Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Dinuclear zinc catalyzed asymmetric [3 + 2] spiroannulation for the synthesis of diverse bispirocyclic saccharines

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General Information

All reactions were carried out under an atmosphere of argon using oven-dried glassware. Super dry solvents, metal catalysts, were purchased from chemical companies and used without further treatment. Flash column chromatography was performed using silica gel (300-400 mesh). ^{1}H NMR ,^{13}C NMR, ^{19}F NMR spectra were recorded in $CDCl_3$ or DMSO-d6 on a 400 MHz spectrometer; chemical shifts are reported in ppm with the solvent signals as reference, and coupling constants (*J*) are given in Hertz. The peak information is described as: s = singlet, d = doublet, t = triplet, q = quartet, m= multiplet. High-resolution mass spectra (HRMS) were recorded on a commercial apparatus (ESI Source). cyclic 1-azadienes[1] and α-Hydroxy-1-indanone[2] were synthesized according to the literature.

General Procedure for optimization of the reaction conditions.

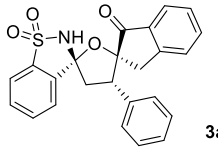
Under a nitrogen atmosphere, a solution of diethylzinc (40 μL, 1.0 M in hexane, 0.04 mmol) was added dropwise to a solution of **L** (0.02 mmol) in solvent (2 mL). After the mixture was stirred for 30 min at room temperature, then, cyclic 1-azadienes **1a** (0.2 mmol) and α-Hydroxy-1-indanone **2a** (0.25 mmol) were added. The reaction mixture was stirred for 36 h at the same temperature. The reaction was quenched with HCl solution (1 M, 2 mL), and the organic layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure by using a rotary evaporator. The residue was purified by flash chromatography with petroleum ether/ethyl acetate (4/1) to afford the desired product **3aa**.

Asymmetric reaction for the synthesis of diverse bispirocyclic saccharines

Under a nitrogen atmosphere, a solution of diethylzinc (40 μL, 1.0 M in hexane, 0.04 mmol) was added dropwise to a solution of **L3c** (0.02 mmol) in THF (2 mL). After the mixture was stirred for 30 min at room temperature, then, cyclic 1-azadienes **1a** (0.2 mmol) and α-Hydroxy-1-indanone **2a** (0.25 mmol) were added. The reaction mixture was stirred for 36 h at 30℃ temperature. The reaction was quenched with HCl solution (1 M, 2 mL), and the organic layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure by using a rotary evaporator. The residue was purified by flash chromatography with petroleum ether/ethyl acetate (4/1) to afford the desired product **3**.

Characterization of 3

(2'*R*,3*R*,3'*S*)-3'-Phenyl-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3aa):

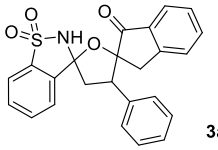


3aa

White solid in 65% isolated yield (54 mg, >20:1 dr); m.p.: 84.1-86.0 ℃. $[\alpha]_D^{20}$ = +121 (c = 1.0, CH_2Cl_2, 99% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79–7.78 (m, 2H), 7.74–7.68 (m, 2H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.17–7.15 (m, 3H), 7.05 (d, *J* = 7.7 Hz, 1H), 6.99–6.90 (m, 2H), 6.45 (s, 1H), 4.27 (dd, *J* = 13.2, 6.1 Hz, 1H), 3.14–3.02 (m, 2H), 2.96 (t, *J* = 12.8 Hz, 1H), 2.82–2.77 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.2, 151.7, 138.0, 137.5, 136.6, 135.2, 134.4, 133.7, 131.4, 128.6, 128.1, 127.8, 127.8, 126.2, 124.7, 124.2, 121.2, 96.8, 91.3, 50.2, 44.5, 36.5;

HRMS (ESI): m/z for $[M+Na]^+$: calcd 440.0927, found 440.0924; **HPLC**: Daicel Chiralpak IA, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 26.32 min and t_{minor} = 42.12 min.

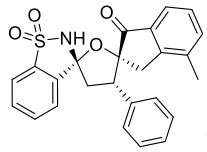
3'-Phenyl-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3aa')：



3aa'

White solid in 14% isolated yield (12 mg, 2:1 dr); m.p.: 84.3-86.5 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.7 Hz, 1H), 7.81–7.64 (m, 3.72H), 7.63–7.55 (m, 1.54H), 7.49–7.40 (m, 2H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.21 (m, 1.68H), 7.18–7.11 (m, 3.80H), 7.11–7.00 (m, 4.52H), 6.92 (s, 0.55H), 5.62 (s, 1H), 4.08 (dd, *J* = 13.8, 5.7 Hz, 1H), 3.94 (dd, *J* = 13.8, 5.7 Hz, 0.56H), 3.64–3.37 (m, 4.70H), 3.05 (dd, *J* = 12.6, 5.6 Hz, 0.52H), 2.71 (dd, *J* = 12.6, 5.6 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.2, 204.6, 150.7, 150.3, 141.1, 139.9, 137.2, 136.1, 135.8, 135.1, 134.8, 134.7, 134.0, 133.8, 133.3, 133.3, 130.9, 128.6, 128.4, 128.1, 127.9, 127.9, 127.8, 127.8, 126.2, 125.9, 125.8, 124.1, 123.9, 123.4, 121.1, 120.5, 97.5, 95.4, 92.4, 91.9, 56.1, 53.5, 44.2, 43.3, 39.7, 38.0; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 440.0927, found 440.0930.

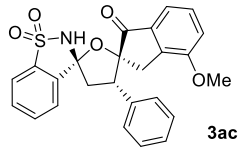
(2'*R*,3*R*,3'*S*)-4''-Methyl-3'-phenyl-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3ab):



3ab

White solid in 60% isolated yield (52 mg, >20:1 dr); m.p.: 182.8-183.9 ℃. $[\alpha]_D^{20}$ = +132 (c = 1.0, $CDCl_3$, 95% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.7 Hz, 1H), 7.75–7.69 (m, 2H), 7.68–7.63 (m, 2H), 7.32–7.27 (m, 2H), 7.17 (d, J = 6.7 Hz, 3H), 6.97–6.90 (m, 2H), 6.45 (s, 1H), 4.26 (dd, *J* = 13.1, 6.2 Hz, 1H), 3.02–2.80 (m, 3H), 2.85–2.80 (m, 1H), 1.96 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.4, 150.5, 138.0, 137.60, 136.80, 135.5, 135.3, 134.2, 133.5, 131.4, 128.4, 128.2, 127.8, 124.1, 122.1, 121.4, 96.8, 91.6, 50.7, 44.6, 35.1, 17.5; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 454.1084, found 454.1085; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 25.83 min and t_{minor} = 19.69 min.

(2'*R*,3*R*,3'*S*)-4''-Methoxy-3'-phenyl-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3ac):

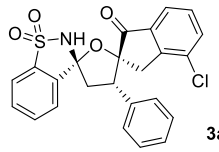


3ac

Yellow solid in 50% isolated yield (45 mg, >20:1 dr); m.p.: 160.2-162.4 ℃. $[\alpha]_D^{20}$ = +82 (c = 1.0, CH_2Cl_2, 91% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.75–7.71 (m, 1H), 7.65 (m, 7.0 Hz, 2H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.20–7.16 (m, 3H), 6.95 (d, *J* = 8.0 Hz, 3H), 6.21 (s, 1H), 4.31 (dd, *J* = 13.2, 6.2 Hz, 1H), 3.71 (s, 3H), 3.10–2.90 (m, 3H), 2.86–2.81 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.8, 156.4, 140.6, 138.3, 137.5, 135.7, 135.3, 133.6, 131.3, 129.5, 128.6, 127.8, 127.7, 124.1, 121.3, 116.7, 116.3, 96.8, 91.1, 55.5, 50.3, 44.7, 33.1; **HRMS** (ESI): m/z

for $[M+Na]^+$: calcd 470.1033, found 470.1039; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 17.11 min and t_{minor} = 12.01 min.

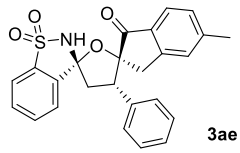
(2'*R*,3*R*,3'*S*)-4''-Chloro-3'-phenyl-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide(3ad):



3ad

White solid in 56% isolated yield (50 mg, >20:1 dr); m.p.: 230.1-232.2 ℃. $[\alpha]_D^{20}$ = +64 (c = 1.0, CH_2Cl_2, 75% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.75–7.70 (m, 3H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.20–7.17 (m, 3H), 6.97–6.95 (m, 2H), 6.22 (s, 1H), 4.29 (dd, *J* = 13.3, 6.1 Hz, 1H), 3.15–2.94 (m, 3H), 2.83 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.2, 149.1, 138.0, 137.5, 136.3, 135.9, 134.7, 133.7, 132.4, 131.5, 129.6, 128.7, 128.1, 127.7, 124.2, 122.9, 121.3, 96.9, 91.1, 50.8, 44.5, 35.4; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 474.0538, found 474.0543; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 27.99 min and t_{minor} = 20.81 min.

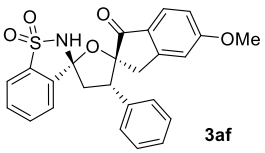
(2'*R*,3*R*,3'*S*)-5''-Methyl-3'-phenyl-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide(3ae):



3ae

Yellow solid in 66% isolated yield (57 mg, >20:1 dr); m.p.: 169.2-170.6 ℃. $[\alpha]_D^{20}$ = +108 (c = 1.0, CH_2Cl_2, 98% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.7 Hz, 1H), 7.73–7.65 (m, 4H), 7.21–7.16 (m, 4H), 6.99–6.92 (m, 2H), 6.87 (s, 1H), 6.47 (s, 1H), 4.32–4.27 (m, 1H), 3.08–2.91 (m, 3H), 2.85–2.80 (m, 1H), 2.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.5, 152.2, 148.2, 137.9, 137.5, 135.6, 133.5, 132.0, 131.4, 129.4, 128.6, 127.8, 127.7, 126.5, 124.7, 124.1, 121.4, 96.7, 91.4, 50.4, 44.7, 36.4, 22.3; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 454.1084, found 454.1082; **HPLC**: Daicel Chiralpak IA, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 31.67 min and t_{minor} = 49.97 min.

(2'*R*,3*R*,3'*S*)-5''-Methoxy-3'-phenyl-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide(3af):

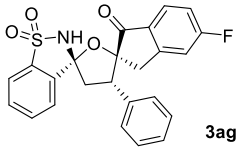


3af

Yellow solid in 52% isolated yield (46 mg, >20:1 dr); m.p.: 153.6-154.7 ℃. $[\alpha]_D^{20}$ = +143 (c = 1.0, CH_2Cl_2, 91% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.7 Hz, 2H), 7.73 (d, *J* = 7.0 Hz, 1H), 7.68 (d, *J* = 6.8 Hz, 1H), 7.66–7.61 (m, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.39–7.33 (m, 1H), 7.12–7.06 (m, 2H), 6.71 (dd, *J* = 8.0, 2.8 Hz, 1H), 6.56 (d, *J* = 8.5 Hz, 1H), 6.45 (s, 1H), 6.38 (s, 1H), 4.25 (dd, *J* = 13.1, 6.2 Hz, 1H), 3.54 (s, 3H), 3.15–3.02 (m, 2H), 2.93 (t, *J* = 12.7 Hz, 1H), 2.80 (dd, *J* = 12.2, 6.2 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.8, 166.7, 154.8, 137.8, 137.5, 135.7, 133.5, 131.4, 128.6, 127.8, 127.7, 127.4, 126.8, 124.1, 121.4, 116.1, 109.4, 96.6, 91.4, 55.7, 50.2, 44.6, 36.6; **HRMS** (ESI):

m/z for $[M+Na]^+$: calcd 470.1033, found 470.1037; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH =70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 24.34 min and t_{minor} = 19.81 min.

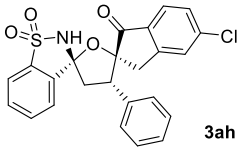
(2'*R*,3*R*,3'*S*)-5''-Fluoro-3'-phenyl-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3ag):



3ag

Yellow solid in 69% isolated yield (60 mg, >20:1 dr); m.p.: 130.6-131.8 ℃. $[\alpha]_D^{20}$ = +107 (c = 1.0, CH_2Cl_2, 96% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87–7.81 (m, 2H), 7.74 (t, *J* = 7.1 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.22–7.20 (m, 3H), 7.11–7.04 (m, 1H), 7.00–6.93 (m, 2H), 6.74 (d, *J* = 8.1 Hz, 1H), 6.35 (s, 1H), 4.29 (dd, *J* = 13.1, 6.2 Hz, 1H), 3.14–3.02 (m, 2H), 2.95 (t, *J* = 12.7 Hz, 1H), 2.85–2.81 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.77; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.2, 168.1 (d, *J* = 259.5 Hz), 154.6 (d, *J* = 10.6 Hz), 137.8, 137.5, 135.1, 133.6, 131.4, 130.8 (d, *J* = 2.1 Hz), 128.7, 128.0, 127.7, 127.4, 127.3, 124.1, 121.4, 116.6 (d, *J* = 23.8 Hz), 113.0 (d, *J* = 22.4 Hz), 96.8, 91.3, 50.6, 44.5, 36.5; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 458.0833, found 458.0838; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 20.06 min and t_{minor} = 15.93 min.

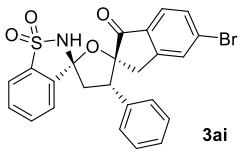
(2'*R*,3*R*,3'*S*)-5''-Chloro-3'-phenyl-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3ah):



3ah

Yellow solid in 54% isolated yield (49 mg, 17:1 dr); m.p.: 189.1-189.9 ℃. $[\alpha]_D^{20}$ = +76 (c = 1.0, CH_2Cl_2, 97% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 1.8 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.69–7.64 (m, 2H), 7.46 (m, 1H), 7.23–7.18 (m, 3H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.95 (m, 2H), 6.23 (s, 1H), 4.28 (dd, *J* = 13.1, 6.3 Hz, 1H), 3.11–2.99 (m, 2H), 2.94 (t, *J* = 12.7 Hz, 1H), 2.86–2.81 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.0, 149.6, 137.9, 137.6, 136.4, 135.8, 134.9, 134.5, 133.6, 131.4, 128.7, 128.0, 127.7, 127.4, 124.4, 124.0, 121.4, 96.8, 91.6, 50.8, 44.5, 36.1; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 474.0538, found 474.0541; **HPLC**: Daicel Chiralpak IA, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 20.97 min and t_{minor} = 48.71 min.

(2'*R*,3*R*,3'*S*)-5''-Bromo-3'-phenyl-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3ai):

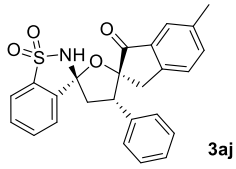


3ai

Yellow solid in 70% isolated yield (69 mg, >20:1 dr); m.p.: 147.5-148.9 ℃. $[\alpha]_D^{20}$ = +83 (c = 1.0, CH_2Cl_2, 85% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88–7.80 (m, 2H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 2H), 7.21 (dd, *J* = 5.0, 2.0 Hz, 3H), 7.07 (td, *J* = 8.7, 2.3 Hz, 1H), 6.96 (dd, *J* = 6.5, 3.2 Hz, 2H), 6.74 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.37 (s, 1H), 4.29 (dd, *J* = 13.1, 6.2 Hz, 1H), 3.12–3.02 (m, 2H), 2.95 (t, *J* = 12.7 Hz, 1H), 2.85–2.81 (m, 1H).; **^{13}C NMR**(101 MHz, $CDCl_3$) δ 205.0, 153.0, 137.8, 137.5, 135.0, 133.6, 133.1, 132.1, 131.9, 131.5, 129.4, 128.8, 128.0, 127.7, 125.9, 124.0, 121.4, 96.8, 91.0, 50.6, 44.5, 36.2; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 518.0033, found 518.0037; **HPLC**:Daicel

Chiralpak IA,*n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 32.25 min and t_{minor} = 55.14 min.

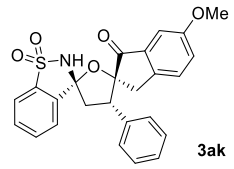
(2'*R*,3*R*,3'*S*)-6''-Methyl-3'-phenyl-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3aj):



3aj

Yellow solid in 60% isolated yield (52 mg, >20:1 dr); m.p.: 129.3-130.2 ℃. $[\alpha]_D^{20}$ = +54 (c = 1.0, CH_2Cl_2, 99% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.69–7.64 (m, 2H), 7.61 (s, 1H), 7.32 (d, *J* = 8.8 Hz, 1H), 7.18 (dd, *J* = 5.0, 1.7 Hz, 3H), 6.95 (d, *J* = 6.9 Hz, 3H), 6.42 (s, 1H), 4.28 (dd, *J* = 13.1, 6.3 Hz, 1H), 3.08–2.91 (m, 3H), 2.82 (dd, *J* = 12.2, 6.3 Hz, 1H), 2.38 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.2, 149.0, 138.2, 138.0, 137.8, 137.6, 135.4, 134.5, 133.5, 131.4, 128.56, 127.8, 127.7, 125.8, 124.6, 124.1, 121.4, 96.7, 91.6, 50.6, 44.6, 36.1, 21.1; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 454.1084, found 454.1088; **HPLC**: Daicel Chiralpak IA, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 23.07 min and t_{minor} = 36.45 min.

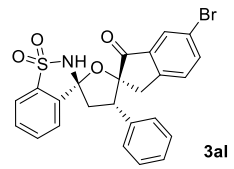
(2'*R*,3*R*,3'*S*)-6''-Methoxy-3'-phenyl-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3ak):



3ak

Yellow solid in 70% isolated yield (63 mg, >20:1 dr); m.p.: 181.3-181.8 ℃. $[\alpha]_D^{20}$ = +64 (c = 1.0, CH_2Cl_2, 90% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.7 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.69–7.63 (m, 2H), 7.24 (d, *J* = 2.4 Hz, 1H), 7.21–7.17 (m, 3H), 7.10 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.98–6.93 (m, 3H), 6.39 (s, 1H), 4.28 (dd, *J* = 13.1, 6.2 Hz, 1H), 3.84 (s, 3H), 3.05–2.91 (m, 3H), 2.83 (dd, *J* = 12.2, 6.2 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.1, 159.7, 144.6, 138.0, 137.6, 135.4, 135.3, 133.5, 131.4, 128.6, 127.8, 127.7, 126.9, 126.0, 124.1, 121.4, 105.6, 96.8, 91.9, 55.7, 50.7, 44.6, 35.8; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 470.1033, found 470.103; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 40.59 min and t_{minor} = 28.64 min.

(2'*R*,3*R*,3'*S*)-6''-Bromo-3'-phenyl-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''H)-one 1,1-dioxide (3al):

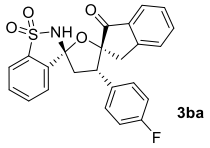


3al

Yellow solid in 63% isolated yield (62 mg, 17:1 dr); m.p.: 192.3-193.4 ℃. $[\alpha]_D^{20}$ = +91 (c = 1.0, CH_2Cl_2, 83% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.67 (t, *J* = 6.6 Hz, 2H), 7.60 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.23–7.18 (m, 3H), 6.96 (dd, *J* = 5.1, 3.0 Hz, 3H), 6.22 (s, 1H), 4.31–4.24 (m, 1H), 3.09–2.90 (m, 3H), 2.83 (dd, *J* = 12.3, 6.3 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.9, 150.0, 139.2, 137.9, 137.6, 136.1, 134.9, 133.6, 131.4, 128.7, 128.0,

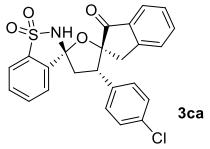
127.7, 127.7, 127.5, 124.0, 122.3, 121.4, 96.8, 91.4, 50.8, 44.5, 36.2; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 518.0033, found 518.0032; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 22.35 min and t_{minor} = 17.24 min.

(2'*R*,3*R*,3'*S*)-3'-(4-fluorophenyl)-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3ba):



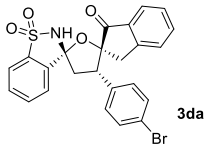
Yellow solid in 62% isolated yield (54 mg, >20:1 dr); m.p.: 177.8-179.0 ℃. $[\alpha]_D^{20}$ = +109 (c = 1.0, CH_2Cl_2, 96% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86–7.80 (m, 2H), 7.77–7.72 (m, 1H), 7.69–7.64 (m, 2H), 7.53 (td, *J* = 7.5, 1.3 Hz, 1H), 7.41–7.36 (m, 1H), 7.09 (d, *J* = 8.6 Hz, 1H), 6.95–6.84 (m, 4H), 6.32 (s, 1H), 4.27 (dd, *J* = 12.7, 6.7 Hz, 1H), 3.10–3.04(m, 2H), 2.93–2.78 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.95; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.8, 162.1 (d, *J* = 247.2 Hz), 151.3, 137.8 (d, *J* = 31.1 Hz), 136.6, 134.4, 133.5, 131.4, 131.0 (d, *J* = 3.3 Hz), 129.4, 129.3, 128.2, 126.2, 124.8, 124.0, 121.4, 115.6, 115.4, 96.7, 91.2, 45.0, 44.9, 36.4; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 458.0833, found 458.0841; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 25.58 min and t_{minor} = 15.44 min.

(2'*R*,3*R*,3'*S*)-3'-(4-chlorophenyl)-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3ca):



Yellow solid in 68% isolated yield (61 mg, >20:1 dr); m.p.: 237.7-238.8 ℃. $[\alpha]_D^{20}$ = +128 (c = 1.0, CH_2Cl_2, 97% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 4.0 Hz, 2H), 7.76–7.72 (m, 1H), 7.70–7.63 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.22–7.14 (m, 2H), 7.11 (d, *J* = 7.7 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.34 (s, 1H), 4.27 (dd, *J* = 12.6, 6.6 Hz, 1H), 3.13–3.03 (m, 2H), 2.94–2.75 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.7, 151.3, 137.9, 137.7, 136.7, 134.3, 133.8, 133.7, 133.5, 131.4, 129.0, 128.8, 128.3, 126.2, 124.8, 124.0, 121.4, 96.7, 91.0, 50.0, 44.7, 36.4; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 474.0538, found 474.0537; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 20.91 min and t_{minor} = 12.79 min.

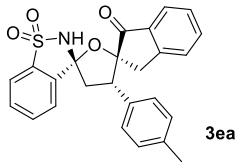
(2'*R*,3*R*,3'*S*)-3'-(4-bromophenyl)-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3da):



Yellow solid in 69% isolated yield (68 mg, 17:1 dr); m.p.: 198.6-199.7 ℃. $[\alpha]_D^{20}$ = +108 (c = 1.0, CH_2Cl_2, 93% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87–7.80 (m, 2H), 7.76–7.71 (m, 1H), 7.67 (t, *J* = 6.3 Hz, 2H), 7.55 (td, *J* = 7.5, 1.3 Hz, 1H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 7.7 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.31 (s, 1H), 4.26 (dd, *J* = 12.6, 6.7 Hz, 1H), 3.12–3.03 (m, 2H), 2.92–2.78 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.7, 151.3, 137.9, 137., 136.8, 134.4, 134.3, 133.5, 131.7, 131.4, 129.4, 128.3, 126.3, 124.9, 124.0, 121.8, 121.4, 96.7, 90.9, 50.0, 44.7, 36.4;

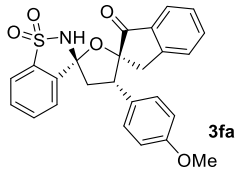
HRMS (ESI): m/z for $[M+Na]^+$: calcd 518.0033, found 518.0029; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 50.11 min and t_{minor} = 31.01 min.

(2'*R*,3*R*,3'*S*)-3'-(P-tolyl)-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3ea):



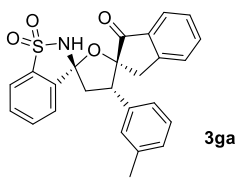
Yellow solid in 60% isolated yield (52 mg, >20:1 dr); m.p.: 115.3-117.1 ℃. $[\alpha]_D^{20}$ = +88 (c = 1.0, $CDCl_3$, 91% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 7.6, 4.1 Hz, 2H), 7.73 (d, *J* = 6.9 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 6.6 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 7.7 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.40 (s, 1H), 4.26 (dd, *J* = 13.1, 6.3 Hz, 1H), 3.15–3.03 (m, 2H), 2.93 (t, *J* = 12.7 Hz, 1H), 2.81 (dd, *J* = 12.2, 6.3 Hz, 1H), 2.25 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.3, 151.7, 138.0, 137.5, 137.5, 136.5, 134.4, 133.5, 132.2, 131.4, 129.3, 128.1, 127.6, 126.2, 124.8, 124.1, 121.37, 96.7, 91.2, 50.2, 44.8, 36.5, 21.0; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 454.1084, found 454.1070; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 14.84 min and t_{minor} = 10.16 min.

(2'*R*,3*R*,3'*S*)-3'-(4-Methoxyphenyl)-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3fa):



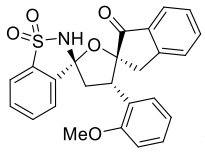
Yellow solid in 55% isolated yield (49 mg, >20:1 dr); m.p.: 158.8-160.2 ℃. $[\alpha]_D^{20}$ = 139 (c = 1.0, CH_2Cl_2, 88% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (t, *J* = 7.1 Hz, 2H), 7.73 (s, 1H), 7.66 (dd, *J* = 7.6, 2.9 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 7.7 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 6.40 (s, 1H), 4.24 (dd, *J* = 13.0, 6.3 Hz, 1H), 3.73 (s, 3H), 3.15–3.07 (m, 2H), 2.89 (t, *J* = 12.6 Hz, 1H), 2.80 (dd, *J* = 12.2, 6.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$)δ 206.3, 159.0, 151.6, 138.1, 137.6, 136.5, 134.4, 133.5, 131.3, 128.8, 128.1, 127.2, 126.2, 124.7, 124.1, 121.4, 113.9, 96.7, 91.4, 55.2, 50.0, 44.9, 36.4; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 470.1033, found 470.1037; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 30.85 min and t_{minor} = 15.29 min.

(2'*R*,3*R*,3'*S*)-3'-(M-tolyl)-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3ga):



Yellow solid in 47% isolated yield (40 mg, >20:1 dr); m.p.: 178.7-180.2 ℃. $[\alpha]_D^{20}$ = +76 (c = 1.0, CH_2Cl_2, 90% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.71–7.63 (m, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.07 (t, *J* = 8.2 Hz, 2H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 6.70 (s, 1H), 6.40 (s, 1H), 4.25 (dd, *J* = 13.1, 6.2 Hz, 1H), 3.12–3.02 (m, 2H), 2.94 (t, *J* = 12.7 Hz, 1H), 2.81 (dd, *J* = 12.2, 6.2 Hz, 1H), 2.16 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.3, 151.8, 138.3, 138.0, 137.5, 136.5, 135.2, 134.4, 133.5, 131.4, 128.7, 128.5, 128.4, 128.0, 126.2, 124.7, 124.7, 124.2, 121.4, 96.8, 91.4, 50.5, 44.5, 36.5, 21.3; **HRMS**. (ESI): m/z for $[M+Na]^+$: calcd 454.1084, found 454.1085; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 25.25 min and t_{minor} = 17.55 min

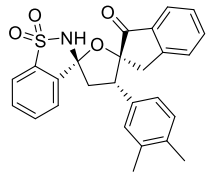
(2'*R*,3*R*,3'*S*)-3'-(2-Methoxyphenyl)-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3ha):



3ha

Yellow solid in 48% isolated yield (43 mg, >20:1 dr); m.p.: 170.2-171.5 ℃. $[\alpha]_D^{20}$ = +131 (c = 1.0, CH_2Cl_2, 93% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 10.7, 7.6 Hz, 2H), 7.67–7.63 (m, 1H), 7.61–7.55 (m, 2H), 7.45–7.40 (m, 1H), 7.32–7.27 (m, 1H), 7.16 (t, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.91 (t, *J* = 6.9 Hz, 1H), 6.64 (s, 1H), 6.51 (d, *J* = 8.0 Hz, 1H), 4.39 (dd, *J* = 13.6, 6.1 Hz, 1H), 3.01 (s, 3H), 2.95–2.83 (m, 3H), 2.69 (dd, *J* = 11.8, 6.2 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.6, 156.9, 151.3, 137.6, 137.5, 135.6, 134.5, 133.4, 131.3, 128.8, 127.6, 126.8, 126.1, 125.3, 124.6, 124.1, 121.4, 120.6, 109.7, 96.4, 90.6, 53.7, 44.6, 43.7, 36.8; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 470.1033, found 470.1038; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 27.43 min and t_{minor} = 23.21 min.

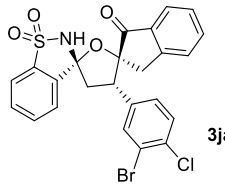
(2'*R*,3*R*,3'*S*)-3'-(3,4-Dimethylphenyl)-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3ia):



3ia

Yellow solid in 50% isolated yield (44 mg, >20:1 dr); m.p.: 172.5-173.8 ℃. $[\alpha]_D^{20}$ = +113 (c = 1.0, CH_2Cl_2, 90% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.7 Hz, 2H), 7.70 (t, *J* = 6.5 Hz, 2H), 7.66–7.61 (m, 1H), 7.53–7.48 (m, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.7 Hz, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.65 (s, 1H), 6.46 (s, 1H), 4.22 (dd, *J* = 13.2, 6.2 Hz, 1H), 3.08 (q, *J* = 17.1 Hz, 2H), 2.93 (t, *J* = 12.7 Hz, 1H), 2.78 (dd, *J* = 12.2, 6.2 Hz, 1H), 2.15 (s, 3H), 2.06 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.5, 151.9, 138.0, 137.4, 136.8, 136.4, 136.1, 134.4, 133.6, 132.6, 131.3, 129.7, 129.1, 128.0, 126.3, 125.0, 124.7, 124.2, 121.3, 96.7, 91.3, 50.1, 44.6, 36.5, 19.7, 19.4; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 468.1240, found 468.1243; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 28.54 min and t_{minor} = 17.48 min.

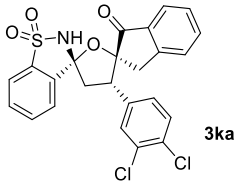
(2'*R*,3*R*,3'*S*)-3'-(3-Bromo-4-chlorophenyl)-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3ja):



3ja

Yellow solid in 60% isolated yield (64 mg, 11:1 dr); m.p.: 169.4-170.5 ℃. $[\alpha]_D^{20}$ = +153 (c = 1.0, CH_2Cl_2, 90% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85–7.82 (m, 2H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.70–7.65 (m, 2H), 7.57 (t, *J* = 8.2 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 1H), 6.78 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.35 (s, 1H), 4.22 (dd, *J* = 12.3, 6.9 Hz, 1H), 3.15–3.02 (m, 2H), 2.91–2.77 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.4, 151.1, 137.8, 137.6, 136.9, 135.7, 134.2, 134.0, 133.6, 132.8, 131.5, 130.3, 128.5, 127.9, 126.3, 124.9, 124.1, 122.8, 121.4, 96.7, 90.9, 49.6, 44.5, 36.4; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 551.9643, found 551.9648; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate =1mL/min, λ =254 nm, t_{major} = 57.68 min and t_{minor} = 28.21 min.

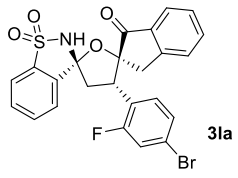
(2'*R*,3*R*,3'*S*)-3'-(3,4-Dichlorophenyl)-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3ka):



3ka

Yellow solid in 65% isolated yield (63 mg, >20:1 dr); m.p.: 188.4-189.3 ℃. $[\alpha]_D^{20}$ = +102 (c = 1.0, CH_2Cl_2, 86% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86–7.81 (m, 1H), 7.76–7.71 (m, 1H), 7.70–7.63 (m, 3H), 7.52 (d, *J* = 6.6 Hz, 1H), 7.22 (dd, *J* = 5.0, 1.9 Hz, 3H), 6.96 (dd, *J* = 6.4, 3.1 Hz, 2H), 6.29 (s, 1H), 4.29 (dd, *J* = 13.2, 6.3 Hz, 1H), 3.12–3.01 (m, 2H), 2.94 (t, *J* = 12.7 Hz, 1H), 2.83 (dd, *J* = 12.2, 6.3 Hz, 1H); **^{13}C NMR**(101 MHz, $CDCl_3$) δ 205.4, 151.1, 137.8, 137.6, 136.9, 135.6, 134.2, 133.6, 132.9, 132.0, 131.5, 130.5, 129.5, 128.4, 127.3, 126.3, 124.9, 124.1, 121.4, 96.6, 90.8, 49.7, 44.6, 36.4; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 508.0148, found 508.0152; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 56.74 min and t_{minor} = 26.59 min.

(2'*R*,3*R*,3'*S*)-3'-(4-Bromo-2-fluorophenyl)-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3la):

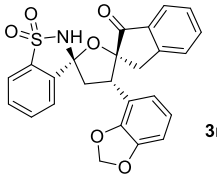


3la

Yellow solid in 80% isolated yield (82 mg, >20:1 dr); m.p.: 218.4-219.3 ℃. $[\alpha]_D^{20}$ = +176 (c =1.0, CH_2Cl_2, 94% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (t, *J* = 7.1 Hz, 2H), 7.75–7.62 (m, 3H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.19–7.09 (m, 2H), 7.02 (d, *J* = 11.5 Hz, 1H), 6.54 (s, 1H), 4.39 (dd, *J* = 13.3, 6.3 Hz, 1H), 3.17–2.94 (m, 3H), 2.78 (dd, *J* = 12.2, 6.3 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.99; **^{13}C NMR**(101 MHz, $CDCl_3$) δ 205.2, 160.8 (d, *J* = 251.8 Hz),150.7, 137.5, 136.5, 133.9, 133.6, 131.5, 130.0 (d, *J* = 4.7 Hz), 128.3, 127.8 (d, *J* = 3.6 Hz), 126.1, 125.0, 124.2, 122.5 (d, *J* = 14.8 Hz), 122.1 (d, *J* = 9.7 Hz), 121.3, 119.4 (d, *J* = 25.5 Hz), 96.6, 90.5, 44.5, 44.1, 36.6; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 535.9938, found 535.9942; **HPLC**: Daicel

Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 21.04 min and t_{minor} = 13.07 min.

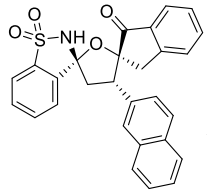
(2'*R*,3*R*,3'*S*)-3'-(Benzo[d][1,3]dioxol-4-yl)-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3ma):



3ma

Yellow solid in 51% isolated yield (47 mg, >20:1 dr); m.p.: 190.5-191.6 ℃. $[\alpha]_D^{20}$ = +88 (c = 1.0, CH_2Cl_2, 91% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85–7.78 (m, 2H), 7.72 (d, *J* = 6.6 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 8.1 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.47 (d, *J* = 1.4 Hz, 1H), 6.43–6.39 (m, 1H), 6.37 (s, 1H), 5.89 (dd, *J* = 12.8, 1.2 Hz, 2H), 4.22 (dd, *J* = 12.7, 6.6 Hz, 1H), 3.21–3.04 (m, 2H), 2.91–2.75 (m, 2H); **^{13}C NMR**(101 MHz, $CDCl_3$) δ 206.1, 151.7, 147.9, 147.1, 138.0, 137.5, 136.6, 134.3, 133.5, 131.4, 129.0, 128.2, 126.2, 124.8, 124.1, 121.4, 121.3, 108.3, 108.0, 101.2, 96.6, 91.1, 50.2, 45.0, 36.4; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 484.0826,found 484.0832; **HPLC**: Daicel Chiralpak IB,*n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 41.72 min and t_{minor} = 21.64 min.

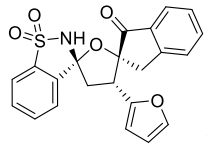
(2'*R*,3*R*,3'*S*)-3'-(Naphthalen-2-yl)-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3na):



3na

Yellow solid in 48% isolated yield (45 mg, >20:1 dr); m.p.: 224.7-226.1 ℃. $[\alpha]_D^{20}$ = +97 (c = 1.0, CH_2Cl_2, 90% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82–7.75 (m, 2H), 7.72–7.56 (m, 6H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.45 (s, 1H), 7.38 (t, *J* = 4.8 Hz, 3H), 7.30 (t, *J* = 7.7 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.86 (m, 1H), 6.35 (s, 1H), 4.41 (dd, *J* = 13.1, 6.1 Hz, 1H), 3.09–2.97 (m, 3H), 2.87 (dd, *J* = 12.2, 6.2 Hz, 1H); **^{13}C NMR**(101 MHz, $CDCl_3$) δ 206.1, 151.7, 138.0, 137.6, 136.6, 134.3, 133.5, 133.1, 133.1, 132.7, 131.4, 128.3, 128.1, 127.7, 127.6, 126.6, 126.4, 126.3, 126.2, 125.8, 124.9, 124.4, 121.4, 96.8, 91.2, 50.6, 44.8, 36.6; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 490.1084, found 490.1080; **HPLC**: Daicel Chiralpak IA, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 20.40 min and t_{minor} = 35.97 min.

(2'*R*,3*R*,3'*S*)-3'-(Furan-2-yl)-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3oa):

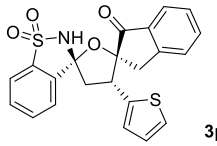


3oa

Yellow solid in 57% isolated yield (46 mg, 10:1 dr); m.p.: 122.5-124.3 ℃. $[\alpha]_D^{20}$ = +65 (c = 1.0, CH_2Cl_2, 93% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 2H), 7.73 (d, *J* = 6.7 Hz, 1H), 7.69–7.63 (m, 2H), 7.59–7.54 (m, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.12 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.84 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.58 (d, *J* = 3.6 Hz, 1H), 6.42 (s, 1H), 4.50–4.42 (m,

1H), 3.28–3.08 (m, 2H), 2.97 (dd, *J* = 12.2, 6.3 Hz, 1H), 2.86 (t, *J* = 12.6 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.8, 152.0, 138.5, 137.7, 137.5, 136.7, 134.1, 133.6, 131.4, 128.2, 127.1, 126.2, 126.1, 124.9, 124.8, 124.2, 121.3, 96.6, 91.3, 46.7, 46.3, 36.6; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 430.0720, found 430.0735; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 15.95 min and t_{minor} = 14.13 min.

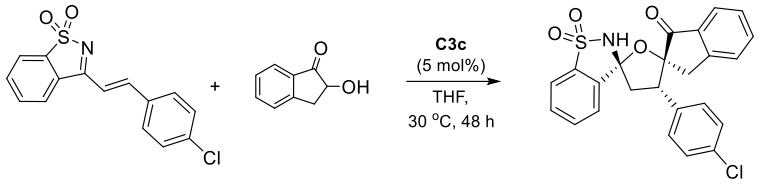
(2'*R*,3*R*,3'*R*)-3'-(Thiophen-2-yl)-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (3pa):



3pa

Brown solid in 63% isolated yield (53 mg, 10:1 dr); m.p.: 92.4-92.9 °C. $[\alpha]_D^{20}$ = + 90 (c = 1.0, CH_2Cl_2, 93% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.5 Hz, 2H), 7.74 (d, *J* = 9.1 Hz, 1H), 7.70–7.64 (m, 2H), 7.57 (t, *J* = 6.8 Hz, 1H), 7.42 (s, 1H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.08 (d, *J* = 2.2 Hz, 1H), 6.73 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.38 (s, 1H), 4.23 (dd, *J* = 12.5, 6.8 Hz, 1H), 3.09 (q, *J* = 17.2 Hz, 2H), 2.94–2.76 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.7, 152.0, 138.6, 137.7, 137.6, 136.7, 134.2, 133.6, 131.4, 128.2, 127.1, 126.2, 126.1, 124.9, 124.7, 124.1, 121.4, 96.6, 91.3, 46.7, 46.3, 36.6; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 446.0492, found 446.0995; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 14.95 min and t_{minor} = 13.13 min.

