Highly Regio- and Enantioselective Monoepoxidation of Conjugated Dienes

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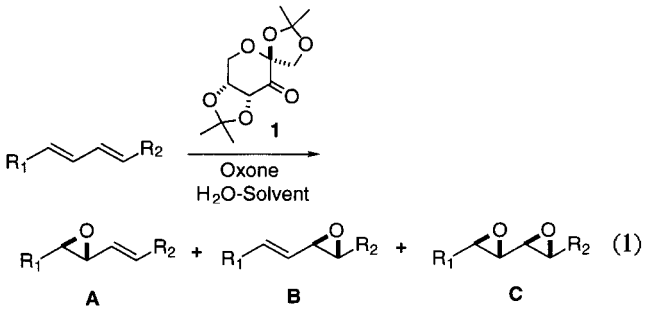
This paper describes a highly effective and mild asymmetric monoepoxidation method for conjugated dienes using a fructose-derived chiral ketone **1** as catalyst and Oxone as oxidant. The regioselectivities and enantioslectivities are very high in most cases. For unsymmetrical dienes, the regioselectivity can be regulated by using steric and electronic control. The olefin substrates include *trans*-disubstituted and trisubstituted olefins that can bear a wide range of functional groups such as hydroxyl groups, TBS ethers, or esters. The enantiomeric excesses for the major monoepoxides range from 89% to 97%. The epoxidation is believed to proceed via a spiro mode.

Enantiomerically enriched vinyl epoxides are very useful synthetic intermediates.[1] Enantioselective monoepoxidation of conjugated dienes presents an efficient approach to these epoxides.[2,3] Recently, we reported a highly enantioselective epoxidation method for *trans*-disubstituted and trisubstituted olefins using a fructose-derived ketone **1** as catalyst and Oxone as oxidant.[4] As part of our continuing effort to expand the scope of this epoxidation, we have been investigating the feasibility of regio- and enantioselective monoepoxidation of conjugated dienes with this catalyst (eq 1). The major issues that need to be addressed for the diene epoxidation include regioselectivity (**A** *vs* **B**), selectivity between monoepoxidation and bisepoxidation (**A** and **B** *vs* **C**), and enantioselectivity.[5] Herein we wish to report our efforts in this area.



(1)

Results and Discussion

Our initial investigation started with a symmetric conjugated diene, *trans,trans*-1,4-diphenyl-1,3-butadiene, as the test substrate (Table 1, entry 1). Subjecting this diene to the epoxidation conditions gave the monoepoxide along with the bisepoxide. The formation of the bisepoxide could be minimized by controlling the amount of catalyst to reduce the further epoxidation of the formed monoepoxide. When 25 mol % of catalyst **1** was used, 94% conversion of the substrate could be achieved at 0 °C with 1.5 h reaction time. The selectivity of monoepoxidation over bisepoxidation remained high (22:1). The high selectivity could be due to the fact that the first epoxide introduced deactivated the remaining olefin by the inductive effect. While the selective monoepoxidation was found to be feasible, the enantiomeric excess for the monoepoxide was also found to be pleasingly high (97%). High conversion and selectivity were also obtained for the symmetric cyclic trisubstituted diene (Table 1, entry 3). It is worth noting that the epoxidations of dienes under the current reaction conditions were generally clean as judged by the ^{1}H NMR of the crude reaction mixtures. The somewhat low isolated yields compared to the substrate conversions in most cases were due to the high sensitivity of these vinyl epoxides toward flash column isolation using silica gel.

The good selectivities obtained with the symmetric dienes encouraged us to further explore the epoxidation of unsymmetrical dienes. As shown in Table 1, the results are very encouraging. In many cases, monoepoxides were predominately obtained if the amount of

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(1) For leading references on synthetic applications of vinyl epoxides see: (a) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1173−1192. (b) Marshall, J. A. *Chem. Rev.* **1989**, *89*, 1503−1511. (c) Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483−2547.

(2) For leading references on enantioselective monoepoxidations of conjugated dienes directed by hydroxyl groups see: (a) Johnson, R. A.; Sharpless, K. B. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993; Chapter 4.1. (b) Katsuki, T.; Martin, V. S. *Org. React.* **1996**, *48*, 1−299.

(3) For leading references on enantioselective epoxidations of *cis*-olefins of conjugated dienes using chiral (salen)Mn catalysts see: (a) Lee, N. H.; Jacobsen, E. N. *Tetrahedron Lett.* **1991**, *32*, 6533−6536. (b) Chang, S.; Lee, N. H.; Jacobsen, E. N. *J. Org. Chem.* **1993**, *58*, 6939−6941. (c) Chang, S.; Heid, R. M.; Jacobsen, E. N. *Tetrahedron Lett.* **1994**, *35*, 669−672. (d) Zhang, W.; Lee, N. H.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1994**, *116*, 425−426. (e) Hamada, T.; Irie, R.; Katsuki, T. *Synlett* **1994**, 479−481. (f) Mikame, D.; Hamada, T.; Irie, R.; Katsuki, T. *Synlett* **1995**, 827−828. (g) Hentemann, M. F.; Fuchs, P. L. *Tetrahedron Lett.* **1997**, *38*, 5615−5618.

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(5) For some examples of racemic epoxidations of conjugated dienes and polyenes with dimethyldioxirane see: (a) Curci, R.; Fiorentino, M.; Troisi, L.; Edwards, J. O.; Pater, R. H. *J. Org. Chem.* **1980**, *45*, 4758−4760. (b) Ebenezer, W.; Pattenden, G. *Tetrahedron Lett.* **1992**, *33*, 4053−4056. (c) Curci, R.; Detomaso, A.; Prencipe, T.; Carpenter, G. B. *J. Am. Chem. Soc.* **1994**, *116*, 8112−8115. (d) Curci, R.; Detomaso, A.; Lattanzio, M. E.; Carpenter, G. B. *J. Am. Chem. Soc.* **1996**, *118*, 11089−11092. (e) Murray, R. W.; Singh, M.; Rath, N. *Tetrahedron Lett.* **1996**, *37*, 8671−8674. (f) Murray, R. W.; Singh, M.; Rath, N. *J. Org. Chem.* **1997**, *62*, 8794−8799. (g) Yang, D.; Wong, M.-K.; Cheung, K.-K.; Chan, E. W. C.; Xie, Y. *Tetrahedron Lett.* **1997**, *38*, 6865−6868.

