Enantioselective Synthesis of Fused Cycloheptadienes by a Tandem Intramolecular Cyclopropanation/Cope Rearrangement Sequence

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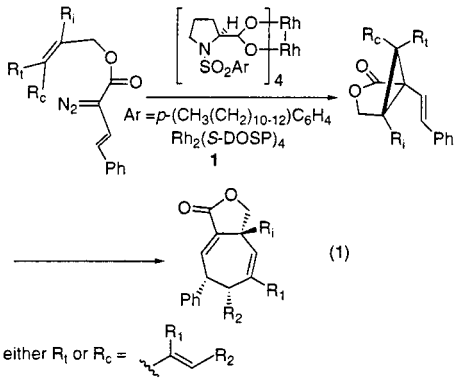
The asymmetric induction in the intramolecular cyclopropanations of allyl vinyldiazoacetates catalyzed by tetrakis[*N*-[4-dodecylphenyl)sulfonyl]-(*S*)-prolinato]dirhodium [Rh_2(*S*-DOSP)$_4$] is very dependent on the allyl substitution pattern. The reactions of *cis*-alkenes result in much higher asymmetric induction than *trans*-alkenes while the highest enantioselectivity was obtained with a disubstituted terminal alkene. The intramolecular cyclopropanation of dienylmethyl vinyldiazoacetates results in the synthesis of fused cycloheptadiene ring systems with full control of relative stereochemistry and variable enantioselectivity. The synthetic utility of this process was demonstrated by a short synthesis of 5-*epi*-tremulenolide in 93% ee.

The 3 + 4 annulation between vinylcarbenoids and dienes is a very general process for the synthesis of seven-membered rings.[1,2] Both inter- and intramolecular versions of the reaction are known, and the reaction is applicable to a vast array of cyclic and acyclic dienes, including furans and pyrroles.[1,3] The annulation occurs by a two-step process, cyclopropanation of the diene to form a *cis*-divinylcyclopropane followed by a Cope rearrangement. As the Cope rearrangement of divinylcyclopropanes proceeds through a well-defined boat transition state, predictable stereocontrol can be achieved at up to three stereogenic centers in the resulting cycloheptadiene.[4] Recently, tetrakis[*N*-[4-dodecylphenyl)sulfonyl]-(*S*)-prolinato]dirhodium (Rh_2(*S*-DOSP)$_4$ (**1**)) has been shown to be an excellent chiral catalyst for the intermolecular version of these transformations such that cycloheptadienes can be obtained with high asymmetric induction.[5] In this paper, we describe a systematic evaluation of Rh_2(*S*-DOSP)$_4$ in intramolecular cyclopropanations of rhodium-stabilized vinylcarbenoids with alkenes and dienes (eq 1), which have culminated in a practical asymmetric 3 + 4 annulation strategy for the construction of fused cycloheptadienes.



Even though no studies have been reported on the asymmetric intramolecular reactions between vinylcarbenoids and alkenes, several excellent chiral catalysts have been developed for other intramolecular carbenoid systems. The most notable are Doyle's dirhodium carboxamide catalysts such as Rh_2(5*S*-MEPY)$_4$, Rh_2(5*S*-MEOX)$_4$, and Rh_2(*S*-MPPIM)$_4$, which have resulted in very high asymmetric cyclopropanation with allyl diazoacetates, homoallyl diazoacetates, *N*-allyl diazoamides, or *N*-homoallyl diazoamides.[6] Various C_2 copper catalysts such as Pfaltz' copper semicorrins, Evans' copper bisoxazolines, and Nishiyama's ruthenium pybox have also proven to be effective for intramolecular cyclopropanation of diazoacetate derivatives.[7,8] As kinetically active dirhodium tetracarboxylates are required for effective decomposition of vinyldiazoacetates to carbenoid intermedi-

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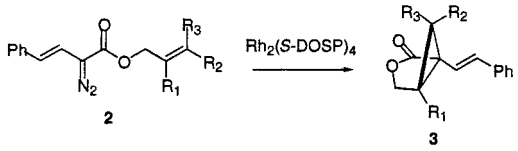
Table 1. Rh_2(*S*-DOSP)$_4$-Catalyzed Decomposition of 2

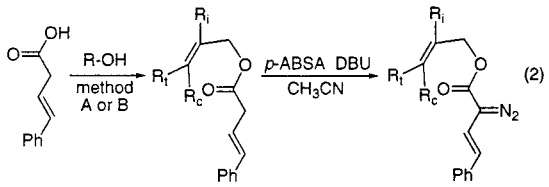


entry	diazo	R_1	R_2	R_3	cyclopropane	ee, %	yield, %
1	**2a**	H	Me	H	**3a**	25	54
2	**2b**	H	Et	H	**3b**	2	55
3	**2c**	H	Pr	H	**3c**	10	75
4	**2d**	H	H	Me	**3d**	72	72
5	**2e**	H	H	Et	**3e**	69	56
6	**2f**	H	H	Pr	**3f**	66	81
7	**2g**	H	H	H	**3g**[a]	28	81
8	**2h**	H	Me	Me	**3h**	74	62
9	**2i**	Me	H	H	**3i**	87	53
10	**2j**	Me	Me	H	**3j**	45	68
11	**2k**	Me	Me	Me	**3k**	60	47

[a] Cyclopropane was prepared using Rh_2(*R*-DOSP)$_4$ as catalyst at 0 °C.

ates,[9] the current study is focused on the use of Rh_2(*S*-DOSP)$_4$ as the chiral catalyst.

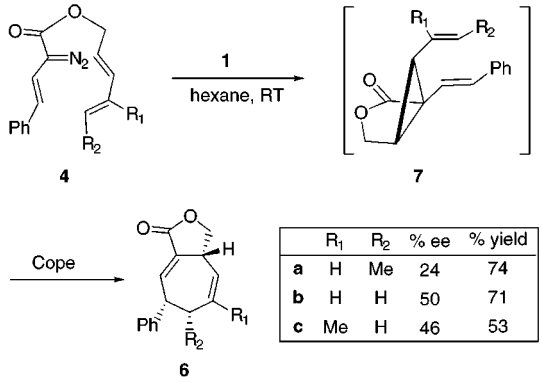
To evaluate the effect of alkene and diene structure on the asymmetric induction in intramolecular vinylcarbenoid cyclopropanations, a series of allyl vinyldiazoacetates and 2,4-pentadienyl vinyldiazoacetates were prepared as summarized in eq 2. Acid chloride (method



A) or DCC (method B) coupling of 4-phenyl-3-butenoic acid with allyl or dienyl alcohols provided the requisite esters. Conversion to the vinyldiazoacetates was readily achieved by a diazo transfer reaction using *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) and DBU as base.[10]

The intramolecular cyclopropanation of the series of allyl vinyldiazoacetates **2** was examined under the standard reaction conditions of Rh_2(*S*-DOSP)$_4$ in hexane at −78 °C. The level of asymmetric induction was found to be very dependent on the substituents around the allyl group as summarized in Table 1. With the trans-substituted allyl systems **2a**−**c**, the enantioselectivity in formation of **3a**−**c** was very low (2−25% ee), but with the cis-substituted allyl systems **2d**−**f**, much higher enantioselectivity was observed (66−73% ee).[11] Moderately low enantioselectivity was observed for the unsubstituted allyl **2g** (25% ee)[12] and the 3,3-disubstituted allyl **2h** (47% ee),[12] while the highest enantioselectivity was observed for the methallyl system **2i** (87% ee). Moderate enantioselectivity was obtained for the more highly substituted systems **2j** (45% ee) and **2k** (60% ee).

