**Catalytic Asymmetric Synthesis of Hydroxy Enolethers:
Approach to a Two-Carbon Homologation of Aldehyde**

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General Methods. All reactions were carried out under a nitrogen atmosphere with oven-dried glassware. The progress of all reactions was monitored by thin layer chromatography. All manipulations involving borane reagents and dimethylzinc were carried out using an inert atmosphere in a Vacuum Atmosphere drybox with an attached MO-40 Dritrain or by using standard Schlenk or vacuum line techniques. Toluene and hexanes were dried through alumina columns. All liquid aldehydes were distilled prior to use and stored under N₂ in glass vessels sealed with Teflon stoppers. Unless otherwise specified, all chemicals were obtained from Acros and Aldrich. Ethyl ethyne ether was purchased from GFS Chemical. All solvents were purchased from Fischer Scientific. NMR spectra were obtained on Brüker 500 and 300 MHz Fourier transform spectrometers at the University of Pennsylvania NMR facility. ¹H and ¹³C{¹H} NMR spectra were referenced to residual solvent in C₆D₆.

Cautionary Note : Caution should be used when handling dialkylzinc reagents.

Synthesis of Substrate Aldehydes.

Preparation of (*tert*-Butyl-dimethyl-silanyloxy)-acetaldehyde. (*tert*-Butyl-dimethyl-silanyloxy)-acetaldehyde was prepared according to literature procedure.¹

Preparation of (*tert*-Butyl-diphenyl-silanyloxy)-acetaldehyde. (*tert*-Butyl-diphenyl-silanyloxy)-acetaldehyde was prepared according to literature procedure.²

Enantio- and Diastereoselective Vinyl Additions to Aldehydes.

General Procedure. An oven-dried 10 mL Schlenk flask that had been thoroughly purged with N₂ was charged with trisvinyl borane (0.4 equiv, 0.4 M in toluene) and cooled to - 10 °C. Me₂Zn (1.4 equiv, 2 M in toluene) was added dropwise over 10 min and allowed to stirred at this temperature for 10 min before the addition of (–)-MIB (4 mol%). The reaction was warmed to 0 °C and a solution of aldehyde (1 equiv, 1 M in toluene) was added over 30 min with the aid of a syringe pump. The reaction was allowed to stir at this temperature for 12 hours and was quenched with ~100 µL H₂O. After stirring for 15 min, MgSO₄ was added followed by 5 mL of diethyl ether. The

resulting suspension was filtered, and successively washed with diethyl ether ($\sim 5 \text{ mL} \times 2$). The organic layer was concentrated and chromatographed on silica gel that had been pretreated with triethylamine (2.5% v/v Et_3N) to afford the desired product.

3-Ethoxy-1-phenyl-prop-2-en-1-ol (S1). The General Procedure was applied to benzaldehyde on 1.0 mmol (106.1 mg, 1 M in toluene) scale. The crude product was purified by column chromatography on silica gel that had been pretreated with triethylamine (2.5 % v/v Et_3N , 20 % ethyl acetate in hexanes) to afford the desired product as colorless oil (175 mg, 98 % yield). $[\alpha]_{\text{D}}^{20} = +18.4$ (c 1.00, MeOH); ^1H NMR (C_6D_6 , 500 MHz): δ 0.96 (t, 3H, $J = 7.0$ Hz), 1.52 (br, 1H), 3.19-3.31 (m, 2H), 4.87-4.92 (m, 2H), 6.36-6.42 (m, 1H), 7.08-7.12 (m, 1H), 7.18-7.22 (m, 2H), and 7.41-7.43 (m, 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz): δ 14.6, 64.3, 72.6, 107.8, 126.3, 127.3, 128.5, 145.1, and 148.9 ppm. IR (neat): 3400, 1650, 1603, 1493, 1478, 1454, and 1394 cm^{-1} . HRMS calcd for $\text{C}_{11}\text{H}_{13}\text{O}$ ($\text{M} - \text{OH}$) $^+$: 161.0967, found 161.0972.

3-Ethoxy-1-(2-methoxy-phenyl)-prop-2-en-1-ol (S2). The General Procedure was applied to *ortho*-methoxybenzaldehyde on 1.0 mmol (136 mg, 1 M in toluene) scale. The crude product was purified by column chromatography on silica gel that had been pretreated with triethylamine (2.5 % v/v Et_3N , 20 % ethyl acetate in hexanes) to afford the desired product as colorless oil (204 mg, 98 % yield). $[\alpha]_{\text{D}}^{20} = -32.4$ ($c = 0.85$, MeOH); ^1H NMR (C_6D_6 , 500 MHz): δ 0.96 (t, 3H, $J = 7.0$ Hz), 2.44 (br, 1H), 3.24 (s, 3H), 3.25-3.37 (m, 2H), 5.17 (dd, 1H, $J = 12.7$ and 7.7 Hz), 5.53 (d, 1H, $J = 7.7$ Hz), 6.51 (d, 1H, $J = 8.2$ Hz), 6.92 (td, 1H, $J = 6.1$ and 1.0 Hz), 7.08 (td, 1H, $J = 8.0$ and 1.7 Hz), and 7.55 (dd, 1H, $J = 7.5$ and 1.7 Hz) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz): δ 14.7, 54.8, 64.3, 68.6, 106.8, 110.7, 121.1, 127.3, 128.3, 133.5, 148.8, and 157.1 cm^{-1} . IR (neat): 3442, 1651, 1600, 1489, 1487, and 1464 cm^{-1} . HRMS calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3$ (M) $^+$: 208.1086, found 208.1089.