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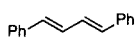
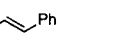
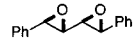
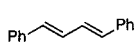
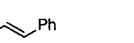
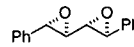
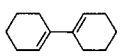
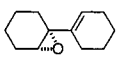
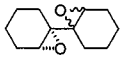
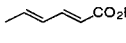
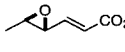
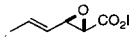
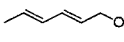
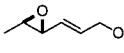
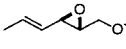
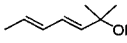
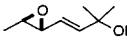
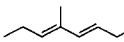
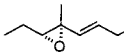
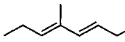
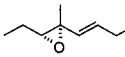
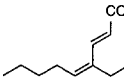
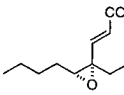
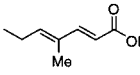
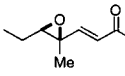
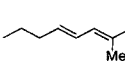
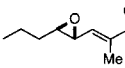
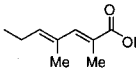
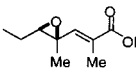
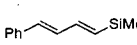
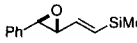
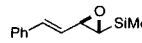
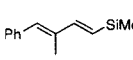
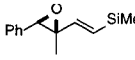
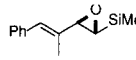
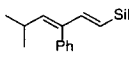
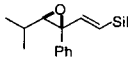
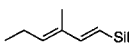
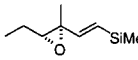
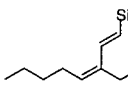
Table 1. Asymmetric Epoxidation of Representative Dienes by Ketone 1 and *ent*-1[a]

Entry	Dienes	Epoxides		Conv[b] (%)	Ratio[c]	Yield[d] (%)	ee[p] (%)
1				94[f]	22:1	77	97[k]
2			 (**ent-1**)	87[e]	26:1	65	97[k]
3				100[e]	12:1	54	95[k]
4				69[g,h]	7:1	41	96[k]
5				100[f]	4.6:1	68(13)	96(91)[l]
6				100[e]		65	89[k]
7				100[f]		68[i]	90[m]
8				100[f]		81[i]	96[n]
9				76[g]		68	95[k]
10				88[g]		82	95[k]
11				72[g]		61	94[k]
12				100[f]		89[i]	94[m]
13				77[g]	1:1	31[i,j]	95[o,q]
14				92[g]	14:1	77[i]	94[o,q]
15				100[g]		81[i]	95[o]
16				100[e]		60[i]	92[o]
17				100[g]		79[i]	95[o]

[a] All reactions were carried out at 0 °C with diene (1 equiv), ketone (0.2−0.3 equiv), Oxone (1.12−1.38 equiv), and K_2CO_3 (5.0−6.2 equiv) in CH_3CN−DMM−0.05 M $Na_2B_4O_7 \cdot 10H_2O$ of aqueous EDTA (4×10^{-4} M) solution (1:2:2, v/v). Oxone was added over 1.5 h unless otherwise stated, and the reactions were stopped immediately. [b] The conversions were determined by the ^{1}H NMR of the crude reaction mixtures. [c] The ratios were determined by the ^{1}H NMR of the crude reaction mixtures. For symmetric dienes the ratio refers to the monoepoxide/bisepoxide ratio (the precise stereochemistry of the bisepoxides has not been determined yet). For unsymmetric dienes it refers to the ratio of the two monoepoxides. For entries 6−12 and 15−17, the other monoepoxide regioisomers were barely detectable by ^{1}H NMR if there was any. [d] The epoxides were purified by flash chromatography and gave satisfactory spectroscopic characterization. The number in parentheses refers to the yield of the minor epoxide. It should be noted that the vinyl epoxides are not very stable, and portions are lost during the column isolation. [e] 0.20 equiv of catalyst used. [f] 0.25 equiv of catalyst used. [g] 0.30 equiv of catalyst used. [h] Oxone was added over 4 h, and the reaction was stopped immediately. [i] Trace amounts of bisepoxide were detected in the crude reaction mixtures by ^{1}H NMR. [j] The epoxide distal to the $SiMe_3$ group was isolated, and the epoxide proximal to the $SiMe_3$ group was detected in the crude reaction mixtures by ^{1}H NMR but decomposed during column isolation. [k] Enantioselectivities were determined by chiral HPLC (Chiralcel OD). [l] The TBS ether was converted to the corresponding alcohol with TBAF, and enantioselectivities were determined by chiral GC (Chiraldex γ-TA column). The number in parentheses refers to the ee of the minor epoxide. [m] Enantioselectivities were determined by chiral HPLC (Chiralcel OB). [n] The TBS ether was converted to the corresponding alcohol with TBAF, and enantioselectivities were determined by chiral HPLC (Chiralcel OB). [o] Enantioselectivities were determined by chiral shift NMR with Eu(hfc)$_3$. [p] The absolute configurations of the epoxides for entries 1 and 10 were determined by comparing to the authentic samples prepared by different routes, and the configurations for the remaining epoxides were tentatively assumed by analogy based on the spiro reaction mode. [q] The number refers to the ee of the epoxide distal to the $SiMe_3$ group.

