Tandem Asymmetric Cyclopropanation/Cope Rearrangement. A Highly Diastereoselective and Enantioselective Method for the Construction of 1,4-Cycloheptadienes

Huw M. L. Davies,* Douglas G. Stafford, Brian D. Doan, and Jeffrey H. Houser

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14260-3000

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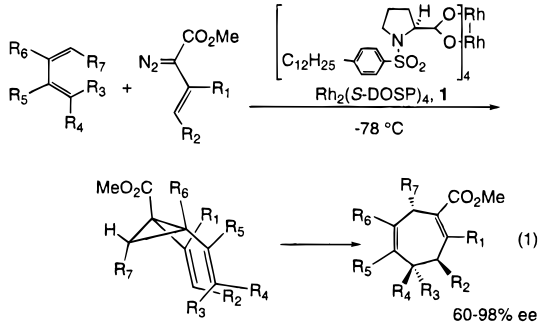
Abstract: Decomposition of vinyldiazoacetates by rhodium(II) (*N*-dodecylbenzenesulfonyl)prolinate (Rh_2(*S*-DOSP)$_4$, **1**) in the presence of dienes results in a direct and highly enantioselective method for the formation of *cis*-divinylcyclopropanes. Combination of this process with a subsequent Cope rearrangement results in a highly enantioselective synthesis of a variety of cycloheptadienes containing multiple stereogenic centers.

The Cope rearrangement of divinylcyclopropanes is an attractive method for the stereoselective synthesis of seven-membered rings.[1−4] Due to the requirement of a boat transition state for this type of Cope rearrangement, multiple stereogenic centers can be formed in a well-defined manner. One major hurdle with this chemistry, however, has been the synthesis of the requisite *cis*-divinylcyclopropanes. A number of ingenious approaches to the *cis*-divinylcyclopropanes have been developed,[2,5] but more often than not, the synthesis has required a cumbersome process lacking stereocontrol.[1] In this paper we describe a direct and highly enantioselective method for the formation of *cis*-divinylcyclopropanes by decomposition of vinyldiazoacetates by rhodium(II) (*N*-dodecylbenzenesulfonyl)-prolinate (Rh_2(*S*-DOSP)$_4$, **1**) in the presence of dienes (eq 1).[6] Combination of this process with a subsequent Cope rearrangement results in a highly enantioselective synthesis of a variety of cycloheptadienes containing multiple stereogenic centers.



(1)

A distinguishing feature of cyclopropanation reactions of vinylcarbenoids derived from vinyldiazoacetates is the excellent diastereoselectivity that is observed.[7] Recently, we have shown that Rh_2(*S*-DOSP)$_4$ (**1**) is an excellent chiral catalyst for the

(1) For general reviews on the Cope rearrangement of divinylcyclopropanes, see: (a) Wong, H. N. C.; Hon, M.-Y.; Tse, C.-W.; Yip, Y. C.; Tanko, J.; Hudlicky, T. *Chem. Rev.* **1989**, *89*, 165. (b) Rhoads, S. J.; Raulinus, N. R. *Org. React.* **1975**, *21*, 1. (c) Hudlicky, T.: Fan, R.; Reed, J. W.; Gadamasetti, K. G. *Org React.* **1992**, *41*, 1. (d) Piers, E. In *Comprehensive Organic Synthesis*; Trost, B. M. Ed.; Pergamon Press: Oxford, 1991; Vol. 5, pp 971−998.

(2) For recent examples of the Cope rearrangement of divinylcyclopropanes, see: (a) Davies, H. M. L.; Matasi, J. J.; Hodges, L. M.; Huby, N. J. S.; Thornley, C.; Kong, N.; Houser, J. H. *J. Org. Chem.* **1997**, *62*, 1095. (b) Davies, H. M. L.; Ahmed, G.; Chruchill, M. R. *J. Am. Chem. Soc.* **1996**, *118*, 10774. (c) Davies, H. M. L.; Doan, B. D. *Tetrahedron Lett.* **1996**, *37*, 3967. (d) Davies, H. M. L.; Matasi, J. J.; Thornley, C. *Tetrahedron Lett.* **1995**, *36*, 7205. (e) Davies, H. M. L.: Calvo, R.; Ahmed G. *Tetrahedron Lett.* **1997**, 38, 1737. (f) Davies, H. M. L.: Matasi J. J.; Ahmed. G. *J. Org. Chem.* **1996**, *61*, 2305. (g) Kohmoto, S.; Nakayama, N.; Takami, J.; Kishikawa, K.; Yamamoto, M.; Yamada, K. *Tetrahedron Lett.* **1996**, *37*, 7761. (h) Lee, J. H.; Kim, H. J.; Cha, J. K. *J. Am. Chem. Soc.* **1995**, *117*, 9919. (i) Takeda, K.; Takeda, M.; Nakajima, A.; Yoshii, E. *J. Am. Chem. Soc.* **1995**, *117*, 6400. (j) Fukuyama, T.; Liu, G. *J. Am. Chem. Soc.* **1996**, *118*, 7426.

(3) Other methods for the construction of seven-membered rings include: *3 + 4 annulations*: (a) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 1. (b) Noyori, R. *Acc. Chem. Res.* **1979**, *12*, 61. (c) Mann, J. *Tetrahedron* **1986**, *42*, 4611. (d) Hosomi, A.; Tominaga, Y. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 5, pp 593−616. (e) Boger, D. L.; Brotherton, C. E. *J. Am. Chem. Soc.* **1986**, *108*, 6695. *5 + 2 annulations* (f) Wender, P. A.; Lee, H. Y.; Wilheim, R. S.; Williams, P. D. *J. Am. Chem. Soc.* **1989**, *111*, 8954. (g) Bromidge, S. M.; Archer, D. A.; Sammes, P. G. *J. Chem. Soc., Perkin Trans. 1* **1990**, 353. (h) Dennis, N.; Katritzky, A. R.; Parton, S. K.; Nomura, Y.; Takahashi, Y.; Takeuchi, Y. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2289. (i) Wender. P. A.; Siggel, L.; Nuss, J. M. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 5, pp 645−674. (j) Rumbo, A.; Mourino, A.; Castedo, L.; Mascarenas, J. L. *J. Org. Chem.* **1996**, *61*, 6114. (k) Marshall, K. A.; Mapp, A. K.; Heathcock, C. H. *J. Org. Chem.* **1996**, *61*, 9135.

