

Supporting Information

NaI/TBHP-Promoted Reaction of Indole-2-thiones with Arylsulfonyl

Hydrazides: Construction of Achiral Axial

3,3'-Biindole-2,2'-dibenzenesulfonylthioate Derivatives

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1. General Information

All commercially available compounds were used without further purification, unless otherwise noted. Solvents for chromatography were analytical grade and used without further purification. Analytical thin-layer chromatography (TLC) was performed on silica gel, visualized by irradiation with UV light. 200-300 mesh silica gel was used for column chromatography. ^1H and ^{13}C NMR spectra were recorded on BRUKER 400 MHz spectrometer in CDCl_3 . Chemical shifts (δ) were reported according to an internal tetramethylsilane (TMS) standard or the CDCl_3 residual peak (δ 7.26) for ^1H NMR. Chemical shifts of ^{13}C NMR were reported relative to CDCl_3 (δ 77.16). Data were reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (J) are in Hertz (Hz). IR spectra were recorded on a BRUKER VERTEX 70 spectrophotometer and are reported in terms of frequency of absorption (cm^{-1}). HRMS spectra were obtained by using BRUKER micrOTOF-Q III instrument with ESI source.

2. Experimental Section

2.1. Preparation of Starting Materials

Take **3a** as example, indole-2-thione (**1a**) were synthesized according to the published methods with minor modifications.¹

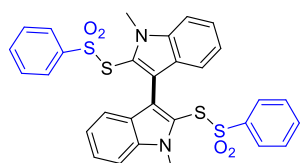
Procedure 1: To a suspension of NaH (0.56 g, 23.3 mmol) in toluene (20 mL) was added 2-oxindole (1.71 g, 10.0 mmol), the resulting mixture was heated at 60 °C oil bath for 30 min. After that, Me₂SO₄ (1.2 mL, 12.0 mmol) was added. After 4 hours, the reaction was quenched with saturated NH₄Cl solution and extracted with ethyl acetate (3×20 mL). The combined organic layers were dried over Na₂SO₄, filtered, concentrated and purified on silica gel chromatography.

Procedure 2: A suspension of P₂S₅ (1.0 g, 2.3 mmol) in THF (25 mL) was allowed to stir for 10 min at room temperature, and then the product of last step was added. The reaction mixture was allowed to stir for 4 hours at room temperature. The reaction mixture was filtered (gravity) and the excess of THF was removed under reduced pressure. Ice-cold water (50 mL) was added to the residue with vigorous stirring to afford a light yellow precipitate that was filtered and air-dried. Sulfonylhydrazide were synthesized according to the published methods with minor modifications.²

2.2. General Procedure for the Synthesis of Products

Take **3a** as example, to a acetonitrile (2 mL) solution of indole-2-thione **1a** (0.2 mmol), sulfonylhydrazide **2a** (0.3 mmol) and NaI (40 mol %) in an oven-dried reactor tube equipped a stir bar was added *tert*-butyl hydroperoxide (70% in aqueous solution, 2.5 equiv.). The reaction mixture was stirred at room temperature for 12 h. The reaction mixture was filtered (gravity) and the solvent was evaporated off and the residue was purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 10:1) to afford Product **3a**.

2.3. Spectra Information of Starting Materials and Products



***S,S'*-(1,1'-dimethyl-1H,1'H-[3,3'-biindole]-2,2'-diyl) dibenzenesulfonylthioate (**3a**)**

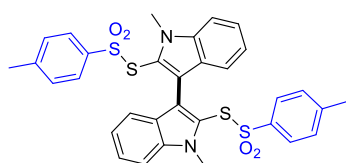
Yellow solid. 0.0532g, 88% total yield, R_f = 0.5 (PE/ EA = 10/1).

¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.33 (m, 4H), 7.15 – 7.11 (m, 6H), 7.03 – 6.99 (m, 2H), 6.79 – 6.74 (m, 2H), 6.65 – 6.59 (m, 4H), 3.91 (s,

6H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 143.5, 139.2, 132.9, 128.0, 126.4, 126.3, 124.9, 122.5, 120.0, 120.0, 118.4, 110.3, 31.3 ppm.

HRMS (ESI) *m/z*: calcd for C₃₀H₂₄N₂NaO₄S₄⁺ [M+Na]⁺ 627.0511, found: 627.0520.

IR (neat, ν): 2926, 1724, 1610, 1447, 1325 cm⁻¹.



***S,S'*-(1,1'-dimethyl-1H,1'H-[3,3'-biindole]-2,2'-diyl) bis(4-methylbenzenesulfonylthioate) (**3b**)**

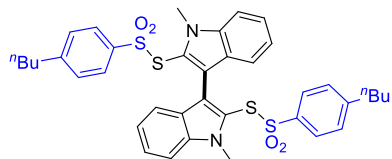
Yellow solid. 0.0499g, 79% total yield, R_f = 0.5 (PE/ EA = 10/1).

¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.34 (m, 4H), 7.12 – 7.09 (m, 2H), 7.04 – 7.01 (m, 2H), 7.00 – 6.97 (m, 4H), 6.45 – 6.40 (m, 4H),

3.94 (s, 6H), 1.94 (s, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 144.2, 140.7, 139.2, 128.8, 126.6, 126.2, 124.8, 122.4, 120.3, 119.9, 118.3, 110.3, 31.3, 21.7 ppm.

HRMS (ESI) m/z : calcd for $C_{32}H_{28}N_2NaO_4S_4^+$ $[M+Na]^+$ 655.0824, found: 655.0829.

IR (neat, ν): 2925, 2360, 1592, 1448, 1326 cm^{-1} .



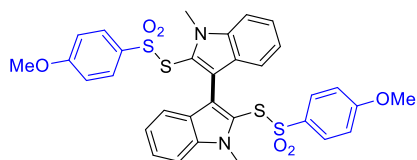
***S,S'*-(1,1'-dimethyl-1H,1'H-[3,3'-biindole]-2,2'-diyl) bis(4-butylbenzenesulfonothioate) (3c)**

Yellow solid. 0.0301g, 42% total yield, $R_f = 0.5$ (PE/EA = 10/1).

1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 4H), 7.21 (s, 2H), 7.09 – 7.00 (m, 6H), 6.49 – 6.39 (m, 4H), 3.90 (s, 6H), 2.27 – 2.16 (m, 4H), 1.32 – 1.23 (m, 5H), 1.22 – 1.17 (m, 3H), 0.87 (t, $J = 7.2$ Hz, 6H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.1, 141.2, 139.2, 128.2, 126.6, 126.5, 124.8, 122.3, 120.6, 120.0, 118.5, 110.3, 35.5, 32.8, 31.3, 22.3, 14.0 ppm.

HRMS (ESI) m/z : calcd for $C_{38}H_{40}N_2NaO_4S_4^+$ $[M+Na]^+$ 739.1763, found: 739.1736.

IR (neat, ν): 2924, 1729, 1591, 1452, 1328 cm^{-1} .



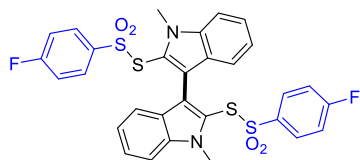
***S,S'*-(1,1'-dimethyl-1H,1'H-[3,3'-biindole]-2,2'-diyl) bis(4-methoxybenzenesulfonothioate) (3d)**

Yellow solid. 0.0498g, 75% total yield, $R_f = 0.4$ (PE/EA = 10/1).

1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 4H), 7.12 – 7.10 (m, 2H), 7.05 – 6.98 (m, 6H), 6.09 – 6.05 (m, 4H), 3.95 (s, 6H), 3.52 (s, 6H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.0, 139.1, 135.2, 128.9, 126.3, 124.7, 122.2, 120.7, 119.8, 118.3, 113.2, 110.2, 55.3, 31.4 ppm.

HRMS (ESI) m/z : calcd for $C_{32}H_{28}N_2NaO_6S_4^+$ $[M+Na]^+$ 687.0722, found: 687.0707.

IR (neat, ν): 2940, 1717, 1589, 1493, 1312 cm^{-1} .



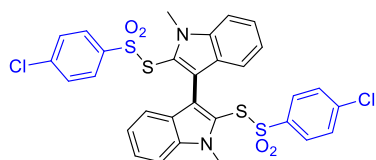
***S,S'*-(1,1'-dimethyl-1H,1'H-[3,3'-biindole]-2,2'-diyl) bis(4-fluorobenzenesulfonothioate) (3e)**

Yellow solid. 0.0179g, 28% total yield, $R_f = 0.5$ (PE/EA = 10/1).

1H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 4H), 7.16 – 7.09 (m, 6H), 7.08 – 7.04 (m, 2H), 6.31 – 6.23 (m, 4H), 3.97 (s, 6H) ppm; **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) $\delta = 164.9$ (d, $J_{C-F} = 256.0$ Hz), 139.4 (d, $J_{C-F} = 3.0$ Hz), 139.2, 129.4 (d, $J_{C-F} = 10.0$ Hz), 126.1, 125.4, 121.2, 120.4, 119.9, 118.3, 115.5 (d, $J_{C-F} = 22.0$ Hz), 110.5, 31.4 ppm.

HRMS (ESI) m/z : calcd for $C_{30}H_{22}F_2N_2NaO_4S_4^+$ $[M+Na]^+$ 663.0323, found: 663.0331.

IR (neat, ν): 2961, 1587, 1488, 1446, 1329 cm^{-1} .



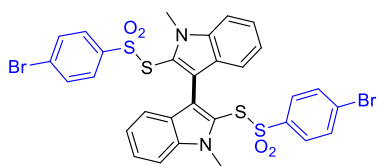
***S,S'*-(1,1'-dimethyl-1H,1'H-[3,3'-biindole]-2,2'-diyl) bis(4-chlorobenzenesulfonothioate) (3f)**

Yellow solid. 0.0436g, 65% total yield, $R_f = 0.5$ (PE/EA = 10/1).

1H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 4H), 7.11 (s, 4H), 7.07 – 6.95 (m, 4H), 6.64 – 6.49 (m, 4H), 3.96 (s, 6H) ppm; **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) δ 142.1, 139.9, 139.2, 128.5, 127.9, 126.2, 125.6, 121.8, 120.7, 119.7, 118.4, 110.7, 31.4 ppm.

HRMS (ESI) m/z : calcd for $C_{30}H_{22}Cl_2N_2NaO_4S_4^+$ $[M+Na]^+$ 694.9732, found: 694.9707.

IR (neat, ν): 2924, 1572, 1446, 1393, 1331 cm^{-1} .



***S,S'*-(1,1'-dimethyl-1H,1'H-[3,3'-biindole]-2,2'-diyl) bis(4-bromobenzenesulfonothioate) (3g)**

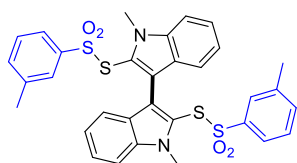
Yellow solid. 0.0464g, 61% total yield, $R_f = 0.5$ (PE/ EA = 10/1).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.46 – 7.41 (m, 4H), 7.14 – 7.11 (m, 4H), 6.99 – 6.95 (m, 4H), 6.76 – 6.72 (m, 4H), 3.95 (s, 6H)

ppm; $^{13}\text{C}\{^1\text{H}\}\text{NMR}$ (100 MHz, CDCl_3) δ 142.8, 139.2, 131.5, 128.6, 127.9, 126.3, 125.7, 121.8, 120.8, 119.7, 118.4, 110.8, 31.4 ppm.

HRMS (ESI) m/z : calcd for $\text{C}_{30}\text{H}_{22}\text{Br}_2\text{N}_2\text{NaO}_4\text{S}_4^+$ $[\text{M}+\text{Na}]^+$ 782.8721, found: 782.8728.

IR (neat, ν): 2927, 1728, 1566, 1448, 1326 cm^{-1} .



***S,S'*-(1,1'-dimethyl-1H,1'H-[3,3'-biindole]-2,2'-diyl) bis(2-methylbenzenesulfonothioate) (3h)**

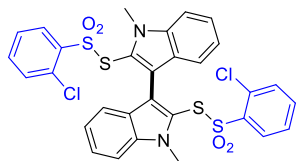
Yellow solid. 0.0525g, 83% total yield, $R_f = 0.5$ (PE/ EA = 10/1).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.35 (s, 4H), 7.12 – 6.93 (m, 6H), 6.92 – 6.80 (m, 2H), 6.63 – 6.37 (m, 4H), 3.96 (s, 6H), 1.87 (s, 6H) ppm;

$^{13}\text{C}\{^1\text{H}\}\text{NMR}$ (100 MHz, CDCl_3) δ 143.0, 139.0, 138.4, 134.0, 127.8, 126.7, 126.2, 124.9, 123.9, 122.3, 120.0, 119.8, 118.5, 110.1, 31.3, 21.0 ppm.

HRMS (ESI) m/z : calcd for $\text{C}_{32}\text{H}_{28}\text{N}_2\text{NaO}_4\text{S}_4^+$ $[\text{M}+\text{Na}]^+$ 655.0824, found: 655.0865.

IR (neat, ν): 2938, 2361, 1452, 1326 cm^{-1} .



***S,S'*-(1,1'-dimethyl-1H,1'H-[3,3'-biindole]-2,2'-diyl) bis(2-chlorobenzenesulfonothioate) (3i)**

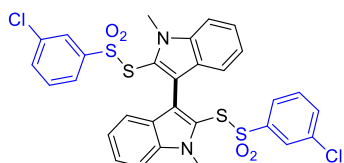
Yellow solid. 0.0262g, 39% total yield, $R_f = 0.5$ (PE/ EA = 10/1).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36 – 7.32 (m, 2H), 7.31 – 7.26 (m, 2H), 7.19 – 7.14 (m, 2H), 6.89 – 6.84 (m, 4H), 6.55 – 6.48 (m, 4H), 6.47 –

6.42 (m, 2H), 4.04 (s, 6H) ppm; $^{13}\text{C}\{^1\text{H}\}\text{NMR}$ (100 MHz, CDCl_3) δ 139.1, 138.8, 133.5, 130.8, 130.7, 130.4, 126.3, 125.7, 124.9, 122.6, 119.7, 119.5, 118.3, 110.2, 31.3 ppm.

HRMS (ESI) m/z : calcd for $\text{C}_{30}\text{H}_{22}\text{Cl}_2\text{N}_2\text{NaO}_4\text{S}_4^+$ $[\text{M}+\text{Na}]^+$ 694.9732, found: 694.9726.

IR (neat, ν): 3052, 2931, 1611, 1570, 1448, 1321 cm^{-1} .



***S,S'*-(1,1'-dimethyl-1H,1'H-[3,3'-biindole]-2,2'-diyl) bis(3-chlorobenzenesulfonothioate) (3j)**

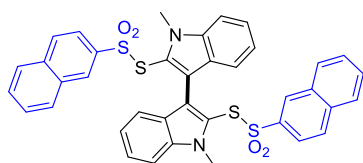
Yellow solid. 0.0174g, 26% total yield, $R_f = 0.5$ (PE/ EA = 10/1).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.42 – 7.34 (m, 4H), 7.19 – 7.14 (m, 2H), 7.05 – 6.98 (m, 4H), 6.97 – 6.92 (m, 2H), 6.56 – 6.49 (m, 2H),

6.46 – 6.39 (m, 2H), 4.02 (s, 6H) ppm; $^{13}\text{C}\{^1\text{H}\}\text{NMR}$ (100 MHz, CDCl_3) δ 144.3, 139.1, 134.2, 132.9, 129.1, 126.3, 125.9, 125.3, 124.8, 122.3, 120.2, 119.0, 118.3, 110.6, 31.5 ppm.

HRMS (ESI) m/z : calcd for $\text{C}_{30}\text{H}_{22}\text{Cl}_2\text{N}_2\text{NaO}_4\text{S}_4^+$ $[\text{M}+\text{Na}]^+$ 694.9732, found: 694.9697.

IR (neat, ν): 3055, 2932, 1731, 1573, 1449, 1329 cm^{-1} .



***S,S'*-(1,1'-dimethyl-1H,1'H-[3,3'-biindole]-2,2'-diyl)bis(naphthalene-2-sulfonylthioate) (3k)**

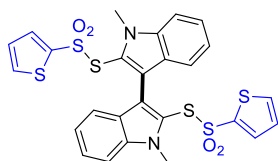
Yellow solid. 0.0493g, 70% total yield, $R_f = 0.5$ (PE/EA = 10/1).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.67 (s, 2H), 7.46 – 7.36 (m, 8H), 7.08 – 6.98 (m, 6H), 6.95 – 6.90 (m, 2H), 6.56 – 6.50 (m, 2H),

6.41 – 6.34 (m, 2H), 3.86 (s, 6H) ppm; $^{13}\text{C}\{^1\text{H}\}\text{NMR}$ (100 MHz, CDCl_3) δ 140.2, 138.7, 134.6, 131.2, 129.2, 128.8, 128.5, 128.1, 127.3, 125.6, 124.9, 121.2, 121.0, 119.7, 119.6, 118.5, 109.7, 31.2 ppm.

HRMS (ESI) m/z : calcd for $\text{C}_{38}\text{H}_{28}\text{N}_2\text{NaO}_4\text{S}_4^+$ $[\text{M}+\text{Na}]^+$ 727.0824, found: 727.0780.

IR (neat, ν): 3053, 2927, 1736, 1610, 1451, 1315 cm^{-1} .



***S,S'*-(1,1'-dimethyl-1H,1'H-[3,3'-biindole]-2,2'-diyl)bis(thiophene-2-sulfonylthioate) (3l)**

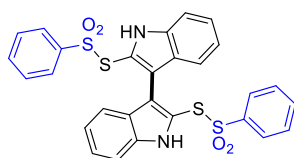
Yellow solid. 0.0185g, 30% total yield, $R_f = 0.5$ (PE/EA = 10/1).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.42 – 7.35 (m, 4H), 7.28 – 7.26 (m, 1H), 7.26 – 7.24 (m, 1H), 7.08 – 7.03 (m, 2H), 6.87 – 6.82 (m, 2H), 6.77 – 6.71

(m, 2H), 6.09 – 6.01 (m, 2H), 3.97 (s, 6H) ppm; $^{13}\text{C}\{^1\text{H}\}\text{NMR}$ (100 MHz, CDCl_3) δ 143.2, 139.4, 133.8, 133.3, 126.5, 126.4, 125.2, 122.8, 120.3, 120.0, 118.7, 110.4, 31.4 ppm.

HRMS (ESI) m/z : calcd for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{NaO}_4\text{S}_6^+$ $[\text{M}+\text{Na}]^+$ 638.9640, found: 638.9613.

IR (neat, ν): 3088, 2925, 1725, 1608, 1448, 1326 cm^{-1} .