1-(4-Chloro-phenyl)-3-ethoxy-prop-2-en-1-ol (S3). The General Procedure was applied to *para*-chlorobenzaldehyde on 1.0 mmol (140 mg, 1 M in toluene) scale. The crude product was purified by column chromatography on silica gel that had been pretreated with triethylamine (2.5 % v/v Et₃N, 20 % ethyl acetate in hexanes) to afford the desired product as colorless oil (198 mg, 93 % yield). $[\alpha]_D^{20} = +23.3$ ($c = 1.21$, MeOH); ¹H NMR (C₆D₆, 500 MHz): δ 0.97 (t, 3H, $J = 7.0$ Hz), 1.36 (br, 1H), 3.20-3.31 (m, 2H), 4.71-4.77 (m, 2H), 6.29 (d, 1H, $J = 11.3$ Hz), 7.10-7.18 (m, 4H) ppm. ¹³C{¹H} NMR (C₆D₆, 125 MHz): δ 14.6, 64.5, 71.9, 107.3, 127.7, 128.6, 133.0, 143.5, and 149.3 ppm. IR (neat): 3398, 1650, 1596, 1493, 1487, 1454, and 1397 cm⁻¹. HRMS calcd for C₁₁H₁₂ClO (M-OH)⁺: 195.0577, found 195.0582.

3-Ethoxy-1-naphthalen-2-yl-prop-2-en-1-ol (S4). The General Procedure was applied to 2-naphthaldehyde on 1 mmol (156 mg, 1 M in toluene) scale. The crude product was purified by column chromatography on silica gel that had been pretreated with triethylamine (2.5% v/v Et₃N, 20% ethyl acetate in hexanes) to afford the desired product as colorless oil (212 mg, 93% yield). $[\alpha]_D^{20} = +18.2$ (c 0.69, MeOH); ¹H NMR (C₆D₆, 500 MHz): δ 0.98 (t, 3H, $J = 7$ Hz), 1.62 (br, 1H), 3.28 (m, 2H), 4.98 (dd, 1H, $J = 12.5$ and 8.2 Hz), 5.06 (d, 1H, $J = 8.2$ Hz), 6.46 (d, 1H, $J = 12.4$ Hz), 7.25 (m, 2H), 7.51 (d, 1H, $J = 8.5$ Hz), 7.61-7.69 (m, 3H), and 7.89 (s, 1H) ppm. ¹³C{¹H} NMR (C₆D₆, 125 MHz): δ 14.6, 64.5, 72.7, 107.0, 124.7, 125.1, 125.9, 126.3, 128.0, 128.3, 128.4, 133.0, 134.0, 142.5, and 149.2 ppm. IR (neat): IR 3401, 3053, 2977, 1667, 1634, 1601, 1505, and 1477 cm⁻¹. HRMS calcd for C₁₅H₁₆O₂ (M)⁺: 228.1150, found 228.1156.

1-Cyclohexyl-3-ethoxy-prop-2-en-1-ol (S5). The General Procedure was applied to cyclohexanecarboxaldehyde on 1 mmol (112 mg, 1 M in toluene) scale. The crude product was purified by column chromatography on silica gel that had been pretreated with triethylamine (2.5% v/v Et₃N, 20% ethyl acetate in hexanes) to

afford the desired product as colorless oil (165 mg, 90% yield). $[\alpha]_D^{20} = -34.0$ ($c = 1.12$, MeOH); ^1H NMR (C_6D_6 , 300 MHz): δ 0.85-1.30 (m, 5H), 1.04 (t, 3H, $J = 7$ Hz), 1.30-1.45 (m, 1H), 1.52-1.80 (m, 5H), 2.01 (m, 1H), 3.39 (m, 2H), 3.61 (dd, 1H, $J = 8.4$ and 6.7 Hz), 4.78 (dd, 1H, $J = 12.7$ and 8.7 Hz), and 6.32 (d, 1H, $J = 12.7$ Hz) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 75 MHz): δ 14.9, 26.7, 27.2, 29.5, 44.9, 64.6, 75.3, 106.2, and 149.1 ppm. IR (neat): 3383, 1746, 1667, 1650, 1478, 1446, and 1393 cm^{-1} . HRMS calcd for $\text{C}_{11}\text{H}_{18}\text{O}$ ($\text{M}-\text{H}_2\text{O}$) $^+$: 166.1358, found 166.1353.

