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Stereospecific Rearrangement of Optically Active Tertiary Allylic Epoxides To Give Optically Active Quaternary Aldehydes: Synthesis of α-Alkyl Amino Aldehydes and Acids

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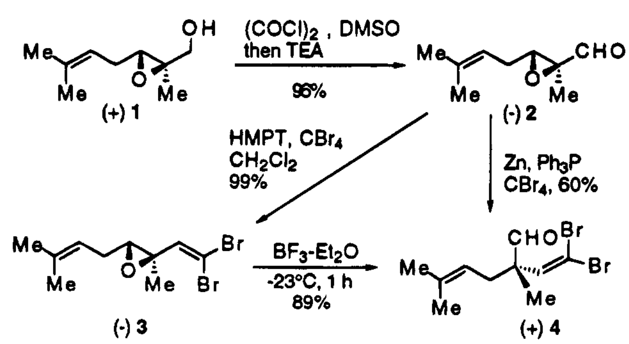
Abstract: 2-Methyl-2-vinyl-3-alkyloxiranes, readily obtained from Sharpless−Katsuki asymmetric epoxidation of allylic alcohols, undergo facile 1,2-alkyl migration with inversion of configuration leading to 2-methyl-2-vinylalkanals, thereby establishing an acyclic quaternary carbon in high yield and optical purity. The reaction conditions necessary for rearrangement are generally quite mild, e.g., $BF_3 \cdot OEt_2$ at −78 °C for 2 min, 5 M $LiClO_4$ in refluxing ether, anhydrous $Zn(OTf)_2$ or $ZnCl_2$, $EtAlCl_2$, silica gel, and sonication. As an application of this methodology, and to prove the stereochemical course of the process, the synthesis of (*S*)-(−)-α-methylphenylalanine [(+)-**16a**] is described. This methodology also permits access to optically active N-protected amino aldehydes [i.e., (−)-**15a** and (−)-**15b**], compounds which are difficult to make by other routes. The key step in each case is the rearrangement of (−)-**8a** or (−)-**8b** to give the quaternary aldehydes (+)-**9a** or (+)-**9b** in good yield and optical purity.

Background and Introduction

Acid-catalyzed reactions of cyclic and acyclic oxiranes enjoy a long history[3] from both synthetic and theoretical points of view.[4] Recent reports demonstrate that optically active epoxides can serve as chiral carbonyl synthons,[5] giving aldehydes and ketones in high yield with good enantioselectivity, including protected aldols. We now report that 2-methyl-2-vinyl-3-alkyloxiranes, readily derived from Sharpless−Katsuki[6] asymmetric epoxidation technology, undergo facile 1,2-alkyl migration, establishing a quaternary carbon in high yield and optical purity. As an application of this methodology, and to prove the stereochemistry course of the process, the synthesis of (*S*)-(−)-α-methylphenylalanine via the corresponding N-protected phenylalanal is described in detail.

Results and Discussion

In the course of a synthesis of the cytotoxic agent aplysiapyranoid A,[7] we required the dibromo olefin **3**, which could be prepared from the readily available epoxy alcohol **1**.[8] Swern oxidation of **1** gave the corresponding aldehyde **2** in 96% yield. Attempted Corey−Fuchs[9] homologation of this aldehyde **2** under conditions using zinc metal with triphenylphosphine and carbon tetrabromide gave not the expected olefin **3**, but rather the aldehyde **4** in good yield (60%). Presumably, the reaction proceeds via the intermediacy of the alkene **3**, but the zinc bromide formed in the reaction is a strong enough Lewis acid to cause the rearrangement of **3** into **4**, by coordination with the epoxide, assistance in the breakage of the tertiary C−O bond, and internal migration of the alkyl group to the cationic center. This mechanism is supported by the following facts. When the triphenylphosphine was replaced with the more reactive hexamethylphosphorus triamide (HMPT) and the zinc metal was omitted, the normal Corey−Fuchs reaction occurred to afford the dibromoalkene **3** in nearly quantitative yield.[10] Exposure of this alkene **3** to boron trifluoride etherate at −23 °C for 1 h then afforded the aldehyde **4** in 89% yield. Thus it is highly likely that **3** is an intermediate in the formation of **4** from **2** in the reaction using zinc metal. Thus one can obtain the optically active quaternary aldehyde in excellent yield in only two or three steps from the epoxy alcohol **1**.



Since there is a scarcity of methods for the preparation of optically active acyclic quaternary centers having extensive functionality, we decided to examine this rearrangement in more detail to determine its generality and applicability to novel

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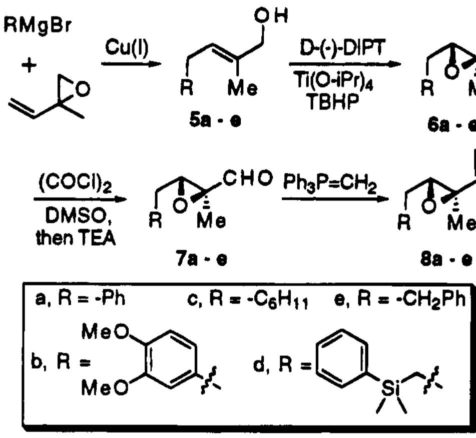
Table 1. Yields for the Preparation of Vinyloxiranes



	% **5** (*E*/*Z*)	% **6** (% ee)	% **7**	% **8**
a	79 (94/6)	93 (92)	82	96
b	68 (95/5)	98 (94)	96	87
c	68 (96/4)	67 (90)	97	97
d	88 (96/4)	91 (96)	84	79[a]
e	87 (95/5)	89 (96)	83	88

[a] Isolated 14% of rearranged aldehyde **9d**.

systems of synthetic and biological interest. The requisite *E*-allylic alcohols were prepared by an application of the chemistry of Normant,[11] namely by addition of a Grignard reagent to isoprene monoepoxide catalyzed by copper(I) salts (Table 1). In this way, the series of *E*-allylic alcohols **5a−e** were prepared in high yield (68−88%) and good stereochemical purity, normally 95% *E* or better. Epoxidation of these alcohols under the catalytic asymmetric epoxidation conditions of Sharpless,[6] using D-(−)-diisopropyl tartrate, yielded the desired optically active epoxy alcohols **6a−e** in generally excellent yield (67−98%) with only the phenethyl derivative **6c** being formed in significantly less than 90% yield. Since the minor *Z*-isomers are epoxidized at a much slower rate than the major *E*-isomers, one can effect a separation of the minor *Z*-isomers at this stage. As expected the optical purities of the alcohols (*R*,*R*) were also excellent, ranging from 90 to 96% ee. The enantiomeric excesses (ee's) were measured by integration of the peaks in the ^{31}P NMR spectra of the corresponding diastereomeric alkoxy tetrahydro-1,3,2-diazaphosphole derivatives of Alexakis[12] (prepared by reaction of the alcohols with the optically active octahydro-*N*,*N*,1,3-tetramethyl-2*H*-1,3,2-benzodiazaphosphol-2-amine). The racemic alcohols and their corresponding *O*-alkyl phosphonodiamidates were also prepared in order to guarantee the separation of the peaks in the ^{31}P NMR. Swern oxidation of the epoxy alcohols **6a−e** afforded the epoxy aldehydes **7a−e** in excellent yields (82−97%). Simple Wittig methylenation using methylenetriphenylphosphorane afforded the desired substrates **8a−e**, again in high yield (79−97%).

With the substrates **8a−e** for the rearrangement in hand, we examined various conditions to define more precisely the requirements for the rearrangement. We first realized that all

(10) Although we can find no references to the use of hexamethylphosphorous triamide with carbon tetrabromide in dibromomethylenation reactions, this reagent has been used with other tetrahalomethanes for dihalomethylenation of aldehydes and ketones. See: (a) Naae, D. G.; Burton, D. J. *Synth. Commun.* **1973**, *3*, 197. (b) Wheeler, T. N. *J. Org. Chem.* **1984**, *49*, 706. (c) Hoffmann, R. W.; Riemann, A.; Mayer, B. *Chem. Ber.* **1985**, *118*, 2493. (d) Verbrugge, P. A.; Kramer, P. A. Eur. Pat. Appl. 2849, 1979; *Chem. Abstr.* **1980**, *92*, P41431j.

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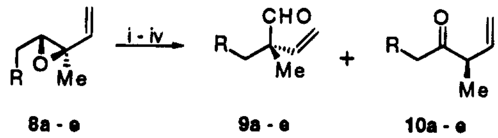
(12) All ee's were measured by the method of Alexakis. Alexakis, A; Mutti, S.; Normant, J. F.; Mangeney, P. *Tetrahedron Asym.* **1990**, *1*, 437. The ^{31}P NMR data is given in the experimental section.

Table 2. Isolated Yields of Carbonyl Compounds

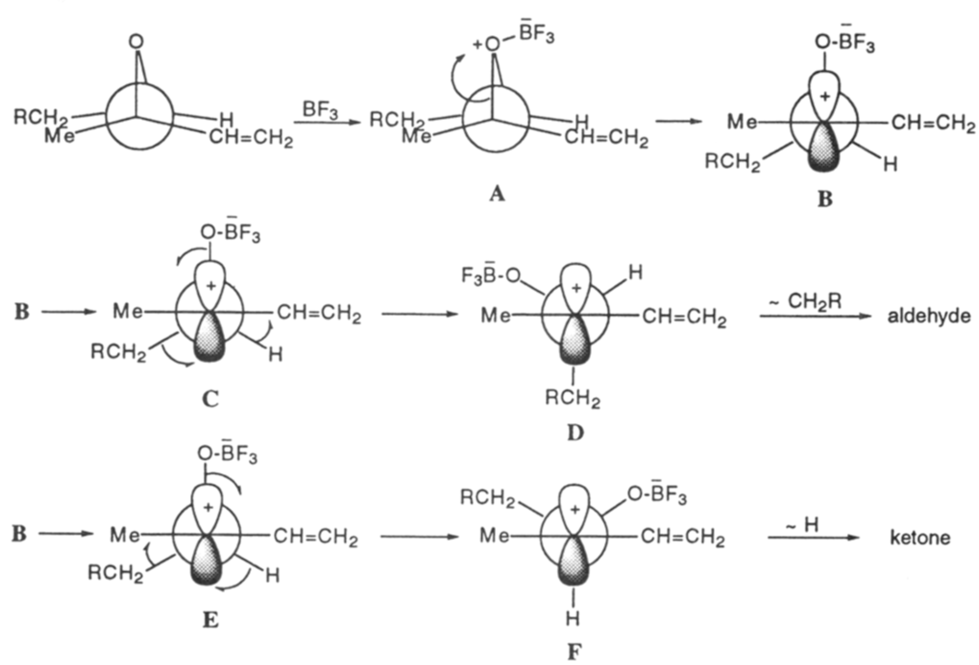


	conditions[a]	% **9**	% **10**
a	i	quant.	
b	i	51	
	ii	91	
c	i	53	
	iii	36	31
	iv	40	31
d	i	98	
e	i	26	21
	iv	30	48

[a] (iv) BF_3·Et_2O, −78 °C, 120 s. (ii) 5 M $LiClO_4$ in Et_2O, reflux. (iii) Et_2AlCl, CH_2Cl_2, −78 °C. (iv) SiO_2, sonication.

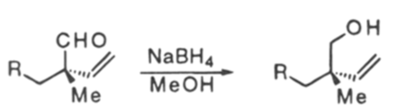
of the substrates rearranged under mild conditions, thereby demonstrating that the bromine atoms on the vinyl group (in compound **3**) are not necessary to effect rearrangement and that a simple vinyl group is sufficient. The reaction conditions necessary for rearrangement are generally quite mild, demonstrating the facile nature of the process. For example, the benzylic substrates **8a** rearranges when treated with boron trifluoride etherate at −78 °C for 2 min to give **9a** in quantitative yield. Likewise the silylethyl substrate **8d** also rearranges under the same conditions to give **9d** in 98% yield. These substrates are so prone to rearrangement that even simple silica gel chromatography of the epoxyalkenes causes some rearrangement, e.g., we isolate 14% of the aldehyde **9d** along with the epoxy alkene **8d** from the Wittig reaction of the silylethyl substrate **7d** (presumably during the silica gel chromatography). Not surprisingly, longer reaction times and higher temperatures led to lower isolated yields. While these conditions also work for other substrates, we have found that the yields are often much lower, e.g., the dimethoxybenzyl substrate **8b** gives 51% of the aldehyde **9b** while the cyclohexylmethyl substrate **8c** affords a similar yield of **9c** (53%) under these conditions. Rearrangement of the substituted benzyl system **8b** proved troublesome, presumably because of the increased propensity of the aryl ring to react with electrophiles. After screening other Lewis acids [anhydrous $Zn(OTf)_2$ and $ZnCl_2$ work as well], satisfactory results were obtained using 5 M $LiClO_4$ in refluxing ether. Attenuation of the ring reactivity may be due in part to chelation of the aryl methoxy groups by the lithium cation. Other Lewis acidic conditions were also tried for the cyclohexylmethyl system **8c**, e.g., diethylaluminum chloride in dichloromethane at −78 °C and sonication with silica gel, but these did not improve the yield of the desired aldehyde. However, with these catalysts, a new reaction pathway was observed, namely hydride migration to give the β,γ-unsaturated ketone **10c**, which was isolated in 31% yield in both cases. It is interesting to note that we isolate only the β,γ-unsaturated ketones from this and subsequent reactions without any evidence of isomerization to the presumably more stable α,β-unsaturated ketones. Also the ketones are isolated in optically active form, another indication that no isomerization of the α center occurred during this rearrangement. The phenethyl substrate was problematic under all reaction conditions. While a complete study of this rearrangement was not undertaken, we found that the standard conditions, boron trifluoride etherate at −78 °C for 2 min, gave 26% of the desired aldehyde **9e** and 21% of the β,γ-unsaturated ketone **10e**. Sonication of **8c** with silica gel afforded a higher yield of the aldehyde **9e** (40%) but also more of the ketone **10e**

Scheme 1



(31%) (Table 2). Thus the rearrangement works very well for epoxyalkenes bearing distal allylic, benzylic, and silylethyl substituents (>90%), but less well for those with simple alkyl substituents.

