Lead-free $Cs_2AgBiBr_6$ double perovskite microcrystals for effective visible-light photocatalytic thio/selenocyanation

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1. General

All commercial reagents were used directly without further purification, unless otherwise stated. 1,4-dioxane was purchased from J & K chemical, stored over 4 Å molecular sieves and handled under N_2. DMSO-d_6 and $CDCl_3$ were purchased from Shanghai aladdin Biochemical Technology Co. The following abbreviations were used to describe NMR signals: s = singlet, d = doublet, t = triplet, m = mulitplet, dd = doublet of doublets, q = quartet.

2. Experimental sections

2.1 Preparation of $Cs_2AgBiBr_6$

CABB was synthesized according to previously reported methods with a slight modification,[1] 2.130 g CsBr (10.0 mmol), 0.940 g AgBr (5.0 mmol) and 2.245 g $BiBr_3$ (5.0 mmol) were added into a 100 ml round bottom flask with 50 mL of 48 % HBr. The mixture was heated to 110 °C for 2 h, then cooled to room temperature. An orange powder precipitated from solution, centrifuged at 8000 rpm for 5 min and dried at 70 °C under reduced pressure for 4 h to obtain the CABB product. The CABB product was dissolved in DMSO giving 50 mM the transparent solution. 1 mL CABB transparent solution was added into 10 mL DCM, then precipitated, centrifuged at 8000 rpm for 5 min and dried at 70 °C under reduced pressure overnight to obtain the CABB nanoparticles.

2.2 characterization of CABB

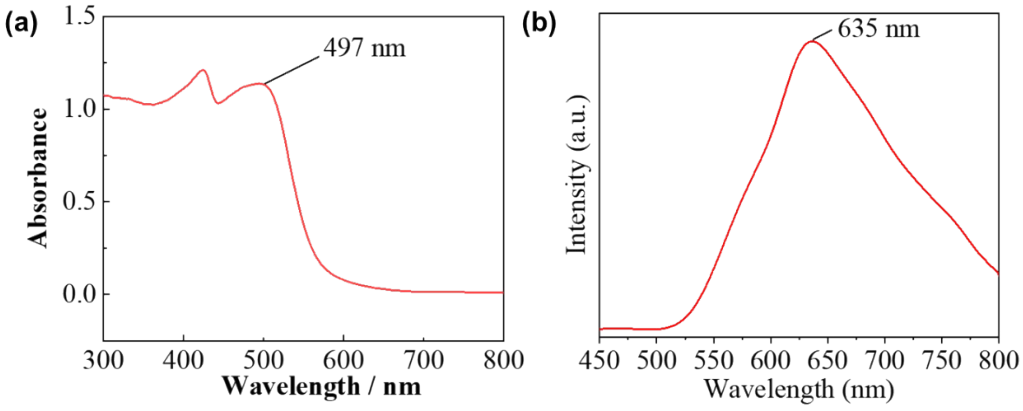


Figure S1 Absorbance spectrum (a) and Tauc plot of UV-Vis absorption data showing the character of an indirect band gap (b)

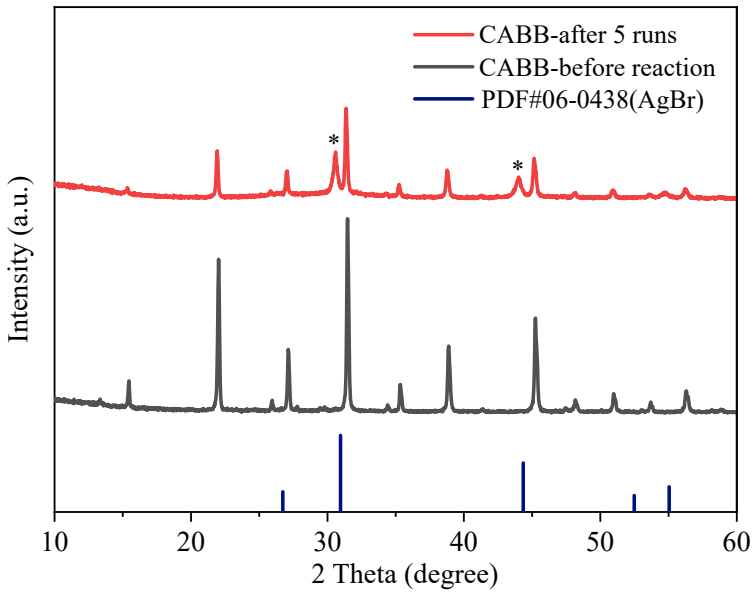


Figure S2 Powder XRD patterns of CABB before and after reactions.

2.3 Fluorescence Quenching Experiments

The fluorescence quenching experiment was conducted using a Perkin Elmer LS55 fluorescence spectrophotometer (USA).

Add CABB powder (1 mg) to 1,4-dioxane (5 mL), 1,4-dioxane of indole (10^{-4} mol/L, 5 mL) and ammonium thiocyanate (10^{-4} mol/L, 5 mL), respectively. Prepare a solution of 1,4-dioxane (5 mL) containing CABB (1 mg). Then they were uniformly dispersed by ultrasound.

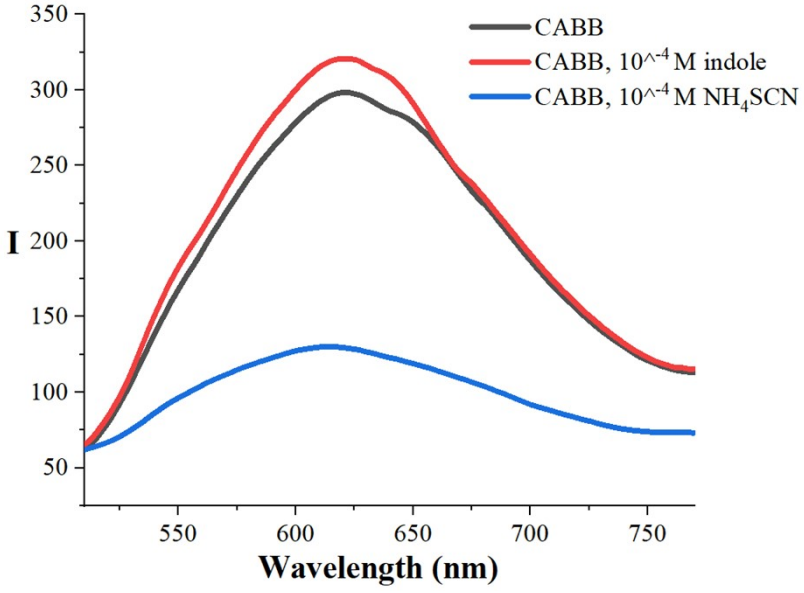
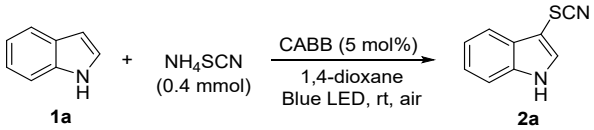


Figure S3 Fluorescence Quenching Experiments

2.4 Optimization of reaction conditions

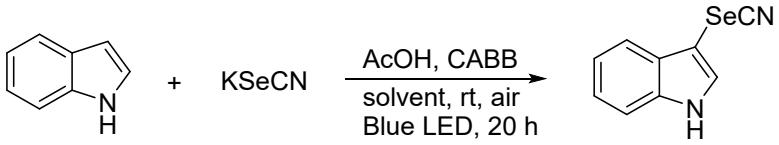
Table S1. Optimization of the reaction conditions[a]



Entry	Variation from the standard conditions	Yield (%)[b]
1	none	97
2	DCE	48
3	MeCN	71
4	EtOH	30
5	EtOAc	78
6	THF	76
7	Without CABB	29
8	AgBr instead of CABB	30
9	$BiBr_3$ instead of CABB	36
10	50 W green LED	32
11	50 W white LED	36
12	dark	nr
13	N_2 atmosphere	6
14	$CsPbBr_3$ was used	82
15	KSCN	37

[a] Standard reaction conditions: indoles **1a** (0.2 mmol), NH_4SCN (0.4 mmol), CABB (5 mol %), solvent (2 mL), 50 W 457 nm Blue LED, r.t., air, 20 h. [b] Isolated yield.

Table S2. Optimization of selenocyanation conditions[a]



Entry	KSeCN (equiv)	CABB (mol%)	AcOH (mol%)	Solvent	Yield (%)[b]
1	1.2	/	/	1,4-dioxane	14
2	1.2	5	/	1,4-dioxane	47
3	1.2	/	5	1,4-dioxane	31
4	1.2	5	5	1,4-dioxane	68
5	1.5	5	5	1,4-dioxane	81
6	2.0	5	5	1,4-dioxane	73
7	1.5	5	5	THF	78
8	1.5	5	5	DCE	32
9	1.5	5	5	MeCN	75

10	1.5	5	5	EtOAc	72

[a] Reaction conditions: indoles (0.2 mmol), NH_4SCN (x mmol), CABB (y mol %), AcOH (z mol%), solvent (2 ml), 50 W 457 nm Blue LED, r.t., air, 20 h. [b] Isolated yield.

2.5 General Procedure for the thiocyanation

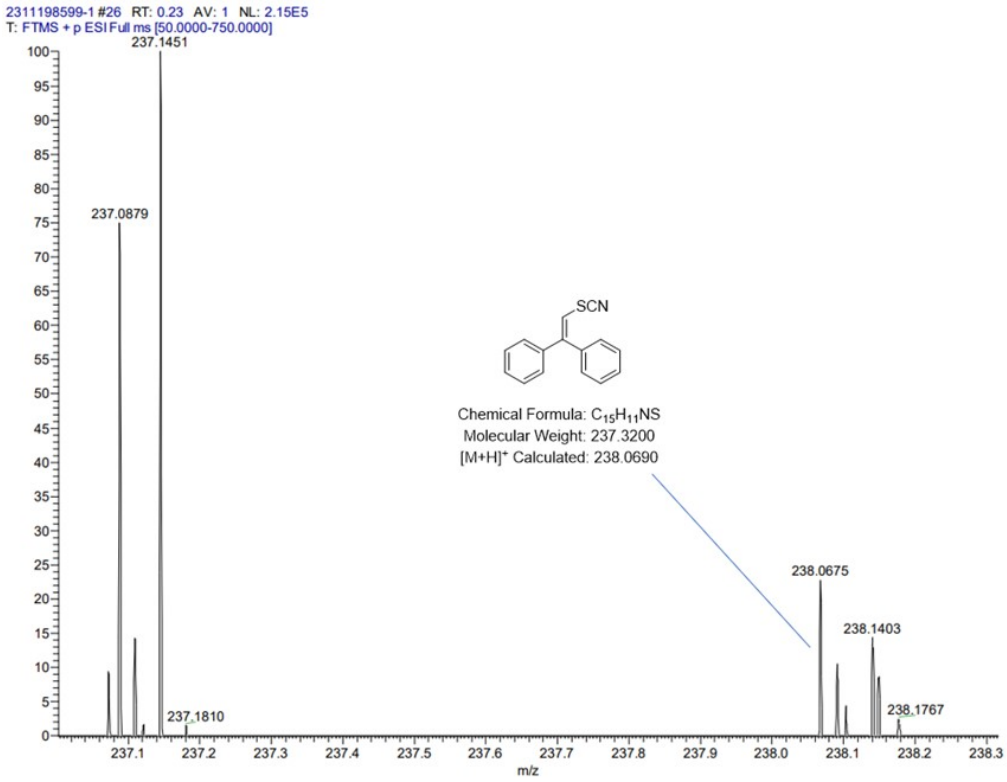
A suspension of indole (0.2 mmol, 1 equiv), NH_4SCN (0.4 mmol, 2 equiv.) and $Cs_2AgBiBr_6$ (10 mg, 5 mol%) in 1,4-dioxane (2 mL) was added to a 10 mL quartz glass tube, and the resulting reaction mixture was stirred under irradiation of a 457 nm Blue LED and an irradiation distance of about 5 cm under air atmosphere at room temperature. After total conversion of the indoles (detected by TLC), the isolated photocatalyst was centrifuged, and the resulting mixture was purified by flash silica gel chromatography (EtOAc/PE = 1/3) to afford the desired products.

2.6 General Procedure for the recycle experiments

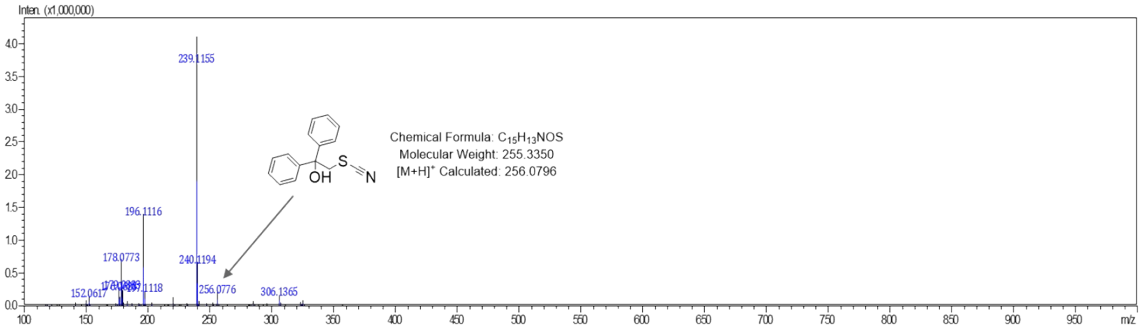
0.2 mmol indole, 0.4 mmol NH_4SCN, 20 mg $Cs_2AgBiBr_6$ and 1,4-dioxane (2 mL) were added to a 10 ml glass tube and irradiated with a 457 nm Blue LED in air at room temperature for 20 h. Upon completion of the reaction, the organic layer was obtained by decantation operation, and the insoluble residue was washed by ethyl acetate (2×10 mL). The combined organic layer was purified by flash silica gel chromatography (EtOAc/PE = 1/3) to afford the thiocyanation products. The resulted residue was dried under vacuum and was charged again with fresh reagents, repeating the process.

2.7 HRMS spectrums of the intermediates

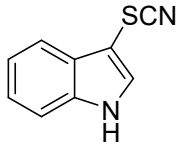
HRMS (ESI) m/z: calcd for $C_{15}H_{11}NS$ $[M + H]^+$: 238.0690, found: 238.0675.



HRMS (ESI) m/z: calcd for $C_{15}H_{13}NOS$ $[M + H]^+$: 256.0796, found: 256.0776.

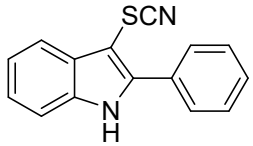


3. Data for the thiocyanation indoles.



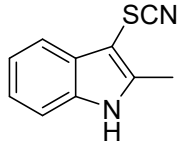
3-thiocyanato-1*H*-indole

2a[2]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a white solid; mp 72.4-74.1 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.78 (dd, *J* = 6.0, 2.9 Hz, 1H), 7.44 (d, *J* = 2.8 Hz, 1H), 7.40 (dd, *J* = 6.1, 2.7 Hz, 1H), 7.29 (dd, *J* = 6.0, 3.0 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.11, 131.30 127.68, 123.83, 121.87, 118.63, 112.43, 112.31, 91.61.



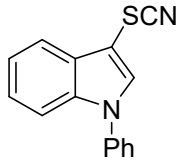
2-phenyl-3-thiocyanato-1*H*-indole

2b[3]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a white solid; mp 168-170 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.42 (s, 1H), 7.86 (d, *J* = 7.4 Hz, 2H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.63 (t, *J* = 7.2 Hz, 2H), 7.56 (d, *J* = 7.1 Hz, 2H), 7.37 – 7.26 (m, 2H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 143.63, 136.29, 130.44, 129.80, 129.62, 129.40, 129.30, 123.88, 121.90, 118.51, 112.95, 112.86, 87.60.



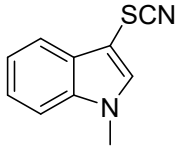
2-methyl-3-thiocyanato-1*H*-indole

2c[3]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a white solid; mp 97.0-98.8 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 6.9 Hz, 1H), 7.26 – 7.17 (m, 2H), 2.47 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.11, 135.14, 128.72, 123.00, 121.58, 118.09, 112.19, 111.28, 88.85, 12.09.



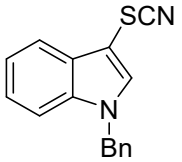
1-phenyl-3-thiocyanato-1*H*-indole

2d[2]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a yellow oil; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.36 (s, 1H), 7.80 (dd, *J* = 5.0, 3.8 Hz, 1H), 7.67 – 7.58 (m, 5H), 7.54 – 7.47 (m, 1H), 7.42 – 7.36 (m, 2H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 138.12, 136.32, 135.80, 130.45, 128.66, 128.28, 125.01, 124.62, 122.76, 119.00, 112.35, 112.07, 92.98.



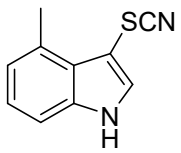
1-methyl-3-thiocyanato-1*H*-indole

2e[2]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a white solid; mp 77-79 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 3.2 Hz, 3H), 7.29 (dd, *J* = 11.7, 4.2 Hz, 1H), 3.74 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.20, 135.16, 128.51, 123.47, 121.64, 118.95, 112.01, 110.29, 89.78, 33.47.



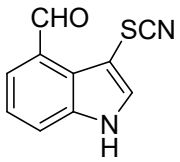
1-benzyl-3-thiocyanato-1*H*-indole

2f[2]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a white solid; mp 84.6-86.2 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.22 (s, 1H), 7.70 (dd, *J* = 6.2, 2.7 Hz, 1H), 7.64 (dd, *J* = 6.3, 2.4 Hz, 1H), 7.38 – 7.21 (m, 7H), 5.50 (s, 2H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 137.56, 136.69, 136.47, 129.17, 128.45, 128.21, 127.80, 123.61, 121.93, 118.61, 112.70, 112.14, 89.74, 50.16.



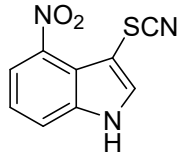
4-methyl-3-thiocyanato-1*H*-indole

2g[3]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a white solid; mp 125.9-126.5 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.44 (d, *J* = 2.6 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 6.98 (d, *J* = 7.0 Hz, 1H), 2.92 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.50, 132.25, 131.01, 125.58, 123.96, 123.51, 113.57, 110.14, 91.92, 19.25.



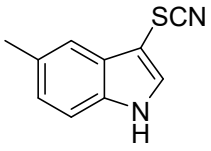
3-thiocyanato-1*H*-indole-4-carbaldehyde

2h: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a white solid; mp 169-171 ℃; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.50 (s, 1H), 10.81 (s, 1H), 8.17 (d, *J* = 2.8 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 191.56, 138.52, 135.93, 129.01, 125.40, 125.04, 122.96, 119.92, 113.53, 91.11.



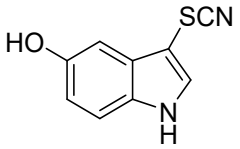
4-nitro-3-thiocyanato-1*H*-indole

2j: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a yellow solid; mp 156-158 ℃; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.82 (s, 1H), 8.29 (s, 1H), 7.97 (dd, *J* = 16.0, 8.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 1H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 141.36, 139.48, 137.56, 122.67, 120.08, 119.04, 118.71, 113.46, 91.07.



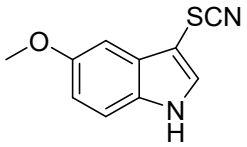
5-methyl-3-thiocyanato-1*H*-indole

2k[3]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a white solid; mp 93.1-94.5 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.56 (s, 1H), 7.39 (dt, *J* = 5.4, 2.8 Hz, 1H), 7.28 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 2.54 – 2.44 (m, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 134.38, 131.52, 131.19, 127.93, 125.52, 118.21, 112.46, 111.91, 91.03, 21.59.



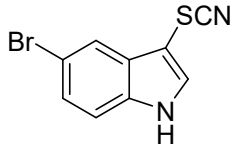
3-thiocyanato-1*H*-indol-5-ol

2l: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a white solid; 128-130℃; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 11.74 (s, 1H), 9.17 (s, 1H), 7.85 (d, J = 2.6 Hz, 1H), 7.32 (d, J = 8.7 Hz, 1H), 6.95 (s, 1H), 6.86 – 6.66 (m, 1H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 152.92, 133.55, 130.90, 128.97, 113.91, 113.71, 112.84, 101.85, 88.12.



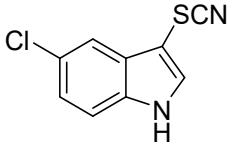
5-methoxy-3-thiocyanato-1*H*-indole

2m[3]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a white solid; mp 119.8-120.7 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.42 (d, J = 2.7 Hz, 1H), 7.27 (d, J = 8.9 Hz, 1H), 7.17 (d, J = 1.9 Hz, 1H), 6.93 (dd, J = 8.8 Hz, 1H), 3.90 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.70, 131.62, 130.92, 128.53, 114.45, 113.17, 112.32, 99.78, 91.14, 55.90.



5-bromo-3-thiocyanato-1*H*-indole

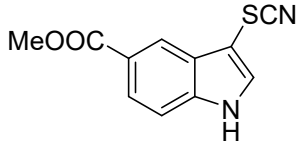
2n[3] Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a white solid; mp 131-133 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.87 (s, 1H), 7.90 (s, 1H), 7.50 (d, J = 2.4 Hz, 1H), 7.37 (d, J = 8.6 Hz, 1H), 7.33 – 7.21 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 134.68, 132.12, 129.41, 127.07, 121.49, 115.47, 113.61, 111.53, 92.15.



5-chloro-3-thiocyanato-1*H*-indole

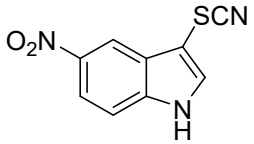
2o[3]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a white solid; mp 130.3-131.9 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$)

δ 8.87 (s, 1H), 7.75 (d, *J* = 1.7 Hz, 1H), 7.52 (d, *J* = 2.7 Hz, 1H), 7.33 (d, *J* = 8.7 Hz, 1H), 7.29 – 7.19 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 134.38, 132.31, 128.85, 127.99, 124.49, 118.38, 113.26, 111.62, 92.17.



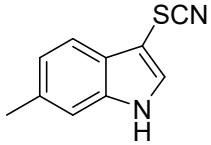
methyl 3-thiocyanato-1*H*-indole-5-carboxylate

2p[6]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a white solid; mp 155.4-157.6 ℃; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.38 (s, 1H), 8.33 (s, 1H), 8.17 (d, *J* = 2.7 Hz, 1H), 7.90 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.65 (d, *J* = 8.6 Hz, 1H), 3.91 (s, 3H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 167.15, 139.45, 135.65, 127.53, 124.19, 123.03, 120.34, 113.52, 112.63, 91.95, 52.51.



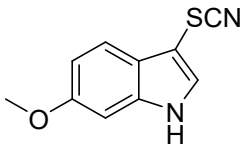
5-nitro-3-thiocyanato-1*H*-indole

2q: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a yellow solid; mp 207-209 ℃ **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.72 (s, 1H), 8.56 (d, *J* = 1.8 Hz, 1H), 8.31 (d, *J* = 2.6 Hz, 1H), 8.16 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.74 (d, *J* = 9.0 Hz, 1H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 142.62, 140.02, 137.60, 127.38, 118.66, 114.90, 114.22, 112.48, 93.65.



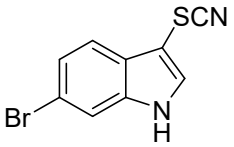
6-methyl-3-thiocyanato-1*H*-indole

2r[3]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a white solid; mp 104.6-106.2 ℃; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 11.88 (s, 1H), 7.90 (d, *J* = 2.5 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.32 (s, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 2.43 (s, 3H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 137.21, 132.98, 132.76, 125.79, 123.29, 117.88, 112.94, 112.80, 89.46, 21.74.



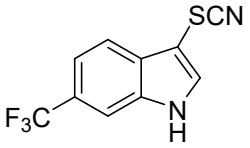
6-methoxy-3-thiocyanato-1*H*-indole

2s[3]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a white solid; mp 114.5-115.6 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.81 (s, 1H), 7.85 (s, 1H), 7.54 (s, 1H), 6.96 (d, *J* = 56.0 Hz, 2H), 3.81 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.13, 137.67, 132.32, 121.93, 118.90, 112.83, 111.92, 95.93, 89.67, 55.76.



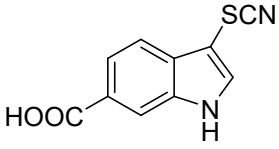
6-bromo-3-thiocyanato-1*H*-indole

2t[3]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a white solid; mp 132.8-134.0 ℃; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.15 (s, 1H), 8.04 (d, *J* = 2.8 Hz, 1H), 7.75 (d, *J* = 1.1 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.40 (dd, *J* = 8.5, 1.5 Hz, 1H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 137.62, 134.66, 126.96, 124.52, 120.05, 116.09, 115.87, 112.59, 90.69.



3-thiocyanato-6-(trifluoromethyl)-1*H*-indole

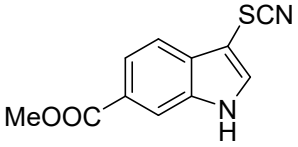
2u[4]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a yellow solid; mp 84.1-86.4 ℃; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.45 (s, 1H), 8.27 (d, *J* = 2.6 Hz, 1H), 7.89 (d, *J* = 8.9 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 1H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 136.82 (s), 135.69 (s), 130.50 (s), 126.52 (s), 124.43 – 123.71 (m), 119.32 (s), 117.87 (d, *J* = 3.4 Hz), 112.55 (s), 110.78 (d, *J* = 4.4 Hz), 91.13 (s). **^{19}F NMR** (DMSO-d_6, 376 MHz, 298 K) δ = -59.23 (s).



3-thiocyanato-1*H*-indole-6-carboxylic acid

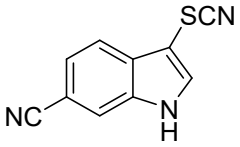
2v: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled

thiocyanation indole as a white solid; mp 262-264 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.87 (s, 1H), 12.37 (s, 1H), 8.20 (d, J = 26.2 Hz, 2H), 7.82 (d, J = 49.4 Hz, 2H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 168.25, 136.71, 136.19, 131.21, 125.76, 122.38, 118.06, 115.19, 112.64, 90.79.



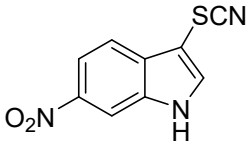
methyl 3-thiocyanato-1*H*-indole-6-carboxylate

2w[6]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a brown solid; mp 135.3-137.2 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.40 (s, 1H), 8.25 (s, 1H), 8.18 (s, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 3.90 (s, 3H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 167.15, 137.04, 136.13, 131.47, 124.54, 122.08, 118.29, 115.10, 112.61, 90.98, 52.56.



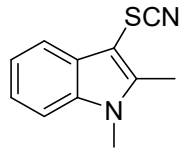
3-thiocyanato-1*H*-indole-6-carbonitrile

2x[3]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a white solid; mp 111-113 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.59 (s, 1H), 8.29 (d, J = 3.6 Hz, 1H), 8.07 (d, J = 5.5 Hz, 1H), 7.89 – 7.80 (m, 1H), 7.60 (dd, J = 7.3, 6.1 Hz, 1H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 137.61, 135.67, 131.07, 124.30, 120.32, 119.50, 118.37, 112.50, 105.11, 91.80.



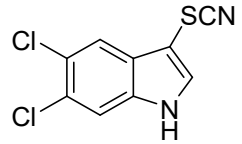
6-nitro-3-thiocyanato-1*H*-indole

2y[5]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a yellow solid; mp 179-180 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.67 (s, 1H), 8.49 – 8.36 (m, 2H), 8.12 (dd, J = 8.8, 1.8 Hz, 1H), 7.87 (d, J = 8.8 Hz, 1H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 143.76, 139.45, 135.32, 132.63, 118.86, 116.60, 112.43, 110.00, 92.22.



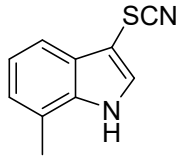
1,2-dimethyl-3-thiocyanato-1*H*-indole

2z[6]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a yellow solid; mp 74.7-76.4 ℃; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.58 (dd, J = 13.8, 7.7 Hz, 2H), 7.32 – 7.18 (m, 2H), 3.74 (s, 3H), 2.56 (s, 3H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 144.80, 137.06, 128.00, 122.72, 121.61, 117.68, 112.58, 111.00, 86.82, 30.94, 11.14.



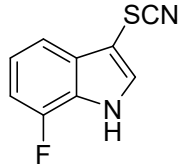
5,6-dichloro-3-thiocyanato-1*H*-indole

2aa: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a brown solid; mp 194.8-196.9 ℃;**^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.28 (s, 1H), 8.14 (s, 1H), 7.88 (s, 1H), 7.81 (s, 1H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 136.37, 135.63, 127.90, 125.96, 124.50, 119.41, 115.03, 112.52, 90.56.



7-methyl-3-thiocyanato-1*H*-indole

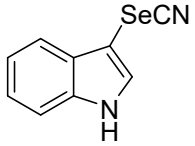
2ab[3]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a white solid; mp 157.2-159.0 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 1.6 Hz, 1H), 7.22 (dd, J = 15.1, 7.6 Hz, 1H), 7.10 (d, J = 7.1 Hz, 1H), 2.47 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.65, 130.77, 127.34, 124.38, 122.08, 121.50, 116.37, 112.37, 92.41, 16.41.



7-fluoro-3-thiocyanato-1*H*-indole

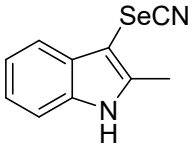
2ac: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a white solid; mp 119-121 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ

8.99 (s, 1H), 7.54 (dd, *J* = 12.4, 5.3 Hz, 2H), 7.33 – 7.12 (m, 1H), 7.02 (dd, *J* = 10.9, 8.0 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.53 (s), 148.57 (s), 131.80, 124.61 (d, *J* = 14.3 Hz), 122.38 (d, *J* = 6.2 Hz), 114.54 (d, *J* = 3.8 Hz), 111.69 (s), 108.80 (d, *J* = 15.9 Hz), 93.34 (d, *J* = 3.4 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz, 298 K) δ = -132.06 (dd, *J* = 11.4, 4.6 Hz).



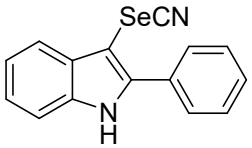
3-selenocyanato-1*H*-indole

3a[4]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a brown solid; mp 108-110 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.74 – 7.65 (m, 1H), 7.34 (dd, *J* = 7.2, 3.9 Hz, 2H), 7.29 – 7.22 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.07, 132.13, 128.70, 123.69, 121.79, 119.43, 112.13, 102.63, 88.93.



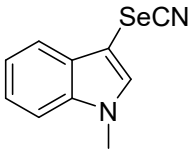
2-methyl-3-selenocyanato-1*H*-indole

3b[8]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a brown oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.83 (s, 1H), 7.43 (d, *J* = 37.5 Hz, 2H), 7.16 (s, 2H), 2.53 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.69, 136.04, 130.07, 122.31, 120.91, 118.58, 111.95, 104.70, 88.33, 13.20.



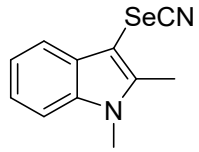
2-phenyl-3-selenocyanato-1*H*-indole

3c[4]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a yellow solid; mp 152.8-154.1 ℃; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.26 (s, 1H), 7.87 (d, *J* = 7.3 Hz, 2H), 7.65 (d, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 2H), 7.56 – 7.49 (m, 2H), 7.31 – 7.24 (m, 2H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 143.23, 136.57, 131.44, 130.93, 129.63, 129.43, 129.14, 123.52, 121.50, 119.70, 112.61, 105.29, 88.68.



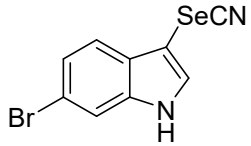
1-methyl-3-selenocyanato-1*H*-indole

3d[7]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a brown solid; mp 106-107 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 7.4 Hz, 1H), 3.84 (s, 3H); **^{13}C NMR** (126 MH z, $CDCl_3$) δ 137.29, 137.22, 129.51, 123.03, 121.35, 119.42, 111.25, 104.90, 88.28, 33.41.



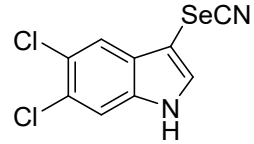
1,2-dimethyl-3-selenocyanato-1*H*-indole

3e[7]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a yellow solid; mp 123-124 ℃; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.52 (t, *J* = 8.6 Hz, 2H), 7.21 (dt, *J* = 15.0, 6.9 Hz, 2H), 3.76 (s, 3H), 2.57 (s, 3H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 143.92, 137.23, 129.25, 122.36, 121.20, 118.79, 110.69, 104.72, 88.23, 30.93, 12.24.



6-bromo-3-selenocyanato-1*H*-indole

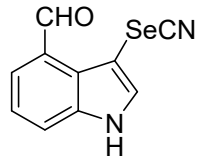
3f[7]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a brown solid; mp 132.2-133.9 ℃; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 11.99 (s, 1H), 7.90 (d, *J* = 2.5 Hz, 1H), 7.71 (s, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.36 (dd, *J* = 8.4, 1.0 Hz, 1H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 137.48, 134.67, 128.25, 124.10, 121.05, 115.71, 115.43, 104.95, 90.35.



5,6-dichloro-3-selenocyanato-1*H*-indole

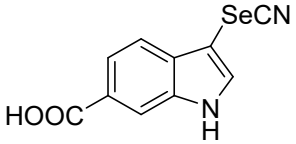
3g: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled

thiocyanation indole as a brown solid; mp 199.5-201.5 ℃; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.13 (s, 1H), 8.00 (d, J = 2.6 Hz, 1H), 7.79 (s, 1H), 7.76 (s, 1H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 136.33, 135.49, 129.22, 125.48, 123.96, 120.27, 114.62, 105.04, 90.15.



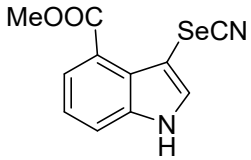
3-selenocyanato-1*H*-indole-4-carbaldehyde

3h: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a yellow solid; mp 142-144 ℃; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.28 (s, 1H), 10.25 (s, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.83 – 7.73 (m, 2H), 7.41 (s, 1H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 194.61, 138.63, 131.65, 128.24, 128.06, 123.96, 122.47, 120.50, 106.44, 90.17.



