

Supporting Information for

Visible-Light-Induced Synthesis of *N*-Disulfanyl Indoles, Pyrroles or Carbazoles via Construction of Stable S-S-N Bonds

Tianfeng Lao,^a Jianxin Chen,^a Xianhang Zhou,^a Ziwu Zhang,^a Gao Cao,^a Zhengquan
Su,^a Yue Yu*^{a,b} and Hua Cao*^{a,b}

*^a School of Chemistry and Chemical Engineering and Guangdong Cosmetics
Engineering & Technology Research Center, Guangdong Pharmaceutical University,
Zhongshan 528458, China.*

*^b Guangdong Pharmaceutical University-University of Hong Kong Joint Biomedical
Innovation Platform, Zhongshan 528437, China.*

E-mail: caohua@gdpu.edu.cn; yuyue@gdpu.edu.cn

List of Contents

I . General considerations

II . General procedure

III. Control Experiments

IV. Characterization data for 3a-3w,5a-5f ,6a-6h

V . NMR spectra

VI. Reference

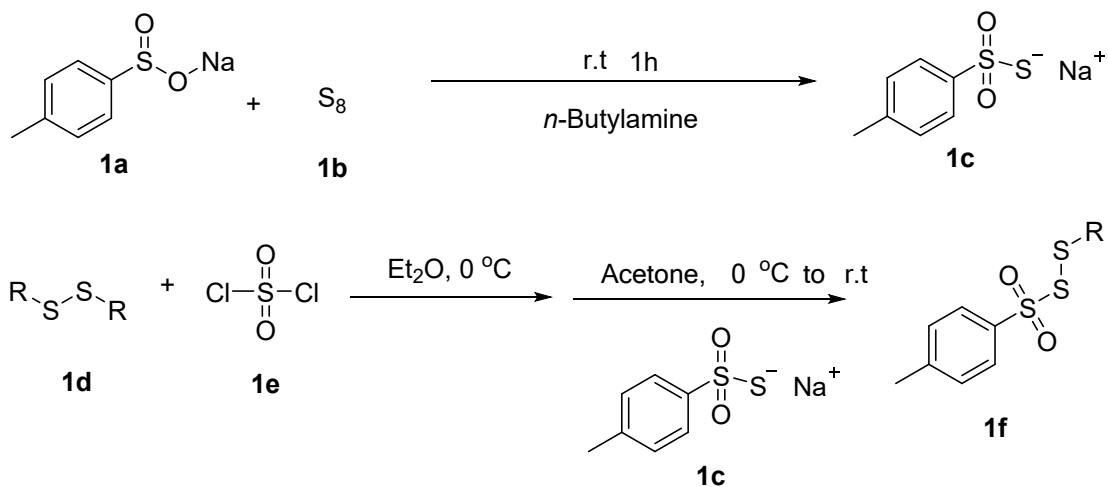
I. General considerations

Analytical thin layer chromatography was carried out using silica gel GF254, visualized under UV light (at 254 nm). ^1H and ^{13}C NMR spectra were recorded using a Bruker DRX-400 spectrometer using CDCl_3 and DMSO as solvents. The chemical shifts are referenced to signals at 7.26, 77.16 ppm and 2.5, 39.6 ppm, respectively. The data of HRMS was carried out on a high-resolution mass spectrometer (ESI-TOF). The data of GC-MS was carried out on a Thermo Scientific Gas Mass Spectrometer (ISQ7000). Analytical thin layer chromatography was performed on 0.20 mm silica gel HSGF-254 plates (Huanghai, China), Column chromatography was performed on 200-300 mesh silica gel (Huanghai, China). Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification.

Photochemical reaction experiment were carried out on a PL-SX100A Model Multi-channel photochemical reaction instrument (the light source is 20 W blue LED, the working current is 0.5-1.7 A, the input power is 120 W, the temperature is controlled by circulating water cooling, and the stirring speed is 0-1500 r/min).

II. General procedure

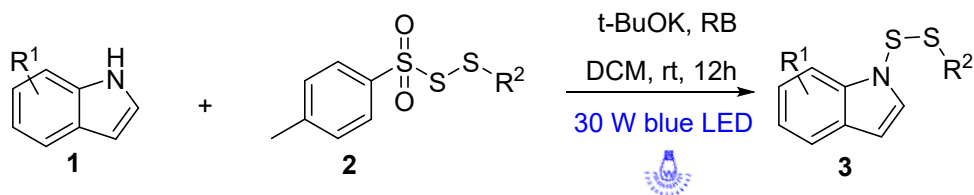
(a) Synthesis of 1a-1f according to the following procedure¹



A mixture of Sodium *p*-tolylsulfinate (3.56 g, 20 mmol) and S₈ (0.64 g, 20 mmol) in *n*-butylamine (20 mL) was stirred at room temperature for 1h. After removal of the solvent under reduced pressure, the residue was washed by Et₂O to obtain a white solid TsSSNa.^[1]

To a solution of disulfide (0.46 mmol) in Et₂O was added sulfonyl chloride (36 μ L, 0.44 mmol) at 0°C. 10 min later, a solution of TsSSNa (2eq) in 2.5 mL of acetone was added dropwise at 0°C. The reaction was then stirred at room temperature for 1h. The mixture was diluted with EtOAc, washed with water and brine, dried over magnesium sulfate, and concentrated in vacuo. The crude residue was purified using silica gel column chromatography.^[2]

(b) General procedure for the synthesis of 3



As exemplified for **3a**: A 25 mL sealed tube was charged with a stirring bar, and indole **1a** (0.0234 g, 2.0 equiv), *SS*-(*tert*-butyl) 4-methylbenzenesulfonyl(dithioperoxoate) **2a** (0.0276 g, 0.1mmol), *t*-BuOK (0.0225 g, 2.0 equiv), rose bengal (0.030 g, 0.03 equiv), DCM (1 mL) were added. The reaction was irradiated with a 30 W blue LED at room temperature stirring for 12 h and monitored by TLC. The

reaction mixture was then diluted with EtOAc and water, extracted with EtOAc. The extract was dried with Na₂SO₄. The solvent was removed with a rotary evaporator. The residue was purified by flash column chromatography (eluent: PE/EtOAc = 60/1, v/v) to give product **3a** (0.0211g, 89% yield).

(c) Large-scale experiment for the synthesis of 3a

An oven-dried 50 mL Schlenk flask was charged with a stirring bar, and indole **1a** (0.9365 g, 2.0 equiv), *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (1.1041 g, 4mmol), *t*-BuOK (0.8977 g, 2.0 equiv), rose bengal (0.1217 g, 0.03 equiv), DCM (15 mL) were added. The reaction was irradiated with a 30 W blue LED at room temperature stirring for 12 h and monitored by TLC. The reaction mixture was then diluted with EtOAc and water, and extracted with EtOAc. The extract was dried with Na₂SO₄. The solvent was removed with a rotary evaporator. The residue was purified by flash column chromatography (eluent: PE/EtOAc = 60/1, v/v) to give product **3a** (0.7395 g, 78% yield).

III. Control Experiments

(a) Radical Capture Experiment

Radical capture experiment were performed using a Thermo Scientific Gas Mass Spectrometer (ISQ7000). Follow the reaction conditions: **2a** (0.2 mmol), 1,1-Diphenylethylene (0.1 mmol), TEMPO (0.1 mmol), RB(3 mol%), DCM(1 mL) was stirred at room temperature and blue LEDs (30 W) for 12 h.

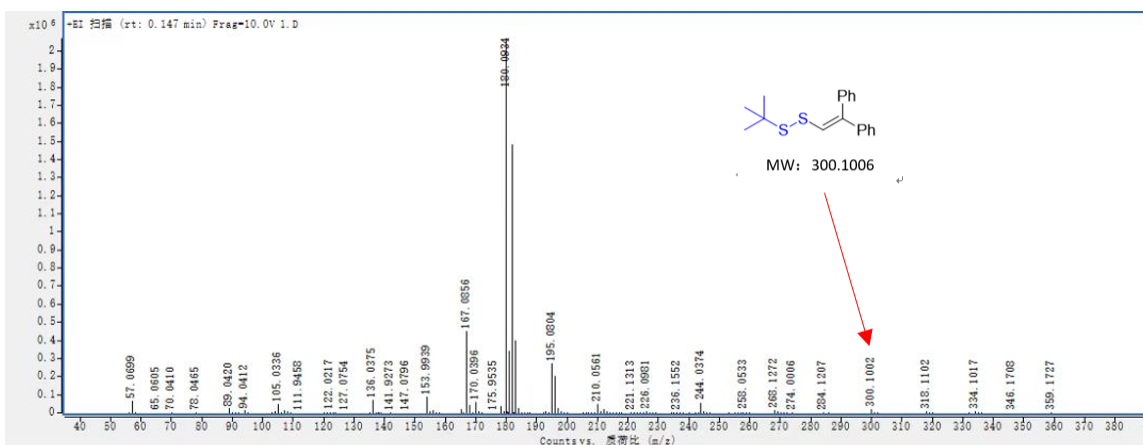
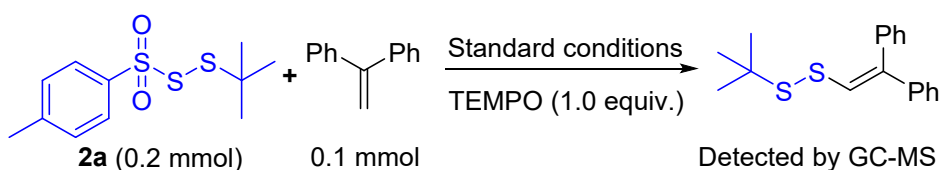


Figure S1. The capture of free radical **2a**

(b) Time profile of the transformation with the light ON/OFF over time

Standard reactions were set up parallel on a 0.40 mmol scale according to the condition. After being irradiated for 2h, an aliquot (200 μ L) from the reaction mixture was transferred into a nuclear magnetic tube charged with 0.5 mL of CDCl_3 . The yield of product **3g** was determined by ^{19}F NMR. Then the reaction mixture was stirred for 2h with light-off. All of the following yields were analyzed in the identical way after a 2 hour light on or off.

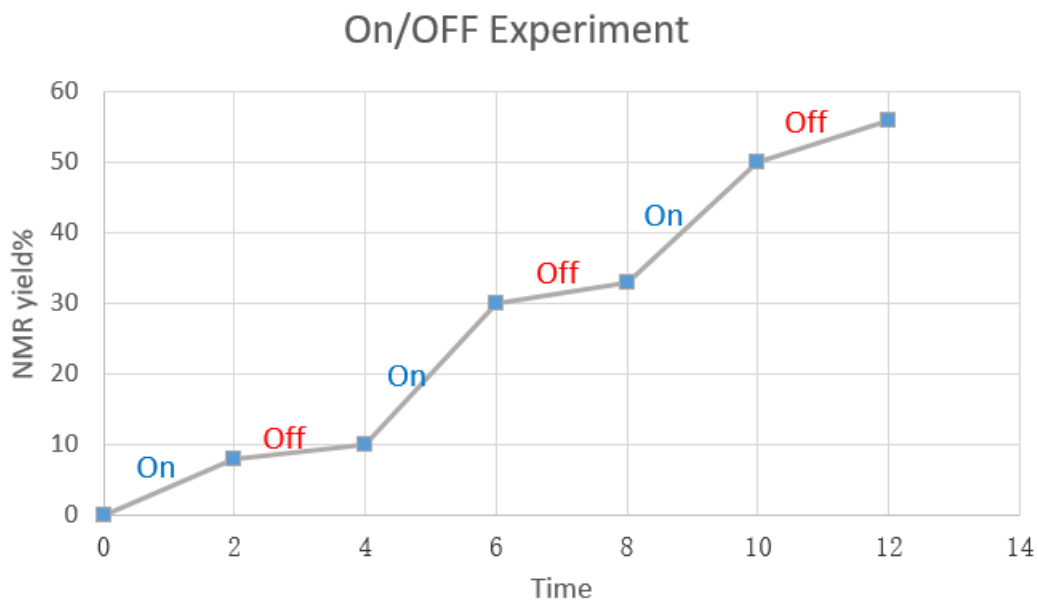


Figure S2. Time profile of the transformation with the light ON/OFF over time.

(c) Fluorescence quenching experimental procedure.

Firstly, a series of DCM solution of indole with concentration of $(0, 1, 3, 5, 7, 9) \times 10^{-3}$ mol/L, which contain RB with concentration of 1×10^{-4} mol/L, were prepared. Then the fluorescence intensity of these solutions was measured and the Stern-Volmer plot was obtained as follow. And we got R^2 value (0.89) and K_{sv} (11286 L/mol) from it.

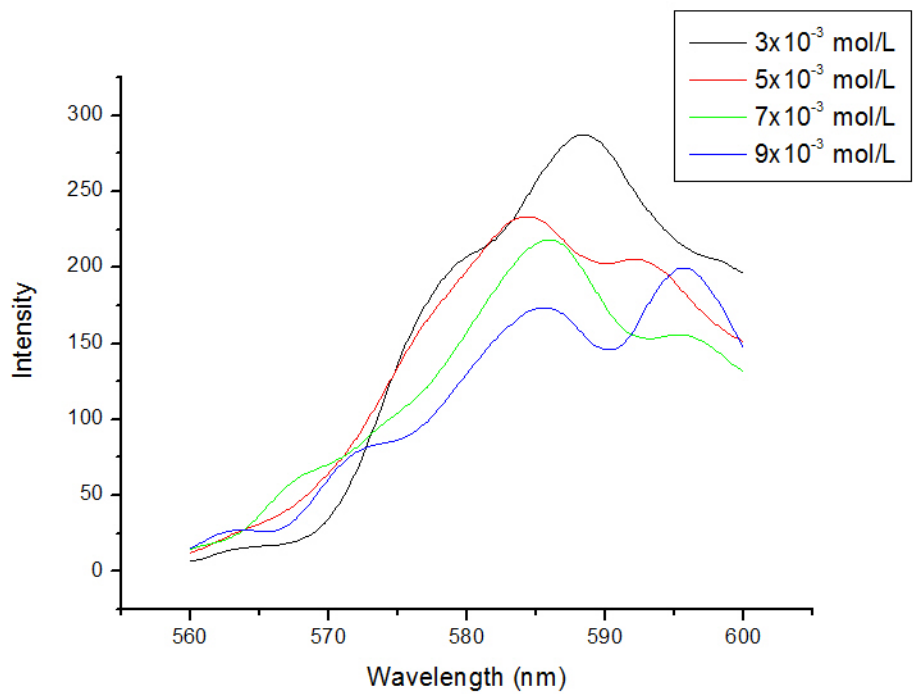
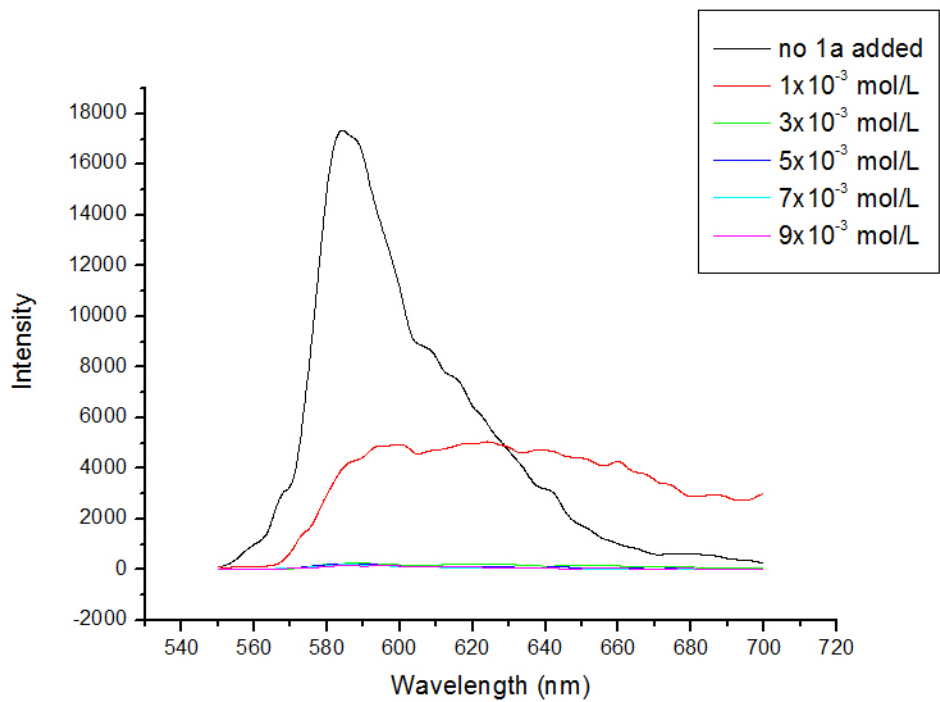


Figure S3. Quenching experiments of RB with indole.

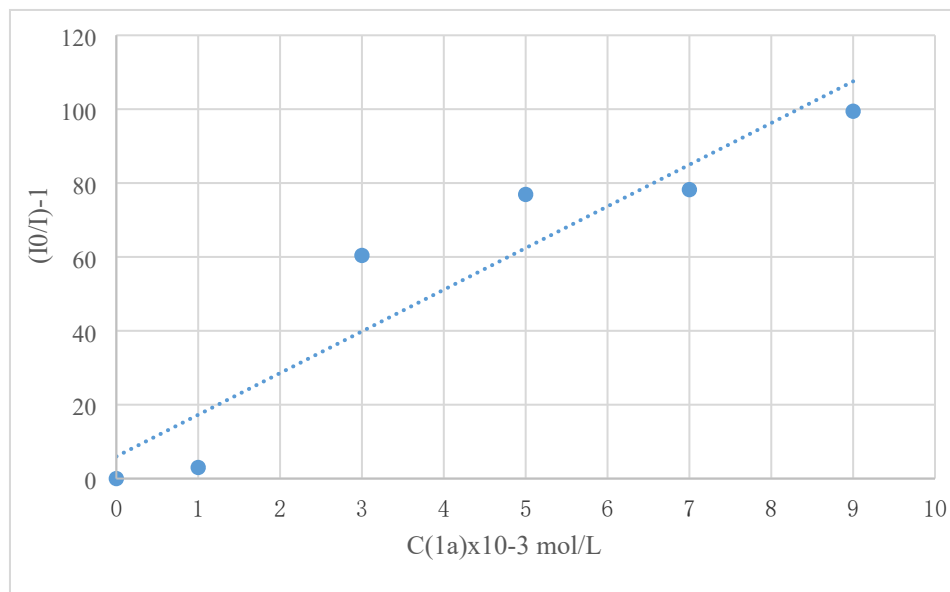


Figure S4. Stern-Volmer Plot of Fluorescence Quenching Experiments

The Stern-Volmer analysis revealed that the excited state of RB photoredox catalysis is efficiently quenched by indole in DCM at room temperature. In addition, indole itself has fluorescence intensity in 560nm-600nm.

(d) Conditional screening experiments

Table 1 Optimization of the reaction conditions^a

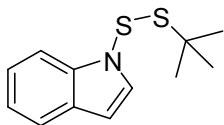
Reaction scheme: 1a + 2a $\xrightarrow[\text{base, solvent}]{\text{photocatalyst}}$ 3a

entry	photocatalyst	base	solvent	yield ^b (%)
15	rose bengal	/	DCM	trace
16 ^c	rose bengal	<i>t</i> -BuOK	DCM	13
17 ^d	/	<i>t</i> -BuOK	DCM	27
18 ^e	rose bengal	<i>t</i> -BuOK	DCM	78

^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), photocatalyst (3 mol%), base (0.2 mmol), solvent (1 mL), and irradiation with a 30 W blue LED for 12 h, room temperature, air atmosphere; ^b Determined by GC-MS.

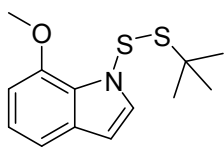
IV. Characterization data for 3a-3q, 5a-5f, 6a-6h

1-(*tert*-butyldisulfanyl)-1*H*-indole (3a)



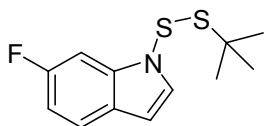
Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **3a**. Brown liquid (63.3mg, 89%) ^1H NMR (400 MHz, CDCl_3) δ ppm 7.61 (d, $J = 8.2$ Hz, 1H), 7.50 (d, $J = 7.8$ Hz, 1H), 7.23 (t, $J = 7.4$ Hz, 1H), 7.15-7.05 (m, 2H), 6.47 (d, $J = 3.4$ Hz, 1H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 139.7, 133.1, 129.8, 122.9, 121.3, 121.1, 111.9, 105.9, 48.6, 30.3. HRMS (ESI): m/z $[\text{M}]^+$ Calcd for $\text{C}_{12}\text{H}_{15}\text{NS}_2$ 237.0646, Found: 237.0643.

1-(tert-butylidisulfanyl)-5-methoxy-1H-indole (3b)



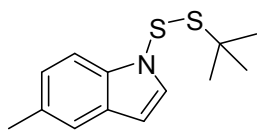
Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **3b**. Brown liquid (64.9 mg, 81%); ^1H NMR (400 MHz, CDCl_3) δ ppm 7.08 (d, $J = 7.8$ Hz, 1H), 7.04-6.96 (m, 2H), 6.64 (d, $J = 7.8$ Hz, 1H), 6.40 (d, $J = 3.2$ Hz, 1H), 3.90 (s, 3H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 148.2, 135.3, 132.5, 128.5, 122.2, 114.0, 106.3, 105.0, 55.7, 48.7, 30.2. HRMS (ESI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{13}\text{H}_{17}\text{NOS}_2$ 267.0752, found: 267.0757.

1-(tert-butylidisulfanyl)-6-fluoro-1H-indole (3c)



Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **3c**. Yellow liquid (59.7 mg, 78%); ^1H NMR (400 MHz, CDCl_3) δ ppm 7.47 (dd, $J = 8.6, 5.2$ Hz, 1H), 7.36 (d, $J = 9.6$ Hz, 1H), 7.17 (d, $J = 3.4$ Hz, 1H), 6.93 (t, $J = 9.1$ Hz, 1H), 6.51 (d, $J = 3.4$ Hz, 1H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 160.4(d, $J = 239.5$ Hz), 140.2(d, $J = 12.0$ Hz), 133.4(d, $J = 4.0$ Hz), 126.1, 121.8(d, $J = 9.8$ Hz), 109.9(d, $J = 24.5$ Hz), 105.8, 98.7(d, $J = 26.9$ Hz), 48.8, 30.3. ^{19}F NMR (376 MHz, CDCl_3) δ ppm -119.06. HRMS (ESI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{12}\text{H}_{14}\text{FNS}_2$ 255.0552, found: 255.0548.

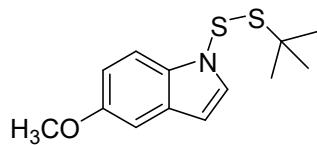
1-(tert-butylidisulfanyl)-5-methyl-1H-indole (3d)



Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **3d**. Brown liquid (64.0 mg, 85%); ^1H NMR (400 MHz, CDCl_3) δ ppm 7.54 (d, $J = 8.4$ Hz, 1H), 7.33 (s, 1H), 7.14-7.07 (m, 2H), 6.44 (d, $J = 3.1$ Hz, 1H), 2.42 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 138.1, 133.3, 130.7, 130.2,

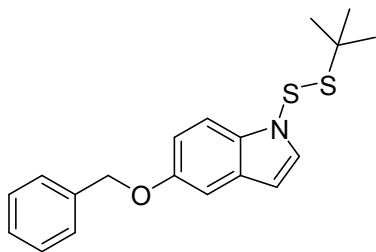
124.5, 121.1, 111.7, 105.6, 48.5, 30.4, 21.5. HRMS (ESI) m/z : $[M]^+$ Calcd for $C_{13}H_{17}NS_2$ 251.0802, found: 251.0796.

1-(*tert*-butyldisulfanyl)-5-methoxy-1*H*-indole (**3e**)



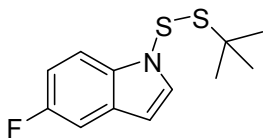
Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **3e**. Brown liquid (67.3 mg, 84%); 1H NMR (400 MHz, $CDCl_3$) δ ppm 7.55 (d, J = 8.9 Hz, 1H), 7.16 (d, J = 3.3 Hz, 1H), 7.04 (d, J = 2.3 Hz, 1H), 6.95 (d, J = 8.9 Hz, 1H), 6.47 (d, J = 3.4 Hz, 1H), 3.84 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 155.3, 134.6, 133.9, 130.4, 112.6, 112.6, 105.7, 103.3, 55.8, 48.5, 30.3. HRMS (ESI) m/z : $[M]^+$ Calcd for $C_{13}H_{17}NOS_2$ 267.0752, found: 267.0750.

SS-benzyl diphenylphosphino(dithioperoxoate) (**3f**)



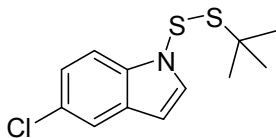
Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **3f**. Brown liquid (74.1 mg, 72%); 1H NMR (400 MHz, $CDCl_3$) δ ppm 7.71 (d, J = 8.9 Hz, 1H), 7.58 (d, J = 5.0 Hz, 2H), 7.55-7.41 (m, 3H), 7.27 (d, J = 16.0 Hz, 2H), 7.17 (d, J = 9.0 Hz, 1H), 6.59 (s, 1H), 5.20 (s, 2H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 154.6, 137.6, 134.9, 134.0, 130.5, 128.7, 128.0, 127.7, 113.5, 112.8, 105.9, 104.9, 70.8, 48.7, 30.5. HRMS (ESI) m/z : $[M]^+$ Calcd for $C_{19}H_{21}NOS_2$ 343.1065, found: 343.1060.

1-(*tert*-butyldisulfanyl)-5-fluoro-1*H*-indole (**3g**)



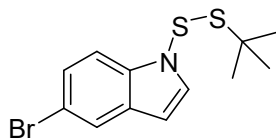
Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **3g**. Yellow liquid (63.5 mg, 83%); 1H NMR (400 MHz, $CDCl_3$) δ ppm 7.57 (dd, J = 8.9, 4.4 Hz, 1H), 7.25-7.17 (m, 2H), 7.03 (t, J = 9.1 Hz, 1H), 6.48 (d, J = 3.2 Hz, 1H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 158.9(d, J = 236.5 Hz), 136.1, 134.8, 130.3(d, J = 10.3 Hz), 112.7(d, J = 9.7 Hz), 111.1(d, J = 26.1 Hz), 106.3(d, J = 23.8 Hz), 105.8(d, J = 4.4 Hz), 48.7, 30.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -123.4. HRMS (ESI) m/z : $[M]^+$ Calcd for $C_{12}H_{14}FNS_2$ 255.0552, found: 255.0558.

1-(*tert*-butyldisulfanyl)-5-chloro-1*H*-indole (**3h**)



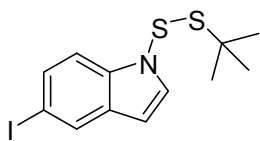
Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **3h**. Yellow liquid (62.6mg, 77%); ^1H NMR (400 MHz, CDCl_3) δ ppm 7.57 (d, $J = 8.7$ Hz, 1H), 7.53 (s, 1H), 7.23 (d, $J = 2.0$ Hz, 1H), 7.21 (d, $J = 3.4$ Hz, 1H), 6.47 (d, $J = 3.2$ Hz, 1H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.1, 134.4, 130.9, 127.1, 123.2, 120.6, 112.9, 105.4, 48.8, 30.3. HRMS (ESI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{12}\text{H}_{14}\text{ClNS}_2$ 271.0256, found: 271.0248.

5-bromo-1-(*tert*-butyldisulfanyl)-1*H*-indole (**3i**)



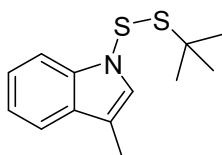
Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **3i**. Yellow liquid (73.7 mg, 78%); ^1H NMR (400 MHz, CDCl_3) δ ppm 7.60 (s, 1H), 7.44 (d, $J = 8.6$ Hz, 1H), 7.28 (d, $J = 8.7$ Hz, 1H), 7.09 (d, $J = 3.4$ Hz, 1H), 6.37 (d, $J = 3.4$ Hz, 1H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 138.4, 134.3, 131.5, 125.8, 123.7, 114.7, 113.4, 105.3, 48.8, 30.3. HRMS (ESI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{12}\text{H}_{14}\text{BrNS}_2$ 314.9751, found: 314.9749.

1-(*tert*-butyldisulfanyl)-5-iodo-1*H*-indole (**3j**)



Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **3j**. Brown liquid (90.4 mg, 83%); ^1H NMR (400 MHz, CDCl_3) δ ppm 7.92 (s, 1H), 7.57 (d, $J = 8.6$ Hz, 1H), 7.45 (d, $J = 8.6$ Hz, 1H), 7.17 (d, $J = 3.4$ Hz, 1H), 6.48 (d, $J = 3.5$ Hz, 1H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 139.0, 133.9, 132.3, 131.3, 130.0, 113.9, 105.0, 85.2, 48.8, 30.3. HRMS (ESI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{12}\text{H}_{14}\text{INS}_2$ 362.9612, found: 362.9611.

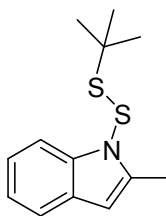
1-(*tert*-butylthio)-3-methyl-1*H*-indole (**3k**)



Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to

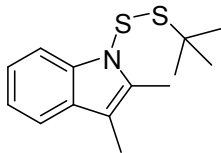
afford **3k**. Purple liquid (61.8 mg, 85%); ^1H NMR (400 MHz, CDCl_3) δ ppm 7.55 (d, $J = 8.2$ Hz, 1H), 7.41 (d, $J = 7.8$ Hz, 1H), 7.20 (t, $J = 7.6$ Hz, 1H), 7.09 (d, $J = 7.6$ Hz, 1H), 6.84 (s, 1H), 2.17 (s, 3H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 140.4, 130.7, 130.1, 122.9, 120.9, 119.2, 115.2, 111.9, 48.4, 30.5, 9.9. HRMS (ESI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{13}\text{H}_{17}\text{NS}_2$ 251.0802; Found: 251.0808.

1-(*tert*-butylthio)-3-methyl-1*H*-indole (**3l**)



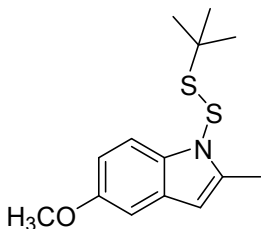
Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **3l**. Purple liquid (60.3 mg, 80%); ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ ppm 7.60 (d, $J = 8.1$ Hz, 1H), 7.45 (d, $J = 7.6$ Hz, 1H), 7.22 (t, $J = 7.6$ Hz, 1H), 7.09 (t, $J = 7.5$ Hz, 1H), 6.44 (s, 1H), 2.52 (s, 3H), 1.26 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 140.8, 140.5, 129.5, 122.2, 121.7, 120.4, 119.9, 112.2, 105.2, 49.1, 30.3, 13.8. HRMS (ESI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{13}\text{H}_{17}\text{NS}_2$ 251.0802; Found: 251.0802.

1-(*tert*-butyldisulfanyl)-2,3-dimethyl-1*H*-indole (**3m**)



Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **3m**. Brown liquid (58.9 mg, 74%); ^1H NMR (400 MHz, CDCl_3) δ ppm 7.53 (d, $J = 8.4$ Hz, 1H), 7.31 (d, $J = 7.9$ Hz, 1H), 7.12 (t, $J = 7.8$ Hz, 1H), 7.08-6.99 (m, 1H), 2.38 (s, 3H), 2.10 (s, 3H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 140.2, 136.0, 130.6, 121.8, 120.9, 118.2, 111.9, 111.5, 48.4, 30.5, 11.3, 9.4. HRMS (ESI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{14}\text{H}_{19}\text{NS}_2$ 265.0959, found: 265.0957.

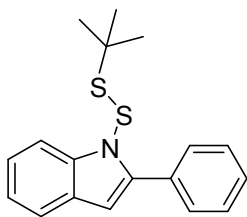
1-(*tert*-butyldisulfanyl)-5-methoxy-2-methyl-1*H*-indole (**3n**)



Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **3n**. Colourless liquid (57.3 mg, 68%); ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ ppm 7.47 (d, $J = 8.8$ Hz, 1H), 6.98 (s, 1H), 6.84 (dd, $J = 8.8$,

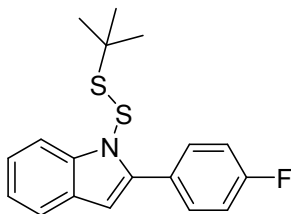
2.4 Hz, 1H), 6.37 (s, 1H), 3.75 (s, 3H), 2.49 (s, 3H), 1.26 (s, 9H). ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$) δ ppm 155.3, 141.5, 135.3, 130.1, 112.7, 111.2, 105.3, 103.1, 55.7, 49.0, 30.3, 13.8. HRMS (ESI) m/z : $[\text{M}]^+$: Calcd for $\text{C}_{14}\text{H}_{19}\text{NOS}_2$ 281.0908, found: 281.0902.

1-(*tert*-butyldisulfanyl)-2-phenyl-1*H*-indole (3o)



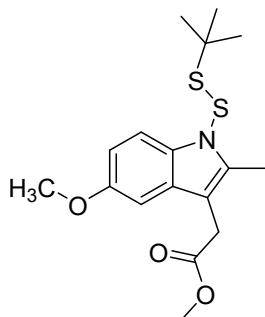
Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **3o**. Yellow liquid (61.1 mg, 65%); ^1H NMR (400 MHz, CDCl_3) δ ppm 7.66 (d, J = 8.2 Hz, 1H), 7.55 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 7.8 Hz, 1H), 7.36 (t, J = 7.5 Hz, 2H), 7.29 (d, J = 7.1 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 6.61 (s, 1H), 0.88 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 145.1, 141.9, 132.4, 130.1, 130.1, 128.3, 128.1, 123.1, 122.1, 120.9, 113.4, 107.0, 48.5, 30.2. HRMS (ESI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{18}\text{H}_{19}\text{NS}_2$ 313.0959, found: 313.0954.

