α-Hydroxy Esters as Chiral Auxiliaries in Asymmetric Cyclopropanations by Rhodium(II)-Stabilized Vinylcarbenoids

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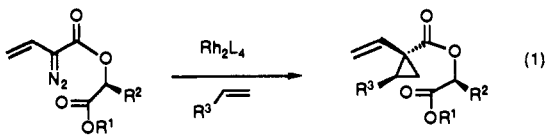
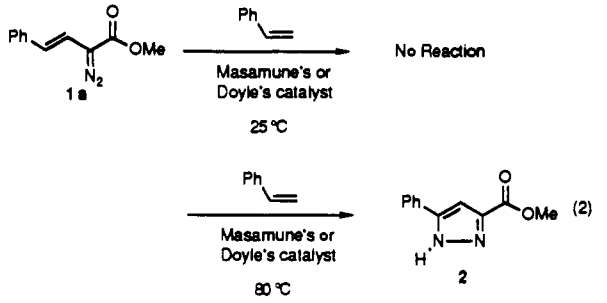
Abstract: The use of several α-hydroxy esters as chiral auxiliaries for asymmetric cyclopropanation with rhodium(II)-stabilized vinylcarbenoids is presented. Use of either (*R*)-pantolactone or (*S*)-lactate allowed entry into both series of enantiomeric vinylcyclopropanes with predictable absolute stereochemistry. Steric and electronic modifications of the chiral auxiliary as well as catalyst structure were shown to have major effects on the asymmetric induction. These results were rationalized on the basis of an interaction between the carbonyl oxygen of the chiral auxiliary and the carbenoid carbon. By combining the asymmetric cyclopropanation with a subsequent Cope rearrangement, an enantioselective entry into hydroazulenes was achieved. The potential of the asymmetric cyclopropanation was illustrated by a short synthesis of (1*R*,2*R*)-2-phenylcyclopropane amino acid **5**.

Due to the versatility of cyclopropanes in organic synthesis[1,2] and the occurrence of a number of important cyclopropane containing natural products and synthetic materials,[3] the asymmetric synthesis of cyclopropanes has drawn considerable attention.[4,5] A number of enantioselective synthetic strategies to cyclopropanes have been developed and the most general of these is the metal catalyzed decomposition of diazoalkanes in the presence of alkenes.[5] α-Diazoacetate derivatives have been the most extensively used carbenoid precursors, but the drawback with this system is that the cyclopropanation is only moderately diastereoselective.[5,6] As we have found that cyclopropanations with vinyldiazomethanes can be highly diastereoselective,[7] a successful enantioselective cyclopropanation with vinyldiazomethanes would enable cyclopropanes to be formed with control of both relative and absolute stereochemistry. This paper describes a highly efficient asymmetric cyclopropanation with vinydiazomethanes, as illustrated in eq 1, using inexpensive α-hydroxy esters as chiral auxiliaries.



At the onset of this work, the most obvious approach for achieving asymmetric cyclopropanations with vinylcarbenoids was considered to be the use of chiral copper[8] and rhodium catalysts[9] that have been successfully developed for other types of carbenoid cyclopropanations. Unfortunately, these catalysts have been principally designed for the decomposition of diazoacetates, and extension of their use to the decomposition of vinyldiazomethane **1a** was unsuccessful. Attempted decomposition of **1a** using either Masamune's *tert*-butyl substituted bisoxazoline copper catalyst[8d] or Doyle's rhodium catalyst[9] at room temperature led to recovery of the starting material, and under more vigorous conditions, rearrangement of **1a** to the pyrazole **2** occurred in preference to decomposition to the carbenoid (eq 2).



Faced with the lack of success in using chiral catalysts, we considered that an alternative strategy for achieving asymmetric control would be by attachment of a chiral auxiliary to the vinylcarbenoid. Previous studies, however, on the use of chiral

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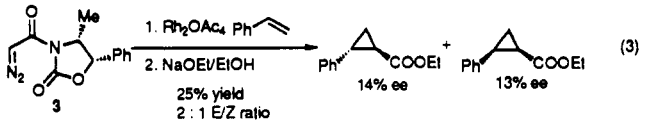
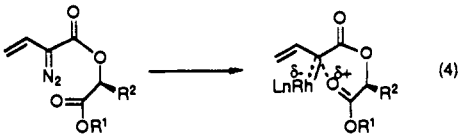
auxiliaries on carbenoids have met with limited success.[10,11] For example, Doyle has shown that rhodium(II) acetate catalyzed decomposition of **3**, containing an oxazolidinone auxiliary, in the presence of styrene resulted in cyclopropanation in poor yield, *cis/trans* ratio, and asymmetric induction.[10]



A major factor against using the traditional menthol and borneol auxiliaries that have been so successful in many other types of asymmetric transformations is that effective blocking of one face of a carbenoid could also easily lead to undesirable side reactions between the carbenoid and the auxiliary. Indeed, naphthylborneol is the only auxiliary that has been reported to be effective in asymmetric carbenoid transformations leading to moderately high levels of asymmetric induction in intramolecular cyclopropanations and C–H insertions.[11] A potential solution to this problem would be to use α-hydroxy esters as chiral auxiliaries, in which the carbenoid would interact with the carbonyl of the auxiliary, generating a rigid intermediate that could lead to a high level of asymmetric induction as illustrated in eq 4.[12] A similar concept was behind Doyle's rationale in the development of the chiral diazoacetic acid **3**.[10] A particularly attractive feature of this approach is that several potential auxiliaries, such as lactate, mandelate, and pantolactone, are very inexpensive and so the cost of using stoichiometric amounts of auxiliary would not be prohibitive in large-scale reactions.



In order to test this basic concept of using α-hydroxy ester auxiliaries for asymmetric cyclopropanation, a series of appropriately substituted vinyldiazomethanes **1** were prepared. The vinyldiazomethanes **1b,e–g** were formed in enantiomerically pure form; **1c,d,h** were produced as racemic mixtures.[13] Rhodium(II) acetate catalyzed decomposition of the (*S*)-methyl lactate derivative **1b** in the presence of styrene in refluxing dichloromethane generated a mixture of two diastereomeric cyclopropanes **4b** in 83% yield with 67% de (Scheme I). Confirmation that both isomers were *E*-cyclopropanes was obtained by methanolysis of the mixture, which generated a pair of enantiomers of the cyclopropane **4a**. As will be described later, the optical rotation of enantiomerically enriched **4a** has been correlated to its absolute stereochemistry and this allowed us to determine that the configuration of the major diastereomer of **4b** formed was 1*S*,2*S*. The lack of evidence of any other isomeric cyclopropanes in the crude cyclopropanation reaction mixture once again demonstrated the remarkable level of *E*/*Z* stereoselectivity exhibited in vinylcarbenoid cyclopropanations.

A study was then carried out to determine what factors influenced the effectiveness of α-hydroxy esters as chiral auxiliaries in these reactions. The results are summarized in Table I. The requirement of a six-membered ring interaction was readily seen by repeating the reaction with the higher homologue **1c**, as this resulted in the formation of **4c** with very low levels of asymmetric induction (12% de). Replacement of the (*S*)-methyl lactate with (±)-mandelate resulted in a slight decrease in diastereoselectivity to give **4d** in 59% de, but improvement of diastereoselectivity was observed on replacing the methyl substituent at the stereogenic center in **1b** with isopropyl (**1e**, 78% de) and *tert*-butyl (**1f**, 79% de). Further enhancement in diastereoselectivity was observed by using a lactone instead of an open chain ester, as the pantolactone derivative **1g** gave the cyclopropane **4g** with 89% de. The importance of the *gem*-dimethyl functionality in pantolactone was readily seen, because cyclopropanation with the (±)-butyrolactone derivative **1h** resulted in the formation of **4h** with only a 42% de.

Having determined that (*R*)-pantolactone was the most effective chiral auxiliary, a study on the effect of catalyst was examined and the results are summarized in Table II. Moderately noncrowded catalysts such as rhodium(II) acetate or rhodium(II) octanoate resulted in the highest levels of asymmetric induction. Increasing the size of the catalyst to rhodium(II) pivalate had a deleterious effect on diastereoselection while rhodium(II) formate gave high levels of diastereoselection but poor yield presumably due to catalyst insolubility. A similar drop of diastereoselection was not seen on going from rhodium(II) acetate to rhodium(II) pivalate with the (*S*)-lactate derivative **1b**. Electronic effects were examined by comparison of the

Scheme I

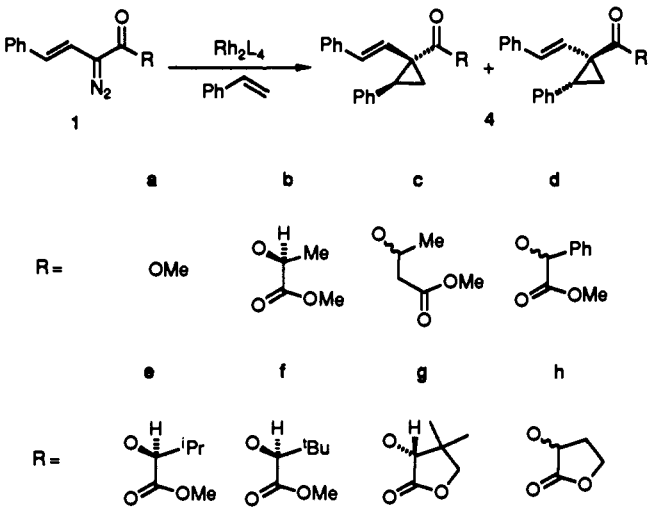


Table I. Effect of Chiral Auxiliary on Asymmetric Cyclopropanation of Styrene by **1**

entry	substrate	de, % (major isomer)	yield, %
1	**1b**	67 (1*S*,2*S*)	83
2	**1c**	12	77
3	**1d**	59	71
4	**1e**	78 (1*S*,2*S*)	82
5	**1f**	79 (1*S*,2*S*)	81
6	**1g**	89 (1*R*,2*R*)	91
7	**1h**	42	90

Table II. Effect of Catalyst on Asymmetric Cyclopropanation of Styrene by **1g**

entry	ligand	de, % (major isomer)	yield, %
1	O_2CCH_3	89 (1*R*,2*R*)	91
2	O_2CCF_3	78 (1*R*,2*R*)	95
3	$O(NH)CCH_3$	78 (1*R*,2*R*)	37
4	$O_2CC(CH_3)_3$	69 (1*R*,2*R*)	95
5	O_2CH	89 (1*R*,1*R*)	42
6	(*S*)-(+)-$O_2CCH(OH)(C_6H_5)$	17 (1*R*,2*R*)	89
7	(*R*)-(−)-$O_2CCH(OH)(C_6H_5)$	80 (1*R*,2*R*)	95
8	$O_2C(CH_2)_6CH_3$	89 (1*R*,2*R*)	84
9	$O_2C(CH_2)_6CH_3$	97 (1*R*,2*R*)[a]	84[a]

[a] Reaction was carried out at 0 °C.

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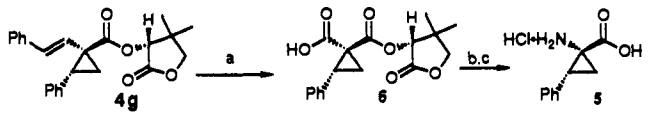
(12) For a preliminary account of a portion of this work, see Davies, H. M. L.; Cantrell, W. R., Jr. *Tetrahedron Lett.* **1991**, *32*, 6509.
(13) Compounds **1c** and **1h** were derived from racemic starting materials. On preparation of **1d** using a diazo-transfer reaction, the mandelate auxiliary underwent racemization.

Scheme II[a]



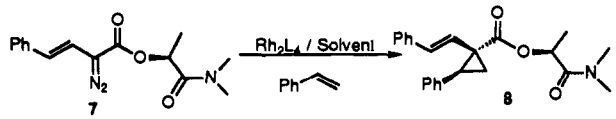
[a] (a) $RuCl_3$, $NaIO_4$, $CCl_4/MeCN/H_2O$; (b) $(PhO)_2P(O)N_3$, NEt_3, toluene, reflux; (c) 6 M HCl, reflux.

rhodium(II) trifluoroacetate and the rhodium(II) acetamide catalysts; neither of these were as effective as the acetate. A brief attempt was also made to determine whether higher levels of asymmetric induction could be achieved through double stereodifferentiation by use of a chiral catalyst. Even though significant double stereoselection was exhibited by the enantiomeric rhodium(II) mandelate catalysts, both are sufficiently bulky that neither catalyst was as effective as rhodium(II) acetate or rhodium(II) octanoate.

Further enhancement of diastereoselectivity was possible by carrying out the reaction at lower temperature. Rhodium(II) octanoate catalyzed decomposition of **1g** at 0 °C resulted in the formation of **4g** with 97% de. A particular advantage of using (*R*)-pantolactone as an auxiliary is that the products tended to be crystalline and, in the case of **4g**, a single recrystallization from 2-propanol resulted in the formation of essentially enantiomerically pure material. The formation of crystalline products is of great utility for the separation of single diastereomers on multigram scale from reactions which give less than complete stereoselectivity.

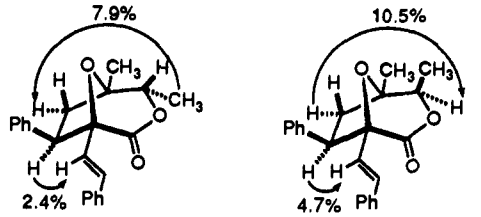
The potential utility of this chemistry was demonstrated through the conversion of **4g** to the conformationally constrained cyclopropane amino acid **5** (Scheme II) of known absolute stereochemistry and optical rotation. Oxidative cleavage of **4g** with sodium perruthenate resulted in the formation of the acid **6**. Further conversion of **6** to the cyclopropane amino acid **5** was achieved by means of a Curtius rearrangement followed by hydrolysis (22% overall yield of **5** from **4g**). The specific optical rotation of +104.6° (*c* 0.26, H_2O) for **5** was in excellent agreement with the reported value and substantiated that the absolute stereochemistry for **4g** was (1*R*,2*R*).[4b] Methanolysis of **4g** gave **4a** with an optical rotation of +157.1° (*c* 1.1, $CHCl_3$), and thus the absolute stereochemistry of the other cyclopropanes could be correlated by their methanolysis to **4a** followed by measurement of the optical rotation.

