

Supporting Information for

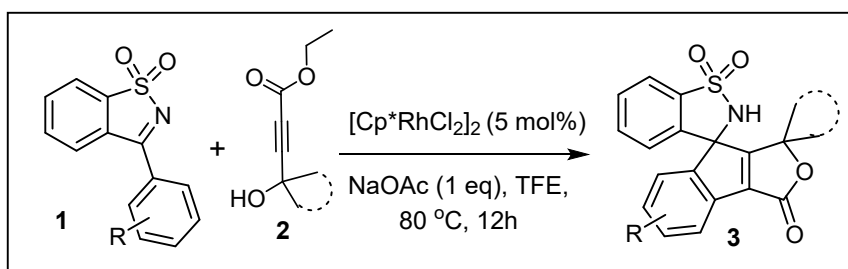
Rh(III)-catalyzed sequential spiroannulation/lactonization of 3-aryl *N*-sulfonyl ketimines with 4-hydroxy-2-alkynoates by C–H bond activation

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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. ¹H and ¹³C NMR (proton-decoupled) spectra were recorded in CDCl₃ 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.

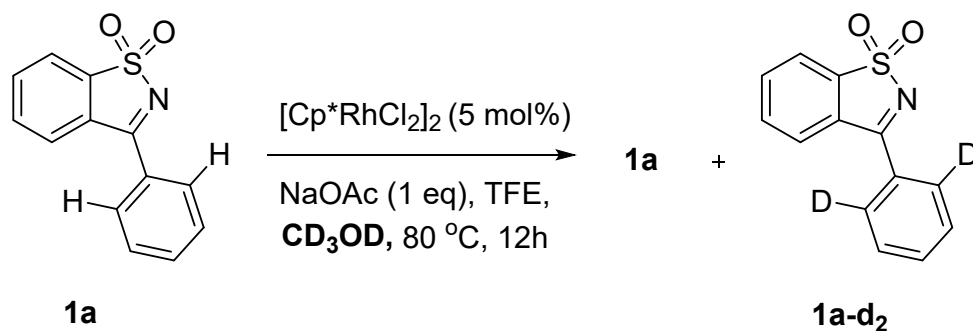
Procedure for the synthesis of 3a-p:

To an oven dried sealed tube equipped with a stir bar were charged with 3-phenylbenzo[*d*]isothiazole 1,1-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*Cl₂]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**.

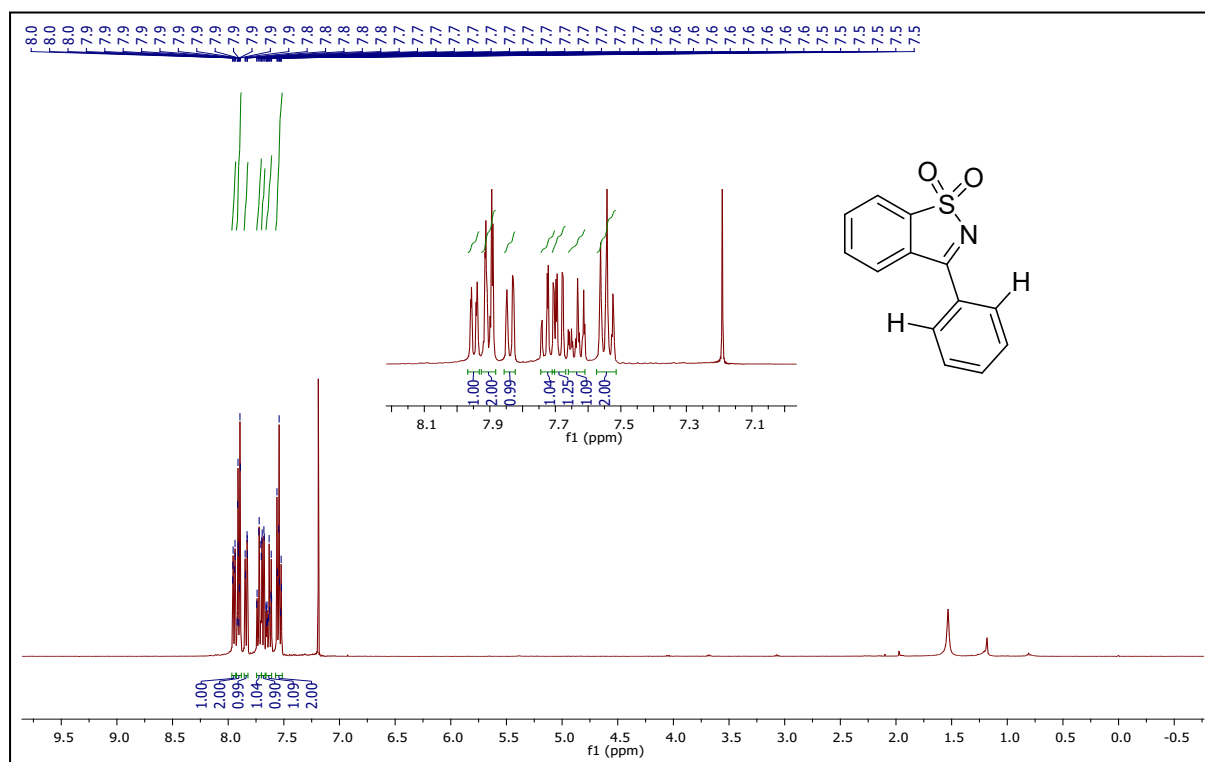
2. Mechanistic studies:

(a) H/D Exchange experiment:

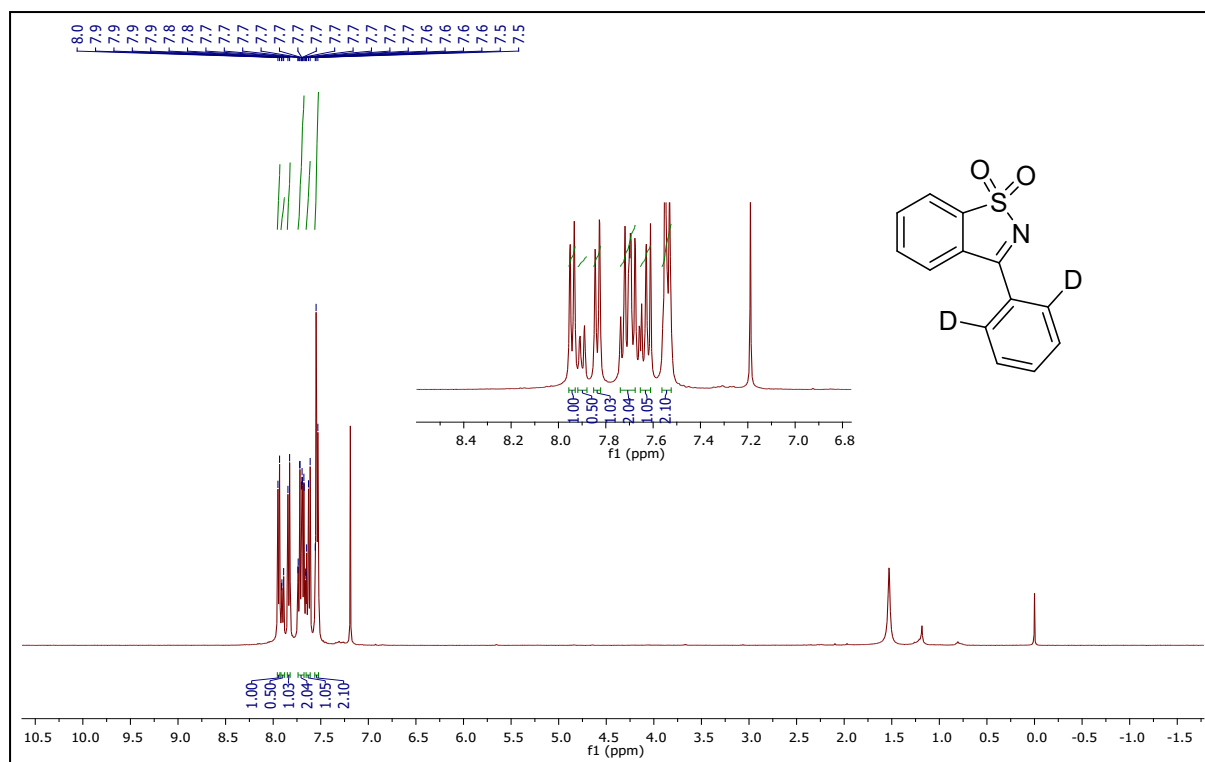
To an oven dried sealed tube was equipped with a stir bar and charged with 3-phenylbenzo[*d*]isothiazole 1,1-dioxide (**1a**, 0.5 mmol) in 3 mL of TFE, followed by addition of [Cp*RhCl₂]₂ (5 mol%) and NaOAc (33 mg, 0.51 mmol) at room temperature. CD₃OD (20 equiv) was added to the above mixture. The resulting 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-d₂**. The deuterium content of the product was 75%, which was determined by ¹H NMR.



¹H NMR (400 MHz, CDCl₃) spectrum of 1a:

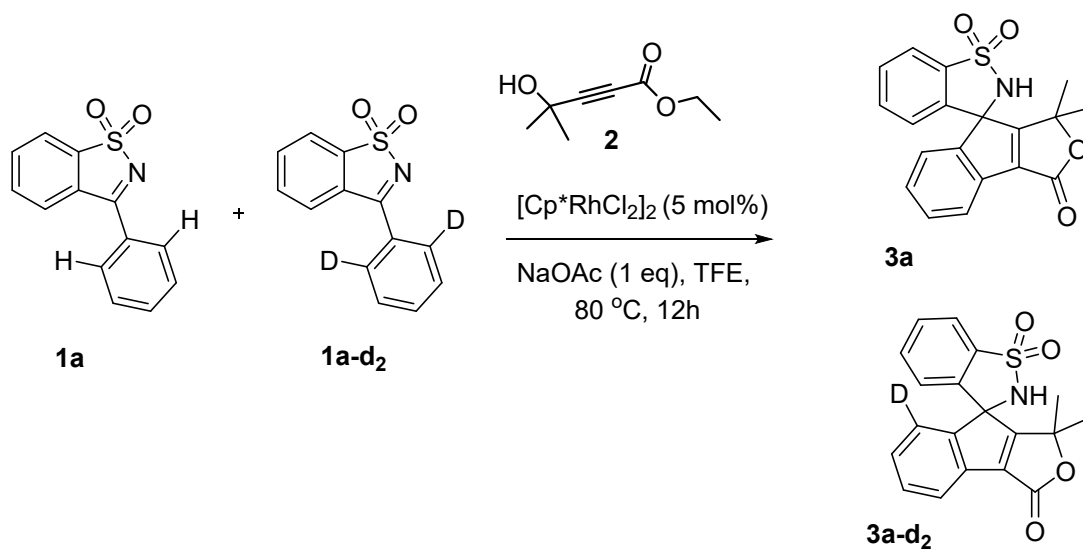


¹H NMR (400 MHz, CDCl₃) spectrum of 1a and 1a-d₂ mixture:

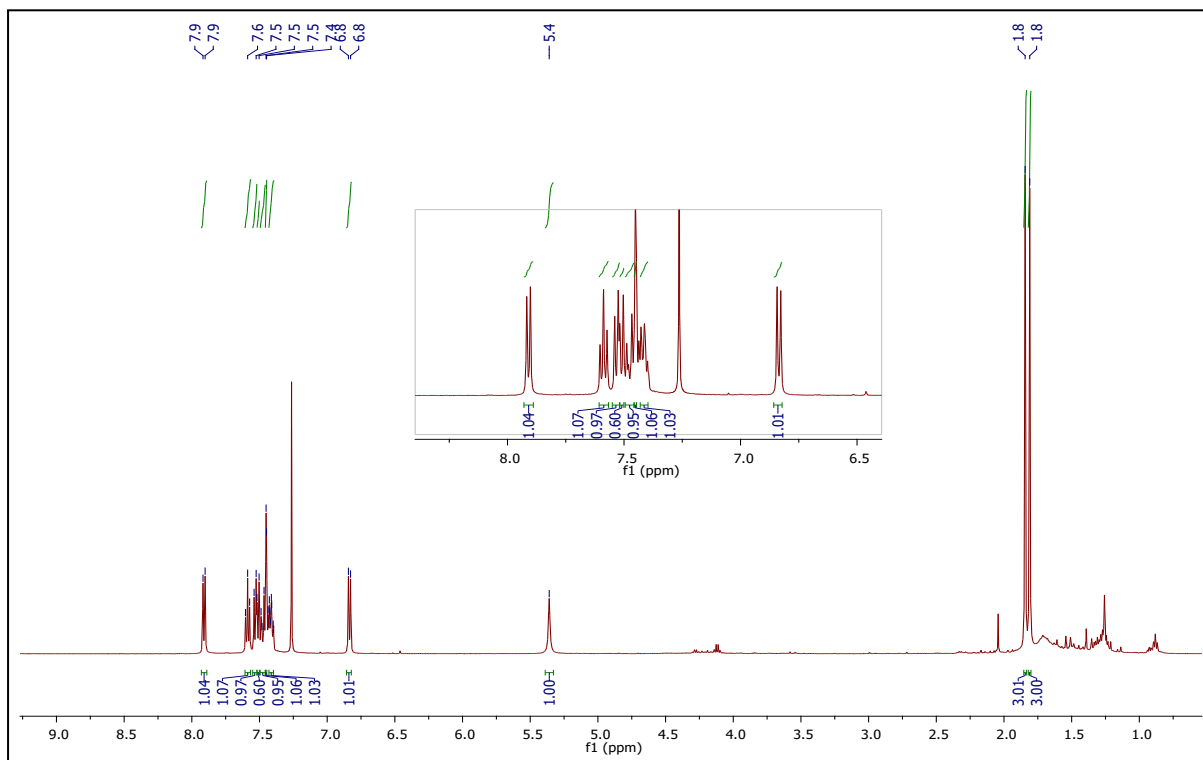


(C) Competitive KIE Experiment between 1a and 1a-d₂:

To an oven dried sealed tube equipped with a stir bar were charged with 3-phenylbenzo[*d*]isothiazole 1,1-dioxide **1a** (100 mg, 0.5 mmol), **1a-d₂** (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*Cl₂]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-d₂**. The ratio of **3a** and **3a-d₂** was determined by ¹H NMR. The calculated K_H/K_D = 1/0.6 = 1.66.