Extension of the study to dienyl vinyldiazoacetates **4** and **5** led to some interesting differences to the reactions of allyl vinyldiazoacetates **2**. The reactions of the *trans*-dienyl systems **4a**−**c** led directly to the formation of the fused cycloheptadienes **6a**−**c**, presumably via the intermediacy of the *cis*-divinylcyclopropane **7** (eq 3). The



	R_1	R_2	% ee	% yield
a	H	Me	24	74
b	H	H	50	71
c	Me	H	46	53

(3)

enantioselectivity in these reactions (24−50% ee) were considerably higher than those that were obtained with the *trans*-allyl derivatives **2a**−**c** (2−25% ee). As expected, cycloheptadienes **6a**−**c** were formed with excellent control of relative stereochemistry due to the requirements of the boat transition state for the Cope rearrangement of divinylcyclopropanes.[4]

The reaction of the *cis*-dienylmethyl systems **5a**−**c** resulted in the formation of isolable *trans*-divinyl cyclopropanes **8a**−**c** in 41−62% ee.[13] Considerable improvement in the enantioselectivity was possible if the reaction was carried out at low temperature, but this also resulted in a severe decrease in the yield. For example, the reaction of **5a** at −78 °C resulted in the formation of **8a** in 85% ee and 29% yield. As the *trans*-divinylcyclopro-

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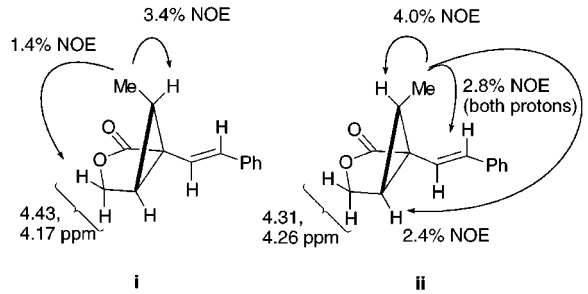
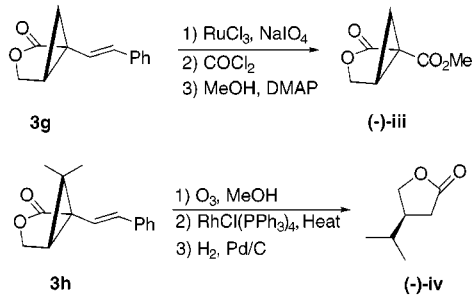
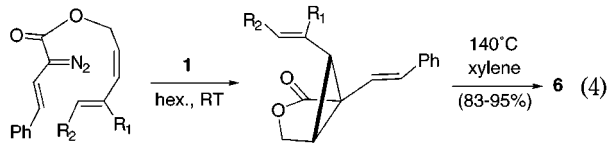
(11) Relative stereochemistry was assigned based on nOe spectral analysis of cyclopropanes **3a,d** as shown in structures **i** and **ii**, respectively. Cyclopropanes **3b,c,e,f,h** were assigned by analogy on the basis of ^{1}H NMR resonances of the lactone methylene. See the Supporting Information for full details.



(12) The absolute stereochemistry for cyclopropane **3g** was determined by conversion to **iii** and comparison to published results. The absolute stereochemistry of cyclopropane **3h** was determined by conversion to isopropyl butyrolactone **iv** and comparison to published results. See the Supporting Information for full details.



panes **8a**−**c** do not contain functionality that would allow a competing 1,5-homodienyl rearrangement to occur, heating **8a**−**c** at 140 °C leads to the smooth conversion to the fused cycloheptadienes **6a**−**c**, the same products that were derived from the *trans*-dienyl systems **4a**−**c**. Presumably, this transformation occurs with the intermediacy of cyclopropane **7**. No change in the enantiomeric excess occurs on conversion of *trans*-divinyl cyclopropanes **8a**−**c** to fused cycloheptadienes **6a**−**c** (eq 4).

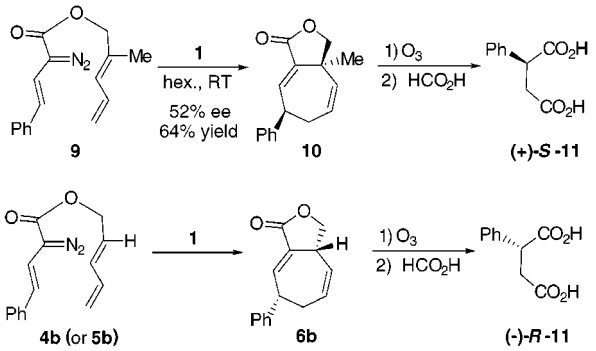


(4)

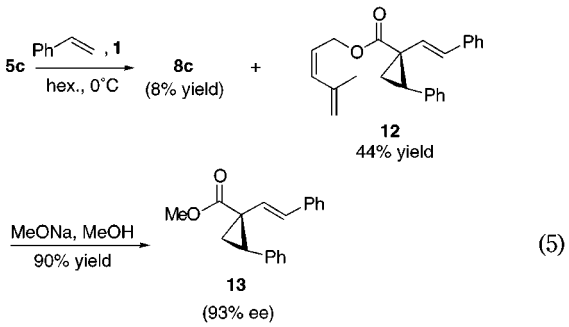
	R_1	R_2	% ee	% yield
a	H	Me	62	78
b	H	H	67	76
c	Me	H	41	63

The sense of asymmetric induction in these reactions was found to be dependent on the dienyl substitution pattern. Rh_2(*S*-DOSP)$_4$-catalyzed decomposition of **9**, which contains an internally substituted diene, resulted in the formation of the fused cycloheptadiene **10** in 52% ee (Scheme 1). The asymmetric induction in the formation of **10** was opposite to that obtained in the formation of **6b** derived from either the *trans*-dienylmethyl vinyldiazoacetate **4b** or the *cis*-dienyl system **5b**. The absolute stereochemistry was determined by conversion of **10** and **6b** to phenylsuccinic acid. The oxidative cleavage of **10** generated the *S*-phenylsuccinic acid ((+)-*S*-**11**) while the oxidative cleavage of the fused cycloheptadiene **6b** derived from either **4b** or **5b** generated *R*-phenylsuccinic acid ((−)-*R*-**11**). Similar change in the sense of asymmetric induction has been found in the intramolecular cyclopropanations of substituted allyl diazoacetates.[14]

Scheme 1

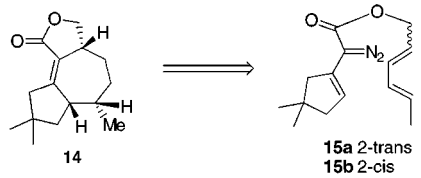


To test the asymmetric influence of the catalyst, a competition study was carried out between inter- and intramolecular reactions by decomposition of **5c** in the presence of 10 equiv of styrene (eq 5). The intramolecular product **8c** was isolated as a minor component (8% yield) while the intermolecular cyclopropanation product **12** was obtained in 44% yield. Conversion to the known methyl ester **13**[15] and analysis revealed that the 1*S*,5*S* isomer was the major component and the asymmetric induction in the formation of **12** was very high (93% ee).



(5)

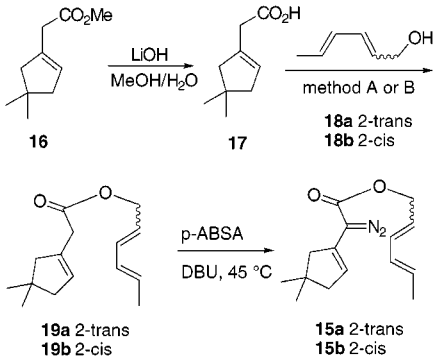
An example of the synthetic potential of the asymmetric intramolecular cyclopropanation was demonstrated by an asymmetric synthesis of 5-*epi*-tremulenolide **14**.[16] It was envisioned that the three stereocenters in **14** could be readily controlled by the tandem cyclopropanation/Cope rearrangement of dienyl vinyldiazoacetates **15a** (2-trans) or **15b** (2-cis) (eq 6).



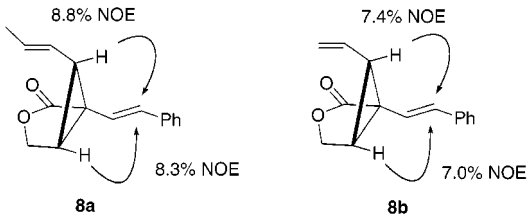
(6)

The vinyldiazoacetates **15a,b** were prepared as outlined in Scheme 2. Hydrolysis of the methyl cyclopentenyl acetate **16** using lithium hydroxide provided the acid **17** in 90−96% yield. Coupling of **17** with either (2*E*,4*E*) or (2*Z*,4*E*) hexadienols (**18a** or **18b**) provided the requisite

Scheme 2



(13) Relative stereochemistry of cyclopropanes **8a,b** was assigned by nOe spectral analysis. Similarities in enhancement between the two cyclopropyl protons and the styrenyl proton suggest the spacial distances are equal and therefore the protons are oriented cis on the cyclopropanes. The relative stereochemistry of **8c** has been previously determined (see ref 26).



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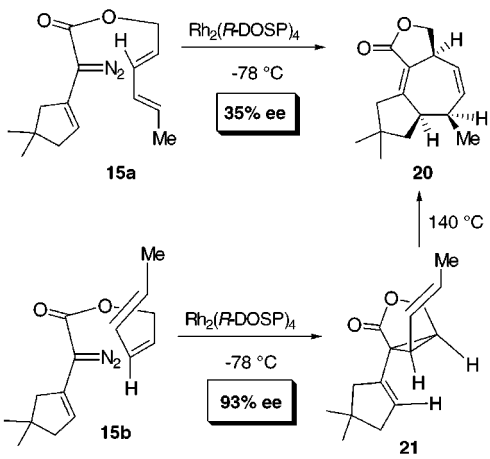
(16) For a preliminary report, see: Davies, H. M. L.; Doan, B. D. *Tetrahedron Lett.* **1996**, *37*, 3967.

esters **19a** or **19b**, respectively, in 80−85% yields. Conversion of **19a** or **19b** to the vinyldiazoacetates **15a** and **15b** was accomplished in 45−55% yield using *p*-ABSA and an excess of DBU at 45 °C.