1-Ethoxy-4-methyl-pent-1-en-3-ol (S6). The General Procedure was applied to isobutyraldehyde on 1 mmol (72 mg, 1 M in toluene) scale. The crude product was purified by column chromatography on silica gel that had been pretreated with triethylamine (2.5% v/v Et_3N , 20% ethyl acetate in hexanes) to afford the desired product as colorless oil (140 mg, 97% yield). $[\alpha]_D^{20} = -35.1$ ($c = 0.65$, MeOH); ^1H NMR (C_6D_6 , 500 MHz): δ 0.90 (d, 3H, $J = 6.8$ Hz), 0.92-1.09 (m, 6H), 1.33 (br, 1H), 1.70 (m, 1H), 3.37 (m, 2H), 3.58 (dd, 1H, $J = 8.2$ and 6.4 Hz), 4.75 (dd, 1H, $J = 12.7$ and 8.6 Hz), and 6.30 (d, 1H, $J = 12.7$ Hz) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz): δ 14.7, 18.5, 18.7, 34.8, 64.4, 75.8, 106.0, and 149.0 ppm. IR (neat): 3410, 1671, 1650, 1469, and 1394 cm^{-1} . HRMS calcd for $\text{C}_8\text{H}_{15}\text{O}$ ($\text{M}-\text{OH}$) $^+$: 127.1078, found 127.1118.

1-Ethoxy-4,4-dimethyl-pent-1-en-3-ol (S7). The General Procedure was applied to pivalaldehyde on 1 mmol (86 mg, 1 M in toluene) scale. The crude product was purified by column chromatography on silica gel that had been pretreated with triethylamine (2.5% v/v Et_3N , 10% ethyl acetate in hexanes) to afford the desired product as colorless oil (130 mg, 82% yield). $[\alpha]_D^{20} = -24.5$ ($c = 1.15$, CH_2Cl_2); ^1H NMR (C_6D_6 , 500 MHz): δ 0.97 (s, 9H), 1.02 (t, 3H, $J = 7$ Hz), 3.36 (q, 2H, $J = 7$ Hz), 3.47 (d, 1H, $J = 9$ Hz), 4.80 (dd, 1H, $J = 12.6$ and 9 Hz), 6.28 (d, 1H, $J = 12.6$ Hz) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz): δ 14.7, 26.1, 35.1, 64.4, 78.5, 104.2, 149.4 ppm. IR (neat): 3457, 2949, 1652, 1473, and 1392 cm^{-1} . HRMS calcd for $\text{C}_9\text{H}_{17}\text{O}$ ($\text{M}-\text{OH}$) $^+$: 141.1279, found 141.1274.

1-Ethoxy-5-methyl-hex-1-en-3-ol (S8). The General Procedure was applied to isovaleraldehyde on 1 mmol (86 mg, 1 M in toluene) scale. The crude product was purified by column chromatography on silica gel that had been pretreated with triethylamine (2.5% v/v Et₃N, 10% ethyl acetate in hexanes) to afford the desired product as colorless oil (155 mg, 98 % yield). $[\alpha]_D^{20} = -15.4$ ($c = 0.91$, MeOH); ¹H NMR (C₆D₆, 500 MHz): δ 0.89 (d, 3H, $J = 6.7$ Hz), 0.92 (d, 3H, $J = 6.7$ Hz), 1.02 (t, 3H, $J = 7.0$ Hz), 1.30 (m, 1H), 1.56 (m, 1H), 1.79 (hep, 1H, $J = 6.7$ Hz), 3.33-3.41 (m, 2H), 3.96 (m, 1H), 4.74 (dd, 1H, $J = 12.7$ and 8.4 Hz), 6.33 (d, 1H, $J = 12.7$ Hz) ppm. ¹³C{¹H} NMR (C₆D₆, 125 MHz): δ 14.7, 22.7, 23.1, 25.0, 47.8, 64.4, 68.8, 108.1, and 148.5 ppm. IR (neat): 3388, 2955, 1671, 1468, 1394, and 1222 cm⁻¹. HRMS calcd for C₉H₁₇O₂ (M-H)⁺: 157.1228, found 157.1385.

1-Ethoxy-5-(naphthalen-2-ylmethoxy)-pent-1-en-3-ol (S9). The General Procedure was applied to 3-(naphthalen-2-ylmethoxy)-propionaldehyde on 1 mmol (214 mg, 1 M in toluene) scale. The crude product was purified by column chromatography on silica gel that had been pretreated with triethylamine (2.5% v/v Et₃N, 20% ethyl acetate in hexanes) to afford the desired product as colorless oil (278 mg, 97% yield). $[\alpha]_D^{20} = -26.5$ (c 1.01, MeOH); ¹H NMR (C₆D₆, 500 MHz): δ 0.99 (t, 3H, $J = 7.0$ Hz), 1.70-1.75 (m, 1H), 1.91 (m, 1H), 2.00 (br, 1H), 3.29-3.33 (m, 2H), 3.41-3.45 (m, 1H), 3.54 (m, 1H), 4.26 (m, 1H), 4.42 (d, 2H, $J = 4.2$ Hz), 4.82 (dd, 1H, $J = 12.6$ and 7.9 Hz), 6.43 (d, 1H, $J = 12.7$ Hz), 7.25 (m, 2H), 7.40 (dd, 1H, $J = 8.4$ and 1.6 Hz), and 7.60-7.67 (m, 4H) ppm. ¹³C{¹H} NMR (C₆D₆, 125 MHz): δ 14.7, 38.6, 64.5, 68.2, 69.0, 73.3, 107.4, 126.0, 126.01, 126.3, 126.6, 128.2, 128.3, 128.5, 133.4, 133.7, 136.5, and 148.6 ppm. IR (neat): 3422, 1651, 1508, 1477, and 1442 cm⁻¹. HRMS calcd for C₁₈H₂₂O₃Na (M+Na)⁺: 309.1467, found 309.1368.

