Supporting Information

Contents

1. General information

All glassware was oven dried at 85 ℃ for hours and cooled down for use. Acetonitrile (MeCN) was dried and distilled from calcium hydride under argon. Starting materials were purchased from Aladdin, Energy Chemical, J & K Scientific, Macklin, and Sinopharm Chemical Reagent limited corporation, and their purities are between 96% and 99%. Unless otherwise stated, materials were used without further purification. The instruments for electrochemical studies are Metrohm Autolab PGSTAT204 (made in The Netherlands) and dual display potentiostat (DJS-292B) (made in China). Both anode and cathode electrode are platinum plate electrodes (1.5×1.5 cm^2). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp.60-90 ℃). Gas chromatographic analyses were performed on an Agilent GC-7820A gas chromatography instrument with FID detector and with reactant **1a** (1*H*-indole) itself as internal standards. ^1H and ^{13}C NMR data were recorded with Bruker AVANCE III (600 MHz) spectrometers with tetramethylsilane (TMS) as the internal standard. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$ = δ 7.26; DMSO = δ 2.50). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.16; DMSO = δ 39.60). GC-MS spectra were recorded on Thermo GC MS TRACE 1300. Melting points were tested by RY-2 Melting Point Instrument.

2. General procedure for thio- and selenocyanation of electron-rich arenes

In an oven-dried undivided four-necked bottle (25 mL) equipped with a stir bar, electron-rich arene (0.5 mmol), NH_4SCN (1.5 mmol) or KSeCN (1.0 mmol) and CH_3CN (10 mL) were combined and added. The bottle was equipped with platinum electrodes (1.5×1.5 cm^2) as both the anode and cathode and was then charged with argon. The reaction mixture was stirred and electrolyzed at a constant current of 18 mA under room temperature for 3 h. When the reaction was finished, the solvent was removed with a rotary evaporator. The pure product was obtained by column chromatography on a silica gel column using petroleum ether: ethyl acetate=10:3.

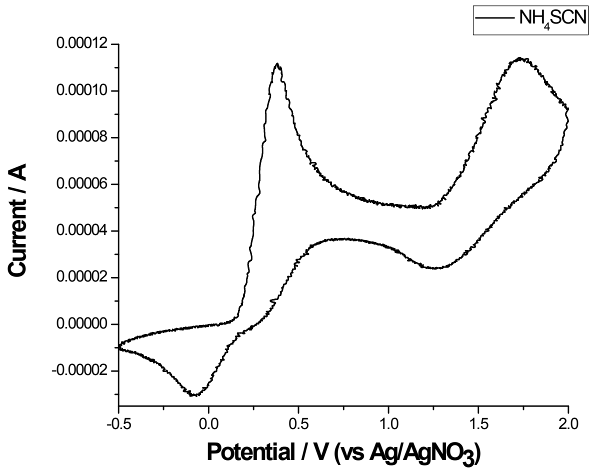
3. Procedure for gram scale synthesis

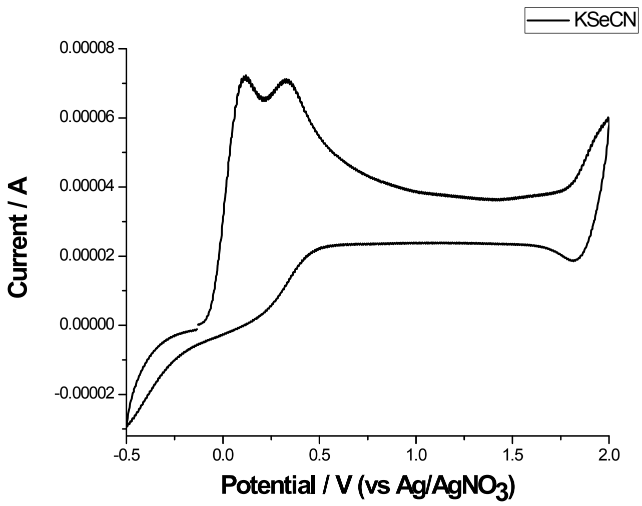
Thiocyanation of indole: In an oven-dried undivided glass cell (100 mL) equipped with a stir bar, indole substrate (10.0 mmol), NH_4SCN (30.0 mmol) and CH_3CN (70 mL) were combined and added. The bottle was equipped with platinum electrodes (2.0×2.0 cm^2) as both the anode and cathode and was then charged with argon. The reaction mixture was stirred and electrolyzed at a constant current of 32 mA (The potentiostat galvanostat was operating in constant current mode) under room temperature. When the reaction was finished, the solvent was removed with a rotary evaporator. The pure product was obtained by flash column chromatography on silica gel.

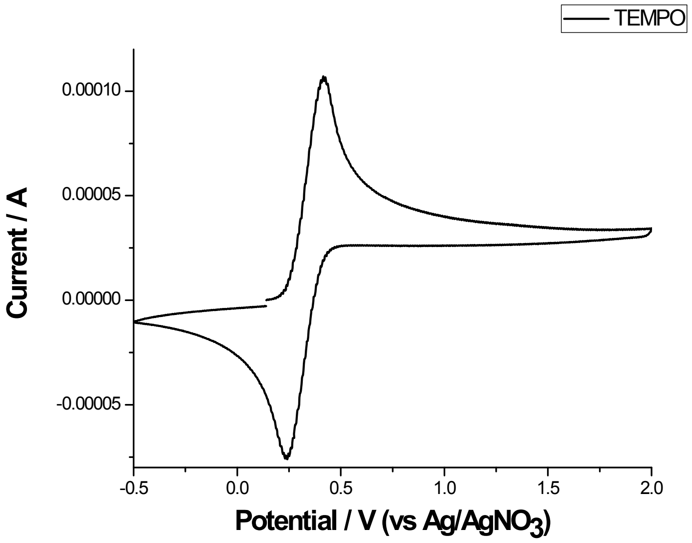
Selenocyanation of indole: In an oven-dried undivided glass cell (100 mL) equipped with a stir bar, indole substrate (10.0 mmol), KSeCN (20.0 mmol) and CH_3CN (70 mL) were combined and added. The bottle was equipped with platinum electrodes (2.0×2.0 cm^2) as both the anode and cathode and was then charged with argon. The reaction mixture was stirred and electrolyzed at a constant current of 32 mA (The potentiostat galvanostat was operating in constant current mode) under room temperature. When the reaction was finished, the solvent was removed with a rotary evaporator. The pure product was obtained by flash column chromatography on silica gel.

4. Voltamometric analysis and voltammograms

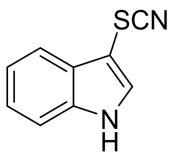
The redox property of each compound was measured in anhydrous acetonitrile (CH_3CN) containing n-tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Cyclic voltammetry was carried out in conventional three-electrode electrochemical cell with Metrohm Autolab PGSTAT204 under argon at room temperature. A glassy carbon disk electrode (diameter is 2.0 mm) was used as the working electrode. A platinum plate electrode (1.5×1.5 cm^2) was used as the counter electrode. The reference Ag/Ag$^+$ electrode was made by immersing a sliver wire in a solution of $AgNO_3$ (0.01 M) - nBu$_4$NPF$_6$ (0.1 M) in CH_3CN, and separated from reaction by a salt bridge. 10mL electrolyte solution containing 0.05 M nBu$_4$NPF$_6$ in CH_3CN was poured into electrochemical cell in all experiments. The concentration of indole sample was 0.01 M. The scan rate was 0.1 V/s, ranging from -0.5 to 2.0 V.



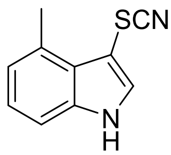




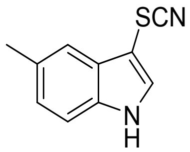
5. Characterization Data



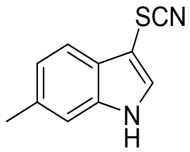
3-Thiocyanato-1H-indole (3aa): yellow solid; Yield – (85 mg, 98%); mp: 70-72 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.00 (s, broad, 1H), 7.98 (d, J = 2.9 Hz, 1H), 7.67 (d, J = 7.5 Hz, 1H), 7.54-7.52 (m, 1H), 7.29-7.23 (m, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 136.43, 133.27, 127.52, 123.04, 121.22, 117.83, 112.93, 112.45, 89.42.



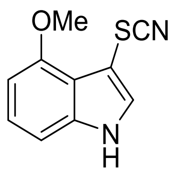
4-Methyl-3-thiocyanato-1H-indole (3ab): yellow solid; Yield – (89 mg, 94%); mp: 127-129 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.60 (s, broad, 1H), 7.50 (d, J = 3.0 Hz, 1H), 7.25 (d, J = 4.2 Hz, 1H), 7.19-7.15 (t, 1H), 7.00 (d, J = 6.6 Hz, 1H), 2.93 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.58, 132.15, 131.26, 125.72, 124.15, 123.68, 113.34, 110.11, 92.55, 19.33.



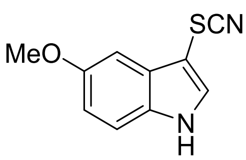
5-Methyl-3-thiocyanato-1H-indole (3ac): yellow solid; Yield – (89 mg, 94%); mp: 89-91 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.56 (s, broad, 1H), 7.59 (s, 1H), 7.46 (d, *J* = 3.0 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.43, 131.72, 131.03, 128.06, 125.72, 118.48, 112.11, 111.84, 91.79, 21.65.



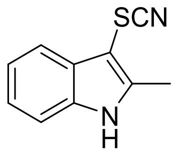
6-Methyl-3-thiocyanato-1H-indole (3ad): white solid; Yield – (93 mg, 99%); mp: 101-104 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (s, broad, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 3.0 Hz, 1H), 7.22 (s, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.59, 134.13, 130.43, 125.64, 123.84, 118.50, 112.11, 112.03, 92.20, 21.81.



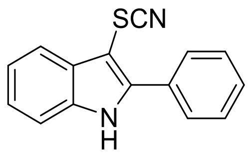
4-Methoxy-3-thiocyanato-1H-indole (3ae): light pink solid; Yield – (101 mg, 99%); mp: 142-144 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.56 (s, broad, 1H), 7.33 (d, *J* = 3.0 Hz, 1H), 7.20-7.17 (t, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.22, 138.00, 128.86, 125.03, 117.13, 113.10, 105.12, 101.86, 92.58, 55.76.



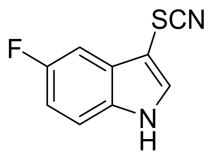
5-Methoxy-3-thiocyanato-1H-indole (3af): yellow solid; Yield – (101 mg, 99%); mp: 123-124 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (s, broad, 1H), 7.47 (d, J = 3.0 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.19 (d, J = 2.4 Hz, 1H), 6.96 (dd, J = 9.0, 2.4 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.92, 131.47, 130.94, 128.65, 114.72, 113.12, 112.06, 99.95, 91.78, 55.97.



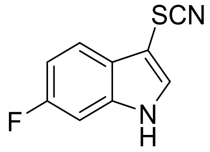
2-Methyl-3-thiocyanato-1H-indole (3ag): yellow solid; Yield – (91 mg, 97%); mp: 87-89 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.95 (s, broad, 1H), 7.57-7.54 (m, 1H), 7.44-7.40 (m, 1H), 7.21-7.16 (m, 2H), 2.54 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 143.14, 135.39, 128.36, 122.28, 120.90, 117.16, 112.20, 111.90, 86.72, 11.75.



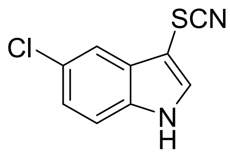
2-Phenyl-3-thiocyanato-1H-indole (3ah): yellow solid; Yield – (120 mg, 96%); mp: 69-71 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.40 (s, broad, 1H), 7.86 (d, J = 7.8 Hz, 2H), 7.72 (d, J = 7.2 Hz, 1H), 7.64-7.61 (m, 2H), 7.56-7.53 (m, 2H), 7.34-7.37 (m, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 143.23, 135.90, 130.05, 129.40, 129.23, 129.00, 128.90, 123.48, 121.50, 118.11, 112.55, 112.43, 87.21.



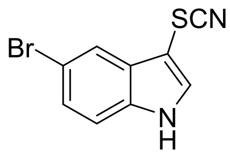
5-Fluoro-3-thiocyanato-1H-indole (3ai): yellow solid; Yield – (85 mg, 88%); mp: 108-109 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.72 (s, broad, 1H), 7.56 (d, J = 3.0 Hz, 1H), 7.44 (dd, J = 9.0, 2.4 Hz, 1H), 7.36 (dd, J = 8.4, 4.2 Hz, 1H), 7.08-7.04 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.19 (d, $J_{C\text{-}F}$ = 239.18 Hz), 132.61 (d, $J_{C\text{-}F}$ = 20.39 Hz), 128.66 (d, $J_{C\text{-}F}$ = 10.57 Hz), 120.01 (d, $J_{C\text{-}F}$ = 10.27 Hz), 112.91, 112.74, 111.71, 104.21 (d, $J_{C\text{-}F}$ = 24.92 Hz), 92.67 (d, $J_{C\text{-}F}$ = 4.83 Hz).



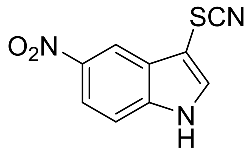
6-Fluoro-3-thiocyanato-1H-indole (3aj): yellow solid; Yield – (93 mg, 97%); mp: 104-106 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (s, broad, 1H), 7.72 (dd, J = 8.4, 4.8 Hz, 1H), 7.51 (d, J = 2.4 Hz, 1H), 7.13-7.06 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.90 (d, $J_{C\text{-}F}$ = 241.45 Hz), 136.18 (d, $J_{C\text{-}F}$ = 12.68 Hz), 131.43 (d, $J_{C\text{-}F}$ = 3.0 Hz), 124.26, 120.01 (d, $J_{C\text{-}F}$ = 10.27 Hz), 111.74, 111.11 (d, $J_{C\text{-}F}$ = 24.92 Hz), 98.69 (d, $J_{C\text{-}F}$ = 26.73 Hz), 92.99.



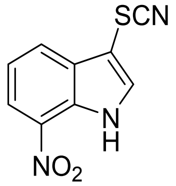
5-Chloro-3-thiocyanato-1H-indole (3ak): yellow solid; Yield – (102 mg, 98%); mp: 123-125 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (s, broad, 1H), 7.77 (d, J = 1.8 Hz, 1H), 7.54 (d, J = 3.0 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.28-7.25(m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.48, 132.34, 128.97, 128.16, 124.65, 118.53, 113.33, 111.64, 92.45.



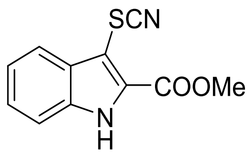
5-Bromo-3-thiocyanato-1H-indole (3al): white solid; Yield – (125 mg, 99%); mp: 138-140 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (s, broad, 1H), 7.93 (d, J = 1.2 Hz, 1H), 7.54 (d, J = 3.0 Hz, 1H), 7.41 (dd, J = 8.4, 1.8 Hz, 1H), 7.31 (d, J = 9.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.80, 132.15, 129.54, 127.25, 121.67, 115.64, 113.67, 111.52, 92.48.



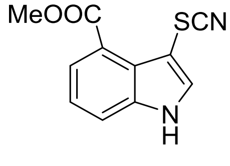
5-Nitro-3-thiocyanato-1H-indole (3am): yellow solid; Yield – (78 mg, 71%); mp: 180-182 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.64 (s, broad, 1H), 8.54 (d, *J* = 1.8 Hz, 1H), 8.28 (d, *J* = 2.4 Hz, 1H), 8.14 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.72 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 142.27, 139.65, 137.20, 127.02, 118.29, 114.53, 113.84, 112.07, 93.30.



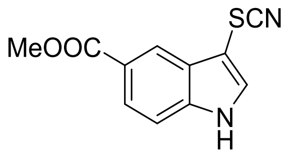
7-Nitro-3-thiocyanato-1H-indole (3an): yellow solid; Yield – (63 mg, 57%); mp: 141-143 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.30 (s, broad, 1H), 8.30 (d, *J* = 7.8 Hz, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 2.4 Hz, 1H), 7.46 (t, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.87, 133.21, 131.11, 129.67, 127.12, 121.69, 121.18, 110.67, 95.60. GC-MS (EI) *m/z* 218.98.



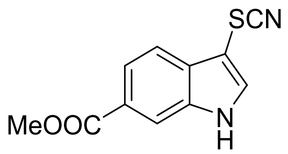
Methyl 3-thiocyanato-1H-indole-2-carboxylate (3ao): white solid; Yield – (50 mg, 43%); mp: 121-122 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.86 (s, broad, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.45-7.42 (m, 1H), 7.33 (t, 1H), 3.97 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 160.26, 136.19, 128.71, 127.54, 126.28, 122.33, 119.63, 113.84, 111.44, 97.00, 52.68. GC-MS (EI) *m/z* 232.00.



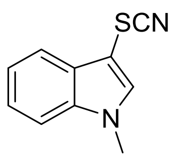
Methyl 3-thiocyanato-1H-indole-4-carboxylate (3ap): yellow solid; Yield – (106 mg, 91%); mp: 114-116 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.37 (s, broad, 1H), 8.07 (d, J = 3.0 Hz, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.65 (d, J = 7.2 Hz, 1H), 7.33 (t, 1H), 3.94(s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 167.51, 137.78, 134.33, 123.85, 123.45, 122.32, 122.21, 117.42, 113.53, 91.15, 52.19. GC-MS (EI) *m/z* 231.98.



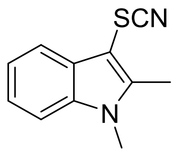
Methyl 3-thiocyanato-1H-indole-5-carboxylate (3aq): yellow solid; Yield – (109 mg, 94%); mp: 154-156 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.37 (s, broad, 1H), 8.31 (s, 1H), 8.15 (d, J = 3.0 Hz, 1H), 7.89 (dd, J = 9.0, 1.8 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 166.80, 139.10, 135.32, 127.18, 123.84, 122.67, 119.99, 113.18, 112.31, 91.61, 52.18.



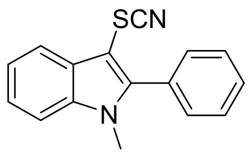
Methyl 3-thiocyanato-1H-indole-6-carboxylate (3ar): white solid; Yield – (103 mg, 89%); mp: 135-137 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.39 (s, broad, 1H), 8.23 (s, 1H), 8.16 (s, 1H), 7.85 (d, J = 9.6 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 3.88(s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 166.85, 136.74, 135.80, 131.15, 124.20, 121.77, 118.00, 114.78, 112.33, 90.67, 52.26. GC-MS (EI) *m/z* 231.97.



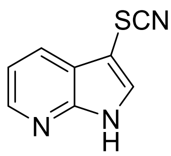
1-Methyl-3-thiocyanato-1H-indole (3as): yellow solid; Yield – (93 mg, 99%); mp: 95-97 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, J = 7.8 Hz, 1H), 7.40-7.31 (m, 4H), 3.82 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.31, 135.18, 128.62, 123.57, 121.74, 119.09, 111.99, 110.32, 90.06, 33.57.



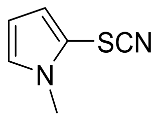
1, 2-Dimethyl-3-thiocyanato-1H-indole (3at): yellow solid; Yield – (92 mg, 91%); mp: 75-77 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.60-7.56 (m, 2H), 7.28-7.22 (m, 2H), 3.76 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 144.42, 136.69, 127.61, 122.33, 121.21, 117.28, 112.15, 110.61, 86.44, 30.56, 10.75. GC-MS (EI) *m/z* 202.03.



1-Methyl-2-phenyl-3-thiocyanato-1H-indole (3au): yellow solid; Yield – (130 mg, 99%); mp: 83-84 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.75 (d, J = 7.8 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.66-7.59 (m, 5H), 7.41-7.33 (m, 2H), 3.71 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 146.17, 136.95, 130.69, 129.68, 128.82, 128.78, 127.75, 123.45, 121.87, 118.07, 112.35, 111.50, 88.52, 31.87.

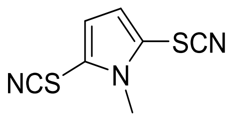


3-Thiocyanato-7-azaindole (3ax): yellow solid; Yield – (56 mg, 64%); mp: 197-199 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.60 (s, broad, 1H), 8.39 (dd, J = 4.2, 1.2 Hz, 1H), 8.17 (s, 1H), 8.11 (dd, J = 7.8, 2.4 Hz, 1H), 7.30 (dd, J = 7.8, 4.8 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 148.44, 144.58, 134.07, 126.57, 119.91, 117.43, 112.22, 89.10.

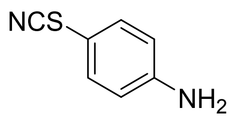


1-Methyl-2-thiocyanato-1H-pyrrole (3ba): colorless liquid; Yield – (50 mg, 72%);

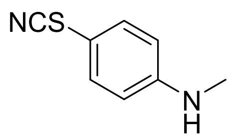
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.92 (t, 1H), 6.63 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.19 (t, 1H), 3.80 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 128.50, 120.97, 110.30, 109.72, 105.42, 34.67.



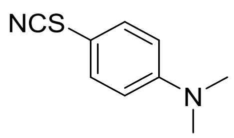
1-Methyl-2, 5-dithiocyanato-1H-pyrrole (3bb): white solid; Yield – (14 mg, 15%); mp: 118-120 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.73 (s, 2H), 3.97 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 120.97, 113.93, 108.53, 32.92. GC-MS (EI) *m/z* 194.97.



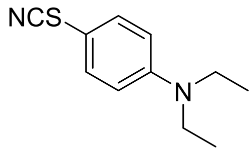
4-Thiocyanatoaniline (3bc): brown yellow solid; Yield – (54 mg, 72%); mp: 50-52 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37-7.34 (m, 2H), 6.68-6.65 (m, 2H), 3.97 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.93, 134.63, 116.20, 112.51, 109.69.



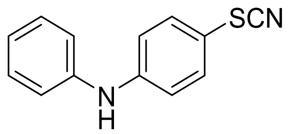
***N*-methyl-4-thiocyanatoaniline (3bd):** yellow liquid; Yield – (75 mg, 91%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 9.0 Hz, 2H), 4.08 (s, broad, 1H), 2.85 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.21, 134.86, 113.49, 112.76, 107.63, 30.36.



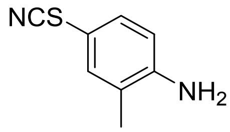
***N, N*-dimethyl-4-thiocyanatoaniline (3be):** yellow solid; Yield – (67 mg, 75%); mp: 73-74 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44-7.40 (m, 2H), 6.69-6.66 (m, 2H), 3.00 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.81, 134.64, 113.27, 112.76, 106.67, 40.28.



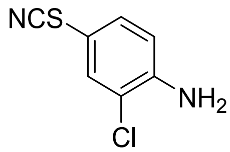
***N, N*-diethyl-4-thiocyanatoaniline (3bf):** yellow liquid; Yield – (95 mg, 92%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41-7.37 (m, 2H), 6.65-6.62 (m, 2H), 3.37 (dd, J = 14.4, 7.2 Hz, 4H), 1.17 (t, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.40, 135.13, 112.95, 112.68, 105.11, 44.60, 12.46.



***N*-phenyl-4-thiocyanatoaniline (3bg):** brown solid; Yield – (103 mg, 91%); mp: 62-64 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44-7.41 (m, 2H), 7.34 (t, 2H), 7.13 (d, J = 7.2 Hz, 2H), 7.07 (t, 1H), 7.04-7.01 (m, 2H), 5.95 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.20, 141.00, 134.25, 129.70, 123.22, 120.23, 117.23, 112.21, 111.55.

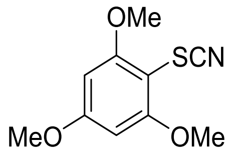


2-Methyl-4-thiocyanatoaniline (3bh): yellow solid; Yield – (80 mg, 98%); mp: 67-68 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.26-7.23 (m, 1H), 6.66 (d, J = 8.4 Hz, 1H), 3.89 (s, broad, 2H), 2.16 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.16, 135.24, 132.27, 124.00, 115.87, 112.70, 109.50, 17.36.

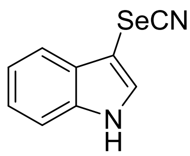


2-Chloro-4-thiocyanatoaniline (3bi): brown yellow solid; Yield – (77 mg, 83%); mp: 60-62 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, J = 2.4 Hz, 1H), 7.29 (dd, J = 8.4, 2.4 Hz, 1H), 6.77 (d, J = 9.0 Hz, 1H), 4.38 (s, broad, 2H). ^{13}C NMR (151 MHz,

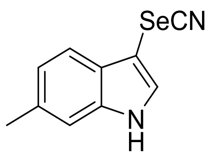
$CDCl_3$) δ 145.40, 134.00, 132.79, 119.80, 116.52, 111.80, 110.15.



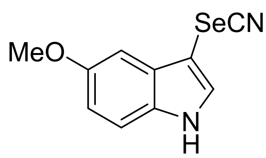
1, 3, 5-Trimethoxy-2-thiocyanatobenzene (3bj): white solid; Yield – (109 mg, 97%); mp: 106-108 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.15 (s, 2H), 3.91 (s, 6H), 3.84 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.39, 161.53, 111.98, 91.45, 89.92, 56.49, 55.72.



3-Selenocyanato-1H-indole (5aa): brown yellow solid; Yield – (103 mg, 94%); mp: 99-101 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 (s, broad, 1H), 7.77-7.73 (m, 1H), 7.48 (d, J = 2.4 Hz, 1H), 7.44-7.40 (m, 1H), 7.32-7.29 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.13, 131.93, 128.84, 123.89, 121.96, 119.70, 112.01, 102.02, 89.64.

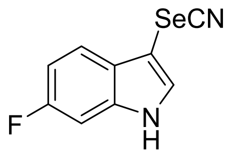


6-Methyl-3-selenocyanato-1H-indole (5ab): yellow solid; Yield – (94 mg, 80%); mp: 121-123 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.71 (s, 1H), 7.76 (d, J = 2.7 Hz, 1H), 7.46 (d, J = 8.1 Hz, 1H), 7.29 (s, 1H), 7.05 (dd, J = 8.1, 0.8 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 136.69, 132.62, 131.91, 126.66, 122.53, 118.45, 112.16, 104.33, 88.73, 21.36. GC-MS (EI) m/z 235.93.

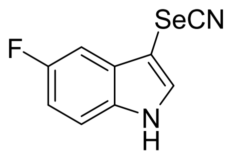


5-Methoxy-3-selenocyanato-1H-indole (5ac): yellow solid; Yield – (88 mg, 70%);

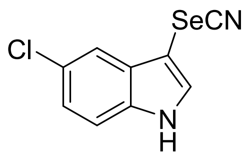
mp: 116-117 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.58 (s, broad, 1H), 7.48 (d, J = 3.0 Hz, 1H), 7.32 (d, J = 9.0 Hz, 1H), 7.14 (d, J = 2.4 Hz, 1H), 6.96 (dd, J = 9.0, 2.4 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.92, 132.27, 130.95, 129.68, 114.63, 112.89, 101.90, 100.85, 89.31, 55.99.



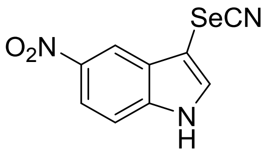
6-Fluoro-3-selenocyanato-1H-indole (5ad): brown yellow solid; Yield – (88 mg, 73%); mp: 117-119 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.66 (dd, J = 8.7, 5.1 Hz, 1H), 7.49 (d, J = 2.7 Hz, 1H), 7.16-7.03 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.88 (d, J_{C-F} = 241.15 Hz), 136.12 (d, J_{C-F} = 12.68 Hz), 132.29 (d, J_{C-F} = 3.17 Hz), 125.33, 120.81 (d, J_{C-F} = 10.27 Hz), 110.99 (d, J_{C-F} = 24.92 Hz), 101.73, 98.44 (d, J_{C-F} = 26.73 Hz), 89.99. GC-MS (EI) *m/z* 239.92.



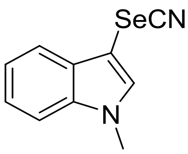
5-Fluoro-3-selenocyanato-1H-indole (5ae): yellow solid; Yield – (109 mg, 91%); mp: 123-125 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.97 (s, 1H), 7.93 (d, J = 2.8 Hz, 1H), 7.52 (dd, J = 8.8, 4.5 Hz, 1H), 7.29 (dd, J = 9.4, 2.5 Hz, 1H), 7.09 (td, J = 9.2, 2.5 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 158.00 (d, J_{C-F} = 234.65 Hz), 135.21, 132.93, 129.45 (d, J_{C-F} = 10.42 Hz), 113.92 (d, J_{C-F} = 9.82 Hz), 110.98 (d, J_{C-F} = 26.12 Hz), 104.45, 103.60 (d, J_{C-F} = 22.65 Hz), 89.36 (d, J_{C-F} = 4.83 Hz). GC-MS (EI) *m/z* 239.91.



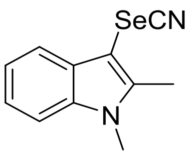
5-Chloro-3-selenocyanato-1H-indole (5af): yellow solid; Yield – (99 mg, 77%); mp: 135-137 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.05 (s, 1H), 7.94 (d, J = 2.7 Hz, 1H), 7.55 (dd, J = 15.1, 5.3 Hz, 2H), 7.25 (dd, J = 8.6, 2.1 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 134.94, 134.82, 130.01, 125.51, 122.68, 117.95, 114.24, 104.49, 89.21. GC-MS (EI) *m/z* 255.88.



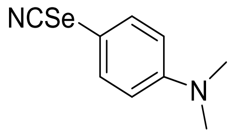
5-Nitro-3-selenocyanato-1H-indole (5ag): yellow solid; Yield – (68 mg, 51%); mp: 162-164 °C; ^1H NMR (600 MHz, DMSO-d_6) δ 12.10 (s, 1H), 8.53 (d, J = 2.3 Hz, 1H), 8.04-7.94 (m, 2H), 7.55 (d, J = 8.9 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 141.33, 139.66, 134.78, 128.75, 117.21, 115.93, 112.78, 100.94. GC-MS (EI) *m/z* 266.97



1-Methyl-3-selenocyanato-1H-indole (3ah): yellow solid; Yield – (48 mg, 41%); mp: 106-108 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, J = 7.8 Hz, 1H), 7.41 (s, 1H), 7.40-7.30 (m, 3H), 3.85 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.34, 136.07, 129.68, 123.46, 121.67, 119.95, 110.15, 101.92, 87.39, 33.52.



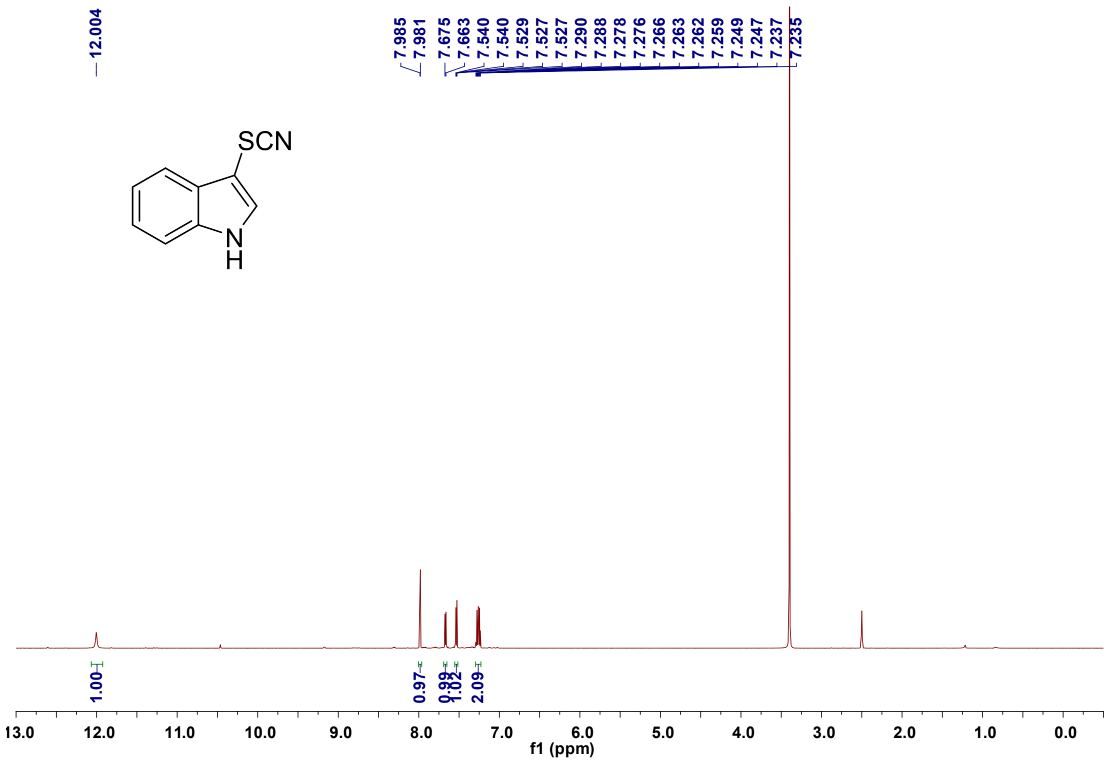
1, 2-Dimethyl-3-selenocyanato-1H-indole (5ai): yellow solid; Yield – (104 mg, 83%); mp: 95-97 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.68-7.64 (m, 1H), 7.33-7.24 (m, 3H), 3.74 (s, 3H), 2.63 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.54, 137.25, 129.45, 122.66, 121.50, 119.25, 109.60, 101.95, 87.12, 30.72, 12.23. GC-MS (EI) *m/z* 249.95.



