Supplementary Information

Graphene Oxide Mediated Thiolation of Indoles in Water: A Green and Sustainable Approach to 3-Sulfenylindoles

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1. General Information

Unless otherwise noted, all reactions were carried out in reaction vessels in sealed tubes. Reactions were carried out without any precautions to extrude moisture or air unless otherwise noted. Solvents used were of analytical purity. All reactions were monitored by thin-layer chromatography (TLC) and were visualized using UV light. Product purification was done using silica gel column chromatography. Thin layer chromatography (TLC) characterization was performed with precoated silica gel GF254 (0.2mm), while column chromatography characterization was performed with silica gel (100-200mesh). ^{1}H and ^{13}C spectra were recorded with tetramethylsilane as the internal standard. ^{13}C were recorded with broadband ^{1}H decoupling model. ^{1}H NMR spectra were recorded at 400 or 600 MHz, ^{13}C NMR spectra were recorded at 100 or 150 MHz. Chemical shifts (δ) were reported as parts per million (ppm) downfield from tetramethylsilane and the following abbreviations were used to identify the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad and all combinations thereof can be explained by their integral parts. HRMS spectra were recorded on a Waters Q-TOF Premier. Commercial reagents were from Best-reagent (Homepage: http://www.best-reagent.com) or Astatech Chemical Technology Co, Ltd. (Homepage: http://www.astabio-chem.com). All reagents were used without further purification.

2. Experimental Procedures and Characterizations

2.1 General procedure for the synthesis of 3 (taking 3aa as an example)

A 15 mL sealed tube, equipped with a magnetic stirring bar and a rubber septum, was charged with indole **1a** (30 mg, 0.26 mmol, 1.0 equiv), thiophenol **2a** (42.3mg, 0.39mmol, 1.5 equiv) and graphene oxide (100 mg). Water was added into the vial, and the resulting solution was stirred at 40℃for 24 h. The reaction mixture was filtrated and the residue was washed with ethyl acetate (3 × 15 mL) monitored by thin-layer chromatography (TLC) until all the organic residuals were completely removed. The combined organic extracts were dried over anhydrous Na_2SO_4, concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using a mixture of PE/EA (100:1) as the eluent to provide the product **3aa** (white solid) with 81% yield.

2.2 Synthesis of GO

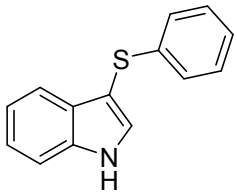
Graphene oxide (GO) used in this work was synthesized from graphite according to the modified Hummers method as reported[1,2]. To begin, 3.0 g of graphite and 1.5 g of $NaNO_3$ were placed in a 500 ml beaker. After adding 69 ml of 98% sulfuric acid, the mixture was stirred until cooled to 0 °C in an ice-water bath. $KMnO_4$ (9.0 g, 99%) was gradually added to the mixture and control the temperature below 20 °C. After complete the adding, the ice-bath was exchanged for an oil-bath and the mixture was heat up to 35 °C and maintain this temperature for 30 min. Then, 138 ml deionized water was added gradually to the reaction and the resulting mixture was heated at 98 °C for 15 min. As the reaction progressed, the reaction mixture was cooled to room temperature and diluted with 420 ml deionized water and 3 ml H_2O_2 (30%) was also added to the reaction. The suspension was filtered and washed with 200 ml of 5% hydrochloric acid solution. Next, the suspension was washed with

deionized water three times until the pH turn nature. The final precipitated GO was dried on vacuum at 60 °C for 24 h for further use.

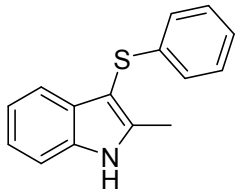
2.3 Synthesis of RGO[3]

GO (100mg) was ultrasonically dispersed in 70 mL of deionized water (DIW). To reduce GO, 2 mL of hydrazine (35 vol %) was slowly added, and the mixture was kept stirring for 24 h at 100 C in a fume cup- board. The boiled mixture was cooled to room temperature and filtered using a vacuum flask and a Buchner funnel. After washing with methanol and DIW, the filtrate was dried in a vacuum oven at room temperature.

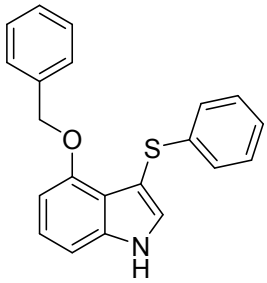
2.4 Characterizations



Compound **3aa**, *3-(phenylthio)-1H-indole*, yield 81%, white solid, m.p150-151℃, **^{1}H NMR** (400 MHz, DMSO-d6) δ 11.70 (s, 1H), 7.76 (d, *J* = 2.4 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.16 (m, 3H), 7.06 (t, *J* = 7.6 Hz, 2H), 7.01 (d, *J* = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 139.7, 137.2, 133.0, 129.3, 129.1, 125.7, 125.2, 122.6, 120.6, 118.8, 112.8, 99.7; **HRMS** (ESI): m/z calculated for $C_{14}H_{11}NS$ [M+Na^+]: 248.0504, found: 248.0527.

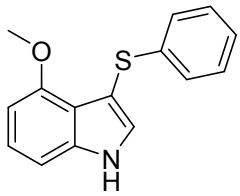


Compound **3ba**, *2-methyl-3-(phenylthio)-1H-indole*, yield 95%, white solid, m.p109-110℃, **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.54 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 3H), 7.09 – 7.04 (m, 2H), 6.98 (d, *J* = 7.6 Hz, 2H), 3.79 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 142.6, 139.6, 136.1, 130.1, 129.4, 125.5, 125.1, 121.9, 120.4, 118.11, 111.8, 96.7, 12.2; **HRMS** (ESI): m/z calculated for $C_{15}H_{13}NS$ [M+Na^+]: 262.0661, found: 262.0662.

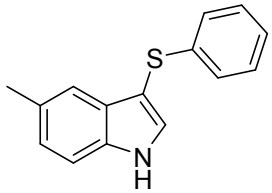


Compound **3ca**, *4-(benzyloxy)-3-(phenylthio)-1H-indole*, yield 60%, green oil, **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.66 (s, 1H), 7.57 (d, *J* = 2.4 Hz, 1H), 7.19–7.12 (m, 7H), 7.08–7.01 (m, 3H), 6.98 (d, *J*

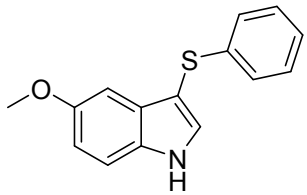
= 7.6 Hz, 2H), 6.61 (dd, *J* = 6.4, 2.4 Hz, 1H), 5.02 (s, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 153.1, 141.8, 139.3, 137.8, 132.4, 129.0, 128.4, 127.5, 127.2, 125.3, 124.6, 123.5, 118.6, 106.1, 102.3, 98.6, 69.1; **HRMS** (ESI): m/z calculated for $C_{21}H_{17}NOS$ [M+Na^+]: 354.0923, found: 354.0924.



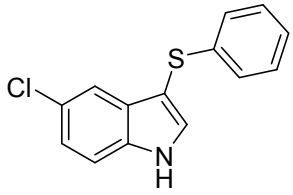
Compound **3da**, *4-methoxy-3-(phenylthio)-1H-indole*, yield 84%, white solid, m.p77-79℃, **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.55 (s, 1H), 7.47 (d, *J* = 2.8 Hz, 1H), 7.14 (t, *J* = 8.0 Hz, 2H), 7.00 (m, 5H), 6.47 (dd, *J* = 6.0, 2.4 Hz, 1H), 3.57 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 154.4, 141.7, 139.1, 131.8, 129.0, 125.9, 124.8, 123.5, 118.6, 105.9, 101.3, 99.4, 55.7; **HRMS** (ESI): m/z calculated for $C_{15}H_{13}NOS$ [M+Na^+]: 278.0610, found: 278.0608.



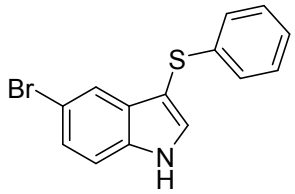
Compound **3ea**, *5-methyl-3-(phenylthio)-1H-indole*, yield 85%, white solid, m.p136-137℃, **^{1}H NMR** (400 MHz, DMSO-d_6) δ11.59 (s, 1H), δ 7.70 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 3H), 7.06 (d, *J* = 6.0 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 3H), 2.33 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 139.9, 135.5, 133.0, 129.4, 129.3, 125.5, 125.1, 124.2, 118.2, 112.6, 98.9, 21.6; **HRMS** (ESI): m/z calculated for $C_{15}H_{13}NS$ [M+Na^+]: 262.0661, found: 262.0663.



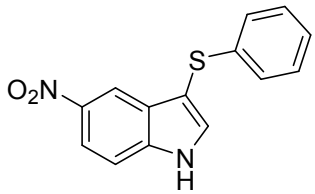
Compound **3fa**, *5-methoxy-3-(phenylthio)-1H-indole*, yield 80%, white solid, m.p77–80℃, **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.57 (s, 1H), 7.70 (d, *J* = 2.8 Hz, 1H), 7.39 (d, *J* = 9.6 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 2H), 6.82 (dd, *J* = 7.2, 2.4 Hz, 2H), 3.68 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 154.7, 139.8, 133.4, 132.1, 129.9, 129.3, 125.61, 125.2, 113.7, 112.7, 100.1, 99.1, 55.7; **HRMS** (ESI): m/z calculated for $C_{15}H_{13}NOS$ [M+Na^+]: 278.0610, found: 278.0612.



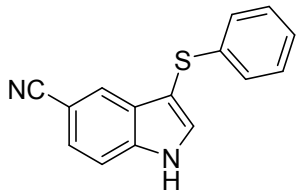
Compound **3ga**, *5-chloro-3-(phenylthio)-1H-indole*, yield 82%, white solid, m.p104-106℃, **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.91 (s, 1H), 7.87 (d, *J* = 2.8 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.33 (d, *J* = 2.0 Hz, 1H), 7.24–7.18 (m, 3H), 7.11–7.06 (m, 1H), 7.04–7.00 (m, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 139.1, 135.7, 134.8, 130.4, 129.5, 125.9, 125.5, 125.4, 122.7, 117.7, 114.6, 99.7; **HRMS** (ESI): m/z calculated for $C_{14}H_{10}ClNS$ [M+Na$^+$]: 282.0115, found: 282.0110.



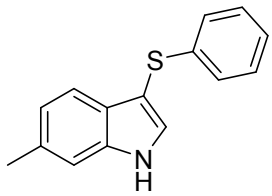
Compound **3ha**, *5-bromo-3-(phenylthio)-1H-indole*, yield 81%, white solid, m.p122-123℃, **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.92 (s, 1H), 7.85 (d, *J* = 2.8 Hz, 1H), 7.48 (dd, *J* = 5.6, 3.6 Hz, 2H), 7.30 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.09 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.03 – 7.00 (m, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 139.1, 135.9, 134.7, 131.1, 129.5, 125.8, 125.5, 125.3, 120.8, 115.0, 113.4, 99.6; **HRMS** (ESI): m/z calculated for $C_{14}H_{10}BrNS$ [M+Na$^+$]: 325.9610, found: 325.9613.



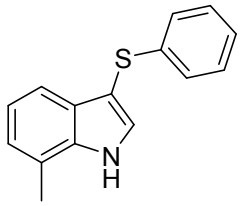
Compound **3ia**, *5-nitro-3-(phenylthio)-1H-indole*, yield 79%, yellow solid, m.p156-158℃, **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.42 (s, 1H), 8.26 (s, 1H), 8.11 – 8.07 (m, 2H), 7.70 (d, *J* = 6.0 Hz, 1H), 7.24 (t, *J* = 5.2 Hz, 2H), 7.12 (t, *J* = 4.8 Hz, 1H), 7.08 (d, *J* = 5.2 Hz, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 142.1, 140.5, 138.4, 137.1, 129.6, 128.6, 126.2, 125.9, 118.1, 115.3, 113.7, 103.1; **HRMS** (ESI): m/z calculated for $C_{14}H_{10}N_2O_2S$ [M+Na$^+$]: 270.0463, found: 270.0458.



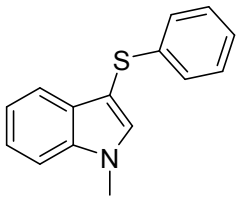
Compound **3ja**, *3-(phenylthio)-1H-indole-5-carbonitrile*, yield 75%, yellow solid, m.p128-130℃, **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.25 (s, 1H), 8.02 (d, *J* = 2.4 Hz, 1H), 7.82 (s, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 139.9, 138.5, 135.6, 131.9, 129.4, 128.9, 126.2, 125.7, 125.4, 123.9, 120.5, 114.3, 102.8; **HRMS** (ESI): m/z calculated for $C_{15}H_{10}N_2S$ [M+Na$^+$]: 250.0565, found: 250.0553.



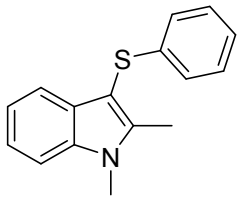
Compound **3ka**, *6-methyl-3-(phenylthio)-1H-indole*, yield 86%, white solid, m.p155-156℃, **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.53 (s, 1H), 7.66 (d, *J* = 2.8 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.18 (t, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 1H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 139.8, 137.6, 132.2, 131.8, 129.3, 127.0, 125.7, 125.2, 122.4, 118.5, 112.6, 99.4, 21.8; **HRMS** (ESI): m/z calculated for $C_{15}H_{13}NS$ [M+Na$^+$]: 262.0661, found: 262.0665.



Compound **3la**, *7-methyl-3-(phenylthio)-1H-indole*, yield 85%, white solid, m.p142-143℃, **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.67 (s, 1H), 7.72 (d, *J* = 2.8 Hz, 1H), 7.22 – 7.12 (m, 3H), 7.03 (d, *J* = 7.6 Hz, 1H), 7.00 – 6.96 (m, 2H), 6.96 – 6.91 (m, 2H), 2.48 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 139.8, 136.7, 132.6, 129.3, 128.9, 125.7, 125.2, 123.1, 122.1, 120.8, 116.4, 100.0, 17.1; **HRMS** (ESI): m/z calculated for $C_{15}H_{13}NS$ [M+Na$^+$]: 262.0661, found: 262.0663.

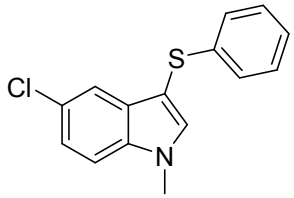


Compound **3ma**, *1-methyl-3-(phenylthio)-1H-indole*, yield 82%, white solid, mp84-88℃, **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.78 (s, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.19 (m ,2H), 7.14 – 7.10 (m, 1H), 7.10 – 7.06 (m, 1H), 7.03 (m, 2H), 3.87 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 139.6, 137.8, 136.7, 129.5, 129.3, 125.8, 125.3, 122.7, 120.78, 118.9, 111.2, 98.6, 33.3; **HRMS** (ESI): m/z calculated for $C_{15}H_{13}NS$ [M+Na$^+$]: 262.0661, found: 262.0571.

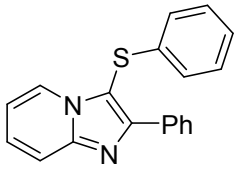


Compound **3na**, *1,2-dimethyl-3-(phenylthio)-1H-indole*, yield 84%, white solid, m.p108-110℃, **^{1}H NMR** (400 MHz, DMSO-d_6) ^{1}H NMR (400 MHz, DMSO) δ 7.49 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 3H), 7.05-7.00 (m, 2H), 6.93 (d, *J* = 7.2 Hz, 2H), 3.75 (s, 3H), 2.46 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 143.9, 139.5, 137.3, 129.4, 129.3, 125.5, 125.1, 121.9, 120.6, 118.2,

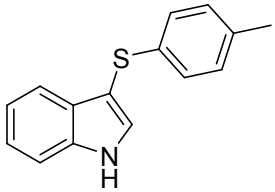
110.4, 96.6, 30.7, 11.0; **HRMS** (ESI): m/z calculated for $C_{16}H_{15}NS$ [M+Na$^+$]: 276.0871, found: 276.0869.



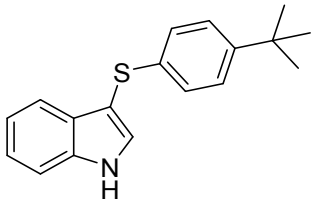
Compound **3oa**, *5-chloro-1-methyl-3-(phenylthio)-1H-indole*, yield 65%, white solid, m.p136-138℃， **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.81 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 2.0 Hz, 1H), 7.20 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.15 (t, *J* = 8.0 Hz, 2H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.99 – 6.95 (m, 2H), 3.81 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 138.9, 138.4, 136.3, 130.7, 129.4, 125.9, 125.7, 125.5, 122.7, 117.9, 113.1, 98.6, 33.5; **HRMS** (ESI): m/z calculated for $C_{15}H_{12}ClNS$ [M+Na$^+$]: 296.0271, found: 296.0275.



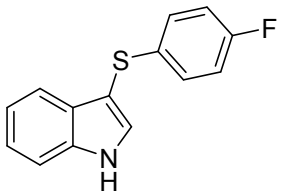
Compound **3pa**, *2-phenyl-3-(phenylthio)imidazo[1,2-a]pyridine*, yield 95%, white solid, m.p92-94℃，**^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.37 (d, *J* = 6.8 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.48 – 7.39 (m, 3H), 7.35 (dd, *J* = 9.6, 7.2 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 6.8 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 150.5, 147.0, 135.2, 133.7, 130.3, 129.1, 129.0, 128.3, 128.0, 126.8, 125.7, 125.2, 117.8, 114.3, 105.9; **HRMS** (ESI): m/z calculated for $C_{19}H_{14}N_2S$ [M+Na$^+$]: 325.0770, found: 325.0778.



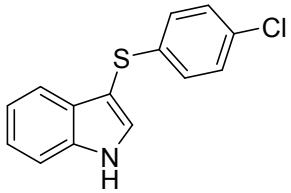
Compound **3ab**, *3-(p-tolylthio)-1H-indole*, yield 82%, white solid, m.p125-126℃, **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.58 (s, 1H), 7.67 (d, *J* = 2.8 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.13 – 7.07 (m, 1H), 7.01 – 6.96 (m, 1H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 2.12 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 137.2, 136.0, 134.6, 132.7, 130.0, 129.1, 126.2, 122.5, 120.5, 118.8, 112.8, 100.4, 20.9; **HRMS** (ESI): m/z calculated for $C_{15}H_{13}NS$ [M+Na$^+$]: 262.0661, found: 262.0669.



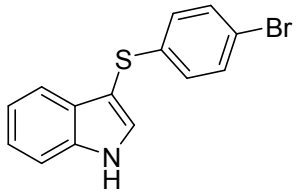
Compound **3ac**, *3-((4-(tert-butyl)phenyl)thio)-1H-indole*, yield 90%, white solid, m.p185-187℃, **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.59 (s, 1H), 7.66 (d, *J* = 2.8 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 7.2 Hz, 1H), 6.99 (t, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 1.12 (s, 9H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 147.9, 137.1, 136.2, 132.8, 129.2, 126.2, 125.9, 122.5, 120.5, 118.8, 112.8, 100.3, 34.5, 31.5; **HRMS** (ESI): m/z calculated for $C_{18}H_{19}NS$ [M+Na$^+$]: 304.1130, found: 304.1135.



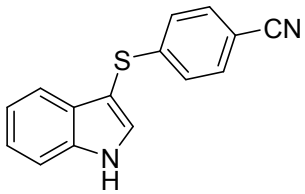
Compound **3ad**, *3-((4-fluorophenyl)thio)-1H-indole*, yield 81%, white solid, m.p138-140℃, **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.76 (s, 1H), 7.83 (d, *J* = 2.4 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.27 – 7.21 (m, 1H), 7.08 – 7.05 (m, 5H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 160.6(d, *J* = 240.0 Hz), 137.2, 135.0 (d, *J* = 3.0 Hz), 132.9, 128.9, 128.0 (d, *J* = 8.0 Hz), 122.7, 119.7(d, *J* = 198.0 Hz), 116.4, 116.3, 112.9, 100.1; **HRMS** (ESI): m/z calculated for $C_{14}H_{10}FNS$ [M+Na$^+$]: 266.0410, found: 266.0416.



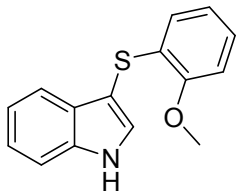
Compound **3ae** *3-((4-chlorophenyl)thio)-1H-indole*, yield 84%, white solid, m.p129-131℃, **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.75 (s, 1H), 7.79 (d, *J* = 2.4 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 138.9, 137.2, 133.2, 129.8, 129.3, 128.9, 127.3, 122.7, 120.7, 118.6, 112.9, 99.1; **HRMS** (ESI): m/z calculated for $C_{14}H_{10}ClNS$ [M+Na$^+$]: 282.0115, found: 282.0122.



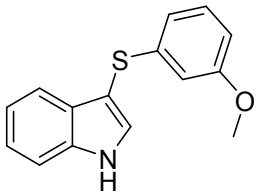
Compound **3af,** *3-((4-bromophenyl)thio)-1H-indole*, yield 84%, white solid, m.p140-142℃, **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.81 (s, 1H), 7.85 (d, *J* = 2.8 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.43 (dd, *J* = 8.8, 6.8 Hz, 3H), 7.25 (t, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 139.5, 137.2, 133.2, 132.1, 128.8, 127.6, 122.7, 120.8, 118.6, 117.9, 112.9, 99.0; **HRMS** (ESI): m/z calculated for $C_{14}H_{10}BrNS$ [M+Na$^+$]: 325.9610, found: 325.9617.



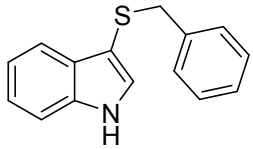
Compound **3ag**, *4-((1H-indol-3-yl)thio)benzonitrile*, yield 78%, light green solid, m.p184-186℃, **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.92 (s, 1H), 7.90 (d, *J* = 2.8 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.30 – 7.28 (t, *J* =7.6 Hz, 1H), 7.19 – 7.12 (m, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 147.6, 137.3, 133.6, 133.0, 128.7, 125.6, 122.9, 121.0, 119.4, 118.5, 113.1, 107.2, 97.3; **HRMS** (ESI): m/z calculated for $C_{15}H_{110}N_2S$ [M+Na$^+$]: 273.0457, found: 273.0462.



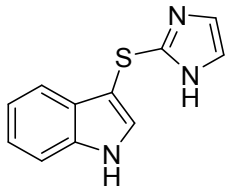
Compound **3ah,** *3-((2-methoxyphenyl)thio)-1H-indole*, yield 84%, white solid, m.p136-138℃, **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.69 (s, 1H), 7.71 (d, *J* = 2.8 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.08 – 7.00 (m, 2H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.67 (t, *J* = 7.6 Hz, 1H), 6.39 (d, *J* = 7.6Hz, 1H), 3.88 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 155.1, 137.3, 133.2, 129.4, 128.1, 125.8, 125.4, 122.6, 121.3, 120.5, 118.8, 112.8, 111.0, 98.4, 56.2; **HRMS** (ESI): m/z calculated for $C_{15}H_{13}NOS$ [M+Na$^+$]: 278.0610, found: 278.0617.



