

Highly Diastereoselective Chelation-Controlled Additions to α -Silyloxy Ketones

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General Methods. All reactions were performed under a nitrogen atmosphere using oven-dried glassware and standard Schlenk or vacuum line techniques. The progress of all reactions was monitored by thin-layer chromatography. Toluene and dichloromethane were dried through alumina columns. Racemic, chiral ketone derivatives were prepared by literature method; nucleophilic addition of Grignard or organolithium reagents to trans-2-methyl-2-butenal was followed by ozonolysis and protection.¹ Enantiopure, chiral ketones were prepared from the enantiopure mandelic acid or methyl lactate according to literature procedure.^{2,3} Alkyl zinc halides were prepared by literature methods.^{4,5} All chemicals were obtained from Acros, Sigma-Aldrich, or GFS Chemicals unless otherwise described. The ¹H NMR and ¹³C{¹H} NMR spectra were obtained using a Brüker AM-500 Fourier transform NMR spectrometer at 500 and 125 MHz, respectively. Chemical shifts are reported in units of parts per million (ppm) downfield from tetramethylsilane and all coupling constants are reported in hertz. The infrared spectra were obtained using a Perkin-Elmer 1600 series spectrometer. Thin-layer chromatography was carried out on Whatman pre-coated silica gel 60 F-254 plates and visualized by ultra-violet light or by staining with ceric ammonium molybdate or 2,4-dinitrophenylhydrazine stain. Silica gel (230-400 mesh, Silicycle) was used for air-flashed chromatography. Analysis of diastereomeric ratios was performed by gas chromatography using a Hewlett-Packard 6990 or Agilent Technologies 7890A GC with a Beta-Dex or Chirasil-Dex Column or by ¹H NMR of the crude reaction products. Analysis of enantiomeric excess was performed using a Hewlett-Packard

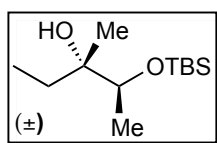
1100 series HPLC and Chiralcel OD-H or Chiralpak AD-H column. High resolution mass spectra were measured using a Waters 2695 Separations Module (1S0RR23444). Relative stereochemistry was determined by comparison to literature values or comparison to corresponding Grignard or organolithium addition. Vinyl lithium⁶ reagents were made from the corresponding vinyl iodides⁷ according to literature procedure.

Caution: Care must be taken when handling pyrophoric dialkylzinc reagents.

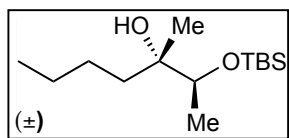
II. Diastereoselective Generation of 1,2-Syn Diols via Alkyl Addition to Chiral Ketones

General Procedure A: A dry 10 mL Schlenk flask, which was evacuated and backfilled with N₂ three times, was charged with the alkyl zinc chloride (1.75 mmol, neat solid), dialkylzinc (0.75 mmol), and toluene (1 mL). The flask was then cooled to -15 °C followed by dropwise addition of ketone solution (0.5 mmol in 0.5 mL toluene). The reaction was monitored by TLC until completion. The reaction mixture was quenched with saturated aq. NH₄Cl (2 mL) followed by addition of Et₂O (5 mL). The organic layer was separated and the aqueous solution extracted with Et₂O (3 × 10 mL). The combined organic layers were successively washed with brine, dried over MgSO₄, and filtered. The filtrate was concentrated *in vacuo* and purified by column chromatography on silica gel.

General Procedure B: A dry 10 mL Schlenk flask, which was evacuated and backfilled with N₂ three times, was charged with the alkyl zinc chloride (2 mmol, neat solid), dialkylzinc (2 mmol), and toluene (1 mL). The ketone solution (0.5 mmol in 0.5 mL toluene) was then added dropwise followed by heating to 50 °C. The reaction was monitored by TLC until completion. The reaction mixture was quenched with saturated aq. NH₄Cl (2 mL) followed by addition of Et₂O (5 mL). The organic layer was separated and the aqueous solution extracted with Et₂O (3 × 10 mL). The combined organic layers were successively washed with brine, dried over MgSO₄, and filtered. The filtrate was concentrated *in vacuo* and purified by column chromatography on silica gel.

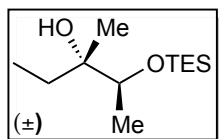


(2SR,3SR)-2-(tert-butyldimethylsilyloxy)-3-methylpentan-3-ol.⁸ General procedure A was applied to EtZnCl (226 mg, 1.75mmol), Et₂Zn (0.4 mL, 2M in toluene) and 3-((tert-butyldimethylsilyloxy)butan-2-one (100 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes/EtOAc, 99:1) to afford the title compound as an oil (105.2 mg, 91% yield, dr >20:1). ¹H NMR (500 MHz, CDCl₃): δ 0.08 (s, 3H), 0.09 (s, 3H), 0.92 (m, 12H), 1.05 (s, 3H), 1.11 (d, *J* = 6.3 Hz, 3H), 1.42–1.51 (m, 2H), 2.22 (s, 1H), 3.68 (q, *J* = 6.3 Hz, 1H). ¹³C{¹H} (CDCl₃, 125 MHz): δ -4.7, -4.0, 8.1, 18.2, 18.3, 20.9, 26.0, 41.4, 73.9, 74.8. IR (neat): 3575, 3488, 2957, 2932, 2885, 2859, 1472, 1463, 1389, 1376, 1254, 1107, 1092, 963, 836, 776 cm⁻¹. HRMS calcd for C₁₂H₂₈O₂Si (M+Na)⁺: 255.1756, found 255.1757. GC (condition 1): t = 13.0 min (major), t = 14.7 min (minor).

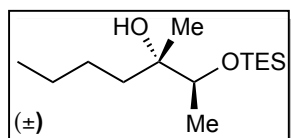


(2SR,3SR)-2-(tert-butyldimethylsilyloxy)-3-methylheptan-3-ol. General procedure A was applied to BuZnCl (276 mg, 1.75mmol), Bu₂Zn (1.50 mL, 1M in pentanes) and 3-((tert-butyldimethylsilyloxy)butan-2-one (100 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc, 99:1) to afford the title compound as an oil (111.7 mg, 86% yield, dr >20:1).

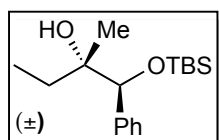
^1H NMR (500 MHz, CDCl_3): δ 0.08 (s, 3H), 0.09 (s, 3H), 0.90 (m, 12H), 1.05 (s, 3H), 1.09 (d, J = 6.3 Hz, 3H), 1.29–1.43 (m, 6H), 2.26 (s, 1H), 3.66 (q, J = 6.3 Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ -5.0, -4.1, 14.0, 17.9, 18.0, 20.8, 23.3, 25.6, 25.7, 38.5, 73.9, 74.3. IR (neat): 3575, 3488, 2957, 2933, 2859, 1472, 1463, 1378, 1255, 1114, 1083, 967, 835, 776 cm^{-1} . HRMS calcd for $\text{C}_{14}\text{H}_{32}\text{O}_2\text{Si}$ (M-OH): 243.2144, found 243.2143. GC (condition 1): t = 23.0 min (major) t = 24.0 min (minor).



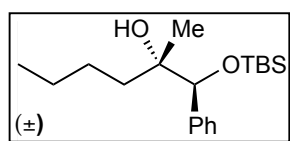
(2SR,3SR)-2-(triethylsilyloxy)-3-methylpentan-3-ol. General procedure A was applied to EtZnCl (226 mg, 1.75mmol), Et_2Zn (0.4 mL, 2M in toluene) and 3-((triethylsilyloxy)oxy)butan-2-one (100 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc, 99:1) to afford the title compound as an oil (111 mg, 96% yield, dr >20:1). ^1H NMR (300 MHz, CDCl_3): δ 0.59–0.67 (q, J = 7.8 Hz, 6H), 0.92 (t, J = 7.5 Hz, 3H), 0.98 (t, J = 7.8 Hz, 9H), 1.04 (s, 3H), 1.11 (d, J = 6.3 Hz, 3H), 1.44–1.49 (q, J = 7.5 Hz, 2H), 2.33 (s, 1H), 3.66–3.72 (q, J = 6.3 Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ 5.4, 7.1, 8.1, 18.4, 20.5, 31.4, 73.8, 74.7. IR (neat): 3572, 3485, 2959, 2941, 2913, 2879, 1459, 1414, 1377, 1239, 1109, 1093, 1058, 1006, 961, 914, 745 cm^{-1} . HRMS calcd for $\text{C}_{12}\text{H}_{28}\text{O}_2\text{Si}$ (M+Na) $^+$: 255.1756, found 255.1759. GC: t = 19 min (major).



