Enantioselective Cyclization/Hydrosilylation of 1,6-Enynes Catalyzed by a Cationic Rhodium Bis(phosphine) Complex

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Supporting Information

Experimental procedures, analytical and spectroscopic data for new enynes and carbocycles and copies of chiral GC traces and chiral NMR spectra for racemic and enantiomerically enriched carbocycles (12 pages).

Experimental

General Methods. Catalytic reactions were performed under an atmosphere of nitrogen employing standard Schlenk techniques. NMR spectra were obtained at 400 MHz for ^1H and at 100 MHz for ^{13}C in CDCl_3 at room temperature unless otherwise specified. IR spectra were obtained on a Bomen MB-100 FT IR spectrometer. Routine gas chromatography was performed on a Hewlett-Packard 5890 gas chromatograph equipped with a 25 m polydimethylsiloxane capillary column. Chiral gas chromatography was performed on a 20 m $\times$ 0.25 mm Chiraldex G-TA column (Advanced Separation Technologies). Flash column chromatography was performed employing 200-400 mesh silica gel (EM). Elemental analyses were performed by Complete Analysis Laboratories (Parsippany, NJ). Silanes were purchased from Aldrich and used as received. CH_2Cl_2 and 1,2-dichloroethane (DCE) were distilled from CaH_2 under nitrogen. Enynes **1**¹ and **17**² were prepared by published procedures.

Enynes

2-Allyl-2-(but-2-ynyl)propane-1,3-diol (S1). A solution of **1** (11.2 g, 50 mmol) in ether (6 mL) was added dropwise to a suspension of LiAlH_4 (2.3 g, 60 mmol) in ether (100 mL) at 0 °C, stirred for 20 min, and then stirred overnight at room temperature. The resulting suspension was treated with aqueous NaOH (1 N, 30 mL) and extracted with ether. The combined ether extracts were washed with brine, concentrated, and distilled under vacuum to give **S1** (2.26 g, 27%) as a colorless oil. TLC (hexane–EtOAc = 2:1): R_f = 0.57. ^1H NMR: δ 5.80 (tdd, J = 7.6, 9.6, 16.8 Hz, 1 H), 5.14–5.07 (m, 2 H), 3.63 (d, J = 10.8 Hz, 2 H), 3.58 (d, J = 11.2 Hz, 2 H), 2.16 (q, J = 2.4 Hz, 2 H), 2.12 (s, 1 H), 2.11 (s, 1 H), 1.78 (t, J = 2.2 Hz, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 133.9, 118.7, 78.5, 75.6, 68.3, 67.8, 42.5, 36.6, 25.9, 22.2, 3.8. IR (neat, cm^{-1}): 3414, 3074, 2917, 1639, 1438, 1030, 917, 861. Anal. calcd (found) for $\text{C}_{10}\text{H}_{16}\text{O}_2$: C, 71.39 (71.39); H, 9.59 (9.52).

4,4-Bis(methoxymethyl)-1-octene-6-yne (9). A suspension of **S1** (1.68 g, 10.0 mmol) and NaH (0.72 g, 30.0 mmol) in THF (50 mL) was stirred for 15 min at 0 °C and then treated with iodomethane (1.87 mL, 30.0 mmol). The resulting solution was stirred at room temperature

overnight, quenched with water, and extracted with ether. The combined ether extracts were washed with brine, dried (MgSO₄), concentrated, and chromatographed (hexanes–EtOAc = 50:1 → 20:1) to give **9** (1.17 g, 60%) as a colorless oil. TLC (hexane–EtOAc = 10:1): R_f = 0.52. ¹H NMR: δ 5.76 (tdd, J = 7.6, 10.0, 17.2 Hz, 1 H), 5.08–5.00 (m, 2 H), 3.29 (s, 6 H), 3.01 (d, J = 8.8 Hz, 2 H), 3.18 (d, J = 8.8 Hz, 2 H), 2.16 (q, J = 2.4 Hz, 2 H), 2.11 (td, J = 1.2, 7.6 Hz, 2 H), 2.09 (q, J = 2.4 Hz, 2 H), 1.76 (t, J = 2.6 Hz, 3 H). ¹³C{¹H} NMR: δ 134.3, 118.0, 77.5, 75.7, 74.7, 59.5, 42.1, 36.6, 22.5, 3.7. IR (neat, cm^{–1}): 3074, 2979, 2919, 2888, 2809, 2749, 1639, 1477, 1439, 1382, 1276, 1198, 1111, 1001, 967, 915. Anal. calcd (found) for C₁₂H₂₀O₂: C, 73.43 (73.29); H, 10.37 (10.19).