Gram-scale reaction and derivations of adducts



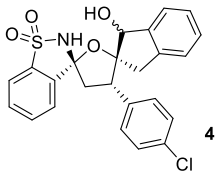
1c (4 mmol, 1.21 g) **2a** (5 mmol, 0.74 g) **3ca** (>20/1 Dr) (66% yield, 92% ee)

Under a nitrogen atmosphere, a solution of diethylzinc (400 μL, 1.0 M in hexane, 0.8 mmol) was added dropwise to a solution of **L3c** (0.2 mmol) in THF (10 mL). After the mixture was stirred for 30 min at room temperature, then, cyclic 1-azadienes **1c** (4.0 mmol) and α-hydroxy-1-indanone **2a** (5.0 mmol) were added. The reaction mixture was stirred for 36 h at the 36℃. The reaction was quenched with HCl solution (1 M, 2 mL), and the organic layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure by using a rotary evaporator. The residue was purified by flash chromatography with petroleum ether/ethyl acetate (4/1) to afford the desired product 1.19g of **3ca**.

Transformation of 3ca to 4

Sodium borohydrside (15 mg, 0.4 mmol, 4 equiv.) was added to a solution of **3ca** (45 mg, 0.1 mmol) in methanol (3 mL) at 0 °C. Then, the resulting reaction mixture was stirred at room temperature for 30 minutes. Saturated aqueous NH_4Cl (3 mL) was then added to quench the reaction. The organic layer was extracted with DCM (3 x 5 mL), then washed with brine, dried over MgSO4 and concentrated under reduced pressure. The crude reaction mixture was purified via column chromatography (petroleum ether/ethyl acetate =1/1) on silica gel to afford pure product **4** as a white solid in 91% yield.

(2'*R*,3*R*,3'*S*)-3'-(4-Chlorophenyl)-1''-hydroxy-1'',3',3'',4'-tetrahydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-indene] 1,1-dioxide (4)



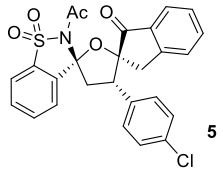
4

Yellow solid in 91% isolated yield (41 mg, >20:1 dr); m.p.: 145.7-147.1 ℃. $[\alpha]_D^{20}$ = +149 (c = 1.0, CH_2Cl_2, 91% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.42–7.38 (m, 1H), 7.27 (t, *J* = 7.7 Hz, 1H), 7.22–7.20 (m, 1H), 7.07 (t, *J* = 8.2 Hz, 1H), 7.02 (d, *J* = 5.9 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.88 (s, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.11 (d, *J* = 2.5 Hz, 1H), 4.92–4.90 (m, 1H), 4.83 (s, 1H), 3.07–3.04 (m, 1H), 2.87 (d, *J* = 17.2 Hz, 1H), 2.69–2.63 (m, 1H), 2.52–2.44 (m, 2H), 1.97 (d, *J* = 17.2 Hz, 1H), 1.74 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.8, 141.4, 140.8, 138.5, 135.4, 132.3, 132.2, 130.3, 129.7, 129.0, 128.2, 127.7, 126.3, 125.9, 124.7, 120.9, 85.3, 81.2, 57.5, 44.8, 43.2, 36.1; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 476.0694, found 476.0683; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 6.74 min and t_{minor} = 8.28 min.

Transformation of 3ca to 5

To a stirred solution of **3ca** (45 mg, 0.1 mmol, 1.0 equiv) and triethylamine (40 uL, 0.3 mmol, 3.0 equiv) in CH_2Cl_2 (3 mL), DMAP (1.2 mg, 0.01 mmol, 0.1 equiv), Acetic anhydride (11 uL, 0.12 mmol, 1.2 equiv) was added at 0 ° C. The reaction mixture was stirred at this temperature for 30 min and further stirred at room temperature for 6 h. Saturated aqueous NH_4Cl (3 mL) was then added to quench the reaction and extracted with CH_2Cl_2 (3 x 10 mL). Drying (Na_2SO_4) and concentrated under reduced pressure. The crude reaction mixture was purified via column chromatography (petroleum ether/ethyl acetate =6/1) on silica gel to afford pure product **5** as a white solid in 81% yield.

(2'*R*,3*R*,3'*S*)-2-Acetyl-3'-(4-chlorophenyl)-3',4'-dihydro-2*H*-dispiro[benzo[*d*]isothiazole-3,5'-furan-2',2''-inden]-1''(3''*H*)-one 1,1-dioxide (5)



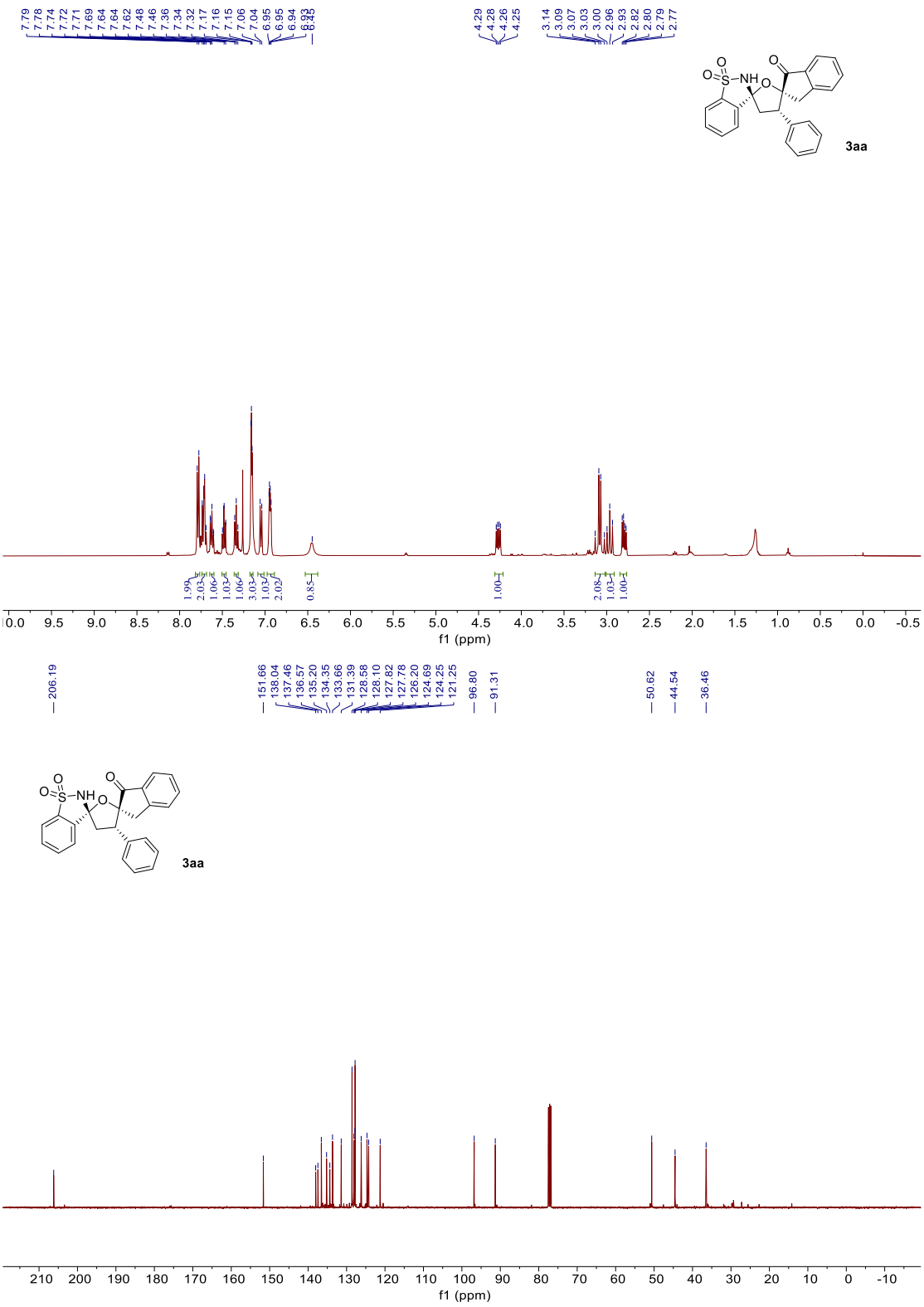
5

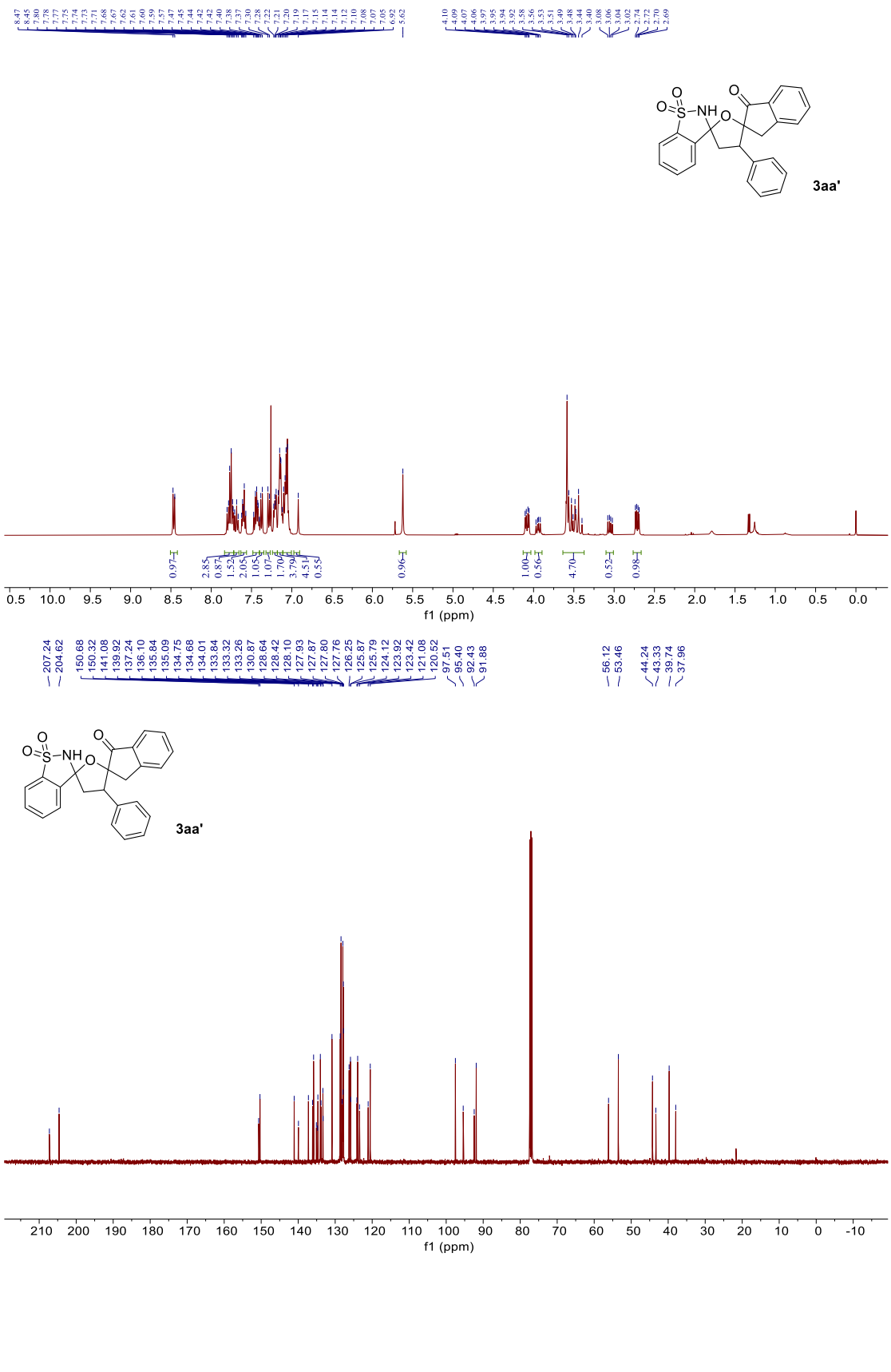
Yellow solid in 81% isolated yield (40 mg, >20:1 dr); m.p.: 144.5-146.1 ℃. $[\alpha]_D^{20}$ = +131 (c = 1.0, CH_2Cl_2, 92% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.0 Hz, 1H), 7.95 (t, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 7.0 Hz, 1H), 7.71 (t, *J* = 8.1 Hz, 2H), 7.49 (t, *J* = 8.1 Hz, 1H), 7.34–7.28 (m, 1H), 7.16 (d, *J* = 8.5 Hz, 3H), 7.09 (d, *J* = 8.6 Hz, 2H), 4.54 (dd, *J* = 13.2, 8.7 Hz, 1H), 3.97 (t, *J* = 13.3 Hz, 1H), 3.37 (m, 2H), 2.81–2.67 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.1, 168.0, 152.9, 139.2, 136.4, 135.5, 134.2, 134.0, 133.6, 131.2, 131.0, 129.6, 128.7, 127.7, 126.4, 125.7, 124.2, 120.6, 98.8, 92.0, 50.9, 40.9, 37.6, 24.9; **HRMS** (ESI): m/z for $[M+Na]^+$: calcd 516.0643, found 516.0645; **HPLC**: Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 7.52 min and t_{minor} = 25.80 min

References

1. R. A. Abramovitch, I. Shinkai, B. J. Mavunkel, K. M. More, S. O'Conner, G. H. Ooi, W. T. Pennington, P. C. Srinivasan and J. R. Stowers, *Tetrahedron*, 1996, **52**, 3339.
2. K. Matsuo and M. Shindo, *Org. Lett.*, 2010, **12**, 5346.

NMR Spectra of compounds

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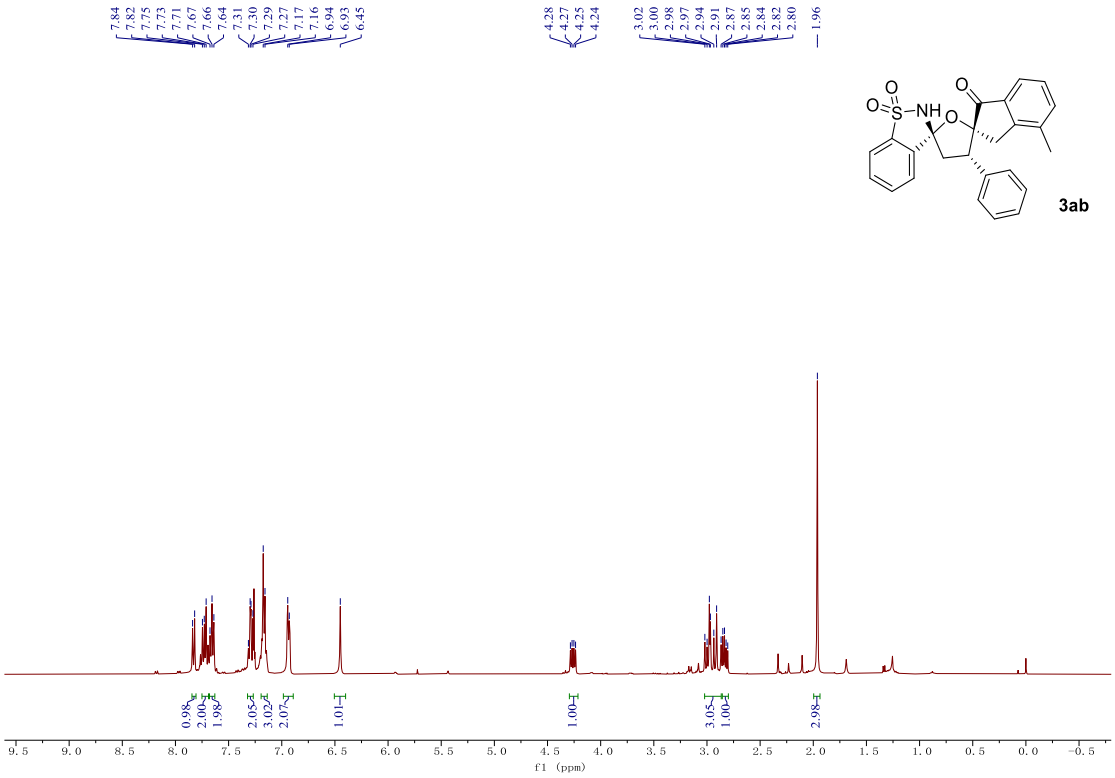
f1 (ppm)
3aa'
f1 (ppm)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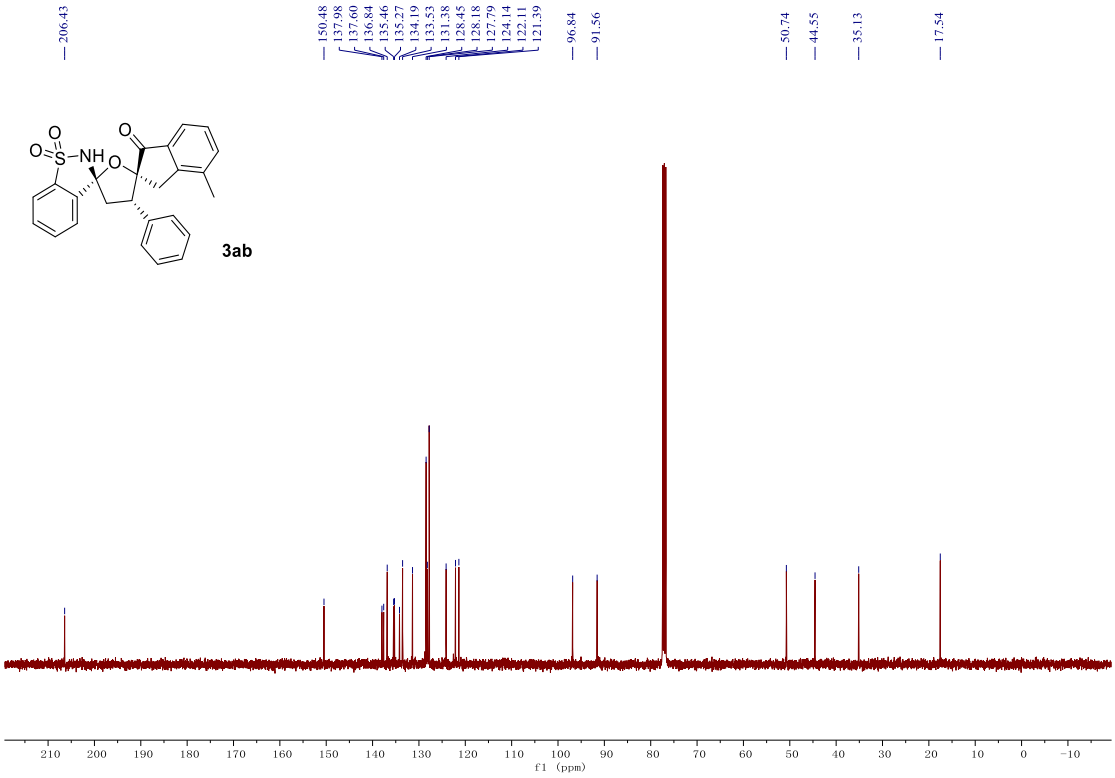
2.98
f1 (ppm)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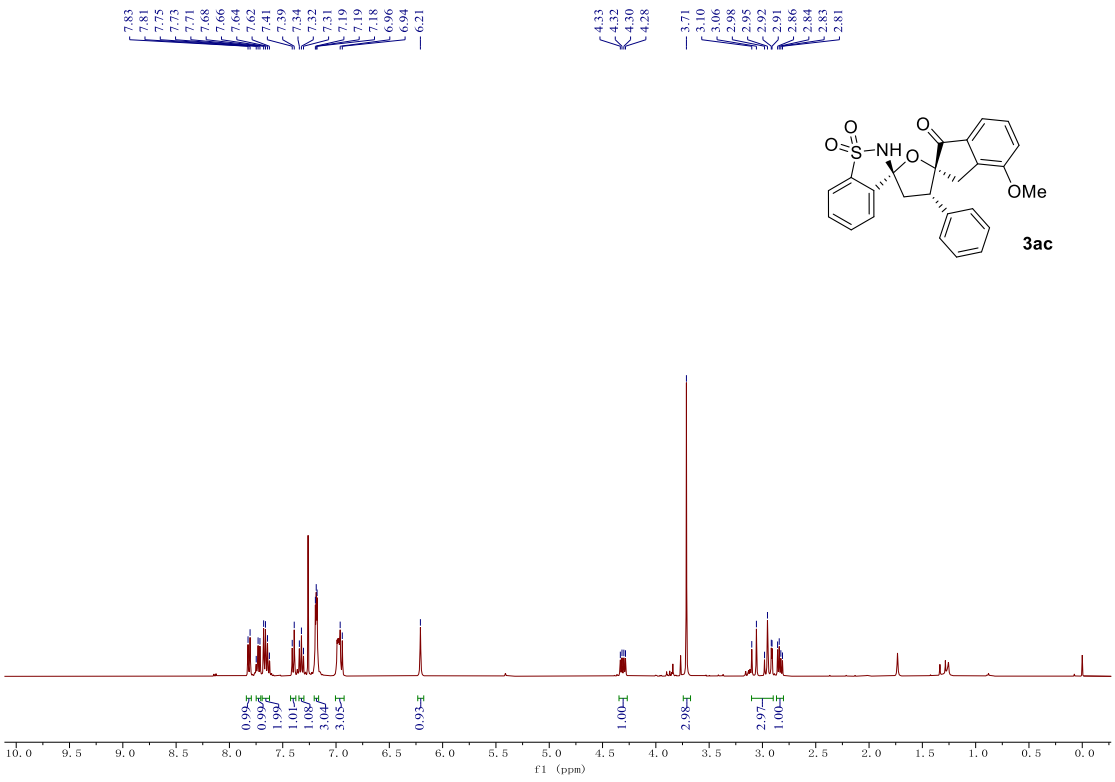
150.48
137.98
137.60
136.84
135.46
135.27
134.19
133.53
131.38
128.45
128.18
127.79
124.14
122.11
121.39
96.84
91.56
50.74
44.55
35.13
17.54
3ab
f1 (ppm)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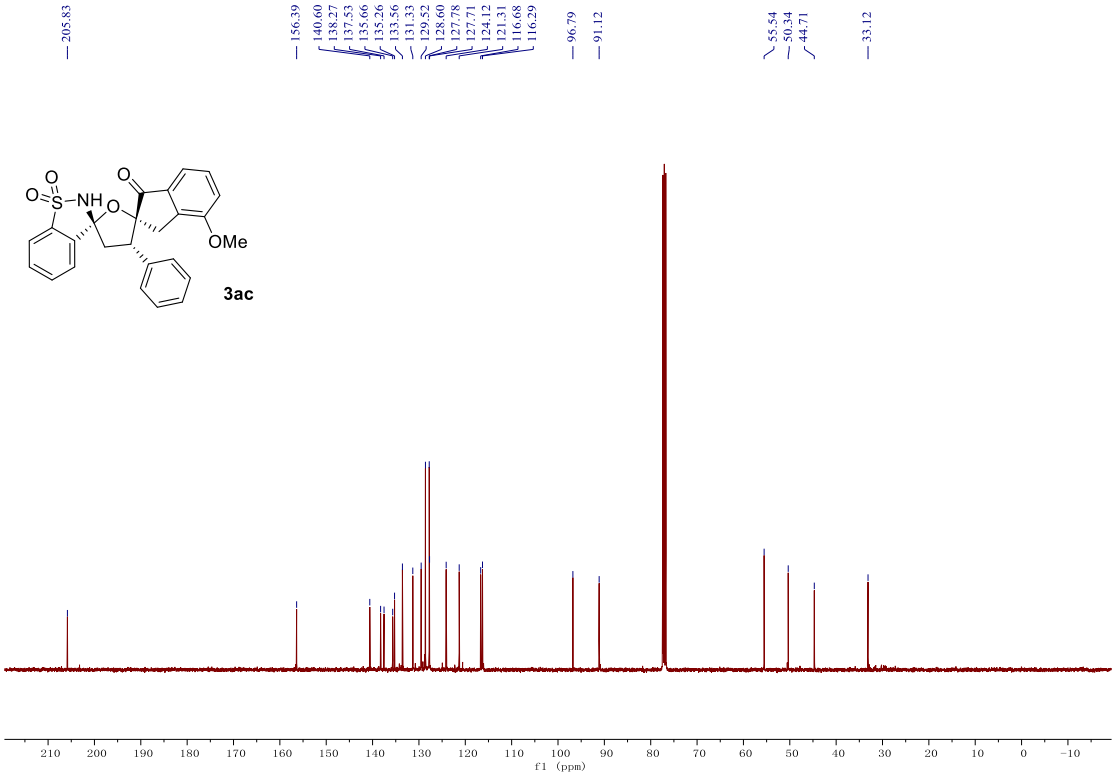
7.81
7.75
7.73
7.71
7.68
7.66
7.64
7.62
7.41
7.39
7.34
7.32
7.31
7.19
7.19
7.18
6.96
6.94
6.21
4.33
4.32
4.30
4.28
3.71
3.10
3.06
2.98
2.95
2.92
2.91
2.86
2.84
2.83
2.81
O
O=S–NH
O
OMe
3ac
0.99
0.99
1.99
1.01
1.08
3.04
3.05
0.93
1.00
2.98
2.97
1.00
f1 (ppm)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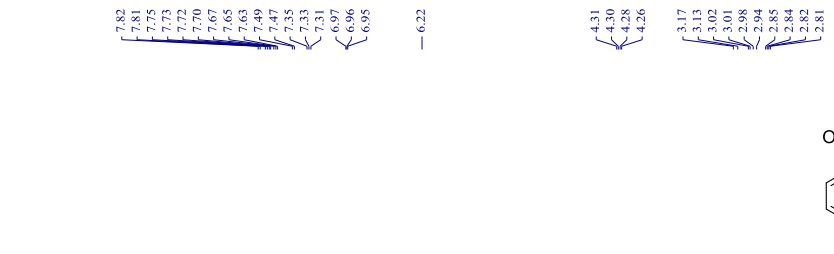
133.56
131.33
129.52
128.60
127.78
127.71
124.12
121.31
116.68
116.29
96.79
91.12
55.54
50.34
44.71
33.12
O
O=S–NH
O
OMe
3ac
f1 (ppm)


7.82
7.81
7.75
7.73
7.72
7.70
7.67
7.65
7.63
7.49
7.47
7.35
7.33
7.31
6.97
6.96
6.95
6.22
4.31
4.30
4.28
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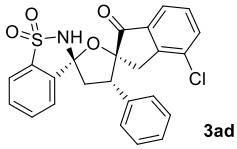
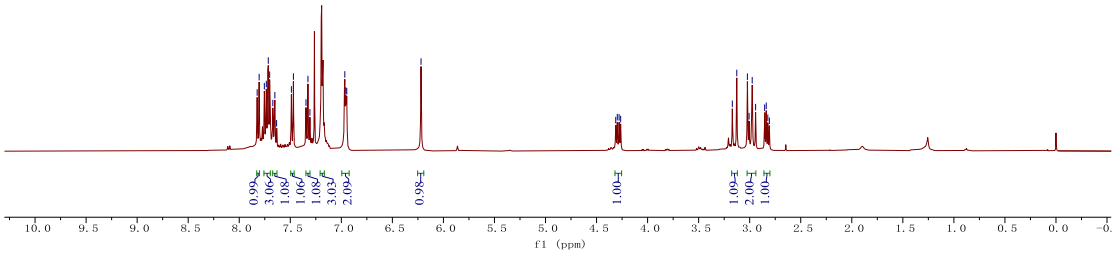
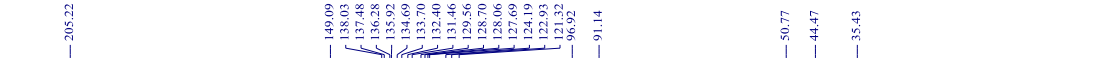
3.17
3.13
3.02
3.01
2.98
2.94
2.85
2.84
2.82
2.81


O
O=S-NH
O
O
Cl

3ad


0.99
3.06
1.08
1.06
1.08
3.03
2.09
0.98
1.00
1.09
2.00
1.00
f1 (ppm)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138.03
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135.92
134.69
133.70
132.40
131.46
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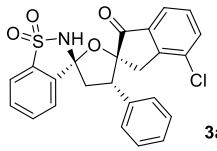
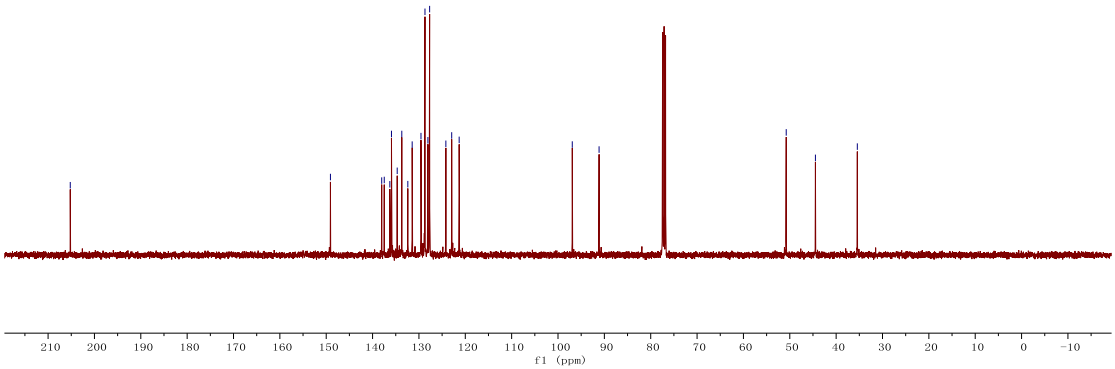
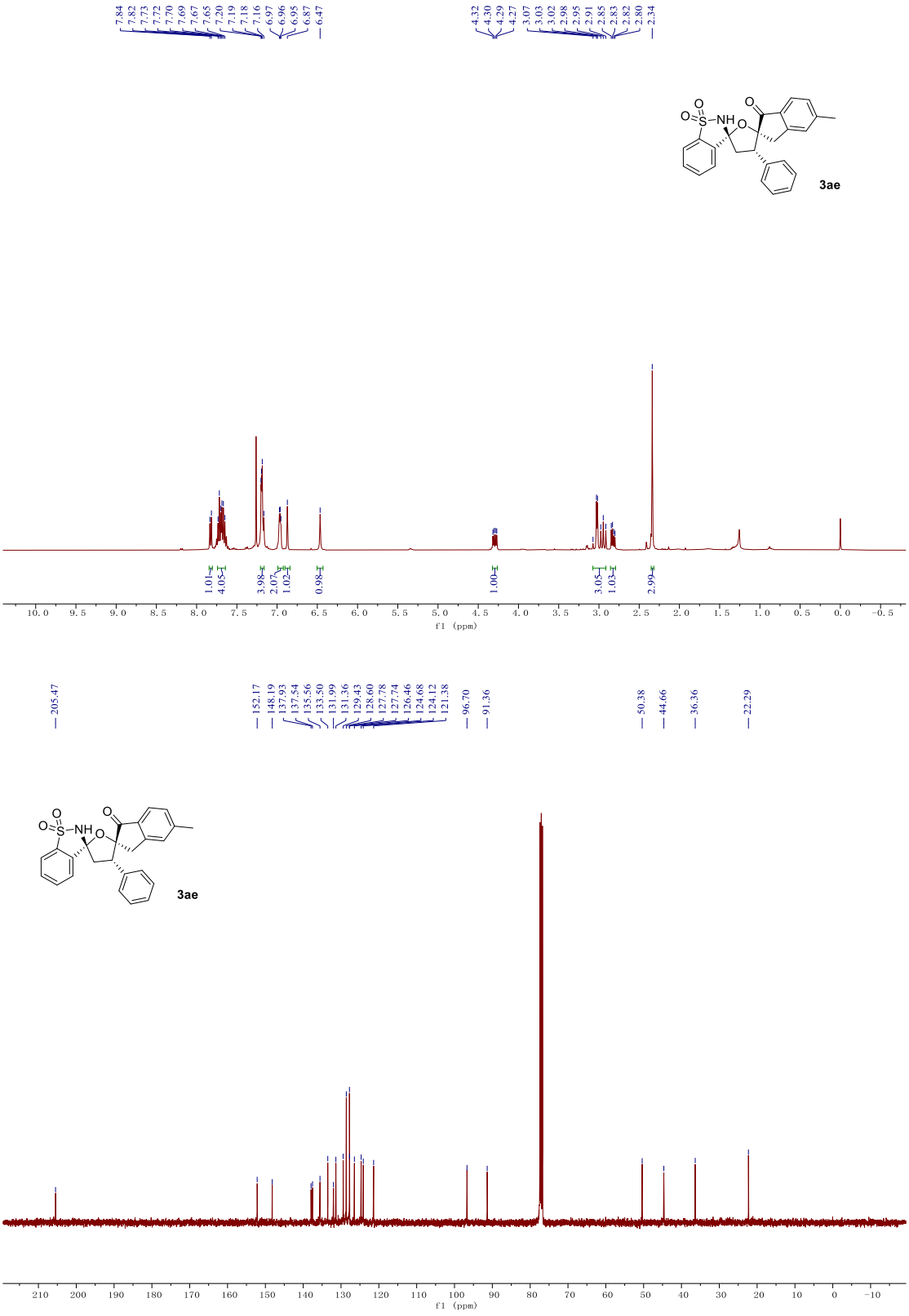
121.32
96.92
91.14
50.77
44.47
35.43


