Supporting Information for

Rh(III)-catalyzed sequential spiroannulation/lactonization of 3-aryl *N*-sulfonyl ketimines with 4-hydroxy-2-alkynoates by C–H bond activation

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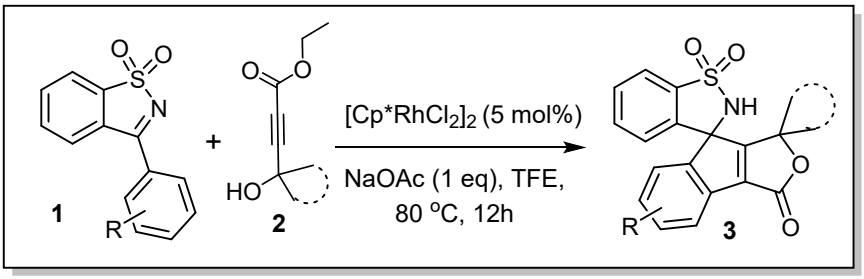


1. Experimental

All solvents were dried by a standard literature procedure. Crude products were purified by column chromatography on silica gel of 60–120 or 100-200 mesh. Thin layer chromatography (**TLC**) plates were visualized by exposure to ultraviolet light at 254 nm, and by exposure to iodine vapors and/or by exposure to methanolic acidic solution of *p*-anisaldehyde followed by heating (<1 min) on a hot plate (~250°C). Organic solvents were concentrated on rotary evaporator at 35–40 °C. Melting points (**m.p.**) were measured on Buchi B-540. **^{1}H** and **^{13}C NMR** (proton-decoupled) spectra were recorded in $CDCl_3$ solvent on 300, 400 or 500 MHz, NMR spectrometer. Chemical shifts (δ) were reported in parts per million (ppm) with respect to TMS as an internal standard. Coupling constants (*J*) are quoted in hertz (Hz). Mass spectra and **HRMS** were recorded on mass spectrometer by Electrospray ionization (ESI) or Atmospheric pressure chemical ionization (APCI) technique.

Procedure for the synthesis of 3a-p:

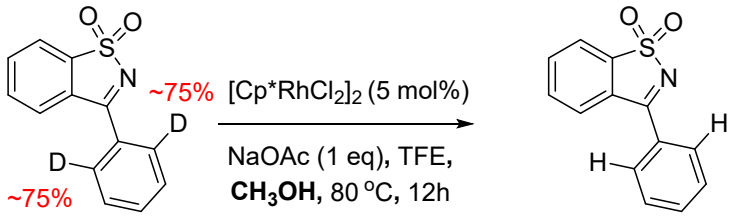
To an oven dried sealed tube equipped with a stir bar were charged with 3-phenylbenzo[*d*]isothiazole1,1-dioxide **1a** (100 mg,0.5 mmol), 4-hydroxy-2-alkynoates **2a** (77 mg, 0.6 mmol) and NaOAc (33 mg, 0.51 mmol), in 3 mL of TFE solvent, followed by $[RhCp^*Cl_2]_2$ (5 mol%) was added at room temperature. The resulting mixture was stirred at 80°C (oil bath) for 12h and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane = 1:2) to afford the pure product as a white solid **3a.**

2. Mechanistic studies:

(a) H/D Exchange experiment: To an oven dried sealed tube was equipped with a stir bar and charged with 3-phenylbenzo[*d*]isothiazole1,1-dioxide (**1a**, 0.5 mmol) in 3 mL of TFE, followed by addition of $[Cp^*RhCl_2]_2$ catalyst (5 mol%) and NaOAc (33 mg, 0.51 mmol) at room temperature. CD_3OD (20 equiv) was added to the above mixture. The resulting mixture was stirred at 80 °C for 16h and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using EtOAc/hexane as an eluent to afford the mixture of product **1a** and **1a-d_2.** The deuterium content of the product was approximately 75%, which was determined by ^{1}H NMR.

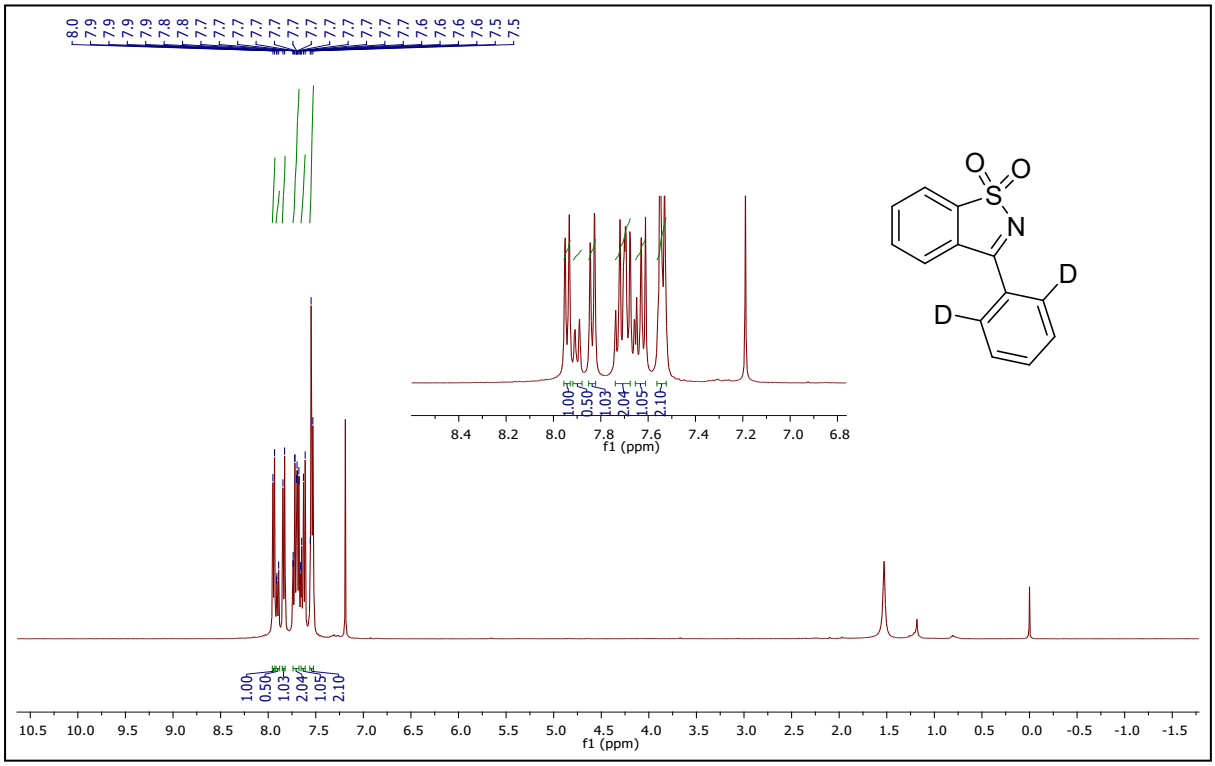
(b) H/D Exchange experiment: To an oven dried sealed tube was equipped with a stir bar and charged with **1a-d_2** (0.5 mmol) in 3 mL of TFE, followed by addition of $[Cp^*RhCl_2]_2$ catalyst (5 mol%) and NaOAc (33 mg, 0.51 mmol) at room temperature. CH_3OH (20 equiv)

was added to the above mixture. The resulting mixture was stirred at 80 °C for 16h and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using EtOAc/hexane as an eluent to afford the of product **1a** without deuterium.

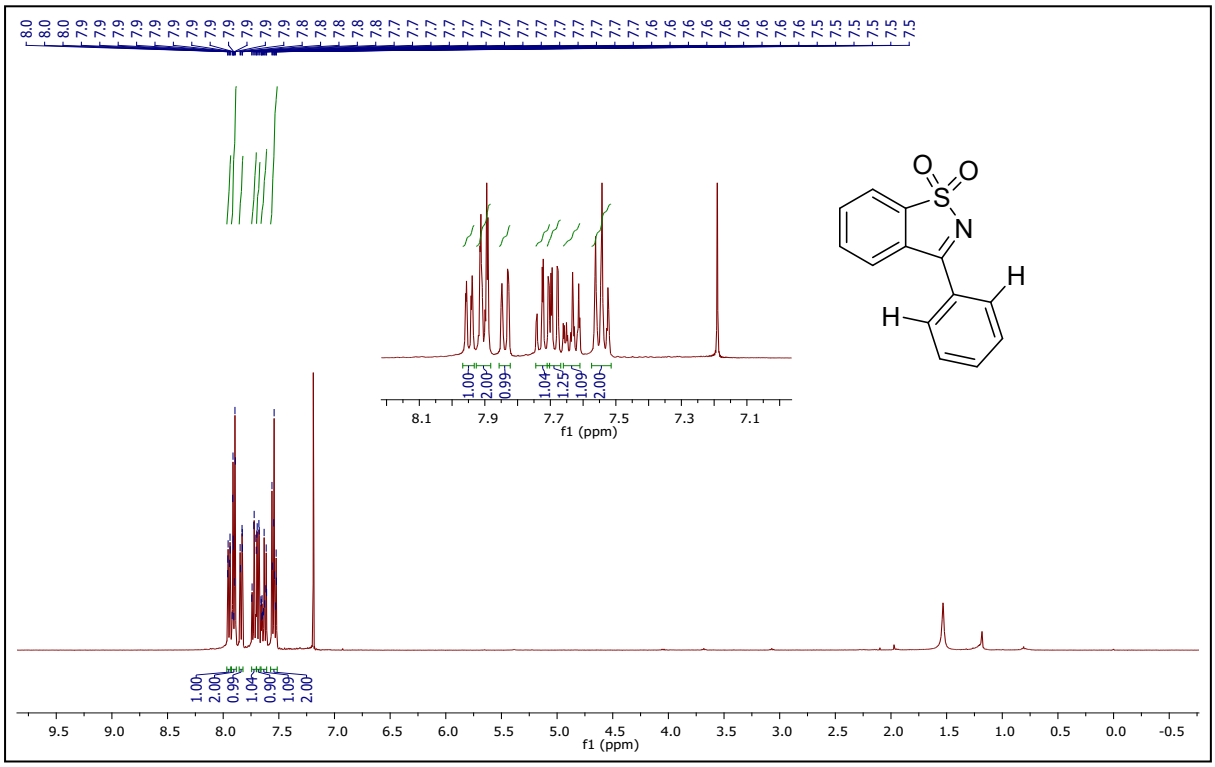


1a-d$_2$ **1a**

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1a and 1a-d$_2$ mixture:

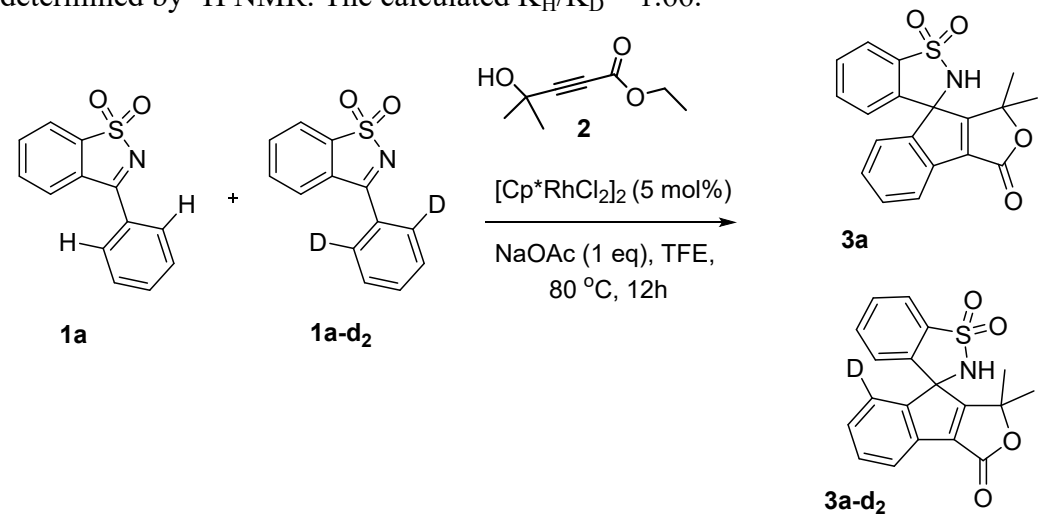


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1a:

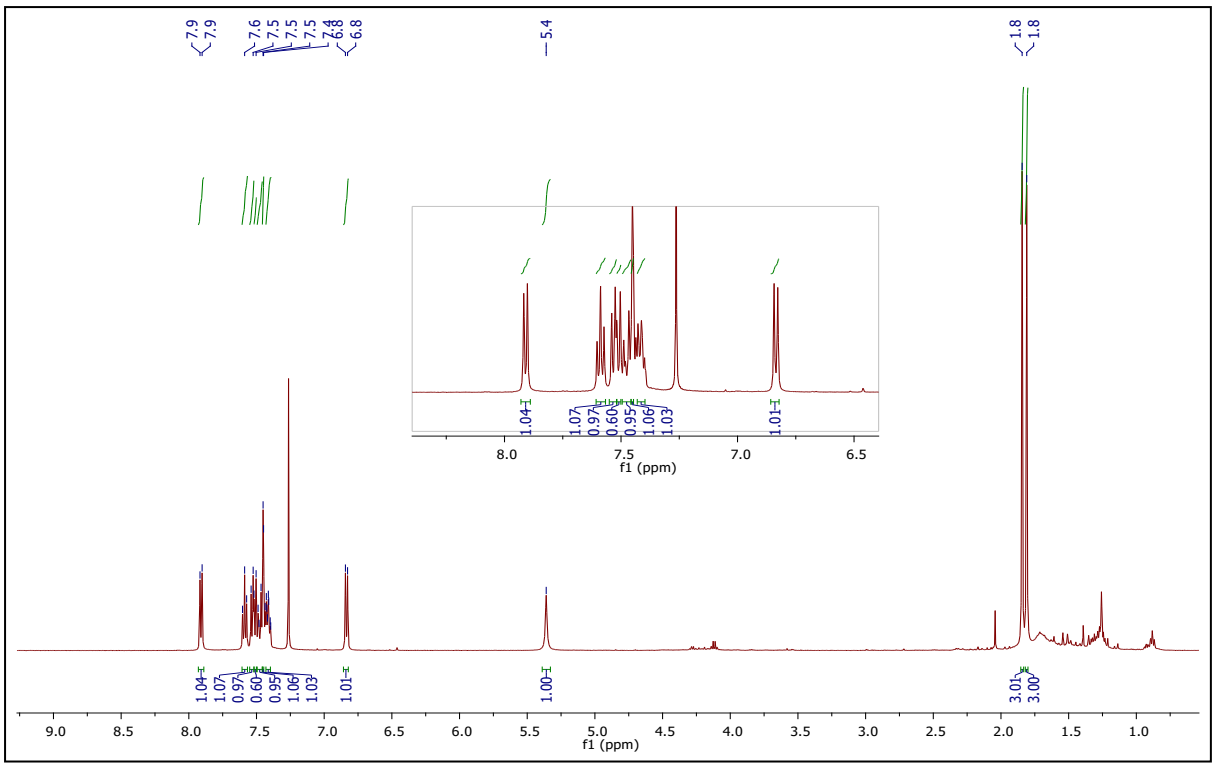


(C) Competitive KIE Experiment between 1a and 1a-d_2:

To an oven dried sealed tube equipped with a stir bar were charged with 3-phenylbenzo[*d*]isothiazole1,1-dioxide **1a** (100 mg,0.5 mmol), **1a-d_2** (100 mg,0.5 mmol), 4-hydroxy-2-alkynoates **2a** (154 mg, 1.2 mmol) and NaOAc (33 mg, 0.51 mmol), in 3 mL of TFE solvent, followed by $[RhCp^*Cl_2]_2$ (5 mol%) was added at room temperature. The resulting mixture was stirred at 80°C (oil bath) for 12h and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane = 1:2) to afford the pure product as a white solid **3a** and **3a-d_2**. The ratio of **3a** and **3a-d_2** was determined by ^{1}H NMR. The calculated K_H/K_D = 1.66.

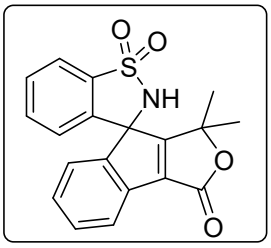


^{1}H NMR (500MHz, $CDCl_3$) spectrum of 3a and 3a-d_2 mixture:



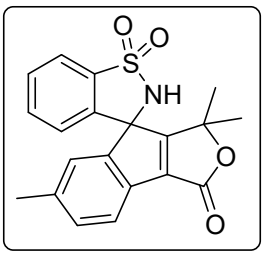
3. Characterization of data:

3',3'-Dimethyl-2*H*-spiro[benzo[*d*]isothiazole-3,8'-indeno[1,2-*c*]furan]-1'(3'*H*)-one-1,1-dioxide:



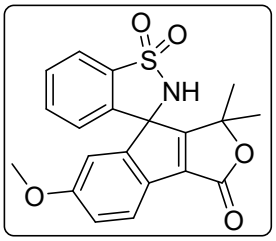
White solid (0.130 g, 90%), m.p.191-193 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 2H), 7.64 (td, *J* = 7.7, 0.9 Hz, 1H), 7.55 (td, *J* = 7.7, 1.1 Hz, 1H), 7.44 (td, *J* = 7.4, 1.3 Hz, 1H), 7.33 – 7.19 (m, 2H), 6.89 (d, *J* = 7.9 Hz, 1H), 5.26 (s, 1H), 1.75 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7, 165.1, 150.4, 137.0, 135.3, 133.9, 132.7, 130.8, 130.3, 128.7, 124.0, 123.8, 122.1, 121.9, 86.3, 69.1, 25.9, 25.6. HRMS calcd for $C_{19}H_{17}NO_4S$: 354.0800 $[M+H]^+$, found: 354.0769.

