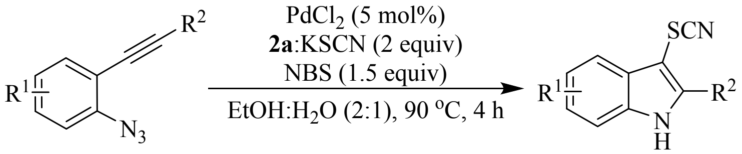
General Considerations

Unless specified, all reactions were carried out in oven-dried glassware with magnetic stirring. All reagents and starting materials were purchased from commercial sources and used as received. Solvents were purified following standard literature procedures. Analytical thin layer chromatography (TLC) was performed using pre-coated silica gel plate. Visualization was achieved by UV light (254 nm). Flash chromatography was performed using silica gel and a gradient solvent system (Ethyl acetate: Petrol ether as eluant). ^{1}H and ^{13}C NMR spectra were measured on 400 and 600 MHz spectrometers. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as: s (singlet), bs (broad singlet), d (doublet), t (triplet), dd (doublet of doublets) or m (multiplet). The number of protons (n) for a given resonance is indicated by nH and coupling constants are reported as a J value in Hz. Infrared spectra were recorded on a FTIR spectrometer. High resolution mass spectra (HRMS) were obtained on a LTQ Orbitrap LC/HRMS mass spectrometer. All the starting materials **1** (2-alkynyl arylazides) were prepared by our reported methods.[1] Analytical reagents with a reaction solvent ethanol mass fraction greater than 99.7%.

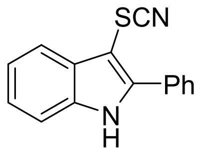
General experimental procedure for the synthesis of 3-thiocyanato-1*H*-indoles 3



1 **3**

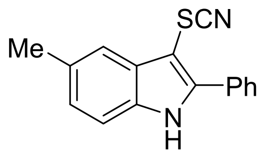
2-Alkynyl arylazides **1** (0.1 mmol, 1 equiv), $PdCl_2$ (5 mol%), KSCN (0.2 mmol, 2 equiv) and NBS (0.15 mmol, 1.5 equiv) were added to a 10 mL round bottom flask with magnetic stir bar in 1 mL mixed solvents of EtOH and H_2O (volume ratio 2:1). The reaction mixture was stirred at 90°C. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction residue was directly subjected to purification by flash column chromatography on silica gel to give the desired products 3-thiocyanato-1*H*-indoles **3**. (eluent: petrol ether: ethyl acetate = 8:1)

2-Phenyl-3-thiocyanato-1*H*-indole (3a)



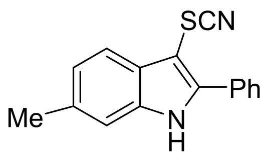
Known compound[2]; isolated yield = 97%; yellow solid; m.p. 169.0-171.0 ℃; ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 12.40 (s, 1 H), 7.85-7.87 (m, 2 H), 7.72 (d, J = 7.4 Hz, 1 H), 7.61-7.64 (m, 2 H), 7.53-7.55 (m, 2 H), 7.27-7.33 (m, 2 H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 143.2, 135.8, 130.0, 129.3, 129.2, 128.9, 128.8, 123.4, 121.4, 118.0, 112.5, 112.3, 87.1.

5-Methyl-2-phenyl-3-thiocyanato-1*H*-indole (3b)



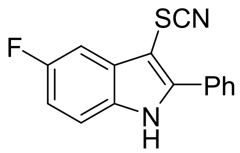
Isolated yield = 95%; yellow solid; m.p. 142.1-143.4 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.67 (s, 1 H), 7.72 (d, J = 7.0 Hz, 2 H), 7.62 (s, 1 H), 7.46-7.55 (m, 3 H), 7.32 (d, J = 8.3 Hz, 1 H), 7.14 (d, J = 8.2 Hz, 1 H), 2.53 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 143.2, 133.8, 131.9, 130.3, 130.1, 129.6, 129.2, 128.7, 125.8, 118.7, 112.2, 111.4, 88.6, 21.7； HRMS (ESI) calcd for $C_{16}H_{13}N_2S$ $[M+H]^+$ 265.0799, found 265.0805.

6-Methyl-2-phenyl-3-thiocyanato-1*H*-indole (3c)



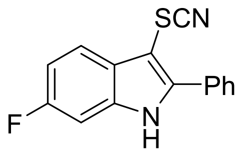
Isolated yield = 83%; yellow solid; m.p. 144.0-145.6 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.64 (s, 1 H), 7.71 (d, J = 7.8 Hz, 3 H), 7.46-7.54 (m, 3 H), 7.22 (s, 1 H), 7.15 (d, J = 8.1 Hz, 1 H), 2.49 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 142.5, 136.0, 134.3, 130.3, 129.5, 129.2, 128.6, 127.7, 124.0, 118.8, 112.1, 111.6, 89.0, 21.9； HRMS (ESI) calcd for $C_{16}H_{13}N_2S$ $[M+H]^+$ 265.0799, found 265.0803.

5-Fluoro-2-phenyl-3-thiocyanato-1*H*-indole (3d)



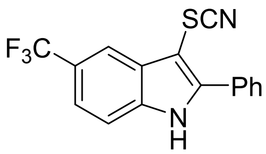
Isolated yield = 98%; yellow solid; m.p. 161.6-162.9 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.87 (s, 1 H), 7.70 (d, J = 7.0 Hz, 2 H), 7.50-7.55 (m, 3 H), 7.46 (d, J = 9.9 Hz, 1 H), 7.33-7.36 (m, 1 H), 7.02-7.07 (m, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.2 (d, J = 237.6 Hz), 145.0, 131.9, 130.7 (d, J = 10.5 Hz), 129.9, 129.8, 129.3, 128.7, 112.9 (d, J = 2.9 Hz), 112.7 (d, J = 18.8 Hz), 111.9, 104.4 (d, J = 24.7 Hz), 89.22; HRMS (ESI) calcd for $C_{15}H_{10}FN_2S$ $[M+H]^+$ 269.0549, found 269.0553.

6-Fluoro-2-phenyl-3-thiocyanato-1*H*-indole (3e)



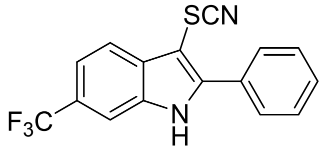
Isolated yield = 87%; yellow solid; m.p. 150.7-152.9 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.83 (s, 1 H), 7.73-7.76 (m, 1 H), 7.69 (d, J = 7.1 Hz, 2 H), 7.47-7.55 (m, 3 H), 7.06-7.12 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 160.8 (d, J = 239.7 Hz), 143.7 (d, J = 3.0 Hz), 135.5 (d, J = 12.5 Hz), 129.9, 129.8, 129.3, 128.6, 126.2, 120.2 (d, J = 10.1 Hz), 111.9, 111.2 (d, J = 24.7 Hz), 98.4 (d, J = 26.6 Hz), 89.4; HRMS (ESI) calcd for $C_{15}H_{10}FN_2S$ $[M+H]^+$ 269.0549, found 269.0555.

2-Phenyl-3-thiocyanato-5-(trifluoromethyl)-1*H*-indole (3f)



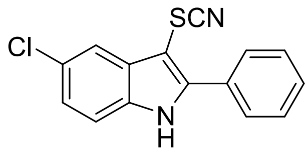
Isolated yield = 87%; yellow solid; m.p. 154.0-155.6 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.09 (s, 1 H), 8.11 (s, 1 H), 7.72 (d, J = 6.5 Hz, 2 H), 7.49-7.57 (m, 5 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 145.2, 137.0, 130.2, 129.4, 128.7, 127.6(d, J = 270.4 Hz), 125.0, 124.8(d, J = 31.8 Hz), 121.0 (d, J = 3.0 Hz), 116.9 (d, J = 8.8 Hz), 112.3, 111.6, 90.4; HRMS (ESI) calcd for $C_{16}H_{10}F_3N_2S$ $[M+H]^+$ 319.0517, found 319.0520.

2-Phenyl-3-thiocyanato-6-(trifluoromethyl)-1*H*-indole (3g)



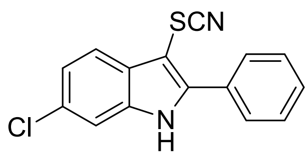
Isolated yield = 92%; yellow solid; m.p. 161.3-162.9 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 12.85 (s, 1 H), 7.87-7.92 (m, 3 H), 7.83 (s, 1 H), 7.63-7.66 (m, 2 H),7.56-7.60 (m, 2 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 146.1, 134.8, 131.8, 129.9, 129.1, 129.0, 126.3, 123.8 (q, *J* = 31.8 Hz), 119.1, 117.8(q, *J* = 3.3 Hz), 112.1, 109.8(q, *J* = 4.3 Hz), 88.5; HRMS (ESI) calcd for $C_{16}H_{10}F_3N_2S$ $[M+H]^+$ 319.0517, found 319.0523.

5-Chloro-2-phenyl-3-thiocyanato-1*H*-indole (3h)



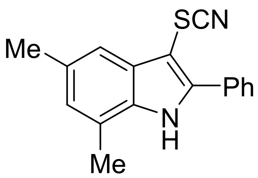
Isolated yield = 91%; yellow solid; m.p. 168.2-170.5 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 12.60 (s, 1 H), 7.85 (d, *J* = 7.5 Hz, 2 H), 7.71 (s, 1 H),7.61-7.65 (m, 2 H), 7.54-7.58 (m, 2 H), 7.32 (d, *J* = 8.6 Hz, 1 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 144.7, 134.4, 130.4, 129.7, 129.6, 129.0, 128.9, 126.1, 123.5, 117.2, 114.2, 112.2, 87.3; HRMS (ESI) calcd for $C_{15}H_{10}ClN_2S$ $[M+H]^+$ 285.0253, found 285.0248.

6-Chloro-2-phenyl-3-thiocyanato-1*H*-indole (3i)



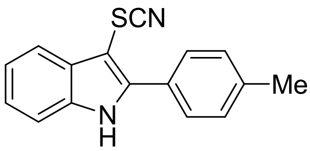
Isolated yield = 87%; yellow solid; m.p. 119.1-121.1 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 12.55 (s, 1 H), 7.84 (d, *J* = 7.6 Hz, 2 H), 7.72 (d, *J* = 8.1 Hz, 1 H), 7.61-7.65 (m, 2 H), 7.54-7.57 (m, 2 H), 7.29-7.32 (m, 1 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 144.1, 136.2, 129.6, 129.0, 128.8, 128.0, 127.9, 121.8, 119.6, 112.2, 112.0, 87.9; HRMS (ESI) calcd for $C_{15}H_{10}ClN_2S$ $[M+H]^+$ 285.0253, found 285.0250.

5,7-Dimethyl-2-phenyl-3-thiocyanato-1*H*-indole (3j)



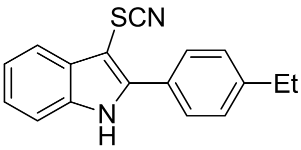
Isolated yield = 78%; yellow solid; m.p. 122.1-123.3 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.52 (s, 1 H), 7.73 (d, J = 7.2 Hz, 2 H), 7.47-7.56 (m, 4 H), 6.97 (s, 1 H), 2.50 (s, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 143.0, 133.4, 132.1, 130.5, 129.8, 129.6, 129.2, 128.8, 126.6, 120.7, 116.4, 112.2, 89.2, 21.7, 16.5; HRMS (ESI) calcd for $C_{17}H_{15}N_2S$ $[M+H]^+$ 279.0956, found 279.0960.

2-Thiocyanato-2-(p-tolyl)-1*H*-indole (3k)



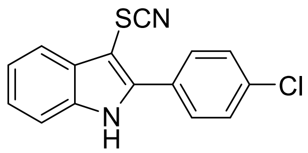
Known compound[2]; isolated yield = 88%; yellow solid; m.p. 151.7-155.7 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.74 (s, 1 H), 7.82-7.84 (m, 1 H), 7.62 (d, J = 7.9 Hz, 2 H), 7.41-7.43 (m, 1 H), 7.31-7.35 (m, 4 H), 2.45 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 143.4, 139.8, 135.4, 129.8, 129.8, 128.5, 127.1, 123.9, 122.0, 119.0, 112.0, 111.6, 88.6.

2-(4-Ethylphenyl)-3-thiocyanato-1H-indole (3l)



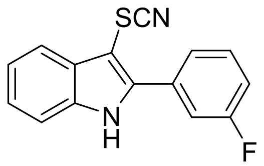
Isolated yield = 87%; yellow solid; m.p. 127.3-129.4 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 12.32 (s, 1 H), 7.77 (d, J = 7.9 Hz, 2 H), 7.70 (d, J = 7.1 Hz, 1 H), 7.53 (d, J = 8.0 Hz, 1 H), 7.45 (d, J = 7.7 Hz, 2 H), 7.25-7.32 (m, 2 H), 2.71 (q, J = 7.6 Hz, 2 H), 1.25 (t, J = 7.6 Hz, 3 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 145.3, 143.3, 135.8, 129.5, 129.2, 128.8, 128.3, 127.4, 123.3, 121.4, 117.9, 112.4, 86.6, 28.0, 15.4; HRMS (ESI) calcd for $C_{17}H_{15}N_2S$ $[M+H]^+$ 279.0956, found 279.0962.

2-(4-Chlorophenyl)-3-thiocyanato-1*H*-indole (3m)



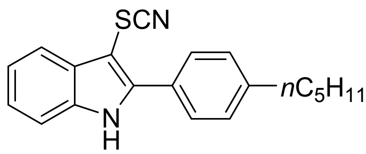
Known compound[2]; isolated yield = 83%; yellow solid; m.p. 122.5-123.9 ℃; ^1H NMR (DMSO-d_6, 400 MHz): δ = 12.45 (s, 1 H), 7.88 (d, J = 8.3 Hz, 2 H), 7.69-7.72 (m, 3 H), 7.55 (d, J = 7.6 Hz, 1 H), 7.27-7.34 (m, 2 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 141.7, 135.9, 134.2, 130.5, 129.1, 129.0, 128.8, 123.6, 121.5, 118.1, 112.5, 112.2, 87.8.

2-(3-Fluorophenyl)-3-thiocyanato-1*H*-indole (3n)



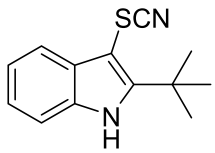
Isolated yield = 81%; yellow solid; m.p. 123.5-125.0 ℃; ^1H NMR (DMSO-d_6, 400 MHz): δ = 12.47 (s, 1 H), 7.65-7.74 (m, 4 H), 7.56 (d, J = 7.6 Hz, 1 H), 7.37-7.42 (m, 1 H), 7.28-7.36 (m, 2 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 162.6 (d, J = 242.7 Hz), 141.9 (d, J = 2.4 Hz), 136.3, 132.6 (d, J = 8.5 Hz), 131.5 (d, J = 8.5 Hz), 129.5, 125.4 (d, J = 2.6 Hz), 124.2, 122.0, 118.7, 116.6 (d, J = 20.8 Hz), 116.0 (d, J = 23.0 Hz), 113.0, 112.7, 86.6; HRMS (ESI) calcd for $C_{15}H_{10}FN_2S$ $[M+H]^+$ 269.0549, found 269.0553.

2-(4-Pentylphenyl)-3-thiocyanato-1*H*-indole (3o)



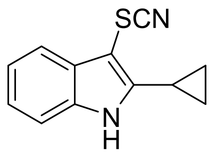
Isolated yield = 73%; yellow liquid; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 12.32 (s, 1 H), 7.76 (d, J = 7.8 Hz, 2 H), 7.70 (d, J = 7.4 Hz, 1 H), 7.52 (d, J = 7.1 Hz, 1 H), 7.43 (d, J = 7.8 Hz, 2 H), 7.25-7.32 (m, 2 H), 2.67 (t, J = 7.5 Hz, 2 H), 1.60-1.67 (m, 2 H), 1.32-1.33 (m, 4 H), 0.88 (t, J = 5.7 Hz, 3 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 143.9, 143.3, 135.8, 129.2, 128.8, 128.7, 127.4, 123.3, 121.4, 117.9, 112.4, 86.6, 34.9, 31.0, 30.5, 22.0, 13.9; HRMS (ESI) calcd for $C_{20}H_{21}N_2S$ $[M+H]^+$ 321.1425, found 321.1430.

2-(*Tert*-butyl)-3-thiocyanato-1*H*-indole (3p)



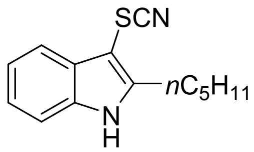
Isolated yield = 99%; yellow solid; m.p. 105.3-107.5 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 11.56 (s, 1 H), 7.58-7.60 (m, 1 H), 7.48-7.50 (m, 1 H), 7.18-7.23 (m, 2 H), 1.55 (s, 9 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 152.8, 134.4, 129.6, 122.3, 121.0, 117.0, 112.5, 112.2, 84.5, 33.5, 29.9; HRMS (ESI) calcd for $C_{13}H_{15}N_2S$ $[M+H]^+$ 231.0956, found 231.0961.

2-Cyclopropyl-3-thiocyanato-1*H*-indole (3q)



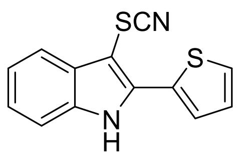
Isolated yield = 97%; yellow solid; m.p. 104.8-106.7 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 11.50 (s, 1 H), 7.53-7.54 (m, 1 H), 7.37-7.39 (m, 1 H), 7.16-7.19 (m, 2 H), 2.33-2.40 (m, 1 H), 1.16-1.21 (m, 2 H), 1.05-1.06 (m, 2 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 148.4, 135.2, 128.6, 122.2, 120.9, 116.8, 112.2, 111.8, 86.6, 8.6, 8.1; HRMS (ESI) calcd for $C_{12}H_{11}N_2S$ $[M+H]^+$ 215.0643, found 215.0638.

2-Pentyl-3-thiocyanato-1*H*-indole (3r)



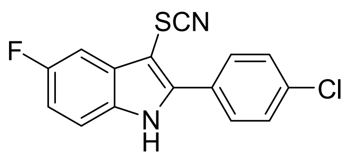
Isolated yield = 89%; yellow solid; m.p. 107.3-109.3 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 11.93 (s, 1 H), 7.56-7.58 (m, 1 H), 7.42-7.44 (m, 1 H), 7.18-7.22 (m, 2 H), 2.91 (t, J = 7.4 Hz, 2 H), 7.70-1.77 (m, 2 H), 1.31-1.34 (m, 2 H), 0.87 (t, J = 6.4 Hz, 3 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 147.2, 135.5, 128.3, 122.3, 120.8, 117.2, 112.2, 112.0, 86.4, 30.7, 28.4, 25.7, 21.8, 13.8; HRMS (ESI) calcd for $C_{15}H_{17}N_2S$ $[M+H]^+$ 257.1112, found 257.1108.

3-Thiocyanato-2-(thiophen-2-yl)-1*H*-indole (3s)



Isolated yield = 86%; yellow solid; m.p. 162.5-165.0 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 12.33 (s, 1 H), 8.21 (s, 1 H), 7.81-7.82 (m, 2 H), 7.68 (d, J = 7.5 Hz, 1 H), 7.52 (d, J = 7.7 Hz, 1 H), 7.24-7.31 (m, 2 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 138.5, 135.6, 130.7, 129.2, 127.6, 126.9, 125.8, 123.4, 121.4, 117.9, 112.3, 112.1, 86.4; HRMS (ESI) calcd for $C_{13}H_9N_2S_2$ $[M+H]^+$ 266.0911, found 266.0915.

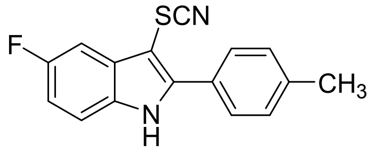
2-(4-Chlorophenyl)-5-fluoro-3-thiocyanato-1*H*-indole (3t)



Isolated yield = 84%; yellow solid; m.p. 147.1-149.1 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 12.58 (s, 1 H), 7.87 (d, J = 7.8 Hz, 1 H), 7.70 (d, J = 7.4 Hz, 1 H), 7.54-7.57 (m, 1 H), 7.45 (d, J = 9.0 Hz, 1 H), 7.15-7.19 (m, 1 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 158.3 (d, J = 234.9 Hz), 143.5, 134.4, 132.4, 130.5, 129.9 (d, J = 10.5 Hz), 129.1, 128.6, 114.4 (d, J = 9.5 Hz), 112.1 (d, J = 7.3 Hz), 111.9, 103.1 (d, J = 24.5 Hz), 88.1; HRMS (ESI) calcd for $C_{15}H_9ClFN_2S$ $[M+H]^+$ 303.0159, found

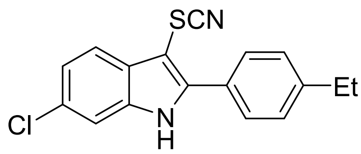
303.0162.

5-Fluoro-3-thiocyanato-2-(p-tolyl)-1*H*-indole (3u)



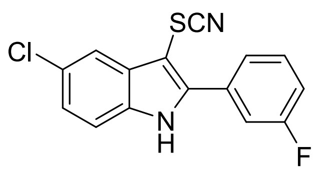
Isolated yield = 82%; yellow solid; m.p. 143.0-144.7 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 12.45 (s, 1 H), 7.75 (d, J = 7.8 Hz, 2 H), 7.51-7.54 (m, 1 H), 7.42 (d, J = 7.7 Hz, 3 H), 7.12-7.16 (m, 1 H), 2.41 (s, 3 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 158.2 (d, J = 233.8 Hz), 145.1, 139.4, 132.3, 130.0 (d, J = 10.2 Hz), 129.5, 128.6, 126.9, 113.9 (d, J = 9.8 Hz), 112.2, 111.6 (d, J = 25.9 Hz), 102.9 (d, J = 24.5 Hz), 87.0, 21.0; HRMS (ESI) calcd for $C_{16}H_{12}FN_2S$ $[M+H]^+$ 283.0705, found 283.0712.