(4) For newer annulation methods for the construction of seven-membered rings, see: (a) Trost, B. M.; MacPherson, D. T. *J. Am. Chem. Soc.* **1987**, *109*, 3483. (b) Molander, G. A.; Shubert, D. C. *J. Am. Chem. Soc.* **1987**, *109*, 6877. (c) Molander, G. A.; Cameron, K. O. *J. Org. Chem.* **1991**, *56*, 2617. (d) Herndon, J. W.; Chatterjee, G.; Patel, M. D.; Matasi, J. J.; Turner, S. U.; Harp, J. J.; Reid, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 7808. (e) Wender, P. A.; Takahashi, H.; Witulski, B. *J. Am. Chem. Soc.* **1995**, *117*, 4720.

(5) (a) Piers, E.; Nagakura, I. *Tetrahedron Lett.* **1976**, 3237. (b) Piers, E.; Morton, H. E.; Nagakura, I.; Thies, R. W. *Can. J. Chem.* **1983**, *61*, 1226. (c) Piers, E.; Burmeister, M. S.; Reissig, H.-U. *Can. J. Chem.* **1986**, *64*, 180. (d) Marino, J. P.; Kaneko, T. *J. Org. Chem.* **1974**, *39*, 3175. (e) Marino, J. P.; Browne, L. J. *Tetrahedron Lett.* **1976**, 3245. (f) Hudlicky, T.; Fleming, A.; Radesca, L. *J. Am. Chem. Soc.* **1989**, *111*, 6691. (g) Hudlicky, T.; Fleming, A.; Heard, N. *J. Org. Chem.* **1990**, *55*, 2570. (h) Wender, P. A.; Eissenstat, M. A.; Filosa, M. P. *J. Am. Chem. Soc.* **1979**, *101*, 2196. (i) Wender, P. A.; Filosa, M. P. *J. Org. Chem.* **1976**, *41*, 3490. (j) Nakamura, E.; Isaka, M.; Matsuzawa, S. *J. Am. Chem. Soc.* **1988**, *110*, 1297. (k) Wulff, W. D.; Yang, D. C.; Murray, C. K. *J. Am. Chem. Soc.* **1988**, *110*, 2653. (l) Padwa, A.; Krumpe, K. E.; Gareau, Y.; Chiacchio, U. *J. Org. Chem.* **1991**, *56*, 2523. (m) Harvey, D. F.; Lund, K. P. *J. Am. Chem. Soc.* **1991**, *113*, 5066.

(6) For a preliminary communication of a portion of this work, see: Davies, H. M. L.; Peng, Z. Q.; Houser, J. H. *Tetrahedron Lett.* **1994**, *35*, 8939.

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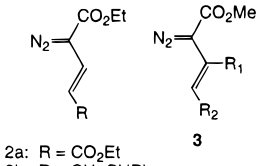
enantioselective cyclopropanation of alkenes by vinyldiazoacetates.[2c,8] The extension of the use of Rh_2(*S*-DOSP)$_4$ to the reaction between vinyldiazoacetates and dienes should lead to a general asymmetric synthesis of highly functionalized cycloheptadienes. Our previous studies on the racemic synthesis of cycloheptadienes by intermolecular reactions of vinylcarbenoids with dienes used only two vinyldiazoacetates (**2a** and **2b**) as vinylcarbenoid precursors.[9] To illustrate the broad scope of the asymmetric synthesis of cycloheptadienes, the current study was carried out with a more extensive range of vinyldiazoacetates (**3a**−**i**). All of these vinyldiazoacetates are methyl ester derivatives as this functionality has been shown to result in the highest levels of asymmetric induction in reactions of vinyldiazoacetates catalyzed by Rh_2(*S*-DOSP)$_4$.[8]

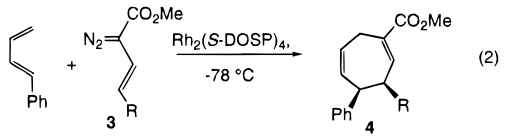


	R_1	R_2
a	H	Me
b	H	Ph
c	H	CH=CHPh
d	H	$CH=CH_2$
e	H	H
f	Me	H
g	OTBDMS	H
h	cyclo C_4H_8	
i	cyclo C_3H_6	

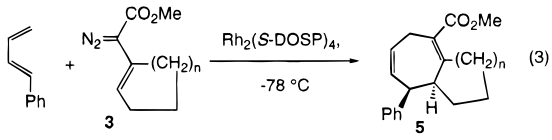
Rh_2(*S*-DOSP)$_4$ has been shown to be active at decomposing vinyldiazoacetates even at −78 °C,[8,10] and by using these lower reaction temperatures, considerable enhancement in enantioselectivity is obtained. Furthermore, solvent has a dramatic effect on the enantioselectivity, with nonpolar solvents being strongly beneficial.[8,10] Therefore, the carbenoid reactions using Rh_2(*S*-DOSP)$_4$ as catalyst described in this paper were carried out at −78 °C using pentane or hexane as solvent.

The vinyldiazoacetates **3a**−**i** were readily prepared using standard published procedures.[9,11] Decomposition of the vinyldiazoacetate **3a** in the presence of *trans*-1-phenyl-1,3-butadiene resulted in the formation of the *cis*-disubstituted cycloheptadienecarboxylate **4a** in 87% yield and 98% ee. Excellent control of regiochemistry was observed in this reaction. Only a single diastereomer of **4a** was formed and this was shown to be the *cis* product by nOe difference analysis. The *cis* diastereomer **4a** is the predicted product for a reaction proceeding by a tandem cyclopropanation/Cope rearrangement. The regiocontrol is consistent with cyclopropanation occurring at the least substituted double bond. Furthermore, the initial cyclopropanation occurs with very high relative stereochemistry as no evidence of the *trans*-divinylcyclopropane was seen in the crude reaction mixture. Highly enantioselective reactions occurred with a series of terminus substituted vinyldiazoacetates **3a**−**d** leading to single diastereomers of the cycloheptadienes **4a**−**d** in 93−98% ee. However, the enantioselectivity dropped to 73% ee in the case of the cycloheptadiene **4e** derived from the vinyldiazoacetate **3e**.

The potential of extending this chemistry to bicyclic systems is illustrated for the cyclic vinyldiazoacateates **3h** and **3i**. Rh_2(*S*-DOSP)$_4$ catalyzed decomposition of **3h** in the presence of cyclopentadiene formed the bicyclo[5.4.0]nonane **5h** in 94% ee, while the reaction with **3i** formed the hexahydroazulene derivative **5i** in 81% ee.