***S,S'*-(1H,1'H-[3,3'-biindole]-2,2'-diyl)dibenzenesulfonylthioate (3m)**

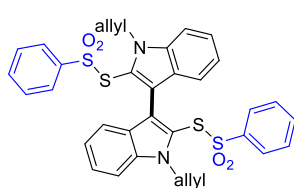
Yellow solid. 0.0263g, 42% total yield, $R_f = 0.5$ (PE/EA = 10/1).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.85 (s, 2H), 7.45 – 7.39 (m, 2H), 7.34 – 7.28 (m, 2H), 7.24 – 7.16 (m, 4H), 7.04 – 6.95 (m, 4H), 6.94 – 6.87 (m,

2H), 6.82 – 6.69 (m, 4H) ppm; $^{13}\text{C}\{^1\text{H}\}\text{NMR}$ (100 MHz, CDCl_3) δ 142.9, 137.8, 133.5, 128.4, 126.8, 126.7, 125.2, 122.0, 120.3, 117.9, 117.7, 111.6 ppm.

HRMS (ESI) m/z : calcd for $\text{C}_{28}\text{H}_{20}\text{N}_2\text{NaO}_4\text{S}_4^+$ $[\text{M}+\text{Na}]^+$ 599.0198, found: 599.0196.

IR (neat, ν): 3333, 1617, 1577, 1447, 1306 cm^{-1} .



***S,S'*-(1,1'-diallyl-1H,1'H-[3,3'-biindole]-2,2'-diyl)dibenzenesulfonylthioate (3n)**

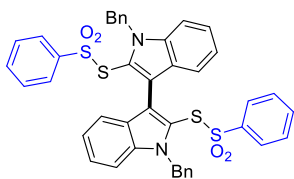
Yellow solid. 0.0413g, 72% total yield, $R_f = 0.5$ (PE/EA = 10/1).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38 – 7.33 (m, 4H), 7.24 – 7.20 (m, 2H), 7.18 – 7.13 (m, 4H), 7.07 – 7.02 (m, 2H), 6.80 – 6.74 (m, 2H), 6.66 –

6.59 (m, 4H), 6.01 – 5.90 (m, 2H), 5.29 (dd, $J = 17.3, 5.0$ Hz, 2H), 5.17 (d, $J = 10.5$ Hz, 2H), 4.91 (dd, $J = 17.2, 5.2$ Hz, 2H), 4.78 (d, $J = 17.2$ Hz, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}\text{NMR}$ (100 MHz, CDCl_3) δ 143.5, 138.6, 133.1, 133.1, 128.3, 128.3, 128.2, 126.5, 126.3, 125.0, 122.5, 120.2, 119.9, 118.7, 116.9, 110.9, 46.9 ppm.

HRMS (ESI) m/z : calcd for $\text{C}_{34}\text{H}_{28}\text{N}_2\text{NaO}_4\text{S}_4^+$ $[\text{M}+\text{Na}]^+$ 679.0824, found: 679.0838.

IR (neat, ν): 3057, 2924, 1730, 1609, 1565, 1444 cm^{-1} .



***S,S'*-(1,1'-dibenzyl-1H,1'H-[3,3'-biindole]-2,2'-diyl) dibenzenesulfonothioate (3o)**

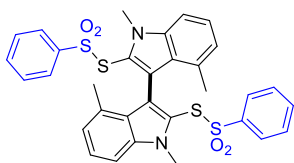
Yellow solid. 0.0302g, 40% total yield, $R_f = 0.5$ (PE/ EA = 10/1).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.40 – 7.27 (m, 11H), 7.21 – 7.17 (m, 2H), 7.15 – 7.09 (m, 7H), 7.04 – 6.99 (m, 2H), 6.67 – 6.61 (m, 2H), 6.51 –

6.41 (m, 4H), 6.07 (d, $J = 16.7$ Hz, 2H), 5.36 (d, $J = 16.7$ Hz, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}\text{NMR}$ (100 MHz, CDCl_3) δ 143.3, 138.5, 137.4, 133.3, 128.8, 128.4, 127.9, 127.0, 126.6, 126.5, 125.2, 122.6, 120.6, 120.2, 119.0, 111.0, 48.1 ppm.

HRMS (ESI) m/z : calcd for $\text{C}_{42}\text{H}_{32}\text{N}_2\text{NaO}_4\text{S}_4^+$ $[\text{M}+\text{Na}]^+$ 779.1137, found: 779.1134.

IR (neat, ν): 3063, 2940, 2339, 1604, 1580, 1447, 1323 cm^{-1} .



***S,S'*-(1,1',4,4'-tetramethyl-1H,1'H-[3,3'-biindole]-2,2'-diyl) dibenzenesulfonothioate (3p)**

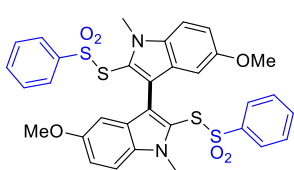
Yellow solid. 0.0209g, 33% total yield, $R_f = 0.5$ (PE/ EA = 10/1).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36 – 7.27 (m, 4H), 7.24 – 7.15 (m, 4H), 7.15 – 7.09 (m, 2H), 6.94 – 6.82 (m, 4H), 6.76 (d, $J = 6.6$ Hz, 2H), 3.79

(s, 6H), 1.83 (s, 6H) ppm; $^{13}\text{C}\{^1\text{H}\}\text{NMR}$ (100 MHz, CDCl_3) δ 144.7, 139.4, 133.4, 133.4, 128.4, 128.3, 126.3, 125.0, 122.5, 122.1, 120.9, 108.0, 31.2, 19.4 ppm.

HRMS (ESI) m/z : calcd for $\text{C}_{32}\text{H}_{28}\text{N}_2\text{NaO}_4\text{S}_4^+$ $[\text{M}+\text{Na}]^+$ 655.0824, found: 655.0845.

IR (neat, ν): 2922, 1731, 1602, 1446, 1325 cm^{-1} .



***S,S'*-(5,5'-dimethoxy-1,1'-dimethyl-1H,1'H-[3,3'-biindole]-2,2'-diyl) dibenzenesulfonothioate (3q)**

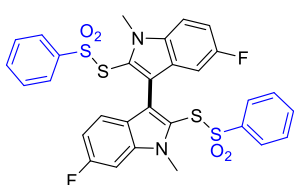
Yellow solid. 0.0359g, 54% total yield, $R_f = 0.5$ (PE/ EA = 10/1).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.30 – 7.26 (m, 2H), 7.20 – 7.14 (m, 4H), 7.05 – 7.03 (m, 1H), 7.03 – 6.98 (m, 1H), 6.90 – 6.83 (m, 2H), 6.70 –

6.63 (m, 4H), 6.47 – 6.43 (m, 2H), 3.92 (s, 6H), 3.69 (s, 6H) ppm; $^{13}\text{C}\{^1\text{H}\}\text{NMR}$ (100 MHz, CDCl_3) δ 154.2, 143.6, 134.8, 132.8, 127.9, 126.5, 126.4, 119.9, 117.8, 116.6, 111.4, 102.4, 55.9, 31.4 ppm.

HRMS (ESI) m/z : calcd for $\text{C}_{32}\text{H}_{28}\text{N}_2\text{NaO}_6\text{S}_4^+$ $[\text{M}+\text{Na}]^+$ 687.0722, found: 687.0701.

IR (neat, ν): 2920, 1726, 1623, 1490, 1445, 1325 cm^{-1} .



***S,S'*-(5,5'-difluoro-1,1'-dimethyl-1H,1'H-[3,3'-biindole]-2,2'-diyl) dibenzenesulfonothioate (3r)**

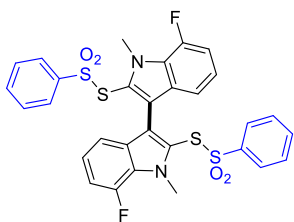
Yellow solid. 0.0160g, 25% total yield, $R_f = 0.5$ (PE/ EA = 10/1).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.32 – 7.27 (m, 2H), 7.19 – 7.07 (m, 6H), 6.92 – 6.85 (m, 2H), 6.78 – 6.68 (m, 4H), 6.62 (m, 2H), 3.92 (s, 6H) ppm;

$^{13}\text{C}\{^1\text{H}\}\text{NMR}$ (100 MHz, CDCl_3) δ 157.8 (d, $J_{C-F} = 238.0$ Hz), 143.3, 135.8, 133.1, 128.1, 126.6, 126.1 (d, $J_{C-F} = 10.0$ Hz), 121.9, 117.7 (d, $J_{C-F} = 5.0$ Hz), 114.1 (d, $J_{C-F} = 26.0$ Hz), 111.5 (d, $J_{C-F} = 9.0$ Hz), 106.6 (d, $J_{C-F} = 23.0$ Hz), 31.7 ppm.

HRMS (ESI) m/z : calcd for $\text{C}_{30}\text{H}_{22}\text{F}_2\text{N}_2\text{NaO}_4\text{S}_4^+$ $[\text{M}+\text{Na}]^+$ 663.0323, found: 663.0324.

IR (neat, ν): 2922, 1722, 1622, 1573, 1486, 1303 cm^{-1} .



***S,S'*-(7,7'-difluoro-1,1'-dimethyl-1H,1'H-[3,3'-biindole]-2,2'-diyl) dibenzenesulfonothioate (3s)**

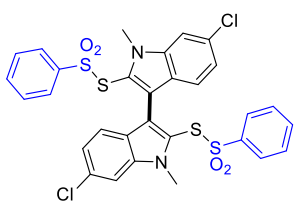
Yellow solid. 0.0275g, 43% total yield, $R_f = 0.5$ (PE/ EA = 10/1).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.20 – 7.15 (m, 4H), 7.03 – 6.97 (m, 2H), 6.94 – 6.84 (m, 6H), 6.78 – 6.72 (m, 4H), 4.09 (s, 6H) ppm;

$^{13}\text{C}\{^1\text{H}\}\text{NMR}$ (100 MHz, CDCl_3) δ 149.9 (d, $J_{\text{C-F}}=245.0$ Hz), 143.7, 133.0, 129.7 (d, $J_{\text{C-F}}=5.0$ Hz), 128.2, 127.7 (d, $J_{\text{C-F}}=10.0$ Hz), 126.4, 122.2, 120.1 (d, $J_{\text{C-F}}=6.0$ Hz), 118.6, 118.1 (d, $J_{\text{C-F}}=4.0$ Hz), 110.1 (d, $J_{\text{C-F}}=18.0$ Hz), 33.9 (d, $J_{\text{C-F}}=7.0$ Hz) ppm.

HRMS (ESI) m/z : calcd for $\text{C}_{30}\text{H}_{22}\text{F}_2\text{N}_2\text{NaO}_4\text{S}_4^+$ [$\text{M}+\text{Na}$] $^+$ 663.0323, found: 663.0322.

IR (neat, ν): 2960, 1727, 1627, 1573, 1509, 1448, 1384, 1319 cm^{-1} .



***S,S'*-(6,6'-dichloro-1,1'-dimethyl-1H,1'H-[3,3'-biindole]-2,2'-diyl) dibenzenesulfonothioate (3t)**

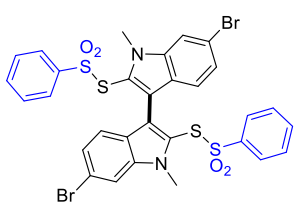
Yellow solid. 0.0248g, 37% total yield, $R_f = 0.5$ (PE/ EA = 10/1).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38 – 7.34 (m, 2H), 7.18 – 7.12 (m, 4H), 7.01 – 6.95 (m, 4H), 6.93 – 6.87 (m, 2H), 6.77 – 6.71 (m, 4H), 3.86 (s, 6H) ppm; $^{13}\text{C}\{^1\text{H}\}\text{NMR}$ (100 MHz, CDCl_3) δ 143.5, 139.4, 133.2, 131.4,

128.3, 126.6, 124.6, 123.1, 121.3, 121.2, 118.1, 110.3, 31.4 ppm.

HRMS (ESI) m/z : calcd for $\text{C}_{30}\text{H}_{22}\text{Cl}_2\text{N}_2\text{NaO}_4\text{S}_4^+$ [$\text{M}+\text{Na}$] $^+$ 694.9732, found: 694.9739.

IR (neat, ν): 2960, 1728, 1605, 1561, 1446, 1320 cm^{-1} .



***S,S'*-(6,6'-dibromo-1,1'-dimethyl-1H,1'H-[3,3'-biindole]-2,2'-diyl) dibenzenesulfonothioate (3u)**

Yellow solid. 0.0266g, 35% total yield, $R_f = 0.5$ (PE/ EA = 10/1).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.53 (s, 2H), 7.18 – 7.09 (m, 6H), 6.94 – 6.86 (m, 4H), 6.78 – 6.70 (m, 4H), 3.86 (s, 6H) ppm; $^{13}\text{C}\{^1\text{H}\}\text{NMR}$ (100 MHz, CDCl_3) δ 143.4, 139.7, 133.2, 128.3, 126.5, 124.9, 123.7, 123.3,

121.2, 119.1, 118.0, 113.4, 31.4 ppm.

HRMS (ESI) m/z : calcd for $\text{C}_{30}\text{H}_{22}\text{Br}_2\text{N}_2\text{NaO}_4\text{S}_4^+$ [$\text{M}+\text{Na}$] $^+$ 782.8721, found: 782.8693.

IR (neat, ν): 2924, 1730, 1601, 1565, 1445, 1321 cm^{-1} .

2.4 References

- (1) Pedras, M.S.C.; Jha, M. *J. Org. Chem.* **2005**, *70*, 1828-1834.
- (2) Tang, L.; Yang, Y.; Wen, L.-X.; Yang, X.-K.; Wang, Z.-Y. *Green Chem.* **2016**, *18*, 1224-1228.

3. X-Ray Crystallographic Data for 3m

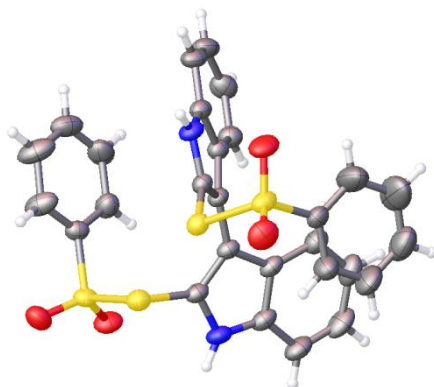


Fig. S1. Single crystal structure of 3m.

Crystal Number: CCDC 2085376

Empirical formula: $C_{28}H_{20}N_2O_4S_4$

Formula weight: 626.98

Unit cell parameters: $a = 20.1470 (13) \text{ \AA}$, $b = 18.1094 (11) \text{ \AA}$, $c = 17.9791 (12) \text{ \AA}$,

$\alpha = 90^\circ$, $\beta = 116.264 (2)^\circ$, $\gamma = 90^\circ$

Temperature: 296 (2) K

Wavelength: 0.71073 \AA

Crystal system: Monoclinic

Volume: 5882.5 (7) \AA^3

Calculated density: 1.406 Mg/m^3

Absorption coefficient: 0.364 mm^{-1}

F (000): 2584

Device: Xcalibur, Atlas, Gemini

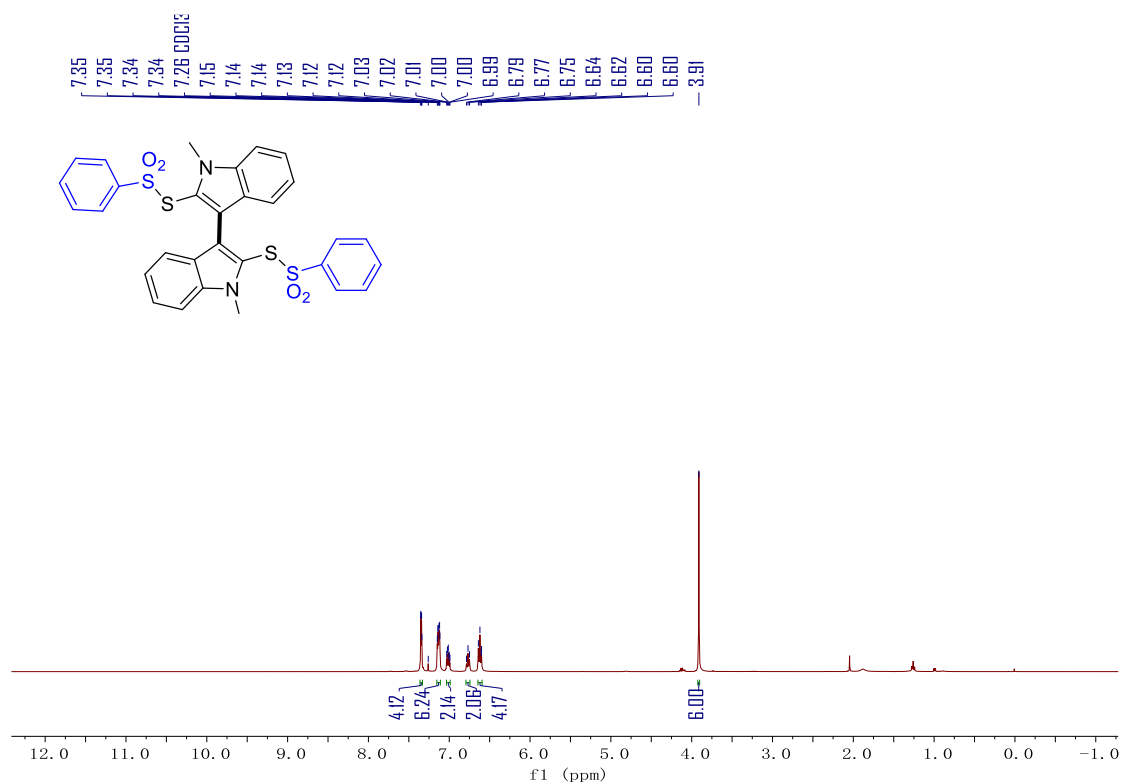
Measurement method: w scans

4. EPR Studies of Interaction

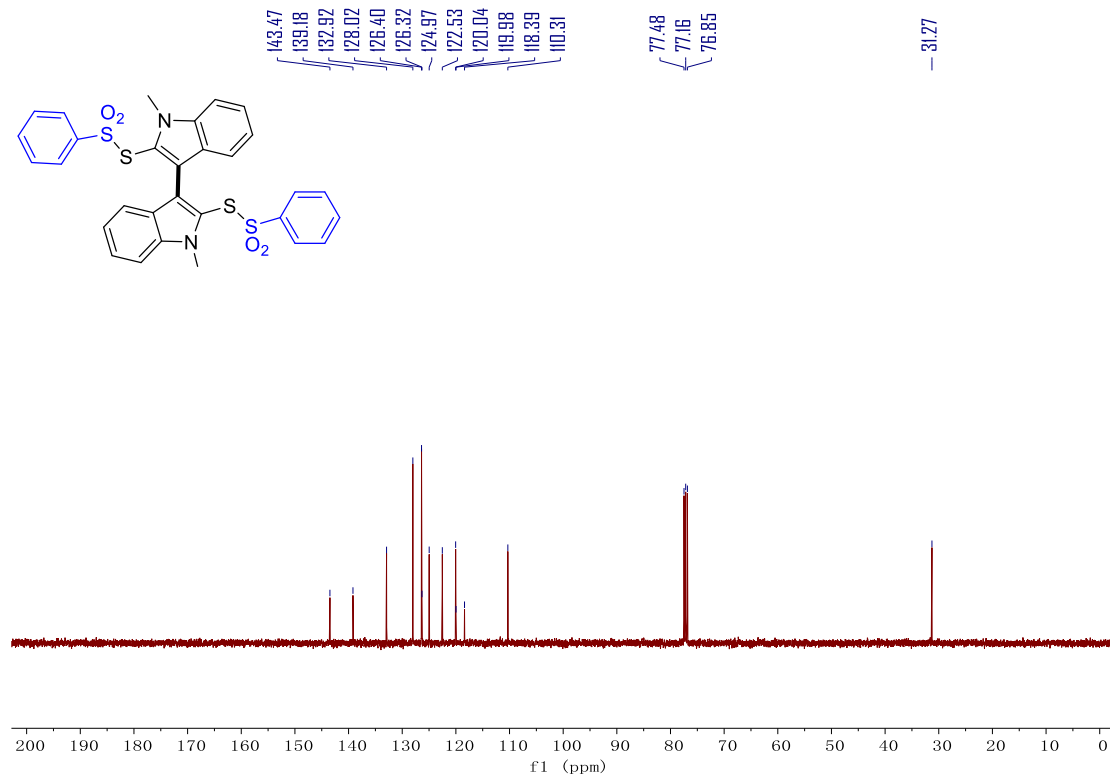
A dried tube equipped with a stir bar was loaded with TBHP (0.50 mmol) or the mixed solution of TBHP and indole-2-thione in 2.0 mL MeCN was stirred at 25 °C. After 5 mins, the solution sample was taken out into a small tube and analyzed by EPR. EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.852 GHz. Typical spectrometer parameters are shown as follows, scan range: 1000 G; center field set: 3400 G; scan time: 35 s.