Again the enantiomeric excess was measured by ^{31}P NMR integration using the method of Alexakis.[12] For example, the aldehydes **9a** and **9d** were reduced to the primary alcohols **11a** and **11d** which were then derivatized using the optically active (dimethylamino)tetrahydro-1,3,2-diazaphosphole to give the alkoxytetrahydro-1,3,2-diazaphosphole derivatives. Integration of the peaks in the ^{31}P NMR spectra afforded the ee's, which were essentially the same (within experimental error) as the ee's of the starting epoxy alcohols, namely 90% ee for **11a** and 96% ee for **11d**. In the latter case, the alkyl phosphodiamidothioate



9a
9d

11a, 92%, 90%ee
11d, 61%, 96%ee

was prepared and analyzed by gas chromatography to ensure the accuracy of the analytical method. Also the enantiomeric series leading to (−)-**9a** was prepared from **5a** and L-(+)-DIPT. Reduction of both aldehydes with $NaBH_4$ gave alcohols (−)-**10** and (+)-**10** in 89.5 and 90.0% ee, respectively, implying that less than 2% of the stereochemical integrity was lost. Thus the rearrangement process is a stereospecific one. The absolute stereochemistry of the products could not be proven by this method, and thus, at this point, it was assumed that the rearrangement had proceeded with inversion of the tertiary epoxide carbon and the structures were based on this assumption. This assumption was shown later to be correct in the case of the phenyl-substituted case **9a** by comparison of the optical rotation of a derivative to the literature value, as described below.

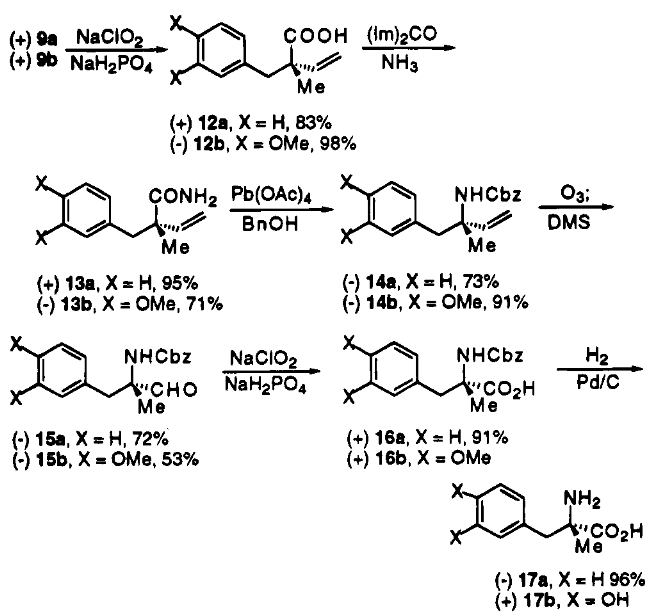
Mechanistic Rationale of Reaction Chemoselectivity. The predominant or, in some cases, complete formation of the product of alkyl group migration, namely the quaternary aldehyde, in preference to the product of hydride migration, namely the β,γ-unsaturated ketone, can be rationalized by examination of the likely mechanism for the transformation. Coordination of the epoxide oxygen with the Lewis acid, e.g., BF_3, would give the complex **A** (Scheme 1) which would then open by rupture of the tertiary C−O bond to relieve the ring strain of the epoxide ring and produce the tertiary allylic cation **B**. This relatively stable cation must then rotate to place either the alkyl group or the hydrogen atom on the oxygen-bearing carbon in the proper orientation for 1,2-shift, namely overlapping with the vacant p orbital on the adjacent carbon. Rotation in a clockwise motion as shown in **C** to align the alkyl group with the p orbital giving **D** requires the hydrogen to pass by the vinyl group, which causes a less serious eclipsing interaction than the alternative shown in **E**, namely the counterclockwise rotation to align the hydrogen atom with the p orbital to give **F**, a process which requires the alkyl group (in all cases a primary carbon chain CH_2R) to pass by the methyl group, thereby causing a more serious eclipsing interaction. Presumably this larger steric eclipsing interaction leading to **F** causes **D** to be formed predominantly, especially in those cases where the migration is favored (allylic, benzylic, or silylethyl groups). Only in the cases where the migratory aptitude of the group is somewhat lower (cyclohexylmethyl, phenethyl) does hydride migration (leading to ketone formation) compete effectively with alkyl migration (leading to aldehyde formation). Other examples of this principle of eclipsing interactions determining product formation have been shown before.[13]

Synthetic Applications and Stereochemical Course of the Reaction: Synthesis of α-Alkylamino Acids and Aldehydes. There are many possible applications of this rearrangement process for the formation of highly functionalized acyclic quaternary centers. We chose to examine only one such application, namely the production of amino acids with α-alkyl groups. These α-branched amino acids have been used extensively in peptide research in a variety of ways, e.g., as effectors of α-helix formation and as more stable analogues of

(13) One might also rationalize the chemoselectivity observed by simple migratory aptitude arguments, although hydrogen migration is often seen in preference to alkyl migration in acyclic cases which is the opposite of what is observed here. For a discussion, see ref 4, pp 742−743.

the natural amino acids.[14] In particular we chose to prepare α-methylphenylalanine **17a** and an analogue of the related dihydroxy derivative L-α-methyl-DOPA **17b** (this latter compound is a well-known antihypertensive agent sold under the name Aldomet).[15] By comparing the optical rotation of our synthetic derivatives with that of the known compounds, we would then also prove the assumption made earlier about the stereochemical course of the reaction, namely that it proceeds with inversion at the tertiary epoxide carbon. Therefore the syntheses of the two amino acids derivatives were undertaken.

The aldehydes (+)-**9a** and (+)-**9b** were oxidized to the acids (+)-**12a** and (−)-**12b** in good yield (83% and 98%, respectively) by the use of buffered sodium chlorite. However, we were unable to effect Curtius rearrangement of these acids to the corresponding isocyanates and their derived carbamates in high yield under various conditions. For example, reaction of **12a** with carbonyldiimidazole, followed by treatment with sodium azide, and heating in the presence of benzyl alcohol afforded 39% yield of the desired *N*-(carbobenzyloxy)carbamate **14a** along with several other unidentified products. This problem was circumvented by a little-used alternative to the traditional Curtius or Hoffmann rearrangement processes. Thus the acids **12ab** were converted (carbonyldiimidazole and ammonia, 96% and 71%, respectively) into the amides (+)-**13a** and (−)-**13b**, which in the presence of benzyl alcohol and lead tetraacetate[16] rearranged smoothly to the carbamates (−)-**14a** and (−)-**14b** in good yield (73% and 91%, respectively). Ozonolysis of the



alkene, followed by reductive workup, provided the protected amino aldehydes (−)-**15a** and (−)-**15b**. Although other methods of alkene cleavage were also investigated (e.g., $KMnO_4$, OsO_4) to give the protected amino acid (+)-**16a**, the best results were obtained by oxidizing (−)-**15a** with sodium chlorite to afford the protected amino acids in excellent yield (91%). Finally, hydrogenolysis with palladium on carbon effected deprotection of (+)-**16a** to give (*S*)-(−)-α-methylphenylalanine (−)-**17a**, the rotation of which matched the literature value,[17] indicating that chirality transfer had occurred with inversion of configuration. Thus our earlier assumption concerning the stereochemical course of the reaction was proven to be correct. We have thereby shown that this epoxide rearrangement can be used easily to produce compounds of biological importance.

Conclusion

Thus, we have demonstrated the efficiency and stereochemical course of the Lewis acid-catalyzed rearrangement of optically active tertiary allylic epoxides and provided an application to biologically relevant molecules. It should be pointed out that this methodology permits access to optically active quaternary N-protected amino aldehydes [i.e., (−)-**15a** and (−)-**15b**], compounds which are difficult to make by other routes.

Experimental Section

General. All temperatures and boiling points (bp) are uncorrected, and reactions were carried out under argon (Ar) with the exclusion of moisture. Dichloromethane (CH_2Cl_2), dimethylformamide (DMF), hexamethylphosphorous triamide (HMPT), dimethyl sulfoxide (DMSO), triethylamine (TEA), and diisopropylethylamine (DIPEA) were distilled from CaH_2. Tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl radical. Titanium(IV) tetraisopropoxide ($Ti(OiPr)_4$) was distilled under vacuum and stored frozen at −23 °C under nitrogen (N_2). Diisopropyl tartrate ((+)- or (−)-DIPT) was distilled under vacuum and stored in a desiccator. Commercial *tert*-butyl hydroperoxide (TBHP) was dried over 4 Å molecular sieves (pellet form) for 2 days at 0 °C and titrated. Boron trifluoride etherate ($BF_3{\cdot}Et_2O$) was stirred over CaH_2, distilled (67 °C at 43 mmHg) with an excess of diethyl ether (Et_2O), and stored at −23 °C under N_2. Chromatography was conducted on 230−400 mesh silica gel (SiO_2), using hexanes (Hex), ethyl acetate (EtOAc), and CH_2Cl_2 as solvents. In general, all reagents were purified, except potassium bis(trimethylsilyl)amide (KHMDS), which was used as supplied from Aldrich Chemical Co.

^1H and ^{13}C nuclear magnetic resonance (NMR) were recorded on a Bruker AM360, AM500, ARX400, or ARX500 with tetramethylsilane as external standard. Enantiomeric purity were determined by reacting the substrates (ca. 0.05−0.1 mmol) in a sealed NMR tube with 750 μL of a 10% C_6D_6 in benzene solution (0.22 M) of chiral phosphonamide for 1 day at 25 °C. The diastereomeric ^{31}P signals were then integrated and reported relative to 85% H_3PO_4 (0.00 ppm) as the external standard. Infrared (IR) spectra were recorded on a Nicolet 510 FT-IR, a Nicolet 205 FT-IR, or a Perkin-Elmer series 1600 spectrometer. Optical rotations were recorded on a Perkin-Elmer 243 polarimeter and were run at ambient temperature. High-resolution mass spectra (MS) were obtained on a VG Autospec at a resolution of 10 000 (10% valley) and are given for the molecular ion unless otherwise stated.

(2*R*,3*R*)-2-Methyl-3-(3-methyl-2-butenyl)oxiranemethanal ((−)-2). To oxalyl chloride (766.5 μL, 8.630 mmol) in 40 mL of dry CH_2Cl_2 at −78 °C was added DMSO (1.2 mL, 17.25 mmol) in 5 mL of CH_2Cl_2 over 10 min and an additional 50 min. Epoxy alcohol (+)-**1** (674.1 mg, 4.315 mmol) in 5 mL of CH_2Cl_2 was added over 20 min *via* syringe pump and reacted for 60 min. Finally, TEA (4.7 mL, 34.53 mmol) was added over 15 min, and the solution was allowed to warm to −30 °C over 60 min, at which time the solution was poured onto 200 mL of Et_2O and 50 mL of 0.05 M pH 7.0 phosphate buffer. The layers were separated, and the aqueous phase was extracted with Et_2O (4 × 25 mL). The combined organic layers were washed successively with H_2O (3 × 10 mL), 5% $NaHCO_3$ (2 × 25 mL), and brine (2 × 25 mL), dried over $MgSO_4$, concentrated, and distilled, yielding 640.0 mg of (−)-**2** as a liquid (4.15 mmol, 96%): ^1H NMR ($CDCl_3$, 500.132 MHz) δ 8.84 (1H, s), 5.13 (1H, tq, *J* = 5.85, 1.44 Hz), 3.14 (1H, t, *J* = 6.32 Hz), 2.49 (1H, m), 2.23 (1H, m), 1.73 (3H, d, *J* = 1.44 Hz), 1.65 (3H, s) and 1.42 (3H, s); ^{13}C NMR ($CDCl_3$, 50.323 MHz) δ 200.1, 135.8, 117.3, 62.3, 59.5, 27.2, 25.7, 18.0, and 10.0; IR (thin film) 2972.3 (s), 2925.0 (s), 2858.2 (m), 2813.9 (m), 2728.8 (w), 1727.3 (s), 1447.0 (s), 1385.4 (m), 1250.0 (w), 1078.4 (m), 1013.6 (w), 922.0 (w), 878.1 (s), and 847.7 (s) cm^{-1}; high-resolution EI MS *m/z* 154.0994, calcd for $C_9H_{14}O_2$ 154.0994; $[\alpha]^{25}_D$ −52.2° (*c* 0.985, CH_2Cl_2); bp 48−49 °C at 0.20 mmHg.

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(2*R*,3*R*)-2-(2,2-Dibromoethenyl)-2-methyl-3-(3-methyl-2-butenyl)-oxirane ((−)-3). Aldehyde (−)-**2** (92.3 mg, 0.598 mmol) and CBr_4 (595.5 mg, 1.796 mmol) were weighed into a dry, 100 mL flask and swept with Ar. Dichloromethane (8 mL) was added, and the solution cooled to −23 °C when HMPT (85% technical, 95 μL, 0.449 mmol) was added over 5 min. After 2 h, an additional 95 μL of HMPT was added, and stirring was continued 2 h, after which 5 mL of H_2O was added and the cooling bath removed. The mixture was partitioned between 10 mL of Et_2O and 5 mL of brine, the layers were separated, and the aqueous phase was extracted with Et_2O (3 × 3 mL). The combined organic extracts were washed with H_2O (2 × 2 mL) and brine (1 × 2 mL) and dried over $MgSO_4$. Removal of the solvent *in vacuo*, followed by chromatography (40 g of SiO_2, 10% EtOAc/90% Hex, R_f = 0.50), yielded 184.3 mg of (−)-**3** as an oil (0.594 mmol, 99%): ^{1}H NMR ($CDCl_3$, 360.130 MHz) δ 6.65 (1H, s), 5.17 (1H, dt, *J* = 5.85, 1.11 Hz), 2.94 (1H, t, *J* = 6.35 Hz), 2.28 (1H, m), 2.17 (1H, m), 1.66 (3H, d, *J* = 1.11 Hz), 1.59 (3H, s), and 1.37 (3H, s); ^{13}C NMR ($CDCl_3$, 90.560 MHz) δ 139.2, 134.6, 118.3, 91.7, 63.9, 61.1, 27.8, 25.7, 17.9, and 16.1; IR (thin film) 2967.6 (m), 2928.0 (s), 2882.4 (m), 2850.3 (m), 1455.5 (s), 1377.8 (s), 1254.0 (m), 1112.9 (w), 1077.6 (s), 934.5 (w), 920.4 (w), 887.0 (w), 813.7 (s), and 699.6 (m) cm^{-1}; $[\alpha]^{25}_D$ −47.1° (*c* 0.675, CH_2Cl_2).