6-Chloro-2-(4-ethylphenyl)-3-thiocyanato-1*H*-indole (3v)



Isolated yield = 75%; yellow solid; m.p. 161.3-163.6 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 12.48 (s, 1 H), 7.77 (d, J = 8.0 Hz, 2 H), 7.70 (d, J = 8.4 Hz, 1 H), 7.54 (s, 1 H), 7.46 (d, J = 7.9 Hz, 2 H), 7.26-7.34 (m, 1 H), 2.71 (q, J = 7.6 Hz, 2 H), 1.25 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 145.6, 144.3, 136.2, 128.7, 128.4, 128.0, 127.8, 127.0, 121.8, 119.4, 112.2, 111.9, 87.4, 28.0, 15.4; HRMS (ESI) calcd for $C_{17}H_{14}ClN_2S$ $[M+H]^+$ 313.0566, found 313.0570.

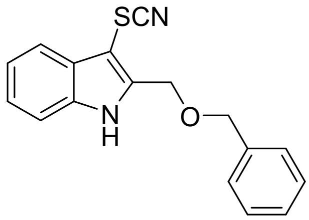
5-Chloro-2-(3-fluorophenyl)-3-thiocyanato-1*H*-indole (3w)



Isolated yield = 97%; yellow solid; m.p. 110.1-113.8 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 12.61 (s, 1 H), 7.66-7.72 (m, 4 H), 7.57 (s, 1 H), 7.39 (s, 1 H), 7.29 (d, J =

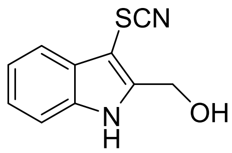
8.3 Hz, 2 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 162.2 (d, J = 242.6 Hz), 142.4 (d, J = 2.4 Hz), 136.2, 131.8 (d, J = 8.3 Hz), 131.2 (d, J = 8.4 Hz), 128.4, 128.0, 125.0, 122.1, 119.7, 119.4 (d, J = 20.6 Hz), 115.6 (d, J = 23,1 Hz), 112.2, 112.1, 88.1； HRMS (ESI) calcd for $C_{15}H_9ClFN_2S$ $[M+H]^+$ 303.0159, found 303.0163.

2-((Benzyloxy)methyl)-3-thiocyanato-1*H*-indole (3x)



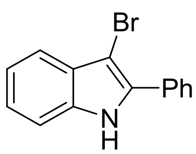
Isolated yield = 71%; yellow liquid; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 12.25 (s, 1 H), 7.65 (d, J = 7.4 Hz, 1 H), 7.51 (d, J = 7.7 Hz, 1 H), 7.35-7.40 (m, 4 H), 7.22-7.32 (m, 3 H), 4.83 (s, 2 H), 4.60 (s, 2 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 141.7, 137.8, 135.8, 128.4, 127.8, 127.8, 127.7, 123.3, 121.2, 117.8, 112.6, 112.0, 88.8, 71.8, 62.4.； HRMS (ESI) calcd for $C_{17}H_{15}N_2OS$ $[M+H]^+$ 295.0905, found 295.0911.

(3-Thiocyanato-1*H*-indol-2-yl)methanol (3y)



Isolated yield = 68%; yellow solid; m.p. 121.5-124.2 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 12.05 (s, 1 H), 7.61 (d, J = 7.6 Hz, 1 H), 7.48 (d, J = 7.0 Hz, 1 H), 7.19-7.25 (m, 2 H), 5.63 (t, J = 5.4 Hz, 1 H), 4.79 (d, J = 5.3 Hz, 2 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 145.7, 135.6, 128.1, 122.7, 121.0, 117.5, 112.5, 112.0, 85.9, 54.8； HRMS (ESI) calcd for $C_{10}H_9N_2OS$ $[M+H]^+$ 214.1140, found 214.1138.

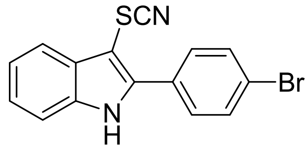
3-Bromo-2-phenyl-1*H*-indole (E)



Known compound[3]; Isolated yield = 51%; yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz):

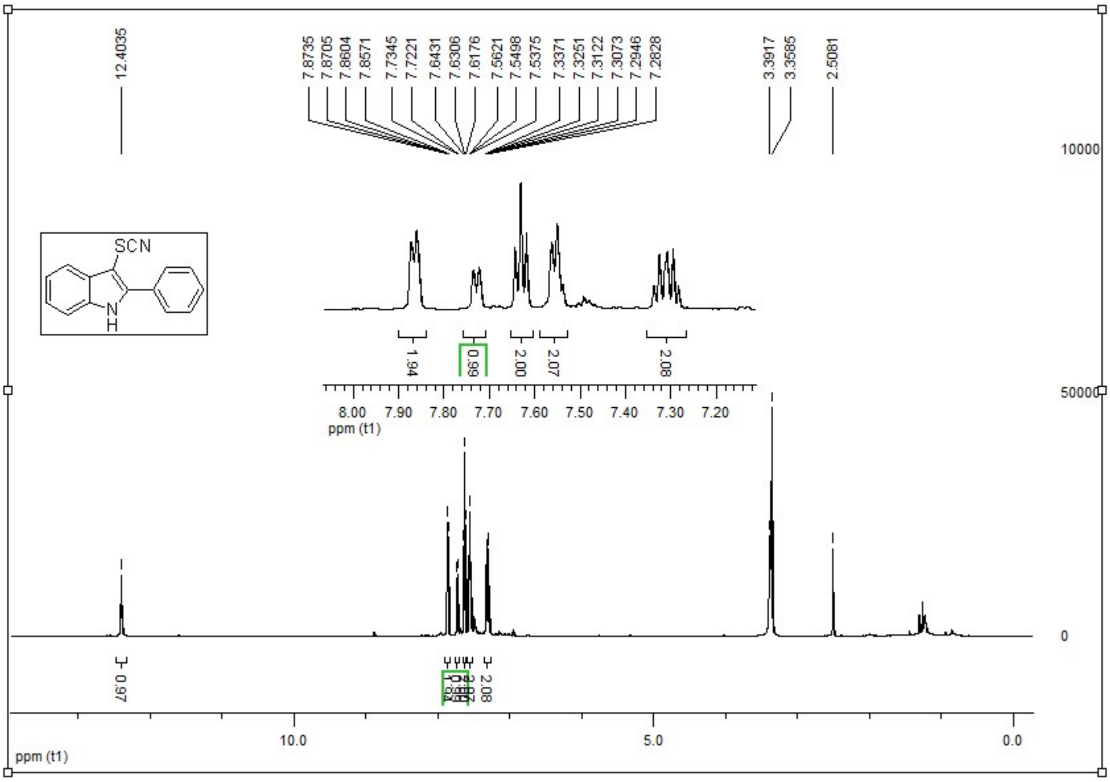
δ = 8.32 (s, 1 H), 7.85 (d, *J* = 4.9 Hz, 2 H), 7.66 (d, *J* = 5.2 Hz, 1 H), 7.53 (m, 2 H), 7.44 (m, 1 H), 7.41 (d, *J* = 5.3 Hz, 1 H), 7.28 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 135.4, 134.4, 131.5, 129.0, 128.9, 128.5, 127.9, 123.6, 121.1, 119.7, 111.2, 90.2.

2-(4-Bromophenyl)-3-thiocyanato-1*H*-indole (3z)



Isolated yield = 71%; yellow solid; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 12.46 (s, 1 H), 7.80-7.85 (m, 4 H), 7.72 (d, *J* = 7.6 Hz, 1 H), 7.56 (d, *J* = 8.0 Hz, 1 H), 7.27-7.34 (m, 2 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 141.7, 135.9, 131.9, 130.7, 129.1, 129.1, 123.6, 122.9, 121.5, 118.1, 112.5, 112.1, 87.7; HRMS (ESI) calcd for $C_{15}H_{10}Br N_2S$ $[M+H]^+$ 328.9748, found 328.9743.

Figure 1. ^{1}H and ^{13}C NMR Spectra of **2-Phenyl-3-thiocyanato-1*H*-indole (3a)**



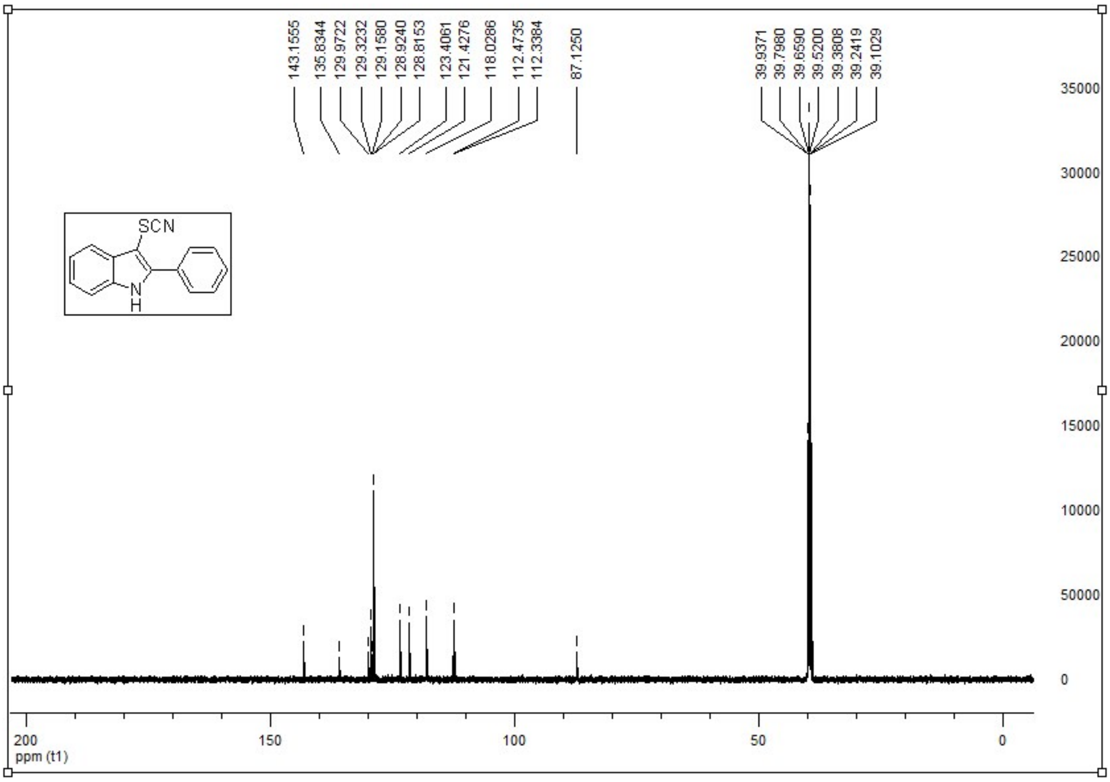
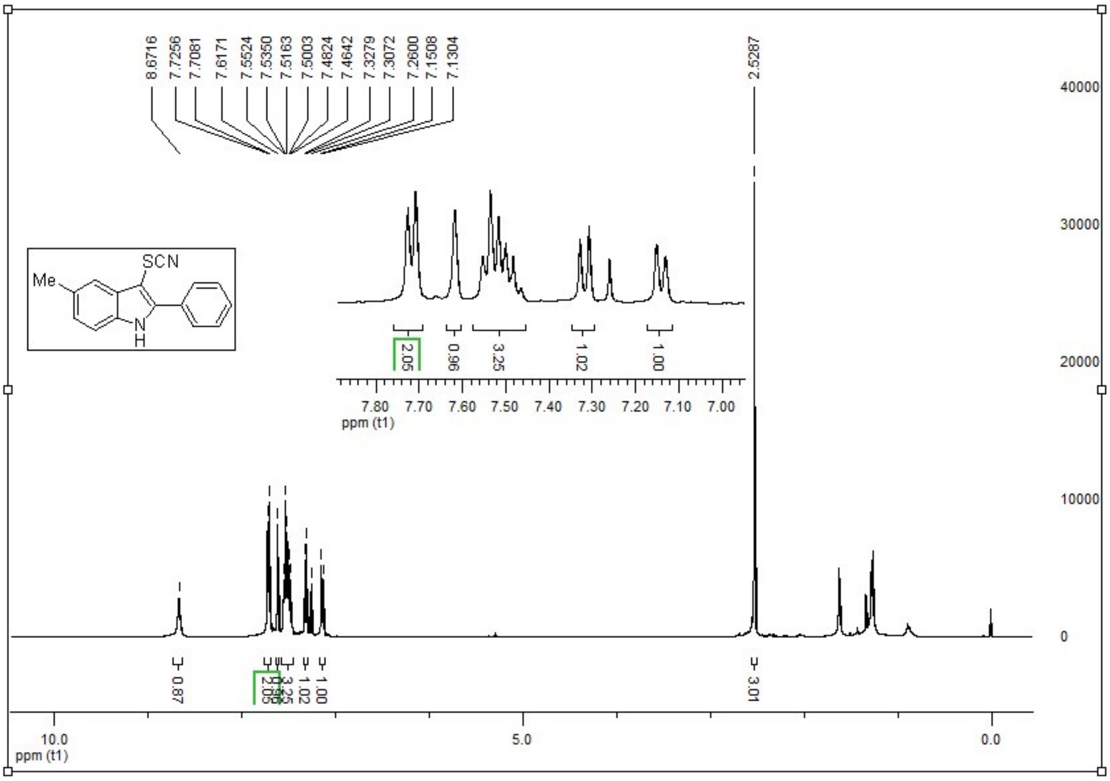


Figure 2. ^{1}H and ^{13}C NMR Spectra of

5-Methyl-2-phenyl-3-thiocyanato-1*H*-indole (3b)



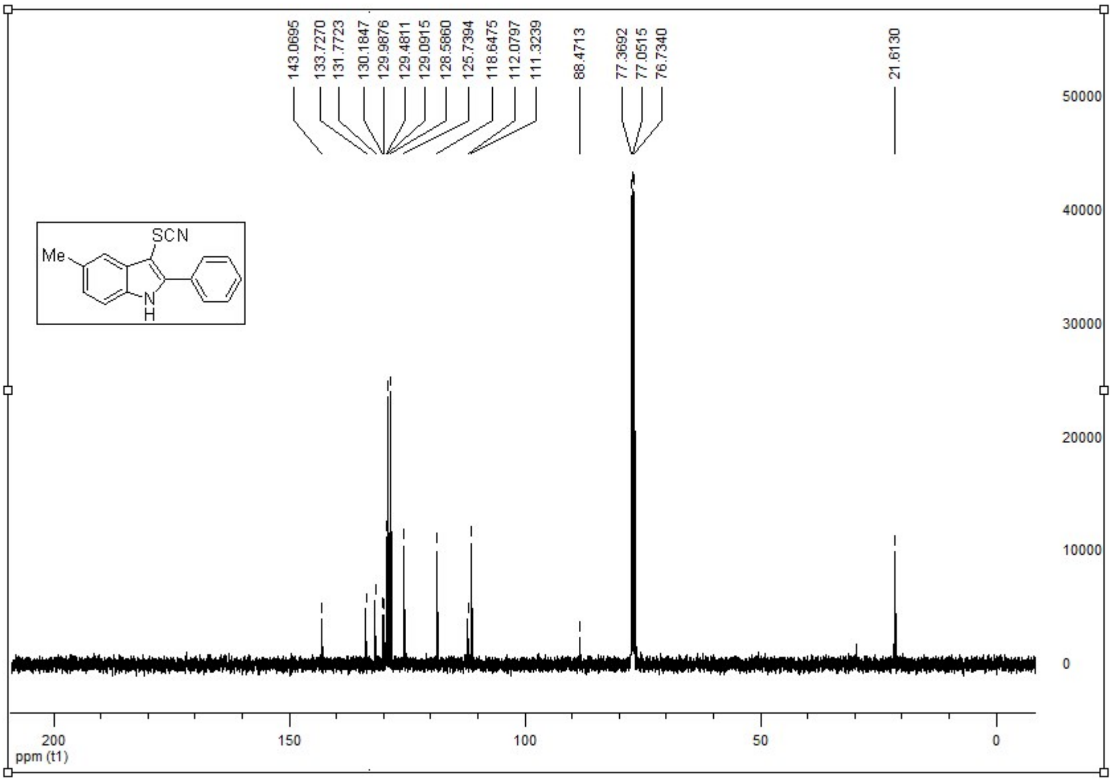
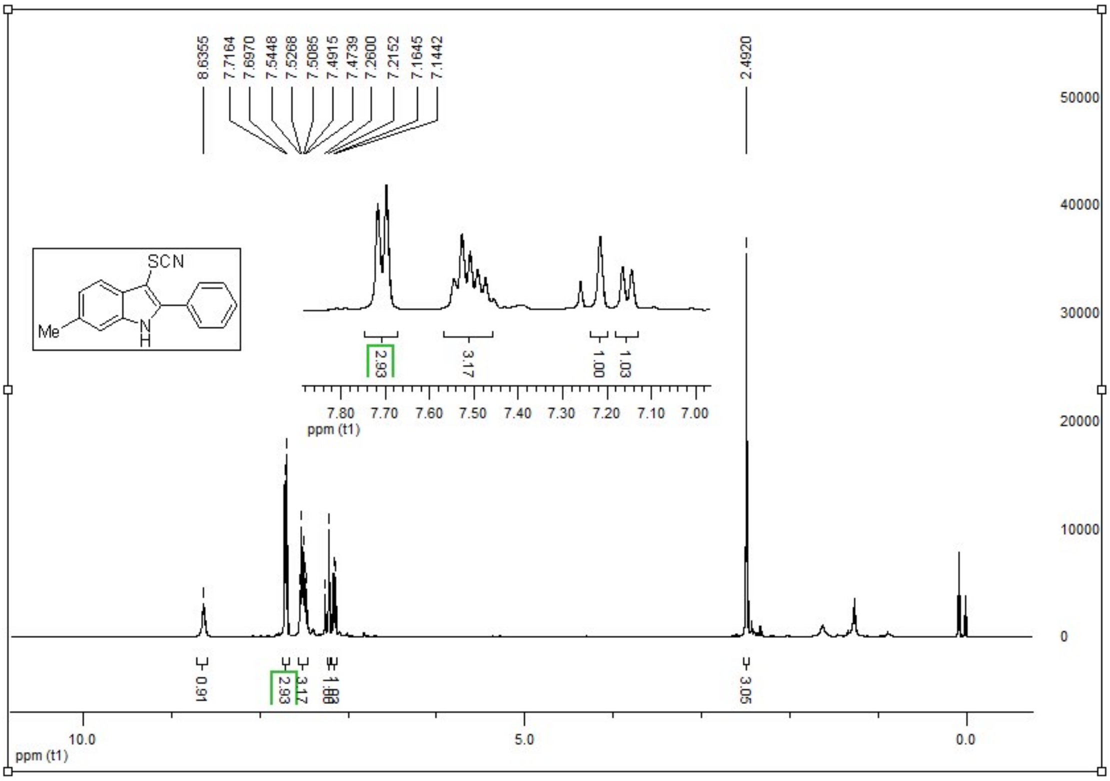


Figure 3. ^{1}H and ^{13}C NMR Spectra of
6-Methyl-2-phenyl-3-thiocyanato-1*H*-indole (3c)



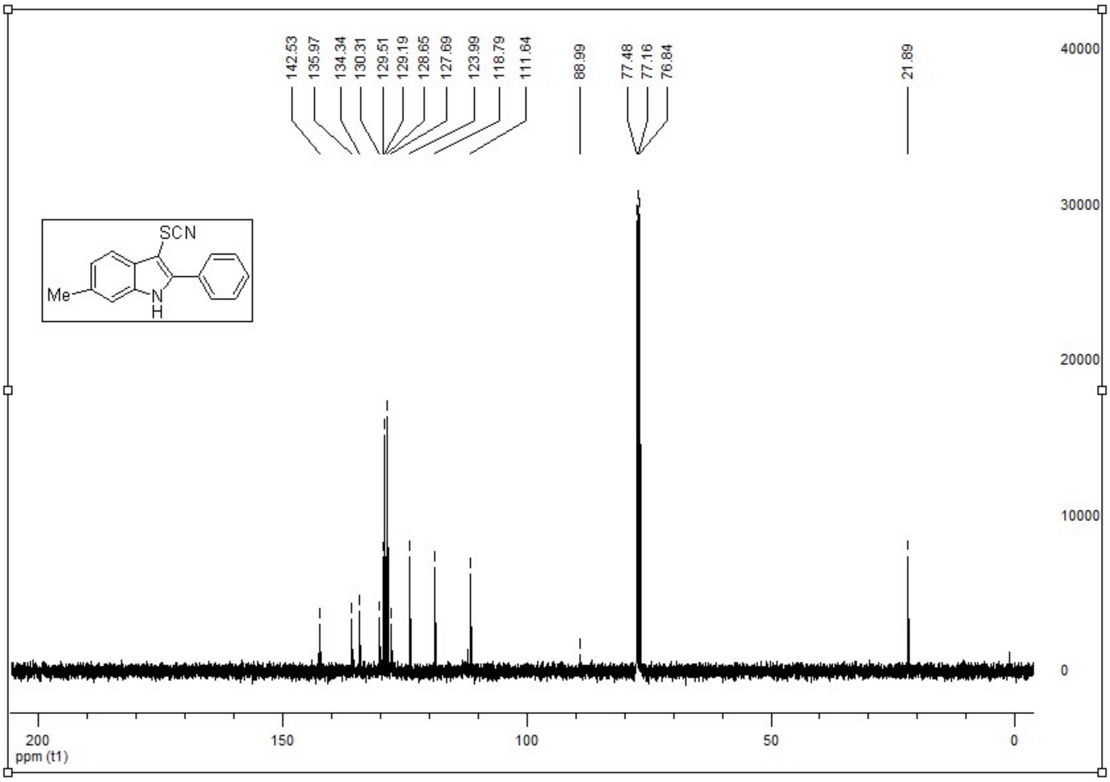
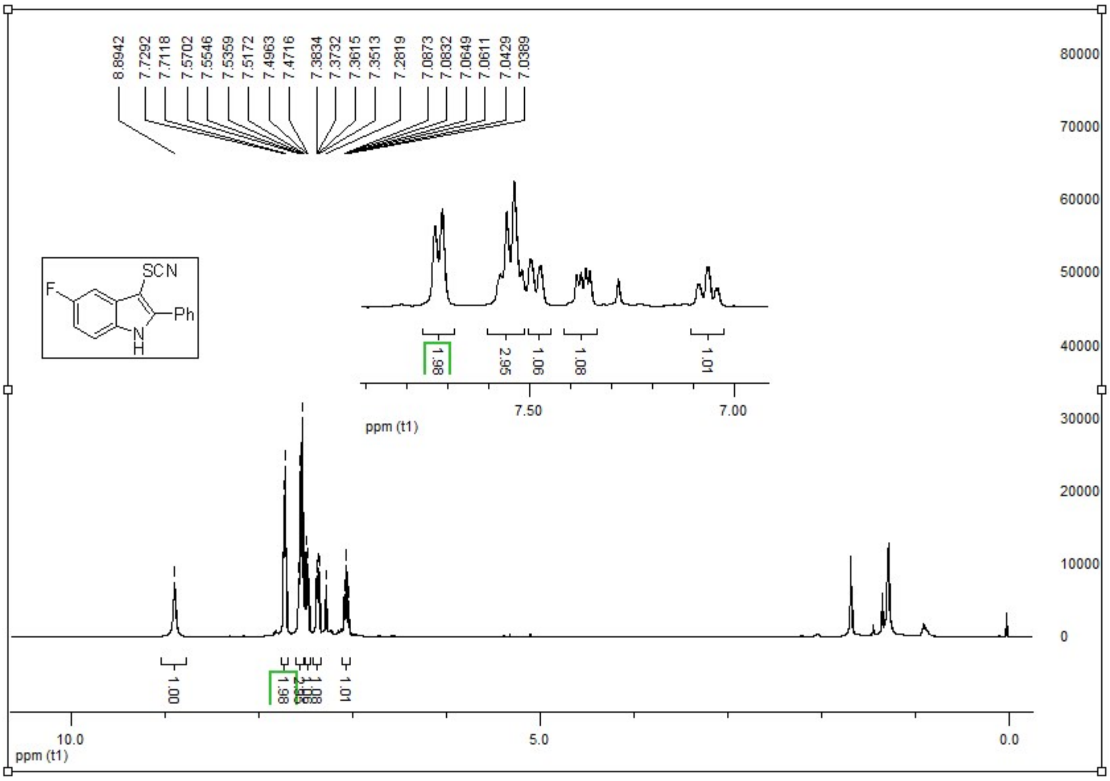