Compound **3ai,** *3-((3-methoxyphenyl)thio)-1H-indole*, yield 87%, colorless oil, **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.72 (s, 1H), 7.77 (d, *J* = 2.8 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.14 – 7.05 (m, 2H), 6.65 (dd, *J* = 8.0, 2.8 Hz, 1H), 6.60 – 6.54 (m, 2H), 3.63 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 160.1, 141.2, 137.2, 133.0, 130.2, 129.1, 122.6, 120.6, 118.8, 118.0, 112.8, 111.5, 110.5, 99.6, 55.4; **HRMS** (ESI): m/z calculated for $C_{15}H_{13}NOS$ [M+Na$^+$]: 278.0610, found: 278.0615.



Compound **3aj** *3-(benzylthio)-1H-indole*, yield 70%, yellow solid, m.p84-85℃, **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.31 (s, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.27 (s, 1H), 7.24–7.18 (m, 3H), 7.15–7.11 (m, 3H), 7.05 (t, *J* = 7.2 Hz, 1H), 3.88 (s, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 139.3, 136.8, 131.1, 129.3 129.3, 128.6, 127.1, 122.2, 120.0, 118.8, 112.5, 103.3, 40.7; **HRMS** (ESI): m/z calculated for $C_{15}H_{13}NS$ [M+Na$^+$]: 262.0661, found: 262.0671.



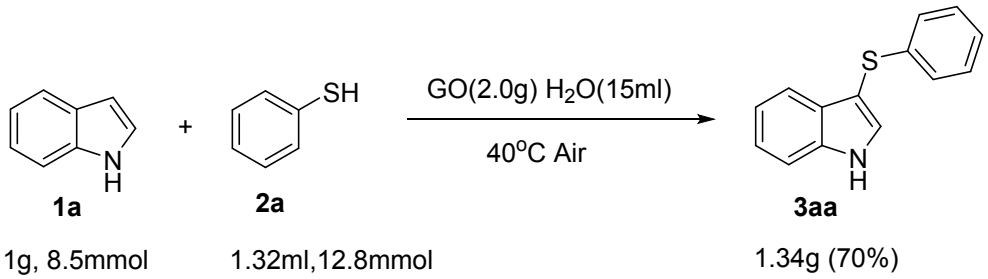
Compound **3ak,** *3-((1H-imidazol-2-yl)thio)-1H-indole*, yield 57%, brown oil, **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.01 (s, 1H), 11.54 (s, 1H), 7.69 (d, *J* = 2.4 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.93 (s, 2H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 140.5, 136.8, 132.4, 128.8, 123.5, 122.5, 120.5, 118.7, 112.6, 98.6; **HRMS** (ESI): m/z calculated for $C_{11}H_9N_3S$ [M+Na$^+$]: 238.0409, found: 238.0417.

3. Catalyst Reuse Study

Indole (**1a**) (0.26mmol) and thiophenol (**2a**) (0.38mmol) were used as the substrates to conducted the recycle experiment with 100 mg GO and 5 ml H_2O. After the reaction, the catalyst was simply separated by filtration and washed with ethyl acetate (3 × 15 mL) until all the organic residuals were completely removed, the residue is GO again, the recovered dry catalyst was recharged with fresh substrate for the next run under the same reaction conditions, this is the first recycle. And GO still can catalyst this reaction well even after 10 times.

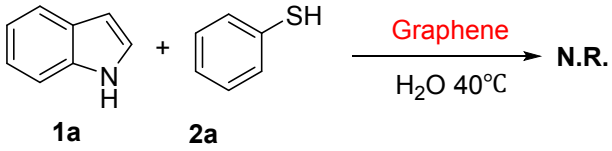
4. Scale-up Experiment

Being inspired by this green simple method, we then attempted to conduct scale-up experiments to examine the synthetic efficiency. When 8.5 mmol indole (**1a**) was subjected for the reaction with 12.8 mmol thiophenol (**2a**) and 2.0g GO, corresponding product **3a** has been afforded with satisfactory yield of 70% (1.34 g), demonstrating the great potential of the present method for large scale synthesis of 3-sulfenylated indole products.



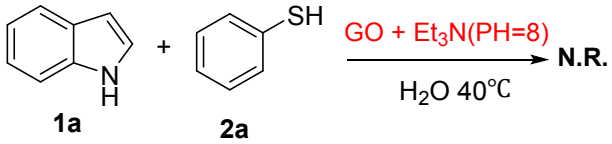
Scheme S1. Scale-up experiment.

5. Experiments on the Reaction Mechanism



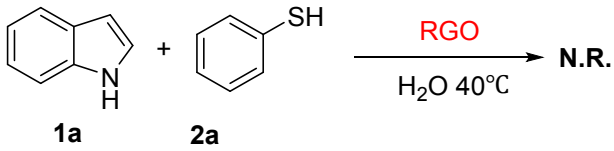
Scheme S2. Scheme showing the reaction does not conduct when using graphene replace graphene oxide.

Indole (**1a**) (0.26 mmol) and thiophenol (**2a**) (0.38 mmol) were used as the substrates to conducted the reaction mechanism experiment with graphene (100 mg) and H_2O (5 ml) under standard conditions. However, there is no product can be detected.



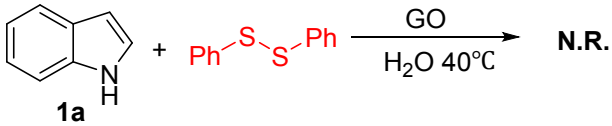
Scheme S3. Scheme showing the reaction does not conduct when Et_3N was added.

A 15 mL sealed tube, equipped with a magnetic stirring bar and a rubber septum, was charged with indole **1a** (30 mg, 0.26 mmol, 1.0 equiv), graphene oxide (100 mg) and water (5 ml), terethylamine was added dropwise until PH to 8, thiophenol **2a** (42.3 mg, 0.39 mmol, 1.5 equiv) was added after that, and the resulting solution was stirred at 40℃. No reaction at all after 24h.



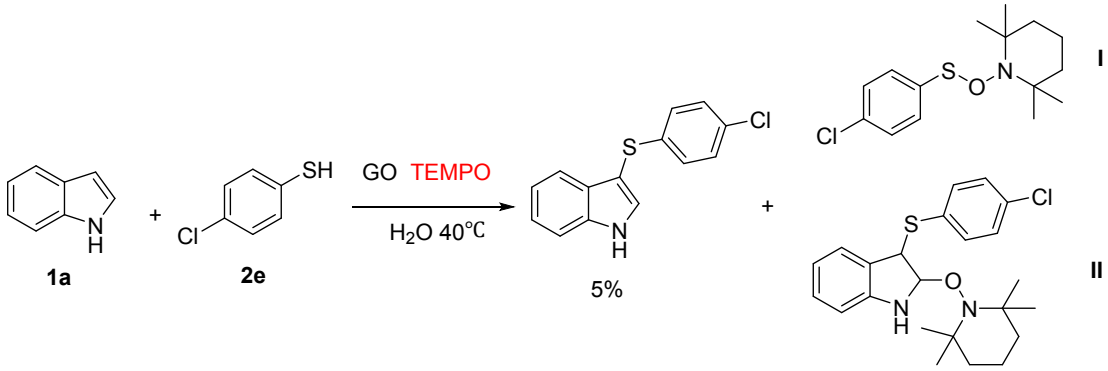
Scheme S4. Scheme showing the reaction does not conduct when using RGO replace graphene oxide.

Indole (**1a**) (0.26 mmol) and thiophenol (**2a**) (0.38 mmol) were used as the substrates to conducted the reaction mechanism experiment with reduced graphene oxide (100 mg) and H_2O (5 ml) under standard conditions. However, there is no product can be detected.



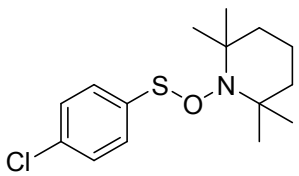
Scheme S5. Scheme showing the reaction does not conduct when thiophenol was replaced by 1, 2-diphenyldisulfane.

A 15 mL sealed tube, equipped with a magnetic stirring bar and a rubber septum, was charged with indole **1a** (30 mg, 0.26 mmol, 1.0 equiv), 1,2-diphenyldisulfane (67 mg, 0.31 mmol, 1.5 equiv) and graphene oxide (100 mg), water (5 ml) was added, and the resulting solution was stirred at standard conditions, also the reaction did not proceed at all.



Scheme S6. Scheme showing that only 5% **3ae** was obtain when TEMPO was added.

A 15 mL sealed tube, equipped with a magnetic stirring bar and a rubber septum, was charged with indole **1a** (30 mg, 0.26 mmol, 1.0 equiv), graphene oxide (100 mg) TEMPO (2equiv) and water (5 ml), thiophenol **2e** (50.5 mg, 0.39 mmol, 1.5 equiv) was added after that, then the resulting solution was stirred at 40℃. Only 5% **3ae** was obtained at all after 24h. After the reaction, the 2,2,6,6-tetramethyl-1-((4-chlorobenzenethiol)oxy)piperidine intermediate was obtained by flash column chromatography and characterize it by ^{1}HNMR and HRMS. At the same time, we also detected 2,2,6,6-tetramethyl-1-((4-chlorobenzenethiol)piperidine (I) and 3-(4-chlorobenzenethiol)-2- ((2,2,6,6-tetramethyl piperidin-1-yl)oxy) indoline (II) by LC-MS.



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 1.85 (d, J = 8.0 Hz, 1H), 1.66 (s, 3H), 1.59 (s, 3H), 1.57 (s, 3H), 1.49 (s, 3H), 1.47 – 1.35 (m, 2H), 1.26 (s, 1H), 0.91 (s, 2H). **HRMS** (ESI): m/z calculated for $C_{15}H_{22}ClNS$ [M+Na$^+$]: 322.1003, found: 322.1007.

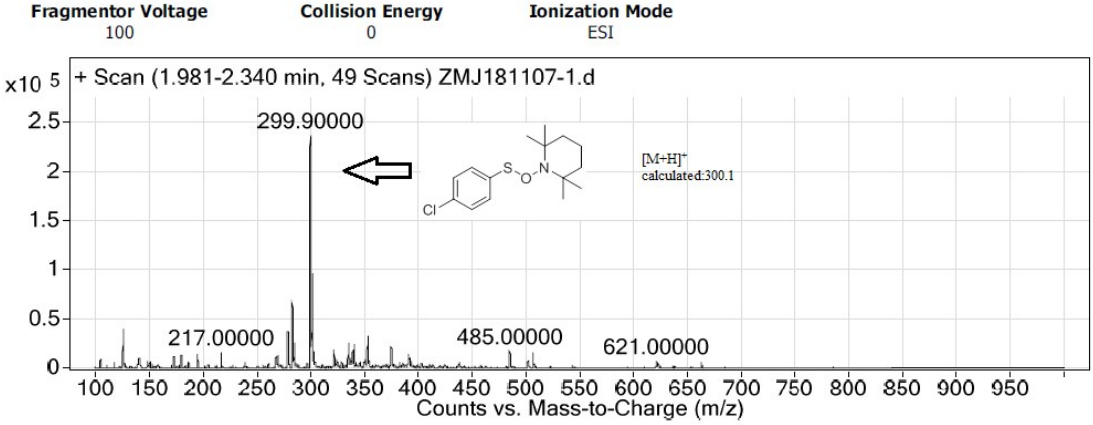


Figure S1. LC-MS data for 2,2,6,6-tetramethyl-1-((4-chlorobenzenethiol)oxy) piperidine.

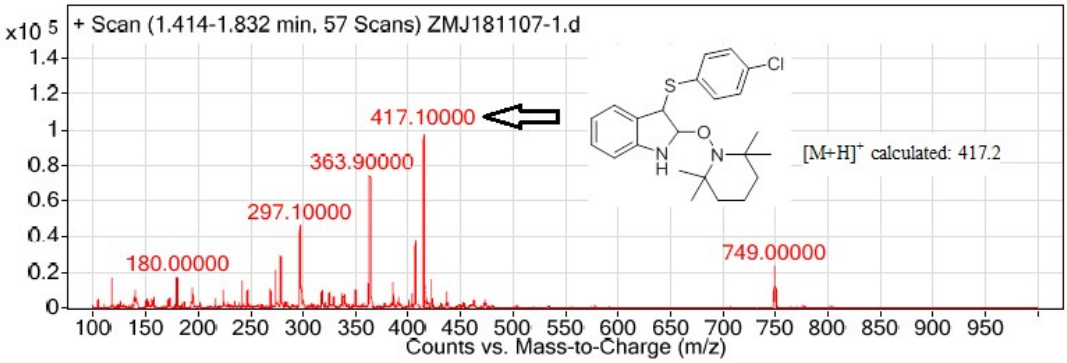


Figure S2. LC-MS data for 3-(4-chlorobenzenethiol)-2-((2,2,6,6-tetramethyl piperidin-1-yl)oxy) indoline (II).

6. NMR Spectra (Figures S3 to S54)

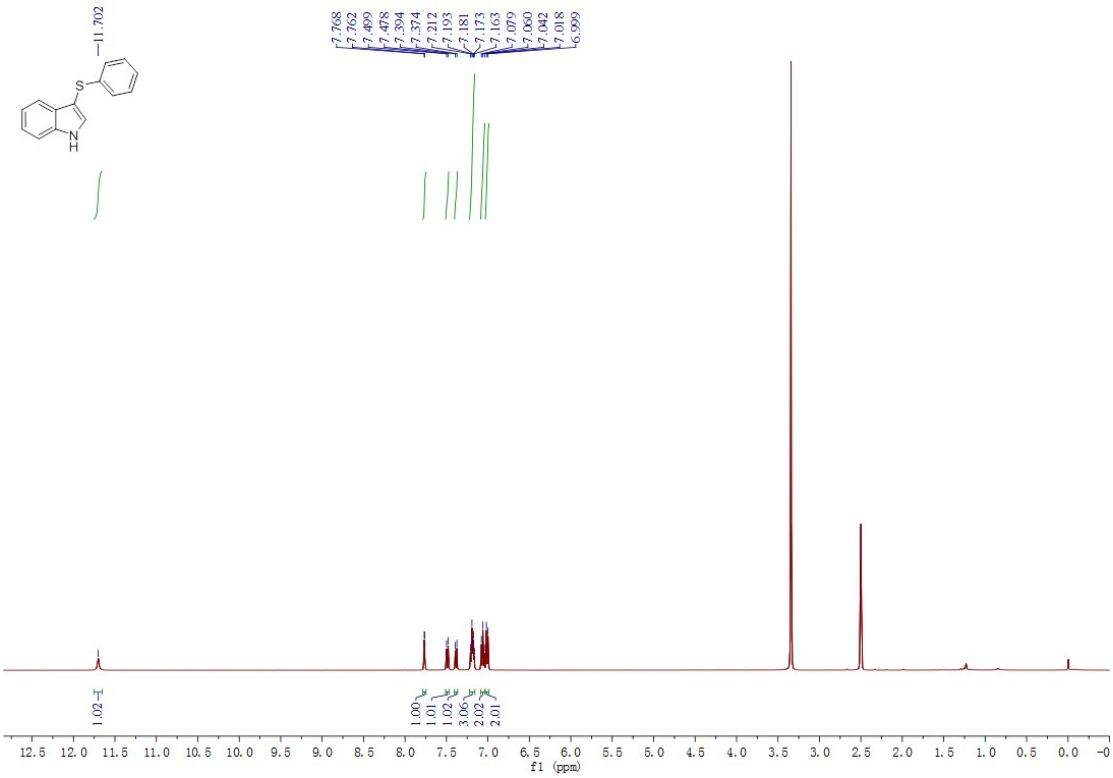


Figure S3. ^{1}H NMR spectrum for **3aa** in DMSO-d_6.

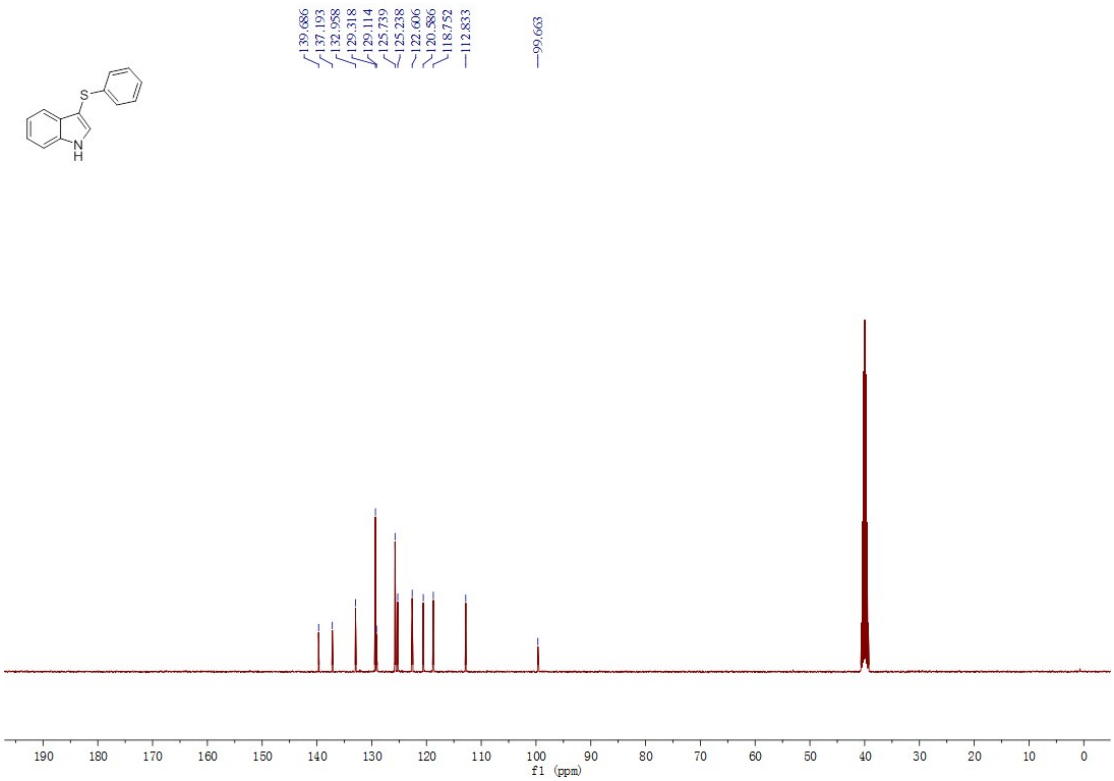


Figure S4. ^{13}C NMR spectrum for **3aa** in DMSO-d_6.

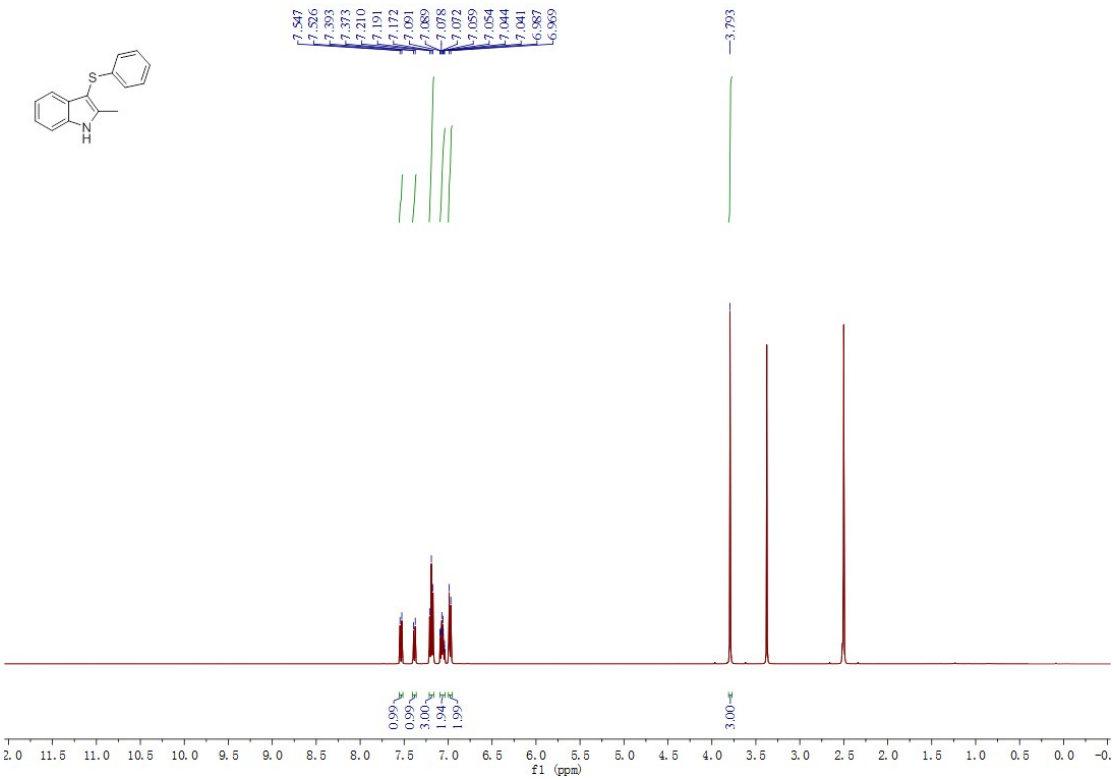


Figure S5. ^{1}H NMR spectrum for **3ba** in DMSO-d_6

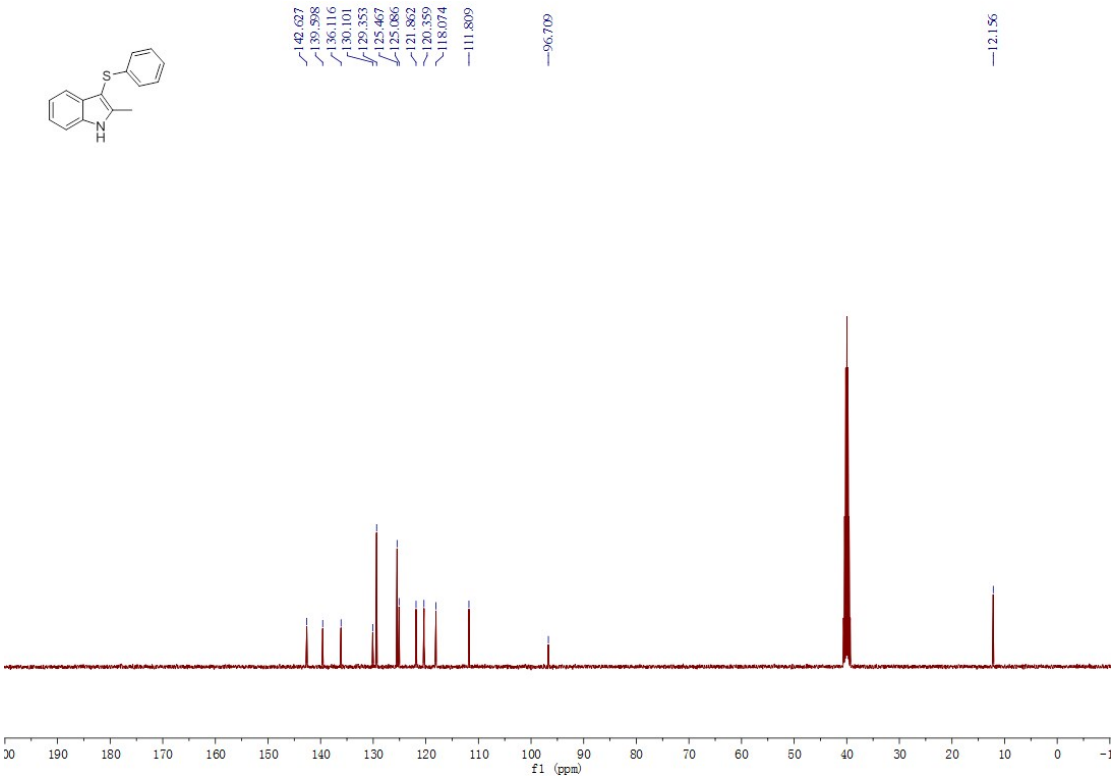


Figure S6. ^{13}C NMR spectrum for **3ba** in DMSO-d_6.

