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Carolyn Cohen 3/24/14

Impact of Silyl Ethyl Esters on the Rhodium(II)-Catalyzed Transformations of Donor/Acceptor Carbenes

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An abstract of
a thesis submitted to the Faculty of Emory College of Arts and Sciences
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Abstract

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By Carolyn M. Cohen

Donor/acceptor carbenes are a privileged class of reagents that are capable of highly site-selective C-H bond functionalization when used in combination with transition metal catalysts. This ability to selectively functionalize a C-H bond has revolutionized organic synthesis in recent years. The transformations of a donor/acceptor carbene substituted with a trialkylsilyl moiety in the acceptor group are investigated. It was discovered that in the presence of the catalyst $Rh_2(TPA)_4$, triisopropylsilyl-substituted ethyl aryldiazoacetates undergo an intramolecular C-H insertion followed by decomposition of the β-lactone intermediate, resulting in preferential formation of the more sterically hindered *Z* allylsilanes. In addition to this unexpected reactivity, the silyl substituted donor/acceptor carbenes are excellent substrates for cyclopropanation using $Rh_2(S\text{-DOSP})_4$. This reaction has been applied to the synthesis of the triarylcyclopropane carboxylate ligand used in the catalyst $Rh_2(R\text{-BTPCP})_4$.

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Introduction to Carbenoid Chemistry

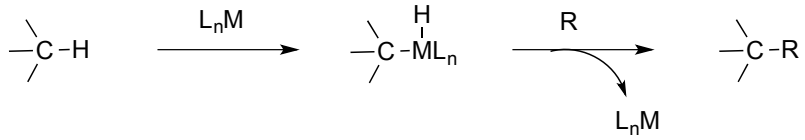
Carbon-hydrogen (C-H) functionalization is a powerful tool that has the potential to revolutionize the synthesis of natural products, pharmaceuticals, and other industrial targets. The ability to selectively functionalize unactivated C-H bonds precludes the need to install functional groups, shortening synthetic pathways and minimizing unwanted byproducts. Issues of cost and waste in large-scale industrial processes demand efficiency in the synthesis of complex molecules, making the possibilities of C-H functionalization chemistry appealing. However, the major challenge in C-H functionalization is achieving selective activation of the desired C-H bond among the many inherent in a single organic molecule[1].

A common method of C-H bond activation is achieved by oxidative addition of a metal complex into a carbon-hydrogen bond (**Eq. 1**)[2]. This is generally achieved with transition metal centers such as palladium, ruthenium, and rhodium[3]. This method is widely used and has a broad substrate scope for both intra- and intermolecular reactions. However, a key problem is the difficulty involved in regenerating the catalyst, resulting in the need for high catalyst loadings, which is environmentally unfavorable. Also, harsh conditions, such as reaction in acetic acid, are often required. Finally, many examples of C-H activation via oxidative insertion require a neighboring group to direct the metal to the desired site, favoring an intramolecular pathway. More recently, C-H functionalization via insertion of metal-bound carbenes, nitrenes, or oxygen into C-H bonds has been probed (**Eq. 2**)[1]. A carbene is an uncharged carbon that has a lone pair and is thus highly reactive. Conveniently, carbenes are easily masked as diazo compounds, which consist of a dinitrogen group bound to a carbene and are stable and easy to prepare. When exposed to a transition metal-based complex, the diazo group decomposes to form a metal

[1] Davies, H. M. L.; Morton, D. *Chem. Soc. Rev.* **2011**, *40*, 1857-1869.
[2] Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154-162.
[3] Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731-1769.

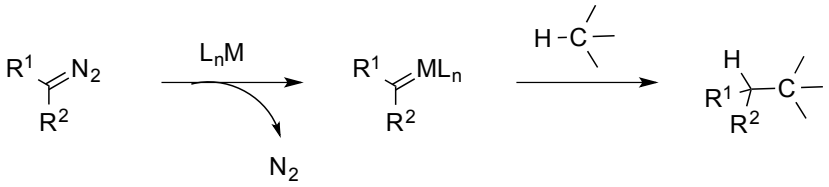
carbenoid, which can then perform the C-H insertion reaction[4]. The ease of preparation of metal-carbenoid complexes is one advantage to this method over the traditional oxidative addition pathway. In addition, the metal complex is easily regenerated following reaction of the metal carbenoid, making this a catalytic process[5]. Finally, while the metal-carbenoid method has been extensively studied in intramolecular reactions, it has also been proven successful in performing selective intermolecular C-H insertion reactions.

Oxidative Addition



(1)

Metal Carbene



(2)

The reactivity of carbenes is dependent upon the substituents that are attached to it. In general, diazo carbonyl compounds are most effective, in conjunction with metal catalysts. Further, carbenes are classified according to the nature of the substituents flanking the carbene. Those that are adjacent to one or two electron-withdrawing groups are called acceptor- and acceptor/acceptor-carbenes, respectively (**Fig.1, 1 and 2**). These carbenes are extremely reactive, since the electron-withdrawing groups pull electron density away from the already electrophilic carbene. Because of this, they are less selective and are more commonly used for intramolecular C-H functionalization reactions[1]. A third class of carbenes is the donor/acceptor group **3**, which consists of one electron withdrawing group and one electron donating group, such as aryl or vinyl groups. The electron-donating group stabilizes the carbene, allowing for more selective C-

[4] Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919-939.
[5] Davies, H. M. L.; Beckwith, R. E. J. *Chem. Rev.* **2003**, *103*, 2861-2903.

H functionalization, including intermolecular transformations. Specifically, the Davies group has extensively studied the reactions of donor/acceptor carbenes from diazo compounds using rhodium(II) catalysts[6].

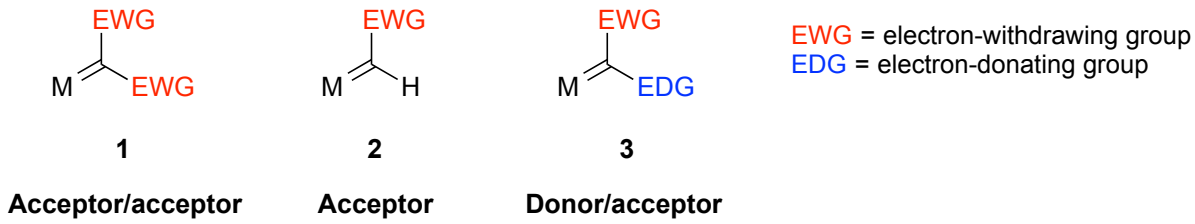


Figure 1. Three classes of carbenes.

Introduction to Dirhodium Catalysts

The metal-catalyzed reactions of diazo compounds have been studied for years, beginning with the use of copper-based catalysts. Nozaki's soluble copper(II) chelates[7] and Moser's (trialkyl and triaryl phosphite)copper(I) catalysts[8] represented the first instance of homogeneous catalysis, and the use of copper catalysts for carbenoid transformations continued. Then, in the 1970s, Teyssié and coworkers introduced rhodium(II) acetate as a catalyst for carbenoid transformations[9]. In a study on carbene additions to aromatic substrates, Teyssié found the most effective catalysts to be dirhodium(II) tetracarboxylates formed from strong acids, such as trifluoroacetic acid[10].

The general structure of Teyssié's catalysts consists of a dirhodium core that is held together by a rhodium-rhodium single bond (**Fig. 2**). Each rhodium atom adopts an octahedral geometry, with four sites for equatorial substituents as well as two axial. The axial sites are

---

[6] Pelphrey, P.; Hansen, J.; Davies, H. M. L. *Chem. Sci.* **2010**, *1*, 254-257.
[7] Nozaki, H.; Takaya, H.; Moriuti, S.; Noyori, R. *Tetrahedron Lett.* **1968**, *24*, 3655-3669.
[8] Moser, W. R. *J. Am. Chem. Soc.* **1969**, *91*, 1135-1140.
[9] Demonceau, A.; Noels, A. F.; Hubert, A. J.; Teyssie, P. *J. Chem. Soc., Chem. Commun.* **1981**, *14*, 688-689.
[10] Anciaux, A. J.; Demonceau, A.; Noels, A. F.; Hubert, A. J.; Warin, R.; Teyssie, P. *J. Org. Chem.* **1981**, *46*, 873-876.

considered to be the active sites for the formation of a metal-bound carbene and subsequent C-H functionalization, while the equatorial ligands are tuned to facilitate asymmetric transformations. It is thought that only one of the rhodium centers can be active at one time, with the second assisting in the reaction by acting as an "electron sink"[5]. This increases the electrophilicity of the carbene, leading to greater reactivity.

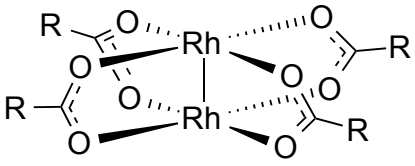


Figure 2. Structure of dirhodium(II) tetracarboxylate catalysts.

The selectivity of C-H functionalization reactions is related to the electronic nature of the catalyst itself, which affects the electrophilicity of the carbene[4]. In addition to having an accessible site for coordination of the diazo, good catalysts interact with the carbene via a combination of σ-bonds as well as π-backbonding interactions, which are stabilizing. Rhodium-based catalysts have held up as the most effective catalysts for C-H functionalization. These complexes are stable to heat, moisture, and air while being exceptionally good catalysts for the formation of metal carbenoids from diazo compounds[11].

The reactivity and selectivity of the catalyst is also highly dependent upon both the electronic and structural features of the equatorial ligands. The high selectivity observed for metal-carbenoid transformations is due to formation of a complex of overall high symmetry from low-symmetry chiral ligands. This results in a single substrate trajectory being most favorable, leading to high diastereo- and enantioselectivity. The four types of chiral catalysts that have proven most successful in enantioselective transformations are rhodium(II) carboxylates, rhodium(II) carboxamidates, rhodium(II) phosphates, and ortho-metalated arylphosphine

[11] Hansen, J.; Davies, H. M. L. *Coord. Chem. Rev.* **2008**, *252*, 545-555.

rhodium(II) complexes[5]. Dirhodium(II) tetracarboxylates are particularly useful catalysts in conjunction with donor/acceptor carbenes derived from diazo compounds. Davies developed the prolinate-derived catalyst rhodium(II) (*S*)-N-(*p*-Dodecylphenyl)sulfonylprolinate Rh_2(*S*-DOSP)$_4$ **4**, which is extremely effective in asymmetric intermolecular C-H insertion reactions with donor/acceptor carbenes[12]. This catalyst is notable for its solubility in hydrocarbon solvents, due to the long hydrocarbon tail on the phenyl group, as well as its ability to remain active at temperatures as low as -78° C.

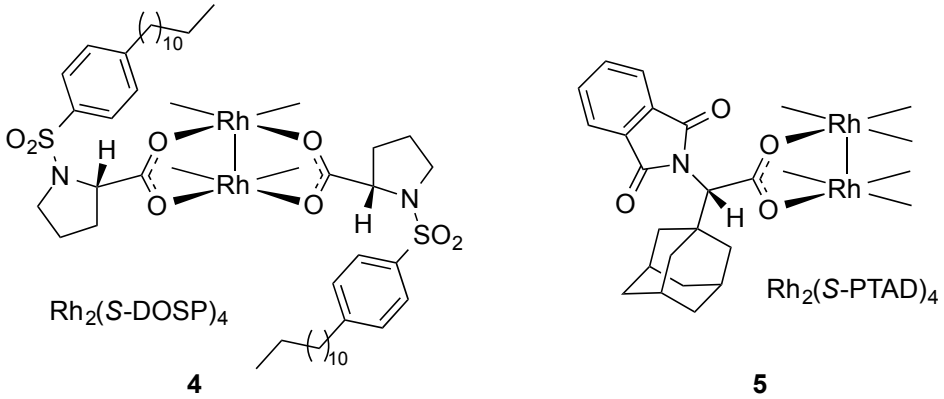
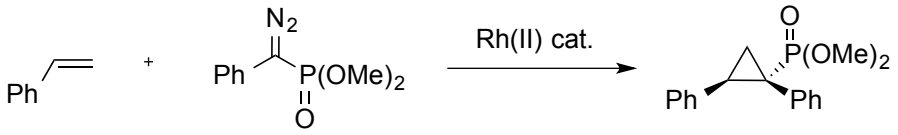


Figure 3. Dirhodium tetracarboxylate catalysts.

More recently, Davies has developed adamantylglycine-derived chiral dirhodium catalysts for carbenoid reactions, building on previous work with phthalimide derivatives[12]. Rh_2(*S*-PTAD)$_4$ **5** was developed as a highly reactive catalyst that is similarly effective at asymmetric carbenoid transformations, achieving up to 99% ee in intramolecular C-H insertion[13]. The chiral ligand was itself prepared via Rh_2(*S*-DOSP)$_4$ catalyzed C-H insertion into adamantane, making use of a previously known method of C-H activation. Rh_2(*S*-PTAD)$_4$ shows complementary reactivity to that of Rh_2(*S*-DOSP)$_4$. For example, Rh_2(*S*-DOSP)$_4$ is tolerant of a range of donor substituents on the donor/acceptor carbenoid, but altering the acceptor group from

[12] Davies, H. M. L.; Hansen, T. *J. Am. Chem. Soc.* **1997**, *119*, 9075-9076.
[13] Reddy, R. P.; Lee, G. H.; Davies, H. M. L. *Org. Lett.* **2006**, *8*, 3437-3440.

a methyl ester can drastically reduce the levels of enantioinduction. However, Rh_2(*S*-PTAD)$_4$ performs exceptionally well in reactions of aryl diazophosphonate **7** (**Eq. 3**).



(3)

6 **7** **8**

Rh_2(*S*-DOSP)$_4$	69% yield, 34% ee
Rh_2(*S*-PTAD)$_4$	86% yield, 99% ee

The design of a third generation of dirhodium catalysts similarly used metal carbenoid chemistry to create new chiral ligands for asymmetric catalysis. As the result of an effort to design a catalyst that would be both easily synthesized and highly selective, the catalyst Rh_2(*R*-BTPCP)$_4$ **9**, consisting of triarylcyclopropanecarboxylate ligands, was developed (**Fig. 4**)[14]. Construction of the ligands was based on the highly enantioselective cyclopropanation reaction of donor/acceptor carbenes, using Rh_2(*S*-DOSP)$_4$ as catalyst[15,16]. Davies et al. postulated that the rigid cyclopropane ring would limit the possible conformations of the ligands, leading to enhanced enantioinduction. Consequently, Rh_2(*R*-BTPCP)$_4$ outperformed Rh_2(*R*-DOSP)$_4$ in the standard cyclopropanation reaction between styryldiazoacetate **10** and styrene **6** when dichloromethane was used as the solvent (**Eq. 4**)[14]. It is tolerant of changes in temperature as well as decreased catalyst loadings, substitutions on the donor group, and various styrene derivatives. Also, in contrast to Rh_2(*S*-DOSP)$_4$, the new catalyst Rh_2(*R*-BTPCP)$_4$ is tolerant of various ester sizes. In fact, the enantioselectivity improves upon increasing the size of the ester from methyl to *tert*-butyl.

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[14] Qin, C.; Boyarskikh, V.; Hansen, J. H.; Hardcastle, K. I.; Musaev, D. G.; Davies, H. M. L. *J. Am. Chem. Soc.* **2011**, *133*, 19198-19204.
[15] Davies, H. M. L.; Bruzinski, P. R.; Fall, M. J. *Tetrahedron Lett.* **1996**, *37*, 4133-4136.
[16] Davies, H. M. L.; Bruzinski, P. R.; Lake, D. H.; Kong, N.; Fall, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 6897-6907.

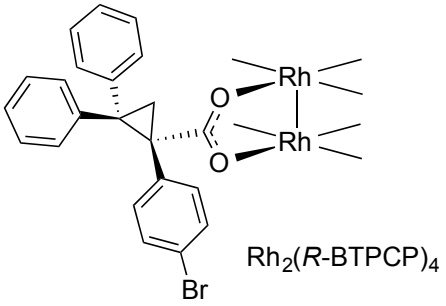

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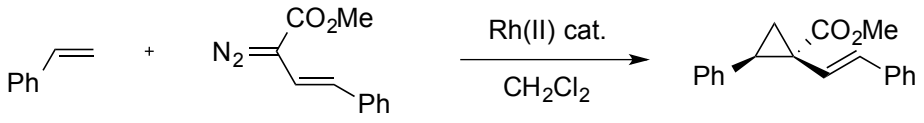
Figure 4. Structure of Rh_2(*R*-BTPCP)$_4$.



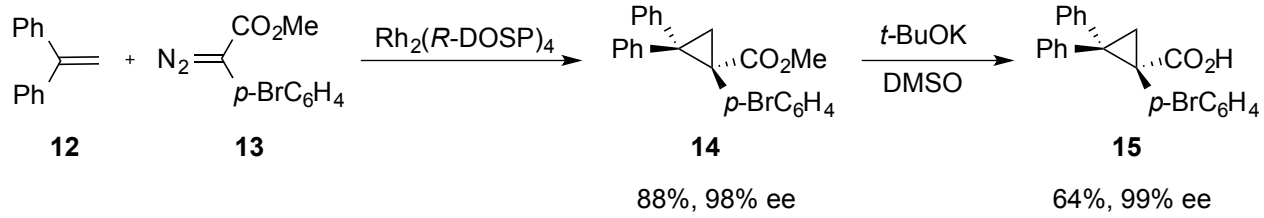
6 **10** **11** (4)

Rh_2(*R*-DOSP)$_4$ 80% yield, 81% ee

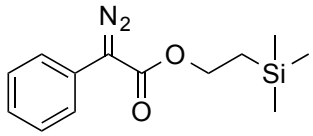
Rh_2(*R*-BTPCP)$_4$ 86% yield, 91% ee

While the synthesis of the triarylcyclopropanecarboxylate ligand is relatively simple and effective, consisting of only three steps (**Scheme 1**), including an enantioselective rhodium(II)-catalyzed cyclopropanation, the removal of the methyl ester to generate the carboxylic acid **15** is less than ideal. This is done using potassium *tert*-butoxide, giving the carboxylic acid in 64% yield after recrystallization when the reaction is performed on a small scale. However, on a large scale, the yield of this reaction drops to approximately 30%, prompting us to investigate a new method to synthesize the ligand.

Scheme 1. Synthesis of triarylcyclopropanecarboxylate ligand.



In an effort to develop a more robust procedure for creating this ligand as well as future cyclopropanecarboxylates, we decided to explore the possibility of using an aryldiazoacetate with a trialkylsilyl substituted ethyl ester in place of the methyl ester (**Fig. 5**). Trialkylsilyl groups are common protecting groups in organic synthesis, and they are easily cleaved by fluoride ion, resulting in the carboxylic acid after acidic quench.



16a

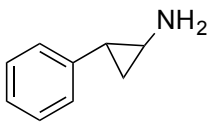
Figure 5. Silyl substituted ethyl aryldiazoacetate

Background: Metal catalyzed cyclopropanation reactions

Cyclopropanes are interesting synthetic units that are found in many natural products, as well as being versatile synthetic intermediates[17]. Many secondary metabolites contain cyclopropane subunits, and a number of these have shown significant biological activity and are thus interesting to the medical community[18]. One biologically active class of molecules is the cyclopropyl amines, which have significant CNS activity. One such compound, tranylcypromine **17**, and its synthetic analogues, has shown activity against the 5-HT_{2C} receptor, which is involved in serotonin mediation, and is thus a target for the treatment of depression, anxiety,

[17] Lebel, H.; Marcoux, J.; Mollinaro, C.; Charette, A. B. *Chem. Rev.* **2003**, *103*, 977-1050.
[18] Wessjohann, L. A.; Brandt, W. *Chem. Rev.* **2003**, *103*, 1625-1647.

chronic pain, and epilepsy, among others[19]. However, our interest in cyclopropanes stems mainly from their demonstrated utility as the basis of ligands for dirhodium(II) tetracarboxylate catalysts such as Rh_2(*R*-BTPCP)$_4$.



Tranylcypromine

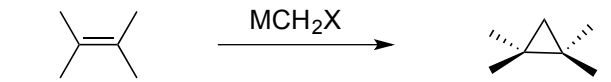
17

Figure 6. Example cyclopropane natural product.