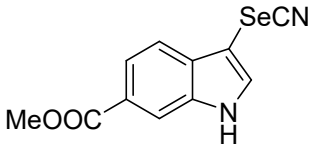
3-selenocyanato-1*H*-indole-6-carboxylic acid

3i: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a yellow solid; mp 269-271 ℃; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.29 (s, 1H), 8.14 (s, 1H), 8.04 (s, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.62 (d, J = 8.2 Hz, 1H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 168.95, 136.53, 136.13, 132.15, 126.66, 122.17, 118.78, 114.81, 104.99, 90.22.



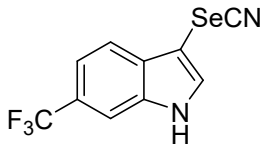
methyl 3-selenocyanato-1*H*-indole-4-carboxylate

3j[4]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a yellow oil; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.18 (s, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.74 (d, J = 7.4 Hz, 1H), 7.71 (d, J = 2.1 Hz, 1H), 7.30 (t, J = 7.8 Hz, 1H), 3.93 (s, 3H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 168.66, 138.58, 129.89, 125.07, 123.57, 122.05, 120.18, 118.74, 106.81, 90.08, 52.97.



methyl 3-selenocyanato-1*H*-indole-6-carboxylate

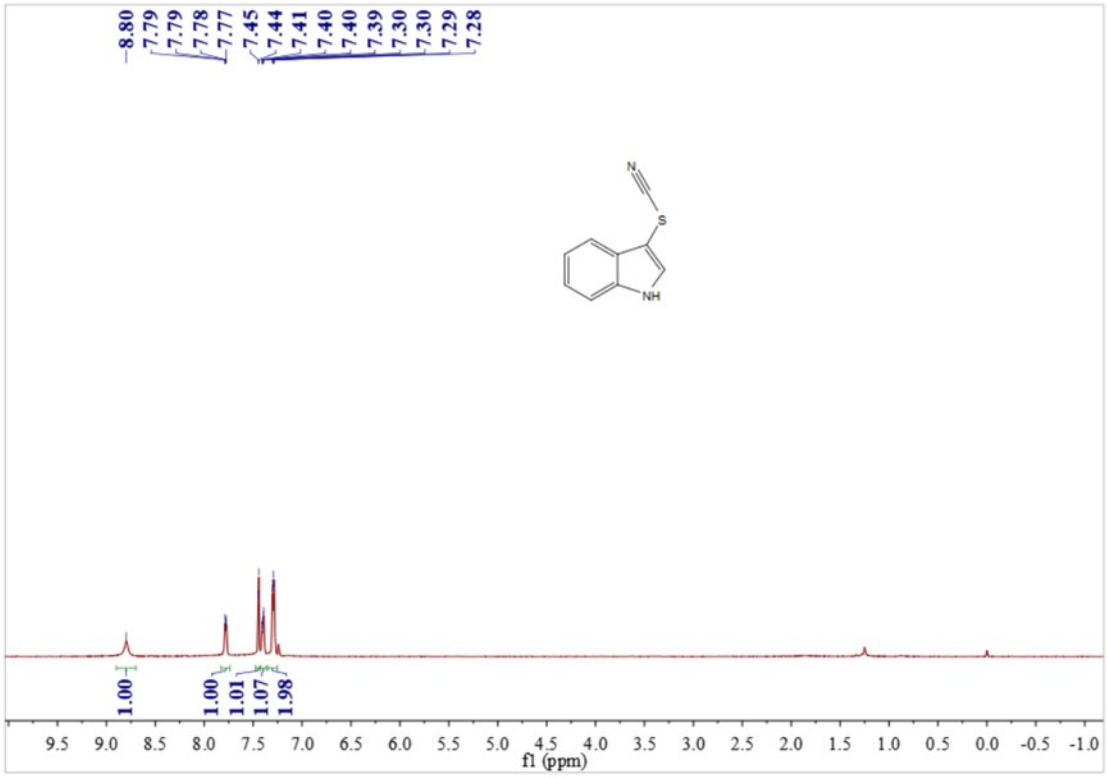
3k[4]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a yellow solid; mp 165.3-167.2 ℃; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.25 (s, 1H), 8.15 (s, 1H), 8.11 (d, J = 2.5 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.69 (d, J = 8.3 Hz, 1H), 3.88 (s, 3H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 167.29, 137.13, 135.99, 132.75, 124.09, 121.70, 119.26, 114.76, 105.02, 90.68, 52.51.

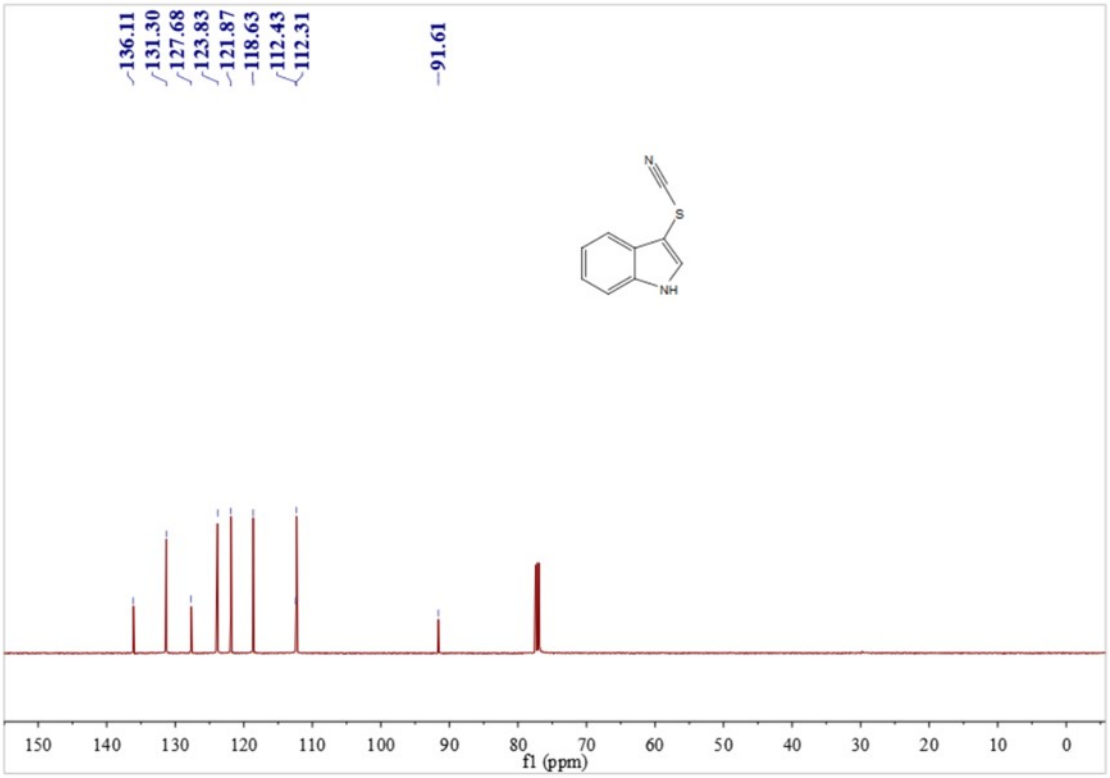


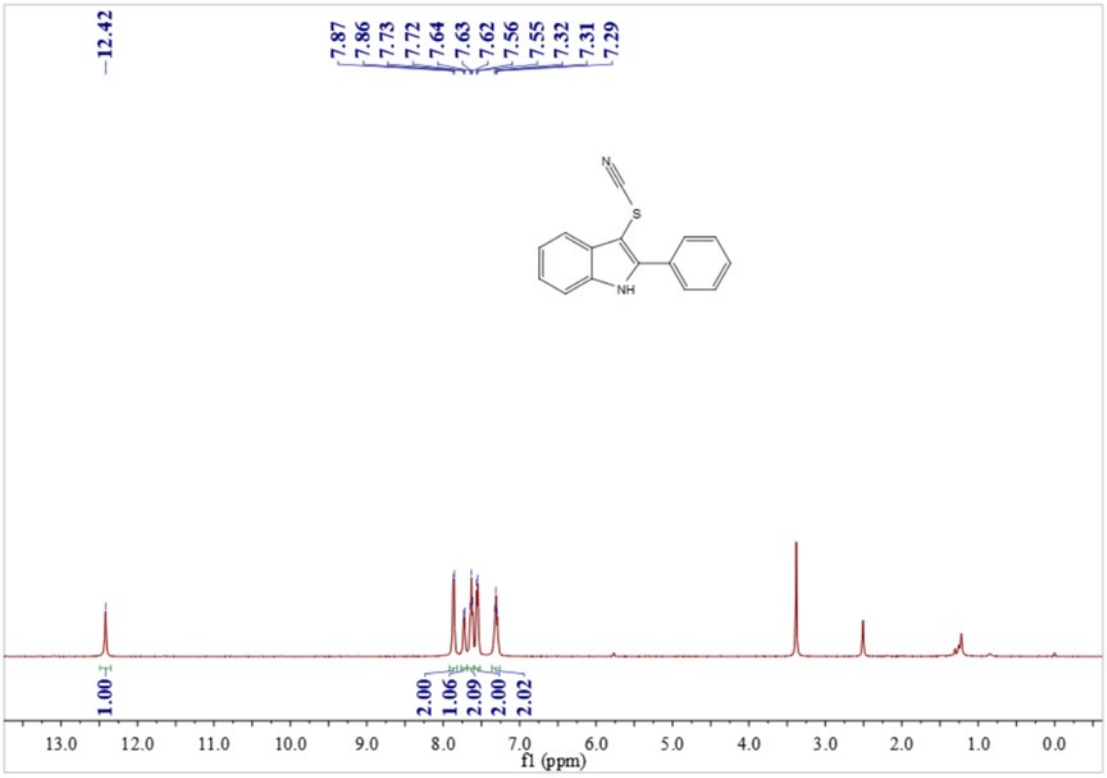
3-selenocyanato-6-(trifluoromethyl)-1*H*-indole

3l[4]: Flash column chromatography (petroleum/ethyl acetate 3:1) afforded the titled thiocyanation indole as a yellow solid; mp 101-103 ℃; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.28 (s, 1H), 8.12 (d, J = 2.6 Hz, 1H), 7.87 (s, 1H), 7.80 (d, J = 8.3 Hz, 1H), 7.52 (d, J = 8.3 Hz, 1H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 136.81 (s), 135.56 (s), 131.76 (s), 126.65 (s), 124.58 – 123.29 (m), 120.25 (s), 117.44 (d, J = 3.4 Hz), 110.37 (d, J = 4.4 Hz), 104.94 (s), 90.73 (s); **^{19}F NMR** (DMSO-d_6, 376 MHz, 298 K) δ = -59.10 (s).

4. ^{1}H NMR, ^{13}CNMR and ^{19}F NMR for the products.



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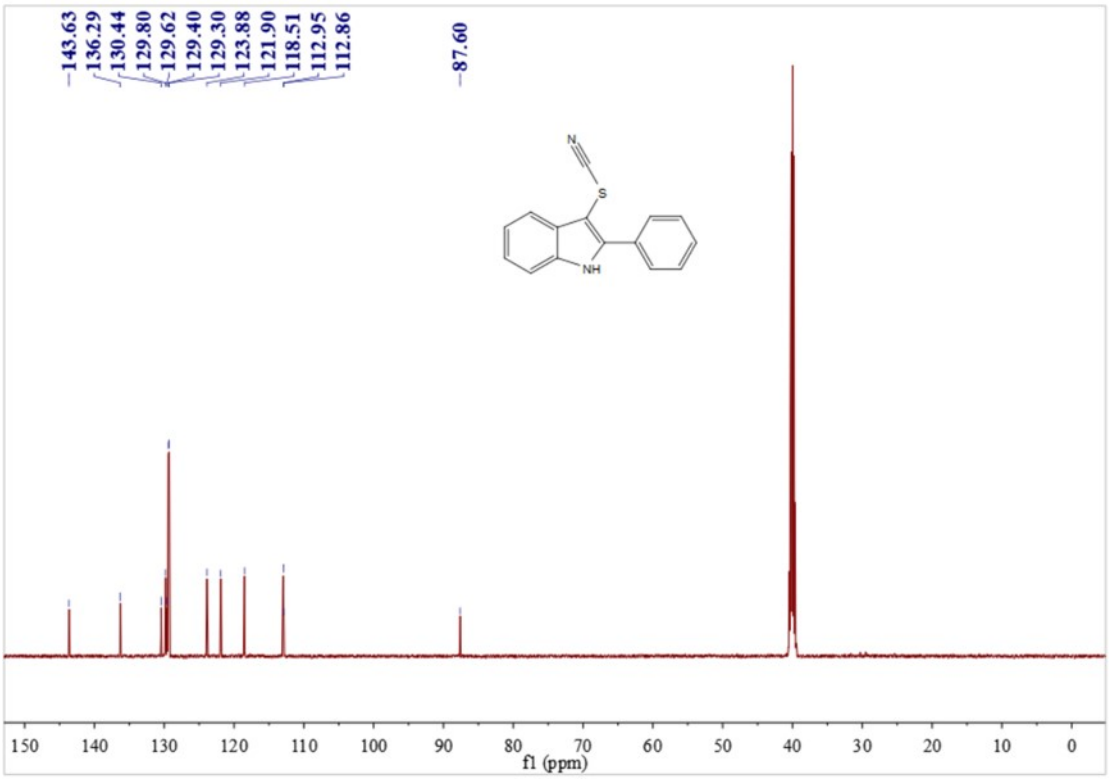
7.87
7.86
7.73
7.72
7.64
7.63
7.62
7.56
7.55
7.32
7.31
7.29
N
S
NH
1.00
2.00
1.06
2.09
2.00
2.02
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


143.63
136.29
130.44
129.80
129.62
129.40
129.30
123.88
121.90
118.51
112.95
112.86
87.60
N
S
NH
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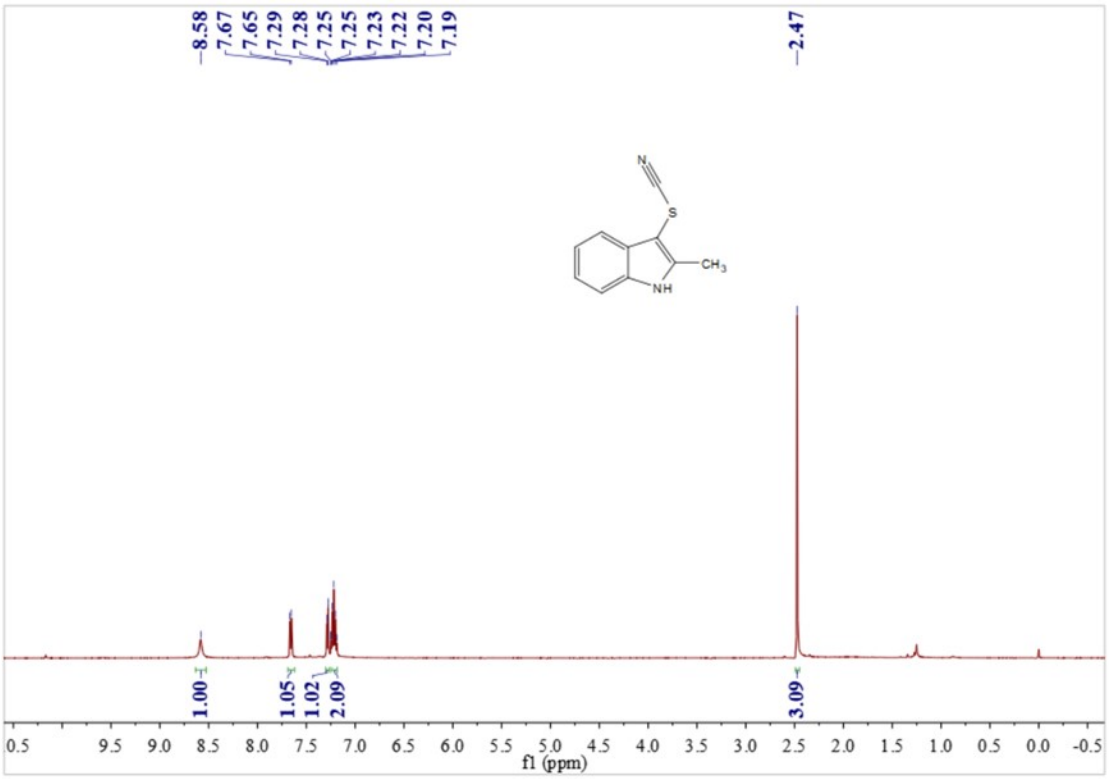
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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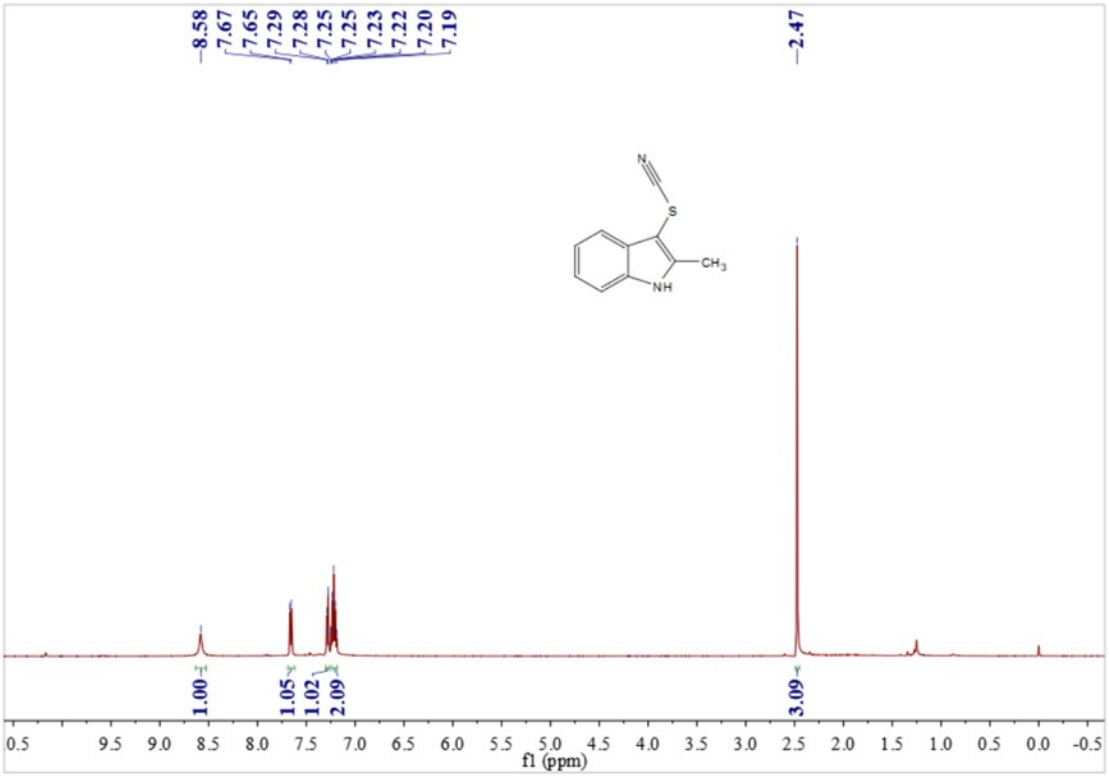
7.67
7.65
7.29
7.28
7.25
7.25
7.23
7.22
7.20
7.19
2.47
N
S
CH3
NH
1.00
1.05
1.02
2.09
3.09
0.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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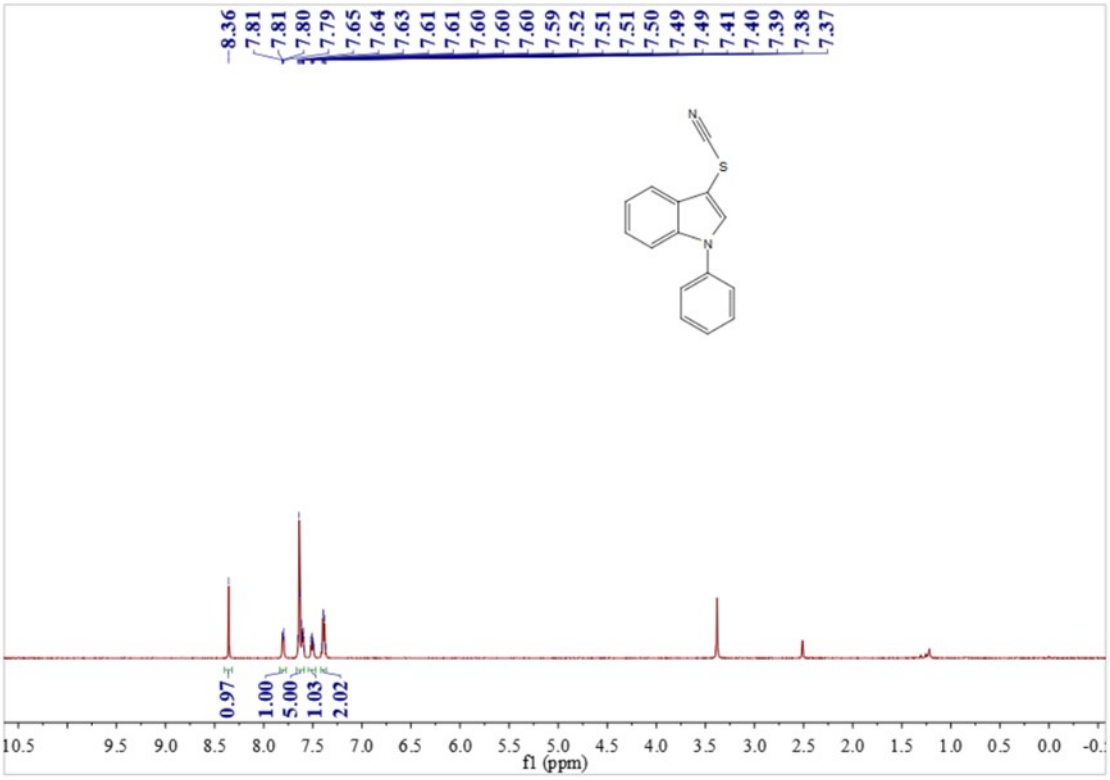
7.67
7.65
7.29
7.28
7.25
7.25
7.23
7.22
7.20
7.19
2.47
N
S
CH3
NH
1.00
1.05
1.02
2.09
3.09
0.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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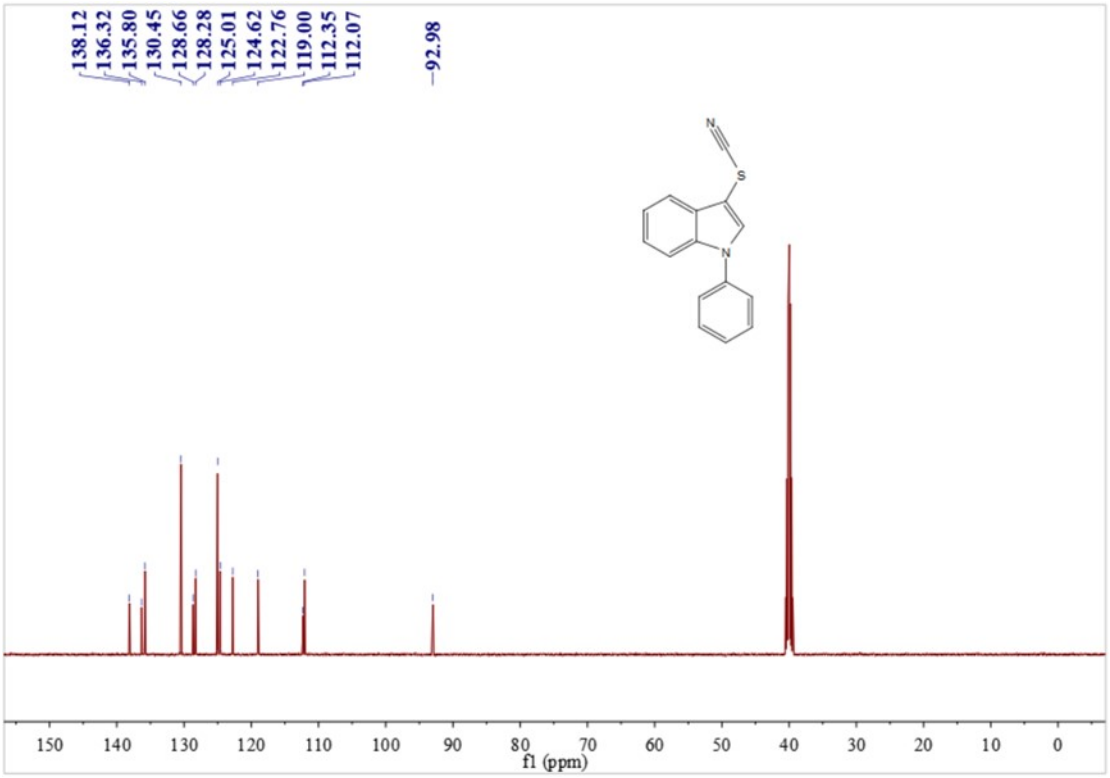
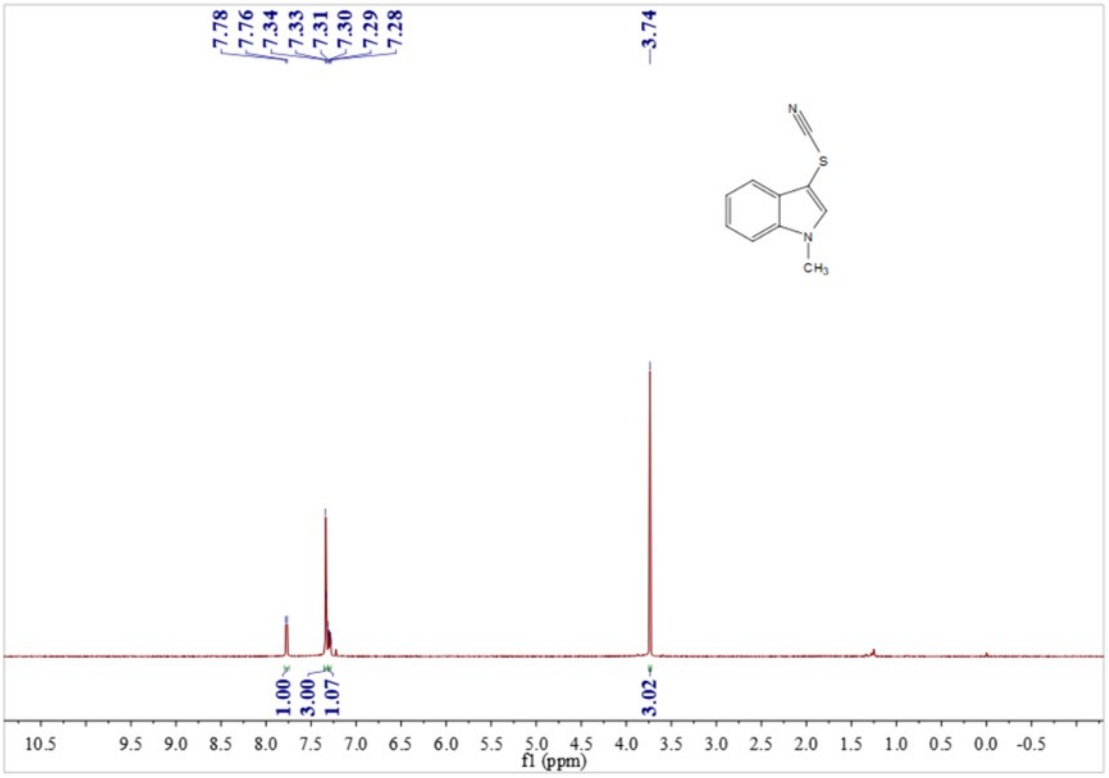
7.65
7.64
7.63
7.61
7.61
7.60
7.60
7.60
7.59
7.52
7.51
7.51
7.50
7.49
7.49
7.41
7.40
7.39
7.38
7.37
N
S
N
0.97
1.00
5.00
1.03
2.02
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