3',3',6'-Trimethyl-2*H*-spiro[benzo[d]isothiazole-3,8'-indeno[1,2-*c*]furan]-1'(3'*H*)-one-1,1-dioxide:



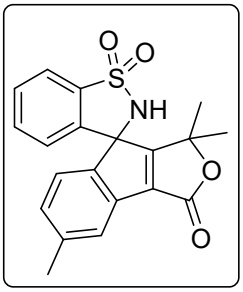
White solid (0.125 g, 88%), m.p. 262-264 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.64 (td, *J* = 7.7, 0.9 Hz, 1H), 7.57 (ddd, *J* = 11.9, 6.4, 5.4 Hz, 2H), 7.24 (dd, *J* = 7.6, 0.6 Hz, 1H), 7.05 (s, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 5.04 (s, 1H), 2.32 (s, 3H), 1.74 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 165.2, 150.6, 139.3, 137.0, 135.7, 135.3, 134.0, 130.9, 130.7, 129.9, 124.6, 123.9, 121.9, 121.8, 86.1, 69.0, 29.7, 26.0, 25.7, 21.5. HRMS calcd for $C_{20}H_{19}NO_4S$: 368.0957 $[M+H]^+$, found: 368.0920.

6'-Methoxy-3',3'-dimethyl-2*H*-spiro[benzo[d]isothiazole-3,8'-indeno[1,2-*c*]furan]-1'(3'*H*)-one-1,1-dioxide:



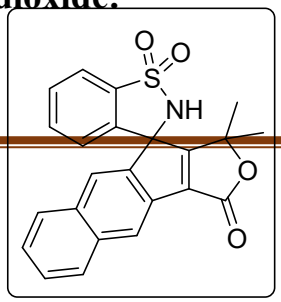
White solid (0.116 g, 83%), m.p. 173-175 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.8 Hz, 1H), 7.68 – 7.58 (m, 2H), 7.26 (dd, *J* = 8.6, 7.3 Hz, 1H), 7.02 – 6.79 (m, 3H), 5.13 (s, 1H), 3.99 (s, 3H), 1.73 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 164.2, 154.5, 152.2, 136.4, 135.5, 135.2, 133.9, 130.8, 130.7, 123.8, 121.9, 120.9, 116.1, 113.5, 85.2, 69.0, 56.2, 26.1, 25.8. HRMS calcd for $C_{20}H_{18}NO_5S$: 384.0852 $[M+H]^+$,found: 384.0864. Purity 99.18% by HPLC.

3',3',5'-Trimethyl-2*H*-spiro[benzo[*d*]isothiazole-3,8'-indeno[1,2-*c*]furan]-1'(3'*H*)-one-1,1-dioxide:



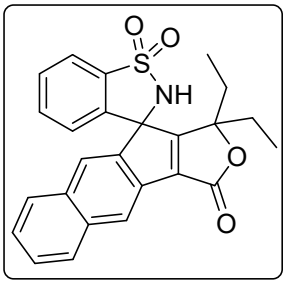
White solid (0.128 g, 90%), m.p. 204-206 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.8 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.57 – 7.51 (m, 2H), 7.10 (q, *J* = 7.8 Hz, 2H), 6.88 (d, *J* = 7.9 Hz, 1H), 5.14 (s, 1H), 2.40 (s, 3H), 1.75 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.0, 165.2, 147.4, 140.9, 136.9, 135.7, 135.3, 133.9, 132.8, 130.7, 129.2, 123.8, 123.5, 122.9, 121.8, 86.3, 68.9, 26.0, 25.6, 21.5. HRMS calcd for $C_{20}H_{19}NO_4S$: 368.0957 $[M+H]^+$, found: 368.0920. Purity 99.53% by HPLC

3',3'-Dimethyl-2*H*-spiro[benzo[*d*]isothiazole-3,10'-benzo[5,6]indeno[1,2-*c*]furan]-1'(3'*H*)-one-1,1-dioxide:



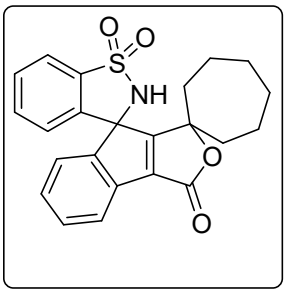
Yellow solid (0.116 g, 85%), m.p. 242-244 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.95 (dd, *J* = 8.5, 7.9 Hz, 2H), 7.77 – 7.64 (m, 3H), 7.62 – 7.48 (m, 3H), 6.95 (d, *J* = 7.8 Hz, 1H), 5.18 (s, 1H), 1.81 (s, 3H), 1.12 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.5, 165.1, 147.7, 136.9, 136.2, 135.2, 134.1, 134.0, 132.7, 130.8, 129.6, 128.8, 128.6, 127.7, 127.3, 124.2, 124.0, 121.8, 121.4, 86.3, 68.9, 26.0, 25.7. HRMS calcd for $C_{23}H_{19}NO_4S$: 404.0957 $[M+H]^+$, found: 404.0916. Purity 99.84% by HPLC

3',3'-Diethyl-2*H*-spiro[benzo[*d*]isothiazole-3,10'-benzo[5,6]indeno[1,2-*c*]furan]-1'(3'*H*)-one-1,1-dioxide:



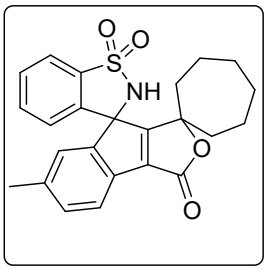
Yellow solid (0.117 g, 80%), m.p. 220-222 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.95 – 7.92 (m, 2H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.65 (s, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 5.32 (s, 1H), 2.26 – 2.11 (m, 2H), 1.44 – 1.54 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.67 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.1, 165.9, 148.0, 139.0, 136.6, 135.3, 134.2, 133.8, 132.7, 130.8, 129.6, 128.8, 128.6, 127.8, 127.4, 124.5, 123.9, 121.8, 121.2, 92.3, 69.2, 30.5, 28.8, 7.9, 7.7. HRMS calcd for $C_{25}H_{22}NO_4S$: 432.1270 $[M+H]^+$, found: 432.1219. Purity 93.12% by HPLC

1'*H*,2*H*-Dispiro[benzo[*d*]isothiazole-3,8'-indeno[1,2-*c*]furan-3',1''-cycloheptan]-1'-one-1,1-dioxide:



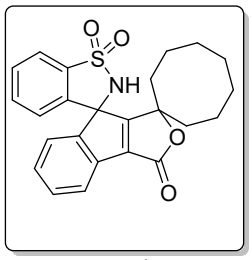
White solid (0.130 g, 78%), m.p.167-169 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.5 Hz, 1H), 7.92 (dd, *J* = 4.3, 3.5 Hz, 1H), 7.84 – 7.74 (m, 1H), 7.62 (m, 1H), 7.59 – 7.53 (m, 1H), 7.41 (ddd, *J* = 7.5, 6.4, 2.3 Hz, 1H), 7.25 (d, *J* = 1.6 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 1H), 5.12 (s, 1H), 2.56 – 2.33 (m, 1H), 1.94 (dd, *J* = 7.5, 7.0 Hz, 1H), 1.85 – 1.61 (m, 4H), 1.44 (dd, *J* = 5.4, 2.6 Hz, 3H), 1.37 – 1.18 (m, 2H), 1.14 – 1.02 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.1, 171.0, 165.5, 150.7, 141.1, 135.2, 133.9, 133.4, 130.7, 129.5, 128.7, 126.6, 123.9, 123.1, 122.0, 92.2, 69.5, 38.2, 37.9, 28.8, 28.4, 22.6, 21.7. HRMS calcdfor$C_{23}H_{123}NO_4S$: 408.1270 $[M+H]^+$, found: 408.1240.

6'-Methyl-1'*H*,2*H*-dispiro[benzo[d]isothiazole-3,8'-indeno[1,2-*c*]furan-3',1''-cycloheptan]-1'-one-1,1-dioxide:



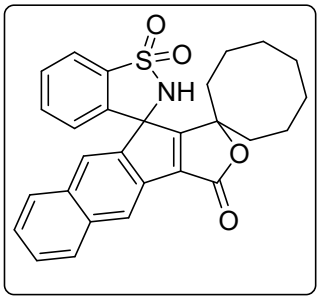
Yellow solid (0.122 g, 75%), m.p. 205-207 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.68 – 7.61 (m, 1H), 7.58 – 7.52 (m, 2H), 7.21 (dd, *J* = 7.6, 0.6 Hz, 1H), 7.05 (s, 1H), 6.91 (d, *J* = 7.9 Hz, 1H), 5.03 (s, 1H), 2.47 – 2.39 (m, 1H), 2.30 (s, 3H), 1.93 (dd, *J* = 4.3, 7.0 Hz, 1H), 1.83 – 1.62 (m, 4H), 1.44 (dd, *J* = 6.8, 4.4 Hz, 3H), 1.39 – 1.29 (m, 1H), 1.29 – 1.20 (m, 1H), 1.13 – 1.00 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.3, 165.6, 151.0, 139.2, 136.4, 135.4, 135.1, 133.9, 130.7, 130.7, 129.7, 124.6, 124.0, 122.0, 121.7, 92.1, 69.4, 38.2, 38.0, 28.8, 28.4, 22.6, 21.7, 21.5. HRMS calcdfor$C_{24}H_{25}NO_4S$: 422.1426 $[M+H]^+$, found: 422.1386.

1'*H*,2*H*-Dispiro[benzo[d]isothiazole-3,8'-indeno[1,2-*c*]furan-3',1''-cyclooctan]-1'-one-1,1-dioxide :



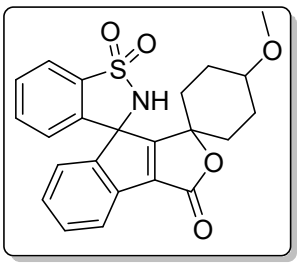
Yellow solid (0.135g, 78%), m.p.145-147 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.91 (m, 2H), 7.77 (ddd, *J* = 11.7, 7.3, 1.1 Hz, 1H), 7.69 (dd, *J* = 7.5, 4.2 Hz, 1H), 7.64 (s, 1H), 7.58 – 7.51 (m, 1H), 7.45 – 7.36 (m, 1H), 6.92 (d, *J* = 7.9 Hz, 1H), 4.98 (s, 1H), 2.52 – 2.40 (m, 1H), 1.82 (dtd, *J* = 26.7, 18.5, 7.4 Hz, 4H), 1.52 (dd, *J* = 8.7, 4.7 Hz, 4H), 1.32 (m, 4H), 1.05 – 0.92 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.9, 150.8, 136.8, 135.2, 134.0, 133.4, 130.7, 130.3, 129.5, 129.2, 128.7, 126.6, 123.8, 123.1, 122.1, 92.1, 69.8, 34.0, 33.9, 27.7, 27.1, 23.5, 22.0, 20.6. HRMS calcd for $C_{24}H_{25}NO_4S$: 422.1426 $[M+H]^+$, found: 422.1386.

1'*H*,2*H*-Dispiro[benzo[*d*]isothiazole-3,10'-benzo[5,6]indeno[1,2-*c*]furan-3',1''-cyclooctan]-1'-one 1,1-dioxide:



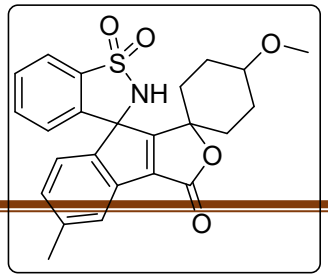
White solid (0.112 g, 70%), m.p.168-170 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.99 (d, *J* = 7.5 Hz, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.73 – 7.65 (m, 3H), 7.56 (t, *J* = 7.4 Hz, 2H), 7.51 (d, *J* = 7.1 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 5.10 (s, 1H), 2.56 – 2.48 (m, 1H), 1.98 – 1.89 (m, 2H), 1.60 – 1.55 (m, 3H), 1.44 (s, 2H), 1.31 (d, *J* = 3.2 Hz, 2H), 1.28 (s, 2H), 1.06 – 1.02 (m, 1H), 0.92 – 0.90 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.8, 165.6, 148.1, 136.6, 136.2, 134.9, 134.0, 132.8, 130.7, 129.4, 128.7, 128.7, 127.6, 127.2, 124.1, 123.9, 122.0, 121.2, 92.2, 69.5, 34.1, 34.0, 27.8, 27.1, 23.5, 22.0, 20.6. HRMS calcd for $C_{28}H_{27}NO_4S$: 472.1583 $[M+H]^+$, found: 472.1545.

4''-Methoxy-1'*H*,2*H*-dispiro[benzo[*d*]isothiazole-3,8'-indeno[1,2-*c*]furan-3',1''-cyclohexan]-1'-one-1,1-dioxide:



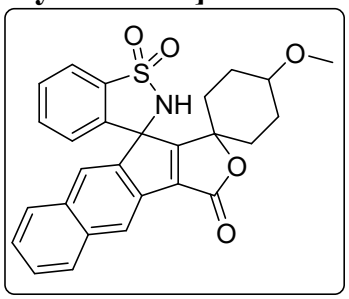
White solid (0.121 g, 70%), m.p. 171-173 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 1H), 7.74 – 7.63 (m, 2H), 7.60 – 7.54 (m, 1H), 7.46 (td, *J* = 7.5, 1.1 Hz, 1H), 7.34 – 7.29 (m, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.9 Hz, 1H), 5.32 (s, 1H), 3.31 (s, 3H), 3.11 (ddd, *J* = 11.1, 7.0, 4.4 Hz, 1H), 2.41 (td, *J* = 4.8, 4.2 Hz, 1H), 1.85 (m, 2H), 1.70 – 1.57 (m, 2H), 1.40 – 1.26 (m, 2H), 1.00 (td, *J* = 5.8, 4.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 165.0, 150.4, 137.3, 135.3, 135.2, 134.0, 132.5, 130.8, 130.4, 128.8, 123.8, 123.7, 122.1, 121.9, 86.9, 69.1, 55.7, 33.4, 29.7, 27.5, 27.4. HRMS calcdfor$C_{23}H_{22}NO_5S$: 424.1038 $[M+H]^+$, found: 424.0984.

4''-Methoxy-5'-methyl-1'*H*,2*H*-dispiro[benzo[*d*]isothiazole-3,8'-indeno[1,2-*c*]furan-3',1''-cyclohexan]-1'-one-1,1-dioxide:



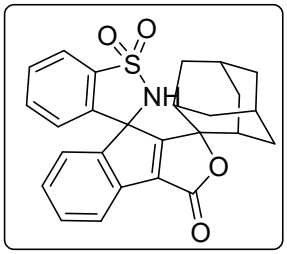
White solid (0.119 g, 68%), m.p.245-247 °C, White solid (0.119 g, 68%), m.p.245-247 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.3 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.53 (s, 2H), 7.08 (s, 2H), 6.85 (d, *J* = 7.5 Hz, 1H), 4.98 (s, 1H), 3.29 (s, 3H), 3.12 – 3.06 (m, 1H), 2.39 (s, 3H), 2.04 (s, 1H), 1.85 – 1.74 (m, 2H), 1.66 (d, *J* = 12.1 Hz, 2H), 1.29 (d, *J* = 27.2 Hz, 2H), 0.98 (d, *J* = 14.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 165.1, 147.4, 141.0, 137.2, 135.8, 135.2, 134.0, 132.6, 130.7, 129.3, 123.7, 123.4, 122.9, 121.9, 86.9, 69.0, 55.7, 33.4, 33.3, 27.6, 27.5, 21.5. Purity 96.74% by HPLC

4''-Methoxy-1'*H*,2*H*-dispiro[benzo[d]isothiazole-3,10'-benzo[5,6] indeno[1,2-*c*]furan-3',1''-cyclohexan]-1'-one-1,1-dioxide :



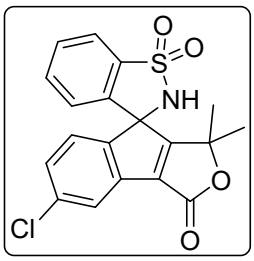
Yellow solid (0.104 g, 65%), m.p. 203-205 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.91 (dd, *J* = 7.1, 7.9 Hz, 2H), 7.70 – 7.61 (m, 3H), 7.57 – 7.46 (m, 3H), 6.89 (d, *J* = 7.9 Hz, 1H), 5.32 (s, 1H), 3.30 (s, 3H), 3.17 – 3.04 (m, 1H), 2.40 (m 1H), 2.08 (d, *J* = 6.2 Hz, 1H), 1.88 (dd, *J* = 8.3, 3.2 Hz, 2H), 1.73 – 1.64 (m, 2H), 0.88 (t, *J* = 7.0 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 165.1, 147.7, 137.2, 136.3, 135.0, 134.1, 132.7, 130.8, 129.5, 128.8, 128.6, 127.7, 127.4, 124.1, 124.0, 121.9, 121.4, 87.0, 68.9, 55.7, 33.5, 27.6, 27.4. HRMS calcd for $C_{27}H_{25}NO_5S$: 474.1375 $[M+H]^+$, found: 474.1368.

1'*H*,2''*H*-Dispiro[adamantane-2,3'-indeno[1,2-*c*]furan-8',3''-benzo[*d*] isothiazol]-1'-one-1'',1''-dioxide:



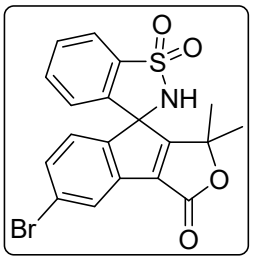
White solid (0.109 g, 60%), m.p.195-197 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.76 – 7.69 (m, 1H), 7.62 (td, *J* = 7.7, 0.9 Hz, 1H), 7.56 – 7.47 (m, 1H), 7.42 – 7.34 (m, 2H), 7.27 (d, *J* = 1.2 Hz, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 4.90 (s, 1H), 2.77 (d, *J* = 4.2 Hz, 1H), 2.39 (dd, *J* = 6.2, 12.8 Hz, 2H), 2.02 (s, 1H), 1.73 (s, 4H), 1.74 – 1.61 (m, 4H), 1.21 – 1.12 (m, 1H), 0.63 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.1, 165.0, 151.9, 135.4, 134.2, 134.1, 130.7, 130., 129.18, 123.4, 122.6, 122.4, 122.0, 96.5, 71.9, 38.6, 37.5, 36.5, 34.9, 34.3, 33.8, 32.9, 26.3, 25.6. HRMS calcd for $C_{26}H_{25}NO_4S$: 446.1426 $[M+H]^+$, found: 446.1373.