1-(*tert*-butyldisulfanyl)-2-(4-fluorophenyl)-1*H*-indole (3p)



Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **3p**. Yellow liquid (59.6mg, 60%); ^1H NMR (400 MHz, CDCl_3) δ ppm 7.74 (d, J = 8.2 Hz, 1H), 7.65-7.53 (m, 3H), 7.37-7.28 (m, 1H), 7.25-7.12 (m, 3H), 6.67 (s, 1H), 1.01 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 162.6(d, J = 248.2 Hz), 143.9, 141.8, 131.7 (d, J = 8.1 Hz), 129.8, 128.5, 128.5, 122.6(d, J = 104.1 Hz), 120.8, 115.4(d, J = 21.6 Hz), 113.3, 107.0, 48.6, 30.2. ^{19}F NMR (376 MHz, CDCl_3) δ ppm -113.93. HRMS (ESI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{18}\text{H}_{18}\text{FNS}_2$ 331.0865, found: 331.0866.

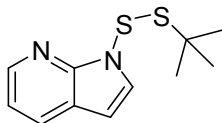
Methyl 2-(1-(*tert*-butyldisulfanyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (3q)



Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **3q**. Colourless liquid (65.7 mg, 62%); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ ppm 7.52 (d, $J = 8.7$ Hz, 1H), 6.96 (s, 1H), 6.88 (d, $J = 8.8$ Hz, 1H), 3.85 (s, 3H), 3.66 (s, 5H), 2.53 (s, 3H), 1.30 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ ppm 171.9, 155.3, 139.1, 134.7, 129.8, 112.6, 111.1, 108.6, 101.0, 55.8, 52.0, 48.5, 30.9, 30.3, 11.5. HRMS (ESI) m/z : $[\text{M}]^+$: Calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_3\text{S}_2$

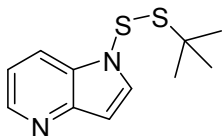
353.1119, found: 353.1112.

1-(*tert*-butyldisulfanyl)-1*H*-pyrrolo[2,3-*b*]pyridine (**3r**)



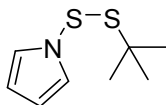
Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **3r**. Yellow liquid (57.1 mg, 80%); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ ppm 8.42 (d, $J = 3.2$ Hz, 1H), 7.90 (d, $J = 7.8$ Hz, 1H), 7.28 (d, $J = 1.5$ Hz, 1H), 7.11 (dd, $J = 7.8, 4.6$ Hz, 1H), 6.54 (d, $J = 3.7$ Hz, 1H), 1.32 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ ppm 151.4, 143.9, 136.4, 129.0, 121.4, 116.9, 102.4, 50.8, 29.1. HRMS (ESI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{S}_2$ 238.0598, found: 238.0601.

1-(*tert*-butyldisulfanyl)-1*H*-pyrrolo[3,2-*b*]pyridine (**3s**)



Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **3s**. Brown liquid (58.6mg, 82%); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ ppm 8.47 (d, $J = 4.7$ Hz, 1H), 7.90 (d, $J = 8.5$ Hz, 1H), 7.36 (d, $J = 3.4$ Hz, 1H), 7.18 (dd, $J = 8.3, 4.7$ Hz, 1H), 6.78 (d, $J = 3.4$ Hz, 1H), 1.29 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ ppm 147.3, 143.9, 139.5, 134.7, 119.2, 117.5, 105.5, 51.2, 29.1. HRMS (ESI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{S}_2$ 238.0598, found: 238.0598.

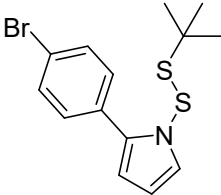
1-(*tert*-butyldisulfanyl)-1*H*-pyrrole (**3t**)



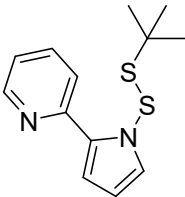
Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford

3t. Brown liquid (44.9 mg, 80%); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ ppm 6.86 (t, $J = 2.2$ Hz, 2H), 6.19 (t, $J = 2.2$ Hz, 2H), 1.38 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ ppm 127.5, 111.3, 49.0, 30.2. HRMS (ESI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_8\text{H}_{13}\text{NS}_2$ 187.0489, found: 187.0488.

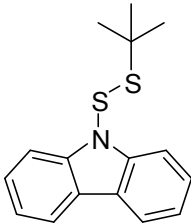
2-(4-bromophenyl)-1-(tert-butylidisulfaneyl)-1H-pyrrole (3u)

 Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **3v**. Colorless liquid (73.7mg, 72%); $^1\text{H NMR}$ (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ ppm 7.56 (d, $J = 9.9$ Hz, 2H), 7.53 (s, 1H), 7.49 (d, $J = 8.4$ Hz, 2H), 7.08 (t, $J = 2.6$ Hz, 1H), 6.65- 6.58 (m, 1H), 1.37 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, $(\text{CD}_3)_2\text{SO}$) δ ppm 134.1, 131.9, 129.7, 127.3, 126.0, 125.2, 119.1, 110.0, 50.0, 30.3. HRMS (ESI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{14}\text{H}_{16}\text{BrNS}_2$ 340.9908, found: 340.9910.

2-(1-(tert-butylidisulfaneyl)-1H-pyrrol-2-yl)pyridine (3v)

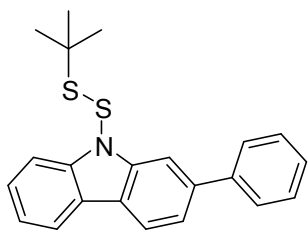
 Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **3w**. Brown liquid (62.8mg, 78%); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ ppm 8.53 (d, $J = 4.9$ Hz, 1H), 7.62 (t, $J = 7.7$ Hz, 1H), 7.49 (s, 1H), 7.44 (d, $J = 8.0$ Hz, 1H), 7.10-7.01 (m, 1H), 6.89 (s, 1H), 6.69 (s, 1H), 1.39 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ ppm 153.5, 149.3, 136.5, 128.7, 127.6, 126.3, 120.8, 119.3, 109.8, 49.4, 30.2. HRMS (ESI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{13}\text{H}_{16}\text{N}_2\text{S}_2$ 264.0755, found: 264.0751.

9-(tert-butylidisulfanyl)-9H-carbazole (5a)

 Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **5a**. Yellow liquid (75.8 mg, 88%); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ ppm 7.98 (d, $J = 7.7$ Hz, 2H), 7.79 (d, $J = 8.2$ Hz, 2H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.28 (t, $J = 7.5$ Hz, 2H), 1.26 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ ppm 142.8, 126.2, 125.1,

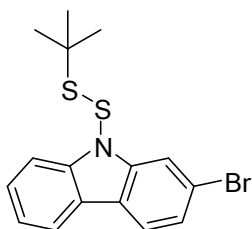
121.4, 120.3, 112.1, 48.2, 30.4. HRMS (ESI) m/z : $[M]^+$ Calcd for $C_{16}H_{17}NS_2$ 287.0802, found:287.0804.

9-(*tert*-butyldisulfanyl)-2-phenyl-9*H*-carbazole (5b)



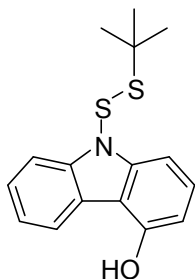
Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **5b**. Yellow liquid (84.9 mg, 78%); 1H NMR (400 MHz, $CDCl_3$) δ ppm 7.98 (d, J = 1.5 Hz, 1H), 7.90 (dd, J = 7.9, 3.6 Hz, 2H), 7.76 (d, J = 8.2 Hz, 1H), 7.69 (d, J = 7.3 Hz, 2H), 7.49-7.40 (m, 4H), 7.31 (t, J = 7.3 Hz, 1H), 7.23 (t, J = 7.5 Hz, 1H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 142.1, 142.0, 140.5, 138.4, 127.7, 126.3, 126.1, 125.0, 123.6, 123.1, 120.3, 119.8, 119.3, 119.1, 110.9, 109.4, 47.0, 29.2. HRMS (ESI) m/z : $[M]^+$ Calcd for $C_{22}H_{21}NS_2$ 363.1115, found: 363.1116.

2-bromo-9-(*tert*-butyldisulfanyl)-9*H*-carbazole (5c)



Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **5c**. Colorless liquid (86.5 mg, 79%); 1H NMR (400 MHz, $CDCl_3$) δ ppm 7.97-7.89 (m, 2H), 7.81 (d, J = 8.3 Hz, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.52 (t, J = 7.7 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 7.29 (t, J = 7.5 Hz, 1H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 143.6, 142.8, 126.7, 124.6, 124.3, 124.1, 121.8, 121.4, 120.3, 119.9, 115.3, 112.2, 48.5, 30.4. HRMS (ESI) m/z : $[M]^+$ Calcd for $C_{16}H_{16}BrNS_2$ 364.9908, found: 364.9908.

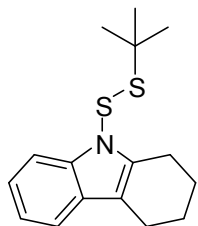
9-(*tert*-butyldisulfanyl)-9*H*-carbazol-4-ol (5d)



Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **5d**. Yellow liquid (68.2 mg, 75%); 1H NMR (400 MHz, $CDCl_3$) δ ppm 8.68

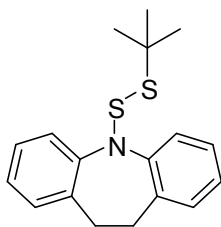
(s, 1H), 8.25 (d, $J = 7.8$ Hz, 1H), 7.54-7.40 (m, 3H), 7.25 (d, $J = 9.3$ Hz, 1H), 6.50 (d, $J = 8.1$ Hz, 1H), 5.67 (s, 1H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 153.0, 142.4, 138.6, 131.5, 125.5, 122.8, 122.6, 120.1, 112.0, 110.7, 110.0, 105.7, 49.2, 30.0. HRMS (ESI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{16}\text{H}_{17}\text{NOS}_2$ 303.0752, found: 303.0750.

9-(*tert*-butyldisulfanyl)-2,3,4,9-tetrahydro-1*H*-carbazole (5e)



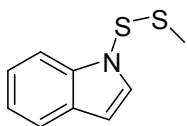
Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **5e**. Yellow liquid (74.2mg, 85%); ^1H NMR (400 MHz, CDCl_3) δ ppm 7.72 (d, $J = 8.1$ Hz, 1H), 7.47 (d, $J = 7.8$ Hz, 1H), 7.30 (t, $J = 7.7$ Hz, 1H), 7.20 (t, $J = 7.4$ Hz, 1H), 2.96 (t, $J = 6.0$ Hz, 2H), 2.73 (t, $J = 6.1$ Hz, 2H), 2.05-1.96 (m, 2H), 1.98-1.87 (m, 2H), 1.38 (d, $J = 2.2$ Hz, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 140.3, 139.2, 129.5, 121.8, 120.8, 118.0, 114.5, 111.8, 48.3, 30.4, 23.3, 23.1, 23.1, 21.3. HRMS (ESI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{16}\text{H}_{21}\text{NS}_2$ 291.1115, found: 291.1112.

5-(*tert*-butyldisulfanyl)-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine (5f)



Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **5f**. Yellow liquid (76.6mg, 81%); ^1H NMR (400 MHz, CDCl_3) δ ppm 7.52 (d, $J = 6.2$ Hz, 1H), 7.39 (s, 1H), 7.13 (t, $J = 6.9$ Hz, 1H), 7.09-6.98 (m, 2H), 6.92 (d, $J = 6.9$ Hz, 1H), 6.81 (t, $J = 8.0$ Hz, 1H), 6.69 (t, $J = 7.6$ Hz, 1H), 3.09 (s, 4H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 143.3, 141.8, 132.9, 131.8, 130.6, 130.0, 128.6, 126.9, 123.2, 119.9, 118.9, 118.9, 49.4, 35.1, 34.8, 30.2. HRMS (ESI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{18}\text{H}_{21}\text{NS}_2$ 315.1115, found: 315.1119.

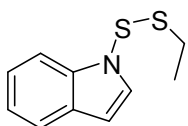
1-(ethyldisulfanyl)-1*H*-indole (6a)



Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **6a**. Colourless liquid (39.2mg, 67%); ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ ppm 7.60 (t, $J = 7.1$ Hz, 2H), 7.39 (d, $J = 3.3$ Hz, 1H), 7.27 (t, $J = 7.4$ Hz, 1H), 7.13 (t, J

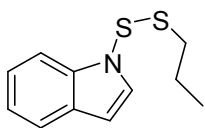
= 7.6 Hz, 1H), 6.60 (d, $J = 3.2$ Hz, 1H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$) δ ppm 139.8, 135.0, 129.6, 123.0, 121.4, 121.1, 111.1, 105.1, 24.0. HRMS (ESI) m/z : $[\text{M}]^+$: Calcd for $\text{C}_9\text{H}_9\text{NS}_2$ 195.0176, found: 195.0172.

1-(ethylidisulfanyl)-1H-indole (6b)



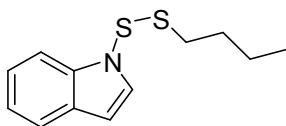
Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **6b**. Colourless liquid 43.9mg, 70%); ^1H NMR (400 MHz, CDCl_3) δ ppm 7.72 (d, $J = 8.2$ Hz, 1H), 7.66 (d, $J = 7.8$ Hz, 1H), 7.34 (t, $J = 7.3$ Hz, 1H), 7.26-7.17 (m, 2H), 6.61 (d, $J = 3.2$ Hz, 1H), 2.94 (q, $J = 7.3$ Hz, 2H), 1.24 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 140.6, 135.2, 129.6, 122.7, 121.0, 120.7, 111.2, 104.5, 34.1, 13.9. HRMS (ESI) m/z : $[\text{M}]^+$: Calcd for $\text{C}_{10}\text{H}_{11}\text{NS}_2$ 209.0333, found: 209.0331.

1-(propyldisulfanyl)-1H-indole (6c)



Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **6c**. Colourless liquid (43.5mg, 65%); ^1H NMR (400 MHz, CDCl_3) δ ppm 7.65 (d, $J = 8.2$ Hz, 1H), 7.59 (d, $J = 7.8$ Hz, 1H), 7.28 (t, $J = 7.6$ Hz, 1H), 7.18-7.10 (m, 2H), 6.54 (d, $J = 3.2$ Hz, 1H), 2.82 (t, $J = 7.3$ Hz, 2H), 1.52 (h, $J = 7.3$ Hz, 2H), 0.97 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 140.5, 135.1, 129.5, 122.6, 121.0, 120.7, 111.2, 104.4, 42.1, 22.0, 13.1. HRMS (ESI) m/z : $[\text{M}]^+$: Calcd for $\text{C}_{11}\text{H}_{13}\text{NS}_2$ 223.0489, found: 223.0481.

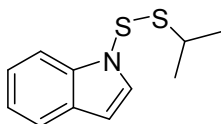
1-(butyldisulfanyl)-1H-indole (6d)



Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **5d**. Colourless liquid (55.5 mg, 78%); ^1H NMR (400 MHz, CDCl_3) δ ppm 7.73 (d, $J = 7.9$ Hz, 1H), 7.67 (d, $J = 7.8$ Hz, 1H), 7.36 (t, $J = 7.6$ Hz, 1H), 7.28-7.18 (m, 2H), 6.62 (d, $J = 3.3$ Hz, 1H), 2.97-2.88 (m, 2H), 1.62-1.50 (m, 2H), 1.47 (h, $J = 7.0$ Hz, 2H), 0.94 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 140.5, 135.1, 129.6,

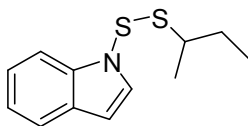
122.7, 121.0, 120.7, 111.2, 104.5, 39.8, 30.6, 21.6, 13.7. HRMS (ESI) m/z : $[M]^+$: Calcd for $C_{12}H_{15}NS_2$ 237.0646, found: 237.0638.

1-(isopropylidisulfanyl)-1H-indole (6e)



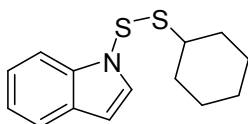
Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **6e**. Black solid (48.8 mg, 73%); 1H NMR (400 MHz, $(CD_3)_2SO$) δ ppm 7.60 (t, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 3.3$ Hz, 1H), 7.25 (t, $J = 7.6$ Hz, 1H), 7.12 (t, $J = 7.5$ Hz, 1H), 6.61 (d, $J = 3.3$ Hz, 1H), 3.44 (h, $J = 6.7$ Hz, 1H), 1.13 (s, 3H), 1.12 (s, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ ppm 141.0, 136.3, 129.4, 123.0, 121.2, 121.0, 111.5, 104.8, 42.6, 21.3. HRMS (ESI) m/z : $[M]^+$: Calcd for $C_{11}H_{13}NS_2$ 223.0489, found: 223.0486.

1-(sec-butylidisulfanyl)-1H-indole (6f)



Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **6f**. Colourless liquid (53.3 mg, 75%); 1H NMR (400 MHz, $CDCl_3$) δ ppm 7.69 (d, $J = 8.2$ Hz, 1H), 7.63 (d, $J = 7.8$ Hz, 1H), 7.31 (t, $J = 7.7$ Hz, 1H), 7.24-7.14 (m, 2H), 6.59 (d, $J = 3.3$ Hz, 1H), 3.17 (h, $J = 6.8$ Hz, 1H), 1.67-1.40 (m, 2H), 1.20 (d, $J = 6.8$ Hz, 3H), 1.05 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 141.1, 135.6, 129.4, 122.6, 120.9, 120.6, 111.4, 104.3, 49.2, 27.6, 18.5, 11.3. HRMS (ESI) (m/z): calcd for $C_{12}H_{15}NS_2$ $[M]^+$: 237.0646, found: 237.0639.

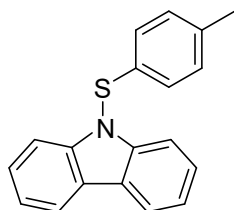
1-(cyclohexylidisulfanyl)-1H-indole (6g)



Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **6g**. Colourless liquid (63.1 mg, 80%); 1H NMR (400 MHz, $(CD_3)_2SO$) δ ppm 7.59 (dd, $J = 10.9, 8.0$ Hz, 2H), 7.33 (d, $J = 3.3$ Hz, 1H), 7.25 (t, $J = 7.6$ Hz, 1H), 7.11 (t, $J = 7.4$ Hz, 1H), 6.60 (d, $J = 3.2$ Hz, 1H), 3.22-3.05 (m, 1H), 1.82-1.74 (m, 2H), 1.71-1.62 (m, 2H), 1.28-1.03 (m, 6H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ ppm 141.1, 136.4, 129.3,

123.0, 121.2, 121.0, 111.6, 104.7, 50.7, 31.5, 25.5, 25.4. HRMS (ESI) m/z : $[M]^+$: Calcd for $C_{14}H_{17}NS_2$ 263.0802, found: 263.0798.

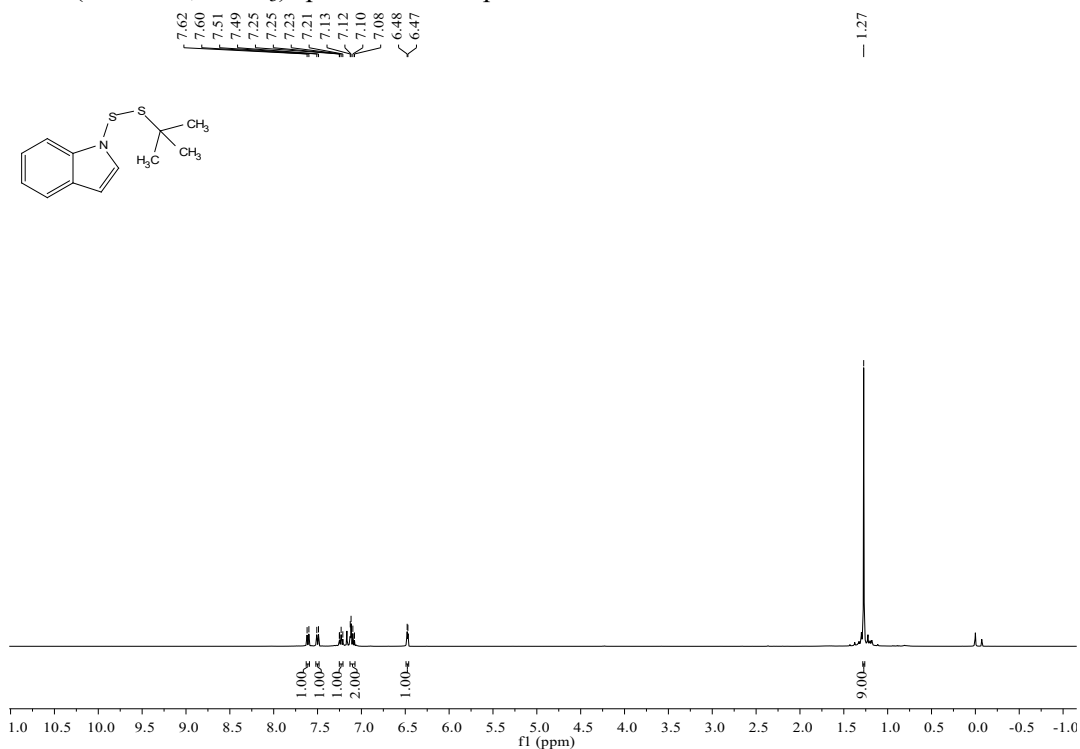
1-(cyclohexyldisulfanyl)-1*H*-indole (**6h**)



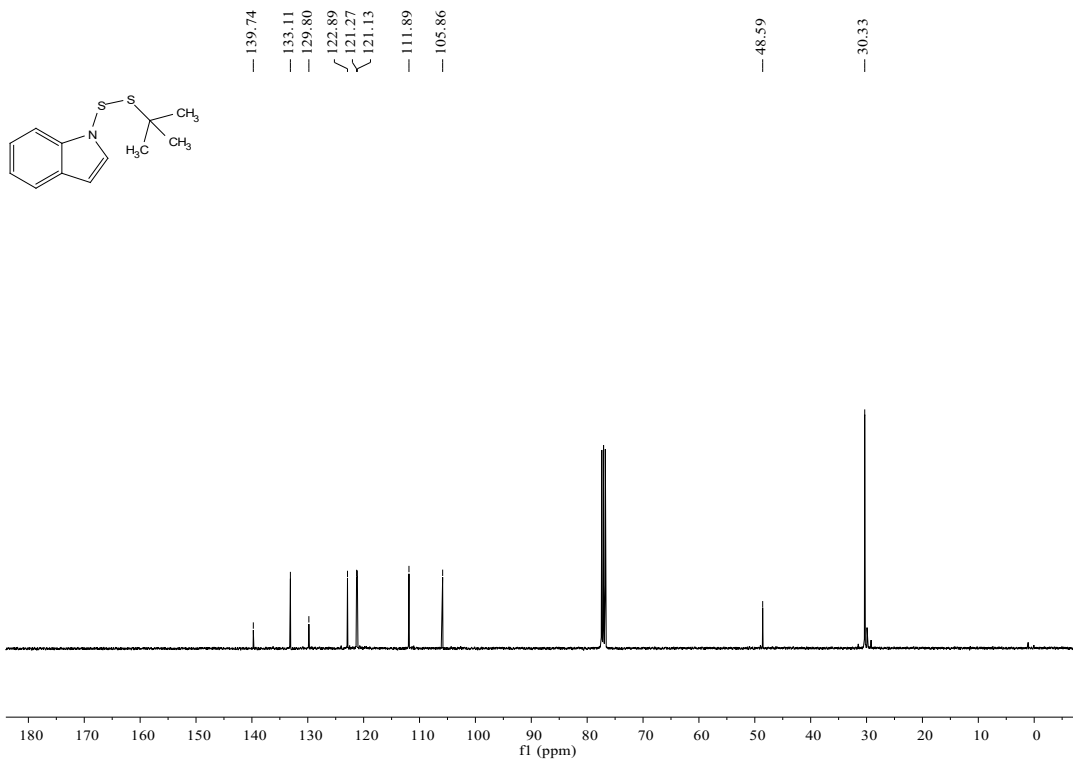
Flash column chromatography on silica gel (eluent: PE/EtOAc = 60/1, v/v) to afford **6h**. Colourless liquid (62.4 mg, 72%); 1H NMR (400 MHz, $CDCl_3$) δ ppm 8.10 (d, $J = 7.7$ Hz, 2H), 7.82 (d, $J = 8.2$ Hz, 2H), 7.52 (t, $J = 7.1$ Hz, 2H), 7.35 (t, $J = 7.5$ Hz, 2H), 7.03 (s, 4H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 143.5, 137.2, 134.3, 130.0, 126.6, 125.4, 124.6, 121.3, 120.3, 111.2, 21.1. HRMS (ESI) m/z : $[M]^+$: Calcd for $C_{19}H_{15}NS_2$ 289.0925, found: 289.0919.

V. NMR spectra

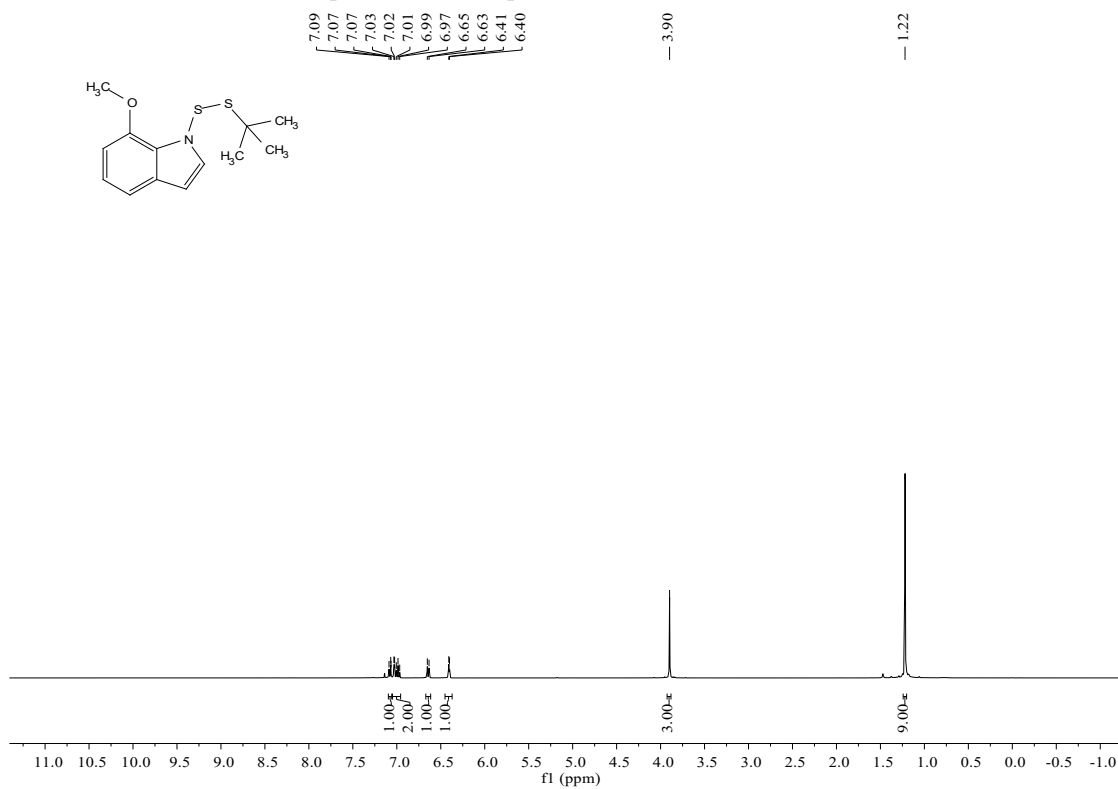
1H NMR (400 MHz, $CDCl_3$) spectrum of compound **3a**



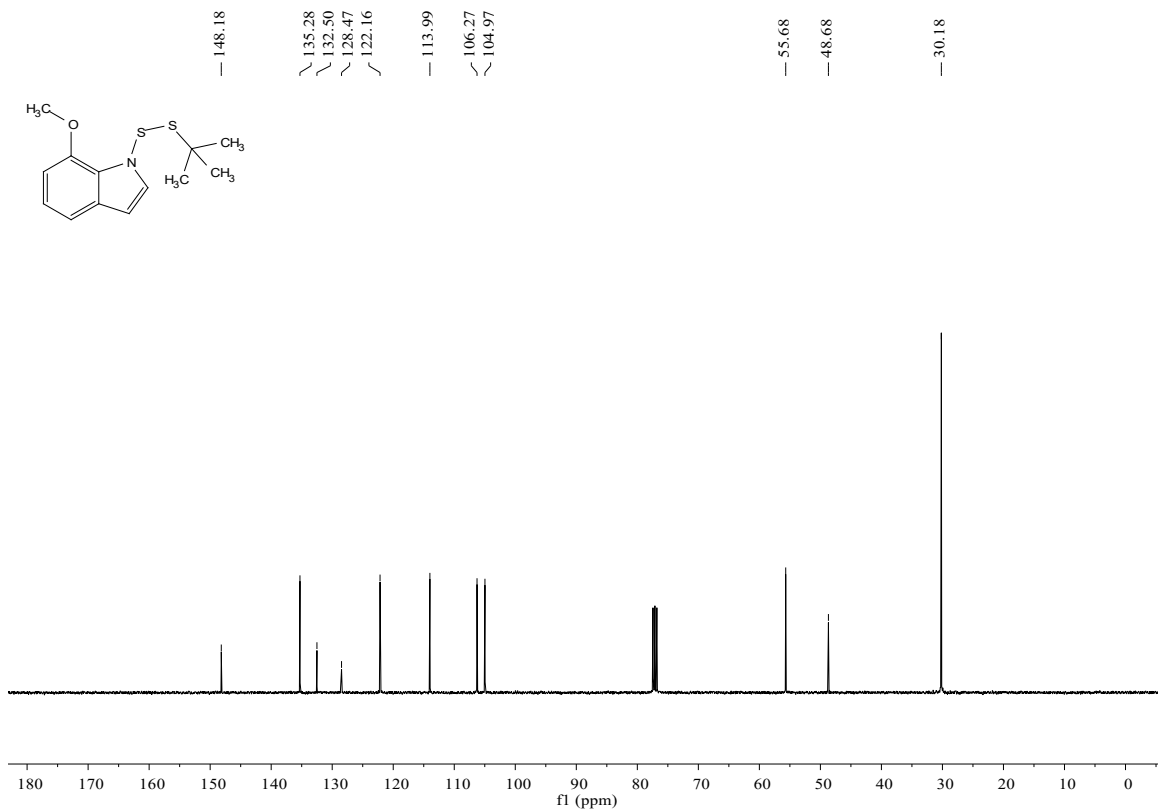
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3a**



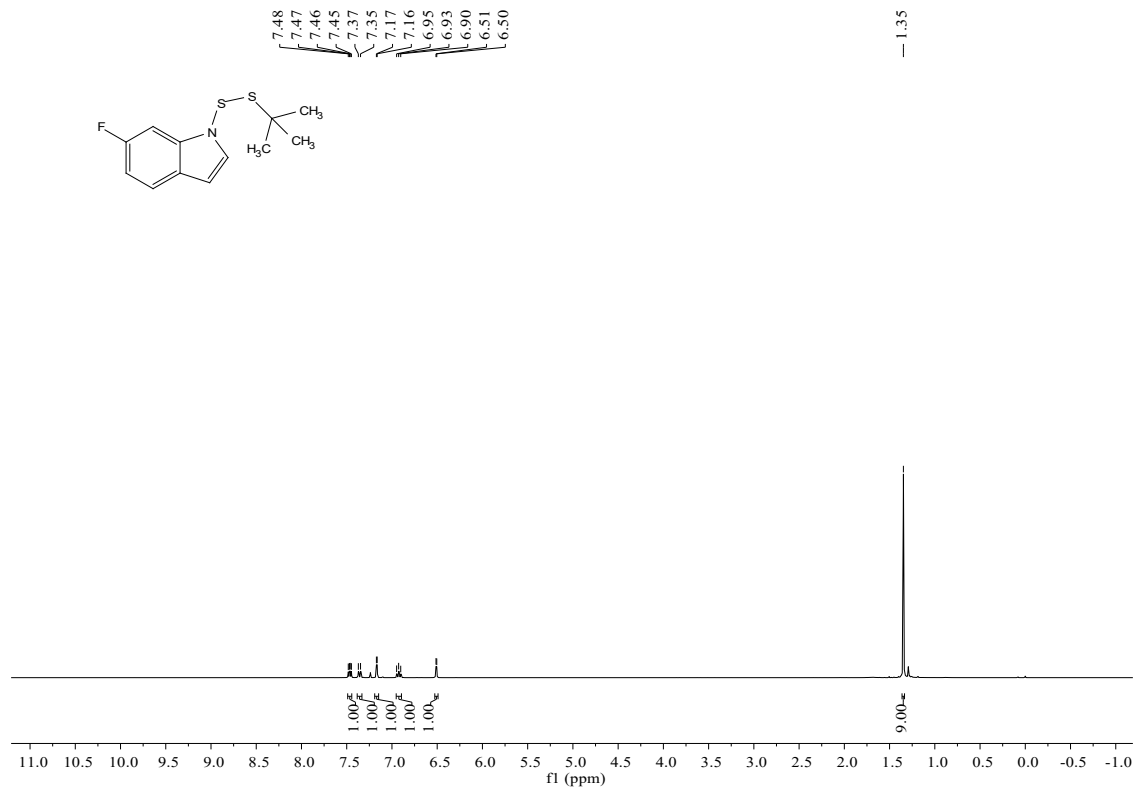
¹H NMR (400 MHz, CDCl₃) spectrum of compound **3b**



