Supporting Information Available

Palladium-Catalyzed Enantioselective 1,3-Rearrangement of Racemic Allylic Sulfinates: Asymmetric Synthesis of Allylic Sulfones and Kinetic Resolution of an Allylic Sulfinate

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General Methods. All reactions were carried out in absolute solvents under an argon atmosphere with syringe and Schlenk techniques in oven-dried glassware. CH_2Cl_2 and NEt_3 were distilled from CaH_2. Bisphosphane **BPA**[4] and $Pd_2(dba)_3{\cdot}CHCl_3$[20] were prepared according to the literature. The racemic acyclic alcohols were prepared by standard procedures from the corresponding unsaturated aldehyds via Grignard reaction,[24] and the racemic cyclic alcohols were synthesized from the corresponding alkenes via Wohl-Ziegler bromination[25] followed by a substitution of the thus obtained allylic bromides with aqueous $NaHCO_3$.[26] 4-Methyl-benzenesulfinylchloride[15b] and 2-methyl-propane-2-sulfinyl-chloride[15a,d] were prepared according to the literature. Column chromatography: silica gel 60 (0.063–0.100 mm). Optical rotations: measurements were made at approximately 22 °C, specific rotations in grad·mL/dm·g, *c* in g/100 mL. Peaks in the ^{1}H NMR spectra are denoted

Peaks in the ^{13}C NMR spectra are denoted as "u" for carbons with zero or two attached protons or "d" for carbons with one or three attached protons, as determined from APT pulse sequence. GC analyses: CP-Sil-8: 30 m × 0.32 mm; 75 kPa H_2, octakis-(2,6-di-*O*-pentyl-3-*O*-butyryl)-γ-cyclodextrin (Lipodex-E): 25 m, 0.25 mm; 100 kPa H_2) and heptakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)-β-cyclodextrin (Hydrodex-β-6-TBDM): 25 m, 0.25 mm; 100 kPa H_2) instruments. HPLC analyses were performed on Chiralcel OD-H and OF columns. IR spectra: only peaks of ν >1000 cm^{-1} are listed. Decisive signals of the MS spectra (CI, 70 ev) and those with an intensity higher than 10% are listed.

2-Methyl-propane-2-sulfinic Acid 1-Methyl-2-butenyl Ester (*rac*-3). Following GP1, the reaction of alcohol *rac*-**1** (0.86 g, 10 mmol) with 2-methyl-propane-2-sulfinyl-chloride (1.41 g, 10 mmol) gave a diastereomeric mixture (1:1, GC and ^{1}H NMR) of the sulfinate *rac*-**3** (1.56 g, 82%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17 (s, 4.5H), 1.18 (s, 4.5H), 1.36 (d, J = 6.4 Hz, 1.5H), 1.39 (d, J = 6.4 Hz, 1.5H), 1.72 (m, 3H), 4.68 (m, 1H), 5.42 (ddq, J = 15.3, J = 7.6, J = 1.7 Hz, 0.5H), 5.57 (ddq, J = 15.3, J = 7.6, J = 1.7 Hz, 0.5H),

5.75 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.6 (d), 21.3 (d), 21.7 (d), 22.2 (d), 56.7 (u), 56.9 (u), 77.0 (u), 77.8 (u), 128.4 (d), 129.3 (d), 131.0 (d), 131.4 (d); MS (CI) *m/z* (relative intensity) 191 [M^++1] (4), 189 (14), 152 (12), 151 (26), 137 (53), 135 (11), 133 (21), 123 (100), 75 (26), 69 (46); IR (film) ν 2978 (m), 2937 (m), 2877 (w), 1479 (m), 1450 (m), 1367 (m), 1286 (s), 1195 (m), 1112 (s), 1013 (m) cm^{-1}. Anal. Cacld for $C_{10}H_{18}O_2S$ (190.29): C, 56.80; H, 9.53. Found: C, 56.63; H, 9.42.

