg) as colorless crystals. ^{1}H NMR (600 MHz) δ 7.27 (m, 3H), 7.13 (m, 3H), 7.04 (dd, 2H, J = 7.8, 1.2 Hz), 6.77 (dd, 2H, J = 7.8, 1.8 Hz), 3.61 (s, 3H), 3.10 (d, 1H, J = 10.2 Hz), 2.38 (dq, 1H, J = 10.2, 7.2 Hz), 1.26 (d, 3H, J = 7.2 Hz). Spectral data is consistent with published results.[17] HPLC: ADH, 0.5% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 6.6 min (mino), 8.0 min (major), 85% ee with (*S*)-DTBM-Segphos$(AuCl)_2$.



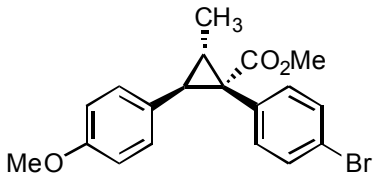
282

(1*S*,2*S*,3*R*)-Methyl 2-methyl-1,3-diphenylcyclopropanecarboxylate (282). Purification by silica gel chromatography (using 20:1 hexane/Et_2O) gave compound **282** in 64% yield (86 mg) as colorless crystals. ^{1}H NMR (600 MHz) δ 7.13 (m, 3Hz), 6.98-7.05 (m, 5H), 6.75 (dd, 2H, J = 7.8, 1.8 Hz), 3.65 (s, 3H), 3.08 (d, 1H, J = 7.2 Hz), 2.25 (dq, 1H, J = 7.2, 6.6 Hz), 1.47 (d, 3H, J = 6.6 Hz). Spectral data is consistent with published results.[17] HPLC: ADH, 1% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 5.8 min (major), 6.7 min (minor), 78% ee with (*S*)-DTBM-Segphos$(AuCl)_2$.



283

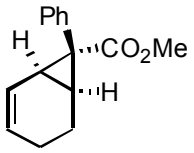
(1*R*,1a*S*,7b*S*)-Methyl 1-phenyl-1a,2,3,7b-tetrahydro-1H-cyclopropa[a]naphthalene-1-carboxylate (283). Purification by silica gel chromatography (using 20:1 hexane/Et_2O) gave compound **283** in 73% yield (102 mg) as colorless oil. ^{1}H NMR (600 MHz) δ 7.45 (d, 1H, *J* = 7.8 Hz), 6.95-7.18 (m, 7H), 6.72 (d, 1H, *J* = 7.8 Hz), 3.62 (s, 3H), 3.04 (d, 1H, *J* = 9.6 Hz), 2.56 (dd, 1H, *J* = 9.6, 4.8 Hz), 2.16 (m, 2H), 1.96 (m, 1H), 1.04 (m, 1H). Spectral data is consistent with published results.[17] HPLC: SS-WHELK, 1% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 9.2 min (minor), 10.0 min (major), 88% ee with (*S*)-DTBM-Segphos$(AuCl)_2$.



286

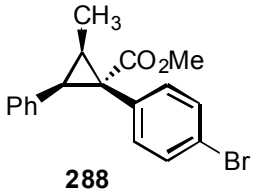
(1S,2R,3S)-Methyl 1-(4-bromophenyl)-2-(4-methoxyphenyl)-3-methylcyclopropane-carboxylate (286). Purification by silica gel chromatography (using 20:1 hexane/Et_2O solvent system) gave compound **286** in 86% yield (161 mg) as colorless oil. IR (neat) 2950, 2835, 1716, 1514, 1247, 1167, 832 cm^{-1}; ^{1}H NMR (600 MHz) δ 7.25 (d, 2H, *J* =

7.8 Hz), 6.86 (d, 2H, J = 7.8 Hz), 6.68 (d, 2H, J = 9.0 Hz), 6.63 (d, 2H, J = 9.0 Hz), 3.74 (s, 3H), 3.64 (s, 3H), 3.04 (d, 1H, J = 7.2 Hz), 2.13 (dq, 1H, J = 7.2, 6.6 Hz), 1.45 (d, 3H, J = 6.0 Hz); ^{13}C-NMR (100 MHz) δ 172.1 (C), 158.3 (C), 135.9 (C), 133.3 (CH), 131.2 (CH), 129.1 (CH), 128.6 (C), 113.6 (CH), 55.3 (CH_3), 52.6 (CH_3), 42.5 (C), 37.6 (CH), 27.8 (CH), 12.9 (CH_3). HRMS (ESI) *m/z* calcd for $C_{19}H_{20}BrO_3$, 375.0551, found 375.0593 $[M+H]^+$. HPLC: ADH, 1% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 8.8 min (major), 9.8 min (minor), 43% ee with (*S*)-DTBM-Segphos$(AuCl)_2$.



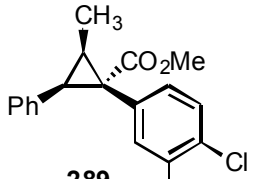
287

(1*R*,6*S*,7*R*)-Methyl 7-phenylbicyclo[4.1.0]hept-2-ene-7-carboxylate (287). Purification by silica gel chromatography (using 20:1 hexane/Et_2O solvent system) gave compound **287** in 74% yield (85 mg) as colorless oil. ^{1}H NMR (400 MHz) δ 7.52 (d, 2H, J = 6.6 Hz), 7.40 (t, 2H, J = 7.2 Hz), 7.35 (m, 2H), 7.23 (m, 1H), 7.15-7.20 (m, 2H), 3.69 (s, 3H), 2.38 (s, 3H). Spectral data is consistent with published results.[17] HPLC: OJH, 1% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 8.5 min (minor), 9.8 min (major), 33% ee with (*S*)-DTBM-Segphos$(AuCl)_2$.



288

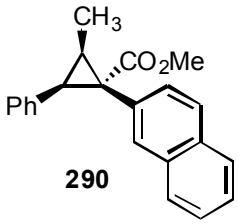
(1*S*,2*R*,3*R*)-Methyl 1-(4-bromophenyl)-2-methyl-3-phenylcyclopropanecarboxylate (288). Purification by silica gel chromatography (using 20:1 hexane/Et_2O solvent system) gave compound **288** in 83% yield (143 mg) as light yellow oil. IR (neat) 3057, 2950, 1722, 1209, 907, 727, 690 cm^{-1}; ^1H NMR (600 MHz) δ 7.39 (d, 2H, J = 8.4 Hz), 7.14 (m, 3H), 6.90 (d, 2H, J = 9.0 Hz), 6.79 (m, 2H), 3.61 (s, 3H), 3.10 (d, 1H, J = 9.6 Hz), 2.38 (dq, 1H, J = 7.2, 3.6 Hz), 1.25 (d, 3H, J = 7.2 Hz); ^{13}C-NMR (100 MHz) δ 175.1 (C), 136.0 (C), 135.1 (CH), 131.8 (C), 131.4 (CH), 130.5 (CH), 127.9 (CH), 126.5 (CH), 121.8 (C), 53.0 (CH_3), 37.7 (C), 36.8 (CH), 28.0 (CH), 11.1 (CH_3). HRMS (ESI) *m/z* calcd for $C_{18}H_{18}BrO_2$, 345.0445, found 345.0486 $[M+H]^+$. HPLC: ADH, 1% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 6.6 min (minor), 7.1 min (major), 94% ee with (*S*)-DTBM-Segphos$(AuCl)_2$; $[\alpha]^{23}_D$ -17.4 (*c* 1.2, $CHCl_3$)



289

(1*S*,2*R*,3*R*)-Methyl 1-(3,4-dichlorophenyl)-2-methyl-3-phenylcyclopropanecarboxylate (289). Purification by silica gel chromatography (using 20:1 hexane/Et_2O solvent system) gave compound **289** in 84% yield (153 mg) as light yellow oil. IR (neat) 2951,

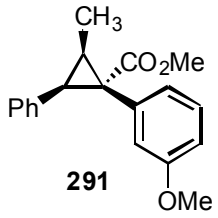
1716, 1243, 1224, 905, 728, 698 cm^{-1}; ^1H NMR (600 MHz) δ 7.30 (d, 2H, *J* = 7.8 Hz), 7.17 (m, 2H), 7.13 (d, 1H, *J* = 1.8 Hz), 6.84 (d, 1H, *J* = 1.8 Hz), 6.82 (m, 2H), 3.62 (s, 3H), 3.11 (d, 1H, *J* = 9.6 Hz), 2.38 (dq, 1H, *J* = 7.2, 3.0 Hz), 1.28 (d, 3H, *J* = 6.6 Hz); ^{13}C-NMR (100 MHz) δ 174.6 (C), 135.7 (C), 135.1 (CH), 133.2 (C), 132.9 (CH), 132.1 (C), 131.8 (C), 130.5 (CH), 130.1 (CH), 128.1 (CH), 126.7 (CH), 53.1 (CH_3), 37.3 (C), 36.9 (CH), 28.1 (CH), 11.1 (CH_3). HRMS (ESI) *m/z* calcd for $C_{18}H_{17}Cl_2O_2$, 335.0561, found 335.0602 $[M+H]^+$. HPLC: ADH, 1% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 6.6 min (minor), 6.8 min (major), 80% ee with (*S*)-DTBM-Segphos($AuCl)_2$; $[\alpha]^{23}_D$ -3.0 (*c* 0.8, $CHCl_3$)



290

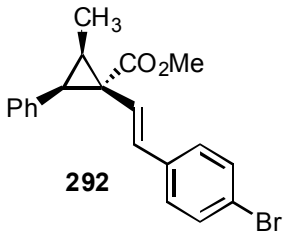
(1*S*,2*R*,3*R*)-Methyl 2-methyl-1-(naphthalen-2-yl)-3-phenylcyclopropanecarboxylate (290). Purification by silica gel chromatography (using 20:1 hexane/Et_2O solvent system) gave compound **288** in 84% yield (133 mg) as light yellow oil. IR (neat) 3026, 2950, 1713, 1241, 1218, 906, 727, 699 cm^{-1}; ^1H NMR (600 MHz) δ 7.81 (d, 1H, *J* = 7.8 Hz), 7.72 (dd, 2H, *J* = 9.0, 8.4 Hz), 7.54 (s, 1H), 7.46 (m, 2H), 7.11 (m, 3H), 6.80 (d, 2H, *J* = 7.8 Hz), 3.59 (s, 3H), 3.17 (d, 1H, *J* = 10.8 Hz), 2.38 (dq, 1H, *J* = 7.2, 3.6 Hz), 1.31 (d, 3H, *J* = 6.6 Hz); ^{13}C-NMR (100 MHz) δ 175.8 (C), 136.4 (C), 133.4 (C), 132.8 (C), 132.3 (CH), 131.6 (CH), 130.6 (CH), 130.4 (C), 128.3 (CH), 127.9 (CH), 127.5 (CH), 126.4

(CH), 126.3 (CH), 126.1 (CH), 53.0 (CH_3), 38.4 (C), 36.9 (CH), 28.3 (CH), 11.2 (CH_3). HRMS (ESI) *m/z* calcd for $C_{22}H_{21}O_2$, 317.1497, found 317.1537 $[M+H]^+$. HPLC: SS-WHELK, 1% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 8.3 min (minor), 9.4 min (major), 92% ee with (*S*)-DTBM-Segphos$(AuCl)_2$; $[\alpha]^{23}_D$ 2.9 (*c* 1.1, $CHCl_3$)



291

(1*S*,2*R*,3*R*)-Methyl 1-(3-methoxyphenyl)-2-methyl-3-phenylcyclopropanecarboxylate (291). Purification by silica gel chromatography (using 20:1 hexane/Et_2O solvent system) gave compound **291** in 81% yield (120 mg) as light yellow oil. IR (neat) 2999, 2951, 2834, 1714, 1236, 1213, 906, 729, 698 cm^{-1}; ^{1}H NMR (600 MHz) δ 7.18 (t, 1H, *J* = 8.4 Hz), 7.13 (m, 3H), 6.82 (m, 3H), 6.65 (d, 1H, *J* = 7.2 Hz), 6.54 (d, 1H, *J* = 2.4 Hz), 3.62 (s, 3H), 3.09 (d, 1H, *J* = 10.2 Hz), 2.38 (dq, 1H, *J* = 6.6, 3.6 Hz), 1.28 (d, 3H, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz) δ 175.6 (C), 159.2 (C), 136.5 (C), 133.9 (CH), 130.6 (CH), 128.9 (CH), 127.7 (C), 126.3 (CH), 125.8 (CH), 118.7 (CH), 113.4 (CH), 55.2 (CH_3), 52.9 (CH_3), 38.3 (C), 36.8 (CH), 28.1 (CH), 11.2 (CH_3). HRMS (ESI) *m/z* calcd for $C_{19}H_{21}O_3$, 297.1446, found 297.1486 $[M+H]^+$. HPLC: ADH, 1% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 8.5 min (minor), 9.5 min (major), 81% ee with (*S*)-DTBM-Segphos$(AuCl)_2$; $[\alpha]^{23}_D$ -86.0 (*c* 1.3, $CHCl_3$)



292

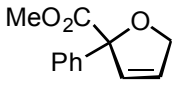
(1*S*,2*R*,3*R*)-Methyl 1-((E)-4-bromostyryl)-2-methyl-3-phenylcyclopropanecarboxylate (292). Purification by silica gel chromatography (using 20:1 hexane/Et_2O solvent system) gave compound **292** in 76% yield (140 mg) as yellow oil. IR (neat) 3026, 2950, 1716, 1487, 1239, 1212, 1072, 905, 728, 702 cm^{-1}; ^1H NMR (600 MHz) δ 7.36 (d, 2H, *J* = 7.8 Hz), 7.31 (t, 1H, *J* = 6.6 Hz), 7.26 (m, 3H), 7.07 (d, 2H, *J* = 8.4 Hz), 6.66 (d, 1H, *J* = 16.2 Hz), 5.81 (d, 1H, *J* = 16.8 Hz), 3.77 (s, 3H), 3.09 (d, 1H, *J* = 9.0 Hz), 2.38 (dq, 1H, *J* = 6.6, 3.0 Hz), 1.19 (d, 3H, *J* = 6.6 Hz); ^{13}C-NMR (100 MHz) δ 174.5 (C), 136.9 (C), 134.6 (C), 133.7 (CH), 131.8 (CH), 131.1 (CH), 128.6 (CH), 127.7 (CH), 126.9 (CH), 123.4 (CH), 121.2 (C), 52.6 (CH_3), 36.6 (CH), 32.9 (C), 28.3 (CH), 11.4 (CH_3). HRMS (ESI) *m/z* calcd for $C_{20}H_{20}BrO_2$, 371.0602, found 371.0644 $[M+H]^+$. HPLC: ADH, 1% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 9.7 min (major), 12.5 min (minor), 91% ee with (*S*)-DTBM-Segphos$(AuCl)_2$; $[\alpha]^{23}_D$ -1.8 (*c* 1.1, $CHCl_3$)

Experimental section for Chapter V: Silver- and Gold-Catalyzed Transformations of Propargyl Alcohols with Aryldiazoacetates

I. General procedure for AgOTf-Catalyzed reaction of propargyl alchols and aryl diazoacetates

A mixture of alcohol (0.6-1.0 mmol) and AgOTf (0.025-0.0.05 mmol) was dissolved in 2 mL degassed DCM and stirred at room temperature under an atmosphere of argon. Aryl diazoacetate (0.5 mmol) in 8 mL DCM was then added to former solution *via* syringe pump over 1 h. After addition, the mixture was stirred for additional 1-3 hrs then concentrated *in vacuo*. The residue was purified on silica using hexane/ether as solvent system in the ratio specified in parenthesis.

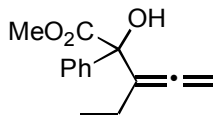
II. Spectral data and full characterization of all dihydrofuran and allenol products



300

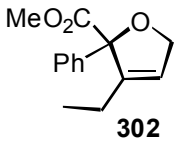
Methyl 2-phenyl-2,5-dihydrofuran-2-carboxylate (300). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **300** in 84% yield (86 mg) as colorless oil. IR (neat) 2952, 2860, 1731, 1236, 1077, 697 cm^{-1}; ^1H NMR (400 MHz) δ 7.64 (dd, 2H, J = 7.2 Hz, 1.2 Hz), 7.24-7.47 (m, 8H), 3.76 (s, 3H), 2.79 (s, 3H); ^{13}C-NMR (100 MHz) δ 175.4 (C), 141.5 (C), 129.6 (CH), 129.2 (CH), 129.1

(CH), 128.8 (CH), 128.5 (CH), 126.9 (C), 126.6 (CH), 111.6 (C), 108.8 (C), 52.2 (CH_3), 35.6 (C), 9.9 (CH_3). HRMS (ESI) *m/z* calcd for $C_{12}H_{13}O_3$, 205.0820, found 205.0858 $[M+H]^+$.



301

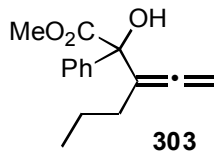
Methyl 3-ethyl-2-hydroxy-2-phenylpenta-3,4-dienoate (301). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **301** in 18% yield (21 mg) as colorless oil. IR (neat) 3415, 2927, 2856, 1733, 1256, 1071, 907, 729, 697 cm^{-1}; ^1H NMR (400 MHz) δ 7.59 (d, 2H, *J* = 6.8 Hz), 7.24-7.36 (m, 3H), 4.88 (app t, 2H, *J* = 4.0 Hz), 3.72 (s, 3H), 3.67 (s, 1H), 1.99 (m, 1H), 1.85 (m, 1H), 0.98 (t, 3H, *J* = 7.6 Hz); ^{13}C-NMR (100 MHz) δ 205.9 (C), 174.6 (C), 139.3 (C), 128.1 (CH), 127.8 (CH), 127.4 (CH), 109.2 (C), 81.4 (C), 79.6 (CH_2), 53.3 (CH_3), 20.1 (CH_2), 12.3 (CH_3). HRMS (ESI) *m/z* calcd for $C_{14}H_{16}O_3Na$, 255.1099, found 255.0992 $[M+Na]^+$.



302

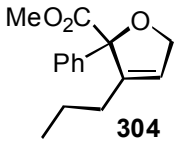
Methyl 3-ethyl-2-phenyl-2,5-dihydrofuran-2-carboxylate (302). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **302** in 74% yield (86 mg) as colorless oil. IR (neat) 2965, 2851, 1728, 1251, 1221, 1069, 758, 698 cm^{-1}; ^1H NMR (600 MHz) δ 7.28-7.39 (m, 5H), 5.76 (t, 1H, *J* = 2.4 Hz), 4.83 (m, 2H), 3.79 (s, 3H), 2.35 (m, 1H), 1.92 (m, 1H), 1.08 (t, 3H, *J* = 7.8 Hz); ^{13}C-NMR (125

MHz) δ 172.3 (C), 144.6 (C), 139.9 (C), 128.5 (CH), 128.3 (CH), 126.3 (CH), 121.9 (CH), 95.3 (C), 75.2 (CH_2), 52.6 (CH_3), 20.3 (CH_2), 12.2 (CH_3). HRMS (ESI) *m/z* calcd for $C_{14}H_{15}O_3$, 231.1099, found 231.1015 $[M-H]^+$.



303

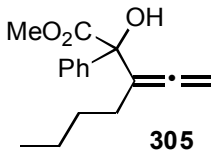
Methyl 2-hydroxy-2-phenyl-3-vinylidenehexanoate (303). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **301** in 16% yield (20 mg) as colorless oil. IR (neat) 3497, 2957, 2872, 1726, 1248, 1062, 849, 743, 699 cm^{-1}; ^1H NMR (600 MHz) δ 7.59 (d, 2H, *J* = 7.8 Hz), 7.36 (m, 2H), 7.30 (t, 1H, *J* = 6.6 Hz), 4.86 (t, 2H, *J* = 3.6 Hz), 3.89 (s, 1H), 3.73 (s, 3H), 1.93 (m, 1H), 1.80 (m, 1H), 1.43 (m, 2H), 0.87 (t, 3H, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz) δ 205.9 (C), 174.6 (C), 139.2 (C), 128.1 (CH), 128.0 (CH), 127.4 (CH), 107.4 (C), 81.5 (C), 79.2 (CH_2), 53.3 (CH_3), 29.0 (CH_2), 21.1 (CH_2) 14.0 (CH_3). HRMS (ESI) *m/z* calcd for $C_{15}H_{17}O_2$, 229.1256, found 229.1221 $[M-OH]^+$.



304

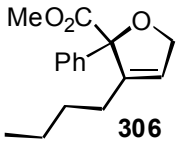
Methyl 2-phenyl-3-propyl-2,5-dihydrofuran-2-carboxylate (304). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **304** in 69% yield (85 mg) as colorless oil. IR (neat) 2956, 2871, 1729, 1252, 1219, 1088, 1069, 698 cm^{-1}; ^1H NMR (400 MHz) δ 7.29-7.39 (m, 5H), 5.77(m, 1H), 4.83 (m, 2H),

3.81 (s, 3H), 2.25 (m, 1H), 1.88 (m, 1H), 1.48 (m, 2H), 0.89 (t, 3H, J = 7.6 Hz); ^{13}C-NMR (100 MHz) δ 172.3 (C), 142.9 (C), 139.9 (C), 128.5 (CH), 128.3 (CH), 126.3 (CH), 122.3 (C), 95.3 (C), 75.3 (CH_2), 52.6 (CH_3), 29.1 (CH_2), 21.2 (CH_2), 14.2 (CH_3). HRMS (ESI) *m/z* calcd for $C_{15}H_{119}O_3$, 247.1289, found 247.1328 $[M-H]^+$.



305

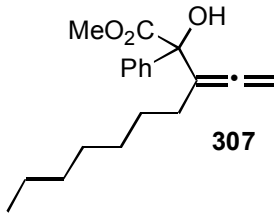
Methyl 2-hydroxy-2-phenyl-3-vinylideneheptanoate (305). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **305** in 15% yield (20 mg) as colorless oil. IR (neat) 3497, 2954, 2930, 2860, 1727, 1186, 850, 698 cm^{-1}; ^{1}H NMR (600 MHz) δ 7.59 (dd, 2H, J = 9.6 Hz, 1.2 Hz), 7.35 (m, 2H), 7.31 (m, 1H), 4.86 (m, 2H), 3.90 (s, 1H), 3.73 (s, 3H), 1.96 (m, 1H), 1.82 (m, 1H), 1.39 (m, 2H), 1.28 (m, 2H), 0.84 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (100 MHz) δ 205.9 (C), 174.6 (C), 139.2 (C), 128.1 (CH), 128.0 (CH), 127.4 (CH), 107.6 (C), 81.5 (C), 79.2 (CH_2), 53.3 (CH_3), 30.0 (CH_2), 26.6 (CH_2), 22.6 (CH_2), 14.2 (CH_3). HRMS (ESI) *m/z* calcd for $C_{16}H_{19}O_2$, 243.1412, found 243.1377 $[M-OH]^+$.



306

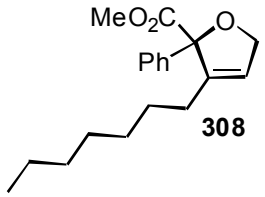
Methyl 3-butyl-2-phenyl-2,5-dihydrofuran-2-carboxylate (306). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **306** in

75% yield (85 mg) as colorless oil. IR (neat) 2954, 2930, 2858, 1731, 1254, 1220, 759, 699 cm^{-1}; ^1H NMR (400 MHz) δ 7.26-7.38 (m, 5H), 5.77 (t, 1H, *J* = 2.0 Hz), 4.83 (m, 2H), 3.81 (s, 3H), 2.26 (m, 1H), 1.90 (m, 1H), 1.44 (m, 2H), 1.32 (quintet, 2H, *J* = 7.6 Hz), 0.86 (t, 3H, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz) δ 172.3 (C), 142.9 (C), 139.9 (C), 128.5 (CH), 128.3 (CH), 126.4 (CH), 122.2 (C), 95.3 (C), 75.3 (CH_2), 52.6 (CH_3), 30.1 (CH_2), 26.7 (CH_2), 22.7 (CH_2), 14.2 (CH_3). HRMS (ESI) *m/z* calcd for $C_{16}H_{21}O_3$, 261.1446, found 261.1485 $[M+H]^+$.



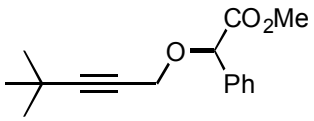
307

Methyl 2-hydroxy-2-phenyl-3-vinylidenedecanoate (307). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **307** in 13% yield (19 mg) as colorless oil. IR (neat) 3502, 2926, 2855, 1729, 1249, 731, 698 cm^{-1}; ^1H NMR (400 MHz) δ 7.59 (dd, 2H, *J* = 7.6 Hz, 1.2 Hz), 7.26-7.35 (m, 3H), 4.86 (t, 2H, *J* = 4.0 Hz), 3.89 (s, 1H), 3.73 (s, 3H), 1.94 (m, 1H), 1.82 (m, 1H), 1.20-1.41 (m, 10H), 0.86 (t, 3H, *J* = 6.4 Hz); ^{13}C-NMR (100 MHz) δ 206.0 (C), 174.6 (C), 139.2 (C), 128.1 (CH), 128.0 (CH), 127.4 (CH), 107.6 (C), 81.5 (C), 79.2 (CH_2), 53.3 (CH_3), 32.0 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 27.9 (CH_2), 26.9 (CH_2), 22.9 (CH_2), 14.3 (CH_3). HRMS (ESI) *m/z* calcd for $C_{19}H_{25}O_2$, 285.1882, found 285.1846 $[M-OH]^+$.



308

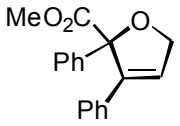
Methyl 3-heptyl-2-phenyl-2,5-dihydrofuran-2-carboxylate (308). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **308** in 80% yield (97 mg) as colorless oil. IR (neat) 2926, 2854, 1731, 1253, 1220, 1089, 1070, 697 cm^{-1}; ^1H NMR (400 MHz) δ 7.26-7.37 (m, 5H), 5.77 (t, 1H, *J* = 2.0 Hz), 4.83 (m, 2H), 3.81 (s, 3H), 2.28 (m, 1H), 1.88 (m, 1H), 1.20-1.53 (m, 10H), 0.86 (t, 3H, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz) δ 172.3 (C), 143.1 (C), 139.9 (C), 128.5 (CH), 128.3 (CH), 126.3 (CH), 122.2 (C), 95.3 (C), 75.3 (CH_2), 52.6 (CH_3), 31.9 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 27.9 (CH_2), 27.0 (CH_2), 22.8 (CH_2), 14.3 (CH_3). HRMS (ESI) *m/z* calcd for $C_{19}H_{27}O_3$, 303.1882, found 303.1956 $[M+H]^+$.



309

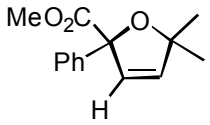
Methyl 2-((4,4-dimethylpent-2-yn-1-yl)oxy)-2-phenylacetate (309). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **309** in 92% yield (120 mg) as colorless oil. IR (neat) 2968, 2867, 1750, 1263, 1097, 1014, 730, 696 cm^{-1}; ^1H NMR (400 MHz) δ 7.64 (dd, 2H, *J* = 8.0 Hz, 2.0 Hz), 7.32-7.38 (m, 3H), 5.19 (2, 1H), 4.29 (d, 1H, *J* = 15.2 Hz), 4.14 (d, 1H, *J* = 15.2 Hz), 3.71 (s, 3H), 1.21 (s, 9H); ^{13}C-NMR (100 MHz) δ 171.3 (C), 136.0 (C), 129.1 (CH), 128.8 (CH), 127.8

(CH), 96.8 (C), 78.5 (CH), 73.3 (C), 57.1 (CH_2), 52.5 (CH_3), 31.1 (CH_3), 27.7 (C). HRMS (ESI) *m/z* calcd for $C_{16}H_{21}O_3$, 261.1412, found 261.1485 $[M-H]^+$.



310

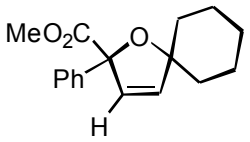
Methyl 2,3-diphenyl-2,5-dihydrofuran-2-carboxylate (310). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **310** in 85% yield (119 mg) as colorless oil. IR (neat) 3059, 2952, 2868, 1737, 1250, 1077, 765, 695 cm^{-1}; ^1H NMR (400 MHz) δ 7.17-7.37 (m, 10H), 6.46 (t, 1H, *J* = 2.0 Hz), 4.97 (dd, 1H, *J* = 14.0, 1.6 Hz), 4.92 (dd, 1H, *J* = 14.0, 1.6 Hz), 3.74 (s, 3H); ^{13}C-NMR (100 MHz) δ 172.1 (C), 141.2 (C), 139.4 (C), 129.7 (C), 128.4 (CH), 128.3 (CH), 127.9 (CH), 127.8 (CH), 127.4 (CH), 126.9 (CH), 94.8 (C), 74.8 (CH_2), 52.6 (CH_3), 35.6 (C), 9.9 (CH_3). HRMS (ESI) *m/z* calcd for $C_{18}H_{15}O_2$, 263.1150, found 263.1076 $[M-H]^+$.



311

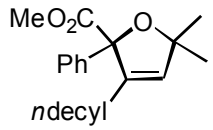
Methyl 5,5-dimethyl-2-phenyl-2,5-dihydrofuran-2-carboxylate (311). Purification by silica gel chromatography (using 10:1 pentane/Et_2O solvent system) gave compound **311** in 93% yield (108 mg) as colorless oil. IR (neat) 2931, 2856, 1728, 1229, 788, 727, 696 cm^{-1}; ^1H NMR (400 MHz) δ 7.50 (d, 2H, *J* = 8.4 Hz, 1.2 Hz), 7.32 (t, 2H, *J* = 7.8 Hz), 7.26 (m, 1H), 6.11 (d, 1H, *J* = 4.0 Hz), 5.90 (d, 1H, *J* = 4.0 Hz), 3.71 (s, 3H), 1.45 (s, 3H), 1.36 (s, 3H); ^{13}C-NMR (125 MHz) δ 173.1 (C), 141.4 (C), 137.0 (C), 136.9 (C),

128.6 (CH), 128.0 (CH), 127.3 (CH), 125.4 (CH), 93.2 (C). 90.2 (C), 52.8 (CH_3), 28.4 (CH_3). HRMS (ESI) *m/z* calcd for $C_{14}H_{17}O_3$, 233.1133, found 233.1175 $[M+H]^+$.



312

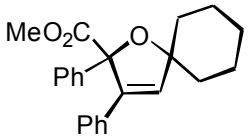
Methyl 2-phenyl-1-oxaspiro[4.5]dec-3-ene-2-carboxylate (312). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **312** in 88% yield (120 mg) as colorless oil. IR (neat) 2931, 2856, 1728, 1447, 1253, 1229, 1052, 697 cm^{-1}; ^1H NMR (400 MHz) δ 7.52 (d, 2H, *J* = 7.2 Hz), 7.34 (t, 2H, *J* = 7.8 Hz), 7.28 (t, 1H, *J* = 7.8 Hz), 6.15 (d, 1H, *J* = 6.6 Hz), 6.09 (d, 1H, *J* = 6.0 Hz), 3.72 (s, 3H), 1.44-1.86 (m, 10H); ^{13}C-NMR (100 MHz) δ 173.3 (C), 141.6 (C), 135.2 (C), 128.6 (CH), 128.1 (C), 127.9 (CH), 125.5 (CH), 92.6 (C), 92.8 (C), 52.7 (CH_3), 37.8 (CH_2), 37.8 (CH_2), 25.5 (CH_2), 23.6 (CH_2), 23.5 (CH_2). HRMS (ESI) *m/z* calcd for $C_{17}H_{21}O_3$, 273.1446, found 273.1486 $[M+H]^+$.



313

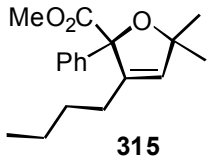
Methyl 3-decyl-5,5-dimethyl-2-phenyl-2,5-dihydrofuran-2-carboxylate (313). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave compound **313** in 93% yield (171 mg) as colorless oil. IR (neat) 2924, 2854, 1731, 1460, 1249, 1055, 908, 731, 697 cm^{-1}; ^1H NMR (400 MHz) δ 7.26-7.39 (m, 5H), 5.62 (t, 1H, *J* = 1.6 Hz), 3.77 (s, 3H), 2.30 (m, 1H), 1.83 (m, 1H), 1.45 (s, 3H), 1.40 (s, 3H), 1.20-1.30

(m, 18H), 0.87 (t, 3H, J = 6.4 Hz); ^{13}C-NMR (100 MHz) δ 173.2 (C), 141.2 (C), 140.2 (C), 131.0 (CH), 128.4 (CH), 128.0 (CH), 126.2 (CH), 94.8 (C), 88.2 (C), 52.5 (CH_3), 32.1 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 28.7 (CH_2), 28.1 (CH_2), 27.9 (CH_2), 26.9 (CH_3), 22.9 (CH_3), 14.3 (CH_3). HRMS (ESI) *m/z* calcd for $C_{24}H_{37}O_3$, 373.2698, found 373.2736 $[M+H]^+$.



314

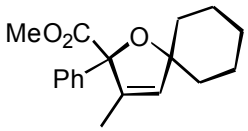
Methyl 2,3-diphenyl-1-oxaspiro[4.5]dec-3-ene-2-carboxylate (314). Purification by silica gel chromatography (using 20:1 hexane/Et_2O solvent system) gave compound **314** in 93% yield (162 mg) as colorless oil. IR (neat) 3058, 2931, 2856, 1732, 1446, 1246, 1213, 761, 694 cm^{-1}; ^{1}H NMR (600 MHz) δ 7.35 (dd, 2H, J = 6.0 Hz, 2.4 Hz), 7.28-7.30 (m, 3H), 7.16-7.20 (m, 5H), 6.43 (s, 1H), 3.77 (s, 3H), 1.82 (m, 7H), 1.53 (m, 5H); ^{13}C-NMR (100 MHz) δ 173.2 (C), 140.4 (C), 133.8 (C), 133.5 (C), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 127.9 (CH), 127.4 (CH), 94.1 (C), 90.2 (C), 52.7 (CH_3), 38.0 (CH_2), 37.4 (CH_2), 25.6 (CH_2), 23.7 (CH_2), 23.6 (CH_2). HRMS (ESI) *m/z* calcd for $C_{23}H_{24}O_3Na$, 371.1725, found 371.1618 $[M+Na]^+$.



315

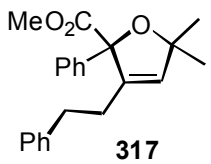
Methyl 3-butyl-5,5-dimethyl-2-phenyl-2,5-dihydrofuran-2-carboxylate (315). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave

compound **315** in 87% yield (125 mg) as colorless oil. IR (neat) 2957, 2872, 1729, 1248, 1054, 910, 730, 697 cm^{-1}; ^1H NMR (400 MHz) δ 7.27-7.39 (m, 5H), 5.63 (t, 1H, *J* = 1.6 Hz), 3.77 (s, 3H), 2.30 (m, 1H), 1.83 (m, 1H), 1.45 (s, 3H), 1.40 (s, 3H), 1.27-1.49 (m, 4H); ^{13}C-NMR (100 MHz) δ 173.2 (C), 141.1 (C), 140.2 (C), 131.0 (CH), 128.4 (CH), 128.1 (CH), 126.2 (CH), 94.8 (C), 88.2 (C), 52.5 (CH_3), 30.1 (CH_2), 28.7 (CH_2), 28.1 (CH_2), 26.7 (CH_3), 22.7 (CH_3), 14.2 (CH_3). HRMS (ESI) *m/z* calcd for $C_{18}H_{25}O_3$, 289.1759, found 289.1797 $[M+H]^+$.



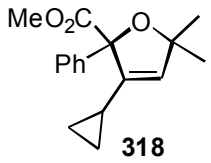
316

Methyl 3-methyl-2-phenyl-1-oxaspiro[4.5]dec-3-ene-2-carboxylate (316). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave compound **316** in 96% yield (123 mg) as colorless oil. IR (neat) 2924, 2856, 1729, 1446, 1235, 1058, 908, 729, 698 cm^{-1}; ^1H NMR (400 MHz) δ 7.64 (dd, 2H, *J* = 8.8 Hz, 1.6 Hz), 7.26-7.37 (m, 3H), 5.74 (d, 1H, *J* = 1.6 Hz), 3.76 (s, 3H), 1.77 (d, 3H, *J* = 1.2 Hz), 1.40-2.05 (m, 10 H); ^{13}C-NMR (100 MHz) δ 173.3 (C), 139.9 (C), 135.9 (C), 132.8 (CH) 128.4 (CH), 128.0 (C), 126.1 (CH), 94.0 (C), 93.4 (C), 52.4 (CH_3), 41.2 (CH_2), 43.3 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 23.0 (CH_2), 22.9 (CH_2), 13.5 (CH_3). HRMS (ESI) *m/z* calcd for $C_{18}H_{15}O_2$, 263.1150, found 263.1076 $[M-H]^+$.



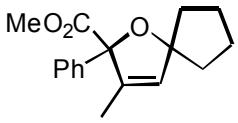
317

Methyl 2-phenyl-1-oxaspiro[4.5]dec-3-ene-2-carboxylate (317). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave compound **317** in 97% yield (161 mg) as colorless oil. IR (neat) 3026, 2972, 1729, 1251, 1056, 909, 797, 692 cm^{-1}; ^1H NMR (400 MHz) δ 7.08-7.38 (m, 10H), 5.65 (t, 1H, *J* = 1.6 Hz), 3.75 (s, 3H), 2.60-2.79 (m, 3H), 2.14-2.21 (m, 1H), 1.46 (s, 3H), 1.40 (s, 3H); ^{13}C-NMR (100 MHz) δ 173.2 (C), 141.7 (C), 140.4 (C), 139.9 (C), 131.8 (CH), 128.6 (CH), 128.5 (CH), 128.6 (CH), 128.2 (CH), 126.2 (CH), 94.8 (C), 88.3 (C), 52.7 (CH_3), 34.4 (CH_2), 28.9 (CH_2), 28.7 (CH_3), 28.2 (CH_3). HRMS (ESI) *m/z* calcd for $C_{22}H_{25}O_3$, 337.1759, found 337.1797 $[M+H]^+$.



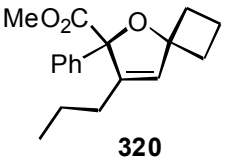
318

Methyl 2-phenyl-1-oxaspiro[4.5]dec-3-ene-2-carboxylate (318). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave compound **318** in 95% yield (129 mg) as colorless oil. IR (neat) 2974, 1734, 1057, 905, 727 cm^{-1}; ^1H NMR (600 MHz) δ 7.48 (d, 2H, *J* = 8.4 Hz), 7.34 (t, 2H, *J* = 7.2 Hz), 7.29 (m, 1H), 5.36 (d, 1H, *J* = 0.6 Hz), 3.80 (s, 3H), 1.44 (m, 1H), 1.39 (d, 3H, *J* = 3.0 Hz), 0.76 (m, 1H), 0.64 (m, 1H), 0.51 (m, 1H), 0.22 (m, 1H); ^{13}C-NMR (100 MHz) δ 173.2 (C), 143.5 (C), 140.5 (C), 128.3 (CH), 128.1 (CH), 128.0 (CH), 126.5 (CH), 94.7 (C), 87.9 (C), 52.6 (CH_3), 28.8 (CH_3), 28.2 (CH_3), 9.0 (CH), 8.5 (CH_2), 8.3 (CH_2) . HRMS (ESI) *m/z* calcd for $C_{17}H_{21}O_3$, 273.1446, found 273.1485 $[M+H]^+$.



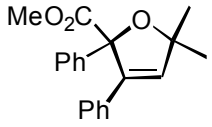
319

Methyl 3-methyl-2-phenyl-1-oxaspiro[4.4]non-3-ene-2-carboxylate (319). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave compound **319** in 97% yield (132 mg) as colorless oil. IR (neat) 2952, 2871, 1728, 1242, 1061, 731, 697 cm^{-1}; ^1H NMR (400 MHz) δ 7.25-7.39 (m, 5H), 5.62 (m, 1H), 3.78 (s, 3H), 1.77 (d, 3H, *J* = 1.2 Hz), 1.77 (d, 3H, *J* = 1.6 Hz), 1.61-1.97 (m, 8 H); ^{13}C-NMR (100 MHz) δ 172.9 (C), 139.8 (C), 136.6 (C), 131.2 (CH) 128.4 (CH), 128.1 (CH), 126.2 (CH), 98.0 (C), 94.5 (C), 52.5 (CH_3), 39.3 (CH_2), 38.7 (CH_2), 24.7 (CH_2), 24.7 (CH_2), 13.4 (CH_3). HRMS (ESI) *m/z* calcd for $C_{17}H_{21}O_3$, 273.1446, found 273.1485 $[M-H]^+$.



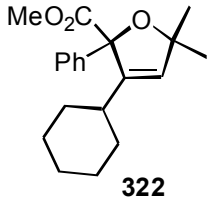
320

Methyl 2-phenyl-1-oxaspiro[4.5]dec-3-ene-2-carboxylate (320). Purification by silica gel chromatography (using 20:1 hexane/Et_2O solvent system) gave compound **320** in 94% yield (134 mg) as colorless oil. IR (neat) 2958, 2934, 2873, 1729, 1447, 1245, 1086, 760, 698` cm^{-1}; ^1H NMR (600 MHz) δ 7.26-7.34 (m, 5H), 5.89 (t, 1H, *J* = 1.8 Hz), 3.78 (s, 3H), 2.59 (m, 2H), 2.27 (m, 2H), 2.1 (m, 1H), 1.79 (m, 2H), 1.48-1.62 (m, 2H), 1.41 (m, 1H), 0.88 (t, 3H, *J* = 7.8 Hz); ^{13}C-NMR (100 MHz) δ 172.4 (C), 141.8 (C), 139.7 (C), 128.4 (CH), 128.1 (CH), 127.8 (CH), 127.7 (CH), 126.1 (CH), 95.1 (C), 90.4 (C), 52.6 (CH_3), 36.7 (CH_2), 36.6 (CH_2), 28.8 (CH_2), 21.1 (CH_2), 14.1 (CH_2), 12.3 (CH_2). HRMS (ESI) *m/z* calcd for $C_{18}H_{22}O_3Na$, 309.1569, found 309.1462 $[M+Na]^+$.



321

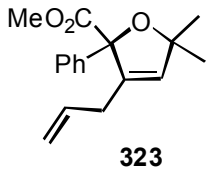
Methyl 5,5-dimethyl-2,3-diphenyl-2,5-dihydrofuran-2-carboxylate (321). Purification by silica gel chromatography (using 20:1 hexane/Et_2O solvent system) gave compound **310** in 90% yield (139 mg) as colorless oil. IR (neat) 3059, 2972, 1732, 1446, 1247, 761, 692 cm^{-1}; ^1H NMR (400 MHz) δ 7.29-7.35 (m, 5H), 7.19-7.21 (m, 5H), 6.30 (s, 1H), 3.77 (s, 3H), 1.52 (s, 3H), 1.49 (s, 3H); ^{13}C-NMR (100 MHz) δ 172.9 (C), 140.3 (C), 139.6 (C), 135.4 (CH), 133.1 (C), 128.4 (CH), 128.3 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.4 (CH), 94.7 (C), 88.2 (C), 52.8 (CH_3), 28.7 (CH_3), 27.9 (CH_3). HRMS (ESI) *m/z* calcd for $C_{20}H_{20}O_3Na$, 331.1412, found 331.1305 $[M+Na]^+$.



322

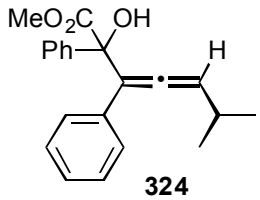
Methyl 3-cyclohexyl-5,5-dimethyl-2-phenyl-2,5-dihydrofuran-2-carboxylate (322). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave compound **322** in 93% yield (146 mg) as colorless oil. IR (neat) 2971, 2926, 2852, 1731, 1246, 729, 692 cm^{-1}; ^1H NMR (400 MHz) δ 7.27-7.39 (m, 5H), 5.64 (s, 1H), 3.77 (s, 3H), 2.03-2.08 (m, 1H), 1.91 (m, 1H), 1.71 (m, 1H), 1.50-1.62 (m, 2H), 1.44 (s, 3H), 1.38 (s, 3H), 0.87-1.27 (m, 6 H); ^{13}C-NMR (100 MHz) δ 173.5 (C), 147.0 (C), 140.5 (C), 130.7 (CH), 128.3 (CH), 128.1 (C), 126.2 (CH), 94.8 (C), 88.1 (C), 52.5 (CH_3), 36.2 (CH), 35.0

(CH_2), 34.4 (CH_2), 28.7 (CH_2), 28.2 (CH_2), 26.9 (CH_2), 26.8 (CH_2), 26.3 (CH_2). HRMS (ESI) *m/z* calcd for $C_{20}H_{27}O_3$, 315.1915, found 315.1954 $[M+H]^+$.



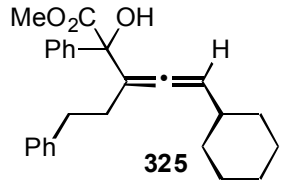
323

Methyl 3-allyl-5,5-dimethyl-2-phenyl-2,5-dihydrofuran-2-carboxylate (323). Purification by silica gel chromatography (using 20:1 hexane/Et_2O solvent system) gave compound **323** in 91% yield (123 mg) as colorless oil. IR (neat) 2974, 1728, 1434, 1252, 1056, 908, 730, 697 cm^{-1}; ^1H NMR (600 MHz) δ 7.28-7.39 (m, 5H), 5.78 (m, 1H), 5.64 (br s, 1H), 5.02 (m, 2H), 3.80 (s, 3H), 3.08 (dd, 1H, *J* = 16.8, 6.6 Hz), 2.60 (dd, 1H, *J* = 17.4, 6.0 Hz), 1.46 (s, 3H), 1.40 (s, 3H); ^{13}C-NMR (100 MHz) δ 173.1 (C), 139.8 (C), 139.4 (C), 135.1 (C), 132.7 (CH), 128.6 (CH), 128.2 (CH), 126.2 (CH), 116.9 (CH_2), 94.5 (C), 88.4 (C), 52.6 (CH_3), 31.8 (CH_2), 28.6 (CH_3), 28.1 (CH_3). HRMS (ESI) *m/z* calcd for $C_{17}H_{20}O_3$, 295.1412, found 295.1305 $[M+Na]^+$.



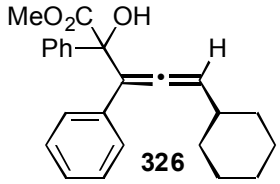
324

Methyl 2-hydroxy-6-methyl-2,3-diphenylhepta-3,4-dienoate (324). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave compound **324** in 81% yield (130 mg) as light yellow oil. IR (neat) 3482, 2960, 2870, 1725, 1255, 908, 730, 695 cm^{-1}; ^1H NMR (400 MHz) δ 7.66 (dd, 2H, *J* = 8.8 Hz, 1.6 Hz), 7.40 (d, 2H, *J* = 8.4 Hz), 7.09-7.30 (m, 6H), 5.56 (d, 1H, *J* = 5.6 Hz), 4.24 (s, 1H), 3.67 (s, 3H), 2.40 (septet, 1H, *J* = 6.4 Hz), 1.06 (d, 6H, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz) δ 203.0 (C), 179.9 (C), 140.1 (C), 134.5 (C), 128.3 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.5 (CH), 126.9 (CH), 110.4 (C), 103.8 (CH), 81.9 (C), 53.5 (CH_3), 28.8 (CH), 22.5 (CH_3), 22.4 (CH_3). HRMS (ESI) *m/z* calcd for $C_{21}H_{22}O_3$, 323.1602, found 323.1638 $[M+H]^+$.



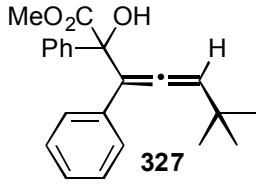
325

Methyl 5-cyclohexyl-2-hydroxy-3-phenethyl-2-phenylpenta-3,4-dienoate (325). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave compound **325** in 75% yield (156 mg) as yellow oil. IR (neat) 3504, 3027, 2924, 2851, 1726, 1255, 907, 729, 697 cm^{-1}; ^1H NMR (400 MHz) δ 7.62 (m, 2H), 7.09-7.35 (m, 8H), 5.29 (dt, 1H, *J* = 3.2, 2.4 Hz), 3.89 (s, 1H), 3.78 (s, 3H), 2.68 (m, 2H), 2.13-2.33 (m, 2H), 1.94 (m, 1H), 1.70 (m, 5H), 0.96-1.31 (m, 5H); ^{13}C-NMR (100 MHz) δ 200.1 (C), 174.7 (C), 142.2 (C), 139.4 (C), 128.7 (CH), 128.4 (CH), 128.1 (CH), 128.0 (CH), 127.5 (CH), 125.9 (CH), 108.6 (C), 102.6 (CH), 81.9 (C), 53.3 (CH_3), 37.9 (CH_2), 34.5 (CH), 33.1 (CH_2), 33.0 (CH_2), 29.1 (CH_2), 26.4 (CH_2), 26.3 (CH_2). HRMS (ESI) *m/z* calcd for $C_{26}H_{29}O_2$, 373.2195, found 373.2159 $[M-OH]^+$.



326

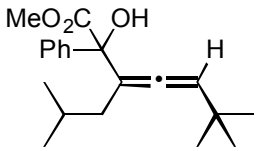
Methyl 5-cyclohexyl-2-hydroxy-2,3-diphenylpenta-3,4-dienoate (326). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave compound **326** in 77% yield (139 mg) as yellowish oil. IR (neat) 3500, 2925, 2852, 1726, 1448, 1256, 906, 728, 695 cm^{-1}; ^1H NMR (400 MHz) δ 7.59 (dd, 2H, J = 8.4 Hz, 1.2 Hz), 7.40 (d, 2H, J = 8.8 Hz), 7.07-7.28 (m, 6H), 5.52 (d, 1H, J = 5.6 Hz), 4.24 (s, 1H), 3.66 (s, 3H), 2.07 (m, 1H), 1.59-1.84 (m, 5H), 1.03-1.32 (m, 5H); ^{13}C-NMR (100 MHz) δ 203.7 (C), 174.9 (C), 140.1 (C), 134.5 (C), 128.3 (CH), 128.2 (CH), 128.1 (CH), 127.5 (CH), 126.9 (CH), 110.1 (C), 102.5 (CH), 81.9 (C), 53.5 (CH_3), 38.1 (CH), 33.0 (CH_2), 32.9 (CH_2), 26.3 (CH_2). HRMS (ESI) *m/z* calcd for $C_{24}H_{25}O_2$, 345.1882, found 345.1847 $[M\text{-}OH]^+$.



327

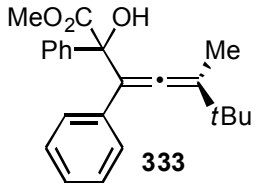
Methyl 2-hydroxy-6,6-dimethyl-2,3-diphenylhepta-3,4-dienoate (327). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave compound **327** in 91% yield (153 mg) as colorless oil. IR (neat) 3491, 2958, 2866, 1725, 1252, 1064, 743, 695 cm^{-1}; ^1H NMR (400 MHz) δ 7.66 (dd, 2H, J = 9.2 Hz, 1.2 Hz), 7.39 (d, 2H, J = 7.6 Hz), 7.09-7.32 (m, 6H), 5.51 (s, 1H), 4.18 (s, 1H), 3.70 (s, 3H), 1.05 (s, 9H); ^{13}C-NMR (100 MHz) δ 202.1 (C), 174.9 (C), 140.2 (C), 134.6 (C), 128.3 (CH), 128.1 (CH),

128.0 (CH), 127.4 (CH), 126.9 (CH), 110.8 (C), 108.3 (CH), 81.7 (C), 53.6 (CH_3), 33.4 (C), 30.1 (CH_3). HRMS (ESI) *m/z* calcd for $C_{22}H_{25}O_3$, 337.1759, found 337.1801 $[M+H]^+$.



328

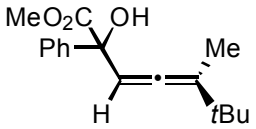
Methyl 2-hydroxy-3-isobutyl-6,6-dimethyl-2-phenylhepta-3,4-dienoate (328). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **328** in 84% yield (133 mg) as colorless oil. IR (neat) 3500, 2953, 2900, 2868, 1726, 1249, 1060, 751, 699 cm^{-1}; ^1H NMR (600 MHz) δ 7.63 (M, 2H), 7.26-7.35 (m, 3H), 5.25 (t, 2H, *J* = 3.6 Hz), 3.81 (s, 1H), 3.72 (s, 3H), 1.78 (m, 2H), 1.74 (m, 1H), 0.99 (m, 9H), 0.87 (app t, 6H, *J* = 6.6 Hz); ^{13}C-NMR (100 MHz) δ 198.4 (C), 174.8 (C), 139.5 (C), 127.9 (CH), 127.5 (CH), 108.7 (C), 107.6 (CH), 81.9 (C), 53.3 (CH_3), 37.1 (CH_2), 32.8 (C), 30.2 (CH_3), 26.8 (CH), 23.2 (CH_3), 22.8 (CH_3). HRMS (ESI) *m/z* calcd for $C_{20}H_{27}O_3$, 315.2038, found 315.1956 $[M-H]^+$.



333

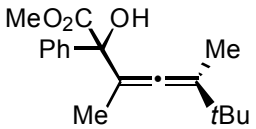
(4*S*)-Methyl 2-hydroxy-5,6,6-trimethyl-2,3-diphenylhepta-3,4-dienoate (333). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave

compound **333** in 71% yield (124 mg) as colorless oil. IR (neat) 3497, 2963, 1725, 1249, 1066, 731, 695 cm^{-1}; ^1H NMR (400 MHz) δ 7.66 (d, 2H, *J* = 6.6 Hz), 7.37 (d, 2H, *J* = 6.6 Hz), 7.29 (t, 2H, *J* = 6.6 Hz), 7.25 (t, 1H, *J* = 7.8 Hz), 7.19 (t, 2H, *J* = 7.2 Hz), 7.11 (t, 1H, *J* = 7.2 Hz), 4.06 (br s, 1H), 3.69 (s, 3H), 1.70 (s, 3H), 0.97 (s, 9H); ^{13}C-NMR (125 MHz) δ 202.2 (C), 175.3 (C), 140.7 (C), 135.6 (C), 128.3 (CH), 127.9 (CH), 127.8 (CH), 127.2 (CH), 126.6 (CH), 114.4 (C), 108.9 (C), 81.8 (C), 53.6 (CH_3), 34.7 (C), 28.9 (CH_3), 14.5 (CH_3). HRMS (ESI) *m/z* calcd for $C_{23}H_{25}O_2$, 333.1882, found 333.1847 $[M\text{-}OH]^+$.