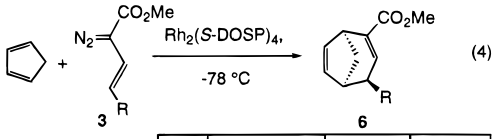


	R	ee, %	yield, %
a	Me	98	87
b	Ph	98	83
c	CH=CHPh	93	84
d	$CH=CH_2$	96	56
e	H	73	41



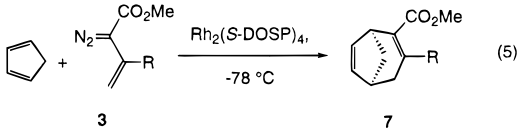
	n	ee, %	yield, %
h	2	94	62
i	1	81	60

The asymmetric synthesis of bicyclo[3.2.1]octadienes **6a**−**d** is readily achieved from the reactions of the vinyldiazoacetates **3a**−**d** with cyclopentadiene. In each case the *endo* bicyclo[3.2.1]octadienes **6a**−**d**[12] were exclusively formed, and the enantioselectivity ranged from 90 to 93% ee. The exclusive formation of the *endo* product is fully consistent with a reaction that proceeds by a tandem cyclopropanation/Cope rearrangement. The enantioselectivity observed in these reactions were considerably higher than what had been observed in the preliminary studies carried out at room temperature using rhodium (*N*-4-(*tert*-butyl)benzenesulfonyl)prolinate as catalyst.[6]



	R	ee, %	yield, %
a	Me	91	47
b	Ph	93	77
c	CH=CHPh	90	80
d	$CH=CH_2$	92	58

The vinyl terminus substituted vinyldiazoacetates were shown to be the ideal substrates by comparing the cyclopentadiene reactions of **3a**−**d** with those of the vinyldiazoacetate **3e**−**g**. The unsubstituted vinyldiazoacetate **3e** generated the bicyclo[3.2.1]octadiene **7e** in 63% ee, while the reactions with 3-substituted vinyldiazoacetates **3f** and **3g** generated **7f** and **7g** in 60% and 74% ee, respectively.



	R	ee, %	yield, %
e	H	63	70
f	Me	62	74
g	OTBS	74	97

Even though the cyclic vinyldiazoacetates formed annulation products in high enantioselectivity with 1-phenylbutadiene the

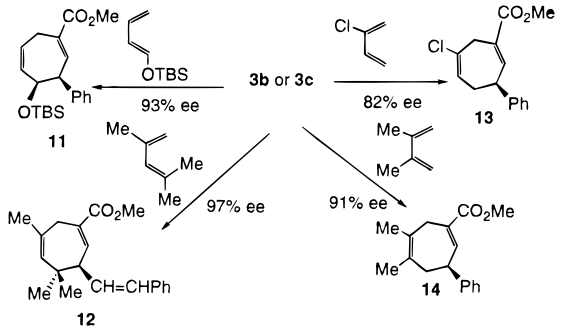
(7) For a review on our earlier studies on vinylcarbenoid cyclopropanations, see: Davies, H. M. L. *Tetrahedron* **1993**, *49*, 5203.

(8) (a) Davies, H. M. L.; Hutcheson, D. K. *Tetrahedron Lett.* **1993**, *34*, 7243. (b) Davies, H. M. L.; Bruzinski, P. R.; Lake, D. H.; Kong, N.; Fall, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 6897.

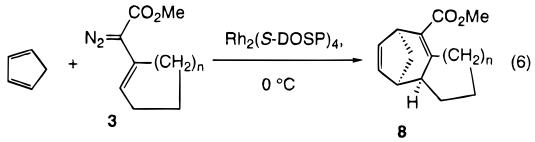
(9) Davies, H. M. L.; Clark, T. J.; Smith, H. D. *J. Org. Chem.* **1991**, *56*, 3817.

(10) Davies, H. M. L.; Hansen, T.; Rutberg, J.; Bruzinski, P. R. *Tetrahedon Lett.* **1997**, *38*, 1741.

Scheme 1

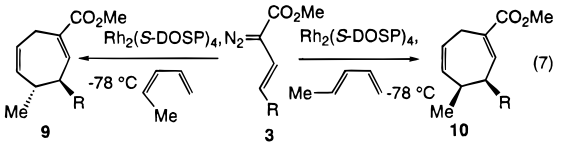


reaction of **3h** and **3i** with cyclopentadiene resulted in the tricyclic products **8** in moderate enantioselectivity. Reactions run at 0 °C resulted in the formation of **8h** and **8i** in 73% and 74% ee, respectively, while no improvement in ee was observed on running these reactions at −78 °C.



	n	ee, %	yield, %
h	2	73	61
i	1	74	66

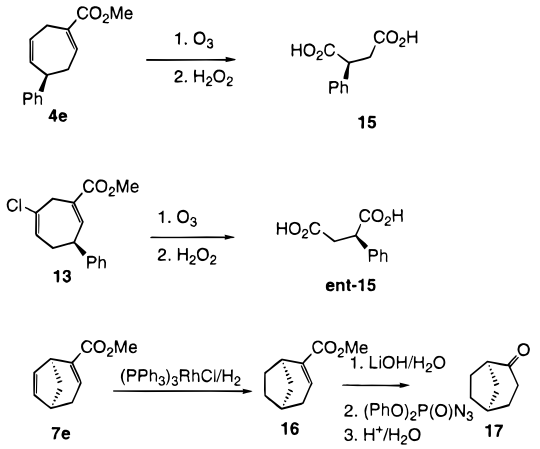
The diastereocontrol that is possible with this chemistry can be readily seen from the reactions of **3b** with the isomers of piperylene. Reactions of **3b** with *cis*-piperylene produced the *trans*-cycloheptadiene **9b** in 96% ee, while the reaction with *trans*-piperylene produced the *cis*-cycloheptadiene **10b** in 98% ee. In the reaction of **3b** with the piperylenes the isolation of the cycloheptadienes products requires careful chromatography because a reasonable amount of the *trans*-divinylcyclopropane (*cis*/*trans* ratios of ∼7:1) was formed as a byproduct. The diastereoselectivity is much higher in the reactions of the carbenoid derived from dienyldiazoacetate **3c** than **3b**.[9] The reactions of **3c** with *cis*- and *trans*-piperylene, resulted in the formation of the cycloheptadienes **9c**[13] and **10c**[13] in 62% yield (98% ee) and 82% yield (95% ee), respectively, without any evidence of *trans*-divinylcyclopropane byproducts.



9, yield, %	**9**, ee, %		R	**10**, ee, %	**10**, yield, %
47	96	**b**	Ph	98	51
62	98	**c**	CH=CHPh	95	82

The reaction can be extended to a range of acyclic dienes as shown in Scheme 1. In all the examples in Scheme 1, the

Scheme 2



cycloheptadienes were formed with excellent control of regiochemistry, diastereoselectivity, and enantioselectivity. Particularly interesting is the fact that effective transformations are possible with dienes containing either an electron releasing group such as siloxy or an electron withdrawing group such as chloro.