Figure 4. ^{1}H and ^{13}C NMR Spectra of
6-Fluoro-2-phenyl-3-thiocyanato-1*H*-indole (3d)



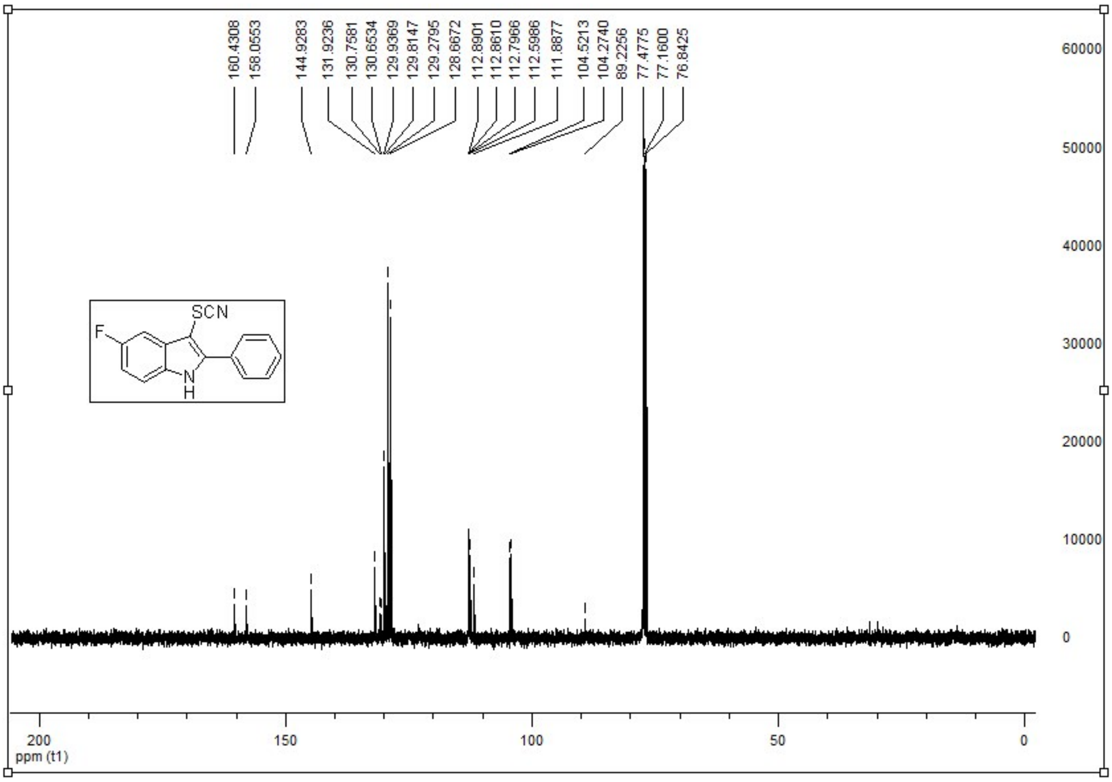
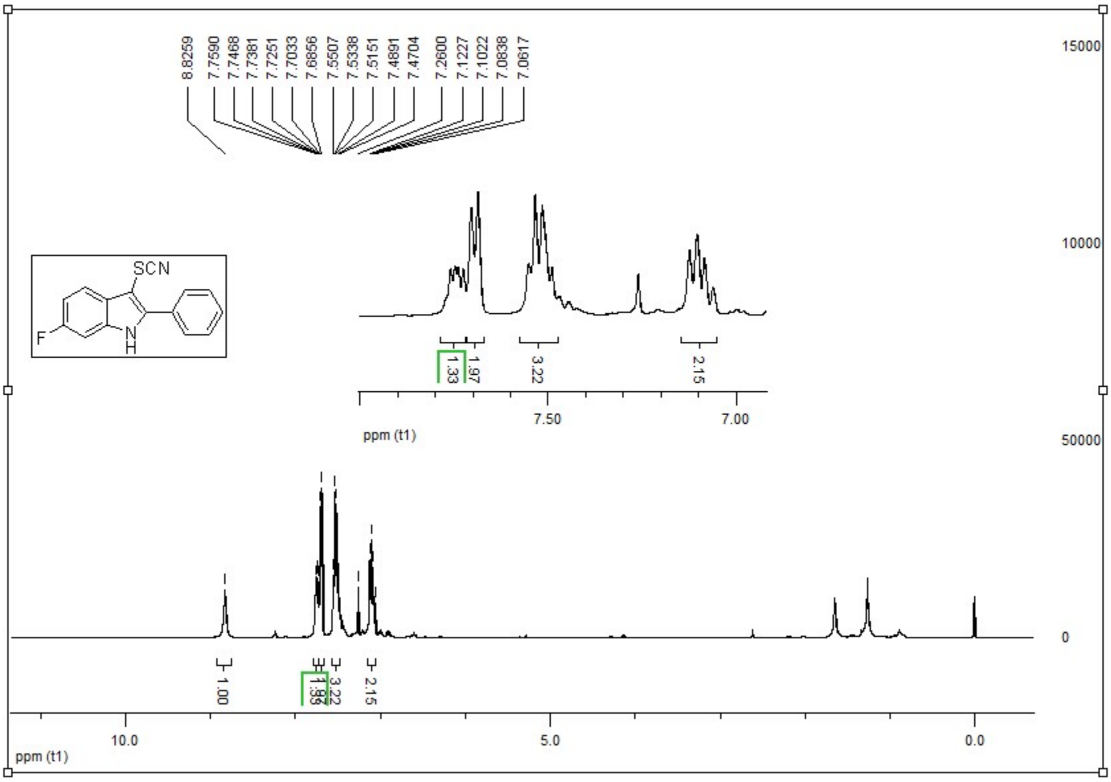


Figure 5. ^{1}H and ^{13}C NMR Spectra of

6-Fluoro-2-phenyl-3-thiocyanato-1*H*-indole (3e)



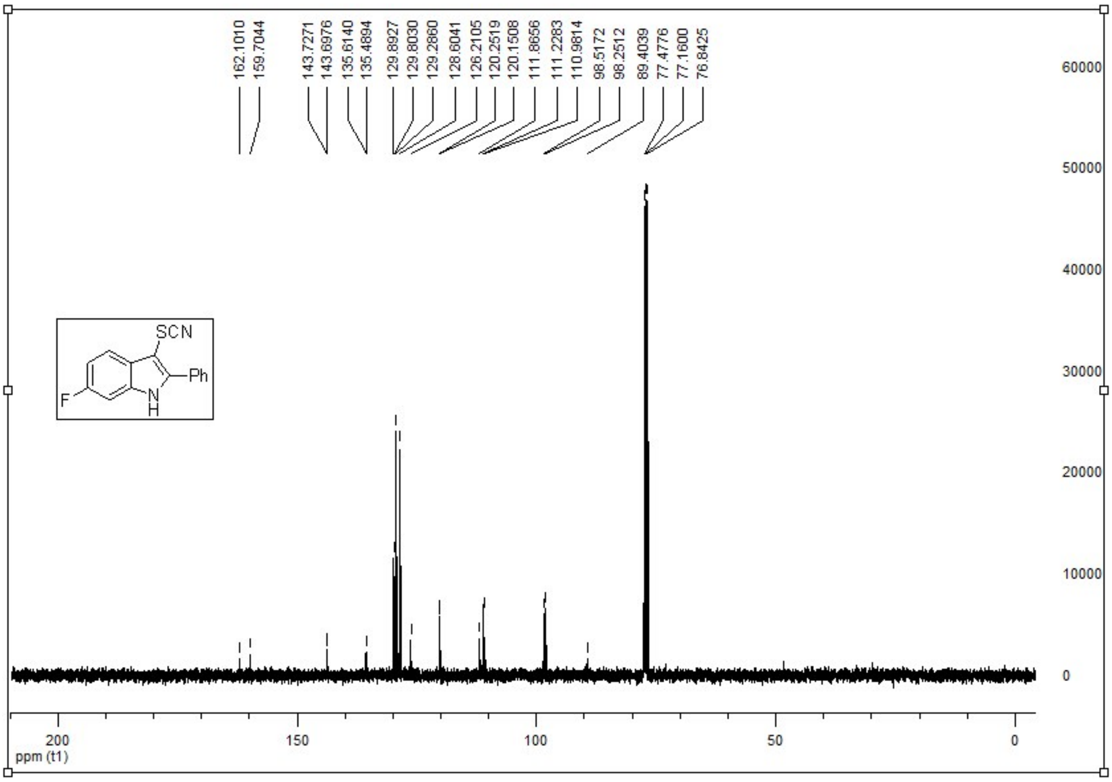
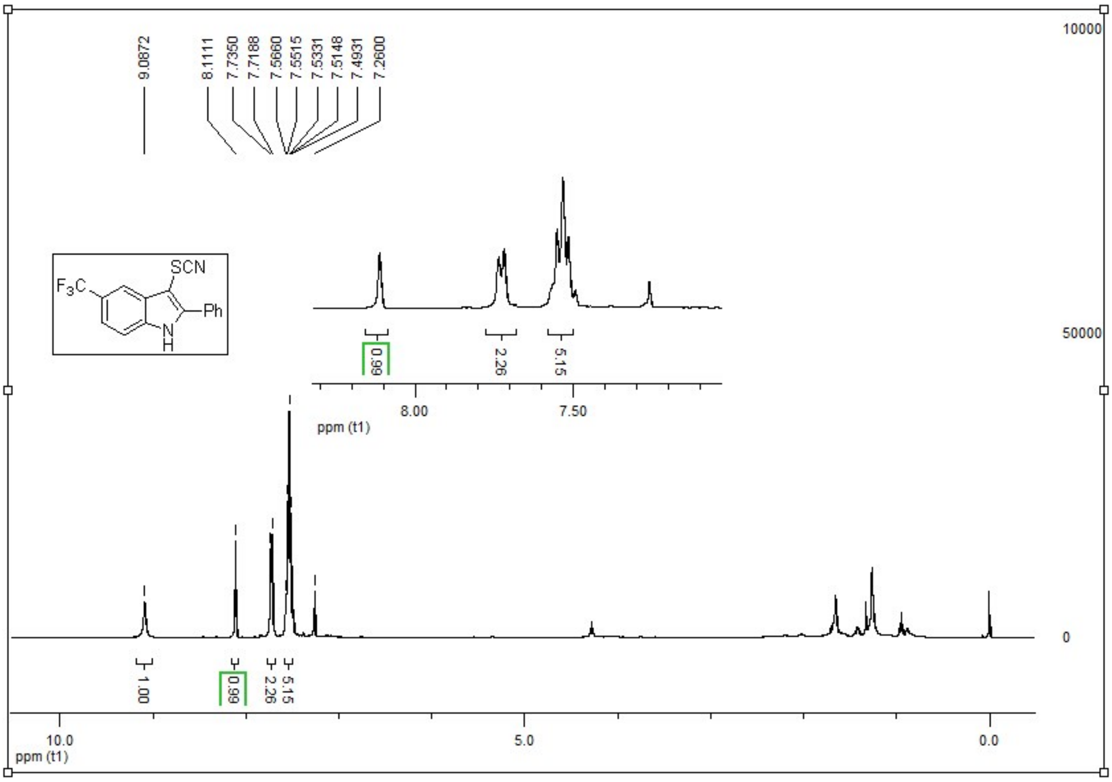


Figure 6. ^{1}H and ^{13}C NMR Spectra of **2-Phenyl-3-thiocyanato-5-(trifluoromethyl)-1*H*-indole (3f)**



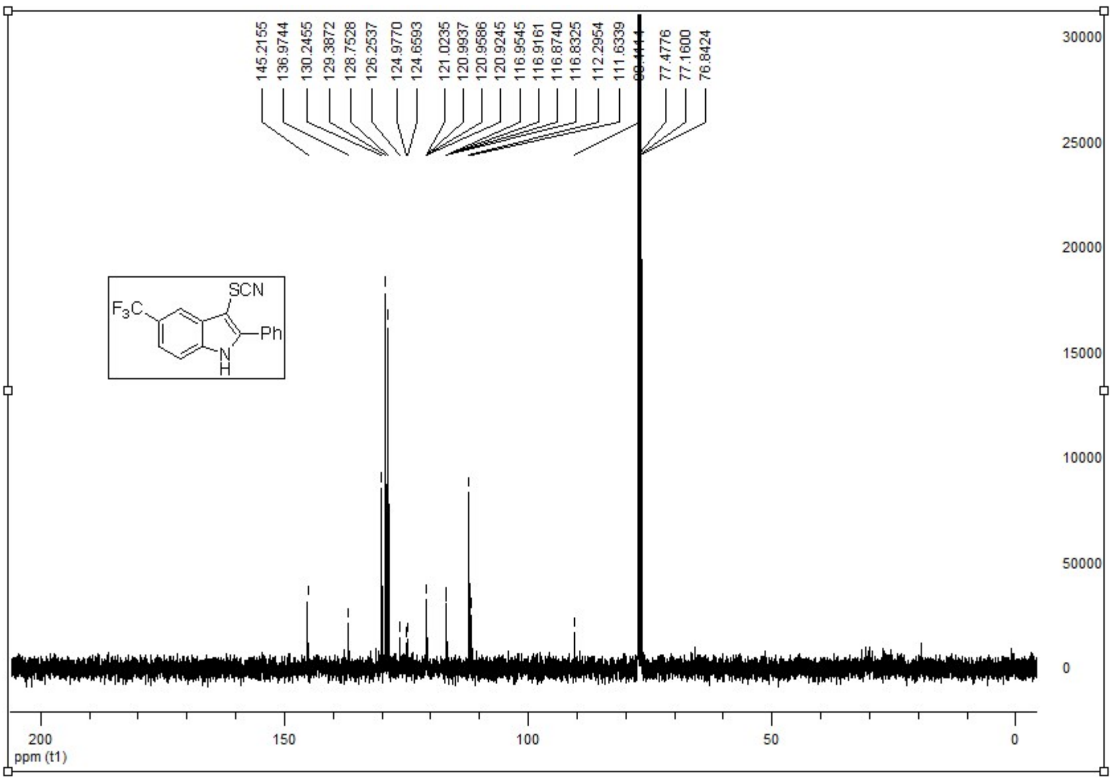
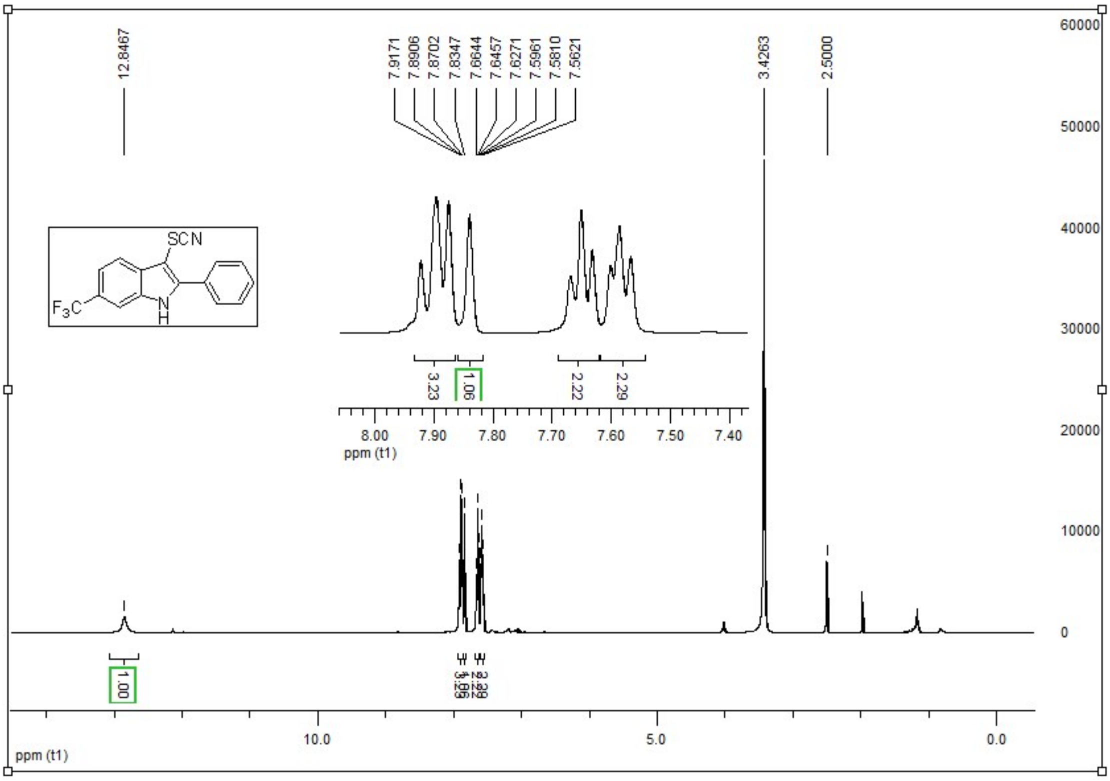


Figure 7. ^{1}H and ^{13}C NMR Spectra of

2-Phenyl-3-thiocyanato-6-(trifluoromethyl)-1*H*-indole (3g)



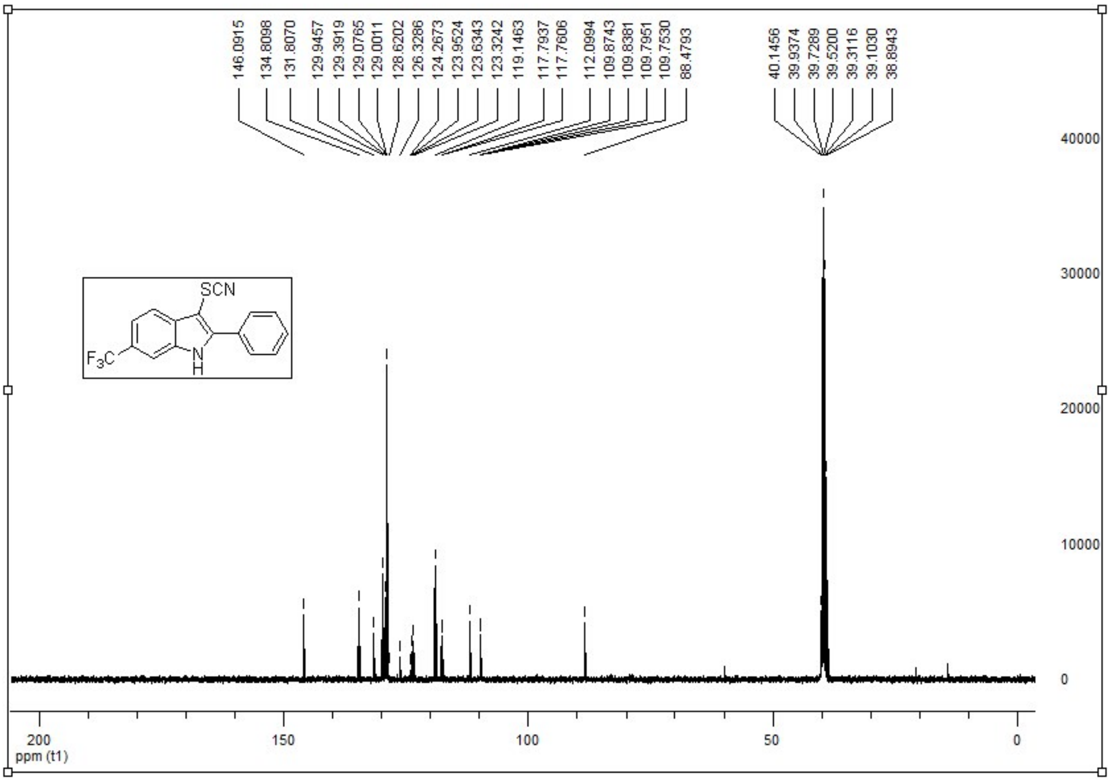
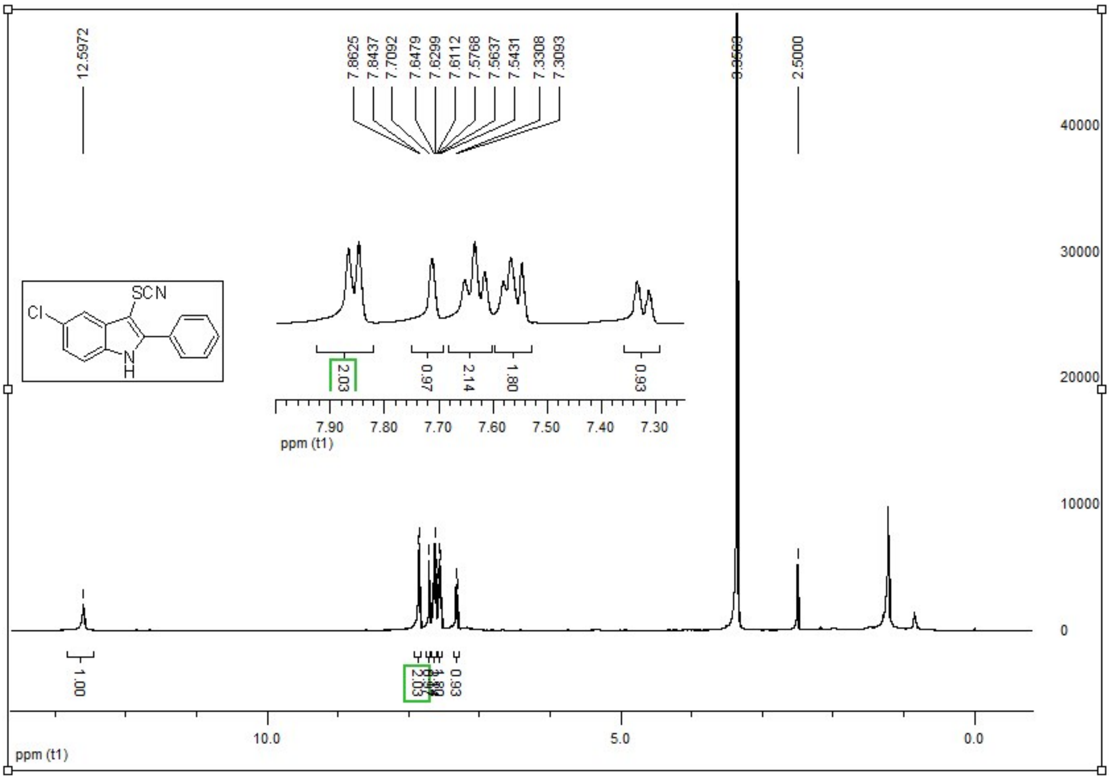