(2SR,3SR)-3-methyl-2-((triethylsilyloxy)oxy)heptan-3-ol . General procedure A was applied to BuZnCl (276 mg, 1.75mmol), Bu_2Zn (1.50 ml, 1M in pentanes) and 3-((triethylsilyloxy)oxy)butan-2-one (100 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:toluene, 1:1) to afford the title compound as an oil (101 mg, 78% yield, dr >20:1). ^1H NMR (500 MHz, CDCl_3): δ 0.62 (q, J = 7.9 Hz, 6H), 0.91 (t, J = 7.2 Hz, 3H), 0.97 (t, J = 7.9 Hz, 9H), 1.09 (s, 3H), 1.10 (d, J = 6.4 Hz, 3H), 1.28–1.56 (m, 6H), 2.35 (s, 1H), 3.68 (q, 6.4 Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ 5.4, 7.1, 14.3, 18.4, 21.0, 23.7, 25.9, 38.8, 74.1, 74.6. IR (neat): 3442, 2958, 2927, 1463, 1272, 1121, 1073, 1016, 965 cm^{-1} . HRMS calcd for $\text{C}_{14}\text{H}_{32}\text{O}_2\text{Si}$ (M+Na) $^+$: 283.2072, found 283.2061.

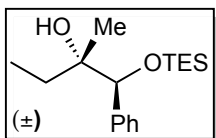


(1SR,2SR)-1-((tert-butyldimethylsilyloxy)oxy)-2-methyl-1-phenylbutan-2-ol . General procedure A was applied to EtZnCl (226 mg, 1.75mmol), Et_2Zn (0.4 mL, 2M in toluene) and 1-((tert-butyldimethylsilyloxy)oxy)-1-phenylpropan-2-one (139 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc, 98:2) to afford the title compound as an oil (130 mg, 88% yield, dr >20:1). ^1H NMR (500 MHz, CDCl_3): δ -0.27 (s, 3H), 0.04 (s, 3H), 0.90 (s, 9H), 0.92–0.96 (m, 6H), 1.43–1.54 (m, 2H), 2.30 (s, 1H), 4.46 (s, 1H), 7.24–7.31 (m, 5H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ -5.0, -4.3, 8.1, 18.4, 21.0, 26.1, 31.2, 75.3, 81.0, 127.6, 127.8, 128.2, 141.3. IR (neat): 3588, 3480, 1463, 1258, 1162, 1087, 1066, 1005, 924, 865, 777, 702 cm^{-1} . HRMS calcd for $\text{C}_{17}\text{H}_{30}\text{O}_2\text{Si}$ (M+Na) $^+$: 317.1915, found 317.1924.



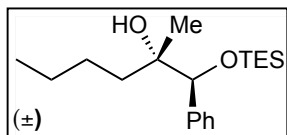
(1SR,2SR)-1-((tert-butyldimethylsilyloxy)oxy)-2-methyl-1-phenylhexan-2-ol . General procedure A was applied to BuZnCl (276 mg, 1.75mmol), Bu_2Zn (1.50 ml, 1M in pentanes) and 1-((tert-butyldimethylsilyloxy)oxy)-1-phenylpropan-2-one (139 mg, 0.5 mmol). The crude product was purified by flash column chromatography on

silica gel (hexanes:toluene, 1:1) to afford the title compound as an oil (131 mg, 81% yield, dr >20:1). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ -0.27 (s, 3H), 0.04 (s, 3H), 0.88–0.92 (m, 12H), 0.96 (s, 3H), 1.26–1.47 (m, 6H), 2.36 (s, 1H), 4.45 (s, 1H), 7.25–7.31 (m, 5H). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ -5.0, -4.3, 14.4, 18.4, 21.7, 23.6, 26.0, 26.1, 38.7, 75.2, 81.2, 127.6, 127.8, 128.2, 141.3. IR (neat): 3575, 3479, 2955, 2931, 2859, 1463, 1388, 1361, 1253, 1093, 1064, 867, 837, 777, 702, 675 cm^{-1} . HRMS calcd for $\text{C}_{17}\text{H}_{34}\text{O}_2\text{Si}$ ($\text{M} + \text{Na}$) $^+$: 345.2228, found 345.2218.



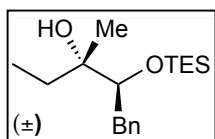
(1SR,2SR)-2-Methyl-1-phenyl-1-((triethylsilyloxy)butan-2-ol. General procedure A was applied to EtZnCl (226 mg, 1.75mmol), Et_2Zn (0.4 mL, 2M in toluene) and 1-phenyl-1-((triethylsilyloxy)propan-2-one (139 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc, 97:3) to afford the title

compound as an oil (125 mg, 85% yield, dr >20:1). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 0.46–0.53 (m, 6H), 0.86 (t, $J = 8.0$ Hz, 9H), 0.93 (s, 3H), 0.94 (t, $J = 7.5$ Hz, 3H), 1.42–1.56 (m, 2H), 2.40 (s, 1H), 4.48 (s, 1H), 7.24–7.33 (m, 5H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ 5.0, 6.9, 8.1, 21.0, 32.3, 75.2, 80.8, 127.6, 127.8, 128.1, 141.5. IR (neat): 3480, 2957, 2912, 1454, 1376, 1240, 1163, 1089, 1066, 1007, 934 cm^{-1} . HRMS calcd for $\text{C}_{17}\text{H}_{30}\text{O}_2\text{Si}$ ($\text{M} + \text{Na}$) $^+$: 317.1915, found 317.1905.



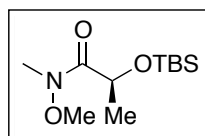
(1SR,2SR)-2-Methyl-1-phenyl-1-((triethylsilyloxy)hexan-2-ol.

General procedure A was applied to BuZnCl (276 mg, 1.75mmol), Bu_2Zn (1.50 mL, 1M in pentanes) and 1-phenyl-1-((triethylsilyloxy)propan-2-one (139 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:toluene, 1:1) to afford the title compound as an oil (126 mg, 78% yield, dr >20:1). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 0.49 (qd, $J = 7.6$ Hz, $J = 3.3$ Hz, 6H), 0.86 (t, $J = 7.6$ Hz, 9H), 0.90 (t, $J = 7.6$ Hz, 3H), 0.94 (s, 3H), 1.26–1.49 (m, 6H), 2.45 (s, 1H), 4.47 (s, 1H), 7.25–7.32 (m, 5H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ 5.0, 6.9, 14.4, 21.6, 23.6, 26.0, 38.7, 75.1, 81.0, 127.6, 127.8, 128.1, 141.5. IR (neat): 3570, 3480, 1454, 1413, 1379, 1239, 1155, 1095, 1064, 1007, 856, 808, 742, 702 cm^{-1} . HRMS calcd for $\text{C}_{19}\text{H}_{34}\text{O}_2\text{Si}$ ($\text{M} + \text{Na}$) $^+$: 345.2228, found 345.2239.



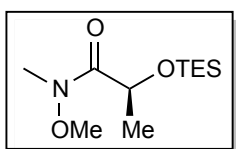
(2SR,3SR)-3-Methyl-1-phenyl-2-((triethylsilyloxy)pentan-3-ol. General procedure A was applied to EtZnCl (226 mg, 1.75mmol), Et_2Zn (0.4 mL, 2M in toluene) and 4-phenyl-3-((triethylsilyloxy)butan-2-one (140 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc, 97:3) to afford the title compound as an oil (105

mg, 68% yield, dr >20:1). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 0.28–0.35 (m, 6H), 0.83 (t, $J = 8.0$ Hz, 9H), 0.96 (t, $J = 7.5$ Hz, 3H), 1.13 (s, 3H), 1.49–1.55 (m, 2H), 2.09 (s, 1H), 2.56 (dd, $J = 8.5$ Hz, $J = 9.0$ Hz, 1H), 2.88 (dd, $J = 14.0$ Hz, $J = 3.5$ Hz, 1H), 3.84 (dd, $J = 9.0$ Hz, $J = 3.5$ Hz, 1H), 7.18–7.29 (m, 5H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ 5.3, 7.2, 8.0, 21.5, 31.6, 39.7, 75.0, 80.3, 126.4, 128.5, 129.8, 140.0. IR (neat): 3479, 2913, 1605, 1456, 1377, 1239, 1097, 1006, 949 cm^{-1} . HRMS calcd for $\text{C}_{18}\text{H}_{32}\text{O}_2\text{Si}$ ($\text{M} + \text{Na}$) $^+$: 331.2072, found 331.2080.



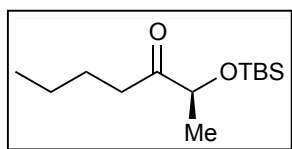
(S)-2-((tert-butyldimethylsilyloxy)-N-methoxy-N-Methylpropanamide. The reaction was conducted according to literature procedure³ by combining

the following reagents: (*S*)-methyl 2-hydroxypropanoate (3.7 mL, 39 mmol), *N,O*-dimethylhydroxylamine hydrochloride (19 g, 194 mmol), and trimethylaluminum (97 mL, 2M in toluene). The crude product was used without further purification. The resulting compound, (*S*)-2-hydroxy-*N*-methoxy-*N*-methylpropanamide (2 g, 15 mmol), was combined with imidazole (1.5 g, 22.5 mmol), and *tert*-butylchlorodimethylsilane (2.5 g, 16.5 mmol) according to literature procedure.³ The crude product was purified by column chromatography on silica gel (hexanes:EtOAc, 4:1) to yield the title compound (3.5 g, 95% yield) as an oil. $[\alpha]_D^{20} = 23.5$ ($c = 1.5$, CHCl₃). ¹H NMR (500 MHz, CDCl₃): δ 0.08 (s, 3H), 0.10 (s, 3H), 0.9 (s, 9H), 1.36 (d, $J = 7.0$ Hz, 3H), 3.21 (s, 3H), 3.70 (s, 3H), 4.65–4.70 (m, 1H). ¹³C{¹H} (CDCl₃, 125 MHz): δ -4.8, -4.5, 18.6, 21.1, 25.9, 26.0, 61.4, 77.2. IR (neat): 2931, 1682, 1472, 1388, 1332, 1253, 1156, 1106, 997, 970, 834, 778 cm⁻¹. HRMS calcd for C₁₁H₂₅NO₃Si (M+H)⁺: 248.1683, found 248.1681.