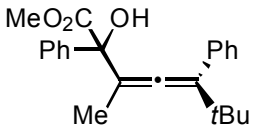
334

(4*S*)-Methyl 2-hydroxy-5,6,6-trimethyl-2-phenylhepta-3,4-dienoate (334). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave compound **334** in 66% yield (90 mg) as light yellow oil. IR (neat) 3500, 3307, 2963, 2909, 2874, 1729, 1370, 1251, 1101, 920, 698 cm^{-1}; ^1H NMR (400 MHz) δ 7.60 (m, 2H), 7.25-7.37 (m, 3H), 5.58 (q, 1H, *J* = 2.8 Hz), 3.74 (s, 3H), 3.72 (s, 1H), 1.70 (d, 3H, *J* = 2.8 Hz), 1.01 (s, 9H); ^{13}C-NMR (100 MHz) δ 199.4 (C), 174.7 (C), 128.2 (CH), 128.1 (CH), 126.8 (CH), 114.5 (C), 95.8 (CH), 78.2 (C), 53.4 (CH_3), 33.9 (C), 29.1 (CH_3), 15.0 (CH_3). HRMS (ESI) *m/z* calcd for $C_{17}H_{23}O_3$, 275.1602, found 275.1641$[M+H]^+$.



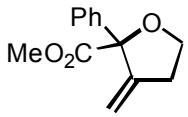
335

(4*S*)-Methyl 2-hydroxy-3,5,6,6-tetramethyl-2-phenylhepta-3,4-dienoate (335). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **335** in 61% yield (92 mg) as colorless oil. IR (neat) 3507, 2961, 2867, 1725, 1248, 730, 699 cm^{-1}; ^1H NMR (400 MHz) δ 7.61 (m, 2H), 7.26-7.34 (m, 3H), 3.81 (s, 1H), 3.73 (s, 3H), 1.66 (s, 3H), 1.63 (s, 3H), 0.93 (s, 3H); ^{13}C-NMR (100 MHz) δ 199.0 (C), 175.1 (C), 139.8 (C), 127.8 (CH), 127.3 (CH), 111.3 (C), 102.1 (C), 81.8 (C), 53.4 (CH_3), 34.1 (CH), 29.0 (CH_3), 15.4 (CH_3), 14.9 (CH_3). HRMS (ESI) *m/z* calcd for $C_{18}H_{25}O_3$, 289.1759, found 289.1801 $[M+H]^+$.



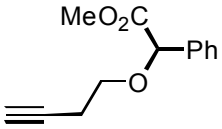
336

(4*R*)-Methyl 2-hydroxy-3,6,6-trimethyl-2,5-diphenylhepta-3,4-dienoate (336). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave compound **336** in 69% yield (121 mg) as white crystals. MP IR (neat) 3507, 2949, 2864, 1723, 1257, 752, 699 cm^{-1}; ^1H NMR (400 MHz) δ 7.47 (m, 2H), 7.24-7.31 (m, 6H), 7.12 (m, 2H), 3.87 (s, 1H), 3.74 (s, 3H), 1.70 (s, 3H), 1.10 (s, 9H); ^{13}C-NMR (100 MHz) δ 200.1 (C), 174.8 (C), 139.6 (C), 137.8 (C), 129.3 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.4 (CH), 126.8 (CH), 118.0 (C), 103.2 (C), 81.5 (C), 53.4 (CH_3), 35.2 (C), 30.1 (CH_3), 15.6 (CH_3). HRMS (ESI) *m/z* calcd for $C_{23}H_{27}O_3$, 351.1915, found 351.1956 $[M+H]^+$.



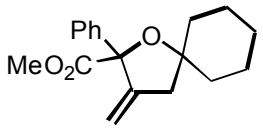
339

Methyl 3-methylene-2-phenyltetrahydrofuran-2-carboxylate (339). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave compound **339** in 48% yield (52 mg) as colorless oil. IR (neat) 3024, 2949, 1716, 1202, 692 cm^{-1}; ^1H NMR (600 MHz) δ 7.55 (d, 2H, *J* = 7.8 Hz), 7.35 (t, 2H, *J* = 7.8 Hz), 7.30 (t, 1H, *J* = 7.2 Hz), 5.48 (app t, 1H, *J* = 2.4 Hz), 5.38 (app t, 1H, *J* = 2.4 Hz), 4.10 (q, 1H, *J* = 7.2 Hz), 4.02 (m, 1H), 3.75 (s, 3H), 2.69 (m, 2H); ^{13}C-NMR (125 MHz) δ 172.1 (C), 148.2 (C), 139.6 (C), 128.5 (CH), 128.3 (CH), 126.5 (CH), 110.9 (CH_2), 87.9 (C), 67.1 (CH_2), 53.1 (CH_3), 33.4 (CH_2). HRMS (ESI) *m/z* calcd for $C_{13}H_{15}O_3$, 219.0976, found 219.1015 $[M+H]^+$.



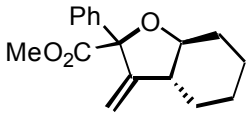
338

Methyl 2-(but-3-yn-1-yloxy)-2-phenylacetate (338). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave compound **338** in 43% yield (98 mg) as colorless oil. IR (neat) 3292, 2953, 1748, 1208, 1116, 729, 697 cm^{-1}; ^1H NMR (400 MHz) δ 7.45 (dd, 2H, *J* = 8.0, 1.6 Hz), 7.32-7.37 (m, 3H), 4.95 (s, 1H), 3.69 (s, 3H), 3.64 (dt, 1H, *J* = 10.0, 6.8 Hz), 3.56 (dt, 1H, *J* = 10.0, 6.8 Hz), 2.54 (m, 2H), 1.97 (t, 1H, *J* = 2.8 Hz); ^{13}C-NMR (100 MHz) δ 171.2 (C), 136.4 (C), 129.0 (CH), 128.9 (CH), 127.4 (CH), 81.2 (CH), 80.9 (C), 69.9 (CH), 67.9 (CH_2), 52.5 (CH_3), 20.0 (CH_2). HRMS (ESI) *m/z* calcd for $C_{13}H_{15}O_3$, 219.0976, found 219.1014 $[M+H]^+$.



342

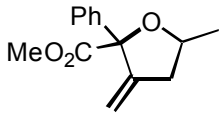
Methyl 3-methylene-2-phenyl-1-oxaspiro[4.5]decane-2-carboxylate (342). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave compound **342** in 75% yield (107 mg) as colorless oil. IR (neat) 2931, 2856, 1731, 1447, 1243, 1064, 699 cm^{-1}; ^1H NMR (400 MHz) δ 7.27-7.39 (m, 5H), 5.63 (t, 1H, J = 1.6 Hz), 3.77 (s, 3H), 2.30 (m, 1H), 1.83 (m, 1H), 1.45 (s, 3H), 1.40 (s, 3H), 1.27-1.49 (m, 4H); ^{13}C-NMR (100 MHz) δ 173.0 (C), 149.2 (C), 141.3 (C), 128.2 (CH), 127.9 (CH), 125.8 (CH), 111.1 (CH_2), 87.3 (C), 83.8 (C), 52.9 (CH_3), 43.6 (CH_2), 38.4 (CH_2), 36.9 (CH_2), 25.6 (CH_2), 24.1 (CH_2), 23.8 (CH_2). HRMS (ESI) *m/z* calcd for $C_{18}H_{25}O_3$, 289.1759, found 289.1797 $[M+H]^+$.



343

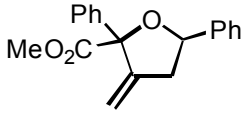
(3a*R*,7a*S*)-Methyl 3-methylene-2-phenyloctahydrobenzofuran-2-carboxylate (343). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave compound **343** in 87% yield (119 mg) as colorless oil. IR (neat) 2935, 2859, 1736, 1254, 1072, 906, 729, 698 cm^{-1}; ^1H NMR (400 MHz) δ 7.50 (m, 2H), 7.25-7.33 (m, 3H), 5.23 (d, 1H, J = 2.8 Hz), 5.16 (d, 1h, J = 2.8 Hz), 3.70 (s, 3H), 3.20 (td, 1H, J = 11.2, 3.6 Hz), 2.10-2.22 (m, 2H), 2.01 (m, 1H), 1.72-1.91 (m, 2H), 1.55 (m, 1H), 1.07-1.30 (m, 3H); ^{13}C-NMR (100 MHz) δ 171.9 (C), 151.3 (C), 140.2 (C), 128.5 (CH), 128.1 (CH), 126.5

(CH), 108.9 (CH_2), 88.6 (C), 81.9 (CH), 53.1 (CH_3), 49.8 (CH), 31.5 (CH_2), 26.6 (CH_2), 25.2 (CH_2), 24.4 (CH_2). HRMS (ESI) *m/z* calcd for $C_{17}H_{221}O_3$, 273.1446, found 273.1483 $[M+H]^+$.[17]



344

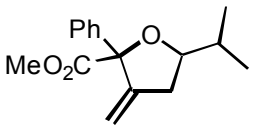
Methyl 5-methyl-3-methylene-2-phenyltetrahydrofuran-2-carboxylate (344). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave compound **344** in 60% yield (70 mg) as colorless oil. IR (neat) 2973, 1734, 1433, 1230, 1096, 1055, 731, 692 cm^{-1}; ^1H NMR (400 MHz) δ 7.55-7.58 (m, 2H), 7.29-7.37 (m, 3H), 5.48 (t, 1H, *J* = 2.4 Hz), 5.32 (t, 1H, *J* = 2.4 Hz), 4.13 (m. 1H), 3.74 (s, 3H), 2.70-2.77 (m, 1H), 2.34-2.41 (m, 1H), 1.37 (d, 3H, *J* = 6.4 Hz); ^{13}C-NMR (100 MHz) δ 171.8 (C), 148.4 (C), 139.8 (C), 128.4 (CH), 128.3 (CH), 126.5 (CH), 110.6 (CH_2), 88.1 (C), 73.7 (C), 53.1 (CH_3), 40.3 (CH_2), 20.9 (CH_3). HRMS (ESI) *m/z* calcd for $C_{14}H_{17}O_3$, 233.1133, found 233.1171 $[M+H]^+$.



345

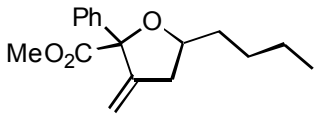
Methyl 3-methylene-2,5-diphenyltetrahydrofuran-2-carboxylate (345). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave compound **315** in 56% yield (83 mg) as colorless oil. IR (neat) 3030, 2951, 1735, 1264, 1069, 734, 697 cm^{-1}; ^1H NMR (400 MHz) δ 7.62-7.65 (m, 2H), 7.47 (d, 2H, *J* = 6.8 Hz), 7.27-7.40

(m, 5H), 5.51 (t, 1H, J = 2.4 Hz), 5.36 (t, 1H, J = 2.4 Hz), 4.98 (dd, 1H, J = 9.2, 7.2 Hz), 3.79 (s, 3H), 3.04-3.07 (m, 1H), 2.69-2.77 (m, 1H); ^{13}C-NMR (100 MHz) δ 172.6 (C), 147.9 (C), 141.5 (C), 139.5 (C), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.1 (CH), 126.7 (CH), 126.5 (CH), 110.7 (CH_2), 88.6 (C), 79.1 (CH), 53.1 (CH_3), 41.7 (CH_2). HRMS (ESI) *m/z* calcd for $C_{19}H_{19}O_3$, 295.1289, found 295.1327 $[M+H]^+$.



346

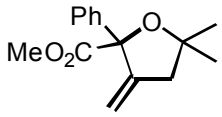
Methyl 5-isopropyl-3-methylene-2-phenyltetrahydrofuran-2-carboxylate (346). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave compound **346** in 65% yield (65 mg) as colorless oil. IR (neat) 2956, 2873, 1734, 1250, 1070, 699 cm^{-1}; ^{1}H NMR (600 MHz) δ 7.56 (m, 2H), 7.229-7.36 (m, 3H), 5.40 (t, 1H, J = 2.4 Hz), 5.29 (t, 1H, J = 2.4 Hz), 3.74 (s, 3H), 3.70 (m, 1H), 2.60 (m, 1H), 2.46-2.51 (m, 1H), 1.92 (m, 1H), 1.04 (d, 3H, J = 6.6), 0.91 (d, 3H, J = 6.6 Hz); ^{13}C-NMR (100 MHz) δ 171.8 (C), 148.8 (C), 139.9 (C), 128.4 (CH), 128.1 (CH), 126.5 (CH), 110.3 (CH_2), 88.0 (C), 82.8 (C), 52.9 (CH_3), 35.8 (CH), 32.5 (CH_2), 19.3 (CH_3), 17.9 (CH_3). HRMS (ESI) *m/z* calcd for $C_{16}H_{20}O_3Na$, 283.1412, found 283.1306 $[M+Na]^+$.



347

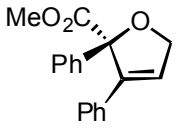
Methyl 5-butyl-3-methylene-2-phenyltetrahydrofuran-2-carboxylate (347). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave

compound **347** in 87% yield (125 mg) as colorless oil. IR (neat) 2953, 2931, 2861, 1735, 1243, 1068, 698 cm^{-1}; ^1H NMR (400 MHz) δ 7.52-7.55 (m, 2H), 7.22-7.31 (m, 3H), 5.43 (t, 1H, *J* = 2.0 Hz), 5.28 (t, 1H, *J* = 2.0 Hz), 3.95 (quintet, 1H, *J* = 6.8 Hz), 3.69 (s, 3H), 2.68 (m, 1H), 2.38 (m, 1H), 1.81 (m, 1H), 1.56 (m, 1H), 1.27-1.49 (m, 4H), 0.89 (t, 3H, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz) δ 171.9 (C), 148.5 (C), 139.9 (C), 128.4 (CH), 128.1 (CH), 126.5 (CH), 110.5 (CH_2), 87.9 (C), 77.8 (CH), 52.9 (CH_3), 38..6 (CH_2), 35.1 (CH_2), 28.1 (CH_2), 22.9 (CH_3), 14.3 (CH_3). HRMS (ESI) *m/z* calcd for $C_{18}H_{25}O_3$, 289.1759, found 289.1797 $[M+H]^+$.



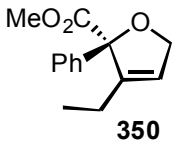
348

Methyl 5,5-dimethyl-3-methylene-2-phenyltetrahydrofuran-2-carboxylate (348). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave compound **348** in 62% yield (76 mg) as colorless oil. IR (neat) 2973, 1732, 1244, 1222, 1065, 699 cm^{-1}; ^1H NMR (600 MHz) δ 7.59 (d, 2H, *J* = 7.8 Hz), 7.27-7.35 (m, 3H), 5.45 (d, 1H, *J* = 1.8 Hz), 5.28 (d, 1H, *J* = 1.8 Hz), 3.74 (s, 3H), 2.51 (s, 2H), 1.41 (s, 3H), 1.36 (s, 3H); ^{13}C-NMR (100 MHz) δ 172.9 (C), 149.3 (C), 141.1 (C), 128.3 (CH), 127.9 (CH), 125.8 (CH), 111.1 (CH_2), 81.7 (C), 70.8 (C), 52.9 (CH_3), 46.1 (CH_2), 28.8 (CH_3), 27.9 (CH_3). HRMS (ESI) *m/z* calcd for $C_{15}H_{18}O_3Na$, 269.1256, found 269.1149 $[M+Na]^+$.



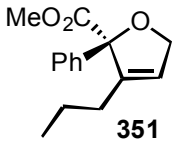
349

(*R*)-Methyl 2,3-diphenyl-2,5-dihydrofuran-2-carboxylate (349). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **310** in 85% yield (119 mg) as colorless oil. ^{1}H NMR (400 MHz) δ 7.17-7.37 (m, 10H), 6.46 (t, 1H, J = 2.0 Hz), 4.97 (dd, 1H, J = 14.0, 1.6 Hz), 4.92 (dd, 1H, J = 14.0, 1.6 Hz), 3.74 (s, 3H); ^{13}C-NMR (100 MHz) δ 172.1 (C), 141.2 (C), 139.4 (C), 129.7 (C), 128.4 (CH), 128.3 (CH), 127.9 (CH), 127.8 (CH), 127.4 (CH), 126.9 (CH), 94.8 (C), 74.8 (CH_2), 52.6 (CH_3), 35.6 (C), 9.9 (CH_3). HPLC: ODH, 0.5% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 3.9 min (major), 4.2 min (minor), 88% ee with (*S*)-xylylBINAP($AuCl)_2$.



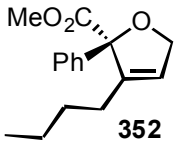
350

(*S*)-Methyl 3-ethyl-2-phenyl-2,5-dihydrofuran-2-carboxylate (350). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **302** in 74% yield (86 mg) as colorless oil. ^{1}H NMR (600 MHz) δ 7.28-7.39 (m, 5H), 5.76 (t, 1H, J = 2.4 Hz), 4.83 (m, 2H), 3.79 (s, 3H), 2.35 (m, 1H), 1.92 (m, 1H), 1.08 (t, 3H, J = 7.8 Hz); ^{13}C-NMR (125 MHz) δ 172.3 (C), 144.6 (C), 139.9 (C), 128.5 (CH), 128.3 (CH), 126.3 (CH), 121.9 (CH), 95.3 (C), 75.2 (CH_2), 52.6 (CH_3), 20.3 (CH_2), 12.2 (CH_3). HPLC: ODH, 0.5% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 3.9 min (major), 4.2 min (minor), 88% ee with (*S*)-xylylBINAP($AuCl)_2$.



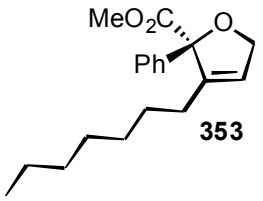
351

(*S*)-Methyl 2-phenyl-3-propyl-2,5-dihydrofuran-2-carboxylate (351). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **304** in 69% yield (85 mg) as colorless oil. ^{1}H NMR (400 MHz) δ 7.29-7.39 (m, 5H), 5.77(m, 1H), 4.83 (m, 2H), 3.81 (s, 3H), 2.25 (m, 1H), 1.88 (m, 1H), 1.48 (m, 2H), 0.89 (t, 3H, *J* = 7.6 Hz); ^{13}C-NMR (100 MHz) δ 172.3 (C), 142.9 (C), 139.9 (C), 128.5 (CH), 128.3 (CH), 126.3 (CH), 122.3 (C), 95.3 (C), 75.3 (CH_2), 52.6 (CH_3), 29.1 (CH_2), 21.2 (CH_2), 14.2 (CH_3). HPLC: ODH, 0.5% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 3.9 min (major), 4.2 min (minor), 88% ee with (*S*)-xylylBINAP($AuCl)_2$.



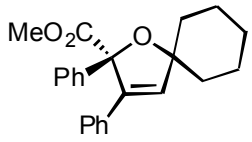
352

(*S*)-Methyl 3-butyl-2-phenyl-2,5-dihydrofuran-2-carboxylate (352). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **306** in 75% yield (85 mg) as colorless oil. ^{1}H NMR (400 MHz) δ 7.26-7.38 (m, 5H), 5.77 (t, 1H, *J* = 2.0 Hz), 4.83 (m, 2H), 3.81 (s, 3H), 2.26 (m, 1H), 1.90 (m, 1H), 1.44 (m, 2H), 1.32 (quintet, 2H, *J* = 7.6 Hz), 0.86 (t, 3H, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz) δ 172.3 (C), 142.9 (C), 139.9 (C), 128.5 (CH), 128.3 (CH), 126.4 (CH), 122.2 (C), 95.3 (C), 75.3 (CH_2), 52.6 (CH_3), 30.1 (CH_2), 26.7 (CH_2), 22.7 (CH_2), 14.2 (CH_3). HPLC: ODH, 0.5% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 3.9 min (major), 4.2 min (minor), 88% ee with (*S*)-xylylBINAP($AuCl)_2$.



353

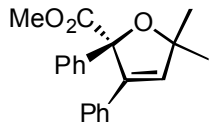
(*S*)-Methyl 3-heptyl-2-phenyl-2,5-dihydrofuran-2-carboxylate (353). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **308** in 80% yield (97 mg) as colorless oil. ^{1}H NMR (400 MHz) δ 7.26-7.37 (m, 5H), 5.77 (t, 1H, J = 2.0 Hz), 4.83 (m, 2H), 3.81 (s, 3H), 2.28 (m, 1H), 1.88 (m, 1H), 1.20-1.53 (m, 10H), 0.86 (t, 3H, J = 6.8 Hz); ^{13}C-NMR (100 MHz) δ 172.3 (C), 143.1 (C), 139.9 (C), 128.5 (CH), 128.3 (CH), 126.3 (CH), 122.2 (C), 95.3 (C), 75.3 (CH_2), 52.6 (CH_3), 31.9 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 27.9 (CH_2), 27.0 (CH_2), 22.8 (CH_2), 14.3 (CH_3). HPLC: ODH, 0.5% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 3.9 min (major), 4.2 min (minor), 88% ee with (*S*)-xylylBINAP(AuCl)$_2$.



357

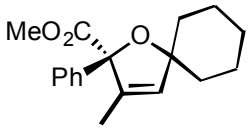
(*R*)-Methyl 2,3-diphenyl-1-oxaspiro[4.5]dec-3-ene-2-carboxylate (357). Purification by silica gel chromatography (using 20:1 hexane/Et_2O solvent system) gave compound **314** in 93% yield (162 mg) as colorless oil. ^{1}H NMR (600 MHz) δ 7.35 (dd, 2H, J = 6.0 Hz, 2.4 Hz), 7.28-7.30 (m, 3H), 7.16-7.20 (m, 5H), 6.43 (s, 1H), 3.77 (s, 3H), 1.82 (m, 7H), 1.53 (m, 5H); ^{13}C-NMR (100 MHz) δ 173.2 (C), 140.4 (C), 133.8 (C), 133.5 (C),

128.4 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 127.9 (CH), 127.4 (CH), 94.1 (C), 90.2 (C), 52.7 (CH_3), 38.0 (CH_2), 37.4 (CH_2), 25.6 (CH_2), 23.7 (CH_2), 23.6 (CH_2). HPLC: ODH, 0.5% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 3.9 min (major), 4.2 min (minor), 88% ee with (*S*)-xylylBINAP($AuCl)_2$.



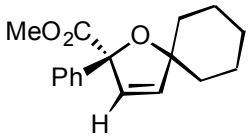
358

(*R*)-Methyl 5,5-dimethyl-2,3-diphenyl-2,5-dihydrofuran-2-carboxylate (358). Purification by silica gel chromatography (using 20:1 hexane/Et_2O solvent system) gave compound **310** in 90% yield (139 mg) as colorless oil. ^{1}H NMR (400 MHz) δ 7.29-7.35 (m, 5H), 7.19-7.21 (m, 5H), 6.30 (s, 1H), 3.77 (s, 3H), 1.52 (s, 3H), 1.49 (s, 3H); ^{13}C-NMR (100 MHz) δ 172.9 (C), 140.3 (C), 139.6 (C), 135.4 (CH), 133.1 (C), 128.4 (CH), 128.3 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.4 (CH), 94.7 (C), 88.2 (C), 52.8 (CH_3), 28.7 (CH_3), 27.9 (CH_3). HPLC: ODH, 0.5% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 3.9 min (major), 4.2 min (minor), 88% ee with (*S*)-xylylBINAP($AuCl)_2$.



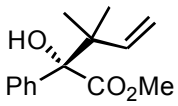
359

(*S*)-Methyl 3-methyl-2-phenyl-1-oxaspiro[4.5]dec-3-ene-2-carboxylate (359). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave compound **316** in 96% yield (123 mg) as colorless oil. ^{1}H NMR (400 MHz) δ 7.64 (dd, 2H, *J* = 8.8 Hz, 1.6 Hz), 7.26-7.37 (m, 3H), 5.74 (d, 1H, *J* = 1.6 Hz), 3.76 (s, 3H), 1.77 (d, 3H, *J* = 1.2 Hz), 1.40-2.05 (m, 10 H); ^{13}C-NMR (100 MHz) δ 173.3 (C), 139.9 (C), 135.9 (C), 132.8 (CH) 128.4 (CH), 128.0 (C), 126.1 (CH), 94.0 (C), 93.4 (C), 52.4 (CH_3), 41.2 (CH_2), 43.3 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 23.0 (CH_2), 22.9 (CH_2), 13.5 (CH_3). HPLC: ODH, 0.5% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 3.9 min (major), 4.2 min (minor), 88% ee with (*S*)-xylylBINAP($AuCl)_2$.



360

(*S*)-Methyl 2-phenyl-1-oxaspiro[4.5]dec-3-ene-2-carboxylate (360). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **312** in 88% yield (120 mg) as colorless oil. ^{1}H NMR (400 MHz) δ 7.52 (d, 2H, *J* = 7.2 Hz), 7.34 (t, 2H, *J* = 7.8 Hz), 7.28 (t, 1H, *J* = 7.8 Hz), 6.15 (d, 1H, *J* = 6.6 Hz), 6.09 (d, 1H, *J* = 6.0 Hz), 3.72 (s, 3H), 1.44-1.86 (m, 10H); ^{13}C-NMR (100 MHz) δ 173.3 (C), 141.6 (C), 135.2 (C), 128.6 (CH), 128.1 (C), 127.9 (CH), 125.5 (CH), 92.6 (C), 92.8 (C), 52.7 (CH_3), 37.8 (CH_2), 37.8 (CH_2), 25.5 (CH_2), 23.6 (CH_2), 23.5 (CH_2). HPLC: ODH, 0.5% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 3.9 min (major), 4.2 min (minor), 88% ee with (*S*)-xylylBINAP($AuCl)_2$.



369

(*S*)-Methyl 2-hydroxy-3,3-dimethyl-2-phenylpent-4-enoate (369). Purification by silica gel chromatography (using 10:1 hexane/Et_2O solvent system) gave compound **369** in 62% yield (76 mg) as colorless oil. IR (neat) 3502, 2953, 1718, 1228, 1161, 1066, 741, 701 cm^{-1}; ^1H NMR (600 MHz) δ 7.69 (d, 2H, J = 7.2 Hz), 7.28-7.33 (m, 3H), 6.06 (dd, 1H, J = 17.4, 10.2 Hz), 5.03 (d, 1H, J = 10.2 Hz), 4.97 (d, 1H, J = 17.4 Hz), 3.84 (s, 3H), 3.70 (s, 1H), 1.09 (s, 3H), 1.07 (s, 3H); ^{13}C-NMR (100 MHz) δ 174.7 (C), 144.2 (C), 138.7 (C), 128.7 (C), 127.9 (CH), 127.7 (CH), 127.4 (CH), 113.6 (CH_2), 82.9 (C), 53.1 (CH_3), 45.1 (C), 23.1 (CH_3), 22.7 (CH_3). HRMS (ESI) *m/z* calcd for $C_{14}H_{19}O_3$, 235.1289, found 235.1327 $[M+H]^+$.

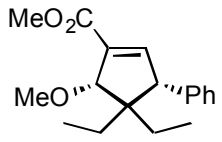
Experimental section for Chapter VI: Gold-Catalyzed Vinylogous [3+2] Cycloaddition of Vinyl Carbenoids and Enol Ethers

I. General procedure for Au-Catalyzed reaction of enol ethers and styryldiazoacetates

A mixture of $AgSbF_6$ (0.015 mmol) and (*R*)-DTBMSegphos$(AuCl)_2$ (0.015) was weighed in a 25-ml one-necked round bottom flask covered with aluminum foil to exclude light.

The mixture was dissolved with 2 mL degassed dichloromethane and stirred at room temperature under an atmosphere of argon for *ca* 20 mins. DCM was degassed either by freeze-pump-thaw method or atmosphere exchange under sonication to exclude oxygen in the reaction mixture. The enol ether (0.5 mmol), which was synthesized *via* Wittig reaction[19], was added via syringe, followed by dropwise addition of phenyl vinyldiazoacetate (0.6 mmol) in 8 mL degassed dichloromethane *via* syringe pump over 1 h. After addition, the mixture was stirred for additional 12 hour then concentrated *in vacuo*. The residue was purified on silica using 20:1 pentane/ether as solvent system to afford the cyclopentene product.

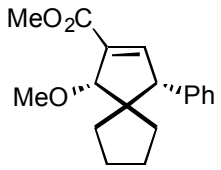
II. Spectral data and characterization of cyclopentene derivatives



377

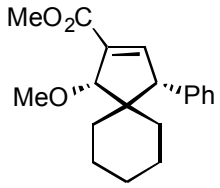
(3*R*,5*S*)-Methyl 4,4-diethyl-5-methoxy-3-phenylcyclopent-1-enecarboxylate (377). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **377** in 73% yield (105 mg) as colorless oil. IR (neat) 2966, 2827, 1716, 1264, 908, 730, 700 cm^{-1}; ^1H NMR (600 MHz) δ 7.19-7.26 (m, 5H), 6.83 (dd, 1H, *J* = 3.6, 1.8 Hz), 4.03 (d, 1H, *J* = 1.8 Hz), 3.79 (s, 3H), 3.53 (s, 3H), 3.49 (d, 1H, *J* = 3.6 Hz), 1.51 (sextet, 1H, *J* = 7.2 Hz), 1.42 (sextet, 1H, *J* = 7.8 Hz), 1.18 (sextet, 1H, *J* = 7.8 Hz), 1.06 (sextet, 1H, *J* = 7.2 Hz), 0.94 (t, 3H, *J* = 7.2 Hz), 0.66 (t, 3H, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz) δ 166.1 (C), 149.4 (CH), 139.3 (C), 136.8 (C), 130.3 (CH), 128.1 (CH), 126.9

(CH), 113.6 (CH_2), 89.7 (CH), 60.2 (CH), 60.1 (CH_3), 53.4 (CH_3), 51.8 (C), 30.3 (CH_2), 21.5 (CH_2), 9.3 (CH_3), 8.6 (CH_3). HRMS (ESI) *m/z* calcd for $C_{18}H_{25}O_3$, 289.1759, found 289.1799 $[M+H]^+$. HPLC: AD-H, 0.3% iPrOH/hexane, 1.0 mlmin^{-1}, UV 230 nm, t_R: 5.0 min (minor), 6.0 min (major), 92% ee with (*R*)-DTBMSegphos$(AuCl)_2$; $[\alpha]^{23}_D$ 254.3 (*c* 1.0, $CHCl_3$).



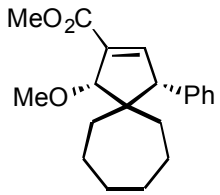
378

(1*S*,4*R*)-Methyl 1-methoxy-4-phenylspiro[4.4]non-2-ene-2-carboxylate (378). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **378** in 68% yield (97 mg) as colorless oil. IR (neat) 2949, 2826, 1718, 1247, 1099, 764, 701 cm^{-1}; ^{1}H NMR (600 MHz) δ 7.20-7.27 (m, 5H), 6.90 (d, 1H, *J* = 3.0 Hz), 4.02 (s, 1H), 3.80 (s, 3H), 3.54 (s, 3H), 3.49 (d, 1H, *J* = 3.0 Hz), 1.48-1.77 (m, 7H), 1.04 (m, 1H); ^{13}C-NMR (100 MHz) δ 165.9 (C), 149.3 (CH), 140.4 (C), 136.9 (C), 129.8 (CH), 128.3 (CH), 126.9 (CH), 90.8 (CH), 60.1 (CH), 60.4 (CH_3), 58.7 (C), 51.8 (CH_3), 42.3 (C), 29.5 (CH_2), 24.1 (CH_2), 24.0 (CH_2). HRMS (ESI) *m/z* calcd for $C_{18}H_{23}O_3$, 287.1602, found 287.1646 $[M+H]^+$. HPLC: ODR, 1% iPrOH/hexane, 1.0 mlmin^{-1}, UV 230 nm, t_R: 4.3 min (minor), 5.0 min (major), 90% ee with (*R*)-DTBMSegphos$(AuCl)_2$; $[\alpha]^{23}_D$ 38.9 (*c* 1.0, $CHCl_3$).



379

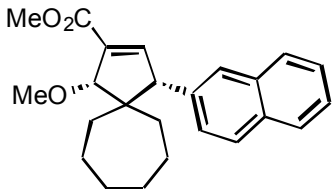
(1*S*,4*R*)-Methyl 1-methoxy-4-phenylspiro[4.5]dec-2-ene-2-carboxylate (379). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **379** in 71% yield (107 mg) as colorless oil. IR (neat) 2926, 2851, 1716, 1093, 751, 700 cm^{-1}; ^1H NMR (600 MHz) δ 7.20-7.28 (m, 5H), 6.83 (d, 1H, J = 3.0 Hz), 4.13 (s, 1H), 3.79 (s, 3H), 3.58 (s, 3H), 3.48 (d, 1H, J = 3.0 Hz), 1.61 (m, 2H), 1.09-1.50 (m, 10H); ^{13}C-NMR (100 MHz) δ 166.2 (C), 149.2 (CH), 139.0 (C), 136.4 (C), 130.4 (CH), 128.1 (CH), 126.9 (CH), 89.9 (CH), 60.1 (CH), 60.5 (CH_3), 51.8 (CH_3), 49.2 (C), 39.3 (CH_2), 29.5 (CH_2), 26.2 (CH_2), 23.8 (CH_2), 23.0 (CH_2). HRMS (ESI) *m/z* calcd for $C_{19}H_{25}O_3$, 301.1759, found 301.1798 $[M+H]^+$. HPLC: AD-H, 1% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 230 nm, t_R: 4.9 min (minor), 5.6 min (major), 90% ee with (*R*)-DTBMSegphos$(AuCl)_2$; $[\alpha]^{23}_D$ 492.0 (*c* 1.0, $CHCl_3$).



380

(1*S*,4*R*)-Methyl 1-methoxy-4-phenylspiro[4.6]undec-2-ene-2-carboxylate (380). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **380** in 81% yield (107 mg) as colorless oil. IR (neat) 2920, 2852, 1716, 1256,

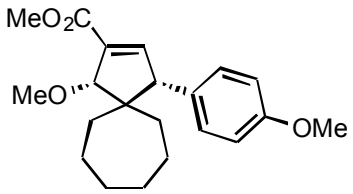
1091, 907, 730, 700 cm^{-1}; ^{1}H NMR (600 MHz) δ 7.18-7.28 (m, 5H), 6.83 (d, 1H, *J* = 3.0 Hz), 3.98 (s, 1H), 3.80 (s, 3H), 3.52 (s, 3H), 3.48 (d, 1H, *J* = 3.0 Hz), 1.22-1.68 (m, 11H), 1.00 (dd, 1H, *J* = 14.4, 9.0 Hz); ^{13}C-NMR (100 MHz) δ 165.9 (C), 148.6 (CH), 139.6 (C), 136.9 (C), 130.3 (CH), 128.2 (CH), 126.9 (CH), 91.7 (CH), 63.4 (CH), 60.4 (CH_3), 53.1 (C), 51.8 (CH_3), 42.7 (C), 31.4 (CH_2), 30.6 (CH_2), 24.1 (CH_2), 23.9 (CH_2). HRMS (ESI) *m/z* calcd for $C_{20}H_{26}O_3K$, 353.1882, found 353.1515 $[M+K]^+$. HPLC: SS-WHELK, 0.3% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 230 nm, t_R: 6.1 min (minor), 6.9 min (major), 88% ee with (*R*)-DTBMSegphos$(AuCl)_2$; $[\alpha]^{23}_D$ 48.6 (*c* 1.0, $CHCl_3$).



381

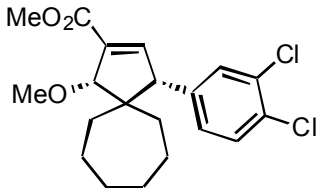
(1*S*,4*R*)-Methyl 1-methoxy-4-(naphthalen-2-yl)spiro[4.6]undec-2-ene-2-carboxylate (381). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **381** in 77% yield (140 mg) as colorless oil. IR (neat) 2920, 2851, 1716, 1259, 1090, 907, 730 cm^{-1}; ^{1}H NMR (600 MHz) δ 7.80 (t, 2H, *J* = 5.4 Hz), 7.41 (d, 1H, *J* = 8.4 Hz), 7.62 (br s, 1H), 7.41-7.46 (m, 2H), 7.39 (dd, 1H, *J* = 9.0, 1.8 Hz), 6.88 (d, 1H, *J* = 3.6 Hz), 4.03 (s, 1H), 3.82 (s, 3H), 3.66 (d, 1H, *J* = 3.0 Hz), 3.55 (s, 3H), 1.20-1.68 (m, 11H), 1.04 (dd, 1H, *J* = 15.0, 9.6 Hz); ^{13}C-NMR (100 MHz) δ 165.9 (C), 148.5 (CH), 137.3 (C), 133.1 (C), 133.5 (C), 132.7 (C), 128.9 (CH), 128.6 (CH), 128.0 (CH), 127.9 (CH), 127.6 (CH), 126.1 (CH), 125.6 (CH), 91.8 (CH), 60.1 (CH), 60.5 (CH_3), 53.3 (CH), 51.9 (CH_3), 42.8 (C), 31.4 (CH_2), 30.7 (CH_2), 24.1 (CH_2), 23.9

(CH_2). HRMS (ESI) *m/z* calcd for $C_{24}H_{27}O_3$, 363.2038, found 363.1967 $[M-H]^+$. HPLC: SS-WHELK, 1% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 10.3 min (major), 11.8 min (minor), 94% ee with (*S*)-xylylBINAP$(AuCl)_2$; $[\alpha]^{23}_D$ -110.7 (*c* 1.1, $CHCl_3$).



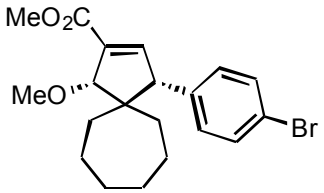
382

(1*S*,4*R*)-Methyl 1-methoxy-4-(4-methoxyphenyl)spiro[4.6]undec-2-ene-2-carboxylate (382). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **382** in 79% yield (137 mg) as colorless oil. IR (neat) 2921, 2852, 1716, 1510, 1249, 1090, 908, 729 cm^{-1}; ^{1}H NMR (600 MHz) δ 7.10 (d, 2H, *J* = 8.4 Hz), 6.80-6.82 (m, 3H), 3.97 (s, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.52 (s, 3H), 3.44 (d, 1H, *J* = 3.0 Hz), 1.26-1.67 (m, 11H), 1.01 (dd, 1H, *J* = 14.4, 10.2 Hz); ^{13}C-NMR (100 MHz) δ 165.9 (C), 158.6 (C), 148.9 (CH), 136.5 (C), 131.6 (C), 131.2 (CH), 113.5 (CH), 91.7 (CH), 62.6 (CH), 60.4 (CH_3), 55.4 (CH), 52.9 (CH_3), 51.8 (CH_3), 42.6 (C), 31.4 (CH_2), 30.7 (CH_2), 24.1 (CH_2), 23.9 (CH_2). HRMS (ESI) *m/z* calcd for $C_{20}H_{22}O_2$, 313.1988, found 313.1799 $[M-OCH_3]^+$. HPLC: SS-WHELK, 1% iPrOH/hexane, 1.0 mlmin^{-1}, UV 254 nm, t_R: 9.6 min (major), 11.7 min (minor), 91% ee with (*S*)-xylylBINAP$(AuCl)_2$; $[\alpha]^{23}_D$ -325.2 (*c* 1.2, $CHCl_3$).



383

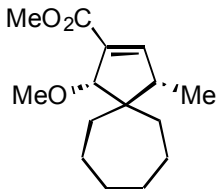
(1*S*,4*R*)-Methyl 4-(3,4-dichlorophenyl)-1-methoxyspiro[4.6]undec-2-ene-2-carboxylate (383). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **383** in 76% yield (146 mg) as yellowish oil. IR (neat) 2926, 2852, 1716, 1435, 1093, 903, 730, 700 cm^{-1}; ^1H NMR (600 MHz) δ 7.32 (d, 1H, *J* = 8.4 Hz), 7.30 (d, 1H, *J* = 1.8 Hz), 7.05 (dd, 1H, *J* = 8.4, 1.8 Hz), 6.76 (d, 1H, *J* = 3.6 Hz), 3.97 (s, 1H), 3.81 (s, 3H), 3.51 (s, 3H), 3.41 (d, 1H, *J* = 2.4 Hz), 1.25-1.69 (m, 11H), 0.96 (dd, 1H, *J* = 15.0, 9.6 Hz); ^{13}C-NMR (100 MHz) δ 165.7 (C), 147.3 (CH), 140.0 (C), 137.9 (C), 132.0 (CH), 130.9 (C), 130.1 (CH), 129.7 (CH), 91.2 (CH), 62.4 (CH), 60.4 (CH_3), 53.1 (C), 51.9 (CH_3), 42.4 (C), 31.2 (CH_2), 30.7 (CH_2), 23.9 (CH_2), 23.8 (CH_2). HRMS (ESI) *m/z* calcd for $C_{19}H_{19}O_2Cl_2$, 351.1103, found 351.0912 $[M\text{-}OCH_3]^+$. HPLC: SS-WHELK, 1% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 230 nm, t_R: 6.5 min (minor), 7.2 min (major), 95% ee with (*R*)-DTBMSegphos$(AuCl)_2$; $[\alpha]^{23}_D$ 311.3 (*c* 1.0, $CHCl_3$).



384

(1*S*,4*R*)-Methyl 4-(4-bromophenyl)-1-methoxyspiro[4.6]undec-2-ene-2-carboxylate (384). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent

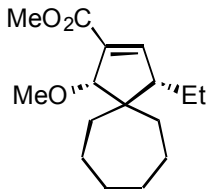
system) gave compound **384** in 84% yield (165 mg) as colorless oil. IR (neat) 2920, 2851, 1717, 1258, 1091, 1010, 754 cm^{-1}; ^1H NMR (600 MHz) δ 7.38 (d, 2H, *J* = 9.0 Hz), 7.07 (d, 2H, *J* = 7.8 Hz), 6.78 (d, 1H, *J* = 3.0 Hz), 3.97 (s, 1H), 3.80 (s, 3H), 3.51 (s, 3H), 3.43 (d, 1H, *J* = 3.6 Hz), 1.25-1.67 (m, 11H), 0.97 (dd, 1H, *J* = 15.0, 10.2 Hz); ^{13}C-NMR (100 MHz) δ 165.7 (C), 147.9 (CH), 138.7 (C), 137.5 (C), 131.9 (CH), 131.3 (CH), 120.9 (C), 91.5 (CH), 62.7 (CH), 60.4 (CH_3), 53.1 (C), 51.8 (CH_3), 42.5 (C), 31.3 (CH_2), 30.7 (CH_2), 24.0 (CH_2), 23.8 (CH_2). HRMS (ESI) *m/z* calcd for $C_{20}H_{24}BrO_3$, 391.0987, found 391.0916 $[M-H]^+$. HPLC: SS-WHELK, 1.0% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 230 nm, t_R: 6.5 min (minor), 7.2 min (major), 93% ee with (*R*)-DTBMSegphos$(AuCl)_2$; $[\alpha]^{23}_D$ 101.7 (*c* 1.0, $CHCl_3$).



385

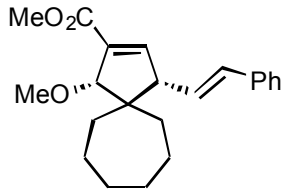
(1*S*,4*S*)-Methyl 1-methoxy-4-methylspiro[4.6]undec-2-ene-2-carboxylate (385). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **385** in 90% yield (114 mg) as colorless oil. IR (neat) 2920, 2853, 1716, 1098, 906, 906, 730 cm^{-1}; ^1H NMR (600 MHz) δ 6.92 (d, 1H, *J* = 3.0 Hz), 3.85 (s, 1H), 3.76 (s, 3H), 3.48 (s, 3H), 2.35 (dq, 1H, *J* = 7.2, 3.0 Hz), 1.83 (m, 1H), 1.34-1.62 (m, 10H), 1.00 (d, 3H, *J* = 1.8 Hz); ^{13}C-NMR (100 MHz) δ 166.1 (C), 153.5 (CH), 135.5 (C), 91.5 (CH), 60.2 (CH_3), 51.6 (CH_3), 51.1 (CH), 50.1 (C), 41.5 (C), 31.3 (CH_2), 31.1 (CH_2), 28.9 (CH_2), 23.7 (CH_2), 23.7 (CH_2), 17.1 (CH_3). HRMS (ESI) *m/z* calcd for $C_{15}H_{24}O_3K$,

291.1725, found 291.1357 $[M+K]^+$. HPLC: SS-WHELK, 1% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 230 nm, t_R: 5.2 min (minor), 5.8 min (major), 91% ee with (*R*)-DTBMSegphos$(AuCl)_2$; $[\alpha]^{23}_D$ 67.6 (*c* 1.2, $CHCl_3$).



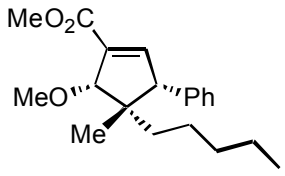
386

(1*S*,4*S*)-Methyl 4-ethyl-1-methoxyspiro[4.6]undec-2-ene-2-carboxylate (386). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **386** in 84% yield (112 mg) as colorless oil. IR (neat) 2920, 2853, 1717, 1248, 1100 cm^{-1}; ^1H NMR (600 MHz) δ 6.92 (d, 1H, *J* = 4.8 Hz), 3.84 (s, 1H), 3.77 (s, 3H), 3.48 (s, 3H), 2.14 (ddd, 1H, *J* = 4.4, 3.2, 1.2 Hz), 1.20-1.77 (m, 14H), 0.93 (t, 3H, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz) δ 166.1 (C), 152.5 (CH), 136.3 (C), 91.3 (CH), 60.1 (CH_3), 57.5 (CH_3), 51.6 (CH_3), 51.5 (C), 41.7 (C), 31.3 (CH_2), 31.2 (CH_2), 28.7 (CH_2), 25.8 (CH_2), 23.7 (CH_2), 23.6 (CH_2), 12.8 (CH_3). HRMS (ESI) *m/z* calcd for $C_{16}H_{26}O_3Na$, 289.1882, found 289.1776 $[M+Na]^+$. HPLC: SS-WHELK, 1% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 230 nm, t_R: 4.8 min (minor), 5.6 min (major), 91% ee with (*R*)-DTBMSegphos$(AuCl)_2$; $[\alpha]^{23}_D$ 119.7 (*c* 1.2, $CHCl_3$).



387

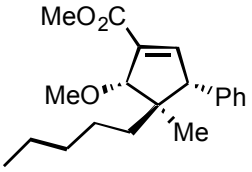
(1*S*,4*S*)-Methyl 1-methoxy-4-((E)-styryl)spiro[4.6]undec-2-ene-2-carboxylate (387). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **387** in 71% yield (107 mg) as colorless oil. IR (neat) 2921, 2852, 1716, 1263, 1098, 73, 692 cm^{-1}; ^1H NMR (600 MHz) δ 7.35 (d, 2H, *J* = 7.8 Hz), 7.19-7.30 (m, 3H), 6.80 (d, 1H, *J* = 3.0 Hz), 6.39 (d, 1H, *J* = 15.6 Hz), 5.96 (dd, 1H, *J* = 16.2, 9.6 Hz), 3.93 (s, 1H), 3.78 (s, 3H), 3.51 (s, 3H), 3.07 (dd, 1H, *J* = 10.2, 3.6 Hz), 1.86 (dd, 1H, *J* = 15.0, 9.0 Hz), 1.43-1.67 (m, 11H); ^{13}C-NMR (100 MHz) δ 166.2 (C), 149.2 (CH), 139.0 (C), 136.4 (C), 130.4 (CH), 128.1 (CH), 126.9 (CH), 89.9 (CH), 60.1 (CH), 60.5 (CH_3), 51.8 (CH_3), 49.2 (C), 39.3 (CH_2), 29.5 (CH_2), 26.2 (CH_2), 23.8 (CH_2), 23.0 (CH_2). HRMS (ESI) *m/z* calcd for $C_{21}H_{25}O_3$, 309.2038, found 309.1848 $[M\text{-}OCH_3]^+$. HPLC: SS-WHELK, 1% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 254 nm, t_R: 7.4 min (major), 8.5 min (minor), 91% ee with (*S*)-xylylBINAP$(AuCl)_2$; $[\alpha]^{23}_D$ -49.9 (*c* 1.0, $CHCl_3$).



375

(3*R*,4*S*,5*S*)-Methyl 5-methoxy-4-methyl-4-pentyl-3-phenylcyclopent-1-enecarboxylate (375). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **375** in 36% yield (57 mg) as colorless oil. IR (neat) 2953, 2928, 1717, 1250, 1098, 700 cm^{-1}; ^1H NMR (600 MHz) δ 7.19-7.27 (m, 5H), 6.85 (d, 1H, *J* = 2.4 Hz), 3.95 (s, 1H), 3.80 (s, 3H), 3.54 (s, 3H), 3.48 (d, 1H, *J* = 2.4

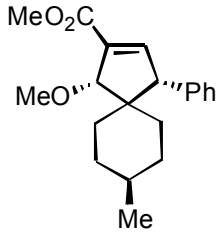
Hz), 1.03-1.17 (m, 4H), 1.12 (s, 3H), 0.88 (m, 1H), 0.74 (t, 3H, J = 702 Hz); ^{13}C-NMR (100 MHz) δ 166.1 (C), 149.2 (CH), 139.2 (C), 136.3 (C), 130.3 (CH), 128.1 (CH), 126.9 (CH), 91.3 (CH), 63.1 (CH), 60.4 (CH_3), 51.8 (CH_3), 48.9 (C), 32.8 (CH_2), 32.6 (CH_2), 28.1 (CH_2), 24.2 (CH_2), 22.6 (CH_3), 14.2 (CH_3). HRMS (ESI) *m/z* calcd for $C_{20}H_{28}O_3Na$, 339.2038, found 339.1934 $[M+Na]^+$. HPLC: SS-WHELK, 1% iPrOH/hexane, 1.0 mlmin^{-1}, UV 230 nm, t_R: 4.9 min (minor), 5.7 min (major), 90% ee with (*R*)-DTBMSegphos$(AuCl)_2$; $[\alpha]^{23}_D$ 44.4 (*c* 1.0, $CHCl_3$).



376

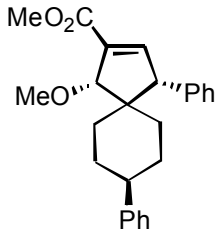
(3*R*,4*R*,5*S*)-Methyl 5-methoxy-4-methyl-4-pentyl-3-phenylcyclopent-1-enecarboxylate (376). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **376** in 39% yield (62 mg) as colorless oil. IR (neat) 2929, 2859, 1717, 1102, 907, 730, 700 cm^{-1}; ^{1}H NMR (600 MHz) δ 7.28 (t, 2H, J = 6.6 Hz), 7.21 (m, 1H), 7.12 (dd, 2H, J = 8.4, 1.8 Hz), 6.82 (d, 1H, J = 3.0 Hz), 4.07 (s, 1H), 3.81 (s, 3H), 3.51 (d, 1H, J = 3.0 Hz), 3.50 (s, 3H), 1.27-1.45 (m, 8H), 0.91 (t, 3H, J = 7.2 Hz), 0.62 (s, 3H); ^{13}C-NMR (100 MHz) δ 165.7 (C), 147.8 (CH), 140.0 (C), 136.9 (C), 129.7 (CH), 128.3 (CH), 126.9 (CH), 90.8 (CH), 60.3 (CH), 60.1 (CH_3), 51.8 (CH_3), 49.9 (C), 43.3 (CH_2), 32.9 (CH_2), 24.9 (CH_2), 22.9 (CH_2), 17.9 (CH_3), 14.3 (CH_3). HRMS (ESI) *m/z* calcd for $C_{20}H_{28}O_3Na$, 339.2038, found 339.1933 $[M+Na]^+$. HPLC:

SS-WHELK, 1% iPrOH/hexane, 1.0 mlmin^{-1}, UV 230 nm, t_R: 5.5 min (minor), 6.2 min (major), 96% ee with (*R*)-DTBMSegphos(AuCl)$_2$; $[\alpha]^{23}_D$ 134.6 (*c* 1.0, $CHCl_3$).



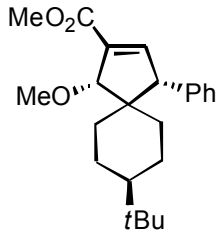
392

(1*S*,4*R*)-Methyl 1-methoxy-8-methyl-4-phenylspiro[4.5]dec-2-ene-2-carboxylate (392). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **392** in 65% yield (102 mg) as colorless oil. IR (neat) 2948, 2817, 2851, 1714, 1252, 1096, 907, 730, 699 cm^{-1}; ^{1}H NMR (600 MHz) δ 7.26 (t, 2H, *J* = 8.4 Hz), 7.21 (m, 1H), 7.16 (d, 2H, *J* = 8.4 Hz), 6.89 (d, 1H, *J* = 3.0 Hz), 4.25 (s, 1H), 3.81 (s, 3H), 3.57 (s, 3H), 3.32 (d, 1H, *J* = 3.6 Hz), 1.60 (m, 2H), 1.20-1.47 (m, 4H), 0.93 (m, 1H), 0.88 (d, 3H, *J* = 6.6 Hz), 0.73 (dt, 1H, *J* = 13.8 Hz, 3.6 Hz); ^{13}C-NMR (100 MHz) δ 166.3 (C), 148.9 (CH), 139.4 (C), 136.9 (C), 130.1 (CH), 128.1 (CH), 126.9 (CH), 86.7 (CH), 64.4 (CH), 60.1 (CH_3), 53.7 (CH), 51.8 (CH_3), 48.8 (C), 38.9 (CH_2), 32.5 (CH_2), 32.4 (CH_2), 32.3 (CH_2), 30.2 (CH_2), 22.7 (CH_3). HRMS (ESI) *m/z* calcd for $C_{20}H_{26}O_3Na$, 337.1882, found 337.1775 $[M+Na]^+$. HPLC: AD-H, 1% iPrOH/hexane, 1.0 mlmin^{-1}, UV 230 nm, t_R: 4.6 min (minor), 5.2 min (major), 93% ee with (*R*)-DTBMSegphos(AuCl)$_2$; $[\alpha]^{23}_D$ 129.8 (*c* 1.0, $CHCl_3$).



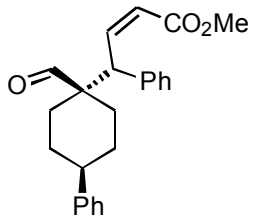
393

(1*S*,4*R*)-Methyl 1-methoxy-4,8-diphenylspiro[4.5]dec-2-ene-2-carboxylate (393). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **393** in 62% yield (122 mg) as colorless crystals. MP 109-110 °C. IR (neat) 3025, 2923, 1716, 1248, 1053, 909, 731, 698 cm^{-1}; ^1H NMR (600 MHz) δ 7.17-7.30 (m, 10H), 6.93 (d, 1H, J = 3.0 Hz), 4.39 (s, 1H), 3.83 (s, 3H), 3.63 (s, 3H), 3.38 (d, 1H, J = 3.0 Hz), 2.45 (m, 1H), 1.42-1.85 (m, 7H), 0.88 (dt, 1H, J = 13.8 Hz, 4.2 Hz); ^{13}C-NMR (100 MHz) δ 166.3 (C), 148.9 (CH), 147.5 (C), 139.4 (C), 136.9 (C), 130.1 (CH), 128.7 (CH), 128.6 (CH), 128.2 (CH), 127.1 (CH), 126.9 (CH), 126.2 (CH), 86.6 (CH), 64.5 (CH), 60.3 (CH_3), 51.9 (CH_3), 48.7 (CH), 44.0 (C), 39.2 (CH_2), 31.6 (CH_2), 31.4 (CH_2), 30.8 (CH_2). HRMS (ESI) *m/z* calcd for $C_{25}H_{29}O_3$, 377.2072, found 377.2113 $[M+H]^+$. HPLC: AD-H, 1% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 230 nm, t_R: 5.9 min (minor), 8.2 min (major), 94% ee with (*S*)-xylylBINAP$(AuCl)_2$, 93% ee with (*R*)-DTBMSegphos$(AuCl)_2$; $[\alpha]^{23}_D$ 72.2 (*c* 1.0, $CHCl_3$).