***N, N*-dimethyl-4-selenocyanatoaniline (3ak):** yellow solid; Yield – (59 mg, 52%); mp: 101-102 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, J = 9.1 Hz, 2H), 6.65 (d, J = 9.0 Hz, 2H), 3.00 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.79, 136.54, 113.44, 104.59, 102.92, 40.26.

NMR spectra

^{1}H NMR



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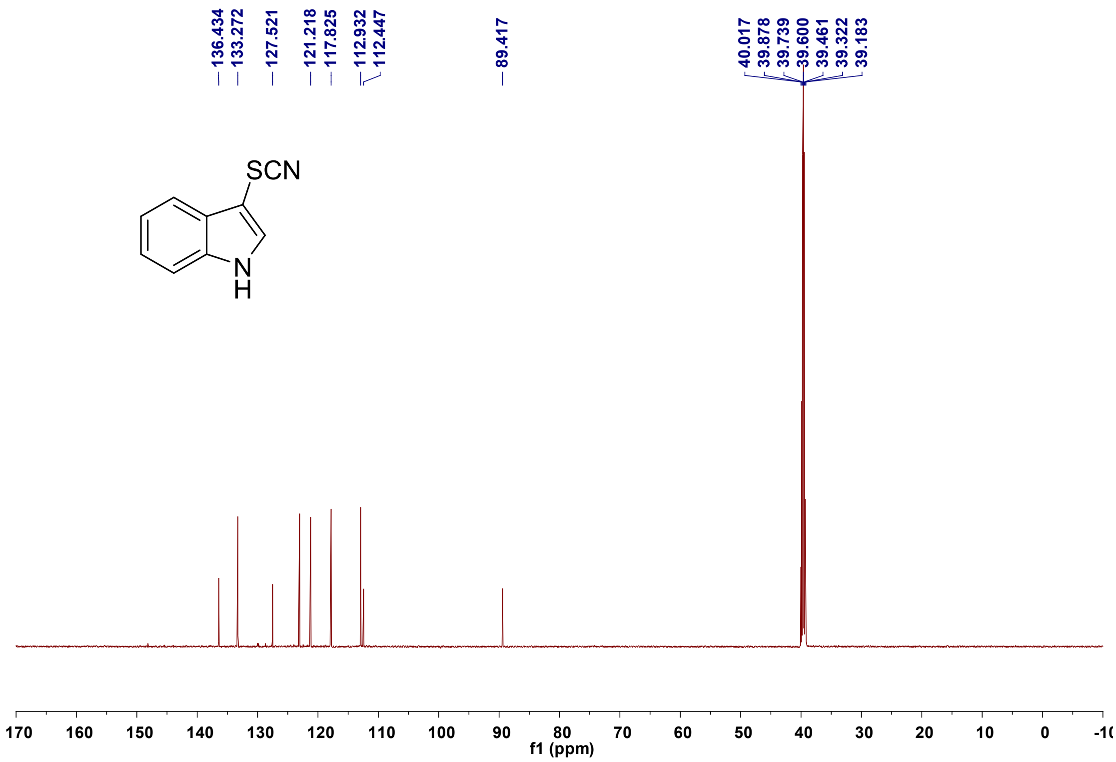

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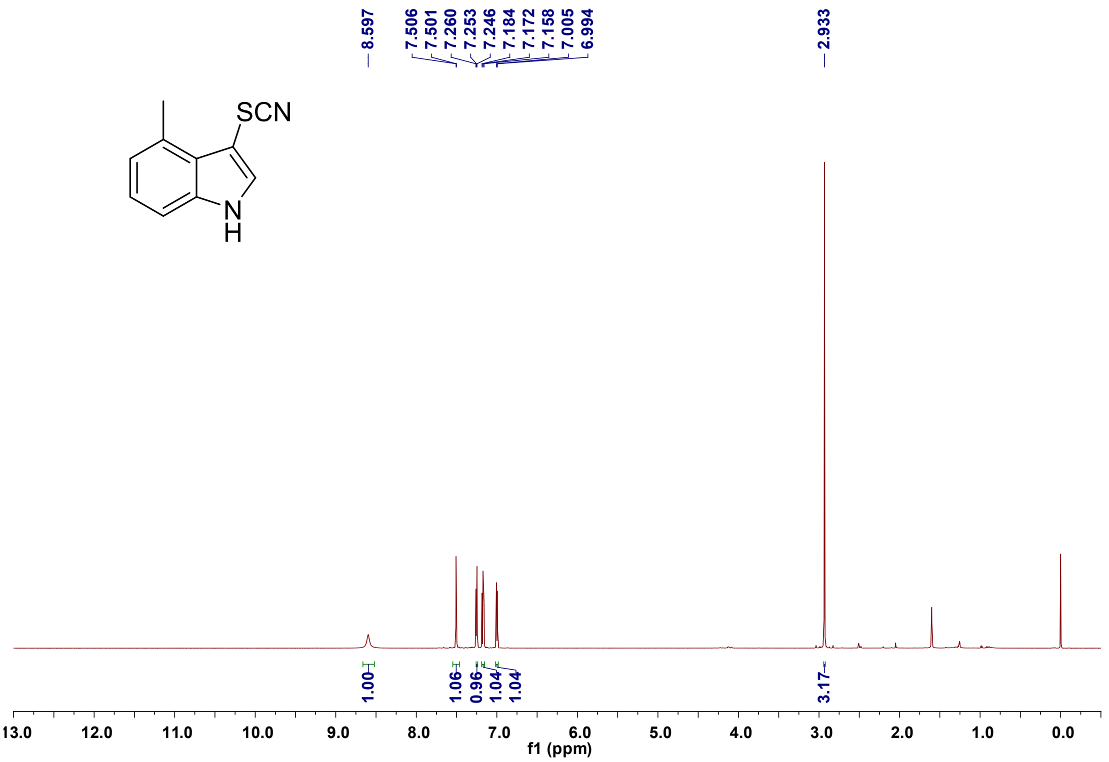

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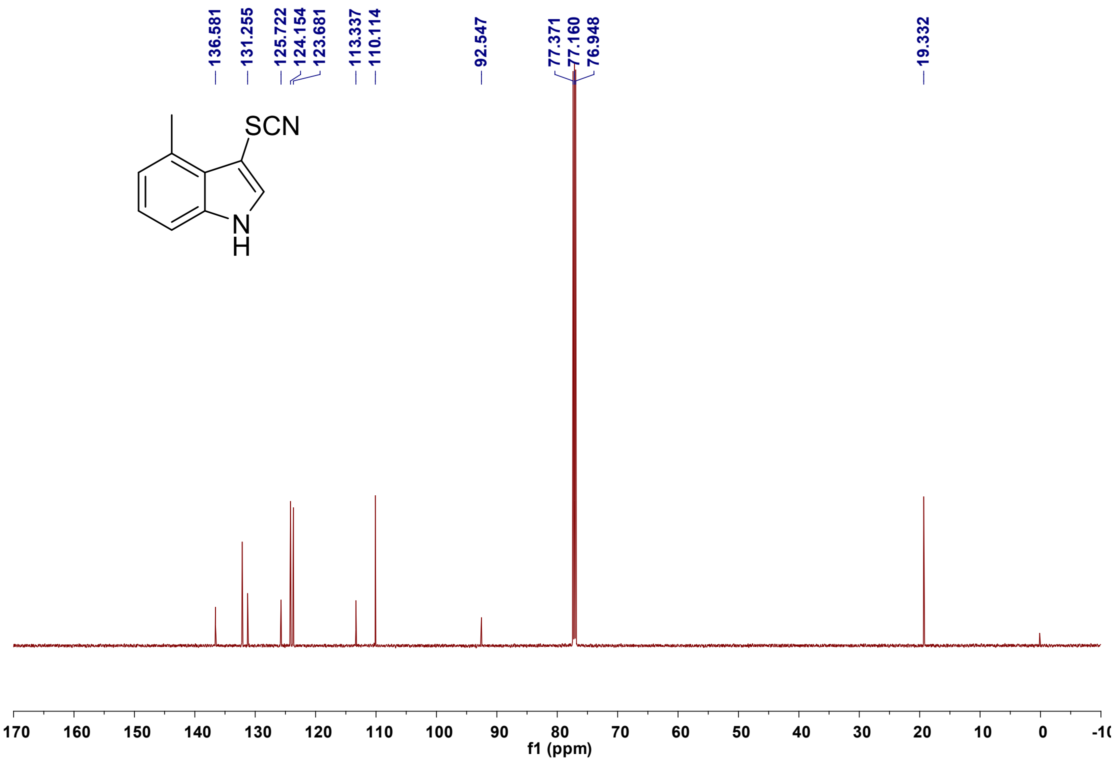

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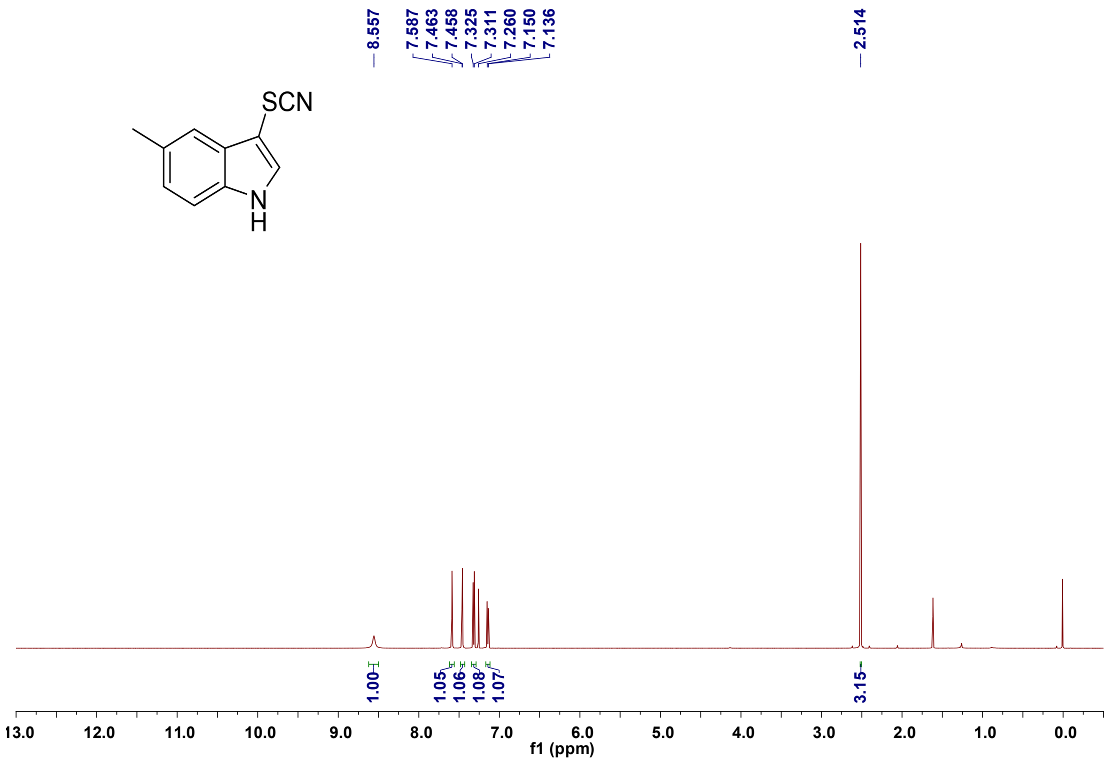

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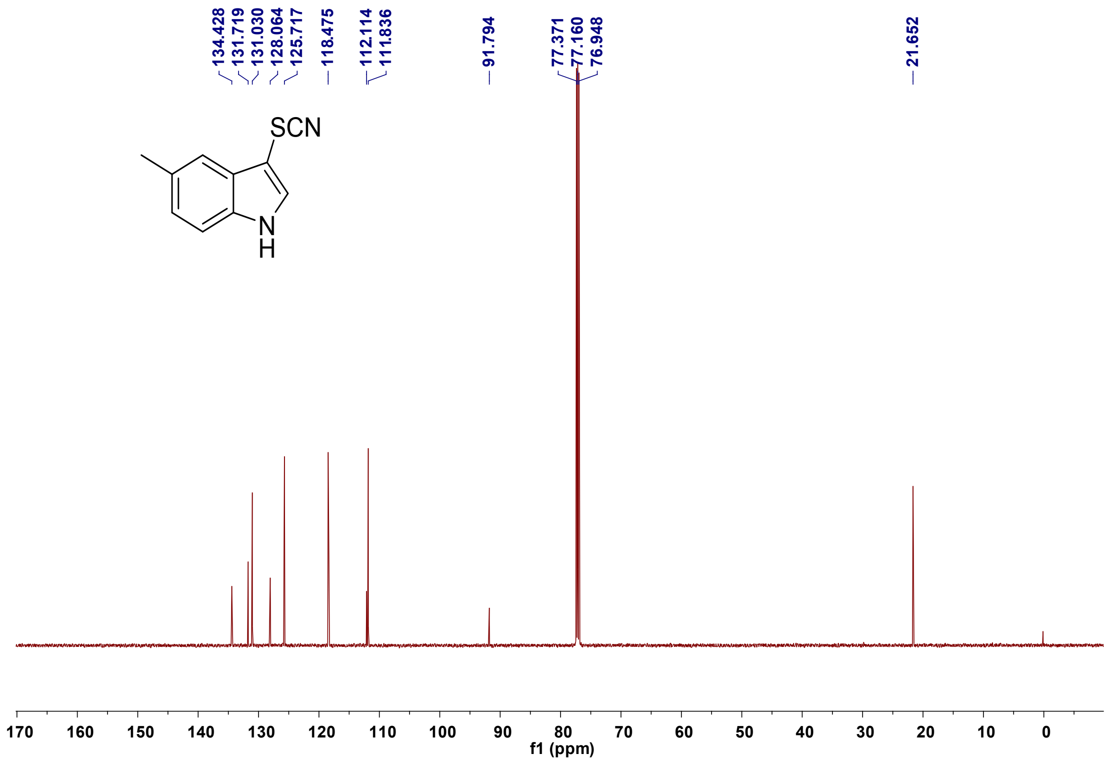

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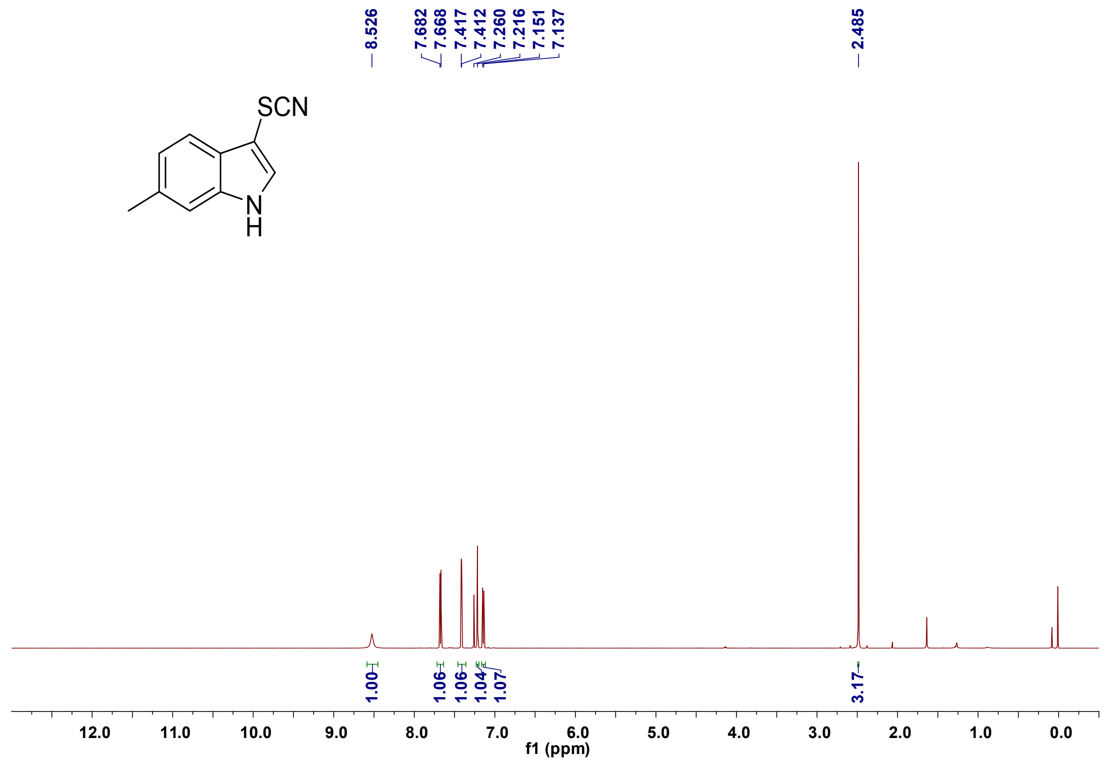

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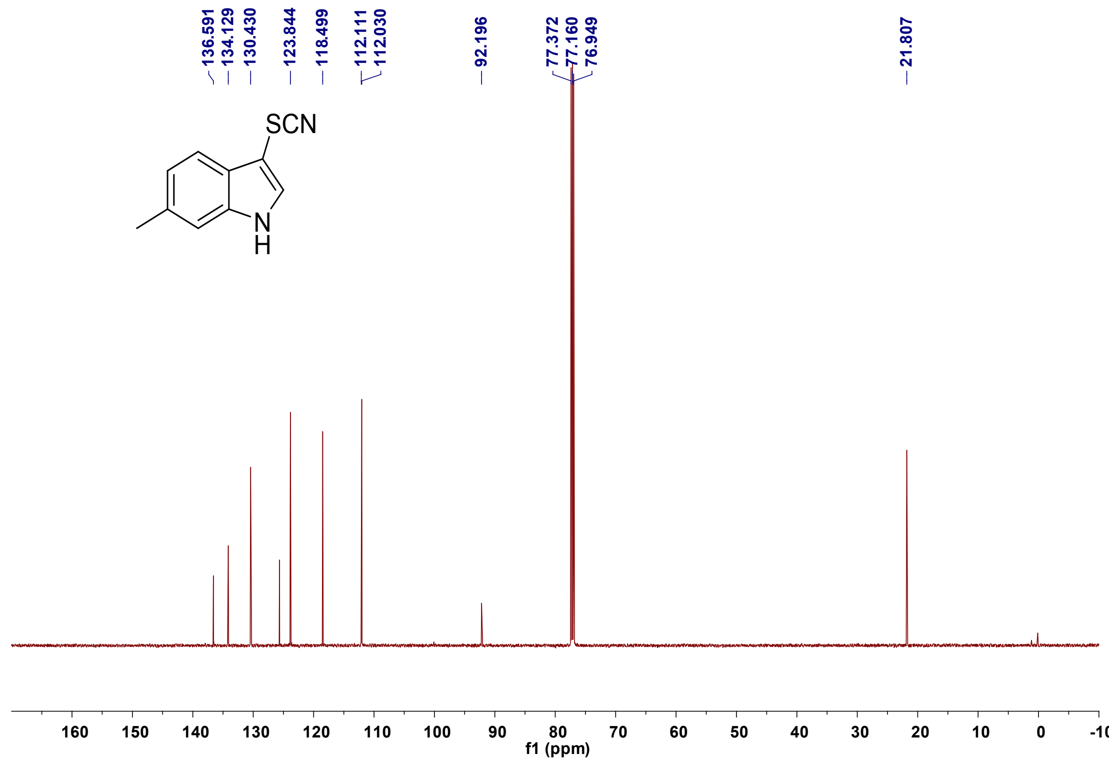

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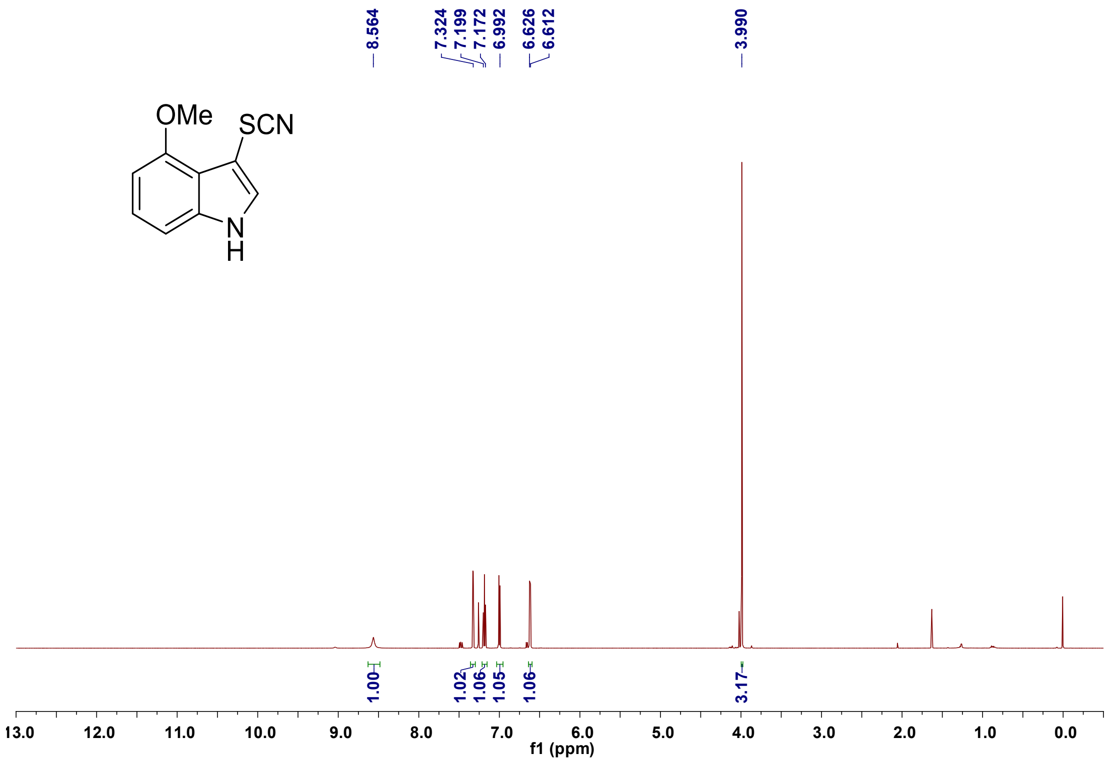

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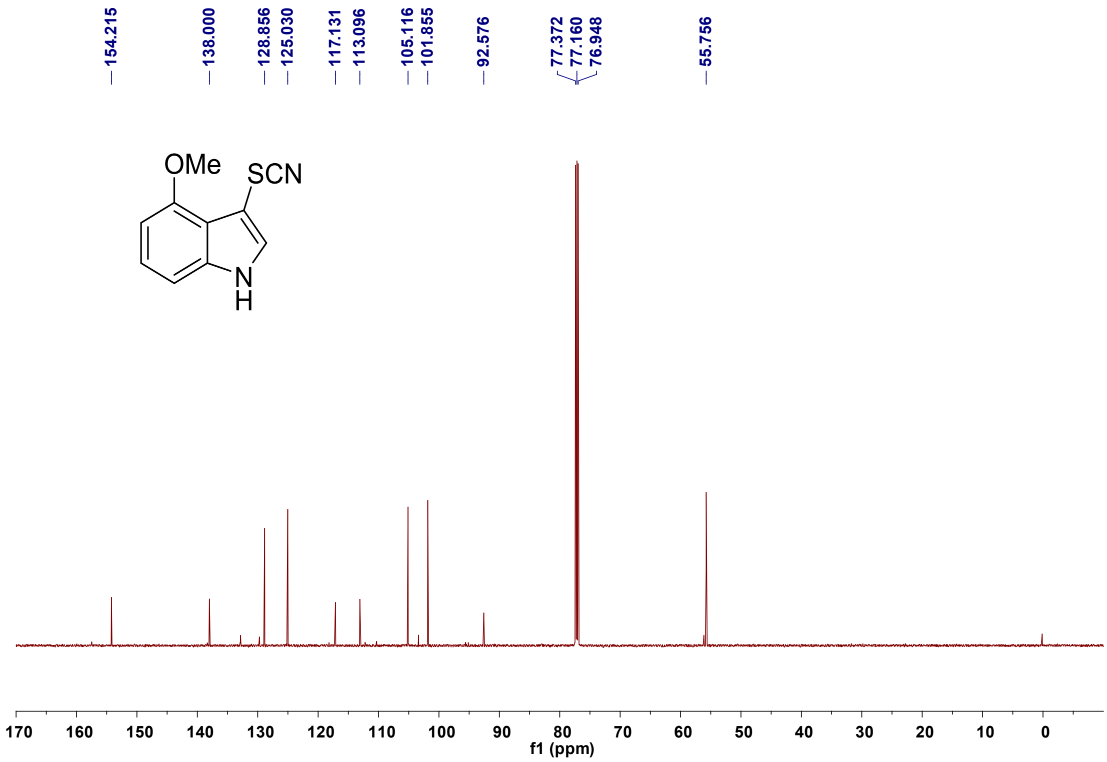

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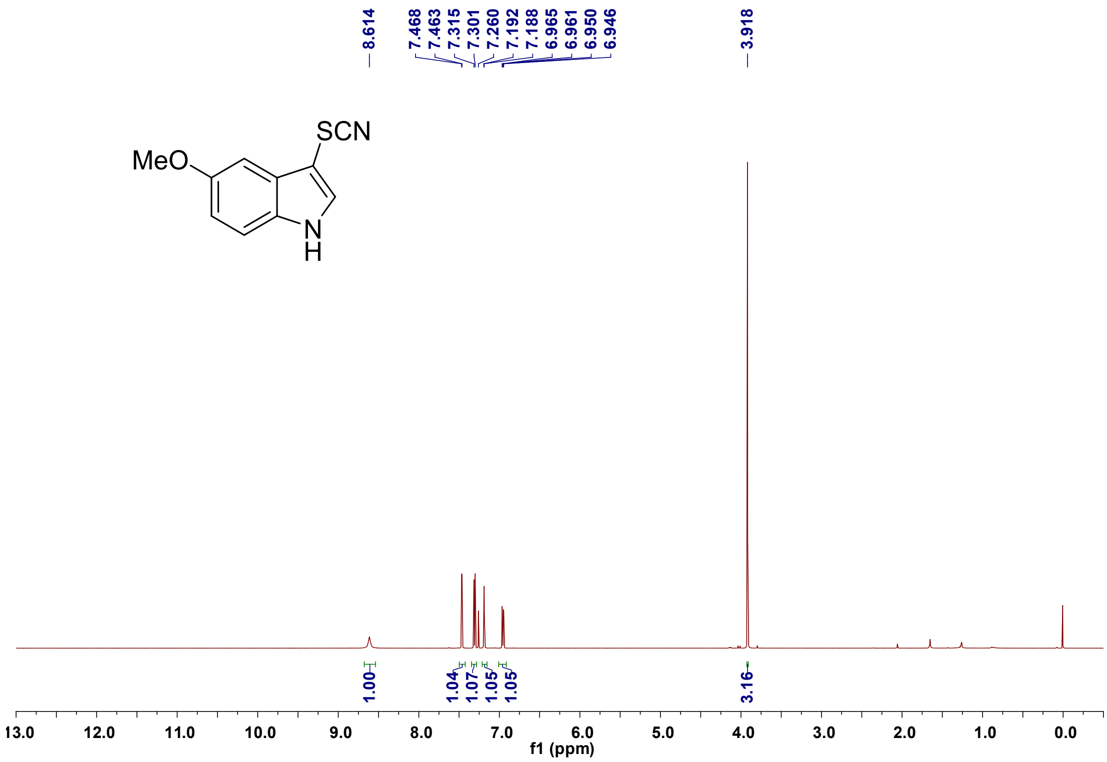

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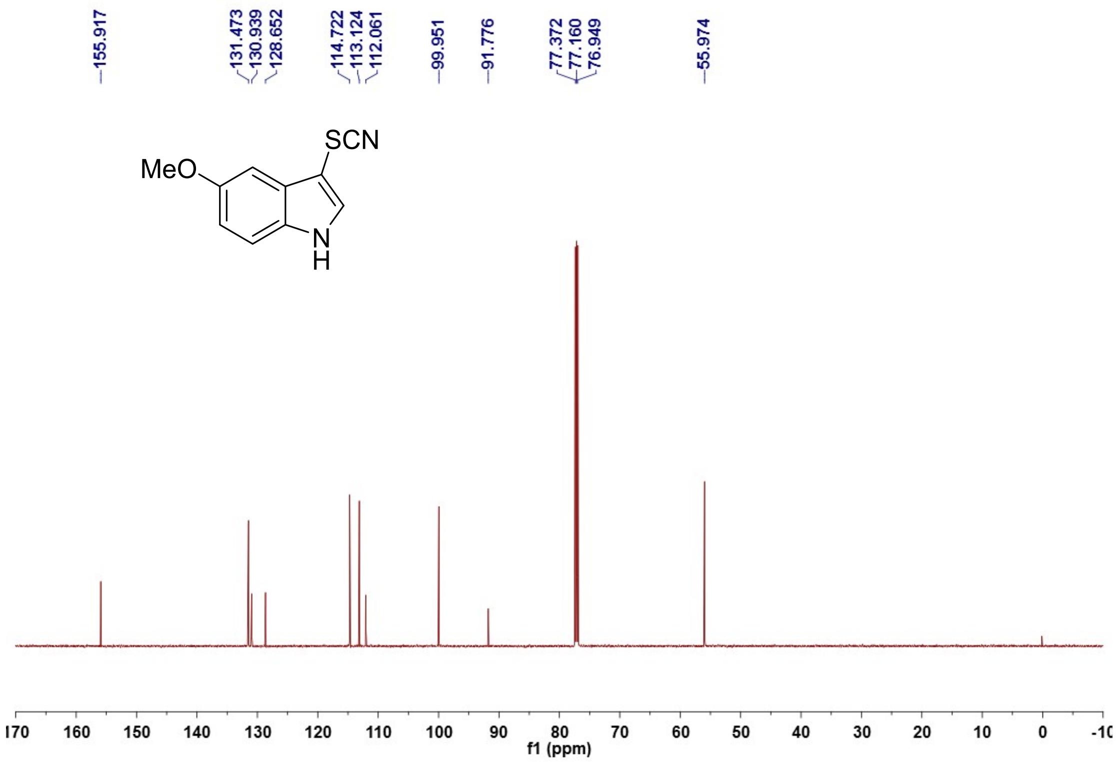