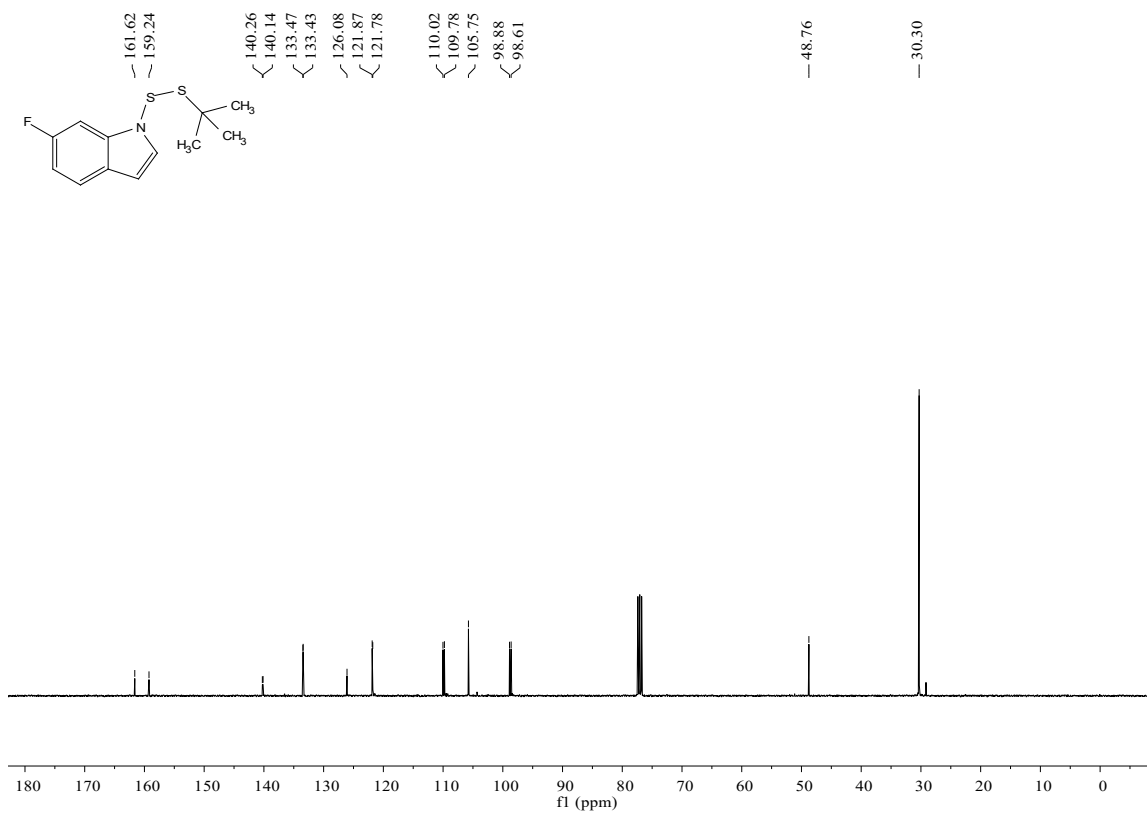
¹³C NMR (100 MHz, CDCl₃) spectrum of compound **3b**



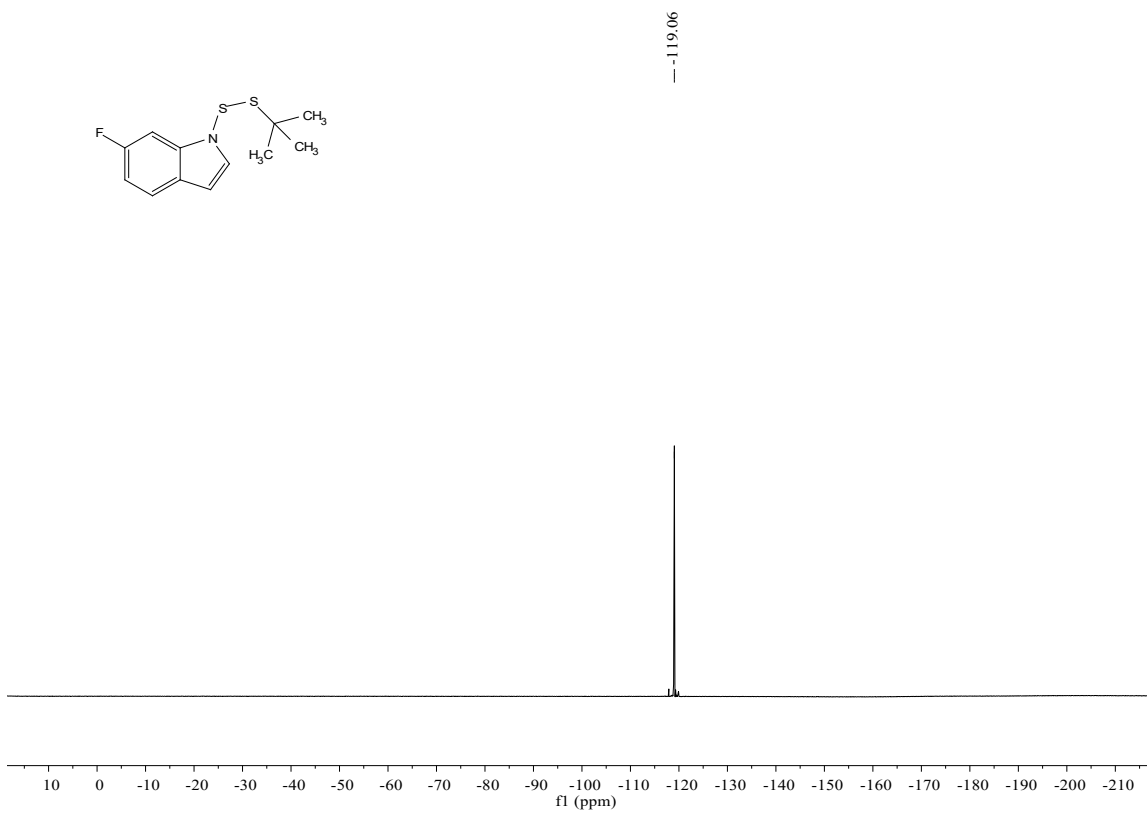
¹H NMR (400 MHz, CDCl₃) spectrum of compound **3c**



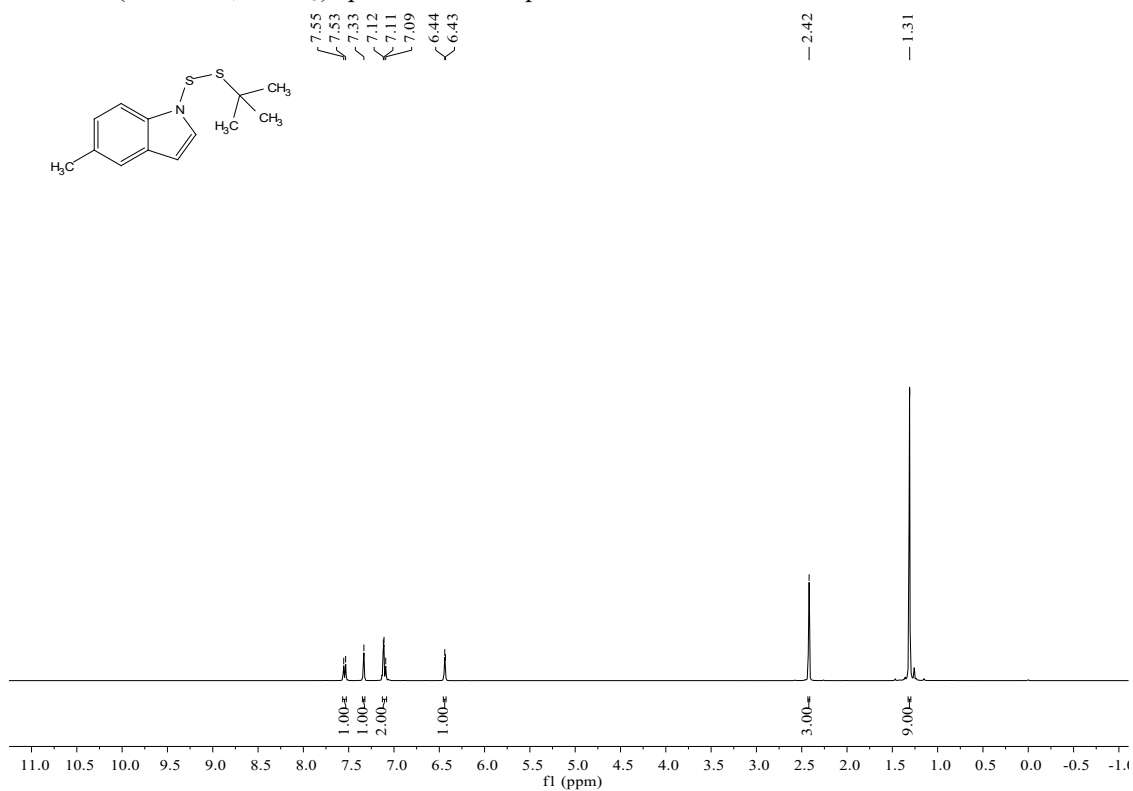
¹³C NMR (100 MHz, CDCl₃) spectrum of compound **3c**



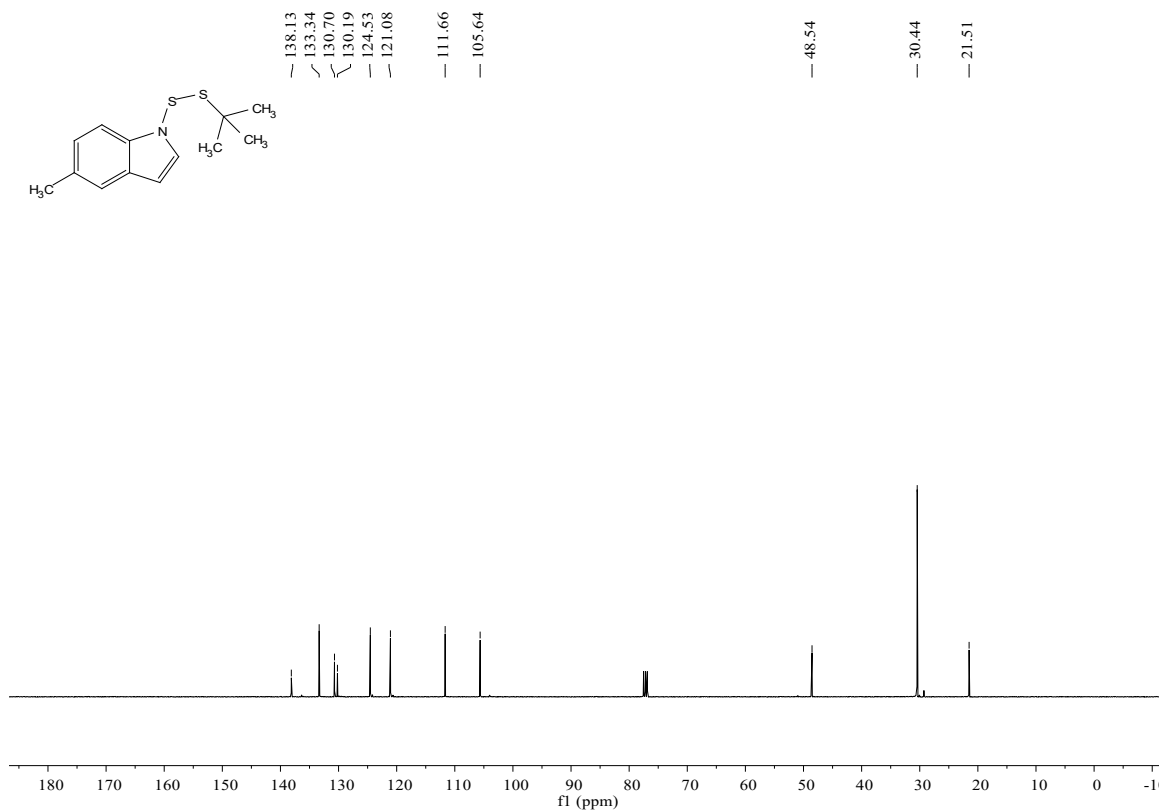
¹⁹F NMR (376 MHz, CDCl₃) spectrum of compound **3c**



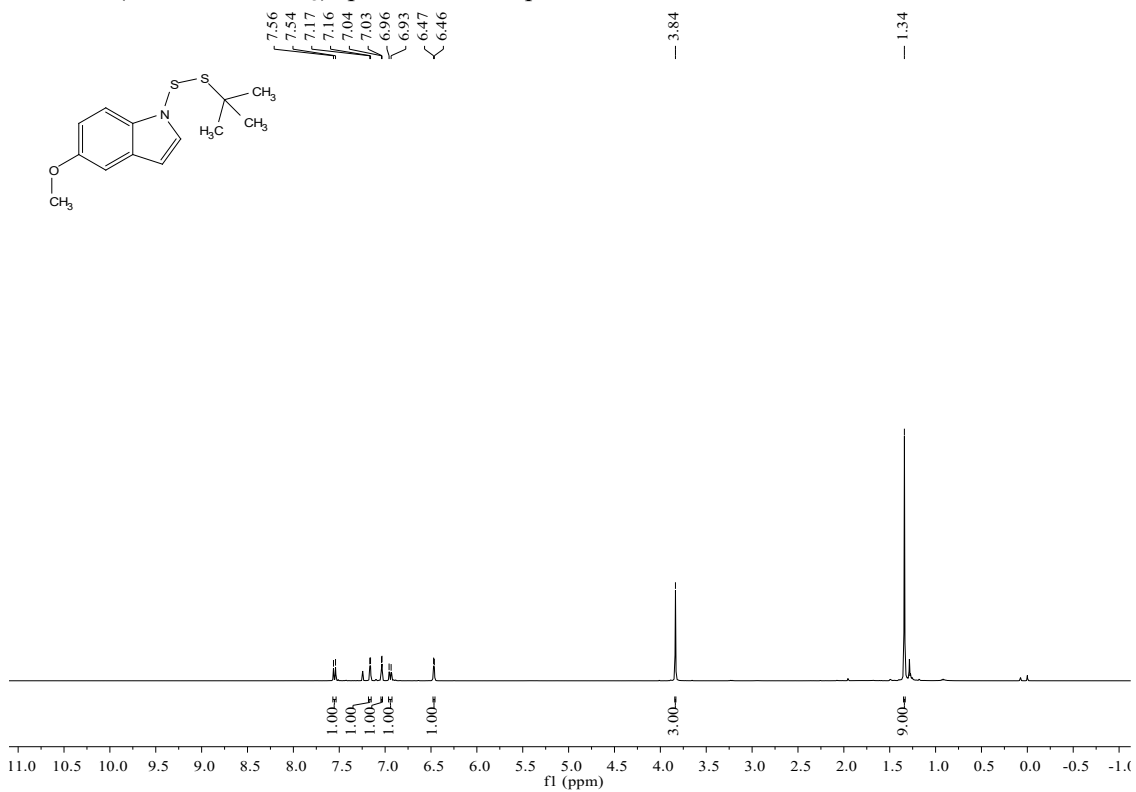
¹H NMR (400 MHz, CDCl₃) spectrum of compound **3d**



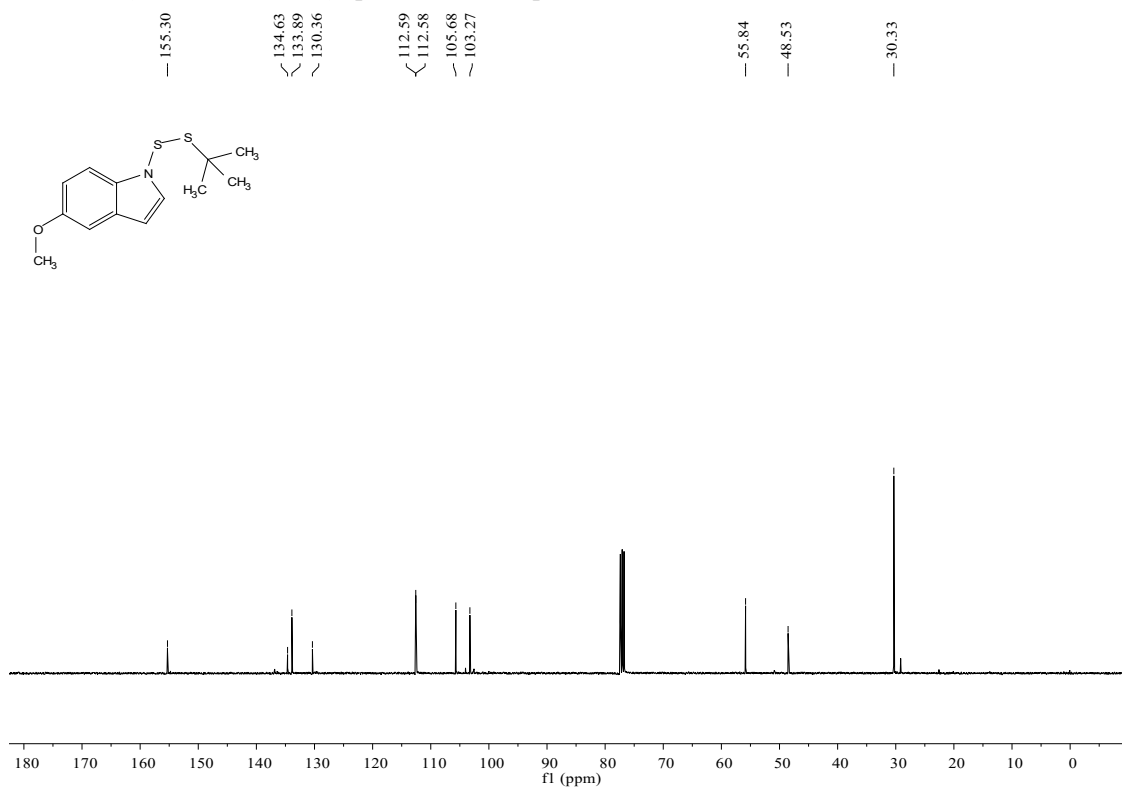
¹³C NMR (100 MHz, CDCl₃) spectrum of compound **3d**



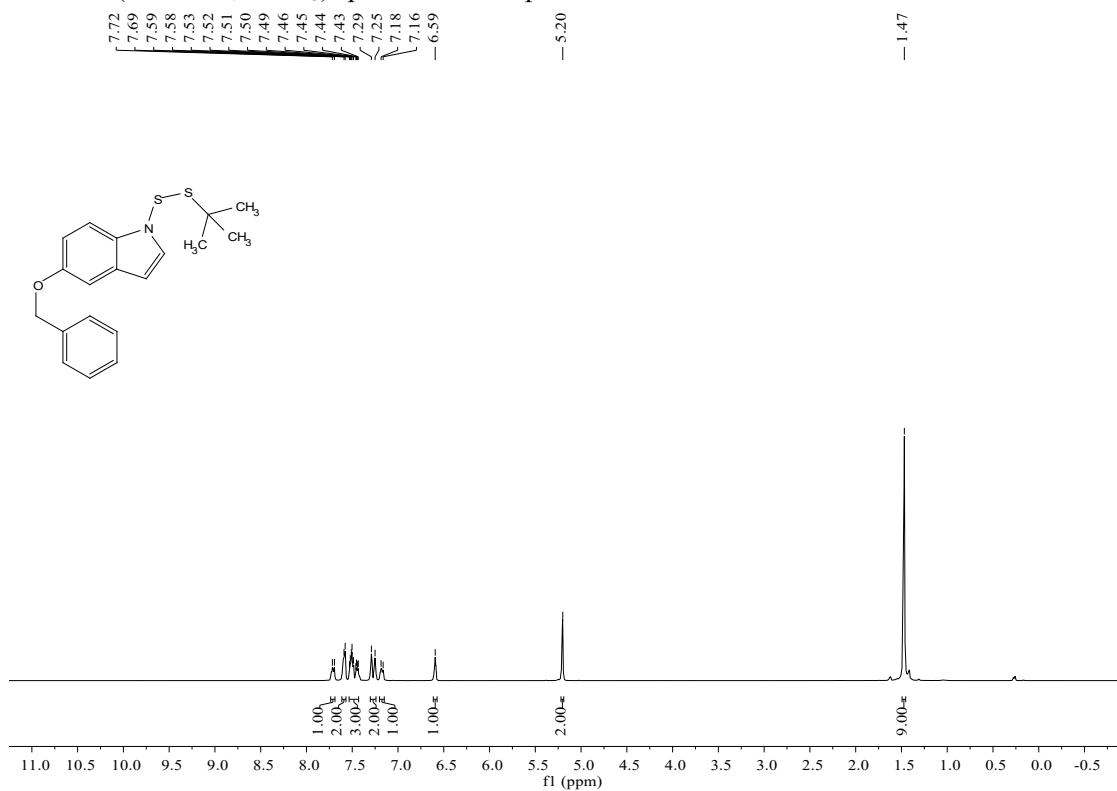
¹H NMR (400 MHz, CDCl₃) spectrum of compound **3e**



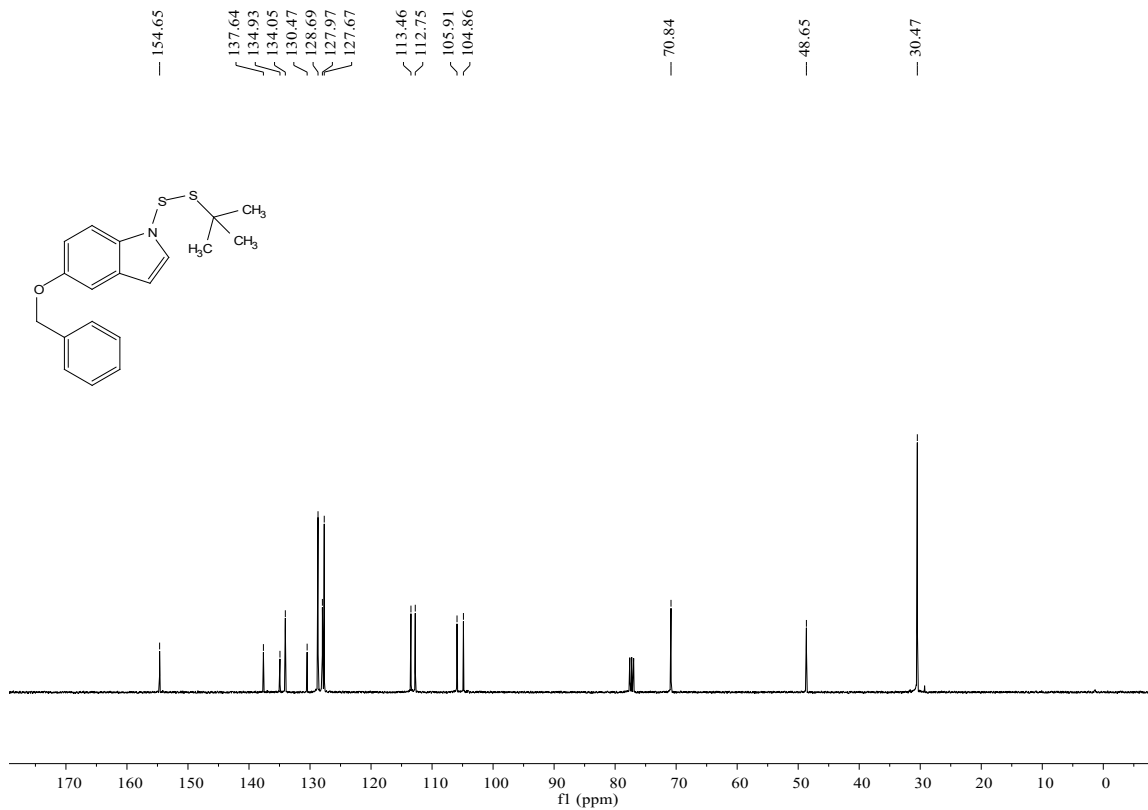
¹³C NMR (100 MHz, CDCl₃) spectrum of compound **3e**



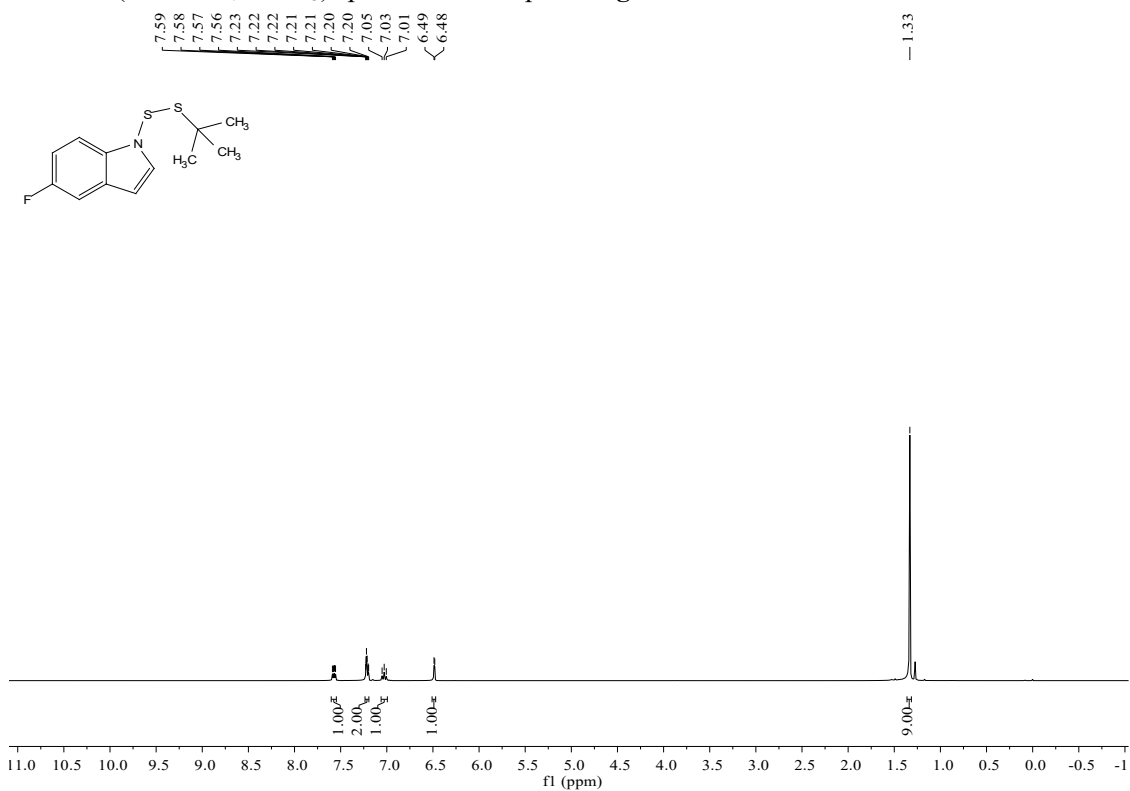
¹H NMR (400 MHz, CDCl₃) spectrum of compound **3f**



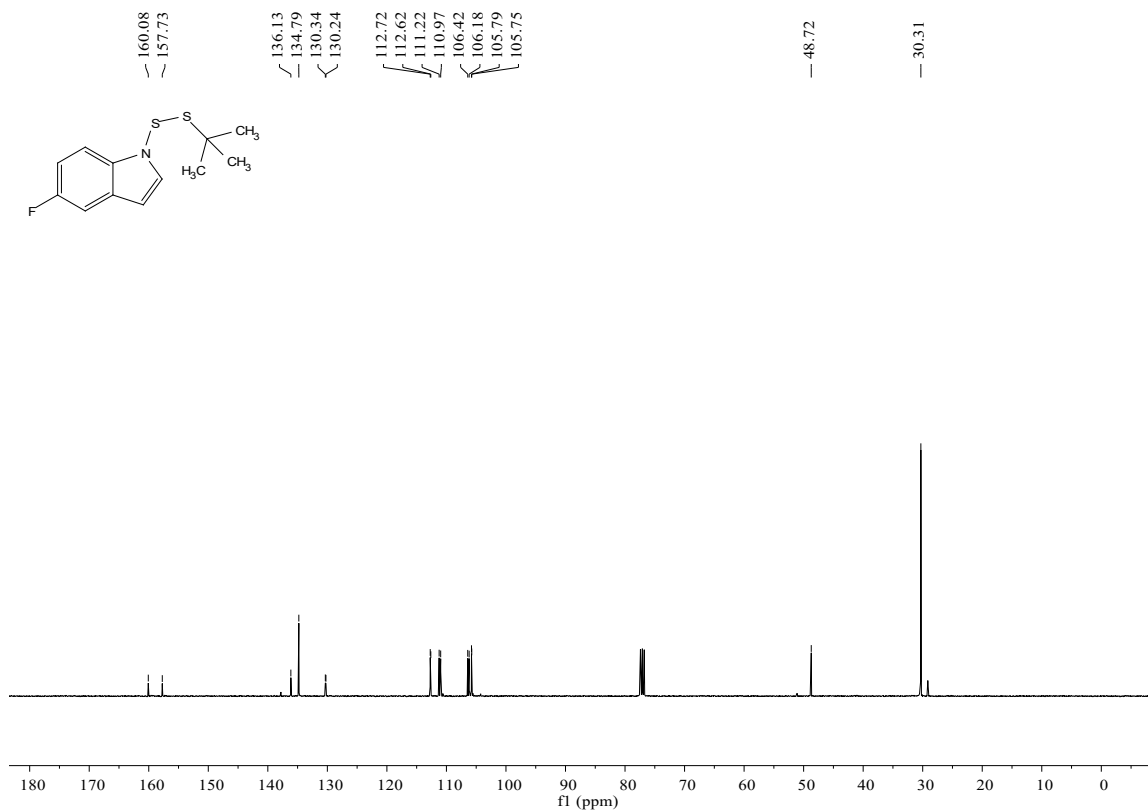
¹³C NMR (100 MHz, CDCl₃) spectrum of compound **3f**



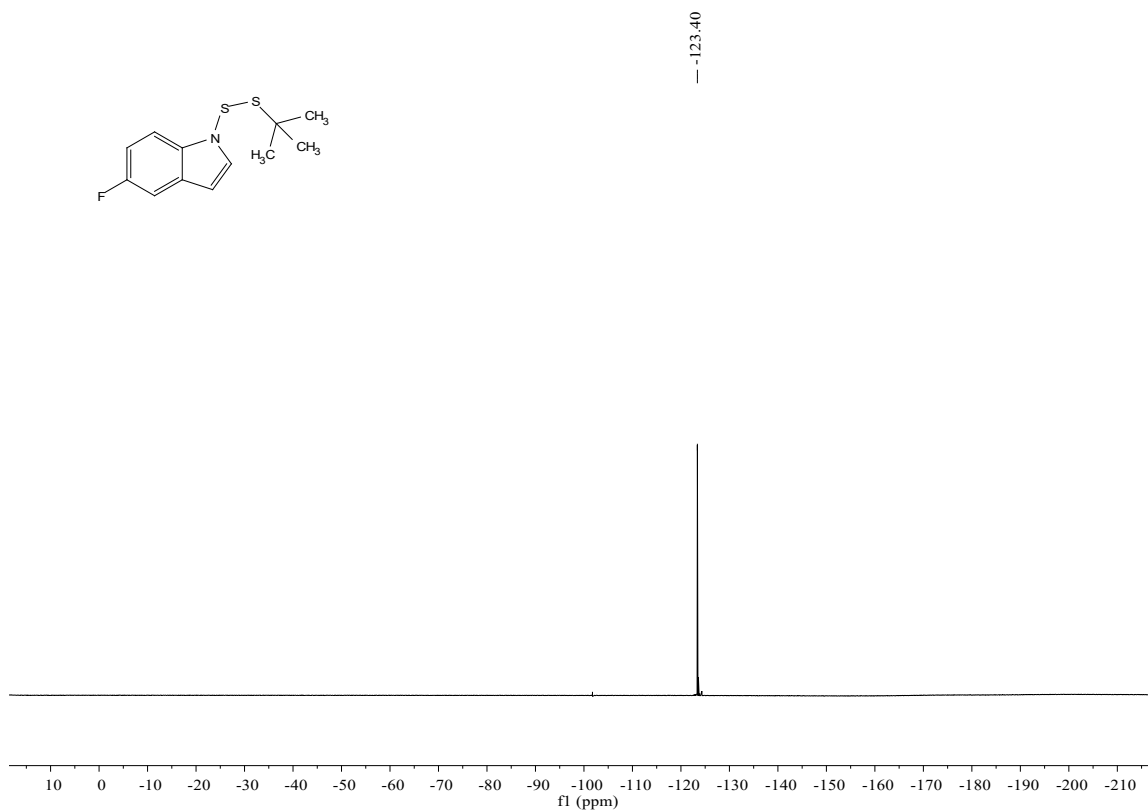
¹H NMR (400 MHz, CDCl₃) spectrum of compound **3g**



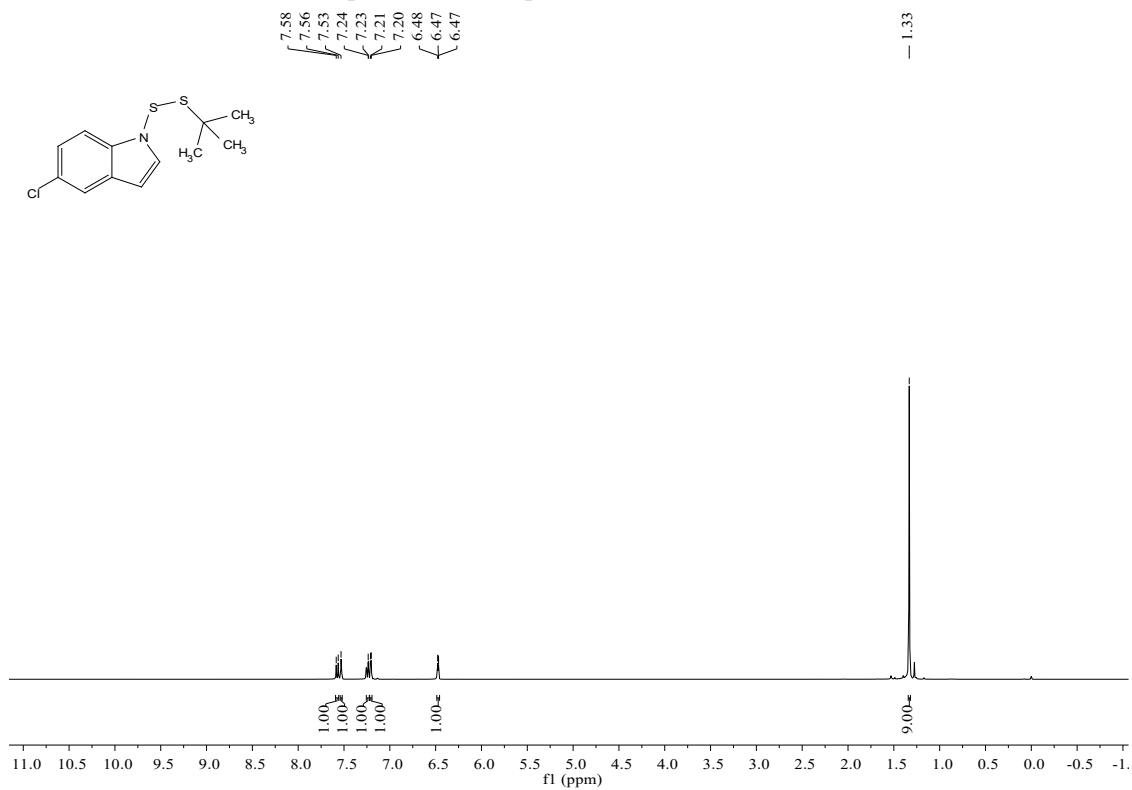
¹³C NMR (100 MHz, CDCl₃) spectrum of compound **3g**