5. Copies of ^1H NMR and ^{13}C NMR Spectra

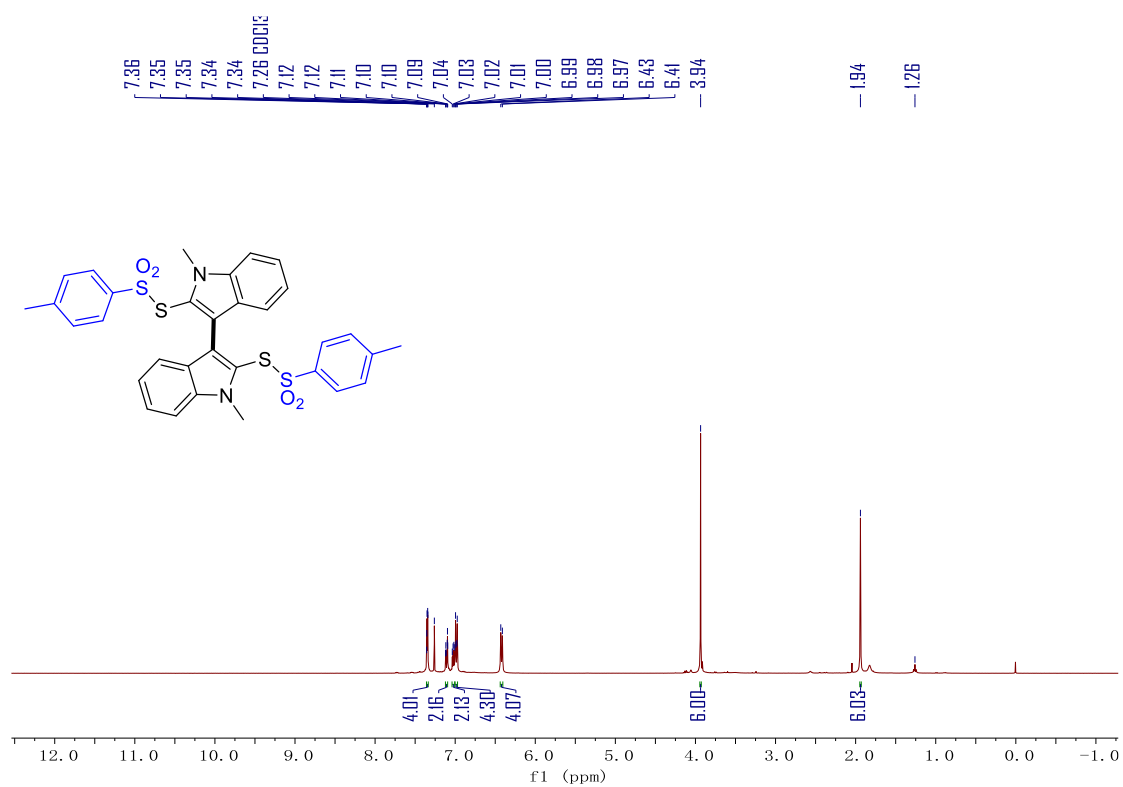
^1H NMR spectra of **3a**



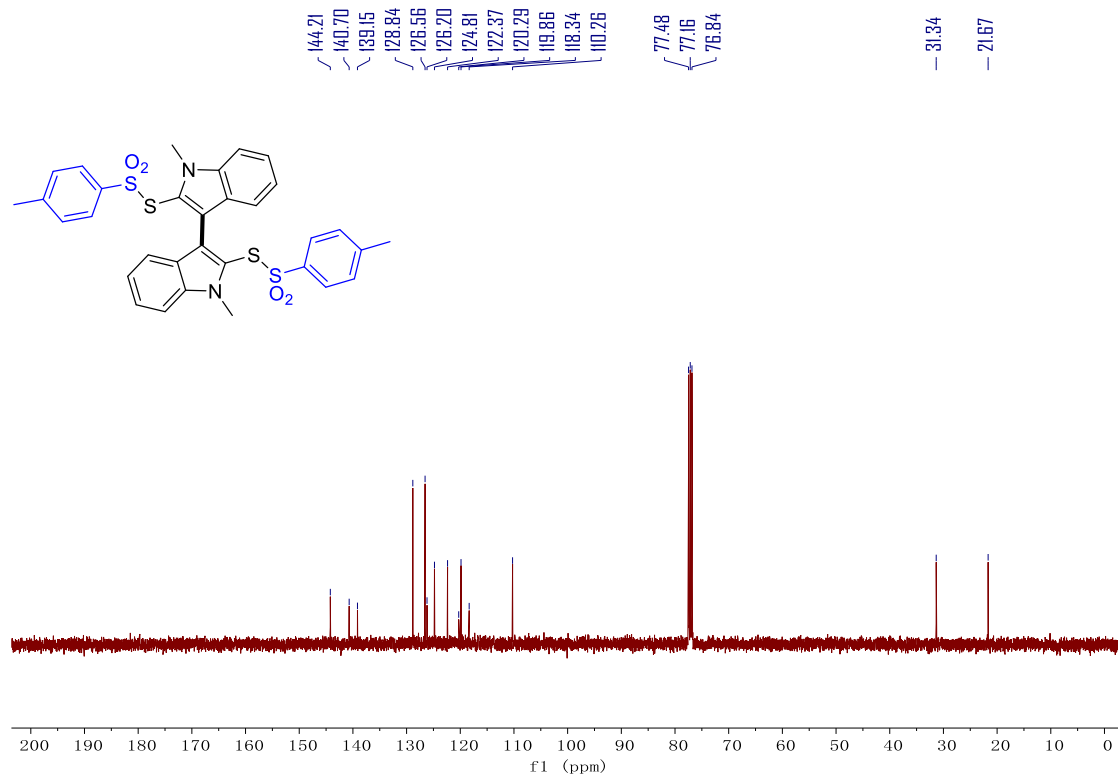
^{13}C NMR spectra of **3a**



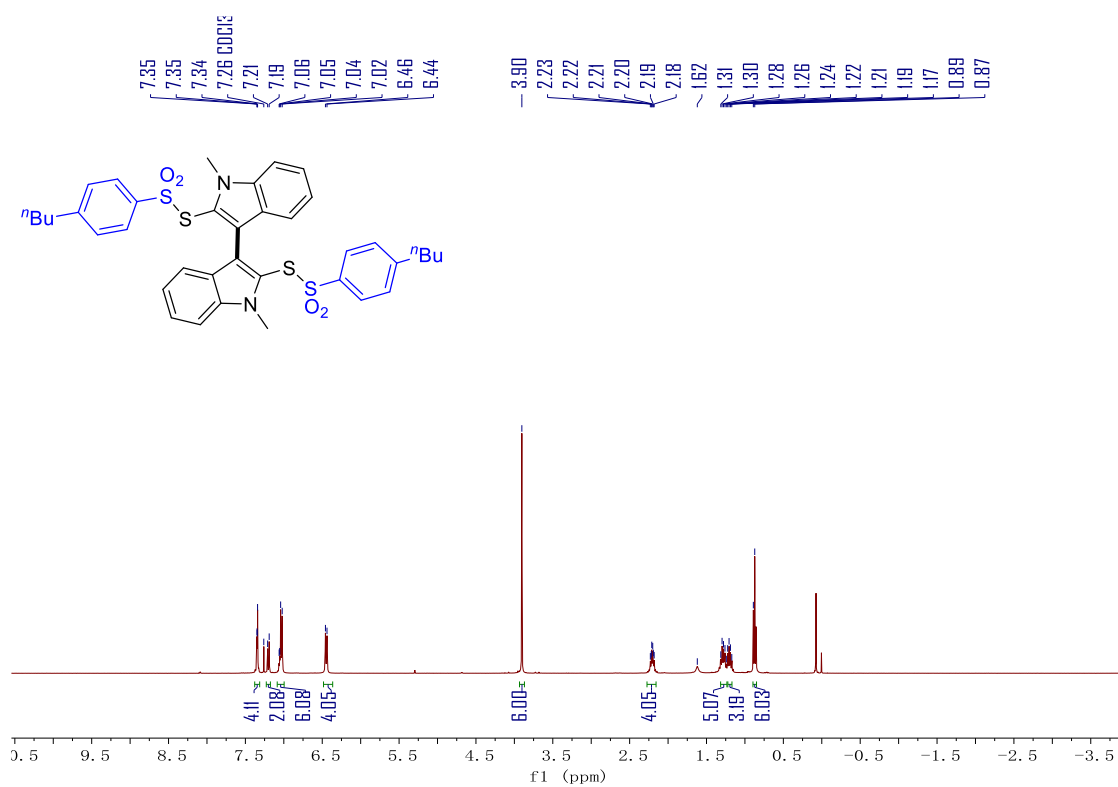
¹H NMR spectra of **3b**



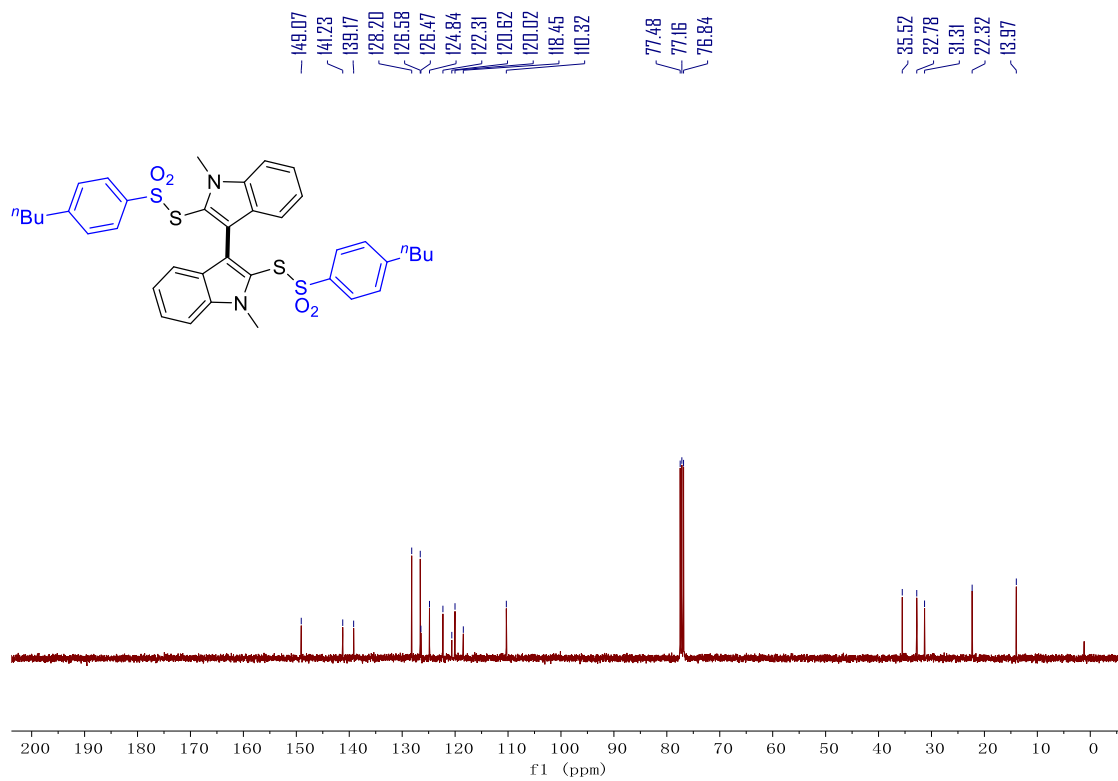
¹³C NMR spectra of **3b**



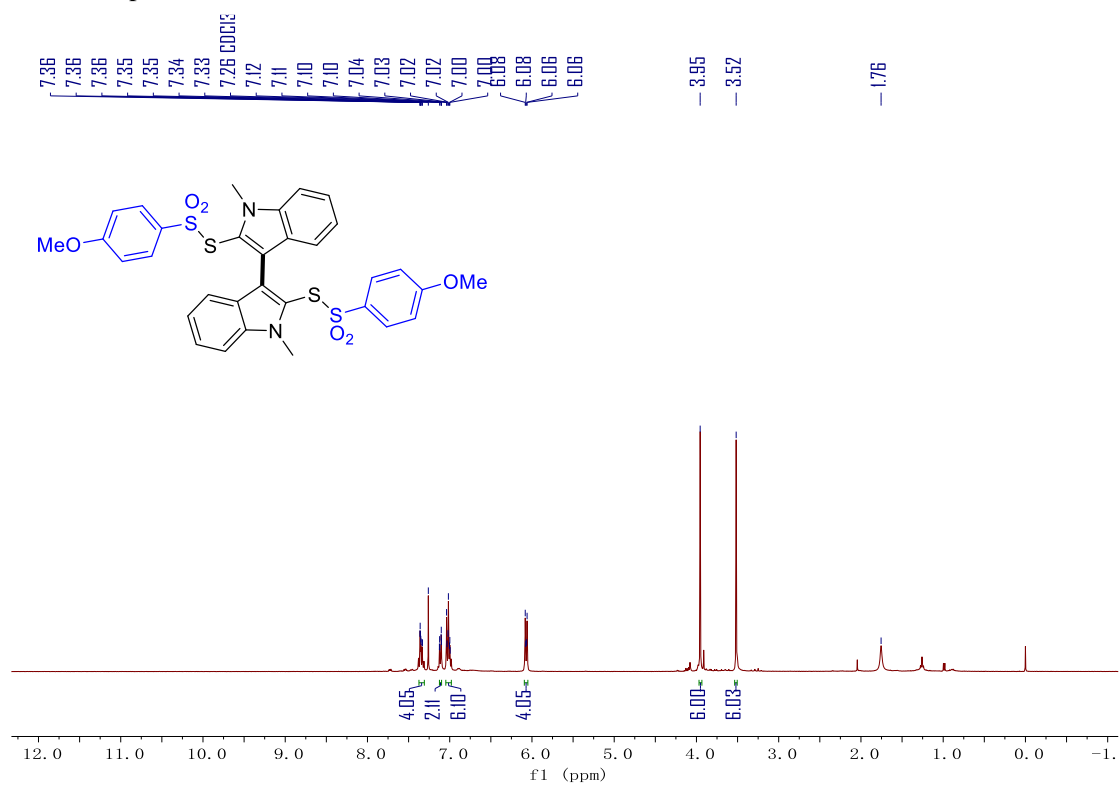
¹H NMR spectra of **3c**



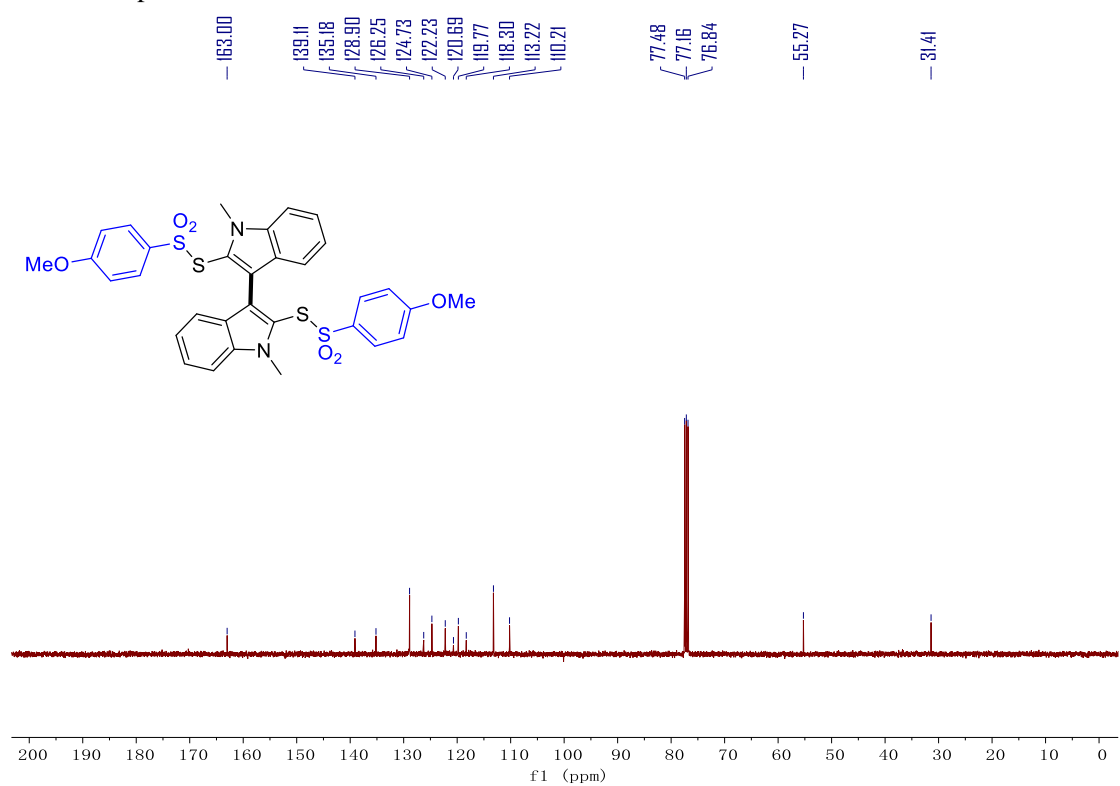
¹³C NMR spectra of **3c**



