Asymmetric Cyclopropanations by Rhodium(II) *N*-(Arylsulfonyl)prolinate Catalyzed Decomposition of Vinyldiazomethanes in the Presence of Alkenes. Practical Enantioselective Synthesis of the Four Stereoisomers of 2-Phenylcyclopropan-1-amino Acid

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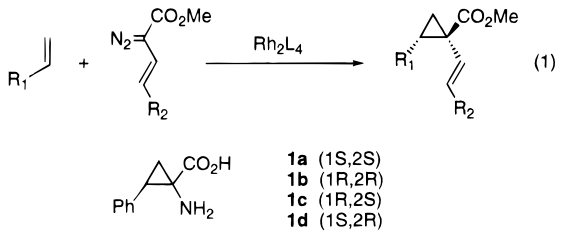
Abstract: The rhodium *N*-(arylsulfonyl)prolinate catalyzed decomposition of vinyldiazomethanes in the presence of alkenes leads to a very general method for the synthesis of functionalized cyclopropanes in a highly diastereoselective and enantioselective mode. A detailed study was undertaken to determine the key factors that control the enantioselectivity of this process. The highest levels of enantioselectivity were obtained using cyclic *N*-(arylsulfonyl)-amino acids as ligands for the dirhodium catalyst, and the optimized catalyst was tetrakis[*N*-[(4-dodecylphenyl)-sulfonyl]-(*L*)-prolinato]dirhodium. The carbenoid structure has a critical effect on the degree of asymmetric induction, and the combination of a small electron-withdrawing group such as a methyl ester and an electron-donating group such as vinyl or phenyl resulted in the highest levels of enantioselectivity. The use of electron neutral alkenes and pentane as solvent also enhanced the enantioselectivity of the process. The synthetic utility of this chemistry was illustrated by its application to the synthesis of all four stereoisomers of 2-phenylcyclopropan-1-amino acid. The occurrence of the highly stereoselective cyclopropanations was rationalized by a model in which the ligands were considered to adopt a D_2 symmetric arrangement.

The cyclopropane ring has drawn great synthetic interest[1] because it is present in a number of useful natural[2] and unnatural products,[3] and can be employed in several stereoselective synthetic processes.[4] In recent years, a number of enantioselective methods have been developed for the construction of the cyclopropane ring.[5−7] A particularly powerful method is the metal-catalyzed decomposition of diazo compounds in the presence of alkenes.[8−10] A new variation of this method is the basis of this paper using vinyldiazomethanes as substrates and chiral rhodium(II) carboxylates as catalysts. This approach leads to the synthesis of highly functionalized vinylcyclopropanes with excellent control of both diastereo- and enantioselectivity (eq 1).[11] The synthetic utility of this chemistry has been illustrated by its application to the synthesis of all four stereoisomers of 2-phenylcyclopropan-1-amino acid (**1**).[7]



Even though the metal-catalyzed asymmetric cyclopropanation of alkenes by diazo compounds has been greatly optimized in recent years through the development of new chiral catalysts, the process still has certain deficiencies. Over the last decade a series of highly effective copper[8] and ruthenium[10] catalysts containing chiral ligands of C_2 symmetry and dimeric rhodium(II) amide complexes of overall C_2 symmetry[9a−h] have been developed. The standard reaction that has been used to evaluate these catalysts has been the asymmetric cyclopropanation of

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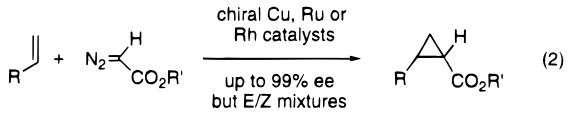
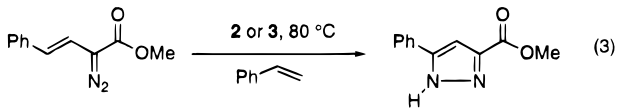
alkenes by diazoacetate derivatives, and many of the catalysts exhibit enantioselectivity of 98% ee or greater (eq 2). In



(2)

general, however, intermolecular cyclopropanations by diazoacetates using rhodium and copper catalysts are not particularly diastereoselective unless extremely bulky ester groups are used,[8e,12] although significant improvements in diastereoselectivity have been recently found using ruthenium catalysis.[10] Furthermore, the chiral catalysts do not have general applicability for asymmetric transformations using other types of diazo compounds. Indeed, the most widely used catalysts for carbenoid transformations are the rhodium(II) carboxylates,[13] but attempts at developing chiral carboxylate catalysts for asymmetric cyclopropanation have met with limited success.[9i,j]

In contrast to diazoacetates, the rhodium(II) carboxylate catalyzed cyclopropanations of vinyldiazomethanes occur with excellent diastereoselectivity.[14] In many instances there is no trace of the second isomer in the ^{1}H NMR spectra of the crude reaction mixtures, and only in the case of alkyl-substituted alkenes and dienes does the diastereoselectivity degrade below 10:1. As the products from these reactions are geminally substituted cyclopropanes that can be further manipulated for the stereoselective construction of other ring systems,[15] we considered that the asymmetric version of this process would be a powerful synthetic transformation. We have previously reported an effective method to achieve asymmetric cyclopropanations with vinyldiazomethanes, but the process required using a stoichiometric amount of a chiral auxiliary on the vinyldiazomethane.[16] In contrast, attempts at chiral catalysis using the traditional chiral catalysts such as Masamune's copper (**2**) and Doyle's rhodium(II) amide (**3**) complexes were unsuccessful because the catalysts were not effective at decomposing vinyldiazomethanes to vinylcarbenoids (eq 3).[16] Consequently, we have explored the possibility of developing chiral rhodium(II) carboxylates as effective catalysts for asymmetric cyclopropanations by vinyldiazomethanes.



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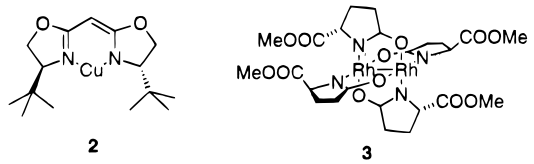

2 **3**

Even though previous attempts at asymmetric cyclopropanation using chiral rhodium(II) carboxylates had not been fruitful, sufficient literature precedence existed to indicate that the rhodium(II) carboxylate scaffold could be employed for the design of useful chiral catalysts.[17,18] Two chiral rhodium(II) carboxylate catalyst systems have shown promise in other asymmetric carbenoid reactions. The prolinate-derived catalyst **4**[17] and the phenylalanine-derived catalyst **5**[18] resulted in moderately high levels of asymmetric induction for intramolecular C−H insertions as illustrated in eqs 4 and 5. Using this precedence as a staring point, we have studied the utilization of these and related catalysts in asymmetric transformations of vinylcarbenoid intermediates. The details of this study are the basis of this paper.

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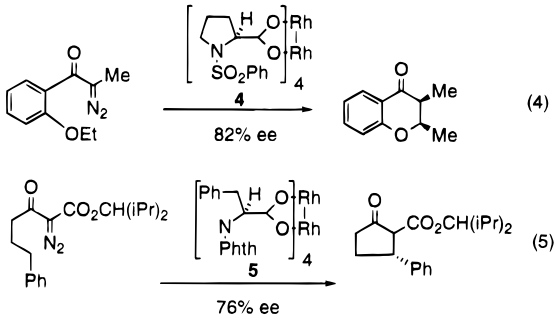
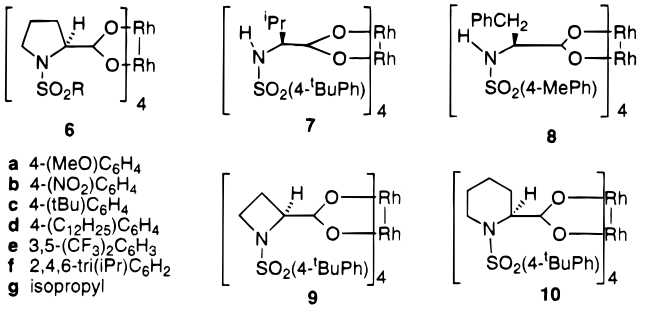
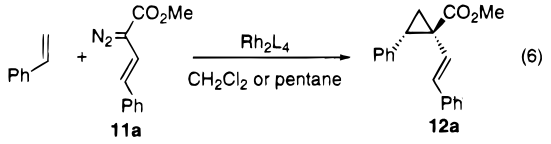


Results

A series of catalysts were readily prepared by high-temperature ligand exchange between the chiral carboxylic acid and rhodium(II) acetate.[19] The majority of these catalysts were prolinate derivatives (**6a**−**i**) that contained different *N*-sulfonyl functionalities. In order to determine how critical the presence of the proline ring would be for high asymmetric induction, the acyclic derivatives **7** and **8**, the azetidinecarboxylate **9** and the picolinate **10** were also prepared.



The evaluation of these catalysts was carried out using the cyclopropanation between methyl 2-diazo-4-phenylbutenoate (**11a**)[20] and styrene with 0.01 equiv of catalyst and dichloromethane as solvent at 25 °C as the standard reaction (eq 6).

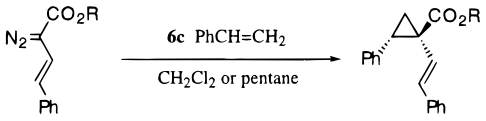


The results are summarized in Table 1. These initial studies were carried out with either 5 or 20 equiv of styrene, but as will be discussed later, either amount of styrene resulted in very similar enantioselectivity and isolated yield of product. In all cases, the diastereoselectivity of these reactions was excellent, favoring the *E*-isomer **12a** over the *Z*-isomer by a ratio of at least 40:1 (typically from 43:1 to 70:1). All the reactions proceeded in moderate to excellent yields ranging from 46% to 91%. Under the traditional conditions for carbenoid reactions using dichloromethane as solvent, all of the *N*-arylsulfonyl prolinate catalysts resulted in the formation of the cyclopropane **12a** with good asymmetric induction (64−83% ee).[21] The absolute stereochemistry of the major isomer of **12a** in all cases was 1*S*,2*S*.[22] Electronic changes on the aryl ring had a minimal effect and high asymmetric induction was obtained with either the 4-methoxyphenyl derivative **6a** (76% ee) or the 4-nitrophenyl derivative **6b** (83% ee). The hydrophobic 4-*tert*-butylphenyl (**6c**) and 4-dodecylphenyl (**6d**) catalysts were prepared in order that the effect of using a hydrocarbon solvent could be explored. The 4-*tert*-butylphenyl catalyst **6c** has rather low solubility in pentane and does not dissolve fully under the catalysis reaction conditions while the 4-dodecylphenyl catalyst **6d** is very soluble in pentane. The change of the reaction solvent from dichloromethane to pentane resulted in a major improvement in enantioselectivity, leading to the formation of **12a** in 90−92% ee. An *N*-arylsulfonyl functionality appears to be a structural requirement for high asymmetric induction because the reaction with the *N*-isopropylsulfonyl catalyst **6g** resulted in the formation of **12a** in only 30% ee. The necessity of the ring system was readily seen from the results with the acyclic derivatives **7** and **8** which also resulted in low levels of enantioselectivity (6−30% ee). Even though a cyclic amino acid derivative is required, certain flexibility in terms of ring size can be tolerated since high levels of asymmetric induction were observed for both the azetidinecarboxylate complex **9** (81% ee) and the pipecolinate complex **10** (81% ee).

