Supporting Information for

tetra-n-Butylammonium Iodide Mediated Reaction of Indoles with Bunte Salts: Efficient 3-Sulfenylation of Indoles under Metal-free Conditions

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Experimental Section

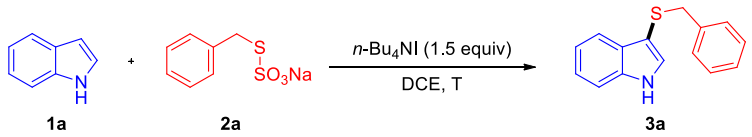
General

All the solvents for routine isolation of products and chromatography were reagent grade. Flash chromatography was performed using silica gel (300−400 mesh) with the indicated solvents. Melting points were recorded on an electrothermal digital melting point apparatus and were uncorrected. IR spectra were recorded on a spectrophotometer using KBr optics. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR) spectrometer using $CDCl_3$ or DMSO-*d*6 as solvent and TMS as internal standard. The ^{1}H NMR data are reported as the chemical shift in parts per million, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant in hertz, and number of protons. High resolution mass spectra were obtained using a high resolution ESI-TOF mass spectrometer.

General Procedure for the construction of 3a

To a mixture of indole (0.5 mmol), sodium *S*-benzyl sulfothioate (0.7 mmol), TBAI (0.75 mmol) were added in 2.5 mL DCE to test tube. The test tube was closed. The reaction mixture was stirred at 85 ^{o}C. When the reactions were completed (checked by TLC), they were cooled to room temperature, washed with 10% $Na_2S_2O_3$ solution (3*15 mL) and extracted with ethyl acetate (3*15 mL). The combined organic layers were dried over Na_2SO_4. Removal of solvent followed by flash column chromatographic purification using petroleum and ethyl acetate afforded products.

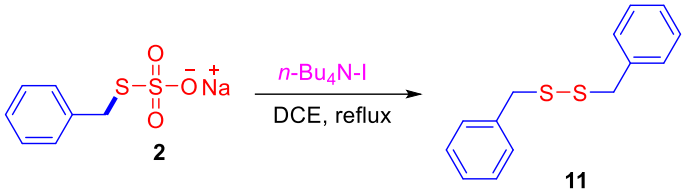
Table S1: Optimization of the reaction conditions [a]



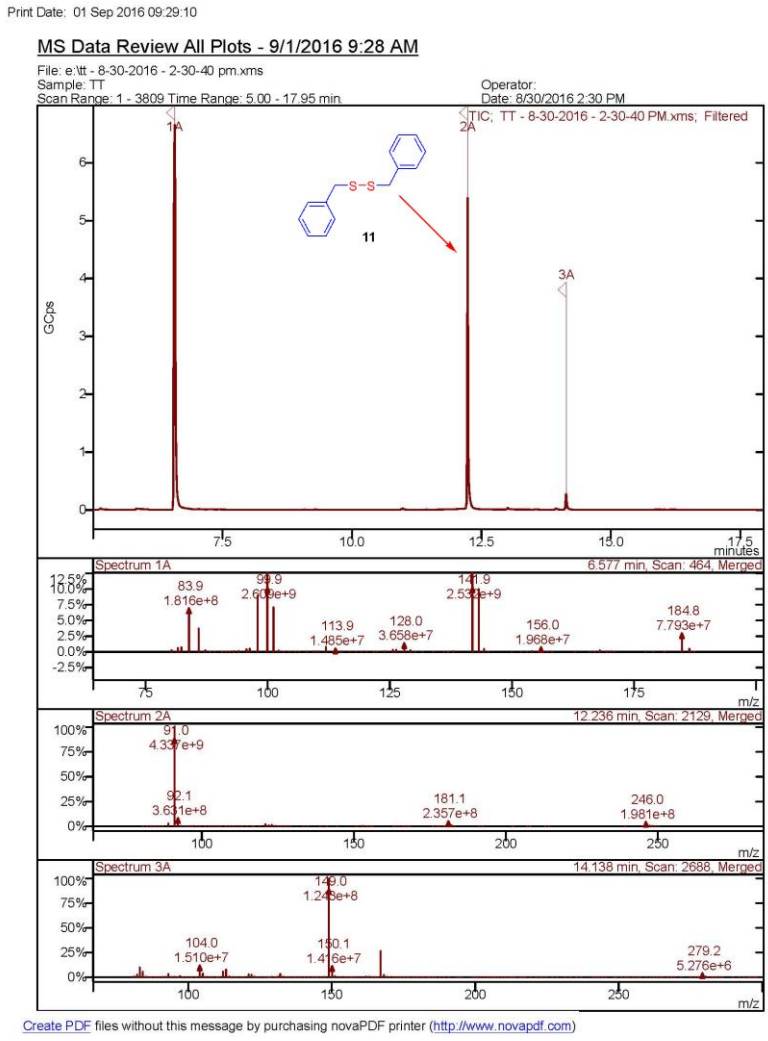
entry	catalyst	solvent	T (°C)	Yied [b](%)
1	TBAI	DCE	80	72
2	I_2	DCE	80	0
3	NIS	DCE	80	0
4	NaI	DCE	80	0
5	PIDA	DCE	80	0
6	CuI	DCE	80	0
7	TBAI	H_2O	80	0
8	TBAI	MeCN	80	0
9	TBAI	EtOH	80	0
10	TBAI	DMF	80	0
11	TBAI	DMSO	80	49
12	TBAI	Dioxane	80	0
13	TBAI	CH_2Cl_2	80	0
14	TBAI	DCE	r.t.	0
15	TBAI	DCE	40	0
16	TBAI	DCE	60	36
17	TBAI	DCE	80	72
18	TBAI	DCE	reflux	86

