Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Metal- and Phosphine-Free Electrophilic Vicinal Chloro-alkylthiolation and Trifluoromethylthiolation of Indoles using Sodium Sulfinate in the Presence of Triphosgene

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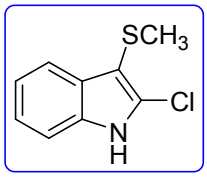
1. General Information

Unless otherwise noted, all reactions were carried out under an atmosphere of argon in oven-dried Schlenk tubes. Dry solvents (water ≤ 50 ppm) were purchased from Energy Chemical and stored over molecular sieves under argon atmosphere. Commercially available chemicals were used without any further purification. The products were purified by column chromatography over silica gel. Analytical thin-layer chromatography was performed on glass plates precoated with silica gel, and compounds were detected by visualization under an ultraviolet lamp (254 nm). ^{1}H, and ^{13}C NMR spectra were recorded on an AVANCE 300 Bruker spectrometer operating at 300 MHz and 75 MHz, respectively. Chemical shifts were reported in ppm. Coupling constants (*J* values) are reported in Hz. Low-resolution mass spectra (EI) were obtained at 70 eV on a 5975C Mass Selective Detector.

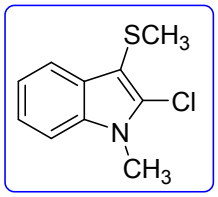
2. Experimental and Characterization of Reaction Products

General procedure for the electrophilic trifluoromethylthiolation of indoles with CH_3SO_2Na(or CF_3SO_2Na):

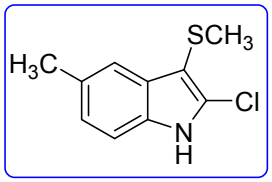
A 10-mL Schlenk tube with a magnetic stirring bar was charged with indoles (0.5 mmol) and sodium trifluoromethanesulfinate (0.6 mmol). The tube was evacuated and backfilled with dry nitrogen (this operation was repeated three times). triphosgene (0.5 mmol) dissolved in dry acetonitrile (2 mL) was added by syringe pump. The resulting mixture was stirred at at -78 °C-rt for 6 h before the solvent was removed under reduced pressure. Purification of the crude product was achieved by column chromatography.



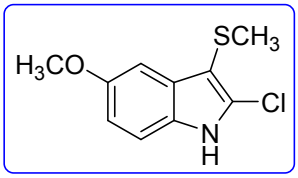
2-chloro-3-(methylthio)-1*H*-indole (2a): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (s, br, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 5.1 Hz, 1H), 7.23 – 7.00 (m, 2H), 2.26 (s, 3H); ^{13}C NMR (75 MHz,) δ 134.35, 129.28, 127.93, 123.09, 121.13, 119.08, 110.81, 105.22, 19.12. HRMS(EI): calcd. for $C_9H_8ClNS[M]^+$: 197.0066, found: 197.0061.



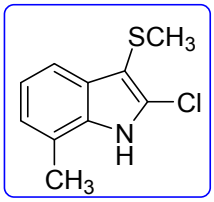
2-chloro-1-methyl-3-(methylthio)-1*H*-indole (2b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.3 Hz, 1H), 7.44 – 7.11 (m, 3H), 3.78 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.99, 130.80, 128.66, 122.54, 120.83, 118.97, 109.34, 104.00, 30.40, 19.15. HRMS(EI): calcd. for $C_{10}H_{10}ClNS[M]^+$: 211.0222, found: 211.0217.



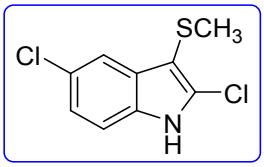
2-chloro-5-methyl-3-(methylthio)-1H-indole (2c): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (s, br, 1H), 7.48 (s, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 7.06 (d, *J* = 8.3 Hz, 1H), 2.47 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.71, 130.63, 129.56, 127.73, 124.57, 118.78, 118.75, 110.37, 21.40, 18.90; HRMS(EI): calcd. for $C_{10}H_{10}ClNS[M]^+$: 211.0222, found: 211.0216.



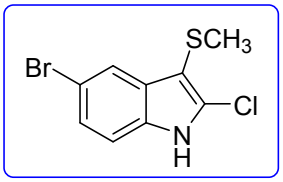
2-chloro-5-methoxy-3-(methylthio)-1H-indole (2d): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (s, br, 1H), 7.16 (dd, *J* = 13.6, 5.5 Hz, 2H), 6.87 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.89 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.23, 130.03, 129.13, 128.23, 113.16, 111.75, 104.88, 100.84, 55.87, 19.10; HRMS(EI): calcd. for $C_{10}H_{10}ClNOS[M]^+$: 227.0172, found: 227.0166.



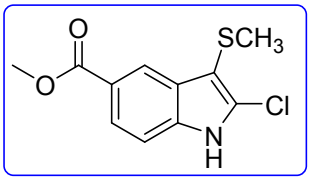
2-chloro-7-methyl-3-(methylthio)-1H-indole(2e): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (s, br, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 6.9 Hz, 1H), 2.47 (s, 3H), 2.34 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.91, 128.88, 127.62, 123.69, 121.30, 120.06, 116.74, 105.67, 19.13, 16.39. HRMS(EI): calcd. for $C_{10}H_{10}ClNS[M]^+$: 211.0222, found: 211.0217.



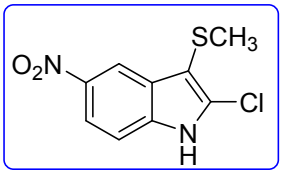
2,5-dichloro-3-(methylthio)-1*H*-indole (2f): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (s, br, 1H), 7.66 (s, 1H), 7.20 (q, *J* = 8.6 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.76, 130.74, 129.22, 128.84, 127.37, 123.49, 118.76, 111.67, 18.76. HRMS(EI): calcd. for $C_9H_7Cl_2NS[M]^+$: 230.9676, found: 230.9670.



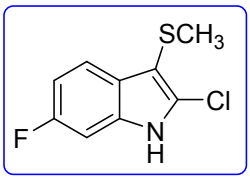
5-bromo-2-chloro-3-(methylthio)-1*H*-indole (2g): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (s, br, 1H), 7.82 (s, 1H), 7.31 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.17 (d, *J* = 8.2 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.99, 131.11, 129.13, 126.06, 121.82, 121.76, 114.72, 112.15, 18.94; HRMS(EI): calcd. for $C_9H_7Cl_2NS[M]^+$: 274.9171, found: 274.9166.



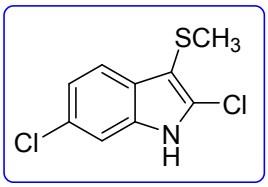
methyl 2-chloro-3-(methylthio)-1*H*-indole-5-carboxylate (2h): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73 (s, br, 1H), 8.44 (s, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 3.96 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.67, 137.03, 129.15, 129.06, 124.54, 123.56, 121.76, 110.44, 51.85, 18.89; HRMS(EI): calcd. for $C_{11}H_{10}ClNO_2S[M]^+$: 255.0121, found: 255.0116.



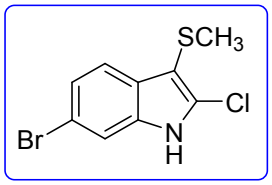
2-chloro-3-(methylthio)-5-nitro-1H-indole (2i): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.64 (s, 1H), 8.15 (d, *J* = 8.3 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.34, 130.97, 129.23, 118.69, 116.01, 110.76, 18.72; HRMS(EI): calcd. for $C_9H_7ClN_2O_2S[M]^+$: 241.9917, found: 241.9912.



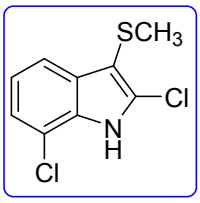
2-chloro-6-fluoro-3-(methylthio)-1H-indole (2J): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (s, br, 1H), 7.60 (dd, *J* = 8.5, 5.2 Hz, 1H), 6.98 (ddd, *J* = 14.3, 9.2, 2.6 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.10, 158.91, 134.2 (d, *J* = 13.5Hz), 127.58, 126.87, 12.06 (d, *J* = 9.8Hz), 109.88 (d, *J* = 24.7Hz), 97.41 (d, *J* = 27Hz), 18.71; HRMS(EI): calcd. for $C_9H_7ClFNS[M]^+$: 214.9972, found: 214.9966.



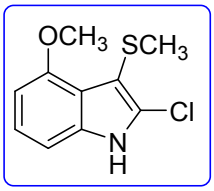
2,6-dichloro-3-(methylthio)-1*H*-indole (2k): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (s, br, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.30 (s, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.66, 129.20, 128.37, 128.01, 121.97, 120.03, 110.77, 110.72, 18.74. HRMS(EI): calcd. for $C_9H_7Cl_2NS[M]^+$: 230.9676, found: 230.9671.



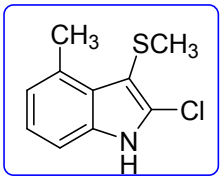
6-bromo-2-chloro-3-(methylthio)-1*H*-indole (2l): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 (s, br, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.43 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.13, 130.80, 128.39, 127.88, 124.59, 120.35, 116.63, 113.69, 18.66; HRMS(EI): calcd. for $C_9H_7Cl_2NS[M]^+$: 274.9171, found: 274.9165.



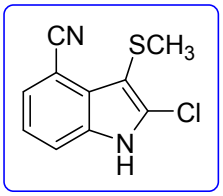
2,7-dichloro-3-(methylthio)-1*H*-indole (2m): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (s, br, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.19 (td, *J* = 15.1, 7.4 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.73, 130.73, 128.80, 122.43, 121.89, 117.71, 116.22, 18.89; HRMS(EI): calcd. for $C_9H_7Cl_2NS[M]^+$: 230.9676, found: 230.9670.



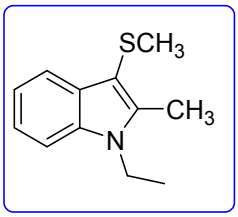
2-chloro-4-methoxy-3-(methylthio)-1H-indole (2p): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (s, br, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.61 (d, *J* = 7.9 Hz, 1H), 3.98 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.93, 136.29, 126.30, 123.78, 119.13, 104.06, 102.35, 55.82, 20.30; HRMS(EI): calcd. for $C_{10}H_{10}ClNOS[M]^+$: 227.0172, found: 227.0167.



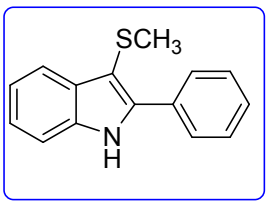
2-chloro-4-methyl-3-(methylthio)-1H-indole (2q): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87 (s, br, 1H), 8.64 (s, 1H), 8.15 (d, *J* = 8.3 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.75, 131.31, 129.03, 128.84, 127.17, 123.11, 122.87, 108.38, 20.77, 18.42. HRMS(EI): calcd. for $C_{10}H_{10}ClNS[M]^+$: 211.0222, found: 211.0217.



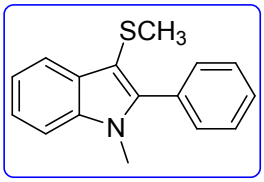
2-chloro-3-(methylthio)-1H-indole-4-carbonitrile (2r): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87 (s, br, 1H), 8.64 (br, 1H), 8.15 (d, *J* = 8.3 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.47, 126.78, 124.31, 121.42, 120.68, 118.49, 116.74, 101.48, 99.63, 20.61; HRMS(EI): calcd. for $C_{10}H_7ClN_2S[M]^+$: 222.0018, found: 222.0013.



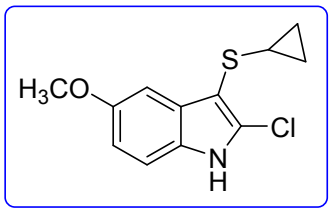
1-ethyl-2-methyl-3-(methylthio)-1H-indole (2s): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 – 7.62 (m, 1H), 7.32 (d, *J* = 7.0 Hz, 1H), 7.20 (tt, *J* = 7.0, 5.6 Hz, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.57 (s, 3H), 2.27 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.72, 135.95, 129.89, 121.36, 119.86, 118.81, 108.89, 103.95, 38.42, 19.81, 14.95, 10.30; HRMS(EI): calcd. for $C_{12}H_{15}NS[M]^+$: 205.0925, found: 205.0920.



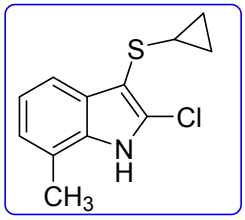
3-(methylthio)-2-phenyl-1*H*-indole (2t): ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.87 (s, br, 1H), 8.91 (d, *J* = 8.3 Hz, 1H), 8.13 (d, *J* = 7.9 Hz, 1H), 8.05 (d, *J* = 7.0 Hz, 2H), 7.69 – 7.46 (m, 5H), 7.17 (t, *J* = 7.7 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (75 MHz, MeOD) δ 165.88, 139.00, 134.80, 131.96, 129.75, 128.82, 127.45, 122.96, 122.82, 121.06, 12.17; HRMS(EI): calcd. for $C_{15}H_{13}NS[M]^+$: 239.0769, found: 239.0764.



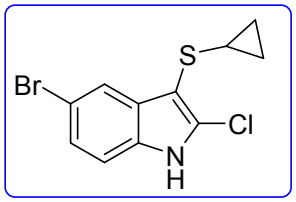
1-methyl-3-(methylthio)-2-phenyl-1H-indole (2u): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.7 Hz, 1H), 7.62 – 7.46 (m, 5H), 7.44-7.26 (m, 3H), 3.68 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.07, 137.51, 131.40, 130.87, 129.76, 128.48, 128.21, 122.51, 120.45, 119.56, 109.68, 105.48, 31.29, 20.04; HRMS(EI): calcd. for $C_{16}H_{15}NS[M]^+$: 253.0925, found: 253.0919.



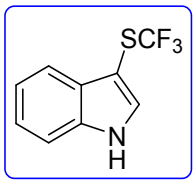
2-chloro-3-(cyclopropylthio)-5-methoxy-1H-indole(2v): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.22 – 7.13 (m, 2H), 6.88 (dd, *J* = 8.8, 2.3 Hz, 1H), 3.89 (s, 3H), 2.25-2.17 (m, 1H), 0.84 – 0.63 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.24, 130.66, 129.14, 128.64, 113.07, 111.71, 104.42, 100.98, 55.93, 16.49, 8.51; HRMS(EI): calcd. for $C_{12}H_{12}ClNOS[M]^+$: 253.0328, found: 253.0325.



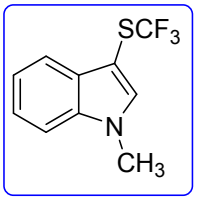
2-chloro-3-(cyclopropylthio)-7-methyl-1H-indole(2w): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.1 Hz, 1H), 2.48 (s, 3H), 2.23 (ddd, *J* = 11.7, 7.3, 4.4 Hz, 1H), 0.85 – 0.59 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.8, 129.5, 128.0, 123.7, 121.4, 120.0, 117.0, 105.3, 16.5, 16.4, 8.6; HRMS(EI): calcd. for $C_{12}H_{12}ClNS[M]^+$: 237.0379, found: 237.0376.



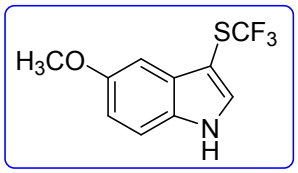
5-bromo-2-chloro-3-(cyclopropylthio)-1H-indole(2x): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.83 (s, 1H), 7.32 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 1H), 2.25-2.21 (m, 1H), 0.82-0.69 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.9, 131.6, 129.5, 126.0, 121.8, 114.7, 112.2, 104.8, 77.5, 77.10, 76.7, 16.4, 8.6; HRMS(EI): calcd. for $C_{11}H_9BrClNS[M]^+$: 300.9328, found: 300.9325.



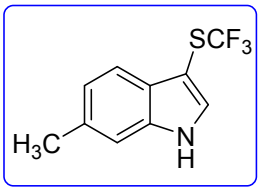
3-((trifluoromethyl)thio)-1*H*-indole [1] **(3a):** ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.49 (s, br, 1H), 7.85–7.82 (m, 1H), 7.52 (d, *J* = 2.8 Hz, 1H), 7.44 (t, *J* = 4.0 Hz, 1H), 7.35–7.28 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.0, 132.9, 129.6 (q, *J* = 308 Hz, 1C), 129.5, 123.5, 121.7, 119.3, 111.8, 95.6(q, *J* = 2 Hz, 1C); HRMS(EI): calcd. for $C_9H_6F_3NS$ $[M]^+$: 217.0173, found: 217.0168.



1-methyl-3-(trifluoromethylthio)-1*H*-indole [2] **(3b):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.6 Hz, 1H), 7.39–7.29 (m, 4H), 3.82 (s, 3H); ^{13}C NMR(75 MHz, $CDCl_3$,) δ 137.20, 136.92, 130.21, 129.44 (q, *J* = 311.2 Hz), 122.92, 121.34, 119.4, 109.97, 93.1 (q, *J* = 2.4 Hz), 33.4. MS (EI): m/z (%) 231, 162 (1 0 0), 106; HRMS(EI): calcd. for $C_{10}H_8F_3NS$ $[M]^+$: 231.0330, found: 231.0325.

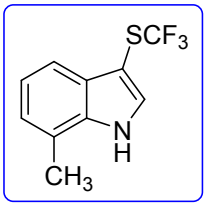


5-methoxy-3-((trifluoromethyl)thio)-1*H*-indole [1] **(3c):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.48 (s, br, 1H), 7.48 (d, *J* = 2.8 Hz, 1H), 7.32-7.25 (m,2H), 6.93 (dd, *J* = 8.8, 1.8 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.6, 133.3, 130.9, 130.4, 129.6 (q, *J* = 309.9 Hz), 114.1, 112.7, 100.6, 95.0 (q, *J* = 2 Hz), 55.9; HRMS(EI): calcd. for $C_{10}H_8F_3NOS$ $[M]^+$: 247.0279, found: 247.0274.

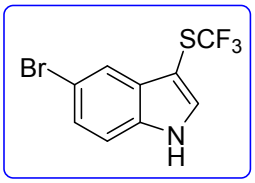


6-methyl-3-((trifluoromethyl)thio)-1H-indole [3] **(3d):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (s, br, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.45 (d, *J* = 2.6 Hz, 1H), 7.22 (s, 1H), 7.13 (d, *J* = 8.2 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.6, 133.6, 132.3, 129.6 (q, *J* = 309.8 Hz), 127.4, 123.6, 119.1, 111.7, 95.4, 21.8; HRMS(EI): calcd. for $C_{10}H_8F_3NS$ $[M]^+$:

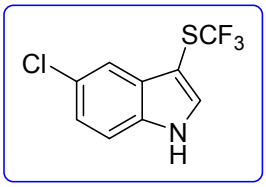
231.0330, found: 231.0325.



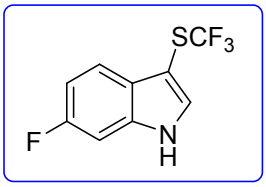
7-methyl-3-((trifluoromethyl)thio)-1*H*-indole [2] (3e): ^{1}H NMR(300 MHz, $CDCl_3$): δ 8.52 (s, br, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 2.8 Hz, 1H), 7.21 (t, *J* = 8.6 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (75 MHz, CDCl3): δ 135.6, 132.5, 129.4 (q, *J* = 308 Hz, 1C), 129.1, 123.9, 121.8, 120.9, 117.1, 96.0 (q, *J* = 2.4 Hz, 1C), 16.3; HRMS(EI): calcd. for $C_{10}H_8F_3NS$ $[M]^+$: 231.0330, found: 231.0325.



5-bromo-3-((trifluoromethyl)thio)-1*H*-indole [2] (3f): ^{1}H NMR (300 MHz, Acetone) δ 8.60 (s, 1H), 7.94 (s, 1H), 7.52 (d, *J* = 2.4 Hz, 1H), 7.37 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.27 (d, *J* = 8.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.8, 133.9, 131.3, 129.3 (q, *J* = 308 Hz, 1C), 126.6, 122.0, 115.2, 113.2, 95.4 (q, *J* = 2.3 Hz, 1C); HRMS(EI): calcd. for $C_9H_5BrF_3NS$ $[M]^+$: 294.9278, found: 294.9273.

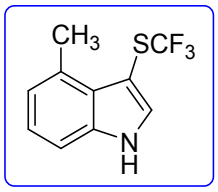


5-chloro-3-((trifluoromethyl)thio)-1H-indole [2] (3g): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (s, br, 1H), 7.78 (s, 1H), 7.55 (d, *J* = 2.4 Hz, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 7.25 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.4, 134.0, 130.7, 129.3 (q, *J* = 310 Hz, 1C), 127.7, 124.0, 118.9, 112.8, 95.5 (q, *J* = 2.3 Hz, 1C); HRMS(EI): calcd. for $C_9H_5ClF_3NS$ $[M]^+$: 250.9783, found: 250.9778.

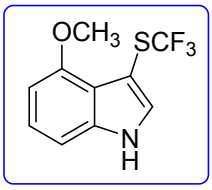


6-fluoro-3-((trifluoromethyl)thio)-1H-indole [2] (3h): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (s, br, 1H), 7.72 (dd, *J* = 8.6, 5.2 Hz, 1H), 7.53 (d, *J* = 2.6 Hz, 1H), 7.13 – 7.01 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.6 (d, *J* = 240.0 Hz), 136.1 (d, *J* = 12.6 Hz), 133.1, 129.4 (q,

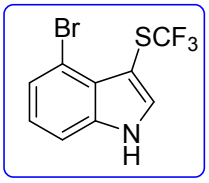
J = 309.9 Hz), 125.9, 120.4 (d, *J* = 10.1 Hz), 110.7 (d, *J* = 24.7 Hz), 98.1 (d, *J* = 26.6 Hz), 96.0 (q, *J* = 2.2 Hz); HRMS(EI): calcd. for $C_9H_5F_4NS$ $[M]^+$: 235.0079, found: 235.0074.



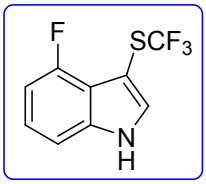
4-methyl-3-((trifluoromethyl)thio)-1H-indole [4] **(3i):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (s, br, 1H), 7.48 (d, *J*= 2.7 Hz, 1H), 7.30-7.28 (m, 2H), 7.14-7.12 (m, 1H), 2.99 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.5, 134.4, 131.7, 129.3 (q, *J* = 309.3Hz), 126.8, 123.5, 110.0, 94.9 (q, *J* = 2.4 Hz), 19.5; HRMS(EI): calcd. for $C_{10}H_8F_3NS$ $[M]^+$: 231.0330, found: 231.0325.



4-methoxy-3-((trifluoromethyl)thio)-1*H*-indole [4] **(3J):** ^{1}H NMR300 MHz, $CDCl_3$) δ 8.43 (s, br, 1H), 7.29 (s, (3c) 1H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6, 137.9, 132.6, 129.6 (q, *J* = 309.4 Hz), 124.4, 118.6, 105.0, 102.2, 94.5 (q, *J* = 2.5 Hz), 55.6;

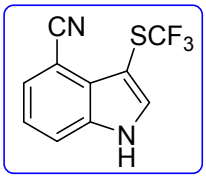


4-bromo-3-((trifluoromethyl)thio)-1*H*-indole [3] **(3k):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (s, br, 1H), 7.56 (d, *J* = 2.5 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.10 (t, *J* = 7.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.1, 135.5, 132.6, 129.1 (q, *J* = 307.5Hz), 126.7, 126.1, 124.3, 114.3, 111.5, 96.1 (q, *J* = 2.5 Hz),

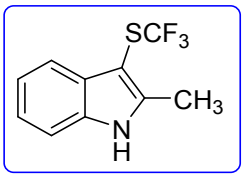


4-fluoro-3-((trifluoromethyl)thio)-1H-indole(3l): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.76 (s, br, 1H), 7.57 (s, 1H), 7.45 – 7.15 (m, 2H), 7.11 – 6.74 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.7 (d, *J* = 249 Hz, 1C), 138.9 (d, *J* = 9 Hz, 1C), 135.4 (d, *J* = 9 Hz, 1C), 129.3 (d, *J* = 307.5 Hz, 1C), 124.1(d, *J* = 8.3 Hz, 1C), 118.0 (d, *J* = 17.3 Hz, 1C), 108.0 (d, *J* = 3.8 Hz, 1C), 107.2 (d, *J* = 19.5 Hz, 1C), 93.3 (q, *J* = 2.5 Hz); HRMS(EI): calcd. for

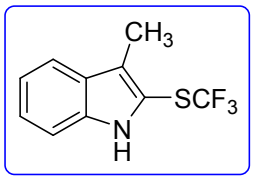
$C_9H_5F_4NS$ $[M]^+$: 235.0079, found: 235.0074.



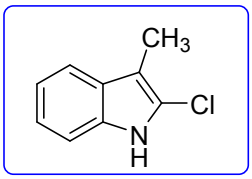
3-((trifluoromethyl)thio)-1H-indole-4-carbonitrile [5] **(3m):** ^{1}H NMR (300 MHz, Acetone) δ 12.42 (s, br, 1H), 8.39 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.9 Hz, 1H); ^{13}C NMR (75 MHz, Acetone) δ 137.7, 133.3, 128.7, 125.9 (q, *J* = 333.0 Hz, 1C), 125.6, 118.9, 118.6, 109.1, 102.0; HRMS(EI): calcd. for $C_{10}H_5F_3N_2S$ $[M]^+$: 242.0126, found: 242.0121.



2-Methyl-3-((trifluoromethyl)thio)-1*H*-indole [4] **(3n):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (s, br, 1H), 7.78 (d, *J* = 7.2 Hz, 1H), 7.33-7.24 (m, 3H), 2.56 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 136.1, 130.6, 129.9 (q, *J* = 309.2 Hz), 122.7, 121.4, 118.7, 110.9, 92.5 (q, *J* = 2.2 Hz), 12.1; HRMS: Calculated for $C_{10}H_8F_3NS$: 231.0330; Found: 231.0325.



3-Methyl-2-((trifluoromethyl)thio)-1*H*-indole [4] **(3o)**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14 (s, br, 1H), 7.63 (d, *J* = 7.2 Hz, 1H), 7.35–7.38 (m, 1H), 7.39–7.30 (m, 1H), 7.21–7.16 (t, *J* = 6.6 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.6, 129.6 (q, *J* = 310 Hz, 1C), 126.7, 124.8, 123.7, 120.1, 119.9, 113.2, 111.1, 9.4; HRMS: Calculated for $C_{10}H_8NF_3S$: 231.0330; Found: 231.0325.



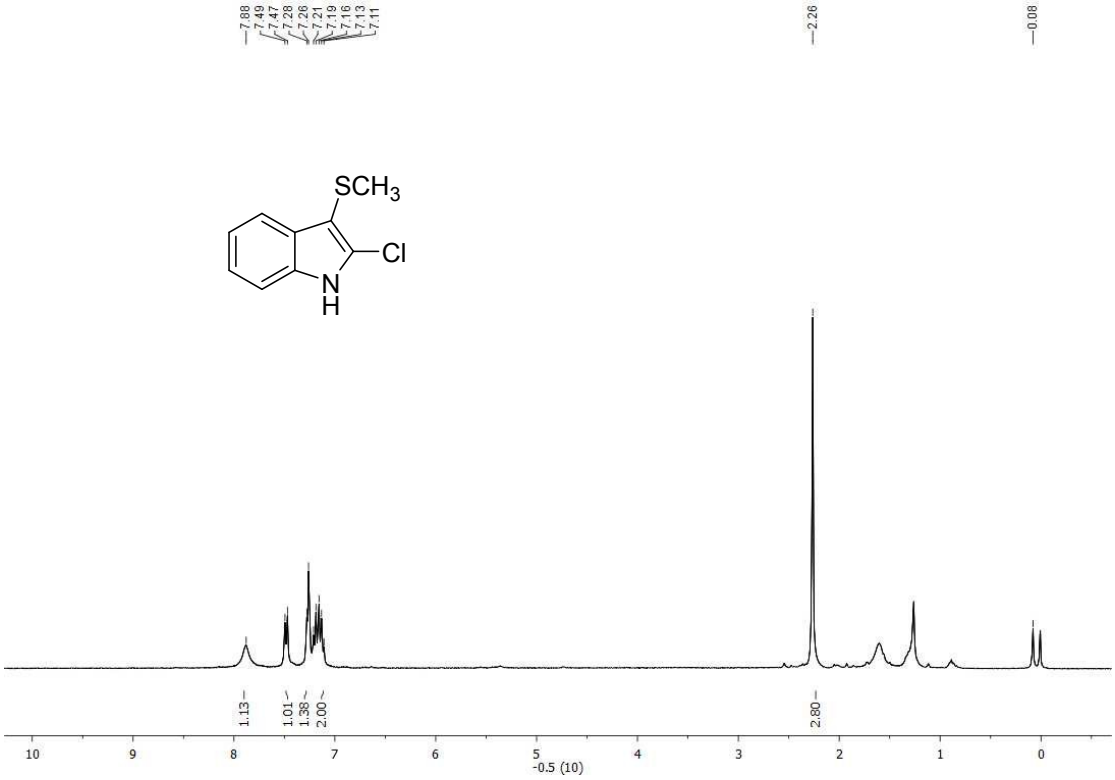
2-chloro-3-methyl-1*H*-indole: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 5.1 Hz, 1H), 7.23 – 6.99 (m, 2H), 2.26 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.6, 1285, 122.3, 120.0, 118.3, 110.2, 108.1, 81. HRMS: Calculated for C_9H_8ClN: 165.0345; Found: 165.034.