The first approach was to synthesize the ring system directly using the *trans*-dienyl system. Rh_2(*R*-DOSP)$_4$-catalyzed decomposition of **15a** in hexane at room temperature resulted in the formation of the tremulane skeleton **20** in 69% yield (eq 7). The enantioselectivity of



(7)

the reaction, however, was low (24% ee) as expected from the model studies. Some improvement in enantioselectivity was possible by carrying out the reactions at lower temperatures (up to 35% ee at −78 °C), but still the overall results were not very satisfactory. Use of the *cis*-dienyl system **15b**, however, resulted in an improvement of enantioselectivity. Rh_2(*R*-DOSP)$_4$-catalyzed decomposition of **15b** in hexane at room temperature resulted in the formation of the expected *trans*-divinylcyclopropane **21** in 79% yield. The *trans*-divinylcyclopropane **21** was stable under ambient conditions, but on heating in refluxing xylene, **21** underwent smooth rearrangement to the tremulane skeleton **20** in 85% yield, presumably though initial equilibration to a *cis*-divinylcyclopropane. By this two-step process, the overall yield of **20** was similar to that obtained from the one-step process starting from the *trans*-diene **15a**. The enantioselectivity, however, of the two-step process from **15b** was 47% ee. Further optimization of enantioselectivity in the formation **20** was obtained by carrying out the decomposition of **15b** at progressively lower temperatures (up to 93% ee (65% yield) at −78 °C). Completion of the synthesis of (+)-5-*epi*-tremulenolide **14** was readily achieved in 76% yield by hydrogenation of **20** using Wilkinson's catalyst.

Discussion

One notable difference between the asymmetric intramolecular and intermolecular cyclopropanations of vinyldiazoacetates is the extent of asymmetric induction. While the intramolecular reactions occurred with moderate enantioselectivity, they fall quite short of what is typically observed in intermolecular vinylcarbenoid reactions (73−99% ee). The formation of the intermolecular cyclopropanation product **12** with high enantioselectivity is indicative that the catalyst is effective at inducing face selectivity in the reaction of carbenoids that contain a dienyl ester functionality. However, due to the conformational demands for the intramolecular cyclopropanation (vide infra), the chiral influence is not as pronounced as in the intermolecular reactions.

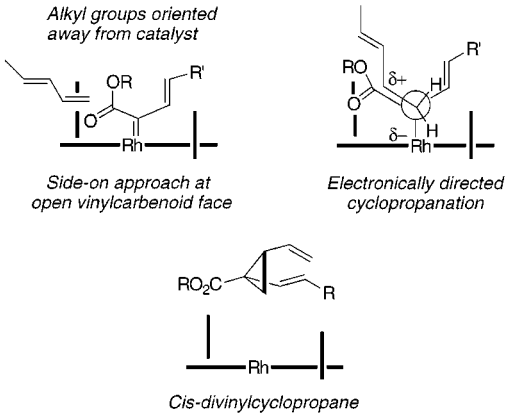


Figure 1.

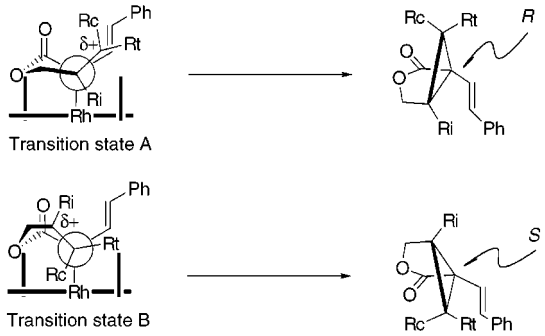


Figure 2.

The sense of asymmetric induction in the intramolecular cyclopropanation reaction can be rationalized by expanding on the model that has been developed for the asymmetric intermolecular cyclopropanations of vinyldiazoacetates. In the intermolecular case, there are several mechanistic imperatives that are believed to account for the observed results as summarized in Figure 1.[15] Rh_2(*S*-DOSP)$_4$ behaves as if it is D_2 symmetric, and so, only one face of the dirhodium complex needs to be considered. The aryl sulfonyl groups (thickened vertical lines in Figure 1) act as blocking groups. The approach of the alkene or diene to the carbenoid occurs over the side of the electron-withdrawing group of the carbenoid in a side-on, nonsynchronous manner. The greater initial bond formation on the alkene occurs at the electronically and/or sterically more favored position. Finally, alkyl groups on the alkene or diene will preferentially point away from the catalyst.

When the model of Figure 1 is extended to intramolecular reactions, the steric demand for formation of the 3-oxobicyclo[3.1.0]hexan-2-one must be imposed on the transition state. This results in two different orientations that are reasonable for approach of the alkene (or diene) as shown in Figure 2 (for the notation R_i, R_c, and R_t, see eq 1). Both transition states lead to the same relative stereochemistry for the cyclopropane products. However, cyclopropanation occurring at opposite faces of the alkene result in the formation of either enantiomer of the cyclopropanes, even though in both orientations the same face of the carbenoid is exposed. The issues that govern which transition state will be involved are dependent on steric interference between the alkene substituents and the catalyst and on the ability of the substituents to

stabilize the partial positive charge buildup. This model has many similarities to that proposed by Doyle to explain the asymmetric induction for allyl diazoacetates except the influence of charge stabilization was not considered as an issue in the Doyle model.[6,17]

The absolute stereochemistry observed in the intramolecular cyclopropanations of vinyldiazoacetates can be rationalized according to Figure 2. In the case of either the *cis*- or *trans*-allyl vinyldiazoacetates (R_i = H), transition states A or B are equally preferred on electronic grounds. A trans substituent does not interfere with either transition state, and so, *trans*-vinyldiazoacetates **2a**−**c** resulted in the formation of vinylcyclopropanes **3a**−**c** with low enantioselectivity. In contrast, cis substituents would interfere in transition state B, and so *cis*-vinyldiazoacetates **2d**−**f** resulted in high asymmetric induction in the formation of vinylcyclopropanes **3d**−**f**. In the case of the dienyl diazoacetates **4** and **5**, transition state A is preferred on electronic grounds for both *trans*- and *cis*-dienyl vinyldiazoacetates. Consequently, reasonable asymmetric induction is exhibited in the reactions of both *trans*-and *cis*-dienyl vinyldiazoacetates **4a**−**c** and **5a**−**c**. The absolute stereochemistry determined for **6b** is consistent with a reaction that proceeds through transition state A.

An internally substituted allyl vinyldiazoacetate would strongly favor transition state B on both electronic and steric grounds. Consequently, the reaction with **2i** occurs with very high asymmetric induction. In the case of dienyl vinyldiazoacetate **9**, structure A would direct the internal methyl group into the catalyst, while transition state B would accommodate the methyl substituent. The determined absolute stereochemistry for **10** is consistent with a reaction proceeding through transition state B.

In the case of the unubstituted allyl vinyldiazoacetate **2g**, both transition state structures are viable on steric grounds, but transition state B is better suited to stabilize the developing positive charge. This is in agreement with the observed absolute stereochemistry in the formation of **3g**.[18] In contrast, in the reaction with dimethylallyl derivative **2h**, transition state A is better suited to stabilize the positive charge, leading to the preferred formation of the 1*R* isomer of **3h**.

One final feature of these reactions is that the thermolysis of *trans*-divinylcyclopropanes to cycloheptadienes (**8a**−**c** to **6a**−**c**) occurs without loss of enantioselectivity. It is generally considered that the rearrangement would occur by homolytic ring opening of the divinylcyclopropane to the diradical **22**.[4] Free rotation of the alkyl group to **23** and then reclosure results in equilibration to the *cis*-divinylcyclopropane **7** as illustrated in Figure 3. Even though two stereocenters in **8** are lost in the diradical intermediate **22**, the third stereocenter is maintained by the lactone ring and is transmitted to the newly formed *cis*-divinylcyclopropane **7**. Thus, the absolute stereochemistry in **8** is maintained through the thermolysis.