catalyst was properly controlled. The enantiomeric excesses for the formed monoepoxides were also high. Some of the reaction features are highlighted as follows. If both olefins were disubstituted, regioselectivity (**A** *vs* **B**) could be regulated by using steric and electronic control. Introducing an electron-withdrawing group deactivated the adjacent olefin, resulting in the formation of the distal epoxide as the major product. For example, a 7:1 ratio was obtained for the epoxidation of ethyl sorbate (Table 1, entry 4). The allylic electron-withdrawing groups such as TBS ether, which was not conjugated to the olefin, could also substantially deactivate the proximal olefin by the inductive effect (Table 1, entry 5). The regioselectivity could be further enhanced by introducing steric hindrance next to one olefin. Such an example is illustrated in entry 6, in which only one monoepoxide was detected. Introducing an additional alkyl group to the olefin could also further regulate the regioselectivity. For example, entries 7 and 8 show that the epoxidation was highly selective for the trisubstituted olefin distal to the hydroxyl group and the TBS ether group. The regioselectivity shown in entry 7 is complementary to the Sharpless asymmetric epoxidation, which selectively epoxidizes the olefin proximal to the hydroxyl group. In the case of diene esters (Table 1, entries 9−12), it is rather interesting to note that the epoxidation regioselectively occurred on the distal olefin regardless of whether the alkyl group was introduced to the distal or to the proximal or both olefins. A possible reason for the observed selectivity could be that the introduced alkyl group(s) prevented full conjugation of the diene due to the $A_{1,3}$ strain, and therefore the distal olefin to the ester group was less electron deficient compared to the proximal olefin.

The epoxidation with dioxiranes is more sensitive to the steric environment around olefins than other epoxidizing reagents such as *m*-CPBA. The reduced reactivity of vinylsilanes for the epoxidation with dioxiranes has been observed due to the steric hindrance of the silyl groups.[6] To further probe the possibility of using the silicon group as a potential controlling element for regioselectivity, a variety of silyl-substituted dienes were prepared and studied (Table 1, entries 13−17).[7] Like the previously discussed dienes, a mixture of two epoxide regioisomers were obtained when both olefins were disubstituted (Table 1, entry 13). However, when the olefin distal to the trimethylsilyl group was trisubstituted, the epoxidation again predominately occurred on the distal olefin with high enantioselectivity.[8] The enantiomerically enriched silyl-substituted vinyl epoxides should be versatile synthetic intermediates.[9] For example, the silyl group could be further utilized as a controlling element for regioselective opening of the epoxide.

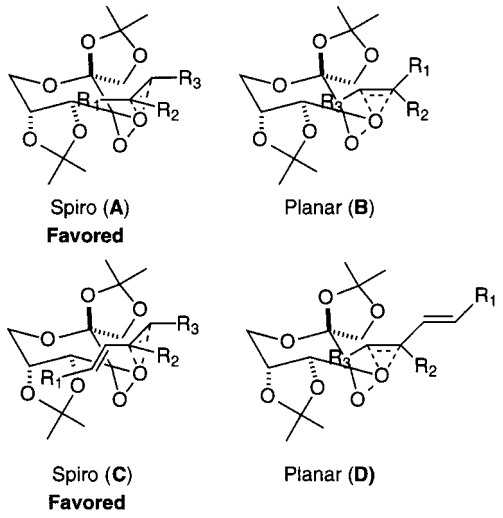


Figure 1. Possible main competing spiro and planar transition states for the epoxidation catalyzed by ketone **1**.

The epoxidation of isolated *trans*-disubstituted and trisubstituted olefins with catalyst **1** has been shown to proceed mainly via spiro transition state **A** (Figure 1).[4a,c,10] The main competing transition state is believed to be planar transition state **B** (Figure 1).[4c] The nature of the substitutents on the olefins have noticeable effects on the competition between the two transition states, consequently affecting the enantioselectivities of the epoxidation.[4c] It is believed that the spiro transition state is generally favored due to the stabilizing interaction of an oxygen lone pair of the dioxirane with the π^* orbital of the alkene.[10c,e] The transition states **C** and **D** are anticipated for the two main competing transition states for the epoxidation of the dienes. As shown in Table 1, the enantioselectivities of the epoxidation of the dienes are high regardless of whether the epoxidized olefin is disubstituted or trisubstituted. This observation shows that the spiro transition state is further favored when a conjugated diene is used as substrate. The increased favorability of the spiro transition state is presumably due to the fact that a conjugated diene has a lower LUMO than an isolated olefin leading to a greater stabilizing interaction between an oxygen lone pair of the dioxirane with the LUMO of the alkene.

As discussed above, the spiro transition state is expected for the epoxidation of dienes. The stereochemistry of the epoxides in Table 1 is assigned on the basis of this model. To further validate the assignment, the absolute configurations of two representative examples (Table 1, entries 1 and 10) were further defined either by converting the vinyl epoxide to an epoxide with known config-

(6) For examples of the epoxidation of vinylsilanes with dimethyldioxirane see: (a) Branan, B. M.; Wang, X.; Jankowski, P.; Wicha, J.; Paquette, L. A. *J. Org. Chem.* **1994**, *59*, 6874−6876. (b) Adam, W.; Prechtl, F.; Richter, M. J.; Smerz, A. K. *Tetrahedron Lett.* **1995**, *36*, 4991−4994.

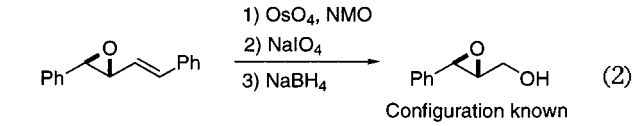
(7) The silyl-substituted dienes were readily prepared on the basis of the reported method: Ni, Z. J.; Yang, P. F.; Ng, D. K. P.; Tzeng, Y. L.; Luh, T. Y. *J. Am. Chem. Soc.* **1990**, *112*, 9356−9364.

(8) In comparison, the diene of entry 17 was epoxidized with *m*-CPBA. The distal epoxide was favored by a 2.5:1 ratio.