4,4-Bis(acetoxymethyl)-1-octene-6-yne (10). A solution of acetic anhydride (4.0 g, 39.0 mmol), **S1** (1.0 g, 6.0 mmol), DMAP (0.36 g, 3.0 mmol), and triethylamine (3.0 g, 3.0 mmol) in CH₂Cl₂ (10 mL) was stirred overnight at room temperature, quenched with water, and extracted with ether. The combined ether extracts were washed with brine, dried (MgSO₄), concentrated, and chromatographed (hexane–EtOAc = 20:1) to give **10** (0.67 g, 45%) as a colorless oil. TLC (hexane–EtOAc = 10:1): R_f = 0.20. ¹H NMR: δ 5.69 (tdd, J = 7.6, 8.8, 16.0 Hz, 1 H), 5.04 (m, 2 H), 3.93 (s, 4 H), 2.14 (d, J = 4.4 Hz, 2 H), 2.12 (q, J = 2.4 Hz, 2 H), 1.99 (s, 6 H), 1.71 (t, J = 2.4 Hz, 3 H). ¹³C{¹H} NMR: δ 171.0, 132.5, 119.4, 78.8, 74.1, 65.8, 40.4, 36.3, 22.6, 21.0, 3.7. IR (neat, cm^{–1}): 3077, 2955, 2920, 2858, 1745, 1640, 1469, 1441, 1382, 1366, 1228, 1040, 921, 874. Anal. calcd (found) for C₁₄H₂₀O₄: C, 66.65 (66.47); H, 7.99 (7.84).

4,4-Bis(propionyloxymethyl)-1-octene-6-yne (11). Enyne **11** was prepared in 67% yield from **S1** as a colorless oil employing a procedure similar to that used to synthesize **10**. TLC (hexane–EtOAc = 10:1): R_f = 0.42. ¹H NMR: δ 5.74 (tdd, J = 7.6, 11.2, 16.0 Hz, 1 H), 5.11–5.07 (m, 2 H), 3.99 (s, 4 H), 2.32 (q, J = 7.6 Hz, 4 H), 2.19 (d, J = 7.2 Hz, 2 H), 2.18 (q, J = 2.4 Hz, 2 H), 1.76 (t, J = 2.6 Hz, 3 H), 1.13 (t, J = 7.6 Hz, 6 H). ¹³C{¹H} NMR: δ 174.4, 132.7, 119.5, 78.8, 74.2, 65.8, 40.6, 36.5, 27.8, 22.8, 9.4, 3.8. IR (neat, cm^{–1}): 2983, 2946, 2922, 1740, 1640, 1462, 1350, 1184, 1083, 1022, 920, 807. Anal. calcd (found) for C₁₆H₂₄O₄: C, 68.54 (68.35); H, 8.63 (8.72).

5-Allyl-5-(2-butynyl)-2,2-dimethyl-1,3-dioxane (12). P₂O₅ (4.26 g, 30.0 mmol) was added in one portion to a solution of **S1** (1.68 g, 10.0 mmol) in acetone (20 mL) at room temperature. The resulting mixture was stirred for 30 min, poured into a mixture of NaOH (5 g) and ice (30 g), and extracted with ether. The combined ether extracts were washed with saturated aqueous NaHCO₃ and brine, dried (MgSO₄), concentrated, and chromatographed (hexane–EtOAc = 50:1) to give **12** (0.93 g, 46%) as a colorless oil. TLC (hexane–EtOAc = 10:1): *R_f* = 0.45. ¹H NMR: δ 5.70 (tdd, *J* = 7.6, 10.4, 16.8 Hz, 1 H), 5.09–5.04 (m, 2 H), 3.58 (s, 4 H), 2.24 (q, *J* = 2.4 Hz, 2 H), 2.09 (d, *J* = 7.6 Hz, 2 H), 1.74 (t, *J* = 2.4 Hz, 3 H), 1.36 (s, 3 H), 1.34 (s, 3 H). ¹³C{¹H} NMR: δ 133.0, 118.9, 98.3, 78.4, 75.4, 67.0, 60.6, 37.3, 35.8, 25.9, 22.9, 22.2, 14.5, 3.7. IR (neat, cm^{–1}): 2986, 2869, 1639, 1444, 1378, 1350, 1197, 1126, 1096, 1050, 932, 827. Anal. calcd (found) for C₁₃H₂₀O₂: C, 74.96 (74.72); H, 9.68 (9.62).