In summary, the intramolecular asymmetric cyclopropanation of allyl or dienylmethyl vinyldiazoacetates catalyzed by Rh_2(*S*-DOSP)$_4$ occurs with higher selectivity

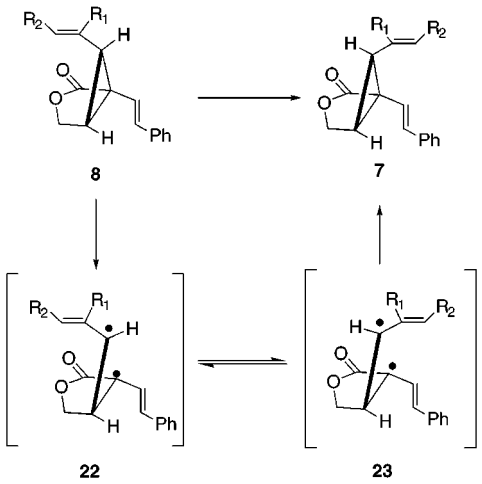


Figure 3.

with *cis*-olefins than with *trans*-olefins. Internally substituted olefins result in highly enantioselective cyclopropanations, but the sense of asymmetric induction is reversed. Furthermore, use of dienes allows for the asymmetric synthesis of fused cycloheptadiene ring systems with excellent control of relative stereochemistry.

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. 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) or by HPLC using a Daicel OJ or OD analytical column (25.0 × 0.46 cm, UV detection at 255 nm).

Glassware was oven-dried at >60 °C prior to use. Reactions were carried out under an atmosphere of argon. Column chromatography was carried out on Merck silica gel 60 (230−400 mesh). Solvent hexanes, THF, and Et_2O were distilled over sodium with triglyme and benzophenone. Acetonitrile and dichloromethane were distilled over calcium hydride prior to use. Reagents were purchased from the Aldrich Chemical Co. and used without additional purification unless noted.

(*E*)-4-Phenyl-3-butenoic acid,[14] *p*-ABSA,[10] Rh_2(*S*-DOSP)$_4$ (**1**),[14] (*E*)-2-methyl-2-butenol,[19] (*Z*)-2-butenol,[20] ethyl 2,3-dimethyl-2-butenoate,[21] 2,3-dimethyl-2-butenol,[22] *E*-2,4-pentadien-1-ol,[23] ethyl (*Z*)-3-iodoacrylate,[24] methyl (*E*)-4-methyl-2,4-pentadienoate,[25] (*E*)-4-methyl-2,4-pentadien-1-ol,[26] ethyl (*Z*)-4-methyl-2,4-pentadienoate,[26] (*Z*)-4-methyl-2,4-pentadien-1-ol,[26] ethyl (*E*)-2-methyl-2,4-pentadienoate,[27] (*E*)-2-methyl-2,4-pentadien-1-ol,[27] (2*E*,4*E*)-2,4-hexadienyl (*E*)-4-phenyl-3-butenoate,[26] (*E*)-2,4-pentadienyl (*E*)-4-phenyl-3-butenoate,[26] (*E*)-4-methyl-2,4-pentadienyl (*E*)-4-phenyl-3-butenoate,[26] (*Z*)-4-methyl-2,4-pentadienyl (*E*)-4-phenyl-3-butenoate,[26] (2*E*,4*E*)-2,4-hexadienyl (*E*)-2-diazo-4-phenyl-3-butenoate (**4a**),[26] (*E*)-2,4-pentadienyl (*E*)-2-diazo-4-phenyl-3-butenoate (**4b**),[26] (*E*)-4-

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(18) Because cyclopropane **3g** was formed using the enantiomer of **1** (Rh_2(*R*-DOSP)$_4$), the absolute stereochemistry depicted for **iii**, is opposite to that predicted using transition state B of Figure 2.

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methyl-2,4-pentadienyl (*E*)-2-diazo-4-phenyl-3-butenoate (**4c**),[26] (*Z*)-4-methyl-2,4-pentadienyl (*E*)-4-phenyl-3-butenoate (**5c**),[26] and methyl 4,4-dimethyl-1-cyclopentyl acetate (**15**)[28] were prepared according to literature procedures. (*Z*)-3-iodo-2-propen-1-ol[29] was prepared by reduction of the corresponding ester, and (*Z*)-2,4-pentadien-1-ol[30] was prepared by Stille coupling.[31]

Ester Synthesis, General Procedure: 2-Propenyl (*E*)-4-Phenyl-3-butenoate. Method A. Oxalyl chloride (4.83 mL, 54.8 mmol) was added neat to a mixture of (*E*)-4-phenyl-3-butenoic acid (8.12 g, 50.1 mmol) in CH_2Cl_2 (50 mL) at 0 °C that was vented through a drying tube ($CaSO_4$). The mixture was stirred 6 h, and then the solvent and excess oxalyl chloride were removed by distillation under reduced pressure. The resulting solid acid chloride was dried in vacuo and then dissolved in CH_2Cl_2 (30 mL). This acid chloride solution was added by cannula to a mixture of allyl alcohol (3.6 g, 53 mmol), pyridine (4.5 mL, 55 mmol), and DMAP (2.45 g, 20.1 mmol) in CH_2Cl_2 (50 mL) at 0 °C. The resulting mixture was stirred overnight, and then saturated $NaHCO_3$ was added. The organics were extracted using Et_2O, and the organic layer was rinsed with saturated $NaHCO_3$ (2×) and then with saturated NaCl. The organic layer was concentrated under reduced pressure to give a yellow oil. Purification by silica gel column chromatography (petroleum ether/Et_2O, 4:1, R_f = 0.47) gave 7.75 g (76%) of 2-propenyl (*E*)-4-phenyl-3-butenoate as a slightly yellow oil: ^{1}H NMR (300 MHz) δ 7.40−7.20 (m, 5 H), 6.52 (d, 1 H, J = 15.9 Hz), 6.32 (dt, 1 H, 15.9, 7.2 Hz), 5.94 (ddt, 1 H, J = 17.2, 10.3, 5.9 Hz), 5.35 (dd, 1 H, J = 17.2, 1.5 Hz), 5.25 (dd, 1 H, J = 10.3, 1.5 Hz), 4.62, (d, 1 H, J = 5.9 Hz), 3.29 (d, 1 H, J = 7.2 Hz); consistent with published results.[32]

3-Methyl-2-butenyl (*E*)-4-Phenyl-3-butenoate. Method B. A solution of DCC in CH_2Cl_2 (1.0 M, 2.6 mL, 2.6 mmol) was added to a mixture of 3-methyl-2-butenol (0.20 g, 2.5 mmol), (*E*)-4-phenyl-3-butenoic acid (0.40 g, 2.5 mmol), and DMAP (30 mg, 0.24 mmol) in CH_2Cl_2 (5 mL) at 0 °C. The mixture was stirred 8 h, and then saturated $NaHCO_3$ and Et_2O were added. The mixture was filtered (paper, vacuum), and the filtrate was extracted using Et_2O. The organic layer was concentrated under reduced pressure to give a yellow oil. Purification by silica gel column chromatography (petroleum ether/Et_2O, 10:1, R_f = 0.34) gave 0.57 g (88%) of 3-methyl-2-butenyl (*E*)-4-phenyl-3-butenoate as a clear, colorless oil: IR (neat) 3022, 2981, 2939, 1739, 1496 cm^{-1}; ^{1}H NMR (500 MHz) δ 7.35 (d, 2 H, J = 7.0 Hz), 7.29 (dd, 2 H, J = 8.1, 7.6 Hz), 7.23−7.18 (m, 1 H), 6.47 (d, 1 H, J = 16.2 Hz), 6.29 (dt, 1 H, J = 16.2, 7.1 Hz), 5.34 (m, 1 H), 4.60 (d, 2 H, J = 7.6 Hz), 3.23 (d, 2 H, J = 7.1 Hz), 1.75 (s, 3 H), 1.70 (s, 3 H); ^{13}C NMR (75 MHz DEPT) δ 171.4 (4°), 139.0 (4°), 136.7 (4°), 133.2 (3°), 128.4 (3°), 127.4 (3°), 126.1 (3°), 121.7 (3°), 118.4 (3°), 61.5 (2°), 38.2 (2°), 25.6 (1°), 17.8 (1°). Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.16; H, 7.83.

