

Indium-Bipyridine-Catalyzed, Enantioselective Thiolytic of *meso*-Epoxides

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Supplementary Information

General Methods: All reactions were performed under an atmosphere of nitrogen in oven dried glassware. ¹H and ¹³C NMR spectra were recorded on a Varian Gemini 2000 (200, 300 or 400 MHz) NMR spectrometer. NMR spectra were obtained using CDCl₃-d as solvent. Chemical shifts are given in the δ scale with tetramethylsilane or the CHCl₃ proton as the internal standard. IR spectra were obtained with a FTIR spectrometer (Genesis ATI Mattson/Unicam). Optical rotations were measured on a polarotronic polarimeter (Schmidt & Haensch). HPLC analyses were performed on a JASCO MD-2010 plus instrument with a chiral stationary phase column (Daicel Chiralcel OD column). Solvents were purified by distillation from appropriate drying agents. The chiral bipyridine ligand **1a** was prepared according to the reported procedure.¹ The corresponding authentic racemic products were prepared using a base-catalyzed (K₂CO₃, EtOH, reflux) thiolytic.

General procedure for the enantioselective ring opening of epoxides with thiols

(1*R*,2*R*)-2-Benzylsulfanyl-1,2-diphenyl-ethanol (4a)²

A solution of InBr₃ (35.4 mg, 10 mol %) and chiral bipyridine **1a** (36 mg, 11 mol %) in CH₂Cl₂ (5 mL) was stirred for 30 min at room temperature. Subsequently *cis*-stilbene oxide (**2a**) (196 mg, 1 mmol) and benzyl mercaptan (186 mg, 1.50 mmol) were added and the solution was stirred for 16 h at room temperature. The solvent was evaporated *in vacuo*, and the crude product was purified by flash column chromatography on silica gel (15% ethyl acetate: hexane) to yield 256 mg (80%) of 1,2-diphenyl-2-benzylsulfanyl-ethanol **4a** as viscous liquid. HPLC (Daicel Chiracel OD, 90:10 *n*-hexane: isopropanol, flow rate 1 mL/min) t_R (*1S,2S*) 14.6 min and t_R (*1R,2R*) 28.3 min (92% ee). IR (film) : 3407, 3055, 3025, 2915, 2891, 1631, 1597, 1488, 1451, 1434, 1334, 1315, 1273, 1196, 1156, 1069, 1047, 1027 cm⁻¹, ¹H NMR (300 MHz, CDCl₃): δ 3.13 (d, *J* = 3.0 Hz, 1H, -OH), 3.53 (d, *J* = 13.0 Hz, 1H, -CH₂), 3.65 (d, *J* = 13.0 Hz, 1H, -CH₂), 3.97 (d, *J* = 8.5 Hz, 1H, -CH-S), 4.88 (dd, *J*₁ = 3.0 Hz, *J*₂ = 8.5 Hz, 1H, -CH-OH), 7.11 – 7.33 (m, 15 H, Ar) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 36.04, 58.68, 77.19, 126.6, 127.0, 127.2, 127.5, 127.8, 128.1, 128.4, 128.7, 129.0, 137.6, 139.2, 141.1 ppm. MS (ESI) [M+ Na]⁺ 343.1. [α]_D²⁵ – 98° (c = 1, CHCl₃).

(1*R*,2*R*)-1,2-Diphenyl-2-phenylsulfanyl-ethanol (4b)³

Yield 81 %, colorless solid, mp. 44 – 45°C, HPLC (Daicel Chiracel OD-phase, 90:10 *n*-hexane: isopropanol, flow rate 1 mL/min) t_R (*1R,2R*) 14.1 min (96 % ee) and t_R (*1S,2S*) 18.4 min. IR (KBr) : 3472, 3025, 2898, 1599, 1581, 1480, 1449, 1438, 1378, 1317, 1294, 1276, 1242, 1229, 1189, 1172, 1159, 1088, 1074, 1056, 1019 cm⁻¹, ¹H NMR (400 MHz, CDCl₃): δ 3.29 (s, 1H, -OH), 4.34 (d, *J* = 8.5 Hz, 1H, -CH-S), 4.93 (d, *J* = 8.5 Hz, 1H, -CH-OH), 7.02 – 7.04 (m, 2H, Ar), 7.13 – 7.25 (m, 11H, Ar), 7.28 – 7.30 (m, 2H, Ar) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 63.87, 76.81, 126.8, 127.2, 127.3, 127.7, 127.9, 128.0, 128.4, 128.8, 132.3, 134.0, 139.1, 140.3 ppm. MS (ESI) [M+ Na]⁺ 329.1. [α]_D²⁵ – 178° (c = 1, CHCl₃).