Even though this chemistry is applicable to a range of dienes, certain limitations exist in the case of dienes in which both ends are functionalized. A striking feature of intermolecular vinylcarbenoid cyclopropanations is the lack of reaction with *trans*-1,2-disubstituted alkenes.[7,9] Therefore, vinylcarbenoids are not trapped by *trans*,*trans*-2,4-hexadiene.[9] In the case of 1,4-disubstituted dienes containing at least one *cis* double bond, the outcome of the chemistry is variable. Cyclopentadiene is an excellent substrate and a highly regioselective reaction of **2b** with *cis*,*trans*-2,4-hexadiene has been reported.[9] However, attempts at the asymmetric reaction of **3b** with cyclohexadiene resulted primarily in the formation of a C−H insertion product rather than the tandem cyclopropanation/Cope rearrangement product.

The absolute configurations of **4e**, **7e**, and **13** were determined as illustrated in Scheme 2. The cycloheptadiene **4e** and **13** were oxidatively cleaved to *S*-phenylsuccinic acid (**15**) and *R*-phenylsuccinic acid (**ent-15**), respectively. Selective catalytic hydrogenation of **7e** using Wilkinson's catalyst resulted in the formation of the bicyclooctene **16**. Hydrolysis of **16** generated the acid which was converted under the Curtius rearrangement reaction conditions followed by hydrolysis to (−)-(*R*,*R*)-bicyclo-[3.2.1]octan-2-one (**17**). The absolute configuration of these products is the predicted result from the model for the asymmetric induction that is discussed below. The absolute stereochemistry of all the other products is tentatively assigned on the basis of this model.

Discussion

A recent paper detailing the asymmetric cyclopropanation of alkenes with vinylcarbenoids demonstrated that a combination of electron donating (such as vinyl or phenyl) and an electron withdrawing (such as ester) functionality on the carbenoid results in systems that are capable of highly diastereoselective cyclopropanations.[14] These results were rationalized by a model in which the cyclopropanation is nonsynchronous and occurs preferentially on the side of the electron withdrawing group.[8b] As *trans* alkenes do not react intermolecularly with carbenoids derived from vinyldiazoacetates,[7,9] the alkene is considered to approach the vinylcarbenoid in a side-on mode. Substituents

(11) (a) Baum, J. S.; Shook, D. A.; Davies, H. M. L.; Smith, H. D. *Synth. Commun.* **1987**, *17*, 1709. (b) Davies, H. M. L.; Saikali, E.; Clark, T. J.; Chee, E. H. *Tetrahedron Lett.* **1990**, *31*, 6299. (c) Davies, H. M. L.; Hougland, P. W.; Cantrell, W. R., Jr. *Synth. Commun.* **1992**, *22*, 971.

(12) The *endo* stereochemistry is readily determined on the basis of the distinctive coupling that exists between the C-4 and C-5 protons in bicyclo-[3.2.1]octa-2,6-dienes. For example, see ref 9.

(13) The relative stereochemistry for the ethyl esters of **9c** and **10c** has been previously determined by NOE difference analysis. See ref 9.

(14) Davies, H. M. L.; Bruzinski, P. R.; Fall, M. J. *Tetrahedron Lett.* **1996**, *37*, 4133.

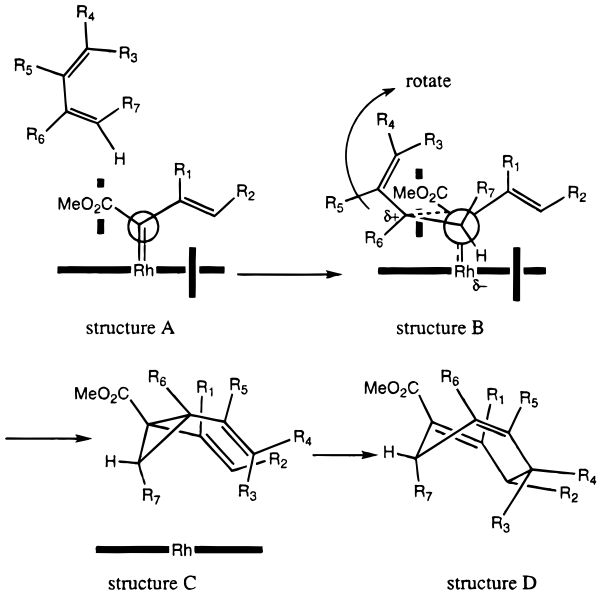


Figure 1.

on the alkene would preferentially point away from the catalyst. The high asymmetric induction achieved by Rh_2(*S*-DOSP)$_4$ has been proposed to be due to a preferential alignment of the ligands such that the catalyst has D_2 symmetry.[8b] This limits the number of possible arrangements between the vinylcarbenoid and the catalyst such that the two metal faces of the dirhodium complex have the same chiral environment. Each face is considered to have two arylsulfonyl blocking groups placed at opposite quadrants, and when the vinylcarbenoid is bound, one blocking group will be in front of the vinylcarbenoid and the other will be behind.[8b]

The extension of this model to the reaction of vinylcarbenoids with dienes would lead to well-defined absolute stereochemistry as shown in Figure 1. In structure A, the rhodium vinylcarbenoid model is shown, with the chiral blocking groups indicated as thick black lines in the back and the front of the structure. The diene would approach side-on from the side of the electron withdrawing group at the initiation of the nonsynchronous cyclopropanation as illustrated in structure B. To complete the cyclopropanation, it is necessary for the diene to rotate away from the catalyst to form the *cis*-divinylcyclopropane in structure C. The Cope rearrangement of the *cis*-divinylcyclopropane through a boat transition state would lead to the cycloheptadiene, structure D.

In summary Rh_2(*S*-DOSP)$_4$ is an effective catalyst for the asymmetric synthesis of cycloheptadiene derivatives of predictable stereochemistry from the reaction of vinyldiazoacetates with dienes. The illustratory examples that are reported here, demonstrate the synthetic potential of this 3 + 4 annulation strategy for the construction of a variety of seven-membered carbocycles in a stereodefined manner. The success of this chemistry is due to the highly stereoselective nature of vinylcarbenoid cyclopropanations which strongly favor the formation of *cis*-divinylcyclopropane intermediates.