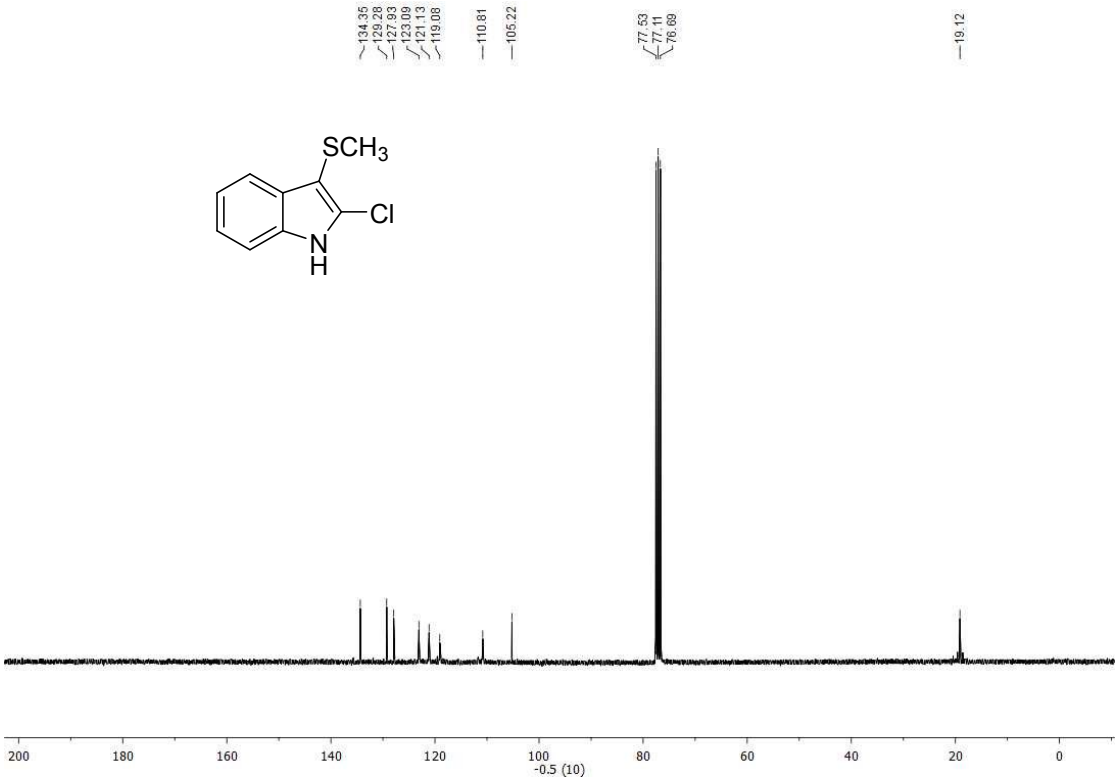
3. References

1. Q. Wang, Z.Qi, F. Xie, X. Li, *Adv. Synth. Catal*. **2015**, 357, 355 – 360.
2. K. Lu, Z. Deng, M. Li, T. Li, X. Zhao, Org. Biomol. Chem., **2017**, 15, 1254–1260.
3. J.-Y. Guo, R.i-H. Dai, W.-C. Xu, R.-X. Wu, S.-K. Tian, *Chem. Commun.*, **2018**, 54, 8980-8982.
4. X. Zhao, A. Wei, B. Yang, T. Li, Q. Li, D. Qiu, K. Lu, *J. Org. Chem.* **2017**, 82, 9175−9181.
5. R. Honeker, J. B. Ernst, F. Glorius, *Chem. Eur. J.* **2015**, 21, 8047 – 8051.
6. S. Tang, J.-H. Li, Y.-X. Xie, N.-X. Wang, Synthesis, **2007**, 1535-1541.

4. Copies of NMR Spectra

2-chloro-3-(methylthio)-1*H*-indole (2a):





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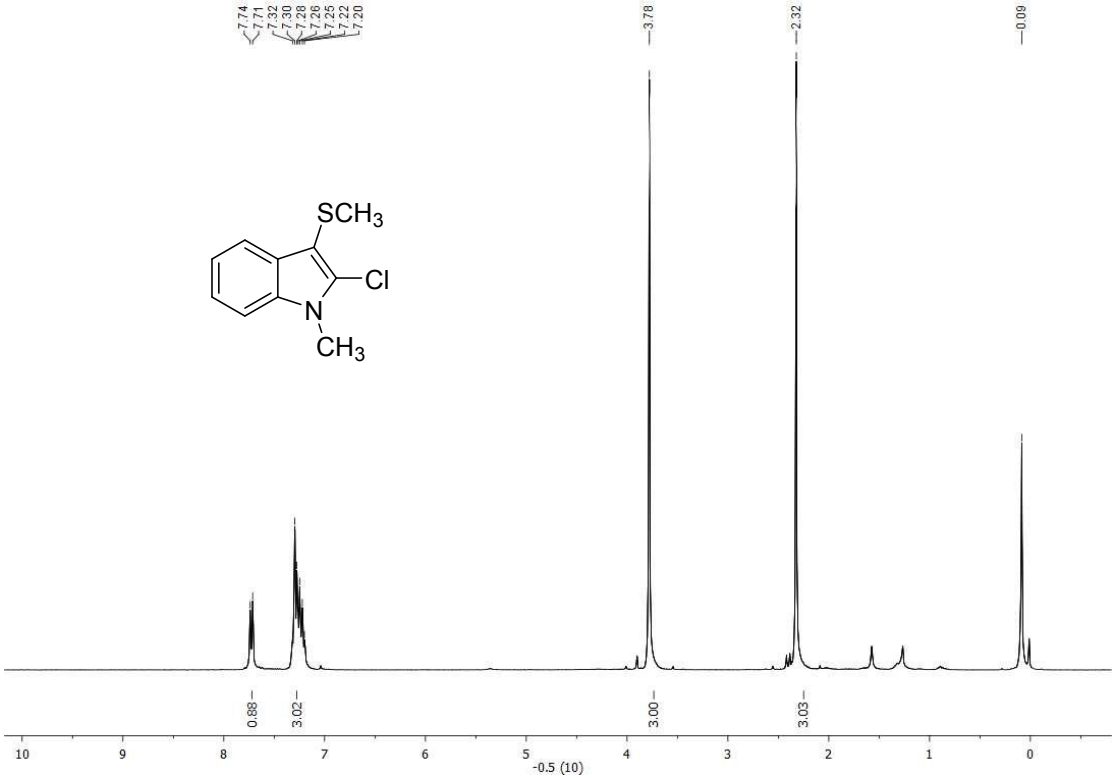
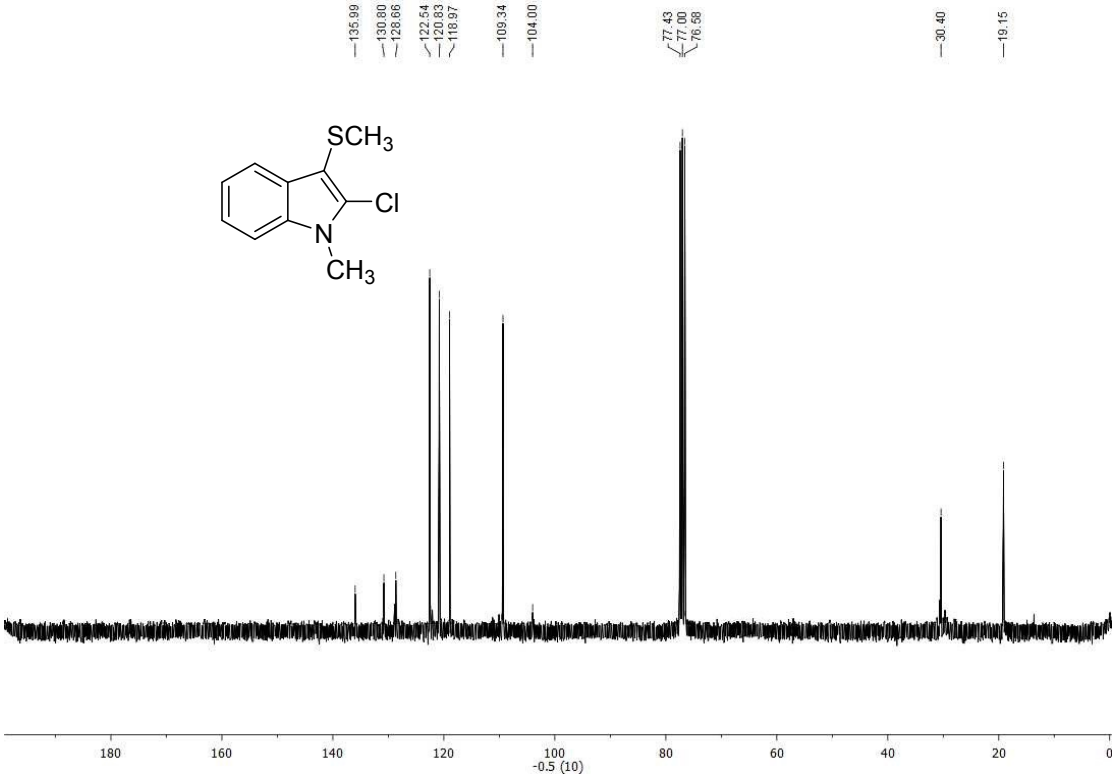
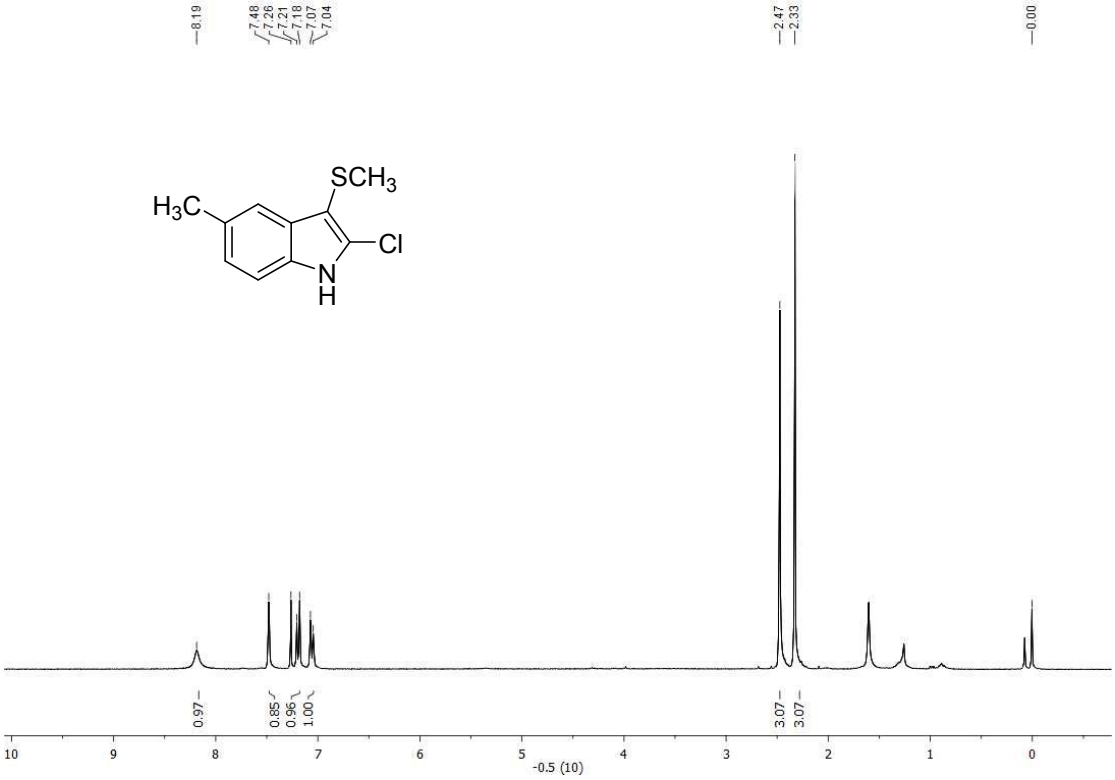
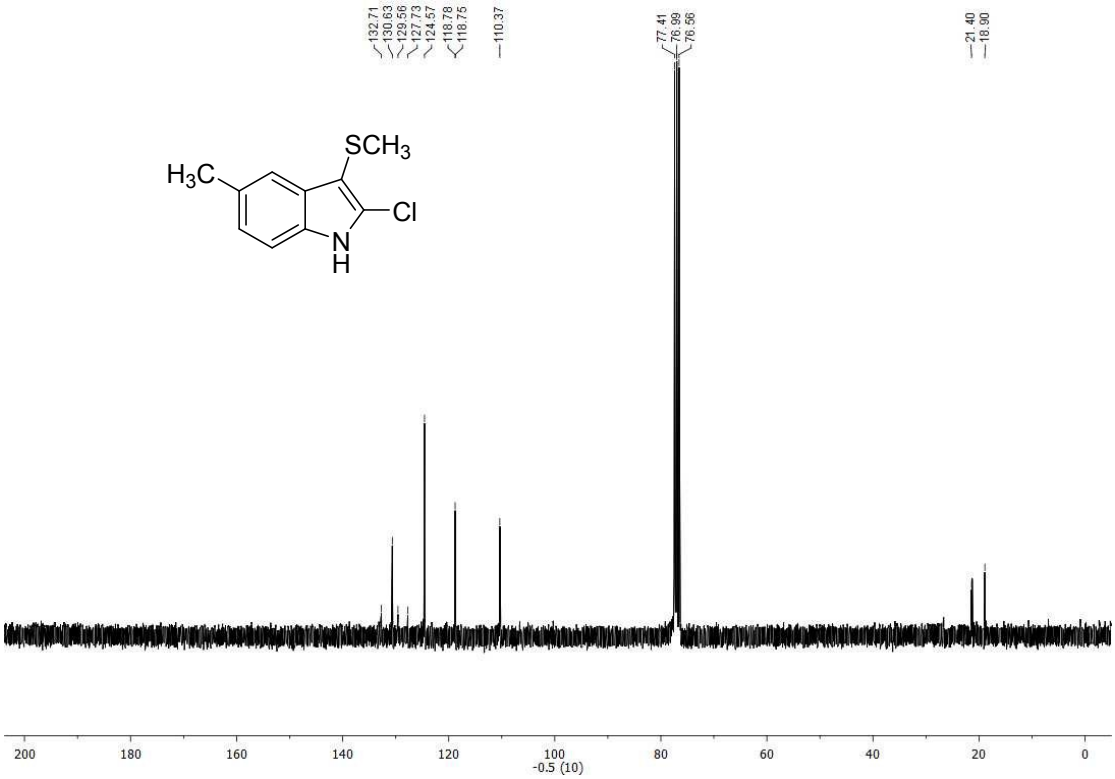




2-chloro-5-methyl-3-(methylthio)-1*H*-indole (2c):





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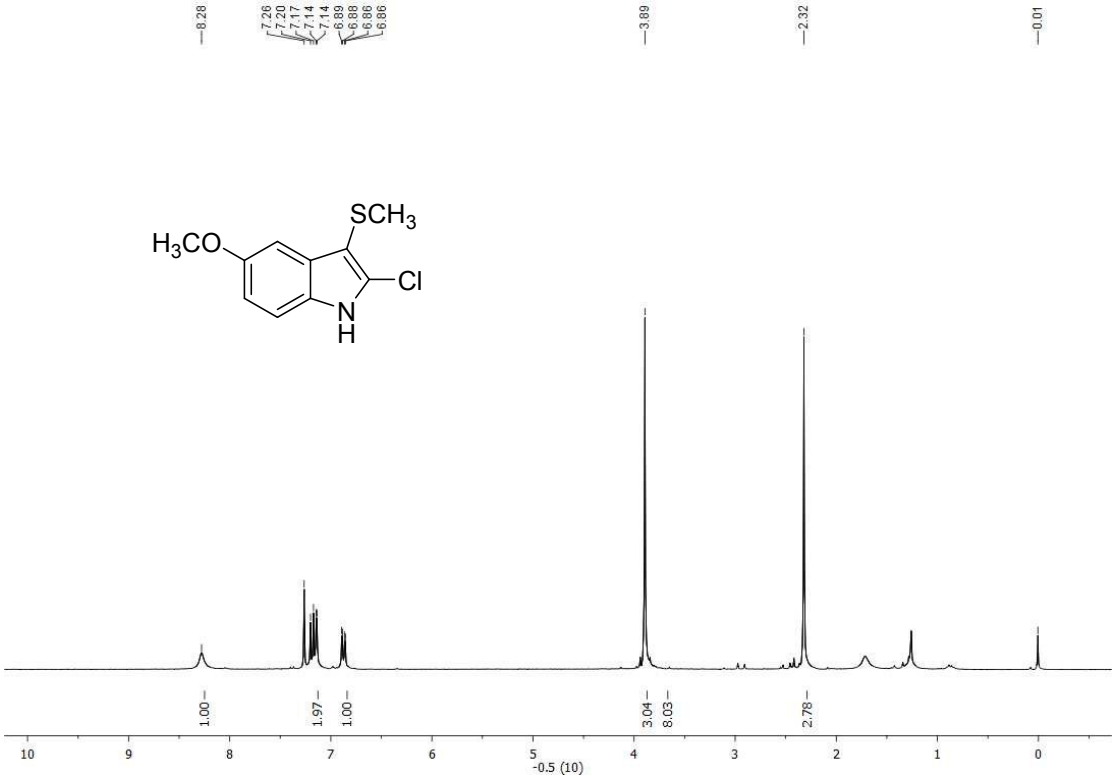

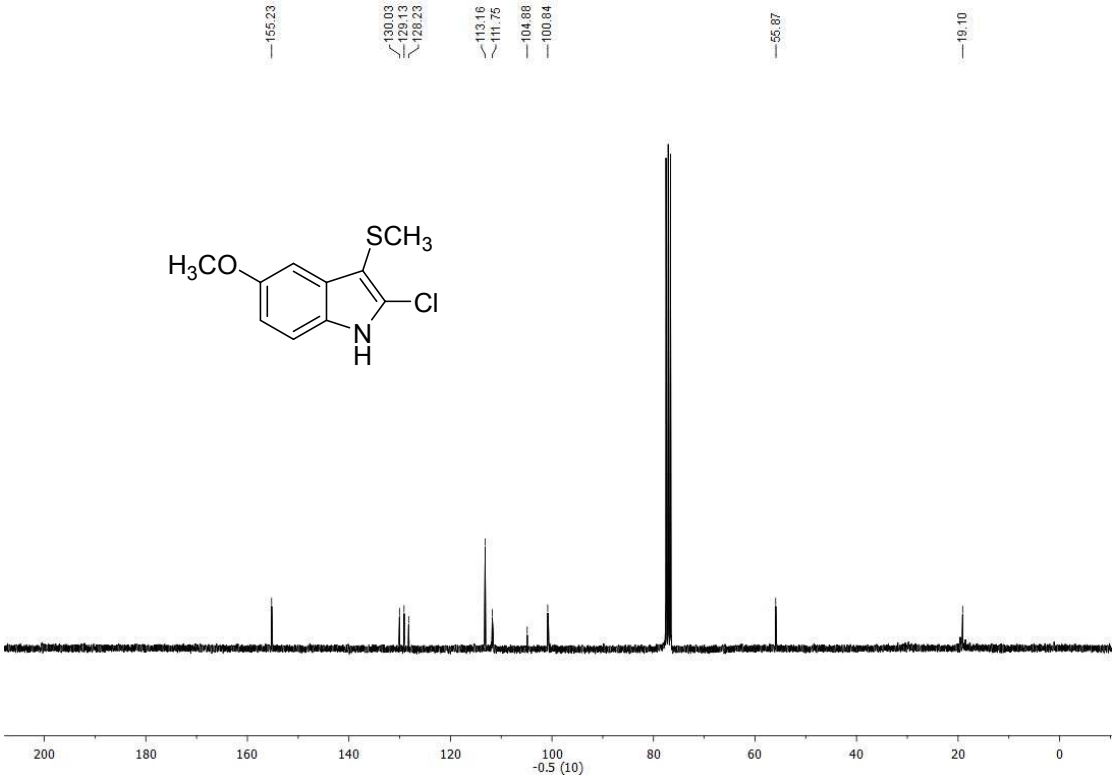

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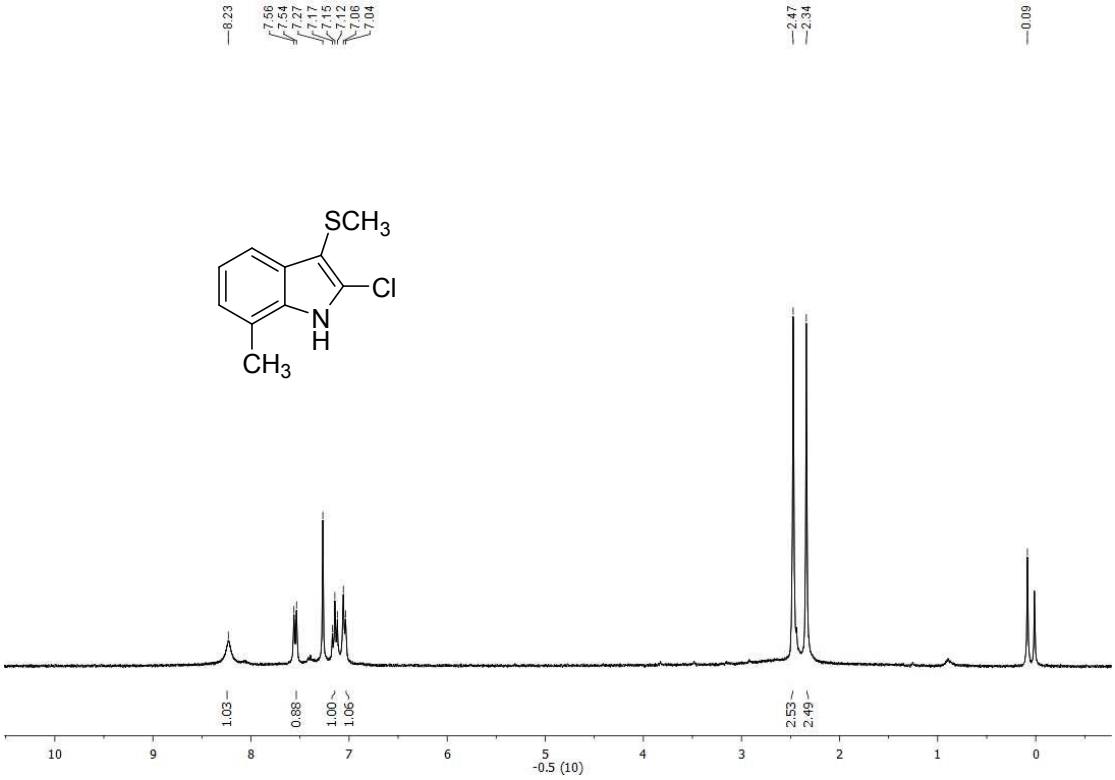
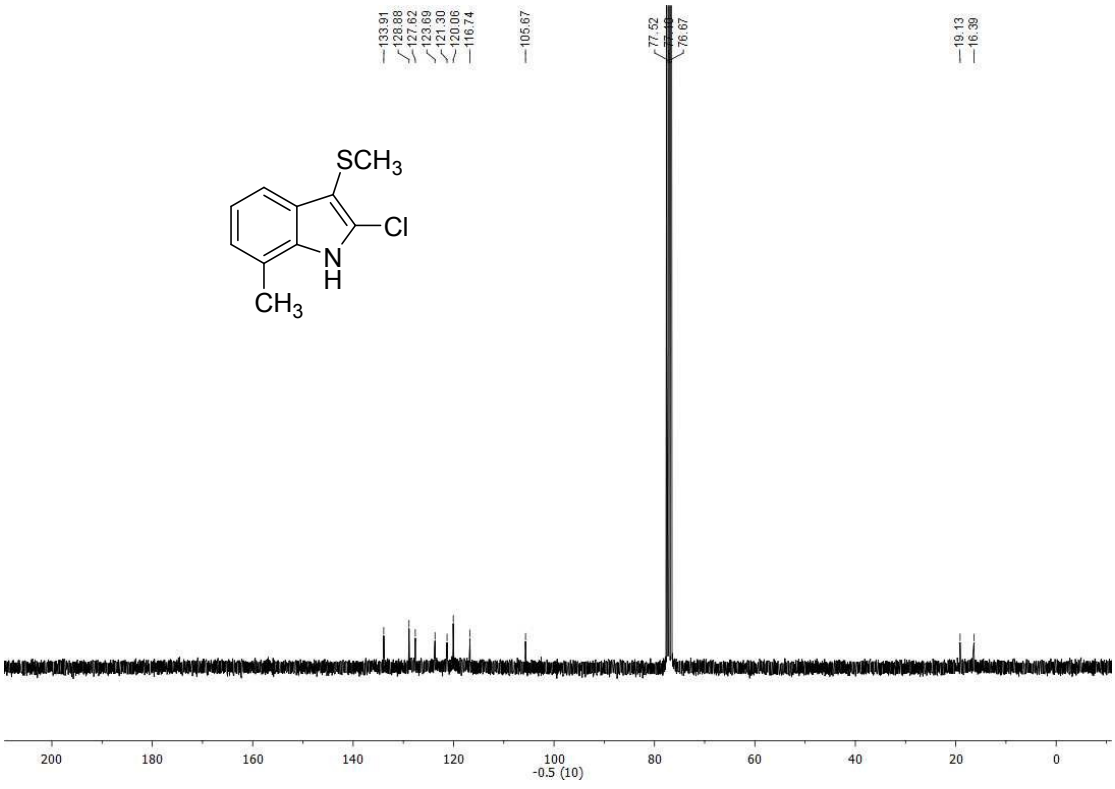
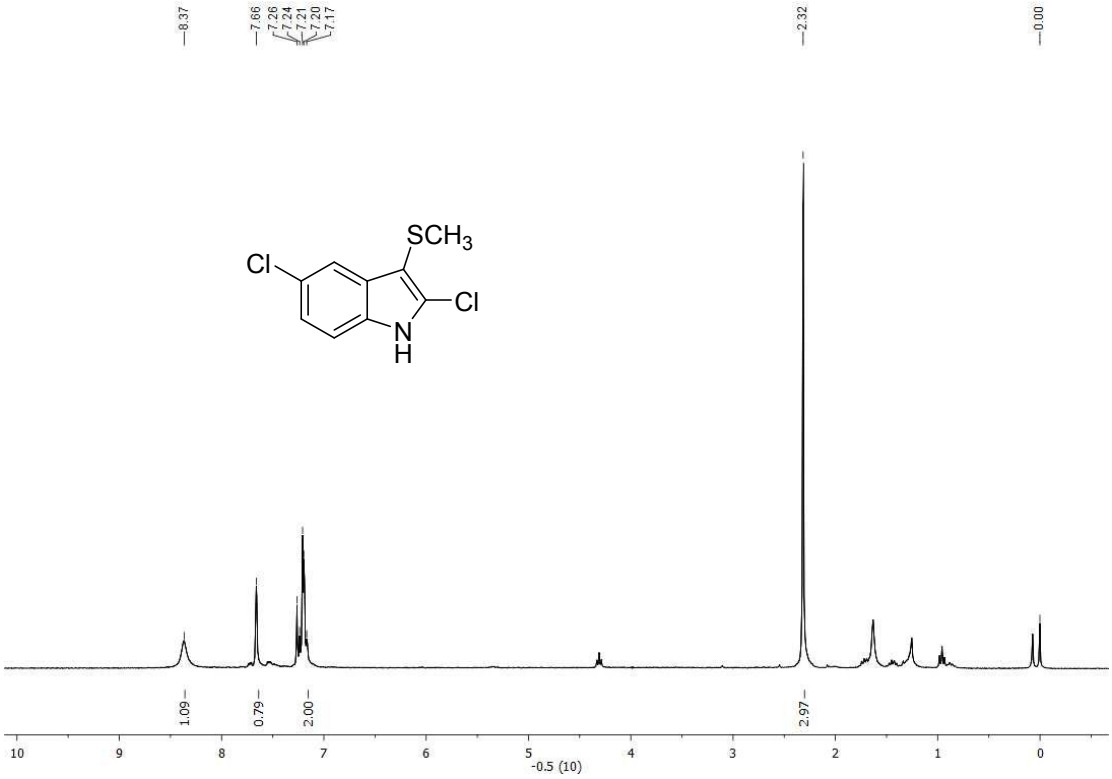
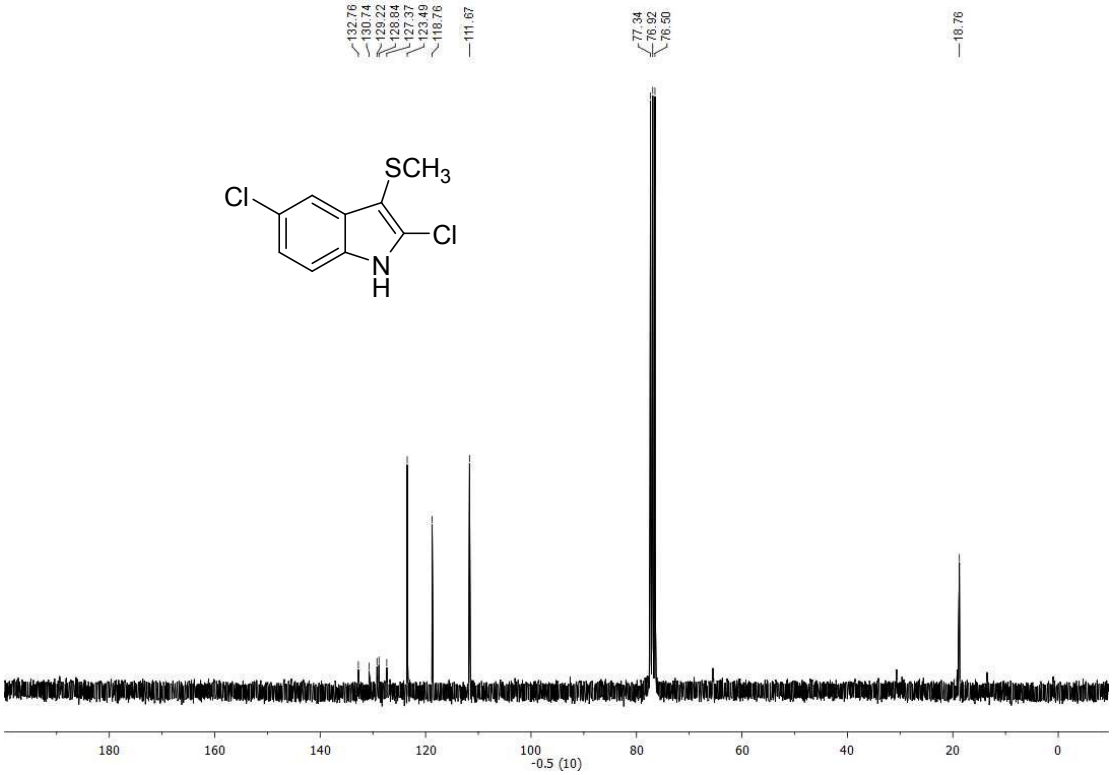