Three major methods of cyclopropanation are outlined in **Equations 5-8**. These are all notable for their ability to control the stereochemistry of the cyclopropane product. The first method involves a species called a halomethylmetal, such as $IZnCH_2I$, which was developed by Simmons and Smith (**Eq. 5**)[20]. The second route is called a Michael-initiated ring closure (MIRC) reaction, which involves a conjugate addition to an electrophilic enolate followed by intramolecular ring closure. There are two types of MIRC reactions, depending on whether the leaving group is present on the alkene (**Eq. 6**) or on the nucleophile (**Eq. 7**). The most prominent type of reagent for this second type is the sulfur ylide, which was developed by Corey[21]. The final method, which is of particular interest to this study, arises from the transition metal-catalyzed decomposition of diazo compounds (**Eq. 8**). Many different metals are available for catalyzing cyclopropanation reactions, depending on the nature of the diazo compound. For example, palladium salts are most effective with diazomethane, while a variety of metals are effective with acceptor-substituted diazos, such as rhodium, ruthenium, cobalt, and copper[19]. As is the case in C-H insertion reactions, dirhodium(II) carboxylates have proven to be the best

[19] Cho, S. J.; Jensen, N. H.; Kurome, T.; Kadari, S.; Manzano, M. L.; Malberg, J. E.; Caldarone, B.; Roth, B. L.; Kozikowski, A. P. *J. Med. Chem.* **2009**, *52*, 1885-1902.
[20] Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1959**, *81*, 4256-4264.
[21] Corey, E. J.; Jautelat, M. *J. Am. Chem. Soc.* **1967**, *89*, 3912-3914.

catalysts for asymmetric cyclopropanation reactions of donor/acceptor carbenes, showing both exceptional diastereocontrol and enantioselectivity[15,16,22,23].



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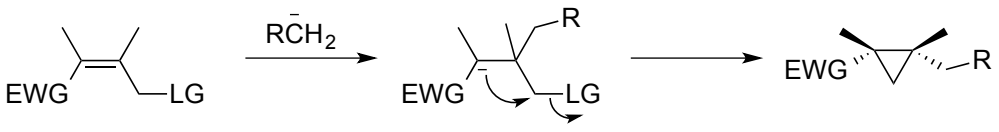

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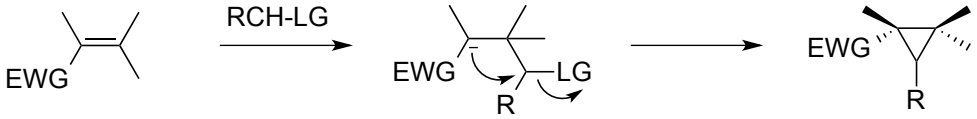

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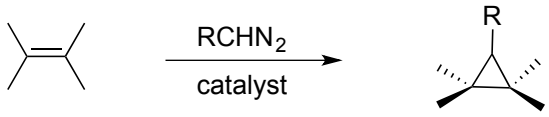


(8)

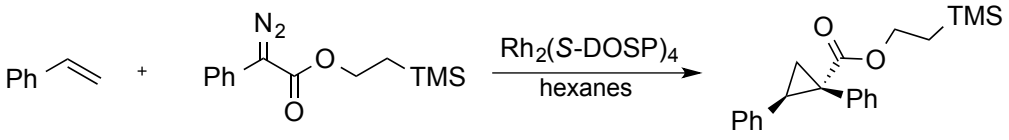
The general reaction of alkyl diazoacetates with alkenes is an effective way to make cyclopropanes, showing reactivity with electron rich, neutral, and even electron deficient alkenes[23]. However, these reactions are not diastereoselective unless a chiral catalyst is employed. In contrast, the donor/acceptor carbenes derived from vinyldiazoacetates and phenyldiazoacetates can only react with mono- and 1,1- or *cis*- disubstituted alkenes, but many of these reactions are diastereoselective, even with the achiral catalyst $Rh_2(OAc)_4$. When the chiral catalyst Rh_2(*S*-DOSP)$_4$ is used, the cyclopropanation proceeds with up to 96% de and 94% ee[15]. This reaction is tolerant of many substutitions on the aryl group of the diazoacetate as well as various styrene derivatives, but requires a methyl ester as acceptor group[24].

[22] Davies, H. M. L.; Clark, J.; Church, L. A. *Tetrahedron Lett.* **1989**, *30*, 5057-5060.
[23] Davies, H. M. L.; Panaro, S. A. *Tetrahedron* **2000**, *56*, 4871-4880.
[24] Chepiga, K. M.; Qin, C.; Alford, J. S.; Chennamadhavuni, S.; Gregg, T. M.; Olson, J. P.; Davies, H. M. L. *Tetrahedron* **2013**, *69*, 5765-5771.

Cyclopropanation with a silyl substituted ester

With the help of graduate student David Guptill, I began an investigation of the cyclopropanation reaction between the silyl substituted diazo compound **16a** and the unsubstituted styrene substrate **6**. As shown in **Scheme 2**, the reaction catalyzed by Rh_2(*S*-DOSP)$_4$ proceeded in both high yield and enantioselectivity (87%, 87% ee). This result was surprising based on previous studies, where only the methyl ester was successful in Rh_2(*S*-DOSP)$_4$-catalyzed transformations.

Scheme 2. Reaction of a silyl substituted diazo with Rh_2(*S*-DOSP)$_4$



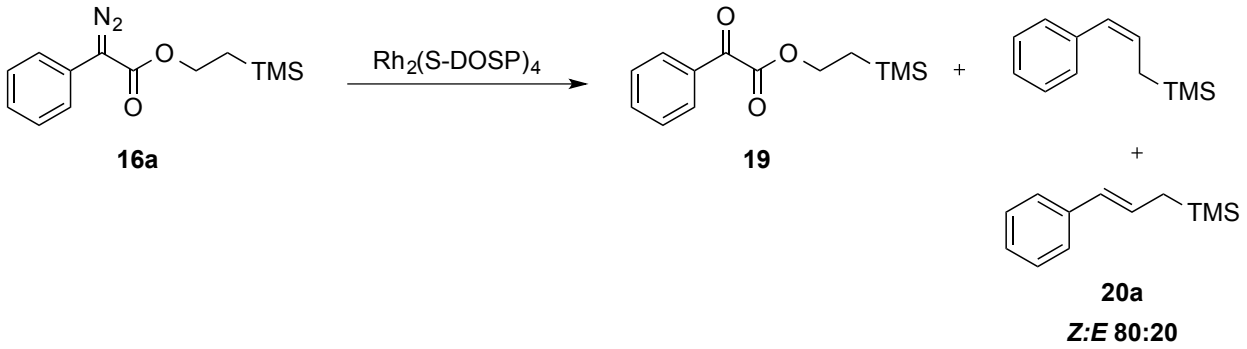
6 **16a** **18**

87% yield, 87% ee

However, further exploration and optimization of this reaction was hindered by the existence of a side product that was evident in the crude ^{1}H NMR of the product. In order to obtain a clean reaction, and to increase the yield of the desired product, we decided to investigate the identity of this other product. We thought that there were two likely possibilities, based on previous experiments with diazo compounds. One possibility was the formation of dimers, which results from two carbenes reacting with each other. This occurs because carbenes are such reactive species that they are able to interact with one another. The other possibility was that, although the reaction was performed under an atmosphere of inert argon gas, there was some oxygen present in the solvent that was reacting with the carbene to form a ketone product. In order to ascertain the identity of the byproduct, we performed a control reaction in which the diazo was reacted with the rhodium catalyst in the absence of a styrene trap (**Scheme 3**). The oxygenated product **19** was in fact observed and verified by IR spectroscopy. In addition, an

unexpected product was formed (**20a)**. The structures of the two isomers of **20a** were elucidated by ^{1}H NMR, and they were determined to be allylsilanes, which were formed by the loss of CO_2 from the original diazo structure. The ratio of *Z:E* isomers was also determined using ^{1}H NMR, by examination of the alkene proton signals.

Scheme 3. Control reaction for byproduct identification



16a **19** **20a**

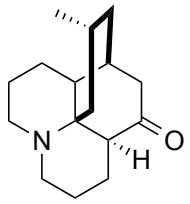
***Z:E* 80:20**

Allylsilanes: Synthetic Applications

This unexpected result warranted further exploration, as the stereoselective synthesis of substituted allylsilanes is a useful synthetic tool. Allylsilanes have many useful synthetic applications in addition to being common protecting groups. They are able to facilitate carbon-carbon bond forming reactions as well as functional group transformations, and often show good stereocontrol[25,26]. But they are particularly useful because they can be easily cleaved afterward by a fluoride source or mild acid. Due to their ability to form furans and pyrrolidines, among other functionalities[27], allylsilanes have found many applications to the total synthesis of natural products. For example, Heathcock's total synthesis of (±)-lycopodine **21**, an alkaloid with cardiovascular and neuromuscular effects, uses a stereoselective allylsilane addition to control the relative stereochemistry at two centers[28]. Because of this utility, we saw this novel

[25] Chan, T. H.; Wang, D. *Chem. Rev.* **1992**, *92*, 995-1006.
[26] Denmark, S. E.; Fu, J. *Chem. Rev.* **2003**, *103*, 2763-2793.
[27] Masse, C. E.; Panek, J. S. *Chem. Rev.* **1995**, *95*, 1293-1316.
[28] Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95*, 1375-1408.

transformation as an excellent opportunity to develop a new method to synthesize allylsilanes. In light of the discovery of this unknown and exciting reactivity, we decided to pursue the allylsilane reaction.



(±)-lycopodine

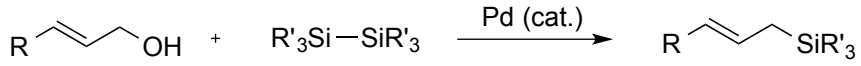
21

Synthesis of Allylsilanes

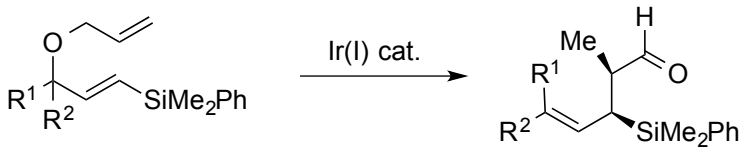
Various methods exist for the preparation of allylsilanes, including those that are regio- and stereoselective. A few recent examples are metal-catalyzed reactions, shown in **eqs 9-11**. The first is a palladium-catalyzed coupling reaction between an allylic alcohol and disilane (**Eq. 9**)[29]. In this reaction, the palladium catalyst serves to activate the C-OH bond, giving the product with high regioselectivity for the linear product as well as high stereoselectivity for the *trans*, or *E*, product. The second gives highly substituted allylsilanes with high stereocontrol from divinyl ethers via an iridium-catalyzed isomerization followed by thermal Claisen rearrangement (**Eq. 10**)[30]. This method generates two contiguous stereocenters, and is selective for the *syn* isomer. A third example is the copper-catalyzed coupling of allylphosphates with silylboronates (**Eq. 11**)[31]. Using a chiral *N*-heterocyclic carbene ligand, this method gives chiral allylsilanes with high enantioselectivity. Generating allylsilanes with defined geometry is valuable for synthesis, and each of these syntheses selectively generates a specific type of allylsilane. We saw our rhodium carbenoid transformation as a complementary method to these syntheses, based on the

[29] Selander, N.; Paasch, J. R.; Szabó, K. J. *J. Am. Chem. Soc.* **2011**, *133*, 409-411.
[30] McLaughlin, M. G.; Cook, M. J.; *J. Org. Chem*. **2012**, *77*, 2058-2063.
[31] Takeda, M.; Shintani, R.; Hayashi, T. *J. Org. Chem.* **2013**, *78*, 5007-5017.

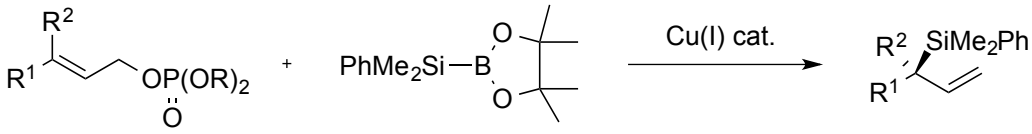
preliminary observation that the more sterically hindered *Z* isomer was favored, which complements the *E* selectivity of the palladium-catalyzed reaction.



(9)



(10)

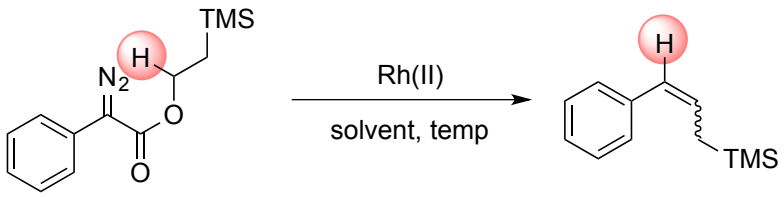


(11)

Results and Discussion

First, a brief solvent study was carried out in order to begin optimization of the reaction conditions, using $Rh_2(OOct)_4$ as catalyst. The control reaction was run in hexanes, and had shown a mixture of the allylsilane products along with the oxygenated product. After dichloromethane gave the same impure product mixture, the reaction was attempted in refluxing dimethyl butane (DMB). It was found that performing the diazo addition in refluxing DMB followed by refluxing the crude product in toluene provided the allylsilane cleanly, however in only 41% yield. Due to this result, I then performed the reaction using trifluorotoluene (TFT) as solvent, with a 3 hour addition of the diazo at reflux, followed by an additional 2 hours of heating at reflux. In addition, the solvent was heated at reflux for 30 minutes before use in an attempt to remove any oxygen. This again yielded the desired product cleanly, in slightly higher (48%) yield. Satisfied with TFT as the solvent, a catalyst optimization study was then carried out (**Table 1**).

Table 1. Catalyst Optimization Study



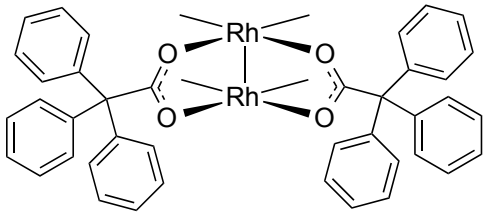
16a **20a**

entry	Rh(II)	solvent	temp (°C)	Z:E Ratio	yield (%)
1	Rh_2(S-DOSP)$_4$	$PhCF_3$	70	80:20	57
2	Rh_2(S-BTPCP)$_4$	$PhCF_3$	70	74:26	45
3	Rh_2(S-PTAD)$_4$	$PhCF_3$	70	83:17	42
4	Rh_2(OOct)$_4$	$PhCF_3$	70	47:53	48
5	Rh_2(OPiv)$_4$	$PhCF_3$	70	48:52	58
6	Rh_2(pfb)$_4$	$PhCF_3$	70	50:50	17
7	Rh_2(TFA)$_4$	$PhCF_3$	70	51:49	25
8	Rh_2(esp)$_2$	$PhCF_3$	70	46:54	42
9	Rh_2(TPA)$_4$	$PhCF_3$	70	84:16	70
10	Rh_2(TPA)$_4$	$PhCF_3$	40	85:15	36
11	Rh_2(TPA)$_4$	$PhCF_3$	23	N/A	--
12[a]	Rh_2(TPA)$_4$	cyclohexane	81	87:13	64
13[a]	**Rh_2(TPA)$_4$**	**1,2-DCE**	**84**	**89:11**	**76**

[a] Reaction performed by David Guptill

The chiral catalysts Rh_2(*S*-BTPCP)$_4$ and Rh_2(*S*-PTAD)$_4$ performed similarly to Rh_2(*S*-DOSP)$_4$, giving both moderate yields and *Z:E* ratios (**entries 1-3**). In general, the achiral catalysts (**entries 4-8**) gave low yields and showed virtually no stereoselectivity. The exceptionally low yields from the reactions with Rh_2(pfb)$_4$ and Rh_2(TFA)$_4$ can be explained by the formation of a significant amount of the oxygenated byproduct. Presumably, the electron-withdrawing nature of the ligands on these catalysts renders the carbene exceptionally reactive, resulting in a rapid reaction with trace amounts of oxygen. The one exception to the trends

observed for the achiral catalysts is rhodium(II) tetrakis(triphenylacetate) **22**, a very bulky catalyst. With this catalyst, the allylsilane product **20a** was formed in 70% yield, with a *Z:E* ratio of 84:16 (**entry 9**). Attempts were made to perform the reaction at lower temperatures, but the yield was much lower at 40°C (**entry 10**), and no product was observed at room temperature (**entry 11**), indicating that the reaction should be performed at high temperature in refluxing solvent. While changing the solvent to cyclohexane increased the *Z:E* ratio, we later found that both the yield and *Z:E* ratio were further increased using 1,2-dichloroethane (**entry 13**).



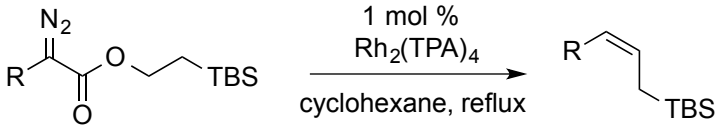
$Rh_2(TPA)_4$

22

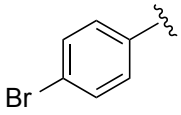
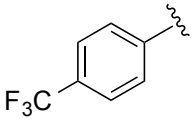
Figure 7. Structure of $Rh_2(TPA)_4$.

Next, the influence of the silyl group was explored. Our initial results indicated that using the *tert*-butyl dimethylsilyl group and cyclohexane as the solvent was optimal, so these were used for the first studies of the substrate scope (**Table 2**). With these conditions, the *para*-bromo and *para*-trifluoromethyl diazo compounds were transformed into allylsilanes **24a** and **24b**, respectively, in moderate yield and 95:5 *Z:E* ratios.

Table 2. Initial Investigation of Reaction Scope

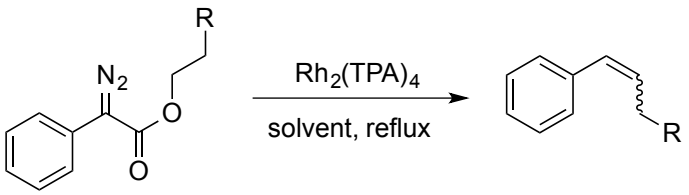


23a-b **24a-b**

entry	R	product	Z:E ratio	yield (%)
1		**24a**	95:5	69
2		**24b**	95:5	50

Initially, the silyl group optimization was performed with trifluorotoluene as the solvent, but after discovering that the reaction was improved in DCE, David repeated the optimization reactions in this solvent (**Table 3**). Upon increasing the size of the silyl group from trimethylsilyl to triisopropylsilyl, an increase in stereoselectivity was observed, with the triisopropyl derivative forming the allylsilane **20d** as almost exclusively the *Z* isomer, also in good yield (82%). Use of an aryl-substituted silyl group had little effect on the yields, but the *Z:E* ratios were not as high (**entries 8-12**). The *tert*-butyldiphenylsilyl group gave a 96:4 ratio of *Z:E* isomers, which is comparable to that of the triisopropylsilyl derivative. However, the formation of the triisopropylsilyl **20d** in 82% yield led to its use in the remainder of our studies.