(1*R*,2*R*)-1,2-Diphenyl-2-*p*-tolylsulfanyl-ethanol (4c)⁴: Yield 79 %, colorless solid, mp. 72 – 74°C, HPLC (Daicel Chiracel OD, 97:3 *n*-hexane: isopropanol, flow rate 1 mL/min) t_R (*1S,2S*) 23.8 min and t_R (*1R,2R*) 25.4 min (96 % ee). IR (KBr) : 3402, 3079, 3059, 3024, 2907, 1953, 1596, 1489, 1450, 1393, 1372, 1336, 1311, 1271, 1228, 1193, 1072, 1054, 1026 cm^{-1} , ^1H NMR (400 MHz, CDCl_3): δ 2.30 (s, 3H, -CH₃), 3.41 (s, 1H, OH), 4.28 (d, J = 8.5 Hz, 1H, -CH-S-), 4.92 (d, J = 8.5 Hz, 1H, -CH-OH), 6.99 – 7.05 (m, 4H, Ar), 7.13 – 7.21 (m, 10H, Ar) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 21.12, 64.47, 76.65, 126.9, 127.1, 127.7, 127.9, 128.0, 128.5, 129.7, 130.1, 133.1, 137.8, 139.3, 140.4 ppm. MS (ESI) $[\text{M} + \text{Na}]^+$ 343.1. $[\alpha]_{\text{D}}^{25} - 166^\circ$ ($c = 1$, CHCl_3).

(1*R*,2*R*)-2-Ethylsulfanyl-1,2-diphenyl-ethanol (4d)⁵: Yield 91 %, viscous liquid, HPLC (Daicel Chiracel OD, 100 % *n*-hexane, flow rate 0.2 mL/min) t_R (*1S,2S*) 164.2 min and t_R (*1R,2R*) 167.5 min (>95 % ee). IR (film) : 3416, 3060, 3028, 2966, 2925, 2870, 1950, 1880, 1807, 1754, 1600, 1584, 1491, 1451, 1384, 1333, 1266, 1192, 1155, 1074, 1045 cm^{-1} , ^1H NMR (300 MHz, CDCl_3): δ 1.17 (t, J = 7.0 Hz, 3H, -CH₃), 2.40 – 2.48 (m, 2H, -CH₂), 3.4 (d, J = 2.5 Hz, 1H, -OH), 4.03 (d, J = 8.5 Hz, 1H, -CH-S-), 4.83 (dd, J = 2.5 Hz, 8.5 Hz, 1H, -CH-OH), 7.12 – 7.20 (m, 10H, Ar) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 14.44, 25.80, 59.65, 76.95, 126.5, 126.9, 127.4, 127.7, 127.9, 128.3, 139.5, 140.8 ppm. MS (ESI) $[\text{M} + \text{Na}]^+$ 281.0. $[\alpha]_{\text{D}}^{25} - 104^\circ$ ($c = 1$, CHCl_3).

(1*R*,2*R*)-2-Butanesulfanyl-1,2-diphenyl-ethanol (4e): Yield 90 %, viscous liquid, HPLC (Daicel Chiracel OD, 97:3 hexane: isopropanol, flow rate 1 mL/min) t_R (*1S,2S*) 15.0 min and t_R (*1R,2R*) 16.4 min (95 % ee). IR (film) : 3431, 3061, 3028, 2956, 2927, 2871, 1948, 1873, 1805, 1727, 1599, 1491, 1452, 1383, 1333, 1294, 1275, 1224, 1191, 1074, 1044 cm^{-1} , ^1H NMR (300 MHz, CDCl_3): δ 0.81 (t, J = 7.0 Hz, 3H, -CH₃), 1.25 – 1.38 (m, 2H, -CH₂), 1.45 – 1.54 (m, 2H, -CH₂), 2.39 (t, J =7.0 Hz, 2H, -CH₂), 3.23 (d, J = 2.5 Hz, 1H, -OH), 3.96 (d, J = 8.5 Hz, 1H, -CH-S), 4.81 (dd, J = 2.5 Hz, 8.5 Hz, 1H, -CH-OH), 7.10 – 7.26 (m, 10H, Ar) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 13.58, 21.89, 31.52, 31.78, 60.42, 77.14, 126.7, 127.1, 127.6, 127.9, 128.1, 128.5, 139.7, 140.9 ppm. MS (ESI) $[\text{M} + \text{Na}]^+$ 309.1. $[\alpha]_{\text{D}}^{25} - 116^\circ$ ($c = 1$, CHCl_3). HRMS (ESI) $[\text{M} + \text{Na}]^+$ cald. for $\text{C}_{18}\text{H}_{22}\text{OS}$: 309.12836, found 309.12848.