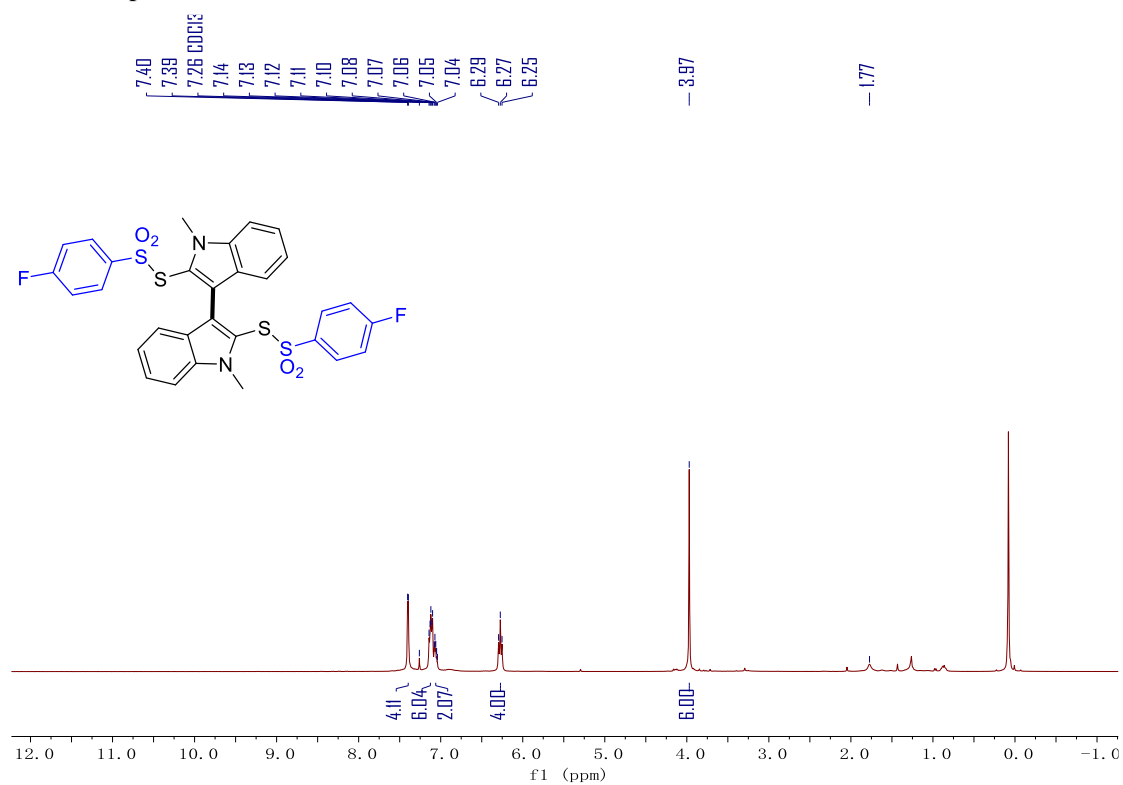
¹H NMR spectra of **3d**



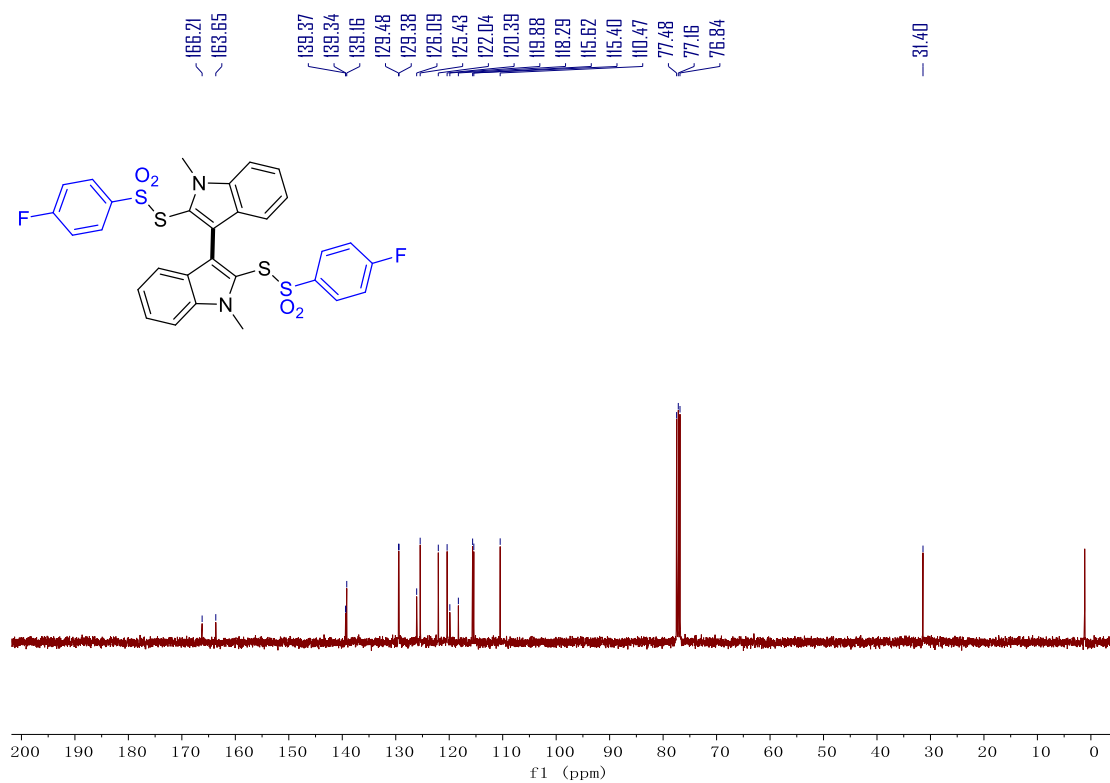
¹³C NMR spectra of **3d**



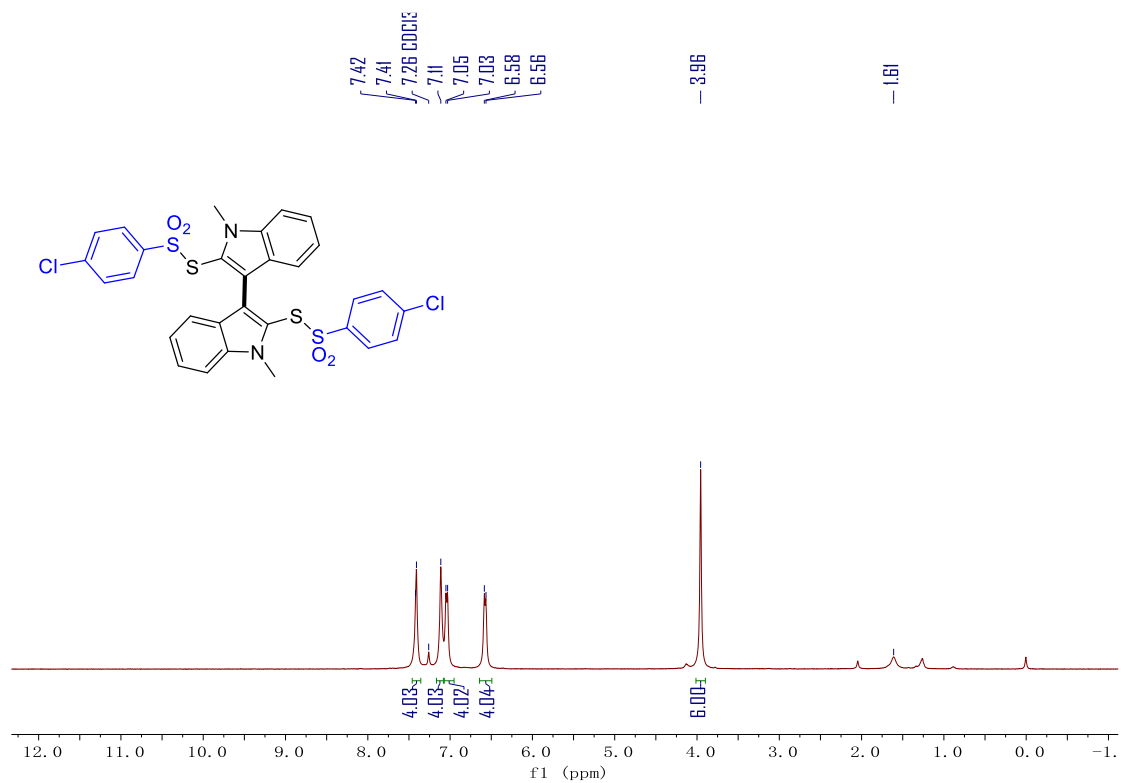
¹H NMR spectra of **3e**



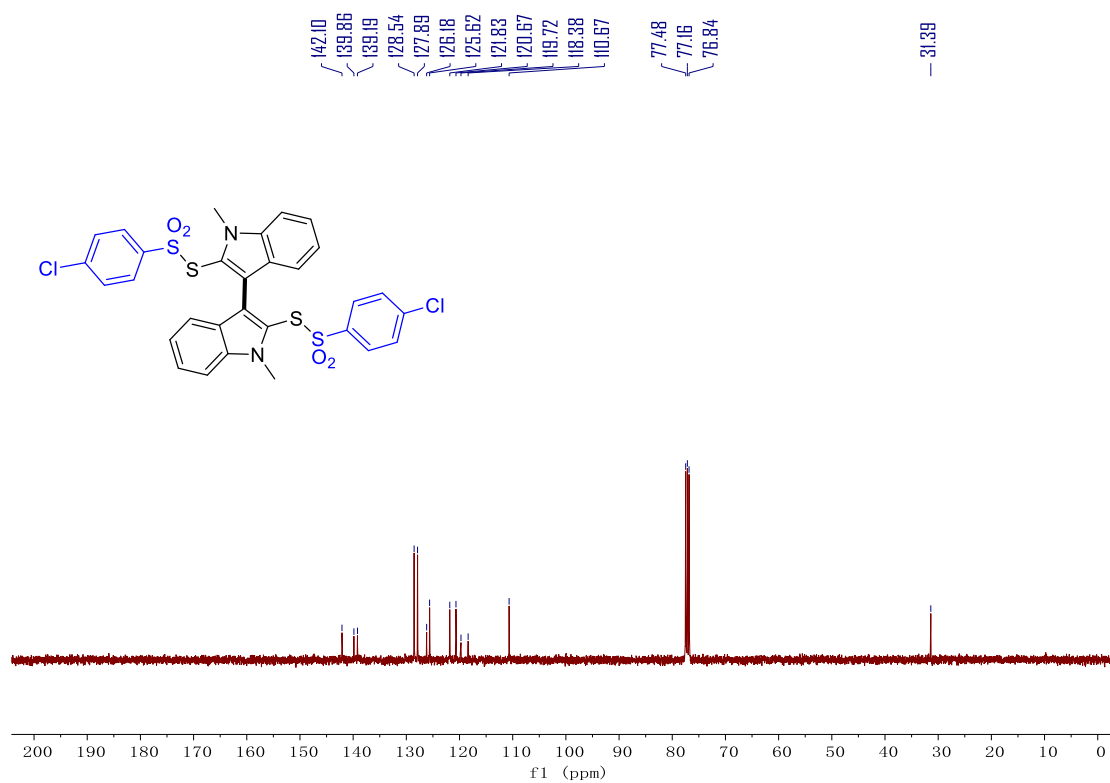
¹³C NMR spectra of **3e**



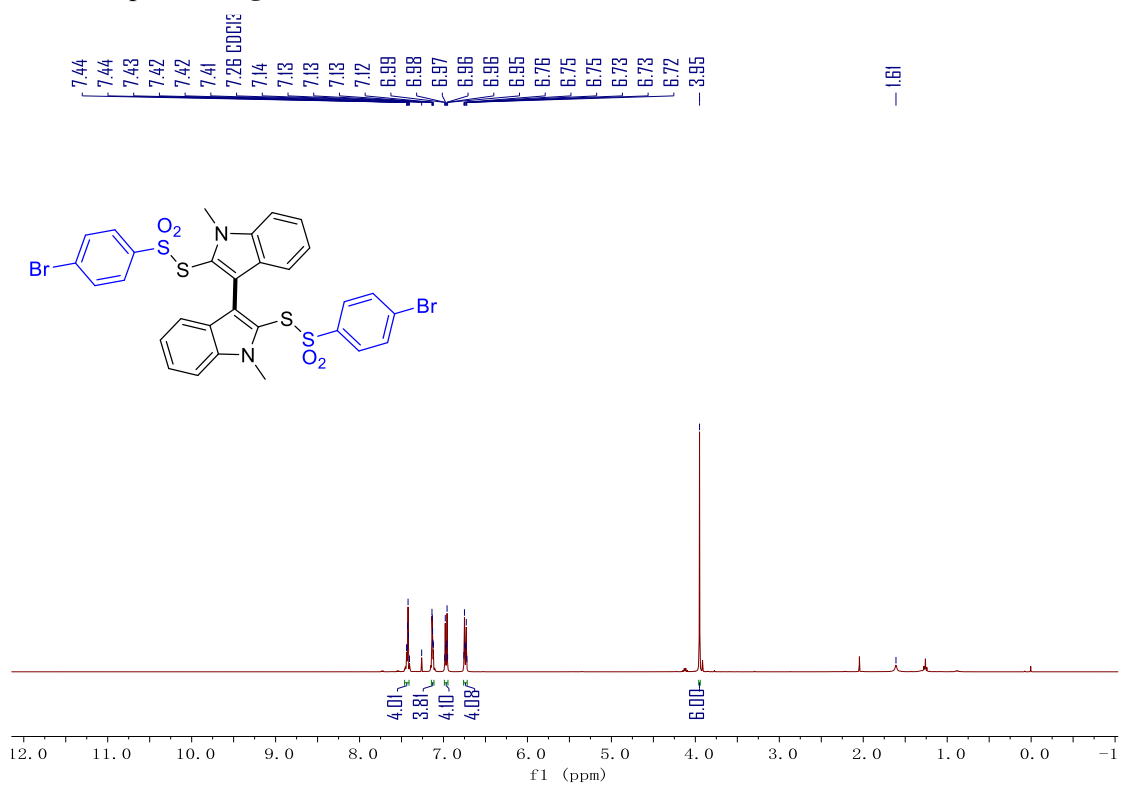
¹H NMR spectra of **3f**



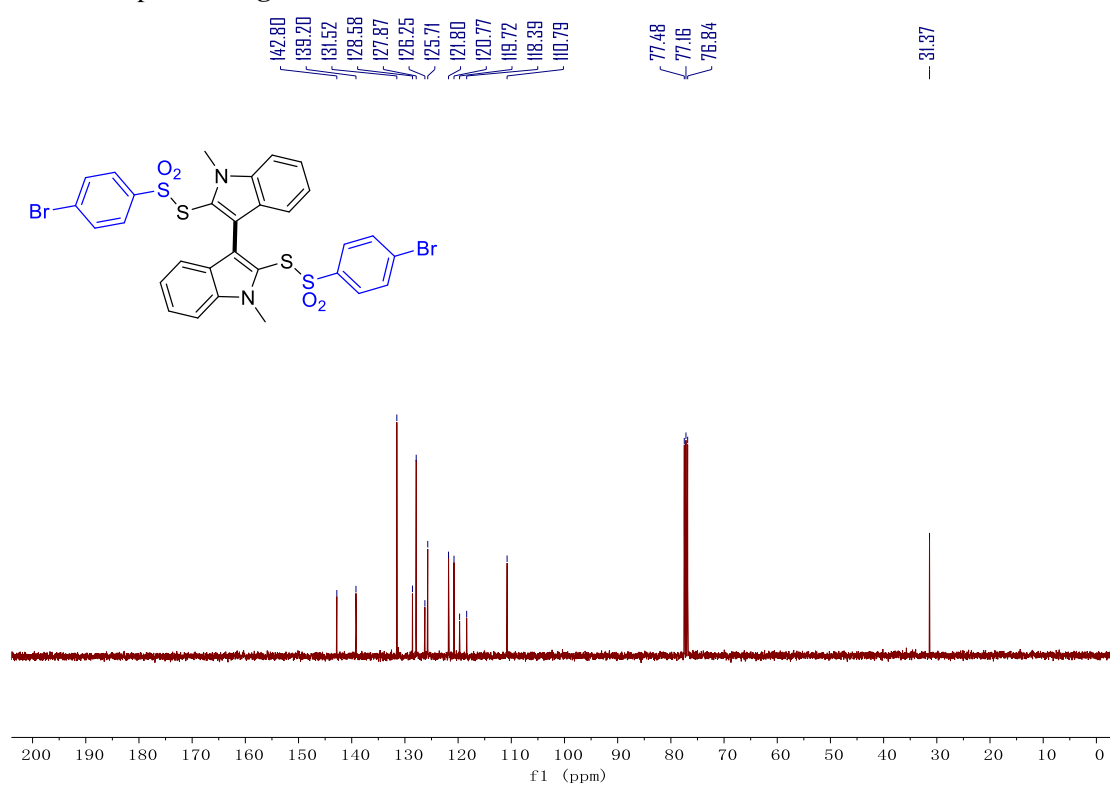
¹³C NMR spectra of **3f**



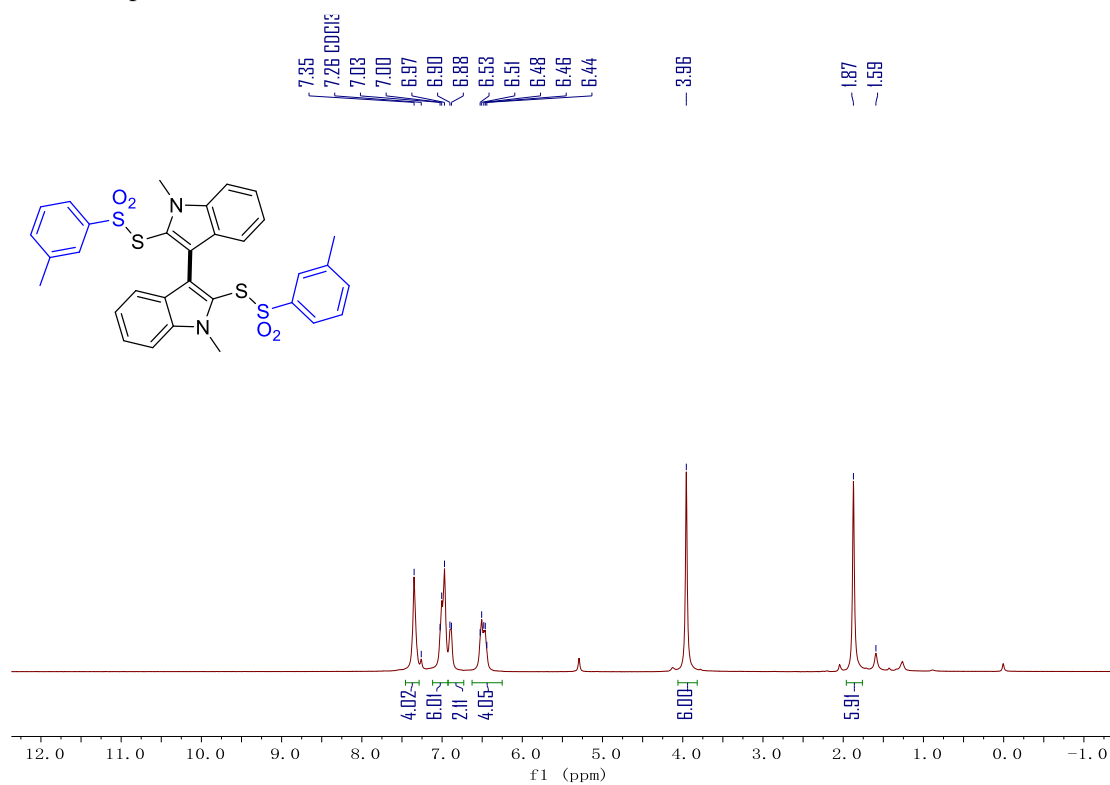
