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Supporting Information

Asymmetric Brønsted Acid-Catalyzed Friedel–Crafts Reaction of Indoles with Cyclic N-Sulfimines

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General Information. Organic solvents were distilled prior to use. Organic solutions were concentrated under reduced pressure using a rotary evaporator. Chromatographic purification of products was accomplished using forced-flow chromatography on ICN 60 32-64 mesh silica gel 63. Thin-layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica gel 60-F plates. Developed chromatograms were visualized by fluorescence quenching and with anisaldehyde stain. ¹H and ¹³C NMR spectra were recorded (400 MHz for ¹H and 100 MHz for ¹³C), and were internally referenced to residual protio solvent signals. Data for ¹H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz) and integration. Data for ¹³C NMR are reported in terms of chemical shift. IR spectra were recorded on an FT IR spectrometer and are reported in wave numbers. Optical rotations were taken on a digital polarimeter. High-resolution mass spectroscopy (HRMS) was performed by electron impact (EI). Enantiomeric excesses were determined using an HPLC instrument with Chiralpak columns as noted.

General Procedure for Friedel–Crafts Reaction of Indoles with Cyclic N-Sulfimines.

To a solution of cyclic *N*-sulfimine **2** (0.1 mmol) in toluene (0.75 mL) was added catalyst **3b** (0.01 mmol). The solution was stirred at -40 °C for 10 min, and then indole **1** (0.15 mmol) was added in one portion. The reaction mixture was stirred at -40 °C until cyclic *N*-sulfimine **2** was complete consumed, as determined by TLC. Then, the resulting mixture was diluted with water and extracted with CH₂Cl₂. The combined organic layer was washed with brine, dried over anhydrous MgSO₄, and concentrated in vacuo. The crude residue was purified by flash column chromatography with EtOAc/hexanes as eluent to afford desired product **4**. The enantiomeric excess was determined using HPLC analysis.



(*S*)-4-(1-Methy-1*H*-indol-3-yl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4a). 29 mg, yield 93%, White solid; m.p. 84-86 °C; $[\alpha]_D^{22} = +64.9$ (*c* = 0.44, CHCl₃); 91% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.40–7.30 (m, 2H), 7.29–7.24 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.17 (s, 1H), 7.12–7.02 (m, 4H), 6.23 (d, *J* = 7.8 Hz, 1H), 4.73 (d, *J* = 7.8 Hz, 1H), 3.82 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 150.15, 136.46,

128.56, 128.35, 127.41, 124.31, 124.19, 121.63, 120.98, 119.16, 117.84, 117.69, 109.69, 108.99, 54.05, 31.98; IR (neat) 3269, 2921, 2851, 1717, 1614, 1550, 1478, 1450, 1412, 1193, 1164, 1098, 1011 cm⁻¹; HRMS (EI) m/z calcd for $[M]^+ C_{16}H_{14}N_2O_3S$: 314.0725 Found: 314.0754; Chiralpak IA column and IA guard column (15% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 17.8$ min and *minor*-isomer $t_r = 11.0$ min.



(*S*)-4-(1-Benzyl-1*H*-indol-3-yl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4b). 30 mg, yield 76%, White solid; m.p. 85-87 °C; $[\alpha]_D^{23} = +28.5$ (*c* = 0.38, CHCl₃); 90% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.37–7.26 (m, 5H), 7.25–7.18 (m, 3H), 7.17–7.12 (m, 2H), 7.10 (d, *J* = 8.2 Hz, 1H), 7.08–7.03 (m, 3H), 6.23 (d, *J* = 8.5 Hz, 1H), 5.32 (s, 2H), 4.77 (d, *J* = 8.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 151.25, 137.20, 136.60, 129.67, 129.00, 128.77, 128.38, 128.06, 126.96, 125.58, 125.29, 122.94, 121.93, 120.50, 119.07, 118.82, 111.41, 110.58, 55.15, 50.3; IR (neat) 3271, 2922, 2852, 1613, 1551, 1450, 1413, 1354, 1281, 1192, 1164, 1097, 1013 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₂₂H₁₈N₂O₃S: 390.1038 Found: 390.1025; Chiralpak IA column and IA guard column (15% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer *t*_r = 18.1 min and *minor*-isomer *t*_r = 22.5 min.



(*S*)-4-(1-Allyl-1*H*-indol-3-yl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4c). 29 mg, yield 85%, White solid; m.p. 115-117 °C; $[\alpha]_D^{21} = +50.4$ (*c* = 0.34, CHCl₃); 92% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, *J* = 8.3 Hz, 1H), 7.32 (ddd, *J* = 9.0, 4.8, 0.7 Hz, 1H), 7.26–7.20 (m, 3H), 7.10 (d, *J* = 8.2 Hz, 1H), 7.08–7.02 (m, 3H), 6.23 (d, *J* = 8.5 Hz, 1H), 6.07–5.95 (m, 1H), 5.26 (dd, *J* = 10.2, 1.2 Hz, 1H), 5.14 (ddd, *J* = 17.1, 2.7, 1.6 Hz, 1H), 4.79–4.70 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.23, 136.98, 132.79, 129.65, 128.41(two peaks overlapping), 125.51, 125.28, 122.77, 121.98, 120.38, 119.02,

118.80, 118.12, 111.15, 110.46, 55.16, 49.03; IR (neat) 3262, 2921, 2851, 1614, 1579, 1551, 1467, 1450, 1412, 1356, 1262, 1193, 1164, 1097, 1011 cm⁻¹; HRMS (EI) m/z calcd for $[M]^+ C_{18}H_{16}N_2O_3S$: 340.0882 Found: 340.0896; Chiralpak IA column and IA guard column (10% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 20.1$ min and *minor*-isomer $t_r = 26.8$ min.



(*S*)-4-(1-Benzyl-5-methoxy-1*H*-indol-3-yl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4d). 40 mg, yield 95%, White solid; m.p. 181-183 °C; $[\alpha]_D^{21} = +58.8$ (*c* = 0.43, CHCl₃); 94% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.36–7.25 (m, 4H), 7.18 (d, *J* = 8.9 Hz, 1H), 7.16 (s, 1H), 7.14–7.05 (m, 5H), 6.84 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.66 (d, *J* = 2.3 Hz, 1H), 6.21 (d, *J* = 8.2 Hz, 1H), 5.26 (s, 2H), 4.81 (d, *J* = 8.3 Hz, 1H), 3.68 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 154.54, 151.30, 136.72, 132.25, 129.65, 129.13, 128.98, 128.48, 128.01, 126.86, 126.25, 125.30, 121.88, 118.79, 113.09, 111.42, 110.98, 100.67, 55.77, 55.09, 50.54; IR (neat) 3260, 2919, 1622, 1580, 1485, 1449, 1363, 1280, 1210, 1165, 1098, 1037cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₂₃H₂₀N₂O₄S: 420.1144 Found: 420.1156; Chiralpak IA column and IA guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer *t*_r = 20.2 min and *minor*-isomer *t*_r = 24.6 min.