O
O=S-NH
O
O
Cl

3ad


f1 (ppm)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7.82
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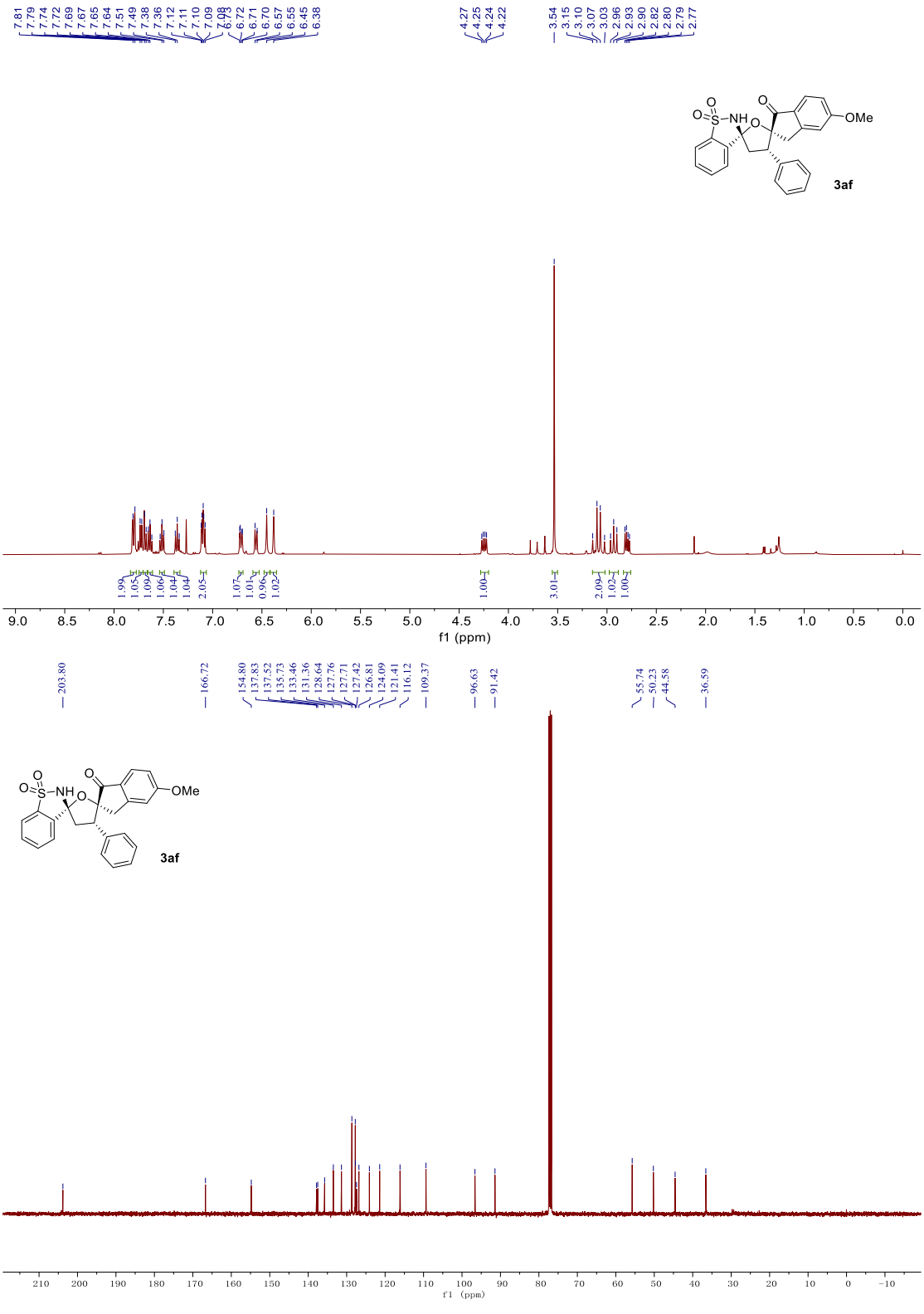
7.69
7.67
7.65
7.20
7.19
7.18
7.16
6.97
6.96
6.95
6.87
6.47
4.32
4.30
4.29
4.27
3.07
3.03
3.02
2.98
2.95
2.91
2.85
2.83
2.82
2.80
2.34
3ae
1.01
4.05
3.98
2.07
1.02
0.98
1.00
3.05
1.03
2.99
f1 (ppm)
205.47
152.17
148.19
137.93
137.54
135.56
133.50
131.99
131.36
129.43
128.60
127.78
127.74
126.46
124.68
124.12
121.38
96.70
91.36
50.38
44.66
36.36
22.29
3ae
f1 (ppm)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7.79
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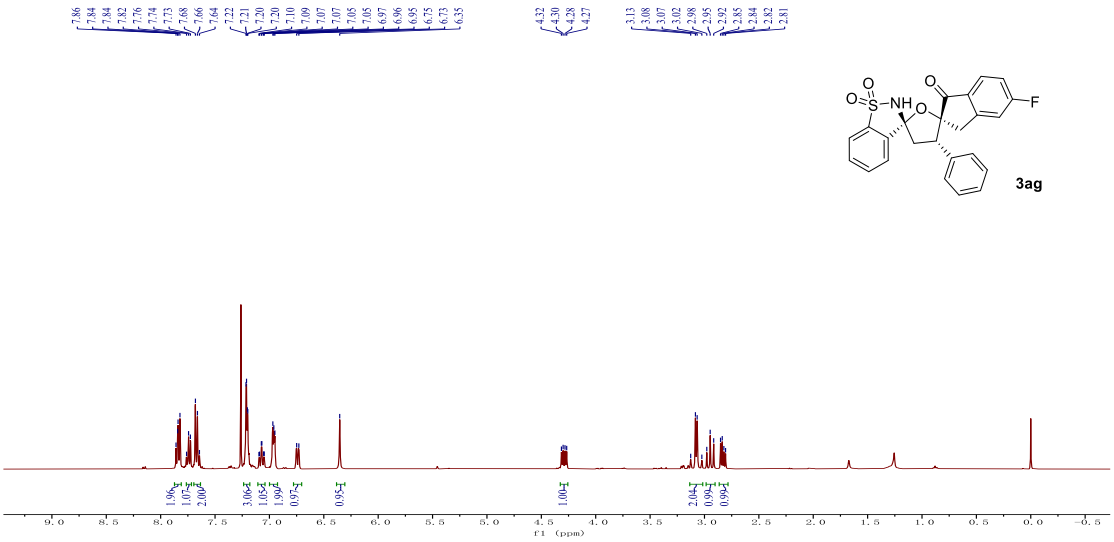
7.67
7.65
7.64
7.51
7.49
7.38
7.36
7.12
7.11
7.10
7.09
6.73
6.72
6.71
6.70
6.57
6.55
6.45
6.38
4.27
4.25
4.24
4.22
3.54
3.15
3.10
3.07
3.03
2.96
2.93
2.90
2.82
2.80
2.79
2.77
OMe
3af
1.99
1.05
1.09
1.06
1.04
1.04
2.05
1.07
1.01
0.96
1.02
1.00
3.01
2.09
1.02
1.00
f1 (ppm)
203.80
166.72
154.80
137.83
137.52
135.73
133.46
131.36
128.64
127.76
127.71
127.42
126.81
124.09
121.41
116.12
109.37
96.63
91.42
55.74
50.23
44.58
36.59
OMe
3af
f1 (ppm)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7.84
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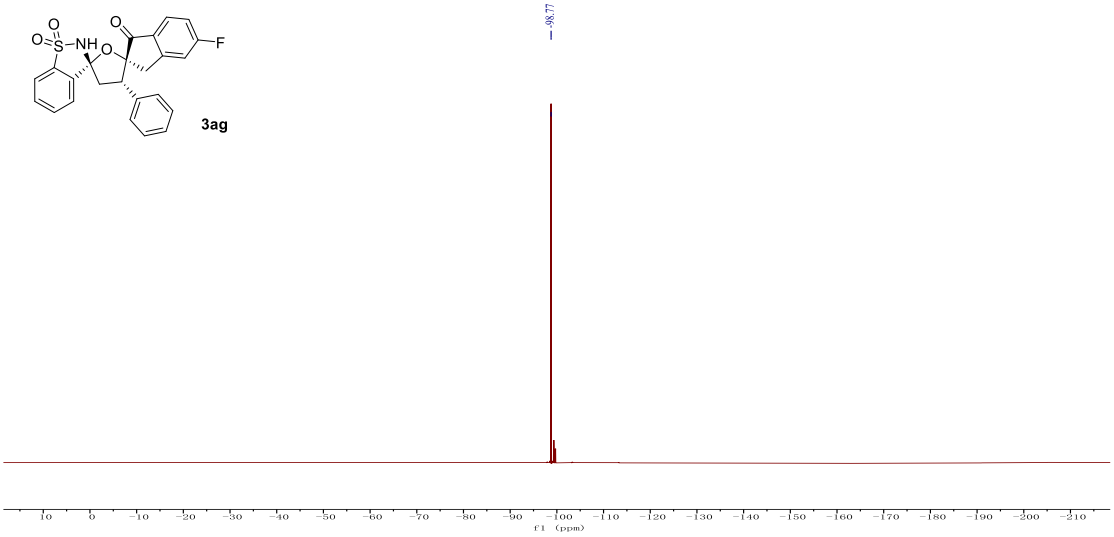
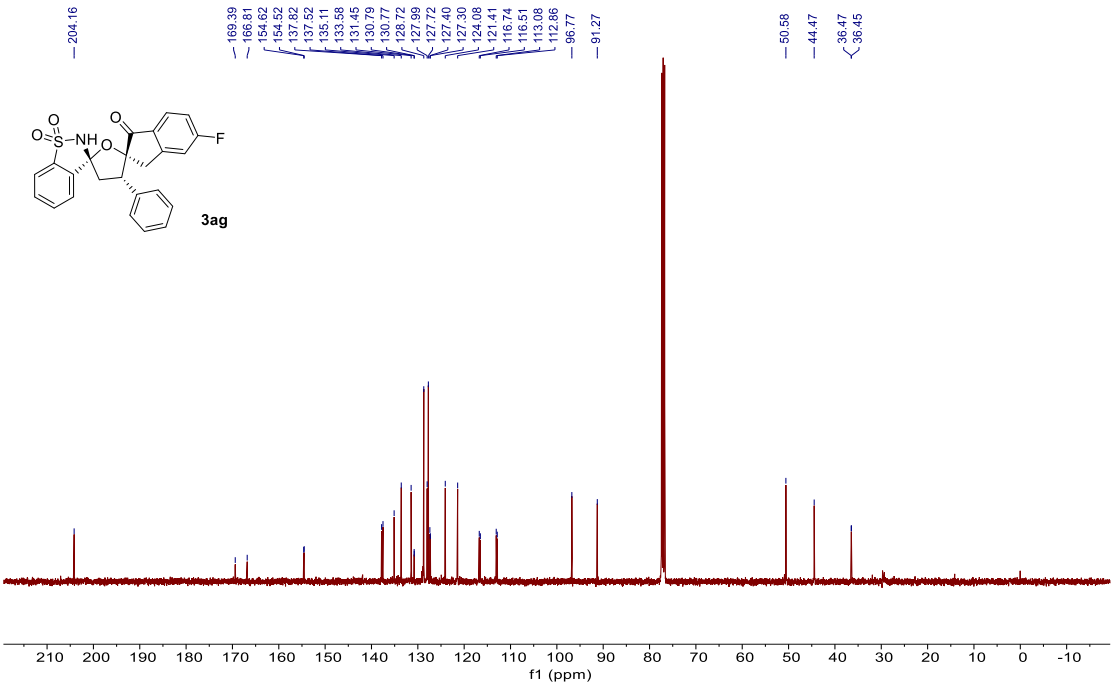
7.73
7.68
7.66
7.64
7.22
7.21
7.20
7.20
7.10
7.09
7.07
7.07
7.05
7.05
6.97
6.96
6.95
6.75
6.73
6.35
4.32
4.30
4.28
4.27
3.13
3.08
3.07
3.02
2.98
2.95
2.92
2.85
2.84
2.82
2.81
O
O
S
NH
O
O
F
3ag
1.96
1.07
2.00
3.06
1.05
1.90
0.97
0.95
1.00
2.04
0.99
0.99
f1 (ppm)


O
O
S
NH
O
O
F
3ag
-98.77
f1 (ppm)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169.39
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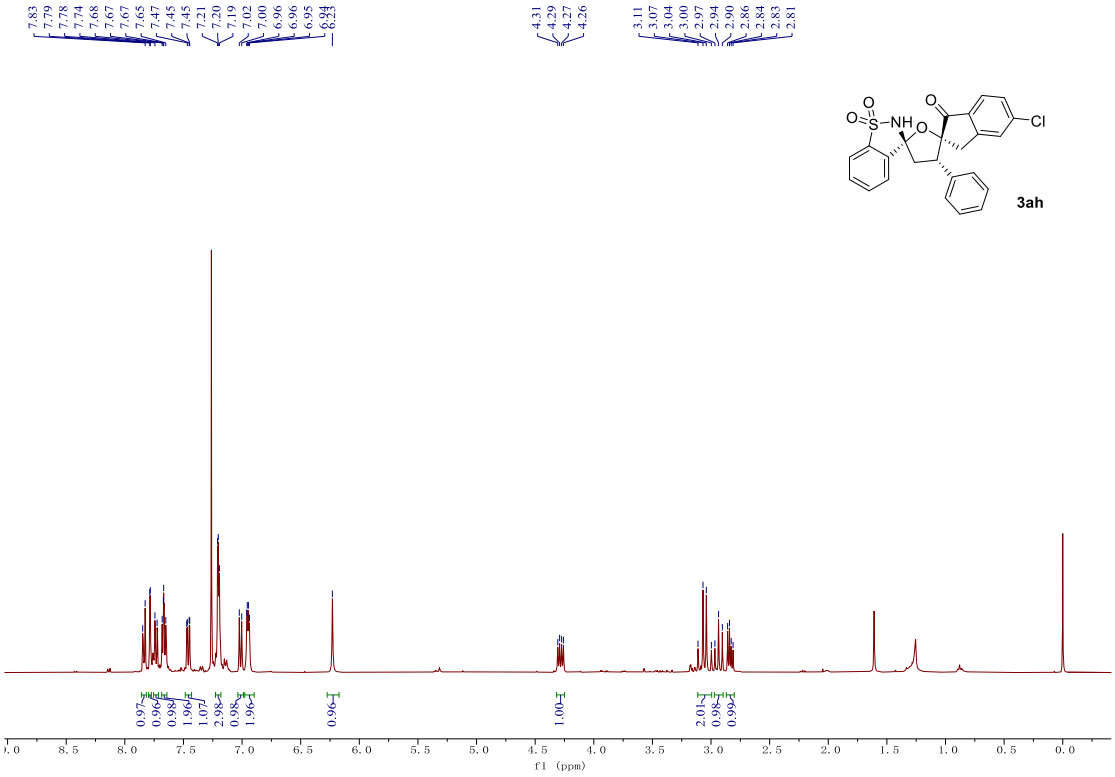
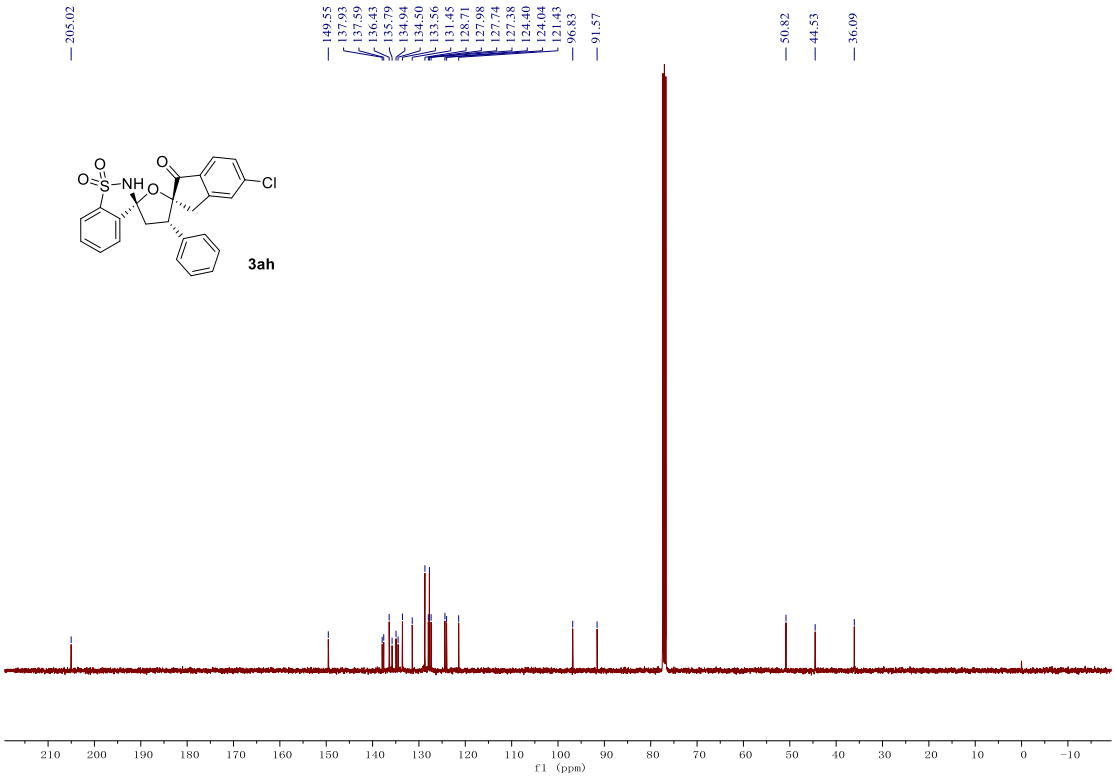
154.52
137.82
137.52
135.11
133.58
131.45
130.79
130.77
128.72
127.99
127.72
127.40
127.30
124.08
121.41
116.74
116.51
113.08
112.86
96.77
91.27
50.58
44.47
36.47
36.45
O
O
S
NH
O
O
F
3ag
f1 (ppm)


7.83
7.79
7.78
7.74
7.68
7.67
7.67
7.65
7.47
7.45
7.45
7.21
7.20
7.19
7.02
7.00
6.96
6.96
6.95
6.94
6.93
4.31
4.29
4.27
4.26
3.11
3.07
3.04
3.00
2.97
2.94
2.90
2.86
2.84
2.83
2.81
O
O=S–NH
O
O
Cl
3ah
0.97
0.96
0.98
1.96
1.07
2.98
0.98
1.96
0.96
1.00
2.01
0.98
0.99
f1 (ppm)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136.43
135.79
134.94
134.50
133.56
131.45
128.71
127.98
127.74
127.38
124.40
124.04
121.43
96.83
91.57
50.82
44.53
36.09
O
O=S–NH
O
O
Cl
3ah
f1 (ppm)


7.86
7.84
7.82
7.74
7.72
7.68
7.66
7.64
7.22
7.21
7.20
7.20
7.10
7.09
7.07
7.07
7.05
7.05
6.97
6.97
6.96
6.95
6.75
6.73
6.73
6.37
4.31
4.30
4.28
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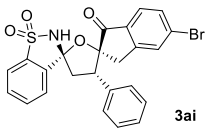
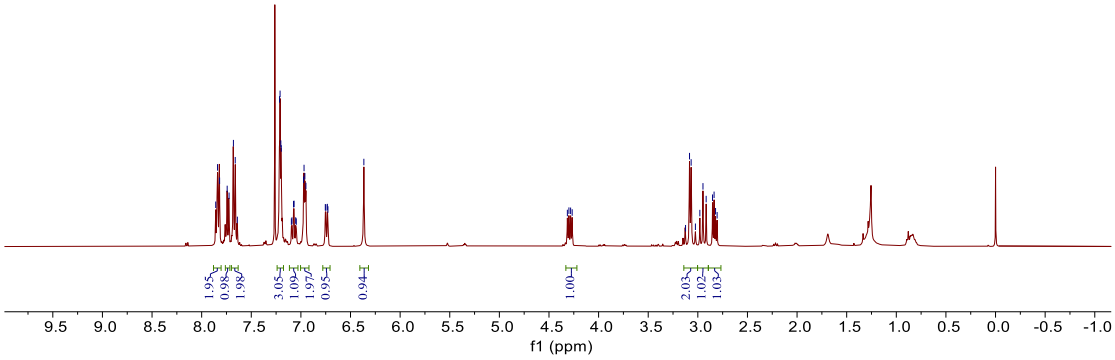
2.95
2.92
2.85
2.84
2.82
2.81


O
O
S
NH
O
O
Br

3ai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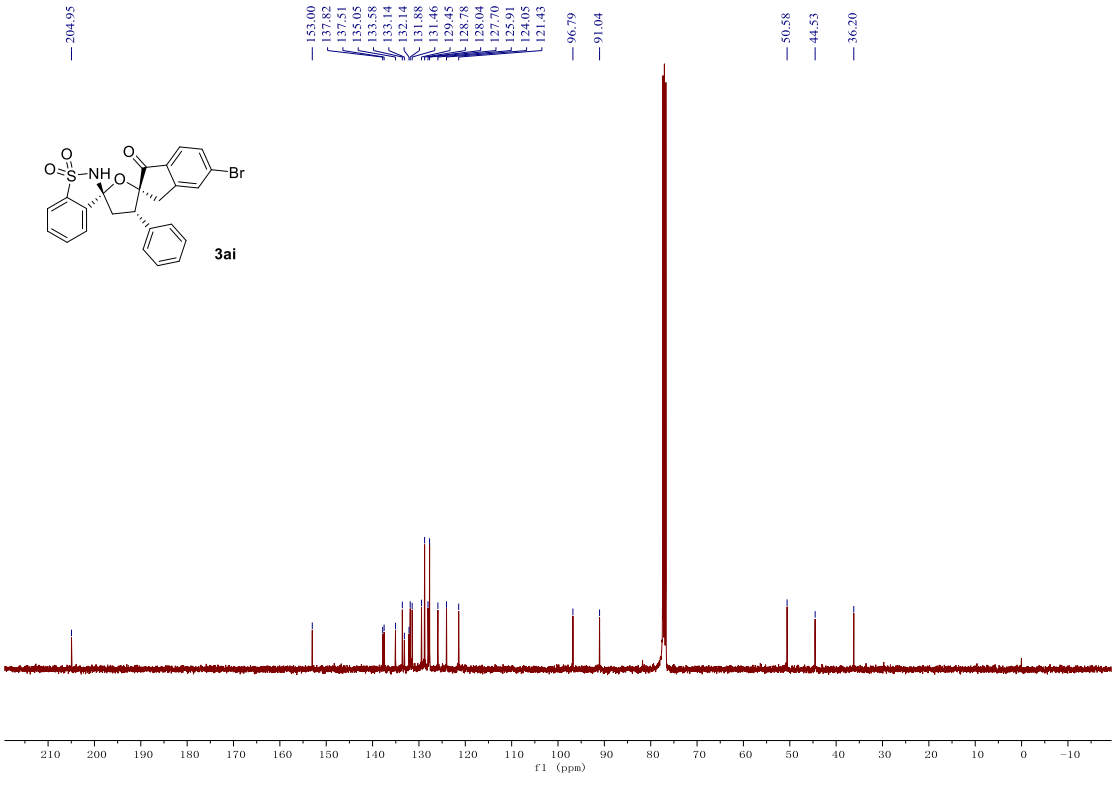
0.98
1.98
3.05
1.09
1.97
0.95
0.94
1.00
2.03
1.02
1.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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133.58
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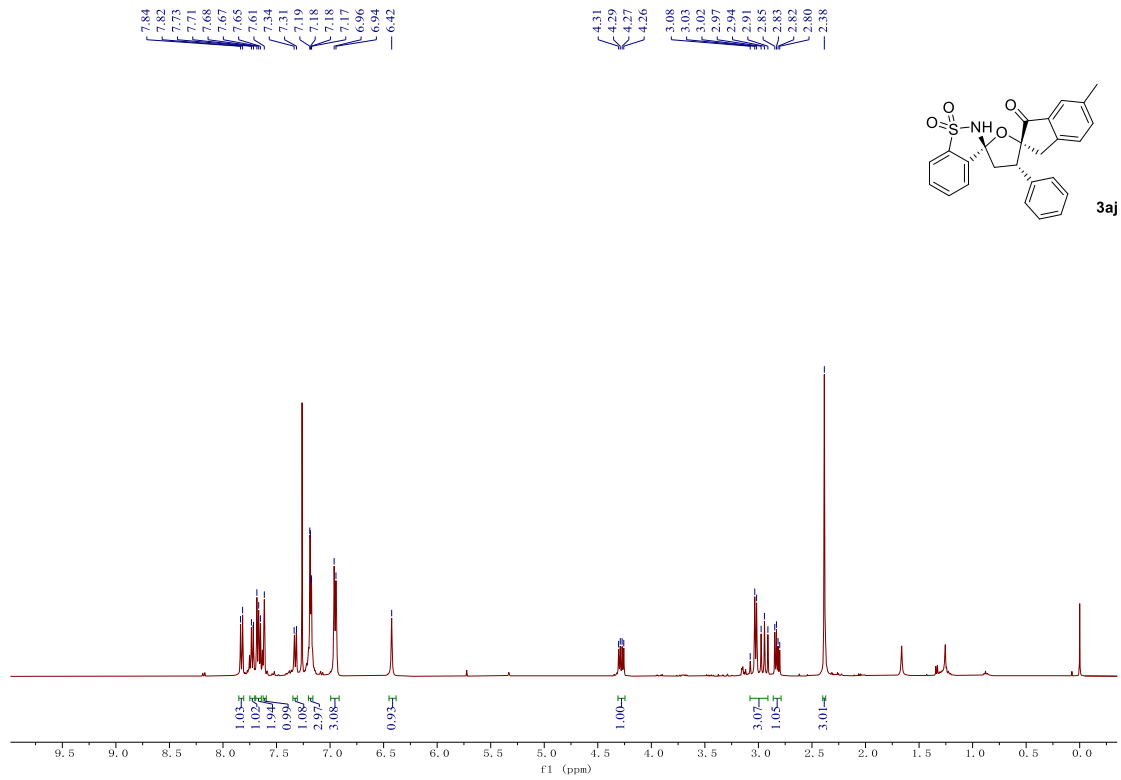
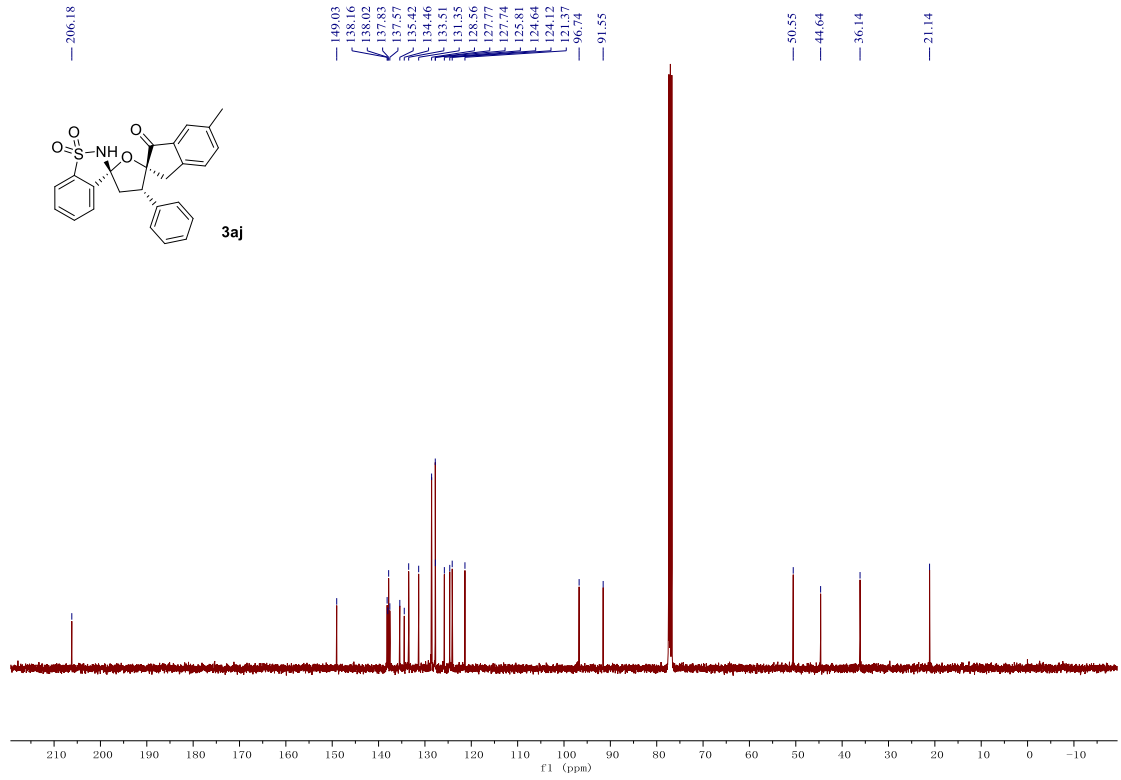
132.14
131.88
131.46
129.45
128.78
128.04
127.70
125.91
124.05
121.43
96.79
91.04
50.58
44.53
36.20
O
O
S
NH
O
O
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3ai


7.84
7.82
7.73
7.71
7.68
7.67
7.65
7.61
7.34
7.31
7.19
7.18
7.18
7.17
6.96
6.94
6.42
4.31
4.29
4.27
4.26
3.08
3.03
3.02
2.97
2.94
2.91
2.85
2.83
2.82
2.80
2.38
3aj
1.03
1.02
1.94
0.99
1.08
2.97
3.08
0.93
1.00
3.07
1.05
3.01
f1 (ppm)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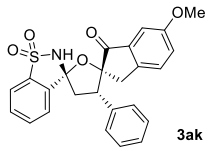
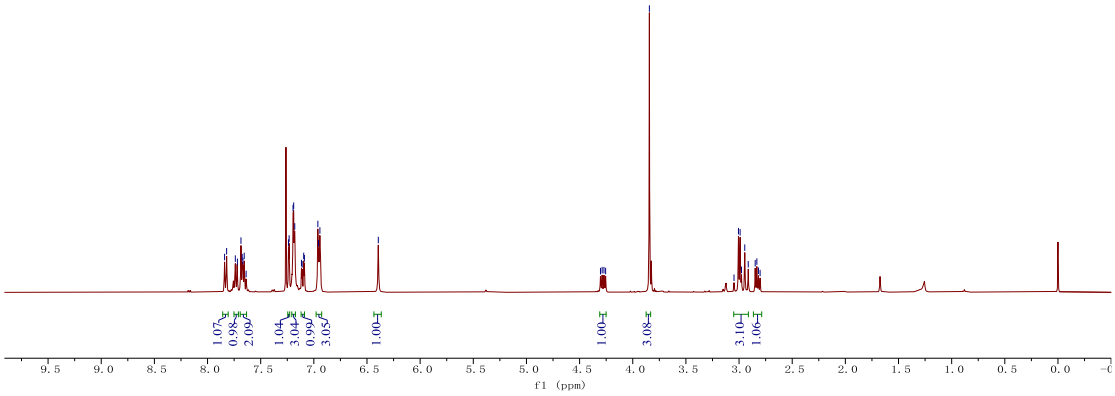
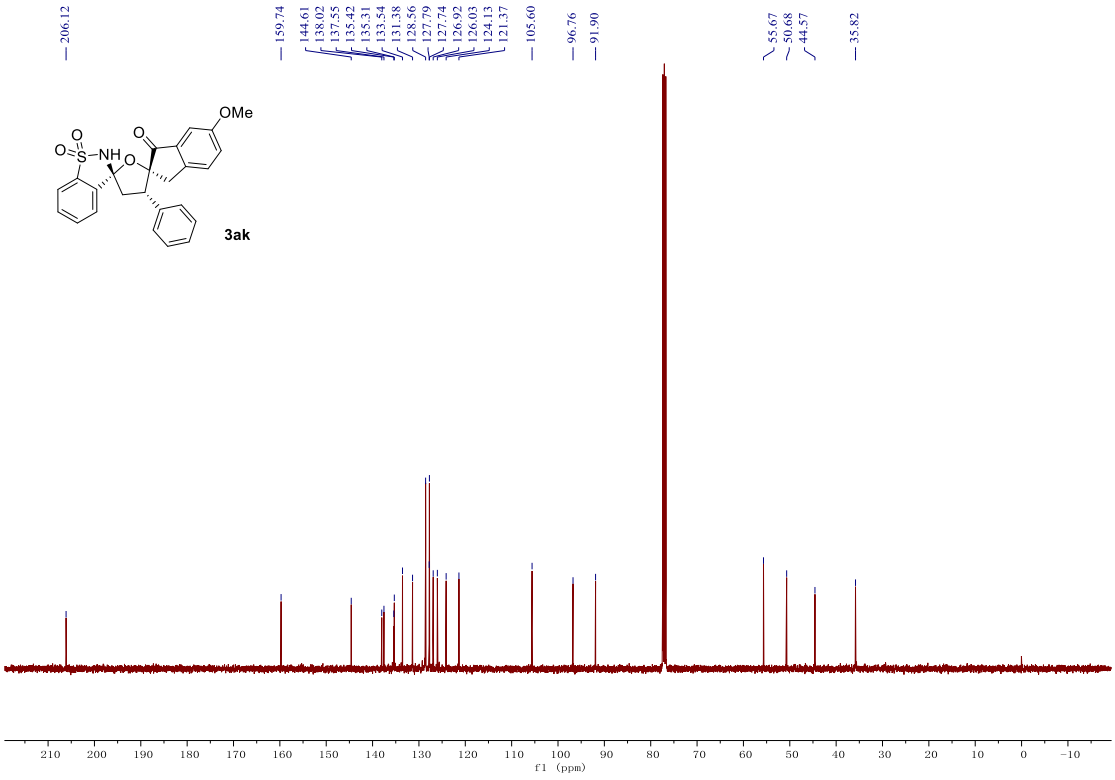
138.02
137.83
137.57
135.42
134.46
133.51
131.35
128.56
127.77
127.74
125.81
124.64
124.12
121.37
96.74
91.55
50.55
44.64
36.14
21.14
3aj
f1 (ppm)


7.84
7.82
7.74
7.72
7.69
7.67
7.67
7.66
7.64
7.24
7.23
7.20
7.19
7.18
7.12
7.11
7.10
7.09
6.96
6.96
6.94
6.39
4.30
4.29
4.27
4.26
3.84
3.05
3.01
2.99
2.98
2.95
2.91
2.85
2.83
2.82
2.80


OMe
O
O
S
NH
O
O

3ak


1.07
0.98
2.09
1.04
3.04
0.99
3.05
1.00
1.00
3.08
3.10
1.06
f1 (ppm)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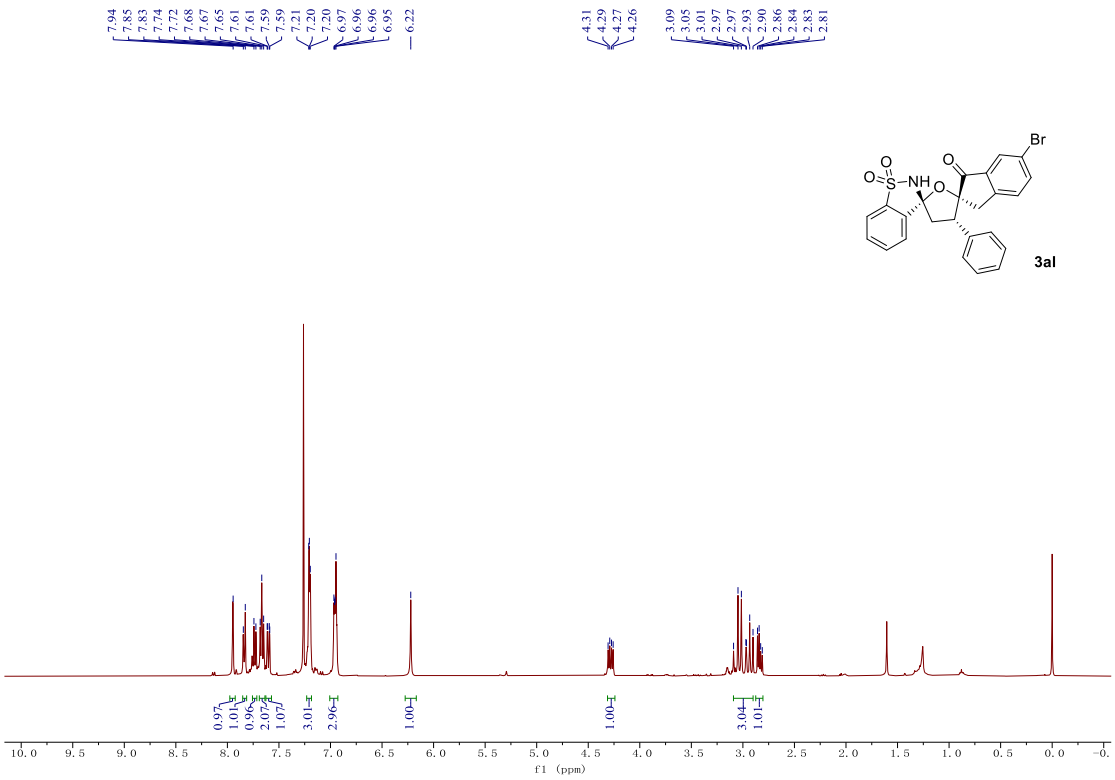
144.61
138.02
137.55
135.42
135.31
133.54
131.38
128.56
127.79
127.74
126.92
126.03
124.13
121.37
105.60
96.76
91.90
55.67
50.68
44.57
35.82
f1 (ppm)

OMe
O
O
S
NH
O
O

3ak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7.85
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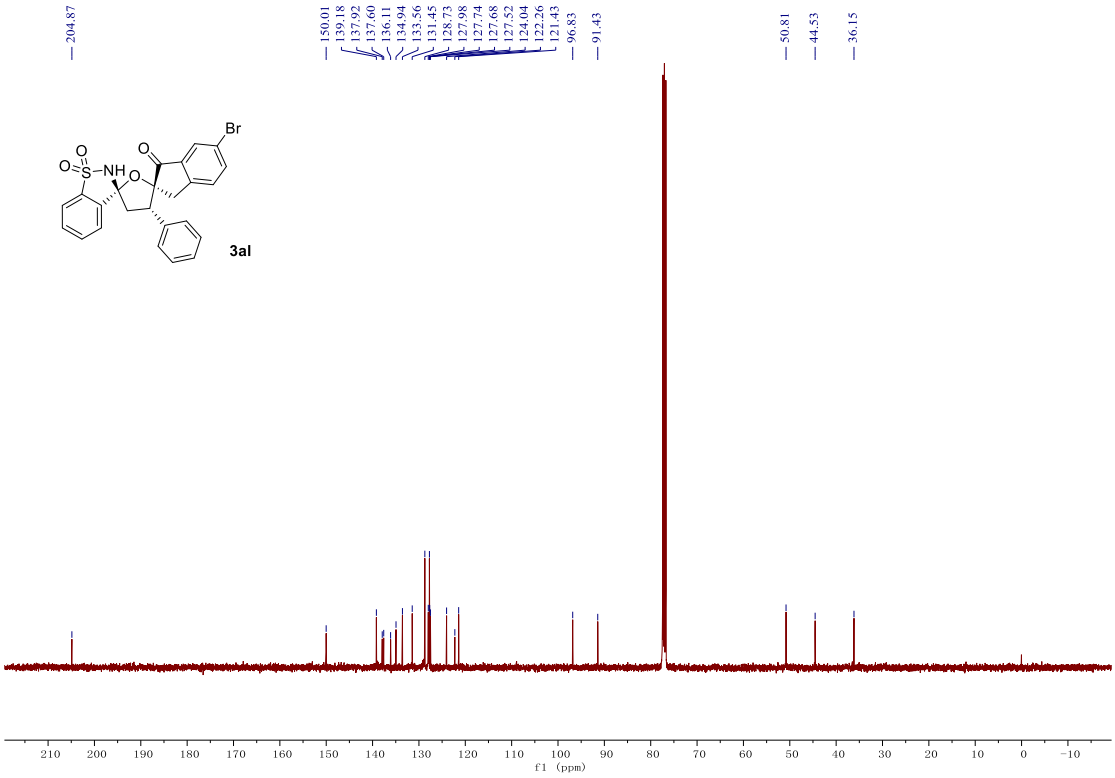
7.74
7.72
7.68
7.67
7.65
7.61
7.61
7.59
7.59
7.21
7.20
7.20
6.97
6.96
6.96
6.95
6.22
4.31
4.29
4.27
4.26
3.09
3.05
3.01
2.97
2.97
2.93
2.90
2.86
2.84
2.83
2.81
Br
O
O
S
NH
O
O
3al
0.97
1.01
0.96
2.07
1.07
3.01
2.96
1.00
1.00
3.04
1.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


