Supplementary Material (ESI) for Green Chemistry

Highly regioselective ring-opening of epoxides with thiophenols in ionic liquids without the use of any catalyst

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SUPPORTING INFORMATION

Contents:

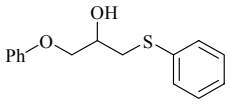
1. General Experimental Details

Chemicals and solvents were either purchased or purified by standard techniques. Melting points were recorded on Digital Melting Point Apparatus WRS-1B and uncorrected. IR spectra was recorded on a AVATAR 370 FI-Infrared Spectrophotometer. Mass spectra were measured with Thermo Finnigan LCQ-Advantage. ^{1}H NMR and ^{13}C NMR spectra were recorded on a VARIAN Mercury plus-400 instrument using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts are given in δ relative to TMS, the coupling constants *J* are given in Hz. Elemental analysis was determined on a Carlo-Erba 1108 instrument. Optical rotations were measured with Autopol IV RUDOLPH RESEARCH ANALYTICAL (U.S.A.) automatic polarimeter in chloroform solution. Enantiomertic excesses (ee) were determined with a HPLC apparatus fitted with a Chiralcel OJ-H (Daicel, Germany) chiral column.

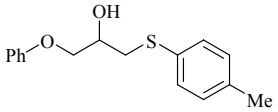
General procedure for thiolysis reaction of epoxides in ionic liquid: To a mixture of epoxides (2 mmol) and thiophenols (2 mmol), [Emim]BF_4 (1 mL) was added. The mixture was stirred at 50 ^{o}C for 10 min. After completion of the reaction, as indicated by TLC, the reaction mixture was extracted with diethyl ether (3×10 mL). The combined ether extracts were concentrated in vacuo and the crude product was obtained. The corresponding purified products were obtained by flash column chormatography. The remainder of the ionic liquid was reused in subsequent runs.

2. Experimental characterisation data for compounds

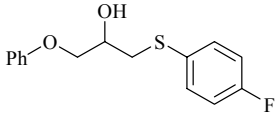
Compounds **1a, 1b, 1i, 2i, 1l, 1o, 1u-v** are known, compounds **1c-e, 1g-h, 1j, 2j, 1m-n, 1p-t** are new and described below.



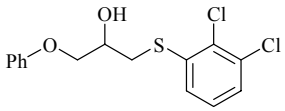
1a (Lit.[1]) : R_f = 0.35 (petroleum ether / EtOAc = 6 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.40 (d, *J* = 7.6 Hz, 2 H, ArH), 7.30 - 7.25 (m, 4 H), 7.20 (t, *J* = 7.2 Hz, 1 H, ArH), 6.96 (t, *J* = 7.2 Hz, 1 H, ArH), 6.88 (d, *J* = 8.4 Hz, 2 H, ArH), 4.14 - 4.02 (m, 3 H), 3.25 (dd, *J* = 13.6, 5.4 Hz, 1 H), 3.15 (dd, *J* = 13.6, 6.6 Hz, 1 H), 2.73 (br s, 1 H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 158.3, 135.0, 129.8, 129.5, 129.1, 126.6, 121.2, 114.5, 70.0, 68.5, 37.5. IR ν_{max} (neat): 3448, 3032, 2930, 2862, 1582, 1455, 1242 cm^{-1}. m / z (EI) 260 (M^+, 100), 167 (63), 109 (6).