2-Methyl-propane-2-sulfinic Acid 1-Ethyl-2-pentenyl Ester (*rac*-4). Following GP1, the reaction of alcohol *rac*-**2** (1.14 g, 10 mmol) with 2-methyl-propane-2-sulfinyl-chloride (1.41 g, 10 mmol) gave a diastereomeric mixture (1:1, GC and ^{1}H NMR) of the sulfinate *rac*-**4** (2.00 g, 92%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (dt, J = 7.4, J = 1.7 Hz, 1.5H), 1.01 (dt, J = 7.4, J = 1.2 Hz, 1.5H), 1.17 (s, 4.5H), 1.19 (s, 4.5H), 1.59–1.80 (m, 1H), 2.08 (m, 1H), 4.42 (m, 1H), 5.32 (dt, J = 15.5, 6.7, 1.7 Hz, 0.5H), 5.48 (dt, J = 15.5, 6.7, 1.7 Hz, 0.5H), 5.73–5.85 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.6 (d), 13.2 (d), 13.3 (d), 21.8 (d), 25.2 (u), 28.7 (u), 29.0 (u), 56.8 (u), 57.3 (u), 82.1 (d), 84.0 (d), 127.6 (d), 128.0 (d), 136.9 (d), 137.6 (d); MS (CI) *m/z* (relative intensity) 219 [M^++1] (0.7), 163 (16), 151 (16), 123 (100), 97 (71), 89 (15), 75 (54), 73 (16); IR (film) ν 2965 (s), 2933 (s), 2876 (s), 1668 (w), 1459 (s), 1363 (m), 1313 (m), 1184 (w), 1127 (s), 1076 (m), 1018 (w) cm^{-1}. Anal. Cacld for $C_{11}H_{20}O_2S$ (218.35): C, 60.51; H, 10.16. Found: C, 60.67; H, 10.28.

2-Methyl-propane-2-sulfinic Acid 2-Cyclohex-1-enyl Ester (*rac*-8a). Following GP1, the reaction of alcohol *rac*-**5** (0.98 g, 10 mmol) with 2-methyl-propane-2-sulfinyl-chloride (1.41 g, 10 mmol) gave a diastereomeric mixture (1:1, GC) of the sulfinate *rac*-**8a** (1.74 g, 86%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (s, 4.5H), 1.19 (s, 4.5H), 1.57–2.14 (m, 6H), 4.70 (m, 1H) 5.73–5.82 (m, 1H), 5.92–6.00 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.5 (u), 18.6 (u), 21.7 (d), 24.8 (u), 24.9 (u), 29.3 (u), 30.3 (u), 56.8 (u), 57.1 (u), 73.6 (d), 74.3 (d), 125.6 (d), 126.6 (d), 132.4 (d), 133.0 (d); MS (EI) *m/z* (relative intensity)

202 [M^+] (0.05), 81 (100), 80 (17), 79 (20), 57 (94); IR (film) ν 3031 (w), 2942 (s), 2867 (m), 2837 (w), 1475 (m), 1457 (m), 1393 (w), 1362 (m), 1322 (w), 1183 (w), 1161 (w), 1126 (s), 1052 (w) cm^{-1}. Anal. Cacld for $C_{10}H_{18}O_2S$ (202.31): C, 59.37; H, 8.97. Found: C, 59.27; H, 8.93.

4-Methyl-benzenesulfinic Acid 2-Cyclohex-1-enyl Ester (*rac*-8b). Following GP1, the reaction of alcohol *rac*-**5** (0.98 g, 10 mmol) with 2-Methyl-benzenesulfinylchloride (2.04 g, 12 mmol) gave a diastereomeric mixture (1:1, ^1H NMR) of the sulfinate *rac*-**8b** (2.01 g, 85%) as a colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 1.50–2.11 (m, 6H), 2.41 (s, 3H), 4.81 (m, 1H), 5.44 (m, 0.5H), 5.81 (m, 0.5H), 5.89 (m, 0.5H), 5.99 (m, 0.5), 7.32 (m, 2H), 7.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.5 (u), 18.6 (u), 21.5 (d), 24.7 (u), 24.7 (u), 30.1 (u), 30.4 (u), 71.5 (d), 72.8 (d), 125.1 (d), 125.2 (d), 126.3 (d), 126.7 (d), 129.6 (d), 129.6 (d), 133.2 (d), 133.3 (d), 142.4 (u), 142.8 (u); MS (CI) *m/z* (relative intensity) 237 [M^++1] (28), 157 (100), 81 (17); IR (film) ν 3031 (m), 2934 (m), 2866 (m), 2834 (w), 1595 (w), 1492 (s), 1450 (w), 1395 (w), 1329 (w), 1132 (s), 1081 (m), 1047 (w), 1002 (m) cm^{-1}. Anal. Cacld for $C_{13}H_{16}O_2S$ (236.32): C, 66.07; H, 6.82. Found: C, 66.14; H, 7.04.