204.87
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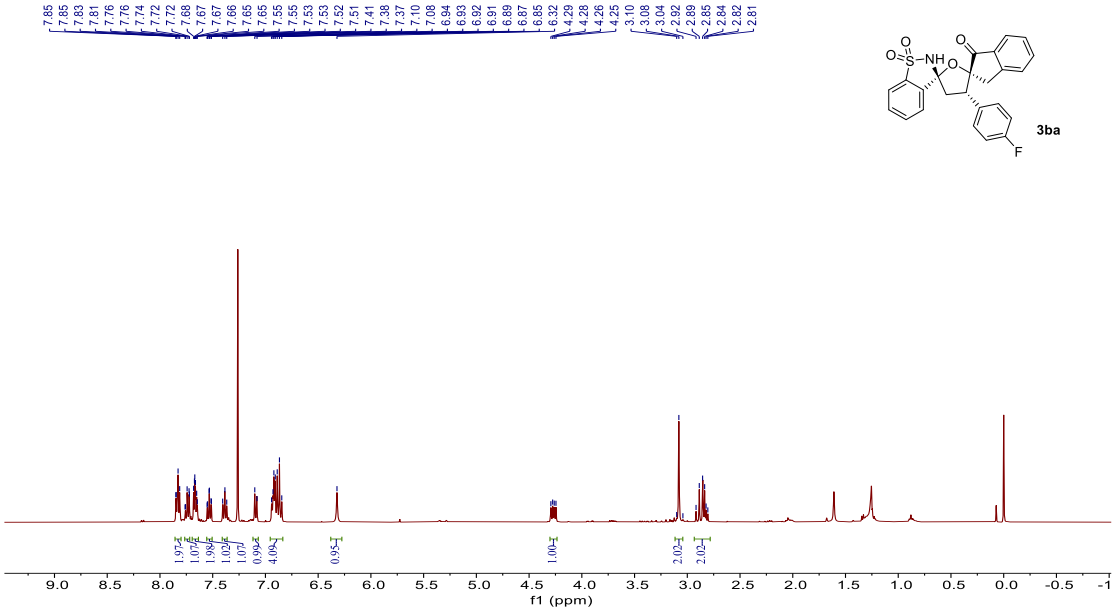
137.60
136.11
134.94
133.56
131.45
128.73
127.98
127.74
127.68
127.52
124.04
122.26
121.43
96.83
91.43
50.81
44.53
36.15
Br
O
O
S
NH
O
O
3al
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.85
7.85
7.83
7.81
7.76
7.76
7.74
7.72
7.72
7.68
7.67
7.67
7.66
7.65
7.65
7.55
7.55
7.53
7.53
7.52
7.51
7.41
7.38
7.37
7.10
7.08
6.94
6.93
6.92
6.91
6.89
6.87
6.85
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3.08
3.04
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2.81
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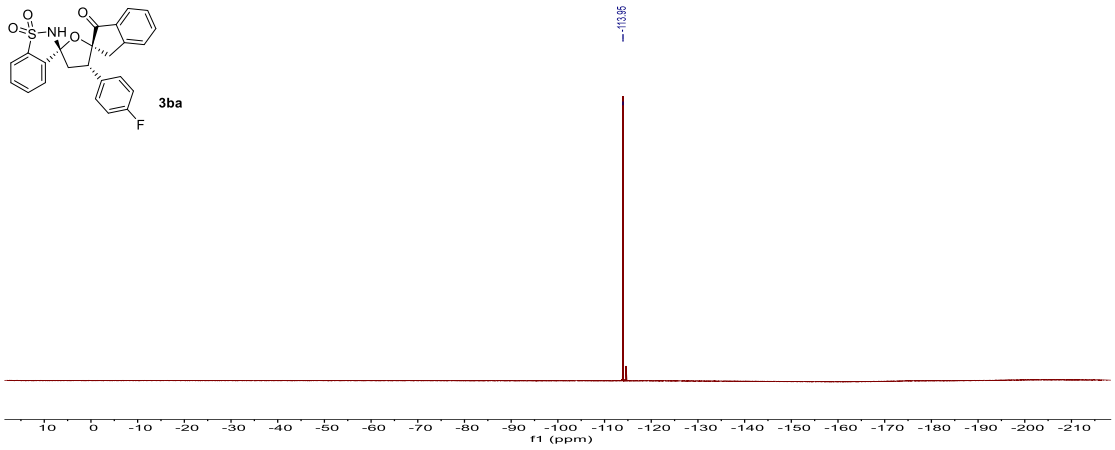
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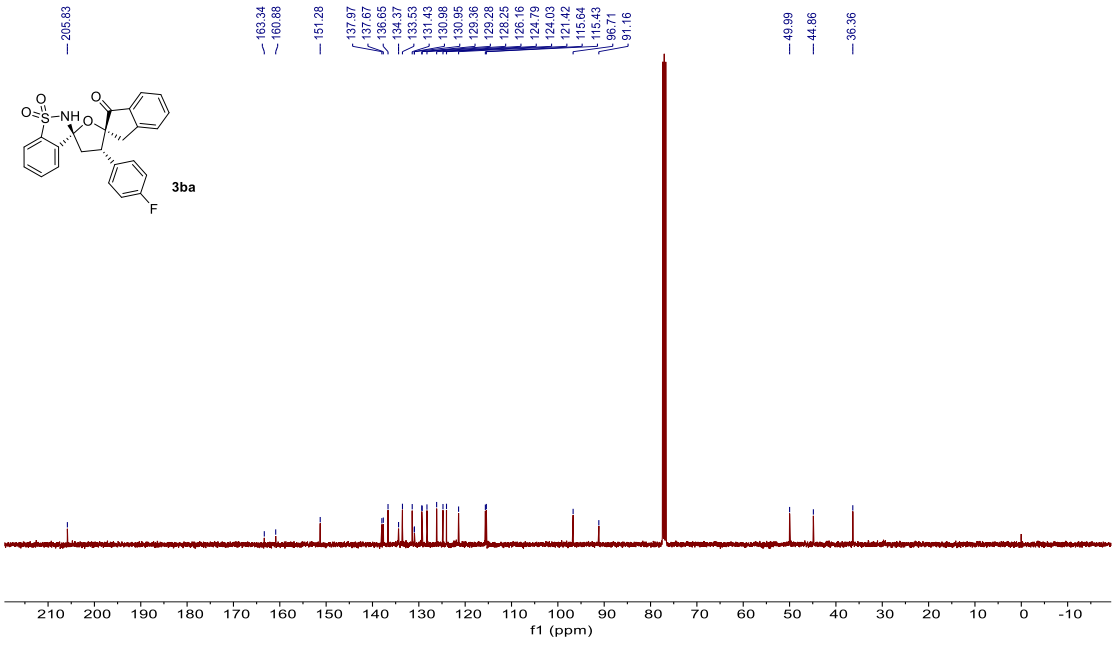
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128.25
126.16
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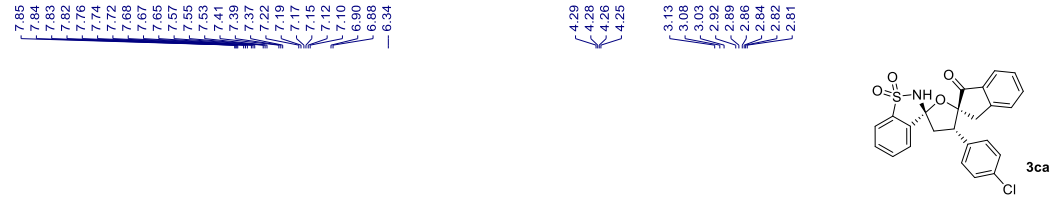
3ba
f1 (ppm)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7.37
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7.17
7.15
7.12
7.10
6.90
6.88
6.34
4.29
4.28
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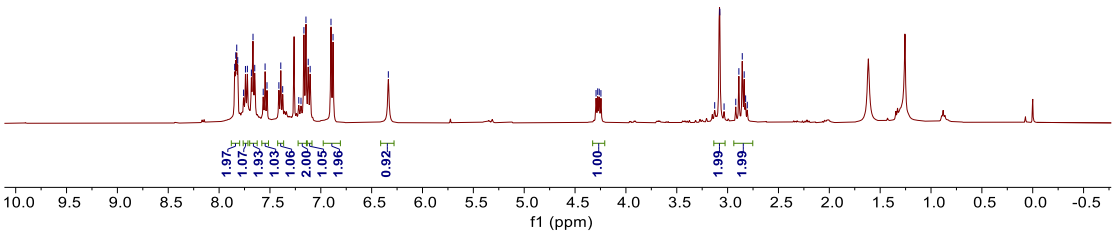
2.81
3ca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0.92
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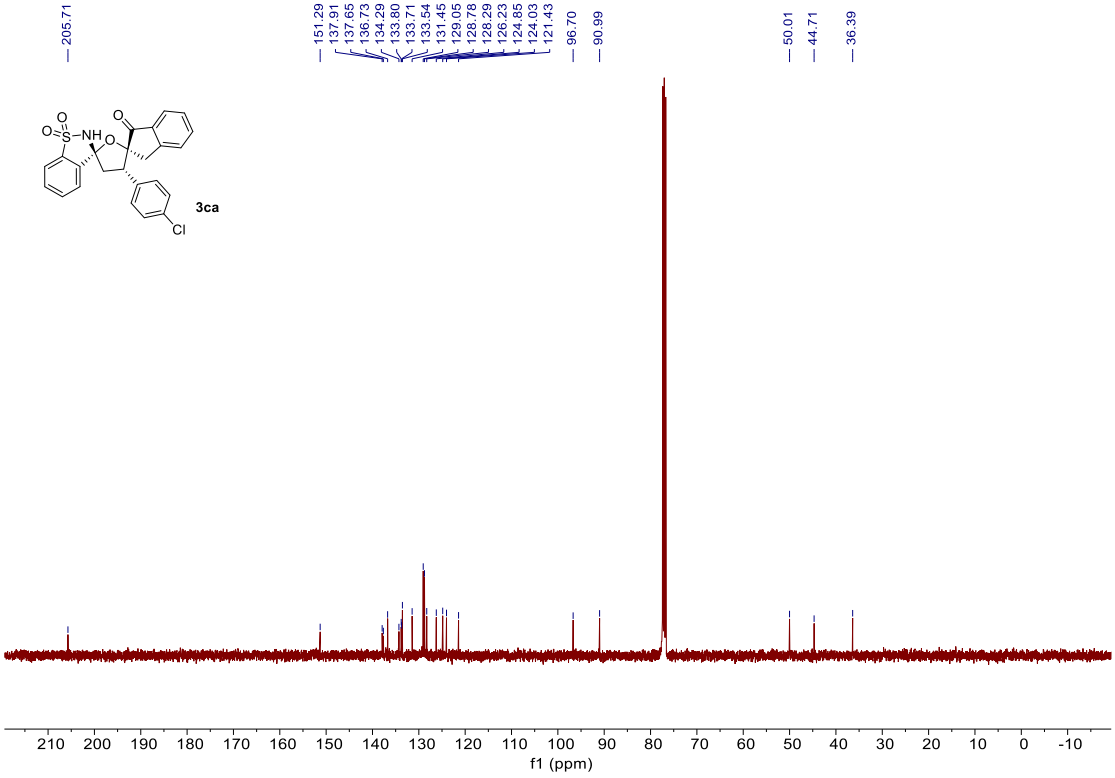
f1 (ppm)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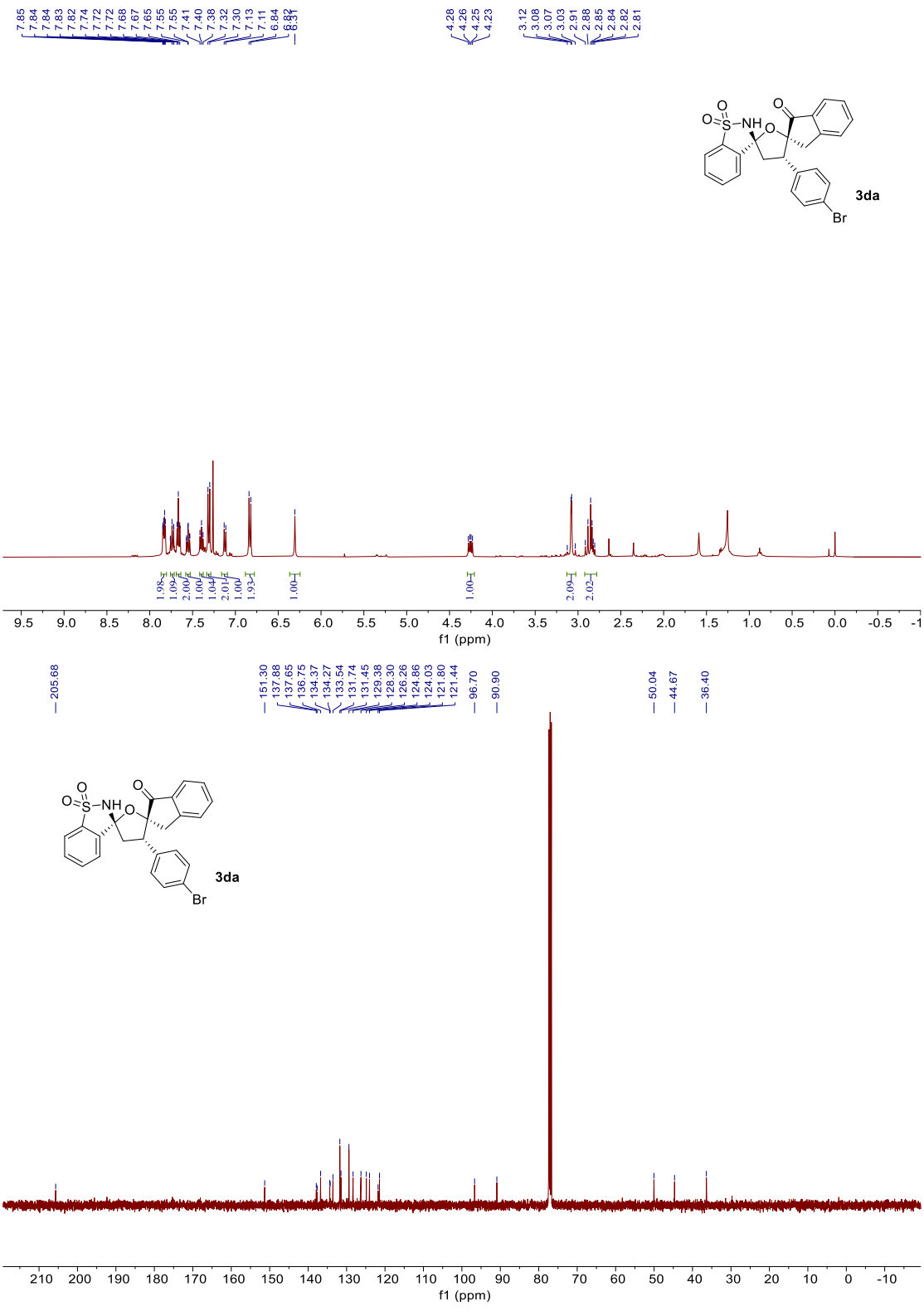
3ca
f1 (ppm)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6.82
6.81
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2.85
2.84
2.82
2.81
3da
Br
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1.09
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1.00
1.04
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1.00
1.93
1.00
1.00
2.09
2.02
f1 (ppm)
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126.26
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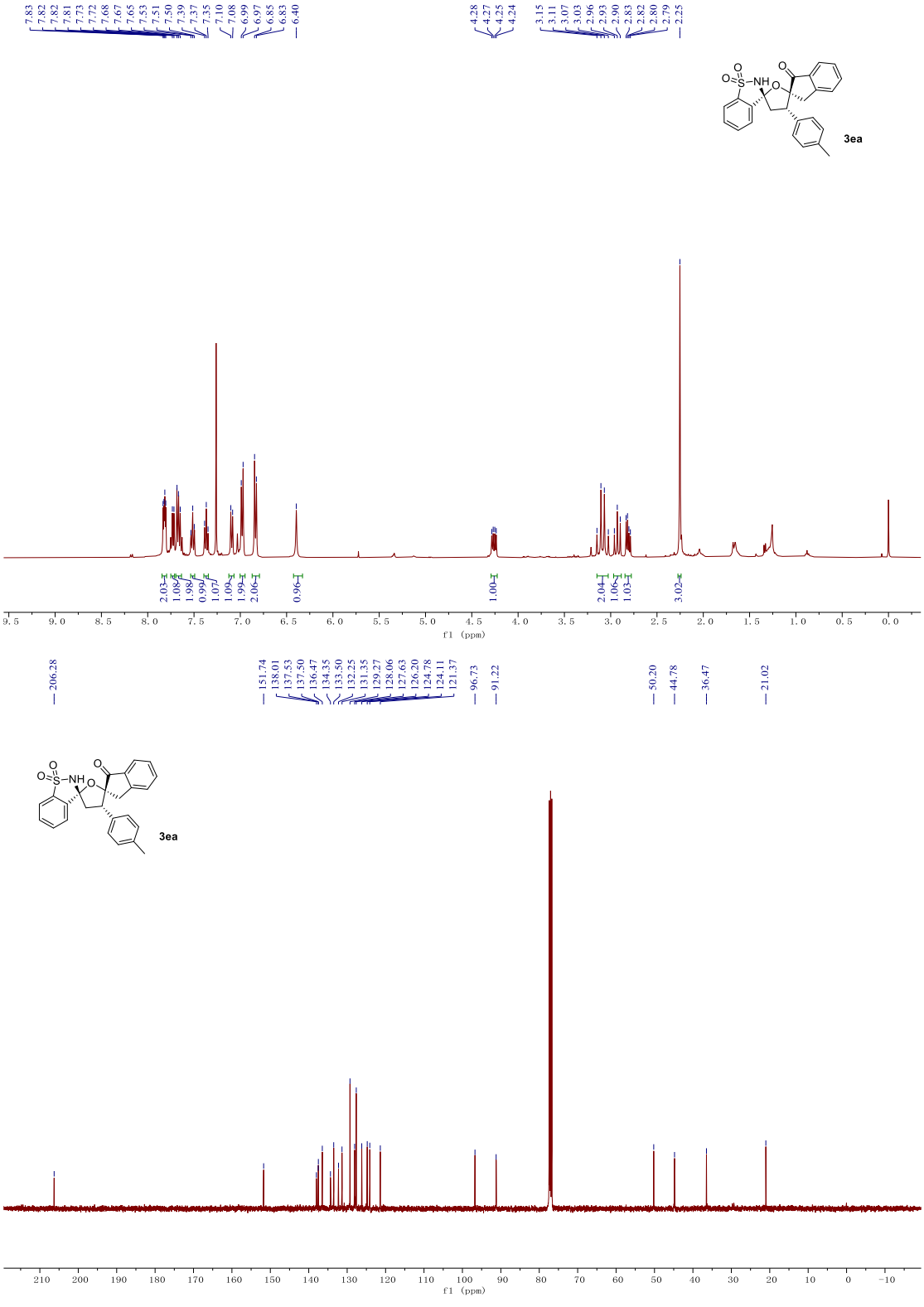
Br
f1 (ppm)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7.35
7.10
7.08
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6.97
6.85
6.83
6.40
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4.24
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3.03
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2.93
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2.82
2.80
2.79
2.25
3ea
2.03
1.08
1.98
0.99
1.07
1.09
1.99
2.06
0.96
1.00
2.04
1.06
1.03
3.02
f1 (ppm)
206.28
151.74
138.01
137.53
137.50
136.47
134.35
133.50
132.25
131.35
129.27
128.06
127.63
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121.37
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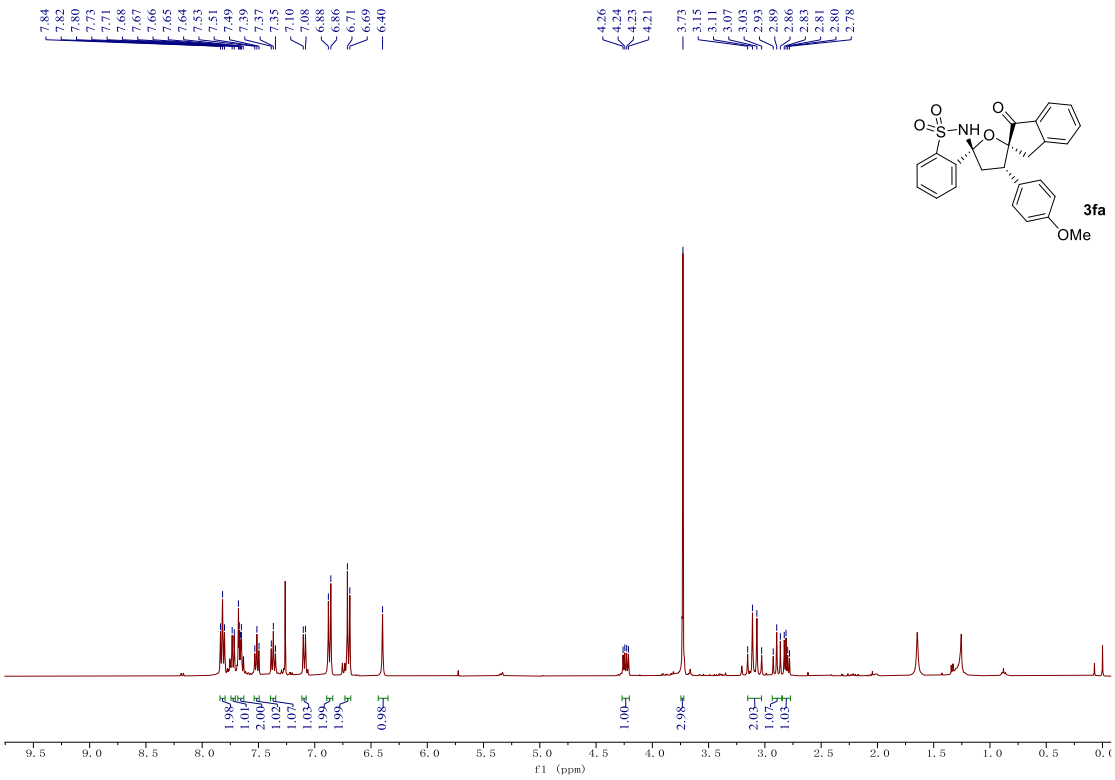
91.22
50.20
44.78
36.47
21.02
3ea
f1 (ppm)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7.10
7.08
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6.86
6.71
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4.23
4.21
3.73
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3.11
3.07
3.03
2.93
2.89
2.86
2.83
2.81
2.80
2.78
3fa
OMe
1.98
1.01
2.00
1.02
1.07
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0.98
1.00
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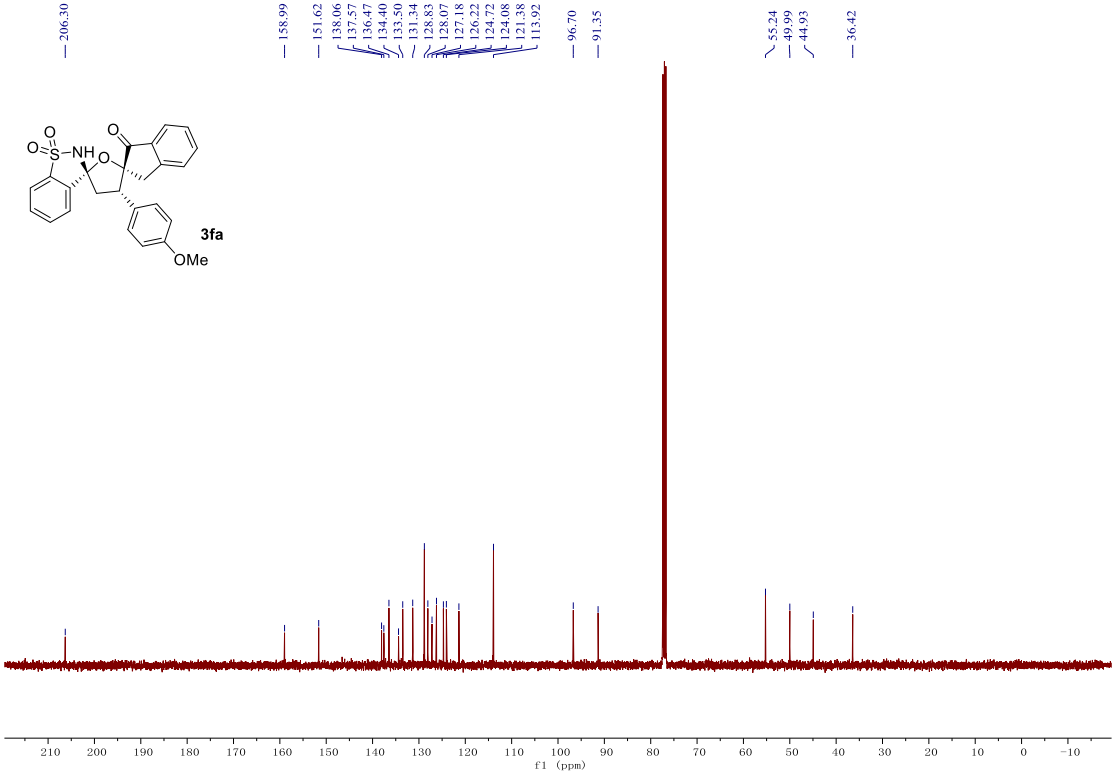
2.03
1.07
1.03
f1 (ppm)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126.22
124.72
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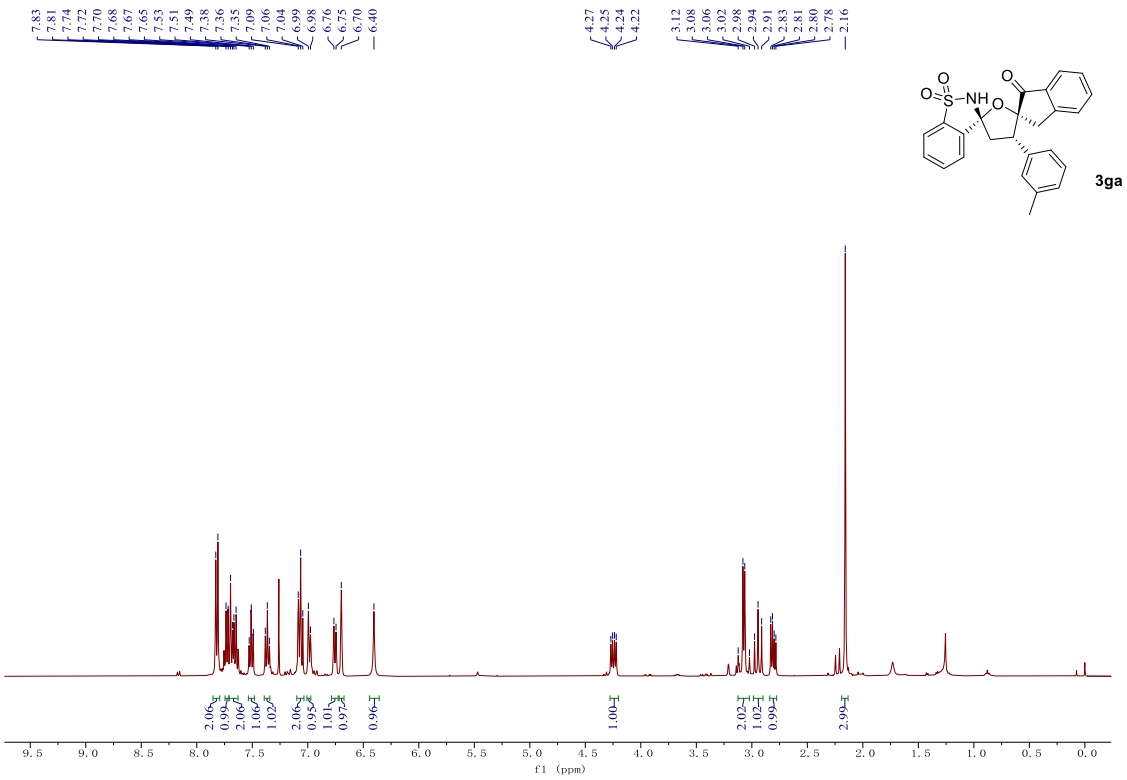
55.24
49.99
44.93
36.42
3fa
OMe
f1 (ppm)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7.35
7.09
7.06
7.04
6.99
6.98
6.76
6.75
6.70
6.40
4.27
4.25
4.24
4.22
3.12
3.08
3.06
3.02
2.98
2.94
2.91
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2.80
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2.16
3ga
2.06
0.99
2.06
1.06
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1.02
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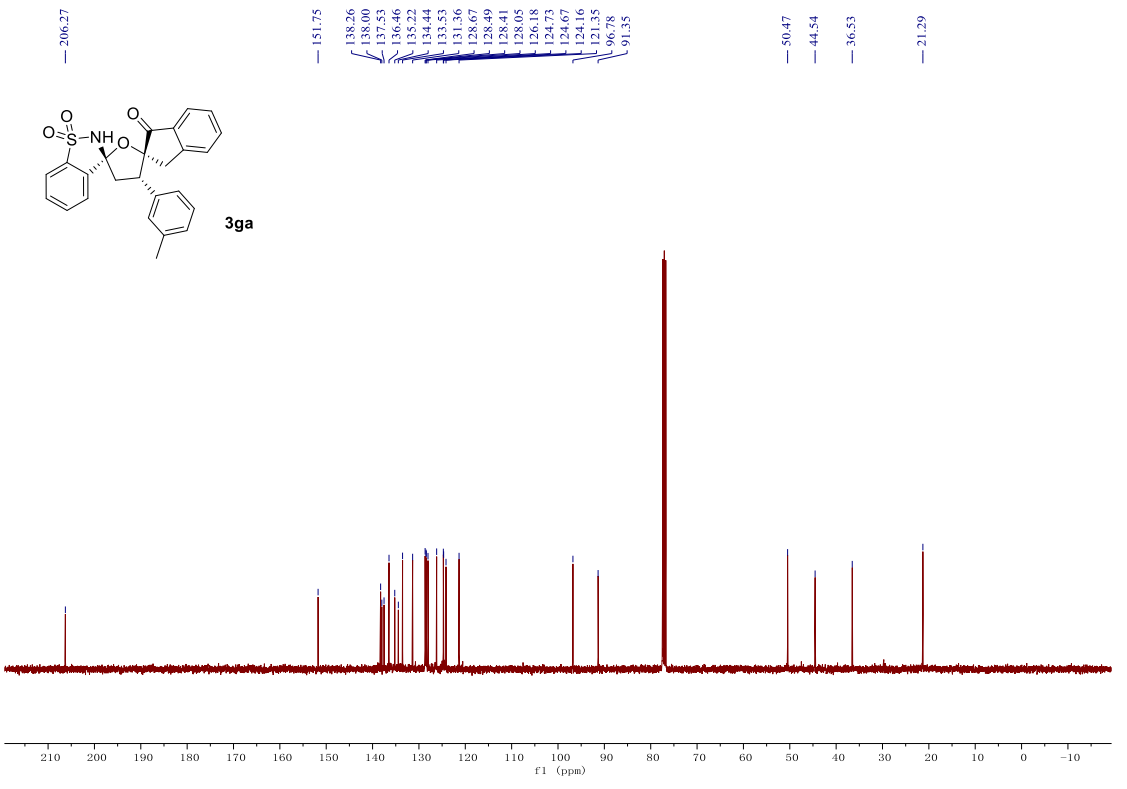
2.99
f1 (ppm)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126.18
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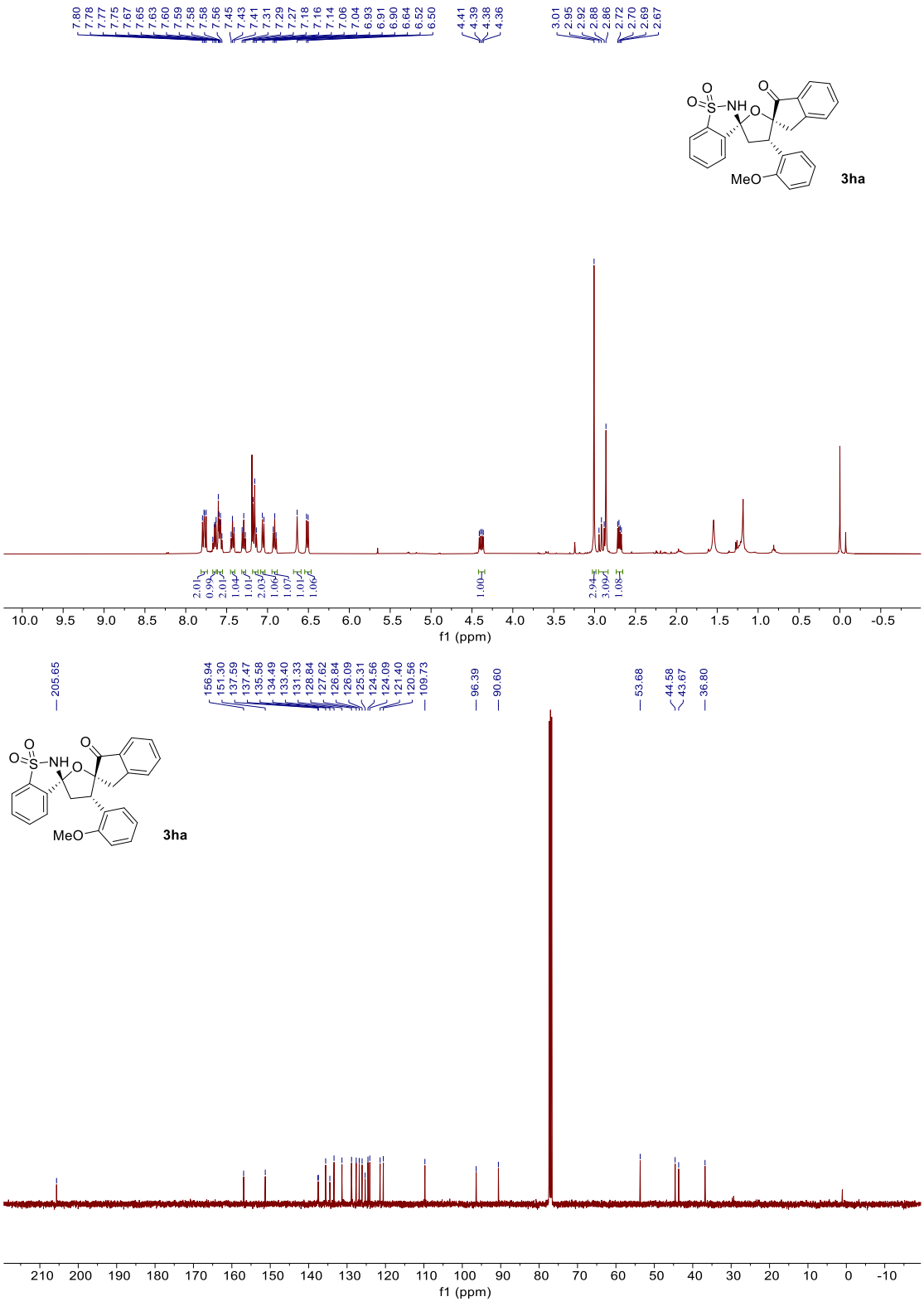
96.78
91.35
50.47
44.54
36.53
21.29
3ga
f1 (ppm)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7.43
7.41
7.31
7.29
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7.18
7.16
7.14
7.06
7.04
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6.91
6.90
6.64
6.52
6.50
4.41
4.39
4.38
4.36
3.01
2.95
2.92
2.88
2.86
2.72
2.70
2.69
2.67
O
O
S
NH
O
O
MeO
3ha
2.01
0.99
2.01
1.04
1.01
2.03
1.06
1.07
1.01
1.06
1.00
2.94
3.09
1.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
205.65
156.94
151.30
137.59
137.47
135.58
134.49
133.40
131.33
128.84
127.62
126.84
126.09
125.31
124.56
124.09
121.40
120.56
109.73
96.39
90.60
53.68
44.58
43.67
36.80
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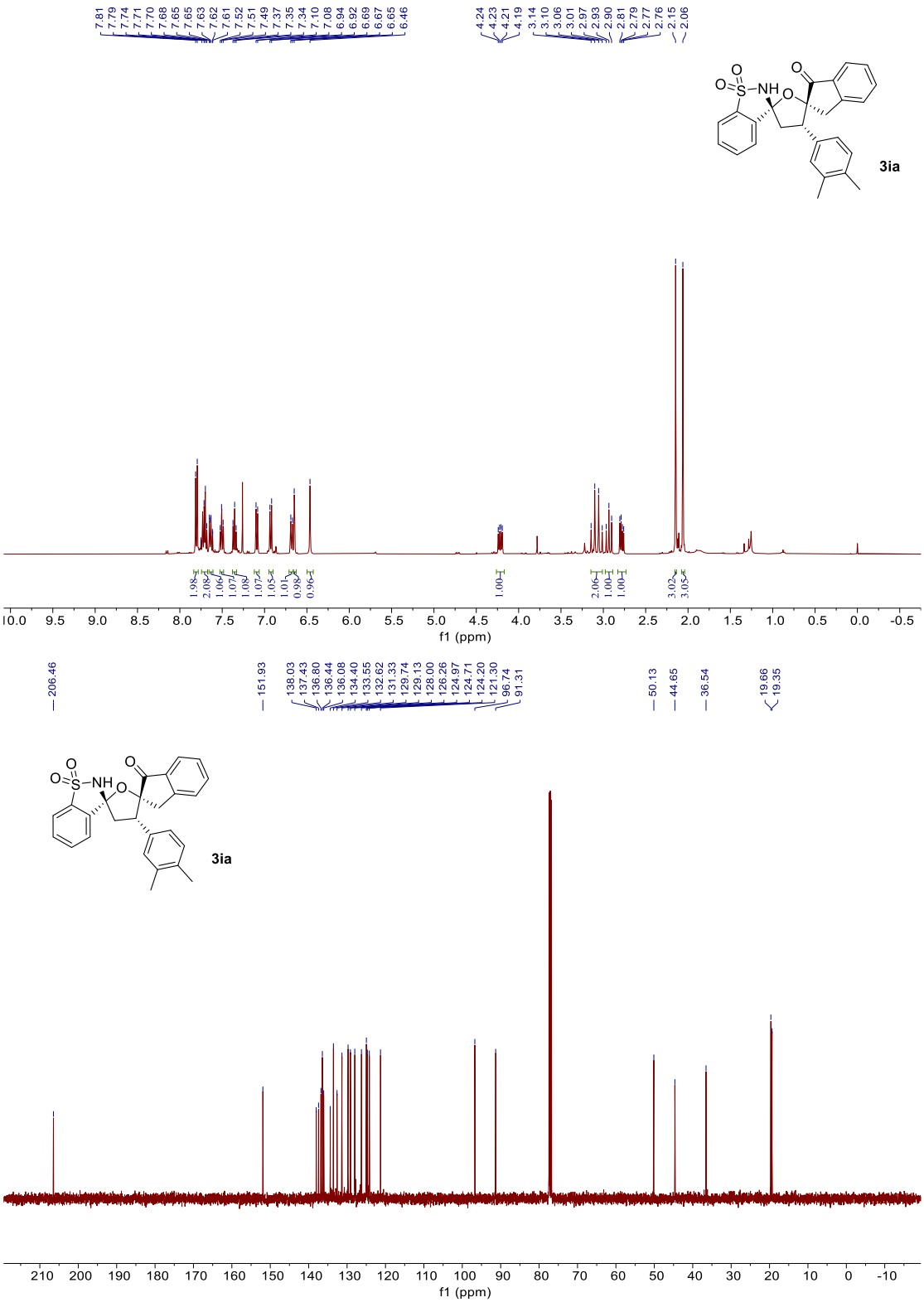
O
S
NH
O
O
MeO
3ha
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.62
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7.52
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7.37
7.35
7.34
7.10
7.08
6.94
6.92
6.69
6.67
6.65
6.46
4.24
4.23
4.21
4.19
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3.10
3.06
3.01
2.97
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2.79
2.77
2.76
2.15
2.06
3ia
1.98
2.08
1.06
1.07
1.08
1.07
1.05
1.01
0.98
0.96
1.00
2.06
1.00
1.00
3.02
3.05
f1 (ppm)
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138.03
137.43
136.80
136.44
136.08
134.40
133.55
132.62
131.33
129.74
129.13
128.00
126.26
124.97
124.71
124.20
121.30
96.74
91.31
50.13
44.65
36.54
19.66
19.35
3ia
f1 (ppm)


7.85
7.85
7.84
7.83
7.82
7.75
7.73
7.73
7.69
7.67
7.67
7.58
7.58
7.41
7.24
7.23
7.21
7.16
7.14
7.14
6.79
6.78
6.77
6.76
6.33


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4.24
4.23
4.21

3.15
3.11
3.06
3.02
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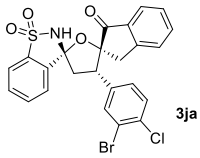
2.85
2.83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Br
Cl
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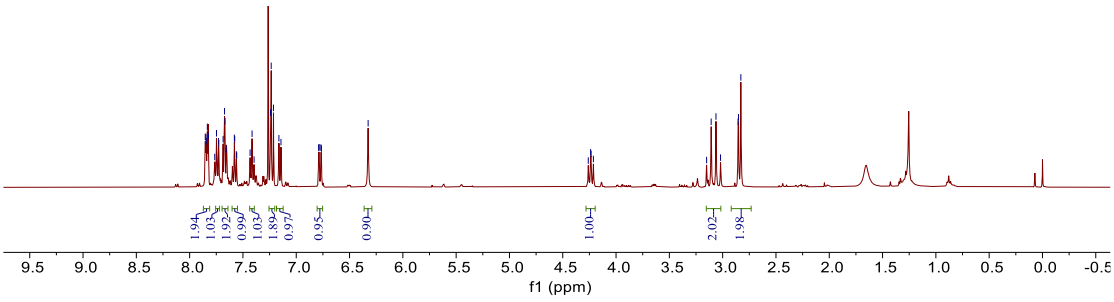
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0.90
1.00
2.02
1.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