Table 1. Effect of Catalysts and Solvent on Asymmetric Induction

catalyst	solvent	ee, % (abs config)	catalyst	solvent	ee, % (abs config)
4	CH_2Cl_2	74 (1*S*,2*S*)	**6e**	CH_2Cl_2	75 (1*S*,2*S*)
6a	CH_2Cl_2	76 (1*S*,2*S*)	**6f**	CH_2Cl_2	61 (1*S*,2*S*)
6b	CH_2Cl_2	83 (1*S*,2*S*)	**6g**	CH_2Cl_2	30 (1*S*,2*S*)
6c	CH_2Cl_2	74 (1*S*,2*S*)	**7**	CH_2Cl_2	30 (1*S*,2*S*)
6c	pentane	90 (1*S*,2*S*)	**8**	CH_2Cl_2	6 (1*S*,2*S*)
6d	CH_2Cl_2	79 (1*S*,2*S*)	**9**	pentane	81 (1*S*,2*S*)
6d	pentane	92 (1*S*,2*S*)	**10**	pentane	81 (1*S*,2*S*)

Table 2. Effect of Ester Size on Asymmetric Induction



substrate	R	solvent	ee, % (abs config)
11a	OMe	CH_2Cl_2	74 (1*S*,2*S*)
11a	OMe	pentane	90 (1*S*,2*S*)
11b	OEt	CH_2Cl_2	68 (1*S*,2*S*)
11b	OEt	pentane	84 (1*S*,2*S*)
11c	O^{i}Pr	CH_2Cl_2	43 (1*S*,2*S*)
11c	O^{i}Pr	pentane	76 (1*S*,2*S*)
11d	O^{t}Bu	CH_2Cl_2	9 (1*S*,2*S*)
11d	O^{t}Bu	pentane	50 (1*S*,2*S*)

For all the chiral catalysts that have been developed for asymmetric cyclopropanation using diazoacetate as substrate, very large improvements in asymmetric induction have been observed on increasing the size of the ester group.[8−10] Consequently, we examined the effect of changing the ester size from methyl to *tert*-butyl with a series of vinyldiazomethane derivatives **11a**−**d**, and the results are summarized in Table 2. In contrast to the previous studies on diazoacetate derivatives, increasing the ester size of the vinyldiazomethanes caused a drastic loss of enantioselectivity while the diastereoselectivity was essentially unaltered. The reactions were carried out in both dichloromethane and pentane as solvent, and in each solvent system a steady drop in enantioselectivity was observed

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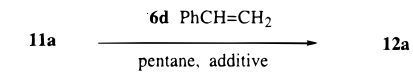
(21) Enantiomeric excesses (% ee) were determined by ^{1}H NMR using tris[3-[(heptafluoropropyl)hydroxymethylene]-(−)-camphorato]praseodymium-(III) as a chiral shift reagent and intergration of the split methoxy signal, or by HPLC using a Diacel Chiralcel OJ analytical column (see ref 29).

(22) The absolute configuration of **12a** was determined by comparison of the optical rotation of **12a** with that of an authentic sample (see ref 16).

(23) The major enantiomer for **12b**−**d** was assigned as (1*S*,2*S*) on the basis of the ORD spectra of **12b**−**d** similar to that of **12a**.

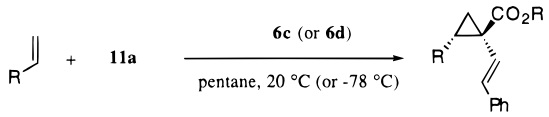
Table 3. Effect of Temperature and Equivalence of Catalyst on Asymmetric Induction



temp, °C	amt of catalyst, equiv	amt of additive, equiv	ee, % (abs config)
25	0.01	−	92 (1*S*,2*S*)
98[a]	0.01	−	82 (1*S*,2*S*)
69[b]	0.01	−	86 (1*S*,2*S*)
35	0.01	−	91 (1*S*,2*S*)
−20	0.01		93 (1*S*,2*S*)
−78	0.01	−	98 (1*S*,2*S*)
25	0.001	−	87 (1*S*,2*S*)
25	0.0001	−	50 (1*S*,2*S*)
25	0.001	acetate (0.01)	89 (1*S*,2*S*)
25	0.001	prolinate (0.01)	90 (1*S*,2*S*)
25	0.0001	acetate (0.01)	67 (1*S*,2*S*)
25	0.0001	prolinate (0.01)	61 (1*S*,2*S*)

[a] Reaction carried out in refluxing heptane. [b] Reaction carried out in refluxing hexane.

Table 4. Effect of Alkene Structure on Asymmetric Induction



catalyst	temp, °C	R	product	ee, % (abs config)	yield, %
6c	25	C_6H_5	**12a**	90 (1*S*,2*S*)	79
6d	−78	C_6H_5	**12a**	98 (1*S*,2*S*)	68
6c	25	*p*-ClC_6H_4	**13**	89 (1*S*,2*S*)	91
6d	−78	*p*-ClC_6H_4	**13**	>97 (1*S*,2*S*)	70
6c	25	*p*-$MeOC_6H_4$	**14**	83 (1*S*,2*S*)	87
6d	−78	*p*-$MeOC_6H_4$	**14**	90 (1*S*,2*S*)	41
6c	25	AcO	**15**	76	40
6d	−78	AcO	**15**	95	26
6c	25	EtO	**16**	59	83
6d	-78	EtO	**16**	93	65
6c	25	^{n}Bu	**17**	>90	63
6c	25	Et	**18**	>95	65
6c	25	^{i}Pr	**19**	95	58

on increasing the size of the ester group from methyl to ethyl to isopropyl to *tert*-butyl (from 74% to 9% ee in dichloromethane and from 90% to 50% ee in pentane).[21,23]

The next series of experiments examined the effects of the reaction temperature and the amount of catalyst on these transformations (Table 3). The 4-dodecylphenylprolinate catalyst **6d** was used because it is the most soluble in hydrocarbon solvents. As can be seen in entries 1−5, the temperature of the reaction (+98 to −78 °C) had a significant effect on the extent of asymmetric induction (82−98% ee). Particularly impressive is the fact that **6d** is still an effectice catalyst even at −78 °C. All of the initial standard reactions were carried out using 0.01 equiv of catalyst. In order to determine the minimum amount of catalyst that would be required in this chemistry, the reaction was examined using decreasing amounts of catalyst. On using 0.001 equiv of **6d** instead of the standard 0.01 equiv, a slight drop in enantioselectivity was observed (from 92% to 87% ee) while on decreasing the amount of catalyst to 0.0001 equiv, the enantioselectivity dropped to 50% ee and the reaction stopped at 50% completion. One possible cause of the drop of enantioselectivity could be dissociation of the carboxylate ligand; therefore, further experiments were carried out with carboxylate ligands as additives. Addition of 0.1 equiv of acetic acid or 0.1 equiv of *N*-[(4-dodecylphenyl)-sulfonyl]proline had very little effect on the asymmetric induction using either 0.001 or 0.0001 equiv of **6d**. This result would indicate that ligand exchange reactions are not the cause of the drop in enantioselectivity when very small quantities of chiral catalyst are used. Instead, general catalyst degradation or poisoning is probably occurring.

Under the standard reaction conditions either 5 or 20 equiv of styrene was used to trap the carbenoid intermediate. Excess styrene was used because with most intermolecular carbenoid reactions, ineffective capture of the carbenoid would occur unless extremely slow rates of diazoalkane addition using syringe pump techniques are employed.[24] Even though the excess styrene can be readily recovered, such an excess of trapping agent would be unacceptable for expensive alkenes. Consequently, the effect of alkene concentration on both the yield and enantioselectivity of cyclopropanation product was examined. Remarkably, both the yield (83−89%) and enantioselectivity (90−92% ee) of the reaction remained virtually unchanged on varying the amount of styrene used from 20 to 1.2 equiv, and this was achieved without resorting to syringe pump techniques for vinyldiazomethane addition.

A series of experiments using monosubstituted alkenes were then carried out to determine the effect of the electronic nature of the alkene on asymmetric induction, and these results are summarized in Table 4. The initial series of experiments were carried out at room temperature using **6c** as catalyst. A steady drop in enantioselectivity was observed with electron rich alkenes as seen for the cyclopropanes **12a**−**16** (90−59% ee), while simple alkyl-substituted alkenes resulted in the formation of the cyclopropanes **17**−**19** with very high levels of enantioselectivity (>90% ee).[25,26] Even though the enantioselectivity is exceptionally high in the case of simple alkenes, some degradation in diastereoselectivity (from >40:1 to ∼15:1) is observed. Further improvement in enantioselectivity was possible by carrying out these reactions at −78 °C using **6d** as catalyst. Under these conditions all the reactions proceeded in >90% ee, although the isolated yields were slightly lower than the reactions carried out at room temperature.

Extension of the reaction to more substituted alkenes was then examined. In the case of a 1,1-disubstituted alkene such as 2-methylpropene, an exceptionally high level of enantioselectivity (95% ee)[26] in the formation of the cyclopropane **20** was observed. We have found that vinylcarbenoids typically fail to react with *trans*-alkenes,[27,28] and this was verified in the rhodium(II) prolinate catalyzed reactions by using *cis*- and *trans*-2-butenes as substrates. Rhodium(II) prolinate **6d** catalyzed decomposition of **11a** in the presence of *cis*-2-butene resulted in the formation of the *meso* compound **21** in 80% yield. In contrast, a mixture of products was formed in the parallel reaction of **11a** with *trans*-2-butene, from which no cyclopropane product was isolable. These results underscore the inability of vinylcarbenoids to react with *trans*-alkenes. A further example of the reaction with a *cis*-alkene was carried out at −78 °C using 2,3-dihydrofuran as substrate, and this resulted in the formation of the fused cyclopropane **23** in 86% ee and 84% yield.

(24) Doyle, M. P.; Van Leusen, D.; Tamblyn, W. H. *Synthesis* **1981**, 787.

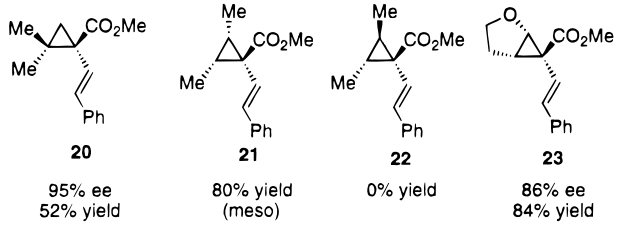
(25) The absolute configurations for **13** and **14** have been assigned on the basis of the ORD spectra of these compounds similar to that of **12a**.

(26) The absolute configurations assigned for **15**−**20** and **23** are tentative and are based on the proposed transition state model for the asymmetric induction.

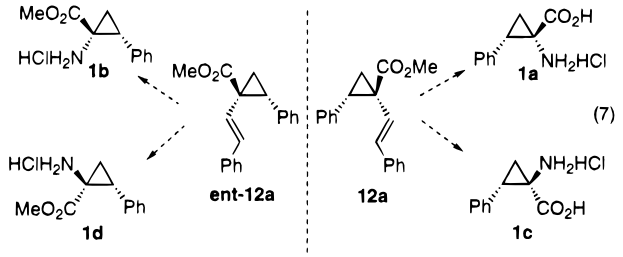
(27) Davies, H. M. L.; Clark, T. J.; Smith, H. D. *J. Org. Chem.* **1991**, *56*, 3817.