In order to more thoroughly test the hypothesis that interaction of the ester carbonyl group with the carbenoid is important for asymmetric induction, a study was carried out on the effect of other carbonyl functionalities in place of the ester. Rhodium(II) acetate catalyzed decomposition of the amide derivative **7** in the presence of styrene using dichloromethane as solvent resulted in a reaction with low chemoselectivity. The cyclopropane **8** was formed in only 33% yield compared to 83% yield for the formation of **4b**, although the diastereoselectivity was still quite reasonable (53% de). A much cleaner reaction was observed by using pentane as solvent, and under these conditions the cyclopropane **8** was isolated in 67% yield with virtually no change in the diastereoselectivity.



Conditions	Yield	d.e.
$Rh_2(OAc)_4$ / CH_2Cl_2	33 %	53 %
$Rh_2(OOct)_4$ / Pentane	67 %	51 %

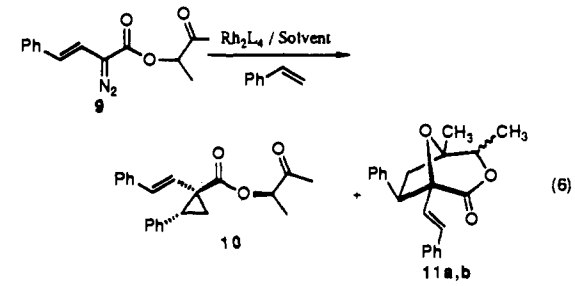
An even more dramatic effect on chemoselectivity was observed in the case of the ketone derivative **9**. Rhodium(II) acetate catalyzed decomposition of **9** in the presence of styrene using dichloromethane as solvent resulted in only a 19% yield of cyclopropanation product **10** (26% de). The major product isolated in this case was the 1,3-dipolar cycloadduct **11** between the presumed carbonyl ylide intermediate and styrene, which was obtained in 52% yield as a mixture of α and β isomers of the methyl group at the C-4 position of **11**. Once again a significant solvent effect on chemoselectivity was observed. When the reaction was repeated using pentane as solvent, the cyclopropane **10** became the dominant product (42% yield) with only a small decrease in diastereoselectivity (22% de).



11a $J(H_{5\alpha}\text{-}H_{5\beta})$ = 14.1 Hz; $J(H_{5\alpha}\text{-}H_{6\alpha})$ = 9.6 Hz; $J(H_{5\beta}\text{-}H_{6\alpha})$ = 3.6 Hz

11b $J(H_{5\alpha}\text{-}H_{5\beta})$ = 13.9 Hz; $J(H_{5\alpha}\text{-}H_{6\alpha})$ = 9.7 Hz; $J(H_{5\beta}\text{-}H_{6\alpha})$ = 3.2 Hz

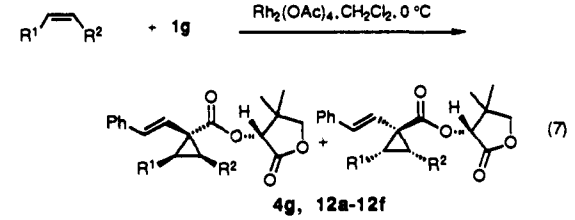
Figure 1.



Conditions	10	11a,b
$Rh_2(OAc)_4$ / CH_2Cl_2	19 %	52 %
$Rh_2(OOct)_4$ / Pentane	42 %	38%

The relative orientation of the C-4 methyl group in **11a** (the major isomer obtained) and **11b** (the minor isomer obtained), as well as the orientation of the phenyl group derived from styrene, was established by characteristic NOE enhancements between the *endo* substituent at C-4 and the homobenzylic substituent orientated *anti* to the phenyl ring (Figure 1). The orientation of the phenyl substituent followed from the distinctive coupling constants between the benzylic and homobenzylic protons.

Having established that (*R*)-pantolactone was the most effective chiral auxiliary, we undertook a study to establish the scope and effectiveness of this particular class of auxiliaries in a range of cyclopropanation reactions (eq 7, Table III). The effect of



4g, 12a-12f

electronically compromised styrenes on the degree of asymmetric induction was addressed through cyclopropanation of 4-chloro- and 4-methoxystyrenes. In both cases only one diastereomer

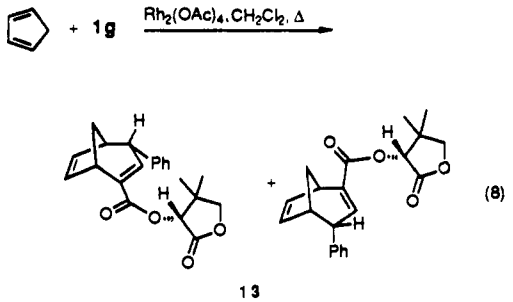
Table III. Asymmetric Cyclopropanation of Various Alkenes with **1g**

entry	R^1	R^2	de, %[a]	yield, %	product
1	Ph	H	97	84	**4g**
2	4-ClC_6H_4	H	>95	92	**12a**
3	4-$MeOC_6H_4$	H	>95	75	**12b**
4	EtO	H	92	71	**12c**
5	OCH_2CH_2		66	86	**12d**
6	$OCH_2CH_2CH_2$		47	65	**12e**
7	AcO	H	90	42	**12f**

[a] Reaction was carried out at 0 °C.

was evident in the ^1H NMR of the crude reaction mixture. Cyclopropanation with ethyl vinyl ether was slightly less diastereoselective but still occurred with a respectable 92% de. However, a trend of decreasing selectivity was observed as the vinyl ether functionality was constrained into a cyclic framework and the bulk of the substrate was increased from dihydrofuran to dihydropyran. Asymmetric cyclopropanation of vinyl acetate with **1g** was accomplished in moderate yield but with a reasonable level of asymmetric induction (90% de). No evidence for *E/Z* mixtures was observed in the crude NMR spectra of any of these reactions. Extension of this reaction to simple alkyl substituted alkenes such as 1-hexene was not successful. Low yields of cyclopropanation products were obtained, and the determination of either *E/Z* ratio or extent of asymmetric induction was inconclusive.

The reaction of vinylcarbenoids with dienes offers a general synthetic approach to highly functionalized seven-membered carbocycles by means of a tandem cyclopropanation/Cope rearrangement sequence.[14] Extension of this chemistry such that the initial cyclopropanation is carried out in an asymmetric mode would be expected to result in control of absolute stereochemistry at several stereogenic centers in the seven-membered carbocycle because the Cope rearrangement of divinylcyclopropanes is highly stereoselective. In order to test this concept, we examined the rhodium(II) acetate catalyzed decomposition of **1g** in the presence of cyclopentadiene in refluxing dichloromethane. A very facile cyclopropanation/Cope rearrangement sequence was observed leading to the formation of the bicyclo[3.2.1]octadiene **13** in 87% yield with 76% de. A further demonstration of the potential of this chemistry has been reported elsewhere, leading to the enantioselective synthesis of tropanes through reaction of vinylcarbenoids with pyrroles.[15]



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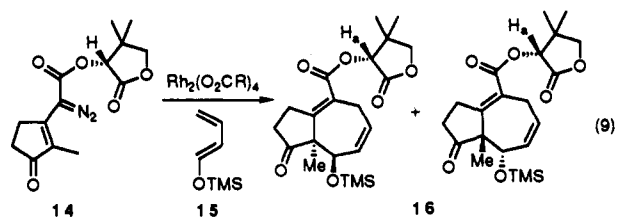
Another example of the asymmetric tandem cyclopropanation/Cope rearrangement using a more elaborate vinylcarbenoid precursor is shown in eq 9. Rhodium(II) carboxylate catalyzed



14 15 16

Table IV. Effect of Reaction Conditions on Formation of **16**

entry	reaction conditions	de, %[a]	yield, %
1	$Rh_2(OAc)_4$, CH_2Cl_2, reflux	+91	60
2	$Rh_2(Piv)_4$, CH_2Cl_2, 0 °C	+68	63
3	$Rh_2(OHex)_4$, CH_2Cl_2, 0 °C	>+90	58
4	$Rh_2(OHex)_4$, CH_2Cl_2, reflux	>+90	80
5	(–)-Rh_2(mandelate)$_4$, CH_2Cl_2, reflux	+38	60
6	(+)-Rh_2(mandelate)$_4$, CH_2Cl_2, reflux	–4	56

[a] de based on ratio of integration for H_a signals in ^1H NMR. A positive values indicates that the downfield signal is larger than the upfield signal.

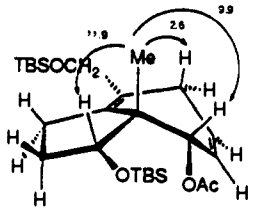
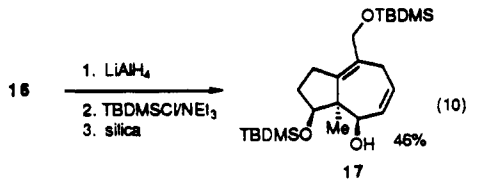


Figure 2.

decomposition of **14** in the presence of *trans*-1-((trimethylsilyl)oxy)-1,3-butadiene (**15**) resulted in the formation of the hydroazulene **16** in respectable yield (Table IV). The regiochemistry and control of hydroazulene relative stereochemistry in the formation of **16** are as expected for a reaction proceeding through a tandem cyclopropanation/Cope rearrangement sequence. As was previously noted for the cyclopropanation of styrene, moderately noncrowded catalysts such as rhodium(II) acetate and hexanoate gave **16** with high levels of diastereoselectivity while the more soluble rhodium(II) hexanoate gave the highest yield. Sterically congested catalysts such as rhodium(II) pivalate and mandelate had a profound effect, leading to poor diastereoselectivity, although the mandelate catalyst did show significant levels of double stereodifferentiation. Under the best conditions studied, rhodium(II) hexanoate/40 °C, **16** was formed in 80% yield and in greater than 90% de.

Hydroazulenes such as **16** are potentially valuable building blocks because they contain the appropriate functionality for eventual elaboration into pseudoguaiane sesquiterpenes.[16] For example, removal of the auxiliary was readily achieved by reduction with lithium aluminum hydride, which also resulted in reduction of the carbonyl from the face opposite to that of the (trimethylsilyl)oxy group. Treatment of the crude reaction mixture with *tert*-butyldimethylsilyl chloride followed by chromatography on silica gave the hydroazulene **17**.[17] Confirmation of the stereochemistry of **17** was achieved by NOE analysis of its acetate as illustrated in Figure 2.



17

Discussion

The high levels of diastereoselectivity observed in the asymmetric cyclopropanations with α-hydroxy esters as auxiliaries

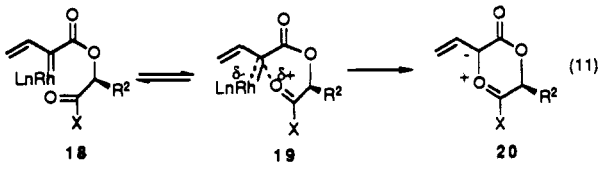
(14) (a) Davies, H. M. L.; Clark, T. J.; Smith, H. D. *J. Org. Chem.* **1991**, *56*, 3817. (b) Cantrell, W. R.; Davies, H. M. L. *J. Org. Chem.* **1991**, *56*, 723. (c) Davies, H. M. L.; McAfee, M. J.; Oldenburg, C. E. M. *J. Org. Chem.* **1989**, *54*, 930.

(15) Davies, H. M. L.; Huby, N. J. S. *Tetrahedron Lett.* **1992**, *33*, 6935.

(16) Heathcock, C. H.; Graham, S. L.; Pirrung, M. C.; Plavac, F.; White, C. T. in *The Total Synthesis of Natural Products*; ApSimon, J., Ed.; Wiley: New York, 1983; Vol. 5, pp 333–384.

(17) The absolute stereochemistry of **17** has not been determined. The drawn stereochemistry for **17** is that predicted on the basis of the model for asymmetric induction shown in Scheme III.

indicate that a fairly rigid transition state must be involved. A plausible explanation for how this rigidity could be obtained is illustrated in eq 11. The critical element of this hypothesis is that



(11)

the carbonyl of the auxiliary interacts with the carbenoid in **18** to generate the dipolar complex **19** prior to the cyclopropanation step. Indications that the carbonyl of the auxiliary is an important element in the asymmetric induction are seen on comparison of the results with the lactate **1b** and the higher homologue **1c**. The very poor diastereoselectivity with **1c** would be consistent with the requirement of formation of a six-membered ring for effective interaction between the carbenoid and the carbonyl. The significant level of double stereodifferentiation that occurs in the case of the rhodium mandelate catalysts is strong evidence that the rhodium is still associated with the dipolar complex during the cyclopropanation step. Thus, the reaction is not considered to proceed through to the uncoordinated ylide **20**, which has been commonly proposed as an intermediate in intramolecular reactions between carbenoids and carbonyls.[18]

A particularly important factor governing the success of the asymmetric cyclopropanation appears to be the extent of the carbenoid/carbonyl interaction, as was demonstrated with the ester auxiliaries. In contrast to the excellent results that were seen with the lactate **1b**, the related amide **7** resulted in a low yield of cyclopropanation when the reaction was carried out in dichloromethane. This would indicate that in this case the dipolar complex **19** tended to go on to the stabilized ylide **20** and, thus, failed to undergo effective cyclopropanation. Evidence to support this hypothesis was seen by repeating the reaction of **7** in pentane, a solvent that has been shown to strongly disfavor the formation of products derived from dipolar intermediates.[19] Under these conditions, a much improved yield of cyclopropanation was achieved although the diastereoselectivity was comparable to the result with dichloromethane as solvent. The formation of a zwitterionic complex that was too stable to exhibit significant carbenoid reactivity was the reason given by Doyle why his earlier studies[10] with the oxazolidinone auxiliaries (eq 3) resulted in such low yields of cyclopropanation products.