205.39
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137.77
137.57
136.94
135.70
134.23
133.98
133.65
132.78
131.51
130.31
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124.91
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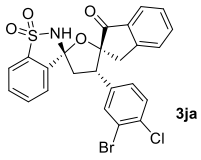
121.37
96.66
90.90
49.61
44.52
36.41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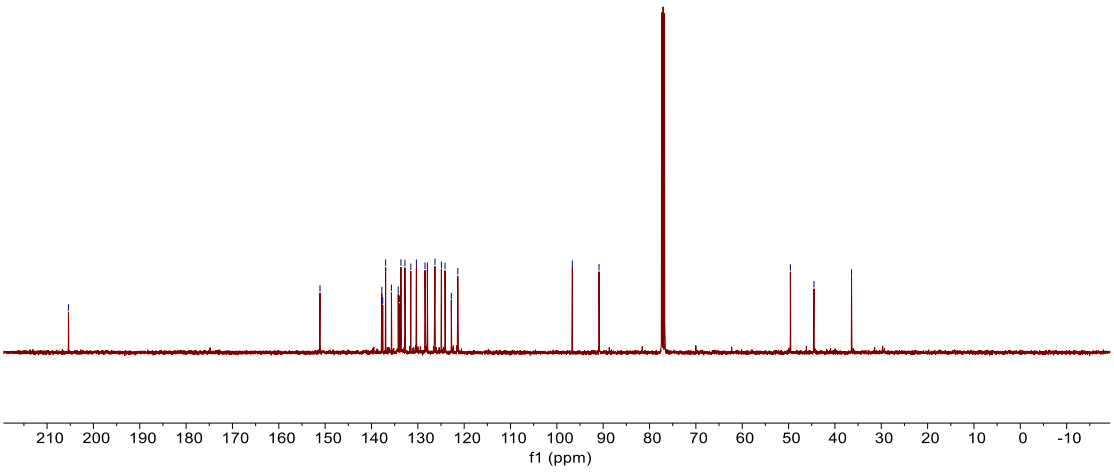
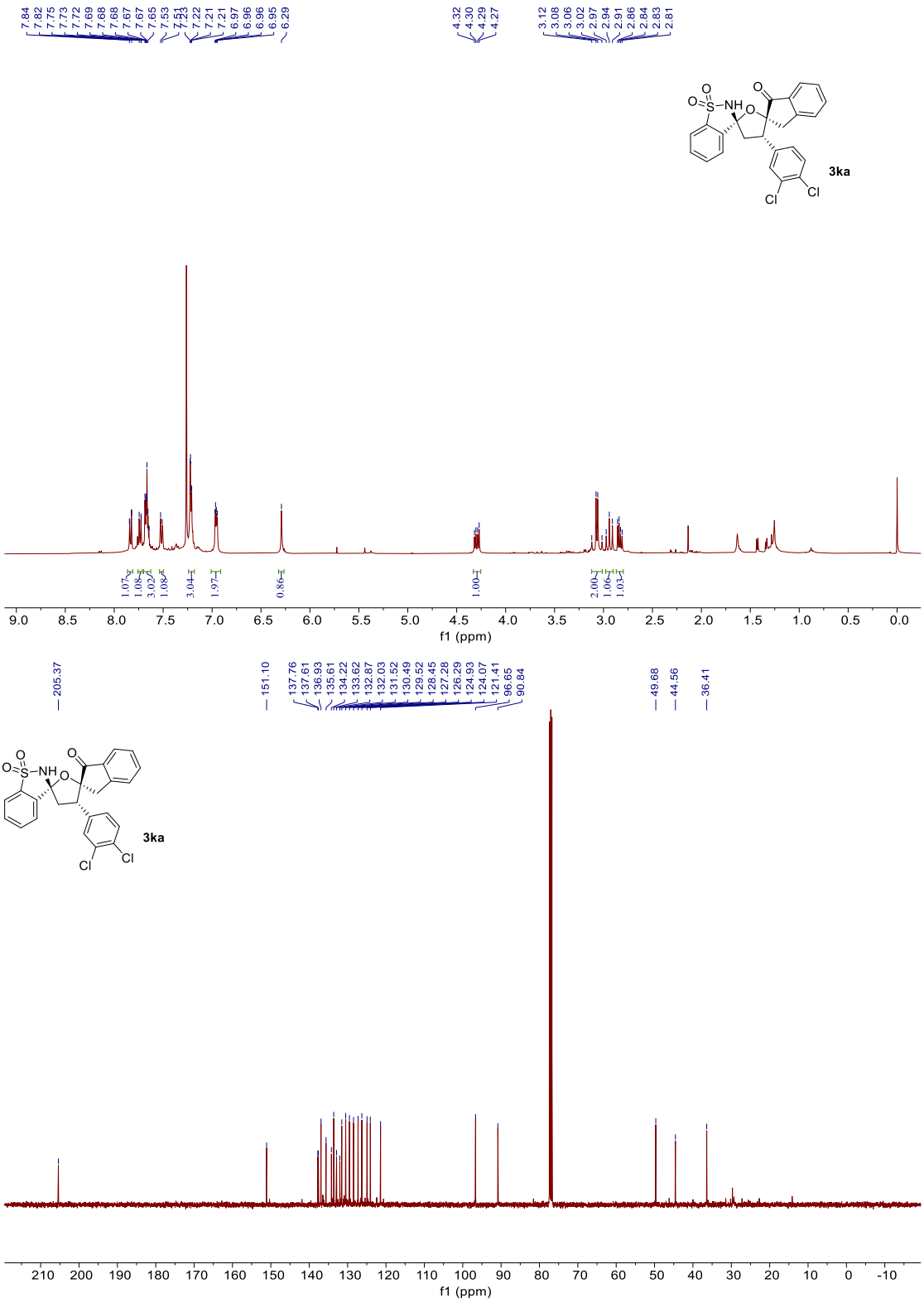
S
NH
O
O
Br
Cl
3ja


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.53
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7.22
7.21
7.21
6.97
6.96
6.96
6.95
6.29
4.32
4.30
4.29
4.27
3.12
3.08
3.06
3.02
2.97
2.94
2.91
2.86
2.84
2.83
2.81
O
O
S
NH
O
O
Cl
Cl
3ka
1.07
1.08
3.02
1.08
3.04
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1.00
2.00
1.06
1.03
9.0
8.5
8.0
7.5
7.0
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6.0
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5.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
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126.29
124.93
124.07
121.41
96.65
90.84
49.68
44.56
36.41
O
O
S
NH
O
O
Cl
Cl
3ka
210
200
190
180
170
160
150
140
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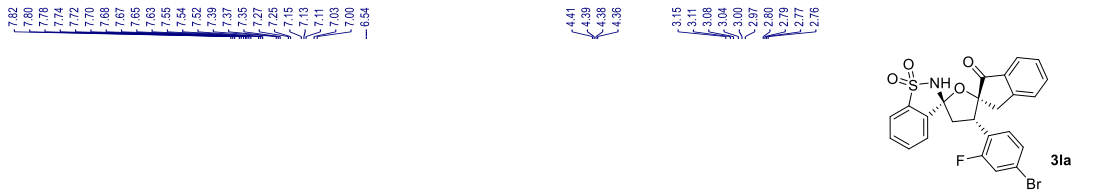
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.39
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7.15
7.13
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7.03
7.00
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4.41
4.39
4.38
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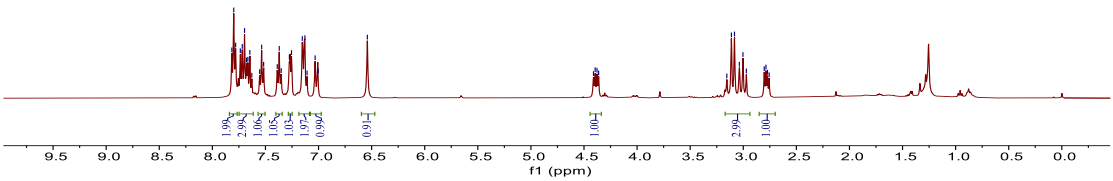
3la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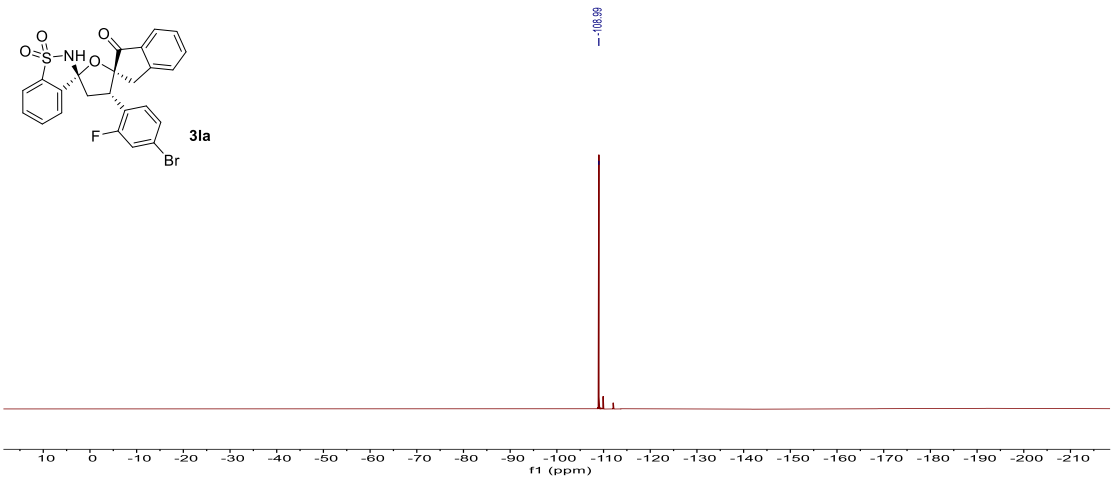
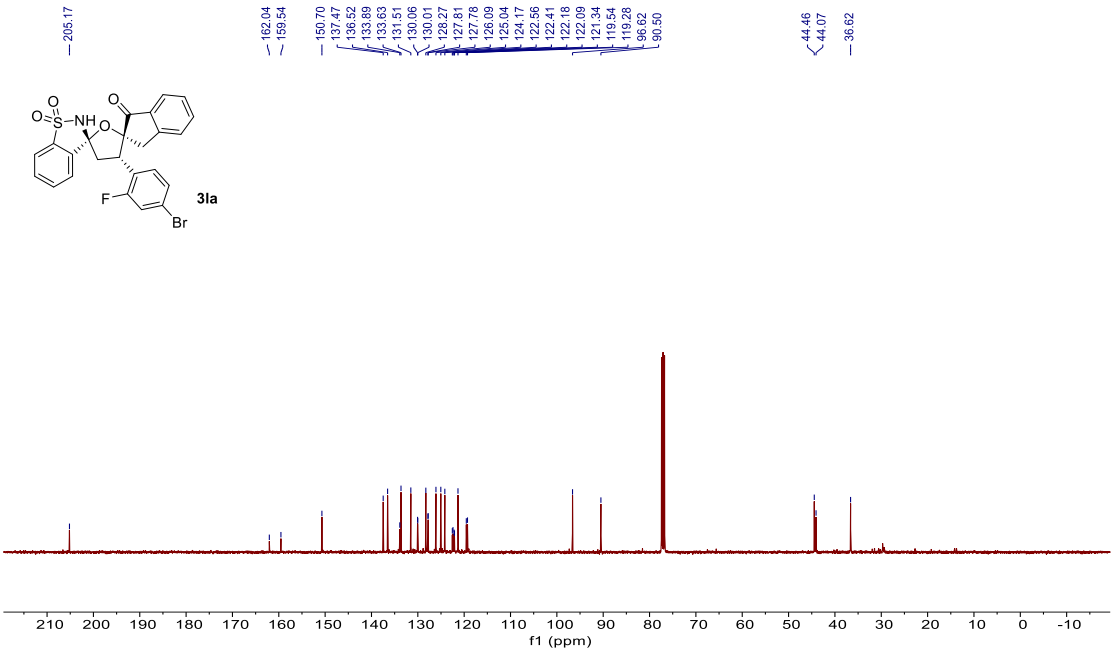
0.99
0.91
1.00
2.99
1.00
f1 (ppm)


-108.99
3la
f1 (ppm)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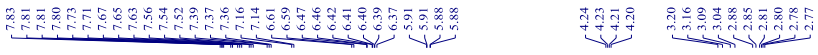
44.07
36.62
3la
f1 (ppm)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6.37
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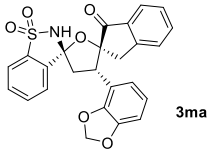
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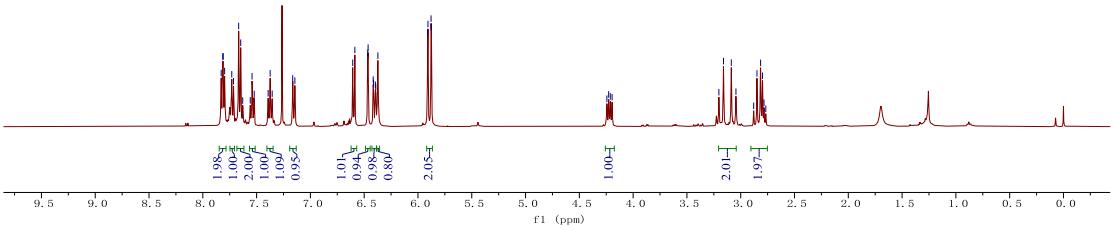
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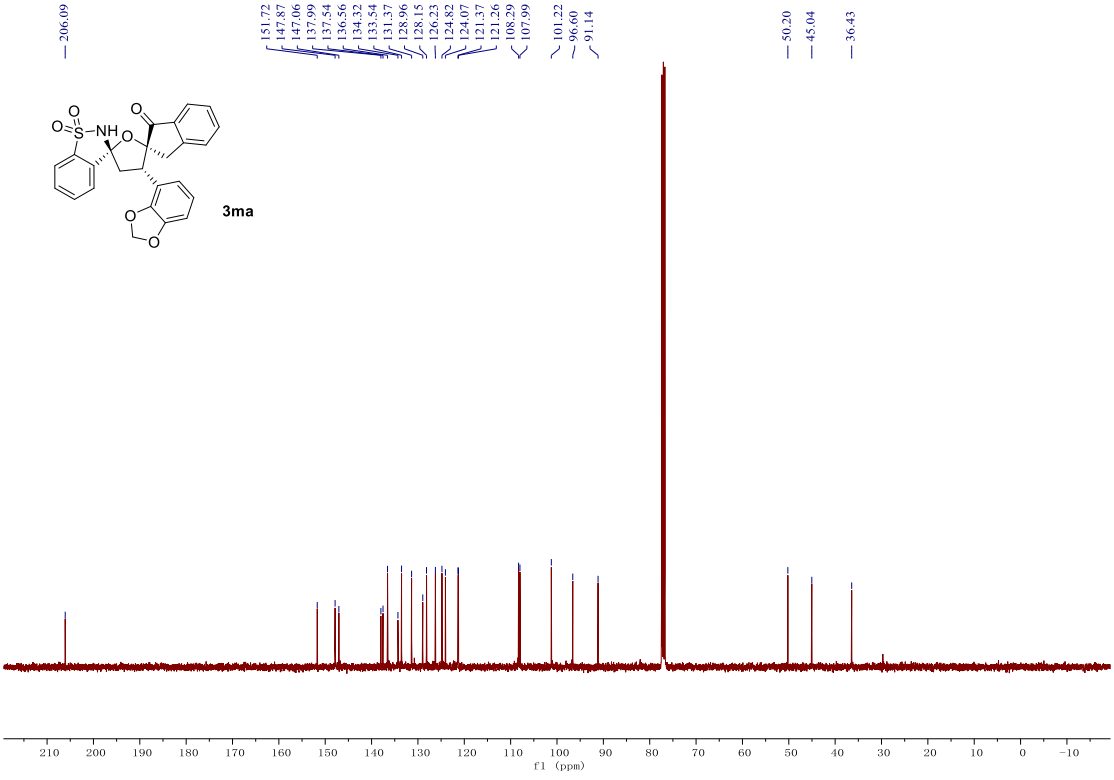
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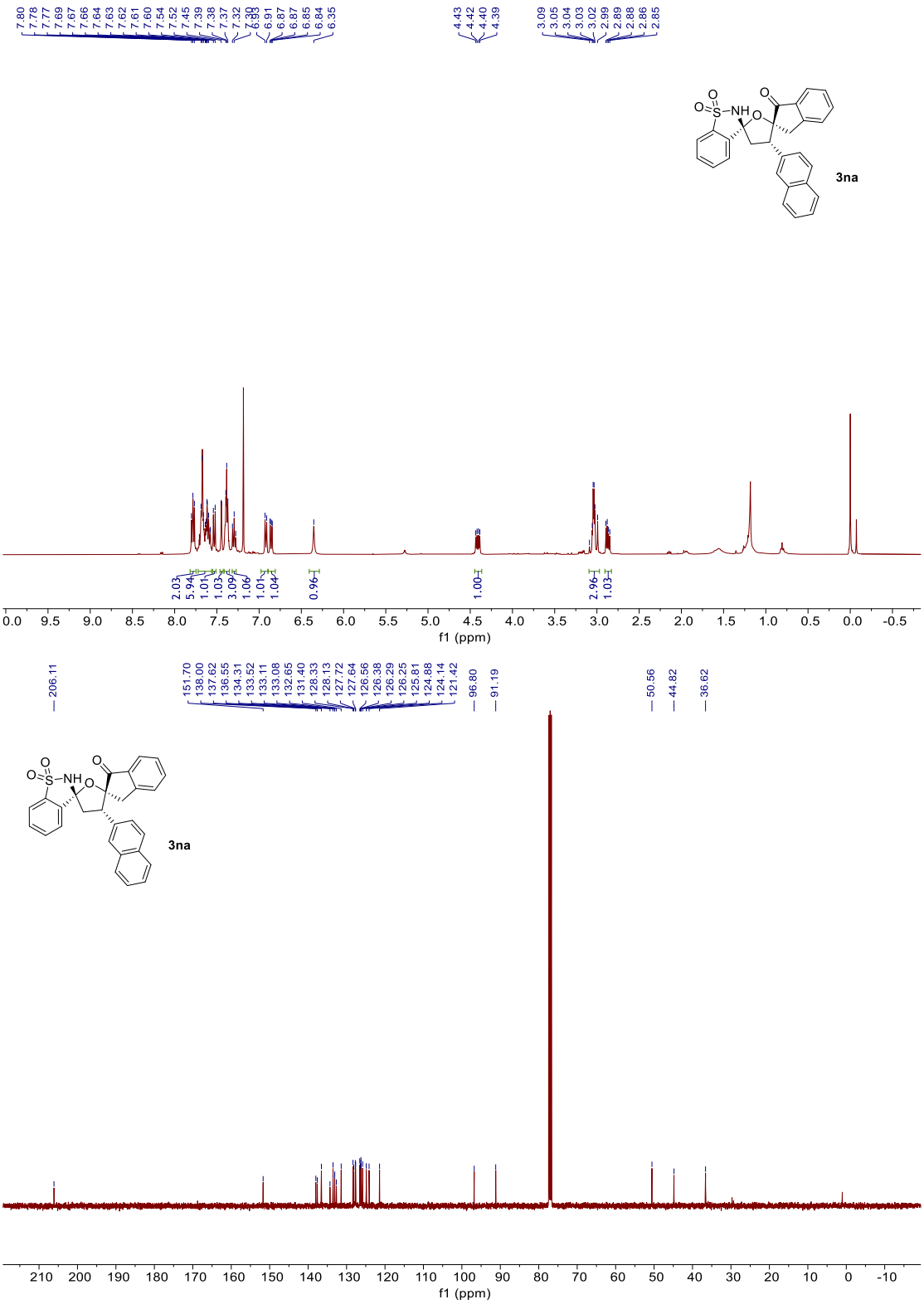
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36.62
3na
f1 (ppm)


7.83
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7.67
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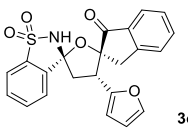
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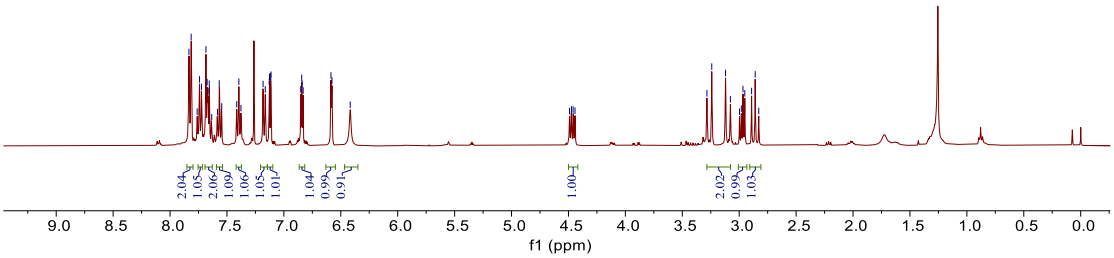
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f1 (ppm)


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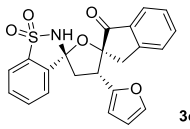
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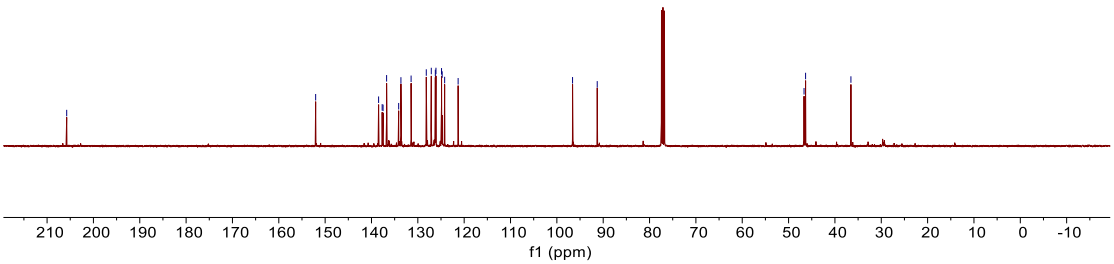
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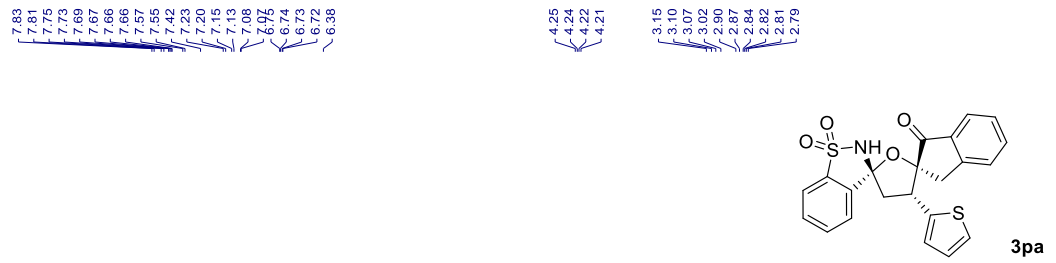
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O
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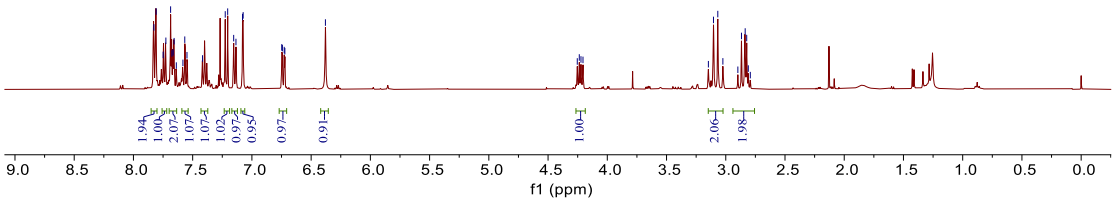
S
3pa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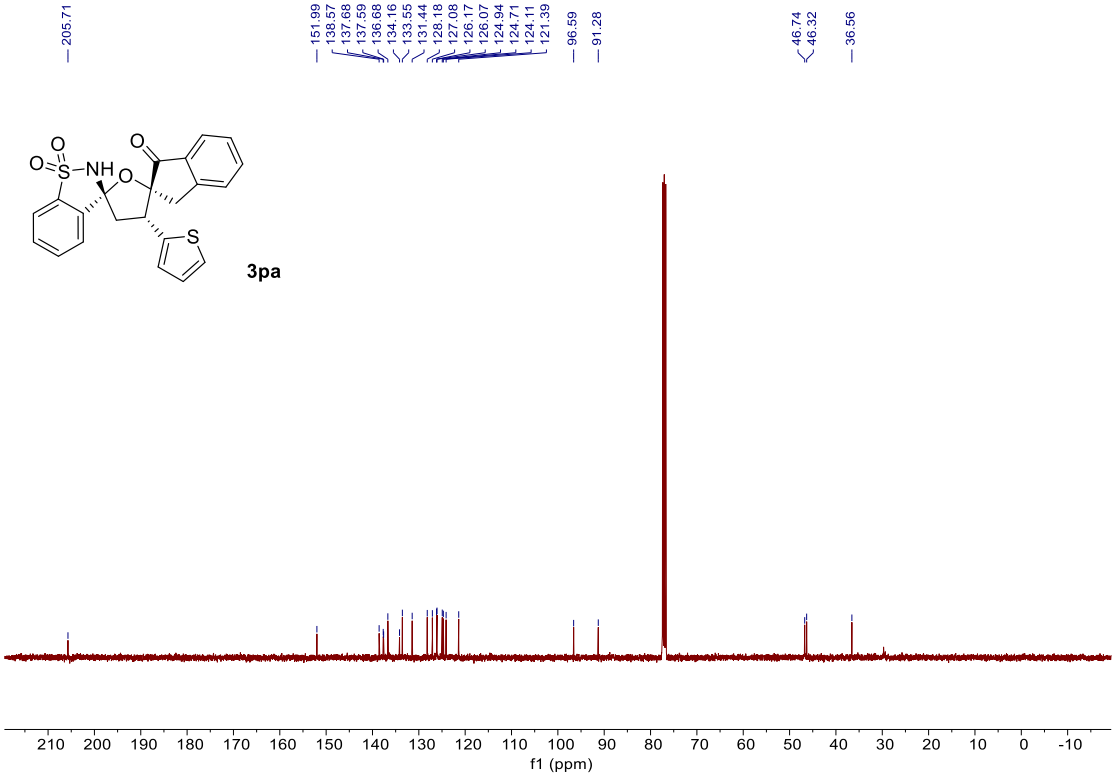
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170
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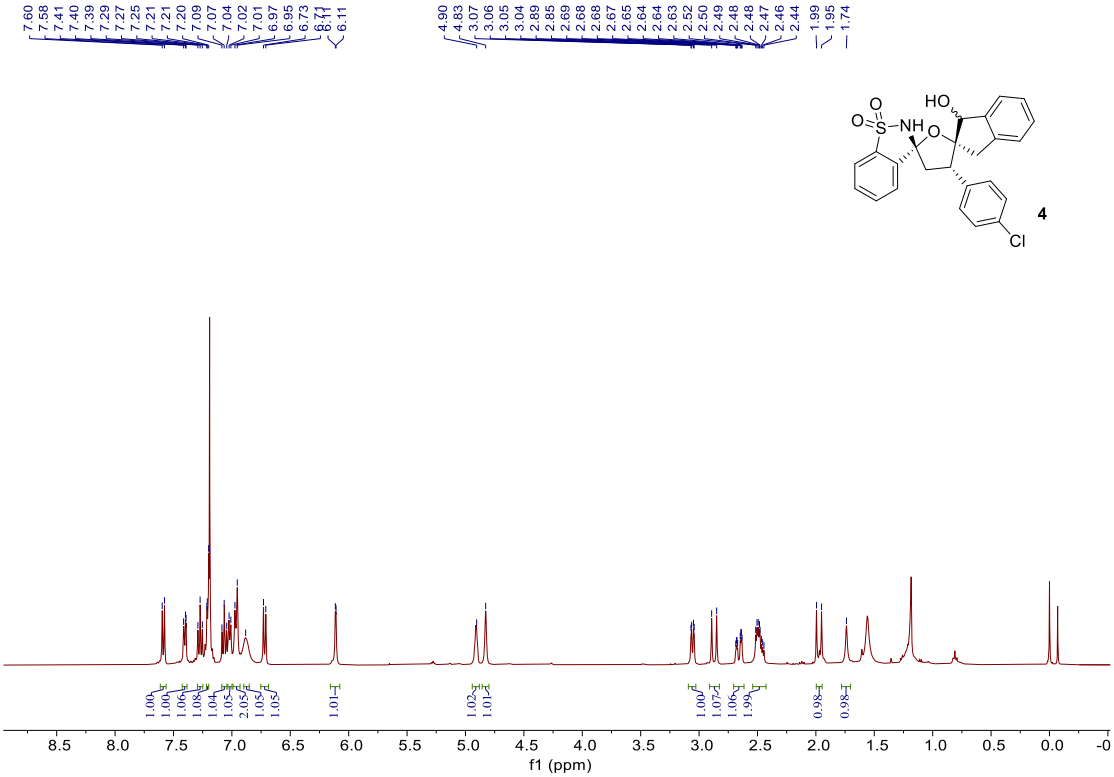
f1 (ppm)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S
NH
O
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Cl
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0.98
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1.0
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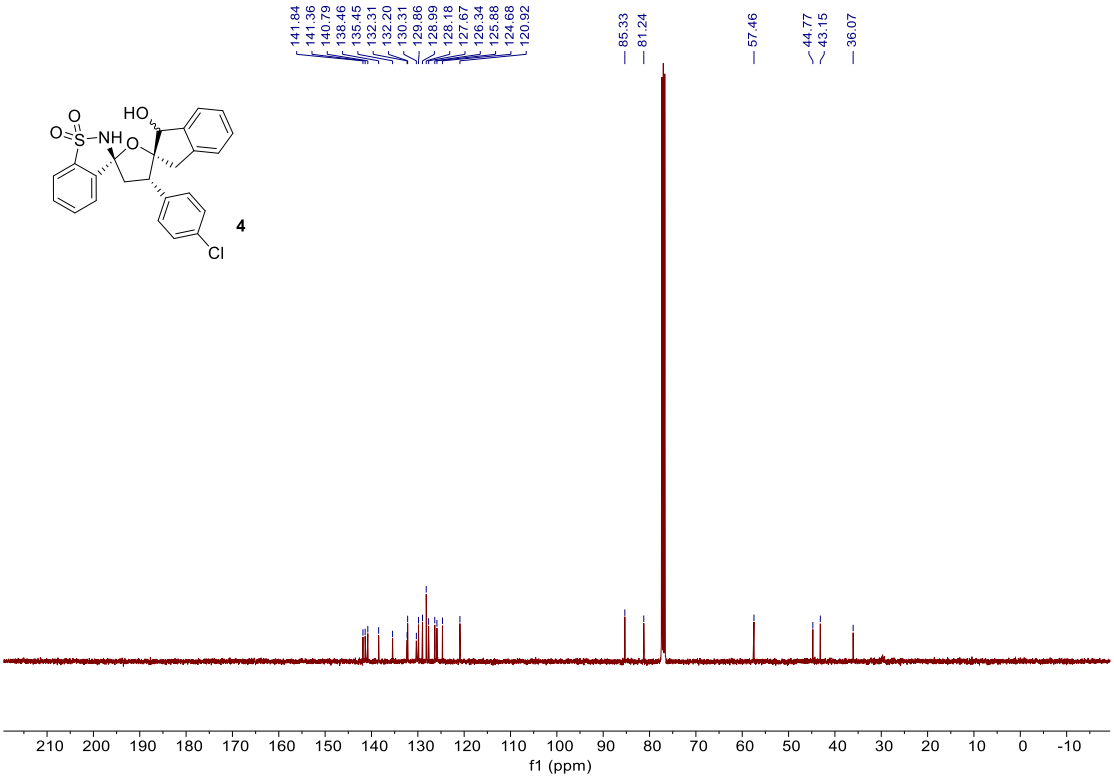
f1 (ppm)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HO
O
S
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O
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200
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180
170
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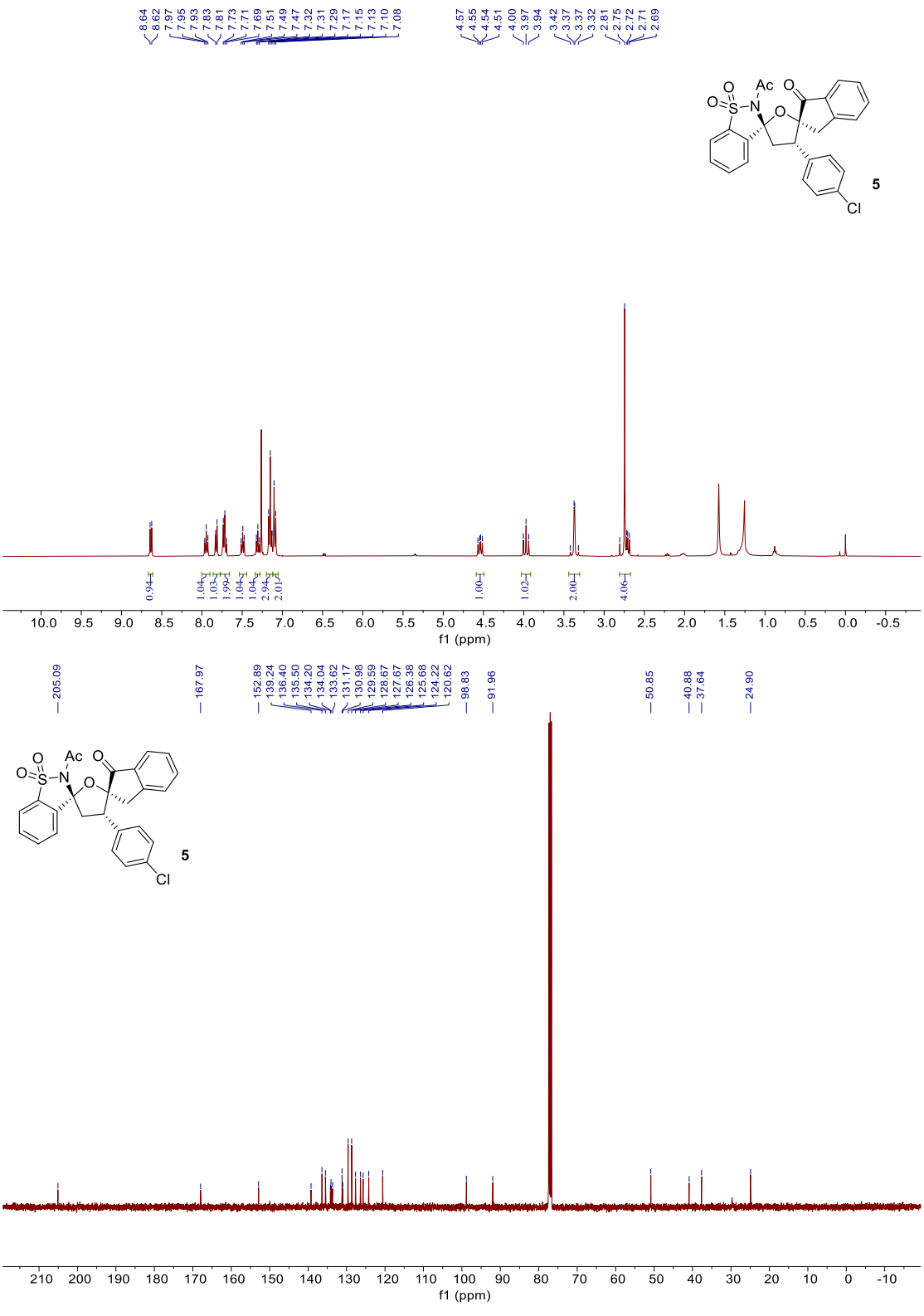
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3.37
3.32
2.81
2.75
2.72
2.71
2.69
Ac
O
O
S
N
O
O
Cl
5
0.94
1.04
1.03
1.99
1.04
1.04
2.94
2.01
1.00
1.02
2.00
4.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
205.09
167.97
152.89
139.24
136.40
135.50
134.20
134.04
133.62
131.17
130.98
129.59
128.67
127.67
126.38
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124.22
120.62
98.83
91.96
50.85
40.88
37.64
24.90
Ac
O
O
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O
Cl
5
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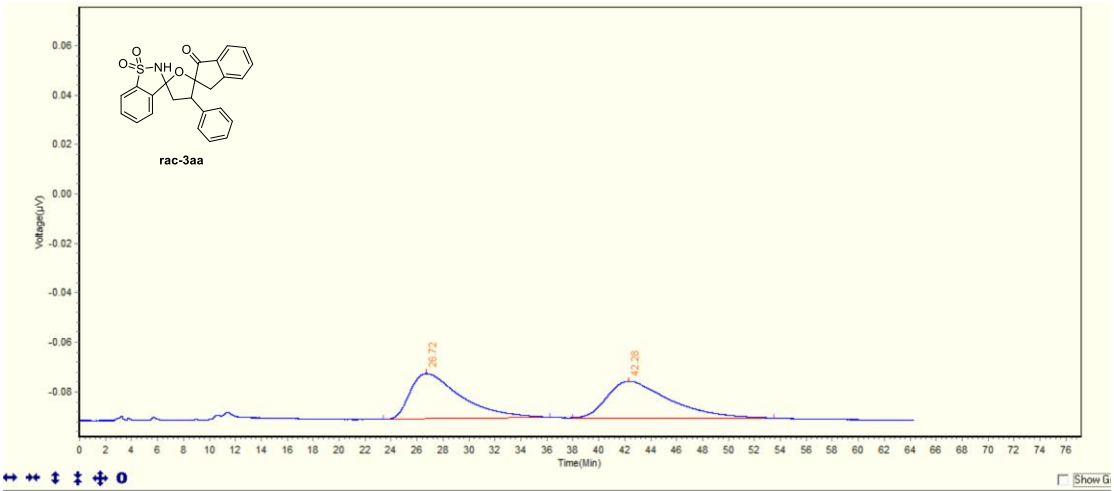
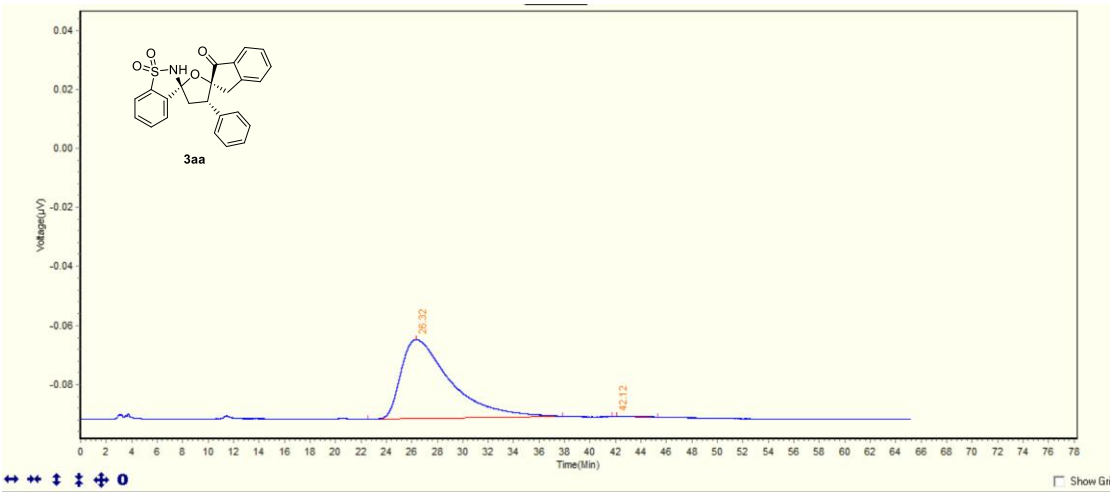
f1 (ppm)

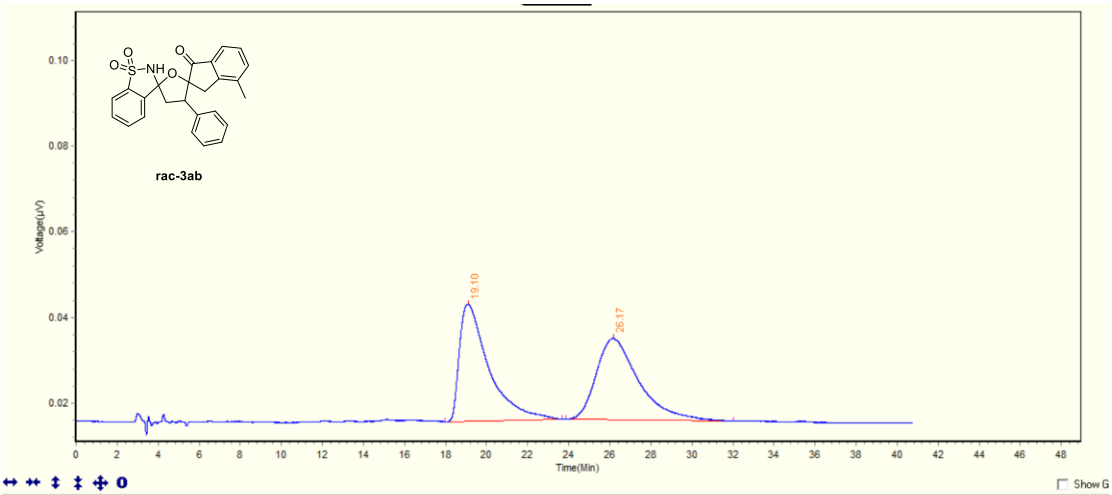
HPLC spectra of compounds



Integration Result	Calculation Result	TimeTable				
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	26.72	2481784	9159	50.13%	12.849	BB
2	42.28	2468750	7429	49.87%	15.521	BB
Total		4,950,534	16,588	100.00%		