2-Propenyl (*E*)-2-Diazo-4-phenyl-3-butenoate (2g). General Procedure. A solution of DBU (2.25 g, 14.8 mmol) in CH_3CN (10 mL) was added via cannula to a mixture of 2-propenyl (*E*)-4-phenyl-3-butenoate (2.5 g, 12 mmol) and *p*-ABSA (3.11 g, 12.9 mmol) in CH_3CN (40 mL) at 0 °C. The resulting red mixture was stirred 4 h, and then saturated NH_4Cl was added. The organics were extracted using Et_2O and then concentrated under reduced pressure. The resulting solid was triturated (petroleum ether/Et_2O, 1:1) and the solid removed by filtration (Celite, vacuum). The resulting filtrate was concentrated under reduced pressure to give a red oil. Purification by silica gel column chromatography (pentane/Et_2O, 1:1, R_f = 0.55) gave 2.15 g (76%) of 2-propenyl (*E*)-2-diazo-4-phenyl-3-butenoate as a red oil: IR (neat) 3023, 2098, 1700 cm^{-1}; ^{1}H NMR (500 MHz) δ 7.36−7.27 (m, 4 H), 7.21−7.16 (m, 1 H), 6.47 (d, 1 H, J = 16.0 Hz), 6.19 (d, 1 H, J = 16.0 Hz), 5.95 (ddt, 1 H, 17.5, 10.5, 6.0 Hz), 5.34 (dd, 1 H, J = 17.5, 2.0 Hz), 5.26 (dd, 1 H, J = 10.5, 2.0 Hz), 4.74 (d, 2 H, 6.0 Hz). The spectral data were consistent with published results.[32] The vinyldiazoacetates are generally not of sufficient stability to obtain elemental analysis.

(1*β*,5*α*,6*β*)-6-Methyl-1-(2-phenylethenyl)-3-oxabicyclo-[3.1.0]hexan-2-one (3a). General Procedure. A solution of **2a** (212.3 mg, 0.8762 mmol) in hexane (15 mL) was added via cannula to a solution of **1** (25 mg, 1.3 × 10−2 mmol) in hexane (15 mL) at −78 °C. The mixture was stirred cold 24 h then slowly warmed to RT (room temperature). The mixture was concentrated under reduced pressure. Purification by silica gel column chromatography (petroleum ether/Et_2O, 1:1, R_f = 0.30) gave 101.0 mg (54%) of **3a** as a white solid (mp 66−71 °C), 25% ee (determined by HPLC: OD column, 10% i-Pr−OH in hexanes, 1.0 mL/min; t_R = 13.5 min (major), 16.8 min (minor)). $[\alpha]^{25}_D$ = 71° (*c* 4.24, $CHCl_3$). Reaction at RT, 18% ee. IR (KBr): 3058, 2991, 2960, 1760 cm^{-1}. ^{1}H NMR (500 MHz): δ 7.39 (d, 2 H, J = 7.5 Hz), 7.13 (dd, 2 H, J = 7.5, 7.5 Hz), 7.25−7.22 (m, 1 H), 6.60 (d, 1 H, J = 16.5 Hz), 6.39 (d, 1 H, J = 16.5 Hz), 4.31 (dd, 1 H, J = 9.0, 4.5 Hz), 4.26 (d, 1 H, J = 9.0 Hz), 2.19 (dd, 1 H, J = 4.5, 4.5 Hz), 1.49 (dq, 1 H, J = 6.0, 4.5 Hz), 1.16 (d, 3 H, J = 6.0 Hz). ^{13}C NMR (75 MHz DEPT): δ 176.2 (4°), 136.4 (4°), 133.4 (3°), 128.6 (3°), 127.7 (3°), 126.2 (3°), 119.1 (3°), 68.0 (2°), 34.1 (4°), 29.5 (3°), 27.6 (3°), 12.0 (1°). MS [*m*/*z* (relative intensity)]: 214 (82), 157 (63), 155 (49), 141 (84), 129 (98), 115 (100), 91 (51), 77 (47), 63 (29), 51 (37). HRMS calcd for $C_{14}H_{14}O_2$, 214.0994, found 214.0998.

(2*Z*,4*E*)-2,4-Hexadienyl (*E*)-4-Phenyl-3-butenoate. General Procedure. A solution of DCC in CH_2Cl_2 (1.0 M, 5.4 mL, 5.4 mmol) was added dropwise via syringe to a mixture of (2*Z*,4*E*)-2,4-hexadien-1-ol (0.50 g, 0.0051 mol), (*E*)-4-phenyl-3-butenoic acid (0.86 g, 0.0053 mol), and DMAP (60 mg, 0.49 mmol) in CH_2Cl_2 (6 mL) at 0 °C. The mixture was stirred 8 h, and then saturated $NaHCO_3$ and Et_2O were added. The mixture was filtered (paper, vacuum), and the filtrate was extracted using Et_2O. The organic layer was concentrated under reduced pressure to give a yellow oil. Purification by silica gel column chromatography (petroleum ether/Et_2O, 10:1, R_f = 0.33) gave 1.02 g (83%) of (2*Z*,4*E*)-2,4-hexadienyl (*E*)-4-phenyl-3-butenoate as a clear, yellow-tinted oil: IR (neat) 3029, 2912, 1731, 1655 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.45−7.27 (m, 4 H), 7.25−7.19 (m, 1 H), 6.49 (d, 1 H, J = 16.2 Hz), 6.34−6.27 (m, 2 H), 6.17 (dd, 1 H, J = 11.1, 10.5 Hz), 5.82 (dq, 1 H, J = 14.6, 6.9 Hz), 5.44 (dt, 1 H, J = 10.5, 7.2), 4.79 (d, 2 H, J = 6.9 Hz), 3.26 (d, 2 H, J = 7.2 Hz), 1.80 (d, 3 H, J = 6.9 Hz); ^{13}C NMR (75 MHz DEPT) δ 171.3 (4°), 136.7 (4°), 133.3 (3°), 133.2 (3°), 132.8 (3°), 128.4 (3°), 127.4 (3°), 126.1 (3°), 125.9 (3°), 121.5 (3°), 121.2 (3°), 60.6 (2°), 38.2 (2°), 18.7 (1°). Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.21; H, 7.54.

(2*Z*,4*E*)-2,4-Hexadienyl (*E*)-2-Diazo-4-phenyl-3-butenoate (5a). General Procedure. A solution of DBU (0.77 g, 0.0051 mol) in CH_3CN (20 mL) was added via syringe to a mixture of (2*Z*,4*E*)-2,4-hexadienyl (*E*)-4-phenyl-3-butenoate (1.02 g, 0.00421 mol) and *p*-ABSA (1.06 g, 0.00442 mol) in CH_3CN (40 mL) at 0 °C. The resulting orange mixture was stirred 12 h, and then saturated NH_4Cl was added. The organics were extracted using Et_2O, and then the organics were concentrated under reduced pressure to give an orange oil. This gum was triturated (petroleum ether/Et_2O, 1:1) and filtered (Celite, vacuum). The filtrate was concentrated under reduced pressure to give an orange oil. Purification by silica gel column chromatography (petroleum ether/Et_2O, 10:1, R_f = 0.29) gave 0.742 g (66%) of **5a** as a viscous, orange oil: IR (neat) 3023, 2962, 2077, 1701, 1630 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.36−7.27 (m, 4 H), 7.21−7.15 (1 H), 6.47 (d, 1 H, J = 16.0 Hz), 6.38 (dd, 1 H, J = 14.8, 11.1 Hz), 6.17 (d, 1 H, J = 16.0 Hz), 6.16 (dd, 1 H, J = 11.1, 10.8 Hz), 5.81 (dq, 1 H, J = 14.8, 6.8 Hz), 5.41 (dt, 1 H, J = 10.8, 7.6 Hz), 4.88 (d, 2 H, J = 7.6 Hz), 1.80 (d, 1 H, J = 6.8 Hz); ^{13}C NMR (75 MHz DEPT) δ 165.1 (4°), 136.8 (4°), 133.5 (3°), 133.2 (3°), 128.6 (3°), 127.0

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(3°), 125.9 (3°), 125.8 (3°), 122.9 (3°), 121.0 (3°), 111.3 (3°), 61.1 (2°), 18.3 1°).