(1*R*,2*R*)-1,2-Diphenyl-[2-(3-methylbutanesulfanyl)]-ethanol (4f): Yield 89 %, viscous liquid, HPLC (Daicel Chiracel OD, 97:3 *n*-hexane: isopropanol, flow rate 1 mL/min) t_R (*1S,2S*) 14.2 min and t_R (*1R,2R*) 16.2 min (96 % ee). IR (film) : 3439, 3062, 3029, 2956, 2925, 2869, 1729, 1600, 1492, 1452, 1384, 1367, 1332, 1278, 1226, 1191, 1074, 1045 cm^{-1} , ^1H NMR (300 MHz, CDCl_3): δ 0.78 (d, $J= 6.5$ Hz, 3H, - CH_3), 0.81 (d, $J= 7.5$ Hz, 3H, - CH_3), 1.36 – 1.43 (m, 2H, - CH_2), 1.51 – 1.64 (m, 1H, -CH), 2.39 (t, $J= 7.5$ Hz, 2H, - CH_2), 3.23 (d, $J= 2.5$ Hz, 1H, -OH), 3.97 (d, $J= 8.5$ Hz, 1H, -CH-S), 4.82 (dd, $J= 2.5$ Hz, 8.5 Hz, 1H, -CH-O), 7.10 – 7.19 (m, 10H, Ar) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 22.09, 22.25, 27.32, 30.11, 38.39, 60.37, 77.10, 126.6, 127.1, 127.6, 127.9, 128.1, 128.5, 139.7, 140.9 ppm. MS (ESI) $[\text{M}+ \text{Na}]^+$ 323.1. $[\alpha]_D^{25} - 118^\circ$ ($c = 1$, CHCl_3). Elemental analysis calcd. for $\text{C}_{19}\text{H}_{24}\text{OS}$: C, 75.95, H, 8.05, found C, 75.66, H, 7.97.

(1*R*,2*R*)-1,2-Dinaphthyl-2-phenylsulfanyl-ethanol (4g): Yield 79 %, colorless solid, mp. 112 – 114°C, HPLC (Daicel Chiracel OD, 90:10 *n*-hexane:isopropanol, flow rate 1 mL/min) t_R (*1R,2R*) 27.2 min (96 % ee) and t_R (*1S,2S*) 40.0 min. IR (KBr) : 3549, 3050, 1627, 1596, 1582, 1504, 1479, 1436, 1403, 1357, 1317, 1272, 1246, 1206, 1189, 1156, 1142, 1121, 1087, 1068, 1041, 1026 cm^{-1} , ^1H NMR (300 MHz, CDCl_3): δ 3.44 (s, 1H, -OH), 4.62 (d, $J= 8.0$ Hz, 1H, -CH-S-), 5.23 (d, $J= 8.0$ Hz, 1H, -CH-OH), 7.16 – 7.18 (m, 3H, Ar), 7.25 – 7.30 (m, 4H, Ar), 7.37 – 7.43 (m, 5H, Ar), 7.57 – 7.73 (m, 7H, Ar) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 63.96, 76.52, 124.5, 125.8, 125.8, 125.9, 126.1, 126.4, 127.4, 127.4, 127.5, 127.5, 127.6, 127.7, 127.9, 128.8, 132.5, 132.6, 132.8, 132.9, 132.9, 133.7, 136.5, 137.8 ppm. MS (ESI) $[\text{M}+ \text{Na}]^+$ 428.9. $[\alpha]_D^{25} - 80^\circ$ ($c = 1$, CHCl_3). HRMS (ESI) $[\text{M}+ \text{Na}]^+$ calcd. for $\text{C}_{28}\text{H}_{22}\text{OS}$: 429.12836, found: 429.12821.