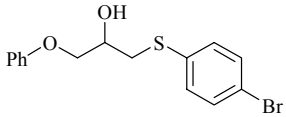
1b (Lit.[2]) : R_f = 0.35 (petroleum ether / EtOAc = 6 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.32 - 7.24 (m, 4 H, ArH), 7.08 (d, *J* = 8.4 Hz, 2 H, ArH), 6.95 (t, *J* = 7.2 Hz, 1 H, ArH), 6.86 (t, *J* = 8.4 Hz, 2 H, ArH), 4.06 – 3.99 (m, 3 H), 3.19 (dd, *J* = 14.0, 5.6 Hz, 1 H), 3.09 (dd, *J* = 14.0, 6.8 Hz, 1 H), 2.82 (br s, 1 H, OH), 2.30 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 158.6, 137.2, 131.5, 130.9, 130.2, 129.7, 121.4, 114.8, 70.3, 68.8, 38.6, 21.3. IR ν_{max} (neat): 3438, 3038, 2922, 2871, 1599, 1494, 1456, 1244, 1079, 1042 cm^{-1}. m / z (EI) 274 (M^+, 100), 257 (34), 181 (38), 163 (39).



1c: R_f = 0.4 (petroleum ether / EtOAc = 6 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39 (t, *J* = 8.4 Hz, 2 H, ArH), 7.27 (t, *J* = 8.4 Hz, 2 H, ArH), 7.00 – 6.94 (m, 3 H, ArH), 6.86 (d, *J* = 8.4 Hz, 2 H, ArH), 4.11 – 3.97 (m, 3 H), 3.18 (dd, *J* = 14.0, 5.2 Hz, 1 H), 3.07 (dd, *J* = 14.0, 6.4 Hz, 1 H), 2.85 (br s, 1 H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.0 (d, $^1J_{CF}$ = 246.2 Hz), 158.2, 132.7 (d, $^3J_{CF}$ = 8.4 Hz), 129.9, 129.5, 121.2, 116.2 (d, $^2J_{CF}$ = 22.0 Hz), 114.4, 69.8, 68.4, 38.7. IR ν_{max} (neat): 3424, 3064, 3040, 2927, 2874, 1589, 1492, 1397, 1243 cm^{-1}. m / z (EI) 278 (M^+, 100), 185 (54), 167 (37), 141 (54), 133 (55), 127 (15). Found: C, 64.86; H, 5.50. Anal. Calcd for $C_{15}H_{15}FO_2S$: C, 64.73; H, 5.43.

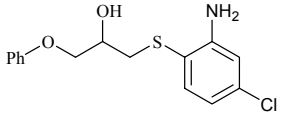


1d: R_f = 0.4 (petroleum ether / EtOAc = 6 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.29 – 7.24 (m, 4 H, ArH), 7.09 (t, *J* = 8.0 Hz, 1 H, ArH), 6.97 (t, *J* = 7.2 Hz, 1 H, ArH), 6.88 (d, *J* = 8.0 Hz, 2 H, ArH), 4.23 – 4.01 (m, 3 H), 3.28 (dd, *J* = 14.0, 5.6 Hz, 1 H), 3.17 (dd, *J* = 14.0, 6.8 Hz, 1 H), 2.95 (br s, 1 H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 158.0, 137.5, 133.6, 131.3, 129.5, 127.5, 127.4, 126.2, 121.3, 114.4, 69.8, 68.4, 36.1. IR ν_{max} (neat): 3417, 3062, 2926, 1599, 1588, 1496, 1435, 1399, 1243 cm^{-1}. m / z (EI) 332 ($[M+4]^+$, 6), 330 ($[M+2]^+$, 32), 328 (M^+, 53), 290 (100), 273 (81), 235 (58), 217 (53). Anal. Calcd for $C_{15}H_{14}C_{l2}O_2S$: C, 54.72; H, 4.29. Found: C, 54.79; H, 4.17.

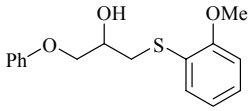


1e: R_f = 0.4 (petroleum ether / EtOAc = 6 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.33 (d, *J* = 8.0 Hz, 2 H, ArH), 7.27 – 7.20 (m, 4 H, ArH), 6.95 (t, *J* = 7.2 Hz, 1 H, ArH), 6.84 (d, *J* = 8.0 Hz, 2 H, ArH), 4.08 – 3.98 (m, 3 H), 3.19 (dd, *J* = 13.6, 5.6 Hz, 1 H), 3.12 (br s, 1 H, OH), 3.09 (dd, *J* = 13.6, 6.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 158.0, 134.4, 131.9, 130.9, 129.4, 121.1, 120.2, 114.3, 69.7, 68.4, 37.2. IR ν_{max} (neat): 3418,