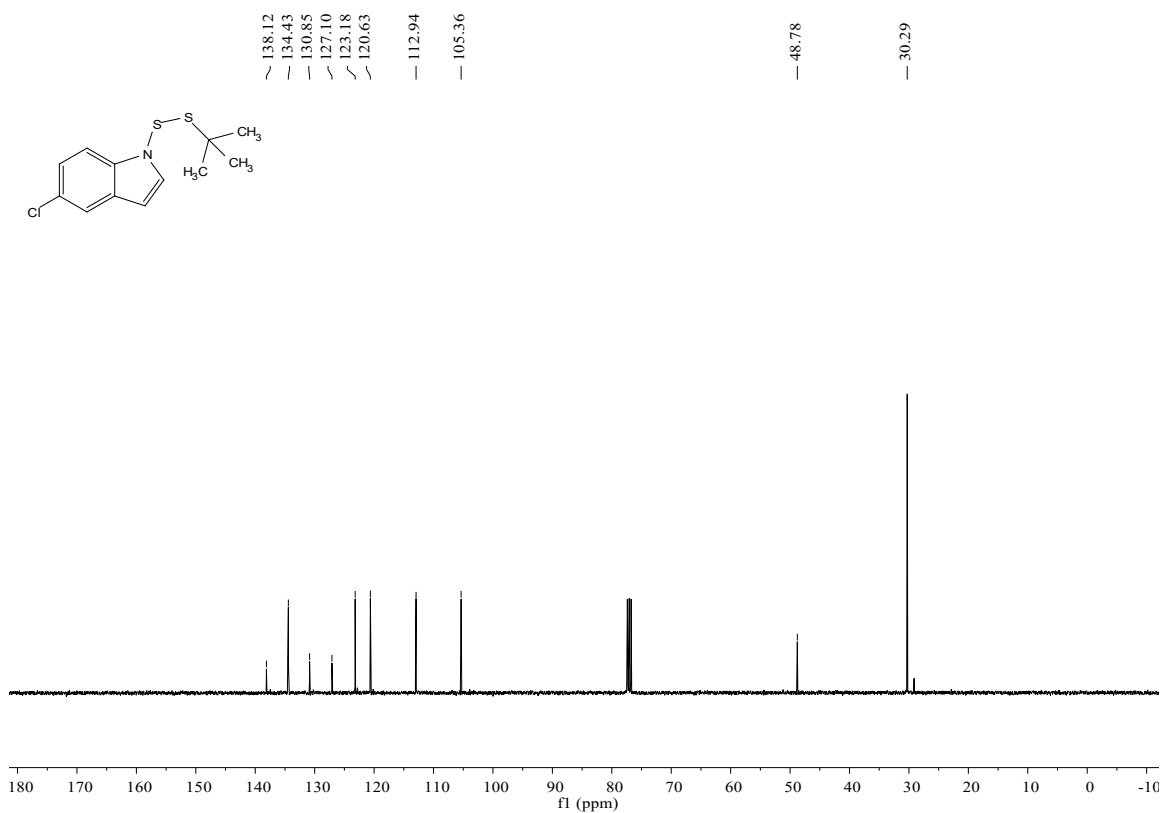
^{19}F NMR (376 MHz, CDCl_3) spectrum of compound **3g**



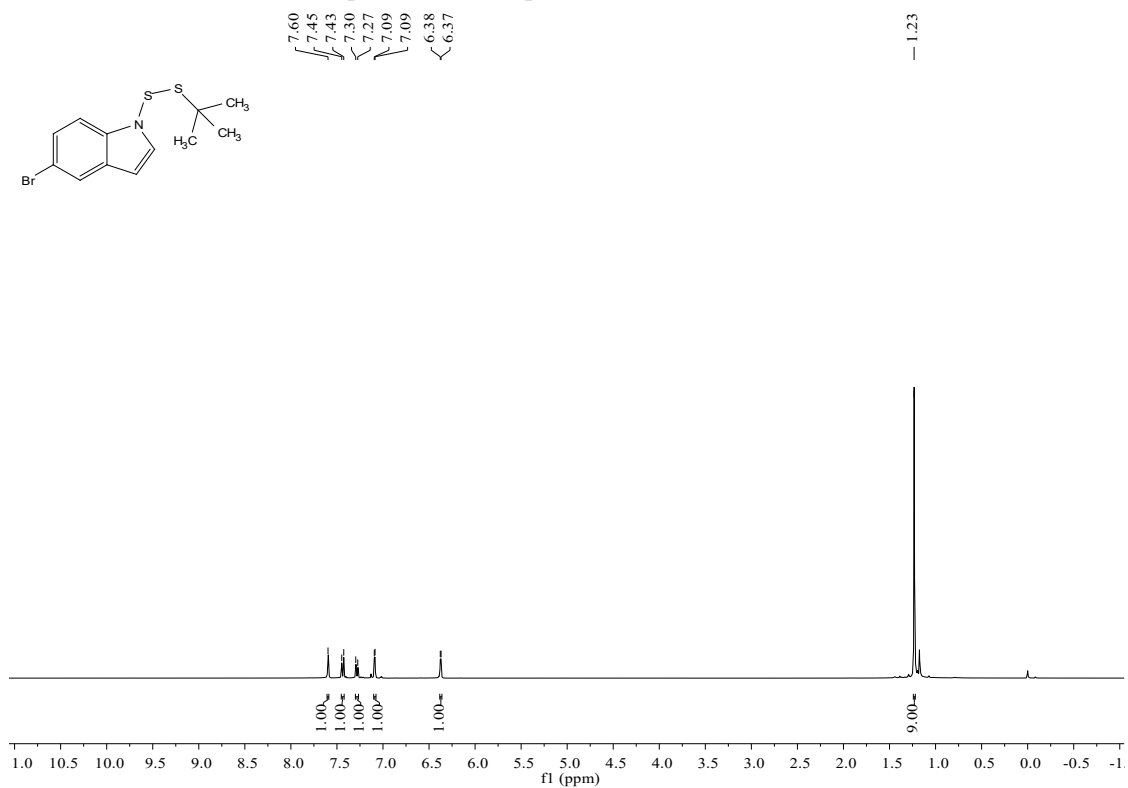
^1H NMR (400 MHz, CDCl_3) spectrum of compound **3h**



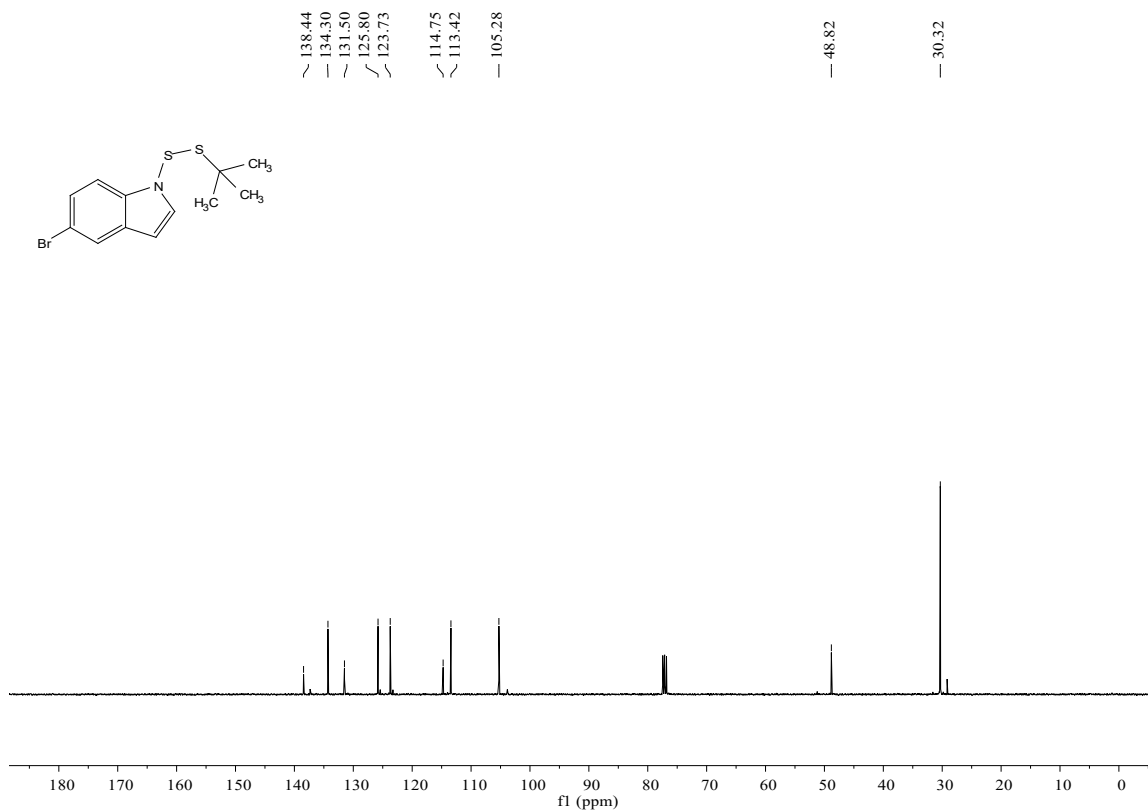
^{13}C NMR (100 MHz, CDCl_3) spectrum of compound **3h**



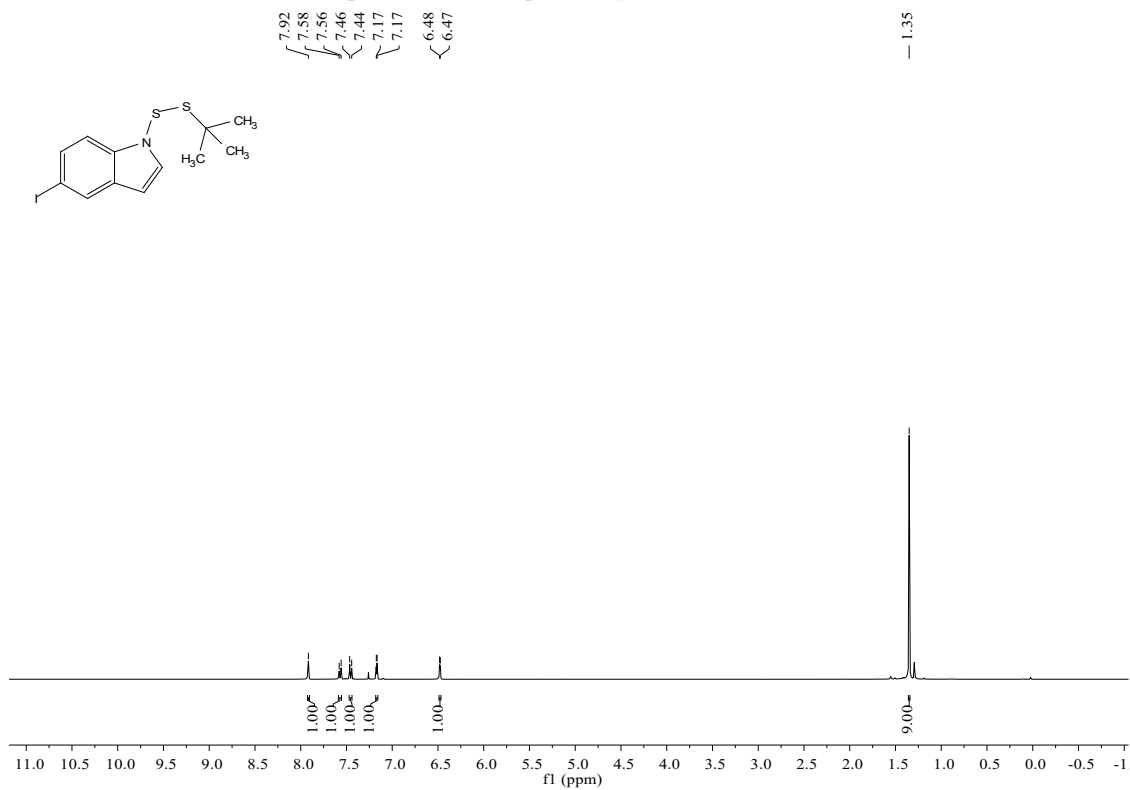
^1H NMR (400 MHz, CDCl_3) spectrum of compound **3i**



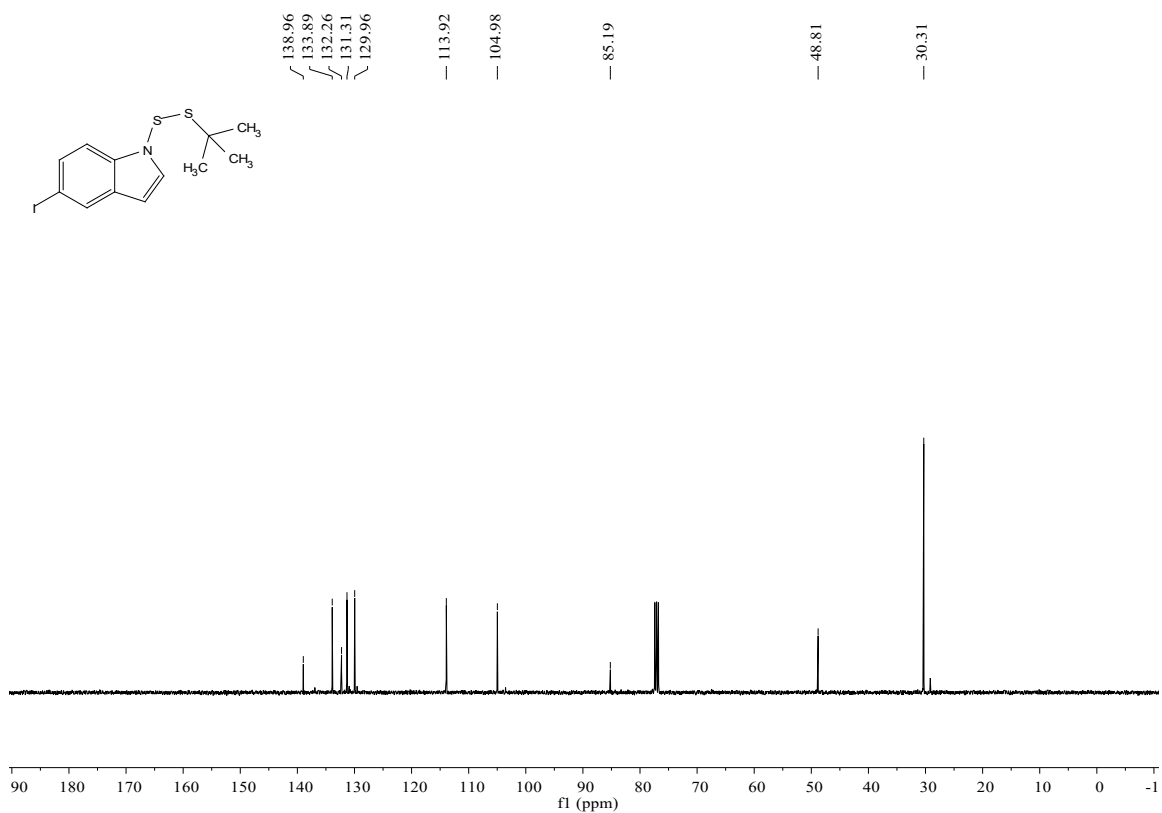
¹³C NMR (100 MHz, CDCl₃) spectrum of compound **3i**



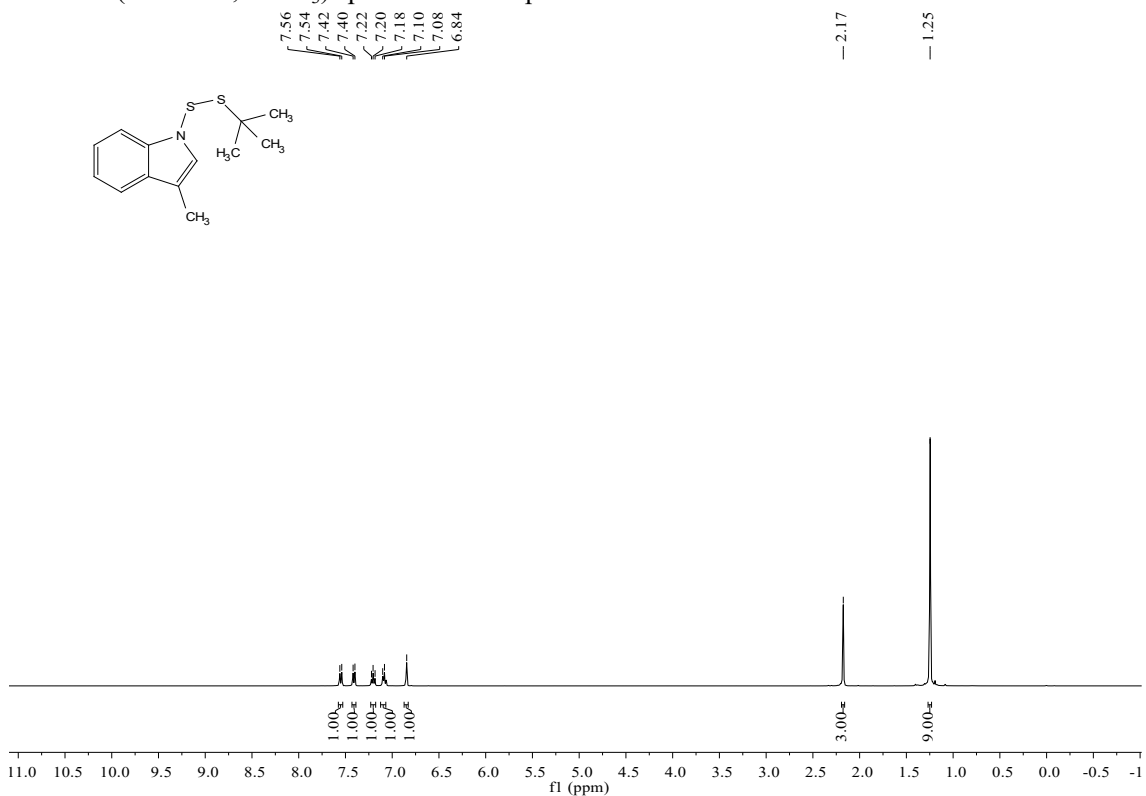
¹H NMR (400 MHz, CDCl₃) spectrum of compound **3j**



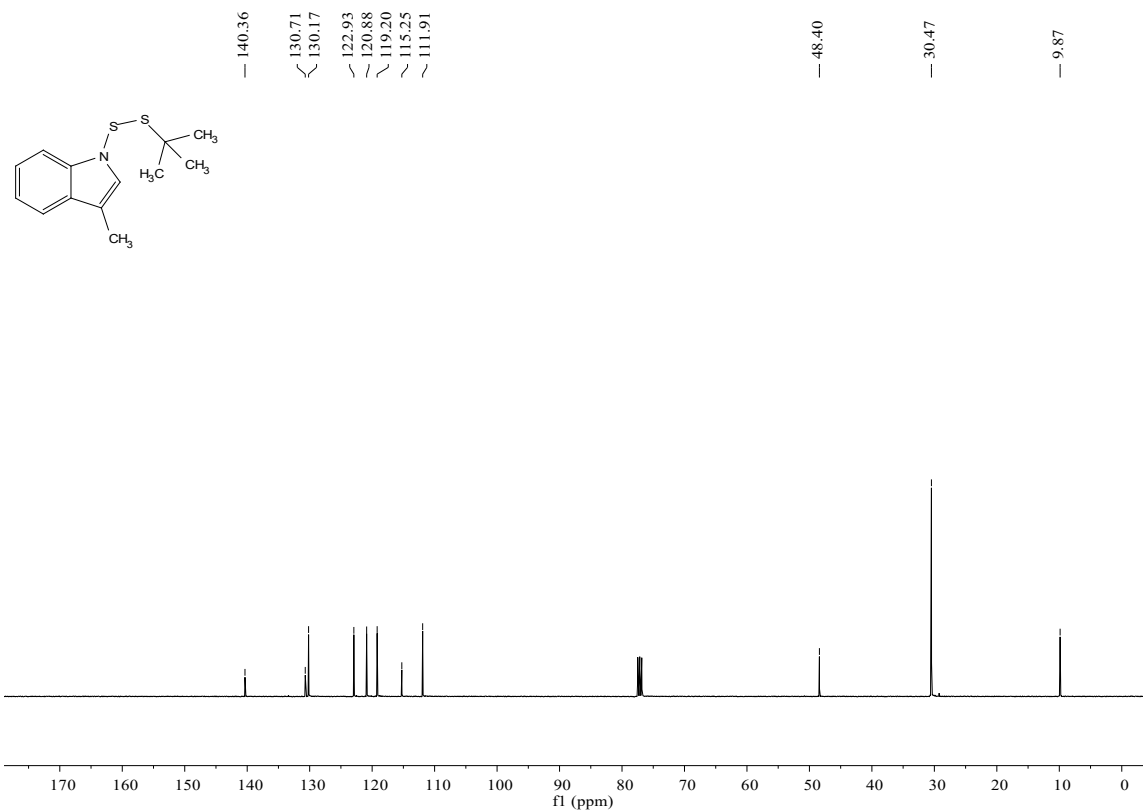
¹³C NMR (100 MHz, CDCl₃) spectrum of compound **3j**



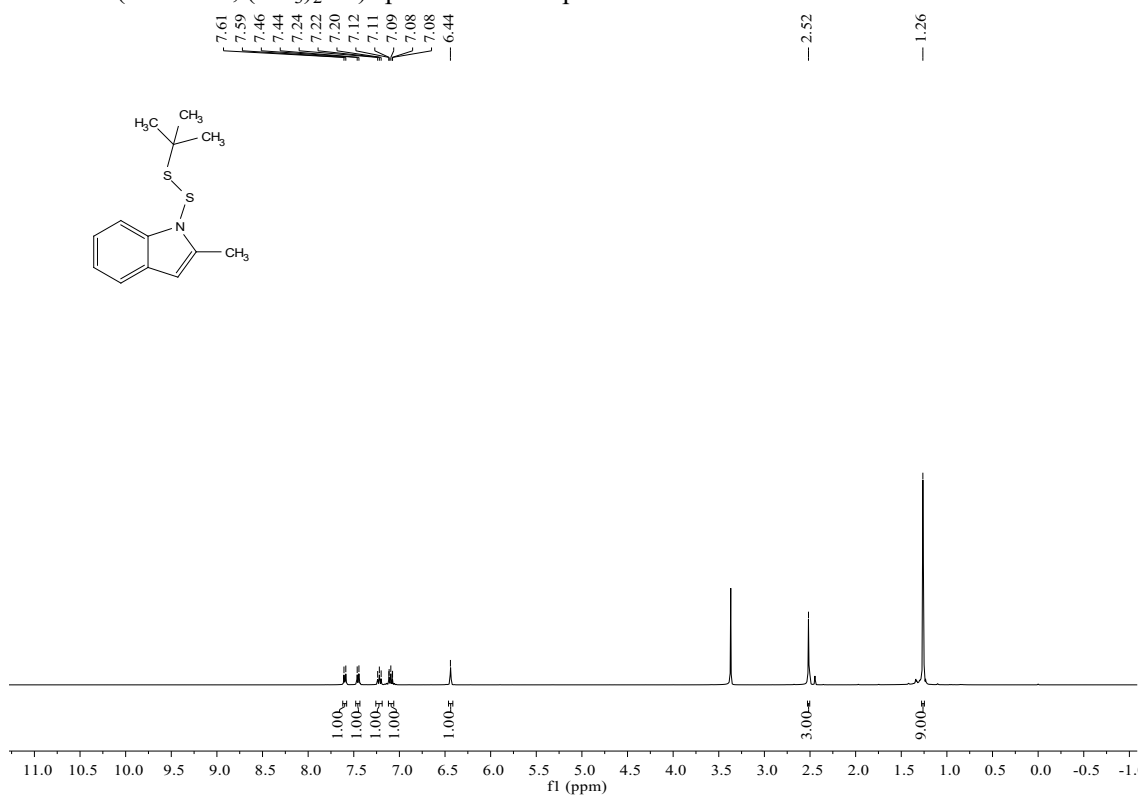
¹H NMR (400 MHz, CDCl₃) spectrum of compound **3k**



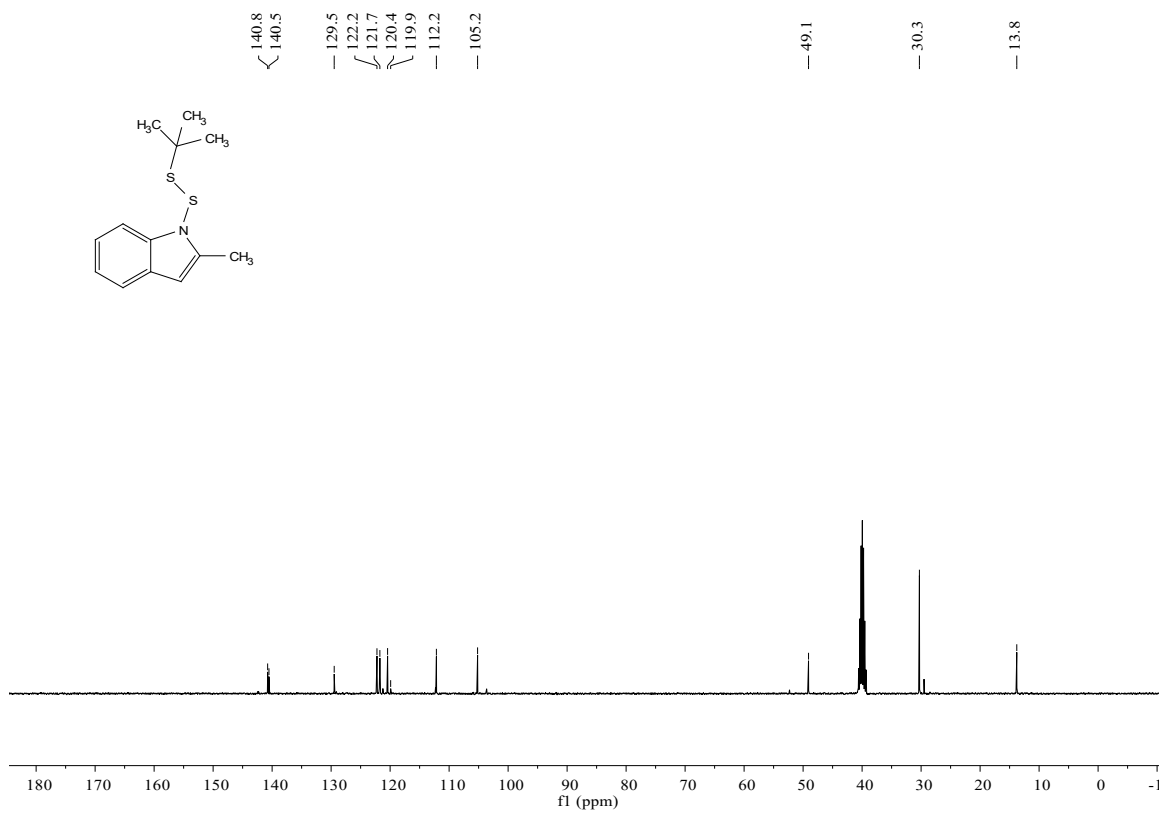
^{13}C NMR (100 MHz, CDCl_3) spectrum of compound **3k**



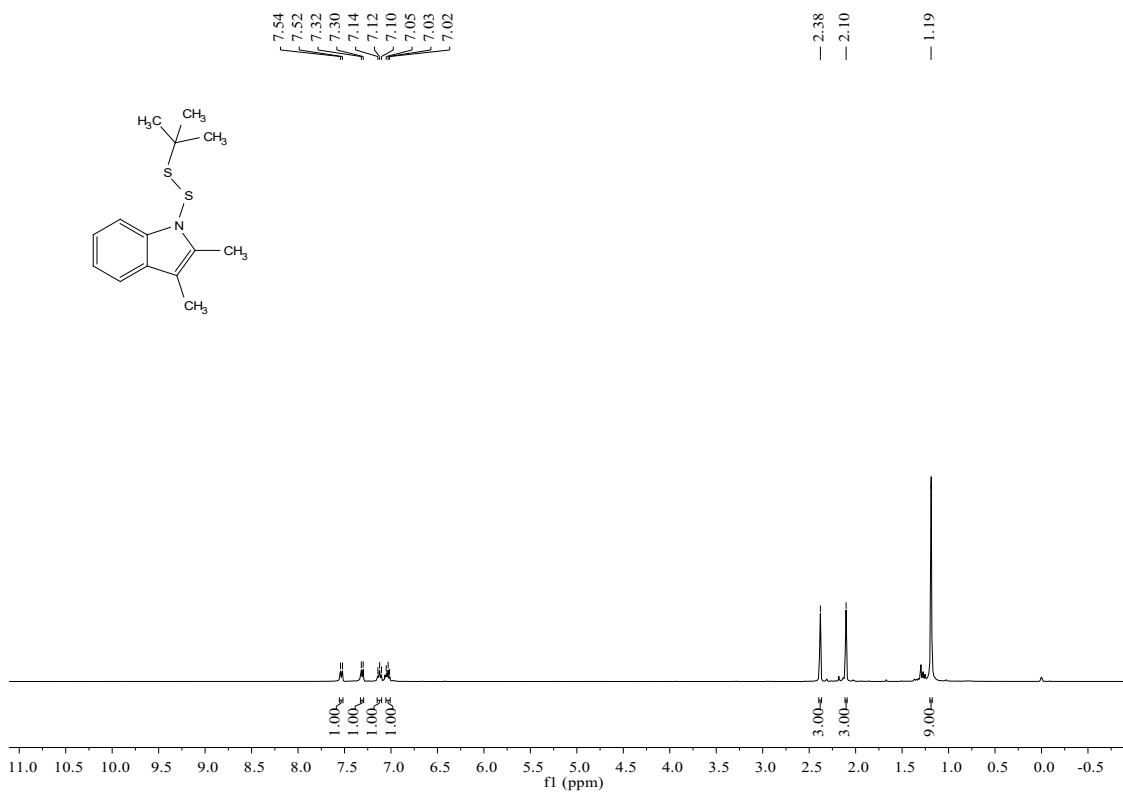
^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) spectrum of compound **3l**



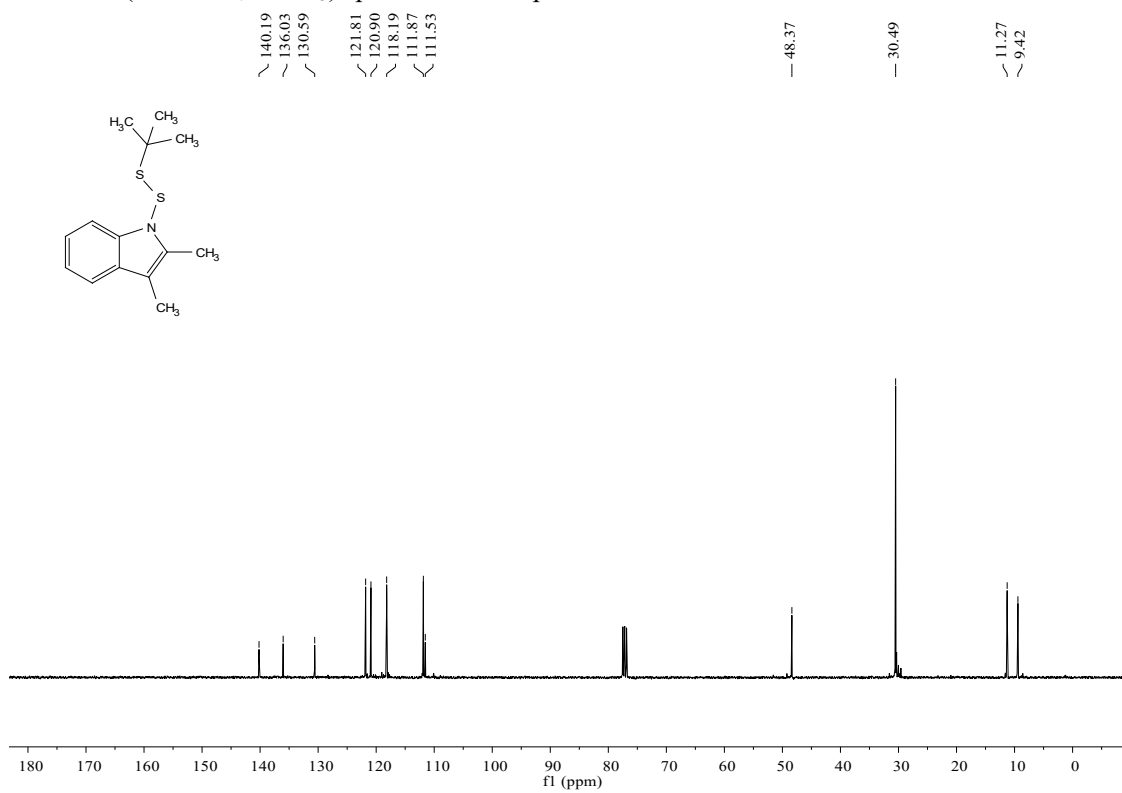
^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$) spectrum of compound **3l**



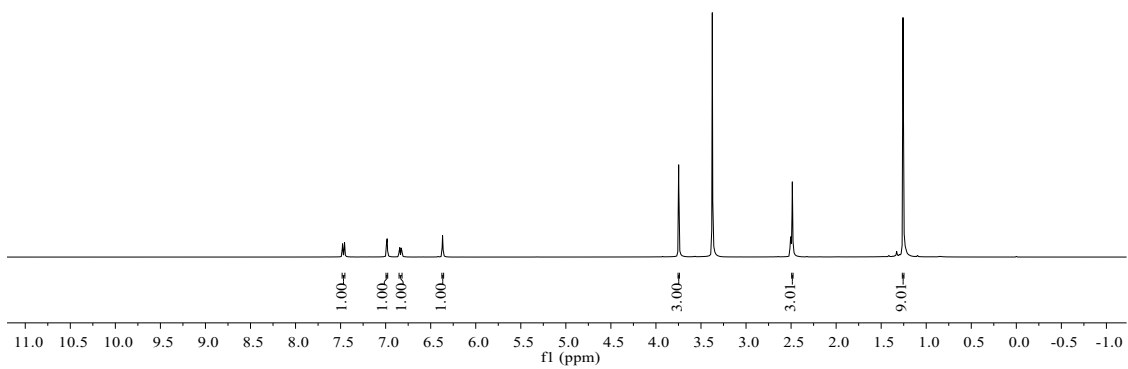
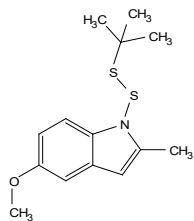
^1H NMR (400 MHz, CDCl_3) spectrum of compound **3m**