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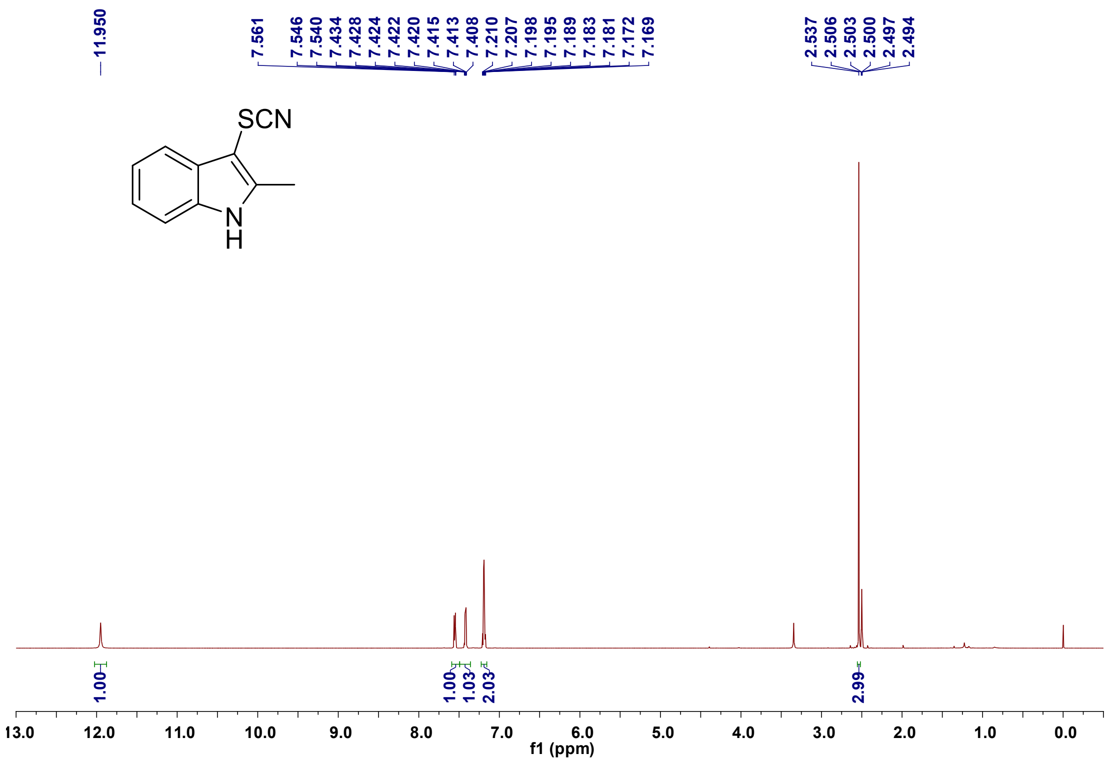

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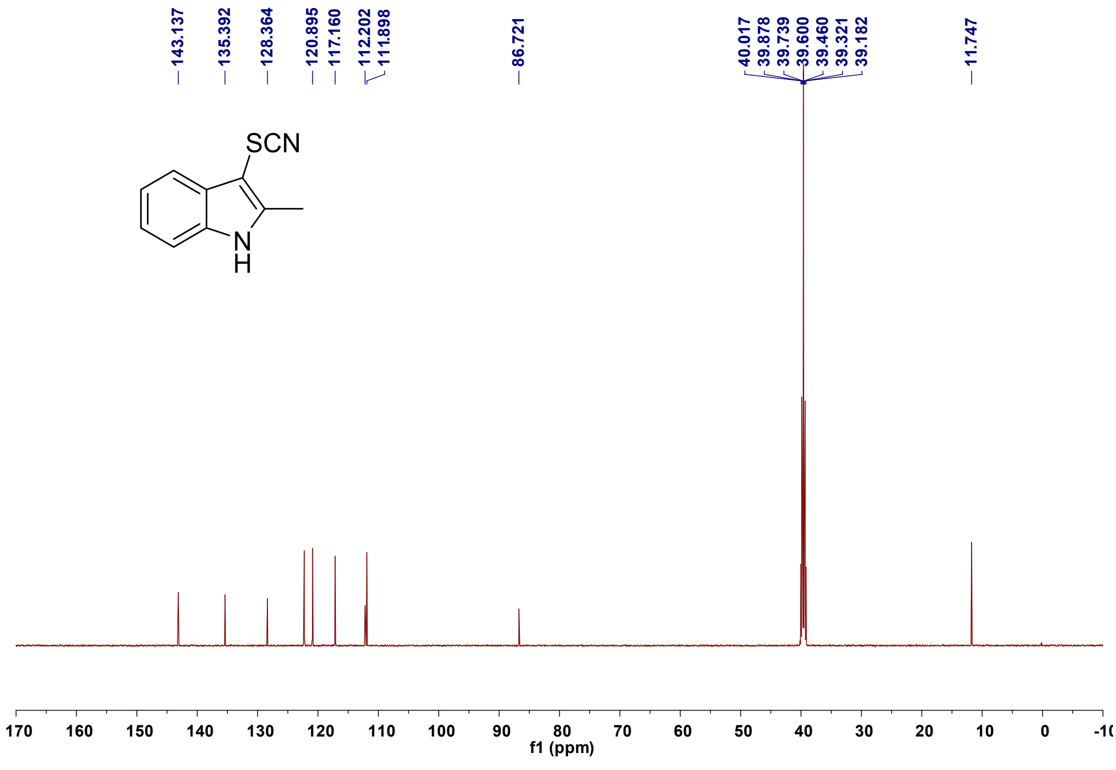
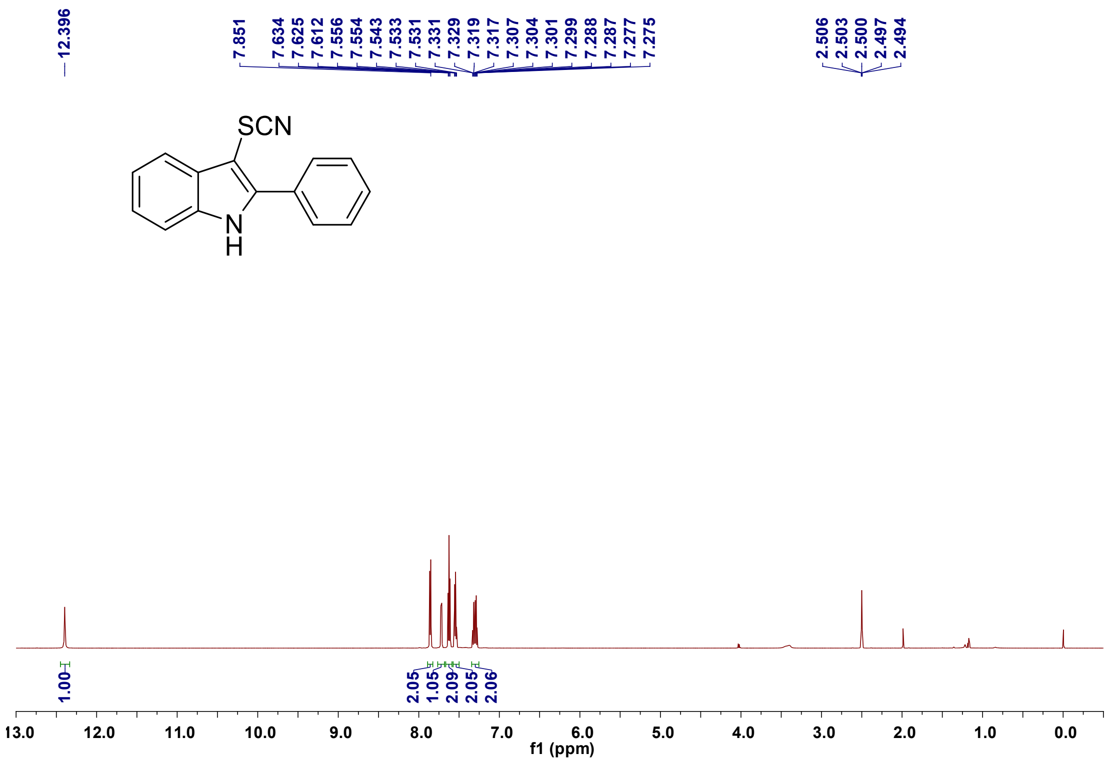


^1H NMR



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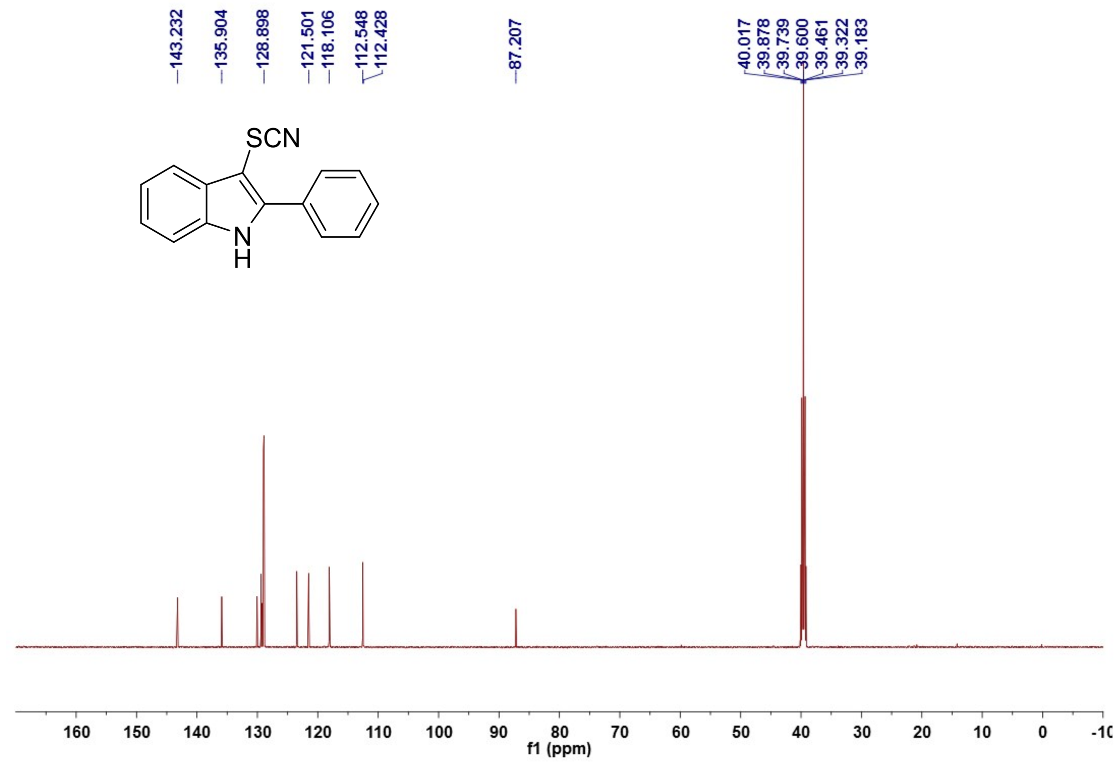

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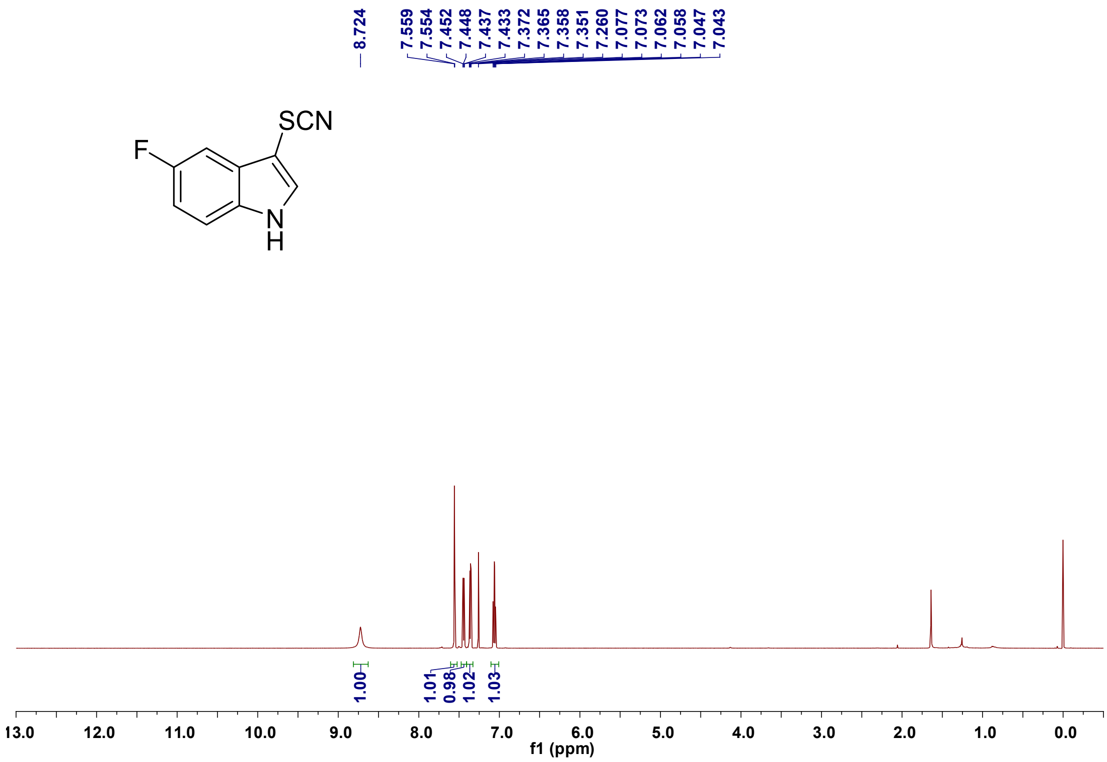

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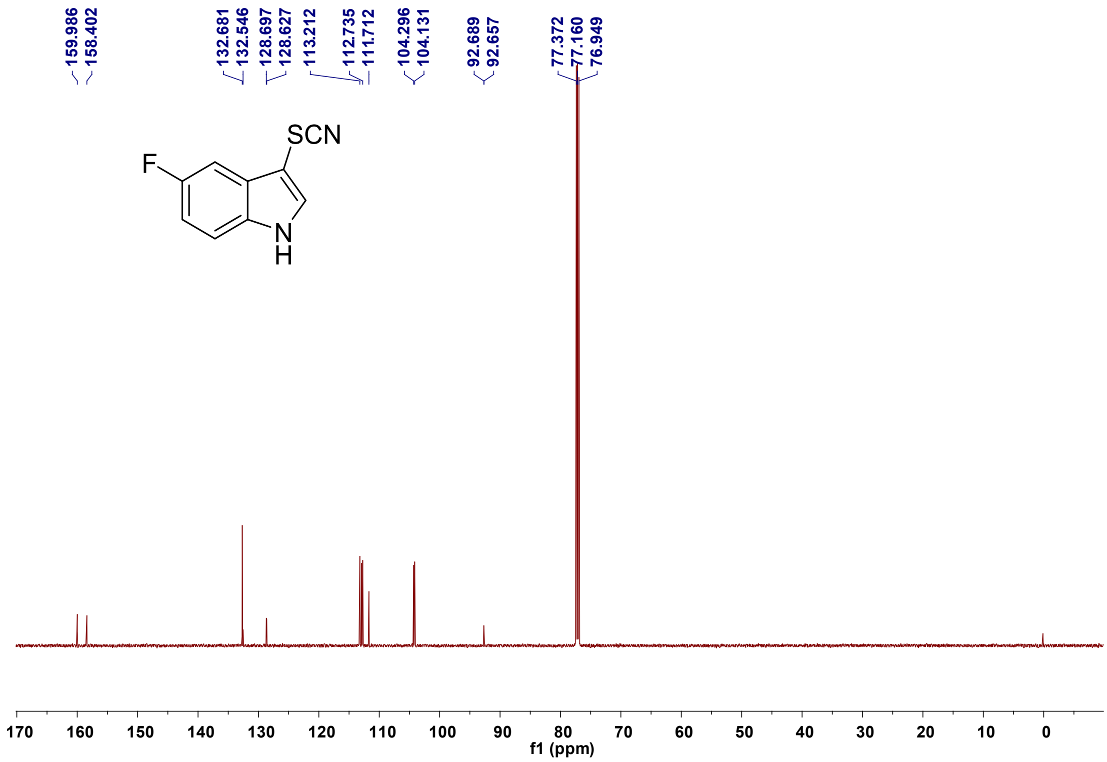

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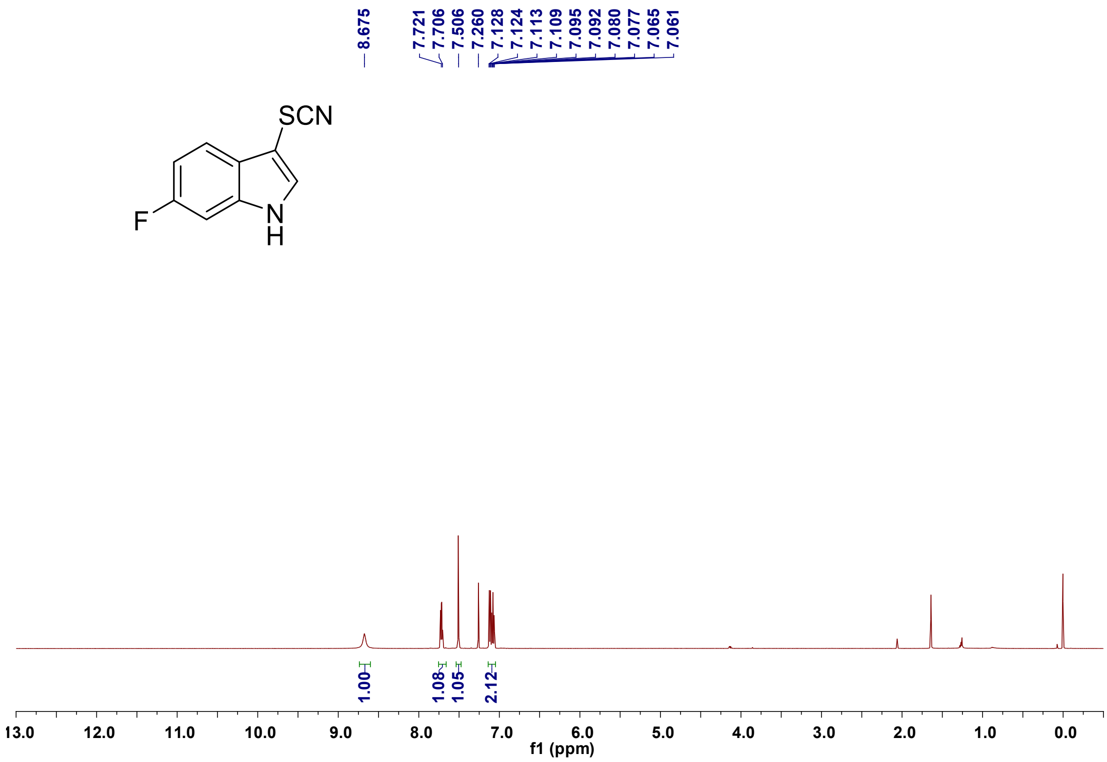
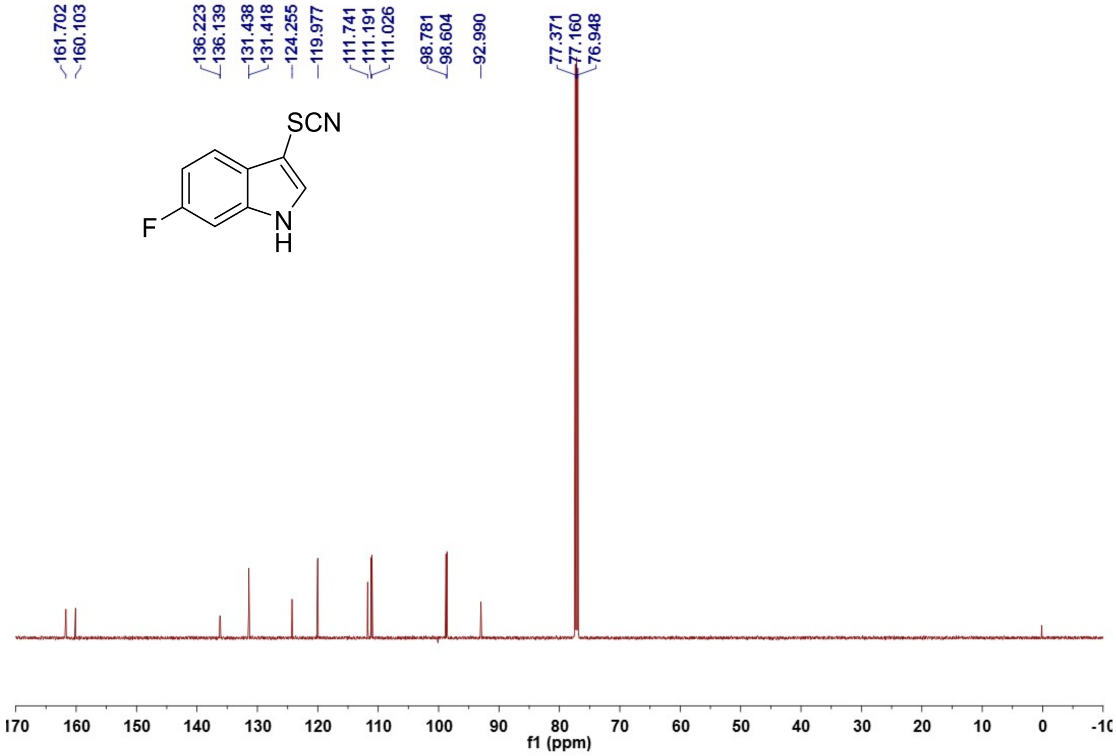


^{13}C NMR



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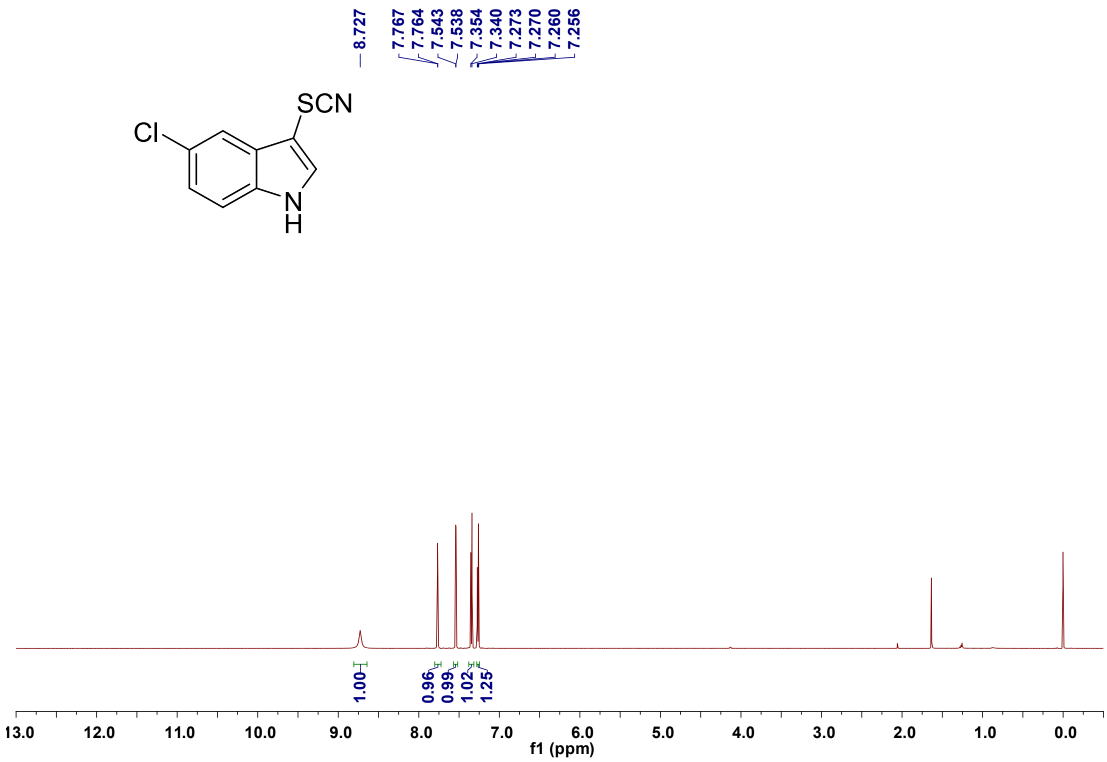

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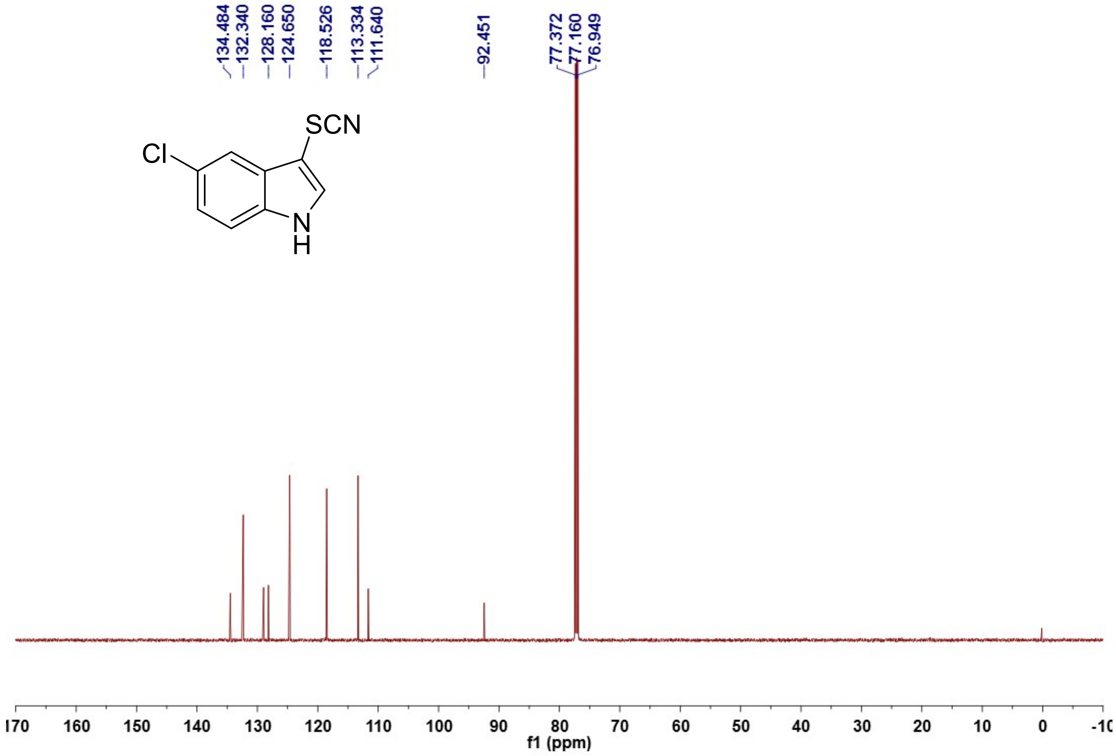

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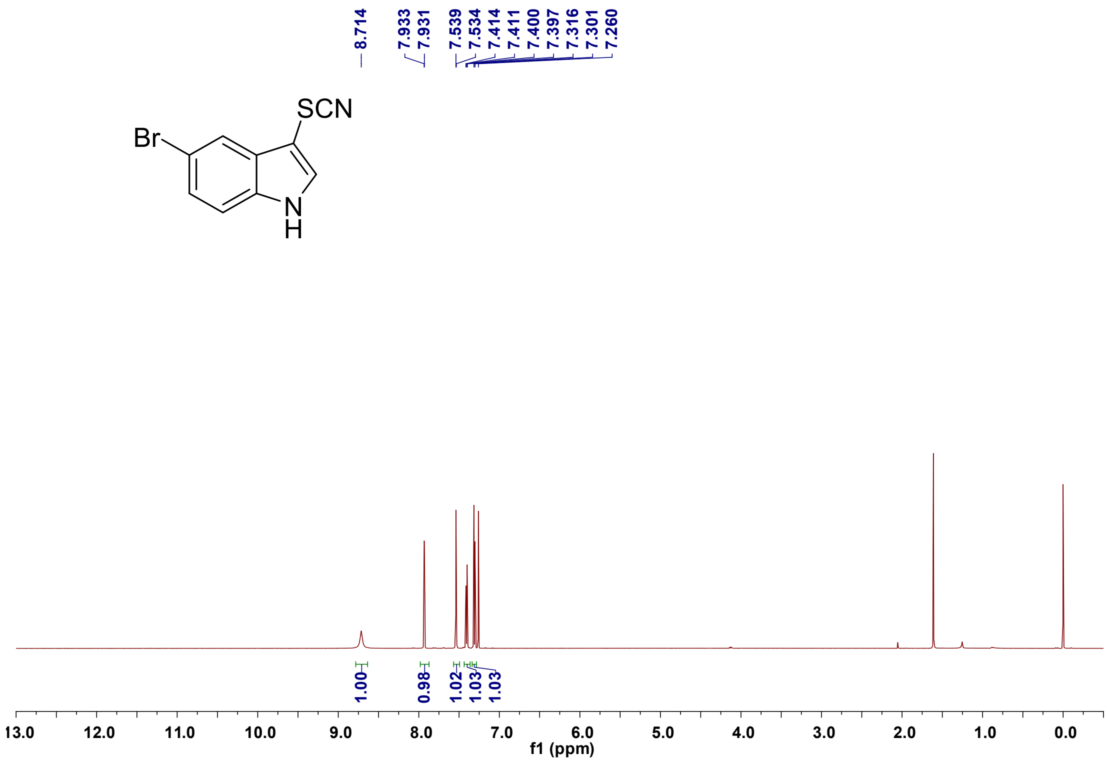

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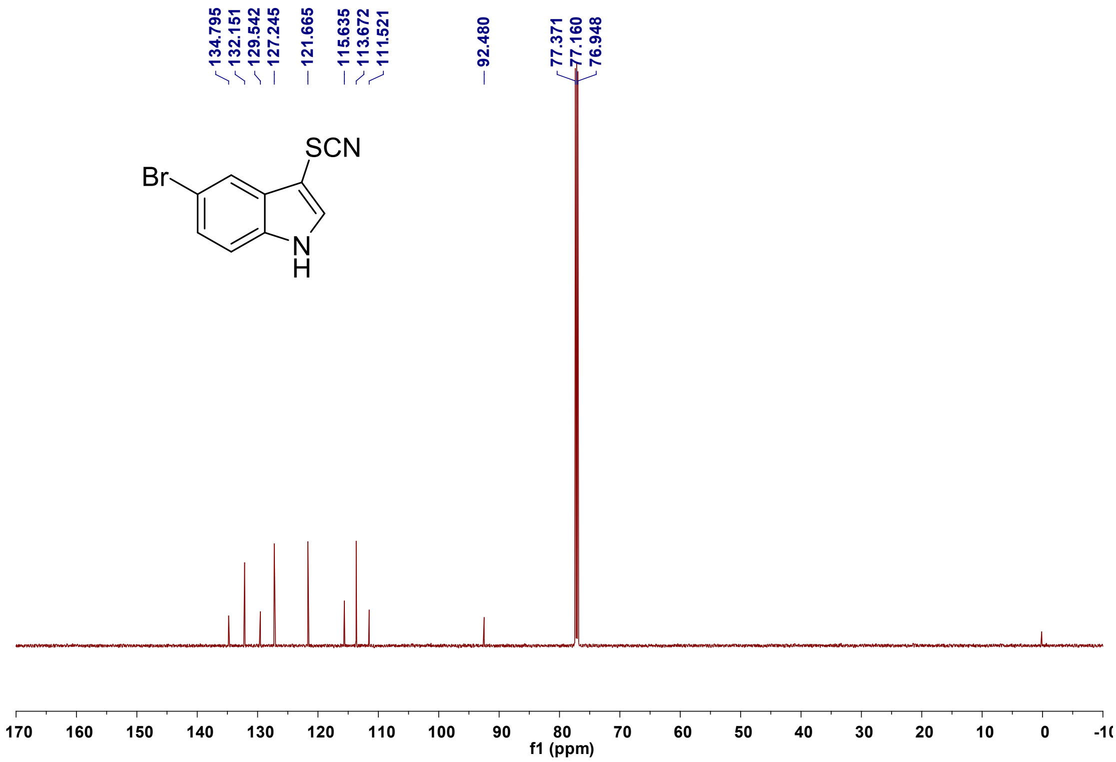