(1*β*,5α,6α)-6-((*E*)-Propenyl)-1-(2-phenylethenyl)-3-oxabicyclo[3.1.0]hexan-2-one (8a). General Procedure. A solution of **5a** (151 mg, 0.562 mmol) in hexane (50 mL) was added over 1 h via cannula to a mixture of **1** (13.0 mg, 0.69 × 10^{-2} mmol) in hexane (50 mL) at RT. The mixture was stirred 1 h, and then toluene (ca. 2 mL) was added and the mixture concentrated to ca. 2 mL volume under reduced pressure. Purification by silica gel column chromatography (petroleum ether/Et_2O, 3:1, R_f = 0.23) gave 105.3 mg (78%) of **8a** as a clear gum, 62% ee (determined by HPLC: OD column, 10% i-Pr−OH in hexanes, 1 mL/min; t_R = 14.0 min (major), 16.2 min (minor)). Enantioselectivites at other temperatures: 0 °C, 73% ee (52% yield) $[\alpha]^{25}_D$ = 15° (*c* 3.75, $CHCl_3$); −40 °C, 78% ee (39% yield); −78 °C, 85% ee (29% yield). IR (neat): 3027, 2965, 2903, 1755 cm^{-1}. ^1H NMR (500 MHz): δ 7.34 (d, 2 H, *J* = 7.5 Hz), 7.29 (dd, 2 H, *J* = 8.0, 7.5 Hz), 7.31−7.19 (m, 1 H), 6.53 (d, 1 H, *J* = 16.5 Hz), 6.43 (d, 1 H, *J* = 16.5 Hz), 5.88 (dq, 1 H, *J* = 15.0, 6.5 Hz), 5.19 (ddq, 1 H, *J* = 15.0, 8.5, 1.5 Hz), 4.45 (dd, 1 H, *J* = 10.0, 5.5 Hz), 4.25 (d, 1 H, *J* = 10.0 Hz), 2.66 (dd, 1 H, *J* = 8.0, 5.0 Hz), 2.28 (dd, 1 H, *J* = 8.5, 8.0 Hz), 1.72 (dd, 3 H, *J* = 6.5, 1.5 Hz). ^{13}C NMR (75 MHz DEPT): δ 173.8 (4°), 136.4 (4°), 132.7 (3°), 130.0 (3°), 128.6 (3°), 127.7 (3°), 126.2 (3°), 123.2 (3°), 121.1 (3°), 65.12 (2°), 36.03 (4°), 35.7 (3°), 31.0 (3°), 18.3 (1°). HRMS calcd for $C_{16}H_{16}O_2$, 240.1150, found 240.1152.

(3aα,6α,7α)]-3,3a,6,7-Tetrahydro-6-methyl-7-phenyl-1*H*-cyclohepta[*c*]-furan-1-one (6a). General Procedure. Thermolysis. A solution of **8a** (58.8 mg, 0.240 mmol (73% ee)) in *o*-xylene (2 mL) was heated to 140 °C for 20 min. The mixture was cooled to RT, and then charcoal and pentane (2 mL) were added. The mixture was stirred 10 min and then filtered (florisil, Celite). The filtrate was concentrated under reduced pressure and then dried in vacuo to give 54.3 mg (92%) of **6a** as a white solid (mp 85−94 °C), 73% ee (determined by HPLC: OD column, 10% i-Pr−OH in hexanes, 1.0 mL/min; t_R = 13.4 min (major), 19.4 min (minor)): $[\alpha]^{25}_D$ = −110° (*c* 2.50, $CHCl_3$); ^1H NMR (500 MHz) δ 7.29−7.23 (m, 3 H), 7.16 (dd, 2 H, *J* = 7.5, 1.5 Hz), 6.92 (dd, 1 H, *J* = 4.5, 3.5 Hz), 5.68 (br d, 1 H, *J* = 9.5 Hz), 5.36 (ddd, 1 H, *J* = 9.5, 6.0, 2.5 Hz), 4.66 (dd, 1 H, *J* = 9.5, 9.0 Hz), 4.22 (m, 1 H), 4.09 (dd, 1 H, *J* = 9.0, 9.0 Hz), 3.68 (m, 1 H), 3.16 (m, 1 H), 0.99 (d, 3 H, *J* = 7.0 Hz); consistent with published results.[26]

Direct Synthesis. A solution of **4a** (258.0 mg, 0.9616 mmol) in hexane (25 mL) was added dropwise over 20 min to a mixture of **1** (27.2 mg, 1.44 × 10^{-2} mmol) in hexane (25 mL) at RT. Toluene (ca. 1 mL) and CH_2Cl_2 (ca. 5 mL) were added, and the mixture was concentrated to ca. 3 mL volume under reduced pressure. Purification by silica gel column chromatography (petroleum ether/Et_2O, 1:1, R_f = 0.15) gave 170.4 mg (74%) of **6a** as a white solid, 24% ee (determined by HPLC: OD column, 10% i-Pr−OH in hexanes, 1.0 mL/min; t_R = 13.7 min (major), 18.6 min (minor)).

(1*S*,2*S*)-(*Z*)-4-Methyl-2,4-pentadienyl 2*β*-Phenyl-1*β*-((*E*)-2-phenylethenyl)cyclopropane-1α-carboxylate (12). A cooled (0 °C) solution of **5c** (130.3 mg, 0.485 mmol) in hexane (30 mL) was added dropwise via cannula over 45 min to a mixture of **1** (18 mg, 9.5 × 10^{-3} mmol) and styrene (0.56 mL, 4.8 mmol) in hexane (25 mL) at 0 °C. The mixture was warmed to RT and then was concentrated to ca. 1 mL volume under reduced pressure to give a green oil. Purification by silica gel column chromatography (petroleum ether/Et_2O, 10:1 (300 mL) and then petroleum ether/Et_2O, 2:1, R_f = 0.35 (petroleum ether/Et_2O, 10:1)) gave 72.5 mg (44%) of **12** as a gum (9.1 mg of **8c** (8% yield) was also isolated from this reaction): IR (neat) 3032, 2970, 1718, 1604 cm^{-1}; ^1H NMR (300 MHz) δ 7.35−7.15 (m, 10 H), 6.39 (d, 1 H, *J* = 16.2 Hz), 6.17 (d, 1 H, *J* = 16.2 Hz), 6.07 (br d, 1 H, *J* = 11.7 Hz), 5.61 (dt, 1 H, *J* = 11.7, 6.3 Hz), 5.08 (br s, 1 H), 4.92 (m, 2 H), 4.85 (br s, 1 H), 3.04 (dd, 1 H, *J* = 9.0, 7.5 Hz), 2.06 (dd, 1 H, *J* = 9.0, 5.0 Hz), 1.90 (s, 3 H), 1.85 (dd, 1 H, *J* = 7.5, 5.0 Hz); ^{13}C NMR (75 MHz DEPT) δ 173.5 (4°), 140.6 (4°), 137.1 (4°), 135.5 (4°), 134.7 (3°), 132.9 (3°), 129.1 (3°), 128.3 (3°), 128.0 (3°), 127.3 (3°), 126.8 (3°), 126.2 (3°), 124.9 (3°), 124.1 (3°), 117.1 (2°), 62.2 (2°), 35.0 (3°), 33.3 (4°), 22.8 (1°), 18.5 (2°). HRMS calcd for $C_{18}H_{15}O_2$ (M − C_6H_9), 263.1072, found 263.1080. HRMS calcd for C_6H_9 (M − $C_{18}H_{15}O_2$), 81.0704, found 81.0710.

(1*S*,2*S*)-Methyl 2*β*-Phenyl-1*β*-((*E*)-2-phenylethenyl)-cyclopropane-1α-carboxylate (13).[9,14] A solution of **12** (55.3 mg, 0.161 mmol) in anhydrous methanol (1.0 mL) was added to a mixture of sodium methoxide (69.4 mg, 1.28 mmol) in anhydrous methanol (1.0 mL) at 0 °C. The mixture was stirred 4 h, and then saturated NH_4Cl was added. The organics were extracted using Et_2O, and the organic layer was concentrated under reduced pressure to give a wet oil. Purification by silica gel column chromatography (petroleum ether/Et_2O, 10:1, R_f = 0.23) gave 40.2 mg (90%) of **13**[9,14] as a white solid (mp 72−76 °C), 93% ee (determined by HPLC: OJ column, 1.5% i-Pr−OH in hexanes, 1.0 mL/min; t_R = 18.1 min (major), 24.8 min (minor)).