(1*R*,2*R*)-2-Benzylsulfanyl-1,2-dinaphthyl-ethanol (4h): Yield 82 %, colorless solid, mp 102 – 104°C, HPLC (Daicel Chiracel OD, 85:15 *n*-hexane:isopropanol, flow rate 1 mL/min) t_R (*1S,2S*) 27.5 min and t_R (*1R,2R*) 46.4 min (96 %). IR (KBr) : 3506, 3048, 2897, 1629, 1597, 1505, 1491, 1451, 1357, 1271, 1234, 1206, 1157, 1120, 1065, 1028, 1015 cm^{-1} , ^1H NMR (200 MHz, CDCl_3): δ 3.08 (d, $J= 3.0$ Hz, 1H, -OH), 3.46 (d, $J= 13.0$ Hz, 1H, CH_2), 3.60 (d, $J= 13.0$ Hz, 1H, CH_2), 4.19 (d, $J= 8.0$ Hz, 1H, -CH-S-), 5.15 (dd,

$J = 3.0$ Hz, 8.0 Hz, 1H , $-\text{CH-OH}$),), $7.13 - 7.25$ (m, 7H , Ar), $7.31 - 7.43$ (m, 5H , Ar), $7.59 - 7.78$ (m, 7H , Ar) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 36.02 , 58.71 , 76.93 , 124.4 , 125.7 , 125.8 , 125.8 , 125.8 , 126.0 , 126.5 , 127.1 , 127.5 , 127.5 , 127.6 , 127.7 , 127.8 , 127.9 , 128.1 , 128.4 , 129.0 , 132.6 , 132.9 , 132.9 , 133.0 , 136.5 , 137.4 , 138.4 ppm. MS (ESI) $[\text{M} + \text{Na}]^+$ 442.9 . $[\alpha]_{\text{D}}^{25} - 153^\circ$ ($c = 1$, CHCl_3). Elemental analysis calcd. for $\text{C}_{29}\text{H}_{24}\text{OS}$ C, 82.82 , H, 5.75 , found C, 82.60 , H, 5.42 .

(1*R*,2*R*)-2-Phenylsulfanyl-1,2-di-*m*-tolyl-ethanol (4i): Yield 67% , viscous liquid, HPLC (Daicel Chiracel OD, $97:3$ *n*-hexane: isopropanol, flow rate 1 mL/min) t_{R} (*1*R*,2*R**) 19.2 min (91% ee) and t_{R} (*1*S*,2*S**) 28.8 min. IR (film) : 3430 , 3021 , 2918 , 2864 , 2732 , 1940 , 1875 , 1789 , 1606 , 1583 , 1479 , 1438 , 1379 , 1296 , 1237 , 1151 , 1089 , 1025 , 1001 cm^{-1} , ^1H NMR (400 MHz, CDCl_3): δ 2.25 (s, 3H , $-\text{CH}_3$), 2.28 (s, 3H , $-\text{CH}_3$), 3.46 (s, 1H , $-\text{OH}$), 4.37 (d, $J = 8.5$ Hz, 1H , $-\text{CH-S-}$), 4.93 (d, $J = 8.5$ Hz, 1H , $-\text{CH-OH}$), $6.88 - 7.11$ (m, 8H , Ar), $7.21 - 7.24$ (m, 3H , Ar), $7.31 - 7.34$ (m, 2H , Ar) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 21.23 , 21.28 , 63.49 , 76.60 , 123.9 , 125.5 , 127.1 , 127.3 , 127.6 , 127.8 , 127.9 , 128.3 , 128.7 , 129.1 , 132.1 , 134.3 , 137.3 , 137.5 , 139.1 , 140.3 ppm. MS (ESI) $[\text{M} + \text{Na}]^+$, 356.9 . $[\alpha]_{\text{D}}^{25} - 130^\circ$ ($c = 1$, CHCl_3). HRMS (ESI) $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_{22}\text{H}_{22}\text{OS}$: 357.12836 , found 357.12861 .