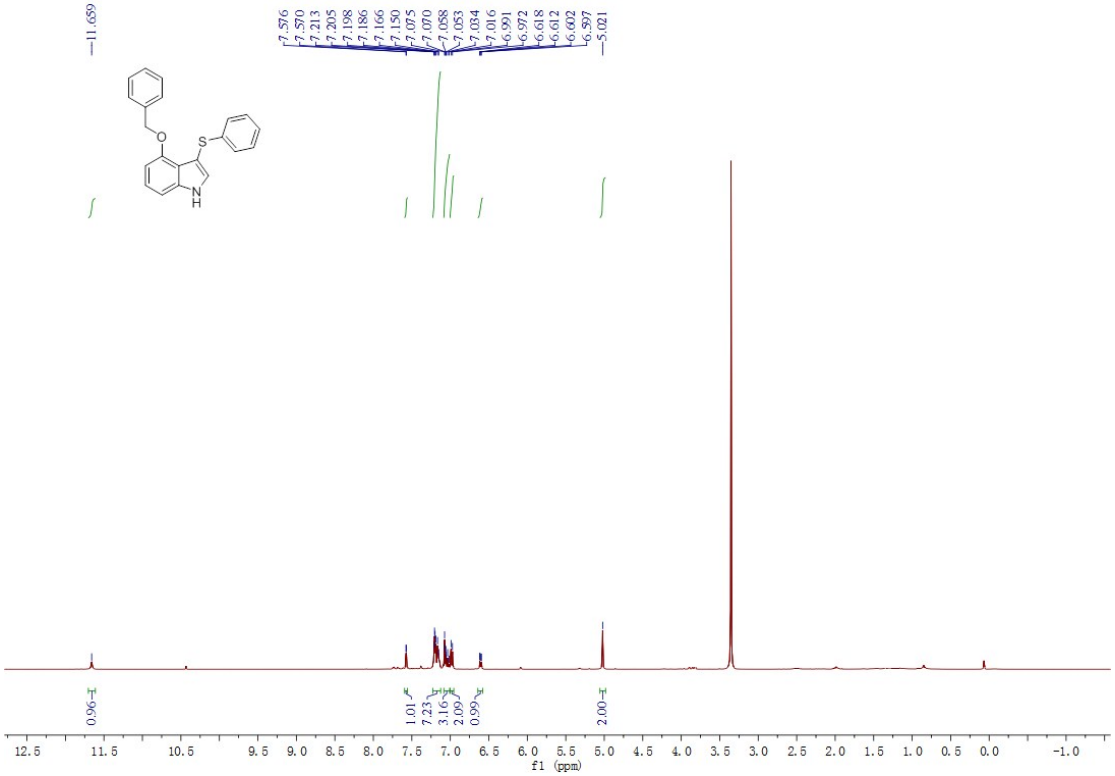


Figure S7. ^{1}H NMR spectrum for **3ca** in DMSO-d_6

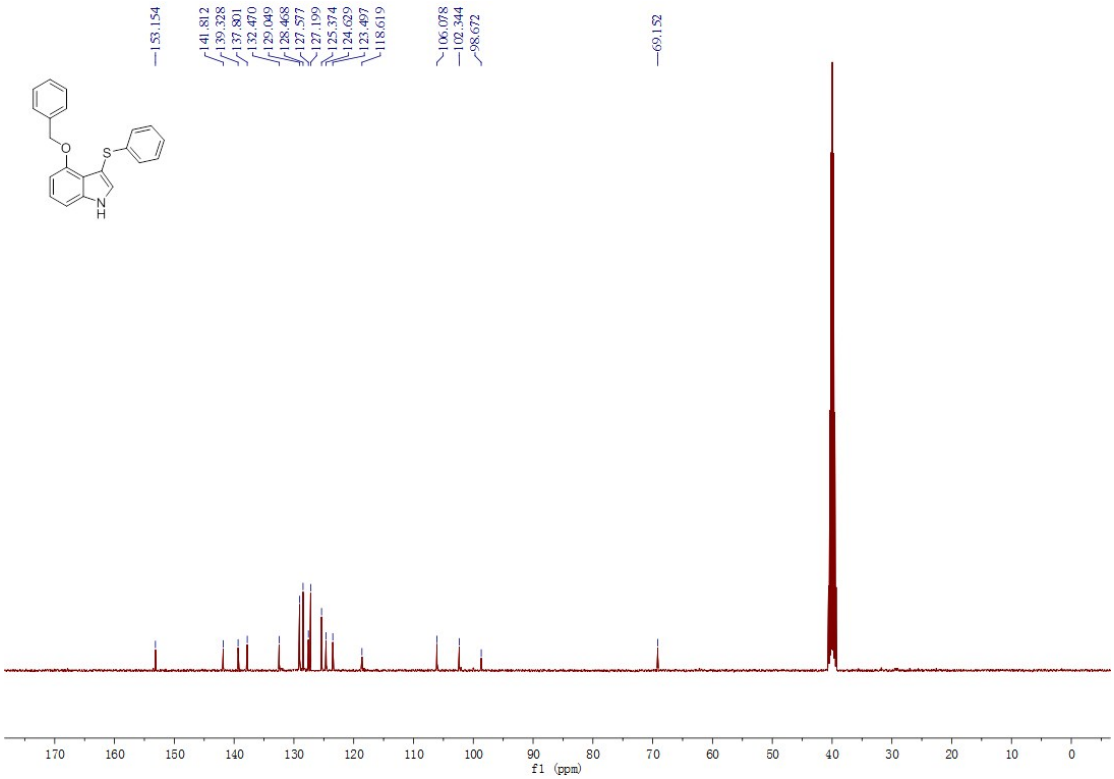


Figure S8. ^{13}C NMR spectrum for **3ca** in DMSO-d_6.

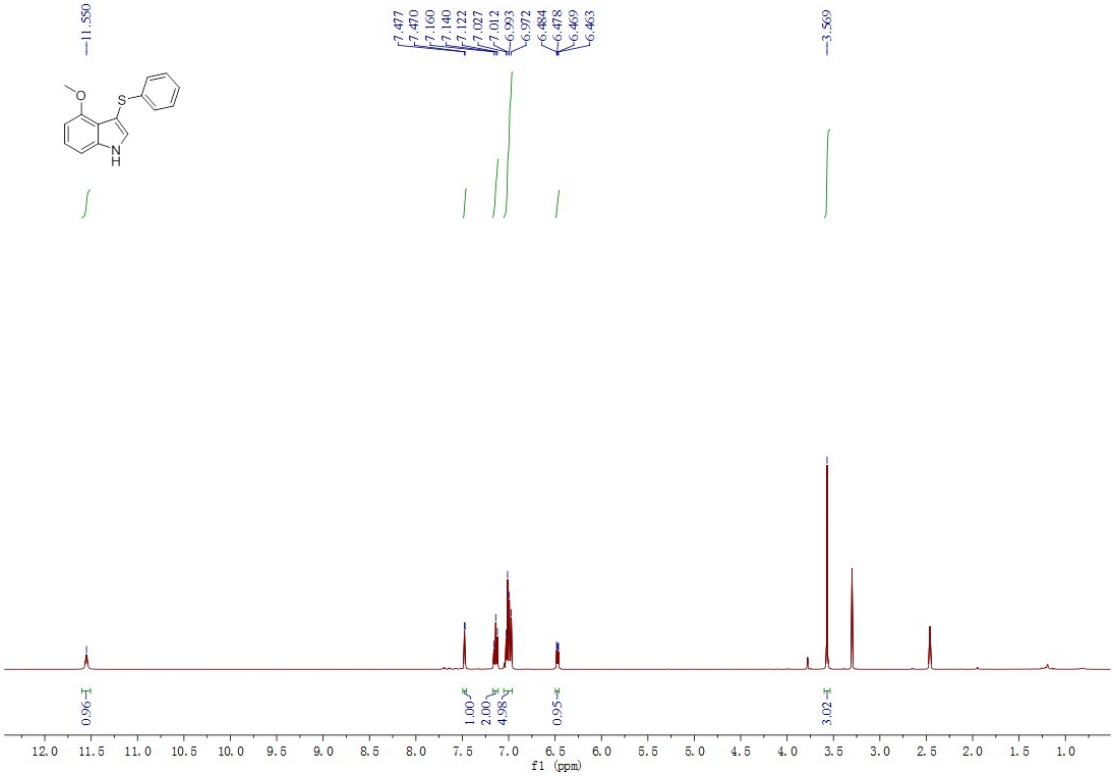


Figure S9. ^{1}H NMR spectrum for **3da** in DMSO-d_6.

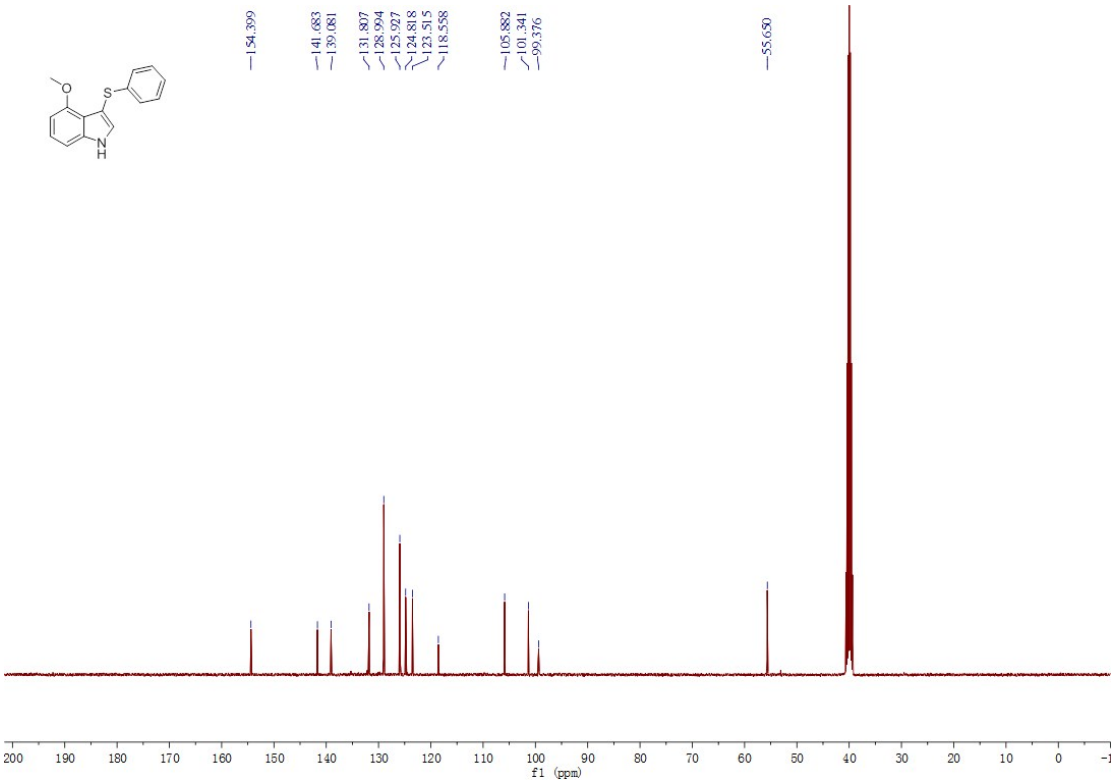


Figure S10. ^{13}C NMR spectrum for **3da** in DMSO-d_6.

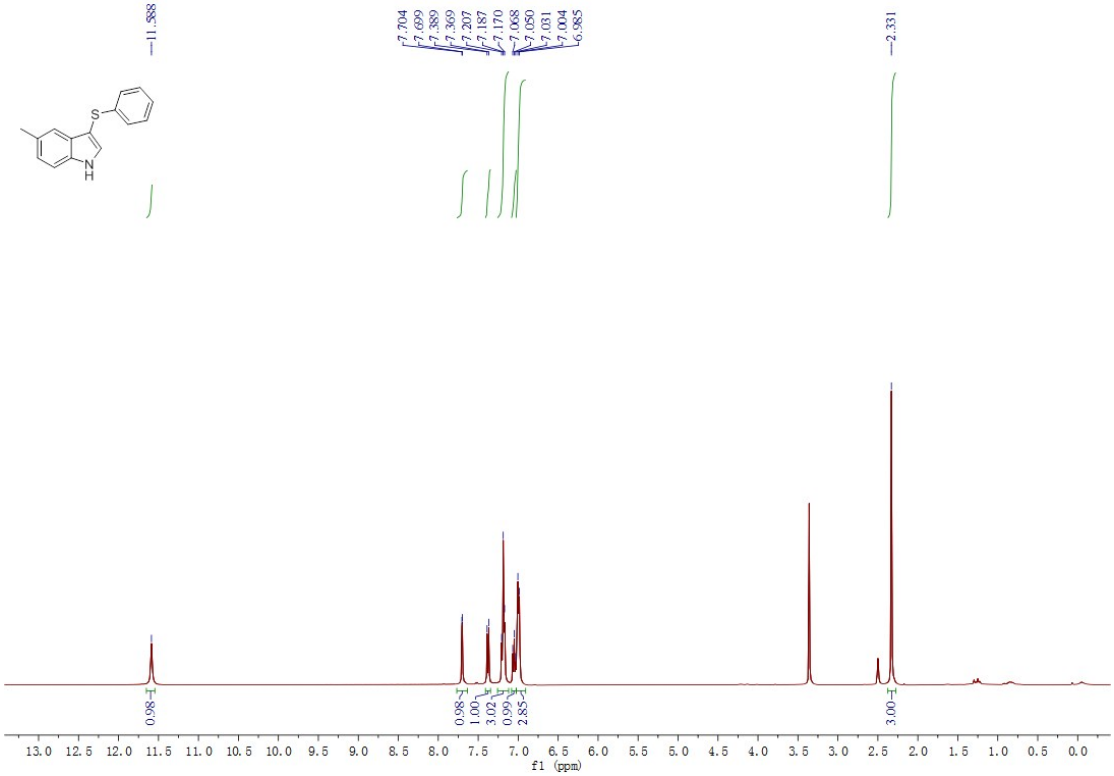


Figure S11. ^{1}H NMR spectrum for **3ea** in DMSO-d_6.

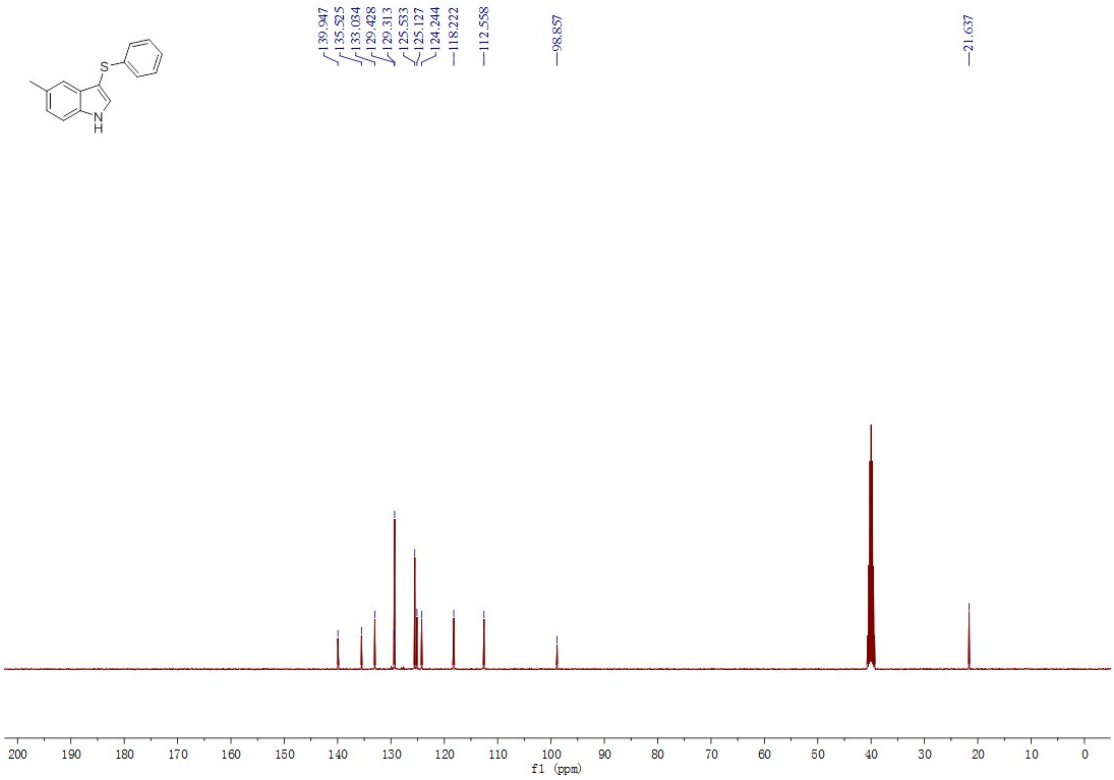


Figure S12. ^{13}C NMR spectrum for **3ea** in DMSO-d_6.

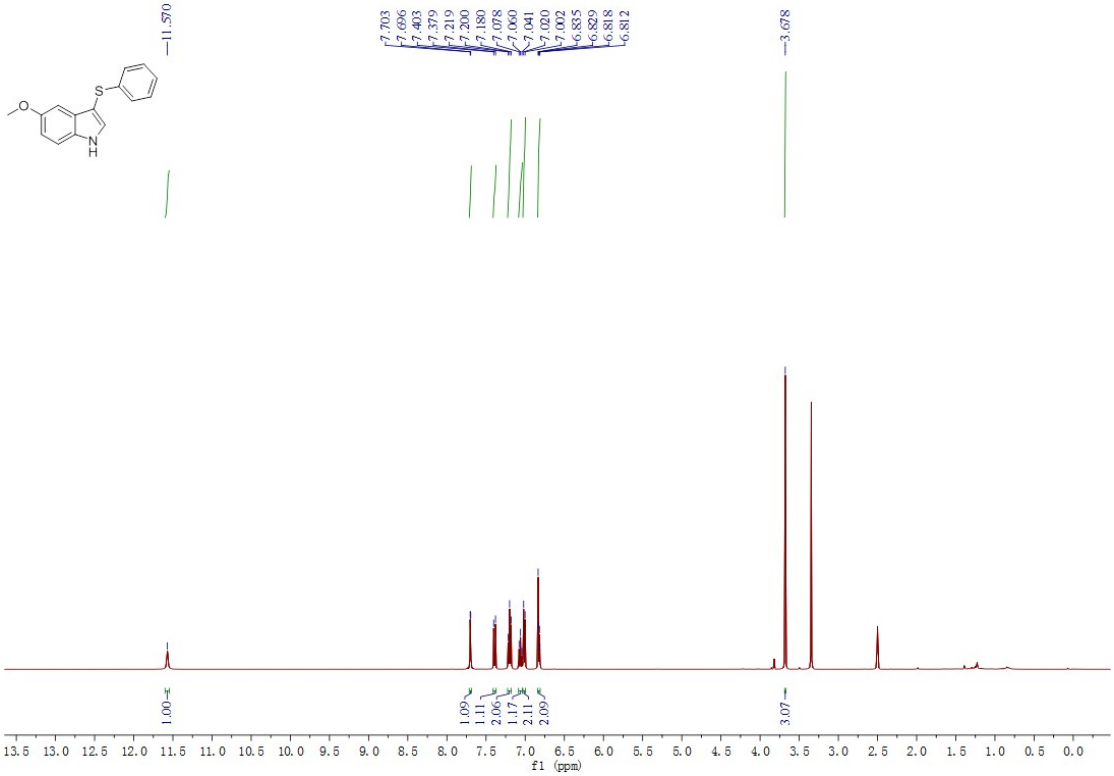


Figure S11. ^{1}H NMR spectrum for **3fa** in DMSO-d_6.

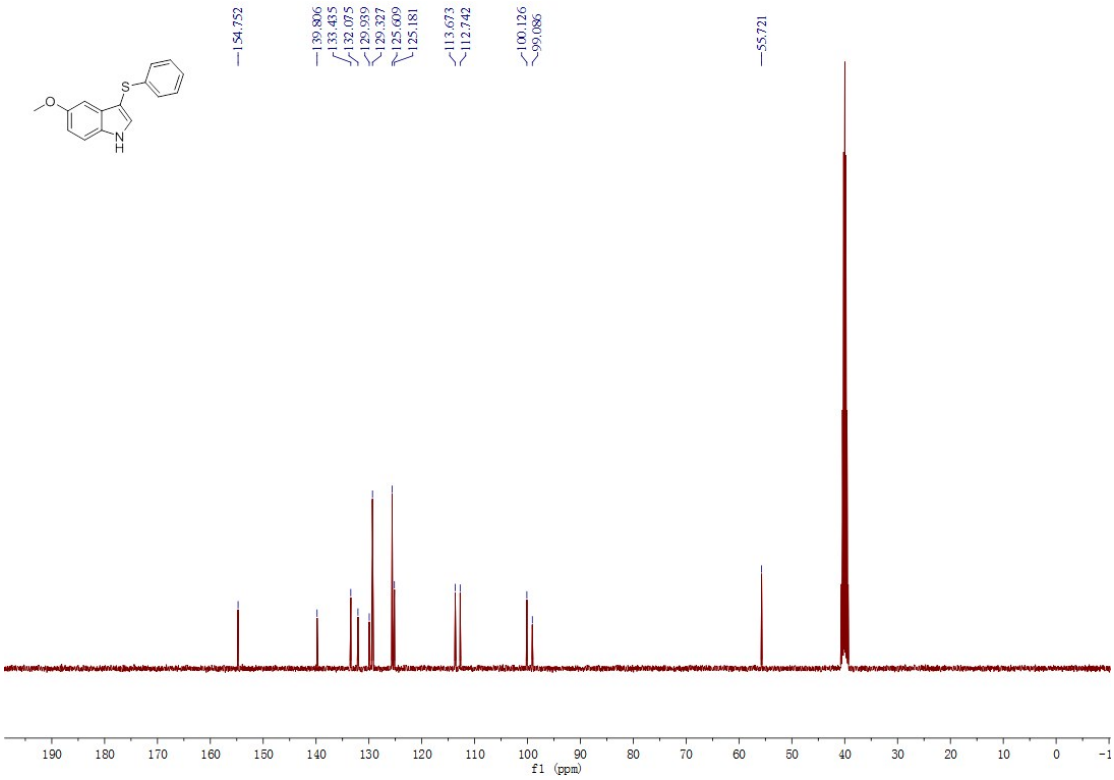


Figure S14. ^{13}C NMR spectrum for **3fa** in DMSO-d_6.