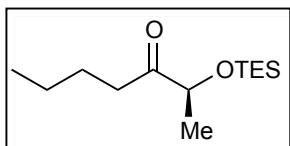
(*S*)-*N*-methoxy-*N*-Methyl-2-((triethylsilyl)oxy)propanamide.

The reaction was conducted according to literature procedure³ by combining the following reagents: The resulting compound, (*S*)-2-hydroxy-*N*-methoxy-*N*-methylpropanamide (1.5 g, 11.3 mmol), was combined with imidazole (1.2 g, 17 mmol), and triethylchlorosilane (2.3 mL, 13.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes:EtOAc, 4:1) to yield the title compound (2.6 g, 95% yield) as an oil. $[\alpha]_D^{20} = 18.0$ ($c = 1.4$, CHCl₃). ¹H NMR (500 MHz, CDCl₃): δ 0.63 (q, $J = 6.7$ Hz, 6H), 0.96 (t, $J = 8.1$ Hz, 9H), 1.37 (d, $J = 6.7$ Hz, 3H), 3.20 (s, 3H), 3.71 (s, 3H), 4.67–4.71 (m, 1H). ¹³C{¹H} (CDCl₃, 125 MHz): δ 4.9, 6.0, 6.8, 6.9, 21.2, 61.4, 77.2. IR (neat): 2955, 2877, 1682, 1460, 1415, 1239, 1155, 1104, 1002, 787, 742 cm⁻¹. HRMS calcd for C₁₁H₂₅NO₃Si (M+H)⁺: 248.1683, found 248.1676.



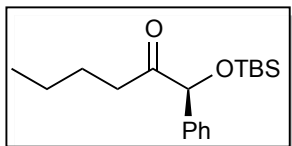
(*S*)-2-((*tert*-butyldimethylsilyl)oxy)Heptan-3-one.

A dry 25 mL Schlenk flask, which was evacuated and backfilled with N₂ three times, was charged with (*S*)-2-((*tert*-butyldimethylsilyl)oxy)-*N*-methoxy-*N*-methylpropanamide (1.5 g, 6 mmol) and Et₂O (15 mL). After cooling the flask to -78 °C, *n*-BuLi (2.9 mL, 2.5M in hexanes) was added slowly. The reaction was monitored by TLC until completion. The reaction mixture was quenched with saturated aq. NH₄Cl (2 mL) followed by addition of Et₂O (5 mL). The organic layer was separated and the aqueous solution extracted with Et₂O (3 × 10 mL). The combined organic layers were successively washed with brine, dried over MgSO₄, and filtered. The filtrate was concentrated *in vacuo* and purified by column chromatography on silica gel (hexanes:EtOAc, 97:3) to yield the title compound (1.26 g, 86% yield) as an oil. $[\alpha]_D^{20} = -7.8$ ($c = 1.0$, CHCl₃). ¹H NMR (500 MHz, CDCl₃): δ 0.08 (s, 6H), 0.91 (t, $J = 7.5$ Hz, 3H), 0.92 (s, 9H), 1.27 (d, $J = 6.9$ Hz, 3H), 1.31 (s, $J = 7.9$ Hz, 2H), 1.54 (q, $J = 7.8$ Hz, 2H), 2.50–2.64 (m, 2H), 4.13 (q, $J = 7.0$ Hz, 1H). ¹³C{¹H} (CDCl₃, 125 MHz): δ -4.8, -4.5, 14.1, 19.3, 21.1, 22.6, 25.5, 25.9, 36.8, 75.1, 214.6. IR (neat): 2957, 2932, 2859, 1719, 1464, 1365, 1257, 1121, 933, 836, 778 cm⁻¹. HRMS calcd for C₁₃H₂₈O₂Si (M-CH₃): 229.1513, found 229.1618.



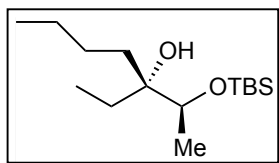
(*S*)-2-((triethylsilyl)oxy)Heptan-3-one. The reaction was conducted according to the procedure above by combining the following reagents: (*S*)-*N*-methoxy-*N*-methyl-2-((triethylsilyl)oxy)propanamide

(1g, 4 mmol) and *n*-BuLi (2 mL, 2.5M in hexanes). The crude product was purified by column chromatograph on silica gel (hexanes:EtOAc, 97:3) to yield the title compound (880 mg, 90% yield) as an oil. $[\alpha]_D^{20} = -7.5$ ($c = 1.1$, CHCl₃). ¹H NMR (500 MHz, CDCl₃): δ 0.62 (q, $J = 8.1$ Hz, 6H), 0.91 (t, $J = 7.5$ Hz, 3H), 0.96 (t, $J = 7.9$ Hz, 9H), 1.28 (d, $J = 7.0$ Hz, 3H), 1.29–1.35 (m, 2H), 1.51–1.57 (m, 2H), 2.53–2.62 (m, 2H), 4.15 (q, $J = 6.9$ Hz, 1H). ¹³C{¹H} (CDCl₃, 125 MHz): δ 5.0, 6.9, 14.1, 21.2, 22.6, 25.6, 35.6, 74.9, 214.6. IR (neat): 2958, 2877, 1719, 1459, 1240, 1171, 1121, 1008, 930, 744 cm⁻¹. HRMS calcd for C₁₃H₂₈O₂Si (M–C₂H₅): 215.1246, found 215.1465.



(S)-1-((*tert*-butyldimethylsilyloxy)-1-Phenylhexan-2-one. The reaction was conducted according to the procedure above by combining the following reagents: (*S*)-2-((*tert*-butyldimethylsilyloxy)-*N*-methoxy-*N*-methyl-2-phenylacetamide)⁹ (520mg, 1.68 mmol) and *n*-BuLi (0.74 mL, 2.5M in hexanes). The

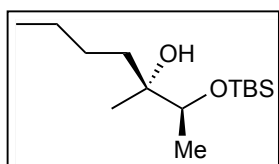
crude product was purified by column chromatograph on silica gel (hexanes:EtOAc, 97:3) to yield the title compound (484 mg, 94% yield) as an oil. $[\alpha]_D^{20} = -56.3$ ($c = 1.2$, CHCl₃). ¹H NMR (500 MHz, CDCl₃): δ –0.02 (s, 3H), 0.07 (s, 3H), 0.79 (t, $J = 7.5$ Hz, 3H), 0.94 (s, 9H), 1.16 (s, $J = 7.5$ Hz, 2H), 1.37–1.47 (m, 2H), 2.39–2.46 (m, 1H), 2.56–2.62 (m, 1H), 5.06 (s, 1H), 7.24–7.42 (m, 5H). ¹³C{¹H} (CDCl₃, 125 MHz): δ –4.9, –4.7, 13.9, 18.4, 22.4, 25.5, 26.0, 35.8, 81.4, 126.0, 128.1, 128.6, 139.0, 210.9. IR (neat): 3097, 3064, 2956, 2859, 1719, 1492, 1471, 1255, 1103, 1069, 870, 779 cm⁻¹. HRMS calcd for C₁₈H₃₀O₂Si (M+H)⁺: 307.2094, found 307.2084.



(2*S*,3*R*)-2-((*tert*-butyldimethylsilyloxy)-3-Ethylheptan-3-ol.⁸

General procedure B was applied to EtZnCl (207 mg, 1.75mmol), Et₂Zn (0.8 mL, 2M in toluene) and (*S*)-2-((*tert*-butyldimethylsilyloxy)heptan-3-one (100 mg, 0.4 mmol). The crude

product was purified by flash column chromatography on silica gel (hexanes:toluene, 4:1) to afford the title compound as an oil (59 mg, 54% yield, dr >20:1). $[\alpha]_D^{20} = 17.7$ ($c = 0.542$, CHCl₃). ¹H NMR (500 MHz, CDCl₃): δ 0.07 (s, 3H), 0.09 (s, 3H), 0.86 (t, $J = 7.5$ Hz, 3H), 0.90 (s, 9H), 0.91 (t, $J = 7.2$ Hz, 3H), 1.10 (d, $J = 6.5$ Hz, 3H), 1.26–1.37 (m, 4H), 1.47–1.54 (m, 4H), 2.13 (s, 1H), 3.72 (q, $J = 6.10$ Hz, 1H). ¹³C{¹H} (CDCl₃, 125 MHz): δ –4.7, –3.8, 8.1, 14.3, 17.9, 18.2, 23.8, 25.7, 26.1, 28.7, 33.4, 72.7, 76.0. IR (neat): 2956, 2859, 1463, 1376, 1255, 1099, 974, 834, 775 cm⁻¹. HRMS calcd for C₁₅H₃₄O₂Si (M–C₄H₉): 217.1751, found 217.1626. GC (condition 2): t = 37.2 min (major), t = 36.9 min (minor).