¹H NMR spectra of **3g**



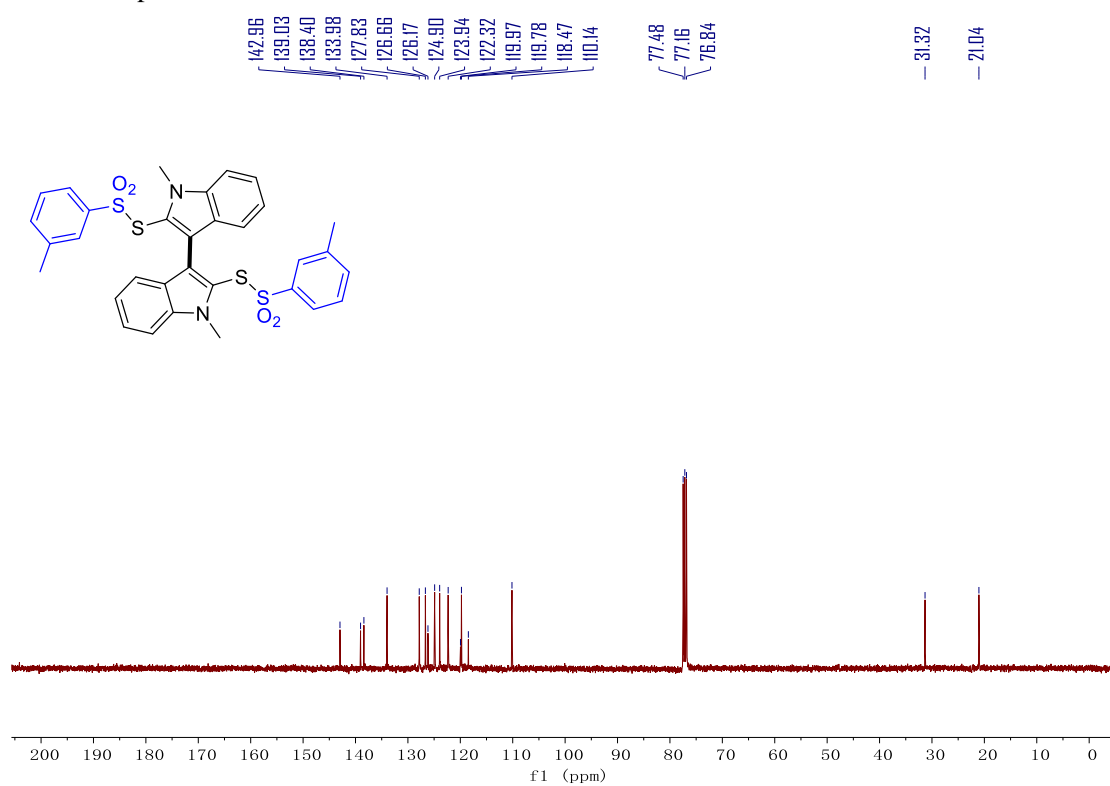
¹³C NMR spectra of **3g**



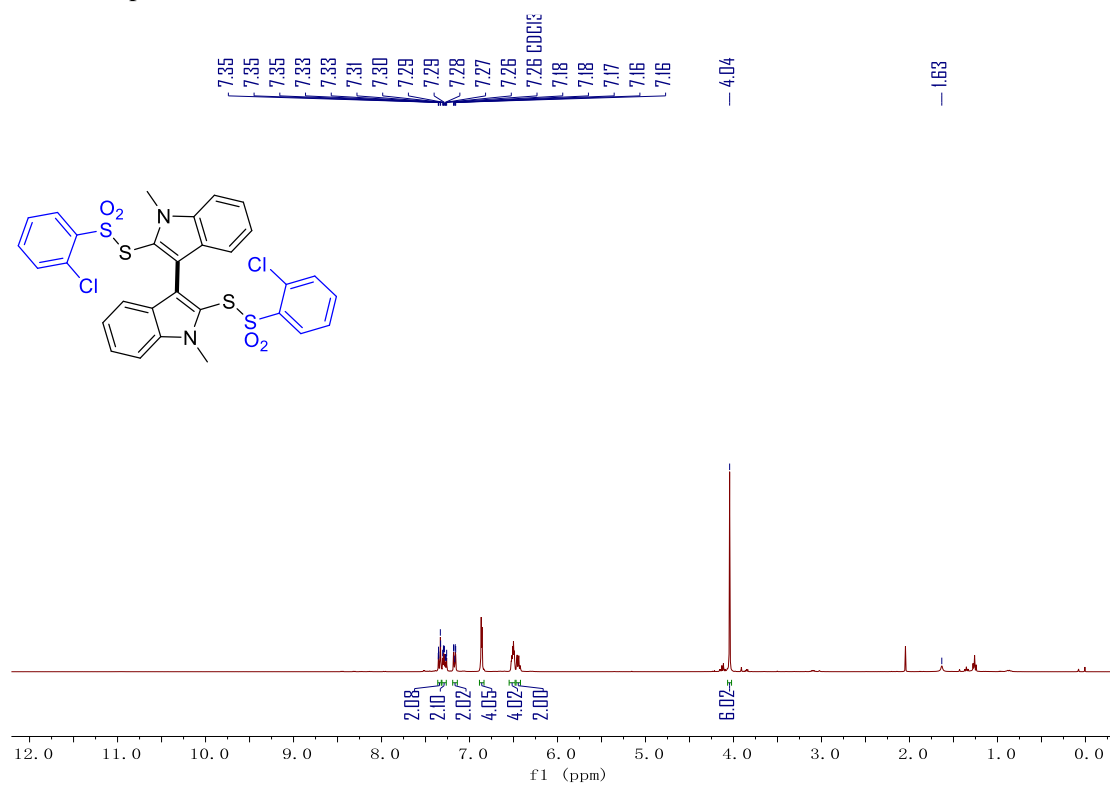
¹H NMR spectra of **3h**



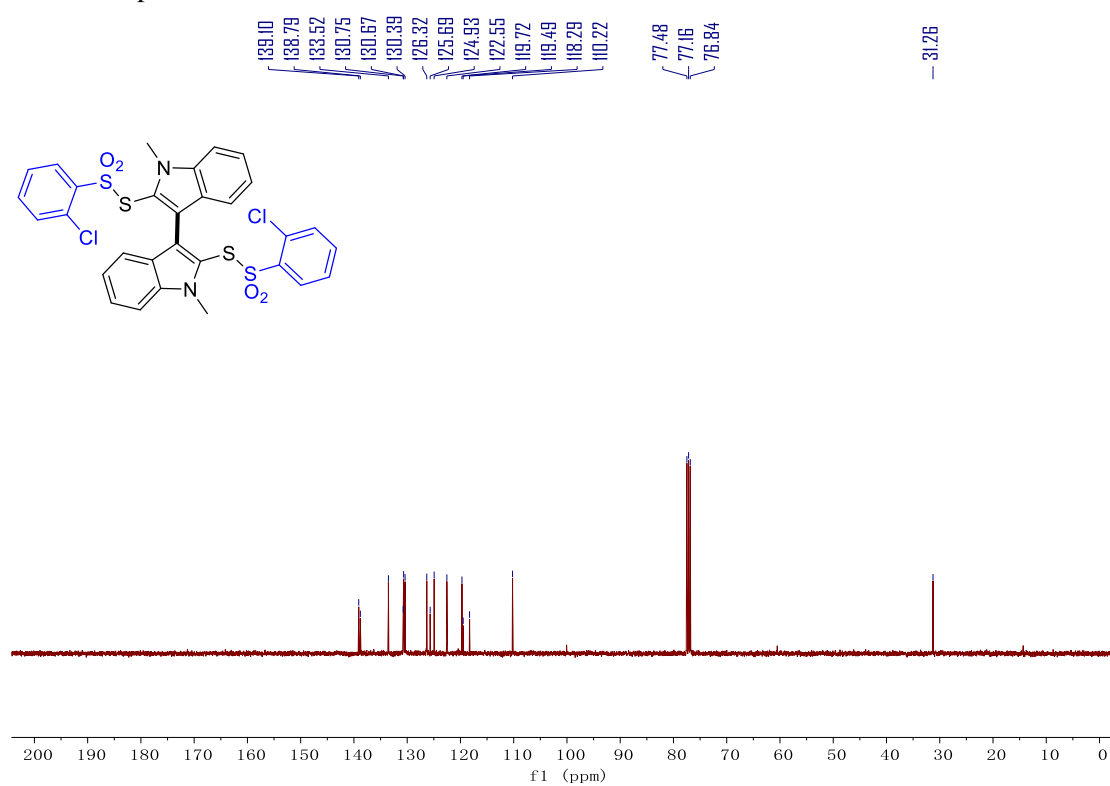
¹³C NMR spectra of **3h**



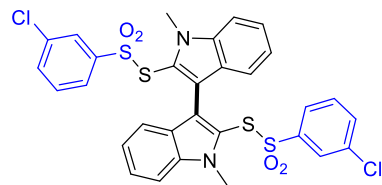
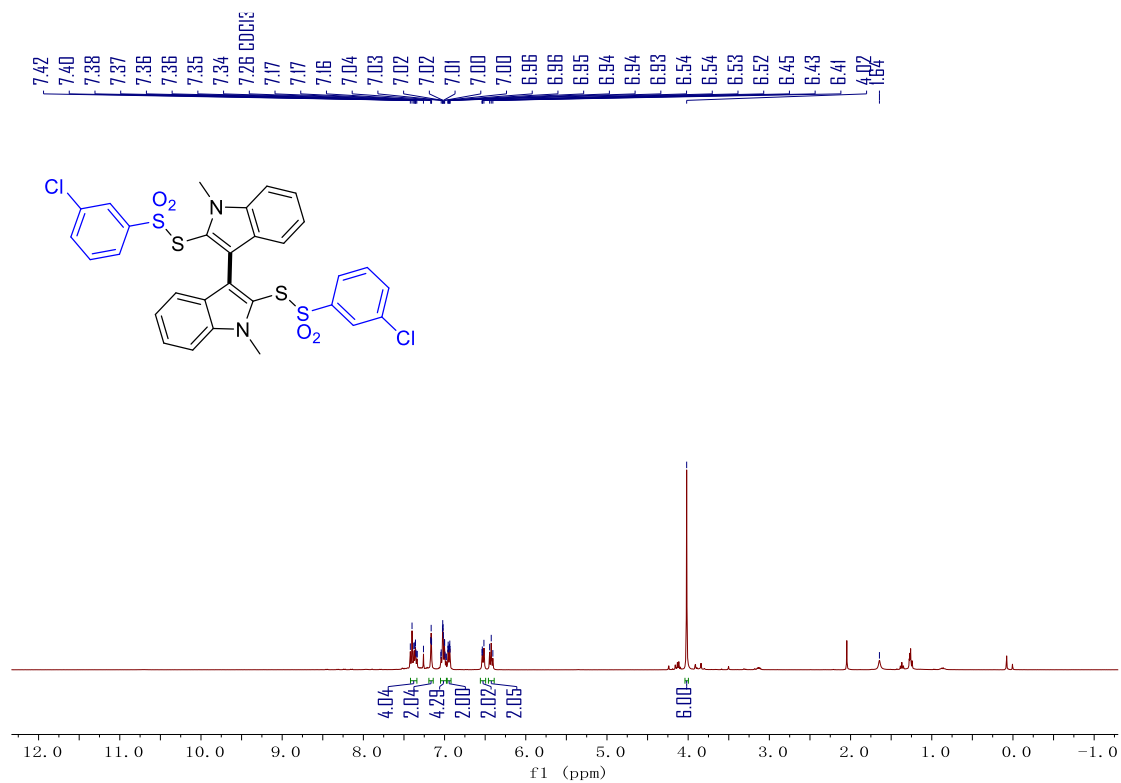
¹H NMR spectra of **3i**



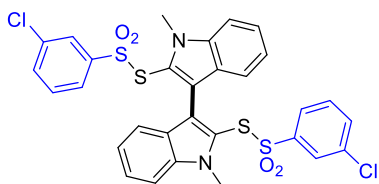
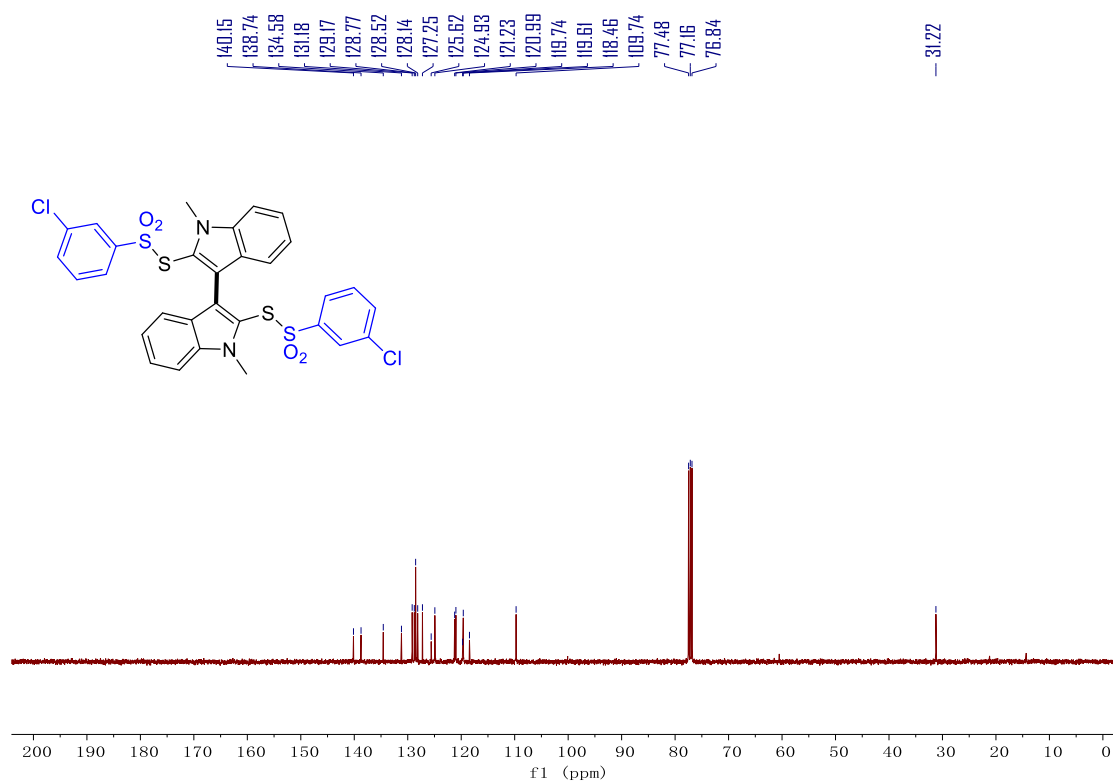
¹³C NMR spectra of **3i**