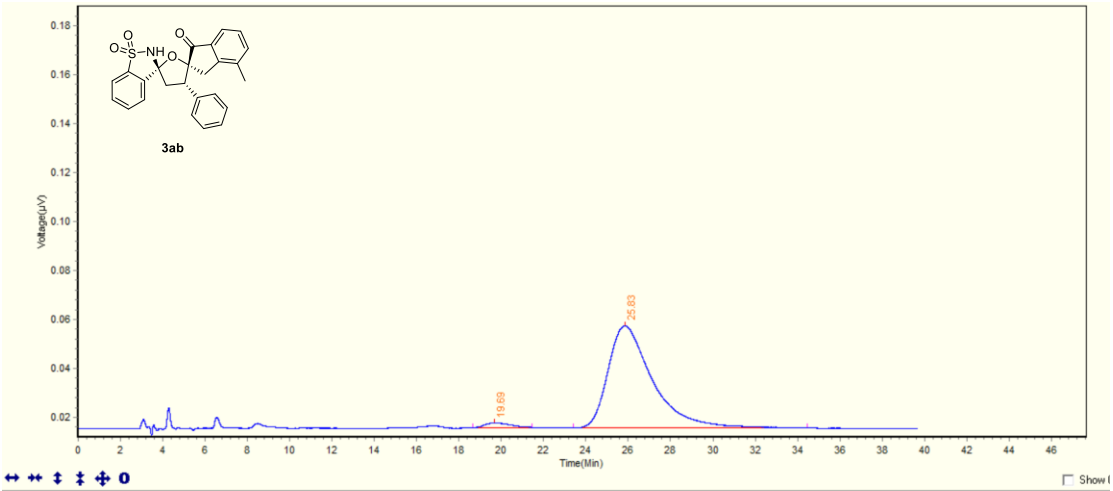


Integration Result	Calculation Result	TimeTable				
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	26.32	3571334	13330	99.76%	15.299	BB
2	42.12	8707	55	0.24%	3.587	BB
Total		3,580,041	13,385	100.00%		



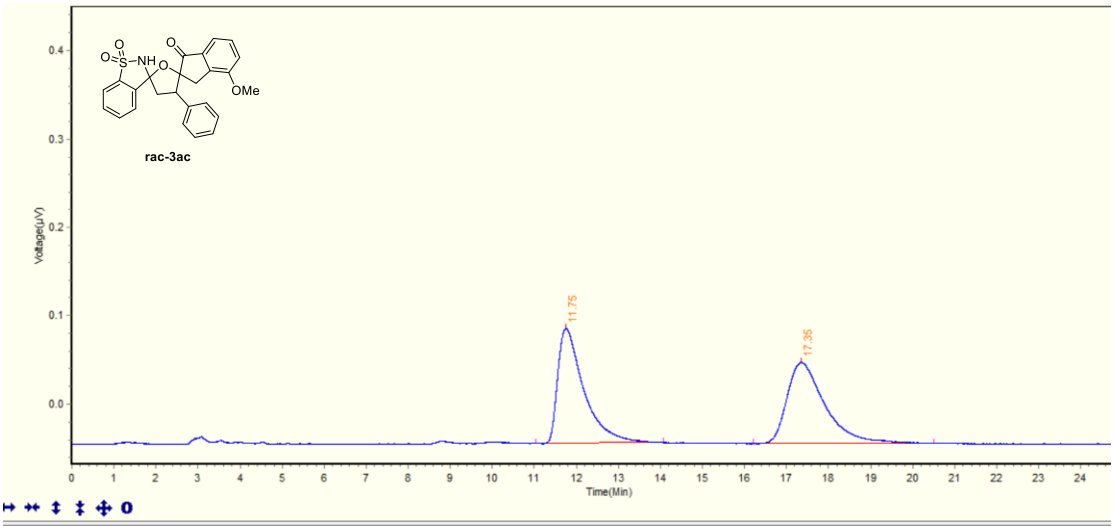
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	19.10	1359980	13642	50.05%	5.702	BB
2	26.17	1357100	9480	49.95%	8.165	BB
Total		2,717,080	23,122	100.00%		



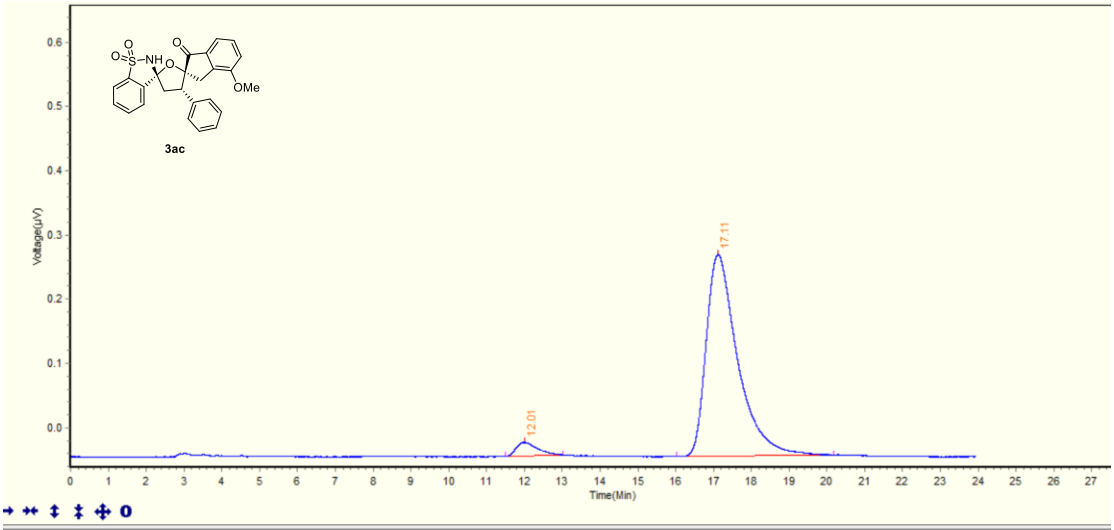
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	19.69	76432	1000	2.46%	2.798	BB
2	25.83	3024732	20833	97.54%	11.058	BB
Total		3,101,164	21,833	100.00%		



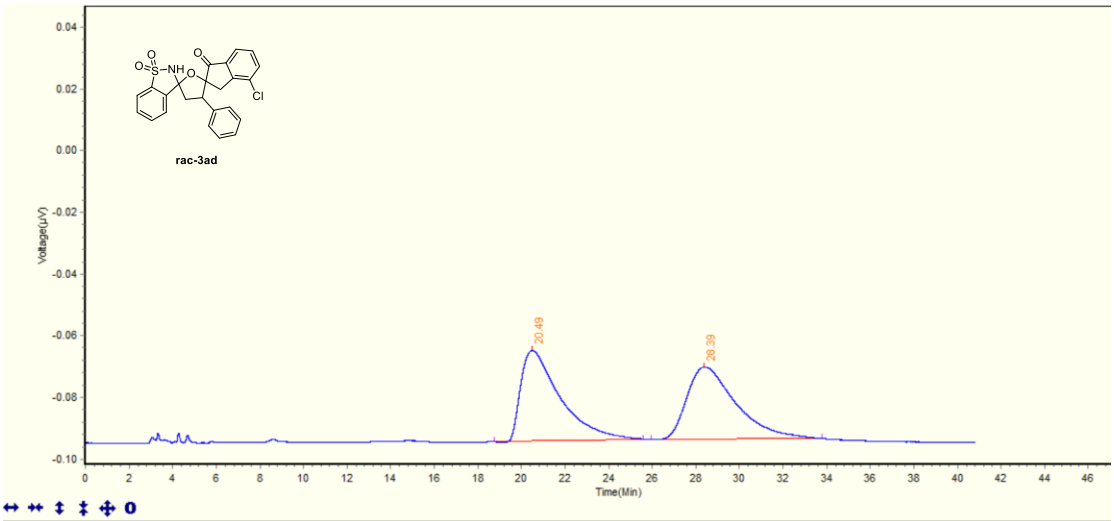
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	11.75	2810121	64972	49.60%	3.035	BB
2	17.35	2855213	45894	50.40%	4.306	BB
Total		5,665,334	110,866	100.00%		



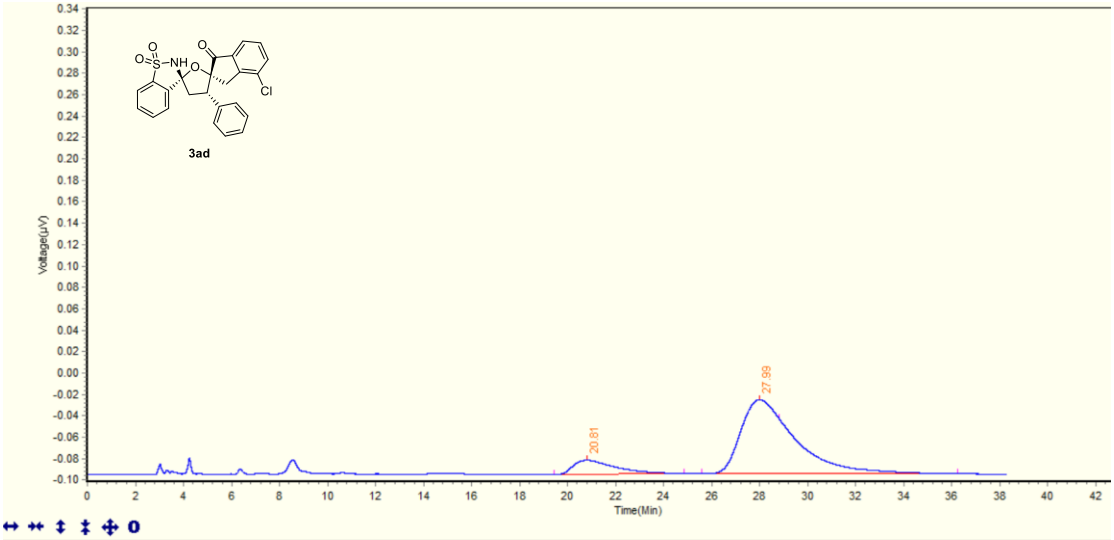
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	12.01	417933	10567	4.41%	1.518	BB
2	17.11	9056710	156714	95.59%	4.153	BB
Total		9,474,643	167,281	100.00%		



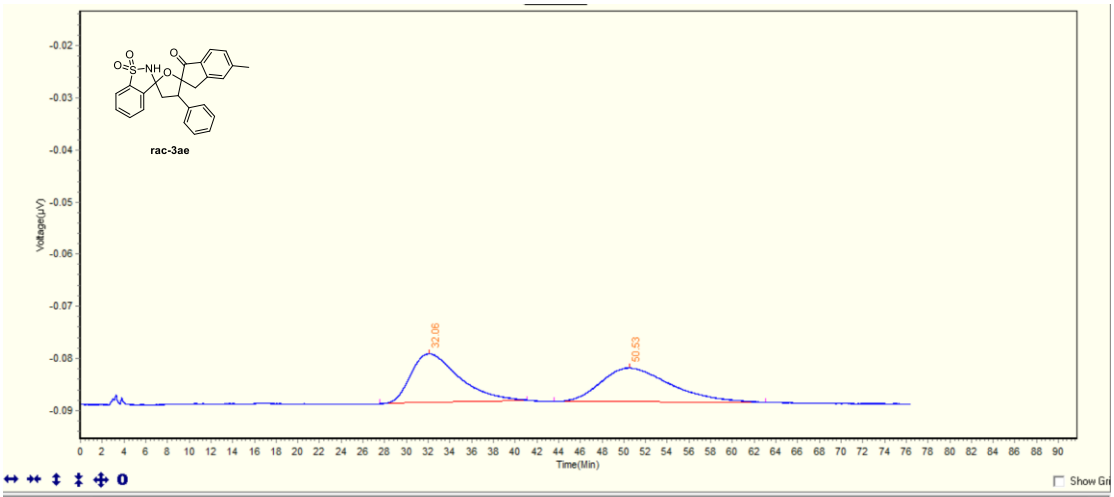
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	20.49	1827661	14690	49.87%	6.831	BB
2	28.39	1837142	11735	50.13%	7.839	BB
Total		3,664,803	26,425	100.00%		



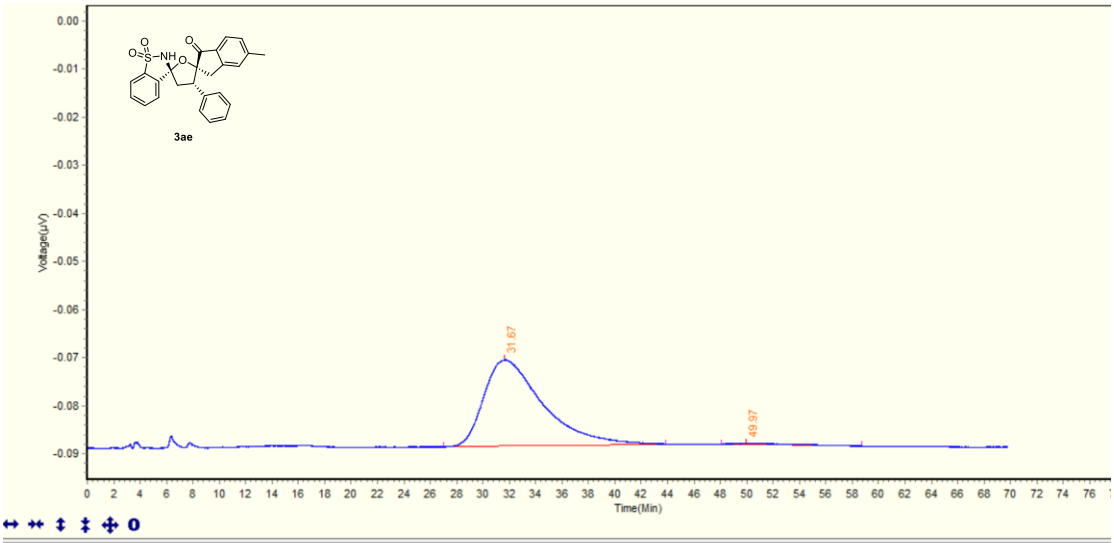
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	20.81	789744	6518	12.65%	5.418	BB
2	27.99	5454011	34586	87.35%	10.664	SBB
3	-17.75	0	-47268	0.00%	0.0	TBB
Total		6,243,755	-6,164	100.00%		



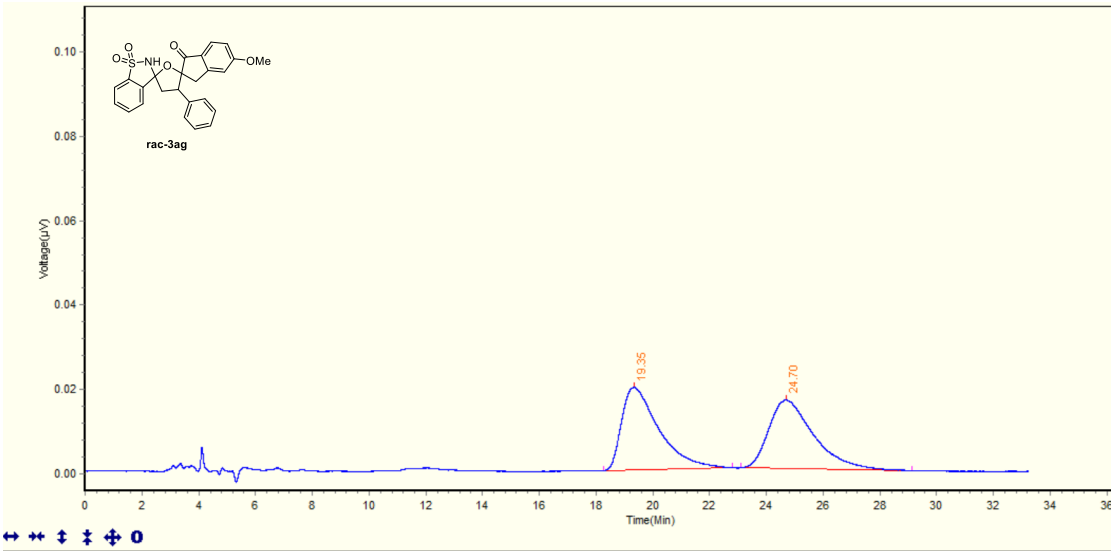
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	32.06	1439504	4688	50.10%	13.555	BB
2	50.53	1434024	3242	49.90%	19.474	BB
Total		2,873,528	7,930	100.00%		



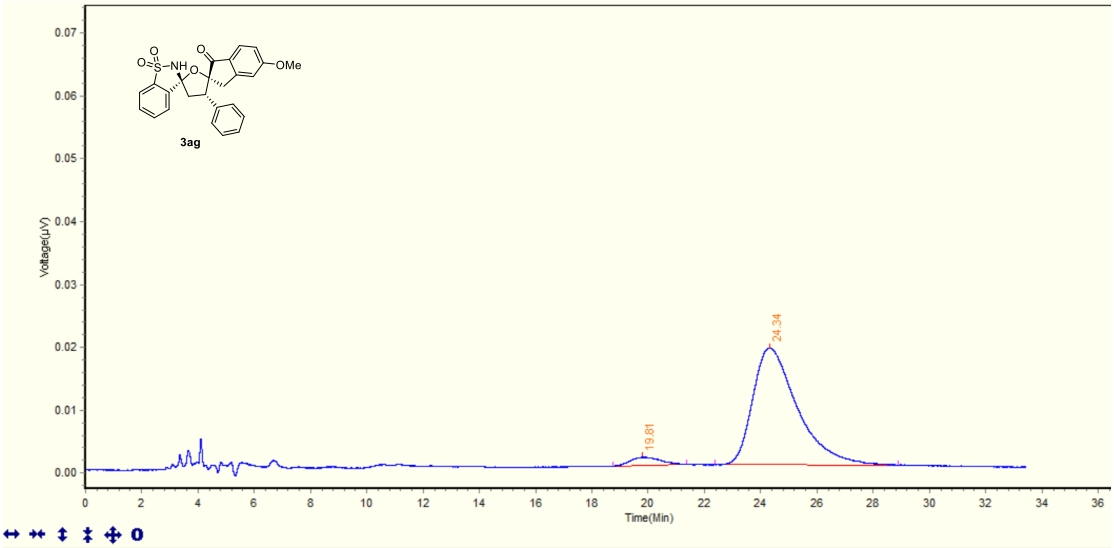
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	31.67	2773431	8939	99.01%	16.831	BB
2	49.97	27700	92	0.99%	10.648	BB
Total		2,801,131	9,031	100.00%		



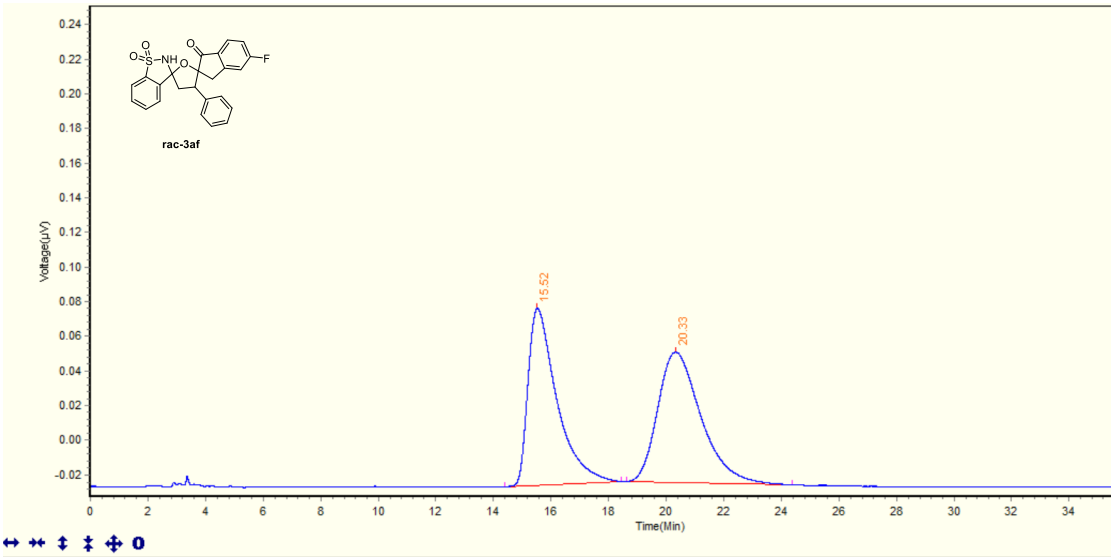
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	19.35	894112	9792	50.03%	4.539	BB
2	24.70	892867	8129	49.97%	6.028	BB
Total		1,786,979	17,921	100.00%		



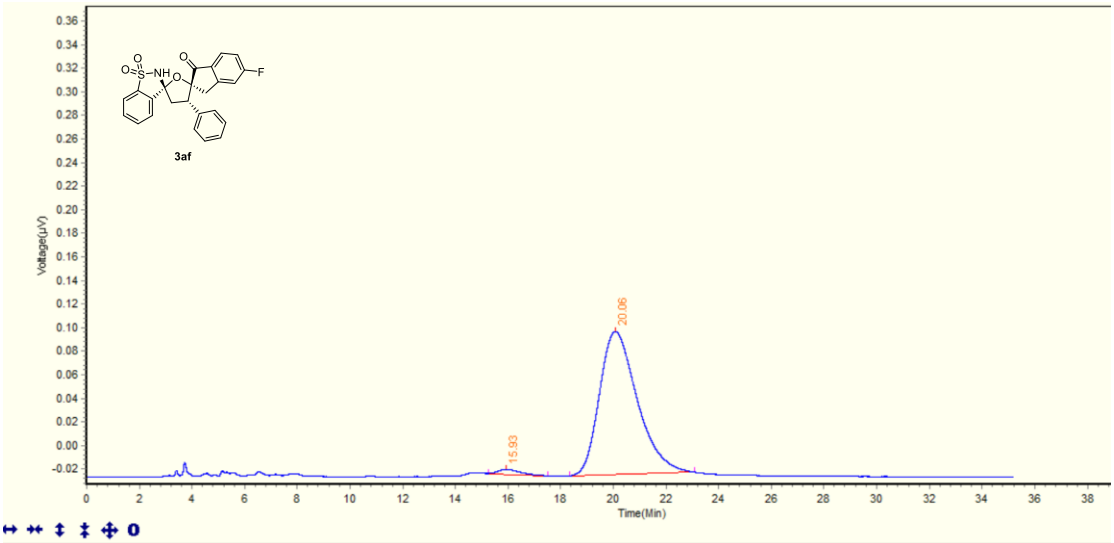
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	19.81	48509	674	4.54%	2.619	BB
2	24.34	1018849	9293	95.46%	6.512	BB
Total		1,067,358	9,967	100.00%		



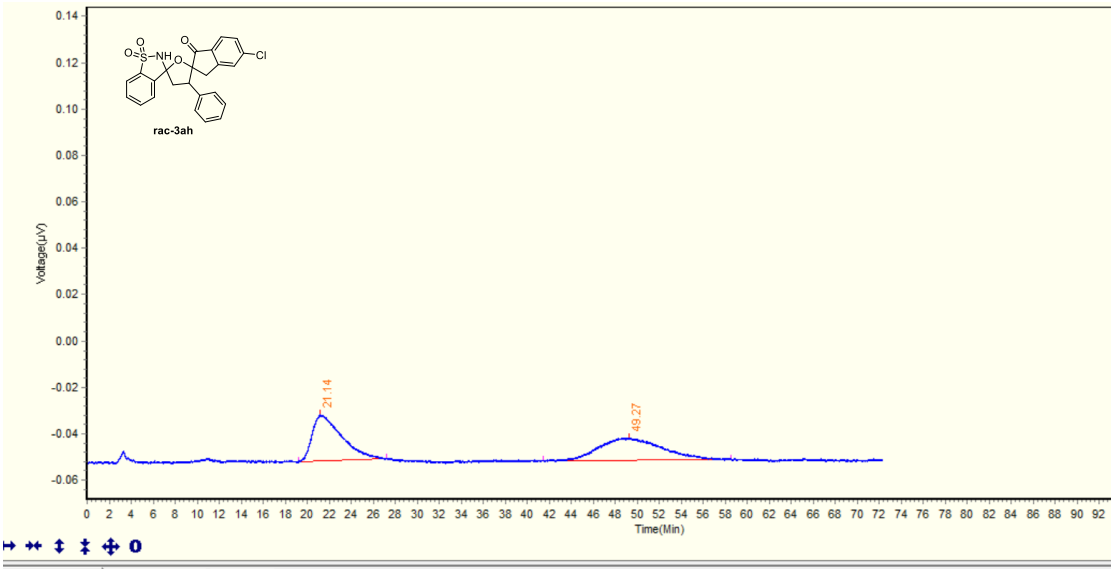
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	15.52	3538099	51014	47.44%	4.043	BB
2	20.33	3919978	37594	52.56%	5.751	BB
Total		7,458,077	88,608	100.00%		



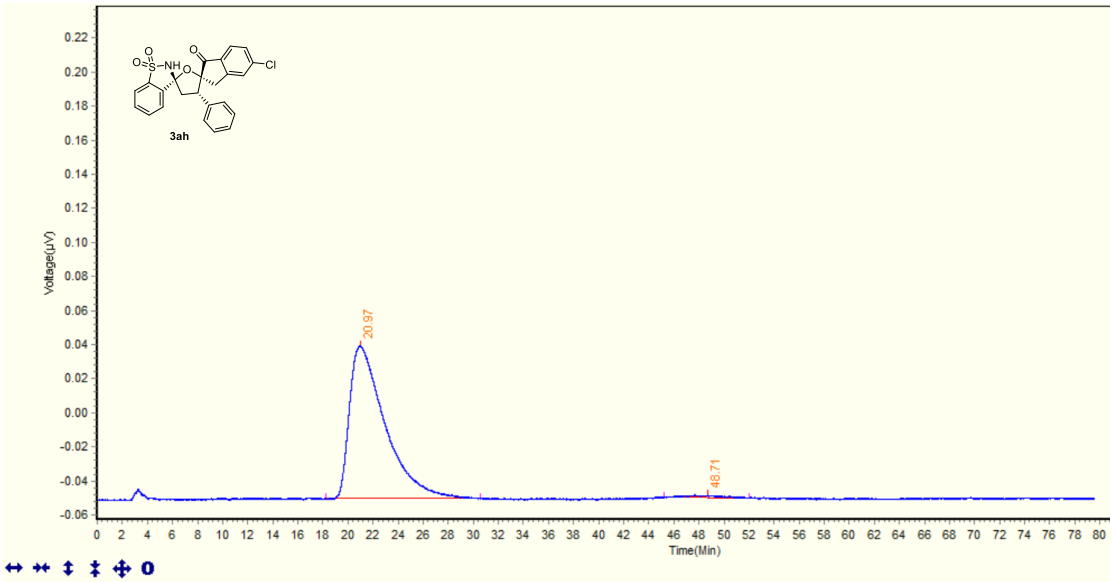
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	15.93	110737	1959	1.80%	2.253	BB
2	20.06	6053793	60623	98.20%	4.743	BB
Total		6,164,530	62,582	100.00%		



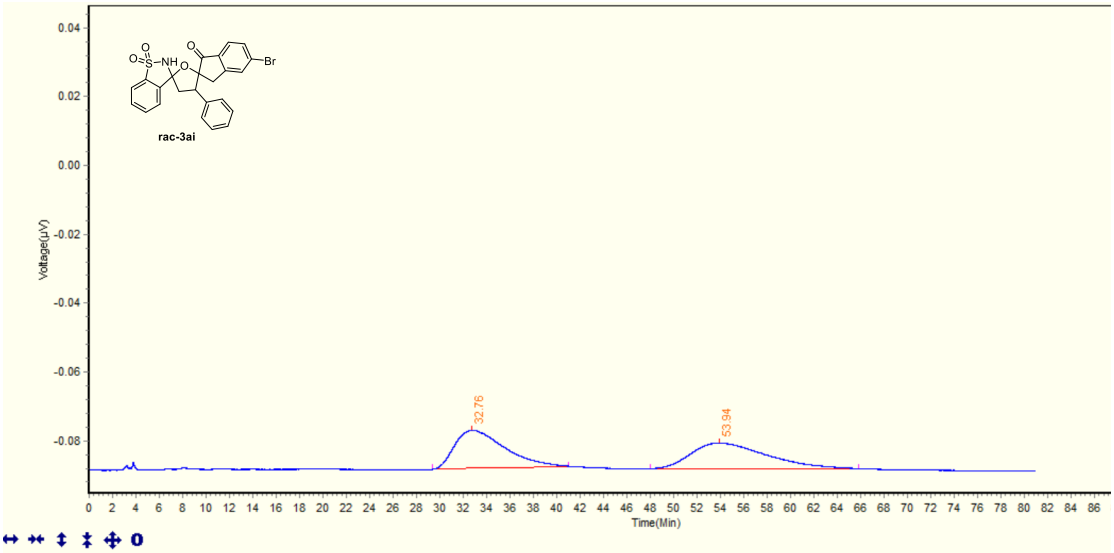
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	21.14	1839948	9979	49.30%	7.996	BB
2	49.27	1892232	4825	50.70%	17.065	BB
Total		3,732,180	14,804	100.00%		



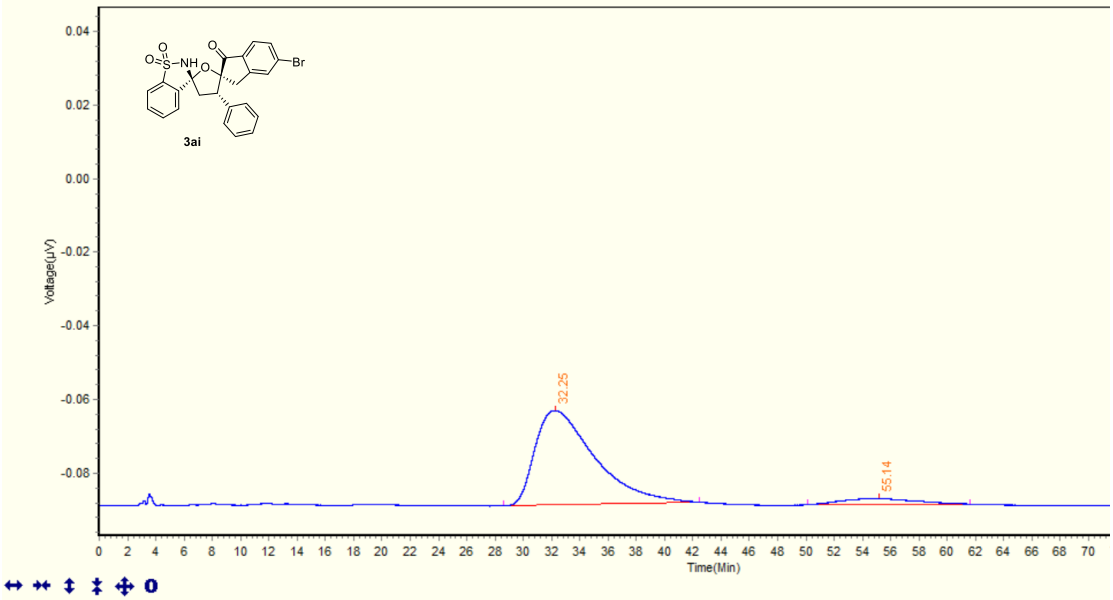
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	20.97	8797059	44753	98.49%	12.332	BB
2	48.71	134812	788	1.51%	6.791	BB
Total		8,931,871	45,541	100.00%		



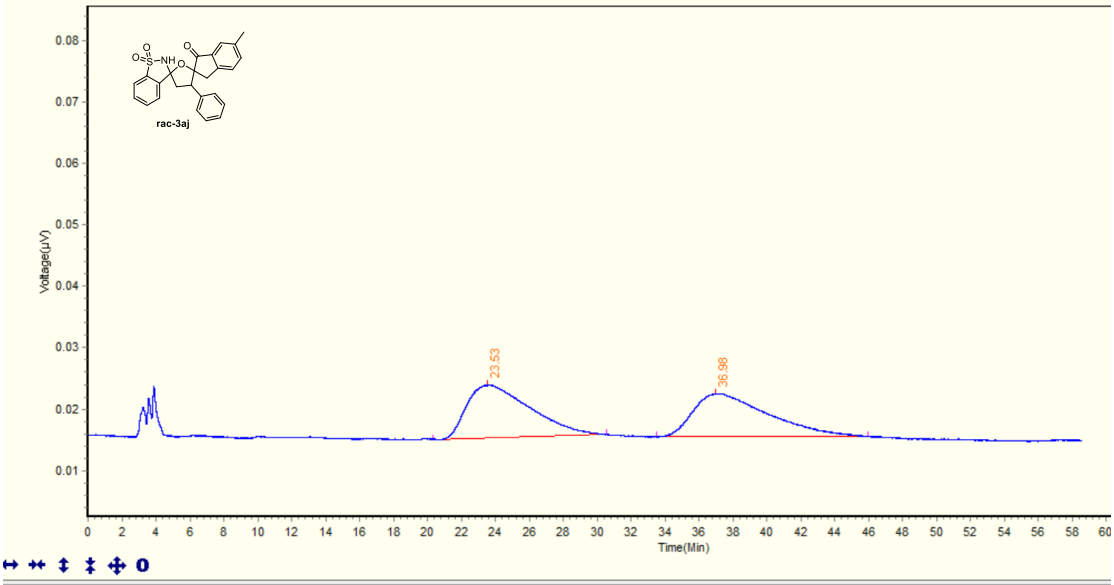
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	32.76	1647323	5539	49.45%	11.637	BB
2	53.94	1683946	3761	50.55%	17.819	BB
Total		3,331,269	9,300	100.00%		



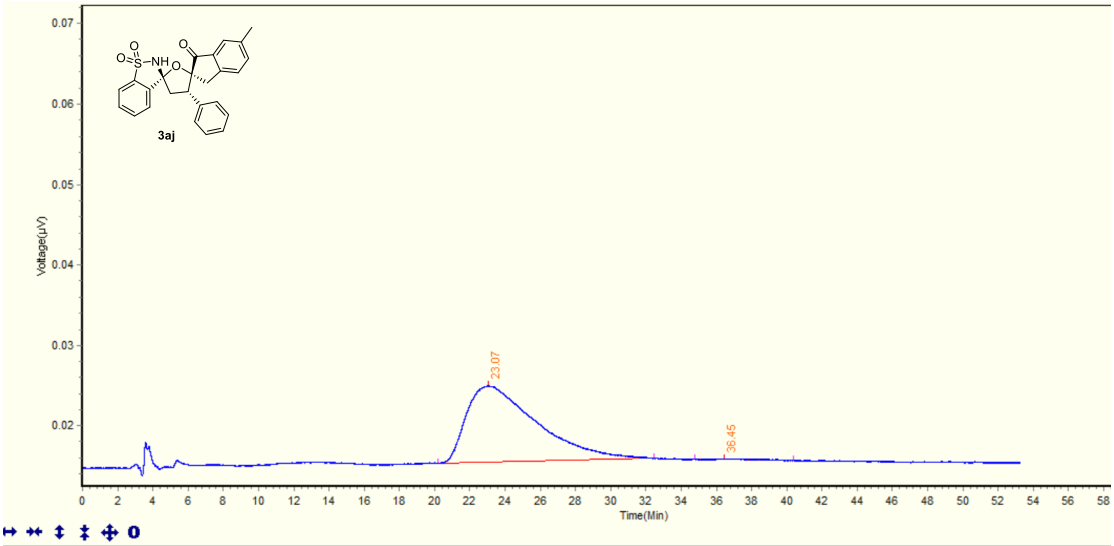
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Ty
1	32.25	3752485	12821	92.87%	13.854	BB
2	55.14	288285	786	7.13%	11.491	BB
Total		4,040,770	13,607	100.00%		



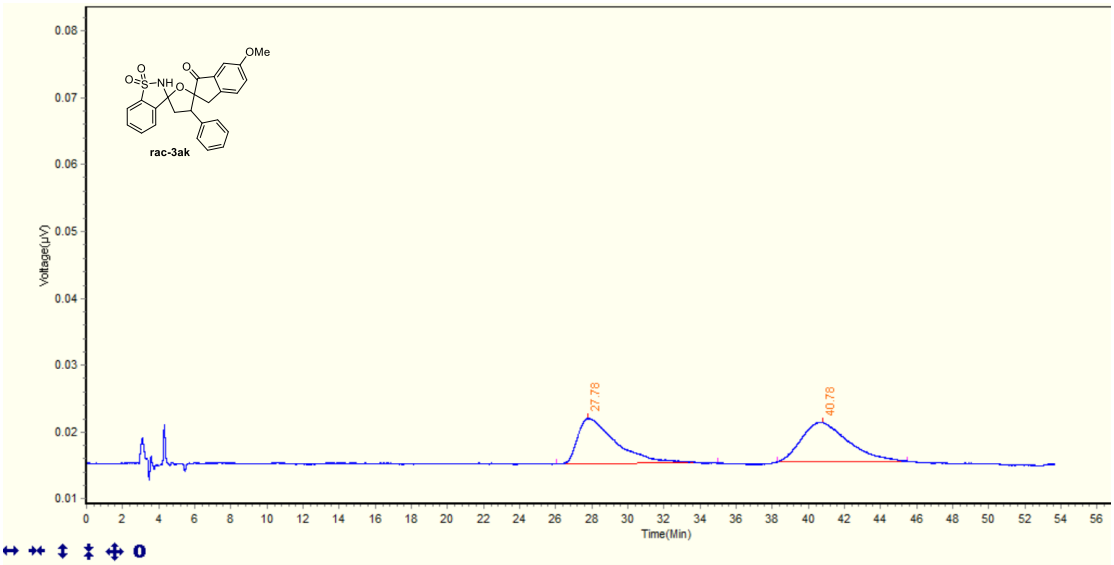
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	23.53	1105318	4296	50.79%	10.225	BB
2	36.98	1071009	3492	49.21%	12.453	BB
Total		2,176,327	7,788	100.00%		



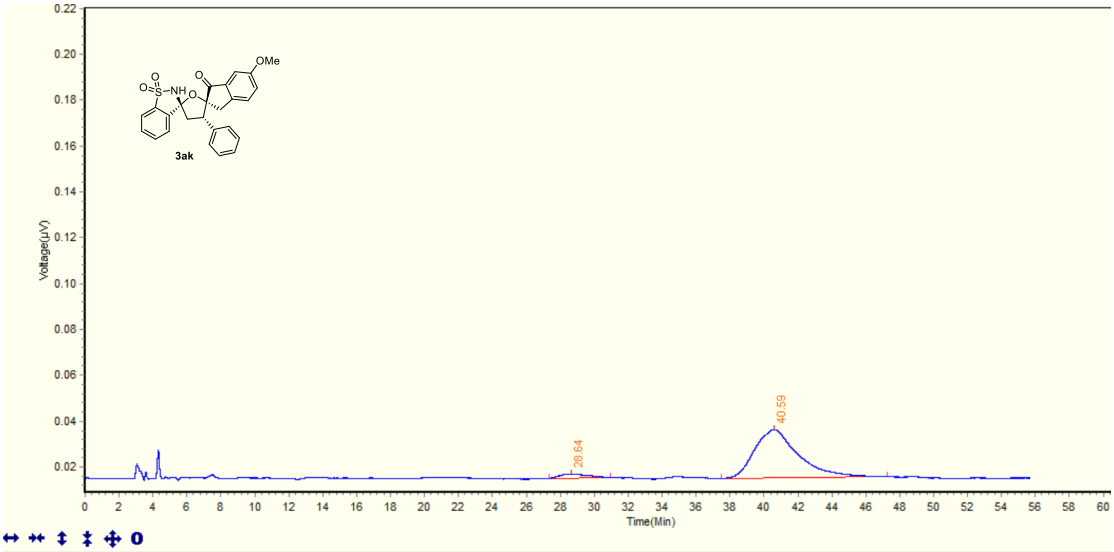
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	23.07	1289986	4714	99.85%	12.267	BB
2	36.45	1896	44	0.15%	5.598	BB
Total		1,291,882	4,758	100.00%		