Silylated Carbocycles

(Z)-1,1-Dicarbomethoxy-4-(1-triethylsilylethylidene)-3-methylcyclopentane (2). A solution of **1** (115 mg, 0.51 mmol), triethylsilane (0.4 mL, 2.5 mmol), [Rh(COD)₂]⁺ SbF₆[–] (14 mg, 0.025 mmol), and (+)-BIPHEMP (15 mg, 0.027 mmol) in DCE (5 mL) was heated at 70 °C for 3 h. The resulting solution was cooled to room temperature, diluted with hexanes (50 mL), filtered through a plug of silica gel, concentrated, and chromatographed (hexane–EtOAc = 50:1 → 10:1) to give **2** (141 mg, 81%) as a colorless oil. TLC (hexane–Et₂O = 2:1): *R_f* = 0.63. ¹H NMR: δ 3.72 (s, 3 H), 3.66 (s, 3 H), 3.09 (d, *J* = 17.2 Hz, 1 H), 2.90 (d, *J* = 17.2 Hz, 1 H), 2.76 (quintet, *J* = 7.2 Hz, 1 H), 2.51 (dd, *J* = 8.0, 13.4 Hz, 1 H), 2.03 (dd, *J* = 2.8, 13.2 Hz, 1 H), 1.61 (m, 3 H), 0.94 (d, *J* = 7.2 Hz, 3 H), 0.88 (d, *J* = 7.6, 8.0 Hz, 9 H), 0.57–0.64 (m, 6 H). ¹³C{¹H} NMR: δ 173.4, 173.0, 156.3, 123.7, 58.4, 52.9, 41.6, 38.5, 37.6, 23.3, 19.5, 7.8, 4.0. IR (neat, cm^{–1}): 2957, 1737, 1731, 1434, 1258, 1202, 1167, 800. Anal. calcd (found) for C₁₈H₃₂O₄Si: C, 63.49 (63.60); H, 9.47 (9.28).

Silylated carbocycles **3-8**, **13-16**, and **18** were prepared using a procedure similar to that used to synthesize **2**.

(Z)-1,1-Dicarbomethoxy-3-methyl-4-(1-benzyl dimethylsilylethylidene)-cyclopentane (3). Colorless oil, 70%. TLC (hexane–Et₂O = 2:1): R_f = 0.58. ¹H NMR: δ 7.16 (t, J = 7.6 Hz, 2 H), 7.03 (t, J = 7.6 Hz, 1 H), 6.94 (d, J = 7.6 Hz, 2 H), 3.73 (s, 3 H), 3.70 (s, 3 H), 3.13 (d, J = 17.2 Hz, 1 H), 2.88 (d, J = 17.2 Hz, 1 H), 2.71 (quintet, J = 7.6 Hz, 2 H), 2.45 (dd, J = 8.0, 9.2 Hz, 1 H), 2.13 (s, 2 H), 2.05 (dd, J = 2.8, 13.2 Hz, 1 H), 1.60 (s, 3 H), 0.85 (d, J = 7.6 Hz, 3 H), 0.09 (s, 3 H), 0.08 (s, 3 H). ¹³C{¹H} NMR: δ 173.5, 173.2, 156.7, 140.5, 128.5, 128.4, 124.3, 58.5, 53.1, 41.6, 38.8, 37.9, 26.3, 23.2, 19.4, –1.4, –1.5. IR (neat, cm^{–1}): 1737, 1733, 1438, 1384, 1293, 1111, 911, 734. Anal. calcd (found) for C₂₁H₃₀O₄Si: C, 67.34 (67.22); H, 8.07 (7.93).