Figure 8. ^{1}H and ^{13}C NMR Spectra of
5-Chloro-2-phenyl-3-thiocyanato-1*H*-indole (3h)



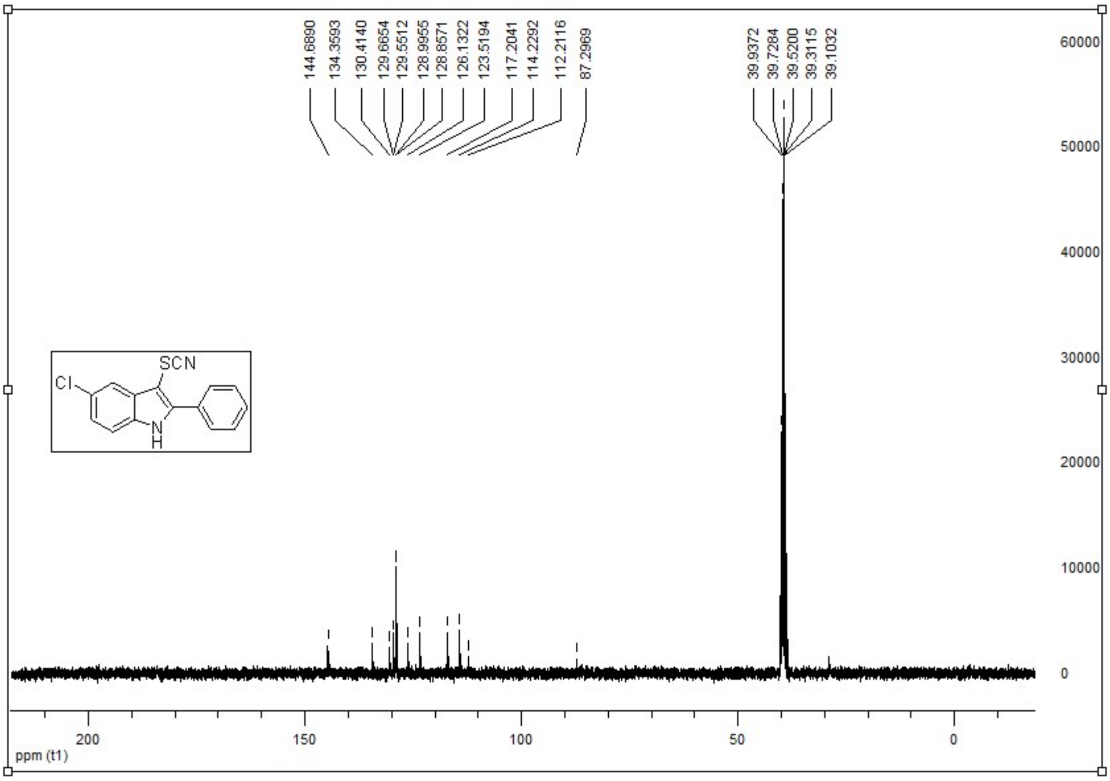
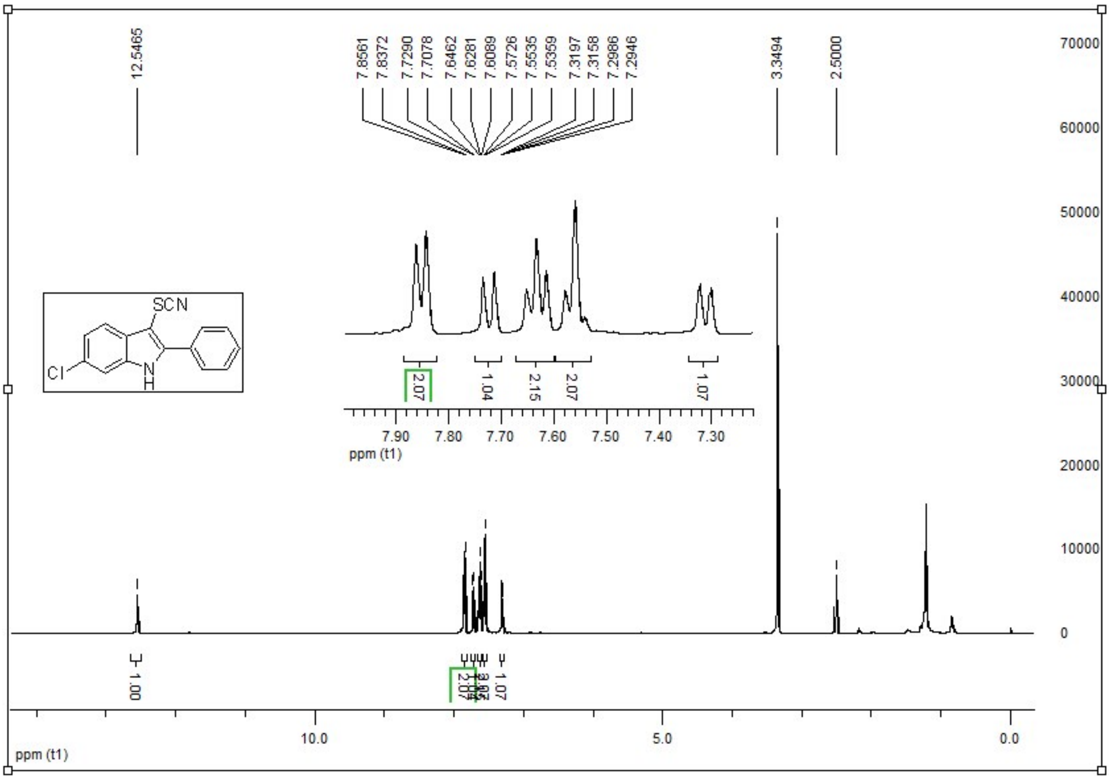


Figure 9. ^{1}H and ^{13}C NMR Spectra of

6-Chloro-2-phenyl-3-thiocyanato-1*H*-indole (3i)



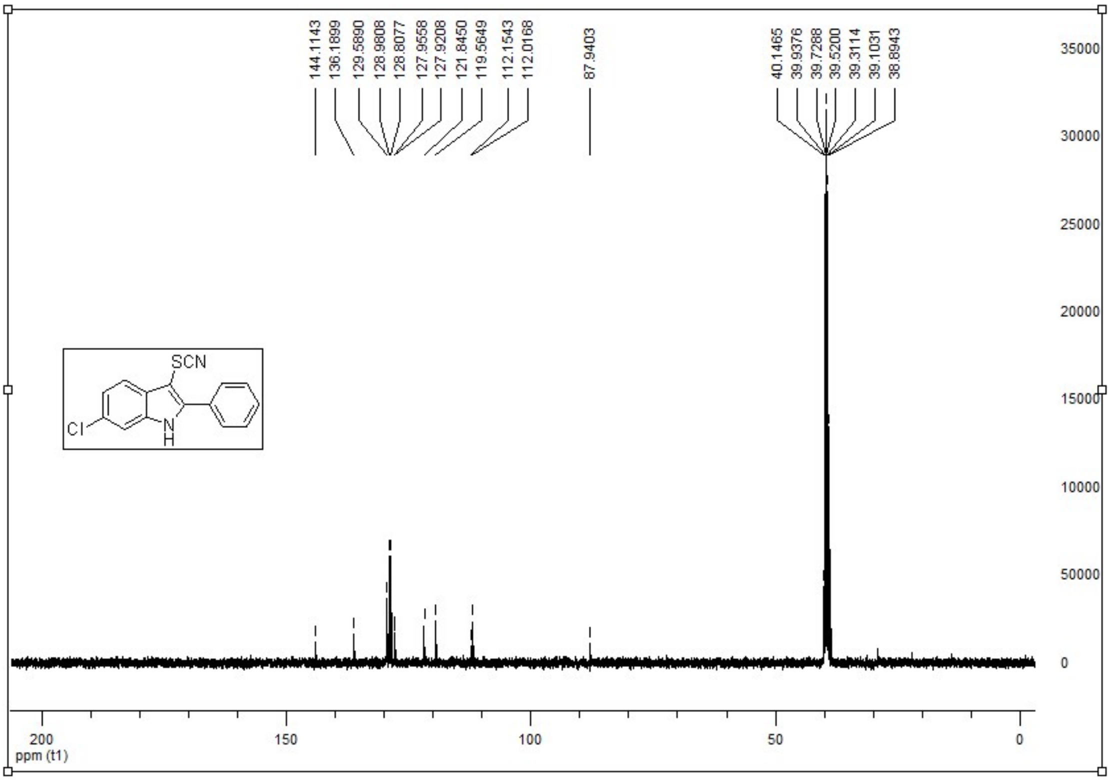
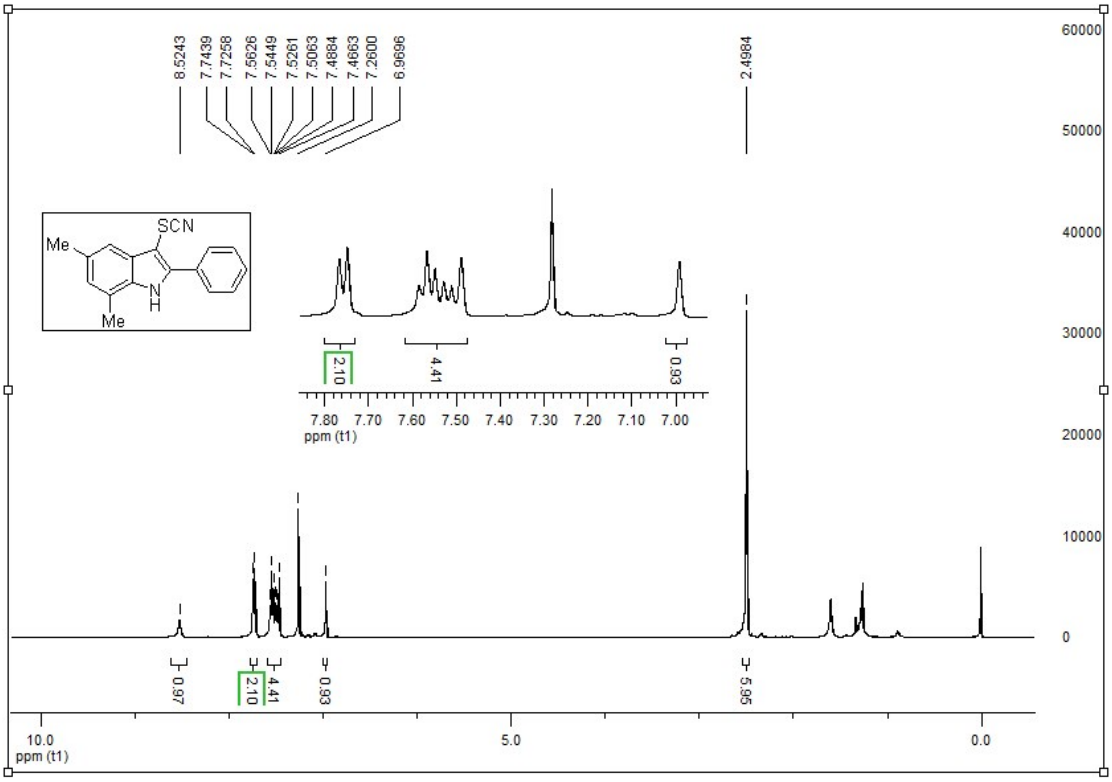


Figure 10. ^1H and ^{13}C NMR Spectra of **5,7-Dimethyl-2-phenyl-3-thiocyanato-1*H*-indole (3j)**



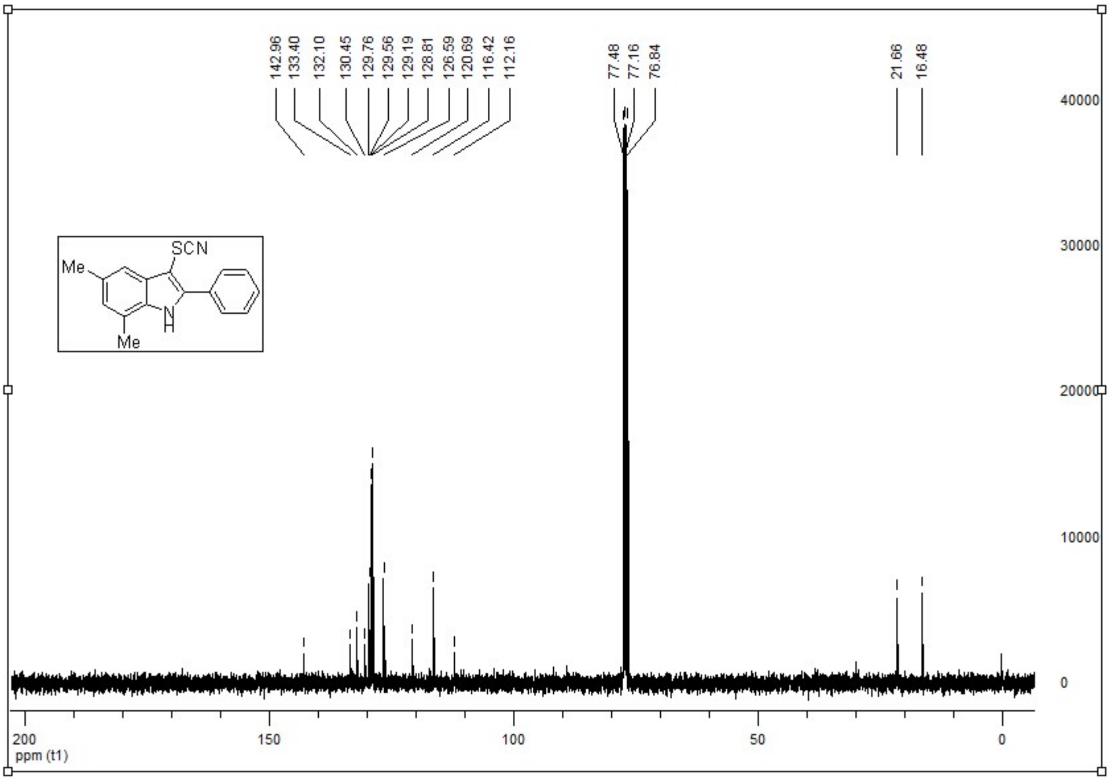
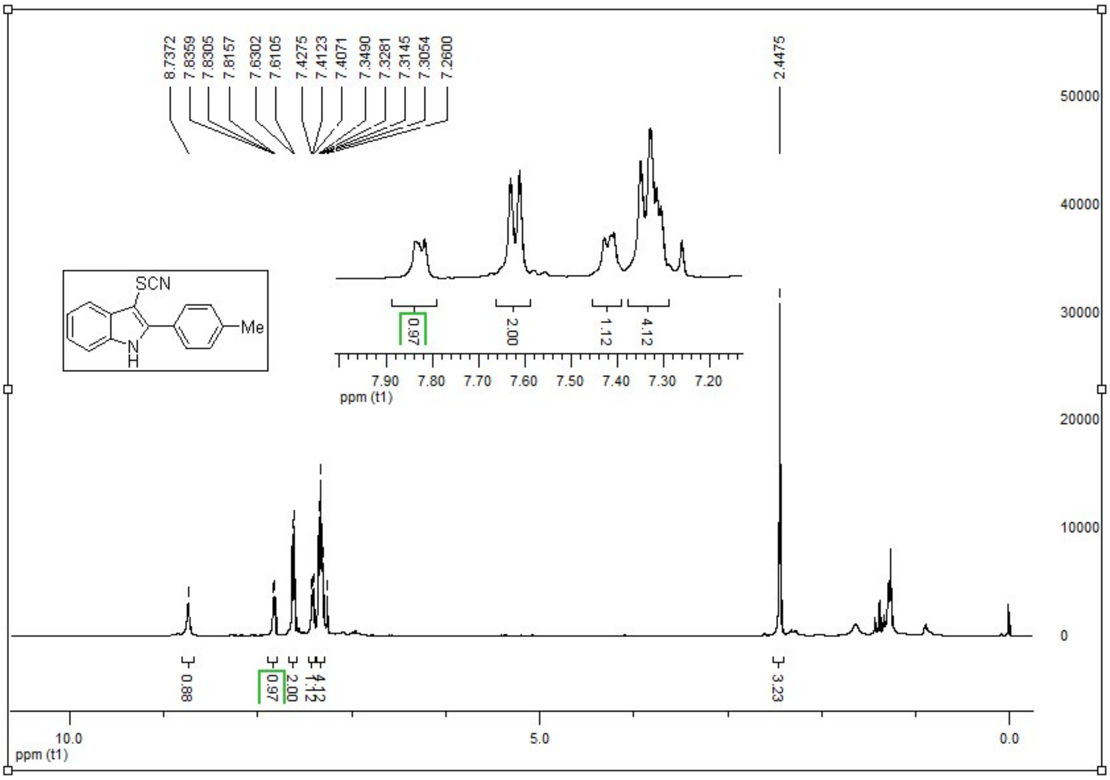


Figure 11. ^{1}H and ^{13}C NMR Spectra of **3-Thiocyanato-2-(p-tolyl)-1*H*-indole (3k)**



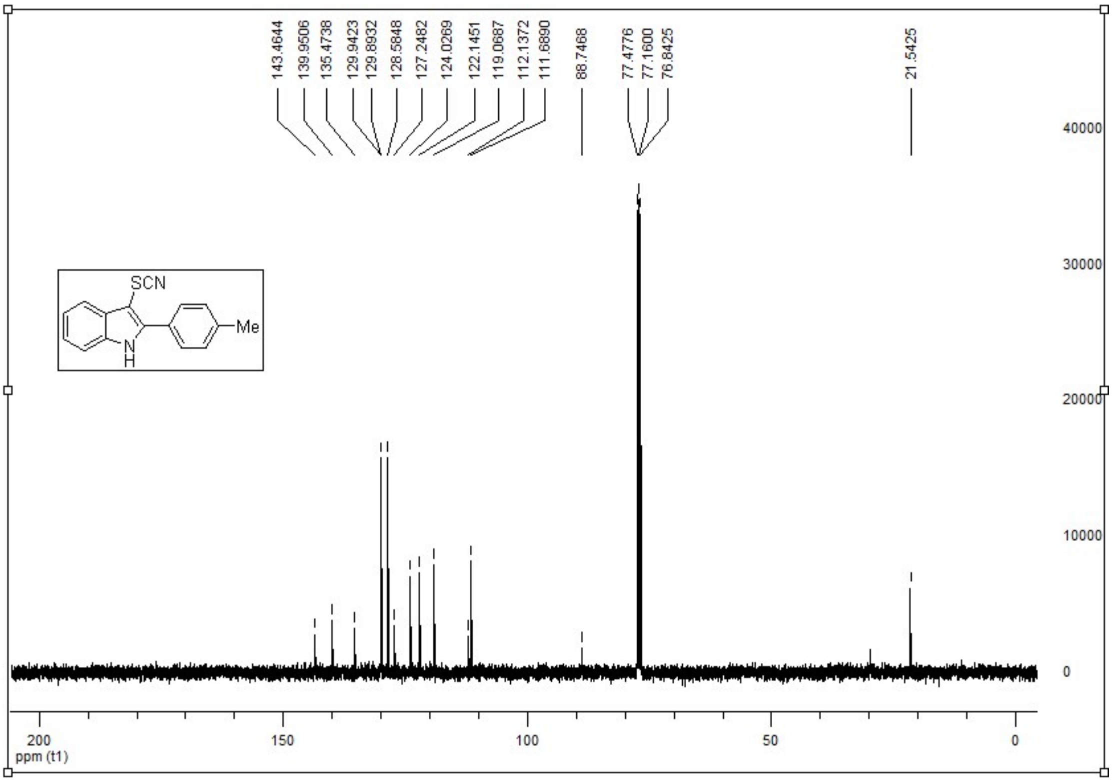
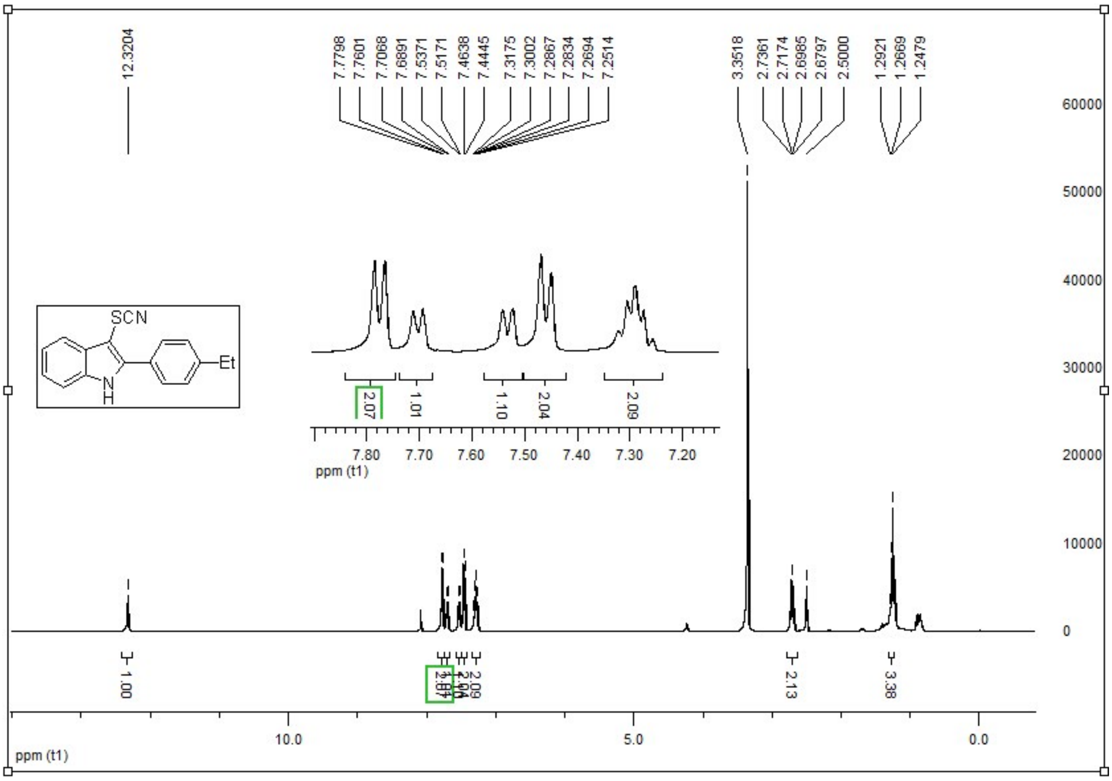