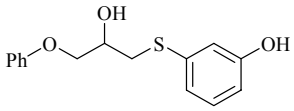
3061, 2925, 1599, 1496, 1474, 1243, 1091, 1007 cm^{-1}. m / z (EI) 340 ($[M+2]^+$, 88), 340 (M^+, 100), 247 (33), 245 (36), 229 (23), 227 (18), 33 (36). Found: C, 53.19; H, 4.50. Anal. Calcd for $C_{15}H_{15}BrO_2S$: C, 53.11; H, 4.46.



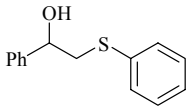
1f: R_f = 0.3 (petroleum ether / EtOAc = 4 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.30 – 7.23 (m, 3 H, ArH), 6.94 (t, *J* = 7.2 Hz, 1 H, ArH), 6.84 (d, *J* = 8.0 Hz, 1 H, ArH), 6.66 (s, 1 H, ArH), 6.62 (d, *J* = 8.0 Hz, 2 H, ArH), 4.02 (br s, 2 H, NH_2), 3.98 – 3.89 (m, 3 H), 2.97 (dd, *J* = 13.2, 4.0 Hz, 1 H), 2.85 (dd, *J* = 13.2, 6.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 158.1, 149.2, 137.2, 135.7, 129.4, 121.1, 118.7, 115.2, 114.7, 114.4, 70.1, 68.6, 38.6. IR ν_{max} (neat): 3454, 3356, 3061, 2925, 1599, 1496, 1477, 1415, 1243, 1092, 1042, 906 cm^{-1}. m / z (EI) 311 ($[M+2]^+$, 38), 309 (M^+, 100), 198 (12), 158 (20), 133 (18). Found: C, 58.07; H, 5.30; N, 4.46. Anal. Calcd for $C_{15}H_{16}ClNO_2S$: C, 58.15; H, 5.21; N, 4.52.



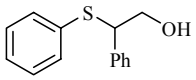
1g: R_f = 0.35 (petroleum ether / EtOAc = 6 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.36 (d, *J* = 8.0 Hz, 1 H, ArH), 7.23 - 7.14 (m, 3 H, ArH), 6.92 - 6.77 (m, 5 H, ArH), 4.09 - 3.93 (m, 3 H), 3.78 (s, 3 H), 3.43 (br s, 1 H, OH), 3.16 (dd, *J* = 13.6, 4.8 Hz, 1 H), 3.07 (dd, *J* = 13.6, 7.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 158.1, 157.7, 131.3, 129.1, 128.1, 122.3, 120.9, 120.7, 114.2, 110.5, 69.8, 68.2, 55.4, 36.4. IR ν_{max} (neat): 3450, 3062, 2933, 2836, 1599, 1477, 1244 cm^{-1}. m / z (EI) 290 (M^+, 100), 273 (14), 197 (20), 153 (23). Found: C, 66.01; H, 6.10. Anal. Calcd for $C_{16}H_{18}O_3S$: C, 66.18; H, 6.25.



1h: R_f = 0.3 (petroleum ether / EtOAc = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.30 – 7.26 (m, 2 H, ArH), 7.13 (t, *J* = 8.0 Hz, 1 H, ArH), 6.99 – 6.88 (m, 5 H, ArH), 6.68 (ddd, *J* = 8.4, 2.4, 0.8 Hz, 1 H, ArH), 5.98 (br s, 1 H, ArOH), 4.15 – 4.02 (m, 3 H), 3.24 (dd, *J* = 14.0, 5.6 Hz, 1 H), 2.85 (dd, *J* = 14.0, 7.2 Hz, 1 H), 2.86 (br s, 1 H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 158.3, 156.3, 136.5, 130.1, 129.5, 121.5, 121.3, 116.1, 114.5, 113.8, 69.9, 68.6, 37.1. IR ν_{max} (neat): 3355, 3063, 2926, 1587, 1496, 1431, 1244 cm^{-1}. m / z (EI) 276 (M^+, 100), 259 (52), 183 (46). Anal. Calcd for $C_{15}H_{16}O_3S$: C, 65.19; H, 5.84. Found: C, 65.31; H, 5.75.