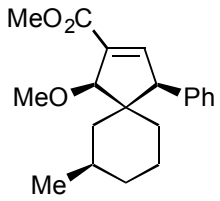
394

(1*S*,4*R*)-Methyl 8-(tert-butyl)-1-methoxy-4-phenylspiro[4.5]dec-2-ene-2-carboxylate (394). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **392** in 70% yield (125 mg) as white needles. MP 92-93 °C. IR (neat) 2940, 2867, 2844, 1717, 1254, 1091, 905, 732, 699 cm^{-1}; ^1H NMR (600 MHz) δ 7.26 (t, 2H, *J* = 7.2 Hz), 7.21 (t, 1H, *J* = 7.2 Hz), 7.16 (d, 2H, *J* = 7.8 Hz), 6.89 (d, 1H, *J* = 3.0 Hz), 4.24 (s, 1H), 3.81 (s, 3H), 3.58 (s, 3H), 3.30 (d, 1H, *J* = 3.0 Hz), 1.65 (d, 2H, *J* = 12.6 Hz), 1.54 (m, 1H), 1.43 (m, 2H), 1.32 (m, 1H), 0.96 (m, 2H), 0.84 (s, 9H), 0.68 (m, 1H); ^{13}C-NMR (100 MHz) δ 166.3 (C), 148.8 (CH), 139.5 (C), 136.9 (C), 130.0 (CH), 128.1 (CH), 126.9 (CH), 86.7 (CH), 64.5 (CH), 60.3 (CH_3), 51.8 (CH_3), 48.8 (C), 47.8 (CH), 39.7 (CH_2), 32.6 (CH_2), 30.9 (C), 27.7 (CH_3), 24.6 (CH_2), 24.5 (CH_3). HRMS (ESI) *m/z* calcd for $C_{23}H_{32}O_3K$, 395.2351, found 395.1986 $[M+K]^+$. HPLC: SS-WHELK, 1% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 230 nm, t_R: 4.6 min (minor), 5.4 min (major), 97% ee with (*R*)-DTBMSegphos$(AuCl)_2$; $[\alpha]^{23}_D$ 171.3 (*c* 1.0, $CHCl_3$).



391

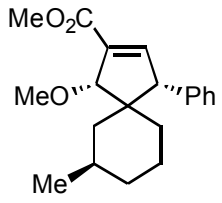
(*S*,*Z*)-Methyl 4-((1s,4R)-1-formyl-4-phenylcyclohexyl)-4-phenylbut-2-enoate (391). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **391** in 6% yield (14 mg) as colorless oil. IR (neat) 3027, 2928, 2857, 1719, 1196, 1175, 907, 699 cm^{-1}; ^1H NMR (600 MHz) δ 9.62 (s, 1H), 7.32 (t, 2H, *J* = 8.4 Hz), 7.26 (m, 3H), 7.19 (d, 2H, *J* = 7.8 Hz), 7.15 (t, 1H, *J* = 6.6 Hz), 7.10 (d, 2H, *J* = 8.4 Hz), 6.65 (t, 1H, *J* = 11.4 Hz), 5.93 (d, 1H, *J* = 12.0 Hz), 4.96 (d, 1H, *J* = 10.8 Hz), 3.69 (s, 3H), 2.38 (tt, 1H, *J* = 12.0, 6.0 Hz,), 2.28 (dd, 1H, *J* = 13.8, 2.4 Hz), 2.18 (dd, 1H, *J* = 13.8, 2.4 Hz), 1.80 (app t, 2H), 1.58 (td, 1H, *J* = 13.2, 3.0 Hz), 1.43 (td, 1H, *J* = 13.8, 4.2 Hz), 1.36 (m, 2H); ^{13}C-NMR (100 MHz) δ 207.7 (CH), 166.5 (C), 147.2 (CH), 146.7 (C), 138.2 (C), 129.6 (CH), 128.7 (CH), 128.6 (CH), 127.5 (CH), 126.9 (CH), 126.3 (CH), 120.9 (CH), 52.7 (C), 51.4 (CH_3), 50.7 (CH), 43.7 (CH), 30.9 (CH_2), 30.8 (CH_2), 30.6 (CH_2), 30.4 (CH_2). HRMS (ESI) *m/z* calcd for $C_{24}H_{27}O_3$, 363.1915, found 363.1243 $[M+H]^+$. HPLC: S4900, 3% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 230 nm, t_R: 5.7 min (major), 6.5 min (minor), 31% ee with (*S*)-xylylBINAP$(AuCl)_2$.



400

(1*R*,4*S*,7*R*)-Methyl 1-methoxy-7-methyl-4-phenylspiro[4.5]dec-2-ene-2-carboxylate (400). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent

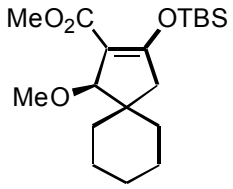
system) gave compound **400** in 70% yield (120 mg) as colorless oil. IR (neat) 2947, 2923, 2843, 1717, 1096, 732, 700 cm^{-1}; ^1H NMR (600 MHz) δ 7.26 (t, 2H, *J* = 7.8 Hz), 7.21 (t, 1H, *J* = 7.2 Hz), 7.15 (d, 2H, *J* = 7.8 Hz), 6.89 (d, 1H, *J* = 3.6 Hz), 4.24 (s, 1H), 3.81 (s, 3H), 3.55 (s, 3H), 3.31 (d, 1H, *J* = 3.0 Hz), 1.56-1.65 (m, 5H), 1.31-1.35 (m, 3H), 0.80 (dq, 1H, *J* = 12.6, 4.8 Hz), 0.72 (d, 3H, *J* = 6.6 Hz), 0.33 (t, 1H, *J* = 12.6 Hz, 3.6 Hz); ^{13}C-NMR (100 MHz) δ 166.4 (C), 149.0 (CH), 139.2 (C), 136.9 (C), 130.1 (CH), 128.1 (CH), 126.9 (CH), 86.6 (CH), 64.9 (CH), 60.1 (CH_3), 51.8 (CH_3), 49.7 (C), 38.9 (CH_2), 37.8 (CH_2), 34.9 (CH_2), 29.8 (CH_2), 23.7 (CH_2), 23.3 (CH_3). HRMS (ESI) *m/z* calcd for $C_{20}H_{26}O_3Na$, 337.1882, found 337.1777 $[M+Na]^+$. Synthesized using (*S*)-DTBMSegphos$(AuCl)_2$; $[\alpha]^{23}_D$ -148.1 (*c* 1.0, $CHCl_3$).



401

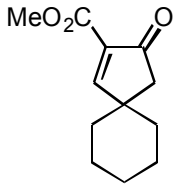
(1*S*,4*R*,7*R*)-Methyl 1-methoxy-7-methyl-4-phenylspiro[4.5]dec-2-ene-2-carboxylate (401). Purification by silica gel chromatography (using 20:1 pentane/Et_2O solvent system) gave compound **401** in 68% yield (117 mg) as colorless oil. IR (neat) 2947, 2923, 2842, 1717, 1096, 732, 700 cm^{-1}; ^1H NMR (600 MHz) δ 7.26 (m, 2H), 7.21 (t, 1H, *J* = 7.2 Hz), 7.16 (d, 2H, *J* = 7.8 Hz), 6.89 (d, 1H, *J* = 3.0 Hz), 4.28 (s, 1H), 3.81 (s, 3H), 3.56 (s, 3H), 3.29 (d, 1H, *J* = 3.0 Hz), 1.67 (m, 2H), 1.59 (m, 1H), 1.51 (m, 1H), 1.38 (dd, 1H, *J* = 13.2, 1.2 Hz), 1.25 (m, 1H), 1.03 (t, 1H, *J* = 12.6 Hz), 0.88 (d, 3H, *J* = 6.0

Hz), 0.80 (dq, 1H, J = 12.6 Hz, 2.4 Hz), 0.59 (dq, 1H, J = 13.2 Hz, 3.6 Hz); ^{13}C-NMR (100 MHz) δ 166.4 (C), 148.9 (CH), 139.4 (C), 136.9 (C), 130.1 (CH), 128.1 (CH), 126.9 (CH), 87.1 (CH), 64.9 (CH), 60.2 (CH_3), 51.8 (CH_3), 49.8 (C), 48.1 (CH), 35.0 (CH_2), 30.2 (CH_2), 29.7 (CH_2), 23.8 (CH_2), 22.9 (CH_3). HRMS (ESI) *m/z* calcd for $C_{20}H_{26}O_3Na$, 337.1882, found 337.1777 $[M+Na]^+$. Synthesized using (*R*)-DTBMSegphos$(AuCl)_2$; $[\alpha]^{23}_D$ 143.4 (*c* 1.0, $CHCl_3$).



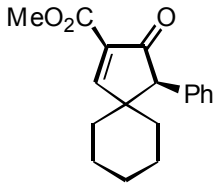
403

(*R*)-Methyl 3-((tert-butyldimethylsilyl)oxy)-1-methoxyspiro[4.5]dec-2-ene-2-carboxylate (403). Purification by silica gel chromatography (using 10:1 pentane/Et_2O solvent system) gave compound **403** in 53% yield (94 mg) as colorless oil. IR (neat) 2927, 2857, 1697, 1624, 1438, 1383, 1222, 838, 781 cm^{-1}; ^{1}H NMR (400 MHz) δ 3.99 (s, 1H), 3.65 (s, 3H), 3.37 (s, 3H), 2.40 (d, 1H, J = 17.2 Hz), 2.05 (d, 1H, J = 17.2 Hz), 1.30-1.60 (m, 10H), 0.91 (s, 9H), 0.15 (s, 3H), 0.14 (s, 3H); ^{13}C-NMR (100 MHz) δ 169.0 (C), 166.0 (CH), 109.9 (C), 89.8 (CH), 59.0 (CH_3), 50.7 (CH_3), 45.8 (C), 42.9 (CH_2), 36.7 (CH_2), 32.2 (CH_2), 26.3 (CH_2), 25.6 (CH_3), 23.5 (CH_2), 23.1 (CH_2), 18.4 (C), -3.7 (CH_3), -3.8(CH_3). HRMS (ESI) *m/z* calcd for $C_{18}H_{31}O_4Si$, 323.2226, found 323.2037 $[M-OCH_3]^+$.



404

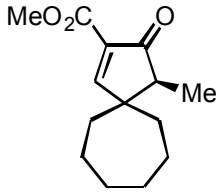
Methyl 3-oxospiro[4.5]dec-1-ene-2-carboxylate (404). Purification by silica gel chromatography (using 10:1 pentane/Et_2O solvent system) gave compound **404** in 36% yield (37 mg) as colorless oil. IR (neat) 2926, 2854, 1749, 1719, 1620, 1023, 766, 727 cm^{-1}; ^1H NMR (400 MHz) δ 8.22 (s, 1H), 3.81 (s, 3H), 2.40 (s, 2H), 1.3-1.8 (m, 10H); ^{13}C-NMR (100 MHz) δ 202.4 (C), 180.3 (CH), 162.7 (C), 134.1 (C), 52.2 (CH_3), 48.7 (CH_2), 43.8 (C), 36.1 (CH_2), 25.3 (CH_2), 23.0 (CH_2). HRMS (ESI) *m/z* calcd for $C_{12}H_{17}O_3$, 209.1133, found 209.1172 $[M+H]^+$.



405

(*R*)-Methyl 3-oxo-4-phenylspiro[4.5]dec-1-ene-2-carboxylate (405). Purification by silica gel chromatography (using 10:1 pentane/Et_2O solvent system) gave compound **405** in 80% yield (114 mg) as colorless oil. IR (neat) 3028, 2930, 2855, 1751, 1722, 1261, 1019, 726, 701 cm^{-1}; ^1H NMR (600 MHz) δ 8.66 (s, 1H), 7.26-7.33 (m, 3H), 7.05 (d, 2H, J = 7.8 Hz), 3.88 (s, 3H), 3.50 (s, 3H), 1.69-1.77 (m, 4H), 1.62 (m, 1H), 1.39 (m, 2H), 1.24 (m, 2H), 1.05 (m, 1H); ^{13}C-NMR (100 MHz) δ 202.3 (C), 177.5 (CH), 162.8 (C), 136.1 (C), 134.8 (C), 130.3 (CH), 128.6 (CH), 127.5 (CH), 66.6 (CH), 52.3 (CH_3), 47.8

(C), 37.2 (CH_2), 34.9 (CH_2), 25.4 (CH_2), 23.0 (CH_2), 22.3 (CH_2). HRMS (ESI) *m/z* calcd for $C_{18}H_{20}O_3K$, 323.1412, found 323.1042 $[M+K]^+$.



406

(*S*)-Methyl 4-methyl-3-oxospiro[4.6]undec-1-ene-2-carboxylate (406). Purification by silica gel chromatography (using 10:1 pentane/Et_2O solvent system) gave compound **406** in 79% yield (89 mg) as colorless oil. IR (neat) 2922, 2853, 1748, 1720, 1617, 1260, 985, 790 cm^{-1}; ^1H NMR (600 MHz) δ 8.32 (s, 1H), 3.83 (s, 3H), 2.25 (q, 1H, *J* = 7.8 Hz), 1.44-1.78 (m, 12H), 1.16 (d, 3H, *J* = 7.8 Hz); ^{13}C-NMR (100 MHz) δ 204.6 (C), 178.2 (CH), 163.0 (C), 132.4 (C), 55.3 (CH), 52.2 (CH_3), 48.7 (C), 39.9 (CH_2), 35.3 (CH_2), 30.9 (CH_2), 30.5 (CH_2), 23.8 (CH_2), 23.6 (CH), 10.4 (CH_3). HRMS (ESI) *m/z* calcd for $C_{14}H_{20}O_3K$, 275.1412, found 275.1048 $[M+K]^+$. HPLC: OB-H, 5% iPrOH/hexane, 1.0 $mlmin^{-1}$, UV 230 nm, t_R: 18.2 min (minor), 23.7 min (major), 79% ee with (*S*)-xylylBINAP$(AuCl)_2$.

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Appendix: X-ray Data

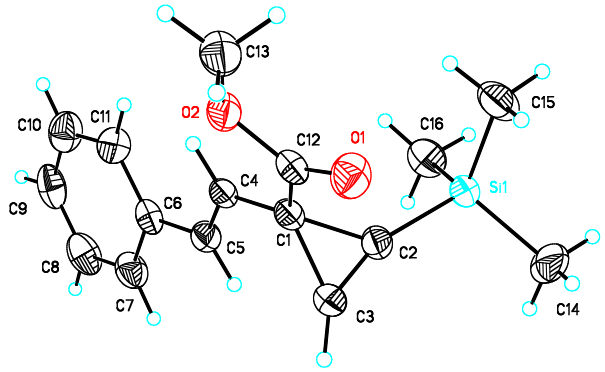

Table 1. Crystal data and structure refinement for **106**

Identification code	**106**	
Empirical formula	C16 H20 O2 Si	
Formula weight	272.41	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 6.3748(3) Å	α= 90°.
	b = 8.6854(3) Å	β= 92.480(3)°.
	c = 14.2983(6) Å	γ = 90°.
Volume	790.93(6) $Å^3$	
Z	2	
Density (calculated)	1.144 Mg/m^3	
Absorption coefficient	1.272 mm^{-1}	
F(000)	292	
Crystal size	0.36 x 0.18 x 0.10 mm^3	
Theta range for data collection	3.09 to 65.99°.	
Index ranges	-6<=h<=7, -10<=k<=8, -16<=l<=16	
Reflections collected	7333	

Independent reflections	2224 [R(int) = 0.0310]
Completeness to theta = 65.99°	95.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8876 and 0.6574
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2224 / 1 / 172
Goodness-of-fit on F^2	1.071
Final R indices [I>2sigma(I)]	R1 = 0.0373, wR2 = 0.1038
R indices (all data)	R1 = 0.0387, wR2 = 0.1050
Absolute structure parameter	0.01(3)
Largest diff. peak and hole	0.448 and -0.194 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for **106**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	6695(4)	9388(3)	8657(2)	34(1)
C(2)	4590(4)	8657(3)	8249(2)	38(1)
C(3)	4457(4)	9903(3)	8727(2)	39(1)
C(4)	8113(4)	10189(3)	8022(2)	33(1)
C(5)	7517(4)	11214(3)	7377(2)	38(1)
C(6)	8866(3)	11993(3)	6720(2)	39(1)
C(7)	8069(5)	13223(3)	6188(2)	50(1)
C(8)	9271(5)	13975(3)	5549(2)	59(1)
C(9)	11323(5)	13533(4)	5428(2)	58(1)
C(10)	12155(5)	12315(4)	5956(2)	58(1)
C(11)	10941(4)	11563(3)	6593(2)	46(1)
C(12)	7630(4)	8566(3)	9489(2)	36(1)
C(13)	10750(4)	7943(3)	10358(2)	52(1)
C(14)	955(4)	6667(5)	7535(3)	78(1)
C(15)	5132(5)	5247(4)	8174(2)	61(1)
C(16)	4824(5)	7168(4)	6370(2)	56(1)
O(1)	6649(3)	7814(2)	10023(1)	52(1)
O(2)	9702(3)	8753(2)	9583(1)	43(1)
Si(1)	3840(1)	6905(1)	7567(1)	40(1)

Table 3. Bond lengths [Å] and angles [°] for **106**.

C(1)-C(4)	1.482(3)	C(4)-C(1)-C(2)	119.67(19)
C(1)-C(12)	1.490(3)	C(12)-C(1)-C(2)	114.1(2)
C(1)-C(3)	1.503(3)	C(3)-C(1)-C(2)	49.30(15)
C(1)-C(2)	1.574(3)	C(3)-C(2)-C(1)	62.47(18)
C(2)-C(3)	1.285(4)	C(3)-C(2)-Si(1)	161.3(2)
C(2)-Si(1)	1.858(3)	C(1)-C(2)-Si(1)	136.09(18)
C(3)-H(3A)	0.9500	C(2)-C(3)-C(1)	68.23(18)
C(4)-C(5)	1.325(3)	C(2)-C(3)-H(3A)	145.9
C(4)-H(4A)	0.9500	C(1)-C(3)-H(3A)	145.9
C(5)-C(6)	1.466(3)	C(5)-C(4)-C(1)	125.3(2)
C(5)-H(5A)	0.9500	C(5)-C(4)-H(4A)	117.4
C(6)-C(11)	1.394(3)	C(1)-C(4)-H(4A)	117.4
C(6)-C(7)	1.395(4)	C(4)-C(5)-C(6)	126.6(2)
C(7)-C(8)	1.381(4)	C(4)-C(5)-H(5A)	116.7
C(7)-H(7A)	0.9500	C(6)-C(5)-H(5A)	116.7
C(8)-C(9)	1.381(4)	C(11)-C(6)-C(7)	117.3(2)
C(8)-H(8A)	0.9500	C(11)-C(6)-C(5)	123.1(2)
C(9)-C(10)	1.391(4)	C(7)-C(6)-C(5)	119.5(2)
C(9)-H(9A)	0.9500	C(8)-C(7)-C(6)	121.5(3)
C(10)-C(11)	1.384(4)	C(8)-C(7)-H(7A)	119.2
C(10)-H(10A)	0.9500	C(6)-C(7)-H(7A)	119.2
C(11)-H(11A)	0.9500	C(7)-C(8)-C(9)	120.4(3)
C(12)-O(1)	1.201(3)	C(7)-C(8)-H(8A)	119.8
C(12)-O(2)	1.332(3)	C(9)-C(8)-H(8A)	119.8
C(13)-O(2)	1.451(3)	C(8)-C(9)-C(10)	119.0(3)
C(13)-H(13A)	0.9800	C(8)-C(9)-H(9A)	120.5
C(13)-H(13B)	0.9800	C(10)-C(9)-H(9A)	120.5
C(13)-H(13C)	0.9800	C(11)-C(10)-C(9)	120.3(3)
C(14)-Si(1)	1.850(3)	C(11)-C(10)-H(10A)	119.8
C(14)-H(14A)	0.9800	C(9)-C(10)-H(10A)	119.8
C(14)-H(14B)	0.9800	C(10)-C(11)-C(6)	121.3(3)
C(14)-H(14C)	0.9800	C(10)-C(11)-H(11A)	119.3
C(15)-Si(1)	1.855(3)	C(6)-C(11)-H(11A)	119.3
C(15)-H(15A)	0.9800	O(1)-C(12)-O(2)	122.9(2)
C(15)-H(15B)	0.9800	O(1)-C(12)-C(1)	124.6(2)
C(15)-H(15C)	0.9800	O(2)-C(12)-C(1)	112.54(19)
C(16)-Si(1)	1.862(3)	O(2)-C(13)-H(13A)	109.5
C(16)-H(16A)	0.9800	O(2)-C(13)-H(13B)	109.5
C(16)-H(16B)	0.9800	H(13A)-C(13)-H(13B)	109.5
C(16)-H(16C)	0.9800	O(2)-C(13)-H(13C)	109.5
		H(13A)-C(13)-H(13C)	109.5
C(4)-C(1)-C(12)	118.7(2)	H(13B)-C(13)-H(13C)	109.5
C(4)-C(1)-C(3)	120.5(2)	Si(1)-C(14)-H(14A)	109.5
C(12)-C(1)-C(3)	115.9(2)	Si(1)-C(14)-H(14B)	109.5

H(14A)-C(14)-H(14B)	109.5
Si(1)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
Si(1)-C(15)-H(15A)	109.5
Si(1)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
Si(1)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
Si(1)-C(16)-H(16A)	109.5
Si(1)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
Si(1)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(12)-O(2)-C(13)	116.11(19)
C(14)-Si(1)-C(15)	110.3(2)
C(14)-Si(1)-C(2)	109.70(14)
C(15)-Si(1)-C(2)	106.96(12)
C(14)-Si(1)-C(16)	111.42(17)
C(15)-Si(1)-C(16)	111.37(15)
C(2)-Si(1)-C(16)	106.99(13)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **106**. 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)	37(1)	26(1)	39(1)	-4(1)	0(1)	-1(1)
C(2)	37(1)	33(1)	42(1)	1(1)	-1(1)	-2(1)
C(3)	40(1)	31(1)	46(1)	0(1)	3(1)	2(1)
C(4)	35(1)	25(1)	39(1)	-4(1)	-2(1)	0(1)
C(5)	38(1)	31(1)	45(1)	3(1)	-1(1)	0(1)
C(6)	50(1)	30(1)	37(1)	-1(1)	-4(1)	-8(1)
C(7)	60(2)	36(1)	54(1)	9(1)	-4(1)	-3(1)
C(8)	87(2)	40(2)	51(2)	11(1)	2(2)	-11(2)
C(9)	80(2)	49(2)	45(1)	-2(1)	10(1)	-27(2)
C(10)	58(2)	66(2)	51(1)	-7(1)	8(1)	-12(2)
C(11)	48(1)	48(2)	42(1)	2(1)	2(1)	-3(1)
C(12)	44(1)	25(1)	40(1)	-3(1)	0(1)	-1(1)
C(13)	56(2)	44(2)	55(1)	11(1)	-15(1)	-2(1)
C(14)	39(1)	77(3)	116(3)	-52(2)	7(2)	-13(2)
C(15)	77(2)	35(1)	70(2)	4(1)	13(2)	4(2)
C(16)	68(2)	52(2)	47(1)	-3(1)	0(1)	2(2)
O(1)	52(1)	52(1)	52(1)	16(1)	2(1)	-5(1)
O(2)	41(1)	36(1)	50(1)	10(1)	-8(1)	-3(1)
Si(1)	37(1)	32(1)	51(1)	-7(1)	2(1)	-2(1)

Table 5. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for **106**.

	x	y	z	U(eq)
H(3A)	3543	10656	8967	47
H(4A)	9566	9949	8081	40
H(5A)	6067	11470	7336	46
H(7A)	6666	13551	6266	60
H(8A)	8682	14802	5190	71
H(9A)	12153	14052	4992	70

H(10A)	13563	11999	5879	69
H(11A)	11535	10737	6950	55
H(13A)	12261	8152	10362	79
H(13B)	10508	6834	10288	79
H(13C)	10189	8295	10949	79
H(14A)	485	6539	8174	116
H(14B)	563	5756	7163	116
H(14C)	287	7581	7251	116
H(15A)	4587	5140	8801	91
H(15B)	6651	5421	8226	91
H(15C)	4840	4305	7815	91
H(16A)	6357	7263	6409	83
H(16B)	4210	8103	6090	83
H(16C)	4424	6276	5982	83

Table 6. Torsion angles [°] for **106**.

C(4)-C(1)-C(2)-C(3)	-106.3(2)
C(12)-C(1)-C(2)-C(3)	104.3(2)
C(4)-C(1)-C(2)-Si(1)	76.2(3)
C(12)-C(1)-C(2)-Si(1)	-73.2(3)
C(3)-C(1)-C(2)-Si(1)	-177.5(3)
Si(1)-C(2)-C(3)-C(1)	174.7(6)
C(4)-C(1)-C(3)-C(2)	104.6(2)
C(12)-C(1)-C(3)-C(2)	-100.4(2)
C(12)-C(1)-C(4)-C(5)	-165.4(2)
C(3)-C(1)-C(4)-C(5)	-11.0(4)
C(2)-C(1)-C(4)-C(5)	46.6(3)
C(1)-C(4)-C(5)-C(6)	-178.1(2)
C(4)-C(5)-C(6)-C(11)	10.6(4)
C(4)-C(5)-C(6)-C(7)	-169.6(2)
C(11)-C(6)-C(7)-C(8)	0.9(4)
C(5)-C(6)-C(7)-C(8)	-178.9(3)
C(6)-C(7)-C(8)-C(9)	-0.7(4)
C(7)-C(8)-C(9)-C(10)	0.3(4)
C(8)-C(9)-C(10)-C(11)	-0.1(4)
C(9)-C(10)-C(11)-C(6)	0.3(4)
C(7)-C(6)-C(11)-C(10)	-0.7(4)
C(5)-C(6)-C(11)-C(10)	179.1(3)
C(4)-C(1)-C(12)-O(1)	-176.0(2)
C(3)-C(1)-C(12)-O(1)	28.5(3)
C(2)-C(1)-C(12)-O(1)	-26.3(3)
C(4)-C(1)-C(12)-O(2)	4.1(3)
C(3)-C(1)-C(12)-O(2)	-151.44(19)
C(2)-C(1)-C(12)-O(2)	153.79(19)

O(1)-C(12)-O(2)-C(13)	2.2(3)
C(1)-C(12)-O(2)-C(13)	-177.8(2)
C(3)-C(2)-Si(1)-C(14)	-3.4(7)
C(1)-C(2)-Si(1)-C(14)	169.8(3)
C(3)-C(2)-Si(1)-C(15)	-123.0(6)
C(1)-C(2)-Si(1)-C(15)	50.2(3)
C(3)-C(2)-Si(1)-C(16)	117.6(6)
C(1)-C(2)-Si(1)-C(16)	-69.2(3)

Symmetry transformations used to generate equivalent atoms:

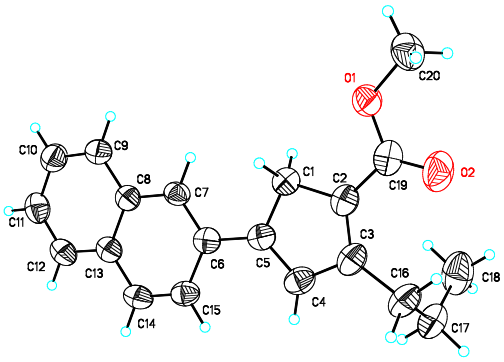

Table 1. Crystal data and structure refinement for **127**.

Identification code	**127**	
Empirical formula	C20 H20 O2	
Formula weight	292.36	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 8.4047(4) Å	α= 90°.
	b = 5.5397(3) Å	β= 91.048(3)°.
	c = 17.0558(7) Å	γ = 90°.
Volume	793.98(7) $Å^3$	
Z	2	
Density (calculated)	1.223 Mg/m^3	
Absorption coefficient	0.609 mm^{-1}	
F(000)	312	
Crystal size	0.32 x 0.31 x 0.04 mm^3	

Theta range for data collection	2.59 to 68.53°.
Index ranges	-10<=h<=10, -6<=k<=5, -20<=l<=18
Reflections collected	4214
Independent reflections	2068 [R(int) = 0.0191]
Completeness to theta = 68.53°	92.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9760 and 0.8289
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2068 / 1 / 199
Goodness-of-fit on F^2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0338, wR2 = 0.0910
R indices (all data)	R1 = 0.0430, wR2 = 0.1016
Absolute structure parameter	0.0(3)
Largest diff. peak and hole	0.127 and -0.168 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for **127**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-6961(2)	-7613(5)	-7753(1)	40(1)
C(2)	-7373(2)	-7275(5)	-6904(1)	43(1)
C(3)	-8396(2)	-5407(5)	-6839(1)	46(1)
C(4)	-8699(2)	-4397(5)	-7616(1)	46(1)
C(5)	-7875(2)	-5632(5)	-8160(1)	39(1)
C(6)	-7824(2)	-5173(4)	-9006(1)	38(1)
C(7)	-7071(2)	-6720(4)	-9510(1)	38(1)
C(8)	-7040(2)	-6281(4)	-10331(1)	39(1)
C(9)	-6248(2)	-7858(5)	-10846(1)	46(1)
C(10)	-6231(3)	-7387(6)	-11635(1)	53(1)
C(11)	-7027(3)	-5358(6)	-11947(1)	52(1)
C(12)	-7791(2)	-3812(5)	-11461(1)	46(1)
C(13)	-7803(2)	-4212(5)	-10639(1)	40(1)
C(14)	-8553(2)	-2606(5)	-10111(1)	44(1)
C(15)	-8556(2)	-3066(5)	-9326(1)	42(1)
C(16)	-9181(3)	-4394(6)	-6126(1)	55(1)
C(17)	-10984(3)	-4759(6)	-6148(1)	58(1)
C(18)	-11451(3)	-7361(8)	-6120(2)	79(1)
C(19)	-6718(2)	-8782(5)	-6268(1)	47(1)
C(20)	-5075(3)	-12122(6)	-5966(1)	60(1)
O(1)	-5794(2)	-10541(4)	-6549(1)	50(1)
O(2)	-6940(2)	-8504(4)	-5577(1)	65(1)

Table 3. Bond lengths [Å] and angles [°] for **127**.

C(1)-C(5)	1.501(3)
C(1)-C(2)	1.507(2)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-C(3)	1.351(4)
C(2)-C(19)	1.469(3)
C(3)-C(4)	1.458(3)
C(3)-C(16)	1.503(3)
C(4)-C(5)	1.353(3)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.468(2)
C(6)-C(7)	1.375(3)
C(6)-C(15)	1.424(3)
C(7)-C(8)	1.422(2)
C(7)-H(7A)	0.9500
C(8)-C(13)	1.410(3)
C(8)-C(9)	1.415(3)
C(9)-C(10)	1.371(3)
C(9)-H(9A)	0.9500
C(10)-C(11)	1.407(4)
C(10)-H(10A)	0.9500
C(11)-C(12)	1.360(4)
C(11)-H(11A)	0.9500
C(12)-C(13)	1.420(3)
C(12)-H(12A)	0.9500
C(13)-C(14)	1.421(3)
C(14)-C(15)	1.363(3)
C(14)-H(14A)	0.9500
C(15)-H(15A)	0.9500
C(16)-C(17)	1.528(3)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-C(18)	1.495(5)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-O(2)	1.206(2)
C(19)-O(1)	1.340(3)
C(20)-O(1)	1.449(3)
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800

C(5)-C(1)-C(2)	103.19(19)

C(5)-C(1)-H(1A)	111.1
C(2)-C(1)-H(1A)	111.1
C(5)-C(1)-H(1B)	111.1
C(2)-C(1)-H(1B)	111.1
H(1A)-C(1)-H(1B)	109.1
C(3)-C(2)-C(19)	127.20(17)
C(3)-C(2)-C(1)	109.4(2)
C(19)-C(2)-C(1)	123.4(2)
C(2)-C(3)-C(4)	108.65(17)
C(2)-C(3)-C(16)	130.0(2)
C(4)-C(3)-C(16)	121.4(2)
C(5)-C(4)-C(3)	110.2(2)
C(5)-C(4)-H(4A)	124.9
C(3)-C(4)-H(4A)	124.9
C(4)-C(5)-C(6)	127.6(2)
C(4)-C(5)-C(1)	108.52(17)
C(6)-C(5)-C(1)	123.83(18)
C(7)-C(6)-C(15)	118.21(17)
C(7)-C(6)-C(5)	121.9(2)
C(15)-C(6)-C(5)	119.92(19)
C(6)-C(7)-C(8)	121.7(2)
C(6)-C(7)-H(7A)	119.2
C(8)-C(7)-H(7A)	119.2
C(13)-C(8)-C(9)	119.08(17)
C(13)-C(8)-C(7)	119.32(19)
C(9)-C(8)-C(7)	121.6(2)
C(10)-C(9)-C(8)	120.4(2)
C(10)-C(9)-H(9A)	119.8
C(8)-C(9)-H(9A)	119.8
C(9)-C(10)-C(11)	120.6(2)
C(9)-C(10)-H(10A)	119.7
C(11)-C(10)-H(10A)	119.7
C(12)-C(11)-C(10)	120.00(19)
C(12)-C(11)-H(11A)	120.0
C(10)-C(11)-H(11A)	120.0
C(11)-C(12)-C(13)	121.0(2)
C(11)-C(12)-H(12A)	119.5
C(13)-C(12)-H(12A)	119.5
C(8)-C(13)-C(12)	118.9(2)
C(8)-C(13)-C(14)	118.47(17)
C(12)-C(13)-C(14)	122.6(2)
C(15)-C(14)-C(13)	120.9(2)
C(15)-C(14)-H(14A)	119.5
C(13)-C(14)-H(14A)	119.5
C(14)-C(15)-C(6)	121.4(2)
C(14)-C(15)-H(15A)	119.3

C(6)-C(15)-H(15A)	119.3
C(3)-C(16)-C(17)	112.28(18)
C(3)-C(16)-H(16A)	109.1
C(17)-C(16)-H(16A)	109.1
C(3)-C(16)-H(16B)	109.1
C(17)-C(16)-H(16B)	109.1
H(16A)-C(16)-H(16B)	107.9
C(18)-C(17)-C(16)	112.8(3)
C(18)-C(17)-H(17A)	109.0
C(16)-C(17)-H(17A)	109.0
C(18)-C(17)-H(17B)	109.0
C(16)-C(17)-H(17B)	109.0
H(17A)-C(17)-H(17B)	107.8
C(17)-C(18)-H(18A)	109.5
C(17)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(17)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
O(2)-C(19)-O(1)	122.9(2)
O(2)-C(19)-C(2)	125.9(2)
O(1)-C(19)-C(2)	111.12(15)
O(1)-C(20)-H(20A)	109.5
O(1)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
O(1)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(19)-O(1)-C(20)	115.50(17)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **127**. 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)	37(1)	43(2)	40(1)	-3(1)	-1(1)	0(1)
C(2)	36(1)	50(2)	41(1)	-4(1)	1(1)	-5(1)
C(3)	37(1)	57(2)	45(1)	-10(1)	3(1)	-5(1)
C(4)	37(1)	47(2)	53(1)	-7(1)	1(1)	1(1)
C(5)	33(1)	37(2)	46(1)	-4(1)	-1(1)	-4(1)
C(6)	30(1)	39(2)	45(1)	-2(1)	-4(1)	-4(1)
C(7)	33(1)	36(2)	44(1)	5(1)	-3(1)	3(1)

C(8)	32(1)	40(2)	43(1)	2(1)	-2(1)	-3(1)
C(9)	45(1)	45(2)	48(1)	4(1)	1(1)	7(1)
C(10)	53(1)	58(2)	48(1)	0(1)	6(1)	4(1)
C(11)	52(1)	60(2)	45(1)	9(1)	0(1)	-5(1)
C(12)	46(1)	42(2)	50(1)	9(1)	-6(1)	-2(1)
C(13)	32(1)	38(2)	49(1)	3(1)	-5(1)	-5(1)
C(14)	41(1)	35(2)	57(1)	3(1)	-7(1)	2(1)
C(15)	36(1)	39(2)	51(1)	-4(1)	-2(1)	1(1)
C(16)	52(1)	60(2)	52(1)	-18(1)	9(1)	-3(1)
C(17)	50(1)	75(3)	49(1)	-7(1)	10(1)	2(1)
C(18)	77(2)	91(3)	69(2)	-7(2)	17(1)	-30(2)
C(19)	42(1)	59(2)	40(1)	-3(1)	0(1)	-9(1)
C(20)	51(1)	77(3)	52(1)	14(1)	-8(1)	1(1)
O(1)	50(1)	60(2)	40(1)	6(1)	-1(1)	8(1)
O(2)	76(1)	83(2)	35(1)	-4(1)	2(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **127**.

	x	y	z	U(eq)
H(1A)	-5803	-7434	-7831	48
H(1B)	-7304	-9220	-7946	48
H(4A)	-9378	-3063	-7726	55
H(7A)	-6560	-8118	-9304	45
H(9A)	-5724	-9252	-10645	55
H(10A)	-5677	-8441	-11975	63
H(11A)	-7030	-5068	-12495	63
H(12A)	-8324	-2444	-11675	56
H(14A)	-9059	-1192	-10309	53
H(15A)	-9058	-1957	-8985	51
H(16A)	-8945	-2646	-6088	66
H(16B)	-8728	-5186	-5651	66
H(17A)	-11453	-3907	-5698	69
H(17B)	-11428	-4029	-6635	69
H(18A)	-12614	-7494	-6141	118
H(18B)	-11044	-8083	-5632	118
H(18C)	-11001	-8212	-6568	118
H(20A)	-4425	-13339	-6226	90
H(20B)	-5913	-12925	-5670	90
H(20C)	-4403	-11171	-5606	90

Table 6. Torsion angles [°] for **127**.

C(5)-C(1)-C(2)-C(3)	1.1(2)
C(5)-C(1)-C(2)-C(19)	-178.4(2)
C(19)-C(2)-C(3)-C(4)	178.7(2)
C(1)-C(2)-C(3)-C(4)	-0.8(2)
C(19)-C(2)-C(3)-C(16)	-1.9(4)
C(1)-C(2)-C(3)-C(16)	178.5(2)
C(2)-C(3)-C(4)-C(5)	0.2(3)
C(16)-C(3)-C(4)-C(5)	-179.2(2)
C(3)-C(4)-C(5)-C(6)	-178.8(2)
C(3)-C(4)-C(5)-C(1)	0.5(3)
C(2)-C(1)-C(5)-C(4)	-1.0(2)
C(2)-C(1)-C(5)-C(6)	178.34(18)
C(4)-C(5)-C(6)-C(7)	-172.9(2)
C(1)-C(5)-C(6)-C(7)	7.9(3)
C(4)-C(5)-C(6)-C(15)	7.6(3)
C(1)-C(5)-C(6)-C(15)	-171.62(19)
C(15)-C(6)-C(7)-C(8)	-1.2(3)
C(5)-C(6)-C(7)-C(8)	179.31(18)
C(6)-C(7)-C(8)-C(13)	-0.2(3)
C(6)-C(7)-C(8)-C(9)	179.17(19)
C(13)-C(8)-C(9)-C(10)	-0.4(3)
C(7)-C(8)-C(9)-C(10)	-179.8(2)
C(8)-C(9)-C(10)-C(11)	-1.3(4)
C(9)-C(10)-C(11)-C(12)	1.5(4)
C(10)-C(11)-C(12)-C(13)	-0.1(3)
C(9)-C(8)-C(13)-C(12)	1.7(3)
C(7)-C(8)-C(13)-C(12)	-178.83(18)
C(9)-C(8)-C(13)-C(14)	-178.16(18)
C(7)-C(8)-C(13)-C(14)	1.3(3)
C(11)-C(12)-C(13)-C(8)	-1.5(3)
C(11)-C(12)-C(13)-C(14)	178.4(2)
C(8)-C(13)-C(14)-C(15)	-0.9(3)
C(12)-C(13)-C(14)-C(15)	179.2(2)
C(13)-C(14)-C(15)-C(6)	-0.5(3)
C(7)-C(6)-C(15)-C(14)	1.6(3)
C(5)-C(6)-C(15)-C(14)	-178.90(19)
C(2)-C(3)-C(16)-C(17)	-113.7(3)
C(4)-C(3)-C(16)-C(17)	65.6(3)
C(3)-C(16)-C(17)-C(18)	64.9(3)
C(3)-C(2)-C(19)-O(2)	-3.8(4)
C(1)-C(2)-C(19)-O(2)	175.7(2)
C(3)-C(2)-C(19)-O(1)	177.2(2)
C(1)-C(2)-C(19)-O(1)	-3.3(3)
O(2)-C(19)-O(1)-C(20)	0.4(3)

C(2)-C(19)-O(1)-C(20)	179.46(19)

Symmetry transformations used to generate equivalent atoms:

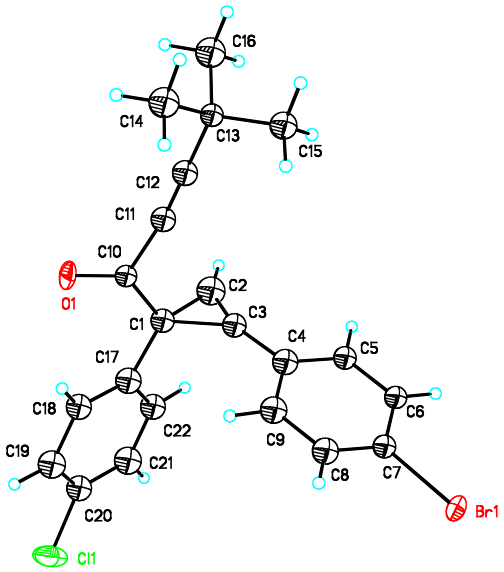

Table 1. Crystal data and structure refinement for **136**.

Identification code	**136**	
Empirical formula	C22 H18 Br Cl O	
Formula weight	413.72	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 5.9266(9) Å	α= 90°.
	b = 10.1987(17) Å	β= 97.890(8)°.
	c = 15.697(2) Å	γ = 90°.
Volume	939.8(3) $Å^3$	
Z	2	
Density (calculated)	1.462 Mg/m^3	
Absorption coefficient	4.327 mm^{-1}	
F(000)	420	
Crystal size	0.46 x 0.14 x 0.13 mm^3	
Theta range for data collection	2.84 to 65.05°.	
Index ranges	-6<=h<=6, 0<=k<=11, 0<=l<=18	
Reflections collected	3293	
Independent reflections	3293 [R(int) = 0.0000]	

Completeness to theta = 65.05°	97.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6031 and 0.2408
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3293 / 1 / 117
Goodness-of-fit on F^2	1.014
Final R indices [I>2sigma(I)]	R1 = 0.1438, wR2 = 0.3278
R indices (all data)	R1 = 0.1947, wR2 = 0.3859
Absolute structure parameter	0.02(12)
Extinction coefficient	0.004(2)
Largest diff. peak and hole	1.875 and -2.664 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for **136**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	13224(4)	261(2)	1817(2)	50(1)
Cl(1)	16339(10)	7196(9)	5789(5)	67(2)
C(1)	7900(40)	6220(20)	3249(14)	37(5)
C(2)	6210(40)	5240(40)	3453(15)	55(6)
C(3)	7650(40)	4790(20)	3000(14)	37(5)
C(4)	8840(40)	3750(20)	2642(14)	42(5)
C(5)	8160(40)	2480(20)	2695(14)	35(5)
C(6)	9370(30)	1410(20)	2455(12)	32(4)
C(7)	11430(30)	1710(20)	2118(12)	32(4)
C(8)	12100(40)	2960(20)	2005(14)	41(5)
C(9)	10880(40)	3980(30)	2306(15)	43(6)
C(10)	6990(30)	7270(20)	2633(12)	30(4)
C(11)	5160(40)	6880(20)	1912(14)	37(5)
C(12)	3860(40)	6760(20)	1265(14)	38(5)
C(13)	2320(30)	6626(19)	465(12)	30(4)
C(14)	2900(40)	7710(20)	-116(16)	49(6)
C(15)	2530(30)	5350(30)	30(12)	41(4)
C(16)	-160(40)	6800(30)	626(17)	53(6)
C(17)	10020(40)	6580(20)	3897(14)	45(5)
C(18)	11470(40)	7550(20)	3720(15)	42(5)
C(19)	13450(50)	7770(30)	4376(18)	51(7)
C(20)	13840(40)	6970(20)	5075(15)	44(5)
C(21)	12360(40)	5990(30)	5212(17)	55(6)
C(22)	10390(40)	5780(20)	4636(14)	45(5)
O(1)	7340(30)	8415(15)	2769(14)	60(5)

Table 3. Bond lengths [Å] and angles [°] for **136**.

Br(1)-C(7)	1.92(2)	C(22)-H(22A)	0.9500
Cl(1)-C(20)	1.75(2)		
C(1)-C(2)	1.48(4)	C(2)-C(1)-C(10)	115.2(19)
C(1)-C(10)	1.49(3)	C(2)-C(1)-C(3)	50.1(18)
C(1)-C(3)	1.52(3)	C(10)-C(1)-C(3)	120.6(19)
C(1)-C(17)	1.55(3)	C(2)-C(1)-C(17)	121.8(19)
C(2)-C(3)	1.27(3)	C(10)-C(1)-C(17)	117(2)
C(2)-H(2A)	0.9500	C(3)-C(1)-C(17)	116(2)
C(3)-C(4)	1.43(3)	C(3)-C(2)-C(1)	66.4(18)
C(4)-C(5)	1.36(3)	C(3)-C(2)-H(2A)	146.8
C(4)-C(9)	1.40(3)	C(1)-C(2)-H(2A)	146.8
C(5)-C(6)	1.38(3)	C(2)-C(3)-C(4)	154(3)
C(5)-H(5A)	0.9500	C(2)-C(3)-C(1)	63(2)
C(6)-C(7)	1.43(3)	C(4)-C(3)-C(1)	141(2)
C(6)-H(6A)	0.9500	C(5)-C(4)-C(9)	118(2)
C(7)-C(8)	1.35(3)	C(5)-C(4)-C(3)	121(2)
C(8)-C(9)	1.39(3)	C(9)-C(4)-C(3)	121(2)
C(8)-H(8A)	0.9500	C(4)-C(5)-C(6)	124(2)
C(9)-H(9A)	0.9500	C(4)-C(5)-H(5A)	118.0
C(10)-O(1)	1.20(3)	C(6)-C(5)-H(5A)	118.0
C(10)-C(11)	1.51(3)	C(5)-C(6)-C(7)	116.1(19)
C(11)-C(12)	1.20(3)	C(5)-C(6)-H(6A)	122.0
C(12)-C(13)	1.45(3)	C(7)-C(6)-H(6A)	122.0
C(13)-C(15)	1.48(3)	C(8)-C(7)-C(6)	122(2)
C(13)-C(14)	1.51(3)	C(8)-C(7)-Br(1)	120.8(16)
C(13)-C(16)	1.53(3)	C(6)-C(7)-Br(1)	117.4(15)
C(14)-H(14A)	0.9800	C(7)-C(8)-C(9)	119(2)
C(14)-H(14B)	0.9800	C(7)-C(8)-H(8A)	120.4
C(14)-H(14C)	0.9800	C(9)-C(8)-H(8A)	120.4
C(15)-H(15A)	0.9800	C(8)-C(9)-C(4)	121(2)
C(15)-H(15B)	0.9800	C(8)-C(9)-H(9A)	119.6
C(15)-H(15C)	0.9800	C(4)-C(9)-H(9A)	119.6
C(16)-H(16A)	0.9800	O(1)-C(10)-C(1)	123(2)
C(16)-H(16B)	0.9800	O(1)-C(10)-C(11)	118.9(19)
C(16)-H(16C)	0.9800	C(1)-C(10)-C(11)	117.1(18)
C(17)-C(18)	1.36(3)	C(12)-C(11)-C(10)	168(2)
C(17)-C(22)	1.41(3)	C(11)-C(12)-C(13)	179(2)
C(18)-C(19)	1.47(3)	C(12)-C(13)-C(15)	113.5(18)
C(18)-H(18A)	0.9500	C(12)-C(13)-C(14)	106.5(18)
C(19)-C(20)	1.36(4)	C(15)-C(13)-C(14)	109.0(17)
C(19)-H(19A)	0.9500	C(12)-C(13)-C(16)	110.5(18)
C(20)-C(21)	1.37(4)	C(15)-C(13)-C(16)	108.5(18)
C(21)-C(22)	1.39(3)	C(14)-C(13)-C(16)	108.7(18)
C(21)-H(21A)	0.9500	C(13)-C(14)-H(14A)	109.5

C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(13)-C(16)-H(16A)	109.5
C(13)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(13)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(18)-C(17)-C(22)	124(2)
C(18)-C(17)-C(1)	121(2)
C(22)-C(17)-C(1)	115(2)
C(17)-C(18)-C(19)	116(2)
C(17)-C(18)-H(18A)	122.1
C(19)-C(18)-H(18A)	122.1
C(20)-C(19)-C(18)	120(2)
C(20)-C(19)-H(19A)	119.9
C(18)-C(19)-H(19A)	119.9
C(19)-C(20)-C(21)	122(2)
C(19)-C(20)-Cl(1)	118(2)
C(21)-C(20)-Cl(1)	120(2)
C(20)-C(21)-C(22)	121(3)
C(20)-C(21)-H(21A)	119.7
C(22)-C(21)-H(21A)	119.7
C(21)-C(22)-C(17)	118(2)
C(21)-C(22)-H(22A)	121.1
C(17)-C(22)-H(22A)	121.1

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **136**. 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)	39(1)	27(1)	82(2)	-17(1)	7(1)	6(1)
Cl(1)	31(3)	98(6)	71(4)	-30(4)	-2(3)	7(4)
O(1)	63(12)	14(8)	93(15)	9(9)	-17(10)	-3(8)

Table 5. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for **136**.

	x	y	z	U(eq)
H(2A)	4914	5071	3733	67
H(5A)	6765	2310	2911	41
H(6A)	8863	539	2511	39
H(8A)	13385	3131	1723	50
H(9A)	11428	4856	2283	52
H(14A)	4477	7606	-231	73
H(14B)	2746	8560	165	73
H(14C)	1869	7681	-659	73
H(15A)	4079	5256	-109	62
H(15B)	1443	5326	-501	62
H(15C)	2191	4641	411	62
H(16A)	-552	6102	1011	80
H(16B)	-1170	6744	78	80
H(16C)	-338	7653	891	80
H(18A)	11213	8047	3205	50
H(19A)	14471	8469	4311	61
H(21A)	12684	5446	5705	65
H(22A)	9322	5120	4739	54

Table 6. Torsion angles [°] for **136**.