(Z)-1,1-Dicarbomethoxy-3-methyl-4-(1-methyldiphenylsilylethylidene)-cyclopentane (4). Colorless oil, 71%. TLC (hexane–Et₂O = 2:1): R_f = 0.50. ¹H NMR: δ 7.48–7.47 (m, 4 H), 7.35–7.29 (m, 6 H), 3.72 (s, 3 H), 3.71 (s, 3 H), 3.00 (d, J = 17.2 Hz, 1 H), 2.56 (m, 1 H), 2.41 (dd, J = 7.6, 13.4 Hz, 1 H), 1.96 (dd, J = 2.8, 13.2 Hz, 1 H), 1.67 (m, 3 H), 0.64 (d, J = 7.2 Hz, 3 H), 0.64 (s, 3 H). ¹³C{¹H} NMR: δ 173.5, 173.2, 159.1, 137.6, 137.5, 135.4, 135.3, 129.4, 128.1, 122.2, 58.5, 53.2, 53.1, 41.6, 39.1, 37.8, 22.6, 20.6, –1.2. IR (neat, cm^{–1}): 1733, 1455, 1255, 911. Anal. calcd (found) for C₂₅H₃₀O₄Si: C, 71.05 (70.98); H, 7.16 (7.05).

(Z)-1,1-Dicarbomethoxy-3-methyl-4-(1-dimethylphenylsilylethylidene)-cyclopentane (5). Colorless oil, 77%. TLC (hexane–Et₂O = 2:1): R_f = 0.64. ¹H NMR: δ 7.46 (m, 2 H), 7.30 (m, 3 H), 3.73 (s, 3 H), 3.70 (s, 3 H), 3.16 (d, J = 17.6 Hz, 1 H), 2.94 (d, J = 17.6 Hz, 1 H), 2.76–2.67 (m, 1 H), 2.49 (dd, J = 7.6, 13.4 Hz, 1 H), 1.66 (s, 3 H), 0.83 (d, J = 7.2 Hz, 3 H), 0.37 (s, 6 H). ¹³C{¹H} NMR: δ 173.5, 173.2, 157.4, 139.9, 134.1, 129.1, 128.0, 124.0, 58.6, 53.1, 41.7, 39.0, 37.7, 23.1, 19.8, –0.57, –0.61. IR (neat, cm^{–1}): 1734, 1428, 1253, 1199, 1108, 701. Anal. calcd (found) for C₂₀H₂₈O₄Si: C, 66.63 (66.52); H, 7.83 (7.76).

(Z)-1,1-Dicarbomethoxy-3-methyl-4-(1-dimethyl-*n*-octylsilylethylidene)-cyclopentane (6). Colorless oil, 74%. TLC (hexane–Et₂O = 2:1): R_f = 0.50. ¹H NMR: δ 3.71 (s, 3 H), 3.67 (s, 3 H), 3.10 (d, J = 17.2 Hz, 1 H), 2.88–2.79 (m, 2 H), 2.49 (dd, J = 8.0, 13.2 Hz, 1 H), 2.04 (dd, J = 2.4, 13.2 Hz, 1 H), 1.59 (s, 3 H), 1.22 (br s, 12 H), 0.92 (d, J = 7.2 Hz, 3 H), 0.84

(t, $J = 6.8$ Hz, 3 H), 0.55-0.51 (m, 2 H), -0.06 (s, 6 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 173.6, 173.2, 155.4, 125.7, 58.6, 53.1, 41.7, 38.8, 37.7, 34.1, 32.3, 29.9, 29.7, 24.4, 23.4, 23.0, 19.4, 16.5, 14.5, -1.3 , -1.4 . IR (neat, cm^{-1}): 2923, 1734, 1249, 911, 836, 734. Anal. calcd (found) for $\text{C}_{22}\text{H}_{40}\text{O}_4\text{Si}$: C, 66.62 (65.64); H, 10.16 (10.22).