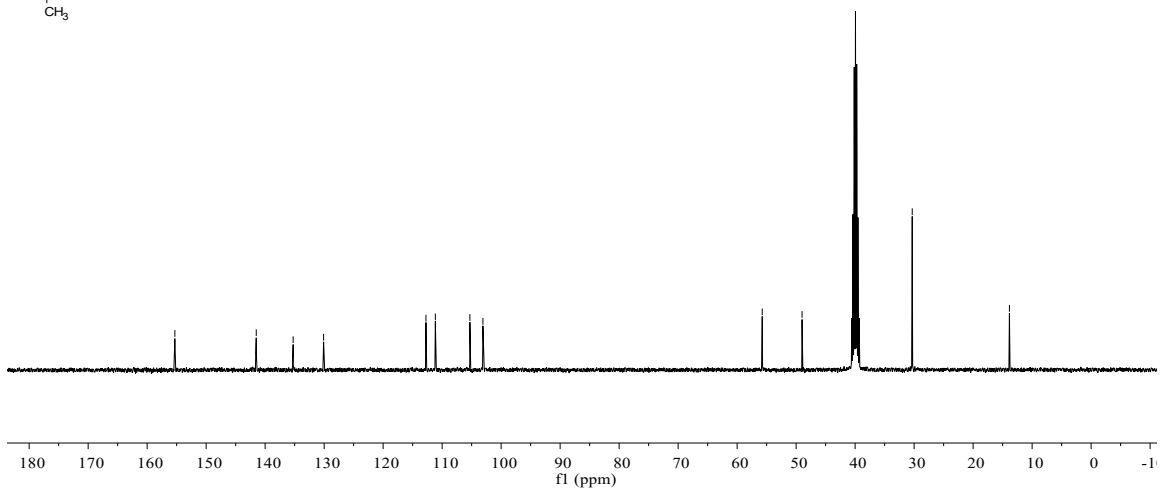
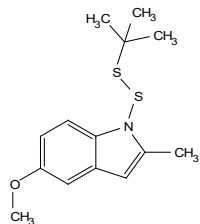
¹³C NMR (100 MHz, CDCl₃) spectrum of compound **3m**



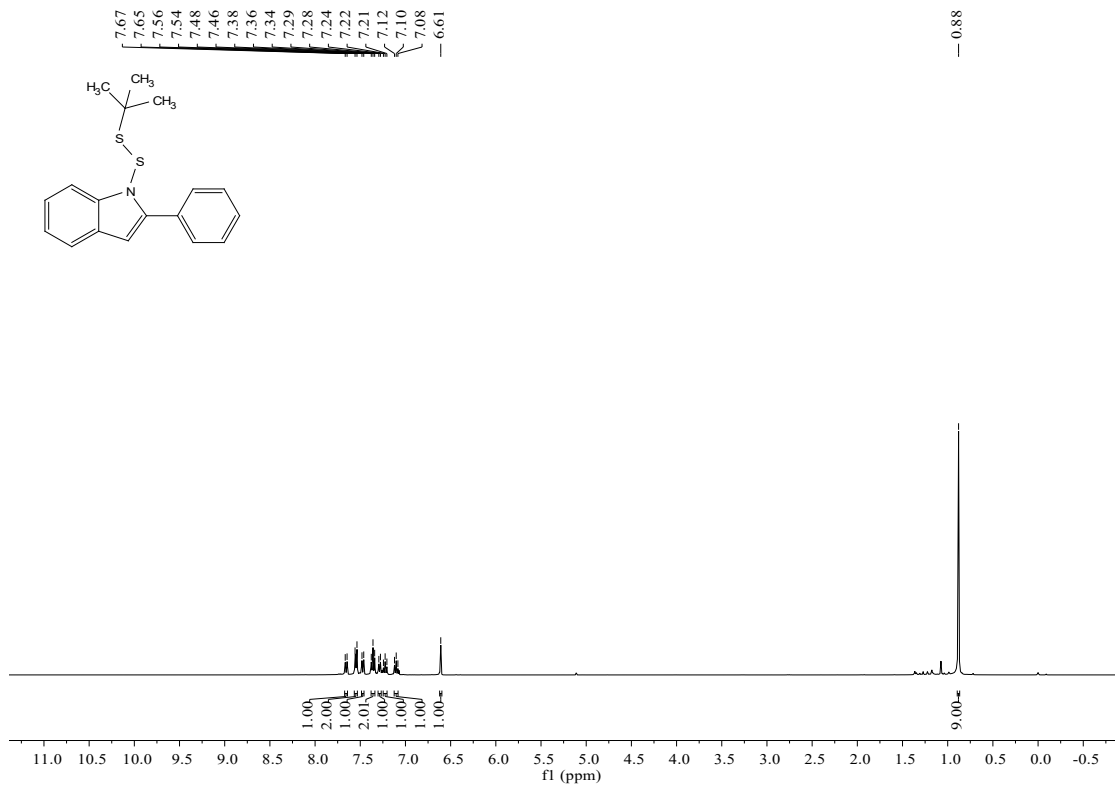
¹H NMR (400 MHz, (CD₃)₂SO) spectrum of compound **3n**



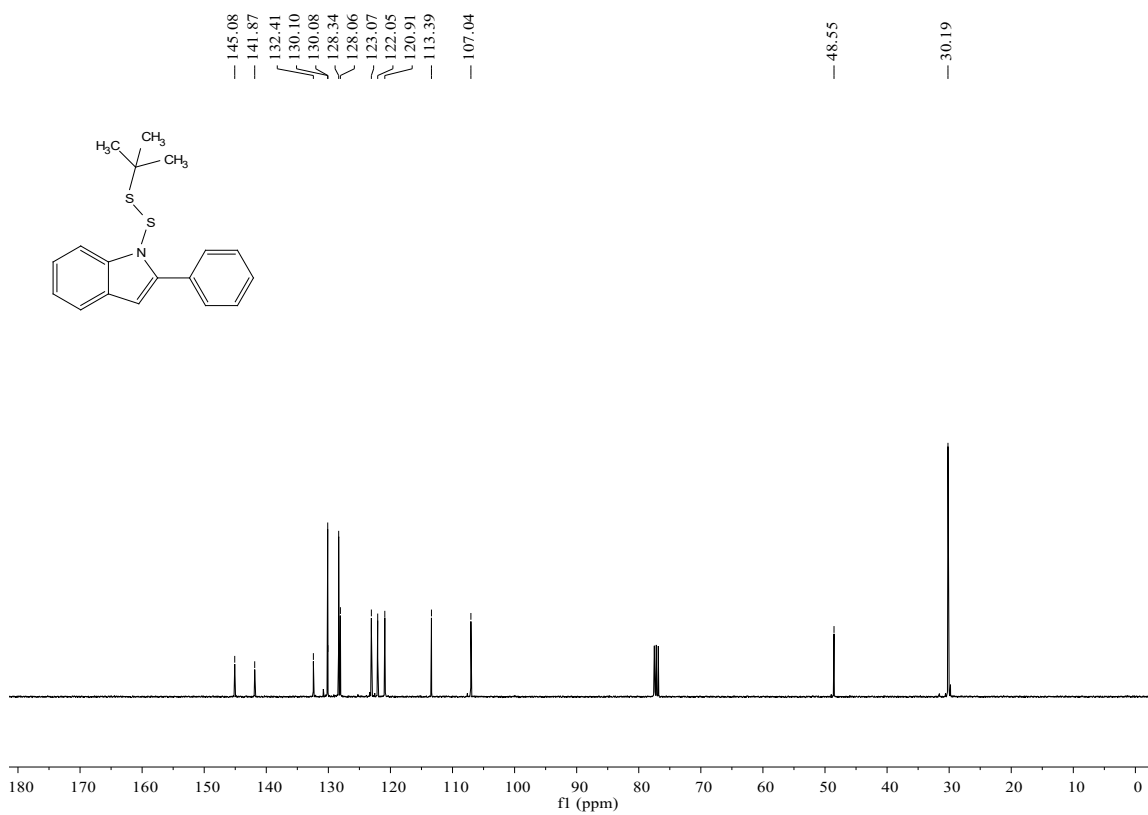
^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$) spectrum of compound **3n**



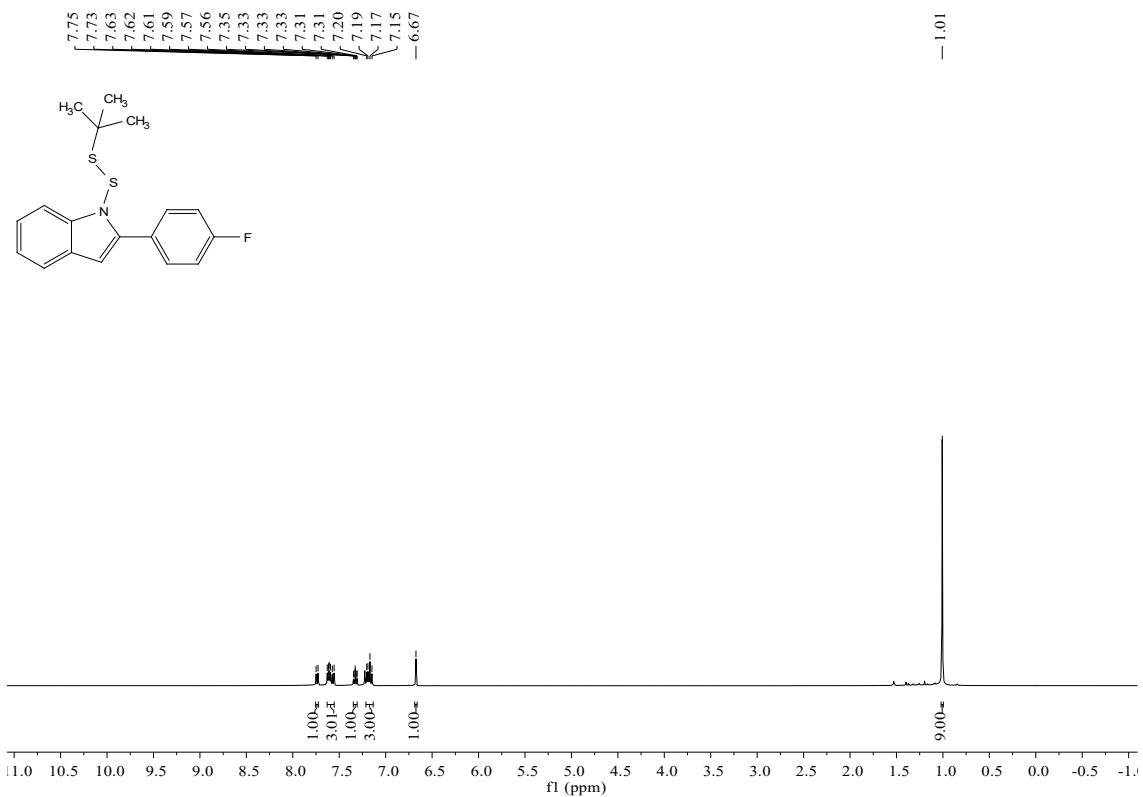
^1H NMR (400 MHz, CDCl_3) spectrum of compound **3o**



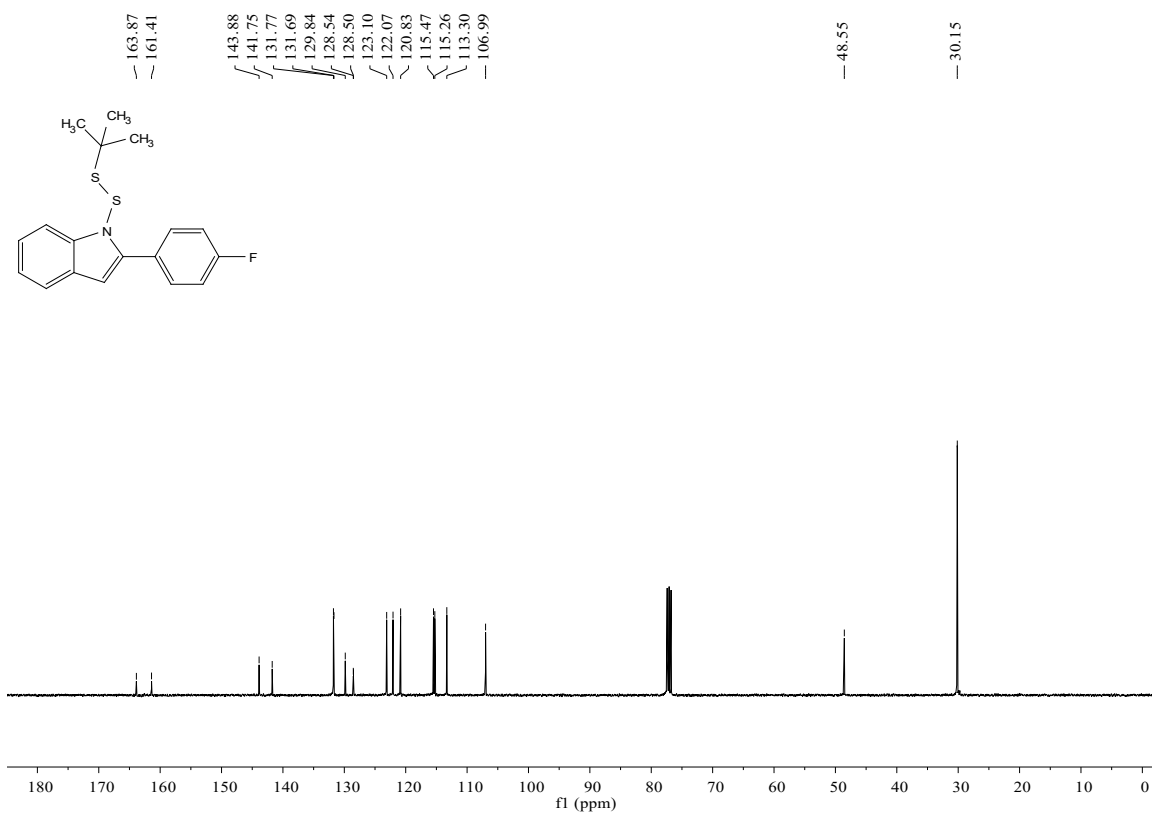
¹³C NMR (100 MHz, CDCl₃) spectrum of compound **3o**



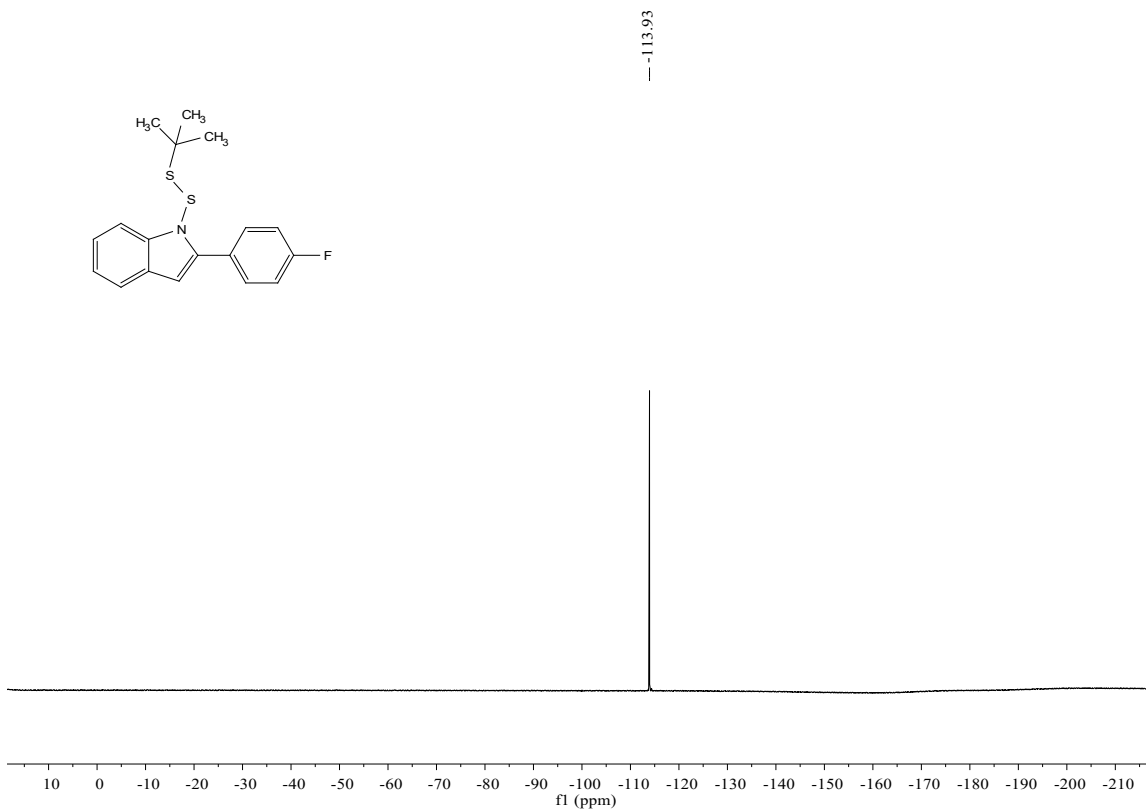
¹H NMR (400 MHz, CDCl₃) spectrum of compound **3p**



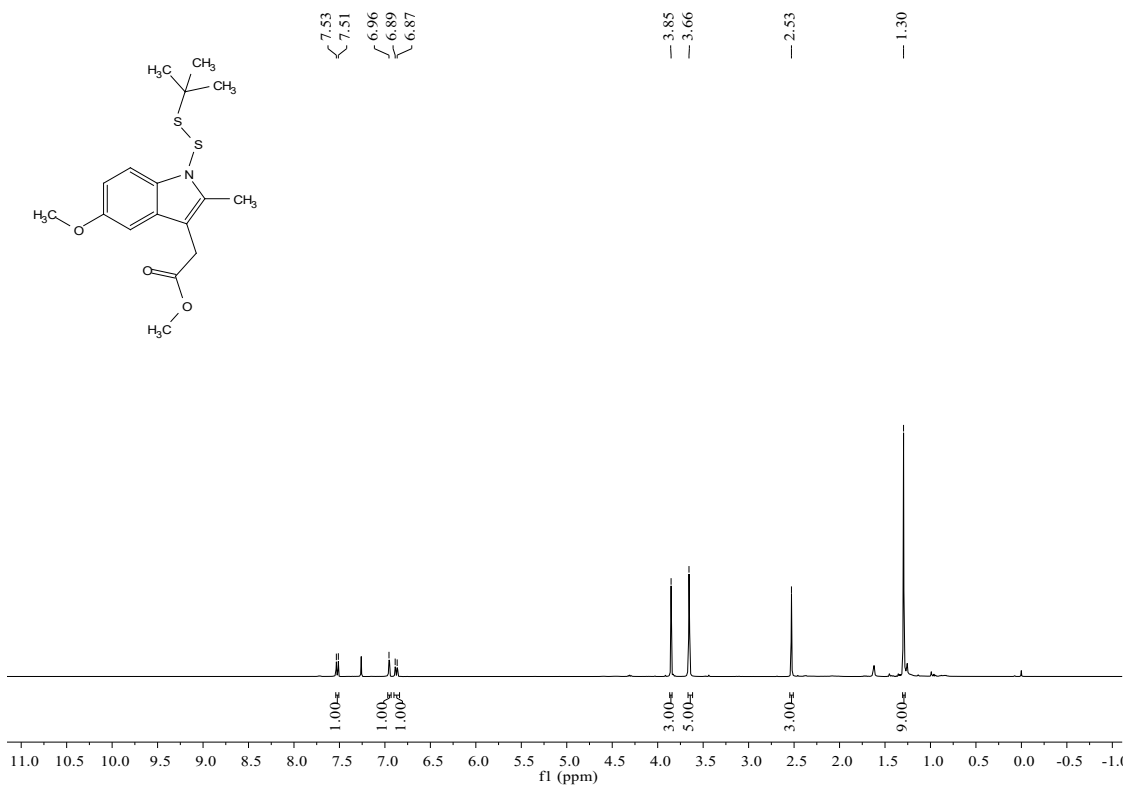
^{13}C NMR (100 MHz, CDCl_3) spectrum of compound **3p**



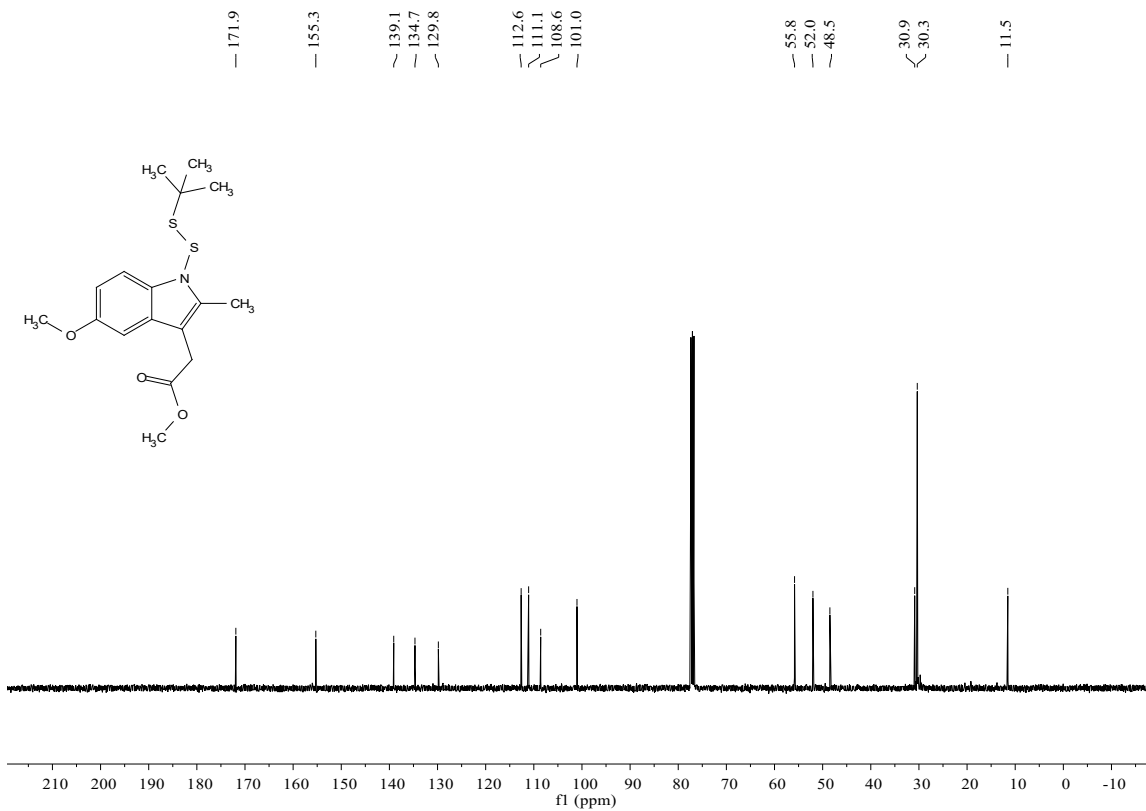
^{19}F NMR (100 MHz, CDCl_3) spectrum of compound **3p**



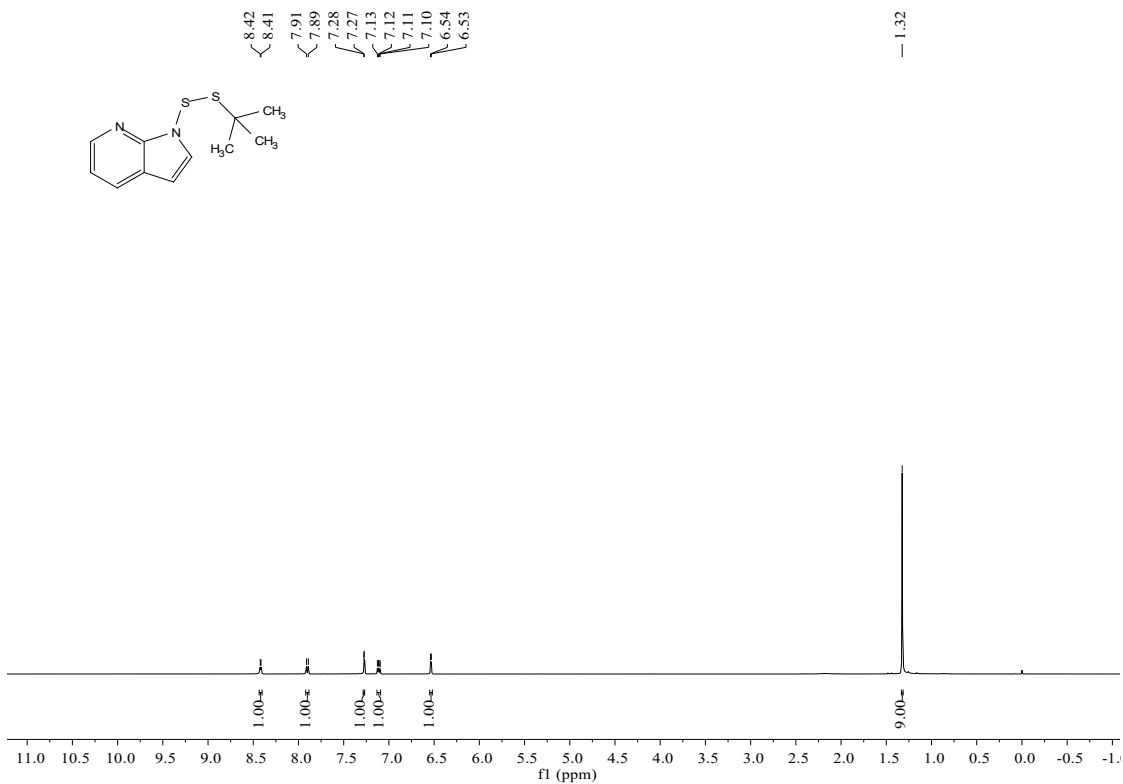
¹H NMR (400 MHz, CDCl₃) spectrum of compound **3q**



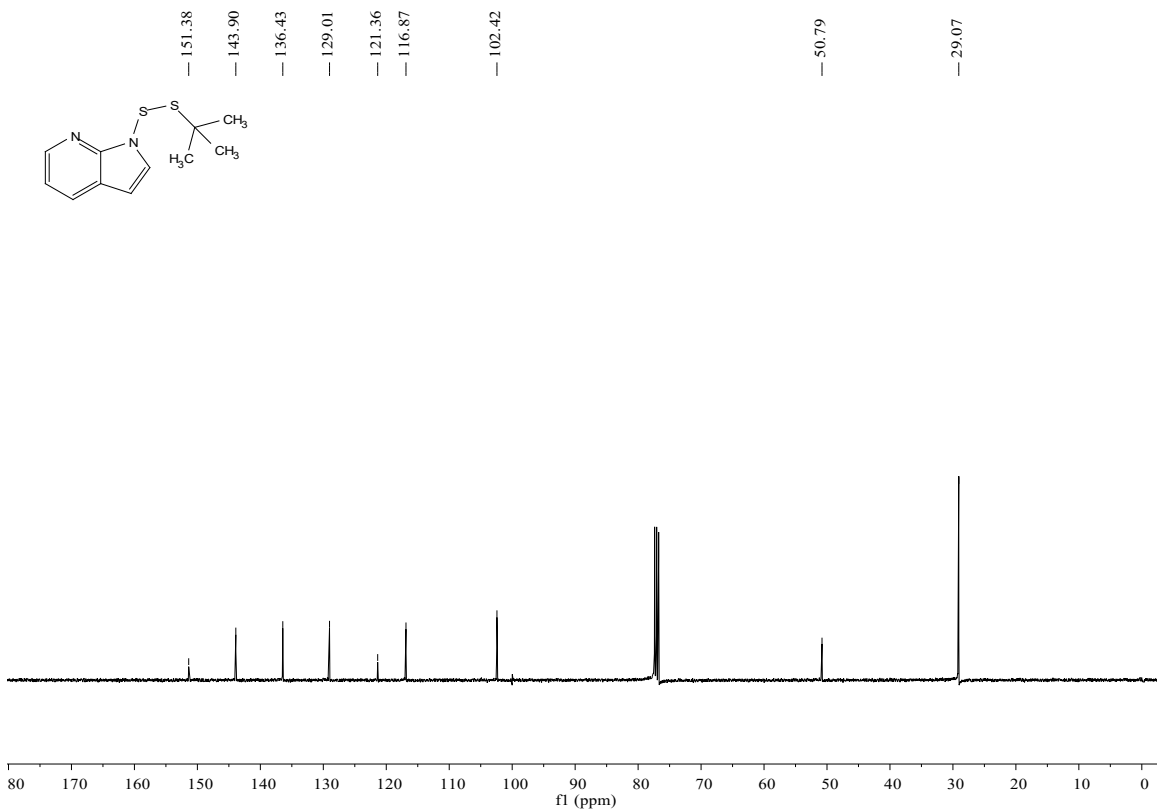
¹³C NMR (100 MHz, CDCl₃) spectrum of compound **3q**



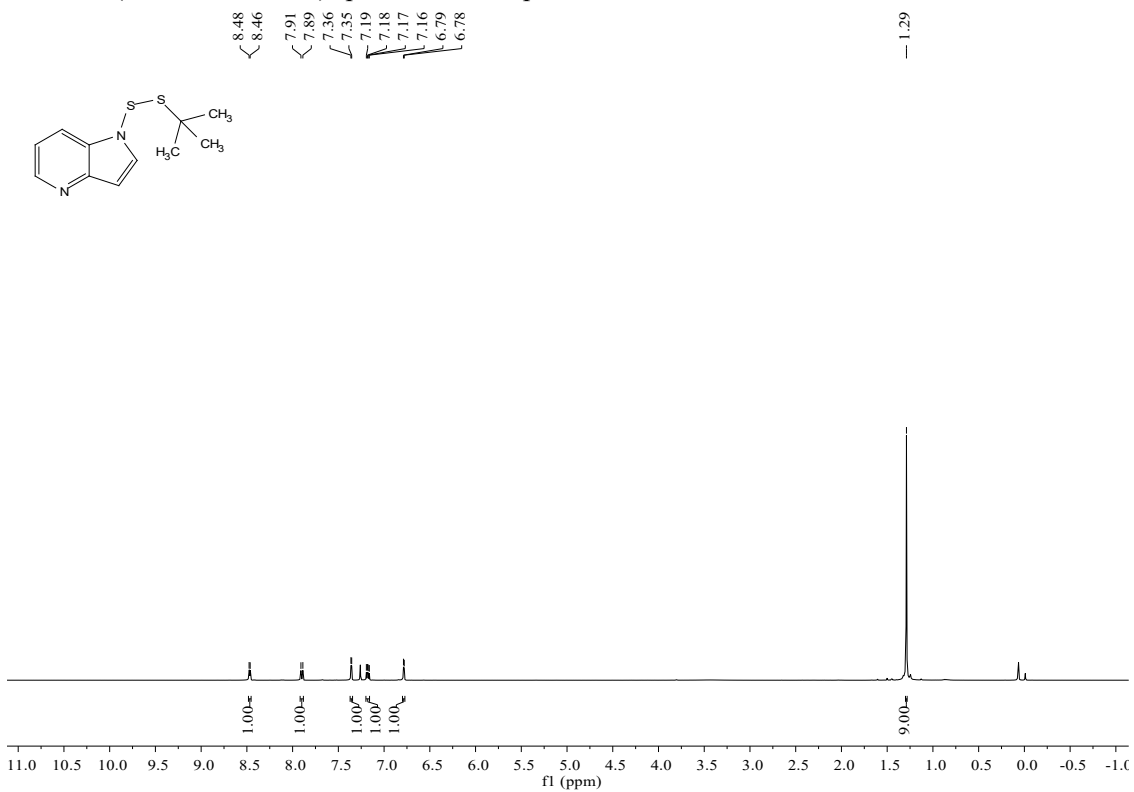
¹H NMR (400 MHz, CDCl₃) spectrum of compound **3r**



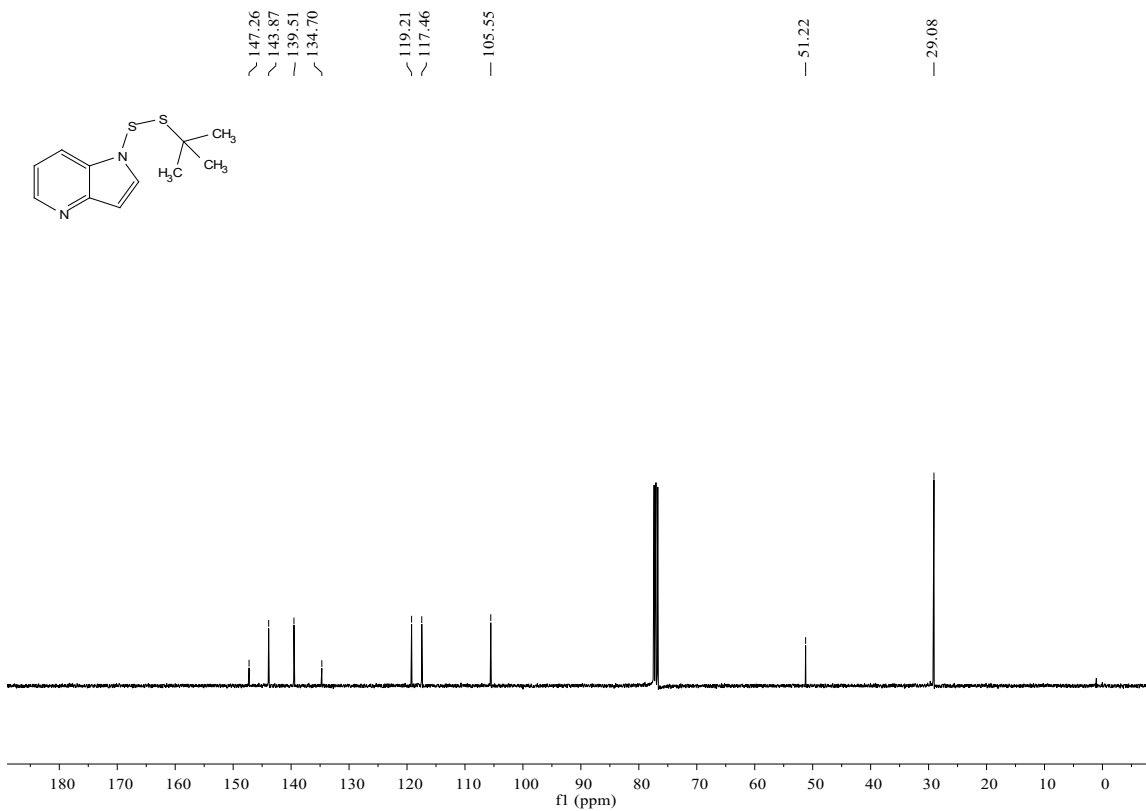
¹³C NMR (100 MHz, CDCl₃) spectrum of compound **3r**