(1*R*,2*R*)-2-Phenylsulfanyl-1,2-bis(*p*-tolyl)-ethanol (4j): Yield 76% , viscous liquid, HPLC (Daicel Chiracel OD, $97:3$ *n*-hexane: isopropanol, flow rate 1 mL/min) t_{R} (*1*R*,2*R**) 19.8 min (85% ee) and t_{R} (*1*S*,2*S**) 35.6 min., IR (KBr) : 3503 , 3049 , 3020 , 2913 , 2878 , 1908 , 1610 , 1581 , 1511 , 1479 , 1438 , 1326 , 1302 , 1268 , 1225 , 1209 , 1168 , 1108 , 1093 , 1049 , 1022 , cm^{-1} , ^1H NMR (200 MHz, CDCl_3): δ 2.23 (s, 6H , $2\times -\text{CH}_3$), 3.18 (d, $J = 2.5$ Hz, 1H , $-\text{OH}$), 4.29 (d, $J = 8.5$ Hz, 1H , $-\text{CH-S-}$),), 4.85 (d, $J = 8.5$ Hz, 2.5 Hz, 1H , $-\text{CH-OH}$), $6.96 - 7.00$ (m, 8H , Ar), $7.16 - 7.27$ (m, 5H , Ar) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 21.04 , 21.09 , 63.34 , 76.52 , 126.7 , 127.2 , 128.3 , 128.6 , 128.7 , 128.7 , 132.2 , 134.3 , 136.1 , 136.7 , 137.2 , 137.4 ppm. MS (ESI) $[\text{M} + \text{Na}]^+$ 356.9 . $[\alpha]_{\text{D}}^{25} - 132^\circ$ ($c = 1$, CHCl_3). HRMS (ESI) $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_{22}\text{H}_{22}\text{OS}$: 357.12836 , found 357.12889 .

(1*R*,2*R*)-2-Benzylsulfanyl-1,2-bis(*p*-tolyl)-ethanol (4k): Yield 68 %, colorless solid, mp. 50 -52°C, HPLC (Diacel Chiracel OD, 90:10 *n*-hexane: isopropanol, flow rate 1 mL/min) t_R (*IS,2S*) 12.4 min and t_R (*IR,2R*) 22.5 min (93 % ee). IR (KBr) : 3427, 3025, 2919, 2893, 1896, 1643, 1511, 1494, 1452, 1376, 1331, 1312, 1196, 1182, 1107, 1064, 1035 cm^{-1} , ^1H NMR (200 MHz, CDCl_3): δ 2.27 (s, 3H, - CH_3), 2.29 (s, 3H, - CH_3), 2.91 (s, 1H, -OH), 3.46 (d, $J = 13.0$ Hz, - CH_2), 3.60 (d, $J = 13.0$ Hz, 1H, - CH_2), 3.90 (d, $J = 8.0$ Hz, 1H, -CH-S-), 4.82 (d, $J = 8.0$ Hz, -CHOH), 6.99 - 7.01 (m, 8H, Ar), 7.16 - 7.29 (m, 5H, Ar) ppm. ^{13}C NMR (50 MHz, CDCl_3): δ 21.07, 21.09, 35.94, 58.33, 76.85, 126.5, 126.5, 127.0, 128.3, 128.3, 128.5, 128.6, 128.6, 128.9, 129.0, 136.2, 136.8, 137.1, 137.7, 138.1 ppm. MS (ESI) $[\text{M} + \text{Na}]^+$ 371.1. $[\alpha]_D^{25} - 86^\circ$ ($c = 1$, CHCl_3). HRMS (ESI) $[\text{M} + \text{Na}]^+$ cald. for $\text{C}_{23}\text{H}_{24}\text{OS}$: 371.14401, found 371.14392.

(1*R*,2*R*)-1,2-Bis-(*p*-chlorophenyl)-2-phenylsulfanyl-ethanol (4l): Yield 84 %, viscous liquid, 6d reaction time, HPLC (Daicel Chiracel OD, 90:10 *n*-hexane: isopropanol, flow rate 1 mL/min) t_R (*IR,2R*) 15.3 min (92 % ee) and t_R (*IS,2S*) 31.6 min. IR (film) : 3438, 2920, 1643, 1596, 1490, 1438, 1407, 1383, 1306, 1283, 1226, 1187, 1091, 1048, 1025, 1014 cm^{-1} , ^1H NMR (300 MHz, CDCl_3): δ 3.25 (d, $J = 2.0$ Hz, 1H, -OH), 4.14 (d, $J = 8.5$ Hz, 1H, -CH-S-), 4.76 (dd, $J = 8.5$ Hz, 2.0 Hz, 1H, -CH-OH), 6.82 - 6.85 (m, 2H, Ar), 6.95 - 6.99 (m, 2H Ar), 7.02 - 7.09 (m, 4H, Ar), 7.13 - 7.21 (m, 5H, Ar) ppm. ^{13}C NMR (50 MHz, CDCl_3): δ 63.20, 75.91, 127.9, 128.1, 128.2, 128.2, 128.3, 128.5, 128.7, 129.0, 129.6, 129.8, 132.7, 137.3, 138.5 ppm. MS (ESI) $[\text{M} + \text{Na}]^+$ 397.0. $[\alpha]_D^{25} - 97^\circ$ ($c = 1$, CHCl_3). HRMS (ESI) $[\text{M} + \text{Na}]^+$ cald. for $\text{C}_{20}\text{H}_{16}\text{Cl}_2\text{OS}$: 397.01911, found 397.01913.