(28) Davies, H. M. L.; Hu, B. *J. Org. Chem.* **1992**, *57*, 3186.

(29) Davies, H. M. L.; Peng, Z.-Q.; Houser, J. H. *Tetrahedron Lett.* **1994**, *35*, 8939.

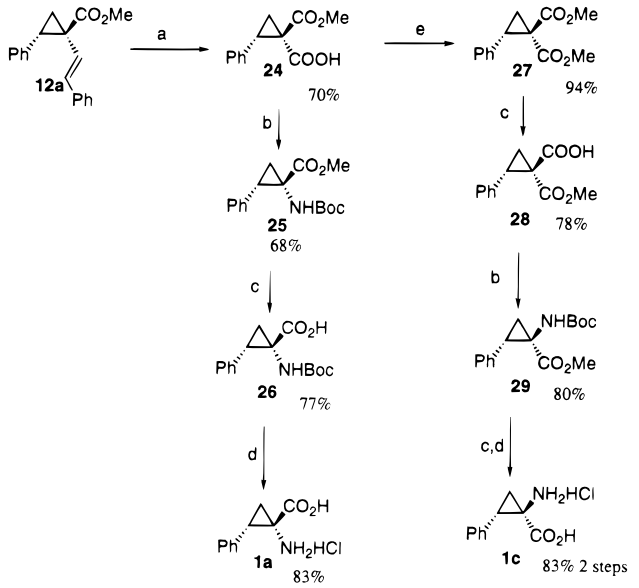


In principle, the asymmetric cyclopropanations between vinylcarbenoids and alkenes offer numerous synthetic opportunities. We have already communicated how the reaction between vinylcarbenoids and dienes can lead to a tandem asymmetric cyclopropanation/Cope rearrangement, leading to a general enantioselective synthesis of seven-membered rings.[29] This study showed that the asymmetric cyclopropanation can be carried out with a variety of diazovinylacetate derivatives and is not limited to the 4-phenyl-2-diazobutenoate system. Another application of this chemistry has recently been described by Corey, leading to the enantioselective synthesis of sertraline.[30] The asymmetric vinylcarbenoid chemistry also appears to offer a very practical approach for the asymmetric construction of cyclopropanamino acids as illustrated for the phenylcyclopropane **12a** (eq 7). Either of the diastereomeric cyclopropanamino acids **1a** and **1c** should be obtainable from **12a** while the corresponding enantiomers **1b** and **1d** should be obtainable from ***ent*-12a**.



The approach that was used to prepare the four phenylcyclopropanamino acids **1a**−**d** is shown in Scheme 1. Either enantiomer of the phenylcyclopropane **12a** or ***ent*-12a** can be obtained enantiomerically pure by decomposition of **11a** in the presence of styrene under the optimized reaction conditions using the appropriate enantiomer of the catalyst **6d** (92% ee, 83% yield), followed by a single recrystallization from 2-propanol (70% recovery). The vinyl portion in the cyclopropane **12a** was oxidatively cleaved with $RuCl_3 \cdot H_2O/NaIO_4$[31] to give the corresponding acid **24** in 70% yield. Treatment of the acid **24** with diphenylphosphoryl azide[32] resulted in a Curtius rearrangement, and the intermediate isocycanate was trapped by *tert*-butyl alcohol. The crude product was treated with di-*tert*-butyl dicarbonate to protect any free amine byproduct that was formed, and this led to the formation of the Boc-protected amine **25** in 68% overall yield after recrystallization. The methyl ester was then hydrolyzed to give the acid **26** in 77% yield, which was then readily converted to the amine **1a** as its hydrochloride salt by treatment in 3 N HCl in EtOAc[33] in 83% yield. The second diastereomer **1c** was readily obtained by first treatment of **24** with Me_2SO_4/K_2CO_3 to form the diester **27** (94% yield). Selective hydrolysis of the ester *trans* to the phenyl ring

Scheme 1[a]



[a] Conditions (a) $RuCl_3/NaIO_4$. (b) (1) NEt_3, DPPA, ^tBuOH; (2) $((CH_3)_3COCO)_2O$. (c) ^-OH. (d) 3 M HCl/EtOAc. (e) K_2CO_3, Me_2SO_4.

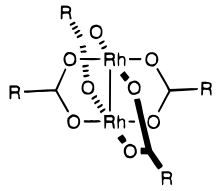


Figure 1.

in **27** was then readily achieved using NaOH in methanol[34] to give **28** in 75% yield after recrystallization. The acid **28** was then converted to the Boc-protected amine **29** in 76% yield using the Curtius rearrangement conditions[32] described above. The ester in **29** was then hydrolyzed with $LiOH \cdot H_2O$ in methanol and water,[7c] and the crude material was directly converted to the amine **1c** as its hydrochloride salt in 83% overall yield with 3 N HCl in EtOAc.[33] The other two stereoisomers of phenylcyclopropanamino acid **1b** and **1d** were readily obtained using the above procedures starting from ***ent*-12a.**

Discussion

Considering that it has been previously suggested that the rhodium carboxylate framework was far from ideal for the development of chiral catalysts,[35] the high levels of asymmetric induction that we have obtained with the rhodium(II) prolinate/vinyldiazomethane system deserve further comment. The basic structure of the rhodium(II) carboxylate core has been well established through a number of X-ray structure determinations.[18b,36] The rhodium complex is dimeric in nature with four bridging carboxylate ligands as shown in Figure 1, and it is generally assumed that the complex remains dimeric during the catalytic process.[13] The empty axial positions have been postulated to be the site of catalytic activity, and as there are two axial sites and all the carboxylate groups are pointing away from these sites, it was considered that chiral carboxylates would not lead to efficient chiral catalysts. Clearly, this is not the case with the rhodium prolinate system, and the issue that needs

(30) Corey, E. J.; Gant, T. G. *Tetrahedron Lett.* **1994**, *35*, 5373.
(31) Carlsen, P. H. J.; Katsuki, T.; Martin, V. S.; Sharpless, K. B. *J. Org. Chem.* **1981**, *46*, 3936.
(32) Ninomiya, K.; Shiori, T.; Yamada, S. *Tetrahedron* **1974**, *30*, 2151.
(33) Stahl, G. L.; Walter, R.; Smith, C. W. *J. Org. Chem.* **1978**, *43*, 2285.
(34) De Kimpe, N.; Boeykens, M.; Tehrani, K. A. *J. Org. Chem.* **1994**, *59*, 8215.
(35) Doyle, M. P. *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 305.
(36) Cotton, F. A.; DeBoer, B. G.; LaPrade, M. D.; Ripal, J. R.; Ucko, D. A. *Acta Crystallogr.* **1971**, *B27*, 1664.

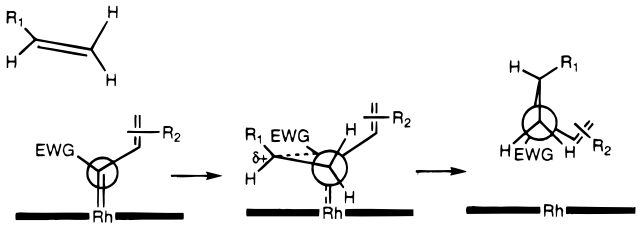


Figure 2.

to be addressed is how the arrangement of the four prolinate ligands around the dirhodium core can lead to a complex that can induce such high enantioselectivity.

The direction of attack of the alkene to the rhodium/vinylcarbenoid complex will be critical in setting up the asymmetric induction. It is generally accepted that the cyclopropanation by rhodium-stabilized carbenoids occurs in a concerted nonsynchronous mode, and models of the approach of the alkene have been postulated to explain the stereochemical preferences in the reactions with diazoacetate derivatives.[37] Rhodium/carbenoid cyclopropanations occur with retention of alkene configuration[37a] while buildup of charge during a nonsynchronous cyclopropanation is consistent with the common occurrence of side products due to the intermediacy of zwitterionic intermediates when the carbenoid is very electron deficient and the alkene is electron rich.[37a,38]

The two most striking features of vinylcarbenoid cyclopropanations are the excellent diastereoselectivity of the process and the total lack of reactivity of vinylcarbenoids toward *trans*-alkenes in intermolecular reaction. This second feature is reminiscent of the epoxidation chemistry of metal oxo species where preferred reaction with *cis*-alkenes has been the basis of a proposal that the attack of the alkene occurs in a side-on approach.[39] In related studies, we have shown that the structure of the carbenoid has a profound effect on the stereoselectivity of the cyclopropanation.[11b] For example, in contrast to vinyldiazomethanes, cyclopropanation of styrene by ethyl diazoacetate using **6c** as catalyst resulted in a 1.2:1 *E*/*Z* mixture of cyclopropanes with the *E*- and *Z*-isomers formed in 6% and 30% ee, respectively. In the case of carbenoids containing both an electron-withdrawing group (such as an ester) and an electron-donating group (such as an alkene or phenyl), highly stereoselective cyclopropanations are routinely observed.

The most reasonable mechanism that is consistent with all these observations is shown in Figure 2. The alkene approaches the vinylcarbenoid side-on in a nonsynchronous mode from the side of the electron-withdrawing group with its bulky functionality pointing away from the face of the rhodium complex. A *trans*-alkene is unreactive because it is unable to avoid having a substituent pointing directly toward the rhodium surface. As the reaction proceeds, the alkene would need to rotate outward to form the cyclopropane ring, where R would end up on the same side as the vinyl group, leading to the observed stereochemistry. The nonsynchronous nature of the reaction appears to be important for the diastereoselection because the highest diastereoselectivity is observed when the alkene is electron rich, a situation that would enhance charge buildup in the transition

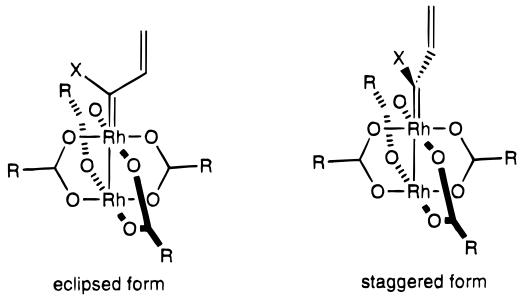


Figure 3.

state. The distinction between the electron-withdrawing group (ester) and the electron-donating group (vinyl or phenyl) on the carbenoid appears to be crucial and is supported by this work and earlier studies,[14] which showed a drop in diastereoselectivity when the vinyl group contained a second electron-withdrawing group. As the site of attack of the alkene on the vinylcarbenoid is dependent on electronic factors (approach on the side of the electron-withdrawing group instead of the electron-donating group), the high diastereoselectivity is not noticeably affected by steric factors either at the vinyl position or on the electron-withdrawing group. Presumably, in carbenoid systems lacking the combination of donor/acceptor functionality, the trajectory for alkene approach is less rigorously defined, leading to lower overall diastereoselectivity.