Experimental Section

^{1}H NMR spectra were run at either 200, 300, 400, or 500 MHz, and ^{13}C NMR at either 50, 75, or 125 MHz in $CDCl_3$ unless otherwise noted. Mass spectral determinations were carried out at 70 eV. Melting points are uncorrected. IR spectra were obtained using a Nicolet Impact series 420 IR. Optical rotations were measured using a Jasco DIP-370 digital polarimeter. Glassware was oven-dried at >60 °C prior to use. Solvent hexanes were distilled over sodium with triglyme and benzophenone. Pentane was dried over activated molecular sieves (4 Å) for 24 h prior to use. Reactions were carried out under an atmosphere of argon. Low temperatures were maintained by use of dry ice/acetone and a Neslab Cryocool immersion cooler. Ozonolyses were carried out using a Welbash T-408 ozone generator. Hydrogenations were carried out using a Parr hydrogenation apparatus. Column chromatography was carried out on Merck silica gel 60 (230−400 mesh). Commercially available reagents were used without additional purification unless noted. Cyclopentadiene was obtained by thermal cracking and distillation from dicyclopentadiene. *p*-Acetamidobenzenesulfonyl azide (*p*-ABSA),[11a] Rh_2(*S*-DOSP)$_4$ **1**,[8b] and the vinyldiazoacetates **3a**−**c**,**e**−**i**[9,11] were prepared by literature procedures.

Methyl 2-Diazo-3,5-hexadieneoate (3d). A solution of DBU (9.4 g, 60 mmol) in CH_3CN (15 mL) was added to a solution of methyl 3,5-hexadienoate (6.5 g, 51 mmol) and *p*-ABSA (13 g, 54 mmol) in CH_3CN (100 mL) cooled to −20 °C. After 2 h, the resulting orange solution was quenched with aqueous NH_4Cl solution, extracted into ether, and concentrated under reduced pressure. The resulting orange solid was triturated with petroleum ether/ether (1:1) and filtered. The filtrate was concentrated, and the residue was chromatographed over silica gel using petroleum ether/Et_2O (10:1) as eluent (R_f = 0.33) to give **3d** in 74% yield (5.8 g) as a viscous red oil. IR (neat) 3002, 2960, 2081, 1709, 1626 cm^{-1}; ^{1}H NMR (300 MHz) δ 6.37 (dddd, 1 H, J = 17.0, 10.0, 7.5, 3.0 Hz), 5.95 (m, 2 H), 5.07 (dd, 1 H, J = 17.0, 1.5 Hz), 4.97 (dd, 1 H, J = 10.0, 1.5 Hz), 3.76 (s, 3 H); ^{13}C NMR (50 MHz, DEPT) δ 178.5 (4°), 165.2 (4°), 136.0 (3°), 124.2 (3°), 115.0 (2°), 114.8 (3°), 52.09 (1°). The product was insufficiently stable for elemental analysis.

Rh_2(*S*-DOSP)$_4$ Catalyzed Decomposition of Vinyldiazomethanes in the Presence of Dienes. **General Procedure**. A solution of vinyldiazoacetate **3** (0.5−1.5 mmol) in dry hexanes (20 mL) was added dropwise over 0.5−2 h to a 100 mL oven-dried Kjeldahl flask containing a stirred solution of Rh_2(*S*-DOSP)$_4$ (0.01 equiv) and the diene (5−16 equiv) in dry hexane (30 mL) cooled to −78 °C. After the addition was complete, the mixture was maintained at −78 °C for an additional 36−48 h and then slowly warmed to room temperature. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel. Enantioselectivities were determined either by ^{1}H NMR using chiral shift reagents, by GC using an Astec Chiraldex β-PH column (20 m × 0.25 mm) unless otherwise noted or by HPLC using a Daicel OJ or OD analytical column (25 cm length).

(3*R*,4*S*)-Methyl 3-Methyl-4-phenylcyclohepta-1,5-diene-1-carboxylate (4a). Purification by silica gel column chromatography (petroleum ether/Et_2O, 9:1, R_f = 0.32) gave **4a** in 87% yield as a white solid (mp 65−66 °C). 98% ee (determined by GC: 125 °C, 22.7 psi, 2.1 mL/min; T_R = 109.9 min (minor), 113.5 min (major)). $[\alpha]^{25}_D$ = +109° (*c* 0.26, $CHCl_3$). IR (neat) 3013, 2960, 2870, 1704 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.30−7.15 (m, 5 H), 6.58 (dd, 1 H, J = 6.7, 2.3 Hz), 5.83 (dddd, 1 H, J = 11.8, 7.5, 2.9, 1.8 Hz), 5.69 (ddd, 1 H, J = 11.8, 5.4, 2.8 Hz), 3.74 (s, 3 H), 3.55 (m, 1 H), 3.36 (dd, 1 H, J = 18.7, 7.5 Hz), 3.25 (m, 2 H), 1.04 (d, 3 H, J = 6.9 Hz); ^{13}C NMR (75 MHz, DEPT) δ 167.7 (4°), 148.1 (3°), 140.5 (4°), 132.9 (3°), 132.4 (4°), 129.7 (3°), 127.9 (3°), 126.7 (3°), 125.6 (3°), 51.8 (1°), 48.7 (3°), 36.4 (3°), 25.9 (2°), 18.5 (1°). Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.24; H, 7.55.

(3*R*,4*S*)-Methyl 3,4-Diphenylcyclohepta-1,5-diene-1-carboxylate (4b). Purification by silica gel column chromatography (hexanes/Et_2O, 19:1, R_f = 0.28) gave **4b** in 83% yield as a clear yellow oil. 98% ee (determined by HPLC: OD, 0.8% *i*-Pr−OH in hexanes, 1 mL/min; T_R = 15.2 min (minor), 8.9 min (major)). $[\alpha]^{25}_D$ = +107° (*c* 2.00, $CHCl_3$). IR (neat) 3028, 2950, 2872, 1714 cm^{-1}; ^{1}H NMR (300 MHz), δ 7.21−7.15 (m, 6 H), 7.10 (dd, 1 H, J = 6.8, 2.7 Hz), 6.88−6.77 (m, 4 H), 5.96 (dddd, 1 H, J = 11.4, 9.9, 7.5, 3.3 Hz), 5.76 (ddd, 1 H, J = 11.4, 5.5, 2.6 Hz), 4.40 (m, 1 H), 3.86 (m, 1 H), 3.76 (s, 3 H), 3.49 (dd, 1 H, J = 18.9, 7.5 Hz), 3.39 (m, 1 H); ^{13}C NMR (75 MHz, DEPT) δ 167.9 (4°), 144.6 (3°), 140.6 (4°), 139.9 (4°), 133.2 (3°), 132.4 (4°), 129.9 (3°), 129.2 (3°), 127.9 (3°), 127.6 (3°), 126.8 (3°), 126.8 (3°), 126.4 (3°), 52.0 (1°), 50.0 (3°), 49.6 (3°), 25.6 (2°). Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.87; H, 6.62. Found: C, 82.91; H, 6.60.