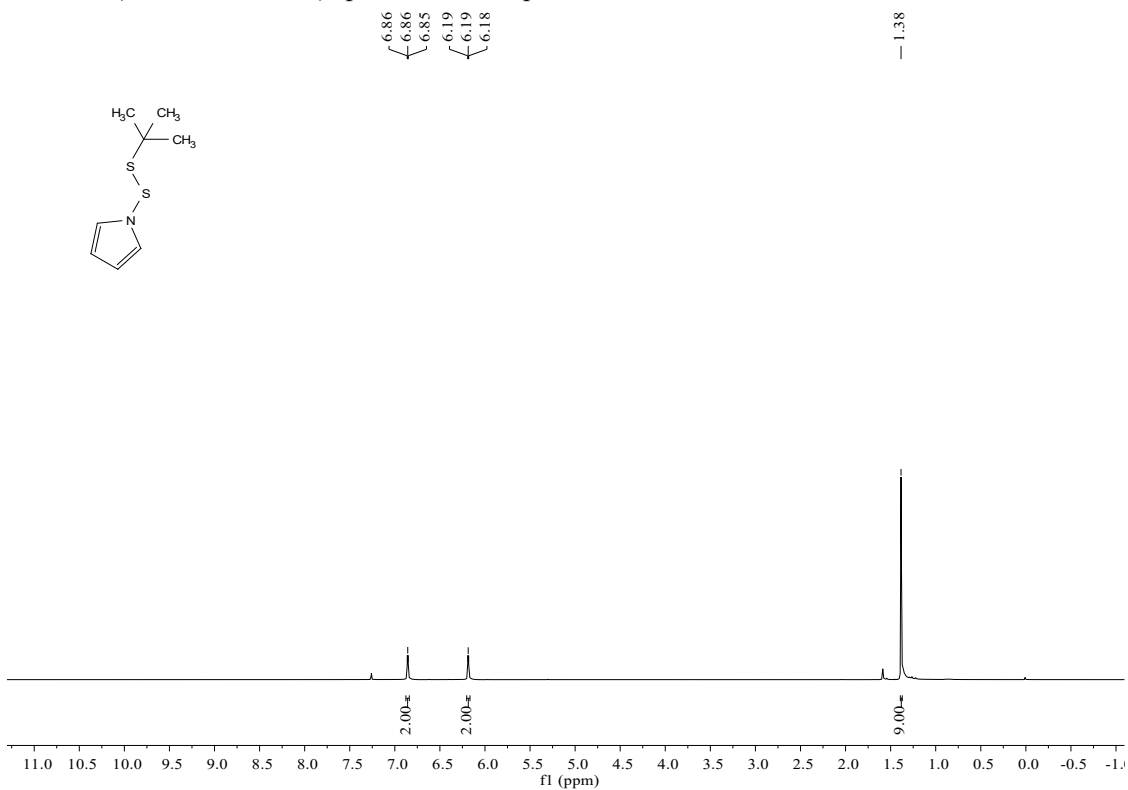
¹H NMR (400 MHz, CDCl₃) spectrum of compound **3s**



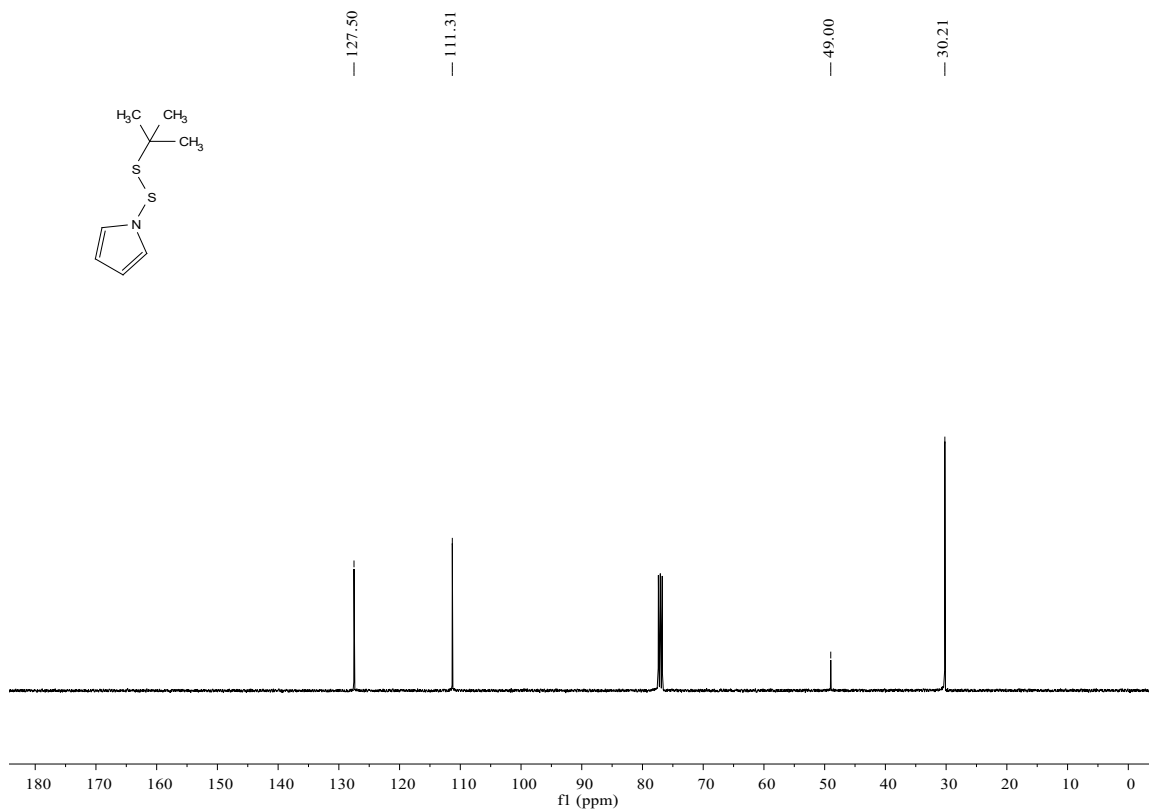
¹³C NMR (100 MHz, CDCl₃) spectrum of compound **3s**

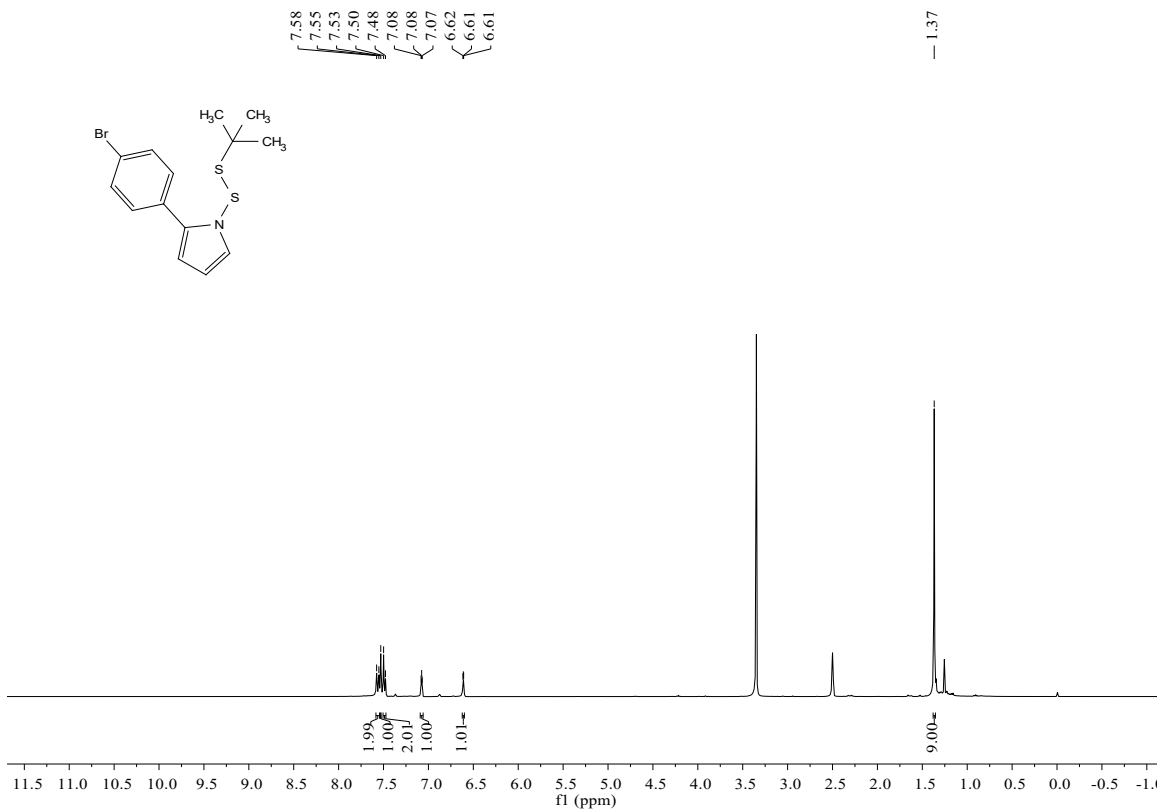


¹H NMR (400 MHz, CDCl₃) spectrum of compound **3t**

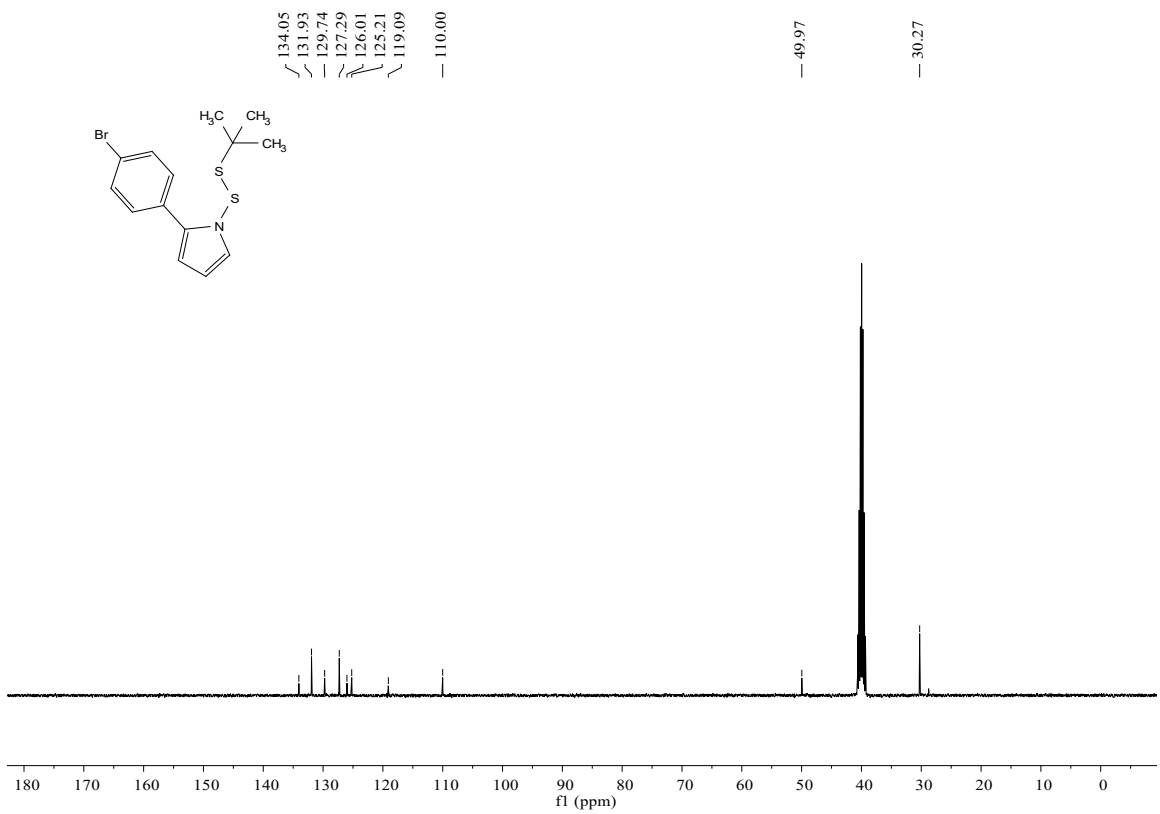


¹³C NMR (100 MHz, CDCl₃) spectrum of compound **3t**

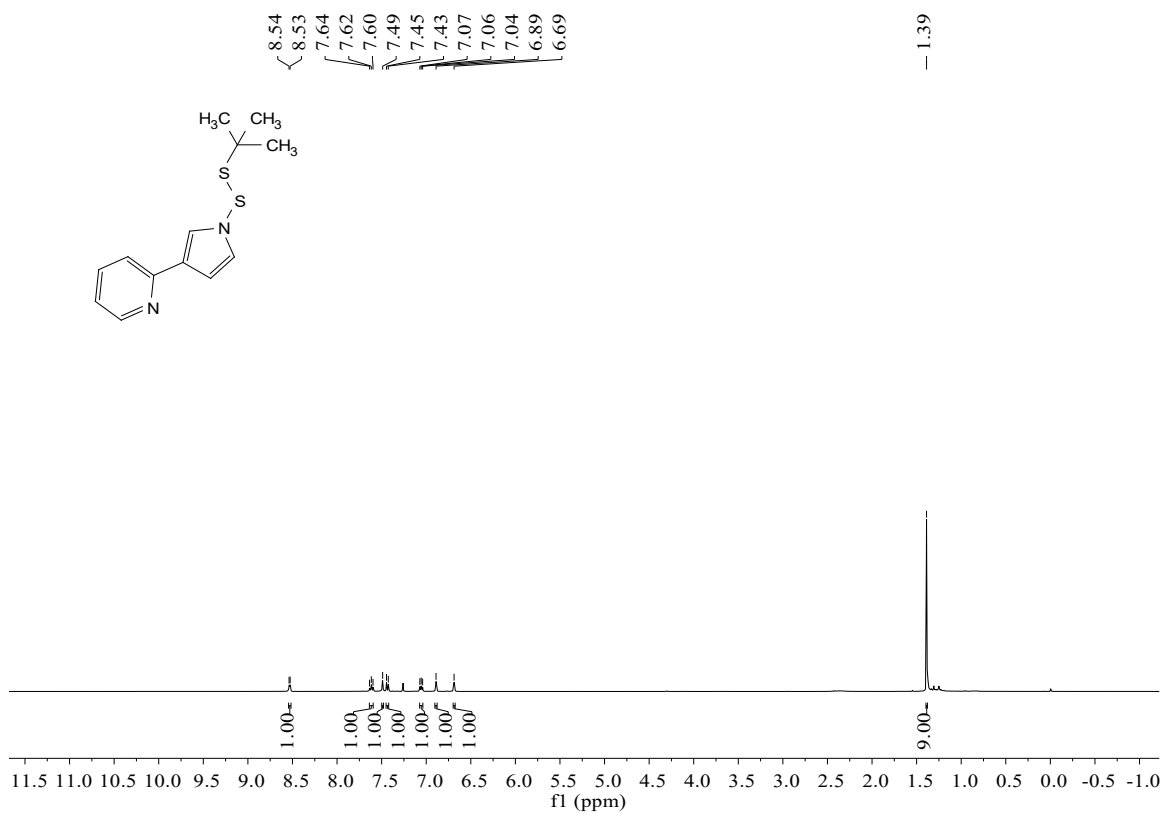




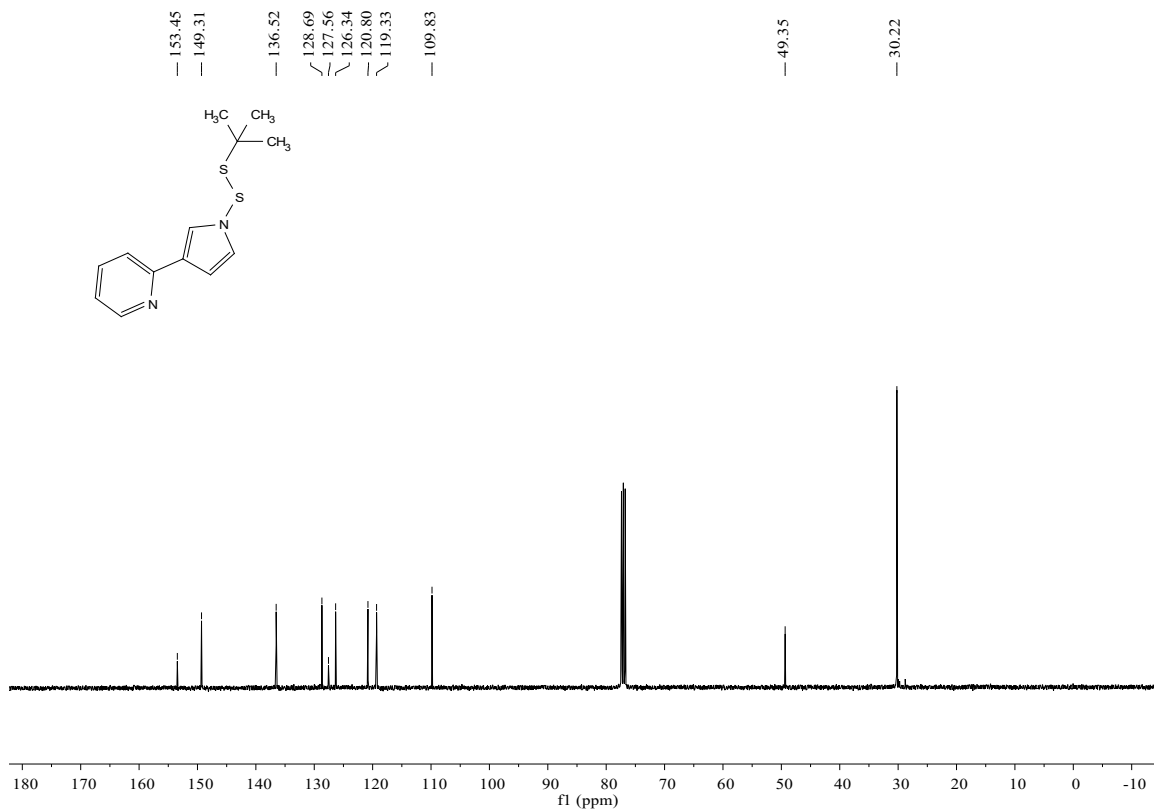
¹³C NMR (100 MHz, (CD₃)₂SO) spectrum of compound **3u**



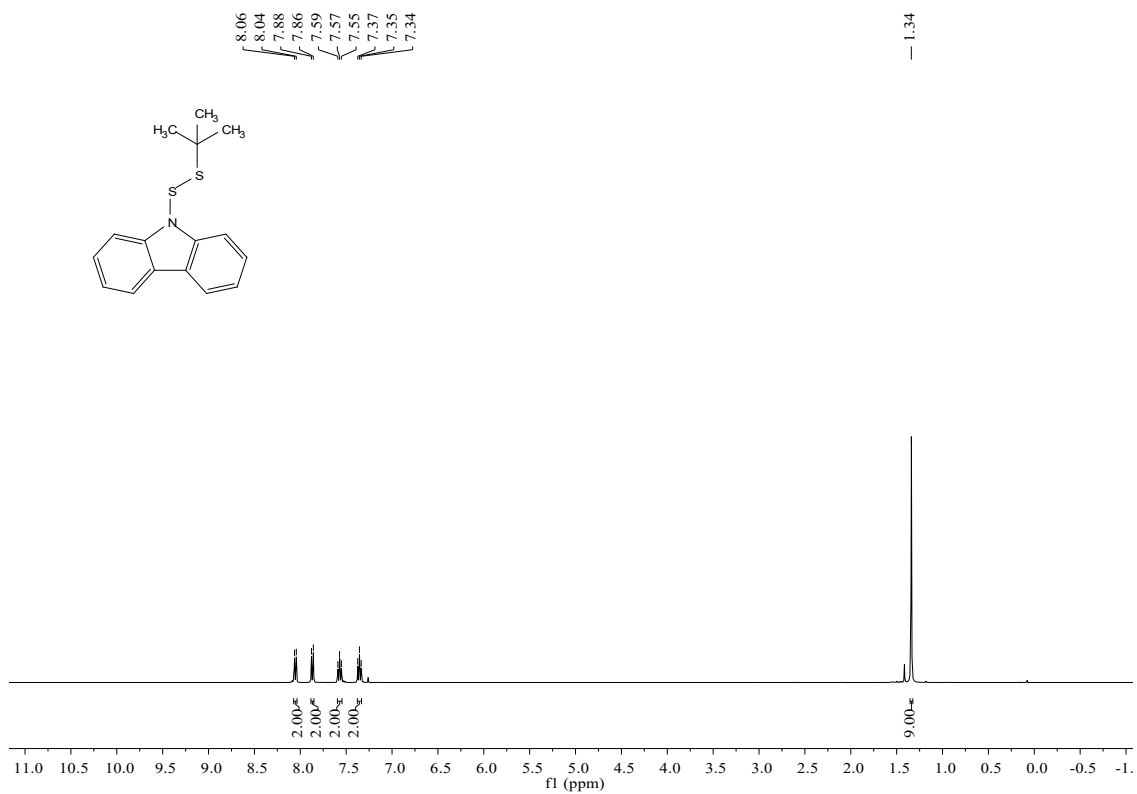
¹H NMR (400 MHz, CDCl₃) spectrum of compound **3v**



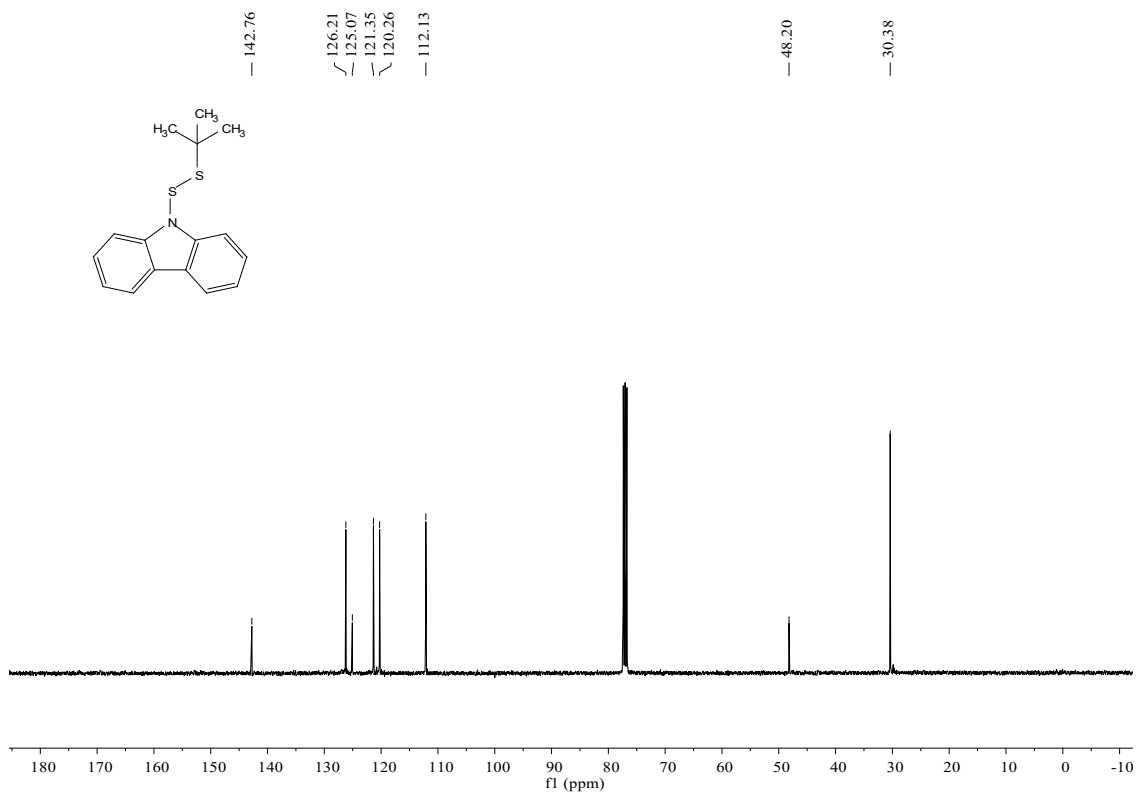
¹³C NMR (100 MHz, CDCl₃) spectrum of compound **3v**



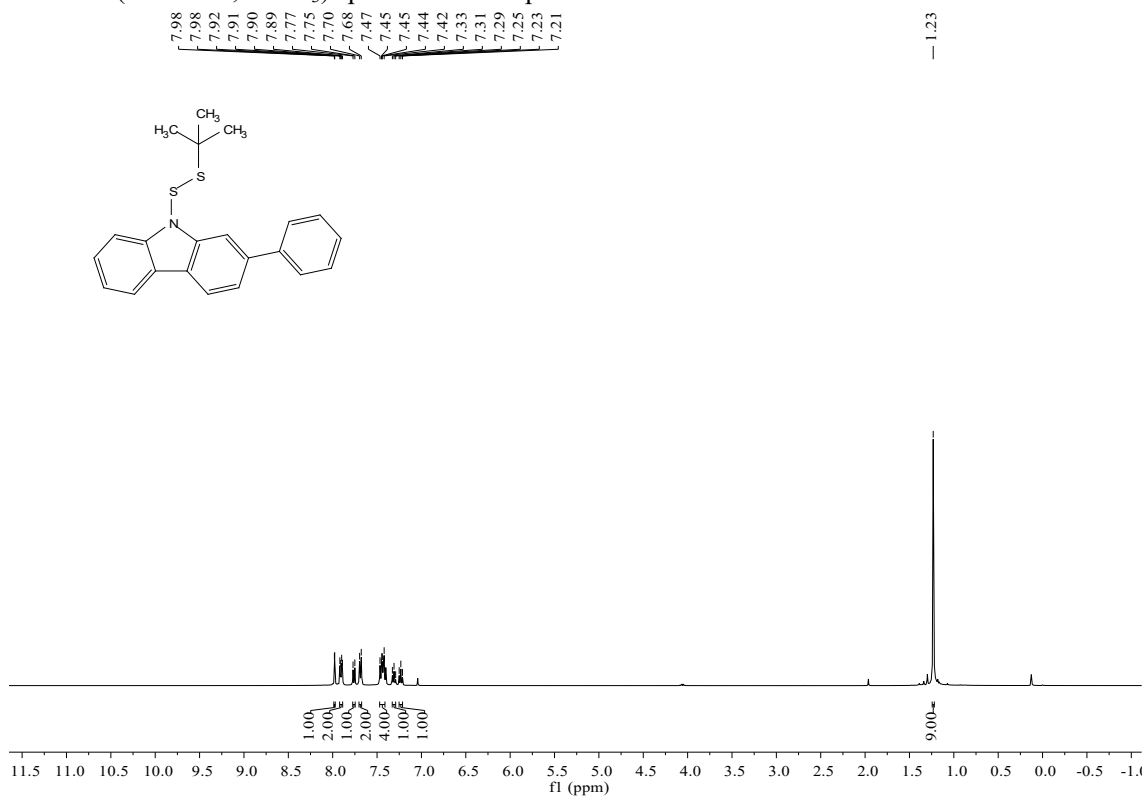
¹H NMR (400 MHz, CDCl₃) spectrum of compound **5a**



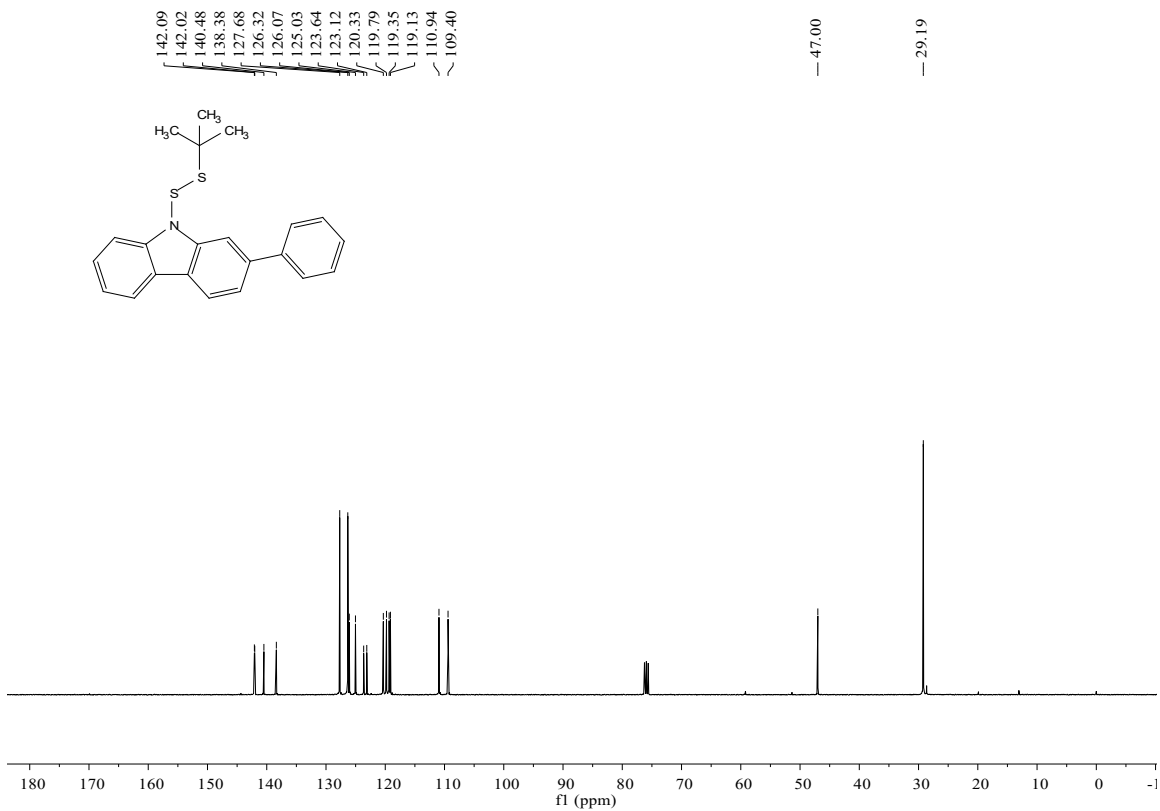
¹³C NMR (100 MHz, CDCl₃) spectrum of compound **5a**



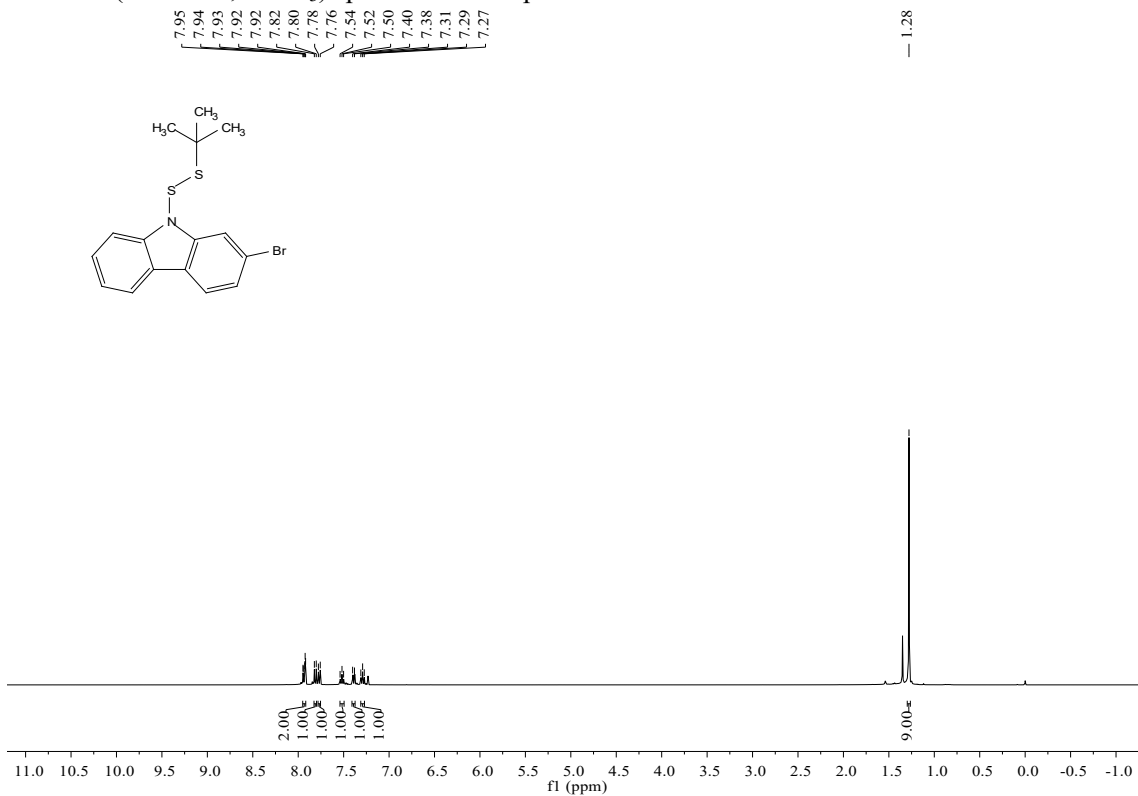
¹H NMR (400 MHz, CDCl₃) spectrum of compound **5b**