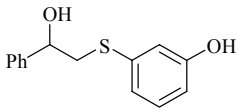


1i (Lit.[3]) : R_f = 0.35 (petroleum ether / EtOAc = 6 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.37 – 7.35 (m, 2 H, ArH), 7.32 – 7.23 (m, 7 H, ArH), 7.21 – 7.17 (m, 1 H, ArH), 4.66 (dd, *J* = 3.6 Hz, 1 H, C*H*OH), 3.25 (dd, *J* = 13.6, 3.6 Hz, 1 H), 3.13 (br s, 1 H, OH), 3.05 (dd, *J* = 13.6, 9.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 142.4, 135.3, 130.2, 129.3, 128.7, 128.1, 126.8, 126.1, 71.9, 43.9. IR ν_{max} (neat): 3425, 3060, 3030, 2922, 1583, 1480, 1439, 1056 cm^{-1}. m / z (EI) 230 (M^+, 57), 213 (100), 196 (16), 124 (26).

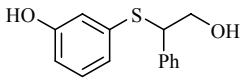


2i (Lit.[3]) : R_f = 0.3 (petroleum ether / EtOAc = 6 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.37 – 7.29 (m, 2 H, ArH), 7.28 – 7.20 (m, 8 H, ArH), 4.27 (t, *J* = 6.8 Hz, 1 H), 3.87 (dd, *J* = 11.2, 5.6 Hz, 1 H), 3.82 (dd, *J* = 11.2, 6.8 Hz, 1 H), 2.41 (br s, 1 H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 138.8, 133.6, 132.3, 128.8, 128.5, 127.9,

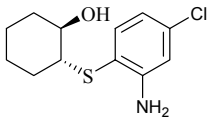
127.6, 127.3, 67.2, 55.6. IR ν_{max} (neat): 3405, 3059, 3028, 2927, 2872, 1583, 1480, 1438, 1055 cm^{-1}. m / z (EI) 230 (M^+, 100), 213 (39), 199 (48), 121 (36).



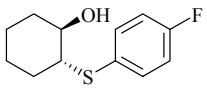
1j: R_f = 0.3 (petroleum ether / EtOAc = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.34 – 7.25 (m, 5 H, ArH), 7.17 – 7.10 (m, 1 H, ArH), 7.01 – 6.93 (m, 1 H, ArH), 6.87 (t, *J* = 2.0 Hz, 1 H, ArH), 6.69 – 6.64 (m, 1 H, ArH), 5.89 (br s, 1 H, ArOH), 4.66 (dd, *J* = 9.6, 3.6 Hz, 1 H, C*H*OH), 3.46 (dd, *J* = 13.6, 3.6 Hz, 1 H), 3.13 (br s, 1 H, OH), 3.05 (dd, *J* = 13.6, 9.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.0, 141.7, 136.1, 130.1, 128.5, 128.0, 125.8, 122.0, 116.6, 113.9, 71.8, 43.3. IR ν_{max} (neat): 3355, 3062, 2922, 1583, 1476, 1493, 1250 cm^{-1}. m / z (EI) 246 (M^+, 100), 229 (92), 140 (12). Found: C, 68.34; H, 5.81. Anal. Calcd for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.73.