Figure 12. ^{1}H and ^{13}C NMR Spectra of
2-(4-Ethylphenyl)-3-thiocyanato-1H-indole (3l)



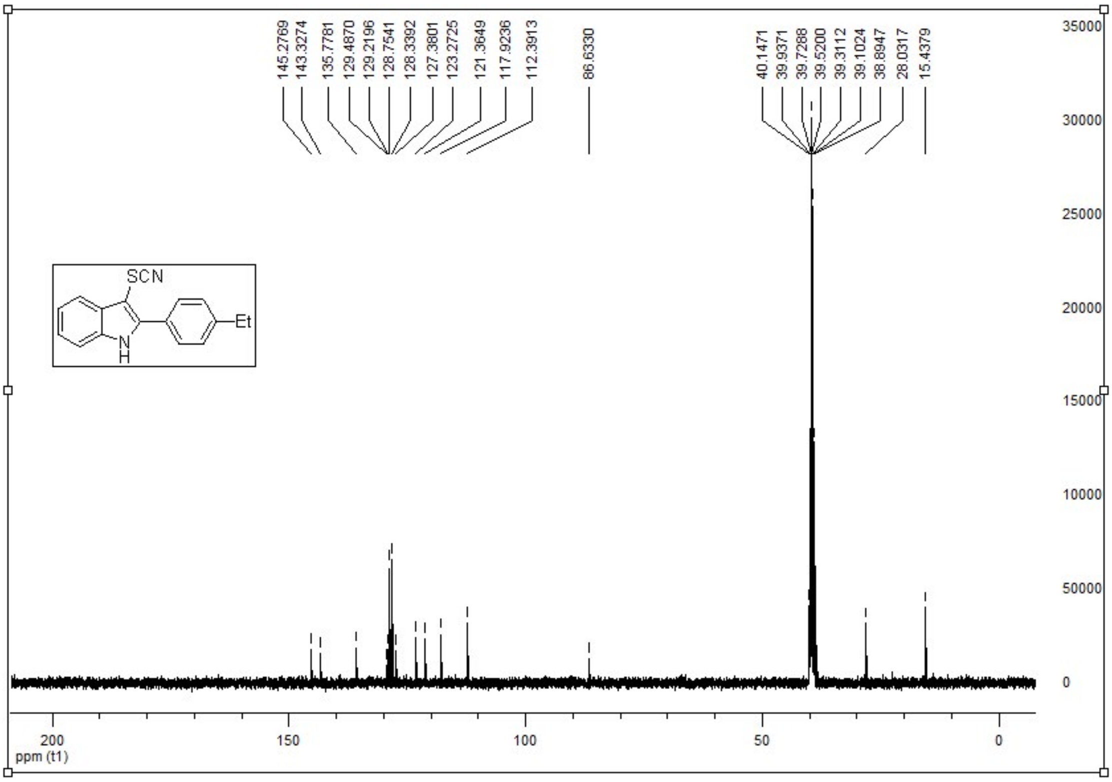
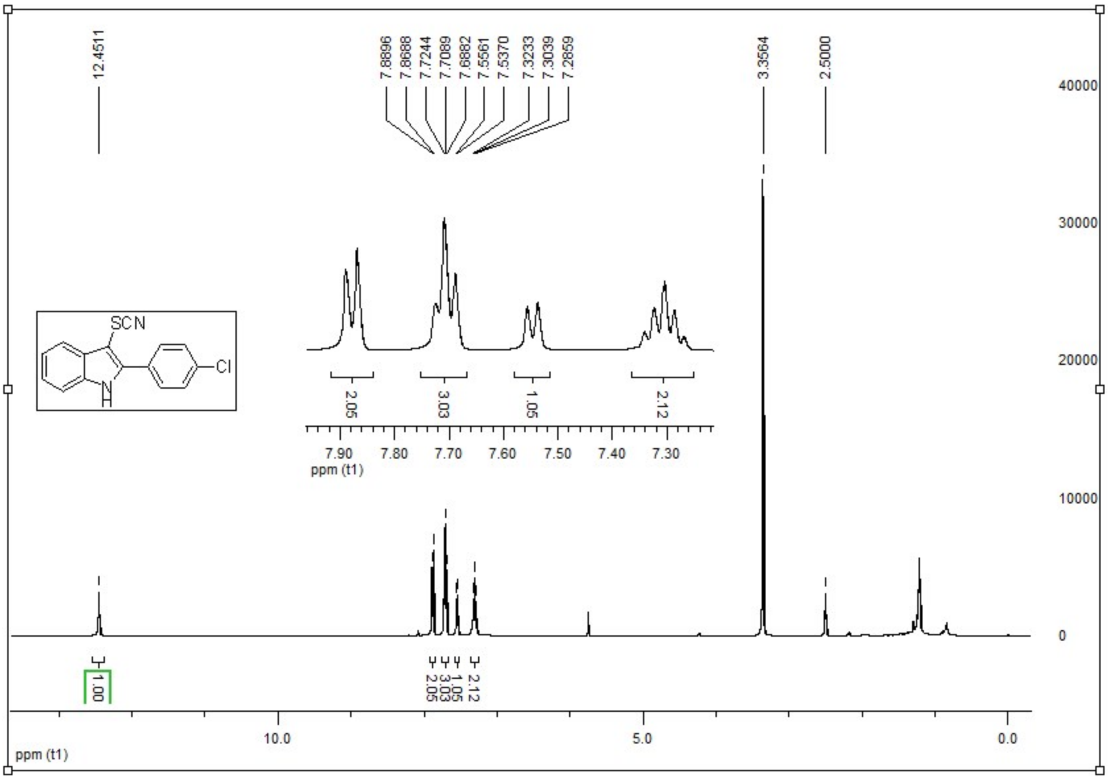


Figure 13. ^{1}H and ^{13}C NMR Spectra of **2-(4-Chlorophenyl)-3-thiocyanato-1*H*-indole (3m)**



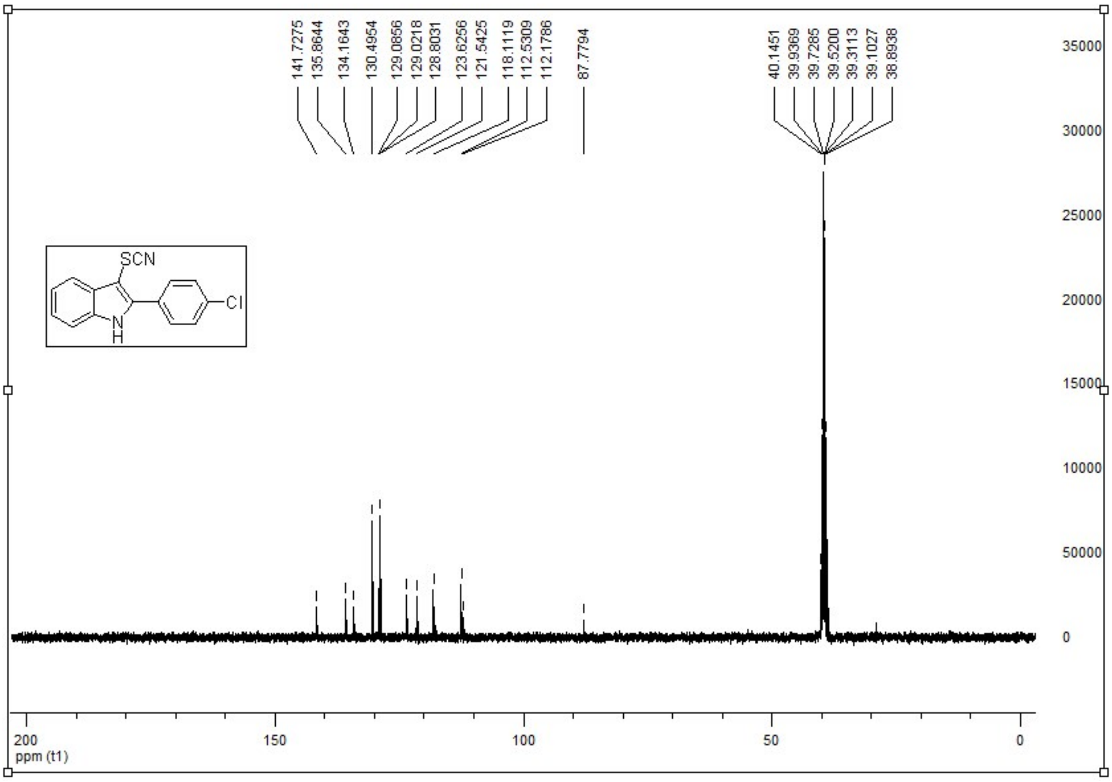
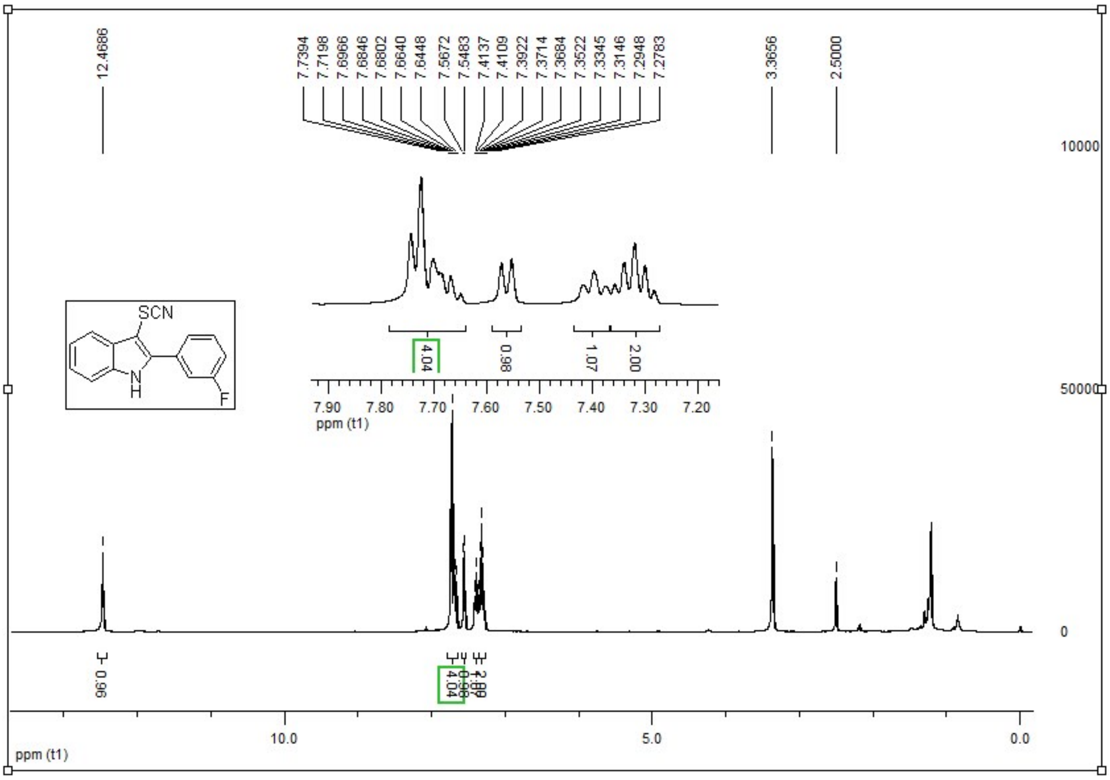


Figure 14. ^{1}H and ^{13}C NMR Spectra of **2-(3-Fluorophenyl)-3-thiocyanato-1*H*-indole (3n)**



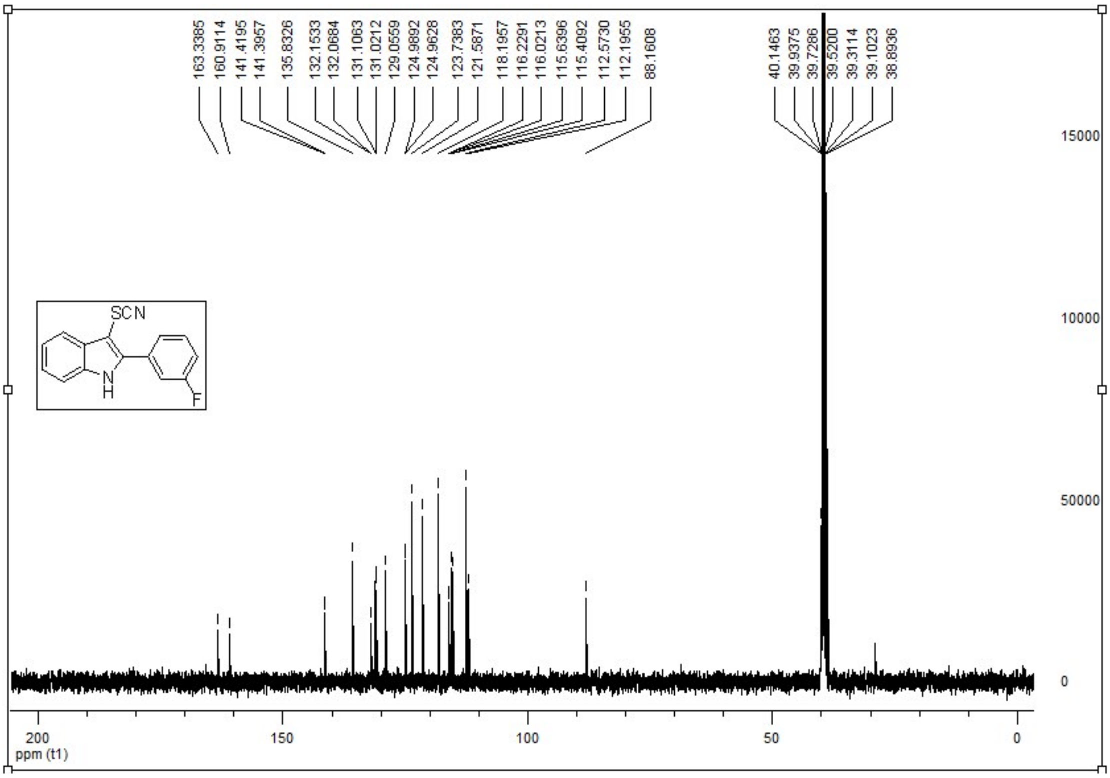
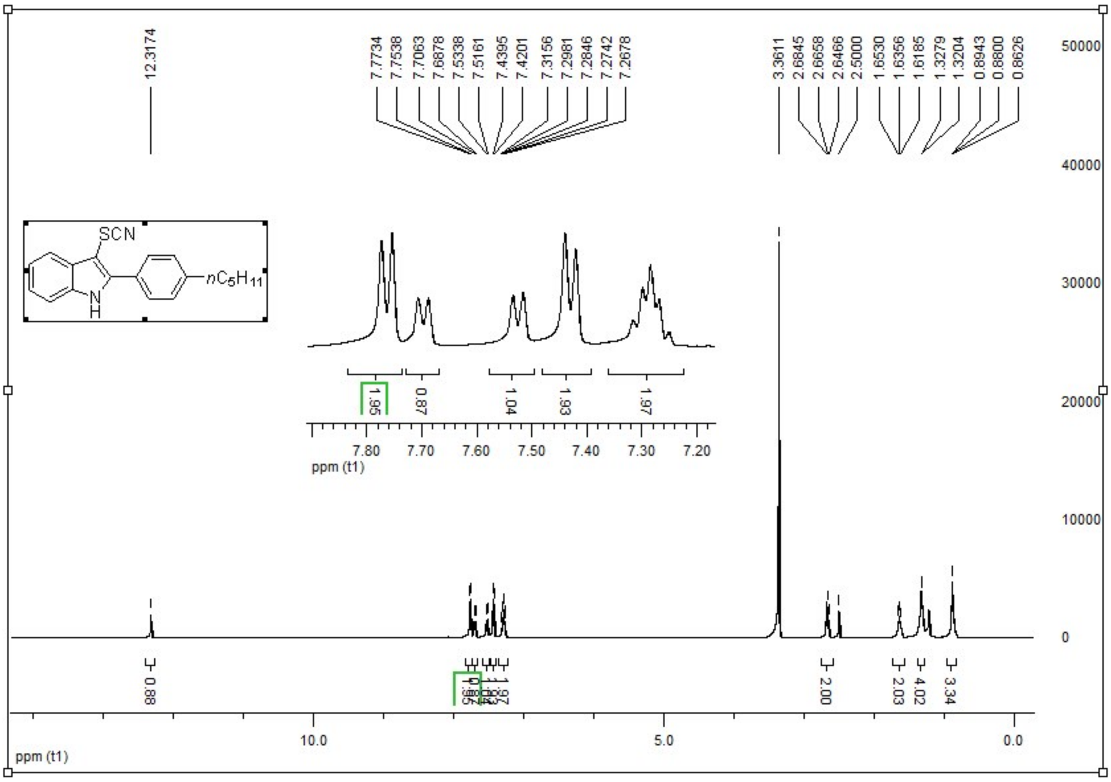


Figure 15. ^{1}H and ^{13}C NMR Spectra of **2-(4-Pentylphenyl)-3-thiocyanato-1*H*-indole (3o)**



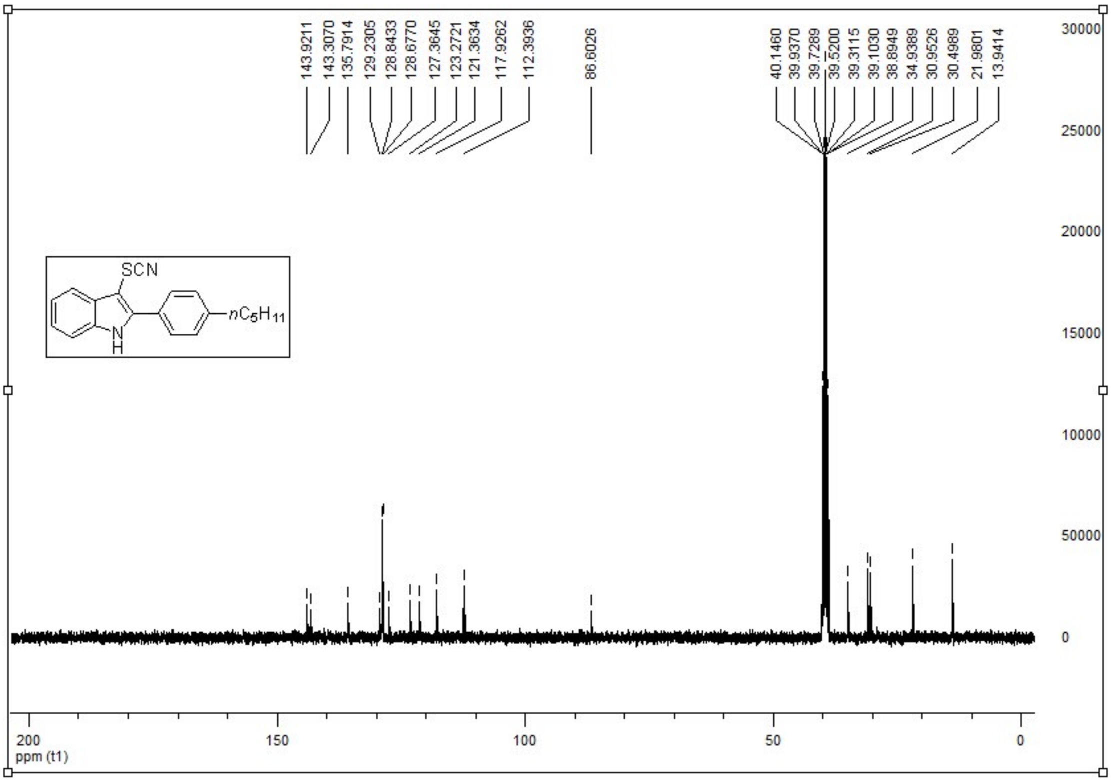
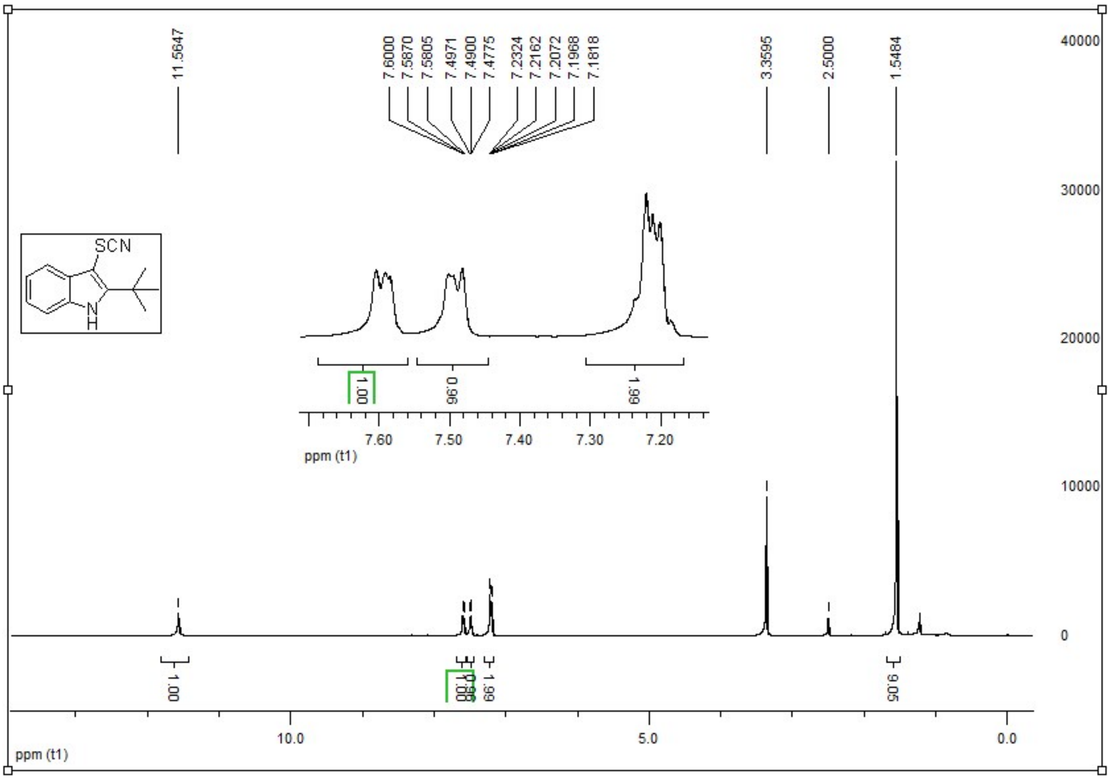