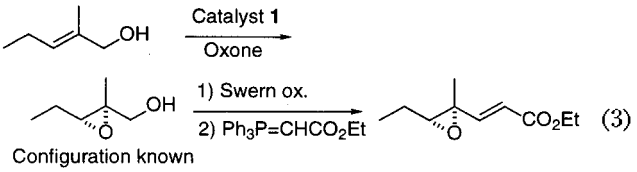
(9) For leading references on the synthesis of silyl-substituted vinyl epoxides by other methods, see: (a) Chou, W.-N.; White, J. B. *Tetrahedron Lett.* **1991**, *32*, 157−160. (b) Chou, W.-N.; White, J. B.; Smith, W. B. *J. Am. Chem. Soc.* **1992**, *114*, 4658−4667. (c) Zhou, Z.-L.; Huang, Y.-Z.; Shi, L.-L. *Tetrahedron Lett.* **1992**, *33*, 5827−5830. (d) Zhou, Y.-G.; Li, A.-H.; Hou, X- L.; Dai, L.-X. *Chem. Commun.* **1996**, 1353−1354.

(10) For leading references on the transition states of the dioxirane-mediated epoxidation see: (a) Baumstark, A. L.; McCloskey, C. J. *Tetrahedron Lett.* **1987**, *28*, 3311−3314. (b) Baumstark, A. L.; Vasquez, P. C. *J. Org. Chem.* **1988**, *53*, 3437−3439. (c) Bach, R. D.; Andres, J. L.; Owensby, A. L.; Schlegel, H. B.; McDouall, J. J. W. *J. Am. Chem. Soc.* **1992**, *114*, 7207−7217. (d) Yang, D.; Wang, X.-C.; Wong, M.-K.; Yip, Y.-C.; Tang, M.-W. *J. Am. Chem. Soc.* **1996**, *118*, 11311−11312. (e) Houk, K. N.; Liu, J.; DeMello, N. C.; Condroski, K. R. *J. Am. Chem. Soc.* **1997**, *119*, 10147−10152. (f) Jenson, C.; Liu, J.; Houk, K. N.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1997**, *119*, 12982−12983.

uration (eq 2)[11] or by preparing an authentic sample from an epoxy alcohol with known configuration following a reported sequence for the exact compound (eq 3).[12,13] In our case, it was found that the route presented in eq 2 was not a very efficient sequence, particularly for the $NaBH_4$ reduction. As a result, the overall yield for the transformation was extremely low. Nevertheless, a small amount of the hydroxy epoxide was obtained, which was sufficient for us to compare with authentic sample by chiral HPLC. The results in both cases support the initial assignment based on the spiro mode.



(2)



(3)

In summary, we report a highly effective and mild epoxidation of conjugated dienes using a fructose-derived chiral ketone **1** as catalyst and Oxone as oxidant. The regioselectivities and enantioslectivities are very high in most cases. As a result, a variety of synthetically useful vinyl epoxides can be readily produced in optically enriched form. The current method is complementary to the selective epoxidation of conjugated dienes catalyzed by chiral (salen)Mn complexes, in which the *cis*-olefins are preferentially epoxidized.[3]

Experimental Section

General Methods. Oxone was purchased from Aldrich (it has been found that the oxidation activity of the purchased Oxone occasionally varies with different batches). All glassware used for the epoxidation was carefully washed to be free of any trace metals, which catalyze the decomposition of Oxone. The 300 MHz ^{1}H NMR and 75.5 MHz ^{13}C NMR spectra were measured on a Bruker ACE-300 spectrometer in $CDCl_3$. Proton chemical shifts (δ) are given relative to internal TMS (0.00 ppm), and carbon chemical shifts are given relative to $CDCl_3$ (77.00 ppm). Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrometer. High-resolution mass spectra were performed by the mass spectrometry facility of Colorado State University. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Optical rotations were measured on an Autopol III automatic polarimeter in a 10 cm cell. Silica gel 60 of E-Merck Co. was employed for all flash chromatography.

General Epoxidation Procedure. To a 150 mL three-necked flask were added buffer (0.05 M $Na_2B_2O_4{\cdot}10\ H_2O$ in 4×10^{-4} M EDTA, 10 mL), dimethoxymethane/acetonitrile (2:1, 15 mL), *trans*,*trans*-1,4-diphenyl-1,3-butadiene (0.206 g, 1 mmol), tetrabutylammonium hydrogen sulfate (0.015 g, 0.04 mmol), and ketone **1** (0.065 g, 0.25 mmol). The reaction mixture was cooled to 0 °C with an ice bath. A solution of Oxone (0.69 g, 1.13 mmol) in aqueous EDTA (4×10^{-4} M, 6.0 mL) and a solution of K_2CO_3 (0.69 g, 4.99 mmol) in water (6.0 mL) were added separately via syringe pump over 1.5 h. The reaction was immediately quenched by the addition of hexanes (15 mL). The aqueous layer was extracted with hexanes (3×25 mL), washed with brine (50 mL), dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography (the silica gel was buffered with 1% Et_3N in hexane; 1% Et_3N in 3:1 CH_2Cl_2/hexane was used as the eluent) to afford (*R*,*R*)-2-phenyl-3-(*trans*-2-phenylvinyl)oxirane as a white solid (0.171 g, 77% yield, 97% ee) (Table 1, entry 1).

(*R*,*R*)-2-Phenyl-3-(*trans*-2-phenylvinyl)oxirane (Table 1, entry 1): white solid; $[\alpha]^{20}_D = +252.2°$ (*c* 0.24, $CHCl_3$); IR (NaCl): 3027, 1953, 1755, 1598, 1489, 1448, 1263 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.4−7.2 (m, 10H), 6.81 (d, J = 15.9 Hz, 1H), 6.09 (dd, J = 15.9, 7.5 Hz, 1H), 3.89 (d, J = 2.1 Hz, 1H), 3.53 (dd, J = 7.5, 2.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.0, 136.0, 134.4, 128.7, 128.5, 128.2, 128.1, 126.5, 126.2, 125.5, 63.12, 60.70. Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.34. Found: C, 86.43; H, 6.55.

(*R*,*R*)-1-Cyclohexenylcyclohexene Oxide (Table 1, entry 3). The diene substrate was prepared by pinacolic coupling of cyclohexanone[14] and dehydration of the resulting diol[15] to give a white solid (36% overall yield): IR (NaCl) 3037, 2924, 2855, 1439 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78 (s, 2H), 2.20−2.05 (m, 8H), 1.70−1.50 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.8, 121.4, 25.85, 25.50, 23.13, 22.51.