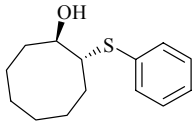
2j: R_f = 0.25 (petroleum ether / EtOAc = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.32 – 7.24 (m, 5 H, ArH), 7.07 (t, *J* = 7.6 Hz, 1 H, ArH), 6.86 – 6.82 (m, 2 H, ArH), 6.69 – 6.66 (m, 1 H, ArH), 5.98 (br s, 1 H, ArOH), 4.30 (t, *J* = 6.8 Hz, 1 H), 3.92 (dd, *J* = 11.6, 6.8 Hz, 1 H), 3.87 (dd, *J* = 11.6, 7.2 Hz, 1 H), 2.64 (br s, 1 H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.4, 141.5, 135.8, 130.3, 128.5, 128.0, 124.2, 123.1, 115.2, 113.4, 68.3, 50.1. IR ν_{max} (neat): 3345, 3061, 3028, 2928, 1584, 1440, 1251, 1053 cm^{-1}. m / z (EI) 246 (M^+, 100), 229 (70), 215 (79), 121 (42), 91 (24). Found: C, 68.19; H, 5.82. Anal. Calcd for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.73.



1k: mp 103.1 – 103.4 °C; R_f = 0.35 (petroleum ether / EtOAc = 4 : 1);^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.29 (d, *J* = 8.0 Hz, 1 H, ArH), 6.74 – 6.65 (m, 2 H, ArH), 4.03 (br s, 2 H, NH_2), 3.31 – 3.25 (m, 1 H), 2.64 – 2.58 (m, 1 H), 2.04 – 1.88 (m, 2 H), 1.66 – 1.65 (m, 2 H), 1.36 – 1.19 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 150.2, 139.0, 136.0, 118.6, 114.8, 113.6, 72.3, 56.6, 34.3, 32.7, 26.0, 24.2. MS (EI): m / z =259 ([M + 2]$^+$, 36), 257 (M^+, 100), 239 (6), 196 (15). IR ν_{max} (KBr): 3370, 3198, 2927, 2854, 1580, 1560, 1475, 1443, 1412, 1092, 1061, 962, 863, 794 cm^{-1}. Found: C, 56.04; H, 6.34; N, 5.49. Anal. Calcd for $C_{12}H_{16}ClNOS$: C, 55.91; H, 6.26; N, 5.43.

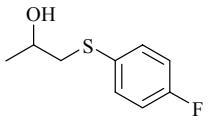


1l (Lit.[4]) : R_f = 0.4 (petroleum ether / EtOAc = 6 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.49 – 7.44 (m, 2 H, ArH), 7.04 – 6.99 (m, 2 H, ArH), 3.31 - 3.26 (m, 1 H, C*H*OH), 3.03 (br s, 1 H, OH), 2.71 – 2.65 (m, 1 H), 2.16 – 2.04 (m, 2 H), 1.73 – 1.64 (m, 2 H), 1.38 – 1.53 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 163.0 (d, $^1J_{CF}$ = 246.4 Hz), 136.8 (d, $^3J_{CF}$ = 8.3 Hz),, 127.3, 116.2 (d, $^2J_{CF}$ = 22.0 Hz),, 71.9, 56.9, 34.0, 32.6, 26.3, 24.5. m / z (EI) 226 (M^+, 100), 209 (85). IR ν_{max} (neat): 3440, 3066, 2934, 2858, 1589, 1550, 1449, 1224, 1068 cm^{-1}.

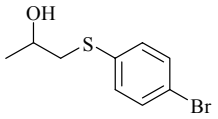


1m (Lit.[5]): R_f = 0.25 (petroleum ether / EtOAc = 6 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39 (d, *J* = 7.6 Hz, 2 H, ArH), 7.30 (d, *J* = 7.6 Hz, 2 H, ArH), 7.23 (d, *J* = 6.8 Hz, 1 H, ArH), 3.85 (br s, 1 H, OH), 3.49 – 3.34 (m, 1 H, C*H*OH), 2.52 - 2.43 (m, 1 H), 1.96 - 1.26 (m, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 135.3, 131.8,

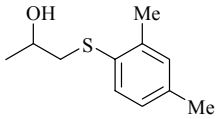
128.8, 126.7, 71.4, 48.0, 33.8, 32.5, 29.7, 27.6, 25.3, 22.7. IR ν_{max} (neat): 3428, 3046, 2956, 2830, 1589, 1550, 1449, 1224, 1068 cm^{-1}. m / z (CI) 237 ($[M+1]^+$, 4), 219 (45), 203 (37), 127 (30), 109 (100), 89 (17).