When the carbonyl of the auxiliary consisted of a ketone functionality, the resulting dipolar complex **19** and the ylide **20** would be expected to be less stable than the corresponding complexes from the amide and ester functionalities. The reaction with **9**, however, resulted in a low yield of cyclopropanation product **10** and poor diastereoselectivity when dichloromethane was used as solvent. The major product was the 1,3-dipolar cycloadduct **11a,b**. These results can be rationalized by assuming that the dipolar rhodium complex in this case has limited stability and proceeds on to a reactive ylide **20**, which is then trapped by styrene. Furthermore, the lower level of diastereoselectivity observed in this case may be indicative of cyclopropanation occurring via the carbenoid complex **18**, without significant carbonyl interaction. A solvent effect was once again observed for **9**, and when the reaction was performed in pentane, cyclopropanation became the dominant reaction pathway but the diastereoselectivity was not improved.

It is of interest to compare the results reported here with the extensive studies of Padwa[18] into the tandem cyclization–cycloaddition reaction of rhodium carbenoids, in which the ylide formed by cyclization through reaction between a carbenoid and a carbonyl is subsequently trapped by means of a 1,3-dipolar cycloaddition. A 1,3-dipolar cycloaddition was seen by us only in the case where the carbonyl consisted of a ketone, and ketones are by far the best systems for the tandem cyclization–cycloaddition reaction. In contrast, when the carbonyl is an ester, effective tandem cyclization–cycloaddition reactions are only observed in systems that were geometrically constrained.[19] Further evidence that ester functionalities may have important interactions with carbenoids is seen with Doyle's chiral rhodium complex, in which a carbenoid/ester carbonyl interaction is considered to be a critical element for the asymmetric induction exhibited by these catalysts.[9a,b]

Having demonstrated that the carbenoid/carbonyl interaction is likely to be involved in obtaining a rigid transition state, the next question that needs to be addressed is how does this lead to the control of absolute stereochemistry? The most reasonable explanation is shown in Scheme III. The central element in this model is the occurrence of steric interaction between the chiral auxiliary and the wall of the catalyst. In the case of (*R*)-pantolactone, conformer **21** is favored over conformer **22**, in which the pantolactone ring points directly toward the catalyst and is in an extremely unfavorable arrangement. Conversely, in the case of (*S*)-lactate, conformer **23** is preferred over conformer **24**. Another factor that needs to be considered is that, in the case of pantolactone, a significant drop in asymmetric induction was seen with more bulky catalysts but this was not seen in the case of lactate. At first sight, this result may appear to be inconsistent with the model, because one would have expected better stereoselectivity as the catalyst ligand imposes greater steric demand. However, cyclopropanation could also occur by means of a carbenoid complex that lacks a weak bond between the carbenoid and the carbonyl of the auxiliary, and this open configuration would be expected to lead to poor levels of asymmetric induction. Examination of molecular models showed that the pantolactone ring could suffer an unfavorable interaction with the catalyst wall even in conformer **21**; thus, the carbenoid/carbonyl interaction would be less favored with a bulky catalyst, and cyclopropanation could occur through a carbenoid complex lacking significant carbonyl interaction. The proposed model is also consistent with the stereochemical result of the asymmetric synthesis of tropanes by a tandem cyclopropanation/Cope rearrangement.[15]

In summary, we have demonstrated that α-hydroxy esters in general and (*R*)-pantolactone in particular are excellent chiral auxiliaries for asymmetric cyclopropanations by vinylcarbenoids. A notable advantage of this approach is that the (*R*)-pantolactone auxiliary adds crystallinity to the products, and often, enantiomerically pure products can be obtained by a single recrystallization.

Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were recorded at 200 and 50.3 MHz, respectively. CH_2Cl_2 was freshly distilled from CaH_2. Column chromatography was carried out on silica gel 60 (230–400 mesh). Methyl (2*S*)-2-hydroxy-3,3-dimethylbutanoate,[20] (2*S*)-2-hydroxy-*N*,*N*-dimethylpropanamide,[21] methyl (*E*)-2-diazo-4-phenyl-3-butenoate (**1a**),[14a] and methyl 2-methyl-3-oxo-1-cyclopentene-1-acetate[14b] were prepared according to literature procedures.

Typical Procedure for Esterification of (*E*)-4-Phenyl-3-butenoic Acid. To a solution of (*E*)-4-phenyl-3-butenoic acid (prepared according to the procedure of Hoye *et al.*[22]) (1.1 equiv) in dry CH_2Cl_2 (≈1.3 L per mol carboxylic acid) was added thionyl

(18) (a) Padwa, A.; Krumpe, K. E. *Tetrahedron* **1992**, *48*, 5385. (b) Padwa, A. *Acc. Chem. Res.* **1991**, *24*, 22.
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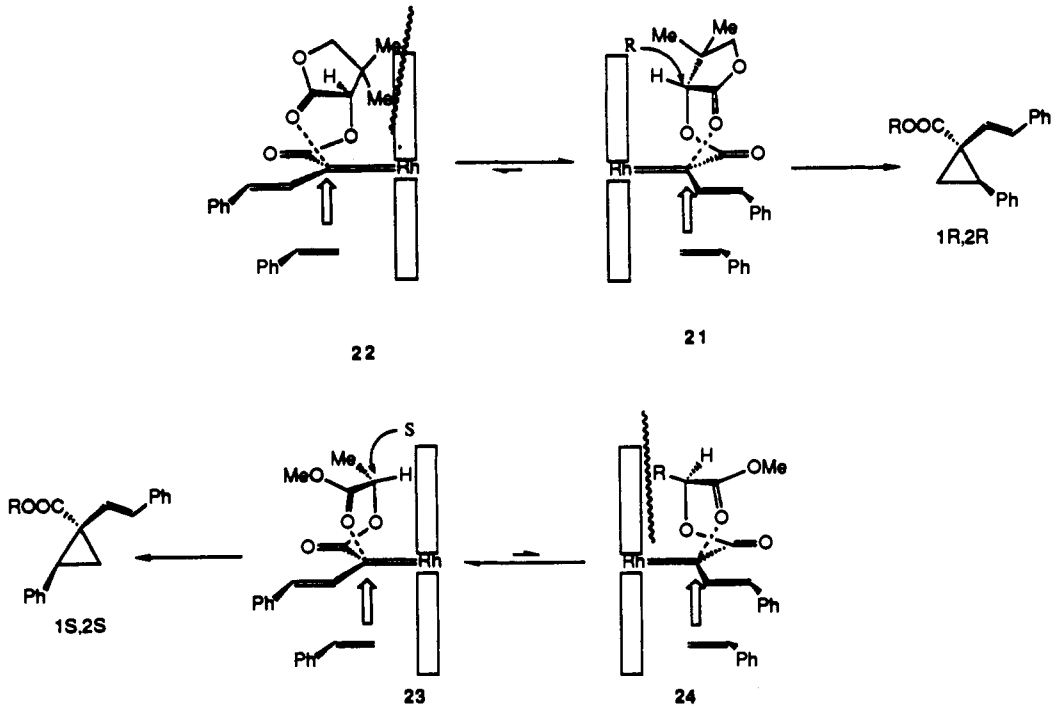
(21) Ratchford, P.; Fisher, C. P. *J. Org. Chem.* **1950**, *15*, 317.
(22) Hoye, T. R.; Richardson, W. S. *J. Org. Chem.* **1989**, *54*, 688.

Scheme III



chloride (1.5 equiv), and the mixture was heated to reflux under argon for 1 h. Concentration *in vacuo* gave the acyl chloride as a yellow solid, which was redissolved in dry CH_2Cl_2 (≈0.8 L per mol of acyl chloride) and added dropwise to a stirred solution of alcohol (1.0 equiv), pyridine (1.1 equiv) and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) (0.05 equiv) in dry CH_2Cl_2 (≈0.5 L per mol of alcohol) at 0 °C and left to warm to ambient temperature and stir overnight (≈12 h). The red reaction mixture was then washed with 2 M aqueous HCl (twice), and saturated aqueous $NaHCO_3$ (twice), dried (Na_2SO_4), and concentrated *in vacuo* to a red oil. Purification by bulb-to-bulb distillation (or silica gel column chromatography if the boiling point was too high to avoid decomposition) gave the (*E*)-4-phenyl-3-butenoate ester as a colorless oil.

(2*S*)-1-Methoxy-1-oxo-2-propyl (*E*)-4-phenyl-3-butenoate was purified by bulb-to-bulb distillation to give the butenoate ester as a clear oil (bp 120–160 °C/0.25 mmHg) (92%): $[\alpha]^{25}_D$ = –31.6 ° (*c* 5.1, $CHCl_3$); IR (neat) 3100, 3085, 3060, 3030, 3000, 2960, 2910, 2850, 1745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.39–7.21 (m, 5 H), 6.51 (d, 1 H, *J* = 15.9 Hz), 6.28 (dt, 1 H, *J* = 15.9, 6.7 Hz), 5.13 (q, 1 H, *J* = 7.1 Hz), 3.73 (s, 3 H), 3.32 (d, 2 H, *J* = 6.7 Hz), 1.50 (d, 3 H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 170.8, 170.6, 136.5, 133.4, 128.2, 127.3, 126.0, 120.9, 68.5, 52.0, 37.6, 16.6. Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.52; H, 6.51.

(±)-1-Methoxy-1-oxo-3-butyl (*E*)-4-phenyl-3-butenoate was purified by bulb-to-bulb distillation to give the butenoate ester as a yellow oil (bp 128–135 °C/0.1 mmHg) (60%): R_f 0.37 (Et_2O/petroleum ether (1:3)); IR (neat) 3020, 2975, 1730, 1595, 1435, 1190, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45–7.15 (m, 5 H), 6.47 (d, 1 H, *J* = 16.1 Hz), 6.28 (dt, 1 H, *J* = 16.1, 6.8 Hz), 5.31 (dqd, 1 H, *J* = 7.4, 6.4, 5.7 Hz), 3.64 (s, 3 H), 3.21 (d, 2 H, *J* = 6.8 Hz), 2.66 (dd, 1 H, *J* = 15.5, 7.4 Hz), 2.54 (dd, 1 H, *J* = 15.5, 5.7 Hz), 1.32 (d, 3 H, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 170.3 (s), 170.2 (s), 136.5 (s), 133.0 (d), 128.2 (d), 127.2 (d), 125.9 (d), 121.4 (d), 67.4 (d), 51.3 (q), 40.1 (t), 38.1 (t), 19.5 (q); MS (EI) *m/z* (relative intensity) 262 (12), 162 (2), 144 (100), 117 (93), 91 (15), 59 (84). Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.69; H, 6.92. Found: C, 68.50; H, 6.91.

(2*S*)-1-Methoxy-1-oxo-2-phenyl-2-ethyl (*E*)-4-phenyl-3-butenoate was purified by silica gel column chromatography to give the butenoate ester as a clear oil (50%): R_f 0.37 (Et_2O/petroleum ether (1:4)); IR (neat) 3075, 3055, 3025, 2950, 2840, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.52–7.23 (m, 10 H), 6.55 (d, 1 H, *J* = 15.9 Hz), 6.32 (dt, 1 H, *J* = 15.9, 6.8 Hz), 5.99 (s, 1 H), 3.73 (s, 3 H), 3.45–3.39 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 170.8, 169.0, 136.6, 133.8, 133.5, 129.2, 128.7, 128.4, 127.5, 127.4, 126.2, 120.8, 74.5, 52.5, 37.7. Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.51; H, 5.88.

(2*S*)-1-Methoxy-3-methyl-1-oxo-2-butyl (*E*)-4-phenyl-3-butenoate was purified by bulb-to-bulb distillation to give the butenoate ester as a yellow oil (bp 130–150 °C/0.2 mmHg) (67%): R_f 0.44 (Et_2O/petroleum ether (1:4)); $[\alpha]_D^{25}$ = –25.4° (*c* 2.03, $CHCl_3$); IR (neat) 3020, 2960, 1735, 1600, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–7.20 (m, 5 H), 6.54 (d, 1 H, *J* = 15.9 Hz), 6.31 (dt, 1 H, *J* = 15.9, 6.8 Hz), 4.89 (d, 1 H, *J* = 4.6 Hz), 3.75 (s, 3 H), 3.36 (d, 1 H, *J* = 6.8 Hz), 2.25 (septd, 1 H, *J* = 6.8, 4.7 Hz), 1.01 (d, 3 H, *J* = 6.8 Hz), 0.99 (d, 3 H, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 170.9 (s), 169.8 (s), 136.6 (s), 133.4 (d), 128.3 (d), 127.3 (d), 126.0 (d), 120.9 (d), 76.7 (d), 51.7 (q), 37.6 (t), 29.8 (d), 18.4 (q), 17.0 (q); MS (EI) *m/z* (relative intensity) 276 (12), 245 (2), 144 (100), 117 (75), 59 (41). Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.30. Found: C, 69.38; H, 7.30.