(−)-(*R*)-Phenylsuccinic Acid (*R*-11).[35] A mixture of **6b** (391.1 mg, 1.728 mmol, ca. 56% ee) in anhydrous methanol (30 mL) was purged with ozone for 20 min. The resulting deep-blue mixture was purged with oxygen until the color had dissipated. The mixture was warmed to RT and then was concentrated under reduced pressure. Formic acid (3.0 mL) was added and the mixture cooled. Hydrogen peroxide solution (1.5 mL, 26 mmol, 30% solution in water) was added and the mixture stirred 2 h at RT. The mixture was heated to reflux for 1 h. Additional formic acid (2 mL) was added and the mixture heated to reflux until a peroxide test (water/AcOH/NaI) was negative. The mixture was cooled to RT, and water (4 mL) was added. The organics were extracted using EtOAc and then were concentrated under reduced pressure. The resulting oil was dried in vacuo to give a gum. This gum was triturated using $CHCl_3$ and pentane to give a white solid. Solvent was removed by pipet and the solid dried in vacuo to give 10.9 mg (10%) of (−)-*R*-**11** as a white solid (mp 153−157 °C). $[\alpha]^{25}_D$ = −112° ± 1 (*c* 0.545, acetone) (lit. value, *S* isomer: $[\alpha]^{25}_D$ = +171.4° ± 1 (*c* 1.0, acetone)).[35]

(+)-(*S*)-Phenylsuccinic acid ((+)-*S*-11).[35] Using the above procedure and **10** (279 mg, 1.16 mmol, ca. 50% ee), 46.1 mg (21%) of (+)-*S*-**11** was obtained as a tan solid (mp 138−140 °C). $[\alpha]^{25}_D$ = 58° ± 1 (*c* 1.45, acetone) (lit. value, *S* isomer: $[\alpha]^{25}_D$ = +171.4° ± 1 (*c* 1.0, acetone)).[35]

4,4-Dimethyl-1-cyclopentylacetic acid (17). A mixture of **16** (4.28 g, 0.0254 mol) in a methanol/water solution (3:1, 11 mL) was added to a mixture of anhydrous $LiOH·H_2O$ (2.13 g, 0.0509 mol) in a methanol/water solution (3:1, 31 mL) cooled to 0 °C. The mixture was stirred 14 h and then was diluted with water (60 mL). The mixture was rinsed with CH_2Cl_2 (20 mL), and the organic layer was discarded. The aqueous solution was acidified to pH 2 using HCl solution (1.0 M, 54 mL). The organics were extracted using Et_2O and then were dried (Na_2SO_4). The organic layer was concentrated under reduced pressure then dried in vacuo to give 3.78 g (96%) of **17** as an amber oil: IR (neat) 3142 (br), 1708 cm^{-1}; ^1H NMR (300 MHz) δ 10.45−10.10 (br s, 1H), 5.40 (s, 1 H), 3.06 (s, 2 H), 2.12 (br s, 4 H), 1.05 (s, 6 H); ^{13}C NMR (75 MHz) δ 178.6, 135.2, 128.0, 50.4, 48.0, 39.1, 37.5, 30.1, 28.5. Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.16; H, 9.20.

(2*E*,4*E*)-2,4-Hexadienyl 4,4-Dimethyl-1-cyclopentenylacetate (19a). Method A. Purification by silica gel column chromatography (petroleum ether/Et_2O, 4:1, R_f = 0.53) gave 2.97 g (82%) of **19a** as a clear, colorless oil: IR (neat) 2939, 1742 cm^{-1}; ^1H NMR (300 MHz) δ 6.22 (dd, 1 H, *J* = 15.2, 10.4 Hz), 6.02 (dd, 1 H, *J* = 15.0, 10.4 Hz), 5.72 (dq, 1 H, *J* = 14.9, 6.8 Hz), 5.59 (dt, 1 H, *J* = 15.2, 6.6 Hz), 5.38 (s, 1 H) 4.55 (d, 2 H, *J* = 6.8 Hz), 3.05 (s, 2 H), 2.10 (br s, 4 H), 1.72 (d, 3 H, *J* = 6.6 Hz), 1.04 (s, 6 H); ^{13}C NMR (75 MHz APT) δ 171.1 (4°), 135.2 (4°), 134.9 (3°), 131.0 (3°), 130.6 (3°), 126.9 (3°), 123.9 (3°), 64.7 (2°), 49.9 (2°), 47.5 (2°), 38.5 (4°), 37.0 (2°), 29.5 (1°), 17.7 (1°). Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.75; H, 9.43.

(2*Z*,4*E*)-2,4-Hexadienyl 4,4-Dimethyl-1-cyclopentenylacetate (19b). Method B. Purification by silica gel column

(35) Krause, H.; Sailer, C. *J. Organomet. Chem.* **1992**, *423*, 271.

chromatography (petroleum ether/Et_2O, 10:1, $R_f = 0.51$) gave 550 mg (90%) of **19b** as a clear, colorless oil: IR (neat) 2950, 1749 cm^{-1}; ^1H NMR (300 MHz) δ 6.3 (dd, 1 H, $J = 13.8, 11.1$ Hz), 6.15 (dd, 1 H, $J = 11.1, 10.6$ Hz), 5.81 (dq, 1 H, $J = 13.8, 6.6$ Hz), 5.42 (s, 1 H), 5.40 (dt, 1 H, $J = 10.6, 7.1$ Hz), 4.73 (d, 2 H, $J = 7.1$ Hz), 3.09 (s, 2 H), 2.14 (br s, 4 H), 1.80 (d, 3 H, $J = 6.6$), 1.08 (s, 6 H); ^{13}C NMR (75 MHz APT) δ 171.6 (4°), 135.3 (4°), 133.3 (3°), 132.8 (3°), 127.1 (3°), 126.3 (3°), 121.6 (3°), 60.4 (2°), 50.0 (2°), 47.6 (2°), 38.6 (4°), 37.1 (2°), 29.6 (1°), 18.0 (1°). Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.83; H, 9.51.

(2*E*,4*E*)-2,4-Hexadienyl 4,4-Dimethyl-1-cyclopentenyl-1-diazoacetate (15a). A solution of DBU (5.8 g, 0.038 mol) in CH_3CN (20 mL) was added via cannula to a mixture of *p*-ABSA (3.66 g, 0.0150 mol) and **19a** (2.97 g, 0.0126 mol) in CH_3CN (30 mL). The mixture was warmed to 40 °C for 4 h, and then the mixture was cooled to 0 °C. Saturated NH_4Cl was added, and then the organics were extracted using Et_2O. The organic layer was concentrated under reduced pressure, and the resulting oil was triturated (petroleum ether/Et_2O, 1:1), and then the solution was decanted away from the solid. This solution was concentrated under reduced pressure to give an orange oil. Purification by silica gel column chromatography (petroleum ether/Et_2O, 30:1, $R_f = 0.24$) gave 1.8 g (55%) of **15a** as an orange oil: IR (neat) 2955. 2076, 1709 cm^{-1}; ^1H NMR (300 MHz) δ 6.22 (dd, 1 H, $J = 15.4, 10.4$ Hz), 6.02 (dd, 1 H, $J = 15.0, 10.4$ Hz), 5.76 (s, 1 H), 5.73 (dq, 1 H, $J = 15.0, 6.6$ Hz), 5.60 (dt, 1 H, $J = 15.4, 6.6$ Hz), 4.66 (d, 2 H, $J = 6.6$ Hz), 2.25 (br s, 4 H), 1.72 (d, 3 H, $J = 6.6$ Hz), 1.07 (s, 6 H); ^{13}C NMR (75 MHz APT) δ 165.6 (4°), 135.0 (3°), 131.0 (3°), 130.6 (3°), 123.8 (3°), 123.1 (3°), 122.9 (4°), 65.0 (2°), 48.7 (2°), 48.3 (2°), 37.8 (4°), 29.4 (1°), 17.8 (1°) (C=N_2 signal missing).

(2*Z*,4*E*)-2,4-Hexadienyl 4,4-Dimethyl-1-cyclopentenyl-1-diazoacetate (15b). A solution of DBU (1.15 g, 7.56 mmol) in CH_3CN (2 mL) was added via cannula to a mixture of **19b** (590 mg, 2.52 mmol) and *p*-ABSA (730 mg, 3.04 mmol) in CH_3CN (8 mL). The mixture was warmed to 40 °C for 4 h, and then the mixture was cooled to 0 °C. Saturated NH_4Cl was added, and then the organics were extracted using Et_2O. The mixture was concentrated under reduced pressure, the resulting oil was triturated (petroleum ether/Et_2O, 1:1), and then the solution was decanted away from the solid. This solution was concentrated under reduced pressure to give an orange oil. Purification by silica gel column chromatography (petroleum ether/Et_2O, 30:1, $R_f = 0.33$) gave 291.4 mg (45%) of **15b** as an orange oil: IR (neat) 2955, 2080, 1699 cm^{-1}; ^1H NMR (300 MHz) δ 6.32 (dd, 1 H, $J = 13.7, 11.0$ Hz), 6.11 (dd, 1 H, $J = 11.0, 11.0$ Hz), 5.77 (dq, 1 H, $J = 13.7, 6.6$ Hz), 5.76 (s, 1 H), 5.37 (dt, 1 H, $J = 11.0, 7.2$ Hz), 4.81 (d, 2 H, $J = 7.2$ Hz), 2.25 (br s, 4 H), 1.76 (d, 3 H, $J = 6.6$ Hz), 1.08 (s, 6 H); ^{13}C NMR (75 MHz) δ 165.6, 133.2, 132.7, 126.2, 123.0, 122.8, 121.5, 60.4, 48.6, 48.2, 37.6, 29.3, 17.9 (C=N_2 signal missing).