C(10)-C(1)-C(2)-C(3)	110(2)
C(17)-C(1)-C(2)-C(3)	-99(3)
C(1)-C(2)-C(3)-C(4)	163(5)
C(10)-C(1)-C(3)-C(2)	-99(2)
C(17)-C(1)-C(3)-C(2)	111(2)
C(2)-C(1)-C(3)-C(4)	-168(4)
C(10)-C(1)-C(3)-C(4)	94(4)
C(17)-C(1)-C(3)-C(4)	-57(4)
C(2)-C(3)-C(4)-C(5)	11(6)
C(1)-C(3)-C(4)-C(5)	165(3)
C(2)-C(3)-C(4)-C(9)	-163(5)
C(1)-C(3)-C(4)-C(9)	-8(5)
C(9)-C(4)-C(5)-C(6)	1(3)
C(3)-C(4)-C(5)-C(6)	-172(2)
C(4)-C(5)-C(6)-C(7)	-1(3)
C(5)-C(6)-C(7)-C(8)	-3(3)
C(5)-C(6)-C(7)-Br(1)	177.7(15)
C(6)-C(7)-C(8)-C(9)	7(3)
Br(1)-C(7)-C(8)-C(9)	-173.8(17)
C(7)-C(8)-C(9)-C(4)	-7(3)
C(5)-C(4)-C(9)-C(8)	3(3)
C(3)-C(4)-C(9)-C(8)	176(2)
C(2)-C(1)-C(10)-O(1)	131(3)
C(3)-C(1)-C(10)-O(1)	-172(2)
C(17)-C(1)-C(10)-O(1)	-22(3)
C(2)-C(1)-C(10)-C(11)	-36(3)
C(3)-C(1)-C(10)-C(11)	21(3)
C(17)-C(1)-C(10)-C(11)	170.6(18)
O(1)-C(10)-C(11)-C(12)	37(11)
C(1)-C(10)-C(11)-C(12)	-155(10)
C(10)-C(11)-C(12)-C(13)	34(100)
C(11)-C(12)-C(13)-C(15)	86(100)
C(11)-C(12)-C(13)-C(14)	-34(100)
C(11)-C(12)-C(13)-C(16)	-151(100)
C(2)-C(1)-C(17)-C(18)	-175(2)
C(10)-C(1)-C(17)-C(18)	-24(3)
C(3)-C(1)-C(17)-C(18)	127(2)
C(2)-C(1)-C(17)-C(22)	8(3)
C(10)-C(1)-C(17)-C(22)	159(2)
C(3)-C(1)-C(17)-C(22)	-49(3)
C(22)-C(17)-C(18)-C(19)	-3(4)
C(1)-C(17)-C(18)-C(19)	-179(2)
C(17)-C(18)-C(19)-C(20)	4(4)
C(18)-C(19)-C(20)-C(21)	-3(4)

C(18)-C(19)-C(20)-Cl(1)	175.0(19)
C(19)-C(20)-C(21)-C(22)	0(4)
Cl(1)-C(20)-C(21)-C(22)	-178.4(19)
C(20)-C(21)-C(22)-C(17)	2(4)
C(18)-C(17)-C(22)-C(21)	-1(4)
C(1)-C(17)-C(22)-C(21)	175(2)

Symmetry transformations used to generate equivalent atoms:

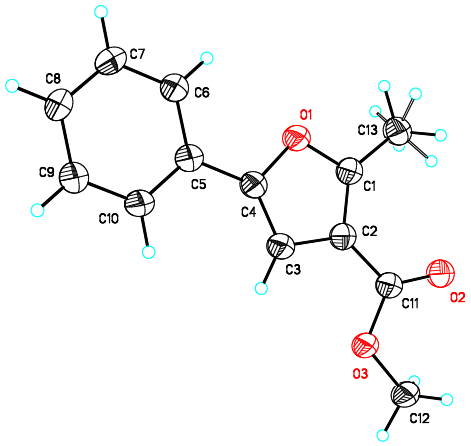

Table 1. Crystal data and structure refinement for **154**

Identification code	**154**	
Empirical formula	C13 H12 O3	
Formula weight	216.23	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.0151(5) Å	α= 90°.
	b = 12.6507(7) Å	β= 93.401(4)°.
	c = 8.3425(5) Å	γ = 90°.
Volume	1055.12(10) $Å^3$	
Z	4	
Density (calculated)	1.361 Mg/m^3	
Absorption coefficient	0.792 mm^{-1}	
F(000)	456	
Crystal size	0.22 x 0.21 x 0.13 mm^3	
Theta range for data collection	4.42 to 64.95°.	
Index ranges	-11<=h<=10, -14<=k<=14, -9<=l<=8	
Reflections collected	4163	
Independent reflections	1542 [R(int) = 0.0259]	
Completeness to theta = 64.95°	86.6 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9041 and 0.8451
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1542 / 0 / 146
Goodness-of-fit on F^2	1.014
Final R indices [I>2sigma(I)]	R1 = 0.0470, wR2 = 0.1394
R indices (all data)	R1 = 0.0609, wR2 = 0.1543
Largest diff. peak and hole	0.271 and -0.200 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for **154**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	8096(2)	3094(2)	855(3)	36(1)
C(2)	8964(2)	3782(2)	1622(3)	35(1)
C(3)	8581(2)	4821(2)	1088(3)	36(1)
C(4)	7527(2)	4707(2)	22(3)	34(1)
C(5)	6691(2)	5431(2)	-961(3)	34(1)
C(6)	5642(2)	5067(2)	-1989(3)	39(1)
C(7)	4872(2)	5766(2)	-2928(3)	42(1)
C(8)	5123(2)	6833(2)	-2856(3)	42(1)
C(9)	6159(2)	7207(2)	-1833(3)	45(1)
C(10)	6936(2)	6514(2)	-891(3)	41(1)
C(11)	10041(2)	3470(2)	2803(3)	35(1)
C(12)	11617(2)	4087(2)	4782(3)	41(1)
C(13)	7910(2)	1929(2)	868(3)	42(1)
O(1)	7215(1)	3642(1)	-135(2)	37(1)
O(2)	10388(2)	2570(1)	3109(2)	44(1)
O(3)	10587(2)	4317(1)	3546(2)	39(1)

Table 3. Bond lengths [Å] and angles [°] for **154**

C(1)-O(1)	1.362(3)	C(11)-O(2)	1.213(3)
C(1)-C(2)	1.363(3)	C(11)-O(3)	1.338(3)
C(1)-C(13)	1.485(3)	C(12)-O(3)	1.444(3)
C(2)-C(3)	1.432(3)	C(12)-H(12A)	0.9800
C(2)-C(11)	1.471(3)	C(12)-H(12B)	0.9800
C(3)-C(4)	1.347(3)	C(12)-H(12C)	0.9800
C(3)-H(3A)	0.9500	C(13)-H(13A)	0.9800
C(4)-O(1)	1.387(3)	C(13)-H(13B)	0.9800
C(4)-C(5)	1.460(3)	C(13)-H(13C)	0.9800
C(5)-C(10)	1.393(3)	C(13)-H(13D)	1.0372
C(5)-C(6)	1.394(3)	C(13)-H(13E)	1.0383
C(6)-C(7)	1.386(3)	C(13)-H(13F)	1.0149
C(6)-H(6A)	0.9500		
C(7)-C(8)	1.374(3)	O(1)-C(1)-C(2)	109.34(19)
C(7)-H(7A)	0.9500	O(1)-C(1)-C(13)	115.63(18)
C(8)-C(9)	1.387(3)	C(2)-C(1)-C(13)	135.0(2)
C(8)-H(8A)	0.9500	C(1)-C(2)-C(3)	106.80(19)
C(9)-C(10)	1.386(3)	C(1)-C(2)-C(11)	124.4(2)
C(9)-H(9A)	0.9500	C(3)-C(2)-C(11)	128.8(2)
C(10)-H(10A)	0.9500	C(4)-C(3)-C(2)	106.97(19)

C(4)-C(3)-H(3A)	126.5
C(2)-C(3)-H(3A)	126.5
C(3)-C(4)-O(1)	109.25(19)
C(3)-C(4)-C(5)	134.8(2)
O(1)-C(4)-C(5)	115.94(18)
C(10)-C(5)-C(6)	118.4(2)
C(10)-C(5)-C(4)	119.97(19)
C(6)-C(5)-C(4)	121.6(2)
C(7)-C(6)-C(5)	120.7(2)
C(7)-C(6)-H(6A)	119.6
C(5)-C(6)-H(6A)	119.6
C(8)-C(7)-C(6)	120.6(2)
C(8)-C(7)-H(7A)	119.7
C(6)-C(7)-H(7A)	119.7
C(7)-C(8)-C(9)	119.4(2)
C(7)-C(8)-H(8A)	120.3
C(9)-C(8)-H(8A)	120.3
C(10)-C(9)-C(8)	120.5(2)
C(10)-C(9)-H(9A)	119.7
C(8)-C(9)-H(9A)	119.7
C(9)-C(10)-C(5)	120.5(2)
C(9)-C(10)-H(10A)	119.8
C(5)-C(10)-H(10A)	119.8
O(2)-C(11)-O(3)	123.34(19)
O(2)-C(11)-C(2)	125.6(2)
O(3)-C(11)-C(2)	111.02(19)
O(3)-C(12)-H(12A)	109.5
O(3)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
O(3)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(1)-C(13)-H(13A)	109.5
C(1)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(1)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(1)-C(13)-H(13D)	109.0
H(13A)-C(13)-H(13D)	59.4
H(13B)-C(13)-H(13D)	53.3
H(13C)-C(13)-H(13D)	141.4
C(1)-C(13)-H(13E)	109.8
H(13A)-C(13)-H(13E)	52.2
H(13B)-C(13)-H(13E)	140.5
H(13C)-C(13)-H(13E)	60.2
H(13D)-C(13)-H(13E)	108.7
C(1)-C(13)-H(13F)	106.7
H(13A)-C(13)-H(13F)	143.8
H(13B)-C(13)-H(13F)	57.5
H(13C)-C(13)-H(13F)	56.1
H(13D)-C(13)-H(13F)	108.9
H(13E)-C(13)-H(13F)	113.7
C(1)-O(1)-C(4)	107.63(16)
C(11)-O(3)-C(12)	115.16(17)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **154**. 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)	33(1)	37(1)	-2(1)	-6(1)	3(1)
C(2)	34(1)	31(1)	38(1)	1(1)	-6(1)	2(1)
C(3)	35(1)	30(1)	40(1)	-2(1)	-7(1)	-3(1)
C(4)	35(1)	26(1)	39(1)	-1(1)	-5(1)	-1(1)
C(5)	33(1)	33(1)	35(1)	-2(1)	-4(1)	1(1)
C(6)	37(1)	32(1)	48(2)	-3(1)	-9(1)	0(1)
C(7)	36(1)	42(1)	48(1)	-3(1)	-14(1)	1(1)
C(8)	39(1)	39(1)	47(1)	2(1)	-12(1)	8(1)
C(9)	47(1)	33(1)	54(2)	-2(1)	-14(1)	4(1)
C(10)	42(1)	36(1)	42(1)	-4(1)	-15(1)	1(1)
C(11)	34(1)	31(1)	39(1)	-2(1)	-5(1)	0(1)
C(12)	40(1)	37(1)	45(1)	-1(1)	-16(1)	1(1)
C(13)	48(1)	30(1)	49(2)	0(1)	-8(1)	0(1)
O(1)	38(1)	30(1)	42(1)	0(1)	-10(1)	-1(1)
O(2)	46(1)	30(1)	54(1)	2(1)	-15(1)	3(1)
O(3)	38(1)	30(1)	47(1)	-1(1)	-17(1)	3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10 ^{3})
For **154**.

	x	y	z	U(eq)
H(3A)	8993	5467	1422	43
H(6A)	5453	4331	-2046	47
H(7A)	4164	5506	-3628	51
H(8A)	4592	7310	-3501	50
H(9A)	6338	7944	-1779	54
H(10A)	7642	6779	-192	49
H(12A)	11897	4744	5326	62
H(12B)	12386	3766	4295	62
H(12C)	11267	3596	5562	62
H(13A)	7155	1737	125	64
H(13B)	7728	1698	1955	64
H(13C)	8724	1583	534	64
H(13D)	6982	1758	1293	64
H(13E)	7942	1634	-290	64
H(13F)	8633	1632	1646	64

Table 6. Torsion angles [°] for **154**

O(1)-C(1)-C(2)-C(3)	0.8(3)
C(13)-C(1)-C(2)-C(3)	-178.9(2)
O(1)-C(1)-C(2)-C(11)	179.00(19)
C(13)-C(1)-C(2)-C(11)	-0.7(4)
C(1)-C(2)-C(3)-C(4)	-0.8(3)
C(11)-C(2)-C(3)-C(4)	-178.9(2)
C(2)-C(3)-C(4)-O(1)	0.5(3)
C(2)-C(3)-C(4)-C(5)	-179.1(2)
C(3)-C(4)-C(5)-C(10)	0.0(4)
O(1)-C(4)-C(5)-C(10)	-179.58(19)
C(3)-C(4)-C(5)-C(6)	179.7(3)
O(1)-C(4)-C(5)-C(6)	0.1(3)
C(10)-C(5)-C(6)-C(7)	0.6(4)
C(4)-C(5)-C(6)-C(7)	-179.1(2)
C(5)-C(6)-C(7)-C(8)	-0.4(4)
C(6)-C(7)-C(8)-C(9)	0.1(4)
C(7)-C(8)-C(9)-C(10)	0.0(4)
C(8)-C(9)-C(10)-C(5)	0.2(4)
C(6)-C(5)-C(10)-C(9)	-0.5(3)
C(4)-C(5)-C(10)-C(9)	179.2(2)
C(1)-C(2)-C(11)-O(2)	8.7(4)
C(3)-C(2)-C(11)-O(2)	-173.5(2)
C(1)-C(2)-C(11)-O(3)	-169.9(2)
C(3)-C(2)-C(11)-O(3)	7.9(3)
C(2)-C(1)-O(1)-C(4)	-0.5(2)
C(13)-C(1)-O(1)-C(4)	179.31(19)
C(3)-C(4)-O(1)-C(1)	-0.1(3)
C(5)-C(4)-O(1)-C(1)	179.65(18)
O(2)-C(11)-O(3)-C(12)	-1.3(3)
C(2)-C(11)-O(3)-C(12)	177.37(19)

Symmetry transformations used to generate equivalent atoms:

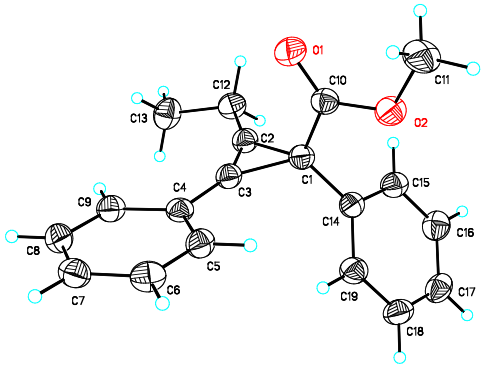

Table 1. Crystal data and structure refinement for **199**.

Identification code	**199**	
Empirical formula	C19 H18 O2	
Formula weight	278.33	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.9829(3) Å	α= 90°.
	b = 7.6696(3) Å	β= 93.905(2)°.
	c = 19.7014(6) Å	γ = 90°.
Volume	1504.93(9) $Å^3$	
Z	4	
Density (calculated)	1.228 Mg/m^3	
Absorption coefficient	0.619 mm^{-1}	
F(000)	592	
Crystal size	0.30 x 0.26 x 0.19 mm^3	
Theta range for data collection	4.44 to 67.83°.	
Index ranges	-11<=h<=11, -9<=k<=8, -23<=l<=23	
Reflections collected	9492	
Independent reflections	2620 [R(int) = 0.0151]	
Completeness to theta = 67.83°	96.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8915 and 0.8361	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2620 / 0 / 190	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2sigma(I)]	R1 = 0.0356, wR2 = 0.0932	
R indices (all data)	R1 = 0.0369, wR2 = 0.0944	
Largest diff. peak and hole	0.169 and -0.204 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for **199**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7613(1)	1253(1)	689(1)	27(1)
C(2)	8235(1)	2400(1)	1254(1)	29(1)
C(3)	6946(1)	2233(1)	1245(1)	28(1)
C(4)	5650(1)	2420(1)	1526(1)	27(1)

C(5)	4524(1)	1586(1)	1221(1)	31(1)
C(6)	3303(1)	1668(2)	1514(1)	35(1)
C(7)	3195(1)	2570(2)	2115(1)	35(1)
C(8)	4310(1)	3414(2)	2420(1)	35(1)
C(9)	5528(1)	3353(1)	2128(1)	31(1)
C(10)	7754(1)	-677(2)	802(1)	29(1)
C(11)	7621(2)	-3460(2)	286(1)	47(1)
C(12)	9552(1)	3039(2)	1538(1)	34(1)
C(13)	9436(1)	4309(2)	2122(1)	41(1)
C(14)	7542(1)	1910(1)	-33(1)	28(1)
C(15)	8699(1)	1936(2)	-390(1)	34(1)
C(16)	8674(1)	2581(2)	-1048(1)	38(1)
C(17)	7487(1)	3214(2)	-1360(1)	39(1)
C(18)	6334(1)	3201(2)	-1011(1)	39(1)
C(19)	6359(1)	2556(2)	-352(1)	33(1)
O(1)	7998(1)	-1353(1)	1349(1)	43(1)
O(2)	7557(1)	-1583(1)	223(1)	38(1)

Table 3. Bond lengths [Å] and angles [°] for **199**.

C(1)-C(10)	1.5023(15)	C(12)-H(12B)	0.9900
C(1)-C(14)	1.5064(15)	C(13)-H(13A)	0.9800
C(1)-C(3)	1.5188(15)	C(13)-H(13B)	0.9800
C(1)-C(2)	1.5192(15)	C(13)-H(13C)	0.9800
C(2)-C(3)	1.2924(16)	C(14)-C(19)	1.3907(16)
C(2)-C(12)	1.4764(16)	C(14)-C(15)	1.3927(16)
C(3)-C(4)	1.4493(15)	C(15)-C(16)	1.3861(17)
C(4)-C(5)	1.3932(16)	C(15)-H(15A)	0.9500
C(4)-C(9)	1.3971(16)	C(16)-C(17)	1.3842(18)
C(5)-C(6)	1.3851(17)	C(16)-H(16A)	0.9500
C(5)-H(5A)	0.9500	C(17)-C(18)	1.3801(18)
C(6)-C(7)	1.3833(17)	C(17)-H(17A)	0.9500
C(6)-H(6A)	0.9500	C(18)-C(19)	1.3885(17)
C(7)-C(8)	1.3879(17)	C(18)-H(18A)	0.9500
C(7)-H(7A)	0.9500	C(19)-H(19A)	0.9500
C(8)-C(9)	1.3807(17)		
C(8)-H(8A)	0.9500	C(10)-C(1)-C(14)	117.91(9)
C(9)-H(9A)	0.9500	C(10)-C(1)-C(3)	114.95(9)
C(10)-O(1)	1.2057(14)	C(14)-C(1)-C(3)	121.37(9)
C(10)-O(2)	1.3390(14)	C(10)-C(1)-C(2)	115.60(9)
C(11)-O(2)	1.4461(15)	C(14)-C(1)-C(2)	119.30(9)
C(11)-H(11A)	0.9800	C(3)-C(1)-C(2)	50.35(7)
C(11)-H(11B)	0.9800	C(3)-C(2)-C(12)	153.99(11)
C(11)-H(11C)	0.9800	C(3)-C(2)-C(1)	64.81(8)
C(12)-C(13)	1.5174(17)	C(12)-C(2)-C(1)	141.16(10)
C(12)-H(12A)	0.9900	C(2)-C(3)-C(4)	154.00(11)

C(2)-C(3)-C(1)	64.84(8)
C(4)-C(3)-C(1)	140.48(10)
C(5)-C(4)-C(9)	119.16(10)
C(5)-C(4)-C(3)	120.26(10)
C(9)-C(4)-C(3)	120.47(10)
C(6)-C(5)-C(4)	120.38(10)
C(6)-C(5)-H(5A)	119.8
C(4)-C(5)-H(5A)	119.8
C(7)-C(6)-C(5)	120.13(11)
C(7)-C(6)-H(6A)	119.9
C(5)-C(6)-H(6A)	119.9
C(6)-C(7)-C(8)	119.80(11)
C(6)-C(7)-H(7A)	120.1
C(8)-C(7)-H(7A)	120.1
C(9)-C(8)-C(7)	120.42(11)
C(9)-C(8)-H(8A)	119.8
C(7)-C(8)-H(8A)	119.8
C(8)-C(9)-C(4)	120.09(11)
C(8)-C(9)-H(9A)	120.0
C(4)-C(9)-H(9A)	120.0
O(1)-C(10)-O(2)	123.23(10)
O(1)-C(10)-C(1)	124.61(10)
O(2)-C(10)-C(1)	112.16(9)
O(2)-C(11)-H(11A)	109.5
O(2)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
O(2)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(2)-C(12)-C(13)	112.83(10)
C(2)-C(12)-H(12A)	109.0
C(13)-C(12)-H(12A)	109.0
C(2)-C(12)-H(12B)	109.0
C(13)-C(12)-H(12B)	109.0
H(12A)-C(12)-H(12B)	107.8
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(19)-C(14)-C(15)	118.38(10)
C(19)-C(14)-C(1)	121.93(10)
C(15)-C(14)-C(1)	119.64(10)
C(16)-C(15)-C(14)	120.96(11)
C(16)-C(15)-H(15A)	119.5
C(14)-C(15)-H(15A)	119.5
C(17)-C(16)-C(15)	120.01(12)
C(17)-C(16)-H(16A)	120.0
C(15)-C(16)-H(16A)	120.0
C(18)-C(17)-C(16)	119.65(11)
C(18)-C(17)-H(17A)	120.2
C(16)-C(17)-H(17A)	120.2
C(17)-C(18)-C(19)	120.38(11)
C(17)-C(18)-H(18A)	119.8
C(19)-C(18)-H(18A)	119.8
C(18)-C(19)-C(14)	120.62(11)
C(18)-C(19)-H(19A)	119.7
C(14)-C(19)-H(19A)	119.7
C(10)-O(2)-C(11)	116.12(9)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **199**. 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)	26(1)	28(1)	0(1)	0(1)	1(1)
C(2)	33(1)	27(1)	28(1)	0(1)	-1(1)	1(1)
C(3)	33(1)	25(1)	26(1)	-1(1)	-2(1)	1(1)
C(4)	31(1)	22(1)	28(1)	2(1)	-1(1)	2(1)
C(5)	36(1)	27(1)	30(1)	-3(1)	-2(1)	-1(1)
C(6)	31(1)	33(1)	40(1)	1(1)	-3(1)	-4(1)
C(7)	33(1)	33(1)	38(1)	5(1)	5(1)	4(1)
C(8)	42(1)	32(1)	31(1)	-3(1)	2(1)	6(1)
C(9)	35(1)	27(1)	31(1)	-3(1)	-4(1)	0(1)
C(10)	27(1)	29(1)	30(1)	2(1)	2(1)	1(1)
C(11)	60(1)	23(1)	56(1)	-2(1)	-6(1)	-1(1)
C(12)	30(1)	36(1)	36(1)	0(1)	-1(1)	-3(1)
C(13)	38(1)	49(1)	37(1)	-7(1)	-2(1)	-10(1)
C(14)	34(1)	20(1)	29(1)	-2(1)	-1(1)	-2(1)
C(15)	35(1)	32(1)	34(1)	3(1)	-1(1)	0(1)
C(16)	44(1)	36(1)	35(1)	3(1)	6(1)	-4(1)
C(17)	56(1)	30(1)	29(1)	3(1)	-2(1)	-3(1)
C(18)	45(1)	33(1)	36(1)	2(1)	-9(1)	4(1)
C(19)	36(1)	29(1)	35(1)	0(1)	-1(1)	1(1)
O(1)	60(1)	35(1)	33(1)	7(1)	3(1)	8(1)
O(2)	53(1)	22(1)	37(1)	-1(1)	-6(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **199**.

	x	y	z	U(eq)
H(5A)	4595	958	809	37
H(6A)	2539	1103	1301	42
H(7A)	2361	2612	2319	42
H(8A)	4235	4037	2832	42
H(9A)	6283	3946	2336	37
H(11A)	7465	-3991	-165	70
H(11B)	6932	-3859	581	70
H(11C)	8510	-3800	483	70
H(12A)	10019	3621	1173	41
H(12B)	10105	2032	1700	41
H(13A)	10335	4689	2291	62
H(13B)	8990	3735	2489	62
H(13C)	8908	5324	1962	62
H(15A)	9518	1505	-180	40
H(16A)	9471	2588	-1286	46
H(17A)	7467	3655	-1811	46
H(18A)	5519	3636	-1223	46
H(19A)	5559	2555	-116	40

Table 6. Torsion angles [°] for **199**.

C(10)-C(1)-C(2)-C(3)	-102.14(11)
C(14)-C(1)-C(2)-C(3)	108.07(11)
C(10)-C(1)-C(2)-C(12)	75.90(18)
C(14)-C(1)-C(2)-C(12)	-73.88(18)
C(3)-C(1)-C(2)-C(12)	178.04(18)
C(12)-C(2)-C(3)-C(4)	-8.3(4)
C(1)-C(2)-C(3)-C(4)	168.9(2)
C(12)-C(2)-C(3)-C(1)	-177.2(3)
C(10)-C(1)-C(3)-C(2)	103.50(11)
C(14)-C(1)-C(3)-C(2)	-103.84(11)
C(10)-C(1)-C(3)-C(4)	-68.86(17)
C(14)-C(1)-C(3)-C(4)	83.80(17)
C(2)-C(1)-C(3)-C(4)	-172.36(17)
C(2)-C(3)-C(4)-C(5)	-169.2(2)

C(1)-C(3)-C(4)-C(5)	-5.2(2)
C(2)-C(3)-C(4)-C(9)	7.1(3)
C(1)-C(3)-C(4)-C(9)	171.18(13)
C(9)-C(4)-C(5)-C(6)	-0.64(16)
C(3)-C(4)-C(5)-C(6)	175.75(10)
C(4)-C(5)-C(6)-C(7)	-0.43(17)
C(5)-C(6)-C(7)-C(8)	0.88(17)
C(6)-C(7)-C(8)-C(9)	-0.25(17)
C(7)-C(8)-C(9)-C(4)	-0.83(17)
C(5)-C(4)-C(9)-C(8)	1.26(16)
C(3)-C(4)-C(9)-C(8)	-175.11(10)
C(14)-C(1)-C(10)-O(1)	169.76(10)
C(3)-C(1)-C(10)-O(1)	-36.58(15)
C(2)-C(1)-C(10)-O(1)	19.54(16)
C(14)-C(1)-C(10)-O(2)	-11.19(14)
C(3)-C(1)-C(10)-O(2)	142.47(9)
C(2)-C(1)-C(10)-O(2)	-161.41(9)
C(3)-C(2)-C(12)-C(13)	-7.4(3)
C(1)-C(2)-C(12)-C(13)	176.67(13)
C(10)-C(1)-C(14)-C(19)	108.57(12)
C(3)-C(1)-C(14)-C(19)	-43.32(15)
C(2)-C(1)-C(14)-C(19)	-102.34(12)
C(10)-C(1)-C(14)-C(15)	-73.75(13)
C(3)-C(1)-C(14)-C(15)	134.36(11)
C(2)-C(1)-C(14)-C(15)	75.34(13)
C(19)-C(14)-C(15)-C(16)	-0.33(17)
C(1)-C(14)-C(15)-C(16)	-178.09(11)
C(14)-C(15)-C(16)-C(17)	0.12(18)
C(15)-C(16)-C(17)-C(18)	0.08(18)
C(16)-C(17)-C(18)-C(19)	-0.07(18)
C(17)-C(18)-C(19)-C(14)	-0.14(18)
C(15)-C(14)-C(19)-C(18)	0.34(16)
C(1)-C(14)-C(19)-C(18)	178.04(10)
O(1)-C(10)-O(2)-C(11)	1.38(16)
C(1)-C(10)-O(2)-C(11)	-177.69(10)

Symmetry transformations used to generate equivalent atoms:

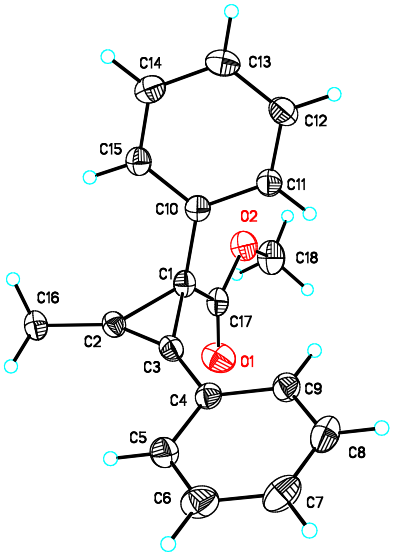

Table 1. Crystal data and structure refinement for **243**.

Identification code	**243**	
Empirical formula	C18 H16 O2	
Formula weight	264.31	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 10.7312(6) Å	α= 90°.
	b = 6.0144(4) Å	β= 103.150(2)°.
	c = 11.0902(7) Å	γ = 90°.
Volume	697.01(7) $Å^3$	
Z	2	
Density (calculated)	1.259 Mg/m^3	
Absorption coefficient	0.642 mm^{-1}	
F(000)	280	
Crystal size	0.44 x 0.22 x 0.18 mm^3	
Theta range for data collection	4.09 to 69.41°.	
Index ranges	-12<=h<=12, -7<=k<=5, -12<=l<=13	
Reflections collected	4247	
Independent reflections	1916 [R(int) = 0.0138]	
Completeness to theta = 69.41°	96.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8932 and 0.7654	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1916 / 1 / 181	

Goodness-of-fit on F^2	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0299, wR2 = 0.0819
R indices (all data)	R1 = 0.0301, wR2 = 0.0821
Absolute structure parameter	0.0(2)
Largest diff. peak and hole	0.156 and -0.207 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for **243**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7459(1)	5929(3)	7819(1)	26(1)
C(2)	8675(1)	4589(3)	8330(1)	27(1)
C(3)	8813(1)	6269(3)	7642(1)	27(1)
C(4)	9591(1)	7814(3)	7131(1)	27(1)
C(5)	10918(1)	7467(3)	7353(1)	34(1)
C(6)	11681(2)	8978(4)	6919(2)	44(1)
C(7)	11152(2)	10825(4)	6268(1)	44(1)
C(8)	9843(2)	11200(3)	6046(1)	40(1)
C(9)	9067(1)	9685(3)	6477(1)	32(1)
C(10)	6955(1)	7490(3)	8652(1)	26(1)
C(11)	6291(1)	9417(3)	8188(1)	32(1)
C(12)	5890(1)	10933(3)	8964(1)	36(1)
C(13)	6146(1)	10536(3)	10235(1)	36(1)
C(14)	6800(1)	8637(3)	10703(1)	34(1)
C(15)	7200(1)	7121(3)	9926(1)	29(1)
C(16)	9192(1)	2711(3)	9146(1)	32(1)
C(17)	6520(1)	4886(3)	6748(1)	29(1)
C(18)	4324(2)	4249(4)	5876(2)	44(1)
O(1)	6798(1)	3834(3)	5932(1)	47(1)
O(2)	5303(1)	5246(2)	6826(1)	36(1)

Table 3. Bond lengths [Å] and angles [°] for **243**.

C(1)-C(10)	1.501(2)
C(1)-C(17)	1.5081(19)
C(1)-C(3)	1.5242(18)
C(1)-C(2)	1.528(2)
C(2)-C(3)	1.295(2)
C(2)-C(16)	1.475(2)
C(3)-C(4)	1.448(2)
C(4)-C(9)	1.387(2)
C(4)-C(5)	1.4042(19)
C(5)-C(6)	1.381(3)
C(5)-H(5A)	0.9500
C(6)-C(7)	1.375(3)
C(6)-H(6A)	0.9500
C(7)-C(8)	1.389(3)
C(7)-H(7A)	0.9500
C(8)-C(9)	1.390(2)
C(8)-H(8A)	0.9500
C(9)-H(9A)	0.9500
C(10)-C(15)	1.3952(19)
C(10)-C(11)	1.396(2)
C(11)-C(12)	1.387(2)
C(11)-H(11A)	0.9500
C(12)-C(13)	1.394(2)
C(12)-H(12A)	0.9500
C(13)-C(14)	1.379(3)
C(13)-H(13A)	0.9500
C(14)-C(15)	1.388(2)
C(14)-H(14A)	0.9500
C(15)-H(15A)	0.9500
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-O(1)	1.197(2)
C(17)-O(2)	1.3454(18)
C(18)-O(2)	1.4386(19)
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(10)-C(1)-C(17)	118.34(12)
C(10)-C(1)-C(3)	118.85(12)
C(17)-C(1)-C(3)	116.14(11)
C(10)-C(1)-C(2)	119.86(11)
C(17)-C(1)-C(2)	115.72(13)

C(3)-C(1)-C(2)	50.21(9)
C(3)-C(2)-C(16)	151.82(13)
C(3)-C(2)-C(1)	64.73(10)
C(16)-C(2)-C(1)	143.31(13)
C(2)-C(3)-C(4)	152.26(13)
C(2)-C(3)-C(1)	65.06(10)
C(4)-C(3)-C(1)	142.02(14)
C(9)-C(4)-C(5)	119.15(15)
C(9)-C(4)-C(3)	121.60(12)
C(5)-C(4)-C(3)	119.17(14)
C(6)-C(5)-C(4)	119.91(16)
C(6)-C(5)-H(5A)	120.0
C(4)-C(5)-H(5A)	120.0
C(7)-C(6)-C(5)	120.55(15)
C(7)-C(6)-H(6A)	119.7
C(5)-C(6)-H(6A)	119.7
C(6)-C(7)-C(8)	120.24(16)
C(6)-C(7)-H(7A)	119.9
C(8)-C(7)-H(7A)	119.9
C(7)-C(8)-C(9)	119.61(17)
C(7)-C(8)-H(8A)	120.2
C(9)-C(8)-H(8A)	120.2
C(4)-C(9)-C(8)	120.53(14)
C(4)-C(9)-H(9A)	119.7
C(8)-C(9)-H(9A)	119.7
C(15)-C(10)-C(11)	117.86(14)
C(15)-C(10)-C(1)	120.83(13)
C(11)-C(10)-C(1)	121.22(12)
C(12)-C(11)-C(10)	121.47(13)
C(12)-C(11)-H(11A)	119.3
C(10)-C(11)-H(11A)	119.3
C(11)-C(12)-C(13)	119.80(16)
C(11)-C(12)-H(12A)	120.1
C(13)-C(12)-H(12A)	120.1
C(14)-C(13)-C(12)	119.27(15)
C(14)-C(13)-H(13A)	120.4
C(12)-C(13)-H(13A)	120.4
C(13)-C(14)-C(15)	120.84(13)
C(13)-C(14)-H(14A)	119.6
C(15)-C(14)-H(14A)	119.6
C(14)-C(15)-C(10)	120.75(15)
C(14)-C(15)-H(15A)	119.6
C(10)-C(15)-H(15A)	119.6
C(2)-C(16)-H(16A)	109.5
C(2)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5

C(2)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
O(1)-C(17)-O(2)	123.12(14)
O(1)-C(17)-C(1)	125.32(13)
O(2)-C(17)-C(1)	111.56(12)
O(2)-C(18)-H(18A)	109.5
O(2)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
O(2)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(17)-O(2)-C(18)	116.36(13)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **243**.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)	25(1)	26(1)	27(1)	3(1)	2(1)	0(1)
C(2)	27(1)	26(1)	26(1)	-2(1)	2(1)	2(1)
C(3)	25(1)	27(1)	27(1)	-2(1)	2(1)	4(1)
C(4)	30(1)	28(1)	22(1)	-3(1)	4(1)	0(1)
C(5)	32(1)	37(1)	33(1)	1(1)	5(1)	3(1)
C(6)	32(1)	58(1)	41(1)	-1(1)	10(1)	-9(1)
C(7)	51(1)	48(1)	36(1)	1(1)	12(1)	-19(1)
C(8)	57(1)	32(1)	30(1)	4(1)	7(1)	-3(1)
C(9)	36(1)	32(1)	27(1)	-1(1)	5(1)	3(1)
C(10)	21(1)	27(1)	30(1)	1(1)	5(1)	-4(1)
C(11)	31(1)	32(1)	33(1)	5(1)	9(1)	3(1)
C(12)	33(1)	31(1)	46(1)	3(1)	14(1)	5(1)
C(13)	30(1)	38(1)	41(1)	-9(1)	13(1)	-3(1)
C(14)	28(1)	44(1)	29(1)	-4(1)	6(1)	-5(1)
C(15)	23(1)	30(1)	31(1)	1(1)	2(1)	-3(1)
C(16)	33(1)	27(1)	32(1)	2(1)	1(1)	4(1)
C(17)	32(1)	25(1)	29(1)	4(1)	2(1)	-1(1)
C(18)	34(1)	46(1)	45(1)	1(1)	-7(1)	-8(1)
O(1)	42(1)	53(1)	42(1)	-17(1)	3(1)	0(1)
O(2)	27(1)	41(1)	36(1)	-2(1)	-2(1)	-3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **243**.

	x	y	z	U(eq)
H(5A)	11290	6194	7802	41
H(6A)	12578	8739	7071	52
H(7A)	11685	11849	5968	53
H(8A)	9479	12483	5603	48
H(9A)	8170	9934	6322	38
H(11A)	6108	9697	7323	38
H(12A)	5443	12238	8630	43
H(13A)	5872	11562	10773	43
H(14A)	6979	8362	11569	40
H(15A)	7645	5818	10265	35
H(16A)	10105	2532	9166	48
H(16B)	8734	1346	8828	48
H(16C)	9082	3006	9984	48
H(18A)	3480	4618	6021	66
H(18B)	4434	2631	5895	66
H(18C)	4389	4819	5065	66

Table 6. Torsion angles [°] for **243**.

C(10)-C(1)-C(2)-C(3)	-104.23(14)
C(17)-C(1)-C(2)-C(3)	103.61(14)
C(10)-C(1)-C(2)-C(16)	72.1(3)
C(17)-C(1)-C(2)-C(16)	-80.1(2)
C(3)-C(1)-C(2)-C(16)	176.3(2)
C(16)-C(2)-C(3)-C(4)	-5.8(5)
C(1)-C(2)-C(3)-C(4)	169.6(3)
C(16)-C(2)-C(3)-C(1)	-175.4(3)
C(10)-C(1)-C(3)-C(2)	106.32(14)
C(17)-C(1)-C(3)-C(2)	-102.73(15)
C(10)-C(1)-C(3)-C(4)	-65.8(2)
C(17)-C(1)-C(3)-C(4)	85.1(2)
C(2)-C(1)-C(3)-C(4)	-172.1(2)
C(2)-C(3)-C(4)-C(9)	-169.8(3)
C(1)-C(3)-C(4)-C(9)	-5.2(3)
C(2)-C(3)-C(4)-C(5)	7.1(4)
C(1)-C(3)-C(4)-C(5)	171.65(16)

C(9)-C(4)-C(5)-C(6)	-0.2(2)
C(3)-C(4)-C(5)-C(6)	-177.15(15)
C(4)-C(5)-C(6)-C(7)	0.0(3)
C(5)-C(6)-C(7)-C(8)	0.4(3)
C(6)-C(7)-C(8)-C(9)	-0.6(3)
C(5)-C(4)-C(9)-C(8)	0.0(2)
C(3)-C(4)-C(9)-C(8)	176.90(13)
C(7)-C(8)-C(9)-C(4)	0.4(2)
C(17)-C(1)-C(10)-C(15)	124.29(15)
C(3)-C(1)-C(10)-C(15)	-85.40(17)
C(2)-C(1)-C(10)-C(15)	-27.2(2)
C(17)-C(1)-C(10)-C(11)	-59.28(19)
C(3)-C(1)-C(10)-C(11)	91.02(16)
C(2)-C(1)-C(10)-C(11)	149.27(14)
C(15)-C(10)-C(11)-C(12)	0.4(2)
C(1)-C(10)-C(11)-C(12)	-176.09(13)
C(10)-C(11)-C(12)-C(13)	-0.3(2)
C(11)-C(12)-C(13)-C(14)	0.2(2)
C(12)-C(13)-C(14)-C(15)	-0.3(2)
C(13)-C(14)-C(15)-C(10)	0.4(2)
C(11)-C(10)-C(15)-C(14)	-0.5(2)
C(1)-C(10)-C(15)-C(14)	176.09(13)
C(10)-C(1)-C(17)-O(1)	170.51(15)
C(3)-C(1)-C(17)-O(1)	19.4(2)
C(2)-C(1)-C(17)-O(1)	-36.9(2)
C(10)-C(1)-C(17)-O(2)	-10.6(2)
C(3)-C(1)-C(17)-O(2)	-161.66(13)
C(2)-C(1)-C(17)-O(2)	142.04(13)
O(1)-C(17)-O(2)-C(18)	1.3(2)
C(1)-C(17)-O(2)-C(18)	-177.68(14)

Symmetry transformations used to generate equivalent atoms:

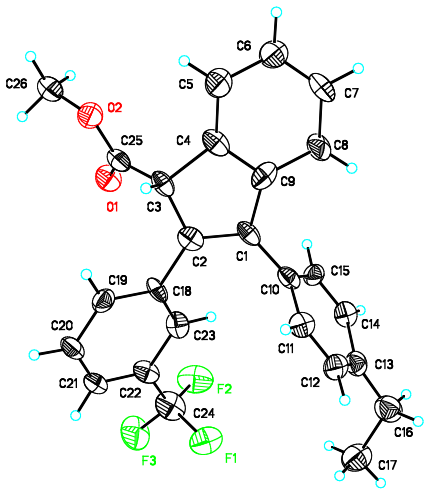

Table 1. Crystal data and structure refinement for **258.**

Identification code	**258**	
Empirical formula	C26 H21 F3 O2	
Formula weight	422.43	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	Pna2(1)	
Unit cell dimensions	a = 17.9833(17) Å	α= 90°.
	b = 5.7116(6) Å	β= 90°.
	c = 40.992(4) Å	γ = 90°.
Volume	4210.4(7) $Å^3$	
Z	8	
Density (calculated)	1.333 Mg/m^3	
Absorption coefficient	0.846 mm^{-1}	
F(000)	1760	
Crystal size	0.32 x 0.11 x 0.08 mm^3	
Theta range for data collection	2.16 to 69.20°.	
Index ranges	-20<=h<=20, -6<=k<=6, -40<=l<=45	
Reflections collected	13689	
Independent reflections	5195 [R(int) = 0.0589]	
Completeness to theta = 69.20°	91.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9354 and 0.7735	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5195 / 1 / 559	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.1049, wR2 = 0.2930	

R indices (all data)	R1 = 0.1403, wR2 = 0.3283
Absolute structure parameter	0.4(6)
Largest diff. peak and hole	0.426 and -0.365 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3)
for **258**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7225(4)	909(17)	9913(3)	46(3)
C(2)	7565(5)	-645(18)	9705(3)	48(3)
C(3)	7254(5)	-502(17)	9367(3)	47(3)
C(4)	6684(5)	1510(20)	9405(3)	55(3)
C(5)	6228(6)	2530(30)	9173(4)	80(5)
C(6)	5780(6)	4480(30)	9268(4)	75(4)
C(7)	5763(6)	5150(20)	9590(4)	67(4)
C(8)	6205(5)	4090(20)	9827(3)	65(3)
C(9)	6674(5)	2160(20)	9730(3)	55(3)
C(10)	7335(5)	1127(19)	10266(3)	49(3)
C(11)	7177(5)	-500(20)	10489(3)	54(3)
C(12)	7335(5)	-330(30)	10811(3)	62(3)
C(13)	7701(6)	1540(20)	10933(3)	56(3)
C(14)	7864(5)	3450(20)	10711(3)	55(3)
C(15)	7687(5)	3190(20)	10391(3)	51(3)
C(16)	7916(8)	1660(30)	11285(4)	80(4)
C(17)	8554(7)	120(30)	11386(4)	89(5)
C(18)	8178(5)	-2270(20)	9790(3)	50(3)
C(19)	8310(6)	-4290(20)	9615(3)	55(3)
C(20)	8897(6)	-5760(20)	9693(3)	56(3)
C(21)	9359(6)	-5250(20)	9947(3)	57(3)
C(22)	9276(5)	-3180(20)	10119(3)	54(3)
C(23)	8676(6)	-1624(19)	10037(3)	54(3)
C(24)	9731(6)	-2570(30)	10393(5)	80(5)
C(25)	7769(6)	-39(18)	9096(3)	53(3)
C(26)	7885(7)	230(20)	8525(3)	70(4)
C(1B)	5189(5)	9140(20)	7534(3)	53(3)
C(2B)	4837(5)	10635(19)	7738(3)	51(3)
C(3B)	5193(6)	10530(30)	8077(3)	62(3)
C(4B)	5751(5)	8460(30)	8047(3)	60(3)
C(5B)	6193(6)	7510(18)	8282(4)	56(3)
C(6B)	6666(6)	5690(20)	8174(4)	66(4)
C(7B)	6658(5)	4990(30)	7855(3)	71(4)
C(8B)	6204(6)	5980(20)	7625(3)	61(3)

C(9B)	5749(5)	7759(19)	7727(3)	50(3)
C(10B)	5057(5)	8750(20)	7183(3)	50(3)
C(11B)	5216(5)	10530(20)	6951(3)	52(3)
C(12B)	5044(6)	10260(20)	6628(3)	55(3)
C(13B)	4686(6)	8090(20)	6516(3)	56(3)
C(14B)	4561(6)	6500(30)	6739(3)	60(3)
C(15B)	4730(6)	6700(20)	7069(3)	59(3)
C(16B)	4488(6)	7920(20)	6166(3)	60(3)
C(17B)	4082(7)	5760(30)	6068(4)	90(5)
C(18B)	4206(5)	12260(20)	7662(3)	53(3)
C(19B)	4108(5)	14311(17)	7837(3)	53(3)
C(20B)	3528(6)	15830(20)	7762(3)	60(3)
C(21B)	3044(5)	15290(20)	7510(3)	63(3)
C(22B)	3148(6)	13160(20)	7337(3)	52(3)
C(23B)	3706(5)	11720(20)	7407(3)	55(3)
C(24B)	2636(6)	12619(18)	7057(3)	49(3)
C(25B)	4634(6)	10110(20)	8355(3)	56(3)
C(26B)	4506(6)	9780(30)	8924(3)	65(4)
F(1)	9471(4)	-3026(17)	10681(2)	84(3)
F(2)	9891(5)	-277(17)	10410(2)	99(3)
F(3)	10417(4)	-3510(20)	10383(2)	110(4)
F(1B)	2920(5)	13120(20)	6771(2)	111(4)
F(2B)	1991(4)	13700(20)	7075(3)	127(4)
F(3B)	2469(5)	10319(15)	7046(2)	91(3)
O(1)	8416(4)	490(15)	9125(2)	64(2)
O(2)	7448(4)	-305(16)	8805(2)	63(2)
O(1B)	4003(4)	9476(18)	8320(2)	71(3)
O(2B)	4969(4)	10378(19)	8640(2)	70(3)

Table 3. Bond lengths [Å] and angles [°] for **258**.

C(1)-C(2)	1.375(16)	C(22)-C(23)	1.439(15)
C(1)-C(9)	1.434(16)	C(23)-H(23A)	0.9500
C(1)-C(10)	1.464(16)	C(24)-F(1)	1.296(19)
C(2)-C(18)	1.482(13)	C(24)-F(2)	1.342(17)
C(2)-C(3)	1.496(16)	C(24)-F(3)	1.349(15)
C(3)-C(25)	1.469(16)	C(25)-O(1)	1.208(13)
C(3)-C(4)	1.548(14)	C(25)-O(2)	1.336(14)
C(3)-H(3A)	1.0000	C(26)-O(2)	1.423(15)
C(4)-C(9)	1.381(17)	C(26)-H(26A)	0.9800
C(4)-C(5)	1.384(18)	C(26)-H(26B)	0.9800
C(5)-C(6)	1.43(2)	C(26)-H(26C)	0.9800
C(5)-H(5A)	0.9500	C(1B)-C(2B)	1.352(16)
C(6)-C(7)	1.38(2)	C(1B)-C(10B)	1.475(16)
C(6)-H(6A)	0.9500	C(1B)-C(9B)	1.507(16)
C(7)-C(8)	1.394(18)	C(2B)-C(18B)	1.497(15)
C(7)-H(7A)	0.9500	C(2B)-C(3B)	1.532(16)
C(8)-C(9)	1.446(18)	C(3B)-C(25B)	1.537(16)
C(8)-H(8A)	0.9500	C(3B)-C(4B)	1.557(18)
C(10)-C(11)	1.335(16)	C(3B)-H(3BA)	1.0000
C(10)-C(15)	1.435(17)	C(4B)-C(5B)	1.361(18)
C(11)-C(12)	1.356(17)	C(4B)-C(9B)	1.372(17)
C(11)-H(11A)	0.9500	C(5B)-C(6B)	1.415(17)
C(12)-C(13)	1.352(18)	C(5B)-H(5BA)	0.9500
C(12)-H(12A)	0.9500	C(6B)-C(7B)	1.366(19)
C(13)-C(14)	1.451(17)	C(6B)-H(6BA)	0.9500
C(13)-C(16)	1.493(19)	C(7B)-C(8B)	1.369(17)
C(14)-C(15)	1.359(17)	C(7B)-H(7BA)	0.9500
C(14)-H(14A)	0.9500	C(8B)-C(9B)	1.371(16)
C(15)-H(15A)	0.9500	C(8B)-H(8BA)	0.9500
C(16)-C(17)	1.506(19)	C(10B)-C(15B)	1.390(16)
C(16)-H(16A)	0.9900	C(10B)-C(11B)	1.419(16)
C(16)-H(16B)	0.9900	C(11B)-C(12B)	1.369(17)
C(17)-H(17A)	0.9800	C(11B)-H(11B)	0.9500
C(17)-H(17B)	0.9800	C(12B)-C(13B)	1.470(18)
C(17)-H(17C)	0.9800	C(12B)-H(12B)	0.9500
C(18)-C(19)	1.377(17)	C(13B)-C(14B)	1.308(18)
C(18)-C(23)	1.402(16)	C(13B)-C(16B)	1.484(17)
C(19)-C(20)	1.388(15)	C(14B)-C(15B)	1.390(17)
C(19)-H(19A)	0.9500	C(14B)-H(14B)	0.9500
C(20)-C(21)	1.364(17)	C(15B)-H(15B)	0.9500
C(20)-H(20A)	0.9500	C(16B)-C(17B)	1.49(2)
C(21)-C(22)	1.381(18)	C(16B)-H(16C)	0.9900
C(21)-H(21A)	0.9500	C(16B)-H(16D)	0.9900
C(22)-C(24)	1.43(2)	C(17B)-H(17D)	0.9800

C(17B)-H(17E)	0.9800	C(8)-C(7)-H(7A)	118.8
C(17B)-H(17F)	0.9800	C(7)-C(8)-C(9)	118.1(13)
C(18B)-C(19B)	1.387(17)	C(7)-C(8)-H(8A)	120.9
C(18B)-C(23B)	1.412(16)	C(9)-C(8)-H(8A)	120.9
C(19B)-C(20B)	1.391(16)	C(4)-C(9)-C(1)	111.3(11)
C(19B)-H(19B)	0.9500	C(4)-C(9)-C(8)	118.6(12)
C(20B)-C(21B)	1.386(18)	C(1)-C(9)-C(8)	129.6(12)
C(20B)-H(20B)	0.9500	C(11)-C(10)-C(15)	115.1(12)
C(21B)-C(22B)	1.419(18)	C(11)-C(10)-C(1)	125.9(11)
C(21B)-H(21B)	0.9500	C(15)-C(10)-C(1)	118.8(10)
C(22B)-C(23B)	1.329(16)	C(10)-C(11)-C(12)	124.9(12)
C(22B)-C(24B)	1.506(17)	C(10)-C(11)-H(11A)	117.6
C(23B)-H(23B)	0.9500	C(12)-C(11)-H(11A)	117.6
C(24B)-F(1B)	1.311(15)	C(13)-C(12)-C(11)	121.4(12)
C(24B)-F(2B)	1.316(13)	C(13)-C(12)-H(12A)	119.3
C(24B)-F(3B)	1.348(12)	C(11)-C(12)-H(12A)	119.3
C(25B)-O(1B)	1.200(14)	C(12)-C(13)-C(14)	117.5(12)
C(25B)-O(2B)	1.324(14)	C(12)-C(13)-C(16)	121.3(12)
C(26B)-O(2B)	1.472(13)	C(14)-C(13)-C(16)	121.2(12)
C(26B)-H(26D)	0.9800	C(15)-C(14)-C(13)	118.5(12)
C(26B)-H(26E)	0.9800	C(15)-C(14)-H(14A)	120.7
C(26B)-H(26F)	0.9800	C(13)-C(14)-H(14A)	120.7
		C(14)-C(15)-C(10)	122.5(11)
C(2)-C(1)-C(9)	107.6(11)	C(14)-C(15)-H(15A)	118.7
C(2)-C(1)-C(10)	127.5(9)	C(10)-C(15)-H(15A)	118.7
C(9)-C(1)-C(10)	124.6(10)	C(13)-C(16)-C(17)	116.0(13)
C(1)-C(2)-C(18)	126.0(11)	C(13)-C(16)-H(16A)	108.3
C(1)-C(2)-C(3)	111.9(9)	C(17)-C(16)-H(16A)	108.3
C(18)-C(2)-C(3)	122.0(10)	C(13)-C(16)-H(16B)	108.3
C(25)-C(3)-C(2)	118.2(8)	C(17)-C(16)-H(16B)	108.3
C(25)-C(3)-C(4)	111.1(9)	H(16A)-C(16)-H(16B)	107.4
C(2)-C(3)-C(4)	101.2(9)	C(16)-C(17)-H(17A)	109.5
C(25)-C(3)-H(3A)	108.6	C(16)-C(17)-H(17B)	109.5
C(2)-C(3)-H(3A)	108.6	H(17A)-C(17)-H(17B)	109.5
C(4)-C(3)-H(3A)	108.6	C(16)-C(17)-H(17C)	109.5
C(9)-C(4)-C(5)	122.8(12)	H(17A)-C(17)-H(17C)	109.5
C(9)-C(4)-C(3)	107.8(11)	H(17B)-C(17)-H(17C)	109.5
C(5)-C(4)-C(3)	129.4(13)	C(19)-C(18)-C(23)	119.0(9)
C(4)-C(5)-C(6)	118.4(14)	C(19)-C(18)-C(2)	122.0(11)
C(4)-C(5)-H(5A)	120.8	C(23)-C(18)-C(2)	118.8(10)
C(6)-C(5)-H(5A)	120.8	C(18)-C(19)-C(20)	121.3(11)
C(7)-C(6)-C(5)	119.5(13)	C(18)-C(19)-H(19A)	119.3
C(7)-C(6)-H(6A)	120.3	C(20)-C(19)-H(19A)	119.3
C(5)-C(6)-H(6A)	120.3	C(21)-C(20)-C(19)	120.5(11)
C(6)-C(7)-C(8)	122.3(12)	C(21)-C(20)-H(20A)	119.7
C(6)-C(7)-H(7A)	118.8	C(19)-C(20)-H(20A)	119.7

C(20)-C(21)-C(22)	120.4(10)	C(6B)-C(7B)-H(7BA)	118.6
C(20)-C(21)-H(21A)	119.8	C(8B)-C(7B)-H(7BA)	118.6
C(22)-C(21)-H(21A)	119.8	C(7B)-C(8B)-C(9B)	116.9(13)
C(21)-C(22)-C(24)	123.2(11)	C(7B)-C(8B)-H(8BA)	121.5
C(21)-C(22)-C(23)	119.4(10)	C(9B)-C(8B)-H(8BA)	121.5
C(24)-C(22)-C(23)	117.2(12)	C(8B)-C(9B)-C(4B)	120.4(12)
C(18)-C(23)-C(22)	119.0(10)	C(8B)-C(9B)-C(1B)	128.8(13)
C(18)-C(23)-H(23A)	120.5	C(4B)-C(9B)-C(1B)	110.7(10)
C(22)-C(23)-H(23A)	120.5	C(15B)-C(10B)-C(11B)	117.6(12)
F(1)-C(24)-F(2)	103.0(14)	C(15B)-C(10B)-C(1B)	121.7(11)
F(1)-C(24)-F(3)	106.1(14)	C(11B)-C(10B)-C(1B)	120.6(11)
F(2)-C(24)-F(3)	101.3(10)	C(12B)-C(11B)-C(10B)	121.4(11)
F(1)-C(24)-C(22)	117.3(10)	C(12B)-C(11B)-H(11B)	119.3
F(2)-C(24)-C(22)	113.8(14)	C(10B)-C(11B)-H(11B)	119.3
F(3)-C(24)-C(22)	113.6(14)	C(11B)-C(12B)-C(13B)	119.7(11)
O(1)-C(25)-O(2)	122.1(11)	C(11B)-C(12B)-H(12B)	120.1
O(1)-C(25)-C(3)	125.4(11)	C(13B)-C(12B)-H(12B)	120.1
O(2)-C(25)-C(3)	112.5(9)	C(14B)-C(13B)-C(12B)	116.3(12)
O(2)-C(26)-H(26A)	109.5	C(14B)-C(13B)-C(16B)	126.1(13)
O(2)-C(26)-H(26B)	109.5	C(12B)-C(13B)-C(16B)	117.6(11)
H(26A)-C(26)-H(26B)	109.5	C(13B)-C(14B)-C(15B)	125.7(14)
O(2)-C(26)-H(26C)	109.5	C(13B)-C(14B)-H(14B)	117.1
H(26A)-C(26)-H(26C)	109.5	C(15B)-C(14B)-H(14B)	117.1
H(26B)-C(26)-H(26C)	109.5	C(10B)-C(15B)-C(14B)	119.3(12)
C(2B)-C(1B)-C(10B)	128.7(11)	C(10B)-C(15B)-H(15B)	120.4
C(2B)-C(1B)-C(9B)	108.5(11)	C(14B)-C(15B)-H(15B)	120.4
C(10B)-C(1B)-C(9B)	122.8(11)	C(13B)-C(16B)-C(17B)	115.7(12)
C(1B)-C(2B)-C(18B)	128.1(11)	C(13B)-C(16B)-H(16C)	108.4
C(1B)-C(2B)-C(3B)	110.0(9)	C(17B)-C(16B)-H(16C)	108.4
C(18B)-C(2B)-C(3B)	121.9(10)	C(13B)-C(16B)-H(16D)	108.4
C(2B)-C(3B)-C(25B)	113.8(9)	C(17B)-C(16B)-H(16D)	108.4
C(2B)-C(3B)-C(4B)	103.2(9)	H(16C)-C(16B)-H(16D)	107.4
C(25B)-C(3B)-C(4B)	111.1(11)	C(16B)-C(17B)-H(17D)	109.5
C(2B)-C(3B)-H(3BA)	109.5	C(16B)-C(17B)-H(17E)	109.5
C(25B)-C(3B)-H(3BA)	109.5	H(17D)-C(17B)-H(17E)	109.5
C(4B)-C(3B)-H(3BA)	109.5	C(16B)-C(17B)-H(17F)	109.5
C(5B)-C(4B)-C(9B)	124.2(12)	H(17D)-C(17B)-H(17F)	109.5
C(5B)-C(4B)-C(3B)	128.6(11)	H(17E)-C(17B)-H(17F)	109.5
C(9B)-C(4B)-C(3B)	107.1(10)	C(19B)-C(18B)-C(23B)	119.0(11)
C(4B)-C(5B)-C(6B)	114.9(13)	C(19B)-C(18B)-C(2B)	120.9(10)
C(4B)-C(5B)-H(5BA)	122.6	C(23B)-C(18B)-C(2B)	120.2(11)
C(6B)-C(5B)-H(5BA)	122.6	C(18B)-C(19B)-C(20B)	120.5(11)
C(7B)-C(6B)-C(5B)	120.7(12)	C(18B)-C(19B)-H(19B)	119.7
C(7B)-C(6B)-H(6BA)	119.6	C(20B)-C(19B)-H(19B)	119.7
C(5B)-C(6B)-H(6BA)	119.6	C(21B)-C(20B)-C(19B)	119.9(12)
C(6B)-C(7B)-C(8B)	122.9(13)	C(21B)-C(20B)-H(20B)	120.0