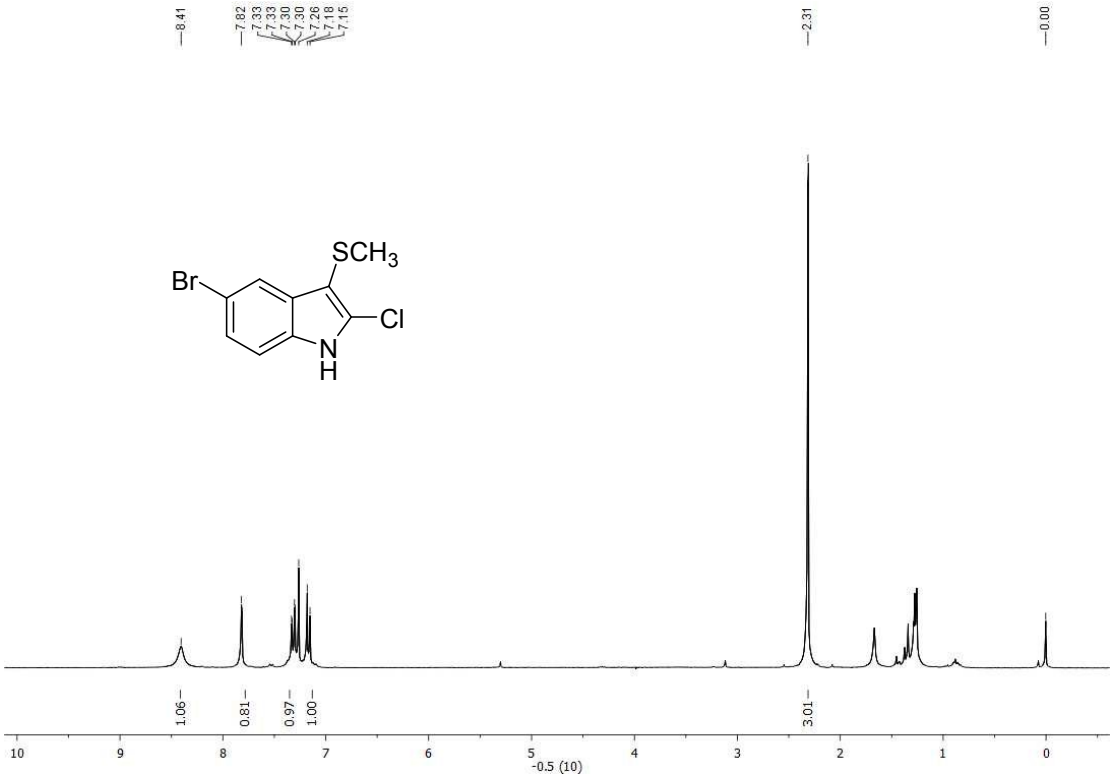


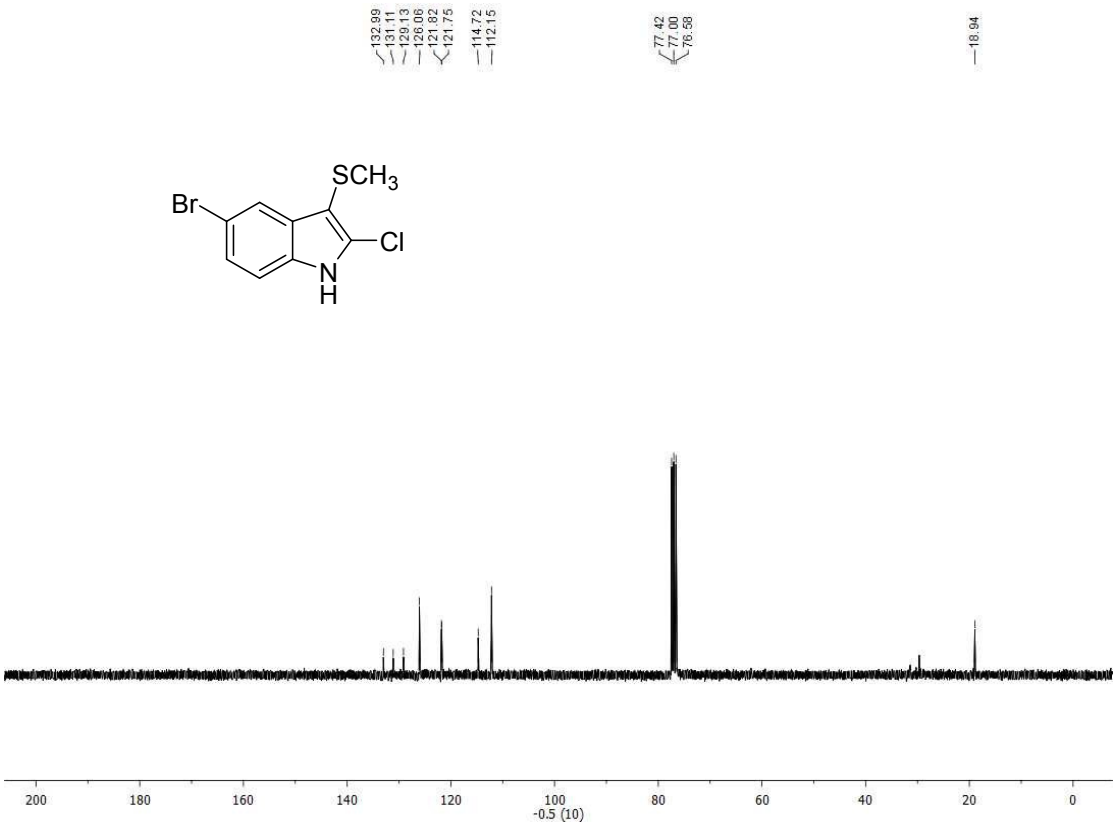
2,5-dichloro-3-(methylthio)-1*H*-indole (2f):



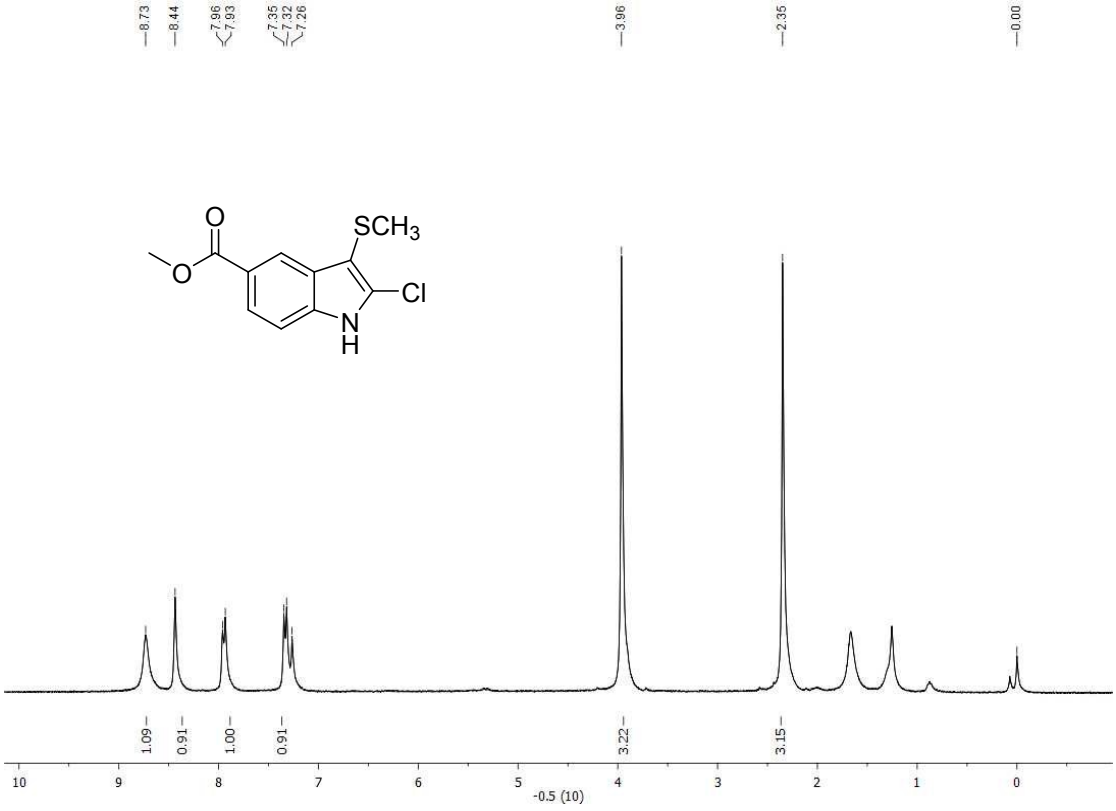


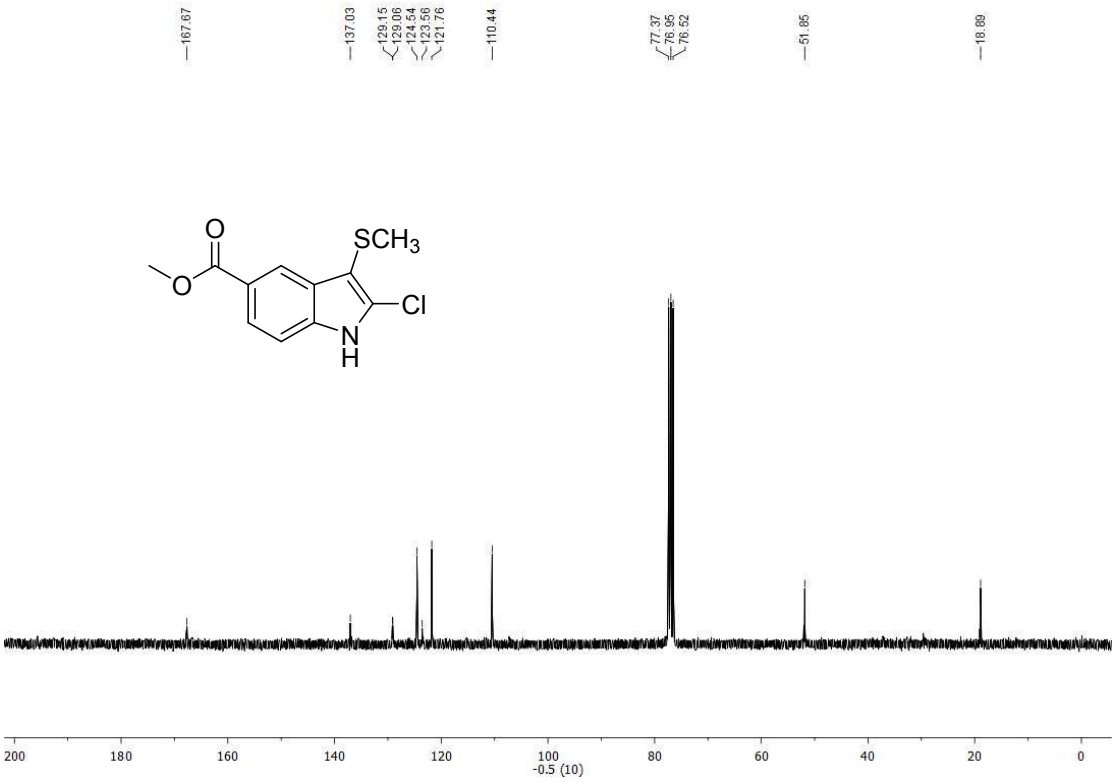
5-bromo-2-chloro-3-(methylthio)-1*H*-indole (2g):



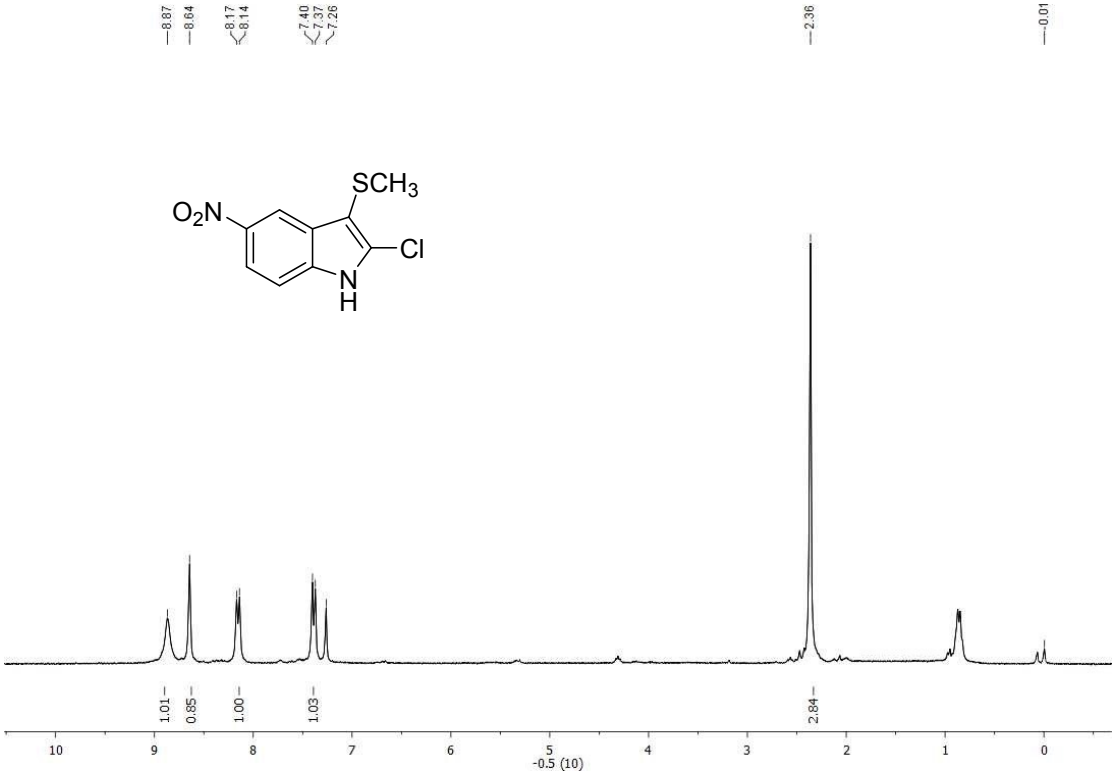


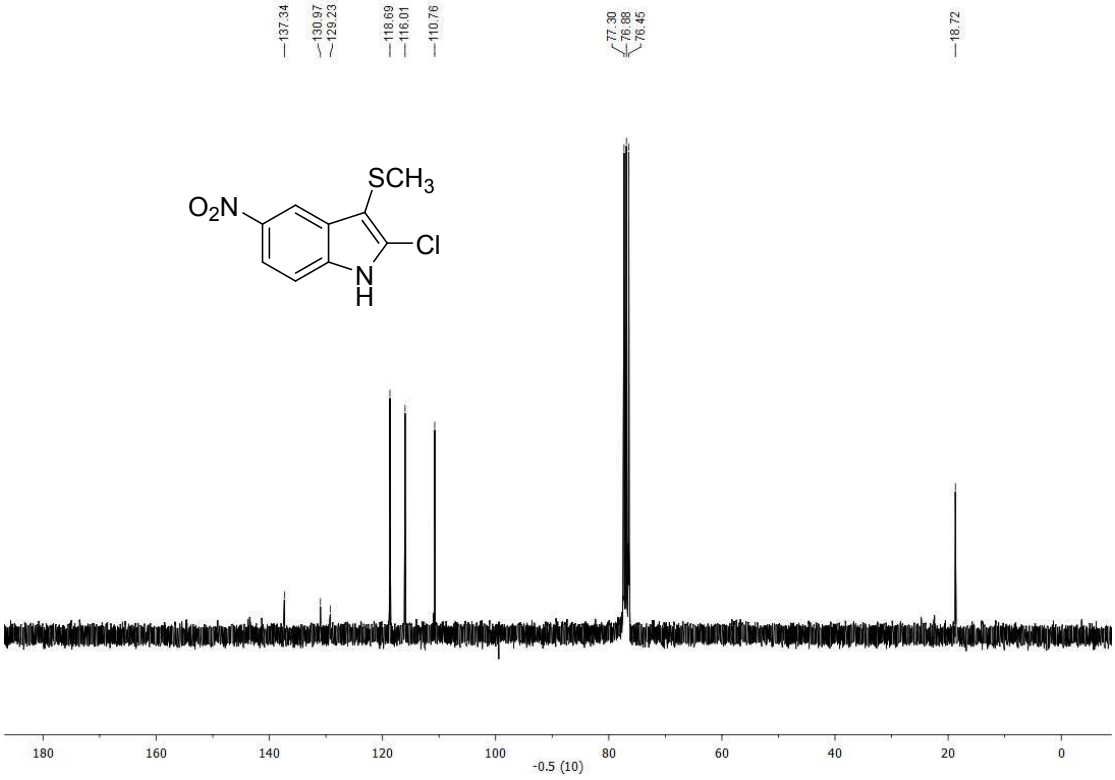
methyl 2-chloro-3-(methylthio)-1*H*-indole-5-carboxylate (2h):



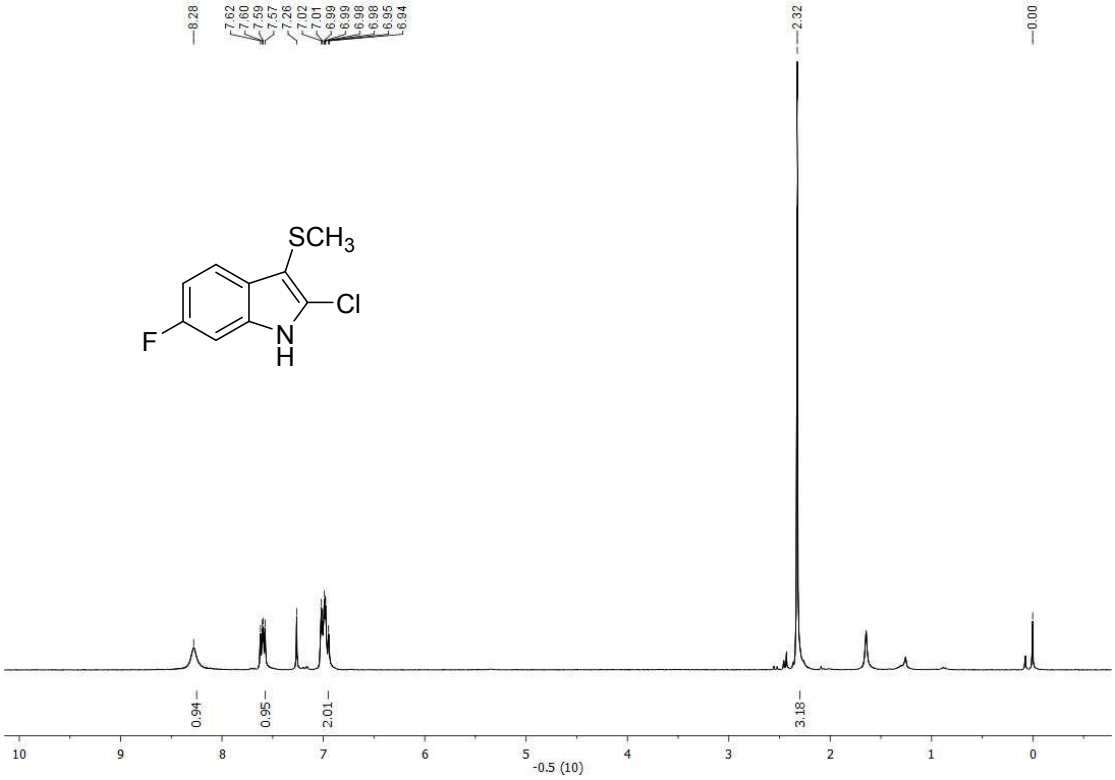


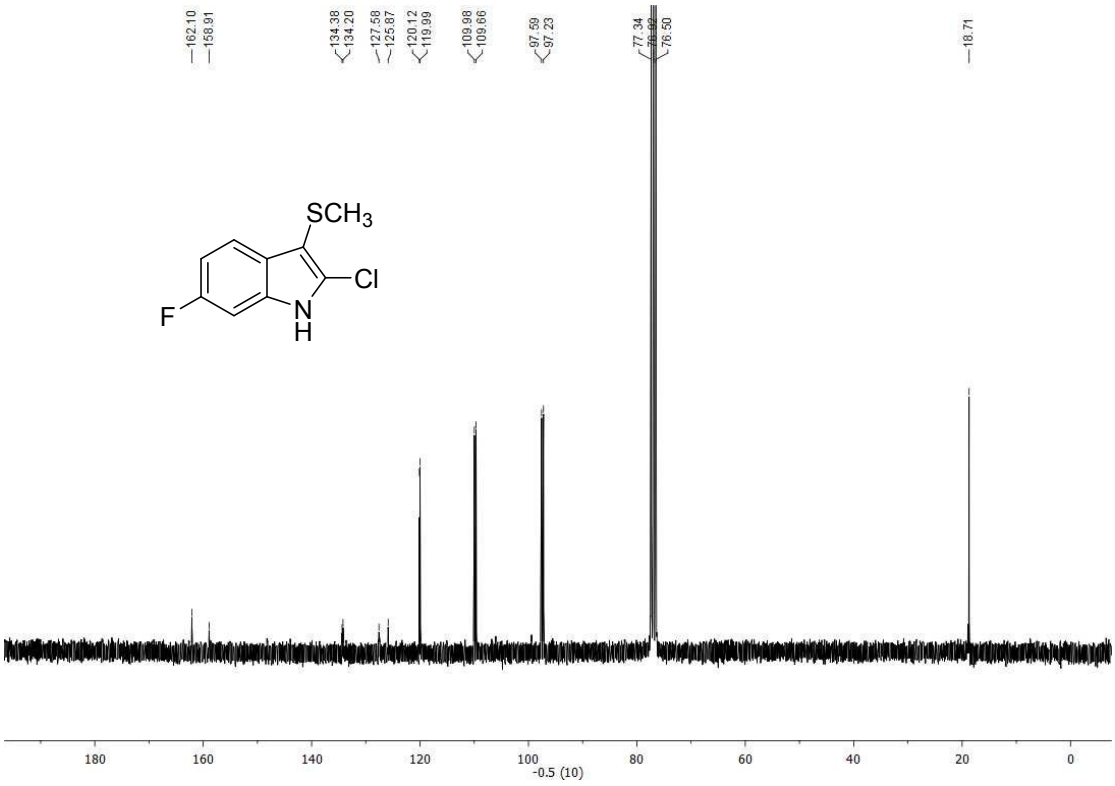
2-chloro-3-(methylthio)-5-nitro-1H-indole (2i):



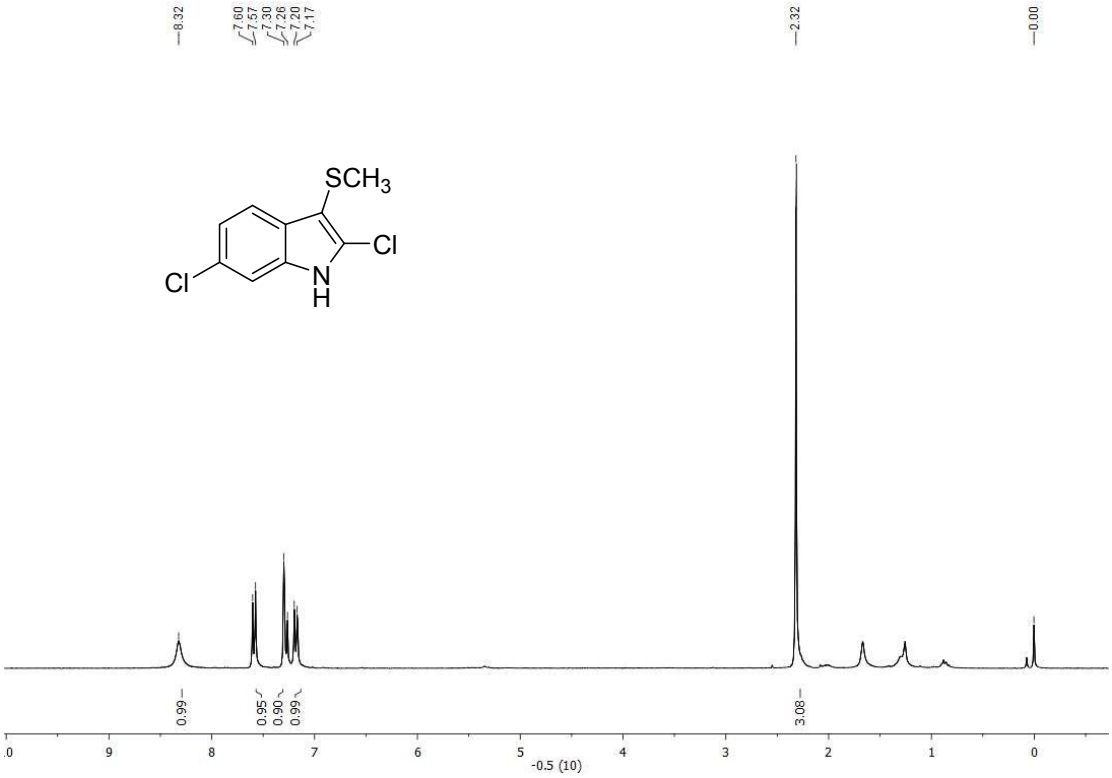


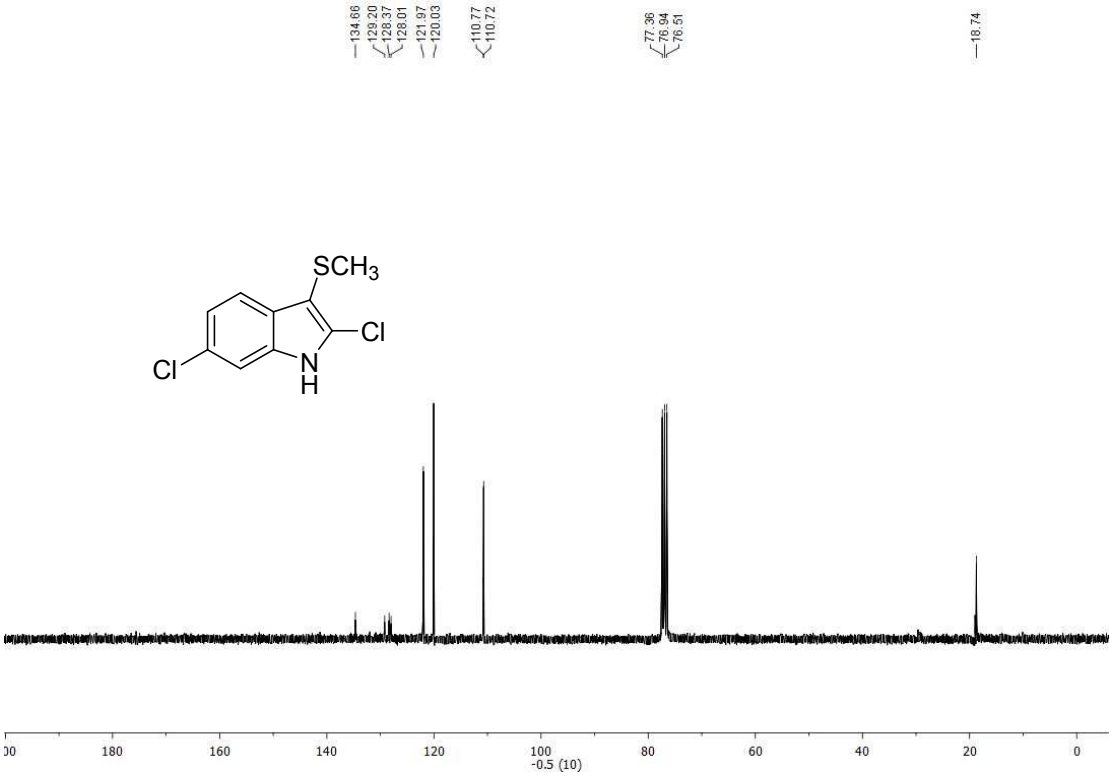
2-chloro-6-fluoro-3-(methylthio)-1H-indole (2j):