The next issue that was considered was what the preferred interaction between the rhodium complex and the carbenoid would be. The answer to this question was approached by MM2 followed by extended Hückel calculations on the interaction between rhodium(II) acetate and a vinylcarbene.[40] The results indicated that the carbene would preferentially line up staggered to the oxygen ligands of the carboxylates rather than in an eclipsed orientation (Figure 3). This would seem reasonable on steric grounds, but also, a staggered arrangement is required for stabilization of the carbenoid ligand by metal back-bonding because at least in the rhodium(II) dimer, the d_{yz} and d_{xz} orbitals are hybridized to from two new orbitals that lie in this staggered position.[41] The staggered arrangement of the carbenoid was also proposed in Doyle's model to explain the enantioselectivity induced by the rhodium(II) carboxamide catalysts,[31] although the requirement of such an arrangement for the occurrence of back-bonding was not considered.[42]

Even with a well-defined approach of the alkene to the vinylcarbenoid complex and with the expectation that the vinylcarbenoid would exist in a staggered arrangement to the dirhodium core, further stereochemical issues must be involved to explain the high enantioselectivity observed in these cyclopropanations. At this stage of the discussion there are eight possible orientations for the bonding of the vinylcarbenoid to the rhodium core. Further insight into the three-dimensional structure of the rhodium(II) prolinate catalysts was obtained by MM2 modeling studies using X-ray-determined bond lengths and angles for the rhodium carboxylate core. Even though the modeling failed to generate well-defined minima, it became clear that the prolinate ligands caused certain steric constraints. In particular, by using a cyclic amino acid ligand such as prolinate, crowding occurs when the NSO_2Ar group adopts a position at

(37) (a) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919. (b) O'Bannon, P. E.; Dailey, W. P. *J. Org. Chem.* **1989**, *54*, 3096. (c) Brown, K. C.; Kodadek, T. *J. Am. Chem. Soc.* **1992**, *114*, 8336.

(38) (a) Alonso, M. E.; Morales, A.; Chitty, A. W. *J. Org. Chem.* **1982**, *47*, 3747. (b) Alonso, M. E.; Jano, P.; Hernandez, M. I.; Greenberg, R. S.; Wenkert, E. *J. Org. Chem.* **1983**, *48*, 3047. (c) Alonso, M. E.; Garcia, M. C. *J. Org. Chem.* **1985**, *50*, 988. (d) Wenkert, E.; Alonso, M. E.; Buckwalter, B. L.; Sanchez, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 2021.

(39) Jacobsen, E. N. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH Publishers: New York, 1993; pp 159−202.

(40) Calculations were carried out on a CAChe STEREO Worksystem using the standard software programs supplied by CAChe Scientific, Beaverton, OR.

(41) (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Clarendon Press: Oxford, 1993; p 672. (b) Norman, J. G., Jr.; Kolari, H. J. *J. Am. Chem. Soc.* **1978**, *100*, 791.

(42) Pirrung, M. C.; Morehead, A. T., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 8991.

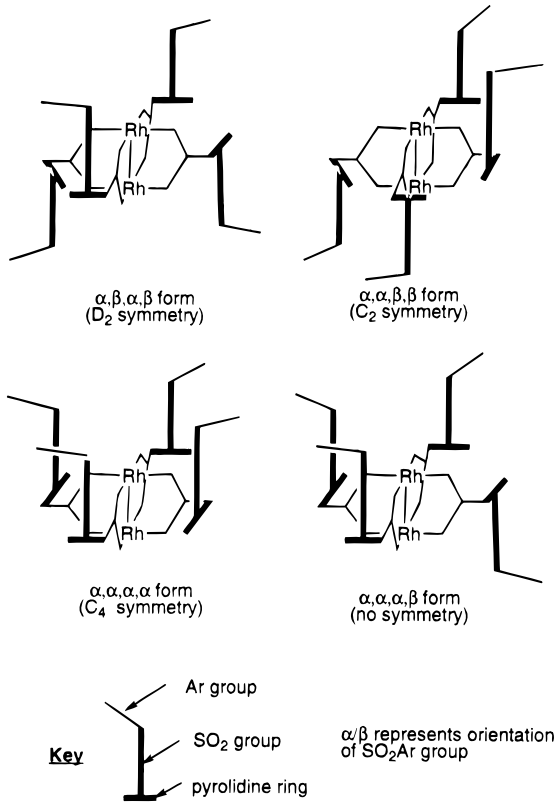


Figure 4.

the periphery of the rhodium carboxylate core. Consequently, the NSO_2Ar group preferentially adopts either an up (α) or a down (β) arrangement. The effect of this is to place the arylsulfonyl groups sufficiently close to influence the site of carbenoid coordination such that a reasonable mechanism for asymmetric induction is possible.

Consideration of this type of arrangement for the NSO_2Ar group for all four ligands would lead to four possible orientations, and these are illustrated in Figure 4. The α, α, α, α form would have C_4 symmetry, the α, α, β, β form would have C_2 symmetry, the α, β, α, β form would have D_2 symmetry, and the α, α, α, β form would lack high symmetry. Two of these forms are highly unlikely to cause the cyclopropanation to occur with high enantioselectivity. The α, α, α, β form lacks any simplifying symmetry elements, and thus cyclopropanation through this form would be expected to have a large number of possible transition states, leading to low overall enantioselectivity. As the α, α, α, α form does not have a symmetry axis of rotation perpendicular to the rhodium−rhodium bond, the two rhodium faces are different; one face is shielded while the other is open but unlikely to exhibit great asymmetric induction. The most promising conformation is the α, β, α, β form. Due to the symmetry of the system both faces of the catalyst would give the same asymmetric induction, and only two distinct staggered orientations are possible, and of these, one is very crowded. The alternative α, α, β, β form is also reasonable as both faces of the catalyst would give the same asymmetric induction, but due to the lower symmetry compared to the α, β, α, β form there are twice as many staggered orientations possible for the carbenoid/rhodium complex.

Even though at this stage it is difficult to rule out all the possible conformations available to the rhodium prolinate catalyst, all the stereochemical results that we have obtained so far can be rationalized by proposing that the catalysis occurs through the D_2 symmetric α, β, α, β conformation of the complex.[13] This can be represented in the diagram shown in

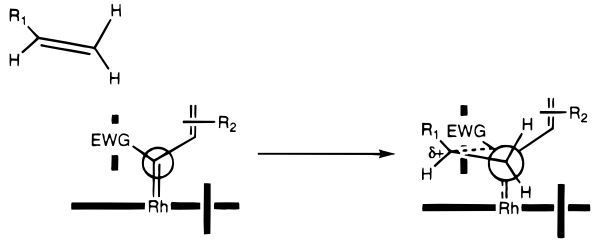


Figure 5.

Figure 5 where the thickened lines represent the steric influence of the arylsulfonyl group. Due to the symmetry of the system only one face of the catalyst needs to be considered. Assuming once again that the alkene approaches side-on over the electron-withdrawing group, then in the model shown in Figure 5, attack from the back is inhibited by the effect of the arylsulfonyl group. The effect of the arylsulfonyl group would be greatest when the transition state requires close approach of the alkene to the carbene, and this would be consistent with the observation that electron rich alkenes result in lowered enantioselectivity as these substrates would be expected to have earlier transition states. Presumably, nonpolar solvents would favor less charge separation[43] and a later transition state, and this is consistent with the significantly enhanced enantioselectivity observed when hydrocarbons are used as solvent instead of dichloromethane. Increasing the size of the ester group causes an unfavorable steric effect between the ester group and the sulfonyl group, and so, the ester is forced to bend away from the SO_2, and this would block the originally open face of the carbenoid. This would explain why bulky ester groups result in significantly lower enantioselectivity. The low enantioselectivity observed with the other diazoacetate systems is presumably because they lack the donor/acceptor functionality combination of the vinyldiazoacetate system. The overall effect of this would be to increase greatly the flexibility on how the alkene can approach the carbene.

In summary, the rhodium prolinate catalyzed decomposition of vinyldiazomethanes in the presence of alkenes leads to a very general method for the synthesis of functionalized cyclopropanes in a highly diastereoselective and enantioselective mode. The synthesis of all four stereoisomers of 2-phenylcyclopropanamino acid underscores the potential of this chemistry for asymmetric synthesis. In a recent review on the synthesis of cyclopropanamino acids, our earlier approach using a chiral auxiliary on the vinylcarbenoid was considered to be "possibly the most practical synthesis of 2*R*,3*R*-cyclo-Phe published to date".[1a] The new approach described herein using a chiral catalyst is much more practical and general than our earlier strategy, and should enable a wide range of cyclopropanamino acids to be readily prepared with high enantioselectivity.

A model has been presented to explain the highly stereoselective cyclopropanations that were observed. The most exciting feature of this model is that it leads to the suggestion that a new approach for designing chiral catalysts of high symmetry would be by appropriate arrangement of fairly simple ligands in a complex instead of by the traditional approach which entails the use of elaborate ligands of defined symmetry. Further studies are in progress to exploit other aspects of these asymmetric cyclopropanations in organic synthesis. Also, we are in the process of testing the working model for asymmetric induction through the design and evaluation of new catalysts

(43) (a) Davies, H. M. L.; Saikali, E.; Clark, T. J.; Chee, E. H. *Tetrahedron Lett.* **1990**, *31*, 6299. (b) Davies, H. M. L.; Saikali, E.; Young, W. B. *J. Org. Chem.* **1991**, *56*, 5696. (c) Padwa, A.; Austin, D. J.; Xu, S. L. *J. Org. Chem.* **1992**, *57*, 1330.

that are conformationally constrained such that they are forced to adopt a D_2 symmetric arrangement.

Experimental Section

General Procedures. ^{1}H NMR spectra were run at 200, 300, 400, or 500 MHz and ^{13}C NMR spectra at either 50.3 or 75 MHz with the sample solvent being $CDCl_3$ unless otherwise noted. Mass spectral determinations were carried out at 70 eV. THF, diethyl ether, and hexanes were dried over and distilled from sodium metal with benzophenone as the indicator. CH_2Cl_2 was dried over and distilled from CaH_2. Pentane was dried over activated molecular sieves (4 Å) for 24 h prior to use. Column chromatography was carried out on silica gel 60 (230−400 mesh). Commercially available reagents were used without additional purification unless noted. Melting points are uncorrected. Ligands for catalysts **6**−**10** were prepared by treatment of the desired amino acid with the appropriate sulfonyl chloride according to the published procedure.[44] The diazo compounds methyl 2-diazo-4-phenyl-3-butenoate (**11a**), ethyl 2-diazo-4-phenyl-3-butenoate (**11b**), isopropyl 2-diazo-4-phenyl-3-butenoate (**11c**), *tert*-butyl 2-diazo-4-phenyl-3-butenoate (**11d**), and tetrakis[*N*-(phenylsulfonyl)-(*L*)-prolinato]dirhodium (**4**)[19] were prepared according to literature procedures.

General Procedure for High-Temperature Ligand Exchange.[19] A mixture of the carboxylate ligand (5−10 equiv) and dirhodium tetraacetate (1 equiv) in chlorobenzene was refluxed through a Soxhlet extractor filled with $CaCO_3$ under an argon atmosphere for 6 days, while the $CaCO_3$ in the thimble was changed every 2 days. The mixture was then concentrated *in vacuo*, and the residue was dissolved in CH_2Cl_2. The mixture was then washed with saturated $NaHCO_3$, dried (Na_2SO_4), and then concentrated *in vacuo*. The residue was purified on silica using ether/petroleum ether as the eluent in the ratio specified in parentheses. The amounts of carboxylate ligand, rhodium acetate, and solvent are presented in that order in abbreviated form.