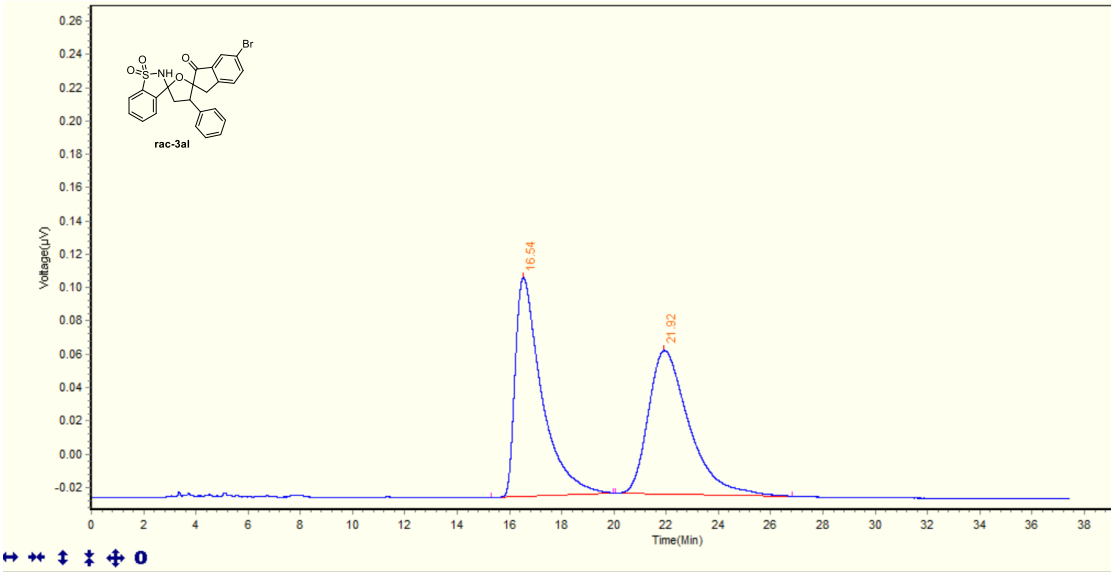
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	27.78	509801	3420	49.15%	8.938	BB
2	40.78	527476	2948	50.85%	7.199	BB
Total		1,037,277	6,368	100.00%		



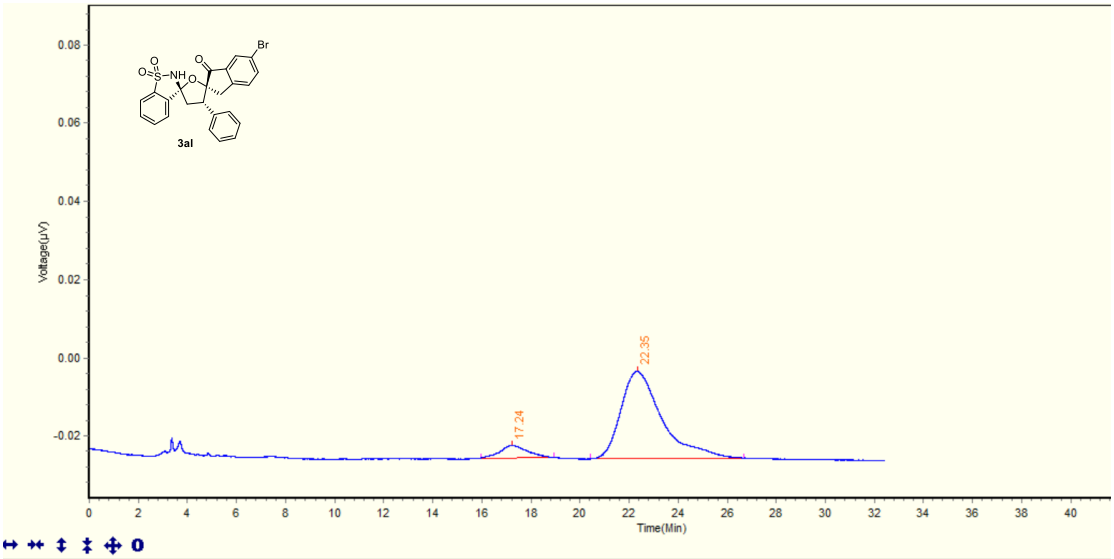
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	28.64	98574	862	4.97%	3.612	BB
2	40.59	1886167	10560	95.03%	9.776	BB
Total		1,984,741	11,422	100.00%		



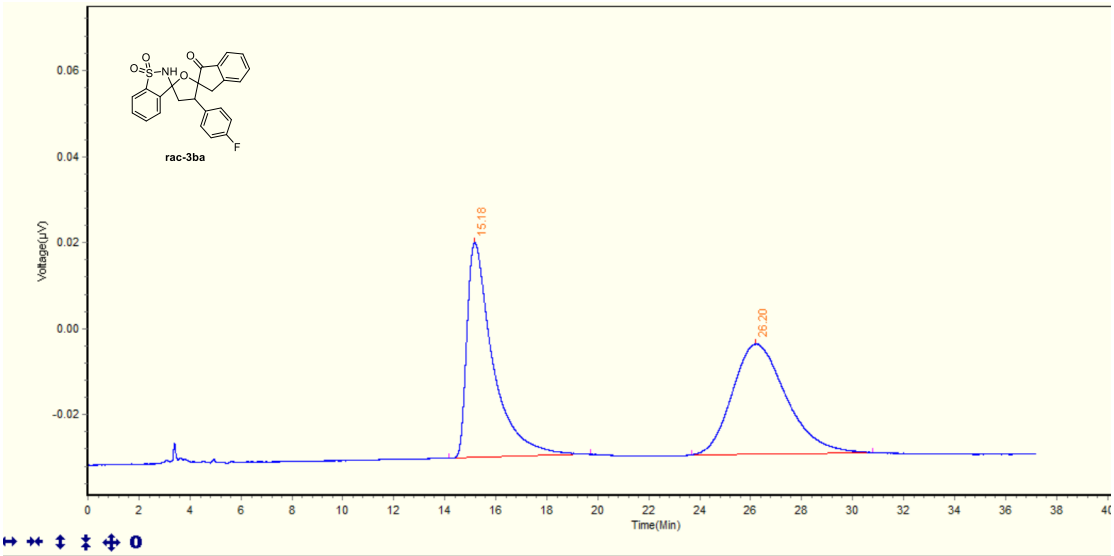
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	16.54	4621138	65712	49.84%	4.666	BB
2	21.92	4651586	43053	50.16%	6.768	BB
Total		9,272,724	108,765	100.00%		



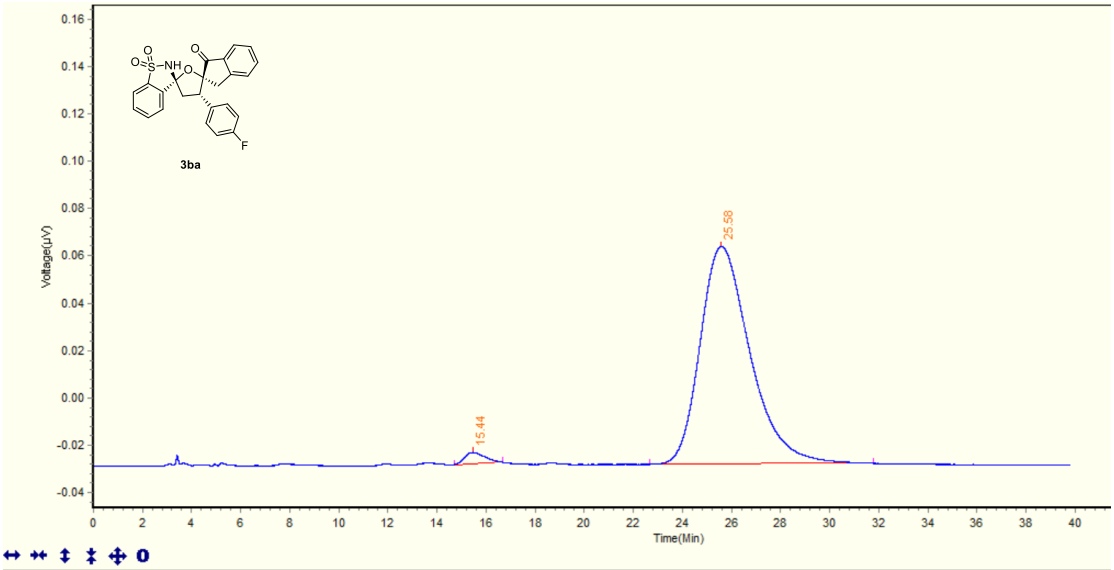
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	17.24	119561	1551	8.46%	2.973	BB
2	22.35	1293833	11148	91.54%	6.254	BB
Total		1,413,394	12,699	100.00%		



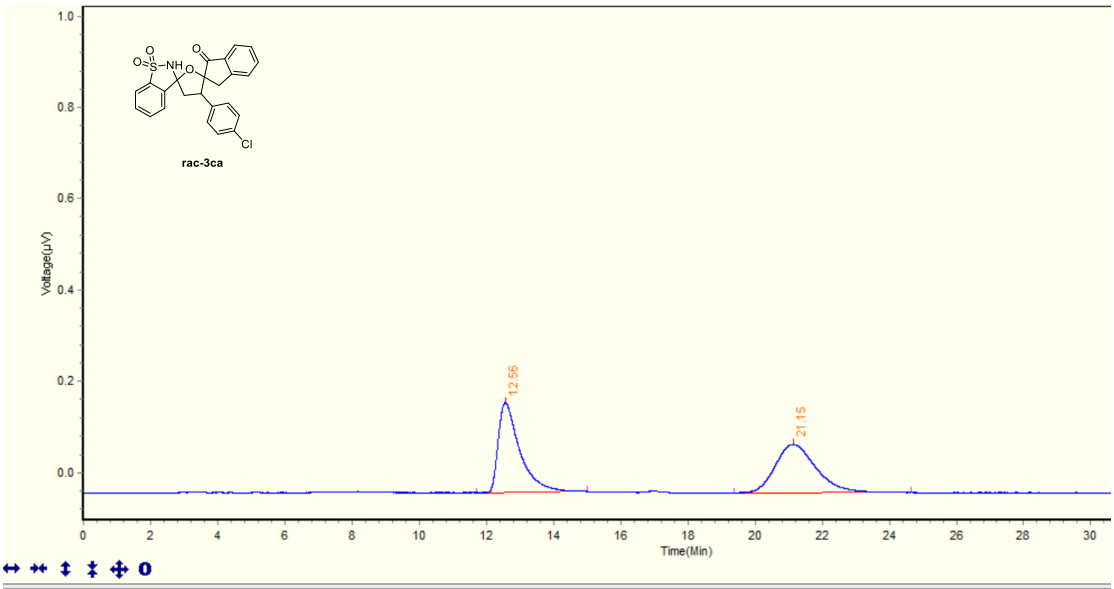
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	15.18	1766443	25011	48.55%	5.556	BB
2	26.20	1872207	12785	51.45%	7.102	BB
Total		3,638,650	37,796	100.00%		



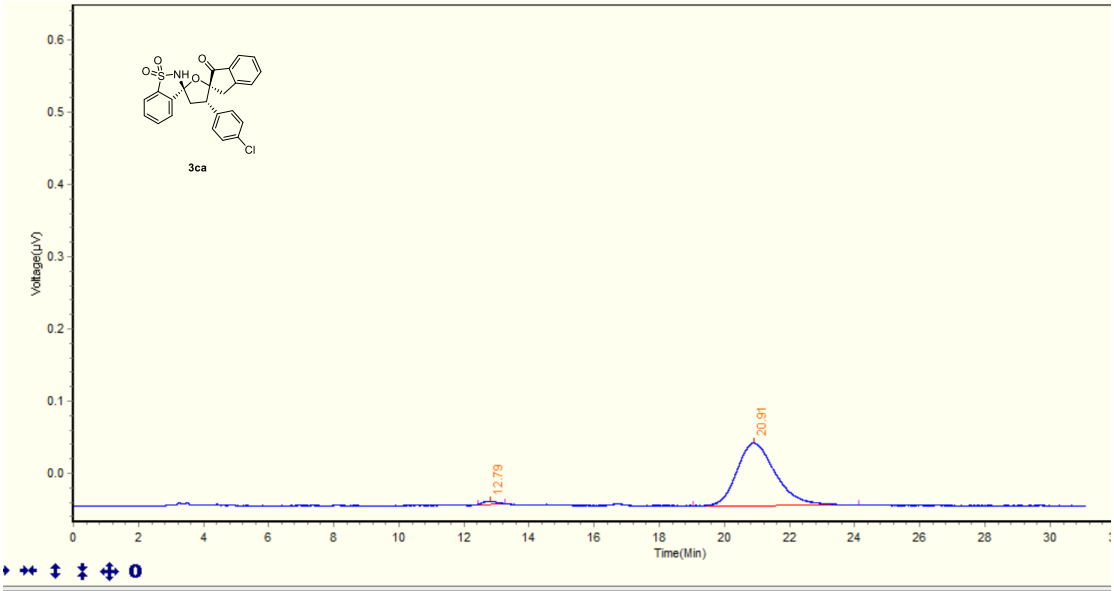
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	15.44	135822	2380	2.04%	1.967	BB
2	25.58	6513219	46072	97.96%	9.118	BB
Total		6,649,041	48,452	100.00%		



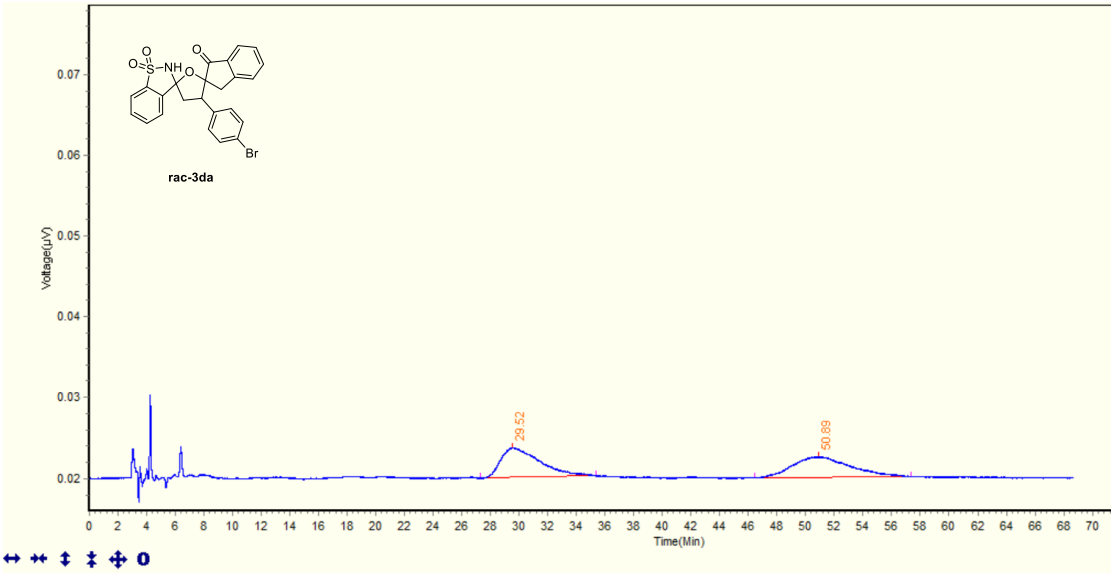
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	12.56	4365877	98140	49.29%	3.278	BB
2	21.15	4491501	53094	50.71%	5.255	BB
Total		8,857,378	151,234	100.00%		



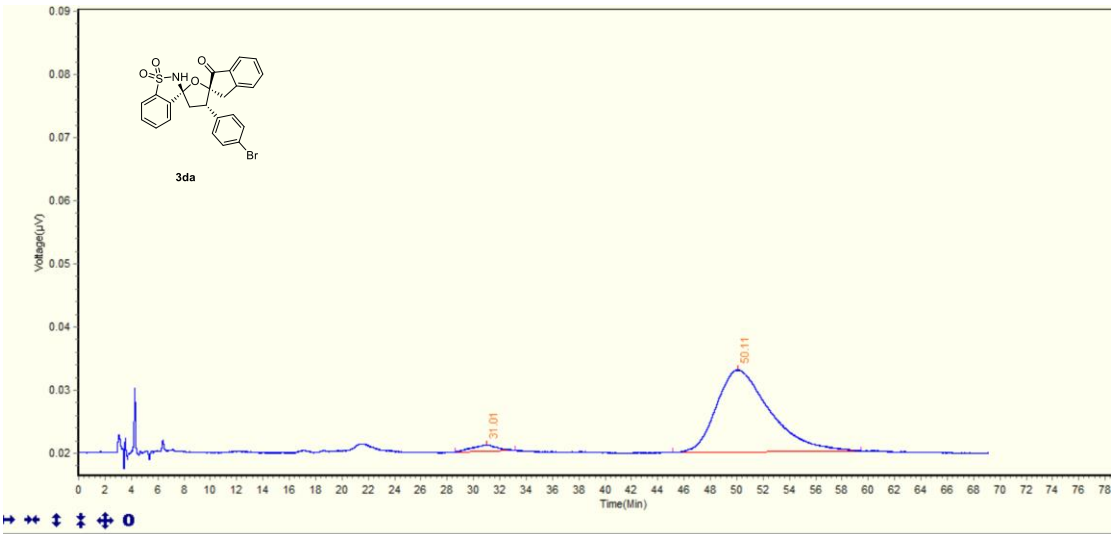
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	12.79	55081	1981	1.51%	0.831	BB
2	20.91	3582608	43352	98.49%	5.101	BB
otal		3,637,689	45,333	100.00%		



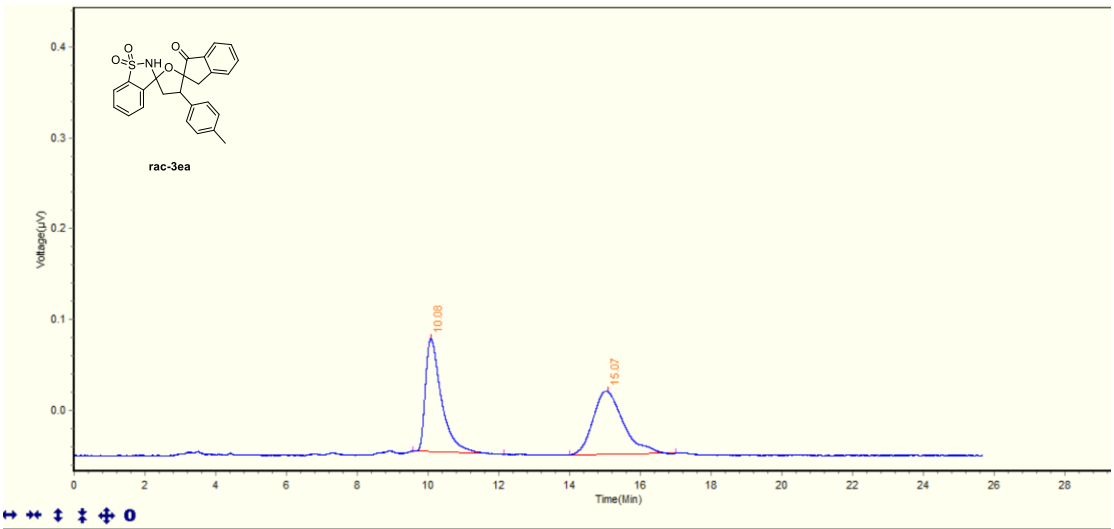
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	29.52	352427	1865	50.64%	8.072	BB
2	50.89	343457	1256	49.36%	10.917	BB
Total		695,884	3,121	100.00%		



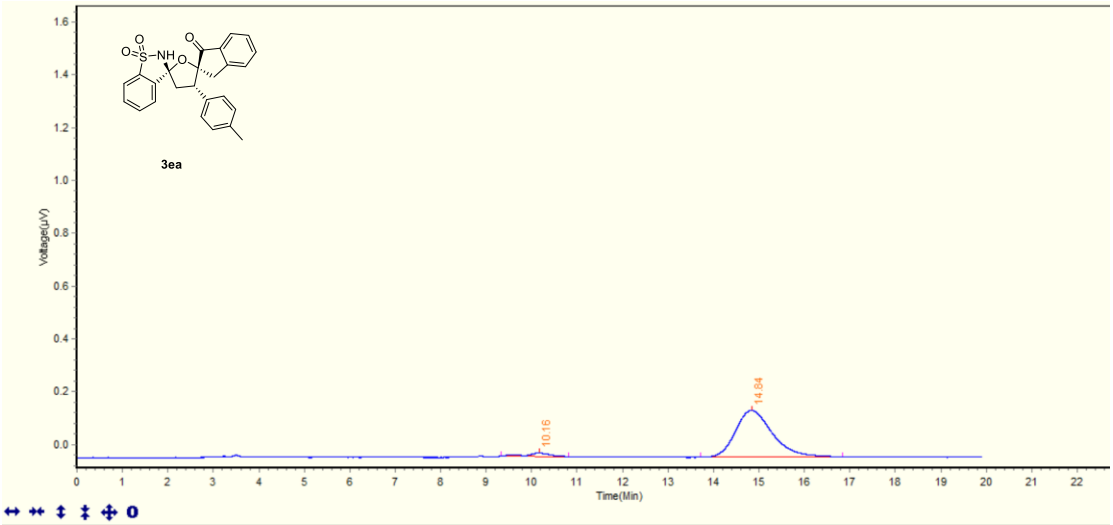
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	31.01	64608	488	3.44%	4.56	BB
2	50.11	1815395	6469	96.56%	14.299	BB
Total		1,880,003	6,957	100.00%		



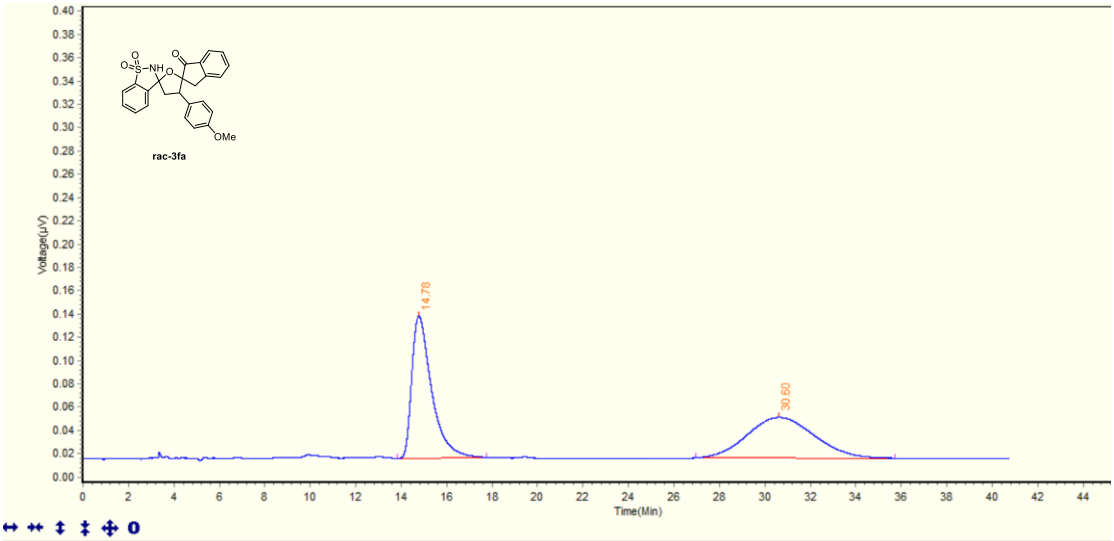
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	10.08	1978710	62407	49.16%	2.571	BB
2	15.07	2046091	34710	50.84%	2.999	BB
Total		4,024,801	97,117	100.00%		



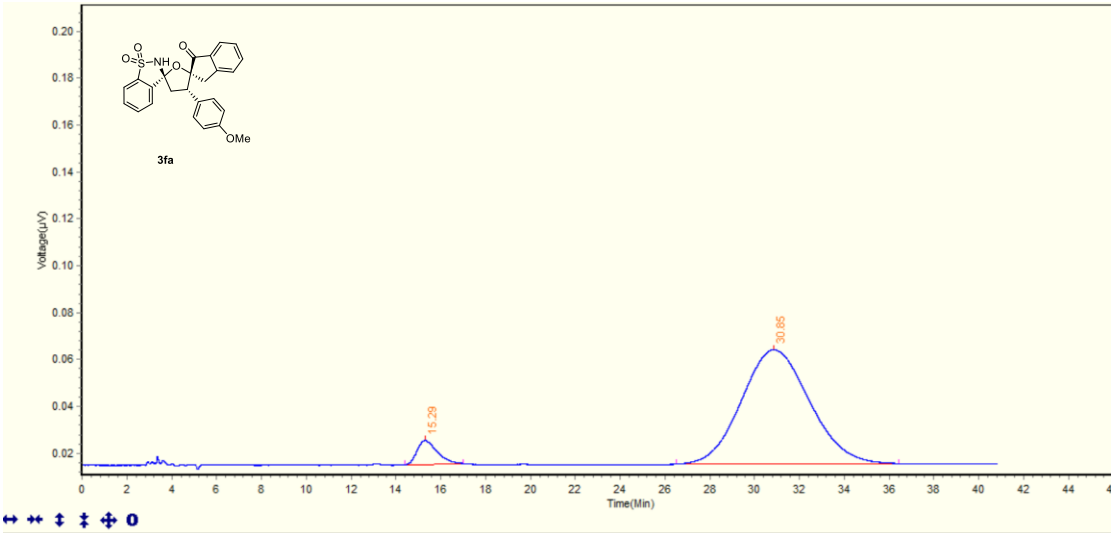
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	10.16	232628	6409	4.49%	1.484	BB
2	14.84	4947142	88107	95.51%	3.131	BB
Total		5,179,770	94,516	100.00%		



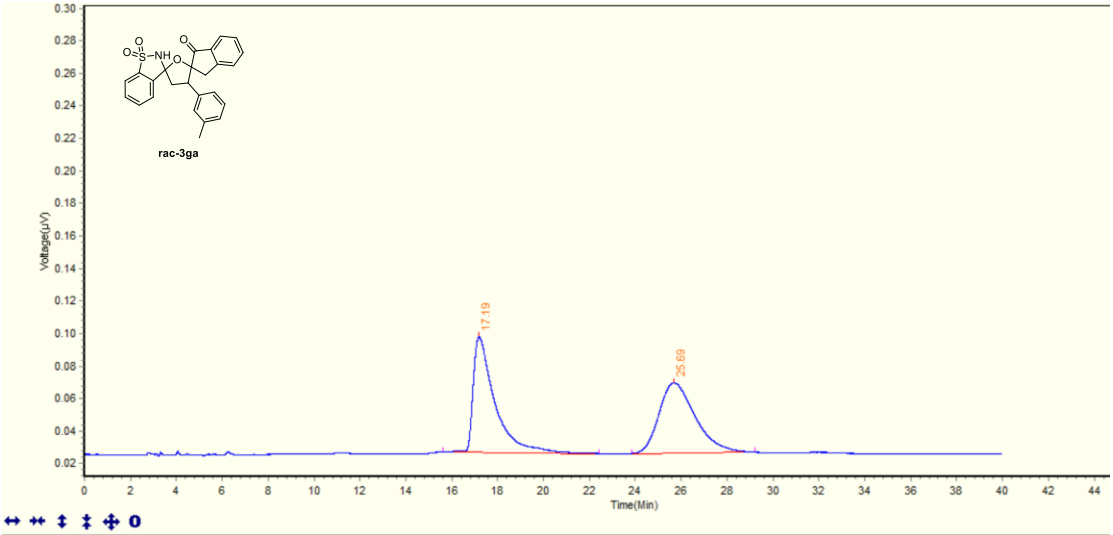
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	14.78	3680394	60970	50.65%	3.923	BB
2	30.60	3586113	17446	49.35%	8.758	BB
Total		7,266,507	78,416	100.00%		



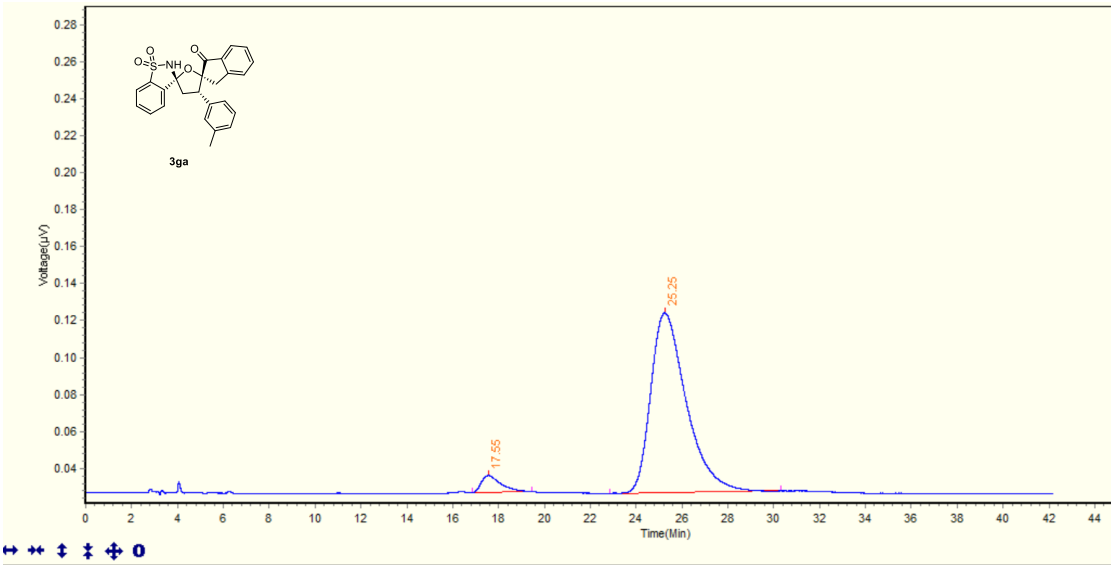
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	15.29	314926	5090	5.77%	2.605	BB
2	30.85	5144975	24325	94.23%	9.919	BB
Total		5,459,901	29,415	100.00%		



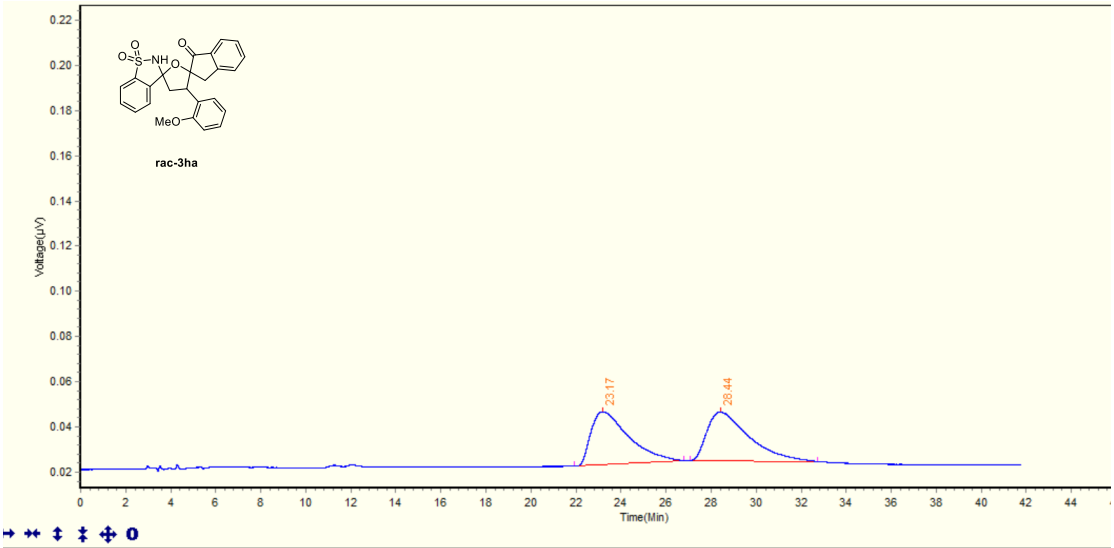
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	17.19	2331040	35498	49.67%	6.801	BB
2	25.69	2361764	21581	50.33%	5.368	BB
Total		4,692,804	57,079	100.00%		



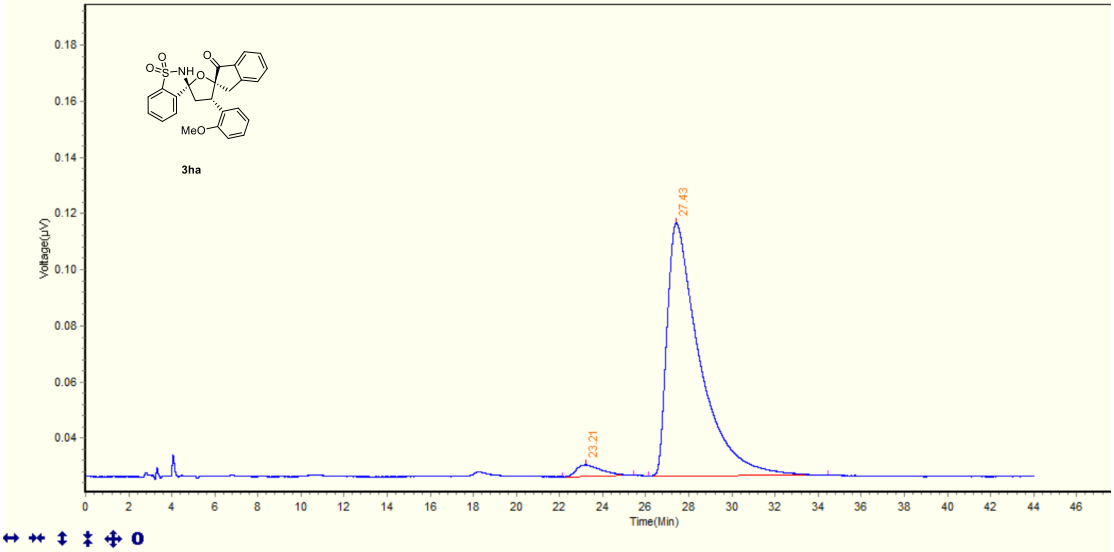
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	17.55	268761	4494	4.88%	2.598	BB
2	25.25	5238660	48676	95.12%	7.46	BB
Total		5,507,421	53,170	100.00%		



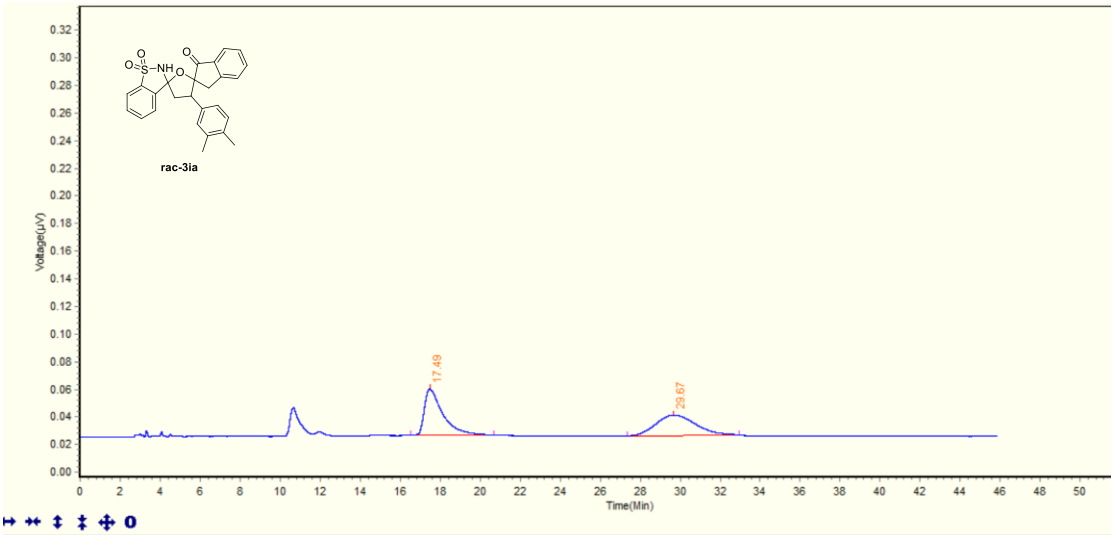
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	23.17	1360637	11743	49.41%	4.863	BB
2	28.44	1393121	10804	50.59%	5.657	BB
Total		2,753,758	22,547	100.00%		



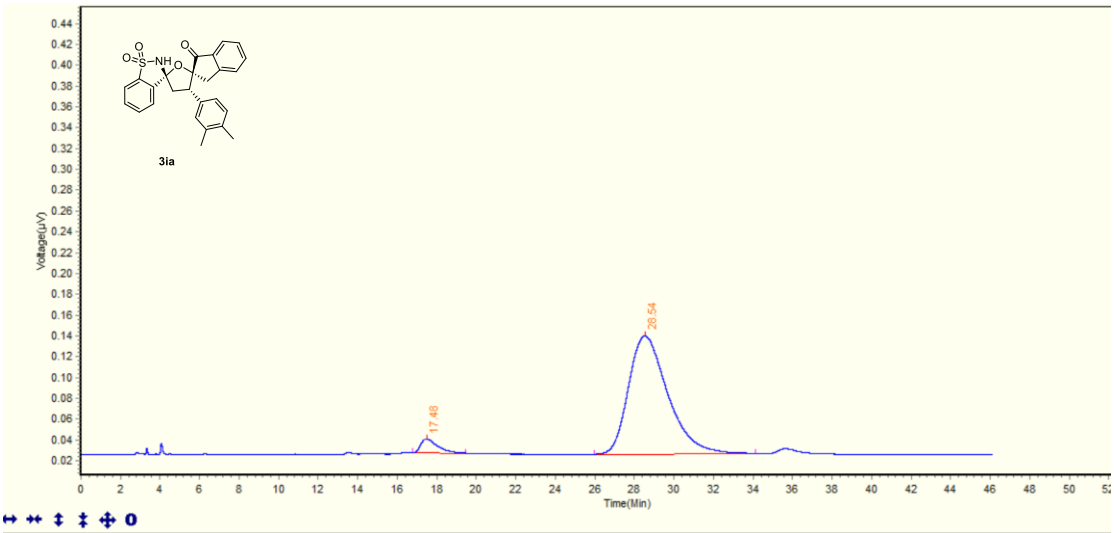
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	23.21	165204	2045	3.38%	3.303	BB
2	27.43	4727783	45104	96.62%	8.33	BB
Total		4,892,987	47,149	100.00%		