(*S*)-4-(5-Benzoyl-1-benzyl-1*H*-indol-3-yl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4e). 36 mg, yield 73%, White solid; m.p. 130-132 °C; $[\alpha]_D^{20} = +45.2$ (*c* = 0.34, CHCl₃); 97% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.39–7.26 (m, 9H), 7.19 (d, *J* = 9.0 Hz, 1H), 7.17 (s, 1H), 7.14–7.03 (m, 5H), 6.92 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.71 (d, *J* = 2.3 Hz, 1H), 6.18 (d, *J* = 8.5 Hz, 1H), 5.26 (s, 2H), 4.92 (s, 2H), 4.71 (d, *J* = 8.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 153.61, 151.26, 137.13, 136.67, 132.44, 129.68, 129.22, 128.99, 128.61, 128.42, 128.04, 127.96, 127.63, 126.90, 126.06, 125.31, 121.81, 118.80, 113.79, 111.45, 110.85, 102.27, 70.70, 55.16, 50.53; IR (neat) 3282, 2922, 2864, 1620, 1578, 1482, 1450, 1417, 1357,

1262, 1189, 1163, 1096, 1024 cm⁻¹; HRMS (EI) m/z calcd for $[M]^+ C_{29}H_{24}N_2O_4S$: 496.1457 Found: 496.1457; Chiralpak IA column and IA guard column (30% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer $t_r = 16.9$ min and *minor*-isomer $t_r = 27.7$ min.



(*S*)-4-(1-Benzyl-5-bromo-1*H*-indol-3-yl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4f). 35 mg, yield 74%, Colorless gum; $[\alpha]_D^{21} = +54.1$ (*c* = 0.37, CHCl₃); 88% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, *J* = 1.5 Hz, 1H), 7.37–7.26 (m, 5H), 7.20 (s, 1H), 7.18 (d, *J* = 8.7 Hz, 1H), 7.13–7.02 (m, 5H), 6.18 (d, *J* = 8.3 Hz, 1H), 5.29 (s, 2H), 4.78 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 151.24, 136.14, 135.76, 129.92(two peaks overlapping), 129.09, 128.22, 128.19, 127.45, 126.84, 125.96, 125.37, 121.63, 121.40, 119.00, 113.93, 112.10, 111.14, 54.77, 50.59; IR (neat) 3274, 2921, 2851, 1610, 1580, 1548, 1468, 1450, 1413, 1301, 1192, 1164, 1097, 1026 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₂₂H₁₇BrN₂O₃S: 468.0143 Found: 468.0114; Chiralpak IA column and IA guard column (15% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer *t*_r = 18.4 min and *minor*-isomer *t*_r = 22.1 min.



(*S*)-4-(5-Methoxy-1-methyl-1*H*-indol-3-yl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4g). 34 mg, yield 98%, White solid; m.p. 84-86 °C; $[\alpha]_D^{18} = +86.2$ (*c* = 0.33, CHCl₃); 89% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.38–7.29 (m, 1H), 7.24 (d, *J* = 8.5 Hz, 1H), 7.14–7.03 (m, 4H), 6.91 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.64 (d, *J* = 2.3 Hz, 1H), 6.21 (d, *J* = 8.2 Hz, 1H), 4.74 (d, *J* = 8.2 Hz, 1H), 3.77 (s, 3H), 3.71 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 154.43, 151.28, 132.70, 129.68, 129.61, 128.54, 125.96, 125.25, 121.96, 118.76, 112.89, 110.85, 110.32, 100.52, 55.80, 55.08, 33.21; IR (neat) 3262, 2920, 1719, 1623, 1579, 1488, 1450, 1421, 1361, 1262, 1165, 1099, 1062, 1017 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺C₁₇H₁₆N₂O₄S: 344.0831 Found: 344.0822; Chiralpak IB column and IB guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *minor*-isomer $t_r = 24.5$ min and *major*-isomer $t_r = 31.2$ min.



(*S*)-4-(5-Benzoyl-1-methyl-1*H*-indol-3-yl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4h). 41 mg, yield 99%, White solid; m.p. 82-84 °C; $[\alpha]_D^{19} = +73.7$ (*c* = 0.38, CHCl₃); 89% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.40–7.27 (m, 6H), 7.24 (d, *J* = 8.9 Hz, 1H), 7.11–7.01 (m, 4H), 6.98 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.69 (d, *J* = 2.3 Hz, 1H), 6.16 (d, *J* = 8.4 Hz, 1H), 4.92 (d, *J* = 6.1 Hz, 2H), 4.71 (d, *J* = 8.5 Hz, 1H), 3.75 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 153.44, 151.24, 137.17, 132.89, 129.83, 129.64, 128.60, 128.51, 127.94, 127.63, 125.80, 125.27, 121.91, 118.75, 113.62, 110.90, 110.20, 102.24, 70.74, 55.13, 33.20; IR (neat) 3268, 2922, 1622, 1578, 1547, 1451, 1415, 1390, 1261, 1189, 1165, 1099, 1020 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₂₃H₂₀N₂O₄S: 420.1144 Found: 420.1125; Chiralpak IA column and IA guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer *t*_r = 26.6 min and *minor*-isomer *t*_r = 46.0 min.



(*S*)-4-(5-Bromo-1-methyl-1*H*-indol-3-yl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4i). 34 mg, yield 87%, White solid; m.p. 164-166 °C; $[\alpha]_D^{19} = +75.2$ (*c* = 0.26, CHCl₃); 68% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.36 (ddd, *J* = 10.4, 7.2, 1.6 Hz, 3H), 7.23 (d, *J* = 8.7 Hz, 1H), 7.15–7.01 (m, 4H), 6.18 (d, *J* = 8.4 Hz, 1H), 4.71 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.22, 136.15, 130.47, 129.88, 128.25, 127.15, 125.73, 125.33, 121.48, 121.42, 118.97, 113.73, 111.56, 110.53, 54.77, 33.27; IR (neat) 3265, 2923, 1729, 1613, 1580, 1545, 1422, 1402, 1359, 1302, 1197, 1072, 1047, 1007 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₁₆H₁₃BrN₂O₃S: 391.9830 Found: 391.9811; Chiralpak IA column and IA guard column (7% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer *t*_r = 37.6 min and *minor*-isomer *t*_r = 42.2 min.