(*S*)-2-(2,2-Dibromoethenyl)-2,5-dimethyl-4-hexenal ((+)-4). Method i. To a stirring suspension of Zn dust (146.6 mg, 2.243 mmol) and PPh_3 (589 mg, 2.243 mmol) in 4 mL of CH_2Cl_2 was added CBr_4 (743 mg, 2.243) in 1 mL of CH_2Cl_2 and stirred under Ar for 15 h at 25 °C. Aldehyde (−)-**2** (117.2 mg, 0.760 mmol) in 2.0 mL of CH_2Cl_2 was then added, and the reaction mixture stirred for 2 h. The solution was diluted to 10 mL with Hex, filtered through a pad of Celite, and concentrated. Chromatography (40 g of SiO_2, 5% EtOAc/95% Hex, R_f = 0.33) gave 140.8 mg of (+)-**4** (0.454 mmol, 60%).

Method ii. To a −23 °C solution of (−)-**3** (26.5 mg, 85.5 μmol) in 2.5 mL of CH_2Cl_2 was added $BF_3 \cdot Et_2O$ (11.0 μL, 89.4 μmol). After 60 min, the reaction mixture was diluted to 5 mL with Et_2O, and the reaction was quenched with 1.0 mL of 5% $NaHCO_3$. The aqueous layer was discarded, and the organic phase was washed with brine (1 × 2 mL) and dried over $MgSO_4$. Removal of solvent gave 23.7 mg of pure (+)-**4** as an oil (76.4 μmol, 89%): ^{1}H NMR ($CDCl_3$, 500.132 MHz) δ 9.15 (1H, s), 6.60 (1H, s), 4.98 (1H, tq, *J* = 7.30, 1.40 Hz), 2.35 (1H, dd, *J* = 14.50, 7.50 Hz), 2.26 (1H, dd, *J* = 14.50, 7.10 Hz), 1.65 (3H, d, *J* = 1.40 Hz), 1.55 (3H, s), and 1.21 (3H, s); ^{13}C NMR ($CDCl_3$, 90.560 MHz) δ 201.0, 139.6, 136.3, 117.2, 90.3, 54.4, 34.4, 26.0, 18.6, and 18.0; IR (thin film) 3020.0 (w), 2972.0 (m), 2930.9 (w), 2915.1 (w), 2873.0 (w), 2856.9 (w), 2808.3 (w), 2712.5 (w), 1731.0 (s), 1590.1 (w), 1455.6 (m), 1377.3 (m), and 810.5 (s) cm^{-1}; low-resolution MS *m/z* (rel intensity) 244 (14.9), 242 (30.4), 240 (16), and 69 (100); high-resolution EI MS *m/z* 306.9333, calcd for $C_{10}H_{13}{}^{79}Br_2O$ 306.9333 (M − H)$^+$; $[\alpha]^{25}_D$ +22.3° (*c* 0.99, CH_2Cl_2).

(*E*)-2-Methyl-4-phenyl-2-buten-1-ol (5a). Phenylmagnesium bromide (from 12.98 mmol of bromobenzene and 13.9 mmol of Mg in 12 mL of dry THF) was added *via* syringe pump over 30 min to a −23 °C of 2-methyl-2-vinyloxirane (Aldrich, 820.4 mg, 9.753 mmol) and CuBr (140 mg, 0.975 mmol) in 40 mL of THF. The solution was stirred for an additional 30 min when 20 mL of saturated NH_4Cl was added and the cooling bath was removed. Distilled water was added to dissolve the solids (ca. 10 mL), and the layers were separated. The aqueous layer was extracted with Et_2O (3 × 10 mL), and the combined organic layers were successively washed with 50% NH_4OH (2 × 5 mL), H_2O (1 × 5 mL), and brine (1 × 5 mL). The ether solution was dried over $MgSO_4$, concentrated, and distilled (96−98 °C at 0.80 mmHg), affording 1.2460 g of **5a** as a 94/6 mixture of *E/Z* isomers (7.728 mmol, 79%): ^{1}H NMR ($CDCl_3$, 500.132 MHz) δ 7.3−7.1 (5H, m), 5.57 (1H, tq, *J* = 7.39, 1.39 Hz), 4.00 (2H, s), 3.35 (2H, d, *J* = 7.31 Hz), 1.73 (3H, d, *J* = 1.36 Hz), and 1.40 (1H, br s); ^{13}C NMR ($CDCl_3$, 90.55 MHz) δ 140.9, 135.6, 128.4, 128.2, 125.9, 124.6, 68.6, 33.8, and 13.7; IR (thin film) 3332.3 (br s), 3083.6 (m), 3061.2 (m), 3026.4 (s), 2974.9 (m), 2914.5 (s), 2859.4 (s), 1602.0 (m), 1494.1 (s), 1453.2 (s), 1071.8 (m), 1029.0 (m), 1015.9 (s), 865.8 (w), 741.1 (s), and 698.0 (s) cm^{-1}; high-resolution EI MS *m/z* 162.1029, calcd for $C_{11}H_{14}O$ 162.1044.

(*E*)-4-(3,4-Dimethoxyphenyl)-2-methyl-2-buten-1-ol (5b). (3,4-Dimethoxyphenyl)magnesium bromide (from 29.37 mmol of veratryl bromide and 44.06 mmol of Mg in 25 mL of dry THF) was added over 3 h *via* syringe pump to a −42 °C solution of 2-methyl-2-vinyloxirane (2.45 mL, 25.00 mmol) and CuBr−DMS (514 mg, 2.50 mmol) in 100 mL of dry THF. The solution was allowed to reach 25 °C overnight and was quenched with 50 mL of saturated NH_4Cl. The mixture was poured onto 200 mL of Et_2O, and 20 mL of H_2O was added to dissolve the solids. The layers were separated, and the aqueous phase was extracted with Et_2O (3 × 40 mL). The combined organic layers were washed with 50% NH_4OH (3 × 25 mL) and brine (1 × 50 mL), dried over $MgSO_4$, and freed of solvent. Short-path distillation (129−158 °C at 0.06 mmHg), yielded 4.098 g of a 95/5 mixture of *E/Z* isomers. Chromatography (100 g of SiO_2, 20% EtOAc/CH_2Cl_2) afforded 3.7891 g of **5b** as a viscous liquid (17.046 mmol, 68%): ^{1}H NMR ($CDCl_3$, 500.132 MHz) δ 6.79 (1H, d, *J* = 8.04 Hz), 6.70 (2H, m), 5.60 (1H, tq, *J* = 7.19, 1.25 Hz), 4.05 (2H, br s), 3.86 (3H, s), 3.85 (3H, s), 3.34 (2H, d, *J* = 7.21 Hz), 1.78 (3H, s), and 1.40 (1H, br s); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ: 148.9, 147.3, 135.5, 133.6, 124.9, 120.0, 111.7, 111.3, 68.7, 55.9, 55.8, 33.5, and 13.8; IR (thin film) 3489.7 (br s), 2997.8 (s), 2936.0 (s), 2912.9 (s), 2835.7 (s), 1591.5 (m), 1515.3 (s), 1465.1 (m), 1416.9 (m), 1260.5 (s), 1230.5 (s), 1152.6 (s), 1138.2 (s), 1029.1 (m), and 764.9 (s) cm^{-1}; high-resolution EI MS *m/z* 222.1256, calcd for $C_{13}H_{18}O_3$ 222.1256.

(*E*)-4-Cyclohexyl-2-methyl-2-buten-1-ol (5c). As in the preparation of **5b**, cyclohexylmagnesium bromide (from 20.0 mmol of bromocyclohexane and 70.0 mmol of Mg in 20 mL of THF), CuBr−DMS (390 mg, 1.897 mmol), and 2-methyl-2-vinyloxirane (1.96 mL, 20.0 mmol) in 40 mL of THF afforded 2.3040 g of **5c** after distillation as a 96/4 mixture of *E/Z* isomers (90−92 °C at 0.41 mmHg, 13.69 mmol, 68%): ^{1}H NMR ($CDCl_3$, 500.132 MHz) δ 5.43 (1H, tq, *J* = 7.40, 1.31 Hz), 4.01 (2H, s), 1.92 (2H, t, *J* = 6.87 Hz), 1.75−1.60 (5H, m), 1.65 (3H, q, *J* = 1.31 Hz), 1.33 (1H, br s), 1.30−1.11 (4H, m), and 0.90 (2H, q, *J* = 11.3 Hz); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 135.0, 125.1, 69.0, 38.2, 35.3, 33.1, 26.4, 26.2, and 13.7; IR (thin film) 3320.9 (br, s), 2923.5 (s), 2853.1 (s), 1449.7 (s), 1387.0 (m), 1269.3 (w), 1226.9 (w), 1069.7 (m), 1012.8 (s), and 866.5 (m) cm^{-1}; high-resolution EI MS *m/z* 168.1510, calcd for $C_{11}H_{20}O$ 168.1510.

(*E*)-5-(Dimethylphenylsilyl)-2-methyl-2-penten-1-ol (5d). As in the preparation of **5b**, (dimethylphenylsilyl)methylmagnesium chloride (from 20.0 mmol of (chloromethyl)dimethylphenylsilane and 100.0 mmol of Mg in 40 mL of THF), 2-methyl-2-vinyloxirane (1.96 mL, 20.0 mmol), and CuBr−DMS (411 mg, 2.0 mmol) in 40 mL of THF yielded 4.1173 g of **5d** after distillation (128−130 °C at 0.67 mmHg, 17.56 mmol, 88%) as a 96/4 mixture of *E/Z* isomers: ^{1}H NMR ($CDCl_3$, 500.132 MHz) δ 7.51 (2H, m), 7.36 (3H, m), 6.37 (1H, tq, *J* = 7.11, 1.30 Hz), 3.92 (2H, s), 2.07 (2H, apparent q, *J* = 7.20 Hz), 1.59 (3H, d, *J* = 1.30 Hz), 0.84 (2H, m), and 0.28 (6H, s); ^{13}C NMR ($CDCl_3$, 125.785 MHz) δ: 139.3, 133.4, 133.2, 129.0, 128.7, 127.6, 68.9, 21.7, 15.6, 13.4, and −3.1; IR (thin film) 3333.4 (br, s), 3070.1 (m), 3050.8 (w), 2999.7 (w), 2955.3 (s), 2913.8 (s), 1427.5 (s), 1306.0 (w), 1248.1 (s), 1113.1 (s), 1011.8 (s), 915.3 (w), 834.3 (s), 769.7 (m), and 700.3 (s) cm^{-1}; high-resolution CI (NH_3) MS *m/z* 234.1432, calcd for $C_{14}H_{22}OSi$ 234.1440; 233.1358, calcd for $C_{14}H_{21}OSi$ 233.1362 (M − H)$^+$.

(*E*)-2-Methyl-5-phenyl-2-penten-1-ol (5e). As in the preparation of **5b**, benzylmagnesium chloride (from 20.0 mmol of benzyl chloride and 100.0 mmol of Mg in 20 mL of THF), 2-methyl-2-vinyloxirane (1.96 mL, 20.0 mmol), and CuBr−DMS (411 mg, 2.0 mmol) in 40 mL of THF afforded 3.0600 g of **5e** after distillation (109−112 °C at 0.84 mmHg, 17.36 mmol, 87%) as a 95/5 mixture of *E/Z* isomers: ^{1}H NMR ($CDCl_3$, 500.132 MHz) δ 7.37 (2H, m), 7.29 (3H, m), 5.55 (1H, tq, *J* = 7.14, 1.34 Hz), 4.05 (2H, s), 2.77 (2H, t, *J* = 7.48 Hz), 2.46 (2H, app. q, *J* = 7.85 Hz), 2.10 (1H, br s), and 1.70 (3H, d, *J* = 1.34 Hz); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 141.9, 135.4, 128.4, 128.2, 125.8, 125.0, 68.6, 35.7, 29.5, and 13.6; IR (thin film) 3335.3 (br, s), 3085.5 (w), 3062.4 (m), 3026.7 (s), 2921.6 (s), 2857.9 (s), 1604.0 (w), 1496.0 (s), 1453.5 (s), 1385.0 (w), 1075.5 (m), 1004.0 (s), 747.5 (s), and 698.3 (s) cm^{-1}; high-resolution EI MS *m/z* 176.1197, calcd for $C_{12}H_{16}O$ 176.1201.

(2*R*,3*R*)-2-Methyl-3-(phenylmethyl)oxiranemethanol ((+)-6a). (−)-DIPT (476.3 mg, 2.033 mmol) and molecular sieves (300.0 mg) were weighed into a dry, 100 mL flask under Ar and dissolved in CH_2Cl_2 (40 mL). The solution was cooled to −10 °C and treated with $Ti(OiPr)_4$ (433.0 μL, 1.452 mmol) and TBHP (4.30 mL of 3.26 M solution, 14.07 mmol) for 10 min. The solution was then cooled to −32 °C, and allylic alcohol **5a** (1.5273 g, 9.383 mmol) in 2.5 mL of CH_2Cl_2 was added *via* syringe pump over 15 min. The cooling bath was removed after 3 h and vigorously stirred overnight with 30 mL of 1/2 saturated Rochelle's salt, after which, 2 mL of 30% NaOH/saturated NaCl was added, and stirring was continued an additional 3 h. The resulting biphasic mixture was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine (2 × 5 mL), dried over $MgSO_4$, and concentrated. Chromatography (100 g of SiO_2, 10% EtOAc/90% CH_2Cl_2, R_f = 0.30) yielded 1.55 g of (+)-**6a** as a viscous oil (8.746 mmol, 93%): ^{1}H NMR ($CDCl_3$, 360.130 MHz) δ 7.40−7.20 (5H, m), 3.69 (1 H, dd, *J* = 12.29, 4.66 Hz), 3.58 (1H, dd, *J* = 12.29, 8.20 Hz), 3.28 (1H, t, *J* = 6.35 Hz), 2.96 (1H, dd, *J* = 14.76, 6.46 Hz), 2.86 (1H, dd, *J* = 14.77, 6.25 Hz), 1.92 (1H, dd, *J* = 8.37, 4.72 Hz), and 1.41 (3H, s); ^{13}C NMR ($CDCl_3$, 90.560 MHz) δ 137.6, 128.68, 128.64, 126.6, 65.3, 61.3, 60.2, 34.6, and 14.4; IR (thin film) 3424.5 (br s), 3085.8 (w), 3061.8 (w), 3027.8 (m), 2997.7 (w), 2983.9 (m), 2925.8 (s), 2868.5 (m), 1604.2 (w), 1495.5 (s), 1453.8 (s), 1384.2 (m), 1072.2 (m), 1036.6 (s), 890.8 (w), 853.3 (w), 741.1 (m), and 699.8 (s) cm^{-1}; high-resolution CI (NH_3) MS *m/z* 179.1064, calcd for $C_{11}H_{15}O_2$ 179.1072 $(M + H)^+$, 196.1340, calcd for $C_{11}H_{18}NO_2$ 196.1337 $(M + NH_4)^+$; $[\alpha]^{25}_D$ + 30.7° (*c* 1.56, CH_2Cl_2); bp 74−76 °C at 0.11 mmHg; ^{31}P NMR (10% C_6D_6 in benzene, 202.427 MHz) δ 137.2 (96%) and 135.3 (4%), 92% ee.