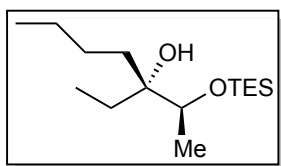


(2*S*,3*R*)-2-((*tert*-butyldimethylsilyloxy)-3-Methylheptan-3-ol.

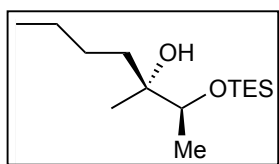
General procedure B was applied to MeZnCl (201 mg, 1.75mmol), Me₂Zn (0.8 mL, 2M in toluene) and (*S*)-2-((*tert*-butyldimethylsilyloxy)heptan-3-one (100 mg, 0.4 mmol). The crude

product was purified by flash column chromatography on silica gel (hexanes:toluene, 4:1) to afford the title compound as an oil (84 mg, 81% yield, dr >20:1). $[\alpha]_D^{20} = 10.6$ ($c = 1.1$, CHCl₃). ¹H NMR (500 MHz, CDCl₃): δ 0.08 (s, 3H), 0.09 (s, 3H), 0.90 (s, 9H), 0.91 (t, $J = 7.3$ Hz, 3H), 1.09–1.12 (m, 6H), 1.24–1.41 (M, 6H), 2.17 (s, 1H), 3.62 (q, $J = 6.6$ Hz,

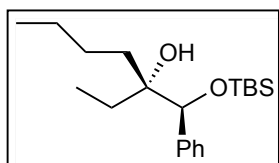
1H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ -4.7, -3.8, 14.3, 18.1, 18.2, 23.7, 23.8, 25.9, 26.1, 36.5, 74.5, 75.1. IR (neat): 3478, 2956, 2931, 2859, 1471, 1377, 1255, 1115, 835, 776, 667 cm^{-1} . HRMS calcd for $\text{C}_{14}\text{H}_{32}\text{O}_2\text{Si}$ (M-OH): 243.2099, found 243.2133. GC (condition 2): t = 26.6 min (major), t = 25.8 min (minor).



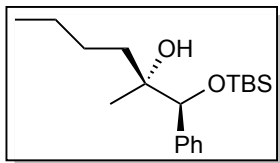
(2*S*,3*R*)-3-ethyl-2-((triethylsilyloxy)heptan-3-yl)heptan-3-ol. General procedure B was applied to EtZnCl (207 mg, 1.75mmol), Et₂Zn (0.8 mL, 2M in toluene) and (*S*)-2-((triethylsilyloxy)heptan-3-yl)heptan-3-one (100 mg, 0.4 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:toluene, 4:1) to afford the title compound as an oil (56 mg, 51% yield, dr >20:1). $[\alpha]_D^{20} = 13.1$ ($c = 1.08$, CHCl_3). ^1H NMR (500 MHz, CDCl_3): δ 0.62 (q, $J = 7.7$ Hz, 6H), 0.86 (t, $J = 7.4$ Hz, 3H), 0.91 (t, $J = 7.4$ Hz, 3H), 0.97 (t, $J = 8.0$ Hz, 9H), 1.11 (d, $J = 6.7$ Hz, 3H), 1.25–1.34 (m, 4H), 1.47–1.53 (m, 4H), 2.19 (s, 1H), 3.74 (q, $J = 6.7$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ 5.4, 7.1, 8.1, 14.3, 17.9, 23.8, 25.7, 28.6, 33.3, 72.6, 75.9. IR (neat): 2957, 2877, 1460, 1377, 1239, 1116, 1006, 946, 791, 744 cm^{-1} . HRMS calcd for $\text{C}_{15}\text{H}_{34}\text{O}_2\text{Si}$ (M-OH): 257.2255, found 257.2285.



(2*S*,3*R*)-3-methyl-2-((triethylsilyloxy)heptan-3-yl)heptan-3-ol. General procedure B was applied to MeZnCl (201 mg, 1.75mmol), Me₂Zn (0.8 mL, 2M in toluene) and (*S*)-2-((triethylsilyloxy)heptan-3-yl)heptan-3-one (100 mg, 0.4 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:toluene, 4:1) to afford the title compound as an oil (90 mg, 86% yield, dr >20:1). $[\alpha]_D^{20} = 19.7$ ($c = 1.1$, CHCl_3). ^1H NMR (500 MHz, CDCl_3): δ 0.62 (q, $J = 8.2$ Hz, 6H), 0.92 (t, $J = 7.4$ Hz, 3H), 0.97 (t, $J = 7.8$ Hz, 9H), 1.11 (s, 3H), 1.12 (d, $J = 6.7$ Hz, 3H), 1.24–1.51 (m, 6H), 2.25 (s, 1H), 3.65 (q, $J = 6.1$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ 5.3, 7.1, 14.3, 18.1, 23.70, 23.73, 25.9, 36.3, 74.5, 75.1. IR (neat): 3477, 2939, 2876, 1459, 1377, 1239, 1116, 1008, 980, 782, 726 cm^{-1} . HRMS calcd for $\text{C}_{14}\text{H}_{32}\text{O}_2\text{Si}$ (M-OH): 243.2099, found 243.2142.



(*R*)-3-((*S*)-((*tert*-butyl dimethylsilyloxy)(phenyl)methyl)heptan-3-yl)heptan-3-ol. General procedure B was applied to EtZnCl (207 mg, 1.75mmol), Et₂Zn (0.8 mL, 2M in toluene) and (*S*)-1-((*tert*-butyl dimethylsilyloxy)-1-phenylhexan-2-one (123 mg, 0.4 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:toluene, 4:1) to afford the title compound as an oil (75 mg, 56% yield, dr >20:1). $[\alpha]_D^{20} = 40.8$ ($c = 1.95$, CHCl_3). ^1H NMR (500 MHz, CDCl_3): δ -0.30 (s, 3H), 0.03 (s, 3H), 0.82 (t, $J = 7.7$ Hz, 3H), 0.89 (s, 9H), 0.92 (t, $J = 7.5$ Hz, 3H), 1.11–1.24 (m, 6H), 1.54–1.66 (m, 2H), 2.23 (s, 1H), 4.52 (s, 1H), 7.24–7.32 (m, 5H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ -5.0, -4.2, 8.4, 14.2, 18.3, 23.5, 25.4, 26.1, 28.6, 33.6, 76.8, 79.1, 127.6, 127.8, 128.4, 141.1. IR (neat): 3572, 2956, 2854, 1246, 1388, 1252, 1086, 866, 777, 701 cm^{-1} . HRMS calcd for $\text{C}_{15}\text{H}_{34}\text{O}_2\text{Si}$ (M-OH): 319.2412, found 319.2470.

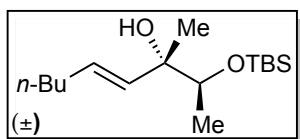


(1S,2R)-1-((*tert*-butyldimethylsilyl)oxy)-2-Methyl-1-phenylhexan-2-ol. General procedure B was applied to MeZnCl (201 mg, 1.75mmol), Me₂Zn (0.8 mL, 2M in toluene) and (*S*)-2-((*tert*-butyldimethylsilyl)oxy)heptan-3-one (99 mg, 0.4 mmol). The crude product was purified by flash column chromatography on silica gel

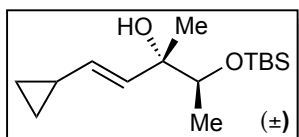
(hexanes:toluene, 4:1) to afford the title compound as an oil (84 mg, 77% yield, dr >20:1). $[\alpha]_D^{20} = 49.3$ ($c = 1.993$, CHCl₃). ¹H NMR (500 MHz, CDCl₃): δ -0.27 (s, 3H), 0.04 (s, 3H), 0.86 (t, $J = 7.2$ Hz, 3H), 0.90 (s, 9H), 1.13 (s, 3H), 1.25–1.30 (m, 4H), 1.38–1.44 (m, 2H), 2.09 (s, 1H), 4.46 (s, 1H), 7.25–7.33 (m, 5H). ¹³C{¹H} (CDCl₃, 125 MHz): δ -5.0, -4.3, 14.3, 18.4, 23.4, 23.6, 25.7, 26.1, 36.7, 75.1, 82.0, 127.6, 127.8, 128.3, 141.1. IR (neat): 3466, 2955, 2859, 1463, 1387, 1257, 1092, 867, 777, 702, 673 cm⁻¹. HRMS calcd for C₁₉H₃₄O₂Si (M–OH): 305.2255, found 305.2310.