C(19B)-C(20B)-H(20B)	120.0
C(20B)-C(21B)-C(22B)	118.6(11)
C(20B)-C(21B)-H(21B)	120.7
C(22B)-C(21B)-H(21B)	120.7
C(23B)-C(22B)-C(21B)	121.5(11)
C(23B)-C(22B)-C(24B)	119.9(11)
C(21B)-C(22B)-C(24B)	118.5(10)
C(22B)-C(23B)-C(18B)	120.5(12)
C(22B)-C(23B)-H(23B)	119.7
C(18B)-C(23B)-H(23B)	119.7
F(1B)-C(24B)-F(2B)	107.0(11)
F(1B)-C(24B)-F(3B)	105.8(11)
F(2B)-C(24B)-F(3B)	105.1(10)
F(1B)-C(24B)-C(22B)	113.6(9)
F(2B)-C(24B)-C(22B)	113.4(11)
F(3B)-C(24B)-C(22B)	111.2(10)
O(1B)-C(25B)-O(2B)	124.6(11)
O(1B)-C(25B)-C(3B)	125.5(11)
O(2B)-C(25B)-C(3B)	109.8(10)
O(2B)-C(26B)-H(26D)	109.5
O(2B)-C(26B)-H(26E)	109.5
H(26D)-C(26B)-H(26E)	109.5
O(2B)-C(26B)-H(26F)	109.5
H(26D)-C(26B)-H(26F)	109.5
H(26E)-C(26B)-H(26F)	109.5
C(25)-O(2)-C(26)	117.4(9)
C(25B)-O(2B)-C(26B)	114.6(9)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **258**. 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)	23(4)	37(5)	77(8)	-1(5)	-1(4)	2(3)
C(2)	39(5)	37(6)	69(8)	8(5)	1(4)	-12(4)
C(3)	41(5)	25(5)	75(8)	-2(5)	6(5)	-1(4)
C(4)	25(4)	50(7)	89(10)	6(6)	3(5)	-4(4)
C(5)	32(5)	139(15)	68(10)	-8(8)	2(5)	14(6)
C(6)	42(6)	116(13)	66(10)	3(8)	-1(5)	2(6)
C(7)	48(6)	51(7)	103(11)	-5(7)	0(6)	16(5)
C(8)	33(5)	85(9)	76(9)	-11(7)	-4(5)	15(5)
C(9)	34(5)	87(9)	44(8)	2(6)	9(4)	-25(5)
C(10)	35(5)	44(6)	68(8)	6(5)	5(4)	10(4)
C(11)	35(5)	66(8)	62(8)	4(6)	-1(4)	-8(5)
C(12)	36(5)	86(10)	63(9)	12(7)	12(5)	1(5)
C(13)	45(5)	60(7)	64(9)	0(7)	10(5)	5(5)
C(14)	46(5)	48(7)	69(9)	-4(6)	7(5)	-11(5)
C(15)	41(5)	71(8)	42(7)	7(6)	7(4)	5(5)
C(16)	81(9)	65(9)	95(12)	11(9)	9(8)	6(7)
C(17)	56(7)	131(14)	79(10)	17(9)	-7(6)	2(8)
C(18)	26(4)	50(6)	75(9)	-6(6)	0(4)	19(4)
C(19)	49(5)	77(9)	39(7)	2(6)	7(4)	7(5)
C(20)	57(6)	39(6)	73(9)	12(6)	13(5)	15(5)
C(21)	61(6)	47(7)	63(8)	5(6)	-5(5)	16(5)
C(22)	24(4)	60(7)	77(9)	11(7)	-2(4)	0(4)
C(23)	53(6)	37(6)	71(8)	-7(6)	8(5)	-15(4)
C(24)	39(6)	85(11)	115(15)	13(9)	9(7)	-10(6)
C(25)	48(6)	43(6)	69(9)	-3(6)	-8(5)	11(4)
C(26)	64(7)	70(9)	76(10)	2(7)	-1(6)	20(6)
C(1B)	39(5)	72(8)	48(7)	0(6)	2(4)	-7(5)
C(2B)	47(5)	49(6)	58(7)	-4(5)	-3(5)	6(4)
C(3B)	43(5)	101(11)	40(7)	-13(6)	2(4)	-7(6)
C(4B)	28(4)	95(10)	56(8)	-12(7)	-4(4)	-6(5)
C(5B)	54(6)	32(6)	81(10)	-4(5)	-11(6)	0(4)
C(6B)	40(5)	67(8)	90(11)	5(7)	-6(5)	4(5)
C(7B)	21(4)	113(11)	79(10)	2(8)	-1(5)	11(5)
C(8B)	45(5)	59(7)	78(9)	11(6)	15(5)	6(5)
C(9B)	37(5)	36(5)	78(10)	1(5)	-2(5)	4(4)
C(10B)	37(5)	54(7)	59(8)	3(6)	1(4)	10(4)
C(11B)	43(5)	50(7)	64(8)	-5(6)	0(5)	-5(4)
C(12B)	47(5)	44(6)	73(9)	7(6)	6(5)	5(4)

C(13B)	44(5)	78(9)	46(7)	1(6)	3(4)	0(5)
C(14B)	59(6)	77(9)	44(8)	3(6)	0(5)	19(6)
C(15B)	46(5)	45(6)	87(10)	-7(7)	6(5)	-11(4)
C(16B)	52(6)	75(9)	54(8)	-5(6)	-1(5)	-4(5)
C(17B)	55(7)	151(16)	64(9)	-26(9)	3(6)	-3(8)
C(18B)	38(5)	66(8)	53(8)	14(6)	-1(4)	-28(5)
C(19B)	44(5)	29(5)	84(9)	1(5)	-1(5)	-8(4)
C(20B)	50(6)	61(7)	68(8)	-9(6)	3(5)	-20(5)
C(21B)	36(5)	74(8)	80(9)	18(7)	10(5)	9(5)
C(22B)	54(6)	40(6)	62(8)	-2(6)	8(5)	-9(5)
C(23B)	32(5)	63(7)	69(8)	6(6)	14(5)	16(4)
C(24B)	55(6)	41(6)	52(8)	2(5)	-13(5)	0(4)
C(25B)	59(7)	50(7)	58(8)	-6(6)	5(5)	13(5)
C(26B)	53(6)	111(11)	31(7)	3(6)	1(4)	-7(6)
F(1)	60(4)	107(7)	85(7)	19(5)	-3(4)	-24(4)
F(2)	84(5)	98(7)	115(8)	10(6)	-38(5)	-24(5)
F(3)	50(4)	158(10)	120(8)	-29(7)	-24(4)	37(5)
F(1B)	99(6)	171(10)	63(7)	18(6)	-19(5)	-47(7)
F(2B)	58(5)	131(9)	192(12)	-45(9)	-41(6)	24(5)
F(3B)	83(5)	91(6)	98(7)	3(5)	-23(4)	-24(4)
O(1)	41(4)	73(6)	78(6)	2(5)	5(3)	-2(3)
O(2)	52(4)	75(6)	61(5)	-5(4)	-3(4)	4(4)
O(1B)	36(4)	109(8)	68(6)	1(5)	1(3)	-20(4)
O(2B)	52(4)	117(8)	42(5)	-5(5)	-8(3)	-2(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **258**.

	x	y	z	U(eq)
H(3A)	6977	-1983	9320	56
H(5A)	6213	1944	8957	96
H(6A)	5496	5301	9110	90
H(7A)	5438	6380	9654	81
H(8A)	6198	4620	10047	78
H(11A)	6936	-1889	10416	65
H(12A)	7186	-1556	10954	74
H(14A)	8089	4850	10788	65
H(15A)	7801	4431	10244	62
H(16A)	7477	1239	11418	96
H(16B)	8047	3300	11337	96
H(17A)	8662	365	11618	133

H(17B)	8995	507	11257	133
H(17C)	8422	-1528	11350	133
H(19A)	7992	-4678	9438	66
H(20A)	8979	-7138	9568	67
H(21A)	9740	-6320	10007	69
H(23A)	8618	-180	10149	64
H(26A)	7593	-74	8327	105
H(26B)	8330	-762	8523	105
H(26C)	8032	1877	8531	105
H(3BA)	5472	12014	8119	74
H(5BA)	6185	8030	8502	67
H(6BA)	6991	4946	8324	79
H(7BA)	6983	3762	7790	85
H(8BA)	6203	5453	7405	73
H(11B)	5448	11933	7022	63
H(12B)	5156	11468	6477	66
H(14B)	4334	5080	6670	72
H(15B)	4624	5451	7215	71
H(16C)	4951	8017	6036	72
H(16D)	4179	9292	6108	72
H(17D)	3977	5818	5833	135
H(17E)	3612	5667	6188	135
H(17F)	4387	4388	6117	135
H(19B)	4440	14686	8010	63
H(20B)	3463	17230	7884	72
H(21B)	2651	16328	7453	76
H(23B)	3770	10328	7285	65
H(26D)	4793	10029	9125	97
H(26E)	4353	8140	8910	97
H(26F)	4064	10786	8927	97

Table 6. Torsion angles [°] for **258**.

C(9)-C(1)-C(2)-C(18)	178.9(9)
C(10)-C(1)-C(2)-C(18)	-7.1(17)
C(9)-C(1)-C(2)-C(3)	0.2(11)
C(10)-C(1)-C(2)-C(3)	174.2(9)
C(1)-C(2)-C(3)-C(25)	123.9(10)
C(18)-C(2)-C(3)-C(25)	-54.9(13)
C(1)-C(2)-C(3)-C(4)	2.4(10)
C(18)-C(2)-C(3)-C(4)	-176.4(9)
C(25)-C(3)-C(4)-C(9)	-130.6(10)
C(2)-C(3)-C(4)-C(9)	-4.3(10)
C(25)-C(3)-C(4)-C(5)	51.6(16)
C(2)-C(3)-C(4)-C(5)	177.9(12)
C(9)-C(4)-C(5)-C(6)	6.2(19)

C(3)-C(4)-C(5)-C(6)	-176.2(11)
C(4)-C(5)-C(6)-C(7)	-6(2)
C(5)-C(6)-C(7)-C(8)	4(2)
C(6)-C(7)-C(8)-C(9)	-2.4(19)
C(5)-C(4)-C(9)-C(1)	-177.2(11)
C(3)-C(4)-C(9)-C(1)	4.7(12)
C(5)-C(4)-C(9)-C(8)	-4.6(17)
C(3)-C(4)-C(9)-C(8)	177.4(9)
C(2)-C(1)-C(9)-C(4)	-3.2(12)
C(10)-C(1)-C(9)-C(4)	-177.4(10)
C(2)-C(1)-C(9)-C(8)	-174.9(11)
C(10)-C(1)-C(9)-C(8)	11.0(18)
C(7)-C(8)-C(9)-C(4)	2.5(16)
C(7)-C(8)-C(9)-C(1)	173.6(11)
C(2)-C(1)-C(10)-C(11)	-63.3(14)
C(9)-C(1)-C(10)-C(11)	109.7(13)
C(2)-C(1)-C(10)-C(15)	112.3(12)
C(9)-C(1)-C(10)-C(15)	-74.7(12)
C(15)-C(10)-C(11)-C(12)	-1.0(15)
C(1)-C(10)-C(11)-C(12)	174.7(10)
C(10)-C(11)-C(12)-C(13)	-2.3(17)
C(11)-C(12)-C(13)-C(14)	4.9(16)
C(11)-C(12)-C(13)-C(16)	-176.1(11)
C(12)-C(13)-C(14)-C(15)	-4.3(15)
C(16)-C(13)-C(14)-C(15)	176.8(10)
C(13)-C(14)-C(15)-C(10)	1.1(15)
C(11)-C(10)-C(15)-C(14)	1.5(14)
C(1)-C(10)-C(15)-C(14)	-174.5(9)
C(12)-C(13)-C(16)-C(17)	73.5(16)
C(14)-C(13)-C(16)-C(17)	-107.6(15)
C(1)-C(2)-C(18)-C(19)	156.2(11)
C(3)-C(2)-C(18)-C(19)	-25.2(16)
C(1)-C(2)-C(18)-C(23)	-29.3(17)
C(3)-C(2)-C(18)-C(23)	149.4(11)
C(23)-C(18)-C(19)-C(20)	3.9(18)
C(2)-C(18)-C(19)-C(20)	178.5(10)
C(18)-C(19)-C(20)-C(21)	0.5(18)
C(19)-C(20)-C(21)-C(22)	-4.0(18)
C(20)-C(21)-C(22)-C(24)	178.5(12)
C(20)-C(21)-C(22)-C(23)	3.0(18)
C(19)-C(18)-C(23)-C(22)	-4.8(17)
C(2)-C(18)-C(23)-C(22)	-179.5(10)
C(21)-C(22)-C(23)-C(18)	1.5(17)
C(24)-C(22)-C(23)-C(18)	-174.3(12)
C(21)-C(22)-C(24)-F(1)	-96.1(16)
C(23)-C(22)-C(24)-F(1)	79.5(16)

C(21)-C(22)-C(24)-F(2)	143.5(13)
C(23)-C(22)-C(24)-F(2)	-40.9(17)
C(21)-C(22)-C(24)-F(3)	28(2)
C(23)-C(22)-C(24)-F(3)	-156.1(12)
C(2)-C(3)-C(25)-O(1)	-8.4(16)
C(4)-C(3)-C(25)-O(1)	107.9(12)
C(2)-C(3)-C(25)-O(2)	170.4(9)
C(4)-C(3)-C(25)-O(2)	-73.3(12)
C(10B)-C(1B)-C(2B)-C(18B)	1(2)
C(9B)-C(1B)-C(2B)-C(18B)	-175.9(10)
C(10B)-C(1B)-C(2B)-C(3B)	-177.1(11)
C(9B)-C(1B)-C(2B)-C(3B)	5.8(13)
C(1B)-C(2B)-C(3B)-C(25B)	-127.9(11)
C(18B)-C(2B)-C(3B)-C(25B)	53.7(15)
C(1B)-C(2B)-C(3B)-C(4B)	-7.3(13)
C(18B)-C(2B)-C(3B)-C(4B)	174.3(10)
C(2B)-C(3B)-C(4B)-C(5B)	-176.3(12)
C(25B)-C(3B)-C(4B)-C(5B)	-53.9(17)
C(2B)-C(3B)-C(4B)-C(9B)	6.0(12)
C(25B)-C(3B)-C(4B)-C(9B)	128.4(10)
C(9B)-C(4B)-C(5B)-C(6B)	-0.1(18)
C(3B)-C(4B)-C(5B)-C(6B)	-177.4(11)
C(4B)-C(5B)-C(6B)-C(7B)	-0.2(18)
C(5B)-C(6B)-C(7B)-C(8B)	0(2)
C(6B)-C(7B)-C(8B)-C(9B)	0.7(19)
C(7B)-C(8B)-C(9B)-C(4B)	-1.0(17)
C(7B)-C(8B)-C(9B)-C(1B)	-179.2(11)
C(5B)-C(4B)-C(9B)-C(8B)	0.8(19)
C(3B)-C(4B)-C(9B)-C(8B)	178.6(10)
C(5B)-C(4B)-C(9B)-C(1B)	179.3(11)
C(3B)-C(4B)-C(9B)-C(1B)	-2.9(13)
C(2B)-C(1B)-C(9B)-C(8B)	176.5(11)
C(10B)-C(1B)-C(9B)-C(8B)	-0.8(18)
C(2B)-C(1B)-C(9B)-C(4B)	-1.8(13)
C(10B)-C(1B)-C(9B)-C(4B)	-179.1(10)
C(2B)-C(1B)-C(10B)-C(15B)	-108.6(15)
C(9B)-C(1B)-C(10B)-C(15B)	68.1(13)
C(2B)-C(1B)-C(10B)-C(11B)	67.3(15)
C(9B)-C(1B)-C(10B)-C(11B)	-116.0(12)
C(15B)-C(10B)-C(11B)-C(12B)	1.1(14)
C(1B)-C(10B)-C(11B)-C(12B)	-174.9(10)
C(10B)-C(11B)-C(12B)-C(13B)	0.0(15)
C(11B)-C(12B)-C(13B)-C(14B)	-0.9(15)
C(11B)-C(12B)-C(13B)-C(16B)	178.0(10)
C(12B)-C(13B)-C(14B)-C(15B)	0.7(17)
C(16B)-C(13B)-C(14B)-C(15B)	-178.1(11)

C(11B)-C(10B)-C(15B)-C(14B)	-1.4(14)
C(1B)-C(10B)-C(15B)-C(14B)	174.6(10)
C(13B)-C(14B)-C(15B)-C(10B)	0.5(17)
C(14B)-C(13B)-C(16B)-C(17B)	2.7(18)
C(12B)-C(13B)-C(16B)-C(17B)	-176.1(10)
C(1B)-C(2B)-C(18B)-C(19B)	-152.0(12)
C(3B)-C(2B)-C(18B)-C(19B)	26.1(15)
C(1B)-C(2B)-C(18B)-C(23B)	27.1(17)
C(3B)-C(2B)-C(18B)-C(23B)	-154.8(11)
C(23B)-C(18B)-C(19B)-C(20B)	-0.1(16)
C(2B)-C(18B)-C(19B)-C(20B)	178.9(10)
C(18B)-C(19B)-C(20B)-C(21B)	-0.2(17)
C(19B)-C(20B)-C(21B)-C(22B)	1.2(17)
C(20B)-C(21B)-C(22B)-C(23B)	-1.9(17)
C(20B)-C(21B)-C(22B)-C(24B)	-178.1(11)
C(21B)-C(22B)-C(23B)-C(18B)	1.5(17)
C(24B)-C(22B)-C(23B)-C(18B)	177.7(10)
C(19B)-C(18B)-C(23B)-C(22B)	-0.5(17)
C(2B)-C(18B)-C(23B)-C(22B)	-179.6(10)
C(23B)-C(22B)-C(24B)-F(1B)	-77.9(14)
C(21B)-C(22B)-C(24B)-F(1B)	98.4(13)
C(23B)-C(22B)-C(24B)-F(2B)	159.5(12)
C(21B)-C(22B)-C(24B)-F(2B)	-24.1(16)
C(23B)-C(22B)-C(24B)-F(3B)	41.3(16)
C(21B)-C(22B)-C(24B)-F(3B)	-142.4(11)
C(2B)-C(3B)-C(25B)-O(1B)	13.7(18)
C(4B)-C(3B)-C(25B)-O(1B)	-102.4(14)
C(2B)-C(3B)-C(25B)-O(2B)	-171.1(10)
C(4B)-C(3B)-C(25B)-O(2B)	72.9(12)
O(1)-C(25)-O(2)-C(26)	-4.5(15)
C(3)-C(25)-O(2)-C(26)	176.6(9)
O(1B)-C(25B)-O(2B)-C(26B)	1.2(18)
C(3B)-C(25B)-O(2B)-C(26B)	-174.1(11)

Symmetry transformations used to generate equivalent atoms:

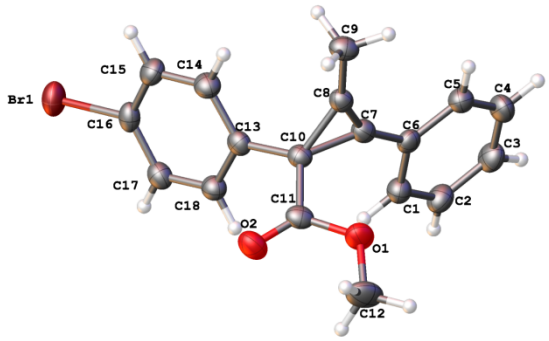

Table 1. Crystal data and structure refinement for **261**.

Identification code	**261**	
Empirical formula	C18 H15 Br O2	
Formula weight	343.21	
Temperature	173.2 K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 5.8806(3) Å	α= 90°.
	b = 12.6232(6) Å	β= 90°.
	c = 20.6562(9) Å	γ = 90°.
Volume	1533.35(13) $Å^3$	
Z	4	
Density (calculated)	1.487 Mg/m^3	
Absorption coefficient	3.662 mm^{-1}	
F(000)	696	
Crystal size	0.485 x 0.324 x 0.254 mm^3	
Theta range for data collection	4.10 to 68.27°.	
Index ranges	-6<=h<=6, -10<=k<=15, -24<=l<=23	
Reflections collected	5531	
Independent reflections	2594 [R(int) = 0.0181]	
Completeness to theta = 68.27°	96.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.4891	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2594 / 0 / 201	
Goodness-of-fit on F^2	1.108	
Final R indices [I>2sigma(I)]	R1 = 0.0254, wR2 = 0.0683	
R indices (all data)	R1 = 0.0255, wR2 = 0.0684	
Absolute structure parameter	0.038(15)	

Largest diff. peak and hole	0.578 and -0.297 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for **261**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	2708(1)	6893(1)	5575(1)	43(1)
C(1)	5262(4)	1384(2)	6728(1)	33(1)
C(2)	3665(4)	580(2)	6757(1)	38(1)
C(3)	3885(4)	-297(2)	6360(1)	40(1)
C(4)	5745(5)	-378(2)	5942(1)	40(1)
C(5)	7346(4)	422(2)	5912(1)	34(1)
C(6)	7110(4)	1318(2)	6304(1)	28(1)
C(7)	8689(4)	2189(2)	6251(1)	28(1)
C(8)	10428(4)	2666(2)	6005(1)	28(1)
C(9)	12382(3)	2720(2)	5556(1)	34(1)
C(10)	9092(3)	3305(2)	6506(1)	27(1)
C(11)	10087(4)	3441(2)	7171(1)	30(1)
C(12)	11792(5)	2558(3)	8054(1)	52(1)
C(13)	7586(4)	4199(2)	6291(1)	28(1)
C(14)	7948(4)	4709(2)	5706(1)	34(1)
C(15)	6514(4)	5509(2)	5490(1)	35(1)
C(16)	4668(4)	5792(2)	5868(1)	32(1)
C(17)	4234(4)	5301(2)	6457(1)	33(1)
C(18)	5706(4)	4518(2)	6662(1)	31(1)
O(1)	10771(3)	2510(1)	7416(1)	41(1)
O(2)	10264(3)	4269(1)	7452(1)	42(1)

Table 3. Bond lengths [Å] and angles [°] for **261**.

Br(1)-C(16)	1.905(2)
O(1)-C(11)	1.341(3)
O(1)-C(12)	1.451(3)
O(2)-C(11)	1.199(3)
C(1)-C(2)	1.384(3)
C(1)-C(6)	1.397(3)
C(2)-C(3)	1.383(3)
C(3)-C(4)	1.397(4)
C(4)-C(5)	1.382(3)
C(5)-C(6)	1.398(3)
C(6)-C(7)	1.443(3)
C(7)-C(8)	1.291(3)
C(7)-C(10)	1.522(3)
C(8)-C(9)	1.478(3)

C(8)-C(10)	1.529(3)
C(10)-C(11)	1.504(3)
C(10)-C(13)	1.502(3)
C(13)-C(14)	1.385(3)
C(13)-C(18)	1.405(3)
C(14)-C(15)	1.390(3)
C(15)-C(16)	1.385(3)
C(16)-C(17)	1.389(3)
C(17)-C(18)	1.380(3)
C(1)-H(1)	0.9500
C(2)-H(2)	0.93(3)
C(3)-H(3)	0.93(3)
C(4)-H(4)	0.9500
C(5)-H(5)	0.9500
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(14)-H(14)	0.9500
C(15)-H(15)	0.9500
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
C(11)-O(1)-C(12)	115.5(2)
C(2)-C(1)-C(6)	120.8(2)
C(1)-C(2)-C(3)	119.9(2)
C(2)-C(3)-C(4)	119.9(2)
C(3)-C(4)-C(5)	120.5(2)
C(4)-C(5)-C(6)	119.9(2)
C(1)-C(6)-C(5)	119.2(2)
C(1)-C(6)-C(7)	120.19(18)
C(5)-C(6)-C(7)	120.6(2)
C(6)-C(7)-C(8)	153.5(2)
C(6)-C(7)-C(10)	141.16(19)
C(8)-C(7)-C(10)	65.25(15)
C(7)-C(8)-C(9)	152.2(2)
C(7)-C(8)-C(10)	64.70(15)
C(9)-C(8)-C(10)	143.05(19)
C(7)-C(10)-C(8)	50.05(13)
C(7)-C(10)-C(11)	118.81(17)
C(7)-C(10)-C(13)	120.10(16)
C(8)-C(10)-C(11)	118.59(17)
C(8)-C(10)-C(13)	119.97(16)
C(11)-C(10)-C(13)	114.46(17)
O(1)-C(11)-O(2)	123.73(19)

O(1)-C(11)-C(10)	111.17(18)
O(2)-C(11)-C(10)	125.1(2)
C(10)-C(13)-C(14)	121.09(19)
C(10)-C(13)-C(18)	121.22(17)
C(14)-C(13)-C(18)	117.64(19)
C(13)-C(14)-C(15)	121.6(2)
C(14)-C(15)-C(16)	118.8(2)
Br(1)-C(16)-C(15)	118.89(16)
Br(1)-C(16)-C(17)	119.53(17)
C(15)-C(16)-C(17)	121.6(2)
C(16)-C(17)-C(18)	118.2(2)
C(13)-C(18)-C(17)	122.13(19)
C(2)-C(1)-H(1)	120.00
C(6)-C(1)-H(1)	120.00
C(1)-C(2)-H(2)	122.9(16)
C(3)-C(2)-H(2)	117.1(16)
C(2)-C(3)-H(3)	125.2(19)
C(4)-C(3)-H(3)	114.9(19)
C(3)-C(4)-H(4)	120.00
C(5)-C(4)-H(4)	120.00
C(4)-C(5)-H(5)	120.00
C(6)-C(5)-H(5)	120.00
C(8)-C(9)-H(9A)	109.00
C(8)-C(9)-H(9B)	109.00
C(8)-C(9)-H(9C)	109.00
H(9A)-C(9)-H(9B)	109.00
H(9A)-C(9)-H(9C)	109.00
H(9B)-C(9)-H(9C)	109.00
O(1)-C(12)-H(12A)	109.00
O(1)-C(12)-H(12B)	109.00
O(1)-C(12)-H(12C)	109.00
H(12A)-C(12)-H(12B)	109.00
H(12A)-C(12)-H(12C)	109.00
H(12B)-C(12)-H(12C)	110.00
C(13)-C(14)-H(14)	119.00
C(15)-C(14)-H(14)	119.00
C(14)-C(15)-H(15)	121.00
C(16)-C(15)-H(15)	121.00
C(16)-C(17)-H(17)	121.00
C(18)-C(17)-H(17)	121.00
C(13)-C(18)-H(18)	119.00
C(17)-C(18)-H(18)	119.00

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **261**. 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}
Br(1)	45(1)	29(1)	55(1)	2(1)	-8(1)	6(1)
C(1)	36(1)	29(1)	34(1)	1(1)	3(1)	1(1)
C(2)	37(1)	35(1)	41(1)	8(1)	6(1)	-1(1)
C(3)	45(1)	32(1)	42(1)	4(1)	-2(1)	-10(1)
C(4)	55(1)	29(1)	37(1)	-5(1)	-1(1)	-3(1)
C(5)	38(1)	32(1)	31(1)	1(1)	2(1)	2(1)
C(6)	31(1)	27(1)	26(1)	4(1)	-4(1)	2(1)
C(7)	28(1)	30(1)	27(1)	-1(1)	-2(1)	4(1)
C(8)	29(1)	28(1)	27(1)	-2(1)	-2(1)	1(1)
C(9)	30(1)	43(1)	30(1)	-3(1)	3(1)	2(1)
C(10)	25(1)	29(1)	27(1)	-1(1)	2(1)	-1(1)
C(11)	23(1)	39(1)	28(1)	-3(1)	4(1)	2(1)
C(12)	54(2)	72(2)	30(1)	-2(1)	-10(1)	17(1)
C(13)	28(1)	26(1)	30(1)	-4(1)	-1(1)	-3(1)
C(14)	33(1)	34(1)	34(1)	0(1)	7(1)	-2(1)
C(15)	39(1)	29(1)	36(1)	5(1)	2(1)	-3(1)
C(16)	33(1)	22(1)	41(1)	-1(1)	-7(1)	0(1)
C(17)	33(1)	30(1)	38(1)	-5(1)	2(1)	-1(1)
C(18)	33(1)	30(1)	31(1)	-1(1)	3(1)	-1(1)
O(1)	50(1)	42(1)	31(1)	-1(1)	-10(1)	9(1)
O(2)	47(1)	40(1)	38(1)	-11(1)	-6(1)	4(1)

Table 5. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for **261**.

	x	y	z	U(eq)
H(1)	5100	1987	6998	40
H(2)	2360(50)	620(20)	7012(14)	45
H(3)	2890(60)	-870(20)	6350(14)	47
H(4)	5910	-987	5676	48
H(5)	8604	363	5626	41
H(9A)	12875	2001	5445	49(8)
H(9B)	13638	3101	5764	51(8)
H(9C)	11929	3095	5161	63(10)
H(12A)	10726	2892	8357	78
H(12B)	13195	2976	8035	78
H(12C)	12143	1839	8203	78

H(14)	9208	4506	5446	41
H(15)	6795	5856	5090	42
H(17)	2959	5499	6712	40
H(18)	5439	4185	7067	37

Table 6. Torsion angles [°] for **261**.

C(12)-O(1)-C(11)-C(10)	179.09(19)
C(12)-O(1)-C(11)-O(2)	-0.7(3)
C(2)-C(1)-C(6)-C(5)	-0.7(3)
C(2)-C(1)-C(6)-C(7)	176.4(2)
C(6)-C(1)-C(2)-C(3)	-0.4(3)
C(1)-C(2)-C(3)-C(4)	1.4(4)
C(2)-C(3)-C(4)-C(5)	-1.3(4)
C(3)-C(4)-C(5)-C(6)	0.2(4)
C(4)-C(5)-C(6)-C(7)	-176.2(2)
C(4)-C(5)-C(6)-C(1)	0.8(3)
C(5)-C(6)-C(7)-C(8)	1.1(6)
C(5)-C(6)-C(7)-C(10)	174.3(2)
C(1)-C(6)-C(7)-C(10)	-2.7(4)
C(1)-C(6)-C(7)-C(8)	-175.9(4)
C(10)-C(7)-C(8)-C(9)	-177.1(4)
C(6)-C(7)-C(8)-C(9)	-1.7(8)
C(6)-C(7)-C(8)-C(10)	175.4(5)
C(6)-C(7)-C(10)-C(13)	-71.2(3)
C(8)-C(7)-C(10)-C(11)	-104.6(2)
C(8)-C(7)-C(10)-C(13)	105.5(2)
C(6)-C(7)-C(10)-C(11)	78.7(3)
C(6)-C(7)-C(10)-C(8)	-176.7(3)
C(7)-C(8)-C(10)-C(13)	-105.8(2)
C(7)-C(8)-C(10)-C(11)	105.0(2)
C(9)-C(8)-C(10)-C(13)	71.9(3)
C(9)-C(8)-C(10)-C(11)	-77.2(3)
C(9)-C(8)-C(10)-C(7)	177.7(3)
C(7)-C(10)-C(11)-O(2)	-171.8(2)
C(7)-C(10)-C(11)-O(1)	8.4(3)
C(13)-C(10)-C(11)-O(1)	159.95(18)
C(8)-C(10)-C(11)-O(1)	-49.2(3)
C(8)-C(10)-C(11)-O(2)	130.5(2)
C(7)-C(10)-C(13)-C(18)	95.6(2)
C(8)-C(10)-C(13)-C(14)	-23.3(3)
C(8)-C(10)-C(13)-C(18)	154.1(2)
C(11)-C(10)-C(13)-C(14)	127.1(2)
C(11)-C(10)-C(13)-C(18)	-55.6(3)
C(13)-C(10)-C(11)-O(2)	-20.3(3)

C(7)-C(10)-C(13)-C(14)	-81.8(3)
C(10)-C(13)-C(14)-C(15)	177.5(2)
C(18)-C(13)-C(14)-C(15)	0.1(3)
C(10)-C(13)-C(18)-C(17)	-176.6(2)
C(14)-C(13)-C(18)-C(17)	0.8(3)
C(13)-C(14)-C(15)-C(16)	-0.7(3)
C(14)-C(15)-C(16)-Br(1)	179.73(17)
C(14)-C(15)-C(16)-C(17)	0.5(3)
Br(1)-C(16)-C(17)-C(18)	-178.94(17)
C(15)-C(16)-C(17)-C(18)	0.3(3)
C(16)-C(17)-C(18)-C(13)	-0.9(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **261** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2)...O(2)#1	0.93(3)	2.55(3)	3.279(3)	135(2)

Symmetry transformations used to generate equivalent atoms:
#1 1/2-x+1,-y-1,1/2+z+1

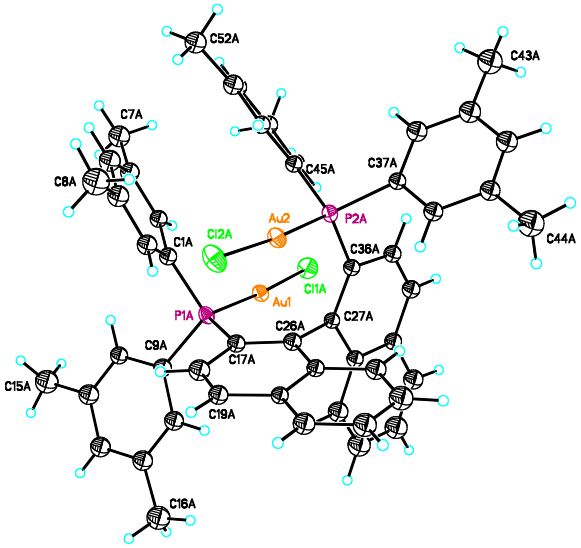

Table 1. Crystal data and structure refinement for **240**.

Identification code	**240**	
Empirical formula	C52 H48 Au2 Cl2 P2	
Formula weight	1199.68	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 12.6094(10) Å	α= 90°.
	b = 19.1881(15) Å	β= 90°.
	c = 38.171(3) Å	γ = 90°.
Volume	9235.4(12) $Å^3$	
Z	8	
Density (calculated)	1.726 Mg/m^3	
Absorption coefficient	6.566 mm^{-1}	
F(000)	4656	
Crystal size	0.27 x 0.09 x 0.06 mm^3	
Theta range for data collection	1.19 to 30.55°.	

Index ranges	-17<=h<=18, -27<=k<=27, -54<=l<=54
Reflections collected	188630
Independent reflections	28250 [R(int) = 0.1279]
Completeness to theta = 30.55°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6941 and 0.2701
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	28250 / 0 / 1035
Goodness-of-fit on F^2	1.025
Final R indices [I>2sigma(I)]	R1 = 0.0614, wR2 = 0.1232
R indices (all data)	R1 = 0.1067, wR2 = 0.1431
Absolute structure parameter	-0.011(7)
Largest diff. peak and hole	8.050 and -4.173 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for **240**.U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	-1341(1)	-589(1)	9603(1)	25(1)
Au(2)	1932(1)	1246(1)	9803(1)	27(1)
Au(1B)	10688(1)	4637(1)	2832(1)	49(1)
Au(2B)	6869(1)	2929(1)	2893(1)	49(1)
C(1A)	-138(8)	-79(5)	10322(2)	27(2)
C(2A)	-1167(8)	80(5)	10432(2)	28(2)
C(3A)	-1388(9)	536(5)	10705(3)	34(2)
C(4A)	-521(10)	854(6)	10864(3)	41(3)
C(5A)	520(9)	738(6)	10762(3)	38(3)
C(6A)	713(8)	263(5)	10498(3)	33(2)
C(7A)	-2479(9)	676(7)	10827(3)	43(3)
C(8A)	1431(11)	1104(8)	10936(4)	61(4)
C(9A)	185(8)	-1564(5)	10120(3)	31(2)
C(10A)	-438(8)	-1800(5)	10402(3)	29(2)
C(11A)	-375(10)	-2502(6)	10508(3)	40(3)
C(12A)	308(8)	-2965(5)	10340(3)	40(3)
C(13A)	916(9)	-2725(6)	10060(3)	39(3)
C(14A)	850(8)	-2036(6)	9955(3)	33(2)
C(15A)	-1100(12)	-2763(6)	10797(4)	57(4)
C(16A)	1630(10)	-3217(6)	9860(4)	52(3)
C(17A)	1358(7)	-490(5)	9776(2)	27(2)
C(18A)	2260(7)	-679(6)	9978(3)	35(2)
C(19A)	3270(8)	-558(5)	9865(3)	31(2)

C(20A)	3444(7)	-265(4)	9525(2)	22(2)
C(21A)	4465(7)	-156(5)	9397(3)	36(3)
C(22A)	4620(9)	113(6)	9069(3)	40(3)
C(23A)	3746(9)	279(7)	8856(3)	44(3)
C(24A)	2734(8)	197(6)	8984(3)	34(2)
C(25A)	2544(7)	-88(5)	9324(3)	25(2)
C(26A)	1486(8)	-191(5)	9450(3)	28(2)
C(27A)	608(7)	-37(5)	9206(2)	22(2)
C(28A)	340(7)	-558(5)	8945(2)	24(2)
C(29A)	824(9)	-1217(6)	8953(3)	36(2)
C(30A)	563(11)	-1712(7)	8711(4)	52(3)
C(31A)	-186(11)	-1568(7)	8454(4)	51(3)
C(32A)	-655(9)	-946(7)	8436(3)	40(3)
C(33A)	-444(7)	-409(6)	8690(2)	30(2)
C(34A)	-908(8)	258(6)	8679(3)	31(2)
C(35A)	-629(7)	754(5)	8911(2)	26(2)
C(36A)	112(7)	614(5)	9181(2)	24(2)
C(37A)	584(7)	2064(5)	9152(2)	23(2)
C(38A)	-207(9)	2571(5)	9099(3)	36(2)
C(39A)	-89(9)	3057(6)	8844(3)	37(3)
C(40A)	804(9)	3039(5)	8627(3)	35(2)
C(41A)	1604(9)	2570(5)	8673(3)	32(2)
C(42A)	1492(8)	2064(5)	8938(2)	28(2)
C(43A)	-950(10)	3577(7)	8781(4)	54(4)
C(44A)	2581(11)	2580(7)	8454(4)	52(3)
C(45A)	-645(8)	1536(5)	9736(2)	25(2)
C(46A)	-1687(7)	1295(5)	9677(2)	25(2)
C(47A)	-2508(8)	1476(5)	9900(3)	32(2)
C(48A)	-2286(8)	1906(5)	10187(3)	31(2)
C(49A)	-1280(9)	2162(6)	10257(3)	33(2)
C(50A)	-461(8)	1962(5)	10029(2)	26(2)
C(51A)	-3601(9)	1188(7)	9850(3)	46(3)
C(52A)	-1026(10)	2601(6)	10577(3)	40(3)
C(1B)	11002(9)	3680(6)	2098(3)	38(3)
C(2B)	11974(10)	3458(6)	2223(4)	44(3)
C(3B)	12709(9)	3173(7)	2000(4)	52(4)
C(4B)	12516(11)	3187(7)	1664(5)	64(4)
C(5B)	11528(11)	3407(7)	1520(3)	50(3)
C(6B)	10783(11)	3643(6)	1746(3)	44(3)
C(7B)	11339(14)	3400(8)	1124(4)	71(4)
C(8B)	13764(15)	2959(10)	2165(5)	88(5)
C(9B)	8880(8)	4313(5)	2210(3)	30(2)
C(10B)	8963(10)	5019(6)	2123(3)	45(3)
C(11B)	8134(11)	5374(6)	1965(3)	51(3)
C(12B)	7195(9)	5015(6)	1913(3)	40(3)
C(13B)	7078(9)	4340(6)	2011(3)	39(3)

C(14B)	7945(9)	3984(6)	2164(3)	37(2)
C(15B)	6040(11)	3966(8)	1956(4)	63(4)
C(16B)	8261(12)	6136(7)	1847(4)	72(5)
C(17B)	9556(9)	3054(5)	2573(3)	33(2)
C(18B)	9335(10)	2556(6)	2306(3)	40(3)
C(19B)	8999(9)	1902(5)	2391(3)	39(3)
C(20B)	8860(9)	1701(6)	2742(3)	38(3)
C(21B)	8524(10)	1019(6)	2830(3)	45(3)
C(22B)	8447(11)	824(6)	3176(4)	52(3)
C(23B)	8692(11)	1277(6)	3440(4)	52(3)
C(24B)	9020(10)	1946(6)	3364(3)	41(3)
C(25B)	9120(9)	2165(5)	3014(3)	33(2)
C(26B)	9436(8)	2882(5)	2927(2)	27(2)
C(27B)	9658(10)	3347(5)	3221(3)	39(3)
C(28B)	10716(11)	3375(5)	3343(3)	40(3)
C(29B)	11541(11)	2998(6)	3186(3)	49(3)
C(30B)	12568(13)	3053(6)	3302(4)	58(4)
C(31B)	12809(13)	3498(7)	3590(4)	61(4)
C(32B)	12003(12)	3852(6)	3753(4)	53(3)
C(33B)	10957(12)	3798(6)	3640(3)	49(3)
C(34B)	10101(12)	4178(6)	3801(3)	47(3)
C(35B)	9144(13)	4149(6)	3684(3)	50(3)
C(36B)	8881(12)	3733(5)	3389(3)	51(4)
C(37B)	6789(12)	3700(7)	3676(3)	51(3)
C(38B)	6904(11)	3074(6)	3857(3)	47(3)
C(39B)	6426(10)	3007(6)	4187(3)	42(3)
C(40B)	5843(10)	3559(6)	4313(3)	43(3)
C(41B)	5743(12)	4168(7)	4147(3)	53(3)
C(42B)	6221(12)	4243(7)	3816(4)	59(4)
C(43B)	6554(12)	2345(7)	4389(4)	62(4)
C(44B)	5084(14)	4766(8)	4292(4)	72(5)
C(45B)	7189(17)	4604(8)	3081(4)	78(6)
C(46B)	6101(18)	4655(9)	2938(5)	96(7)
C(47B)	5763(18)	5291(10)	2803(5)	92(6)
C(48B)	6531(17)	5781(8)	2779(5)	82(6)
C(49B)	7497(13)	5779(9)	2922(4)	67(4)
C(50B)	7873(18)	5131(8)	3081(4)	87(7)
C(51B)	4550(30)	5336(18)	2632(7)	230(20)
C(52B)	8330(20)	6333(11)	2925(7)	155(13)
Cl(1A)	-2842(2)	-486(2)	9273(1)	40(1)
Cl(2A)	3358(2)	1187(2)	10176(1)	43(1)
Cl(1B)	11407(5)	5424(2)	3214(1)	98(2)
Cl(2B)	6127(3)	2160(2)	2516(1)	67(1)
P(1A)	50(2)	-674(1)	9959(1)	24(1)
P(2A)	486(2)	1347(1)	9468(1)	23(1)
P(1B)	10006(2)	3916(1)	2432(1)	33(1)

P(2B)	7470(3)	3745(2)	3257(1)	50(1)

Table 3. Bond lengths [Å] and angles [°] for **240**.

Au(1)-P(1A)	2.225(2)
Au(1)-Cl(1A)	2.284(2)
Au(2)-P(2A)	2.237(2)
Au(2)-Cl(2A)	2.294(2)
Au(1B)-P(1B)	2.231(3)
Au(1B)-Cl(1B)	2.287(3)
Au(2B)-P(2B)	2.224(4)
Au(2B)-Cl(2B)	2.265(4)
C(1A)-C(2A)	1.398(14)
C(1A)-C(6A)	1.427(14)
C(1A)-P(1A)	1.810(10)
C(2A)-C(3A)	1.389(14)
C(2A)-H(2AA)	0.9500
C(3A)-C(4A)	1.391(17)
C(3A)-C(7A)	1.477(15)
C(4A)-C(5A)	1.387(17)
C(4A)-H(4AA)	0.9500
C(5A)-C(6A)	1.381(16)
C(5A)-C(8A)	1.500(16)
C(6A)-H(6AA)	0.9500
C(7A)-H(7AA)	0.9800
C(7A)-H(7AB)	0.9800
C(7A)-H(7AC)	0.9800
C(8A)-H(8AA)	0.9800
C(8A)-H(8AB)	0.9800
C(8A)-H(8AC)	0.9800
C(9A)-C(14A)	1.385(15)
C(9A)-C(10A)	1.409(14)
C(9A)-P(1A)	1.823(10)
C(10A)-C(11A)	1.409(14)
C(10A)-H(10A)	0.9500
C(11A)-C(12A)	1.395(16)
C(11A)-C(15A)	1.516(17)
C(12A)-C(13A)	1.393(17)
C(12A)-H(12A)	0.9500
C(13A)-C(14A)	1.386(15)
C(13A)-C(16A)	1.510(16)
C(14A)-H(14A)	0.9500
C(15A)-H(15A)	0.9800
C(15A)-H(15B)	0.9800
C(15A)-H(15C)	0.9800

C(16A)-H(16A)	0.9800
C(16A)-H(16B)	0.9800
C(16A)-H(16C)	0.9800
C(17A)-C(26A)	1.377(14)
C(17A)-C(18A)	1.422(13)
C(17A)-P(1A)	1.826(10)
C(18A)-C(19A)	1.364(14)
C(18A)-H(18A)	0.9500
C(19A)-C(20A)	1.430(13)
C(19A)-H(19A)	0.9500
C(20A)-C(21A)	1.394(13)
C(20A)-C(25A)	1.412(13)
C(21A)-C(22A)	1.365(16)
C(21A)-H(21A)	0.9500
C(22A)-C(23A)	1.408(16)
C(22A)-H(22A)	0.9500
C(23A)-C(24A)	1.376(15)
C(23A)-H(23A)	0.9500
C(24A)-C(25A)	1.427(14)
C(24A)-H(24A)	0.9500
C(25A)-C(26A)	1.433(14)
C(26A)-C(27A)	1.476(13)
C(27A)-C(36A)	1.400(13)
C(27A)-C(28A)	1.450(13)
C(28A)-C(29A)	1.406(14)
C(28A)-C(33A)	1.418(13)
C(29A)-C(30A)	1.366(16)
C(29A)-H(29A)	0.9500
C(30A)-C(31A)	1.390(19)
C(30A)-H(30A)	0.9500
C(31A)-C(32A)	1.334(18)
C(31A)-H(31A)	0.9500
C(32A)-C(33A)	1.438(14)
C(32A)-H(32A)	0.9500
C(33A)-C(34A)	1.407(15)
C(34A)-C(35A)	1.347(14)
C(34A)-H(34A)	0.9500
C(35A)-C(36A)	1.417(13)
C(35A)-H(35A)	0.9500
C(36A)-P(2A)	1.843(10)
C(37A)-C(42A)	1.407(13)
C(37A)-C(38A)	1.408(14)
C(37A)-P(2A)	1.833(9)
C(38A)-C(39A)	1.357(15)
C(38A)-H(38A)	0.9500
C(39A)-C(40A)	1.398(16)

C(39A)-C(43A)	1.494(15)
C(40A)-C(41A)	1.363(15)
C(40A)-H(40A)	0.9500
C(41A)-C(42A)	1.409(14)
C(41A)-C(44A)	1.488(16)
C(42A)-H(42A)	0.9500
C(43A)-H(43A)	0.9800
C(43A)-H(43B)	0.9800
C(43A)-H(43C)	0.9800
C(44A)-H(44A)	0.9800
C(44A)-H(44B)	0.9800
C(44A)-H(44C)	0.9800
C(45A)-C(50A)	1.402(13)
C(45A)-C(46A)	1.411(13)
C(45A)-P(2A)	1.794(10)
C(46A)-C(47A)	1.385(14)
C(46A)-H(46A)	0.9500
C(47A)-C(48A)	1.400(15)
C(47A)-C(51A)	1.496(15)
C(48A)-C(49A)	1.387(15)
C(48A)-H(48A)	0.9500
C(49A)-C(50A)	1.405(14)
C(49A)-C(52A)	1.517(15)
C(50A)-H(50A)	0.9500
C(51A)-H(51A)	0.9800
C(51A)-H(51B)	0.9800
C(51A)-H(51C)	0.9800
C(52A)-H(52A)	0.9800
C(52A)-H(52B)	0.9800
C(52A)-H(52C)	0.9800
C(1B)-C(6B)	1.374(16)
C(1B)-C(2B)	1.384(16)
C(1B)-P(1B)	1.847(12)
C(2B)-C(3B)	1.373(19)
C(2B)-H(2BA)	0.9500
C(3B)-C(4B)	1.31(2)
C(3B)-C(8B)	1.53(2)
C(4B)-C(5B)	1.42(2)
C(4B)-H(4BA)	0.9500
C(5B)-C(6B)	1.353(17)
C(5B)-C(7B)	1.530(19)
C(6B)-H(6BA)	0.9500
C(7B)-H(7BA)	0.9800
C(7B)-H(7BB)	0.9800
C(7B)-H(7BC)	0.9800
C(8B)-H(8BA)	0.9800

C(8B)-H(8BB)	0.9800
C(8B)-H(8BC)	0.9800
C(9B)-C(14B)	1.349(15)
C(9B)-C(10B)	1.398(15)
C(9B)-P(1B)	1.822(10)
C(10B)-C(11B)	1.386(17)
C(10B)-H(10B)	0.9500
C(11B)-C(12B)	1.385(18)
C(11B)-C(16B)	1.538(17)
C(12B)-C(13B)	1.356(15)
C(12B)-H(12B)	0.9500
C(13B)-C(14B)	1.416(15)
C(13B)-C(15B)	1.507(17)
C(14B)-H(14B)	0.9500
C(15B)-H(15D)	0.9800
C(15B)-H(15E)	0.9800
C(15B)-H(15F)	0.9800
C(16B)-H(16D)	0.9800
C(16B)-H(16E)	0.9800
C(16B)-H(16F)	0.9800
C(17B)-C(26B)	1.400(14)
C(17B)-C(18B)	1.424(14)
C(17B)-P(1B)	1.828(11)
C(18B)-C(19B)	1.364(15)
C(18B)-H(18B)	0.9500
C(19B)-C(20B)	1.409(15)
C(19B)-H(19B)	0.9500
C(20B)-C(25B)	1.405(15)
C(20B)-C(21B)	1.415(15)
C(21B)-C(22B)	1.377(18)
C(21B)-H(21B)	0.9500
C(22B)-C(23B)	1.367(19)
C(22B)-H(22B)	0.9500
C(23B)-C(24B)	1.378(17)
C(23B)-H(23B)	0.9500
C(24B)-C(25B)	1.407(14)
C(24B)-H(24B)	0.9500
C(25B)-C(26B)	1.470(14)
C(26B)-C(27B)	1.462(15)
C(27B)-C(36B)	1.385(17)
C(27B)-C(28B)	1.415(18)
C(28B)-C(29B)	1.402(18)
C(28B)-C(33B)	1.426(16)
C(29B)-C(30B)	1.374(19)
C(29B)-H(29B)	0.9500
C(30B)-C(31B)	1.422(19)

C(30B)-H(30B)	0.9500
C(31B)-C(32B)	1.37(2)
C(31B)-H(31B)	0.9500
C(32B)-C(33B)	1.391(19)
C(32B)-H(32B)	0.9500
C(33B)-C(34B)	1.439(19)
C(34B)-C(35B)	1.288(19)
C(34B)-H(34B)	0.9500
C(35B)-C(36B)	1.419(16)
C(35B)-H(35B)	0.9500
C(36B)-P(2B)	1.851(16)
C(37B)-C(42B)	1.373(18)
C(37B)-C(38B)	1.392(16)
C(37B)-P(2B)	1.820(13)
C(38B)-C(39B)	1.404(16)
C(38B)-H(38B)	0.9500
C(39B)-C(40B)	1.375(16)
C(39B)-C(43B)	1.495(16)
C(40B)-C(41B)	1.336(17)
C(40B)-H(40B)	0.9500
C(41B)-C(42B)	1.404(18)
C(41B)-C(44B)	1.522(17)
C(42B)-H(42B)	0.9500
C(43B)-H(43D)	0.9800
C(43B)-H(43E)	0.9800
C(43B)-H(43F)	0.9800
C(44B)-H(44D)	0.9800
C(44B)-H(44E)	0.9800
C(44B)-H(44F)	0.9800
C(45B)-C(50B)	1.33(3)
C(45B)-C(46B)	1.48(3)
C(45B)-P(2B)	1.815(15)
C(46B)-C(47B)	1.39(2)
C(46B)-H(46B)	0.9500
C(47B)-C(48B)	1.35(3)
C(47B)-C(51B)	1.66(4)
C(48B)-C(49B)	1.34(2)
C(48B)-H(48B)	0.9500
C(49B)-C(50B)	1.46(2)
C(49B)-C(52B)	1.49(3)
C(50B)-H(50B)	0.9500
C(51B)-H(51D)	0.9800
C(51B)-H(51E)	0.9800
C(51B)-H(51F)	0.9800
C(52B)-H(52D)	0.9800
C(52B)-H(52E)	0.9800