(3*R*,4*S*)-Methyl 3-(2-Phenylethenyl)-4-phenylcyclohepta-1,5-diene-1-carboxylate (4c). Purification by silica gel column chromatography (hexanes/Et_2O, 19:1, $R_f = 0.24$) gave **4c** in 84% yield as a clear oil. 93% ee (determined by HPLC: OD, 0.5% *i*-Pr−OH in hexanes, 1.2 mL/min; $T_R = 24.8$ min (minor), 26.8 min (major)). $[\alpha]^{25}_D = +60°$ (*c* 0.71, $CHCl_3$). IR (neat) 3033, 2945, 2867, 1714, cm^{-1}; ^1H NMR (300 MHz) δ 7.31−7.18 (m, 10 H), 6.83 (dd, 1 H, $J = 6.9$, 2.2 Hz), 6.41 (d, 1 H, $J = 15.9$ Hz), 6.14 (dd, 1 H, $J = 15.9$, 8.6 Hz), 5.90 (dddd, 1 H, $J = 11.7$, 7.1, 3.3, 1.6 Hz), 5.76 (ddd, 1 H, $J = 11.7$, 5.1, 2.6 Hz), 3.91 (m, 1 H), 3.84 (m, 1 H), 3.75 (s, 3 H), 3.42 (dd 1 H, $J = 19.4$, 7.3 Hz), 3.33 (br d, 1 H, $J = 19.4$ Hz); ^{13}C NMR (75 MHz) δ 167.7, 144.5, 140.6, 137.3, 132.9, 132.3, 131.7, 130.1, 129.5, 128.6, 128.0, 127.5, 126.8, 126.3, 126.2, 52.0, 48.9, 46.7, 26.1. Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.47; H, 6.74.

(3*R*,4*S*)-Methyl 3-Ethenyl-4-phenylcyclohepta-1,5-diene-1-carboxylate (4d). Purification by silica gel column chromatography (hexanes/Et_2O, 19:1, $R_f = 0.19$) gave **4d** in 56% yield as a clear oil. 96% ee (determined by HPLC: OD, 0.8% *i*-Pr−OH in hexanes, 1.2 mL/min; $T_R = 6.3$ min (minor), 6.8 min (major)). $[\alpha]^{25}_D = +39°$ (*c* 1.40, $CHCl_3$). IR (neat) 3084, 3017, 2950, 2867, 1724 cm^{-1}; ^1H NMR (300 MHz) δ 7.30−7.16 (m, 5 H), 6.76 (dd, 1 H, $J = 6.7$, 2.1 Hz), 5.86 (dddd, 1 H, $J = 11.4$, 7.7, 3.2, 1.6 Hz), 5.78 (ddd, 1 H, $J = 16.4$, 8.7, 2.9 Hz), 5.71 (ddd, 1 H, $J = 11.4$, 4.9, 2.3 Hz), 5.10 (s, 1 H), 5.05 (br d, 1 H, $J = 7.5$ Hz), 3.81−3.75 (m, 2 H), 3.75 (s, 3 H), 3.39 (dd, 1 H, $J = 19.2$, 7.7 Hz), 3.29 (br d, 1 H, $J = 19.2$ Hz); ^{13}C NMR (75 MHz, DEPT) δ 167.6 (4°), 144.3 (3°), 140.4 (4°), 138.5 (3°), 132.8 (3°), 132.4 (4°), 129.5 (3°), 127.9 (3°), 126.7 (3°), 126.0 (3°), 116.4 (2°), 51.9 (1°), 48.5 (3°), 47.1 (3°), 26.0 (2°). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.25; H, 7.14.

(4*R*)-Methyl 4-Phenylcyclohepta-1,5-diene-1-carboxylate (4e). Purification by silica gel column chromatography (petroleum ether/Et_2O, 19:1, $R_f = 0.16$) gave **4e** in 41% yield as a white solid (mp 31−33 °C). 73% ee (determined by HPLC: OD, 0.6% *i*-Pr−OH in hexanes, 0.8 mL/min; $T_R = 17.2$ min (major), 18.1 min (minor)). $[\alpha]^{25}_D = -25.4°$ (*c* 3.05, $CHCl_3$). IR (neat) 3029, 2944, 2864, 1711, 1654 cm^{-1}; ^1H NMR (300 MHz) δ 7.34−7.23 (m, 5 H), 7.08 (dd, 1 H, $J = 7.2$, 6.6 Hz), 5.81 (dddd, 1 H, $J = 11.5$, 5.1, 5.1, 2.2 Hz), 5.69 (dd, 1 H, $J = 11.5$, 2.6 Hz), 3.75 (s, 3 H), 3.69−3.65 (m, 1 H), 3.30 (d, 2 H, $J = 5.1$ Hz), 2.75 (ddd, 1 H, $J = 14.5$, 10.5, 6.6 Hz), 2.62 (ddd, 1 H, $J = 14.5$, 7.2, 3.5 Hz); ^{13}C NMR (75 MHz, DEPT) δ 167.7 (4°), 145.1 (4°), 141.3 (3°), 134.5 (4°), 134.1 (3°), 128.5 (3°), 127.5 (3°), 126.4 (3°), 126.2 (3°), 51.8 (1°), 42.2 (3°), 34.8 (2°), 25.6 (2°). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.99; H, 7.11.

(7*S*,6*S*)-Methyl 6-Phenylbicyclo[5.4.0]undeca-1,4-diene-2-carboxylate (5h). Purification by silica gel column chromatography (petroleum ether/Et_2O, 19:1, $R_f = 0.28$) gave **5h** in 62% yield as a white solid (mp 74−75 °C). 94% ee (determined by HPLC: OD, 0.4% *i*-Pr−OH in hexanes, 1 mL/min; $T_R = 10.1$ min (major), 12.7 min (minor)). $[\alpha]^{25}_D = -81°$ (*c* 1.88, $CHCl_3$). IR (neat) 3012, 2933, 2859, 1714 cm^{-1}; ^1H NMR (300 MHz) δ 7.31−7.20 (m, 5 H), 5.89 (dddd, 1 H, $J = 11.3$, 8.4, 3.0, 1.7 Hz), 5.76 (ddd, 1 H, $J = 16.5$, 11.3, 5.4 Hz), 3.75 (s, 3 H), 3.75 (m, 1 H), 3.44 (dd, 1 H, $J = 16.5$, 1.7 Hz), 3.06 (m, 1 H), 2.98 (dd, 1 H, $J = 18.0$, 8.4 Hz), 2.51 (m, 1 H), 1.68−1.60 (m, 1 H), 1.54−1.39 (m, 5 H), 1.28−1.17 (m, 1 H). Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found: C, 80.94; H, 7.79.

