Chiral Ketone Catalyzed Highly Chemo- and Enantioselective Epoxidation of Conjugated Enynes

Zhi-Xian Wang, Guo-An Cao, and Yian Shi*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

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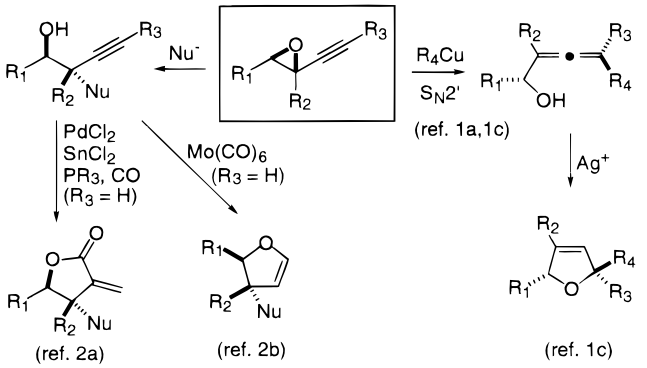
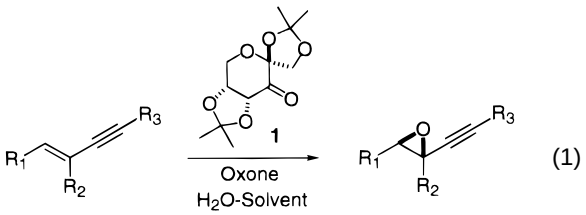
Chiral alkynyloxiranes are very useful synthetic intermediates. The alkynyl group is a synthetically versatile functional group, and it provides a controlling group for regioselective opening of the epoxide (Scheme 1).[1,2] In addition, some important natural products contain alkynyloxiranes (for example, the antitumor agent neocarzinostatin[3]). Enantioselective epoxidation of enynes would provide a direct approach to alkynyloxiranes.[4,5]

Recently we reported a highly enantioselective epoxidation method for trans- and trisubstituted olefins using a fructose-derived ketone **1** as catalyst and Oxone as oxidant.[6] In an effort to expand the scope of this epoxidation, we have been investigating the feasibility of chemo- and enantioselective epoxidation of enynes with this catalyst (eq 1). Although dioxiranes are known to be able to epoxidize C−C triple bonds,[7] chemoselective epoxidation of the enynes using dimethyldioxirane has been observed.[8] Herein we report our detailed studies on

Scheme 1



the asymmetric epoxidation of enynes using ketone **1** as catalyst and Oxone as oxidant.[9]



(1)

Results and Discussion

The enyne substrates were readily synthesized by known procedures. The substituted 6-membered cyclic enynes were prepared from commercially available 1-ethynylcyclohexene (Table 1, entries 3−5). The other cyclic enynes were prepared by reacting a ketone and an acetylide to give the propargyl alcohol, which was then converted to its carbonate. The resulting carbonate was converted to an enyne by Pd(0) catalyst.[10] The acyclic enynes were prepared from readily available α,β-unsaturated aldehydes using the Corey−Fuchs procedure.[11]

Our investigation started with 1-ethynylcyclohexene as the test substrate (Table 1, entry 1). Subjecting this enyne to the epoxidation conditions led to a chemoselective epoxidation of the double bond. The analysis of the epoxide using chiral GC (Chiraldex B-TA column) showed 93% ee. Further studies demonstrated that the acetylene could bear different substituents such as alkyl, TMS, and ester groups (Table 1, entries 3−5). The epoxidation could also extend to many other enynes. The ^{1}H NMR spectra of the crude reaction mixtures in all cases were very clean and showed that the epoxidations chemoselectively occurred at the double bond. Among cyclic enynes, the 5- and 12-membered systems gave somewhat lower ee than the 6- and 8-membered systems. Most of the tested acyclic disubstituted and trisubstituted enynes gave high enantioselectivities. In contrast to certain isolated trisubsti-

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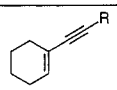
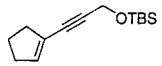
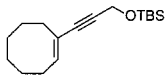
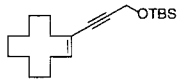
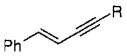
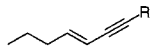
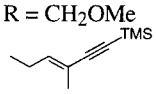
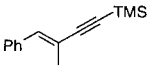
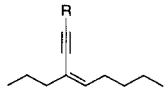
Table 1. Asymmetric Epoxidation of Enynes Catalyzed by Ketone 1 & ent-1[a]

entry	substrate	T (°C)	t (h)	yield (%)[c]	ee (%)	config.
						