(2*S*)-1-Methoxy-3,3-dimethyl-1-oxo-2-butyl (*E*)-4-phenyl-3-butenoate was purified by bulb-to-bulb distillation to give the butenoate ester as a yellow oil (bp 128–135 °C/0.1 mmHg) (44%). On standing, a pale-yellow solid was formed (mp 54–55 °C): R_f 0.76 (Et_2O/petroleum ether (1:1)); $[\alpha]^{25}_D$ = –21.0° (*c* 4.03, $CHCl_3$); IR (neat) 3010, 2950, 1730, 1595, 1430, 1210, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–7.15 (m, 5 H), 6.52 (d, 1 H, *J* = 15.9 Hz), 6.31 (dt, 1 H, *J* = 15.9, 6.9 Hz), 4.64 (s, 1 H), 3.74 (s, 3 H), 3.35 (d, 2 H, *J* = 6.8 Hz), 1.04 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 171.0 (s), 169.3 (s), 136.7 (s), 133.5 (d), 128.4 (d), 127.4 (d), 126.1 (d), 121.0 (d), 80.1 (d), 51.6 (q), 37.7 (t), 33.5 (s), 26.0 (q); MS (EI) *m/z* (relative intensity) 290 (8), 144 (100), 117 (56), 91 (8), 59 (9), 57 (7). Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.29; H, 7.65.

(±)-3-(2-Oxotetrahydrofuranyl) (*E*)-4-phenyl-3-butenoate was purified by recrystallization (ethyl acetate/hexanes) to give the butenoate ester as a colorless solid (mp 78–80 °C) (55%): IR ($CHCl_3$) 3110, 3085, 3065, 3030, 2925, 1785, 1740 cm^{-1}; ^1H

NMR ($CDCl_3$) δ 7.37–7.12 (m, 5 H), 6.50 (d, 1 H, J = 15.9 Hz), 6.26 (dt, 1 H, J = 15.9, 6.8 Hz), 5.43 (dd, 1 H, J = 9.7, 8.7 Hz), 4.48 (m, 2 H), 3.33 (d, 2 H, J = 6.8 Hz), 2.73–2.57 (m, 1 H), 2.36–2.14 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 172.4, 170.0, 136.2, 133.6, 128.2, 127.3, 125.9, 120.3, 67.7, 64.8, 37.4, 28.4. Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.25; H, 5.77.

(3*R*)-3-(4,4-Dimethyl-2-oxotetrahydrofuranyl) (*E*)-4-phenyl-3-butenoate was purified by silica gel column chromatography to give the butenoate ester as a clear oil (84%): R_f 0.44 (Et_2O/petroleum ether (2:3)); $[\alpha]^{25}_D$ = 7.1° (*c* 2.13, $CHCl_3$); IR (neat) 3090, 3060, 3030, 2970, 2940, 2910, 2880, 1790, 1745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–7.23 (m, 5 H), 6.55 (d, 1 H, J = 15.9 Hz), 6.29 (dt, 1 H, J = 15.9, 6.9 Hz), 5.39 (s, 1 H), 4.05 (d, 1 H, J = 9.1 Hz), 4.00 (d, 1 H, J = 9.1 Hz), 3.40 (d, 2 H, J = 6.9 Hz), 1.19 (s, 3 H), 1.11 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 172.1, 170.1, 136.4, 133.8, 128.3, 127.5, 126.1, 120.5, 75.9, 75.0, 39.9, 37.4, 22.6, 19.6. Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 70.04; H, 6.64.

(2*S*)-1-(*N*,*N*-Dimethylamino)-1-oxo-2-propanyl (*E*)-4-phenyl-3-butenoate was purified by bulb-to-bulb distillation to give the butenoate ester as a yellow oil (bp 160–165 °C/0.4 mmHg) (56%): R_f 0.09 (Et_2O/petroleum ether (1:1)); $[\alpha]^{25}_D$ = −26.7° (*c* 2.95, $CHCl_3$); IR (neat) 3450 (br), 2930, 1725 (s), 1650 (s), 1155 (s), 1075 (s), 745, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.50–7.10 (m, 5 H), 6.51 (d, 1 H, J = 16.0 Hz), 6.29 (dt, 1 H, J = 16.0, 6.8 Hz), 5.41 (q, 1 H, J = 6.7 Hz), 3.34 (d, 2 H, J = 6.8 Hz), 3.06 (s, 3 H), 2.97 (s, 3 H), 1.46 (d, 3 H, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$) δ 170.8 (s), 169.8 (s), 136.5 (s), 133.3 (d), 128.2 (d), 127.2 (d), 126.0 (d), 121.0 (d), 66.9 (d), 37.5 (t), 36.4 (q), 35.5 (q), 16.2 (q); MS (EI) *m/z* (relative intensity) 261 (2), 216 (18), 144 (100), 117 (51), 91 (12). Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.69; H, 7.30; N, 5.34.

(±)-2-Hydroxy-3-butyl (*E*)-4-Phenyl-3-butenoate. The reaction was carried out at −40 °C for 4 h before warming to ambient temperature and stirring for 10 h. The product was purified by bulb-to-bulb distillation (bp 142–155 °C/0.1 mmHg) (46%): R_f 0.42 (Et_2O/petroleum ether (3:2)); IR (neat) 3430 (br), 3010, 2965, 1715, 1595, 1440, 1365, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45–7.20 (m, 5 H), 6.50 (d, 1 H, J = 15.9 Hz), 6.30 (dt, 1 H, J = 15.9, 6.8 Hz), 4.91 (qd, 1 H, J = 6.5, 3.4 Hz), 3.90 (qd, 1 H, J = 6.5, 3.4 Hz), 3.26 (d, 2 H, J = 6.8 Hz), 1.98 (s br, 3 H), 1.23 (d, 3 H, J = 6.5 Hz), 1.17 (d, 3 H, J = 6.5 Hz); ^{13}C NMR ($CDCl_3$) δ 171.2 (s), 136.6 (s), 133.4 (d), 128.4 (d), 127.4 (d), 126.1 (d), 121.4 (d), 74.6 (d), 69.2 (d), 38.2 (t), 17.8 (q), 14.2 (q); MS (EI) *m/z* (relative intensity) 234 (31), 190 (2), 162 (10), 144 (28), 117 (100), 73 (30); HRMS calcd for $C_{14}H_{18}O_3$ 234.1255, found 234.1255.

(±)-2-Oxo-3-butyl (*E*)-4-Phenyl-3-butenoate. To a stirred solution of 2-hydroxy-3-butyl (*E*)-4-phenyl-3-butenoate (2.50 g, 10.7 mmol) in dry CH_2Cl_2 (50 mL) at ambient temperature under argon was added pyridinium chlorochromate (PCC) (3.45 g, 16.0 mmol). After 3 h further PCC (3.45 g, 16.0 mmol) was added and stirring continued overnight (10 h). Dry Et_2O (50 mL) was added, the mixture filtered through Celite, and the precipitate washed with Et_2O (100 mL). The filtrate was concentrated *in vacuo* to a dark brown oil. Purification by bulb-to-bulb distillation gave the butenoate ester as a yellow oil (bp 114–120 °C/0.1 mmHg) (2.05 g, 83%). On standing, colorless crystals were formed (mp 25 °C): R_f 0.55 (Et_2O/petroleum ether (1:1)); IR (neat) 3015, 2985, 1720, 1645, 1595, 1440, 1355, 1155 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45–7.15 (m, 5 H), 6.53 (d, 1 H, J = 15.9 Hz), 6.31 (dt, 1 H, J = 15.9, 6.9 Hz), 5.12 (q, 1 H, J = 7.1 Hz), 3.34 (d, 2 H, J = 6.9 Hz), 2.18 (s, 3 H), 1.43 (d, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 205.0 (s), 170.6 (s), 136.5 (s), 133.5 (d), 128.3 (d), 127.4 (d), 126.0 (d), 120.8 (d), 74.9 (d), 37.6 (t), 25.3 (q), 15.6 (q); MS (EI) *m/z* (relative intensity) 232 (7), 144 (64), 117 (100), 91 (13). Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.15; H, 6.98.

Typical Procedure for Diazo Transfer to (*E*)-4-Phenyl-3-butenoate Esters. To a solution of (*E*)-4-phenyl-3-butenoate ester (1.0 equiv) and *p*-acetamidobenzenesulfonyl azide (ABSA) (1.1 equiv) in dry MeCN (≈10 L per mol of ester) at 0 °C under argon was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.95 equiv) in dry MeCN (≈4 L per mol). After 1 h the red reaction mixture was poured into saturated aqueous NH_4Cl to quench the reaction, extracted with CH_2Cl_2, dried (Na_2SO_4), and concentrated *in vacuo* to an orange solid. The bulk of the solid sulfonamide byproduct could be removed as a colorless solid by trituration with 1:1 Et_2O/petroleum ether. Silica gel column chromatography gave the pure (*E*)-2-diazo-4-phenyl-3-butenoate ester. Noncrystalline derivatives were of insufficient stability for elemental composition analysis.

(2*S*)-1-Methoxy-1-oxo-2-propyl (*E*)-2-diazo-4-phenyl-3-butenoate (1b): orange solid (mp 63–65 °C) (85%); R_f 0.60 (Et_2O/petroleum ether (1:1)); $[\alpha]^{25}_D$ = +18.6° (*c* 2.0, $CHCl_3$); IR ($CHCl_3$) 3080, 3060, 3025, 2960, 2080, 1750, 1695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.36–7.18 (m, 5 H), 6.46 (d, 1 H, J = 16.3 Hz), 6.21 (d, 1 H, J = 16.3 Hz), 5.25 (q, 1 H, J = 7.1 Hz), 3.76 (s, 3 H), 1.54 (d, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 170.9, 164.3, 136.6, 128.6, 127.0, 125.8, 123.3, 110.8, 69.1, 63.8, 52.3, 16.9. Anal. Calcd for $C_{14}H_{14}N_2O_4$: C, 61.31; H, 5.15; N, 10.21. Found: C, 61.38; H, 5.19; N, 10.14.

(±)-1-Methoxy-1-oxo-3-butyl (*E*)-2-diazo-4-phenyl-3-butenoate (1c): red oil (76%); R_f 0.39 (Et_2O/petroleum ether (1:3)); IR (neat) 2985, 2080, 1735, 1700, 1630, 1375, 1245, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–7.15 (m, 5 H), 6.45 (d, 1H, J = 16.4 Hz), 6.20 (d, 1 H, J = 16.4 Hz), 5.44 (dqd, 1 H, J = 7.3, 6.3, 5.8 Hz), 3.70 (s, 3H), 2.70 (dd, 1 H, J = 15.6, 7.3 Hz), 2.59 (dd, 1 H, J = 15.6, 5.8 Hz), 1.30 (d, 3 H, J = 6.3 Hz); ^{13}C NMR ($CDCl_3$) δ 170.1 (s), 164.0 (s), 136.5 (s), 128.4 (d), 126.8 (d), 125.6 (d), 122.9 (d), 111.0 (d), 68.3 (d), 63.6 (s), 51.5 (q), 40.3 (t), 19.8 (q).

(±)-1-Methoxy-1-oxo-2-phenyl-2-ethyl (*E*)-2-diazo-4-phenyl-3-butenoate (1d): orange solid (mp 75.5–76.5 °C) (64%); R_f 0.67 (Et_2O/petroleum ether (1:1)); IR ($CHCl_3$) 3050, 3015, 2950, 2080, 1745, 1695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.51–7.18 (m, 10 H), 6.48 (d, 1 H, J = 16.3 Hz), 6.24 (d, 1 H, J = 16.3 Hz), 6.09 (s, 1 H), 3.75 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 169.0, 164.3, 136.5, 133.4, 129.3, 128.8, 128.6, 127.4, 127.1, 125.8, 123.6, 110.6, 74.7, 64.0, 52.6. Anal. Calcd for $C_{19}H_{16}N_2O_4$: C, 67.85; H, 4.80; N, 8.33. Found: C, 67.79; H, 4.82; N, 8.25.

(2*S*)-1-Methoxy-3-methyl-1-oxo-2-butyl (*E*)-2-diazo-4-phenyl-3-butenoate (1e): viscous red oil (73%); R_f 0.52 (Et_2O/petroleum ether (1:4)); $[\alpha]^{25}_D$ = +4.6° (*c* 1.00, $CHCl_3$); IR (neat) 2955, 2075, 1740, 1690, 1620, 1440, 1365, 1200, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45–7.15 (m, 5 H), 6.45 (d, 1 H, J = 16.4 Hz), 6.26 (d, 1 H, J = 16.4 Hz), 5.00 (d, 1 H, J = 4.5 Hz), 3.78 (s, 3 H), 2.30 (septd, 1 H, J = 6.9, 4.5 Hz), 1.04 (d, 3 H, J = 6.9 Hz), 1.00 (d, 3 H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 169.7 (s), 164.3 (s), 136.5 (s), 128.4 (d), 126.9 (d), 125.6 (d), 123.3 (d), 110.6 (d), 77.0 (d), 63.7 (s), 51.9 (q), 30.0 (d), 18.5 (q), 16.9 (q).

(2*S*)-1-Methoxy-3,3-dimethyl-1-oxo-2-butyl (*E*)-2-diazo-4-phenyl-3-butenoate (1f): red oil (83%); R_f 0.57 (Et_2O/petroleum ether (1:4)); $[\alpha]^{25}_D$ = +12.3° (*c* 0.81, $CHCl_3$); IR (neat) 3010, 2960, 2070, 1745, 1695, 1625, 1445, 1365, 1210, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–7.15 (m, 5 H), 6.44 (d, 1 H, J = 16.3 Hz), 6.26 (d, 1 H, J = 16.3 Hz), 4.75 (s, 1 H), 3.77 (s, 3 H), 1.05 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 169.2 (s), 164.5 (s), 136.6 (s), 128.6 (d), 127.0 (d), 125.7 (d), 123.5 (d), 110.6 (d), 80.4 (d), 63.8 (s), 51.7 (q), 33.7 (s), 26.0 (q).