(*S*)-4-(5-Cyano-1-methyl-1*H*-indol-3-yl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4j). 15 mg, yield 45%, White solid; m.p. 227-229 °C; $[\alpha]_D^{19} = +115.6$ (*c* = 0.15, CHCl₃); 84% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.61 (s, 1H), 7.49 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.45–7.35 (m, 2H), 7.29 (s, 1H), 7.17–7.07 (m, 2H), 7.02 (d, *J* = 7.7 Hz, 1H), 6.23 (d, *J* = 8.3 Hz, 1H), 4.87 (d, *J* = 8.3 Hz, 1H), 3.86 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.23, 138.95, 131.79, 130.15, 128.06, 125.65, 125.42, 125.32, 124.67, 121.05, 120.09, 119.18, 112.24, 110.99, 103.51, 54.49, 33.38; IR (neat) 3188, 2221, 1615, 1581, 1485, 1453, 1433, 1381, 1363, 1281, 1164, 1098, 1015 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₁₇H₁₃N₃O₃S: 339.0678 Found: 339.0674; Chiralpak IA column and IA guard column (13% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer *t*_r = 35.8 min and *minor*-isomer *t*_r = 61.6 min.



(*S*)-4-(5-Methoxycarbonyl-1-methyl-1*H*-indol-3-yl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2dioxide (4k). 32 mg, yield 85%, White solid; m.p. 210-212 °C; $[\alpha]_D^{19} = +97.38$ (*c* = 0.41, CHCl₃); 88% ee; ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 0.9 Hz, 1H), 7.96 (dd, *J* = 8.7, 1.4 Hz, 1H), 7.43–7.32 (m, 2H), 7.17 (s, 1H), 7.15–7.02 (m, 3H), 6.28 (d, *J* = 8.5 Hz, 1H), 4.91 (d, *J* = 8.6 Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.68, 151.32, 139.77, 130.76, 129.85, 128.24, 125.28, 125.23, 124.11, 122.35, 121.65, 121.59, 118.98, 112.76, 109.71, 54.57, 52.01, 33.29; IR (neat) 3152, 2948, 2923, 2849, 1684, 1612, 1453, 1411, 1369, 1246, 1196, 1173, 1096, 1021 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₁₈H₁₆N₂O₅S: 372.0780 Found: 372.0764; Chiralpak IA column and IA guard column (20% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer *t*_r = 23.9 min and *minor*-isomer *t*_r = 27.8 min.



(*S*)-4-(1-Methyl-5-nitro-1*H*-indol-3-yl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4l). 32 mg, yield 88%, White solid; m.p. 227-229 °C; $[\alpha]_D^{19} = -169.3$ (*c* = 0.22, CHCl₃); 78% ee; ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, *J* = 2.1 Hz, 1H), 8.15 (dd, *J* = 9.1, 2.2 Hz, 1H), 7.45–7.35 (m, 2H), 7.27 (s, 1H), 7.16–7.09 (m, 2H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.28 (d, *J* = 7.9 Hz, 1H), 4.96 (d, *J* = 8.1 Hz, 1H), 3.88 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.30, 141.99, 140.06, 132.64, 130.15, 128.08, 125.38, 125.07, 120.94, 119.21, 118.31, 116.19, 114.06, 110.12, 54.28, 33.61; IR (neat) 3253, 2922, 2852, 1728, 1578, 1548, 1516, 1483, 1450, 1363, 1331, 1196, 1090, 1044 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₁₆H₁₃N₃O₅S: 359.0576 Found: 359.0570; Chiralpak IA column and IA guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer *t*_r = 21.9 min and *minor*-isomer *t*_r = 29.6 min.



(*S*)-4-(6-Chloro-1-methyl-1*H*-indol-3-yl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4m). 17 mg, yield 48%, White solid; m.p. 100-102 °C; $[\alpha]_D^{19} = +71.5$ (*c* = 0.12, CHCl₃); 78% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.38–7.31 (m, 2H), 7.16 (s, 1H), 7.11 (dd, *J* = 8.4, 6.2 Hz, 2H), 7.09–7.00 (m, 3H), 6.20 (d, *J* = 8.4 Hz, 1H), 4.70 (d, *J* = 8.4 Hz, 1H), 3.78 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.22, 137.97, 130.02, 129.80, 128.94, 128.29, 125.29, 123.93, 121.67, 121.01, 119.86, 118.90, 111.17, 110.14, 54.88, 33.16; IR (neat) 3270, 2923, 2853, 1716, 1580, 1477, 1451, 1416, 1360, 1329, 1256, 1192, 1165, 1099, 1067, 1010 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₁₆H₁₃ClN₂O₃S: 348.0335 Found: 348.0332; Chiralpak IA column and IA guard column (10% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer *t*_r = 27.4 min and *minor*-isomer *t*_r = 32.7 min.



(*S*)-4-(6-Fluoro-1-methyl-1*H*-indol-3-yl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4n). 29 mg, yield 88%, White solid; m.p. 182-184 °C; $[\alpha]_D^{19} = -11.2$ (*c* = 0.28, CHCl₃); 85% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.38–7.31 (m, 1H), 7.16–7.04 (m, 5H), 7.03 (dd, *J* = 9.5, 2.2 Hz, 1H), 6.83 (td, *J* = 9.3, 2.3 Hz, 1H), 6.20 (d, *J* = 8.3 Hz, 1H), 4.72 (d, *J* = 8.2 Hz, 1H), 3.77 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 160.23 (d, *J*^{*l*} = 240.0 Hz), 159.04, 151.21, 137.68 (d, *J*³ = 11.9 Hz), 129.76, 128.35, 125.28, 121.86, 121.76, 119.92, 119.82, 118.86, 111.12, 109.12 (d, *J*² = 24.7 Hz), 96.53 (d, *J*² = 26.2 Hz), 54.97, 33.18; IR (neat) 3251, 2959, 2923, 1730, 1625, 1578, 1547, 1477, 1413, 1338, 1287, 1205, 1163, 1103, 1002 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₁₆H₁₃FN₂O₃S: 332.0631 Found: 332.0636; Chiralpak IA column and IA guard column (15% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer *t*_r = 16.7 min and *minor*-isomer *t*_r = 19.4 min.



(*S*)-4-(1,7-Dimethyl-1*H*-indol-3-yl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4o). 26 mg, yield 79%, White solid; m.p. 148-150 °C; $[\alpha]_D^{19} = +43.8$ (*c* = 0.37, CHCl₃); 88% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.32 (dtd, *J* = 8.2, 4.2, 2.2 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 7.08–7.02 (m, 4H), 6.98–6.88 (m, 2H), 6.19 (d, *J* = 8.4 Hz, 1H), 4.71 (d, *J* = 8.4 Hz, 1H), 4.07 (s, 3H), 2.77 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.22, 136.29, 130.94, 129.60, 128.41, 126.42, 125.35, 125.27, 122.20, 122.01, 120.53, 118.78, 116.88, 110.37, 55.08, 37.09, 19.72; IR (neat) 3256, 2925, 1605, 1580, 1480, 1450, 1406, 1372, 1253, 1195, 1165, 1095, 1011 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₁₇H₁₆N₂O₃S: 328.0882 Found: 328.0898; Chiralpak IA column and IA guard column (15% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer *t*_r = 18.9 min and *minor*-isomer *t*_r = 23.8 min.