(7*S*,6*S*)-Methyl 6-Phenylbicyclo[5.3.0]deca-1,4-diene-2-carboxylate (5i). Purification by silica gel column chromatography (hexane/Et_2O, 19:1, $R_f = 0.27$) gave **5i** in 60% yield as a clear yellow oil. 81% ee (determined by HPLC: OD, 0.3% *i*-Pr−OH in hexanes, 0.9 mL/min; $T_R = 10.7$ min (major), 12.3 min (minor)). $[\alpha]^{25}_D = +143°$ (*c* 2.86, $CHCl_3$). IR (neat) 3012, 2955, 2867, 1714 cm^{-1}; ^1H NMR (300 MHz) δ 7.28−7.17 (m, 5 H), 5.80 (dddd, 1 H, $J = 11.7$, 7.3, 3.3, 1.5 Hz), 5.56 (ddd, 1 H, $J = 11.7$, 5.1, 2.6 Hz), 3.74 (s, 3 H), 3.65−3.58 (m, 1 H), 3.47 (br d, 1 H, $J = 4.0$ Hz), 3.36 (dd, 1 H, $J = 17.9$, 7.7 Hz), 3.32−3.23 (m, 1 H), 2.62−2.49 (m, 1 H), 2.24−2.12 (m, 1 H), 1.93−1.80 (m, 1 H), 1.64−1.54 (m, 1 H), 1.36−1.23 (m, 1 H), 0.73−0.56 (m, 1 H); ^{13}C NMR (75 MHz) δ 168.1 (4°), 164.9 (4°), 141.4 (4°), 132.5 (3°), 129.6 (3°), 128.0 (3°), 126.7 (3°), 125.4 (3°), 124.2 (4°), 51.3 (1°), 48.4 (3°), 47.8 (3°), 35.0 (2°), 30.1 (2°), 27.7 (2°), 24.7 (2°),. Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.64; H, 7.50.

(1*S*,4*S*,5*R*)-Methyl 4-Methylbicyclo[3.2.1]octa-2,6-diene-2-carboxylate (6a). Purification by silica gel column chromatography (petroleum ether/Et_2O, 10:1, $R_f = 0.33$) gave **6a** in 47% yield as a clear oil. 91% ee (determined by ^1H NMR (500 MHz) using chiral shift (20% mol Yb(hfc)$_3$); δ 6.67 (minor), δ 6.56 (major) ppm). $[\alpha]^{25}_D = -127°$ (*c* 1.42, $CHCl_3$). IR (neat) 3063, 2962, 2870, 1717, 1696, 1627 cm^{-1}; ^1H NMR (500 MHz) δ 6.35 (dd, 1 H, $J = 5.5$, 3.0 Hz), 6.32 (br m, 1 H), 5.65 (dd, 1 H, $J = 5.5$, 3.0 Hz), 3.71 (s, 3 H), 3.18 (dd, 1 H, $J = 4.0$, 3.5 Hz), 2.74 (br m, 1 H), 2.54 (ddq, 1 H, $J = 7.5$, 4.5, 3.0 Hz), 2.13 (dq, 1 H, $J = 5.0$, 5.0 Hz), 1.75 (d, 1 H, $J = 9.5$ Hz), 0.94 (d, 3 H, $J = 7.5$ Hz); ^{13}C NMR (50 MHz) δ 166.6, 142.1, 141.7, 136.8, 129.8, 51.2, 43.8, 42.3, 37.7, 33.5, 15.4; MS *m*/*z* (relative intensity): 178 (17), 146 (23), 119 (48), 103 (22), 91 (100), 77 (38), 65 (32), 51 (27). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.12; H, 7.92. Found: C, 73.89; H, 7.90.

(1*S*,4*S*,5*R*)-Methyl 4-Phenylbicyclo[3.2.1]octa-2,6-diene-2-carboxylate (6b). Purification by silica gel column chromotography (petroleum ether/Et_2O, 9:1, $R_f = 0.48$) gave **6b** in 77% yield as a yellow oil. 93% ee (determined by GC: 160 °C, $T_R = 22.6$ min (minor), 24.6 min (major)). $[\alpha]^{25}_D = -28°$ (*c* 0.87, $CHCl_3$). IR (neat) 2949, 2360, 2341, 1712, 1261 cm^{-1}; ^1H NMR (300 MHz) δ 7.32−7.16 (m, 3 H), 7.06 (d, 2 H, $J = 6.6$ Hz), 6.63 (s, 1 H), 6.35 (dd, 1 H, $J = 5.4$, 2.7 Hz), 5.27 (dd, 1 H, $J = 5.4$, 2.7 Hz), 3.78 (dd, 1 H, $J = 4.2$, 3.3 Hz), 3.76 (s, 3 H), 3.32 (t, 1 H, $J = 3.8$ Hz), 3.02 (ddd, 1 H, $J = 4.7$, 4.6, 2.4 Hz), 2.24 (ddd, 1 H, $J = 9.9$, 4.8, 4.8 Hz), 1.98 (d, 1 H, $J = 9.9$ Hz); ^{13}C NMR (50 MHz) δ 166.9, 141.1, 140.2, 139.3, 138.2, 130.5, 128.2, 127.8, 126.6, 51.7, 45.8, 44.3, 43.0, 37.8; MS *m*/*z* (relative intensity): 240 (100), 208 (35), 181 (76), 165 (50), 115 (47), 77 (28), 51 (20). HRMS calcd for $C_{16}H_{16}O_2$, 240.1150, found, 240.1155.

(1*S*,4*S*,5*R*)-Methyl 4-(2-Phenylethenyl)bicyclo[3.2.1]octa-2,6-diene-2-carboxylate (6c). Purification by silica gel column chromatography (petroleum ether/Et_2O, 10:1, $R_f = 0.25$) gave **6c** in 80% yield as a clear, colorless oil. 90% ee (determined by HPLC: OJ, 10% *i*-Pr−OH in hexanes, 0.5 mL/min; $T_R = 19.6$ min (major), 21.65 min (minor)). $[\alpha]^{25}_D = -40°$ (*c* 2.65, $CHCl_3$). IR (neat) 3062, 3026, 2994, 2862 1709, 1613 cm^{-1}; ^1H NMR (500 MHz) δ 7.35−7.19 (m, 5 H), 6.49 (br s, 1 H), 6.44 (d, 1 H, $J = 16.6$ Hz), 6.40 (dd, 1 H, $J = 5.6$, 3.2 Hz), 6.09 (dd, 1 H, $J = 16.6$, 8.0 Hz), 5.78 (dd, 1 H, $J = 5.6$, 2.3 Hz), 3.75 (s, 3 H), 3.31 (m, 2 H), 2.96 (m, 1 H), 2.21 (ddd, 1 H, $J = 10.0$, 5.2, 4.8 Hz), 1.85 (d, 1 H, $J = 10.0$ Hz); ^{13}C NMR (75 MHz, DEPT) δ 166.8 (4°), 142.1 (3°), 138.7 (3°), 138.1 (4°), 137.1 (4°), 130.9 (3°), 130.5 (3°), 128.5 (3°), 128.1 (3°), 127.3 (3°), 126.1 (3°), 51.7 (1°), 43.7 (3°), 42.2 (2°), 42.2 (3°), 37.9 (3°); MS *m*/*z* (relative intensity): 266 (58), 234 (19), 207 (44), 191 (18), 178 (21), 165 (31), 141 (16), 129 (36), 115 (48), 103 (18), 91 (100). HRMS calcd for $C_{18}H_{18}O_2$, 266.1307, found, 266.1298. Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.3; H, 6.86.