(3*R*)-3-(4,4-Dimethyl-2-oxotetrahydrofuranyl) 2-diazo-4-phenyl-3-butenoate (1g): orange solid (mp 95.5–98 °C) (81%); R_f 0.53 (Et_2O/petroleum ether (1:1)); $[\alpha]^{25}_D$ = +8.2° (*c* 2.2, $CHCl_3$); IR ($CHCl_3$) 3080, 3060, 3020, 2970, 2930, 2910, 2880,

2080, 1790, 1695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38–7.21 (m, 5 H), 6.46 (d, 1 H, J = 16.3 Hz), 6.25 (d, 1 H, J = 16.3 Hz), 5.50 (s, 1 H), 4.07 (s, 2 H), 1.25 (s, 3 H), 1.14 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 172.0, 163.7, 136.4, 128.6, 127.2, 125.8, 123.8, 110.3, 76.0, 75.4, 63.9, 40.1, 22.8, 19.7. Anal. Calcd for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N, 9.33. Found: C, 63.99; H, 5.38; N, 9.35.

(±)-3-(2-Oxotetrahydrofuranyl) (*E*)-2-diazo-4-phenyl-3-butenoate (1h): orange gum (52%); R_f 0.27 (Et_2O/petroleum ether (1:1)); IR ($CHCl_3$) 3090, 3070, 3040, 2925, 2080, 1785, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38–7.16 (m, 5 H), 6.44 (d, 1 H, J = 16.4 Hz), 6.22 (d, 1 H, J = 16.4 Hz), 5.58 (apparent t, 1 H, J = 9.3 Hz), 4.54–4.24 (m, 2 H), 2.82–2.65 (m, 1 H), 2.49–2.28 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 172.2, 163.4, 136.1, 128.3, 126.9, 125.5, 123.4, 110.0, 68.0, 64.8, 63.7, 28.5.

Typical Procedure for the Rhodium(II) Carboxylate Catalyzed Decomposition of Vinyldiazoacetates in the Presence of Alkenes. The vinyldiazoacetate (0.5 mmol) in dry CH_2Cl_2 (15 mL) was added dropwise to a refluxing mixture of the alkene (10 mmol) and rhodium(II) acetate (0.005 mmol) in dry CH_2Cl_2 (15 mL) under an atmosphere of argon. After the addition was complete, the mixture was refluxed for an additional 30 min whereupon the solvent was removed *in vacuo* and the unreacted styrene removed by bulb-to-bulb distillation (25–40 °C/0.5 mmHg). At this point, the crude reaction was examined by ^1H NMR to reveal the extent of asymmetric induction. Diastereomeric excess (de) was typically determined by comparison of the integrals for the signals arising due to the alkenyl protons at δ ≈6.30 and ≈6.10. The crude product was purified by silica gel column chromatography using ether/petroleum ether mixtures as solvent to give the cyclopropane.

(2*S*)-1-Methoxy-1-oxo-2-propanyl 2α-phenyl-1α-((*E*)-2-phenylethenyl)-1β-cyclopropanecarboxylate (4b): de = 67% before purification; clear oil (83%); R_f 0.37 (Et_2O/petroleum ether (1:1)); IR (neat) 3080, 3060, 3020, 2990, 2950, 1745, 1715 cm^{-1}; ^1H NMR ($CDCl_3$) (major diastereomer) δ 7.29–7.12 (m, 10 H), 6.40 (d, 1 H, J = 16.0 Hz), 6.12 (d, 1 H, J = 16.0 Hz), 5.18 (q, 1 H, J = 7.1 Hz), 3.78 (s, 3 H), 3.17 (dd, 1 H, J = 9.1, 7.5 Hz), 2.12 (dd, 1 H, J = 9.1, 5.2 Hz), 1.88 (dd, 1 H, J = 7.4, 5.2 Hz), 1.53 (d, 3 H, J = 7.1 Hz); ^1H NMR ($CDCl_3$) (minor diastereomer, resolvable signals at 200 MHz) δ 6.37 (d, 1 H, J = 16.0 Hz), 6.17 (d, 1 H, J = 16.0 Hz), 5.17 (q, 1 H, J = 7.1 Hz), 3.80 (s, 3 H), 3.06 (dd, 1 H, J = 9.1, 7.5 Hz), 1.53 (d, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 172.3, 170.7, 136.7, 134.9, 132.7, 128.9, 128.0, 127.6, 126.9, 126.5, 125.8, 123.3, 68.7, 51.9, 35.2, 32.8, 18.2, 16.6; MS (EI) m/z (relative intensity) 350 (7), 246 (100), 217 (52), 159 (9), 141 (24), 115 (45), 91 (65); HRMS calcd for $C_{22}H_{22}O_4$ 350.1518, found 350.1525. Anal. Calcd for $C_{22}H_{22}O_4$: C, 75.41; H, 6.33. Found: C, 75.29; H, 6.36. Methanolysis of **4b** gave enantiomerically enriched **4a**: $[\alpha]^{25}_D$ = −84.5° (*c* 0.71, $CHCl_3$).

(±)-1-Methoxy-1-oxo-3-butanyl 2α-phenyl-1α-((*E*)-2-phenylethenyl)-1β-cyclopropanecarboxylate (4c): de = 12% before purification; colorless oil (77%); R_f 0.37 (Et_2O/petroleum ether (1:3)); IR (neat) 3050, 2970, 2940, 1740, 1710, 1595, 1485, 1440, 1365 cm^{-1}; ^1H NMR ($CDCl_3$) (major diastereomer) δ 7.40–7.05 (m, 10 H), 6.32 (d, 1 H, J = 16.0 Hz), 6.10 (d, 1 H, J = 16.0 Hz), 5.33 (m, 1 H), 3.61 (s, 3 H), 2.95 (m, 1 H), 2.68 (dd, 1 H, J = 15.4, 7.4 Hz), 2.57 (dd, 1 H, J = 15.4, 5.6 Hz), 2.04 (apparent t, 1 H, J = 5.6 Hz), 1.79 (dd, 1 H, J = 7.3, 5.1 Hz), 1.36 (d, 3 H, J = 6.3 Hz); ^1H NMR ($CDCl_3$) (minor diastereomer, resolvable signals at 200 MHz) δ 6.30 (d, 1 H, J = 16.0 Hz), 6.08 (d, 1 H, J = 16.0 Hz), 3.69 (s, 3 H), 3.00 (m, 1 H), 2.65 (dd, 1 H, J = 15.4, 7.4 Hz), 2.55 (dd, 1 H, J = 15.4, 5.6 Hz), 1.99 (apparent t, 1 H, J = 5.6 Hz), 1.80 (dd, 1 H, J = 7.3, 5.1 Hz), 1.34 (d, 3 H, J = 6.3 Hz); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 172.4 (s), 170.5 (s), 137.0 (s), 135.4 (s), 132.6 (d), 128.9 (d), 128.2 (d), 127.8 (d), 127.1 (d), 126.6 (d), 126.0 (d), 123.9 (d), 68.1 (d), 51.5 (q), 40.4 (t), 34.8 (d), 33.2 (s), 19.7 (q), 18.2 (t); MS (EI) m/z (relative intensity) 364 (61), 264 (16), 246 (100), 219 (23), 173 (13), 141 (11), 129 (28), 91 (42); HRMS calcd for $C_{23}H_{24}O_4$ 364.1675, found 364.1675.

(±)-1-Methoxy-1-oxo-2-phenyl-2-ethyl 2α-phenyl-1α-((*E*)-2-phenylethenyl)-1β-cyclopropanecarboxylate (4d): de = 59% before purification; clear oil (71%); R_f 0.74 (Et_2O/petroleum ether (1:1)); IR (neat) 3090, 3060, 3035, 2980, 2960, 1750, 1715 cm^{-1}; ^1H NMR ($CDCl_3$) (major diastereomer) δ 7.52–7.11, (m, 15 H), 6.47 (d, 1 H, J = 16.1 Hz), 6.15 (d, 1 H, J = 16.1 Hz), 6.03 (s, 1 H), 3.74 (s, 3 H), 3.27 (dd, 1 H, J = 9.2, 7.6 Hz), 2.17 (dd, 1 H, J = 9.2, 5.1 Hz), 1.90 (dd, 1 H, J = 7.6, 5.1 Hz); ^1H NMR ($CDCl_3$) (minor diastereomer, resolvable signals at 200 MHz) δ 6.41 (d, 1 H, J = 16.1 Hz), 6.20 (d, 1 H, J = 16.1 Hz), 3.76 (s, 3 H), 3.14 (dd, 1 H, J = 9.1, 7.5 Hz), 2.20 (dd, 1 H, J = 9.1, 4.6 Hz), 1.92 (dd, 1 H, J = 7.5, 4.6 Hz); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 172.5, 169.0, 136.9, 135.0, 133.6, 133.2, 129.0, 128.6, 128.2, 127.8, 127.3, 127.2, 127.1, 126.7, 126.0, 123.2, 74.6, 52.5, 35.5, 33.0, 18.8; MS (EI) m/z (relative intensity) 412 (29), 263 (79), 217 (43), 159 (61), 129 (81), 91 (100); HRMS calcd for $C_{27}H_{24}O_4$ 412.1674, found 412.1639.

(2*S*)-1-Methoxy-3-methyl-1-oxo-2-butanyl 2α-phenyl-1α-((*E*)-2-phenylethenyl)-1β-cyclopropanecarboxylate (4e): de = 78% before purification; yellow oil (82%); R_f 0.47 (Et_2O/petroleum ether (1:4)); $[\alpha]^{25}_D$ = −55.1° (*c* 1.60, $CHCl_3$); IR (neat) 3010, 2950, 2865, 1740, 1715, 1595, 1485, 1445, 1235, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) (major diastereomer) δ 7.35–7.05 (m, 10 H), 6.40 (d, 1 H, J = 16.1 Hz), 6.11 (d, 1 H, J = 16.1 Hz), 4.92 (d, 1 H, J = 4.4 Hz), 3.77 (s, 3 H), 3.19 (dd, 1 H, J = 9.3, 7.5 Hz), 2.28 (septd, 1 H, J = 6.9, 4.4 Hz), 2.10 (dd, 1 H, J = 9.3, 5.2 Hz), 1.85 (dd, 1 H, J = 7.5, 5.2 Hz), 1.04 (d, 3 H, J = 6.9 Hz), 0.98 (d, 3 H, J = 6.9 Hz); ^1H NMR ($CDCl_3$) (minor diastereomer, resolvable signals at 200 MHz) δ 6.38 (d, 1 H, J = 16.1 Hz), 6.17 (d, 1 H, J = 16.1 Hz), 3.78 (s, 3 H), 3.05 (dd, 1 H, J = 9.3, 7.5 Hz); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 172.7 (s), 170.0 (s), 137.0 (s), 135.2 (s), 133.0 (d), 129.1 (d), 128.2 (d), 127.9 (d), 127.1 (d), 126.7 (d), 126.0 (d), 123.4 (d), 76.9 (d), 51.9 (q), 35.2 (d), 33.0 (s), 30.0 (d), 18.8 (q), 18.6 (t), 17.1 (q); MS (EI) m/z (relative intensity) 378 (39), 347 (2), 246 (100), 219 (9), 115 (10), 91 (27). Anal. Calcd for $C_{24}H_{26}O_4$: C, 76.17; H, 6.92. Found: C, 76.22; H, 6.94. Methanolysis of **4e** gave enantiomerically enriched **4a**: $[\alpha]^{25}_D$ = −131.4° (*c* 1.71, $CHCl_3$).

(2*S*)-1-Methoxy-3,3-dimethyl-1-oxo-2-butanyl 2α-phenyl-1α-((*E*)-2-phenylethenyl)-1β-cyclopropanecarboxylate (4f): de = 79% before purification; yellow oil (81%); R_f 0.41 (Et_2O/petroleum ether (1:4)); $[\alpha]^{25}_D$ = −43.6° (*c* 4.00, $CHCl_3$); IR (neat) 3010, 2950, 2860, 1735, 1715, 1595, 1485, 1445, 1205, 1130 cm^{-1}; ^1H NMR ($CDCl_3$) (major diastereomer) δ 7.30–7.05 (m, 10 H), 6.40 (d, 1 H, J = 16.1 Hz), 6.10 (d, 1 H, J = 16.1 Hz), 4.65 (s, 1 H), 3.77 (s, 3 H), 3.18 (dd, 1 H, J = 9.2, 7.6 Hz), 2.09 (dd, 1 H, J = 9.2, 5.2 Hz), 1.85 (dd, 1 H, J = 7.6, 5.2 Hz), 1.04 (s, 9 H); ^1H NMR ($CDCl_3$) (minor diastereomer, resolvable signals at 200 MHz) δ 6.38 (d, 1 H, J = 16.1 Hz), 6.16 (d, 1 H, J = 16.1 Hz), 4.64 (s, 1 H), 3.03 (dd, 1 H, J = 9.2, 7.6 Hz); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 172.8 (s), 169.5 (s), 137.1 (s), 135.3 (s), 133.2 (d), 129.1 (d), 128.3 (d), 128.0 (d), 127.2 (d), 126.8 (d), 126.1 (d), 123.4 (d), 80.4 (d), 51.7 (q), 35.1 (d), 33.7 (s), 33.0 (s), 26.2 (q), 18.7 (t); MS (EI) m/z (relative intensity) 392 (51), 264 (25), 246 (100), 219 (19), 173 (15), 129 (20), 91 (39). Anal. Calcd for $C_{25}H_{28}O_4$: C, 76.50; H, 7.19. Found: C, 76.41; H, 7.23. Methanolysis of **4f** gave enantiomerically enriched **4a**: $[\alpha]^{25}_D$ = −120.6° (*c* 1.08, $CHCl_3$).