1-(*tert*-Butyl-dimethyl-silanyloxy)-4-ethoxy-but-3-en-2-ol (S10). The General Procedure was applied to (*tert*-butyl-dimethyl-silanyloxy)-acetaldehyde on 1 mmol (174

mg, 1 M in toluene) scale. The crude product was purified by column chromatography on silica gel that had been pretreated with triethylamine (2.5% v/v Et₃N, 10% ethyl acetate in hexanes) to afford the desired product as colorless oil (222 mg, 90% yield). $[\alpha]_D^{20} = -8.59$ ($c = 0.85$, MeOH); ¹H NMR (C₆D₆, 500 MHz): δ 0.02 (s, 6H), 0.92 (s, 9H), 1.0 (t, 3H, $J = 7.0$ Hz), 2.33 (br, 1H), 3.38 (m, 1H), 3.45 (dd, 1H, $J = 9.9$ and 3.0 Hz), 3.52 (dd, 1H, $J = 9.9$ and 4.0 Hz), 4.10 (m, 1H), 4.79 (dd, 1H, $J = 12.7$ and 7.8 Hz), and 6.52 (d, 1H, $J = 12.7$ Hz) ppm. ¹³C{¹H} NMR (C₆D₆, 125 MHz): δ -5.27, -5.23, 14.7, 18.5, 26.0, 64.5, 68.7, 71.0, 102.9, and 149.8 ppm. IR (neat): 3439, 1650, 1472, 1392, and 1361 cm⁻¹. HRMS calcd for C₁₂H₂₄O₂Si (M-H₂O)⁺: 228.1546, found 228.1543.

1-(*tert*-Butyl-diphenyl-silanyloxy)-4-ethoxy-but-3-en-2-ol (S11). The General Procedure was applied to (*tert*-butyl-diphenyl-silanyloxy)-acetaldehyde on 1 mmol

(298 mg, 1 M in toluene) scale. The crude product was purified by column chromatography on silica gel that had been pretreated with triethylamine (2.5% v/v Et₃N, 10% ethyl acetate in hexanes) to afford the desired product as colorless oil (363 mg, 98% yield). $[\alpha]_D^{20} = -6.18$ ($c = 1.03$, MeOH); ¹H NMR (C₆D₆, 500 MHz): δ 0.97 (t, 3H, $J = 7.0$ Hz), 1.13 (s, 9H), 2.32 (br, 1H), 3.32 (m, 2H), 3.66 (m, 2H), 4.17 (m, 1H), 4.70 (dd, 1H, $J = 12.7$ and 7.8 Hz), 6.46 (d, 1H, $J = 12.7$ Hz), 7.21 (m, 6H), and 7.76 (m, 4H) ppm. ¹³C{¹H} NMR (C₆D₆, 125 MHz): δ 14.7, 19.5, 27.1, 64.5, 69.5, 71.2, 102.9, 128.2, 130.1, 133.9, 136.0, and 149.9 ppm. IR (neat): 3430, 1660, 1589, 1470, and 1427 cm⁻¹. HRMS calcd for C₂₂H₃₀O₃NaSi (M+Na)⁺: 393.1862, found 393.1847.

***tert*-Butyl-(1-cyclohexyl-3-ethoxy-allyloxy)-dimethylsilane (S12).** 1-Cyclohexyl-3-ethoxy-prop-2-en-1-ol (S5) (708 mg, 3.84 mmol) was dissolved in 5 mL CH₂Cl₂. Imidazole (523 mg, 7.68 mmol) and TBSCl (868 mg, 5.76

mmol) were added successively to the solution at 0 °C. The reaction was then warmed to

rt and stirred for 2 h. The resulting solution was poured into 30 mL water, extracted twice with 10 mL CH₂Cl₂, dried over MgSO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel that had been pretreated with triethylamine (2.5% v/v Et₃N, 2% ethyl acetate in hexanes) to afford the desired product as colorless oil (1.08 g, 94% yield). $[\alpha]_D^{20} = +6.84$ ($c = 1.19$, MeOH); ¹H NMR (C₆D₆, 300 MHz): δ 0.12 (s, 3H), 0.14 (s, 3H), 1.03 (s, 9H), 1.04 (t, 3H, $J = 7.0$ Hz), 0.95-1.30 (m, 4H), 1.31-1.50 (m, 2H), 1.61-1.83 (m, 4H), 1.96-2.08 (m, 1H), 3.34-3.49 (m, 2H), 3.67-3.75 (m, 1H), 4.79 (dd, 1H, $J = 12.7$ and 8.6 Hz), and 6.32 (d, 1H, $J = 12.8$ Hz), ppm. ¹³C{¹H} NMR (C₆D₆, 75 MHz): δ -4.3, -3.2, 14.9, 18.6, 26.4, 26.8, 26.9, 27.3, 29.6, 29.7, 46.0, 64.5, 76.7, 106.5, and 148.3 ppm. IR (neat): 2928, 2856, 1652, 1453, 1392, 1253, and 1182 cm⁻¹. HRMS calcd for C₁₇H₃₅O₂Si (MH)⁺: 299.2406, found 299.2400.