[a] General conditions : **1a** (0.5mmol), **2a** (0.7 mmol), TBAI (0.75 mmol). [b] GC yield

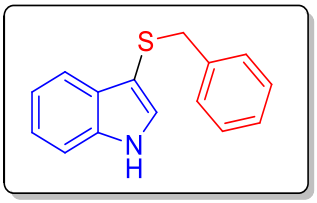
Control Experiment:



Bunte salt **2** undergoes transformations to give disulfide **11** under reflux conditions, which can be detected by GC-MS.

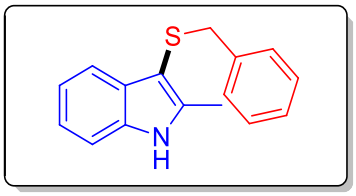


Characterization Data of Compounds:



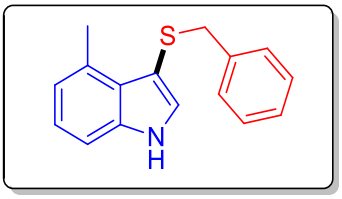
3-(Benzylthio)-1*H*-indole (3a)

White solid, mp: 67.2-68.4 ℃
IR (neat, *v*, cm^{-1}): 3403, 3056, 3030, 2925, 1453, 704 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.19 (qd, *J* = 4.7, 1.3 Hz, 5H), 7.07 (dd, *J* = 7.4, 1.9 Hz, 2H), 7.00 (d, *J* = 2.5 Hz, 1H), 3.86 (s, 2H).ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 136.4, 130.0, 129.4, 129.2, 128.4, 126.9, 122.8, 120.7, 119.5, 111.6, 105.4, 41.2.ppm;
HRMS (ESI) *m/z*: calcd for $C_{15}H_{13}NNaS$: $(M+Na)^+$ 262.0661, found: 262.0653.



3-(Benzylthio)-2-methyl-1*H*-indole (3b)

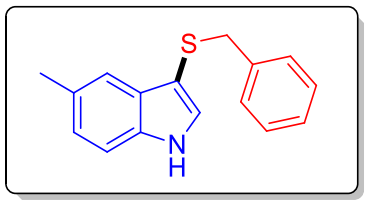
Brown solid, mp: 62.8-63.2 ℃
IR (neat, *v*, cm^{-1}): 3320, 3026, 1453, 743 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.69 – 7.62 (m, 1H), 7.30 – 7.26 (m, 1H), 7.20 – 7.12 (m, 5H), 6.95 (dd, *J* = 6.4, 3.0 Hz, 2H), 3.75 (s, 2H), 1.98 (s, 3H).ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 139.4, 135.5, 130.6, 129.2, 128.3, 126.8, 122.0, 120.5, 118.8, 110.7, 101.5, 40.5, 11.7.ppm;
HRMS (ESI) *m/z*: calcd for $C_{16}H_{15}NNaS$: $(M+Na)^+$ 276.0817, found: 276.0802.