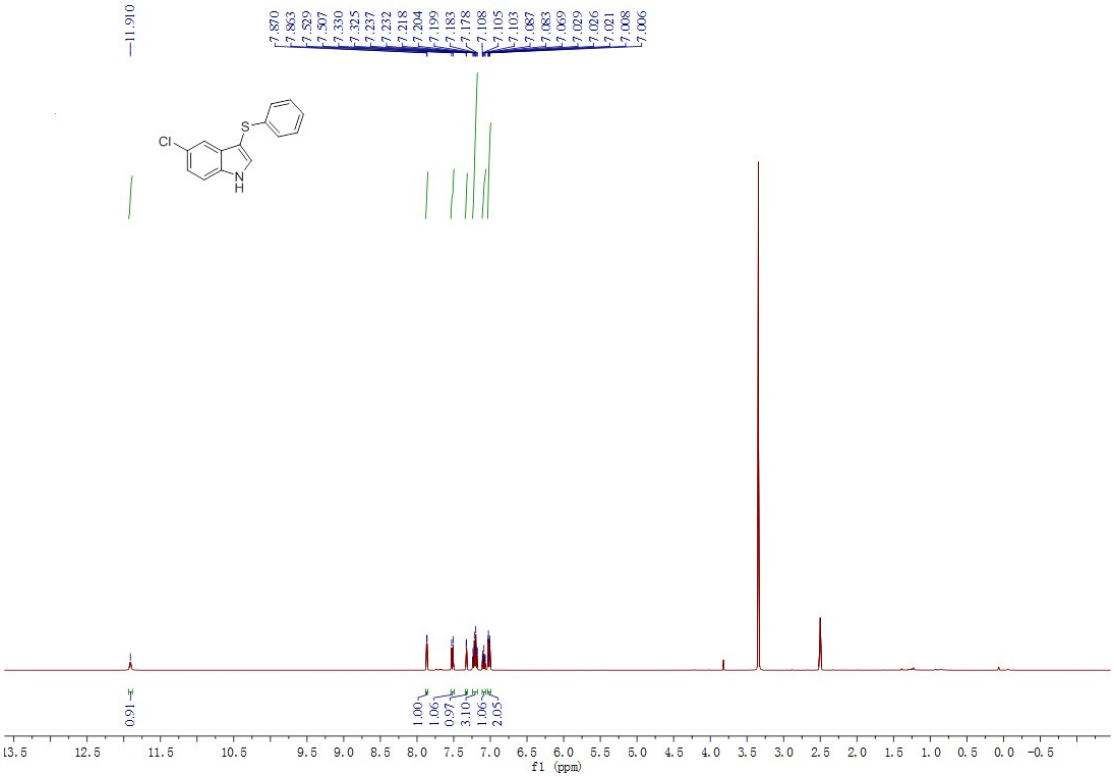


Figure S15. ^{1}H NMR spectrum for **3ga** in DMSO-d_6.

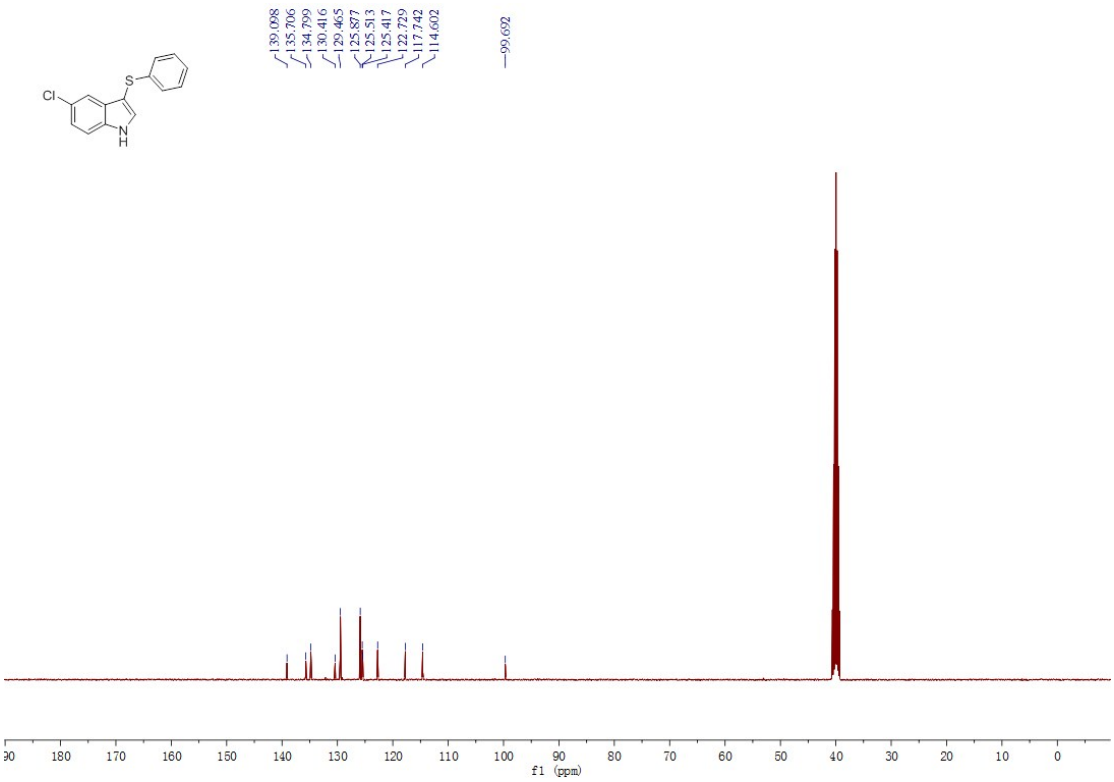


Figure S16. ^{13}C NMR spectrum for **3ga** in DMSO-d6.

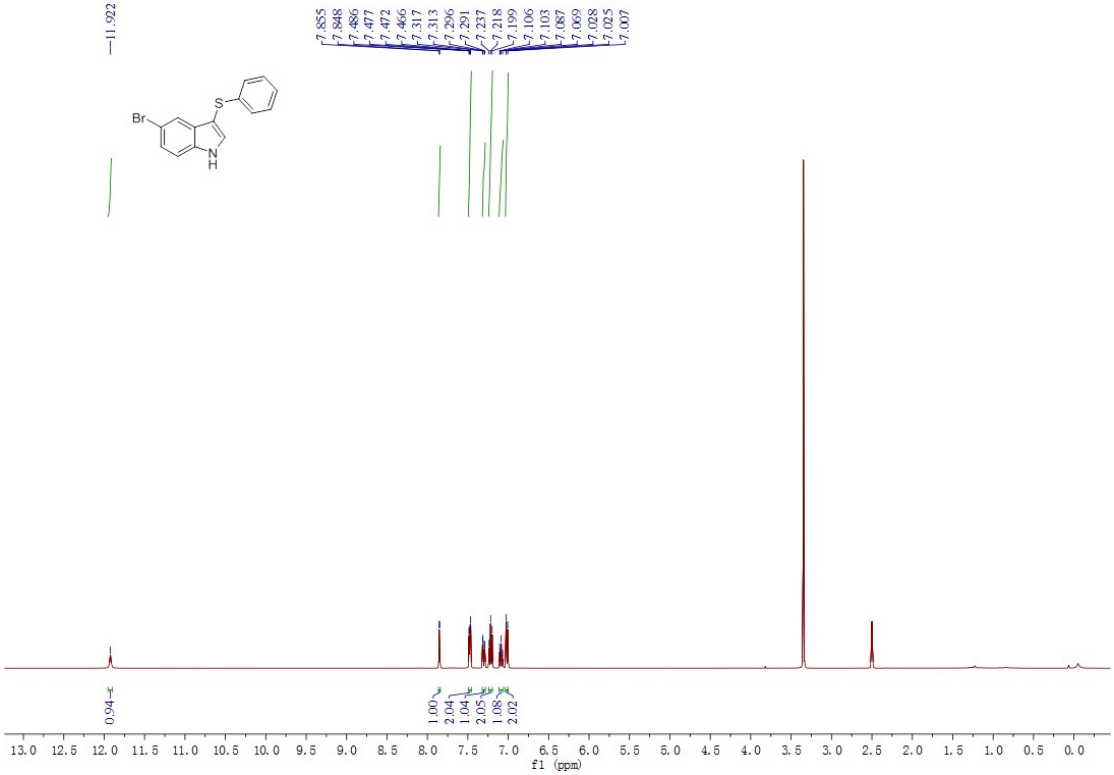


Figure S17. ^{1}H NMR spectrum for **3ha** in DMSO-d_6.

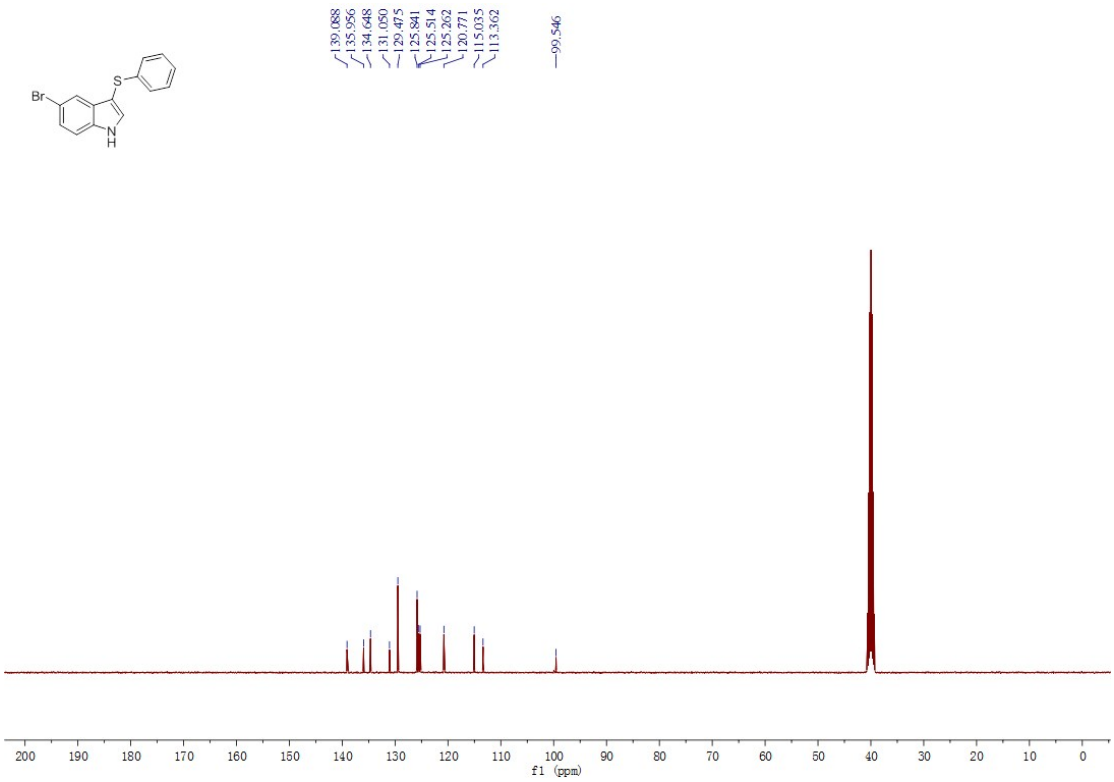


Figure S18. ^{13}C NMR spectrum for **3ha** in DMSO-d_6.

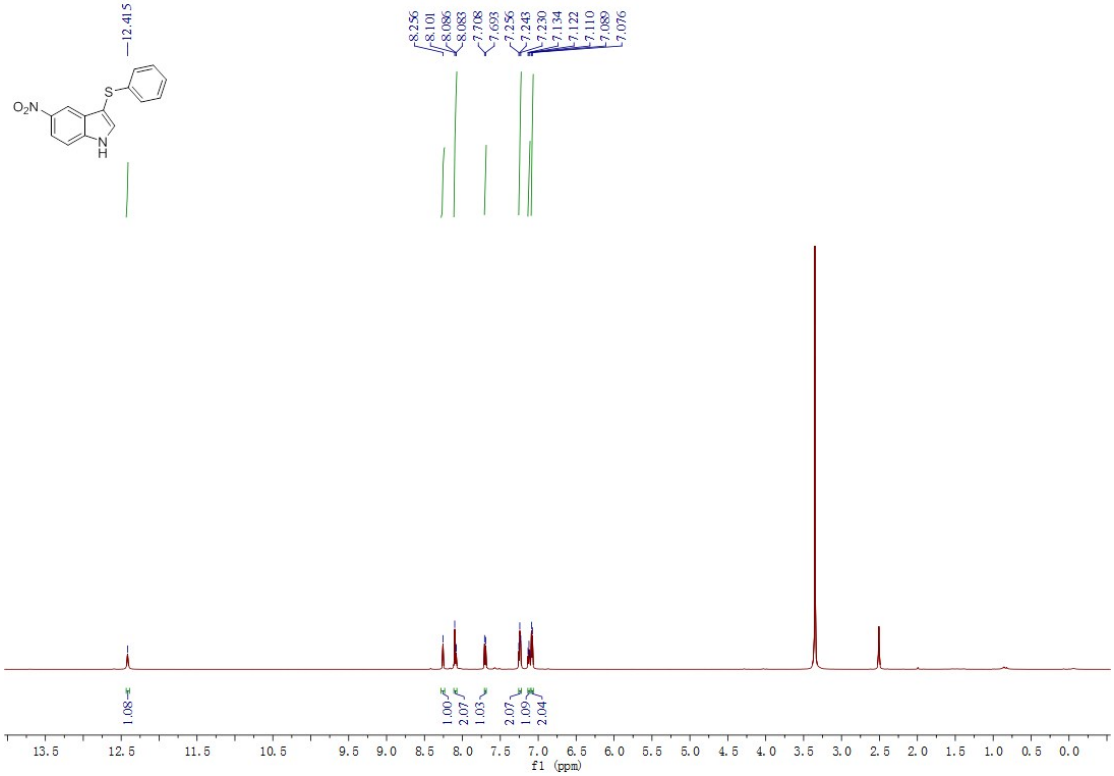


Figure S19. ^{1}H NMR spectrum for **3ia** in DMSO-d_6.

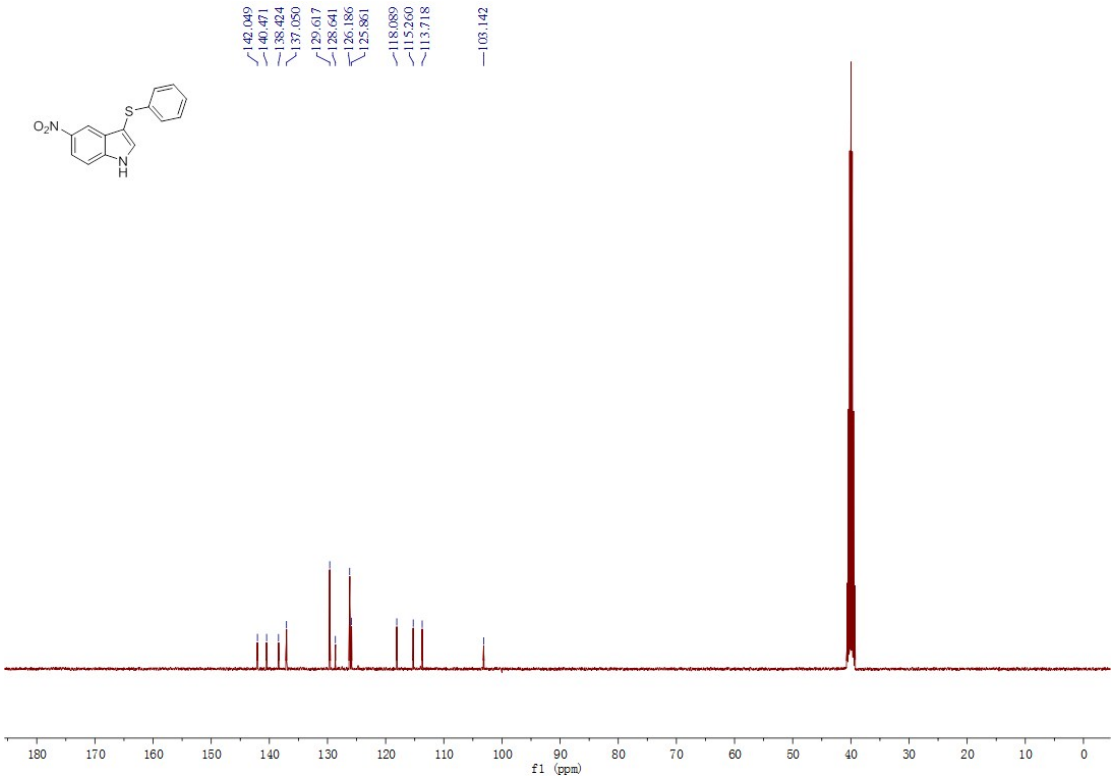


Figure S20. ^{13}C NMR spectrum for **3ia** in DMSO-d_6.

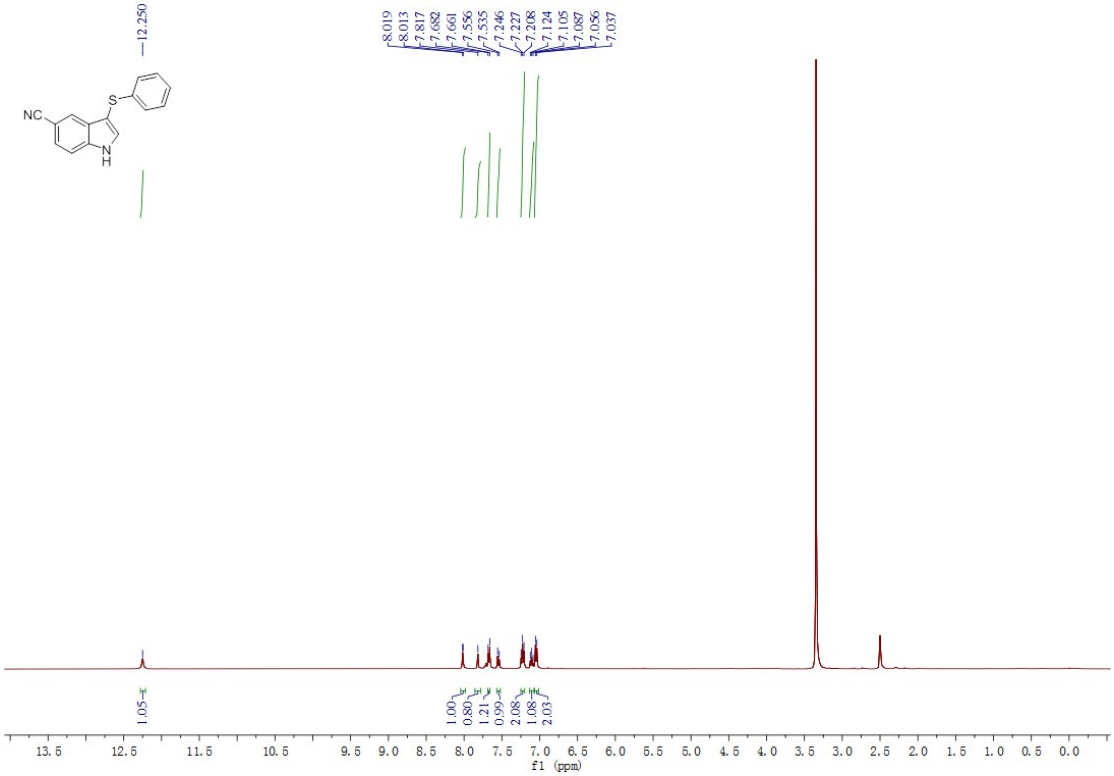


Figure S21. ^{1}H NMR spectrum for **3ja** in DMSO-d_6.

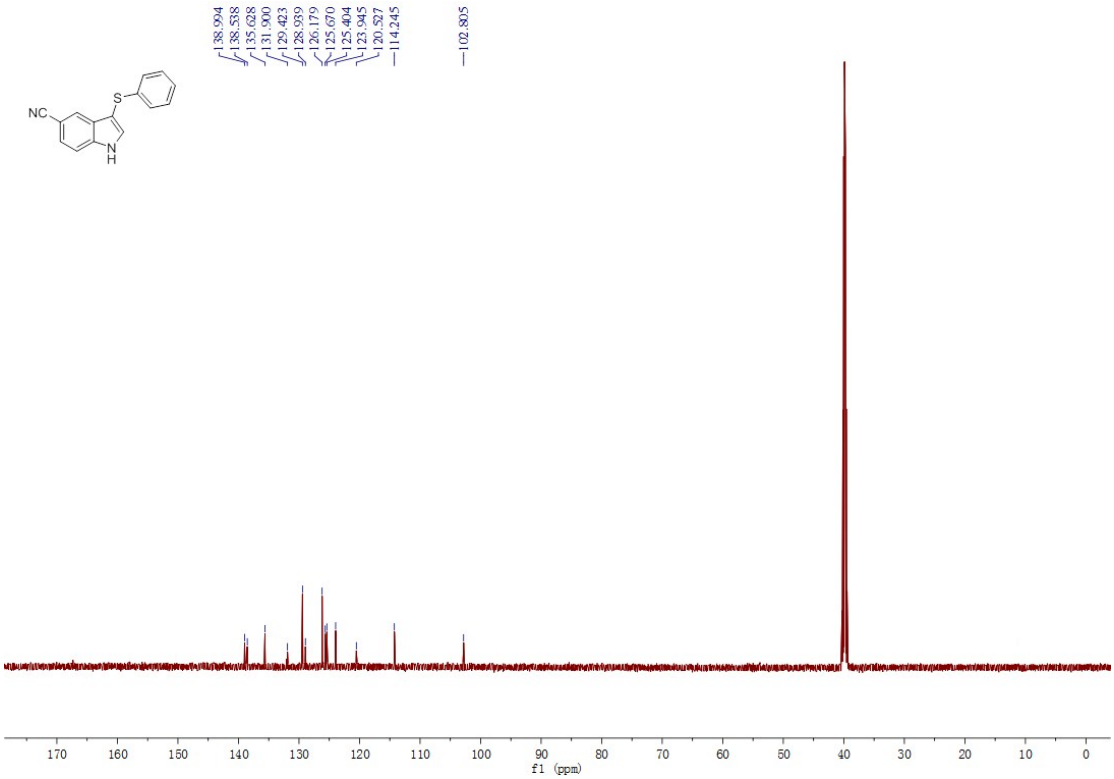


Figure S22. ^{13}C NMR spectrum for **3ja** in DMSO-d$_6$.