Figure 16. ^{1}H and ^{13}C NMR Spectra of **2-(Tert-butyl)-3-thiocyanato-1*H*-indole (3p)**



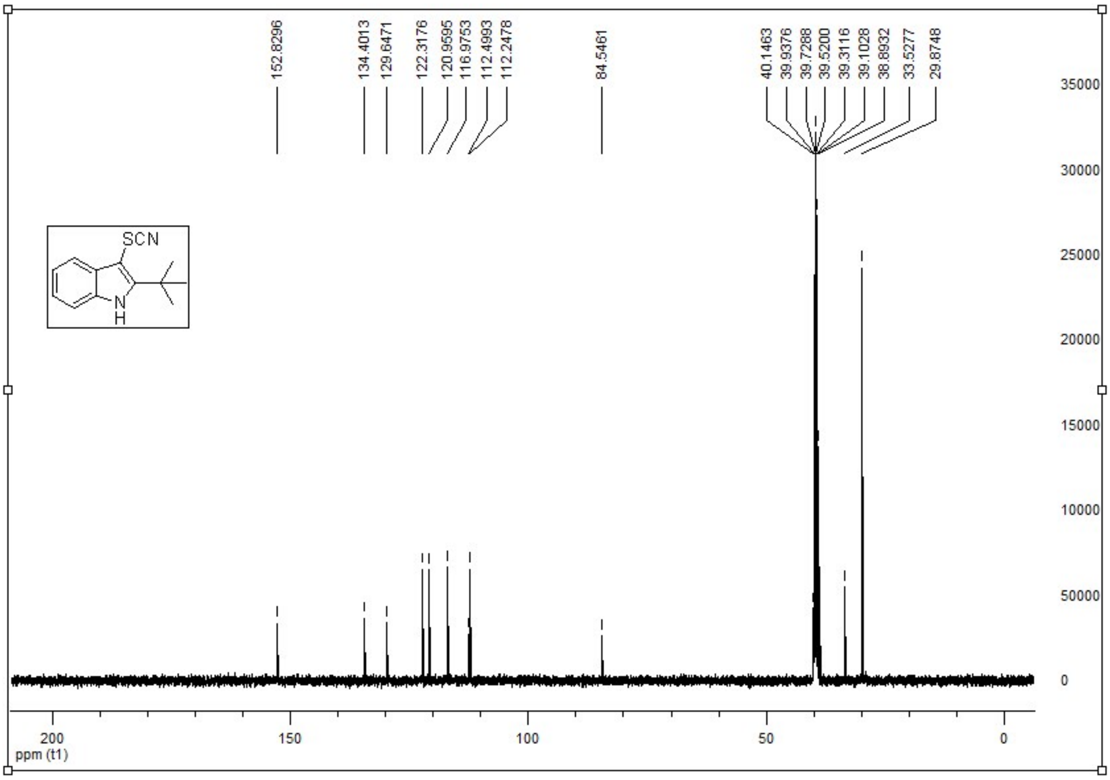
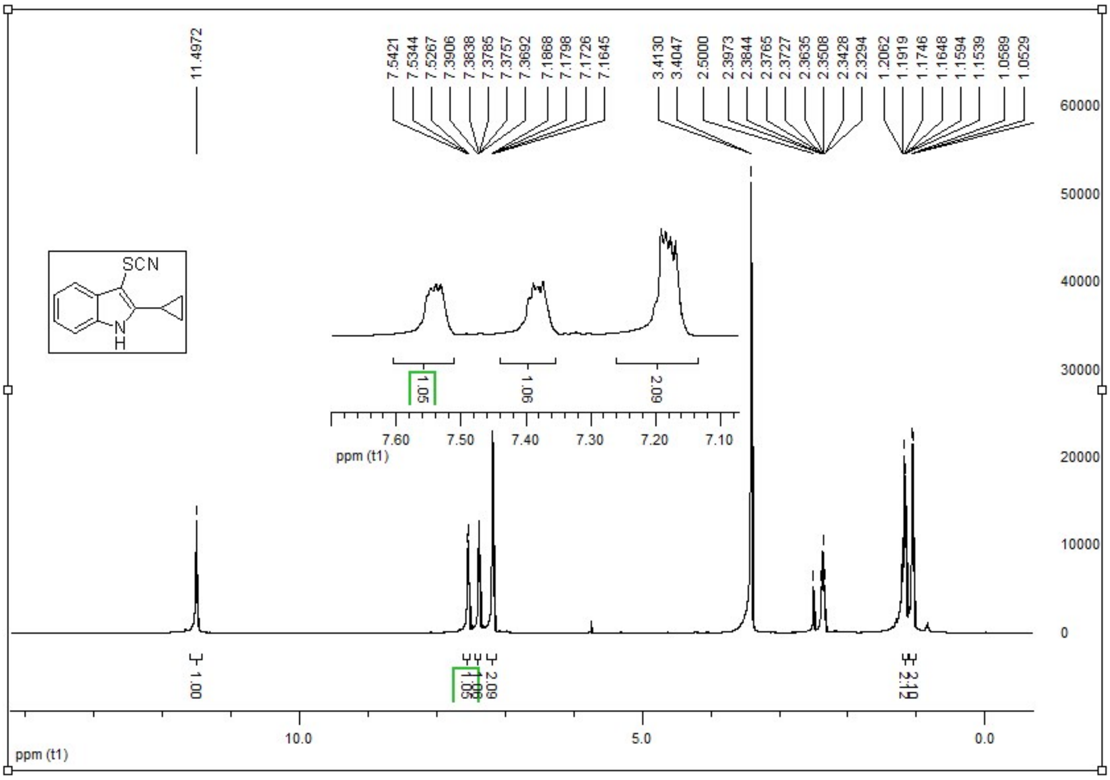


Figure 17. ¹H and ¹³C NMR Spectra of
2-Cyclopropyl-3-thiocyanato-1*H*-indole (3q)



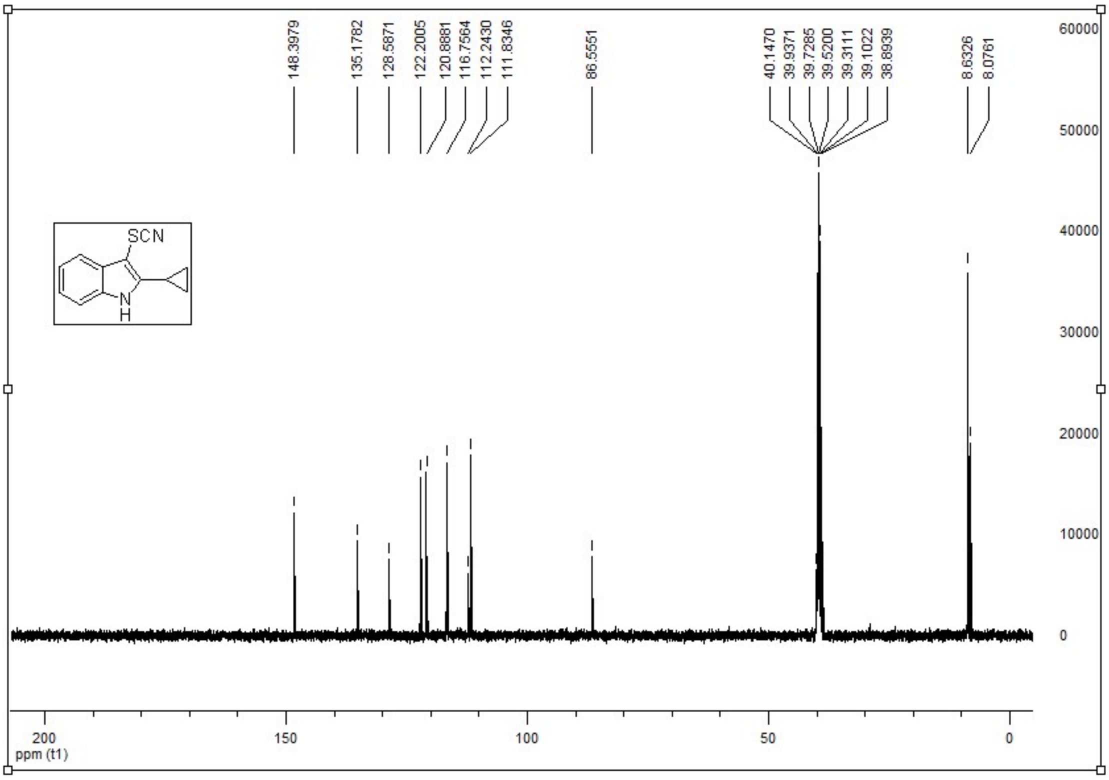
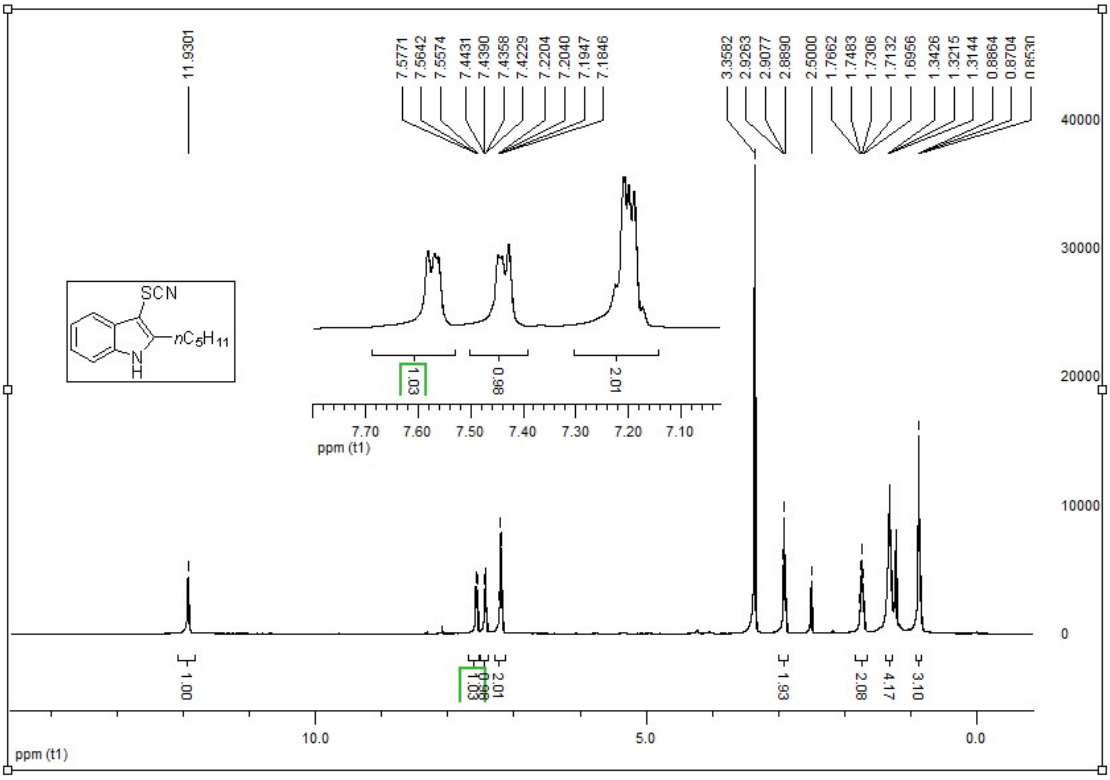


Figure 18. ^{1}H and ^{13}C NMR Spectra of **2-Pentyl-3-thiocyanato-1*H*-indole (3r)**



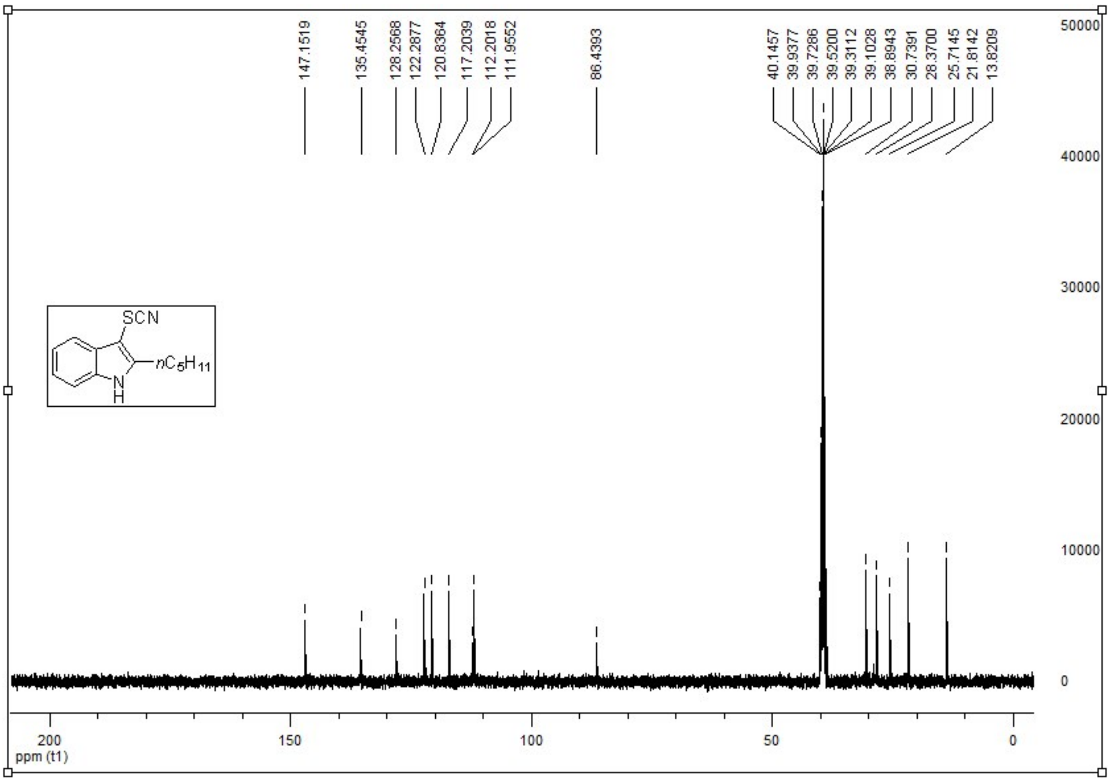
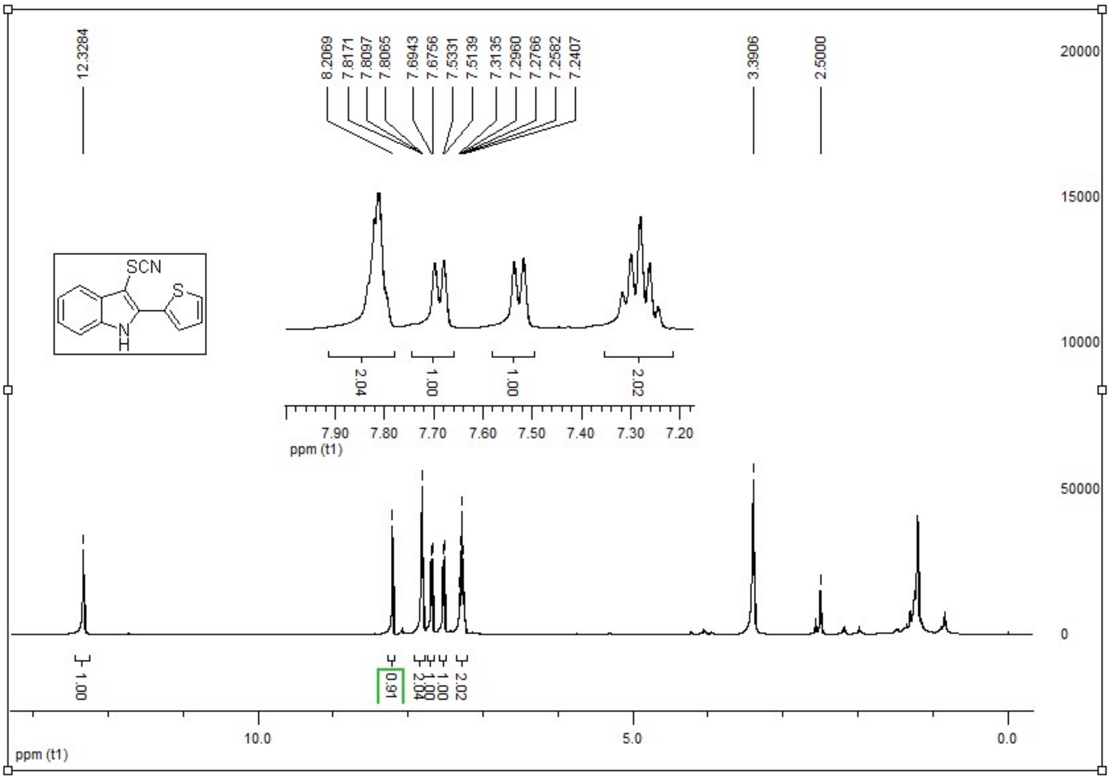


Figure 19. ^{1}H and ^{13}C NMR Spectra of
3-Thiocyanato-2-(thiophen-2-yl)-1*H*-indole (3s)



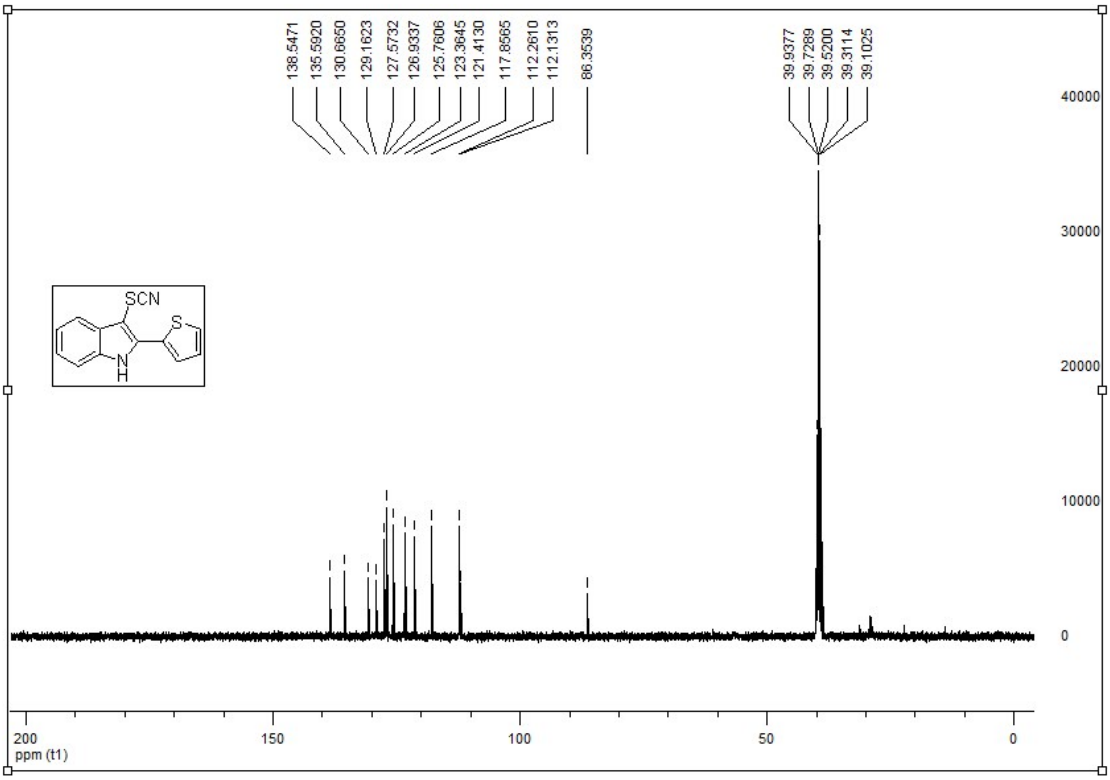
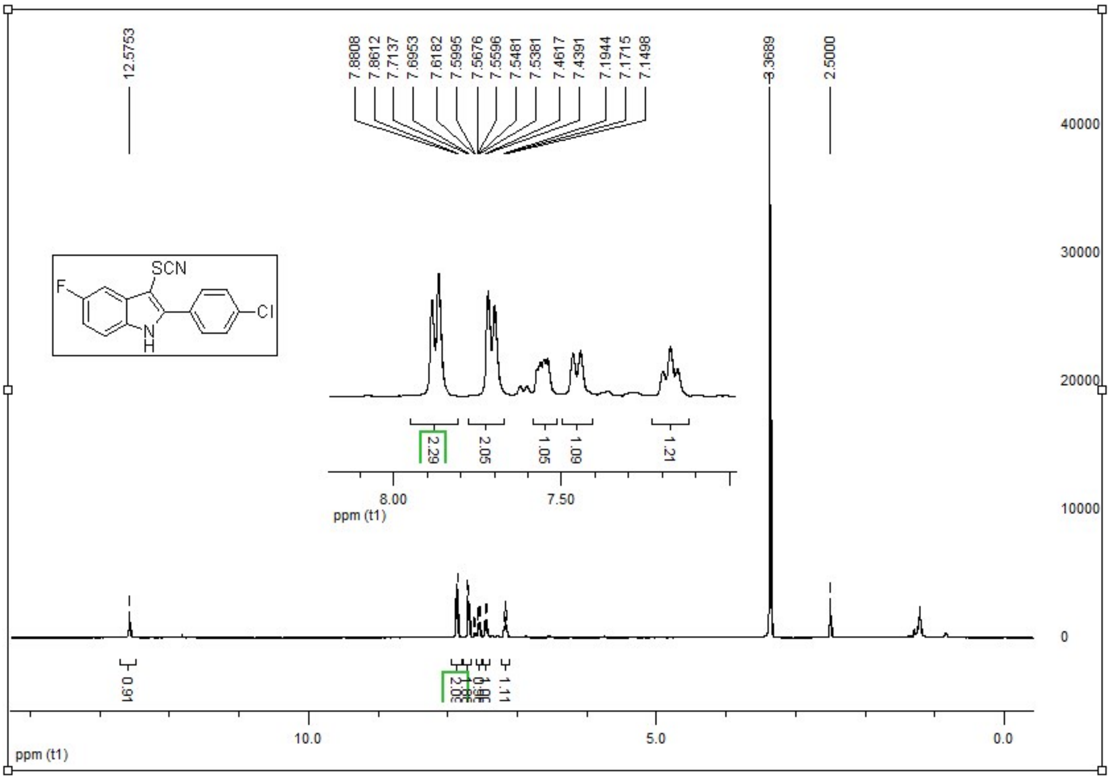


Figure 20. ^{1}H and ^{13}C NMR Spectra of **2-(4-Chlorophenyl)-5-fluoro-3-thiocyanato-1*H*-indole (3t)**



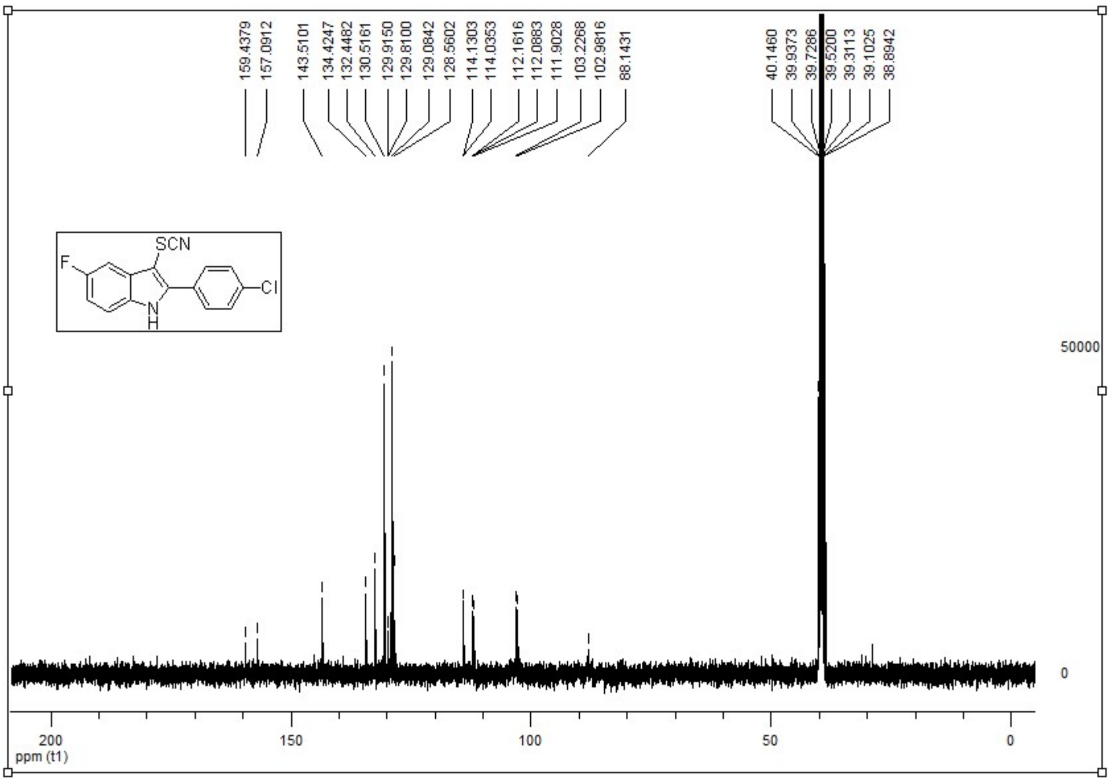
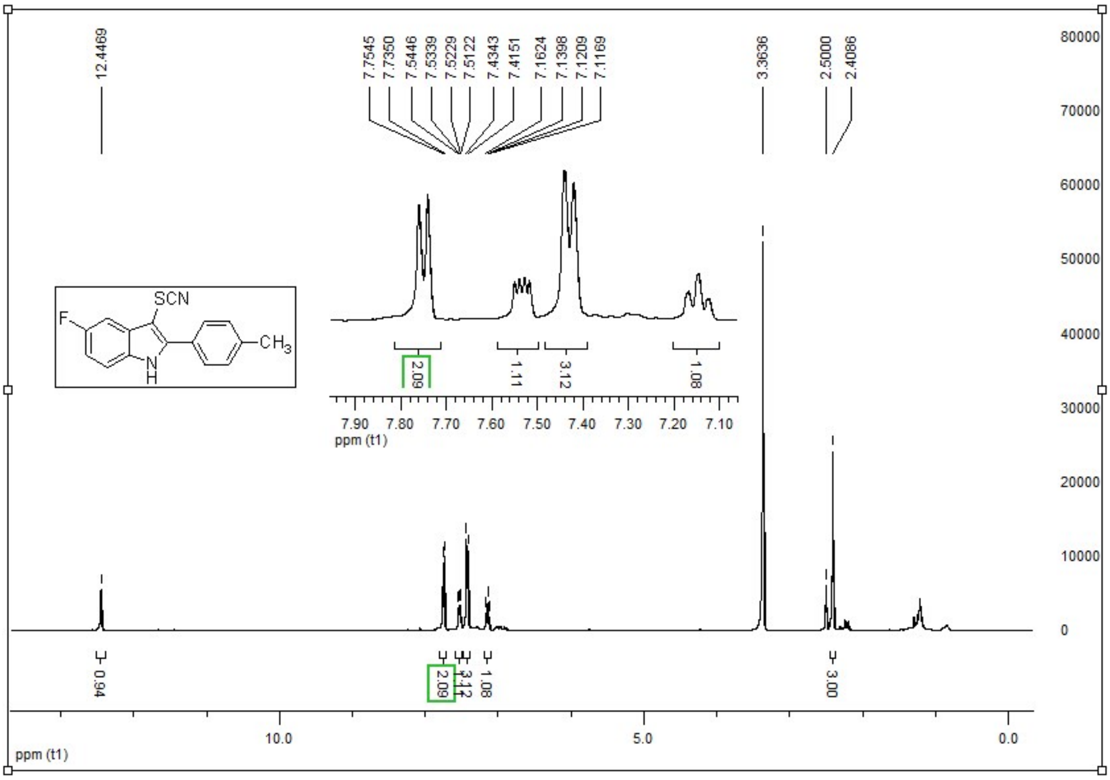


Figure 21. ^{1}H and ^{13}C NMR Spectra of **5-Fluoro-3-thiocyanato-2-(p-tolyl)-1*H*-indole (3u)**



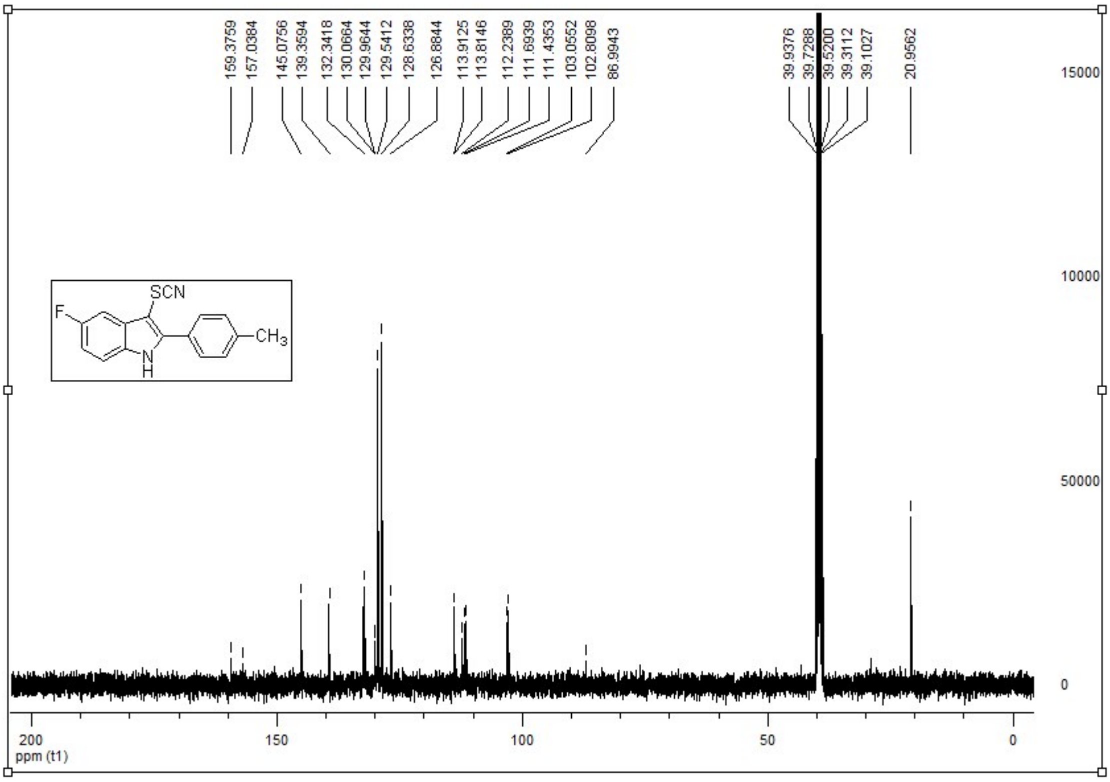
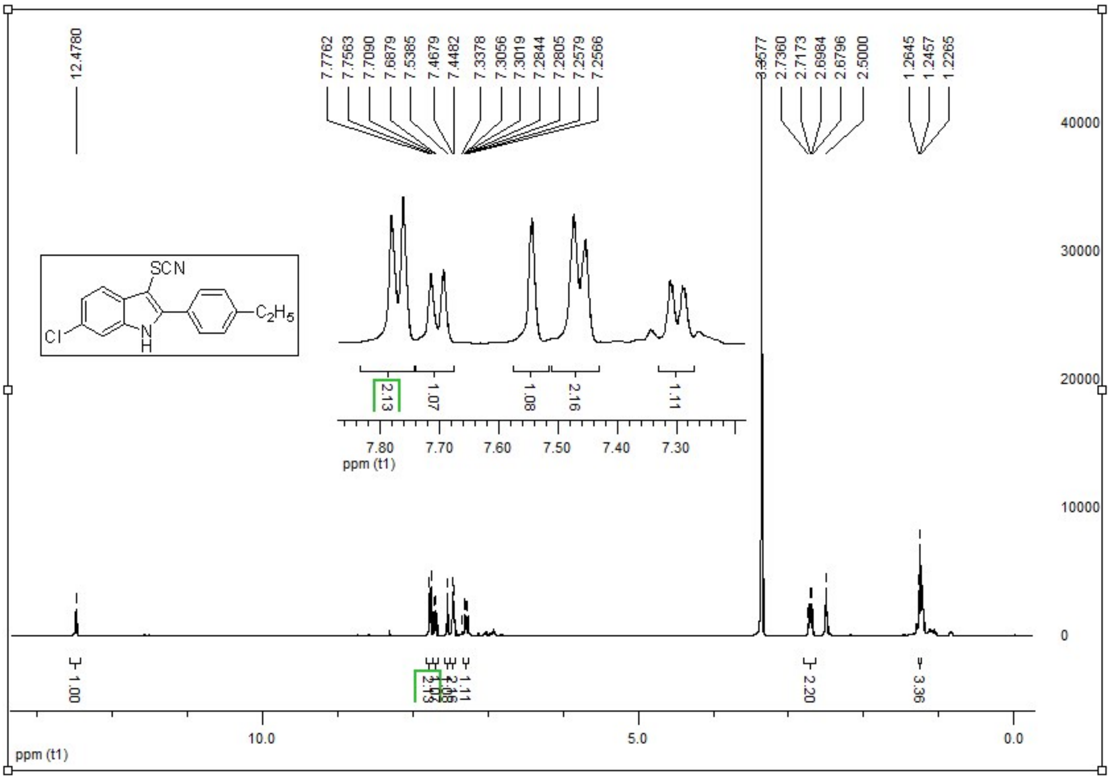


Figure 22. ^1H and ^{13}C NMR Spectra of **6-Chloro-2-(4-ethylphenyl)-3-thiocyanato-1*H*-indole (3v)**



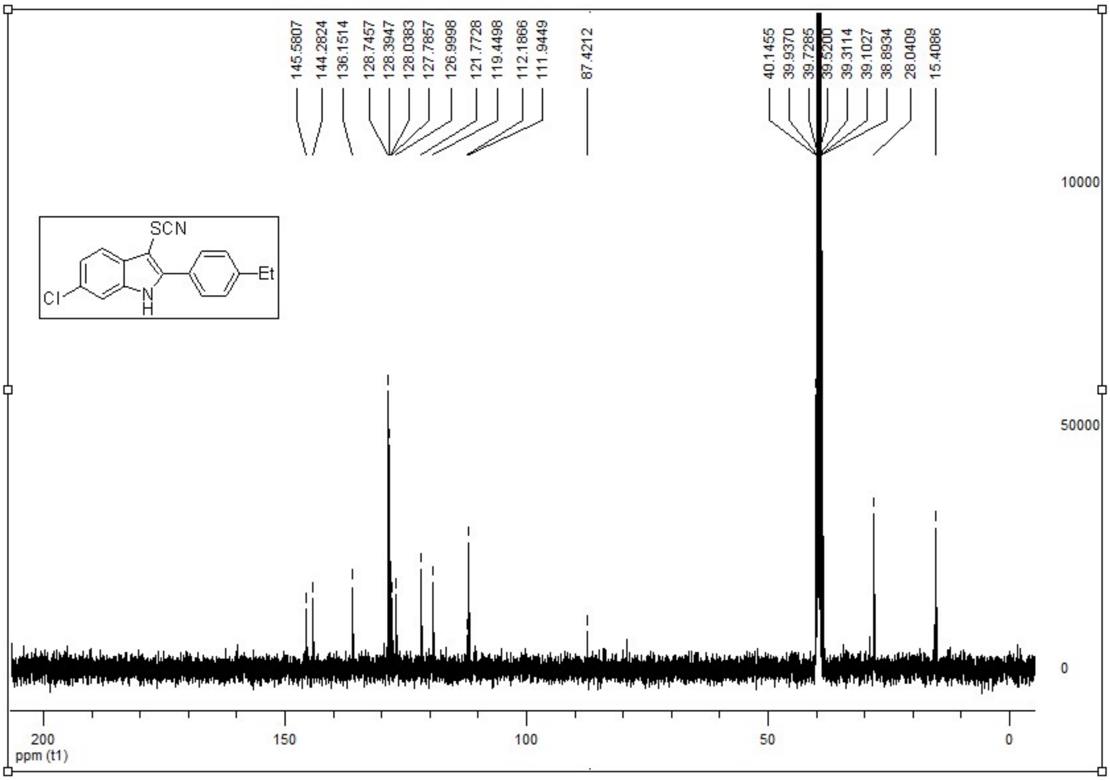
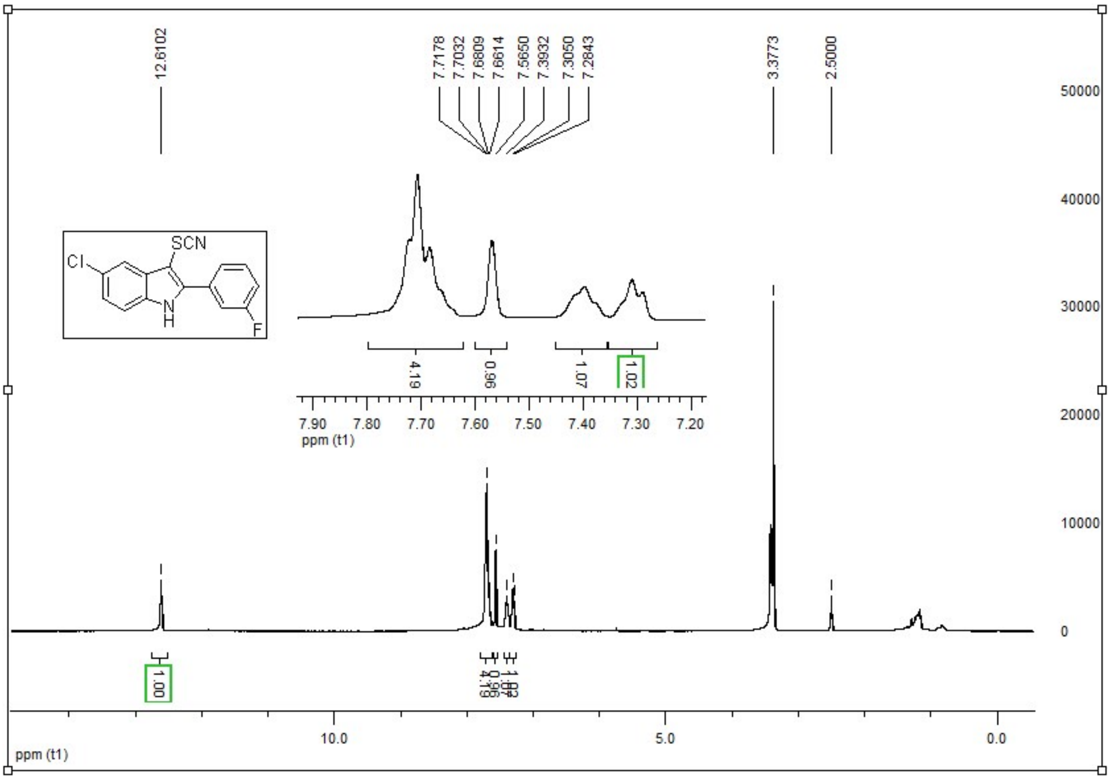


Figure 23. ^{1}H and ^{13}C NMR Spectra of **5-Chloro-2-(3-fluorophenyl)-3-thiocyanato-1*H*-indole (3w)**



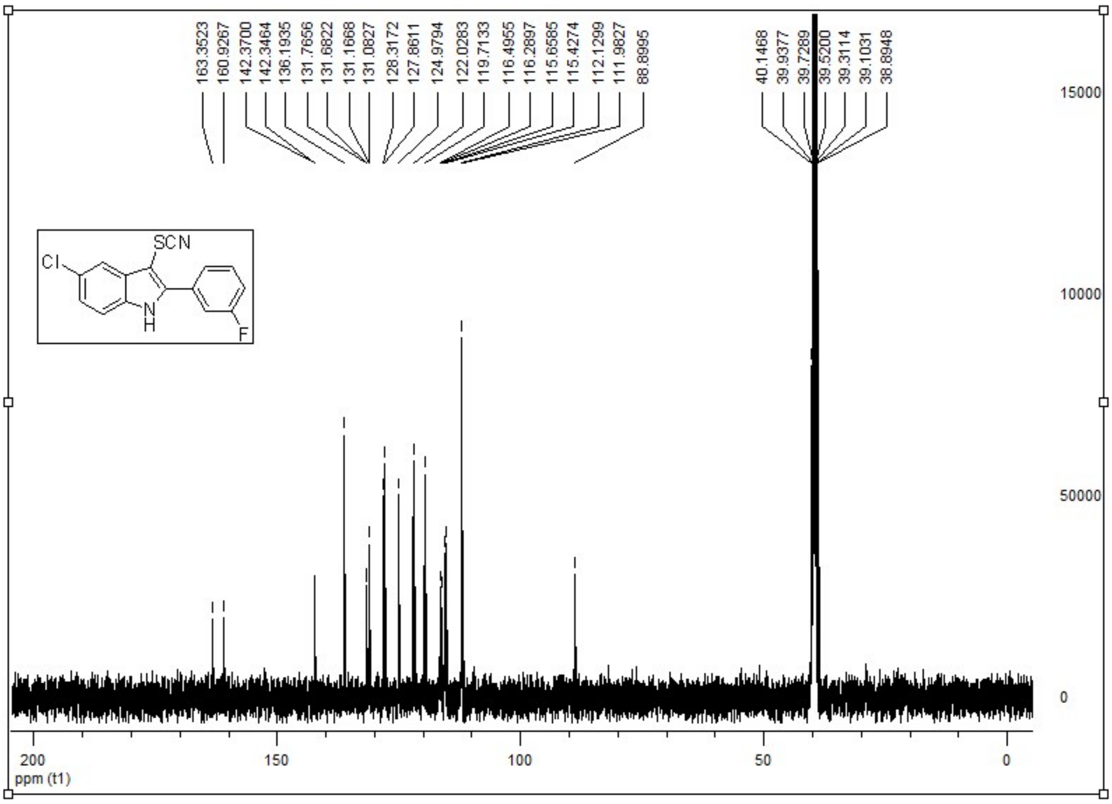
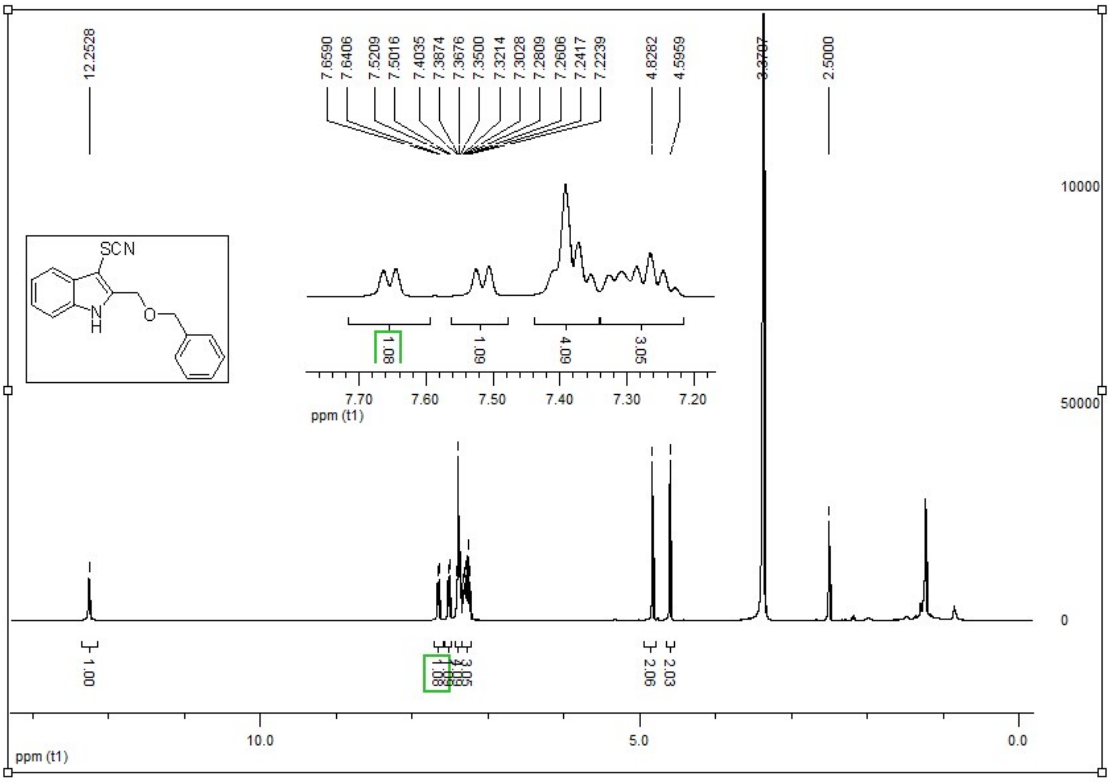