(3*R*)-3-(4,4-Dimethyl-2-oxotetrahydrofuranyl) 2α-phenyl-1α-((*E*)-2-phenylethenyl)-1β-cyclopropanecarboxylate (4g): de = 89% before purification; colorless solid (mp 97–98 °C) (91%). Recrystallization from 2-isopropanol gave essentially one diastereomer as determined by ^1H NMR (64%): R_f 0.40 (Et_2O/petroleum ether (1:1)); $[\alpha]^{25}_D$ = +99.3° (*c* 2.0, enriched diastereomer, $CHCl_3$); IR ($CHCl_3$) 3040, 3020, 2970, 2930, 2860,

1790, 1715 cm^{-1}; ^{1}H NMR ($CDCl_3$) (major diastereomer) δ 7.28–7.07 (m, 10 H), 6.39 (d, 1 H, J = 16.1 Hz), 6.06 (d, 1 H, J = 16.1 Hz), 5.42 (s, 1 H), 4.04 (s, 2 H), 3.18 (dd, 1 H, J = 9.1, 7.5 Hz), 2.13 (dd, 1 H, J = 9.1, 5.2 Hz), 1.90 (dd, 1 H, J = 7.5, 5.2 Hz), 1.24 (s, 3 H), 1.12 (s, 3 H); ^{1}H NMR ($CDCl_3$) (minor diastereomer, resolvable signals at 200 MHz) δ 6.12 (d, 1 H, J = 16.1 Hz), 4.03 (s, 2 H), 3.08 (dd, 1 H, J = 9.2, 7.5 Hz), 2.11 (dd, 1 H, J = 9.2, 5.2 Hz), 1.19 (s, 3 H), 1.08 (s, 3 H); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 172.1, 136.8, 134.9, 133.5, 129.1, 128.3, 128.0, 127.3, 126.9, 126.1, 123.0, 76.0, 75.3, 40.0, 35.6, 32.9, 23.0, 19.9, 19.1. Anal. Calcd for $C_{24}H_{24}O_4$: C, 76.57; H, 6.43. Found: C, 76.48; H, 6.45.

(±)-3-(2-Oxotetrahydrofuranyl) 2α-phenyl-1α-((*E*)-2-phenylethenyl)-1β-cyclopropanecarboxylate (4h): de = 42% before purification; colorless solid (mp 107.5–110 °C) (90%); R_f 0.21 (Et_2O/petroleum ether (1:1)); IR ($CHCl_3$) 3085, 3060, 3025, 3010, 2975, 2925, 1780, 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) (major diastereomer) δ 7.28–7.09 (m, 10 H), 6.39 (d, 1 H, J = 15.8 Hz), 6.07 (d, 1 H, J = 15.8 Hz), 5.50 (apparent t, 1 H, J = 9.1 Hz), 4.55–4.22 (m, 2 H), 3.14 (dd, 1 H, J = 9.3, 7.6 Hz), 2.79–2.64 (m, 1 H), 2.47–2.26 (m, 1 H), 2.11 (dd, 1 H, J = 9.3, 5.2 Hz), 1.90 (dd, 1 H, J = 7.6, 5.2 Hz); ^{1}H NMR ($CDCl_3$) (minor diastereomer, resolvable signals at 200 MHz) δ 6.37 (d, 1 H, J = 15.8 Hz), 6.11 (d, 1 H, J = 15.8 Hz), 5.52 (apparent t, 1 H, J = 9.1 Hz), 3.09 (dd, 1 H, J = 9.9, 7.7 Hz), 2.13 (dd, 1 H, J = 9.9, 5.1 Hz), 1.92 (dd, 1 H, J = 7.7, 5.1 Hz); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 172.4, 172.1, 136.6, 134.7, 133.4, 129.0, 128.1, 127.8, 127.2, 126.7, 126.0, 122.9, 68.0, 64.8, 35.5, 32.8, 28.5, 18.9. Anal. Calcd for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79. Found: C, 75.76; H, 5.85.

Methyl 2α-Phenyl-1α-((*E*)-2-phenylethenyl)-1β-cyclopropanecarboxylate (4a). Sodium metal (0.30 g, 13.0 mmol) was washed with hexanes and then added to dry MeOH (15 mL) with stirring. After dissolution of the sodium, recrystallized **4g** (0.96 g, 2.55 mmol) in dry MeOH (15 mL) was added to the methoxide solution and the mixture was allowed to stir for 12 h. The solvent was removed *in vacuo*, and CH_2Cl_2 and saturated aqueous NH_4Cl were added to the residue. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2×). The combined organic extracts were dried ($MgSO_4$), and the solvent was removed *in vacuo* to give the crude product. Purification by silica gel column chromatography gave **4a** as a colorless solid (mp 77–78 °C) (0.57 g, 81%): R_f 0.43 (Et_2O/petroleum ether (1:4)); $[\alpha]^{25}_D$ = +157.1° (*c* 1.1, $CHCl_3$); IR ($CHCl_3$) 3110, 3090, 3060, 2980, 2950, 2880, 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.28–7.12 (m, 10 H), 6.37 (d, 1 H, J = 15.9 Hz), 6.15 (d, 1 H, J = 15.9 Hz), 3.77 (s, 3 H), 3.04 (dd, 1 H, J = 9.1, 7.3 Hz), 2.05 (dd, 1 H, J = 9.1, 5.1 Hz), 1.85 (dd, 1 H, J = 7.3, 5.1 Hz); ^{13}C NMR ($CDCl_3$) δ 174.0, 137.0, 135.4, 133.0, 129.0, 128.3, 127.9, 127.2, 126.7, 126.1, 124.0, 52.3, 34.9, 33.2, 18.5. Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.74; H, 6.53.

1α-Amino-2α-phenyl-1β-cyclopropanecarboxylic Acid Hydrochloride Salt (5).[4b] $RuCl_3 \cdot H_2O$ (0.0156 g, 0.0692 mmol) was added to a rapidly stirred mixture of recrystallized **4g** (1.30 g, 3.46 mmol) and $NaIO_4$ (5.93 g, 27.7 mmol) in CCl_4 (6.9 mL, 2 mL mmol^{-1}), CH_3CN (6.9 mL, 2 mL mmol^{-1}), and H_2O (10.4 mL, 3 mL mmol^{-1}) at ambient temperature. After stirring for 2 h, the mixture was filtered, the precipitate was washed with H_2O and CH_2Cl_2, and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$), and the solvent was removed *in vacuo* to yield the crude product **6** and benzoic acid, which were used in the next step without purification. A mixture of benzoic acid and crude carboxylic acid **6** (1.02 g, 2.32 mmol), diphenyl phosphorylazidate (0.70 g, 2.55 mmol), and triethylamine (0.28 g, 2.78 mmol) was dissolved in toluene, and the mixture was heated to reflux for 12 h. The mixture was then cooled, and the solvent was removed under vacuum. HCl (6 M, 20 mL) was added to the residue, and the mixture was heated to reflux for 12 h. The mixture was cooled and washed with CH_2Cl_2. NaOH (10%) was added to the aqueous layer until pH = 12, and the mixture was then washed with CH_2Cl_2. Concentrated HCl was added to the aqueous layer until pH = 2, and the solvent was removed *in vacuo*. The residue was triturated with EtOH, and the filtrate was reduced *in vacuo* to yield the crude product. Purification by recrystallization (EtOH/Et_2O) gave the cyclopropane amino acid **5** as a colorless solid (mp 197–199 °C dec) (0.137 g, 27%): $[\alpha]^{25}_D$ = +104.6° (*c* 0.26, H_2O); IR (KBr) 3440, 2940, 1725, 1580 cm^{-1}; ^{1}H NMR (D_2O) δ 7.37–7.16 (m, 5 H), 3.07 (t, 1 H, J = 9.1 Hz), 1.87 (dd, 1 H, J = 9.9, 6.9 Hz), 1.7 (t, 1 H, J = 7.7 Hz).

(2*S*)-1-(*N*,*N*-Dimethylamino)-1-oxo-2-propanyl (*E*)-2-diazo-4-phenyl-3-butenoate (7): red viscous oil (77%); R_f 0.27 (Et_2O/petroleum ether (3:1)); $[\alpha]^{25}_D$ = +54.7° (*c* 0.817, $CHCl_3$); IR (neat) 3260, 3040, 2975, 2925, 2110, 2080, 1640 (br), 1585, 1490, 1365, 1235 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.45–7.15 (m, 5 H), 6.45 (d, 1 H, J = 16.3 Hz), 6.20 (d, 1 H, J = 16.3 Hz), 5.53 (q, 1 H, J = 6.8 Hz), 3.09 (s, 3 H), 2.99 (s, 3 H), 1.49 (d, 3 H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 169.6 (s), 164.3 (s), 136.4 (s), 128.3 (d), 126.7 (d), 125.5 (d), 122.9 (d), 110.7 (d), 67.4 (d), 63.8 (s), 36.3 (q), 35.5 (q), 16.3 (q).

(2*S*)-1-(*N*,*N*-dimethylamino)-1-oxo-2-propyl 2α-phenyl-1α-((*E*)-2-phenylethenyl)-1β-cyclopropanecarboxylate (8). Cyclopropanation with styrene was performed as per the typical procedure (*vide supra*) except that dry pentane was used as solvent in place of CH_2Cl_2, rhodium(II) octanoate was used as catalyst in place of rhodium(II) acetate, and **7** was added in a solution of 1:1 toluene/pentane so that the vinyldiazomethane remained in solution. de = 51% (53% in CH_2Cl_2 reaction) before purification; colorless gum (67%) (33% in CH_2Cl_2 reaction); R_f 0.45 (Et_2O/petroleum ether (9:1)); $[\alpha]^{25}_D$ = –42.6° (*c* 2.07, $CHCl_3$); IR (neat) 3010, 2980, 2925, 1710, 1650, 1595, 1485, 1445, 1235, 1135 cm^{-1}; ^{1}H NMR ($CDCl_3$) (major diastereomer) δ 7.35–7.05 (m, 10 H), 6.37 (d, 1 H, J = 16.1 Hz), 6.13 (d, 1 H, J = 16.1 Hz), 5.40 (q, 1 H, J = 6.8 Hz), 3.19 (apparent t, 1 H, J = 8.3 Hz), 3.03 (s, 3 H), 2.95 (s, 3 H), 2.10 (dd, 1 H, J = 9.2, 5.1 Hz), 1.83 (dd, 1 H, J = 7.5, 5.1 Hz), 1.45 (d, 3 H, J = 6.8 Hz); ^{1}H NMR ($CDCl_3$) (minor diastereomer, resolvable signals at 200 MHz) δ 6.33 (d, 1 H, J = 16.1 Hz), 6.19 (d, 1 H, J = 16.1 Hz), 3.04 (s, 3 H), 2.96 (s, 3 H); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 172.6 (s), 169.8 (s), 136.8 (s), 135.1 (s), 132.6 (d), 128.9 (d), 128.0 (d), 127.6 (d), 126.9 (d), 126.4 (d), 125.9 (d), 123.5 (d), 67.2 (d), 36.3 (q), 35.5 (q), 35.0 (d), 32.7 (s), 18.3 (t), 16.2 (q); MS m/z (relative intensity) 363 (38), 318 (12), 246 (100), 217 (13), 202 (9), 115 (14), 91 (26); HRMS calcd for $C_{23}H_{25}NO_3$ 363.1834, found 363.1831. Methanolysis of **8** gave enantiomerically enriched **4a**: $[\alpha]^{25}_D$ = –93.5° (*c* 1.29, $CHCl_3$).

(±)-2-Oxo-3-butanyl (*E*)-2-diazo-4-phenyl-3-butenoate (9): orange solid (mp 49.5–51.5 °C) (23%); R_f 0.60 (Et_2O/petroleum ether (1:1)); IR (neat) 2990, 2080, 1695, 1660, 1445, 1365, 1245 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.45–7.15 (m, 5 H), 6.45 (d, 1 H, J = 16.4 Hz), 6.25 (d, 1 H, J = 16.4 Hz), 5.24 (q, 1 H, J = 7.1 Hz), 2.21 (s, 3 H), 1.47 (d, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 204.7 (s), 164.1 (s), 136.4 (s), 128.4 (d), 126.9 (d), 125.6 (d), 123.3 (d), 110.5 (d), 75.3 (d), 63.8 (s), 25.3 (q), 15.8 (q).

Decomposition of 9 in the Presence of Styrene. The reaction was performed as per the typical procedure (*vide supra*). Analysis of the crude reaction mixture by ^{1}H NMR indicated the presence of three products, **10**, **11a**, and **11b**, in a 1.79:1.96:1.00 ratio. When the reaction was performed in pentane as solvent with rhodium(II) octanoate as catalyst, the product distribution was 5.41:2.35:1.00. Silica gel column chromatography was employed to separate the three components.

(±)-2-Oxo-3-butanyl 2α-phenyl-1α-((*E*)-2-phenylethenyl)-1β-cyclopropanecarboxylate (10): de = 26% (22% in pentane reaction); pale-yellow, viscous oil (19%) (42% from pentane

reaction); R_f 0.59 (Et_2O/petroleum ether (1:1)); IR (neat) 3015, 2980, 1710, 1595, 1440, 1350, 1235 cm^{-1}; ^1H NMR ($CDCl_3$) (major diastereomer) δ 7.35–7.05 (m, 10 H), 6.39 (d, 1 H, J = 15.9 Hz), 6.13 (d, 1 H, J = 15.9 Hz), 5.15 (q, 1 H, J = 7.1 Hz), 3.11 (apparent t, 1 H, J = 8.3 Hz), 2.17 (s, 3 H), 2.09 (dd, 1 H, J = 9.2, 5.2 Hz), 1.87 (dd, 1 H, J = 7.3, 5.2 Hz), 1.44 (d, 3 H, J = 7.1 Hz); ^1H NMR ($CDCl_3$) (minor diastereomer, resolvable signals at 200 MHz) δ 6.36 (d, 1 H, J = 15.9 Hz), 6.16 (d, 1 H, J = 15.9 Hz), 3.03 (apparent t, 1 H, J = 8.1 Hz), 2.21 (s, 3 H), 1.43 (d, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 205.7, 172.9, 137.0, 135.2, 133.4, 129.1, 128.3, 128.0, 127.3, 126.8, 126.2, 123.5, 75.5, 65.8, 58.3, 35.2, 33.0, 25.6, 18.8, 16.0; MS (EI) m/z (relative intensity) 334 (49), 246 (100), 217 (17), 115 (21), 91 (48). Anal. Calcd for $C_{22}H_{22}O_3$: C, 79.02; H, 6.63. Found: C, 79.10; H, 6.65.