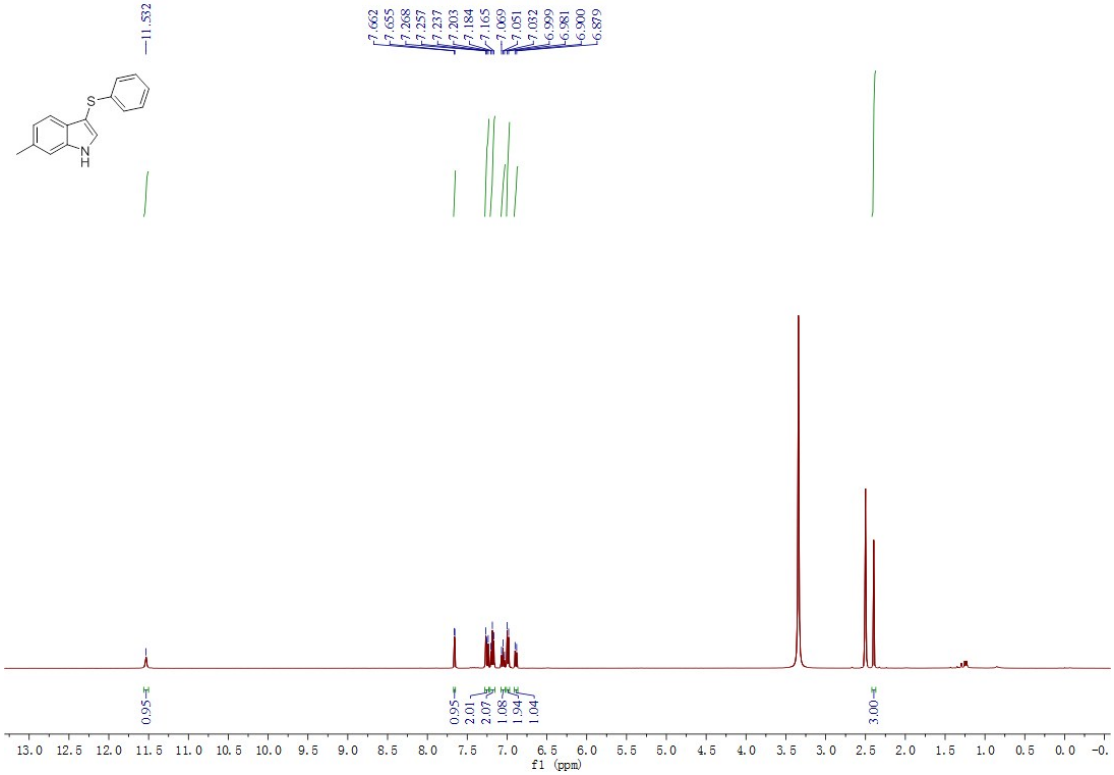


Figure S23. ^{1}H NMR spectrum for **3ka** in DMSO-d$_6$.

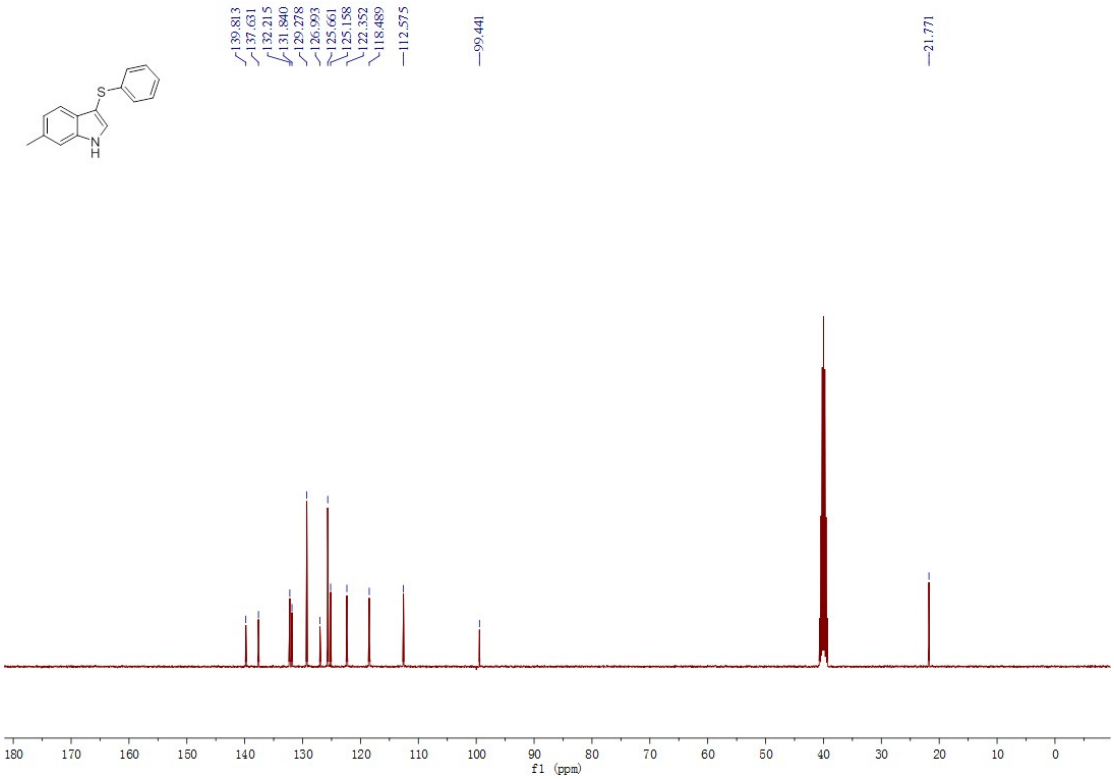


Figure S24. ^{13}C NMR spectrum for **3ka** in DMSO-d_6.

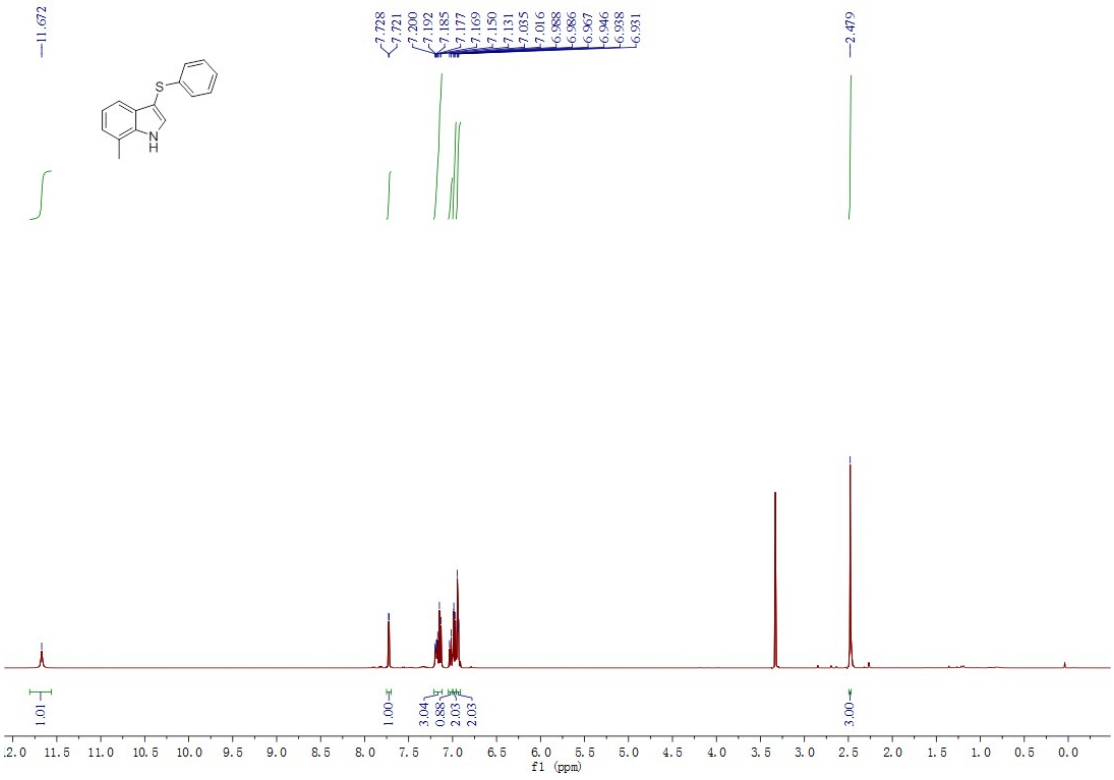


Figure S25. ^{1}H NMR spectrum for **3la** in DMSO-d_6.

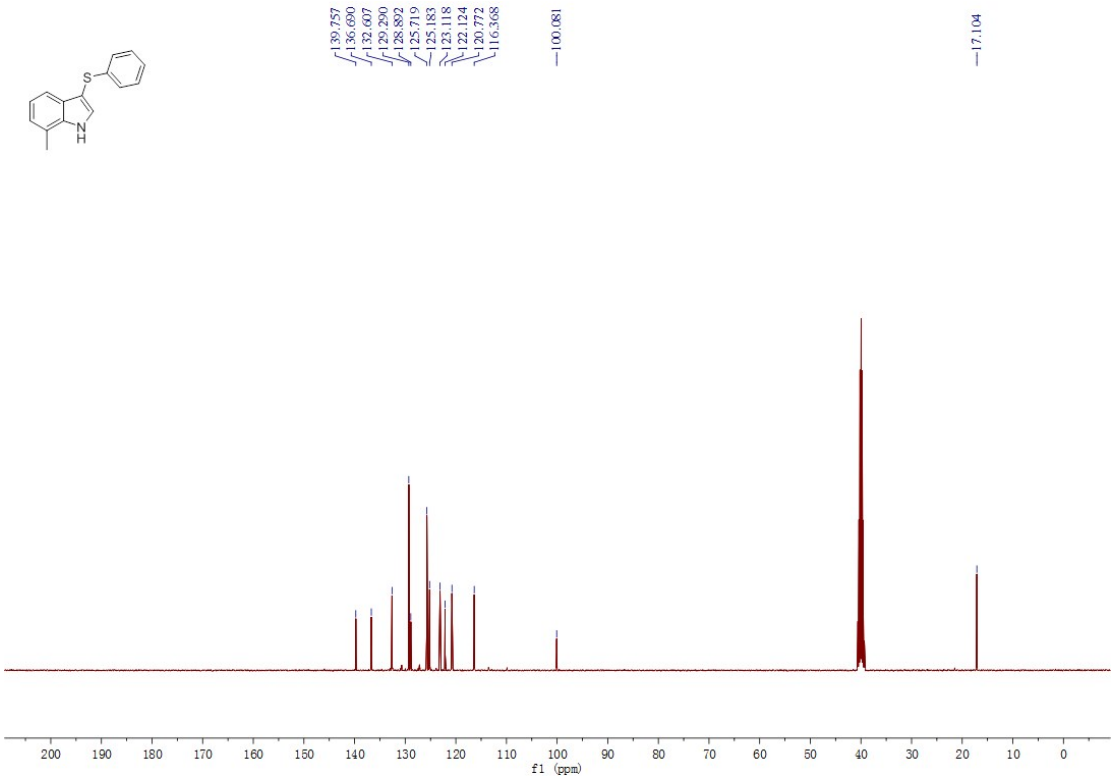


Figure S26. ^{13}C NMR spectrum for **3la** in DMSO-d_6.

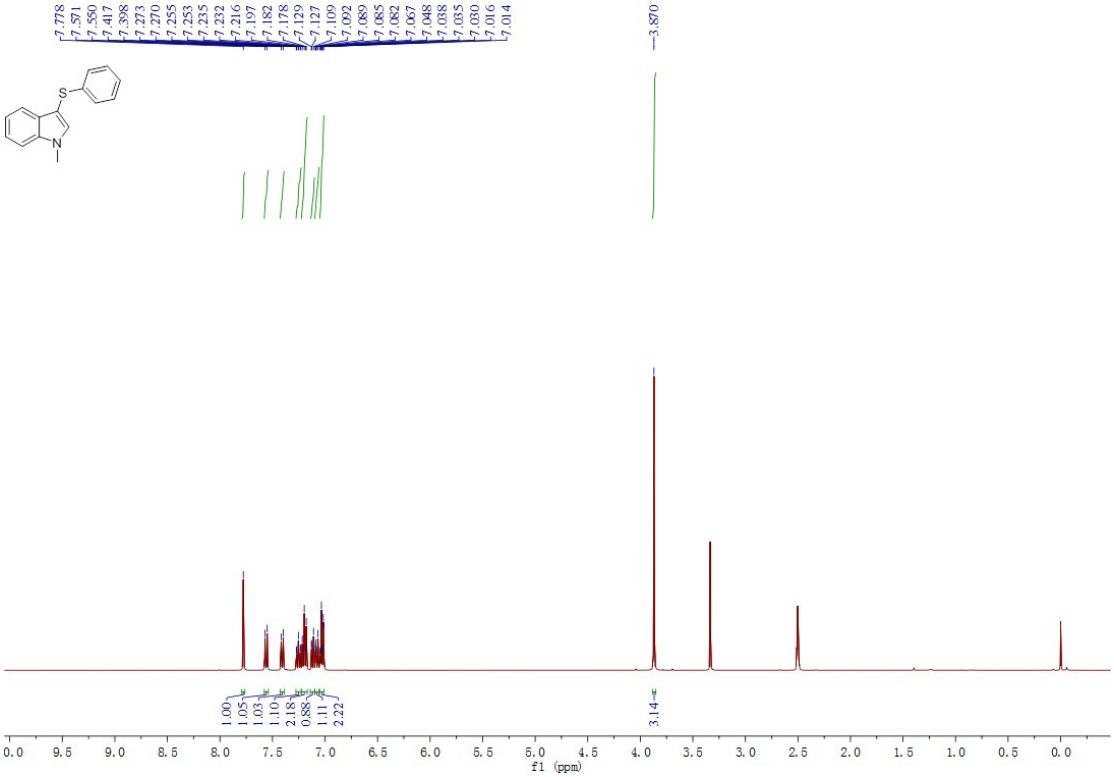


Figure S27. ^{1}H NMR spectrum for **3ma** in DMSO-d_6.

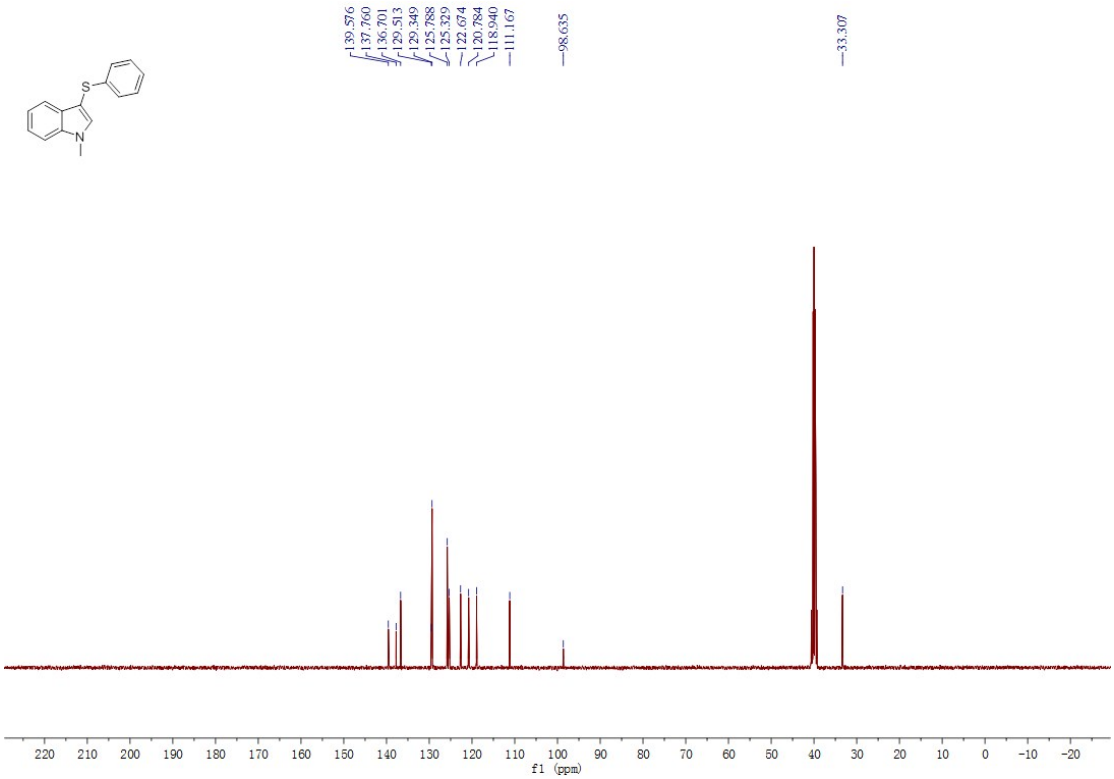


Figure S28. ^{13}C NMR spectrum for **3ma** in DMSO-d_6.

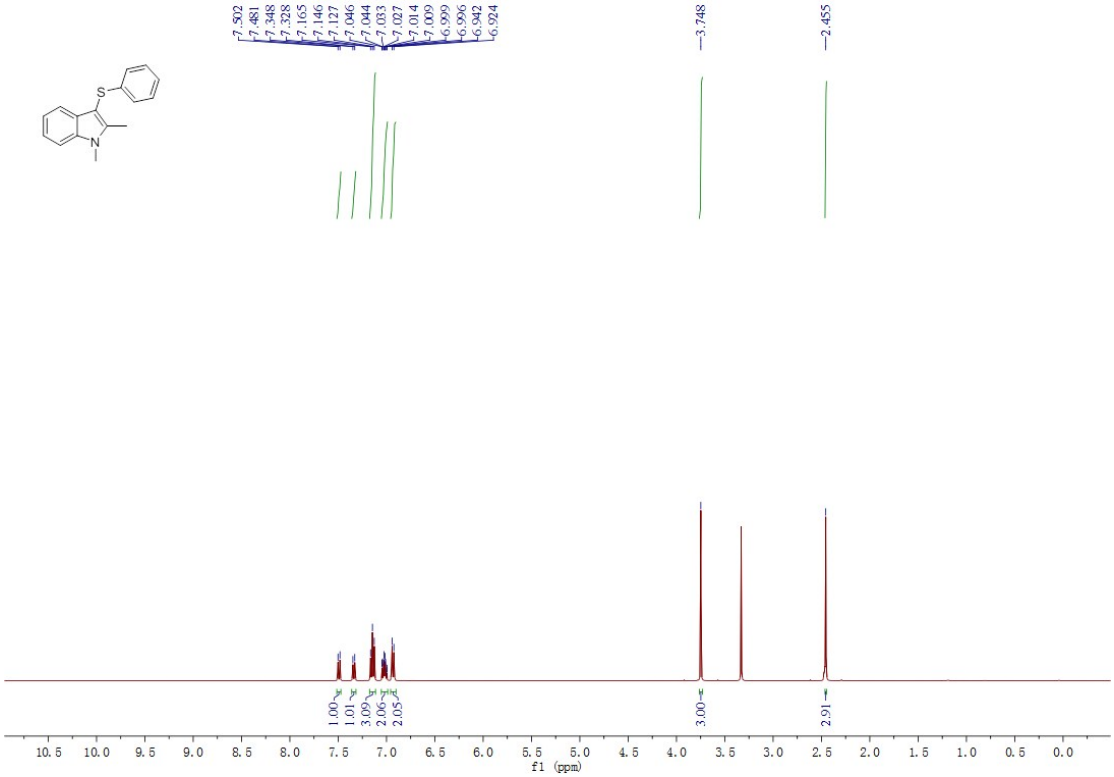


Figure S29. ^{1}H NMR spectrum for **3na** in DMSO-d_6.

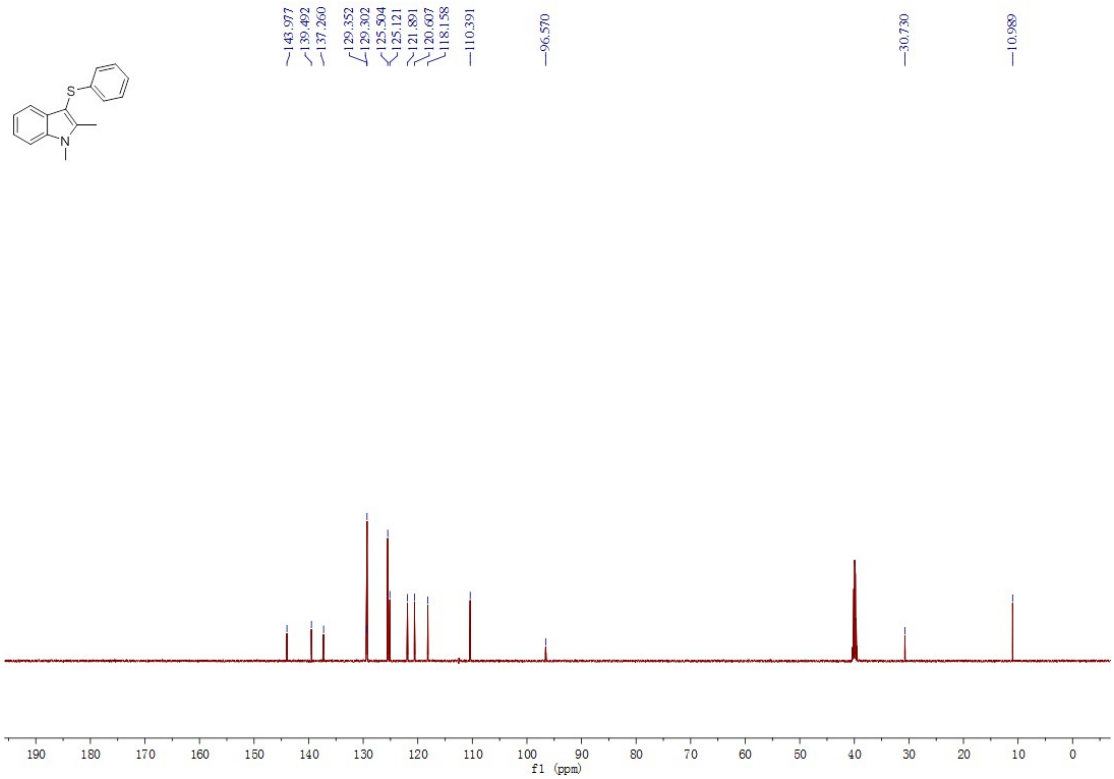


Figure S30. ^{13}C NMR spectrum for **3na** in DMSO-d_6.