C(52B)-H(52F)	0.9800

P(1A)-Au(1)-Cl(1A)	175.86(10)
P(2A)-Au(2)-Cl(2A)	176.16(10)
P(1B)-Au(1B)-Cl(1B)	176.45(12)
P(2B)-Au(2B)-Cl(2B)	174.85(14)
C(2A)-C(1A)-C(6A)	117.1(9)
C(2A)-C(1A)-P(1A)	119.4(8)
C(6A)-C(1A)-P(1A)	123.4(7)
C(3A)-C(2A)-C(1A)	123.4(10)
C(3A)-C(2A)-H(2AA)	118.3
C(1A)-C(2A)-H(2AA)	118.3
C(2A)-C(3A)-C(4A)	116.5(10)
C(2A)-C(3A)-C(7A)	122.5(10)
C(4A)-C(3A)-C(7A)	121.0(10)
C(3A)-C(4A)-C(5A)	123.4(11)
C(3A)-C(4A)-H(4AA)	118.3
C(5A)-C(4A)-H(4AA)	118.3
C(6A)-C(5A)-C(4A)	118.5(10)
C(6A)-C(5A)-C(8A)	119.7(11)
C(4A)-C(5A)-C(8A)	121.7(11)
C(5A)-C(6A)-C(1A)	121.0(10)
C(5A)-C(6A)-H(6AA)	119.5
C(1A)-C(6A)-H(6AA)	119.5
C(3A)-C(7A)-H(7AA)	109.5
C(3A)-C(7A)-H(7AB)	109.5
H(7AA)-C(7A)-H(7AB)	109.5
C(3A)-C(7A)-H(7AC)	109.5
H(7AA)-C(7A)-H(7AC)	109.5
H(7AB)-C(7A)-H(7AC)	109.5
C(5A)-C(8A)-H(8AA)	109.5
C(5A)-C(8A)-H(8AB)	109.5
H(8AA)-C(8A)-H(8AB)	109.5
C(5A)-C(8A)-H(8AC)	109.5
H(8AA)-C(8A)-H(8AC)	109.5
H(8AB)-C(8A)-H(8AC)	109.5
C(14A)-C(9A)-C(10A)	118.5(9)
C(14A)-C(9A)-P(1A)	121.0(8)
C(10A)-C(9A)-P(1A)	120.4(8)
C(11A)-C(10A)-C(9A)	119.7(10)
C(11A)-C(10A)-H(10A)	120.2
C(9A)-C(10A)-H(10A)	120.2
C(12A)-C(11A)-C(10A)	120.8(10)
C(12A)-C(11A)-C(15A)	119.7(10)
C(10A)-C(11A)-C(15A)	119.4(11)
C(11A)-C(12A)-C(13A)	118.9(10)

C(11A)-C(12A)-H(12A)	120.6
C(13A)-C(12A)-H(12A)	120.6
C(14A)-C(13A)-C(12A)	120.3(10)
C(14A)-C(13A)-C(16A)	119.1(11)
C(12A)-C(13A)-C(16A)	120.6(10)
C(9A)-C(14A)-C(13A)	121.9(10)
C(9A)-C(14A)-H(14A)	119.0
C(13A)-C(14A)-H(14A)	119.0
C(11A)-C(15A)-H(15A)	109.5
C(11A)-C(15A)-H(15B)	109.5
H(15A)-C(15A)-H(15B)	109.5
C(11A)-C(15A)-H(15C)	109.5
H(15A)-C(15A)-H(15C)	109.5
H(15B)-C(15A)-H(15C)	109.5
C(13A)-C(16A)-H(16A)	109.5
C(13A)-C(16A)-H(16B)	109.5
H(16A)-C(16A)-H(16B)	109.5
C(13A)-C(16A)-H(16C)	109.5
H(16A)-C(16A)-H(16C)	109.5
H(16B)-C(16A)-H(16C)	109.5
C(26A)-C(17A)-C(18A)	120.2(9)
C(26A)-C(17A)-P(1A)	122.1(7)
C(18A)-C(17A)-P(1A)	117.7(7)
C(19A)-C(18A)-C(17A)	122.1(10)
C(19A)-C(18A)-H(18A)	119.0
C(17A)-C(18A)-H(18A)	119.0
C(18A)-C(19A)-C(20A)	119.8(9)
C(18A)-C(19A)-H(19A)	120.1
C(20A)-C(19A)-H(19A)	120.1
C(21A)-C(20A)-C(25A)	121.0(9)
C(21A)-C(20A)-C(19A)	121.4(9)
C(25A)-C(20A)-C(19A)	117.7(8)
C(22A)-C(21A)-C(20A)	120.7(10)
C(22A)-C(21A)-H(21A)	119.6
C(20A)-C(21A)-H(21A)	119.6
C(21A)-C(22A)-C(23A)	120.2(10)
C(21A)-C(22A)-H(22A)	119.9
C(23A)-C(22A)-H(22A)	119.9
C(24A)-C(23A)-C(22A)	119.6(10)
C(24A)-C(23A)-H(23A)	120.2
C(22A)-C(23A)-H(23A)	120.2
C(23A)-C(24A)-C(25A)	121.6(10)
C(23A)-C(24A)-H(24A)	119.2
C(25A)-C(24A)-H(24A)	119.2
C(20A)-C(25A)-C(24A)	116.8(9)
C(20A)-C(25A)-C(26A)	122.1(9)

C(24A)-C(25A)-C(26A) 121.0(9)
C(17A)-C(26A)-C(25A) 118.0(9)
C(17A)-C(26A)-C(27A) 124.4(9)
C(25A)-C(26A)-C(27A) 117.3(9)
C(36A)-C(27A)-C(28A) 117.6(8)
C(36A)-C(27A)-C(26A) 123.8(8)
C(28A)-C(27A)-C(26A) 118.0(8)
C(29A)-C(28A)-C(33A) 119.9(9)
C(29A)-C(28A)-C(27A) 120.3(9)
C(33A)-C(28A)-C(27A) 119.8(9)
C(30A)-C(29A)-C(28A) 120.5(11)
C(30A)-C(29A)-H(29A) 119.8
C(28A)-C(29A)-H(29A) 119.8
C(29A)-C(30A)-C(31A) 120.2(12)
C(29A)-C(30A)-H(30A) 119.9
C(31A)-C(30A)-H(30A) 119.9
C(32A)-C(31A)-C(30A) 121.1(11)
C(32A)-C(31A)-H(31A) 119.5
C(30A)-C(31A)-H(31A) 119.5
C(31A)-C(32A)-C(33A) 121.6(11)
C(31A)-C(32A)-H(32A) 119.2
C(33A)-C(32A)-H(32A) 119.2
C(34A)-C(33A)-C(28A) 119.4(9)
C(34A)-C(33A)-C(32A) 123.8(10)
C(28A)-C(33A)-C(32A) 116.6(10)
C(35A)-C(34A)-C(33A) 121.1(9)
C(35A)-C(34A)-H(34A) 119.4
C(33A)-C(34A)-H(34A) 119.4
C(34A)-C(35A)-C(36A) 121.0(9)
C(34A)-C(35A)-H(35A) 119.5
C(36A)-C(35A)-H(35A) 119.5
C(27A)-C(36A)-C(35A) 120.9(9)
C(27A)-C(36A)-P(2A) 121.8(7)
C(35A)-C(36A)-P(2A) 117.0(7)
C(42A)-C(37A)-C(38A) 119.5(9)
C(42A)-C(37A)-P(2A) 115.9(7)
C(38A)-C(37A)-P(2A) 124.4(7)
C(39A)-C(38A)-C(37A) 120.0(10)
C(39A)-C(38A)-H(38A) 120.0
C(37A)-C(38A)-H(38A) 120.0
C(38A)-C(39A)-C(40A) 119.8(10)
C(38A)-C(39A)-C(43A) 119.7(11)
C(40A)-C(39A)-C(43A) 120.4(10)
C(41A)-C(40A)-C(39A) 122.5(10)
C(41A)-C(40A)-H(40A) 118.8
C(39A)-C(40A)-H(40A) 118.8

C(40A)-C(41A)-C(42A) 118.2(10)
C(40A)-C(41A)-C(44A) 122.2(10)
C(42A)-C(41A)-C(44A) 119.6(10)
C(37A)-C(42A)-C(41A) 119.9(9)
C(37A)-C(42A)-H(42A) 120.0
C(41A)-C(42A)-H(42A) 120.0
C(39A)-C(43A)-H(43A) 109.5
C(39A)-C(43A)-H(43B) 109.5
H(43A)-C(43A)-H(43B) 109.5
C(39A)-C(43A)-H(43C) 109.5
H(43A)-C(43A)-H(43C) 109.5
H(43B)-C(43A)-H(43C) 109.5
C(41A)-C(44A)-H(44A) 109.5
C(41A)-C(44A)-H(44B) 109.5
H(44A)-C(44A)-H(44B) 109.5
C(41A)-C(44A)-H(44C) 109.5
H(44A)-C(44A)-H(44C) 109.5
H(44B)-C(44A)-H(44C) 109.5
C(50A)-C(45A)-C(46A) 118.2(9)
C(50A)-C(45A)-P(2A) 116.2(7)
C(46A)-C(45A)-P(2A) 125.6(7)
C(47A)-C(46A)-C(45A) 121.0(9)
C(47A)-C(46A)-H(46A) 119.5
C(45A)-C(46A)-H(46A) 119.5
C(46A)-C(47A)-C(48A) 118.7(10)
C(46A)-C(47A)-C(51A) 121.1(10)
C(48A)-C(47A)-C(51A) 120.1(10)
C(49A)-C(48A)-C(47A) 122.8(10)
C(49A)-C(48A)-H(48A) 118.6
C(47A)-C(48A)-H(48A) 118.6
C(48A)-C(49A)-C(50A) 117.2(9)
C(48A)-C(49A)-C(52A) 123.0(10)
C(50A)-C(49A)-C(52A) 119.7(10)
C(45A)-C(50A)-C(49A) 122.1(9)
C(45A)-C(50A)-H(50A) 119.0
C(49A)-C(50A)-H(50A) 119.0
C(47A)-C(51A)-H(51A) 109.5
C(47A)-C(51A)-H(51B) 109.5
H(51A)-C(51A)-H(51B) 109.5
C(47A)-C(51A)-H(51C) 109.5
H(51A)-C(51A)-H(51C) 109.5
H(51B)-C(51A)-H(51C) 109.5
C(49A)-C(52A)-H(52A) 109.3
C(49A)-C(52A)-H(52B) 109.5
H(52A)-C(52A)-H(52B) 109.5
C(49A)-C(52A)-H(52C) 109.6

H(52A)-C(52A)-H(52C)	109.5
H(52B)-C(52A)-H(52C)	109.5
C(6B)-C(1B)-C(2B)	120.1(12)
C(6B)-C(1B)-P(1B)	123.5(9)
C(2B)-C(1B)-P(1B)	116.0(9)
C(3B)-C(2B)-C(1B)	120.4(12)
C(3B)-C(2B)-H(2BA)	119.8
C(1B)-C(2B)-H(2BA)	119.8
C(4B)-C(3B)-C(2B)	118.4(12)
C(4B)-C(3B)-C(8B)	125.0(15)
C(2B)-C(3B)-C(8B)	116.0(14)
C(3B)-C(4B)-C(5B)	123.2(14)
C(3B)-C(4B)-H(4BA)	118.4
C(5B)-C(4B)-H(4BA)	118.4
C(6B)-C(5B)-C(4B)	117.5(13)
C(6B)-C(5B)-C(7B)	121.5(13)
C(4B)-C(5B)-C(7B)	121.0(13)
C(5B)-C(6B)-C(1B)	120.0(12)
C(5B)-C(6B)-H(6BA)	120.0
C(1B)-C(6B)-H(6BA)	120.0
C(5B)-C(7B)-H(7BA)	109.5
C(5B)-C(7B)-H(7BB)	109.5
H(7BA)-C(7B)-H(7BB)	109.5
C(5B)-C(7B)-H(7BC)	109.5
H(7BA)-C(7B)-H(7BC)	109.5
H(7BB)-C(7B)-H(7BC)	109.5
C(3B)-C(8B)-H(8BA)	109.5
C(3B)-C(8B)-H(8BB)	109.5
H(8BA)-C(8B)-H(8BB)	109.5
C(3B)-C(8B)-H(8BC)	109.5
H(8BA)-C(8B)-H(8BC)	109.5
H(8BB)-C(8B)-H(8BC)	109.5
C(14B)-C(9B)-C(10B)	119.2(10)
C(14B)-C(9B)-P(1B)	123.0(8)
C(10B)-C(9B)-P(1B)	117.2(8)
C(11B)-C(10B)-C(9B)	121.5(11)
C(11B)-C(10B)-H(10B)	119.2
C(9B)-C(10B)-H(10B)	119.2
C(10B)-C(11B)-C(12B)	117.6(11)
C(10B)-C(11B)-C(16B)	121.1(12)
C(12B)-C(11B)-C(16B)	121.3(11)
C(13B)-C(12B)-C(11B)	121.9(11)
C(13B)-C(12B)-H(12B)	119.0
C(11B)-C(12B)-H(12B)	119.0
C(12B)-C(13B)-C(14B)	119.4(11)
C(12B)-C(13B)-C(15B)	120.7(11)

C(14B)-C(13B)-C(15B) 119.9(10)
C(9B)-C(14B)-C(13B) 120.2(10)
C(9B)-C(14B)-H(14B) 119.9
C(13B)-C(14B)-H(14B) 119.9
C(13B)-C(15B)-H(15D) 109.5
C(13B)-C(15B)-H(15E) 109.5
H(15D)-C(15B)-H(15E) 109.5
C(13B)-C(15B)-H(15F) 109.5
H(15D)-C(15B)-H(15F) 109.5
H(15E)-C(15B)-H(15F) 109.5
C(11B)-C(16B)-H(16D) 109.5
C(11B)-C(16B)-H(16E) 109.5
H(16D)-C(16B)-H(16E) 109.5
C(11B)-C(16B)-H(16F) 109.5
H(16D)-C(16B)-H(16F) 109.5
H(16E)-C(16B)-H(16F) 109.5
C(26B)-C(17B)-C(18B) 120.8(10)
C(26B)-C(17B)-P(1B) 122.0(8)
C(18B)-C(17B)-P(1B) 117.2(8)
C(19B)-C(18B)-C(17B) 120.5(10)
C(19B)-C(18B)-H(18B) 119.7
C(17B)-C(18B)-H(18B) 119.7
C(18B)-C(19B)-C(20B) 121.2(10)
C(18B)-C(19B)-H(19B) 119.4
C(20B)-C(19B)-H(19B) 119.4
C(25B)-C(20B)-C(19B) 120.1(10)
C(25B)-C(20B)-C(21B) 118.8(11)
C(19B)-C(20B)-C(21B) 121.0(10)
C(22B)-C(21B)-C(20B) 119.9(11)
C(22B)-C(21B)-H(21B) 120.0
C(20B)-C(21B)-H(21B) 120.0
C(23B)-C(22B)-C(21B) 121.2(11)
C(23B)-C(22B)-H(22B) 119.4
C(21B)-C(22B)-H(22B) 119.4
C(22B)-C(23B)-C(24B) 120.4(12)
C(22B)-C(23B)-H(23B) 119.8
C(24B)-C(23B)-H(23B) 119.8
C(23B)-C(24B)-C(25B) 120.3(12)
C(23B)-C(24B)-H(24B) 119.9
C(25B)-C(24B)-H(24B) 119.9
C(20B)-C(25B)-C(24B) 119.4(10)
C(20B)-C(25B)-C(26B) 119.2(9)
C(24B)-C(25B)-C(26B) 121.3(10)
C(17B)-C(26B)-C(27B) 125.2(9)
C(17B)-C(26B)-C(25B) 118.0(9)
C(27B)-C(26B)-C(25B) 116.7(8)

C(36B)-C(27B)-C(28B) 119.6(11)
C(36B)-C(27B)-C(26B) 123.1(11)
C(28B)-C(27B)-C(26B) 117.2(11)
C(29B)-C(28B)-C(27B) 122.6(11)
C(29B)-C(28B)-C(33B) 118.5(12)
C(27B)-C(28B)-C(33B) 119.0(12)
C(30B)-C(29B)-C(28B) 121.3(12)
C(30B)-C(29B)-H(29B) 119.3
C(28B)-C(29B)-H(29B) 119.3
C(29B)-C(30B)-C(31B) 119.8(15)
C(29B)-C(30B)-H(30B) 120.1
C(31B)-C(30B)-H(30B) 120.1
C(32B)-C(31B)-C(30B) 119.3(13)
C(32B)-C(31B)-H(31B) 120.4
C(30B)-C(31B)-H(31B) 120.4
C(31B)-C(32B)-C(33B) 121.7(13)
C(31B)-C(32B)-H(32B) 119.2
C(33B)-C(32B)-H(32B) 119.2
C(32B)-C(33B)-C(28B) 119.3(13)
C(32B)-C(33B)-C(34B) 122.8(12)
C(28B)-C(33B)-C(34B) 117.8(12)
C(35B)-C(34B)-C(33B) 122.3(12)
C(35B)-C(34B)-H(34B) 118.9
C(33B)-C(34B)-H(34B) 118.9
C(34B)-C(35B)-C(36B) 121.1(14)
C(34B)-C(35B)-H(35B) 119.4
C(36B)-C(35B)-H(35B) 119.4
C(27B)-C(36B)-C(35B) 120.2(14)
C(27B)-C(36B)-P(2B) 124.1(9)
C(35B)-C(36B)-P(2B) 115.7(11)
C(42B)-C(37B)-C(38B) 121.1(12)
C(42B)-C(37B)-P(2B) 123.6(10)
C(38B)-C(37B)-P(2B) 115.3(10)
C(37B)-C(38B)-C(39B) 118.6(11)
C(37B)-C(38B)-H(38B) 120.7
C(39B)-C(38B)-H(38B) 120.7
C(40B)-C(39B)-C(38B) 118.1(11)
C(40B)-C(39B)-C(43B) 122.2(11)
C(38B)-C(39B)-C(43B) 119.7(11)
C(41B)-C(40B)-C(39B) 124.0(12)
C(41B)-C(40B)-H(40B) 118.0
C(39B)-C(40B)-H(40B) 118.0
C(40B)-C(41B)-C(42B) 118.4(12)
C(40B)-C(41B)-C(44B) 122.5(12)
C(42B)-C(41B)-C(44B) 119.0(12)
C(37B)-C(42B)-C(41B) 119.7(12)

C(37B)-C(42B)-H(42B) 120.2
C(41B)-C(42B)-H(42B) 120.2
C(39B)-C(43B)-H(43D) 109.5
C(39B)-C(43B)-H(43E) 109.5
H(43D)-C(43B)-H(43E) 109.5
C(39B)-C(43B)-H(43F) 109.5
H(43D)-C(43B)-H(43F) 109.5
H(43E)-C(43B)-H(43F) 109.5
C(41B)-C(44B)-H(44D) 109.5
C(41B)-C(44B)-H(44E) 109.5
H(44D)-C(44B)-H(44E) 109.5
C(41B)-C(44B)-H(44F) 109.5
H(44D)-C(44B)-H(44F) 109.5
H(44E)-C(44B)-H(44F) 109.5
C(50B)-C(45B)-C(46B) 123.4(16)
C(50B)-C(45B)-P(2B) 124.5(16)
C(46B)-C(45B)-P(2B) 112.1(15)
C(47B)-C(46B)-C(45B) 119(2)
C(47B)-C(46B)-H(46B) 120.7
C(45B)-C(46B)-H(46B) 120.7
C(48B)-C(47B)-C(46B) 114(2)
C(48B)-C(47B)-C(51B) 127(2)
C(46B)-C(47B)-C(51B) 118(2)
C(49B)-C(48B)-C(47B) 128.6(17)
C(49B)-C(48B)-H(48B) 115.7
C(47B)-C(48B)-H(48B) 115.7
C(48B)-C(49B)-C(50B) 117.8(18)
C(48B)-C(49B)-C(52B) 130.0(18)
C(50B)-C(49B)-C(52B) 112.0(17)
C(45B)-C(50B)-C(49B) 116(2)
C(45B)-C(50B)-H(50B) 122.0
C(49B)-C(50B)-H(50B) 122.0
C(47B)-C(51B)-H(51D) 109.5
C(47B)-C(51B)-H(51E) 109.5
H(51D)-C(51B)-H(51E) 109.5
C(47B)-C(51B)-H(51F) 109.5
H(51D)-C(51B)-H(51F) 109.5
H(51E)-C(51B)-H(51F) 109.5
C(49B)-C(52B)-H(52D) 109.5
C(49B)-C(52B)-H(52E) 109.5
H(52D)-C(52B)-H(52E) 109.5
C(49B)-C(52B)-H(52F) 109.5
H(52D)-C(52B)-H(52F) 109.5
H(52E)-C(52B)-H(52F) 109.5
C(1A)-P(1A)-C(9A) 110.2(5)
C(1A)-P(1A)-C(17A) 106.9(5)

C(9A)-P(1A)-C(17A)	103.1(5)
C(1A)-P(1A)-Au(1)	108.5(3)
C(9A)-P(1A)-Au(1)	110.3(3)
C(17A)-P(1A)-Au(1)	117.6(3)
C(45A)-P(2A)-C(37A)	106.1(4)
C(45A)-P(2A)-C(36A)	106.8(4)
C(37A)-P(2A)-C(36A)	101.6(4)
C(45A)-P(2A)-Au(2)	109.7(3)
C(37A)-P(2A)-Au(2)	112.8(3)
C(36A)-P(2A)-Au(2)	118.8(3)
C(9B)-P(1B)-C(17B)	105.9(5)
C(9B)-P(1B)-C(1B)	108.0(5)
C(17B)-P(1B)-C(1B)	101.1(5)
C(9B)-P(1B)-Au(1B)	111.1(3)
C(17B)-P(1B)-Au(1B)	118.7(3)
C(1B)-P(1B)-Au(1B)	111.3(4)
C(45B)-P(2B)-C(37B)	106.0(6)
C(45B)-P(2B)-C(36B)	107.4(8)
C(37B)-P(2B)-C(36B)	102.3(6)
C(45B)-P(2B)-Au(2B)	110.1(6)
C(37B)-P(2B)-Au(2B)	110.8(5)
C(36B)-P(2B)-Au(2B)	119.3(4)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **240**. 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}
Au(1)	19(1)	29(1)	29(1)	4(1)	1(1)	1(1)
Au(2)	25(1)	27(1)	30(1)	4(1)	-4(1)	-2(1)
Au(1B)	92(1)	24(1)	30(1)	4(1)	-23(1)	-8(1)
Au(2B)	61(1)	51(1)	35(1)	3(1)	-5(1)	20(1)
C(1A)	28(5)	28(5)	23(5)	3(4)	-2(4)	8(4)
C(2A)	36(6)	24(5)	25(5)	13(4)	-1(4)	2(4)
C(3A)	38(5)	24(5)	39(6)	12(4)	0(5)	9(5)
C(4A)	61(8)	37(6)	25(5)	8(4)	4(5)	5(6)
C(5A)	40(6)	40(6)	35(6)	9(5)	1(5)	-18(5)
C(6A)	22(5)	35(6)	43(6)	5(5)	2(4)	-4(4)
C(7A)	38(6)	52(7)	40(6)	-3(6)	0(5)	11(6)
C(8A)	45(7)	90(11)	50(8)	-10(7)	6(6)	-27(8)
C(9A)	33(5)	31(5)	29(5)	9(4)	-2(4)	-5(4)
C(10A)	34(5)	23(5)	30(5)	4(4)	-3(5)	-7(4)
C(11A)	48(7)	32(6)	39(6)	13(5)	-6(5)	-6(5)
C(12A)	37(6)	12(5)	72(8)	-4(5)	-2(6)	4(4)
C(13A)	34(6)	43(7)	39(6)	-1(5)	-9(5)	15(5)
C(14A)	32(5)	33(6)	36(5)	0(4)	5(4)	2(5)
C(15A)	78(10)	31(7)	62(8)	15(6)	5(7)	-8(6)
C(16A)	41(7)	37(7)	77(9)	0(6)	3(6)	16(5)
C(17A)	25(4)	29(5)	29(5)	7(4)	-9(4)	2(4)
C(18A)	22(5)	39(6)	43(6)	4(5)	1(4)	-1(4)
C(19A)	27(5)	28(5)	37(5)	5(4)	-8(4)	10(4)
C(20A)	21(4)	13(4)	33(5)	-1(3)	1(4)	7(3)
C(21A)	10(4)	30(6)	68(8)	1(5)	-4(5)	0(4)
C(22A)	27(6)	43(7)	50(7)	5(5)	14(5)	-3(5)
C(23A)	28(6)	62(8)	42(6)	10(6)	10(5)	-2(6)
C(24A)	29(5)	42(7)	32(5)	7(5)	5(4)	-3(4)
C(25A)	20(4)	19(5)	37(5)	-1(4)	0(4)	8(4)
C(26A)	29(5)	20(5)	35(5)	-7(4)	-4(4)	9(4)
C(27A)	20(4)	24(5)	22(4)	1(4)	-1(4)	-3(4)
C(28A)	21(4)	22(5)	29(5)	-4(4)	3(4)	-3(4)
C(29A)	35(6)	41(6)	33(5)	1(5)	0(5)	0(5)
C(30A)	60(8)	37(7)	58(8)	-10(6)	5(7)	3(6)
C(31A)	57(8)	42(7)	54(8)	-25(6)	4(7)	-8(6)
C(32A)	35(6)	58(8)	28(5)	-8(5)	-5(5)	-13(6)
C(33A)	18(4)	46(6)	25(5)	-4(4)	7(4)	-11(4)
C(34A)	28(5)	42(6)	23(5)	5(4)	5(4)	3(4)
C(35A)	19(4)	33(5)	26(5)	5(4)	1(4)	-2(4)
C(36A)	21(4)	31(5)	18(4)	2(4)	6(3)	3(4)
C(37A)	24(5)	19(4)	27(5)	3(4)	1(4)	-6(4)

C(38A)	31(6)	30(6)	45(6)	9(5)	3(5)	0(4)
C(39A)	40(6)	26(6)	44(6)	8(5)	-3(5)	1(5)
C(40A)	46(6)	20(5)	38(6)	1(4)	2(5)	1(5)
C(41A)	50(7)	26(5)	21(5)	-2(4)	7(4)	-3(4)
C(42A)	32(5)	29(5)	24(5)	0(4)	2(4)	5(4)
C(43A)	44(7)	51(8)	68(9)	34(7)	2(6)	21(6)
C(44A)	58(8)	39(7)	60(8)	2(6)	15(7)	-6(6)
C(45A)	25(5)	24(5)	26(5)	15(4)	-6(4)	1(4)
C(46A)	29(5)	13(4)	32(5)	5(4)	3(4)	3(4)
C(47A)	27(5)	34(6)	34(5)	16(4)	0(4)	6(4)
C(48A)	32(5)	25(5)	35(5)	6(4)	5(4)	10(4)
C(49A)	37(5)	38(6)	23(5)	5(4)	4(4)	4(5)
C(50A)	25(5)	25(5)	29(5)	1(4)	1(4)	-1(4)
C(51A)	32(6)	58(8)	48(7)	-11(6)	2(5)	5(6)
C(52A)	53(7)	41(7)	27(5)	-1(5)	8(5)	6(5)
C(1B)	40(6)	26(5)	48(6)	9(5)	-3(5)	-9(4)
C(2B)	39(6)	31(6)	63(8)	9(5)	-12(6)	-6(5)
C(3B)	23(6)	53(8)	81(10)	11(7)	-13(6)	-10(5)
C(4B)	46(8)	34(7)	112(14)	25(8)	30(9)	-8(6)
C(5B)	47(8)	51(8)	53(8)	11(6)	4(6)	-17(6)
C(6B)	60(8)	41(7)	31(6)	7(5)	8(5)	16(6)
C(7B)	93(12)	58(9)	61(9)	0(7)	24(9)	17(9)
C(9B)	41(6)	23(5)	27(5)	7(4)	-2(4)	2(4)
C(10B)	48(7)	36(6)	51(7)	3(5)	-8(6)	-3(5)
C(11B)	52(7)	37(6)	63(8)	9(6)	0(7)	16(6)
C(12B)	41(7)	35(6)	44(6)	8(5)	0(5)	10(5)
C(13B)	41(6)	47(7)	30(5)	13(5)	-6(5)	-2(5)
C(14B)	43(6)	34(6)	33(5)	5(5)	-3(5)	8(5)
C(15B)	60(9)	60(9)	68(9)	20(7)	-23(7)	-3(7)
C(16B)	64(9)	44(8)	107(12)	37(8)	-35(9)	-19(7)
C(17B)	41(6)	28(5)	31(5)	1(4)	-17(5)	13(5)
C(18B)	63(8)	37(6)	20(5)	-5(4)	-3(5)	4(6)
C(19B)	57(7)	23(5)	37(6)	-9(4)	-12(5)	-9(5)
C(20B)	41(7)	32(6)	39(6)	-1(5)	-12(5)	0(5)
C(21B)	56(8)	24(5)	54(7)	-6(5)	-1(6)	-2(5)
C(22B)	59(9)	20(6)	77(10)	12(6)	16(7)	-6(5)
C(23B)	59(8)	34(7)	64(8)	19(6)	3(7)	6(7)
C(24B)	55(7)	36(6)	33(6)	10(5)	5(5)	16(5)
C(25B)	42(6)	25(5)	31(5)	-2(4)	-3(5)	7(4)
C(27B)	67(8)	22(5)	30(5)	12(4)	-6(5)	0(5)
C(28B)	67(8)	17(5)	35(6)	10(4)	-18(6)	4(5)
C(29B)	71(9)	23(6)	55(7)	10(5)	-31(7)	-4(6)
C(30B)	87(10)	22(6)	65(9)	14(6)	-27(8)	-2(6)
C(31B)	74(11)	45(8)	64(9)	15(7)	-43(8)	-20(7)
C(32B)	68(9)	35(7)	55(8)	6(6)	-13(7)	6(7)
C(33B)	84(10)	29(6)	33(6)	10(5)	-13(6)	-18(6)

C(34B)	74(9)	28(6)	38(7)	-3(5)	0(6)	-4(6)
C(35B)	97(11)	25(6)	28(6)	-2(4)	-3(7)	2(6)
C(36B)	112(12)	11(5)	30(5)	0(4)	19(6)	-15(6)
C(37B)	83(10)	43(7)	26(5)	-4(5)	-6(6)	9(7)
C(38B)	69(8)	36(6)	37(6)	0(5)	-2(6)	22(6)
C(39B)	46(7)	45(7)	36(6)	1(5)	-8(5)	10(6)
C(40B)	43(7)	49(7)	38(6)	-4(5)	-5(5)	4(6)
C(41B)	63(9)	56(8)	39(7)	-4(6)	7(6)	16(7)
C(42B)	82(10)	48(8)	47(8)	1(6)	-7(7)	25(7)
C(43B)	71(10)	45(8)	71(9)	23(7)	15(8)	23(7)
C(44B)	91(12)	66(10)	59(9)	-9(7)	6(8)	48(9)
C(45B)	147(18)	53(9)	34(7)	-3(6)	13(9)	41(11)
C(46B)	160(20)	53(10)	79(12)	11(9)	-15(12)	45(11)
C(47B)	118(16)	83(13)	76(12)	-3(10)	-5(12)	27(13)
C(48B)	124(17)	40(8)	82(12)	24(8)	37(12)	14(9)
C(49B)	50(9)	89(13)	61(9)	1(8)	25(7)	19(8)
C(50B)	154(18)	41(8)	67(10)	9(7)	70(12)	21(10)
C(51B)	360(60)	220(40)	110(20)	30(20)	-30(30)	190(40)
C(52B)	220(30)	73(14)	170(20)	66(15)	100(20)	63(17)
Cl(1A)	20(1)	55(2)	43(1)	0(1)	-8(1)	2(1)
Cl(2A)	37(1)	43(2)	50(2)	8(1)	-21(1)	-5(1)
Cl(1B)	217(6)	33(2)	43(2)	8(1)	-56(3)	-38(3)
Cl(2B)	75(3)	70(2)	56(2)	3(2)	-14(2)	2(2)
P(1A)	19(1)	26(1)	27(1)	7(1)	1(1)	0(1)
P(2A)	21(1)	24(1)	23(1)	3(1)	0(1)	-1(1)
P(1B)	48(2)	24(1)	26(1)	1(1)	-12(1)	4(1)
P(2B)	80(2)	37(2)	33(2)	4(1)	2(2)	21(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **240**.

	x	y	z	U(eq)
H(2AA)	-1745	-134	10314	34
H(4AA)	-649	1168	11052	49
H(6AA)	1424	164	10432	40
H(7AA)	-2460	1017	11018	65
H(7AB)	-2799	242	10912	65
H(7AC)	-2902	861	10633	65
H(8AA)	1161	1419	11117	92
H(8AB)	1824	1374	10760	92
H(8AC)	1905	759	11043	92

H(10A)	-899	-1487	10521	35
H(12A)	357	-3437	10414	48
H(14A)	1273	-1882	9764	40
H(15A)	-962	-3259	10839	85
H(15B)	-1841	-2700	10726	85
H(15C)	-965	-2500	11012	85
H(16A)	1999	-2960	9675	77
H(16B)	1202	-3589	9756	77
H(16C)	2151	-3421	10021	77
H(18A)	2157	-895	10199	41
H(19A)	3856	-669	10011	37
H(21A)	5060	-269	9538	43
H(22A)	5320	188	8985	48
H(23A)	3854	445	8624	53
H(24A)	2149	335	8844	41
H(29A)	1336	-1320	9128	44
H(30A)	894	-2157	8718	62
H(31A)	-366	-1917	8288	62
H(32A)	-1141	-855	8251	48
H(34A)	-1426	359	8506	37
H(35A)	-934	1206	8893	32
H(38A)	-822	2574	9243	43
H(40A)	856	3367	8441	42
H(42A)	2028	1723	8971	34
H(43A)	-1513	3513	8955	82
H(43B)	-1242	3511	8545	82
H(43C)	-660	4049	8801	82
H(44A)	2537	2961	8284	79
H(44B)	2649	2136	8329	79
H(44C)	3202	2649	8605	79
H(46A)	-1827	1003	9482	30
H(48A)	-2849	2028	10341	37
H(50A)	240	2119	10074	32
H(51A)	-3618	900	9638	68
H(51B)	-4107	1573	9826	68
H(51C)	-3793	903	10054	68
H(52A)	-1549	2506	10760	61
H(52B)	-1050	3096	10514	61
H(52C)	-316	2484	10663	61
H(2BA)	12135	3504	2466	53
H(4BA)	13060	3043	1508	77
H(6BA)	10107	3783	1661	52
H(7BA)	10621	3569	1074	106
H(7BB)	11417	2924	1035	106
H(7BC)	11857	3704	1009	106
H(8BA)	14231	2767	1984	133

H(8BB)	13637	2605	2345	133
H(8BC)	14101	3367	2272	133
H(10B)	9603	5261	2173	54
H(12B)	6615	5248	1806	48
H(14B)	7868	3513	2236	44
H(15D)	5526	4286	1850	94
H(15E)	5769	3803	2182	94
H(15F)	6149	3566	1801	94
H(16D)	8978	6298	1903	107
H(16E)	7741	6428	1970	107
H(16F)	8143	6168	1594	107
H(18B)	9423	2681	2067	48
H(19B)	8855	1577	2209	47
H(21B)	8352	697	2650	54
H(22B)	8220	366	3232	62
H(23B)	8635	1131	3677	63
H(24B)	9180	2260	3550	50
H(29B)	11386	2698	2994	59
H(30B)	13116	2795	3192	70
H(31B)	13520	3550	3668	73
H(32B)	12163	4140	3948	63
H(34B)	10248	4460	3999	56
H(35B)	8604	4411	3797	60
H(38B)	7298	2700	3758	57
H(40B)	5491	3503	4531	52
H(42B)	6152	4668	3691	71
H(43D)	6167	2380	4611	94
H(43E)	7308	2265	4437	94
H(43F)	6271	1955	4252	94
H(44D)	4801	4635	4522	108
H(44E)	4497	4867	4132	108
H(44F)	5531	5181	4317	108
H(46B)	5643	4262	2938	115
H(48B)	6361	6179	2642	99
H(50B)	8564	5089	3177	105
H(51D)	4428	5806	2541	347
H(51E)	4027	5230	2814	347
H(51F)	4488	4997	2441	347
H(52D)	8047	6758	2817	233
H(52E)	8949	6173	2793	233
H(52F)	8538	6432	3167	233

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Table 6. Torsion angles [°] for **240**.

C(6A)-C(1A)-C(2A)-C(3A)	-1.5(14)
P(1A)-C(1A)-C(2A)-C(3A)	-179.3(7)
C(1A)-C(2A)-C(3A)-C(4A)	1.8(14)
C(1A)-C(2A)-C(3A)-C(7A)	-177.4(10)
C(2A)-C(3A)-C(4A)-C(5A)	0.2(15)
C(7A)-C(3A)-C(4A)-C(5A)	179.4(11)
C(3A)-C(4A)-C(5A)-C(6A)	-2.3(16)
C(3A)-C(4A)-C(5A)-C(8A)	178.6(11)
C(4A)-C(5A)-C(6A)-C(1A)	2.6(16)
C(8A)-C(5A)-C(6A)-C(1A)	-178.3(11)
C(2A)-C(1A)-C(6A)-C(5A)	-0.7(15)
P(1A)-C(1A)-C(6A)-C(5A)	176.9(8)
C(14A)-C(9A)-C(10A)-C(11A)	-0.2(15)
P(1A)-C(9A)-C(10A)-C(11A)	175.9(8)
C(9A)-C(10A)-C(11A)-C(12A)	0.8(16)
C(9A)-C(10A)-C(11A)-C(15A)	-176.0(11)
C(10A)-C(11A)-C(12A)-C(13A)	-1.0(17)
C(15A)-C(11A)-C(12A)-C(13A)	175.7(11)
C(11A)-C(12A)-C(13A)-C(14A)	0.7(17)
C(11A)-C(12A)-C(13A)-C(16A)	-177.4(11)
C(10A)-C(9A)-C(14A)-C(13A)	0.0(16)
P(1A)-C(9A)-C(14A)-C(13A)	-176.1(9)
C(12A)-C(13A)-C(14A)-C(9A)	-0.2(17)
C(16A)-C(13A)-C(14A)-C(9A)	177.9(10)
C(26A)-C(17A)-C(18A)-C(19A)	1.7(16)
P(1A)-C(17A)-C(18A)-C(19A)	-179.5(9)
C(17A)-C(18A)-C(19A)-C(20A)	-3.2(16)
C(18A)-C(19A)-C(20A)-C(21A)	-178.0(10)
C(18A)-C(19A)-C(20A)-C(25A)	2.2(14)
C(25A)-C(20A)-C(21A)-C(22A)	-1.3(15)
C(19A)-C(20A)-C(21A)-C(22A)	178.8(10)
C(20A)-C(21A)-C(22A)-C(23A)	-0.4(17)
C(21A)-C(22A)-C(23A)-C(24A)	2.9(19)
C(22A)-C(23A)-C(24A)-C(25A)	-3.5(18)
C(21A)-C(20A)-C(25A)-C(24A)	0.7(14)
C(19A)-C(20A)-C(25A)-C(24A)	-179.4(9)
C(21A)-C(20A)-C(25A)-C(26A)	-179.7(9)
C(19A)-C(20A)-C(25A)-C(26A)	0.2(14)
C(23A)-C(24A)-C(25A)-C(20A)	1.7(16)
C(23A)-C(24A)-C(25A)-C(26A)	-177.9(11)
C(18A)-C(17A)-C(26A)-C(25A)	0.7(14)
P(1A)-C(17A)-C(26A)-C(25A)	-178.0(7)
C(18A)-C(17A)-C(26A)-C(27A)	174.0(9)
P(1A)-C(17A)-C(26A)-C(27A)	-4.7(14)

C(20A)-C(25A)-C(26A)-C(17A)	-1.6(14)
C(24A)-C(25A)-C(26A)-C(17A)	178.0(9)
C(20A)-C(25A)-C(26A)-C(27A)	-175.4(8)
C(24A)-C(25A)-C(26A)-C(27A)	4.2(14)
C(17A)-C(26A)-C(27A)-C(36A)	95.5(12)
C(25A)-C(26A)-C(27A)-C(36A)	-91.2(11)
C(17A)-C(26A)-C(27A)-C(28A)	-93.2(11)
C(25A)-C(26A)-C(27A)-C(28A)	80.1(11)
C(36A)-C(27A)-C(28A)-C(29A)	179.0(9)
C(26A)-C(27A)-C(28A)-C(29A)	7.2(13)
C(36A)-C(27A)-C(28A)-C(33A)	-3.5(13)
C(26A)-C(27A)-C(28A)-C(33A)	-175.3(8)
C(33A)-C(28A)-C(29A)-C(30A)	1.6(15)
C(27A)-C(28A)-C(29A)-C(30A)	179.1(10)
C(28A)-C(29A)-C(30A)-C(31A)	0.0(18)
C(29A)-C(30A)-C(31A)-C(32A)	1(2)
C(30A)-C(31A)-C(32A)-C(33A)	-2.7(19)
C(29A)-C(28A)-C(33A)-C(34A)	-178.7(9)
C(27A)-C(28A)-C(33A)-C(34A)	3.8(13)
C(29A)-C(28A)-C(33A)-C(32A)	-3.5(13)
C(27A)-C(28A)-C(33A)-C(32A)	179.0(9)
C(31A)-C(32A)-C(33A)-C(34A)	179.1(11)
C(31A)-C(32A)-C(33A)-C(28A)	4.1(16)
C(28A)-C(33A)-C(34A)-C(35A)	-0.9(14)
C(32A)-C(33A)-C(34A)-C(35A)	-175.7(9)
C(33A)-C(34A)-C(35A)-C(36A)	-2.3(14)
C(28A)-C(27A)-C(36A)-C(35A)	0.3(13)
C(26A)-C(27A)-C(36A)-C(35A)	171.7(9)
C(28A)-C(27A)-C(36A)-P(2A)	-173.5(7)
C(26A)-C(27A)-C(36A)-P(2A)	-2.1(13)
C(34A)-C(35A)-C(36A)-C(27A)	2.6(14)
C(34A)-C(35A)-C(36A)-P(2A)	176.7(7)
C(42A)-C(37A)-C(38A)-C(39A)	-0.1(16)
P(2A)-C(37A)-C(38A)-C(39A)	-175.8(8)
C(37A)-C(38A)-C(39A)-C(40A)	1.7(17)
C(37A)-C(38A)-C(39A)-C(43A)	177.8(11)
C(38A)-C(39A)-C(40A)-C(41A)	-3.4(17)
C(43A)-C(39A)-C(40A)-C(41A)	-179.4(11)
C(39A)-C(40A)-C(41A)-C(42A)	3.2(16)
C(39A)-C(40A)-C(41A)-C(44A)	-176.5(11)
C(38A)-C(37A)-C(42A)-C(41A)	0.1(15)
P(2A)-C(37A)-C(42A)-C(41A)	176.1(8)
C(40A)-C(41A)-C(42A)-C(37A)	-1.6(15)
C(44A)-C(41A)-C(42A)-C(37A)	178.1(10)
C(50A)-C(45A)-C(46A)-C(47A)	0.5(13)
P(2A)-C(45A)-C(46A)-C(47A)	-179.5(7)

C(45A)-C(46A)-C(47A)-C(48A)	-0.1(14)
C(45A)-C(46A)-C(47A)-C(51A)	-176.4(9)
C(46A)-C(47A)-C(48A)-C(49A)	0.4(15)
C(51A)-C(47A)-C(48A)-C(49A)	176.8(10)
C(47A)-C(48A)-C(49A)-C(50A)	-1.2(15)
C(47A)-C(48A)-C(49A)-C(52A)	-177.1(9)
C(46A)-C(45A)-C(50A)-C(49A)	-1.3(13)
P(2A)-C(45A)-C(50A)-C(49A)	178.7(8)
C(48A)-C(49A)-C(50A)-C(45A)	1.7(14)
C(52A)-C(49A)-C(50A)-C(45A)	177.7(9)
C(6B)-C(1B)-C(2B)-C(3B)	-2.8(17)
P(1B)-C(1B)-C(2B)-C(3B)	170.1(9)
C(1B)-C(2B)-C(3B)-C(4B)	7.4(18)
C(1B)-C(2B)-C(3B)-C(8B)	178.9(12)
C(2B)-C(3B)-C(4B)-C(5B)	-8(2)
C(8B)-C(3B)-C(4B)-C(5B)	-178.4(14)
C(3B)-C(4B)-C(5B)-C(6B)	3(2)
C(3B)-C(4B)-C(5B)-C(7B)	-178.9(14)
C(4B)-C(5B)-C(6B)-C(1B)	1.7(18)
C(7B)-C(5B)-C(6B)-C(1B)	-176.2(12)
C(2B)-C(1B)-C(6B)-C(5B)	-1.8(18)
P(1B)-C(1B)-C(6B)-C(5B)	-174.1(9)
C(14B)-C(9B)-C(10B)-C(11B)	-5.2(18)
P(1B)-C(9B)-C(10B)-C(11B)	-177.5(10)
C(9B)-C(10B)-C(11B)-C(12B)	3.3(19)
C(9B)-C(10B)-C(11B)-C(16B)	-175.7(13)
C(10B)-C(11B)-C(12B)-C(13B)	-0.1(19)
C(16B)-C(11B)-C(12B)-C(13B)	178.9(13)
C(11B)-C(12B)-C(13B)-C(14B)	-1.2(18)
C(11B)-C(12B)-C(13B)-C(15B)	178.9(13)
C(10B)-C(9B)-C(14B)-C(13B)	3.8(17)
P(1B)-C(9B)-C(14B)-C(13B)	175.6(8)
C(12B)-C(13B)-C(14B)-C(9B)	-0.6(17)
C(15B)-C(13B)-C(14B)-C(9B)	179.2(11)
C(26B)-C(17B)-C(18B)-C(19B)	0.2(17)
P(1B)-C(17B)-C(18B)-C(19B)	179.8(9)
C(17B)-C(18B)-C(19B)-C(20B)	0.0(19)
C(18B)-C(19B)-C(20B)-C(25B)	-3.2(18)
C(18B)-C(19B)-C(20B)-C(21B)	-179.2(12)
C(25B)-C(20B)-C(21B)-C(22B)	0.7(18)
C(19B)-C(20B)-C(21B)-C(22B)	176.6(12)
C(20B)-C(21B)-C(22B)-C(23B)	0(2)
C(21B)-C(22B)-C(23B)-C(24B)	0(2)
C(22B)-C(23B)-C(24B)-C(25B)	-0.9(19)
C(19B)-C(20B)-C(25B)-C(24B)	-177.3(11)
C(21B)-C(20B)-C(25B)-C(24B)	-1.3(16)

C(19B)-C(20B)-C(25B)-C(26B)	6.0(16)
C(21B)-C(20B)-C(25B)-C(26B)	-178.0(10)
C(23B)-C(24B)-C(25B)-C(20B)	1.4(17)
C(23B)-C(24B)-C(25B)-C(26B)	178.0(11)
C(18B)-C(17B)-C(26B)-C(27B)	178.9(11)
P(1B)-C(17B)-C(26B)-C(27B)	-0.7(15)
C(18B)-C(17B)-C(26B)-C(25B)	2.5(15)
P(1B)-C(17B)-C(26B)-C(25B)	-177.1(7)
C(20B)-C(25B)-C(26B)-C(17B)	-5.6(15)
C(24B)-C(25B)-C(26B)-C(17B)	177.7(10)
C(20B)-C(25B)-C(26B)-C(27B)	177.7(10)
C(24B)-C(25B)-C(26B)-C(27B)	1.1(15)
C(17B)-C(26B)-C(27B)-C(36B)	96.9(14)
C(25B)-C(26B)-C(27B)-C(36B)	-86.7(12)
C(17B)-C(26B)-C(27B)-C(28B)	-85.6(13)
C(25B)-C(26B)-C(27B)-C(28B)	90.8(12)
C(36B)-C(27B)-C(28B)-C(29B)	-180.0(10)
C(26B)-C(27B)-C(28B)-C(29B)	2.4(15)
C(36B)-C(27B)-C(28B)-C(33B)	0.4(15)
C(26B)-C(27B)-C(28B)-C(33B)	-177.2(9)
C(27B)-C(28B)-C(29B)-C(30B)	177.7(11)
C(33B)-C(28B)-C(29B)-C(30B)	-2.6(17)
C(28B)-C(29B)-C(30B)-C(31B)	0.2(18)
C(29B)-C(30B)-C(31B)-C(32B)	1.9(19)
C(30B)-C(31B)-C(32B)-C(33B)	-1(2)
C(31B)-C(32B)-C(33B)-C(28B)	-1.0(18)
C(31B)-C(32B)-C(33B)-C(34B)	-178.3(12)
C(29B)-C(28B)-C(33B)-C(32B)	3.1(16)
C(27B)-C(28B)-C(33B)-C(32B)	-177.3(10)
C(29B)-C(28B)-C(33B)-C(34B)	-179.6(10)
C(27B)-C(28B)-C(33B)-C(34B)	0.1(15)
C(32B)-C(33B)-C(34B)-C(35B)	176.8(12)
C(28B)-C(33B)-C(34B)-C(35B)	-0.5(17)
C(33B)-C(34B)-C(35B)-C(36B)	0.5(19)
C(28B)-C(27B)-C(36B)-C(35B)	-0.4(15)
C(26B)-C(27B)-C(36B)-C(35B)	177.0(9)
C(28B)-C(27B)-C(36B)-P(2B)	180.0(8)
C(26B)-C(27B)-C(36B)-P(2B)	-2.6(15)
C(34B)-C(35B)-C(36B)-C(27B)	0.0(17)
C(34B)-C(35B)-C(36B)-P(2B)	179.6(10)
C(42B)-C(37B)-C(38B)-C(39B)	0(2)
P(2B)-C(37B)-C(38B)-C(39B)	178.3(10)
C(37B)-C(38B)-C(39B)-C(40B)	1.6(19)
C(37B)-C(38B)-C(39B)-C(43B)	-178.9(13)
C(38B)-C(39B)-C(40B)-C(41B)	-3(2)
C(43B)-C(39B)-C(40B)-C(41B)	177.4(14)

C(39B)-C(40B)-C(41B)-C(42B)	3(2)
C(39B)-C(40B)-C(41B)-C(44B)	179.6(13)
C(38B)-C(37B)-C(42B)-C(41B)	0(2)
P(2B)-C(37B)-C(42B)-C(41B)	-178.4(12)
C(40B)-C(41B)-C(42B)-C(37B)	-1(2)
C(44B)-C(41B)-C(42B)-C(37B)	-177.9(14)
C(50B)-C(45B)-C(46B)-C(47B)	-2(2)
P(2B)-C(45B)-C(46B)-C(47B)	178.3(14)
C(45B)-C(46B)-C(47B)-C(48B)	8(3)
C(45B)-C(46B)-C(47B)-C(51B)	178.3(17)
C(46B)-C(47B)-C(48B)-C(49B)	-13(3)
C(51B)-C(47B)-C(48B)-C(49B)	177(2)
C(47B)-C(48B)-C(49B)-C(50B)	11(3)
C(47B)-C(48B)-C(49B)-C(52B)	-175(2)
C(46B)-C(45B)-C(50B)-C(49B)	-1(2)
P(2B)-C(45B)-C(50B)-C(49B)	179.2(10)
C(48B)-C(49B)-C(50B)-C(45B)	-3(2)
C(52B)-C(49B)-C(50B)-C(45B)	-178.5(15)
C(2A)-C(1A)-P(1A)-C(9A)	-91.4(8)
C(6A)-C(1A)-P(1A)-C(9A)	91.0(9)
C(2A)-C(1A)-P(1A)-C(17A)	157.2(7)
C(6A)-C(1A)-P(1A)-C(17A)	-20.4(9)
C(2A)-C(1A)-P(1A)-Au(1)	29.5(8)
C(6A)-C(1A)-P(1A)-Au(1)	-148.1(8)
C(14A)-C(9A)-P(1A)-C(1A)	-145.3(9)
C(10A)-C(9A)-P(1A)-C(1A)	38.7(10)
C(14A)-C(9A)-P(1A)-C(17A)	-31.5(10)
C(10A)-C(9A)-P(1A)-C(17A)	152.5(8)
C(14A)-C(9A)-P(1A)-Au(1)	94.9(9)
C(10A)-C(9A)-P(1A)-Au(1)	-81.1(9)
C(26A)-C(17A)-P(1A)-C(1A)	-110.9(8)
C(18A)-C(17A)-P(1A)-C(1A)	70.4(9)
C(26A)-C(17A)-P(1A)-C(9A)	132.9(8)
C(18A)-C(17A)-P(1A)-C(9A)	-45.8(9)
C(26A)-C(17A)-P(1A)-Au(1)	11.3(10)
C(18A)-C(17A)-P(1A)-Au(1)	-167.4(7)
Cl(1A)-Au(1)-P(1A)-C(1A)	-33.2(16)
Cl(1A)-Au(1)-P(1A)-C(9A)	87.6(15)
Cl(1A)-Au(1)-P(1A)-C(17A)	-154.6(14)
C(50A)-C(45A)-P(2A)-C(37A)	-86.9(7)
C(46A)-C(45A)-P(2A)-C(37A)	93.1(8)
C(50A)-C(45A)-P(2A)-C(36A)	165.3(7)
C(46A)-C(45A)-P(2A)-C(36A)	-14.7(9)
C(50A)-C(45A)-P(2A)-Au(2)	35.3(7)
C(46A)-C(45A)-P(2A)-Au(2)	-144.7(7)
C(42A)-C(37A)-P(2A)-C(45A)	173.2(7)

C(38A)-C(37A)-P(2A)-C(45A)	-10.9(10)
C(42A)-C(37A)-P(2A)-C(36A)	-75.2(8)
C(38A)-C(37A)-P(2A)-C(36A)	100.6(9)
C(42A)-C(37A)-P(2A)-Au(2)	53.0(8)
C(38A)-C(37A)-P(2A)-Au(2)	-131.1(8)
C(27A)-C(36A)-P(2A)-C(45A)	-115.0(8)
C(35A)-C(36A)-P(2A)-C(45A)	70.9(8)
C(27A)-C(36A)-P(2A)-C(37A)	134.0(8)
C(35A)-C(36A)-P(2A)-C(37A)	-40.1(8)
C(27A)-C(36A)-P(2A)-Au(2)	9.7(9)
C(35A)-C(36A)-P(2A)-Au(2)	-164.4(6)
Cl(2A)-Au(2)-P(2A)-C(45A)	-23.3(16)
Cl(2A)-Au(2)-P(2A)-C(37A)	94.8(15)
Cl(2A)-Au(2)-P(2A)-C(36A)	-146.6(14)
C(14B)-C(9B)-P(1B)-C(17B)	-1.4(11)
C(10B)-C(9B)-P(1B)-C(17B)	170.5(9)
C(14B)-C(9B)-P(1B)-C(1B)	106.2(10)
C(10B)-C(9B)-P(1B)-C(1B)	-81.8(10)
C(14B)-C(9B)-P(1B)-Au(1B)	-131.5(9)
C(10B)-C(9B)-P(1B)-Au(1B)	40.5(10)
C(26B)-C(17B)-P(1B)-C(9B)	-113.1(9)
C(18B)-C(17B)-P(1B)-C(9B)	67.3(10)
C(26B)-C(17B)-P(1B)-C(1B)	134.3(9)
C(18B)-C(17B)-P(1B)-C(1B)	-45.3(10)
C(26B)-C(17B)-P(1B)-Au(1B)	12.4(10)
C(18B)-C(17B)-P(1B)-Au(1B)	-167.2(7)
C(6B)-C(1B)-P(1B)-C(9B)	-15.9(11)
C(2B)-C(1B)-P(1B)-C(9B)	171.5(8)
C(6B)-C(1B)-P(1B)-C(17B)	95.0(10)
C(2B)-C(1B)-P(1B)-C(17B)	-77.7(9)
C(6B)-C(1B)-P(1B)-Au(1B)	-138.1(9)
C(2B)-C(1B)-P(1B)-Au(1B)	49.3(9)
Cl(1B)-Au(1B)-P(1B)-C(9B)	-60(3)
Cl(1B)-Au(1B)-P(1B)-C(17B)	177(3)
Cl(1B)-Au(1B)-P(1B)-C(1B)	60(3)
C(50B)-C(45B)-P(2B)-C(37B)	103.7(14)
C(46B)-C(45B)-P(2B)-C(37B)	-76.2(12)
C(50B)-C(45B)-P(2B)-C(36B)	-5.0(14)
C(46B)-C(45B)-P(2B)-C(36B)	175.0(10)
C(50B)-C(45B)-P(2B)-Au(2B)	-136.4(11)
C(46B)-C(45B)-P(2B)-Au(2B)	43.7(12)
C(42B)-C(37B)-P(2B)-C(45B)	-1.7(16)
C(38B)-C(37B)-P(2B)-C(45B)	180.0(12)
C(42B)-C(37B)-P(2B)-C(36B)	110.7(13)
C(38B)-C(37B)-P(2B)-C(36B)	-67.6(12)
C(42B)-C(37B)-P(2B)-Au(2B)	-121.1(12)

C(38B)-C(37B)-P(2B)-Au(2B)	60.6(12)
C(27B)-C(36B)-P(2B)-C(45B)	-111.1(10)
C(35B)-C(36B)-P(2B)-C(45B)	69.3(9)
C(27B)-C(36B)-P(2B)-C(37B)	137.6(9)
C(35B)-C(36B)-P(2B)-C(37B)	-42.1(9)
C(27B)-C(36B)-P(2B)-Au(2B)	14.9(11)
C(35B)-C(36B)-P(2B)-Au(2B)	-164.7(7)
Cl(2B)-Au(2B)-P(2B)-C(45B)	-39.8(18)
Cl(2B)-Au(2B)-P(2B)-C(37B)	77.1(16)
Cl(2B)-Au(2B)-P(2B)-C(36B)	-164.6(15)

Symmetry transformations used to generate equivalent atoms:

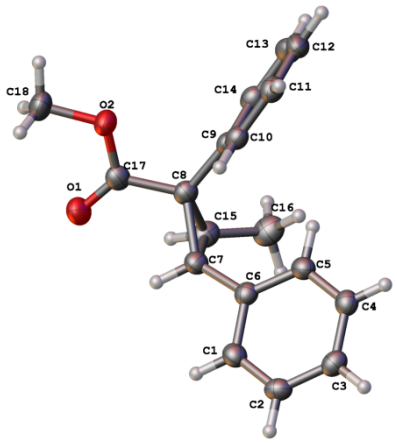

Table 1. Crystal data and structure refinement for **280**.