(Z)-1,1-Dicarbomethoxy-4-(1-ethyldimethylsilylethylidene)-3-methylcyclopentane

(7). Colorless oil, 75%. TLC (hexane– $\text{Et}_2\text{O} = 2:1$): $R_f = 0.55$. ^1H NMR: δ 3.72 (s, 3 H), 3.67 (s, 3 H), 3.11 (d, $J = 17.2$ Hz, 1 H), 2.87 (d, $J = 17.2$ Hz, 1 H), 2.82 (m, 1 H), 2.52 (dd, $J = 8.0$, 13.4 Hz, 1 H), 2.06 (dd, $J = 2.8$, 13.2 Hz, 1 H), 1.60 (s, 3 H), 0.93 (d, $J = 7.2$ Hz, 3 H), 0.87 (m, 3 H), 0.56 (d, $J = 7.6$ Hz, 1 H), 0.53 (d, $J = 8.0$ Hz, 1 H), 0.07 (s, 6 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 173.6, 173.2, 155.5, 125.4, 58.6, 53.1, 41.7, 38.8, 37.6, 23.4, 19.4, 8.1, 7.9, -1.8 , -1.9 . IR (neat, cm^{-1}): 1733, 1489, 1446, 1383, 1351. Anal. calcd (found) for $\text{C}_{16}\text{H}_{28}\text{O}_4\text{Si}$: C, 61.50 (61.39); H, 9.03 (9.09).

(Z)-1,1-Dicarbomethoxy-4-(1-diethylmethylsilylethylidene)-3-methylcyclopentane

(8). Colorless oil, 76%. TLC (hexane– $\text{Et}_2\text{O} = 2:1$): $R_f = 0.60$. ^1H NMR: δ 3.71 (s, 3 H), 3.66 (s, 3 H), 3.09 (d, $J = 17.2$ Hz, 1 H), 2.85 (d, $J = 17.2$ Hz, 1 H), 2.78 (quintet, $J = 7.6$ Hz, 1 H), 2.51 (dd, $J = 7.6$, 12.9 Hz, 1 H), 2.03 (dd, $J = 2.8$, 13.6 Hz, 1 H), 1.58 (m, 3 H), 0.93 (d, $J = 7.2$ Hz, 3 H), 0.86 (dt, $J = 3.6$, 7.8 Hz, 6 H), 0.59-0.52 (m, 4 H), 0.07 (s, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 173.6, 173.2, 156.0, 124.6, 58.6, 53.1, 41.7, 38.7, 37.7, 23.4, 19.5, 7.9, 6.3, 6.2, -4.2 . IR (neat, cm^{-1}): 2953, 2910, 2873, 2256, 1734, 1623, 1458, 1435, 1253, 1200, 1173, 1110, 909, 795. Anal. calcd (found) for $\text{C}_{17}\text{H}_{30}\text{O}_4\text{Si}$: C, 62.54 (62.61); H, 9.26 (9.34).

(Z)-1,1-Bis(methoxymethyl)-4-(1-triethylsilylethylidene)-3-methylcyclopentane

(14). Colorless oil, 65%. TLC (hexane– $\text{EtOAc} = 10:1$): $R_f = 0.55$. ^1H NMR: δ 3.36 (s, 3 H), 3.34 (s, 2 H), 3.30 (s, 3 H), 3.07 (s, 2 H), 2.67 (m, 1 H), 2.40 (d, $J = 16.4$ Hz, 1 H), 2.12 (d, $J = 16.0$ Hz, 1 H), 1.72 (dd, $J = 8.2$, 13.4 Hz, 1 H), 1.62 (s, 6 H), 1.24 (dd, $J = 3.6$, 13.6 Hz, 1 H), 1.04 (d, $J = 7.2$ Hz, 3 H), 0.92 (t, $J = 7.8$ Hz, 9 H), 0.64 (q, $J = 8.0$ Hz, 6 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 159.7, 122.5, 78.1, 76.4, 59.6, 46.0, 39.7, 37.1, 36.7, 25.4, 19.9, 8.1, 4.3. IR (neat, cm^{-1}): 2953, 2904, 2866, 1454, 1383, 1200, 1020, 730. Anal. calcd (found) for $\text{C}_{18}\text{H}_{36}\text{O}_2\text{Si}$: C, 69.17 (68.97); H, 11.61 (11.70).