2-Methyl-propane-2-sulfinic Acid 2-Cyclohept-1-enyl Ester (*rac*-9a). Following GP1, the reaction of alcohol *rac*-**6** (1.12 g, 9.9 mmol) with 2-methyl-propane-2-sulfinyl-chloride (1.41 g, 10 mmol) gave a diastereomeric mixture (1.2:1, GC) of the sulfinate *rac*-**9a** (1.88 g, 87%) as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 1.20 (s, 9H), 1.40–2.28 (m, 8H), 4.85 (m, 1H), 5.70–5.92 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7 (d), 26.1 (u), 26.25 (u), 26.5 (u), 28.4 (u), 28.5 (u), 33.7 (u), 34.6 (u), 57.1 (u), 57.1 (u), 78.0 (d), 80.0 (d), 131.8 (d), 132.8 (d), 133.2 (d), 134.0 (d); MS (CI) *m/z* (relative intensity) 217 [M^++1] (10), 123 (100); IR (film) ν 3031 (w), 2942 (s), 2867 (m), 2837 (w), 1475 (m), 1457 (m), 1393 (w), 1362 (m), 1322 (w), 1183 (w), 1161 (w), 1126 (s), 1052 (w) cm^{-1}. Anal. Cacld for $C_{11}H_{20}O_2S$ (216.28): C, 61.09; H, 9.32. Found: C, 61.17; H, 9.34.

4-Methyl-benzenesulfinic Acid 2-Cyclohept-1-enyl Ester (*rac*-9b). Following GP1, the reaction of alcohol *rac*-**6** (1.06 g, 9.5 mmol) with 2-methyl-benzenesulfinylchloride (2.08 g, 12 mmol) gave a diastereomeric mixture (1:1, ^{1}H NMR) of the sulfinate *rac*-**9b** (2.27 g, 96%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ1.35–2.24 (m, 8H), 2.41 (s, 3H), 4.97 (m, 1H), 5.54–5.91 (m, 2H), 7.31 (m, 2H), 7.61 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ21.5 (d), 25.9 (u), 26.1 (u), 26.4 (u), 26.0 (u), 28.4 (u), 28.4 (u), 34.5 (u), 34.8 (u), 78.0 (d), 78.6 (d), 125.0 (d), 125.4 (d), 129.6 (d), 132.2 (d), 132.6 (d), 133.5 (d), 133.8 (d), 142.5 (u), 142.6 (u), 142.8 (u); MS (CI) *m/z* (relative intensity) 251 [M^++1] (28), 157 (100); IR (film) ν3026 (m), 2857 (m), 1651 (w), 1596 (m), 1492 (w), 1447 (m), 1397 (w), 1135 (s), 1082 (m) cm^{-1}. Anal. Cacld for $C_{14}H_{18}O_2S$ (250.35): C, 67.16; H, 7.25. Found: C, 67.09; H, 7.48.

(–)-(*R,E*)-5-(2-Methyl-propane-2-sulfonyl)-hept-3-ene (12). Following GP2, rearrangement of sulfinate *rac*-**4** (224 mg, 1.03 mmol) in the presence of **BPA** (133 mg, 0.19 mmol) and $Pd_2(dba)_3{\cdot}CHCl_3$ (66 mg, 0.06 mmol) for 24 h gave sulfone **12** (190 mg, 84%) as a colorless oil: 97% ee (GC, Lipodex-E, t_R (**12**) = 35.9 min, t_R (*ent*-**12**) = 36.1 min); $[\alpha]_D$ = –31.0 (*c* 1.02, EtOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ0.94 (t, J = 7.4, 3H), 1.03 (t, J = 7.7 Hz, 3H), 1.42 (s, 9H), 1.60/1.75 (m, 1H), 2.08/2.28 (m, 3H), 3.56 (dt, J = 3.2, J = 10.1 Hz, 1H), 5.45 (ddt, J = 9.9, J = 15.6, J = 1.5 Hz, 1H), 5.75 (dt, J =15.6, J = 6.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ10.81 (d), 13.04 (d), 20.45 (u), 24.55 (d), 25.58 (u), 61.65 (u), 64.78 (d), 123.90 (d), 138.91 (d); MS (CI) *m/z* (relative intensity) 219 [M^++1] (100), 123 (95), 97 (10); IR (film) ν 2969 (s), 2935 (s), 2876 (m), 1479 (m), 1461 (m), 1367 (w), 1279 (s), 1197 (w), 1113 (s), 1073 (w), 1054 (w) cm^{-1}. Anal. Cacld for $C_{11}H_{22}O_2S$ (218.35): C, 60.51; H, 10.16. Found: C, 60.70; H, 10.05.