4α,5-Dimethyl-3,8-dioxa-1-((*E*)-2-phenylethenyl)-7β-phenylbicyclo[3.2.1]octan-2-one (11a): obtained in 38% yield (24% from pentane reaction). Recrystallization (Et_2O/petroleum ether) gave the bicyclic ketone as a colorless solid (mp 149 °C): R_f 0.52 (Et_2O/petroleum ether (1:1)); IR (neat) 3010, 2970, 1730, 1595, 1440, 1375, 1225, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35–7.00 (m, 10 H), 6.51 (d, 1 H, J = 16.3 Hz), 6.09 (d, 1 H, J = 16.3 Hz), 4.70 (q, 1 H, J = 6.6 Hz), 3.69 (dd, 1 H, J = 9.6, 3.6 Hz), 2.96 (dd, 1 H, J = 14.1, 9.6 Hz), 2.00 (dd, 1 H, J = 14.1, 3.6 Hz), 1.60 (s, 3 H), 1.37 (d, 3 H, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$) δ 170.2, 141.3, 136.6, 130.9, 128.3, 128.2, 127.4, 127.1, 126.4, 123.4, 87.5, 84.0, 81.1, 55.2, 38.4, 21.9, 16.4; MS (EI) m/z (relative intensity) 334 (3), 290 (18), 199 (24), 159 (4), 131 (100), 103 (24), 91 (14). Anal. Calcd for $C_{22}H_{22}O_3$: C, 79.02; H, 6.63. Found: C, 78.84; H, 6.65.

4β,5-Dimethyl-3,8-dioxa-1-((*E*)-2-phenylethenyl)-7β-phenylbicyclo[3.2.1]octan-2-one (11b): obtained in 14% yield (14% from pentane reaction). Recrystallization from Et_2O/petroleum ether gave the bicyclic ketone as a colorless solid (mp 119–121 °C): R_f 0.46 (Et_2O/petroleum ether (1:1)); IR (neat) 3050, 3020, 2975, 1730, 1595, 1490, 1445, 1360, 1215, 1155 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35–7.00 (m, 10 H), 6.52 (d, 1 H, J = 16.1 Hz), 6.10 (d, 1 H, J = 16.1 Hz), 4.44 (q, 1 H, J = 6.4 Hz), 3.74 (dd, 1 H, J = 9.7, 3.2 Hz), 2.92 (dd, 1 H, J = 13.9, 9.7 Hz), 2.26 (dd, 1 H, J = 13.9, 3.2 Hz), 1.60 (s, 3 H), 1.53 (d, 3 H, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 141.3, 136.6, 131.0, 128.3, 128.2, 127.4, 127.1, 126.4, 123.2, 88.1, 84.8, 79.3, 55.3, 45.8, 21.6, 17.4; MS (EI) m/z (relative intensity) 334 (4), 290 (28), 262 (2), 219 (4), 199 (37), 159 (4), 131 (100), 103 (25), 91 (15). Anal. Calcd for $C_{22}H_{22}O_3$: C, 79.02; H, 6.63. Found: C, 78.85; H, 6.64.

(3*R*)-3-(4,4-Dimethyl-2-oxotetrahydrofuranyl) 2α-(4-Chlorophenyl)-1α-((*E*)-2-phenylethenyl)-1β-cyclopropanecarboxylate (12a). The reaction was carried out with 4-chlorostyrene in CH_2Cl_2 at 0 °C with $Rh_2(OAc)_4$ as catalyst: de >95% before purification; pale-yellow solid (92%). Recrystallization from EtOAc/hexanes gave pure cyclopropanecarboxylate **12a** as fine colorless needles (mp 138–139 °C) (61%): R_f 0.37 (Et_2O/petroleum ether (1:1)); $[\alpha]^{25}_D$ = +101.1° (*c* 2.48, $CHCl_3$); IR (neat) 3010, 2955, 1790, 1715, 1485, 1370, 1235, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–7.00 (m, 9 H), 6.40 (d, 1 H, J = 16.1 Hz), 6.09 (d, 1 H, J = 16.1 Hz), 5.42 (s, 1 H), 4.04 (s, 2 H), 3.15 (apparent t, 1 H, J = 8.3 Hz), 2.12 (dd, 1 H, J = 9.1, 5.4 Hz), 1.87 (apparent t, 1 H, J = 6.4 Hz), 1.24 (s, 3 H), 1.12 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 172.1, 172.0, 136.6, 134.0, 133.6, 132.8, 130.4, 128.4, 128.2, 127.6, 126.2, 122.6, 76.1, 75.5, 40.1, 34.7, 33.1, 23.0, 19.9, 19.1; MS (EI) m/z (relative intensity) 412 (14), 410 (40), 299 (3), 297 (8), 282 (32), 280 (100), 245 (31), 217 (19), 127 (9), 125 (23), 91 (19). Anal. Calcd for $C_{24}H_{23}ClO_4$: C, 70.15; H, 5.64. Found: C, 70.24; H, 5.71.

(3*R*)-3-(4,4-Dimethyl-2-oxotetrahydrofuranyl) 2α-(4-Methoxyphenyl)-1α-((*E*)-2-phenylethenyl)-1β-cyclopropanecarboxylate (12b). The reaction was carried out with 4-methoxystyrene in CH_2Cl_2 at 0 °C with $Rh_2(OAc)_4$ as catalyst: de >95% before purification; pale-yellow solid (75%). Recrystallization from EtOAc/hexanes gave essentially a single diastereomer of **12b** as fine colorless needles (mp 122 °C) (40%): R_f 0.35 (Et_2O/petroleum ether (1:1)); $[\alpha]^{25}_D$ = +106.7° (*c* 2.49, $CHCl_3$); IR (neat) 2960, 1790, 1715, 1605, 1505, 1370, 1240 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35–7.00 (m, 7 H), 6.83–6.70 (m, 2H), 6.39 (d, 1 H, J = 16.1 Hz), 6.11 (d, 1 H, J = 16.1 Hz), 5.42 (s, 1 H), 4.03 (s, 2 H), 3.73 (s, 3H), 3.14 (apparent t, 1 H, J = 8.4 Hz), 2.10 (dd, 1 H, J = 9.2, 5.8 Hz), 1.84 (apparent t, 1 H, J = 6.3 Hz), 1.23 (s, 3 H), 1.12 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 172.24, 172.18, 158.5, 136.9, 133.3, 130.2, 128.3, 127.3, 126.9, 126.2, 123.2, 113.5, 76.1, 75.3, 55.1, 40.1, 35.3, 32.8, 23.0, 19.9, 19.3; MS (EI) m/z (relative intensity) 406 (35), 293 (38), 276 (100), 247 (16), 189 (8), 121 (21), 91 (19). Anal. Calcd for $C_{25}H_{26}O_5$: C, 73.87; H, 6.45. Found: C, 73.85; H, 6.52.

(3*R*)-3-(4,4-Dimethyl-2-oxotetrahydrofuranyl) 2α-ethoxy-1α-((*E*)-2-phenylethenyl)-1β-cyclopropanecarboxylate (12c). The reaction was carried out with ethyl vinyl ether in CH_2Cl_2 at 0 °C using $Rh_2(OOct)_4$ as catalyst: de = 92% before purification. Chromatography gave the vinylcyclopropane as a colorless solid (71%). Recrystallization from Et_2O gave essentially a single diastereomer of vinylcyclopropane **12c** as a colorless solid (mp 97.5 °C); R_f 0.38 (Et_2O/petroleum ether (1:1)); $[\alpha]^{25}_D$ = −50.0° (*c* 2.0, $CHCl_3$); IR (neat) 3020, 2970, 1780, 1720, 1440, 1370, 1235, 1115 cm^{-1}; ^1H NMR ($CDCl_3$) (major diastereomer) δ 7.42–7.10 (m, 5 H), 6.72 (d, 1 H, J = 16.4 Hz), 6.52 (d, 1 H, J = 16.4 Hz), 5.41 (s, 1 H), 4.05 (s, 2 H), 3.99 (dd, 1 H, J = 7.0, 5.1 Hz), 3.58 (dq, 1 H, J = 9.3, 7.0 Hz), 3.40 (dq, 1 H, J = 9.3, 7.0 Hz), 1.99 (apparent t, 1 H, J = 6.7 Hz), 1.72 (apparent t, 1 H, J = 5.8 Hz), 1.22 (s, 3 H), 1.13 (t, 3 H, J = 7.0 Hz), 1.11 (s, 3 H); ^1H NMR ($CDCl_3$) (minor diastereomer, resolvable signals at 200 MHz) δ 6.47 (d, 1 H, J = 16.4 Hz), 3.82 (dd, 1 H, J = 7.0, 5.1 Hz), 2.11 (apparent t, 1 H, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 172.2, 170.9, 137.4, 129.9, 128.5, 127.1, 126.1, 121.0, 76.0, 75.1, 68.6, 67.3, 40.1, 31.6, 22.9, 22.3, 19.9, 14.7; MS (EI) m/z (relative intensity) 344 (6), 298 (16), 214 (55), 185 (99), 168 (60), 157 (100), 129 (53). Anal. Calcd for $C_{20}H_{24}O_5$: C, 69.75; H, 7.02. Found: C, 69.71; H, 7.05.

***cis*-(3*R*)-3-(4,4-Dimethyl-2-oxotetrahydrofuranyl) 6-((*E*)-2-Phenylethenyl)-2-oxabicyclo[3.1.0]hexane-6-carboxylate (12d)**. The reaction was carried out with 2,3-dihydrofuran in CH_2Cl_2 at 0 °C using $Rh_2(OAc)_4$ as catalyst: de = 66% before purification; pale-yellow foam (86%). Trituration with pentane gave a small sample of vinylcyclopropane **12d** as a pale-yellow solid (mp 102–103 °C): R_f 0.29 (Et_2O/petroleum ether (1:1)); IR (neat) 3045, 3015, 2960, 1775, 1715, 1595, 1445, 1365, 1290, 1215, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) (major diastereomer) δ 7.45–7.25 (m, 5 H), 6.82 (d, 1 H, J = 16.4 Hz), 6.20 (d, 1 H, J = 16.4 Hz), 5.31 (s, 1 H), 4.49 (d, 1 H, J = 5.6 Hz), 4.20–4.00 (m, 1 H), 4.00 (s, 2 H), 3.64 (dd, 1 H, J = 16.3, 8.8 Hz), 2.61 (apparent t, 1 H, J = 5.9 Hz), 2.40–2.20 (m, 1 H), 2.12–1.94 (m, 1 H), 1.17 (s, 3 H), 1.04 (s, 3 H); ^1H NMR ($CDCl_3$) (minor diastereomer, resolvable signals at 200 MHz) δ 6.19 (d, 1 H, J = 16.4 Hz), 4.45 (d, 1 H, J = 5.6 Hz), 3.90–3.72 (m, 1 H), 2.70 (apparent t, 1 H, J = 5.9 Hz), 1.05 (s, 3 H); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 172.2 (s), 169.7 (s), 137.9 (d), 137.0 (s), 128.4 (d), 127.7 (d), 126.1 (d), 117.7 (d), 76.0 (t), 75.1 (d), 71.6 (t), 70.5 (d), 39.9 (s), 34.7 (s), 33.7 (d), 25.2 (t), 22.7 (q), 19.7 (q); MS (EI) m/z (relative intensity) 227 (79), 195 (44), 183 (37), 168 (45), 152 (26), 96 (100). Anal. Calcd for $C_{20}H_{22}O_5$: C, 70.16; H, 6.45. Found: C, 70.02; H, 6.54.

***cis*-(3*R*)-3-(4,4-Dimethyl-2-oxotetrahydrofuranyl) 7-((*E*)-2-Phenylethenyl)-2-oxabicyclo[4.1.0]heptane-7-carboxylate (12e)**. The reaction was carried out with 3,4-dihydro-2*H*-pyran in CH_2Cl_2 at 0 °C using $Rh_2(OAc)_4$ as catalyst: de = 47% before purification; yellow solid (65%). Recrystallization (Et_2O/petroleum ether) gave essentially a single diastereomer of **12e** as

a colorless solid (mp 128–129 °C): R_f 0.28 (Et_2O/petroleum ether (1:1)); $[\alpha]^{25}_D$ = +13.2° (*c* 0.61, $CHCl_3$); IR (neat) 3020, 2960, 1785, 1715, 1595, 1445, 1230, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) (major diastereomer) δ 7.45–7.15 (m, 5 H), 6.82 (d, 1 H, *J* = 16.6 Hz), 6.14 (d, 1 H, *J* = 16.6 Hz), 5.29 (s, 1 H), 4.15 (d, 1 H, *J* = 7.3 Hz), 3.97 (s, 2 H), 3.69 (dt, 1 H, *J* = 10.8, 3.2 Hz), 3.45–3.25 (m, 1 H), 2.30–1.75 (m, 3 H), 1.45–1.25 (m, 2 H), 1.15 (s, 3 H), 1.02 (s, 3 H); ^1H NMR ($CDCl_3$) (minor diastereomer, resolvable signals at 200 MHz) δ 6.78 (d, 1 H, *J* = 16.6 Hz), 6.18 (d, 1 H, *J* = 16.6 Hz), 1.17 (s, 3 H), 1.04 (s, 3 H); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 172.2, 170.9, 137.4, 137.2, 128.4, 127.4, 126.0, 119.4, 76.0, 75.0, 64.7, 62.2, 40.0, 31.7, 26.1, 22.9, 21.6, 19.8, 16.3; MS (EI) *m/z* (relative intensity) 243 (41), 200 (71), 172 (10), 143 (7), 96 (52), 82 (100). Anal. Calcd for $C_{21}H_{24}O_5$: C, 70.77; H, 6.79. Found: C, 70.56; H, 6.81.