1	R = H	-10	3	78	93[d]	(R,R)[i]
2	R = H (**ent-1**)	-10	3	75	94[d]	(S,S)[i]
3	R = CH_3	-10	3	88	90[d]	(R,R)[j]
4	R = TMS	-10	3	86	93[e]	(R,R)[i]
5	R = CO_2Et	0	2	71	93[f]	(R,R)[j]
						
6		-10	3	97	77[g]	(R,R)[j]
						
7		-10	3	98	96[g]	(R,R)[j]
						
8		-10	3	99	86[g]	(R,R)[j]
						
9[b]	R = TMS	0	4	59	96[g]	(R,R)[i]
10[b]	R = TBS	0	4	60	96[g]	(R,R)[i]
11[b]	R = Me	0	3	35	94[h]	(R,R)[j]
						
12	R = TMS	-10	4	71	89[g]	(R,R)[i]
13	R = TBS	-10	4	69	89[g]	(R,R)[i]
14	R = CH_2OMe	-10	4	35	89[g]	(R,R)[j]
						
15		-10	3	84	95[g]	(R,R)[i]
						
16		0	2	64	94[g]	(R,R)[i]
						
17	R = H	-10	3	60	93[f]	(R,R)[j]
18	R = TMS	-10	3	83	97[g]	(R,R)[j]
19	R = TBS	-10	2	93	97[g]	(R,R)[j]

[a] All reactions except entries 9−11 were carried out with substrate (1 equiv), ketone (0.3 equiv), Oxone (1.38 equiv), and K_2CO_3 (5.8 equiv) in CH_3CN−DMM−aqueous K_2CO_3/AcOH solution (prepared by adding 0.5 mL of AcOH to 100 mL of 0.1 M aqueous K_2CO_3, pH 9.3) (1:2:2, v/v). [b] The reaction was run with substrate (1 equiv), ketone (0.5 equiv), Oxone (2.07 equiv), and K_2CO_3 (8.7 equiv) in CH_3CN−DMM−aqueous K_2CO_3/AcOH solution (1:2:2, v/v). [c] The epoxides were purified by flash chromatography and gave satisfactory spectroscopic characterization. [d] Enantioselectivity was determined by chiral GC (Chiraldex B-TA column). [e] Enantioselectivity was determined by chiral GC (Chiraldex B-TA column) after desilylation. [f] Enantioselectivity was determined by ^1H NMR shift analysis of the epoxide products directly with $Eu(hfc)_3$. [g] Enantioselectivity was determined by chiral HPLC (Chiralcel OD). [h] Enantioselectivity was determined by chiral GC (Chiraldex G-TA column). [i] The absolute configuration was determined by a correlation of the epoxide with a prepared authentic sample (see text). [j] The absolute configuration was tentatively assumed by analogy based on the spiro reaction mode.

tuted olefins,[6c] the enantioselectivity for the trisubstitued enynes is certainly high, which indicates that the alkyne groups are beneficial for chiral induction.

To determine the absolute configurations of the epoxides, correlations of representative cyclic, disubstituted, and trisubstituted enyne epoxides (Table 1, entries 1, 2, 4, 9, 10, 12, 13, 15, and 16) were made with authentic samples prepared from epoxy alcohols with known configuration.[6e,12] In the cases of silyl-substituted epoxides, the comparisons were made after the silyl groups were removed by TBAF. A represetative reaction sequence for the preparation of the authentic sample is shown in eq 2. The chiral epoxy alcohol obtained from the epoxidation of the allylic alcohol was oxidized to the aldehyde, which was subsequently converted to the alkyne.[13] In all of these cases, the configurations obtained are consistent with the spiro transition state.[6,14]

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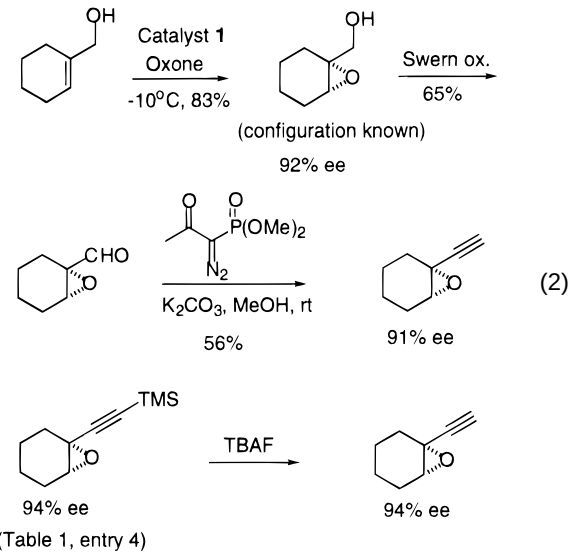