(2*S*,3*S*)-2-Methyl-3-(phenylmethyl)oxiranemethanol ((−)-6a). As in the preparation of (+)-**6a**, allylic alcohol **5a** (2.5917 g, 15.98 mmol), (+)-DIPT (631.1 mg, 2.694 mmol), $Ti(OiPr)_4$ (573 μL, 1.924 mmol), TBHP (6.20 mL of a 3.28 M solution, 20.33 mmol), and 491.4 mg of molecular sieves afforded 2.1776 g of (−)-**6a** (12.29 mmol, 77%); ^{1}H NMR, ^{13}C NMR, IR, and MS are identical to those of (+)-**6a**; $[\alpha]^{25}_D$ −30.6° (*c* 1.56, CH_2Cl_2); ^{31}P NMR (10% C_6D_6 in benzene, 202.427 MHz) δ 135.3 (96%) and 137.2 (4%), 92% ee.

(2*R*,3*R*)-3-[(3,4-Dimethoxyphenyl)methyl]-2-methyloxiranemethanol ((+)-6b). As in the preparation of (+)-**6a**, alcohol **5b** (309.5 mg, 1.3923 mmol), (−)-DIPT (49.0 mg, 0.209 mmol), $Ti(OiPr)_4$ (44 μL, 0.149 mmol), TBHP (397 μL of a 5.26 M solution, 2.08 mmol), and 32 mg of molecular sieves yielded, after chromatography (45 g of SiO_2, 20% EtOAc/80% CH_2Cl_2), 325.1 mg of (+)-**6b** (1.364 mmol, 98%): ^{1}H NMR ($CDCl_3$, 500.132 MHz) δ 6.82 (1H, d, *J* = 8.59 Hz), 6.80−6.70 (2H, m), 3.88 (3H, s), 3.86 (3H, s), 3.70 (1H, dd, *J* = 12.24, 4.53 Hz), 3.60 (1H, dd, *J* = 12.24, 8.58 Hz), 3.27 (1H, t, *J* = 6.29 Hz), 2.88 (1H, dd, *J* = 14.78, 6.17 Hz), 2.82 (1H, dd, *J* = 14.79, 5.86 Hz), 1.72 (1H, dd, *J* = 8.51, 4.60 Hz, D_2O exchangeable), and 1.41 (3H, s); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 149.0, 147.8, 130.2, 120.6, 111.9, 111.4, 65.3, 61.1, 60.5, 55.9, 55.8, 34.3, and 14.5; IR (thin film) 3477.1 (br s), 2998.7 (m), 2936.0 (m), 2836.7 (m), 1591.5 (m), 1517.2 (m), 1465.1 (s), 1262.7 (s), 1238.5 (s), 1156.4 (m), 1142.0 (m), 1028.2 (s), and 765.8 (m) cm^{-1}; high-resolution EI MS *m/z* 238.1206, calcd for $C_{13}H_{18}O_4$ 238.1205; $[\alpha]^{25}_D$ +24.1° (*c* 1.16, CH_2Cl_2); ^{31}P NMR (10% C_6D_6 in benzene, 202.427 MHz) δ 136.0 (97%) and 134.5 (3%), 94% ee. Signals were verified by *m*-CPBA epoxidation of **5b**, providing (±)-**6b** in a straightforward manner.

(2*R*,3*R*)-3-(Cyclohexylmethyl)-2-methyloxiranemethanol ((+)-6c). As in the preparation of (+)-**6a**, allylic alcohol **5c** (3.46 g, 20.576 mmol), (−)-DIPT (861 mg, 3.67 mmol), $Ti(OiPr)_4$ (781 μL, 2.625 mmol), and TBHP (5.8 mL of 5.28 M solution, 30.86 mmol) in 60 mL of CH_2Cl_2 afforded 2.6313 g of (+)-**6c** after chromatography (125 g of SiO_2, gradient from CH_2Cl_2 to 5% EtOAc/95% CH_2Cl_2, 14.27 mmol, 67%): ^{1}H NMR ($CDCl_3$, 500.132 MHz) δ 3.68 (1H, dd, *J* = 12.15, 4.43 Hz), 3.57 (1H, dd, *J* = 12.15, 8.63 Hz), 3.09 (1H, t, *J* = 5.52 Hz), 1.85−1.60 (5H, m), 1.63 (1H, br s), 1.55−1.40 (3H, m), 1.35−1.10 (3H, m), 1.27 (3H, s), and 1.05−0.85 (2H, m); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 65.2, 60.5, 58.8, 35.9, 35.4, 33.5, 33.0, 26.2, 26.12, 26.09, and 14.3; IR (thin film) 3432.8 (br s), 2923.5 (s), 2853.1 (s), 1746.8 (w), 1449.7 (s), 1384.1 (m), 1075.5 (m), 1038.8 (s), 872.9 (m), and 681.0 (w) cm^{-1}; high-resolution CI (NH_3) MS *m/z* 185.1536, calcd for $C_{11}H_{21}O_2$ 185.1541; $[\alpha]^{25}_D$ + 24.7° (*c* 1.46, CH_2Cl_2); ^{31}P NMR (10% C_6D_6 in benzene, 202.427 MHz) δ 137.5 (95%) and 135.4 (5%), 90% ee. Signals were verified by epoxidation of **5c** under vanadium acetylacetonate catalysis, providing (±)-**6c** in a straightforward manner.

(2*R*,3*R*)-3-[2-(Dimethylphenylsilyl)ethyl]-2-methyloxiranemethanol ((+)-6d). As in the preparation of (+)-**6a**, allylic alcohol **5d** (3.40 g, 14.50 mmol), (−)-DIPT (767 mg, 3.28 mmol), $Ti(OiPr)_4$ (694 μL, 2.34 mmol), and TBHP (4.1 mL of 5.28 mmol, 21.76 mmol) in 40 mL of CH_2Cl_2 afforded 3.2933 g of (+)-**6d** after chromatography (125 g of SiO_2, 5% EtOAc/CH_2Cl_2, 13.15 mmol, 91%): ^{1}H NMR ($CDCl_3$, 500.132 Hz) δ 7.50 (2H, m), 7.35 (3H, m), 3.63 (1H, dd, *J* = 12.15, 3.46 Hz), 3.52 (1H, dd, *J* = 12.12, 8.06 Hz), 3.00 (1H, t, *J* = 6.40 Hz), 1.69 (1H, br s), 1.64 (1H, m), 1.48 (1H, m), 1.21 (3H, s), 0.93 (1H, ddd, *J* = 14.51, 12.35, 5.17 Hz), 0.77 (1H, ddd, *J* = 14.51, 12.25, 4.74 Hz), and 0.29 (6H, s); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ: 138.5, 133.4, 128.9, 127.7, 65.3, 62.0, 61.1, 22.6, 13.9, 11.9, −3.3, and −3.4; IR (thin film) 3433.7 (br s), 3069.1 (m), 2998.7 (m), 2954.4 (s), 1427.5 (s), 1383.1 (w), 1249.1 (s), 1183.5 (w), 1114.0 (s), 1073.5 (m), 1039.7 (s), 838.2 (s), and 701.2 (s); high-resolution CI (NH_3) MS *m/z* 235.1155, calcd for $C_{13}H_{19}O_2Si$ 235.1154 $(M - CH_3)^+$; $[\alpha]^{25}_D$ + 16.5° (*c* 0.48, CH_2Cl_2); ^{31}P NMR (10% C_6D_6 in benzene, 202.427 MHz) δ 136.7 (98%) and 135.1 (2%), 96% ee. Signals were verified by epoxidation of **5d** under vanadium aceetylacetonate catalysis, providing (±)-**6d** in a straightforward manner.

(2*R*,3*R*)-2-Methyl-3-(phenylethyl)oxiranemethanol ((+)-6e). As in the preparation of (+)-**6a**, allylic alcohol **5e** (2.994 g, 16.99 mmol), DIPT (877 mg, 3.746 mmol), $Ti(OiPr)_4$ (796 μL, 2.676 mmol), and TBHP (4.8 mL of 5.29 M solution, 25.479 mmol) in 40 mL of CH_2Cl_2 afforded 2.90 g of (+)-**6e** after chromatography (200 g of SiO_2, 10% EtOAc/90% CH_2Cl_2, 15.08 mmol, 89%): ^{1}H NMR ($CDCl_3$, 500.132 MHz) δ 7.35 (2H, m), 7.26 (3H, m), 3.67 (1H, dd, *J* = 12.23, 4.65 Hz), 3.56 (1H, dd, *J* = 12.23, 8.46 Hz), 3.14 (1H, t, *J* = 6.34 Hz), 2.91 (1H, ddd, *J* = 14.08, 8.85, 5.58 Hz), 2.77 (1H, dt, *J* = 13.82, 8.14 Hz), 2.28 (1H, br), 2.02 (1H, dddd, *J* = 19.7, 8.6, 6.6, 5.7 Hz), 1.89 (1H, dddd, *J* = 20.0, 8.8, 7.8, 6.1 Hz), and 1.18 (3H, s); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 141.0, 128.3, 126.3, 126.0, 65.2, 61.2, 59.6, 32.6, 29.9, and 13.9; IR (thin film) 3429.9 (br s), 3086.5 (w), 3062.4 (m), 3026.7 (s), 2998.7 (s), 2928.3 (s), 2860.8 (s), 1604.0 (w), 1496.0 (s), 1454.5 (s), 1384.1 (s), 1039.8 (s), 876.1 (m), and 700.3 (s) cm^{-1}; high-resolution EI MS *m/z* 192.1152 calcd for $C_{12}H_{16}O_2$ 192.1150; $[\alpha]^{25}_D$ + 29.1° (*c* 0.77, CH_2Cl_2); ^{31}P NMR (10% C_6D_6 in benzene, 202.427 MHz) δ 137.1 (98%) and 135.1 (2%), 96% ee. Signals were verified by epoxidation of **5e** under vanadium acetylacetonate catalysis, providing (±)-**6e** in straightforward manner.

(2*R*,3*R*)-2-Methyl-3-(phenylmethyl)oxiranecarboxaldehyde ((−)-7a). Oxalyl chloride (1.58 mL, 17.79 mmol) in 80 mL of dry CH_2Cl_2 was cooled to −78 °C under Ar and treated with DMSO (2.52 mL, 35.58 mmol) in 8 mL of CH_2Cl_2 over 15 min *via* syringe pump. Epoxy alcohol (+)-**6a** (1.5763 g, 8.894 mmol) in 10 mL of CH_2Cl_2 was then added over a period of 30 min. After the mixture was stirred at this temperature 30 min, TEA (10.0 mL, 71.7 mmol) was added over 15 min, and the resulting mixture was allowed to warm to −30 °C over 1 h. The solution was poured onto 100 mL of pentane and shaken with pH 7 buffer (25 mL). The layers were separated, and the aqueous phase was extracted with pentane (3 × 50 mL). The combined extracts were washed with 1.0 M $NaHSO_4$ (2 × 25 mL), H_2O (2 × 20 mL), 5% $NaHCO_3$ (2 × 10 mL), and brine (1 × 10 mL) and dried over $MgSO_4$. Removal of the solvent and short-path distillation provided 1.2885 g of (−)-**7a** as a liquid (7.312 mmol, 82%): ^{1}H NMR ($CDCl_3$, 360.130 MHz) δ 8.86 (1H, s), 7.40−7.20 (5H, m), 3.39 (1 H, dd, *J* = 6.39, 5.83 Hz), 3.03 (1H, dd, *J* = 14.89, 6.39 Hz), 2.94 (1H, dd, *J* = 14.86, 5.83 Hz), and 1.54 (3H, s); ^{13}C NMR ($CDCl_3$, 90.560 MHz) δ 199.7, 136.3, 128.8, 128.7, 127.5, 62.5, 60.1, 34.3, and 10.3; IR (thin film) 3063.3 (w), 3030.6 (w), 2974.6 (w), 2934.1 (w), 2818.4 (w), 1728.4 (s), 1495.0 (w), 1454.5 (w), 1082.2 (w), 738.8 (m), and 700.3 (m) cm^{-1}; high-resolution CI (NH_3) MS *m/z* 176.0834, calcd for $C_{11}H_{12}O_2$ 176.0837; $[\alpha]^{25}_D$ −30.5° (*c* 1.74, CH_2Cl_2); bp 82−85 °C at 0.30 mmHg.

(2*S*,3*S*)-2-Methyl-3-(phenylmethyl)oxiranecarboxaldehyde ((+)-7a). As in the preparation of (−)-**7a**, epoxy alcohol (−)-**6a** (2.1243 g, 11.987 mmol), oxalyl chloride (2.13 mL, 22.97 mmol), DMSO (3.40 mL, 47.95 mmol), and TEA (13.0 mL, 95.32 mmol) afforded 1.59 g of (+)-**7a** after distillation (9.023 mmol, 75%); ^{1}H NMR, ^{13}C NMR, IR, and MS are identical to those of (−)-**7a**; $[\alpha]^{25}_D$ +30.6° (*c* 1.65, CH_2Cl_2).