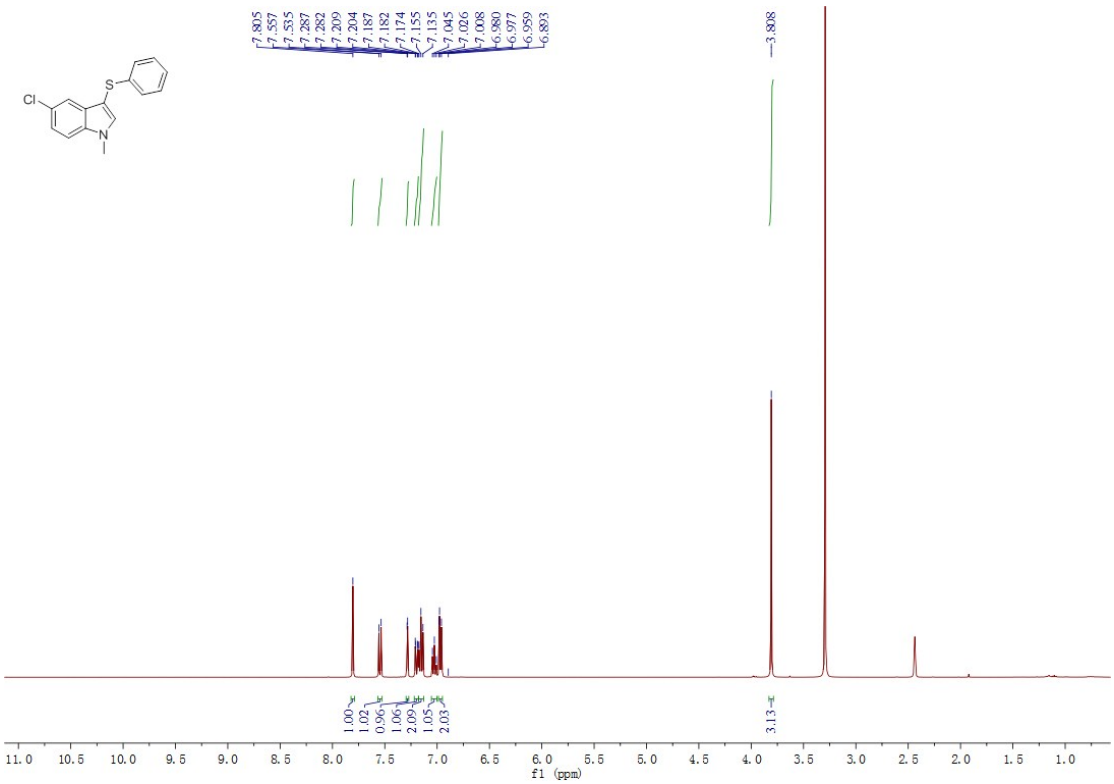


Figure S31. ^{1}H NMR spectrum for **3oa** in DMSO-d_6.

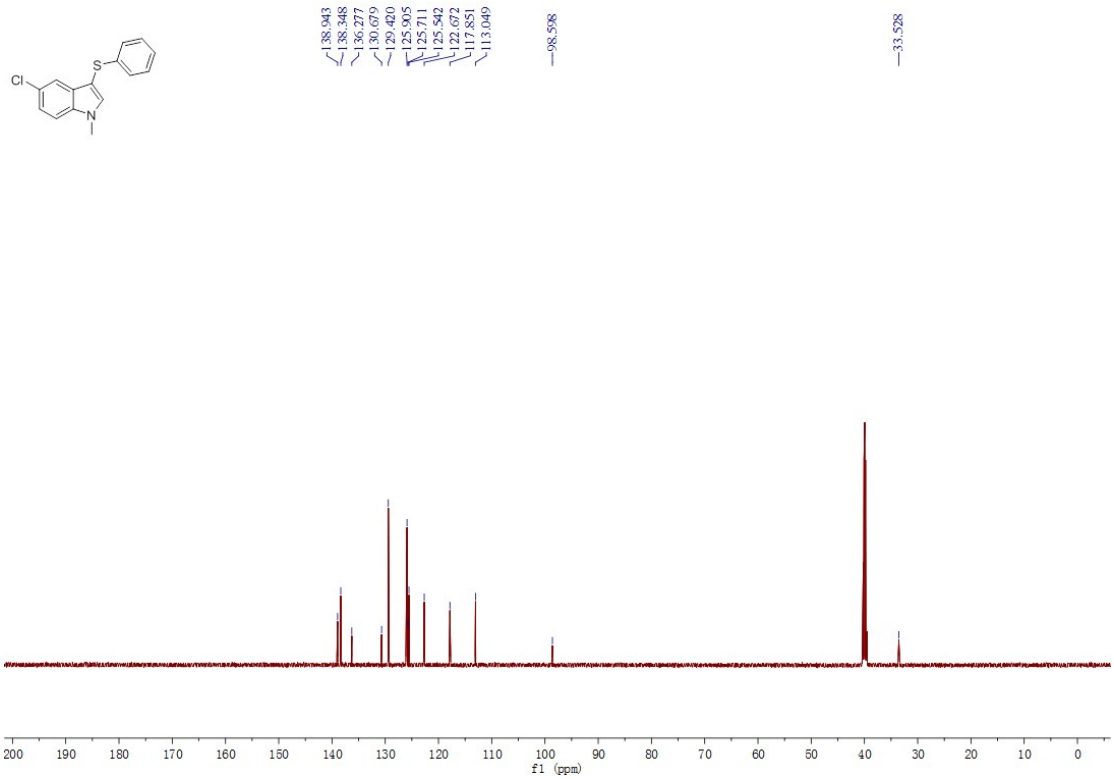


Figure S32. ^{13}C NMR spectrum for **3oa** in DMSO-d_6.

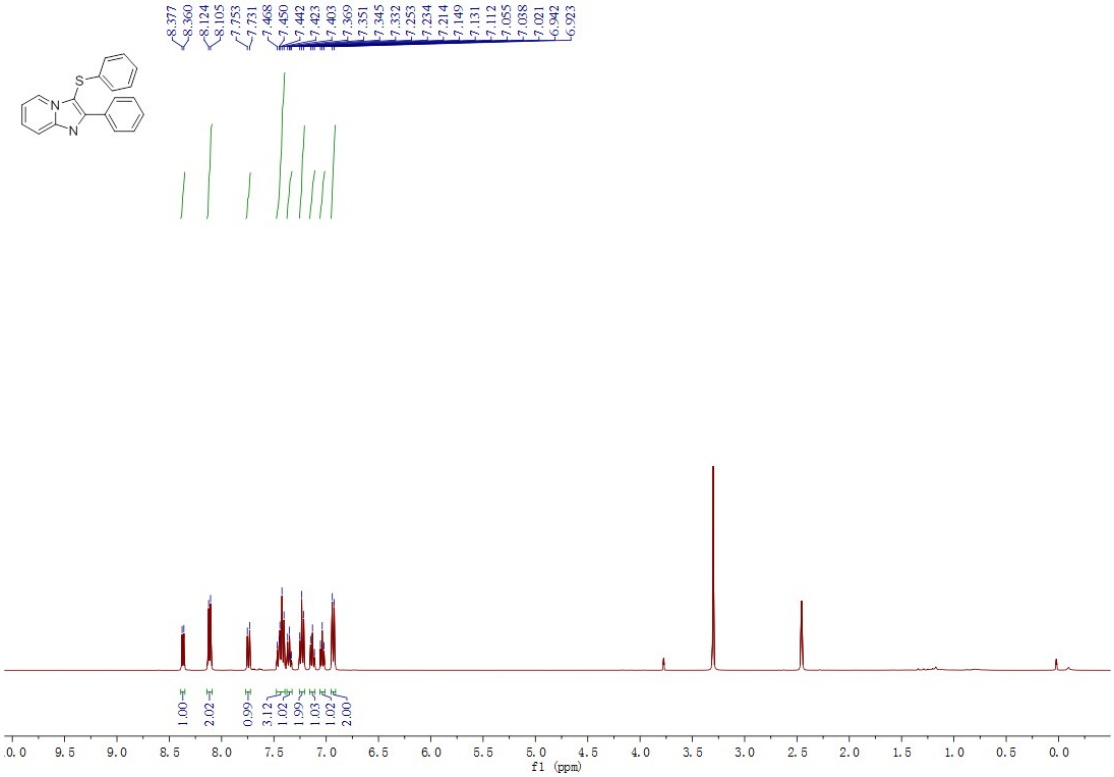


Figure S33. ^{1}H NMR spectrum for **3pa** in DMSO-d_6.

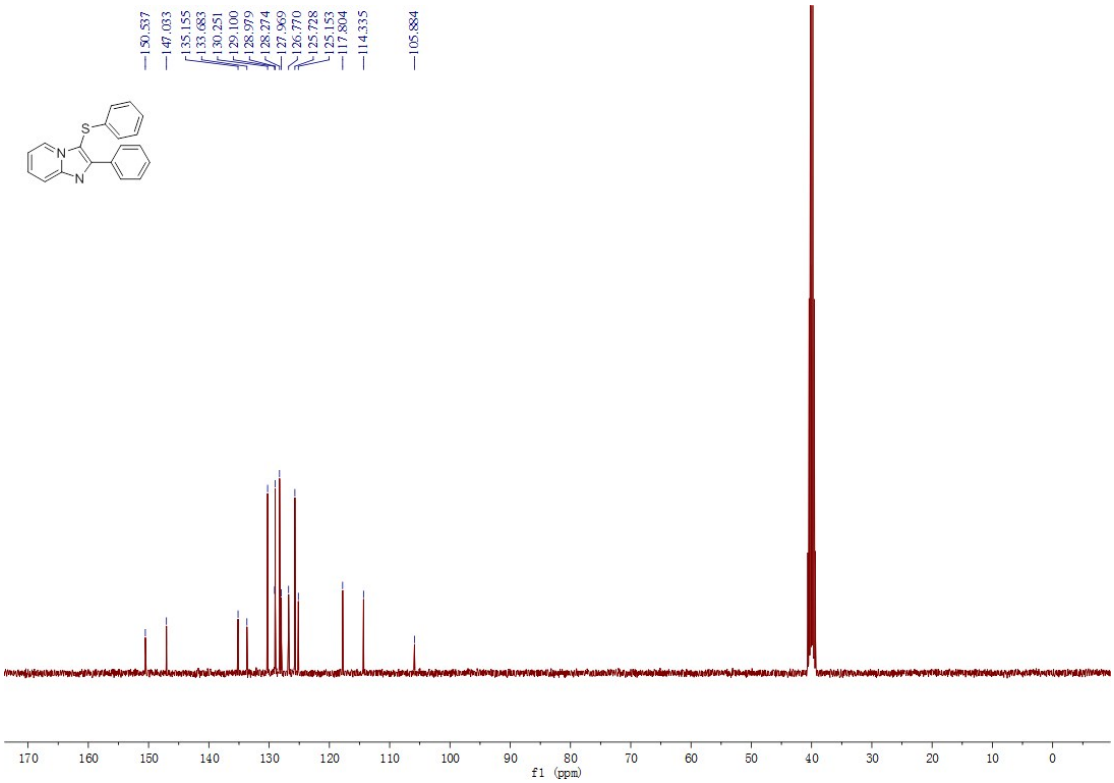


Figure S34. ^{13}C NMR spectrum for **3pa** in DMSO-d_6.

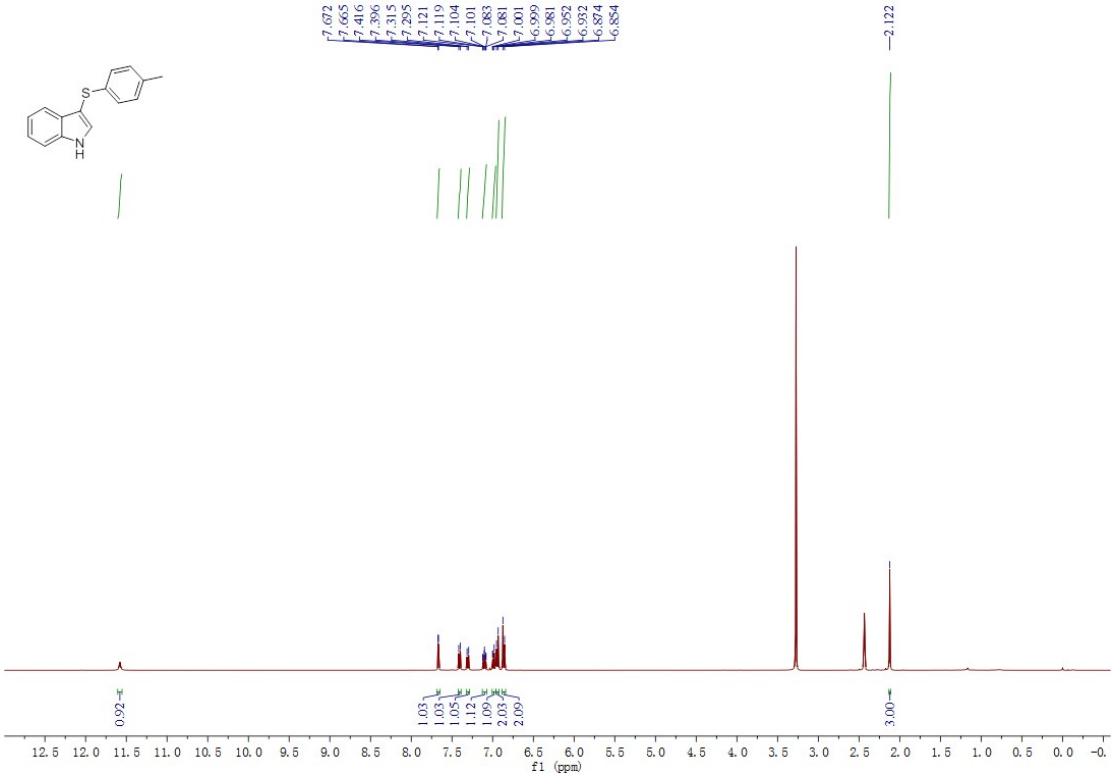


Figure S35. ^{1}H NMR spectrum for **3ab** in DMSO-d_6.

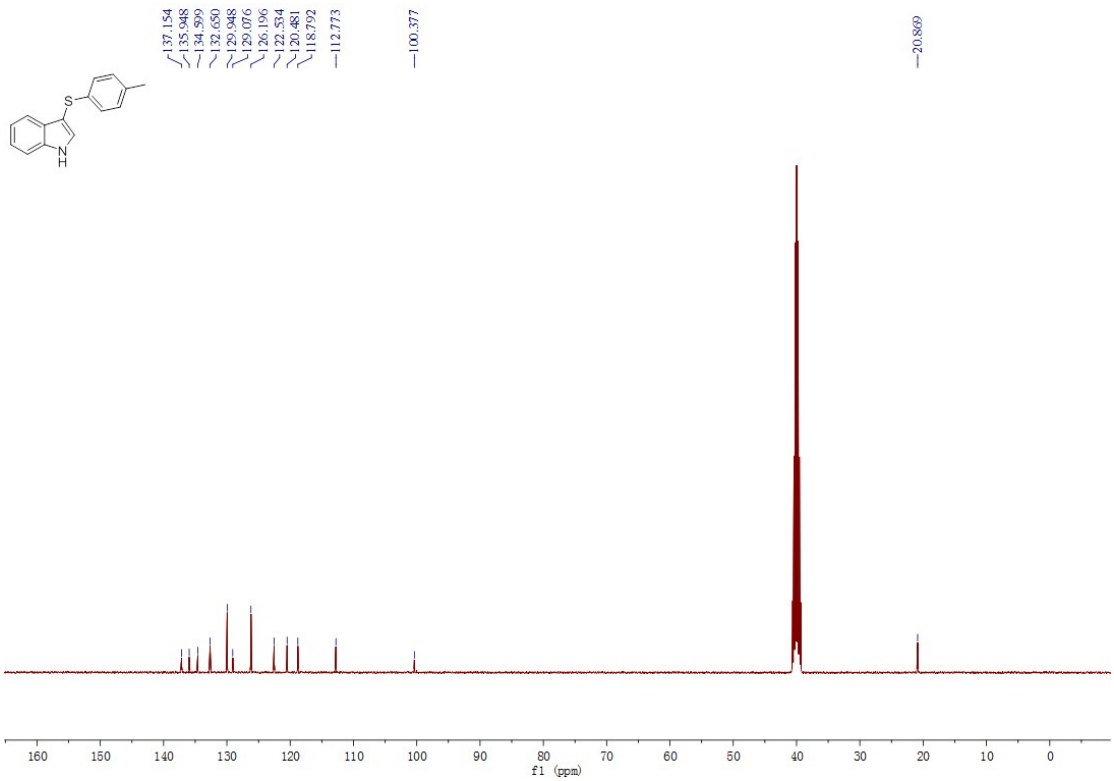


Figure S36. ^{13}C NMR spectrum for **3ab** in DMSO-d_6.

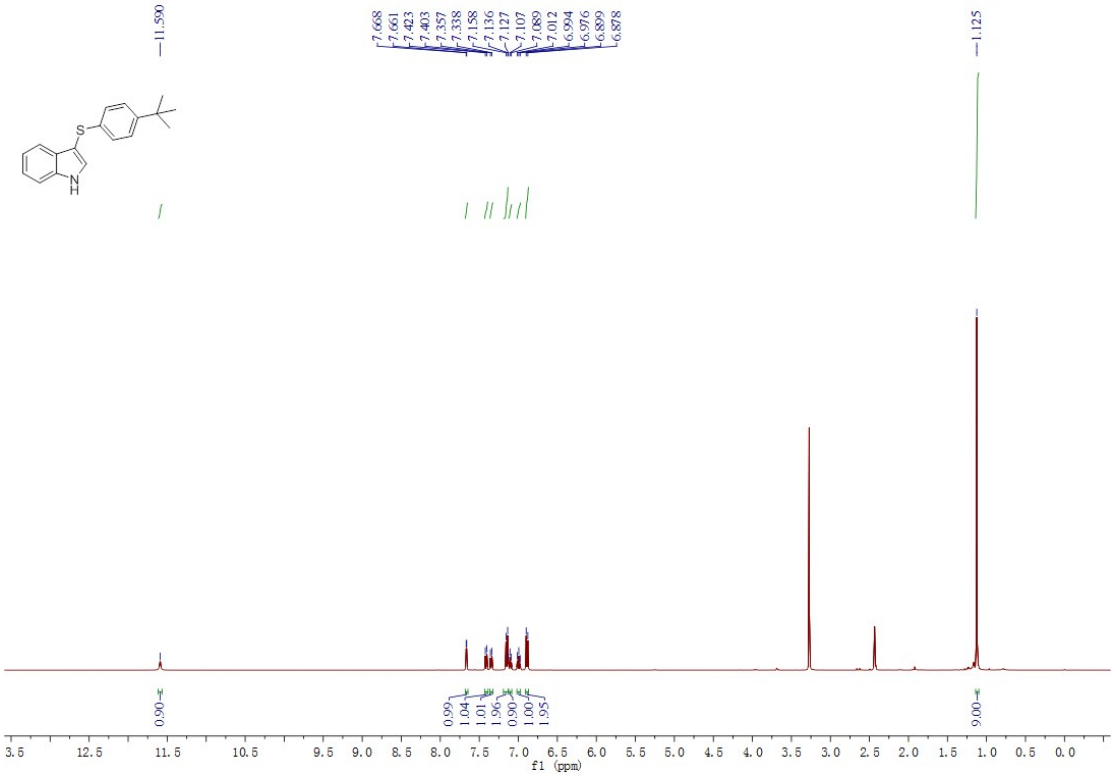


Figure S37. ^{1}H NMR spectrum for **3ac** in DMSO-d_6.

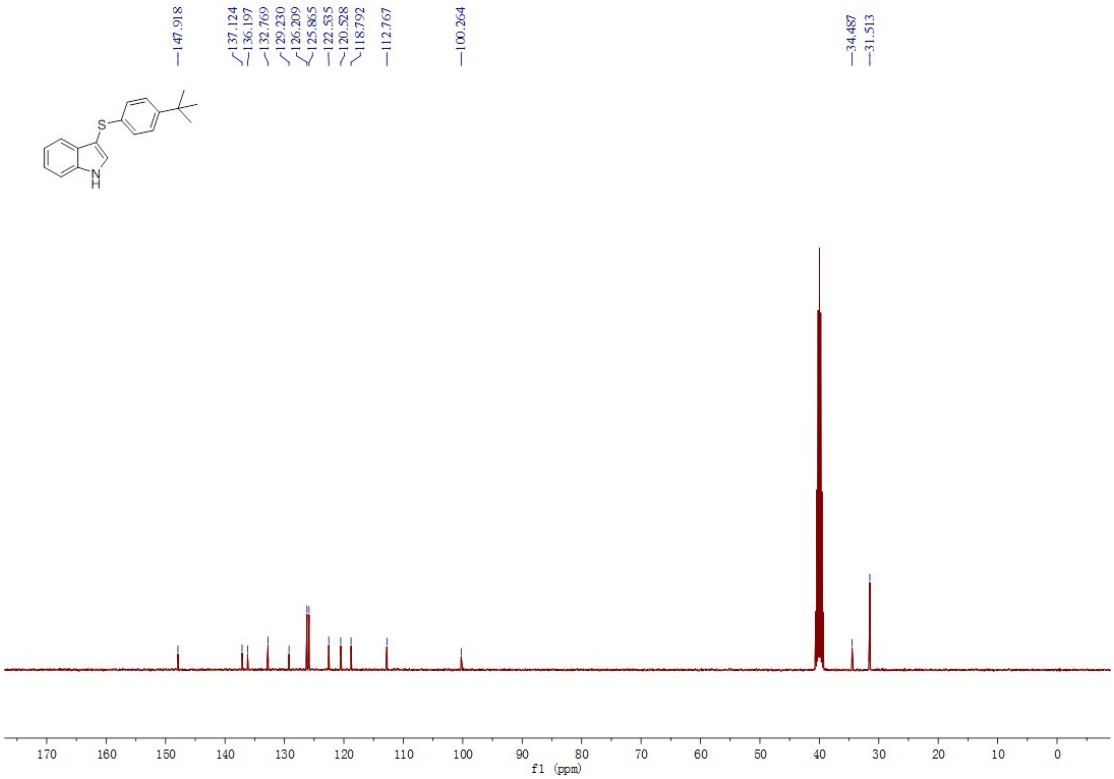


Figure S38. ^{13}C NMR spectrum for **3ac** in DMSO-d6.

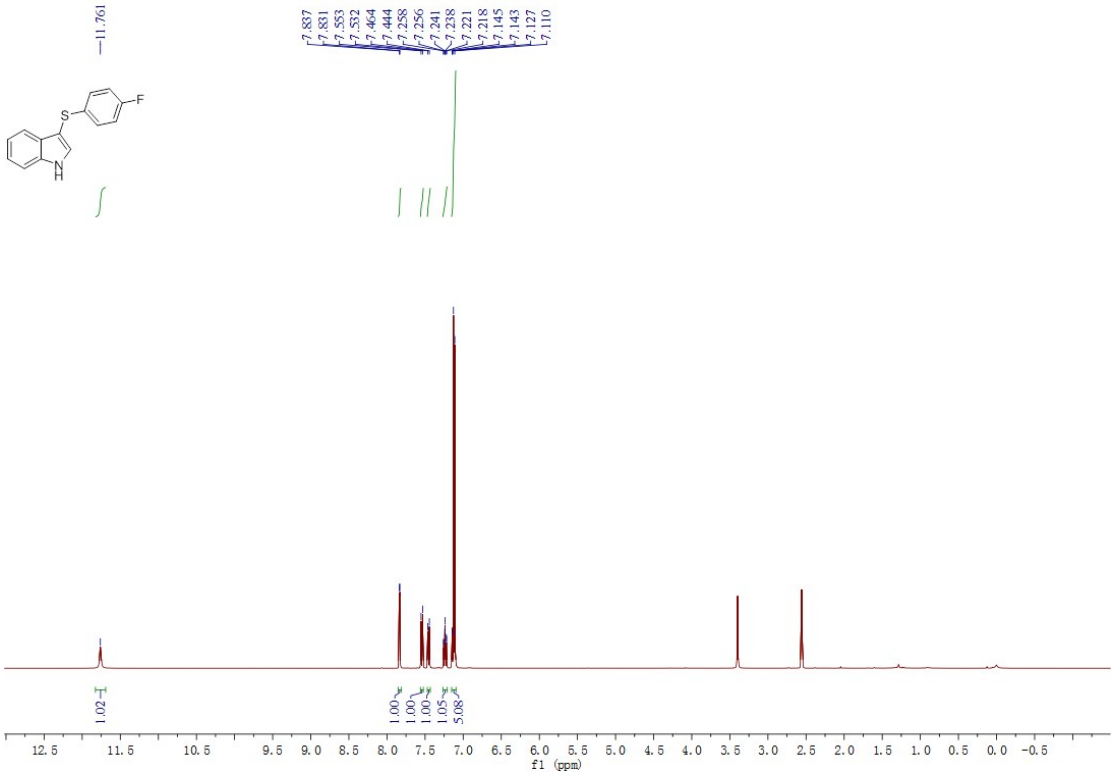


Figure S39. 1H NMR spectrum for **3ad** in DMSO-d6.

