SUPPORTING INFORMATION

Asymmetric reduction of α -(trimethylsilyl)methyl- β -ketosulfoxide with DIBAL under basic conditions

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General. All reactions were performed in oven- and flame-dried glassware under a positive pressure of argon. Air- and moisture sensitive reagents and solvents were transferred *via* syringe or cannula, and were introduced into the reaction vessels through a rubber septum. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under a nitrogen atmosphere before use. The TLC plates were visualized with UV light and 7% phosphomolybdic acid or *p*-anisaldehyde in ethanol/heat.

(1*R*,2*R*,3*S*)-1-Phenyl-2-(*p*-tolylsulfinyl)-3-(trimethylsilyl)propan-1-ol (5a).¹ To a solution of diisopropylamine (0.04 mL, 0.28 mmol) in THF (0.25 mL) was added *n*-butyllithium (1.49 mol dm⁻³ in hexane, 0.18 mL, 0.27 mmol) at 0 °C and the mixture was stirred for 10 min. The reaction mixture was cooled to -78 °C, and then a solution of (*R*)-*p*-tolyl 2-trimethylsilylethyl sulfoxide (**1**) (51 mg, 0.21 mmol) in THF (0.25 mL) was added dropwise over a period of 20 min. A solution of ethyl benzoate (0.05 mL, 0.35 mmol) in THF (0.3 mL) was added, and the mixture was stirred for 30 min. A solution of DIBAL (0.95 mol dm⁻³ in hexane, 0.35 mL, 0.34 mmol) was then added, and the mixture was stirred for an additional 1 h. Saturated aqueous NH₄Cl was added and the mixture was extracted with CH₂Cl₂. The combined organic extracts were washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure to leave a residue which was purified by column chromatography (silica gel 12 g, CH₂Cl₂/Et₂O =90:10) to afford **5a** (44 mg, 60%) and **4a** (27.6 mg, 38%). **5a**; *R*_f=0.50; (CH₂Cl₂/Et₂O =90:10); ¹H NMR δ -0.55 (s, 9H), 0.80 (dd, 1H, *J* = 4.4, 16.2 Hz), 0.94 (dd, 1H, *J* = 6.6, 16.2 Hz), 2.41 (s, 3H), 2.86 (ddd, 1H, *J* = 3.3, 4.4, 6.6 Hz), 2.90 (d, 1H, *J* = 2.2 Hz), 5.50 (dd, 1H, *J* = 2.2, 3.3 Hz), 7.29-7.49 (m, 9H).

(*R,R*)- and (*S,R*)-1-Phenyl-2-(*p*-tolylsulfinyl)-3-(trimethylsilyl)propan-1-one (4a).

$R_f=0.67$; ($\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}=90:10$); $^1\text{H NMR}$ δ -0.15 (s, 9H, (*R,R*)), 0.00 (s, 9H, (*S,R*)), 0.60 - 0.90 (m, 2H), 2.41 (s, 3H), 4.50 - 4.70 (m, 1H), 7.29 - 7.92 (m, 9H); IR (neat) 2950 , 1650 , 1080 cm^{-1} ; MS (SIMS) m/e 204 ($\text{M}^+-\text{CH}_3\text{C}_6\text{H}_4\text{SOH}$, 100), 92 (80), 71 (55); Anal. Calcd for $\text{C}_{19}\text{H}_{24}\text{O}_2\text{SSi}$: C, 66.24; H, 7.02; Found: C, 66.20; H 7.09.

(2*R*,3*R*,*R*)-3-(*p*-Tolylsulfinyl)-4-(trimethylsilyl)butan-2-ol (5b). $R_f=0.15$; (hexane/ethyl

acetate= $70:30$); $^1\text{H NMR}$ δ -0.17 (s, 9H), 0.70 (dd, 1H, $J = 3.8, 15.5\text{ Hz}$), 0.85 (dd, 1H, $J = 8.9, 15.5\text{ Hz}$), 1.20 (3H, d, $J = 7.0\text{ Hz}$), 2.42 (s, 3H), 2.70 (ddd, 1H, $J = 3.8, 4.5, 8.9\text{ Hz}$), 2.70 (br, 1H), 4.08 - 4.25 (m, 1H), 7.28 (d, 2H, $J = 8.4\text{ Hz}$), 7.40 (d, 2H, $J = 8.4\text{ Hz}$); IR (neat) 3580 , 2970 , 1420 , 1080 cm^{-1} ; MS (EI) m/e 296 (M^+ , 10), 156 (100), 92 (72); Anal. Calcd for $\text{C}_{15}\text{H}_{24}\text{O}_2\text{SSi}$: C, 60.76; H, 8.16. Found: C, 60.57; H, 8.22.