Table 3. Silyl Group Optimization



16a-g **20a-g**

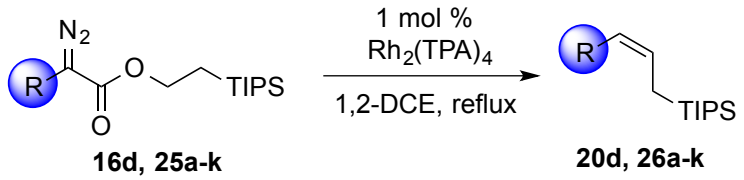
entry	R	solvent	product	Z:E ratio	yield (%)
1	$SiMe_3$	$PhCF_3$	**20a**	88:12	68
2[a]	$SiMe_3$	DCE	**20a**	89:11	76
3	$SiEt_3$	$PhCF_3$	**20b**	93:7	60
4[a]	$SiEt_3$	DCE	**20b**	91:9	76
5	$SiMe_2$t-Bu	$PhCF_3$	**20c**	95:5	52
6[a]	$SiMe_2$t-Bu	DCE	**20c**	95:5	73
7[a]	**Si(*i*-Pr)$_3$**	**DCE**	**20d**	**>97:3**	**82**
8	$SiMe_2Ph$	$PhCF_3$	**20e**	90:10	63
9[a]	$SiMe_2Ph$	DCE	**20e**	88:12	80
10	$SiMePh_2$	$PhCF_3$	**20f**	96:4	55
11[a]	$SiMePh_2$	DCE	**20f**	89:11	70
12[a]	$SiPh_2$*t*-Bu	DCE	**20g**	96:4	68

[a] Study performed by David Guptill

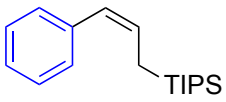
Once the optimized conditions and substrate were obtained, a full investigation of substrate scope in regard to the donor group on the diazo compound was undertaken (**Scheme 4**). The reactions highlighted in red were performed by David. Similar to the results for the Rh_2(*S*-DOSP)$_4$-catalyzed cyclopropanation reactions[24], the reaction was very tolerant of various substitutions on the donor group. Both electron-donating (**26b**) and electron-withdrawing (**26c, 26h**) diazo substituents gave good yields and good *Z:E* ratios. Halogenated substituents were also well-tolerated, giving the products **26a**, **26d**, and **26e** in up to >97:3 *Z:E*. The

stereoselectivity dropped slightly with the *ortho*- substituted aryl groups, giving lower *Z:E* ratios for the formation of **26f** and **26g**. One reason for this drop may be the steric interactions between the *ortho*- substituent and the triisopropylsilyl group in the *Z* configuration. David also explored substrates with a 2-naphthyl aryl group (**26i**) as well as conjugated polyenes (**26j**, **26k**), which also gave high *Z:E* ratios. The low yield of product **26k** may be due to its instability.

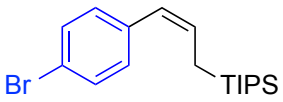
Scheme 4. Exploration of Diazo Substrate Scope.



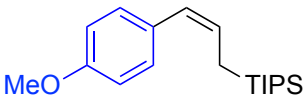
16d, 25a-k **20d, 26a-k**



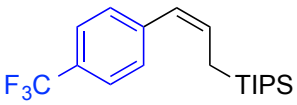
20d, 82% yield
>97:3 *Z:E*



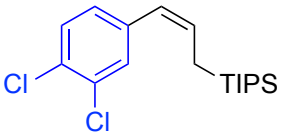
26a, 74% yield
>97:3 *Z:E*



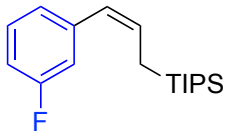
26b, 76% yield
>97:3 *Z:E*



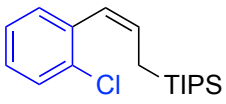
26c, 73% yield
>97:3 *Z:E*



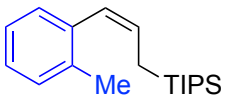
26d, 61% yield
96:4 *Z:E*



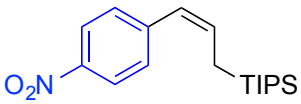
26e, 68% yield
>97:3 *Z:E*



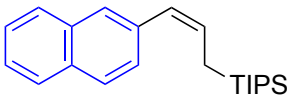
26f, 73% yield
92:8 *Z:E*



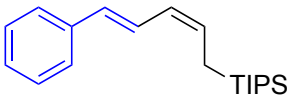
26g, 74% yield
91:9 *Z:E*



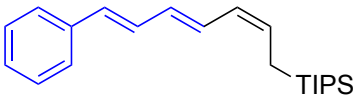
26h, 60% yield
95:5 *Z:E*



26i, 74% yield
>97:3 *Z:E*



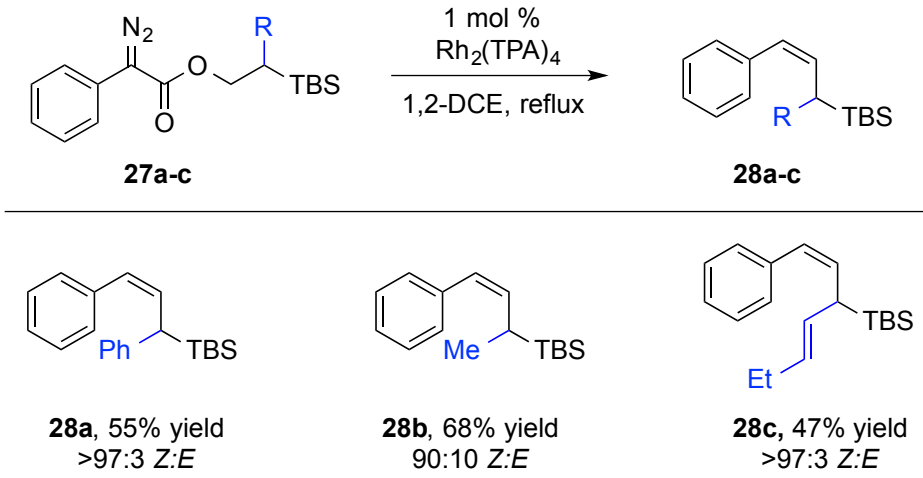
26j, 60% yield
95:5 *Z:E*



26k, 37% yield
93:7 *Z:E*

In addition, David was interested in the synthesis of chiral allylsilanes, using diazo compounds derived from chiral alcohols (**Scheme 5**). The chiral products **28a-c** were formed in moderate yield, as well as in good *Z:E* ratios. The bulkier phenyl and ethyl vinyl substituents gave a >97:3 ratio of *Z:E* isomers, compared to the smaller methyl group (90:10 ratio).

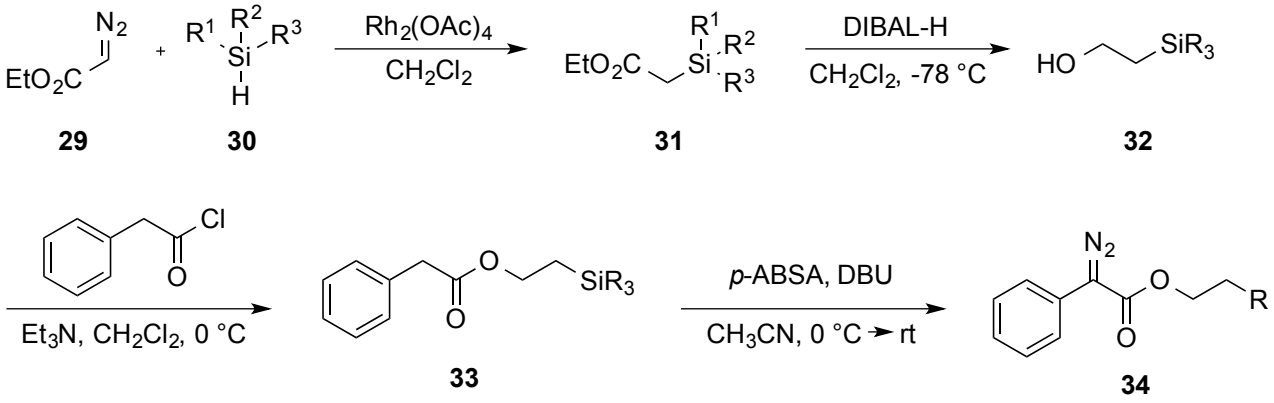
Scheme 5. Synthesis of Chiral Allylsilanes



Synthesis of Diazo Compounds

The general method used to synthesize the silyl-substituted aryldiazoacetates is shown in **Scheme 6**. Starting from the silane, $Rh_2(OAc)_4$-catalyzed C-H insertion into ethyldiazoacetate gave the ester **31**, which was reduced to the corresponding alcohol **32**. Transesterification with phenylacetyl chloride afforded ester **33**, which was subsequently submitted to diazo transfer to afford the diazo compound. The aryl substituted diazo compounds were synthesized by the same procedure starting from commercially available substituted phenylacetyl chloride compounds.

Scheme 6. General Synthesis of Diazo Compounds

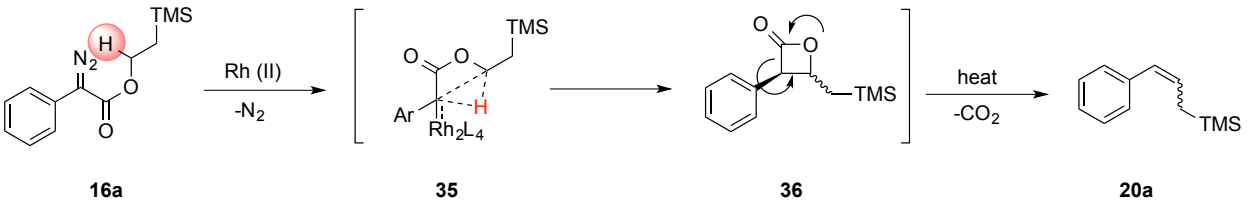


Discussion

The likely mechanism of the allylsilane transformation is shown in **Scheme 7**. Following nitrogen extrusion and formation of the rhodium carbenoid, this carbenoid then performs an intramolecular C-H insertion at the *β*-position to silicon, forming a *β*-lactone (**36**). Intramolecular rhodium(II) carboxylate catalyzed C-H insertion to form beta-lactones has been previously shown[32], and Doyle has observed that formation of 4-membered rings is common when there is an adjacent heteroatom to electronically activate the C-H bond, especially with alkyl esters[33]. In addition, Doyle found that Rh_2(*S*-DOSP)$_4$ gave the most selectivity in these intramolecular C-H insertions. In our silyl-substituted diazoacetate substrate, the C-H insertion is aided by the electron-donating ability of silicon, as is the last step, in which the *β*-lactone decomposes to the allylsilane, releasing CO_2.

[32] Doyle, M. P.; Shanklin, M. S.; Oon, S. M.; Pho, H. Q.; van der Heide, F. R.; Veal, W. R. *J. Org. Chem.* **1988**, *53*, 3384-3386.
[33] Doyle, M. P.; Davies, S. B.; May, E. J. *J. Org. Chem.* **2001**, *66*, 8112-8119.

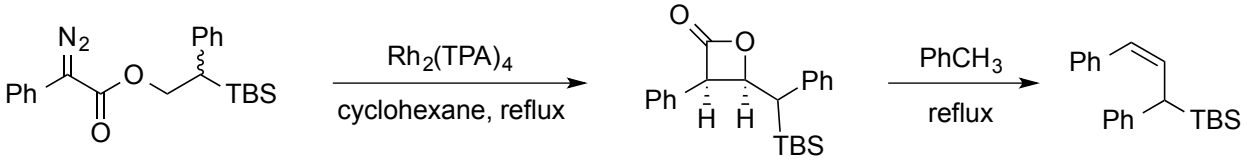
Scheme 7. Proposed Mechanism for Allylsilane Formation.



16a **35** **36** **20a**

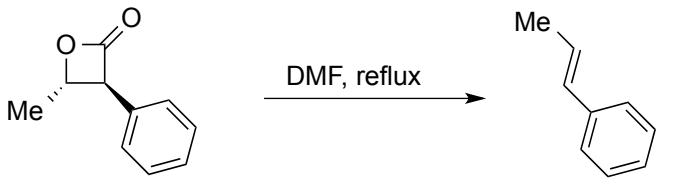
In support of this theory, David was able to isolate one of these *β*-lactone intermediates that contained a substituent *α*- to the silicon (**Scheme 8**). Most of the other diazo substrates without this *α*- substituent could be observed in the crude NMR, however they proved not to be isolable. The *β*-lactone **38** was formed in a single diastereomer, which then rearranged to form the allylsilane **39** as exclusively the *Z* isomer. This implies that the rearrangement step is stereospecific, which has precedence in the literature[34,35]. **Equation 12** is an example of the stereoselective synthesis of *E* olefins via a beta-lactone intermediate. Formation of the *trans* lactone gives almost exclusively the *E* product. In another study (**Equation 13**), it was shown that a mixture of *cis* and *trans* lactones led to a mixture of *Z* and *E* olefins, but the ratio of products was preserved. Thus, the stereochemistry of the allylsilane product is likely predetermined by the stereoselectivity of the C-H insertion step.

Scheme 8. Control Reaction to Isolate *β*-lactone Intermediate



37 **38** **39**

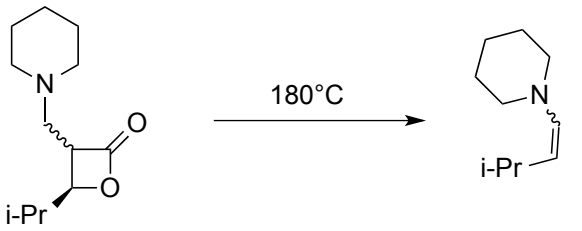
[34] Mulzer, J.; Pointner, A.; Chucholowski, A.; Brüntrup, G. *J. C. S. Chem. Comm.* **1979**, *2*, 52-54.
[35] Adam, W.; Nava-Salgado, V. O. *J. Org. Chem*. **1995**, *60*, 578-584.



40 **41**

E:Z >99:1
63% yield

(12)



42 **43**

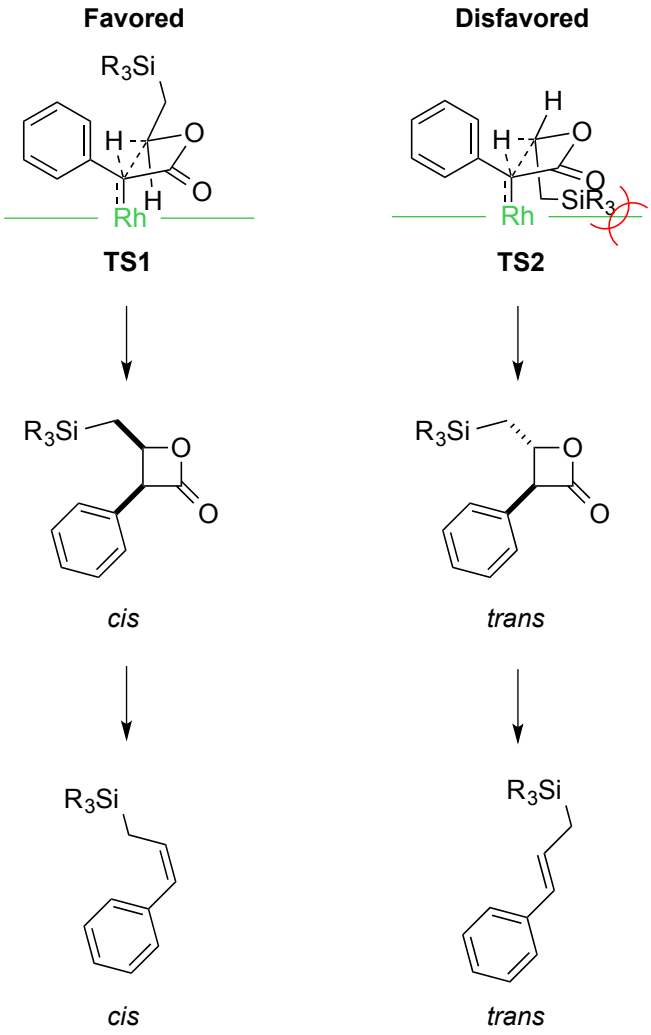
Z:E 66:34 ***Z:E 64:36***
73% yield

(13)

The rationale for the stereoselectivity of the C-H insertion is outlined in **Scheme 9**. There are two possible transition states for the orientation of the catalyst-bound substrate, **TS1** and **TS2**. In these figures, the catalyst is represented for simplicity as a flat surface. In TS1, the bulky triisopropylsilyl group is oriented away from the face of the rhodium catalyst as well as from the bulky triphenylacetate ligands. In contrast, in transition state 2, the trialkylsilyl group is positioned in proximity to the catalyst, which is disfavored due to steric interactions. The favorable transition state **TS1** leads to the *cis β*-lactone, and thus to the *Z* isomer. This model is consistent with the observation that *Z*-selectivity increased upon increasing the size of the silyl group as well as of the carboxylate ligands on the catalyst. The steric basis of this model also explains why the achiral catalyst is capable of excellent stereoinduction. These studies on the synthesis of allylsilanes were compiled into a paper written by David Guptill and published in *Organic Letters*[36].

[36] Guptill, D. M.; Cohen, C. M.; Davies, H. M. L. *Org. Lett*. **2013**, *15*, 6120-6123.

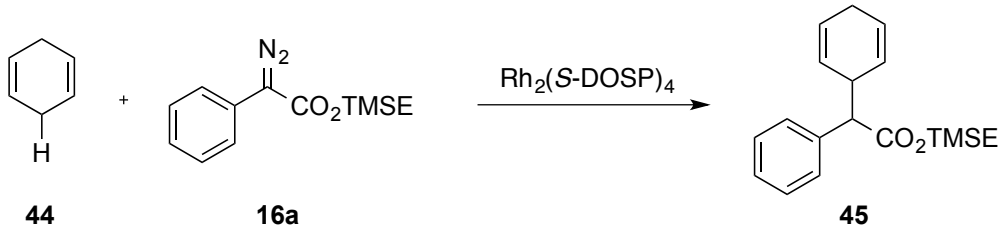
Scheme 9. Explanation of Observed Stereochemistry



Revisiting the Cyclopropanation Reaction with a Silyl-Substituted Diazo

We were still interested in the ability of the trialkylsilyl-substituted aryldiazoacetate **16a** to perform cyclopropanation reactions, which was tentatively explored before the intramolecular C-H insertion was discovered (see **Scheme 2**). Ultimately, our goal is to use this reaction to easily synthesize various cyclopropanecarboxylate ligands to create dirhodium(II) carboxylate catalysts with varied reactivity profiles. In addition to being a good substrate for cyclopropanation, diazo **16a** proved capable of intermolecular C-H insertion in a test reaction with cyclohexadiene

(**Equation 14**). The product was formed in 74% yield, but attempts to determine the enantioselectivity by chiral HPLC were unsuccessful.



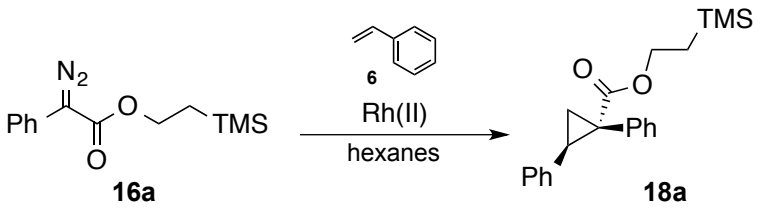
44 **16a** **45**

74% yield

(14)

Because we were more interested in the cyclopropanation reaction, we then sought to optimize the conditions for the reaction of **16a** with styrene, as shown in **Scheme 2**. We observed that the reaction proceeded in good yield and enantioselectivity with Rh_2(*S*-DOSP)$_4$, which is surprising based on previous results with this catalyst. Usually, changing the ester substituent from methyl results in low enantioselectivity, but the cyclopropane **18a** was formed in 87% ee, which is nearly equivalent to the 88% ee observed using the methyl ester[24]. A further exploration of different chiral dirhodium catalysts yielded no better results, showing both low yields and low enantioselectivity (**Table 4, entries 2-4**). Thus, we proceeded in all further studies using the catalyst Rh_2(*S*-DOSP)$_4$.

Table 4. Catalyst Optimization for Cyclopropanation

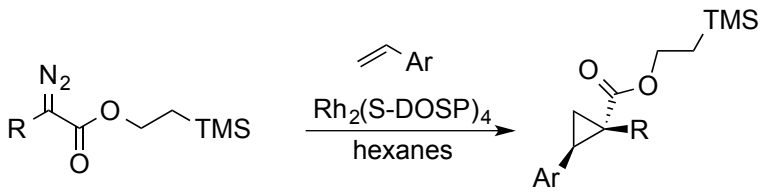


Entry	Catalyst	Yield (%)	ee (%)
1	Rh_2(S-DOSP)$_4$	87	87
2	Rh_2(S-PTAD)$_4$	46[1]	35
3	Rh_2(S-BTPCP)	67[1]	43
4	Rh_2(S-NTTL)$_4$	35[1]	51

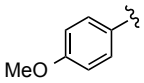
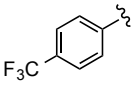
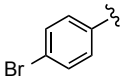
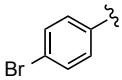
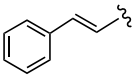
[1] Yields using unoptimized conditions.