II. Diastereoselective Generation of (*E*)-Di- and (*E*)-Trisubstituted Allylic Alcohols via Addition to Chiral Ketones

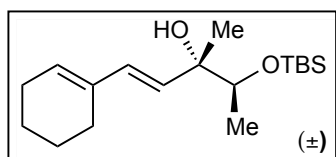
General Procedure C: A dry 10 mL Schlenk flask, which was evacuated under vacuum and backfilled with N₂ (g) three times, was charged with dicyclohexylborane (Cy₂BH) (125 mg, 0.7 mmol) and toluene (1.5 mL). The solution was cooled to 0 °C followed by slow addition of alkyne (0.7 mmol). After 5 min the reaction was warmed to room temperature and stirred for an additional 15 min. The solution was cooled to -78 °C and dimethylzinc (Me₂Zn) (0.4 mL, 2M in toluene) was added. After stirring at -78 °C for 30 minutes, the reaction flask was warmed to -30 °C and EtZnCl (1.05 mmol) was added under a steady flow of N₂ (g). Immediately thereafter, the ketone (0.35 mmol, in 0.2 mL toluene) was added. The reaction mixture stirred at -30 °C and was monitored by TLC until completion (usually 36–48 h). The reaction mixture was quenched with saturated aq. NH₄Cl (2 mL) and 2N HCl (1 mL) followed by addition of 5 mL Et₂O. The organic layer was separated and the aqueous layer was extracted successively with Et₂O (2 × 5 mL). The combined organic layers were successively washed with aq. NaHCO₃ and brine, dried over MgSO₄, and filtered. The filtrate was concentrated in vacuo and purified by column chromatography on silica gel



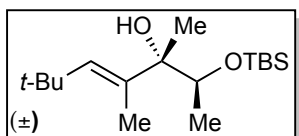
(2SR,3SR,*E*)-2-((*tert*-butyldimethylsilyloxy)-3-Methylnon-4-en-3-ol. General procedure C was applied to Cy₂BH (125 mg, 0.7 mmol), 1-hexyne (81 μ L, 0.70 mmol), Me₂Zn (0.35 mL, 2M in toluene), EtZnCl (136 mg, 1.05 mmol), and 3-((*tert*-butyldimethylsilyl)oxy)butan-2-one (71 mg, 0.35 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes) to afford the title compound as an oil (88 mg, 88% yield, dr >20:1). ¹H NMR (300 MHz, CDCl₃) δ 0.07(s, 3H), 0.08 (s, 3H), 0.90 (m, 12H), 1.09 (d, $J = 6.3$ Hz, 3H), 1.17 (s, 3H), 1.31–1.36 (m, 4H), 2.01–2.05 (m, 2H), 2.43 (s, 1H), 3.62 (q, $J = 6.0$ Hz, 1H), 5.46 (d, $J = 15.6$ Hz, 1H), 5.64–5.74 (td, $J = 15.6$ Hz, $J = 6.6$ Hz, 1H). ¹³C{¹H} (CDCl₃, 125 MHz): δ -4.7, -4.0, 14.2, 18.2, 18.3, 22.4, 22.5, 26.0, 31.6, 32.3, 74.9, 75.0, 129.9, 134.9. IR (neat) 3563, 3478, 2957, 2930, 2858, 1471, 1463, 1376, 1362, 1255, 1090, 973, 836, 776, 669 cm⁻¹. HRMS calcd for C₁₆H₃₄O₂Si (M+Na)⁺: 309.2226, found 303.2229.



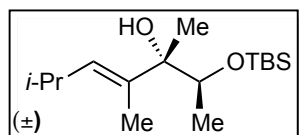
(3SR,4SR,E)-4-(tert-butyldimethylsilyloxy)-1-cyclopropyl-3-methylpent-1-en-3-ol. General procedure C was applied to Cy₂BH (1.8 g, 5 mmol), cyclopropylacetylene (847 μ L, 0.70 mmol), Me₂Zn (5 mL, 2M in toluene), EtZnCl (136 mg, 1.05 mmol), and 3-((tert-butyldimethylsilyl)oxy)butan-2-one (1.0 g, 5 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc, 98:2) to afford the title compound as an oil (1.1 g, 81% yield, dr >20:1). ¹H NMR (500 MHz, CDCl₃): δ 0.07 (s, 3H), 0.08 (s, 3H), 0.34–0.38 (m, 2H), 0.67–0.71 (m, 2H), 0.90 (s, 9H), 1.10 (d, J = 6.0 Hz, 3H), 1.15 (s, 3H), 1.36–1.39 (m, 1H), 2.43 (s, 1H), 3.58–3.65 (q, J = 6.3 Hz, 1H), 5.19 (dd, J = 15.6 Hz, J = 8.7 Hz, 1H), 5.53 (d, J = 15.6 Hz, 1H). ¹³C{¹H} (CDCl₃, 125 MHz): δ -4.6, -4.0, 6.7, 6.8, 13.9, 18.2, 18.3, 22.4, 26.0, 74.8, 74.9, 132.7, 133.4. IR (neat) 3558, 3474, 3082, 2956, 2931, 2885, 2859, 1472, 1463, 1255, 1090, 967, 835, 812, 776 cm⁻¹. HRMS calcd for C₁₅H₃₀O₂Si (M+Na)⁺: 293.1913, found 293.1918.



(3SR,4SR,E)-4-(tert-butyldimethylsilyloxy)-1-cyclohexenyl-3-methylpent-1-en-3-ol. General procedure C was applied to Cy₂BH (125 mg, 0.7 mmol), 1-ethynylcyclohexene (82 μ L, 0.70 mmol), Me₂Zn (0.35 mL, 2M in toluene), EtZnCl (136 mg, 1.05 mmol), and 3-((tert-butyldimethylsilyl)oxy)butan-2-one (71 mg, 0.35 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:dichloromethane, 99:1) to afford the title compound as an oil (90 mg, 83% yield, dr = 18:1). ¹H NMR (300 MHz, CDCl₃): δ 0.05 (s, 3H), 0.08 (s, 3H), 0.91 (s, 9H), 1.10 (d, J = 6.3 Hz, 3H), 1.21 (s, 3H), 1.58–1.69 (m, 4H), 2.09–2.13 (m, 4H), 2.49 (s, 1H), 3.67 (q, J = 6.3 Hz, 1H), 5.54 (d, J = 15.6 Hz, 1H), 5.76 (bs, 1H), 6.29 (d, J = 15.9 Hz, 1H). ¹³C{¹H} (CDCl₃, 125 MHz): δ -5.0, -4.3, 17.9, 18.1, 22.3, 22.4, 22.5, 24.5, 25.7, 25.8, 74.8, 75.0, 129.1, 130.2, 132.1, 135.0. IR (neat) 3557, 3468, 2953, 2929, 2858, 1649, 1472, 1462, 1448, 1375, 1255, 1090, 970, 835, 776 cm⁻¹. HRMS calcd for C₁₈H₃₄O₂Si (M+Na)⁺: 333.2226, found 333.2210.

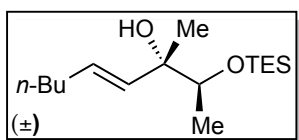


(2SR,3SR,E)-2-(tert-butyldimethylsilyloxy)-3,4,6,6-tetramethylhept-4-en-3-ol. General procedure C was applied to Cy₂BH (157 mg, 0.88 mmol), 4,4-dimethyl-2-pentyne (118 μ L, 0.88 mmol), Me₂Zn (0.50 mL, 2M in toluene), EtZnCl (136 mg, 1.05 mmol), and 3-((tert-butyldimethylsilyl)oxy)butan-2-one (71 mg, 0.35 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:dichloromethane, 99:1) to afford the title compound as an oil (82 mg, 78% yield, dr >20:1). ¹H NMR (300 MHz, CDCl₃): δ 0.06 (s, 3H), 0.08 (s, 3H), 0.89 (s, 9H), 1.08 (d, J = 6.3 Hz, 3H), 1.21 (s, 9H), 1.73 (d, J = 0.9 Hz, 3H), 2.49 (s, 1H), 3.89 (q, J = 6.3 Hz, 1H), 5.55 (q, J = 1.2 Hz, 1H). ¹³C{¹H} (CDCl₃, 125 MHz): δ -4.6, -3.7, 14.1, 18.2, 18.4, 22.4, 26.1, 31.2, 32.2, 72.1, 78.0, 134.8, 137.6. IR (neat) 3556, 3480, 2956, 2932, 2903, 2859, 1472, 1464, 1375, 1362, 1255, 1100, 1090, 964, 838, 776 cm⁻¹. HRMS calcd for C₁₇H₃₆O₂Si (M+Na)⁺: 323.2382, found 323.2369.



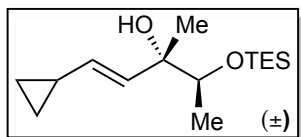
(2SR,3SR,E)-2-(tert-butyldimethylsilyloxy)-3,4,6-trimethylhept-4-en-3-ol. General procedure C was applied to Cy₂BH (157 mg, 0.88 mmol), 4-dimethyl-2-pentyne (100 μ L, 0.88 mmol), Me₂Zn (0.50 mL, 2M in toluene), EtZnCl (136 mg, 1.05 mmol), and 3-((tert-

butyldimethylsilyloxy)butan-2-one (80 mg, 0.35 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:dichloromethane, 99:1) to afford the title compound as an oil (65 mg, 65% yield, dr >20:1). ^1H NMR (300 MHz, CDCl_3): δ 0.05 (s, 3H), 0.08 (s, 3H), 0.88 (s, 9H), 0.94 (d, $J = 5.1$ Hz, 3H), 0.96 (d, $J = 4.8$ Hz, 3H), 1.07 (d, $J = 6.3$ Hz, 3H), 1.65 (s, 3H), 2.48 (s, 1H), 2.49–2.54 (m, 1H), 3.74 (q, $J = 6.3$ Hz, 1H), 5.33 (d, $J = 8.7$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ -4.7, -3.8, 13.2, 18.2, 18.3, 22.1, 23.1, 23.2, 26.0, 27.3, 71.2, 132.7, 136.4. IR (neat) 3558, 3479, 2957, 2931, 2898, 2859, 1464, 1375, 1361, 1313, 1255, 1091, 964, 836, 776 cm^{-1} . HRMS calcd for $\text{C}_{16}\text{H}_{34}\text{O}_2\text{Si}$ ($\text{M}+\text{Na}$) $^+$: 309.2226, found 309.2225.