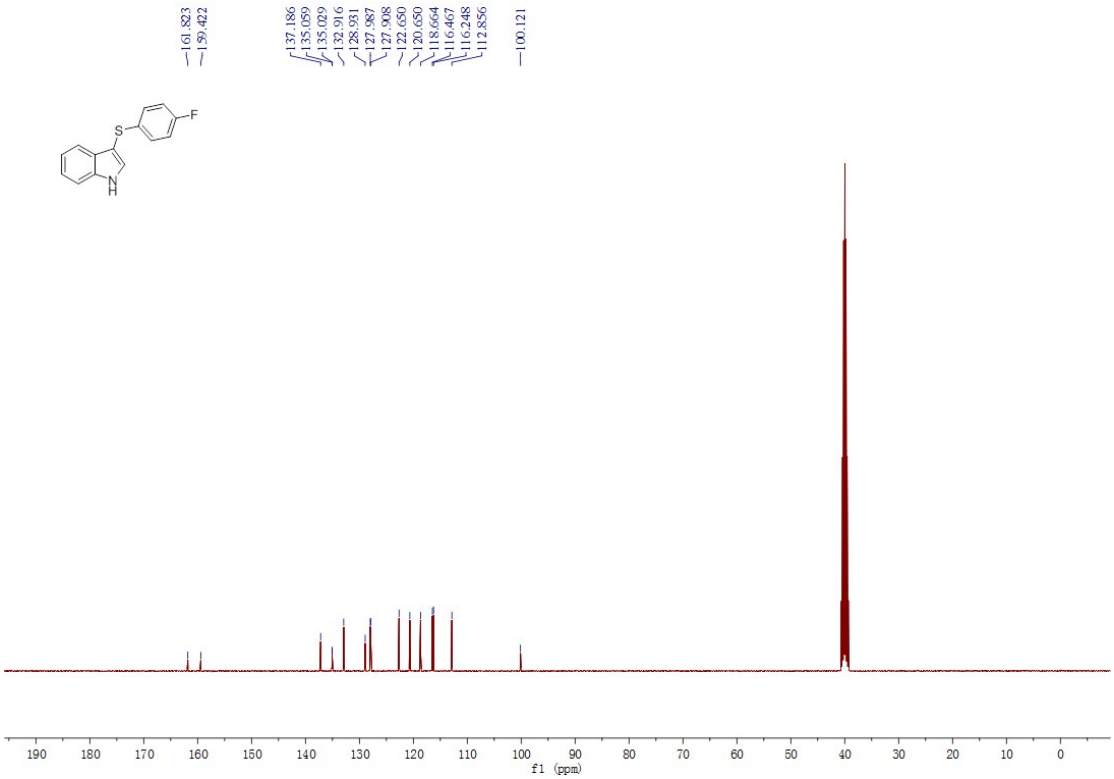


Figure S40. ^{13}C NMR spectrum for **3ad** in DMSO-d_6.

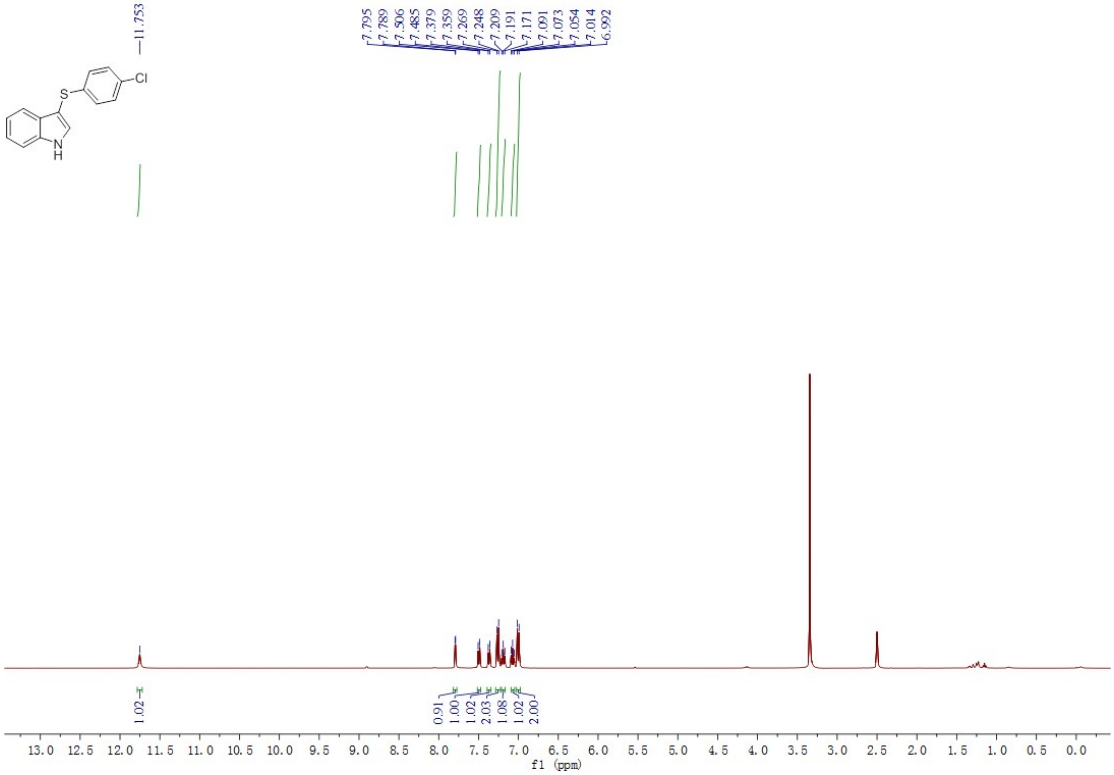


Figure S41. ^{1}H NMR spectrum for **3ae** in DMSO-d_6.

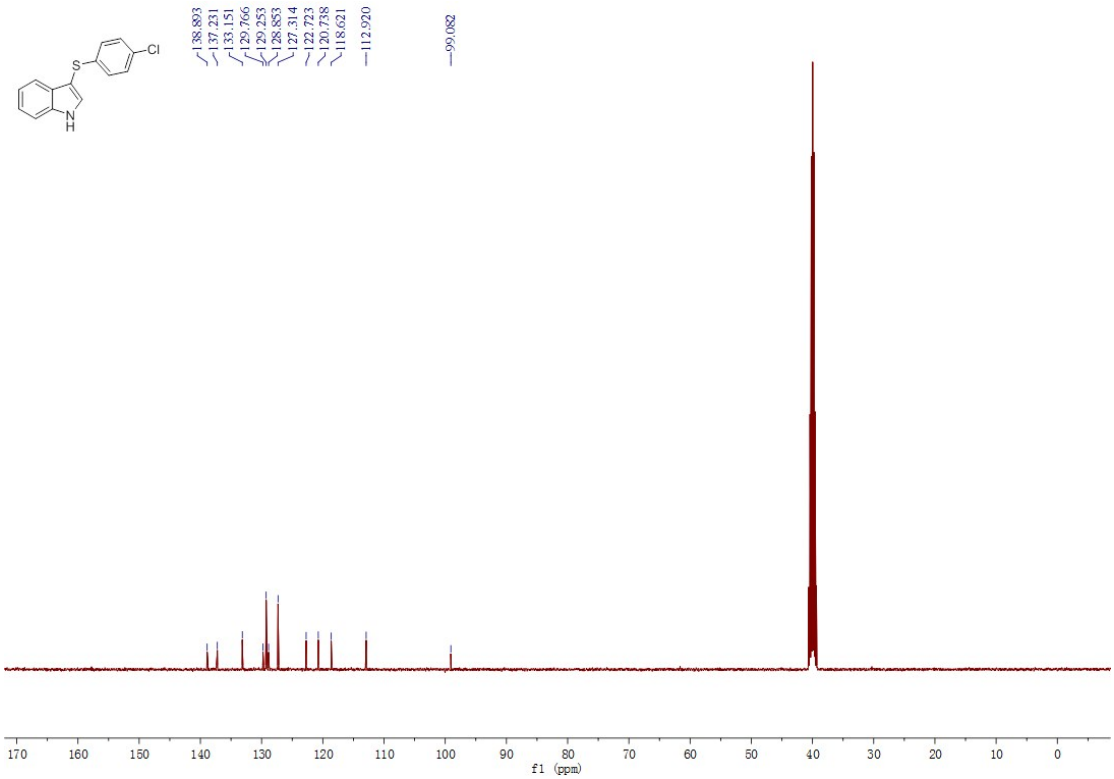


Figure S42. ^{13}C NMR spectrum for **3ae** in DMSO-d$_6$.

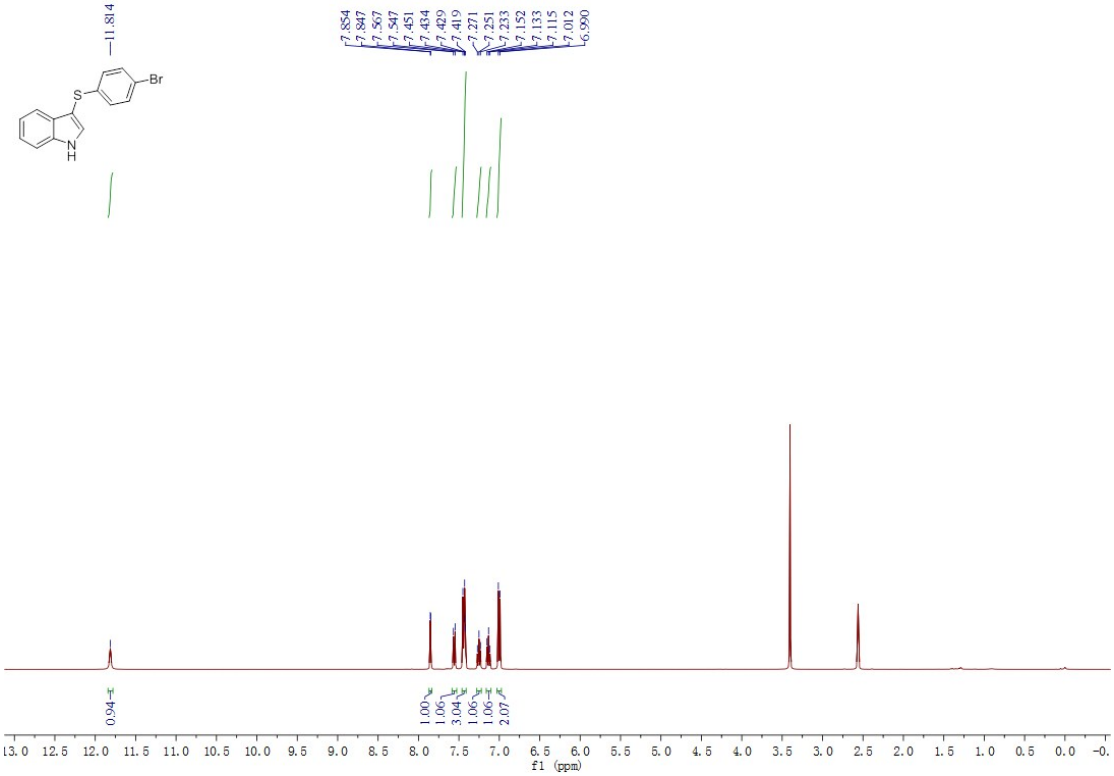


Figure S43. ^{1}H NMR spectrum for **3af** in DMSO-d$_6$.

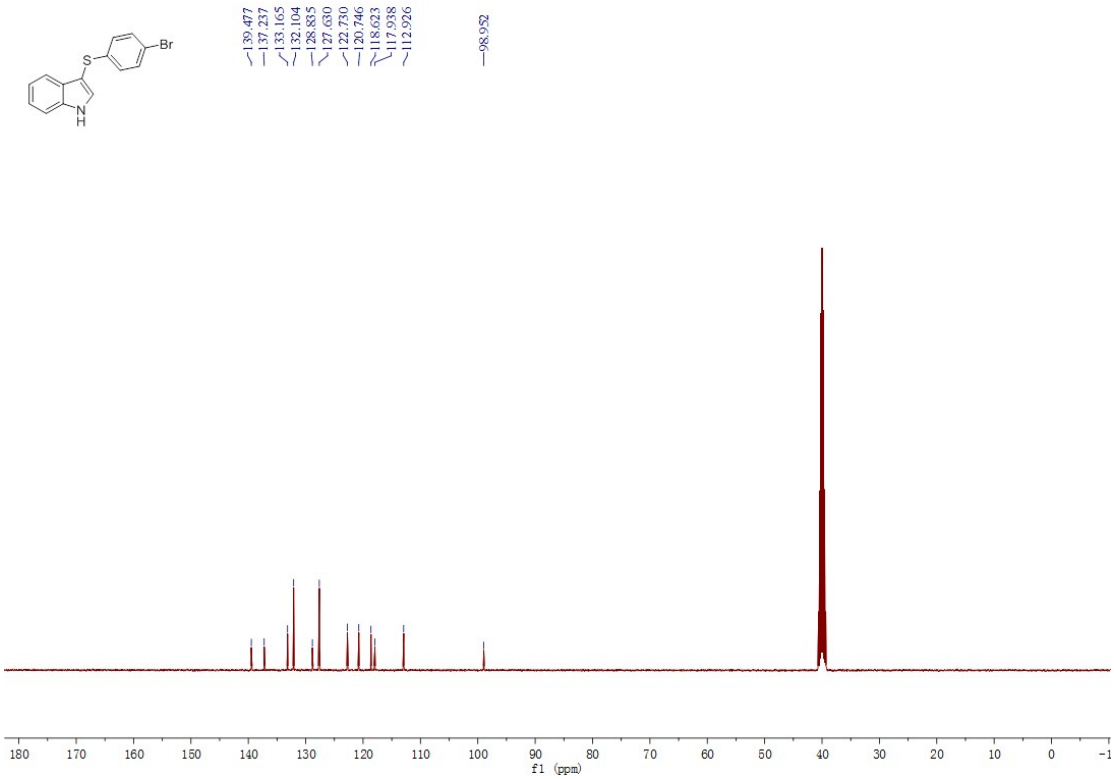


Figure S44. ^{13}C NMR spectrum for **3af** in DMSO-d$_6$.

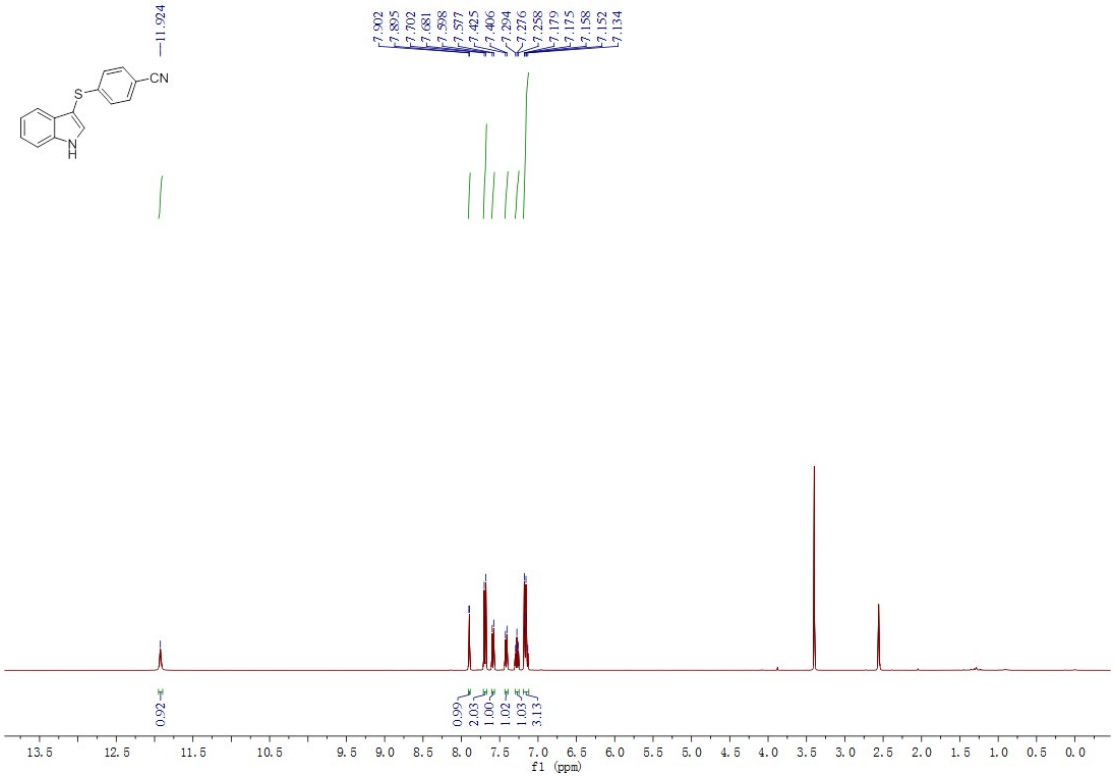


Figure S45. ^{1}H NMR spectrum for **3ag** in DMSO-d$_6$.

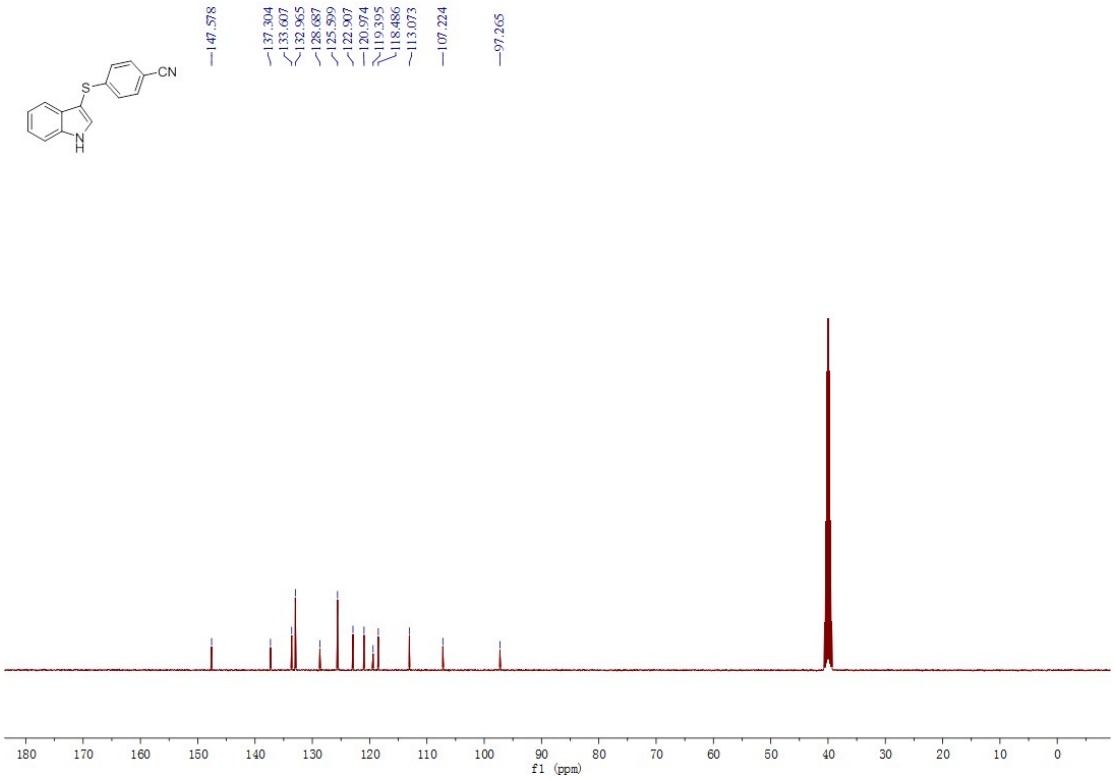


Figure S46. ^{13}C NMR spectrum for **3ag** in DMSO-d$_6$.

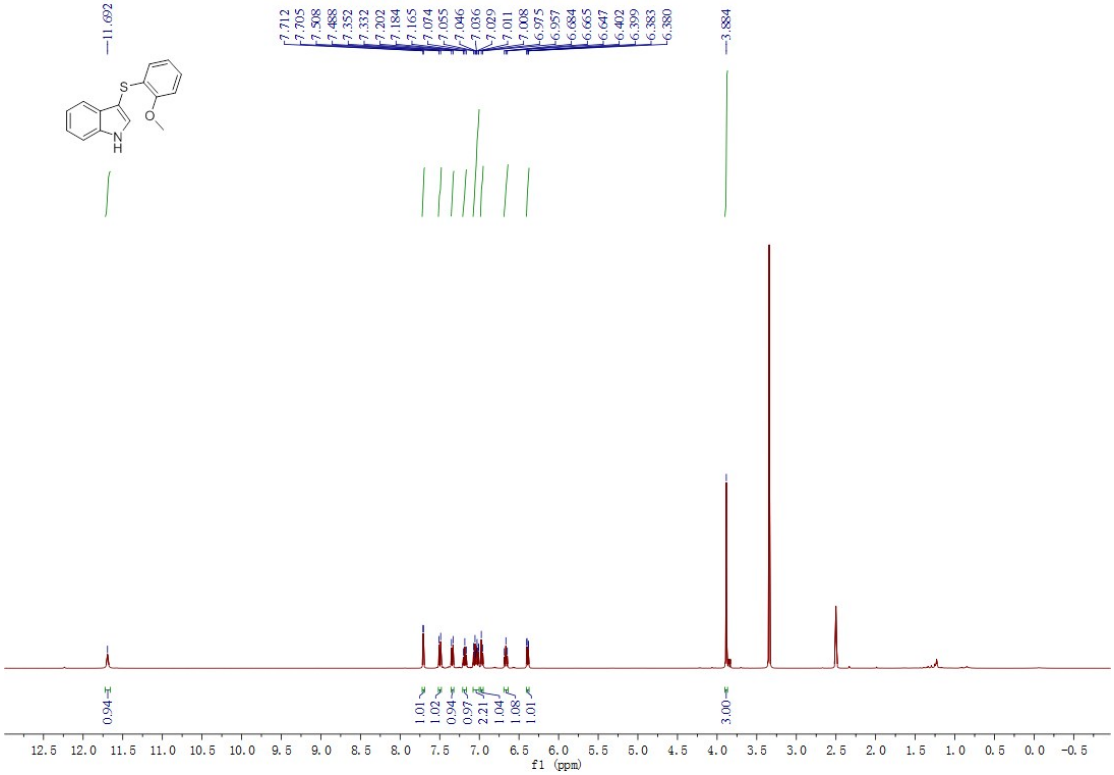


Figure S47. ^{1}H NMR spectrum for **3ah** in DMSO-d$_6$.