***tert*-Butyl-(3-ethoxy-1-isopropyl-allyloxy)-dimethyl-silane**

(S13). 1-Ethoxy-4-methyl-pent-1-en-3-ol (**S6**) (205 mg, 1.42 mmol) was dissolved in 4 mL CH₂Cl₂. Imidazole (194 mg, 2.80 mmol) and TBSCl (321 mg, 2.13 mmol) were added

successively to the solution at 0 °C. The reaction was then warmed to rt and stirred for 2 h. The resulting solution was poured into 30 mL water, extracted twice with 10 mL CH₂Cl₂, dried over MgSO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel that had been pretreated with triethylamine (2.5% v/v Et₃N, 2% ethyl acetate in hexanes) to afford the desired product as colorless oil (332 mg, 91% yield). $[\alpha]_D^{20} = +11.5$ ($c = 1.06$, CH₂Cl₂); ¹H NMR (C₆D₆, 500 MHz): δ 0.10 (s, 3H), 0.11 (s, 3H), 0.93 (d, 3H, $J = 6.5$ Hz), 0.97 (d, 3H, $J = 6.5$ Hz), 1.01 (t, 3H, $J = 7$ Hz), 1.02 (s, 9H), 1.72-1.75 (m, 1H), 3.38-3.44 (m, 2H), 3.72 (dd, 1H, $J = 8.5$ and 5.5 Hz), and 4.78 (dd, 1H, $J = 12.5$ and 8.5 Hz), and 6.32 (d, 1H, $J = 12.5$ Hz) ppm. ¹³C{¹H} NMR (C₆D₆, 125 MHz): δ -4.6, -3.5, 14.7, 18.4, 18.5, 18.5, 26.2, 35.9, 64.3, 77.0, 105.7, and 148.2 ppm. IR (neat): 2956, 1652, 1467, 1252, and 1185 cm⁻¹. HRMS calcd for C₁₃H₂₇O₂Si (M-CH₃)⁺: 243.1780, found 243.1777.

(3-Ethoxy-1-isopropyl-allyloxymethyl)-benzene (S14). To a stirred solution of 1-ethoxy-4-methyl-pent-1-en-3-ol (**S6**) (262 mg, 1.82 mmol) in THF (5 mL) were added a 60% dispersion of sodium hydride in mineral oil (146 mg, 3.64 mmol), benzyl bromide (0.324 mL, 2.73 mmol), and tetrabutylammoniumiodide (11 mg, 1 mol%) at 0 °C. The solution was then warmed to rt and stirred overnight. The reaction was quenched by the slow addition of water, extracted with EtOAc, and concentrated. The crude product was purified by column chromatography on silica gel that had been pretreated with triethylamine (2.5% v/v Et₃N, 20% ethyl acetate in hexanes) to afford the desired product as colorless oil (350 mg, 82% yield). $[\alpha]_D^{20} = +42.7$ ($c = 1.07$, CH₂Cl₂); ¹H NMR (C₆D₆, 500 MHz): δ 0.97 (d, 3H, $J = 6.7$ Hz), 1.02 (t, 3H, $J = 7$ Hz), 1.05 (d, 3H, $J = 6.7$ Hz), 1.86-1.96 (m, 1H), 3.28 (dd, 1H, $J = 9.6$ Hz), 3.38 (q, 2H, $J = 7$ Hz), 4.27 (d, 1H, $J = 12.2$ Hz), 4.63 (d, 1H, $J = 12.2$ Hz), 4.66 (dd, 1H, $J = 12.8$ and 9 Hz), 6.28 (d, 1H, $J = 12.8$ Hz), 7.07-7.14 (m, 1H), 7.15-7.23 (m, 3H), and 7.35-7.40 (m, 1H) ppm. ¹³C{¹H} NMR (C₆D₆, 125 MHz): δ 14.7, 18.9, 19.2, 34.1, 64.4, 69.5, 83.0, 102.3, 127.4, 128.4, 128.5, 140.2, and 150.2 ppm. IR (neat): 3061, 3031, 2961, 2873, 1649, 1458, and 1186 cm⁻¹. HRMS calcd for C₁₅H₂₁O₂ (M-H)⁺: 233.1542, found 233.1549.

Hydrolysis of Vinyl Ethers.

Preparation of 3-(*tert*-Butyl-dimethyl-silanyloxy)-4-methyl-pentanal.³ A stirred solution of *tert*-butyl-(3-ethoxy-1-isopropyl-allyloxy)-dimethyl-silane (**S13**) (258 mg, 1 mmol) in a 9:1 mixture of THF-H₂O (5 mL) was treated with Hg(OAc)₂ (381 mg, 1.2 mmol). After the reaction was stirred for 1 h, saturated aqueous KI (freshly prepared) was added. After 10 min, the reaction mixture was extracted twice with diethyl ether, washed with Na₂S₂O₄, dried over MgSO₄, and concentrated in vacuo. Purification by flash chromatography (5% ethyl acetate in hexanes) afforded the title aldehyde (164 mg, 71% yield).

Preparation of 3-Benzoyloxy-4-methyl-pentanal.⁴ The same procedure described above was applied to (3-ethoxy-1-isopropyl-allyloxymethyl)-benzene (**S14**) (234 mg, 1

mmol). Purification by flash chromatography (5% ethyl acetate in hexanes) afforded the title aldehyde (147 mg, 71% yield). $[\alpha]_D^{20} = -34.5$ (c 1.0, CHCl_3). [Published $[\alpha]_D^{20} = -34.7$ (c 0.96, CHCl_3)].