Epoxide: colorless oil; $[\alpha]^{20}_D = +6.67°$ (*c* 0.29, $CHCl_3$); IR (NaCl) 2932, 2857, 1439, 1344, 1220, 1136, 980, 920, 834 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.73 (m, 1H), 3.04 (dd, J = 3.6, 1.5 Hz, 1H), 2.1−1.1 (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3, 122.6, 61.81, 58.81, 27.39, 24.93, 24.80, 24.55, 22.62, 22.33, 20.09, 19.91; HRMS calcd for $C_{12}H_{19}O$ ($M^+ + 1$) 179.1437, found 179.1437.

(*R*,*R*)-2-[*trans*-2-(Ethoxycarbonyl)vinyl]-3-methyloxirane (Table 1, entry 4): colorless oil; $[\alpha]^{20}_D = +12.64°$ (*c* 0.48, $CHCl_3$); IR (NaCl) 2984, 2933, 1721, 1655, 1446, 1370, 1340, 1188, 1144 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.67 (dd, J = 15.6, 7.2 Hz, 1H), 6.13 (d, J = 15.6 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 3.18 (dd, J = 7.2, 1.8 Hz, 1H), 2.98 (qd, J = 5.1, 1.8 Hz, 1H), 1.39 (d, J = 5.1 Hz, 3H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 144.6, 123.7, 60.50, 57.37, 57.21, 17.50, 14.19; HRMS calcd for $C_8H_{13}O_3$ ($M^+ + 1$) 157.0864, found 157.0865.

(*R*,*R*)-2-[*trans*-2-[(*tert*-Butyldimethylsiloxy)methyl]vinyl]-3-methyloxirane (Table 1, entry 5). The diene substrate was prepared from (*E*,*E*)-2,4-hexadien-1-ol and *tert*-butyldimethylsilyl chloride[16] to give a colorless oil (99% yield): IR (NaCl) 3020, 2954, 2931, 2856, 1467, 1379, 1255, 1111 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.25−6.00 (m, 2H), 5.75−5.55 (m, 2H), 4.19 (d, J = 4.5 Hz, 2H), 1.75 (d, J = 6.6 Hz, 3H), 0.91 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.0, 130.3, 129.9, 129.0, 63.70, 26.00, 18.46, 18.11, −5.13.

Epoxide: colorless oil; $[\alpha]^{20}_D = +28.6°$ (*c* 0.71, EtOH); IR (NaCl) 2956, 2931, 2857, 1620, 1468, 1381, 1255, 1125 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.98 (dt, J = 15.3, 4.5 Hz, 1H), 5.45 (ddtd, J = 15.3, 8.1, 1.8, 0.9 Hz, 1H), 4.19 (dd, J = 4.5, 1.8 Hz, 2H), 3.09 (dd, J = 8.1, 2.1 Hz, 1H), 2.91 (qdd, J = 5.1, 2.1, 0.9 Hz, 1H), 1.34 (d, J = 5.1 Hz, 3H), 0.91, (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.5, 127.2, 62.87, 59.08. 56.40, 25.89, 18.36, 17.54, −5.41. Anal. Calcd for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.59. Found: C, 62.96; H, 10.30..

(*R*,*R*)-2-[(*tert*-Butyldimethylsiloxy)methyl]-3-(*trans*-2-methylvinyl)oxirane (Table 1, entry 5): colorless oil; $[\alpha]^{20}_D = +17.7°$ (*c* 0.45, EtOH); IR (NaCl) 3051, 2955, 2928, 2857, 1464, 1382, 1260, 1109 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.94 (dq, J = 15.3, 6.6 Hz, 1H), 5.22 (ddq, J = 15.3, 8.1, 1.8 Hz, 1H), 3.84 (dd, J = 12.3, 3.6 Hz, 1H), 3.70 (dd, J = 12.3, 4.5 Hz, 1H), 3.24 (dd, J = 8.1, 2.4 Hz, 1H), 3.02−2.97 (m, 1H), 1.74 (dd, J = 6.6, 1.8 Hz, 3H), 0.90 (s, 9H), 0.08 (s, 3H), 0.072

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(16) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190−6191.

(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.8, 128.2, 63.23, 60.17, 56.16, 25.88, 18.30, 17.86, −5.31. Anal. Calcd for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.59. Found: C, 63.02; H, 10.46.

(*R,R*)-2-[*trans*-2-(1-Methoxy-1-methylethyl)vinyl]-3-methyloxirane (Table 1, entry 6). The diene substrate was prepared from ethyl sorbate by treatment with MeLi (2 equiv) and then NaH/MeI[17] to give a colorless oil (39% yield): IR (NaCl) 3017, 2922, 2856, 1454, 1373, 1241, 1161, 1073, 992 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.15−6.00 (m, 2H), 5.76−5.64 (m, 1H), 5.57−5.45 (m, 1H), 3.14 (s, 3H), 1.76 (d, J = 6.6, 0.6 Hz, 3H), 1.27 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.0, 131.1, 129.7, 129.2, 74.80, 50.27, 25.82, 18.00.

Epoxide: colorless oil; $[\alpha]^{20}_D$ = +22.0° (*c* 0.20, $CHCl_3$); IR (NaCl) δ 2977, 2934, 2825, 1455, 1378, 1246, 1169, 1075 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.89 (d, J = 15.9 Hz, 1H), 5.30 (dd, J = 15.9, 8.1 Hz, 1H), 3.16 (s, 3H), 3.08 (dd, J = 8.1, 1.8 Hz, 1H), 2.93 (dq, J = 5.1, 1.8 Hz, 1H), 1.35 (d, J = 5.1 Hz, 3H), 1.27 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.7, 127.4, 74.51, 59.24, 56.39, 50.43, 25.61, 17.51; HRMS calcd for $C_9H_{17}O_2$ (M^+ + 1) 157.1228, found 157.1225.