It is widely believed that the spiro transition state is favored due to a stabilizing interaction of an oxygen lone pair of the dioxirane with the π^* orbital of the olefin.[14c,e] In the present case, the conjugation of an alkyne to the olefin results in a lowering of the olefin's LUMO. As a result, the overlap of the oxygen lone pair with the olefin's LUMO in the spiro transition state becomes even more favorable. Previously we have shown that the main competing transition state with this system is the planar transition state **B** (Scheme 2).[6c] The competition between spiro **A** and planar **B** is affected by the steric bulk of substituents on the olefin. Higher ee can be obtained by decreasing the size of R_a (favoring spiro **A**) and increasing the size of R_c (disfavoring planar **B**). The epoxidation of the enynes in Table 1 is expected to proceed via spiro transition states **C** and **D**. The sterically less demanding acetylene groups should favor the spiro transition states, particularly spiro **C**.

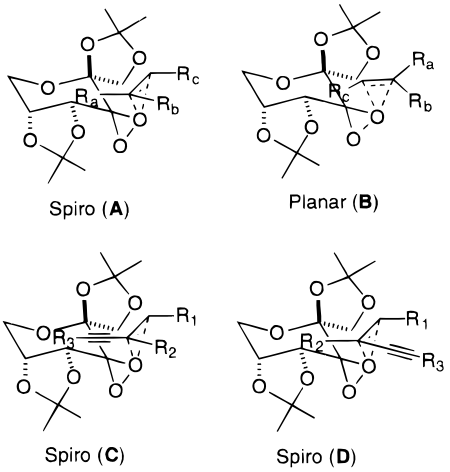
In summary, we have found that the epoxidation of conjugated enynes using a fructose-derived chiral ketone **1** as catalyst and Oxone as oxidant is highly chemo-, enantioselective, and stereospecific. The alkyne groups are beneficial for the enantioselectivity due to both electronic and steric effects. The availability of these enantiomerically enriched enyne epoxides provides opportunities for potential synthetic applications.

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. Elemental analyses were performed by M−H−W Laboratories, Phoenix, AZ. Silica gel 60 of E-Merck Co. was employed for all flash chromatography.

General Epoxidation Procedure. To a mixture of 1-ethynylcyclohexene (0.53 g, 5 mmol) and ketone **1** (0.387 g, 1.5 mmol) in DMM−CH_3CN (40 mL, 2:1 v/v) were added aqueous K_2CO_3/AcOH (prepared by adding 0.5 mL AcOH to 100 mL of 0.1 M aqueous K_2CO_3, pH 9.3) (25 mL) and a catalytic amount of Bu_4NHSO_4. After the mixture was cooled to −10 °C, a solution of Oxone (4.25 g, 6.9 mmol) in 20 mL of aqueous Na_2(EDTA) (4×10^{-4} M) and a solution of K_2CO_3 (4.0 g, 29 mmol) in 20 mL of water were added dropwise simultaneously from separate syringes via syringe pump(s) over 3 h. The reaction was then quenched by adding pentane (40 mL) and water (30 mL). The aqueous layer was extracted with pentane (3×40 mL). The combined extracts were washed with brine, dried (Na_2SO_4), concentrated, and purified by flash chromatography (pentane−ether, 1:0 to 10:1 v/v) to give (*R*,*R*)-1-ethynylcyclohexene oxide[1a,5b] as a colorless oil (0.48 g, 78% yield, 93% ee) (Table 1, entry 1). $[\alpha]^{23}_D = +22.36$ (*c* 0.93, $CHCl_3$).

Scheme 2



(*S*,*S*)-1-Ethynylcyclohexene Oxide[1a,5b] (Table 1, entry 2). Colorless oil. $[\alpha]^{23}_D = -22.44$ (*c* 1.1, $CHCl_3$).

(*R*,*R*)-1-(1′-Propynyl)cyclohexene Oxide (Table 1, entry 3). Enyne. Colorless liquid. ^{1}H NMR δ: 5.99 (br s, 1H), 2.10−2.03 (m, 4H), 1.93 (s, 3H), 1.64−1.53 (m, 4H). ^{13}C NMR δ: 133.1, 121.1, 82.7, 81.6, 29.6, 25.6, 22.5, 21.7, 4.11.

Epoxide. Colorless oil. $[\alpha]^{23}_D = +14.8$ (*c* 1.02, $CHCl_3$). IR: 2249 cm^{-1} ^{1}H NMR δ: 3.27 (br s, 1H), 2.10 (dt, J = 15.1, 6.0 Hz, 1H), 2.00−1.85 (m, 3H), 1.82 (s, 3H), 1.44−1.16 (m, 4H). ^{13}C NMR δ: 80.0, 78.6, 60.1, 50.7, 30.1, 24.4, 19.6, 19.1, 3.8. Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.51; H, 8.73.