Tetrakis[*N*-[(4-methoxyphenyl)sulfonyl]-(*L*)-prolinato]dirhodium (6a): (0.531 g, 1.9 mmol), (0.08 g, 0.19 mmol), (40 mL), (1:0); yield 0.212 g of a green solid (mp 202−205 °C) (85%); IR ($CDCl_3$) 3162, 2946, 1730, 1602 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.73 (d, 8 H, J = 8.2 Hz), 7.03 (d, 8 H, J = 8.2 Hz), 4.43−4.28 (br s, 4 H), 3.87 (s, 12 H), 3.35−3.00 (m, 8 H), 2.20−1.73 (m, 12 H), 1.70−1.50 (s, 4 H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 192.6, 162.7, 130.2, 139.7, 114.2, 61.8, 55.7, 48.2, 31.3, 24.9. Anal. Calcd for $C_{48}H_{56}N_4O_{20}Rh_2S_4$: C, 42.93; H, 4.20; N, 4.17. Found: C, 43.05; H, 4.35; N, 4.14.

Tetrakis[*N*-[(4-nitrophenyl)sulfonyl]-(*L*)-prolinato]dirhodium (6b): (0.435 g, 1.8 mmol), (0.08 g, 0.18 mmol), (40 mL), (1:0); yield 0.048 g of a green solid (mp 228−230 °C) (19%); IR ($CDCl_3$) 2974, 1729, 1603 1532 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.35 (d, 8 H, J = 8.70 Hz), 8.00 (d, 8 H, J = 8.70 Hz), 4.40−4.28 (m, 4 H), 3.37−3.15 (m, 12 H), 2.10−1.78 (m, 12 H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 191.9, 150.0, 144.1, 128.7, 124.3, 61.9, 44.3, 31.4, 24.9; HRMS (FAB) calcd for $C_{44}H_{45}N_8O_{24}Rh_2S_4$ (m + H), 1402.9539, found (m + H) 1402.9600.

Tetrakis[*N*-[(4-*tert*-butylphenyl)sulfonyl]-(*L*)-prolinato]dirhodium (6c): (7.204 g, 231.3 mmol), (2.00 g, 4.62 mmol), (180 mL), (50:50, 750 mL; 60:40, 500 mL; 70:30, 750 mL); yield 3.78 g of a green solid (mp 279 °C dec) (56%); IR ($CDCl_3$) 3686, 2960, 1604, 1347 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.74 (d, 8 H, J = 9.2 Hz), 7.53 (d, 8 H, J = 9.2 Hz), 4.35 (m, 4 H), 3.27 (m, 4 H), 3.09 (m, 4 H), 2.07 (m, 4 H), 1.81 (m, 8 H), 1.52 (m, 4 H), 1.35 (s, 36 H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 192.45, 156.13, 135.48, 127.39, 125.89, 76.37, 61.74, 48.25, 35.18, 31.18, 24.85; HRMS (FAB) calcd for $C_{60}H_{81}N_4O_{16}Rh_2S_4$ (m + H), 1447.2641, found (m + H) 1447.2617.

Tetrakis[*N*-[(4-dodecylphenyl)sulfonyl]-(*L*)-prolinato]dirhodium (6d). The linear alkylbenzenesulfonic acid used was obtained from Alpha Research Chemicals and consisted of a mixture of 1% C_{10}, 40% C_{11}, 28% C_{12}, and 31% C_{13}: (14.3 g, 33.9 mmol), (3.00 g, 6.8 mmol), (180 mL), (50:50, 500 mL; 60:40, 1000 mL; 70:30, 1000 mL); yield 8.8 g of a green solid (mp 190−194 °C) (69%); IR ($CDCl_3$) 2928, 2856, 1605, 1156 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.74 (d, 8 H, J = 9.23 Hz), 7.53 (d, 8 H, J = 9.23 Hz), 4.32 (m, 4 H), 3.25 (m, 4 H), 3.05 (m, 4 H), 2.07 (m, 4 H), 1.85 (m, 4 H), 1.57 (m, 8 H), 1.25 (bs, 36 H), 0.85 (m, 10 H); HRMS (FAB) (% relative abundance) 1881.7361 (60, $C_{91}H_{143}N_4O_{16}Rh_2S_4$); 1867.7227 (88, $C_{90}H_{141}N_4O_{16}Rh_2S_4$); 1853.7089 (100, $C_{89}H_{139}N_4O_{16}Rh_2S_4$); 1839.6975 (84, $C_{88}H_{137}N_4O_{16}Rh_2S_4$); 1825.6819 (50, $C_{87}H_{135}N_4O_{16}Rh_2S_4$).

Tetrakis[*N*-[[3,5-Bis(trifluoromethyl)phenyl]sulfonyl]-(*L*)-prolinato]dirhodium (6e): (1.55 g, 3.95 mmol), (0.35 g, 0.79 mmol), (50 mL), (40:60); yield 0.56 g of a green solid (mp 306−309 °C) (40%); IR ($CDCl_3$) 3154, 2984, 2900, 1819, 1684 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.23 (s, 8 H), 8.02 (s, 4 H), 4.25 (br d, 4 H, J = 9.62 Hz), 3.65−3.51 (m, 4 H), 2.25−1.58 (m, 20 H). Anal. Calcd for $C_{52}H_{40}F_{24}N_4O_{16}Rh_2S_4$: C, 35.35; H, 2.28; N, 3.17. Found: C, 35.36; H, 2.39; N, 3.20.

Tetrakis[*N*-[(2,4,6-triisopropylphenyl)sulfonyl]-(*L*)-prolinato]-dirhodium (6f): (0.5 g, 1.3 mmol), (0.058 g, 0.13 mmol), (30 mL), (50:50); yield 0.21 g of a green solid (mp 177−181 °C) (93%); IR ($CDCl_3$) 3501, 2963, 1604, 1313 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.12 (s, 8 H), 4.34 (br d, 4 H, J = 8.2 Hz), 4.20−4.00 (m, 8 H), 3.48−3.30 (m, 4 H), 3.05−2.85 (m, 8 H), 2.20−1.80 (m, 12 H), 1.75−1.60 (m, 4 H), 1.30−1.18 (3 s, 72 H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 192.3, 152.5, 151.2, 132.1, 123.7, 61.3, 46.9, 37.1, 31.1, 29.4, 25.0, 24.8, 24.2, 23.5; HRMS (FAB) calcd for $C_{80}H_{121}N_4O_{16}Rh_2S_4$ (m + H), 1727.5771, found (m + H) 1727.5792.

Tetrakis[*N*-(isopropylsulfonyl)-(*L*)-prolinato]dirhodium (6g): (0.4 g, 1.8 mmol), (0.079 g, 0.18 mmol), (50 mL), (100:0); yield 0.116 g of a green solid (mp 219−222 °C) (59%); IR ($CDCl_3$) 3000, 2982, 1683, 1699 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.35 (dd, 4 H, J = 9.06, 3.02 Hz), 4.15 (br s, 4 H), 3.59−3.30 (m, 8H), 3.22 (quin, 4 H, J = 6.8 Hz), 2.02−1.68 (m, 12 H), 1.34 (app t, 24 H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 193.05, 61.94, 53.87, 48.02, 31.49, 25.13, 16.74, 16.35. Anal. Calcd for $C_{32}H_{56}N_4O_{16}Rh_2S_4$: C, 35.36; H, 5.19; N, 5.15. Found: C, 35.37; H, 5.37; N, 5.06.

Tetrakis[*N*-[(4-*tert*-butylphenyl)sulfonyl]-(*L*)-valinato]dirhodium (7): (1.08 g, 3.38 mmol), (0.2954 g, 0.68 mmol), (30 mL), (60:40); yield 0.723 g of a green solid (mp 235−238 °C dec) (72%); IR ($CDCl_3$) 3278, 2966, 2260, 1597, 1466 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.74 (d, 8 H, J = 8.2 Hz), 7.43 (d, 8 H, J = 8.2 Hz), 6.25−5.79 (bs, 4 H), 3.75−3.63 (m, 4 H), 2.60−2.29 (m, 12 H), 2.05−1.85 (m, 4 H), 1.29 (s, 36 H), 0.58 (d, 12 H, J = 6.12 Hz); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 191.1, 155.9, 137.8, 127.1, 125.7, 62.4, 35.0, 31.4, 31.0, 18.9, 17.6. Anal. Calcd for $C_{60}H_{88}N_4O_{16}Rh_2S_4$: C, 49.52; H, 6.09; N, 3.85. Found: C, 49.50; H, 6.23 N, 3.75.

Tetrakis[*N*-[(4-methylphenyl)sulfonyl]-(*L*)-phenylalinato]dirhodium (8): (1.08 g, 0.34 mmol), (0.29 g, 0.68 mmol), (30 mL), (60:40); yield 0.723 g of a green solid (mp 270−273 °C dec) (72%); IR ($CDCl_3$) 3343, 2927, 1710, 1601, 1160 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.43 (d, 4 H, J = 9.2 Hz), 6.95 (m, 32 H), 6.15 (br s, 4 H), 3.95 (m, 4 H), 2.80 (m, 8H), 2.28 (s, 12 H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 191.4, 142.6, 136.9, 136.7, 125.6, 129.5, 129.2, 128.1, 126.8, 126.2; HRMS (FAB) calcd for $C_{64}H_{65}N_4O_{16}Rh_2S_4$ (m + H), 1479.1389, found (m + H) 1479.1426.

Tetrakis[*N*-[(4-*tert*-butylphenyl)sulfonyl]-(*L*)-2-azetidinecarboxylato]dirhodium (9): (70.3 mg, 0.236 mmol), (26.1 mg, 59.0 μmol), (40 mL), (70:30); yield 50.0 mg of a green solid (mp 181−184 °C) (63%); IR (neat) 2964, 1607, 1428, 1345, 1308, 1166, 1113, 1089 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.82−7.69 (d, 8 H, J = 8.0 Hz), 7.69−7.49 (d, 8 H, J = 10.0 Hz), 4.48−4.23 (m, 4 H), 3.80−3.45 (m, 4 H), 3.31−3.11 (m, 4 H), 2.39−1.93 (m, 8 H), 1.36 (s, 36 H); $[\alpha]^{25}_D$ = −187.36° (*c* 0.095, $CHCl_3$). Anal. Calcd for $C_{56}H_{72}O_{16}N_4Rh_2S_4$: C, 48.35; H, 5.22; N, 4.03. Found: C, 48.20; H, 5.29; N, 3.98.

Tetrakis[*N*-[(4-*tert*-butylphenyl)sulfonyl]-(*L*)-2-pipecolinato]dirhodium (10): (40.0 mg, 0.123 mmol), (13.6 mg, 30.7 μmol), (40 mL), (40:60); yield 40.0 mg of a green solid (mp 293−295 °C dec) (80%); IR (neat) 2962, 1599, 1410, 1337, 1263, 1157, 1115, 1090 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.74−7.66 (d, 8 H, J = 8.0 Hz), 7.53−7.44 (d, 8 H, J = 8.0 Hz), 4.71−4.6 (m, 4 H), 3.40−3.24 (m, 4 H), 3.18−2.90 (m, 4 H, 2.58−2.41 (m, 4 H), 2.28−2.01 (m, 4 H), 1.57−0.74 (m, 52 H); HRMS (FAB) calcd for $C_{64}H_{89}N_4O_{16}Rh_2S_4$ (m + H), 1503.3267, found (m + H) 1503.3276.