(2*R*,3*R*)-3-[(3,4-Dimethoxyphenyl)methyl]-2-methyloxiranecarboxaldehyde ((−)-7b). As in the preparation of (−)-**7a**, alcohol (+)-**6b** (659.2 mg, 2.766 mmol), oxalyl chloride (507 μL, 5.707 mmol), DMSO (810.6 μL, 11.4149 mmol), and TEA (3.2 mL, 22.82 mmol) provided, after chromatography (30 g of SiO_2, brine), 627.5 mg of (−)-**7b** (2.656 mmol, 96%): ^{1}H NMR ($CDCl_3$, 500.132 MHz) δ 8.83 (1H, s), 6.85−6.70 (3H, m), 3.88 (3H, s), 3.83 (3H, s), 3.33 (1H, dd *J* = 6.45, 5.67 Hz), 2.94 (1H, dd, *J* = 14.80, 6.45 Hz), 2.89 (1H, dd, *J* = 14.80, 5.58 Hz), and 1.53 (3H, s); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 199.6, 149.0, 148.0, 128.7, 120.5, 111.7, 111.3, 62.4, 60.2, 55.8, 55.7, 33.8, and 10.2; IR (thin film) 3000.7 (w), 2958.0 (m), 2836.7 (m), 1728.5 (s), 1591.5 (w), 1517.2 (s), 1466.1 (m), 1282.6 (s), 1237.5 (s), 1157.4 (s), 1028.2 (s), and 765.8 (w) cm^{-1}; high-resolution EI MS (*m/z*) 236.1045, calcd for $C_{13}H_{16}O_4$ 236.1048; $[\alpha]^{25}_D$ −34.9° (*c* 1.45, CH_2Cl_2); bp 124−126 °C at 0.05 mmHg.

(2*R*,3*R*)-3-(Cyclohexylmethyl)-2-methyloxiranecarboxaldehyde ((−)-7c). As in the preparation of (−)-**7a**, epoxy alcohol (+)-**6c** (1.267 g, 6.875 mmol), oxalyl chloride (1.2 mL, 13.75 mmol), DMSO (2.5 mL, 13.75 mmol), and TEA (7.7 mL, 55.00 mmol) in 30 mL of CH_2Cl_2 afforded 1.2192 g of (−)-**7c** after chromatography (125 g of SiO_2, gradient from 20% CH_2Cl_2/80% Hex to 30% CH_2Cl_2/70% Hex, 6.689 mmol, 97%): ^{1}H NMR ($CDCl_3$, 500.132 MHz) δ 8.86 (1H, s), 3.19 (1H, t, *J* = 5.82 Hz), 1.75−1.60 (5H, m), 1.55−1.50 (3H, m), 1.39 (3H, s), 1.30−1.10 (3H, m), and 1.05−0.95 (2H, m); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 200.3, 62.0, 58.7, 35.9, 35.1, 33.3, 33.0, 26.10, 26.01, 25.0, and 10.1; IR (thin film) 2925.4 (s), 2853.1 (s), 1730.4 (s), 1449.7 (m), 1390.8 (w), 1252.0 (w), and 1080.3 (w) cm^{-1}; high-resolution EI MS *m/z* 182.1309, calcd for $C_{11}H_{18}O_2$ 182.1307; $[\alpha]^{25}_D$ −40.6° (*c* 1.87, CH_2Cl_2); bp 68−70 °C at 0.90 mmHg.

(2*R*,3*R*)-3-[2-(Dimethylphenylsilyl)ethyl]-2-methyloxiranecarboxaldehyde ((−)-7d). As in the preparation of (−)-**7a**, epoxy alcohol (+)-**6d** (276.6 mg, 1.105 mmol), oxalyl chloride (197 μL, 2.209 mmol), DMSO (314 μL, 4.418 mmol), and TEA (1.23 mL, 8.837 mmol) in 8 mL of CH_2Cl_2 afforded 231.2 mg of (−)-**7d** after chromatography (40 g of SiO_2, 40% CH_2Cl_2/60% Hex, 0.931 mmol, 84%): ^{1}H NMR ($CDCl_3$, 500.132 MHz) δ 8.80 (1H, s), 7.49 (2H, m), 7.36 (3H, m), 3.10 (1H, t, *J* = 6.24 Hz), 1.73 (1H, dddd, *J* = 14.21, 12.78, 6.14, 5.18 Hz), 1.54 (1H, dddd, *J* = 14.21, 12.52, 6.28, 4.62 Hz), 1.33 (3H, s), 0.95 (1H, ddd, *J* = 14.46, 12.53, 5.15 Hz), 0.79 (1H, ddd, *J* = 14.46, 12.39, 4.65 Hz), and 0.31 (6H, s); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 200.0, 138.0, 133.3, 129.1, 127.8, 62.5, 61.7, 22.5, 11.9, 9.6, −3.4, and −3.5; IR (thin film) 3071.1 (m), 3010.3 (m), 2957.2 (s), 2901.3 (m), 2808.7 (m), 1729.4 (s), 1427.5 (s), 1390.8 (m), 1250.0 (s), 1115.0 (s), 1082.2 (m), 838.2 (s), 780.8 (s), 734.0 (s), and 702.2 (s) cm^{-1}; high-resolution CI (NH_3) MS (*m/z*) 233.0994, calcd for $C_{13}H_{17}O_2Si$ 233.0998 $(M - CH_3)^+$; $[\alpha]^{25}_D$ −45.6° (*c* 1.24, CH_2Cl_2).

(2*R*,3*R*)-2-Methyl-3-(2-phenylethyl)oxiranecarboxaldehyde ((−)-7e). As in the preparation of (−)-**7a**, epoxy alcohol (+)-**6e** (328.8 mg, 1.710 mmol), oxalyl chloride (305 μL, 3.420 mmol), DMSO (486 μL, 6.841 mmol), and TEA (1.9 mL, 1.419 mmol) in 8 mL of CH_2Cl_2 afforded 270.0 mg of (−)-**7e** after chromatography (40 g of SiO_2, 50% CH_2Cl_2/50% Hex, 1.419 mmol, 83%): ^{1}H NMR ($CDCl_3$, 500.132 MHz) δ 8.88 (1H, s), 7.36 (2H, t, *J* = 7.35 Hz), 7.27 (1H, t, *J* = 7.39 Hz), 7.25 (2H, t, *J* = 7.13 Hz), 3.23 (1H, t, *J* = 6.00 Hz), 2.93 (1H, ddd, *J* = 14.28, 8.72, 5.91 Hz), 2.84 (1H, dt, *J* = 13.87, 7.98 Hz), 2.06 (1H, m), 1.98 (1H, m), and 1.35 (3H, s); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 199.8, 140.2, 128.5, 128.3, 126.3, 62.3, 59.2, 32.4, 29.6, and 9.8; IR (thin film) 3027.7 (w), 2934.1 (m), 2813.5 (w), 1727.5 (s), 1495.5 (m), 1390.8 (w), 1082.2 (w), 1019.5 (w), 885.4 (w), 853.6 (m), 749.4 (m), and 699.3 (s) cm^{-1}; high-resolution EI MS *m/z* 190.0995, calcd for $C_{12}H_{14}O_2$ 190.0994; $[\alpha]^{25}_D$ −71.6° (*c* 1.15, CH_2Cl_2).

(2*R*,3*R*)-2-Ethenyl-2-methyl-3-(phenylmethyl)oxirane ((−)-8a). To a slurry of methyltriphenylphosphonium bromide (768.0 mg, 2.150 mmol) in 15 mL of dry THF was added solid KHMDS (370.0 mg, 1.864 mmol) in one portion. After 1 h at 25 °C, aldehyde (−)-**7a** (252.7 mg, 1.434 mmol) in 2.5 mL of THF was added dropwise, and the mixture was stirred at this temperature for 1 h. The solution was poured onto 15 mL of CH_2Cl_2, filtered through SiO_2 (10 g, rinsed with CH_2Cl_2), and concentrated. Chromatography (50 g of SiO_2, 6% EtOAc/94% Hex, R_f = 0.40) yielded 240.4 mg of (−)-**8a** as a liquid (1.3774 mmol, 96.1%): ^{1}H NMR ($CDCl_3$, 500.134 MHz) δ 7.40−7.20 (5H, m), 5.69 (1H, dd, *J* = 21.70, 13.40 Hz), 5.35 (1H, dd, *J* = 21.70, 1.37 Hz), 5.19 (1H, dd, *J* = 13.40, 1.35 Hz), 3.06 (1H, t, *J* = 7.73 Hz), 2.99 (1H, dd, *J* = 18.40, 7.60 Hz), 2.90 (1H, dd, *J* = 18.40, 7.90 Hz), and 1.53 (3H, s); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 140.5, 137.6, 128.7, 128.6, 126.5, 116.1, 65.3, 59.8, 35.1, and 15.2; IR (thin film) 3089.4 (w), 3065.3 (w), 3030.6 (m), 3002.6 (w), 2969.8 (m), 2928.3 (w), 1497.0 (m), 1454.5 (m), 1410.1 (w), 1384.1 (w), 1073.5 (m), 990.6 (m), 746.5 (m), and 701.2 (s) cm^{-1}; $[\alpha]^{25}_D$ −24.8° (*c* 1.165, CH_2Cl_2).

(2*S*,3*S*)-2-Ethenyl-2-methyl-3-(phenylmethyl)oxirane ((+)-8a). As in the preparation of (−)-**8a**, aldehyde (+)-**7a** (391.0 mg, 2.219 mmol), methyltriphenylphosphonium bromide (951.0 mg, 2.663 mmol), and KHMDS (484.4 mg, 2.441 mmol) in 10 mL of THF afforded, after chromatography (45 g of SiO_2, 1% TEA/99% CH_2Cl_2), 385.0 mg of (+)-**8a** (2.210 mmol, quant): ^{1}H NMR, ^{13}C NMR, and IR are identical to those of (−)-**8a**; $[\alpha]^{25}_D$ +23.7° (*c* 1.165, CH_2Cl_2).

(2*R*,3*R*)-3-[(3,4-Dimethoxyphenyl)methyl]-2-ethenyl-2-methyloxirane ((−)-8b). As in the preparation of (−)-**8a**, aldehyde (−)-**7b** (283.0 mg, 1.198 mmol), methyltriphenylphosphonium bromide (514.0 mg, 1.439 mmol), and KHMDS (284.3 mg, 1.436 mmol) provided, after chromatography (40 g of SiO_2, 1% TEA/99% CH_2Cl_2, R_f = 0.28), 243.8 mg of (−)-**8b** as a liquid (1.041 mmol, 87%): ^{1}H NMR ($CDCl_3$, 500.132 MHz) δ 6.90−6.70 (3H, m), 5.67 (1H, dd, *J* = 17.35, 10.75 Hz), 5.33 (1H, d, *J* = 17.33 Hz), 5.19 (1H, d, *J* = 10.88 Hz), 3.87 (3H, s), 3.86 (3H, s), 3.02 (1H, t, *J* = 6.19 Hz), 2.90 (1H, dd, *J* = 18.00, 6.32 Hz), 2.85 (1H, dd, *J* = 18.00, 6.04 Hz), and 1.51 (3H, s); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 148.9, 147.6, 140.5, 130.1, 120.5, 116.0, 111.8, 111.3, 65.4, 59.6, 55.8, 55.7, 34.6, and 15.1; IR (thin film) 2999.7 (m), 2963.0 (s), 2936.0 (s), 2835.7 (s), 1591.5 (m), 1516.2 (s), 1465.1 (s), 1417.9 (m), 1262.6 (s), 1237.5 (s), 1156.5 (s), 1142.0 (s), 1077.4 (m), 1029.2 (s), and 923.1 (m) cm^{-1}; high-resolution EI MS *m/z* 234.1251, calcd for $C_{14}H_{18}O_3$ 234.1256; $[\alpha]^{25}_D$ −23.5° (*c* 1.20, CH_2Cl_2).

(2*R*,3*R*)-3-(Cyclohexylmethyl)-2-ethenyl-2-methyloxirane ((−)-8c). As in the preparation of (−)-**8a**, aldehyde (−)-**7c** (915.9 mg, 5.025 mmol), methyltriphenylphosphonium bromide (2.5 g, 7.03 mmol), and KHMDS (1.2 g, 6.03 mmol) in 25 mL of THF afforded 876.3 mg of vinyl oxirane (−)-**8c** after chromatography (125 g of SiO_2, gradient from 20% CH_2Cl_2/79.9% Hex/0.1% DIPEA to 40% CH_2Cl_2/59.9% Hex/0.1% DIPEA, 4.86 mmol, 97%): ^{1}H NMR ($CDCl_3$, 500.132 MHz) δ 5.65 (1H, dd, *J* = 17.41, 10.76 Hz), 5.30 (1H, dd, *J* = 17.42, 1.06 Hz), 5.16 (1H, dd, *J* = 10.77, 1.06 Hz), 2.82 (1H, t, *J* = 5.69 Hz), 1.80−1.60 (5H, m), 1.55−1.40 (3H, m), 1.36 (3H, s), 1.30−1.10 (3H, m), and 1.05−0.95 (2H, m); ^{13}C NMR ($CDCl_3$) 125.767 MHz) δ 141.0, 115.5, 64.1, 59.2, 35.93, 35.88, 33.5, 33.0, 26.26, 26.14, 26.10, and 15.0; IR (thin film) 3091.3 (w), 3000.7 (w), 2924.5 (s), 2853.1 (s), 1639.7 (w), 1449.7 (m), 1381.2 (w), 1071.6 (w), 989.6 (w), 916.3 (m), 871.9 (m), and 679.0 (w) cm^{-1}; high-resolution CI (NH_3) MS *m/z* 180.1508, calcd for $C_{12}H_{20}O$ 180.1514; 181.1583, calcd for $C_{12}H_{21}O$ 181.1592 $(M + H)^+$; $[\alpha]^{25}_D$ −4.4° (*c* 1.075, CH_2Cl_2).

(2*R*,3*R*)-3-[2-(Dimethylphenylsilyl)ethyl]-2-ethenyl-2-methyloxirane ((+)-8d). As in the preparation of (−)-**8a**, aldehyde (−)-**7d** (218.0 mg, 0.878 mmol), methyltriphenylphosphonium bromide (407 g, 1.141 mmol), and KHMDS (210.0 mg, 1.053 mmol) in 5 mL of THF afforded 171.6 mg of vinyloxirane (+)-**8d** after chromatography (40 g of SiO_2, 40% CH_2Cl_2/60% Hex, 0.696 mmol, 79%) along with 29.7 mg of rearranged aldehyde (+)-**9d** (0.121 mmol, 14%): ^{1}H NMR ($CDCl_3$, 500.132 MHz) δ 7.51 (2H, m), 7.35 (3H, m), 5.63 (1H, dd, *J* = 17.40, 10.75 Hz), 5.29 (1H, dd, *J* = 17.42, 1.10 Hz), 5.15 (1H, dd, *J* = 10.77, 1.10 Hz), 2.78 (1H, t, *J* = 6.34 Hz), 1.65 (1H, m), 1.53 (1H, m), 1.33 (3H, s), 0.95 (1H, ddd, *J* = 14.50, 12.48, 5.16 Hz), 0.78 (1H, ddd, *J* = 14.50, 12.40, 4.72 Hz), and 0.30 (6H, s); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 140.9, 138.5, 133.4, 128.9, 127.7, 115.5, 67.2, 59.7, 23.1, 14.6, 11.9, −3.2, and −3.4; IR (thin film) 3090.4 (w), 3070.1 (m), 3050.8 (m), 3000.7 (m), 2958.2 (s), 1427.5 (s), 1413.0 (w), 1249.1 (s), 1114.0 (s), 918.2 (m), 828.2 (s), 730.1 (s), and 700.3 (s) cm^{-1}; high-resolution CI (NH_3) MS *m/z* 231.1203, calcd for $C_{14}H_{19}OSi$ 231.1205 $(M - CH_3)^+$; $[\alpha]^{25}_D$ + 0.4° (*c* 1.04 CH_2Cl_2).