Figure 24. ^{1}H and ^{13}C NMR Spectra of **2-((Benzyloxy)methyl)-3-thiocyanato-1*H*-indole (3x)**



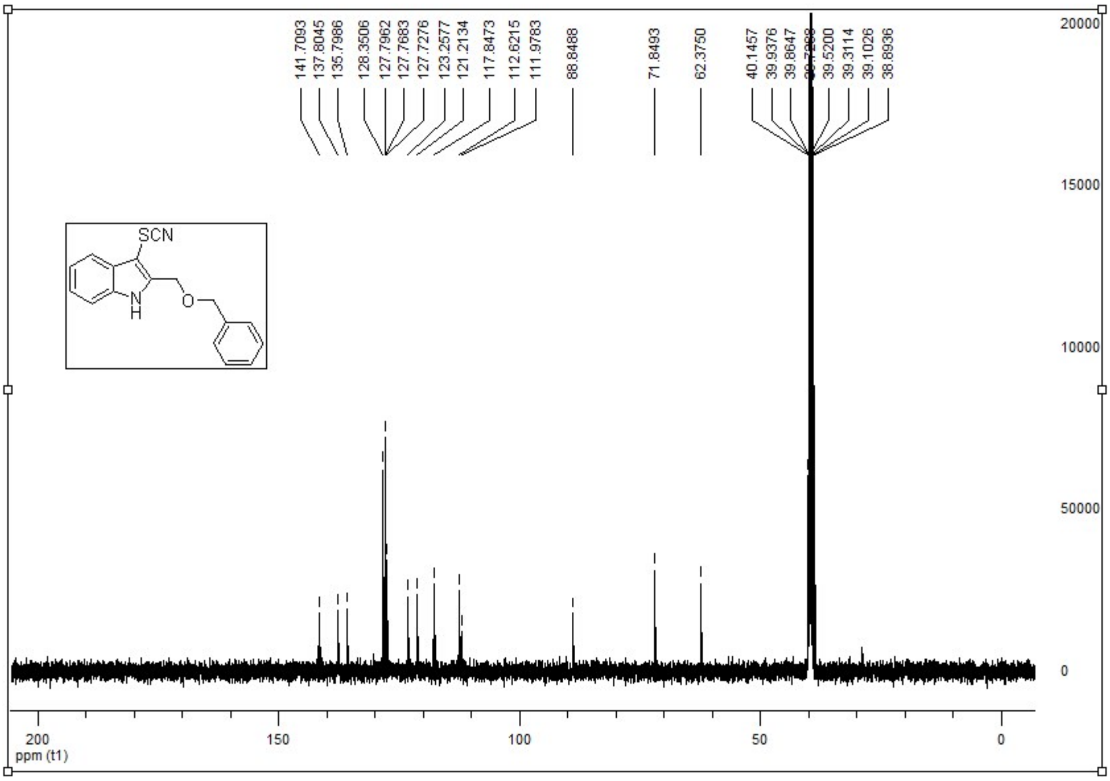
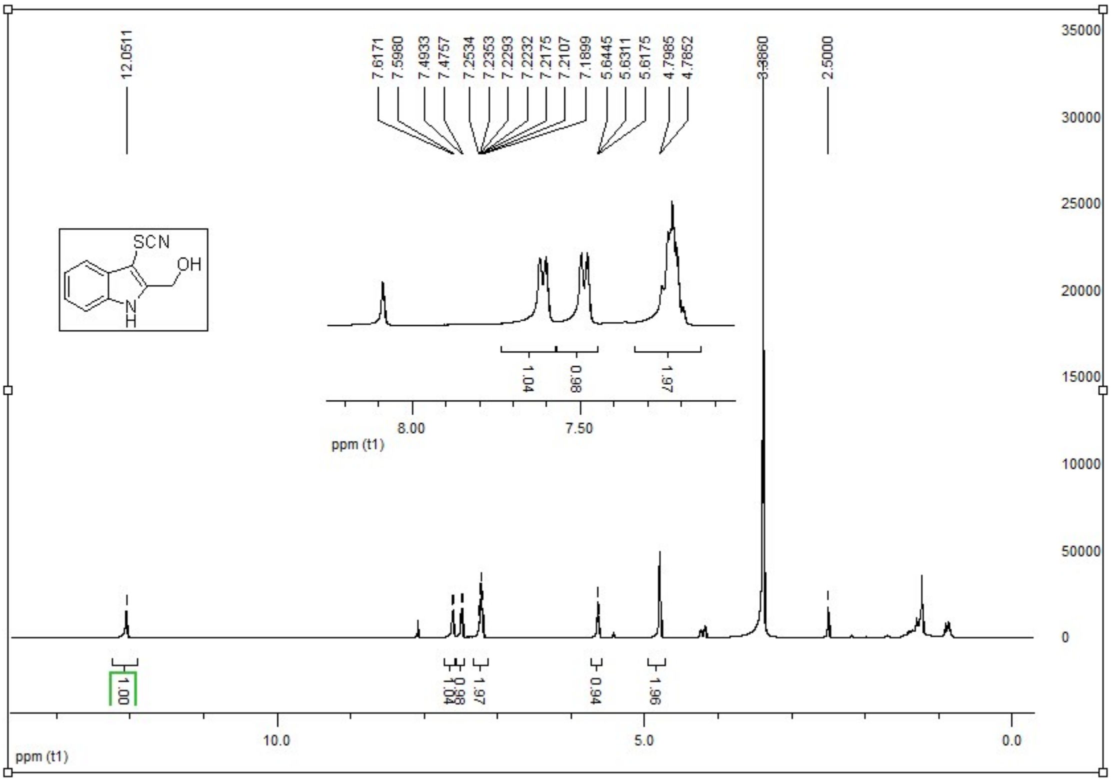


Figure 25. ^{1}H and ^{13}C NMR Spectra of

(3-Thiocyanato-1*H*-indol-2-yl)methanol (3y)



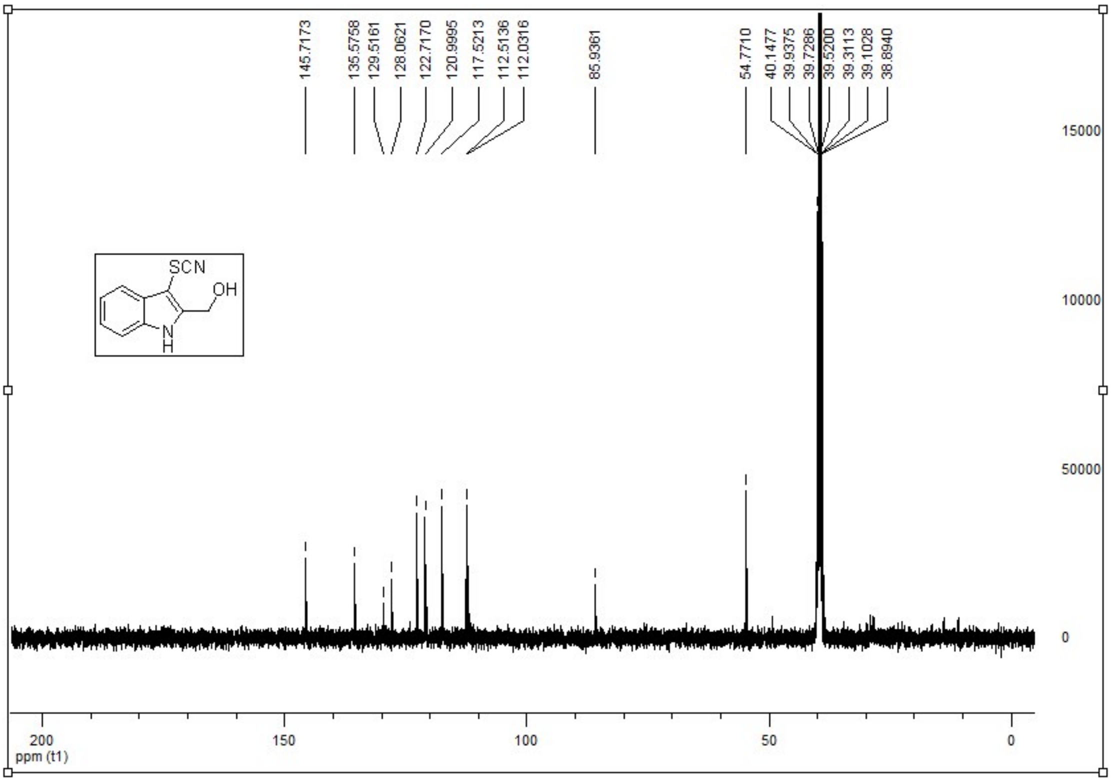
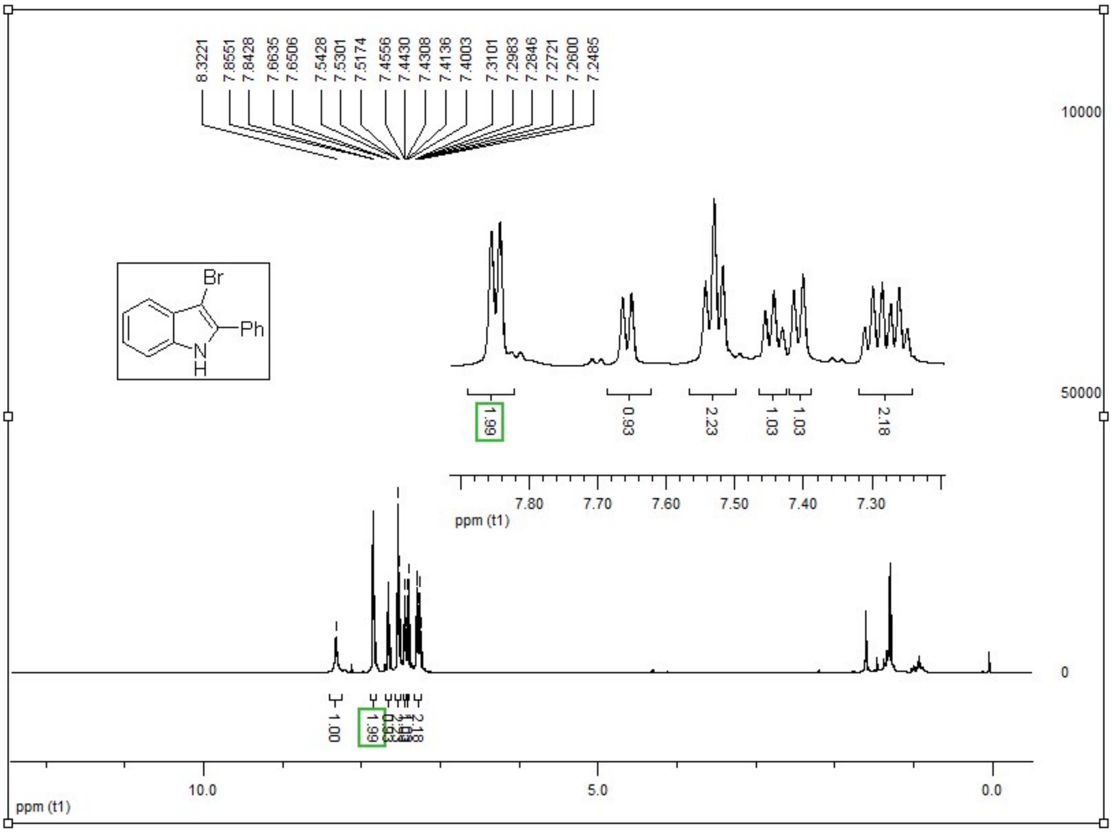


Figure 26. ^{1}H and ^{13}C NMR Spectra of **3-Bromo-2-phenyl-1*H*-indole**



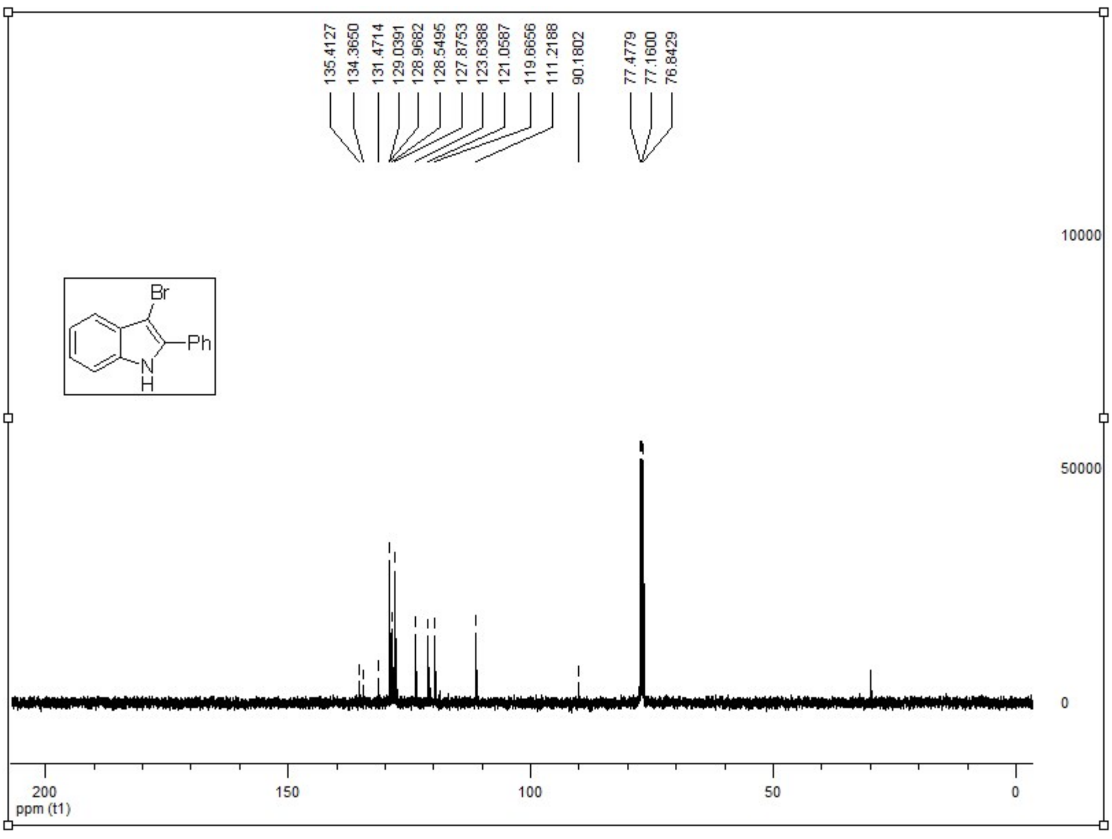
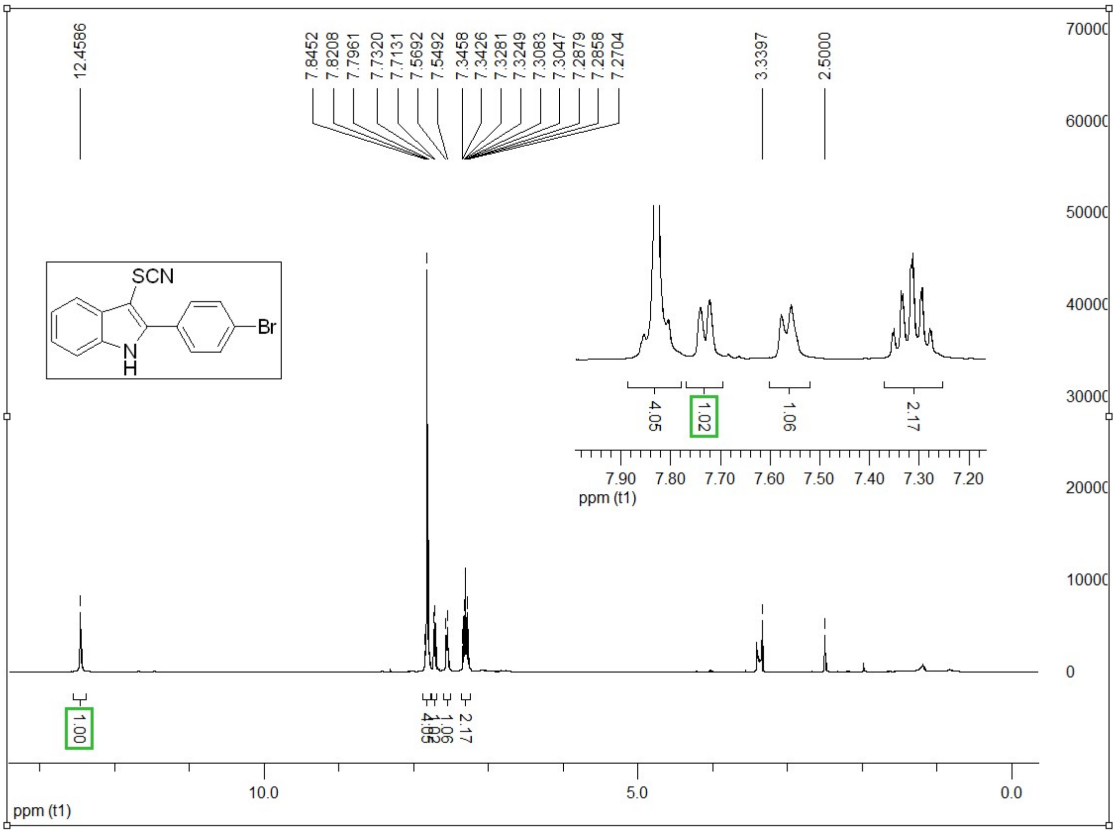
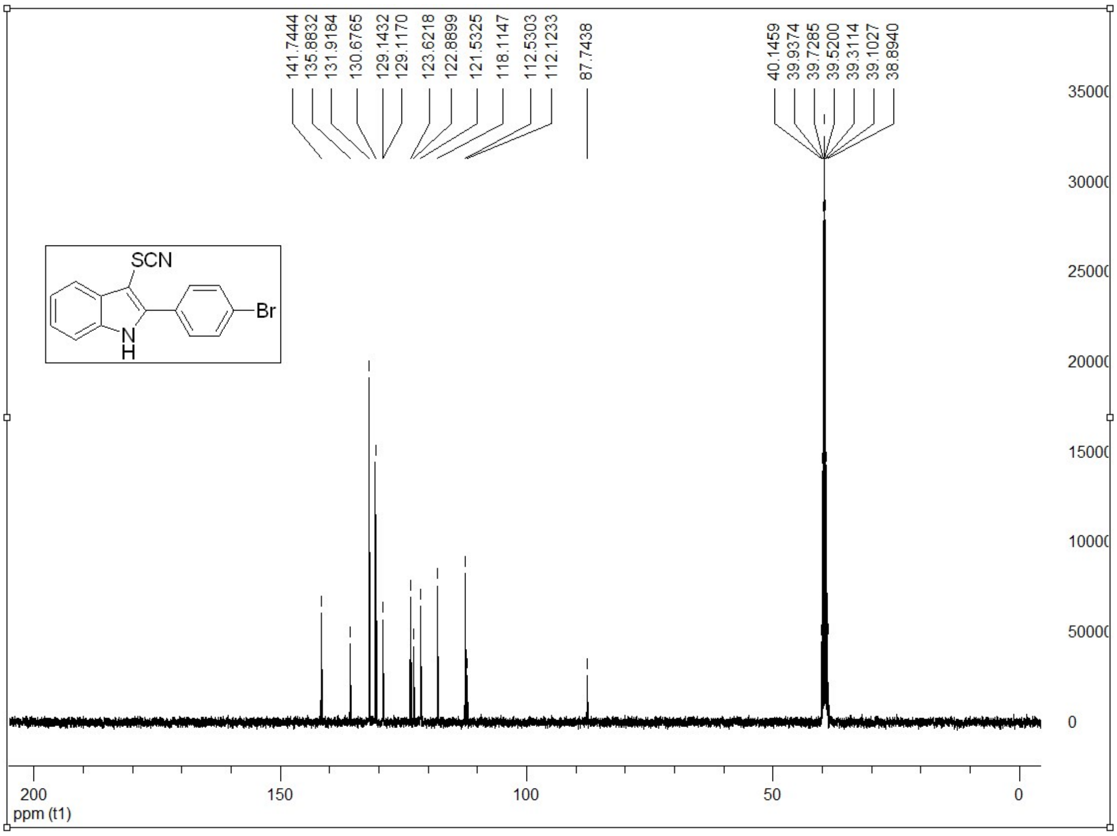


Figure 27. ^{1}H and ^{13}C NMR Spectra of 2-**(4-Bromophenyl)-3-thiocyanato-1*H*-indole (3z)**





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