(Z)-1,1-Bis(acetoxymethyl)-4-(1-triethylsilylethylidene)-3-methylcyclopentane

(15). Colorless oil, 58%. TLC (hexane–EtOAc = 10:1): R_f = 0.25. ^1H NMR: δ 4.04 (dd, J = 11.2, 14.0 Hz, 2 H), 3.79 (dd, J = 10.8, 17.6 Hz, 2 H), 2.70 (m, 1 H), 2.41 (d, J = 15.6 Hz, 1 H), 2.21–2.15 (m, 1 H), 2.04 (s, 3 H), 2.01 (s, 3 H), 1.78 (dd, J = 8.4, 13.6 Hz, 1 H), 1.59 (s, 3 H), 1.26 (dd, J = 4.0, 13.6 Hz, 1 H), 1.04 (d, J = 7.2 Hz, 3 H), 0.89 (t, J = 8.0 Hz, 9 H), 0.61 (q, J = 8.0 Hz, 6 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 171.5, 157.5, 124.0, 68.7, 67.1, 44.0, 39.5, 36.9, 36.3, 25.1, 21.2, 19.9, 8.0, 4.3. IR (neat, cm^{-1}): 2952, 2873, 1744, 1458, 1378, 1363, 1227, 1035, 732. Anal. calcd (found) for $\text{C}_{20}\text{H}_{36}\text{O}_4\text{Si}$: C, 65.17 (65.22); H, 9.84 (9.94).

(Z)-1,1-Bis(propoxymethyl)-4-(1-triethylsilylethylidene)-3-methylcyclopentane

(16). Colorless oil, 49%. TLC (hexane–EtOAc = 10:1): R_f = 0.48. ^1H NMR: δ 4.10 (d, J = 11.2 Hz, 1 H), 4.06 (d, J = 11.2 Hz, 1 H), 3.85 (d, J = 10.8 Hz, 1 H), 3.80 (d, J = 11.2 Hz, 1 H), 2.72 (m, 1 H), 2.44 (d, J = 16.0 Hz, 1 H), 2.35 (q, J = 7.6 Hz, 2 H), 2.31 (d, J = 7.6 Hz, 2 H), 2.20 (d, J = 16.4 Hz, 1 H), 1.80 (dd, J = 8.2, 13.4 Hz, 1 H), 1.62 (s, 3 H), 1.30 (dd, J = 3.6, 13.6 Hz, 1 H), 1.15 (t, J = 7.8 Hz, 3 H), 1.13 (t, J = 7.8 Hz, 3 H), 0.92 (t, J = 7.8 Hz, 9 H), 0.65 (q, J = 8.0 Hz, 6 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 174.8, 157.6, 124.0, 68.5, 67.0, 44.2, 39.6, 37.0, 36.3, 27.9, 25.2, 19.9, 9.5, 8.0, 4.3. IR (neat, cm^{-1}): 2951, 2873, 1742, 1462, 1379, 1348, 1180, 1083, 1017, 732. Anal. calcd (found) for $\text{C}_{22}\text{H}_{40}\text{O}_4\text{Si}$: C, 66.62 (66.40); H, 10.16 (10.19).

(Z)-3-(1-Triethylsilylethylidene)-4,8,8-trimethyl-7,9-dioxaspiro[4.5]decane (17).

Colorless oil, 48%. TLC (hexane–EtOAc = 10:1): R_f = 0.50. ^1H NMR: δ 3.72 (d, J = 11.2 Hz, 1 H), 3.67 (d, J = 11.2 Hz, 1 H), 3.46 (d, J = 11.2 Hz, 1 H), 3.39 (d, J = 11.2 Hz, 1 H), 2.67 (m, 1 H), 2.59 (d, J = 16.4 Hz, 1 H), 2.16 (d, J = 16.4 Hz, 1 H), 1.72 (dd, J = 8.2, 13.4 Hz, 1 H), 1.62 (m, 3 H), 1.39 (s, 6 H), 1.19 (dd, J = 3.6, 13.4 Hz, 1 H), 1.01 (d, J = 6.8 Hz, 3 H), 0.88 (q, J = 8.0 Hz, 9 H), 0.94–0.58 (m, 6 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 158.5, 123.4, 98.0, 70.9, 69.4, 67.7, 40.9, 40.0, 38.1, 37.0, 25.6, 25.3, 22.8, 19.9, 8.1, 7.8, 4.3. IR (neat, cm^{-1}): 2955, 2901, 2869, 1455, 1416, 1380, 1240, 1200, 1017, 730. Anal. calcd (found) for $\text{C}_{19}\text{H}_{36}\text{O}_2\text{Si}$: C, 70.31 (70.24); H, 11.18 (11.12).