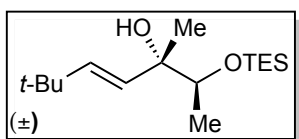
(2SR,3SR,E)-3-Methyl-2-((triethylsilyloxy)non-4-en-3-ol. General procedure C was applied to Cy_2BH (125 mg, 0.7 mmol), 1-hexyne (81 μL , 0.70 mmol), Me_2Zn (0.35 mL, 2M in toluene), EtZnCl (136 mg, 1.05 mmol), and 3-((triethylsilyloxy)butan-2-one (71 mg, 0.35 mmol). The crude product was purified by flash column

chromatography on silica gel (hexanes:EtOAc, 97:3) to afford the title compound as an oil (91 mg, 91% yield, dr >20:1). ^1H NMR (500 MHz, CDCl_3): δ 0.61 (q, $J = 8.0$ Hz, 6H), 0.89 (t, $J = 7.0$ Hz, 3H), 0.96 (t, $J = 7.9$, 9H), 1.09 (d, $J = 6.2$ Hz, 3H), 1.16 (s, 3H), 1.29–1.37 (m, 4H), 2.03 (q, $J = 6.9$ Hz, 2H), 2.51 (s, 1H), 3.63 (q, $J = 6.1$ Hz, 1H), 5.46 (d, $J = 16.1$ Hz, 1H), 5.68 (dt, $J = 15.8$ Hz, $J = 7.0$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ 5.3, 7.1, 14.2, 18.4, 22.1, 22.5, 31.7, 32.3, 74.9, 75.0, 130.0, 134.8. IR (neat): 3563, 3479, 2957, 2932, 2877, 1457, 1377, 1239, 1091, 1006, 974, 778, 741, 676 cm^{-1} . HRMS calcd for $\text{C}_{16}\text{H}_{34}\text{O}_2\text{Si}$ ($\text{M}+\text{Na}$) $^+$: 309.2228, found 309.2235.



(3SR,4SR,E)-1-Cyclopropyl-3-methyl-4-((triethylsilyloxy)pent-1-en-3-ol. General procedure C was applied to Cy_2BH (125 mg, 0.7 mmol), cyclopropylacetylene (60 μL , 0.70 mmol), Me_2Zn (0.35 mL, 2M in toluene), EtZnCl (136 mg, 1.05 mmol), and 3-((triethylsilyloxy)butan-2-one (71 mg, 0.35 mmol). The crude

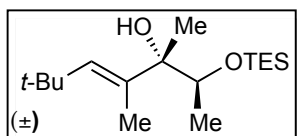
product was purified by flash column chromatography on silica gel (hexanes:EtOAc, 98:2) to afford the title compound as an oil (64 mg, 68% yield, dr >20:1). ^1H NMR (500 MHz, CDCl_3): δ 0.35–0.38 (m, 2H), 0.6 (q, $J = 8.0$ Hz, 6H), 0.67–0.69 (m, 2H), 0.96 (t, $J = 8.0$ Hz, 9H), 1.10 (d, $J = 6.0$ Hz, 3H), 1.15 (s, 3H), 1.34–1.41 (m, 1H), 2.48 (s, 1H), 3.63 (q, $J = 6.0$ Hz, 1H), 5.21 (dd, $J = 15.5$ Hz, $J = 9.0$ Hz, 1H), 5.54 (d, $J = 15.5$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ 5.3, 6.7, 6.8, 7.1, 13.9, 18.5, 22.2, 74.9, 132.6, 133.5. IR (neat): 3472, 2956, 1667, 1456, 1377, 1239, 1091, 1017, 966 cm^{-1} . HRMS calcd for $\text{C}_{15}\text{H}_{30}\text{O}_2\text{Si}$ ($\text{M}-\text{OH}$): 253.1946, found 253.1983.



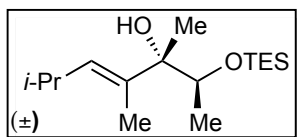
(2SR,3SR,E)-3,6,6-Trimethyl-2-((triethylsilyloxy)hept-4-en-3-ol. General procedure C was applied to Cy_2BH (125 mg, 0.7 mmol), 3,3-dimethyl-1-butyne (86 μL , 0.70 mmol), Me_2Zn (0.35 mL, 2M in toluene), EtZnCl (136 mg, 1.05 mmol), and 3-((triethylsilyloxy)butan-2-one (71 mg, 0.35 mmol). The crude

product was purified by flash column chromatography on silica gel (hexanes:EtOAc, 98:2) to afford the title compound as an oil (64 mg, 64% yield, dr >20:1). ^1H NMR (500 MHz, CDCl_3): δ 0.61 (q, $J = 8.2$ Hz, 6H), 0.97 (t, $J = 8.6$ Hz, 9H), 1.00 (s, 9H), 1.09 (d, $J = 6.3$ Hz, 3H), 1.16 (s, 3H), 2.51 (s, 1H), 3.64 (q, $J = 6.5$ Hz, 1H), 5.37 (d, $J = 15.9$ Hz, 1H), 5.70 (d, $J = 15.9$ Hz, 1H).

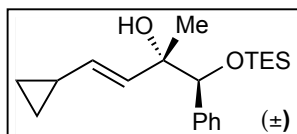
$^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ 5.9, 7.1, 18.4, 22.2, 29.8, 32.9, 74.9, 75.0, 129.7, 140.6. IR (neat): 3480, 2958, 2877, 1459, 1363, 1239, 1091, 1007, 978, 787, 739 cm^{-1} . HRMS calcd for $\text{C}_{16}\text{H}_{34}\text{O}_2\text{Si}$ ($\text{M}+\text{Na}$) $^+$: 309.2228, found 309.2238.



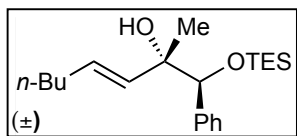
(2SR,3SR,E)-3,4,6,6-Tetramethyl-2-((triethylsilyloxy)hept-4-en-3-ol. General procedure C was applied to Cy_2BH (157 mg, 0.88 mmol), 4,4-dimethyl-2-pentyne (118 μL , 0.88 mmol), Me_2Zn (0.50 mL, 2M in toluene), EtZnCl (136 mg, 1.05 mmol), and 3-((triethylsilyloxy)butan-2-one (71 mg, 0.35 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc, 99:1) to afford the title compound as an oil (85 mg, 81% yield, dr >20:1). ^1H NMR (500 MHz, CDCl_3): δ 0.60 (q, J = 8.3 Hz, 6H), 0.95 (t, J = 8.0 Hz, 9H), 1.08 (d, J = 6.3 Hz, 3H), 1.12 (s, 9H), 1.15 (s, 3H), 1.73 (s, 3H), 2.57 (s, 1H), 3.90 (q, J = 6.8 Hz, 1H), 5.52 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ 5.4, 7.1, 14.1, 18.5, 22.0, 31.2, 32.2, 72.1, 78.0, 135.0, 137.6. IR (neat): 3467, 2912, 1647, 1463, 1374, 1311, 1090, 1006, 962 cm^{-1} . HRMS calcd for $\text{C}_{17}\text{H}_{36}\text{O}_2\text{Si}$ ($\text{M}-\text{OH}$): 283.2416, found 283.2462.



(2SR,3SR,E)-3,4,6-Trimethyl-2-((triethylsilyloxy)hept-4-en-3-ol. General procedure C was applied to Cy_2BH (157 mg, 0.88 mmol), 4-dimethyl-2-pentyne (100 μL , 0.88 mmol), Me_2Zn (0.50 mL, 2M in toluene), EtZnCl (136 mg, 1.05 mmol), and 3-((triethylsilyloxy)butan-2-one (80 mg, 0.35 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:dichloromethane, 99:1) to afford the title compound as an oil (80 mg, 80% yield, dr >20:1). ^1H NMR (500 MHz, CDCl_3): δ 0.59 (q, J = 7.6 Hz, 6H), 0.93–0.97 (m, 15H), 1.07 (d, J = 6.3 Hz, 3H), 1.16 (s, 3H), 1.63 (d, J = 1.3 Hz, 3H), 2.50–2.53 (m, 1H), 2.57 (s, 1H), 3.88 (q, J = 6.5 Hz, 1H), 5.3 (dd, J = 9.0 Hz, J = 1.3 Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ 5.3, 7.1, 13.1, 18.4, 21.7, 23.0, 23.1, 27.3, 72.1, 77.4, 132.9, 136.3. IR (neat): 3460, 2936, 1638, 1448, 1333, 1303, 1070, 1083, 974 cm^{-1} . HRMS calcd for $\text{C}_{16}\text{H}_{34}\text{O}_2\text{Si}$ ($\text{M}+\text{Na}$) $^+$: 309.2228, found 309.2219.