(*R*,*R*)-1-(Trimethylsilylethynyl)cyclohexene Oxide (Table 1, entry 4). Enyne. IR: 2146 cm^{-1}. ^{1}H NMR δ: 6.18 (br s, 1H), 2.15−2.05 (m, 4H), 1.67−1.52 (m, 4H), 0.18 (s, 9H). ^{13}C NMR δ: 136.4, 120.9, 107.5, 91.0, 29.3, 25.8, 22.4, 21.6, 0.29.

Epoxide. Colorless oil. $[\alpha]^{23}_D = +11.7$ (*c* 1.02, $CHCl_3$). IR: 2170 cm^{-1}. ^{1}H NMR δ: 3.31 (t, J = 2.4 Hz, 1H), 2.1 (dt, J = 15.2, 6.2 Hz, 1H), 1.99 (ddd, J = 15.2, 7.5, 5.7 Hz, 1H), 1.88 (td, J = 6.3, 2.4 Hz, 2H), 1.44−1.16 (m, 4H), 0.14 (s, 9H). ^{13}C NMR δ: 106.0, 87.0, 60.3, 50.5, 29.7, 24.3, 19.6, 19.0, −0.03. Anal. Calcd for $C_{11}H_{18}OSi$: C, 67.98; H, 9.34. Found: C, 67.95; H, 9.13.

(*R*,*R*)-1-[(Ethoxycarbonyl)ethynyl]cyclohexene Oxide (Table 1, entry 5). Enyne. IR: 2207, 1708, 1625 cm^{-1}. ^{1}H NMR δ: 6.39 (br s, 1H), 4.18 (q, J = 7.2 Hz, 2H), 2.13−2.07 (m, 4H), 1.62−1.53 (m, 4H), 1.26 (t, J = 7.2 Hz, 3H). ^{13}C NMR δ: 154.3, 142.0, 118.5, 88.3, 78.7, 61.8, 28.2, 26.0, 22.0, 21.2, 14.1.

Epoxide. Colorless oil. $[\alpha]^{23}_D = +9.1$ (*c* 0.78, $CHCl_3$). IR: 2240, 1713 cm^{-1}. ^{1}H NMR δ: 4.23 (q, J = 7.2 Hz, 2H), 3.42 (br s, 1H), 2.16 (dt, J = 15.3, 6.2 Hz, 1H), 2.06 (ddd, J = 15.3, 6.7, 5.8 Hz, 1H), 2.00−1.90 (m, 2H), 1.49−1.19 (m, 4H), 1.30 (t, J = 7.2 Hz, 3H). ^{13}C NMR δ: 153.2, 87.0, 73.6, 62.3, 60.0, 49.4, 28.7, 24.0, 19.2, 18.6, 14.1. Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.19; H, 7.00.

(*R*,*R*)-1-[3′-(*tert*-Butyldimethylsiloxy)-1′-propynyl]cyclopentene Oxide (Table 1, entry 6). Enyne. Colorless liquid. IR: 2225, 1634 cm^{-1}. ^{1}H NMR δ: 6.02 (br s, 1H), 4.46 (s, 2H), 2.48−2.42 (m, 4H), 1.90 (quintet, J = 7.5 Hz, 2H), 0.92 (s, 9H), 0.14 (s, 6H). ^{13}C NMR δ: 137.9, 124.4, 89.2, 82.5, 52.5, 36.4, 33.4, 26.1, 23.4, 18.6, −4.85.

Epoxide. Colorless oil. $[\alpha]^{23}_D = -7.5$ (*c* 1.75, $CHCl_3$). IR: 2242 cm^{-1}. ^{1}H NMR δ: 4.33 (s, 2H), 3.61 (s, 1H), 2.13 (dd, J = 13.9, 8.3 Hz, 1H), 1.98 (dd, J = 13.9, 8.3 Hz, 1H), 1.79 (ddd, J = 13.9, 10.4, 8.4 Hz, 1H), 1.75−1.31 (m, 3H), 0.89 (s, 9H), 0.09 (s, 6H). ^{13}H NMR δ: 83.1, 81.5, 65.1, 55.9, 51.9, 31.7, 27.6, 26.0, 19.2, 18.4, −4.9. Anal. Calcd for $C_{14}H_{24}O_2Si$: C, 66.61; H, 9.58. Found: C, 66.83; H, 9.47.