General Procedure for Rhodium(II)-Catalyzed Decompositions of Vinyldiazomethanes in the Presence of Alkenes. A mixture of the alkene (1.2−20 equiv) and Rh(II) catalyst (0.01 equiv) in CH_2Cl_2 or pentane was stirred at room temperature under an argon atmosphere. To this solution was added the vinyl diazomethane (1 equiv, 0.12 M)

(44) Rapoport, H.; Cupps, T. L.; Boutin, R. H. *J. Org. Chem.* **1985**, *50*, 3972.

in CH_2Cl_2 or pentane over 10 min, and the mixture was then stirred for 1−8 h. The mixture was then concentrated *in vacuo*, and the residue was purified on silica using ether/petroleum ether as the eluent in the ratio specified in parentheses. The amounts of diazo compound, rhodium(II), alkene, and solvent are presented in that order in abbreviated form. In reactions carried out at −78 °C, the diazo compound was added over 30 min and the reaction was the maintained at −78 °C for 24−36 h. Compounds **18**−**21** were prepared from alkenes obtained as gases by condensing a large excess of alkene with a dry ice/acetone cup condenser into a chilled (0 °C) solvent/catalyst solution, followed by addition of the diazo compound, and warming to room temperature, and the reaction was worked up as above. Enantiomeric excesses (% ee) were determined by ^{1}H NMR at 200 or 500 MHz using tris[3-[(heptafluoropropyl)hydroxymethylene]-(−)-camphorato]praseodymium(III) derivative (0.10−0.35 equiv) and intergration of the split signals due to the methoxy or the vinyl group, or by HPLC using a Diacel Chiralcel OJ analytical column where noted.

(1*S*,2*S*)-Methyl 2*β*-Phenyl-1*β*-(2-(*Z*)-styryl)cyclopropane-1α-carboxylate (12a): 11a (17.2 g, 84.8 mmol), **6d** (1.58 g, 0.85 mmol), (44.2 g, 424 mmol), (pentane, 350 mL), (0:100 to 10:90); yield 19.62 g (83%); mp 57−60 °C; 92% ee, determined by ^{1}H NMR and by chiral HPLC;[30] flow rate 1.0 mL/min, 1.5% 2-propanol in hexane; UV 254 nm; T_R = 17 min (1*S*,2*S*), 27 min (1*R*,2*R*) (100% ee after 1 recrystallization from 2-propanol, giving a 70% recovery of fine white crystals); $[\alpha]^{25}_D = -166°$ (*c* 1.1, $CHCl_3$) (lit. $[\alpha]^{25}_D = -169°$ (*c* 1.1, $CHCl_3$),[30] for enantiomer $[\alpha]^{25}_D = +157.1°$ (*c* 1.1, $CHCl_3$)[16]); CD λ (mdeg) 202 (−2.9), 220 (+1.1), 255 (−1.0) (*c* 2.7 × 10^{-4} M, EtOH); reaction at −78 °C, (68%) 98% ee. The spectral data were consistent with the previously reported data.[16]

(1*R*,2*R*)-Methyl 2*β*-Phenyl-1*β*-(2-(*Z*)-styryl)cyclopropane-1α-carboxylate (*ent*-12a) was prepared by a procedure similar to that described above using ***ent*-6d** as catalyst. $[\alpha]^{25}_D = +164°$ (*c* 1.1, $CHCl_3$) (lit. $[\alpha]^{25}_D = +157.1°$ (*c* 1.1, $CHCl_3$)); CD λ (mdeg) 202 (+2.9), 220 (−1.1), 255 (+1.0) (*c* 2.7 × 10^{-4} M, EtOH).[16]

(1*S*,2*S*)-Ethyl 2*β*-Phenyl-1*β*-(2-(*Z*)-styryl)cyclopropane-1α-carboxylate (12b). 11b (0.35 g, 1.62 mmol), **6c** (10.7 mg, 7.4 mmol), (3.37 g, 32.4 mmol), (pentane, 50 mL), (2:98); yield 0.35 g as a pale yellow solid (mp 37−40 °C) (73%); 84% ee, $[\alpha]^{25}_D = -98°$ (*c* 0.301, MeOH); IR (neat) 3027, 2980, 1713, 1246 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.28−7.08 (m, 10 H), 6.34 (d, 1 H, *J* = 15.9 Hz), 6.13 (d, 1 H, *J* = 15.9 Hz), 4.21 (q, 2 H, *J* = 7.1 Hz), 2.02 (dd, 1 H, *J* = 9.1, 5.0 Hz), 3.00 (dd, 1H, *J* = 9.0, 7.3 Hz), 1.81 (dd, 1 H, *J* = 7.3, 5.1 Hz), 1.29 (t, 3 H, *J* = 7.1 Hz); CD λ (mdeg) 200 (−3.2), 220 (+1.2), 256 (−1.0) (*c* 2.5 × 10^{-4} M, EtOH). Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 82.11; H, 6.87.

(1*S*,2*S*)-1-Methylethyl 2*β*-Phenyl-1*β*-(2-(*Z*)-styryl)cyclopropane-1α-carboxylate (12c). 11c (0.25 g, 1.09 mmol), **6c** (10.7 mg, 7.4 mmol), (2.27 g, 21.8 mmol), (pentane, 50 mL), (10:90); yield 0.25 g as a pale yellow solid (mp 38−41 °C) (76%); 76% ee, $[\alpha]^{25}_D = -109°$ (*c* 0.633, MeOH); IR (neat) 2361, 1715, 1250 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.45−7.05 (m, 10 H), 6.31 (d, 1 H, *J* = 16.0 Hz), 6.12 (d, 1 H, *J* = 16.0 Hz), 5.10 (m, 1 H), 2.98 (app t, 1 H, *J* = 8.1 Hz), 2.00 (dd, 1 H, *J* = 9.2, 5.1 Hz), 1.79 (dd, 1 H, *J* = 7.1, 5.1 Hz), 1.28 (t, 6 H, *J* = 8.2 Hz); CD λ (mdeg) 202 (−2.2), 220 (+0.9), 255 (−1.0) (*c* 2.7 × 10^{-4} M, EtOH). Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.17; H, 7.22.

(1*S*,2*S*)-1,1-Dimethylethyl 2*β*-Phenyl-1*β*-(2-(*Z*)-styryl)cyclopropane-1α-carboxylate (12d). 11d (0.20 g, 0.82 mmol), **6c** (10.7 mg, 7.4 mmol), (1.71 g, 16.4 mmol), (pentane, 50 mL), (10:90); yield 75% as a pale yellow solid (mp 71−74 °C); 50% ee, $[\alpha]^{25}_D = -45°$ (*c* 0.444, MeOH); IR (neat) 2978, 2361, 2342, 1709, 1144 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.26−7.08 (m, 10 H), 6.30 (d, 1 H, *J* = 16.1 Hz), 6.12 (d, 1 H, *J* = 16.1 Hz), 2.92 (dd, 1 H, *J* = 9.0, 7.4 Hz), 1.95 (dd, 1 H, *J* = 9.0, 5.0 Hz), 1.73 (dd, 1 H, *J* = 7.4, 5.0 Hz), 1.50 (s, 9 H); CD λ (mdeg) 202 (−1.1), 222 (+3.8), 255 (−0.3) (*c* 2.3 × 10^{-4} M, EtOH); HRMS (EI) calcd for $C_{18}H_{16}O_2$ (*m* − C_4H_8), 264.1150, found (*m* − C_4H_8) 264.1156. Anal. Calcd for $C_{22}H_{24}O_2 \cdot 0.3H_2O$: C, 80.95; H, 7.62. Found: C, 80.94; H, 7.43.

(1*S*,2*S*)-Methyl 2*β*-(4-Chlorophenyl)-1*β*-(2-(*Z*)-styryl)cyclopropane-1α-carboxylate (13). 11a (0.15 g, 0.74 mmol), **6c** (10.7 mg, 7.4 mmol), (2.05 g, 14.8 mmol), (pentane, 30 mL), (5:95); yield 0.21 g as a yellow oil (91%); 89% ee, $[\alpha]^{25}_D = -101°$ (*c* 2.118, MeOH); reaction at −78 °C, (70%) >97% ee; IR (neat) 1721, 1495, 1435, 1250, 737 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.29−7.02 (m, 9 H), 6.35 (d, 1 H, *J* = 15.9 Hz), 6.11 (d, 1 H, *J* = 15.9 Hz), 3.75 (s, 3 H), 2.95 (app t, 1 H, *J* = 8.5), 2.01 (dd, 1 H, *J* = 9.1, 5.1 Hz), 1.77 (dd, 1 H, *J* = 7.1, 5.1 Hz); CD λ (mdeg) 202 (−2.1), 224 (+0.9), 258 (−0.8) (*c* 2.4 × 10^{-4} M, EtOH); HRMS (EI) calcd for $C_{19}H_{17}O_2Cl$, 312.0917, found 312.0907.

(1*S*,2*S*)-Methyl 2*β*-(4-Methoxyphenyl)-1*β*-(2-(*Z*)-styryl)cyclopropane-1α-carboxylate (14). 11a (0.15 g, 0.74 mmol), **6c** (10.7 mg, 7.4 mmol), (1.99 g, 14.8 mmol), (pentane, 30 mL), (5:95); yield 0.20 g (87%); 83% ee, $[\alpha]^{25}_D = -123°$ (*c* 1.184, MeOH); reaction at −78 °C, (41%) 90% ee; IR (neat) 2952, 1718, 1515, 1303, 1283, 1248, 1179, 1145, 910 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.20−7.13 (m 5 H), 7.03 (d, 2 H, *J* = 8.5 Hz), 6.74 (d, 2 H, *J* = 8.6 Hz), 6.33 (d, 1 H, *J* = 16.0 Hz), 6.14 (d, 1 H, *J* = 16.0 Hz), 3.73 (s, 3 H), 3.70 (s, 3 H), 2.95 (app t, 1 H, *J* = 8.6, Hz), 1.99 (dd, 1 H, *J* = 9.3, 5.1 Hz), 1.74 (dd, 1 H, *J* = 7.3, 5.1 Hz); ^{13}C NMR (50.3 MHz, DEPT, $CDCl_3$) δ 174.0 (4°), 158.3 (4°), 137.0 (4°), 132.7 (3°), 130.0 (4°), 128.3 (3°), 127.3 (4°), 127.2 (3°), 126.1 (3°), 124.1 (3°), 113.3 (3°), 55.0, 52.2 (1°), 34.5 (3°), 33.0 (4°), 18.6 (2°); CD λ (mdeg) 204 (−2.3), 221 (+0.7), 256 (−0.9) (*c* 2.4 × 10^{-4} M, EtOH); HRMS (EI) calcd for $C_{20}H_{20}O_3$, 308.1412, found 308.1398.

Methyl 2*β*-Acetoxy1-1*β*-(2-(*Z*)-styryl)cyclopropane-1α-carboxylate (15). 11a (0.12 g, 0.593 mmol), **6c** (8.5 mg, 5.95 mmol), (1.02 g, 11.86 mmol), (pentane, 30 mL), (10:90); yield 0.06 g as an oil (40%); 76% ee, $[\alpha]^{25}_D = +55°$ (*c* 0.221, MeOH); reaction at −78 °C, (26%) 95% ee; IR (neat) 3050, 2950, 1751, 1724, 1254, 1221 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.42−7.23 (m, 5 H), 6.54 (d, 1 H, *J* = 16.1 Hz), 6.36 (d, 1 H, *J* = 16.1 Hz), 4.44 (dd, 1 H, *J* = 6.9, 4.6 Hz), 3.75 (s, 3 H), 1.95 (s, 3 H), 1.89 (dd, 1 H, *J* = 6.9, 6.2 Hz), 1.68 (dd, 1 H, *J* = 6.2, 4.6 Hz); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 172.1, 170.9, 136.8, 132.0, 128.6, 127.6, 126.3, 121.0, 59.5, 52.5, 31.1, 20.4, 18.3; HRMS (EI) calcd for $C_{15}H_{16}O_4$, 260.1049, found 260.1038.