138.12
136.32
135.80
130.45
128.66
128.28
125.01
124.62
122.76
119.00
112.35
112.07
92.98
N
S
N
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.76
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7.33
7.31
7.30
7.29
7.28
3.74
N
S
N
CH3
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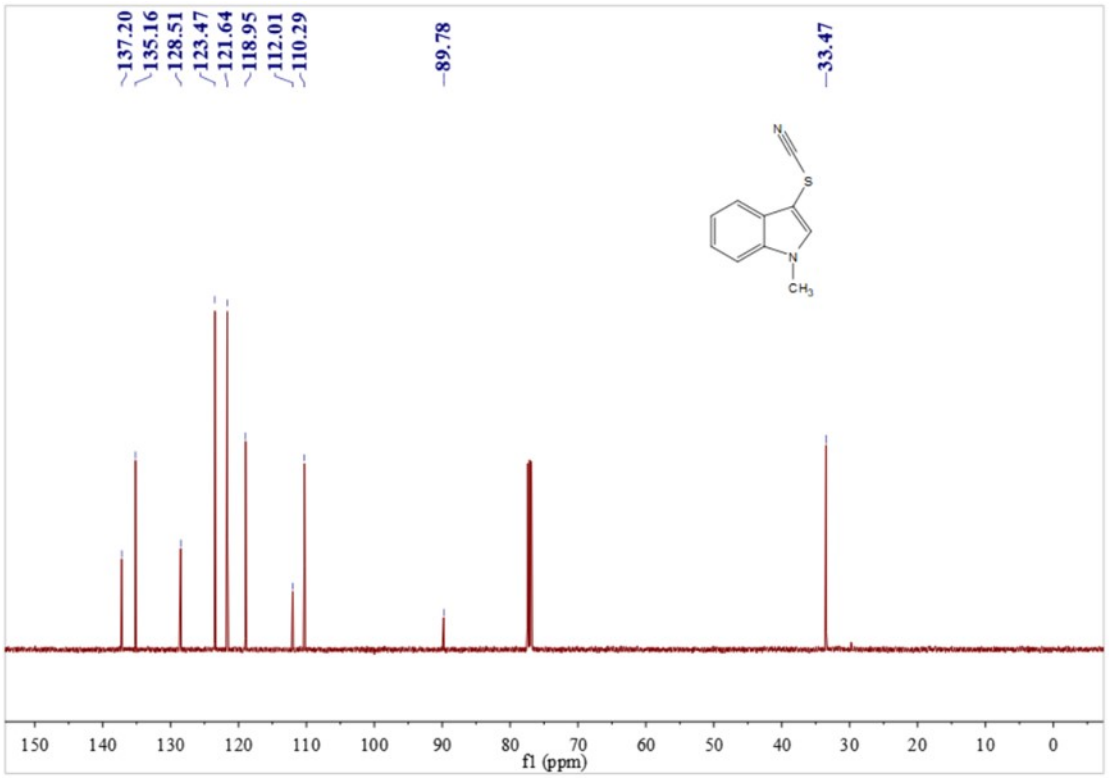
3.00
1.07
3.02
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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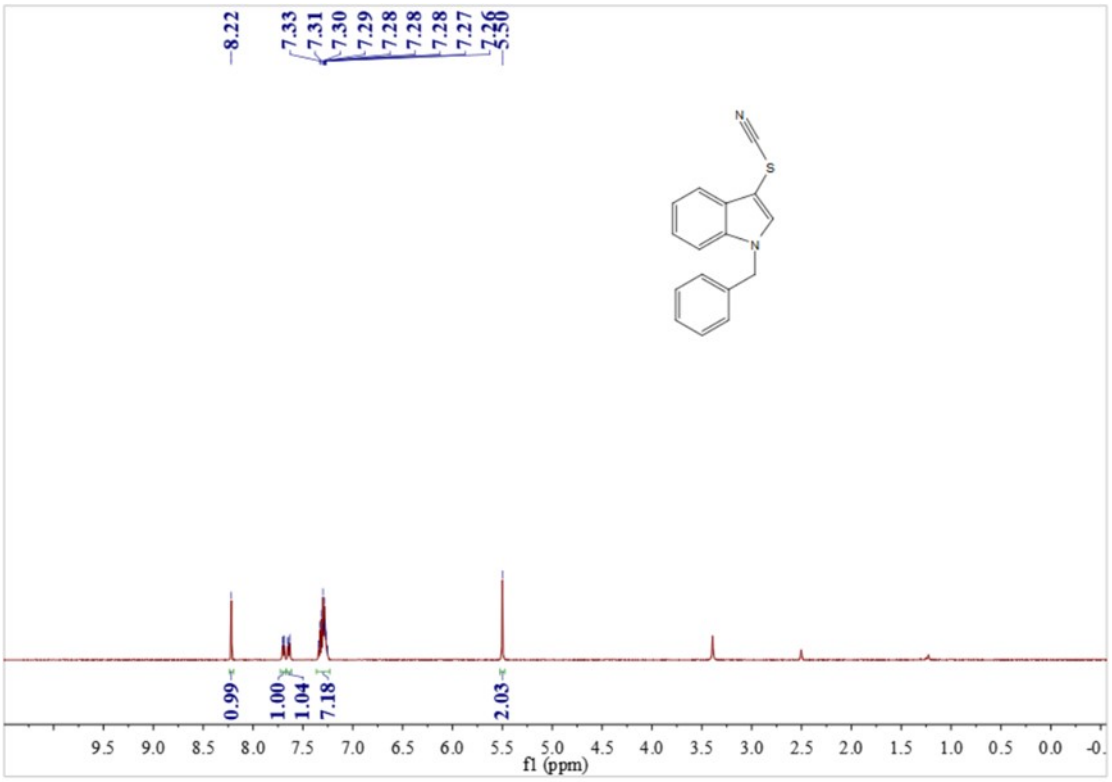
135.16
128.51
123.47
121.64
118.95
112.01
110.29
89.78
33.47
N
S
N
CH3
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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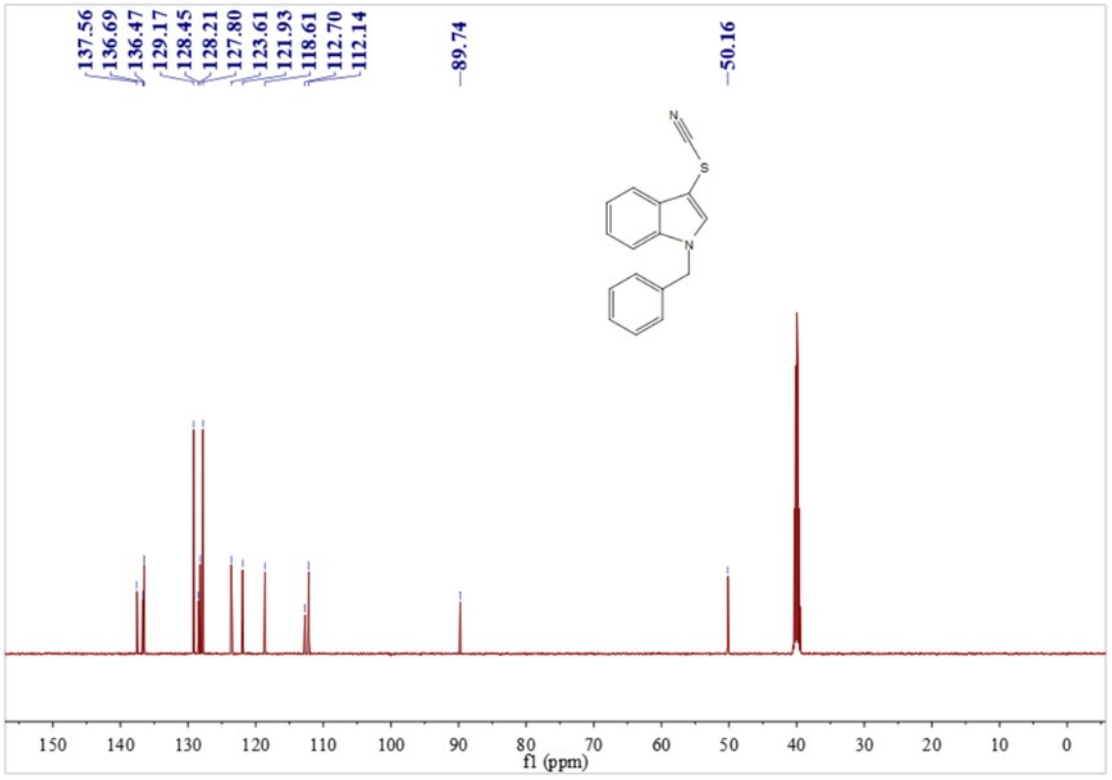
7.33
7.31
7.30
7.29
7.28
7.28
7.28
7.27
7.26
5.50
N
S
N
0.99
1.00
1.04
7.18
2.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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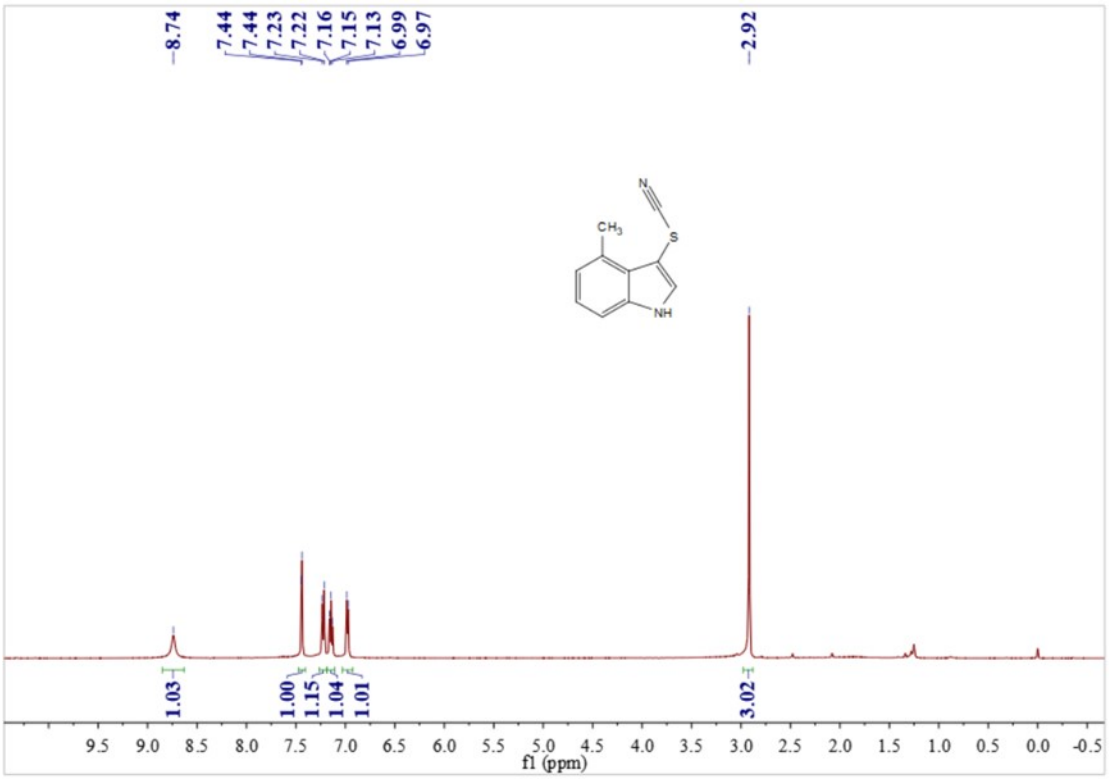
136.69
136.47
129.17
128.45
128.21
127.80
123.61
121.93
118.61
112.70
112.14
89.74
50.16
N
S
N
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.74
7.44
7.44
7.23
7.22
7.16
7.15
7.13
6.99
6.97
2.92
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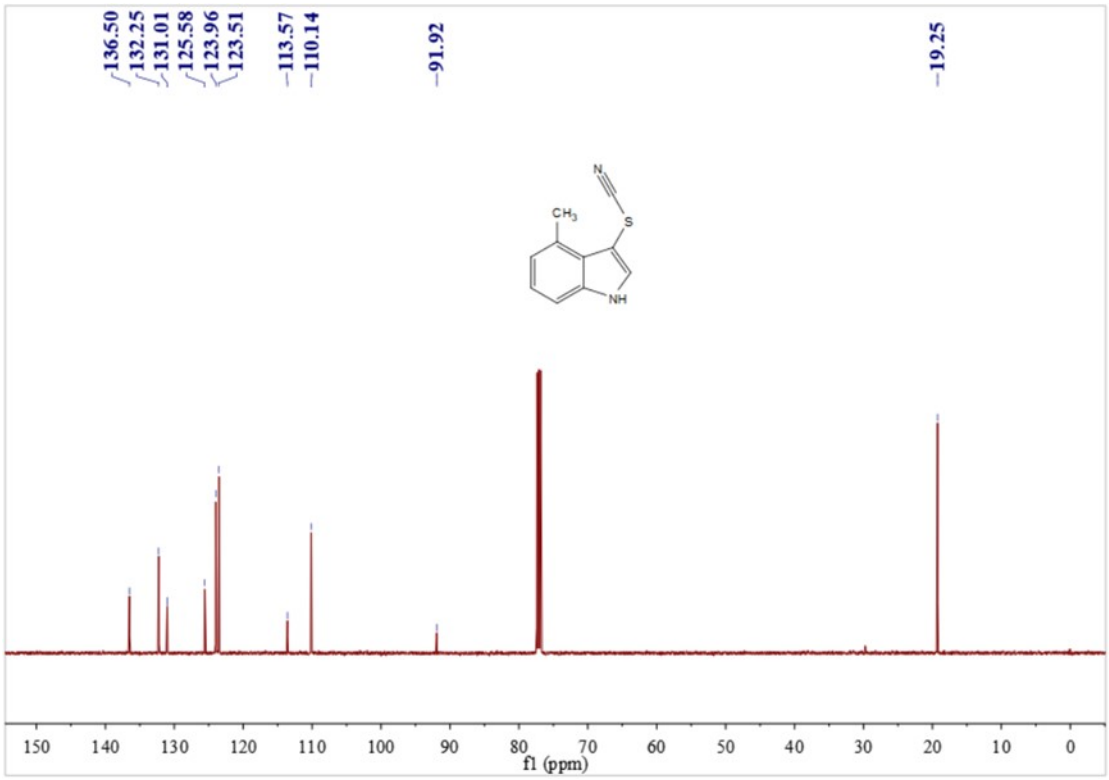
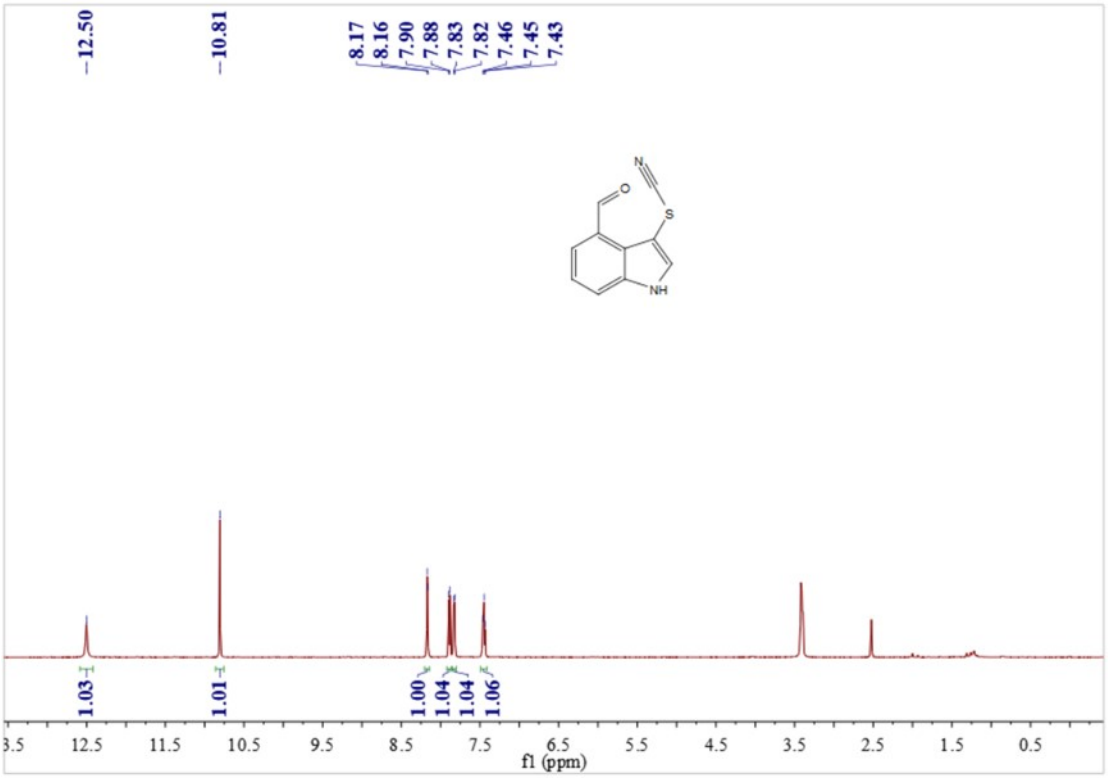
S
CH3
NH
1.03
1.00
1.15
1.04
1.01
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


136.50
132.25
131.01
125.58
123.96
123.51
113.57
110.14
91.92
19.25
N
S
CH3
NH
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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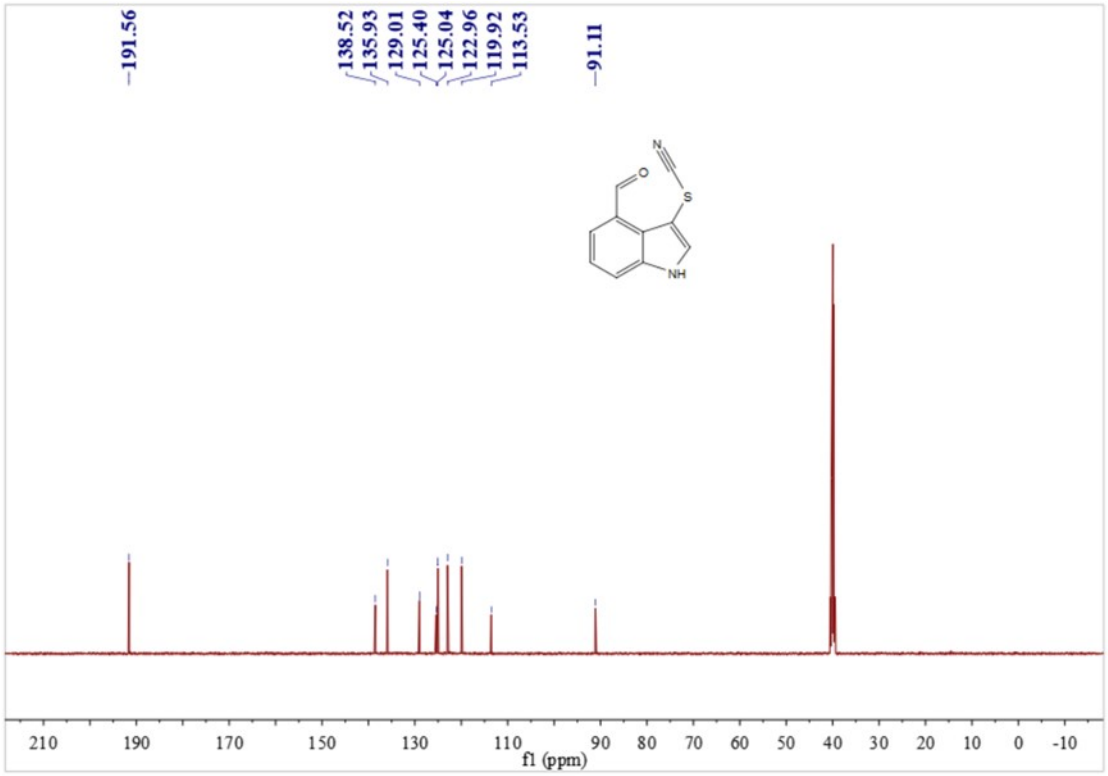
10.81
8.17
8.16
7.90
7.88
7.83
7.82
7.46
7.45
7.43
O
N
S
NH
1.03
1.01
1.00
1.04
1.04
1.06
3.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


191.56
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135.93
129.01
125.40
125.04
122.96
119.92
113.53
91.11
O
N
S
NH
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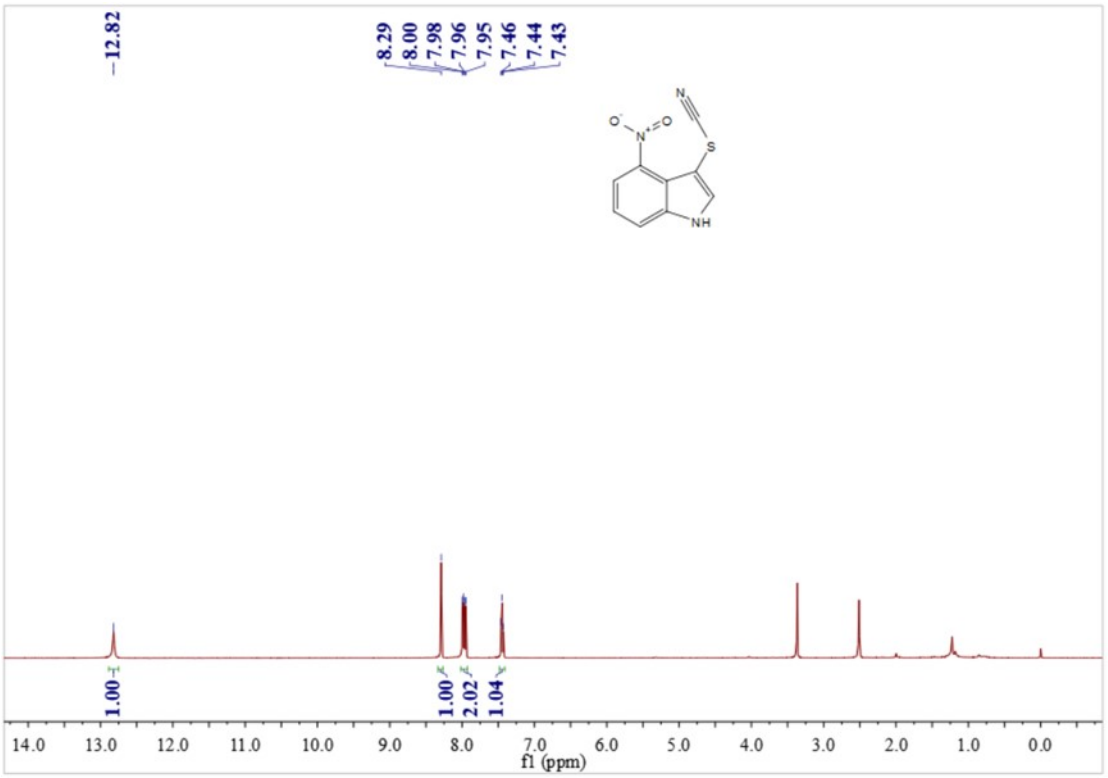
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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8.00
7.98
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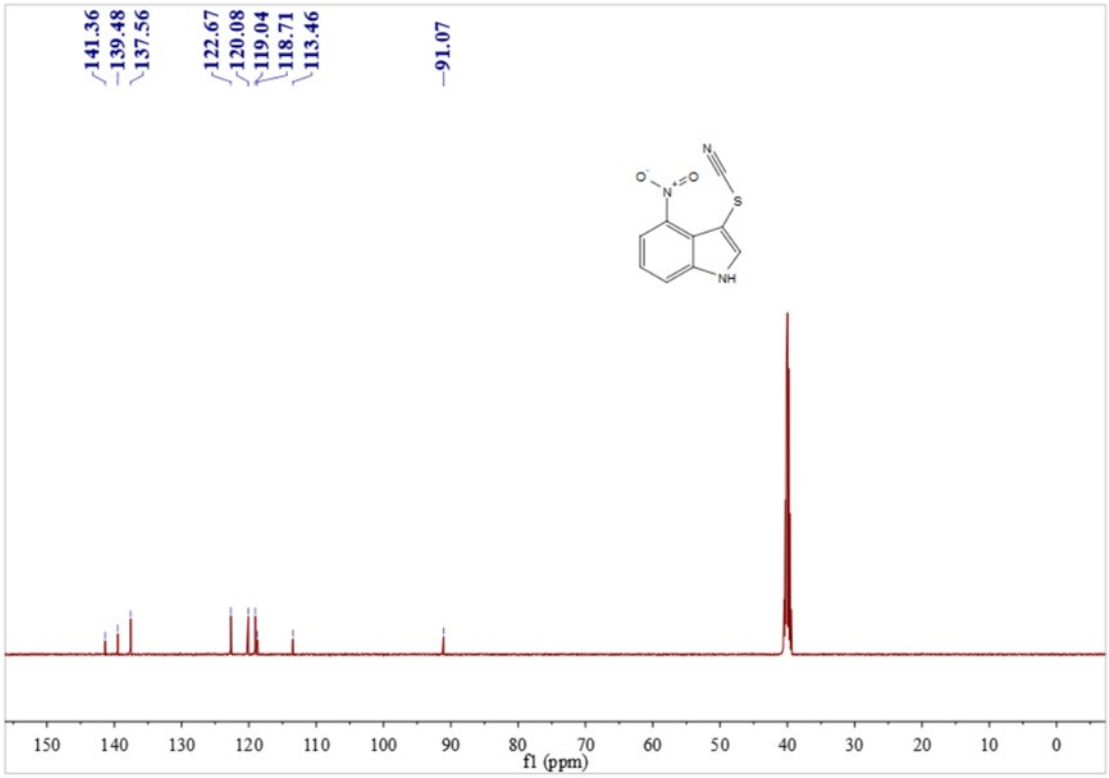
7.95
7.46
7.44
7.43
1.00
1.00
2.02
1.04
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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119.04
118.71
113.46
91.07
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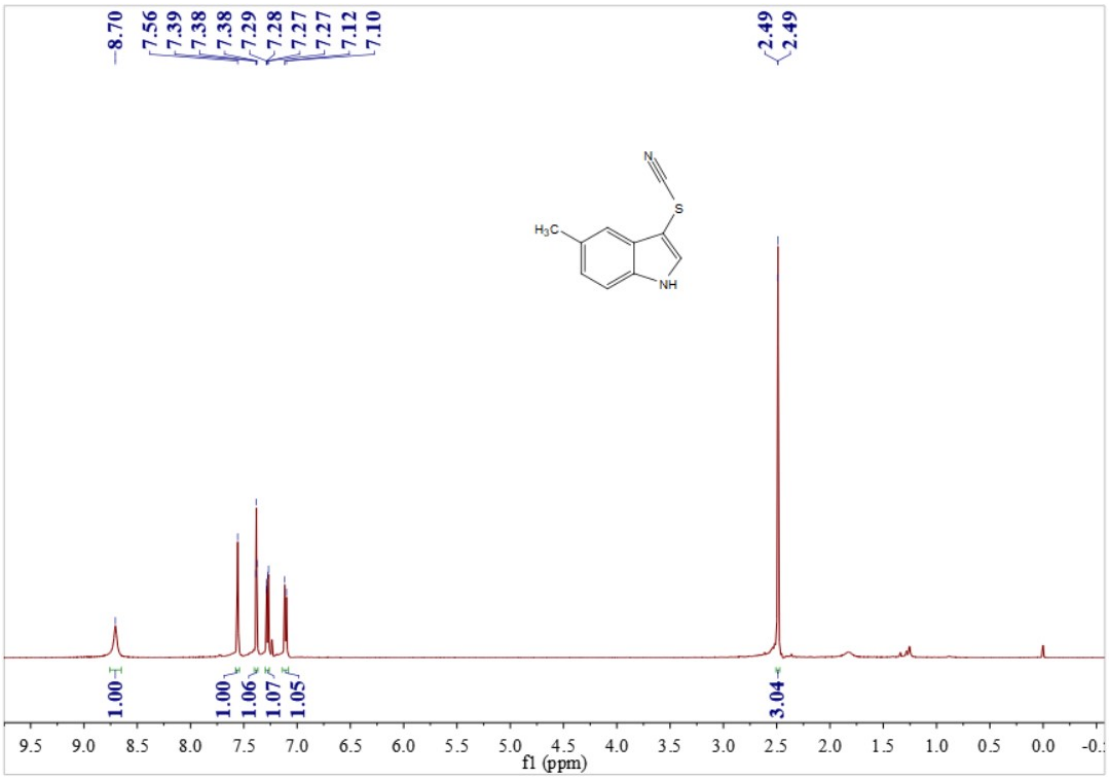
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.27
7.27
7.12
7.10
2.49
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H3C
NH
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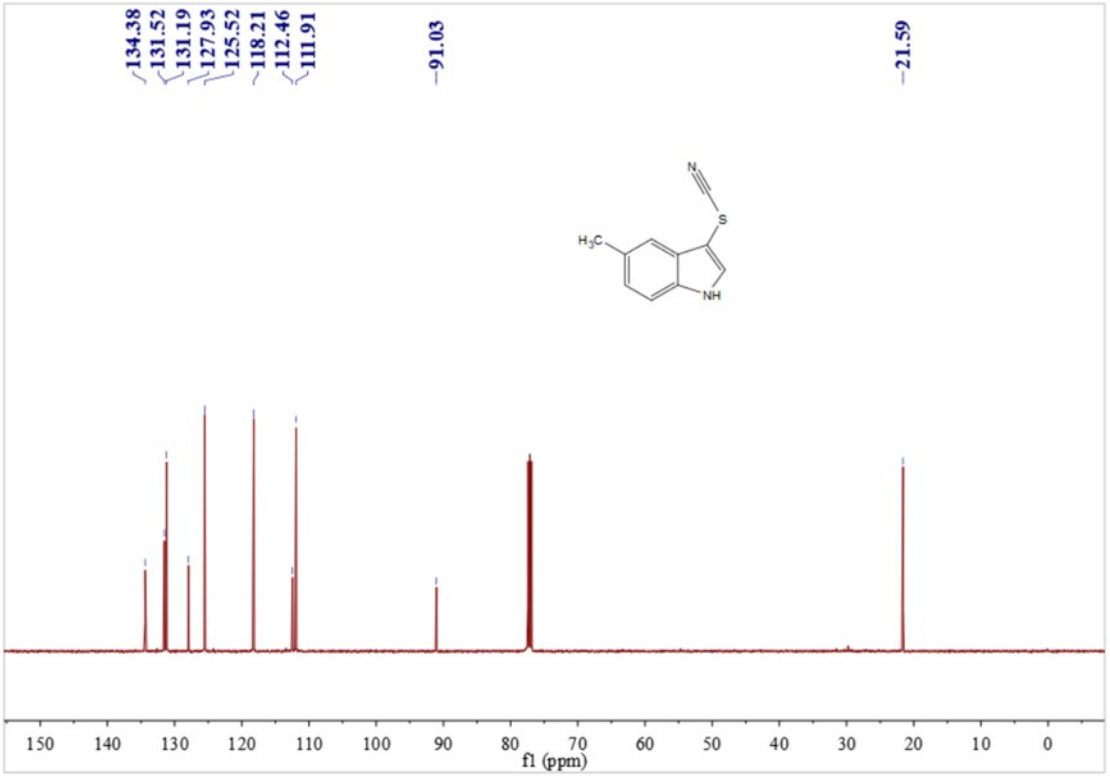
1.00
1.06
1.07
1.05
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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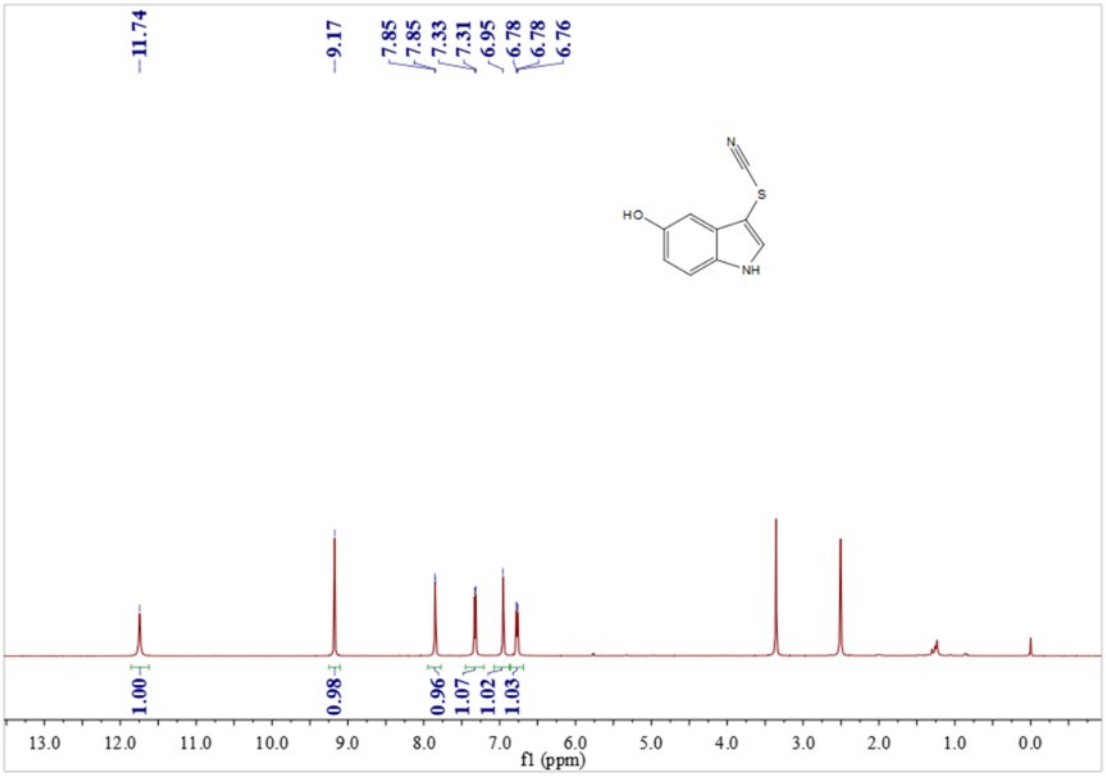
131.19
127.93
125.52
118.21
112.46
111.91
91.03
21.59
N
S
H3C
NH
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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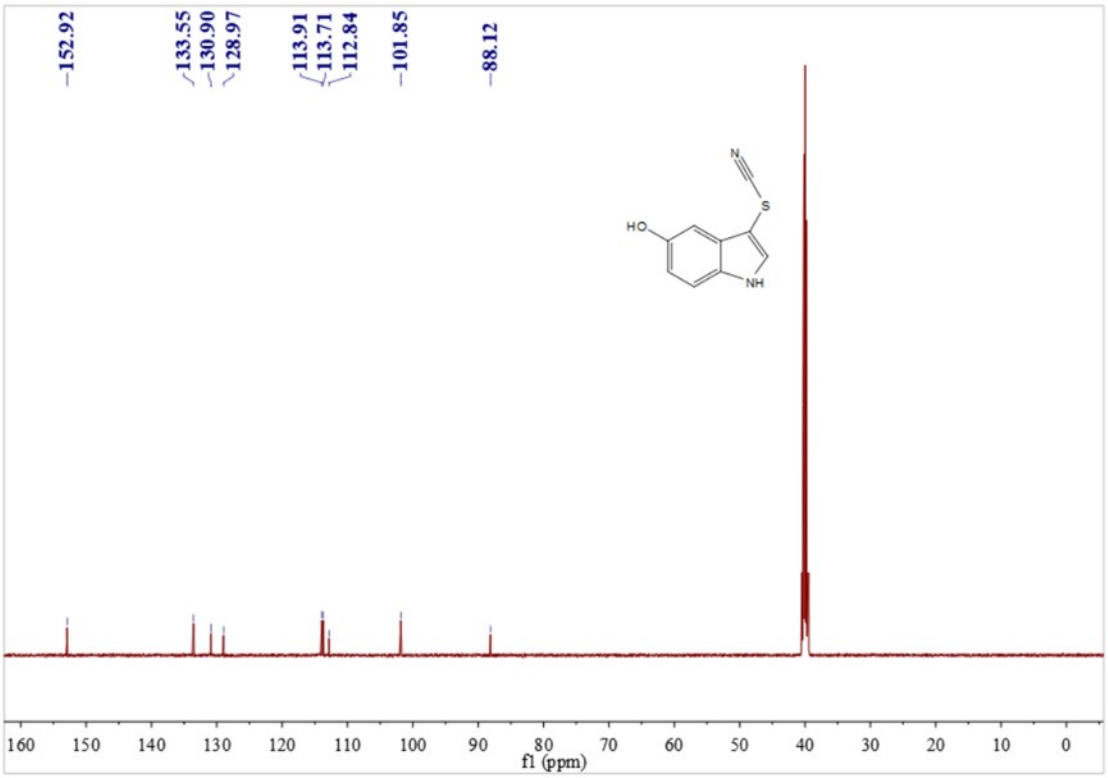
9.17
7.85
7.85
7.33
7.31
6.95
6.78
6.78
6.76
N
S
HO
NH
1.00
0.98
0.96
1.07
1.02
1.03
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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112.84
101.85
88.12
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S
HO
NH
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90
80
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60
50
40
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20
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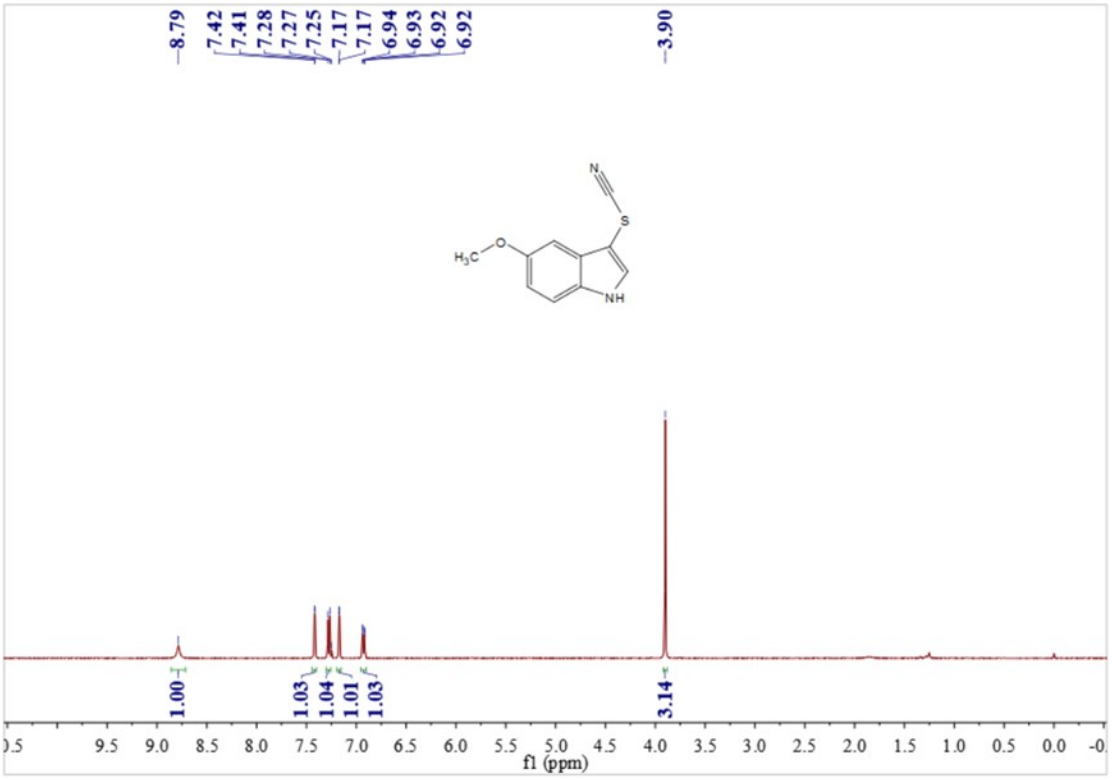
0
f1 (ppm)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7.17
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6.92
6.92
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S
H3C
O
NH
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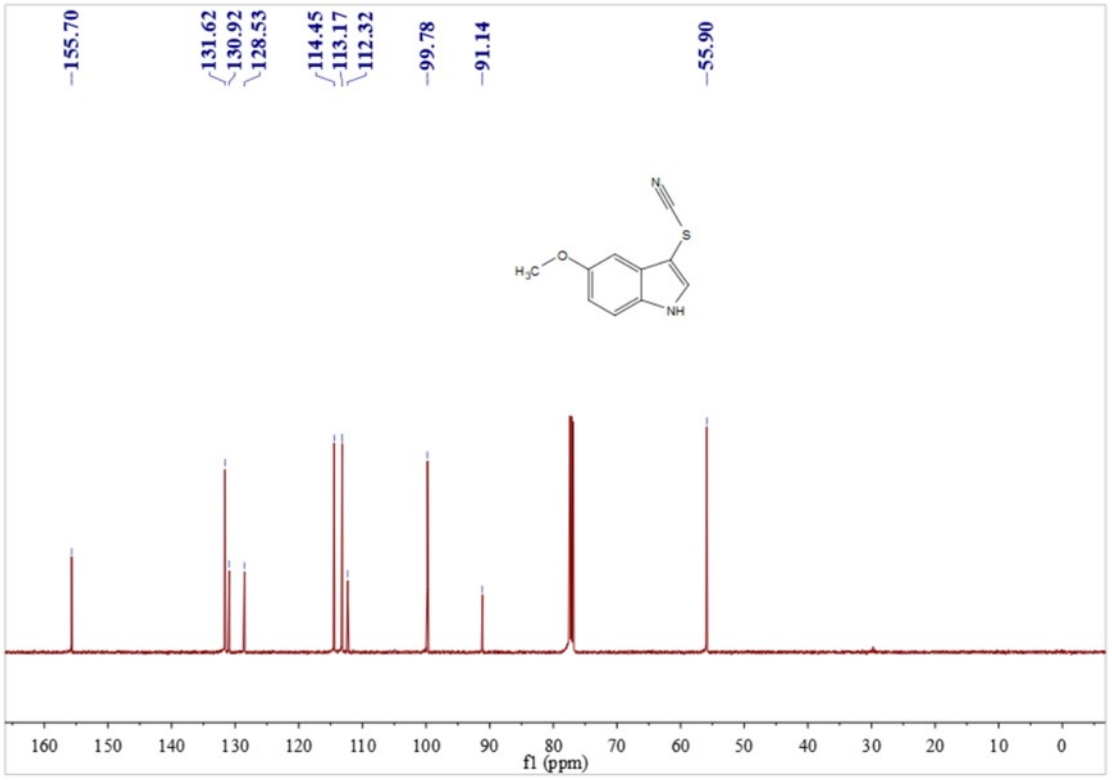
1.03
1.04
1.01
1.03
3.14
f1 (ppm)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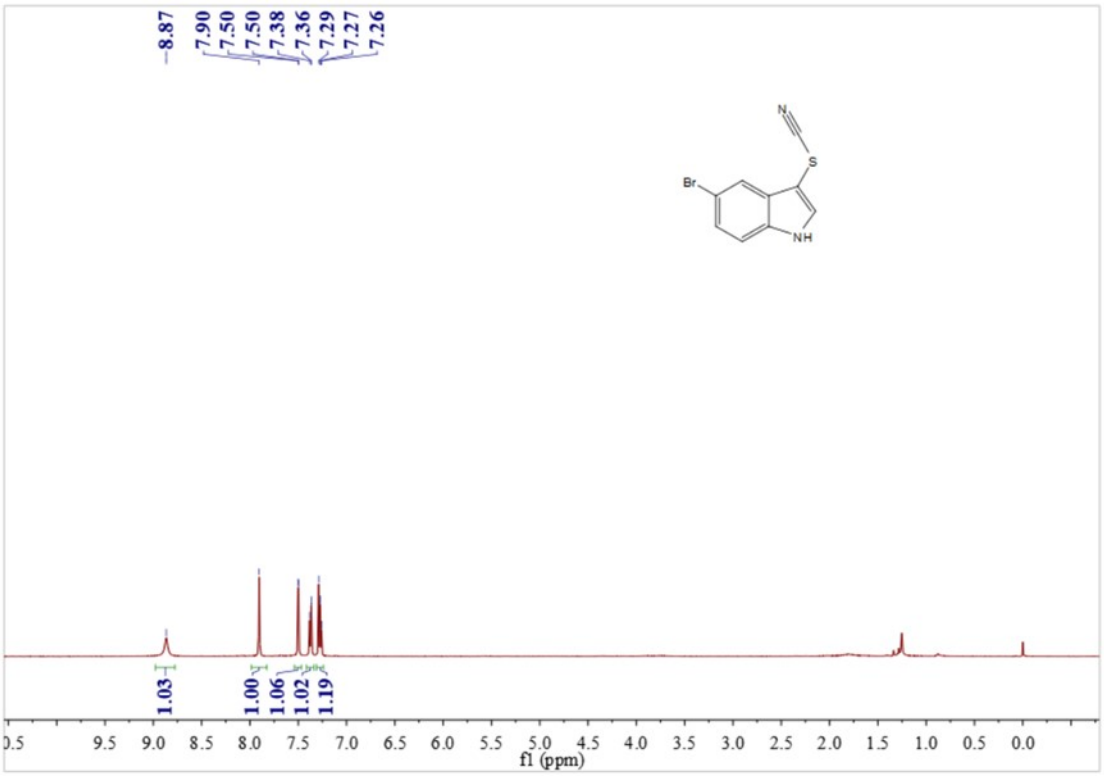
113.17
112.32
99.78
91.14
55.90
N
S
H3C
O
NH
f1 (ppm)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7.90
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7.50
7.38
7.36
7.29
7.27
7.26
N
S
Br
NH
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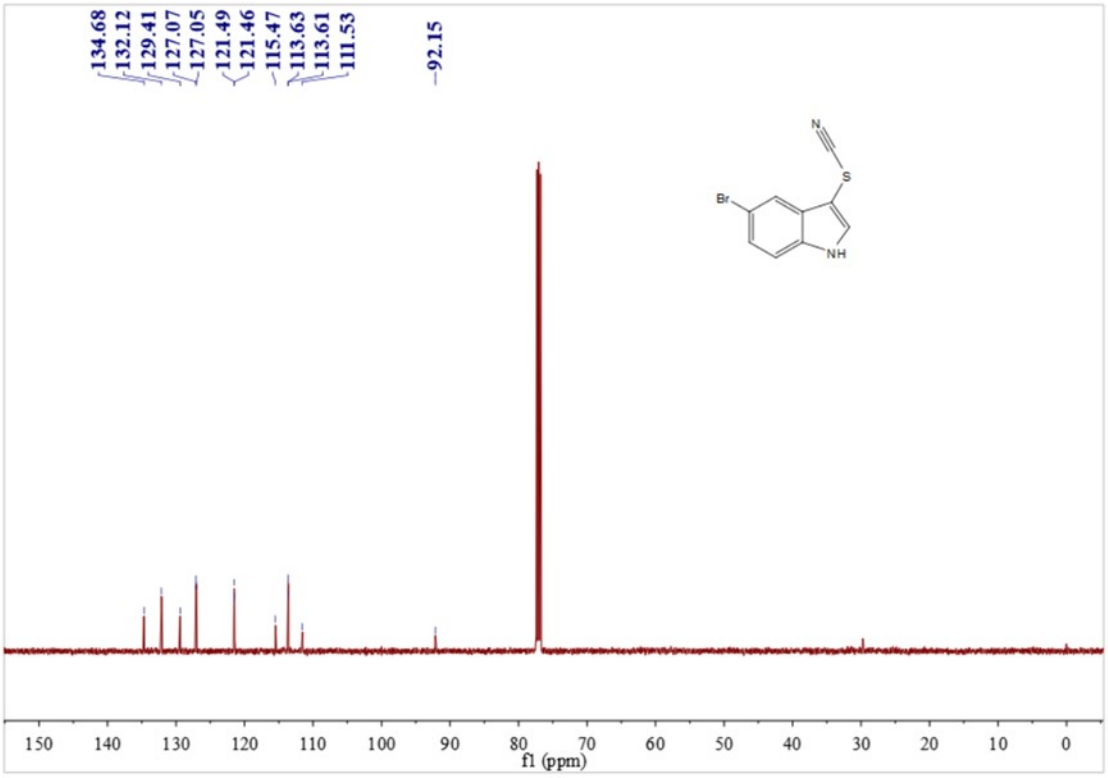
1.00
1.06
1.02
1.19
f1 (ppm)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115.47
113.63
113.61
111.53
92.15
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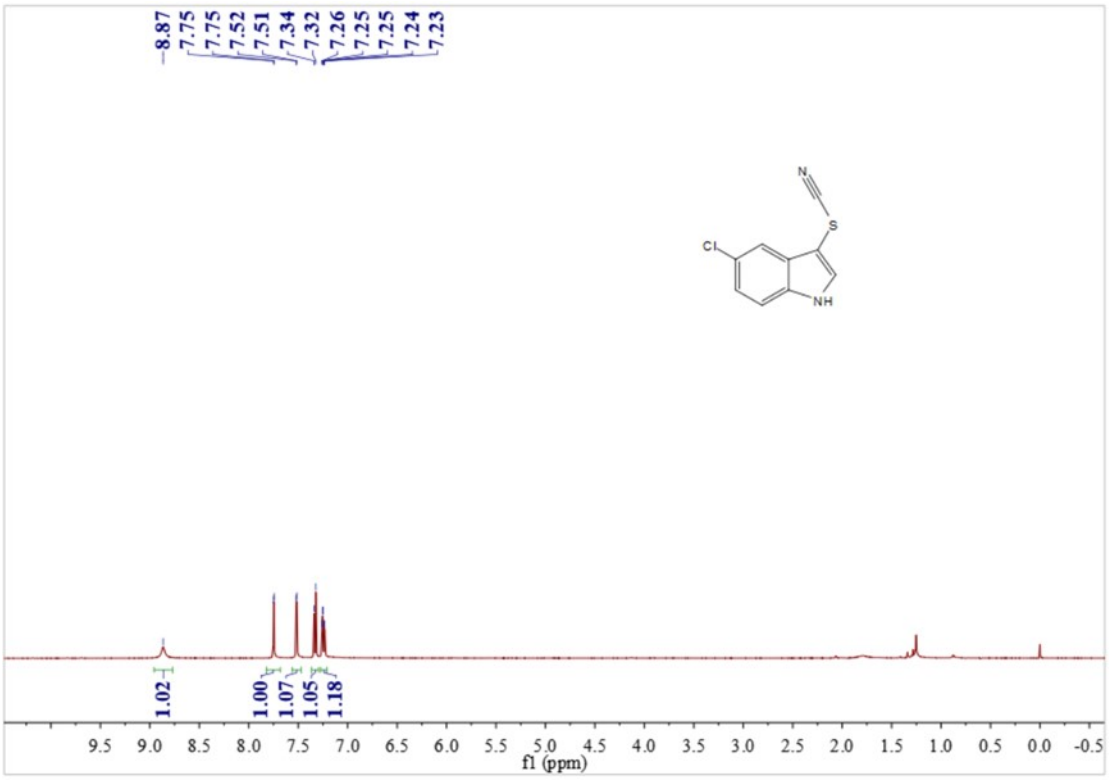
S
Br
NH
f1 (ppm)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7.25
7.24
7.23
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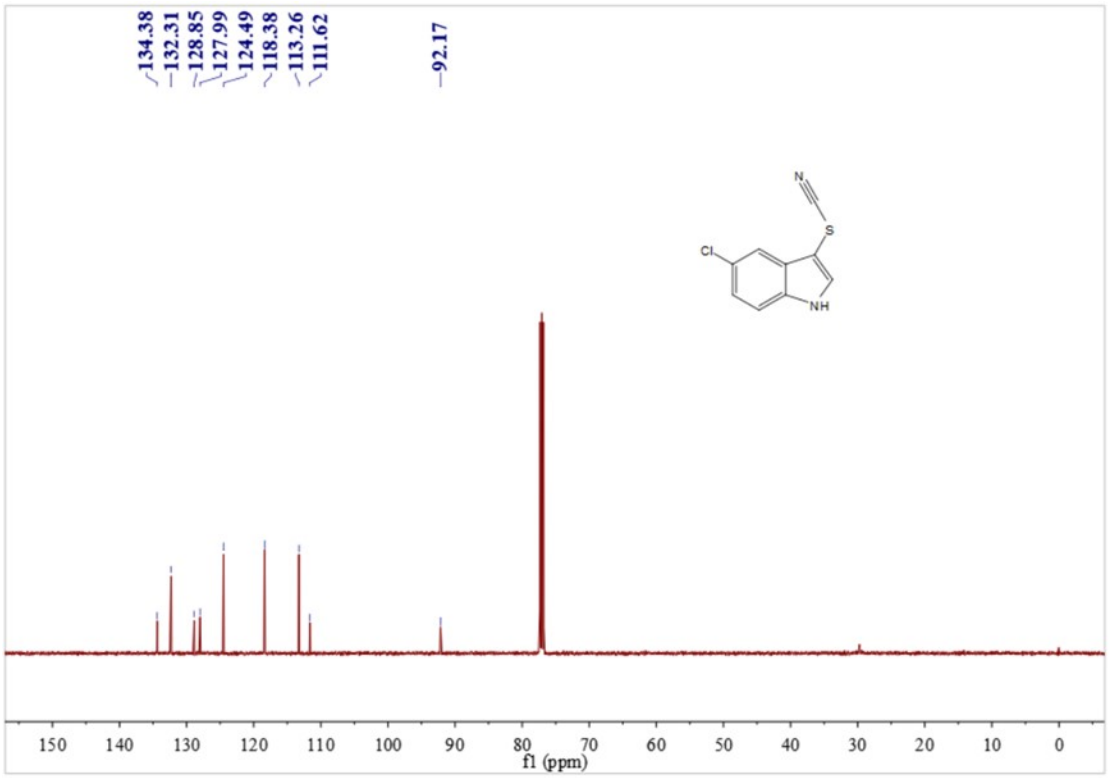
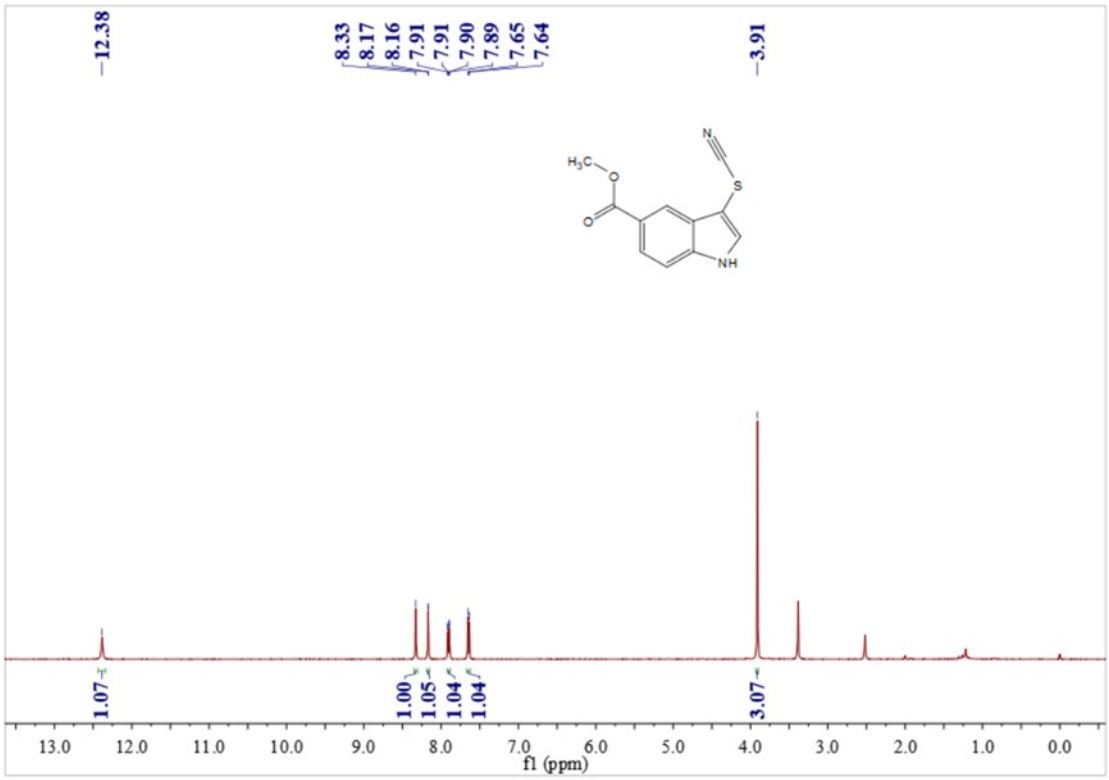
S
Cl
NH
1.02
1.00
1.07
1.05
1.18
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