(*R*,*R*)-1-[3′-(*tert*-Butyldimethylsiloxy)-1′-propynyl]cyclooctene Oxide (Table 1, entry 7). Enyne. Colorless oil. IR: 2214, 1639 cm^{-1}. ^{1}H NMR δ: 6.07 (t, J = 8.3 Hz, 1H), 4.44 (s, 2H), 2.31−2.27 (m, 2H), 2.17−2.14 (m, 2H), 1.59−1.49 (m, 8H),

0.93 (s, 9H), 0.14 (s, 6H). ^{13}C NMR δ: 137.8, 123.6, 87.5, 84.9, 52.5, 30.0, 29.9, 28.6, 27.1, 26.6, 26.2, 26.0, 18.5, −4.83.

Epoxide. Colorless oil. $[\alpha]^{23}_D = +9.2$ (*c* 1.2, $CHCl_3$). IR: 2248 cm^{-1}. ^{1}H NMR δ: 4.32 (s, 2H), 3.05 (dd, *J* = 10.4, 4.2 Hz, 1H), 2.16 (dt, *J* = 13.7, 3.3 Hz, 2H), 1.78−1.16 (m, 10H), 0.89 (s, 9H), 0.10 (s, 6H). ^{13}C NMR δ: 84.5, 81.4, 63.6, 53.8, 51.9, 30.6, 27.2, 26.5, 26.2, 25.9, 25.87, 25.3, 18.4, −4.93. Anal. Calcd for $C_{17}H_{30}O_2Si$: C, 69.33; H, 10.27. Found: C, 69.58; H, 10.58.

(*R*,*R*)-1-[3′-(*tert*-Butyldimethylsiloxy)-1′-propynyl]cyclododecene Oxide (Table 1, entry 8). Enyne. Colorless oil. IR: 2215, 1633 cm^{-1}. ^{1}H NMR δ: 5.79 (t, *J* = 7.7 Hz, 1H), 4.51 (s, 2H), 2.31 (td, *J* = 6.5, 4.1 Hz, 2H), 2.18 (t, *J* = 5.9 Hz, 2H), 1.57−1.51 (m, 4H), 1.40−1.29 (m, 12H), 0.93 (s, 9H), 0.15 (s, 6H). ^{13}C NMR δ: 140.3, 122.0, 92.0, 83.6, 52.6, 36.4, 30.4, 27.2, 26.4, 26.1, 26.0, 25.5, 24.9, 24.8, 24.5, 24.4, 18.5, −4.85.

Epoxide. Colorless oil. $[\alpha]^{23}_D = -31.8$ (*c* 1.2, $CHCl_3$). ^{1}H NMR δ: 4.37 (s, 2H), 3.00 (dd, *J* = 9.6, 2.6 Hz, 1H), 2.34−2.27 (m, 2H), 2.09−2.04 (m, 2H), 1.76−1.11 (m, 16H), 0.91 (s, 9H), 0.12 (s, 6H). ^{13}C NMR δ: 84.8, 81.9, 66.0, 56.6, 51.9, 35.9, 29.7, 27.2, 26.8, 25.9, 25.8, 25.3, 25.2, 24.3, 23.6, 23.5, 18.4, −5.0. Anal. Calcd for $C_{21}H_{38}O_2Si$: C, 71.94; H, 10.92. Found: C, 71.79; H, 10.73.

(*R*,*R*)-2-Phenyl-3-(trimethylsilylethynyl)oxirane[5a] (Table 1, entry 9). Enyne. Colorless oil. IR: 2167, 2120 cm^{-1}. ^{1}H NMR δ: 7.37−7.25 (m, 5H), 6.99 (d, *J* = 16.4 Hz, 1H), 6.16 (d, *J* = 16.4 Hz, 1H), 0.22 (s, 9H). ^{13}C NMR δ: 142.6, 136.3, 128.92, 128.89, 126.5, 108.2, 104.6, 97.1, 0.2.

Epoxide. Colorless oil. $[\alpha]^{23}_D = +140.1$ (*c* 0.52, $CHCl_3$). IR: 2176 cm^{-1}. ^{1}H NMR δ: 7.36−7.25 (m, 5H), 4.03 (d, *J* = 2.0 Hz, 1H), 3.34 (d, *J* = 2.0 Hz, 1H), 0.205 (s, 9H). ^{13}C NMR δ: 135.9, 128.9, 128.8, 125.8, 101.4, 90.0, 60.4, 49.7, −0.11.