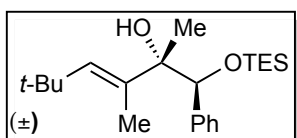


(1SR,2SR,E)-4-Cyclopropyl-2-methyl-1-phenyl-1-((triethylsilyloxy)but-3-en-2-ol. General procedure C was applied to Cy_2BH (125 mg, 0.7 mmol), cyclopropylacetylene (60 μL , 0.70 mmol), Me_2Zn (0.35 mL, 2M in toluene), EtZnCl (136 mg, 1.05 mmol), and 1-phenyl-1-((triethylsilyloxy)propan-2-one (92 mg, 0.35 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc, 98:2) to afford the title compound as an oil (83 mg, 71% yield, dr >20:1). ^1H NMR (500 MHz, CDCl_3): δ 0.33–0.35 (m, 2H), 0.47–0.52 (m, 6H), 0.66–0.69 (m, 2H), 0.86 (t, J = 8.2 Hz, 9H), 1.06 (s, 3H), 1.35–1.40 (m, 1H), 2.50 (s, 1H), 4.44 (s, 1H), 5.13 (dd, J = 15.5 Hz, J = 9.1 Hz, 1H), 5.58 (d, J = 15.5 Hz, 1H), 7.24–7.31 (m, 5H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ 5.0, 6.7, 6.7, 6.9, 13.7, 25.6, 75.2, 81.6, 127.6, 127.7, 128.2, 132.3, 133.3, 141.0. IR (neat): 3564, 3479, 1667, 1494, 1455, 1414, 1378, 1310, 1240, 1190, 1159, 1091, 1065, 1006, 978, 856, 811, 743, 701 cm^{-1} . HRMS calcd for $\text{C}_{20}\text{H}_{32}\text{O}_2\text{Si}$ ($\text{M}+\text{Na}$) $^+$: 333.2077, found 355.2072.



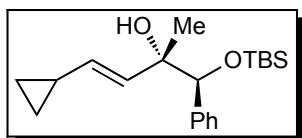
(1SR,2SR,E)-2-Methyl-1-phenyl-1-((triethylsilyloxy)oct-3-en-2-ol. General procedure C was applied to Cy_2BH (125 mg, 0.7 mmol), 1-

hexyne (81 μL , 0.70 mmol), Me_2Zn (0.35 mL, 2M in toluene), EtZnCl (136 mg, 1.05 mmol), and 1-phenyl-1-((triethylsilyl)oxy)propan-2-one (92 mg, 0.35 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc, 98:2) to afford the title compound as an oil (101 mg, 83% yield, dr >20:1). ^1H NMR (500 MHz, CDCl_3): δ 0.49 (qd, $J = 7.8$ Hz, $J = 2.9$ Hz, 6H), 0.86 (t, $J = 7.9$ Hz, 9H), 0.89 (t, $J = 6.9$ Hz, 3H), 1.08 (s, 3H), 1.26–1.36 (m, 4H), 2.02 (q, $J = 6.9$ Hz, 2H), 2.47 (s, 1H), 4.45 (s, 1H), 5.50–5.60 (m, 2H), 7.23–7.30 (m, 5H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ 5.0, 6.9, 14.2, 22.4, 23.5, 31.6, 32.2, 75.3, 81.7, 127.6, 127.7, 128.2, 129.8, 134.5, 141.0. IR (neat) 3562, 3479, 2956, 2931, 2876, 1455, 1433, 1377, 1309, 1239, 1174, 1090, 1006, 975, 846, 743 cm^{-1} . HRMS calcd for $\text{C}_{21}\text{H}_{36}\text{O}_2\text{Si}$ ($\text{M}+\text{Na}$) $^+$: 371.2385, found 371.2380.



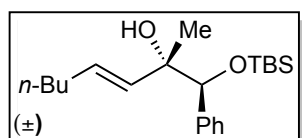
(1SR,2SR,E)-2,3,5,5-Tetramethyl-1-phenyl-1-((triethylsilyl)oxy)hex-3-en-2-ol. General procedure C was applied to Cy_2BH (125 mg, 0.7 mmol), 4,4-dimethyl-2-pentyne (141 μL , 1.05 mmol), Me_2Zn (0.35 mL, 2M in toluene), EtZnCl (136 mg, 1.05 mmol), and 1-phenyl-1-((triethylsilyl)oxy)propan-2-one (92 mg, 0.35

mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc, 98:2) to afford the title compound as an oil (80 mg, 63% yield, dr >20:1). ^1H NMR (500 MHz, CDCl_3): δ 0.48 (q, $J = 8.3$ Hz, 6H), 0.86 (t, $J = 7.9$ Hz, 9H), 0.98 (s, 3H), 1.09 (s, 9H), 1.76 (d, $J = 1.4$ Hz, 3H), 2.83 (s, 1H), 4.64 (s, 1H), 5.38 (d, $J = 1.3$ Hz, 1H), 7.22–7.28 (m, 5H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ 5.0, 7.0, 14.6, 22.7, 31.1, 32.2, 78.4, 79.2, 127.4, 127.5, 128.1, 135.8, 136.8, 141.2. IR (neat) 2955, 1463, 1362, 1253, 1088, 1062, 863, 837, 777, 732, 700 cm^{-1} . HRMS calcd for $\text{C}_{22}\text{H}_{38}\text{O}_2\text{Si}$ ($\text{M}+\text{Na}$) $^+$: 385.2539, found 385.2540.



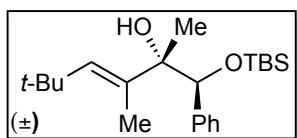
(1SR,2SR,E)-1-((tert-butyldimethylsilyl)oxy)-4-cyclopropyl-2-methyl-1-phenylbut-3-en-2-ol. General procedure C was applied to Cy_2BH (125 mg, 0.7 mmol), cyclopropylacetylene (60 μL , 0.70 mmol), Me_2Zn (0.35 mL, 2M in toluene), EtZnCl (136 mg, 1.05

mmol), and (*S*)-1-((tert-butyldimethylsilyl)oxy)-1-phenylpropan-2-one (92 mg, 0.35 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc, 98:2) to afford the title compound as an oil (86 mg, 74% yield, dr >20:1). $[\alpha]_D^{20} = 25.8$ ($c = 2.2$, CHCl_3). ^1H NMR (500 MHz, CDCl_3): δ -0.24 (s, 3H), 0.03 (s, 3H), 0.32–0.35 (m, 2H), 0.66–0.69 (m, 2H), 0.89 (s, 9H), 1.06 (s, 3H), 1.34–1.41 (m, 1H), 2.41 (s, 1H), 4.42 (s, 1H), 5.12 (dd, $J = 15.7$ Hz, $J = 8.8$ Hz, 1H), 5.57 (d, $J = 15.5$ Hz, 1H), 7.23–7.28 (m, 5H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ -4.9, -4.4, 6.6, 6.7, 13.7, 18.4, 23.8, 26.0, 75.3, 81.7, 127.6, 127.7, 128.3, 132.4, 133.3, 140.8. IR (neat): 3564, 3479, 3083, 3065, 3029, 2955, 2930, 2886, 1667, 1472, 1455, 1361, 1253, 1190, 1091, 1066, 968, 866, 837, 777 cm^{-1} . HRMS calcd for $\text{C}_{20}\text{H}_{32}\text{O}_2\text{Si}$ ($\text{M}+\text{Na}$) $^+$: 355.2072, found 355.2074. HPLC conditions: Chiralpak AD-H, $t_1 = 12.3$ min (major), $t_2 = 13.3$ min (hexanes/2-propanol: 99/1, 0.5 mL/min).



(1SR,2SR,E)-1-((tert-butyldimethylsilyl)oxy)-2-methyl-1-phenyloct-3-en-2-ol. General procedure C was applied to Cy_2BH (125 mg, 0.7 mmol), 1-hexyne (81 μL , 0.70 mmol), Me_2Zn (0.35 mL, 2M in toluene), EtZnCl (136 mg, 1.05 mmol), and 1-((tert-

butyldimethylsilyloxy)-1-phenylpropan-2-one (93 mg, 0.35 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:toluene, 1:1) to afford the title compound as an oil (101 mg, 76% yield, dr >20:1). ^1H NMR (500 MHz, CDCl_3): δ -0.28 (s, 3H), 0.03 (s, 3H), 0.88 (t, $J = 7.0$ Hz, 3H), 0.89 (s, 9H), 1.09 (s, 3H), 1.26–1.36 (m, 4H), 2.02 (q, $J = 6.5$ Hz, 2H), 2.37 (s, 1H), 4.43 (s, 1H), 5.50–5.60 (m, 2H), 7.23–7.28 (m, 5H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ -5.0, -4.4, 14.2, 18.4, 22.5, 23.8, 26.0, 31.6, 32.2, 75.4, 81.8, 127.6, 127.7, 128.3, 129.8, 134.5, 140.8. IR(neat): 3565, 3480, 3030, 2956, 2858, 1463, 1361, 1252, 1176, 1090, 1066, 975, 938, 868, 837, 777, 748, 701, 676, 615 cm^{-1} . HRMS calcd for $\text{C}_{21}\text{H}_{36}\text{O}_2\text{Si}$ ($\text{M}+\text{Na}$) $^+$: 371.2385, found 370.2392.