134.38
132.31
128.85
127.99
124.49
118.38
113.26
111.62
92.17
N
S
Cl
NH
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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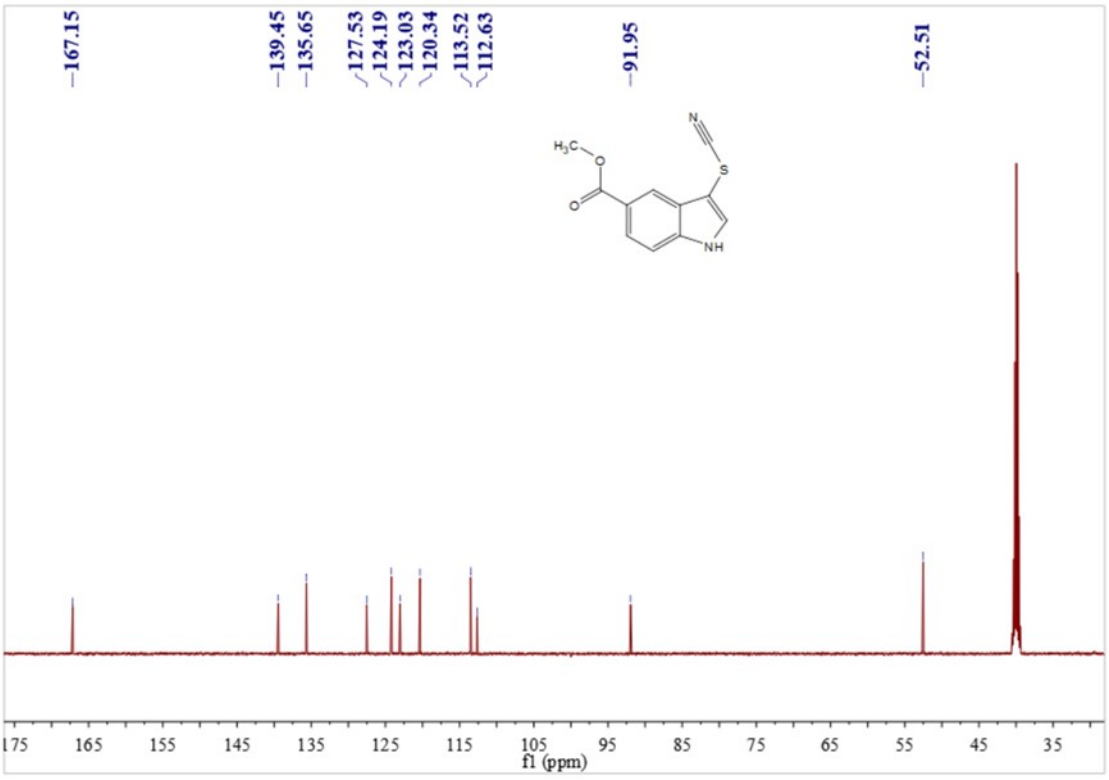
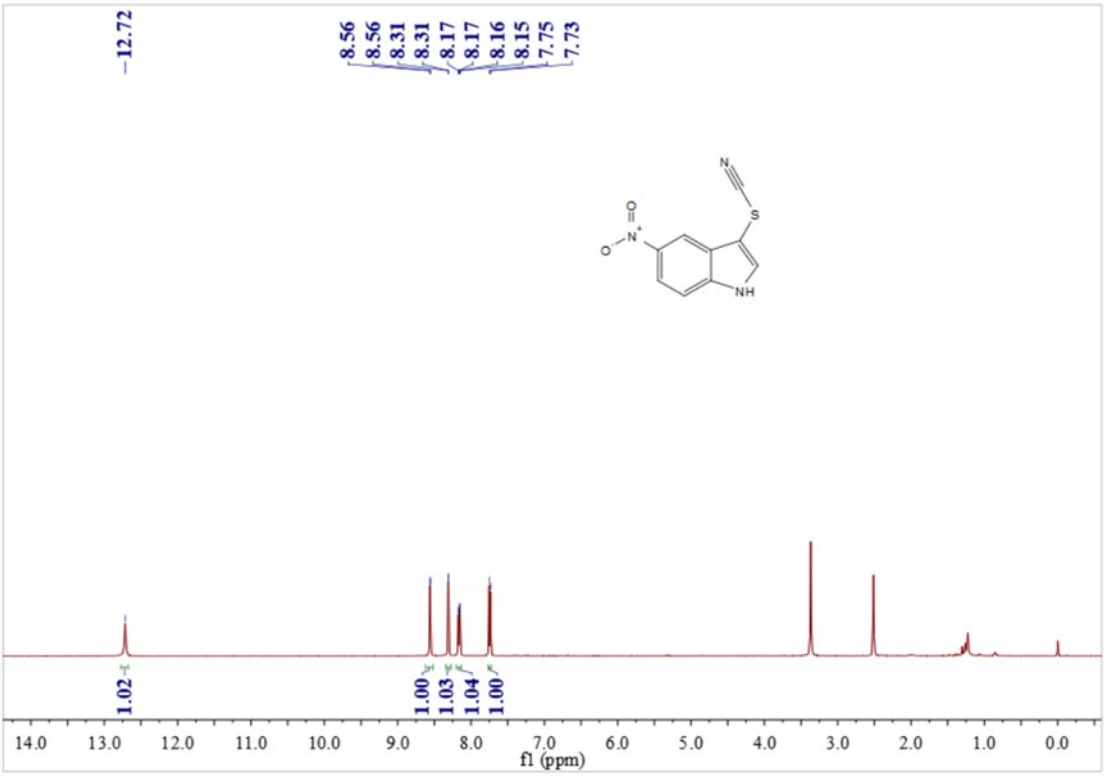
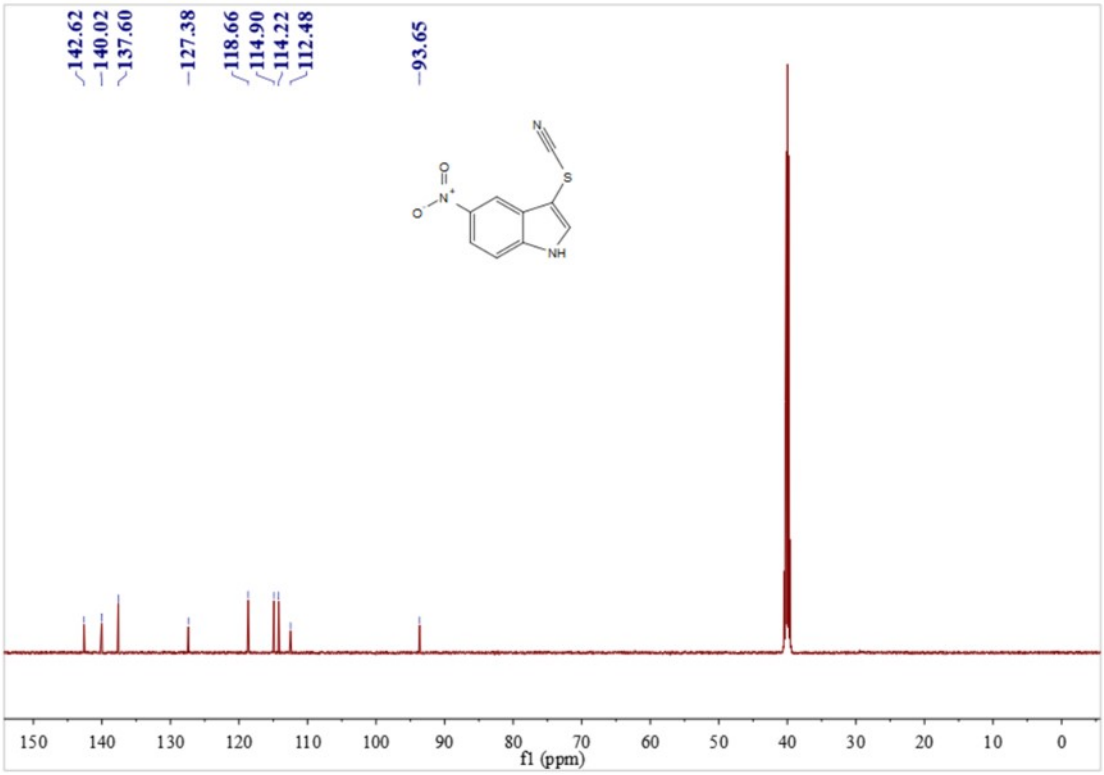
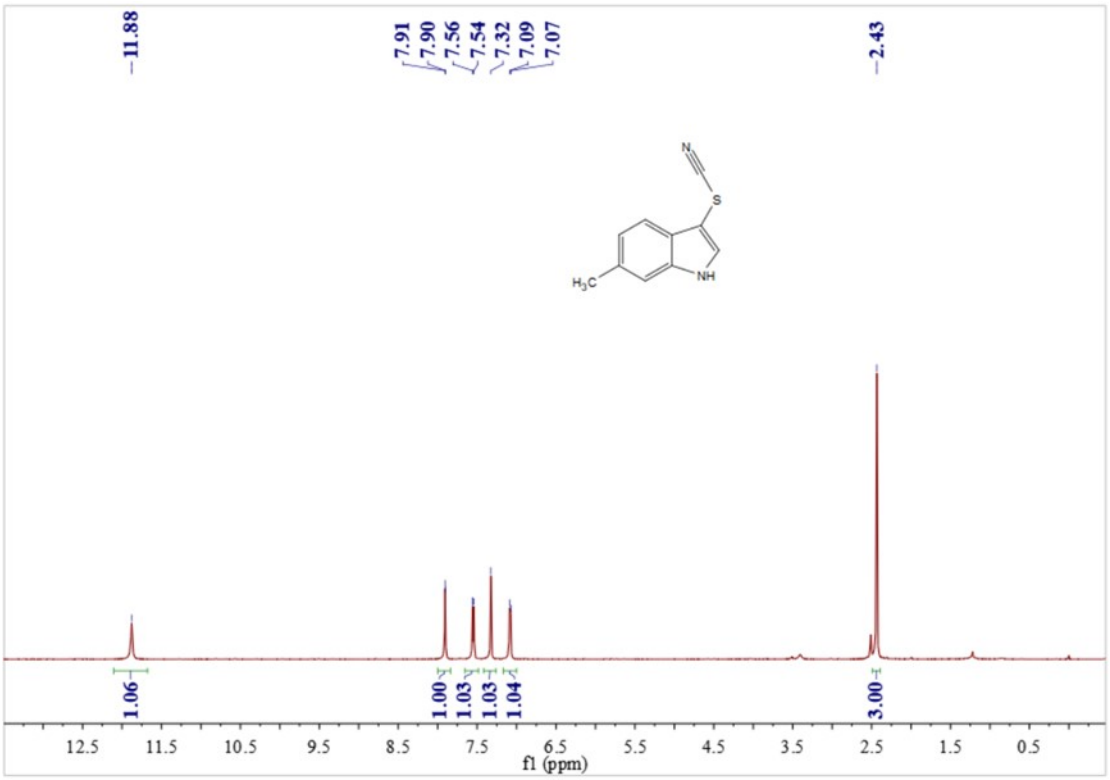
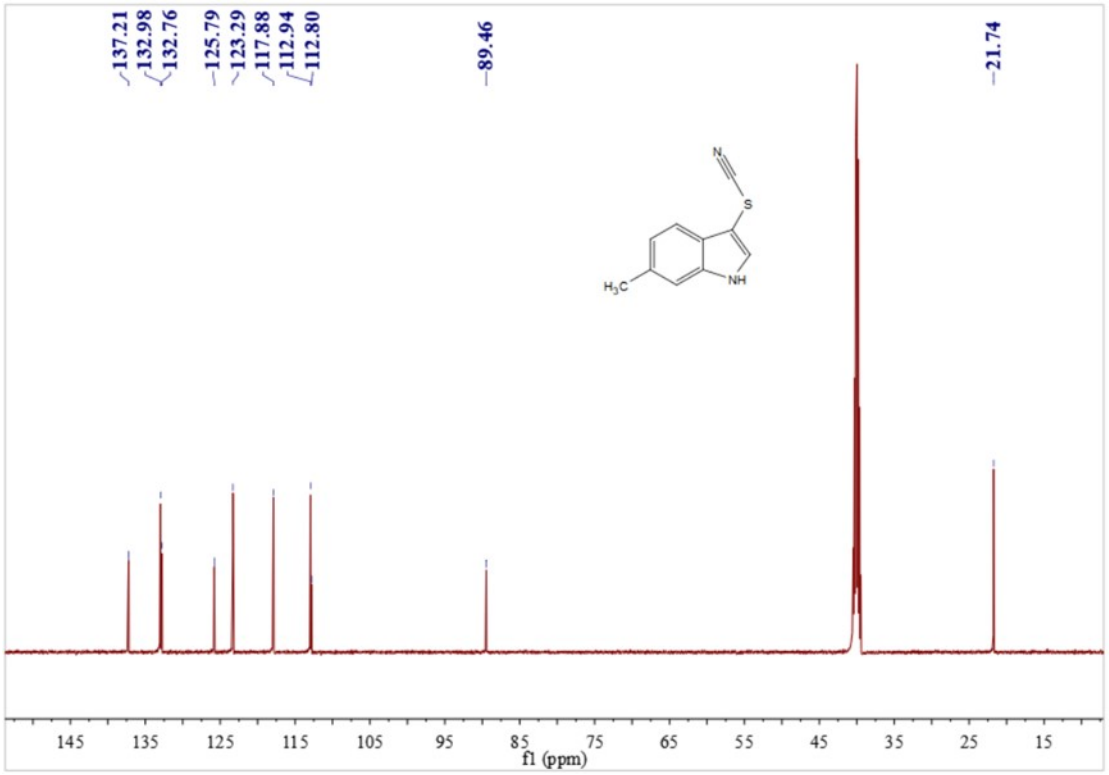
8.33
8.17
8.16
7.91
7.91
7.90
7.89
7.65
7.64
3.91
1.07
1.00
1.05
1.04
1.04
3.07
f1 (ppm)

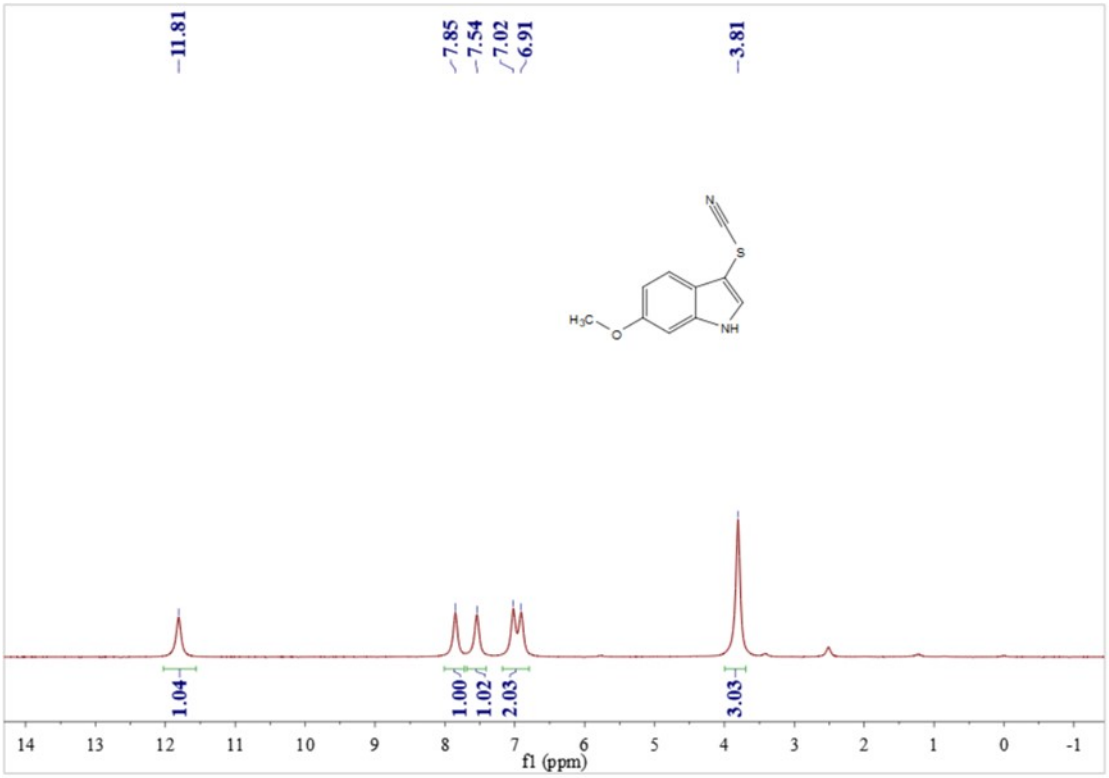

167.15
139.45
135.65
127.53
124.19
123.03
120.34
113.52
112.63
91.95
52.51
f1 (ppm)