Preparation of 3-(*tert*-Butyl-dimethyl-silanyloxy)-3-cyclohexyl-propionaldehyde.⁵

The same procedure described above was applied to *tert*-butyl-(1-cyclohexyl-3-ethoxyallyloxy)-dimethyl-silane (**S12**) (299 mg, 1 mmol). Purification by flash chromatography (5% ethyl acetate in hexanes) afforded the title aldehyde (191 mg, 71% yield).

5-(*tert*-Butyl-dimethyl-silanyloxy)-5-cyclohexyl-1-ethoxy-pent-1-en-3-ol (S15**, 1,3-*anti* major diastereomer).** The General Procedure was applied to (*S*)-3-(*tert*-butyl-dimethyl-silanyloxy)-3-

cyclohexyl-propionaldehyde on 0.5 mmol (135.2 mg, 1 M in toluene) scale with (+)-MIB. The crude product was purified by column chromatography on silica gel that had been pretreated with triethylamine (2.5% v/v Et_3N , 20% ethyl acetate in hexanes) to afford the desired product as colorless oil (163 mg, 95% yield). $[\alpha]_D^{20} = -12.5$ (c = 0.66, MeOH); ^1H NMR (C_6D_6 , 500 MHz): δ 0.12 (s, 3H), 0.18 (s, 3H), 0.95-1.00 (m, 1H), 1.01 (s, 9H), 1.03 (t, 3H, J = 7 Hz), 1.05-1.14 (m, 2H), 1.15-1.26 (m, 2H), 1.52-1.60 (m, 1H), 1.60-1.66 (m, 1H), 1.65-1.81 (m, 6H), 1.95 (br, 1H), 3.41 (q, 2H, J = 7 Hz), 3.81-3.84 (m, 1H), 4.32-4.37 (m, 1H), 4.87 (dd, 1H, J = 12.7 and 7.9 Hz), and 6.49 (d, 1H, J = 12.5 Hz) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz): δ -4.2, -4.2, 14.7, 18.4, 26.2, 26.8, 26.9, 27.1, 28.6, 29.3, 41.9, 44.1, 64.5, 67.2, 74.5, and 108.2 ppm. IR (neat): 3436, 2929, 2855, 1651, 1392, and 1253 cm^{-1} . HRMS calcd for $\text{C}_{19}\text{H}_{36}\text{O}_2\text{Si}$ ($\text{M}-\text{H}_2\text{O}$)⁺: 324.2512, found 324.2500.

For 1,3-*syn* minor diastereomer (S16**),** The General Procedure was applied with (-)-MIB. $[\alpha]_D^{20} = -11.5$ (c = 0.49, MeOH); ^1H NMR (C_6D_6 , 500 MHz): δ 0.10 (s, 3H), 0.14 (s, 3H), 1.01 (s, 9H), 1.03 (t, 3H, J = 6.5 Hz), 1.02-1.05 (m, 1H), 1.10-1.26 (m, 4H), 1.49-1.60 (m, 2H), 1.61-1.69 (m, 2H), 1.69-1.84 (m, 4H), 1.84-1.92 (m, 1H), 3.41 (q, 2H, J = 7 Hz), 3.75-3.78 (m, 1H), 4.16-4.21 (m, 1H), 4.85 (dd, 1H, J = 13 and 8 Hz), and 6.50 (d,

1H, $J = 13$ Hz) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz): δ -4.1, -3.96, 14.8, 18.4, 26.25, 26.31, 27.0, 27.1, 27.2, 28.5, 42.1, 44.2, 64.6, 69.0, 75.7, and 108.1 ppm.

5-(*tert*-Butyl-dimethyl-silanyloxy)-1-ethoxy-6-methyl-hept-1-en-3-ol (S17, 1,3-*anti* major diastereomer).

The General Procedure was applied to (*S*)-3-(*tert*-butyl-dimethyl-silanyloxy)-4-methyl-pentanal on 0.25 mmol (58 mg, 1 M in toluene) scale with (+)-MIB. The crude product was purified by column chromatography on silica gel that had been pretreated with triethylamine (2.5% v/v Et_3N , 20% ethyl acetate in hexanes) to afford the desired product as colorless oil (72 mg, 95% yield). $[\alpha]_{\text{D}}^{20} = -9.82$ ($c = 0.82$, CH_2Cl_2); ^1H NMR (C_6D_6 , 500 MHz): δ 0.09 (s, 3H), 0.17 (s, 3H), 0.88 (d, 3H, $J = 5$ Hz), 0.89 (d, 3H, $J = 5$ Hz), 1.00 (s, 9H), 1.02 (t, 3H, $J = 7$ Hz), 1.59-1.67 (m, 2H), 1.75 (br, 1H), 1.81-1.89 (m, 2H), 3.40 (q, 2H, $J = 7$ Hz), 3.83-3.86 (m, 1H), 4.24-4.31 (m, 1H), 4.84 (dd, 1H, $J = 12.5$ and 8 Hz), and 6.45 (d, 1H, $J = 12.5$ Hz) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz): δ -4.3, -4.2, 14.7, 17.5, 18.37, 18.4, 26.2, 33.7, 41.3, 64.5, 67.0, 74.4, 107.9, and 148.2 ppm. IR (neat): 3428, 2956, 1653, 1467, 1389, and 1253 cm^{-1} . HRMS calcd for $\text{C}_{16}\text{H}_{34}\text{O}_3\text{SiNa}$ ($\text{M}+\text{Na}$) $^+$: 325.2174, found 325.2163.