Methyl 2*β*-Ethoxy-1*β*-(2-(*Z*)-styryl)cyclopropane-1α-carboxylate (16). 11a (0.15 g, 0.742 mmol), **6c** (10.7 mg, 7.4 mmol), (1.07 g, 14.8 mmol), (pentane, 30 mL), (5:95); yield 0.15 g as an oil (83%); 59% ee, $[\alpha]^{25}_D = -7°$ (*c* 0.997, MeOH); reaction at −78 °C, (65%) 93% ee; IR (neat) 2978, 1717, 1437, 1348, 1290, 1250 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.43−7.21 (m, 5 H), 6.74 (d, 1 H, *J* = 16.3 Hz), 6.33 (d, 1 H, *J* = 16.2 Hz), 4.45 (dd, 1 H, *J* = 7.0, 4.9 Hz), 3.74 (s, 3 H), 3.33 (q, 2 H, *J* = 7.2 Hz), 1.88 (dd, 1 H, *J* = 7.0, 5.5 Hz), 1.64 (dd, 1 H, *J* = 5.5, 4.9 Hz), 1.11 (t, 3 H, *J* = 7.1 Hz); ^{13}C NMR (50.3 MHz, DEPT, $CDCl_3$) δ 172.7 (4°), 137.5 (4°), 129.5 (3°), 128.4 (3°), 127.0 (3°), 126.0 (3°), 121.6 (3°), 67.9 (3°), 67.1 (2°), 52.0 (1°), 31.6 (4°), 21.6 (2°), 14.7 (1°). Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 72.87; H, 7.38.

Methyl 2*β*-Butyl-1*β*-(2-(*Z*)-styryl)cyclopropane-1α-carboxylate (17). 11a (0.15 g, 0.742 mmol), **6c** (10.7 mg, 7.4 mmol), (25 g, 14.8 mmol), (pentane, 30 mL), (5:95); yield 0.12 g as an oil (63%); >90% ee, $[\alpha]^{25}_D = -93°$ (*c* 0.255, MeOH); IR (neat) 2955, 2930, 1724, 1246 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.41−7.22 (m, 5 H), 6.65 (d, 1 H, *J* = 16.0 Hz), 6.32 (d, 1 H, *J* = 16.0 Hz), 3.70 (s, 3 H), 1.62−1.58 (m, 3 H), 1.32−1.26 (m, 5 H), 1.14−1.11 (m, 1 H), 0.89−0.82 (m, 3 H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 175.0, 137.1, 131.7, 128.5, 127.4, 126.3, 124.7, 52.2, 31.7, 31.6, 30.5, 27.8, 22.4, 19.4, 14.0; HRMS (EI) calcd for $C_{17}H_{22}O_2$, 258.1620, found 258.1616.

Methyl 2*β*-Ethyl-1*β*-(2-(*Z*)-styryl)cyclopropane-1α-carboxylate (18). 11a (0.20 g, 0.989 mmol), **6c** (14.2 mg, 9.8 mmol), 1-butene in excess, (pentane, 25 mL), (2:98 to 5:95); yield 0.16 g as a yellow oil; (69%); >95% ee, $[\alpha]^{25}_D = -128°$ (*c* 0.53, MeOH); IR (neat) 2960, 1720, 1250, 1150, 965 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.32−7.14 (m, 5 H), 6.80 (d, 1 H, *J* = 16.2 Hz), 6.15 (d, 1 H, *J* = 16.2 Hz), 3.68 (s, 3 H), 1.53−1.20 (m, 5 H), 0.91 (t, 3 H, *J* = 7.2 Hz); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 174.9, 137.0, 131.6, 128.5, 127.3, 126.2, 124.5, 52.1, 33.3, 30.6, 21.5, 19.3, 13.7; MS (EI) *m*/*z* (relative intensity) 230 (33), 199 (9), 187 (62), 171 (36), 141 (24), 129 (100), 115 (47), 91 (99), 65 (31), 55 (36); HRMS (EI) calcd for $C_{15}H_{18}O_2$: 230.1307, found 230.1307.

Methyl 2*β*-(1-Methylethyl)-1*β*-(2-(*Z*)-styryl)cyclopropane-1α-carboxylate (19). 11a (0.20 g, 0.989 mmol), **6c** (14.2 mg, 9.8 mmol), 3-methyl-1-butene in excess, (pentane, 30 mL), (2:98 to 5:95); yield 0.14 g as a yellow oil; (58%); 95% ee, $[\alpha]^{25}_D = -115°$ (*c* 0.186,

MeOH); IR (neat) 3026, 2956, 2928, 2870, 1723, 1435, 1294, 1247, 1202, 1149, 968 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.44−7.19 (m, 5 H), 6.74 (d, 1 H, J = 18.0 Hz), 6.35 (d, 1 H, J = 18.0 Hz), 3.71 (s, 3 H), 1.62−1.38 (m, 2 H), 1.29−1.06 (m, 2 H), 1.02 (d, 3 H, J = 8.0 Hz), 0.95−0.91 (d, 3 H, J = 8.0 Hz); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 174.8, 137.0, 131.4, 128.5, 127.3, 126.2, 124.5, 52.1, 39.7, 30.9, 28.0, 22.4, 22.0, 18.7; MS *m*/*z* (relative intensity) 244 (19), 188 (21), 169 (5), 155 (7), 129 (100), 115 (12), 91 (5), 77 (4), 41 (12); HRMS calcd for $C_{16}H_{20}O_2$, 244.1463, found 244.1474.

Methyl 2,2-Dimethyl-1*β*-(2-(*Z*)-styryl)cyclopropane-1α-carboxylate (20). 11a (0.20 g, 0.989 mmol), **6c** (14.7 mg, 9.8 μmol), 2-methylpropene in excess, (pentane, 30 mL), (2:98 to 5:95); yield 0.12 g as a yellow oil; (52%); 95% ee; IR (neat) 3027, 3000, 2984, 2950, 1728, 1434, 1294, 1231, 1196, 1187, 1106 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.40−7.25 (m, 5 H), 6.71−6.63 (d, 1 H, J = 16.0 Hz), 6.36 (d, 1 H, J = 16.0 Hz), 3.71 (s, 3 H), 1.53 (d, 1 H, J = 5.0 Hz), 1.21 (s, 3 H) 1.13 (d, 1 H, J = 5.0 Hz), 1.11 (s, 3 H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 172.5, 137.1, 128.5, 127.3, 126.7, 126.2, 51.8, 37.2, 27.9, 23.6, 21.5, 20.9; MS (EI) *m*/*z* (relative intensity) 230 (64), 197 (16), 183 (32), 171 (22), 155 (41), 128 (32), 115 (43), 91 (100), 65 (37), 41 (53). Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.08; H, 7.96.

Methyl 2*β*,3*β*-Dimethyl-1*β*-(2-(*Z*)-styryl)cyclopropane-1α-carboxylate (21). 11a (0.50 g, 2.5 mmol), **6d** (46.6 mg, 2.5 μmol), *cis*-2-butene in excess (approximately 5 mL), (pentane, 40 mL), (5:95); yield 0.46 g as a yellow oil; (80%); IR ($CDCl_3$) 3029, 2933, 1710 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.44−7.23 (m, 5 H), 6.59 (d, 1 H, J = 16.4 Hz), 6.02 (d, 1 H, J = 16.4 Hz), 3.65 (s, 3 H), 1.85 (m, 2 H), 1.10−1.05 (m, 6 H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 175.4, 137.4, 137.1, 128.5, 127.4, 126.1, 121.0, 52.1, 30.8, 26.2, 8.9. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.13; H, 7.93.

Methyl 6-(2-(*Z*)-Styryl)-2-oxabicyclo[3.1.0]hexane-6-carboxylate (23). 11a (0.15 g, 0.74 mmol), **6c** (10.7 mg, 7.4 μmol), (1.04 g, 14.8 mmol), (40 mL), (10:90 to 20:80); yield 0.17 g as an oil (94%); 68% ee; reaction at −78 °C, (84%) 86% ee; IR (neat) 3020, 2950, 2890, 1710, 1430, 1290, 1230, 1110, 1070, 965, 940 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.45−7.20 (m, 5 H), 6.75 (d, 1 H, J = 16.2 Hz), 6.21 (d, 1 H, J = 16.2 Hz), 4.36 (d, 1 H, J = 5.6 Hz), 4.06 (ddd, 1 H, J = 10.1, 6.9, 5.0 Hz), 3.79−3.54 (m, 1 H), 3.64 (s, 3 H), 2.52 (dd, 1 H, J = 6.0, 5.6 Hz), 2.36−2.18 (m, 1 H), 1.97 (ddd, 1 H, J = 13.0, 9.2, 5.0 Hz); MS (EI) *m*/*z* (relative intensity) 244 (100), 212 (20), 185 (37), 155 (33), 129 (40), 115 (41), 91 (30), 77 (35), 51 (24). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.48; H, 6.65.

(1*R*,2*S*)-(*E*)-1-Carboxy-1-(methoxycarbonyl)-2-phenylcyclopropane (24). A mixture of **12a** (8.46 g, 30.3 mmol), CH_3CN (60 mL, 2 mL/mmol), CCl_4 (60 mL, 2 mL/mmol), H_2O (90 mL, 3 mL/mmol), and $NaIO_4$ (52.03 g, 243.4 mmol) was stirred to a uniform suspension. $RuCl_3 \cdot H_2O$ (0.2145 g, 0.91 mmol) was added, and the reaction was stirred for 8 h at rt.[31] The reaction was quenched with 2 M HCl (400 mL) and then extracted with EtOAc (4 × 200 mL). The organic layers were filtered through a Celite/charcoal cake, dried ($MgSO_4$), and reduced. The crude material was purified by chromatography on a silica column using EtOAc/hexanes/AcOH (14:85:1) as the eluent, and then recrystallized from ethyl acetate/hexenes to form 4.68 g of a white solid (94−96 °C) (70%): $[\alpha]^{25}_D$ = −124.2° (*c* 1.1, PhH); (lit. $[\alpha]^{23}_D$ = −104.2° (*c* 0.89, PhH)). The spectral data were in agreement with previously reported data.[30]

(1*S*,2*R*)-(E)-1-Carboxy-1-(methoxycarbonyl)-2-phenylcyclopropane (*ent*-24) was prepared by a procedure similar to that described above using ***ent*-12a** as substrate (69%): $[\alpha]^{25}_D$ = +125.6° (*c* 1.0, PhH).