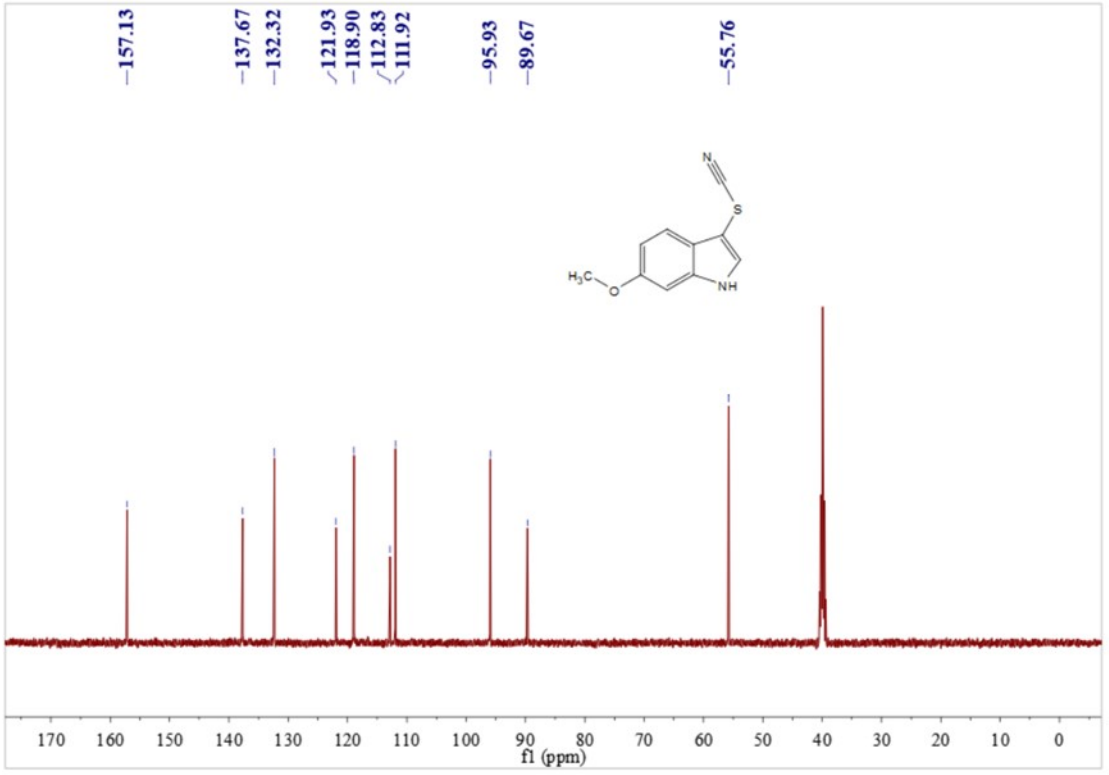

12.72
8.56
8.56
8.31
8.31
8.17
8.17
8.16
8.15
7.75
7.73
1.02
1.00
1.03
1.04
1.00
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

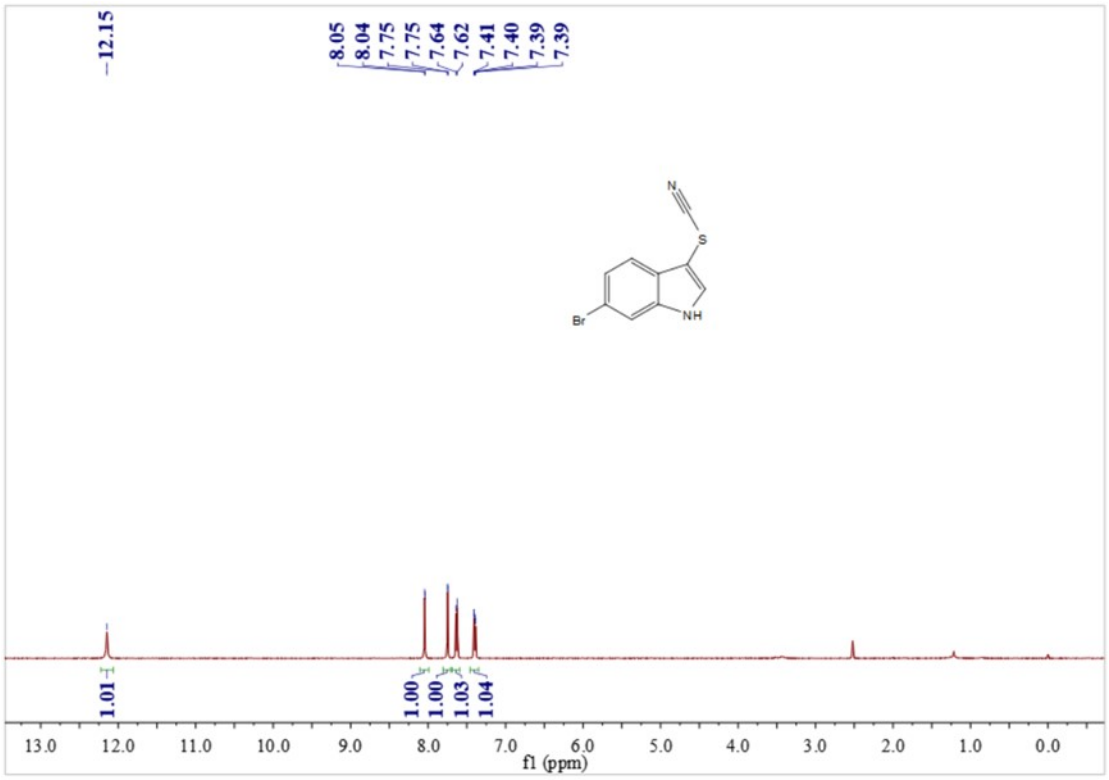

142.62
140.02
137.60
127.38
118.66
114.90
114.22
112.48
93.65
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

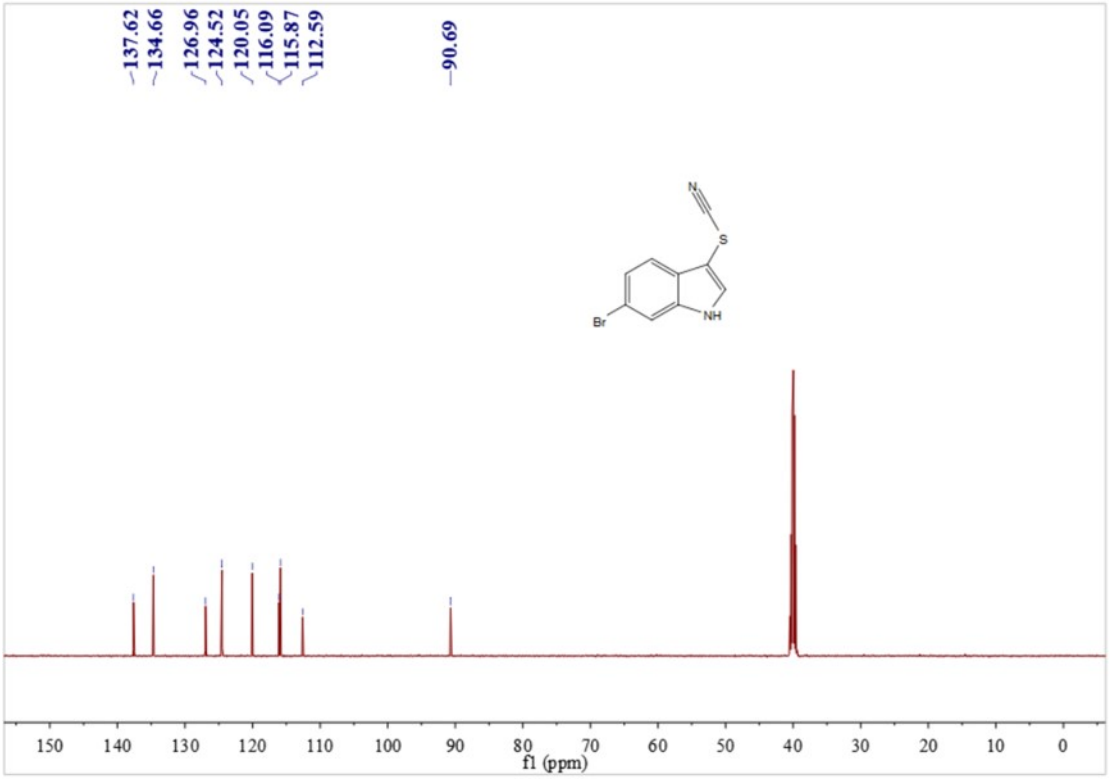

11.88
7.91
7.90
7.56
7.54
7.32
7.09
7.07
2.43
N
S
NH
H3C
1.06
1.00
1.03
1.03
1.04
3.00
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

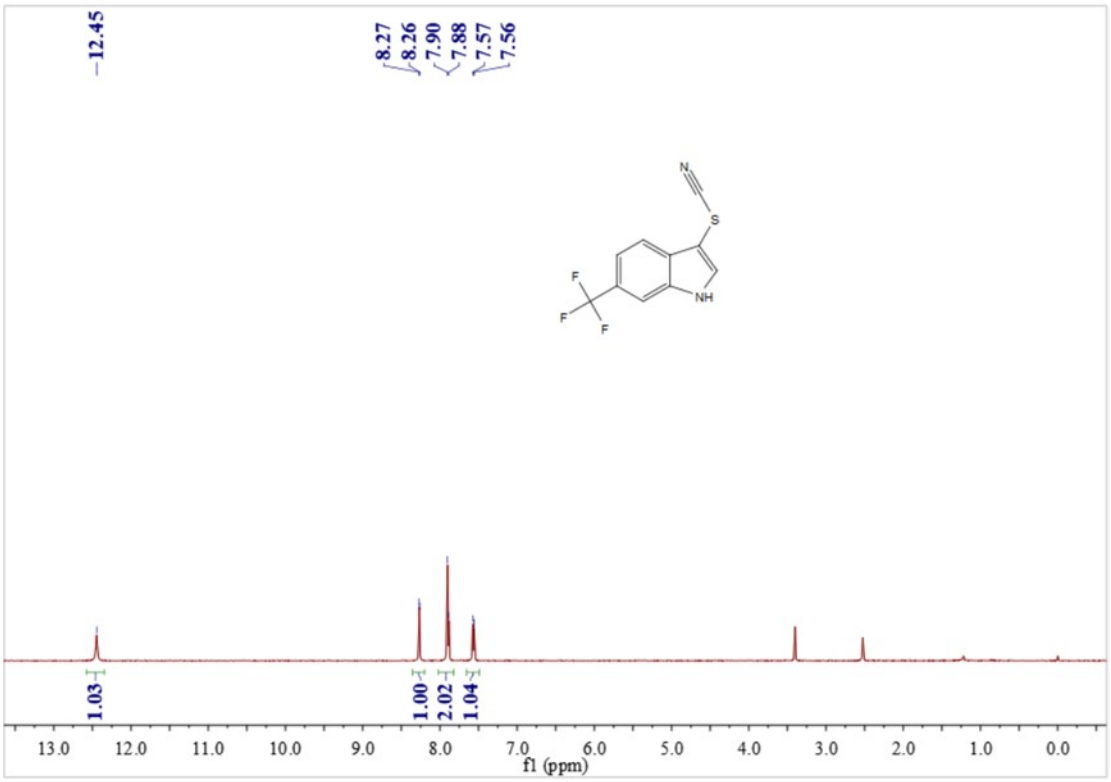

137.21
132.98
132.76
125.79
123.29
117.88
112.94
112.80
89.46
21.74
N
S
NH
H3C
145
135
125
115
105
95
85
75
65
55
45
35
25
15
f1 (ppm)

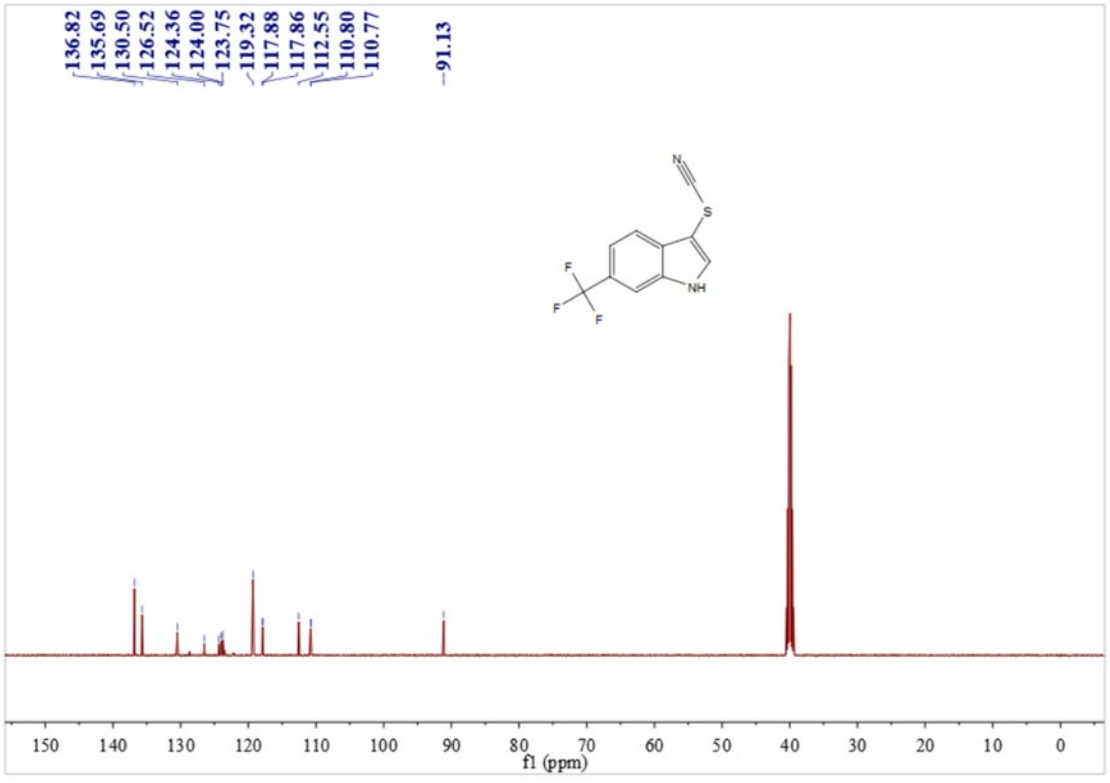

11.81
7.85
7.54
7.02
6.91
3.81
N
S
H3C
O
NH
1.04
1.00
1.02
2.03
3.03
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

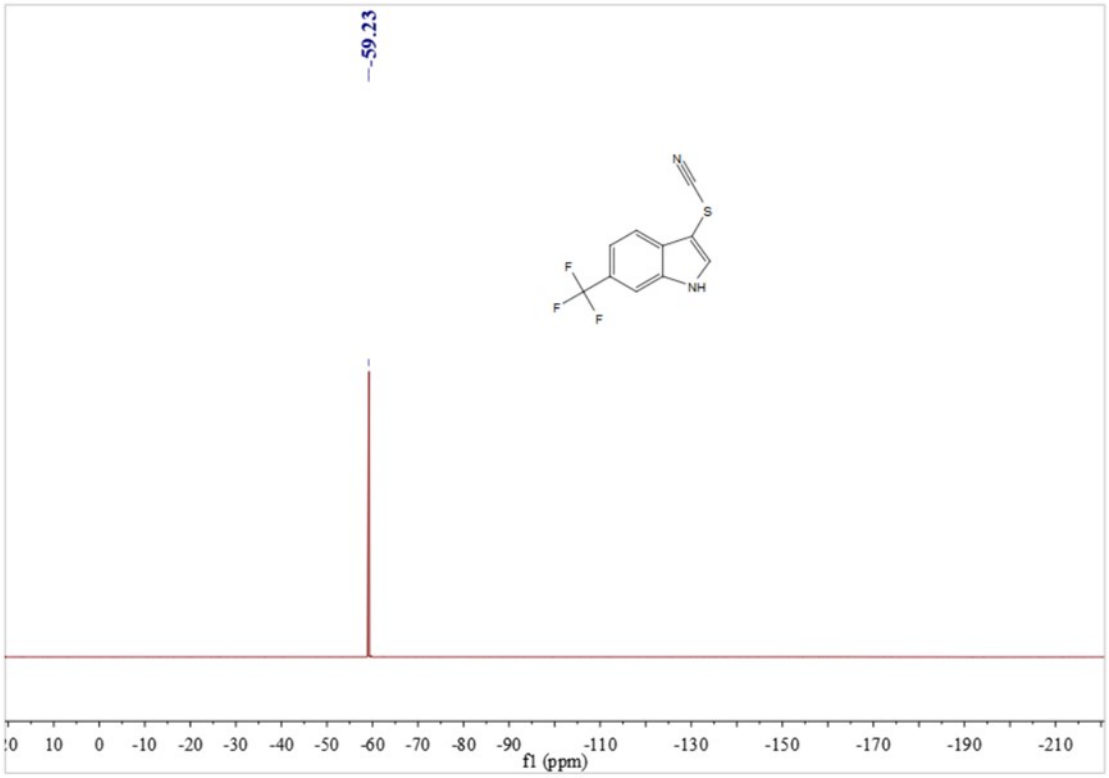

157.13
137.67
132.32
121.93
118.90
112.83
111.92
95.93
89.67
55.76
N
S
H3C
O
NH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

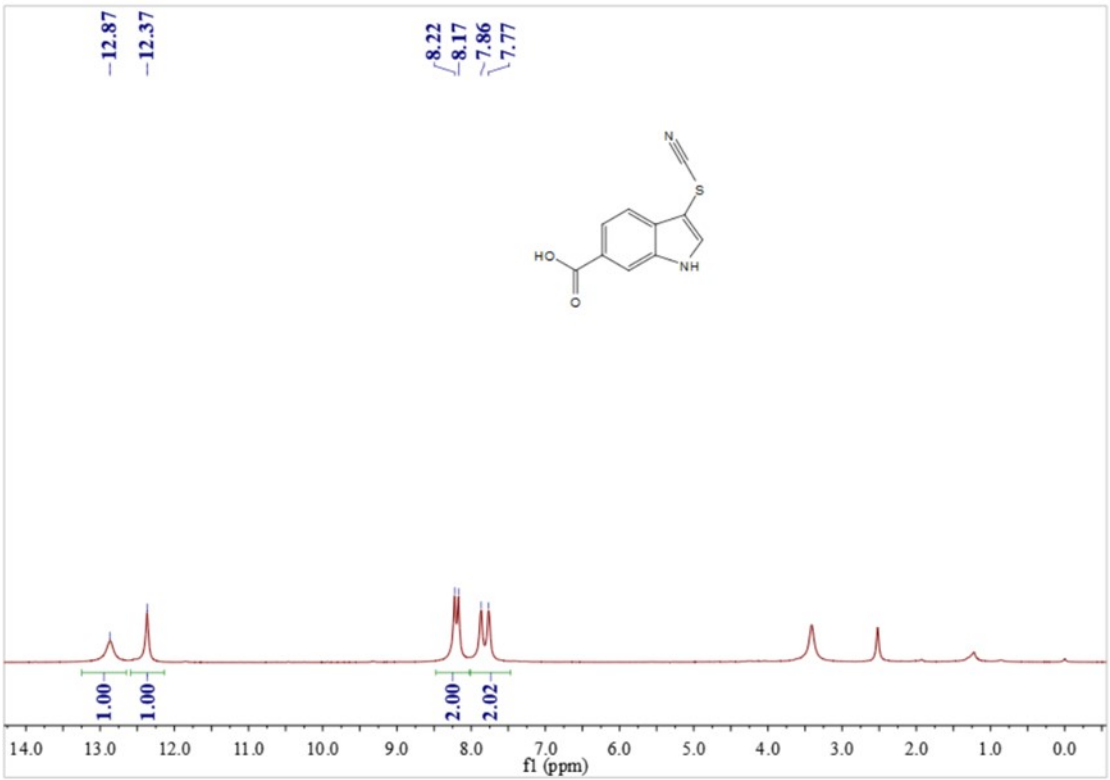

12.15
8.05
8.04
7.75
7.75
7.64
7.62
7.41
7.40
7.39
7.39
N
S
Br
NH
1.01
1.00
1.00
1.03
1.04
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

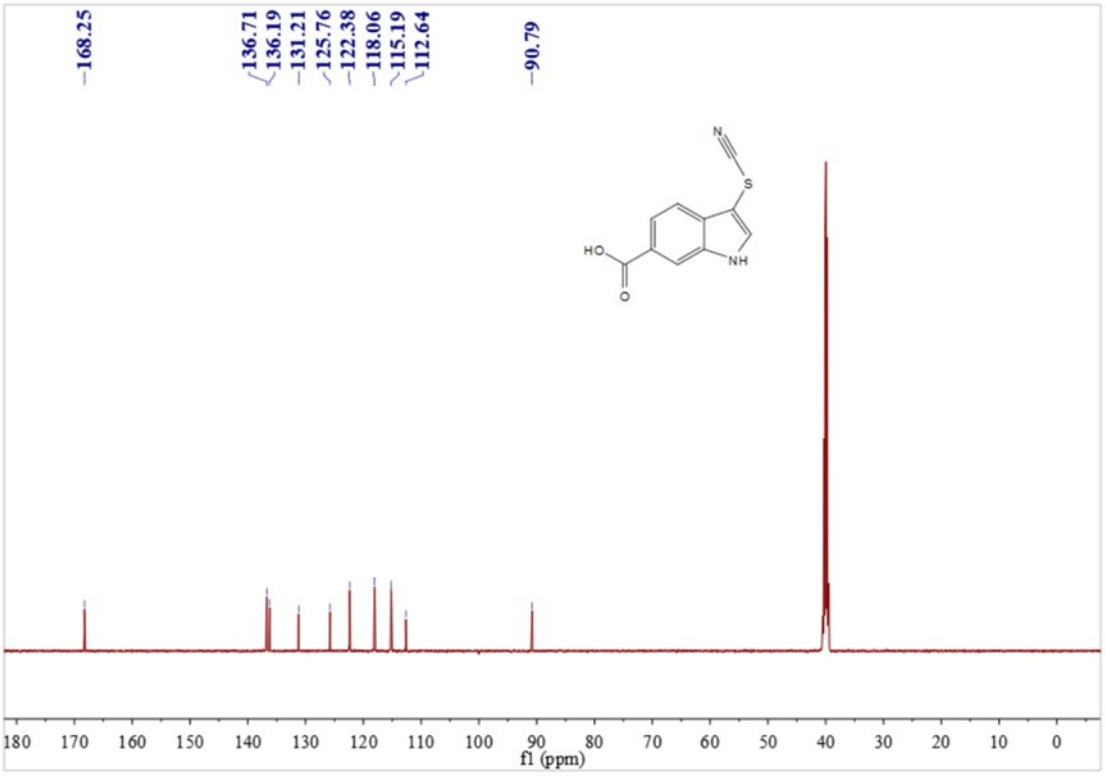

137.62
134.66
126.96
124.52
120.05
116.09
115.87
112.59
90.69
N
S
Br
NH
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

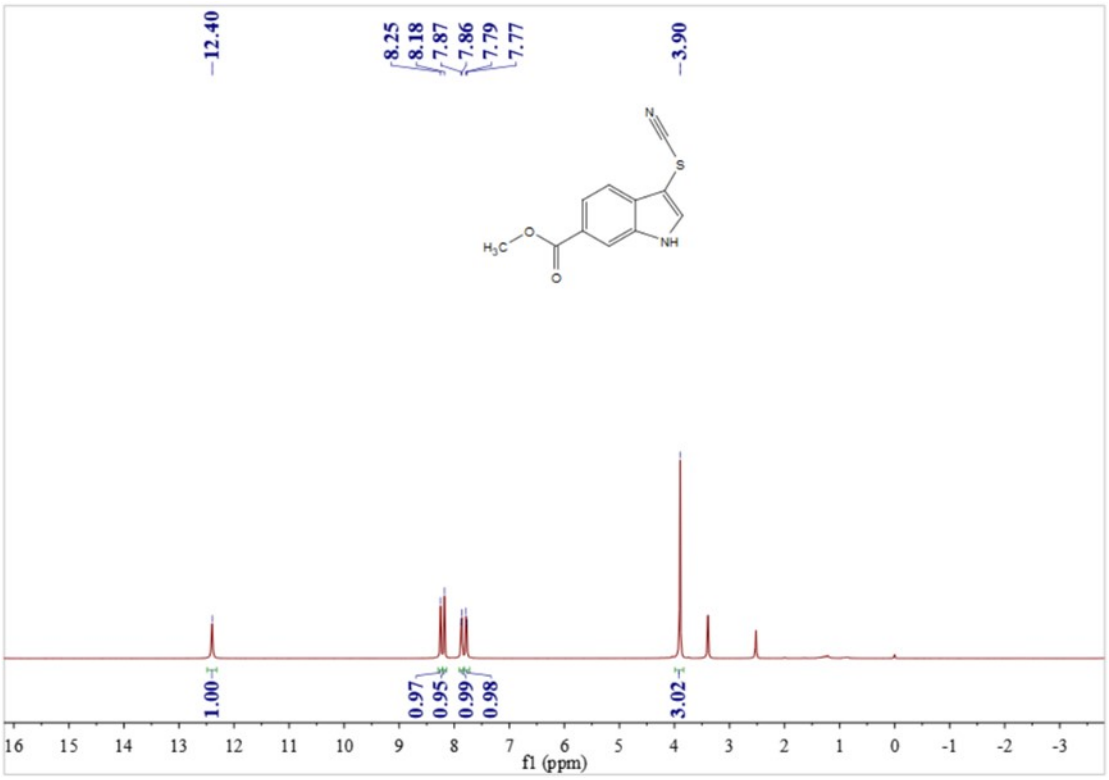

12.45
8.27
8.26
7.90
7.88
7.57
7.56
N
S
F
F
F
NH
1.03
1.00
2.02
1.04
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

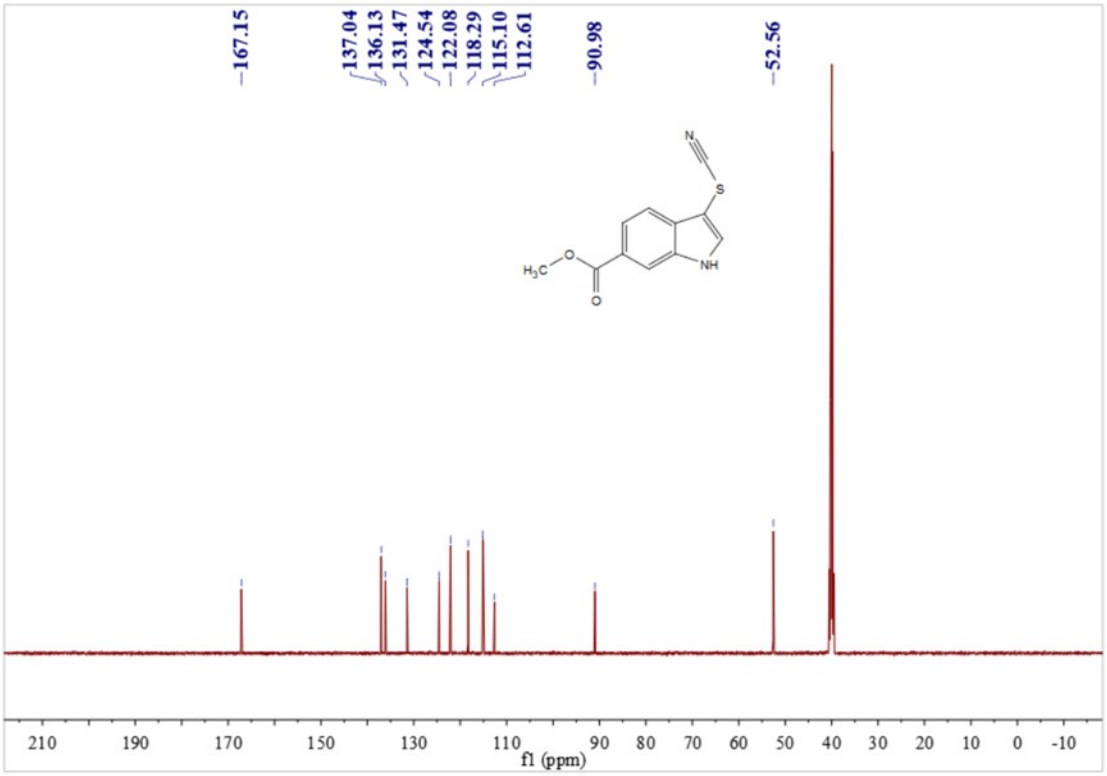

136.82
135.69
130.50
126.52
124.36
124.00
123.75
119.32
117.88
117.86
112.55
110.80
110.77
91.13
N
S
F
F
F
NH
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

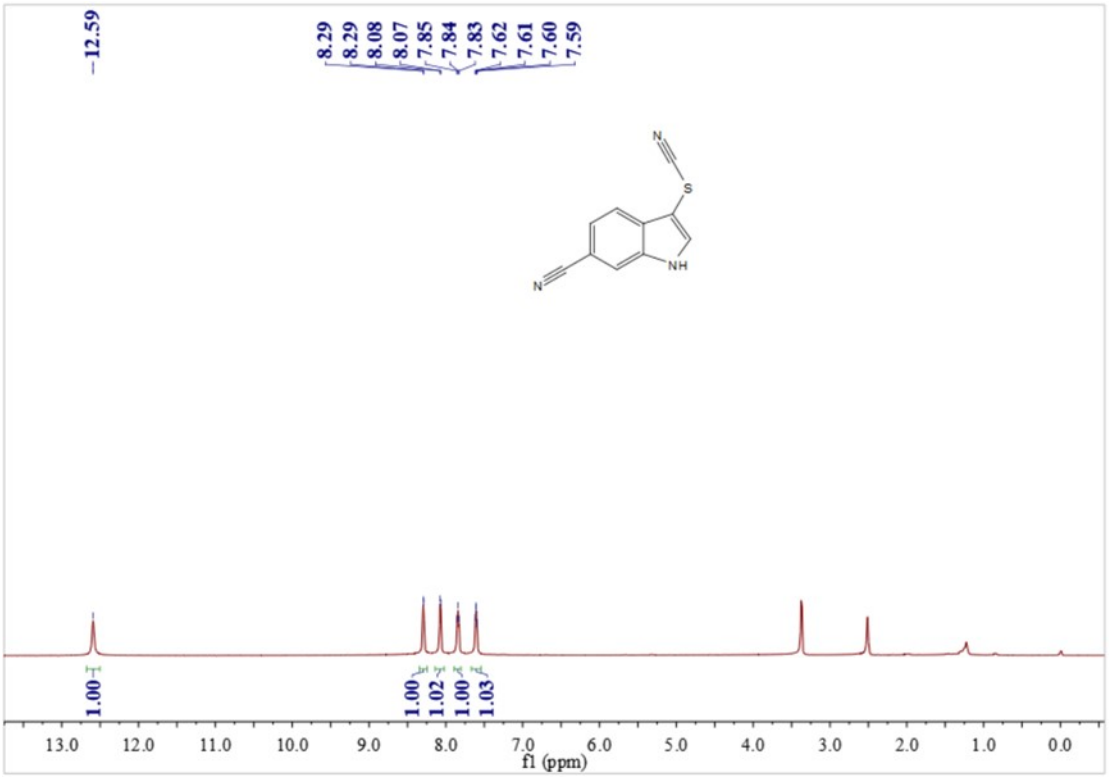

-59.23
N
S
F
F
F
NH
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

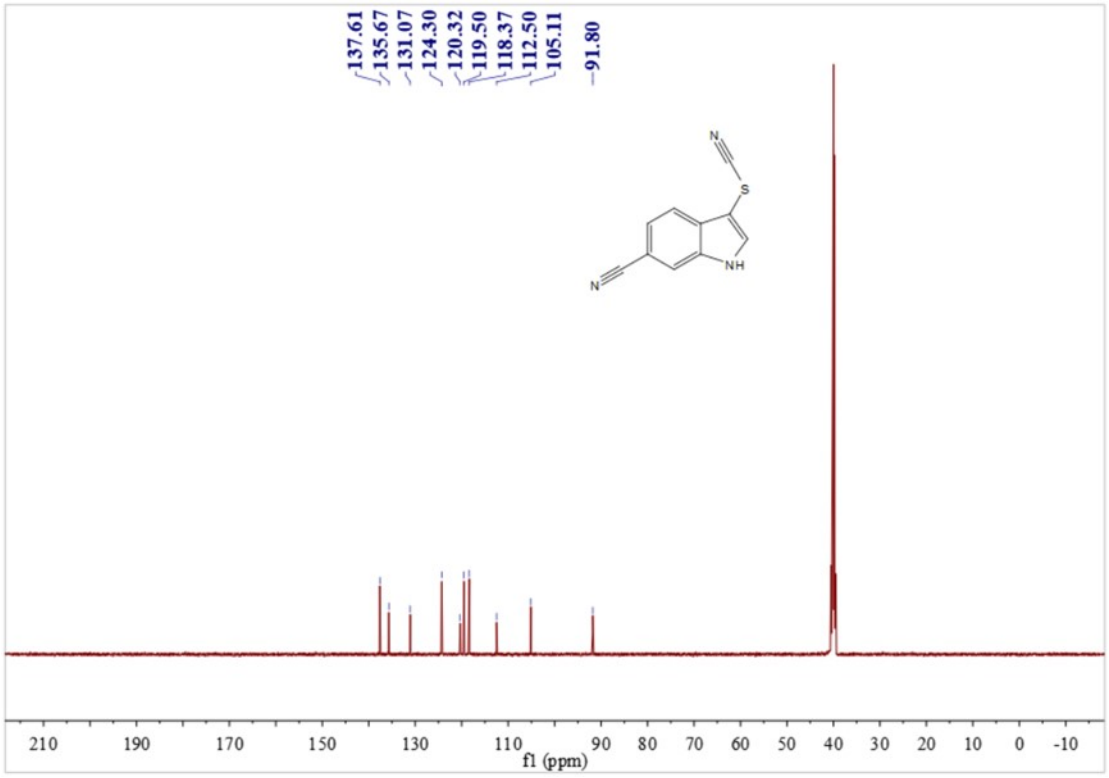

12.87
12.37
8.22
8.17
7.86
7.77
N
S
HO
O
NH
1.00
1.00
2.00
2.02
14.0 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