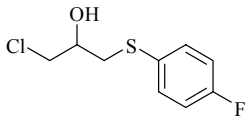
1n: R_f = 0.4 (petroleum ether / EtOAc = 6 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.41 – 7.38 (m, 2 H, ArH), 7.00 (t, *J* = 8.4 Hz, 2 H, ArH), 3.85 – 3.77 (m, 1 H, C*H*OH), 3.04 (dd, *J* = 13.6, 3.6 Hz, 1 H), 2.81 (dd, *J* = 13.6, 8.4 Hz, 1 H), 2.67 (br s, 1 H, OH), 1.25 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.0 (d, $^1J_{CF}$ = 245.7 Hz), 133.0 (d, $^3J_{CF}$ = 8.3 Hz), 130.0, 116.1 (d, $^2J_{CF}$ = 21.2 Hz), 65.4, 44.7, 21.8. IR ν_{max} (neat): 3404, 2971, 2926, 1590, 1491, 1456, 1228, 1157, 1090 cm^{-1}. m / z (EI) 186 (M^+, 100), 169 (77), 141 (13). Anal. Calcd for $C_9H_{11}FOS$: C, 58.04; H, 5.95. Found: C, 58.12; H, 5.86.



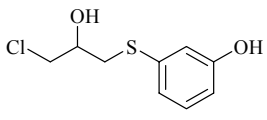
1o (Lit.[6]) : R_f = 0.4 (petroleum ether / EtOAc = 6 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.42 – 7.38 (m, 2 H), 7.25 – 7.22 (m, 2 H), 3.89 – 3.81 (m, 1 H), 3.06 (dd, *J* = 14.0, 3.6 Hz, 1 H), 2.85 (dd, *J* = 14.0, 8.0 Hz, 1 H), 2.55 (br s, 1 H, OH), 1.26 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 134.6, 132.0, 131.3, 120.3, 65.5, 43.3, 22.0. IR ν_{max} (neat): 3395, 3077, 2970, 2925, 1474, 1386, 1091, 1007 cm^{-1}. m / z (EI) 248 ($[M+2]^+$, 85), 246 (M^+, 100), 231 (43), 229 (48), 150 (22).



1p: R_f = 0.4 (petroleum ether / EtOAc = 6 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.27 – 7.25 (m, 1 H, ArH), 7.03 – 6.95 (m, 2 H, ArH), 3.84 – 3.77 (m, 1 H, C*H*OH), 3.01 (dd, *J* = 13.6, 4.0 Hz, 1 H), 2.77 (dd, *J* = 13.6, 8.8 Hz, 1 H), 2.40 (s, 1 H), 2.29 (s, 3 H), 1.25 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 138.8, 136.8, 131.2, 130.7, 130.3, 127.2, 65.4, 43.4, 21.8, 20.8, 20.5. IR ν_{max} (neat): 3397, 2969, 2923, 2856, 1578, 1453, 1057 cm^{-1}. m / z (EI) 196 (M^+, 100), 179 (60), 151 (47), 137 (32), 105 (33). Found: C, 67.26; H, 8.30. Anal. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.22.