(E)-3-Methyl-1-(toluene-4-sulfonyl)-4-(1-dimethylphenylethylidene)pyrrolidine

(18). Pale yellow oil, 73 %. TLC (hexane–EtOAc = 2:1): R_f = 0.73. ^1H NMR: δ 7.70–7.21 (m,

9 H), 4.02 (d, $J = 14.4$ Hz, 1 H), 3.49 (d, $J = 14.8$ Hz, 1 H), 3.18 (d, $J = 9.2$ Hz, 1 H), 2.90 (dd, $J = 5.8, 9.0$ Hz, 1 H), 2.69 (m, 1 H), 2.42 (s, 3 H), 1.56 (s, 3 H), 0.93 (d, $J = 6.8$ Hz, 3 H), 0.36 (s, 3 H), 0.35 (s, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 152.2, 143.9, 138.9, 133.9, 133.0, 129.8, 129.2, 128.0, 125.3, 55.3, 50.7, 37.4, 31.8, 22.9, 21.5, 21.4, 18.9, 14.1, -1.4 , -1.6 . IR (neat, cm^{-1}): 2959, 2855, 1346, 1163, 815, 664. Anal. calcd (found) for $\text{C}_{22}\text{H}_{29}\text{NO}_2\text{SSi}$: C, 66.12 (65.97); H, 7.31 (7.19).

Determination of enantiomeric excess

The enantiomeric excesses of cyclopentanes **2** - **8** were determined by conversion to 1,1-dicarbomethoxy-3-ethylidene-4-methyl-cyclopentane¹ (**S2**) via protodesilylation followed by chiral GC (Figure S1); ee was determined by cutting and weighing the peaks corresponding to the major and minor enantiomers. The enantiomeric excess of **13** was determined by conversion to (*Z*)-1,1-bis(methoxymethyl)-3-methyl-4-ethylidenecyclopentane (**S3**) (Scheme S1), followed by chiral GC analysis (Figure S2); ee was determined from the computer integration of the peaks corresponding to the major and minor enantiomers. The enantiomeric excesses of **14-16** were determined by conversion to **S3** in three steps (Scheme S2) followed by chiral GC analysis. The enantiomeric excess of **18** was determined by chiral ^1H NMR spectroscopy in CDCl_3 employing $\text{Eu}(\text{hfc})_3$ as a chiral shift reagent (Figure S3); ee was determined by cutting and weighing the peaks corresponding to the major and minor enantiomers.

Scheme S1

Protodesilylation. A solution of **2** (79 mg, 0.252 mmol) and TFA (0.1 mL) in CH₂Cl₂ (3 mL) was stirred at room temperature for 40 min. Ether (100 mL) and saturated aqueous sodium carbonate (100 mL) were added to the resulting solution and the layers were separated. The organic fraction was washed with brine (50 mL), dried (MgSO₄), concentrated, and chromatographed (hexane–Et₂O = 50:1 → 10:1) to give **S2** (44 mg) as a colorless oil. Protodesilylation of cyclopentanes **3** - **8** to give **S2** and protodesilylation of **13** to give **S3** were performed employing a similar procedure.

Conversion of 14 to (Z)-1,1-bis(hydroxymethyl)-3-methyl-4-(1-triethylsilyl ethylidene)cyclopentane (S4). A suspension of **14** (92 mg, 0.25 mmol), K₂CO₃ (200 mg, 1.40 mmol) in methanol/water (9:1, 5 mL) was stirred for 30 min at room temperature and then extracted with ether. The combined ether extracts were washed with brine, concentrated, and chromatographed (hexane–EtOAc = 10:1 → 2:1) to give **S4** (64 mg, 90%) as a colorless oil (Scheme S1). Carbocycle **15** was converted to **S4** employing a similar procedure.