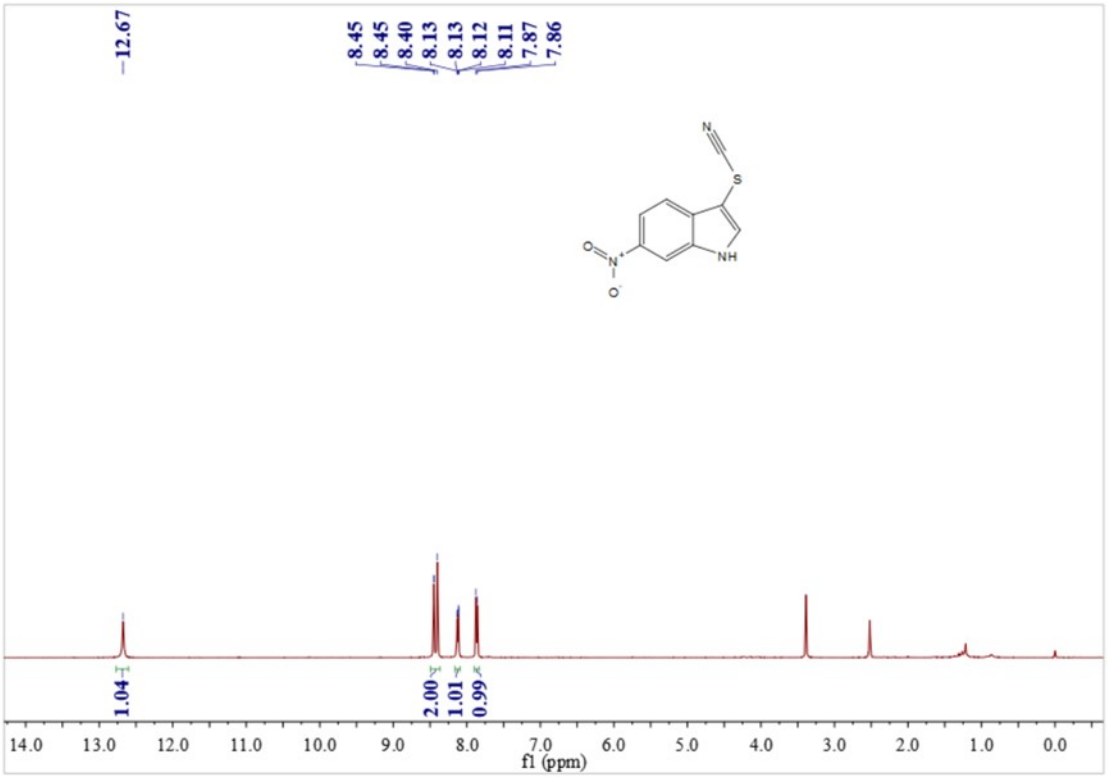

168.25
136.71
136.19
131.21
125.76
122.38
118.06
115.19
112.64
90.79
N
S
HO
NH
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

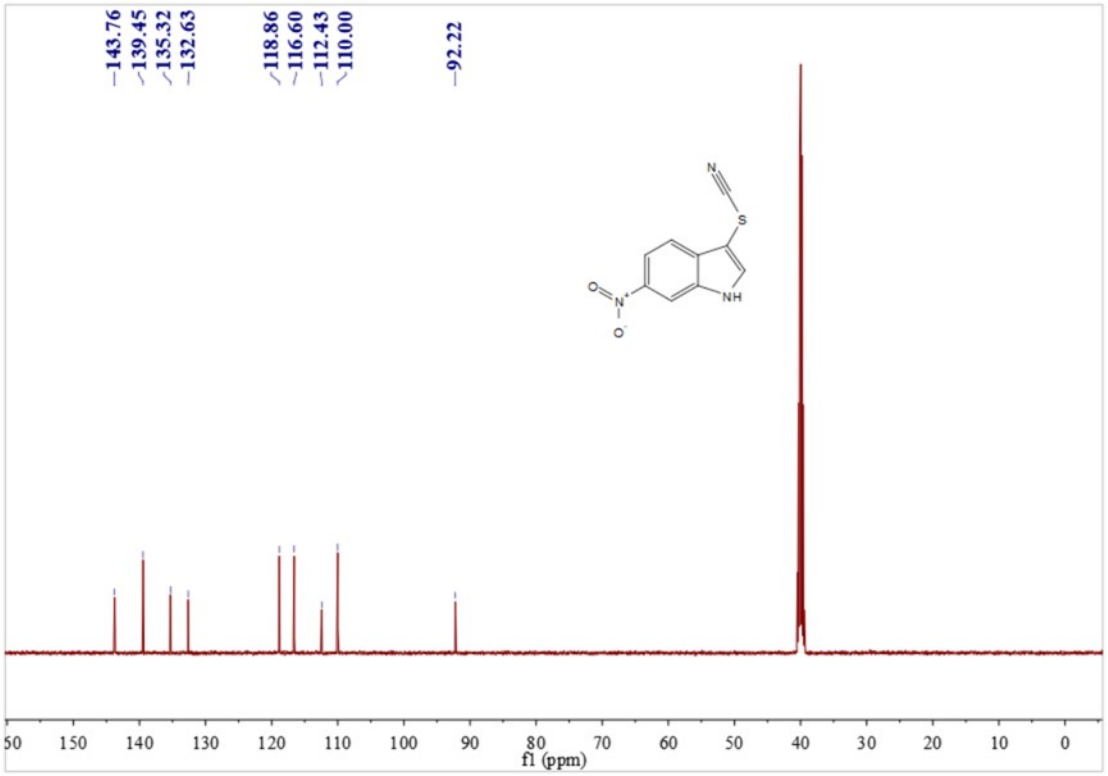

12.40
8.25
8.18
7.87
7.86
7.79
7.77
3.90
N
S
H3C
O
NH
O
1.00
0.97
0.95
0.99
0.98
3.02
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

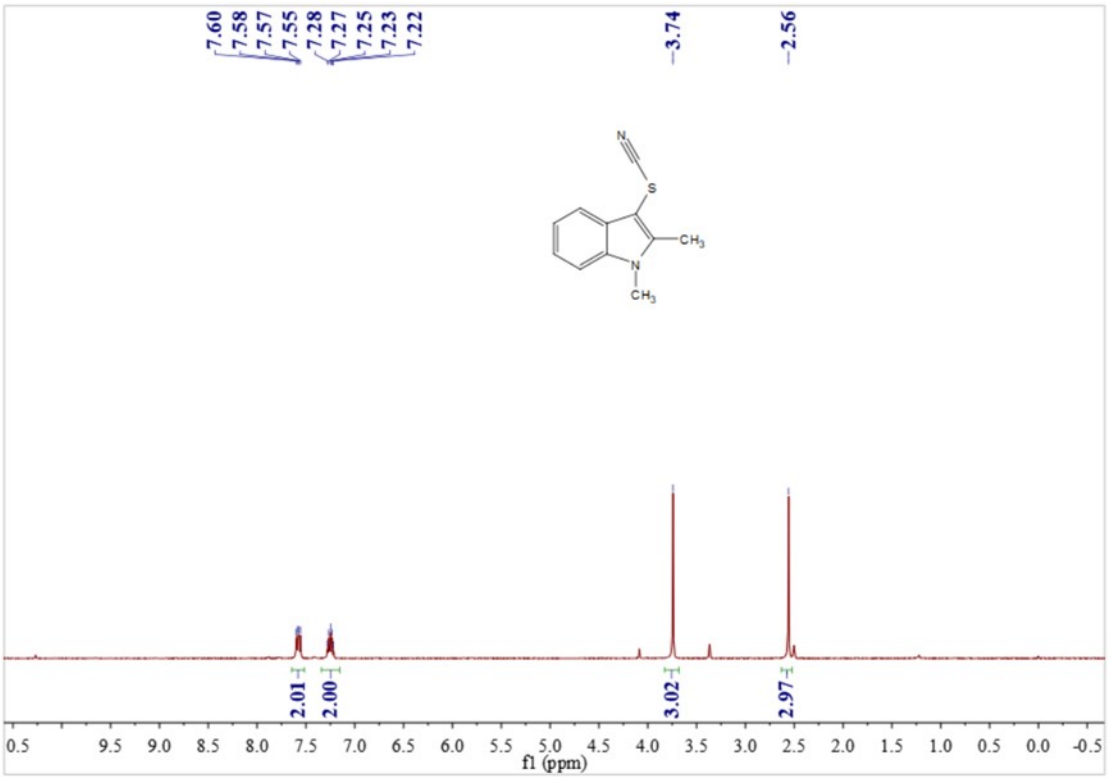

167.15
137.04
136.13
131.47
124.54
122.08
118.29
115.10
112.61
90.98
52.56
N
S
NH
H3C
O
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

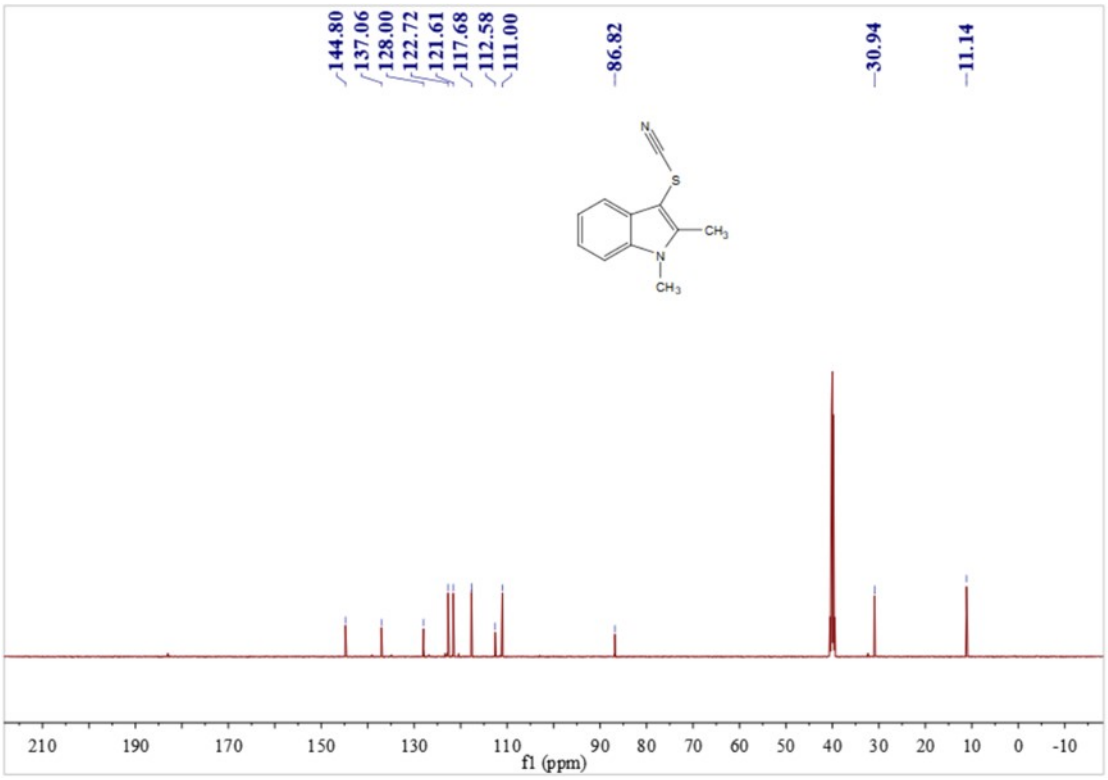

12.59
8.29
8.29
8.08
8.07
7.85
7.84
7.83
7.62
7.61
7.60
7.59
N
S
NH
N
1.00
1.00
1.02
1.00
1.03
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

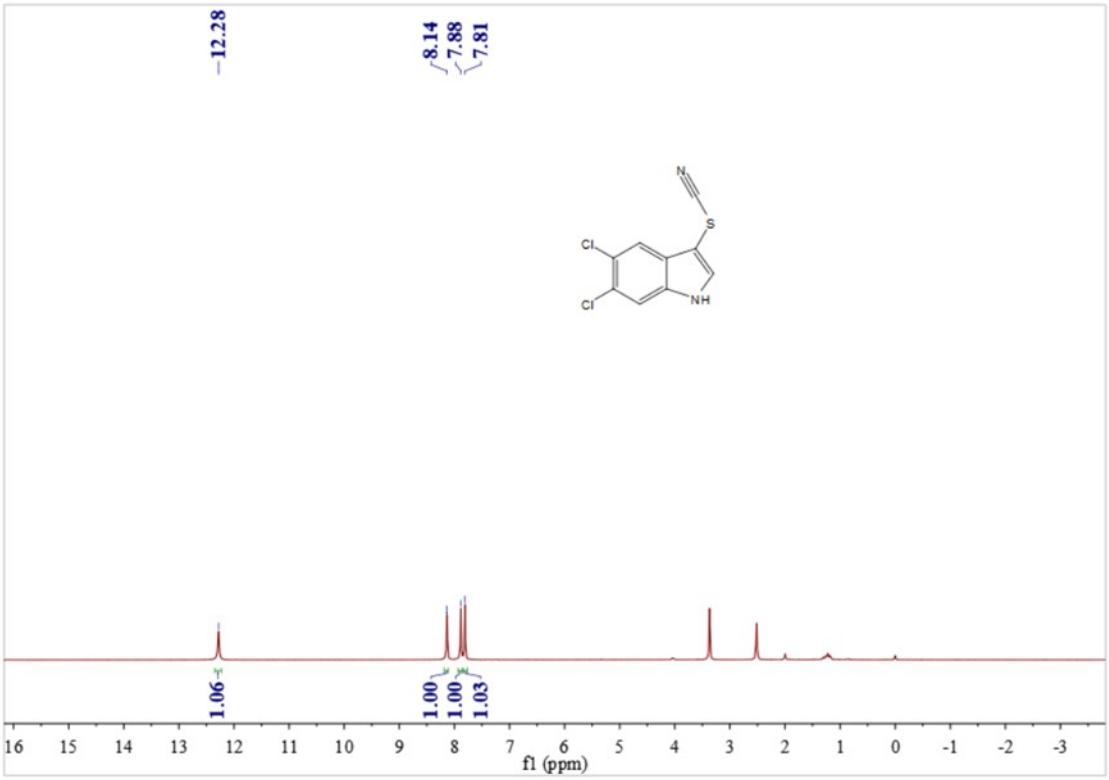

137.61
135.67
131.07
124.30
120.32
119.50
118.37
112.50
105.11
91.80
N
S
NH
N
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

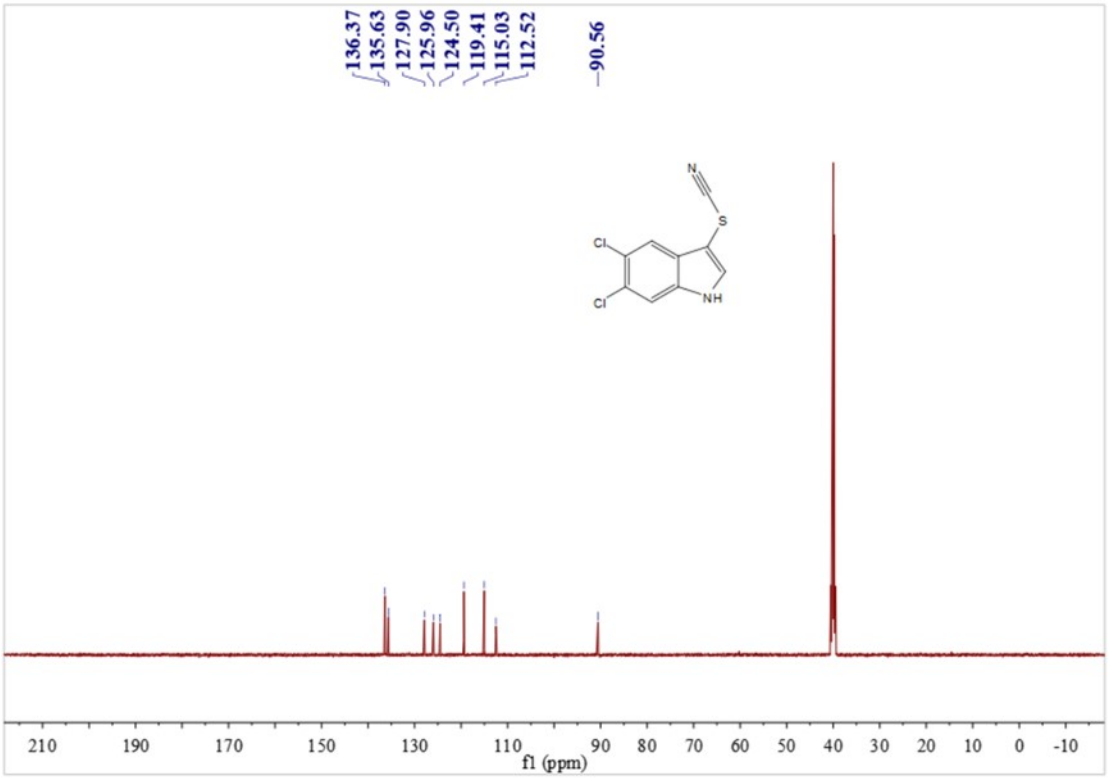

12.67
8.45
8.45
8.40
8.13
8.13
8.12
8.11
7.87
7.86
N
S
NH
O
N+
O-
1.04
2.00
1.01
0.99
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

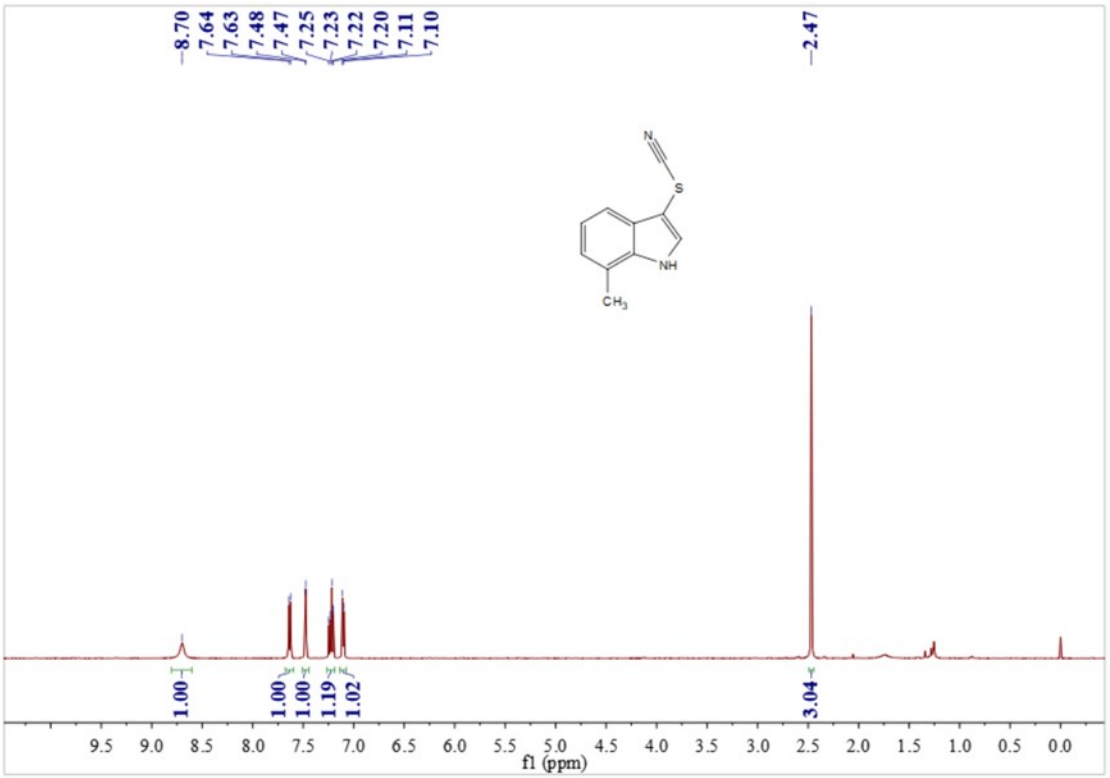

143.76
139.45
135.32
132.63
118.86
116.60
112.43
110.00
92.22
N
S
NH
O
N+
O-
50 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

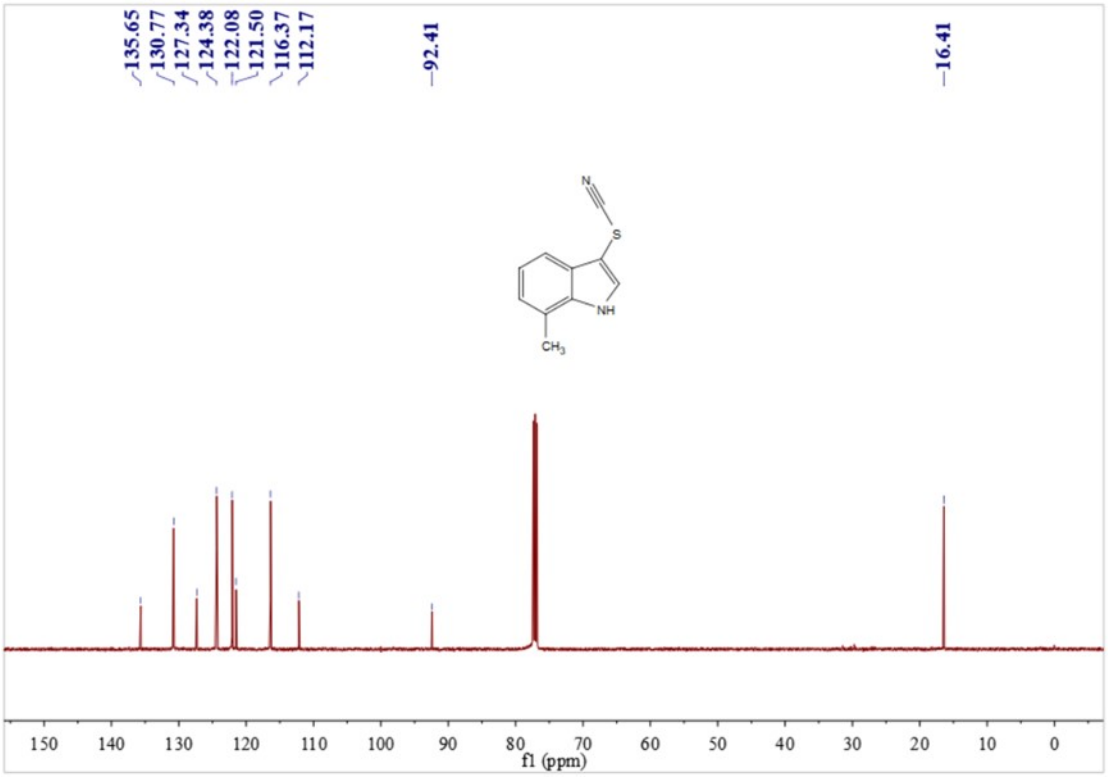

7.60
7.58
7.57
7.55
7.28
7.27
7.25
7.23
7.22
3.74
2.56
N
S
CH3
N
CH3
2.01
2.00
3.02
2.97
0.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

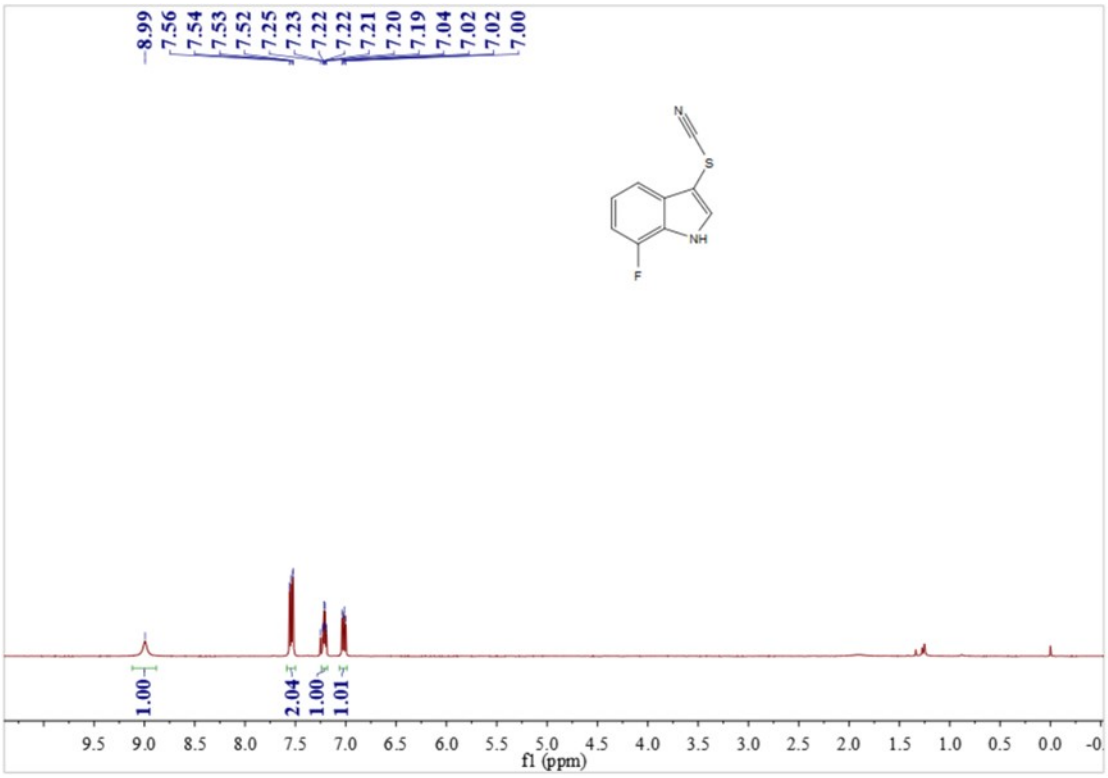

144.80
137.06
128.00
122.72
121.61
117.68
112.58
111.00
86.82
30.94
11.14
N
S
CH3
N
CH3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

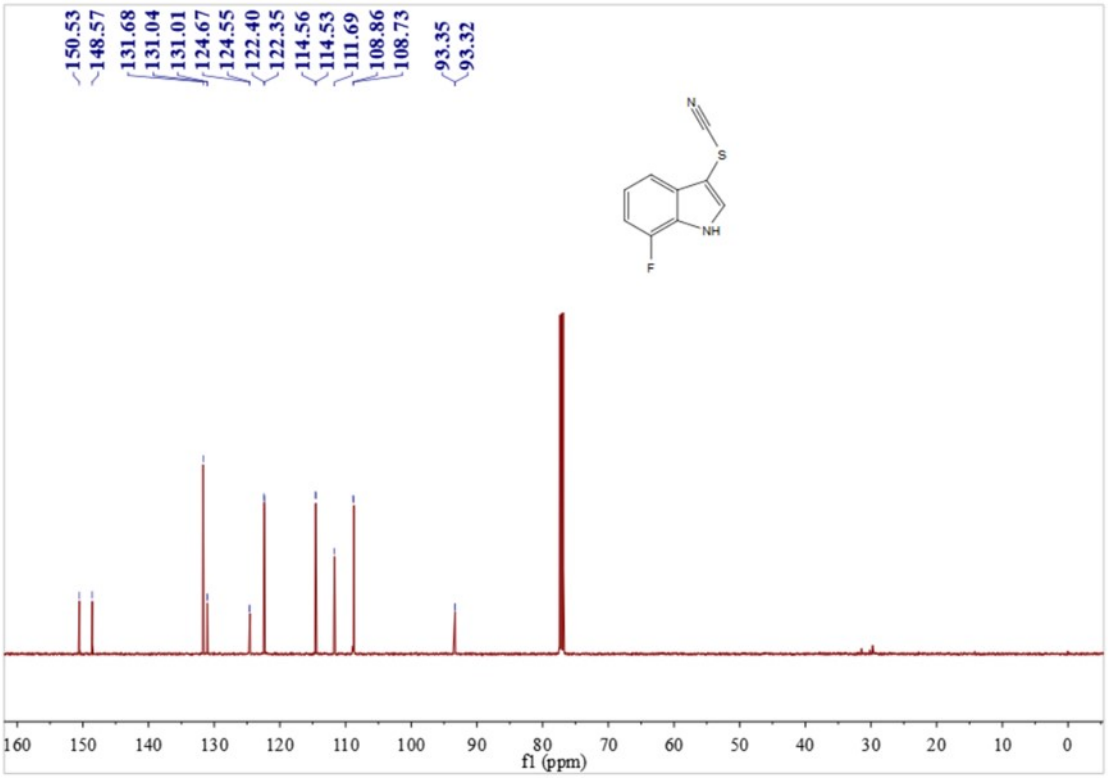

12.28
8.14
7.88
7.81
N
S
Cl
Cl
NH
1.06
1.00
1.00
1.03
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

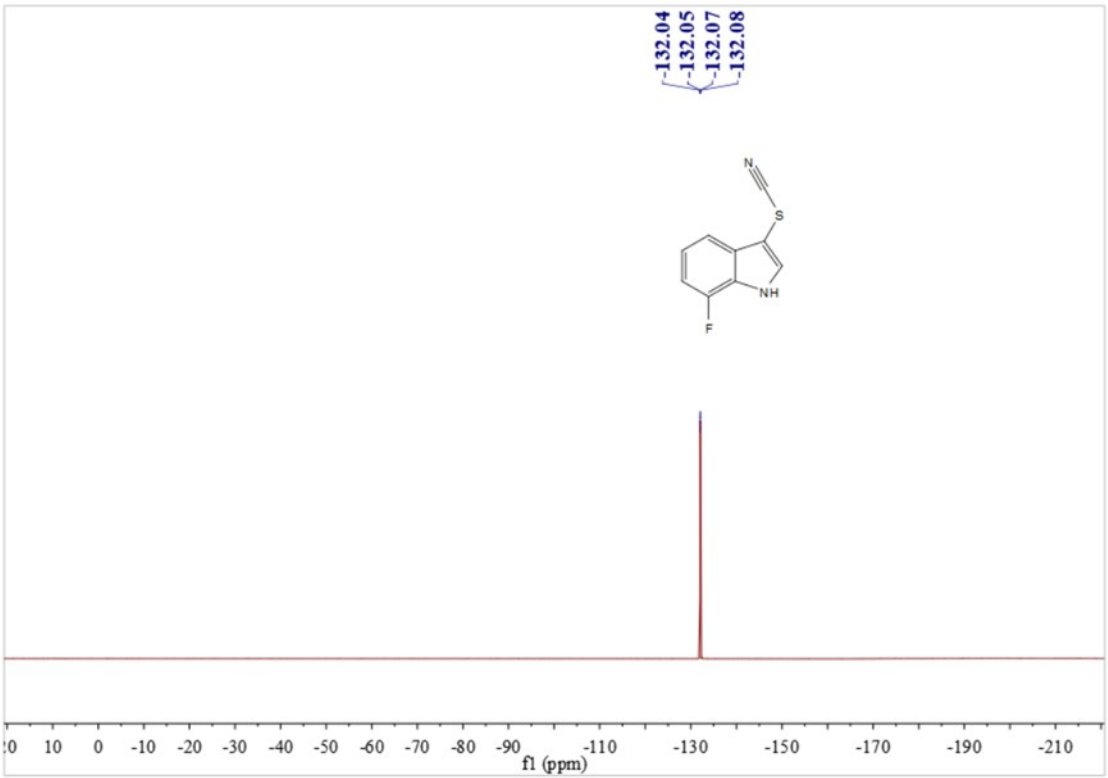

136.37
135.63
127.90
125.96
124.50
119.41
115.03
112.52
90.56
N
S
Cl
Cl
NH
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

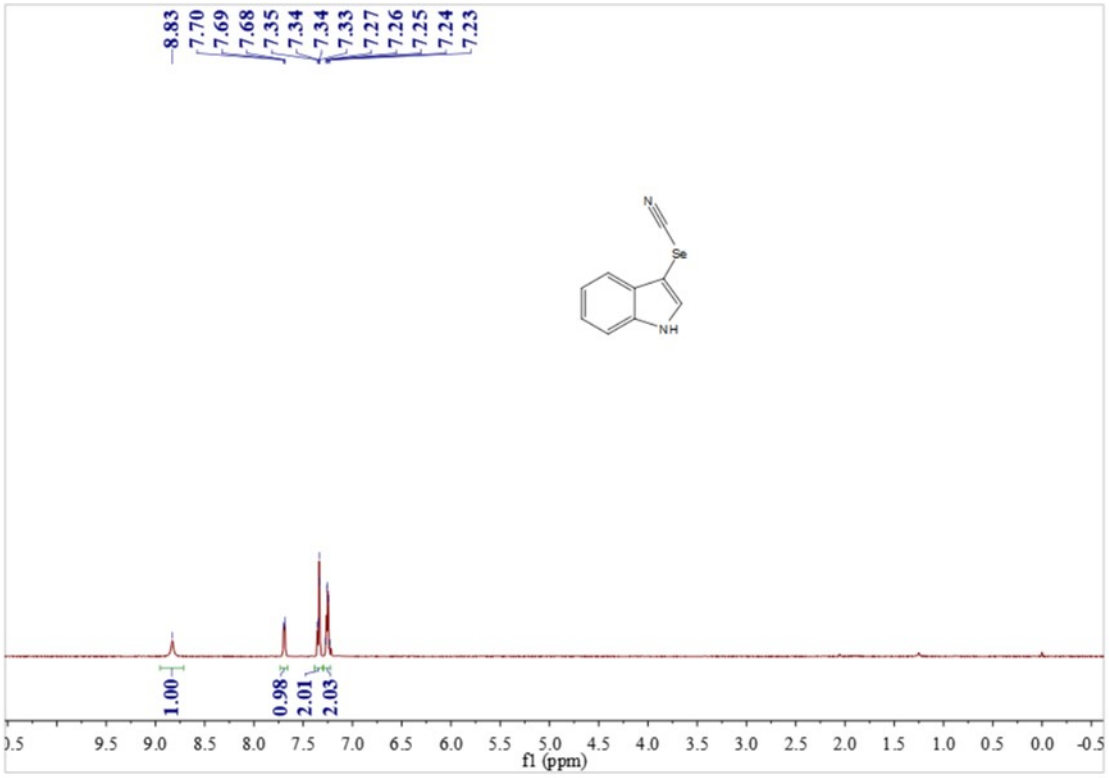

8.70
7.64
7.63
7.48
7.47
7.25
7.23
7.22
7.20
7.11
7.10
2.47
N
S
NH
CH3
1.00
1.00
1.00
1.19
1.02
3.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