3-(Benzylthio)-4-methyl-1*H*-indole (3c)

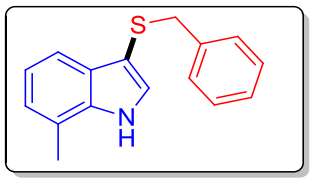
Black solid, mp: 46.6-47.1 ℃

IR (neat, *v*, cm^{-1}): 3433, 2919, 700 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.24 – 7.15 (m, 4H), 7.09 (dd, *J* = 15.4, 7.5 Hz, 3H), 6.96 – 6.80 (m, 2H), 3.84 (s, 2H), 2.91 (s, 3H).ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 136.8, 132.0, 131.0, 129.3, 128.4, 128.3, 126.9, 122.8, 122.4, 109.5, 105.5, 100.1, 43.6, 19.3.ppm;
HRMS (ESI) *m/z*: calcd for $C_{16}H_{15}NNaS$: $(M+Na)^+$ 276.0817, found: 276.0807.



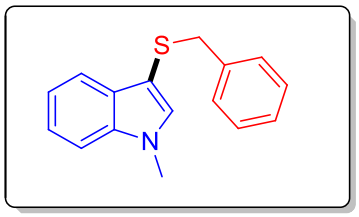
3-(Benzylthio)-5-methyl-1*H*-indole (3d)

Light yellow solid, mp: 97.7-98.8 ℃
IR (neat, *v*, cm^{-1}): 3387, 3117, 3026, 2914, 2856, 796 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.44 (s, 1H), 7.21 (dd, *J* = 13.3, 7.4 Hz, 4H), 7.11 – 7.02 (m, 3H), 6.94 (d, *J* = 2.4 Hz, 1H), 3.84 (s, 2H), 2.46 (s, 3H).ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 134.7, 130.2, 130.0, 129.7, 129.2, 128.4, 126.9, 124.4, 119.1, 111.3, 104.75, 41.2, 21.7.ppm;
HRMS (ESI) *m/z*: calcd for $C_{16}H_{15}NNaS$: $(M+Na)^+$ 276.0817, found: 276.0809.



3-(Benzylthio)-7-methyl-1*H*-indole (3e)

Light yellow solid, mp: 69.6-71.4 ℃
IR (neat, *v*, cm^{-1}): 3303, 1417, 697 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.23 – 7.15 (m, 3H), 7.09 (dt, *J* = 6.8, 4.4 Hz, 3H), 7.02 (d, *J* = 7.1 Hz, 1H), 6.97 (d, *J* = 2.6 Hz, 1H), 3.85 (s, 2H), 2.44 (s, 3H).ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 136.0, 129.7, 129.2, 129.0, 128.4, 126.9, 123.4, 120.8, 120.8, 117.2, 106.0, 41.2, 16.6.ppm;
HRMS (ESI) *m/z*: calcd for $C_{16}H_5NNaS$: $(M+Na)^+$ 276.0817, found: 276.0815.



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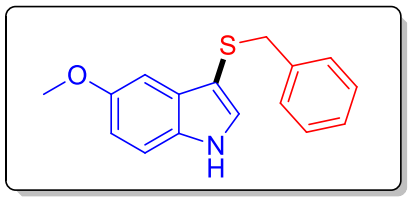
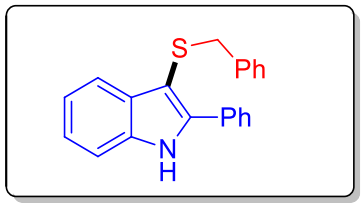
3-(Benzylthio)-1-methyl-1*H*-indole (3f)

Red oil
IR (neat, *v*, cm^{-1}): 2977, 2929, 1720, 1288, 1123, 739 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.9 Hz, 1H), 7.29 (dd, *J* = 19.0, 7.5 Hz, 2H), 7.19 (dd, *J* = 19.1, 7.5 Hz, 4H), 7.13 – 7.05 (m, 2H), 6.89 (s, 1H), 3.85 (s, 2H), 3.71 (s, 3H).ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 137.4, 134.5, 130.1, 129.2, 128.4, 126.9, 122.4, 120.2, 119.6, 109.7, 103.5, 41.7, 33.1.ppm;
HRMS (ESI) *m/z*: calcd for $C_{16}H_{15}NNaS$: $(M+Na)^+$ 276.0817, found: 276.0808.



3-(Benzylthio)-5-methoxy-1*H*-indole (3g)

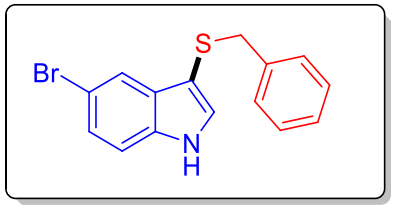
Grown oil
IR (neat, *v*, cm^{-1}): 3410, 2941, 2829, 1481, 1203, 1166, 797, 698 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.23 – 7.14 (m, 4H), 7.05 (dd, *J* = 8.8, 7.0 Hz, 3H), 6.96 (s, 1H), 6.85 (d, *J* = 8.8 Hz, 1H), 3.82 (s, 5H).ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 139.4, 131.2, 130.8, 130.2, 129.2, 128.4, 126.9, 113.3, 112.4, 104.8, 100.7, 55.9, 41.4.ppm;
HRMS (ESI) *m/z*: calcd for $C_{16}H_{15}NONaS$: $(M+Na)^+$ 292.0767, found: 292.0756.



3-(Benzylthio)-2-phenyl-1*H*-indole (3h)

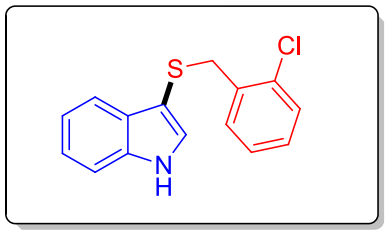
Grown oil
IR (neat, *v*, cm^{-1}): 3404, 3057, 3027, 1453, 741, 692 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.51 (dt, *J* = 4.0, 2.2 Hz, 2H), 7.41 – 7.28 (m, 4H), 7.27 – 7.16 (m, 2H), 7.12 – 7.02 (m, 3H), 6.95 (dd, *J* = 6.7, 2.7 Hz, 2H),

3.84 (s, 2H).ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 138.5, 135.8, 131.9, 131.5, 129.1, 128.6, 128.4, 128.4, 128.3, 126.9, 123.6, 120.9, 119.9, 111.3, 102.6, 40.8.ppm;
HRMS (ESI) *m/z*: calcd for $C_{21}H_{17}NNaS$: $(M+Na)^+$ 338.0974, found: 338.0968.



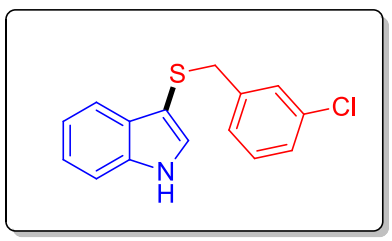
3-(Benzylthio)-5-bromo-1*H*-indole (3i)

Light yellow solid, mp: 112.8-113.8 ℃
IR (neat, *v*, cm^{-1}): 3301, 1452, 975 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.72 (d, *J* = 1.3 Hz, 1H), 7.28 (d, *J* = 8.6 Hz, 1H), 7.22 – 7.17 (m, 4H), 7.04 (dd, *J* = 6.4, 2.8 Hz, 2H), 6.97 (d, *J* = 2.6 Hz, 1H), 3.81 (s, 2H).ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 134.9, 131.3, 131.2, 129.2, 128.4, 127.1, 125.8, 122.2, 114.2, 113.1, 105.2, 41.2.ppm;
HRMS (ESI) *m/z*: calcd for $C_{15}H_{12}B_rNNaS$: $(M+Na)^+$ 339.9766, found: 339.9755.



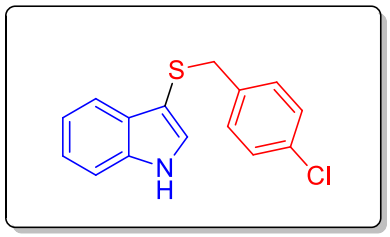
3-((2-Chlorobenzyl)thio)-1*H*-indole (5a)

Yellow solid, mp: 76.6-77.4 ℃
IR (neat, *v*, cm^{-1}): 3298, 1412, 1234, 1051, 738 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 8.1 Hz, 2H), 7.24 – 7.08 (m, 3H), 7.08 – 6.95 (m, 2H), 6.80 (d, *J* = 7.6 Hz, 1H), 3.97 (s, 2H).ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.7, 136.4, 134.1, 131.2, 130.4, 129.7, 129.6, 128.4, 126.5, 122.9, 120.7, 119.5, 111.6, 105.1, 38.9.ppm;
HRMS (ESI) *m/z*: calcd for $C_{15}H_{12}ClNNaS$: $(M+Na)^+$ 296.0271, found: 296.0266.



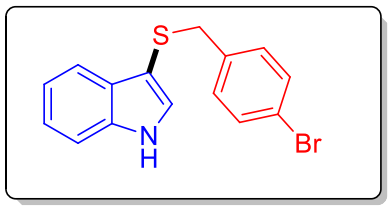
3-((3-Chlorobenzyl)thio)-1*H*-indole (5b)

Grown solid, mp: 70.7-71.3 ℃
IR (neat, *v*, cm^{-1}): 3404, 3377, 798, 742 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.22 – 7.17 (m, 1H), 7.17 – 7.13 (m, 1H), 7.10 (t, *J* = 7.7 Hz, 1H), 7.05 (s, 1H), 7.02 (d, *J* = 2.6 Hz, 1H), 6.91 (d, *J* = 7.4 Hz, 1H), 3.80 (s, 2H).ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 136.4, 134.1, 130.2, 129.6, 129.3, 129.2, 127.3, 127.1, 123.0, 120.8, 119.4, 111.7, 104.9, 40.6.ppm;
HRMS (ESI) *m/z*: calcd for $C_{15}H_{12}ClNNaS$: $(M+Na)^+$ 296.0271, found: 296.0268.



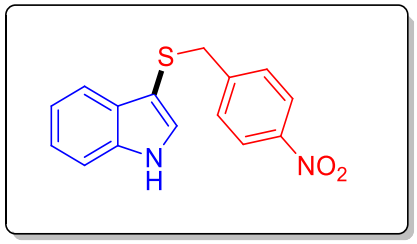
3-((4-Chlorobenzyl)thio)-1H-indole (5c)

Yellow solid, mp: 44.2-45.0℃
IR (neat, *v*, cm^{-1}): 3376, 3322, 3110, 1657, 762 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.28 – 7.10 (m, 4H), 6.96 (dd, *J* = 12.0, 5.5 Hz, 3H), 3.80 (s, 2H).ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 136.4, 132.7, 130.5, 130.2, 129.3, 128.5, 123.0, 120.8, 119.4, 111.7, 104.9, 40.3.ppm;
HRMS (ESI) *m/z*: calcd for $C_{15}H_{12}ClNNaS$: $(M+H)^+$296.0271, found: 296.0275.



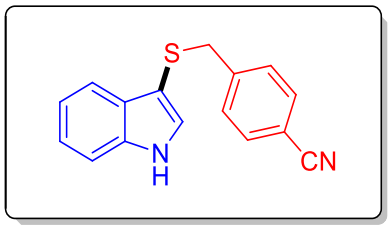
3-((4-Bromobenzyl)thio)-1*H*-indole (5d)

Light yellow Solid, mp: 114.2-115.3 ℃
IR (neat, *v*, cm^{-1}): 3272, 1651, 1595, 1474 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.25 – 7.17 (m, 2H), 6.97 (d, *J* = 2.6 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 2H), 3.78 (s, 2H).ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 136.4, 131.4, 130.9, 130.3, 129.3, 122.9, 120.8, 119.4, 111.7, 104.7, 40.3.ppm;
HRMS (ESI) *m/z*: calcd for $C_{15}H_{12}BrNNaS$: $(M+Na)^+$ 339.9766, found: 339.9757.