5'-Chloro-1',1'-dimethyl-2*H*-spiro[benzo[d]isothiazole-3,8'-indeno[1,2-*c*]furan]-3'(1'*H*)-one 1,1-dioxide



Yellow solid (0.075g, 56%) m.p. 208-210 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 1.7 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 1.8 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 5.24 (s, 1H), 1.76 (s, 3H), 1.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.03, 164.48, 148.52, 136.72, 136.20, 135.29, 134.61, 134.30, 134.13, 131.06, 128.72, 125.01, 123.71, 122.66, 122.10, 86.41, 68.80, 25.95, 25.60. HRMS calcd for $C_{19}H_{15}NO_4SCl$:388.0434 $[M+H]^+$, found: 388.0448. Purity 98.7% by HPLC

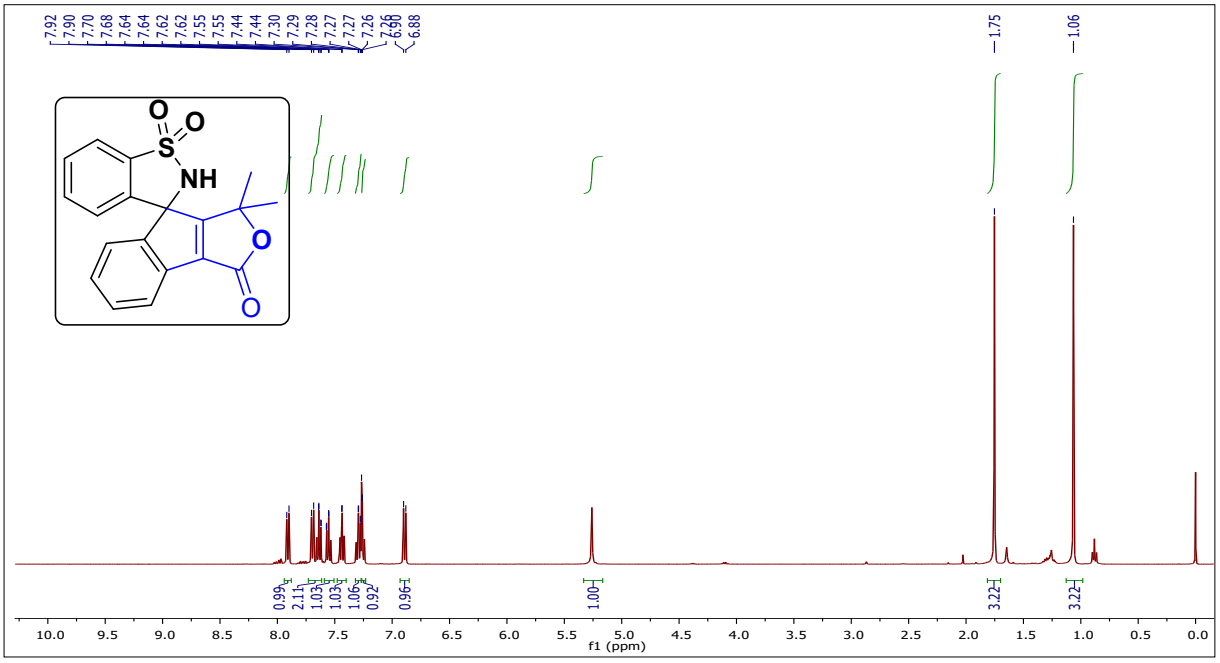
5'-Bromo-1',1'-dimethyl-2*H*-spiro[benzo[*d*]isothiazole-3,8'-indeno[1,2-c]furan]-3'(1'*H*)-one 1,1-dioxide:



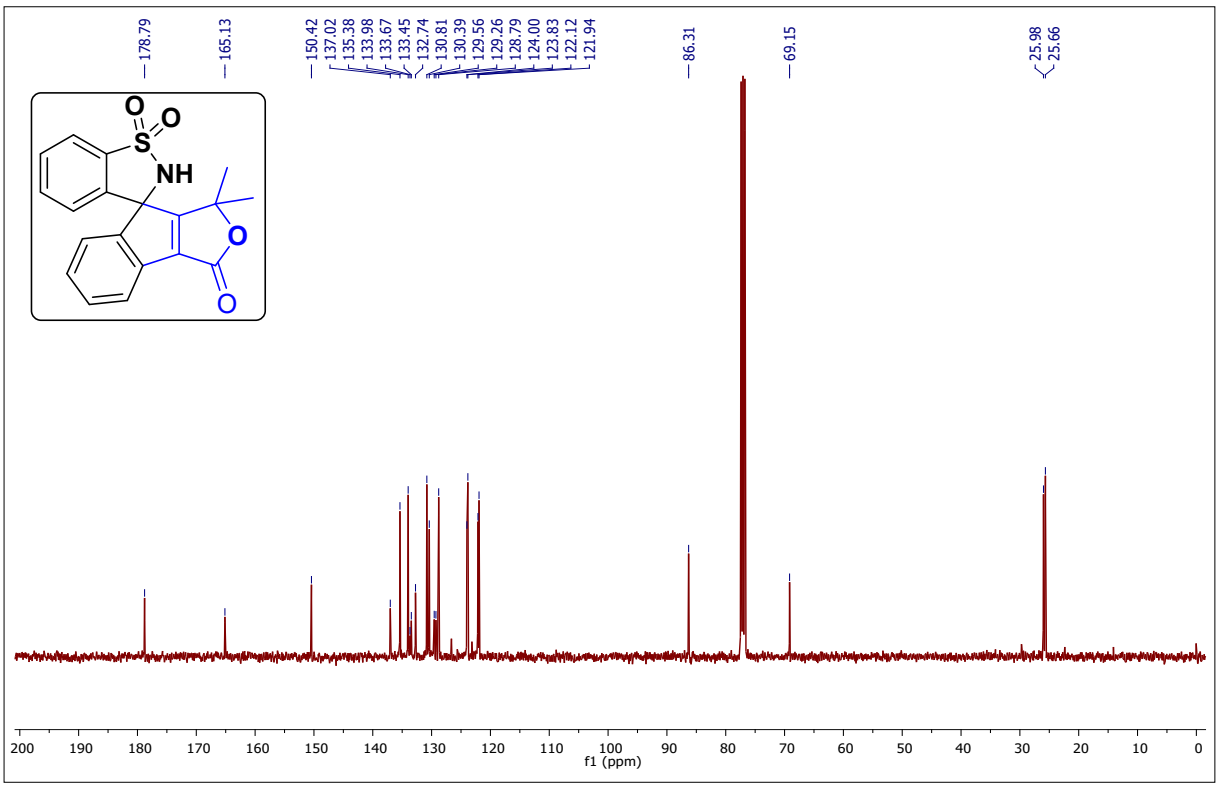
Yellow solid (0.062g, 46%) m.p. 213-215 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 6.1 Hz, 2H), 7.45 (s, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 6.76 (d, *J* = 7.7 Hz, 1H), 5.34 (s, 1H), 1.77 (s, 3H), 1.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7, 163.7, 153.1, 136.8, 136.0, 135.4, 134.2, 133.9, 133.7, 130.7, 127.0, 125.6, 124.0, 122.5, 122.3, 83.2, 67.0, 26.2, 25.5. HRMS calcd for $C_{19}H_{15}NO_4SBr$:431.9967 $[M+H]^+$, found: 431.9983. Purity 97.36% by HPLC

4. NMR spectra of products:

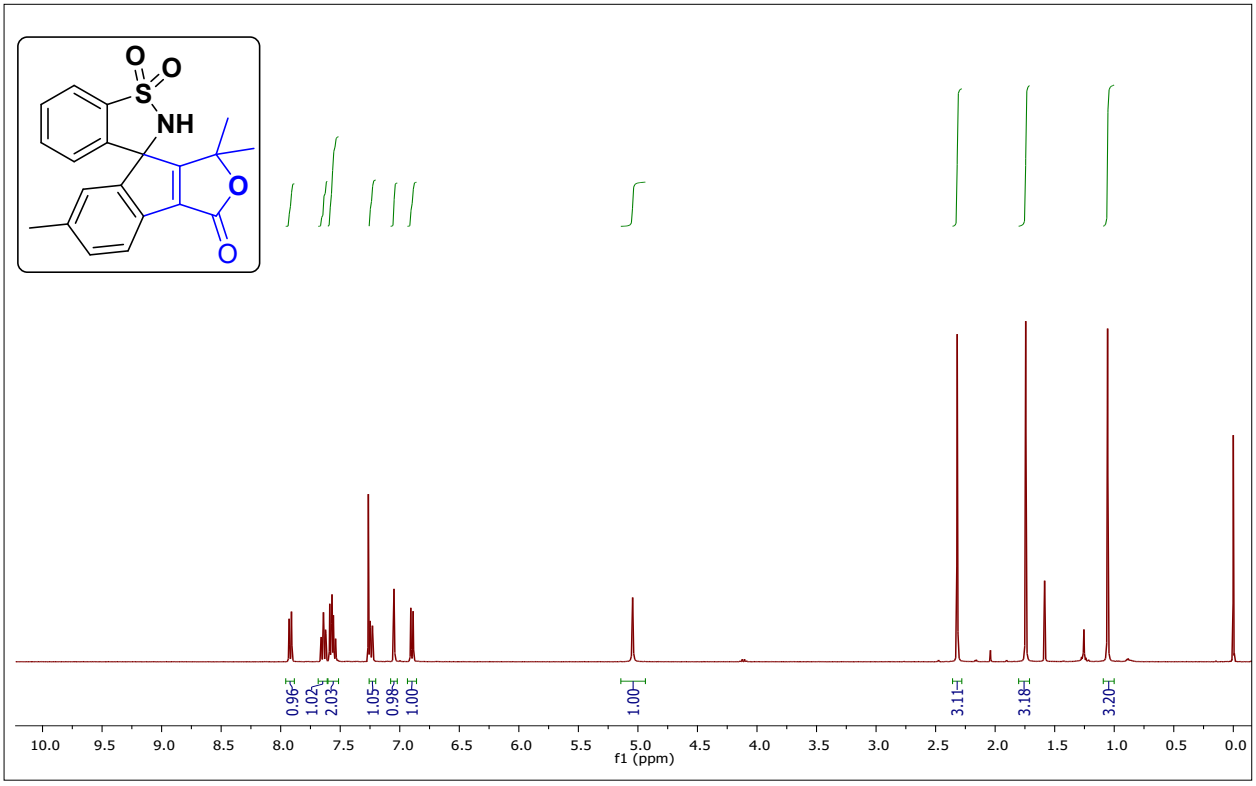
^{1}H NMR (400MHz, $CDCl_3$) spectrum of 3a:



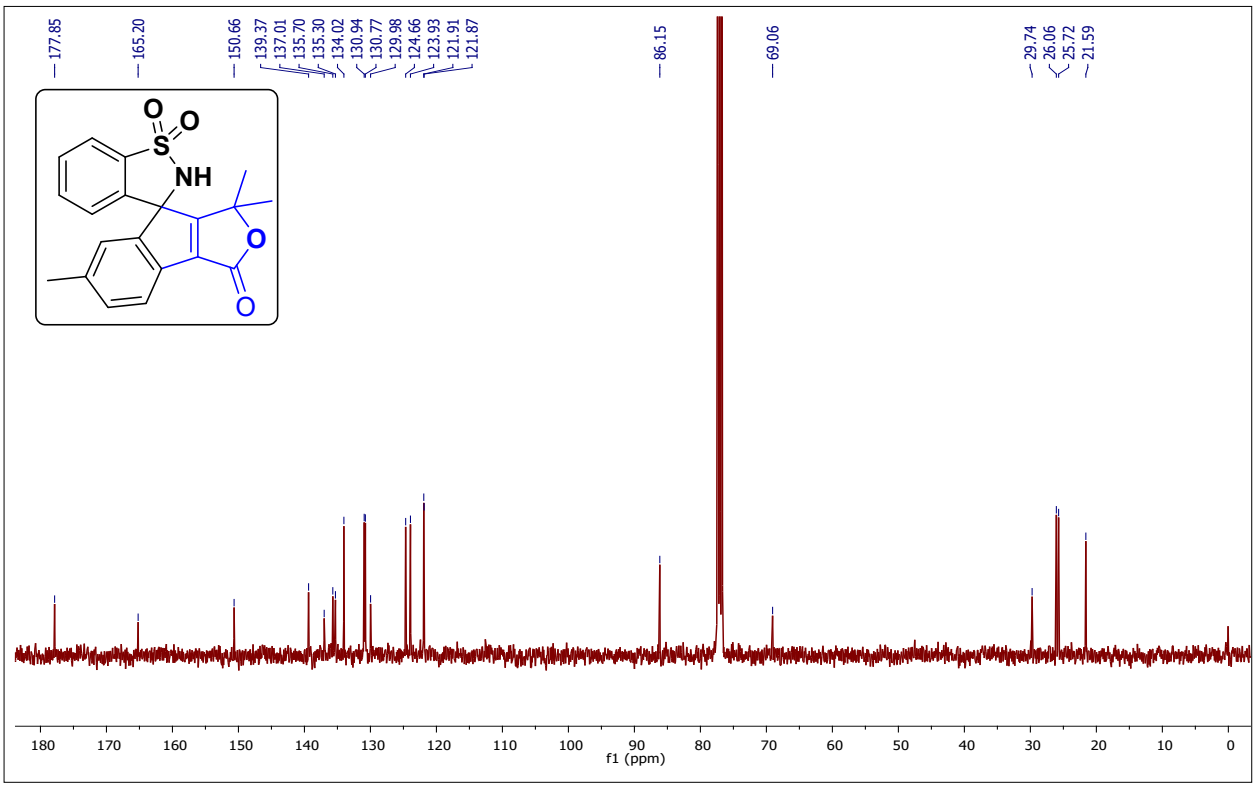
^{13}C NMR(101 MHz,$CDCl_3$) spectrum of 3a:



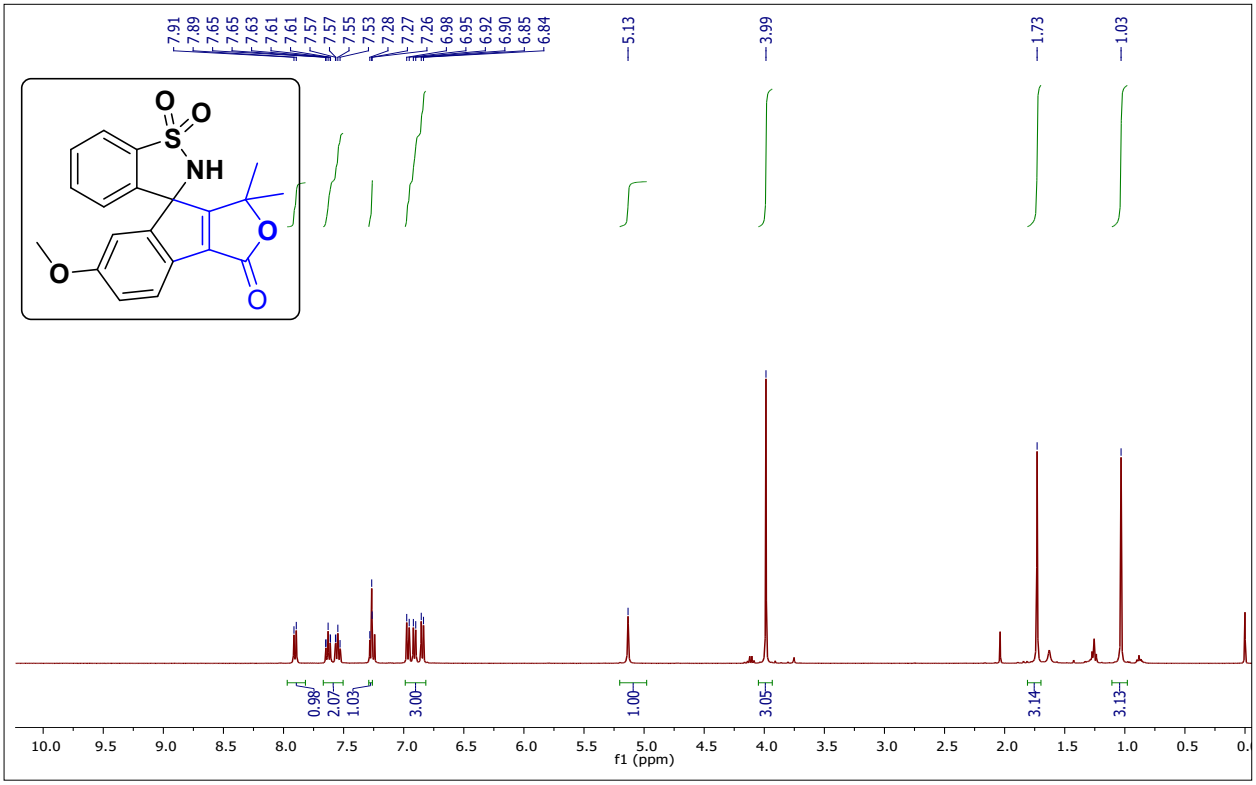
^{1}H NMR (400MHz, $CDCl_3$) spectrum of 3b:



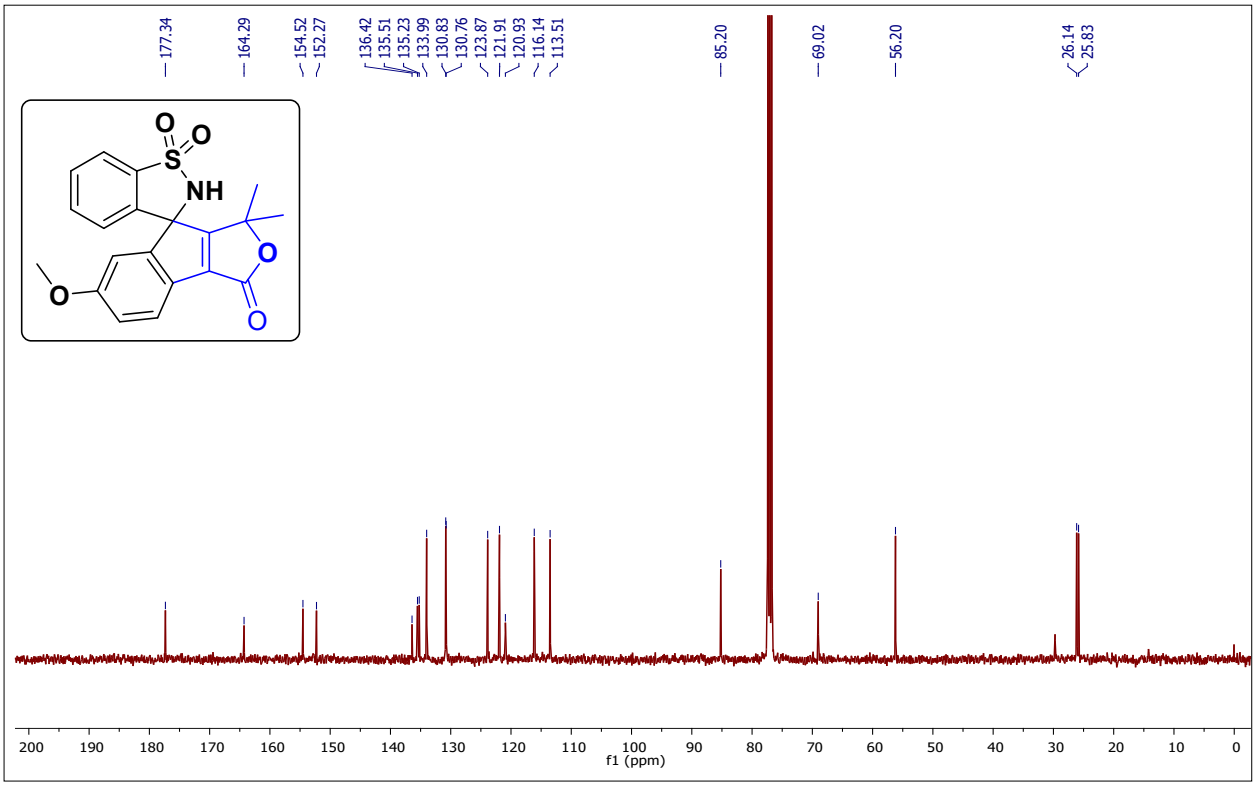
^{13}C NMR(101 MHz,$CDCl_3$) spectrum of 3b:



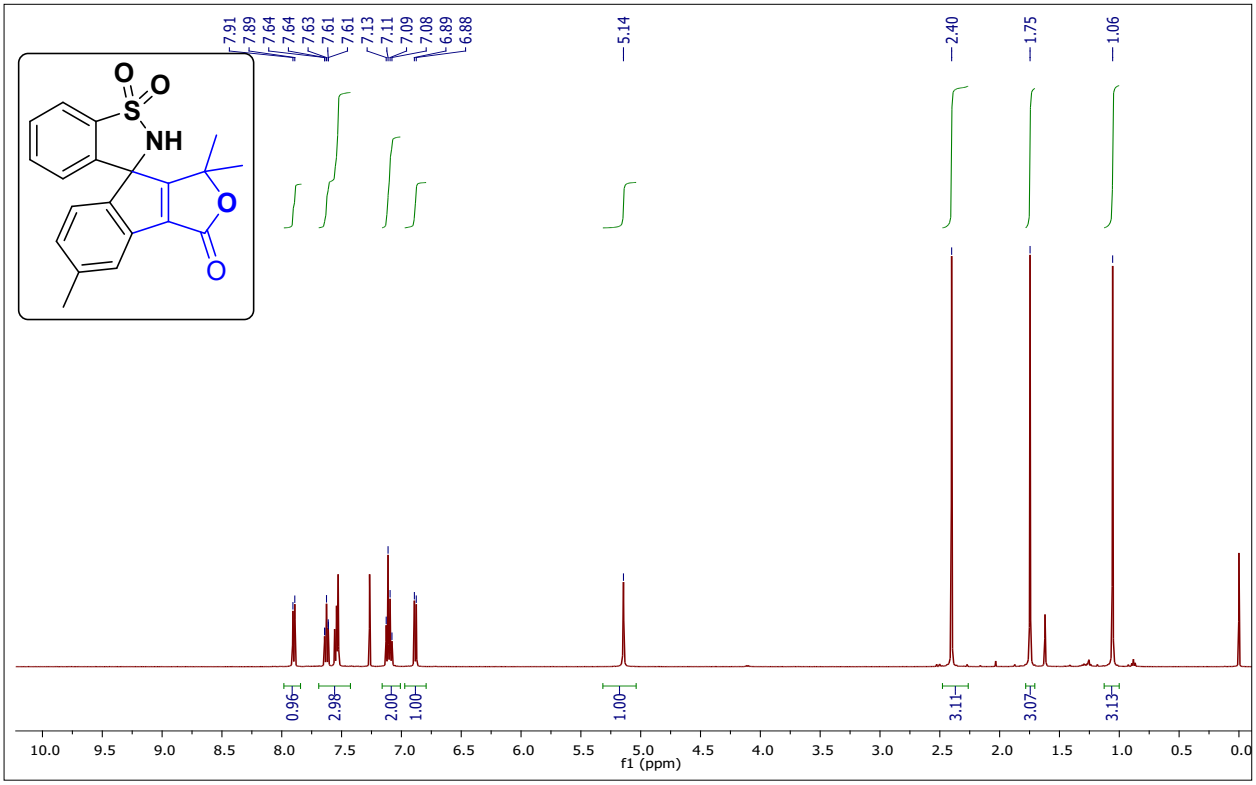
^{1}H NMR (400MHz, $CDCl_3$) spectrum of 3c:



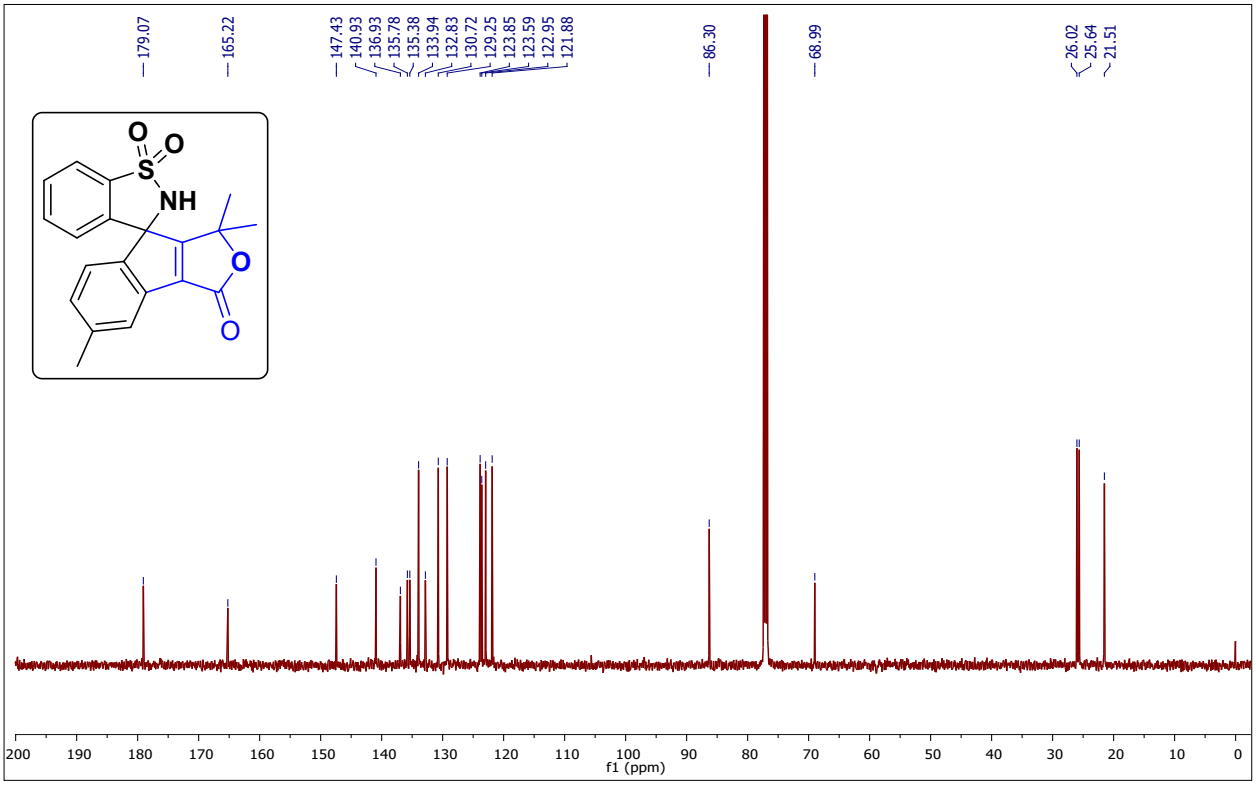
^{13}C NMR(101 MHz,$CDCl_3$) spectrum of 3c:



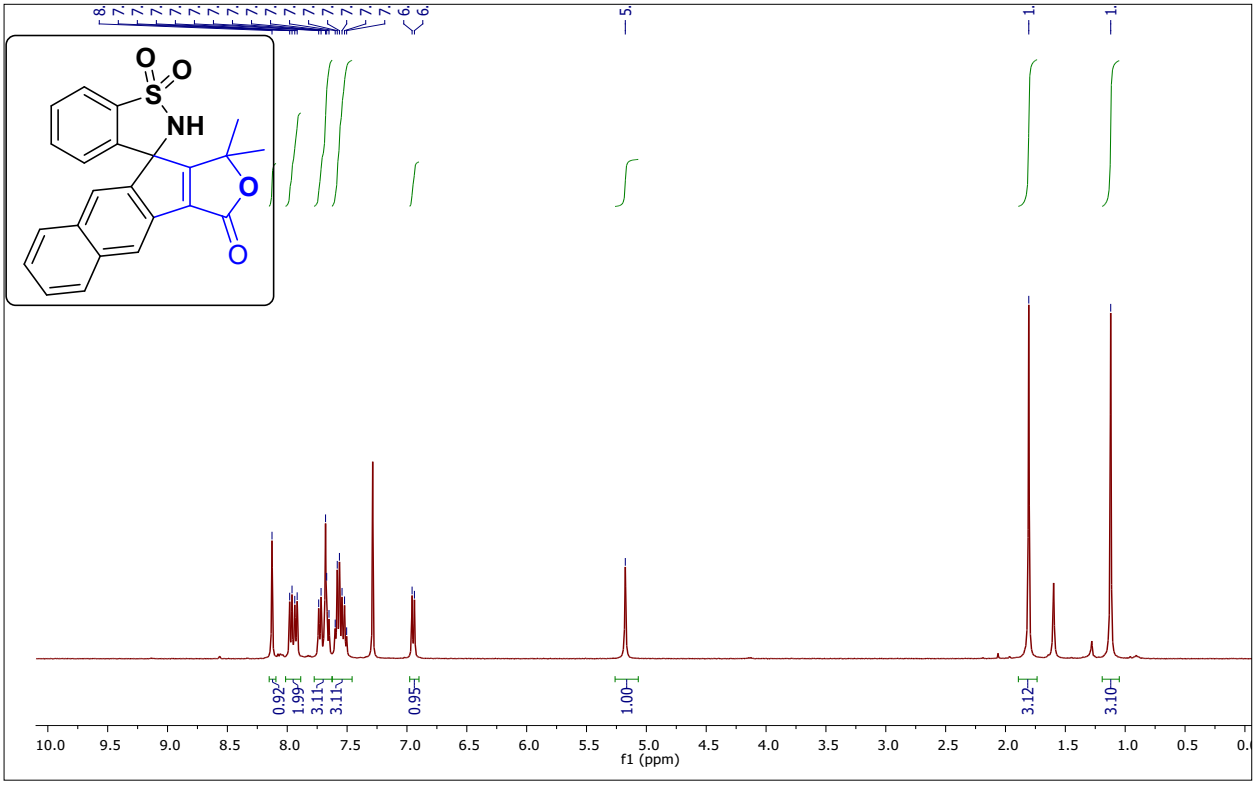
^{1}H NMR (500MHz, $CDCl_3$) spectrum of 3d:



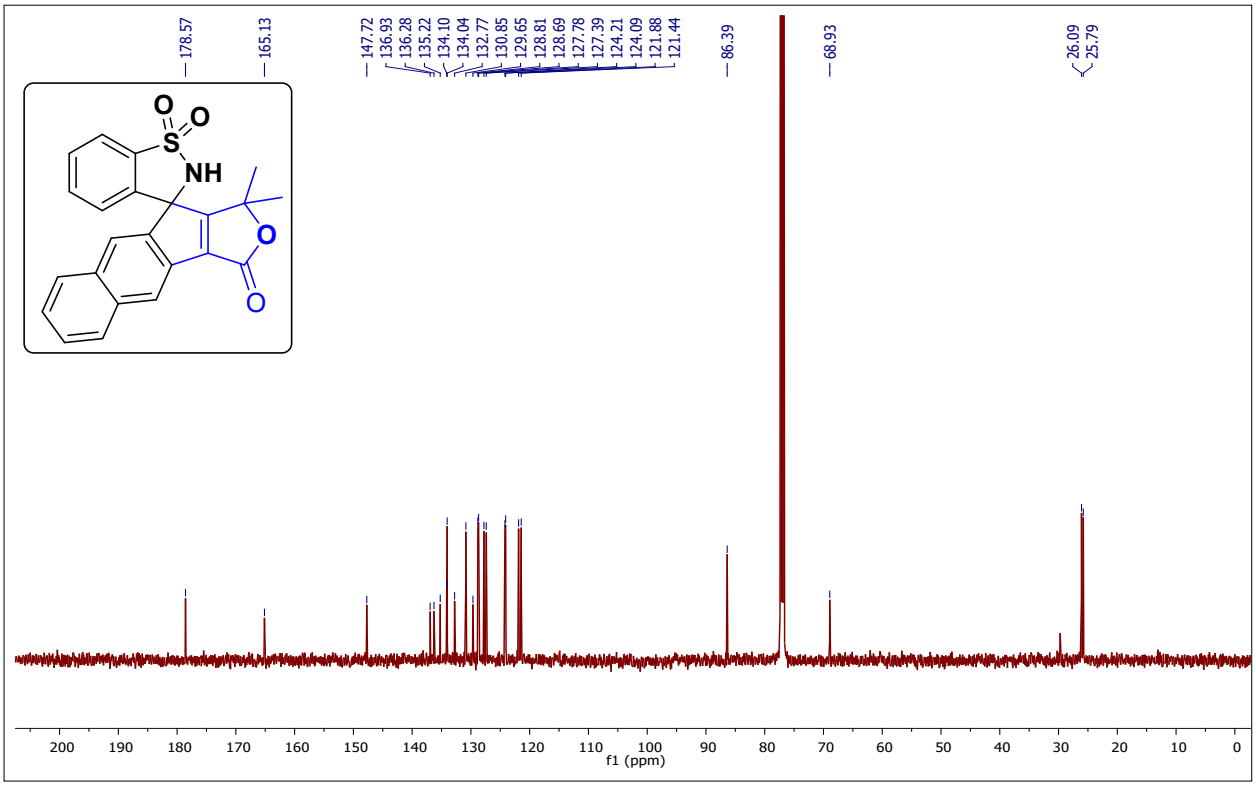
^{13}C NMR(126 MHz,$CDCl_3$) spectrum of 3d:



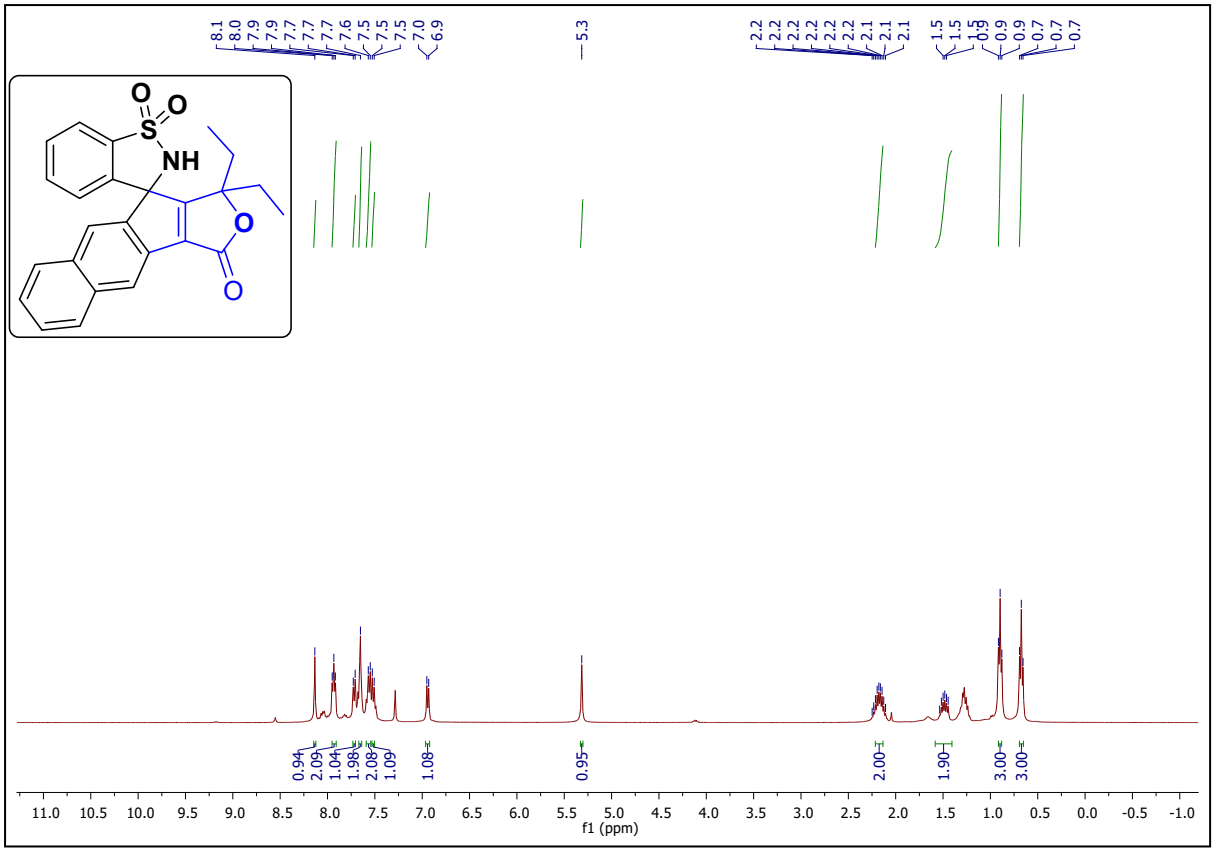
^{1}H NMR (400MHz, $CDCl_3$) spectrum of 3e:



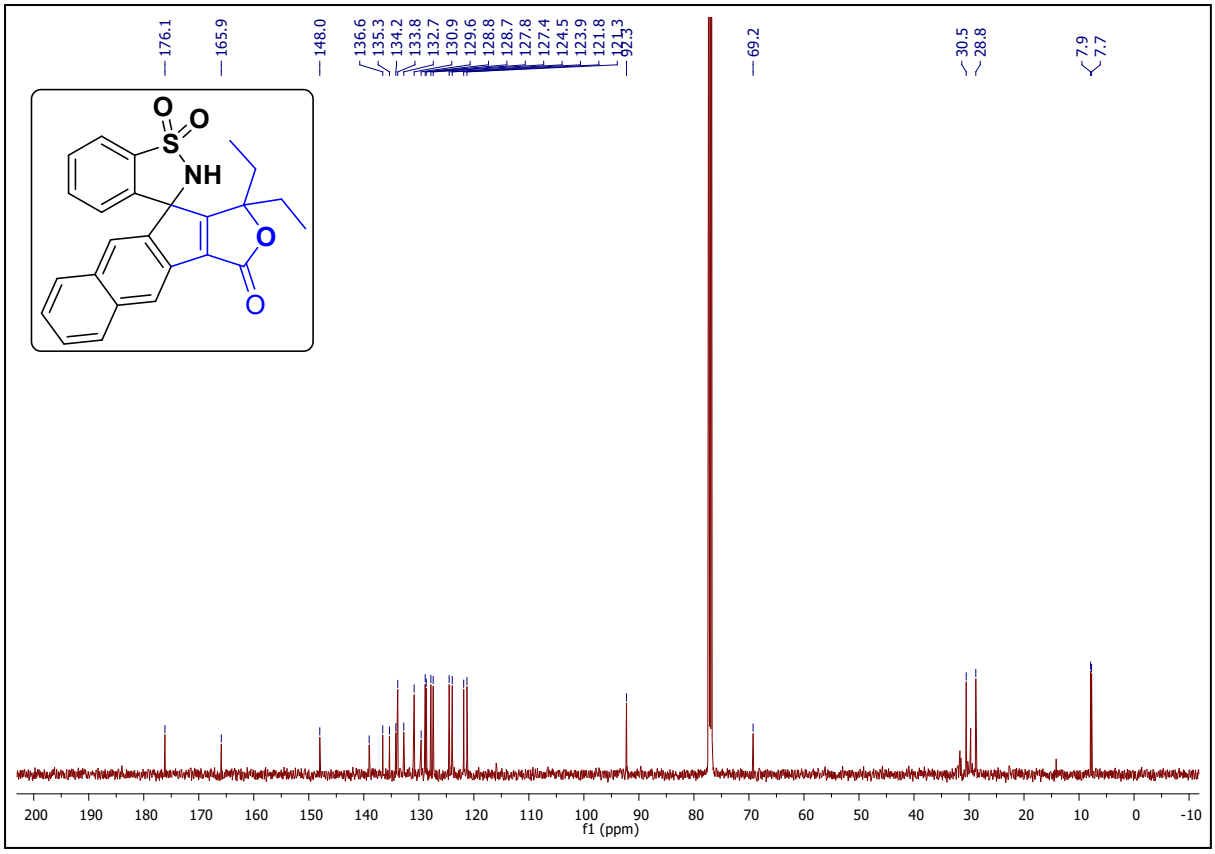
^{13}C NMR(101 MHz,$CDCl_3$) spectrum of 3e:



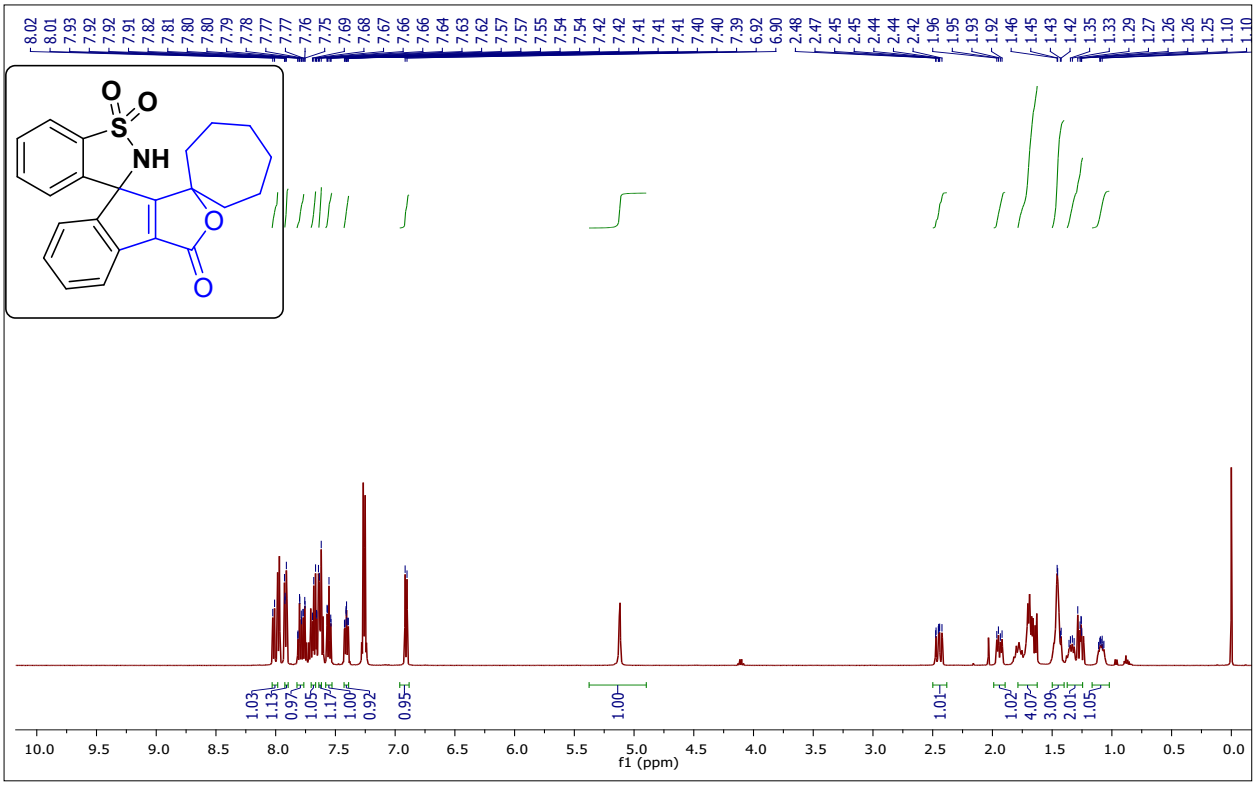
^{1}H NMR (400MHz, $CDCl_3$) spectrum of 3f:



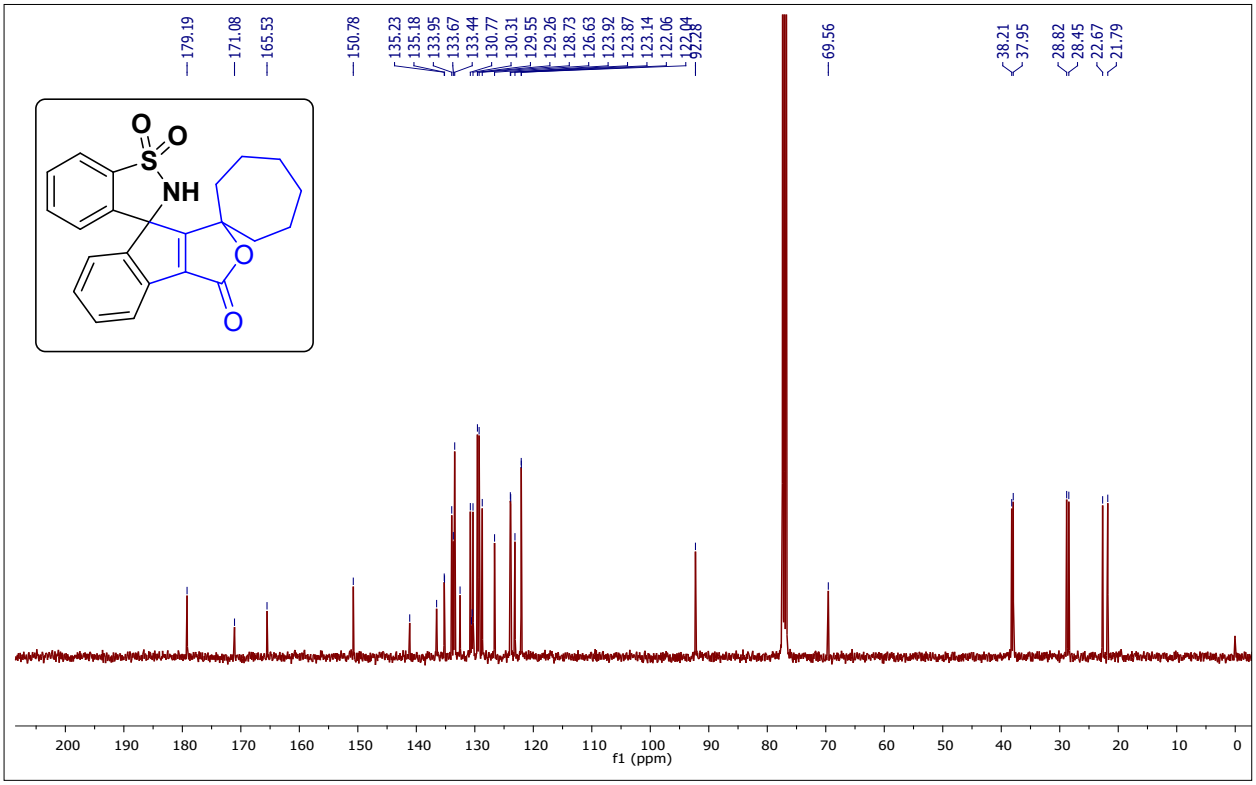
^{13}C NMR(101 MHz,$CDCl_3$) spectrum of 3f:



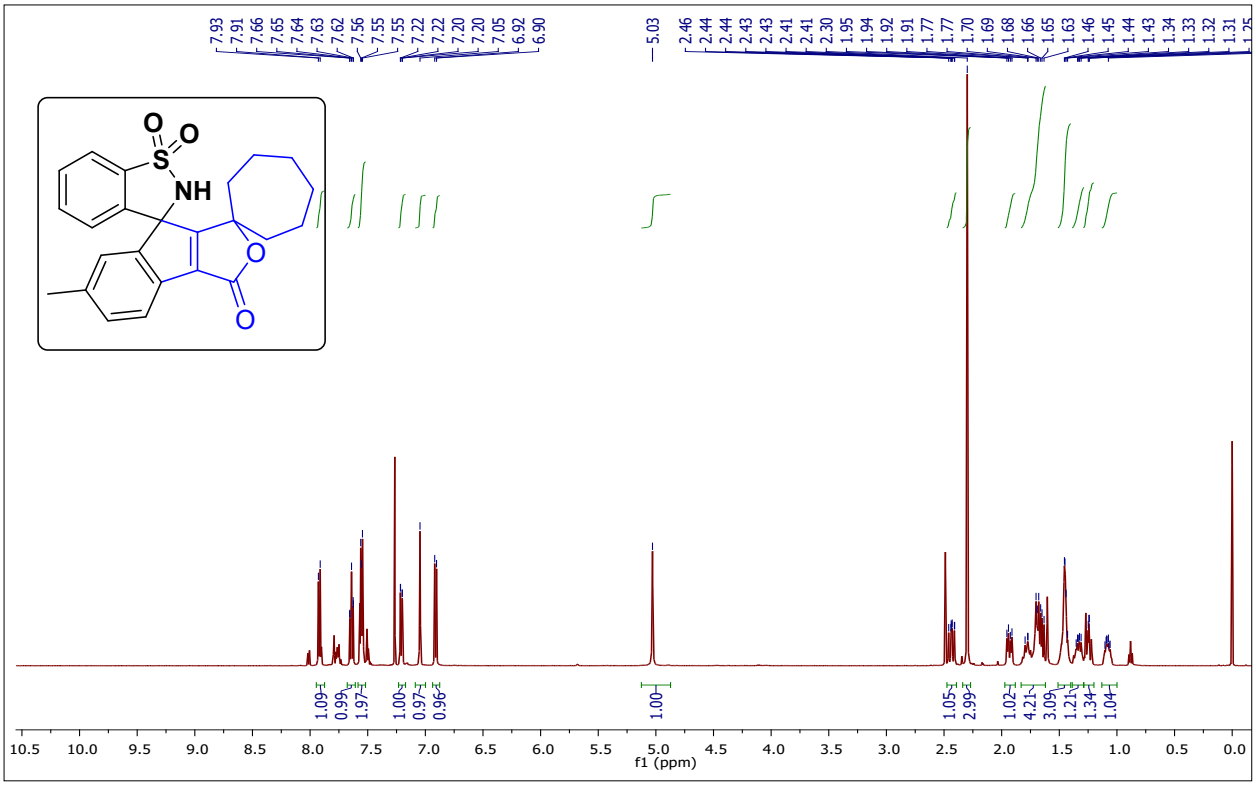
^{1}H NMR (500MHz, $CDCl_3$) spectrum of 3g:



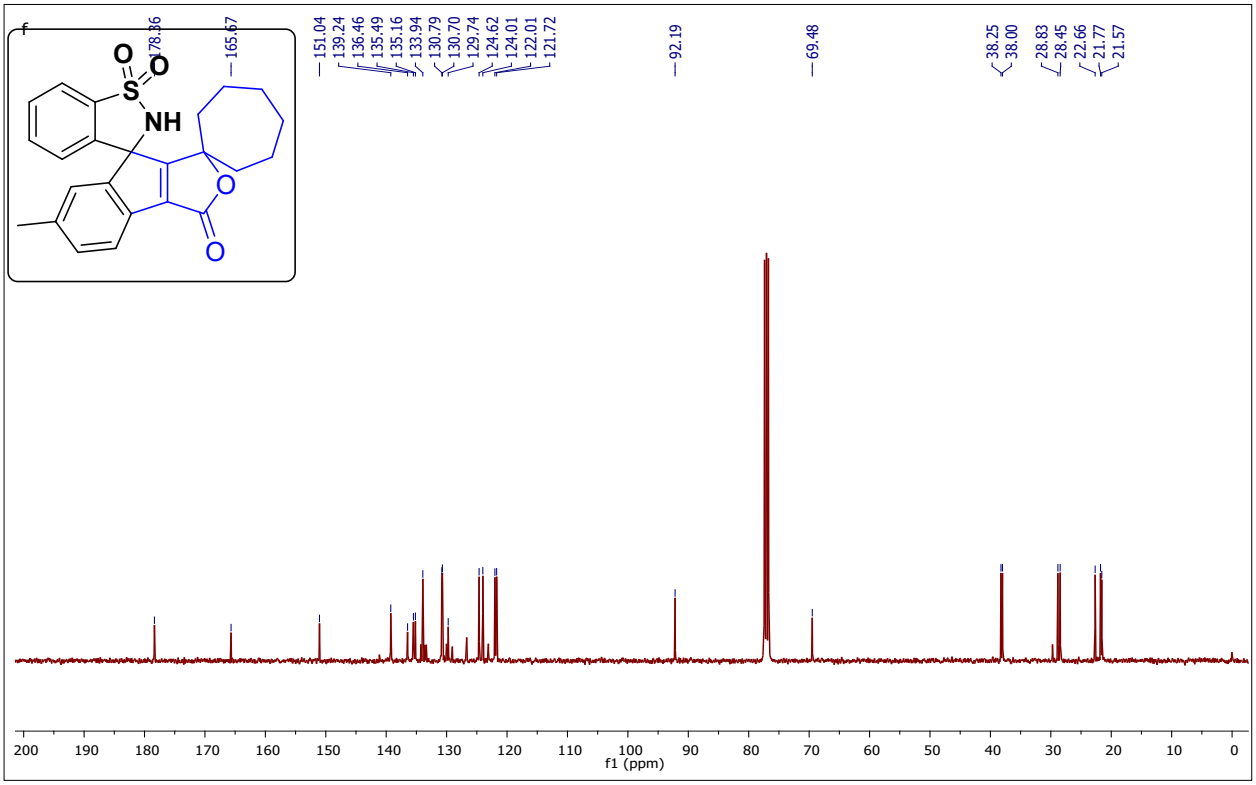
^{13}C NMR(126 MHz,$CDCl_3$) spectrum of 3g:



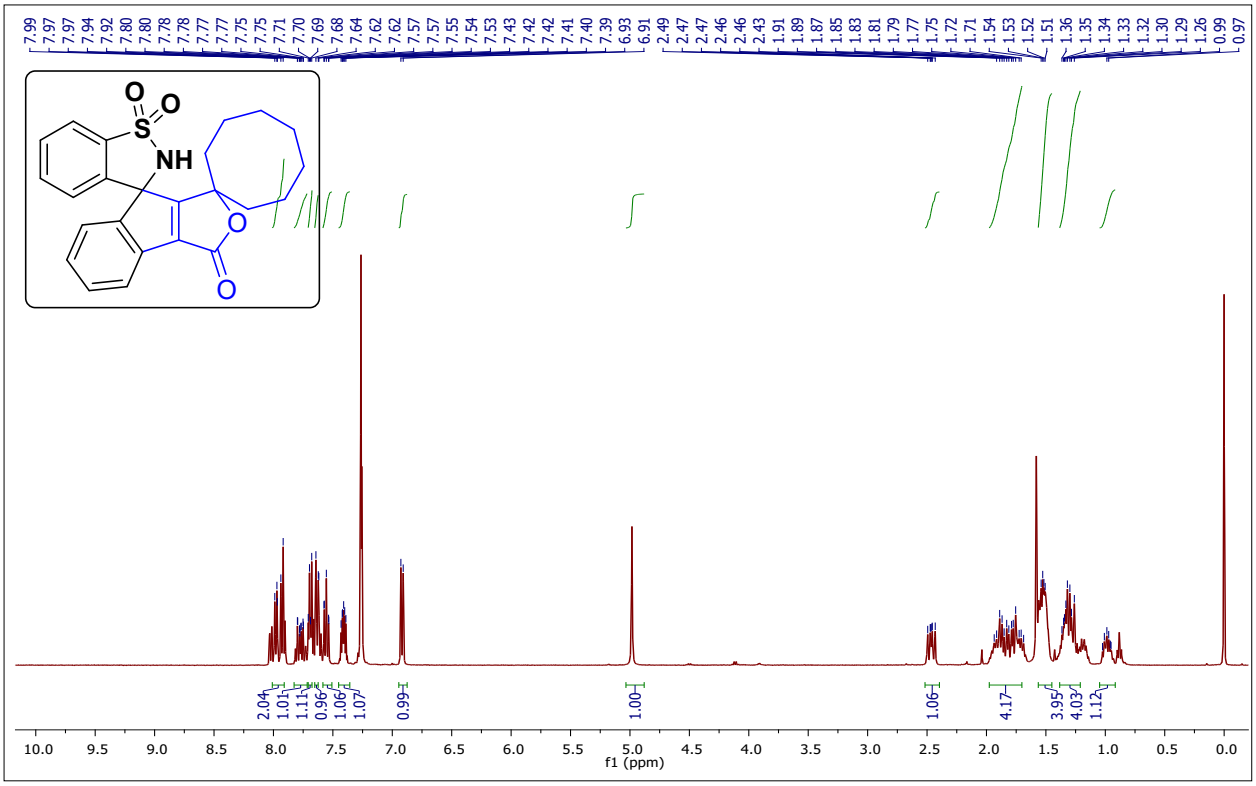
^{1}H NMR (500MHz, $CDCl_3$) spectrum of 3h:



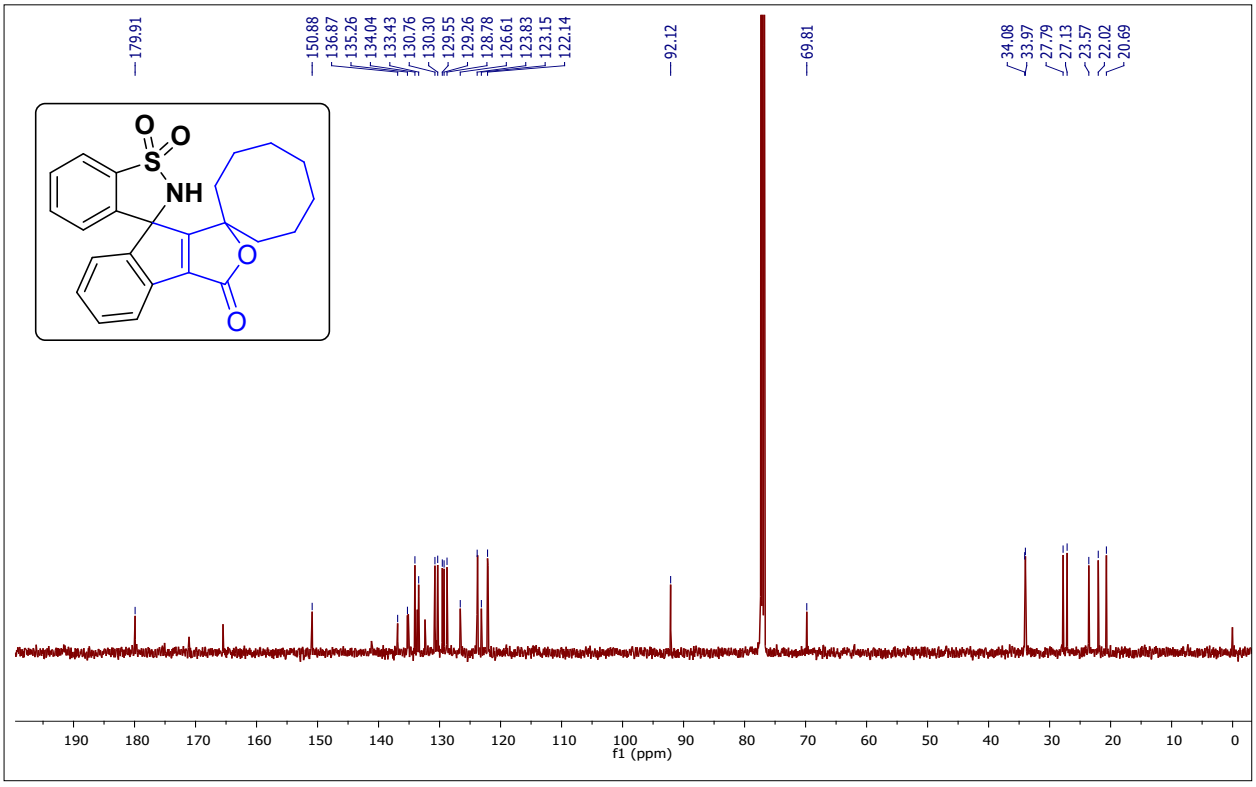
^{13}C NMR(126 MHz,$CDCl_3$) spectrum of 3h:



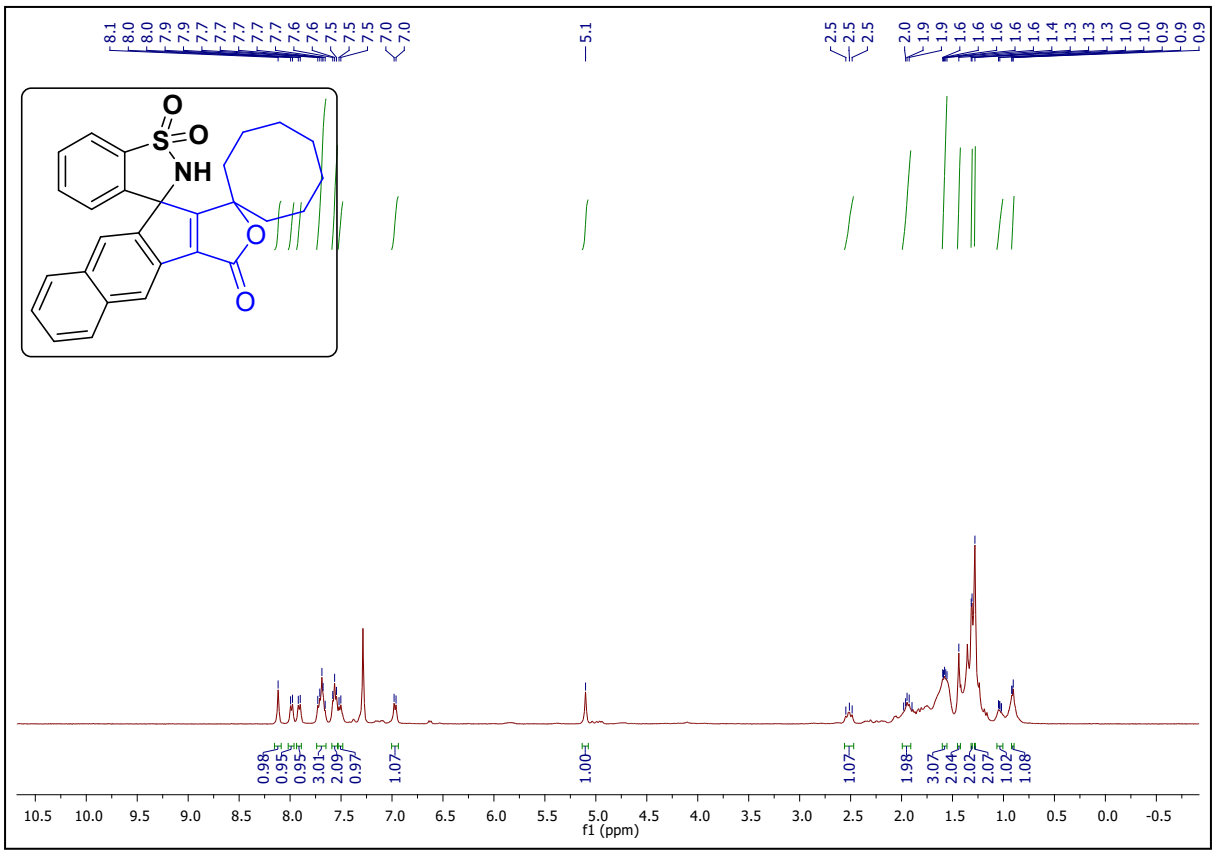
^{1}H NMR (400MHz, $CDCl_3$) spectrum of 3i:



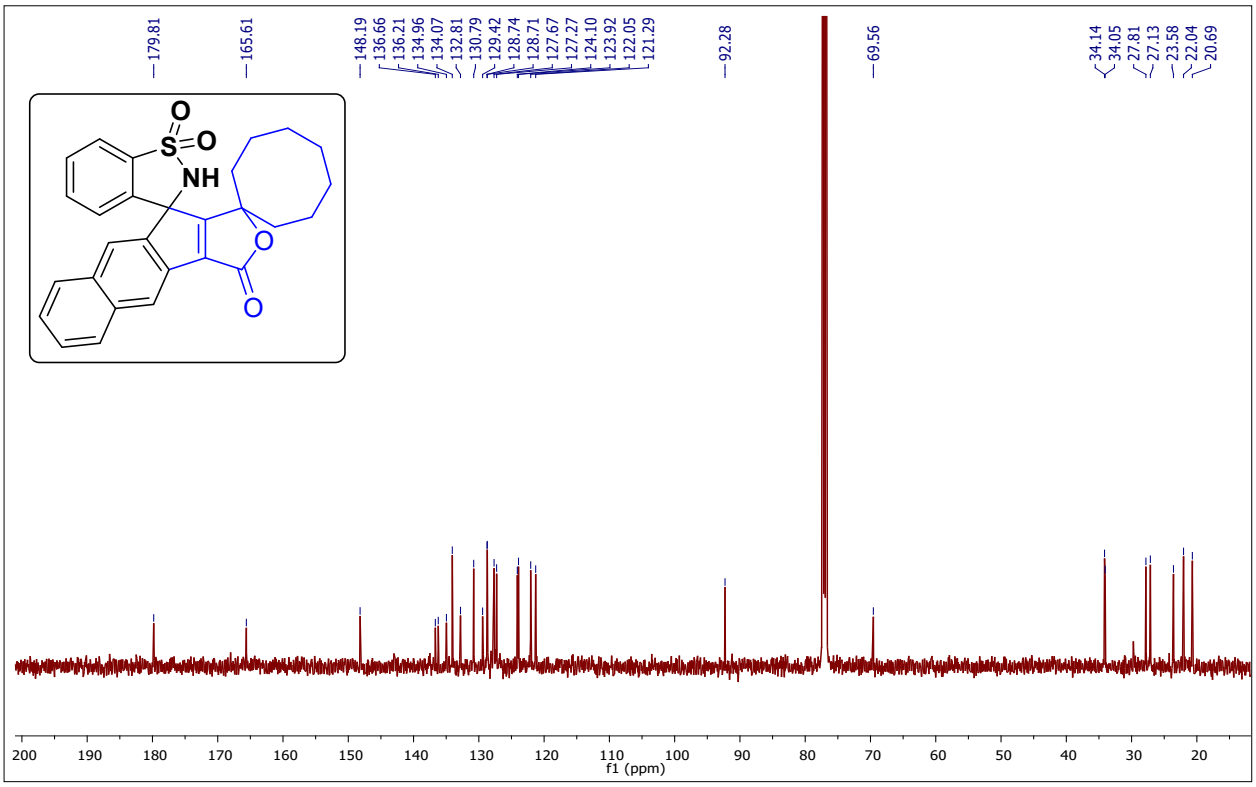
^{13}C NMR(101 MHz,$CDCl_3$) spectrum of 3i:



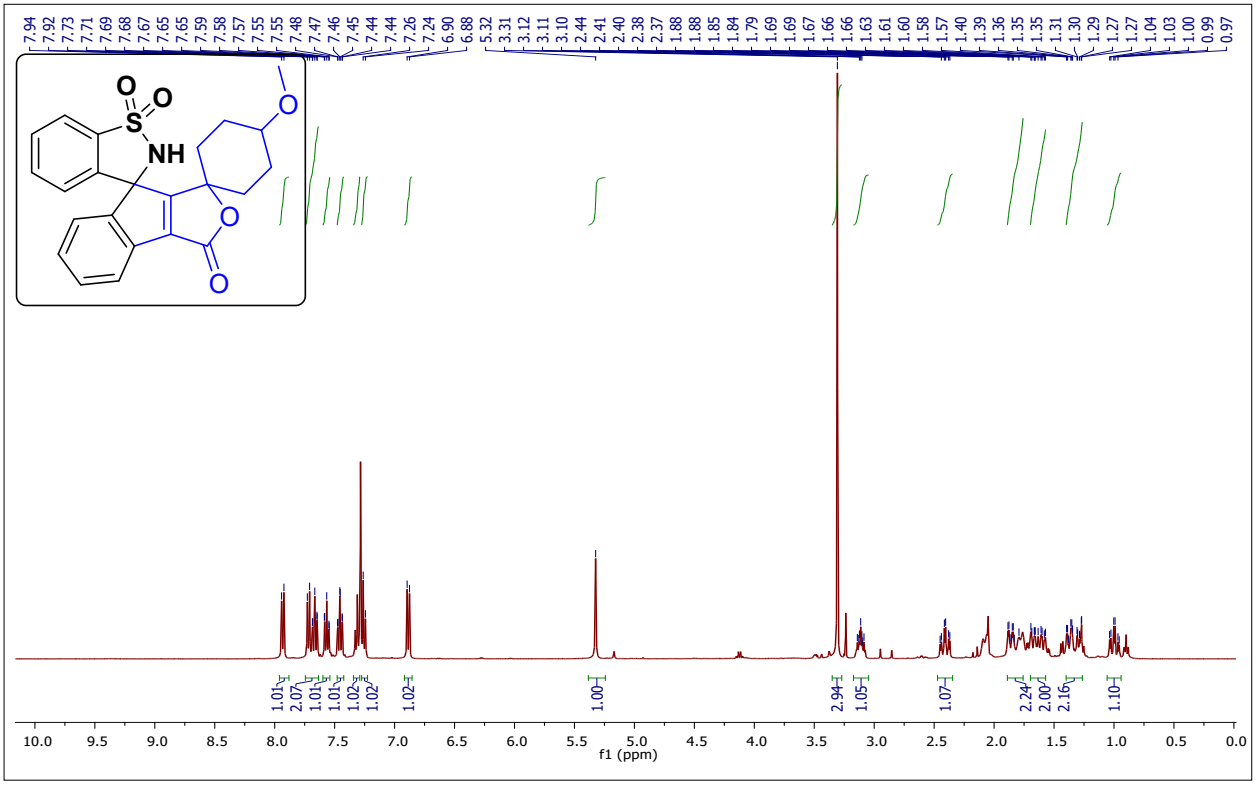
^{1}H NMR (500MHz, $CDCl_3$) spectrum of 3j:



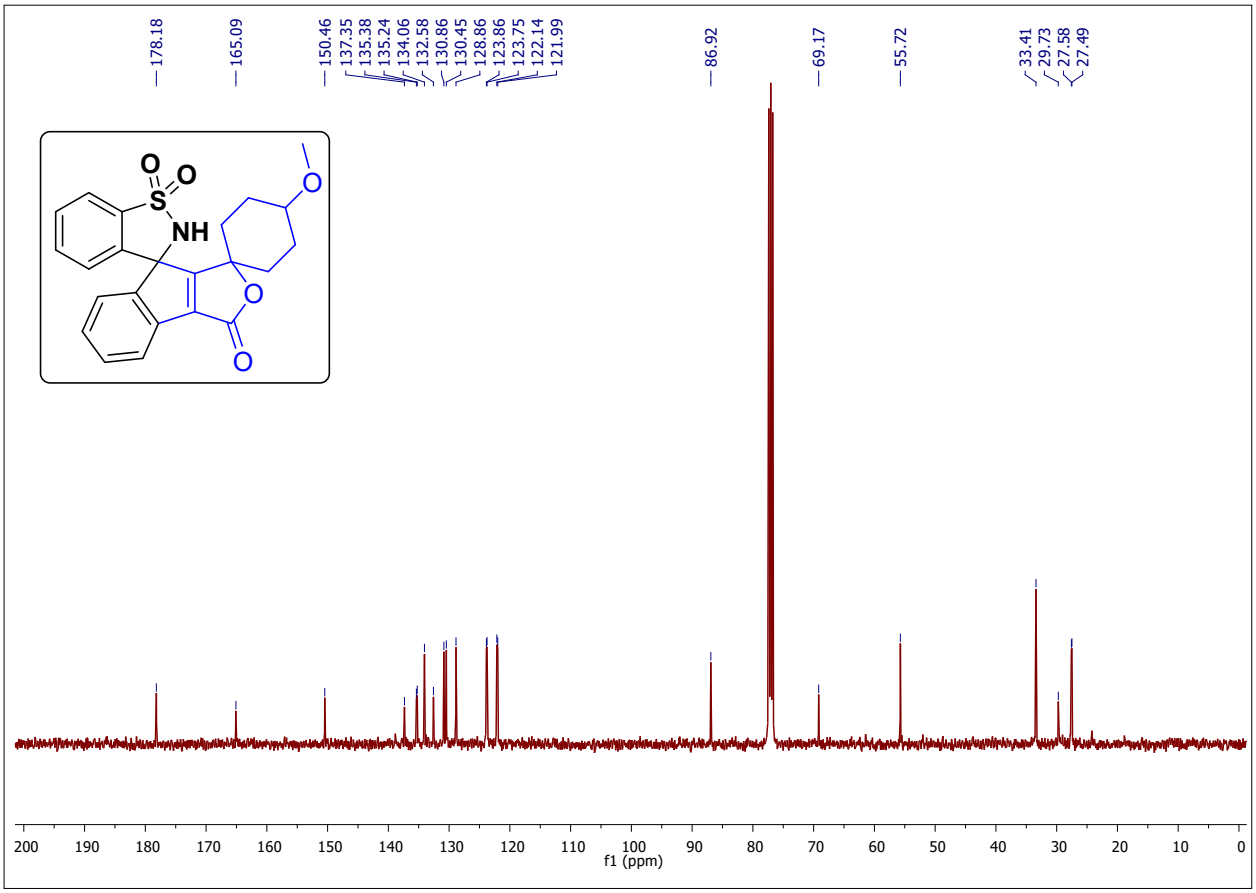
^{13}C NMR(126 MHz,$CDCl_3$) spectrum of 3j:



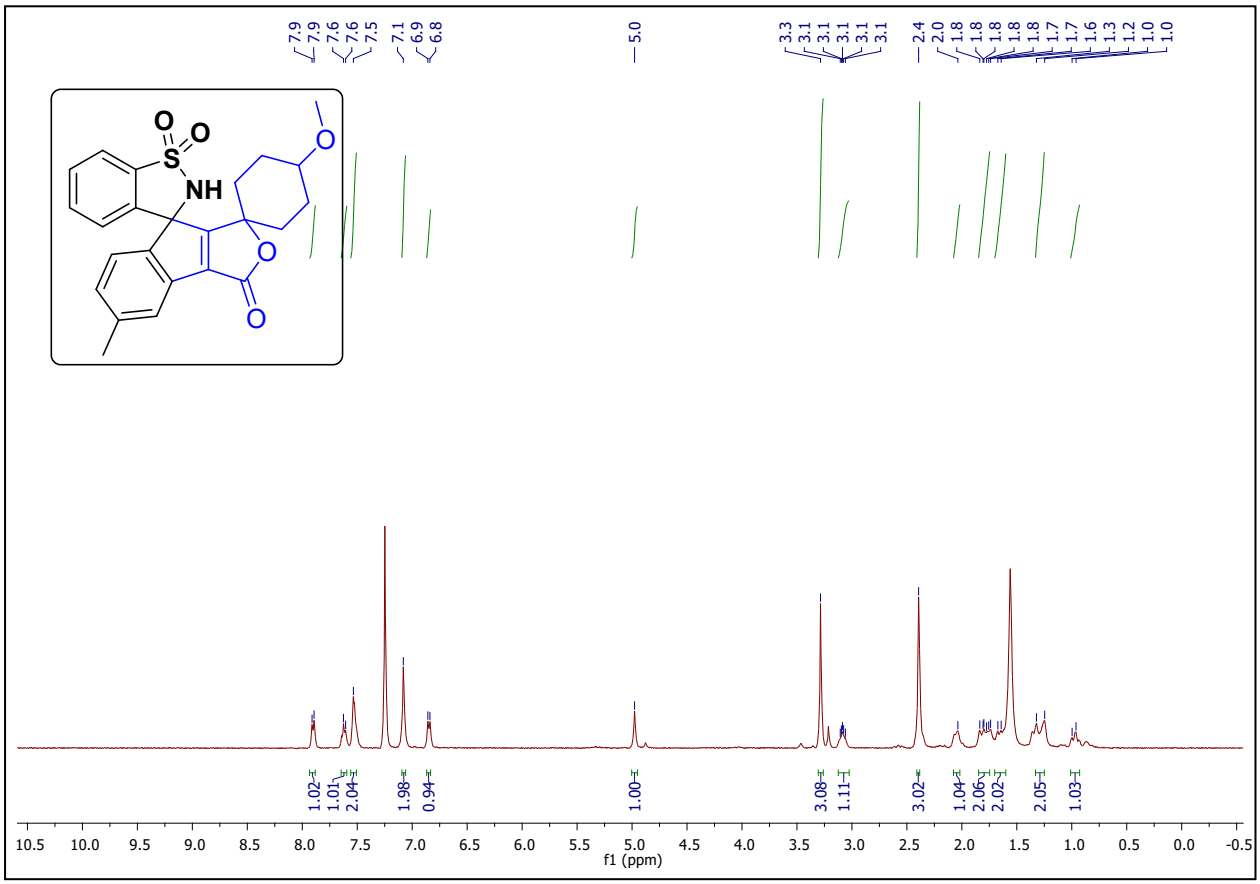
^{1}H NMR (400MHz, $CDCl_3$) spectrum of 3k:



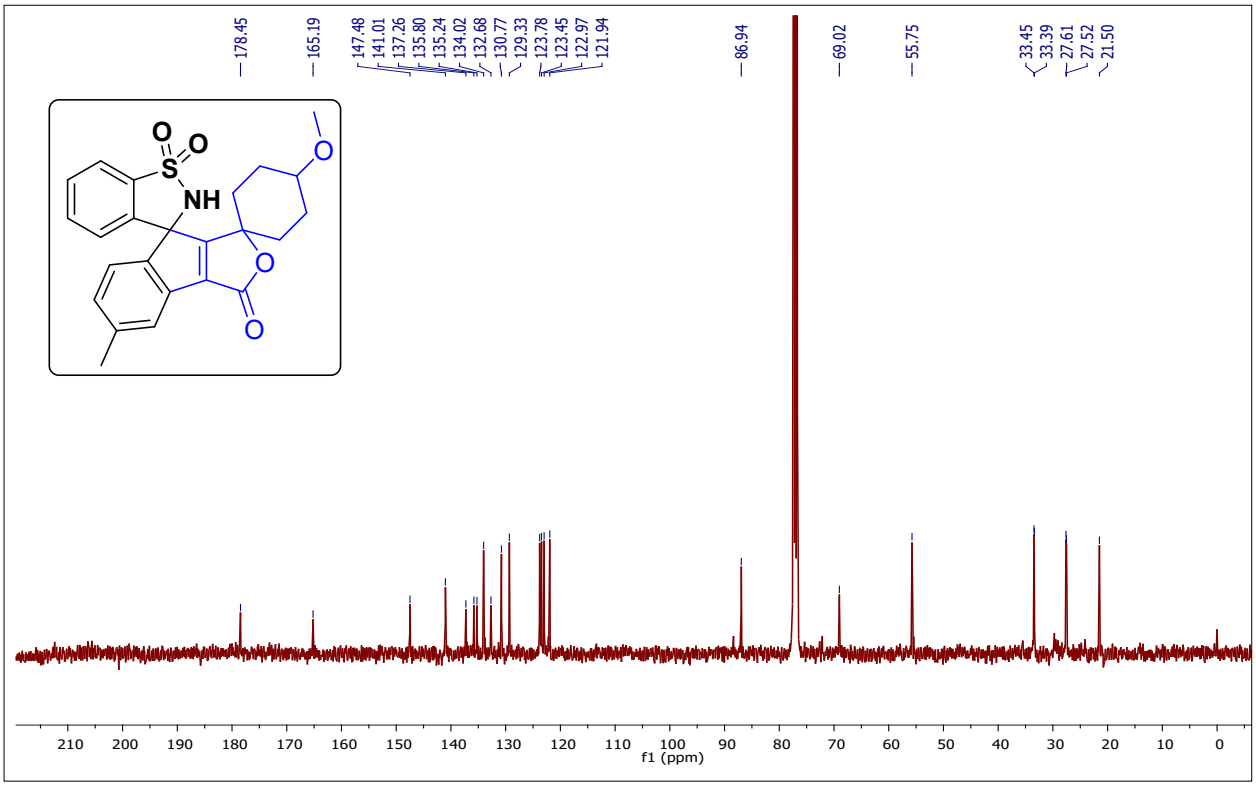
^{13}C NMR(101 MHz,$CDCl_3$) spectrum of 3k:



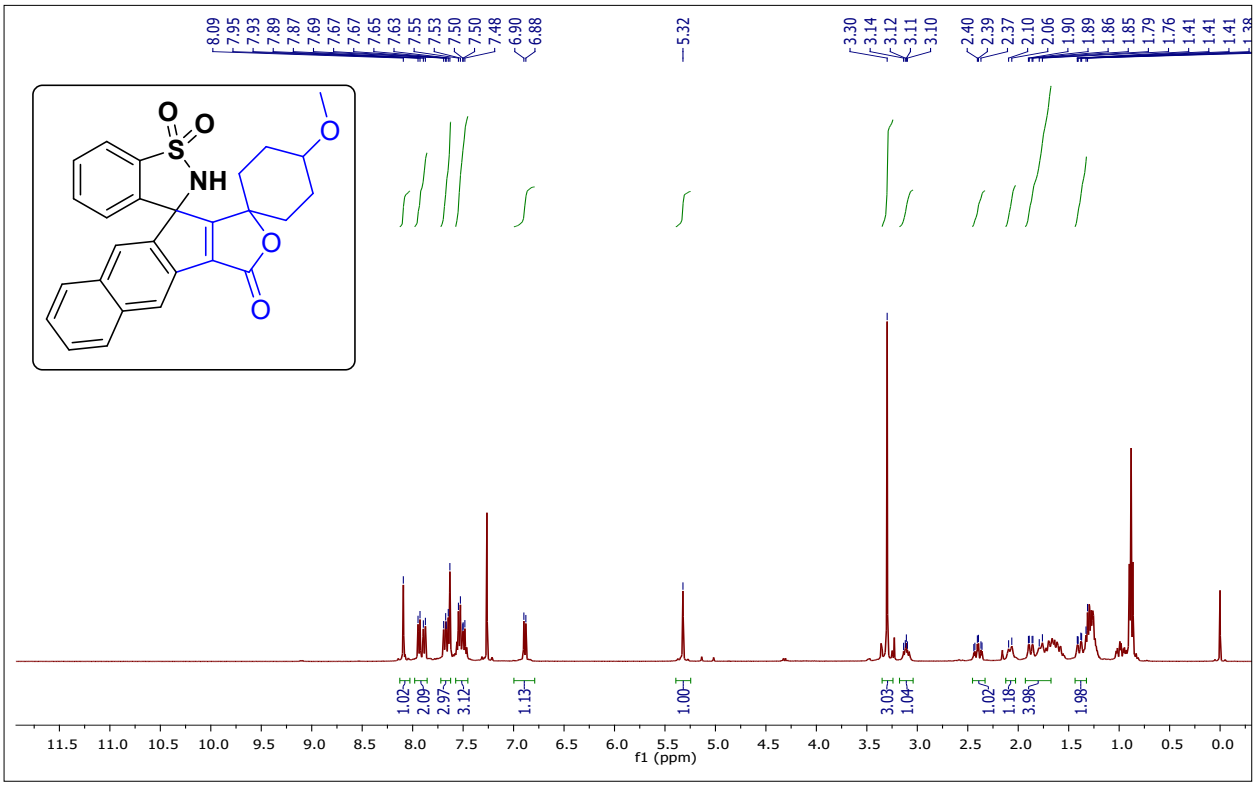
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound 3l:



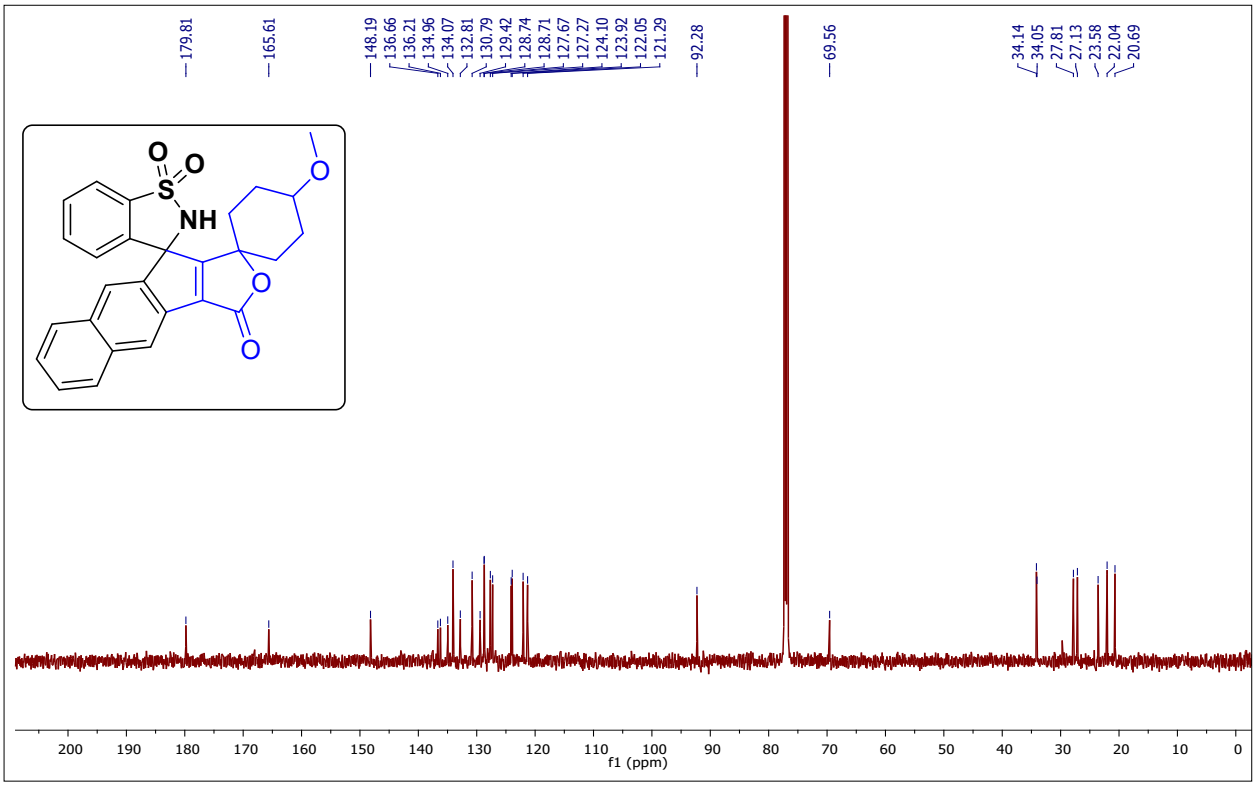
^{13}C NMR(101 MHz,$CDCl_3$) spectrum of compound 3l:



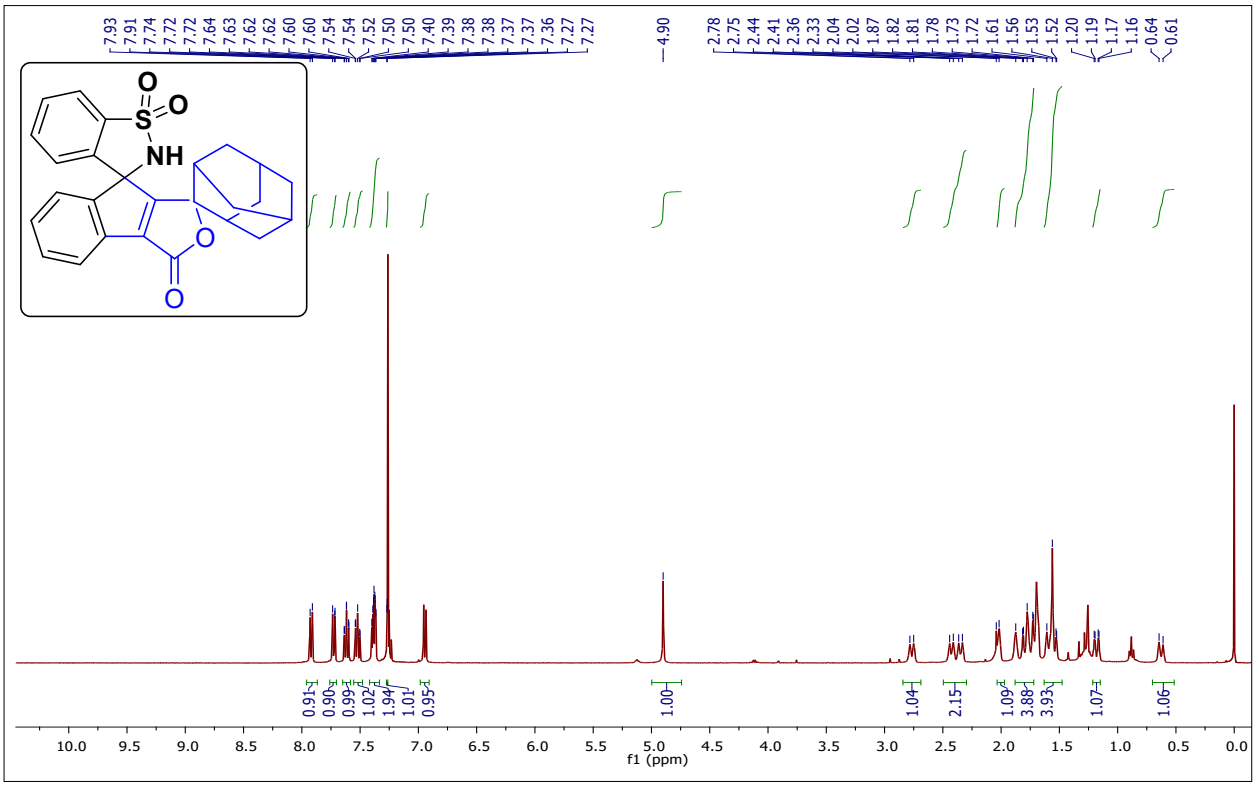
^{1}H NMR (400MHz, $CDCl_3$) spectrum of 3m:



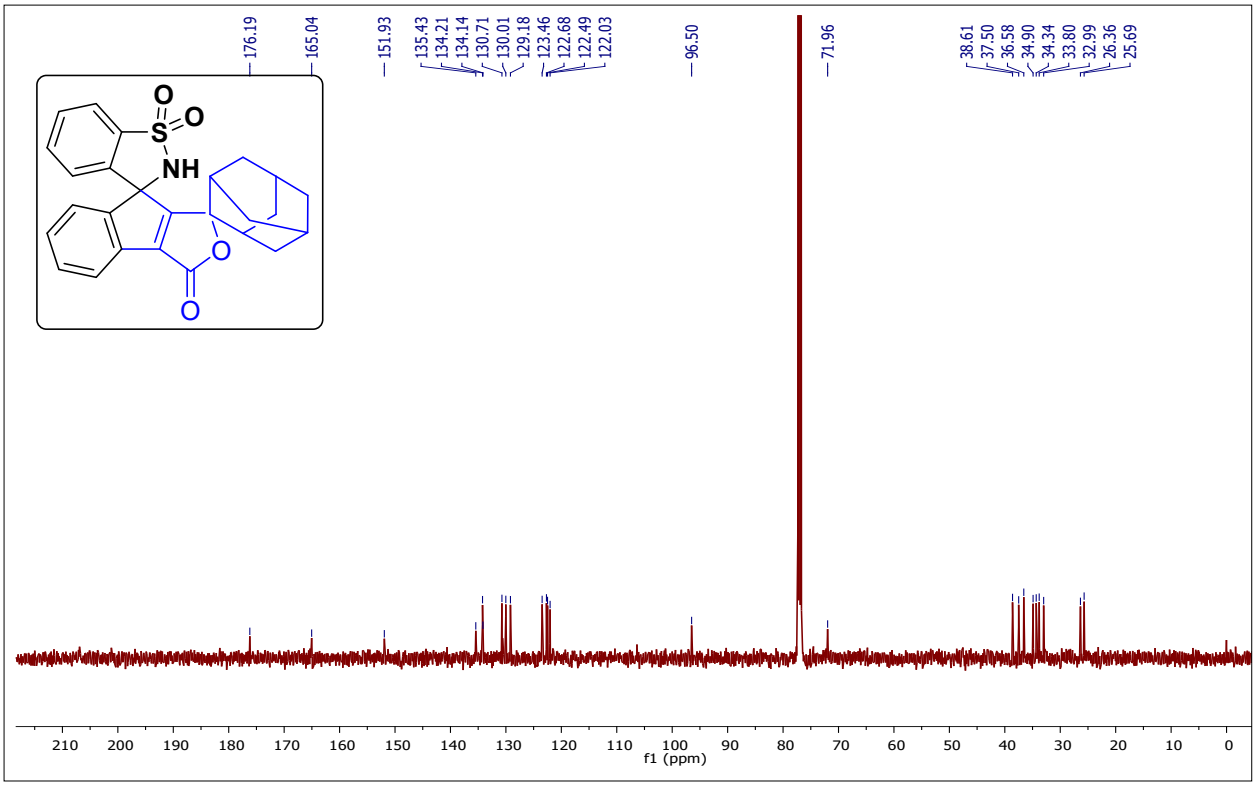
^{13}C NMR(101 MHz,$CDCl_3$) spectrum of 3m:



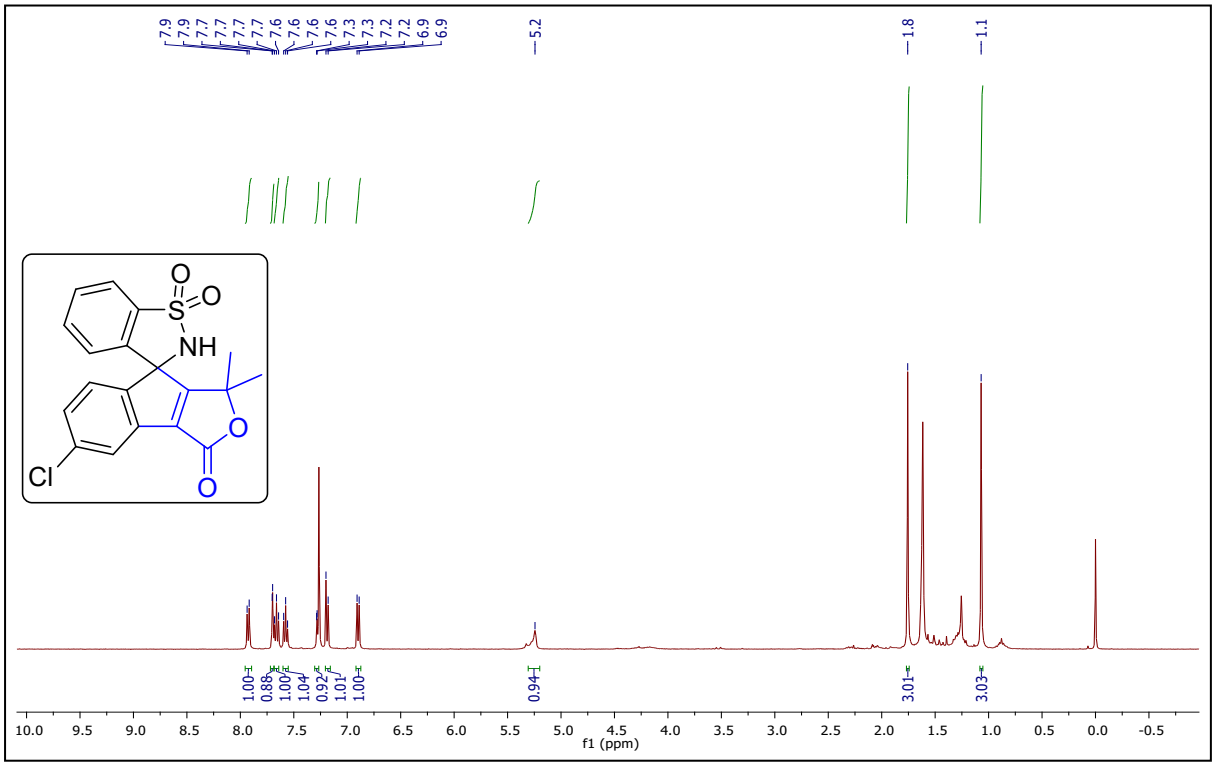
^{1}H NMR (400MHz, $CDCl_3$) spectrum of 3n:



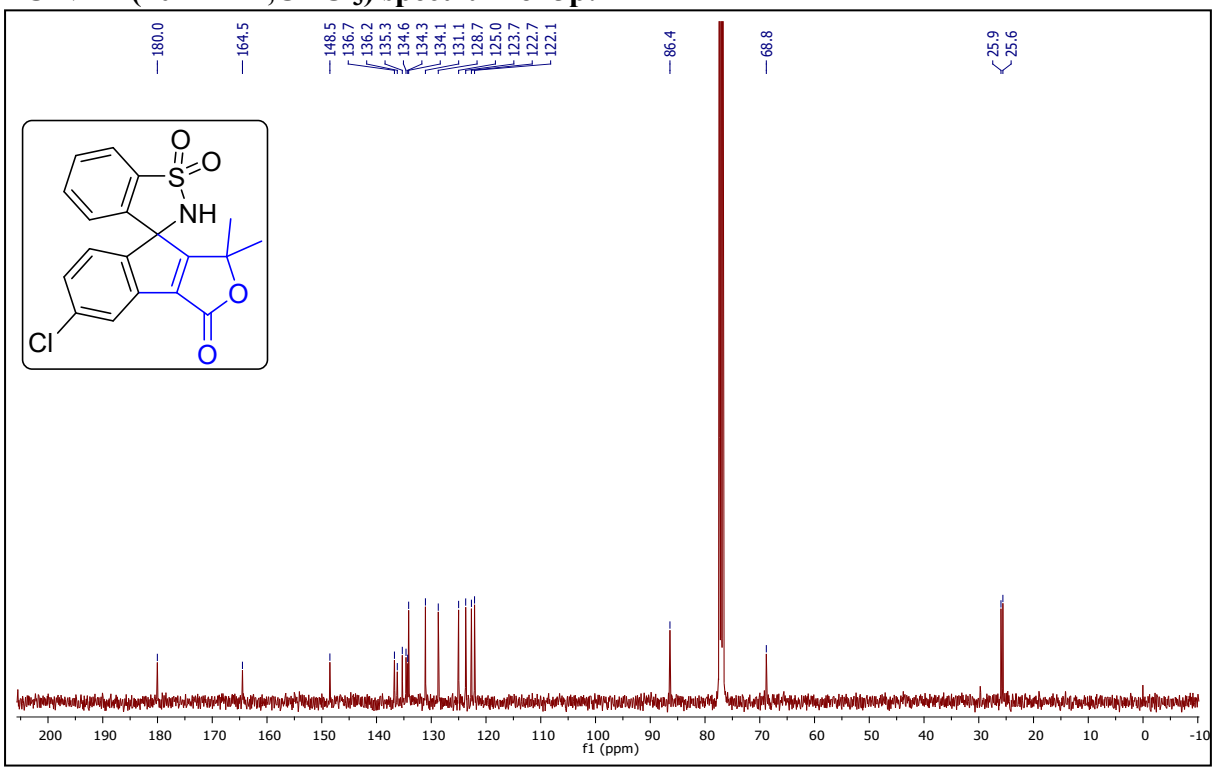
^{13}C NMR(101 MHz,$CDCl_3$) spectrum of 3n:



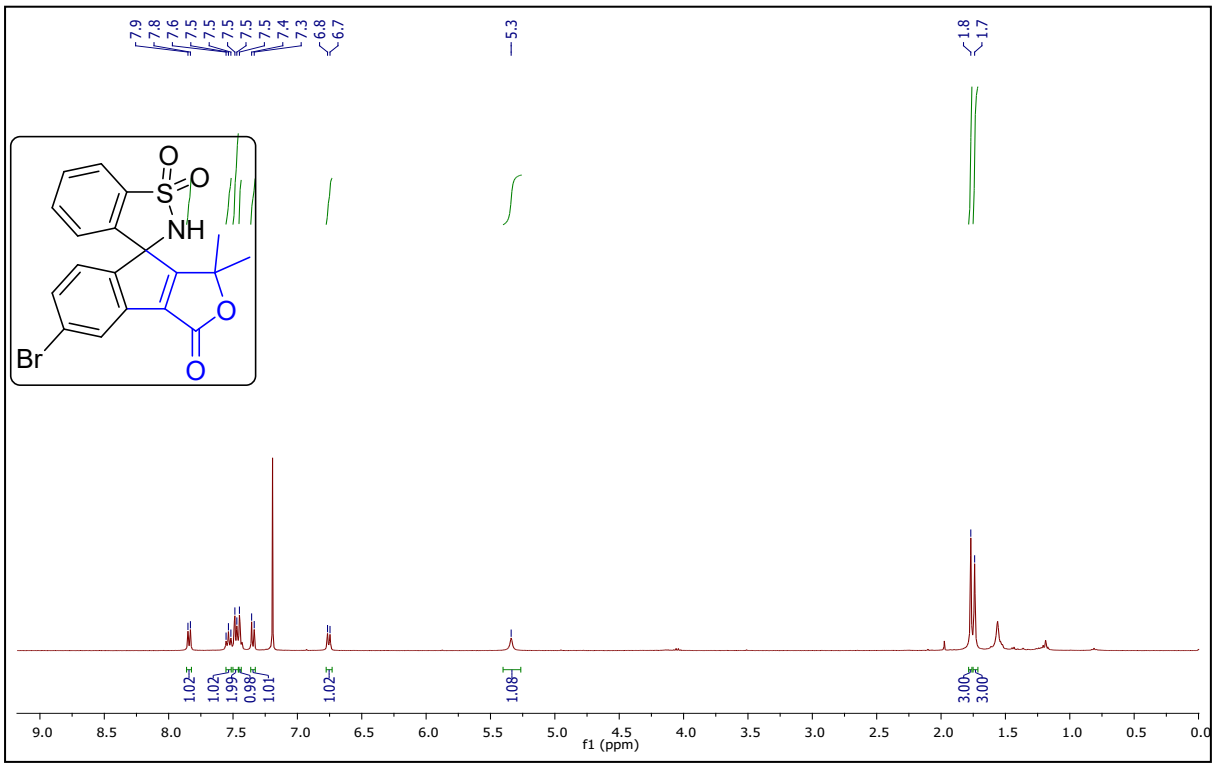
^{1}H NMR (400MHz, $CDCl_3$) spectrum of 3p:



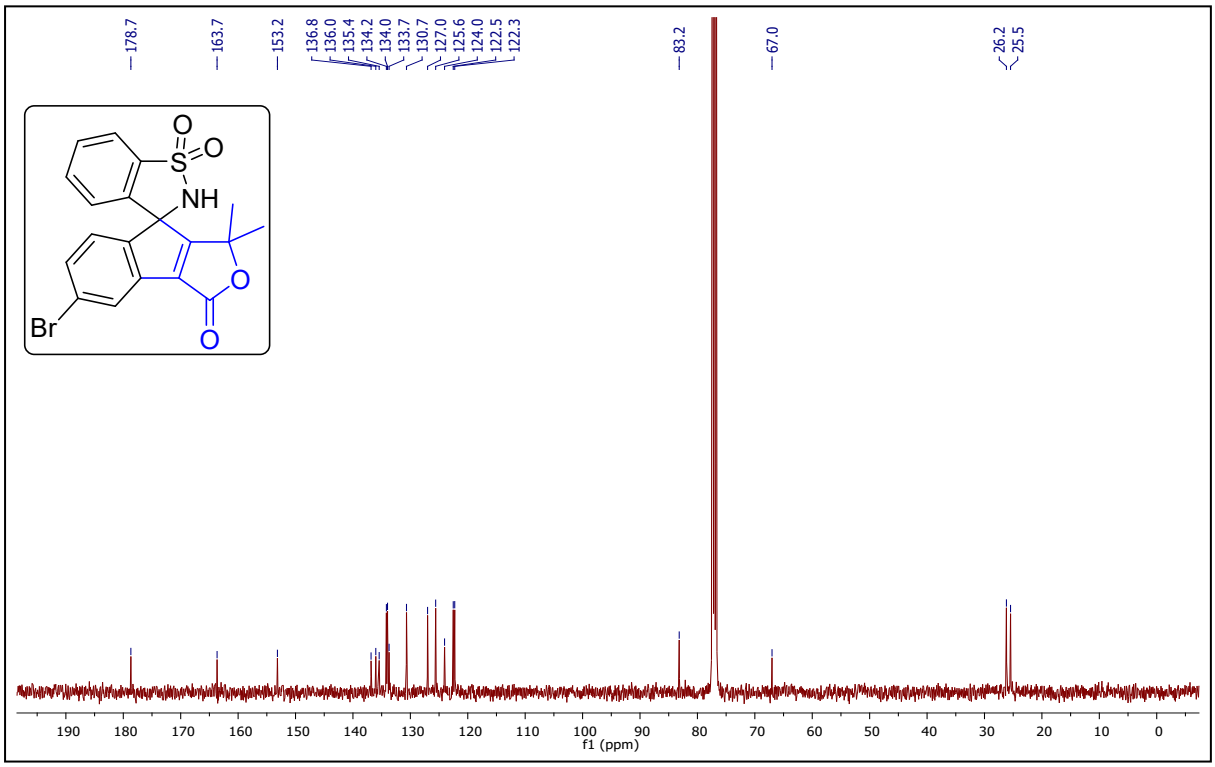
^{13}C NMR(101 MHz,$CDCl_3$) spectrum of 3p:



^{1}H NMR (400MHz, $CDCl_3$) spectrum of 3q:



^{13}C NMR(101 MHz,$CDCl_3$) spectrum of 3q:



5. X-ray Crystallography:

X-ray data for the compound was collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-III detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs [1]. The structure was solved using intrinsic phasing method [2] and further refined with the SHELXL [2] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. The N-H atoms were located in the difference Fourier map and its positions and isotropic displacement parameters were refined. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms].

Crystal structure determination of 3b

Crystal Data for $C_{20}H_{17}NO_4S$ (*M* =367.40 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 11.908(2) Å, *b* = 10.3611(19) Å, *c* = 14.976(2) Å, *β* = 97.885(7)°, *V* = 1830.3(5) $Å^3$, *Z* = 4, *T* = 294.15 K, μ(MoKα) = 0.202 mm^{-1}, *Dcalc* = 1.333 g/cm^3, 21574 reflections measured (4.796° ≤ 2Θ ≤ 61.206°), 5552 unique (R_{int} = 0.0335, R_{sigma} = 0.0354) which were used in all calculations. The final R_1 was 0.0415 (I > 2σ(I)) and wR_2 was 0.1174 (all data). **CCDC 2293494** deposition number contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

1. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.
2. Sheldrick G. M. (2015). ActaCrystallogr C71: 3-8.

Figure caption: ORTEP diagram of **3b** compound with the atom-numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.