(1*R*,2*R*)-1,2-Bis-(*p*-chlorophenyl)-2-benzylsulfanyl-ethanol (4m): Yield 67 %, viscous liquid, 6d reaction time, HPLC (Daicel Chiracel OD, 90:10 *n*-hexane: isopropanol, flow rate 1 mL/min) t_R (*IS,2S*) 19.8 min and t_R (*IR,2R*) 34.0 min (93 % ee). IR (film) : 3417, 3084, 3061, 3028, 2915, 2283, 1900, 1778, 1727, 1644, 1596, 1485, 1453, 1410, 1384, 1307, 1283, 1240, 1178, 1090, 1015 cm^{-1} , ^1H NMR (400 MHz, CDCl_3): δ 3.06 (d, $J = 2.5$ Hz, 1H, -OH), 3.49 (d, $J = 13.0$ Hz, 1H, - CH_2), 3.63 (d, $J = 13.0$ Hz, 1H, - CH_2), 3.79 (d, $J = 8.0$ Hz, 1H, -CH-S-), 4.73 (dd, $J_1 = 2.5$ Hz, 8.0 Hz, 1H, -CH-OH) 6.93 - 7.00 (m, 5H Ar), 7.13(m, 5H Ar), 7.25 - 7.29 (m, 3H, Ar) ppm. ^{13}C NMR (50 MHz, CDCl_3): δ 36.03,

57.95, 76.47, 127.2, 127.9, 128.1, 128.4, 128.5, 128.9, 130.0, 133.1, 133.5, 137.1, 137.4, 139.0 ppm. MS (ESI) $[M+Na]^+$ 411.0. $[\alpha]_D^{25} - 162^\circ$ (c 1, CHCl₃). HRMS (ESI) $[M+Na]^+$ calcd. for C₂₁H₁₈Cl₂OS: 411.03476, found 411.03483.

Preparation of single X-ray crystal of [InBr₂.1a.H₂O] Br.THF.4H₂O complex

To a solution of InBr₃ (17.7 mg, 50 μmol) in dry THF (1.5 mL) was added **1a** (16.6 mg, 50 μmol) and stirred the reaction mixture at room temperature for 10 minutes. To the clear solution was added 20 μL of water and heated the reaction mixture at 66°C for 2h. The resulting solution was cooled to room temperature and slow evaporation of the solvent under atmospheric pressure afforded the crystals.

Desulfurization of 4a with nickel boride – preparation of (1S)-1,2-diphenyl ethanol 5⁶

The 1,2-mercapto alcohol **4a** (0.48 mmol) and NiCl₂.6H₂O (3.9 mmol) were dissolved in 20 mL of methanol-THF (3:1) mixture at 0°C. Sodium borohydride (11.7 mmol) was added in small portions for a period of 10 minutes and the mixture was stirred for another 15 minutes at 0°C. The black precipitate was then filtered through a celite column and washed with MeOH-THF mixture. The solvent was removed and crude mixture was purified by column chromatography on silica gel (15 % ethyl acetate: hexane) yielded 70 mg (72 %) of 1, 2-diphenyl ethanol as a colorless solid, mp. 55 – 57°C. HPLC (Daicel Chiracel OD, 95:5 *n*-hexane: isopropanol, flow rate 1 mL/min) t_R (*1S*) 15.3 min and t_R (*1R*) 18.4 min (91 % ee). IR (KBr): 3340, 3083, 3062, 3024, 2913, 2861, 1949, 1630, 1601, 1493, 1453, 1394, 1315, 1268, 1198, 1150, 1071, 1021. NMR (400 MHz, CDCl₃): δ 2.02 (d, J= 3.0 Hz, 1H, -OH), 2.99 – 3.10 (m, 2H, -CH₂), 4.90 – 4.94 (m, 1H, -CH-OH), 7.21 – 7.39 (m, 10H Ar) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 46.2, 75.4, 126.0, 126.7, 127.7, 128.5, 128.6, 129.6, 138.1, 143.9.

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