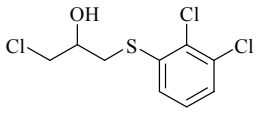


1q: R_f = 0.4 (petroleum ether / EtOAc = 6 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.41 (t, *J* = 6.4 Hz, 2 H, ArH), 7.02 (t, *J* = 8.4 Hz, 2 H, ArH), 3.90 – 3.87 (m, 1 H, C*H*OH), 3.70 - 3.63 (m, 2 H, CH_2Cl), 3.11 (dd, *J* = 14.0, 5.6 Hz, 1 H), 3.02 (dd, *J* = 14.0, 7.2 Hz, 1 H), 2.77 (br s, 1 H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.1 (d, $^1J_{CF}$ = 246.5 Hz), 133.0 (d, $^3J_{CF}$ = 8.3 Hz), 129.4, 116.3 (d, $^2J_{CF}$ = 22.0 Hz), 69.3, 47.8, 39.3. IR ν_{max} (neat): 3367, 2935, 2912, 1555, 1457, 1408, 1235 cm^{-1}. m / z (EI) 222 ($[M+2]^+$, 20), 220 (M^+, 57), 205 (5), 203 (18), 141 (72), 84 (100). Found: C, 49.22; H, 4.34. Anal. Calcd for $C_9H_{10}ClFOS$: C, 48.98; H, 4.57.

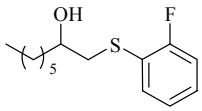


1r: R_f = 0.3 (petroleum ether / EtOAc = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.14 (t, *J* = 7.6 Hz, 1 H, ArH), 6.92 – 6.87 (m, 2 H, ArH), 6.70 (dd, *J* = 8.4, 2.4 Hz, 1 H, ArH), 6.62 (br s, 1 H, ArOH), 3.99 – 3.94 (m, 1

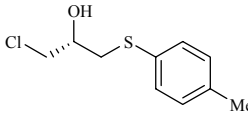
H, C*H*OH), 3.69 (dd, *J* =11.2, 4.4 Hz, 1 H), 3.65 (dd, *J* = 11.2, 5.2 Hz, 1 H), 3.15 (br s, 1 H, OH), 3.13 (dd, *J* = 14.4, 5.6 Hz, 1 H), 3.11 (dd, *J* = 14.4, 7.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.1, 135.8, 130.2, 121.7, 116.2, 114.1, 69.5, 47.8, 37.5. IR ν_{max} (neat): 3362, 2955, 2924, 1583, 1476, 1437, 1042, 775, 686 cm^{-1}. m / z (EI) 220 ([M + 2]$^+$, 46), 218 (M$^+$, 100), 184 (72), 183 (28), 182 (22), 167 (30). Found: C, 49.35; H, 5.18. Anal. Calcd for $C_9H_{11}ClO_2S$: C, 49.43; H, 5.07.



1s: R_f = 0.4 (petroleum ether / EtOAc = 6 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.32 – 7.35 (m, 2 H, ArH), 7.21 – 7.10 (m, 1 H, ArH), 4.04 – 3.98 (m, 1 H, C*H*OH), 3.72 (d, *J* = 4.8 Hz, 2 H), 3.22 (dd, *J* = 14.0, 5.6 Hz, 1 H), 3.12 (dd, *J* = 14.0, 6.8 Hz, 1 H), 2.83 (br s, 1 H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 137.0, 133.7, 131.7, 127.9, 127.5, 126.6, 69.3, 48.0, 36.8. IR ν_{max} (neat): 3388, 2955, 2923, 1565, 1435, 1399 cm^{-1}. m / z (EI) 276 ([M+6]$^+$, 5), 274 ([M+4]$^+$, 33), 272 ([M+2]$^+$, 94), 270 (M$^+$, 100), 255 (42), 253 (48), 193 (46), 191 (74), 142 (31). Found: C, 39.86; H, 3.26. Anal. Calcd for $C_9H_9Cl_3OS$: C, 39.80; H, 3.34.