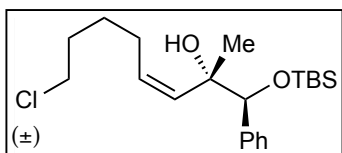


(1SR,2SR,E)-1-((tert-butyldimethylsilyloxy)-2,3,5,5-Tetramethyl-1-phenylhex-3-en-2-ol. General procedure C was applied to Cy_2BH (125 mg, 0.7 mmol), 4,4-dimethyl-2-pentyne (141 μL , 1.05 mmol), Me_2Zn (0.35 mL, 2M in toluene), EtZnCl (136 mg, 1.05 mmol), and 1-((tert-butyldimethylsilyloxy)-1-phenylpropan-2-one (92 mg, 0.35

mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc, 98:2) to afford the title compound as an oil (74 mg, 58% yield, dr >20:1). ^1H NMR (500 MHz, CDCl_3): δ -0.28 (s, 3H), 0.03 (s, 3H), 0.88 (s, 9H), 0.98 (s, 3H), 1.10 (s, 9H), 1.76 (d, $J = 1.4$ Hz, 3H), 2.76 (s, 1H), 4.62 (s, 1H), 5.42 (d, $J = 1.4$ Hz, 1H), 7.22–7.28 (m, 5H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ -5.0, -4.3, 14.6, 18.3, 23.0, 26.1, 31.1, 32.2, 78.4, 79.1, 127.6, 128.2, 135.5, 136.9, 141.1. IR (neat) 2955, 1454, 1362, 1239, 1092, 1063, 1004, 853, 700 cm^{-1} . HRMS calcd for $\text{C}_{22}\text{H}_{38}\text{O}_2\text{Si}$ ($\text{M}+\text{Na}$) $^+$: 385.2539, found 385.2520.

III. Diastereoselective Generation of (Z)-Disubstituted Allylic Alcohols via Addition to Chiral Ketones

General Procedure D: A dry 10 mL Schlenk flask, which was evacuated under vacuum and backfilled with N_2 (g) three times, was charged with diethylborane (0.88 mL, 1M toluene) and 1 mL dry THF. After cooling the flask to 0 $^\circ\text{C}$, the bromoalkyne (0.88 mmol) was added dropwise and the flask was stirred at room temperature for 20 minutes. $t\text{-BuLi}$ (0.51 mL, 1.7 M in pentanes) was added to the flask at -78 $^\circ\text{C}$ and stirred for 35 minutes, warmed to room temperature and stirred for an additional 40 minutes. The volatiles were then removed under vacuum over 30 minutes and the residue redissolved in toluene (2 mL). Dimethylzinc (0.44 mL, 2M in toluene) was slowly added to the reaction mixture at -78 $^\circ\text{C}$ and stirred for 30 minutes. The EtZnCl (136 mg, 1.05 mmol) was then added followed by the ketone solution (0.35 mmol, in 0.2 mL toluene). The reaction mixture stirred at -30 $^\circ\text{C}$ and was monitored by TLC until completion. The reaction mixture was quenched with saturated aq. NH_4Cl (2 mL) and 2N HCl (1 mL) followed by addition of 5 mL Et_2O . The organic layer was separated and the aqueous layer was extracted successively with Et_2O (2 \times 5 mL). The combined organic layers were successively washed with aq. NaHCO_3 and brine, dried over MgSO_4 , and filtered. The filtrate was concentrated *in vacuo* and purified column chromatography on silica gel.

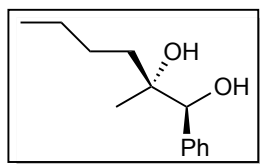


(1SR,2SR,Z)-1-((tert-butyldimethylsilyloxy)-8-Chloro-2-methyl-1-phenyloct-3-en-2-ol. General procedure D was applied to Et_2BH (0.88 mL, 1M in hexanes), $t\text{-BuLi}$ (0.51 mL, 1.7 M in pentanes), Me_2Zn (0.44 mL, 2M toluene), EtZnCl (136mg, 1.05 mmol), and 1-((tert-butyldimethylsilyloxy)-1-phenylpropan-2-

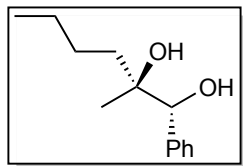
one (93 mg, 0.35 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc, 98:2) to afford the title compound as an oil (78 mg, 58% yield, dr >20:1). ^1H NMR (500 MHz, CDCl_3): δ -0.23 (s, 3H), 0.05 (s, 3H), 0.90 (s, 9H), 1.15 (s, 3H), 1.47 (q, $J = 7.5$ Hz, 2H), 1.76 (q, $J = 7.8$ Hz, 2H), 2.34 (q, $J = 7.5$ Hz, 2H), 2.42 (s, 1H), 3.5 (t, $J = 6.4$ Hz, 2H), 4.52 (s, 1H), 5.35–5.41 (m, 2H), 7.23–7.32 (m, 5H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ -5.0, -4.3, 18.4, 24.5, 26.0, 27.5, 32.4, 45.2, 76.9, 81.8, 127.8, 128.2, 132.2, 133.9, 140.8. IR (neat): 3564, 2954, 2858, 1728, 1471, 1454, 1361, 1311, 1258, 1088, 1065, 1006, 938, 865, 837, 778, 703, 671 cm^{-1} . HRMS calcd for $\text{C}_{21}\text{H}_{35}\text{ClO}_2\text{Si}$ ($\text{M}+\text{Na}$) $^+$: 405.1995, found 405.1991.

Determine of Chiral Purity for Additions to Enantioenriched Ketones

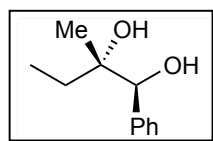
General Procedure E: After the addition following general procedure A or B, the silyl group was removed from the crude addition product using tetrabutylammonium fluoride (1M solution in THF). The diol was then purified by flash column chromatography on silica gel (hexanes:EtOAc, 85:15) and analyzed by HPLC.



(1*S*,2*R*)-2-Methyl-1-phenylhexane-1,2-diol. $[\alpha]_D^{20} = 36.1$ ($c = 1.8$, CHCl_3). ^1H NMR (500 MHz, CDCl_3): δ 0.86 (t, $J = 6.9$ Hz, 3H), 1.20 (s, 3H), 1.22–1.51 (m, 6H), 1.92 (s, 1H), 2.55 (s, 1H), 4.54 (s, 1H), 7.27–7.38 (m, 5H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ 14.3, 23.5, 23.6, 25.6, 36.3, 75.2, 80.9, 127.8, 128.0, 128.2, 140.7. IR (neat): 3401, 2956, 2872, 1709, 1604, 1455, 1380, 1220, 1162, 1087, 1024, 956, 918, 848 cm^{-1} . HRMS calcd for $\text{C}_{13}\text{H}_{20}\text{O}_2$ ($\text{M}+\text{Na}$) $^+$: 231.1361, found 231.1362. HPLC conditions: Chiralcel OD-H, $t_1 = 31.4$ min (major), $t_2 = 34.8$ min (hexanes/2-propanol: 97/3, 0.5 mL/min).



(1*R*,2*S*)-2-Methyl-1-phenylhexane-1,2-diol. $[\alpha]_D^{20} = -40.6$ ($c = 1.8$, CHCl_3). This compound was prepared using the same method that was used to prepare its enantiomer above.



(1*S*,2*S*)-2-Methyl-1-phenylbutane-1,2-diol. $[\alpha]_D^{20} = 22.7$ ($c = 2.2$, CHCl_3). ^1H NMR (500 MHz, CDCl_3): δ 0.96 (t, $J = 7.7$ Hz, 3H), 0.99 (s, 3H), 1.50–1.60 (m, 2H), 2.12 (bs, 1H), 2.73 (bs, 1H), 4.52 (s, 1H), 7.26–7.36 (m, 5H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ 8.0, 21.0, 31.5, 75.6, 80.0, 127.8, 128.0, 128.2, 140.8. IR (neat): 3418, 2978, 1709, 1604, 1463, 1381, 1274, 1165, 1085, 1016, 920, 845 cm^{-1} . HRMS calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2$ ($\text{M}+\text{Na}$) $^+$: 203.1048, found 208.1021. HPLC conditions: Chiralcel OD-H, $t_1 = 40.2$ min, $t_2 = 48.5$ min (major) (hexanes/2-propanol: 97/3, 0.5 mL/min).

Conditions for Determination of Diastereomeric Ratio by Gas Chromatography for (2*SR*,3*SR*)-2-(*tert*-butyldimethylsilyloxy)-3-Methylpentan-3-ol and (2*S*,3*R*)-2-(*tert*-butyldimethylsilyloxy)-3-Ethylheptan-3-ol.

Condition 1: WCOT fused silica 25m x 0.25mm coating CP CHIRASIL-Dex CB, DF = 0.25 (oven: 100 $^{\circ}\text{C}$, flow = 1.6 mL/min).

Condition 2: WCOT fused silica 25m x 0.25mm coating CP CHIRASIL-Dex CB, DF = 0.25 (oven: 100 °C hold 20 min, ramp 5 °C/min to 130 °C, flow = 1.8 mL/min).

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