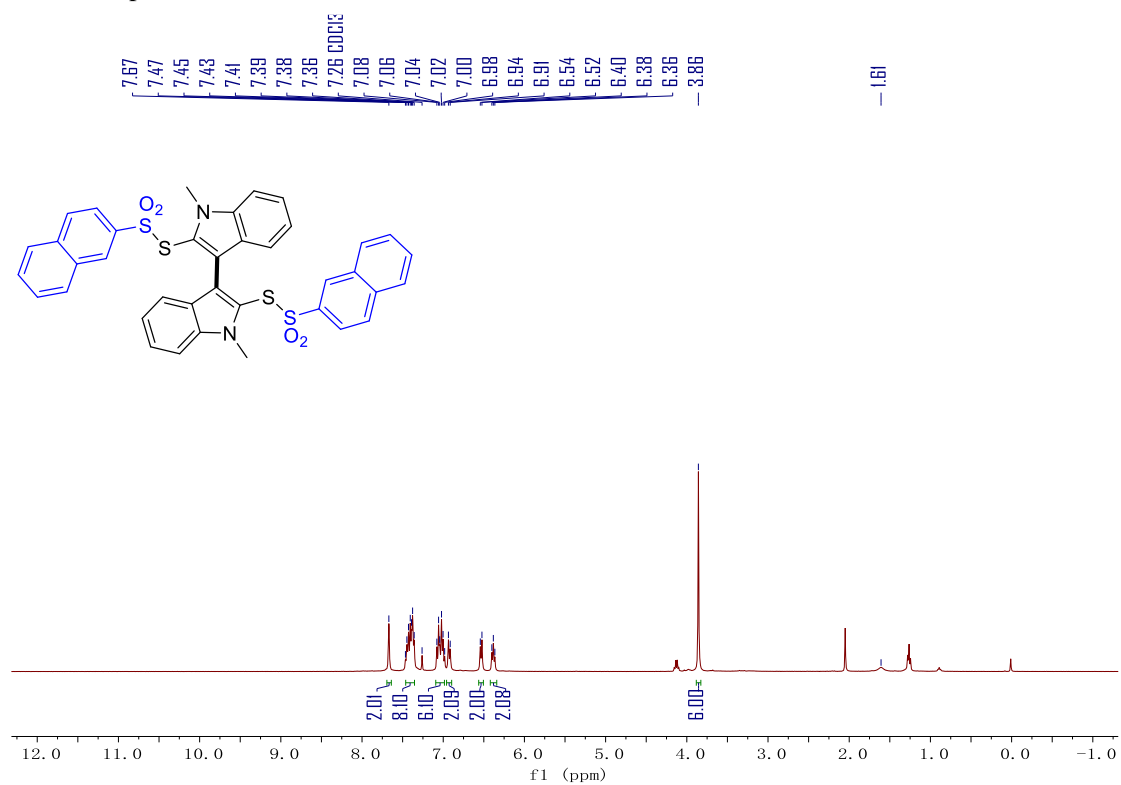
¹H NMR spectra of **3j**



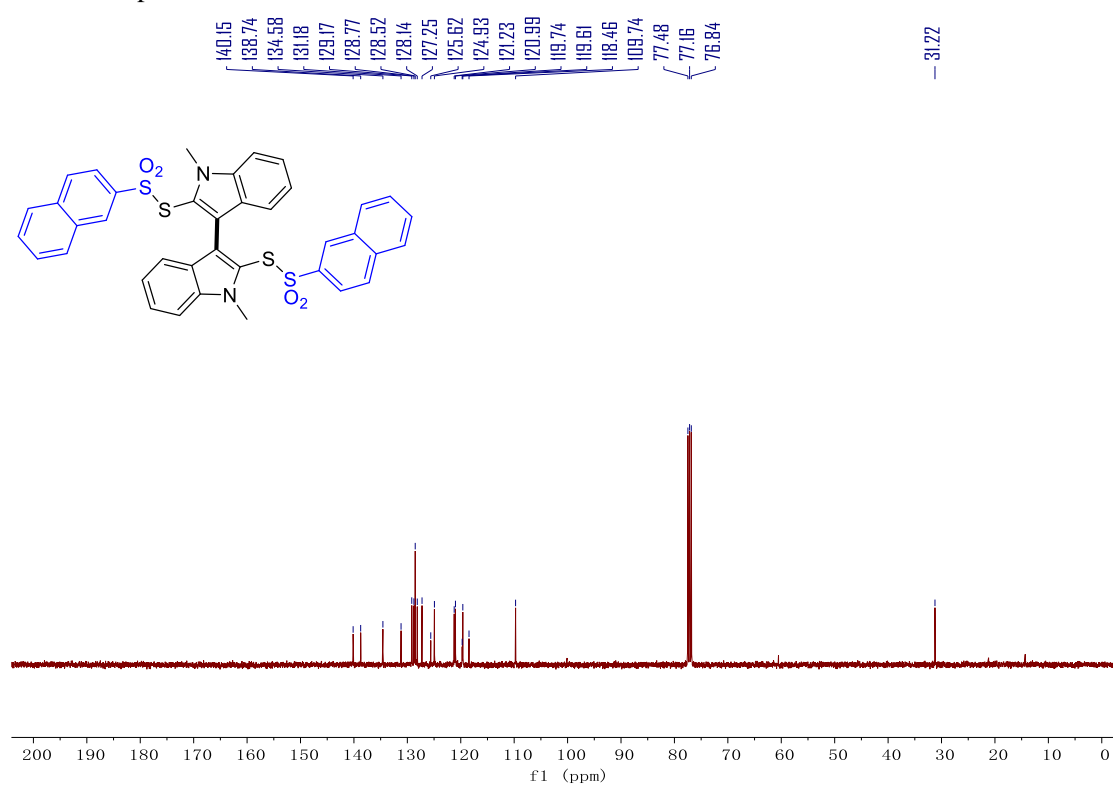
¹³C NMR spectra of **3j**



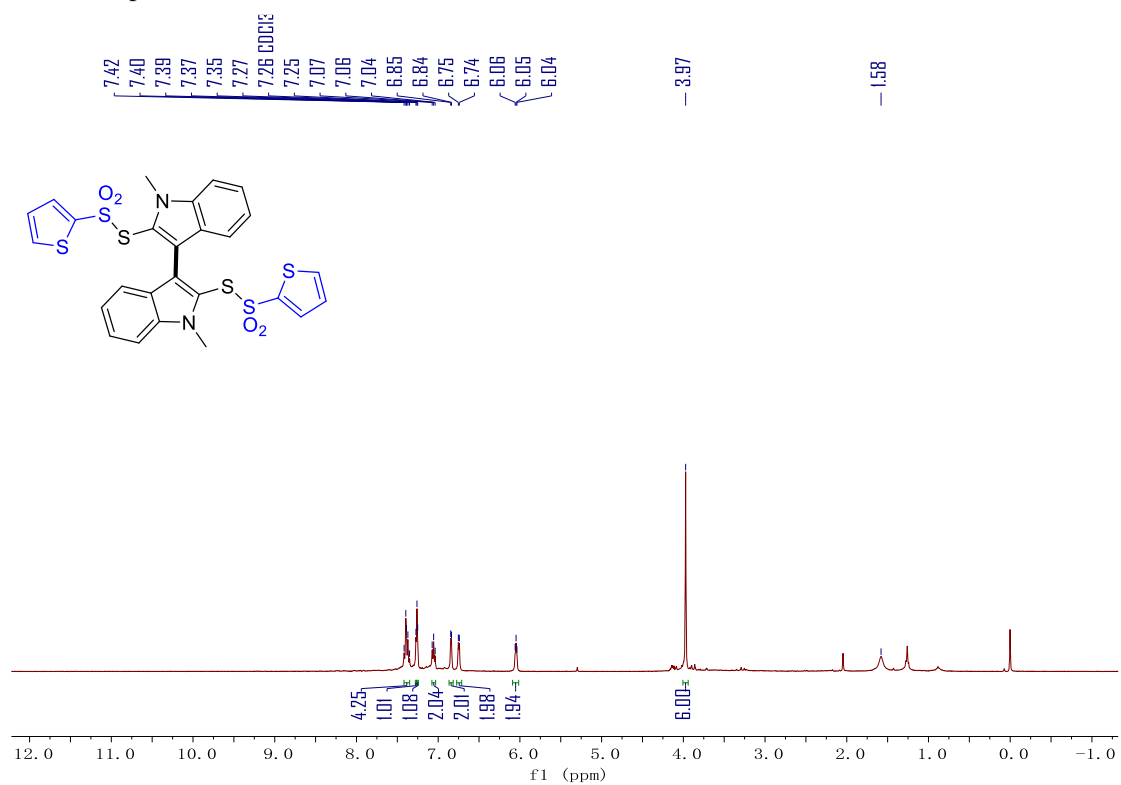
¹H NMR spectra of **3k**



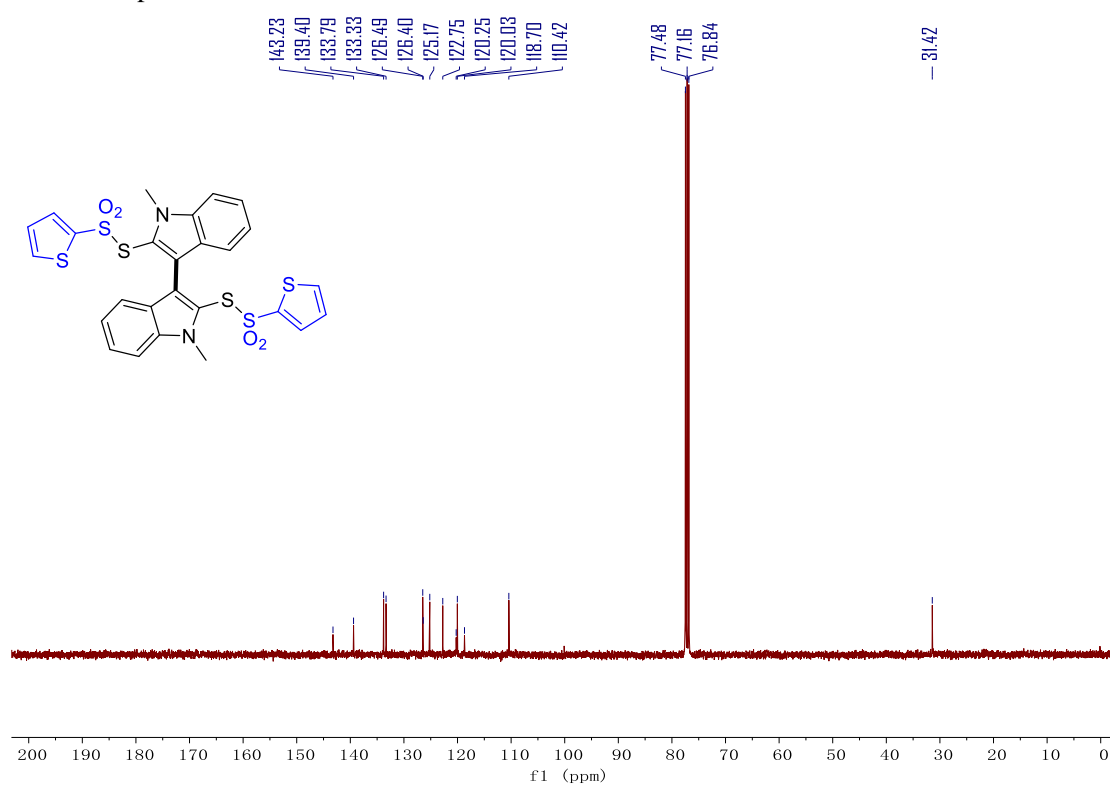
¹³C NMR spectra of **3k**



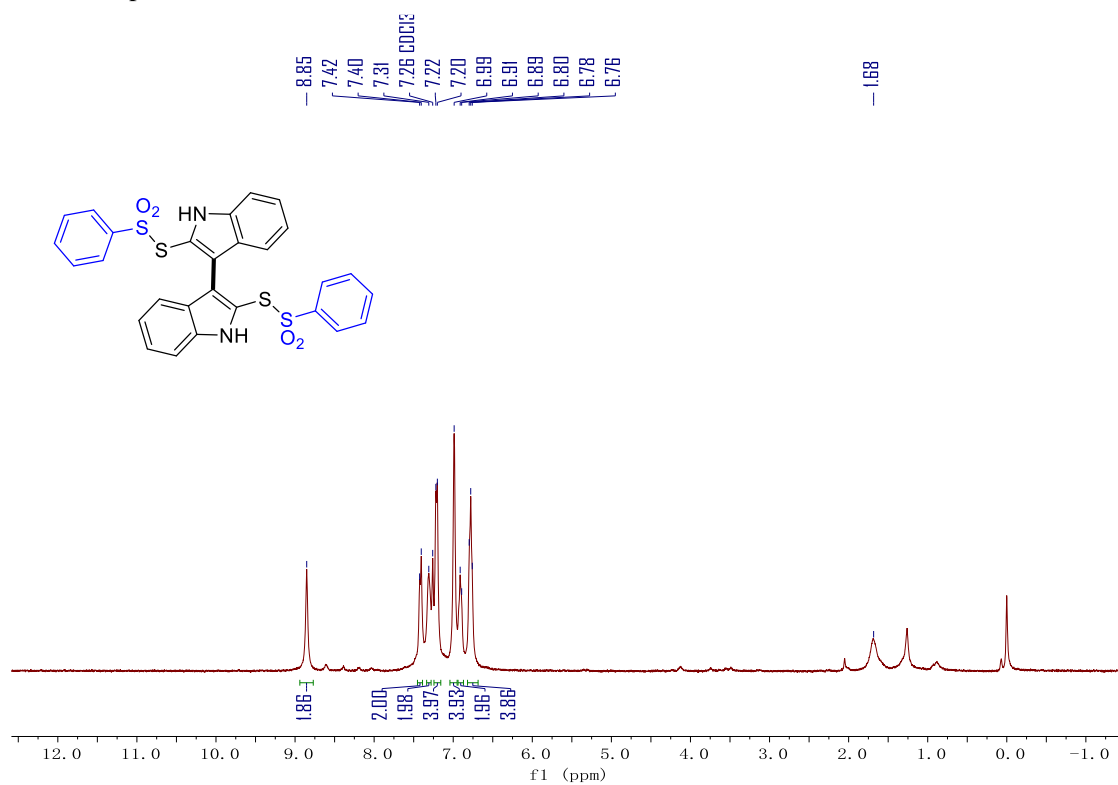
¹H NMR spectra of **31**



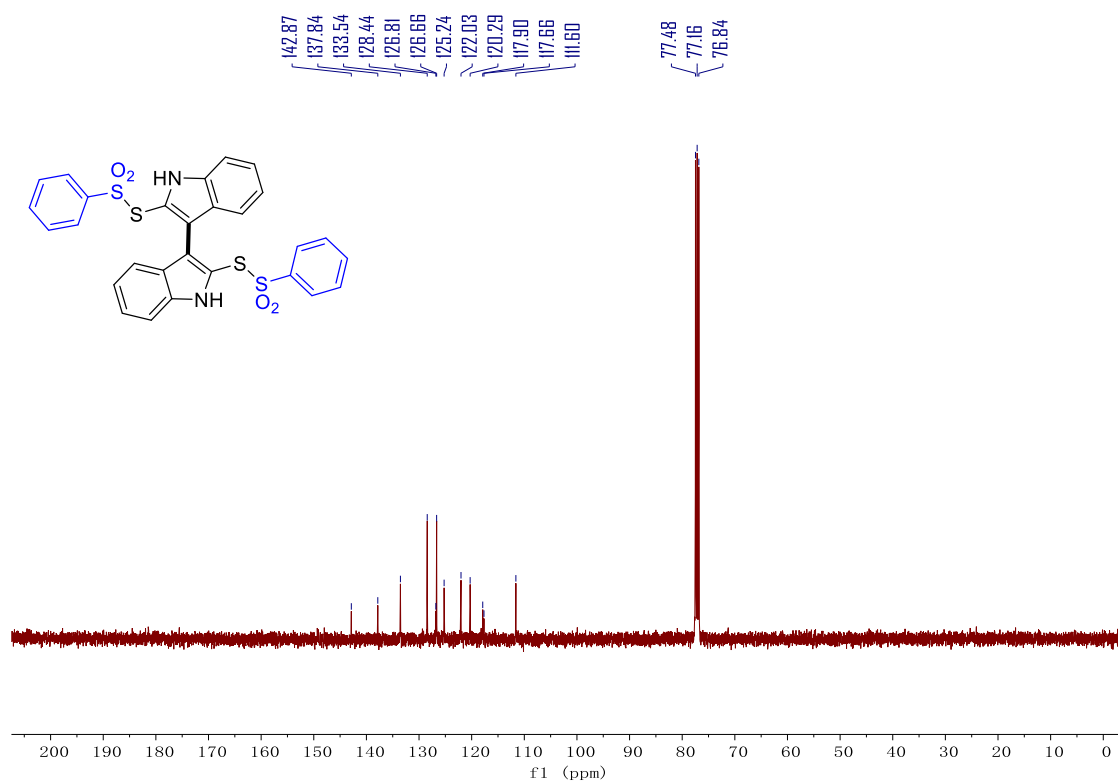
¹³C NMR spectra of **31**



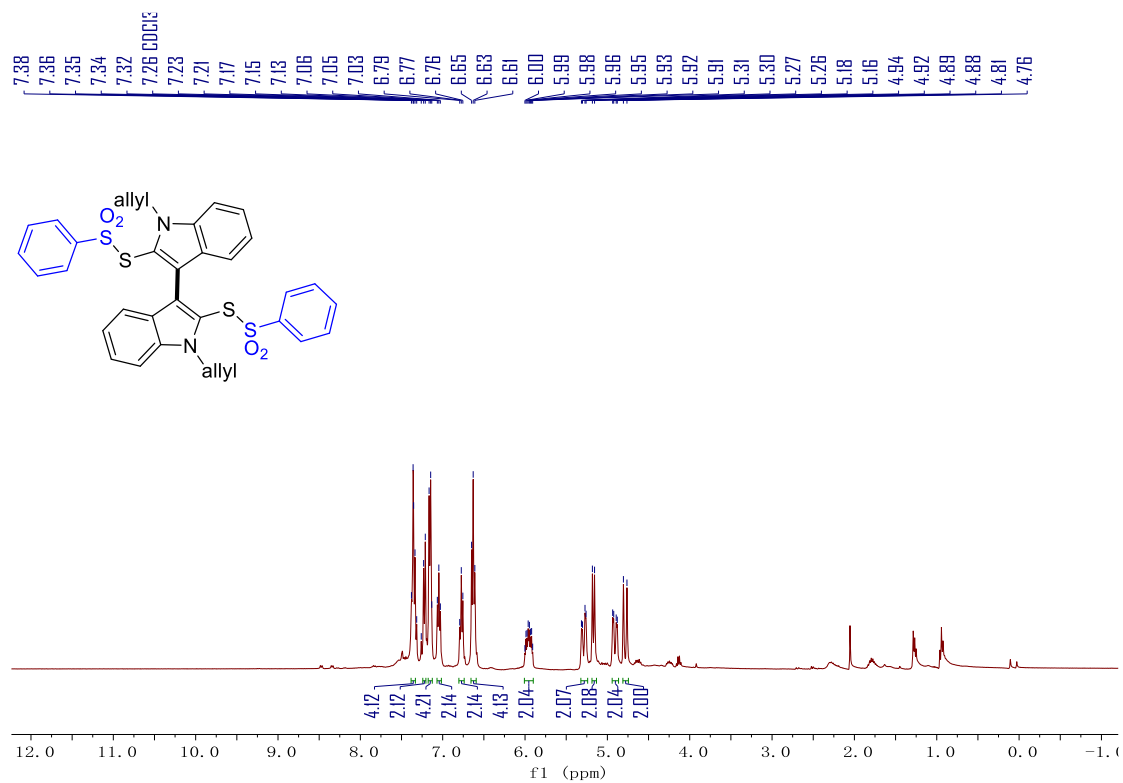
¹H NMR spectra of **3m**



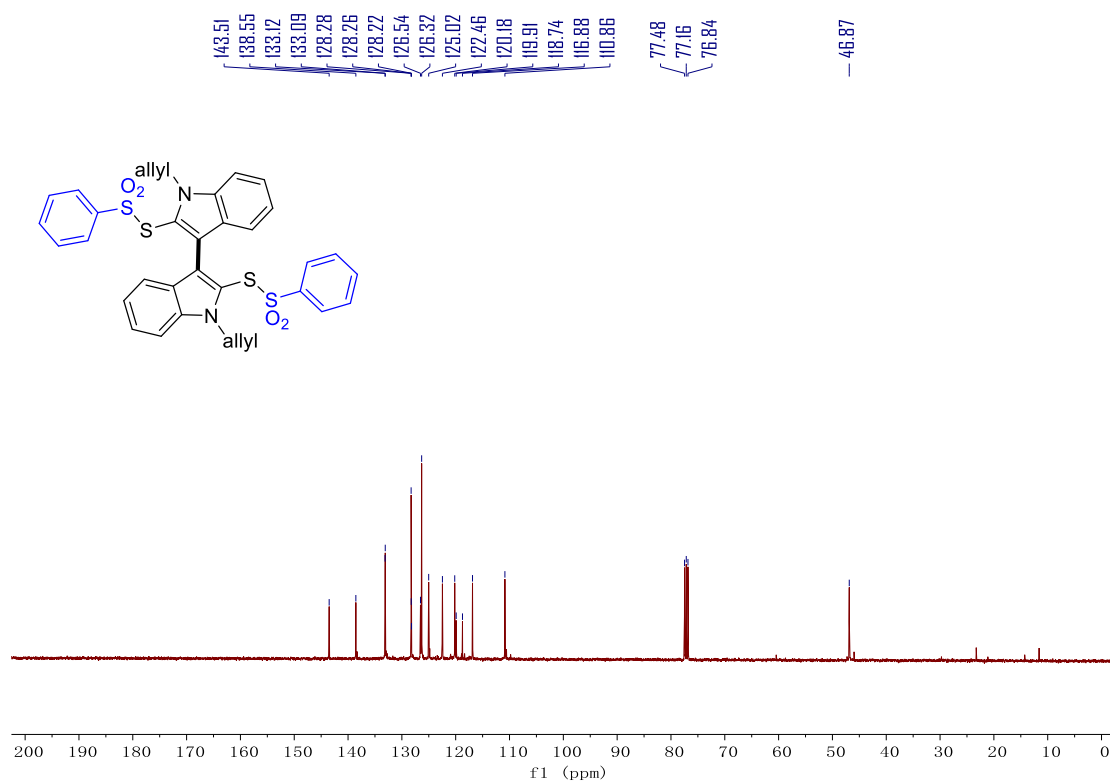