(–)-(S)-3-(2-Methyl-propane-2-sulfonyl)-cyclohexene (13a). Following GP2, rearrangement of sulfinate *rac*-**8a** (225 mg, 1.11 mmol) in the presence of **BPA** (41 mg, 0.06 mmol) and $Pd_2(dba)_3{\cdot}CHCl_3$ (21 mg, 0.02 mmol) for 3.5 h gave sulfone **13a** (208 mg, 92%) as

a colorless solid: 95% ee (^{1}H NMR, 400 MHz, $CDCl_3$, 30 mol %, Eu(hfc)$_3$, δ (*t*Bu) (**13a**) = 2.04 ppm, δ (*t*Bu)-(*ent*-**13a**) = 2.07 ppm); mp 55 °C; $[\alpha]_D = -179.2$ (*c* 1.06, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45 (s, 9H), 1.60/1.70 (m, 1H), 1.94/2.28 (m, 5H), 3.93 (m, 1H), 5.82 (dq, J = 10.2, J = 2.2 Hz, 1H), 6.12 (dq, J = 10.2, J = 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.06 (u), 23.81 (u), 24.21 (d), 24.28 (u), 55.14 (u), 61.13 (u), 119.50 (d), 134.41 (d); MS (CI) *m/z* (relative intensity) 203 [M^++1] (100), 123 (19); IR (KBr) ν 3491 (m), 3042 (w), 2939 (s), 2875 (m), 2836 (w), 1650 (w), 1479 (m), 1398 (w), 1368 (w), 1281 (s), 1197 (w), 1108 (s), 1040 (w) cm^{-1}. Anal. Cacld for $C_{10}H_{18}O_2S$ (202.31): C, 59.37; H, 8.97. Found: C, 59.35; H, 9.13.

(–)-(*S*)-1-((2-Cyclohex-1-ene)sulfonyl)-4-methylbenzene (13b). Following GP2, rearrangement of sulfinate *rac*-**8b** (248 mg, 1.05 mmol) in the presence of **BPA** (45 mg, 0.06 mmol) and $Pd_2(dba)_3 \cdot CHCl_3$ (21 mg, 0.02 mmol) for 15 h gave sulfone **13b** (239 mg, 96%) as a colorless solid: ≥ 99% ee (HPLC, Chiralcel OD-H column *n*-heptane/EtOH, 99:1, t_R (**13b**) = 25.9 min; $[\alpha]_D = -132.2$ (*c* 1.105, CH_2Cl_2) ;^{1}H NMR (300 MHz, $CDCl_3$) δ 1.42/1.56 (m, 1H), 1.70/2.03 (m, 5H), 2.45 (s, 3H), 3.74 (m, 1H), 5.78 (dq, J = 10.1, J = 2.2 Hz, 1H), 6.08 (dq, J = 10.1, J = 2.5 Hz, 1H), 7.35 (m, 2H), 7.74 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.50 (u), 21.60 (d), 22.68 (u), 24.32 (u), 61.71 (d), 118.49 (d), 128.92 (d), 129.36 (d), 134.15 (u), 134.86 (d), 144.30 (u); MS (CI) *m/z* (relative intensity) 237 [M^++1] (100), 157 (40); IR (film) ν 3033 (w), 2938 (m), 2868 (m), 2836 (w), 1597 (m), 1449 (m), 1402 (w), 1301 (s), 1238 (w), 1212 (w), 1183 (w), 1143 (s), 1087 (s) cm^{-1}. Anal. Cacld for $C_{13}H_{16}O_2S$ (236.37): C, 66.07; H, 6.82. Found: C, 65.93; H, 6.95.