Conversion of 16 to S4. A solution **16** (51 mg, 0.16 mmol) HCl (5 mL of a 1 N HCl aqueous solution) in THF (5 mL) was then stirred for 1 h at room temperature and extracted with

ether. The combined ether extracts were washed with brine and concentrated, and chromatographed (hexane–EtOAc = 10:1 → 2:1) to give **S4** (32 mg, 70%).

Conversion of S4 to 9. A suspension of NaH (48 mg, 2.0 mmol) and **S4** (57 mg, 0.20 mmol) in THF (6 mL) was stirred at 0 °C for 15 min and treated with iodomethane (0.12 mL, 2.0 mmol). The reaction mixture was stirred at room temperature overnight, quenched with water, and extracted with ether. The combined ether extracts were washed with brine, dried (MgSO₄), concentrated, and chromatographed (hexane–EtOAc = 50:1) to give **9** (37 mg, 60%) (Scheme S1).

For S2:¹ ¹H NMR: δ 5.18 (m, 1 H), 3.705 (s, 3 H), 3.702 (s, 3 H), 2.96–3.00 (m, 1 H), 2.79–2.84 (m, 1 H), 2.46–2.52 (m, 2 H), 1.64–1.71 (m, 1 H), 1.56–1.59 (m, 3 H). ¹³C{¹H} NMR: δ 172.9, 144.1, 115.5, 58.6, 53.1, 53.0, 42.8, 37.5, 37.4, 18.3, 14.8.

For S3: Colorless oil. TLC (hexane–EtOAc = 10:1): *R_f* = 0.45. ¹H NMR: δ 5.17 (qq, *J* = 2.6, 6.6 Hz, 1 H), 3.34 (s, 3 H), 3.33 (s, 3 H), 3.29 (d, *J* = 8.8 Hz, 1 H), 3.24 (d, *J* = 9.6 Hz, 1 H), 3.23 (s, 3 H), 2.49 (m, 1 H), 2.16 (m, 2 H), 1.85 (dd, *J* = 7.6, 12.8 Hz, 1 H), 1.57 (tdd, *J* = 1.6, 2.4, 6.8 Hz, 3 H), 1.03 (d, *J* = 6.8 Hz, 3 H). ¹³C{¹H}: δ 147.3, 114.4, 78.1, 75.8, 59.6, 45.8, 41.0, 36.8, 36.1, 19.0, 14.8. IR (neat, cm^{−1}): 2954, 2926, 2871, 1456, 1197, 1108. HRMS calcd. (found) for C₁₂H₂₂O₂ (M⁺): 198.1619 (198.1616).

For S4: TLC (hexane–EtOAc = 2:1): *R_f* = 0.24. ¹H NMR: δ 3.74 (s, 2 H), 3.46 (s, 2 H), 2.71 (m, 1 H), 2.50 (d, *J* = 16.0 Hz, 1 H), 2.41 (s, 2 H), 2.12 (quintet of doublets, *J* = 1.6, 16.0 Hz, 1 H), 1.75 (dd, *J* = 8.4, 13.6 Hz, 1 H), 1.64 (s, 3 H), 1.21 (dd, *J* = 4.0, 13.6 Hz, 1 H), 1.06 (d, *J* = 6.8 Hz, 3 H), 0.91 (t, *J* = 7.8 Hz, 9 H), 0.64 (q, *J* = 7.6 Hz, 6 H). ¹³C{¹H} NMR: δ 158.6, 123.3, 72.3, 70.2, 46.7, 39.2, 37.1, 36.0, 25.3, 20.0, 8.1, 4.3. IR (neat, cm^{−1}): 3344, 2950, 2872, 1618, 1457, 1415, 1375, 1236, 1017, 810, 731, 412, 404. Anal. calcd (found) for C₁₆H₃₂O₂: C, 67.54 (67.39); H, 11.34 (11.18).

Figure S1. Portions of the chiral GC of racemic (left trace) and enantiomerically enriched (right trace) **S2** at 75 °C and 20 psi.

Figure S2. Chiral GC of racemic (left trace) and enantiomerically enriched (right trace) **S3** at 70 °C and 15 psi. Note that the chart speed of the left trace is twice that of the right trace.

Figure S3. Portions of the ^1H NMR spectra of racemic (left spectrum) and enantiomerically enriched (right spectrum) **18** in CDCl_3 in the presence of $\text{Eu}(\text{hfc})_3$.

References

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