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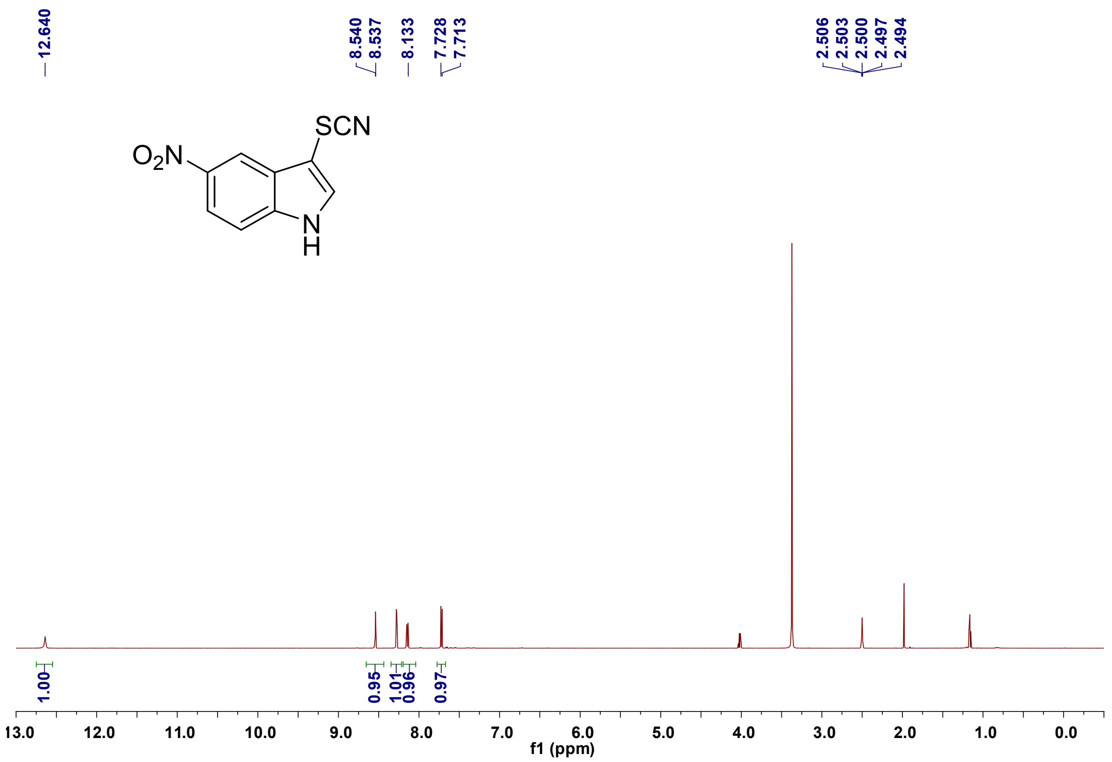

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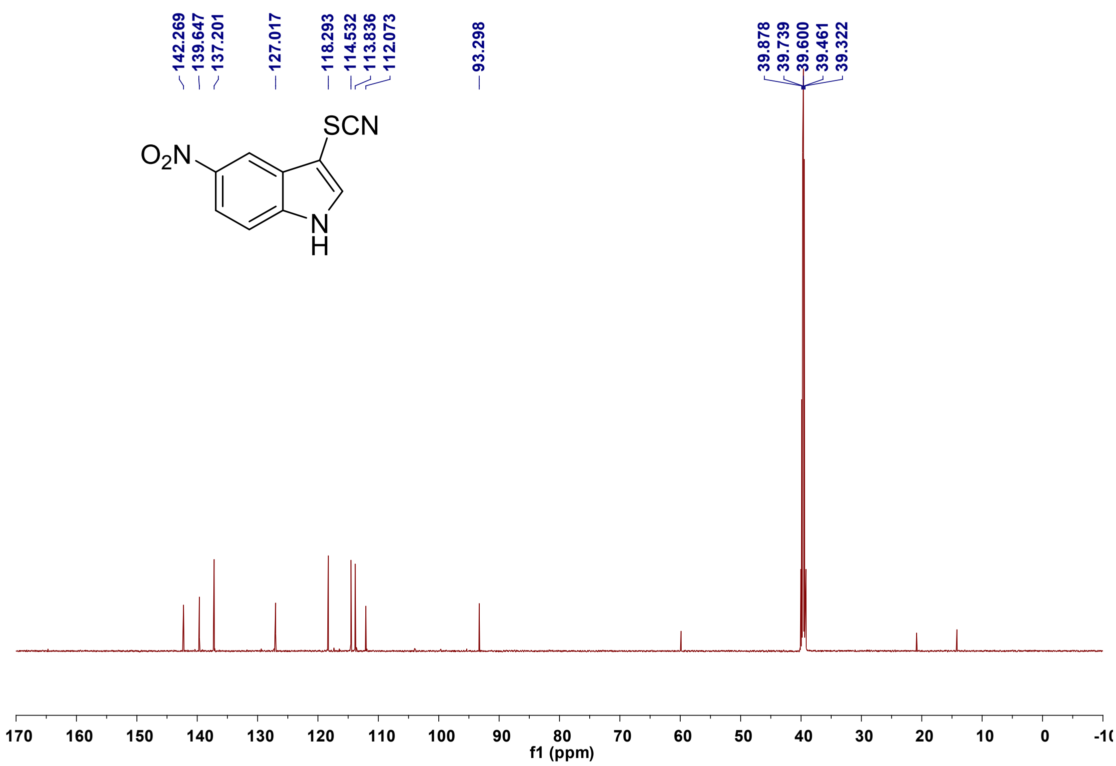

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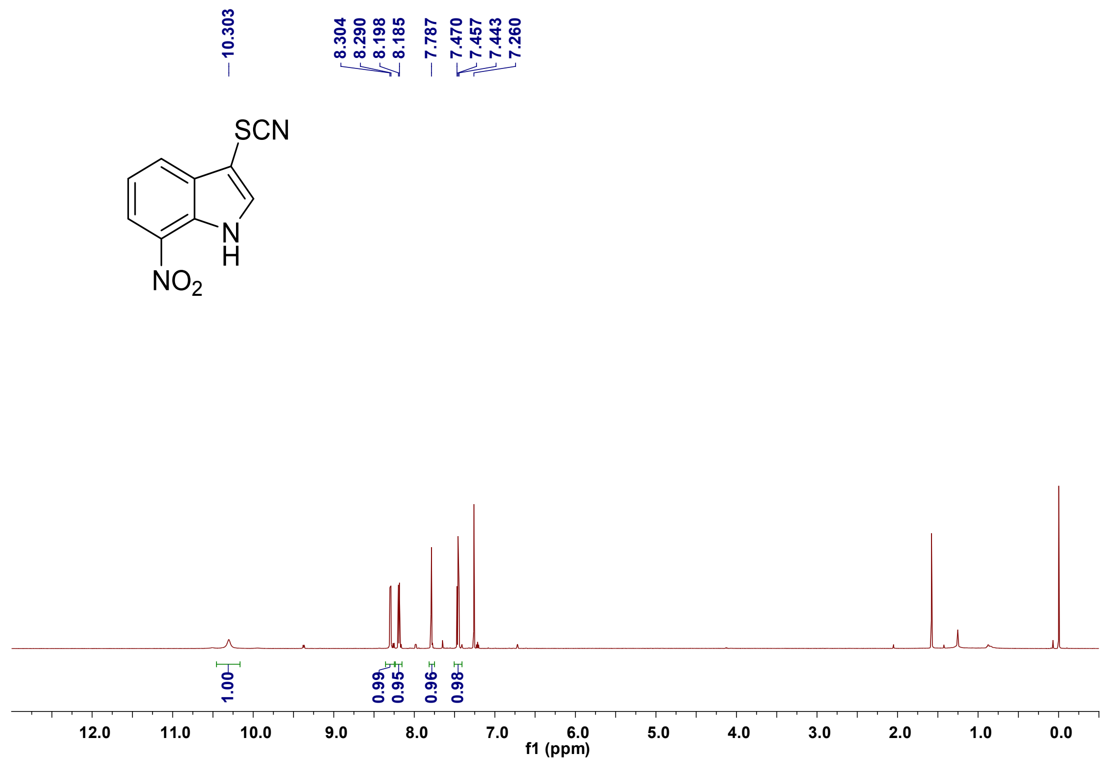

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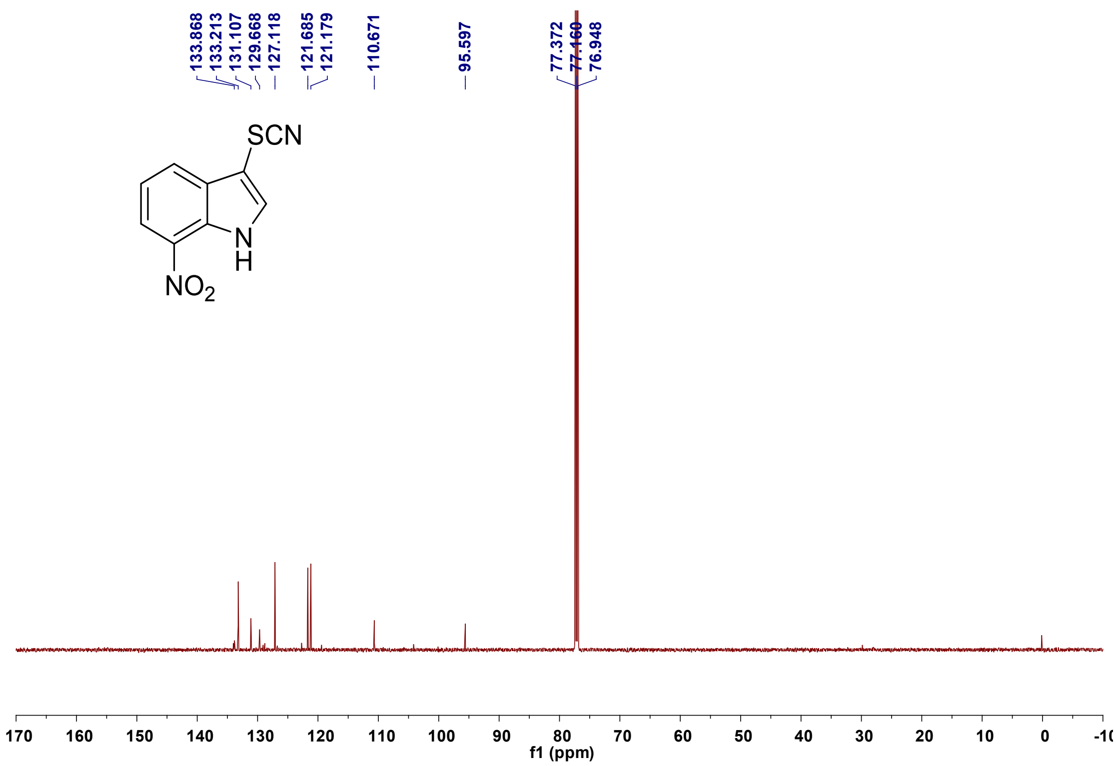

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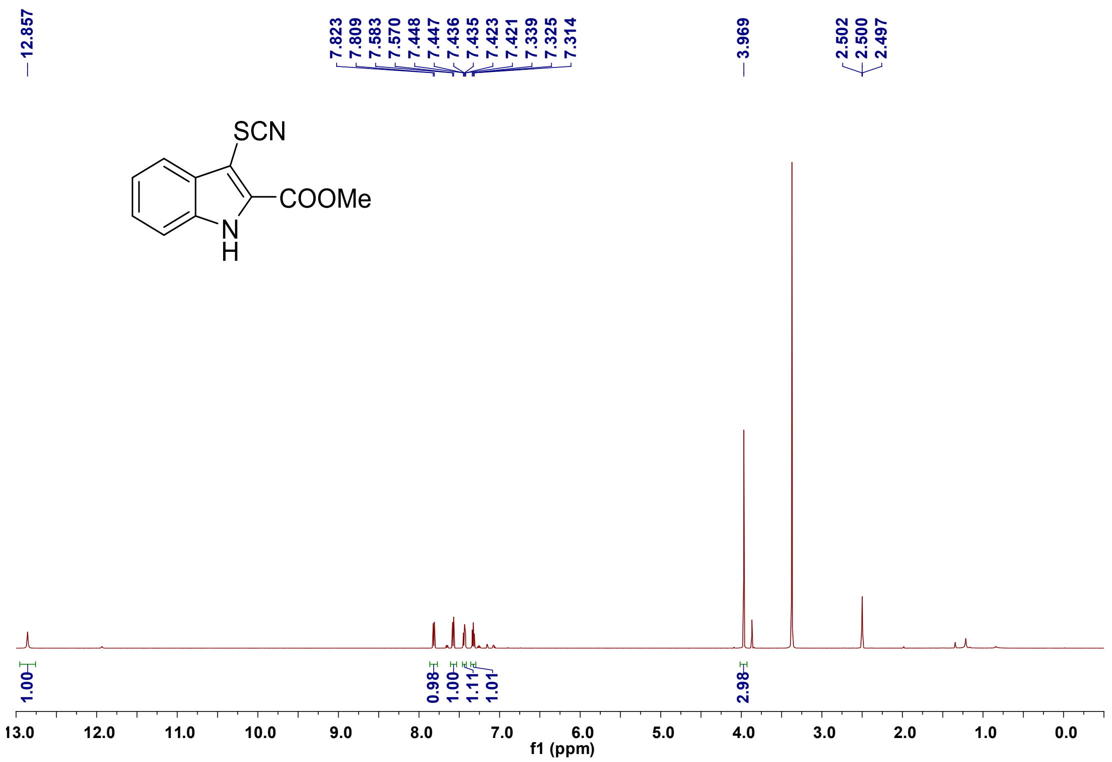

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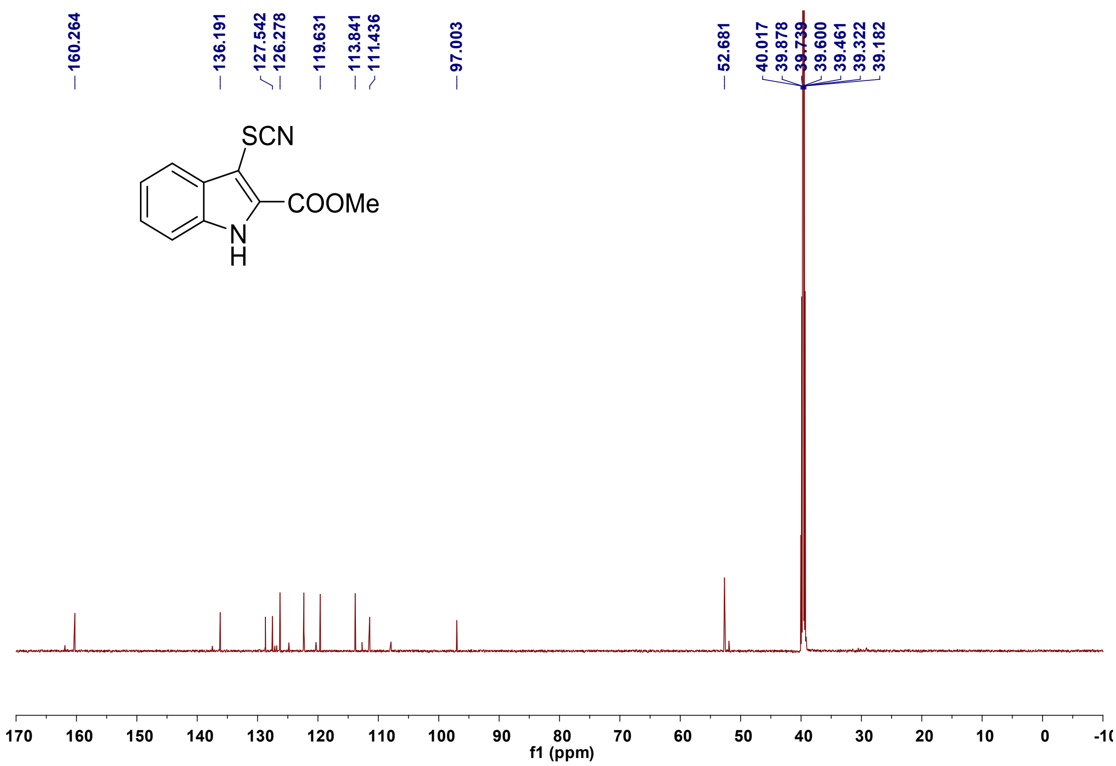

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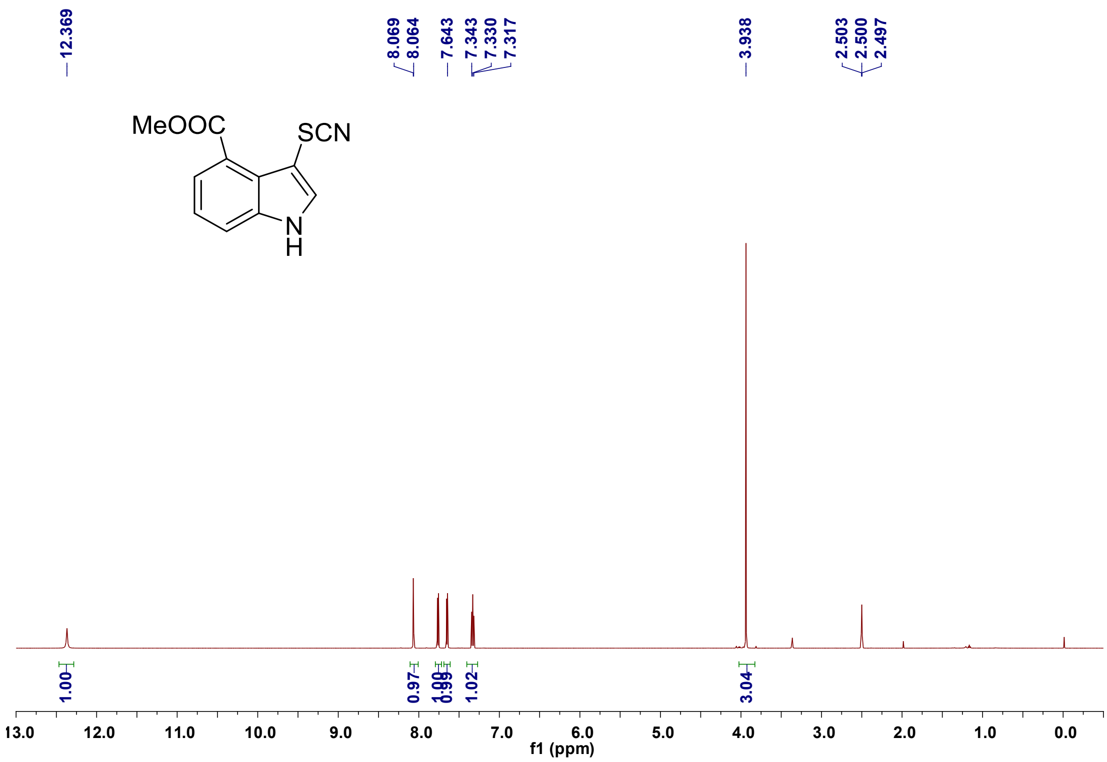

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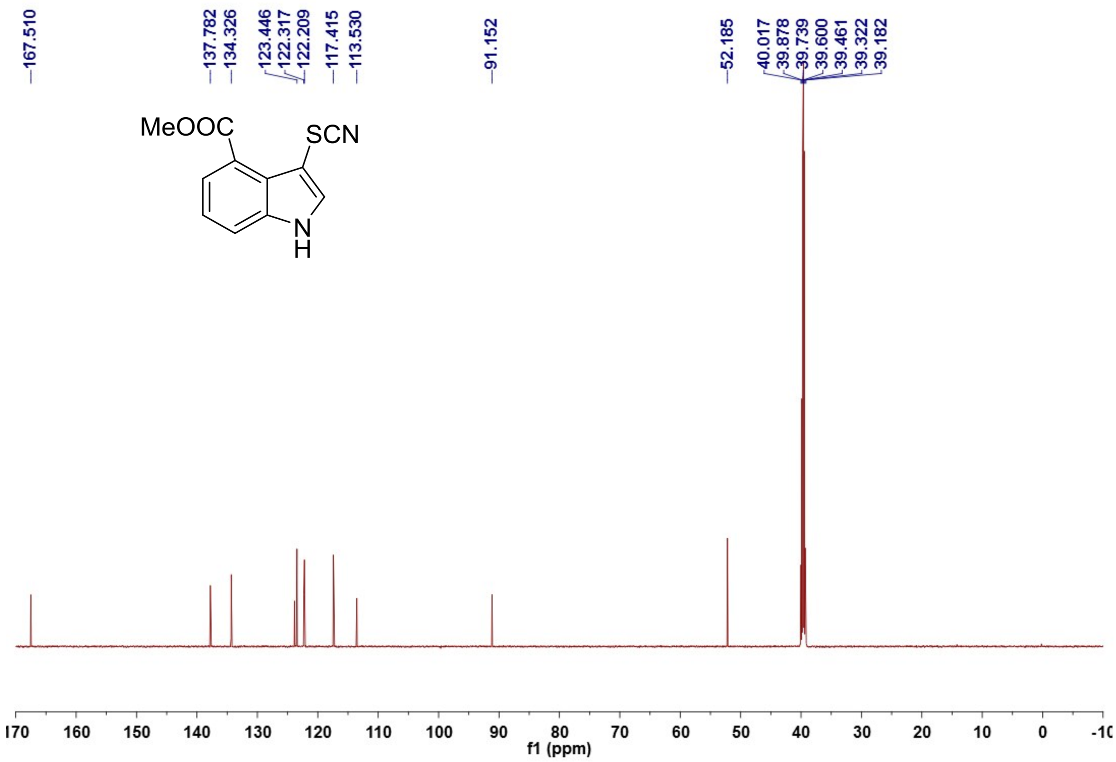

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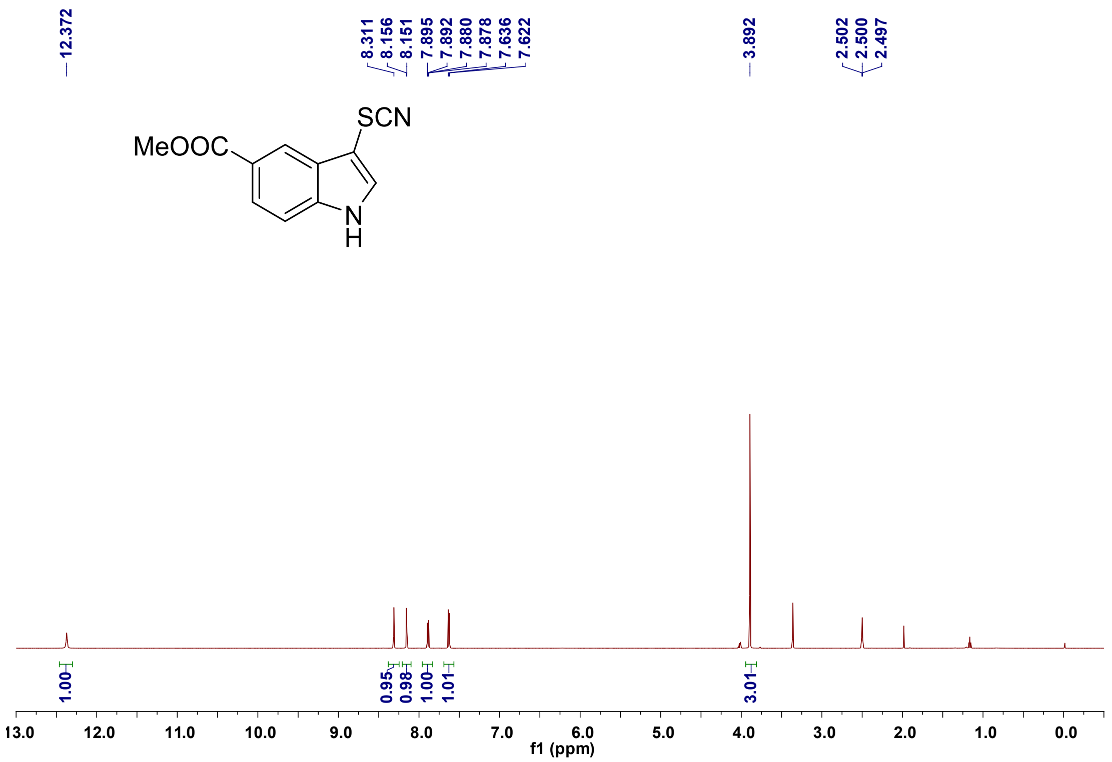

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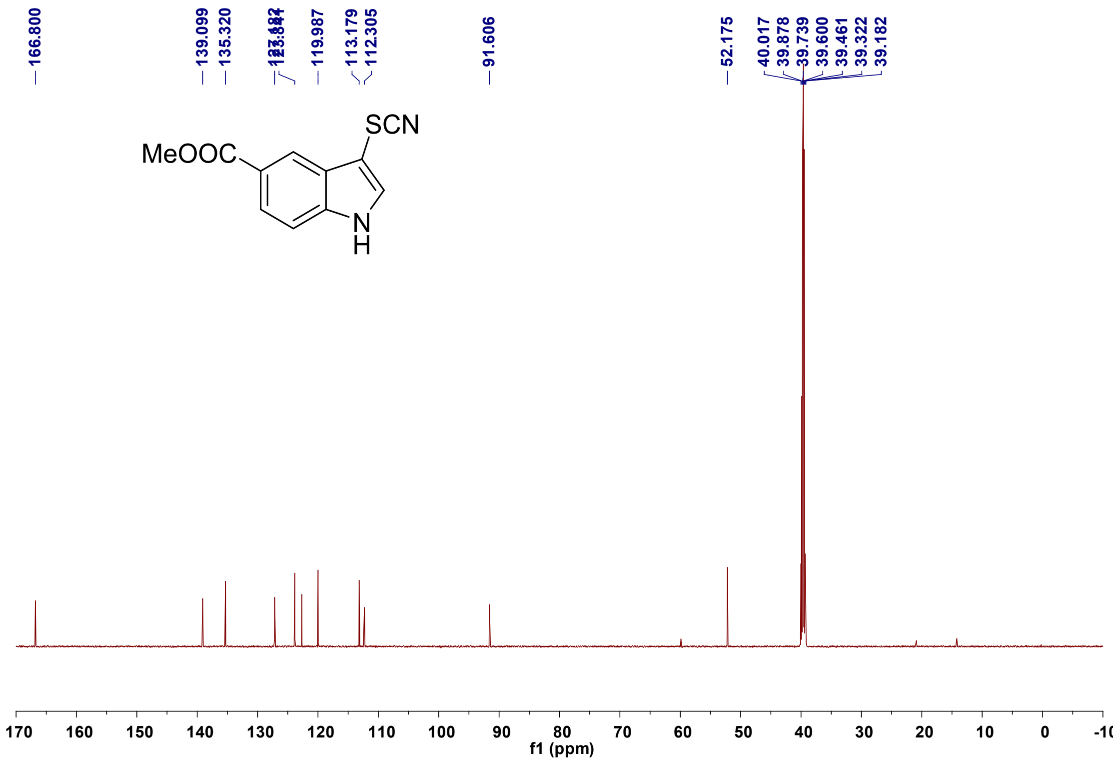

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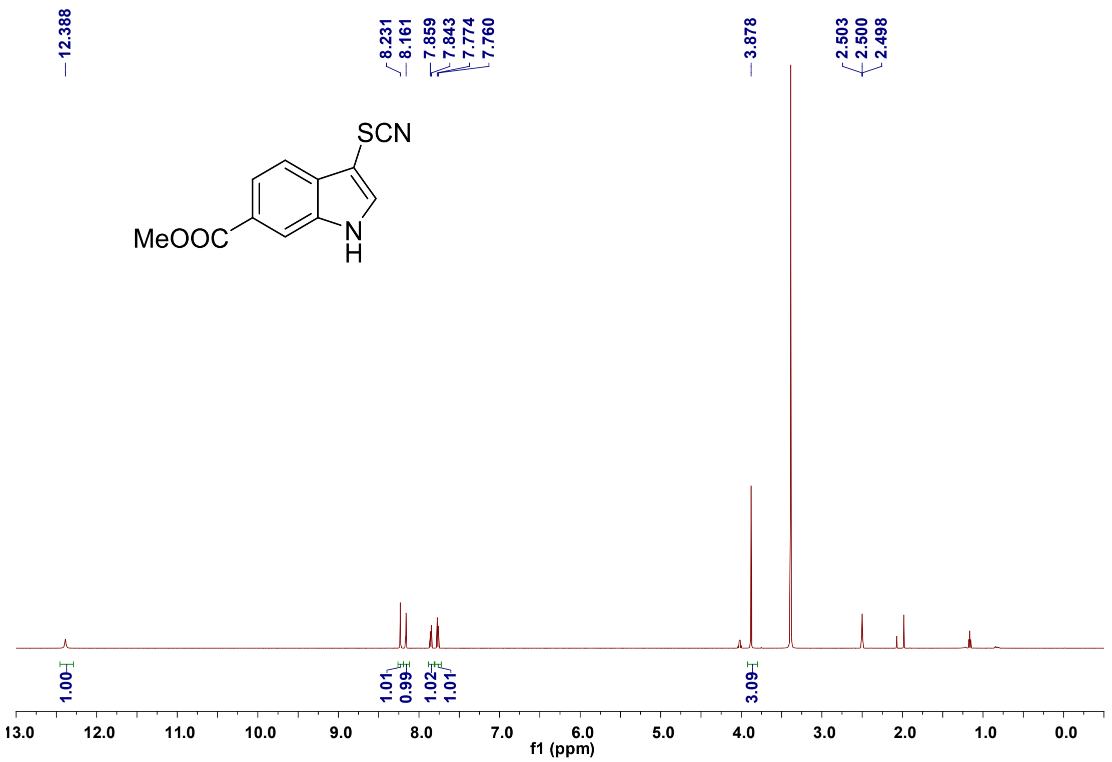

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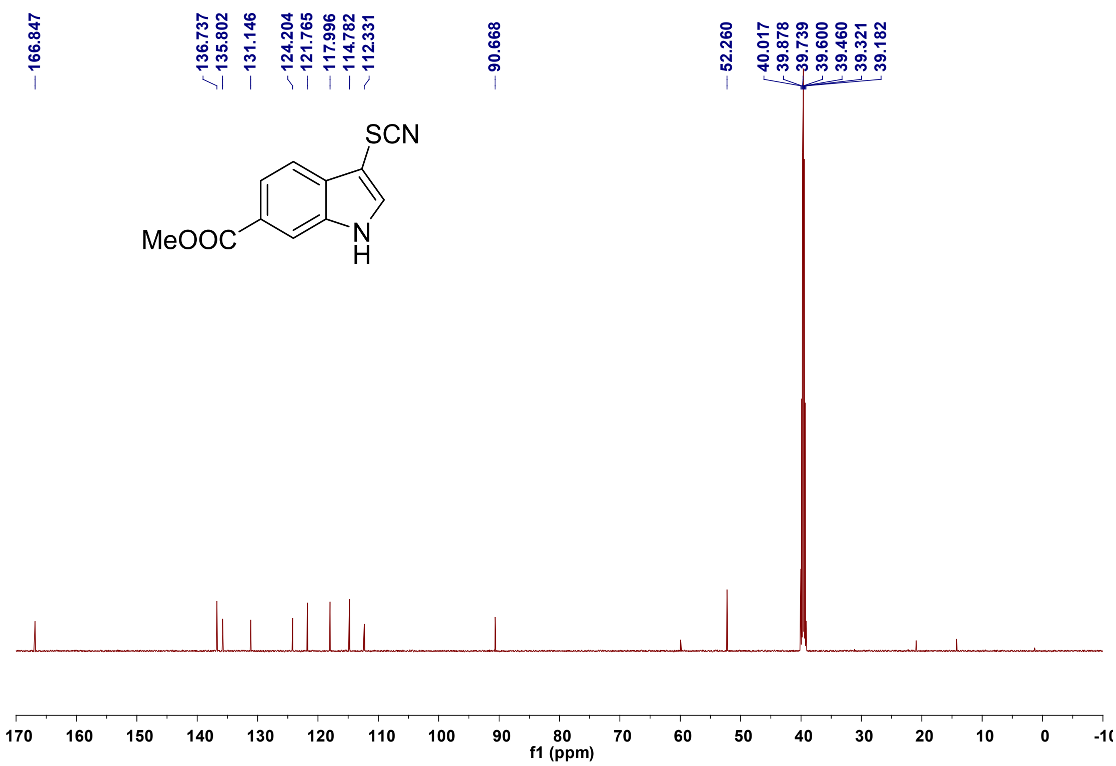