The next study (**Table 5**) investigated different styrene derivatives, including electron-donating (**entry 2, 4**) and electron-withdrawing (**entry 3**) substituents. The levels of enantioinduction were relatively unaffected by the nature of the substituent on styrene, however the lowest ee was found with *para*-methoxystyrene. This result is consistent with the finding that electron rich alkenes give lower enantioselectivity[16], albeit to a very small extent. The yields for these reactions also remained high (70-73%). The *para*-bromo phenyldiazoacetate **46a** and phenylvinyl diazoacetate **43b** also showed good reactivity and enantioselectivity in the reaction with styrene. The products **18e** and **18f** were formed in high yield and equally high enantioselectivity as compared to the reaction with the aryldiazoacetate substrate **16a**.

Table 5. Exploration of Substrate Scope



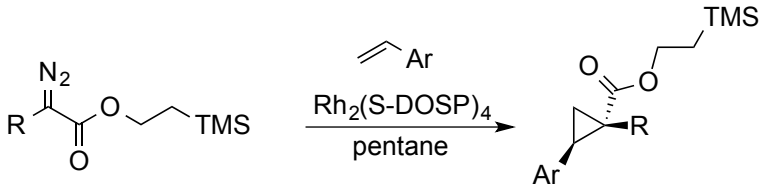
16a, 46a-b **18a-f**

Entry	R	Ar	Product	Yield (%)	ee(%)
1			**18a**	87	87
2			**18b**	70	84
3			**18c**	74	86
4			**18d**	73	88
5			**18e**	83	87
6			**18f**	77	88

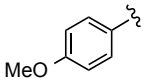
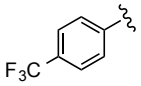
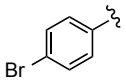
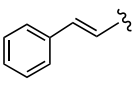
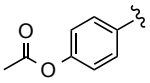
However, despite the efficiency of this reaction, we were still observing a noticeable amount of the side product arising from oxygenation of the diazo. In an attempt to reduce this side product, we tried the reaction in pentane, following the same procedure as before where the solvent was heated at reflux prior to its use to remove oxygen. The results are summarized in **Table 6**. While there was no observed change in yield, and a slight drop in enantioselectivity, the reactions were slightly cleaner. Also, some of the products could be completely separated from the oxygenated side product by chromatography, although some could not and mixtures were obtained.

Another variable that was examined was reaction temperature, which proved to be an important factor. We had observed that the unsubstituted cyclopropane **18a** could be formed in 95% ee when the temperature was lowered from room temperature to -40 °C, which was a significant increase. In addition, the enantioinduction of the vinyldiazoacetate increased at low temperature. It then followed that reaction with the remainder of the styrene derivatives gave cyclopropanes **18b-d** at increased levels of enantioinduction at low temperature. In general, the ee increased by 10% upon lowering the reaction temperature. Also, the 4-acetoxystyrene was added to this study (**entry 6**), and it also performed well in the reaction (84% yield, 95% ee).

Table 6. Substrate Scope with Optimized Conditions



16a,46b **18a-d,f,g**

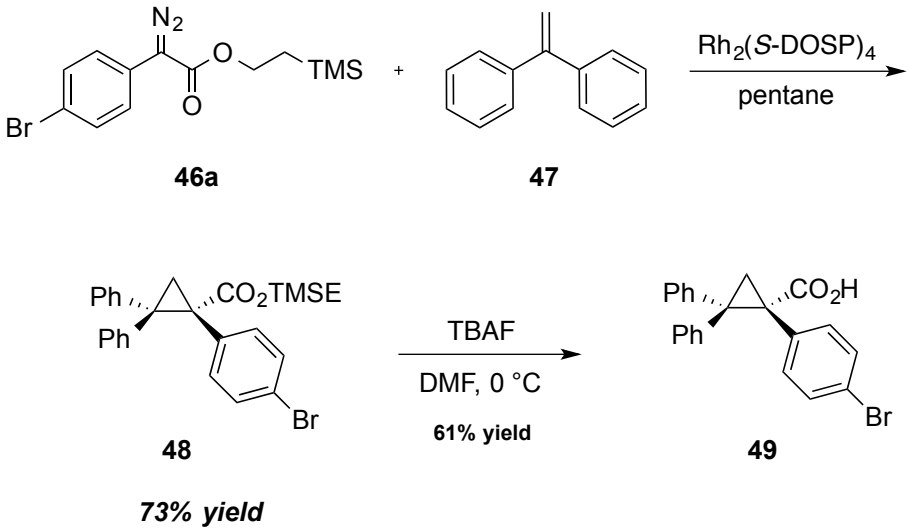
Entry	R	Ar	Product	Yield/ee (%) (**23°C**)	Yield/ee (%) (**-40°C**)
1[a]			**18a**	87/87	73/95
2			**18b**	72/81	~75/91
3			**18c**	72/85	50/96
4			**18d**	74/86	67/96
5[a]			**18f**	77/88	78/92
6			**18g**	49/84	84/95

[a] Solvent was hexanes

Preliminary Investigation of Ligand Synthesis

After confirming that the silyl substituted diazo was a good substrate for cyclopropanation, we began to explore the synthesis of the Rh_2(*R*-BTPCP)$_4$ ligand, which is currently used as an effective catalyst for asymmetric transformations. The first step, cyclopropanation of the *para*-bromo substituted aryldiazoacetate **46a** with 1,1-diphenylethylene proceeded with good yield (**Scheme 10**). The enantioselectivity for this step has not been determined at this time. The next step is the desilylation reaction with tetrabutylammonium fluoride (TBAF). Initial trials have indicated that using dimethylformamide (DMF) as solvent gives modest yields of product **49**, up to 61% on a small scale. Efforts to optimize this reaction are ongoing, as this route holds promise as a milder and more efficient route to the BTPCP ligand.

Scheme 10. Synthesis of Triarylcyclopropanecarboxylate

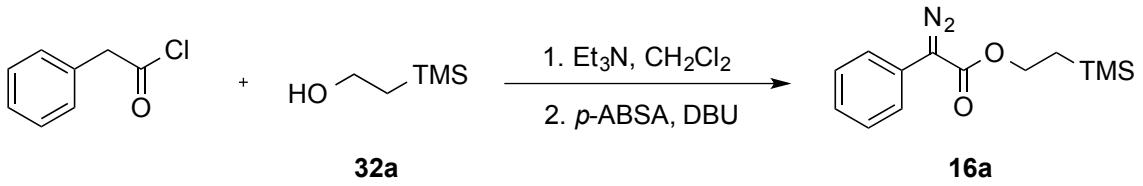


Conclusion

The versatility of ethyl aryl- and vinyldiazoacetates substituted in the ester position with trialkylsilyl groups has been demonstrated. With dirhodium catalysts, *Z* allylsilanes can effectively be synthesized via an intramolecular pathway. The reaction involves C-H insertion of

a rhodium(II) carbenoid species into the site β- to silicon to generate a β-lactone intermediate. The C-H insertion step, as well as the decomposition and release of CO_2 that follows, is enabled by the electronically stabilizing presence of silicon. Using the bulky dirhodium catalyst $Rh_2(TPA)_4$ in conjunction with a triisopropylsilyl group, steric factors favor the selective formation of *Z* allylsilanes. The reaction is tolerant of many varied substitutions on the donor group, encompassing electron-rich groups as well as electron-poor groups and conjugated alkenes. In addition, this methodology can be used to generate chiral allylsilanes from chiral starting materials. This work represents a new and efficient method to selectively create *Z* allylsilanes, which are synthetically interesting substrates. In addition, the silyl substituted diazo compounds are ideal substrates for cyclopropanation reactions with $Rh_2(S\text{-DOSP})_4$, achieving up to 96% ee with a variety of substituted styrene compounds. This method of cyclopropanation has been used to synthesize the appropriate ligand for the catalyst $Rh_2(R\text{-BTPCP})_4$ in a method that is milder than that which has previously been used.

Experimental Data



32a **16a**

2-(trimethylsilyl)ethyl 2-diazo-2-phenylacetate (16a)

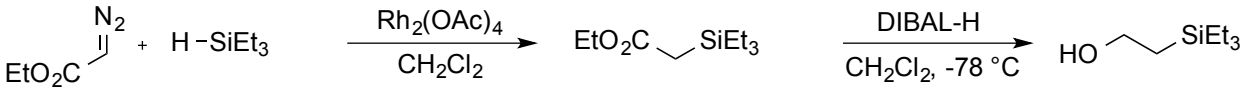
Step 1: To a solution of 2-(trimethylsilyl)ethanol **32a** (1.2g, 10.0 mmol, 1.0 equiv.) and triethylamine (2.1 mL, 15.0 mmol, 1.5 equiv.) in CH_2Cl_2 (80 mL) was added phenylacetyl chloride (1.5 mL, 11.0 mmol, 1.1 equiv.) dropwise. The reaction was stirred at room temperature for 1 hour, then quenched with distilled H_2O (5 mL) and extracted 2x with dichloromethane. The combined extracts were dried over $MgSO_4$, filtered and concentrated. The crude material was used without purification in *Step 2*: The crude ester (2.2 g, 9.1 mmol, 1.0 equiv.) was dissolved in acetonitrile (90 mL) along with *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (3.3 g, 13.7 mmol, 1.5 equiv.) and cooled to 0 °C in an ice bath. Next, 1,8-diazabicycloundec-7-ene (DBU) (2.7 mL, 18.2 mmol, 2.0 equiv) was added dropwise. The mixture was allowed to warm to room temperature and then stirred overnight. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl (5 mL) and water (2 mL). The organic layer was extracted 3x with diethyl ether, and the combined extracts were dried over $MgSO_4$, filtered and concentrated. The crude material was purified by column chromatography (3% Et_2O in pentane), yielding diazo **16a** as an orange oil (1.6 g, 59% yield over two steps).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.51 (dd, 2H, J = 8.5, 1.1 Hz), 7.40 (t, 2H, J = 7.9 Hz), 7.19 (m, 1H), 4.43-4.37 (m, 2H), 1.14-1.07 (m, 2H), 0.09 (s, 9H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 129.8, 129.0, 125.9, 124.1, 63.5, 17.8, -1.3 (resonance resulting from the diazo carbon was not detected)

IR (neat): 2954, 2080, 1698, 1150 cm^{-1}

HRMS (NSI) calcd for $C_{13}H_{18}O_2N_2NaSi$ ($[M+Na]^+$) 285.1029, found 285.1032

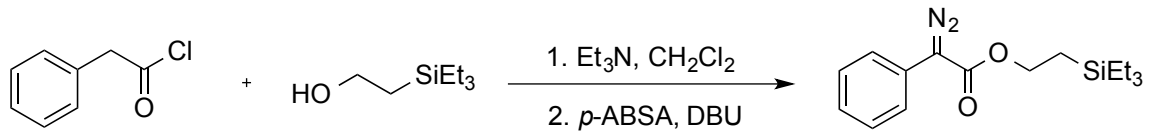


31b **32b**

2-(triethylsilyl)ethanol (32b)

A solution of ethyl diazoacetate (0.7 mL, 80% by mass in CH_2Cl_2, 6.0 mmol, 1.0 equiv.) in CH_2Cl_2 (15 mL) was added dropwise over 2 hours to a solution of triethylsilane (1.9 mL, 12.0 mmol, 2.0 equiv.) and $Rh_2(OAc)_4$ (26.5 mg, 0.06 mmol, 1 mol %) in CH_2Cl_2 (15 mL). The volatiles were removed by rotary evaporation, and the crude mixture was purified by column chromatography (5% Et_2O in pentane), giving the ester **31b** as a clear oil. This oil (1.2 g, 6.0 mmol, 1.0 equiv) was dissolved in 30 mL CH_2Cl_2, and this solution was cooled to -78 °C in a bath of dry ice and acetone. Diisobutylaluminum hydride (DIBAL-H) (1.0 M in CH_2Cl_2, 13.4 mL, 13.4 mmol, 2.2 equiv.) was added slowly and the reaction was maintained at -78 °C for 45 minutes. The reaction was then warmed to room temperature and stirred overnight. The mixture was quenched with methanol added dropwise. Then, an aqueous solution of Rochelle's salt was added with vigorous stirring for 10 minutes. The product was extracted in CH_2Cl_2, dried over Na_2SO_4, filtered, and concentrated, giving the alcohol **32b** (0.85 g, 88% yield over two steps) pure enough for the next step. The spectral data were consistent with the literature[37].

[37] Soderquist, J. A.; Rivera, I.; Negron, A. *J. Org. Chem.* **1989**, *54*, 4051-4055.



32b **16b**

2-(triethylsilyl)ethyl 2-diazo-2-phenylacetate (16b)

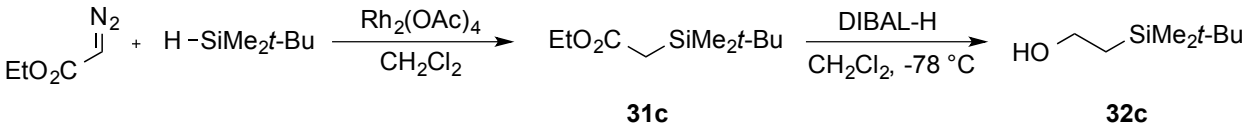
Prepared analogously to **16a**. *Step 1*: To a solution of 2-(triethylsilyl)ethanol **32b** (0.8 g, 5.3 mmol, 1.0 equiv.) and triethylamine (1.1 mL, 8.0 mmol, 1.5 equiv.) in CH_2Cl_2 (50 mL) was added phenylacetyl chloride (0.8 mL, 5.8 mmol, 1.1 equiv.) dropwise. The reaction was stirred at room temperature for 1 hour, then quenched with distilled H_2O (5 mL) and extracted 2x with dichloromethane. The combined extracts were dried over $MgSO_4$, filtered and concentrated. The crude material was used without purification in *Step 2*: The crude ester (1.3 g, 4.7 mmol, 1.0 equiv.) was dissolved in acetonitrile (50 mL) along with *p*-ABSA (1.7 g, 7.1 mmol, 1.5 equiv.) and cooled to 0 °C in an ice bath. Next, DBU (1.3 mL, 9.4 mmol, 2.0 equiv) was added dropwise. The mixture was allowed to warm to room temperature and then stirred for 48 hours. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl. The organic layer was extracted 3x with diethyl ether, and the combined extracts were dried over $MgSO_4$, filtered and concentrated. The crude material was purified by column chromatography (3% Et_2O in pentane), giving the diazo **16b** as a red oil (0.185 g, 13% yield over two steps).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.51 (dd, 2H, J = 8.6, 1.2 Hz), 7.42-7.37 (m, 2H), 7.19 (tt, 1H, J = 7.8, 1.2 Hz), 4.41-4.36 (m, 2H), 1.15-1.09 (m, 2H), 0.98 (t, 9H, J = 7.9 Hz), 0.58 (q, 6H, J = 7.9 Hz)

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 129.1, 125.9 (2 signals), 124.2, 63.5, 13.1, 7.6, 3.6 (resonance resulting from the diazo carbon was not detected)

IR (film): 2953, 2874, 2080, 1699, 1150 cm^{-1}

HRMS (NSI) calcd for $C_{16}H_{24}O_2N_2Si$ ($[M]^+$) 304.1602, found 304.1588

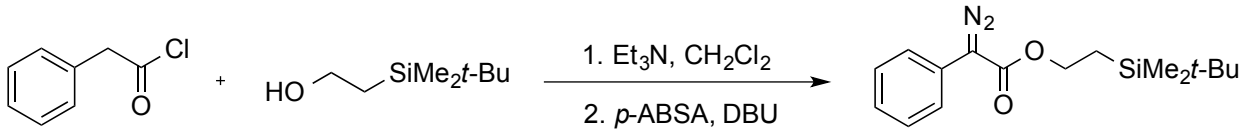


31c **32c**

2-(*tert*-butyldimethylsilyl)ethanol (32c)

Prepared analogously to **32b**. A solution of ethyl diazoacetate (0.7 mL, 80% by mass in CH_2Cl_2, 6.0 mmol, 1.0 equiv.) in CH_2Cl_2 (15 mL) was added dropwise over 4 hours to a solution of *tert*-butyldimethylsilane (2.0 mL, 12.0 mmol, 2.0 equiv.) and $Rh_2(OAc)_4$ (26.5 mg, 0.06 mmol, 1 mol %) in CH_2Cl_2 (20 mL). The volatiles were removed by rotary evaporation, and the crude mixture was purified by column chromatography (3% Et_2O in pentane), giving the ester **31c** as a clear oil. This oil (0.7 g, 3.5 mmol, 1.0 equiv) was dissolved in 20 mL CH_2Cl_2, and this solution was cooled to -78 °C in a bath of dry ice and acetone. DIBAL-H (1.0 M in CH_2Cl_2, 7.7 mL, 7.7 mmol, 2.2 equiv.) was added slowly and the reaction was maintained at -78 °C for 30 minutes. The reaction was then warmed to room temperature. The mixture was quenched with methanol added dropwise. Then, an aqueous solution of Rochelle's salt was added with vigorous stirring for 10 minutes. The product was extracted in CH_2Cl_2, dried over Na_2SO_4, filtered, and concentrated, giving the alcohol **32c** (0.5 g, 52% yield over two steps) pure enough for the next step. The spectral data were consistent with the literature[38].

[38] Kumada, M.; Imaki, N.; Yamamoto, K. *J. Organomet. Chem.* **1966**, *6*, 490-495.



32c **16c**

2-(*tert*-butyldimethylsilyl)ethyl 2-diazo-2-phenylacetate (16c)

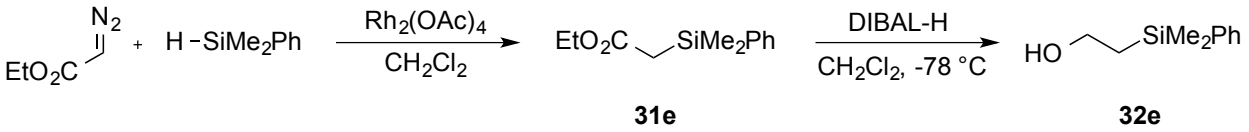
Prepared analogously to **16a**. *Step 1*: To a solution of 2-(*tert*-butyldimethylsilyl)ethanol **32c** (0.5 g, 3.1 mmol, 1.0 equiv.) and triethylamine (0.64 mL, 4.6 mmol, 1.5 equiv.) in CH_2Cl_2 (25 mL) was added phenylacetyl chloride (0.45 mL, 3.4 mmol, 1.1 equiv.) dropwise. The reaction was stirred at room temperature for 1 hour, then quenched with distilled H_2O and extracted 2x with dichloromethane. The combined extracts were dried over $MgSO_4$, filtered and concentrated. The crude material was used without purification in *Step 2*: The crude ester (0.8 g, 3.0 mmol, 1.0 equiv.) was dissolved in acetonitrile (30 mL) along with *p*-ABSA (1.1 g, 4.5 mmol, 1.5 equiv.) and cooled to 0 °C in an ice bath. Next, DBU (0.8 mL, 6.0 mmol, 2.0 equiv) was added dropwise. The mixture was allowed to warm to room temperature and then stirred for 48 hours. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl. The organic layer was extracted 3x with diethyl ether, and the combined extracts were dried over $MgSO_4$, filtered and concentrated. The crude material was purified by column chromatography (1% Et_2O in pentane), giving the diazo **16c** as a red oil (0.467 g, 48% yield over two steps).