(*R*,*R*)-2-[(*tert*-Butyldimethylsilyl)ethynyl]-3-phenyloxirane (Table 1, entry 10). Enyne. Colorless oil. IR: 2166, 2120 cm^{-1}. ^{1}H NMR δ: 7.38−7.26 (m, 5H), 6.99 (d, *J* = 16.3 Hz, 1H), 6.18 (d, *J* = 16.3 Hz, 1H), 0.98 (s, 9H), 0.16 (s, 6H). ^{13}C NMR δ: 142.5, 136.3, 128.9, 126.5, 108.4, 105.2, 95.4, 26.4, 16.9, −4.37.

Epoxide. Colorless oil. $[\alpha]^{23}_D = +147.3$ (*c* 0.75, $CHCl_3$). IR: 2175 cm^{-1}. ^{1}H NMR δ: 7.36−7.25 (m, 5H), 4.02 (d, *J* = 2.0 Hz, 1H), 3.35 (d, *J* = 2.0 Hz, 1H), 0.954 (s, 9H), 0.138 (s, 6H). ^{13}C NMR δ: 135.9, 128.9, 128.8, 125.8, 102.1, 88.3, 60.4, 49.8, 26.2, 16.7, −4.6. Anal. Calcd for $C_{16}H_{22}OSi$: C, 74.36; H, 8.58. Found: C, 74.31; H, 8.45.

(*R*,*R*)-2-Phenyl-3-(1′-propynyl)oxirane (Table 1, entry 11). Enyne. Colorless oil. IR: 2216 cm^{-1}. ^{1}H NMR δ: 7.37−7.25 (m, 5H), 6.86 (d, *J* = 16.3 Hz, 1H), 6.13 (dq, *J* = 16.3, 2.2 Hz, 1H), 2.01 (d, *J* = 2.2 Hz, 3H). ^{13}C NMR δ: 140.3, 136.7, 128.9, 128.5, 126.3, 109.0, 88.5, 79.1, 4.75.

Epoxide. Colorless oil. $[\alpha]^{23}_D = +154.5$ (*c* 0.8, $CHCl_3$). IR: 2243 cm^{-1}. ^{1}H NMR δ: 7.37−7.24 (m, 5H), 3.97 (d, *J* = 1.7 Hz, 1H), 3.29 (m, 1H), 1.88 (d, *J* = 1.7 Hz, 3H). ^{13}C NMR δ: 136.1, 128.7, 128.7, 125.7, 80.9, 75.7, 60.1, 49.9, 3.8. Anal. Calcd for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found: C, 83.24; H, 6.40.

(*R*,*R*)-2-Propyl-3-(trimethylsilylethynyl)oxirane (Table 1, entry 12). Enyne. Colorless oil. IR: 2176, 2143 cm^{-1}. ^{1}H NMR δ: 6.22 (dt, *J* = 15.9, 7.1 Hz, 1H), 5.51 (dt, *J* = 15.9, 1.4 Hz, 1H), 2.08 (tdd, *J* = 7.4, 7.1, 1.4 Hz, 2H), 1.42 (sextet, *J* = 7.4 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H), 0.184 (s, 9H). ^{13}C NMR δ: 146.3, 109.9, 104.4, 92.7, 35.3, 22.0, 13.8, 0.19.

Epoxide. Colorless oil. $[\alpha]^{23}_D = +3.9$ (*c* 0.75, $CHCl_3$). IR: 2180 cm^{-1}. ^{1}H NMR δ: 3.12−3.08 (m, 2H), 1.57−1.46 (m, 4H), 0.97 (t, *J* = 7.2 Hz, 3H), 0.18 (s, 9H). ^{13}C NMR δ: 102.2, 89.3, 60.8, 45.6, 33.9, 19.2, 14.0, −0.10. Anal. Calcd for $C_{10}H_{18}OSi$: C, 65.87; H, 9.95. Found: C, 65.69; H, 10.01.

(*R*,*R*)-2-[(*tert*-Butyldimethylsilyl)ethynyl]-3-propyloxirane (Table 1, entry 13). Enyne. Colorless oil. IR: 2175, 2142 cm^{-1}. ^{1}H NMR δ: 6.22 (dt, *J* = 15.9, 7.2 Hz, 1H), 5.51 (dt, *J* = 15.9, 1.2 Hz, 1H), 2.09 (qd, *J* = 7.2, 1.2 Hz, 2H), 1.43 (sextet, *J* = 7.2 Hz, 2H), 0.95 (s, 9H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.12 (s, 6H). ^{13}C NMR δ: 146.1, 110.1, 105.0, 90.9, 35.4, 26.3, 22.1, 16.9, 13.9, −4.33.