(*R,R*)-3-Ethyl-2-[*trans*-2-(hydroxymethyl)vinyl]-2-methyloxirane (Table 1, entry 7). The diene substrate was prepared by DIBAL reduction of (*E,E*)-ethyl-4-methyl-2,4-heptadienoate to give a colorless oil (81% yield): IR (NaCl) 3332, 3027, 2961, 2925, 2867, 1646, 1450, 1392, 1305, 1087, 963 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.24 (d, J = 15.6 Hz, 1H), 5.71 (dt, J = 15.6, 6.3 Hz, 1H), 5.49 (t, J = 7.4 Hz, 1H), 4.18 (d, J = 6.3 Hz, 2H), 2.14 (quintet, J = 7.4 Hz, 2H), 1.78 (br s, 1H), 1.75 (s, 3H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.7, 135.1, 132.3, 125.1, 63.87, 21.45, 13.90, 12.17.

Epoxide: colorless oil; $[\alpha]^{20}_D$ = −8.14° (*c* 0.52, $CHCl_3$); IR (NaCl) 3416, 2970, 2934, 2875, 1670, 1460, 1385, 1276, 1222, 1096, 1071, 1013, 971, 880 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (dt, J = 15.9, 5.1 Hz, 1H), 5.53 (d, J = 15.9 Hz, 1H), 4.12 (t, J = 5.1 Hz, 2H), 2.76 (t, J = 6.3 Hz, 1H), 2.29 (br s, 1H), 1.65−1.5 (m, 2H), 1.37 (s, 3H), 1.01 (t, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.9, 130.7, 66.61, 62.65, 59.07, 21.89, 15.24, 10.32; HRMS calcd for $C_8H_{15}O_2$ (M^+ + 1) 143.1073, found 143.1073.

(*R,R*)-3-Ethyl-2-[*trans*-2-[(*tert*-butyldimethylsiloxy)methyl]vinyl]-2-methyloxirane (Table 1, entry 8). The diene substrate was prepared from (*E,E*)-4-methyl-2,4-heptadien-1-ol and *tert*-butyldimethylsilyl chloride[16] to give a colorless oil (82% yield): IR (NaCl) 3034, 2954, 2925, 2852, 1646, 1465, 1377, 1297, 1254, 1123, 1072, 963, 840, 724 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.23 (d, J = 15.6 Hz, 1H), 5.63 (dt, J = 15.6, 5.7 Hz, 1H), 5.46 (t, J = 6.9 Hz, 1H), 4.25 (d, J = 5.7 Hz, 2H), 2.14 (qd, J = 7.5, 6.9 Hz, 2H), 1.75 (s, 3H), 0.99 (t, J = 7.5 Hz, 3H), 0.92 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.0, 134.2, 132.5, 125.7, 64.17, 25.98, 21.45, 18.42, 14.01, 12.24, −5.133.

Epoxide: colorless oil; $[\alpha]^{20}_D$ = −9.2° (*c* 1.57, $CHCl_3$); IR (NaCl) 2959, 2935, 2857, 1456, 1386, 1252, 1118, 1071, 961, 835, 772 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.83 (dt, J = 15.6, 4.5 Hz, 1H), 5.54 (dt, J = 15.6, 1.8 Hz, 1H), 4.19 (dd, J = 4.5, 1.8 Hz, 2H), 2.77 (t, J = 6.0 Hz, 1H), 1.61 (m, 2H), 1.39 (s, 3H), 1.04 (t, J = 8.4 Hz, 3H), 0.91 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.7, 130.8, 66.64, 63.21, 59.10, 25.97, 22.06, 18.43, 15.48, 10.45, −5.21. Anal. Calcd for $C_{14}H_{28}O_2Si$: C, 65.57; H, 11.01. Found: C, 65.70; H, 10.84.

(2*S*,3*R*)-3-Butyl-2-[*trans*-2-(ethoxycarbonyl)vinyl]-2-propyloxirane (Table 1, entry 9). The diene substrate was prepared by treatment of (*Z*)-2-propyl-2-heptenal with NaH and triethyl phophonoacetate to produce a colorless oil (85% yield): IR (NaCl) 2959, 2931, 2871, 1714, 1624, 1463, 1367, 1301, 1258, 1168 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, J = 15.9 Hz, 1H), 5.88 (t, J = 7.5 Hz, 1H), 5.79 (d, J = 15.9 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 2.25−2.15 (m, 4H), 1.48−1.27 (m, 9H), 0.96−0.88 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.7, 149.0, 142.6, 137.2, 115.1, 60.08, 31.37, 28.60, 28.46, 22.42, 21.92, 14.31, 14.16, 13.88.

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Epoxide: colorless oil; $[\alpha]^{20}_D$ = −58.8° (*c* 0.39, $CHCl_3$); IR (NaCl) 2961, 2932, 2872, 1722, 1655, 1464, 1367, 1305, 1265, 1165, 1041, 980 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.96 (d, J = 15.6 Hz, 1H), 6.00 (d, J = 15.6 Hz, 1H), 4.19 (q, J = 7.2 Hz, 2H), 2.74 (t, J = 6.3 Hz, 1H), 1.8−1.32 (m, 13H), 1.0−0.9 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 148.5, 120.9, 67.11, 61.90, 60.44, 32.02, 28.55, 28.17, 22.50, 18.75, 14.28, 14.21, 13.93. Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07. Found: C, 70.17; H, 9.97.

(*R,R*)-2-[*trans*-2-(Ethoxycarbonyl)vinyl]-3-ethyl-2-methyloxirane (Table 1, entry 10). The diene substrate was prepared by Wittig reaction of (*E*)-2-methyl-2-pentenal and (carbethoxymethylene)triphenylphosphorane to give a colorless oil (99% yield): IR (NaCl) 3066, 2971, 2935, 2874, 1713, 1625, 1294, 1263, 1170 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, J = 15.6 Hz, 1H), 5.89 (t, J = 7.2 Hz, 1H), 5.79 (d, J = 15.6 Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 2.21 (quintet, J = 7.2 Hz, 2H), 1.77 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H), 1.03 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.5, 149.6, 143.6, 132.2, 115.5, 60.08, 22.05, 14.31, 13.45, 11.93.