^{1}H NMR (600 MHz; $CDCl_3$): δ 7.51 (dd, 2H, J = 8.5, 1.0 Hz), 7.40 (t, 2H, J = 8 Hz), 7.19 (t, 1H, J = 7.4 Hz), 4.42-4.37 (m, 2H), 1.13-1.09 (m, 2H), 0.92 (s, 9H), 0.03 (s, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 129.1, 125.9 (2 signals), 124.2, 63.8, 26.6, 16.6, 14.1, -5.8 (resonance resulting from the diazo carbon was not detected)

IR (neat): 2953, 2856, 2080, 1699 cm^{-1}

HRMS (NSI) calcd for $C_{16}H_{24}O_2N_2NaSi$ ($[M+Na]^+$) 327.1499, found 327.1501

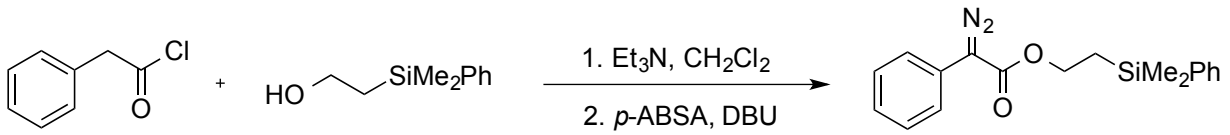


31e **32e**

2-(dimethyl(phenyl)silyl)ethanol (32e)

Prepared analogously to **32b**. A solution of ethyl diazoacetate (0.7 mL, 80% by mass in CH_2Cl_2, 6.0 mmol, 1.0 equiv.) in CH_2Cl_2 (15 mL) was added dropwise over 4 hours to a solution of dimethyl(phenyl)silane (1.9 mL, 12.0 mmol, 2.0 equiv.) and $Rh_2(OAc)_4$ (26.5 mg, 0.06 mmol, 1 mol %) in CH_2Cl_2 (20 mL). The volatiles were removed by rotary evaporation, and the crude mixture was purified by column chromatography (5% Et_2O in pentane), giving the ester **31e** as a clear oil. This oil (1.1 g, 5.1 mmol, 1.0 equiv) was dissolved in 25 mL CH_2Cl_2, and this solution was cooled to -78 °C in a bath of dry ice and acetone. DIBAL-H (1.0 M in CH_2Cl_2, 11.2 mL, 11.2 mmol, 2.2 equiv.) was added slowly and the reaction was maintained at -78 °C for 30 minutes. The reaction was then warmed to room temperature. The mixture was quenched with methanol added dropwise. Then, an aqueous solution of Rochelle's salt was added with vigorous stirring for 10 minutes. The product was extracted in CH_2Cl_2, dried over $MgSO_4$, filtered, and concentrated, giving the alcohol **32e** (0.8 g, 73% yield over two steps) pure enough for the next step. The spectral data were consistent with the literature[39].

[39] Celebuski, J. E.; Chan, C. *J. Org. Chem.* **1992**, *57*, 5535-5538.



32e **16e**

2-(dimethyl(phenyl)silyl)ethyl 2-diazo-2-phenylacetate (16e)

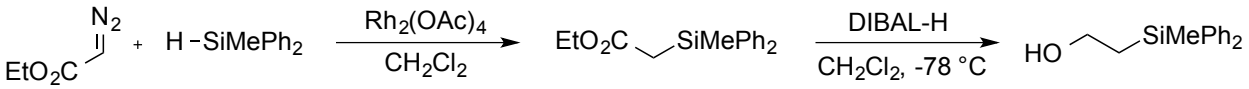
Prepared analogously to **16a**. *Step 1*: To a solution of 2-(dimethyl(phenyl)silyl)ethanol **32e** (0.8 g, 4.5 mmol, 1.0 equiv.) and triethylamine (0.94 mL, 6.8 mmol, 1.5 equiv.) in CH_2Cl_2 (30 mL) was added phenylacetyl chloride (0.66 mL, 5.0 mmol, 1.1 equiv.) dropwise. The reaction was stirred at room temperature for 1 hour, then quenched with distilled H_2O and extracted 2x with dichloromethane. The combined extracts were dried over $MgSO_4$, filtered and concentrated. The crude material was used without purification in *Step 2*: The crude ester (1.3 g, 4.5 mmol, 1.0 equiv.) was dissolved in acetonitrile (40 mL) along with *p*-ABSA (1.6 g, 6.8 mmol, 1.5 equiv.) and cooled to 0 °C in an ice bath. Next, DBU (1.3 mL, 9.0 mmol, 2.0 equiv) was added dropwise. The mixture was allowed to warm to room temperature and then stirred for 48 hours. The reaction mixture was then quenched by addition of saturated aqueous NH_4Cl. The organic layer was extracted 3x with diethyl ether, and the combined extracts were dried over $MgSO_4$, filtered and concentrated. The crude material was purified by column chromatography (2% Et_2O in pentane), giving the diazo **16e** as a red oil (0.43 g, 29% yield over two steps).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.55-7.50 (m, 2H), 7.47 (d, 2H, J = 8.8 Hz), 7.41-7.33 (m, 5H), 7.17 (td, 1H, J = 7.4, 1.2 Hz), 4.37 (m, 2H), 1.34 (m, 2H), 0.35 (s, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 138.0, 133.6, 129.4, 129.1, 128.1, 125.9, 125.8, 124.1, 63.2, 17.1, -2.7 (resonance resulting from the diazo carbon was not detected)

IR (film): 2954, 2080, 1697, 1243, 1150 cm^{-1}

HRMS (NSI) calcd for $C_{18}H_{20}O_2N_2NaSi$ ($[M+Na]^+$) 347.1186, found 347.1187

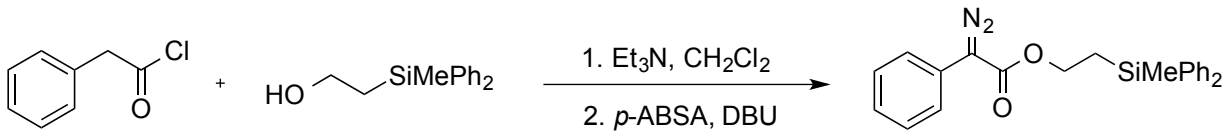


31f **32f**

2-(methyldiphenylsilyl)ethanol (32f)

Prepared analogously to **32b**. A solution of ethyl diazoacetate (1.4 mL, 80% by mass in CH_2Cl_2, 12.0 mmol, 1.0 equiv.) in CH_2Cl_2 (15 mL) was added dropwise over 4 hours to a solution of methyldiphenylsilane (4.8 mL, 24.0 mmol, 2.0 equiv.) and $Rh_2(OAc)_4$ (53 mg, 0.12 mmol, 1 mol %) in CH_2Cl_2 (40 mL). The volatiles were removed by rotary evaporation, and the crude mixture was purified by column chromatography (4% Et_2O in pentane), giving the ester **31f** as a clear oil. This oil (3.2 g, 11.3 mmol, 1.0 equiv) was dissolved in 50 mL CH_2Cl_2, and this solution was cooled to -78 °C in a bath of dry ice and acetone. DIBAL-H (1.0 M in CH_2Cl_2, 24.8 mL, 24.8 mmol, 2.2 equiv.) was added slowly and the reaction was maintained at -78 °C for 30 minutes. The reaction was then warmed to room temperature and the mixture was quenched with methanol added dropwise. Then, an aqueous solution of Rochelle's salt was added and stirred vigorously for 10 minutes. The product was extracted in CH_2Cl_2, dried over $MgSO_4$, filtered, and concentrated, giving the alcohol **32f** (1.7 g, 60% yield over two steps) pure enough for the next step. The spectral data were consistent with the literature[40].

[40] Chao, G.; Bernatowicz, M. S.; Reiss, P. D.; Matsueda, G. R. *J. Org. Chem.* **1994**, *59*, 6687-6691.



32f **16f**

2-(methyldiphenylsilyl)ethyl 2-diazo-2-phenylacetate (16f)

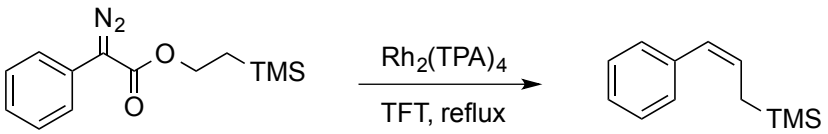
Prepared analogously to **16a**. *Step 1*: To a solution of 2-(methyldiphenylsilyl)ethanol **32f** (1.7 g, 7.2 mmol, 1.0 equiv.) and triethylamine (1.5 mL, 10.8 mmol, 1.5 equiv.) in CH_2Cl_2 (60 mL) was added phenylacetyl chloride (1.0 mL, 7.9 mmol, 1.1 equiv.) dropwise. The reaction was stirred at room temperature for 1 hour, then quenched with distilled H_2O and extracted 2x with dichloromethane. The combined extracts were dried over $MgSO_4$, filtered and concentrated. The crude material was used without purification in *Step 2*: The ester (2.6 g, 7.2 mmol, 1.0 equiv.) was dissolved in acetonitrile (60 mL) along with *p*-ABSA (2.6 g, 10.8 mmol, 1.5 equiv.) and cooled to 0 °C in an ice bath. Next, DBU (2.0 mL, 14.4 mmol, 2.0 equiv) was added dropwise. The mixture was allowed to warm to room temperature and then stirred overnight. The reaction mixture was then quenched by addition of saturated aqueous NH_4Cl. The organic layer was extracted 3x with diethyl ether, and the combined extracts were dried over $MgSO_4$, filtered and concentrated. The crude material was purified by column chromatography (3% EtOAc in hexanes), giving the diazo **16f** as a red oil (1.9 g, 68% yield over two steps).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.58-7.53 (m, 4H), 7.49-7.44 (m, 2H), 7.43-7.35 (m, 8H), 7.22-7.17 (m, 1H), 4.48-4.41 (m, 2H), 1.71-1.64 (m, 2H), 0.65 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 136.0, 134.5, 129.7, 129.1, 128.2, 125.9, 125.8, 124.1, 63, 15.8, -3.9 (resonance resulting from the diazo carbon was not detected)

IR (neat): 3068, 2955, 2081, 1696, 1150 cm^{-1}

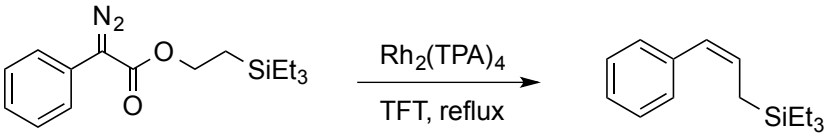
HRMS (NSI) calcd for $C_{23}H_{22}O_2N_2NaSi$ ([M+Na]$^+$) 409.1343, found 409.1343



16a **20a**

(*Z*)-trimethyl(3-phenylallyl)silane (20a)

A solution of the diazo **16a** (131 mg, 0.5 mmol, 1.0 equiv.) in 4 mL trifluorotoluene (TFT) was added dropwise over 3 hours to a solution of $Rh_2(TPA)_4$ (7 mg, 0.005 mmol, 1 mol %) in TFT (2 mL) at reflux. The mixture was stirred at reflux for an additional 2 hours, cooled to room temperature, and concentrated. The crude was purified by column chromatography (hexanes) to give **20a** as a colorless oil (65 mg, 68% yield) as a 88:12 mixture of *Z*:*E* isomers. Both the *Z*[41] and *E*[42] isomers of this compound are known in the literature.



16b **20b**

(*Z*)-triethyl(3-phenylallyl)silane (20b)

A solution of the diazo **16b** (152 mg, 0.5 mmol, 1.0 equiv.) in 4 mL trifluorotoluene (TFT) was added dropwise over 3 hours to a solution of $Rh_2(TPA)_4$ (7 mg, 0.005 mmol, 1 mol %) in TFT (2 mL) at reflux. The mixture was stirred at reflux for an additional 2 hours, cooled to room

[41] Seyferth, D.; Wursthorn, K. R.; Lim, T. F. O.; Sepelak, D. J. *J. Organomet. Chem.* **1979**, *181*, 293-302.
[42] Moser, R.; Nishikata, T.; Lipshutz, B. H. *Org. Lett.* **2010**, *12*, 28-31.

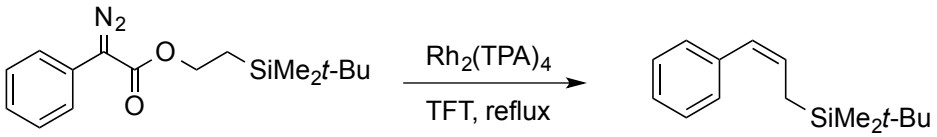
temperature, and concentrated. The crude was purified by column chromatography (hexanes) to give **20b** as a colorless oil (70 mg, 60% yield) as a 93:7 mixture of *Z*:*E* isomers.

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.37-7.31 (m, 4H), 7.25-7.18 (m, 1H), 6.34 (dt, 1H, *J* = 11.6, 1.6 Hz), 5.76 (dt, 1H, *J* = 11.6, 9.1 Hz), 1.89 (dd, 2H, *J* = 9.1, 1.6 Hz), 0.94 (t, 9H, *J* = 7.9 Hz), 0.58 (q, 6H, *J* = 7.9 Hz)

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 129.4, 128.8, 128.3, 126.9, 126.2, 14.8, 7.5, 3.6

IR (neat): 2951, 2909, 2874, 1446 cm^{-1}

HRMS (APCI) calcd for $C_{15}H_{25}Si$ ($[M+H]^+$) 233.1720, found 233.1718



16c **20c**

(*Z*)-*tert*-butyldimethyl(3-phenylallyl)silane (20c)

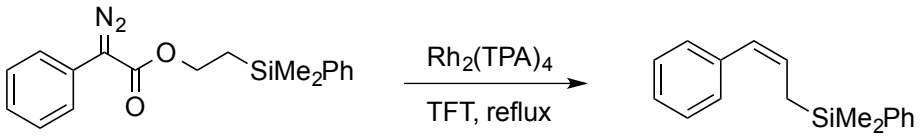
A solution of the diazo **16c** (152 mg, 0.5 mmol, 1.0 equiv.) in 4 mL trifluorotoluene (TFT) was added dropwise over 3 hours to a solution of $Rh_2(TPA)_4$ (7 mg, 0.005 mmol, 1 mol %) in TFT (2 mL) at reflux. The mixture was stirred at reflux for an additional 2 hours, cooled to room temperature, and concentrated. The crude was purified by column chromatography (hexanes) to give **20c** as a colorless oil (60 mg, 52% yield) as a 95:5 mixture of *Z*:*E* isomers.

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.37-7.29 (m, 4H), 7.23-7.18 (m, 1H), 6.34 (d, 1H, *J* = 11.6 Hz), 5.75 (dt, 1H, *J* = 11.6, 9.1 Hz), 1.88 (dd, 2H, *J* = 9.1, 1.4 Hz), 0.90 (s, 9H), 0.00 (s, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 129.6, 128.8, 128.3, 127.0, 126.2, 26.7, 17.1, 15.7, -6.0

IR (neat): 2952, 2927, 2882, 2855, 1248 cm^{-1}

HRMS (APCI) calcd for $C_{15}H_{25}Si$ ([M+H]$^+$) 233.1720, found 233.1722



16e **20e**

(*Z*)-dimethyl(phenyl)(3-phenylallyl)silane (20e)

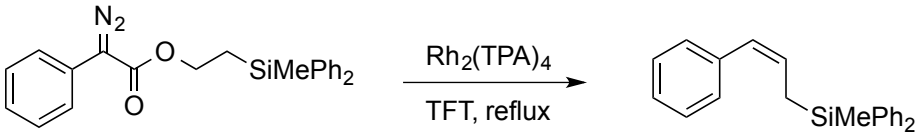
A solution of the diazo **16e** (162 mg, 0.5 mmol, 1.0 equiv.) in 4 mL trifluorotoluene (TFT) was added dropwise over 3 hours to a solution of $Rh_2(TPA)_4$ (7 mg, 0.005 mmol, 1 mol %) in TFT (2 mL) at reflux. The mixture was stirred at reflux for an additional 2 hours, cooled to room temperature, and concentrated. The crude was purified by column chromatography (hexanes) to give **20e** as a colorless oil (80 mg, 63% yield) as a 90:10 mixture of *Z*:*E* isomers.

Characterization of Z isomer: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.57-7.52 (m, 2H), 7.42-7.28 (m, 5H), 7.27-7.17 (m, 3H), 6.38 (d, 1H, *J* = 11.6 Hz), 5.73 (dt, 1H, *J* = 11.6, 9.0 Hz), 2.10 (dd, 2H, *J* = 9.0, 1.3 Hz), 0.34 (s, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 138.2, 133.8, 129.3, 128.0, 127.7, 126.3, 18.9, -2.9

IR (neat): 3068, 3008, 2955, 1248, 1112 cm^{-1}

HRMS (NSI) calcd for $C_{17}H_{21}Si$ ([M+H]$^+$) 253.1407, found 253.1411



16f **20f**

(*Z*)-methyldiphenyl(3-phenylallyl)silane (20f)

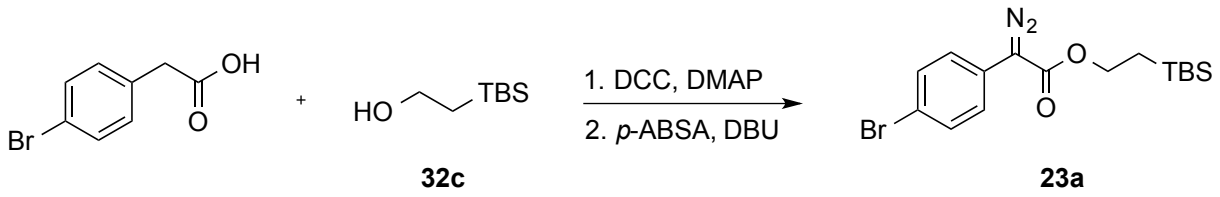
A solution of the diazo **16f** (193 mg, 0.5 mmol, 1.0 equiv.) in 4 mL trifluorotoluene (TFT) was added dropwise over 3 hours to a solution of $Rh_2(TPA)_4$ (7 mg, 0.005 mmol, 1 mol %) in TFT (2 mL) at reflux. The mixture was stirred at reflux for an additional 2 hours, cooled to room temperature, and concentrated. The crude was purified by column chromatography (hexanes) to give **20f** as a colorless oil (87 mg, 55% yield) as a 96:4 mixture of *Z*:*E* isomers.