(3*R*)-3-(4,4-Dimethyl-2-oxotetrahydrofuranyl) 2α-Acetoxy-1α-((*E*)-2-phenylethenyl)-1β-cyclopropanecarboxylate (12f). The reaction was carried out with vinyl acetate in CH_2Cl_2 at 0 °C with $Rh_2(OAc)_4$ as catalyst: de = 90% before purification; colorless oil (42%); R_f 0.25 (Et_2O/petroleum ether (1:1)); $[\alpha]^{25}_D$ = −73.4° (*c* 1.30, $CHCl_3$); IR (neat) 3050, 3015, 2960, 1780, 1750, 1730, 1595, 1460, 1365, 1215 cm^{-1}; ^1H NMR ($CDCl_3$) (major diastereomer) δ 7.40–7.20 (m, 5 H), 6.48 (d, 1 H, *J* = 16.2 Hz), 6.42 (d, 1 H, *J* = 16.2 Hz), 5.41 (s, 1 H), 4.44 (dd, 1 H, *J* = 7.1, 4.9 Hz), 4.07 (d, 1 H, *J* = 8.9 Hz), 4.04 (d, 1 H, *J* = 8.9 Hz), 2.01 (apparent t, 1 H, *J* = 6.9 Hz), 1.97 (s, 3 H), 1.78 (dd, 1 H, *J* = 6.5, 4.9 Hz), 1.25 (s, 3 H), 1.17 (s, 3 H); ^1H NMR ($CDCl_3$) (minor diastereomer, resolvable signals at 200 MHz) δ 4.58 (dd, 1 H, *J* = 7.1, 4.9 Hz); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 171.9, 170.72, 170.65, 136.5, 132.6, 128.5, 127.6, 126.2, 119.8, 76.1, 75.7, 60.1, 40.2, 31.0, 22.9, 20.3, 19.8, 18.8; MS (EI) *m/z* (relative intensity) 358 (4), 316 (10), 298 (17), 186 (41), 168 (100), 158 (58), 141 (26), 129 (21). Anal. Calcd for $C_{20}H_{22}O_6$: C, 67.03; H, 6.19. Found: C, 66.85; H, 6.14.

***endo*-(3*R*)-3-(4,4-Dimethyl-2-oxotetrahydrofuranyl) 4-Phenylbicyclo[3.2.1]octa-2,6-diene-2-carboxylate (13).** To a solution of freshly distilled cyclopentadiene (0.25 mL, ≈3.0 mmol) and rhodium(II) acetate (1.5 mg, 0.003 mmol) in dry CH_2Cl_2 (10 mL) under argon at reflux was added vinyldiazo acetate **1g** (100.1 mg, 0.33 mmol) in dry CH_2Cl_2 (10 mL) over ≈30 min. After a further 30 min at reflux the reaction mixture was concentrated *in vacuo* to a green oil: de = 76% before purification. Chromatography gave **13** as a colorless waxy solid (87%): R_f 0.50 (Et_2O/petroleum ether (1:1)); IR (neat) 3050, 2960, 1785, 1715, 1650, 1250, 1195, 1090 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) (major diastereomer) δ 7.35–7.00 (m, 5 H), 6.80 (s br, 1 H), 6.41 (dd, 1 H, *J* = 5.6, 2.9 Hz), 5.47 (s, 1 H), 5.31 (dd, 1 H, *J* = 5.6, 2.7 Hz), 4.06 (s, 2 H), 3.84 (apparent t, 1 H, *J* = 4.4 Hz), 3.35 (apparent t, 1 H, *J* = 3.7 Hz), 3.05 (m, 1 H), 2.35–2.22 (m, 1 H), 2.06 (d, 1 H, *J* = 10.0 Hz), 1.25 (s, 3 H), 1.14 (s, 3 H); ^1H NMR ($CDCl_3$) (minor diastereomer, resolvable signals at 500 MHz) δ 6.38 (dd, 1 H, *J* = 5.6, 2.9 Hz), 2.05 (d, 1 H, *J* = 10.0 Hz); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 172.5, 164.9, 141.6, 141.1, 139.9, 137.2, 130.8, 128.4, 127.7, 126.7, 76.2, 75.0, 45.8, 44.5, 42.9, 40.4, 37.9, 23.1, 20.0; MS (EI) *m/z* (relative intensity) 338 (11), 225 (8), 208 (100), 181 (24), 165 (19), 115 (18). Anal. Calcd for $C_{21}H_{22}O_4$: C, 74.54; H, 6.55. Found C, 73.46; H, 6.55.

2-Methyl-3-oxo-1-cyclopentene-1-acetic Acid. NaOH (0.71 g, 17.9 mmol) was dissolved in H_2O (25 mL) and then added to a mixture of methyl 2-methyl-3-oxo-1-cyclopentene-1-acetate (1.00 g, 5.95 mmol) in H_2O (25 mL) at 0 °C. After the reaction mixture was stirred for 1 h, dilute HCl was added until pH = 2. The mixture was then extracted with ether (6×), dried ($MgSO_4$), and concentrated under vacuum. Recrystallization (hexanes) gave the productas a colorless solid (mp 100–101 °C) (0.80 g, 87%): IR ($CHCl_3$) 3010, 2920, 1700, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.81 (br s, 1 H), 3.45 (s, 2 H), 2.69–2.58 (m, 2 H), 2.47–2.40 (m, 2 H), 1.72 (t, 3 H, *J* = 2.1 Hz); ^{13}C NMR ($CDCl_3$) δ 211.1, 171.8, 165.6, 138.4, 36.2, 33.7, 29.7, 7.6. Anal. Calcd for $C_8H_{10}O_3$: C, 62.33; H, 6.54. Found: C, 62.41; H, 6.55.

(3*R*)-3-(4,4-Dimethyl-2-oxotetrahydrofuranyl) 2-Methyl-3-oxo-1-cyclopentene-1-acetate. A solution of *N*,*N*-dicyclohexylcarbodiimide (DCC) (1.03 g, 4.98 mmol) in dry THF (20 mL) was added to stirred mixture of the carboxylic acid (0.73 g, 4.74 mmol) and (*R*)-(−)-pantolactone (0.62 g, 4.74 mmol) in dry THF at room temperature. The reaction flask was fitted with a drying tube, and the reaction mixture was stirred for 24 h. The reaction mixture was concentrated *in vacuo*, cold acetone was added to the residue, and the mixture was vacuum filtered. The filtrate was concentrated *in vacuo* to yield the crude product. Purification by silica gel column chromatography gave the (*R*)-pantolactonyl ester as a clear oil (0.90 g, 71%): R_f 0.41 (EtOAc/hexanes (1:1)); $[\alpha]^{25}_D$ = +6.6° (*c* 2.0, $CHCl_3$); IR (neat) 2970, 2925, 2880, 1790, 1745, 1690, 1645 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.36 (s, 1 H), 4.03 (s, 2 H), 3.58 (s, 2 H), 2.70–2.61 (m, 2 H), 2.44–2.38 (m, 2 H), 1.72 (t, 3 H, *J* = 1.9 Hz), 1.20 (s, 3 H), 1.08 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 208.3, 171.3, 167.3, 162.2, 138.5, 75.6, 75.2, 39.6, 35.9, 33.7, 29.2, 22.3, 19.4, 7.6. Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.20; H, 6.84.

(3*R*)-3-(4,4-Dimethyl-2-oxotetrahydrofuranyl) 2-Methyl-3-oxo-1-cyclopentene-1-(2-diazoacetate) (14). Triethylamine (1.14 g, 11.3 mmol) was added rapidly to a stirred mixture of the (*R*)-pantolactonyl ester (1.00 g, 3.76 mmol) and *n*-dodecylbenzenesulfonyl azide (1.46 g, 4.14 mmol) in acetonitrile (50 mL) at 0 °C. The mixture was warmed to room temperature and then stirred for 12 h, whereupon the reaction mixture was concentrated *in vacuo* to give the crude product. Purification by silica gel column chromatography gave **14** as a yellow solid (mp 113–114.5 °C) (0.84 g, 76%): R_f 0.29 (Et_2O); $[\alpha]^{25}_D$ = +6.2° (*c* 2.7, $CHCl_3$); IR ($CHCl_3$) 3030, 2980, 2945, 2890, 2115, 1790, 1705, 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.48 (s, 1 H), 4.07 (s, 2 H), 2.93–2.85 (m, 2 H), 2.47–2.40 (m, 2 H), 1.81 (t, 3 H, *J* = 1.9 Hz), 1.26 (s, 3 H), 1.12 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 206.7, 171.7, 161.8, 152.2, 131.0, 75.9, 75.6, 65.1, 40.0, 33.2, 28.2, 22.6, 19.7, 8.2. Anal. Calcd for $C_{14}H_{16}N_2O_5$: C, 57.53; H, 5.52; N, 9.58. Found: C, 57.58; H, 5.47; N, 9.63.

(3*R*)-3-(4,4-Dimethyl-2-oxotetrahydrofuranyl) 8aβ-Methyl-1-oxo-8α-(trimethylsilyl)oxy-2,3,8,8α-tetrahydro-4(5*H*)-azulenecarboxylate (16). For yields and percent diastereomeric excess refer to Table IV. In a typical procedure **14** (0.0347 g, 0.119 mmol) in a solution of dry CH_2Cl_2 (25 mL) was added to a refluxing mixture of *trans*-1-((trimethylsilyl)oxy)-1,3-butadiene (**15**) (0.844 g, 0.594 mmol) and rhodium(II) acetate (0.5 mg, 0.0012 mmol) in CH_2Cl_2 (25 mL) under an atmosphere of argon. The reaction was allowed to reflux for 30 min, whereupon the reaction mixture was concentrated *in vacuo* to yield the crude product. At this point, a ^1H NMR was obtained and the percent de was determined by measurement of the integration of the peaks at approximately δ 5.48 (de = 91%). Purification by silica gel column chromatography gave **16** as a colorless oil (28.9 mg, 60%): R_f 0.51 (Et_2O/petroleum ether (1:1)); $[\alpha]^{25}_D$ = −146.8° (*c* 1.0, $CHCl_3$); IR (neat) 3015, 2955, 2925, 2875, 1790, 1745, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ (major diastereomer) 5.85–5.60 (m, 2 H), 5.49 (s, 1 H), 4.30 (dd, 1 H, *J* = 6.1, 1.8 Hz), 4.06 (s, 2 H), 3.54 (dd, 1 H, *J* = 21.3, 5.8 Hz), 3.30–3.02 (m, 3 H), 2.50–2.38 (m, 2 H), 1.24 (s, 3 H), 1.19 (s, 3 H), 1.13 (s, 3 H), 0.03 (s, 9 H); ^1H NMR ($CDCl_3$) δ (minor diastereomer, resolvable signals at 200 MHz) 5.46 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 220.8, 172.6, 166.2, 161.4, 129.2, 127.6, 123.8, 76.2, 75.3, 72.9, 58.8, 40.2, 36.8, 29.6, 28.8, 23.1, 20.3, 17.4, 0.3. Anal. Calcd for $C_{21}H_{30}O_6Si$: C, 62.04; H, 7.44. Found: C, 62.32; H, 7.63.

8α-Hydroxy-8aβ-methyl-1-((*tert*-butyldimethylsilyl)oxy)-4β-(((*tert*-butyldimethylsilyl)-oxy)methyl)-1,2,3,5,8,8a-hexahydroa-

zulene (17). The cycloadduct **16** (0.33 g, 0.813 mmol) in dry ether (10 mL) was added dropwise to a stirred suspension of lithium aluminum hydride (0.12 g, 3.25 mmol) in dry ether (15 mL) at −78 °C under an atmosphere of argon. After addition was complete, the mixture was slowly warmed to room temperature over 3 h and then stirred for 1 h at room temperature. Saturated NH_4Cl (25 mL) was added slowly to quench the reaction, and the mixture was filtered. The layers were separated, the aqueous layer was extracted with EtOAc (3×) combined with the ether layer and dried (Na_2SO_4), and the solvent was removed *in vacuo* to give the crude diol, which was not purified but used in the next step without purification. The crude product (0.17 g, 0.603 mmol, 74% recovery) was combined with *tert*-butyldimethylchlorosilane (0.44 g, 2.89 mmol) and imidazole (0.21 g, 3.02 mmol) in dry DMF (0.6 mL) at room temperature under an atmosphere of argon. The mixture was stirred for 12 h, whereupon H_2O (30 mL) was added, the mixture was extracted with pentane (3×) and dried ($MgSO_4$), and the solvent was removed under vacuum. Purification by chromatography gave **17** as a clear oil (0.17 g, 46%): R_f 0.43 (Et_2O/petroleum ether (1:9)); $[\alpha]^{25}_D = -37.2°$ (*c* 0.67, $CHCl_3$); IR (neat) 3560, 3500, 3020, 2960, 2935, 2890, 2860, 1460 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.79–5.76 (m, 2 H), 4.21–4.18 (m, 1 H), 4.18 (d, 1 H, J = 11.8 Hz), 4.08 (d, 1 H, J = 11.8 Hz), 3.92 (dd, 1 H, J = 5.3, 5.3 Hz), 2.98 (br s, 1 H), 2.61–2.45 (m, 1 H), 2.39–2.24 (m, 1 H), 2.14–1.80 (m, 1 **H**), 1.73–1.57 (m, 1 H), 1.00 (s, 3 H), 0.89 (s, 9 H), 0.86 (s, 9 H), 0.11 (s, 3 H), 0.09 (s, 3 H), 0.03 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 139.8, 131.0, 129.6, 127.6, 85.0, 71.6, 65.4, 51.5, 33.0, 31.6, 28.1, 25.8, 25.6, 25.5, 23.1, 18.1, 17.7, −3.7, −4.7, −5.1, −5.3; MS (EI) m/z (relative intensity) 438 (13), 306 (6), 275 (14), 237 (12), 157 (34), 119 (24), 73 (100); HRMS calcd for $C_{24}H_{46}O_3Si_2$ 438.2986, found 438.3048.

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