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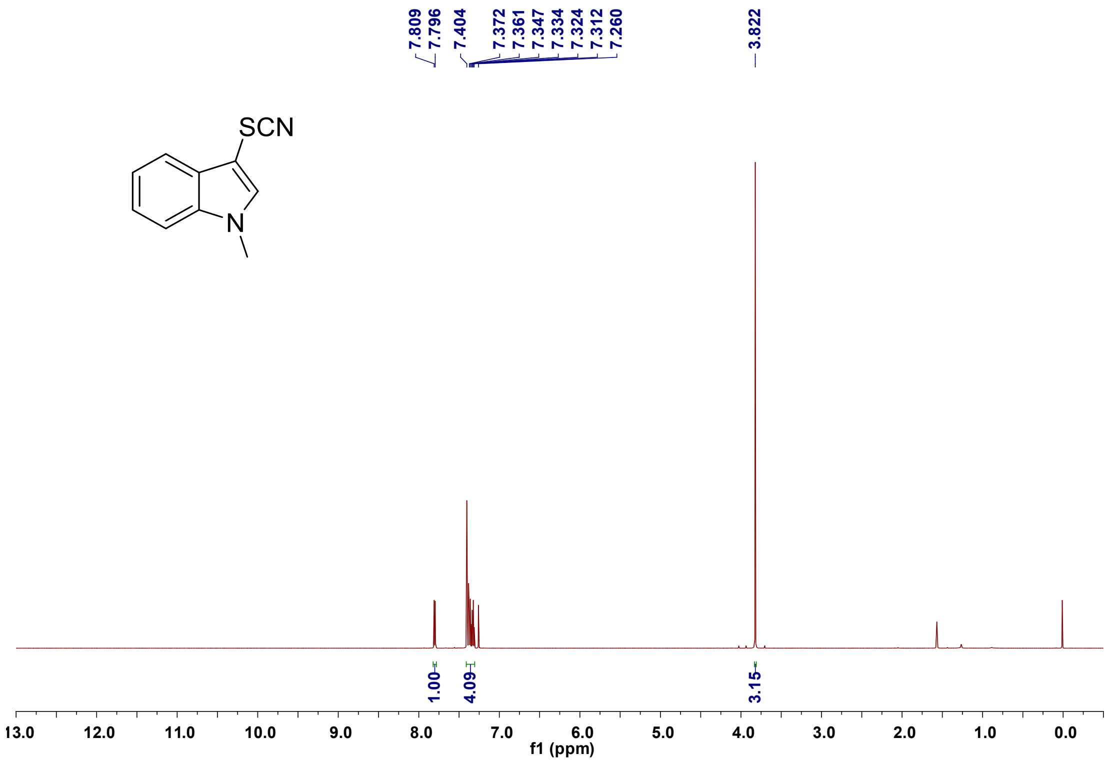

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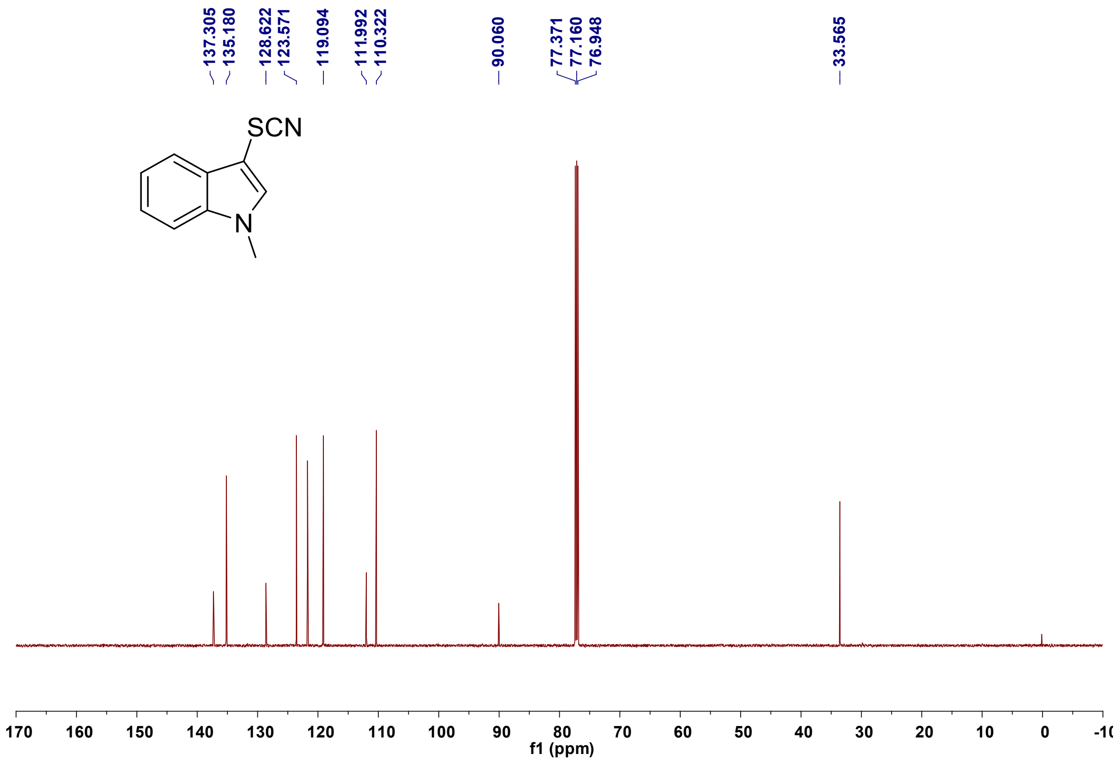

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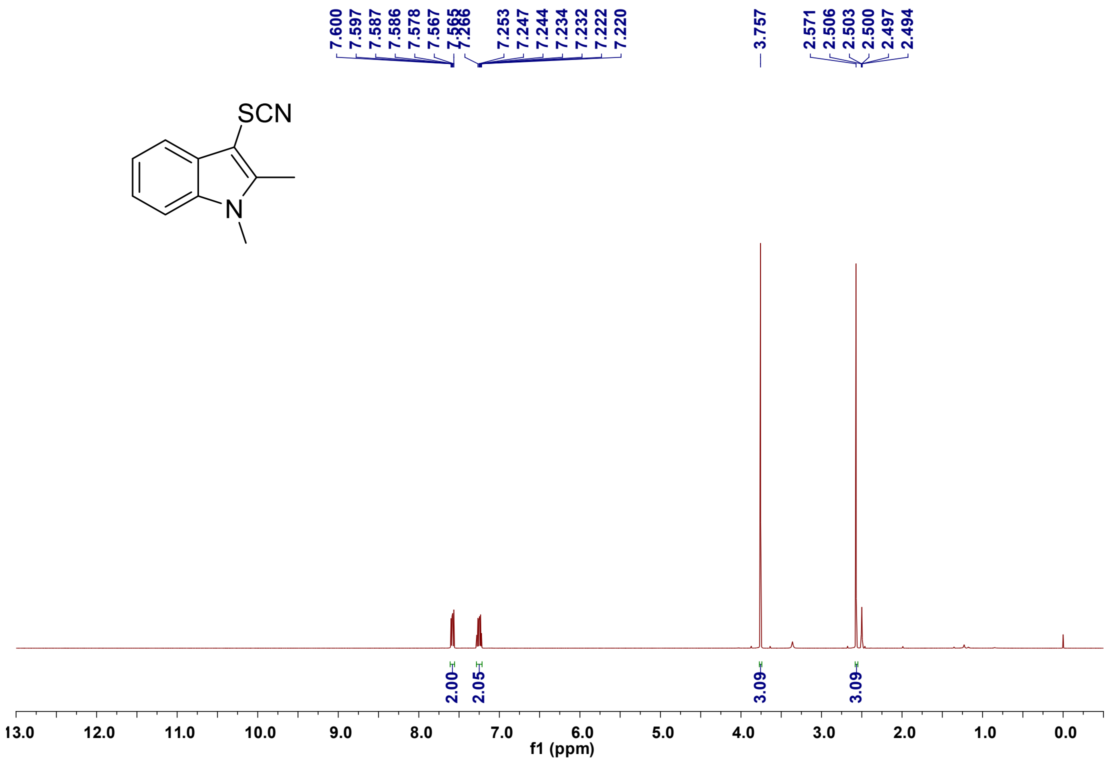

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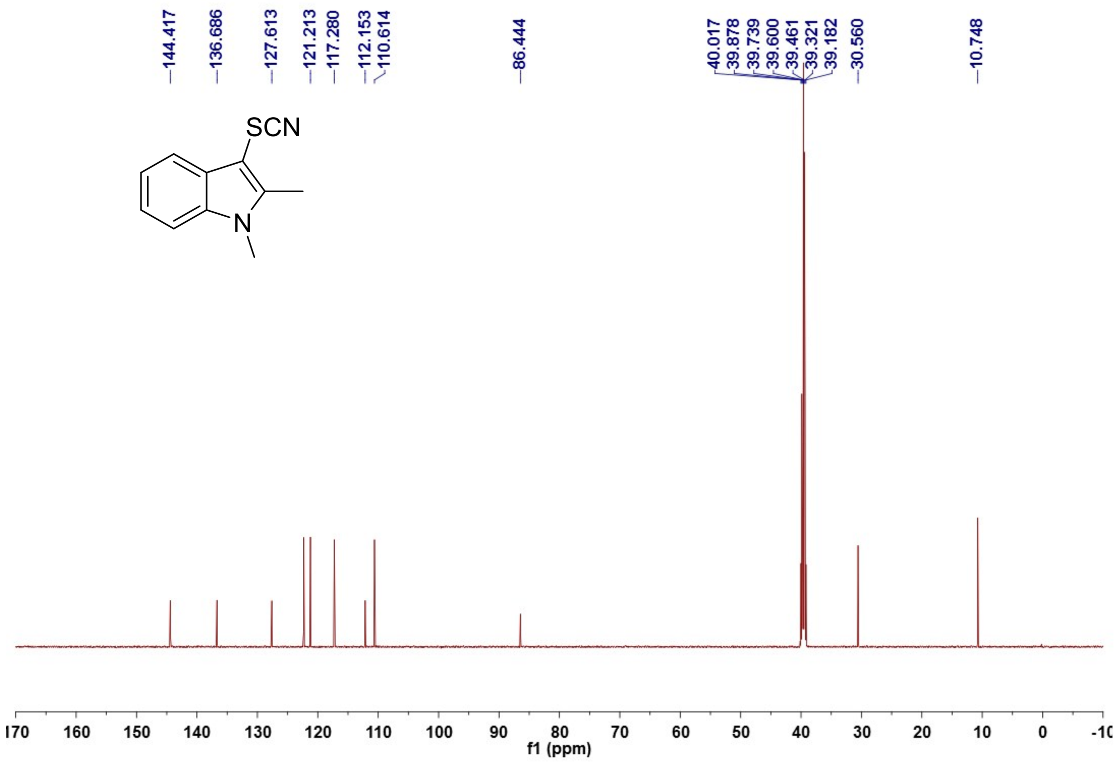

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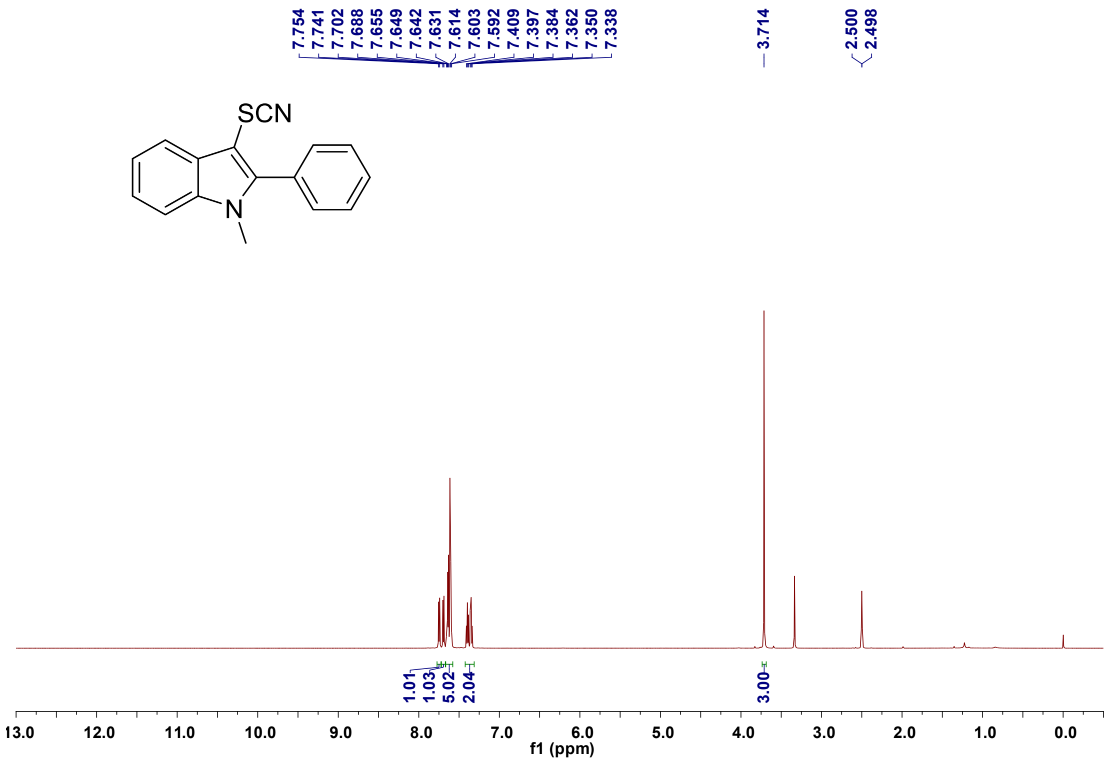

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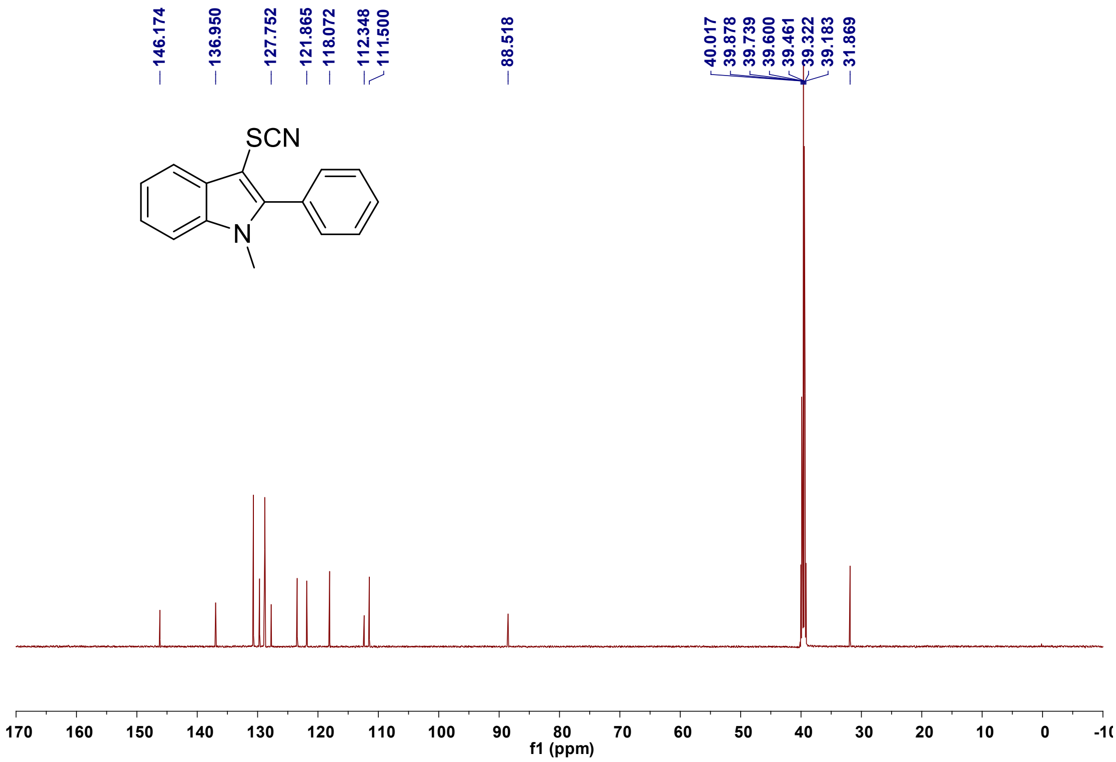

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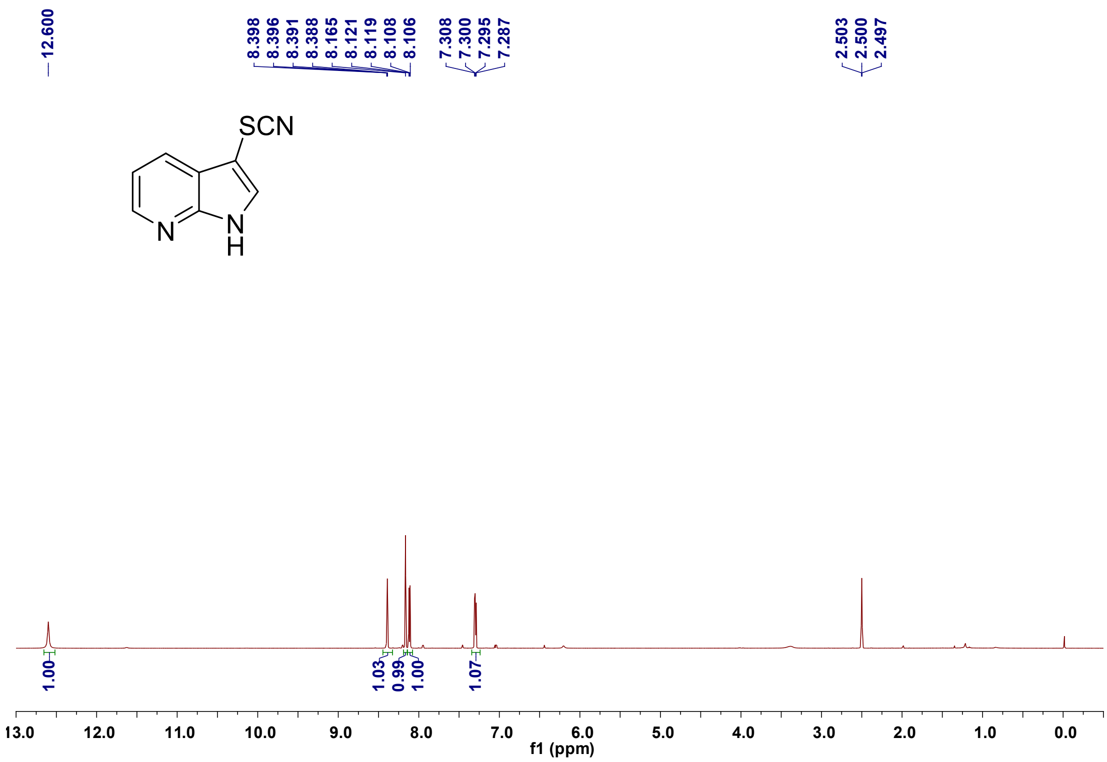

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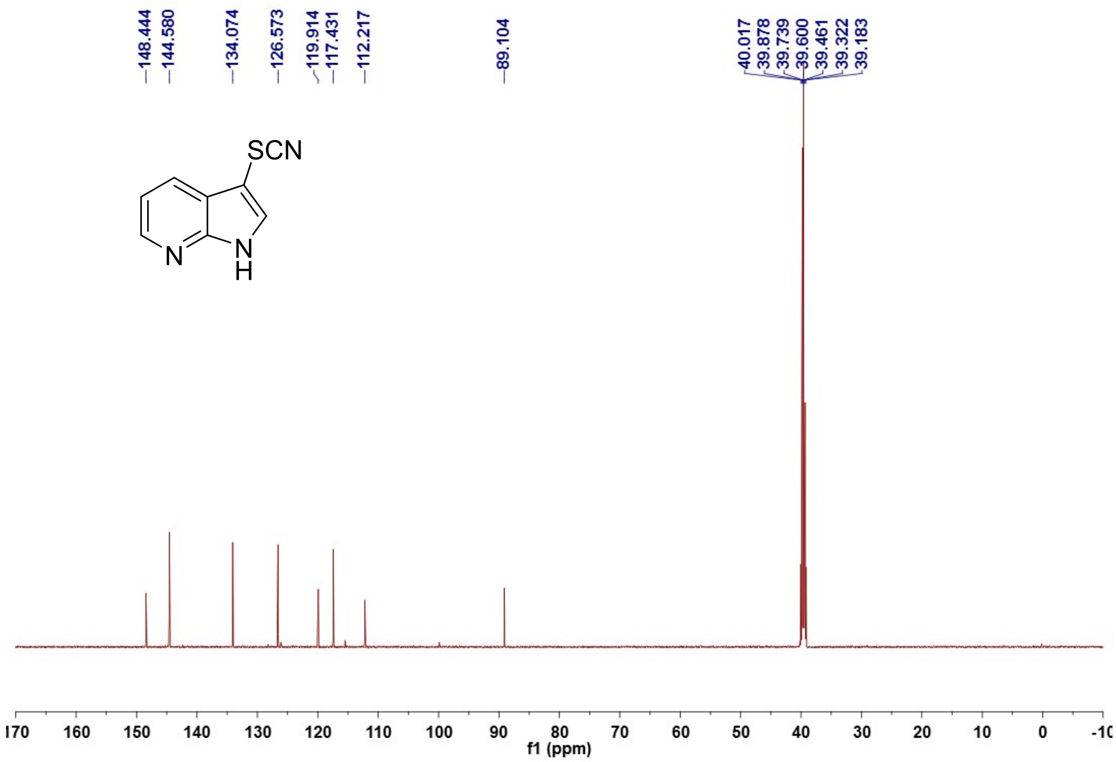

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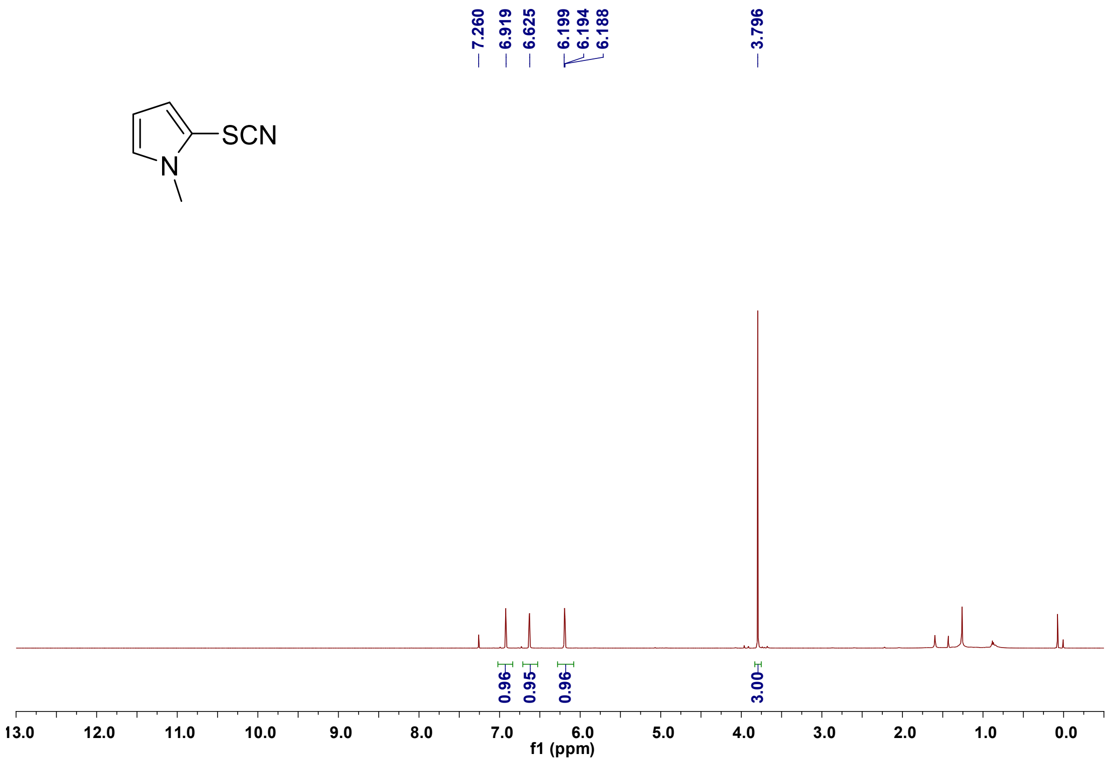

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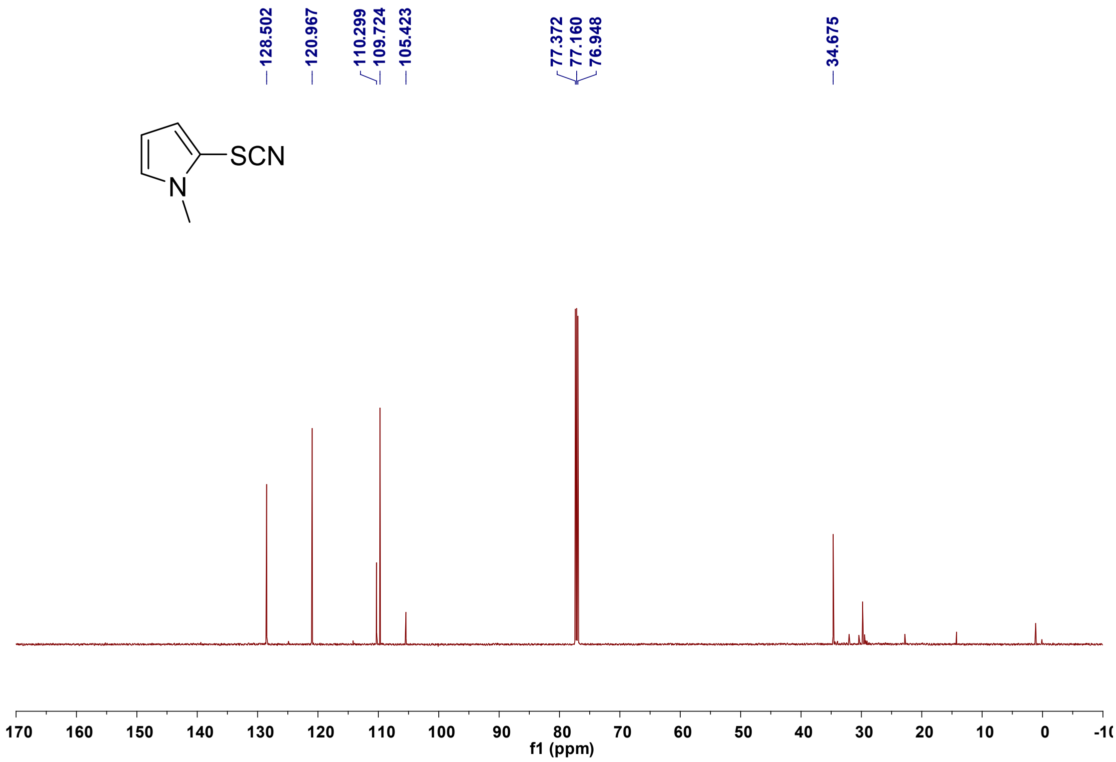

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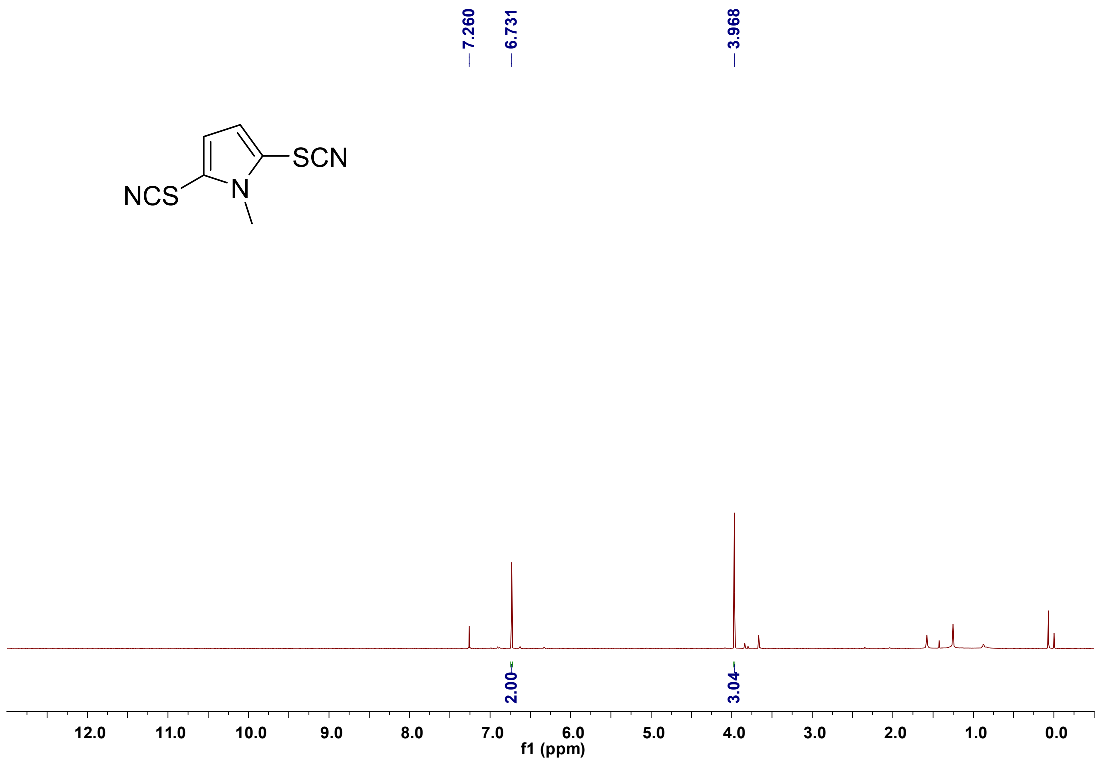

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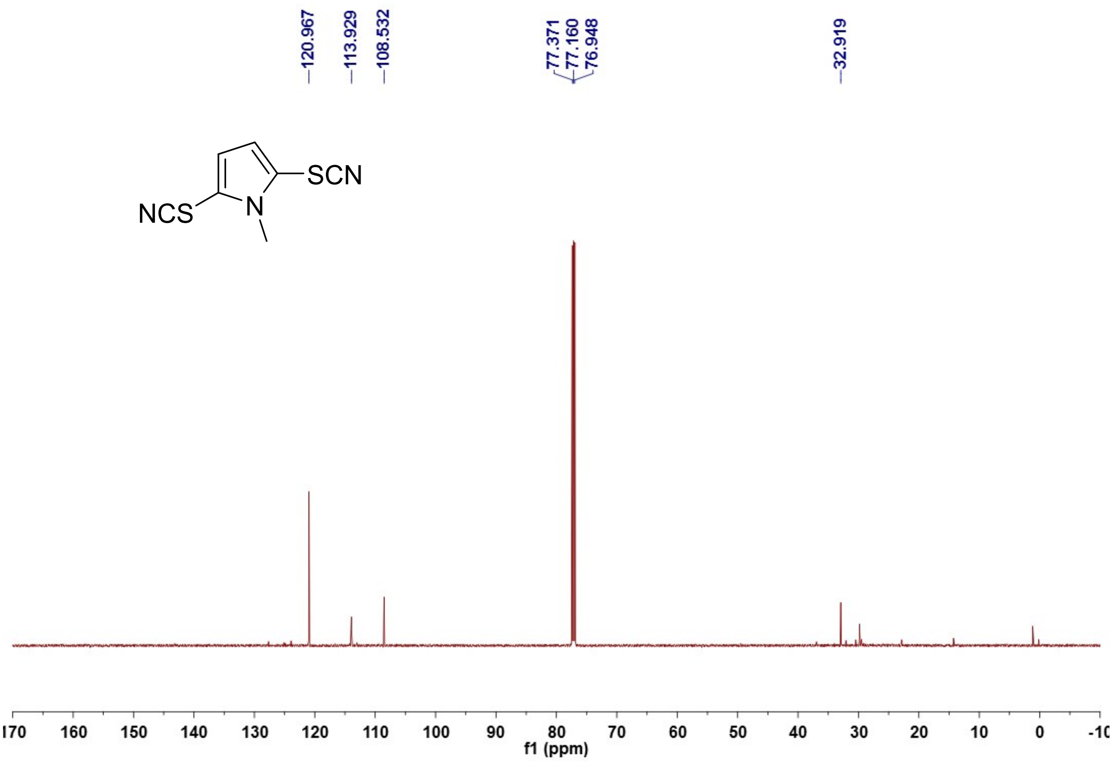