Identification code	**280**	
Empirical formula	C18 H18 O2	
Formula weight	266.32	
Temperature	173.2 K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 8.5588(2) Å	α= 90°.
	b = 9.7751(2) Å	β= 90°.
	c = 17.3323(4) Å	γ = 90°.
Volume	1450.07(6) $Å^3$	
Z	4	
Density (calculated)	1.220 Mg/m^3	
Absorption coefficient	0.617 mm^{-1}	
F(000)	568	
Crystal size	0.448 x 0.236 x 0.229 mm^3	
Theta range for data collection	5.10 to 69.16°.	

Index ranges	-9<=h<=10, -10<=k<=11, -19<=l<=20
Reflections collected	8880
Independent reflections	2552 [R(int) = 0.0158]
Completeness to theta = 69.16°	96.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.9447
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2552 / 0 / 209
Goodness-of-fit on F^2	1.072
Final R indices [I>2sigma(I)]	R1 = 0.0264, wR2 = 0.0691
R indices (all data)	R1 = 0.0268, wR2 = 0.0695
Absolute structure parameter	0.12(18)
Largest diff. peak and hole	0.130 and -0.166 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for **280**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	4725(1)	-2028(1)	5281(1)	32(1)
C(2)	5439(2)	-2453(1)	5956(1)	33(1)
C(3)	6633(2)	-1689(1)	6277(1)	32(1)
C(4)	7116(1)	-501(1)	5915(1)	31(1)
C(5)	6414(1)	-76(1)	5233(1)	30(1)
C(6)	5200(1)	-830(1)	4903(1)	28(1)
C(7)	4370(2)	-514(1)	4166(1)	30(1)
C(8)	4260(1)	875(1)	3742(1)	29(1)
C(9)	5039(1)	2162(1)	4011(1)	28(1)
C(10)	4702(1)	2719(1)	4731(1)	29(1)
C(11)	5355(2)	3961(1)	4953(1)	34(1)
C(12)	6342(2)	4661(1)	4460(1)	38(1)
C(13)	6683(2)	4119(2)	3742(1)	39(1)
C(14)	6037(1)	2880(1)	3521(1)	33(1)
C(15)	5186(2)	-321(1)	3401(1)	35(1)
C(16)	6935(2)	-325(2)	3337(1)	44(1)
C(17)	2680(1)	1048(1)	3374(1)	31(1)
C(18)	662(2)	2589(2)	3058(1)	43(1)
O(1)	1928(1)	127(1)	3097(1)	41(1)
O(2)	2194(1)	2347(1)	3385(1)	36(1)

Table 3. Bond lengths [Å] and angles [°] for **280**.

O(1)-C(17)	1.2059(16)
O(2)-C(17)	1.3366(15)
O(2)-C(18)	1.4478(18)
C(1)-C(2)	1.3845(17)
C(1)-C(6)	1.4019(17)
C(2)-C(3)	1.3821(18)
C(3)-C(4)	1.3831(18)
C(4)-C(5)	1.3894(17)
C(5)-C(6)	1.3953(17)
C(6)-C(7)	1.4944(16)
C(7)-C(8)	1.5465(17)
C(7)-C(15)	1.5105(17)
C(8)-C(9)	1.4989(17)
C(8)-C(15)	1.5307(18)
C(8)-C(17)	1.5049(17)

C(9)-C(10)	1.3919(16)
C(9)-C(14)	1.3947(17)
C(10)-C(11)	1.3902(18)
C(11)-C(12)	1.3832(18)
C(12)-C(13)	1.384(2)
C(13)-C(14)	1.386(2)
C(15)-C(16)	1.5015(19)
C(1)-H(1)	0.9500
C(2)-H(2)	0.9500
C(3)-H(3)	0.9500
C(4)-H(4)	0.9500
C(5)-H(5)	0.9500
C(7)-H(7)	0.9600
C(10)-H(10)	0.9500
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-H(13)	0.9500
C(14)-H(14)	0.9500
C(15)-H(15)	0.9700
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(18)-H(18A)	0.919(19)
C(18)-H(18B)	0.93(2)
C(18)-H(18C)	0.99(2)

C(17)-O(2)-C(18)	115.52(11)
C(2)-C(1)-C(6)	121.14(11)
C(1)-C(2)-C(3)	120.28(12)
C(2)-C(3)-C(4)	119.49(11)
C(3)-C(4)-C(5)	120.48(11)
C(4)-C(5)-C(6)	120.85(11)
C(1)-C(6)-C(5)	117.76(11)
C(1)-C(6)-C(7)	115.69(10)
C(5)-C(6)-C(7)	126.52(11)
C(6)-C(7)-C(8)	128.07(10)
C(6)-C(7)-C(15)	123.82(11)
C(8)-C(7)-C(15)	60.08(8)
C(7)-C(8)-C(9)	124.18(9)
C(7)-C(8)-C(15)	58.79(8)
C(7)-C(8)-C(17)	110.80(10)
C(9)-C(8)-C(15)	122.05(10)
C(9)-C(8)-C(17)	115.96(10)
C(15)-C(8)-C(17)	112.79(10)
C(8)-C(9)-C(10)	121.03(10)
C(8)-C(9)-C(14)	120.34(10)

C(10)-C(9)-C(14)	118.48(11)
C(9)-C(10)-C(11)	120.42(11)
C(10)-C(11)-C(12)	120.41(12)
C(11)-C(12)-C(13)	119.72(12)
C(12)-C(13)-C(14)	119.95(13)
C(9)-C(14)-C(13)	121.02(12)
C(7)-C(15)-C(8)	61.13(8)
C(7)-C(15)-C(16)	121.71(11)
C(8)-C(15)-C(16)	123.17(12)
O(1)-C(17)-O(2)	123.30(11)
O(1)-C(17)-C(8)	124.36(12)
O(2)-C(17)-C(8)	112.33(10)
C(2)-C(1)-H(1)	119.00
C(6)-C(1)-H(1)	119.00
C(1)-C(2)-H(2)	120.00
C(3)-C(2)-H(2)	120.00
C(2)-C(3)-H(3)	120.00
C(4)-C(3)-H(3)	120.00
C(3)-C(4)-H(4)	120.00
C(5)-C(4)-H(4)	120.00
C(4)-C(5)-H(5)	120.00
C(6)-C(5)-H(5)	120.00
C(6)-C(7)-H(7)	117.00
C(8)-C(7)-H(7)	107.00
C(15)-C(7)-H(7)	108.00
C(9)-C(10)-H(10)	120.00
C(11)-C(10)-H(10)	120.00
C(10)-C(11)-H(11)	120.00
C(12)-C(11)-H(11)	120.00
C(11)-C(12)-H(12)	120.00
C(13)-C(12)-H(12)	120.00
C(12)-C(13)-H(13)	120.00
C(14)-C(13)-H(13)	120.00
C(9)-C(14)-H(14)	119.00
C(13)-C(14)-H(14)	120.00
C(7)-C(15)-H(15)	114.00
C(8)-C(15)-H(15)	108.00
C(16)-C(15)-H(15)	117.00
C(15)-C(16)-H(16A)	109.00
C(15)-C(16)-H(16B)	109.00
C(15)-C(16)-H(16C)	109.00
H(16A)-C(16)-H(16B)	109.00
H(16A)-C(16)-H(16C)	109.00
H(16B)-C(16)-H(16C)	109.00
O(2)-C(18)-H(18A)	109.3(12)
O(2)-C(18)-H(18B)	109.7(11)

O(2)-C(18)-H(18C)	106.4(10)
H(18A)-C(18)-H(18B)	111.0(17)
H(18A)-C(18)-H(18C)	112.8(16)
H(18B)-C(18)-H(18C)	107.4(16)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **280**. 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)	31(1)	28(1)	36(1)	-3(1)	-1(1)	-1(1)
C(2)	37(1)	27(1)	35(1)	4(1)	5(1)	1(1)
C(3)	34(1)	35(1)	27(1)	0(1)	0(1)	6(1)
C(4)	28(1)	32(1)	34(1)	-3(1)	-1(1)	2(1)
C(5)	29(1)	27(1)	35(1)	2(1)	1(1)	0(1)
C(6)	28(1)	27(1)	30(1)	-2(1)	0(1)	3(1)
C(7)	32(1)	27(1)	33(1)	-2(1)	-4(1)	-1(1)
C(8)	31(1)	31(1)	26(1)	1(1)	0(1)	1(1)
C(9)	26(1)	30(1)	28(1)	5(1)	-4(1)	2(1)
C(10)	26(1)	31(1)	31(1)	4(1)	-1(1)	2(1)
C(11)	33(1)	34(1)	34(1)	-3(1)	-6(1)	3(1)
C(12)	32(1)	30(1)	51(1)	2(1)	-10(1)	-4(1)
C(13)	31(1)	40(1)	47(1)	13(1)	1(1)	-4(1)
C(14)	31(1)	38(1)	31(1)	4(1)	1(1)	2(1)
C(15)	41(1)	35(1)	29(1)	-4(1)	-1(1)	5(1)
C(16)	44(1)	48(1)	41(1)	-1(1)	8(1)	12(1)
C(17)	34(1)	34(1)	24(1)	2(1)	-1(1)	-3(1)
C(18)	33(1)	50(1)	47(1)	8(1)	-12(1)	0(1)
O(1)	41(1)	40(1)	41(1)	0(1)	-12(1)	-6(1)
O(2)	31(1)	35(1)	42(1)	1(1)	-10(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **280**.

	x	y	z	U(eq)
H(1)	3899	-2558	5069	35(4)
H(2)	5106	-3273	6201	37(4)
H(3)	7119	-1978	6742	34(4)
H(4)	7933	29	6134	36(4)
H(5)	6764	737	4988	32(4)
H(7)	3411	-994	4075	32(3)
H(10)	4021	2249	5073	28(3)
H(11)	5123	4330	5447	35(4)
H(12)	6784	5510	4613	50(4)
H(13)	7359	4597	3401	43(4)
H(14)	6278	2513	3027	37(4)
H(15)	4608	-661	2963	36(4)
H(16A)	7381	249	3745	51(5)
H(16B)	7243	36	2832	59(5)
H(16C)	7323	-1263	3392	59(5)
H(18A)	-80(20)	2170(20)	3360(12)	67(6)
H(18B)	630(20)	2261(19)	2557(12)	62(5)
H(18C)	530(20)	3590(20)	3034(10)	62(5)

Table 6. Torsion angles [°] for **280**.

C(18)-O(2)-C(17)-C(8)	-178.43(11)
C(18)-O(2)-C(17)-O(1)	1.70(18)
C(2)-C(1)-C(6)-C(7)	178.01(11)
C(2)-C(1)-C(6)-C(5)	-0.24(18)
C(6)-C(1)-C(2)-C(3)	0.61(19)
C(1)-C(2)-C(3)-C(4)	-0.34(19)
C(2)-C(3)-C(4)-C(5)	-0.27(19)
C(3)-C(4)-C(5)-C(6)	0.64(19)
C(4)-C(5)-C(6)-C(1)	-0.38(18)
C(4)-C(5)-C(6)-C(7)	-178.41(12)
C(1)-C(6)-C(7)-C(15)	-122.93(13)
C(5)-C(6)-C(7)-C(8)	-21.1(2)
C(1)-C(6)-C(7)-C(8)	160.82(12)
C(5)-C(6)-C(7)-C(15)	55.14(18)
C(6)-C(7)-C(8)-C(15)	111.41(14)
C(6)-C(7)-C(8)-C(9)	1.62(19)
C(15)-C(7)-C(8)-C(17)	104.73(11)

C(6)-C(7)-C(15)-C(8)	-118.09(13)
C(6)-C(7)-C(15)-C(16)	-4.90(19)
C(8)-C(7)-C(15)-C(16)	113.19(14)
C(6)-C(7)-C(8)-C(17)	-143.87(12)
C(15)-C(7)-C(8)-C(9)	-109.79(13)
C(15)-C(8)-C(9)-C(10)	-131.25(12)
C(7)-C(8)-C(9)-C(10)	-59.54(16)
C(7)-C(8)-C(9)-C(14)	125.08(12)
C(17)-C(8)-C(9)-C(14)	-91.01(14)
C(7)-C(8)-C(15)-C(16)	-110.89(13)
C(9)-C(8)-C(15)-C(7)	113.30(12)
C(9)-C(8)-C(15)-C(16)	2.41(17)
C(17)-C(8)-C(15)-C(7)	-101.30(11)
C(15)-C(8)-C(9)-C(14)	53.37(16)
C(17)-C(8)-C(9)-C(10)	84.36(14)
C(7)-C(8)-C(17)-O(2)	145.36(10)
C(9)-C(8)-C(17)-O(1)	176.66(11)
C(9)-C(8)-C(17)-O(2)	-3.22(14)
C(15)-C(8)-C(17)-O(1)	29.03(17)
C(15)-C(8)-C(17)-O(2)	-150.85(11)
C(17)-C(8)-C(15)-C(16)	147.81(12)
C(7)-C(8)-C(17)-O(1)	-34.77(16)
C(8)-C(9)-C(10)-C(11)	-175.76(11)
C(10)-C(9)-C(14)-C(13)	0.08(18)
C(14)-C(9)-C(10)-C(11)	-0.30(18)
C(8)-C(9)-C(14)-C(13)	175.57(12)
C(9)-C(10)-C(11)-C(12)	0.34(19)
C(10)-C(11)-C(12)-C(13)	-0.2(2)
C(11)-C(12)-C(13)-C(14)	-0.1(2)
C(12)-C(13)-C(14)-C(9)	0.1(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **280** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(7)-H(7)...O(1)	0.9600	2.3800	2.8628(15)	110.00
C(15)-H(15)...O(1)	0.9700	2.4300	2.8714(16)	107.00

Symmetry transformations used to generate equivalent atoms:

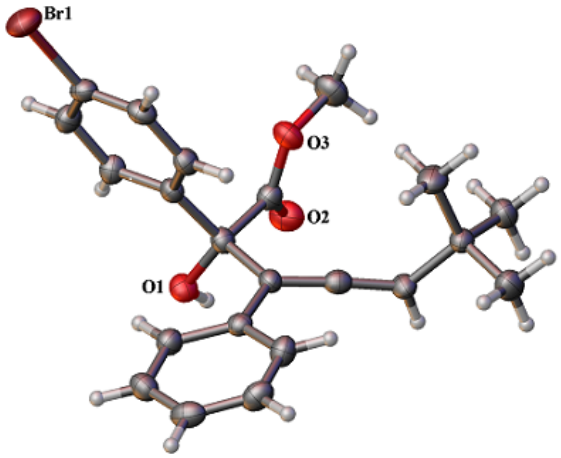

Table 1 Crystal data and structure refinement for 327-Br

Identification code	**327-Br**
Empirical formula	$C_{22}H_{23}BrO_3$
Formula weight	415.31
Temperature/K	173(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.3961(14)
b/Å	17.500(2)
c/Å	20.188(2)
α/°	90
β/°	91.912(2)
γ/°	90
Volume/Å^3	4024.0(8)
Z	8
ρ_{calc}mg/mm^3	1.371
m/mm^{-1}	2.061
F(000)	1712.0
Crystal size/mm^3	0.837 × 0.284 × 0.204
2Θ range for data collection	3.08 to 61.014°
Index ranges	$-16 \le h \le 16$, $-24 \le k \le 25$, $-28 \le l \le 28$
Reflections collected	46338
Independent reflections	12267[R(int) = 0.0589]
Data/restraints/parameters	12267/0/479
Goodness-of-fit on F^2	1.004
Final R indexes [I>=2σ (I)]	R_1 = 0.0504, wR_2 = 0.1057
Final R indexes [all data]	R_1 = 0.1142, wR_2 = 0.1273
Largest diff. peak/hole / e Å^{-3}	0.89/-0.48

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for . U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	5373.6(2)	9107.36(17)	6967.61(14)	44.29(9)
Br1B	3658.1(3)	9139.38(18)	1429.97(15)	50.76(10)
O1	247.2(14)	8568.2(9)	5220.2(8)	31.1(4)
O1B	8810.8(14)	8457.3(10)	3119.4(8)	31.9(4)
O3	2762.0(14)	8621.7(10)	4227.8(8)	33.7(4)
O3B	6368.0(15)	8514.9(10)	4171.5(8)	38.2(4)
O2	903.9(15)	8979.9(10)	3991.7(9)	39.6(4)
O2B	8238.6(15)	8859.5(11)	4341.8(9)	40.6(4)
C18	4114(2)	8839.2(14)	6376.0(12)	28.8(5)
C18B	4924(2)	8835.5(15)	2004.4(12)	31.5(5)
C15B	6758(2)	8373.7(13)	2843.9(11)	25.6(5)
C1	1150.9(19)	7395.1(13)	4846.5(11)	24.7(5)
C8	923.0(19)	6843.2(13)	5392.8(11)	25.6(5)
C21	1618(2)	8660.3(13)	4346.1(11)	28.2(5)
C15	2275.6(19)	8429.1(13)	5513.4(11)	24.5(5)
C14	1311(2)	8252.6(13)	4995.6(11)	26.0(5)
C3	1109.7(19)	7167.6(13)	4224.3(12)	27.9(5)
C4	1006(2)	6945.5(13)	3611.5(11)	28.1(5)
C14B	7734.5(19)	8156.1(13)	3340.4(11)	26.7(5)
C1B	7848.0(19)	7286.3(13)	3443.1(11)	26.3(5)
C5	1965.3(19)	6641.0(14)	3182.0(11)	27.7(5)
C20	3223(2)	7943.4(13)	5621.9(11)	28.9(5)
C8B	8053.9(19)	6781.3(13)	2863.7(11)	27.6(5)
C21B	7490(2)	8544.2(13)	4011.2(12)	29.9(5)
C3B	7851.2(19)	7005.2(13)	4050.3(12)	28.8(5)
C19	4137(2)	8141.7(14)	6058.2(12)	30.1(5)
C17	3179(2)	9334.6(14)	6278.7(12)	31.8(6)
C19B	4825(2)	8165.3(15)	2356.9(12)	32.4(6)
C12	613(2)	7077.4(14)	6018.7(12)	30.1(5)
C13	2251(2)	9125.3(13)	5848.0(11)	28.5(5)
C12B	8303(2)	7062.5(14)	2237.9(12)	31.4(5)
C1A	318(2)	6545.0(15)	6498.0(12)	34.2(6)
C20B	5746(2)	7936.7(14)	2776.9(11)	30.0(5)

C4B	7893(2)	6729.6(14)	4645.7(12)	32.2(6)
C2	973(2)	6060.3(14)	5266.3(13)	33.3(6)
C1C	339(2)	5774.2(15)	6358.9(13)	36.7(6)
C1D	677(2)	5534.5(15)	5741.3(12)	36.6(6)
C17B	5927(2)	9272.8(14)	2055.3(12)	34.6(6)
C13B	6854(2)	9039.9(13)	2475.1(12)	28.8(5)
C1BB	8033(2)	5988.7(14)	2943.9(13)	35.4(6)
C1DB	8296(2)	5504.9(15)	2425.1(13)	40.4(7)
C5B	6873(2)	6432.8(15)	5036.4(12)	35.1(6)
C1CB	8578(2)	5795.2(15)	1813.5(14)	39.8(6)
C1E	1921(2)	7101.9(15)	2537.6(12)	37.5(6)
C1AB	8563(2)	6577.0(16)	1723.4(13)	37.6(6)
C1F	1700(2)	5809.3(14)	3014.5(14)	40.5(6)
C1G	3134(3)	9003.4(15)	3630.4(13)	42.5(7)
C1H	3171(2)	6701.7(16)	3531.9(13)	40.6(6)
C1HB	5715(2)	6526(2)	4648.4(16)	56.9(9)
C1GB	6071(3)	8905.2(17)	4779.9(13)	46.1(7)
C1FB	7088(3)	5602.5(16)	5205.8(14)	44.5(7)
C1EB	6857(3)	6896.1(17)	5682.1(14)	52.5(8)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for . The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka×b×U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	33.76(15)	49.11(18)	49.14(18)	-1.35(13)	-11.68(12)	-8.09(12)
Br1B	42.67(18)	57.9(2)	50.48(19)	-1.14(15)	-16.37(14)	16.54(14)
O1	25.7(9)	36.2(10)	31.3(9)	1.3(8)	-0.6(7)	6.9(7)
O1B	24.5(9)	39.5(10)	31.7(9)	1.5(8)	0.0(7)	-7.9(7)
O3	32.1(10)	39(1)	30.5(10)	7.6(8)	7.2(7)	2.6(8)
O3B	33.3(10)	49.8(11)	31.9(10)	-4.6(8)	8.5(8)	-1.8(8)
O2	35.7(10)	44.3(11)	38.4(11)	13.4(8)	-3.1(8)	1.4(8)
O2B	34.5(10)	46.7(11)	39.9(11)	-10.7(9)	-6.6(8)	1.2(8)
C18	24.7(12)	32.9(13)	28.6(13)	3.2(10)	-0.7(10)	-5(1)
C18B	30.5(13)	36.6(14)	27.3(13)	-6.6(11)	-2.7(10)	9.8(11)
C15B	25.1(12)	28.0(12)	24.0(12)	-1.4(10)	3.2(9)	0.7(10)
C1	22.2(11)	28.6(12)	23.2(12)	-1.5(9)	2.0(9)	-0.2(9)
C8	21.1(11)	29.4(12)	26.0(12)	1.1(9)	-2.3(9)	-1.7(9)
C21	30.2(13)	26.2(12)	27.9(13)	-0.1(10)	-1.6(10)	-0.8(10)
C15	25.7(12)	25.9(12)	22.2(12)	1.6(9)	3.1(9)	0.3(9)
C14	26.4(12)	27.9(12)	23.8(12)	0.6(9)	1.5(9)	3.7(10)

C3	22.8(12)	27.0(12)	33.8(14)	2.6(10)	0.8(10)	1(1)
C4	22.6(11)	36.5(14)	25.0(12)	-1.5(10)	-1.5(9)	0.4(10)
C14B	22.2(11)	31.2(13)	26.9(12)	3(1)	2.2(9)	-3.5(10)
C1B	19.8(11)	29.5(12)	29.5(13)	3(1)	0.4(9)	0.2(9)
C5	23.0(11)	32.0(13)	28.1(12)	-4.8(10)	1.0(9)	-0.1(10)
C20	29.2(13)	28.3(12)	29.5(13)	-1(1)	4.7(10)	3.4(10)
C8B	19.4(11)	32.8(13)	30.2(13)	0.7(10)	-2.8(9)	0.1(10)
C21B	31.2(13)	30.3(13)	28.1(13)	5.3(10)	0.4(10)	4(1)
C3B	22.4(12)	31.0(13)	33.0(14)	-0.2(10)	2.8(10)	0.9(10)
C19	22.9(12)	35.2(14)	32.4(13)	5.5(11)	3.1(10)	3.5(10)
C17	36.8(14)	26.0(12)	32.4(14)	-2.1(10)	-0.7(11)	-1.6(10)
C19B	22.6(12)	39.8(14)	34.9(14)	-1.1(11)	2(1)	-0.1(10)
C12	30.0(13)	29.6(13)	30.6(13)	-1.7(10)	0.7(10)	-0.9(10)
C13	33.7(13)	24.4(12)	27.1(12)	2(1)	-1.9(10)	4.1(10)
C12B	30.2(13)	31.5(13)	33.0(14)	-0.2(11)	7.1(10)	-4(1)
C1A	31.0(13)	41.9(15)	29.9(13)	3.8(11)	3.9(10)	1.2(11)
C20B	27.7(12)	31.4(13)	31.0(13)	4.6(10)	4.5(10)	-2.3(10)
C4B	25.4(12)	40.6(15)	30.4(13)	3.0(11)	0.1(10)	4.6(11)
C2	38.3(14)	31.8(14)	29.7(14)	-3.3(10)	-3.1(11)	1.5(11)
C1C	31.2(13)	39.0(15)	39.2(16)	12.8(12)	-5.5(11)	-5.9(11)
C1D	41.8(16)	28.0(13)	39.5(16)	3.0(11)	-7.2(12)	-4.4(11)
C17B	41.9(15)	31.7(14)	30.2(14)	1.7(10)	-1.6(11)	2.6(11)
C13B	31.3(12)	26.3(12)	28.8(13)	0.3(10)	-0.1(10)	-2.1(10)
C1BB	37.3(14)	34.7(14)	33.7(14)	2.7(11)	-6.3(11)	-1.5(11)
C1DB	42.9(16)	30.9(14)	46.3(17)	-3.7(12)	-15.4(13)	3.7(12)
C5B	32.2(14)	41.5(15)	31.8(14)	10.9(11)	4.8(11)	4.2(11)
C1CB	30.8(13)	43.8(16)	44.6(17)	-14.5(13)	-2.6(12)	2.9(12)
C1E	40.2(15)	39.9(15)	32.6(14)	-1.9(12)	6.4(11)	-2.9(12)
C1AB	33.5(14)	45.1(16)	34.6(15)	-4.0(12)	6.1(11)	-3.6(12)
C1F	45.4(16)	35.2(15)	41.3(16)	-5.3(12)	7.0(13)	-5.1(12)
C1G	47.0(17)	42.7(16)	38.3(16)	10.1(12)	10.4(13)	-1.9(13)
C1H	24.5(13)	51.0(17)	46.2(16)	-9.6(13)	-0.6(11)	3.0(12)
C1HB	30.5(15)	74(2)	66(2)	28.4(18)	2.5(14)	-3.1(14)
C1GB	55.5(19)	51.4(18)	32.6(15)	-7.2(13)	18.6(13)	-5.4(14)
C1FB	47.7(17)	43.3(16)	43.0(17)	8.6(13)	9.7(13)	7.9(13)
C1EB	65(2)	46.7(18)	46.9(18)	7.3(14)	24.7(15)	10.4(15)

Table 4 Bond Lengths for 327-Br

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C18	1.895(2)	C4	C5	1.515(3)

Br1B	C18B	1.897(2)	C14B	C1B	1.541(3)
O1	C14	1.421(3)	C14B	C21B	1.548(3)
O1B	C14B	1.421(3)	C1B	C8B	1.491(3)
O3	C21	1.335(3)	C1B	C3B	1.321(3)
O3	C1G	1.454(3)	C5	C1E	1.530(3)
O3B	C21B	1.330(3)	C5	C1F	1.522(3)
O3B	C1GB	1.455(3)	C5	C1H	1.527(3)
O2	C21	1.203(3)	C20	C19	1.386(3)
O2B	C21B	1.200(3)	C8B	C12B	1.394(3)
C18	C19	1.380(3)	C8B	C1BB	1.397(3)
C18	C17	1.382(3)	C3B	C4B	1.295(3)
C18B	C19B	1.378(3)	C17	C13	1.396(3)
C18B	C17B	1.377(4)	C19B	C20B	1.386(3)
C15B	C14B	1.521(3)	C12	C1A	1.392(3)
C15B	C20B	1.387(3)	C12B	C1AB	1.382(3)
C15B	C13B	1.390(3)	C1A	C1C	1.378(3)
C1	C8	1.495(3)	C4B	C5B	1.518(3)
C1	C14	1.540(3)	C2	C1D	1.379(3)
C1	C3	1.317(3)	C1C	C1D	1.382(4)
C8	C12	1.385(3)	C17B	C13B	1.393(3)
C8	C2	1.395(3)	C1BB	C1DB	1.387(4)
C21	C14	1.543(3)	C1DB	C1CB	1.383(4)
C15	C14	1.523(3)	C5B	C1HB	1.521(4)
C15	C20	1.386(3)	C5B	C1FB	1.511(4)
C15	C13	1.394(3)	C5B	C1EB	1.536(4)
C3	C4	1.298(3)	C1CB	C1AB	1.380(4)

Table 5 Bond Angles for 327-Br

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C21	O3	C1G	116.03(19)	C3B	C1B	C8B	120.8(2)
C21B	O3B	C1GB	116.1(2)	C4	C5	C1E	107.28(19)
C19	C18	Br1	119.10(18)	C4	C5	C1F	108.8(2)
C19	C18	C17	121.0(2)	C4	C5	C1H	111.47(19)
C17	C18	Br1	119.88(19)	C1F	C5	C1E	108.3(2)
C19B	C18B	Br1B	118.71(19)	C1F	C5	C1H	109.8(2)
C17B	C18B	Br1B	120.2(2)	C1H	C5	C1E	111.1(2)
C17B	C18B	C19B	121.1(2)	C15	C20	C19	120.8(2)
C20B	C15B	C14B	120.9(2)	C12B	C8B	C1B	123.0(2)
C20B	C15B	C13B	119.4(2)	C12B	C8B	C1BB	117.4(2)
C13B	C15B	C14B	119.6(2)	C1BB	C8B	C1B	119.6(2)

C8	C1	C14	120.51(19)	O3B	C21B	C14B	113.5(2)
C3	C1	C8	120.4(2)	O2B	C21B	O3B	123.6(2)
C3	C1	C14	118.8(2)	O2B	C21B	C14B	122.9(2)
C12	C8	C1	122.5(2)	C4B	C3B	C1B	178.0(2)
C12	C8	C2	118.1(2)	C18	C19	C20	119.4(2)
C2	C8	C1	119.4(2)	C18	C17	C13	119.3(2)
O3	C21	C14	112.25(19)	C18B	C19B	C20B	119.2(2)
O2	C21	O3	124.2(2)	C8	C12	C1A	120.7(2)
O2	C21	C14	123.6(2)	C15	C13	C17	120.3(2)
C20	C15	C14	121.6(2)	C1AB	C12B	C8B	121.3(2)
C20	C15	C13	119.2(2)	C1C	C1A	C12	120.5(2)
C13	C15	C14	118.9(2)	C19B	C20B	C15B	120.7(2)
O1	C14	C1	110.13(18)	C3B	C4B	C5B	127.2(2)
O1	C14	C21	108.13(18)	C1D	C2	C8	121.0(2)
O1	C14	C15	107.83(18)	C1A	C1C	C1D	119.2(2)
C1	C14	C21	108.25(18)	C2	C1D	C1C	120.4(2)
C15	C14	C1	114.21(18)	C18B	C17B	C13B	119.6(2)
C15	C14	C21	108.12(18)	C15B	C13B	C17B	120.0(2)
C4	C3	C1	176.8(2)	C1DB	C1BB	C8B	120.9(2)
C3	C4	C5	127.3(2)	C1CB	C1DB	C1BB	120.8(2)
O1B	C14B	C15B	108.69(18)	C4B	C5B	C1HB	111.2(2)
O1B	C14B	C1B	109.84(18)	C4B	C5B	C1EB	106.9(2)
O1B	C14B	C21B	107.12(18)	C1HB	C5B	C1EB	110.3(2)
C15B	C14B	C1B	113.09(19)	C1FB	C5B	C4B	109.0(2)
C15B	C14B	C21B	108.51(18)	C1FB	C5B	C1HB	110.6(2)
C1B	C14B	C21B	109.41(18)	C1FB	C5B	C1EB	108.8(2)
C8B	C1B	C14B	119.7(2)	C1AB	C1CB	C1DB	118.7(2)
C3B	C1B	C14B	119.4(2)	C1CB	C1AB	C12B	120.8(3)

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 327-Br

Atom	*x*	*y*	*z*	U(eq)
H1	-176	8687	4900	47
H1B	9236	8568	3441	48
H4	258	6977	3414	34
H20	3245	7479	5399	35
H19	4761	7807	6136	36
H17	3169	9802	6498	38
H19B	4148	7870	2313	39
H12	601	7596	6120	36

H13	1613	9452	5784	34
H12B	8295	7587	2165	38
H1A	106	6711	6915	41
H20B	5684	7485	3016	36
H4B	8630	6711	4858	39
H2	1209	5890	4855	40
H1C	128	5420	6677	44
H1D	706	5015	5646	44
H17B	5986	9721	1811	42
H13B	7537	9330	2509	35
H1BB	7840	5783	3351	42
H1DB	8282	4979	2489	48
H1CB	8774	5470	1470	48
H1ED	1162	7044	2322	56
H1EE	2514	6919	2251	56
H1EF	2058	7632	2636	56
H1AB	8730	6779	1311	45
H1FD	1728	5511	3414	61
H1FE	2274	5621	2718	61
H1FF	932	5772	2807	61
H1GD	2638	8848	3261	64
H1GE	3933	8868	3549	64
H1GF	3078	9547	3687	64
H1HD	3333	7227	3638	61
H1HE	3760	6511	3246	61
H1HF	3177	6406	3932	61
H1HA	5592	7056	4544	85
H1HB	5084	6345	4910	85
H1HC	5737	6236	4245	85
H1GA	6176	9446	4726	69
H1GB	6572	8726	5138	69
H1GC	5267	8802	4877	69
H1FA	7085	5306	4806	67
H1FB	6481	5422	5485	67
H1FC	7836	5551	5435	67
H1EA	7591	6831	5923	79
H1EB	6228	6720	5947	79
H1EC	6743	7427	5580	79

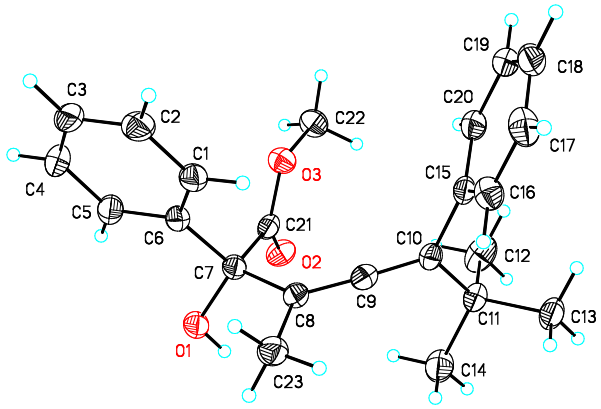

Table 1. Crystal data and structure refinement for **336**

Identification code	**336**	
Empirical formula	C23 H26 O3	
Formula weight	350.44	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.7601(2) Å	a= 90°.
	b = 15.1294(4) Å	b= 99.9440(10)°.
	c = 13.3607(3) Å	g = 90°.
Volume	1943.26(8) $Å^3$	
Z	4	
Density (calculated)	1.198 Mg/m^3	
Absorption coefficient	0.617 mm^{-1}	
F(000)	752	
Crystal size	0.36 x 0.30 x 0.27 mm^3	
Theta range for data collection	4.45 to 69.58°.	
Index ranges	-11<=h<=11, -14<=k<=17, -16<=l<=16	
Reflections collected	12830	
Independent reflections	3368 [R(int) = 0.0212]	
Completeness to theta = 69.58°	92.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8511 and 0.8085	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3368 / 0 / 235	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0392, wR2 = 0.1008	
R indices (all data)	R1 = 0.0410, wR2 = 0.1023	
Largest diff. peak and hole	0.167 and -0.165 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for **336** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	8696(1)	63(1)	6043(1)	34(1)
C(2)	8554(2)	-401(1)	5138(1)	41(1)
C(3)	8813(2)	-1296(1)	5144(1)	45(1)
C(4)	9183(2)	-1732(1)	6061(1)	45(1)
C(5)	9298(2)	-1276(1)	6971(1)	38(1)
C(6)	9063(1)	-367(1)	6966(1)	30(1)
C(7)	9291(1)	140(1)	7972(1)	29(1)
C(8)	8525(1)	1032(1)	7907(1)	29(1)
C(9)	9210(1)	1776(1)	8066(1)	30(1)
C(10)	9926(1)	2512(1)	8205(1)	28(1)
C(11)	10378(1)	2932(1)	9262(1)	33(1)
C(12)	11956(2)	2863(1)	9586(1)	52(1)
C(13)	9947(2)	3907(1)	9220(1)	42(1)
C(14)	9672(2)	2458(1)	10044(1)	46(1)
C(15)	10250(1)	2982(1)	7286(1)	30(1)
C(16)	9179(1)	3404(1)	6635(1)	37(1)
C(17)	9440(2)	3843(1)	5776(1)	45(1)
C(18)	10767(2)	3867(1)	5556(1)	48(1)
C(19)	11845(2)	3457(1)	6201(1)	47(1)
C(20)	11592(2)	3018(1)	7059(1)	39(1)
C(21)	10853(1)	317(1)	8327(1)	29(1)
C(22)	12963(1)	738(1)	7822(1)	39(1)
C(23)	6952(1)	982(1)	7700(1)	39(1)
O(1)	8808(1)	-417(1)	8691(1)	37(1)
O(2)	11409(1)	273(1)	9204(1)	38(1)
O(3)	11498(1)	533(1)	7565(1)	34(1)

Table 3. Bond lengths [Å] and angles [°] for **336**

C(1)-C(2)	1.3845(19)
C(1)-C(6)	1.3845(19)
C(1)-H(1A)	0.9500
C(2)-C(3)	1.378(2)
C(2)-H(2A)	0.9500
C(3)-C(4)	1.384(2)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.386(2)
C(4)-H(4A)	0.9500

C(5)-C(6)	1.3939(19)
C(5)-H(5A)	0.9500
C(6)-C(7)	1.5297(17)
C(7)-O(1)	1.4172(15)
C(7)-C(8)	1.5379(18)
C(7)-C(21)	1.5399(17)
C(8)-C(9)	1.3080(18)
C(8)-C(23)	1.5141(18)
C(9)-C(10)	1.3113(18)
C(10)-C(15)	1.4989(18)
C(10)-C(11)	1.5413(17)
C(11)-C(14)	1.526(2)
C(11)-C(12)	1.530(2)
C(11)-C(13)	1.5326(18)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-C(16)	1.3943(18)
C(15)-C(20)	1.3956(19)
C(16)-C(17)	1.387(2)
C(16)-H(16A)	0.9500
C(17)-C(18)	1.378(2)
C(17)-H(17A)	0.9500
C(18)-C(19)	1.386(2)
C(18)-H(18A)	0.9500
C(19)-C(20)	1.383(2)
C(19)-H(19A)	0.9500
C(20)-H(20A)	0.9500
C(21)-O(2)	1.2051(15)
C(21)-O(3)	1.3274(15)
C(22)-O(3)	1.4452(16)
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
O(1)-H(1B)	0.8400

C(2)-C(1)-C(6)	120.77(13)

C(2)-C(1)-H(1A)	119.6
C(6)-C(1)-H(1A)	119.6
C(3)-C(2)-C(1)	120.16(14)
C(3)-C(2)-H(2A)	119.9
C(1)-C(2)-H(2A)	119.9
C(2)-C(3)-C(4)	119.58(13)
C(2)-C(3)-H(3A)	120.2
C(4)-C(3)-H(3A)	120.2
C(3)-C(4)-C(5)	120.54(14)
C(3)-C(4)-H(4A)	119.7
C(5)-C(4)-H(4A)	119.7
C(4)-C(5)-C(6)	119.95(14)
C(4)-C(5)-H(5A)	120.0
C(6)-C(5)-H(5A)	120.0
C(1)-C(6)-C(5)	118.98(12)
C(1)-C(6)-C(7)	121.55(11)
C(5)-C(6)-C(7)	119.39(12)
O(1)-C(7)-C(6)	106.46(10)
O(1)-C(7)-C(8)	110.13(10)
C(6)-C(7)-C(8)	113.20(10)
O(1)-C(7)-C(21)	108.79(10)
C(6)-C(7)-C(21)	110.14(10)
C(8)-C(7)-C(21)	108.05(10)
C(9)-C(8)-C(23)	123.08(12)
C(9)-C(8)-C(7)	121.13(11)
C(23)-C(8)-C(7)	115.73(11)
C(8)-C(9)-C(10)	177.97(13)
C(9)-C(10)-C(15)	117.97(11)
C(9)-C(10)-C(11)	122.75(11)
C(15)-C(10)-C(11)	119.21(10)
C(14)-C(11)-C(12)	109.04(12)
C(14)-C(11)-C(13)	108.93(12)
C(12)-C(11)-C(13)	109.43(12)
C(14)-C(11)-C(10)	109.98(11)
C(12)-C(11)-C(10)	110.24(11)
C(13)-C(11)-C(10)	109.20(11)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(11)-C(13)-H(13A)	109.5
C(11)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(11)-C(13)-H(13C)	109.5

H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(11)-C(14)-H(14A)	109.5
C(11)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(11)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(16)-C(15)-C(20)	118.46(13)
C(16)-C(15)-C(10)	119.14(12)
C(20)-C(15)-C(10)	122.40(12)
C(17)-C(16)-C(15)	120.72(14)
C(17)-C(16)-H(16A)	119.6
C(15)-C(16)-H(16A)	119.6
C(18)-C(17)-C(16)	120.19(14)
C(18)-C(17)-H(17A)	119.9
C(16)-C(17)-H(17A)	119.9
C(17)-C(18)-C(19)	119.77(14)
C(17)-C(18)-H(18A)	120.1
C(19)-C(18)-H(18A)	120.1
C(20)-C(19)-C(18)	120.31(14)
C(20)-C(19)-H(19A)	119.8
C(18)-C(19)-H(19A)	119.8
C(19)-C(20)-C(15)	120.55(14)
C(19)-C(20)-H(20A)	119.7
C(15)-C(20)-H(20A)	119.7
O(2)-C(21)-O(3)	124.46(12)
O(2)-C(21)-C(7)	123.08(11)
O(3)-C(21)-C(7)	112.45(10)
O(3)-C(22)-H(22A)	109.5
O(3)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
O(3)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(8)-C(23)-H(23A)	109.5
C(8)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(8)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(7)-O(1)-H(1B)	109.5
C(21)-O(3)-C(22)	116.83(10)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **336**. 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)	38(1)	35(1)	30(1)	-1(1)	8(1)	-5(1)
C(2)	44(1)	53(1)	28(1)	-4(1)	7(1)	-11(1)
C(3)	49(1)	54(1)	36(1)	-18(1)	14(1)	-18(1)
C(4)	54(1)	35(1)	50(1)	-15(1)	15(1)	-7(1)
C(5)	46(1)	31(1)	36(1)	-3(1)	8(1)	-4(1)
C(6)	31(1)	30(1)	30(1)	-4(1)	7(1)	-6(1)
C(7)	36(1)	26(1)	25(1)	1(1)	7(1)	-3(1)
C(8)	34(1)	29(1)	26(1)	-2(1)	7(1)	-2(1)
C(9)	32(1)	31(1)	26(1)	0(1)	5(1)	5(1)
C(10)	29(1)	24(1)	31(1)	-1(1)	4(1)	4(1)
C(11)	39(1)	27(1)	32(1)	-4(1)	3(1)	3(1)
C(12)	45(1)	57(1)	50(1)	-19(1)	-8(1)	6(1)
C(13)	59(1)	28(1)	40(1)	-5(1)	11(1)	4(1)
C(14)	68(1)	38(1)	31(1)	1(1)	9(1)	0(1)
C(15)	37(1)	21(1)	32(1)	-4(1)	6(1)	-1(1)
C(16)	39(1)	35(1)	34(1)	1(1)	1(1)	-5(1)
C(17)	61(1)	37(1)	33(1)	3(1)	-3(1)	-8(1)
C(18)	80(1)	32(1)	35(1)	-2(1)	19(1)	-12(1)
C(19)	59(1)	31(1)	59(1)	-6(1)	32(1)	-4(1)
C(20)	42(1)	27(1)	50(1)	0(1)	14(1)	3(1)
C(21)	38(1)	23(1)	26(1)	-3(1)	6(1)	3(1)
C(22)	32(1)	43(1)	41(1)	2(1)	4(1)	-2(1)
C(23)	34(1)	41(1)	42(1)	-6(1)	9(1)	-2(1)
O(1)	52(1)	32(1)	27(1)	0(1)	12(1)	-8(1)
O(2)	41(1)	45(1)	26(1)	-3(1)	2(1)	5(1)
O(3)	33(1)	39(1)	29(1)	1(1)	4(1)	-3(1)

Table 5. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for **336**

	x	y	z	U(eq)
H(1A)	8540	683	6032	41
H(2A)	8279	-100	4511	50
H(3A)	8737	-1612	4522	54
H(4A)	9361	-2350	6067	55
H(5A)	9536	-1582	7598	45

H(12A)	12231	3131	10258	79
H(12B)	12417	3173	9092	79
H(12C)	12232	2239	9615	79
H(13A)	10233	4176	9890	63
H(13B)	8935	3951	9021	63
H(13C)	10399	4217	8720	63
H(14A)	9965	2728	10713	69
H(14B)	9938	1832	10073	69
H(14C)	8660	2508	9847	69
H(16A)	8261	3391	6781	44
H(17A)	8701	4128	5339	54
H(18A)	10943	4163	4964	57
H(19A)	12763	3478	6054	56
H(20A)	12337	2740	7497	47
H(22A)	13324	884	7202	58
H(22B)	13464	225	8151	58
H(22C)	13094	1243	8287	58
H(23A)	6565	1581	7670	58
H(23B)	6632	650	8246	58
H(23C)	6642	682	7050	58
H(1B)	8899	-157	9254	55

—

Table 6. Torsion angles [°] for **336**.

C(6)-C(1)-C(2)-C(3)	-1.7(2)
C(1)-C(2)-C(3)-C(4)	1.5(2)
C(2)-C(3)-C(4)-C(5)	-0.1(2)
C(3)-C(4)-C(5)-C(6)	-1.2(2)
C(2)-C(1)-C(6)-C(5)	0.41(19)
C(2)-C(1)-C(6)-C(7)	177.10(12)
C(4)-C(5)-C(6)-C(1)	1.0(2)
C(4)-C(5)-C(6)-C(7)	-175.78(12)
C(1)-C(6)-C(7)-O(1)	144.88(12)
C(5)-C(6)-C(7)-O(1)	-38.46(15)
C(1)-C(6)-C(7)-C(8)	23.74(16)
C(5)-C(6)-C(7)-C(8)	-159.60(11)
C(1)-C(6)-C(7)-C(21)	-97.34(14)
C(5)-C(6)-C(7)-C(21)	79.33(14)
O(1)-C(7)-C(8)-C(9)	123.46(12)
C(6)-C(7)-C(8)-C(9)	-117.50(13)
C(21)-C(7)-C(8)-C(9)	4.75(15)
O(1)-C(7)-C(8)-C(23)	-53.70(14)
C(6)-C(7)-C(8)-C(23)	65.34(14)
C(21)-C(7)-C(8)-C(23)	-172.40(10)
C(23)-C(8)-C(9)-C(10)	-137(4)
C(7)-C(8)-C(9)-C(10)	46(4)
C(8)-C(9)-C(10)-C(15)	50(4)
C(8)-C(9)-C(10)-C(11)	-133(4)
C(9)-C(10)-C(11)-C(14)	-9.38(17)
C(15)-C(10)-C(11)-C(14)	167.46(11)
C(9)-C(10)-C(11)-C(12)	110.89(14)
C(15)-C(10)-C(11)-C(12)	-72.27(15)
C(9)-C(10)-C(11)-C(13)	-128.85(13)
C(15)-C(10)-C(11)-C(13)	47.98(15)
C(9)-C(10)-C(15)-C(16)	70.97(15)
C(11)-C(10)-C(15)-C(16)	-106.02(14)
C(9)-C(10)-C(15)-C(20)	-109.53(14)
C(11)-C(10)-C(15)-C(20)	73.48(16)
C(20)-C(15)-C(16)-C(17)	0.65(19)
C(10)-C(15)-C(16)-C(17)	-179.84(12)
C(15)-C(16)-C(17)-C(18)	0.0(2)
C(16)-C(17)-C(18)-C(19)	-0.6(2)
C(17)-C(18)-C(19)-C(20)	0.6(2)
C(18)-C(19)-C(20)-C(15)	0.0(2)
C(16)-C(15)-C(20)-C(19)	-0.6(2)
C(10)-C(15)-C(20)-C(19)	179.88(12)
O(1)-C(7)-C(21)-O(2)	-24.65(16)
C(6)-C(7)-C(21)-O(2)	-140.98(12)

C(8)-C(7)-C(21)-O(2)	94.91(14)
O(1)-C(7)-C(21)-O(3)	156.15(10)
C(6)-C(7)-C(21)-O(3)	39.82(14)
C(8)-C(7)-C(21)-O(3)	-84.30(12)
O(2)-C(21)-O(3)-C(22)	-0.90(18)
C(7)-C(21)-O(3)-C(22)	178.29(10)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **336** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1B)...O(2)#1	0.84	2.14	2.8650(13)	144.5

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y,-z+2

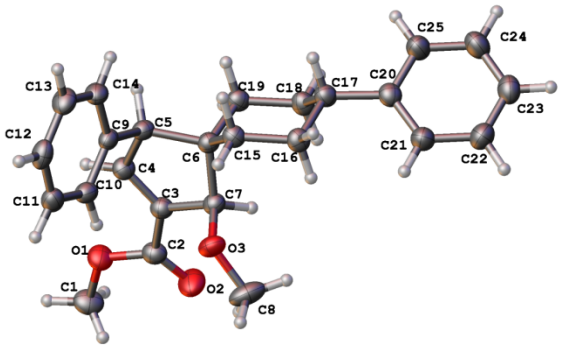

Table 1. Crystal data and structure refinement for **390**

Identification code	**390**	
Empirical formula	C25 H28 O3	
Formula weight	376.47	
Temperature	173.2 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 6.3511(2) Å	α= 90°.
	b = 9.9513(3) Å	β= 90°.
	c = 32.7486(10) Å	γ = 90°.