¹³C NMR spectra of **3m**



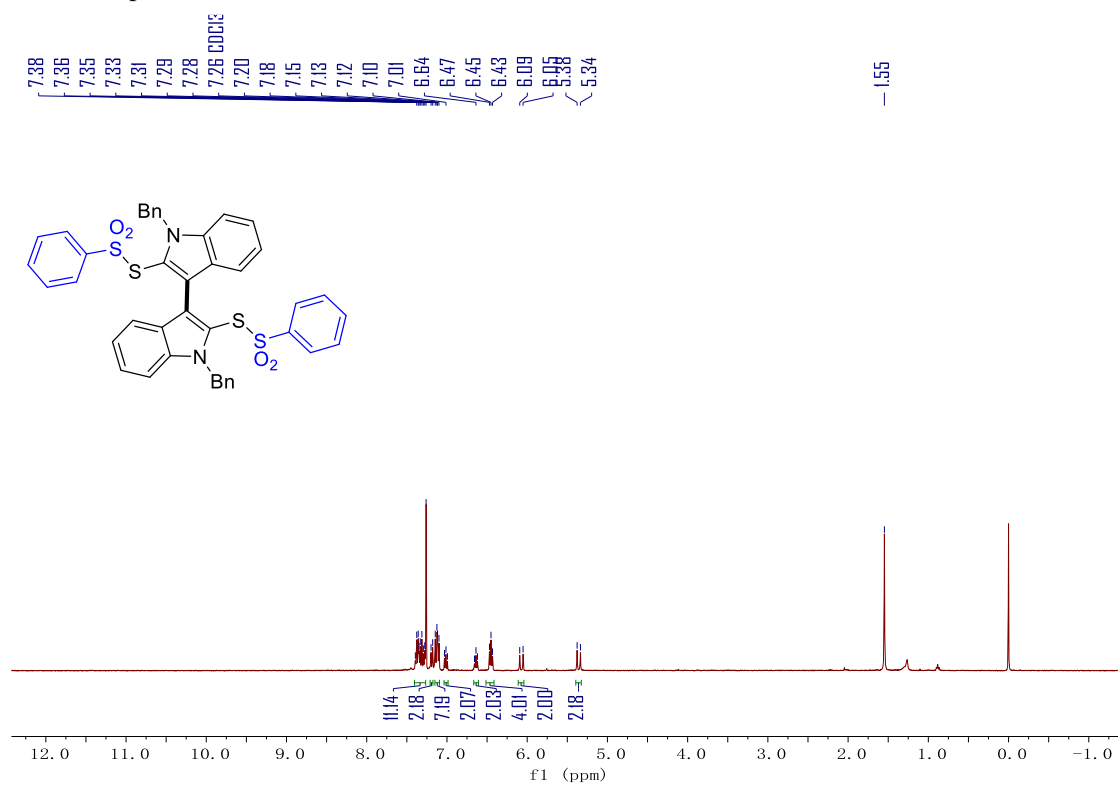
¹H NMR spectra of **3n**



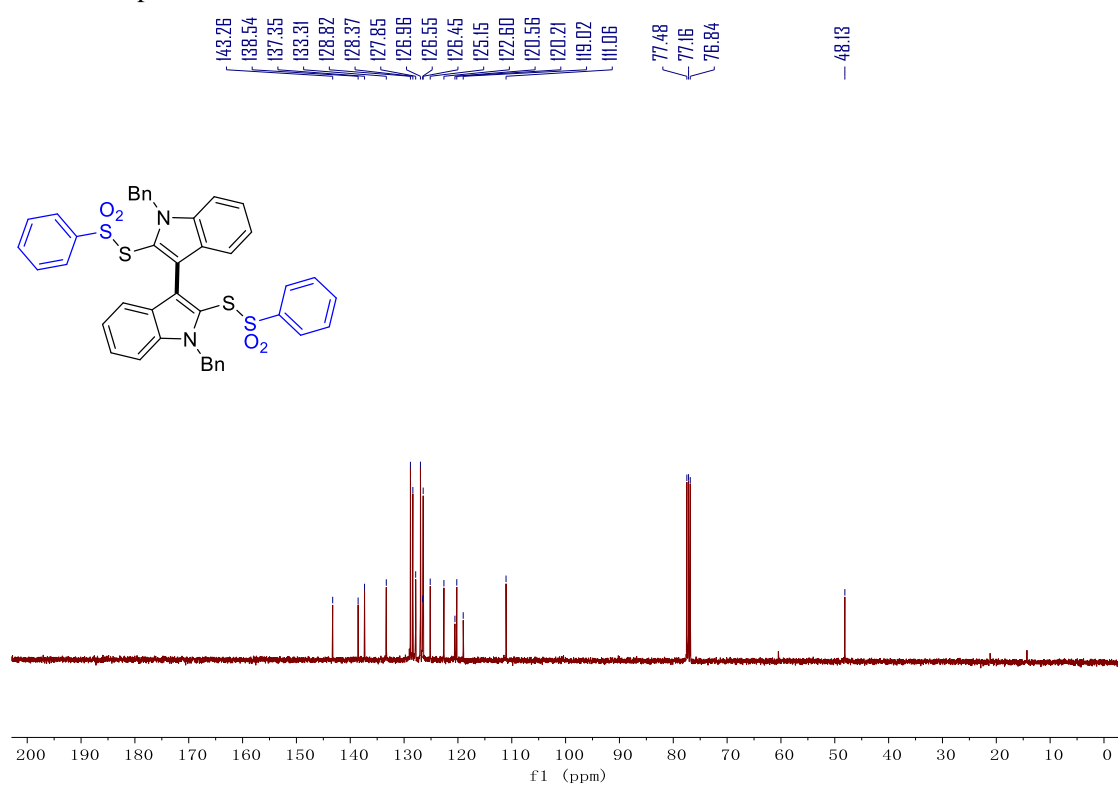
¹³C NMR spectra of **3n**



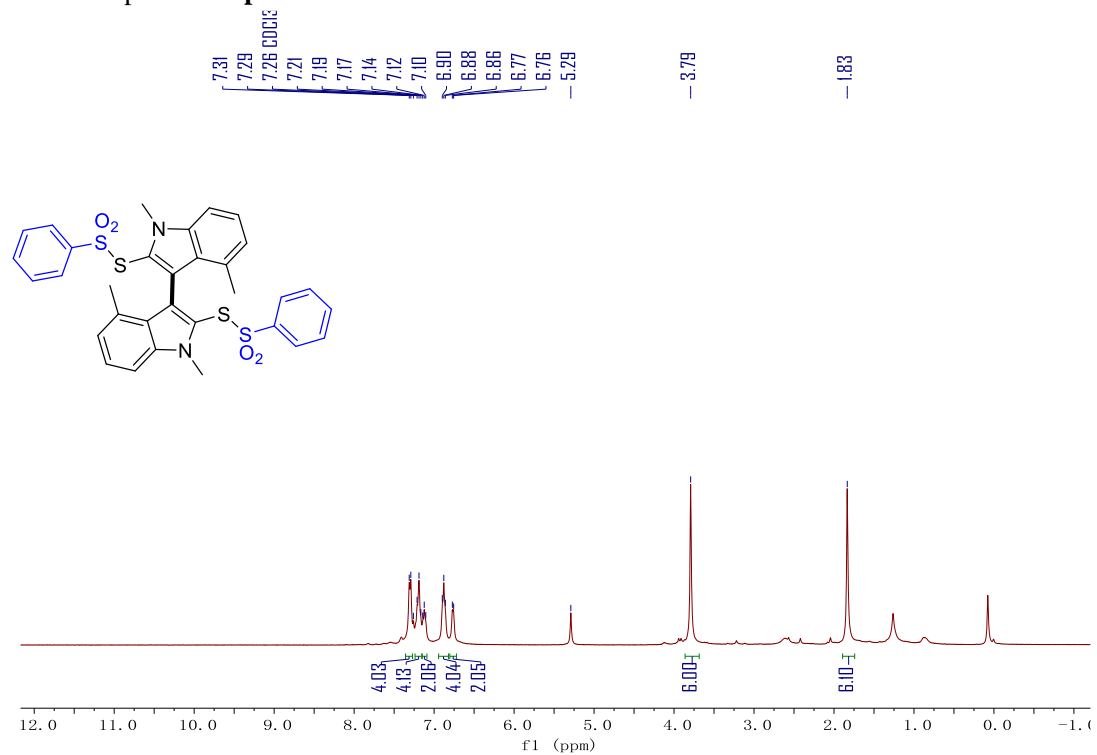
¹H NMR spectra of **3o**



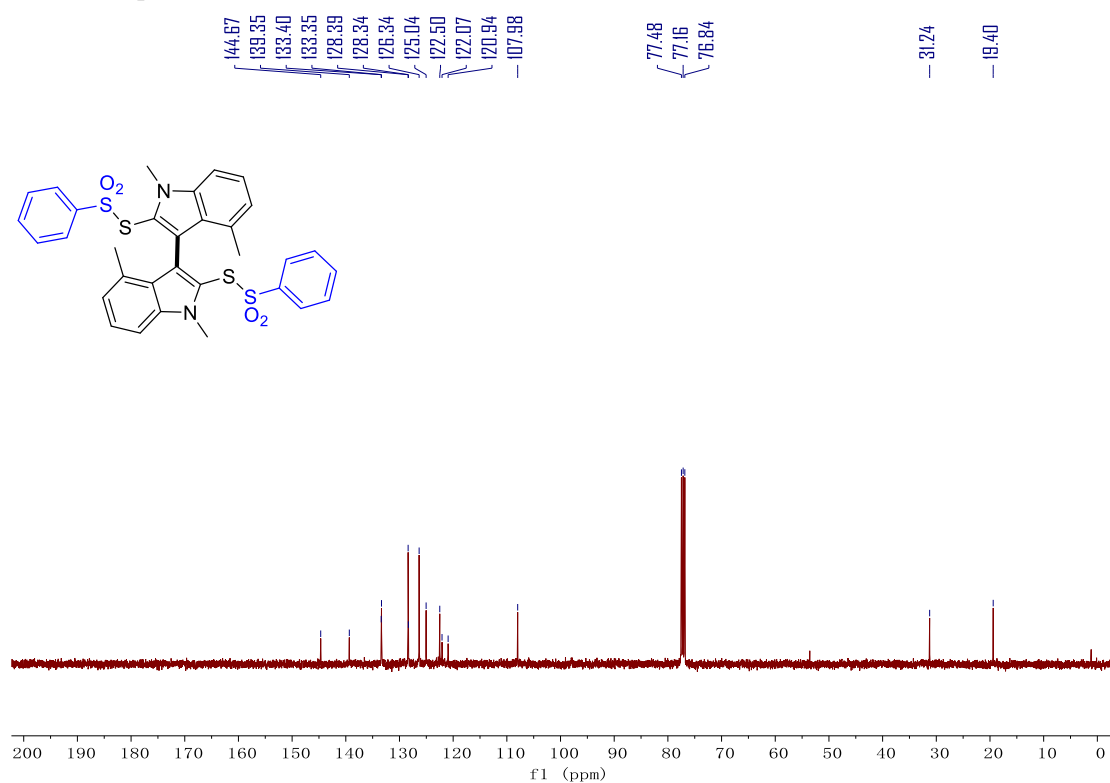
¹³C NMR spectra of **3o**



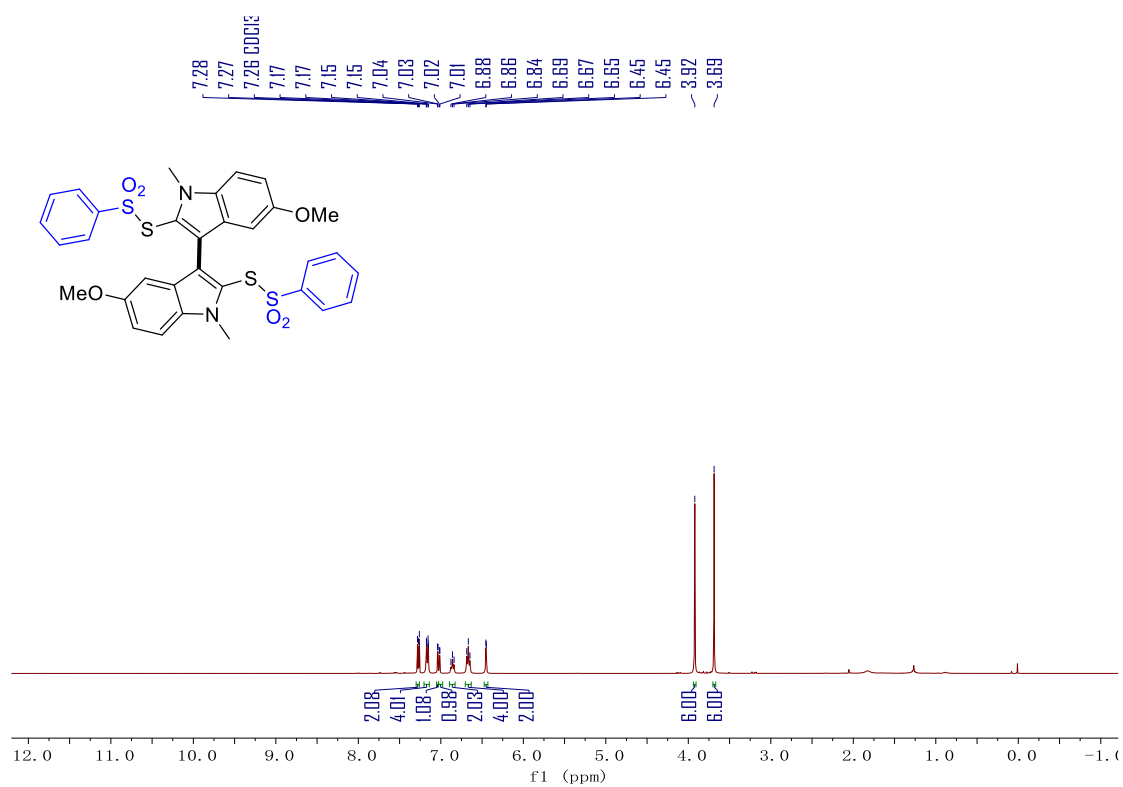
¹H NMR spectra of **3p**



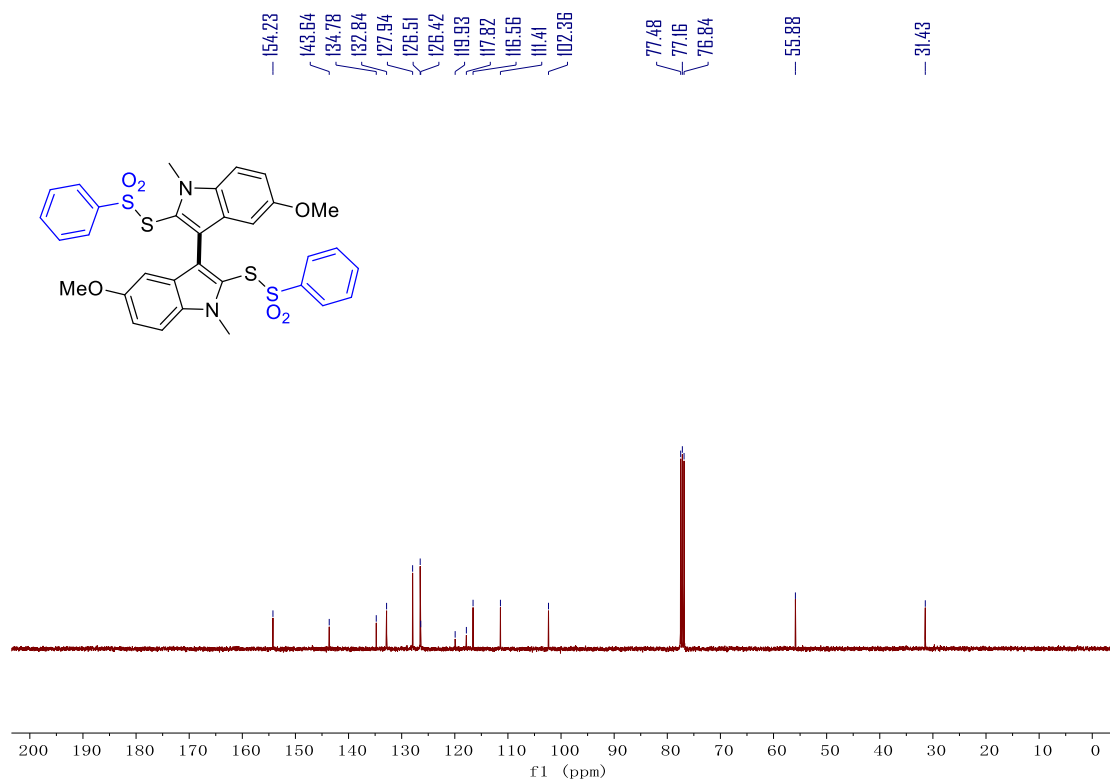
¹³C NMR spectra of **3p**



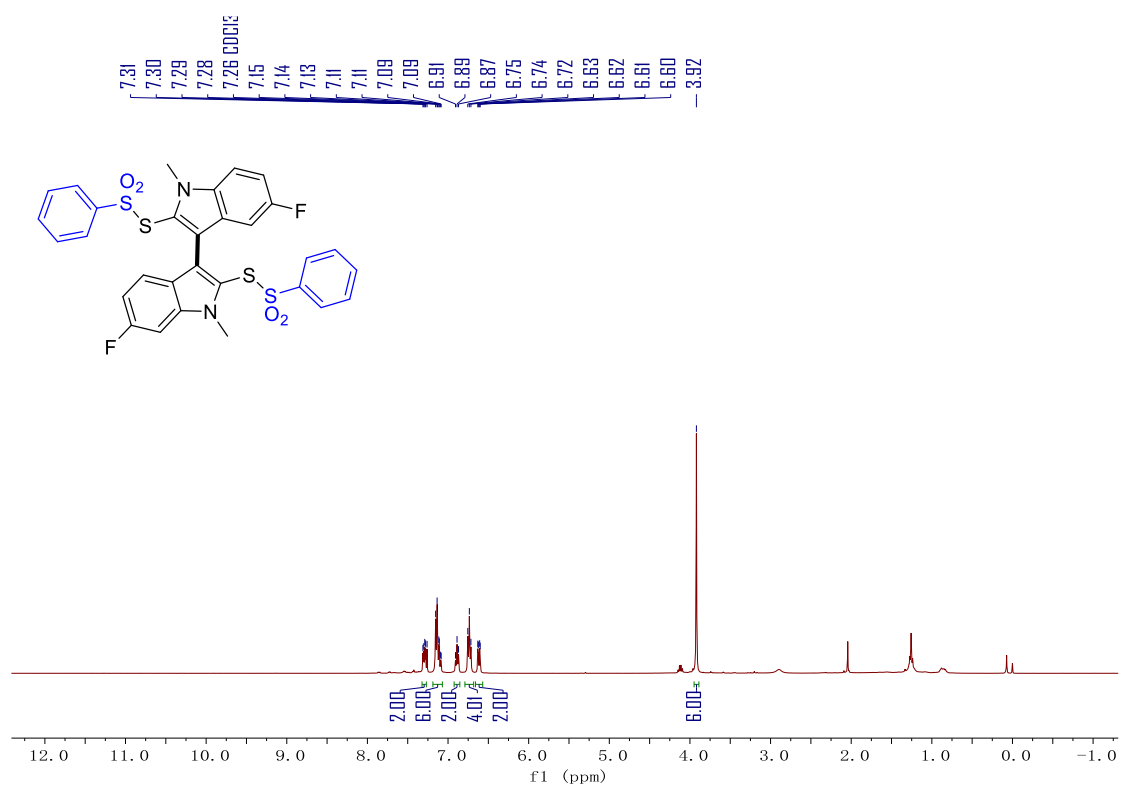
¹H NMR spectra of **3q**