(1β,5α,6α)-6-((*E*)-Propenyl)-1-(4,4-dimethyl-1-pentenyl)-3-oxabicyclo[3.1.0]hexan-2-one (21). A cold (−78 °C) solution of **15b** (109.2 mg, 0.419 mmol) in hexane (5 mL, dried over Na_2SO_4) was added via cannula to a solution of Rh_2(*R*-DOSP)$_4$ (18.9 mg, 0.0100 mmol) in hexane (5 mL) in a Kjeldahl flash (100 mL) at −78 °C. The mixture was stirred cold for 24 h and then slowly warmed to RT. Toluene (ca. 2 mL) was added and the mixture concentrated to ca. 1 mL volume under reduced pressure to give a green oil. Purification by silica gel column chromatography (petroleum ether/Et_2O, 4:1, $R_f = 0.32$) gave 63.1 mg (65%) of **21** as a clear, colorless oil, 93% ee (determined by thermolysis to **19** and then analysis by HPLC: OJ column, 0.5% i-Pr−OH in hexanes, 1.0 mL/min; t_R = 12.7 min (minor), 13.9 min (major)). $[\alpha]^{25}_D = 32°$ (*c* 3.155, $CHCl_3$). Enantioselectivites at other temperatures: RT, 47% ee (79% yield); 0 °C 59% ee; −20 °C, 63% ee; −40 °C, 77% ee. IR (neat): 2950, 2836, 1768 cm^{-1}. ^1H NMR (500 MHz) δ 5.84 (dq, 1 H, $J = 15.0, 6.5$ Hz), 5.71 (m, 1 H), 5.15 (ddq, 1 H, $J = 15.0, 8.5, 1.5$ Hz), 4.38 (dd, 1 H, $J = 9.5, 5.0$ Hz), 4.16 (d, 1 H, $J = 9.5$ Hz), 2.39 (dd, 1 H, $J = 7.0, 5.0$ Hz), 2.23 (dd, 1 H, $J = 8.5, 7.0$ Hz), 2.18 (dm, 1 H, $J = 15.0$ Hz), 2.18−2.16 (m, 2 H), 2.05 (dm, 1 H, $J = 15.0$ Hz), 1.70 (dd, 3 H, $J = 6.5, 1.5$ Hz). 1.07 (s, 3 H), 1.06 (s, 3 H). ^{13}C NMR (75 MHz DEPT): δ 174.0 (4°), 135.0 (4°), 132.0 (3°), 126.9 (3°), 121.5 (3°), 65.0 (2°), 48.0 (2°), 47.7 (2°), 38.2 (4°), 35.3 (4°), 30.8 (3°), 29.7 (1°), 29.7 (3°), 29.6 (1°), 18.2 (1°). HRMS calcd for $C_{15}H_{20}O_2$, 232.1463, found 232.1466.

(3aα,6β,6aα)]-6,8,8-Trimethyl-3a,6,6a,7,8,9-hexahydroazuleno[4,5-*c*]furan-1(3*H*)-one (20). Thermolysis. A solution of **21** (62.8 mg, 0.272 mg) in *o*-xylene (2 mL) was heated to 140 °C for 45 min. The mixture was cooled to RT, and then charcoal and pentane (2 mL) were added. The mixture was stirred 10 min and then filtered (florisil, Celite). The filtrate was concentrated under reduced pressure then dried in vacuo to give a yellow gum. Purification by silica gel column chromatography (petroleum ether/Et_2O, 4:1, $R_f = 0.29$) gave 46.3 mg (73%) of **20** as a white solid (mp 96−100 °C), 93% ee (determined by HPLC: OJ column, 0.5% i-Pr−OH in hexanes, 1.0 mL/min; t_R = 12.7 min (minor), 13.9 min (major)): $[\alpha]^{25}_D = -220°$ (*c* 2.219, $CHCl_3$); IR (neat) 2949, 2870, 1751, 1683, 1468 cm^{-1}; ^1H NMR (500 MHz) δ 5.75 (ddd, 1 H, $J = 12.0, 7.0, 2.5$ Hz), 5.21 (dd, 1 H, $J = 12.0, 2.0$ Hz) Hz, 1H), 4.49 (dd, 1 H, $J = 9.5, 8.0$ Hz), 3.99 (m, 1 H), 3.77 (dd, 1 H, $J = 9.5, 8.0$ Hz), 3.38 (m, 1 H), 3.32 (d, 1 H, $J = 17.0$ Hz), 2.30 (m, 1 H), 2.08 (ddd, 1 H, $J = 17.0, 5.0, 2.5$ Hz), 1.62 (ddd, 1 H, $J = 13.0, 8.5, 2.0$ Hz), 1.46 (dd, 1 H, $J = 13.0, 10.0$ Hz), 1.16 (s, 3 H), 0.95 (d, 3 H, $J = 7.0$ Hz), 0.87 (s, 3 H); ^{13}C NMR (75 MHz APT) δ 170.9 (4°), 164.9 (4°), 137.0 (3°), 124.0 (3°), 120.4 (4°), 70.6 (2°), 47.4 (2°), 47.2 (3°), 43.0 (2°), 39.8 (3°), 39.4 (4°), 34.8 (3°), 28.7 (1°), 27.8 (1°), 15.8 (1°); MS *m*/*z* (relative intensity) 232 (34), 217 (100), 131 (27), 117 (25), 91 (36). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.46; H, 8.64.

Direct Synthesis. A solution of **15a** (90.8 mg, 0.349 mmol) in hexane (6 mL) was added to a mixture of (*ent*)-1 (6.6 mg, 3.5×10^{-3} mmol) in hexane (10 mL) at RT. The mixture was stirred 1 h, and then the mixture was concentrated under reduced pressure to give a green gum. Purification by silica gel column chromatography (petroleum ether/Et_2O, 4:1, R_f = 0.29) gave 56.2 mg (69%) of **20** as a white solid, 24% ee (determined by HPLC: OJ column, 0.5% i-Pr−OH in hexanes, 1.0 mL/min; t_R = 12.8 min (minor), 14.2 min (major)). Reactions at other temperatures: −20 °C, 33% ee (50% yield); −78 °C, 35% ee.

(+)-(3aα,6β,6aα)-6,8,8-Trimethyl-3a,4,5,6,6a,7,8,9-octahydroazuleno[4,5-*c*]furan-1(3*H*)one ((+)-*epi*-5-Tremulenolide A) ((+)-14). A solution of **20** (111 mg, 0.476 mmol, 87% ee) and chlorotris(triphenylphosphine)rhodium(I) (5.5 mg, 5.9 $\times 10^{-3}$ mmol) in EtOH (20 mL) was shaken under H_2 (35 psi) for 12 h. The mixture was then concentrated under reduced pressure to give a yellow solid. Purification by silica gel column chromatography (petroleum ether/Et_2O, 4:1, $R_f = 0.17$) gave 85 mg (76%) of (+)-**14** as a white solid (mp 101−103 °C): $[\alpha]^{25}_D = 25°$ (*c* 0.63, $CHCl_3$); IR (neat) 2950, 2870, 1751, 1683, 1468 cm^{-1}; ^1H NMR (500 MHz) δ 4.46 (dd, 1 H, $J = 9.5, 9.0$ Hz), 3.80 (dd, 1 H, $J = 9.0, 7.0$ Hz), 3.29 (dm, 1 H, $J = 17.0$ Hz), 3.10 (m, 1 H), 2.99 (dddd, 1 H, $J = 8.0, 2.4, 2.3, 1.9$ Hz), 2.06 (ddd, 1 H, $J = 17.5, 4.5, 3.0$ Hz), 1.94−1.85 (m, 2 H), 1.82−1.74 (m, 1 H), 1.62−1.52 (m, 2 H), 1.50−1.42 (m, 2 H), 1.12 (s, 3 H), 0.83 (d, 3 H, $J = 7.0$ Hz), 0.82 (s, 3 H); ^{13}C NMR (75 MHz APT) δ 171.1 (4°), 165.5 (4°), 121.8 (4°), 70.7 (2°), 50.5 (3°), 47.5 (2°), 44.1 (2°), 40.3 (3°), 38.1 (4°), 36.3 (2°), 31.4 (3°), 28.3 (1°), 26.9 (1°), 25.5 (2°), 11.9 (1°); MS *m*/*z* (relative intensity) 234 (12), 219 (100), 105 (14), 91 (19). Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.71; H, 9.41.

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Supporting Information Available: Experimental and spectral data for allyl and dienyl (*E*)-4-phenyl-3-butenoates, **2a**−**f**,**h**−**k**, **3b**−**k**, **5b**, **6b**, **6c**, **8b**, **8c**, **9**, **10**, **iii**, and **iv**. This material is available free of charge via the Internet at http://pubs.acs.org.

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