(*S*)-4-(1-Methyl-1*H*-indol-3-yl)-6-methyl-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4p). 31 mg, yield 95%, White solid; m.p. 104-106 °C; $[\alpha]_D^{20} = +61.2$ (*c* = 0.36, CHCl₃); 91% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.40–7.34 (m, 1H), 7.29–7.24 (m, 2H), 7.15 (s, 1H), 7.13–7.04 (m, 2H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.85 (s, 1H), 6.17 (d, *J* = 8.4 Hz, 1H), 4.68 (d, *J* = 8.4 Hz, 1H), 3.82 (s, 3H), 2.17 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 149.13, 137.51, 135.03, 130.27, 129.29, 128.51, 125.42, 122.67, 121.59, 120.22, 118.92, 118.53, 111.02, 110.02, 55.11, 33.06, 20.77; IR (neat) 3267, 2921, 1550, 1486, 1411, 1376, 1333, 1280, 1257, 1203, 1173, 1106, 1064, 1014 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₁₇H₁₆N₂O₃S: 328.0882 Found: 328.0894; Chiralpak IA column and IA guard column (10% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer *t*_r = 25.6 min and *minor*-isomer *t*_r = 32.9 min.



(*S*)-4-(1-Methyl-1*H*-indol-3-yl)-6-methoxy-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4q). 34 mg, yield 99%, White solid; m.p. 167-169 °C; $[\alpha]_D^{20} = +71.5$ (*c* = 0.31, CHCl₃); 93% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, *J* = 8.2 Hz, 1H), 7.30–7.24 (m, 2H), 7.15 (s, 1H), 7.11–7.05 (m, 1H), 7.03 (d, *J* = 9.0 Hz, 1H), 6.85 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.58–6.53 (m, 1H), 6.18 (d, *J* = 8.4 Hz, 1H), 4.67 (d, *J* = 8.4 Hz, 1H), 3.81 (s, 3H), 3.61 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.57, 145.03, 137.51, 129.27, 125.39, 122.91, 122.72, 120.27, 119.68, 118.88, 115.10, 113.12, 110.79, 110.03, 55.71, 55.21, 33.06; IR (neat) 3246, 2928, 2842, 1615, 1551, 1490, 1415, 1390, 1335, 1286, 1253, 1160, 1066, 1008 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₁₇H₁₆N₂O₄S: 344.0831 Found: 344.00798; Chiralpak IA column and IA guard column (15% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer *t*_r = 19.4 min and *minor*-isomer *t*_r = 22.8 min.



(*S*)-4-(1-Methyl-1*H*-indol-3-yl)-6-fluoro-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4r). 32 mg, yield 96%, White solid; m.p. 91-93 °C; $[\alpha]_D^{20} = +21.7$ (*c* = 0.38, CHCl₃); 84% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, *J* = 8.3 Hz, 1H), 7.31–7.26 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.19 (s, 1H), 7.12–7.06 (m, 2H), 7.06–6.99 (m, 1H), 6.77 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.18 (d, *J* = 8.4 Hz, 1H), 4.73 (d, *J* = 8.4 Hz, 1H), 3.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 159.26 (d, *J*^{*l*} = 245.3 Hz), 147.06, 137.57, 129.40, 125.12, 123.86 (d, *J*³ = 7.2 Hz), 120.43, 120.3 (d, *J*³ = 8.3 Hz), 118.69, 116.77 (d, *J*² = 23.9 Hz), 114.89 (d, *J*² = 25.0 Hz), 110.19, 110.02, 55.10, 33.10; IR (neat) 3266, 2920, 1617, 1550, 1480, 1415, 1388, 1334, 1254, 1200, 1156, 1095, 1065 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₁₆H₁₃FN₂O₃S: 332.0631 Found: 332.0659; Chiralpak IA column and IA guard column (10% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer *t*_r = 20.1 min and *minor*-isomer *t*_r = 22.9 min.



(*S*)-4-(1-Methyl-1*H*-indol-3-yl)-6-chloro-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4s). 34 mg, yield 99%, White solid; m.p. 144-146 °C; $[\alpha]_D^{20} = +78.0$ (*c* = 0.38, CHCl₃); 84% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, *J* = 8.3 Hz, 1H), 7.33–7.26 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.18 (s, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.07–7.01 (m, 2H), 6.17 (d, *J* = 8.4 Hz, 1H), 4.76 (d, *J* = 8.4 Hz, 1H), 3.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 149.68, 137.56, 130.51, 129.79, 129.40, 128.19, 125.14, 123.81, 122.88, 120.47, 120.24, 118.65, 110.21, 109.95, 54.96, 33.13; IR (neat) 3270, 2930, 1550, 1471, 1414, 1388, 1334, 1293, 1273, 1252, 1192, 1162, 1108, 1064 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₁₆H₁₃ClN₂O₃S: 348.0335 Found: 348.0345; Chiralpak IB column and IB guard column (20% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer *t*_r = 14.2 min and *minor*-isomer *t*_r = 17.6 min.



(*S*)-4-(1-Methyl-1*H*-indol-3-yl)-6-bromo-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4t). 36 mg, yield 92%, White solid; m.p. 108-110 °C; $[\alpha]_D^{20} = +88.6$ (*c* = 0.19, CHCl₃); 83% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.43 (ddd, *J* = 8.7, 2.4, 0.7 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.31–7.26 (m, 1H), 7.25–7.21 (m, 1H), 7.19 (dd, *J* = 2.3, 0.9 Hz, 1H), 7.17 (s, 1H), 7.12–7.06 (m, 1H), 6.98 (d, *J* = 8.8 Hz, 1H), 6.17 (d, *J* = 8.1 Hz, 1H), 4.77 (d, *J* = 8.2 Hz, 1H), 3.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 150.25, 137.56, 132.71, 131.09, 129.38, 125.13, 124.19, 122.90, 120.58, 120.48, 118.64, 118.00, 110.21, 109.96, 54.87, 33.13; IR (neat) 3264, 2919, 1549, 1468, 1414, 1388, 1322, 1254, 1189, 1163, 1107, 1077, 1030, 1014 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₁₆H₁₃BrN₂O₃S: 391.9830 Found: 391.9814; Chiralpak IA column and IA guard column (7% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer *t*_r = 37.6 min.