For 1,3-*syn* minor diastereomer (S18), The General Procedure was applied with (-)-MIB. $[\alpha]_{\text{D}}^{20} = -23.4$ ($c = 1.25$, CH_2Cl_2); ^1H NMR (C_6D_6 , 300 MHz): δ 0.07 (s, 3H), 0.12 (s, 3H), 0.81 (d, 3H, $J = 7$ Hz), 0.95 (d, 3H, $J = 7$ Hz), 0.99 (s, 9H), 1.03 (t, 3H, $J = 7$ Hz), 1.59-1.69 (m, 1H), 1.73-1.91 (m, 3H), 3.40 (q, 2H, $J = 7$ Hz), 3.73-3.79 (m, 1H), 4.12-4.23 (m, 1H), 4.82 (dd, 1H, $J = 12.7$ and 8 Hz), and 6.50 (d, 1H, $J = 12.7$ Hz) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz): δ -4.06, -3.93, 14.9, 17.6, 17.7, 18.5, 26.3, 33.4, 41.3, 64.7, 69.1, 75.9, 108.1, and 148.8 ppm.

5-Benzyloxy-1-ethoxy-6-methyl-hept-1-en-3-ol (S19, 1,3-*anti* major diastereomer).

The General Procedure was applied to (*S*)-3-benzyloxy-4-methyl-pentanal on 0.3 mmol (62 mg, 1 M in toluene) scale with (+)-MIB. The crude product was purified by column chromatography on silica gel that had been pretreated with triethylamine (2.5% v/v Et_3N , 20% ethyl acetate in hexanes) to afford the desired product as colorless oil (80 mg, 96%

yield). $[\alpha]_D^{20} = -2.73$ ($c = 1.1$, MeOH); ^1H NMR (C_6D_6 , 500 MHz): δ 0.89 (d, 3H, $J = 6.7$ Hz), 0.90 (d, 3H, $J = 6.7$ Hz), 1.02 (t, 3H, $J = 7$ Hz), 1.61-1.74 (m, 2H), 1.80 (br, 1H), 1.87-1.95 (m, 1H), 3.37 (q, 2H, $J = 7$ Hz), 3.49-3.57 (m, 1H), 4.30-4.37 (m, 1H), 4.48 (s, 2H), 4.85 (dd, 1H, $J = 12.5$ and 8 Hz), 6.38 (d, 1H, $J = 12.5$ Hz), 7.05-7.11 (m, 1H), 7.14-7.21 (m, 2H), and 7.35-7.40 (m, 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz): δ 14.7, 17.6, 18.6, 30.8, 39.0, 64.6, 67.5, 72.2, 81.4, 108.1, 127.5, 127.8, 128.5, 139.7, and 148.3 ppm. IR (neat): 3444, 3032, 2960, 1653, 1460, and 1392 cm^{-1} . HRMS calcd for $\text{C}_{17}\text{H}_{26}\text{O}_3\text{Na}$ ($\text{M}+\text{Na}^+$): 301.1780, found 301.1782.

For 1,3-syn minor diastereomer (S20), The General Procedure was applied with (-)-MIB. $[\alpha]_D^{20} = -88.3$ ($c = 0.75$, CH_2Cl_2); ^1H NMR (C_6D_6 , 500 MHz): δ 0.78 (d, 3H, $J = 6.8$ Hz), 0.89 (d, 3H, $J = 6.8$ Hz), 1.02 (t, 3H, $J = 7$ Hz), 1.51-1.58 (m, 1H), 1.82-1.95 (m, 2H), 2.53 (br, 1H), 3.29-3.36 (m, 1H), 3.37-3.44 (m, 2H), 4.22-4.27 (m, 1H), 4.25 (d, 1H, $J = 11.5$ Hz), 4.39 (d, 1H, $J = 11.5$ Hz), 4.85 (dd, 1H, $J = 12.5$ and 7.5 Hz), 6.45 (d, 1H, $J = 12.5$ Hz), 7.05-7.10 (m, 1H), 7.12-7.21 (m, 2H), and 7.26-7.32 (m, 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz): δ 14.7, 16.8, 18.3, 29.9, 38.5, 64.5, 69.7, 71.2, 83.1, 107.8, 127.7, 127.9, 128.6, 139.2, and 148.5 ppm.

Conditions for the Determination of Enantiomeric Excesses.

The racemic hydroxy enolethers were prepared by addition of trisvinyl borane reagents to the corresponding aldehydes with racemic MIB. Due to the sensitivity of resulting hydroxy enolethers, **S1-S4** were converted to the 1,2-diols by ozonolysis and reduction with NaBH_4 , then analyzed by chiral HPLC. **S5** was converted to the 1,2-diol, transformed into the trifluoroacetate, and then analyzed by chiral GC. **S9** was protected with TBS group before ee determination by chiral HPLC. **S6-S8** and **S10** were analyzed directly by chiral GC. **S11** was analyzed directly by chiral HPLC.