Epoxide. Colorless oil. $[\alpha]^{23}_D = +4.2$ (*c* 1.1, $CHCl_3$). IR: 2178 cm^{-1}. ^{1}H NMR δ: 3.09−3.06 (m, 2H), 1.60−1.44 (m, 4H), 0.97 (t, *J* = 6.9 Hz, 3H), 0.93 (s, 9H), 0.11 (s, 6H). ^{13}C NMR δ: 103.0, 87.4, 60.8, 45.6, 33.9, 26.2, 19.2, 16.6, 14.0, −4.6. Anal. Calcd for $C_{13}H_{24}OSi$: C, 69.57; H, 10.78. Found: C, 69.70; H, 10.76.

(*R*,*R*)-2-(3′-Methoxy-1′-propynyl)-3-propyloxirane (Table 1, entry 14). Enyne. Colorless oil. IR: 2213, 1634 cm^{-1}. ^{1}H NMR δ: 6.16 (dt, *J* = 15.9, 7.2 Hz, 1H), 5.50 (d, *J* = 15.9 Hz, 1H), 4.20 (s, 2H), 3.38 (s, 3H), 2.09 (q, *J* = 7.2 Hz, 2H), 1.42 (sextet, *J* = 7.2 Hz, 2H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR δ: 145.6, 109.2, 85.4, 83.4, 60.6, 57.7, 35.2, 22.0, 13.7.

Epoxide. Colorless oil. $[\alpha]^{23}_D = -2.5$ (*c* 1.14, $CHCl_3$). ^{1}H NMR δ: 4.11 (s, 2H), 3.37 (s, 3H), 3.14 (br s, 1H), 3.10 (m, 1H), 1.58−1.44 (m, 4H), 0.97 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR δ: 83.4, 79.6, 60.5, 60.0, 57.9, 45.3, 33.8, 19.1, 14.0. Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.22; H, 9.39.

(*R*,*R*)-3-Ethyl-2-methyl-2-(trimethylsilylethynyl)oxirane (Table 1, entry 15). Enyne. Colorless oil. IR: 2146 cm^{-1}. ^{1}H NMR δ: 5.92 (td, *J* = 7.4, 1.4 Hz, 1H), 2.08 (qd, *J* = 7.6, 7.4 Hz, 2H), 1.77 (d, *J* = 0.6 Hz, 3H), 0.98 (t, *J* = 7.6 Hz, 3H), 0.18 (s, 9H). ^{13}C NMR δ: 141.4, 117.5, 108.8, 89.9, 22.0, 17.1, 13.6, 0.31.

Epoxide. Colorless oil. $[\alpha]^{23}_D = -8.1$ (*c* 1.0, $CHCl_3$). IR: 2175 cm^{-1}. ^{1}H NMR δ: 3.10 (t, *J* = 6.3 Hz, 1H), 1.55 (qd, *J* = 7.6, 6.3 Hz, 2H), 1.48 (s, 3H), 1.06 (t, *J* = 7.6 Hz, 3H), 0.164 (s, 9H). ^{13}C NMR δ: 106.4, 86.5, 66.2, 51.1, 21.8, 18.3, 10.4, −0.05. Anal. Calcd for $C_{10}H_{18}OSi$: C, 65.87; H, 9.95. Found: C, 65.70; H, 9.76.

(*R*,*R*)-2-Methyl-3-phenyl-2-(trimethylsilylethynyl)oxirane (Table 1, entry 16). Enyne. Colorless oil. A mixture of *E* and *Z* isomers (*E*/*Z* = 2.8/1 by ^{1}H NMR). ^{1}H NMR δ (*E*)-isomer: 7.3−7.2 (m, 5H), 6.81 (br s, 1H), 1.96 (s, 3H), 0.14 (s, 9H). ^{1}H MR δ (*Z*)-isomer: 7.3−7.2 (m, 5H), 6.45 (br s, 1H), 1.97 (s, 3H), 0.16 (s, 9H).

Epoxide. Colorless oil. $[\alpha]^{23}_D = +103.7$ (*c* 1.05, $CHCl_3$). IR: 2179, 1605 cm^{-1}. ^{1}H NMR δ: 7.4−7.25 (m, 5H), 4.29 (s, 1H), 1.29 (s, 3H), 0.22 (s, 9H). ^{13}C NMR δ: 134.5, 128.4, 128.2, 126.9, 105.8, 87.4, 65.2, 53.5, 17.9, 0.01. Anal. Calcd for $C_{14}H_{18}OSi$: C, 72.99; H, 7.87. Found: C, 72.88; H, 7.89.