(–)-(*S*)-3-(2-Methyl-propane-2-sulfonyl)-cycloheptene (14a). Following GP2, rearrangement of sulfinate *rac*-**9a** (226 mg, 1.04 mmol) in the presence of **11** (41 mg, 0.06 mmol) and $Pd_2(dba)_3 \cdot CHCl_3$ (21 mg, 0.02 mmol) for 19.5 h gave sulfone **14a** (185 mg, 82%) as a colorless solid: 98% ee (GC, Lipodex-E, t_R (**14a**) = 102.9 min, t_R (*ent*-**14a**) = 103.2 min); $[\alpha]_D$

= –99.0 (*c* 1.00, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 1.43 (s, 9H), 1.45/1.91 (m, 4H), 2.11/2.38 (m, 4H) 3.97 (m, 1H), 5.96/6.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.43 (d), 25.79 (u), 26.48 (u), 27.96 (u), 29.43 (u), 59.10 (d), 61.39 (u), 126.95 (d),135.32 (d); MS (CI) *m/z* (relative intensity) 217 [M^++1] (67), 123 (100); IR (KBr) ν 3453 (m), 3034 (w), 2929 (s), 2859 (m), 1473 (m), 1447 (m), 1398 (w), 1367 (w), 1281 (s), 1231 (m), 1192 (w), 1147 (w), 1106 (s), 1066 (w) cm^{-1}. Anal. Cacld for $C_{11}H_{20}O_2S$ (216.28): C, 61.09; H, 9.32. Found: C, 61.09; H, 9.42.

(–)-(*S*)-1-((2-Cyclohep-1-ene)sulfonyl)-4-methylbenzene (14b). Following GP2, rearrangement of sulfinate *rac*-**9b** (268 mg, 1.07 mmol) in the presence of **BPA** (42 mg, 0.06 mmol) and $Pd_2(dba)_3{\cdot}CHCl_3$ (21 mg, 0.02 mmol) for 24 h gave sulfone **14b** (233 mg, 87%) as a colorless solid: ≥ 99% ee (HPLC, Chiralcel OD-H column *n*-heptane/EtOH, 99:1, t_R (**14b**) = 40.5 min; $[\alpha]_D$ = –91.2 (*c* 1.04, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 1.38/1.49 (m, 1H), 1.55/1.74 (m, 3H), 2.00/2.10 (m, 2H), 2.15/2.25 (m, 2H), 2.45 (s, 3H), 3.81 (m, 1H), 5.81 (m, 1H), 6.01 (m, 1H), 7.35 (m, 2H), 7.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.64 (d), 25.99 (u), 26.93 (u), 27.98 (u), 27.98 (u), 66.30 (d), 124.05 (d), 129.08 (d), 129.69 (d), 134.79 (u), 136.67 (d), 144.55 (u); MS (CI) *m/z* (relative intensity) 251 [M^++1] (100), 157 (81); IR (FILM) ν 3676 (w), 3652 (w), 3631 (w), 3433 (m), 3034 (w), 2964 (m), 2926 (s), 2854 (m), 1645 (w), 1595 (m), 1495 (w), 1443 (m), 1404 (w), 1385 (w), 1309 (s), 1243 (s), 1143 (s), 1106 (m), 1086 (s), 1019 (w) cm^{-1}. Anal. Cacld for $C_{14}H_{18}O_2S$ (250.35): C, 67.16; H, 7.25. Found: C, 67.11; H, 7.44.

Rearrangement of Mixtures of Sulfinates *rac*-8b and *rac*-9a and of Sulfones 13a and 14b. Following GP2, treatment of a mixture of sulfinates *rac*-**8b** and *rac*-**9a** and of a mixture of sulfones **13a** and **14b** both with **BPA** and $Pd_2(dba)_3{\cdot}CHCl_3$ for 1 h gave in both cases a mixture of sulfones **13a**, **13b**, **14a** and **14b** according to GC analysis (CP-Sil-8: 30 m × 0.32 mm; 75 kPa H_2, t_R (**13a**) = 9.7, t_R (**14a**) = 10.3, t_R (**13b**) = 13.3, t_R (**14b**) = 14.0 min).

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