Volume	2069.77(11) $Å^3$
Z	4
Density (calculated)	1.208 Mg/m^3
Absorption coefficient	0.614 mm^{-1}
F(000)	808
Crystal size	0.385 x 0.342 x 0.304 mm^3
Theta range for data collection	2.70 to 68.92°.
Index ranges	-7<=h<=7, -11<=k<=12, -39<=l<=36
Reflections collected	11082
Independent reflections	3702 [R(int) = 0.0219]
Completeness to theta = 68.92°	98.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7532 and 0.6364
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3702 / 0 / 365
Goodness-of-fit on F^2	1.067
Final R indices [I>2sigma(I)]	R1 = 0.0321, wR2 = 0.0848
R indices (all data)	R1 = 0.0328, wR2 = 0.0855
Absolute structure parameter	0.02(18)
Largest diff. peak and hole	0.155 and -0.165 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for **390**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	8146(3)	8479(2)	5016(1)	43(1)
C(2)	7874(2)	7276(1)	4396(1)	33(1)
C(3)	7701(2)	5927(1)	4209(1)	30(1)
C(4)	8093(2)	4774(1)	4396(1)	30(1)
C(5)	7714(2)	3579(1)	4127(1)	28(1)
C(6)	7597(2)	4229(1)	3691(1)	28(1)
C(7)	6940(2)	5716(1)	3776(1)	29(1)
C(8)	4008(3)	7102(2)	3594(1)	54(1)
C(9)	5820(2)	2770(1)	4273(1)	28(1)
C(10)	4104(2)	3379(1)	4462(1)	32(1)
C(11)	2444(3)	2626(2)	4611(1)	37(1)
C(12)	2414(3)	1243(2)	4557(1)	40(1)
C(13)	4101(3)	625(2)	4368(1)	41(1)
C(14)	5805(3)	1378(1)	4231(1)	35(1)
C(15)	6130(2)	3478(1)	3398(1)	30(1)
C(16)	6270(2)	3996(2)	2958(1)	32(1)
C(17)	8512(2)	3912(2)	2793(1)	32(1)
C(18)	9988(2)	4724(2)	3074(1)	33(1)
C(19)	9851(2)	4233(2)	3514(1)	31(1)
C(20)	8765(2)	4344(1)	2351(1)	34(1)
C(21)	7261(3)	5074(2)	2140(1)	41(1)
C(22)	7575(3)	5455(2)	1734(1)	45(1)
C(23)	9412(3)	5115(2)	1537(1)	43(1)
C(24)	10935(3)	4388(2)	1741(1)	48(1)
C(25)	10608(3)	4005(2)	2144(1)	42(1)
O(1)	8046(2)	7207(1)	4804(1)	38(1)
O(2)	7855(2)	8317(1)	4212(1)	51(1)
O(3)	4697(2)	5870(1)	3760(1)	37(1)

Table 3. Bond lengths [Å] and angles [°] for **390**

O(1)-C(1)	1.445(2)
O(1)-C(2)	1.3404(19)
O(2)-C(2)	1.1987(18)
O(3)-C(7)	1.4337(17)
O(3)-C(8)	1.410(2)
C(2)-C(3)	1.4805(19)
C(3)-C(4)	1.3245(19)
C(3)-C(7)	1.5131(18)
C(4)-C(5)	1.4995(19)
C(5)-C(6)	1.5689(18)
C(5)-C(9)	1.5252(18)
C(6)-C(7)	1.5621(18)
C(6)-C(15)	1.5323(18)
C(6)-C(19)	1.5442(18)
C(9)-C(10)	1.3922(18)
C(9)-C(14)	1.3921(19)
C(10)-C(11)	1.382(2)
C(11)-C(12)	1.388(2)
C(12)-C(13)	1.382(3)
C(13)-C(14)	1.391(2)
C(15)-C(16)	1.5299(19)
C(16)-C(17)	1.5261(18)
C(17)-C(18)	1.542(2)
C(17)-C(20)	1.5176(19)
C(18)-C(19)	1.525(2)
C(20)-C(21)	1.385(2)
C(20)-C(25)	1.395(2)
C(21)-C(22)	1.397(2)
C(22)-C(23)	1.376(3)
C(23)-C(24)	1.380(3)
C(24)-C(25)	1.390(2)
C(1)-H(1A)	0.96(2)
C(1)-H(1B)	0.95(2)
C(1)-H(1C)	0.99(2)
C(4)-H(4)	0.98(2)
C(5)-H(5)	0.986(18)
C(7)-H(7)	1.012(17)
C(8)-H(8A)	0.98(3)
C(8)-H(8B)	1.00(3)
C(8)-H(8C)	0.98(3)
C(10)-H(10)	0.96(2)
C(11)-H(11)	0.977(18)
C(12)-H(12)	0.991(18)
C(13)-H(13)	0.96(2)

C(14)-H(14)	0.935(18)
C(15)-H(15A)	0.936(19)
C(15)-H(15B)	0.999(17)
C(16)-H(16A)	0.971(18)
C(16)-H(16B)	1.004(18)
C(17)-H(17)	0.979(18)
C(18)-H(18A)	0.954(19)
C(18)-H(18B)	0.957(19)
C(19)-H(19A)	0.967(17)
C(19)-H(19B)	1.001(18)
C(21)-H(21)	0.959(19)
C(22)-H(22)	0.991(19)
C(23)-H(23)	0.98(2)
C(24)-H(24)	0.97(2)
C(25)-H(25)	0.97(2)

C(1)-O(1)-C(2)	115.89(12)
C(7)-O(3)-C(8)	114.57(12)
O(1)-C(2)-O(2)	123.12(14)
O(1)-C(2)-C(3)	111.86(12)
O(2)-C(2)-C(3)	125.03(15)
C(2)-C(3)-C(4)	125.46(13)
C(2)-C(3)-C(7)	122.59(12)
C(4)-C(3)-C(7)	111.90(12)
C(3)-C(4)-C(5)	112.63(12)
C(4)-C(5)-C(6)	102.48(10)
C(4)-C(5)-C(9)	111.08(11)
C(6)-C(5)-C(9)	117.84(11)
C(5)-C(6)-C(7)	103.93(10)
C(5)-C(6)-C(15)	113.44(11)
C(5)-C(6)-C(19)	107.35(10)
C(7)-C(6)-C(15)	114.28(11)
C(7)-C(6)-C(19)	108.20(11)
C(15)-C(6)-C(19)	109.27(11)
O(3)-C(7)-C(3)	109.72(10)
O(3)-C(7)-C(6)	111.11(10)
C(3)-C(7)-C(6)	102.33(10)
C(5)-C(9)-C(10)	121.87(12)
C(5)-C(9)-C(14)	119.94(12)
C(10)-C(9)-C(14)	118.17(13)
C(9)-C(10)-C(11)	121.18(13)
C(10)-C(11)-C(12)	120.23(16)
C(11)-C(12)-C(13)	119.19(16)
C(12)-C(13)-C(14)	120.53(14)
C(9)-C(14)-C(13)	120.64(15)
C(6)-C(15)-C(16)	112.92(11)

C(15)-C(16)-C(17)	111.72(11)
C(16)-C(17)-C(18)	109.06(11)
C(16)-C(17)-C(20)	114.98(11)
C(18)-C(17)-C(20)	110.84(12)
C(17)-C(18)-C(19)	111.19(12)
C(6)-C(19)-C(18)	114.09(11)
C(17)-C(20)-C(21)	123.45(13)
C(17)-C(20)-C(25)	118.99(12)
C(21)-C(20)-C(25)	117.56(14)
C(20)-C(21)-C(22)	121.25(16)
C(21)-C(22)-C(23)	120.11(16)
C(22)-C(23)-C(24)	119.71(16)
C(23)-C(24)-C(25)	119.92(17)
C(20)-C(25)-C(24)	121.45(16)
O(1)-C(1)-H(1A)	110.5(13)
O(1)-C(1)-H(1B)	110.7(13)
O(1)-C(1)-H(1C)	105.5(12)
H(1A)-C(1)-H(1B)	111.1(19)
H(1A)-C(1)-H(1C)	103(2)
H(1B)-C(1)-H(1C)	115(2)
C(3)-C(4)-H(4)	126.0(11)
C(5)-C(4)-H(4)	121.3(11)
C(4)-C(5)-H(5)	110.8(9)
C(6)-C(5)-H(5)	109.8(8)
C(9)-C(5)-H(5)	104.9(10)
O(3)-C(7)-H(7)	108.4(11)
C(3)-C(7)-H(7)	115.1(10)
C(6)-C(7)-H(7)	110.1(10)
O(3)-C(8)-H(8A)	109.0(17)
O(3)-C(8)-H(8B)	111.0(17)
O(3)-C(8)-H(8C)	108.2(18)
H(8A)-C(8)-H(8B)	108(2)
H(8A)-C(8)-H(8C)	116(2)
H(8B)-C(8)-H(8C)	104(2)
C(9)-C(10)-H(10)	117.9(12)
C(11)-C(10)-H(10)	120.9(12)
C(10)-C(11)-H(11)	119.2(10)
C(12)-C(11)-H(11)	120.6(10)
C(11)-C(12)-H(12)	118.2(11)
C(13)-C(12)-H(12)	122.6(11)
C(12)-C(13)-H(13)	120.1(11)
C(14)-C(13)-H(13)	119.4(11)
C(9)-C(14)-H(14)	119.9(11)
C(13)-C(14)-H(14)	119.5(11)
C(6)-C(15)-H(15A)	108.3(10)
C(6)-C(15)-H(15B)	108.0(10)

C(16)-C(15)-H(15A)	110.2(10)
C(16)-C(15)-H(15B)	108.3(10)
H(15A)-C(15)-H(15B)	109.0(14)
C(15)-C(16)-H(16A)	110.7(10)
C(15)-C(16)-H(16B)	109.4(10)
C(17)-C(16)-H(16A)	109.0(11)
C(17)-C(16)-H(16B)	108.0(11)
H(16A)-C(16)-H(16B)	107.9(15)
C(16)-C(17)-H(17)	107.6(11)
C(18)-C(17)-H(17)	106.8(11)
C(20)-C(17)-H(17)	107.1(10)
C(17)-C(18)-H(18A)	106.6(11)
C(17)-C(18)-H(18B)	109.0(12)
C(19)-C(18)-H(18A)	112.5(10)
C(19)-C(18)-H(18B)	110.6(12)
H(18A)-C(18)-H(18B)	106.8(16)
C(6)-C(19)-H(19A)	106.9(11)
C(6)-C(19)-H(19B)	110.8(10)
C(18)-C(19)-H(19A)	109.8(10)
C(18)-C(19)-H(19B)	111.1(10)
H(19A)-C(19)-H(19B)	103.5(15)
C(20)-C(21)-H(21)	119.0(10)
C(22)-C(21)-H(21)	119.8(10)
C(21)-C(22)-H(22)	119.1(12)
C(23)-C(22)-H(22)	120.8(11)
C(22)-C(23)-H(23)	119.8(11)
C(24)-C(23)-H(23)	120.4(11)
C(23)-C(24)-H(24)	118.9(12)
C(25)-C(24)-H(24)	121.1(12)
C(20)-C(25)-H(25)	117.7(14)
C(24)-C(25)-H(25)	120.9(14)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **390** 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)	35(1)	49(1)	-14(1)	-4(1)	-3(1)
C(2)	32(1)	29(1)	38(1)	-2(1)	2(1)	-1(1)
C(3)	30(1)	27(1)	33(1)	-1(1)	0(1)	0(1)
C(4)	32(1)	30(1)	30(1)	-3(1)	-3(1)	-1(1)
C(5)	31(1)	25(1)	30(1)	-1(1)	-4(1)	3(1)
C(6)	27(1)	26(1)	29(1)	0(1)	-1(1)	0(1)
C(7)	29(1)	26(1)	32(1)	2(1)	0(1)	0(1)

C(8)	48(1)	34(1)	81(1)	2(1)	-20(1)	9(1)
C(9)	35(1)	26(1)	24(1)	2(1)	-4(1)	2(1)
C(10)	37(1)	28(1)	32(1)	-1(1)	-4(1)	5(1)
C(11)	34(1)	44(1)	33(1)	5(1)	0(1)	6(1)
C(12)	40(1)	45(1)	34(1)	11(1)	-3(1)	-8(1)
C(13)	55(1)	28(1)	40(1)	4(1)	-1(1)	-5(1)
C(14)	44(1)	27(1)	33(1)	-2(1)	1(1)	3(1)
C(15)	27(1)	31(1)	30(1)	-2(1)	-1(1)	-2(1)
C(16)	30(1)	36(1)	31(1)	-2(1)	-4(1)	-2(1)
C(17)	32(1)	35(1)	30(1)	-2(1)	-1(1)	2(1)
C(18)	28(1)	39(1)	33(1)	0(1)	2(1)	-2(1)
C(19)	27(1)	34(1)	31(1)	-2(1)	-2(1)	2(1)
C(20)	37(1)	32(1)	32(1)	-3(1)	0(1)	-1(1)
C(21)	42(1)	44(1)	36(1)	2(1)	3(1)	9(1)
C(22)	50(1)	44(1)	40(1)	8(1)	-2(1)	7(1)
C(23)	53(1)	43(1)	33(1)	3(1)	3(1)	-4(1)
C(24)	47(1)	58(1)	38(1)	-2(1)	9(1)	6(1)
C(25)	40(1)	51(1)	35(1)	2(1)	2(1)	10(1)
O(1)	49(1)	30(1)	36(1)	-7(1)	-2(1)	-4(1)
O(2)	81(1)	25(1)	47(1)	0(1)	4(1)	-1(1)
O(3)	31(1)	32(1)	48(1)	5(1)	-2(1)	6(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **390**

	x	y	z	U(eq)
H(1A)	9470(40)	8910(20)	4967(7)	64(6)
H(1B)	7010(40)	9040(20)	4938(7)	61(6)
H(1C)	8210(40)	8250(20)	5309(7)	60(6)
H(4)	8540(30)	4667(18)	4681(6)	39(5)
H(5)	8910(30)	2949(16)	4140(4)	22(3)
H(7)	7590(30)	6333(17)	3565(5)	31(4)
H(8A)	2480(50)	7160(30)	3621(8)	78(8)
H(8B)	4640(50)	7880(30)	3744(8)	79(7)
H(8C)	4570(50)	7180(30)	3317(8)	82(8)
H(10)	4080(30)	4340(20)	4476(6)	50(5)
H(11)	1320(30)	3075(17)	4762(5)	37(4)
H(12)	1180(30)	736(18)	4660(5)	39(5)
H(13)	4100(30)	-330(20)	4328(5)	43(5)
H(14)	6950(30)	943(18)	4110(5)	34(4)
H(15A)	4750(30)	3559(16)	3495(5)	31(4)
H(15B)	6540(30)	2509(17)	3399(5)	30(4)
H(16A)	5790(30)	4920(18)	2942(5)	36(4)
H(16B)	5340(30)	3436(19)	2778(5)	40(5)
H(17)	8960(30)	2972(18)	2810(5)	33(4)
H(18A)	9590(30)	5644(19)	3046(5)	39(5)
H(18B)	11400(30)	4650(20)	2974(6)	44(5)
H(19A)	10370(30)	3321(17)	3532(5)	32(4)
H(19B)	10830(30)	4749(17)	3695(5)	32(4)
H(21)	5970(30)	5302(18)	2275(5)	40(5)
H(22)	6490(30)	6008(19)	1596(6)	42(5)
H(23)	9600(30)	5350(20)	1247(6)	48(5)
H(24)	12190(40)	4120(20)	1595(6)	53(5)
H(25)	11650(40)	3480(20)	2289(7)	59(6)

Table 6. Torsion angles [°] for **390**

C(1)-O(1)-C(2)-O(2)	1.9(2)
C(1)-O(1)-C(2)-C(3)	-177.81(12)
C(8)-O(3)-C(7)-C(3)	103.42(15)
C(8)-O(3)-C(7)-C(6)	-144.14(14)
O(2)-C(2)-C(3)-C(4)	167.17(14)
O(1)-C(2)-C(3)-C(4)	-13.18(19)
O(1)-C(2)-C(3)-C(7)	163.92(12)
O(2)-C(2)-C(3)-C(7)	-15.7(2)
C(2)-C(3)-C(7)-O(3)	-76.16(15)
C(2)-C(3)-C(7)-C(6)	165.80(11)
C(4)-C(3)-C(7)-O(3)	101.29(13)
C(4)-C(3)-C(7)-C(6)	-16.75(14)
C(2)-C(3)-C(4)-C(5)	178.36(12)
C(7)-C(3)-C(4)-C(5)	0.99(16)
C(3)-C(4)-C(5)-C(9)	-111.56(13)
C(3)-C(4)-C(5)-C(6)	15.16(14)
C(4)-C(5)-C(6)-C(19)	90.34(12)
C(9)-C(5)-C(6)-C(7)	98.08(12)
C(9)-C(5)-C(6)-C(15)	-26.62(16)
C(9)-C(5)-C(6)-C(19)	-147.43(11)
C(4)-C(5)-C(9)-C(10)	32.18(17)
C(4)-C(5)-C(6)-C(7)	-24.16(12)
C(4)-C(5)-C(6)-C(15)	-148.85(11)
C(6)-C(5)-C(9)-C(14)	96.42(15)
C(6)-C(5)-C(9)-C(10)	-85.55(16)
C(4)-C(5)-C(9)-C(14)	-145.84(13)
C(5)-C(6)-C(7)-C(3)	24.61(12)
C(5)-C(6)-C(7)-O(3)	-92.43(12)
C(19)-C(6)-C(7)-O(3)	153.68(10)
C(15)-C(6)-C(7)-O(3)	31.72(15)
C(15)-C(6)-C(7)-C(3)	148.76(11)
C(7)-C(6)-C(15)-C(16)	69.39(14)
C(19)-C(6)-C(15)-C(16)	-51.98(14)
C(5)-C(6)-C(19)-C(18)	174.94(12)
C(7)-C(6)-C(19)-C(18)	-73.46(14)
C(15)-C(6)-C(19)-C(18)	51.53(15)
C(19)-C(6)-C(7)-C(3)	-89.28(12)
C(5)-C(6)-C(15)-C(16)	-171.71(11)
C(5)-C(9)-C(10)-C(11)	-176.90(13)
C(14)-C(9)-C(10)-C(11)	1.2(2)
C(5)-C(9)-C(14)-C(13)	179.22(13)
C(10)-C(9)-C(14)-C(13)	1.1(2)
C(9)-C(10)-C(11)-C(12)	-3.0(2)
C(10)-C(11)-C(12)-C(13)	2.6(2)

C(11)-C(12)-C(13)-C(14)	-0.3(3)
C(12)-C(13)-C(14)-C(9)	-1.5(2)
C(6)-C(15)-C(16)-C(17)	57.32(15)
C(15)-C(16)-C(17)-C(18)	-57.66(16)
C(15)-C(16)-C(17)-C(20)	177.17(12)
C(16)-C(17)-C(18)-C(19)	56.22(15)
C(20)-C(17)-C(18)-C(19)	-176.23(11)
C(16)-C(17)-C(20)-C(21)	15.9(2)
C(16)-C(17)-C(20)-C(25)	-164.71(14)
C(18)-C(17)-C(20)-C(21)	-108.36(15)
C(18)-C(17)-C(20)-C(25)	71.04(17)
C(17)-C(18)-C(19)-C(6)	-54.96(16)
C(17)-C(20)-C(21)-C(22)	179.60(15)
C(25)-C(20)-C(21)-C(22)	0.2(2)
C(17)-C(20)-C(25)-C(24)	-179.22(15)
C(21)-C(20)-C(25)-C(24)	0.2(2)
C(20)-C(21)-C(22)-C(23)	-0.5(3)
C(21)-C(22)-C(23)-C(24)	0.4(3)
C(22)-C(23)-C(24)-C(25)	0.0(3)
C(23)-C(24)-C(25)-C(20)	-0.3(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **390** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(8)-H(8B)...O(2)	1.00(3)	2.59(3)	3.396(3)	137(2)
C(15)-H(15A)...O(3)	0.936(19)	2.458(16)	2.8104(17)	102.3(12)

Symmetry transformations used to generate equivalent atoms:

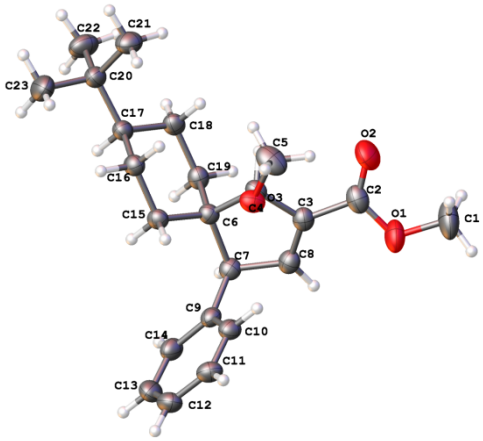

Table 1. Crystal data and structure refinement for ***ent*-394**

Identification code	***ent*-394**	
Empirical formula	C23 H32 O3	
Formula weight	356.49	
Temperature	173.2 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 10.8332(2) Å	α= 90°.
	b = 6.12720(10) Å	β= 90.0220(10)°.
	c = 15.5015(3) Å	γ = 90°.
Volume	1028.95(3) $Å^3$	
Z	2	
Density (calculated)	1.151 Mg/m^3	
Absorption coefficient	0.583 mm^{-1}	
F(000)	388	
Crystal size	0.562 x 0.531 x 0.376 mm^3	
Theta range for data collection	2.85 to 60.00°.	
Index ranges	-12<=h<=11, -6<=k<=6, -17<=l<=17	
Reflections collected	5613	
Independent reflections	2538 [R(int) = 0.0155]	

Completeness to theta = 60.00°	94.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7531 and 0.7153
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2538 / 1 / 240
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0322, wR2 = 0.0838
R indices (all data)	R1 = 0.0323, wR2 = 0.0839
Absolute structure parameter	-0.1(2)
Largest diff. peak and hole	0.123 and -0.171 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for ***ent*-394**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-1014(2)	3005(5)	101(2)	71(1)
C(2)	168(2)	3766(3)	1346(1)	42(1)
C(3)	1414(2)	4075(3)	1713(1)	35(1)
C(4)	1593(2)	5379(3)	2536(1)	32(1)
C(5)	326(2)	8552(4)	2582(2)	57(1)
C(6)	2922(2)	4756(3)	2818(1)	30(1)
C(7)	3562(2)	3935(3)	1961(1)	33(1)
C(8)	2476(2)	3369(3)	1399(1)	36(1)
C(9)	4435(2)	5558(3)	1541(1)	32(1)
C(10)	4006(2)	7389(3)	1105(1)	35(1)
C(11)	4816(2)	8917(3)	770(1)	41(1)
C(12)	6072(2)	8650(4)	874(1)	46(1)
C(13)	6515(2)	6831(4)	1296(1)	48(1)
C(14)	5705(2)	5285(4)	1619(1)	40(1)
C(15)	3631(2)	6600(3)	3261(1)	32(1)
C(16)	3088(2)	7214(3)	4139(1)	34(1)
C(17)	3031(2)	5267(3)	4763(1)	34(1)
C(18)	2311(2)	3415(3)	4330(1)	35(1)
C(19)	2833(2)	2812(3)	3447(1)	34(1)
C(20)	2564(2)	5887(3)	5681(1)	40(1)
C(21)	1256(2)	6819(4)	5667(1)	48(1)
C(22)	2588(2)	3875(4)	6264(1)	55(1)
C(23)	3421(2)	7618(5)	6072(1)	63(1)
O(1)	188(1)	3183(3)	513(1)	57(1)
O(2)	-770(1)	4020(3)	1746(1)	61(1)
O(3)	1476(1)	7657(2)	2354(1)	37(1)

Table 3. Bond lengths [Å] and angles [°] for ***ent*-394**.

O(1)-C(1)	1.454(3)
O(1)-C(2)	1.340(2)
O(2)-C(2)	1.201(2)
O(3)-C(4)	1.430(2)
O(3)-C(5)	1.407(2)
C(2)-C(3)	1.477(2)
C(3)-C(4)	1.517(2)
C(3)-C(8)	1.322(2)
C(4)-C(6)	1.553(2)
C(6)-C(7)	1.580(2)
C(6)-C(15)	1.529(2)
C(6)-C(19)	1.543(2)
C(7)-C(8)	1.504(2)
C(7)-C(9)	1.520(2)
C(9)-C(10)	1.390(2)
C(9)-C(14)	1.391(2)
C(10)-C(11)	1.385(2)
C(11)-C(12)	1.380(3)
C(12)-C(13)	1.379(3)
C(13)-C(14)	1.385(3)
C(15)-C(16)	1.530(2)
C(16)-C(17)	1.537(2)
C(17)-C(18)	1.532(2)
C(17)-C(20)	1.558(2)
C(18)-C(19)	1.526(2)
C(20)-C(21)	1.529(3)
C(20)-C(22)	1.528(3)
C(20)-C(23)	1.534(3)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(4)-H(4)	1.0000
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(7)-H(7)	1.0000
C(8)-H(8)	0.9500
C(10)-H(10)	0.9500
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-H(13)	0.9500
C(14)-H(14)	0.9500
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900

C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-H(17)	1.0000
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800

C(1)-O(1)-C(2)	115.38(16)
C(4)-O(3)-C(5)	114.14(14)
O(1)-C(2)-O(2)	123.07(17)
O(1)-C(2)-C(3)	112.99(15)
O(2)-C(2)-C(3)	123.93(17)
C(2)-C(3)-C(4)	120.53(14)
C(2)-C(3)-C(8)	127.70(16)
C(4)-C(3)-C(8)	111.76(14)
O(3)-C(4)-C(3)	109.71(13)
O(3)-C(4)-C(6)	112.17(14)
C(3)-C(4)-C(6)	103.02(13)
C(4)-C(6)-C(7)	104.41(12)
C(4)-C(6)-C(15)	114.21(15)
C(4)-C(6)-C(19)	108.04(13)
C(7)-C(6)-C(15)	113.13(13)
C(7)-C(6)-C(19)	108.27(14)
C(15)-C(6)-C(19)	108.51(13)
C(6)-C(7)-C(8)	102.53(13)
C(6)-C(7)-C(9)	115.15(14)
C(8)-C(7)-C(9)	112.95(13)
C(3)-C(8)-C(7)	113.07(14)
C(7)-C(9)-C(10)	121.89(15)
C(7)-C(9)-C(14)	120.01(16)
C(10)-C(9)-C(14)	118.04(17)
C(9)-C(10)-C(11)	121.09(15)
C(10)-C(11)-C(12)	120.07(17)
C(11)-C(12)-C(13)	119.66(19)
C(12)-C(13)-C(14)	120.22(18)
C(9)-C(14)-C(13)	120.88(19)

C(6)-C(15)-C(16)	112.86(14)
C(15)-C(16)-C(17)	112.61(15)
C(16)-C(17)-C(18)	108.65(13)
C(16)-C(17)-C(20)	113.50(14)
C(18)-C(17)-C(20)	114.56(14)
C(17)-C(18)-C(19)	112.54(14)
C(6)-C(19)-C(18)	113.81(15)
C(17)-C(20)-C(21)	112.29(14)
C(17)-C(20)-C(22)	109.75(15)
C(17)-C(20)-C(23)	109.43(15)
C(21)-C(20)-C(22)	108.97(15)
C(21)-C(20)-C(23)	107.97(17)
C(22)-C(20)-C(23)	108.34(16)
O(1)-C(1)-H(1A)	109.00
O(1)-C(1)-H(1B)	109.00
O(1)-C(1)-H(1C)	109.00
H(1A)-C(1)-H(1B)	110.00
H(1A)-C(1)-H(1C)	110.00
H(1B)-C(1)-H(1C)	109.00
O(3)-C(4)-H(4)	111.00
C(3)-C(4)-H(4)	111.00
C(6)-C(4)-H(4)	111.00
O(3)-C(5)-H(5A)	109.00
O(3)-C(5)-H(5B)	110.00
O(3)-C(5)-H(5C)	109.00
H(5A)-C(5)-H(5B)	109.00
H(5A)-C(5)-H(5C)	109.00
H(5B)-C(5)-H(5C)	109.00
C(6)-C(7)-H(7)	109.00
C(8)-C(7)-H(7)	109.00
C(9)-C(7)-H(7)	109.00
C(3)-C(8)-H(8)	123.00
C(7)-C(8)-H(8)	123.00
C(9)-C(10)-H(10)	119.00
C(11)-C(10)-H(10)	119.00
C(10)-C(11)-H(11)	120.00
C(12)-C(11)-H(11)	120.00
C(11)-C(12)-H(12)	120.00
C(13)-C(12)-H(12)	120.00
C(12)-C(13)-H(13)	120.00
C(14)-C(13)-H(13)	120.00
C(9)-C(14)-H(14)	120.00
C(13)-C(14)-H(14)	120.00
C(6)-C(15)-H(15A)	109.00
C(6)-C(15)-H(15B)	109.00
C(16)-C(15)-H(15A)	109.00

C(16)-C(15)-H(15B)	109.00
H(15A)-C(15)-H(15B)	108.00
C(15)-C(16)-H(16A)	109.00
C(15)-C(16)-H(16B)	109.00
C(17)-C(16)-H(16A)	109.00
C(17)-C(16)-H(16B)	109.00
H(16A)-C(16)-H(16B)	108.00
C(16)-C(17)-H(17)	107.00
C(18)-C(17)-H(17)	107.00
C(20)-C(17)-H(17)	106.00
C(17)-C(18)-H(18A)	109.00
C(17)-C(18)-H(18B)	109.00
C(19)-C(18)-H(18A)	109.00
C(19)-C(18)-H(18B)	109.00
H(18A)-C(18)-H(18B)	108.00
C(6)-C(19)-H(19A)	109.00
C(6)-C(19)-H(19B)	109.00
C(18)-C(19)-H(19A)	109.00
C(18)-C(19)-H(19B)	109.00
H(19A)-C(19)-H(19B)	108.00
C(20)-C(21)-H(21A)	109.00
C(20)-C(21)-H(21B)	109.00
C(20)-C(21)-H(21C)	109.00
H(21A)-C(21)-H(21B)	109.00
H(21A)-C(21)-H(21C)	110.00
H(21B)-C(21)-H(21C)	109.00
C(20)-C(22)-H(22A)	109.00
C(20)-C(22)-H(22B)	109.00
C(20)-C(22)-H(22C)	109.00
H(22A)-C(22)-H(22B)	110.00
H(22A)-C(22)-H(22C)	109.00
H(22B)-C(22)-H(22C)	109.00
C(20)-C(23)-H(23A)	109.00
C(20)-C(23)-H(23B)	109.00
C(20)-C(23)-H(23C)	109.00
H(23A)-C(23)-H(23B)	110.00
H(23A)-C(23)-H(23C)	109.00
H(23B)-C(23)-H(23C)	109.00

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for ***ent*-394**. 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)	59(1)	71(2)	83(2)	-21(1)	-34(1)	-2(1)
C(2)	40(1)	31(1)	55(1)	1(1)	-8(1)	0(1)
C(3)	37(1)	31(1)	37(1)	3(1)	-4(1)	0(1)
C(4)	30(1)	31(1)	36(1)	4(1)	1(1)	-2(1)
C(5)	40(1)	43(1)	87(1)	-4(1)	4(1)	12(1)
C(6)	30(1)	29(1)	32(1)	1(1)	0(1)	1(1)
C(7)	33(1)	32(1)	35(1)	0(1)	0(1)	7(1)
C(8)	42(1)	30(1)	36(1)	-1(1)	-3(1)	-1(1)
C(9)	31(1)	40(1)	26(1)	-3(1)	0(1)	5(1)
C(10)	31(1)	42(1)	33(1)	1(1)	2(1)	5(1)
C(11)	45(1)	42(1)	36(1)	4(1)	7(1)	2(1)
C(12)	42(1)	55(1)	40(1)	-1(1)	9(1)	-7(1)
C(13)	29(1)	72(2)	41(1)	-2(1)	2(1)	1(1)
C(14)	37(1)	53(1)	32(1)	2(1)	-2(1)	8(1)
C(15)	32(1)	29(1)	33(1)	3(1)	1(1)	-2(1)
C(16)	34(1)	34(1)	34(1)	-2(1)	1(1)	-4(1)
C(17)	28(1)	42(1)	33(1)	4(1)	1(1)	0(1)
C(18)	35(1)	35(1)	35(1)	8(1)	-1(1)	-3(1)
C(19)	34(1)	30(1)	39(1)	3(1)	-4(1)	0(1)
C(20)	34(1)	53(1)	34(1)	2(1)	-1(1)	-2(1)
C(21)	44(1)	59(1)	41(1)	0(1)	7(1)	6(1)
C(22)	54(1)	73(2)	38(1)	14(1)	6(1)	11(1)
C(23)	58(1)	89(2)	41(1)	-13(1)	1(1)	-15(1)
O(1)	50(1)	61(1)	60(1)	-18(1)	-20(1)	0(1)
O(2)	36(1)	78(1)	69(1)	-3(1)	-8(1)	2(1)
O(3)	34(1)	33(1)	44(1)	5(1)	4(1)	8(1)

Table 5. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for ***ent*-394**.

	x	y	z	U(eq)
H(1A)	-1427	1675	301	106
H(1B)	-907	2940	-526	106
H(1C)	-1516	4279	251	106
H(4)	981	4923	2983	39
H(5A)	160	8256	3193	85

H(5B)	-324	7892	2228	85
H(5C)	339	10133	2486	85
H(7)	4029	2567	2091	40
H(8)	2546	2584	873	43
H(10)	3142	7596	1036	42
H(11)	4507	10150	468	49
H(12)	6628	9713	655	55
H(13)	7380	6639	1366	57
H(14)	6021	4021	1897	49
H(15A)	3624	7902	2883	38
H(15B)	4501	6147	3339	38
H(16A)	2244	7799	4055	41
H(16B)	3597	8383	4400	41
H(17)	3898	4735	4834	41
H(18A)	2331	2113	4708	42
H(18B)	1438	3863	4263	42
H(19A)	2304	1672	3187	41
H(19B)	3667	2181	3526	41
H(21A)	1232	8106	5292	72
H(21B)	1013	7235	6253	72
H(21C)	683	5712	5447	72
H(22A)	1960	2833	6070	82
H(22B)	2415	4312	6860	82
H(22C)	3404	3190	6235	82
H(23A)	4275	7095	6053	94
H(23B)	3182	7893	6671	94
H(23C)	3352	8974	5739	94

Table 6. Torsion angles [°] for ***ent*-394**.

C(1)-O(1)-C(2)-O(2)	3.7(3)
C(1)-O(1)-C(2)-C(3)	-175.86(19)
C(5)-O(3)-C(4)-C(3)	101.14(17)
C(5)-O(3)-C(4)-C(6)	-145.01(15)
O(2)-C(2)-C(3)-C(4)	-18.6(3)
O(1)-C(2)-C(3)-C(4)	161.01(16)
O(1)-C(2)-C(3)-C(8)	-17.4(3)
O(2)-C(2)-C(3)-C(8)	163.0(2)
C(2)-C(3)-C(4)-C(6)	164.85(15)
C(8)-C(3)-C(4)-O(3)	103.13(17)
C(2)-C(3)-C(8)-C(7)	-178.33(17)
C(4)-C(3)-C(8)-C(7)	3.1(2)
C(8)-C(3)-C(4)-C(6)	-16.49(19)
C(2)-C(3)-C(4)-O(3)	-75.52(19)
O(3)-C(4)-C(6)-C(7)	-95.76(15)
O(3)-C(4)-C(6)-C(15)	28.31(18)

O(3)-C(4)-C(6)-C(19)	149.15(13)
C(3)-C(4)-C(6)-C(7)	22.15(17)
C(3)-C(4)-C(6)-C(15)	146.22(14)
C(3)-C(4)-C(6)-C(19)	-92.94(15)
C(4)-C(6)-C(7)-C(8)	-20.51(17)
C(4)-C(6)-C(7)-C(9)	102.56(16)
C(15)-C(6)-C(7)-C(8)	-145.27(14)
C(15)-C(6)-C(7)-C(9)	-22.2(2)
C(19)-C(6)-C(7)-C(8)	94.42(15)
C(19)-C(6)-C(7)-C(9)	-142.51(14)
C(4)-C(6)-C(15)-C(16)	67.15(18)
C(7)-C(6)-C(15)-C(16)	-173.59(14)
C(19)-C(6)-C(15)-C(16)	-53.43(18)
C(4)-C(6)-C(19)-C(18)	-71.47(17)
C(7)-C(6)-C(19)-C(18)	176.00(13)
C(15)-C(6)-C(19)-C(18)	52.86(18)
C(6)-C(7)-C(8)-C(3)	11.4(2)
C(9)-C(7)-C(8)-C(3)	-113.15(17)
C(6)-C(7)-C(9)-C(10)	-73.40(19)
C(6)-C(7)-C(9)-C(14)	103.78(18)
C(8)-C(7)-C(9)-C(10)	43.9(2)
C(8)-C(7)-C(9)-C(14)	-138.89(16)
C(7)-C(9)-C(10)-C(11)	176.19(15)
C(14)-C(9)-C(10)-C(11)	-1.1(2)
C(7)-C(9)-C(14)-C(13)	-175.17(16)
C(10)-C(9)-C(14)-C(13)	2.1(3)
C(9)-C(10)-C(11)-C(12)	-0.7(3)
C(10)-C(11)-C(12)-C(13)	1.4(3)
C(11)-C(12)-C(13)-C(14)	-0.3(3)
C(12)-C(13)-C(14)-C(9)	-1.5(3)
C(6)-C(15)-C(16)-C(17)	57.25(18)
C(15)-C(16)-C(17)-C(18)	-55.22(18)
C(15)-C(16)-C(17)-C(20)	176.10(14)
C(16)-C(17)-C(18)-C(19)	54.07(18)
C(20)-C(17)-C(18)-C(19)	-177.85(14)
C(16)-C(17)-C(20)-C(21)	60.9(2)
C(16)-C(17)-C(20)-C(22)	-177.77(14)
C(16)-C(17)-C(20)-C(23)	-59.0(2)
C(18)-C(17)-C(20)-C(21)	-64.7(2)
C(18)-C(17)-C(20)-C(22)	56.64(19)
C(18)-C(17)-C(20)-C(23)	175.40(16)
C(17)-C(18)-C(19)-C(6)	-55.29(19)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for ***ent*-394** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(5)-H(5B)...O(2)	0.9800	2.5300	3.287(3)	134.00

Symmetry transformations used to generate equivalent atoms:

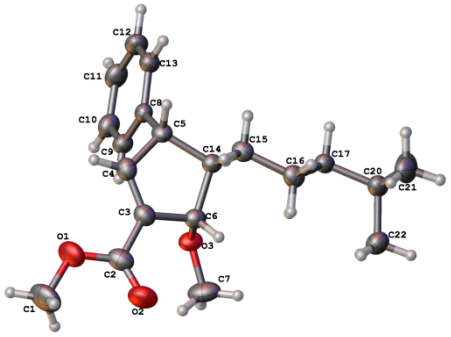

Table 1. Crystal data and structure refinement for **394**

Identification code	**394**	
Empirical formula	C23 H32 O3	
Formula weight	356.49	
Temperature	173.2 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 10.8266(4) Å	a= 90°.
	b = 6.1262(3) Å	b= 90.055(2)°.
	c = 15.5226(6) Å	g = 90°.
Volume	1029.55(7) $Å^3$	
Z	2	
Density (calculated)	1.150 Mg/m^3	
Absorption coefficient	0.583 mm^{-1}	
F(000)	388	
Crystal size	0.468 x 0.176 x 0.162 mm^3	
Theta range for data collection	2.85 to 66.55°.	
Index ranges	-12<=h<=12, -7<=k<=7, -18<=l<=18	
Reflections collected	7089	
Independent reflections	3109 [R(int) = 0.0183]	
Completeness to theta = 66.55°	97.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.6925	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	3109 / 1 / 308
Goodness-of-fit on F^2	1.060
Final R indices [I>2sigma(I)]	R1 = 0.0316, wR2 = 0.0807
R indices (all data)	R1 = 0.0326, wR2 = 0.0816
Absolute structure parameter	0.0(2)
Largest diff. peak and hole	0.126 and -0.161 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3)
for **394**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	6013(2)	8873(5)	9900(2)	71(1)
C(2)	4834(2)	8106(3)	8654(1)	42(1)
C(3)	3587(2)	7794(3)	8286(1)	35(1)
C(4)	2524(2)	8510(3)	8600(1)	35(1)
C(5)	1442(1)	7938(3)	8039(1)	33(1)
C(6)	3407(2)	6500(3)	7465(1)	32(1)
C(7)	4673(2)	3322(4)	7417(2)	56(1)
C(8)	566(1)	6318(3)	8459(1)	32(1)
C(9)	995(2)	4485(3)	8894(1)	35(1)
C(10)	186(2)	2956(3)	9230(1)	41(1)
C(11)	-1073(2)	3223(4)	9127(1)	45(1)
C(12)	-1518(2)	5048(4)	8704(1)	48(1)
C(13)	-707(2)	6593(4)	8381(1)	40(1)
C(14)	2076(1)	7122(3)	7182(1)	30(1)
C(15)	2167(2)	9058(3)	6554(1)	34(1)
C(16)	2689(2)	8458(3)	5670(1)	35(1)
C(17)	1966(2)	6603(3)	5239(1)	33(1)
C(18)	1914(2)	4662(3)	5860(1)	34(1)
C(19)	1371(2)	5272(3)	6738(1)	31(1)
C(20)	2432(2)	5989(3)	4321(1)	39(1)
C(21)	2412(2)	8001(4)	3738(1)	55(1)
C(22)	3746(2)	5054(4)	4332(1)	48(1)
C(23)	1581(2)	4257(5)	3927(1)	62(1)
O(1)	4814(1)	8693(3)	9486(1)	56(1)
O(2)	5772(1)	7849(3)	8252(1)	61(1)
O(3)	3522(1)	4215(2)	7646(1)	37(1)

Table 3. Bond lengths [Å] and angles [°] for **394**

O(1)-C(1)	1.452(3)
O(1)-C(2)	1.340(2)

O(2)-C(2)	1.203(2)
O(3)-C(6)	1.433(2)
O(3)-C(7)	1.407(2)
C(2)-C(3)	1.478(2)
C(3)-C(4)	1.325(2)
C(3)-C(6)	1.513(2)
C(4)-C(5)	1.500(2)
C(5)-C(8)	1.521(2)
C(5)-C(14)	1.578(2)
C(6)-C(14)	1.553(2)
C(8)-C(9)	1.390(2)
C(8)-C(13)	1.393(2)
C(9)-C(10)	1.385(2)
C(10)-C(11)	1.382(3)
C(11)-C(12)	1.383(3)
C(12)-C(13)	1.386(3)
C(14)-C(15)	1.539(2)
C(14)-C(19)	1.530(2)
C(15)-C(16)	1.529(2)
C(16)-C(17)	1.534(2)
C(17)-C(18)	1.532(2)
C(17)-C(20)	1.558(2)
C(18)-C(19)	1.531(2)
C(20)-C(21)	1.530(3)
C(20)-C(22)	1.533(3)
C(20)-C(23)	1.532(3)
C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600
C(1)-H(1C)	0.9600
C(4)-H(4)	0.948(19)
C(5)-H(5)	0.955(18)
C(6)-H(6)	0.978(17)
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
C(9)-H(9)	0.96(2)
C(10)-H(10)	0.98(2)
C(11)-H(11)	0.96(2)
C(12)-H(12)	0.96(2)
C(13)-H(13)	0.96(2)
C(15)-H(15A)	0.937(18)
C(15)-H(15B)	0.97(2)
C(16)-H(16A)	0.979(18)
C(16)-H(16B)	0.97(2)
C(17)-H(17)	0.982(18)
C(18)-H(18A)	0.953(17)

C(18)-H(18B)	0.98(2)
C(19)-H(19A)	0.959(18)
C(19)-H(19B)	0.977(19)
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600

C(1)-O(1)-C(2)	115.60(16)
C(6)-O(3)-C(7)	114.00(14)
O(1)-C(2)-O(2)	123.28(17)
O(1)-C(2)-C(3)	113.07(15)
O(2)-C(2)-C(3)	123.65(17)
C(2)-C(3)-C(4)	127.51(16)
C(2)-C(3)-C(6)	120.69(14)
C(4)-C(3)-C(6)	111.79(15)
C(3)-C(4)-C(5)	112.82(15)
C(4)-C(5)-C(8)	113.02(13)
C(4)-C(5)-C(14)	102.87(12)
C(8)-C(5)-C(14)	115.26(14)
O(3)-C(6)-C(3)	109.61(13)
O(3)-C(6)-C(14)	112.04(14)
C(3)-C(6)-C(14)	103.20(13)
C(5)-C(8)-C(9)	121.79(14)
C(5)-C(8)-C(13)	120.11(16)
C(9)-C(8)-C(13)	118.04(16)
C(8)-C(9)-C(10)	121.20(15)
C(9)-C(10)-C(11)	120.02(17)
C(10)-C(11)-C(12)	119.62(19)
C(11)-C(12)-C(13)	120.18(17)
C(8)-C(13)-C(12)	120.91(19)
C(5)-C(14)-C(6)	104.11(12)
C(5)-C(14)-C(15)	108.55(14)
C(5)-C(14)-C(19)	113.38(13)
C(6)-C(14)-C(15)	107.97(13)
C(6)-C(14)-C(19)	114.08(14)
C(15)-C(14)-C(19)	108.50(13)
C(14)-C(15)-C(16)	114.04(15)
C(15)-C(16)-C(17)	112.38(14)
C(16)-C(17)-C(18)	108.62(13)
C(16)-C(17)-C(20)	114.37(14)

C(18)-C(17)-C(20)	113.61(14)
C(17)-C(18)-C(19)	112.66(15)
C(14)-C(19)-C(18)	112.94(14)
C(17)-C(20)-C(21)	110.02(15)
C(17)-C(20)-C(22)	112.36(14)
C(17)-C(20)-C(23)	109.68(14)
C(21)-C(20)-C(22)	108.73(15)
C(21)-C(20)-C(23)	108.28(16)
C(22)-C(20)-C(23)	107.67(17)
O(1)-C(1)-H(1A)	109.00
O(1)-C(1)-H(1B)	109.00
O(1)-C(1)-H(1C)	109.00
H(1A)-C(1)-H(1B)	109.00
H(1A)-C(1)-H(1C)	109.00
H(1B)-C(1)-H(1C)	110.00
C(3)-C(4)-H(4)	124.7(10)
C(5)-C(4)-H(4)	122.3(10)
C(4)-C(5)-H(5)	109.8(10)
C(8)-C(5)-H(5)	106.9(10)
C(14)-C(5)-H(5)	108.9(9)
O(3)-C(6)-H(6)	110.7(11)
C(3)-C(6)-H(6)	111.9(11)
C(14)-C(6)-H(6)	109.2(10)
O(3)-C(7)-H(7A)	109.00
O(3)-C(7)-H(7B)	109.00
O(3)-C(7)-H(7C)	109.00
H(7A)-C(7)-H(7B)	109.00
H(7A)-C(7)-H(7C)	109.00
H(7B)-C(7)-H(7C)	109.00
C(8)-C(9)-H(9)	119.5(14)
C(10)-C(9)-H(9)	119.3(14)
C(9)-C(10)-H(10)	121.1(11)
C(11)-C(10)-H(10)	118.9(11)
C(10)-C(11)-H(11)	121.3(13)
C(12)-C(11)-H(11)	119.1(13)
C(11)-C(12)-H(12)	120.8(14)
C(13)-C(12)-H(12)	119.1(14)
C(8)-C(13)-H(13)	118.2(12)
C(12)-C(13)-H(13)	120.9(12)
C(14)-C(15)-H(15A)	108.0(11)
C(14)-C(15)-H(15B)	110.5(11)
C(16)-C(15)-H(15A)	107.5(11)
C(16)-C(15)-H(15B)	111.2(10)
H(15A)-C(15)-H(15B)	105.2(16)
C(15)-C(16)-H(16A)	110.8(10)
C(15)-C(16)-H(16B)	108.0(12)

C(17)-C(16)-H(16A)	109.2(11)
C(17)-C(16)-H(16B)	110.2(12)
H(16A)-C(16)-H(16B)	106.0(15)
C(16)-C(17)-H(17)	106.2(11)
C(18)-C(17)-H(17)	108.2(10)
C(20)-C(17)-H(17)	105.4(10)
C(17)-C(18)-H(18A)	110.7(10)
C(17)-C(18)-H(18B)	109.8(13)
C(19)-C(18)-H(18A)	108.0(10)
C(19)-C(18)-H(18B)	108.7(11)
H(18A)-C(18)-H(18B)	106.7(17)
C(14)-C(19)-H(19A)	109.5(10)
C(14)-C(19)-H(19B)	108.7(11)
C(18)-C(19)-H(19A)	110.4(10)
C(18)-C(19)-H(19B)	109.9(10)
H(19A)-C(19)-H(19B)	105.2(14)
C(20)-C(21)-H(21A)	109.00
C(20)-C(21)-H(21B)	109.00
C(20)-C(21)-H(21C)	109.00
H(21A)-C(21)-H(21B)	110.00
H(21A)-C(21)-H(21C)	109.00
H(21B)-C(21)-H(21C)	109.00
C(20)-C(22)-H(22A)	109.00
C(20)-C(22)-H(22B)	109.00
C(20)-C(22)-H(22C)	109.00
H(22A)-C(22)-H(22B)	109.00
H(22A)-C(22)-H(22C)	109.00
H(22B)-C(22)-H(22C)	110.00
C(20)-C(23)-H(23A)	109.00
C(20)-C(23)-H(23B)	109.00
C(20)-C(23)-H(23C)	109.00
H(23A)-C(23)-H(23B)	110.00
H(23A)-C(23)-H(23C)	109.00
H(23B)-C(23)-H(23C)	109.00

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **394** 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)	59(1)	73(2)	82(2)	-22(1)	-33(1)	-2(1)
C(2)	40(1)	32(1)	56(1)	1(1)	-10(1)	0(1)
C(3)	37(1)	30(1)	37(1)	2(1)	-4(1)	-1(1)
C(4)	42(1)	30(1)	34(1)	-1(1)	-3(1)	-1(1)

C(5)	33(1)	30(1)	35(1)	-1(1)	-1(1)	6(1)
C(6)	30(1)	30(1)	36(1)	4(1)	2(1)	0(1)
C(7)	40(1)	43(1)	86(1)	-5(1)	6(1)	11(1)
C(8)	31(1)	38(1)	26(1)	-3(1)	1(1)	4(1)
C(9)	32(1)	40(1)	33(1)	0(1)	3(1)	4(1)
C(10)	46(1)	41(1)	35(1)	4(1)	7(1)	2(1)
C(11)	40(1)	55(1)	41(1)	-2(1)	10(1)	-9(1)
C(12)	30(1)	72(2)	42(1)	-2(1)	3(1)	0(1)
C(13)	35(1)	53(1)	32(1)	1(1)	-1(1)	8(1)
C(14)	28(1)	29(1)	32(1)	1(1)	1(1)	0(1)
C(15)	33(1)	29(1)	39(1)	1(1)	-5(1)	-1(1)
C(16)	35(1)	34(1)	36(1)	7(1)	0(1)	-3(1)
C(17)	28(1)	40(1)	31(1)	3(1)	0(1)	0(1)
C(18)	34(1)	32(1)	34(1)	-2(1)	0(1)	-3(1)
C(19)	31(1)	29(1)	33(1)	3(1)	1(1)	-2(1)
C(20)	33(1)	50(1)	33(1)	2(1)	1(1)	-1(1)
C(21)	56(1)	72(2)	38(1)	14(1)	6(1)	11(1)
C(22)	44(1)	58(1)	41(1)	0(1)	7(1)	7(1)
C(23)	59(1)	88(2)	41(1)	-12(1)	-1(1)	-16(1)
O(1)	49(1)	60(1)	60(1)	-18(1)	-20(1)	-1(1)
O(2)	35(1)	77(1)	71(1)	-3(1)	-8(1)	2(1)
O(3)	34(1)	31(1)	44(1)	5(1)	4(1)	7(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **394**

	x	y	z	U(eq)
H(1A)	6489	7585	9783	107
H(1B)	5903	9025	10511	107
H(1C)	6439	10129	9680	107
H(4)	2430(15)	9210(30)	9140(12)	30(4)
H(5)	973(15)	9220(30)	7916(10)	26(4)
H(6)	3989(16)	6940(30)	7016(11)	30(4)
H(7A)	5315	4027	7741	85
H(7B)	4813	3544	6812	85
H(7C)	4676	1787	7540	85
H(9)	1869(19)	4250(40)	8947(12)	45(5)
H(10)	490(16)	1670(40)	9539(12)	36(5)
H(11)	-1644(19)	2150(40)	9329(13)	50(6)
H(12)	-2390(20)	5280(40)	8640(14)	58(6)
H(13)	-1006(17)	7880(40)	8096(12)	38(5)
H(15A)	1369(17)	9610(30)	6468(11)	30(4)
H(15B)	2629(16)	10250(40)	6813(11)	33(4)
H(16A)	3560(17)	8040(30)	5715(11)	35(4)
H(16B)	2669(17)	9770(40)	5310(12)	43(5)
H(17)	1122(16)	7150(30)	5156(11)	29(4)
H(18A)	1428(15)	3510(30)	5625(10)	26(4)
H(18B)	2749(18)	4070(40)	5948(12)	41(5)
H(19A)	1352(15)	4020(30)	7109(11)	30(4)
H(19B)	509(18)	5710(30)	6671(11)	39(5)
H(21A)	1602	8638	3745	83
H(21B)	2618	7580	3160	83
H(21C)	3003	9048	3942	83
H(22A)	3769	3785	4695	72
H(22B)	4306	6133	4553	72
H(22C)	3984	4660	3758	72
H(23A)	1830	3971	3344	94
H(23B)	745	4778	3932	94
H(23C)	1636	2937	4258	94

Table 6. Torsion angles [°] for **394**

C(1)-O(1)-C(2)-O(2)	-3.8(3)
C(1)-O(1)-C(2)-C(3)	175.82(19)
C(7)-O(3)-C(6)-C(3)	-101.16(17)
C(7)-O(3)-C(6)-C(14)	144.90(15)
O(1)-C(2)-C(3)-C(4)	17.6(3)
O(1)-C(2)-C(3)-C(6)	-161.33(16)
O(2)-C(2)-C(3)-C(4)	-162.8(2)
O(2)-C(2)-C(3)-C(6)	18.3(3)
C(2)-C(3)-C(4)-C(5)	178.35(17)
C(6)-C(3)-C(4)-C(5)	-2.6(2)
C(2)-C(3)-C(6)-O(3)	75.73(19)
C(2)-C(3)-C(6)-C(14)	-164.75(15)
C(4)-C(3)-C(6)-O(3)	-103.36(17)
C(4)-C(3)-C(6)-C(14)	16.16(19)
C(3)-C(4)-C(5)-C(8)	113.09(17)
C(3)-C(4)-C(5)-C(14)	-11.9(2)
C(4)-C(5)-C(8)-C(9)	-44.3(2)
C(4)-C(5)-C(8)-C(13)	138.61(16)
C(14)-C(5)-C(8)-C(9)	73.61(19)
C(14)-C(5)-C(8)-C(13)	-103.48(18)
C(4)-C(5)-C(14)-C(6)	20.69(17)
C(4)-C(5)-C(14)-C(15)	-94.14(15)
C(4)-C(5)-C(14)-C(19)	145.22(14)
C(8)-C(5)-C(14)-C(6)	-102.77(15)
C(8)-C(5)-C(14)-C(15)	142.40(14)
C(8)-C(5)-C(14)-C(19)	21.76(19)
O(3)-C(6)-C(14)-C(5)	95.78(15)
O(3)-C(6)-C(14)-C(15)	-148.98(13)
O(3)-C(6)-C(14)-C(19)	-28.30(18)
C(3)-C(6)-C(14)-C(5)	-22.05(17)
C(3)-C(6)-C(14)-C(15)	93.19(15)
C(3)-C(6)-C(14)-C(19)	-146.13(14)
C(5)-C(8)-C(9)-C(10)	-176.18(15)
C(13)-C(8)-C(9)-C(10)	1.0(2)
C(5)-C(8)-C(13)-C(12)	175.12(17)
C(9)-C(8)-C(13)-C(12)	-2.1(3)
C(8)-C(9)-C(10)-C(11)	0.8(3)
C(9)-C(10)-C(11)-C(12)	-1.5(3)
C(10)-C(11)-C(12)-C(13)	0.4(3)
C(11)-C(12)-C(13)-C(8)	1.4(3)
C(5)-C(14)-C(15)-C(16)	-176.16(13)
C(6)-C(14)-C(15)-C(16)	71.56(17)
C(19)-C(14)-C(15)-C(16)	-52.55(18)
C(5)-C(14)-C(19)-C(18)	173.74(14)

C(6)-C(14)-C(19)-C(18)	-67.31(18)
C(15)-C(14)-C(19)-C(18)	53.07(18)
C(14)-C(15)-C(16)-C(17)	55.17(19)
C(15)-C(16)-C(17)-C(18)	-54.12(18)
C(15)-C(16)-C(17)-C(20)	177.82(14)
C(16)-C(17)-C(18)-C(19)	55.44(18)
C(20)-C(17)-C(18)-C(19)	-176.07(13)
C(16)-C(17)-C(20)-C(21)	-56.46(19)
C(16)-C(17)-C(20)-C(22)	64.8(2)
C(16)-C(17)-C(20)-C(23)	-175.46(16)
C(18)-C(17)-C(20)-C(21)	178.06(14)
C(18)-C(17)-C(20)-C(22)	-60.7(2)
C(18)-C(17)-C(20)-C(23)	59.1(2)
C(17)-C(18)-C(19)-C(14)	-57.23(18)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **394** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(7)-H(7A)...O(2)	0.9600	2.5200	3.285(3)	136.00

Symmetry transformations used to generate equivalent atoms: