Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Catalyst-free sulfenylation of indoles with sulfinic esters in ethanol

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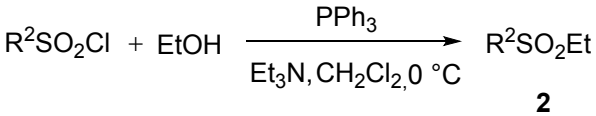
Table of Contents

General Information

All reactions were performed in dry solvents under an open air atmosphere and anhydrous conditions unless otherwise stated. All other reagents were used as received from commercial sources. Reactions were monitored through thin layer chromatography (TLC) on 0.30 mm SiliCycle silica gel plates and visualized under UV light. NMR spectra of the new products were recorded using Bruker AC-300 or Bruker AC-500 instruments, calibrated to $CDCl_3$ as the internal reference. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. The following abbreviations indicate the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High resolution mass spectrometry (HRMS) was obtained on a Thermo Scientific LTQ Orbitrap XL Instrument equipped with an ESI source.

Experimental Procedure

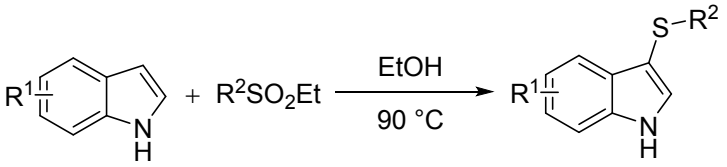
Preparation of sulfinate ester



2

To a solution of sulfonyl chloride (10 mmol) in CH_2Cl_2 (20 mL) was added ethanol (0.88 mL, 15 mmol), triethylamine (2.09 mL, 15 mmol) at 0 °C. Triphenylphosphine (2.6 g, 10 mmol) was dissolved in CH_2Cl_2 (10 mL) and it was slowly added dropwise using a dropping funnel. Reaction progress was monitored by TLC. After completion of the reaction, purified by flash column chromatography on silica gel, eluting with ethyl acetate/petroleum ether (1:10) to give the desired product **2**.

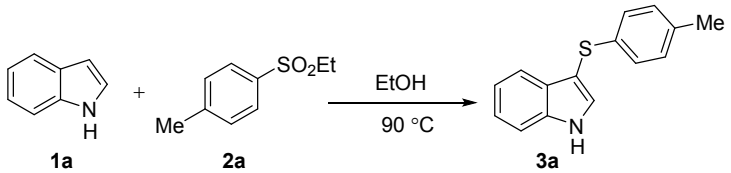
General procedure for catalyst-free sulfenylation of indoles with sulfinic esters



1 **2** **3 or 4**

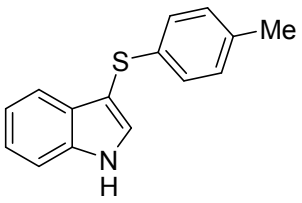
To a solution of sulfinate ester **2** (0.2 mmol) in ethanol (0.5 mL) was added indoles **1** (0.36 mmol). The resulting mixture was stirred at 90 °C under air for 12h, cooled to room temperature, and purified by silica gel column chromatography, eluting with ethyl acetate/petroleum ether (1:10) to give mainly desired product **3** or **4**.

Procedure for a gram-scale synthesis of indole thioether 3a



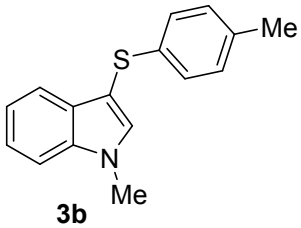
To a solution of sulfinate ester **2a** (0.9 mL, 6 mmol) in ethanol (10 mL) was added indole **1a** (1.26 g, 10.8 mmol). The resulting mixture was stirred at 90 °C under air for 12h, cooled to room temperature, and purified by silica gel column chromatography, eluting with ethyl acetate/petroleum ether (1:10) to give mainly desired product **3a**. (1.14 g, 79% yield)

Analytical Data for the Products



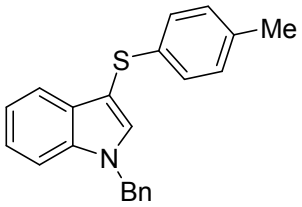
3a

3-(*p*-Tolylthio)-1*H*-indole (**3a**),[1] white solid (42.1 mg, 88%), m.p. 124-126 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (s, br, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.41-7.34 (m, 2H), 7.28-7.18 (m, 1H), 7.18-7.08 (m, 1H), 7.03 (d, J = 8.1 Hz, 2H), 6.95 (d, J = 8.1 Hz, 2H), 2.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.5, 135.5, 134.7, 130.6, 129.6, 129.1, 126.2, 123.0, 120.9, 119.7, 111.6, 103.3, 20.9.



3b

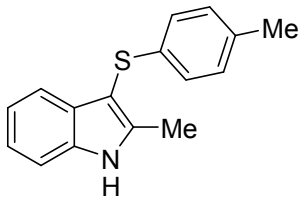
1-Methyl-3-(*p*-tolylthio)-1*H*-indole (**3b**),[3] white solid (41.8 mg, 82%), m.p. 86-88 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, J = 7.8 Hz, 1H), 7.36 (d, J = 8.1 Hz, 1H), 7.32-7.21 (m, 2H), 7.15 (t, J = 7.2 Hz, 1H), 7.01 (d, J = 8.1Hz, 2H), 6.95 (d, J = 8.1 Hz, 2H), 3.80 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.6 , 136.0, 134.8, 134.6, 129.9, 129.5, 126.3, 122.5, 120.4, 119.8, 109.7, 101.4, 33.1, 20.9.



3c

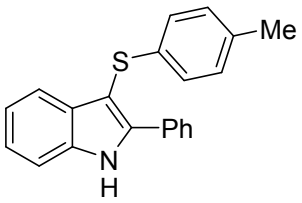
1-Benzyl-3-(*p*-tolylthio)-1*H*-indole (**3c**), light yellow oil (47.3 mg, 72%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, J = 7.5 Hz, 1H), 7.37 (s, 1H), 7.35-7.25 (m, 4H),

7.24-7.17 (m, 1H), 7.17-7.09 (m, 3H), 7.05-6.92 (m, 4H), 5.31 (s, 2H), 2.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2, 136.7, 135.8, 134.6, 134.3, 130.1, 129.5, 129.0, 128.0, 127.0, 126.2, 122.7, 120.7, 120.0, 110.3, 102.1, 50.5, 20.9. HRMS (ESI) calcd for $C_{22}H_{20}NS^+$ $(M+H)^+$ 330.4685, found 330.4683.



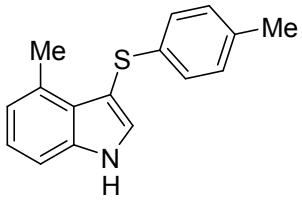
3d

2-Methyl-3-(*p*-tolylthio)-1*H*-indole (**3d**),[4] white solid (28.8 mg, 57%), m.p. 94-96 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (s, br, 1H), 7.54 (d, J = 7.5 Hz, 1H), 7.31-7.23 (m, 1H), 7.22-7.05 (m, 2H), 6.98-6.89 (m, 4H), 2.45 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.9, 135.7, 135.5, 134.3, 130.4, 129.5, 125.9, 122.1, 120.7, 119.0, 110.6, 100.1, 20.8, 12.1.



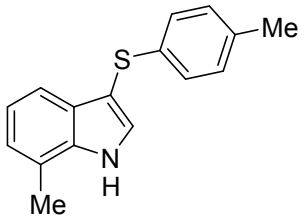
3e

2-Phenyl-3-(*p*-tolylthio)-1*H*-indole (**3e**),[3] colorless oil (42.2 mg, 67%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (s, br, 1H), 7.79-7.70 (m, 2H), 7.63 (d, J = 7.8 Hz, 1H), 7.45 -7.32 (m, 4H), 7.28-7.18 (m, 1H), 7.17-7.09 (m, 1H), 7.00 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 2.22 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.8, 135.9, 135.6, 134.4, 131.6, 131.3, 129.6, 128.7, 128.6, 128.1, 126.0, 123.3, 121.1, 120.1, 111.1, 100.3, 20.8.



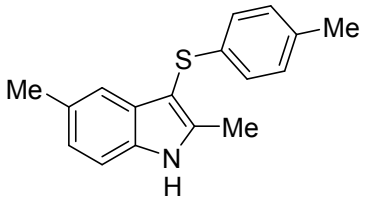
3f

4-Methyl-3-(*p*-tolylthio)-1*H*-indole (**3f**),[3] white solid (39.4 mg, 78%), m.p. 109-111 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (s, br, 1H), 7.40 (s, 1H), 7.25 (d, J = 7.8 Hz, 1H), 7.13 (t, J = 7.8 Hz, 1H), 7.05-6.91 (m, 4H), 6.88 (d, J = 7.2 Hz, 1H), 2.64 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.9, 137.1, 134.3, 132.2, 131.7, 129.6, 127.1, 125.5, 123.1, 122.5, 109.4, 103.0, 20.9, 18.7.



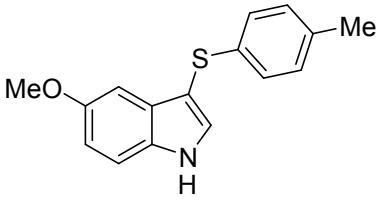
3g

7-Methyl-3-(p-tolylthio)-*1H*-indole (**3g**),[4] yellow solid (38.3 mg, 76%), m.p. 93-95 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (s, br, 1H), 7.45 (d, J = 6.0 Hz, 2H), 7.11 - 7.03 (m, 2H), 7.02 (d, J = 8.1 Hz, 2H), 6.96 (d, J = 8.1 Hz, 2H), 2.51 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.1, 135.6, 134.6, 130.1, 129.5, 128.8, 126.3, 123.6, 121.0, 120.7, 117.4, 104.1, 20.9, 16.4.



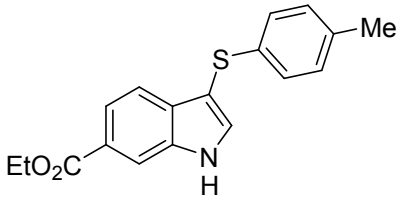
3h

2,5-Dimethyl-3-(*p*-tolylthio)-1*H*-indole (**3h**), white solid (37.5 mg, 70%), m.p. 130-132 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (s, br, 1H), 7.34 (s, 1H), 7.23-7.14 (m, 1H), 7.06-6.89 (m, 5H), 2.45 (s, 3H), 2.38 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 136.0, 134.2, 133.8, 130.7, 130.1, 129.5, 125.7, 123.6, 118.7, 110.4, 99.2, 21.5, 20.8, 12.1. HRMS (ESI) calcd for $C_{17}H_{18}NS^+$ $(M+H)^+$ 268.1154, found 268.1152.



3i

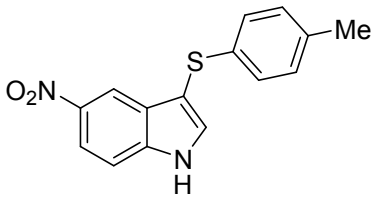
5-Methoxy-3-(*p*-tolylthio)-1*H*-indole (**3i**),[3] white solid (38.2 mg, 71%), m.p. 77-79 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (s, br, 1H), 7.38 (d, J = 2.4 Hz,1H), 7.26 (t, J = 8.7 Hz, 1H), 7.07-6.94 (m, 5H), 6.92-6.85 (m, 1H), 3.77 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1, 135.7, 134.6, 131.4, 131.2, 130.0, 129.5, 126.2, 113.5, 112.4, 102.9, 101.0, 55.9, 20.9.



3j

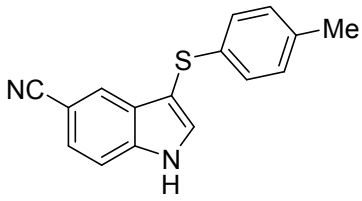
Eethyl 3-(*p*-tolylthio)-1*H*-indole-6-carboxylate (**3j**), white solid (33.1 mg, 53%), m.p. 130-132 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.77 (s, br, 1H), 8.22 (s, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.70-7.50 (m, 2H), 7.17-6.72 (m, 4H), 4.41 (q, J = 7.2 Hz, 2H), 2.25

(s, 3H), 1.41 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4, 135.9, 135.0, 134.9, 133.3, 132.8, 129.6, 126.6, 125.3, 121.8, 119.4, 113.9, 104.6, 60.9, 20.9, 14.4. HRMS (ESI) calcd for $C_{18}H_{18}NO_2S^+$ $(M+H)^+$ 312.1053, found 312.1054.



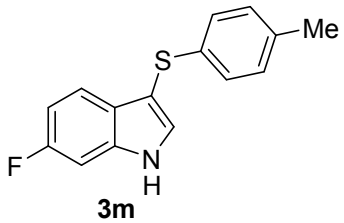
3k

5-Nitro-3-(*p*-tolylthio)-1*H*-indole (**3k**),[6] yellow solid (30.1 mg, 53%), m.p. 156-157 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.85 (s, br, 1H), 8.57 (d, J = 2.1 Hz, 1H), 8.16 (dd, J = 9.0, 2.1 Hz, 1H), 7.64 (d, J = 2.4 Hz, 1H), 7.49 (d, J = 9.0 Hz, 1H), 7.10-6.97 (m, 4H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.8, 139.4, 135.6, 134.0, 133.2, 129.8, 128.8, 127.1, 118.7, 116.95, 111.8, 107.5, 20.9.



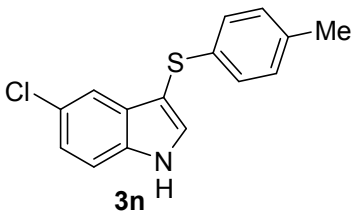
3l

3-(*p*-tolylthio)-1*H*-indole-5-carbonitrile (**3l**),[7] white solid, (20.1 mg, 38%), m.p. 202-203 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69 (s, br, 1H), 7.94 (s, 1H), 7.60 (d, J = 2.4 Hz, 1H), 7.49 (s, 2H), 7.09-6.94 (m, 4H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 139.1, 135.3, 134.9, 130.1, 129.0, 126.9, 125.4, 124.1, 120.7, 114.3, 102.8, 102.5, 20.9.



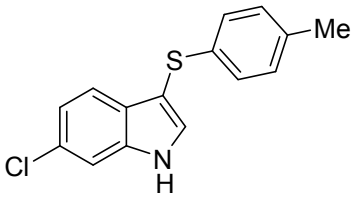
3m

6-Fluoro-3-(*p*-tolylthio)-1*H*-indole (**3m**),[4] white solid (39.0 mg, 76%), m.p. 124-126 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (s, br, 1H), 7.59-7.50 (m, 1H), 7.39 (d, J = 2.7 Hz, 1H), 7.09-7.04 (m, 1H), 7.04-6.95 (m, 4H), 6.93-6.84 (m, 1H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.5 (d, J = 239.4 Hz), 136.4 (d, J = 12.9 Hz), 135.1, 135.0, 130.5 (d, J = 3.3 Hz), 129.5, 126.6, 125.6, 120.7 (d, J = 10.2 Hz), 109.7 (d, J = 24.6 Hz), 104.4, 97.9 (d, J = 26.4 Hz), 20.8.



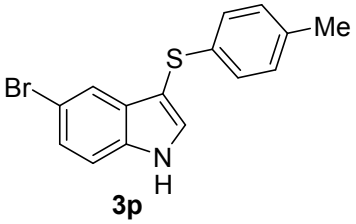
3n

5-Chloro-3-(*p*-tolylthio)-1*H*-indole (**3n**),[4] white solid (41.9mg, 77%), m.p. 133-135 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (s, br, 1H), 7.58 (s, 1H), 7.46 (s, 1H), 7.32 (d, J = 8.7 Hz, 1H), 7.21 (t, J = 9.9 Hz, 1H), 7.04-6.95 (m, 4H), 2.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.0, 134.9, 131.7, 130.4, 129.6, 126.9, 126.5, 123.5, 119.2, 112.6, 103.7, 20.9.



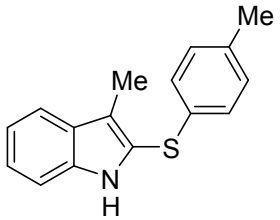
3o

6-Chloro-3-(*p*-tolylthio)-1*H*-indole (**3o**),[3] colorless oil (32.0 mg, 59%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (s, br, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.43 (s, 1H), 7.39 (s, 1H), 7.10 (d, J = 8.4 Hz, 1H), 7.03-6.95 (m, 4H), 2.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.8, 135.0, 130.9, 129.6, 129.0, 127.7, 126.5, 121.7, 120.7, 111.6, 104.3, 20.9.



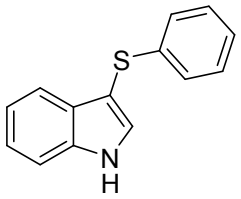
3p

5-Bromo-3-(*p*-tolylthio)-1*H*-indole (**3p**),[4] white solid (38.1 mg, 60%), m.p. 144-146 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (s, br, 1H), 7.75 (s, 1H), 7.47 (s, 1H), 7.37-7.31 (m, 1H), 7.30-7.23 (m, 1H), 7.14-6.79 (m, 4H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.1, 135.0, 131.6, 131.0, 129.7, 126.4, 126.1, 122.3, 114.4, 113.1, 103.5, 20.9;



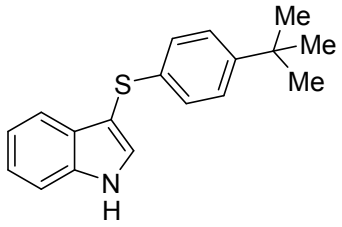
3q

3-Methyl-2-(*p*-tolylthio)-1*H*-indole (**3q**),[3] colorless oil (29 mg, 57%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (s, br, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.30-7.18 (m, 2H), 7.17-7.07 (m, 1H), 7.03-6.90 (m, 4H), 2.39 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.9, 135.9, 133.3, 129.9, 128.6, 127.2, 123.4, 122.4, 119.6, 119.4, 119.3, 110.8, 20.9, 9.4.



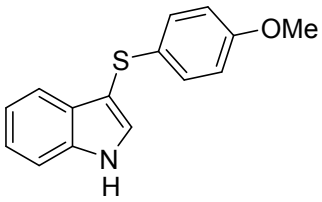
4a

3-(Phenylthio)-1*H*-indole (**4a**),[1] white solid (32.6 mg, 72%), m.p. 151-152 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 (s, br, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.48-7.40 (m, 2H), 7.30-7.23 (m, 1H), 7.19-7.04 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.2, 136.5, 130.7, 129.1, 128.7, 125.9, 124.8, 123.1, 120.9, 119.7, 111.6, 103.0.



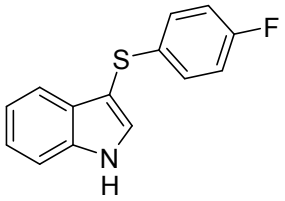
4b

3-(4-tert-butylphenylthio)-1*H*-indole (**4b**),[2] white solid (30.0 mg, 53%), m.p. 185-186 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (s, br, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.44-7.36 (m, 2H), 7.28-7.21 (m, 1H), 7.20-7.12 (m, 3H), 7.05 (d, J = 8.4 Hz, 2H), 1.24 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.0, 136.4, 135.8, 130.7, 129.3, 125.8, 125.7, 123.0, 120.9, 119.7, 111.6, 103.2, 34.4, 31.4.



4c

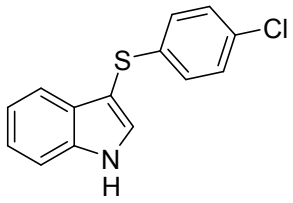
3-((4-Methoxyphenyl)thio)-1*H*-indole (**4c**),[1] yellow solid (37.6 mg, 74%), m.p. 111-112 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (s, br, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.44-7.36 (m, 2H), 7.24 (t, J = 7.5 Hz, 1H), 7.18-7.09 (m, 3H), 6.73 (d, J = 7.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.9, 136.5, 130.0, 129.6, 129.1, 128.7, 123.0, 120.8, 119.7, 114.5, 111.5, 104.8, 55.4.



4d

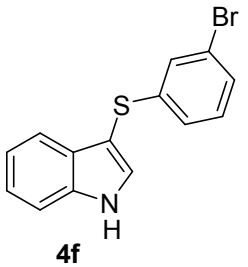
3-((4-Fluorophenyl)thio)-1*H*-indole (**4d**),[1] white solid (31.0 mg, 64%), m.p. 132-134 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (s, br, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.45 (d, J = 2.6 Hz, 1H), 7.41 (d, J = 8.1 Hz, 1H), 7.30-7.21 (m, 1H), 7.20-7.12 (m, 1H), 7.12-7.04 (m, 2H), 6.90-6.80 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9 (d, J =

243.9 Hz), 136.5 , 134.0 (d, J = 3.0 Hz), 130.6, 128.9, 127.8 (d, J = 7.8 Hz), 123.2, 121.0, 119.5, 115.8 (d, J = 22.2 Hz), 111.7, 103.3.



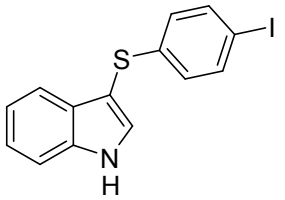
4e

3-((4-Chlorophenyl)thio)-1*H*-indole (**4e**),[1] white solid (40.3 mg, 78%), m.p. 130-131^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (s, br, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.48 (d, J = 2.6 Hz, 1H), 7.44 (d, J = 8.1 Hz, 1H), 7.31-7.24 (m, 1H), 7.17 (t, J = 7.5 Hz, 1H), 7.11 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9, 136.6, 130.7, 130.6, 128.9, 128.8, 127.2, 123.2, 121.1, 119.5, 111.7, 102.6.



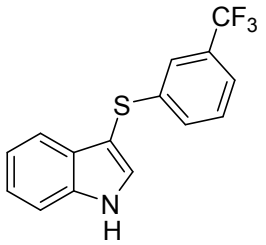
4f

3-((3-Bromophenyl)thio)-1*H*-indole (**4f**), white solid (30.3 mg, 50%), m.p. 93-95 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (s, br, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.48 (d, J = 2.6 Hz, 1H), 7.44 (d, J = 8.1 Hz, 1H), 7.29 (d, J = 7.2 Hz, 1H), 7.25 (d, J = 3.0 Hz, 1H), 7.19-7.14 (m, 2H), 6.99 (d, J = 4.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 136.6, 131.0, 130.0, 128.9, 128.3, 127.9, 124.4, 123.3, 122.9, 121.2, 119.5, 111.7, 101.9. HRMS (ESI) calcd for $C_{14}H_{11}BrNS^{+}$ $(M+H)^{+}$ 303.9790, found 303.9797.



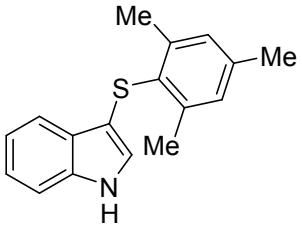
4g

3-((4-Iodophenyl)thio)-1*H*-indole (**4g**),[1] white solid (37.1 mg, 53%), m.p. 135-137 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (s, br, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.49-7.40 (m, 4H), 7.35-7.22 (m, 1H), 7.21-7.11 (m, 1H), 6.80 (d, J = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6, 137.5, 136.6, 130.8, 128.8, 127.7, 123.3, 121.1, 119.5, 111.7, 102.2, 89.0.



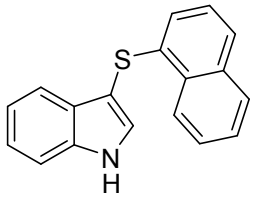
4h

3-((3-trifluoromethyl)phenyl)thio)-1H-indole (**4h**),[5] white solid (34.2mg, 58%), m.p. 130-132 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (s, br, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 2.4 Hz, 1H), 7.45 (d, J = 8.1Hz, 1H), 7.39 (s, 1H), 7.32-7.25 (m, 2H), 7.24-7.13 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.0, 136.6, 131.0, 129.1, 128.9, 125.8, 123.3, 122.4 (q, J = 3.9 Hz), 121.5 (q, J = 3.9 Hz), 121.2, 119.4, 114.6, 111.8, 101.6.



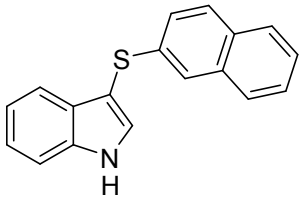
4i

3-(Mesitylthio)-1*H*-indole (**4i**),[1] white solid (39.2 mg, 73%), m.p. 125-127 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (s, br, 1H), 7.50 (d, J = 7.8 Hz, 1H), 7.32 (d, J = 8.1 Hz, 1H), 7.23-7.12 (m, 1H), 7.11-6.92 (m, 2H), 6.90 (s, 2H), 2.52 (s, 6H), 2.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.3, 137.8, 136.2, 130.1, 129.2, 128.2, 125.5, 122.5, 120.1, 119.5, 111.3, 108.2, 22.1, 21.0.



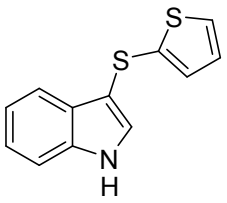
4j

3-(Naphthalen-1-ylthio)-1*H*-indole (**4j**),[2] white solid (42.3 mg, 77%), m.p. 166-168 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (d, J = 8.4 Hz, 1H), 8.41 (s, br, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.60-7.50 (m, 5H), 7.45 (d, J = 8.1 Hz, 1H), 7.32-7.22 (m, 1H), 7.19-7.10 (m, 2H), 6.95 (d, J = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.7, 136.2, 133.8, 130.9, 130.8, 129.1, 128.5, 126.1, 126.0, 125.7, 125.3, 124.1, 123.6, 123.1, 121.0, 119.8, 111.6, 102.5.



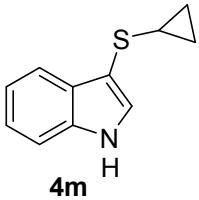
4k

3-(Naphthalen-2-ylthio)-1*H*-indole (**4k**),[1] white solid (46.2 mg, 84%), m.p. 141-143 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (s, br, 1H), 7.74-7.67 (m, 1H), 7.65-7.59 (m, 2H), 7.58-7.51 (m, 2H), 7.50-7.42 (m, 2H), 7.40-7.31 (m, 2H), 7.30-7.22(m, 2H), 7.17-7.10 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.7, 136.6, 133.8, 131.4, 130.6, 129.2, 128.2, 127.7, 126.9, 126.3, 125.0, 124.8, 123.7, 123.1, 121.0, 119.7, 111.6, 103.1.



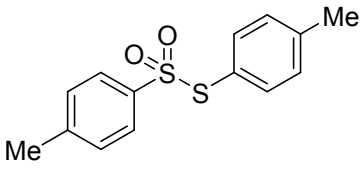
4l

3-(Thiophen-2-ylthio)-1*H*-indole (**4l**),[1] white solid (20.0 mg, 43%), m.p. 106-107 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (s, br, 1H), 7.79 (d, J = 7.5 Hz, 1H), 7.43 (s, 1H), 7.36 (d, J = 7.5 Hz, 1H), 7.29-7.05 (m, 4H), 6.89-6.80 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0, 136.2, 129.8, 129.2, 128.6, 127.3, 127.2, 123.0, 120.9, 119.5, 111.5, 106.8.



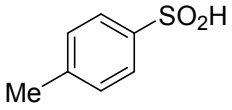
4m

3-(1-cyclopropylthio)-1*H*-indole (**4m**), yellow oil (20.5 mg, 54%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (s, br, 1H), 7.84-7.55 (m, 1H), 7.32-7.25 (m, 1H), 7.23-7.17 (m, 1H), 7.16-7.07 (m, 2H), 2.25-1.94 (m, 1H), 0.75-0.66 (m, 2H), 0.62-0.54 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.3, 129.3, 128.2, 122.7, 120.4, 119.6, 111.4, 107.4, 16.7, 8.6. HRMS (ESI) calcd for $C_{11}H_{12}NS^{+}$ $(M+H)^{+}$ 190.0685, found 190.0689.



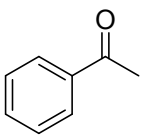
5

S-(*p*-tolyl) 4-Methyl-benzenesulfonothioate (**5**),[2] white solid (20.0 mg, 72%), m.p. 91-92 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, J = 8.4 Hz, 1H), 7.25-7.17 (m, 4H), 7.13 (d, J = 8.1 Hz, 2H), 2.41 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.7, 142.1, 140.4, 136.5, 130.2, 129.4, 127.6, 124.5, 21.7, 21.5.



6

4-Methyl-benzenesulfinic acid (**6**),[8] white solid (6.2 mg, 20%), m.p. 85-86 ^{o}C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.55 (s, 1H), 7.56 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) 146.3, 141.8, 129.9, 125.0, 21.4.



7

Acetophenone (**7**),[9] colorless oil (11.5 mg, 48%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98- 7.90 (m, 2H), 7.59-7.50 (m, 1H), 7.48-7.40 (m, 2H), 2.59 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.2, 137.1, 133.1, 128.6, 128.3, 26.6.

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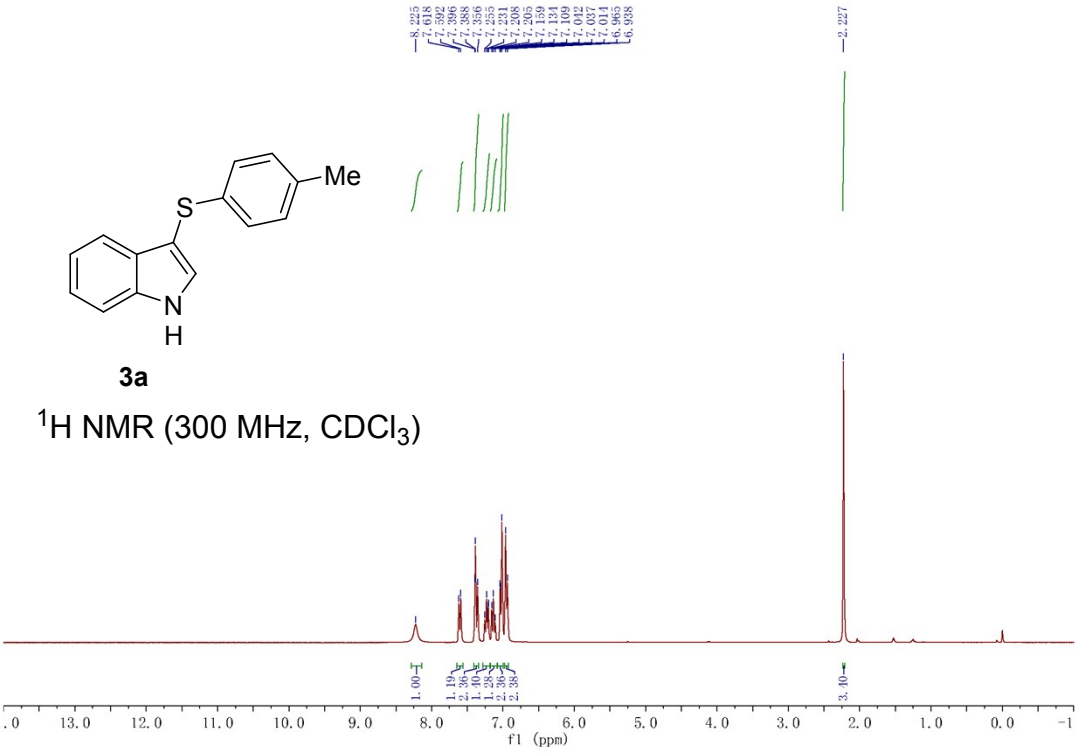
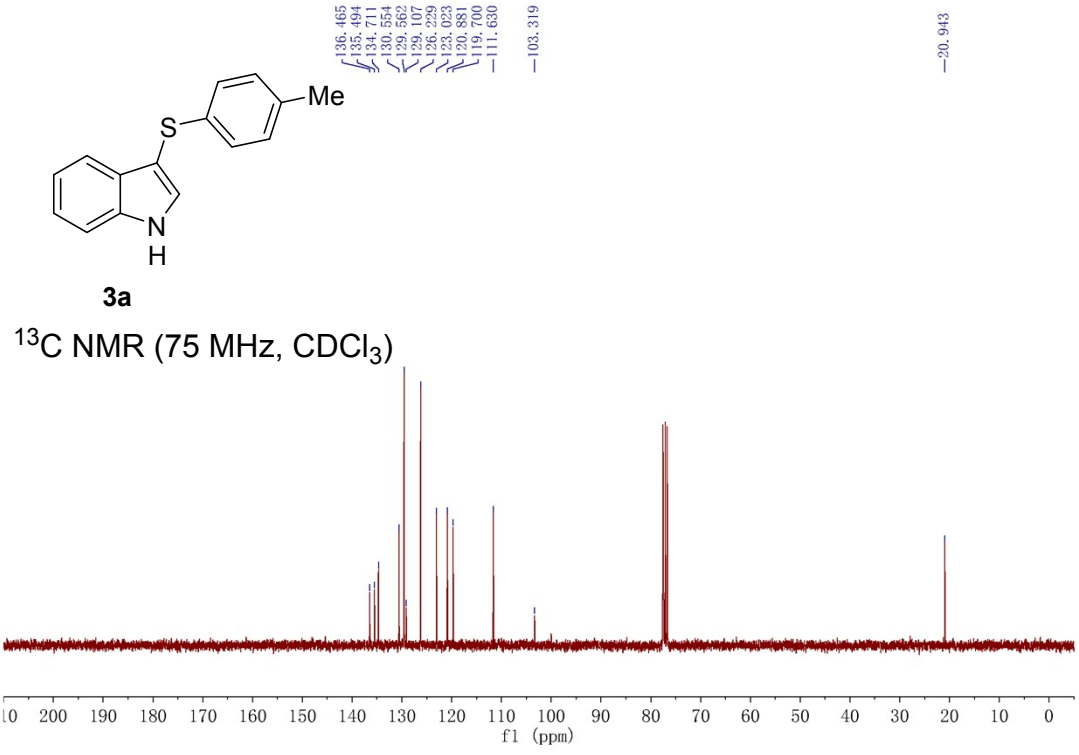
Copies of ^{1}H NMR and ^{13}C NMR spectra



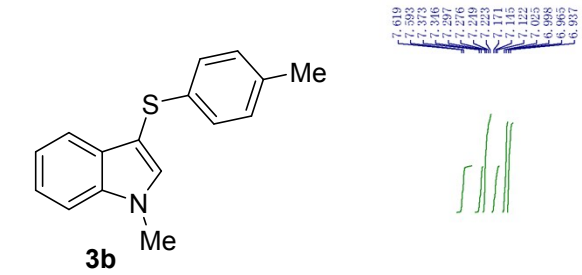
3a

^{1}H NMR (300 MHz, $CDCl_3$)



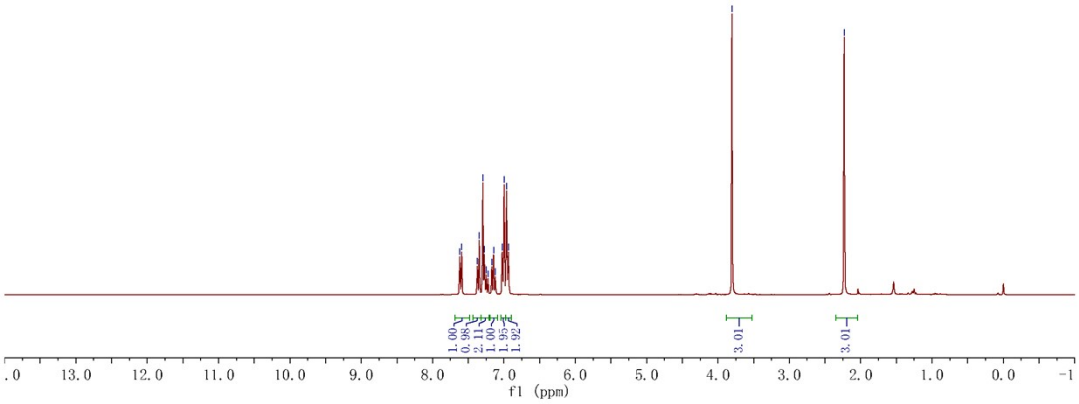
3a

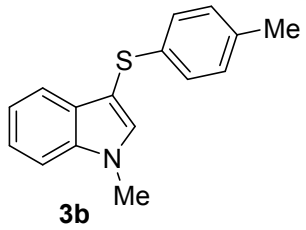
^{13}C NMR (75 MHz, $CDCl_3$)



3b

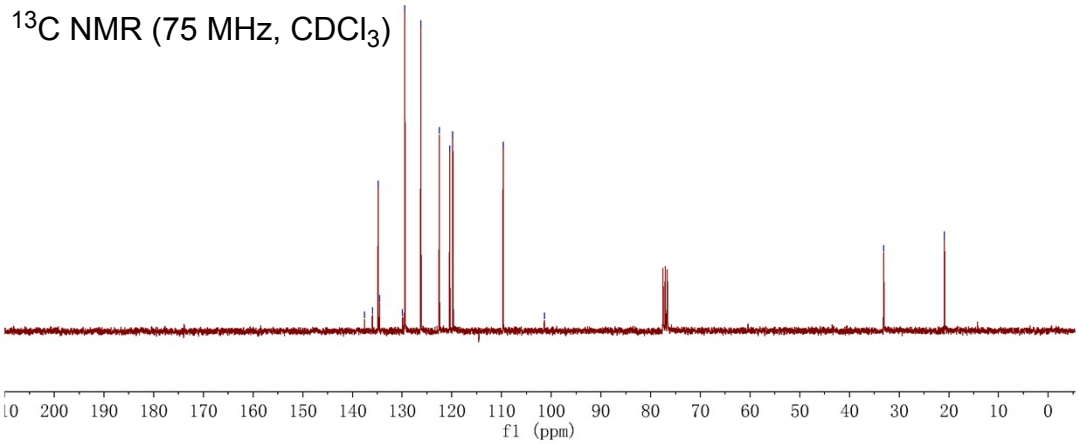
^{1}H NMR (300 MHz, $CDCl_3$)

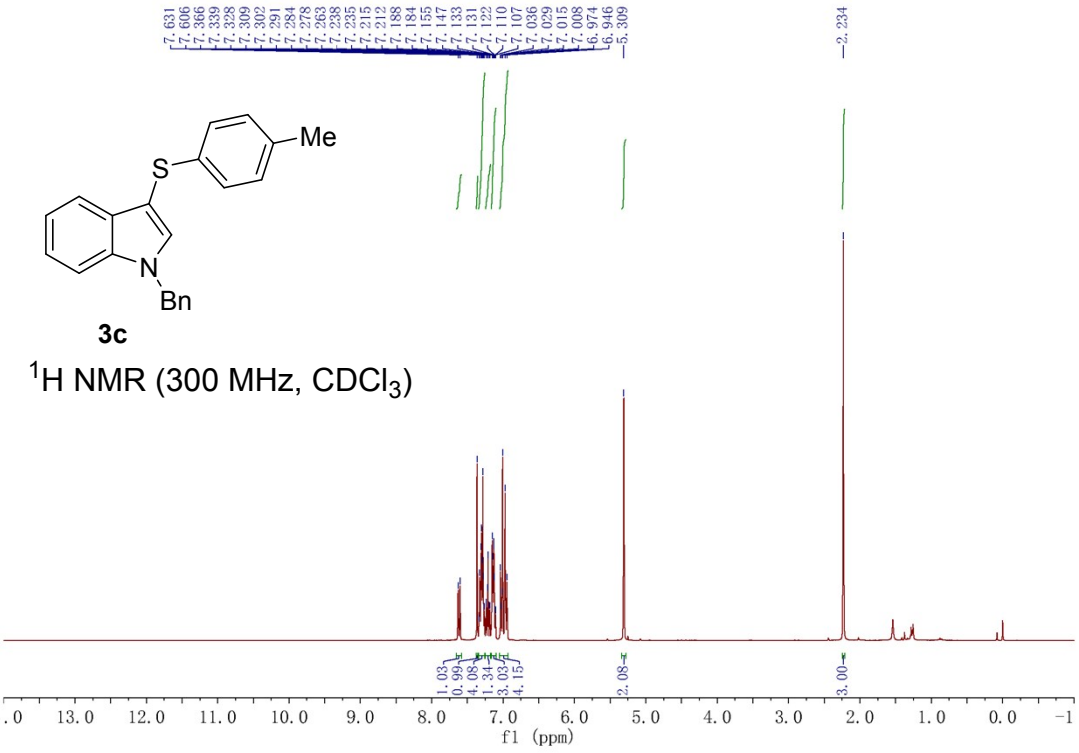




3b

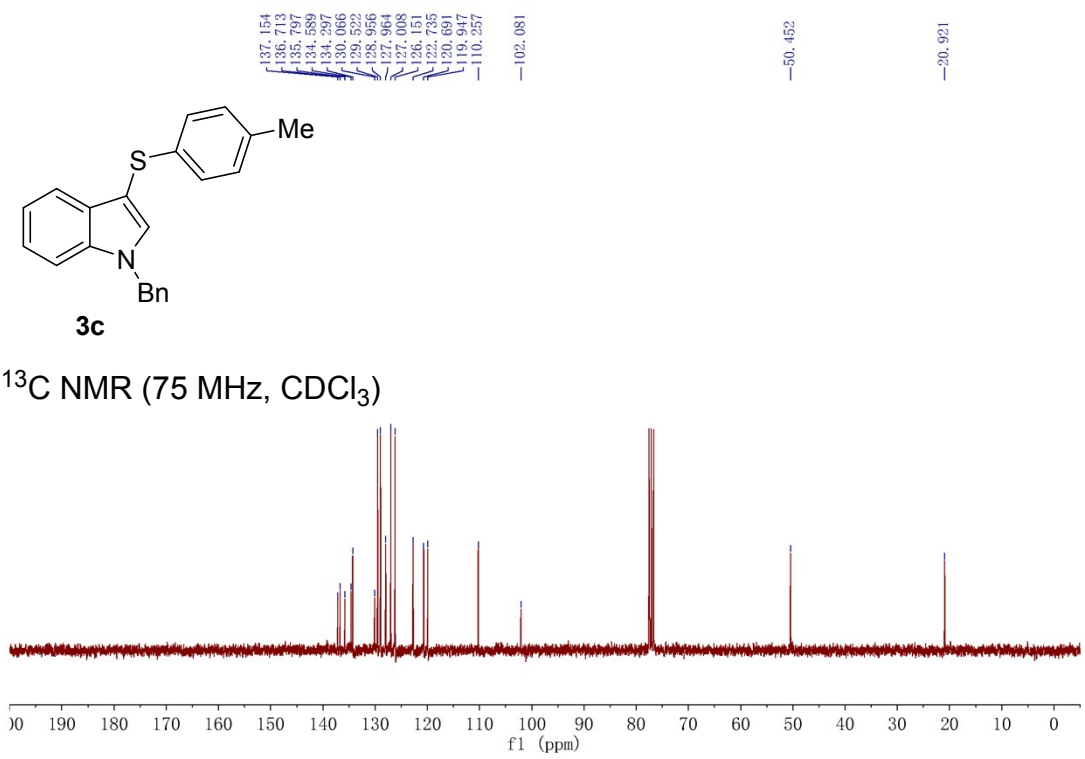
^{13}C NMR (75 MHz, $CDCl_3$)





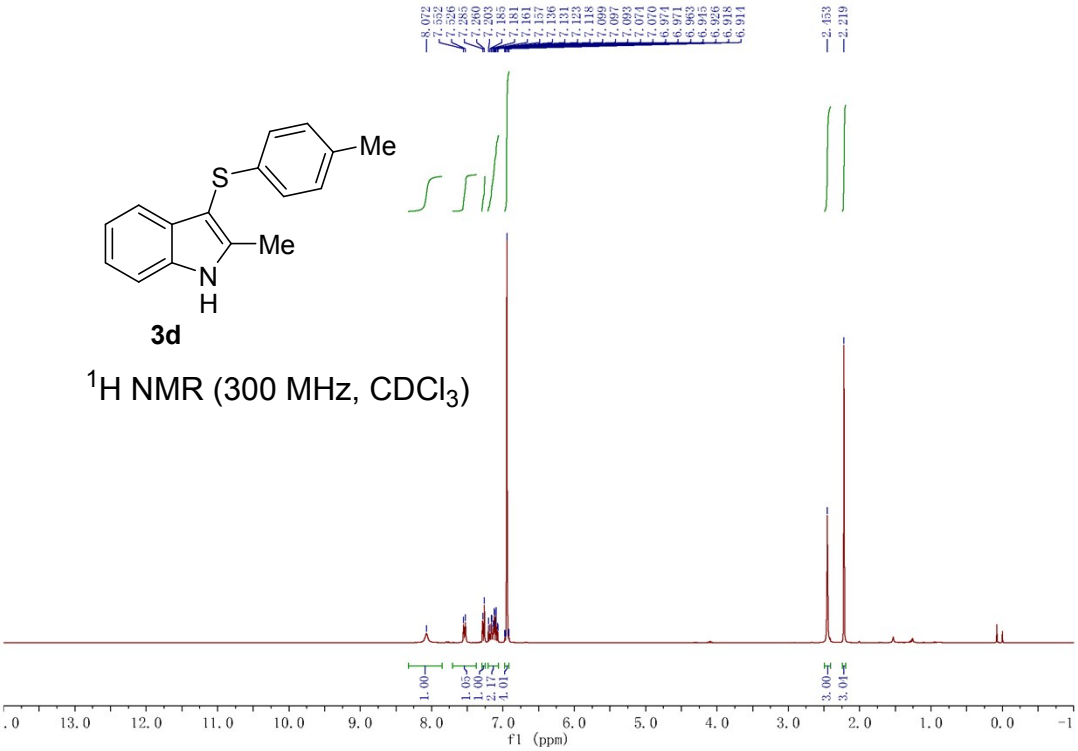
3c

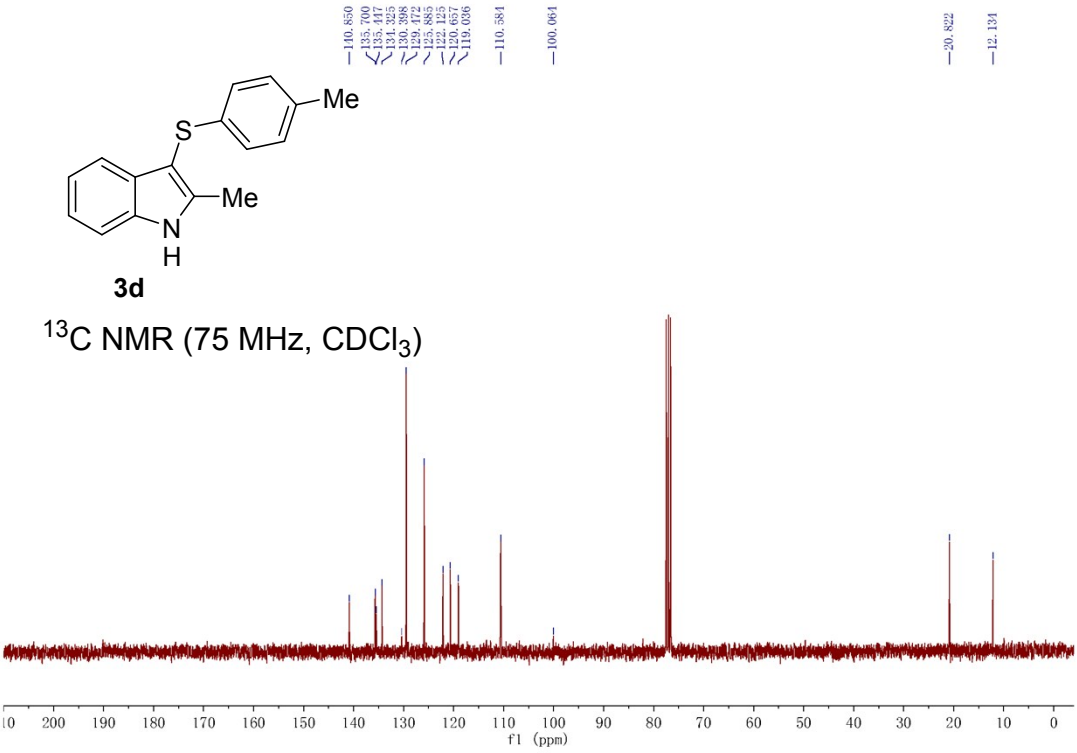
^{1}H NMR (300 MHz, $CDCl_3$)

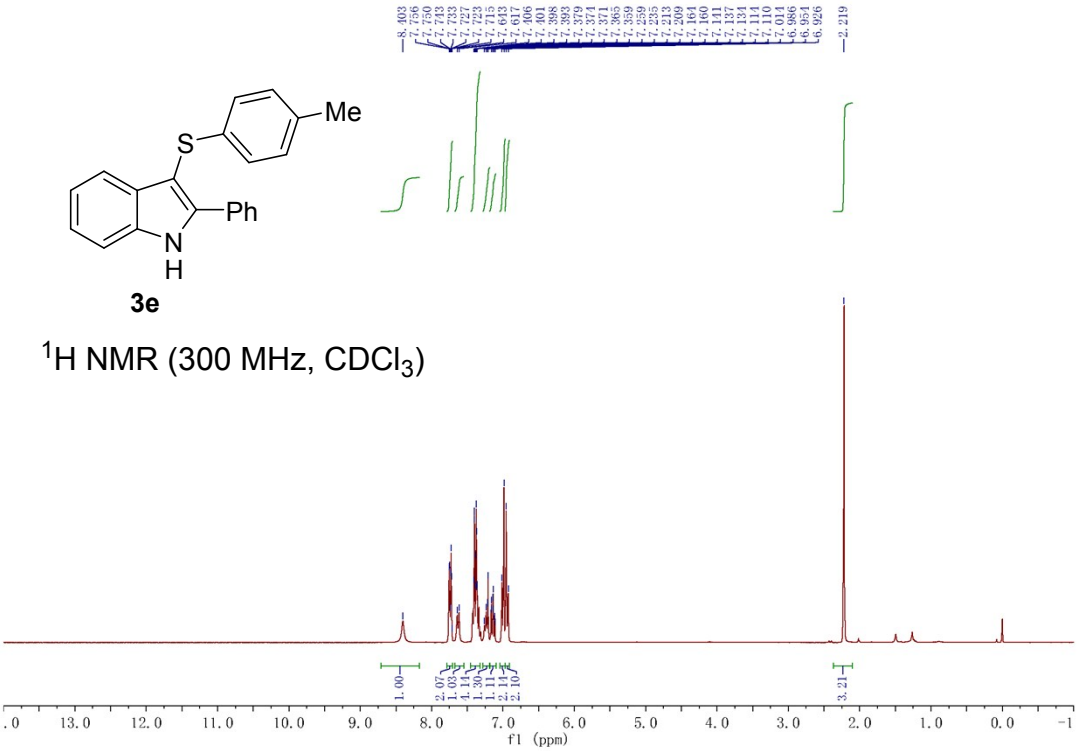


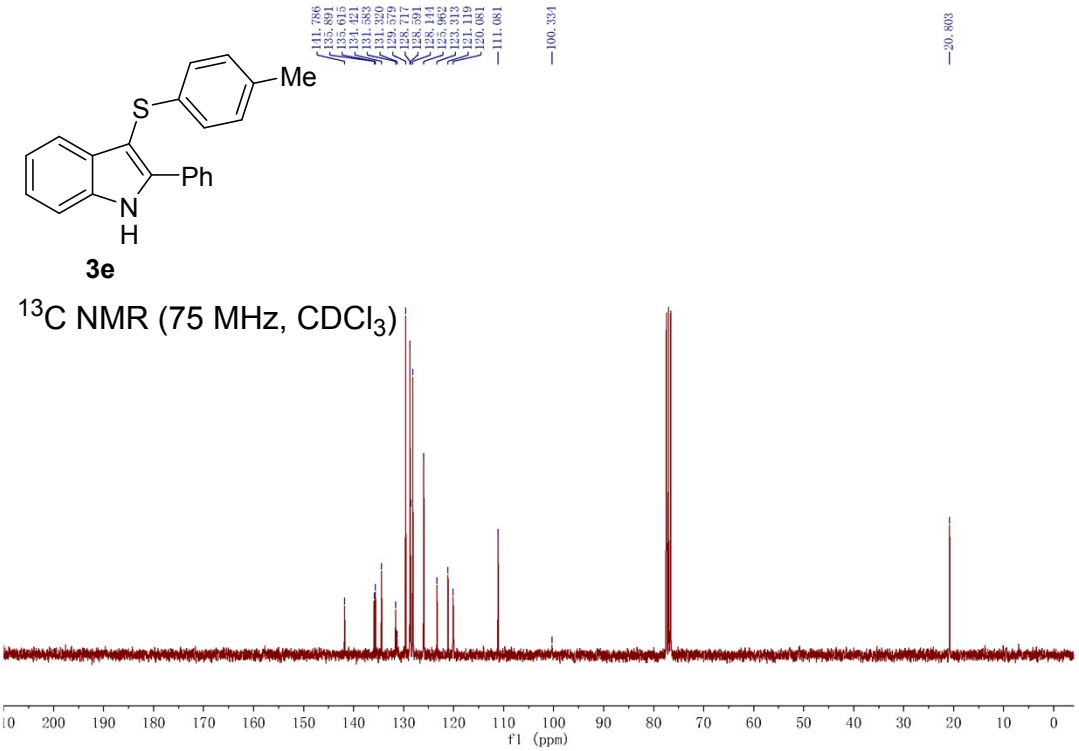
3c

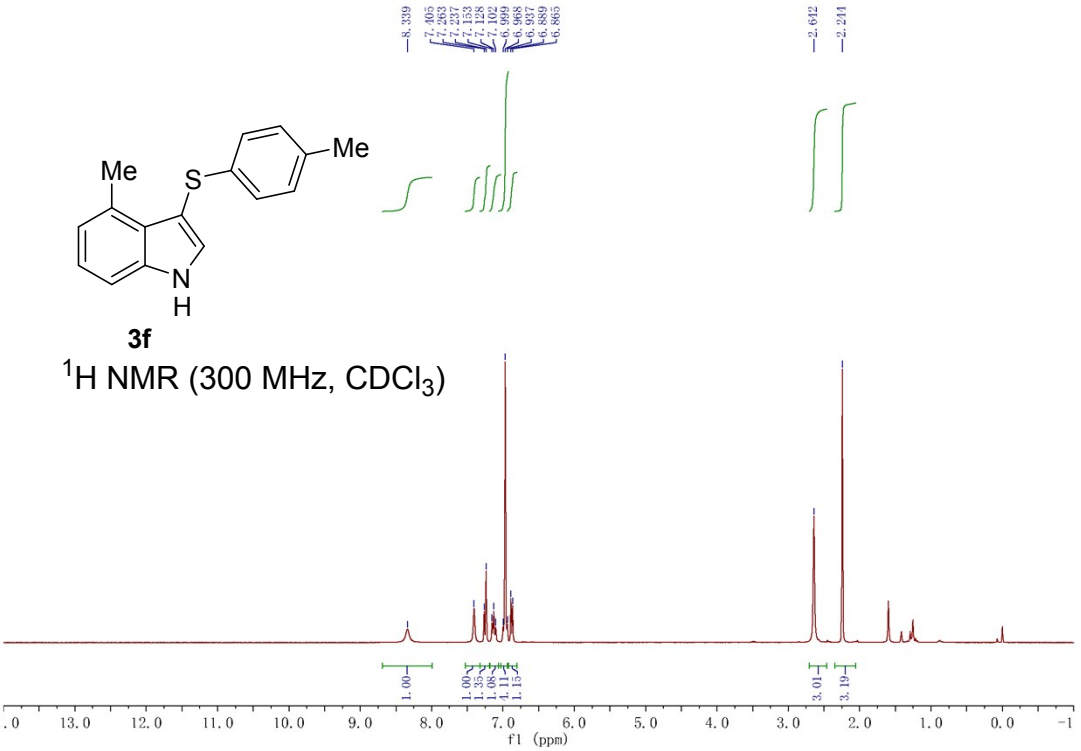
^{13}C NMR (75 MHz, $CDCl_3$)


Me
S
Me
N
H
3d
1H NMR (300 MHz, CDCl3)
f1 (ppm)


Me
S
Me
N
H
3d
13C NMR (75 MHz, CDCl3)
f1 (ppm)

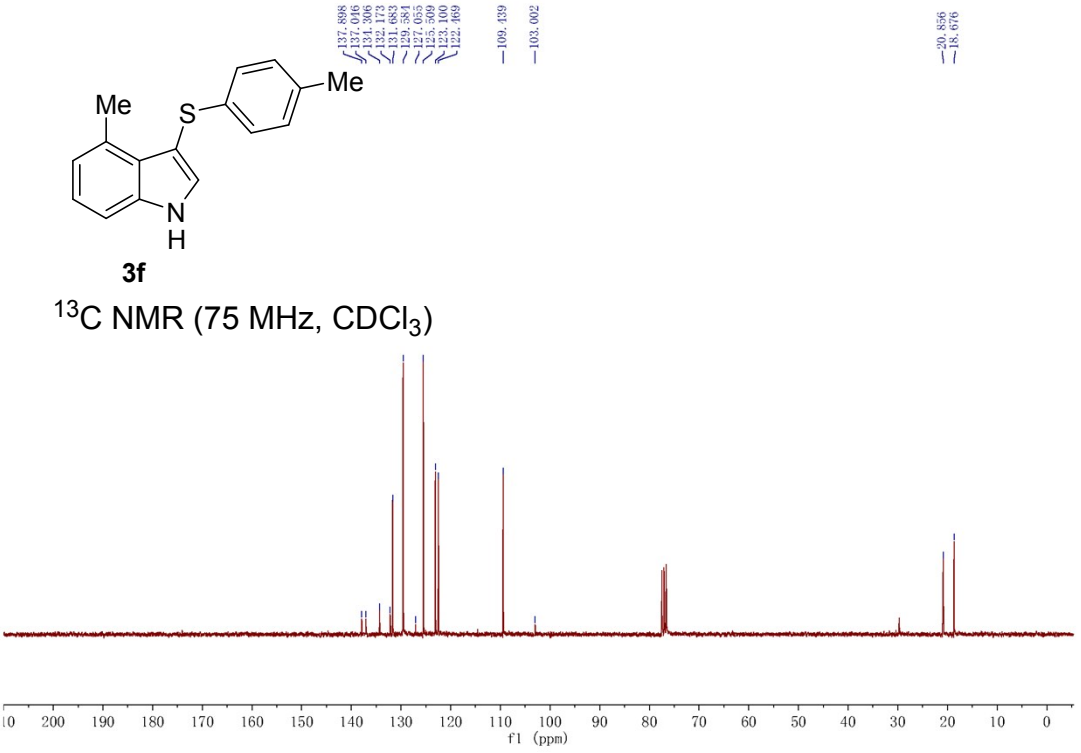

Me
S
Ph
N
H
3e
1H NMR (300 MHz, CDCl3)
f1 (ppm)


Me
S
Ph
N
H
3e
13C NMR (75 MHz, CDCl3)
f1 (ppm)



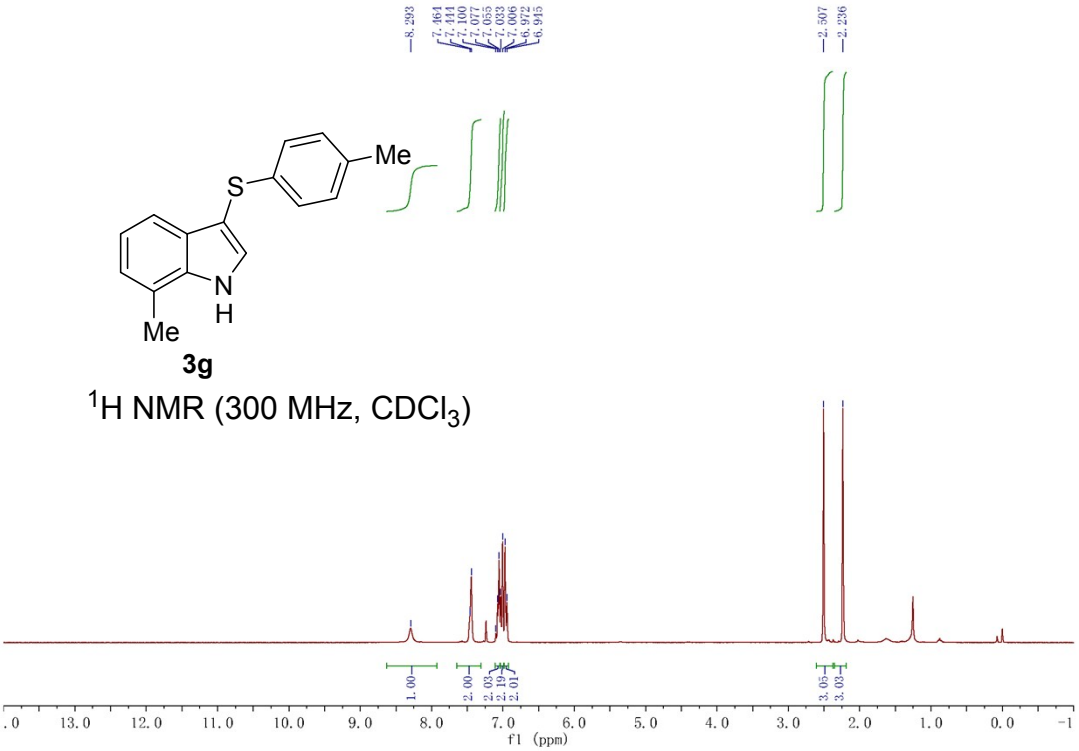
3f

^{1}H NMR (300 MHz, $CDCl_3$)



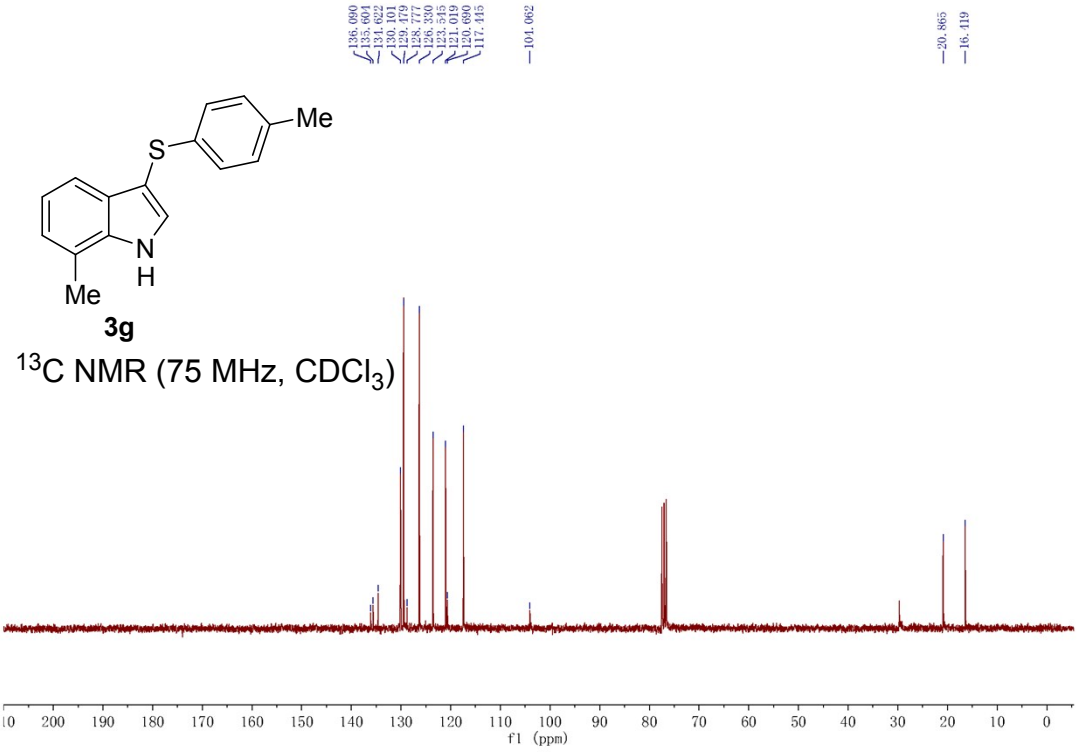
3f

^{13}C NMR (75 MHz, $CDCl_3$)



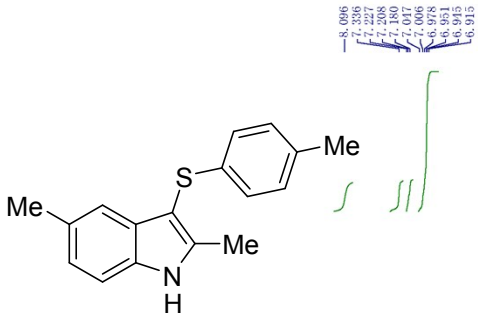
3g

^{1}H NMR (300 MHz, $CDCl_3$)



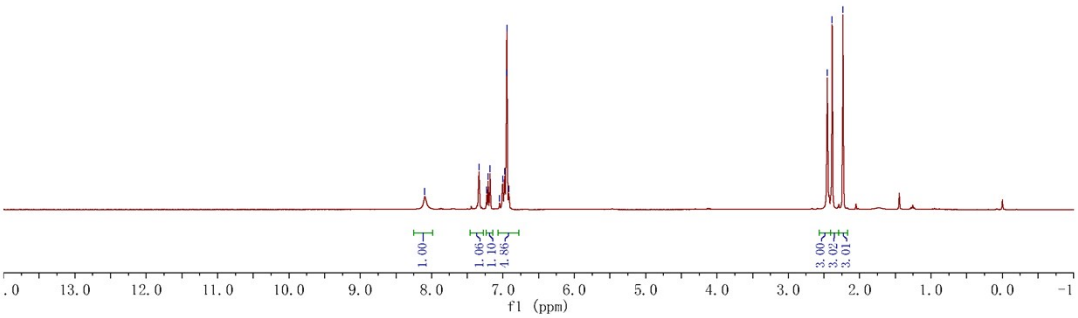
3g

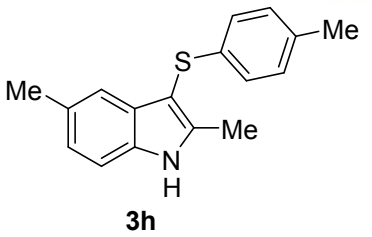
^{13}C NMR (75 MHz, $CDCl_3$)



3h

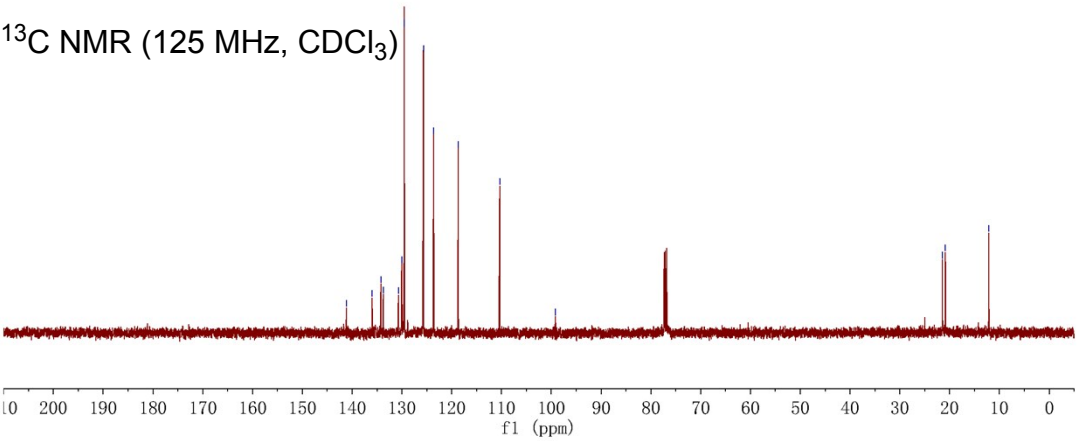
^{1}H NMR (300 MHz, $CDCl_3$)

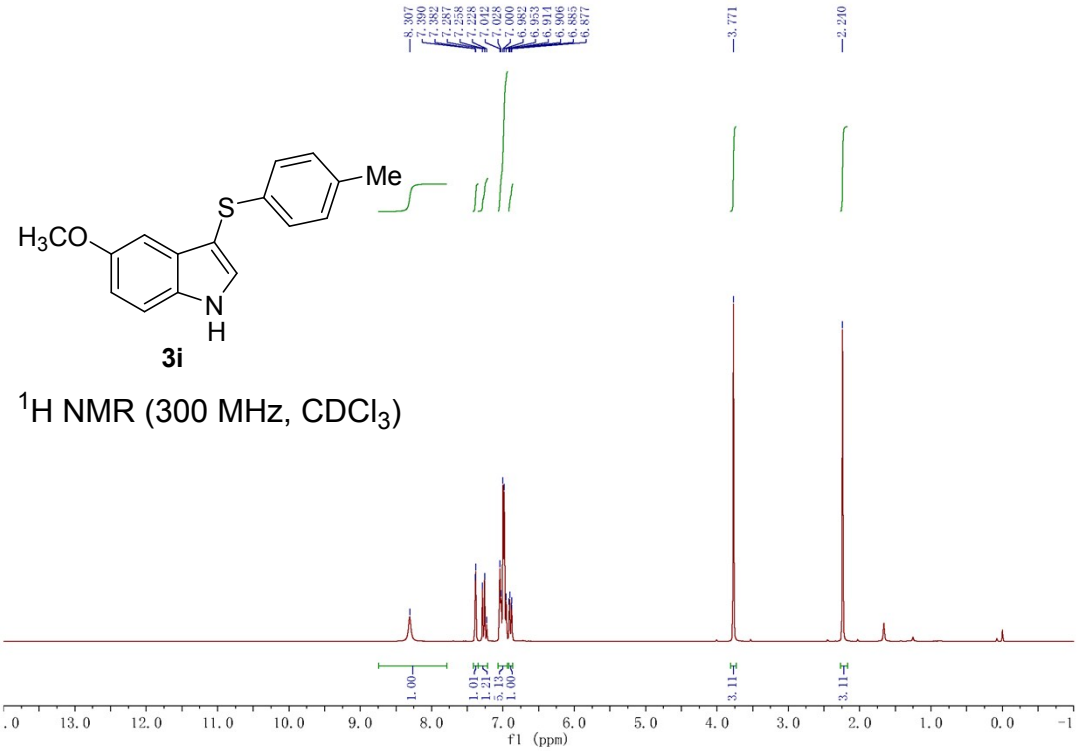




3h

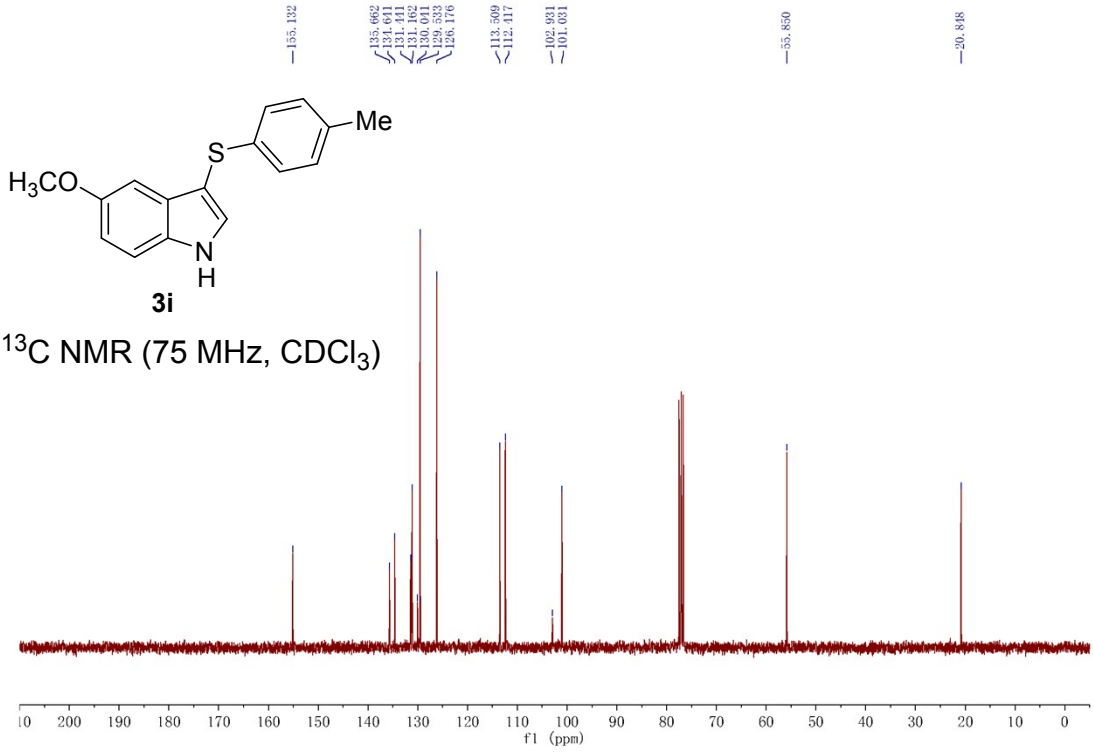
^{13}C NMR (125 MHz, $CDCl_3$)





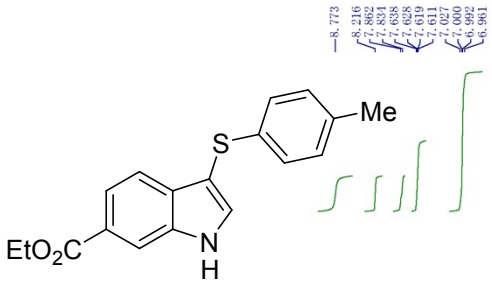
3i

^{1}H NMR (300 MHz, $CDCl_3$)



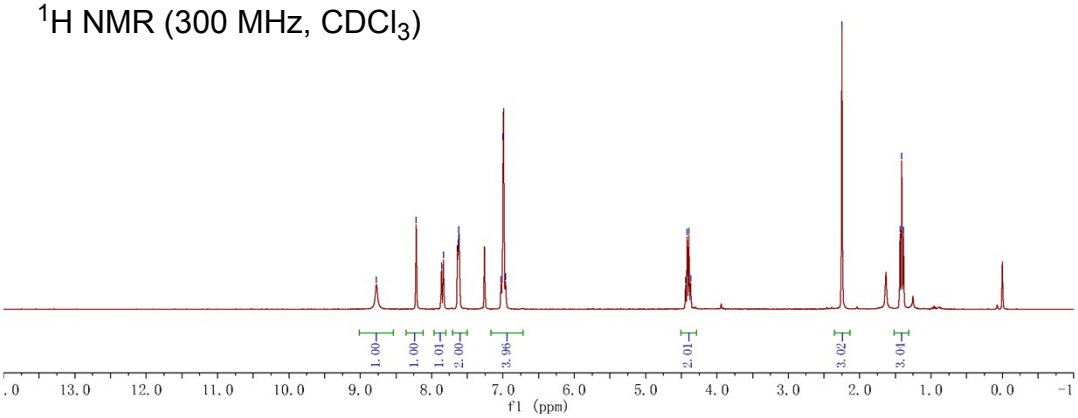
3i

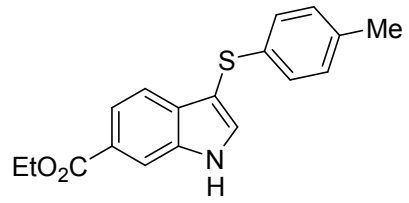
^{13}C NMR (75 MHz, $CDCl_3$)



3j

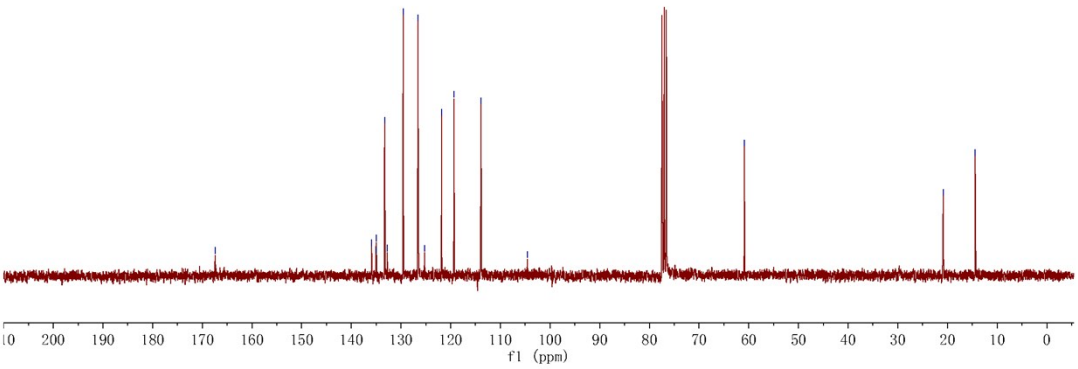
^{1}H NMR (300 MHz, $CDCl_3$)

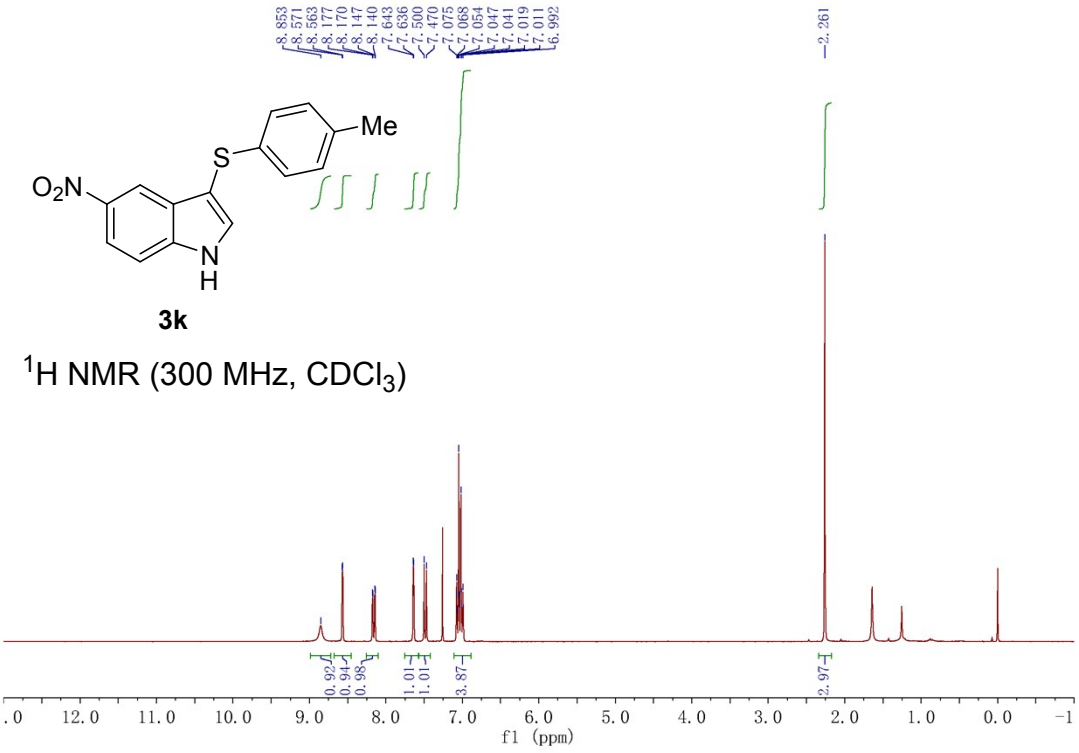




3j

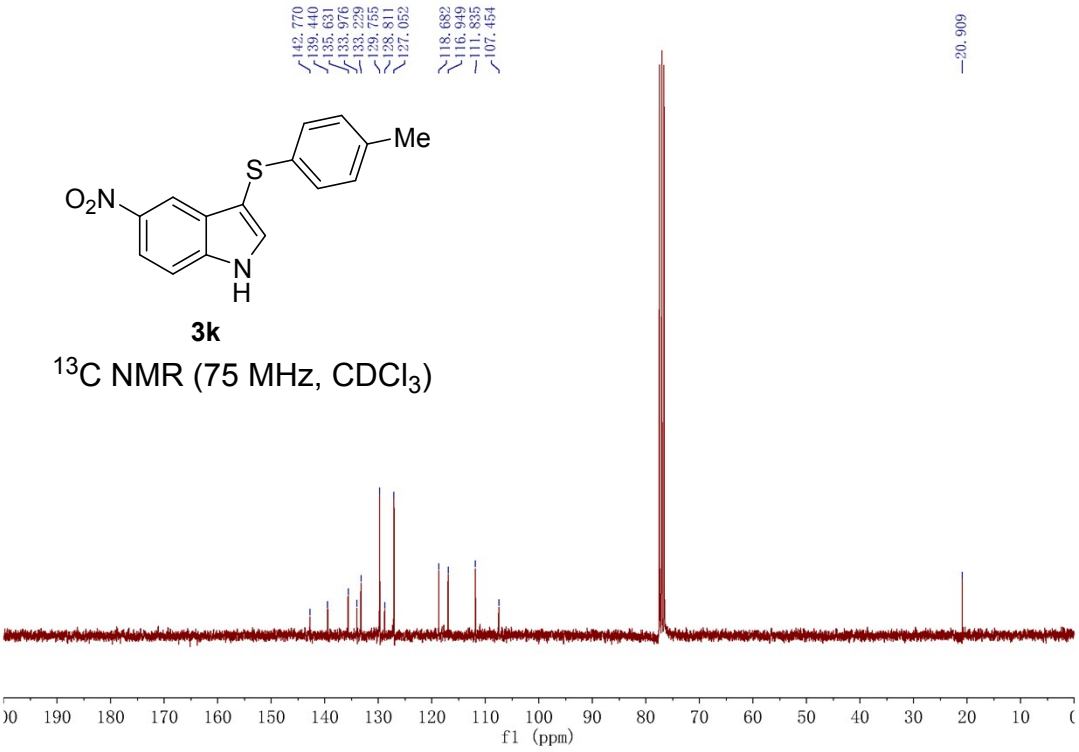
^{13}C NMR (75 MHz, $CDCl_3$)





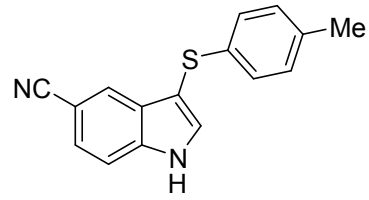
3k

^{1}H NMR (300 MHz, $CDCl_3$)



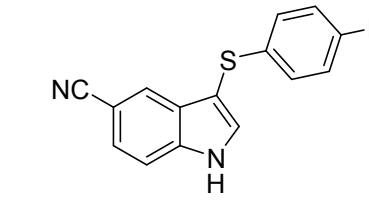
3k

^{13}C NMR (75 MHz, $CDCl_3$)



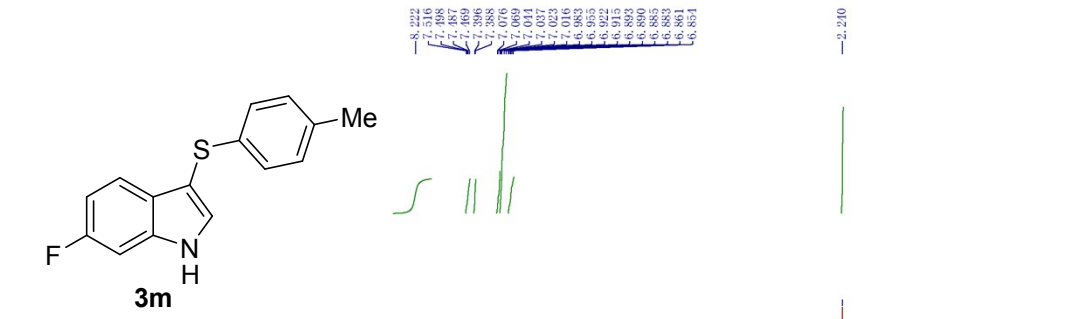
3l

^{1}H NMR (300 MHz, $CDCl_3$)



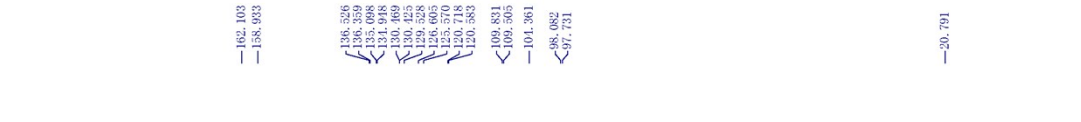
3l

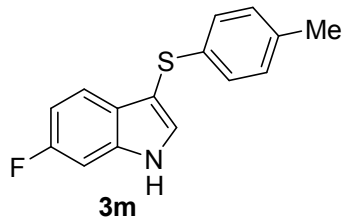
^{13}C NMR (125 MHz, DMSO-d_6)



3m

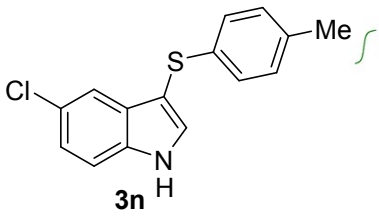
^{1}H NMR (300 MHz, $CDCl_3$)





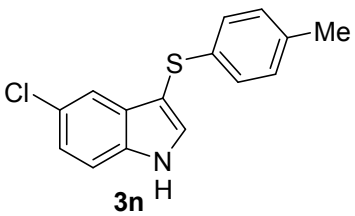
3m

^{13}C NMR (75 MHz, $CDCl_3$)



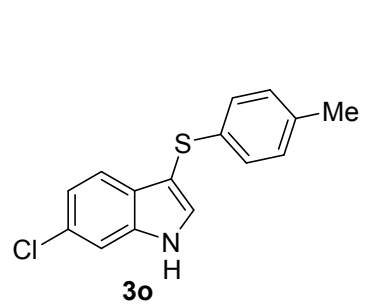
3n

^{1}H NMR (300 MHz, $CDCl_3$)



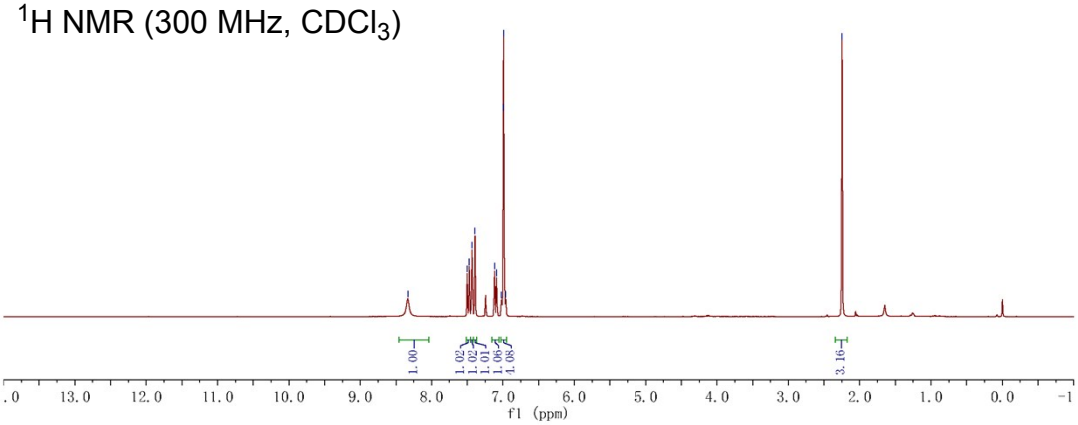
3n

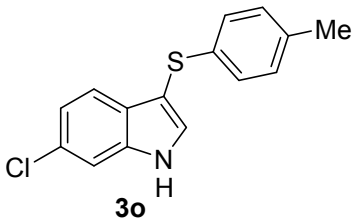
^{13}C NMR (125 MHz, $CDCl_3$)



3o

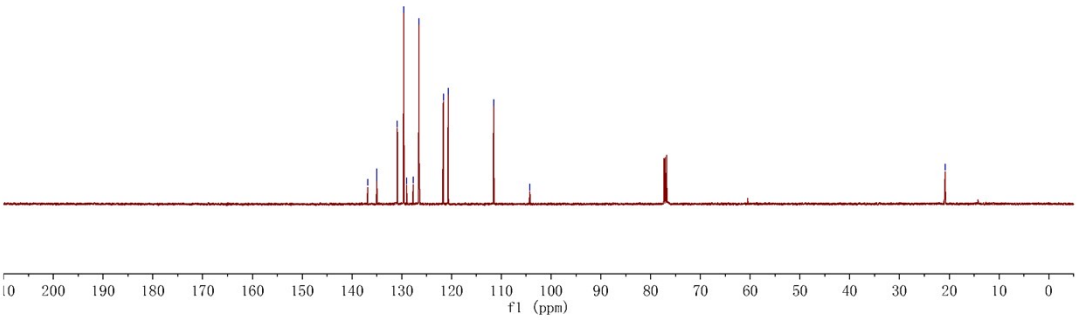
^{1}H NMR (300 MHz, $CDCl_3$)

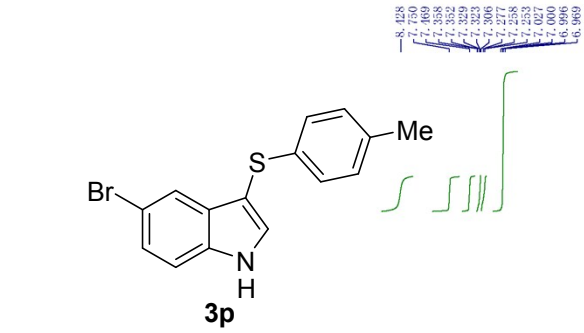




3o

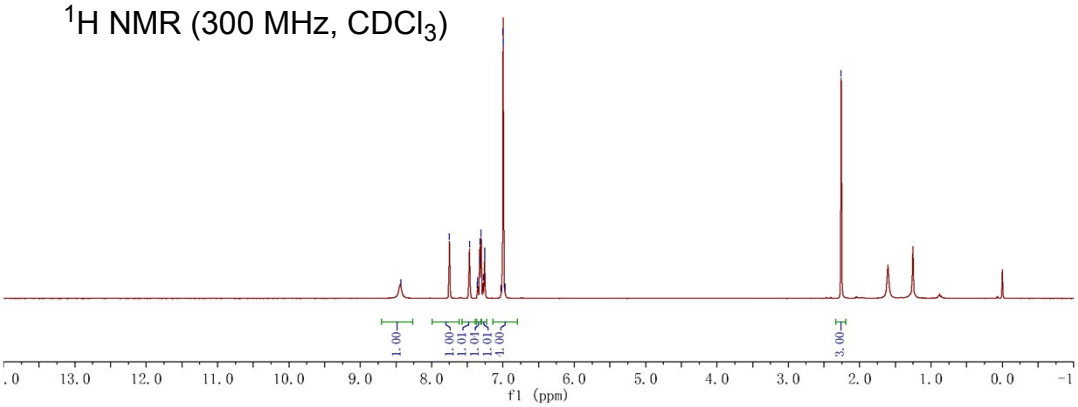
^{13}C NMR (125 MHz, $CDCl_3$)

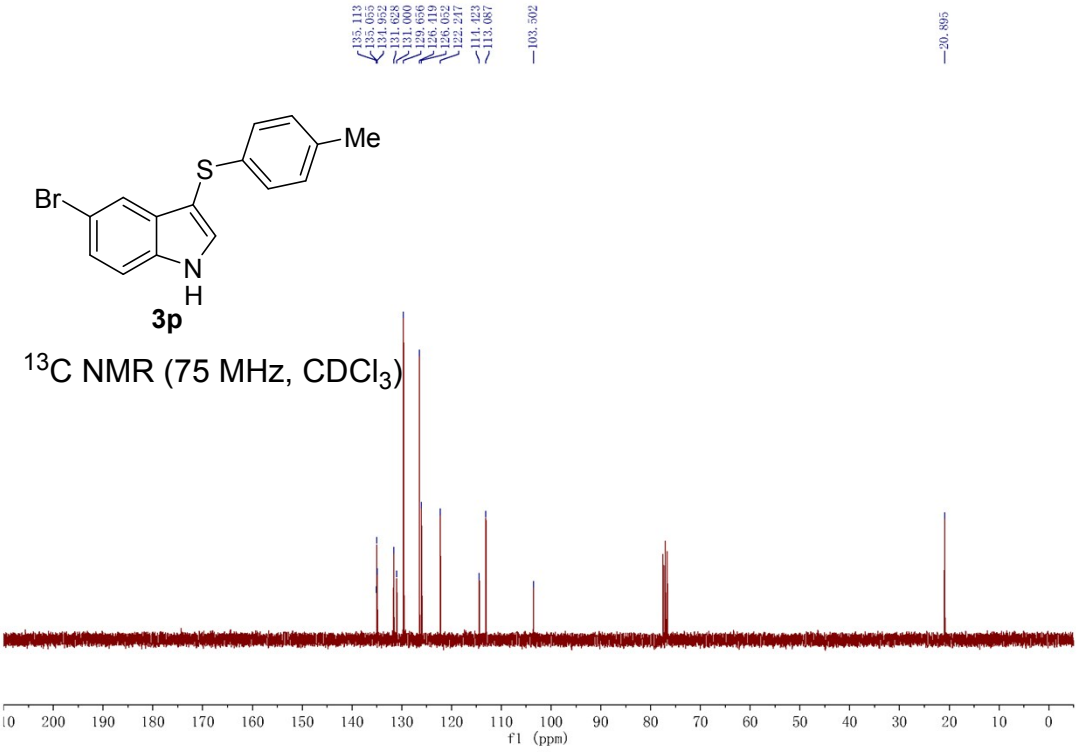




3p

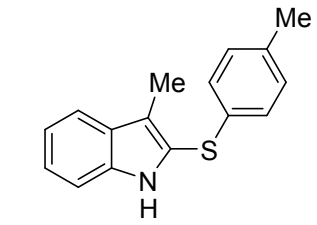
^{1}H NMR (300 MHz, $CDCl_3$)





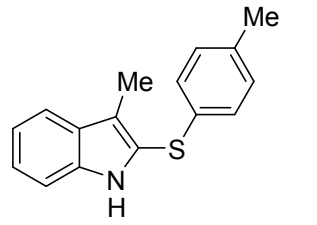
3p

^{13}C NMR (75 MHz, $CDCl_3$)



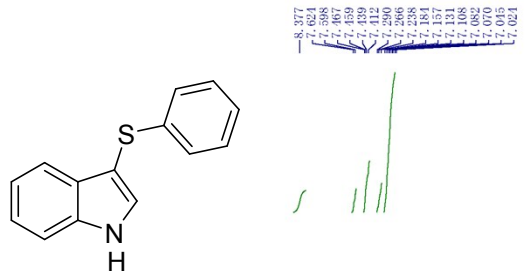
3q

^{1}H NMR (300 MHz, $CDCl_3$)



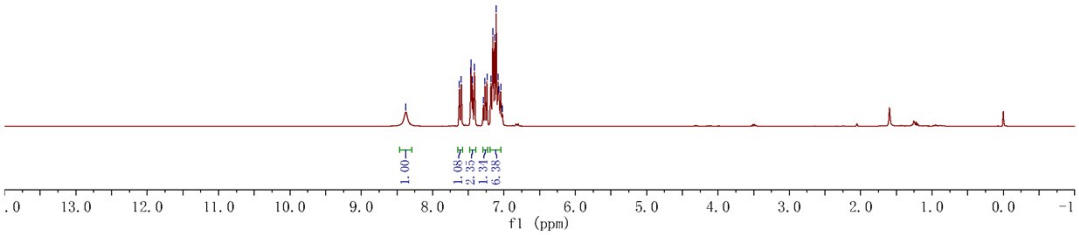
3q

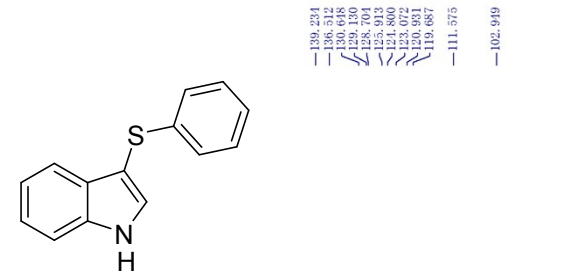
^{13}C NMR (125 MHz, $CDCl_3$)



4a

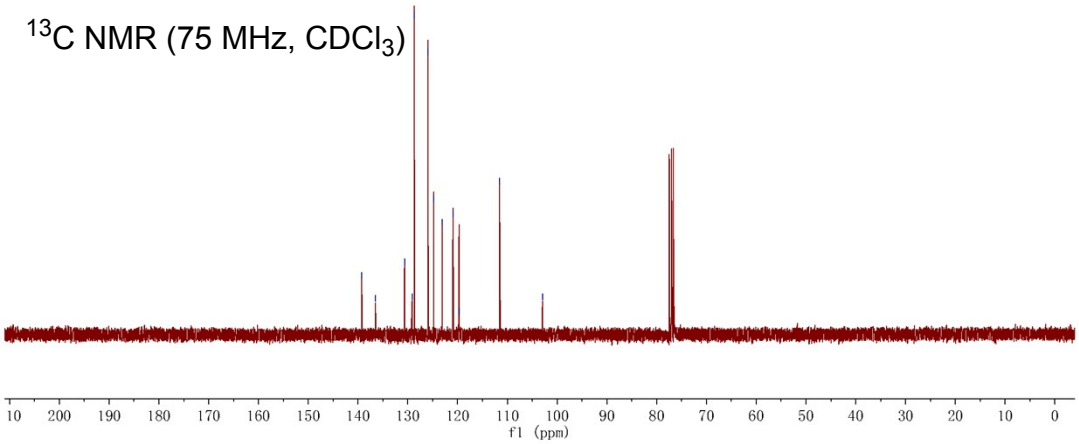
^{1}H NMR (300 MHz, $CDCl_3$)

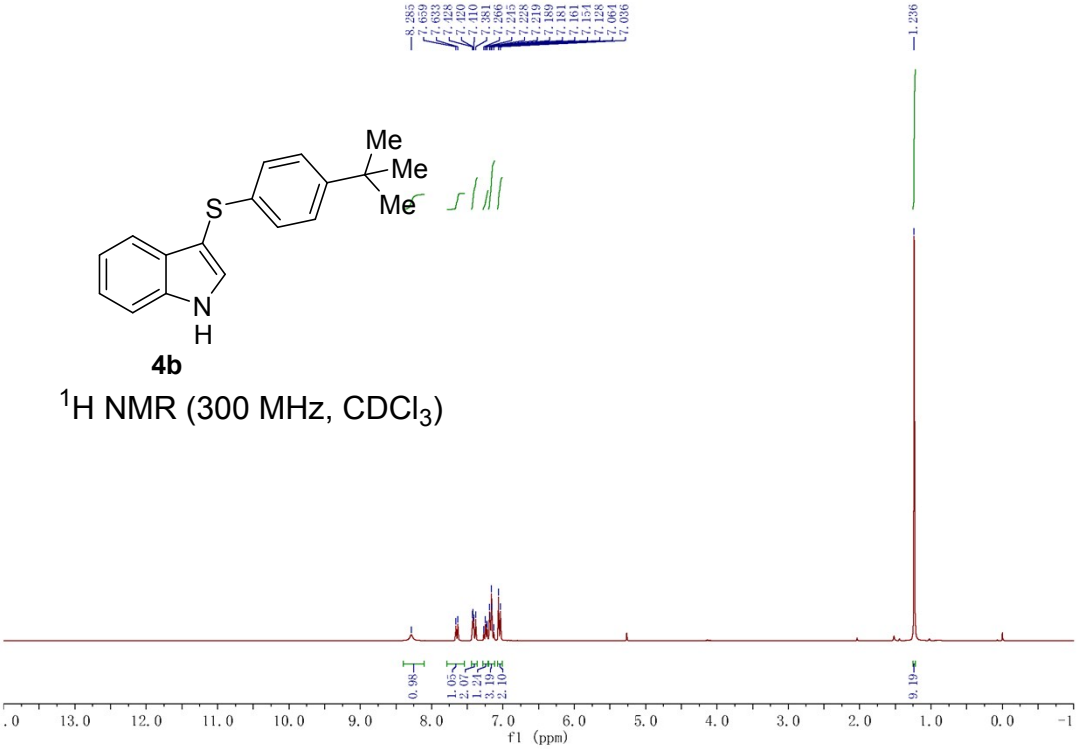




4a

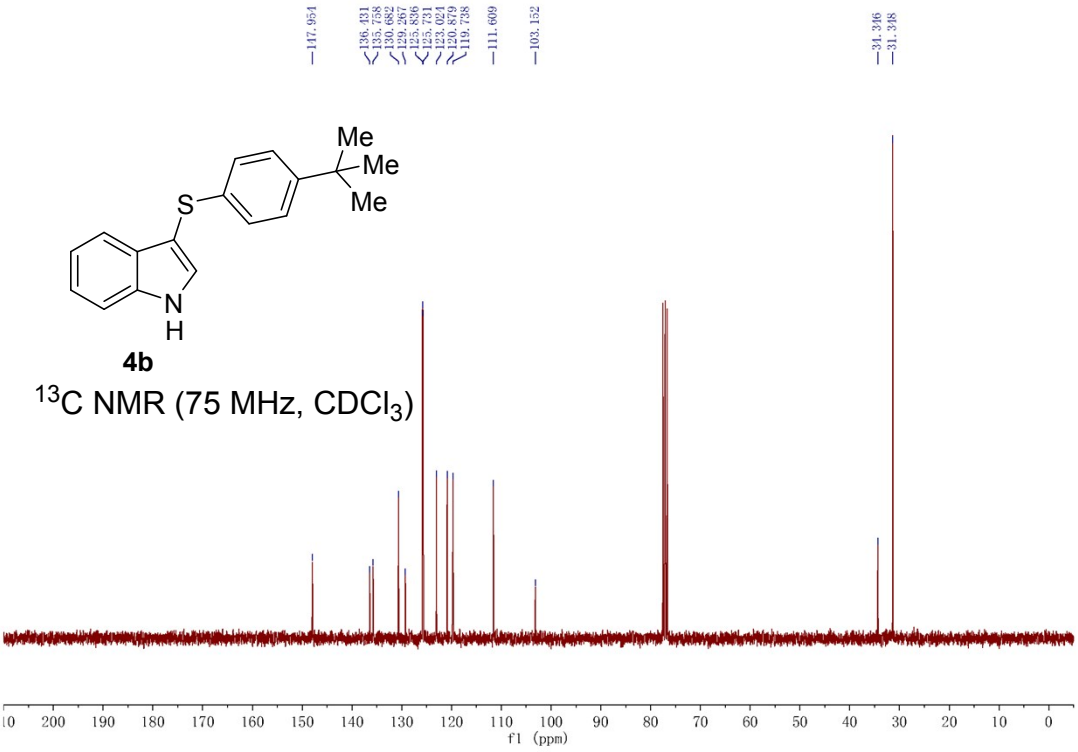
^{13}C NMR (75 MHz, $CDCl_3$)





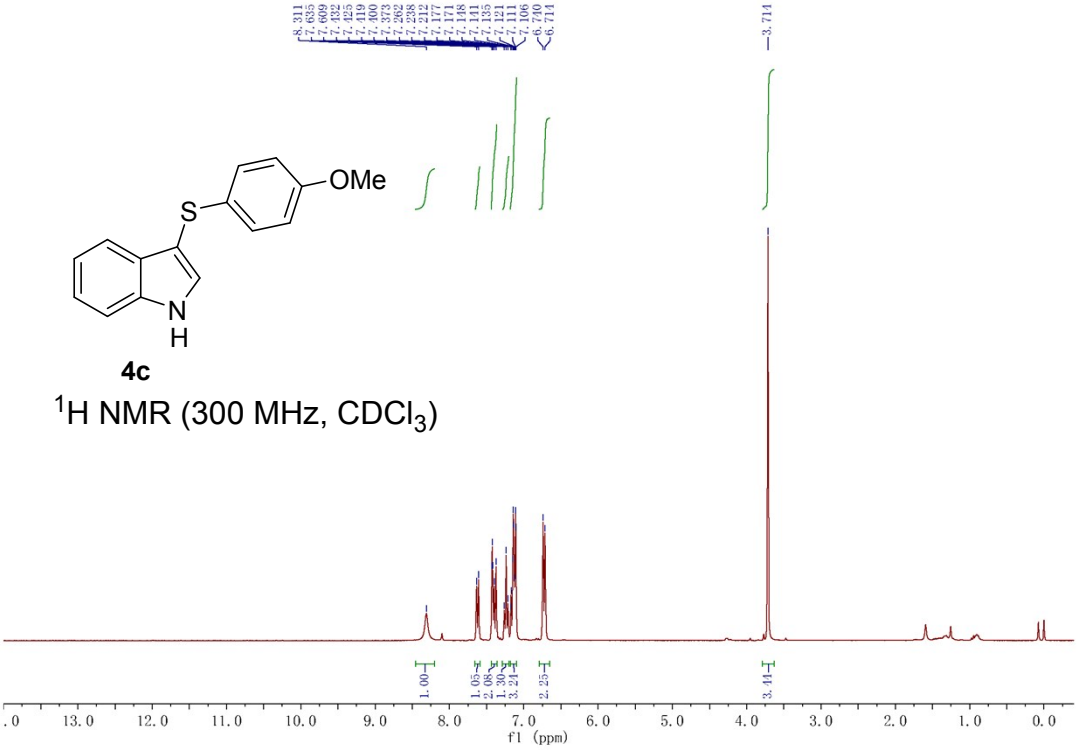
4b

^{1}H NMR (300 MHz, $CDCl_3$)



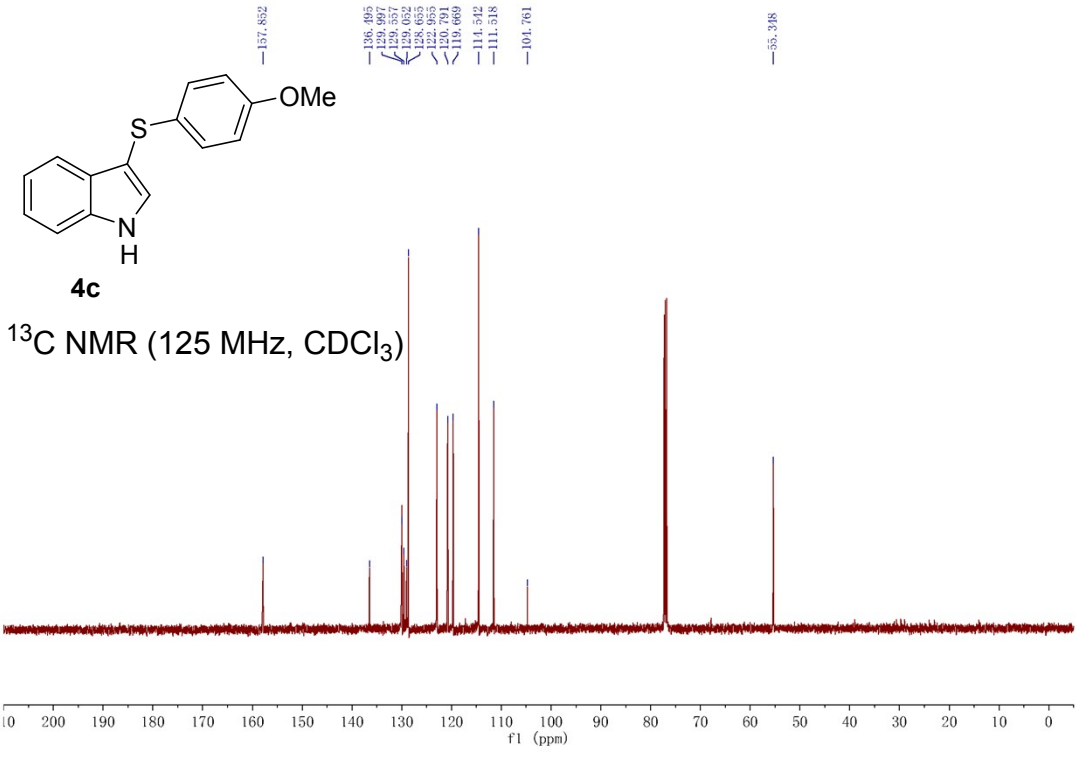
4b

^{13}C NMR (75 MHz, $CDCl_3$)



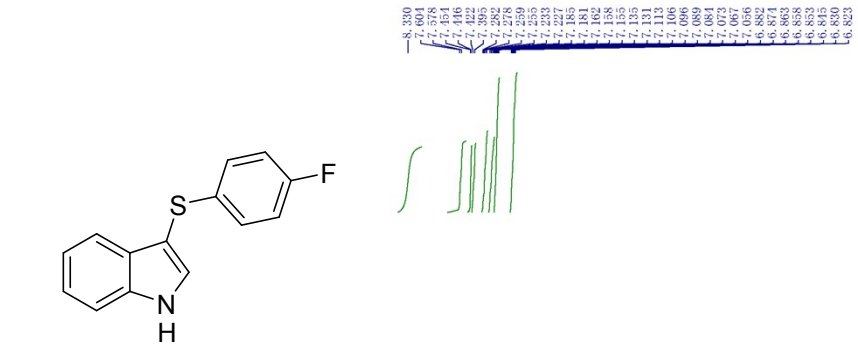
4c

^{1}H NMR (300 MHz, $CDCl_3$)



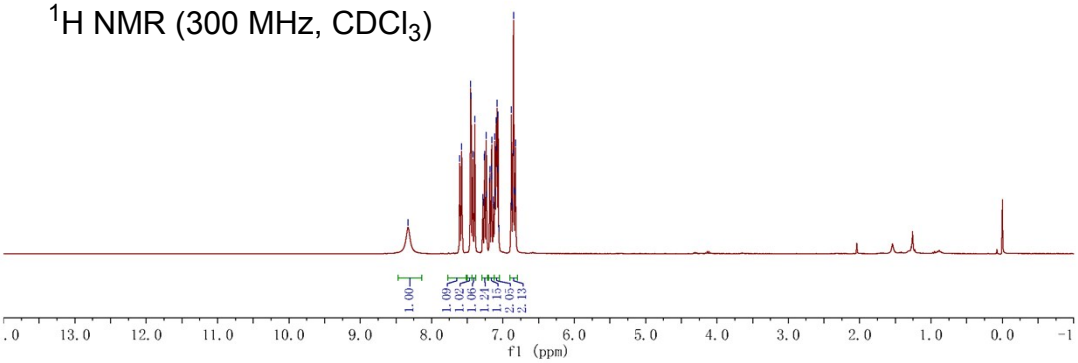
4c

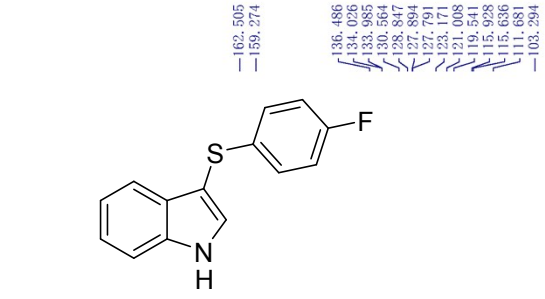
^{13}C NMR (125 MHz, $CDCl_3$)



4d

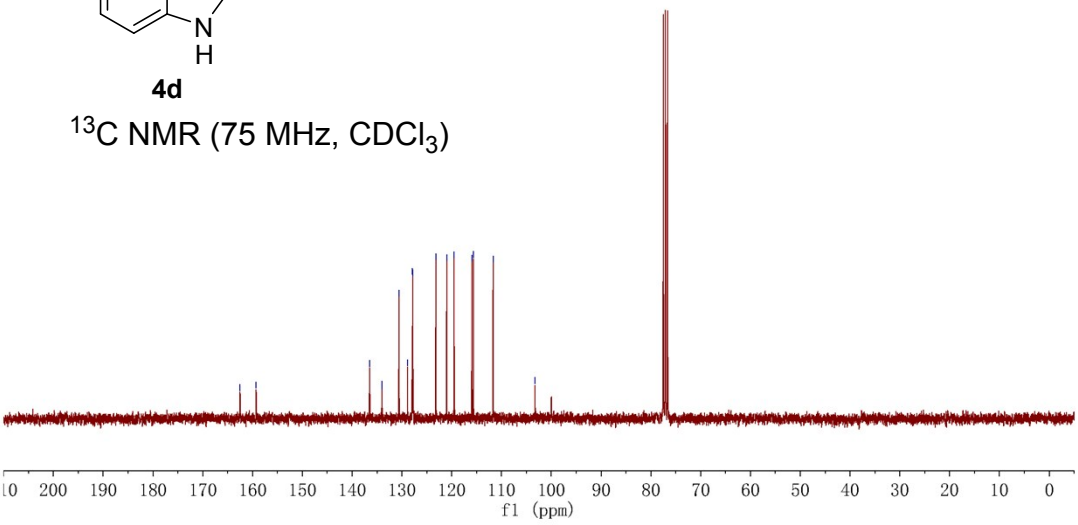
^{1}H NMR (300 MHz, $CDCl_3$)

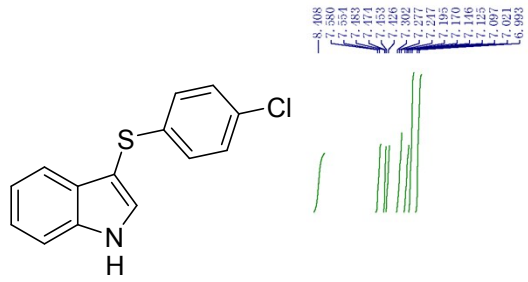




4d

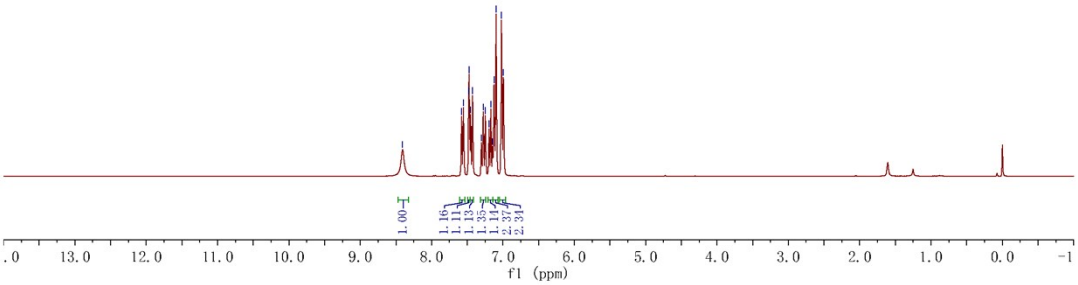
^{13}C NMR (75 MHz, $CDCl_3$)

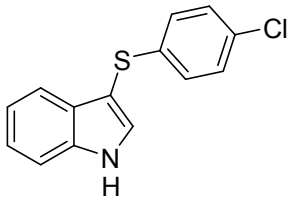




4e

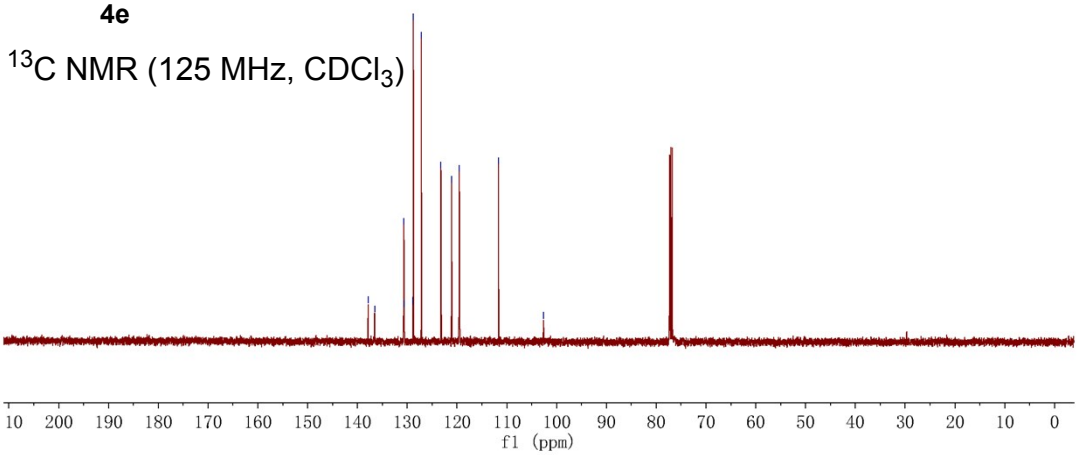
^{1}H NMR (300 MHz, $CDCl_3$)

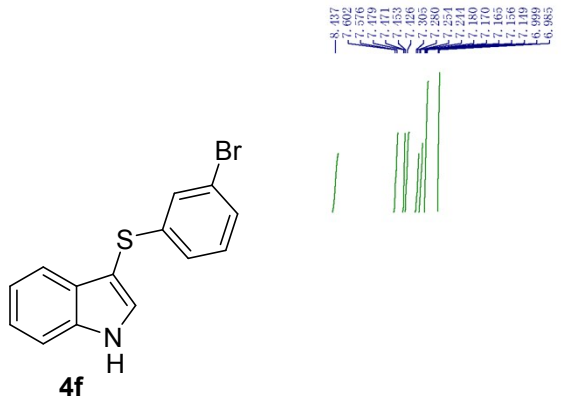




4e

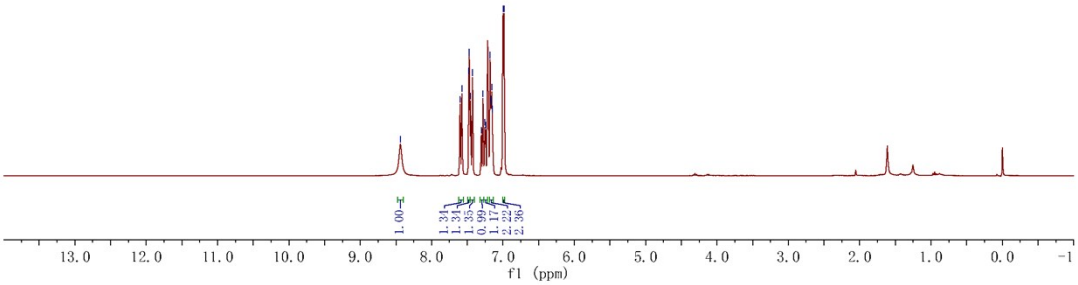
^{13}C NMR (125 MHz, $CDCl_3$)

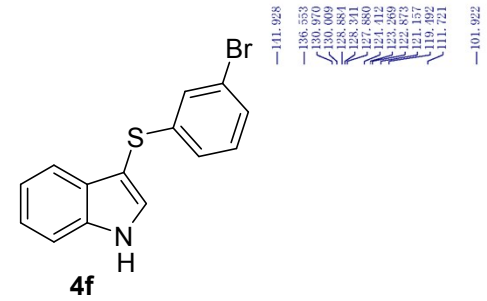




4f

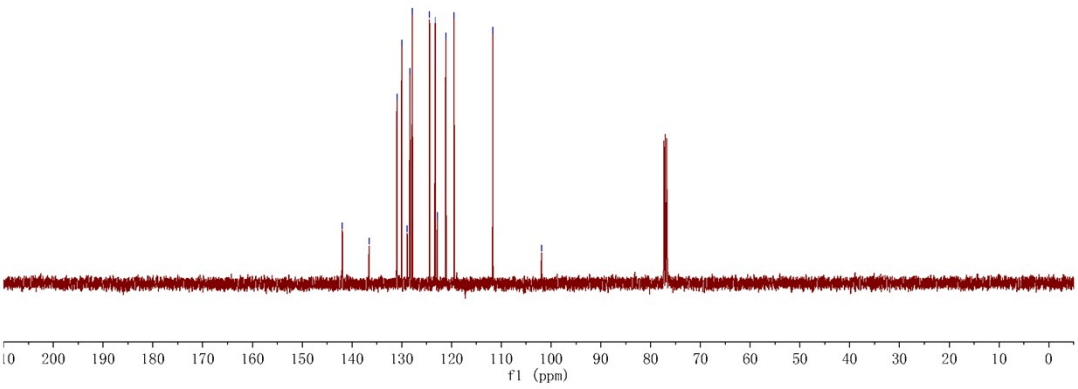
^{1}H NMR (300 MHz, $CDCl_3$)

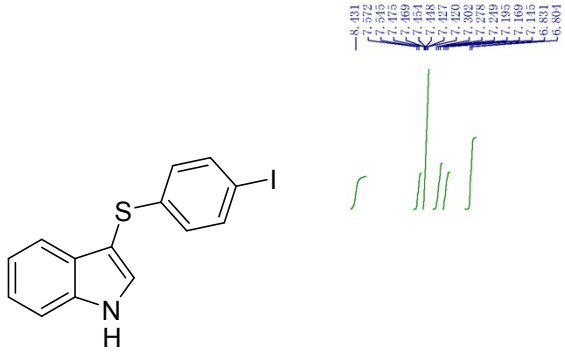




4f

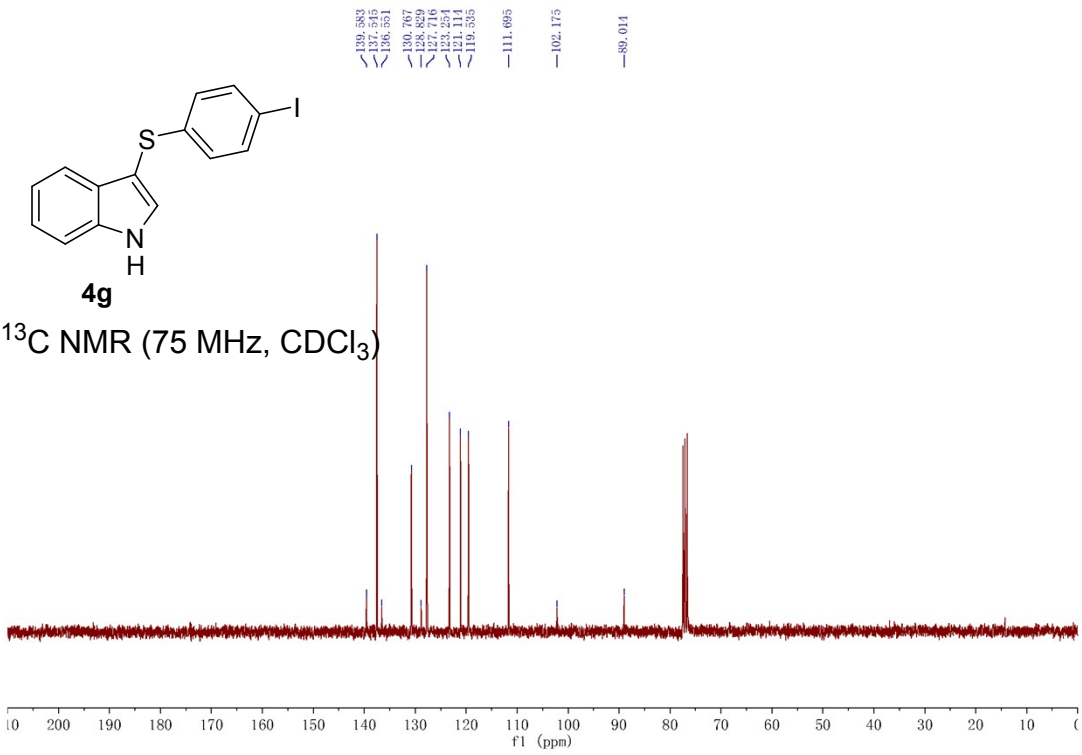
^{13}C NMR (125 MHz, $CDCl_3$)





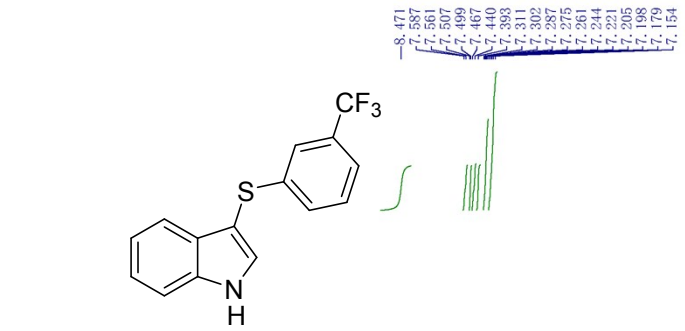
4g

^{1}H NMR (300 MHz, $CDCl_3$)



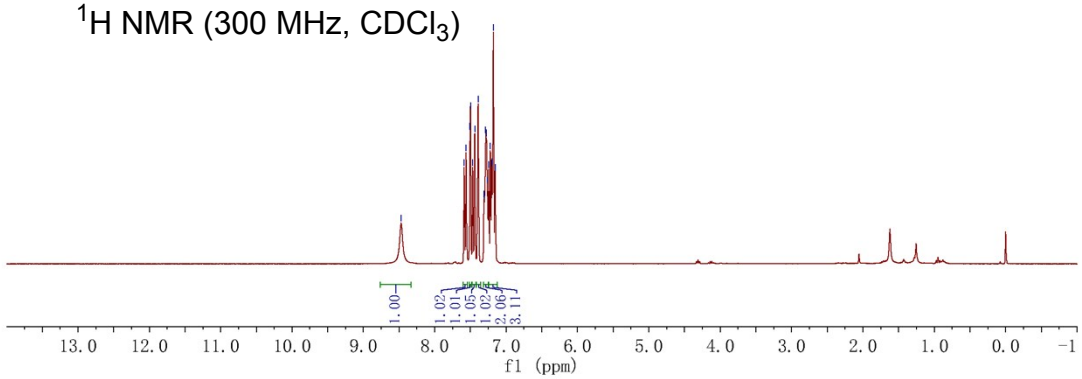
4g

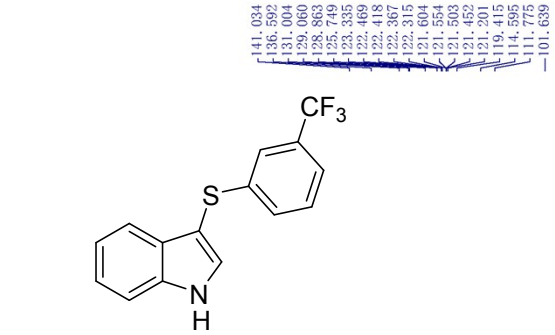
^{13}C NMR (75 MHz, $CDCl_3$)



4h

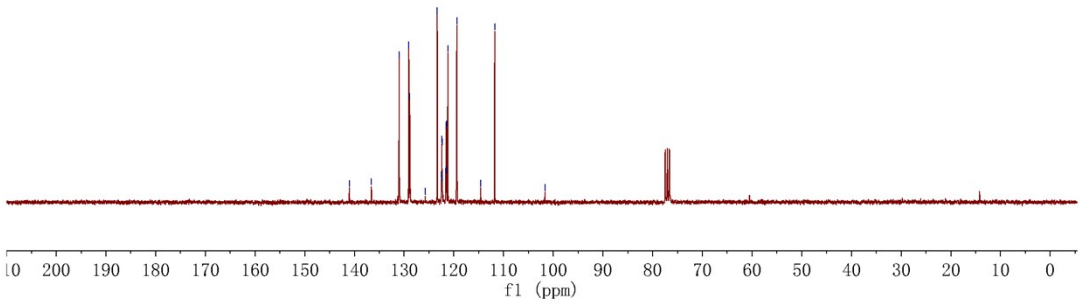
^{1}H NMR (300 MHz, $CDCl_3$)

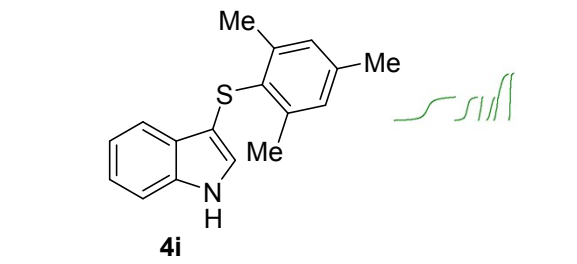




4h

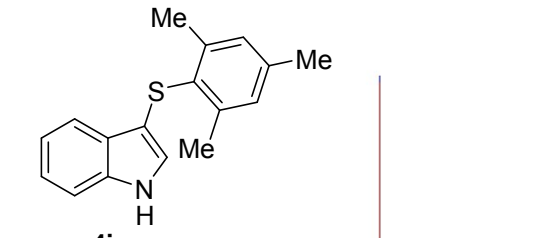
^{13}C NMR (75 MHz, $CDCl_3$)





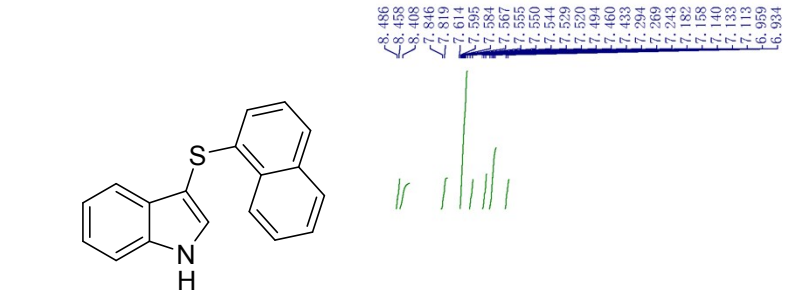
4i

^{1}H NMR (300 MHz, $CDCl_3$)



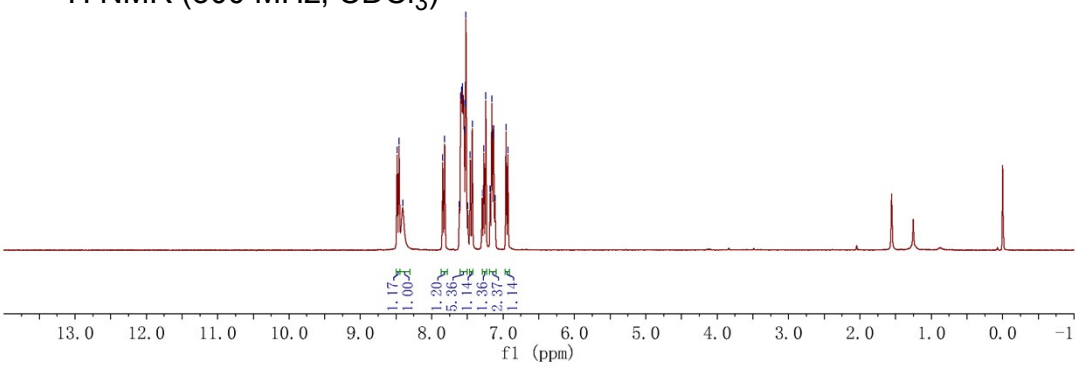
4i

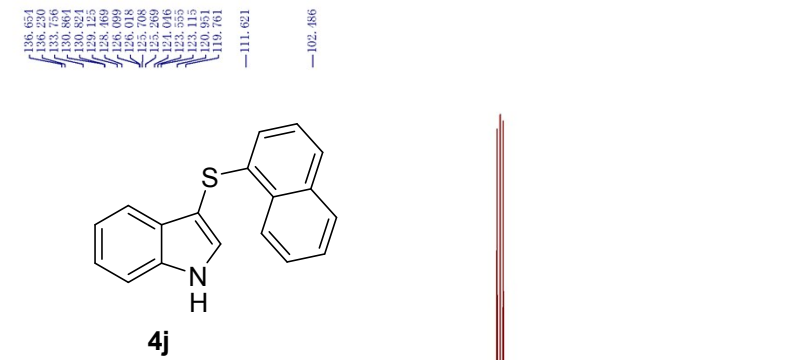
^{13}C NMR (75 MHz, $CDCl_3$)



4j

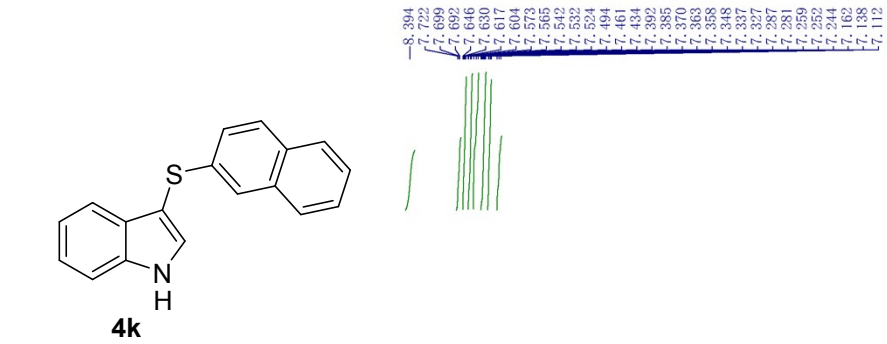
^{1}H NMR (300 MHz, $CDCl_3$)





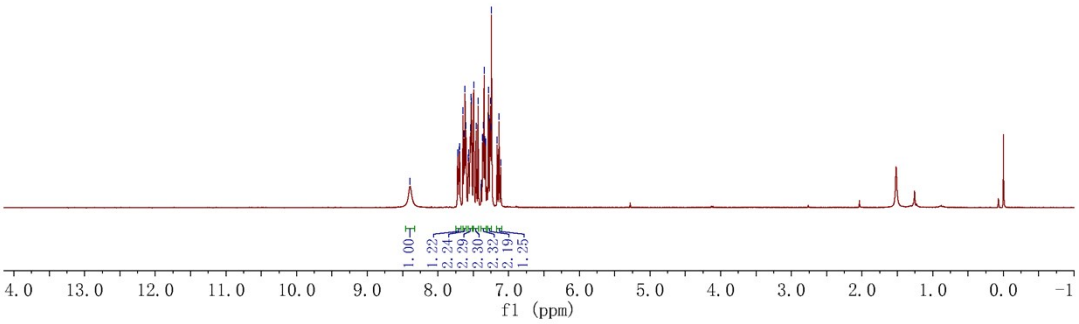
4j

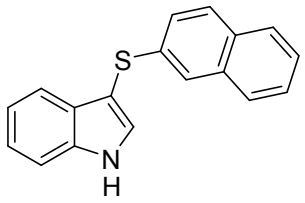
^{13}C NMR (75 MHz, $CDCl_3$)



4k

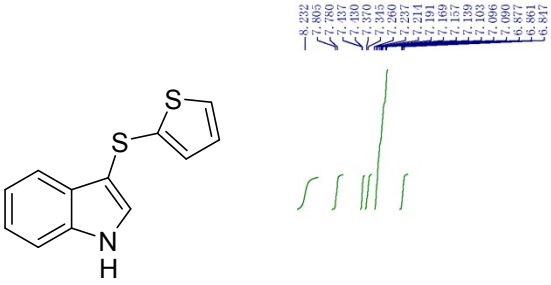
^{1}H NMR (300 MHz, $CDCl_3$)





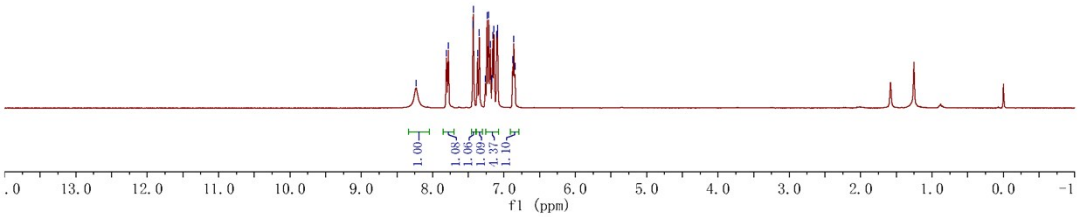
4k

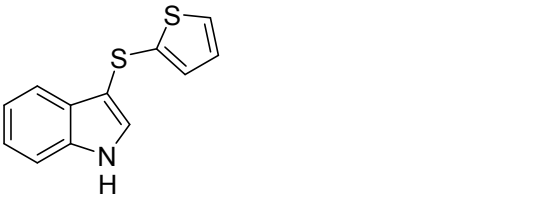
^{13}C NMR (75 MHz, $CDCl_3$)



4l

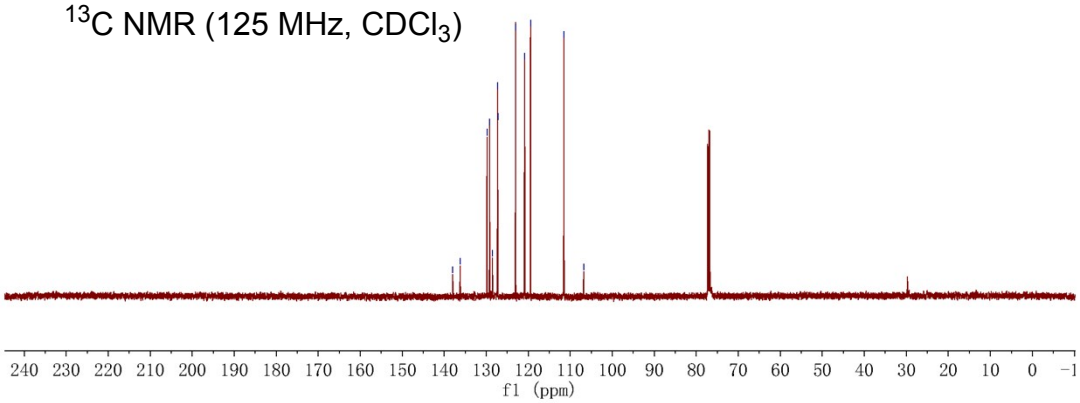
^{1}H NMR (300 MHz, $CDCl_3$)

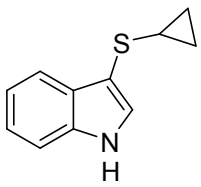




4l

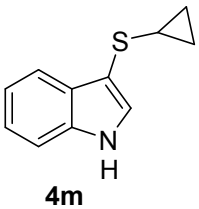
^{13}C NMR (125 MHz, $CDCl_3$)





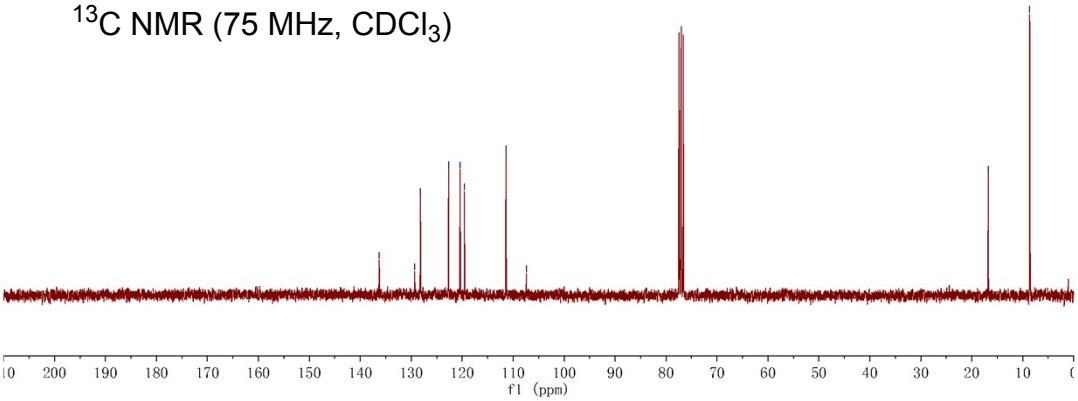
4m

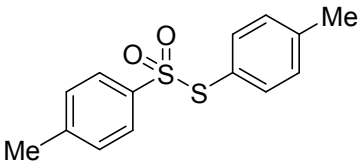
^{1}H NMR (300 MHz, $CDCl_3$)



4m

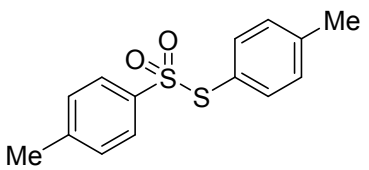
^{13}C NMR (75 MHz, $CDCl_3$)





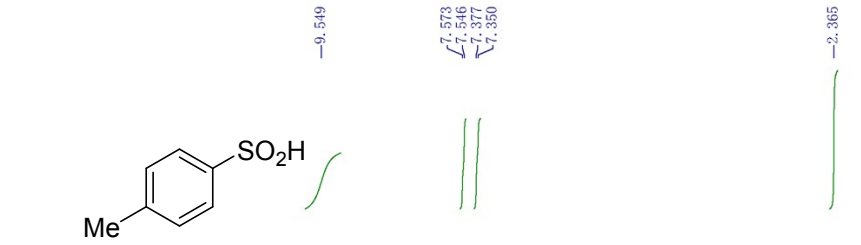
5

^{1}H NMR (300 MHz, $CDCl_3$)



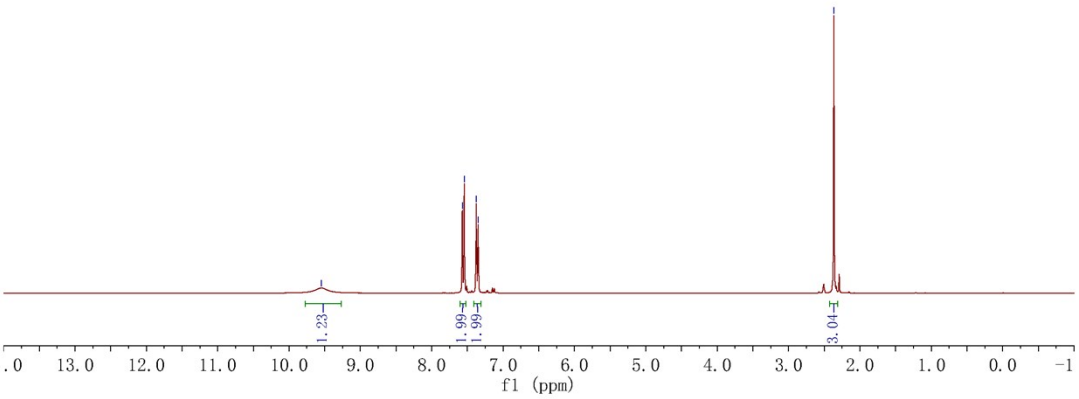
5

^{13}C NMR (75 MHz, $CDCl_3$)



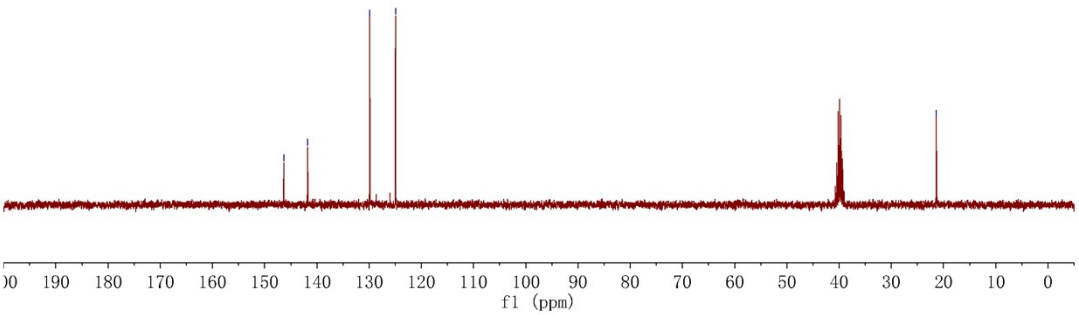
6

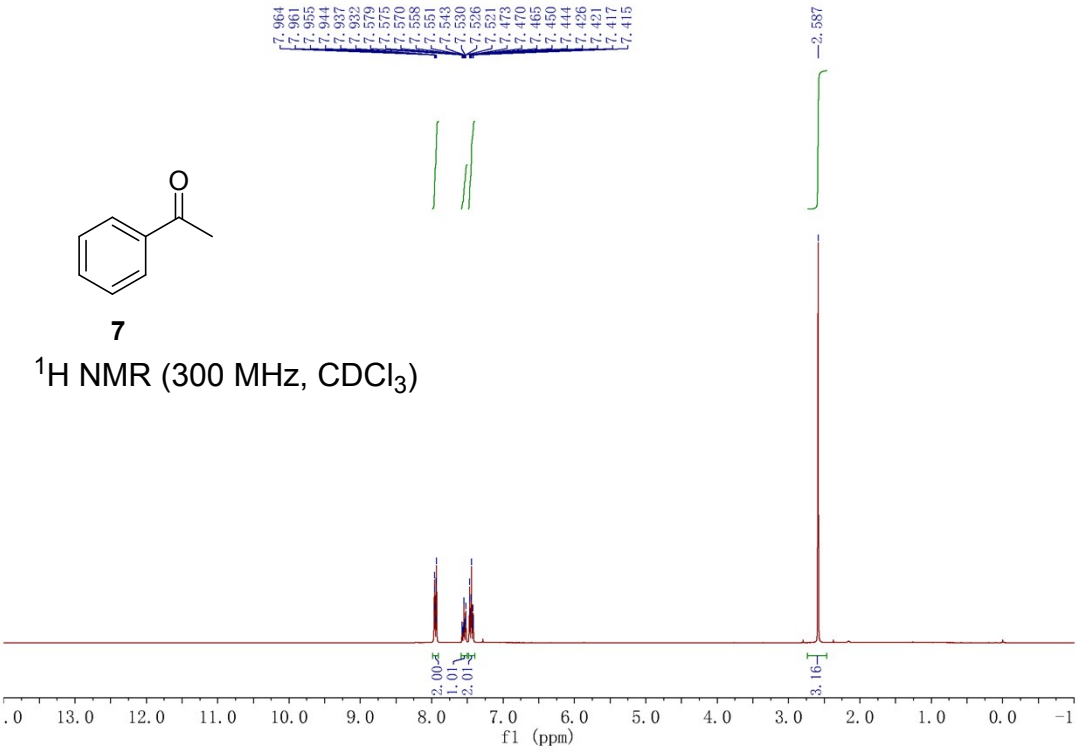
^{1}H NMR (300 MHz, $CDCl_3$)



6

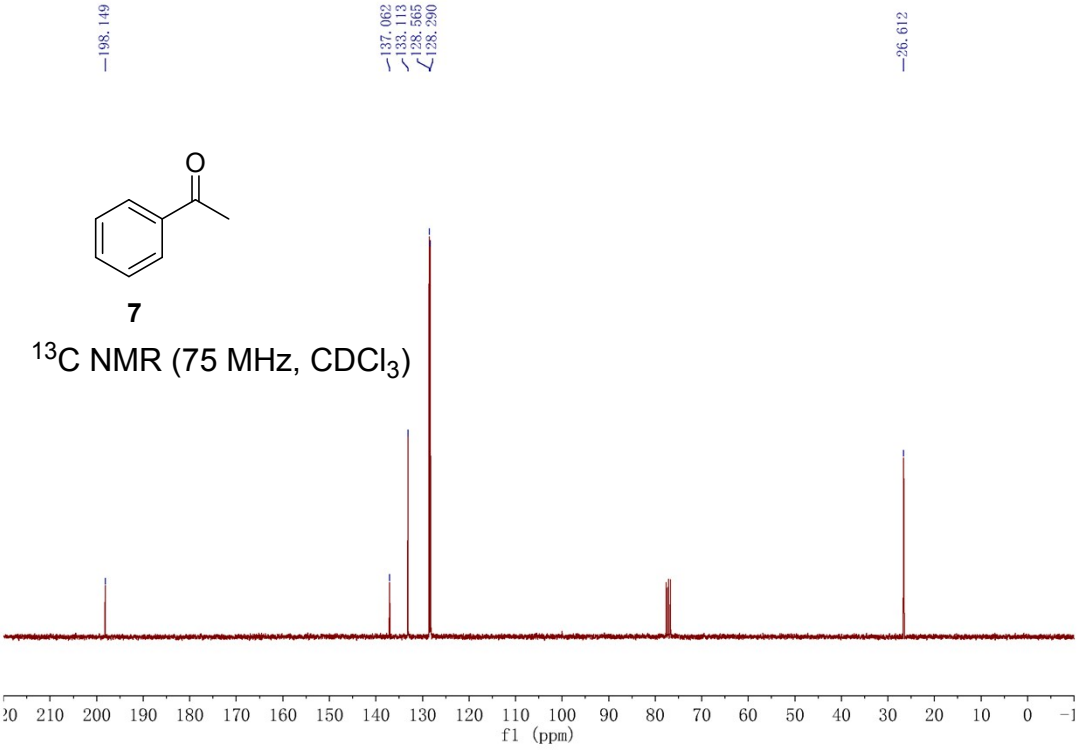
^{13}C NMR (75 MHz, DMSO-d_6)





7

^{1}H NMR (300 MHz, $CDCl_3$)



7

^{13}C NMR (75 MHz, $CDCl_3$)