(*R,R*)- and (*S,R*)-3-(*p*-Tolylsulfinyl)-4-(trimethylsilyl)butan-2-one (4b). $R_f=0.65$;

($\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}=90:10$); $^1\text{H NMR}$ δ -0.20 (s, 9H, major), -0.05 (s, 9H, minor), 0.65 (dd, 1H, $J = 4.3, 15.6\text{ Hz}$), 0.86 (dd, 1H, $J = 8.8, 15.6\text{ Hz}$), 2.41 (s, 3H), 2.45 (s, 3H), 4.55 (dd, 1H, $J = 4.3, 8.8\text{ Hz}$), 7.28 - 7.95 (m, 4H); IR (neat) 2950 , 1640 , 1080 cm^{-1} ; MS (SIMS) m/e 154 ($\text{M}^+-\text{CH}_3\text{C}_6\text{H}_4\text{SOH}$, 100), 92 (60), 71 (40); Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{O}_2\text{SSi}$: C, 61.18; H, 7.53; Found: C, 61.22; H 7.46.

(2*R*,3*R*,*R*)-2-(*p*-Tolylsulfinyl)-1-(trimethylsilyl)octan-3-ol (5c). $^1\text{H NMR}$ δ -0.18 (s, 9H),

0.72 (dd, 1H, $J = 4.2, 15.7\text{ Hz}$), 0.85 (dd, 1H, $J = 8.9, 15.7\text{ Hz}$), 0.90 (3H, t, $J = 6.5\text{ Hz}$), 1.24 - 1.41 (m, 6H), 1.52 - 1.71 (m, 2H), 2.20 (d, 1H, $J = 4.3\text{ Hz}$), 2.41 (s, 3H), 2.69 (ddd, 1H, $J = 2.8, 4.2, 8.9\text{ Hz}$), 4.08 - 4.20 (m, 1H), 7.32 (d, 2H, $J = 8.4\text{ Hz}$), 7.44 (d, 2H, $J = 8.4\text{ Hz}$).

(*R,R*)- and (*S,R*)-2-(*p*-Tolylsulfinyl)-1-(trimethylsilyl)octan-3-one (4c). $R_f=0.65$;

($\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}=90:10$); $^1\text{H NMR}$ δ -0.15 (s, 9H, major), -0.17 (s, 9H, minor), 0.68 (dd, 1H, $J = 4.5, 14.8\text{ Hz}$), 0.89 (dd, 1H, $J = 8.8, 14.8\text{ Hz}$), 0.90 (t, 3H, $J = 6.5\text{ Hz}$), 1.21 - 1.60 (m, 6H),

2.41 (s, 3H), 2.45 (t, 2H, $J = 7.0$ Hz), 4.60 (dd, 1H, $J = 4.5, 8.8$ Hz), 7.25-7.90 (m, 4H); IR (neat) 2950, 1650, 1080 cm^{-1} ; MS (SIMS) m/e 198 ($\text{M}^+ - \text{CH}_3\text{C}_6\text{H}_4\text{SOH}$, 100), 92 (81), 71 (30); Anal. Calcd for $\text{C}_{18}\text{H}_{30}\text{O}_2\text{SSi}$: C, 63.85; H, 8.93; Found: C, 64.01; H 8.88.

(2*R*,3*R*,*R*_S)-4-Methyl-2-(*p*-tolylsulfinyl)-1-(trimethylsilyl)pentan-3-ol (5d).¹ $R_f=0.42$; ($\text{CHCl}_3/\text{Et}_2\text{O}=80:20$); ^1H NMR δ -0.18 (s, 9H), 0.79 (dd, 1H, $J = 5.1, 16.2$ Hz), 0.93 (d, 3H, $J = 6.7$ Hz), 0.94 (dd, 1H, $J = 6.5, 16.2$ Hz), 1.03 (d, 3H, $J = 6.7$ Hz), 1.86 (dq, 1H, $J = 6.7, 7.6$ Hz), 2.17 (br, 1H), 2.42 (s, 3H), 2.82 (ddd, 1H, $J = 3.2, 5.1, 6.5$ Hz), 3.90 (dd, 1H, $J = 3.2, 7.6$ Hz), 7.33 (d, 2H, $J = 8.5$ Hz), 7.45 (d, 2H, $J = 8.5$ Hz).