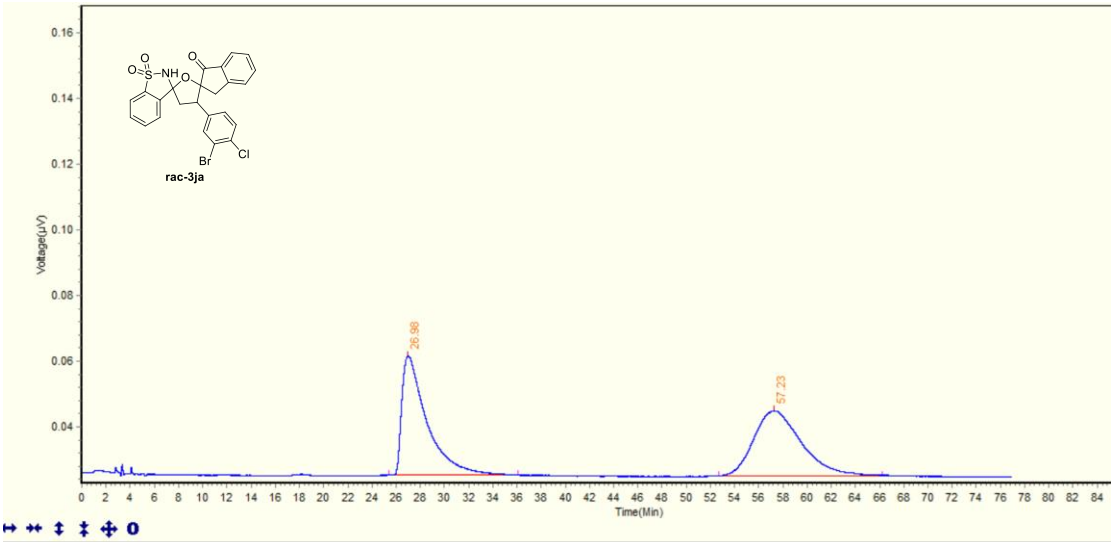
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	17.49	1048880	16560	50.38%	4.157	BB
2	29.67	1033081	7453	49.62%	5.594	BB
Total		2,081,961	24,013	100.00%		



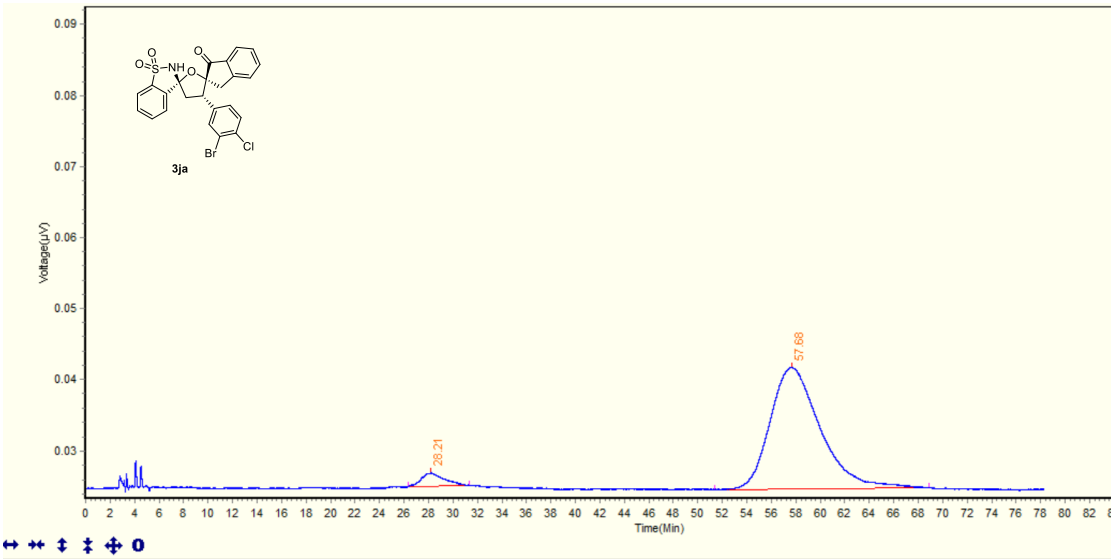
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	17.48	388684	6649	4.74%	2.684	BB
2	28.54	7814416	56518	95.26%	8.157	BB
Total		8,203,100	63,167	100.00%		



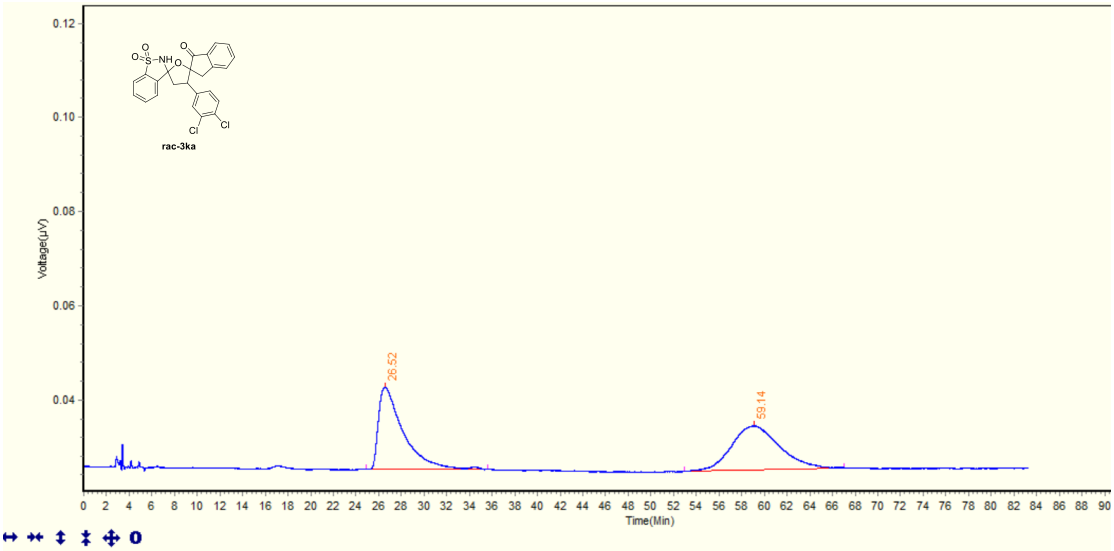
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	26.98	2621357	18168	49.40%	10.678	BB
2	57.23	2684537	9905	50.60%	13.518	BB
Total		5,305,894	28,073	100.00%		



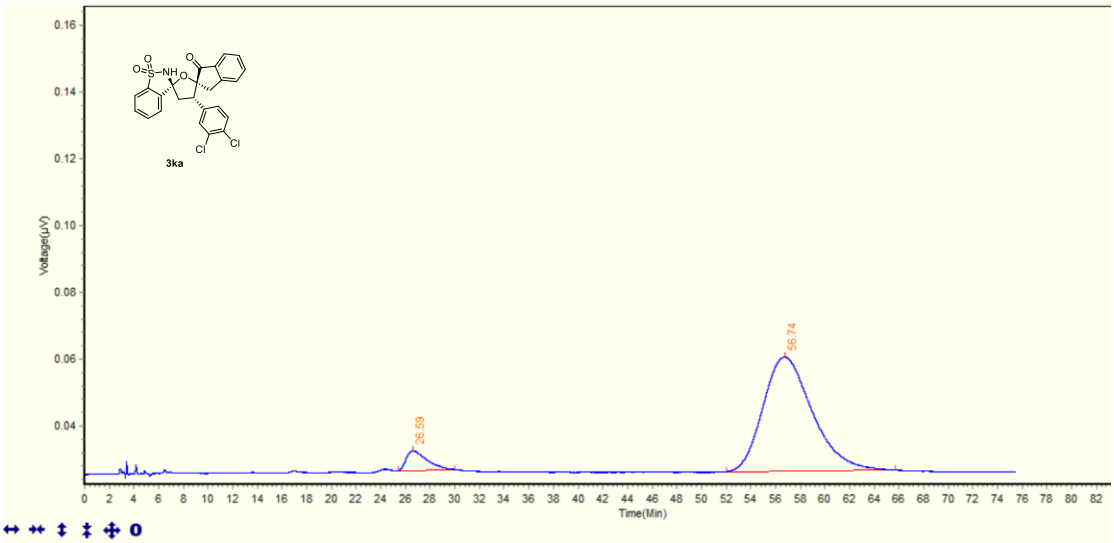
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	28.21	122219	942	4.79%	4.988	BB
2	57.68	2430431	8544	95.21%	17.503	BB
Total		2,552,650	9,486	100.00%		



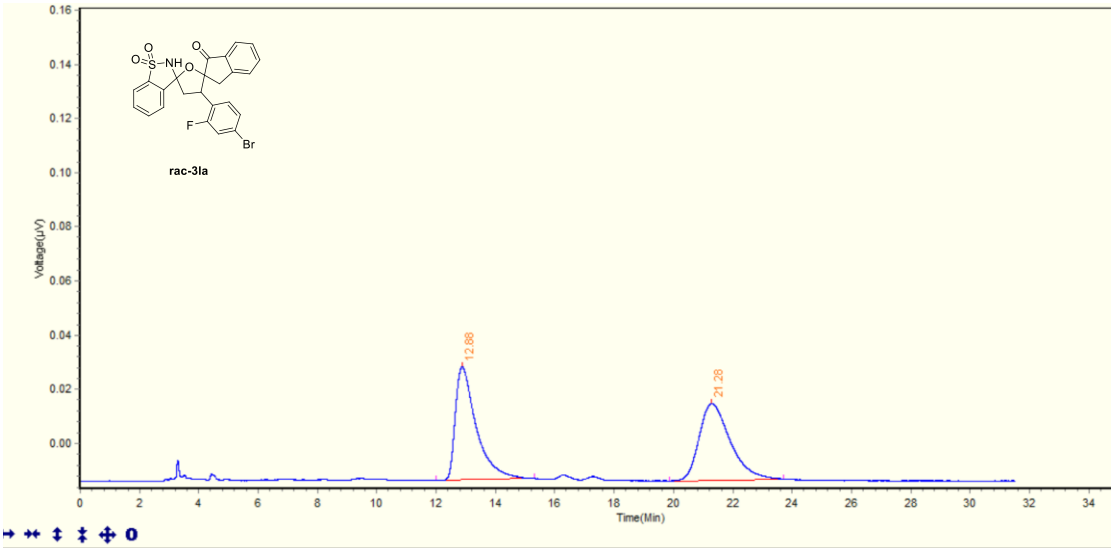
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	26.52	1318571	8746	49.17%	10.719	BB
2	59.14	1363083	4670	50.83%	14.075	BB
Total		2,681,654	13,416	100.00%		



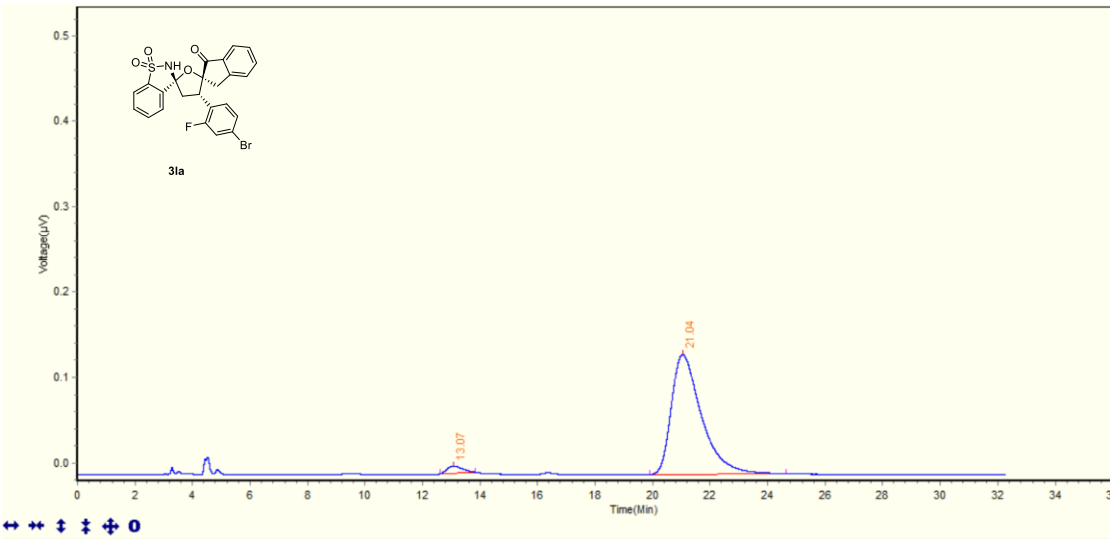
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	26.59	348839	2992	6.87%	4.562	BB
2	56.74	4726777	17073	93.13%	13.685	BB
Total		5,075,616	20,065	100.00%		



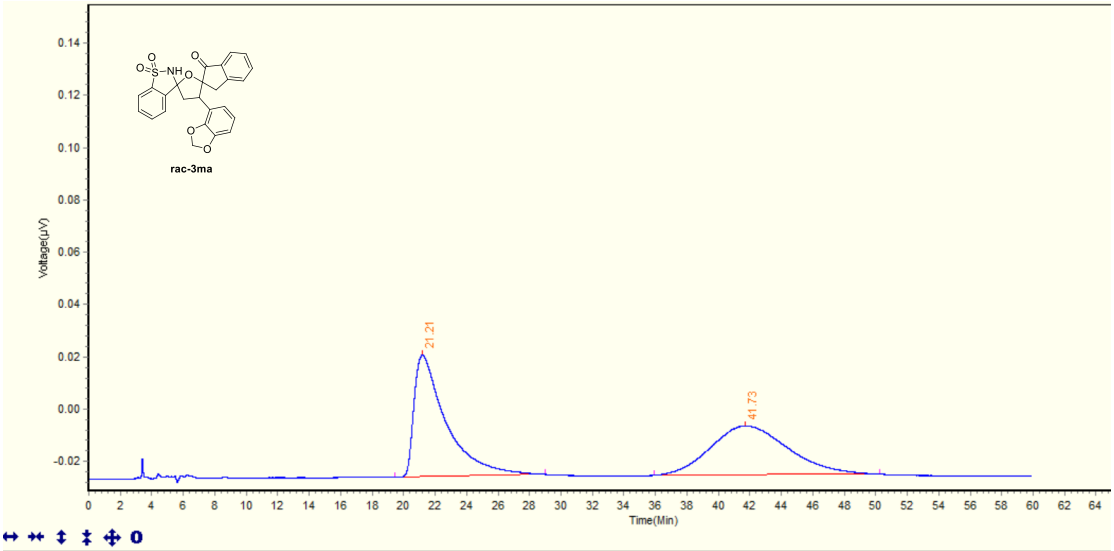
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	12.88	1023868	20944	49.78%	3.317	BB
2	21.28	1032722	14197	50.22%	3.846	BB
Total		2,056,590	35,141	100.00%		



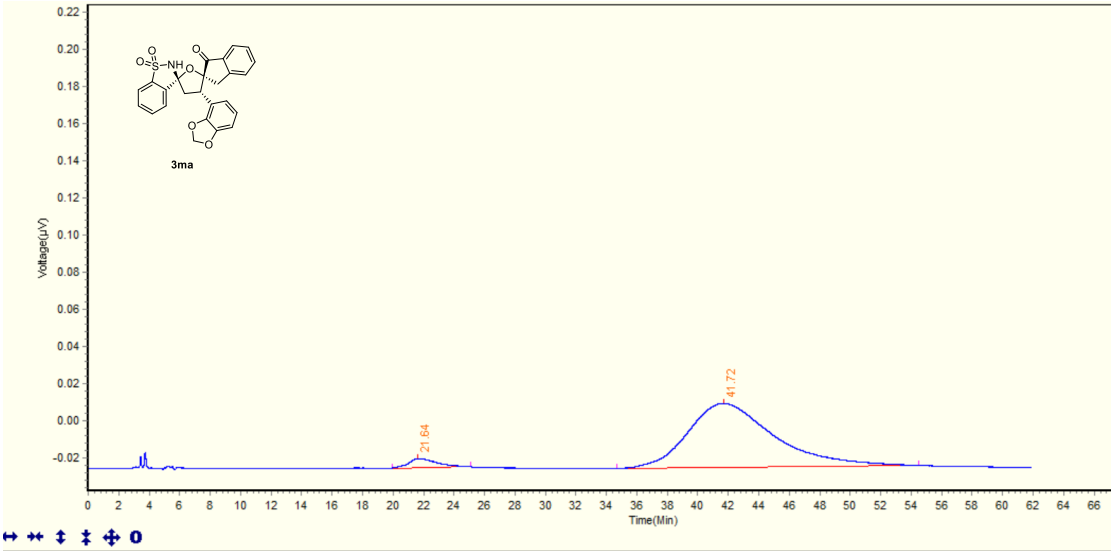
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	13.07	157977	4195	3.00%	1.222	BB
2	21.04	5099323	70023	97.00%	4.742	BB
Total		5,257,300	74,218	100.00%		



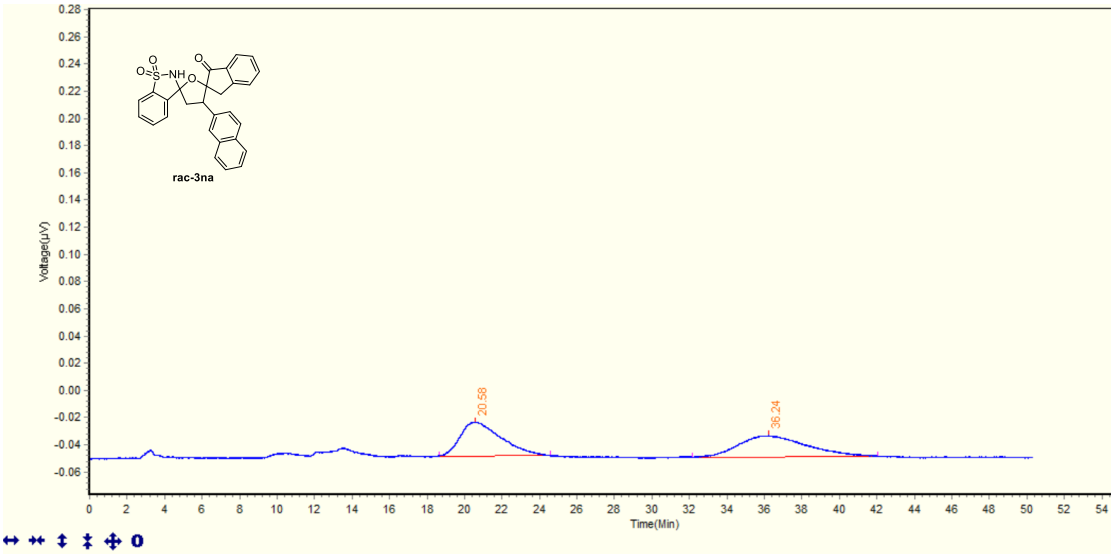
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	21.21	3281319	23234	50.62%	9.552	BB
2	41.73	3200740	9384	49.38%	14.328	BB
Total		6,482,059	32,618	100.00%		



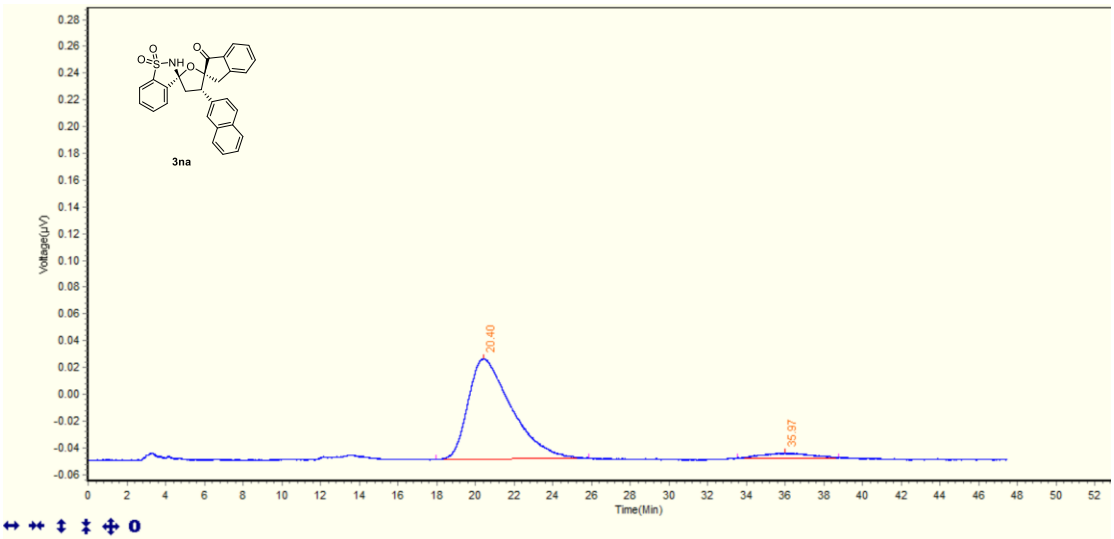
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	21.64	314133	2446	4.45%	5.143	BB
2	41.72	6742813	17208	95.55%	19.809	BB
Total		7,056,946	19,654	100.00%		



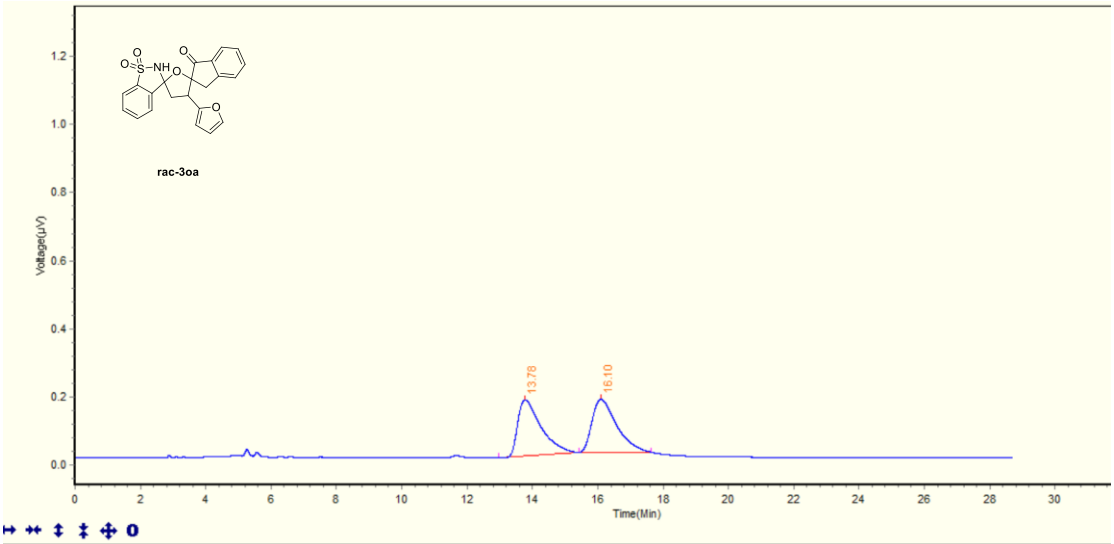
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	20.58	1880103	12354	49.38%	5.934	BB
2	36.24	1927069	7796	50.62%	9.89	BB
Total		3,807,172	20,150	100.00%		



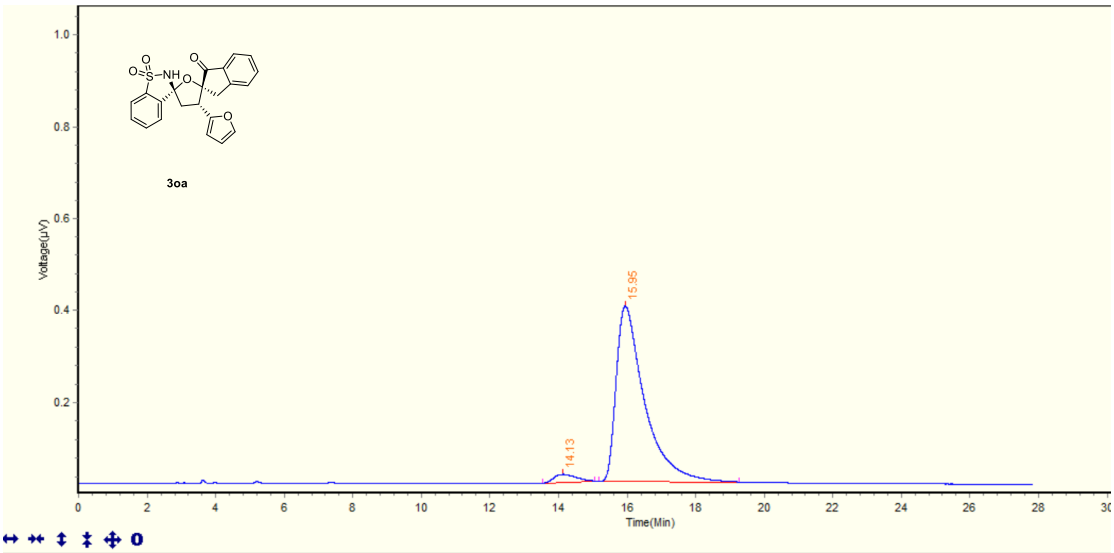
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	20.40	5823355	37534	95.13%	7.892	BB
2	35.97	297973	1882	4.87%	5.225	BB
Total		6,121,328	39,416	100.00%		



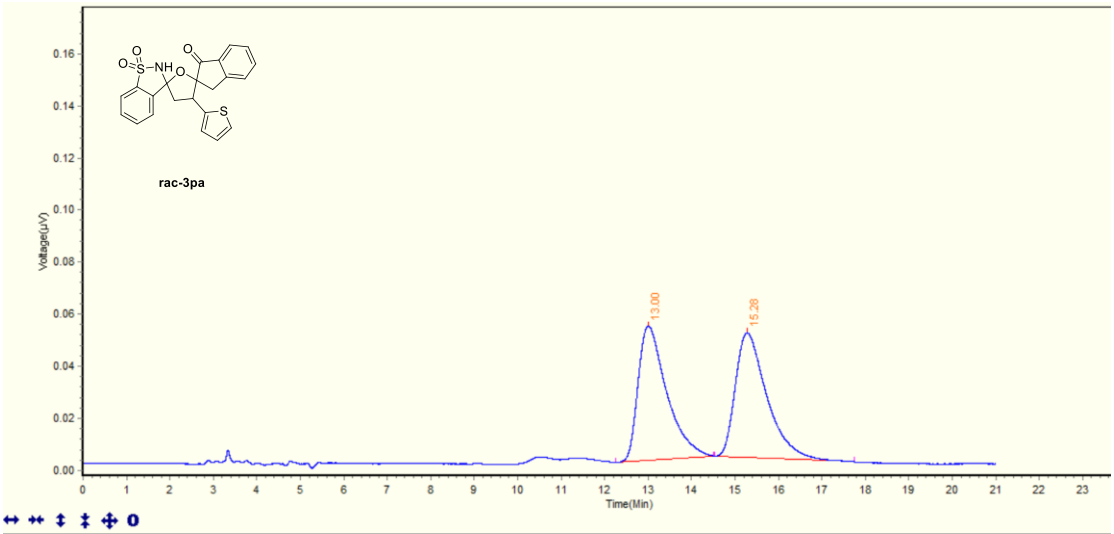
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	13.78	4039657	82367	49.88%	2.459	BB
2	16.10	4058881	77580	50.12%	2.204	BB
Total		8,098,538	159,947	100.00%		



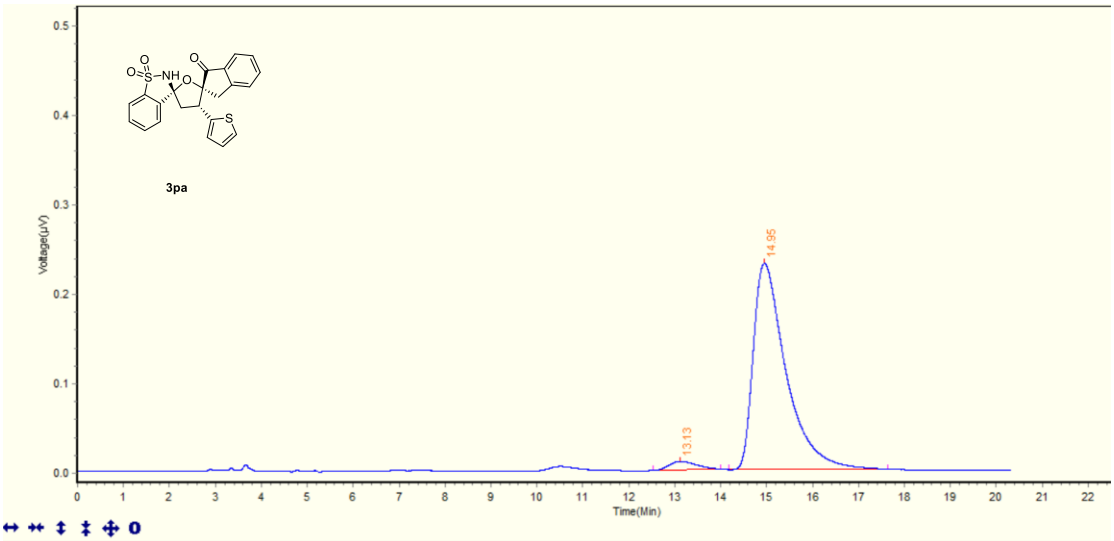
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	14.13	389708	8712	3.44%	1.518	BB
2	15.95	10943225	191137	96.56%	4.088	BB
Total		11,332,933	199,849	100.00%		



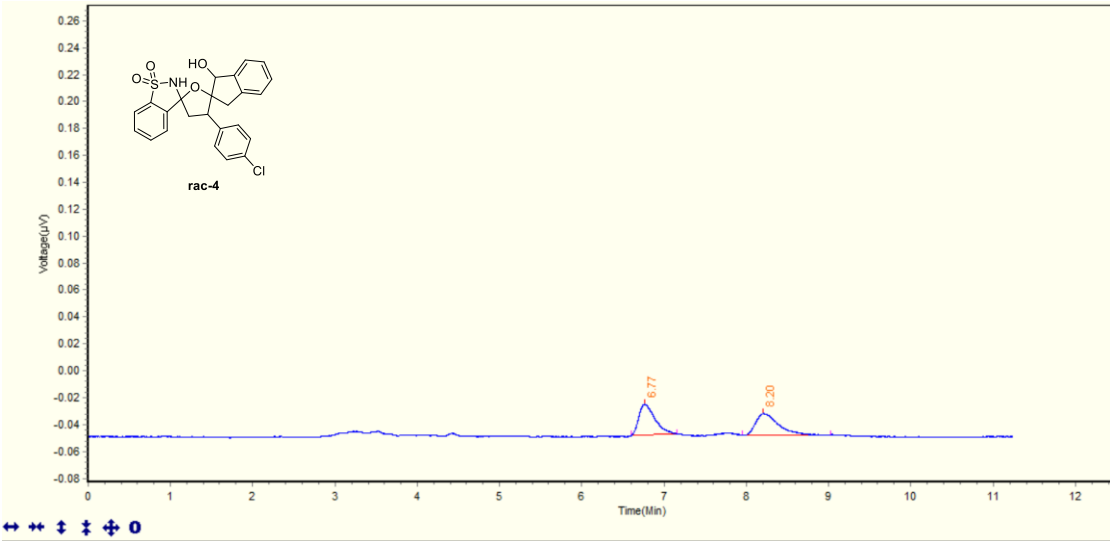
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	13.00	1175099	25774	49.27%	2.254	BB
2	15.28	1210155	23935	50.73%	3.216	BB
Total		2,385,254	49,709	100.00%		



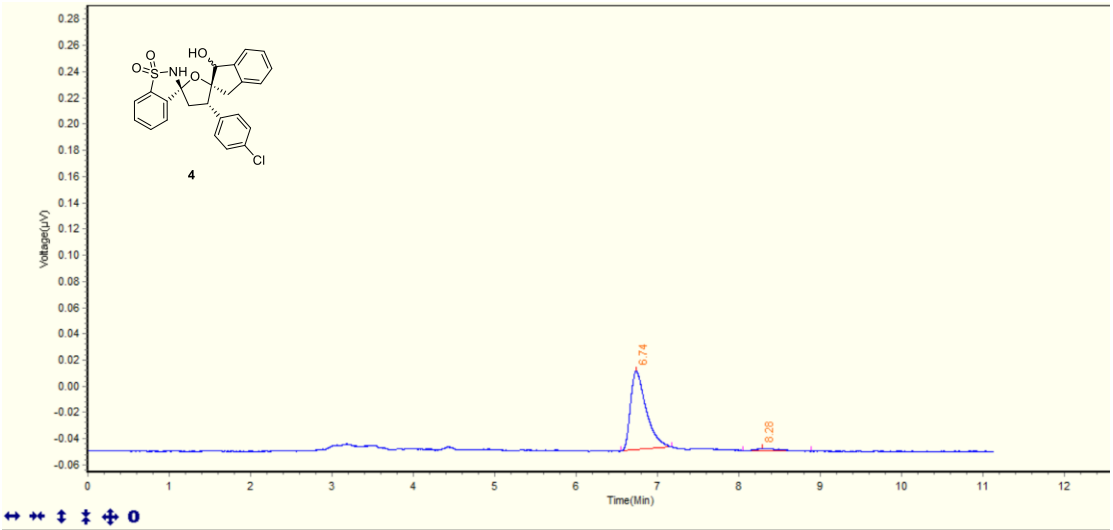
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	13.13	199031	4825	3.37%	1.47	BB
2	14.95	5701893	115160	96.63%	3.46	BB
Total		5,900,924	119,985	100.00%		



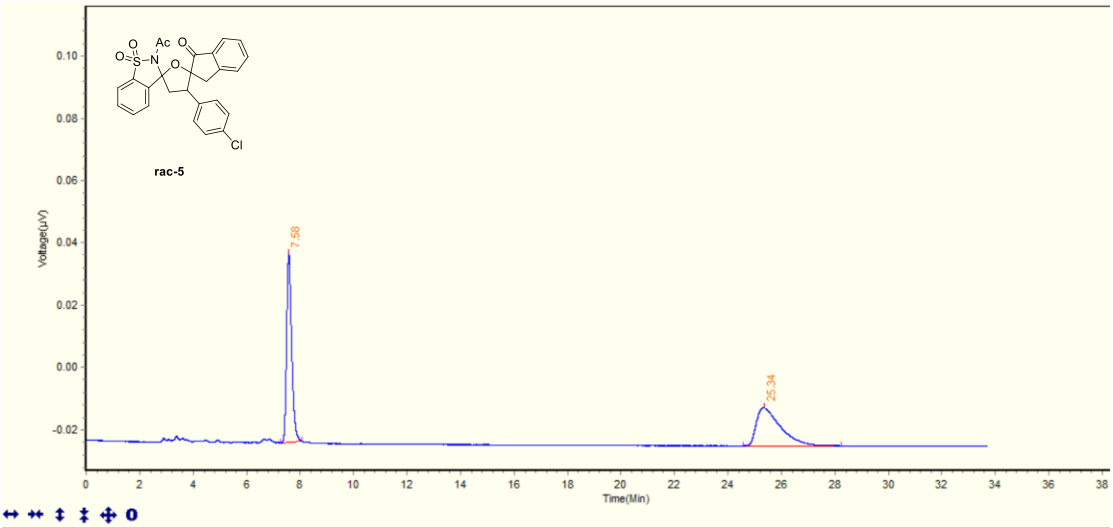
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	6.77	155328	11430	50.43%	0.556	BB
2	8.20	152650	7978	49.57%	1.073	BB
Total		307,978	19,408	100.00%		



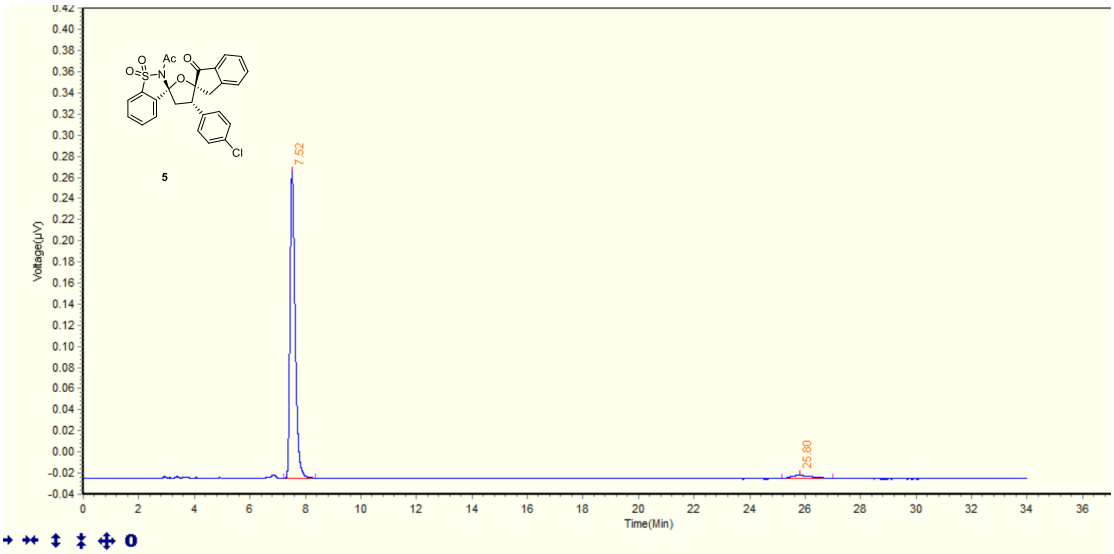
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	6.74	402690	30036	95.49%	0.625	BB
2	8.28	19014	985	4.51%	0.837	BB
Total		421,704	31,021	100.00%		



Integration Result | Calculation Result | TimeTable

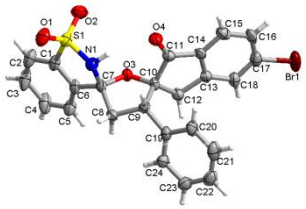
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	7.58	396672	30306	50.77%	0.795	BB
2	25.34	384568	6121	49.23%	3.672	BB
Total		781,240	36,427	100.00%		



Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	Peak Type
1	7.52	1875111	145154	96.01%	1.146	BB
2	25.80	78003	1485	3.99%	1.833	BB
Total		1,953,114	146,639	100.00%		

Single-crystal X-ray diffraction of 3ai (CCDC 2175173)



Datablock: 20220326

Bond precision: C-C = 0.0130 A Wavelength=1.54184

Cell: a=7.4992(11) b=14.135(2) c=20.507(3)
alpha=90 beta=90 gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	2173.8(5)	2173.8(6)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C24 H18 Br N O4 S	C24 H18 Br N O4 S
Sum formula	C24 H18 Br N O4 S	C24 H18 Br N O4 S
Mr	496.35	496.36
Dx,g cm-3	1.517	1.517
Z	4	4
Mu (mm-1)	3.741	3.741
F000	1008.0	1008.0
F000'	1009.18	
h,k,lmax	9,17,25	8,17,24
Nref	4308[2471]	4087
Tmin,Tmax	0.613,0.688	0.828,1.000
Tmin'	0.543	

Correction method= # Reported T Limits: Tmin=0.828 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.65/0.95 Theta(max)= 72.415

R(reflections)= 0.0504(2876) wR2(reflections)= 0.1351(4087)

S = 1.077 Npar= 284

```
The following ALERTS were generated. Each ALERT has the format
      test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

Alert level C

```
PLAT234_ALERT_4_C Large Hirshfeld Difference C16      --C17      .       0.17 Ang.
PLAT341_ALERT_3_C Low Bond Precision on  C-C Bonds ...............      0.013 Ang.
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         10 Report
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite          2 Note
PLAT012_ALERT_1_G No       _shelx_res_checksum Found in CIF ......     Please Check
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records          1 Report
PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)        293 Check
PLAT200_ALERT_1_G Reported   _diffrn_ambient_temperature ..... (K)        293 Check
PLAT791_ALERT_4_G Model has Chirality at C7          (Sohnke SpGr)          R Verify
PLAT791_ALERT_4_G Model has Chirality at C9          (Sohnke SpGr)          S Verify
PLAT791_ALERT_4_G Model has Chirality at C10         (Sohnke SpGr)          R Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............          1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         75 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        3.5 Low
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          0 Info
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
  3 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 12 ALERT level G = General information/check it is not something unexpected

  3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  2 ALERT type 2 Indicator that the structure model may be wrong or deficient
  4 ALERT type 3 Indicator that the structure quality may be low
  6 ALERT type 4 Improvement, methodology, query or suggestion
  0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.