(1*S*,4*S*,5*R*)-Methyl 4-Ethenylbicyclo[3.2.1]octa-2-carboxylate (6d). Purification by silica gel chromatography (petroleum ether/Et_2O, 10:1, $R_f = 0.22$) gave **6d** in 58% yield as a clear, colorless gum. 92% ee (enantioselectivity determined by ^1H NMR (500 MHz) using chiral shift (20% mol Yb(hfc)$_3$); δ 6.76 (minor), δ 6.63 (major) ppm). $[\alpha]^{25}_D = -142°$ (*c* 1.06, $CHCl_3$). IR (neat) 2950, 1738, 1603, 1445 cm^{-1}; ^1H NMR (500 MHz) δ 6.41 (br m, 1 H), 6.34 (dd, 1 H, $J = 5.5$, 3.0 Hz), 5.69 (ddd, 1 H, $J = 17.5$, 10.0, 8.0 Hz), 5.63 (dd, 1 H, $J = 5.5$, 2.5 Hz), 5.07 (d, 1 H, $J = 17.5$ Hz), 5.03 (d, 1 H, $J = 10.0$ Hz), 3.72 (s, 3 H), 3.24 (br m, 1 H), 3.14 (br q, 1 H), 2.87 (br m, 1 H), 2.16 (dq, 1 H, $J = 5.0$, 5.0 Hz), 1.78 (d, 1 H, $J = 10.5$ Hz); ^{13}C NMR (50 MHz) δ 163.5, 143.2, 141.1, 137.1, 134.0, 132.6, 130.1, 58.9, 56.7, 52.1, 43.3, 38.6; MS *m*/*z* (relative intensity): 190 (7), 175 (17), 145 (17), 131 (96), 115 (44), 103 (23), 91 (100), 77 (43), 65 (36), 51 (28). HRMS calcd for $C_{12}H_{14}O_2$, 190.0994, found, 190.0983.

(*S*)-Phenylsuccinic Acid (15). A solution of **4e** (0.625 g, 2.74 mmol, 73% ee) in anhydrous methanol (50 mL) was cooled to −78 °C and treated with ozone for 1 h. The solution was purged with oxygen, and the solvent was removed via rotovap (0 °C bath). The clear oil obtained was cooled to −78 °C, and formic acid (50 mL, 88%) and then H_2O_2 (18 mL, 30% solution in water) were added with stirring, and the mixture was slowly warmed to room temperature and then brought to reflux over 3 h. Water (600 mL) was added, and the mixture was extracted with EtOAc (4 × 75 mL). The solution was concentrated to

dryness, and the resulting solid was triturated (2 × 15 mL) with chloroform/petroleum ether (1:1) to give **15** as a white solid in 19% (102 mg) yield: mp 172−173 °C (lit. mp 173−174 °C)[15]; $[\alpha]^{25}_D$ = +127° (*c* 1.59, acetone) (lit. $[\alpha]^{15.4}_D$ = +171° (*c* 2.00, acetone)[15], $[\alpha]^{20}_D$ = +181° (*c* 0.20, acetone)[16]).

(*R*)-Phenylsuccinic Acid (ent-15). Decomposition of compound **13** (0.362 g, 1.38 mmol, 80% ee) to **ent-15** was accomplished by an ozonolysis procedure similar to that described above using **4e** as substrate. Trituration with chloroform gave **ent-5** in 7% yield (18.0 mg) as a white solid. (Mp 159−161 °C (lit. mp 167−168 °C)[16]). $[\alpha]^{25}_D$ = −156° (*c* 0.36, acetone) (lit. $[\alpha]^{20}_D$ = −190° (*c* 0.2, acetone)[16]).

(*R*,*R*)-Bicyclo[3.2.1]octan-2-one (17). A hydrogenation vessel charged with **7e** (463 mg, 2.82 mmol), Wilkinson's catalyst (26 mg, 1 mol %), and absolute ethanol (40 mL) was hydrogenated (40 psi H_2) for 4.5 h. The solvent was removed, and the residue was purified by silica gel column chromatography (petroleum ether/Et_2O, 19:1, R_f = 0.34) to give **16**. Lithium hydroxide (63.0 mg, 2.62 mmol) was added to a solution of **16** in water (5 mL) and methanol (10 mL), and the mixture was heated under reflux for 48 h. Water (100 mL) was added, and the aqueous layer was extracted with CH_2Cl_2 (2 × 75 mL), acidified with 2.4 M HCl solution (50 mL), and then extracted with CH_2Cl_2 (4 × 30 mL). The second organic extract was dried over sodium sulfate and concentrated under reduced pressure. This residue was dissolved in mesitylene (5 mL) and triethylamine (0.16 mL, 1.2 mmol) at 0 °C. Diphenylphosphoryl azide (0.25 mL, 1.2 mmol) was slowly added over 10 min, and then the mixture warmed to room temperature over 3.5 h. Water (5 mL), dioxane (5 mL), and ammonium chloride (138 mg) were then added and the mixture was heated at reflux for 5 h. The mixture was cooled to room temperature, water (50 mL) was added, and the aqueous solution was extracted into CH_2Cl_2 (4 × 40 mL). The combined organics were dried over sodium sulfate and then concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (pentane/Et_2O, gradient to 3:1) as eluent gave **17** (44.0 mg) whose ^1H and ^{13}C NMR were identical to reported values.[17] $[\alpha]^{25}_D$ = −68° (*c* 0.88, chloroform). For *S*,*S* enantiomer (lit. $[\alpha]^{25}_D$ = +130° (chloroform),[18] $[\alpha]^{25}_D$ = +149° (*c* 2.6, chloroform)[19]).

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Supporting Information Available: Experimental data for **7e**−**h**, **8a**, **8i**, **9b**, **9c**, **10b**, **10c**, and **11**−**14**, copies of ^1H NMR spectra of **6b**, **6d**, **7g**, **8h**, **8i**, **9b**, and **10b**, NOE data for **4a**, and representative examples of enantiomeric excess determinations (14 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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