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.60-7.51 (m, 4H), 7.45-7.15 (m, 11H), 6.40 (d, 1H, J = 11.6 Hz), 5.76 (dt, 1H, J = 11.6, 8.8 Hz), 2.40 (dd, 2H, J = 8.8, 1.6), 0.60 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1, 134.8, 129.7, 128.9, 128.5, 128.4, 128.2, 127.9, 126.5, -4.2

IR (neat): 3067, 3009, 1427, 1110, 694 cm^{-1}

HRMS (NSI) calcd for $C_{22}H_{22}NaSi$ ($[M+Na]^+$) 337.1383, found 337.1386



32c **23a**

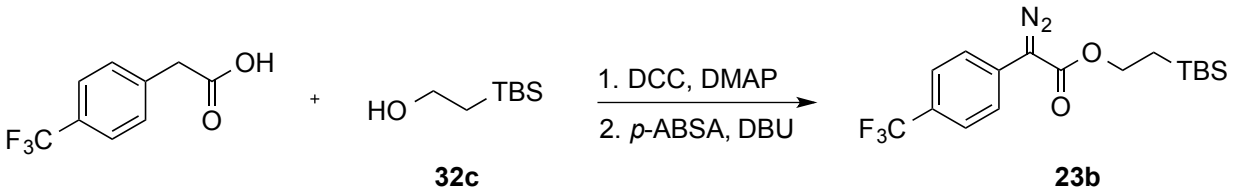
2-(*tert*-butyldimethylsilyl)ethyl 2-(4-bromophenyl)-2-diazoacetate (23a)

A solution of 4-bromophenylacetic acid (1.1g, 5.2 mmol, 1.0 equiv.), *N,N*-dimethyl-4-aminopyridine (DMAP) (63 mg, 0.52 mmol, 10 mol %), and 2-(*tert*-butyldimethylsilyl)ethanol **32c** (1.0 g, 6.2 mmol, 1.2 equiv.) in CH_2Cl_2 (3 mL) was cooled to 0 °C. Then, a solution of *N,N*-dicyclohexylcarbodiimide (DCC) (1.2g, 5.7 mmol, 1.1 equiv.) in CH_2Cl_2 (2 mL) was added slowly. The mixture was stirred and warmed slowly to room temperature over 2 hours. The white precipitate was removed by filtration, washing several times with Et_2O. The filtrate was concentrated by rotary evaporation and the crude residue was purified by column chromatography (3% EtOAc in hexanes). The ester was isolated as a colorless oil and used in the diazo transfer: The ester (1.4 g, 4.0 mmol, 1.0 equiv.) was dissolved in CH_3CN (40 mL), followed by *p*-ABSA (1.4 g, 6.0 mmol, 1.5 equiv.). The mixture was cooled to 0 °C and DBU (1.1 mL, 8.0 mmol, 2.0 equiv.) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 72 hours. The reaction was quenched with saturated aqueous NH_4Cl and H_2O. The mixture was extracted with Et_2O, and the ether layer was dried over $MgSO_4$, filtered and concentrated. The crude residue was purified by column chromatography (1% Et_2O in pentane) to give the diazo **23a** as an orange oil (1.2 g, 62% yield over two steps).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 – 7.47 (m, 2H), 7.42 – 7.35 (m, 2H), 4.42 – 4.35 (m, 2H), 1.13 – 1.06 (m, 2H), 0.91 (d, J = 1.4 Hz, 9H), 0.02 (d, J = 1.4 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.21, 132.18, 125.52, 125.12, 119.41, 64.04, 26.56, 16.63, 14.06, -5.78

*partially characterized compound



32c **23b**

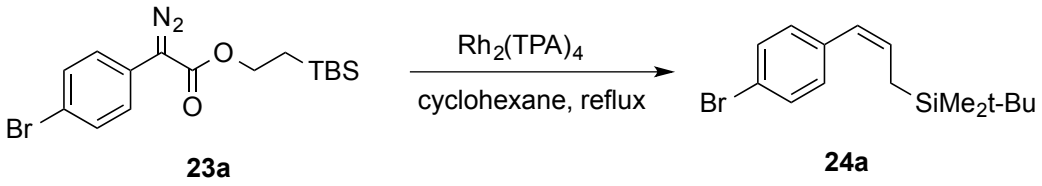
2-(*tert*-butyldimethylsilyl)ethyl 2-(4-(trifluoromethyl)phenyl)-2-diazoacetate (23b)

A solution of 4-bromophenylacetic acid (1.1g, 5.2 mmol, 1.0 equiv.), *N,N*-dimethyl-4-aminopyridine (DMAP) (63 mg, 0.52 mmol, 10 mol %), and 2-(*tert*-butyldimethylsilyl)ethanol **32c** (1.0 g, 6.2 mmol, 1.2 equiv.) in CH_2Cl_2 (3 mL) was cooled to 0 °C. Then, a solution of *N,N*-dicyclohexylcarbodiimide (DCC) (1.2g, 5.7 mmol, 1.1 equiv.) in CH_2Cl_2 (2 mL) was added slowly. The mixture was stirred and warmed slowly to room temperature over 2 hours. The white precipitate was removed by filtration, washing several times with Et_2O. The filtrate was concentrated by rotary evaporation and the crude residue was purified by column chromatography (3% EtOAc in hexanes). The ester was isolated as a colorless oil and used in the diazo transfer: The ester (0.9 g, 2.6 mmol, 1.0 equiv.) was dissolved in CH_3CN (25 mL), followed by *p*-ABSA (0.9 g, 3.9 mmol, 1.5 equiv.). The mixture was cooled to 0 °C and DBU (0.7 mL, 5.2 mmol, 2.0 equiv.) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 72 hours. The reaction was quenched with saturated aqueous NH_4Cl and H_2O. The mixture was extracted with Et_2O, and the ether layer was dried over $MgSO_4$,

filtered and concentrated. The crude residue was purified by column chromatography (1% Et_2O in pentane) to give the diazo **23b** as an orange oil (0.78 g, 40% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 0.5 Hz, 4H), 4.43 – 4.36 (m, 2H), 1.13 – 1.06 (m, 2H), 0.90 (d, *J* = 0.5 Hz, 9H), 0.05 – -0.02 (m, 6H)

*partially characterized compound



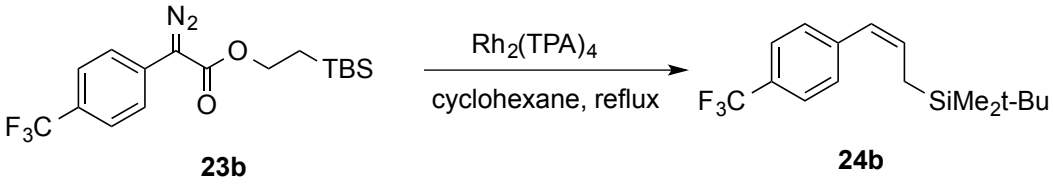
23a **24a**

(*Z*)-(3-(4-bromophenyl)allyl)*tert*-butyldimethylsilane (24a)

A solution of the diazo **23a** (192 mg, 0.5 mmol, 1.0 equiv.) in cyclohexane (4 mL) was added dropwise over 3 hours to a solution of $Rh_2(TPA)_4$ (7 mg, 0.005 mmol, 1 mol %) in cyclohexane (2 mL) at reflux. The volatiles were evaporated by rotary evaporation, and the mixture was redissolved in trifluorotoluene (TFT) and stirred at reflux for an additional 10 minutes, cooled to room temperature, and concentrated. The crude was purified by column chromatography (hexanes) to give **24a** as a colorless oil (107 mg, 69% yield) as a 95:5 mixture of *Z*:*E* isomers.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (dd, *J* = 8.6, 2.3 Hz, 2H), 7.15 (dd, *J* = 8.5, 2.2 Hz, 2H), 6.23 (d, *J* = 11.7 Hz, 1H), 5.75 (dt, *J* = 11.8, 9.1 Hz, 1H), 1.81 (d, *J* = 8.3 Hz, 2H), 0.87 (s, 9H), -0.04 (s, 6H)

*partially characterized compound



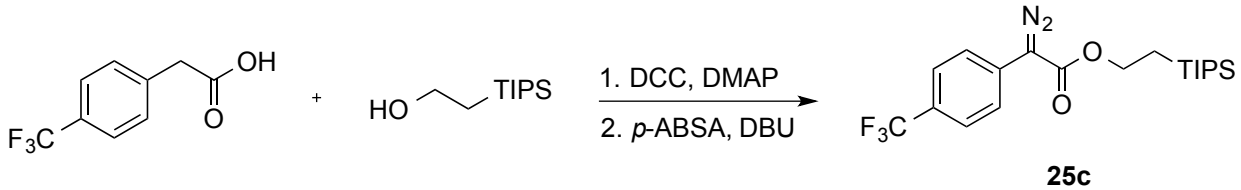
23b **24b**

(*Z*)-(3-(4-(trifluoromethyl)phenyl)allyl)*tert*-butyldimethylsilane (24b)

A solution of the diazo **23b** (150 mg, 0.4 mmol, 1.0 equiv.) in cyclohexane (4 mL) was added dropwise over 3 hours to a solution of $Rh_2(TPA)_4$ (6 mg, 0.004 mmol, 1 mol %) in cyclohexane (2 mL) at reflux. The volatiles were evaporated by rotary evaporation, and the mixture was redissolved in trifluorotoluene (TFT) and stirred at reflux for an additional 10 minutes, cooled to room temperature, and concentrated. The crude was purified by column chromatography (hexanes) to give **24b** as a colorless oil (61 mg, 50% yield) as a 95:5 mixture of *Z*:*E* isomers.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.32 (d, *J* = 11.7 Hz, 1H), 5.84 (dt, *J* = 11.7, 9.2 Hz, 1H), 1.85 (dd, *J* = 9.2, 1.6 Hz, 2H), 0.88 (s, 9H), -0.03 (s, 6H)

*partially characterized compound



25c

2-(triisopropylsilyl)ethyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate (25c)

Prepared analogously to **23a**. *Step 1*: A solution of 4-(trifluoromethyl)phenylacetic acid (1.0 g, 4.9 mmol, 1.0 equiv.), DMAP (72 mg, 0.59 mmol, 0.1 equiv.), and 2-(triisopropylsilyl)ethanol

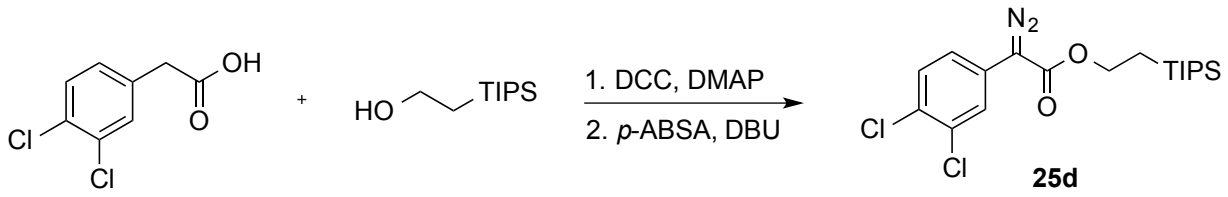
(1.2 g, 5.9 mmol, 1.2 equiv.) in CH_2Cl_2 (3 mL) was cooled to 0 °C. To this mixture, a solution of DCC (1.1g, 5.4 mmol, 1.1 equiv.) in CH_2Cl_2 (2 mL) was added slowly. The mixture was stirred and warmed slowly to room temperature over 2 hours. The white precipitate was removed by filtration, washing several times with Et_2O. The filtrate was concentrated by rotary evaporation and the crude residue was purified by column chromatography (3% EtOAc in hexanes). The ester was isolated as a colorless oil and used in *Step 2*: The ester (0.8 g, 2.1 mmol, 1.0 equiv.) was dissolved in CH_3CN (25 mL), followed by *p*-ABSA (0.77 g, 3.2 mmol, 1.5 equiv.). The mixture was cooled to 0 °C and DBU (0.59 mL, 4.2 mmol, 2.0 equiv.) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 72 hours. The reaction was quenched with saturated aqueous NH_4Cl and H_2O. The mixture was extracted with Et_2O, and the ether layer was dried over $MgSO_4$, filtered and concentrated. The crude residue was purified by column chromatography (0.5% Et_2O in pentane) to give the product **25c** as an orange solid (730 mg, 37% yield over two steps).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.63 (s, 4H), 4.49-4.41 (m, 2H), 1.22-1.15 (m, 2H), 1.11-1.06 (m, 21H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 130.6, 127.6 (q, J = 32.8 Hz), 126 (q, J = 3.7 Hz), 124.3, (q, J = 271.6 Hz), 123.6, 64.1, 18.9, 11.4, 11.2 (resonance resulting from the diazo carbon was not detected)

IR (neat): 2943, 2866, 2087, 1702, 1322 cm^{-1}

HRMS (NSI) calcd for $C_{20}H_{29}O_2N_2F_3NaSi$ ($[M+Na]^+$) 437.1843, found 437.1838



25d

2-(triisopropylsilyl)ethyl 2-diazo-2-(3,4-dichlorophenyl)acetate (25d)

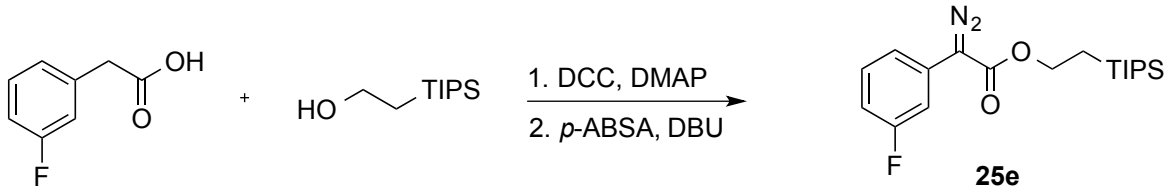
Prepared analogously to **23a**. *Step 1*: A solution of 3,4-dichlorophenylacetic acid (1.0 g, 5.0 mmol, 1.0 equiv.), DMAP (61 mg, 0.5 mmol, 0.1 equiv.), and 2-(triisopropylsilyl)ethanol (1.2 g, 5.9 mmol, 1.2 equiv.) in CH_2Cl_2 (3 mL) was cooled to 0 °C. To this mixture, a solution of DCC (1.1g, 5.5 mmol, 1.1 equiv.) in CH_2Cl_2 (2 mL) was added slowly. The mixture was stirred and warmed slowly to room temperature over 2 hours. The white precipitate was removed by filtration, washing several times with Et_2O. The filtrate was concentrated by rotary evaporation and the crude residue was purified by column chromatography (3% EtOAc in hexanes). The ester was isolated as a colorless oil and used in *Step 2*: The ester (1.5 g, 3.8 mmol, 1.0 equiv.) was dissolved in CH_3CN (35 mL), followed by *p*-ABSA (1.4 g, 5.7 mmol, 1.5 equiv.). The mixture was cooled to 0 °C and DBU (1.1 mL, 7.6 mmol, 2.0 equiv.) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 72 hours. The reaction was quenched with saturated aqueous NH_4Cl and H_2O. The mixture was extracted with Et_2O, and the ether layer was dried over $MgSO_4$, filtered and concentrated. The crude residue was purified by column chromatography (0.5% Et_2O in pentane) to give the product **25d** as an orange solid (1.4 g, 67% yield over two steps).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.66 (d, 1H, J = 2.3 Hz), 7.42 (d, 1H, J = 8.6 Hz), 7.30 (dd, 1H, J = 8.6, 2.3 Hz), 4.47-4.39 (m, 2H), 1.21-1.04 (m, 23H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 133.4, 130.8, 129.4, 126.5, 125.4, 122.8, 64.1, 18.9, 11.4, 11.1

IR (film): 2941, 2865, 2085, 1699, 1159 cm^{-1}

HRMS (APCI) calcd for $C_{19}H_{29}O_2N_2Cl_2Si$ ($[M+H]^+$) 415.1370, found 415.1360; Anal. calcd for $C_{19}H_{29}O_2N_2Cl_2Si$: C 54.93, H 6.79, N 6.74, found C 54.92, H 6.80, N 6.66



2-(triisopropylsilyl)ethyl 2-diazo-2-(3-fluorophenyl)acetate (25e)

Prepared analogously to **23a**. *Step 1*: A solution of 3-fluorophenylacetic acid (0.76 g, 4.9 mmol, 1.0 equiv.), DMAP (72 mg, 0.59 mmol, 0.1 equiv.), and 2-(triisopropylsilyl)ethanol (1.2 g, 5.9 mmol, 1.2 equiv.) in CH_2Cl_2 (3 mL) was cooled to 0 °C. To this mixture, a solution of DCC (1.1g, 5.4 mmol, 1.1 equiv.) in CH_2Cl_2 (2 mL) was added slowly. The mixture was stirred and warmed slowly to room temperature over 2 hours. The white precipitate was removed by filtration, washing several times with CH_2Cl_2. The filtrate was concentrated by rotary evaporation and the crude residue was purified by column chromatography (3% EtOAc in hexanes). The ester was isolated as a colorless oil and used in *Step 2*: The ester (1.0 g, 3.0 mmol, 1.0 equiv.) was dissolved in CH_3CN (30 mL), followed by *p*-ABSA (1.1 g, 4.5 mmol, 1.5 equiv.). The mixture was cooled to 0 °C and DBU (0.84 mL, 6.0 mmol, 2.0 equiv.) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 72 hours. The reaction was quenched with saturated aqueous NH_4Cl and H_2O. The mixture was extracted with

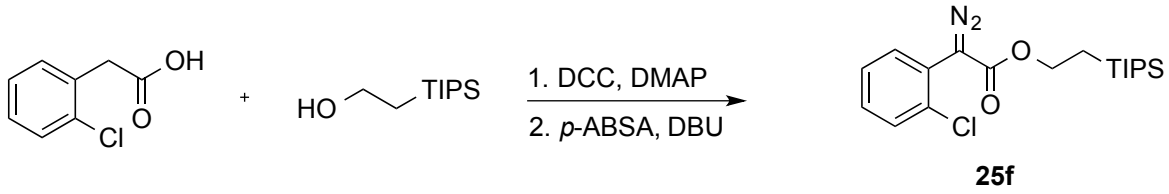
Et_2O, and the ether layer was dried over $MgSO_4$, filtered and concentrated. The crude residue was purified by column chromatography (1% Et_2O in pentane) to give the product **25e** as an orange oil (0.9 g, 50% yield over two steps).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.41-7.30 (m, 2H), 7.18 (ddd, 1H, J = 8.0, 1.8, 0.9 Hz), 6.86 (tdd, 1H, J = 8.3, 2.5, 0.9 Hz), 4.48-4.40 (m, 2H), 1.25-1.03 (m, 23H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 165, 163.4 (d, $^1J_{CF}$ = 245 Hz), 130.5 (d, $^3J_{CF}$ = 8.8 Hz), 128.5 (d, $^3J_{CF}$ = 9.4 Hz), 119 (d, $^4J_{CF}$ = 2.6 Hz), 112.5 (d, $^2J_{CF}$ = 21.3 Hz), 111.3 (d, $^2J_{CF}$ = 25.3 Hz), 63.9, 18.9, 11.4, 11.1

IR (film): 2942, 2865, 2082, 1700, 1244 cm^{-1}

HRMS (NSI) calcd for $C_{19}H_{29}O_2N_2FNaSi$ ([M+Na]$^+$) 387.1875, found 387.1879



25f

2-(triisopropylsilyl)ethyl 2-(2-chlorophenyl)-2-diazoacetate (25f)

Prepared analogously to **23a**. *Step 1*: A solution of 2-chlorophenylacetic acid (0.85 g, 5.0 mmol, 1.0 equiv.), DMAP (61 mg, 0.5 mmol, 0.1 equiv.), and 2-(triisopropylsilyl)ethanol (1.2 g, 5.9 mmol, 1.2 equiv.) in CH_2Cl_2 (3 mL) was cooled to 0 °C. To this mixture, a solution of DCC (1.1g, 5.5 mmol, 1.1 equiv.) in CH_2Cl_2 (2 mL) was added slowly. The mixture was stirred and warmed slowly to room temperature over 2 hours. The white precipitate was removed by filtration, washing several times with Et_2O. The filtrate was concentrated by rotary evaporation

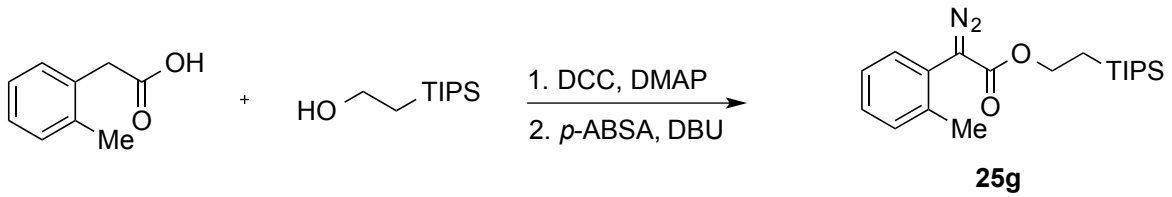
and the crude residue was purified by column chromatography (3% EtOAc in hexanes). The ester was isolated as a colorless oil and used in *Step 2*: The ester (1.2 g, 3.3 mmol, 1.0 equiv.) was dissolved in CH_3CN (30 mL), followed by *p*-ABSA (1.2 g, 5.0 mmol, 1.5 equiv.). The mixture was cooled to 0 °C and DBU (0.93 mL, 6.6 mmol, 2.0 equiv.) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 72 hours. The reaction was quenched with saturated aqueous NH_4Cl and H_2O. The mixture was extracted with Et_2O, and the ether layer was dried over $MgSO_4$, filtered and concentrated. The crude residue was purified by column chromatography (1% Et_2O in pentane) to give the product **25f** as a yellow oil (1.1 g, 58% yield over two steps).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.55 (dd, 1H, J = 7.7, 1.8 Hz), 7.40 (dd, 1H, J = 7.9, 1.6 Hz), 7.34-7.22 (m, 2H), 4.42-4.35 (m, 2H), 1.18-1.01 (m, 23H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 133.9, 132.5, 130.2, 129.7, 127.3, 124.3, 64.0, 18.9, 11.4, 11.2