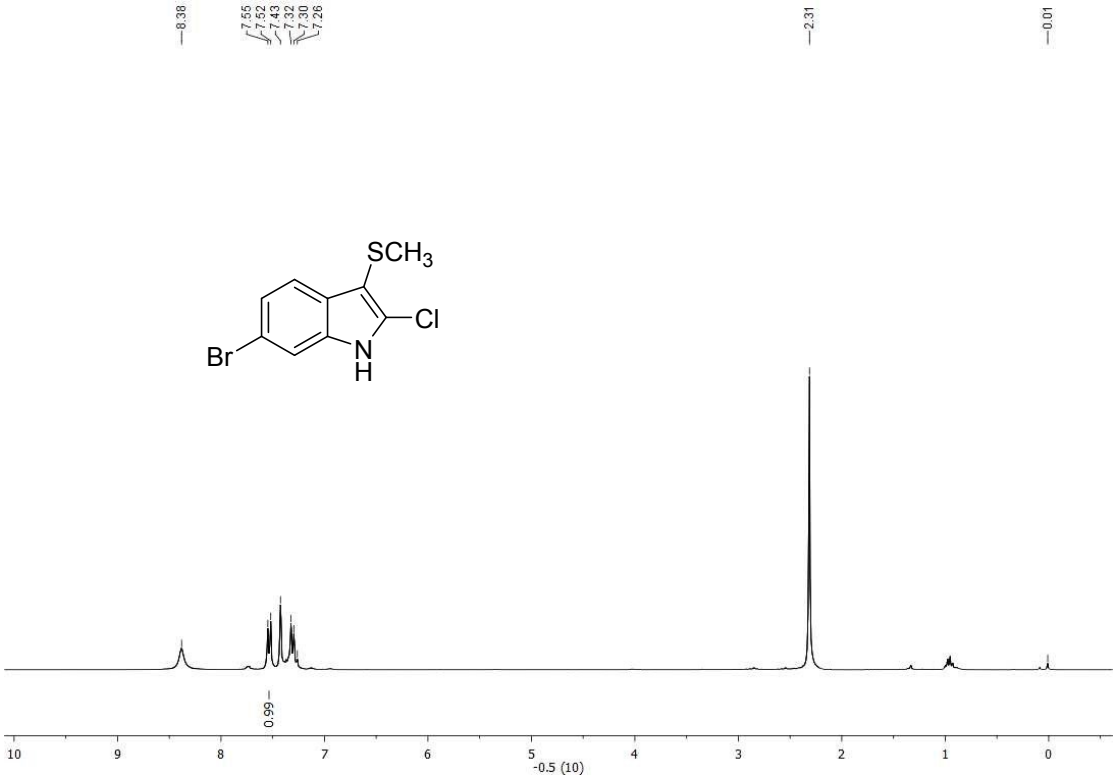


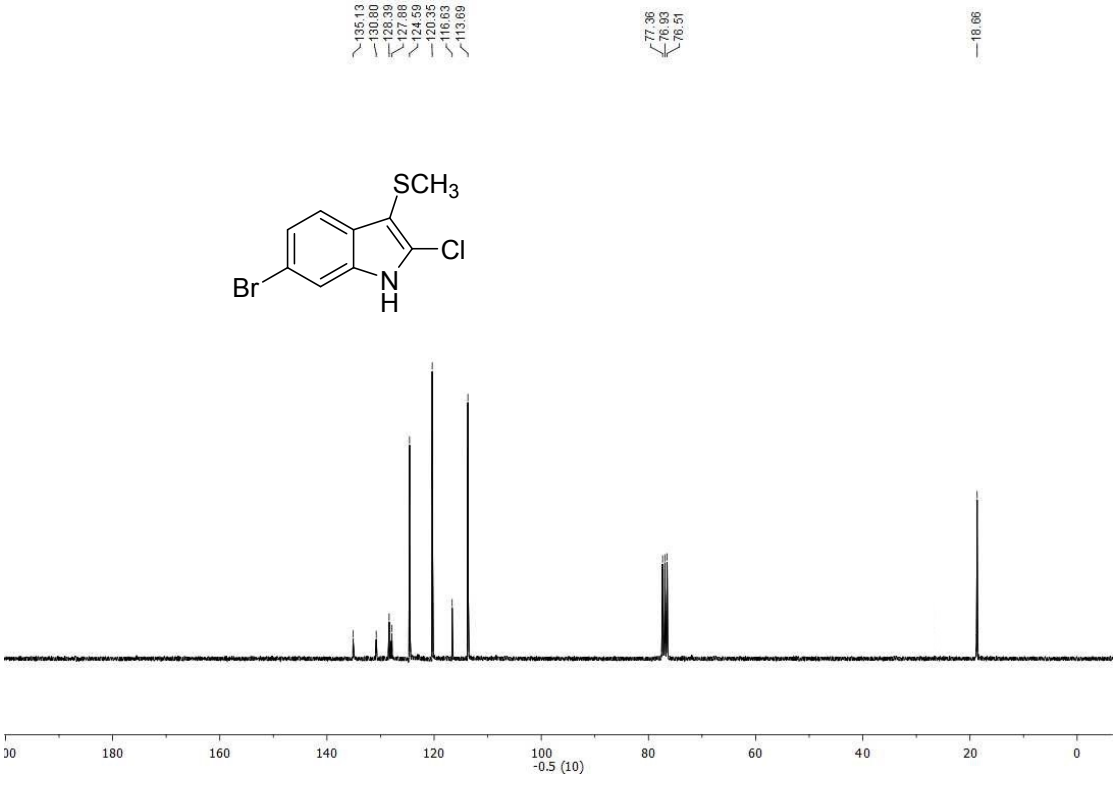
2,6-dichloro-3-(methylthio)-1*H*-indole (2k):



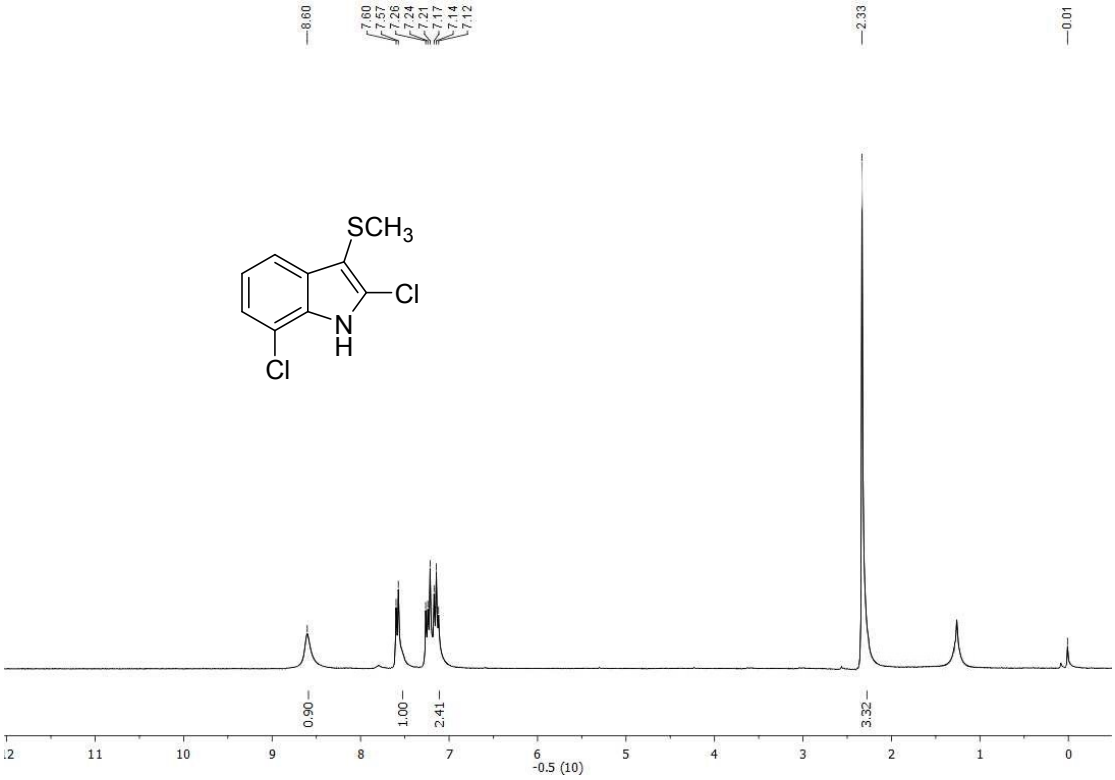


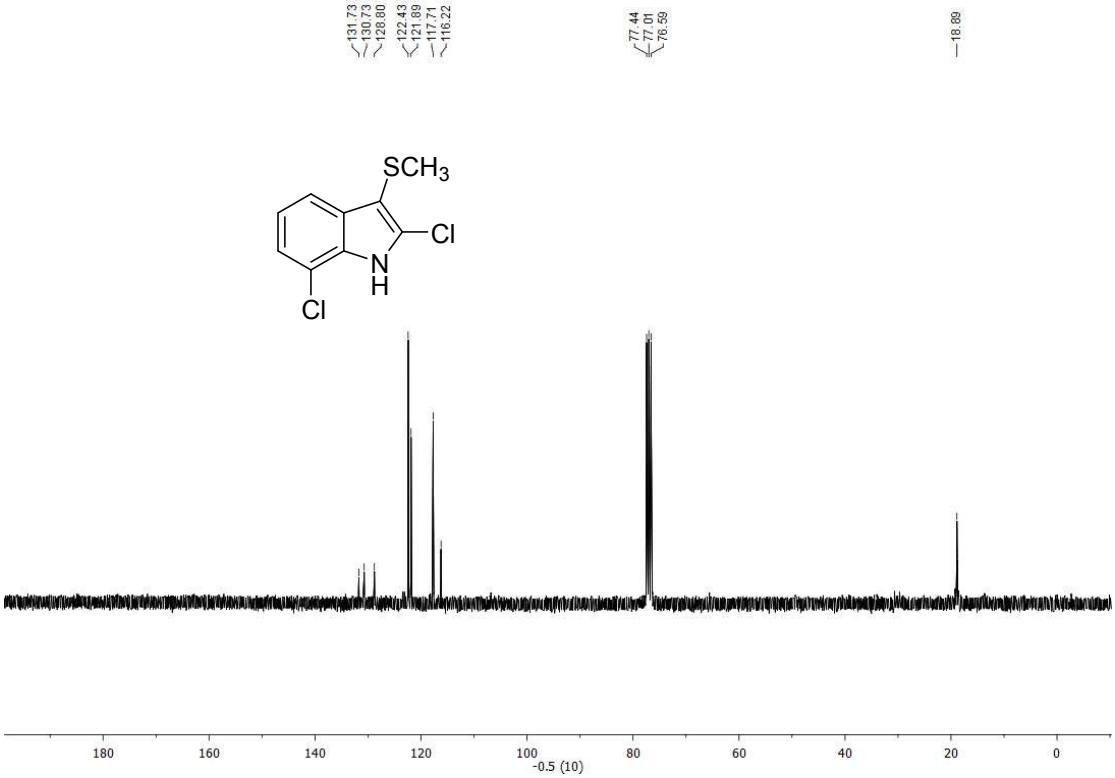
6-bromo-2-chloro-3-(methylthio)-1*H*-indole (2l):



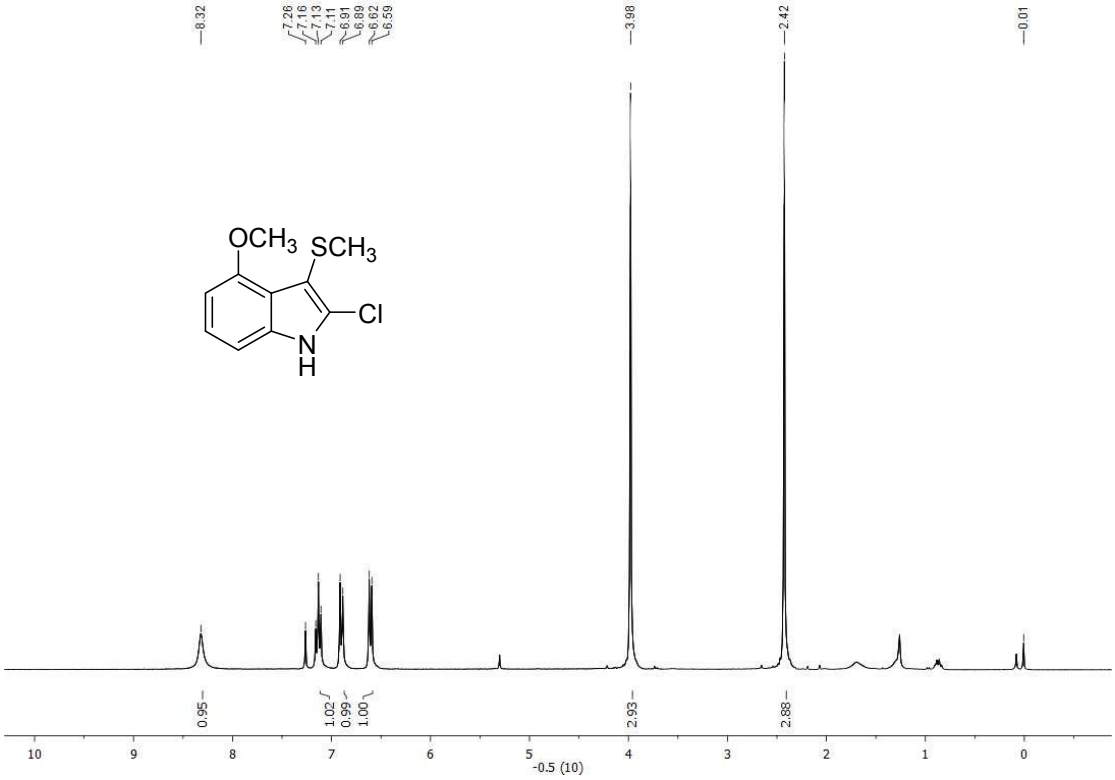


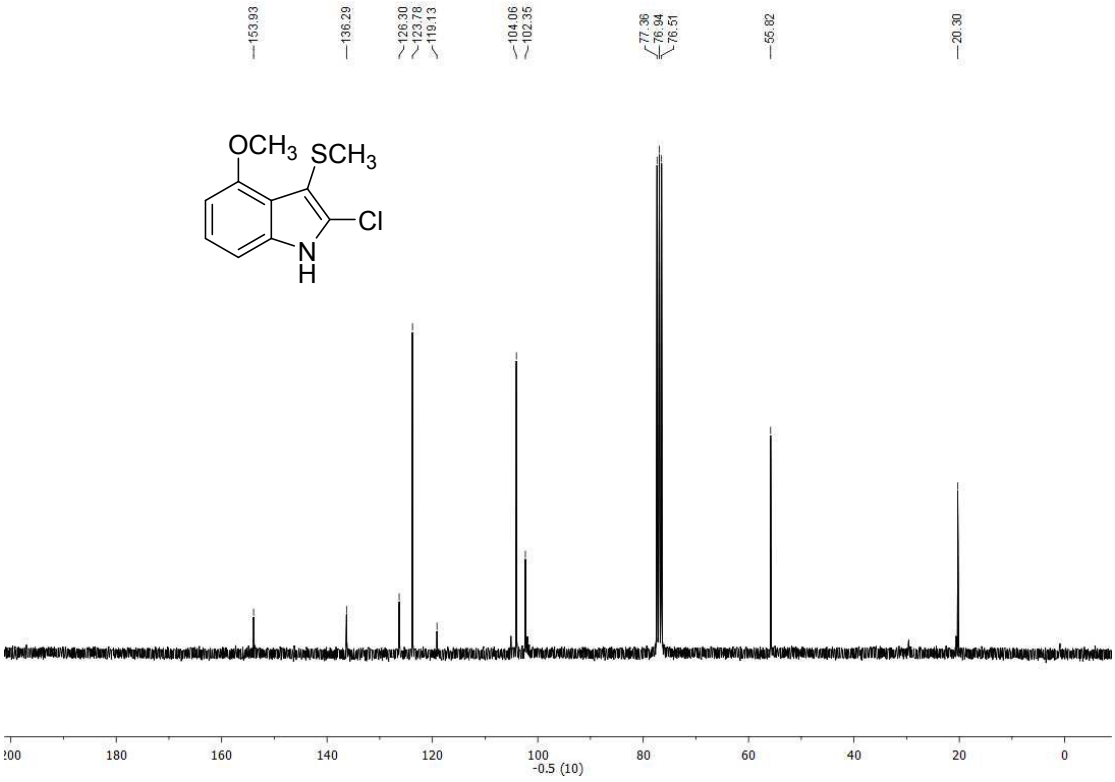
2,7-dichloro-3-(methylthio)-1*H*-indole (2m):



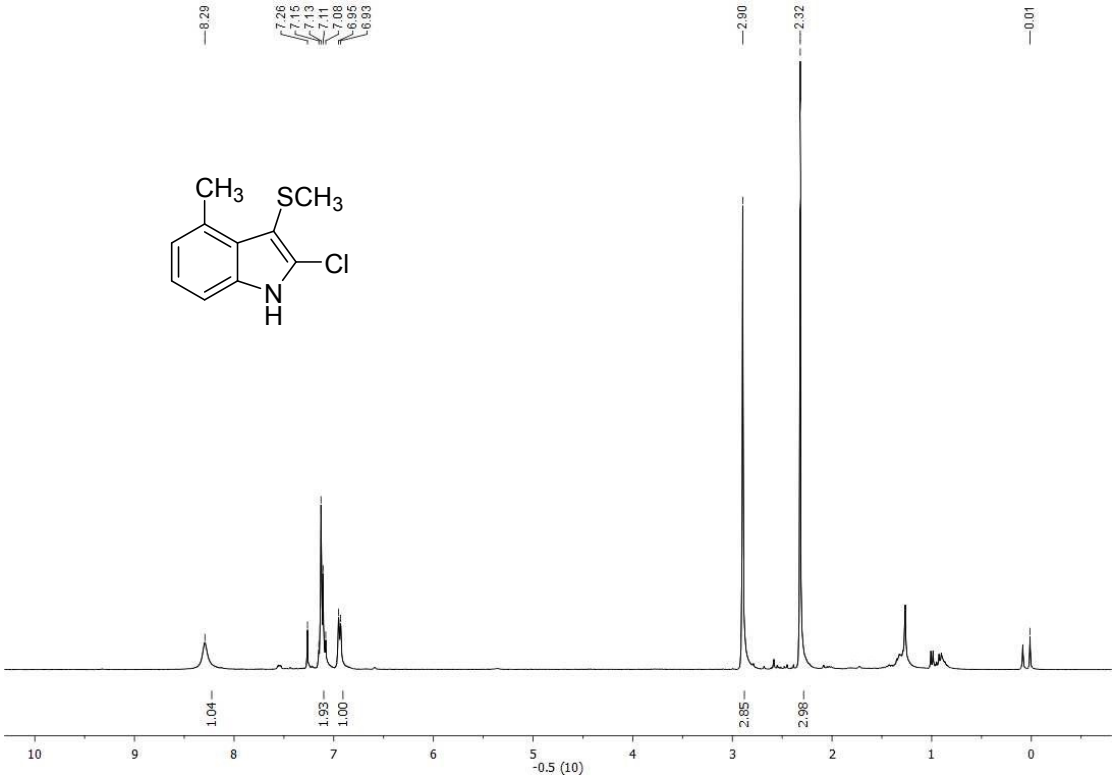


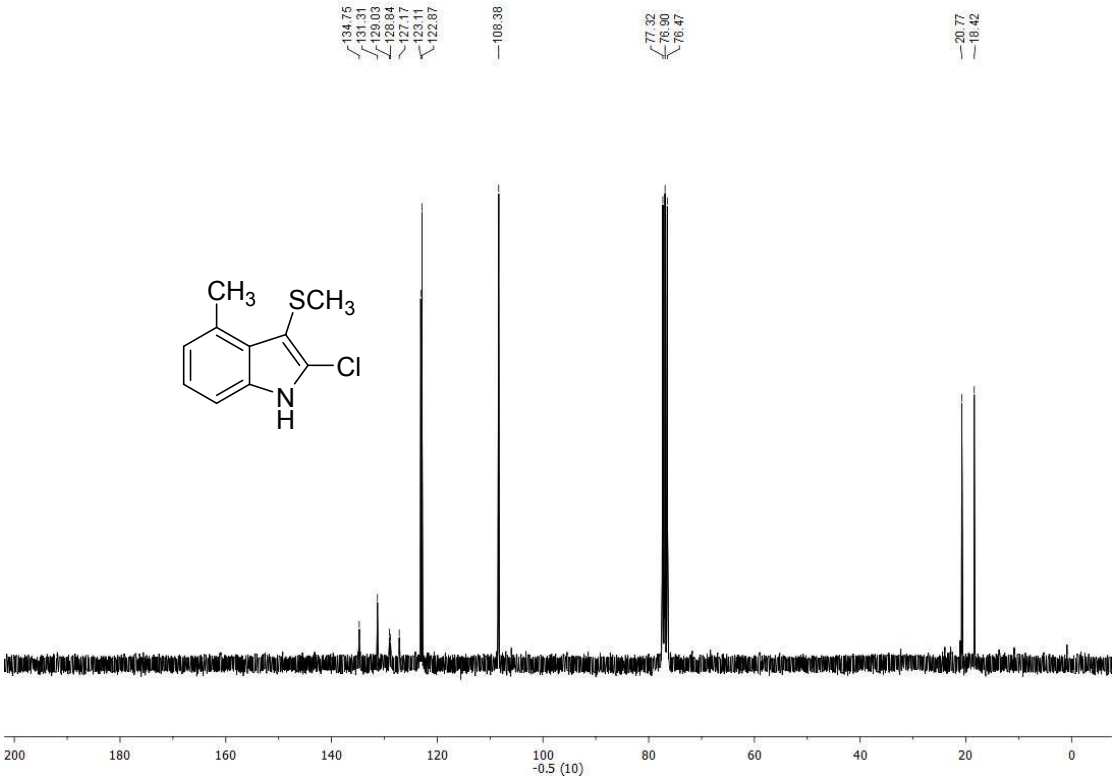
2-chloro-4-methoxy-3-(methylthio)-1H-indole (2p):



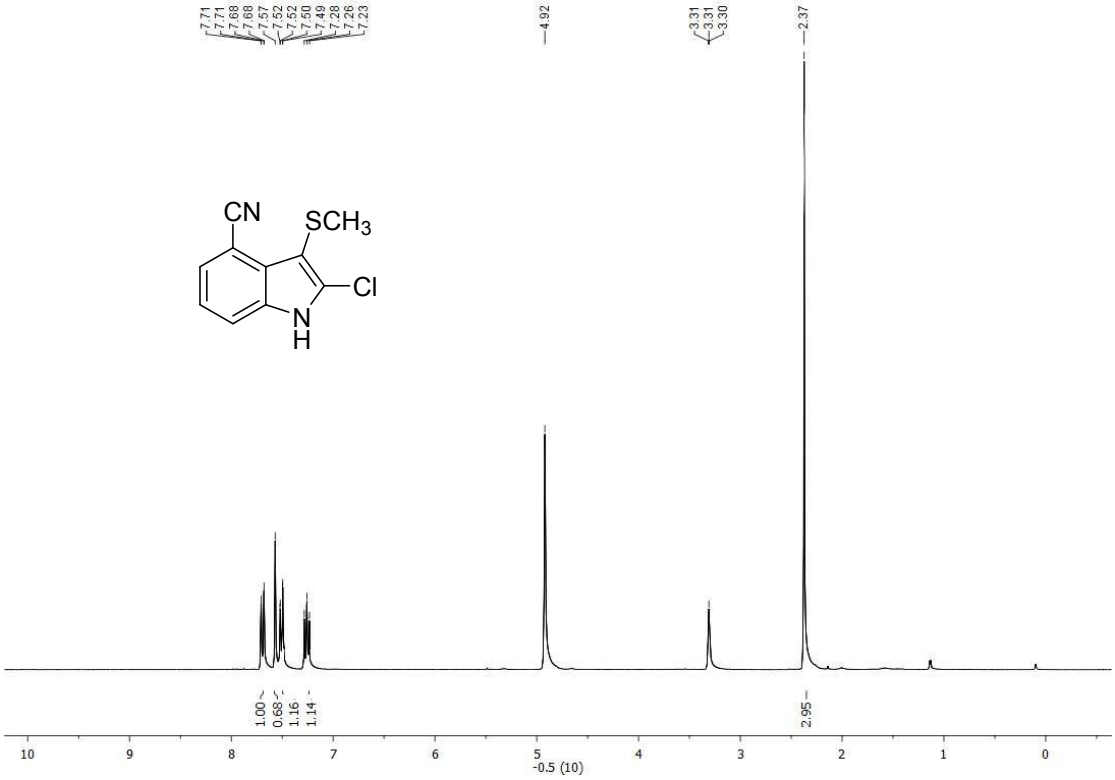


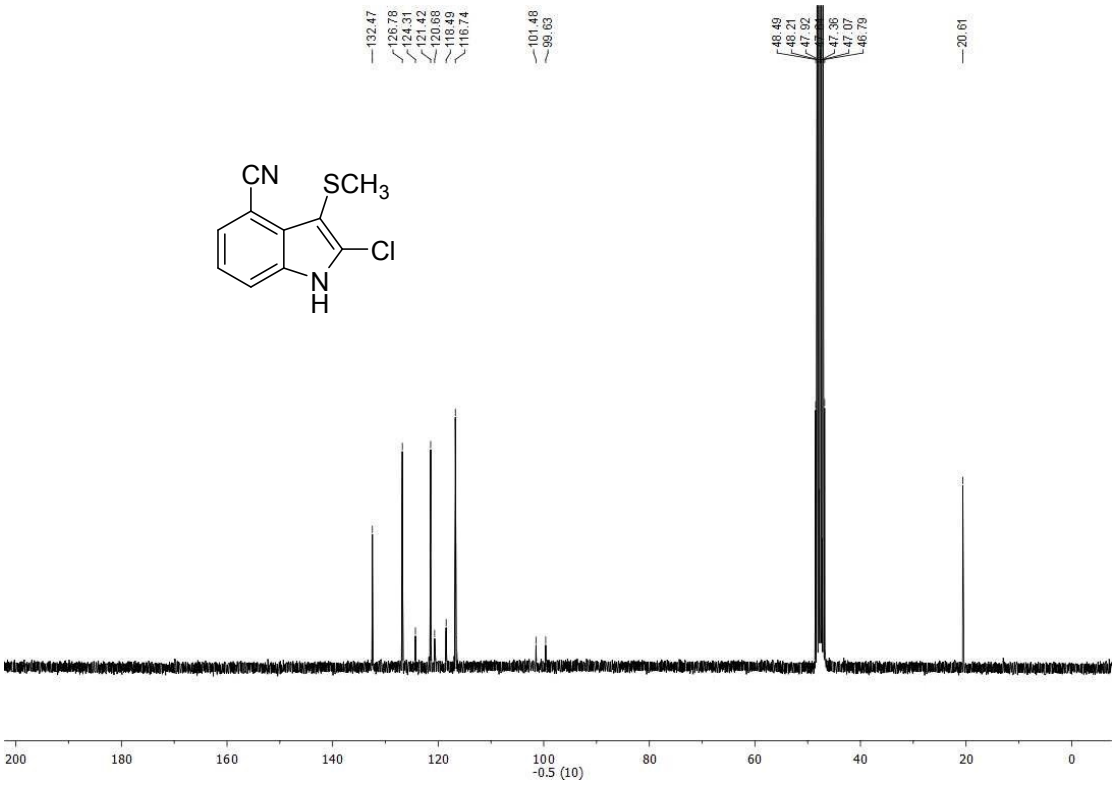
2-chloro-4-methyl-3-(methylthio)-1H-indole (2q):



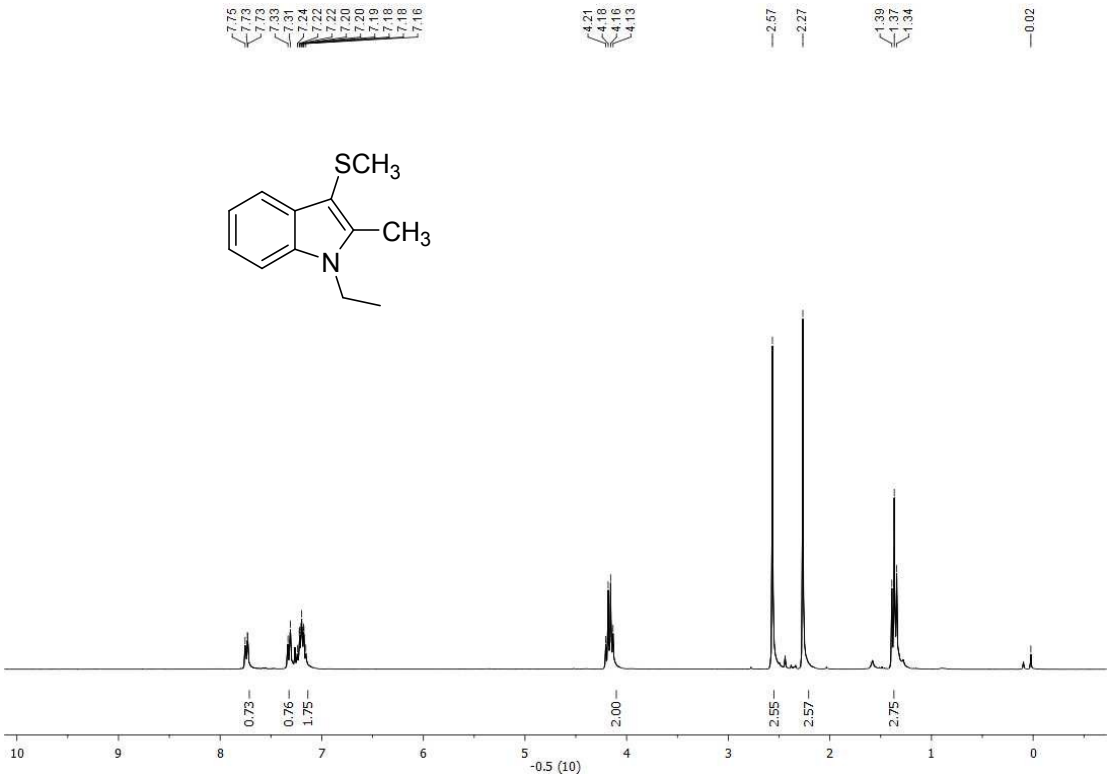


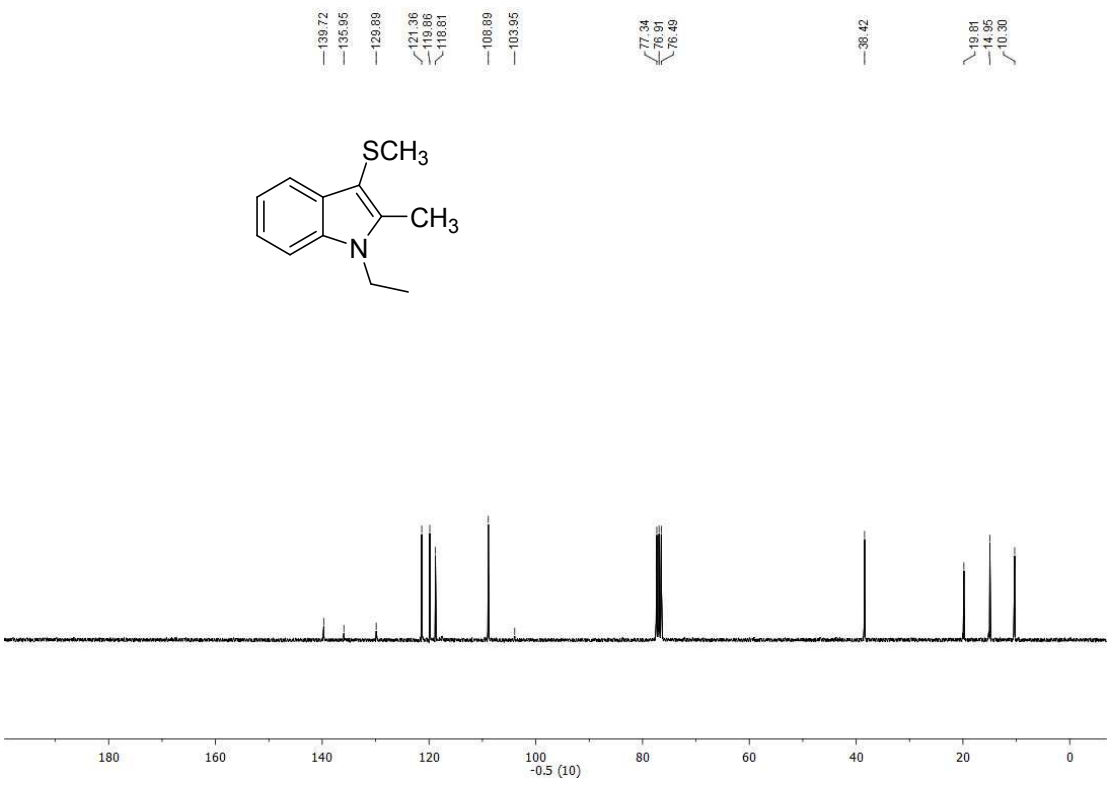
2-chloro-3-(methylthio)-1H-indole-4-carbonitrile (2r):