Epoxide:[13a] colorless oil; $[\alpha]^{20}_D$ = −36.8° (*c* 0.65, $CHCl_3$).

(*R,R*)-2-[(*E*)-2-(Ethoxycarbonyl)-2-methylvinyl]-3-propyloxirane (Table 1, entry 11). The diene substrate was prepared by Wittig reaction of 2-(carbethoxyethyl)triphenylphosphonium bromide with *trans*-2-hexenal to produce a colorless oil (59% yield): IR (NaCl) 2960, 2931, 2872, 1705, 1641, 1610, 1464, 1389, 1367, 1291, 1238, 1167, 1103, 1038, 971, 749 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (d, J = 11.1 Hz, 1H), 6.34 (dd, J = 15.0, 11.1 Hz, 1H), 6.06 (dt, J = 15.0, 7.2 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 2.18 (dt, J = 7.2, 6.6 Hz, 2H), 1.93 (s, 3H), 1.55−1.40 (m, 2H), 1.30 (t, J = 7.2 Hz, 3H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.5, 142.7, 138.4, 126.0, 124.9, 60.35, 35.30, 22.17, 14.33, 13.67, 12.53.

Epoxide: colorless oil; $[\alpha]^{20}_D$ = +40.6° (*c* 1.61, $CHCl_3$); IR (NaCl) 2962, 2934, 2874, 1714, 1654, 1465, 1368, 1311, 1253, 1236, 1160, 1103, 1033, 976, 914, 858, 747 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.30 (d, J = 8.4 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 3.38 (dd, J = 8.4, 1.8 Hz, 1H), 2.96 (td, J = 5.7, 1.8 Hz, 1H), 2.00 (s, 3H), 1.65−1.40 (m, 4H), 1.29 (t, J = 7.2 Hz, 3H), 0.98 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 137.9, 132.0, 60.72, 59.99, 54.43, 33.91, 19.19, 14.17, 13.84, 12.75. Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.77; H, 8.96.

(*R,R*)-2-[(*E*)-2-(Ethoxycarbonyl)-2-methylvinyl]-3-ethyl-2-methyloxirane (Table 1, entry 12). The diene was prepared by Wittig reaction of 2-(carbethoxyethyl)triphenylphosphonium bromide with *trans*-2-methyl-2-pentenal to give a colorless oil (91% yield): IR (NaCl) 2966, 2933, 2872, 1703, 1626, 1456, 1364, 1246, 1108, 1031, 1010, 923, 872, 749, 667 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (s, 1H), 5.62 (t, J = 7.2 Hz, 1H), 4.19 (q, J = 6.9 Hz, 2H), 2.15 (quintet, J = 6.9 Hz, 2H), 2.01 (s, 3H), 1.84 (s, 3H), 1.30 (t, J = 6.9 Hz, 3H), 1.02 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.0, 142.8, 138.2, 131.4, 124.9, 60.40, 21.63, 16.03, 14.26, 13.89, 13.66.

Epoxide: colorless oil; $[\alpha]^{20}_D$ = −90.7° (*c* 1.63, $CHCl_3$) [lit.[13b] $[\alpha]^{23}_D$ = +78.3° (*c* 1.15, $CHCl_3$) for (*S,S*)].

(*R,R*)-2-[*trans*-2-(Trimethylsilyl)vinyl]-3-phenyloxirane (Table 1, entry 13). The diene substrate was prepared by Ni-catalyzed coupling of an allylic dithioacetal with [(trimethylsilyl)methyl]magnesium chloride[7] to give a white solid (88% yield): mp 38−40 °C; IR (NaCl) 3077, 3017, 2957, 2897, 1572, 1445, 1243, 1010, 868, 839, 734, 689 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, J = 8.7 Hz, 2H), 7.35 (t, J = 7.2 Hz, 2H), 7.26 (m, 1H), 6.71 (dd, J = 17.4, 10.2 Hz, 1H), 6.82 (dd, J = 15.3, 10.2 Hz, 1H), 6.61 (d, J = 15.3 Hz, 1H), 6.01 (d, J = 17.4 Hz, 1H), 0.15 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 137.2, 135.0, 132.9, 131.6, 128.6, 127.6, 126.5, −1.28.

Epoxide: colorless oil; $[\alpha]^{20}_D$ = +137.4° (*c* 0.915, $CHCl_3$); IR (NaCl) 3063, 3034, 2953, 2912, 1615, 1494, 1453, 1251, 989, 850, 757, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (m, 5H), 6.23 (d, J = 18.6 Hz 1H), 5.87 (dd, J = 18.6, 7.2 Hz, 1H), 3.81 (d, J = 2.1 Hz, 1H), 3.35 (dd, J = 7.2, 2.1 Hz, 1H), 0.11 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0, 137.1, 136.4, 128.4,

128.1, 125.4, 64.49, 60.28, −1.55. Anal. Calcd for $C_{13}H_{18}OSi$: C, 71.50; H, 8.31. Found: C, 71.41; H, 8.27.

(*R*,*R*)-2-Methyl-2-[*trans*-2-(trimethylsilyl)vinyl]-3-phenyloxirane (Table 1, entry 14). The diene substrate was prepared by Ni-catalyzed coupling of an allylic dithioacetal with [(trimethylsilyl)methyl]magnesium chloride[7] to give a colorless oil (53% yield): IR (NaCl) 3077, 3056, 3019, 2954, 2889, 1600, 1579, 1491, 1444, 1257, 983, 871, 836, 730, 697 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.33 (m, 5H), 6.75 (d, J = 18.9 Hz, 1H), 6.60 (s, 1H), 5.99 (d, J = 18.9 Hz, 1H), 2.03 (s, 3H), 0.15 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.8, 137.9, 137.1, 132.3, 129.2, 128.5, 128.1, 126.6, 13.37, −1.12.