Chiral HPLC analyses of **S1-S4**, **S9**, and **S11** were performed using a Chiralcel OD-H column.

(S)-3-Ethoxy-1-phenyl-prop-2-en-1-ol (S1). $t_1 = 34.3$ min, $t_2 = 40.2$ min (hexanes / 2-propanol : 95 / 5, 0.5 mL/min).

(S)-3-Ethoxy-1-(2-methoxy-phenyl)-prop-2-en-1-ol (S2). $t_1 = 22.9$ min, $t_2 = 35.5$ min (hexanes / 2-propanol : 90 / 10, 0.5 mL/min).

(S)-1-(4-Chloro-phenyl)-3-ethoxy-prop-2-en-1-ol (S3). $t_1 = 33.2$ min, $t_2 = 38.2$ min (hexanes / 2-propanol : 95 / 5, 0.5 mL/min).

3-Ethoxy-1-naphthalen-2-yl-prop-2-en-1-ol (S4). $t_1 = 14.2$ min, $t_2 = 16.6$ min (hexanes / 2-propanol : 80 / 20, 0.5 mL/min).

1-Ethoxy-5-(naphthalen-2-ylmethoxy)-pent-1-en-3-ol (S9). $t_1 = 14.2$ min, $t_2 = 15.7$ min (hexanes / 2-propanol : 97 / 3, 0.3 mL/min).

1-(tert-Butyl-diphenyl-silanyloxy)-4-ethoxy-but-3-en-2-ol (S11). $t_1 = 12.9$ min, $t_2 = 16.2$ min (hexanes / 2-propanol : 95 / 5, 0.5 mL/min).

The specifications for the GC analyses were as follows: Fused silica chiral capillary column (Supelco β -Dex 120): 30 m $\times$ 0.25 mm (id) $\times$ 0.25 μ m film thickness. Carrier gas: nitrogen. Inlet temperature: 250 $^{\circ}$ C. Detector: FID, 270 $^{\circ}$ C. The conditions for the resolution of the racemates by GC are given below.

1-Cyclohexyl-3-ethoxy-prop-2-en-1-ol (S5). $t_1 = 58.4$ min, $t_2 = 64.1$ min (73 $^{\circ}$ C, 1.6 mL/min).

1-Ethoxy-4-methyl-pent-1-en-3-ol (S6). $t_1 = 16.7$ min, $t_2 = 18.6$ min (80 $^{\circ}$ C, 1.6 mL/min).

(S,E)-1-Ethoxy-4,4-dimethylpent-1-en-3-ol (S7). $t_1 = 74.7$ min, $t_2 = 82.3$ min (80 $^{\circ}$ C, 1.6 mL/min).

1-Ethoxy-5-methylhex-1-en-3-ol (S8). $t_1 = 123.8$ min, $t_2 = 132.0$ min (60 $^{\circ}$ C, 1.6 mL/min).

1-(tert-Butyl-dimethyl-silanyloxy)-4-ethoxy-but-3-en-2-ol (S10). $t_1 = 55.5$ min, $t_2 = 58.3$ min (100 $^{\circ}$ C, 1.5 mL/min).

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3-Ethoxy-1-phenyl-prop-2-en-1-ol

3-Ethoxy-1-(2-methoxy-phenyl)-prop-2-en-1-ol

3-Ethoxy-1-(2-methoxy-phenyl)-prop-2-en-1-ol

1-(4-Chloro-phenyl)-3-ethoxy-prop-2-en-1-ol

1-(4-Chloro-phenyl)-3-ethoxy-prop-2-en-1-ol

3-Ethoxy-1-naphthalen-2-yl-prop-2-en-1-ol

1-Cyclohexyl-3-ethoxy-prop-2-en-1-ol

1-Cyclohexyl-3-ethoxy-prop-2-en-1-ol

1-Ethoxy-4-methyl-pent-1-en-3-ol

1-Ethoxy-4-methyl-pent-1-en-3-ol

1-Ethoxy-4,4-dimethyl-pent-1-en-3-ol

1-Ethoxy-5-(naphthalen-2-ylmethoxy)-pent-1-en-3-ol

1-(*tert*-Butyl-dimethyl-silyloxy)-4-ethoxy-but-3-en-2-ol

1-(*tert*-Butyl-diphenyl-silanyloxy)-4-ethoxy-but-3-en-2-ol

tert-Butyl-(1-cyclohexyl-3-ethoxy-allyloxy)-dimethyl-silane

tert-Butyl-(3-ethoxy-1-isopropyl-allyloxy)-dimethyl-silane

(3-Ethoxy-1-isopropyl-allyloxymethyl)-benzene

5-(*tert*-Butyl-dimethyl-silanyloxy)-5-cyclohexyl-1-ethoxy-pent-1-en-3-ol

5-(*tert*-Butyl-dimethyl-silanyloxy)-5-cyclohexyl-1-ethoxy-pent-1-en-3-ol

5-(*tert*-Butyl-dimethyl-silanyloxy)-1-ethoxy-6-methyl-hept-1-en-3-ol

5-(*tert*-Butyl-dimethyl-silanyloxy)-1-ethoxy-6-methyl-hept-1-en-3-ol

5-Benzyloxy-1-ethoxy-6-methyl-hept-1-en-3-ol

5-Benzyloxy-1-ethoxy-6-methyl-hept-1-en-3-ol