IR (neat): 2941, 2865, 1093, 1698, 1239 cm^{-1}

HRMS (NSI) calcd for $C_{19}H_{29}O_2N_2ClNaSi$ ($[M+Na]^+$) 403.1579, found 403.1577; Anal. calcd for $C_{19}H_{29}O_2N_2SiCl$: C 59.90, H 7.67, N 7.35, found C 60.12, H 7.59, N 7.17



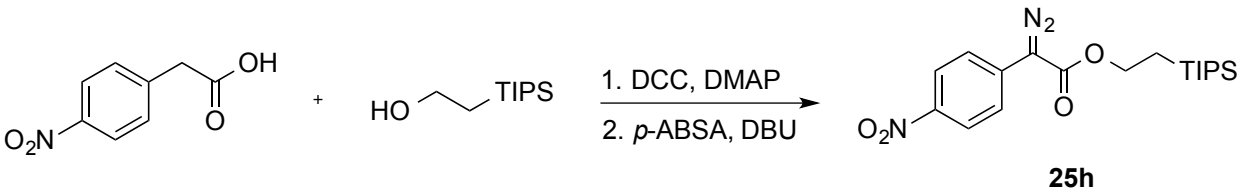
25g

2-(triisopropylsilyl)ethyl 2-(2-methylphenyl)-2-diazoacetate (25g)

Prepared analogously to **23a**. *Step 1*: A solution of 2-methylphenylacetic acid (0.71 g, 4.7 mmol, 1.0 equiv.), DMAP (57 mg, 0.47 mmol, 0.1 equiv.), and 2-(triisopropylsilyl)ethanol (1.1 g, 5.6 mmol, 1.2 equiv.) in CH_2Cl_2 (3 mL) was cooled to 0 °C. To this mixture, a solution of DCC (1.1g, 5.2 mmol, 1.1 equiv.) in CH_2Cl_2 (2 mL) was added slowly. The mixture was stirred and warmed slowly to room temperature over 2 hours. The white precipitate was removed by filtration, washing several times with Et_2O. The filtrate was concentrated by rotary evaporation and the crude residue was purified by column chromatography (3% EtOAc in hexanes). The ester was isolated as a colorless oil and used in *Step 2*: The ester (1.1 g, 3.3 mmol, 1.0 equiv.) was dissolved in CH_3CN (30 mL), followed by *p*-ABSA (1.2 g, 5.0 mmol, 1.5 equiv.). The mixture was cooled to 0 °C and DBU (0.93 mL, 6.6 mmol, 2.0 equiv.) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 72 hours. The reaction was quenched with saturated aqueous NH_4Cl and H_2O. The mixture was extracted with Et_2O, and the ether layer was dried over $MgSO_4$, filtered and concentrated. The crude residue was purified by column chromatography (1% Et_2O in pentane) to give the product **25g** as an orange oil (0.95 g, 55% yield over two steps).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43 – 7.38 (m, 1H), 7.29 – 7.22 (m, 2H), 4.43 – 4.36 (m, 3H), 2.31 (s, 3H), 1.18 – 1.11 (m, 2H), 1.10 – 1.00 (m, 21H)

*partially characterized compound



25h

2-(triisopropylsilyl)ethyl 2-(4-nitrophenyl)-2-diazoacetate (25h)

Prepared analogously to **23a**. *Step 1*: A solution of 4-nitrophenylacetic acid (0.91 g, 5.0 mmol, 1.0 equiv.), DMAP (61 mg, 0.5 mmol, 0.1 equiv.), and 2-(triisopropylsilyl)ethanol (1.2 g, 5.9 mmol, 1.2 equiv.) in CH_2Cl_2 (3 mL) was cooled to 0 °C. To this mixture, a solution of DCC (1.1g, 5.5 mmol, 1.1 equiv.) in CH_2Cl_2 (2 mL) was added slowly. The mixture was stirred and warmed slowly to room temperature over 2 hours. The white precipitate was removed by filtration, washing several times with Et_2O. The filtrate was concentrated by rotary evaporation and the crude residue was purified by column chromatography (5% EtOAc in hexanes). The ester was isolated as a colorless oil and used in *Step 2*: The ester (1.2 g, 3.2 mmol, 1.0 equiv.) was dissolved in CH_3CN (30 mL), followed by *p*-ABSA (1.2 g, 4.8 mmol, 1.5 equiv.). The mixture was cooled to 0 °C and DBU (0.90 mL, 6.4 mmol, 2.0 equiv.) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 72 hours. The reaction was quenched with saturated aqueous NH_4Cl and H_2O. The mixture was extracted with Et_2O, and the ether layer was dried over $MgSO_4$, filtered and concentrated. The crude residue was purified by column chromatography (2% Et_2O in pentane) to give the product **25h** as an orange solid (0.87 g, 44% yield over two steps).

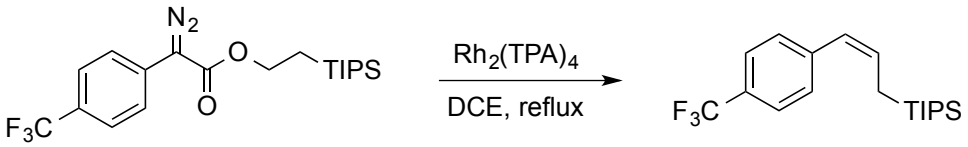
^{1}H NMR (400 MHz; $CDCl_3$): δ 8.23-8.18 (m, 2H), 7.69-7.63 (m, 2H), 4.47-4.40 (m, 2H), 1.20-0.99 (m, 23H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 145.1, 134.4, 124.5, 123.3, 64.4, 18.9, 11.4, 11.1

(resonance resulting from the diazo carbon was not detected)

IR (film): 2942, 2846, 2091, 1697, 1330 cm^{-1}

HRMS (NSI) calcd for $C_{19}H_{29}O_4N_2NaSi$ ([M+Na]$^+$) 414.1820, found 414.1815



25c **26c**

(*Z*)-(3-(4-(trifluoromethyl)phenyl)allyl)triisopropylsilane (26c)

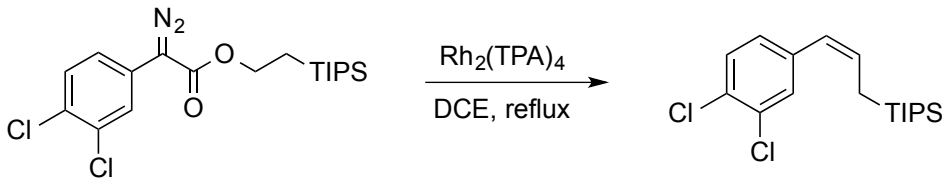
A solution of the diazo **25c** (145 mg, 0.35 mmol, 1.0 equiv.) in 4 mL 1,2-dichloroethane (DCE) was added dropwise over 3 hours to a solution of $Rh_2(TPA)_4$ (5 mg, 0.0035 mmol, 1 mol %) in DCE (2 mL) at reflux. The mixture was stirred at reflux for an additional 15 minutes, cooled to room temperature, and concentrated. The crude was purified by column chromatography (hexanes) to give **26c** as a colorless oil (78 mg, 65% yield).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.59 (d, 2H, *J* = 8.2 Hz), 7.43 (d, 2H, *J* = 8.2 Hz), 6.31 (d, 1H, *J* = 11.7 Hz), 5.94 (dt, 1H, *J* = 11.7, 8.9 Hz), 1.92 (dd, 2H, *J* = 8.9, 1.8 Hz), 1.13-0.98 (m, 21H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 132.4, 129.1, 128.2 (q, *J* = 32 Hz), 125.8, 125.3 (q, *J* = 3.7 Hz), 124.6 (q, *J* = 272 Hz), 18.8, 12.5, 11.4

IR (film): 2942, 2866, 1323, 1123 cm^{-1}

HRMS (APCI) calcd for $C_{19}H_{29}F_2Si$ ([M+H-HF]$^+$) 323.2001, found 323.2002



25d **26d**

(*Z*)-(3-(3,4-dichlorophenyl)allyl)triisopropylsilane (26d)

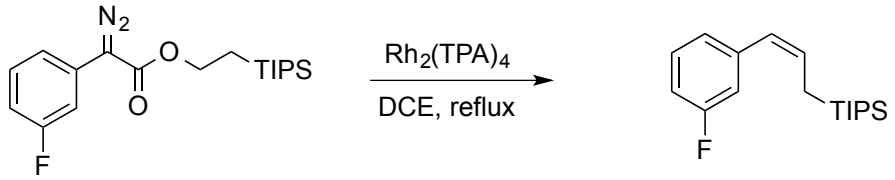
A solution of the diazo **25d** (207 mg, 0.5 mmol, 1.0 equiv.) in 4 mL DCE was added dropwise over 3 hours to a solution of $Rh_2(TPA)_4$ (7.2 mg, 0.005 mmol, 1 mol %) in DCE (2 mL) at reflux. The mixture was stirred at reflux for an additional 15 minutes, cooled to room temperature, and concentrated. The crude was purified by column chromatography (hexanes) to give **26d** as a colorless oil (105 mg, 61% yield).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.42 (s, 1H), 7.39 (d, 1H, J = 8.3 Hz), 7.17 (d, 1H, J = 8.3 Hz), 6.18 (d, 1H, J = 11.4 Hz), 5.89 (dt, 1H, J = 11.4, 8.9 Hz), 1.88 (d, 2H, J = 8.9 Hz), 1.12-1.00 (m, 21H)

^{13}C NMR (150 MHz, $CDCl_3$): δ 138.5, 132.3, 132.2, 130.6, 130.3, 129.9, 128.2, 124.7, 18.8, 12.4, 11.4

IR (neat): 2941, 2864, 1470 cm^{-1}

HRMS (APCI) calcd for $C_{18}H_{29}Cl_2Si$ ($[M+H]^+$) 343.1410, found 343.1415



25e **26e**

(*Z*)-(3-(3-fluorophenyl)allyl)triisopropylsilane (26e)

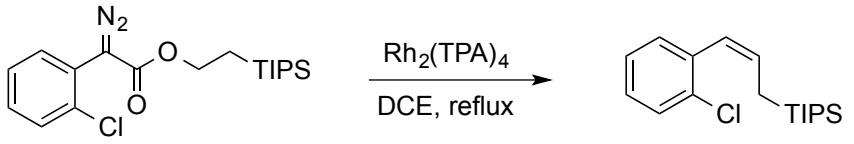
A solution of the diazo **25e** (150 mg, 0.4 mmol, 1.0 equiv.) in 4 mL DCE was added dropwise over 3 hours to a solution of $Rh_2(TPA)_4$ (5.7 mg, 0.004 mmol, 1 mol %) in DCE (2 mL) at reflux. The mixture was stirred at reflux for an additional 15 minutes, cooled to room temperature, and concentrated. The crude was purified by column chromatography (hexanes) to give **26e** as a colorless oil (80 mg, 68% yield).

^{1}H NMR (600 MHz; $CDCl_3$): δ 7.26 (q, 1H, *J* = 7.2 Hz), 7.08 (d, 1H, *J* = 7.7 Hz), 7.02 (d, 1H, *J* = 10.1 Hz), 6.88 (t, 1H, *J* = 8.4 Hz), 6.24 (d, 1H, *J* = 11.6 Hz), 5.88-5.81 (m, 1H), 1.90 (d, 2H, *J* = 8.8 Hz), 1.09-0.98 (m, 21H)

^{13}C NMR (150 MHz, $CDCl_3$): δ 163 (d, *J* = 245 Hz), 140.7 (d, *J* = 7.7 Hz), 131.3, 129.7 (d, *J* = 8.4 Hz), 125.9 (d, *J* = 1.7 Hz), 124.6, 115.5 (d, *J* = 21.2 Hz), 113.1 (d, *J* = 21.1 Hz), 18.8, 12.3, 11.3

IR (neat): 2941, 2865, 1580, 880 cm^{-1}

HRMS (APCI) calcd for $C_{18}H_{30}FSi$ ($[M+H]^+$) 293.2095, found 293.2097



25f **26f**

(*Z*)-(3-(2-chlorophenyl)allyl)triisopropylsilane (26f)

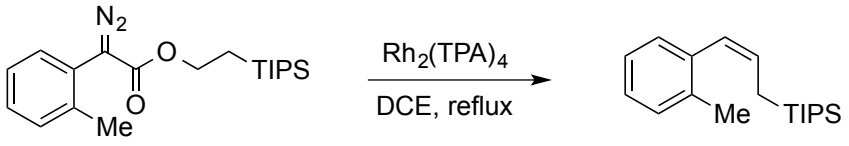
A solution of the diazo **25f** (190 mg, 0.5 mmol, 1.0 equiv.) in 4 mL DCE was added dropwise over 3 hours to a solution of $Rh_2(TPA)_4$ (7.2 mg, 0.005 mmol, 1 mol %) in DCE (2 mL) at reflux. The mixture was stirred at reflux for an additional 15 minutes, cooled to room temperature, and concentrated. The crude was purified by column chromatography (hexanes) to give **26f** as a colorless oil (113 mg, 73% yield).

^{1}H NMR (600 MHz; $CDCl_3$): δ 7.44 (dd 1H, *J* = 7.6, 1.5 Hz), 7.39 (dd, 1H, *J* = 7.9, 1.2 Hz), 7.24 (td, 1H, *J* = 7.6, 1.2 Hz), 7.17 (td, 1H, *J* = 7.9, 1.5 Hz), 6.36 (d, 1H, *J* = 11.4 Hz), 5.96 (dt, 1H, *J* = 11.4, 8.7 Hz), 1.82 (dd, 2H, *J* = 8.7, 1.7 Hz), 1.14-0.97 (m, 21H)

^{13}C NMR (150 MHz, $CDCl_3$): δ 136.4, 134.0, 131.3, 130.8, 129.7, 126.3, 124.4, 18.8, 12.0, 11.3

IR (neat): 2940, 2864, 1469 cm^{-1}

HRMS (APCI) calcd for $C_{18}H_{30}ClSi$ ($[M+H]^+$) 309.1800, found 309, 1803



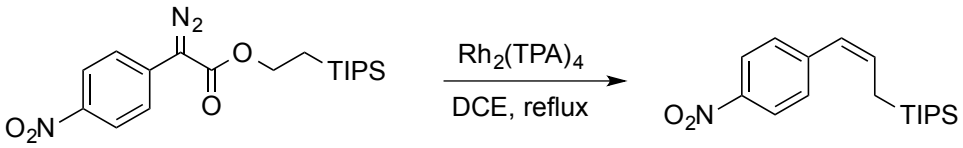
25g **26g**

(*Z*)-(3-(2-methylphenyl)allyl)triisopropylsilane (26g)

A solution of the diazo **25g** (150 mg, 0.42 mmol, 1.0 equiv.) in 4 mL DCE was added dropwise over 3 hours to a solution of $Rh_2(TPA)_4$ (6 mg, 0.0042 mmol, 1 mol %) in DCE (2 mL) at reflux. The mixture was stirred at reflux for an additional 15 minutes, cooled to room temperature, and concentrated. The crude was purified by column chromatography (hexanes) to give **26g** as a colorless oil (89 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.27 (m, 1H), 7.20 – 7.08 (m, 3H), 6.29 (d, *J* = 11.4 Hz, 1H), 5.86 (dt, *J* = 11.4, 8.6 Hz, 1H), 2.24 (s, 3H), 1.76 (dd, *J* = 8.5, 1.8 Hz, 2H), 1.15 – 0.84 (m, 21H)

*partially characterized compound



25h **26h**

(*Z*)-(3-(4-nitrophenyl)allyl)triisopropylsilane (26h)

A solution of the diazo **25h** (150 mg, 0.38 mmol, 1.0 equiv.) in 4 mL DCE was added dropwise over 3 hours to a solution of $Rh_2(TPA)_4$ (5.4 mg, 0.0038 mmol, 1 mol %) in DCE (2 mL) at reflux. The mixture was stirred at reflux for an additional 20 minutes, cooled to room

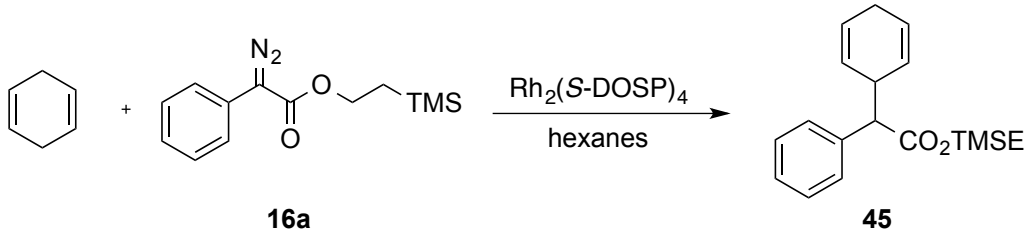
temperature, and concentrated. The crude was purified by column chromatography (pentane) to give **26h** as a colorless oil (72 mg, 60% yield).

^{1}H NMR (600 MHz; $CDCl_3$): δ 8.20 (d, 2H, *J* = 8.7 Hz), 7.47 (d, 2H, *J* = 8.7 Hz), 6.32 (d, 1H, *J* = 11.6 Hz), 6.03 (dt, 1H, *J* = 11.6, 9.0 Hz), 1.95 (dd, 2H, *J* = 9.0, 1.8 Hz), 1.12-0.96 (m, 21H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 145.5, 134.5, 129.4, 125.0, 123.8, 18.8, 13.0, 11.3

IR (neat): 2941, 2889, 2864, 1514, 1338 cm^{-1}

HRMS (APCI) calcd for $C_{18}H_{30}O_2NSi$ ($[M+H]^+$) 320.2040, found 320.2044



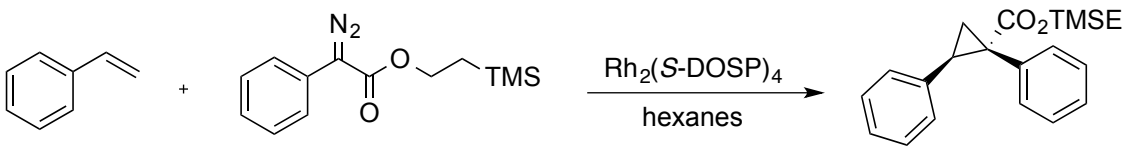
16a **45**

2-(trimethylsilyl)ethyl 2-cyclohexadienyl-2-phenylacetate (45)

A solution of the diazo **16a** (131 mg, 0.5 mmol, 1.0 equiv.) in hexanes (3 mL) was added dropwise over 1 hour to Rh_2(*S*-DOSP)$_4$ (9.3 mg, 0.005 mmol, 1 mol %) and cyclohexadiene (0.24 mL, 2.5 mmol, 5.0 equiv.) in hexanes (3 mL). The volatiles were removed by rotary evaporation, and the crude residue was purified by column chromatography (2% Et_2O in pentane) to give the product **45** as a clear oil (116 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.21 (m, 5H), 5.85 – 5.63 (m, 4H), 5.25 (ddd, *J* = 10.3, 3.5, 1.9 Hz, 1H), 4.27 – 4.06 (m, 2H), 3.37 (d, *J* = 10.5 Hz, 1H), 2.66 – 2.57 (m, 2H), 1.08 – 0.84 (m, 2H), 0.01 – -0.02 (m, 9H)

*partially characterized compound



16a **18a**

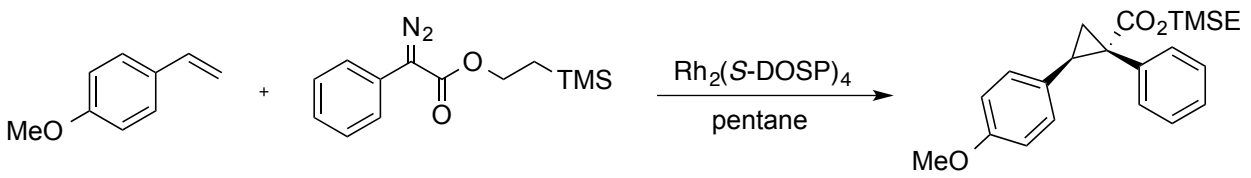
(1*R*,2*S*)-2-(trimethylsilyl)ethyl 1,2-diphenylcyclopropanecarboxylate (18a)