(2*R*,3*R*)-2-Ethenyl-2-methyl-3-(2-phenylethyl)oxirane ((+)-8e). As in the preparation of (−)-**8a**, aldehyde (−)-**7e** (253.8 mg, 1.334 mmol), methyltriphenylphosphonium bromide (535.8 mg, 1.50 mmol), and KHMDS (278.8 mg, 1.45 mol) in 4 mL of THF afforded 220.9 mg of (+)-**8e** after chromatography (40 g of SiO_2, 40% CH_2Cl_2/60% Hex, 1.173 mmol, 88%): ^{1}H NMR ($CDCl_3$, 500.132 MHz) δ 7.36−7.32 (2H, m), 7.26−7.24 (3H, m), 5.68 (1H, dd, *J* = 17.40, 10.70 Hz), 5.32 (1H, dd, *J* = 17.40, 0.69 Hz), 5.21 (1H, dd, *J* = 10.70, 0.69 Hz), 2.91 (1H, ddd, *J* = 13.80, 8.80, 5.70 Hz), 2.90 (1H, t, *J* = 6.15 Hz), 2.78 (1H, dt, J = 13.80, 8.1 Hz), 2.01 (1H, m), 1.94 (1H, m), and 1.31 (3H, s); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 141.1, 140.7, 128.34, 128.33, 126.0, 115.7, 64.6, 59.6, 32.5, 30.5, and 14.7; IR (thin film) 3087.5 (w), 3063.4 (w), 3027.7 (m), 3001.6 (w), 2965.0 (m), 2930.2 (m), 2860.8 (w), 1496.0 (m), 1454.5 (s), 1410.9 (w), 1074.5 (m), 989.6 (w), 920.1 (m), 750.4 (s), and 700.3 (s) cm^{-1}; high-resolution EI MS m/z 188.1201, calcd for $C_{13}H_{16}O$ 188.1201; $[\alpha]^{25}_D$ + 15.3° (c 1.15, CH_2Cl_2).

(S)-2-Methyl-2-(phenylmethyl)-3-butenal ((+)-9a). Method i. To a −78 °C solution of vinyloxirane (−)-**8a** (678.6 mg, 3.895 mmol) in 50 mL of CH_2Cl_2 was added $BF_3 \cdot Et_2O$ (503 μL, 4.09 mmol), and after exactly 2.0 min, the solution was poured onto 100 mL of Et_2O and shaken with 10 mL of 5% $NaHCO_3$. The layers were separated, and the aqueous phase was extracted with Et_2O (3 × 2 mL). The combined ether extracts were washed with brine (2 × 5 mL), dried over $MgSO_4$, and concentrated to give 680.0 mg of pure (+)-**9a** as an oil (3.903 mmol, quant): ^{1}H NMR ($CDCl_3$, 400.132 MHz) δ 9.52 (1H, s), 7.30−7.05 (5H, m), 5.87 (1H, dd, J = 17.60, 10.78 Hz), 5.29 (1H, dd, J = 10.78, 0.62 Hz), 5.10 (1H, dd, J = 17.60, 0.61 Hz), 2.98 (1H, d, J = 13.57 Hz), 2.89 (1H, d, J = 13.57 Hz), and 1.14 (3H, s); ^{13}C NMR ($CDCl_3$, 100.625 MHz) δ 202.4, 138.4, 136.4, 130.3, 128.0, 126.6, 117.1, 53.7, 42.0, and 17.8; IR (thin film) 3088.4 (w), 3085.3 (w), 3031.5 (m), 2980.4 (w), 2933.1 (w), 2810.6 (br w), 2711.3 (br w), 1728.5 (s), 1496.9 (m), 1454.5 (m), 1000.2 (w), 925.0 (m), and 702.2 (s) cm^{-1}; high-resolution CI (NH_3) MS m/z 175.1112, calcd for $C_{12}H_{15}O$ 175.1122 (M + H)$^+$; $[\alpha]^{25}_D$ +48.6° (c 1.70, CH_2Cl_2).

(R)-2-Methyl-2-(phenylmethyl)-3-butenal ((−)-9a). Method i. As in the preparation of (+)-**9a**, vinyloxirane (+)-**8a** (385.0 mg, 2.219 mmol) and $BF_3 \cdot Et_2O$ (273 μL, 2.219 mmol) yielded 380.0 mg of (−)-**9a** (2.181 mmol, 98%): ^{1}H NMR, ^{13}C NMR, IR, and MS are identical to those of (+)-**9a**; $[\alpha]^{25}_D$ −49.0° (c 1.82, CH_2Cl_2).

***(S)-2-[(3,4-Dimethoxyphenyl)methyl]-2-methyl-3-butenal* ((+)-9b). Method i.** As in the preparation of (+)-**9a**, vinyloxirane (−)-**8b** (410.0 mg, 1.750 mmol) and $BF_3 \cdot Et_2O$ (215 μL, 1.750 mmol) were reacted at −78 °C for 60 s in 17 mL of CH_2Cl_2 to yield 208.0 mg of (+)-**9b** after chromatography (40 g of SiO_2, CH_2Cl_2, 0.888 mmol, 51%).

Method ii. Vinyloxirane (−)-**8b** (235.0 mg, 1.003 mmol) was treated with 5 mL of freshly prepared 5 M anhydrous $LiClO_4$ in Et_2O and refluxed for 14 h. The solution was diluted to 50 mL with Et_2O and shaken with 10 mL of H_2O. The layers were separated, and the aqueous layer was extracted with Et_2O (2 × 2 mL). The combined extracts were washed with 5% $NaHCO_3$ (2 × 5 mL) and brine (1 × 5 mL), dried over $MgSO_4$, and concentrated. Chromatography (50 g of SiO_2, CH_2Cl_2) afforded 212.7 mg of (+)-**9b** as an oil (0.908 mmol, 91%): ^{1}H NMR ($CDCl_3$, 500.132 MHz) δ 9.50 (1H, s), 6.76 (1H, d, J = 8.06 Hz), 6.70−6.50 (2H, m), 5.86 (1H, dd, J = 17.51, 10.75 Hz), 5.28 (1H, d, J = 10.54 Hz), 5.09 (1H, d, J = 17.73 Hz), 3.85 (3H, s), 3.84 (3H, s), 2.92 (1H, d, J = 13.76 Hz), 2.82 (1H, d, J = 13.86 Hz), and 1.13 (3H, s); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 202.6, 148.2, 147.6, 138.5, 128.8, 122.3, 116.9, 113.5, 110.7, 55.7 (2 overlapping signals), 53.7, 41.6, and 17.7; IR (thin film) 2936.0 (m), 2835.7 (m), 1724.6 (s), 1590.9 (w), 1517.2 (s), 1465.1 (m), 1418.8 (m), 1261.6 (m), 1238.5 (s), 1158.4 (m), 1028.4 (m), and 766.8 (w) cm^{-1}; high-resolution EI MS m/z 234.1256, calcd for $C_{14}H_{18}O_3$ 234.1256; $[\alpha]^{25}_D$ +28.1° (c 1.025, CH_2Cl_2).

(S)-2-(Cyclohexylmethyl)-2-methyl-3-butenal ((+)-9c). Method i. As in the preparation of (−)-**9a**, vinyloxirane (−)-**8c** (83.0 mg, 0.460 mmol) and $BF_3 \cdot Et_2O$ (60 μL, 0.483 mmol) in 5 mL of CH_2Cl_2 afforded 44.0 mg of (+)-**9c** after chromatography (40 g of SiO_2, gradient from 20% CH_2Cl_2/80% Hex to 30% CH_2Cl_2/70% Hex, 0.244 mmol, 53%).

Method iii. Vinyloxirane (−)-**8c** (128.6 mg, 0.713 mmol) in 8 mL of CH_2Cl_2 at −78 °C was treated with a 1.8 M solution of Et_2AlCl (Aldrich, 416 μL, 0.749 mmol). After 5 min, 1 mL of 1/2 saturated Rochelle's salt was added and the cooling bath removed. Stirring was continued for 12 h, when the layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 1 mL). The combined extracts were dried over $MgSO_4$, concentrated, and chromatographed (40 g of SiO_2, gradient from 20% CH_2Cl_2/80% Hex to 33% CH_2Cl_2/67% Hex), affording 46.5 mg of (+)-**9c** (0.255 mmol, 36%) and 40.0 mg of (+)-**10c** (0.222 mmol, 31%).

Method iv. Vinyloxirane (−)-**8c** (90.7 mg, 0.503 mmol) in 100 μL of CH_2Cl_2 was added to 50 mg of dry SiO_2 in a conical vial. The vial was placed in a sonication bath and sonicated for 24 h under inert atmosphere. By the end of the reaction, all of the solvent had evaporated. The SiO_2 was rinse with CH_2Cl_2, filtered, freed of solvent, and chromatographed (35 g of SiO_2, gradient from 20% CH_2Cl_2/80% Hex to 30% CH_2Cl_2/70% Hex), affording 36.2 mg of (+)-**9c** (0.201 mmol, 40%) and 27.8 mg of (+)-**10c** (0.154 mmol, 31%).

Physical properties of (+)-**9c**: ^{1}H NMR ($CDCl_3$, 500.132 MHz) δ 9.39 (1H, s), 5.80 (1H, dd, J = 17.62, 10.79 Hz), 5.23 (1H, d, J = 10.77 Hz), 5.11 (1H, d, J = 17.63 Hz), 1.70−1.60 (7H, m), 1.40−1.30 (1H, m), 1.20−1.05 (3H, m), 1.18 (3H, s), and 1.00−0.80 (2H, m); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 203.0, 139.3, 116.0, 52.6, 43.5, 34.8, 34.4, 33.8, 26.19, 26.16, 26.01, and 18.2; IR (thin film) 3087.5 (w), 2924.5 (s), 2853.1 (m), 2797.1 (w), 2699.8 (w), 1729.4 (s), 1449.7 (m), and 920.2 (w) cm^{-1}; high-resolution EI MS m/z 180.1498, calcd for $C_{12}H_{20}O$ 180.1514; 179.1441, calcd for $C_{12}H_{19}O$ 179.1436 (M − H)$^+$; $[\alpha]^{25}_D$ +2.3° (c 1.635, CH_2Cl_2).

Physical properties of (R)-1-Cyclohexyl-3-methyl-4-penten-2-one ((+)-**10c**): ^{1}H NMR ($CDCl_3$, 500.132 MHz) δ 5.78 (1H, ddd, J = 17.14, 10.18, 8.12 Hz), 5.15 (1H, dt, J = 17.20, 1.17 Hz), 5.13 (1H, dt, J = 10.10, 1.17 Hz), 3.17 (1H, p, J = 6.92 Hz), 2.35 (1H, dd, J = 16.28, 7.03 Hz), 2.30 (1H, dd, J = 16.28, 6.60 Hz), 1.80 (1H, m), 1.70−1.60 (5H, m), 1.30−1.20 (2H, m), 1.16 (3H, d, J = 6.88 Hz), and 0.90−0.80 (2H, m); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 211.2, 137.4, 116.6, 51.6, 48.3, 33.4, 33.1, 33.0, 26.1, 25.99, 25.97, and 15.5; IR (thin film) 3081.7 (w), 2975.6 (m), 2924.5 (s), 2853.1 (s), 1714.0 (s), 1634.9 (w), 1449.7 (w), 1406.3 (w), 1372.5 (w), 1359.2 (w), 1283.8 (w), 1017.6 (w), 993.5 (w), 961.6 (w), and 917.3 (w) cm^{-1}; high-resolution CI (NH_3) MS m/z 180.1515, calcd for $C_{12}H_{20}O$ 180.1514; 181.1593, calcd for $C_{12}H_{21}O$ 181.1592 (M + H)$^+$; $[\alpha]^{25}_D$ +113.7° (c 0.30, CH_2Cl_2).

(S)-2-[2-(Dimethylphenylsilyl)ethyl]-2-methyl-3-butenal ((+)-9d). Method i. As in the preparation of (+)-**9a**, vinyloxirane (+)-**8d** (52.2 mg, 0.212 mmol) and $BF_3 \cdot Et_2O$ (27.3 μL, 0.222 mmol) in 3 mL of CH_2Cl_2 afforded 51.2 mg of (+)-**9d** (0.208 mmol, 98%): ^{1}H NMR ($CDCl_3$, 500.132 MHz) δ 9.42 (1H, s), 7.53 (2H, m), 7.40 (3H, m), 5.81 (1H, dd, J = 17.70, 10.80 Hz), 5.30 (1H, dd, J = 10.80, 0.70 Hz), 5.13 (1H, dd, J = 17.70, 0.70 Hz), 1.60 (2H, m), 1.19 (3H, s), 0.69 (2H, m), and 0.32 (6H, s); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 203.1, 138.50, 138.46, 133.4, 128.9, 127.7, 116.6, 53.7, 29.5, 17.0, 9.1, −3.43, and −3.45; IR (thin film) 3070.1 (w), 3050.8 (w), 3000.7 (m), 2925.4 (w), 2804.9 (w), 2697.8 (w), 1727.5 (s), 1427.5 (m), 1249.1 (m), 923.1 (w), 838.2 (s), 817.0 (s), 778.4 (m), 730.2 (s), and 700.3 (s) cm^{-1}; high-resolution CI (NH_3) MS m/z 245.1354, calcd for $C_{15}H_{21}OSi$ 245.1362; $[\alpha]^{25}_D$ +20.4° (c 0.715, CH_2Cl_2).