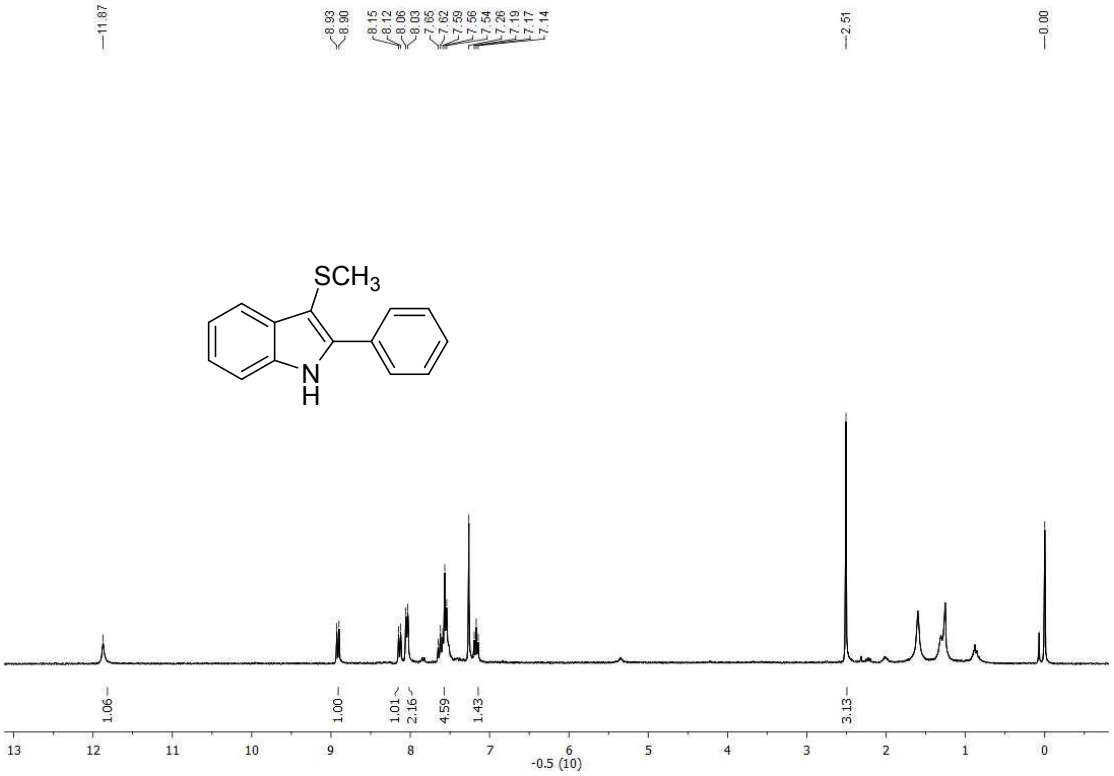


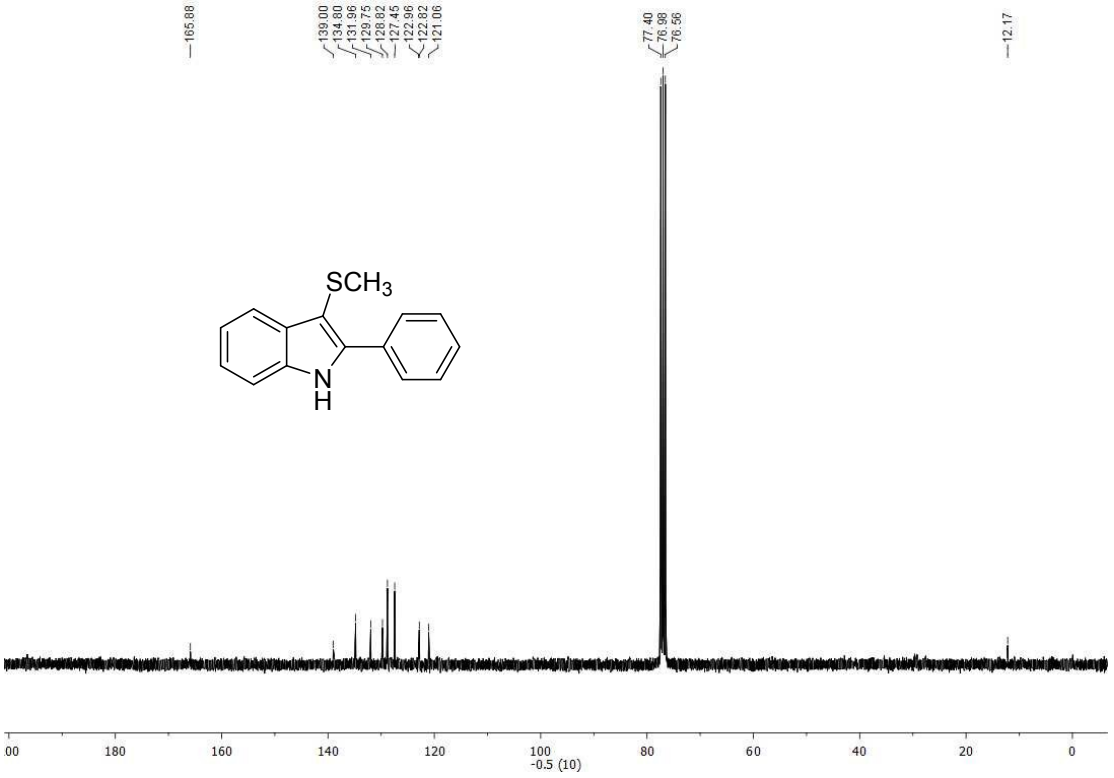
1-ethyl-2-methyl-3-(methylthio)-1H-indole (2s):



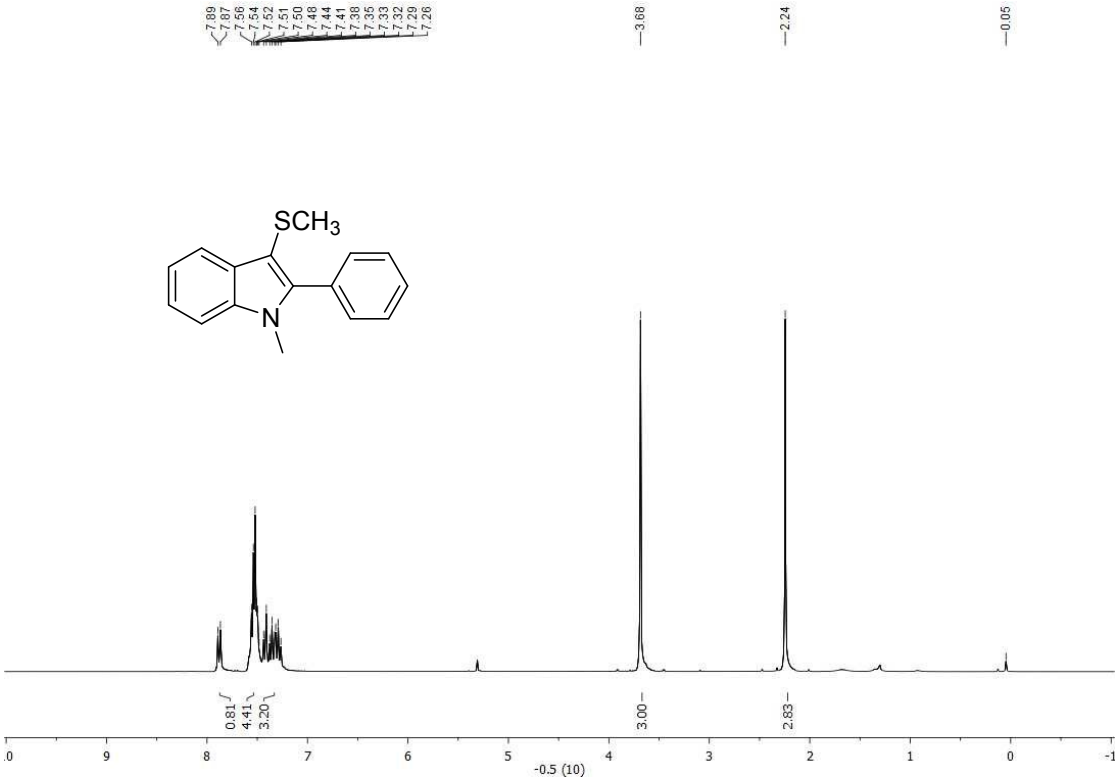


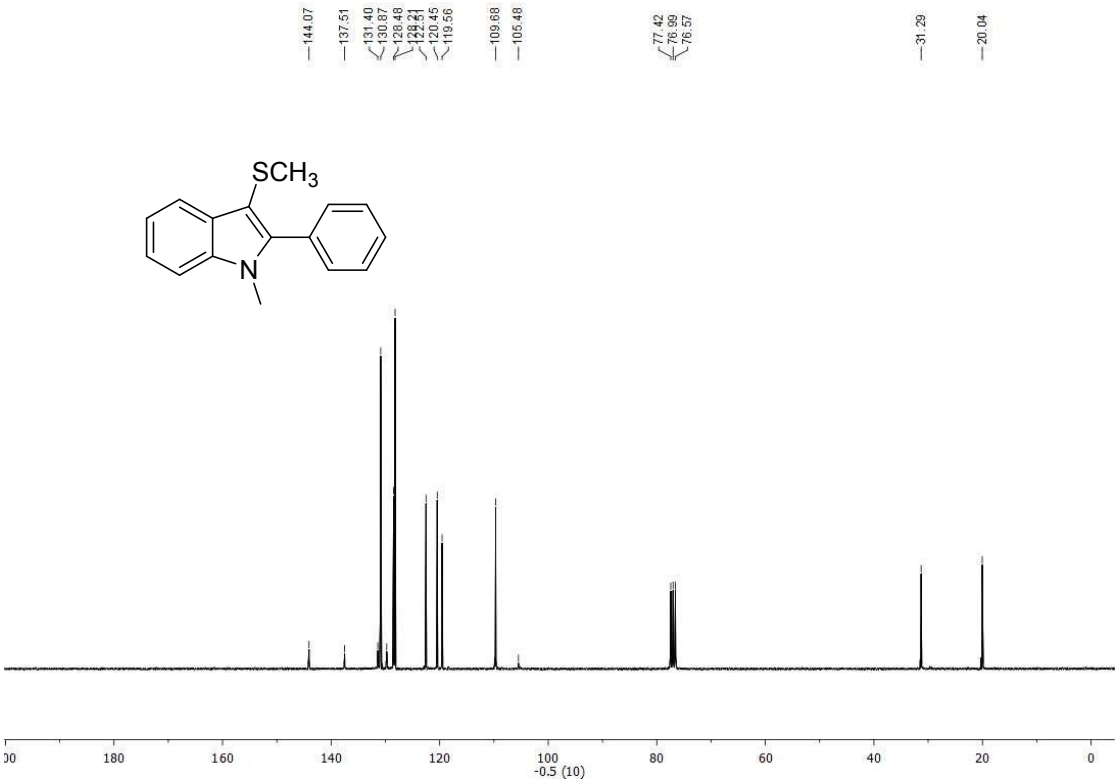
3-(methylthio)-2-phenyl-1*H*-indole (2t):



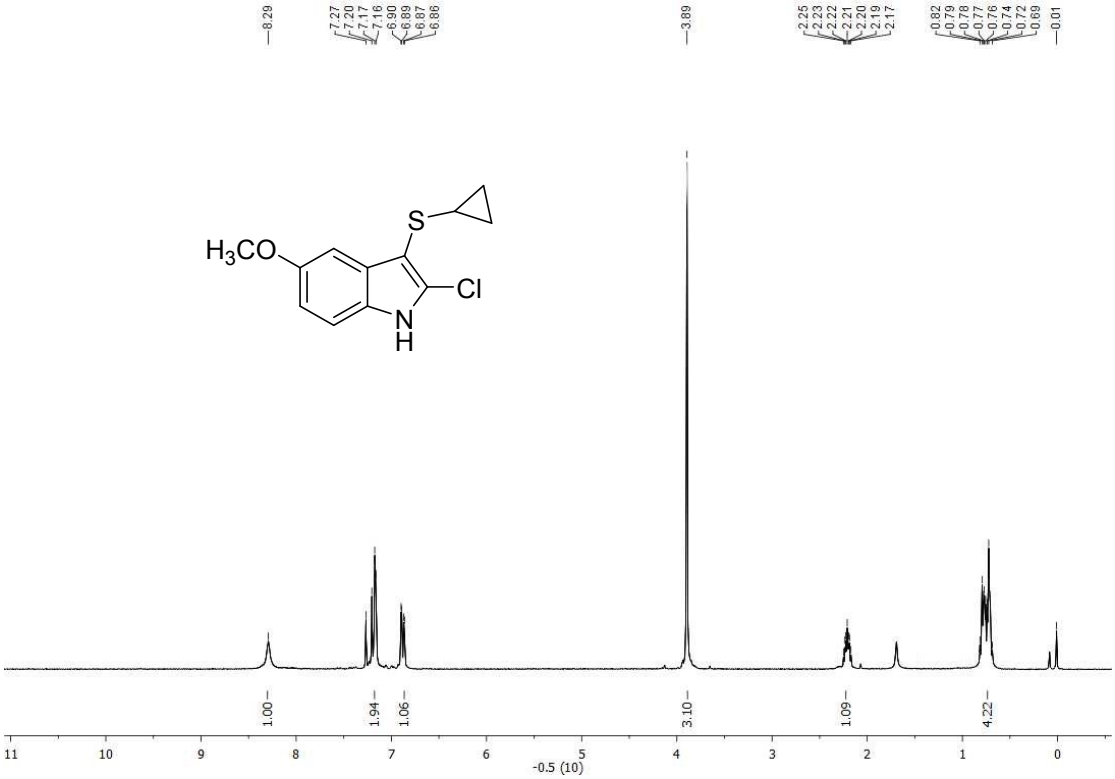


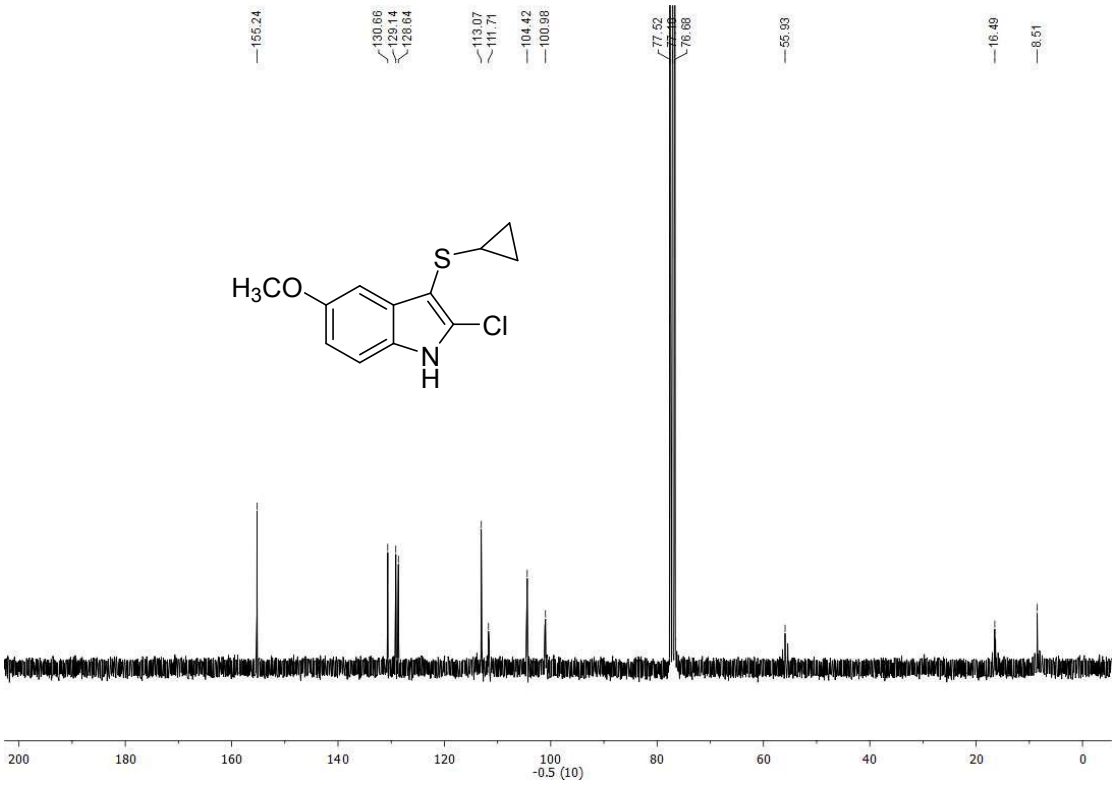
1-methyl-3-(methylthio)-2-phenyl-1H-indole (2u):



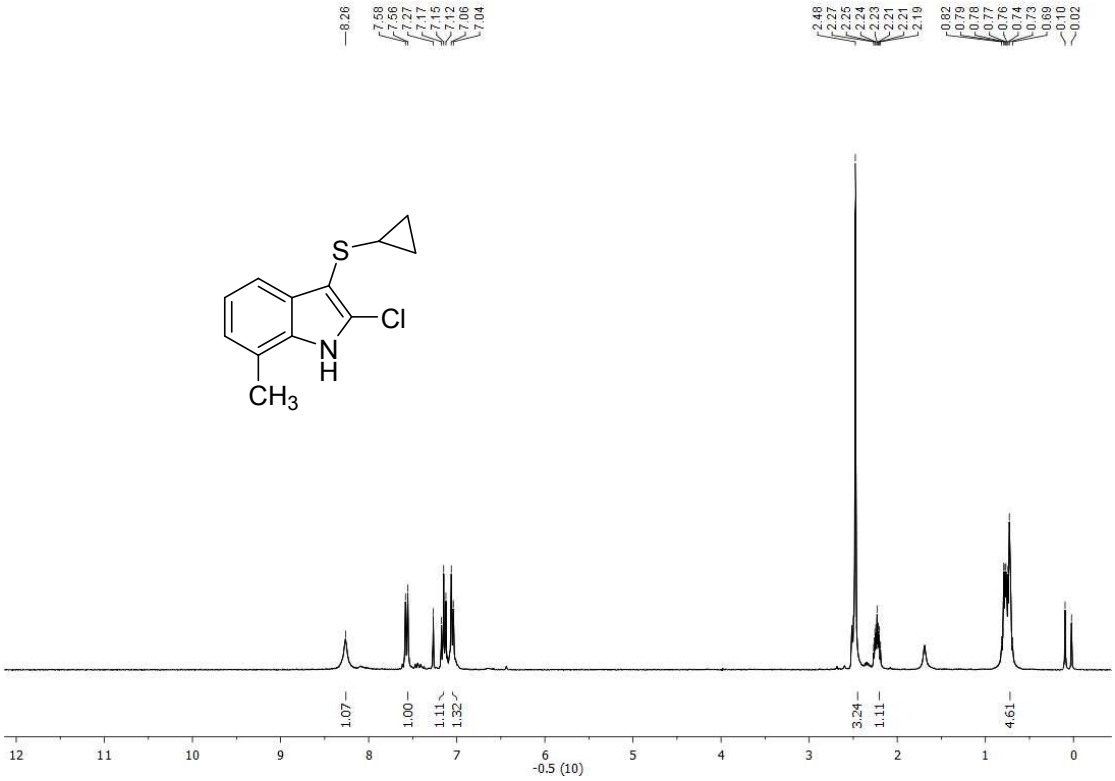


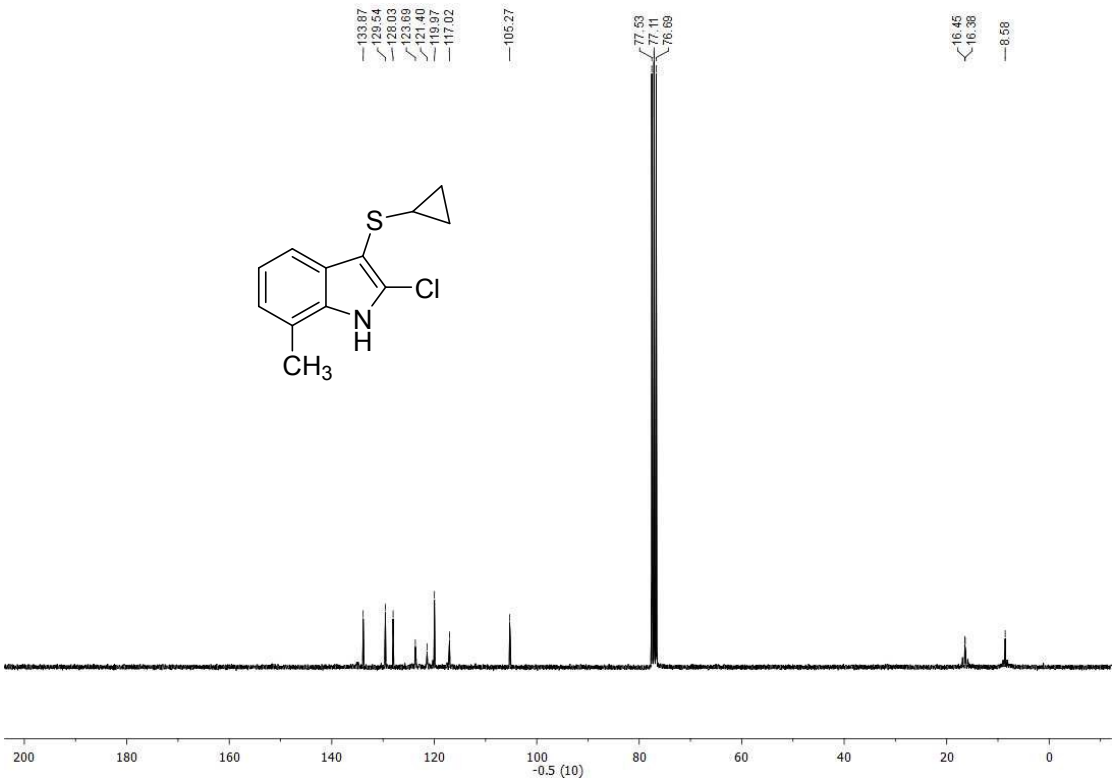
2-chloro-3-(cyclopropylthio)-5-methoxy-1H-indole(2v):



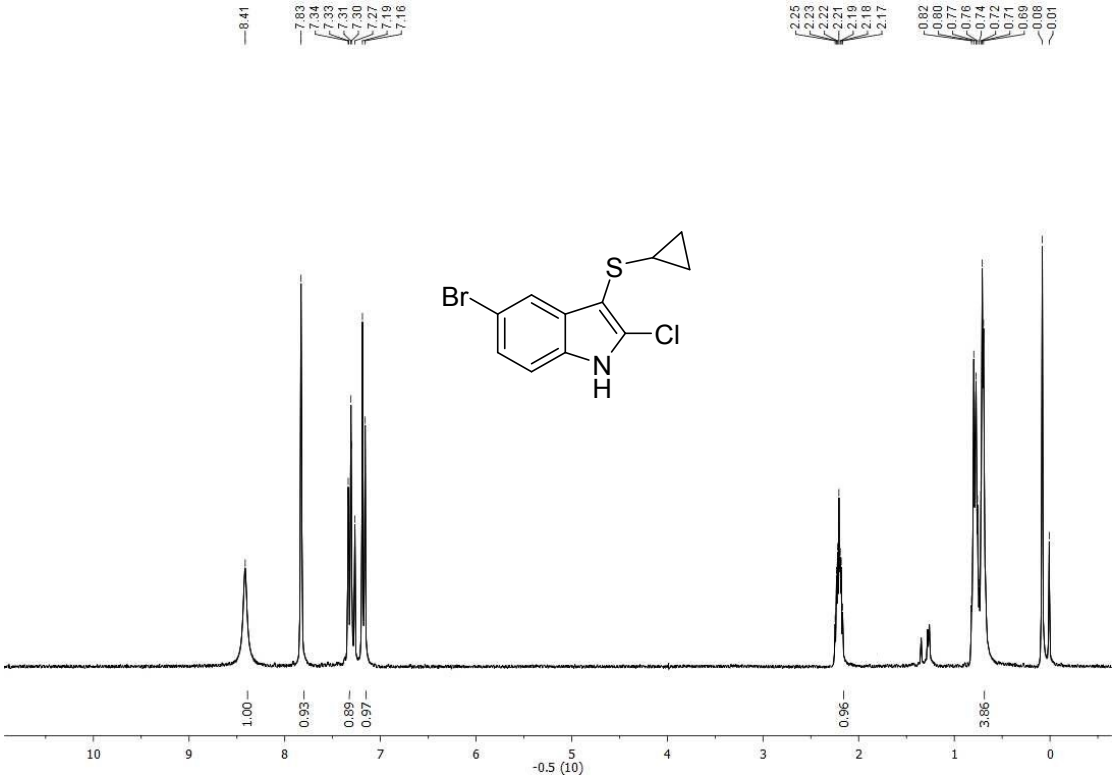


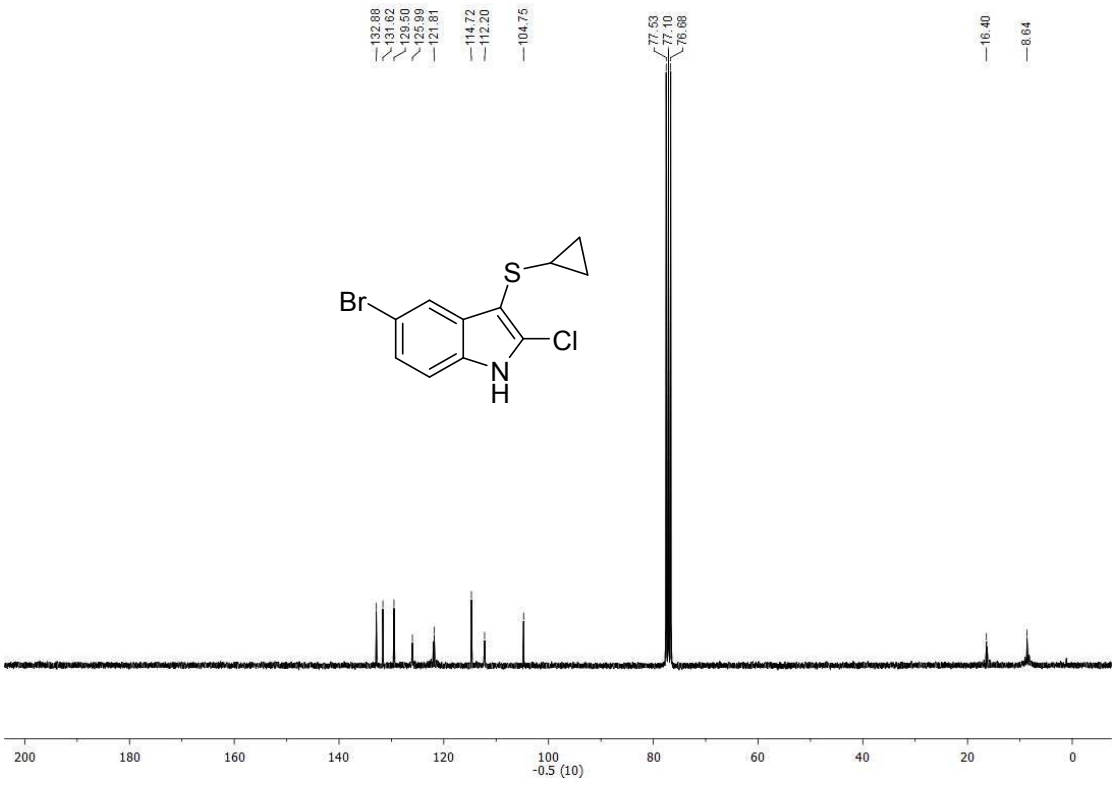
2-chloro-3-(cyclopropylthio)-7-methyl-1H-indole(2w):