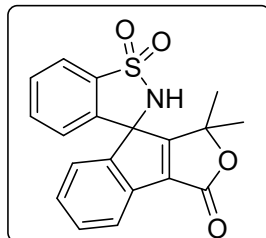


¹H NMR (500MHz, CDCl₃) spectrum of **3a** and **3a-d₂** mixture:



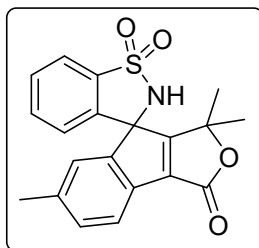
3. Characterization of data:

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



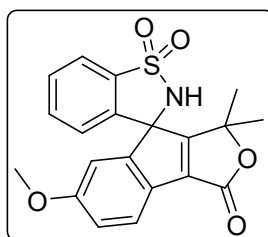
White solid (0.130 g, 90%), m.p. 191-193 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 2H), 7.64 (td, *J* = 7.7, 0.9 Hz, 1H), 7.55 (td, *J* = 7.7, 1.1 Hz, 1H), 7.44 (td, *J* = 7.4, 1.3 Hz, 1H), 7.33 – 7.19 (m, 2H), 6.89 (d, *J* = 7.9 Hz, 1H), 5.26 (s, 1H), 1.75 (s, 3H), 1.06 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) 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 C₁₉H₁₇NO₄S: 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:



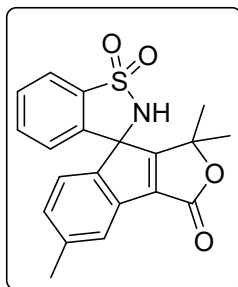
White solid (0.125 g, 88%), m.p. 262-264 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.64 (td, *J* = 7.7, 0.9 Hz, 1H), 7.57 (ddd, *J* = 11.9, 6.4, 5.4 Hz, 2H), 7.24 (dd, *J* = 7.6, 0.6 Hz, 1H), 7.05 (s, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 5.04 (s, 1H), 2.32 (s, 3H), 1.74 (s, 3H), 1.06 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) 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 C₂₀H₁₉NO₄S: 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:



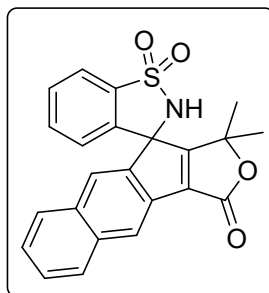
White solid (0.116 g, 83%), m.p. 173-175 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, $J = 7.8$ Hz, 1H), 7.68 – 7.58 (m, 2H), 7.26 (dd, $J = 8.6, 7.3$ Hz, 1H), 7.02 – 6.79 (m, 3H), 5.13 (s, 1H), 3.99 (s, 3H), 1.73 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.3, 164.2, 154.5, 152.2, 136.4, 135.5, 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 $\text{C}_{20}\text{H}_{18}\text{NO}_5\text{S}$: 384.0852 $[\text{M}+\text{H}]^+$, 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:



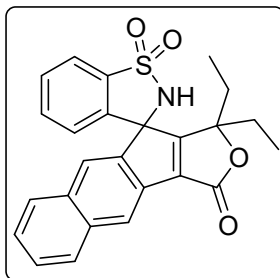
White solid (0.128 g, 90%), m.p. 204-206 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.90 (d, $J = 7.8$ Hz, 1H), 7.65 – 7.61 (m, 1H), 7.57 – 7.51 (m, 2H), 7.10 (q, $J = 7.8$ Hz, 2H), 6.88 (d, $J = 7.9$ Hz, 1H), 5.14 (s, 1H), 2.40 (s, 3H), 1.75 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 179.0, 165.2, 147.4, 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 $\text{C}_{20}\text{H}_{19}\text{NO}_4\text{S}$: 368.0957 $[\text{M}+\text{H}]^+$, 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:



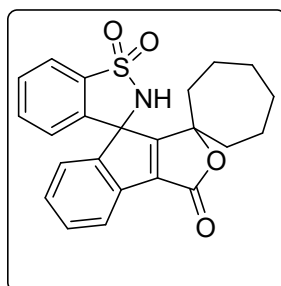
Yellow solid (0.116 g, 85%), m.p. 242-244 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.13 (s, 1H), 7.95 (dd, $J = 8.5, 7.9$ Hz, 2H), 7.77 – 7.64 (m, 3H), 7.62 – 7.48 (m, 3H), 6.95 (d, $J = 7.8$ Hz, 1H), 5.18 (s, 1H), 1.81 (s, 3H), 1.12 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 178.5, 165.1, 147.7, 136.9, 136.2, 135.2, 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 $\text{C}_{23}\text{H}_{19}\text{NO}_4\text{S}$: 404.0957 $[\text{M}+\text{H}]^+$, 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:



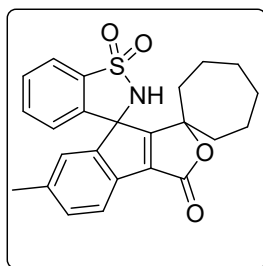
Yellow solid (0.117 g, 80%), m.p. 220-222 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.13 (s, 1H), 7.95 – 7.92 (m, 2H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.65 (s, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 5.32 (s, 1H), 2.26 – 2.11 (m, 2H), 1.44 – 1.54 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.67 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) 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 C₂₅H₂₂NO₄S: 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:



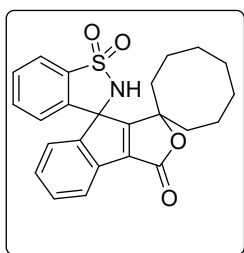
White solid (0.130 g, 78%), m.p. 167-169 °C, ¹H NMR (500 MHz, CDCl₃) δ 8.02 (d, *J* = 7.5 Hz, 1H), 7.92 (dd, *J* = 4.3, 3.5 Hz, 1H), 7.84 – 7.74 (m, 1H), 7.62 (m, 1H), 7.59 – 7.53 (m, 1H), 7.41 (ddd, *J* = 7.5, 6.4, 2.3 Hz, 1H), 7.25 (d, *J* = 1.6 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 1H), 5.12 (s, 1H), 2.56 – 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). ¹³C NMR (126 MHz, CDCl₃) 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 calcd for C₂₃H₁₂₃NO₄S: 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:



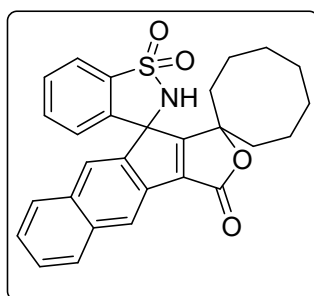
Yellow solid (0.122 g, 75%), m.p. 205-207 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.92 (d, $J = 7.8$ Hz, 1H), 7.68 – 7.61 (m, 1H), 7.58 – 7.52 (m, 2H), 7.21 (dd, $J = 7.6, 0.6$ Hz, 1H), 7.05 (s, 1H), 6.91 (d, $J = 7.9$ Hz, 1H), 5.03 (s, 1H), 2.47 – 2.39 (m, 1H), 2.30 (s, 3H), 1.93 (dd, $J = 4.3, 7.0$ Hz, 1H), 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 calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_4\text{S}$: 422.1426 $[\text{M}+\text{H}]^+$, found: 422.1386.

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



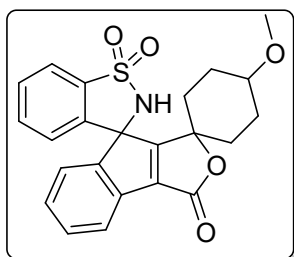
Yellow solid (0.135g, 78%), m.p. 145-147 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.01 – 7.91 (m, 2H), 7.77 (ddd, $J = 11.7, 7.3, 1.1$ Hz, 1H), 7.69 (dd, $J = 7.5, 4.2$ Hz, 1H), 7.64 (s, 1H), 7.58 – 7.51 (m, 1H), 7.45 – 7.36 (m, 1H), 6.92 (d, $J = 7.9$ Hz, 1H), 4.98 (s, 1H), 2.52 – 2.40 (m, 1H), 1.82 (dtd, $J = 26.7, 18.5, 7.4$ 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 $\text{C}_{24}\text{H}_{25}\text{NO}_4\text{S}$: 422.1426 $[\text{M}+\text{H}]^+$, found: 422.1386.

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



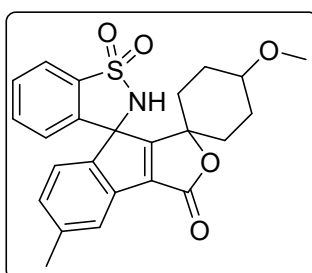
White solid (0.112 g, 70%), m.p.168-170 °C ^1H NMR (400 MHz, CDCl_3) δ 8.12 (s, 1H), 7.99 (d, $J = 7.5$ Hz, 1H), 7.91 (d, $J = 7.7$ Hz, 1H), 7.73 – 7.65 (m, 3H), 7.56 (t, $J = 7.4$ Hz, 2H), 7.51 (d, $J = 7.1$ Hz, 1H), 6.97 (d, $J = 7.6$ Hz, 1H), 5.10 (s, 1H), 2.56 – 2.48 (m, 1H), 1.98 – 1.89 (m, 2H), 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 $\text{C}_{28}\text{H}_{27}\text{NO}_4\text{S}$: 472.1583 $[\text{M}+\text{H}]^+$, found: 472.1545.

4''-Methoxy-1'H,2H-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, ^1H 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 calcd for $\text{C}_{23}\text{H}_{22}\text{NO}_5\text{S}$: 424.1038 $[\text{M}+\text{H}]^+$, found: 424.0984.

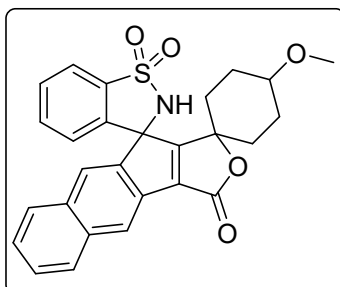
4''-Methoxy-5'-methyl-1'H,2H-dispiro[benzo[d]isothiazole-3,8'-indeno[1,2-c]furan-3',1''-cyclohexan]-1'-one-1,1-dioxide:



White solid (0.119 g, 68%), m.p.245-247 °C. White solid (0.119 g, 68%), m.p.245-247 °C. ^1H 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,

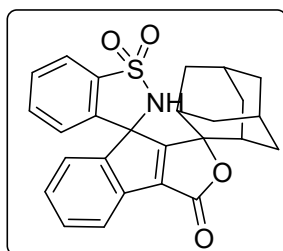
135.2, 134.0, 132.6, 130.7, 129.3, 123.7, 123.4, 122.9, 121.9, 86.9, 69.0, 55.7, 33.4, 33.3, 27.6, 27.5, 21.5. Purity 96.74% by HPLC

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 :



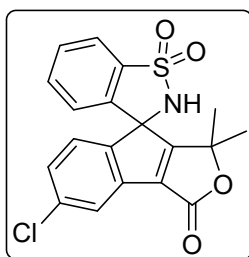
Yellow solid (0.104 g, 65%), m.p. 203-205 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.09 (s, 1H), 7.91 (dd, *J* = 7.1, 7.9 Hz, 2H), 7.70 – 7.61 (m, 3H), 7.57 – 7.46 (m, 3H), 6.89 (d, *J* = 7.9 Hz, 1H), 5.32 (s, 1H), 3.30 (s, 3H), 3.17 – 3.04 (m, 1H), 2.40 (m 1H), 2.08 (d, *J* = 6.2 Hz, 1H), 1.88 (dd, *J* = 8.3, 3.2 Hz, 2H), 1.73 – 1.64 (m, 2H), 0.88 (t, *J* = 7.0 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) 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 C₂₇H₂₅NO₅S: 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:



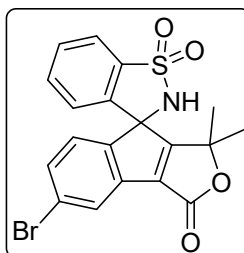
White solid (0.109 g, 60%), m.p.195-197 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.76 – 7.69 (m, 1H), 7.62 (td, *J* = 7.7, 0.9 Hz, 1H), 7.56 – 7.47 (m, 1H), 7.42 – 7.34 (m, 2H), 7.27 (d, *J* = 1.2 Hz, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 4.90 (s, 1H), 2.77 (d, *J* = 4.2 Hz, 1H), 2.39 (dd, *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). ¹³C NMR (126 MHz, CDCl₃) 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 C₂₆H₂₅NO₄S: 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



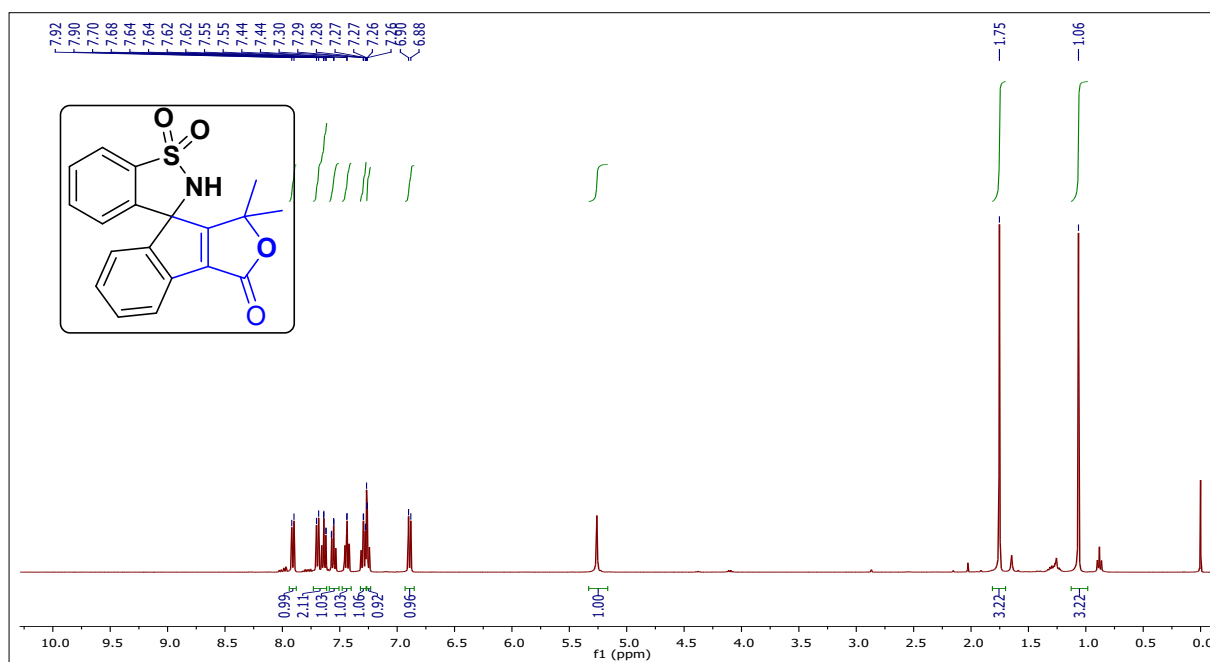
Yellow solid (0.075g, 56%) m.p. 208-210 °C, ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 7.8$ Hz, 1H), 7.70 (d, $J = 1.7$ Hz, 1H), 7.66 (t, $J = 7.5$ Hz, 1H), 7.58 (t, $J = 7.3$ Hz, 1H), 7.28 (d, $J = 1.8$ Hz, 1H), 7.19 (d, $J = 8.1$ Hz, 1H), 6.90 (d, $J = 7.8$ Hz, 1H), 5.24 (s, 1H), 1.76 (s, 3H), 1.07 (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 $\text{C}_{19}\text{H}_{15}\text{NO}_4\text{S}$:388.0434 $[\text{M}+\text{H}]^+$, found: 388.0448. Purity 98.7% by HPLC

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

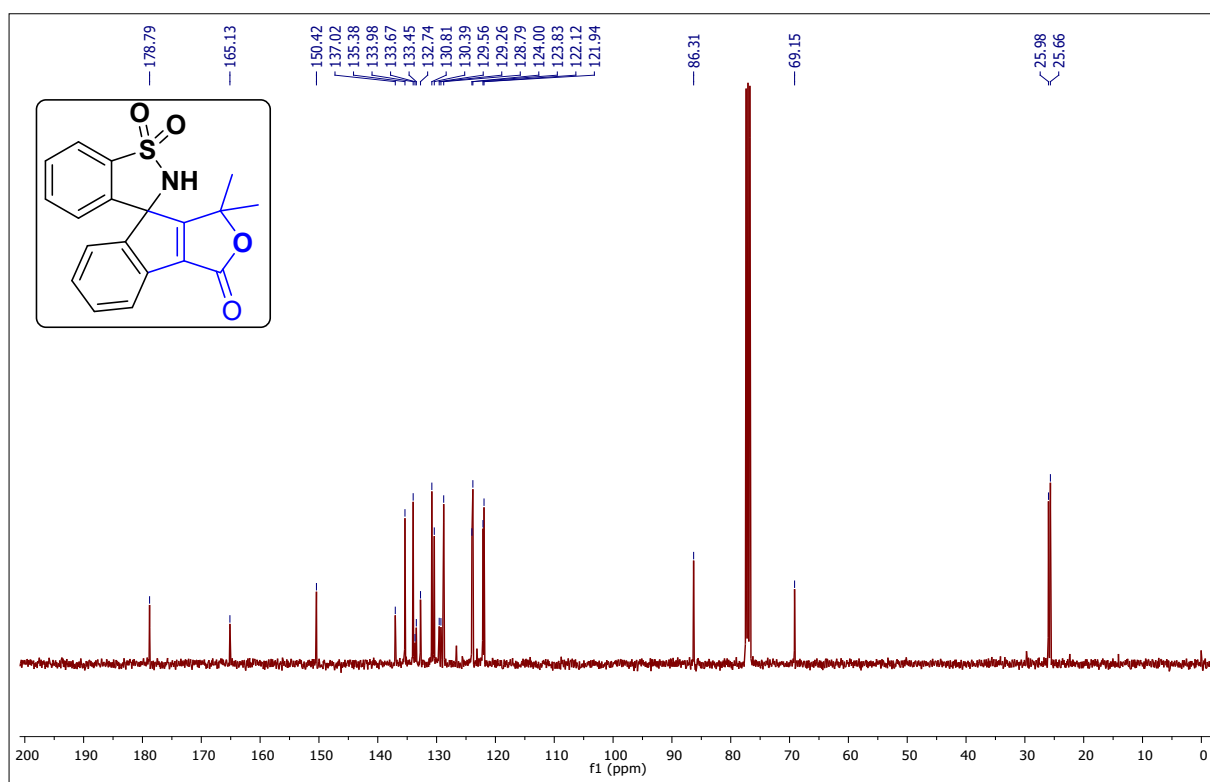


Yellow solid (0.062g, 46%) m.p. 213-215 °C, ^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, $J = 7.7$ Hz, 1H), 7.54 (t, $J = 7.5$ Hz, 1H), 7.48 (d, $J = 6.1$ Hz, 2H), 7.45 (s, 1H), 7.35 (d, $J = 8.1$ Hz, 1H), 6.76 (d, $J = 7.7$ Hz, 1H), 5.34 (s, 1H), 1.77 (s, 3H), 1.74 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 178.7, 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 $\text{C}_{19}\text{H}_{15}\text{NO}_4\text{SBr}$:431.9967 $[\text{M}+\text{H}]^+$, found: 431.9983. Purity 97.36% by HPLC