Epoxide: colorless oil; $[\alpha]^{20}_D$ = +63.6° (*c* 0.905, $CHCl_3$); IR (NaCl) 3002, 3021, 2956, 1610, 1245, 982, 866, 839, 723 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.6−7.4 (m, 5H), 6.09 (d, J = 18.9 Hz, 1H), 5.95 (d, J = 18.9 Hz, 1H), 3.95 (s, 1H), 1.19 (s, 3H), 0.11 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.1, 135.9, 131.9, 128.0, 127.5, 126.5, 65.62, 62.99, 14.18, −1.38. Anal. Calcd for $C_{14}H_{20}OSi$: C, 72.35; H, 8.67. Found: C, 72.35; H, 8.75.

(2*S*,3*R*)-3-Isopropyl-2-[*trans*-2-(trimethylsilyl)vinyl]-2-phenyloxirane (Table 1, entry 15). The diene substrate was prepared by Ni-catalyzed coupling of an allylic dithioacetal with [(trimethylsilyl)methyl]magnesium chloride[7] to give a semicrystalline solid (86% yield): IR (NaCl) 3077, 3054, 3024, 2957, 2927, 2897, 2867, 1580, 1235, 988, 867, 839, 704 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35 (m, 3H), 7.10 (dt, J = 6.6, 1.5 Hz, 2H), 6.7 (dd, J = 18.9, 0.6 Hz, 1H), 5.58 (d, J = 10.2 Hz, 1H), 5.32 (d, J = 18.9 Hz, 1H), 2.25 (m, 1H), 0.935 (d, J = 6.6 Hz, 6H), 0.04 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.0, 142.3, 140.8, 138.5, 130.1, 129.8, 128.2, 126.9, 28.53, 23.21, −0.952.

Epoxide: colorless oil; $[\alpha]^{20}_D$ = −29.7° (*c* 0.93, $CHCl_3$); IR (NaCl) 3061, 3030, 2958, 1610, 1466, 1449, 1248, 987, 864, 840, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35 (m, 5H), 6.12 (d, J = 18.9 Hz, 1H), 5.88 (d, J = 18.9 Hz, 1H), 2.80 (d, J = 8.7 Hz, 1H), 1.02 (d, J = 5.1 Hz, 3H), 1.0−0.9 (m, 1H), 0.812 (d, J = 6.2 Hz, 3H), 0.08 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.8, 136.5, 132.9, 127.9, 127.5, 127.3, 73.09, 66.45, 27.8, 19.76, 17.87, −1.42. Anal. Calcd for $C_{16}H_{24}OSi$: C, 73.78; H, 9.29. Found: C, 73.41; H, 8.96.

(*R*,*R*)-3-Ethyl-2-methyl-2-[*trans*-2-(trimethylsilyl)vinyl]oxirane (Table 1, entry 16). The diene substrate was prepared by Ni-catalyzed coupling of an allylic dithioacetal with [(trimethylsilyl)methyl]magnesium chloride[7] to give a colorless oil (64% yield): IR (NaCl) 2957, 2893, 2874, 1677, 1632, 1581, 1453, 1289, 1248, 1203, 986, 864, 832, 755, 730, 685 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.55 (d, J = 18.9 Hz, 1H), 5.73 (d, J = 18.9 Hz, 1H), 5.56 (t, J = 7.5 Hz, 1H), 2.17 (quintet, J = 7.5 Hz, 2H), 1.75 (s, 3H), 1.01 (t, J = 7.5, 3H), 0.01 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.7, 136.0, 134.71, 125.4, 21.68, 13.96, 11.67, 0.71.

Epoxide: colorless oil; $[\alpha]^{20}_D$ = −16.1° (*c* 0.99, $CHCl_3$); IR (NaCl) 2960, 2898, 1614, 1383, 1249, 1198, 988, 869, 840, 730, 694 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.98 (d, J = 18.9 Hz, 1H), 5.79 (d, J = 18.9 Hz, 1H), 2.77 (t, J = 6.3 Hz, 1H), 1.74−1.55 (m, 2H), 1.4 (s, 3H), 1.05 (t, J = 7.8 Hz, 3H), 0.08 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.2, 131.0, 66.60, 60.36, 22.1, 14.74, 10.51, −1.38. Anal. Calcd for $C_{10}H_{20}OSi$: C, 65.15; H, 10.93. Found: C, 65.30; H, 10.75.

(2*S*,3*R*)-3-Butyl-2-[*trans*-2-(trimethylsilyl)vinyl]-2-propyloxirane (Table 1, entry 17). The diene substrate was prepared by Ni-catalyzed coupling of an allylic dithioacetal with [(trimethylsilyl)methyl]magnesium chloride[7] to give a colorless oil (79% yield): IR (NaCl) 2957, 2932, 2874, 1677, 1626, 1581, 1466, 1370, 1248, 1203, 986, 864, 838, 742, 691, 621 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.44 (d, J = 18.9 Hz, 1H), 5.72 (d, J = 18.9 Hz, 1H), 5.53 (t, J = 7.5 Hz, 1H), 2.15 (m, 4H), 1.37 (m, 6H), 0.92 (m, 6H), 0.09 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7, 139.8, 134.5, 124.8, 31.86, 28.3, 28.09, 22.48, 22.24, 14.37, 13.96, −1.10.

Epoxide: colorless oil; $[\alpha]^{20}_D$ = −26.2° (*c* 1.04, EtOH); IR (NaCl) 2958, 2870, 1615, 1248, 989, 865, 834 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.93 (s, 2H), 2.72 (dd, J = 6.6, 5.4 Hz, 1H), 1.75−1.35 (m, 10H), 0.965 (t, J = 7.2 Hz, 3H), 0.92 (t, J = 7.2 Hz, 3H), 0.07 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 130.4, 66.68, 63.74, 32.22, 29.01, 28.59, 22.85, 19.02, 14.71, −1.09. Anal. Calcd for $C_{14}H_{28}OSi$: C, 69.93; H, 11.74. Found: C, 69.87; H, 11.51.

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Supporting Information Available: The NMR spectral, GC, and HPLC data for the determination of the enantiomeric excess of the formed epoxides (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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