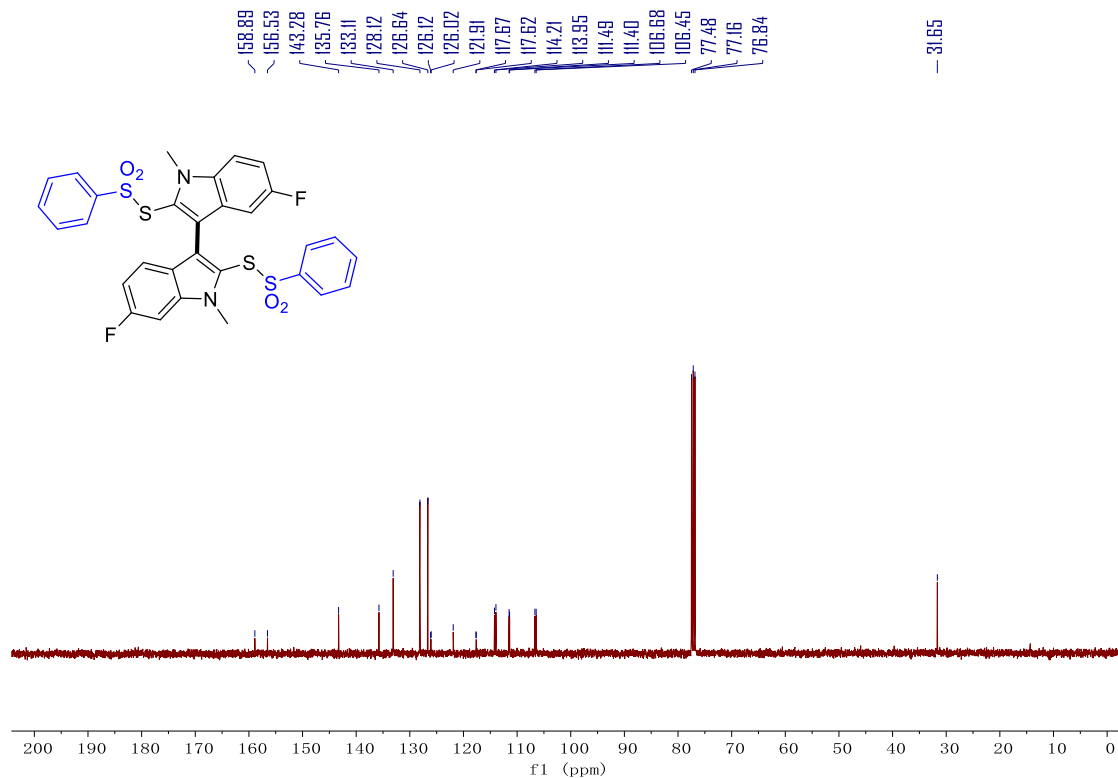
¹³C NMR spectra of **3q**



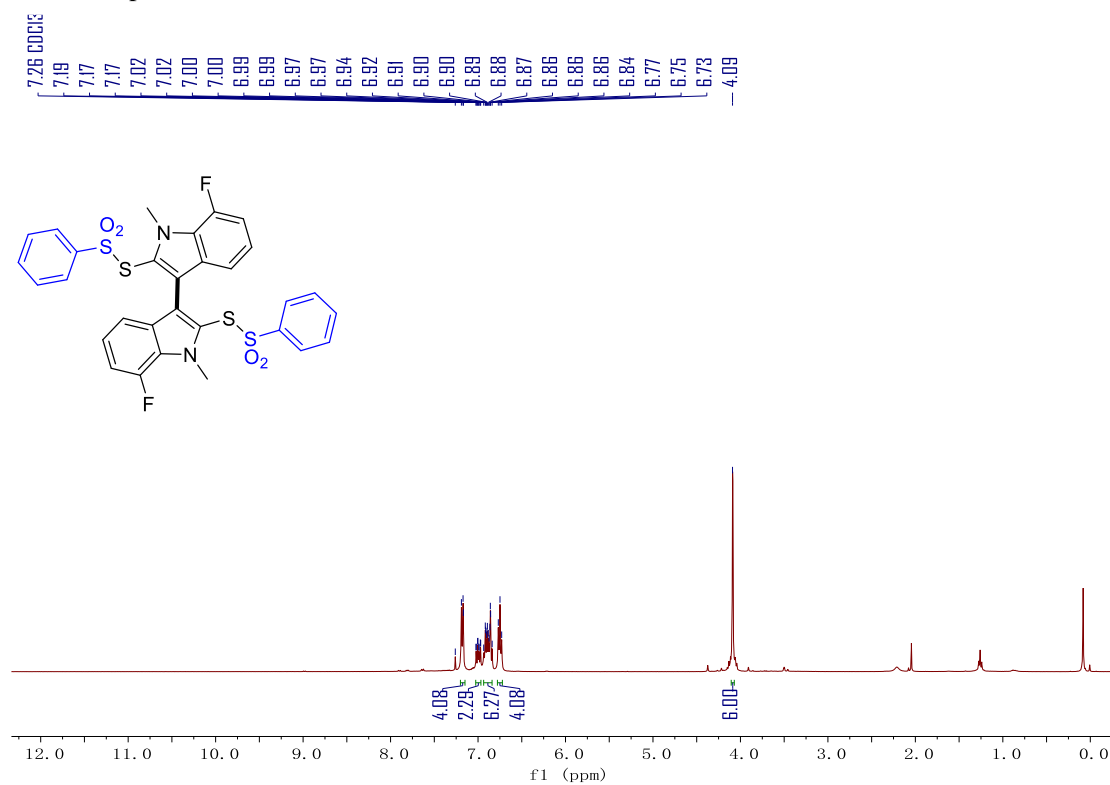
¹H NMR spectra of **3r**



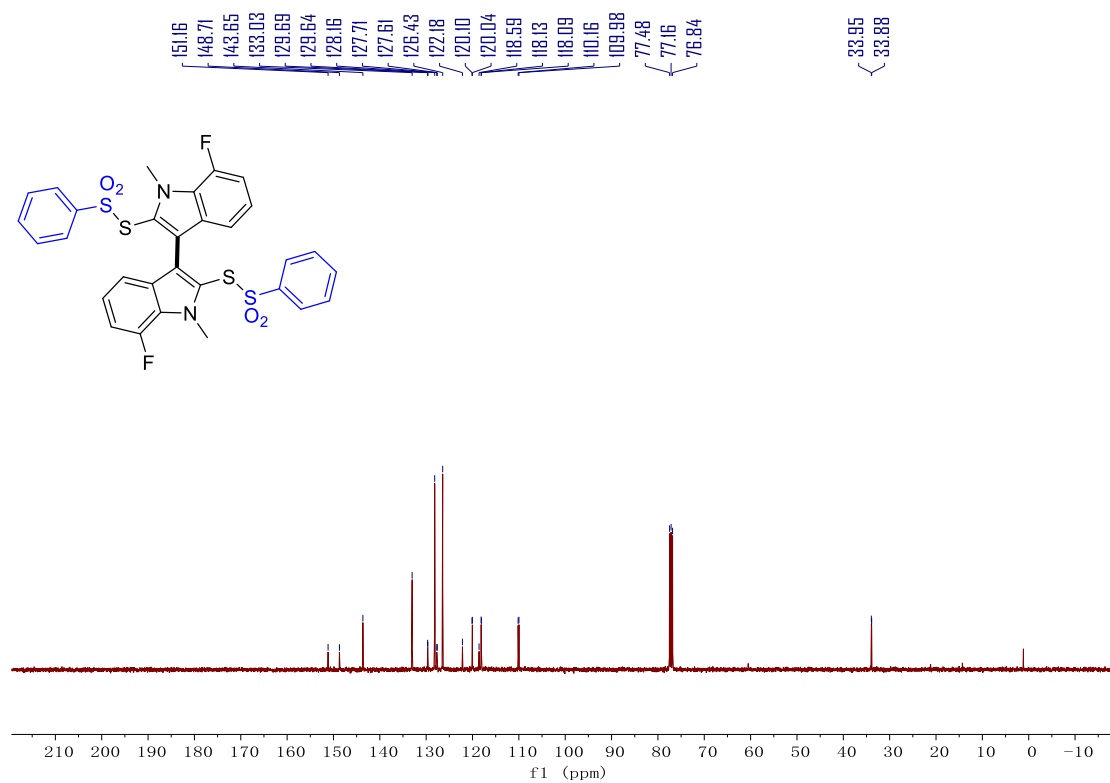
¹³C NMR spectra of **3r**



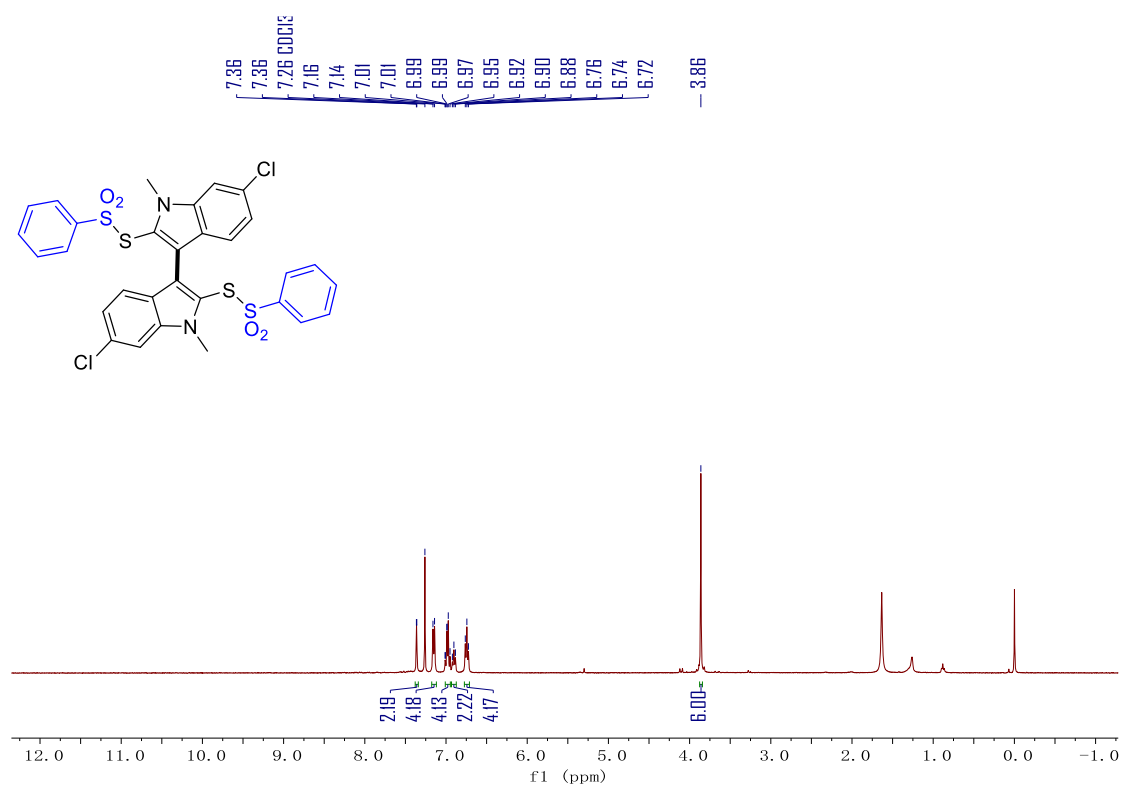
¹H NMR spectra of **3s**



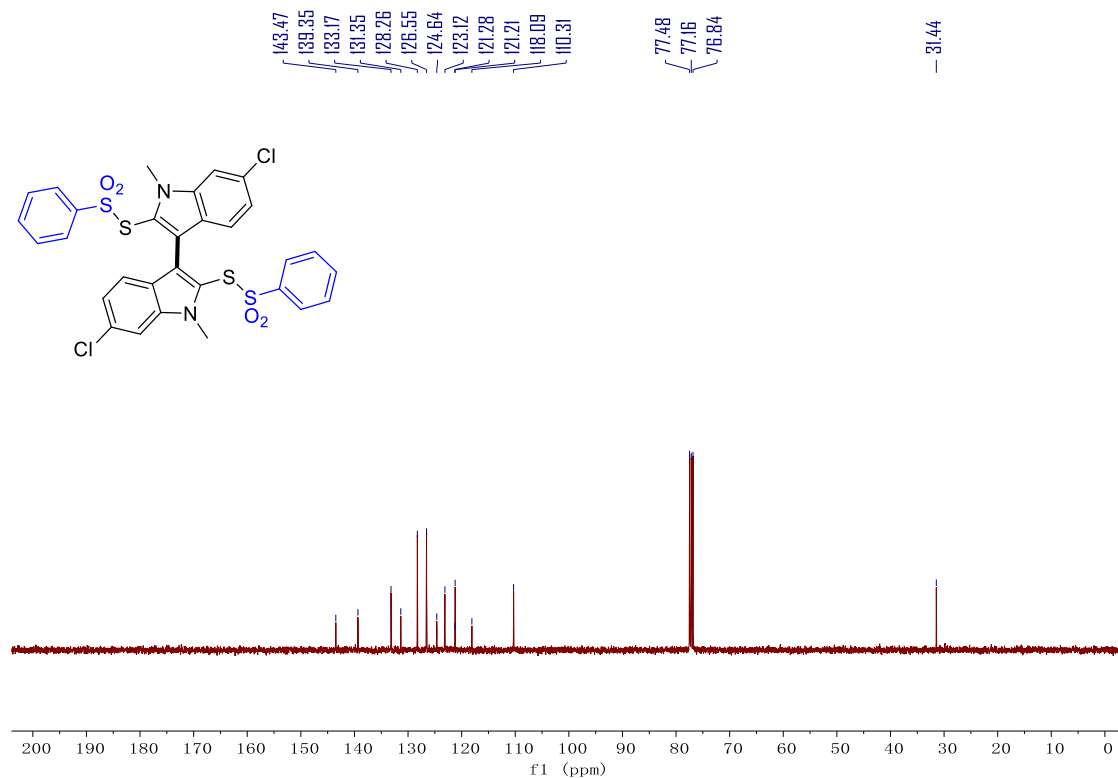
¹³C NMR spectra of **3s**



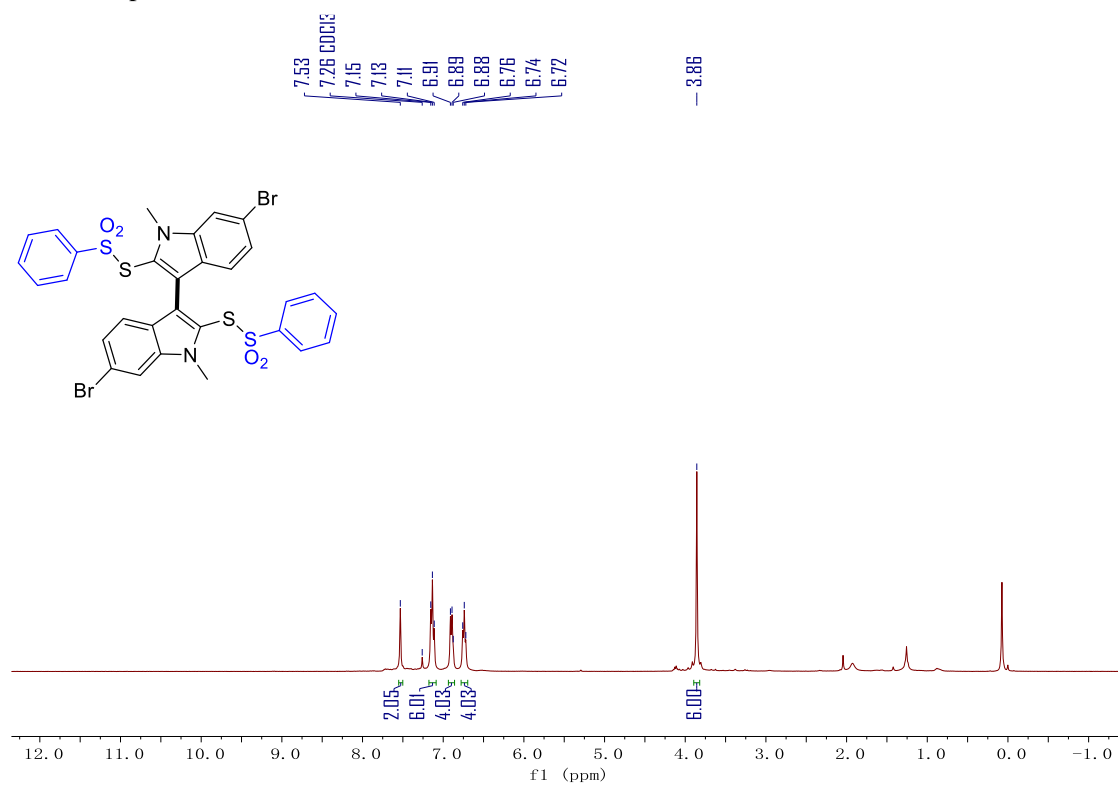
¹H NMR spectra of **3t**



¹³C NMR spectra of **3t**



¹H NMR spectra of **3u**



¹³C NMR spectra of **3u**