(S)-2-Methyl-2-(2-phenylethyl)-3-butenal ((+)-9e). Method i. As in the preparation of (+)-**9a**, vinyloxirane (+)-**8e** (69.3 mg, 0.368 mmol) and $BF_3 \cdot Et_2O$ (48 μL, 0.386 mmol) in 3 mL of CH_2Cl_2 afforded 17.7 mg of **9e** (0.094 mmol, 26%), 14.6 mg of **10e** (0.078 mmol, 21%), and 18.6 mg of diols after prep plate chromatography (500 μm thickness, one elution with 50% CH_2Cl_2/50% Hex).

Method iv. As in the preparation of (+)-**9c**, vinyloxirane (+)-**8e** (43.0 mg, 0.228 mmol) afforded 13.0 mg of (+)-**9e** (0.690 mmol, 30%) and 20.6 mg of (+)-**10e** (0.109 mmol, 48%) after chromatography (30 g of SiO_2, gradient from 20% CH_2Cl_2/80% Hex to 30% CH_2Cl_2/70% Hex).

Physical properties of (+)-**9e**: ^{1}H NMR ($CDCl_3$, 500.134 MHz) δ 9.48 (1H, s), 7.28−7.25 (2H, m), 7.23−7.20 (3H, m), 5.85 (1H, dd, J = 17.61, 10.78 Hz), 5.33 (1H, dd, J = 10.80, 0.50 Hz), 5.19 (1H, dd, J = 17.63, 0.50 Hz), 2.55 (2H, m), 1.91 (2H, m), and 1.26 (3H, s); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ: 202.3, 141.7, 138.3, 128.4, 128.2, 125.9, 117.0, 52.7, 37.3, 30.3, and 17.7; IR (thin film) 3087.5 (w), 3027.7 (w), 2977.5 (w), 2933.1 (w), 2862.7 (w), 2806.8 (w), 2705.5 (w), 1727.5 (s), 1632.9 (w), 1604.0 (w), 1497.9 (m), 1454.5 (m), 997.3 (w), 924.0 (m), and 699.3 (s) cm^{-1}; high-resolution CI (NH_3) MS m/z 188.1204, calcd for $C_{13}H_{16}O$ 188.1201; $[\alpha]^{25}_D$ + 25.8° (c 0.41, CH_2Cl_2).

Physical properties of (R)-4-methyl-1-phenyl-5-hexen-3-one ((+)-**10e**): ^{1}H NMR ($CDCl_3$, 500.132 MHz) δ 7.30−7.25 (2H, m), 7.21−7.15 (3H, m), 5.78 (1H, ddd, J = 17.12, 10.17, 8.12 Hz), 5.14 (1H, dt, J = 17.12, 1.23 Hz), 5.12 (1H, ddd, J = 10.17, 1.23, 0.90 Hz), 3.18 (1H, br p, J = 6.94 Hz), 2.90−2.70 (4H, m), and 1.16 (3H, d, J = 6.87 Hz); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 210.4, 141.1, 137.2, 128.3, 128.2, 125.9, 116.9, 51.4, 42.2, 29.6, and 15.5; IR (thin film) 3064.3 (w), 3028.6 (w), 2977.5 (m), 2933.1 (w), 1714.9 (s), 1634.9 (w), 1605.0 (w), 1497.9 (w), 1453.6 (m), 1409.2 (w), 1371.6 (w), 1262.6 (w), 995.4 (m), 921.1 (m), 749.4 (m), and 699.3 (s) cm^{-1}; high-resolution CI (NH_3) MS *m/z* 188.1207, calcd for $C_{13}H_{16}O$ 188.1201; $[\alpha]^{25}_D$ + 21.3° (*c* 0.61, CH_2Cl_2).

(*S*)-2-Methyl-2-(phenylmethyl)-3-buten-1-ol ((−)-11a). Aldehyde (+)-**9a** (32.9 mg, 0.188 mmol) in 2.2 mL of MeOH at 0 °C was treated with $NaBH_4$ (5.4 mg, 0.143 mmol) for 2 h, at which time the solution was poured onto 10 mL of Et_2O and shaken with 5 mL of H_2O. The layers were separated, and the aqueous layer was extracted with Et_2O (3 × 2 mL). The combined extracts were dried over $MgSO_4$ and freed of solvent. Preparative TLC (500 μM thickness, CH_2Cl_2, one elution) gave 30.4 mg of (−)-**11a** as an oil (0.173 mmol, 92%): ^1H NMR ($CDCl_3$, 500.132 MHz) δ 7.40−7.10 (5H, m), 5.89 (1 H, dd, *J* = 17.62, 10.90 Hz), 5.22 (1H, dd, *J* = 10.95, 0.98 Hz), 5.07 (1H, dd, *J* = 17.72, 0.94 Hz), 3.47 (1H, d, *J* = 10.69 Hz), 3.42 (1H, d, *J* = 10.70 Hz), 2.77 (1H, d, *J* = 13.12 Hz), 2.69 (1H, d, *J* = 13.11 Hz), 1.54 (1H, br s), and 1.02 (3H, s); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 143.7, 137.7, 130.5, 127.7, 126.0, 114.6, 68.8, 43.1, 43.0, and 20.0; IR (thin film) 3399.0 (br s), 3085.5 (m), 3064.3 (w), 3029.6 (m), 2965.0 (s), 2925.4 (s), 2873.3 (m), 1496.0 (m), 1453.6 (m), 1415.9 (m), 1042.7 (m), 916.3 (m), and 703.1 (s) cm^{-1}; high-resolution CI (NH_3) MS *m/z* 176.1201, calcd for $C_{12}H_{16}O$ 176.1204; $[\alpha]^{25}_D$ −4.0° (*c* 1.15, CH_2Cl_2); ^{31}P NMR (10% C_6D_6 in benzene, 202.427 MHz) δ 131.8 (95%) and 131.5 (5%), 90% ee.

(*R*)-2-Methyl-2-(phenylmethyl)-3-buten-1-ol ((+)-11a). As in the preparation of (−)-**11a**, aldehyde (−)-**9a** (34.0 mg, 0.195 mmol) and $NaBH_4$ (10.0 mg, 0.264 mmol) yielded 20.1 mg of (+)-**11a** after preparative TLC (0.114 mmol, 58%): ^1H NMR, ^{13}C NMR, IR, and MS are identical to those of (−)-**11a**; $[\alpha]^{25}_D$ +4.1° (*c* 1.20, CH_2Cl_2); ^{31}P NMR (10% C_6D_6 in benzene, 202.427 MHz) δ 131.5 (95.0%) and 131.8 (5.0%), 90.0 % ee.

(*S*)-2-[2-(Dimethylphenylsilyl)ethyl]-2-methyl-3-buten-1-ol ((−)-11d). As in the preparation of (−)-**11a**, aldehyde (+)-**9d** (50.0 mg, 0.203 mmol) and $NaBH_4$ (7.6 mg, 0.203 mmol) in 3 mL of MeOH yielded 30.6 mg of (−)-**11d** after prep plate chromatography (500 μm, one elution with CH_2Cl_2, 0.123 mmol, 61%): ^1H NMR ($CDCl_3$, 500.132 MHz) δ 7.50 (2H, m), 7.36 (3H, m), 5.66 (1H, dd, *J* = 17.64, 10.87 Hz), 5.18 (1H, dd, *J* = 10.86, 1.30 Hz), 5.03 (1H, dd, *J* = 17.64, 1.30 Hz), 3.37 (1H, d, *J* = 10.63 Hz), 3.34 (1H, d, *J* = 10.63 Hz), 1.34 (2H, m), 0.99 (3H, s), 0.67 (2H, m), and 0.27 (6H, s); ^{13}C NMR ($CDCl_3$, 125.785 MHz) δ 143.8, 139.0, 133.4, 128.8, 127.6, 114.8, 69.8, 43.2, 30.8, 19.0, 8.8, −3.31, and −3.36; IR (thin film) 3375.9 (br s), 3070.1 (m), 2999.0 (w), 2957.3 (s), 2920.6 (s), 1427.5 (s), 1248.1 (s), 1114.1 (s), 1043.6 (s), 913.4 (m), 838.2 (s), 815.0 (s), 777.4 (s), and 699.3 (s) cm^{-1}; high-resolution CI (NH_3) MS *m/z* 233.1370, calcd for $C_{14}H_{21}OSi$ 233.1361 $(M - CH_3)^+$; $[\alpha]^{25}_D$ −11.6° (*c* 1.455, CH_2Cl_2); ^{31}P NMR (10% C_6D_6 in benzene, 202.427 MHz) δ 133.6 (98%) and 133.2 (2%), 96% ee.

(*S*)-2-Methyl-2-(phenylmethyl)-3-butenoic Acid ((+)-12a). To a 10 °C solution of (+)-**9a** (680.0 mg, 3.903 mmol) and 2-methyl-2-butene (500 μL) in 4 mL of *tert*-butyl alcohol were added $NaClO_2$ (80% technical, 880.0 mg, 7.789 mmol) and NaH_2PO_4 (1.10 g, 7.97 mmol) in 3 mL of H_2O over 25 min. The temperature was allowed to warm to 25 °C over 1 h, at which time the reaction mixture was concentrated *in vacuo* to approximately 1/2 volume. The concentrate was diluted to 10 mL with H_2O and washed with pentane (2 × 2 mL). The H_2O layer was acidified to pH 2.0 with 1 M HCl, saturated with NaCl and extracted with Et_2O (3 × 5 mL). The ether extracts were washed with brine (2 × 2 mL), dried over $MgSO_4$, and concentrated. Heating to 40 °C at 0.03 mmHg (to remove excess *tert*-butyl alcohol) afforded 618.2 mg of (+)-**12a** as an oil which solidified on standing (3.250 mmol, 83%): ^1H NMR ($CDCl_3$, 400.130 MHz) δ 9.50 (1H, v br), 7.30−7.10 (5H, m), 6.13 (1H, dd, *J* = 17.49, 10.76 Hz), 5.21 (1H, dd, *J* = 10.73, 0.53 Hz), 5.15 (1H, dd, *J* = 17.52, 0.53 Hz), 3.13 (1H, d, *J* = 13.26 Hz), 2.93 (1 H, d, *J* = 13.26 Hz), and 1.28 (3H, s); ^{13}C NMR ($CDCl_3$, 100.623 MHz) δ 181.8, 140.7, 136.8, 130.4, 128.0, 126.7, 114.7, 49.7, 45.1, and 19.6; IR (thin film) 3100 (v br), 3088.4 (m), 3084.3 (m), 3030.6 (m), 2985.2 (m), 2929.3 (m), 2639.0 (br m), 1702.0 (s), 1497.0 (m), 1454.5 (w), 1280.9 (m), 1216.3 (m), 1000.2 (w), 924.0 (m), and 701.2 (s) cm^{-1}; high-resolution CI (NH_3) MS *m/z* 190.0987, calcd for $C_{12}H_{14}O_2$ 190.0994; 208.1334, calcd for $C_{12}H_{18}NO_2$ 208.1337 $(M + NH_4)^+$; $[\alpha]^{25}_D$ +2.9° (*c* 3.10, CH_2Cl_2).

(*S*)-2-[(3,4-Dimethoxyphenyl)methyl]-2-methyl-3-butenoic Acid ((−)-12b). As in the preparation of (+)-**12a**, aldehyde (+)-**9b** (200.0 mg, 0.854 mmol), $NaClO_2$ (80% technical, 193.0 mg, 1.707 mmol), NaH_2PO_4 (236.0 mg, 1.707 mmol), and 2-methyl-2-butene (1 mL) afforded 210.0 mg of (−)-**12b** (0.839 mmol, 98%): ^1H NMR ($CDCl_3$, 500.132 MHz) δ 6.80−6.60 (3H, m), 6.09 (1H, dd, *J* = 17.45, 10.73 Hz), 5.18 (1H, d, *J* = 10.76 Hz), 5.12 (1H, d, *J* = 17.39 Hz), 3.85 (3H, s), 3.81 (3H, s), 3.04 (1H, d, *J* = 13.48 Hz), 2.83 (1H, d, *J* = 13.45 Hz), and 1.24 (3H, s); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 181.3, 148.2, 147.7, 140.7, 129.2, 122.4, 114.5, 113.4, 110.6, 55.69, 55.62, 49.7, 44.8, and 19.6; IR (thin film) 3300 (br), 3000.0 (m), 2938.0 (m), 2836.7 (m), 1698.3 (s), 1590.5 (w), 1517.2 (s), 1464.2 (m), 1264.5 (s), 1238.5 (m), 1142.9 (m), 1029.9 (m), and 767.8 (w) cm^{-1}; high-resolution (EI) MS *m/z* 250.1201, calcd for $C_{14}H_{18}O_4$ 250.1205; $[\alpha]^{25}_D$ −10.7° (*c* 0.84, CH_2Cl_2).

(*S*)-2-Methyl-2-(phenylmethyl)-3-butenamide ((+)-13a). To a stirring solution of acid (+)-**12a** (240.0 mg, 1.262 mmol) in 5 mL of CH_2Cl_2 at 25 °C under Ar was added carbonyldiimidazole (245.4 mg, 1.514 mmol) in one portion, and the mixture was stirred 1.5 h. The flask was then fitted with an ammonia condenser and cooled to −78 °C. Approximately 30−40 drops of anhydrous NH_3 was condensed into the solution, and the apparatus was allowed to warm to 25 °C overnight with the excess gas being released into an inert atmosphere. The solution was poured onto 10 mL of Et_2O and 3 mL of 5% $NaHCO_3$. The aqueous layer was discarded, and the ether phase was washed with H_2O (2 × 1 mL) and brine (2 × 1 mL) and dried over $MgSO_4$. Evaporation of solvent yielded 227.5 mg of (+)-**12a** (1.202 mmol, 95%): ^1H NMR ($CDCl_3$, 500.132 MHz) δ 7.40−7.20 (5H, m), 6.11 (1H, dd, *J* = 17.54, 10.79 Hz), 5.80 (1H, br), 5.71 (1H, br), 5.29 (1H, dd, *J* = 10.80, 0.83 Hz), 5.23 (1H, dd, *J* = 17.65, 0.85 Hz), 3.12 (1H, d, *J* = 13.29 Hz), 2.98 (1H, d, *J* = 13.27 Hz), and 1.33 (3H, s); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 177.8, 141.1, 137.2, 130.4, 127.8, 126.3, 115.8, 49.7, 44.4, and 21.5; IR (thin film) 3474.2 (br), 3191.6 (br), 3086.5 (m), 3062.4 (m), 3029.6 (m), 2980.4 (m), 2926.4 (br), 1666.7 (s), 1495.0 (w), 1372.6 (m), 1119.8 (w), 924.0 (w), 701.2 (m) cm^{-1}; high-resolution CI (NH_3) MS *m/z* 189.1144, calcd for $C_{12}H_{15}NO$ 189.1154; 190.1227, calcd for $C_{12}H_{16}NO$ 190.1232 $(M + H)^+$; $[\alpha]^{25}_D$ +3.9° (*c* 0.915, CH_2Cl_2).