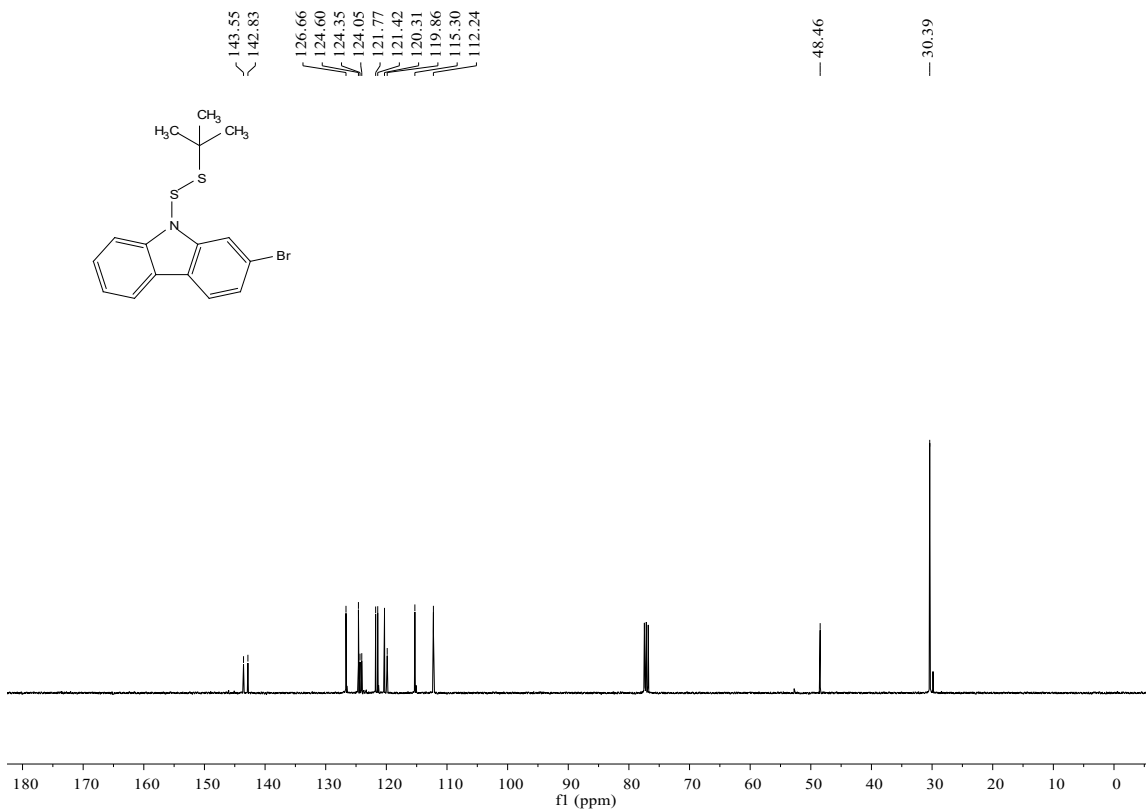
¹³C NMR (100 MHz, CDCl₃) spectrum of compound **5b**



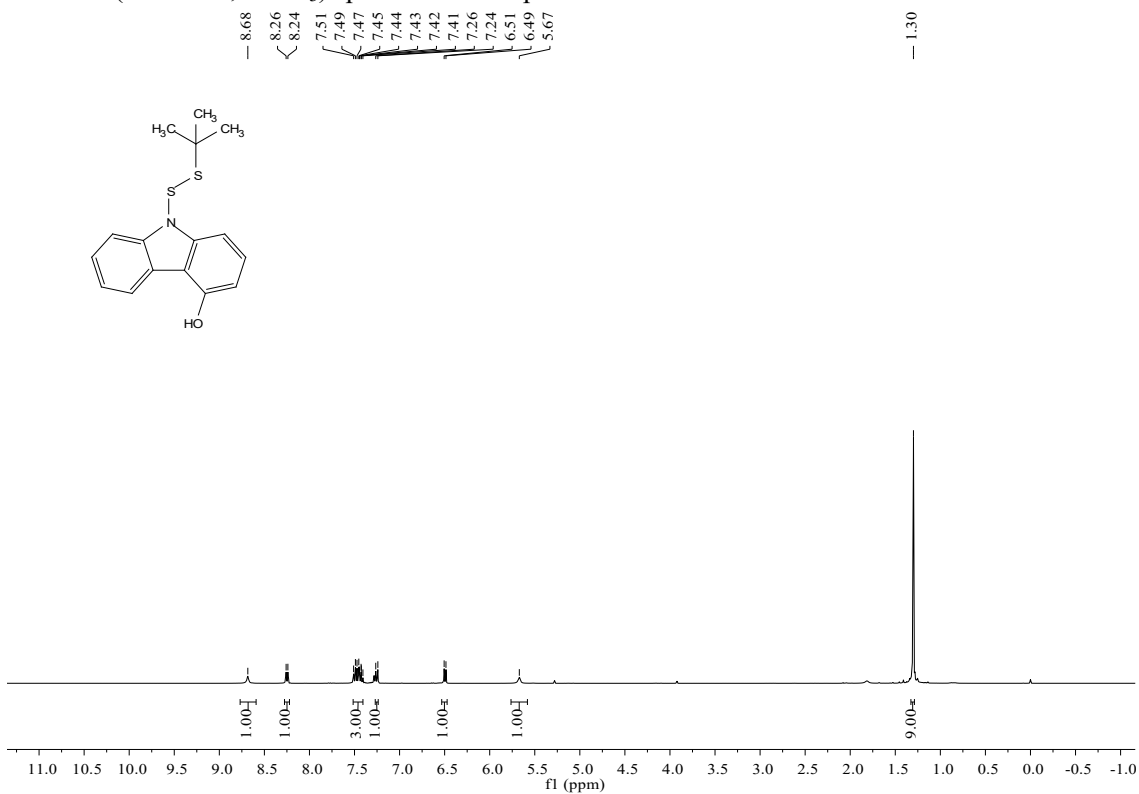
¹H NMR (400 MHz, CDCl₃) spectrum of compound **5c**



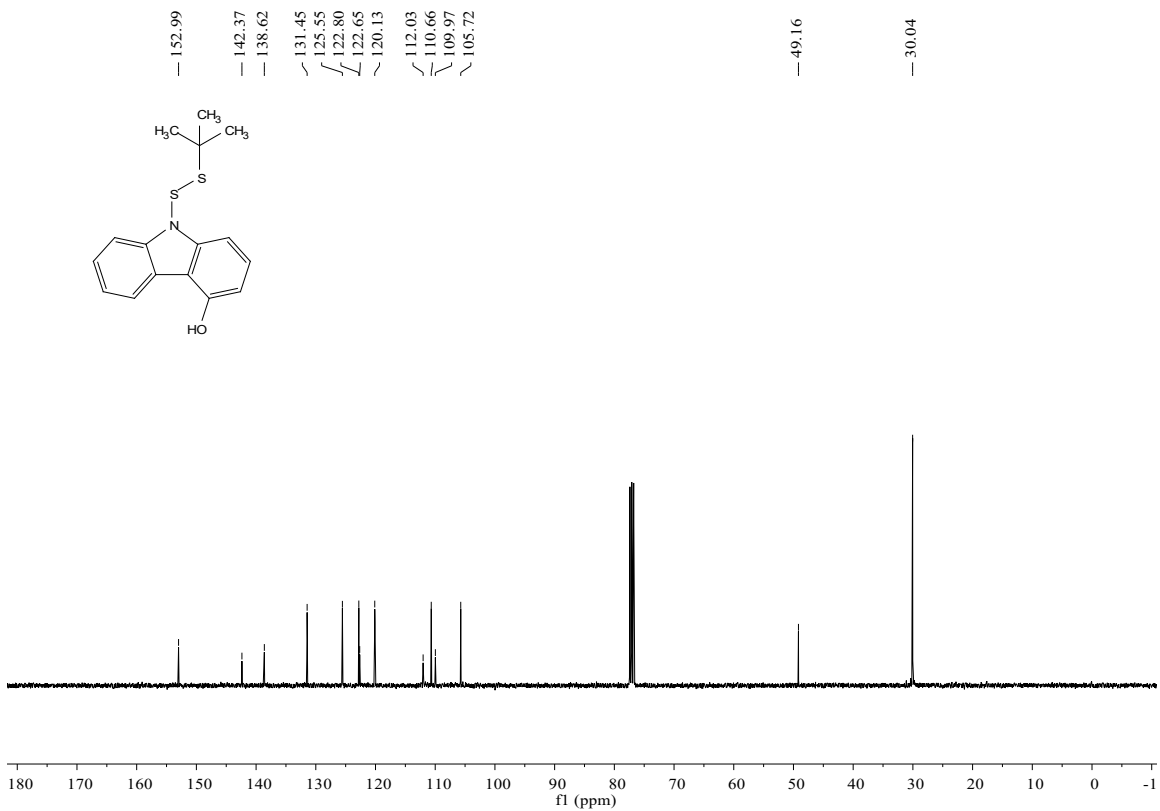
¹³C NMR (100 MHz, CDCl₃) spectrum of compound **5c**



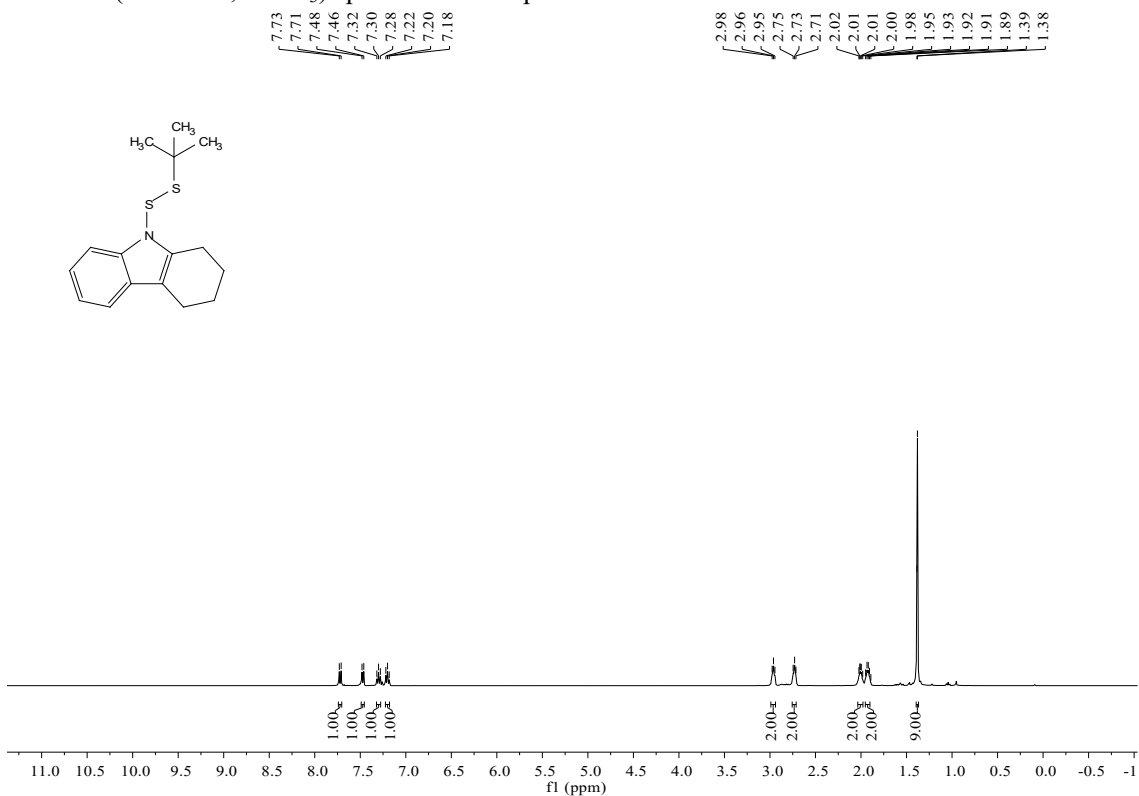
¹H NMR (400 MHz, CDCl₃) spectrum of compound **5d**



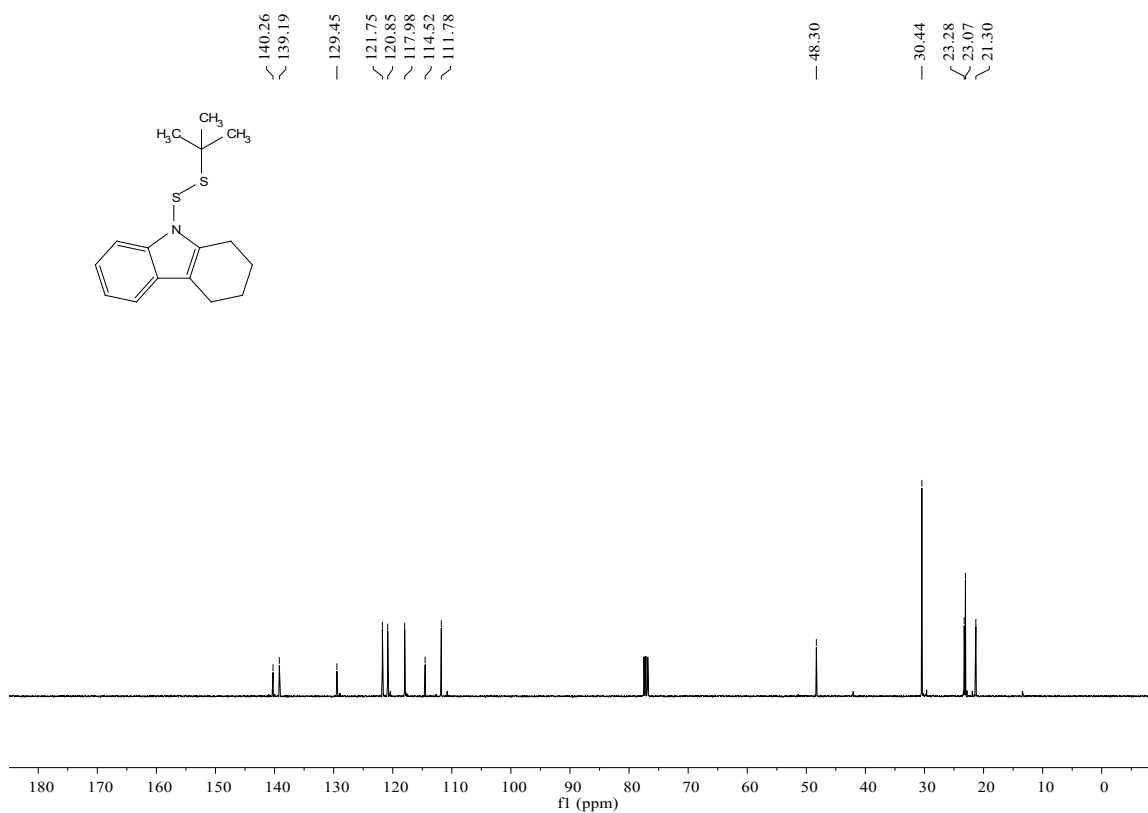
¹³C NMR (100 MHz, CDCl₃) spectrum of compound **5d**



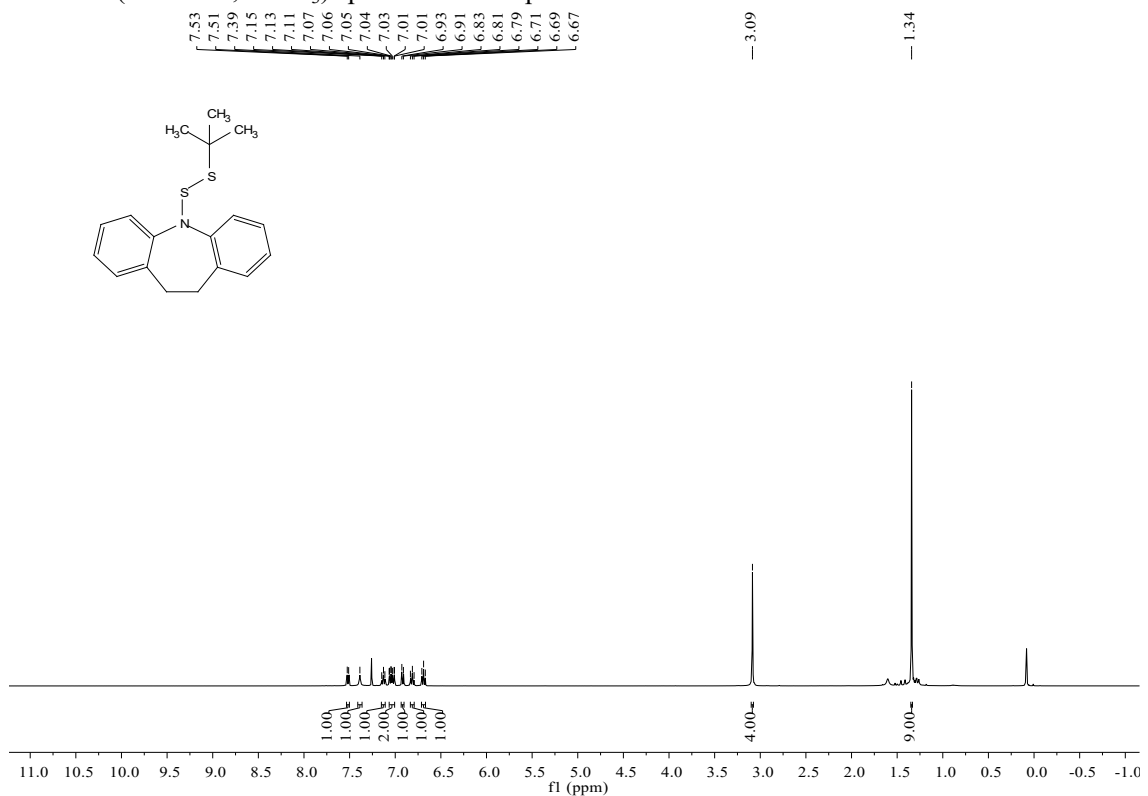
¹H NMR (400 MHz, CDCl₃) spectrum of compound 5e



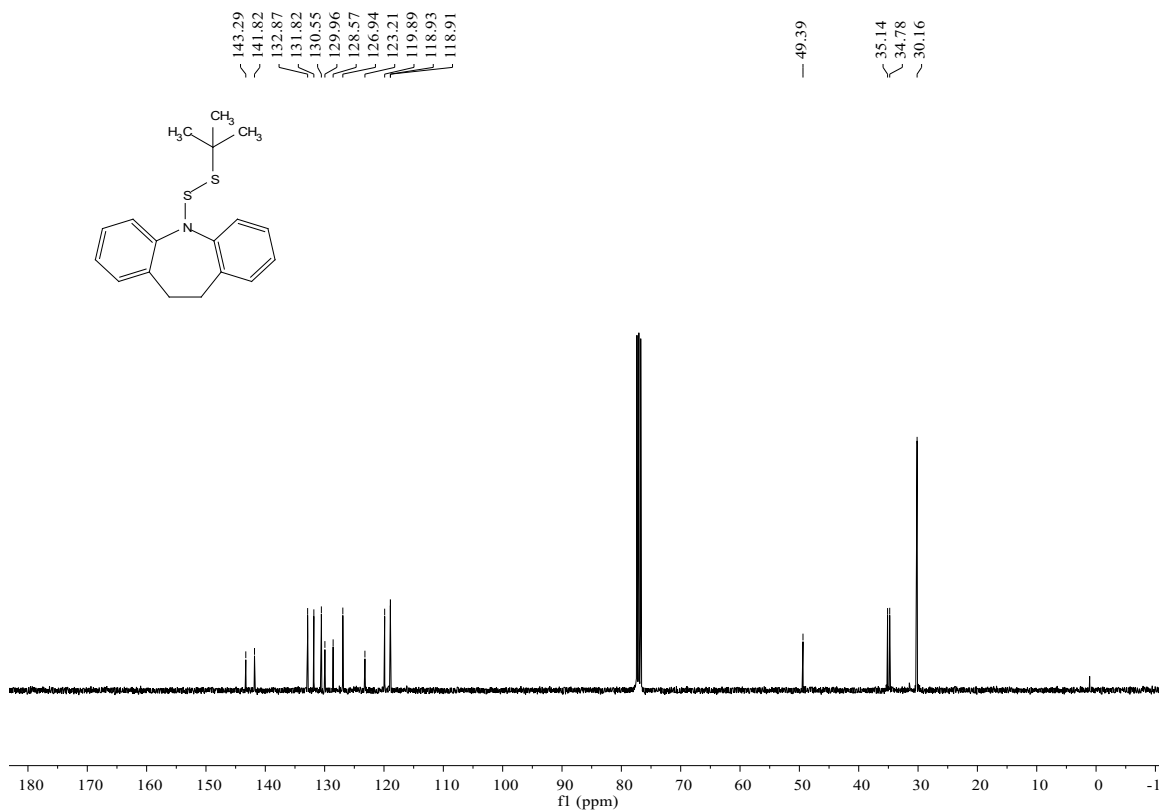
^{13}C NMR (100 MHz, CDCl_3) spectrum of compound **5e**



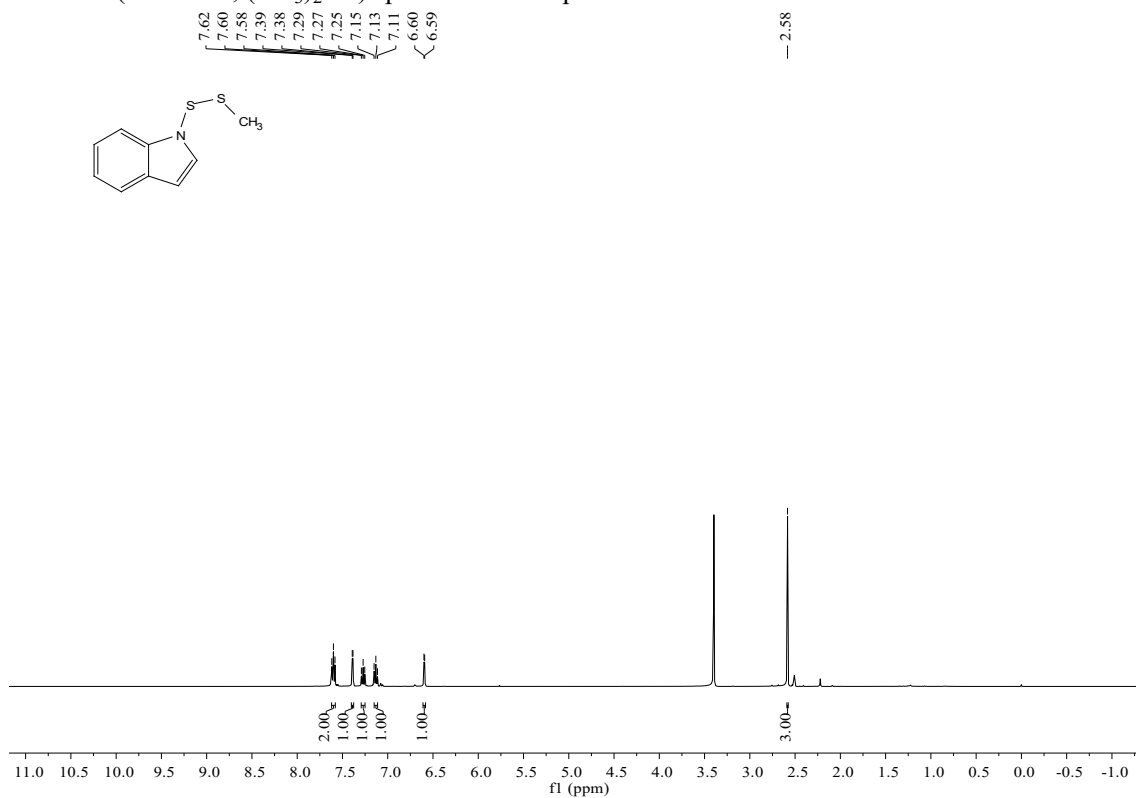
^1H NMR (400 MHz, CDCl_3) spectrum of compound **5f**



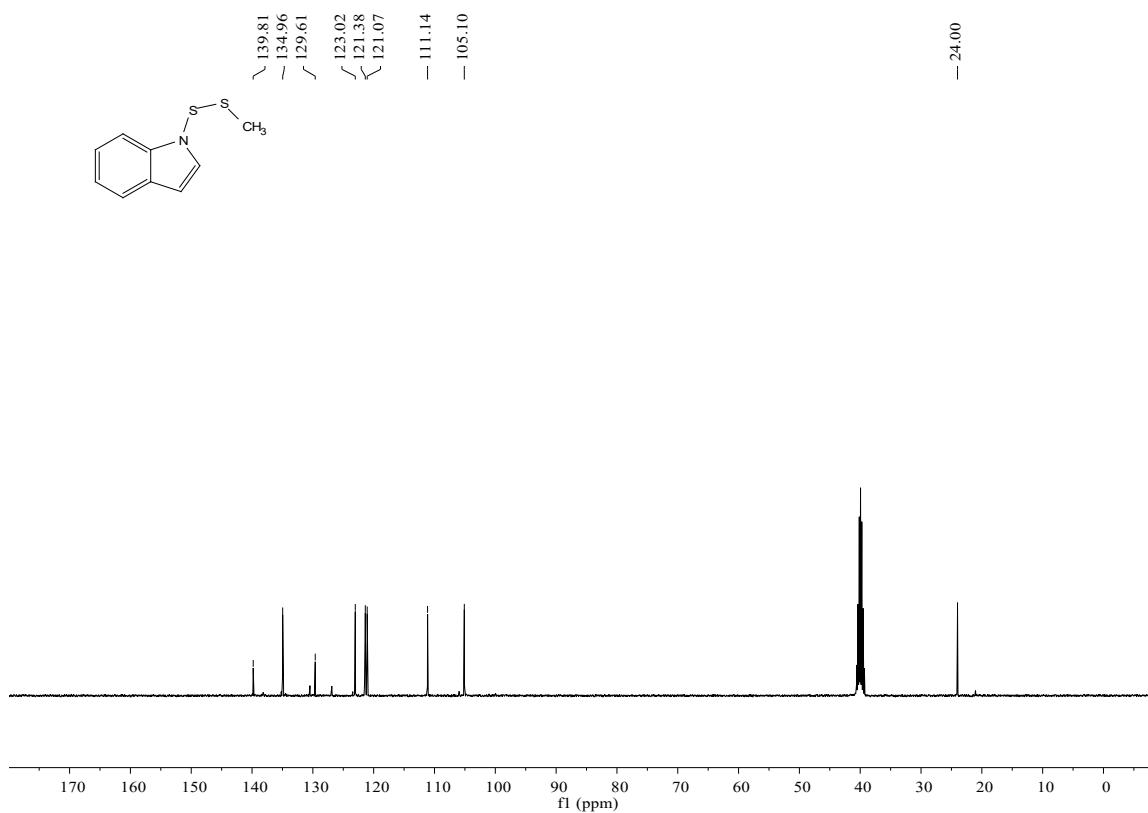
^{13}C NMR (100 MHz, CDCl_3) spectrum of compound **5f**



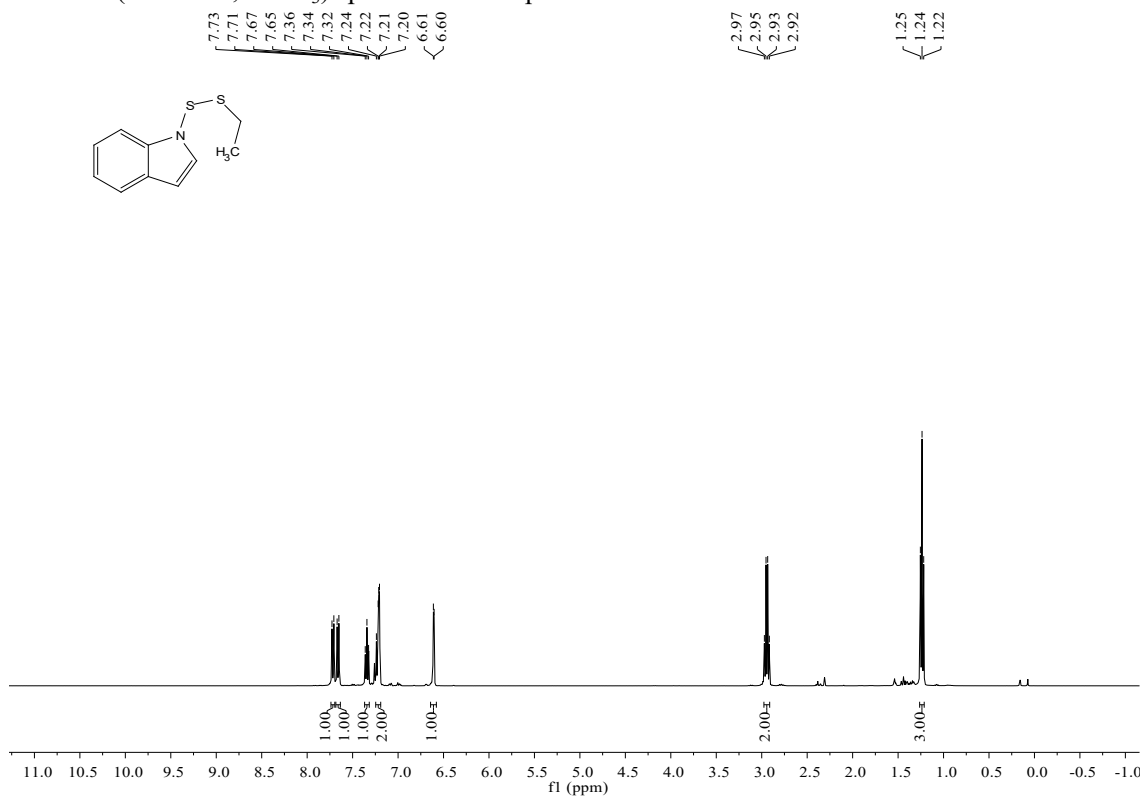
^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) spectrum of compound **6a**



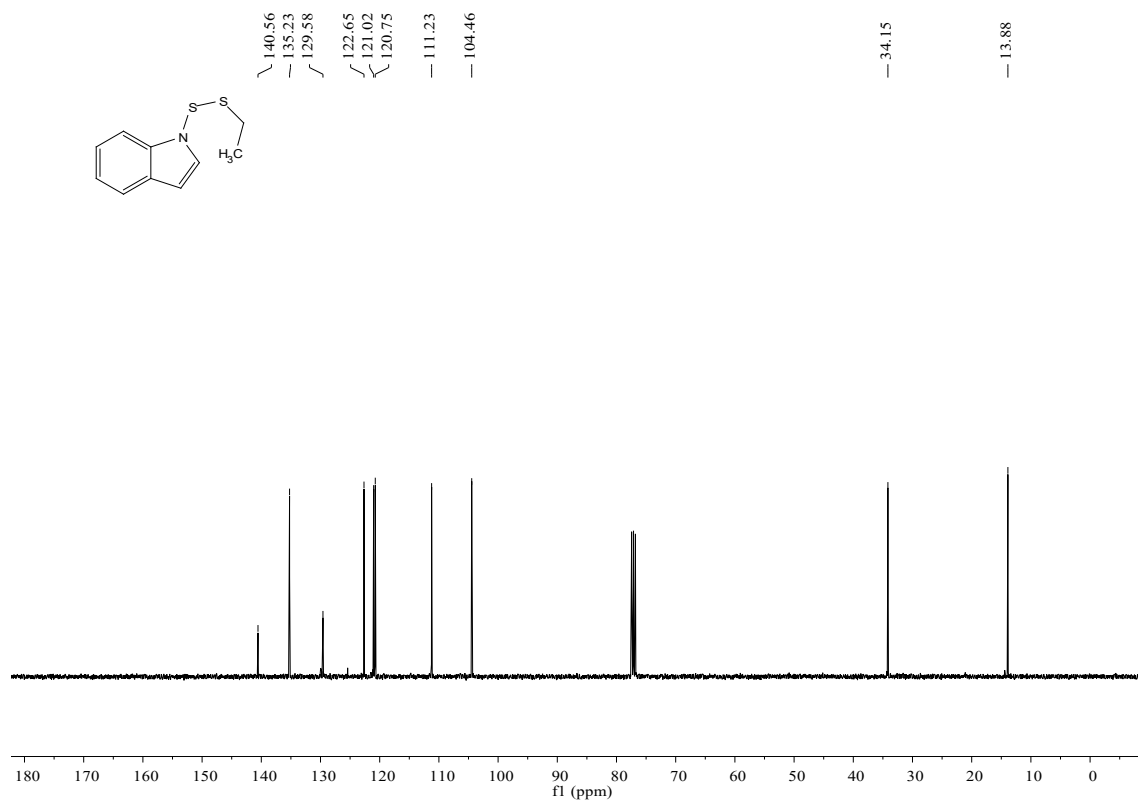
^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$) spectrum of compound **6a**



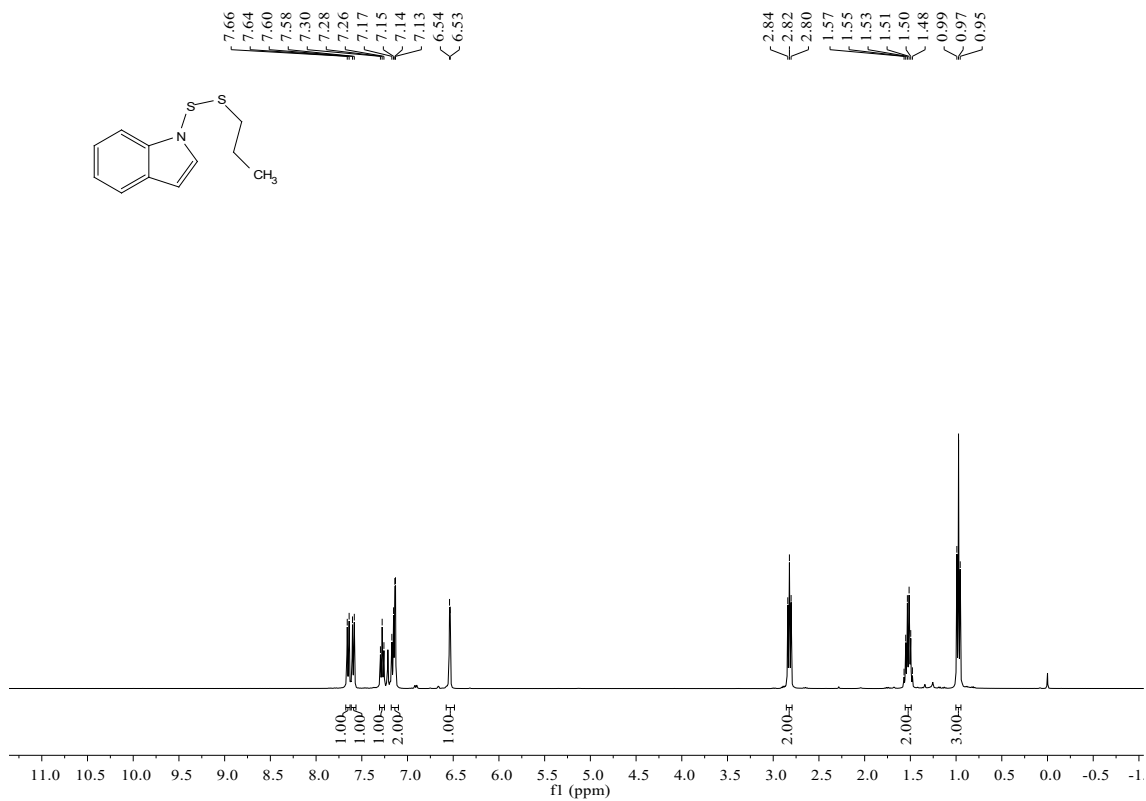
^1H NMR (400 MHz, CDCl_3) spectrum of compound **6b**