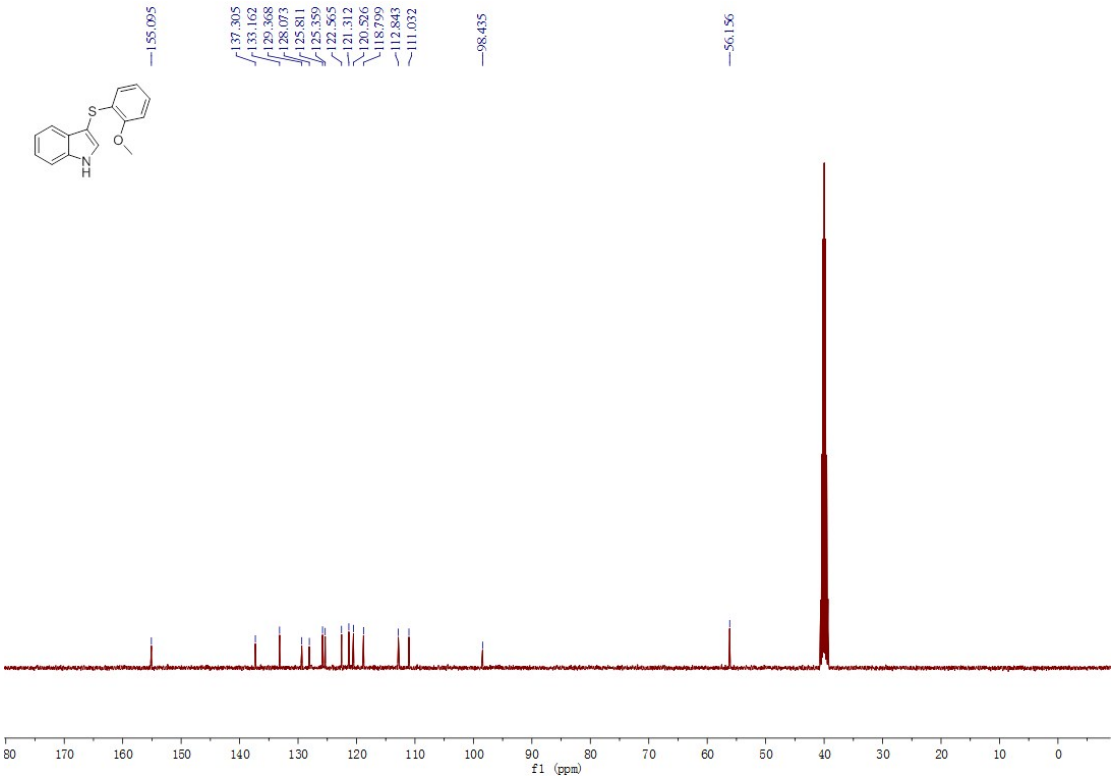


Figure S48. ^{13}C NMR spectrum for **3ah** in DMSO-d_6.

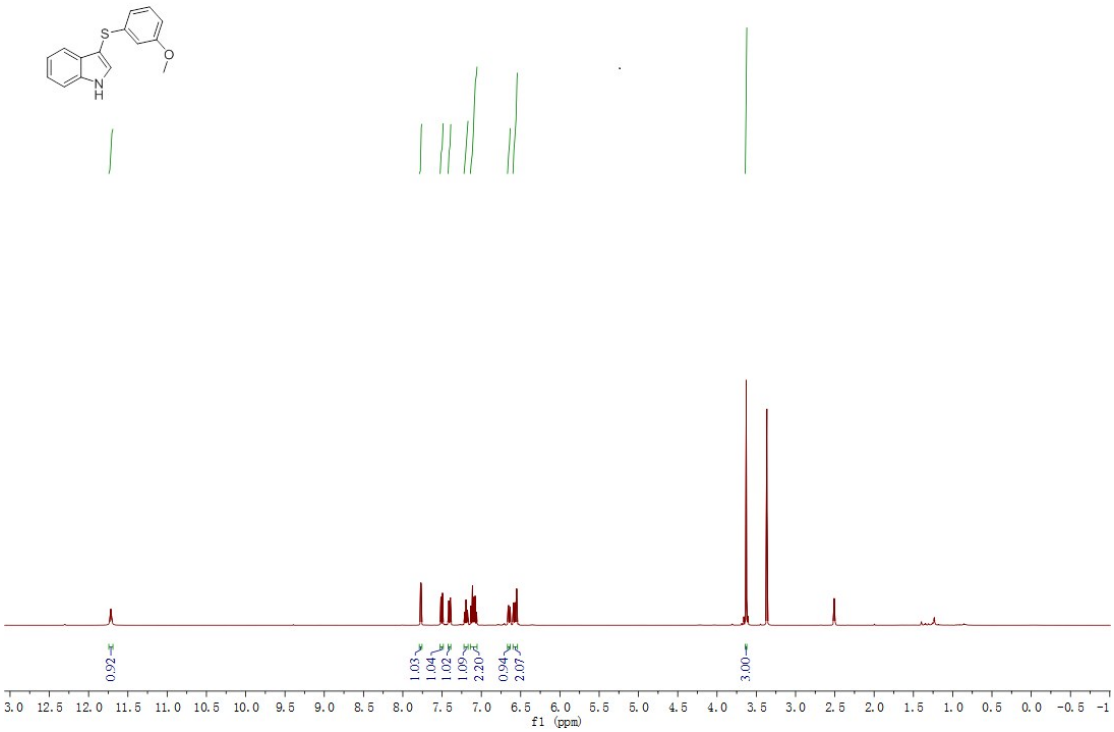


Figure S49. ^{1}H NMR spectrum for **3ai** in DMSO-d_6.

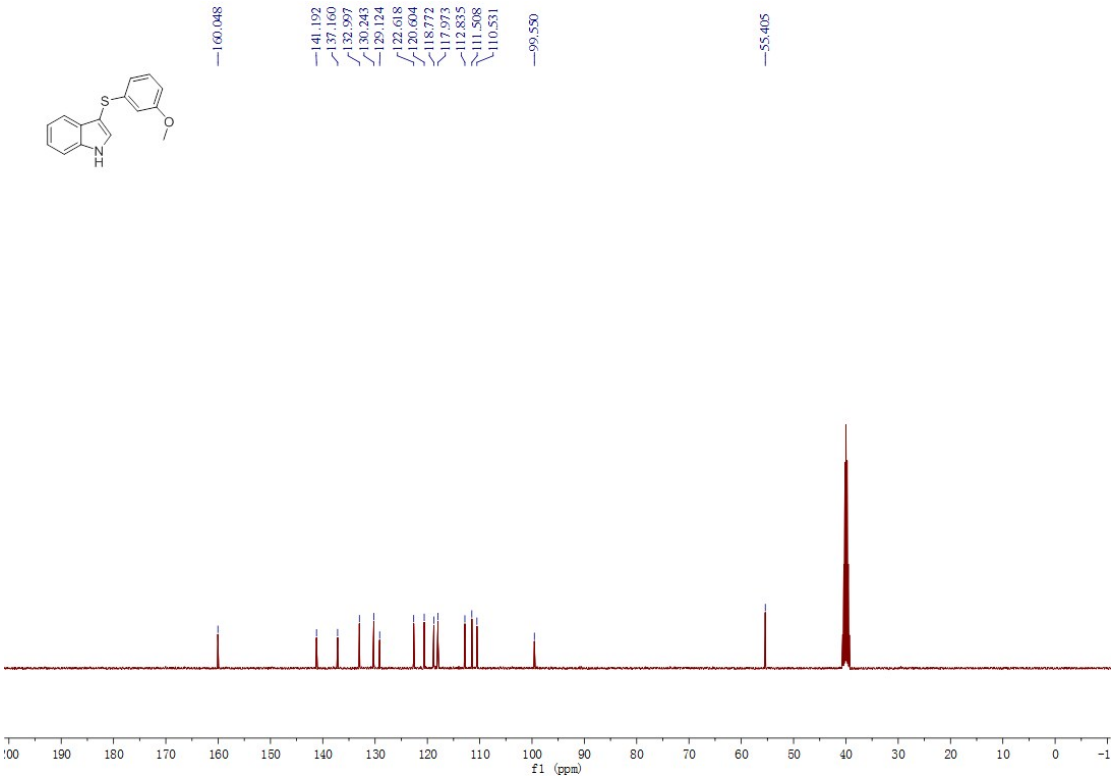


Figure S50. ^{13}C NMR spectrum for **3ai** in DMSO-d_6.

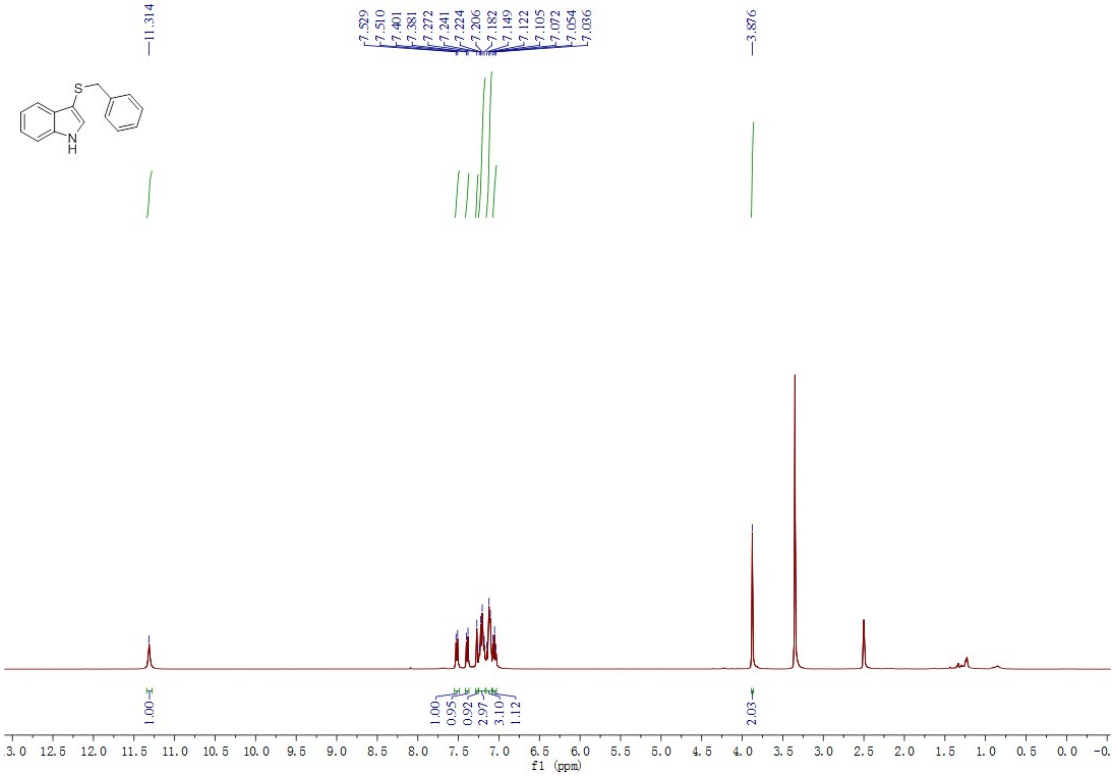


Figure S51. ^{1}H NMR spectrum for **3aj** in DMSO-d_6.

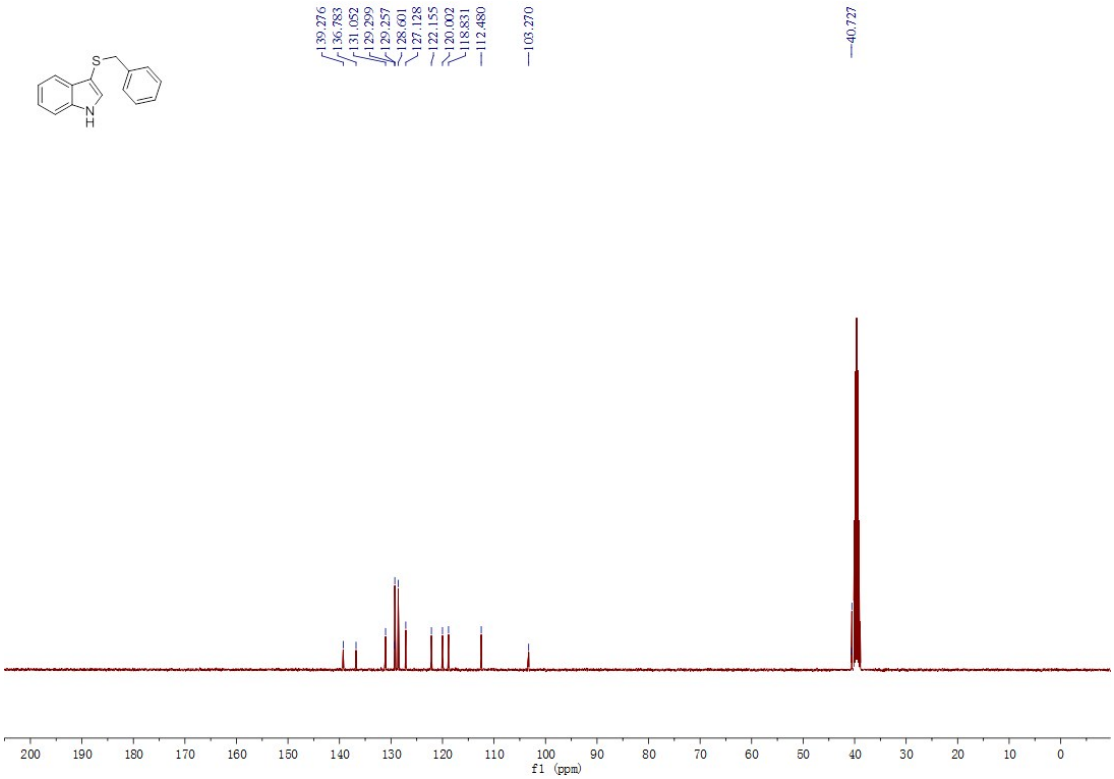


Figure S52. ^{13}C NMR spectrum for **3aj** in DMSO-d$_6$.

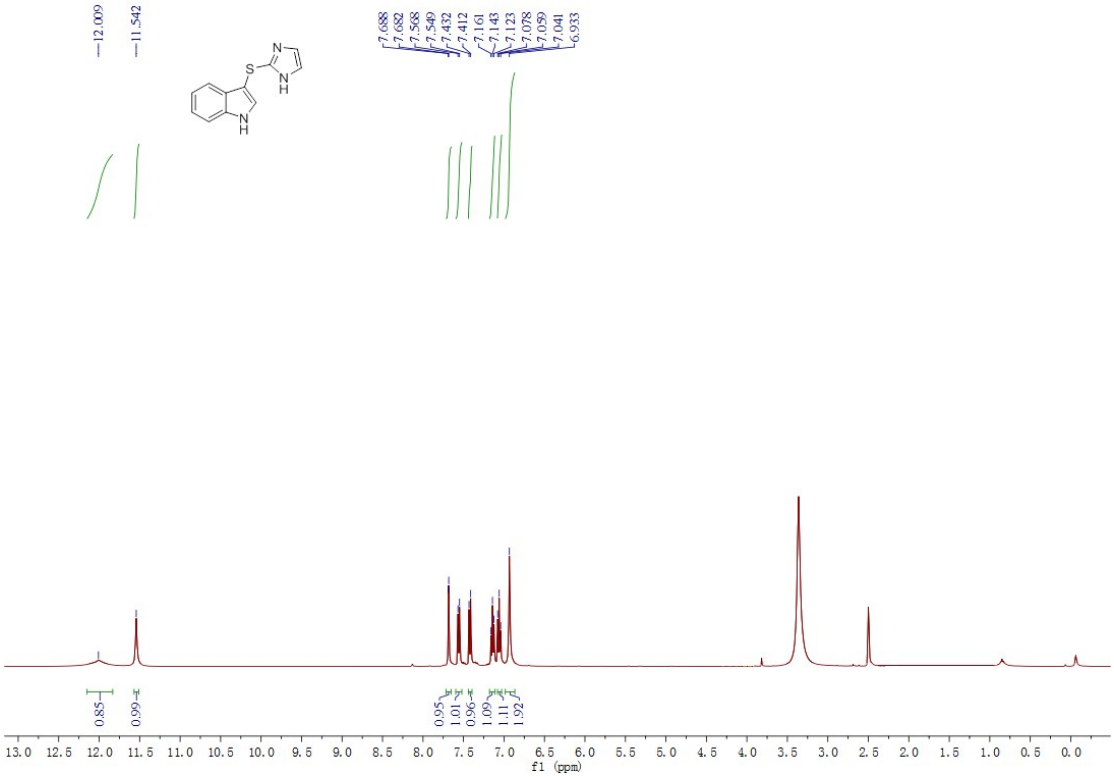


Figure S53. ^{1}H NMR spectrum for **3ak** in DMSO-d$_6$.

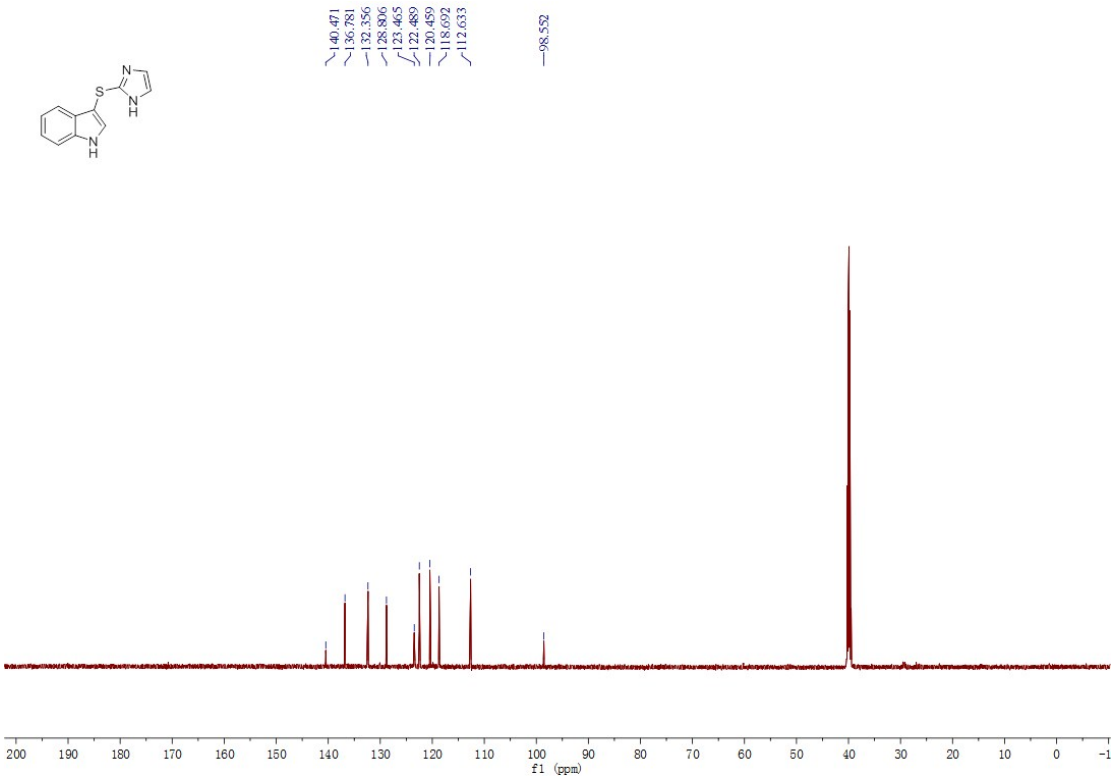


Figure S54. ^{13}C NMR spectrum for **3ak** in DMSO-d_6.

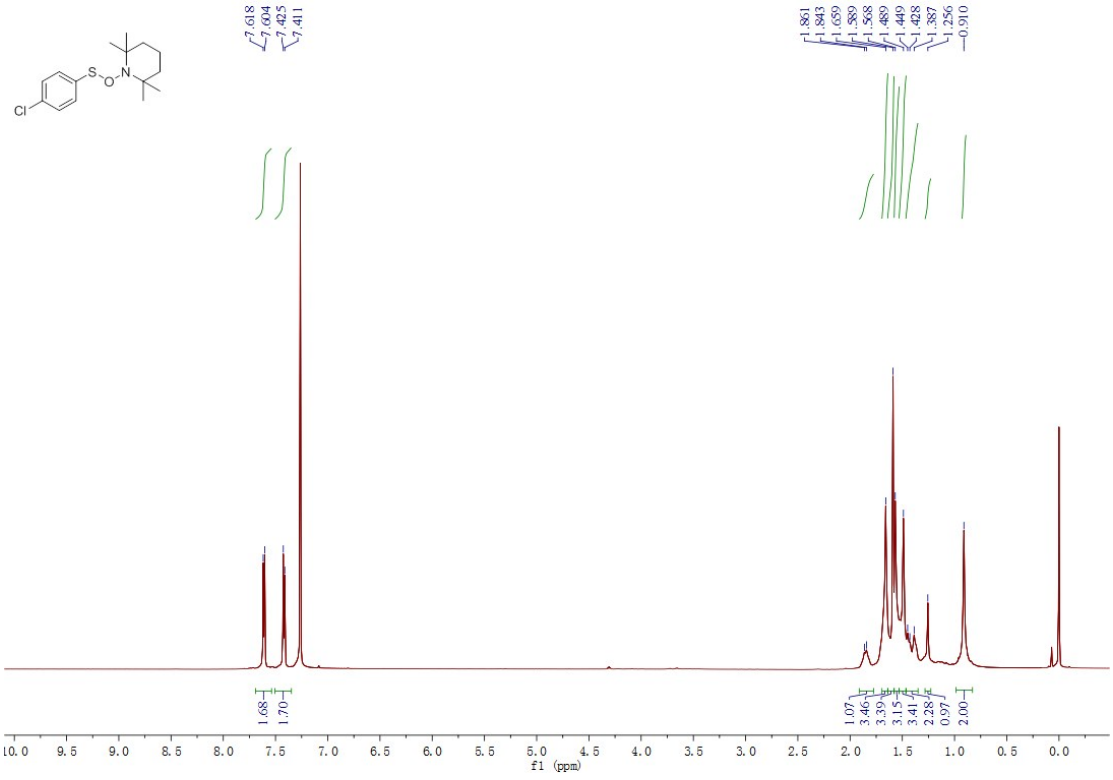


Figure S55. ^{1}HNMR of 2,2,6,6-tetramethyl-1-((4-chlorobenzenethiol)oxy) piperidine.

7. Reference

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2. J. Liu, H. Jeong, J. Liu, K. Lee, J.-Y. Park and Y.H. Ahn, *Carbon.* 2010, **48**, 2282.
3. D. Kaya and N. Alemdar, *J. APPL. POLYM. SCI.*, 2018, 46905.