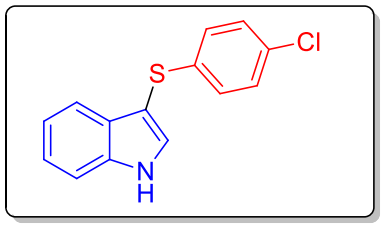
3-((4-Nitrobenzyl)thio)-1*H*-indole (5e)

Yellow solid, mp: 112.0-112.9 ℃
IR (neat, *v*, cm^{-1}): 3424, 2929, 149, 1348, 1095, 743 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.02 (d, *J* = 8.7 Hz, 2H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 2.6 Hz, 1H), 3.89 (s, 2H).ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 146.9, 136.4, 130.5, 129.9, 129.2 123.6, 123.2, 121.0, 119.2, 111.9, 104.0, 40.2.ppm;
HRMS (ESI) *m/z*: calcd for $C_{15}H_{12}N_2NaO_2S$: $(M+Na)^+$ 307.0512, found: 307.0502.



4-(((1*H*-Indol-3-yl)thio)methyl)benzonitrile (5f)

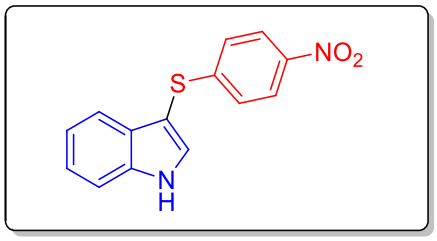
Grown oil
IR (neat, *v*, cm-^{1}): 3309, 3065, 2913, 2226, 1414, 737 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.41 (dd, *J* = 26.0, 8.1 Hz, 3H), 7.26 – 7.16 (m, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.97 (d, *J* = 2.6 Hz, 1H), 3.84 (s, 2H).ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 136.4, 132.1, 130.4, 129.8, 129.2, 123.1, 120.9, 119.2, 111.8, 110.5, 104.1, 40.6.ppm;
HRMS (ESI) *m/z*: calcd for $C_{16}H_{12}N_2NaS$: $(M+Na)^+$ 287.0613, found: 287.0613.



3-((4-Chlorophenyl)thio)-1*H*-indole (5g)

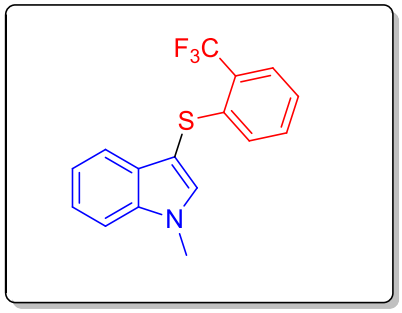
White solid, mp: 137.0-137.7 ℃

IR (neat, *v*, cm^{-1}): 3405, 1474, 1090, 748 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 2.6 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.40 – 7.27 (m, 1H), 7.20 – 7.15 (m, 1H), 7.15 – 7.06 (m, 2H), 7.06 – 6.97 (m, 2H).ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 136.7, 130.9, 130.8, 129.0, 129.0, 127.3, 123.4, 121.3, 119.7, 111.9.ppm;
HRMS (ESI) *m/z*: calcd for $C_{14}H_{10}ClNNaS$: $(M+Na)^+$ 282.0115, found:282.0117.



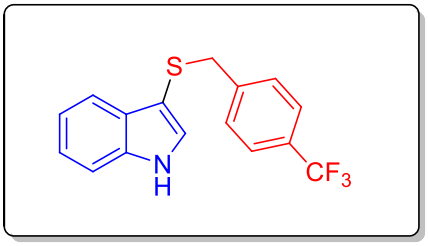
3-((4-Nitrophenyl)thio)-1*H*-indole (5h)

Yellow solid, mp: 126.5-126.9 ℃
IR (neat, *v*, cm^{-1}): 3419, 3101, 1325, 1088, 739 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.07 – 7.94 (m, 2H), 7.61 – 7.43 (m, 3H), 7.34 – 7.29 (m, 1H), 7.23 – 7.17 (m, 1H), 7.16 – 7.07 (m, 2H).ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 136.8, 131.4, 128.6, 125.3, 124.1, 123.8, 121.7, 119.4, 112.2, 100.5.ppm;
HRMS (ESI) *m/z*: calcd for $C_{14}H_{10}N_2NaO_2S$: $(M+Na)^+$ 293.0355, found: 293.0352.