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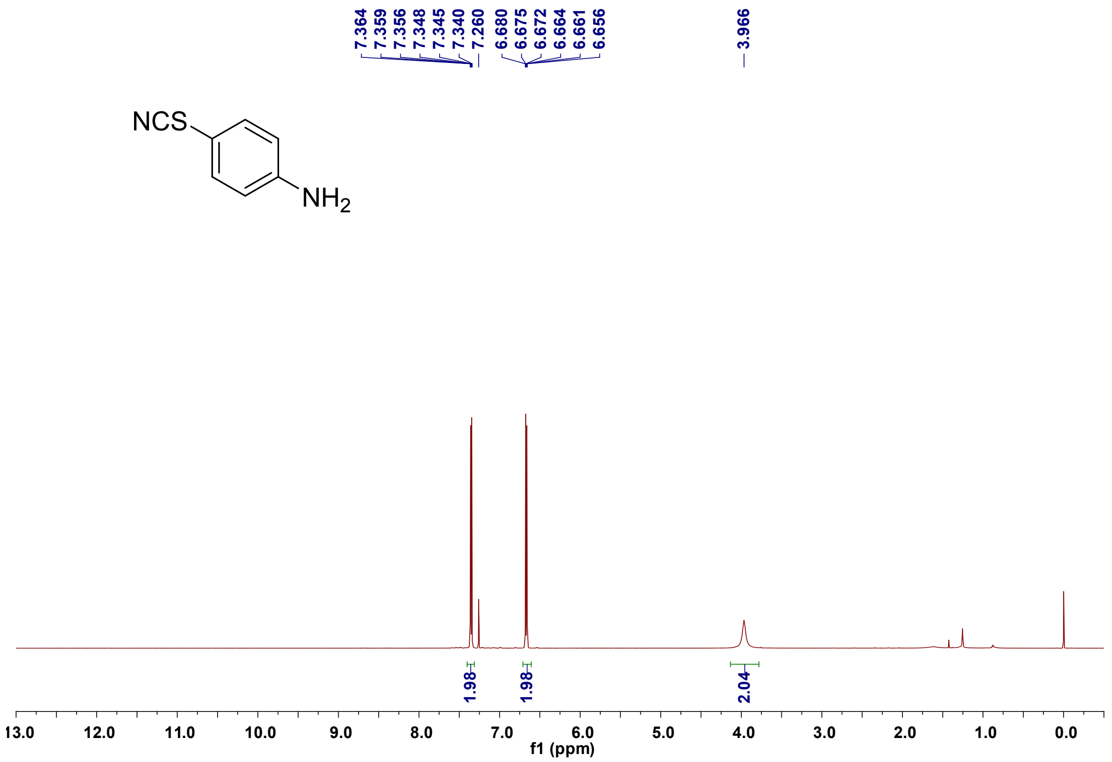

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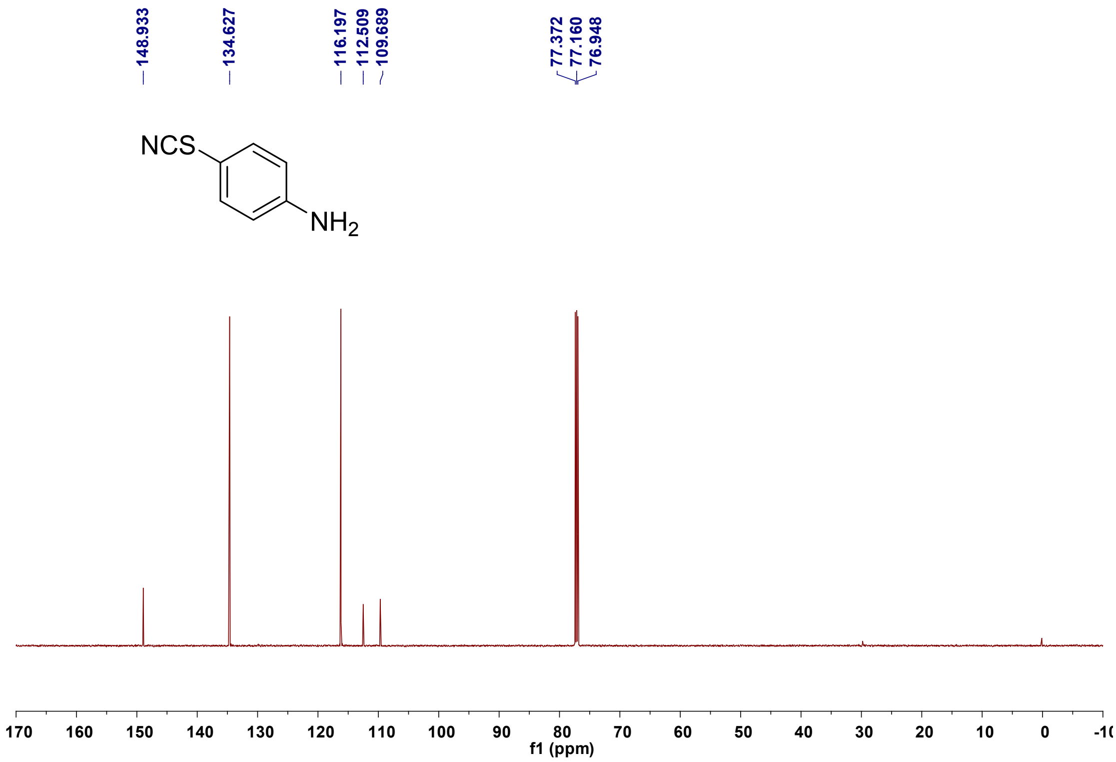

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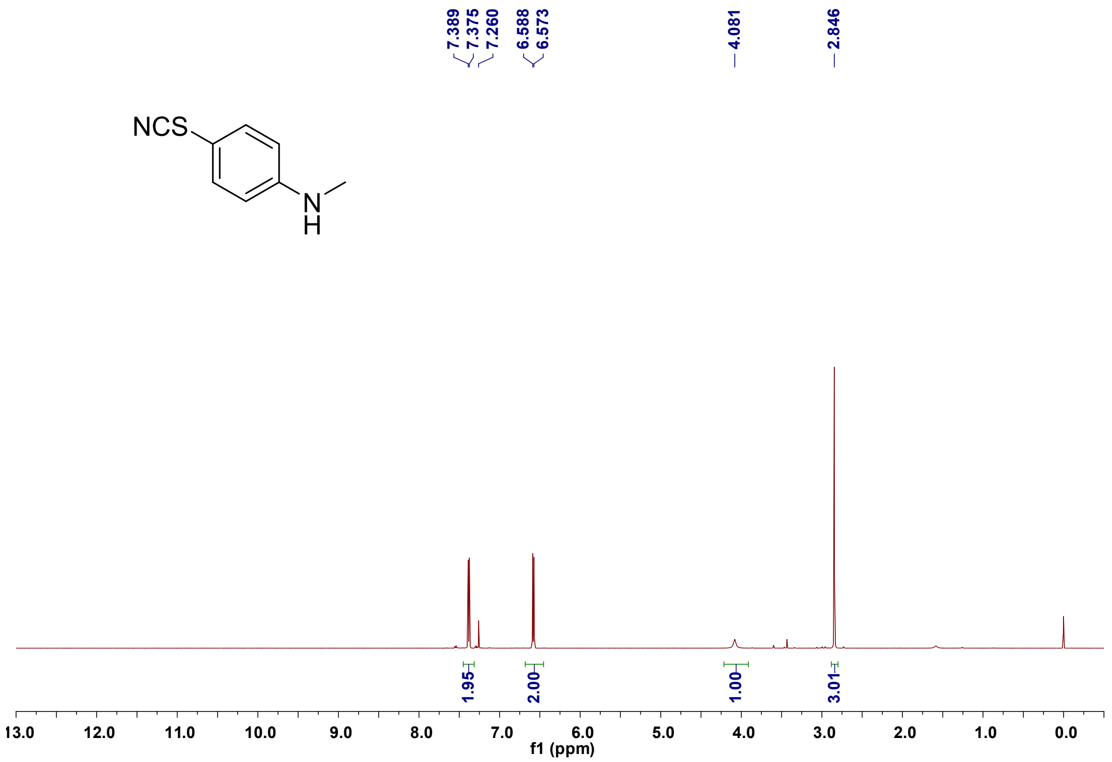

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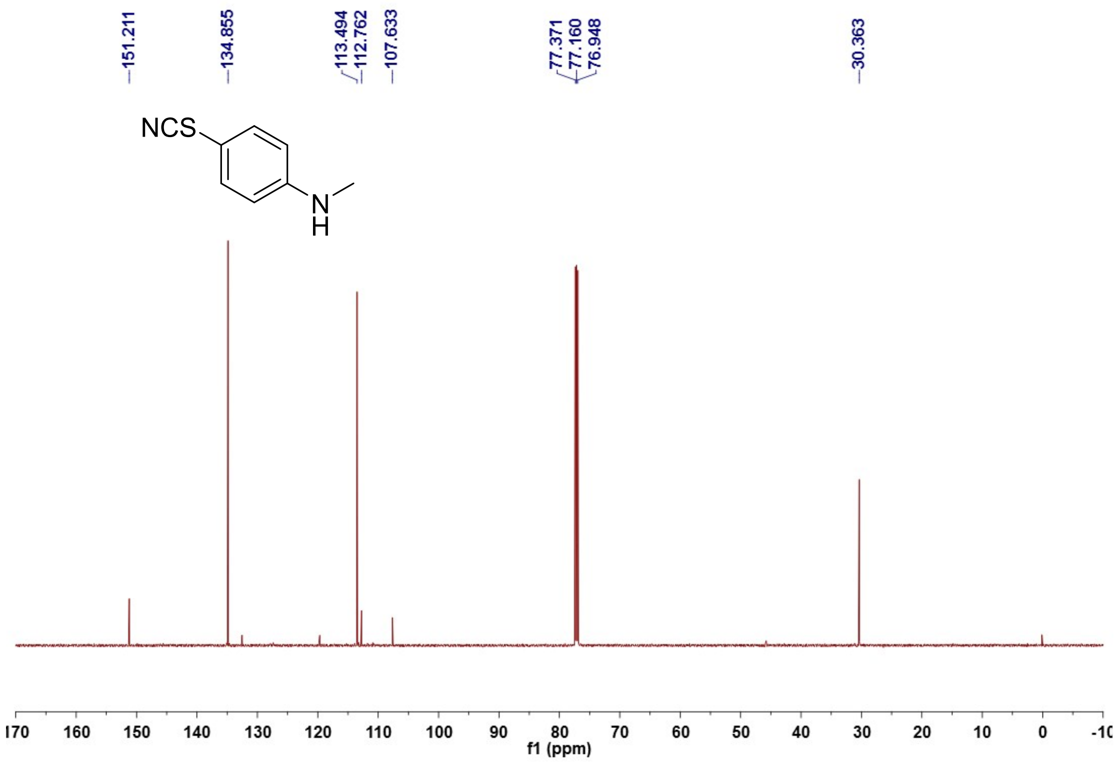

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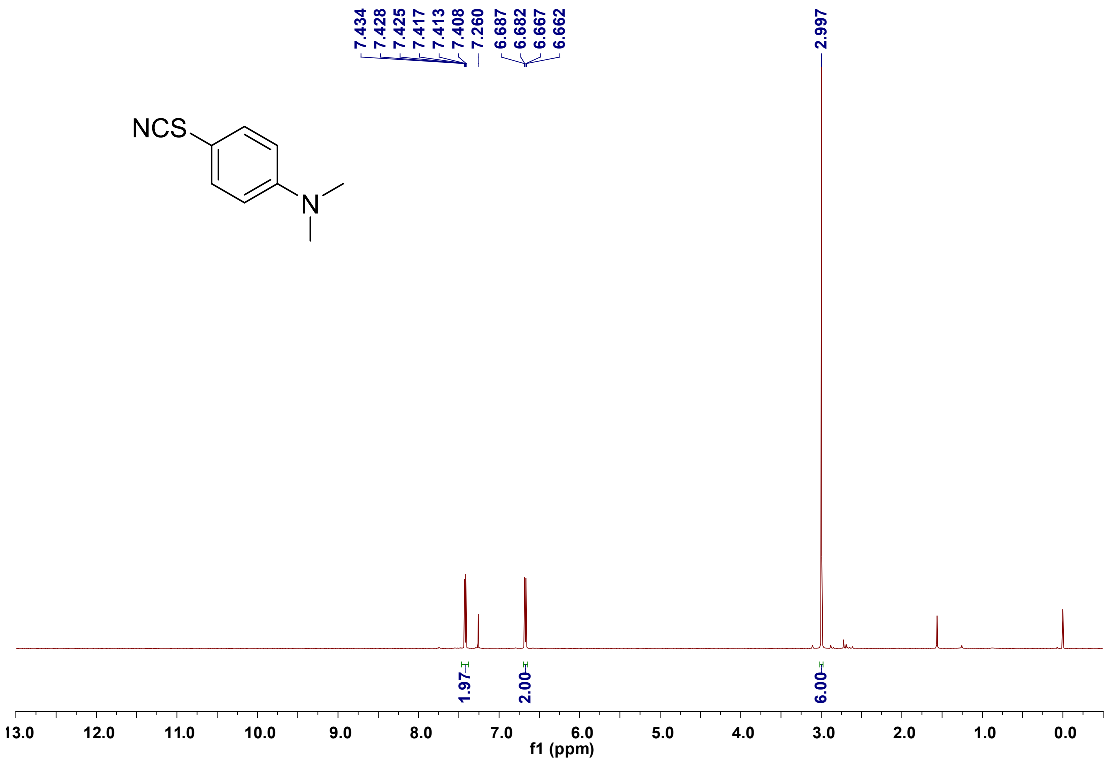

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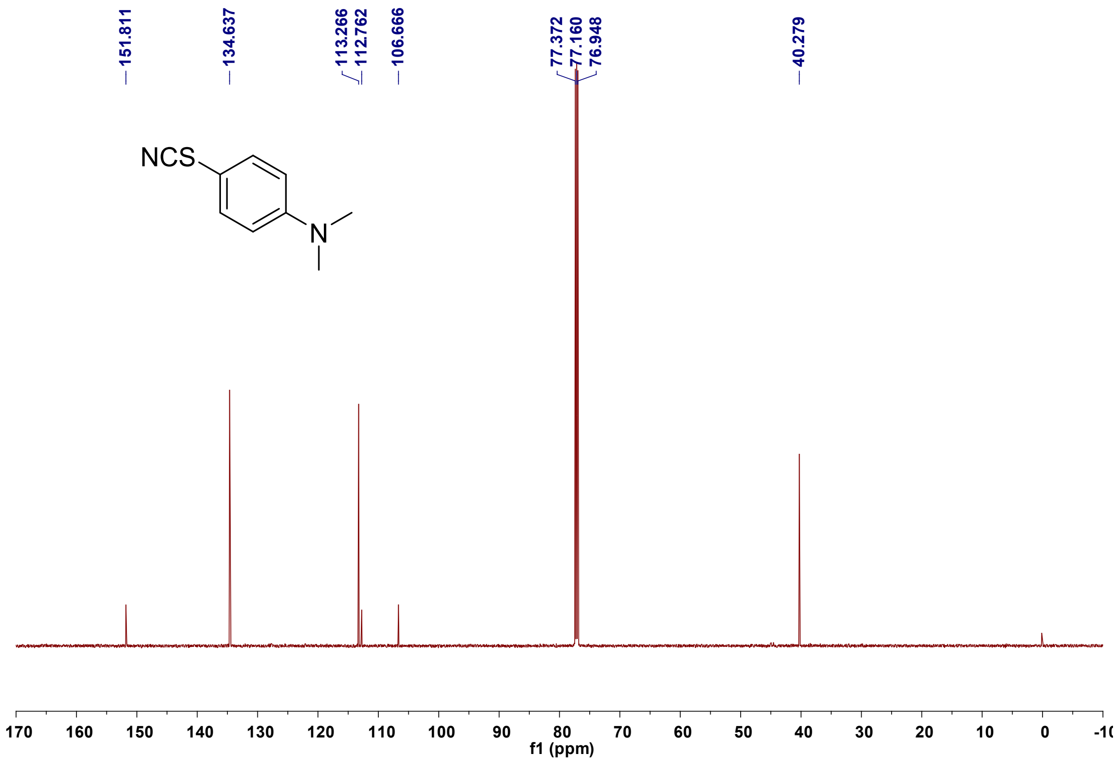

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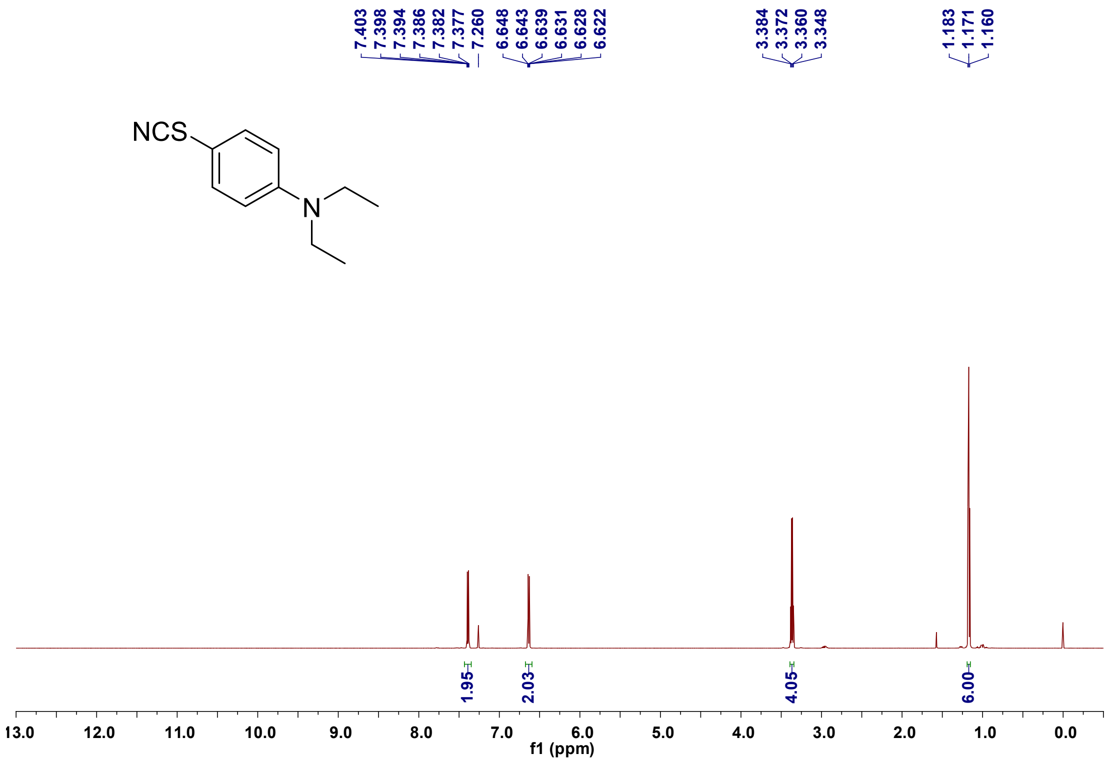

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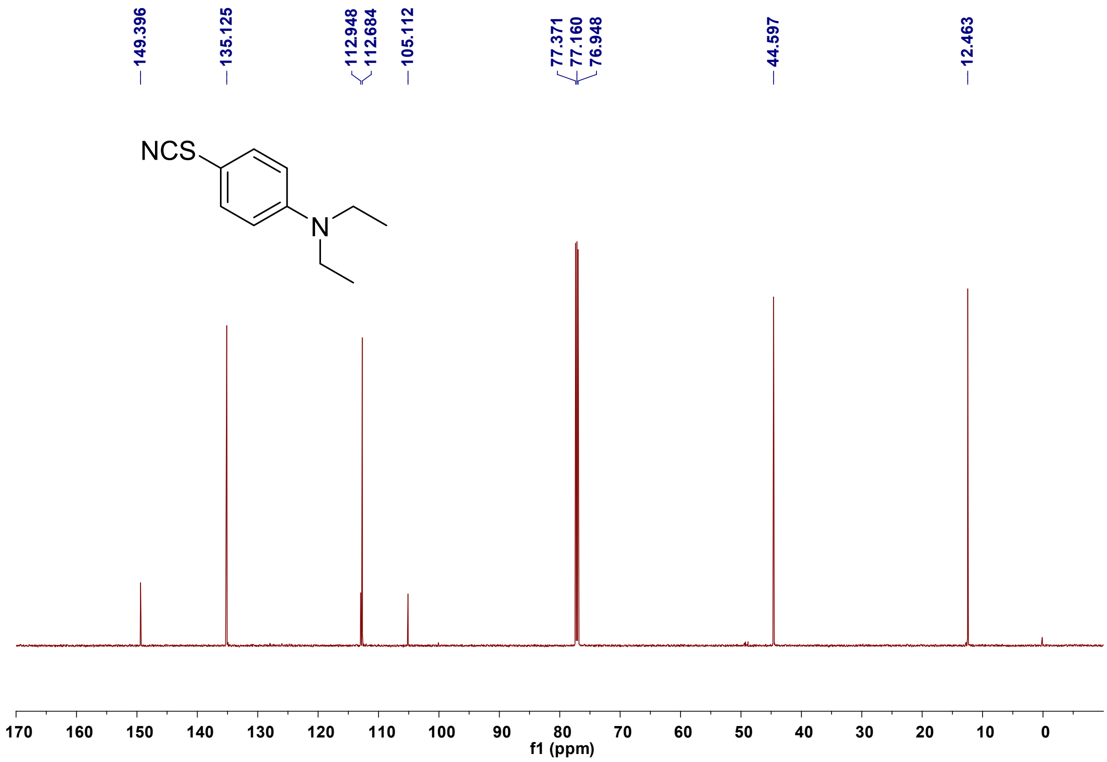

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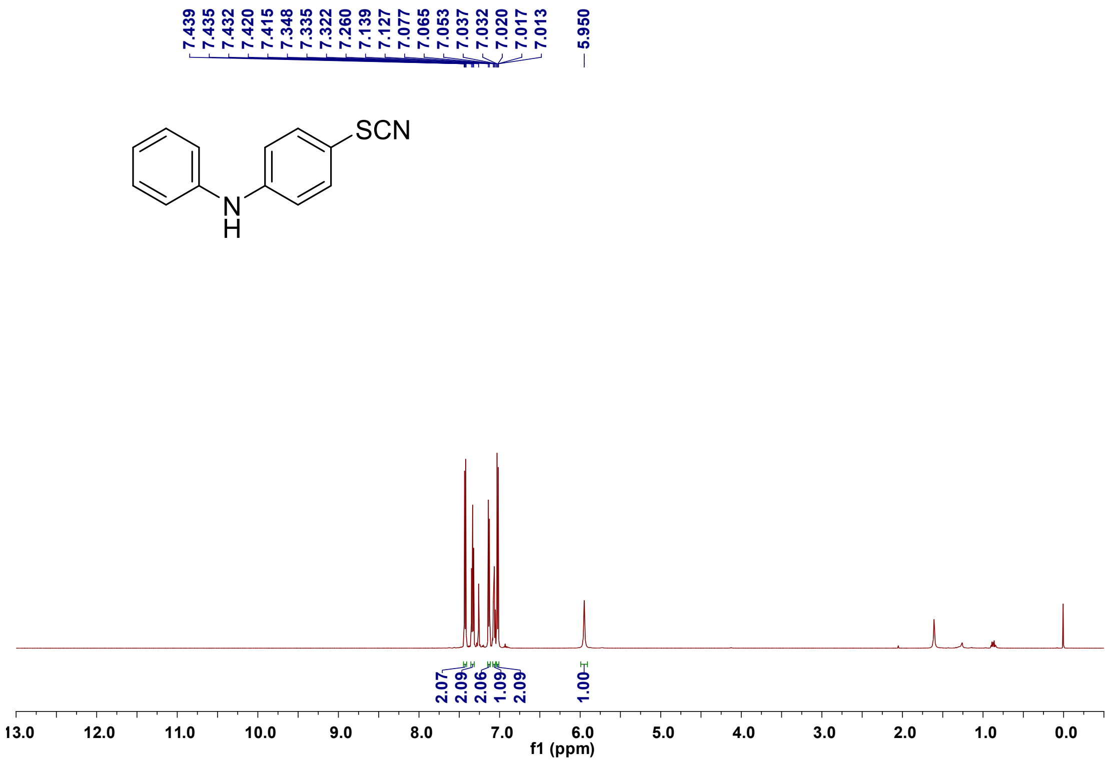

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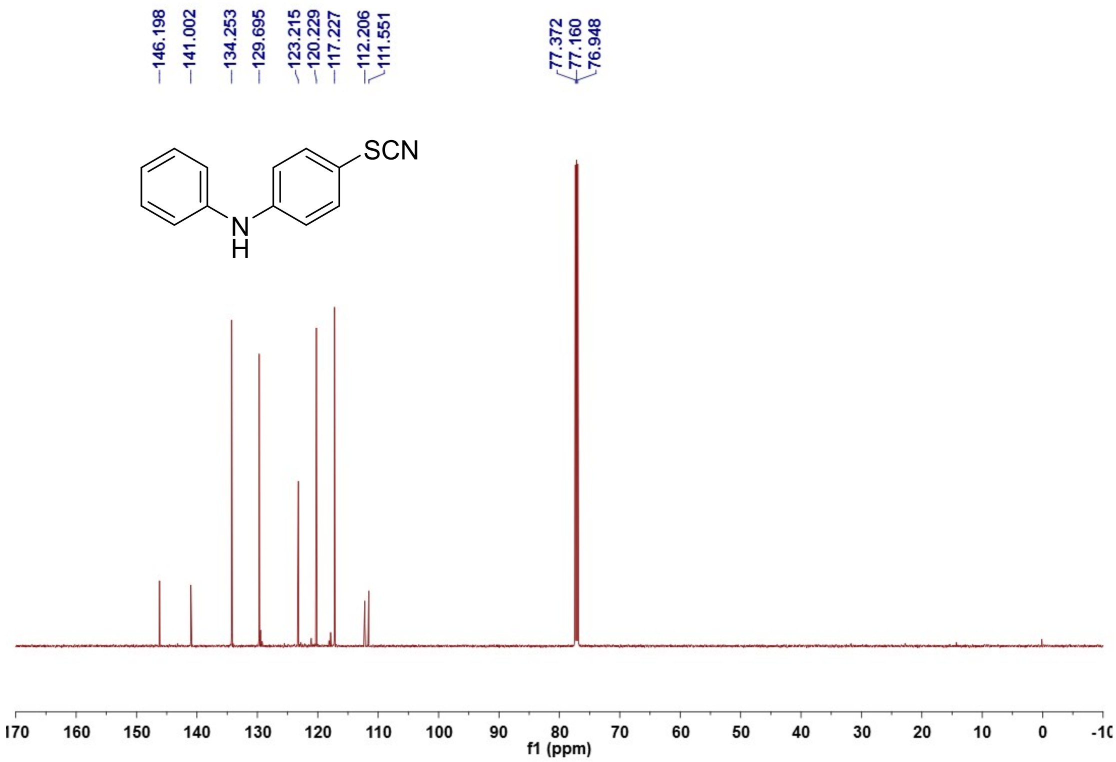

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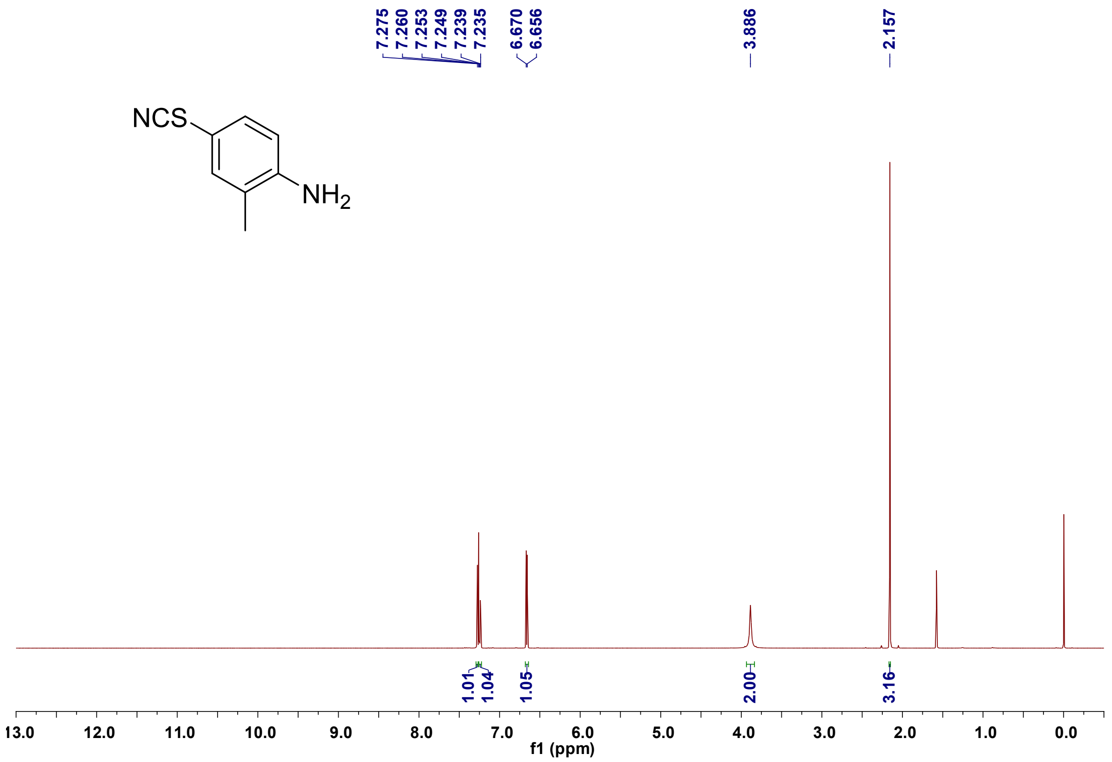

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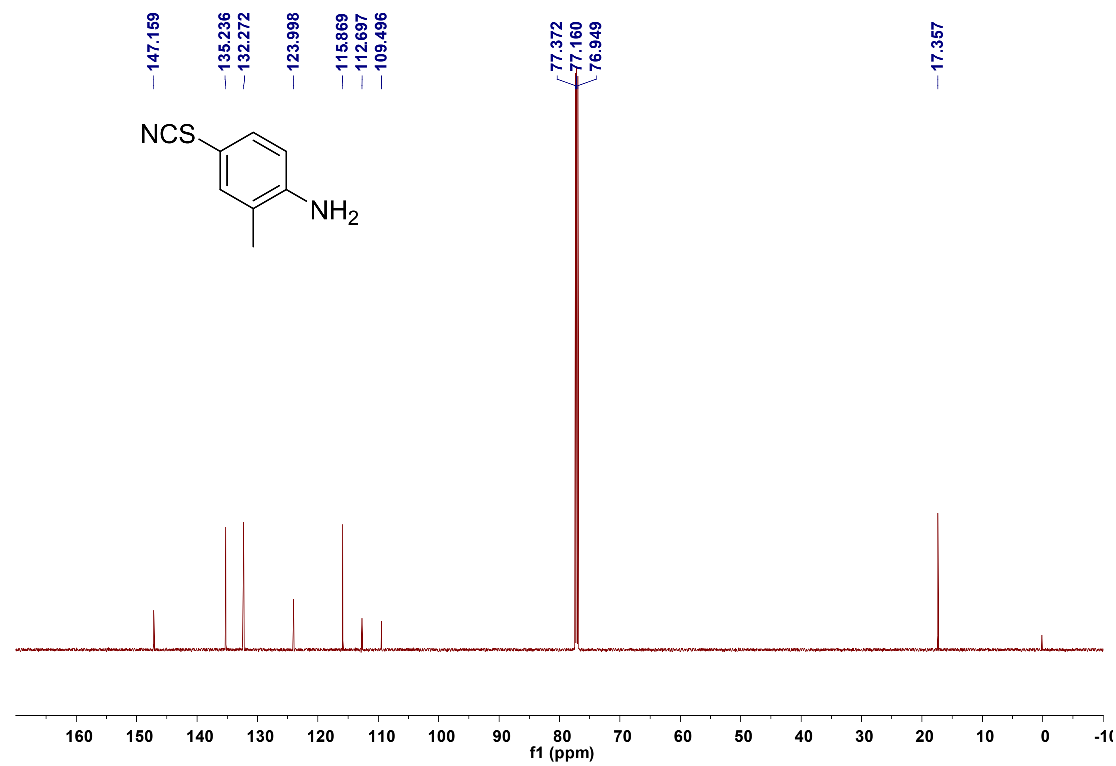

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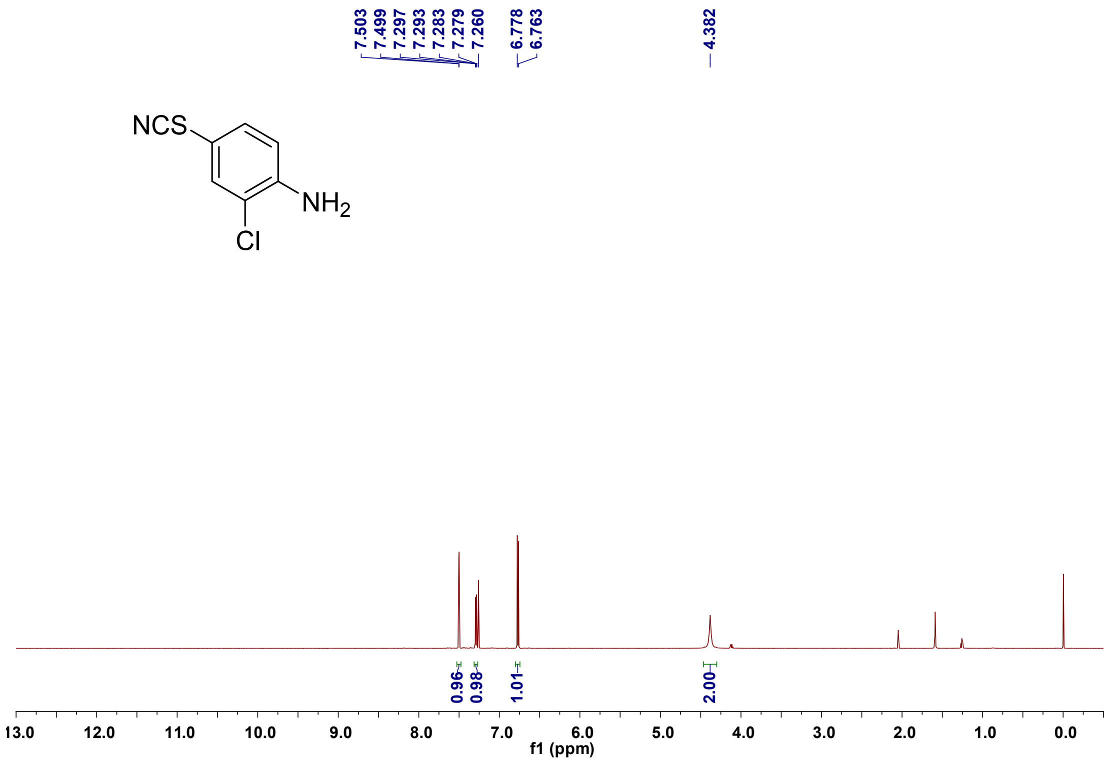

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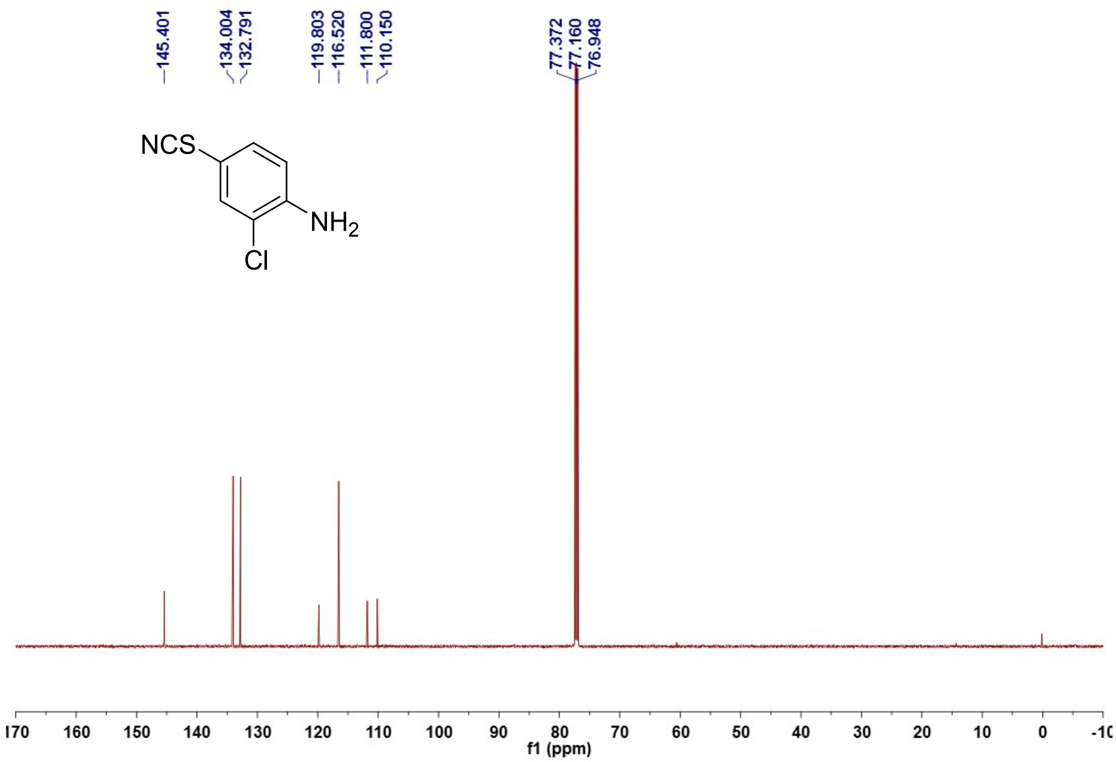

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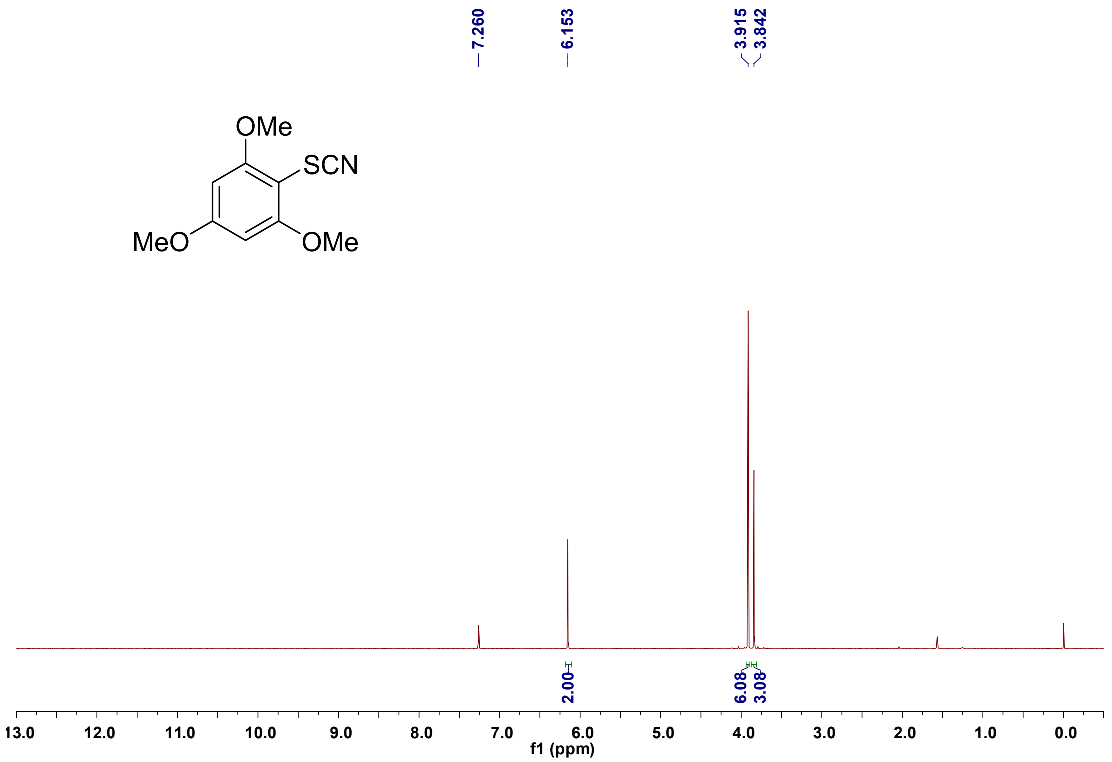

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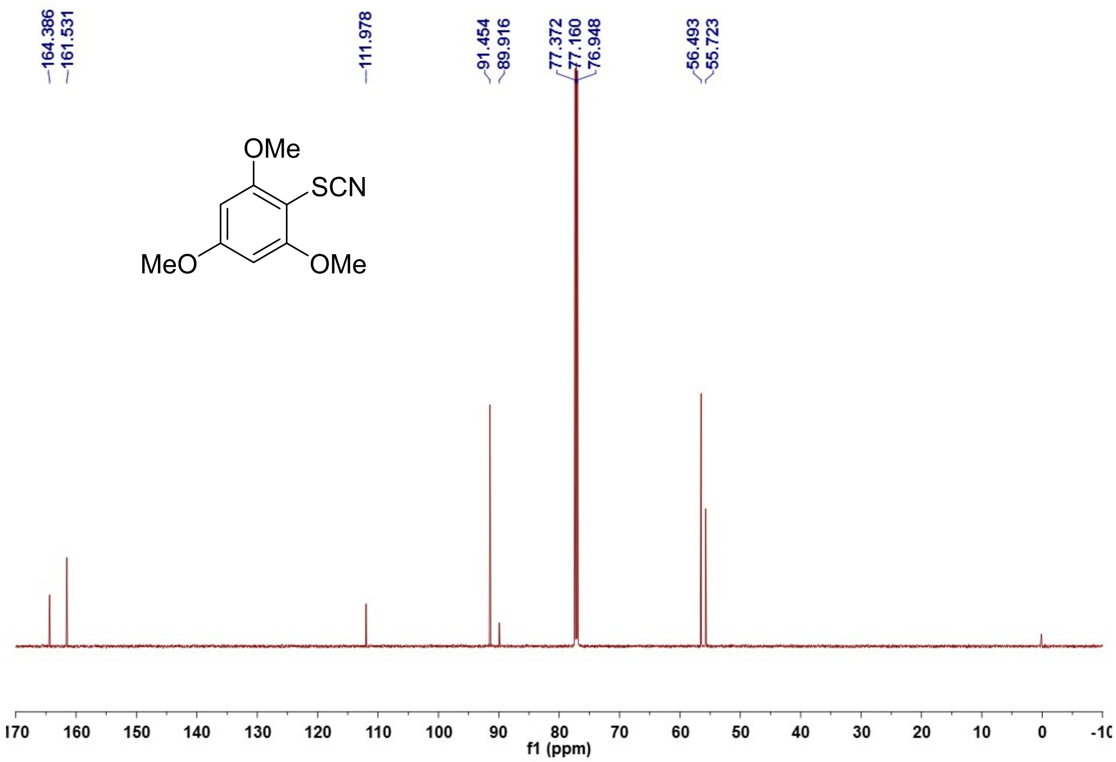

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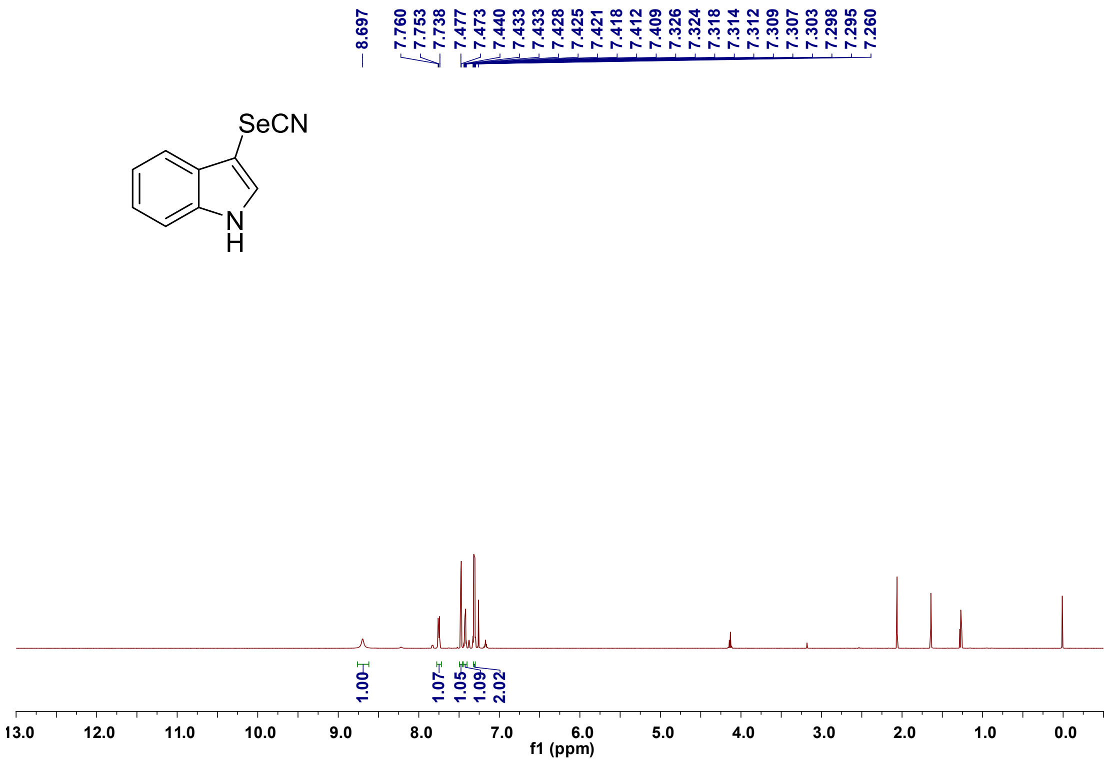

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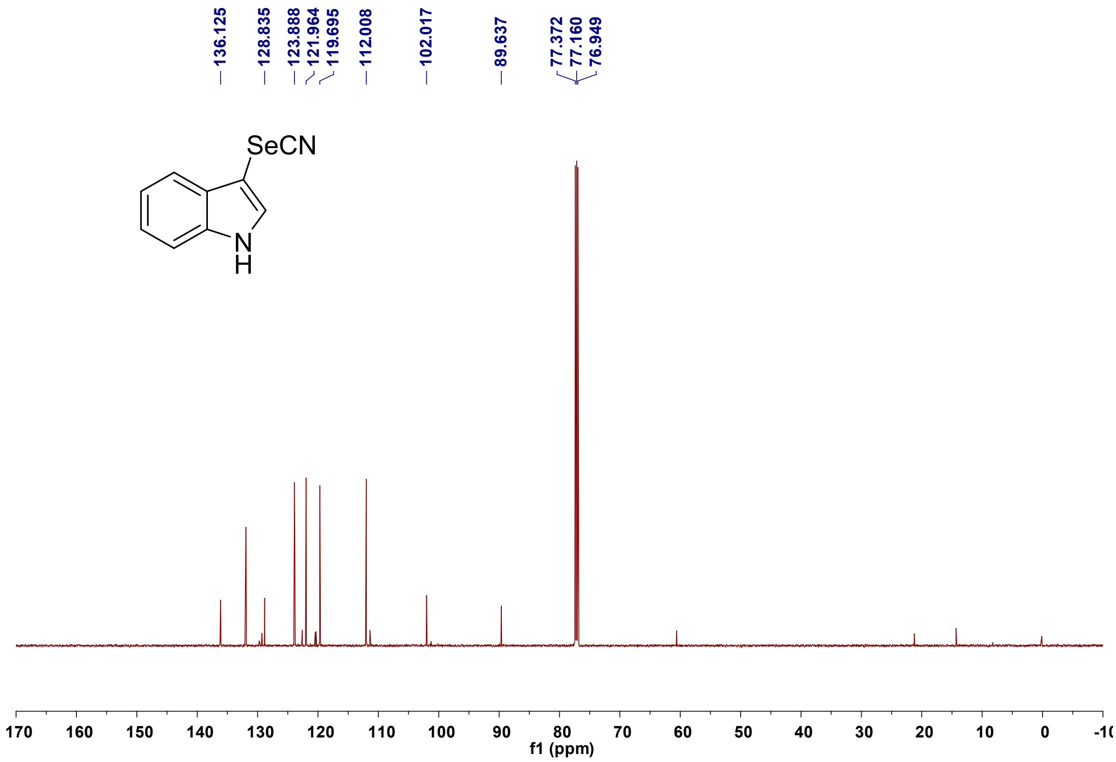

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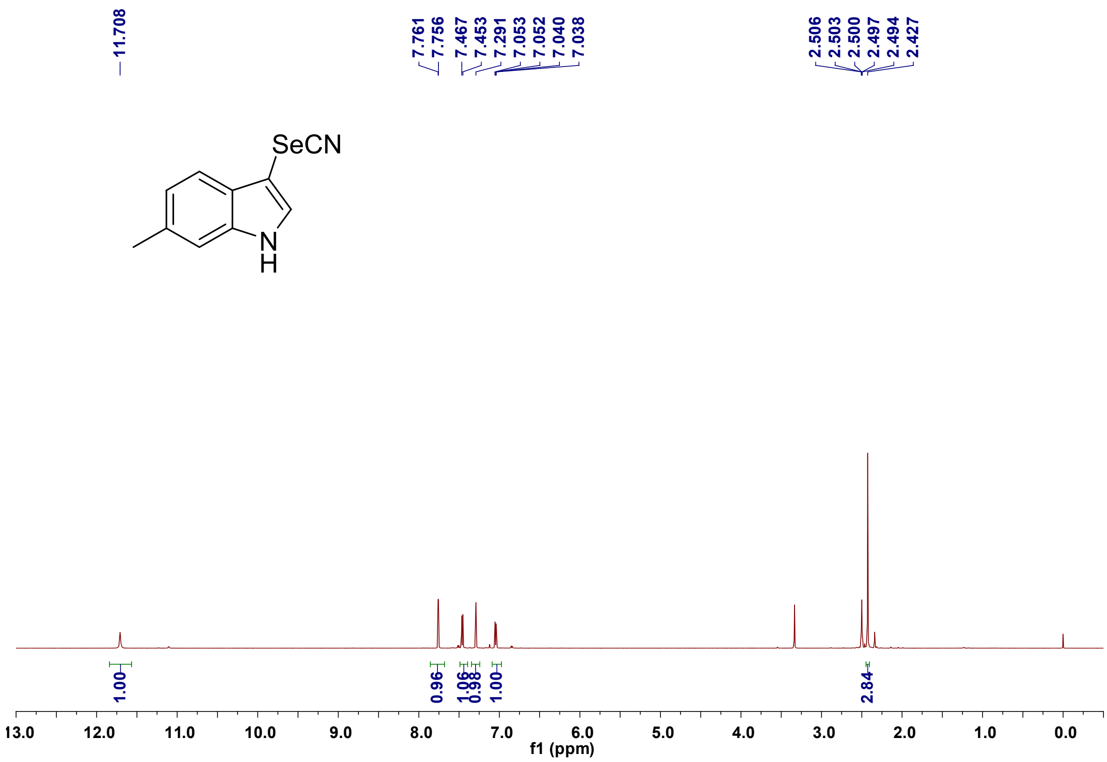

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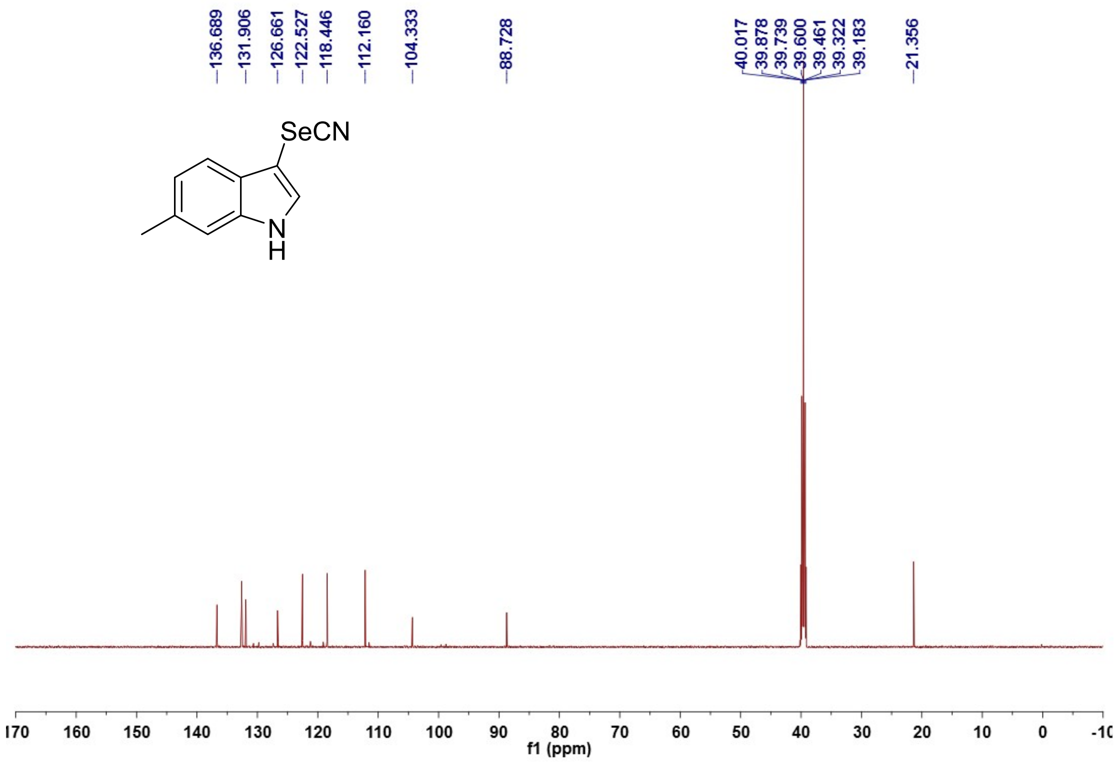

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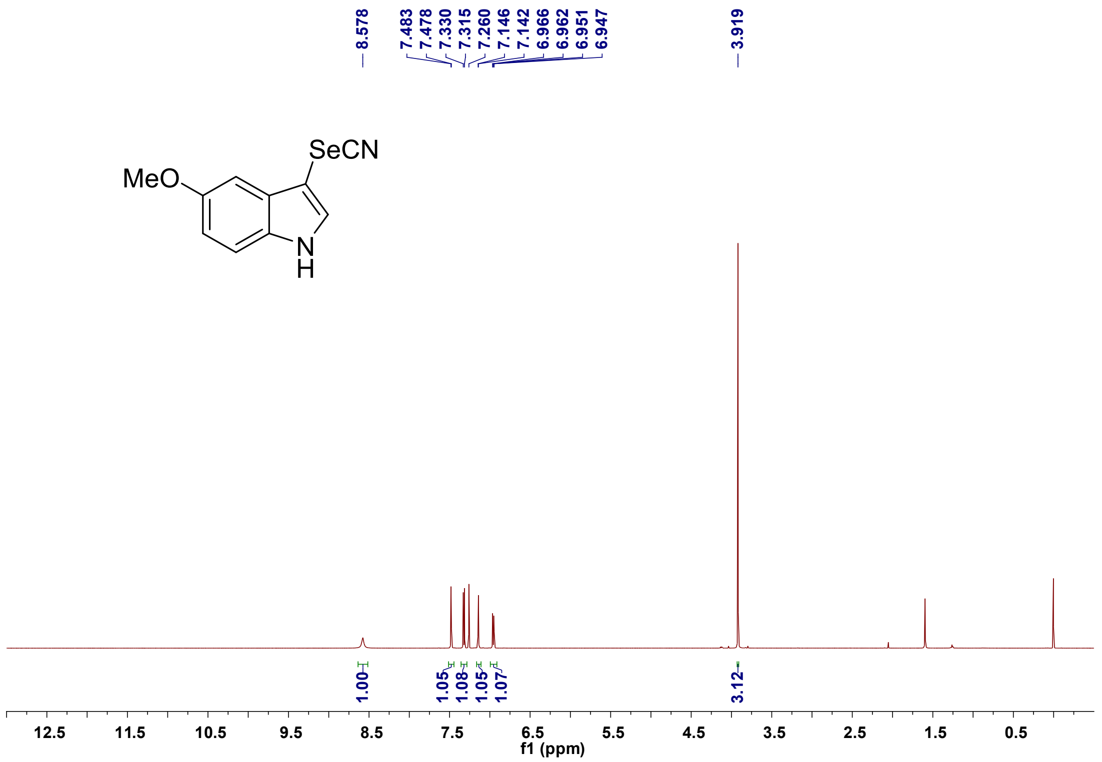

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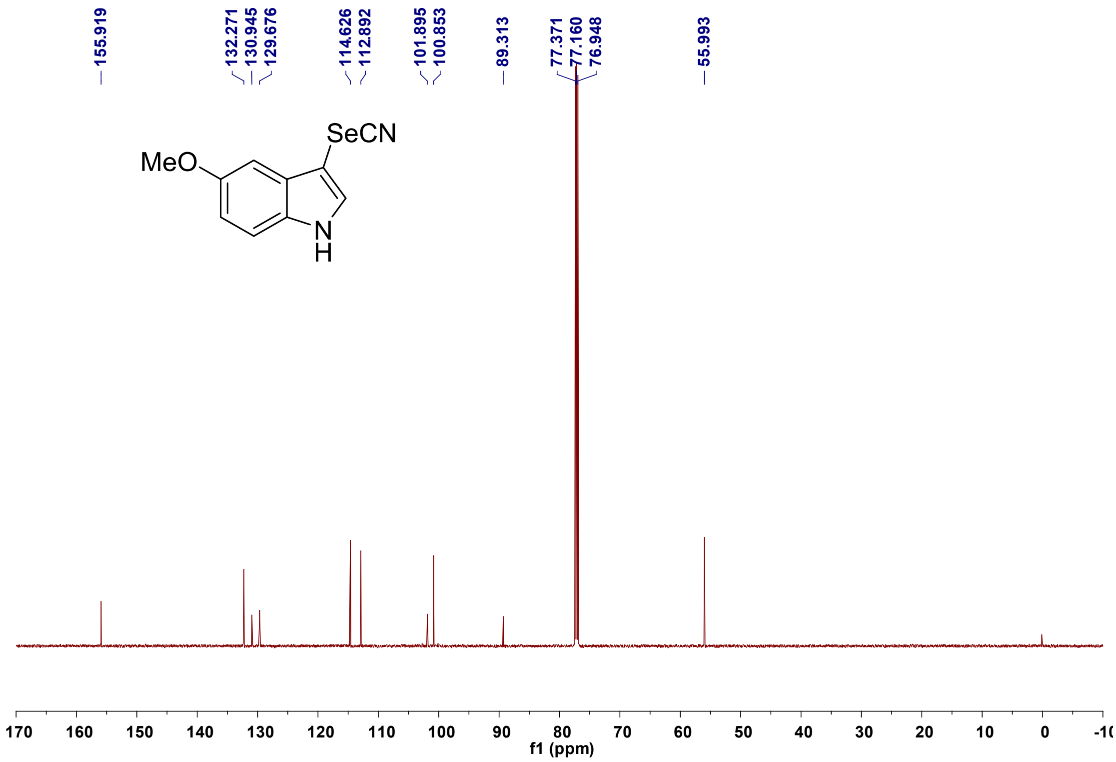

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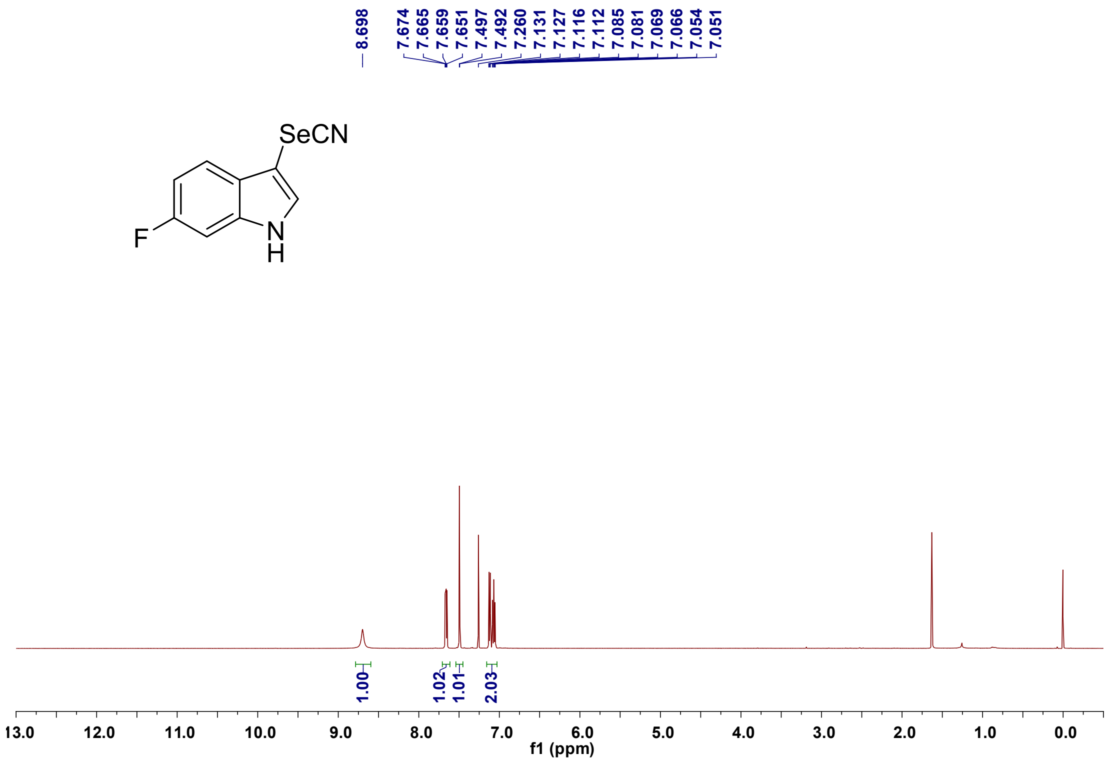

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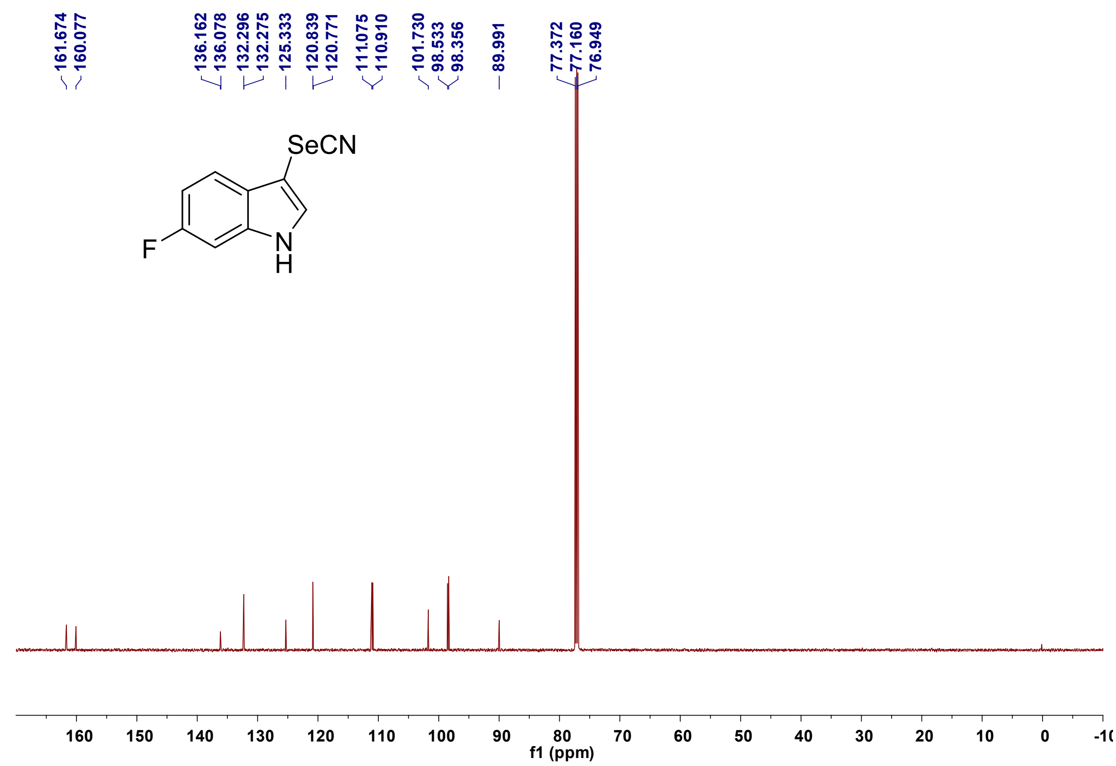