(*S*)-4-(1-Methyl-1*H*-indol-3-yl)-7-methyl-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4u). 30 mg, yield 93%, White solid; m.p. 94-96 °C; $[\alpha]_D^{20} = +41.3$ (*c* = 0.36, CHCl₃); 89% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, *J* = 8.3 Hz, 1H), 7.25 (td, *J* = 8.0, 3.1 Hz, 2H), 7.14 (s, 1H), 7.09–7.02 (m, 1H), 6.95–6.89 (m, 2H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.17 (d, *J* = 8.4 Hz, 1H), 4.68 (d, *J* = 8.5 Hz, 1H), 3.80 (s, 3H), 2.34 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.02, 140.14, 137.53, 129.36, 128.16, 126.19, 125.41, 122.67, 120.18, 118.97(two peaks overlapping), 118.89, 110.95, 110.02, 54.96, 33.04, 21.04; IR (neat) 3262, 2920, 1624, 1550, 1501, 1475, 1410, 1261, 1188, 1149, 1099, 1065, 1012 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₁₇H₁N₂O₃S: 328.0882 Found: 328.0880; Chiralpak IA column and IA guard column (15% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer *t*_r = 13.6 min and *minor*-isomer *t*_r = 18.2 min.



(*S*)-4-(1-Methyl-1*H*-indol-3-yl)-7-methoxy-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4v). 15 mg, yield 45%, White solid; m.p. 144-146 °C; $[\alpha]_D^{20} = +36.7$ (*c* = 0.22, CHCl₃); 80% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, *J* = 8.3 Hz, 1H), 7.30–7.26 (m, 1H), 7.25–7.22 (m, 1H), 7.17 (s, 1H), 7.08 (dd, *J* = 11.0, 4.0 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.65–6.60 (m, 2H), 6.17 (d, *J* = 8.5 Hz, 1H), 4.66 (d, *J* = 8.6 Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 160.37, 151.87, 137.55, 129.35, 129.08, 125.33, 122.69, 120.21, 119.00, 113.69, 112.18, 110.95, 110.03, 103.35, 55.64, 54.75, 33.06; IR (neat) 3255, 2920, 2850, 1734, 1622, 1575, 1502, 1466, 1416, 1357, 1269, 1235, 1200, 1187, 1152, 1088, 1029 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₁₇H₁₆N₂O₄S: 344.0831 Found: 344.0851; Chiralpak IA column and IA guard column (20% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer *t*_r = 13.5 min and *minor*-isomer *t*_r = 18.0 min.



(*S*)-4-(1-Methyl-1*H*-indol-3-yl)-6,8-dichloro-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4w). 35 mg, yield 91%, White solid; m.p. 101-103 °C; $[\alpha]_D^{24} = +64.4$ (*c* = 0.26, CHCl₃); 81% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.44–7.36 (m, 2H), 7.33–7.26 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.20 (s, 1H), 7.15–7.08 (m, 1H), 6.95 (dd, *J* = 2.4, 1.0 Hz, 1H), 6.17 (d, *J* = 8.4 Hz, 1H), 4.90 (d, *J* = 8.5 Hz, 1H), 3.84 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.89, 137.56, 130.20, 130.16, 129.45, 126.63, 125.25, 124.94, 124.71, 123.02, 120.62, 118.55, 110.29, 109.48, 55.20, 33.17; IR (neat) 3272, 2923, 1550, 1444, 1423, 1389, 1335, 1267, 1199, 1156, 1093, 1033, 1015 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₁₆H₁₂Cl₂N₂O₃S: 381.9946 Found: 381.9930; Chiralpak IB column and IB guard column (10% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer *t*_r = 32.1 min and *minor*-isomer *t*_r = 42.5 min.



(*S*)-4-(1-Methyl-1*H*-indol-3-yl)-6,8-dibromo-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4x). 44 mg, yield 94%, White solid; m.p. 113-115 °C; $[\alpha]_D^{22} = +59.4$ (*c* = 0.39, CHCl₃); 84% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.70 (dd, *J* = 2.3, 0.8 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.32–7.26 (m, 1H), 7.26–7.22 (m, 1H), 7.19 (s, 1H), 7.12 (ddd, *J* = 15.1, 5.1, 0.9 Hz, 2H), 6.17 (d, *J* = 6.7 Hz, 1H), 4.92 (d, *J* = 7.1 Hz, 1H), 3.84 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 147.34, 137.55, 135.83, 130.26, 129.46, 125.70, 124.97, 123.01, 120.62, 118.57, 117.85, 113.55, 110.28, 109.51, 55.12, 33.18; IR (neat) 3268, 2924, 1707, 1616, 1552, 1475, 1420, 1388, 1291, 1266, 1192, 1146, 1089, 1066 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₁₆H₁₂Br₂N₂O₃S: 469.8935 Found: 469.8945; Chiralpak AD-H column and AD-H guard column (10% EtOH:hexanes, 1.0 mL/min flow, λ = 220 nm); *major*-isomer *t*_r = 20.5 min and *minor*-isomer *t*_r = 25.4 min.



(*S*)-4-(1-Methyl-1*H*-indol-3-yl)-8-methoxy-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4y). 33 mg, yield 96%, White solid; m.p. 169-171 °C; $[\alpha]_D^{25} = +64.2$ (*c* = 0.32, CHCl₃); 85% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.38–7.34 (m, 1H), 7.28–7.23 (m, 2H), 7.16 (s, 1H), 7.06 (td, *J* = 7.3, 0.9 Hz, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.66–6.58 (m, 1H), 6.22 (d, *J* = 8.5 Hz, 1H), 4.75 (d, *J* = 8.5 Hz, 1H), 3.91 (s, 3H), 3.81 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 148.77, 140.92, 137.48, 129.36, 125.36, 124.72, 123.04, 122.66, 120.19, 119.53, 118.93, 111.73, 110.83, 110.03, 56.25, 55.25, 33.06; IR (neat) 3299, 3237, 2932, 1614, 1581, 1550, 1475, 1403, 1354, 1272, 1200, 1151, 1079, 1009 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₁₇H₁₆N₂O₄S: 344.0831 Found: 344.0831; Chiralpak IA column and IA guard column (20% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer *t*_r = 16.2 min and *minor*-isomer *t*_r = 20.5 min.

Enantioselective Friedel–Crafts Reaction of *N*-Benzylpyrrole 5 with Cyclic *N*-Sulfimine 2a.

To a solution of cyclic *N*-sulfimine **2** (0.1 mmol) in toluene (0.75 mL) was added catalyst **3d** (0.01 mmol). The solution was stirred at -20 °C for 10 min, and then *N*-benzylpyrrole **5** (0.15 mmol) was added in one portion. The reaction mixture was stirred at -20 °C for 72 h. Then, the resulting mixture was diluted with water and extracted with CH₂Cl₂. The combined organic layer was washed with brine, dried over anhydrous MgSO₄, and concentrated in vacuo. The crude residue was purified by flash column chromatography with EtOAc/hexanes as eluent to afford desired product **6**. The enantiomeric excess was determined using HPLC analysis.