(1*S*,2*S*)-(*Z*)-Methyl 1-[*N*-[[(1,1-Dimethylethyl)oxy]carbonyl]amino]-2-phenylcyclopropane-1-carboxylate (25). A two-neck 100 mL flask, which was thoroughly dried, pumped, and purged with argon, was charged with **24** (0.50 g, 2.3 mmol), dry hexanes (25 mL), NEt_3 (0.364 mL, 2.6 mmol, freshly distilled from CaH_2), *t*-BuOH (2.2 mL, 23 mmol, fractionally distilled from CaH_2), and diphenylphosphoryl azide (0.52 mL, 2.5 mmol, freshly distilled via vacuum short path 140 °C at 2 mmHg).[32] The mixture was heated under reflux for 18 h under argon and then di-*tert*-butyl dicarbonate (0.783 mL, 3.4 mmol) was added, and the mixture was refluxed for a further 2 h. The reaction was then cooled to room temperature, and the solvent was removed, leaving a thick oil. Ethyl acetate (40 mL) was added, and the organic layer was washed successively with 5% citric acid, H_2O, $NaHCO_3$ (saturated aqueous solution), and brine (25 mL each). The excess dicarbonate was removed by Kugelrohr distillation (80 °C at 0.7 mmHg), and the residue was purified by chromatography on silica using EtOAc/hexanes (0:100 to 20:80) to give 0.453 g of a white solid (68%): $[\alpha]^{25}_D$ = −86.8° (*c* 0.98, CH_2Cl_2); IR (neat) 3367, 2987, 2954, 1721, 1693 cm^{-1}; ^1H NMR (400 MHz, DMSO, 125 °C) δ 7.23−7.17 (m, 5 H), 6.76 (br s, 1 H), 3.66 (s, 3 H), 3.01−2.91 (m, 1 H), 1.66 (br s, 2 H), 1.14 (s, 9 H); ^{13}C (75 MHz, $CDCl_3$) δ 173.1, 155.7, 134.7, 128.8, 128.4, 127.3, 79.8, 52.3, 39.6, 32.6, 27.9, 21.0. Anal. Calcd for $C_{16}H_{21}NO_4$: C, 65.96; H, 7.27; N, 4.81. Found: C, 65.85; H, 7.25; N, 4.88.

(1*R*,2*R*)-(*Z*)-Methyl 1-[*N*-[[(1,1-Dimethylethyl)oxy]carbonyl]amino]-2-phenylcyclopropane-1-carboxylate (*ent*-25) was prepared by a procedure similar to that described above using ***ent*-24** as substrate (83%): $[\alpha]^{25}_D$ = +88.6° (*c* 1.2, CH_2Cl_2).

(1*S*,2*S*)-(*Z*)-1-[*N*-[[(1,1-Dimethylethyl)oxy]carbonyl]amino]-2-phenylcyclopropane-1-carboxylic Acid (26). KOH (0.34 g, 6.1 mmol) was added to a solution of **25** (0.443 g, 1.5 mmol) in THF/H_2O (20 mL, 1:1), and the resulting mixture was stirred at ambient temperature for 18 h. H_2O (10 mL), followed by a small portion of 2 M HCl, was added, and the resulting mixture was extracted with ethyl acetate. The process was repeated until the aqueous layer was acidified to pH 2. The combined organic layers were dried ($MgSO_4$) and reduced. The crude material was recrystallized (EtOAc/hexanes) to give 0.323 g of fine white crystals (mp 179−181 °C) (77%): $[\alpha]^{25}_D$ = −106.8° (*c* 1.4, CH_2Cl_2); IR (neat) 3263, 2979, 2929, 1703 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39−7.17 (m, 5 H), 4.62 (br s, 1 H), 3.03 (t, 1 H, J = 9.87 Hz), 2.15 (br s, 1 H), 1.80 (br s, 1 H), 1.33 (s, 9 H); ^{13}C (75 MHz, $CDCl_3$) δ 178.2, 156.3, 134.6, 128.9, 128.4, 127.4, 80.1, 39.5, 33.2, 27.9, 21.6. Anal. Calcd for $C_{15}H_{19}NO_4$: C, 64.97; H, 6.91; N, 5.05. Found: C, 64.89; H, 6.88; N, 5.01.

(1*R*,2*R*)-(*Z*)-1-[*N*-[[(1,1-Dimethylethyl)oxy]carbonyl]amino]-2-phenylcyclopropane-1-carboxylic Acid (*ent*-26) was prepared by a procedure similar to that described above using ***ent*-25** as substrate (90%): $[\alpha]^{25}_D$ = +108.9° (*c* 1.1, CH_2Cl_2).

(1*S*,2*S*)-(*Z*)-(−)-1-Amino-2-phenyl-1-cyclopropane-1-carboxylic Acid (1a) Hydrochloride Salt. 26 (0.050 g, 0.18 mmol) was dissolved in 3 M HCl (2.5 mL, concentrated HCl diluted in ethyl acetate[33]), and stirred at room temperature for 1 h. The solvent was removed under reduced pressure, and the crude material was recrystallized (EtOH/Et_2O) to give 0.031 g of fine white crystals (mp 199−202 °C dec (lit. mp 199 °C dec)) (83%): $[\alpha]^{25}_D$ = −112.1° (*c* 0.81, H_2O) (lit. $[\alpha]^{23}_D$ = −103° (*c* 0.76, H_2O),[7c] $[\alpha]^{25}_D$ = −104.6° (*c* 0.26, H_2O)[16]). The spectral data were consistent with the previously reported data.[16]

(1*R*,2*R*)-(*Z*)-(+)-1-Amino-2-phenyl-1-cyclopropane-1-carboxylic Acid (1b) Hydrochloride Salt was prepared by a procedure similar to that described above using ***ent*-26** as substrate (84%): $[\alpha]^{25}_D$ = +112.3° (*c* 1.2, H_2O).

(*S*)-1,1-Bis(methoxycarbonyl)-2-phenylcyclopropane (27) was prepared from **24** (3.00 g, 13.6 mmol) by the procedure described by Corey:[30] mp 63−65 °C (lit. mp 61−62 °C[30]); $[\alpha]^{25}_D$ = −137.2° (*c* 1.1, PhH) (lit. $[\alpha]^{23}_D$ = −124° (*c* 2.2, PhH)[30]). The spectral data were consistent with the previously reported data.[30]

(*R*)-1,1-Bis(methoxycarbonyl)-2-phenylcyclopropane (*ent*-27) was prepared by a procedure similar to that described above using ***ent*-24** as substrate (91%): $[\alpha]^{25}_D$ = +137.5° (*c* 1.0, PhH). Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02. Found: C, 66.52; H, 6.04.

(1*S*,2*S*)-(*Z*)-1-Carboxy-1-(methoxycarbonyl)-2-phenylcyclopropane (28). NaOH (1 N) (16.61 mL, 16.6 mmol) was added to a stirred mixture of **27** (2.99 g, 12.7 mmol) in MeOH (20 mL), and the resulting solution was stirred at ambient temperature for 2 h.[34] The mixture was reduced to dryness, H_2O (50 mL) was added, and the resulting mixture was extracted with ethyl acetate (3 × 75 mL). The combined organic layers were dried ($MgSO_4$) and reduced. The crude material was recrystallized (EtOAc/hexanes) to give 2.12 g of fine white crystals (mp 60−62 °C) (75%): $[\alpha]^{25}_D$ = −146.2° (*c* 1.1, PhH); IR (neat) 3032, 2948, 1739, 1688, 1429 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.23 (m, 5 H), 3.41 (dd, 1 H, J = 8.8, 7.8 Hz), 3.25 (s, 3 H), 2.41 (dd, 1 H J = 7.8, 4.9 Hz), 1.31 (dd, 1 H J = 8.8, 4.9 Hz); ^{13}C (75 MHz, $CDCl_3$) δ 172.6, 171.6, 134.1, 129.1, 128.4, 127.9, 52.3, 39.4, 33.9, 20.7. Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.45; H, 5.49. Found: C, 65.42; H, 5.53.

(1*R*,2*R*)-(*Z*)-1-Carboxy-1-(methoxycarbonyl)-2-phenylcyclopropane (*ent*-28) was prepared by a procedure similar to that described above using ***ent*-27** as substrate (73%): $[\alpha]^{25}_D = +147.6°$ (*c* 1.0, PhH).

(1*R*,2*S*)-(*E*)-Methyl 1-[*N*-[[(1,1-Dimethylethyl)oxy]carbonyl]amino]-2-phenylcyclopropane-1-carboxylate (29) was prepared from **28** (1.00 g, 4.5 mmol) by a procedure similar to that used to prepare **25**[32] to give 1.00 g of a white solid (mp 85−86 °C) (76%): $[\alpha]^{25}_D = -79.6°$ (*c* 0.95, CH_2Cl_2) (lit. for enantiomer $[\alpha]^{25}_D = +74.8°$ (95% ee) (*c* 1.1, CH_2Cl_2)[7b]); IR (neat) 3353, 2972, 1721, 1498 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34−7.21 (m, 5 H), 5.37 (br s, 1 H), 3.57 (s, 3 H), 2.85 (dd, 1 H, $J = 9.5, 8.2$ Hz), 2.18 (dd, 1 H $J = 8.2, 5.7$ Hz), 1.61 (dd, 1 H $J = 9.5, 5.7$ Hz), 1.14 (s, 9 H); ^{13}C (75 MHz, $CDCl_3$) δ 170.7, 156.0, 135.4, 129.1, 127.7, 126.7, 79.5, 51.3, 40.7, 34.5, 27.9, 20.0. Anal. $C_{16}H_{21}NO_4$: C, 65.96; H, 7.27; N, 4.81. Found: C, 65.82; H, 7.26; N, 4.87.

(1*S*,2*R*)-(*E*)-Methyl 1-[*N*-[[(1,1-Dimethylethyl)oxy]carbonyl]amino]-2-phenylcyclopropane-1-carboxylate (*ent*-29)[7b] was prepared by a procedure similar to that described above using ***ent*-28** as substrate (75%): $[\alpha]^{25}_D = +88.6°$ (*c* 1.2, CH_2Cl_2).

(1*R*,2*S*)-(*E*)-(−)-1-Amino-2-phenyl-1-cyclopropane-1-carboxylic Acid (1c) Hydrochloride Salt. $LiOH·H_2O$ (0.3104 g, 7.4 mmol) was added to a solution of **29** (0.2155 g, 0.74 mmol) in $MeOH/H_2O$ (9 mL, 2/1), and the resulting solution was heated under reflux for 2.5 h.[7c] The reaction was then cooled, and the solvent was evaporated under reduced pressure. The residue was dissolved in H_2O (10 mL), and the resulting solution was acidified to pH 2 with 2M HCl and then extracted with ethyl acetate (4 × 30 mL). The organic layer was dried ($MgSO_4$) and reduced. The crude material was dissolved in 3 M HCl (10 mL, concentrated HCl diluted in ethyl acetate), and the resulting solution was stirred at rt for 1 h.[33] The solvent was then removed under reduced pressure, and the crude material was recrystallized ($EtOH/Et_2O$) to give 0.132 g of fine white crystals (mp 219−221 °C) (83%): $[\alpha]^{25}_D = -80.9°$ (*c* 1.2, H_2O) (enantiomer lit. $[\alpha]^{25}_D = +74.4°$ (*c* 1.0, H_2O),[7d] lit. $[\alpha]^{25}_D = +72.7°$ (95% ee) (*c* 1.0, H_2O)[7d]). The spectral data were consistent with the previously reported data.[30]

(1*S*,2*R*)-(*E*)-(+)-1-Amino-2-phenyl-1-cyclopropane-1-carboxylic Acid (1d) Hydrochloride Salt was prepared by a procedure similar to that described above using ***ent*-29** as substrate (92%): $[\alpha]^{25}_D = +80.3°$ (*c* 1.2, H_2O).

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