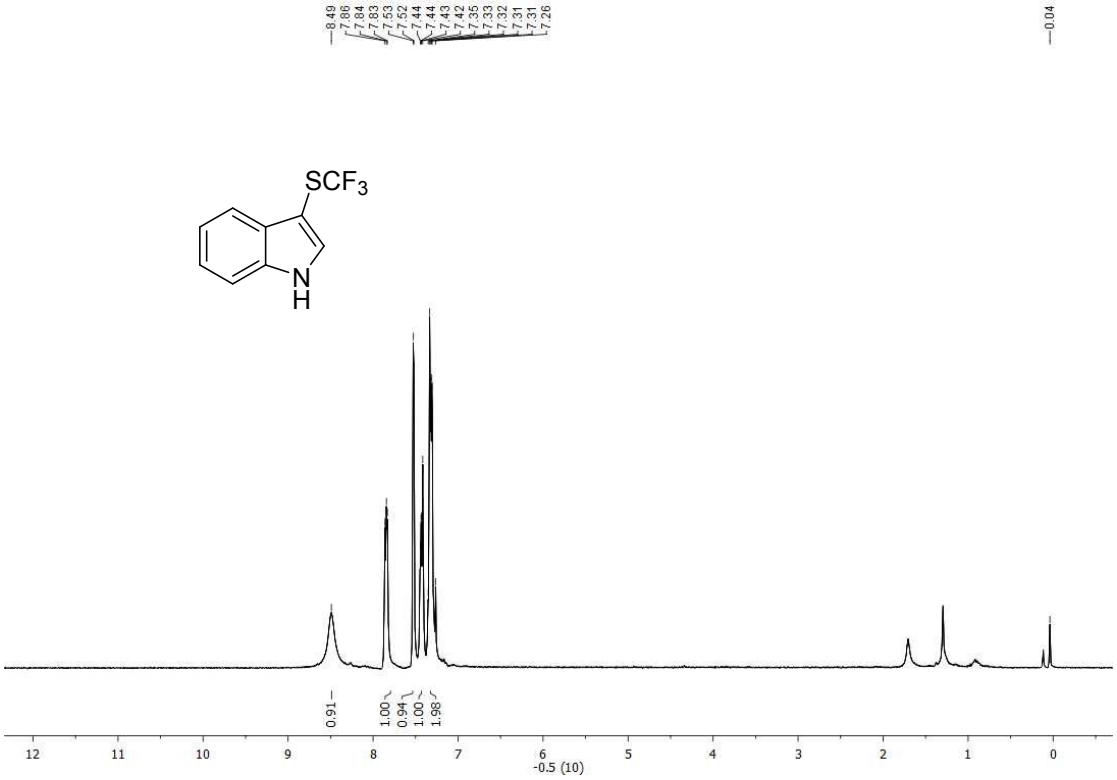


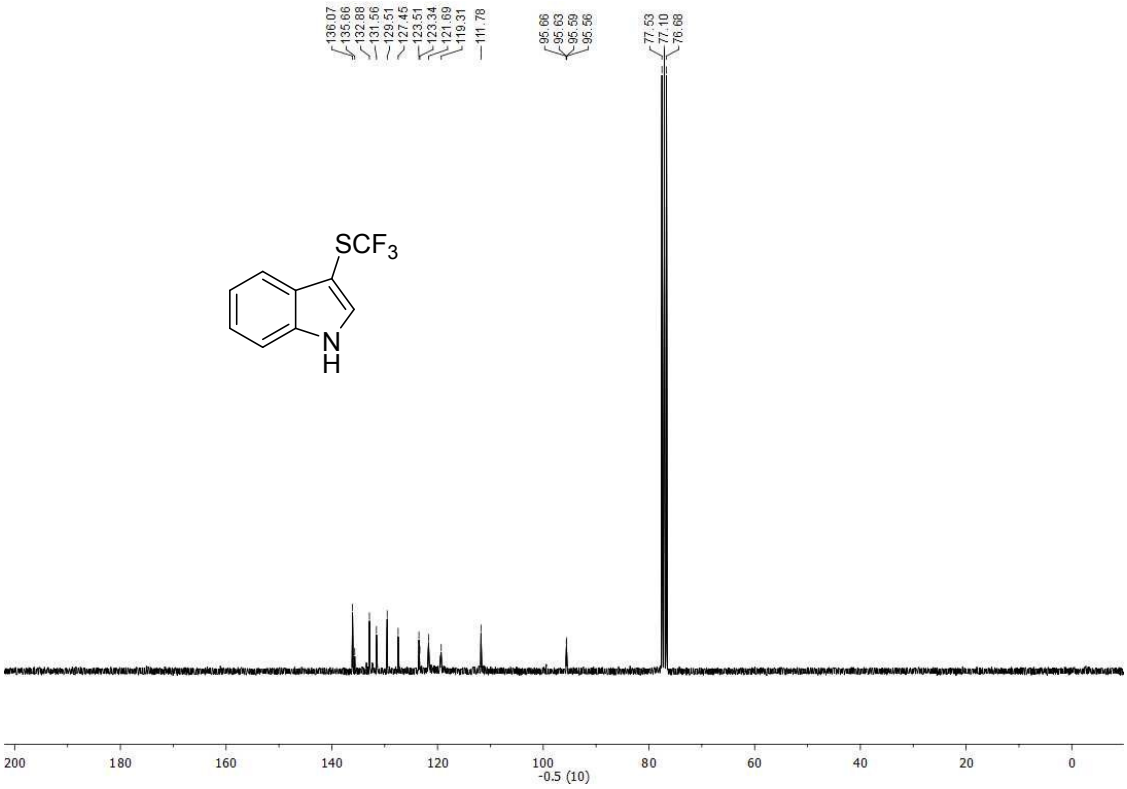
5-bromo-2-chloro-3-(cyclopropylthio)-1H-indole(2x):



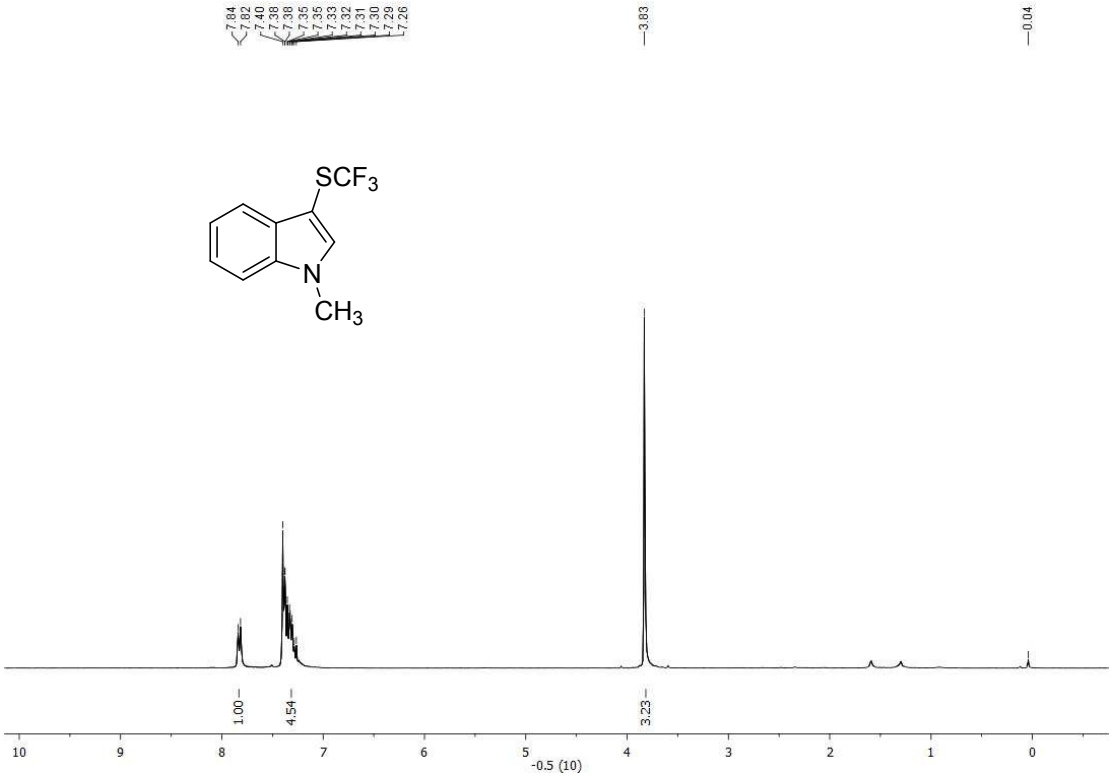


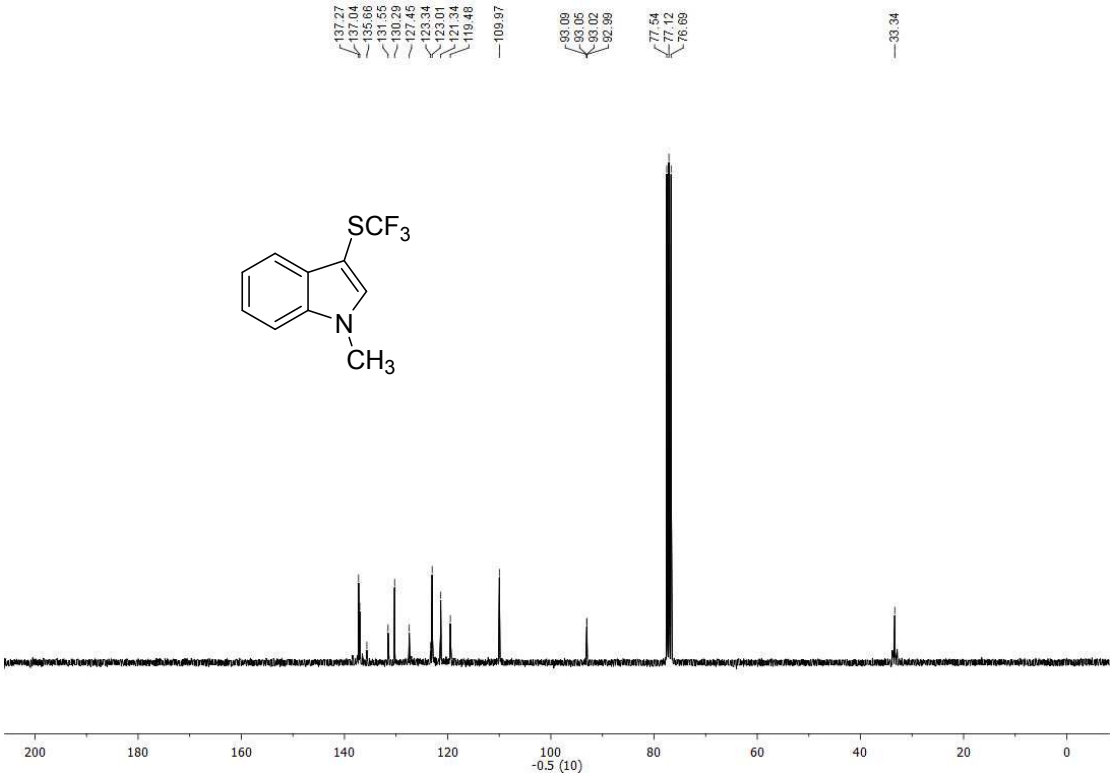
3-((trifluoromethyl)thio)-1*H*-indole (3a):



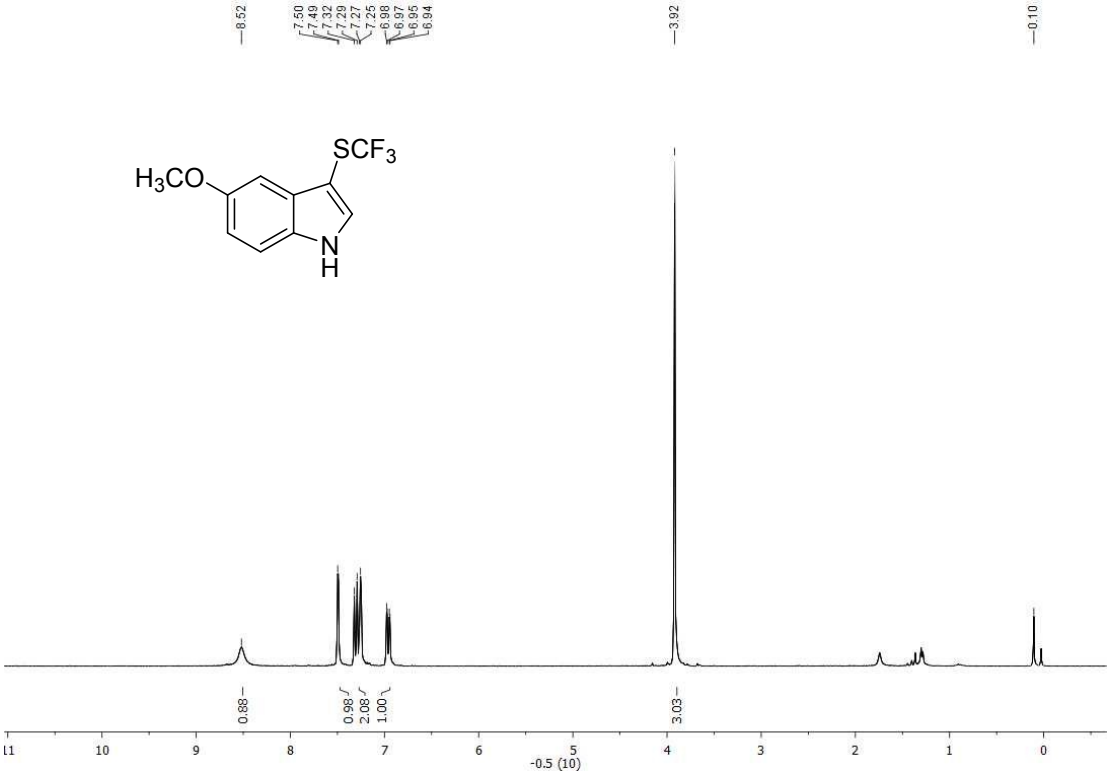


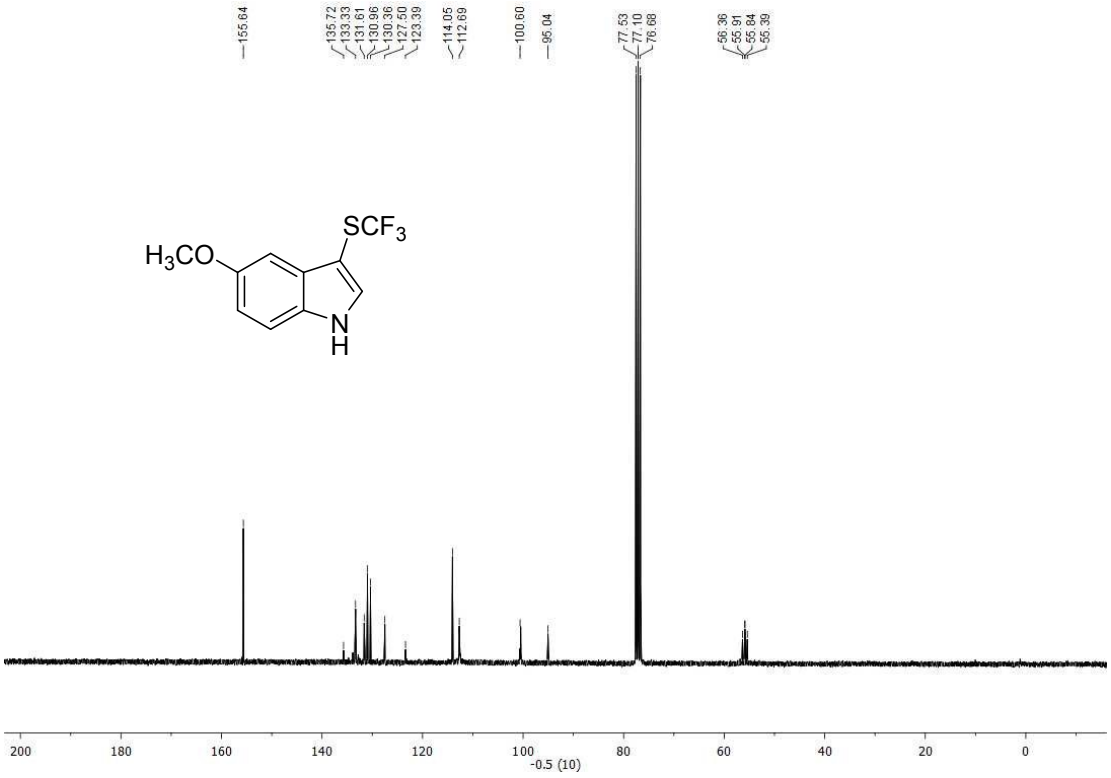
1-methyl-3-(trifluoromethylthio)-1*H*-indole (3b):



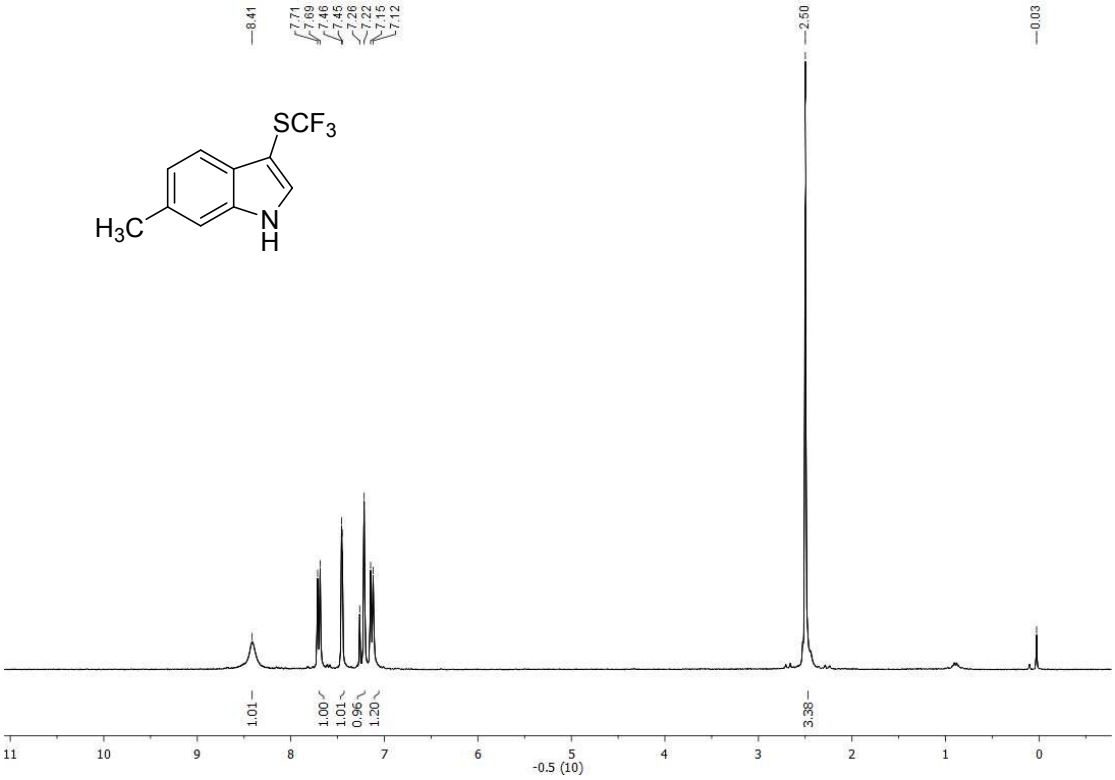


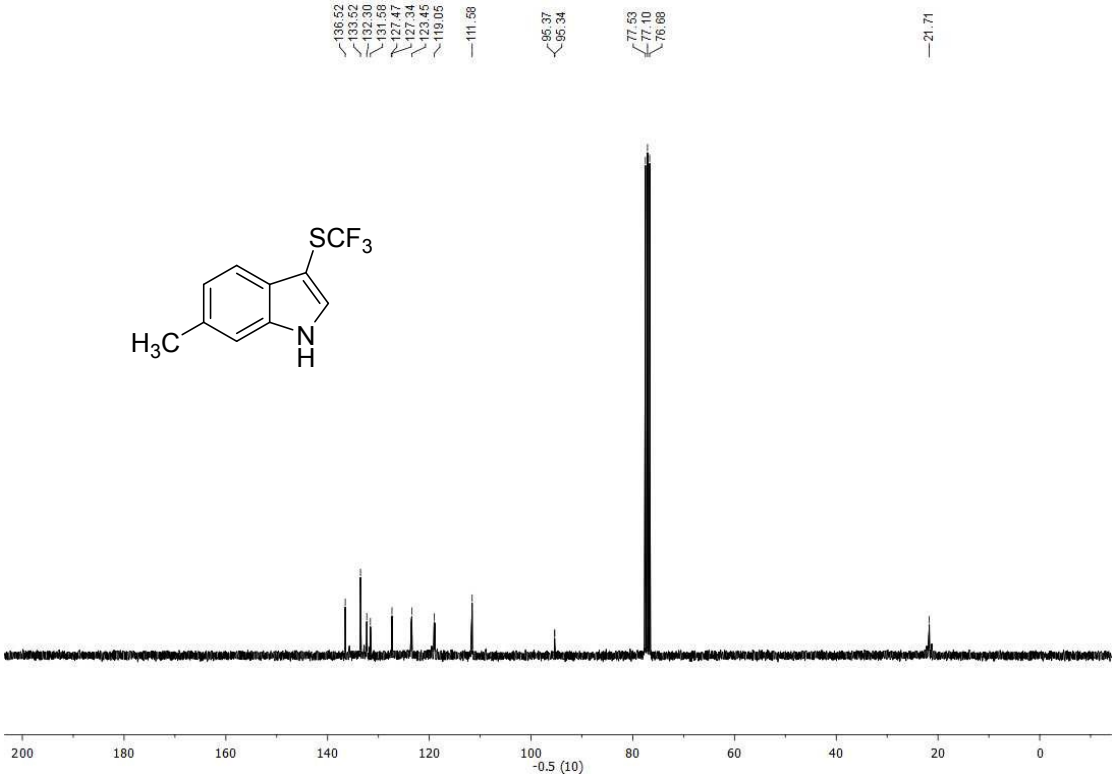
5-methoxy-3-((trifluoromethyl)thio)-1*H*-indole (3c):



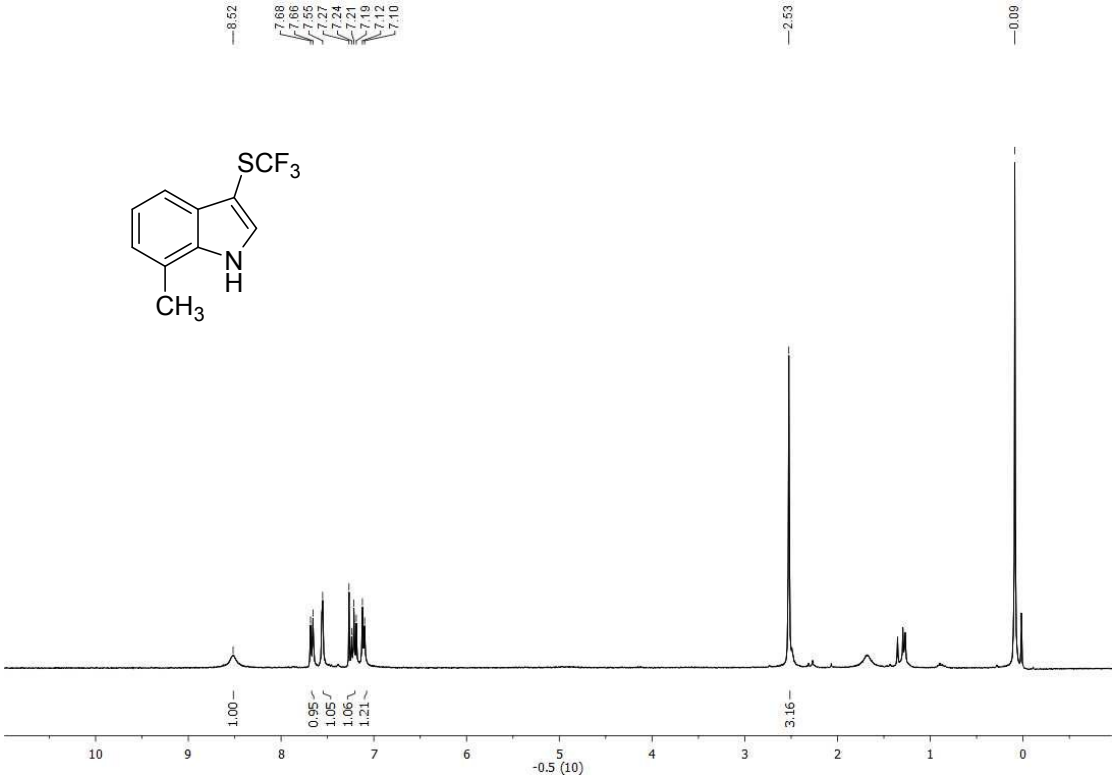


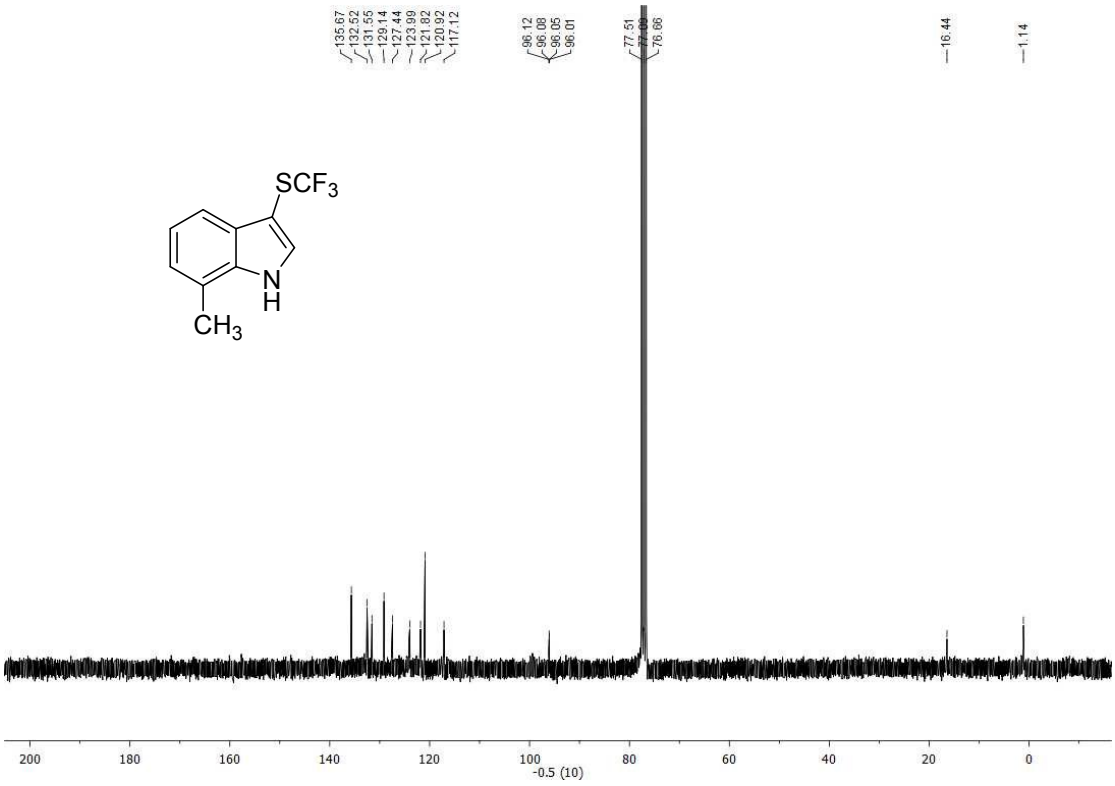
6-methyl-3-((trifluoromethyl)thio)-1H-indole (3d):