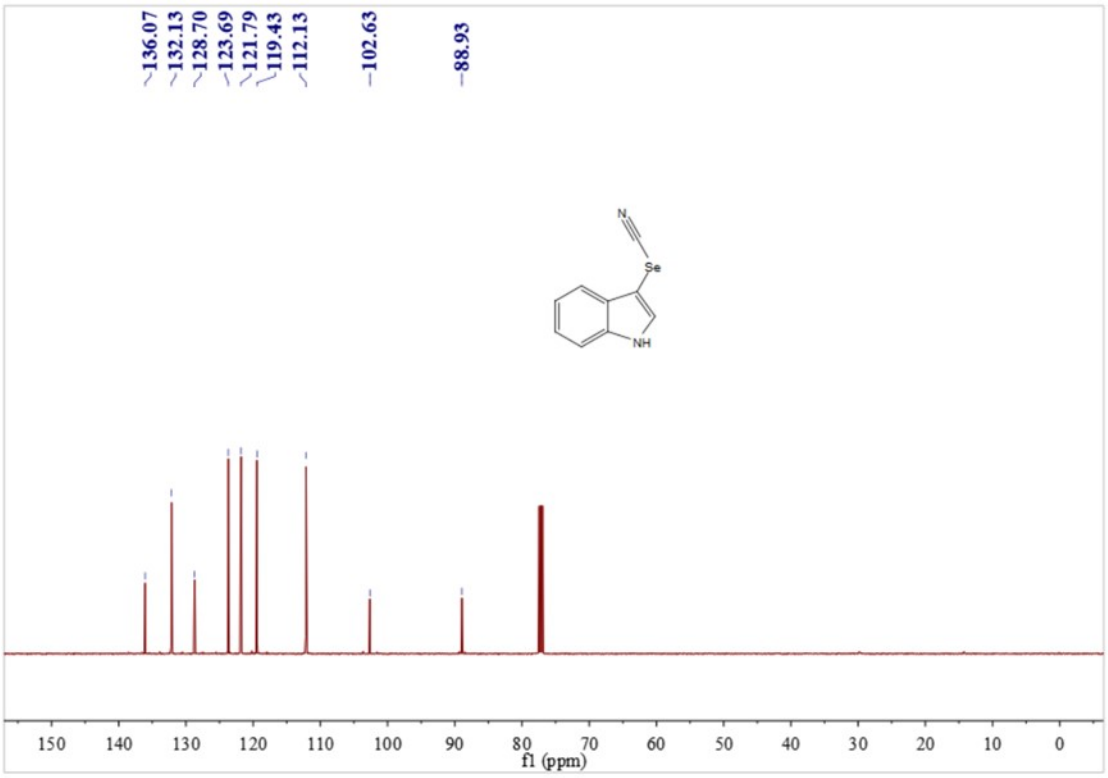

135.65
130.77
127.34
124.38
122.08
121.50
116.37
112.17
92.41
16.41
N
S
NH
CH3
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

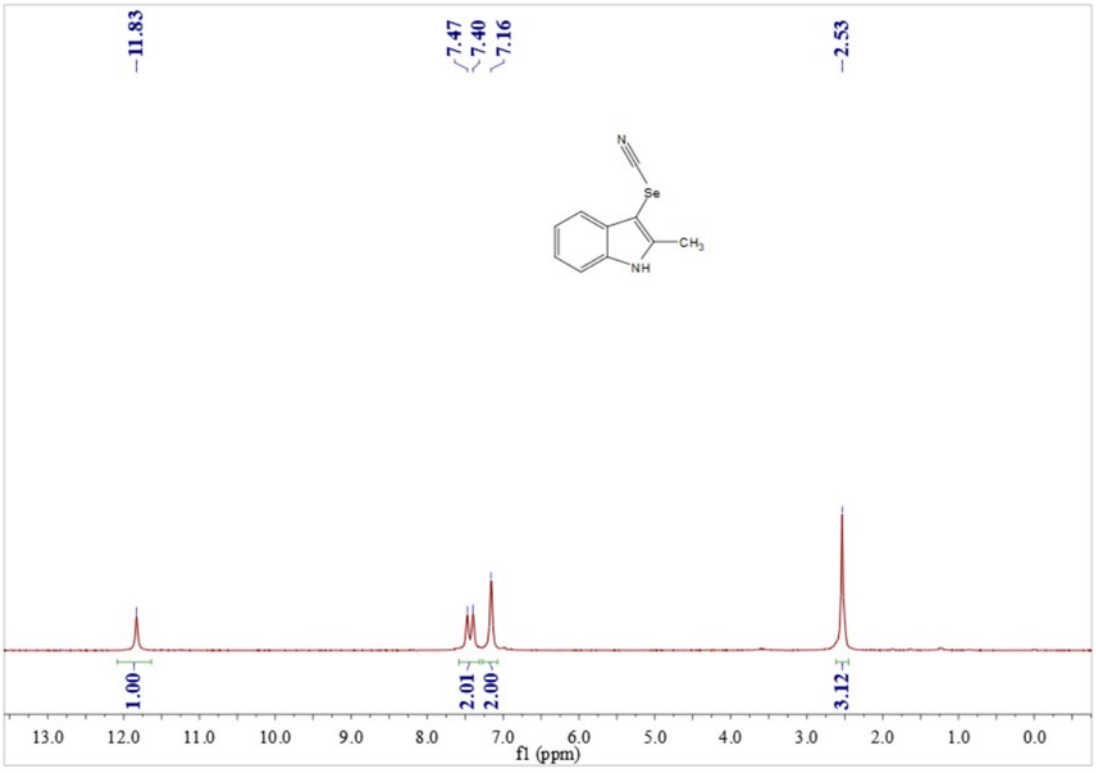

8.99
7.56
7.54
7.53
7.52
7.25
7.23
7.22
7.22
7.21
7.20
7.19
7.04
7.02
7.02
7.00
N
S
NH
F
1.00
2.04
1.00
1.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

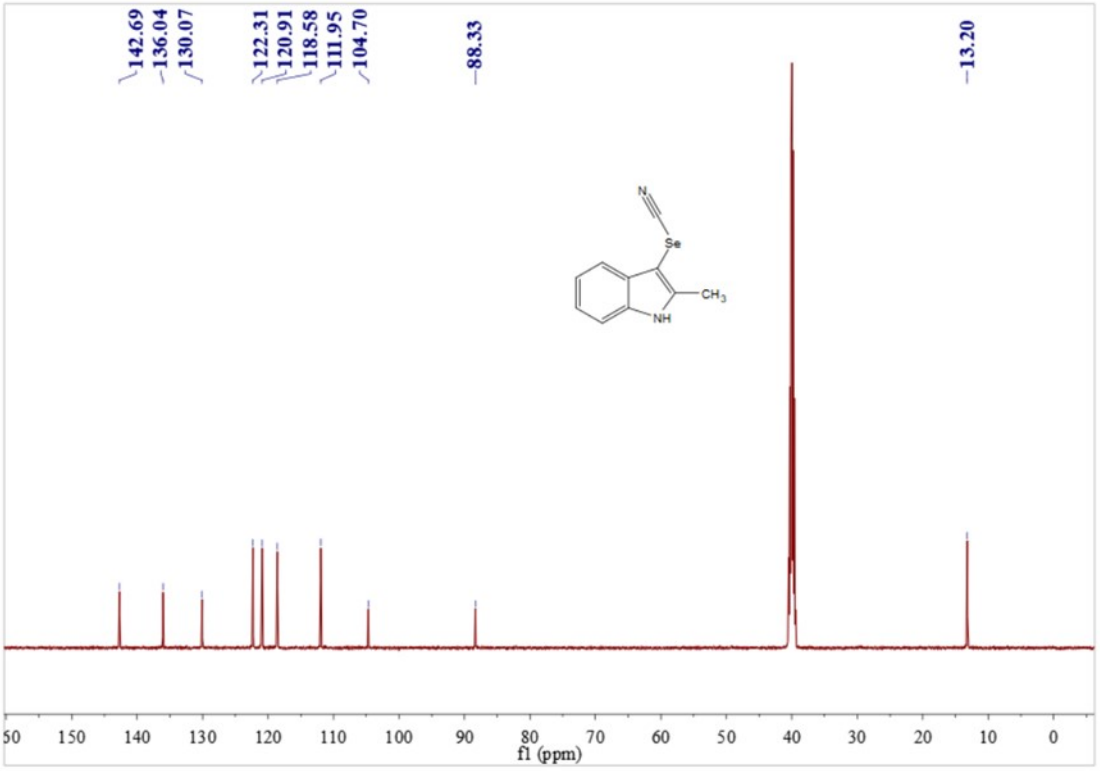

150.53
148.57
131.68
131.04
131.01
124.67
124.55
122.40
122.35
114.56
114.53
111.69
108.86
108.73
93.35
93.32
N
S
NH
F
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

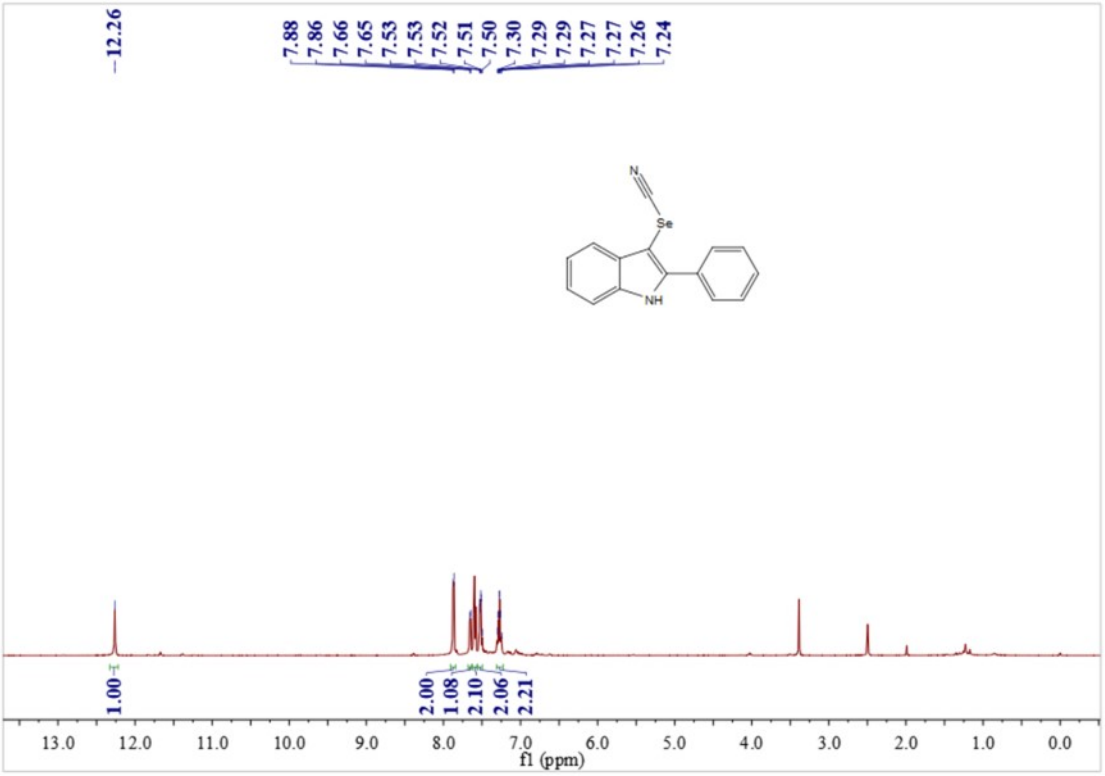

-132.04
-132.05
-132.07
-132.08
N
S
NH
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

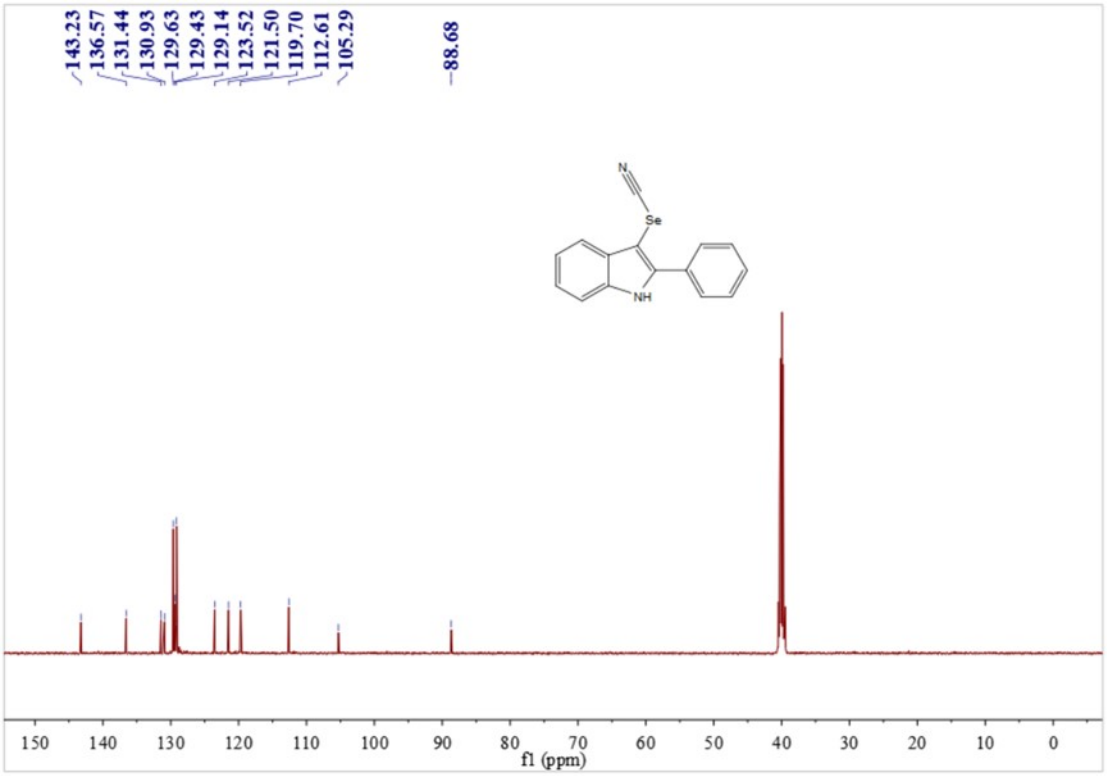

8.83
7.70
7.69
7.68
7.35
7.34
7.34
7.33
7.27
7.26
7.25
7.24
7.23
N
Se
NH
1.00
0.98
2.01
2.03
f1 (ppm)

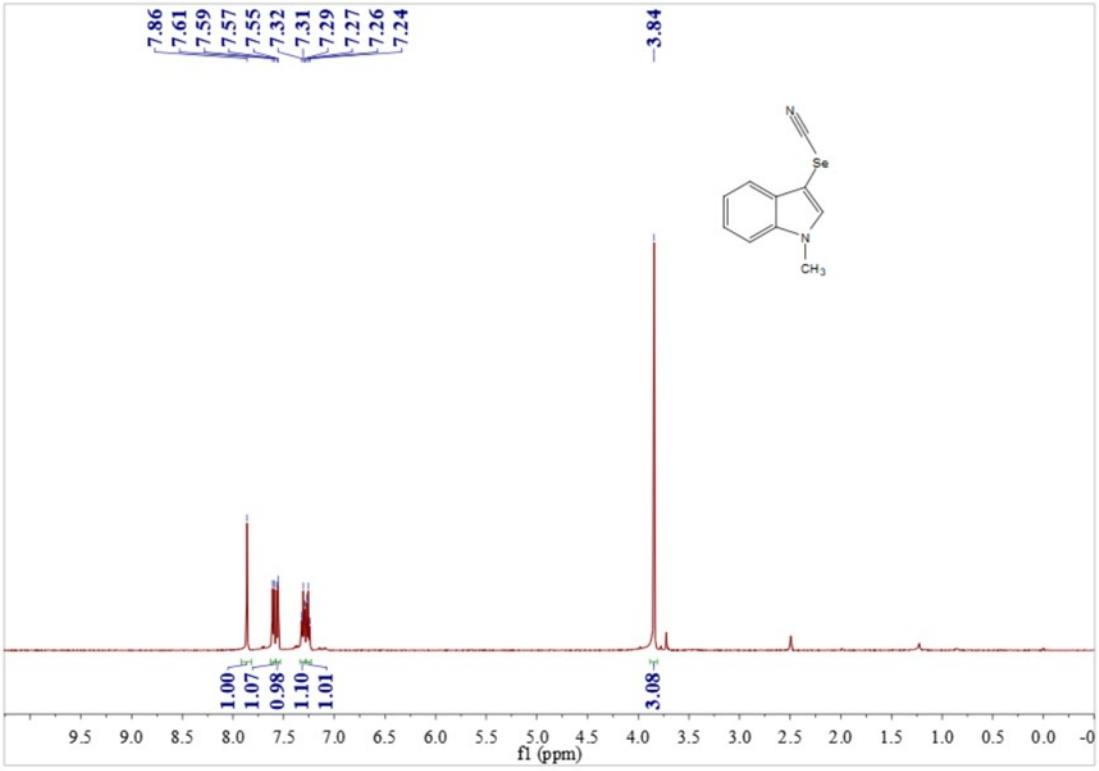

136.07
132.13
128.70
123.69
121.79
119.43
112.13
102.63
88.93
N
Se
NH
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

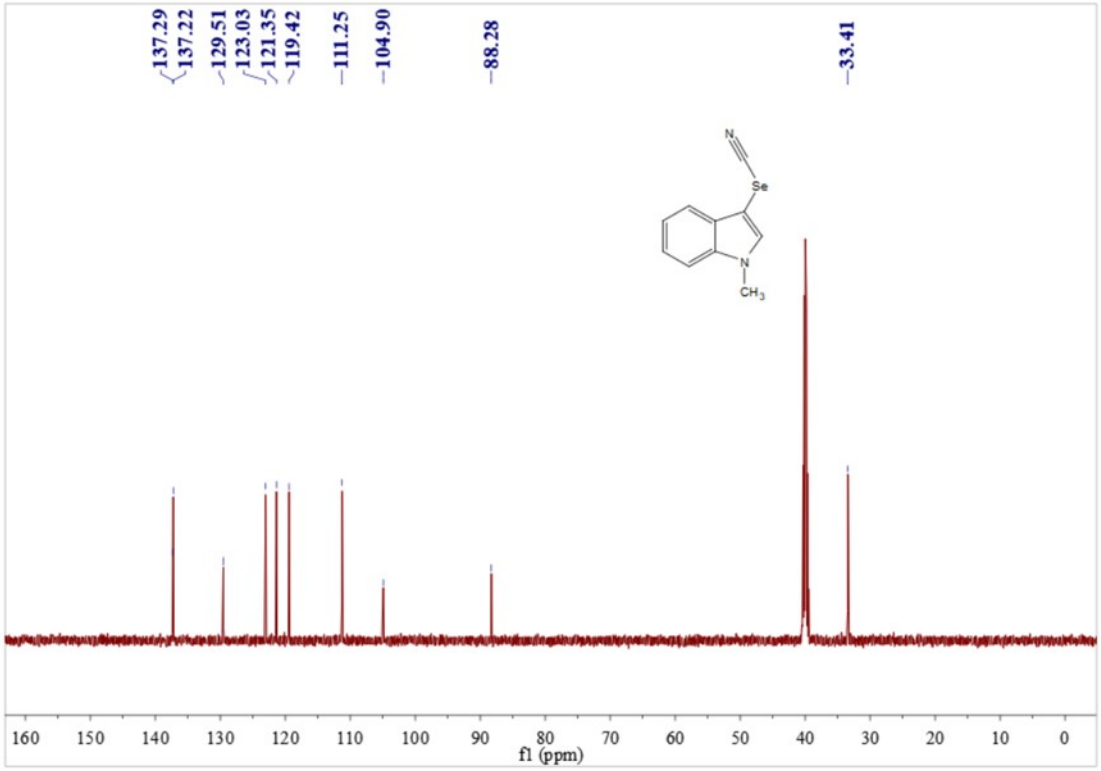

11.83
7.47
7.40
7.16
2.53
N
Se
CH3
NH
1.00
2.01
2.00
3.12
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

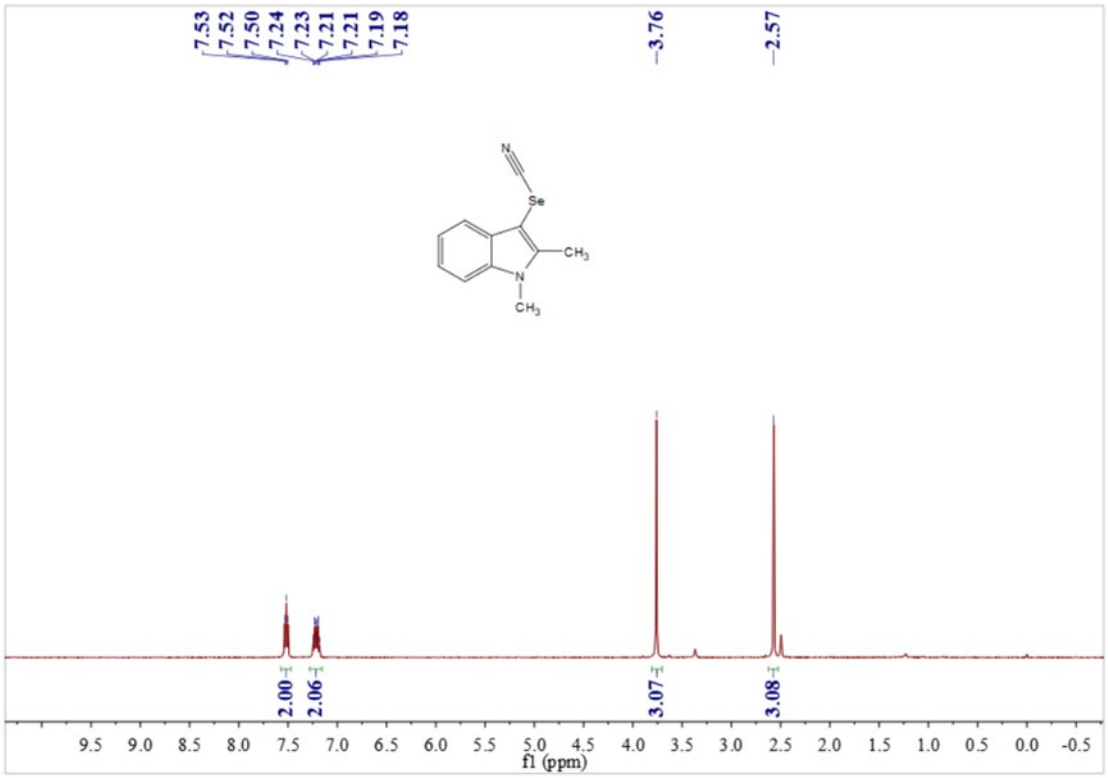

142.69
136.04
130.07
122.31
120.91
118.58
111.95
104.70
88.33
13.20
N
Se
CH3
NH
50 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

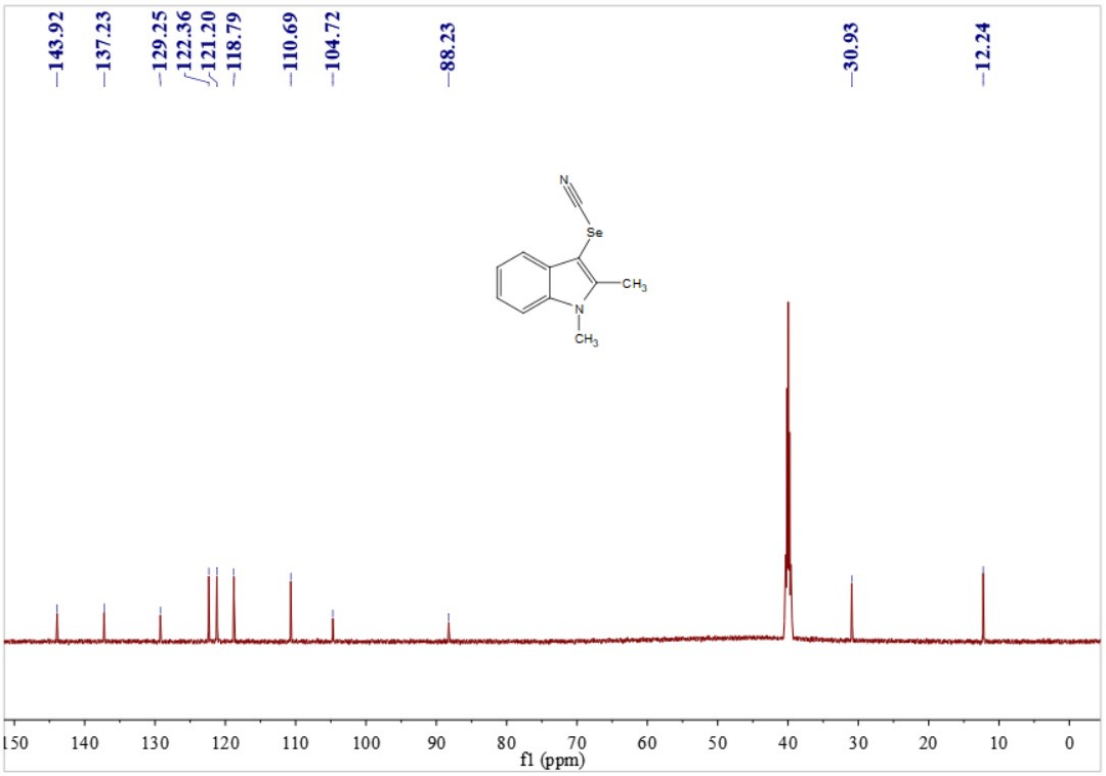

12.26
7.88
7.86
7.66
7.65
7.53
7.53
7.52
7.51
7.50
7.30
7.29
7.29
7.27
7.27
7.26
7.24
N
Se
NH
1.00
2.00
1.08
2.10
2.06
2.21
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

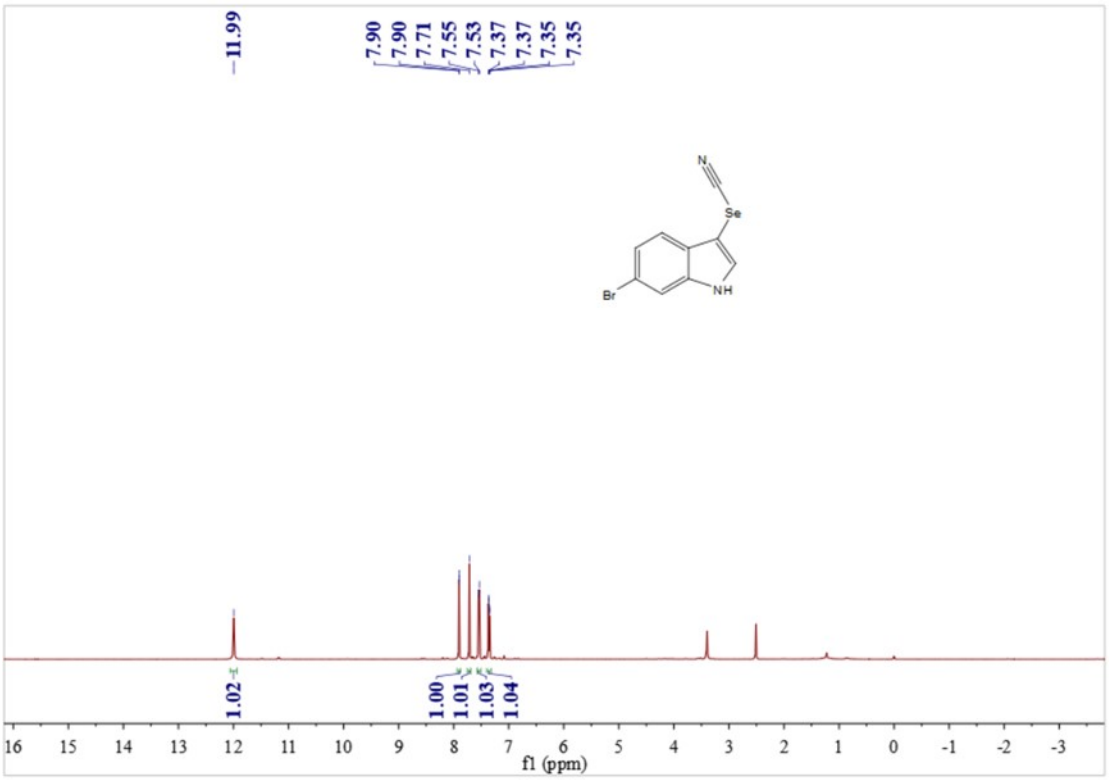

143.23
136.57
131.44
130.93
129.63
129.43
129.14
123.52
121.50
119.70
112.61
105.29
88.68
N
Se
NH
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

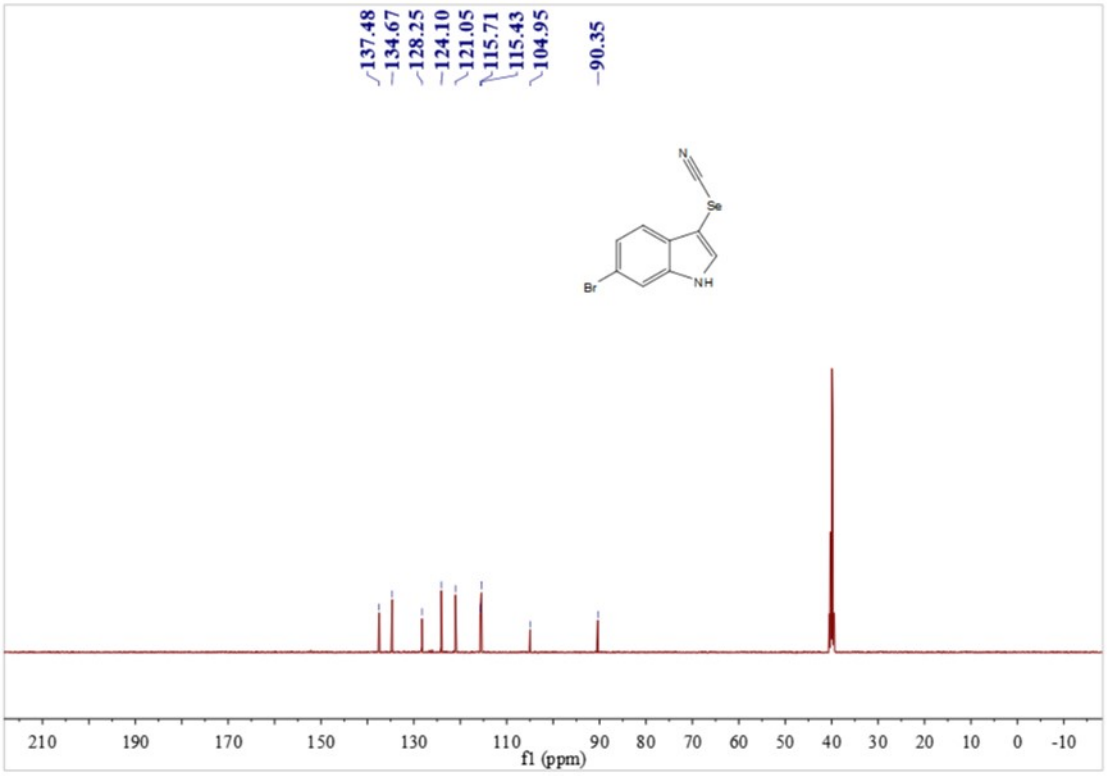

7.86
7.61
7.59
7.57
7.55
7.32
7.31
7.29
7.27
7.26
7.24
3.84
N
Se
N
CH3
1.00
1.07
0.98
1.10
1.01
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

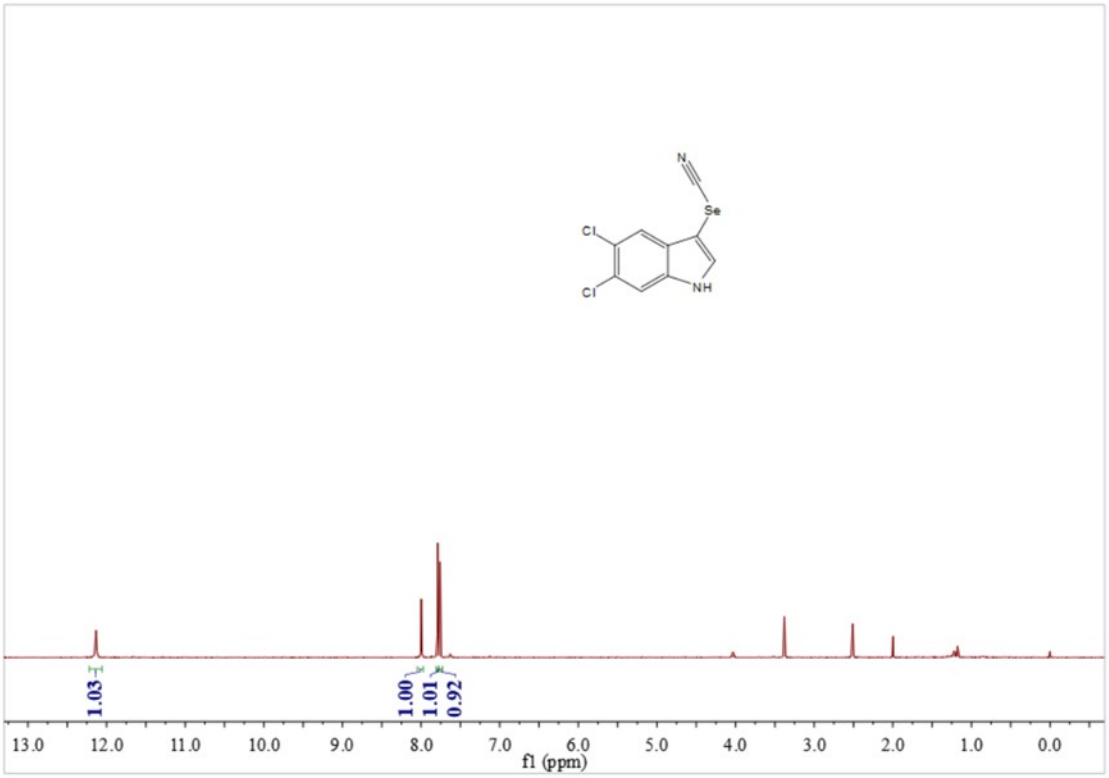

137.29
137.22
129.51
123.03
121.35
119.42
111.25
104.90
88.28
33.41
N
Se
N
CH3
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