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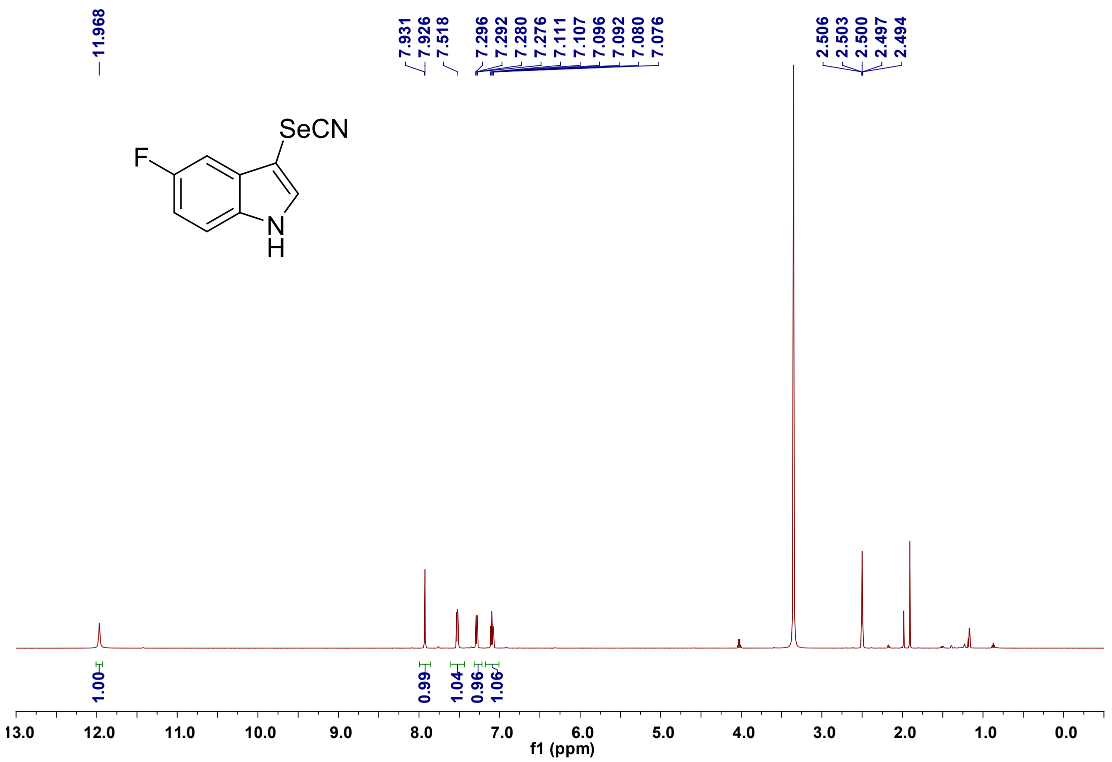

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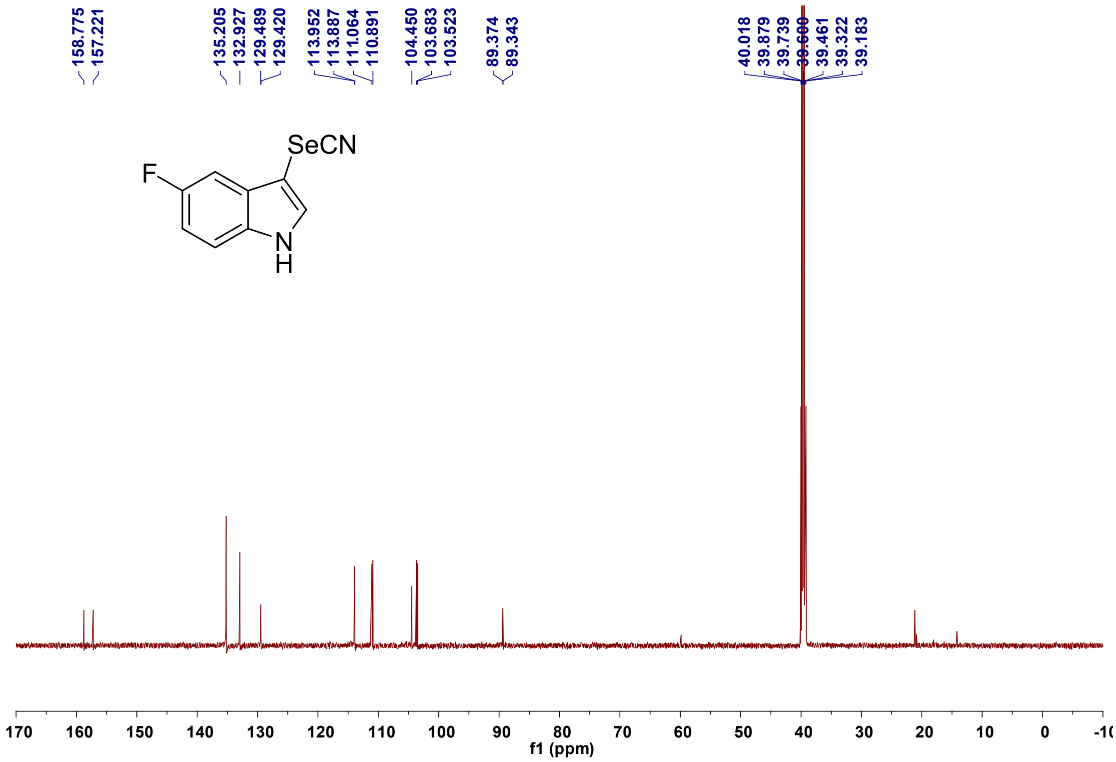

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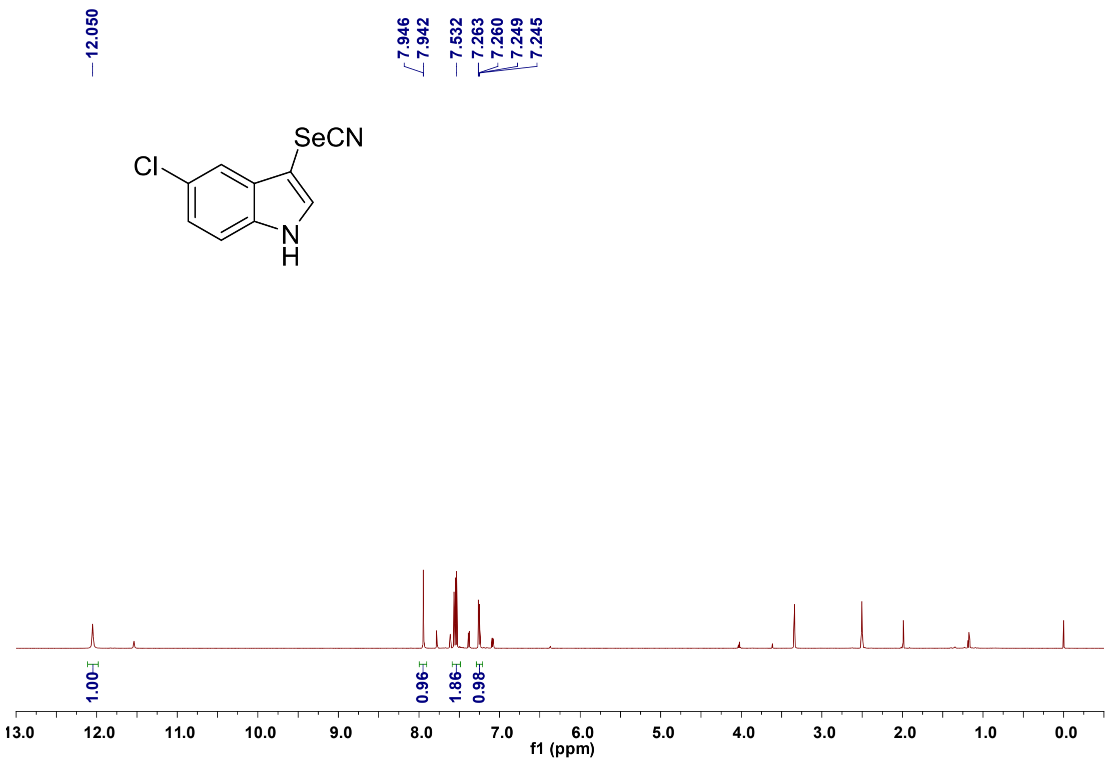

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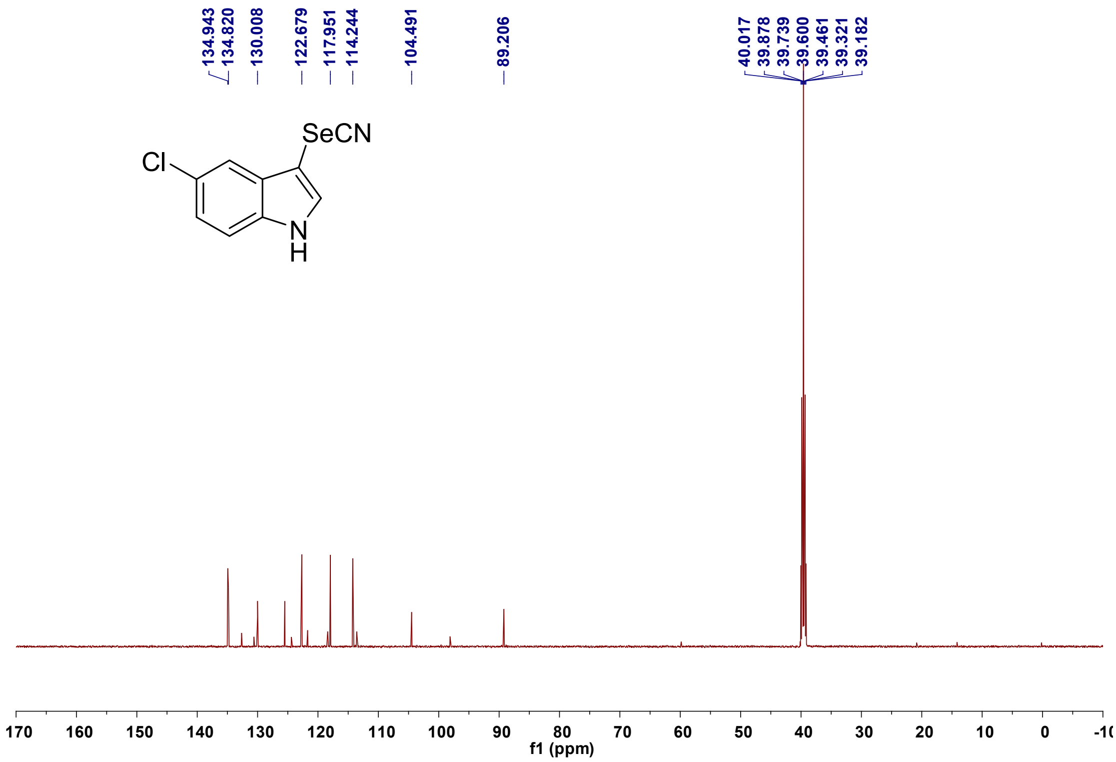

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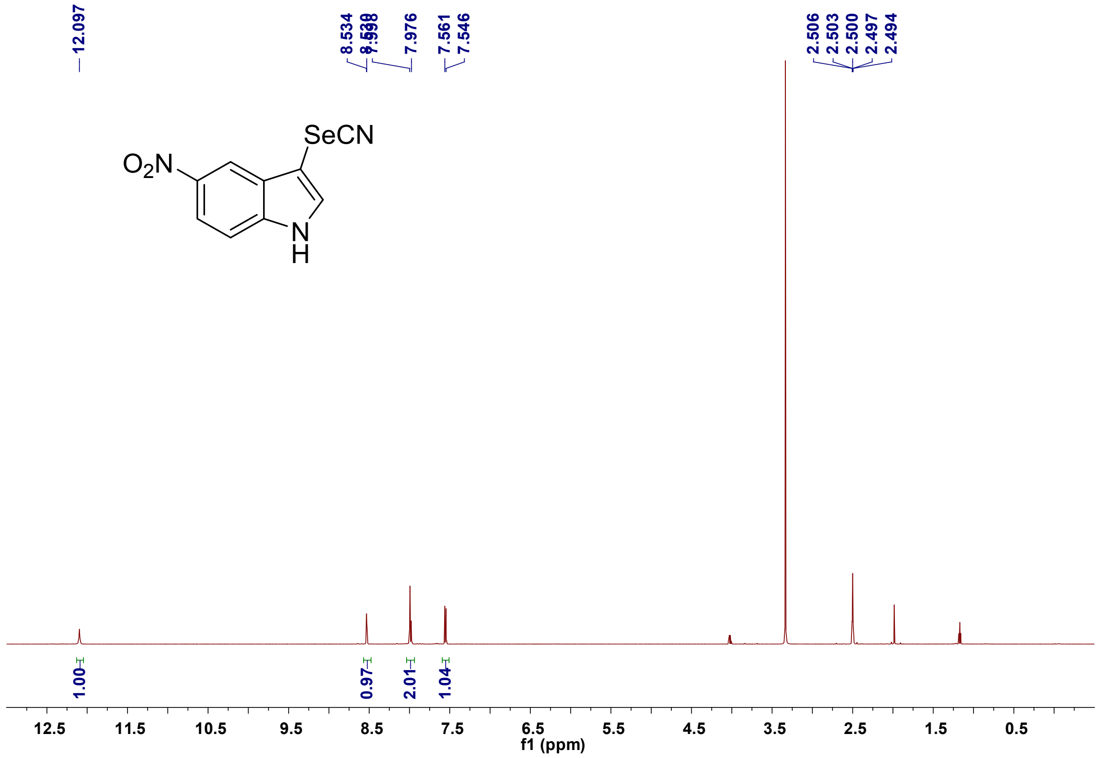

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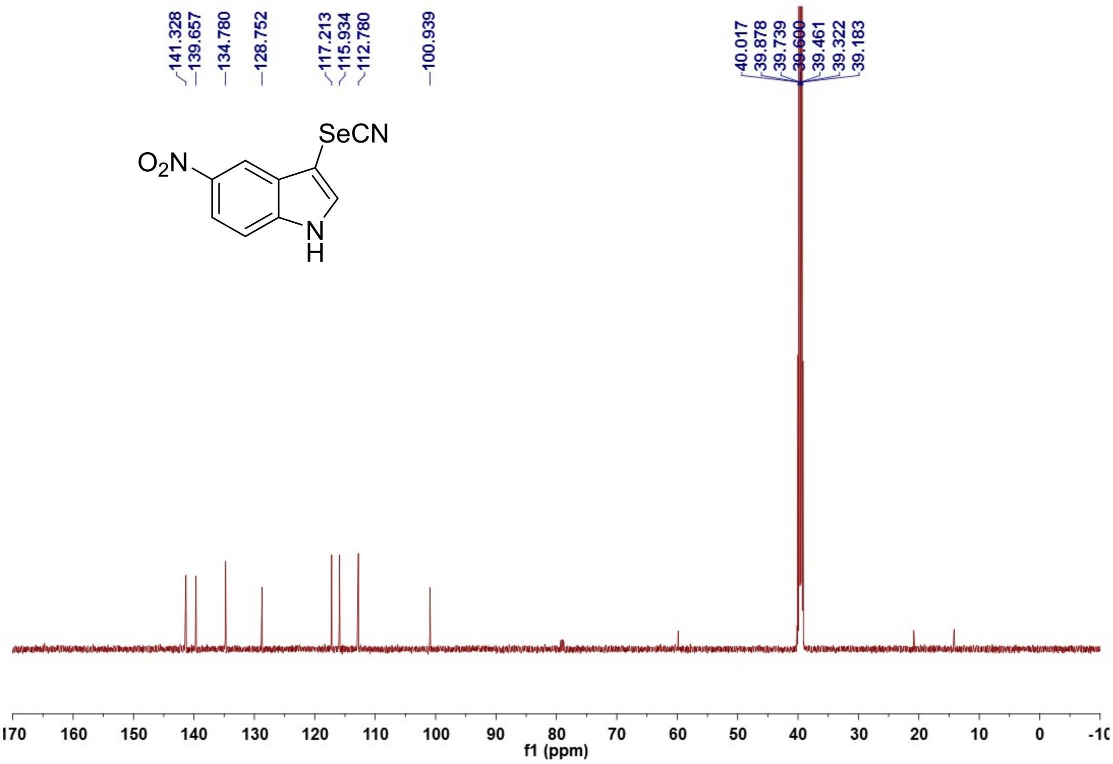

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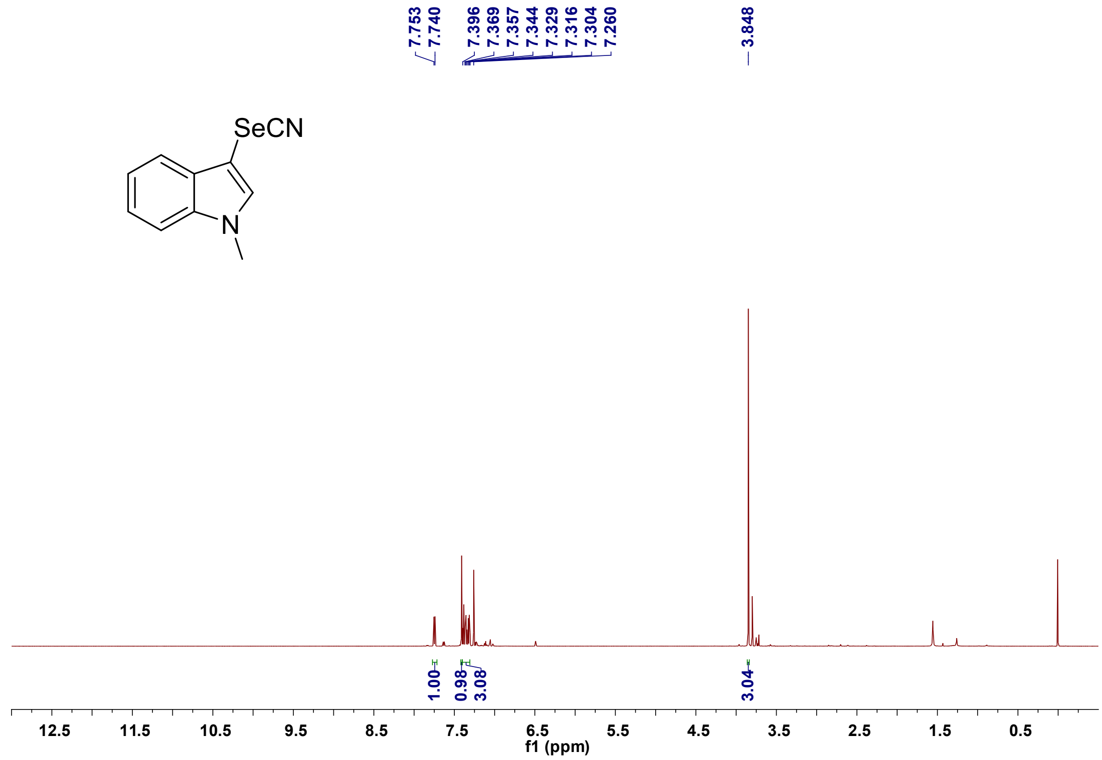

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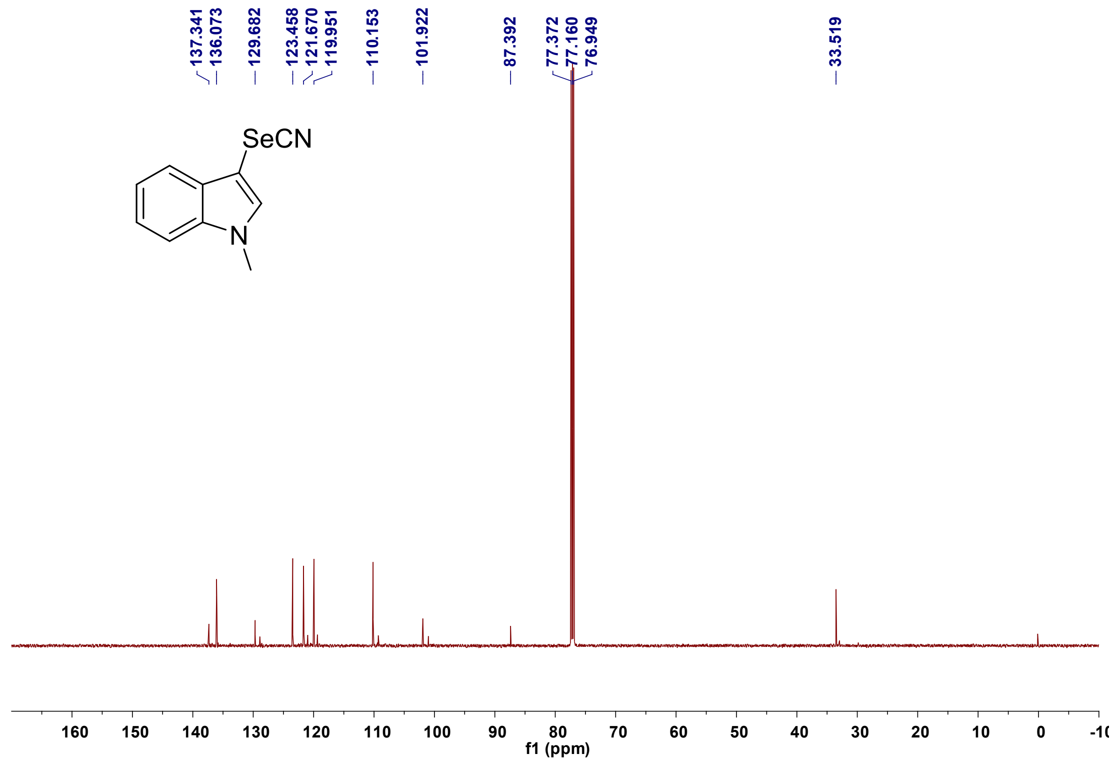

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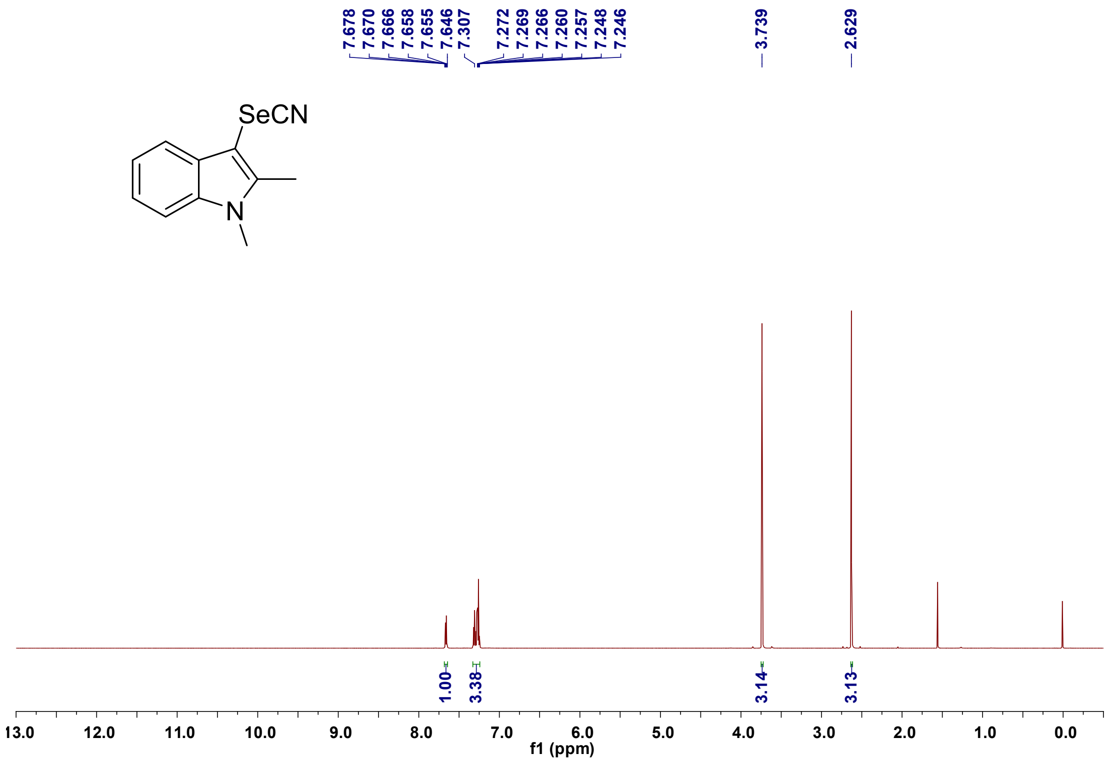

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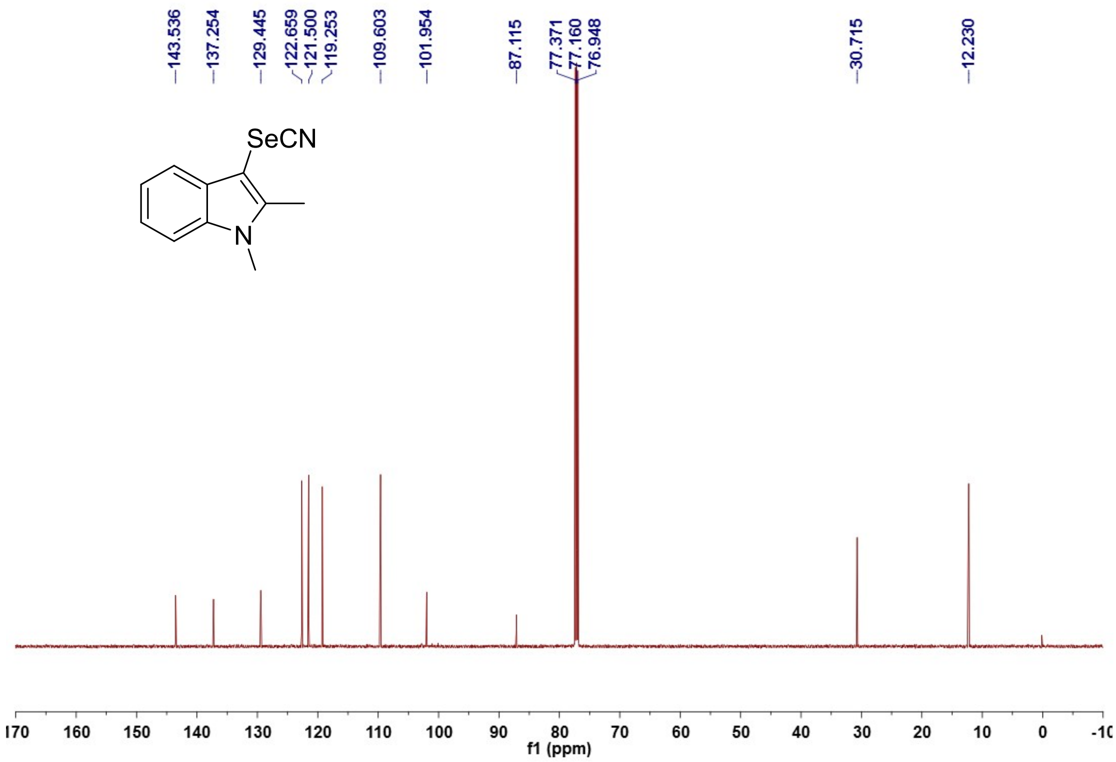

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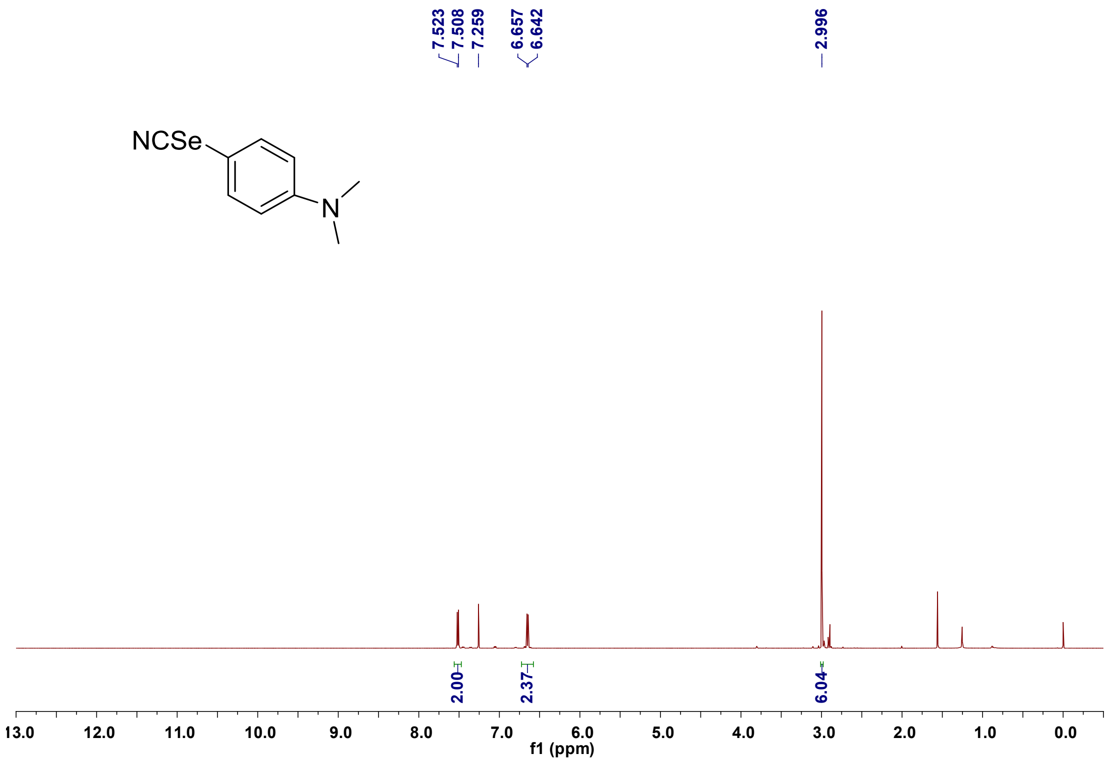
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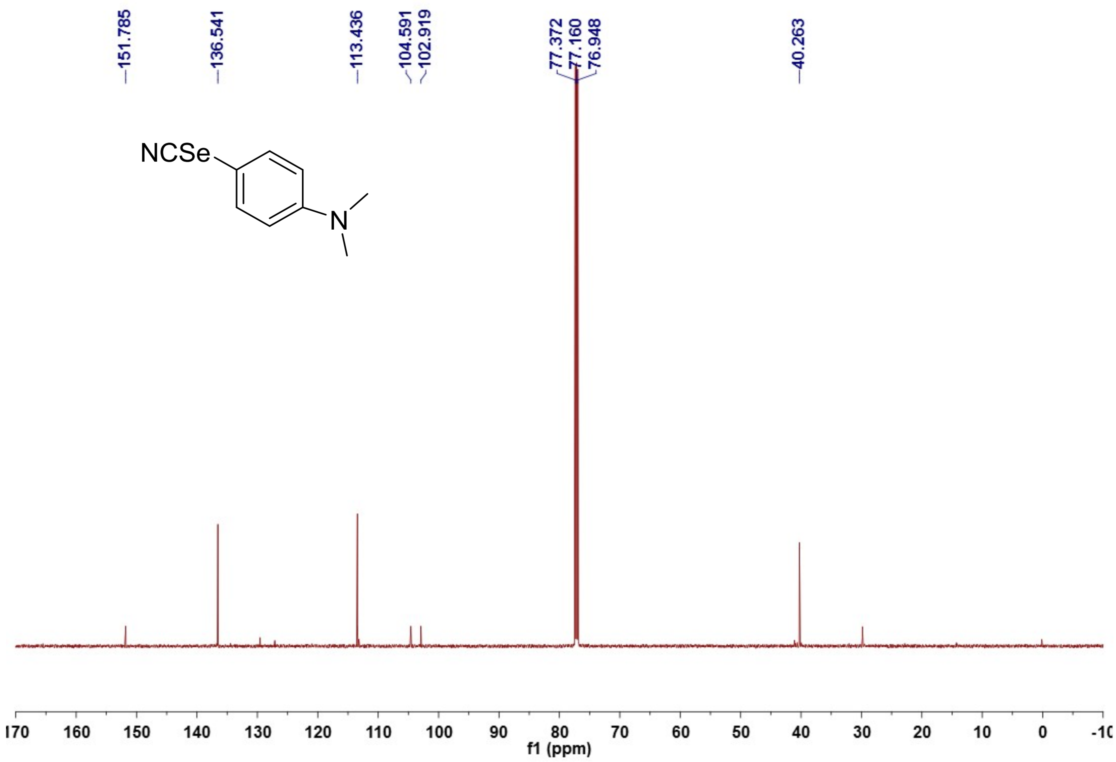
f1 (ppm)

^{13}C NMR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f1 (ppm)