(*S*)-4-(1-Benzyl-1*H*-pyrrol-2-yl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (6). 19 mg, yield 57%, Colorless gum; $[\alpha]_D^{22} = +91.9$ (*c* = 0.24, CHCl₃); 74% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.42–7.27 (m, 4H), 7.16–7.01 (m, 5H), 6.85 (dd, *J* = 2.6, 1.8 Hz, 1H), 6.24–6.15 (m, 1H), 6.10 (dd, *J* = 3.6, 1.6 Hz, 1H), 5.94 (s, 1H), 5.13 (q, *J* = 16.2 Hz, 2H), 4.30 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 151.43, 137.32, 129.94, 129.20, 128.33, 128.20, 127.64, 126.46, 125.09, 124.80, 120.42, 118.90, 111.83, 108.00, 77.35, 77.03, 76.72, 54.47, 51.0; IR (neat) 3274, 2924, 2853, 1481, 1451, 1417, 1362, 1286, 1197, 1166, 1099 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₁₈H₁₆N₂O₃S: 340.0882 Found: 340.0874; Chiralpak IB column and IB guard column (3% EtOH:hexanes, 1.0 mL/min flow, $\lambda = 254$ nm); *major*-isomer *t*_r = 21.6 min and *minor*-isomer *t*_r = 20.7 min.





S16































S24























S31

Area Percent Report

| Peak | RetTime | Туре | Width | A: | rea | Hei | ght | Area |
|-------|---------|------|--------|------|--------|------|-------|---------|
| # | [min] | | [min] | mAU | *s | [mAU |] | % |
| 1 | 17.884 | BB | 0.8826 | 908 | .84515 | 15. | 89358 | 50.1630 |
| 2 | 21.461 | BB | | 902 | .94049 | 14. | 05030 | 49.8370 |
| Total | ls : | | | 1811 | .78564 | 29. | 94388 | |

Area Percent Report

| Peak RetTime # [min] | Туре | Width [min] | A1 mAU | rea *s | Heic [mAU | jht] | Area % |
|-------------------------|----------------|------------------|---------------|----------------|--------------|--------------|-------------------|
| 1 17.777 2 20.991 | MM MM MM | 0.8549 0.8929 | 2719. 122. | 33398 66618 | 53.0 | 1590 8965 | 95.6838 4.3162 |
| Totals : | | | 2842. | 00017 | 55.3 | 80556 | |

S42

| Peak RetTime Ty | ype Width | Area | Height | Area |
|-----------------|-----------|------------|------------|---------|
| # [min] | [min] | mAU *s | [mAU] | % |
| | | | | |
| 1 18.068 BH | B 0.8642 | 966.98730 | 17.74891 | 95.1675 |
| 2 22.520 MM | M 0.9601 | 49.10224 | 8.52400e-1 | 4.8325 |
| Totals : | | 1016.08954 | 18.60131 | |

S43

racemic

chiral

Totals :

Area Percent Report

1433.08521

24.68648

| Peak RetTime | Туре | Width | A: | rea | Heig | ght | Area |
|--------------|------|--------|------|--------|------|-------|---------|
| # [min] | | [min] | mAU | *s | [mAU |] | % |
| 1 20.064 | MM | 0.8928 | 1643 | .07434 | 30.0 | 57374 | 95.7267 |
| 2 26.841 | MM | | 73 | .34764 | 1.1 | 18809 | 4.2733 |
| Totals : | | | 1716 | 42198 | 31.8 | 36183 | |

| Peak # | RetTime [min] | Туре | Width [min] | A: mAU | rea *s | Height [mAU] | Area % |
|-----------|------------------|------|----------------|-----------|-----------|-----------------|---------------|
| | 10 204 | | 0.0765 | 21.04 | 01440 | 20 22226 | [50 1611 |
| 2 | 21.981 | BB | 1.0341 | 2194 | .92432 | 32.57351 | 49.8389 |
| Total | ls : | | | 4373 | .93872 | 71.90577 | |

chiral

| Peak # | RetTime [min] | Туре | Width [min] | A1 mAU | rea *s | Height [mAU] | Area % |
|------------|------------------|----------|----------------|---------------|-----------|---------------------|-------------------|
| 1 2 | 18.366 22.135 | BB BB | 0.8609 | 2233. 149. | 20117 | 40.64035 2.24146 | 93.7365 6.2635 |
| Total | s: | | | 2382. | 42464 | 42.88182 | |

racemic

Totals :

Area Percent Report

1638.37451

25.78321

| Peak | RetTime | Туре | Width | A: | rea | Hei | ght | Area |
|-------|---------|------|--------|------|--------|------|-------|---------|
| # | [min] | | [min] | mAU | *s | [mAU |] | % |
| | | | | | | | | |
| 1 | 20.151 | BB | 0.9139 | 3666 | .11230 | 62. | 94955 | 96.7582 |
| 2 | 24.614 | BB | 0.8167 | 122 | .82885 | 1. | 78002 | 3.2418 |
| Total | s: | | | 3788 | .94115 | 64. | 72957 | |

racemic

chiral

| Peak i | RetTime | Туре | Width | A1 | rea | Height | Area |
|--------|---------|------|--------|-------|-------|------------|---------|
| # | [min] | | [min] | mAU | *s | [mAU] | % |
| 1 | 16.869 | BB | 1.0232 | 2349 | 05151 | 35.52917 | 98.3564 |
| 2 | 27.664 | MM | 1.2056 | 39 | | 5.42662e-1 | 1.6436 |
| Total | s: | | | 2388. | 30629 | 36.07183 | |

racemic

 Peak RetTime Type
 Width
 Area
 Height
 Area

 #
 [min]
 [min]
 mAU
 *s
 [mAU
 \$

 --- ---- ---- ----- ----- ----- \$

 1
 24.102
 MM
 1.2790
 1072.89246
 13.98033
 50.5144

 2
 31.201
 MM
 1.4162
 1051.04004
 12.36967
 49.4856

 Totals :
 2123.93250
 26.35000
 26.35000
 26.35000

chiral

| Peak | RetTime | Туре | Width | Area | | Height | | Area | |
|-------|---------|------|--------|--------|--------|--------|-------|---------|--|
| # | [min] | | [min] | mAU *s | | [mAU] | | % | |
| 1 | 26.618 | BB | 0.9915 | 1923 | .68835 | 29.5 | 8697 | 50.2933 | |
| 2 | 45.547 | BB | 1.3389 | 1901 | .25488 | 19.9 | 2603 | 49.7067 | |
| Total | ls : | | | 3824 | .94324 | 49.5 | 51300 | | |