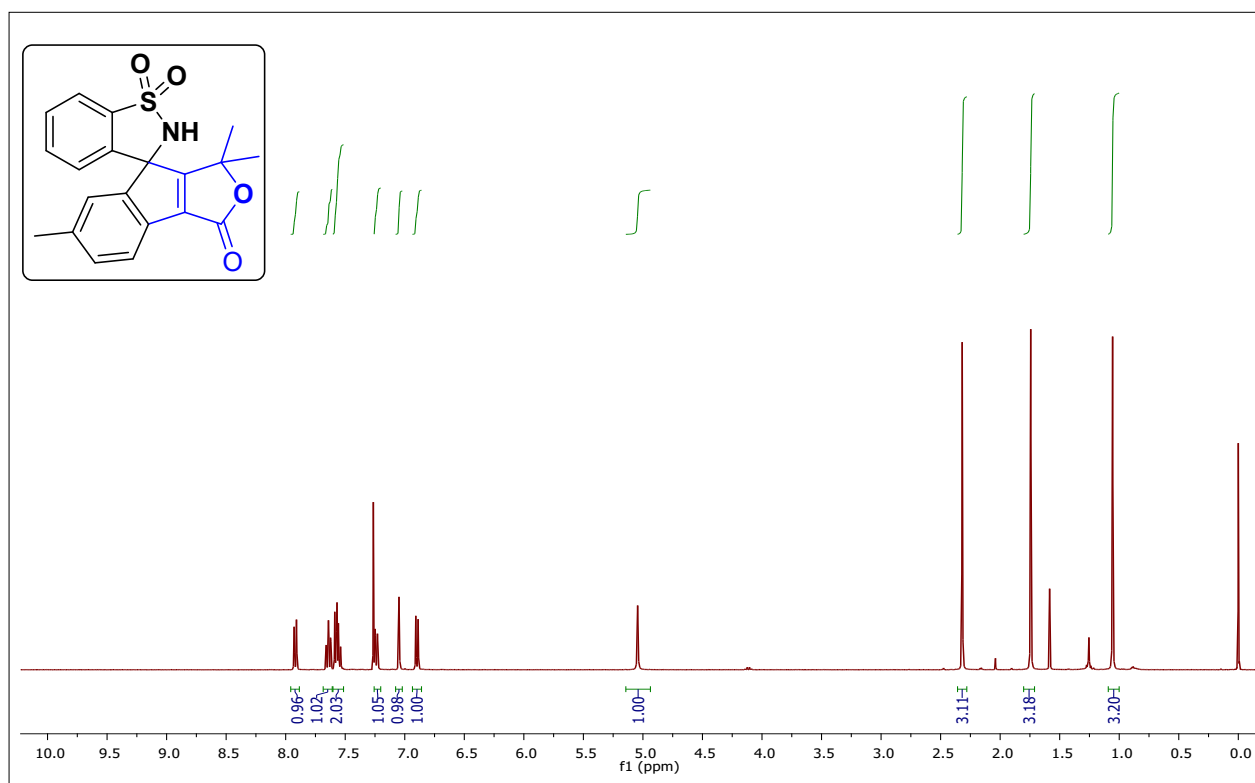
4. NMR spectra of products: ^1H NMR (400MHz, CDCl_3) spectrum of 3a:



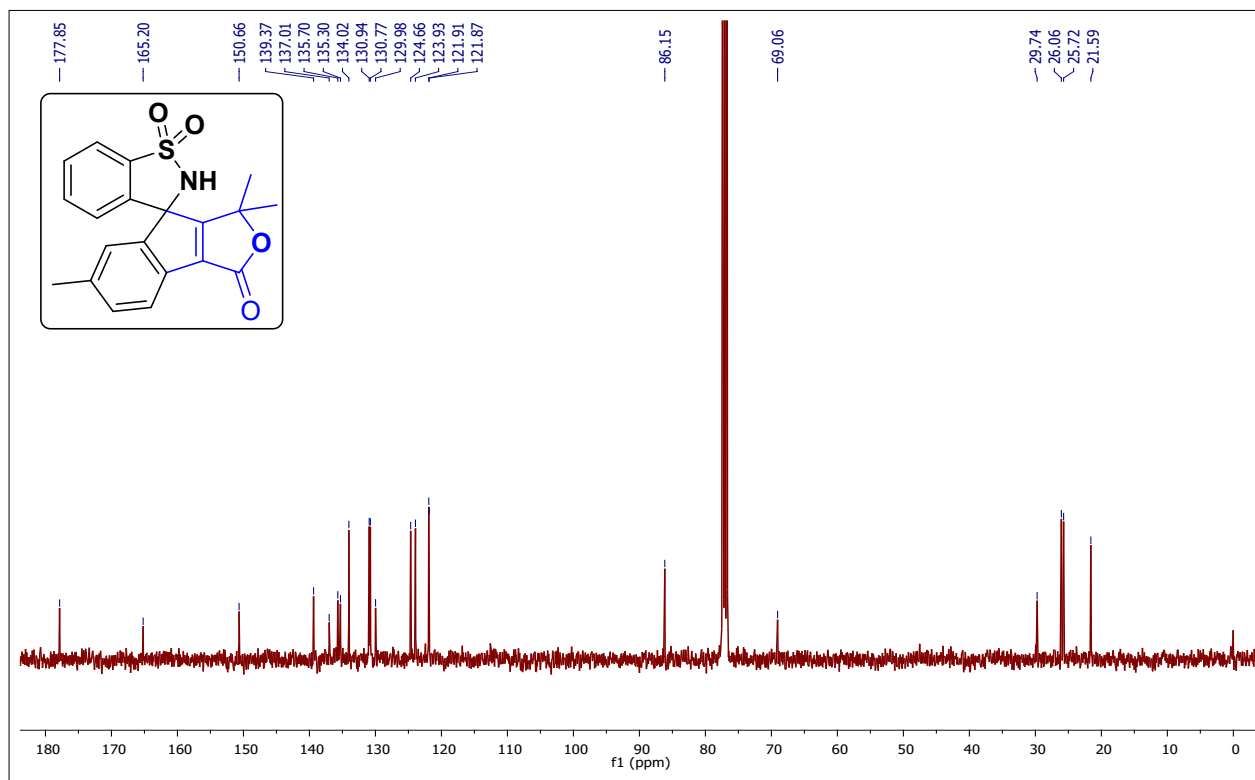
^{13}C NMR (101 MHz, CDCl_3) spectrum of 3a:



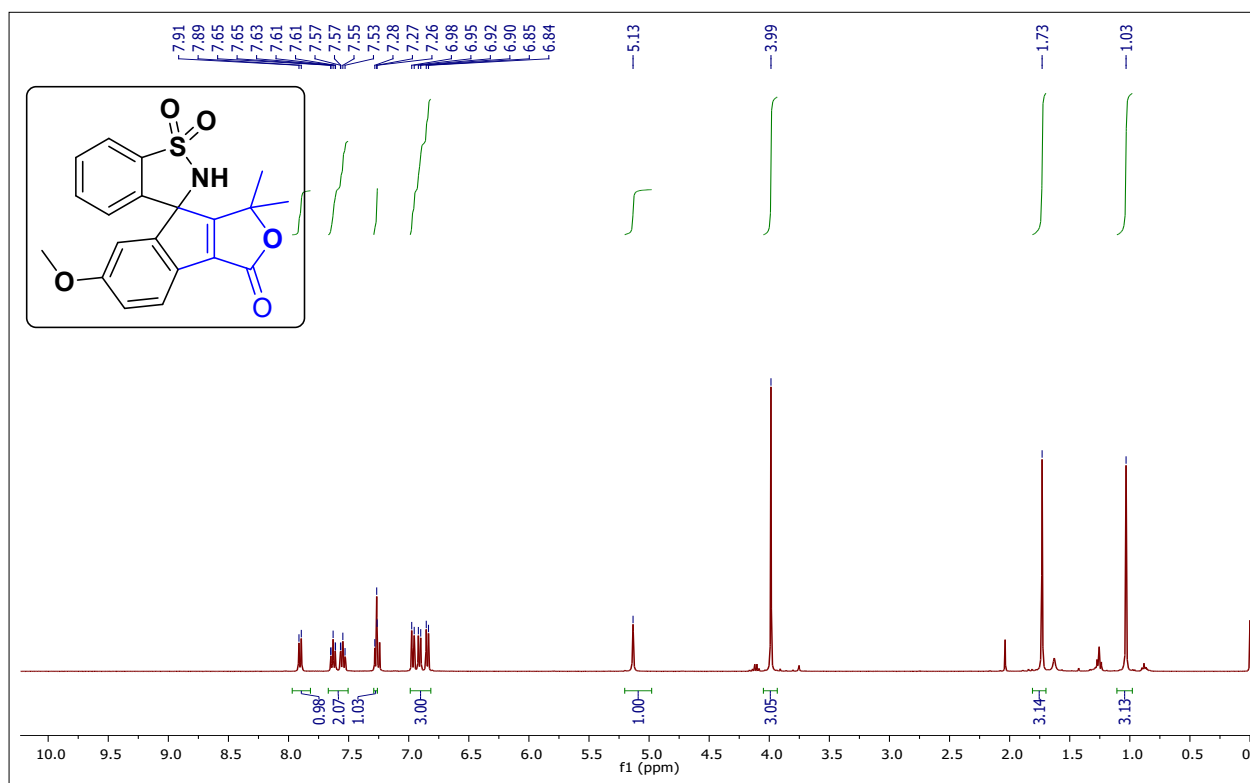
¹H NMR (400MHz, CDCl₃) spectrum of 3b:



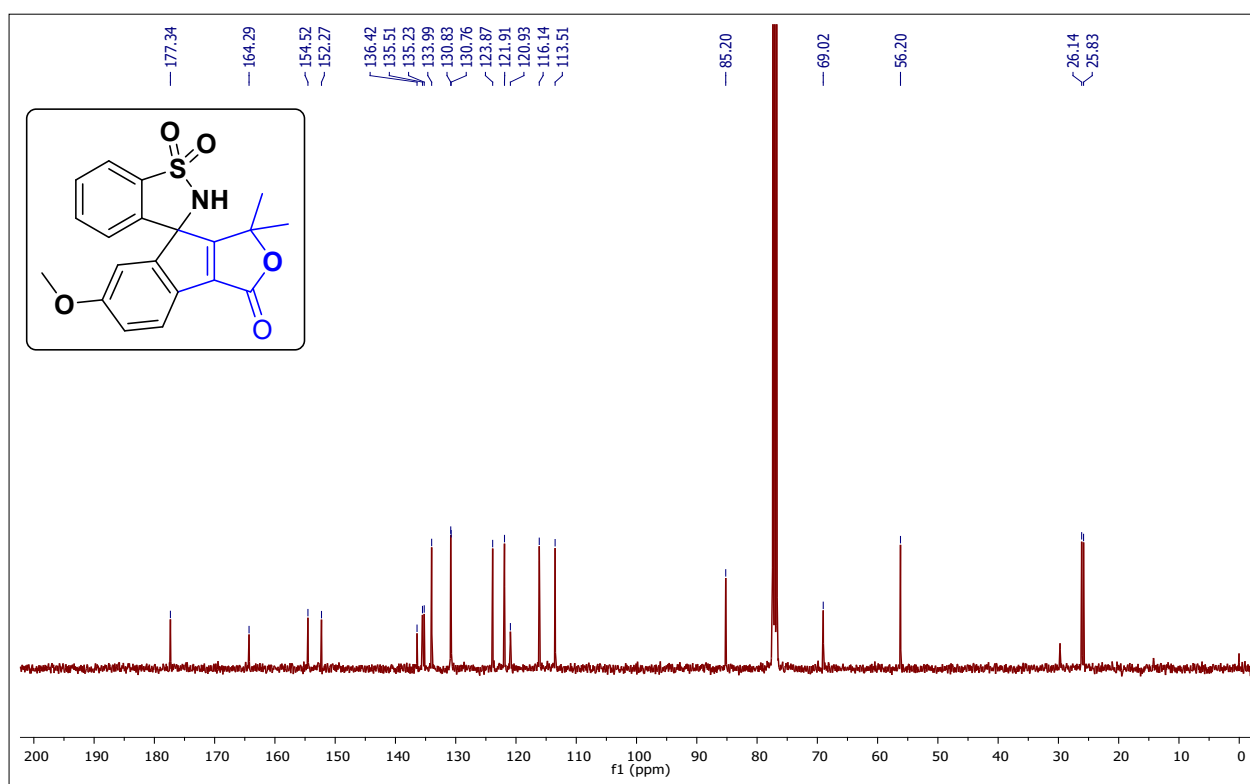
¹³C NMR(101 MHz,CDCl₃) spectrum of 3b:



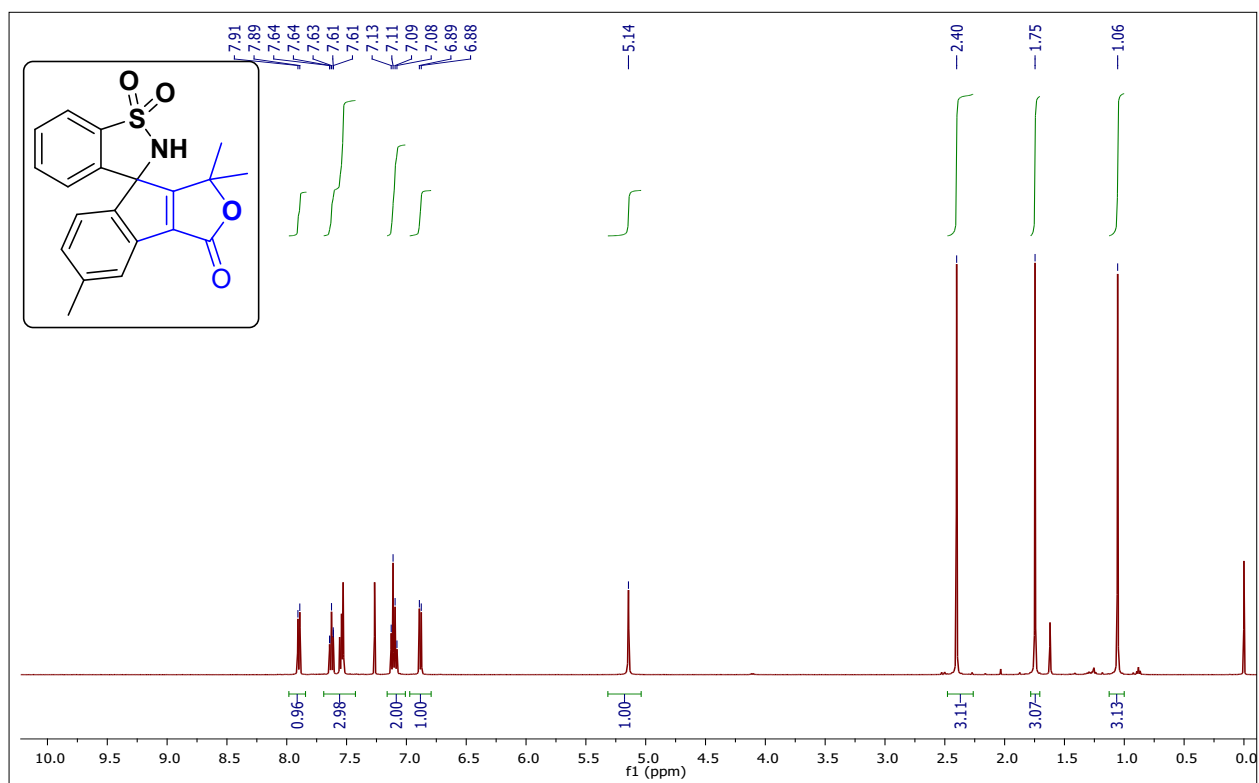
¹H NMR (400MHz, CDCl₃) spectrum of 3c:



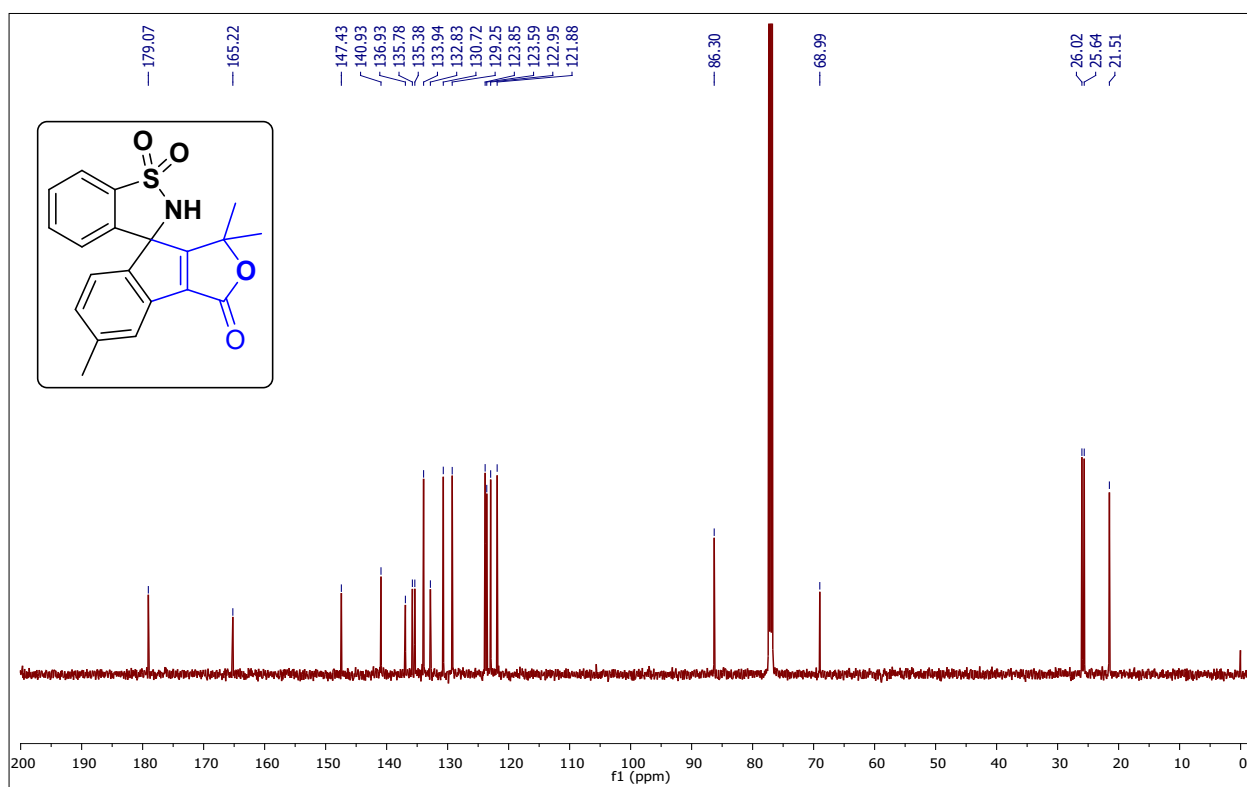
¹³C NMR(101 MHz,CDCl₃) spectrum of 3c:



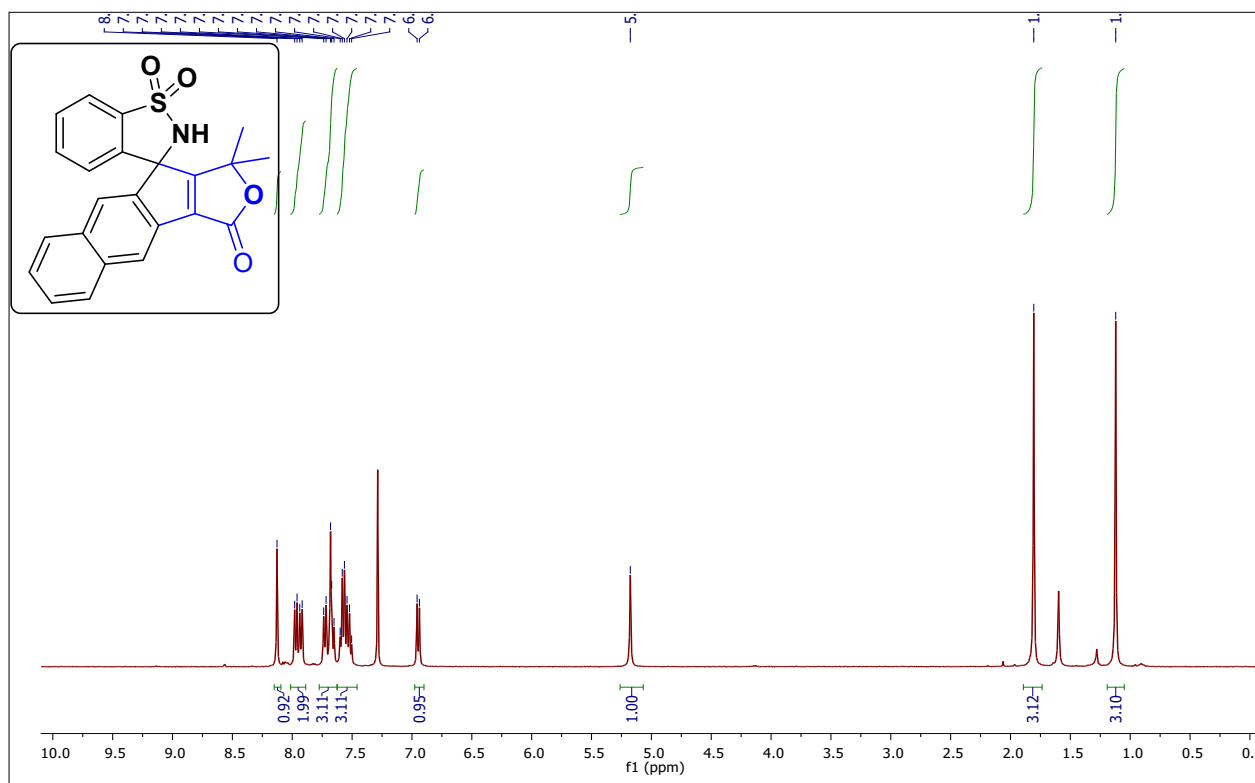
¹H NMR (500MHz, CDCl₃) spectrum of 3d:



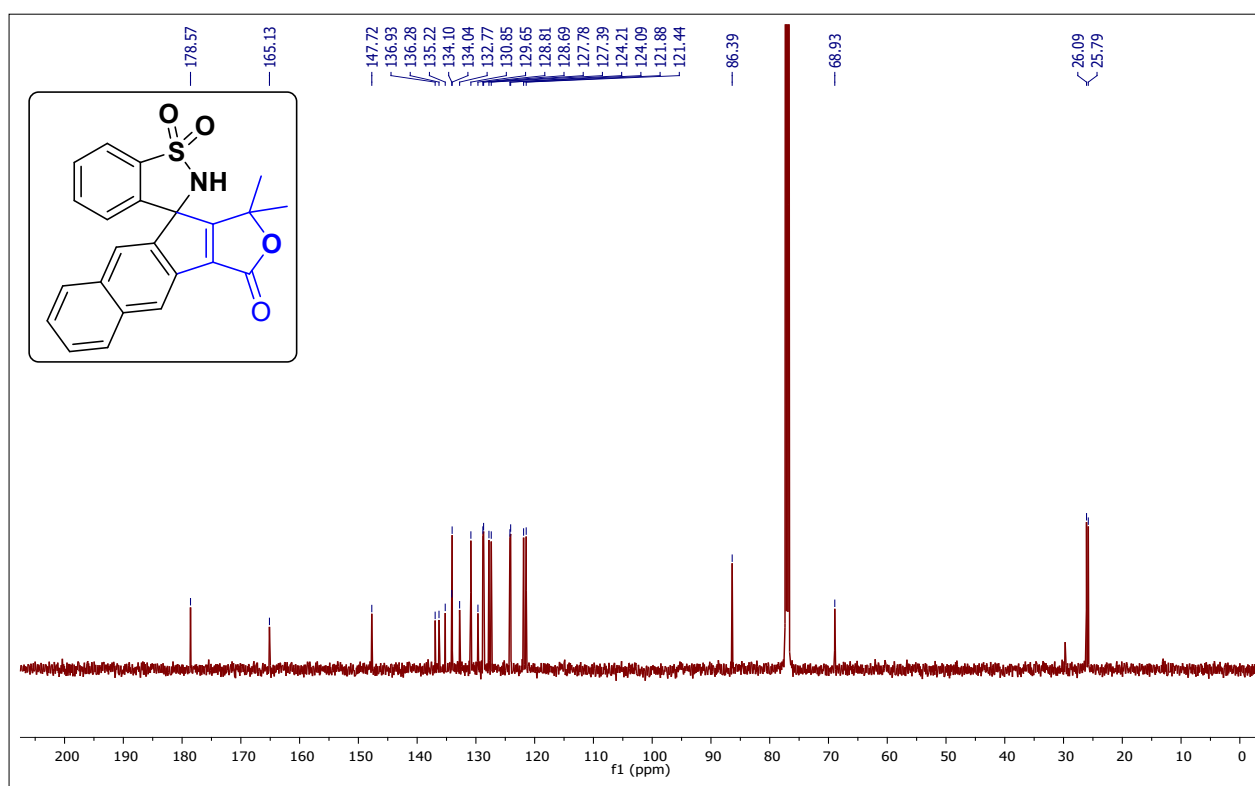
¹³C NMR (126 MHz, CDCl₃) spectrum of 3d:



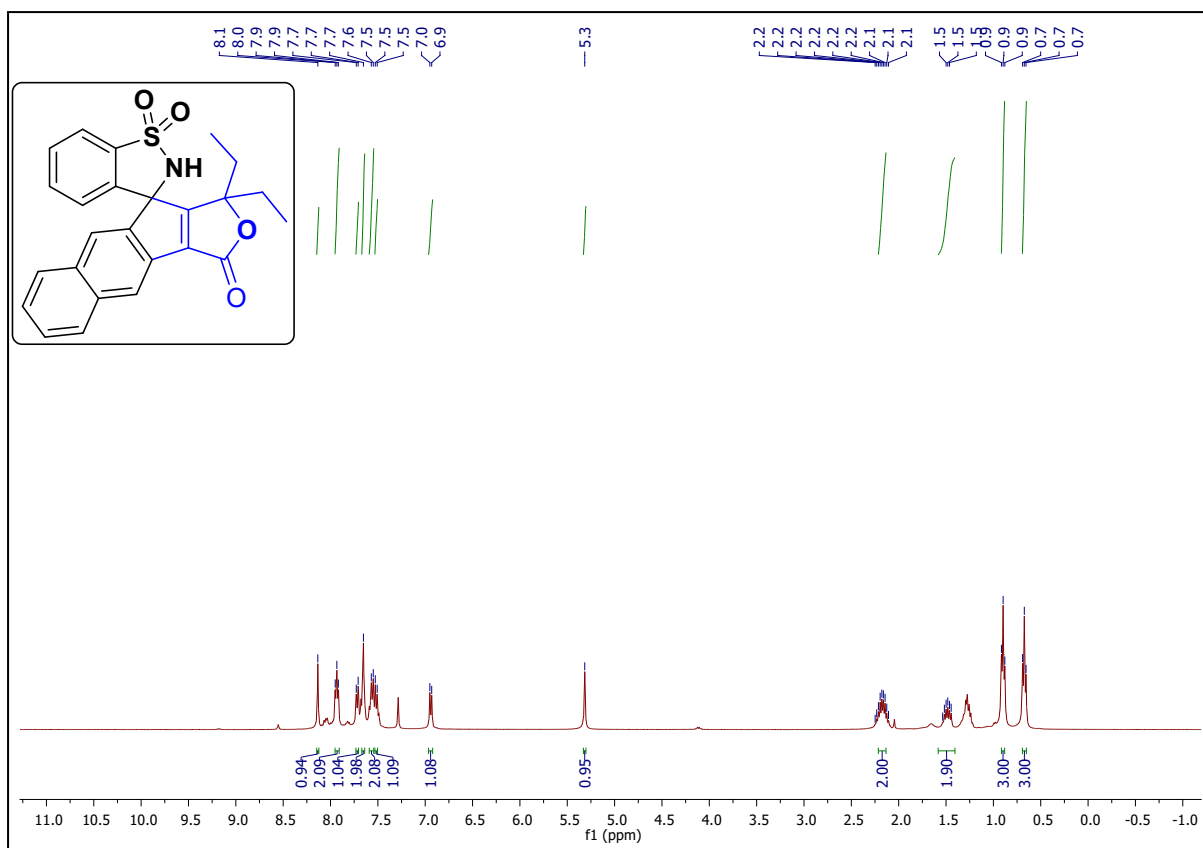
¹H NMR (400MHz, CDCl₃) spectrum of 3e:



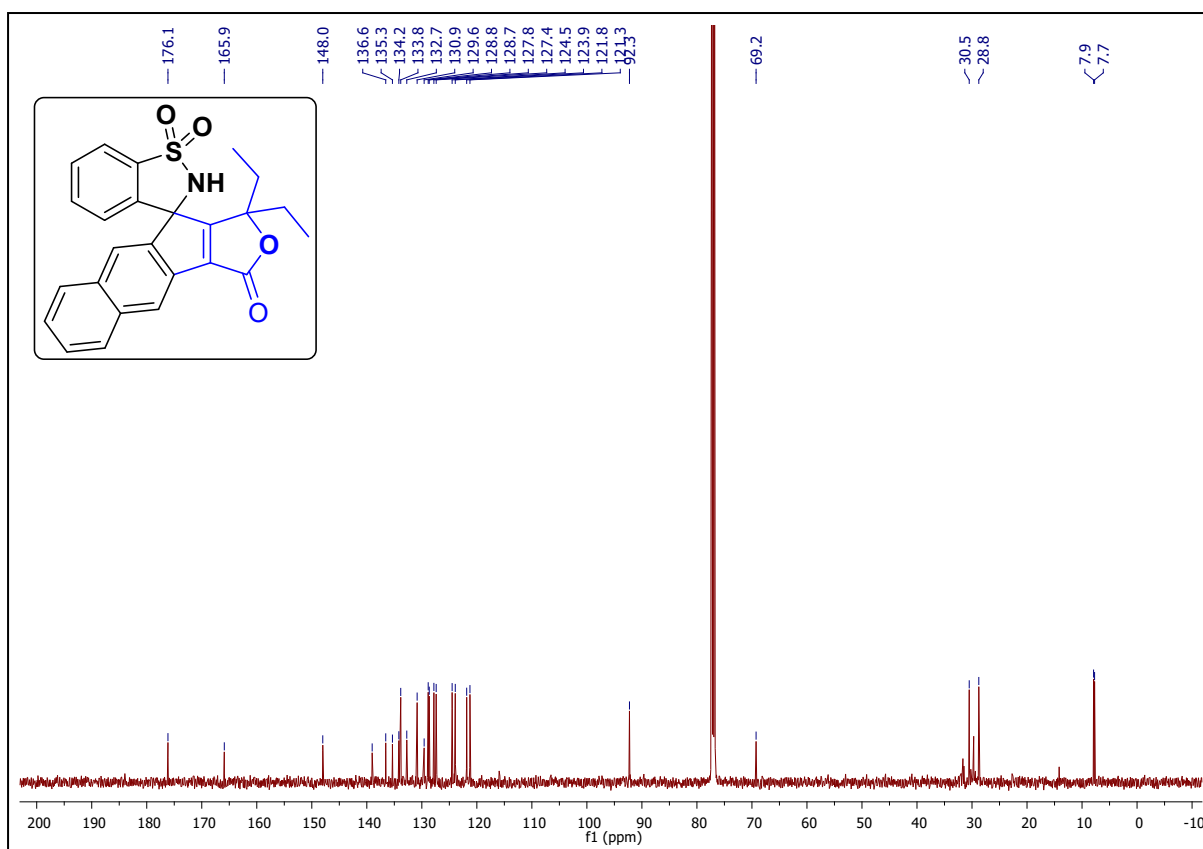
¹³C NMR(101 MHz,CDCl₃) spectrum of 3e:



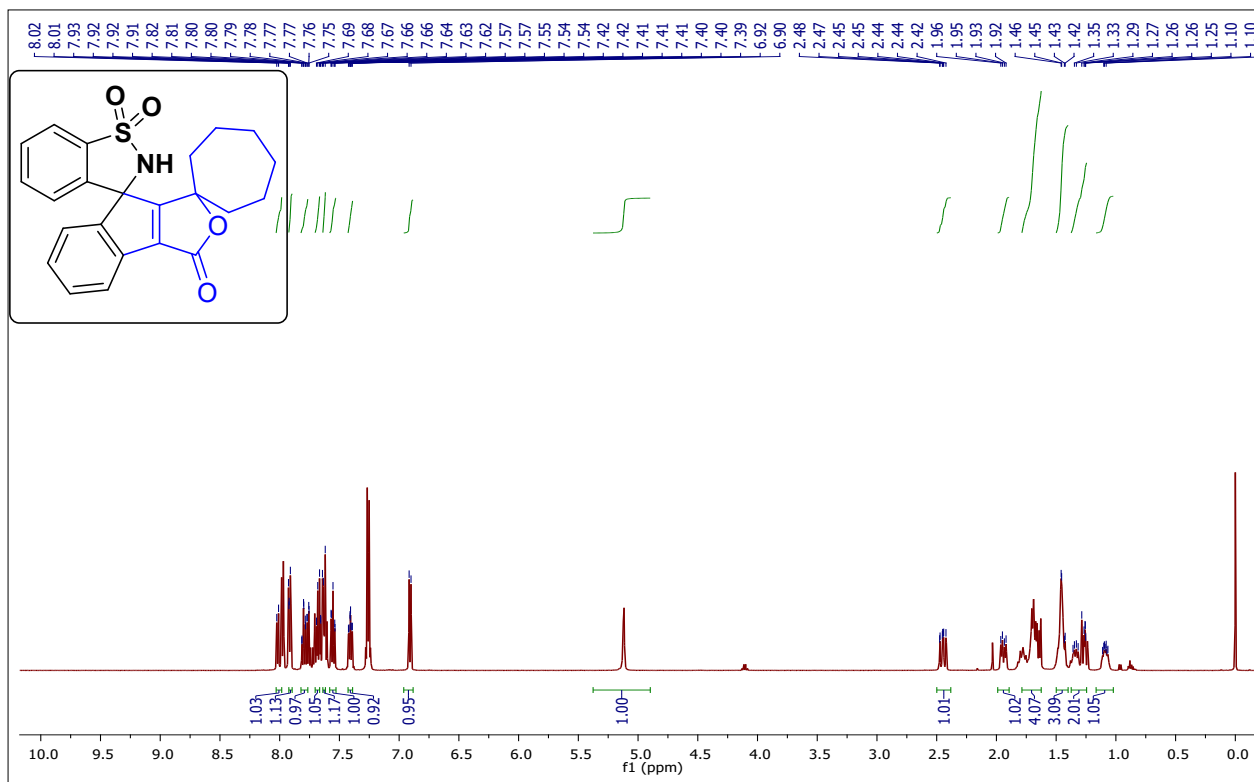
¹H NMR (400MHz, CDCl₃) spectrum of 3f:



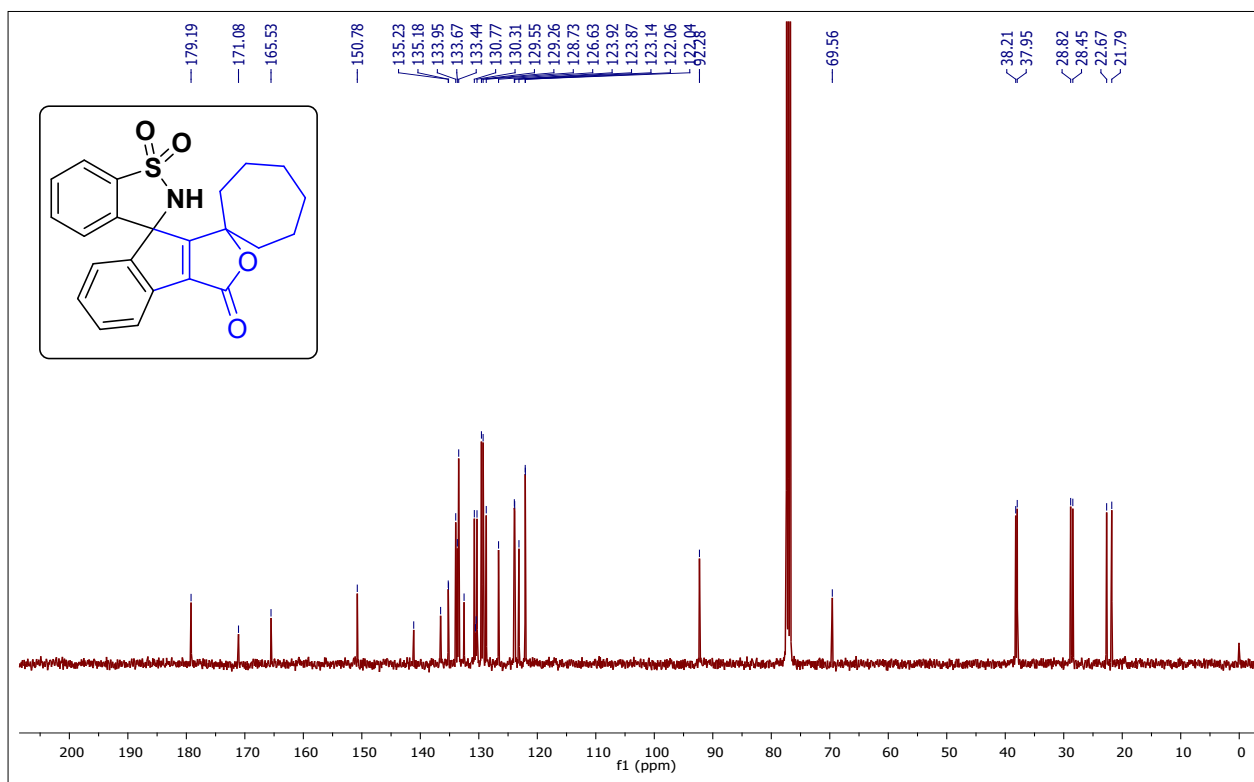
¹³C NMR(101 MHz,CDCl₃) spectrum of 3f:



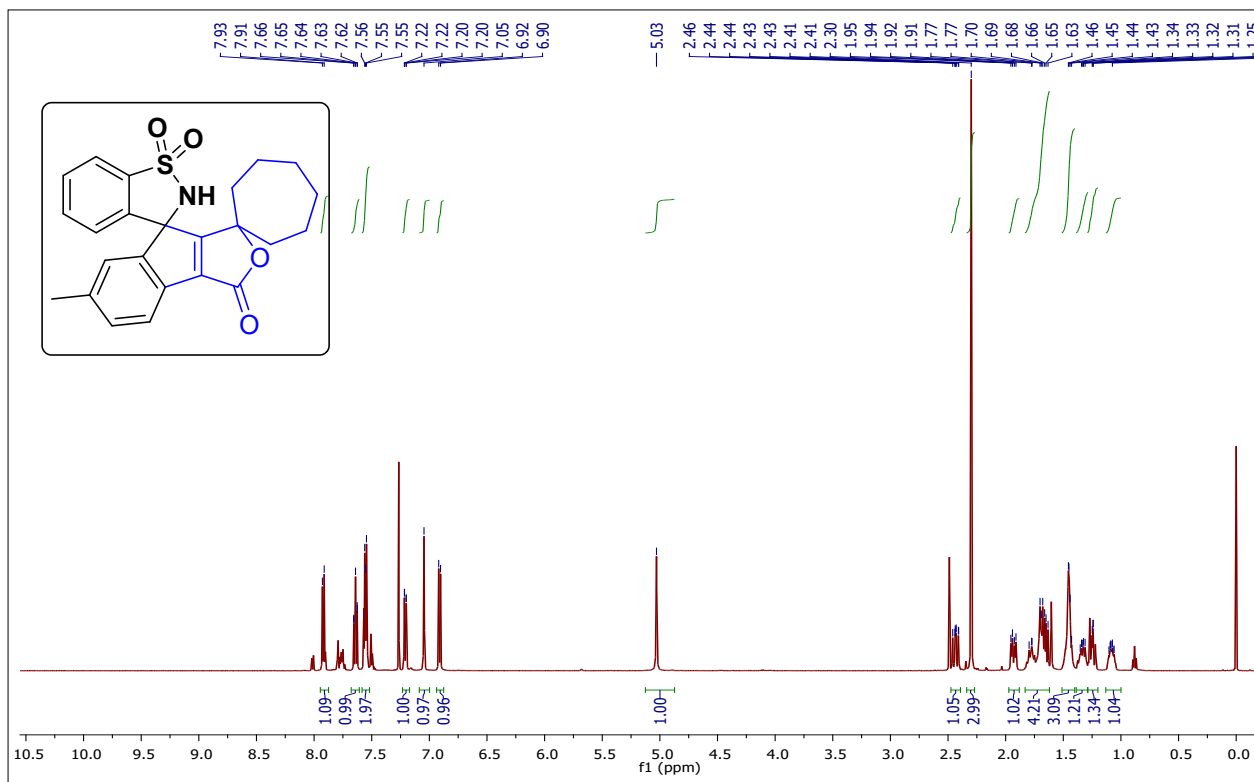
¹H NMR (500MHz, CDCl₃) spectrum of 3g:



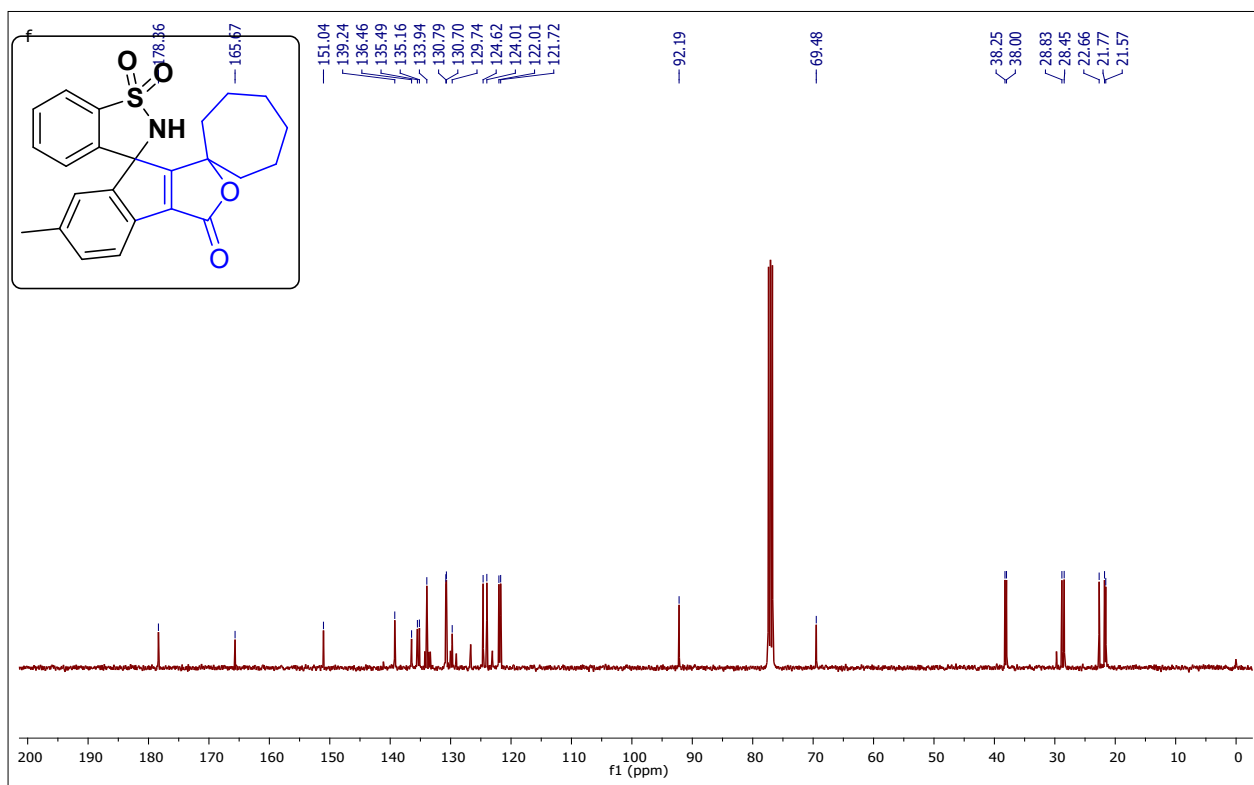
¹³C NMR(126 MHz,CDCl₃) spectrum of 3g:



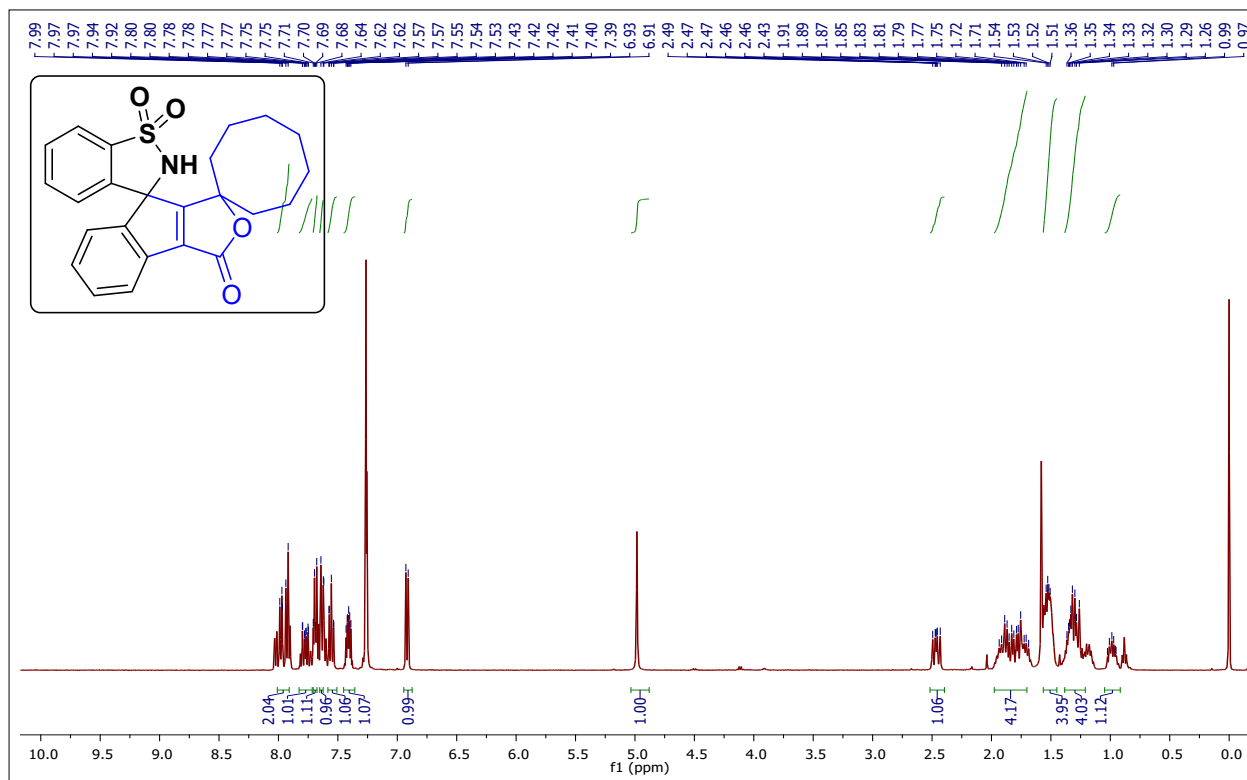
¹H NMR (500MHz, CDCl₃) spectrum of 3h:



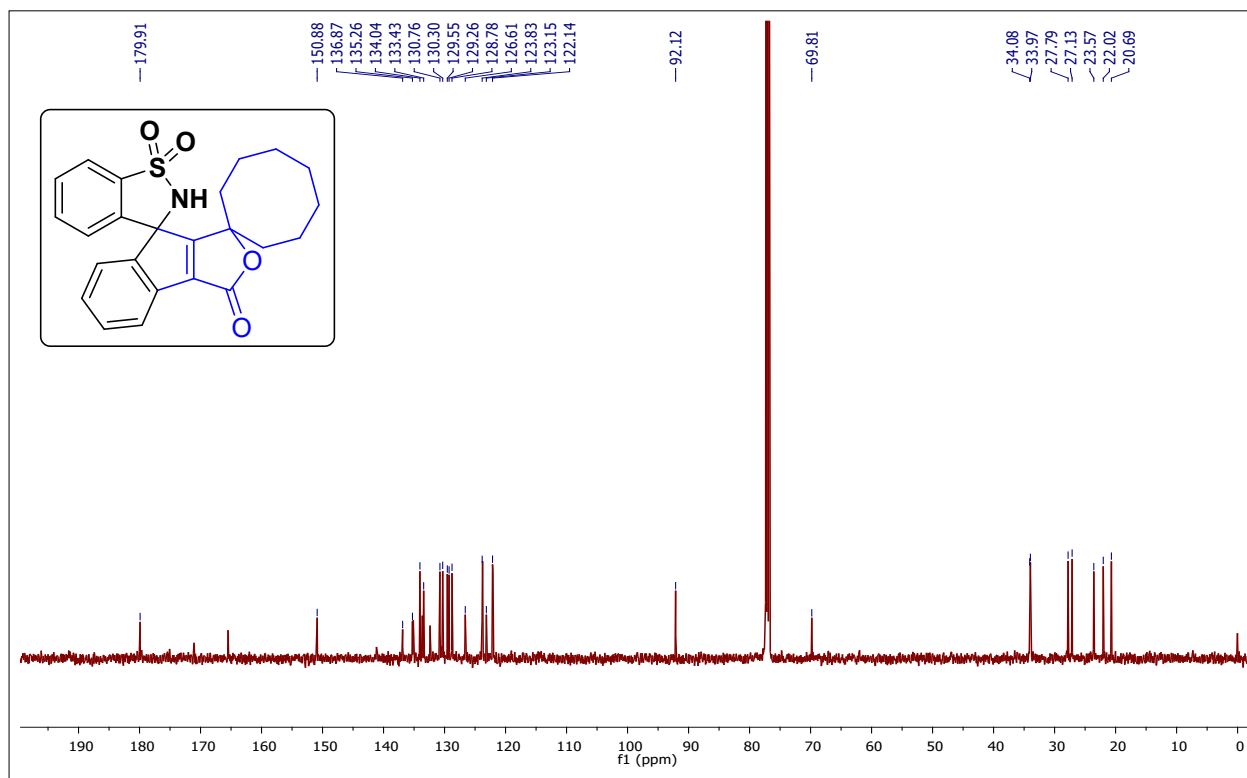
¹³C NMR(126 MHz,CDCl₃) spectrum of 3h:



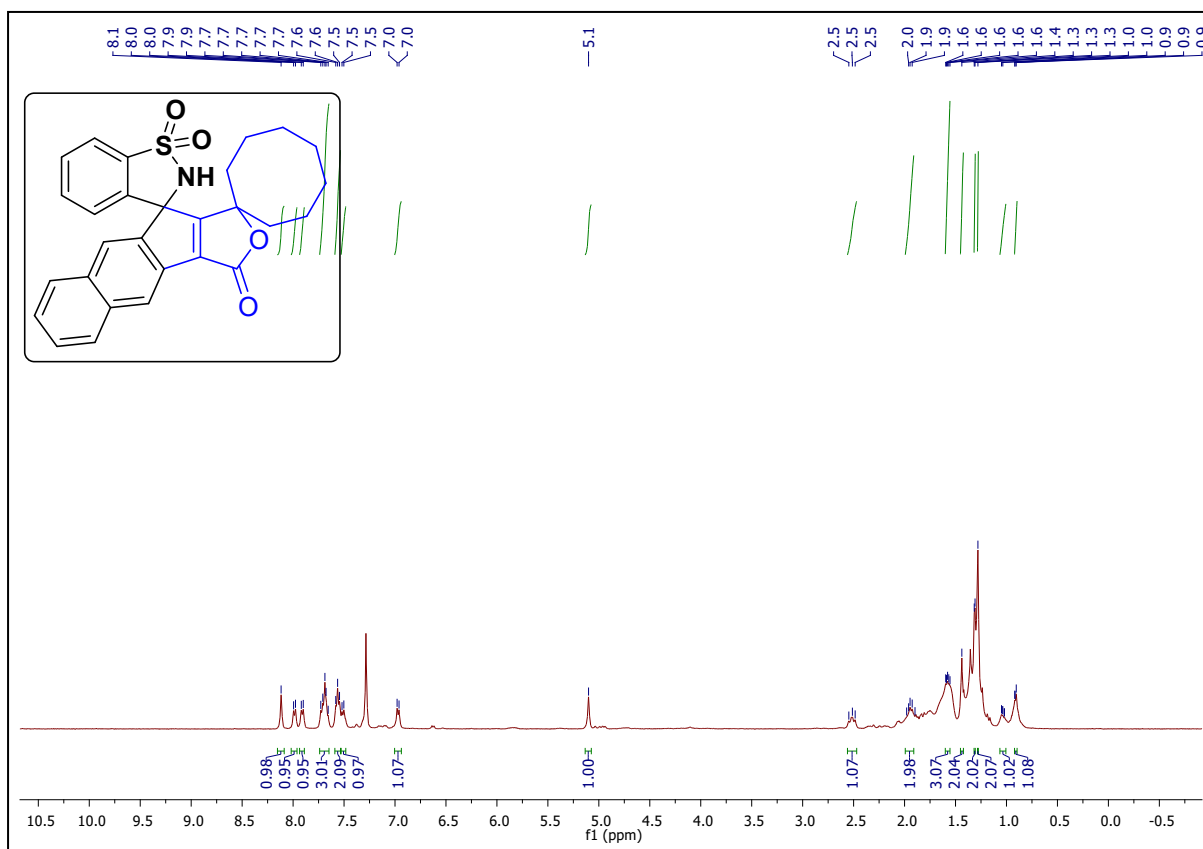
¹H NMR (400MHz, CDCl₃) spectrum of 3i:



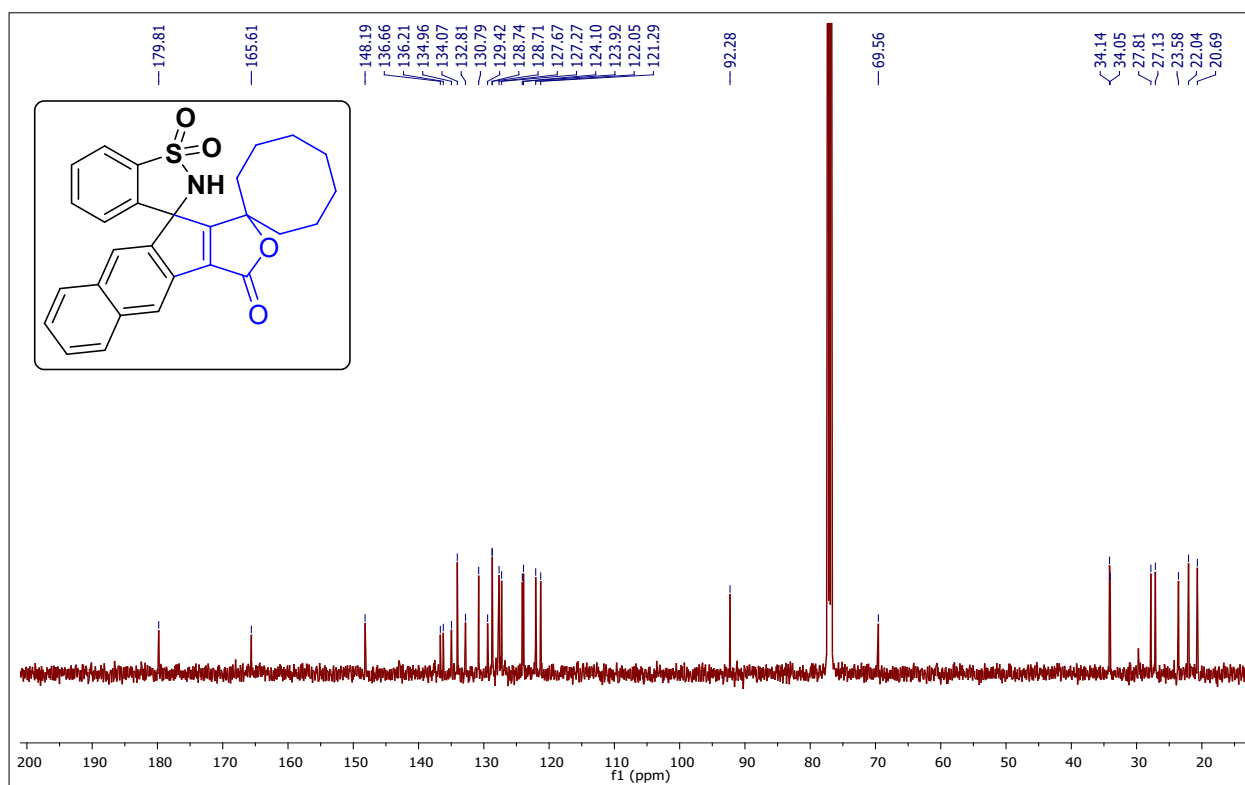
¹³C NMR (101 MHz, CDCl₃) spectrum of 3i:



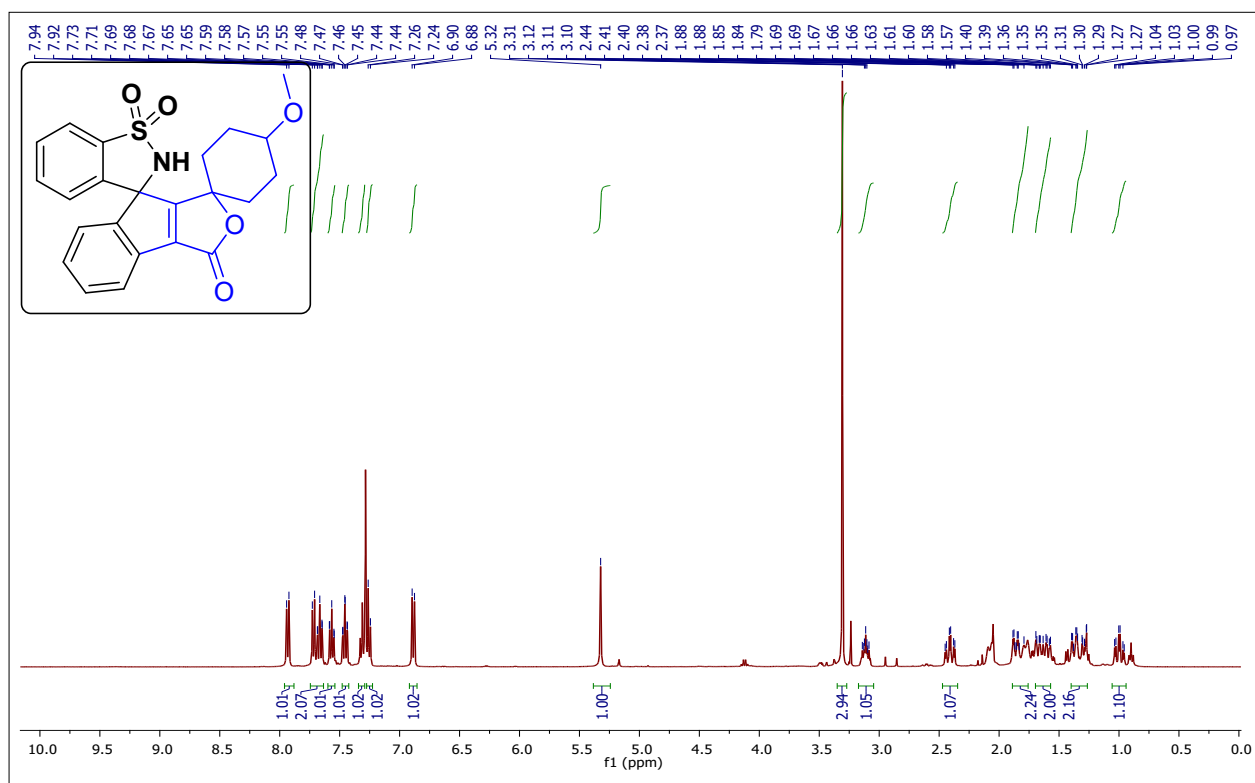
¹H NMR (500MHz, CDCl₃) spectrum of 3j:



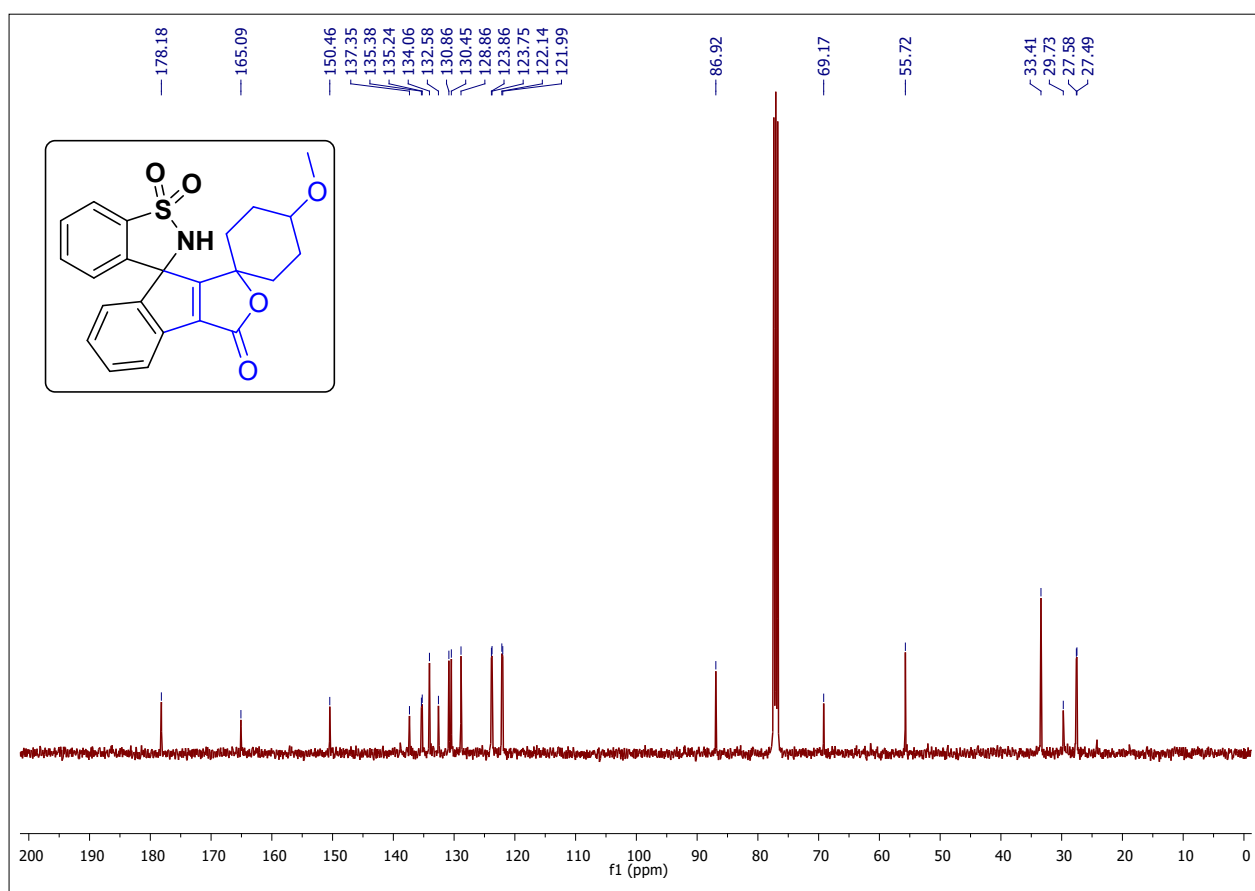
¹³C NMR(126 MHz,CDCl₃) spectrum of 3j:



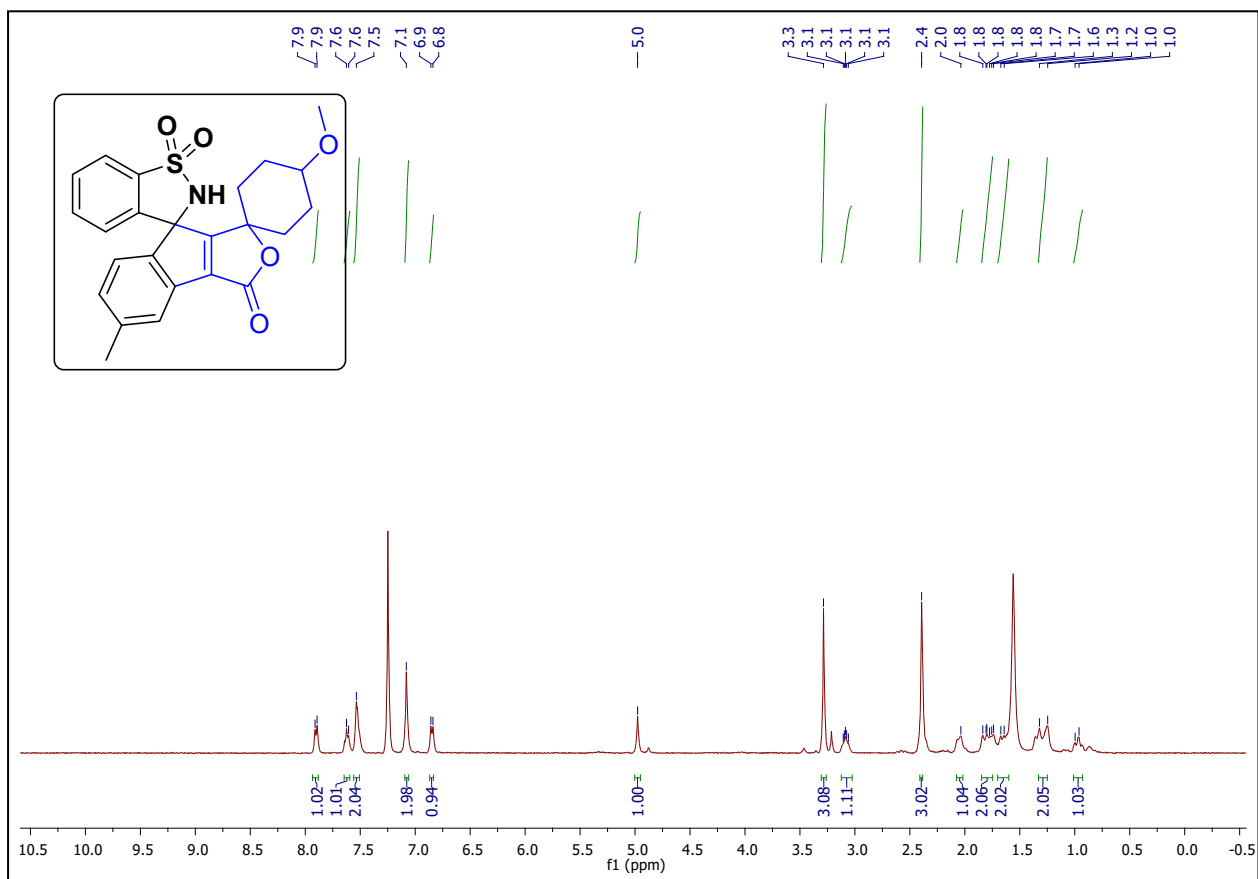
¹H NMR (400MHz, CDCl₃) spectrum of 3k:



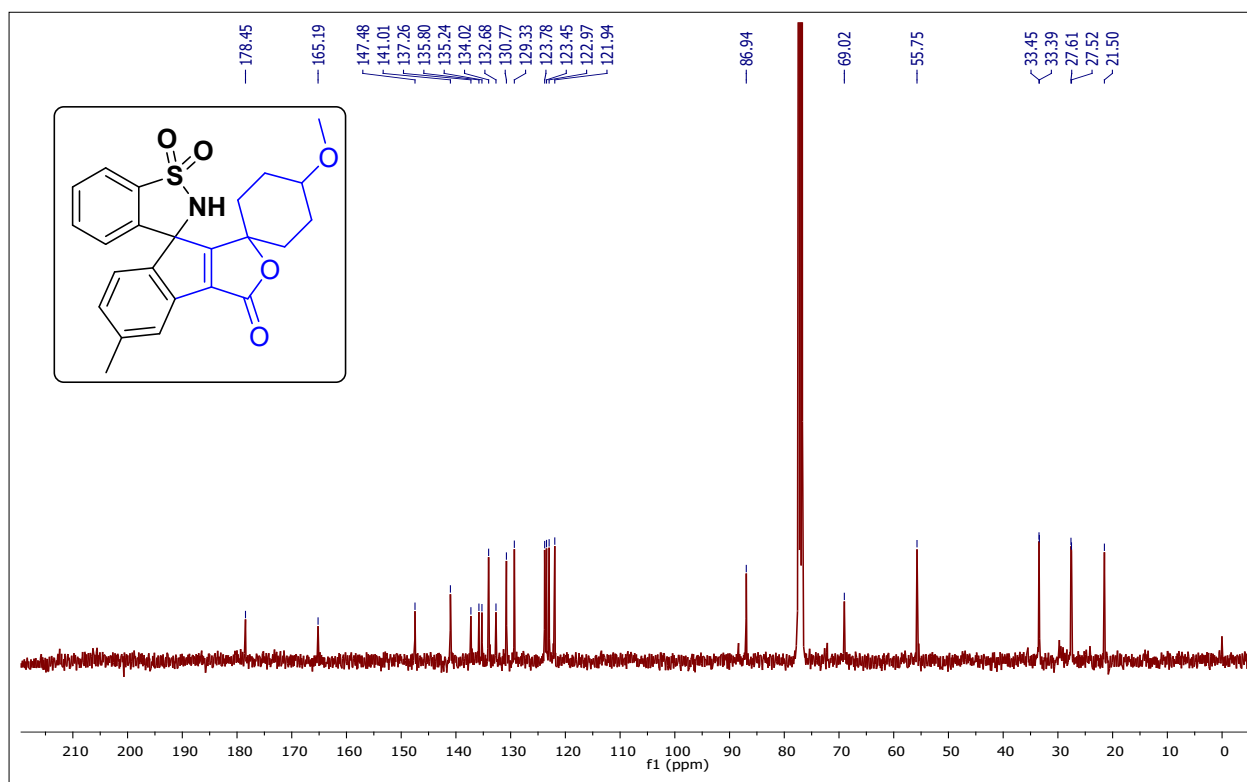
¹³C NMR(101 MHz,CDCl₃) spectrum of 3k:



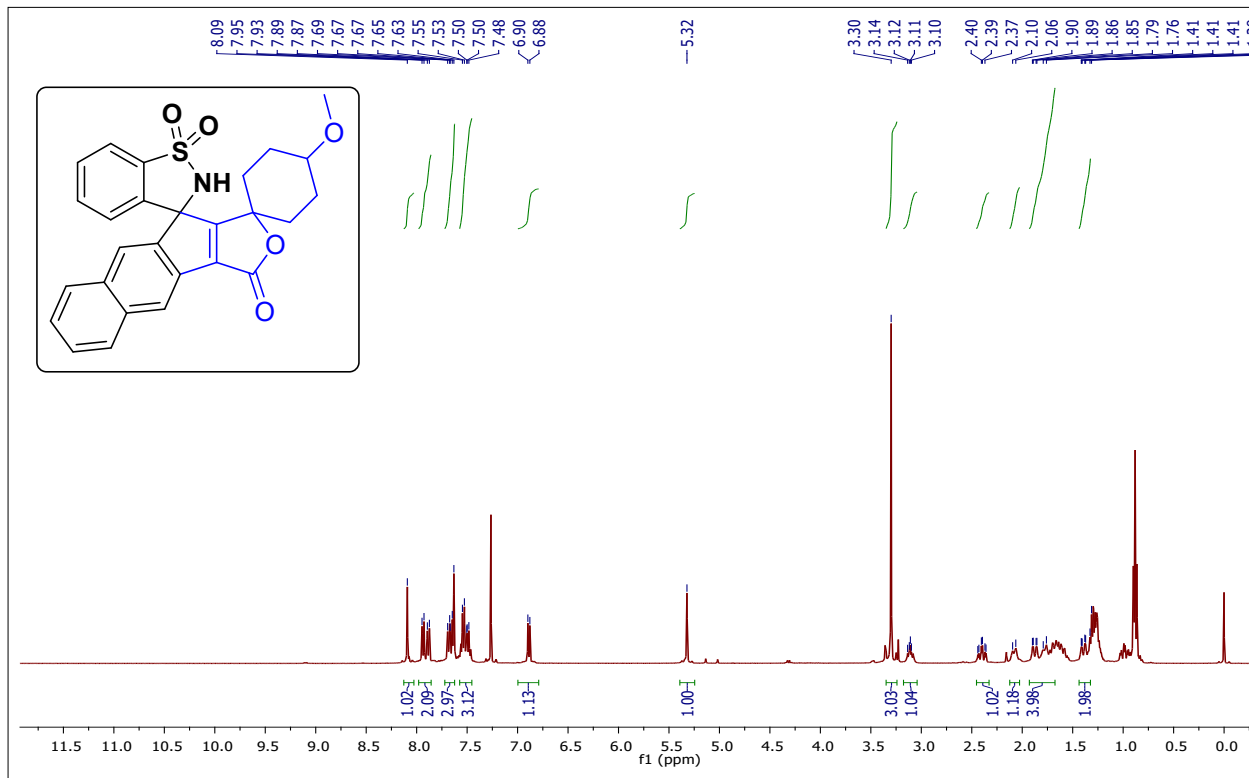
¹H NMR (400MHz, CDCl₃) spectrum of compound 3l:



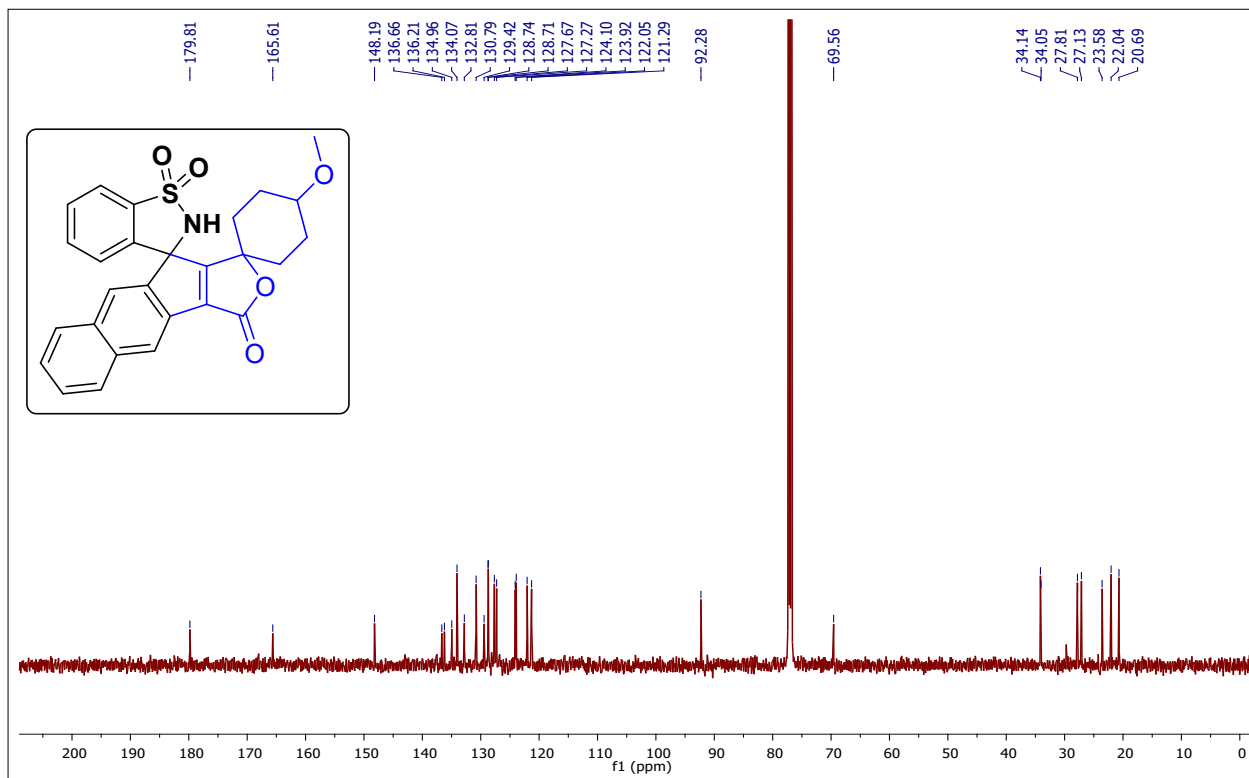
¹³C NMR(101 MHz,CDCl₃) spectrum of compound 3l:



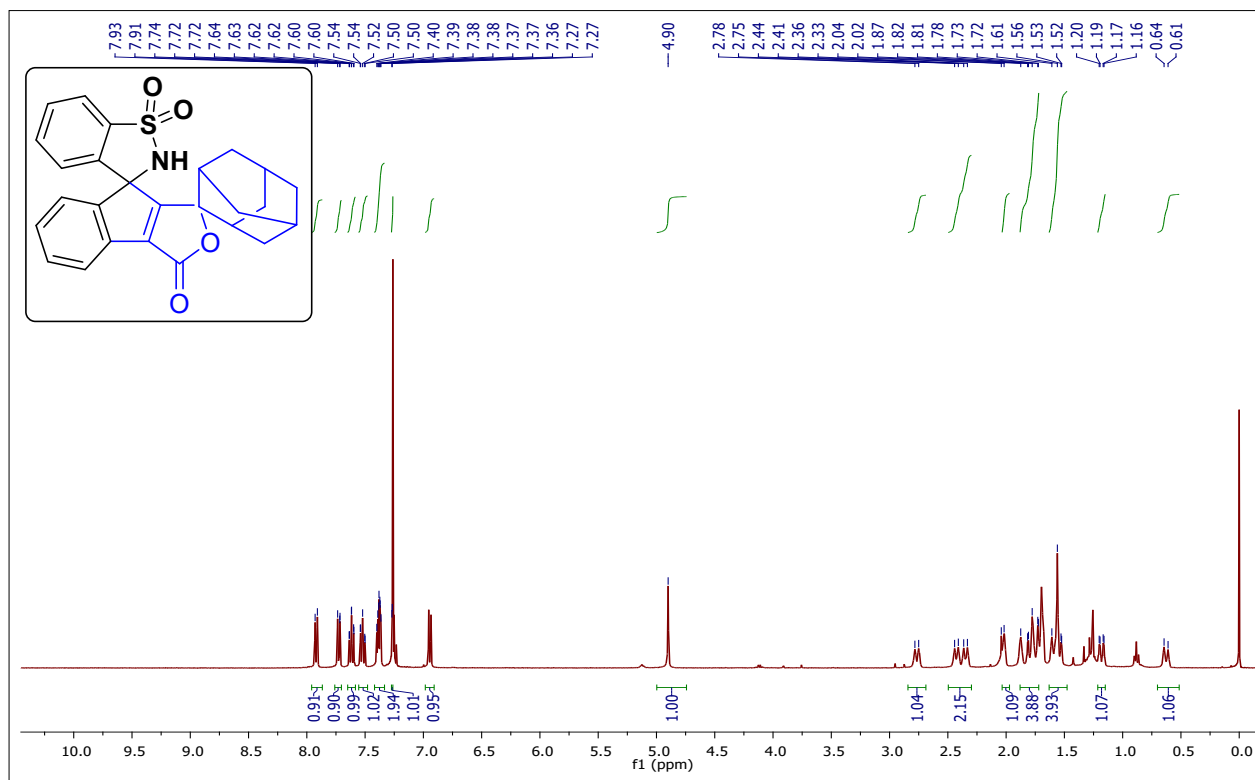
¹H NMR (400MHz, CDCl₃) spectrum of 3m:



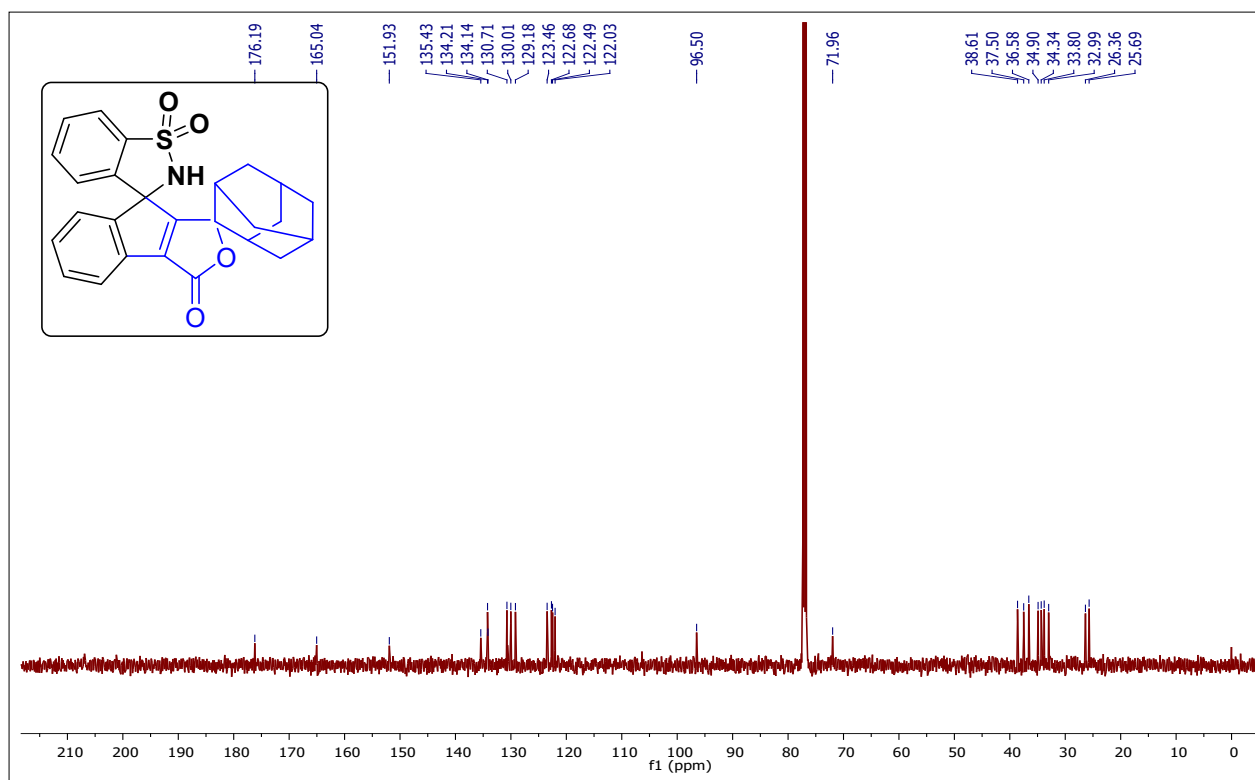
¹³C NMR(101 MHz,CDCl₃) spectrum of 3m:



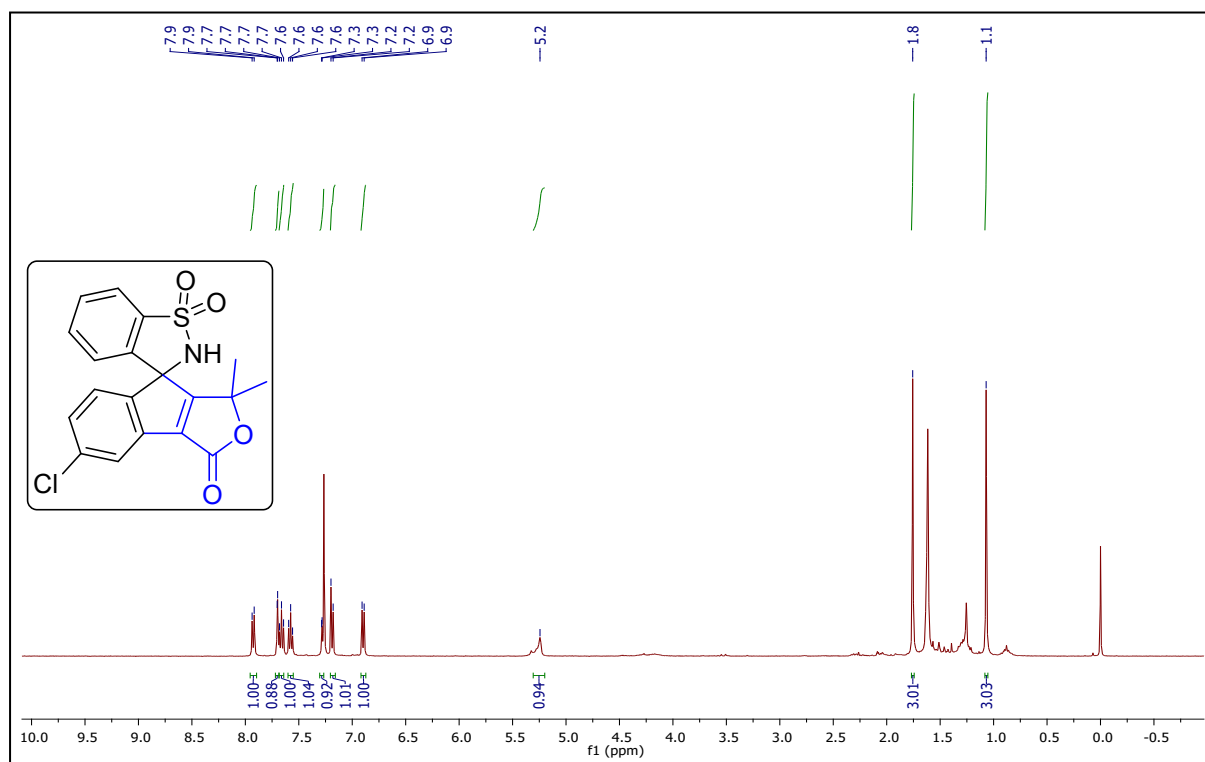
¹H NMR (400MHz, CDCl₃) spectrum of 3n:



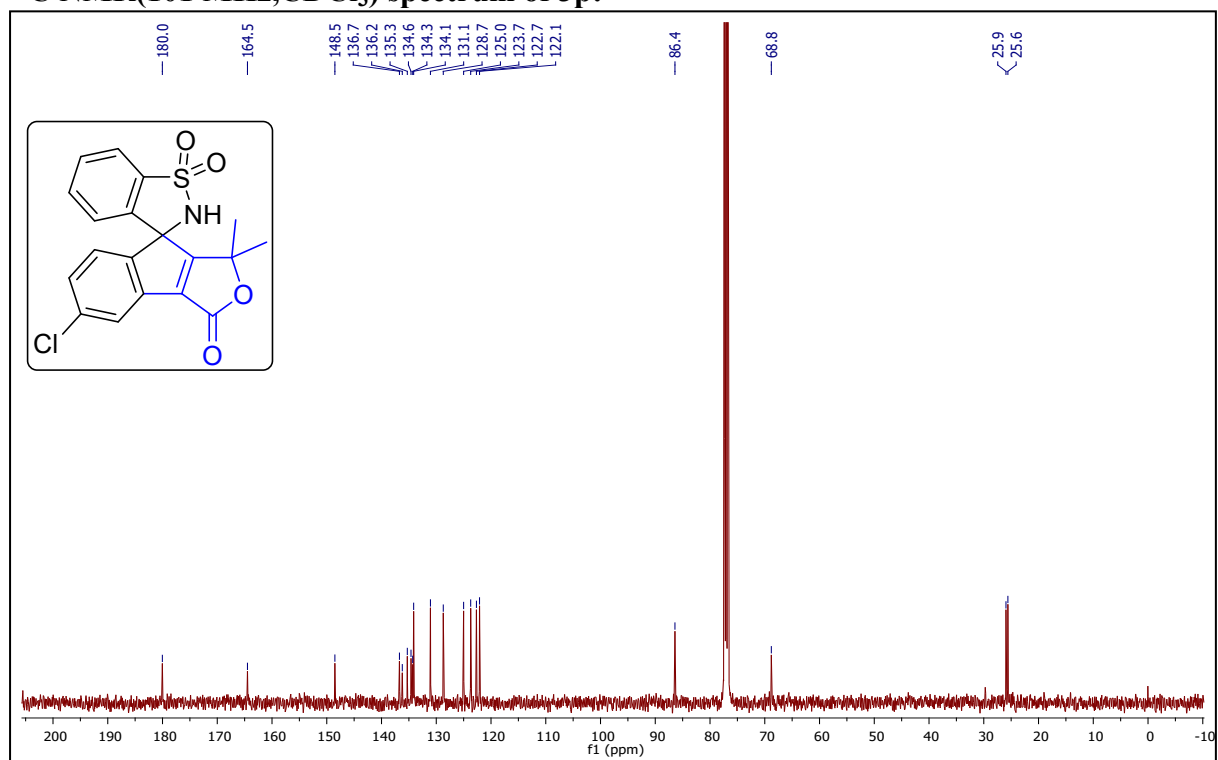
¹³C NMR (101 MHz, CDCl₃) spectrum of 3n:



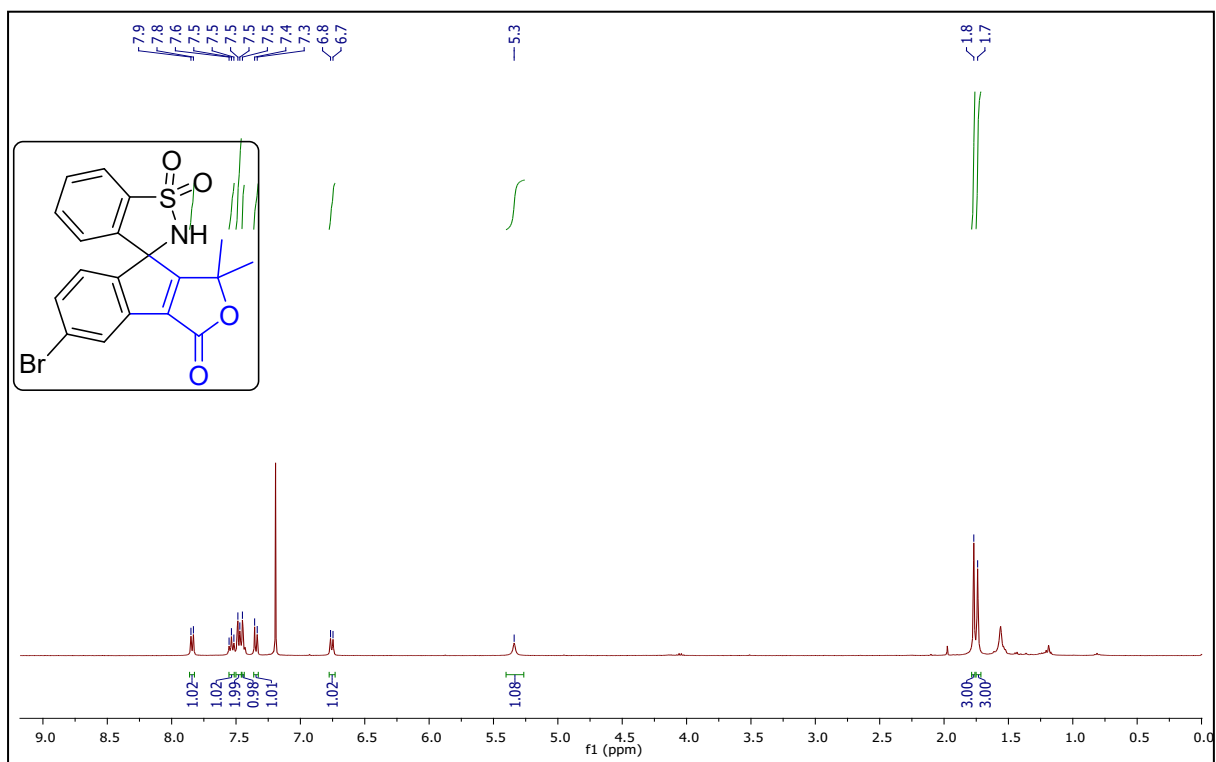
¹H NMR (400MHz, CDCl₃) spectrum of 3p:



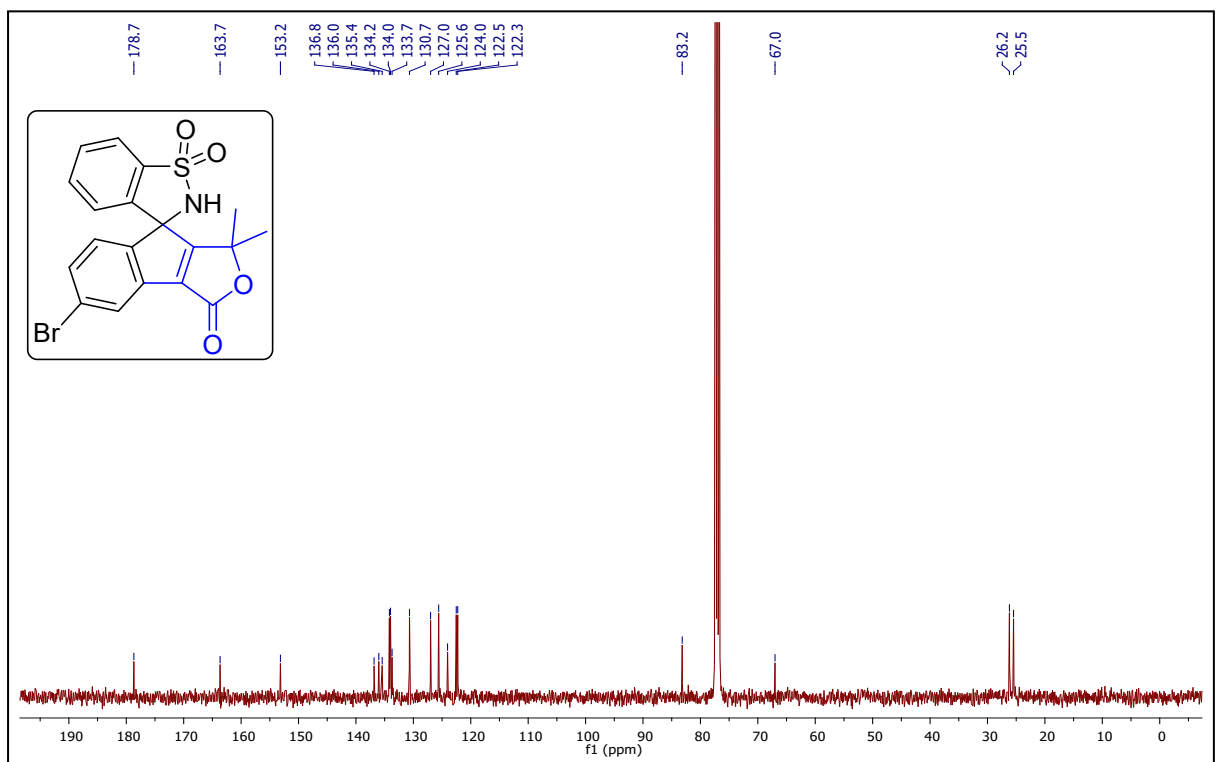
¹³C NMR(101 MHz,CDCl₃) spectrum of 3p:



¹H NMR (400MHz, CDCl₃) spectrum of 3q:



¹³C NMR(101 MHz,CDCl₃) 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 I μ S Mo microsource ($\lambda = 0.7107$ Å) 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 C₂₀H₁₇NO₄S ($M = 367.40$ g/mol): monoclinic, space group P2₁/c (no. 14), $a = 11.908(2)$ Å, $b = 10.3611(19)$ Å, $c = 14.976(2)$ Å, $\beta = 97.885(7)^\circ$, $V = 1830.3(5)$ Å³, $Z = 4$, $T = 294.15$ K, $\mu(\text{MoK}\alpha) = 0.202$ mm⁻¹, $D_{\text{calc}} = 1.333$ g/cm³, 21574 reflections measured ($4.796^\circ \leq 2\theta \leq 61.206^\circ$), 5552 unique ($R_{\text{int}} = 0.0335$, $R_{\text{sigma}} = 0.0354$) which were used in all calculations. The final R_1 was 0.0415 ($I > 2\sigma(I)$) 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.