(*S*)-2-[(3,4-Dimethoxyphenyl)methyl]-2-methyl-3-butenamide ((−)-13b). As in the preparation of (+)-**13a**, (−)-**12b** (141.9 mg, 0.567 mmol), carbonyldiimidazole (110.0 mg, 0.680 mmol), and anhydrous NH_3 (20−30 drops) afforded, after chromatography (35 g of SiO_2, 30% EtOAc/CH_2Cl_2), 100.0 mg of (−)-**12b** (0.401 mmol, 71%): ^1H NMR ($CDCl_3$, 500.132 MHz) δ 6.80−6.60 (3H, m), 6.06 (1H, dd, *J* = 17.56, 10.81 Hz), 5.62 (1H, br), 5.56 (1H, br), 5.24 (1H, dd, *J* = 10.81, 0.82 Hz), 5.20 (1H, dd, *J* = 17.58, 0.82 Hz), 3.84 (3H, s), 3.83 (3H, s), 3.04 (1H, d, *J* = 13.43 Hz), 2.84 (1H, d, *J* = 13.44 Hz), and 1.28 (3H, s); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 177.7, 148.2, 147.5, 141.3, 129.9, 122.5, 115.7, 113.7, 110.5, 55.68, 55.67, 49.8, 44.2, and 21.6; IR (thin film) 3400 (br), 3340.2 (br), 3185.4 (br), 2936.0 (m), 1666.7 (s), 1590.5 (m), 1516.2 (s), 1464.2 (m), 1266.5 (s), 1236.5 (s), 1158.4 (m), 1142.6 (m), 1062.9 (w), 1028.2 (m), and 664.6 (w) cm^{-1}; high-resolution EI MS *m/z* 249.1367, calcd for $C_{14}H_{19}NO_3$ 249.1365; $[\alpha]^{25}_D$ −6.30° (*c* 0.54, CH_2Cl_2).

(*R*)-Phenylmethyl *N*-(1-Ethenyl-1-methyl-2-phenylethyl)carbamate ((−)-14a). To a 40 °C solution of amide (+)-**13a** (210.0 mg, 1.110 mmol) and benzyl alcohol (1.10 mL, 11.096 mmol) in 4 mL of dry DMF was added lead tetraacetate (2.58 g, 5.61 mmol) in one portion. A reflux condenser with an Ar needle was quickly fitted, and the solution was heated to 100−110 °C for 1 h. The solution was cooled to 25 °C, poured onto a SiO_2 plug (30 g), and rinsed with Et_2O (75 mL). The ethereal solution was washed with 5% NaOH (2 × 10 mL), H_2O (2 × 5 mL), and brine (1 × 5 mL), dried over $MgSO_4$, and freed of solvent. Evacuation of the crude (0.05 mmHg) at 50 °C (to remove benzyl alcohol and benzaldehyde) followed by chromatography (45 g of SiO_2, 7% EtOAc/93% Hex) gave 240.0 mg of (−)-**14a** as an oil (0.813 mmol, 73%): ^1H NMR ($CDCl_3$, 400.130 MHz) δ 7.40−7.30 (5H, m), 7.24−7.15 (3H, m), 7.12−7.00 (2H, m), 6.02 (1H, dd, *J* = 17.46, 10.80 Hz), 5.20−5.00 (4H, m), 4.68 (1H, br s), 3.17 (1H, d, *J* = 13.30 Hz), 2.94 (1H, d, *J* = 13.30 Hz), and 1.36 (3H, s); ^{13}C NMR

$CDCl_3$, 125.767 MHz) δ 154.6. 142.9, 136.7, 136.6, 130.6, 128.4, 128.1, 128.0, 127.9, 126.4, 112.6, 66.1, 56.6, 44.3, and 25.0; IR (thin film) 3418.3 (br), 3348.5 (br), 3086.5 (m), 3063.4 (m), 3030.5 (m), 2980.4 (m), 2934.1 (br w), 1724.5 (s), 1496.9 (s), 1454.5 (m), 1259.7 (s), 1228.8 (s), 1078.3 (s), 918.2 (w), 736.9 (m), and 700.3 (w) cm^{-1}; high-resolution CI (NH_3) MS *m/z* 296.1650, calcd for $C_{19}H_{22}NO_2$ 296.1639 $(M + H)^+$; $[\alpha]^{25}{}_D$ −16.0° (*c* 0.90, CH_2Cl_2).

(*R*)-Phenylmethyl *N*-[1-Ethenyl-2-(3,4-dimethoxyphenyl)-1-methylethyl]carbamate ((−)-14b). As in the preparation of (−)-**14a**, amide (−)-**12b** (82.0 mg, 0.329 mmol) lead tetraacetate (729.0 mg, 1.645 mmol) and benzyl alcohol (340 μL, 3.289 mmol) gave, after chromatography (30 g SiO_2, CH_2Cl_2), 106.7 mg of (−)-**14b** (0.300 mmol, 91%): ^1H NMR ($CDCl_3$, 500.132 MHz) δ 7.50−7.25 (5H, m), 6.72 (1H, d, *J* = 8.39 Hz), 6.63 (1H, d, *J* = 8.39 Hz), 6.62 (1H, br s), 6.02 (1H, dd, *J* = 17.46, 10.84 Hz), 5.12 (1H, d, *J* = 10.79 Hz), 5.06 (1H, d, *J* = 17.57 Hz), 5.09 (2H, s), 4.69 (1H, br s), 3.85 (3H, s), 3.75 (3H, s), 3.12 (1H, d, *J* = 13.47 Hz), 2.89 (1H, d, *J* = 13.52 Hz), and 1.37 (3H, s); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 154.6, 148.2, 147.6, 143.0, 136.5, 129.1, 128.4, 128.1, 128.0, 122.6, 113.7, 112.6, 110.6, 66.1, 56.6, 55.7, 55.6, 44.1, and 25.1; IR (thin film) 3358.5 (br), 3064.2 (w), 3033.4 (w), 2936.0 (m), 2834.8 (w), 1722.6 (s), 1640.7 (w), 1607.9 (w), 1589.6 (w), 1517.2 (s), 1464.2 (m), 1455.5 (m), 1264.5 (s), 1237.5 (s), 1158.4 (m), 1142.4 (m), 1067.7 (m), 1029.1 (s), 918.2 (w), 743.6 (w), and 698.3 (w) cm^{-1}; high-resolution EI MS *m/z* 355.1772, calcd for $C_{21}H_{25}NO_4$ 355.1784; $[\alpha]^{25}{}_D$ −7.70° (*c* 1.25, CH_2Cl_2).

(*S*)-*N*-(Phenylmethoxycarbonyl)-α-methylphenylalanal ((−)-15a). To a −78 °C solution of (−)-**13** (175.8 mg, 0.595 mmol) in 5 mL of CH_2Cl_2 was bubbled ozone until a faint blue appeared. Stirring continued at this temperature an additional 15 min when 500 μL of dimethyl sulfide (excess) was added, and the solution was warmed to 25 °C overnight. The crude product was diluted to 10 mL with Et_2O, washed with H_2O (1 × 1 mL), 5% $NaHCO_3$ (2 × 1 mL), and brine (1 × 1 mL), dried over $MgSO_4$, and concentrated. Chromatography (30 g of SiO_2, gradient from 10% EtOAc/90% Hex to 20% EtOAc/80% Hex) yielded 128.0 mg of (−)-**15a** (0.430 mmol, 72%): ^1H NMR ($CDCl_3$, 500.132 MHz), δ 9.53 (1H, s), 7.50−7.30 (5H, m), 7.30−7.10 (3H, m), 7.10−6.90 (2H, m), 5.19 (1H, br s), 5.15 (2H, s), 3.23 (1H, d, *J* = 13.94 Hz), 3.19 (1H, d, *J* = 13.94 Hz), and 1.35 (3H, s); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 199.9, 155.1, 136.2, 135.1, 130.1, 128.5, 128.3, 128.2, 126.9, 66.7, 62.8, 39.0, and 20.0: IR (thin film) 3402.9 (br), 3339.2 (br), 3088.4 (w), 3063.4 (w), 3030.6 (m), 2972.7 (m), 2937.9 (w), 2812.6 (br), 2708.4 (w), 1738.1 (s), 1713.1 (s), 1512.4 (w), 1454.5 (m), 1381.2 (w), 1267.4 (s), 1238.5 (m), 1086.1 (m), 1057.1 (m), and 700.2 (s) cm^{-1}; high-resolution EI MS *m/z* 297.1363, calcd for $C_{18}H_{19}NO_3$ 297.1365; $[\alpha]^{25}{}_D$ −20.8° (*c* 0.93, CH_2Cl_2).

(*S*)-*N*-(Phenylmethoxycarbonyl)-3,4-dimethoxy-α-methylphenylalanal ((−)-15b). As in the preparation of (−)-**15a**, carbamate (−)-**14b** (87.8 mg, 0.247 mmol) yielded, after prep plate chromatography (500 μm thickness, 5% EtOAc/95% CH_2Cl_2, two elutions), 46.4 mg of (−)-**15b** (0.130 mmol, 53%): ^1H NMR ($CDCl_3$, 500.132 MHz) δ 9.52 (1H, s), 7.50−7.30 (5H, m), 6.71 (1H, d, *J* = 8.13 Hz), 6.55 (1H, d, *J* = 8.13 Hz), 6.52 (1H, s), 5.23 (1H, br), 5.12 (2H, s), 3.83 (3H, s), 3.70 (3H, s), 3.11 (2H, s), and 1.37 (3H, s); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 200.0, 155.0, 148.6, 147.9, 136.0, 128.5, 128.23, 128.22, 127.5, 122.1, 113.1, 110.9, 66.7, 65.0, 62.9, 55.7, 55.6, and 38.9; IR (thin film) 3352.7 (br), 3033.5 (w), 2952.4 (m), 2833.8 (w), 1721.7 (s), 1605.9 (m), 1515.3 (s), 1455.5 (m), 1439.1 (m), 1403.4 (w), 1352.3 (w), 1273.2 (s), 1236.5 (s), 1194.1 (s), 1173.9 (s), 1070.6 (m), and 699.3 (w) cm^{-1}; high-resolution EI MS *m/z* 360.1440, calcd for $C_{19}H_{22}NO_6$ 360.1447 $(M - CHO)^+$; $[\alpha]^{25}{}_D$ −22.0° (*c* 1.835, CH_2Cl_2).

(*S*)-*N*-[(Phenylmethoxy)carbonyl]-α-methylphenylalanine ((+)-16a). To aldehyde (−)-**15a** (125.0 mg, 0.420 mmol) and 1 mL of 2-methyl-2-butene in 2 mL of *tert*-butyl alcohol at 10 °C were added $NaClO_2$ (80% technical, 95.0 mg, 0.841 mmol) and NaH_2PO_4 (116.0 mg, 0.841 mmol) in 1.8 mL of H_2O over 20 min. The mixture stirred at 25 °C for 24 h. The solution was concentrated to approximately $^1/_2$ the volume, diluted to 20 mL with H_2O, and washed with Hex (2 × 3 mL). The aqueous phase was acidified to pH 2 with 1 M HCl, saturated with NaCl, and extracted with Et_2O (3 × 10 mL). The ether layer was washed with brine (2 × 5 mL) and dried over $MgSO_4$. Removal of solvent, followed by heating to 40 °C *in vacuo* (0.03 mmHg), afforded 120.9 mg of (+)-**16a** (0.386 mmol, 92%): ^1H NMR ($CDCl_3$, 500.132 MHz) δ 10.40 (1H, v br), 7.50−7.30 (5H, m), 7.30−7.15 (3H, m), 7.10−7.00 (2H, m), 5.48 (1H, br), 5.24 (1H, m), 5.16 (1H, m), 3.46 (1H, m), 3.32 (1H, m), and 1.72 (3H, s); ^{13}C NMR ($CDCl_3$, 125.767 MHz) δ 178.8, 154.8, 136.3, 135.6, 129.9, 128.4, 128.2, 128.1 (2), 126.9, 66.6, 60.4, 41.2, and 23.4; IR (thin film) 3412.5 (m), 3200 (br s), 3065.3 (w), 3032.5 (m), 2944.7 (w), 1712.0 (s), 1503.7 (m), 1453.5 (m), 1276.1 (m), 1079.4 (m), 1057.1 (m), 779.3 (w), 738.8 (w), and 700.3 (s) cm^{-1}; high-resolution EI MS *m/z* 313.1319, calcd for $C_{18}H_{19}NO_4$ 313.1314; $[\alpha]^{25}{}_D$ + 2.3° (*c* 1.58, CH_2Cl_2).

(*S*)-Methylphenylalanine ((−)-17a). Carbamate (+)-**16a** (97.2 mg, 0.310 mmol) was dissolved in 5 mL of dry MeOH and fitted with a H_2 balloon. To this stirring solution at 25 °C was added 10 mg of 9% Pd/C, and the stirring continued for 2 h. The slurry was filtered through a pipette of Celite on cotton, concentrated, and evacuated (0.03 mmHg). The crude product was dissolved in 1 mL of MeOH and triturated with 500 μL of Et_2O. The solvent was removed via microsyringe, yielding 53.2 mg of crystalline (−)-**17a** after drying *in vacuo* (0.297 mmol, 96%). The physical data was in accord with literature values: ^1H NMR (D_2O, 500.132 MHz) δ 7.60−7.30 (5H, m), 3.38 (1H, d, *J* = 14.24 Hz), 3.07 (1H, d, *J* = 14.23 Hz), and 1.63 (3H, s); ^{13}C NMR (D_2O, 125.767 MHz) δ 178.6, 136.8, 132.6, 131.5, 130.4, 64.7, 45.2, and 24.9; high-resolution EI MS *m/z* 178.0876, calcd for $C_{10}H_{12}NO$ 178.0868; $[\alpha]^{25}{}_D$ −21.6° (*c* 1.00, H_2O); mp 307 − 309 °C dec.

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