(*R*,*R*)-3-Butyl-2-ethynyl-2-propyloxirane (Table 1, entry 17). Enyne. Colorless oil. IR: 3309, 2094, 1636 cm^{-1}. ^{1}H NMR δ: 5.96 (t, *J* = 7.6 Hz, 1H), 2.74 (s, 1H), 2.11 (t, *J* = 7.3 Hz, 2H), 2.10 (dt, *J* = 7.6, 7.3 Hz, 2H), 1.53 (sextet, *J* = 7.3 Hz, 2H), 1.38−1.29 (m, 4H), 0.92 (t, *J* = 7.3 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR δ: 140.3, 122.1, 86.3, 74.1, 32.6, 31.5, 28.2, 22.6, 21.6, 14.1, 13.8.

Epoxide. Colorless oil. $[\alpha]^{23}_D = -3.08$ (*c* 0.91, $CHCl_3$). IR: 3307, 2116 cm^{-1}. ^{1}H NMR δ: 3.14 (t, *J* = 5.6 Hz, 1H), 2.29 (s, 1H), 1.70−1.33 (m, 10H), 0.99 (t, *J* = 7.0 Hz, 3H), 0.93 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR δ: 83.9, 70.8, 65.0, 54.5, 33.6, 28.7, 27.8, 22.7, 19.1, 14.2, 14.1. Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.43; H, 10.75.

(*R*,*R*)-3-Butyl-2-propyl-2-(trimethylsilylethynyl)oxirane (Table 1, entry 18). Enyne. Colorless oil. IR: 2143 cm^{-1}. ^{1}H NMR δ: 5.93 (t, *J* = 7.5 Hz, 1H), 2.09 (t, *J* = 7.3 Hz, 2H), 2.08 (dt, *J* = 7.5, 7.3 Hz, 2H), 1.53 (qt, *J* = 7.5, 7.3 Hz, 2H), 1.36−1.26 (m, 4H), 0.92 (t, *J* = 7.5 Hz, 3H), 0.89 (t, *J* = 7.5 Hz, 3H), 0.17 (s, 9H). ^{13}C NMR δ: 139.8, 123.2, 108.0, 90.7, 32.7, 31.6, 28.2, 22.6, 21.7, 14.1, 13.9, 0.3.

Epoxide. Colorless oil. $[\alpha]^{23}_D = +7.16$ (*c* 1.41, $CHCl_3$). IR: 2169 cm^{-1}. ^{1}H NMR δ: 3.12 (t, *J* = 5.5 Hz, 1H), 1.66−1.37 (m, 10H), 0.98 (t, *J* = 7.0 Hz, 3H), 0.92 (t, *J* = 7.0 Hz, 3H), 0.16 (s, 9H). ^{13}C NMR δ:105.5, 87.8, 65.5, 55.0, 33.8, 28.8, 28.0, 22.7, 19.3, 14.3, 14.2, 0.05. Anal. Calcd for $C_{14}H_{26}OSi$: C, 70.52; H, 10.99. Found: C, 70.44; H, 11.07.

(*R*,*R*)-3-Butyl-2-[(*tert*-butyldimethylsilyl)ethynyl]-2-propyloxirane (Table 1, entry 19). Enyne. Colorless oil. IR: 2141 cm^{-1}. ^{1}H NMR δ: 5.93 (t, *J* = 7.4 Hz, 1H), 2.10 (t, *J* = 7.4 Hz, 2H), 2.07 (q, *J* = 7.4 Hz, 2H), 1.54 (tq, *J* = 7.4, 7.2 Hz, 2H), 1.37−1.26 (m, 4H), 0.94 (s, 9H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.88 (td, *J* = 7.2, 2.4 Hz, 3H), 0.11 (s, 6H). ^{13}C NMR δ: 139.6, 123.3, 108.7, 88.9, 32.8, 31.7, 28.3, 26.4, 22.7, 21.8, 17.0, 14.2, 13.9, −4.2.

Epoxide. Colorless oil. $[\alpha]^{23}_D = +16.7$ (*c* 0.6, EtOH). IR: 2168 cm^{-1}. ^{1}H NMR δ: 3.12 (t, *J* = 5.5 Hz, 1H), 1.69−1.33 (m, 10H), 0.96 (t, *J* = 7.0 Hz, 3H), 0.931 (s, 9H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.10 (s, 6H). ^{13}C NMR δ: 106.2, 86.1, 65.4, 55.0, 33.8, 28.8, 28.0, 26.2, 26.2, 22.8, 19.3, 16.7, 14.2, −4.5. Anal. Calcd for $C_{17}H_{32}OSi$: C, 72.79; H, 11.50. Found: C, 72.71; H, 11.67.

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Supporting Information Available: NMR spectral, GC, and HPLC data for the determination of the enantiomeric excess of the epoxides along with the preparation of the enyne substrates and the authentic epoxides for the determination of absolute configurations. This material is available free of charge via the Internet at http://pubs.acs.org.

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