| Peak RetTime Typ | e Width | Area | Height | Area |
|------------------|---------|------------|----------|---------|
| # [min] | [min] | mAU *s | [mAU] | % |
| 1 26.633 MM | 1.0984 | 2008.81140 | 30.48024 | 94.6189 |
| 2 46.010 MM | 1.5421 | 114.24424 | 1.23476 | 5.3811 |
| Totals : | | 2123.05564 | 31.71501 | |

racemic

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | | Heig [mAU | iht 1 | Area % | |
|-----------|------------------|----------|------------------|----------------|----------------|--------------|----------------|--------------------|--|
| | | | | | | · | | | |
| 1 2 | 38.948 42.564 | BB BB | 1.0664 1.1741 | 2760. 2694. | 70435 13135 | 38.9 33.6 | 91726 55879 | 50.6102 49.3898 | |
| Total | ls : | | | 5454. | 83569 | 72.5 | 57605 | | |

| Peak Ret # [r | tTime nin] | Туре | Width [min] | A1 mAU | rea *s | Heig [mAU | jht] | Area % |
|------------------|---------------|------|----------------|-----------|-----------|--------------|----------|-----------|
| | | - | | | | | | |
| 1 3 | 7.606 | BB | 1.0714 | 2614. | 87378 | 37.1 | 5883 | 83.8056 |
| 2 42 | 2.194 | BB | 1.0491 | 505. | 29242 | 6.4 | 3131 | 16.1944 |
| | | | | | | | | |
| Totals | | | | 3120. | 16620 | 43.5 | 59014 | |

racemic

| Peak # | RetTime [min] | Туре | Width [min] | A mAU | rea *s | Hei [mAU | ght] | Area % |
|-----------|------------------|------|----------------|----------|-----------|-------------|----------|-----------|
| | | | | | | | | |
| 1 | 35.248 | MM | 1.5029 | 650 | .46289 | 7.3 | 21326 | 49.3614 |
| 2 | 59.000 | MM | 2.3115 | 667 | .29218 | 4. | 81134 | 50.6386 |
| Total | ls : | | | 1317 | .75507 | 12. | 02461 | |

| Peak RetTime # [min] | Туре | Width [min] | A: mAU | rea *s | Heig [mAU | ght] | Area % |
|-------------------------|--------------|------------------|-------------|------------------|--------------|--------------|-------------------|
| 1 35.841 2 61.565 | MM MM | 1.5221 2.5834 | 2015 174 | .92847 .67722 | 22.0 | 7368 2690 | 92.0261 7.9739 |
| Totals : | | | 2190 | .60568 | 23.2 | 20058 | |

chiral

| Peak RetTime # [min] | Туре | Width [min] | A mAU | rea *s | Heig [mAU | ght] | Area % |
|-------------------------|------|----------------|----------|-----------|--------------|----------|-----------|
| | | | | | | | |
| 1 23.898 | MM | 1.3738 | 6771 | .12402 | 82.1 | L4424 | 93.2814 |
| 2 27.795 | MM | 1.5733 | 487 | .69339 | 5.1 | L6628 | 6.7186 |
| Totals : | | | 7258 | .81741 | 87.3 | 31052 | |

racemic

chiral

Area Percent Report

| Peak RetT | ime Type n] | Width [min] | Are mAU | *s | Heig [mAU | nt] | Area % |
|-----------|----------------|----------------|------------|-------|--------------|---------|-----------|
| 1 21. | 909 MM | 1.0750 | 6578.3 | 81787 | 101.9 | 8546 | 89.0282 |
| 2 29. | 590 BB | 1.1417 | 810.7 | 71136 | 9.7 | 0799 | 10.9718 |

```
Totals :
```

7389.02924 111.69345

racemic

| Peak | RetTime | Туре | Width | A | rea | Hei | ght | Area |
|--------|------------------|----------|------------------|------------|------------------|----------|----------------|--------------------|
| # | [min] | | [min] | mAU | *s | [mAU | | * |
| 1 2 | 28.581 33.952 | MM MM | 1.0459 1.4271 | 244 237 | .74998 .26993 | 3. 2. | 90019 77093 | 50.7759 49.2241 |
| Total | ls : | | | 482 | .01991 | 6. | 67112 | |

| Peak RetTime Type | Width | Area | Height | Area |
|-------------------|--------|------------|----------|---------|
| # [min] | [min] | mAU *s | [mAU] | % |
| 1 27.395 MM | 1.0101 | 1537.64856 | 25.37234 | 89.0850 |
| 2 32.719 BB | 0.9300 | 188.39717 | 2.42807 | 10.9150 |
| Totals : | | 1726.04573 | 27.80041 | |

racemic

Totals :

chiral

Area Percent Report

1865.09845

34.63132

| Peak RetTime Type | Width | Area | Height | Area |
|-------------------|---------|------------|----------|---------|
| # [min] | [min] 1 | mAU *s | [mAU] | % |
| 1 16.668 MM | 0.8317 | 1998.96997 | 40.05807 | 92.4165 |
| 2 19.399 MM | | 164.03189 | 3.02956 | 7.5835 |
| Totals : | | 2163.00186 | 43.08763 | |

racemic

| Peak # | RetTime [min] | Type | Width [min] | Ar mAU | ea *s | Heig [mAU | ght] | Area % |
|-----------|------------------|----------|----------------|--------------|----------------|--------------|---------------|--------------------|
| 1 2 | 18.779 23.515 | BB BB | 0.8046 | 411. 406. | 64883 53339 | 7.8 | 87951 5131 | 50.3126 49.6874 |
| Total | ls : | | | 818. | 18222 | 14.9 | 93082 | |

chiral

| Peak # | RetTime [min] | Туре | Width [min] | A: mAU | rea *s | Heig [mAU | ght] | Area % |
|-----------|------------------|------|----------------|-----------|-----------|--------------|----------|-----------|
| | | | | | | | | |
| 1 | 18.896 | MM | 0.8823 | 1707 | .21240 | 32.2 | 25107 | 93.9893 |
| 2 | 23.806 | MM | 0.9403 | 109 | .17730 | 1.5 | 93517 | 6.0107 |
| | | | | | | | | |
| Total | s: | | | 1816 | .38970 | 34. | 18623 | |

chiral

Totals :

| | | -100 | | | | | | |
|--------|------------------|----------|------------------|-------------|------------------|-------------|--------------|-------------------|
| # | [min] | | [min] | mAU | *s | [mAU |] | 8 |
| | | | | | | | | |
| 1 2 | 25.614 32.862 | MM MM | 0.9378 0.9970 | 2255 105 | .69849 .66940 | 40.0 1.7 | 9018 6648 | 95.5251 4.4749 |
| Total | .s : | | | 2361 | .36789 | 41.8 | 5666 | |