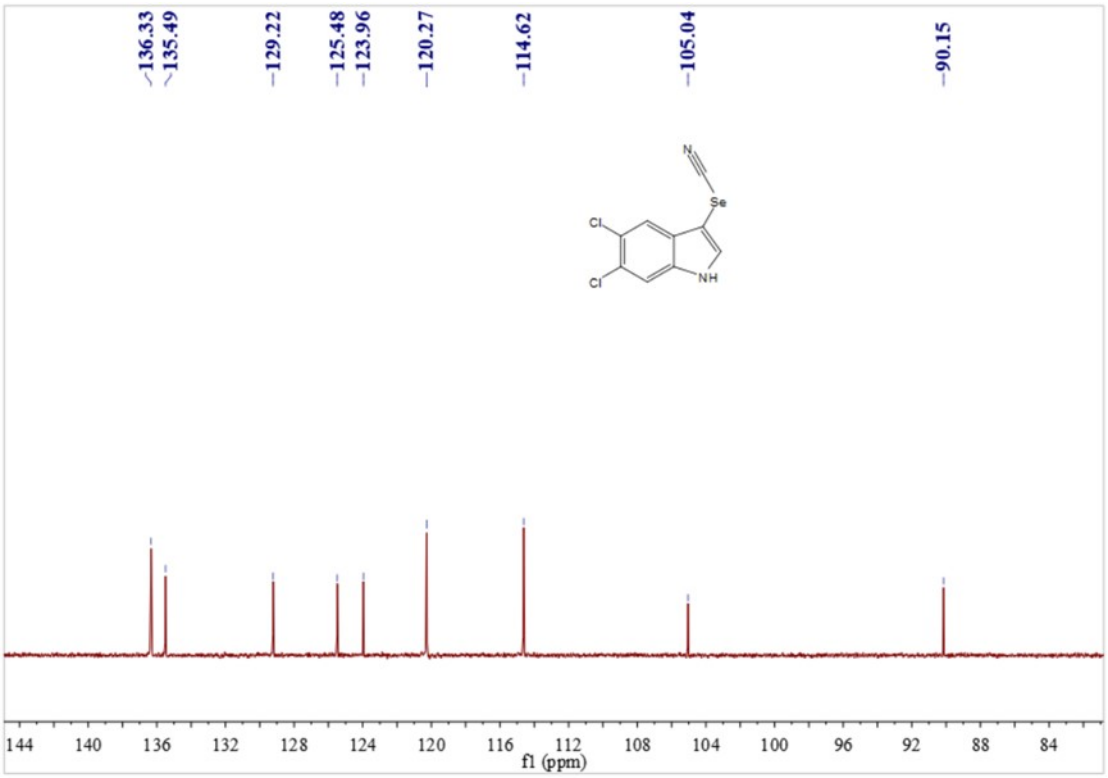

7.53
7.52
7.50
7.24
7.23
7.21
7.21
7.19
7.18
3.76
2.57
N
Se
CH3
N
CH3
2.00
2.06
3.07
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

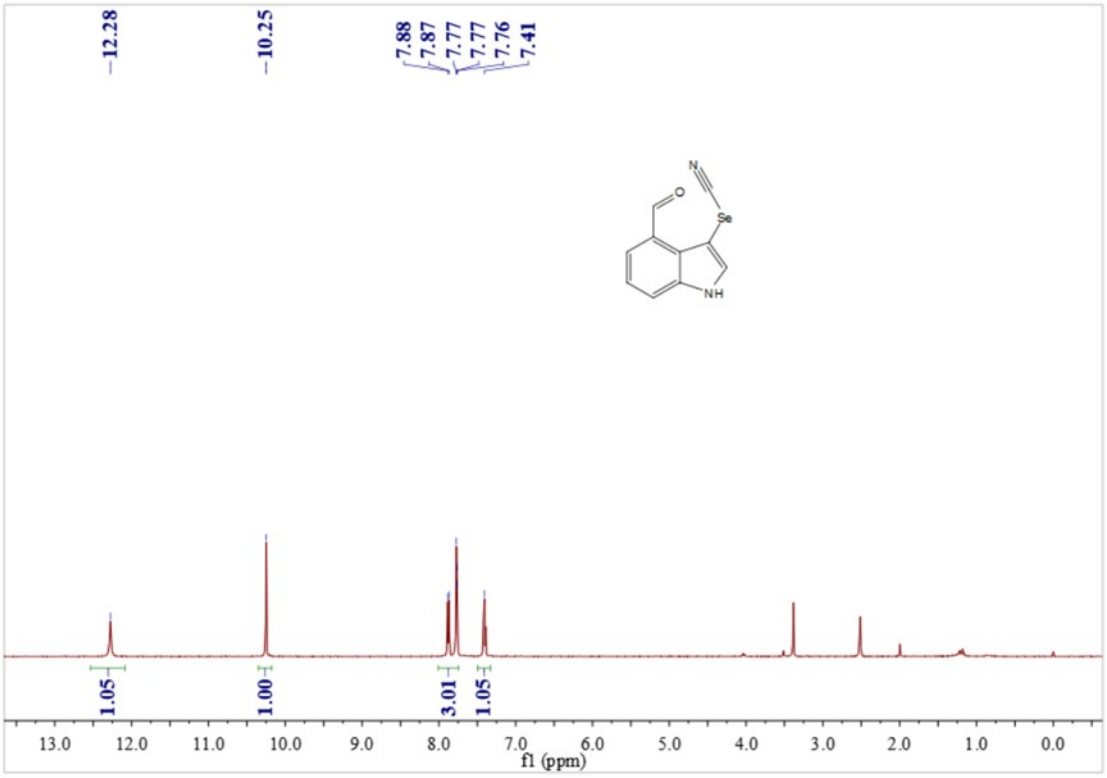

143.92
137.23
129.25
122.36
121.20
118.79
110.69
104.72
88.23
30.93
12.24
N
Se
CH3
N
CH3
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

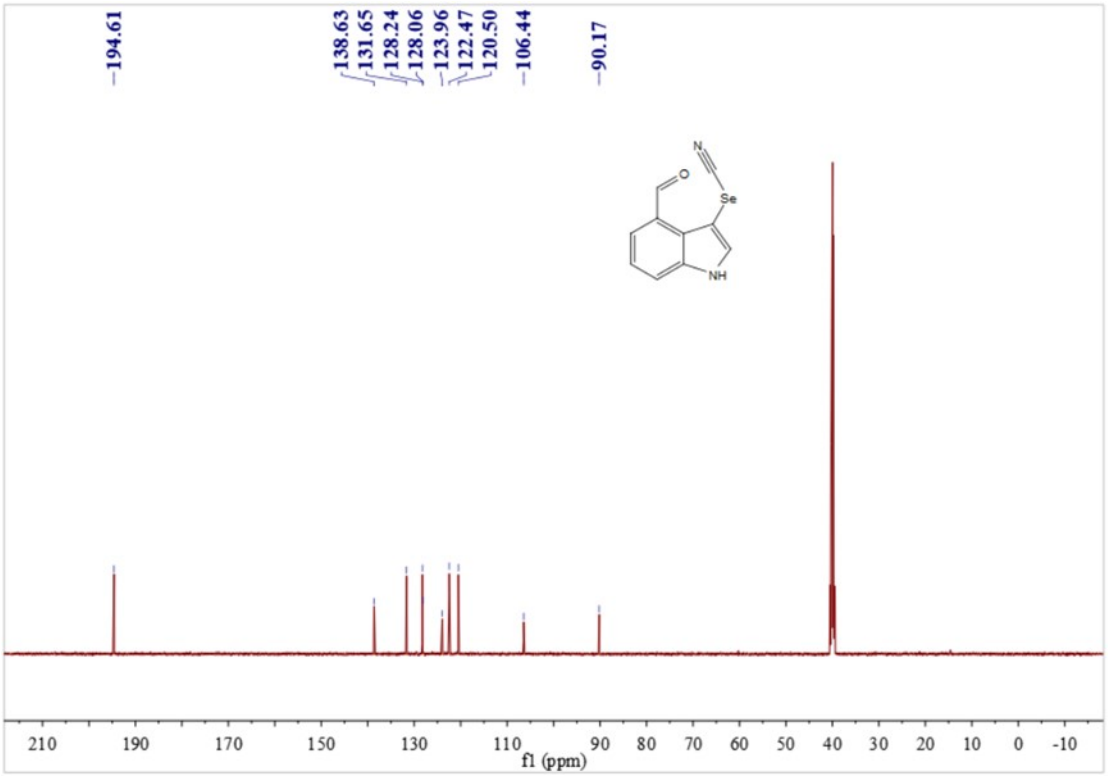

11.99
7.90
7.90
7.71
7.55
7.53
7.37
7.37
7.35
7.35
N
Se
Br
NH
1.02
1.00
1.01
1.03
1.04
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

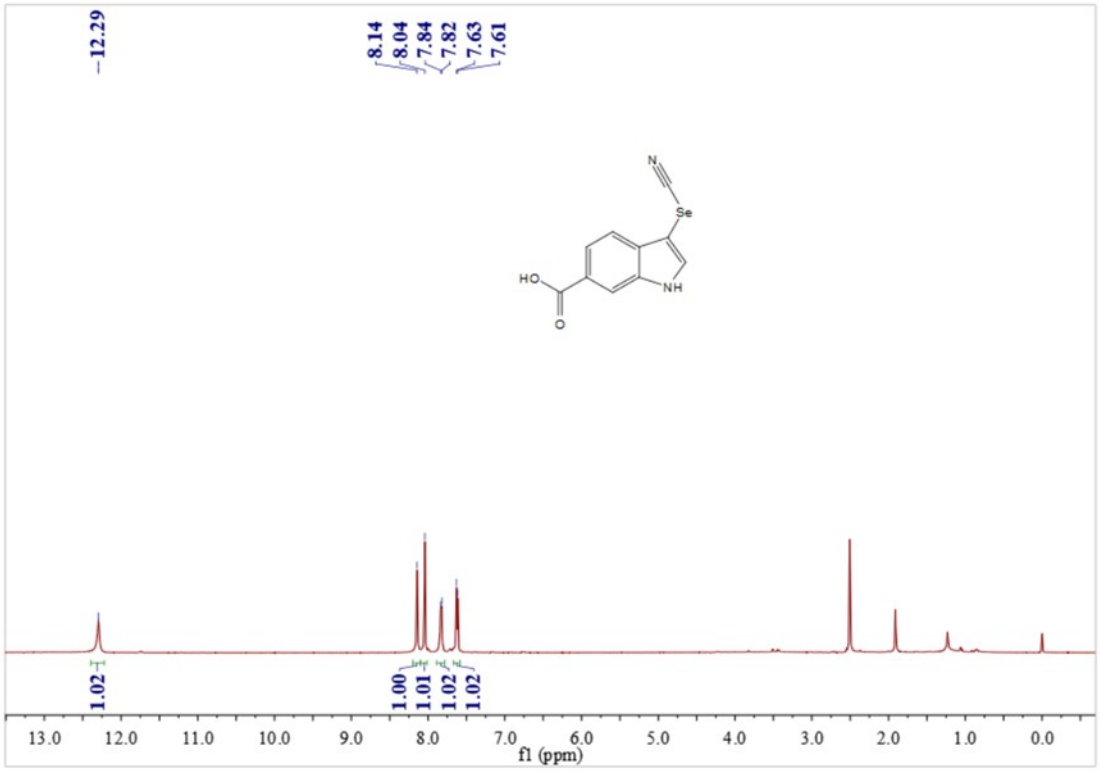

137.48
134.67
128.25
124.10
121.05
115.71
115.43
104.95
90.35
N
Se
Br
NH
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

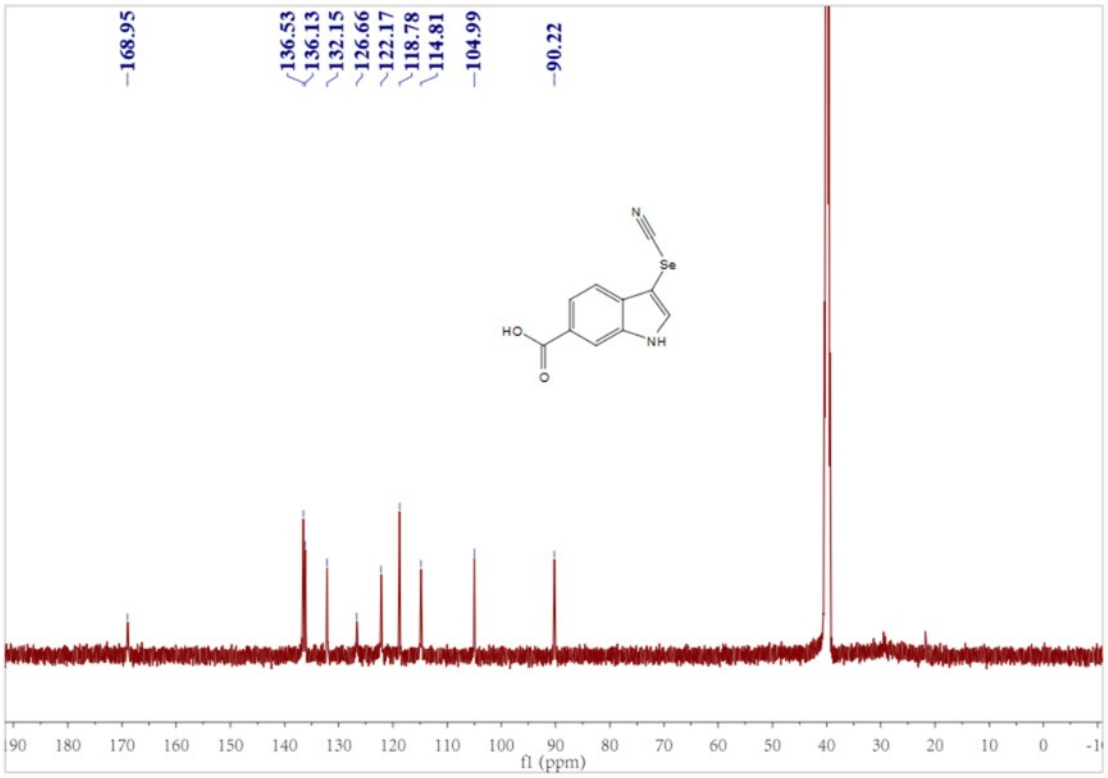

N
Se
Cl
Cl
NH
1.03
1.00
1.01
0.92
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

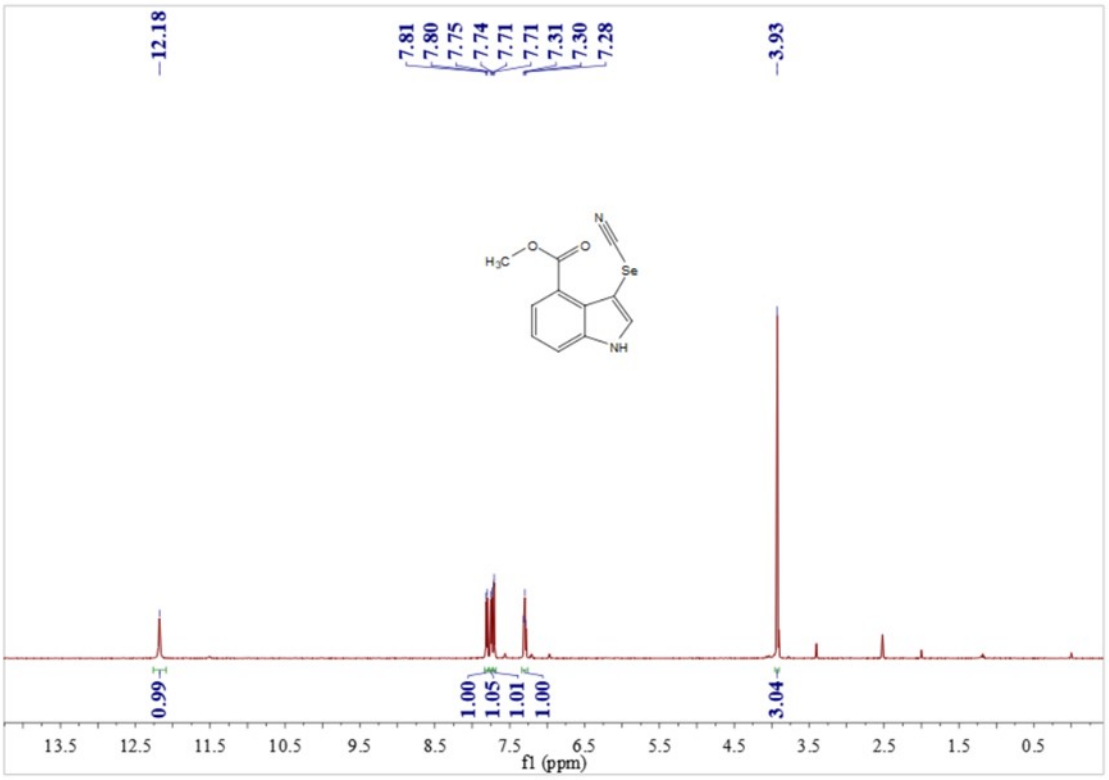

136.33
135.49
129.22
125.48
123.96
120.27
114.62
105.04
90.15
N
Se
Cl
Cl
NH
144 140 136 132 128 124 120 116 112 108 104 100 96 92 88 84
f1 (ppm)

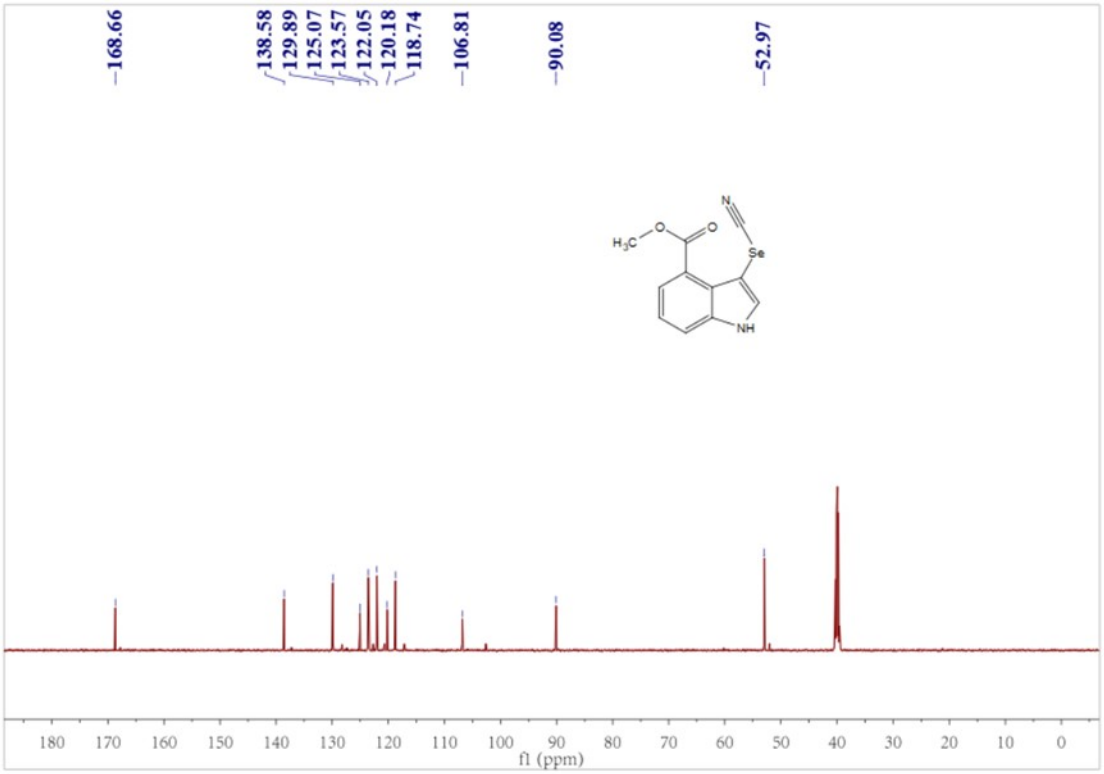

12.28
10.25
7.88
7.87
7.77
7.77
7.76
7.41
N
O
Se
NH
1.05
1.00
3.01
1.05
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

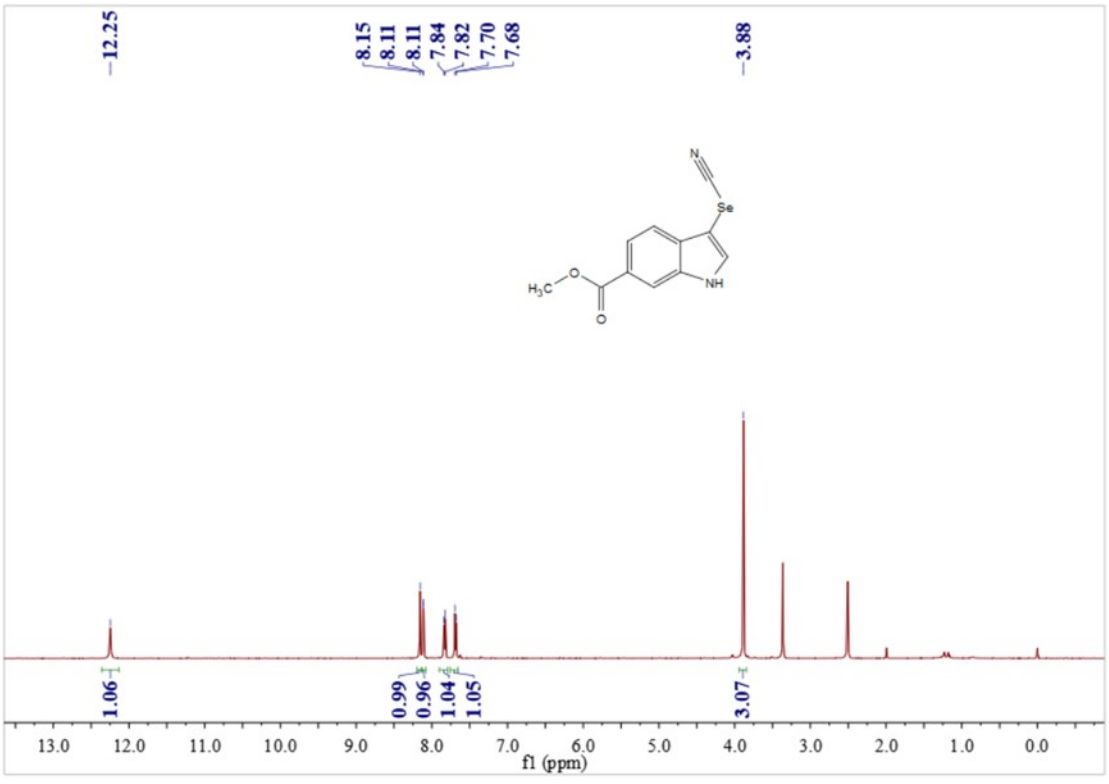

194.61
138.63
131.65
128.24
128.06
123.96
122.47
120.50
106.44
90.17
N
O
Se
NH
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

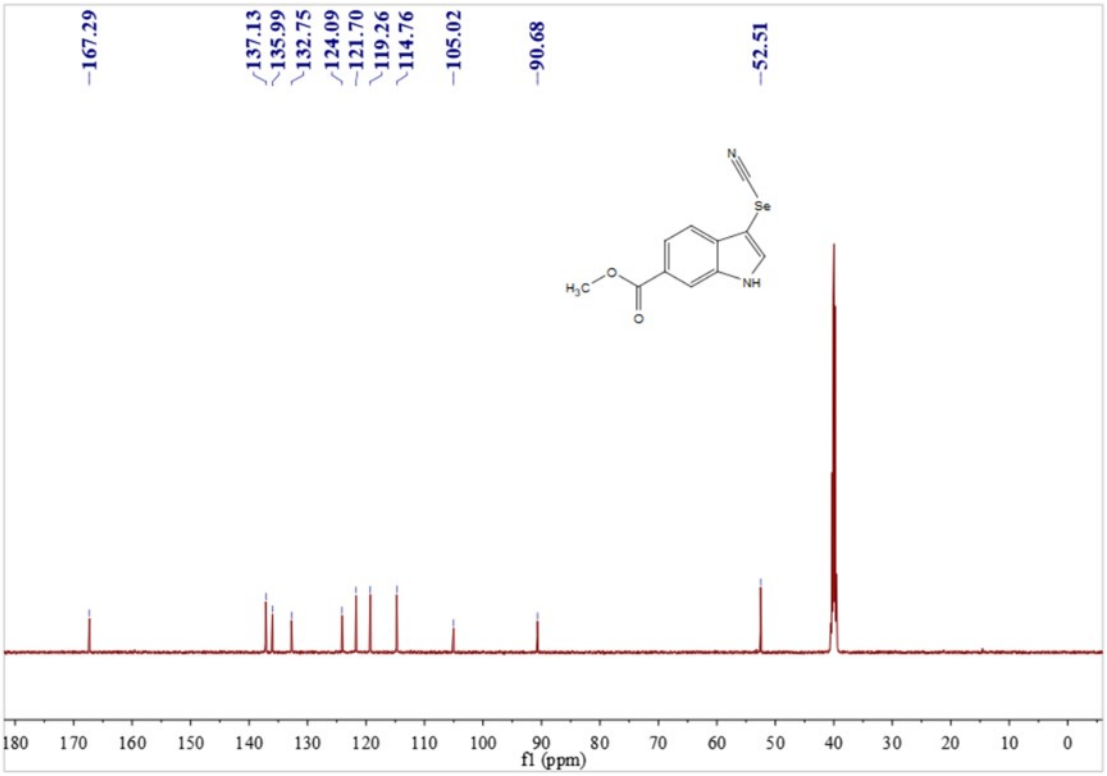

12.29
8.14
8.04
7.84
7.82
7.63
7.61
N
Se
HO
O
NH
1.02
1.00
1.01
1.02
1.02
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

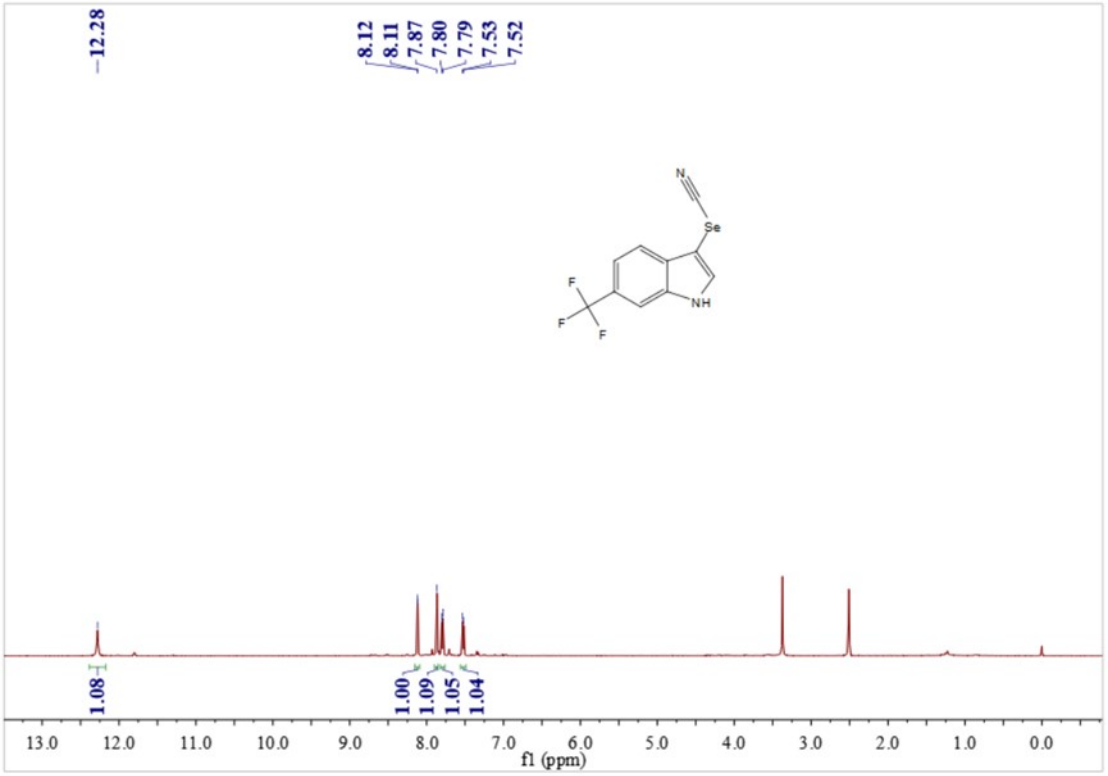

168.95
136.53
136.13
132.15
126.66
122.17
118.78
114.81
104.99
90.22
N
Se
HO
NH
O
f1 (ppm)

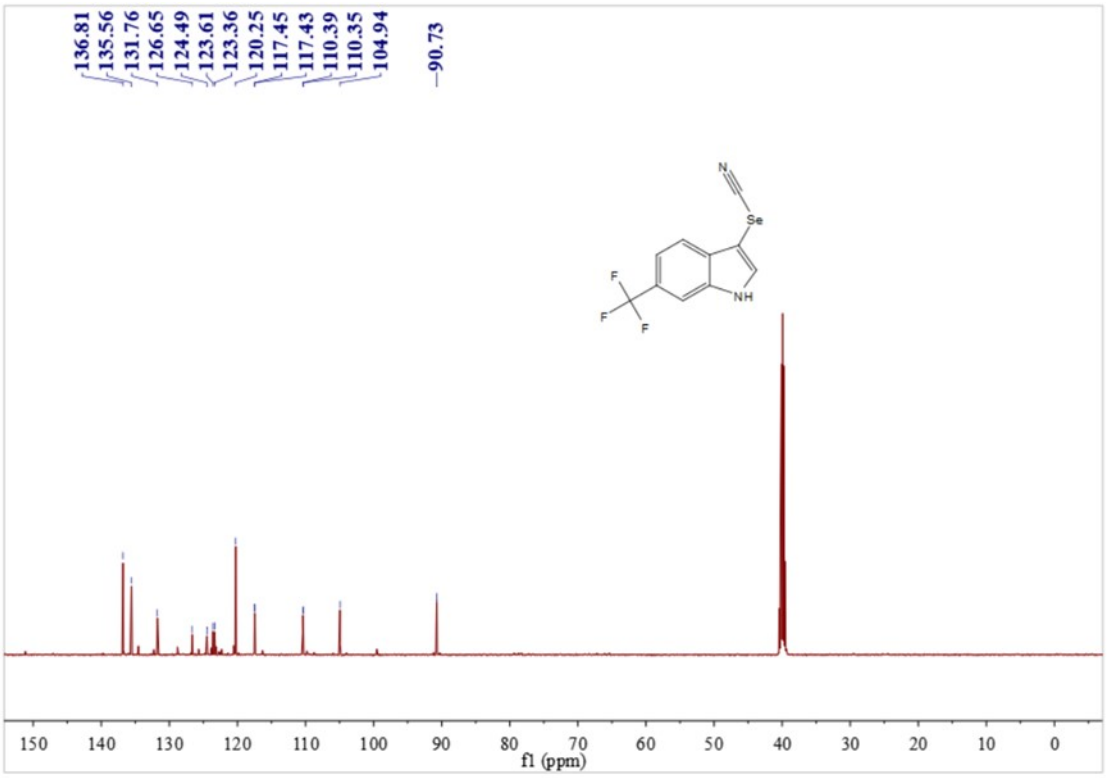

12.18
7.81
7.80
7.75
7.74
7.71
7.71
7.31
7.30
7.28
3.93
N
H3C
O
O
Se
NH
0.99
1.00
1.05
1.01
1.00
3.04
f1 (ppm)

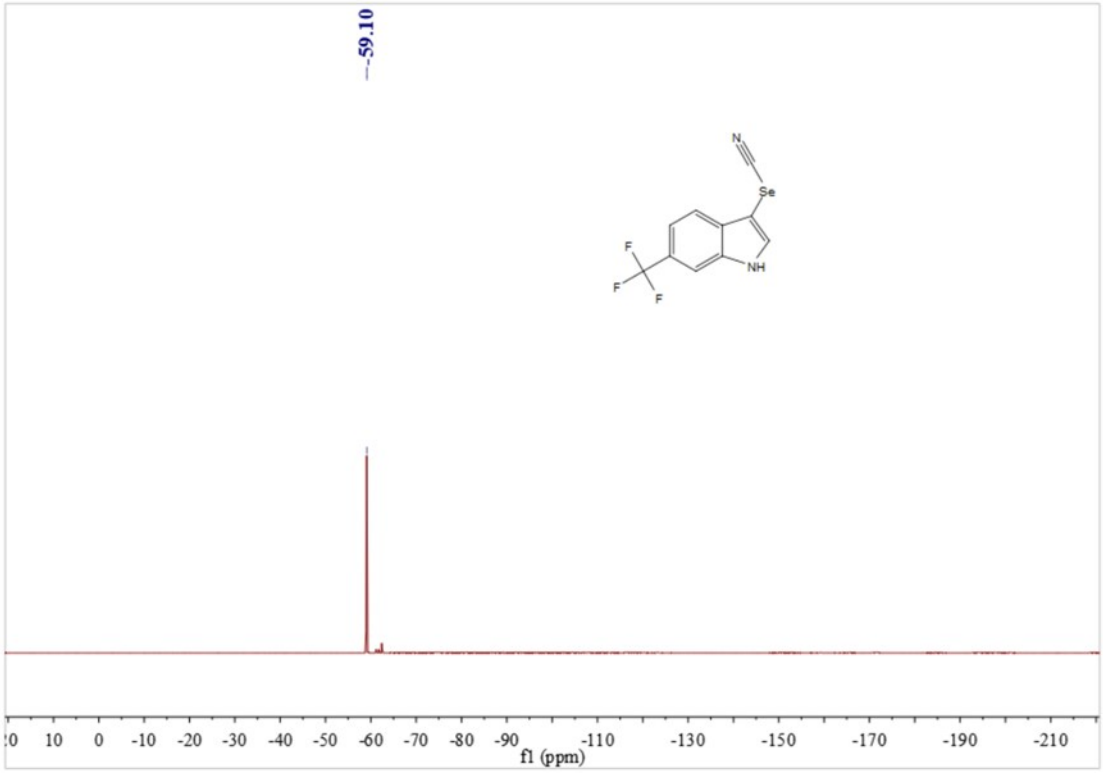

168.66
138.58
129.89
125.07
123.57
122.05
120.18
118.74
106.81
90.08
52.97
N
Se
NH
H3C
O
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


12.25
8.15
8.11
8.11
7.84
7.82
7.70
7.68
3.88
N
Se
NH
H3C
O
O
1.06
0.99
0.96
1.04
1.05
3.07
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


167.29
137.13
135.99
132.75
124.09
121.70
119.26
114.76
105.02
90.68
52.51
N
Se
NH
O
O
H3C
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


12.28
8.12
8.11
7.87
7.80
7.79
7.53
7.52
N
Se
NH
F
F
F
1.08
1.00
1.09
1.05
1.04
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


136.81
135.56
131.76
126.65
124.49
123.61
123.36
120.25
117.45
117.43
110.39
110.35
104.94
90.73
N
Se
F
F
F
NH
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


59.10
N
Se
F
F
F
NH
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

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