(*R*,*R*_S)- and (*S*,*R*_S)-4-Methyl-2-(*p*-tolylsulfinyl)-1-(trimethylsilyl)pentan-3-one (4d). $R_f=0.60$; ($\text{CHCl}_3/\text{Et}_2\text{O}=80:20$); ^1H NMR δ -0.15 (s, 9H, major), 0.00 (s, 9H, minor), 0.80 (dd, 1H, $J = 5.3, 16.6$ Hz), 0.95 (d, 3H, $J = 6.7$ Hz), 0.94 (dd, 1H, $J = 6.6, 16.6$ Hz), 1.03 (d, 3H, $J = 6.7$ Hz), 1.86 (qq, 1H, $J = 6.7, 6.7$ Hz), 2.43 (s, 3H), 3.05 (dd, 1H, $J = 5.1, 6.5$ Hz), 7.35 (d, 2H, $J = 8.4$ Hz), 7.45 (d, 2H, $J = 8.4$ Hz); IR (neat) 2950, 1630, 1080 cm^{-1} ; MS (SIMS) m/e 170 ($\text{M}^+ - \text{CH}_3\text{C}_6\text{H}_4\text{SOH}$, 100), 92 (60), 71 (80); Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{O}_2\text{SSi}$: C, 61.89; H, 8.44; Found: C, 61.88; H 8.43.

(2*R*,3*S*,*R*_S)- and (2*R*,3*R*,*R*_S)-3-(*p*-Tolylsulfinyl)butan-2-ol (5e).² $R_f = 0.30$ (hexane/ethyl acetate = 40:60); ^1H NMR δ 0.85-1.45 (m, 6H), 2.35-2.80 (m, 1H), 2.44 (s, 3H), 2.80-2.90 (br, 1H, (2*R*,3*S*,*R*_S)), 3.98-4.10 (br, 1H, (2*R*,3*R*,*R*_S)), 3.95-4.60 (m, 1H), 7.25-7.70 (m, 4H); IR (neat) 3600, 2970, 1450, 1070 cm^{-1} ; MS (EI) m/e 212 (M^+ , 5), 140 (100), 92 (20); Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2\text{S}$: C, 62.23; H, 7.60. Found: C, 62.00; H, 7.70.

(*R*,*R*_S)- and (*S*,*R*_S)-3-(*p*-Tolylsulfinyl)butan-2-one (4e).² $R_f = 0.40$ (hexane/ethyl acetate = 40:60); ^1H NMR δ 1.25 (d, 1H, $J = 7.0$ Hz, (*R*,*R*_S)), 1.35 (d, 1H, $J = 7.0$ Hz, (*S*,*R*_S)), 2.16 (s, 3H, (*S*,*R*_S)), 2.25 (s, 3H, (*R*,*R*_S)), 2.42 (s, 3H), 3.69 (q, 1H, $J = 7.0$ Hz, (*S*,*R*_S)), 3.75 (q, 1H, $J = 7.0$ Hz, (*R*,*R*_S)), 7.32-7.50 (m, 4H).

(1*R*,2*S*,*R*_S)- and (1*R*,2*R*, *R*_S)-4,4-Dimethyl-1-phenyl-2-(*p*-tolylsulfinyl)pentan-1-ol (5f).

$R_f = 0.52$ (hexane/ethyl acetate = 50:50); $^1\text{H NMR}$ δ 0.69 (s, 9H), 1.80-2.10 (m, 2H), 2.35-2.50 (m, 1H), 2.44 (s, 3H, (1*R*,2*R*, *R*_S)), 2.50 (s, 3H, (1*R*,2*S*,*R*_S)), 4.72 (s, 1H, (1*R*,2*S*,*R*_S)), 4.85-4.98 (m, 1H, (1*R*,2*R*, *R*_S)), 5.30 (br, 1H), 6.81-7.30 (m, 5H), 7.40-7.70 (m, 4H); IR (neat) 3600, 2980, 1490, 1080 cm^{-1} ; MS (EI) m/e 330 (M^+ , 5), 315 (21), 140 (60), 92 (100); Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{O}_2\text{S}$: C, 72.69; H, 7.93. Found: C, 72.82; H, 7.88.