2076.99731

34.28676

racemic

chiral

| Peak # | RetTime [min] | Туре | Width [min] | A mAU | rea *s | Hei [mAU | ght] | Area % |
|-----------|------------------|------|----------------|----------|-----------|-------------|----------|-----------|
| | | | | | | | | |
| 1 | 19.436 | BB | 0.5234 | 2023 | .01636 | 59. | 06198 | 96.5158 |
| 2 | 22.813 | BB | 0.5720 | 73 | .03020 | 1. | 91959 | 3.4842 |
| | | | | | | | | |
| Total | s : | | | 2096 | .04656 | 60. | 98158 | |

racemic

| Fear I | Retrime | Type | Widen | | rea | Height | | Area | |
|----------|---------|------|--------|------|--------|--------|-------|---------|--|
| # | [min] | | [min] | mAU | *s | MAU | 1 | 8 | |
| | | | | | | · | | | |
| 1 | 19.118 | MM | 0.5730 | 1544 | .48645 | 44. | 92115 | 49.9216 | |
| 2 | 21.392 | MM | 0.6429 | 1549 | .33569 | 40. | 16604 | 50.0784 | |
| | | | | | | | | | |
| Totals : | | | | 3093 | .82214 | 85. | 08719 | | |
| | | | | | | | | | |

chiral

_____ Area Percent Report _____ _____

| Peak # | RetTime [min] | туре | Width [min] | A: mAU | rea *s | Hei [mAU | ght] | Area % |
|-----------|------------------|------|----------------|-----------|-----------|-------------|----------|-----------|
| | | | | | | | | |
| 1 | 20.051 | BB | 0.5694 | 6470 | .82861 | 172. | 22542 | 92.1623 |
| 2 | 22.869 | BB | 0.6158 | 550 | .29614 | 13. | 52716 | 7.8377 |
| | | | | | | | | |
| Total | ls : | | | 7021 | .12476 | 185. | 75258 | |

```
S59
```

1549.34

19-118 392%

20

15

25

n

Area Percent Report

| Peak # | RetTime [min] | Туре | Width [min] | A: mAU | rea *s | Heig [mAU | ght] | Area % |
|-----------|------------------|----------|------------------|------------|-----------|--------------|----------------|--------------------|
| 1 2 | 14.186 17.839 | BB BB | 0.7737 0.7871 | 893 895 | .74347 | 17.7 | 79776 50254 | 49.9531 50.0469 |
| Total | ls : | | | 1789 | .16669 | 35.4 | 0031 | |

chiral

| Peak RetTime Type | Width Area | Height | Area |
|-------------------|-------------------|-----------|---------|
| # [min] | [min] mAU *s | [mAU] | % |
| 1 14.183 BB | 0.7836 4714.30420 | 94.39548 | 91.8068 |
| 2 17.649 BB | 0.7552 420.72095 | 8.31007 | 8.1932 |
| Totals : | 5135.02515 | 102.70555 | |

20 -

15 -

10 -

5-

0

20

| Peak RetTime | | Type | Width | Area | | Height | | Area | |
|--------------|--------|------|--------|------|--------|--------|-------|---------|--|
| # | [min] | | [min] | mAU | *s | [mAU |] | 8 | |
| | | | | | | | | | |
| 1 | 30.865 | MM | 0.9173 | 1931 | .62134 | 35. | 09717 | 91.3006 | |
| 2 | 37.633 | MM | 1.1013 | 184 | .05180 | 2. | 78536 | 8.6994 | |
| | | | | | | | | | |
| Total | s : | | | 2115 | .67314 | 37. | 88253 | | |

10

69. Ange. 184.052

40

35

30

| Peak # | RetTime [min] | Туре | Width [min] | A: mAU | rea *s | Hei [mAU | ght] | Area % |
|-----------|------------------|------|----------------|-----------|-----------|-------------|----------|-----------|
| | | | | | | | | |
| 1 | 13.649 | BB | 0.3776 | 846 | .85669 | 34. | 03638 | 94.4874 |
| 2 | 18.174 | MM | 0.5545 | 49 | .40727 | 1. | 48498 | 5.5126 |
| Total | ls : | | | 896 | .26396 | 35. | 52136 | |

racemic

chiral

Totals :

| Peak # | RetTime [min] | Туре | Width [min] | Area mAU *s | Height [mAU] | Area % |
|-----------|------------------|------|----------------|----------------|------------------|-----------|
| | | | | | | |
| 1 | 31.613 | MM | 2.2946 | 3143.87939 | 22.83542 | 49.2606 |
| 2 | 40.292 | MM | 2.1535 | 3238.26245 | 25.06144 | 50.7394 |
| | | | | | | |

Totals : 6382.14185 47.89686

| Peak RetTime Type | Width | Area | Height | Area |
|-------------------|--------|------------|----------|---------|
| # [min] | [min] | mAU *s | [mAU] | % |
| 1 32.125 MM | 2.5824 | 3063.42969 | 19.77143 | 90.6918 |
| 2 42.510 MM | 2.5460 | 314.41663 | 2.05825 | 9.3082 |
| Totals : | | 3377.84631 | 21.82969 | |

chiral

Area Percent Report

| Peak RetTime Type | Width | Area | Height | Area |
|-------------------|--------|------------|----------|---------|
| # [min] | [min] | mAU *s | [mAU] | % |
| 1 16.236 MM | 0.5560 | 2861.60376 | 85.77186 | 92.3053 |
| 2 20.543 MM | 0.7355 | 238.54846 | 5.40554 | 7.6947 |
| Totals : | | 3100.15222 | 91,17740 | |

| Peak # | RetTime [min] | Туре | Width [min] | A mAU | rea *s | Heig [mAU | ght] | Area % |
|-----------|------------------|------|----------------|----------|-----------|--------------|----------|-----------|
| 1 | 22.096 | вв | 0.6892 | 507 | .46777 | 10.0 | 60673 | 50.3242 |
| 2 | 26.086 | BB | 0.7234 | 500 | .93005 | 10.2 | 24447 | 49.6758 |
| Total | ls : | | | 1008 | .39783 | 20.8 | 35120 | |

chiral

| Peak # | RetTime [min] | туре | Width [min] | Area mAU *s | | Height [mAU] | | Area % |
|-----------|------------------|------|----------------|----------------|--------|-----------------|-------|-----------|
| | | | | | | | | |
| 1 | 21.556 | MM | 0.8204 | 458 | .40491 | 9. | 31218 | 86.9741 |
| 2 | 25.660 | MM | 0.7926 | 68. | .65408 | 1. | 44371 | 13.0259 |
| | | | | | | | | |
| Total | ls : | | | 527 | .05898 | 10. | /5589 | |