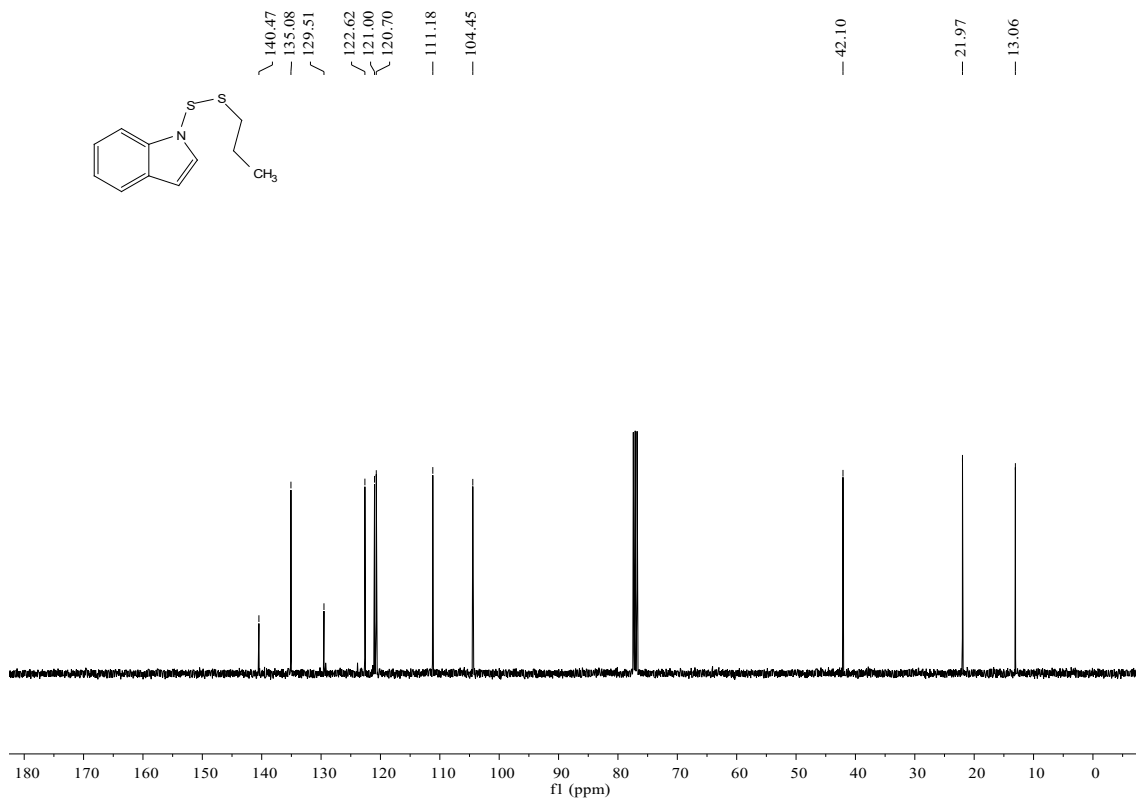
^{13}C NMR (100 MHz, CDCl_3) spectrum of compound **6b**



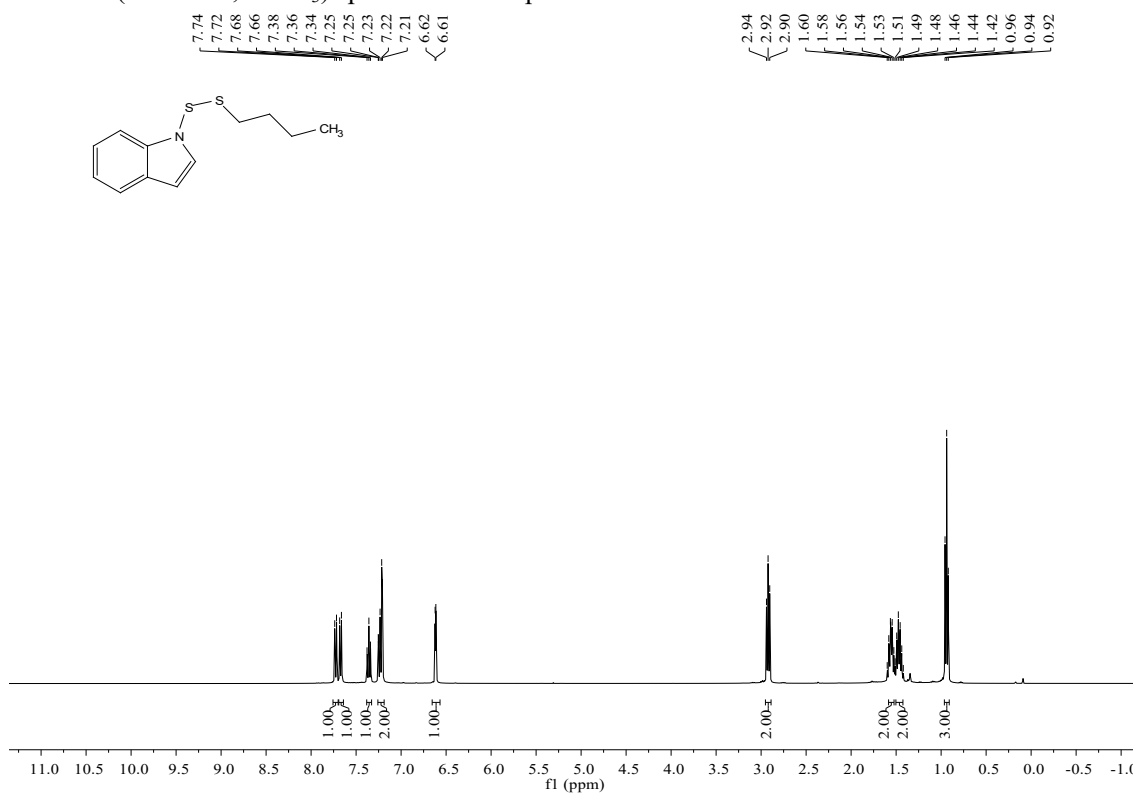
^1H NMR (400 MHz, CDCl_3) spectrum of compound **6c**



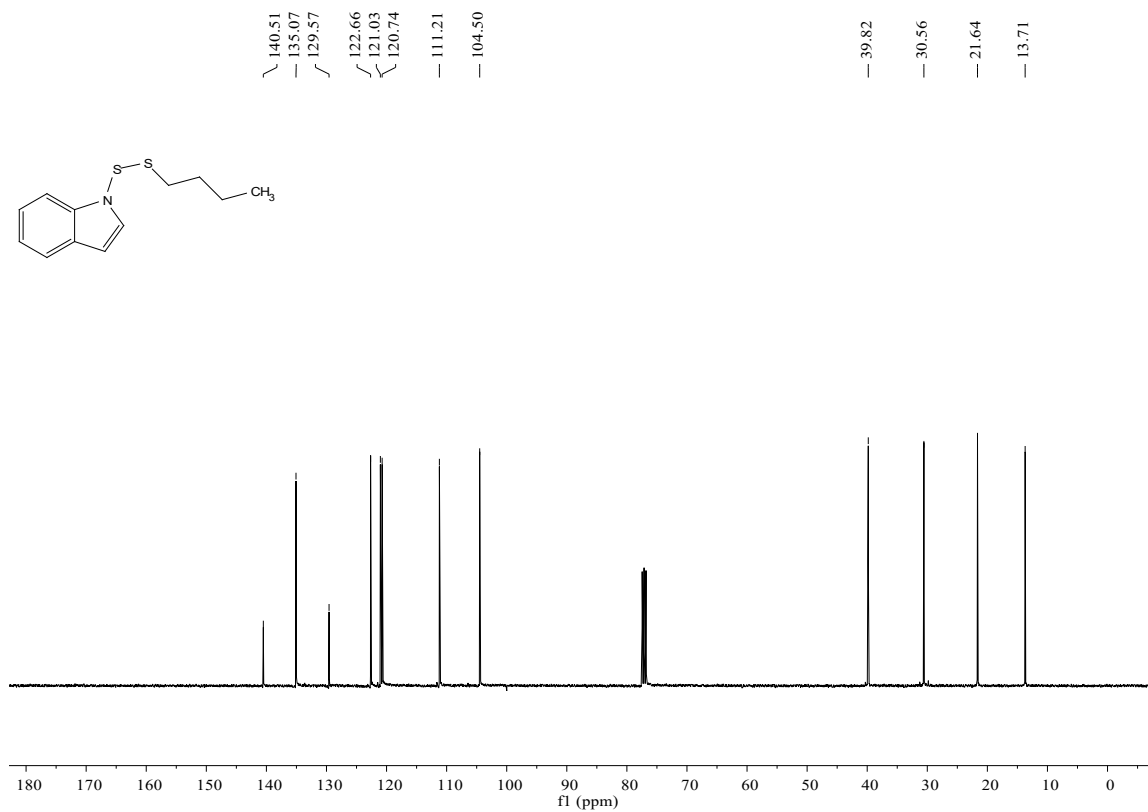
^{13}C NMR (100 MHz, CDCl_3) spectrum of compound **6c**



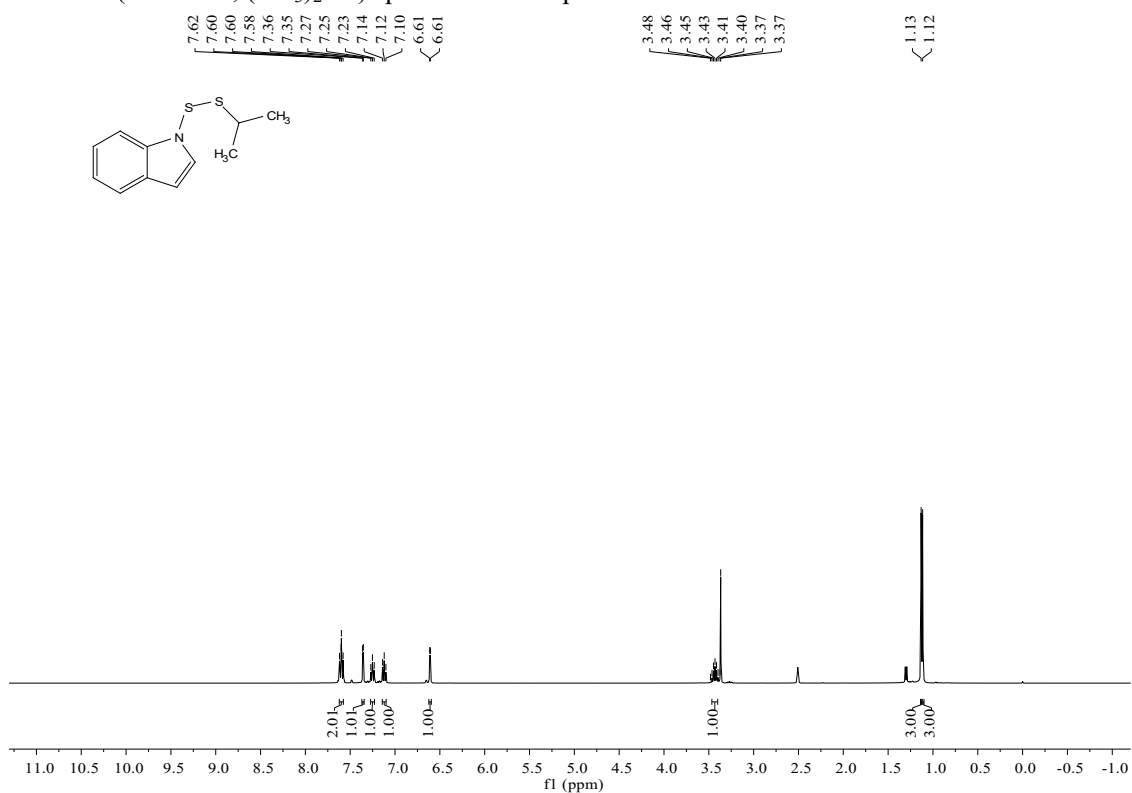
¹H NMR (400 MHz, CDCl₃) spectrum of compound **6d**



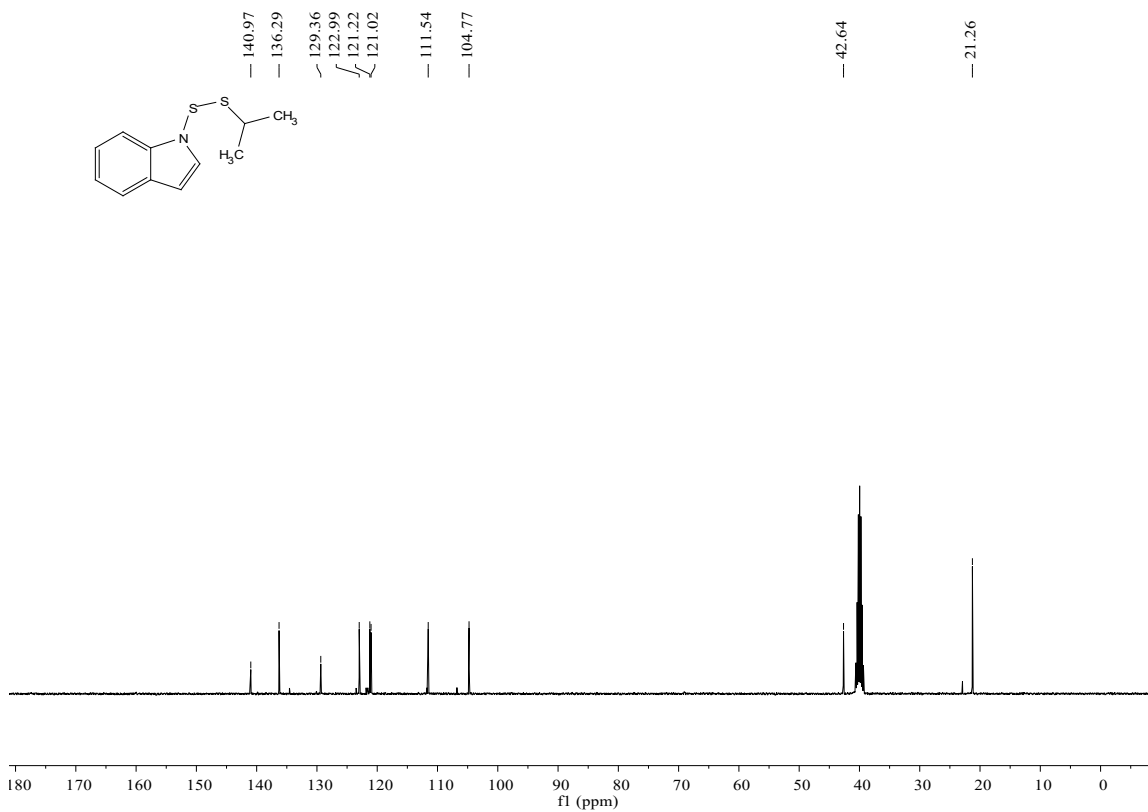
¹³C NMR (100 MHz, CDCl₃) spectrum of compound **6d**



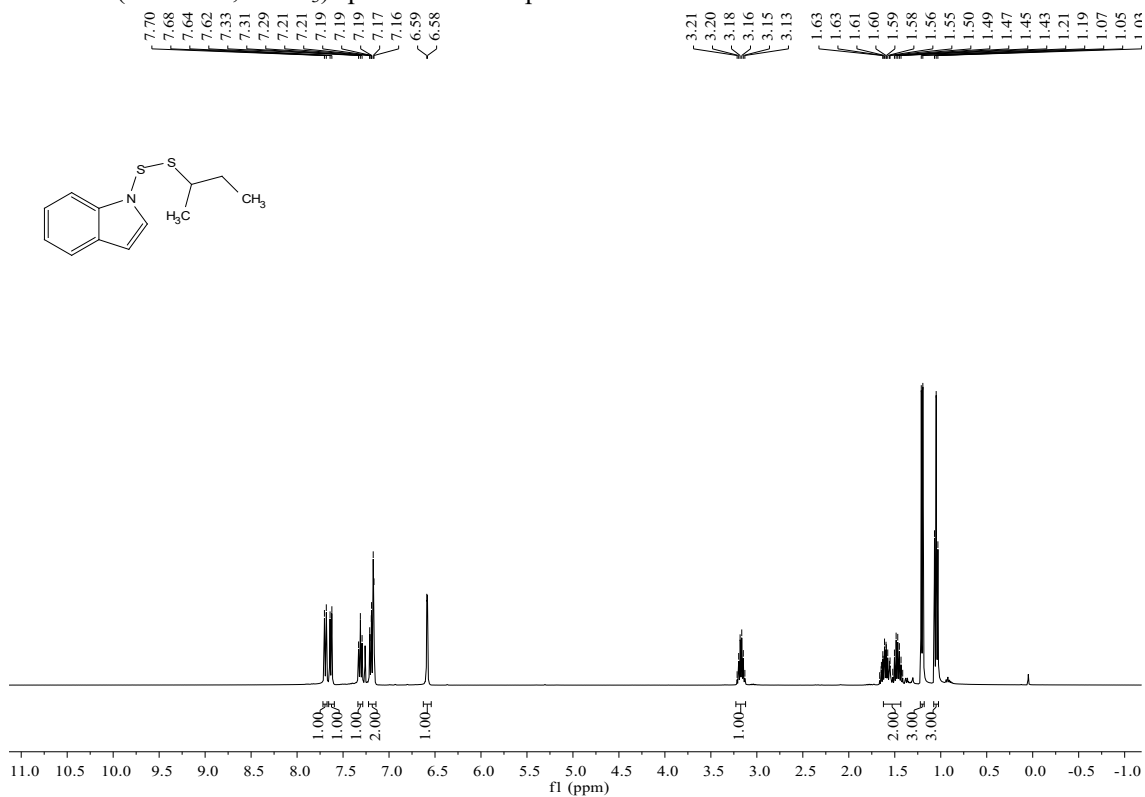
¹H NMR (400 MHz, (CD₃)₂SO) spectrum of compound **6e**



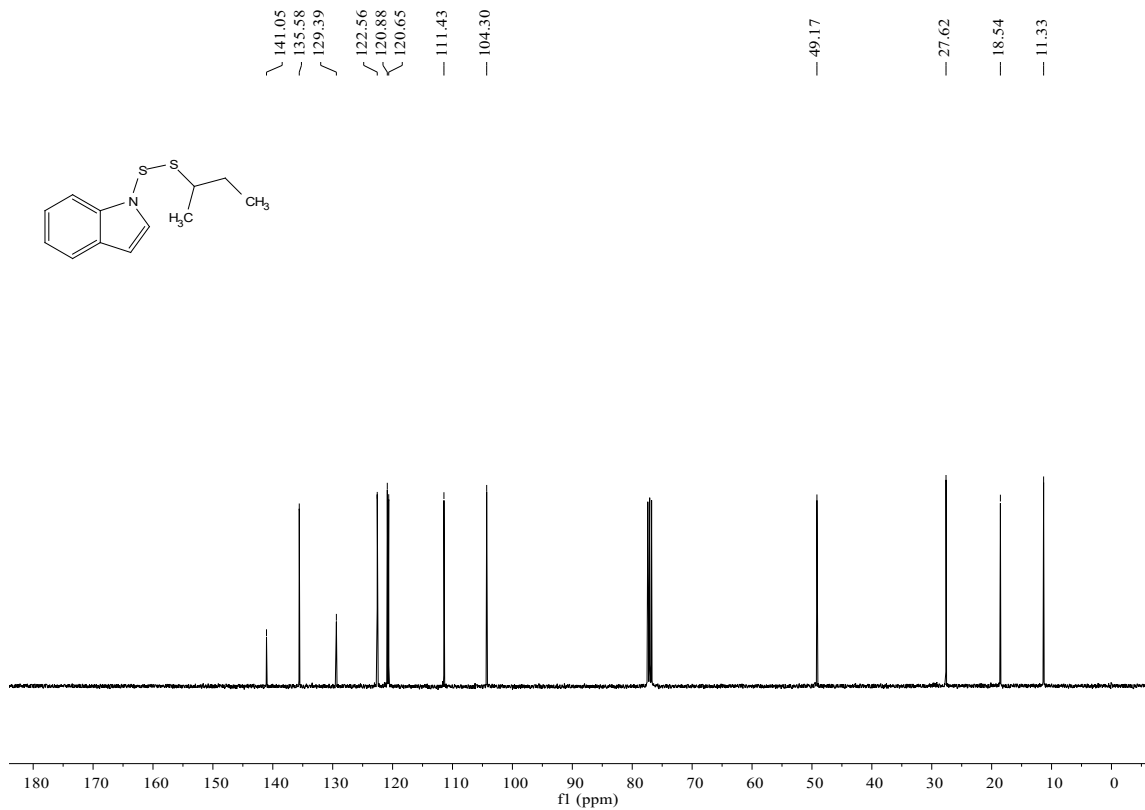
¹³C NMR (100 MHz, (CD₃)₂SO) spectrum of compound **6e**



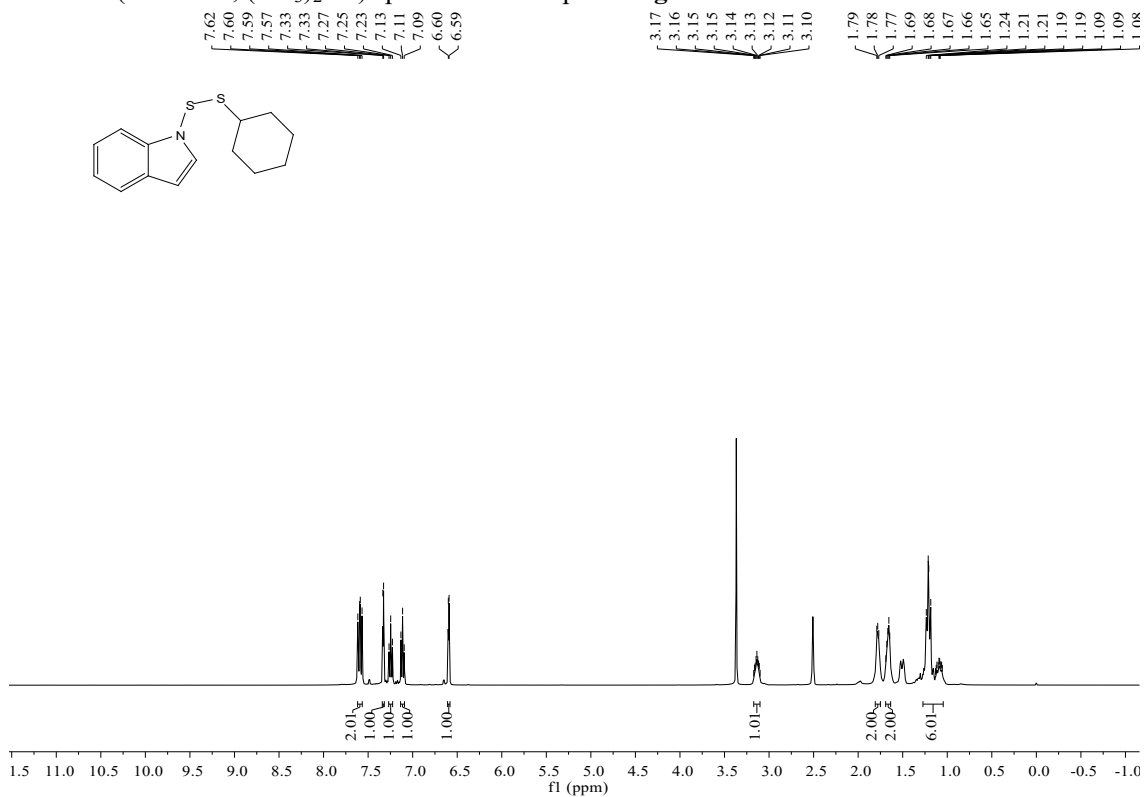
¹H NMR (400 MHz, CDCl₃) spectrum of compound **6f**



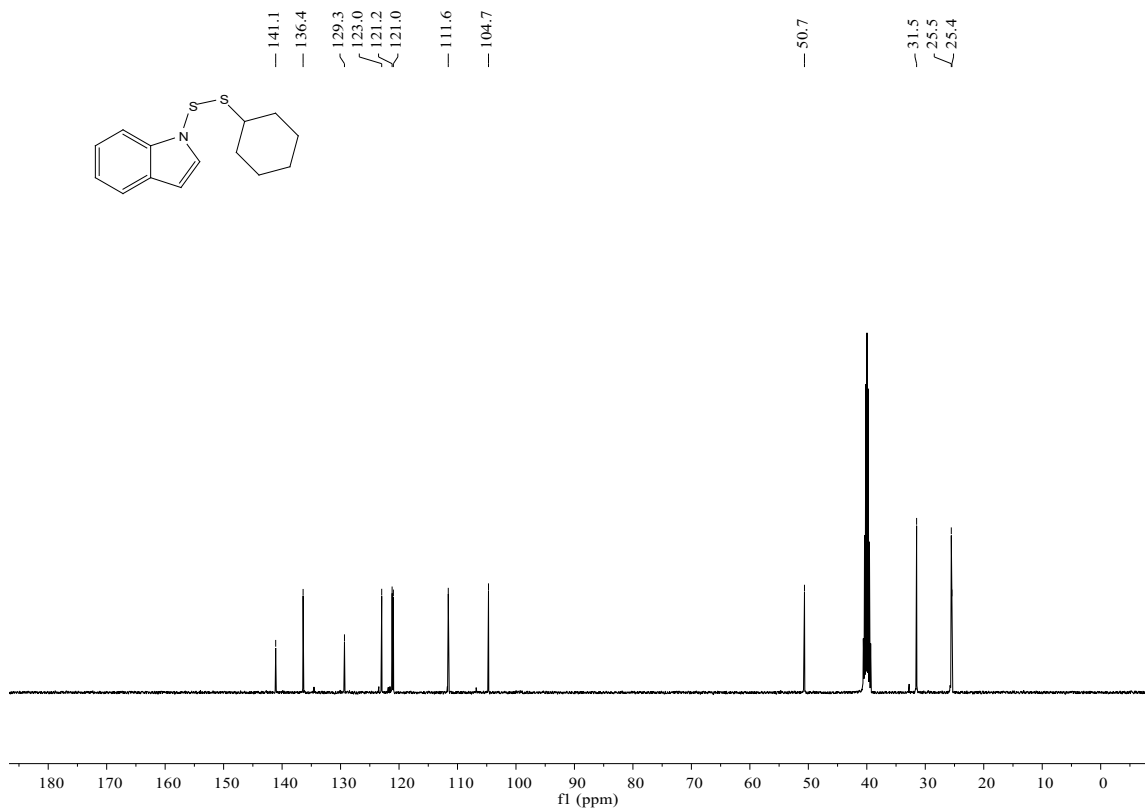
¹³C NMR (100 MHz, CDCl₃) spectrum of compound **6f**



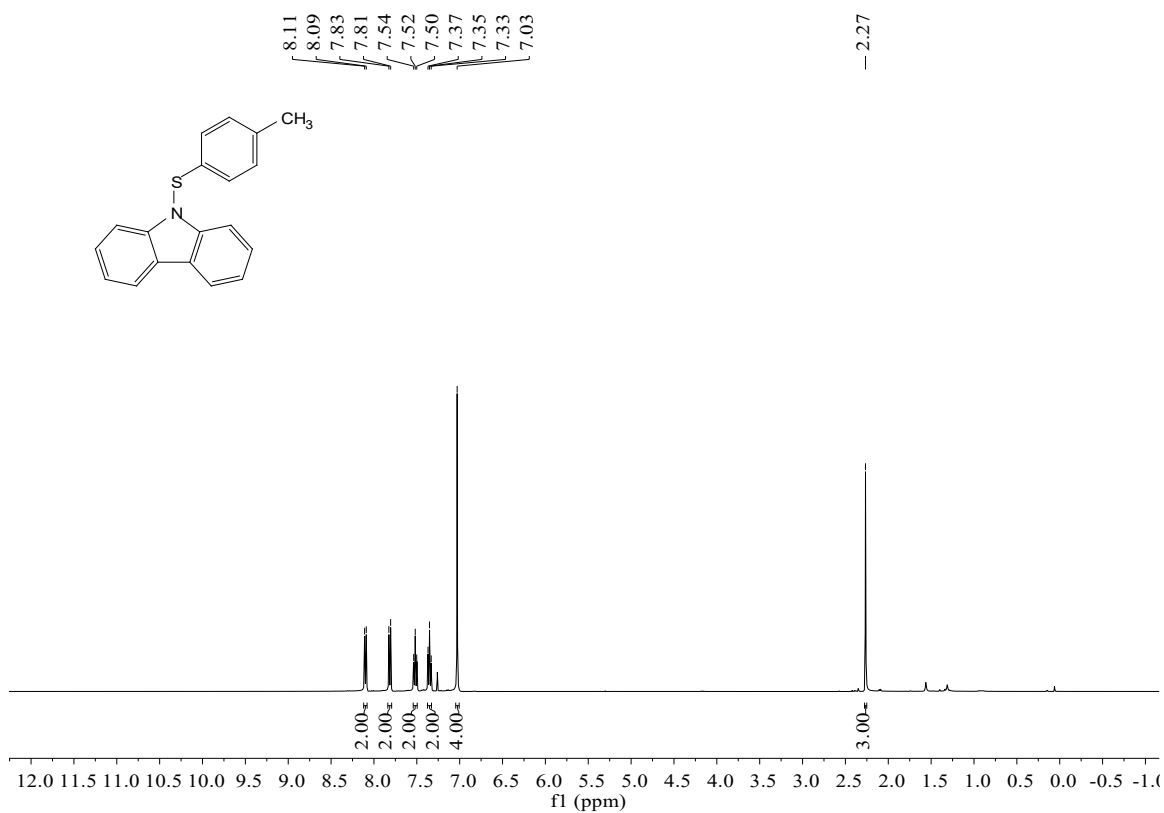
¹H NMR (400 MHz, (CD₃)₂SO) spectrum of compound **6g**



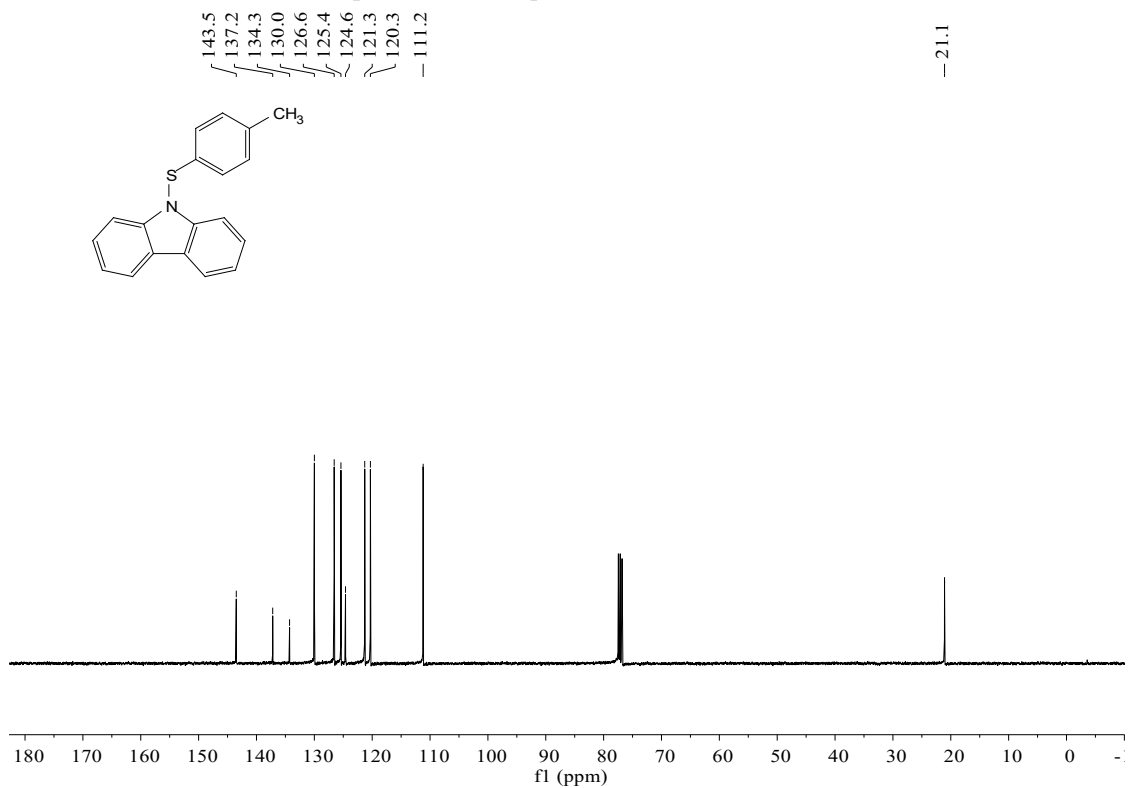
¹³C NMR (100 MHz, (CD₃)₂SO) spectrum of compound **6g**



¹H NMR (400 MHz, CDCl₃) spectrum of compound **6h**



¹³C NMR (100 MHz, CDCl₃) spectrum of compound **6h**



VI. References

1. S. Huang, H. Y. Li, T. Xie, F. Wei, *Org. Chem. Front.*, 2019, **6**, 1663.
2. Z. Wu, D. A. Pratt, *Angew. Chem. Int. Ed.*, 2021, **60**, 15598.