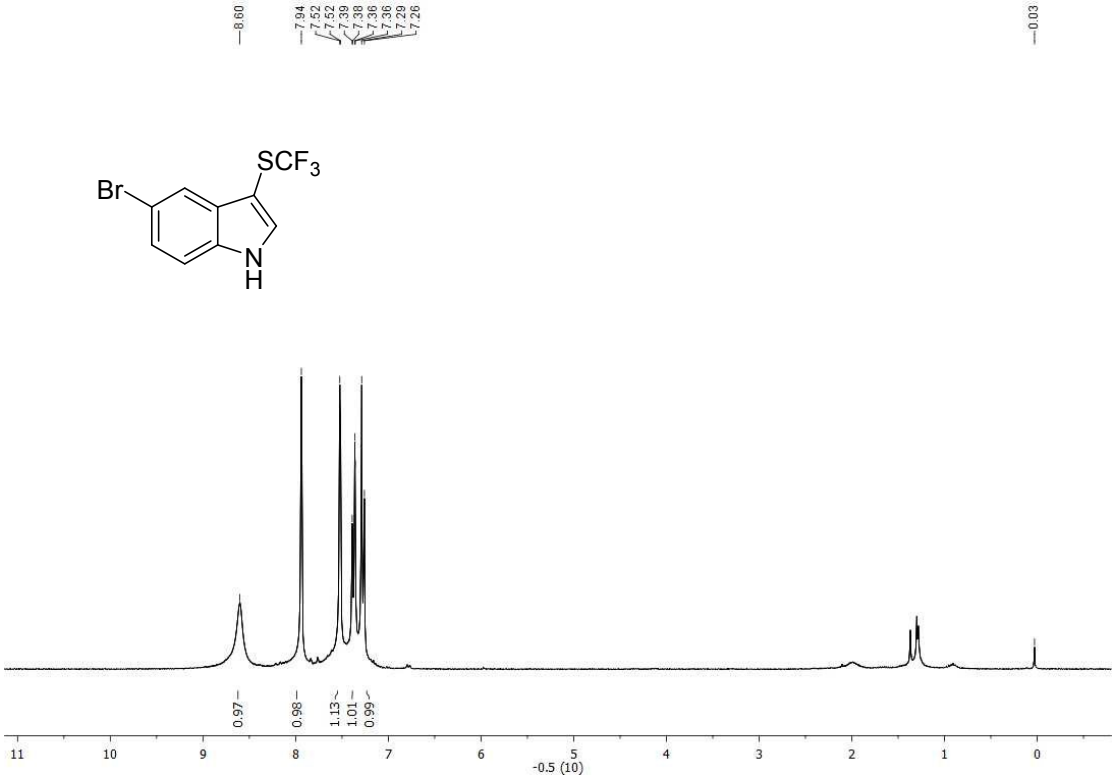


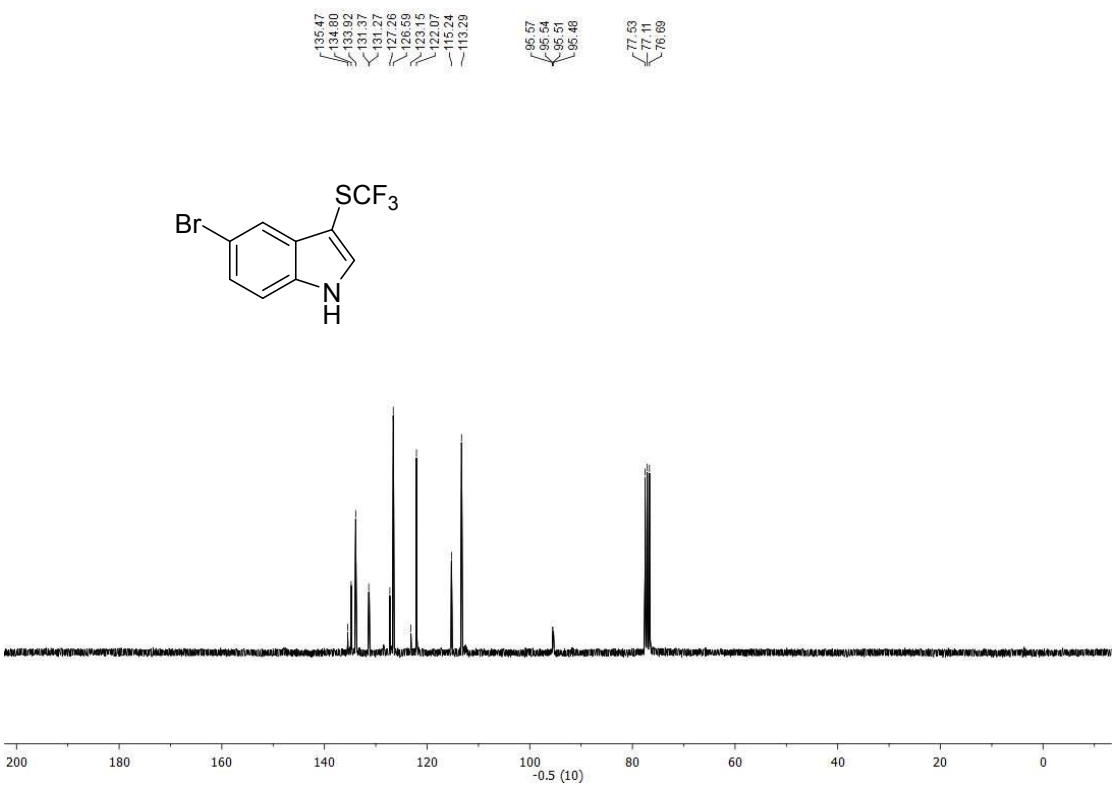
7-methyl-3-((trifluoromethyl)thio)-1*H*-indole (3e):



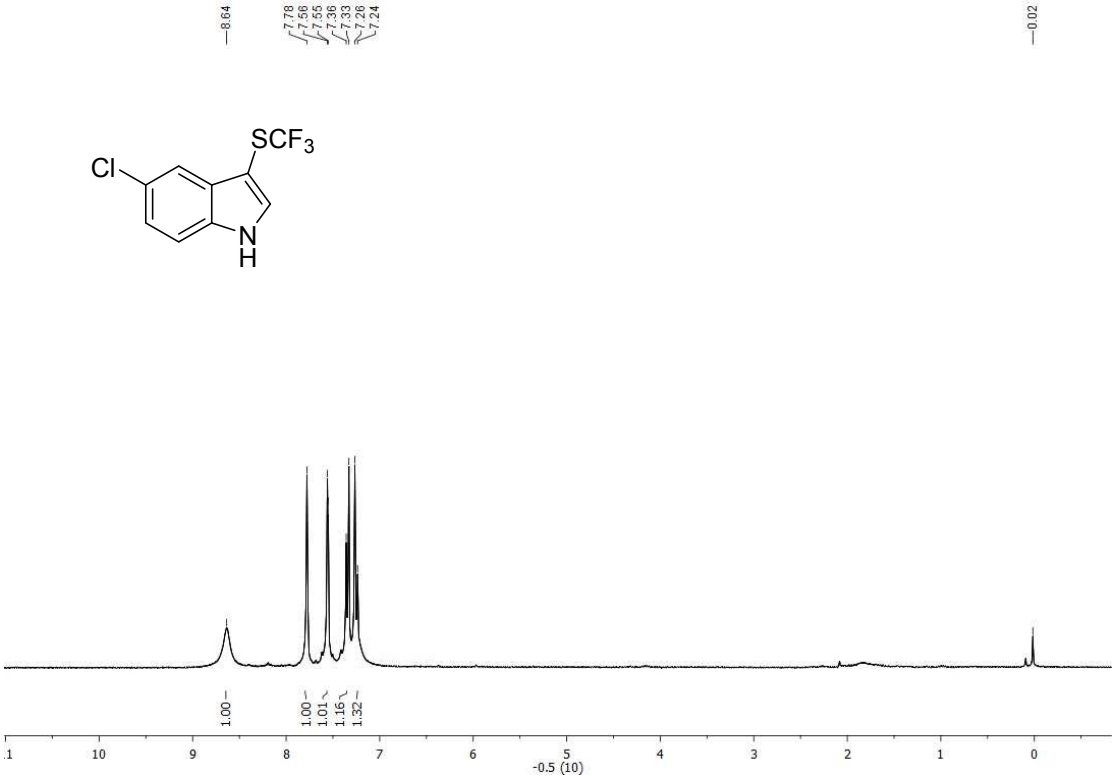


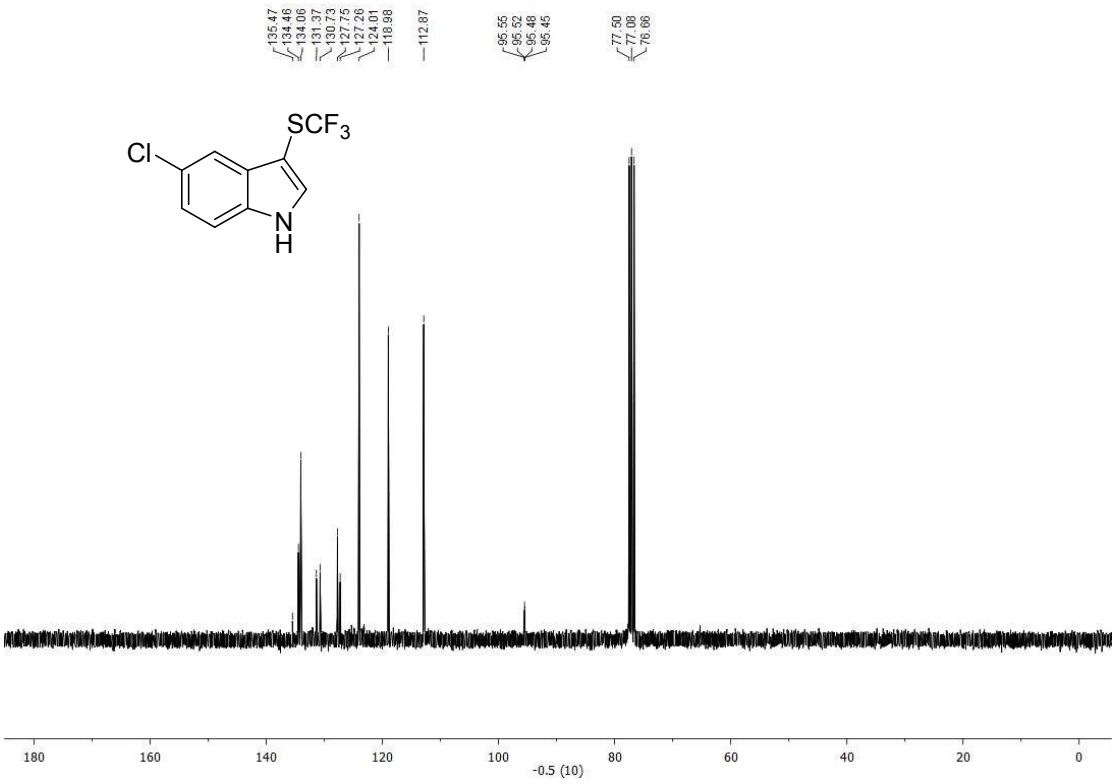
5-bromo-3-((trifluoromethyl)thio)-1*H*-indole (3f):



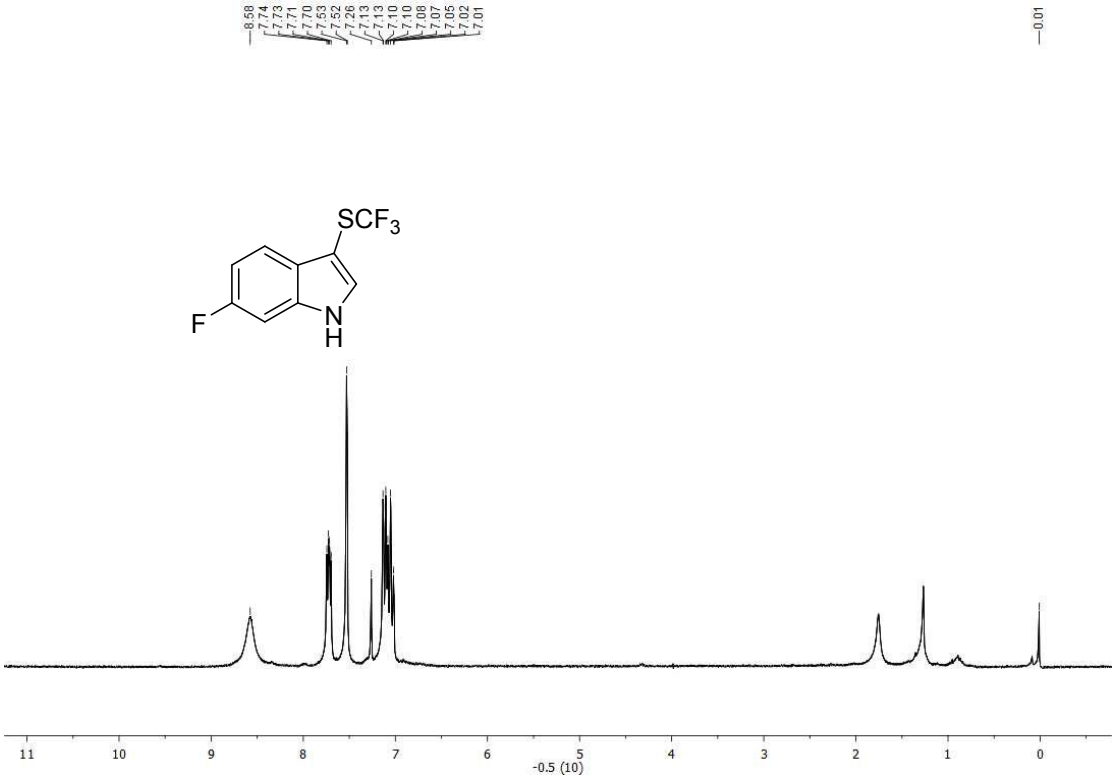


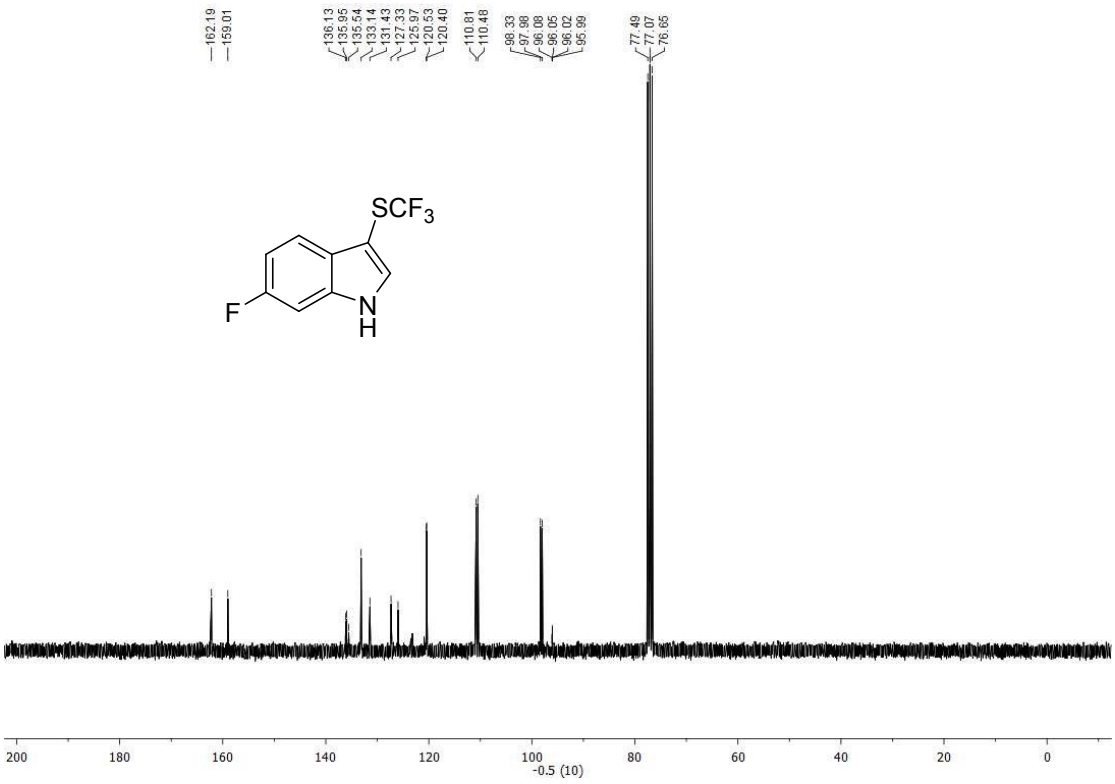
5-chloro-3-((trifluoromethyl)thio)-1H-indole (3g):



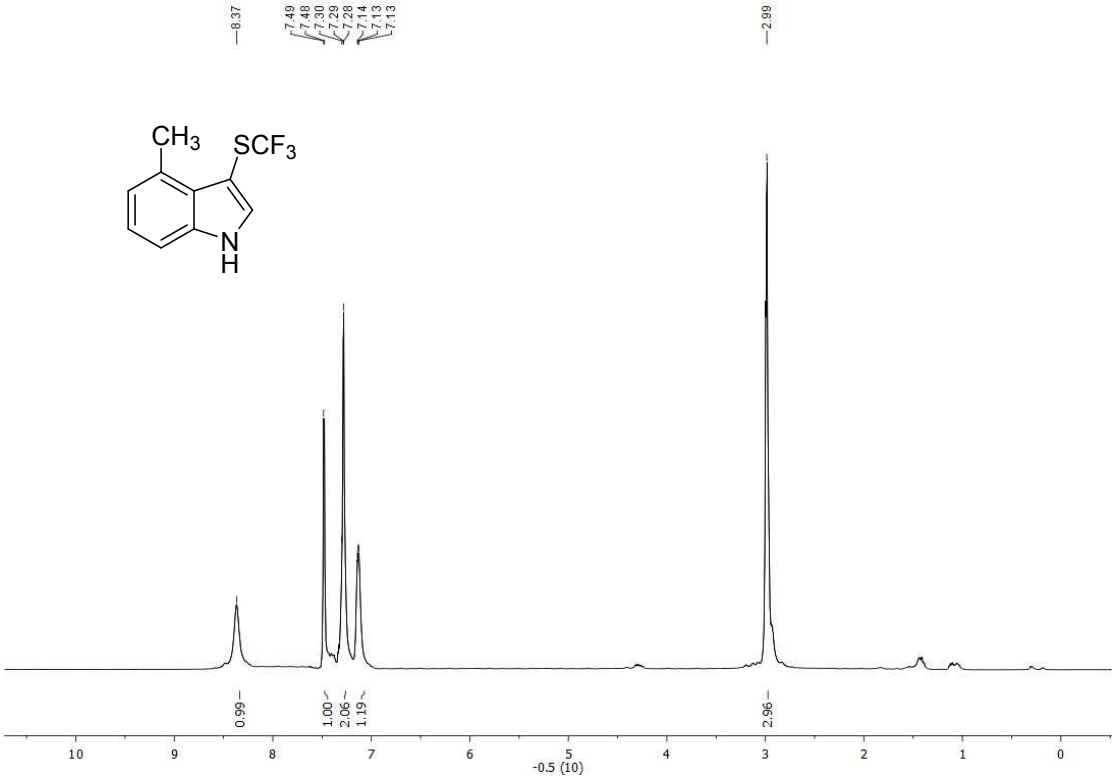


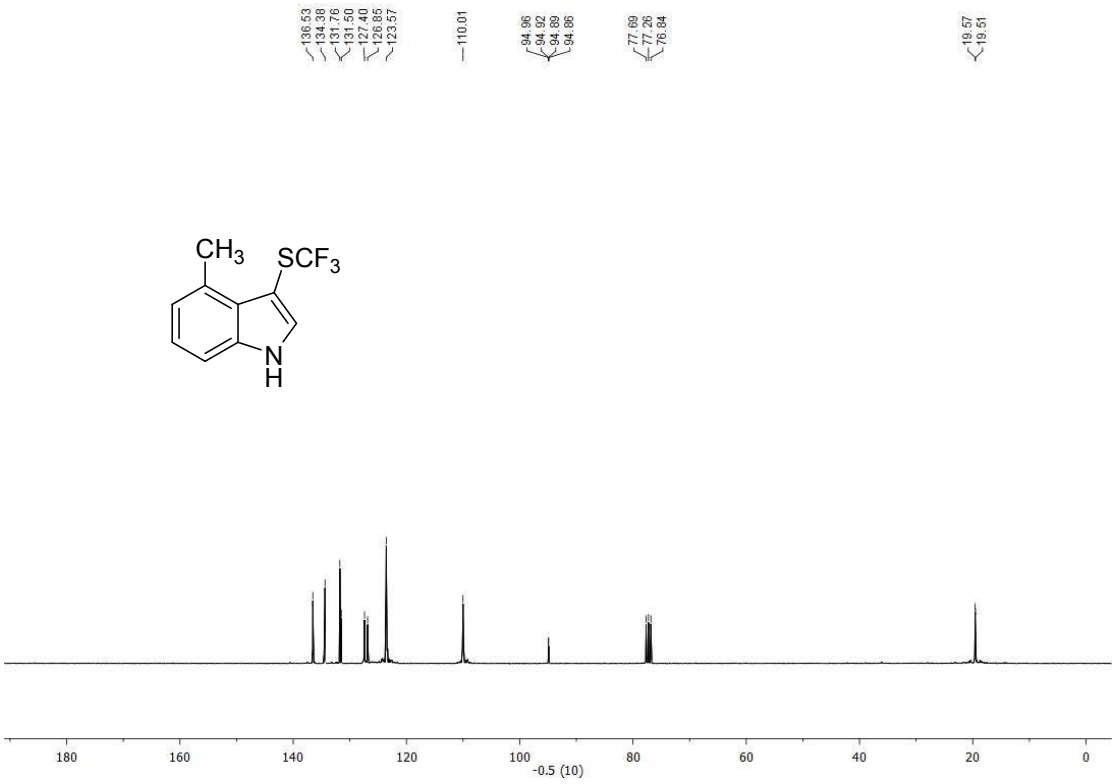
6-fluoro-3-((trifluoromethyl)thio)-1H-indole (3h):



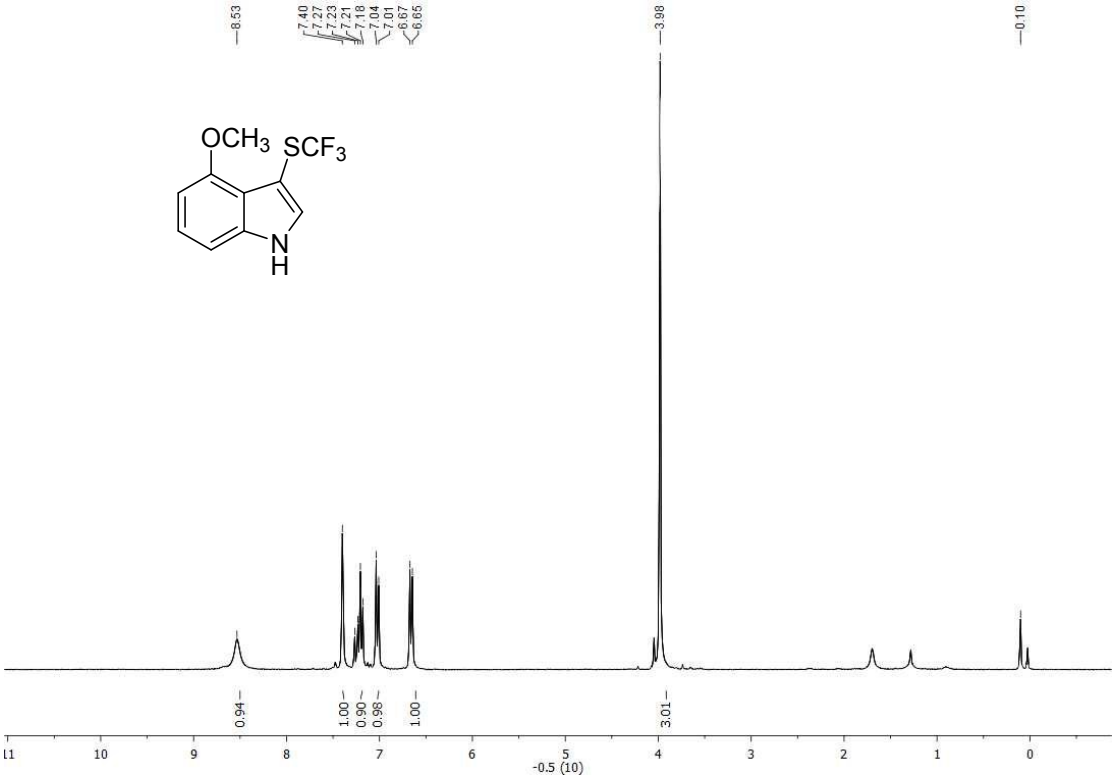


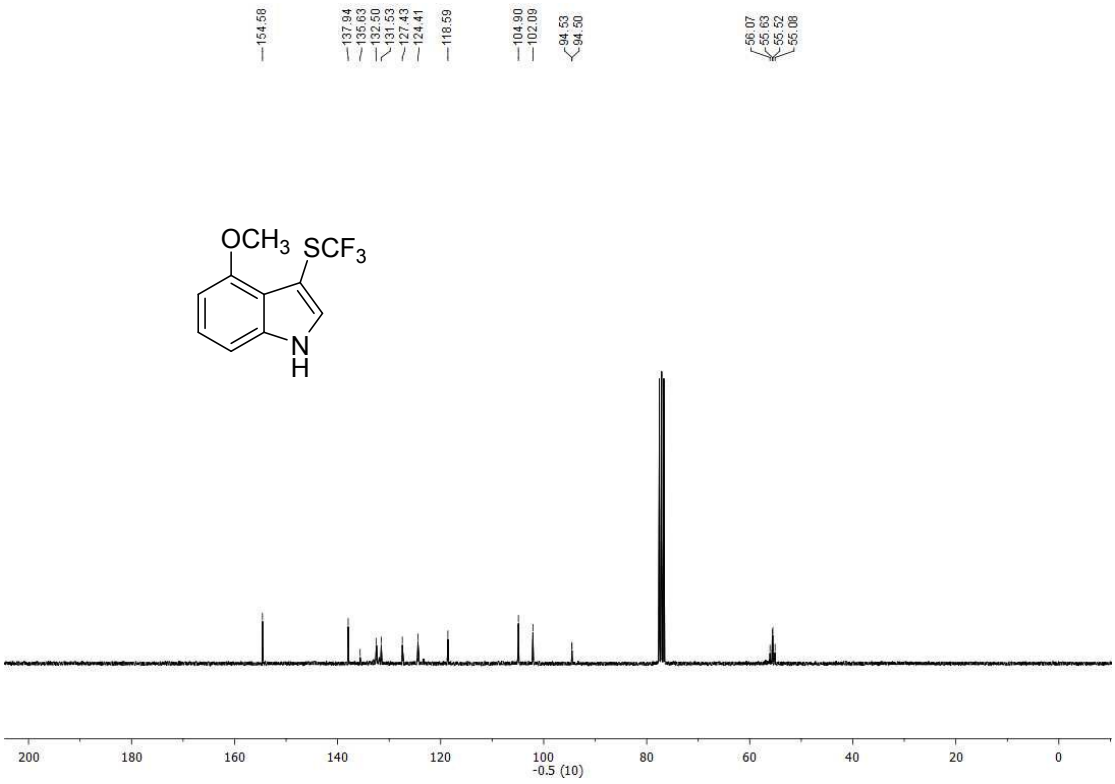
4-methyl-3-((trifluoromethyl)thio)-1H-indole (3i):



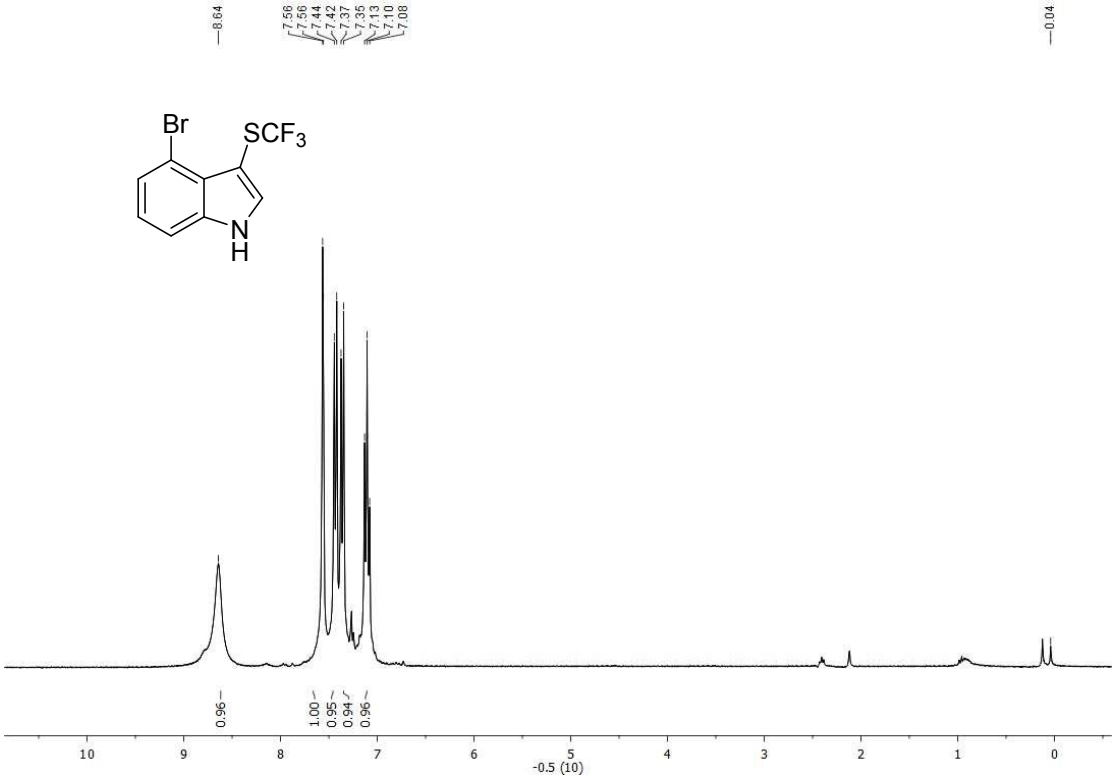


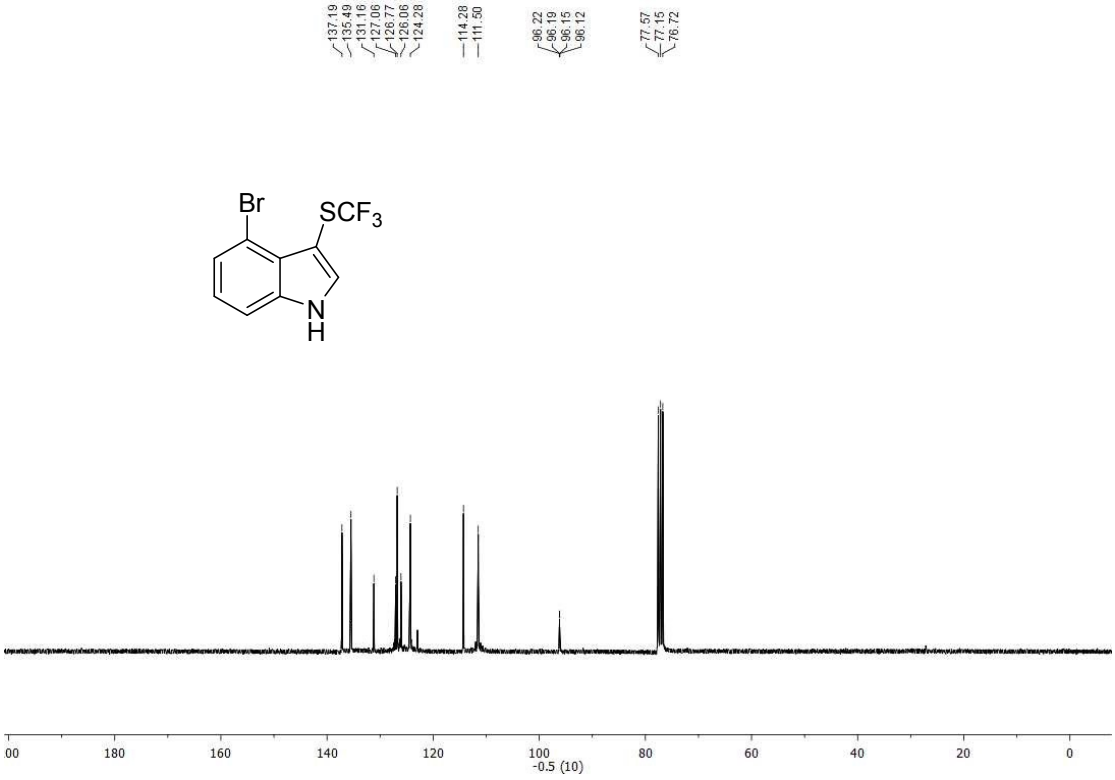
4-methoxy-3-((trifluoromethyl)thio)-1*H*-indole(3j):