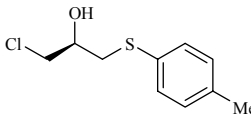


1t: R_f = 0.4 (petroleum ether / EtOAc = 6 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.44 (t, *J* = 7.6 Hz, 1 H, ArH), 7.26 – 7.23 (m, 1 H, ArH), 7.11 – 7.05 (m, 2 H, ArH), 3.61 – 3.60 (m, 1 H, C*H*OH), 3.12 (dd, *J* = 13.2, 2.8 Hz, 1 H), 2.80 (dd, *J* = 13.2, 8.8 Hz, 1 H), 2.48 (br s, 1 H, OH), 1.52 – 1.26 (m, 10 H), 0.87 (t, *J* = 6.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 161.9 (d, $^1J_{CF}$ = 244.2 Hz, *C*F), 133.3, 129.1 (d, $^3J_{CF}$ = 7.5 Hz, *C*H_{Ar}), 124.6 (d, $^3J_{CF}$ = 3.8 Hz, *C*H_{Ar}), 121.9 (d, $^2J_{CF}$ = 16.5 Hz, *C*SCH_2), 115.8 (d, $^2J_{CF}$ = 22.8 Hz, *C*H_{Ar}), 69.5, 41.9, 35.4, 31.7, 29.2, 25.6, 22.5, 14.0. IR ν_{max} (neat): 3392, 2935, 2847, 1587, 1461, 1240 cm^{-1}. m / z (EI) 256 (M$^+$, 100), 239 (76), 142 (64). Found: C, 65.45; H, 8.31. Anal. Calcd for $C_{14}H_{21}FOS$: C, 65.59; H, 8.26.



(R)

1u (Lit.[7]): R_f = 0.4 (petroleum ether / EtOAc = 6 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.30 (d, 2 H, ArH), 7.11 (d, 2 H, ArH), 3.89 -3.87 (m, 1 H, C*H*OH), 3.68 – 3.61 (m, 2 H), 3.10 (dd, *J* = 13.6, 4.8 Hz, 1 H), 3.01 (dd, *J* = 13.6, 7.2 Hz, 1 H), 2.80 (br s, 1 H, OH), 2.32 (s, 3 H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 137.2, 130.8, 130.7, 129.9, 69.4, 47.9, 38.8, 21.0. IR ν_{max} (neat): 3422, 3020, 2954, 2921, 1493, 1425, 1043 cm^{-1}. m / z (EI) 218 ([M+2]$^+$, 17), 272 (M$^+$, 47), 201 (33), 199 (100), 137 (39), 89 (52). $[\alpha]_D^{20}$ +26.4 (*c* 0.99 in $CHCl_3$), R; {lit.[7] $[\alpha]_D^{22}$ +27.8 (*c* 0.99 in $CHCl_3$), R, 99% ee}. HPLC analysis using a Chiracel OJ-H column [*iso*-PrOH/hexane: 1/99; flow rate: 0.8 mL/min; detector: 254 nm] showed it to 97% ee [t_R(S) 39.50 min and t_R(R) 41.63 min].



(S)

1v (Lit.[7]): R_f = 0.4 (petroleum ether / EtOAc = 6 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.30 (d, 2 H, ArH), 7.11 (d, 2 H, ArH), 3.89 -3.87 (m, 1 H, C*H*OH), 3.68 – 3.61 (m, 2 H), 3.10 (dd, *J* = 13.6, 4.8 Hz, 1 H), 3.01 (dd, *J* = 13.6, 7.2 Hz, 1 H), 2.80 (br s, 1 H, OH), 2.32 (s, 3 H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 137.2, 130.8, 130.7, 129.9, 69.4, 47.9, 38.8, 21.0. IR ν_{max} (neat): 3422, 3020, 2954, 2921, 1493, 1425, 1043 cm^{-1}. m / z (EI) 218 ([M+2]$^+$, 17), 272 (M$^+$, 47), 201 (33), 199 (100), 137 (39), 89 (52). $[\alpha]_D^{20}$ -25.9 (*c* 0.99 in $CHCl_3$), R. HPLC analysis using a Chiralcel OJ-H column [*iso*-PrOH/hexane: 1/99; flow rate: 0.8 mL/min; detector: 254

nm] showed it to 95% ee [t_S(S) 39.56 min and t_S(R) 42.56 min].

3. References

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