(*S*,*R*_S)- and (*R*,*R*_S)-4,4-Dimethyl-1-phenyl-2-(*p*-tolylsulfinyl)pentan-1-one (4f). $R_f = 0.56$

(hexane/ethyl acetate = 50:50); $^1\text{H NMR}$ δ 0.70 (s, 9H, (*S*,*R*_S)), 0.72 (s, 9H, (*R*,*R*_S)), 1.80-2.10 (m, 2H), 2.44 (s, 3H), 4.50-4.60 (m, 1H), 6.90-7.70 (m, 9H); IR (neat) 3600, 2980, 1490, 1080 cm^{-1} ; MS (EI) m/e 330 (M^+ , 5), 315 (21), 140 (60), 92 (100); Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_2\text{S}$: C, 71.13; H, 7.36. Found: C, 71.20; H, 7.30.

(*S*)-1-Phenylprop-2-en-1-ol (6).¹ $[\alpha]_{\text{D}}^{10} + 8.3$ (c 2.87, benzene); $^1\text{H NMR}$ δ 1.95 (br, 1H), 5.20 (d, 1H, $J = 10$ Hz), 5.22 (d, 1H, $J = 6.0$ Hz), 5.36 (d, 1H, $J = 17.0$ Hz), 6.05 (ddd, 1H, $J = 6.0, 10.0, 17.0$ Hz), 7.26-7.40 (m, 5H).

(*R*)-(E)-Trimethylsilylbut-1-en-2-ol (7).³ $[\alpha]_{\text{D}}^{20} - 5.3$ (c 0.20, CHCl_3); $^1\text{H NMR}$ δ 0.07 (s, 9H), 1.28 (d, 3H, $J = 6.8$ Hz), 1.61 (br, 1H), 4.30 (dq, 1H, $J = 5.1, 6.8$ Hz), 5.83 (dd, 1H, $J = 2.0, 17.0$ Hz), 6.08 (dd, $J = 5.1, 17.0$ Hz).

(*R*)- Oct-1-en-3-ol (8).¹ $[\alpha]_{\text{D}}^{15} - 10.0$ (c 1.67, CHCl_3); $^1\text{H NMR}$ δ 1.89 (t, 3H, $J = 6.8$ Hz), 1.22-1.60 (m, 8H), 1.44 (d, 1H, $J = 4.5$ Hz), 4.03-4.17 (m, 1H), 5.10 (ddd, 1H, $J = 1.4, 1.4, 10.3$ Hz), 5.22 (ddd, 1H, $J = 1.4, 1.4, 17.2$ Hz), 5.87 (ddd, 1H, $J = 6.1, 10.3, 17.2$ Hz).

(*R*)-(E)-1-Trimethylsilyloct-1-en-3-ol (9).¹ $[\alpha]_{\text{D}}^{20} - 10.9$ (c 1.01, CHCl_3); $^1\text{H NMR}$ δ 0.07 (s, 9H), 0.88 (t, 3H, $J = 6.4$ Hz), 1.23-1.58 (m, 8H), 1.52 (d, 1H, $J = 4.3$ Hz), 4.01-4.18 (m, 1H), 5.82 (dd, 1H, $J = 1.1, 18.7$ Hz), 6.04 (dd, 1H, $J = 5.1, 18.7$ Hz).

(R)-(E)-4-Methyl-1-trimethylsilylpent-1-en-3-ol (10).⁴ $[\alpha]_{\text{D}}^{25} - 22.0$ (*c* 0.50, CHCl₃).); ¹H NMR δ 0.08 (s, 9H), 0.90 (d, 3H, *J* = 6.6 Hz), 0.92 (d, 3H, *J* = 6.6 Hz), 1.55 (d, 1H, *J* = 3.0 Hz), 1.70-1.80 (m, 1H), 3.78-3.88 (m, 1H), 5.85 (dd, 1H, *J* = 1.2, 18.6 Hz), 6.04 (dd, 1H, *J* = 5.5, 18.6 Hz),

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