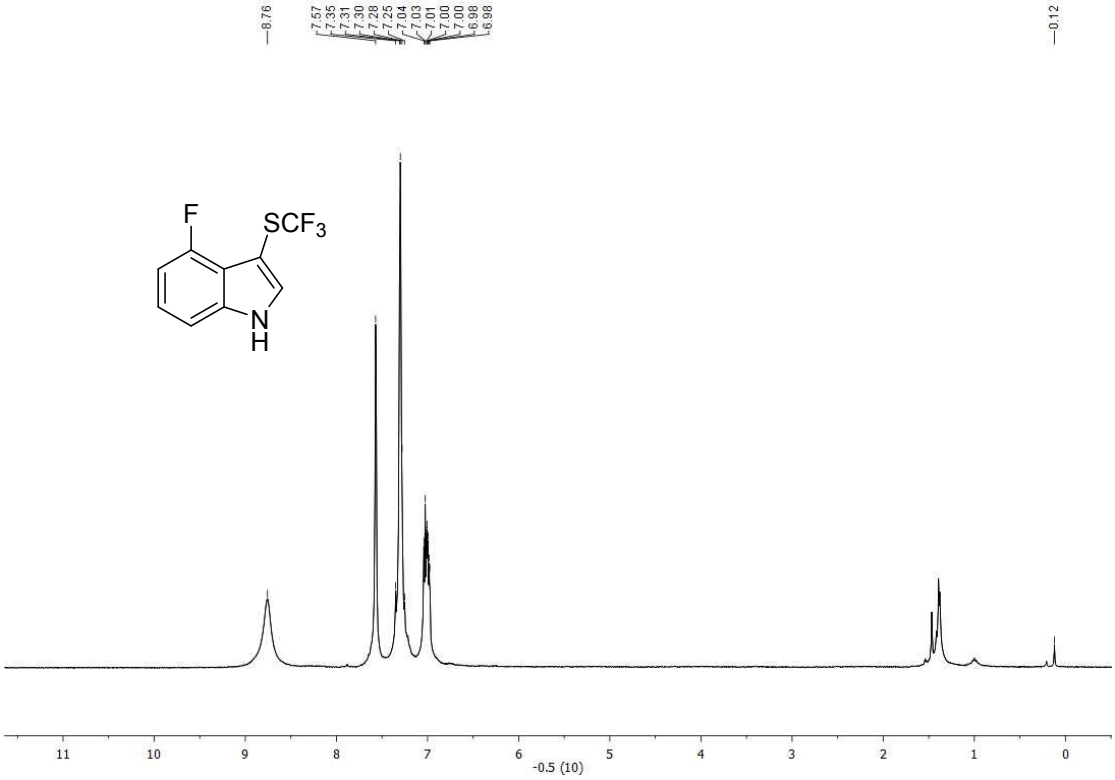


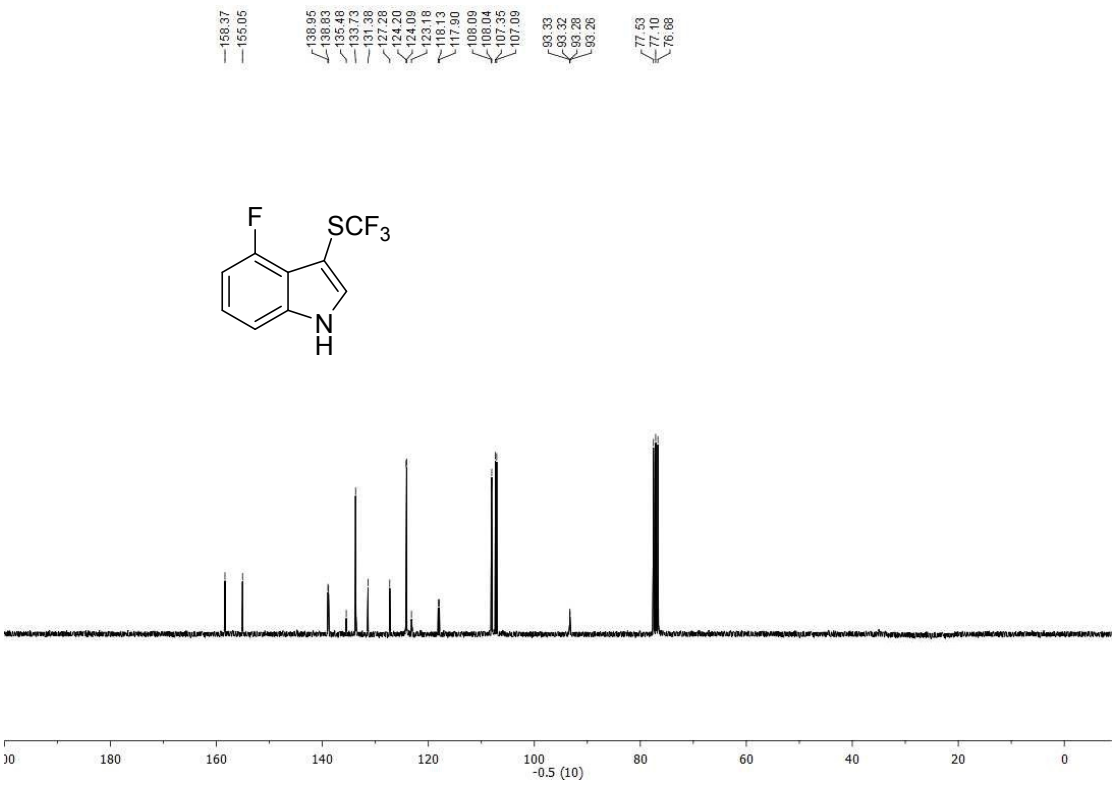
4-bromo-3-((trifluoromethyl)thio)-1*H*-indole(3k):



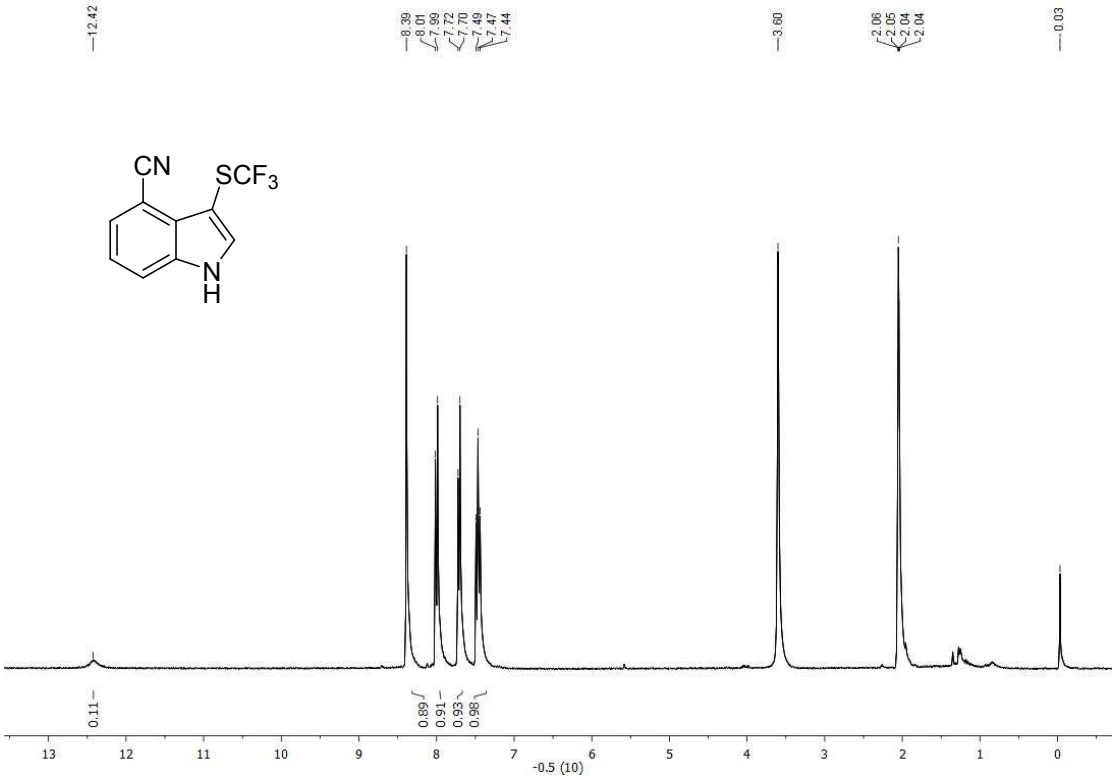


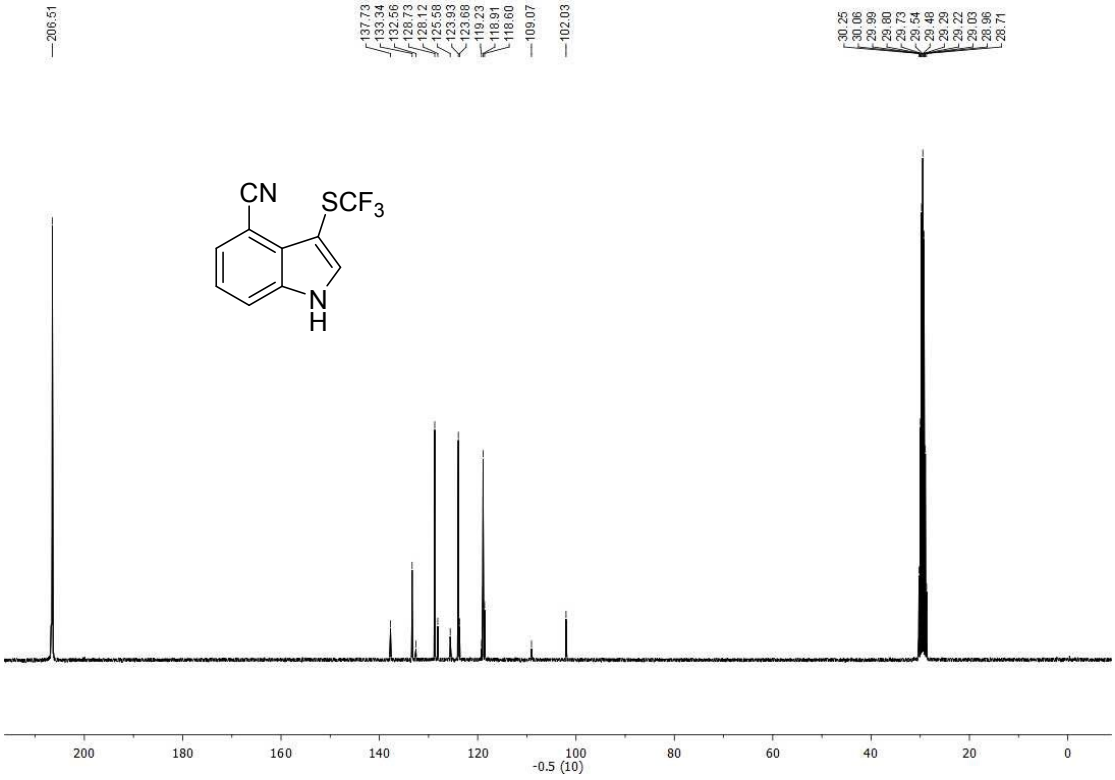
4-fluoro-3-((trifluoromethyl)thio)-1H-indole(3l):



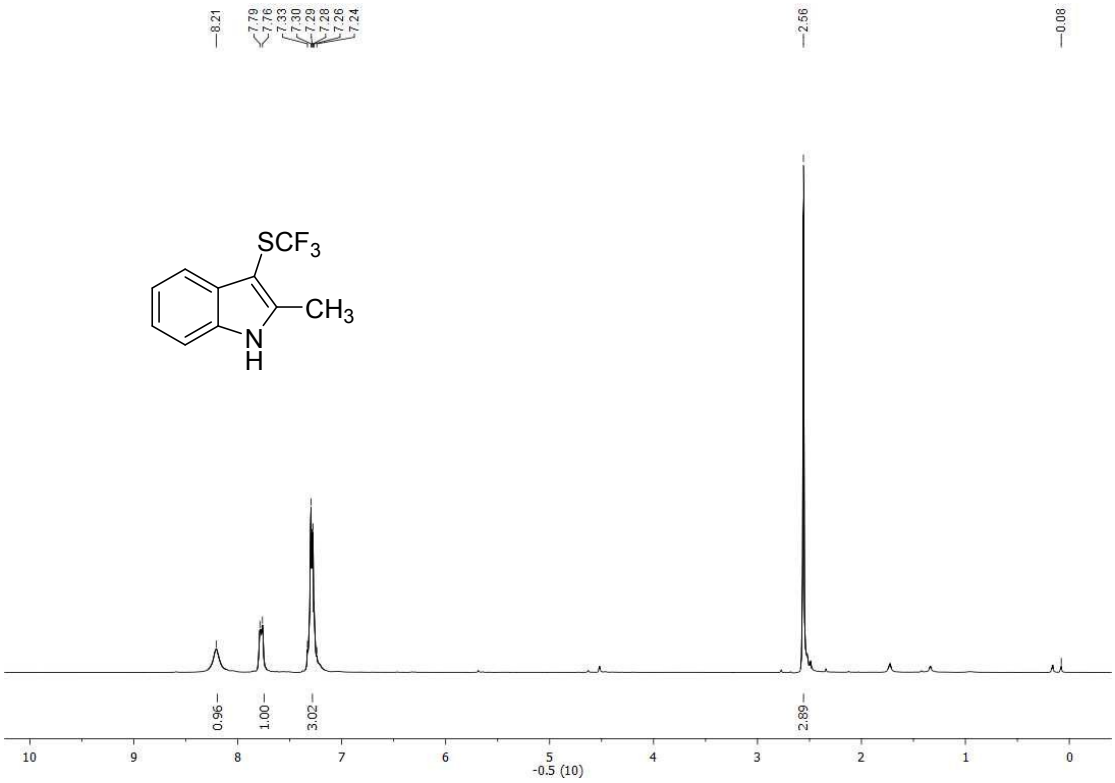


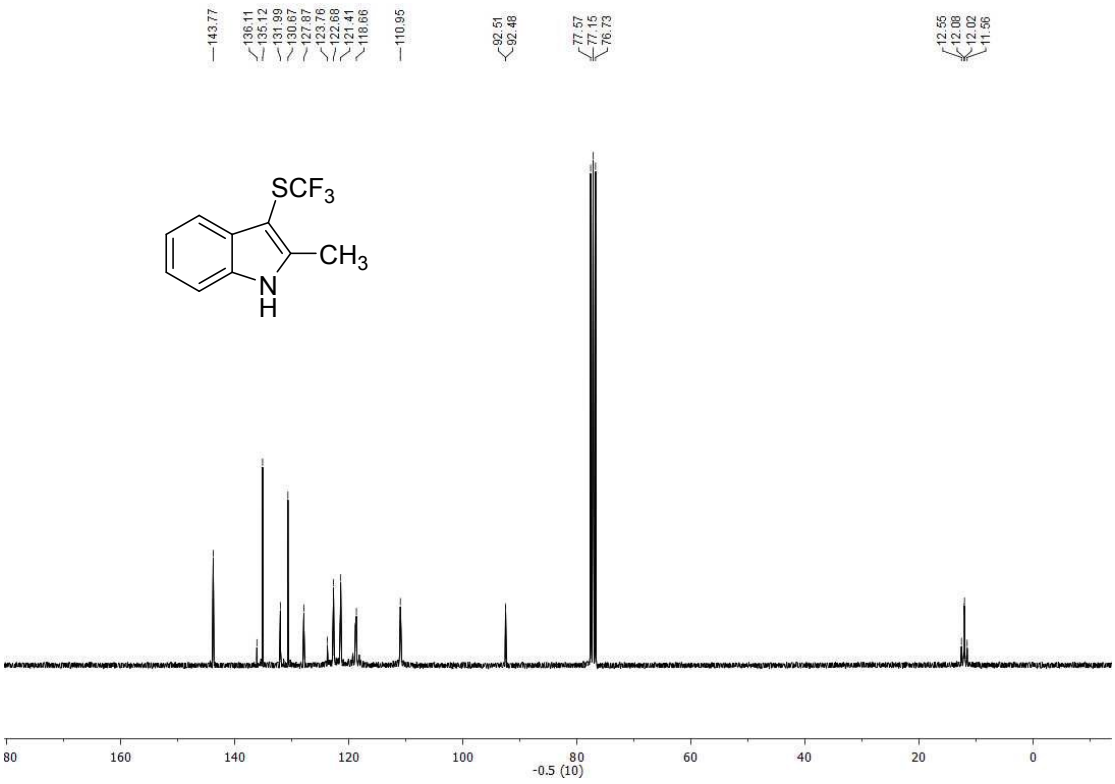
3-((trifluoromethyl)thio)-1*H*-indole-4-carbonitrile (3m):



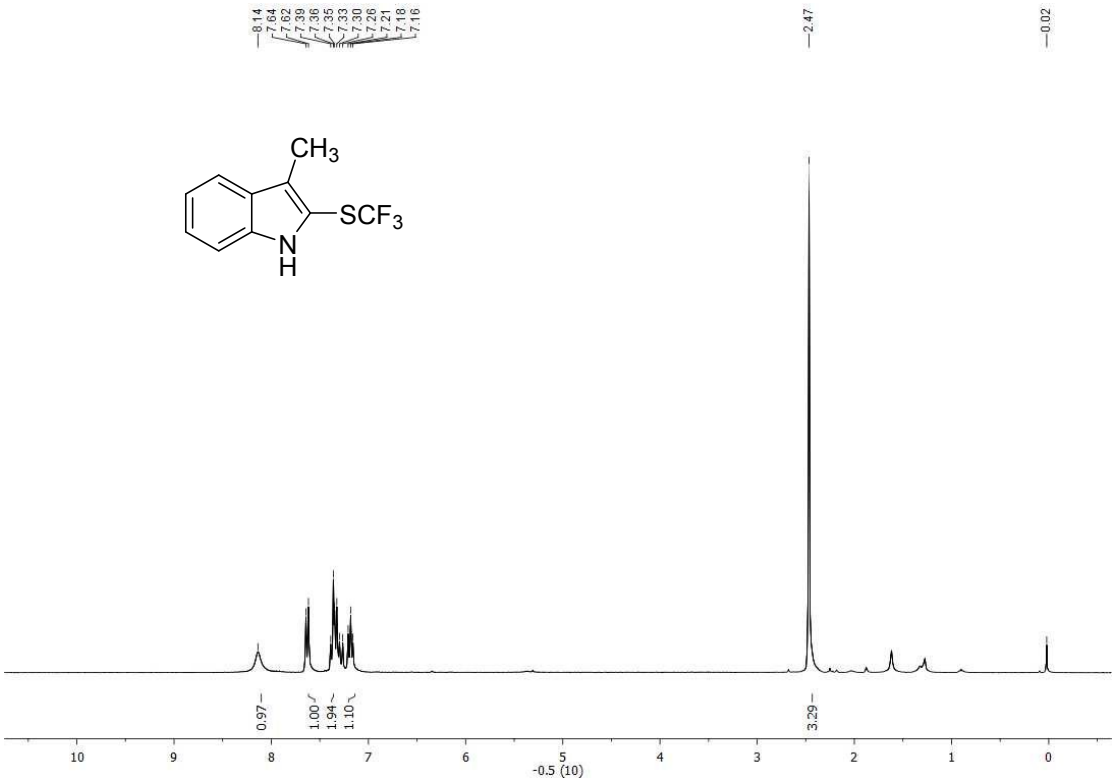


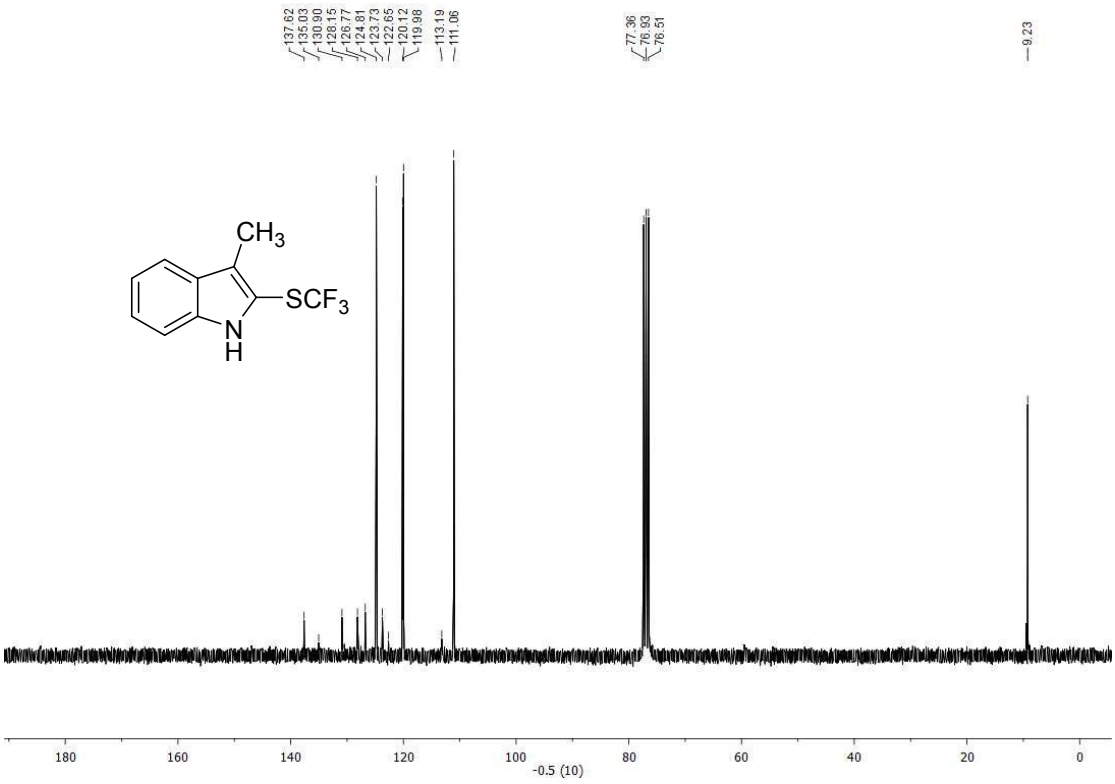
2-Methyl-3-((trifluoromethyl)thio)-1*H*-indole (3n):

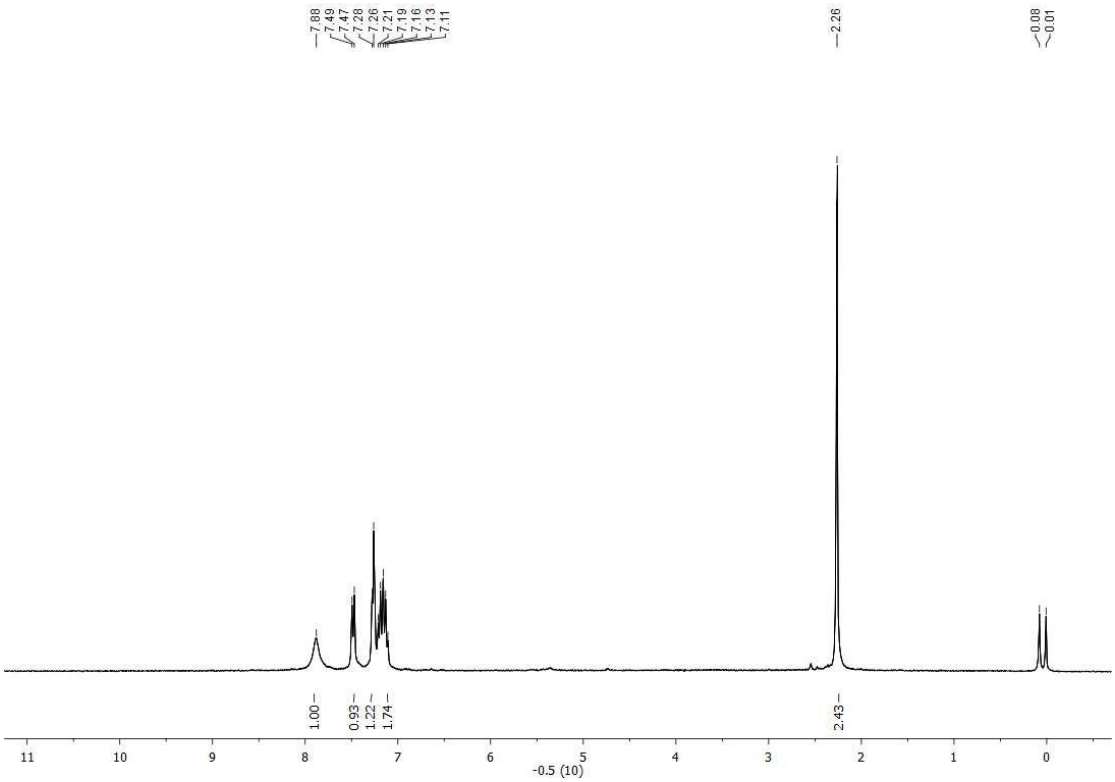




3-Methyl-2-((trifluoromethyl)thio)-1*H*-indole (3o):



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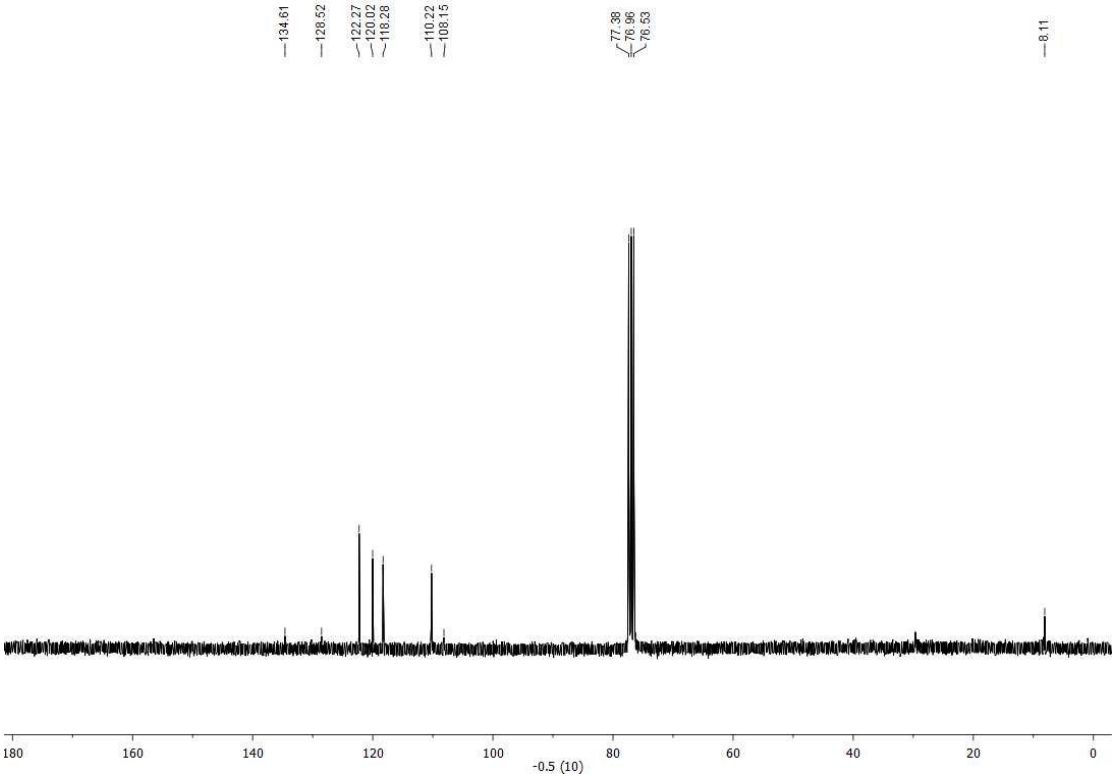
7.49
7.47
7.28
7.26
7.21
7.19
7.16
7.13
7.11
2.26
0.08
0.01
1.00
0.93
1.22
1.74
2.43
11
10
9
8
7
6
5
4
3
2
1
0
-0.5 (10)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128.52
122.27
120.02
118.28
110.22
108.15
77.38
76.96
76.53
8.11
180
160
140
120
100
80
60
40
20
0
-0.5 (10)