In a 25-mL round bottom flask equipped with a magnetic stir bar, Rh_2(*S*-DOSP)$_4$ (9.28 mg, 0.005 mmol, 1 mol %) and styrene (0.29 mL, 2.5 mmol, 5.0 equiv.) were dissolved in hexanes (3 mL). To this was added a solution of diazo **16a** (131 mg, 0.5 mmol, 1.0 equiv.) in hexanes (3 mL) dropwise over 1 hour. The volatiles were removed by rotary evaporation, and the crude residue was purified by column chromatography (3% EtOAc in hexanes), giving the product **18a** as a clear oil (147 mg, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (m, 3H), 7.09 – 7.04 (m, 3H), 7.04 – 6.98 (m, 2H), 6.82 – 6.73 (m, 2H), 4.27 – 4.10 (m, 2H), 3.11 (dd, *J* = 9.3, 7.3 Hz, 1H), 2.13 (dd, *J* = 9.3, 4.9 Hz, 1H), 1.87 (dd, *J* = 7.2, 4.9 Hz, 1H), 1.00 – 0.84 (m, 2H), -0.03 (s, 9H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.21, 136.76, 135.10, 132.20, 128.27, 127.89, 127.83, 127.12, 126.45, 63.87, 37.92, 33.16, 20.50, 17.44, -1.26

*partially characterized compound



16a **18b**

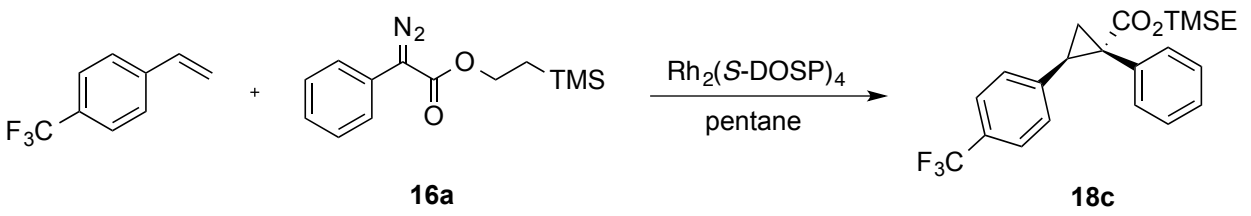
(1*R*,2*S*)-2-(trimethylsilyl)ethyl 2-(4-methoxyphenyl)-1-phenylcyclopropanecarboxylate (18b)

In a 25-mL round bottom flask equipped with a magnetic stir bar, Rh_2(*S*-DOSP)$_4$ (9.28 mg, 0.005 mmol, 1 mol %) and 4-methoxystyrene (0.33 mL, 2.5 mmol, 5.0 equiv.) were dissolved in pentane (3 mL). To this was added a solution of diazo **16a** (131 mg, 0.5 mmol, 1.0 equiv.) in pentane (3 mL) dropwise over 1 hour. The volatiles were removed by rotary evaporation, and the crude residue was purified by column chromatography (3% Et_2O in pentane), giving the product **18b** as a clear oil (133 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 – 7.08 (m, 3H), 7.08 – 6.98 (m, 2H), 6.72 – 6.65 (m, 2H), 6.65 – 6.57 (m, 2H), 4.26 – 4.09 (m, 2H), 3.70 (s, 3H), 3.05 (dd, *J* = 9.4, 7.3 Hz, 1H), 2.10 (dd, *J* = 9.4, 4.9 Hz, 1H), 1.79 (dd, *J* = 7.3, 4.8 Hz, 1H), 0.96 – 0.85 (m, 2H), -0.03 (d, *J* = 0.7 Hz, 9H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.04, 158.00, 135.02, 131.99, 128.97, 128.49, 127.59, 126.79, 113.12, 63.52, 37.31, 32.41, 20.32, 17.18, -1.54

*partially characterized compound



16a **18c**

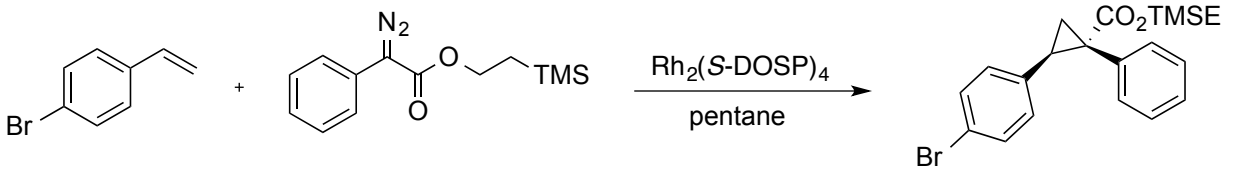
(1*R*,2*S*)-2-(trimethylsilyl)ethyl 1-phenyl-2-(4-(trifluoromethyl)phenyl)cyclopropanecarboxylate (18c)

In a 25-mL round bottom flask equipped with a magnetic stir bar, Rh_2(*S*-DOSP)$_4$ (9.28 mg, 0.005 mmol, 1 mol %) and 4-(trifluoromethyl)styrene (0.37 mL, 2.5 mmol, 5.0 equiv.) were dissolved in pentane (3 mL). To this was added a solution of diazo **16a** (131 mg, 0.5 mmol, 1.0 equiv.) in pentane (3 mL) dropwise over 1 hour. The volatiles were removed by rotary evaporation, and the crude residue was purified by column chromatography (4% Et_2O in pentane), giving the product **18c** as a clear oil (146 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 18.5 Hz, 2H), 7.18 – 7.08 (m, 3H), 7.05 – 6.96 (m, 2H), 6.84 (d, *J* = 8.1 Hz, 2H), 4.26 – 4.10 (m, 2H), 3.13 (dd, *J* = 9.2, 7.1 Hz, 1H), 2.17 (dd, *J* = 9.2, 5.0 Hz, 1H), 1.87 (dd, *J* = 7.2, 5.0 Hz, 1H), 0.96 – 0.84 (m, 2H), -0.04 (s, 9H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.53, 141.01, 134.19, 131.80, 128.16, 127.83, 127.22, 124.51, 63.87, 38.19, 32.22, 20.69, 17.16, -1.58

*partially characterized compound



16a **18d**

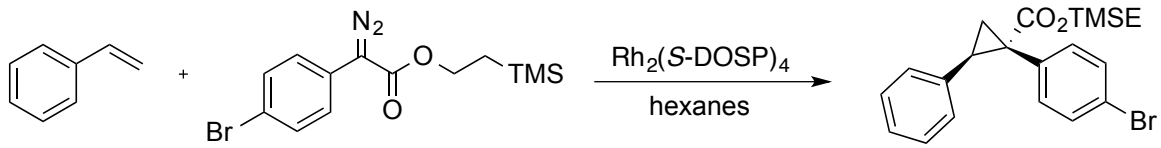
(1*R*,2*S*)-2-(trimethylsilyl)ethyl 2-(4-bromophenyl)-1-phenylcyclopropanecarboxylate (18d)

In a 25-mL round bottom flask equipped with a magnetic stir bar, Rh_2(*S*-DOSP)$_4$ (9.28 mg, 0.005 mmol, 1 mol %) and 4-bromostyrene (0.33 mL, 2.5 mmol, 5.0 equiv.) were dissolved in pentane (3 mL). To this was added a solution of diazo **16a** (131 mg, 0.5 mmol, 1.0 equiv.) in pentane (3 mL) dropwise over 1 hour. The volatiles were removed by rotary evaporation, and the crude residue was purified by column chromatography (3% Et_2O in pentane), giving the product **18d** as a clear oil (154 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 – 7.08 (m, 5H), 7.05 – 6.96 (m, 2H), 6.62 (d, *J* = 8.7 Hz, 2H), 4.25 – 4.07 (m, 2H), 3.04 (dd, *J* = 9.3, 7.2 Hz, 1H), 2.12 (ddd, *J* = 9.3, 5.0, 0.7 Hz, 1H), 1.80 (ddd, *J* = 7.2, 4.9, 0.7 Hz, 1H), 0.95 – 0.84 (m, 2H), 0.03 – -0.07 (m, 9H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.69, 135.76, 134.41, 131.85, 130.72, 129.59, 127.79, 127.10, 120.08, 63.77, 37.75, 32.17, 20.46, 17.17, -1.55

*partially characterized compound



46a **18e**

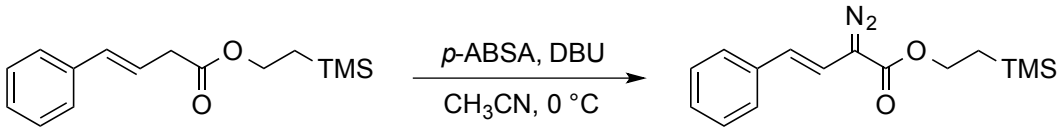
(1*R*,2*S*)-2-(trimethylsilyl)ethyl 1-(4-bromophenyl)-2-phenylcyclopropanecarboxylate (18e)

In a 25-mL round bottom flask equipped with a magnetic stir bar, Rh_2(*S*-DOSP)$_4$ (9.28 mg, 0.005 mmol, 1 mol %) and styrene (0.29 mL, 2.5 mmol, 5.0 equiv.) were dissolved in hexanes (3 mL). To this was added a solution of diazo **46a** (171 mg, 0.5 mmol, 1.0 equiv.) in hexanes (3 mL) dropwise over 1 hour. The volatiles were removed by rotary evaporation, and the crude residue was purified by column chromatography (3% EtOAc in hexanes), giving the product **18e** as a clear oil (173 mg, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 – 7.16 (m, 2H), 7.12 – 7.00 (m, 3H), 6.93 – 6.83 (m, 2H), 6.81 – 6.71 (m, 2H), 4.23 – 4.06 (m, 2H), 3.08 (dd, *J* = 9.3, 7.3 Hz, 1H), 2.11 (dd, *J* = 9.3, 5.0 Hz, 1H), 1.80 (dd, *J* = 7.3, 5.0 Hz, 1H), 0.99 – 0.80 (m, 2H), -0.05 (s, 9H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.39, 135.99, 134.11, 133.60, 130.80, 127.99, 127.87, 126.47, 121.05, 63.81, 37.03, 32.91, 20.12, 17.20, -1.54

*partially characterized compound



46b

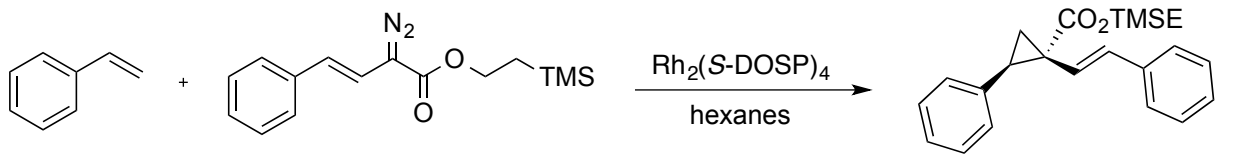
(*E*)-2-(trimethylsilyl)ethyl 2-diazo-4-phenylbut-3-enoate (46b)

The ester (1.0 g, 3.8 mmol, 1.0 equiv.) was dissolved in 50 mL CH_3CN. To this was added *p*-ABSA (1.4 g, 5.7 mmol, 1.5 equiv.), and the mixture was cooled to 0 °C. DBU (1.1 mL, 7.6 mmol, 2.0 equiv.) was added, and the mixture was stirred for 3 hours. The reaction was quenched with saturated aqueous NH_4Cl and extracted with ether, dried over $MgSO_4$, filtered and concentrated. The crude residue was purified by column chromatography (3% Et_2O in pentane), giving the product **46b** as a red solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.28 (m, 4H), 7.24 – 7.16 (m, 1H), 6.49 (d, J = 16.3 Hz, 1H), 6.19 (d, J = 16.3 Hz, 1H), 4.40 – 4.32 (m, 2H), 1.10 – 1.01 (m, 2H), 0.10 – -0.02 (m, 9H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.31, 136.83, 128.67, 127.00, 125.80, 122.83, 111.49, 63.73, 17.60, -1.46 (the resonance resulting from the diazo carbon was not detected)

*partially characterized compound



46b **18f**

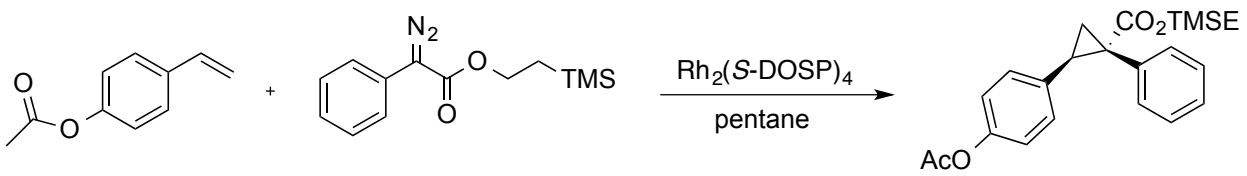
(1*R*,2*S*)-2-(trimethylsilyl)ethyl 1-phenylvinyl-2-phenylcyclopropanecarboxylate (18f)

In a 25-mL round bottom flask equipped with a magnetic stir bar, Rh_2(*S*-DOSP)$_4$ (9.28 mg, 0.005 mmol, 1 mol %) and styrene (0.29 mL, 2.5 mmol, 5.0 equiv.) were dissolved in hexanes (3 mL). To this was added a solution of diazo **46b** (144 mg, 0.5 mmol, 1.0 equiv.) in hexanes (3 mL) dropwise over 1 hour. The volatiles were removed by rotary evaporation, and the crude residue was purified by column chromatography (3% EtOAc in hexanes), giving the product **18f** as a clear oil (141 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 – 7.09 (m, 10H), 6.33 (d, *J* = 16.0 Hz, 1H), 6.14 (d, *J* = 16.0 Hz, 1H), 4.34 – 4.18 (m, 2H), 2.99 (dd, *J* = 9.1, 7.3 Hz, 1H), 2.05 – 1.96 (m, 1H), 1.80 (dd, *J* = 7.3, 5.0 Hz, 1H), 1.03 (t, *J* = 8.4 Hz, 2H), 0.06 – 0.03 (m, 9H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.83, 137.17, 135.66, 132.87, 129.12, 128.36, 127.98, 127.26, 126.72, 126.25, 124.32, 63.59, 34.91, 33.51, 18.47, 17.37, -1.39

*partially characterized compound



16a **18g**

(1*R*,2*S*)-2-(trimethylsilyl)ethyl 2-(4-acetoxyphenyl)-1-phenylcyclopropanecarboxylate (18g)

In a 25-mL round bottom flask equipped with a magnetic stir bar, Rh_2(*S*-DOSP)$_4$ (9.28 mg, 0.005 mmol, 1 mol %) and 4-acetoxystyrene (0.38 mL, 2.5 mmol, 5.0 equiv.) were dissolved in pentane (3 mL). To this was added a solution of diazo **16a** (131 mg, 0.5 mmol, 1.0 equiv.) in pentane (3 mL) dropwise over 1 hour. The volatiles were removed by rotary evaporation, and the crude residue was purified by column chromatography (10% Et_2O in pentane), giving the product **18f** as a clear oil (97 mg, 49% yield).

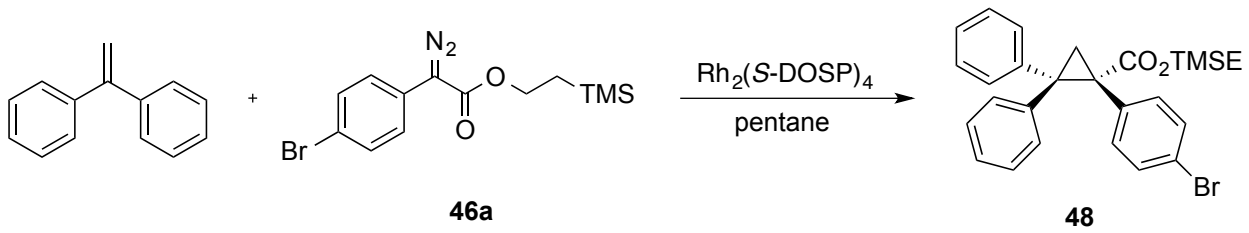
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 – 7.08 (m, 3H), 7.09 – 6.98 (m, 2H), 6.83 – 6.66 (m, 4H), 4.23 – 4.09 (m, 2H), 3.08 (dd, *J* = 8.5, 7.0 Hz, 1H), 2.34 – 2.18 (m, 3H), 2.12 (dd, *J* = 9.4, 4.9 Hz, 1H), 1.81 (dd, *J* = 7.2, 4.9 Hz, 1H), 1.01 – 0.81 (m, 2H), -0.04 (d, *J* = 1.3 Hz, 9H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.81, 169.27, 149.00, 134.61, 134.19, 131.92, 128.84, 127.68, 126.99, 120.69, 63.67, 37.61, 32.22, 21.08, 20.52, 17.17, -1.55

*partially characterized compound

Procedure for low-temperature cyclopropanation studies:

The same procedure was followed as for the preceding cyclopropanation reactions, with cooling of the catalyst and styrene mixture to -40 °C in a bath of dry ice and acetonitrile. The diazo solution was then added at -40 °C, and following addition the mixture was allowed to warm slowly to room temperature.



46a **48**

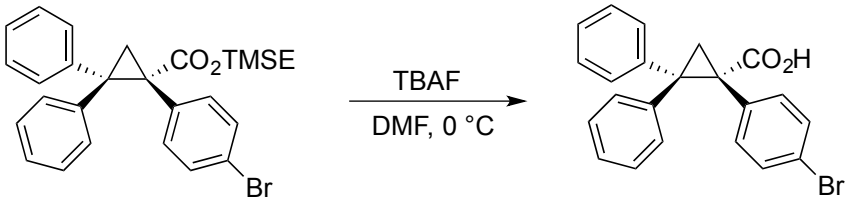
(*R*)-2-(trimethylsilyl)ethyl 1-(4-bromophenyl)-2,2-diphenylcyclopropanecarboxylate (48)

In a 25-mL round bottom flask equipped with a magnetic stir bar, Rh_2(*S*-DOSP)$_4$ (9.28 mg, 0.005 mmol, 1 mol %) and 1,1-diphenylethylene (0.18 mL, 1.0 mmol, 2.0 equiv.) were dissolved in pentane (3 mL). To this was added a solution of diazo **46a** (171 mg, 0.5 mmol, 1.0 equiv.) in pentane (3 mL) dropwise over 1 hour. The volatiles were removed by rotary evaporation, and the crude residue was purified by column chromatography (3% Et_2O in pentane), giving the product **48** as a clear oil (170 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.21 (m, 3H), 7.19 (dd, *J* = 8.6, 1.1 Hz, 2H), 7.05 – 6.91 (m, 5H), 3.87 (ddd, *J* = 11.8, 10.8, 5.8 Hz, 1H), 3.69 (ddd, *J* = 11.9, 10.8, 5.4 Hz, 1H), 2.67 (d, *J* = 5.6 Hz, 1H), 2.36 (d, *J* = 5.6 Hz, 1H), 0.61 (ddd, *J* = 13.6, 11.9, 5.8 Hz, 1H), 0.48 (ddd, *J* = 13.7, 11.8, 5.4 Hz, 1H), -0.09 (d, *J* = 1.1 Hz, 9H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.65, 141.86, 139.38, 135.05, 133.53, 130.58, 130.02, 128.65, 128.30, 127.79, 126.99, 126.33, 121.05, 63.53, 44.54, 42.50, 22.50, 16.84, -1.63

*partially characterized compound



48 **49**

(*R*)-1-(4-bromophenyl)-2,2-diphenylcyclopropanecarboxylic acid (49)

Tetrabutylammonium fluoride hydrate (TBAF) (112 mg, 0.4 mmol, 2.0 equiv.) was added to a solution of cyclopropane **48** (0.1 g, 0.2 mmol, 1.0 equiv.) in 2 mL dimethylformamide (DMF) at 0 ºC, and the reaction was stirred overnight. The reaction was quenched with dH_2O (2 mL) and 6M HCl (1 mL) and stirred for 20 minutes. The reaction was extracted 3x with EtOAc, and the combined extracts were washed 3x with dH_2O, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (25% EtOAc in hexanes), giving the carboxylic acid **49** as a white solid (48 mg, 61% yield).

The spectral data were consistent with that found in the literature[14].