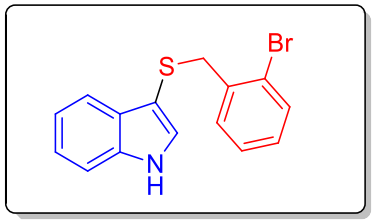
3-((2-(Trifluoromethyl)phenyl)thio)-1*H*-indole (5i)

Light yellow solid, mp: 120.4-121.9 ℃
IR (neat, *v*, cm^{-1}): 2919, 2852, 1313, 1109, 732 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.54 (m, 2H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.35 (s, 1H), 7.33 – 7.28 (m, 1H), 7.20 – 7.06 (m, 3H), 6.93 (d, *J* = 7.4 Hz, 1H), 3.85 (s, 3H).ppm;
^{13}C NMR (101 MHz, CDCl3) δ 139.9, 137.9, 136.0, 132.0, 130.0, 128.9 ($J_{C\text{-}F}$ = 272Hz), 127.84, 126.6 ($J_{C\text{-}F}$ = 31Hz), 126.6 ($J_{C\text{-}F}$ = 4Hz), 124.4, 123.0, 121.0, 119.8, 110.1, 99.3 ($J_{C\text{-}F}$ =2Hz), 33.5.ppm;
^{19}F NMR (376 MHz, CDCl3) δ -61.28;
HRMS (ESI) *m/z*: calcd for $C_{16}H_{12}F_3NNaS$: $(M+Na)^+$ 330.0535, found: 330.0524.



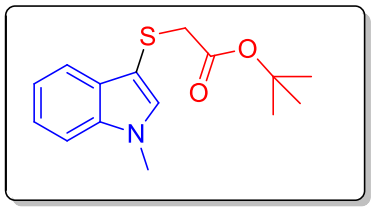
3-((4-(Trifluoromethyl)benzyl)thio)-1*H*-indole (5j)

White solid, mp: 84.0-86.4 ℃
IR (neat, *v*, cm^{-1}): 3409, 2926, 1615, 1115, 749 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.40 (dd, *J* = 21.5, 8.0 Hz, 3H), 7.23 – 7.08 (m, 4H), 6.99 (d, *J* = 2.6 Hz, 1H), 3.87 (s, 2H).ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 136.4, 130.3, 129.4, 129.3, 129.1 (J_{C-F} = 33Hz), 125.3 (J_{C-F} = 4Hz), 124.4 (J_{C-F} = 270Hz) 123.0, 120.9, 119.3, 111.7, 104.6, 40.5.ppm;
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.35;
HRMS (ESI) *m/z*: calcd for $C_{16}H_{12}F_3NNaS$: $(M+Na)^+$ 330.0535, found: 330.0529.



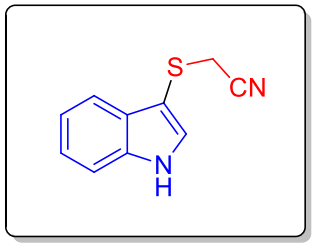
3-((2-Bromobenzyl)thio)-1*H*-indole (5k)

Yellow solid, mp: 69.7-71.2 ℃
IR (neat, *v*, cm-^{1}): 3304, 3055, 2962, 1024, 737, 707 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.57 – 7.47 (m, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.14 (m, 2H), 7.09 – 6.97 (m, 3H), 6.80 (dd, *J* = 4.0, 2.5 Hz, 1H), 3.98 (s, 2H).ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 136.4, 133.1, 131.2, 130.4, 129.6, 128.6, 127.1, 124.7, 122.9, 120.7, 119.5, 111.6, 105.1, 41.5.ppm;
HRMS (ESI) calcd for $C_{15}H_{12}BrNNaS$: $(M+Na)^+$ 339.9766, *m/z*: found: 339.9756.



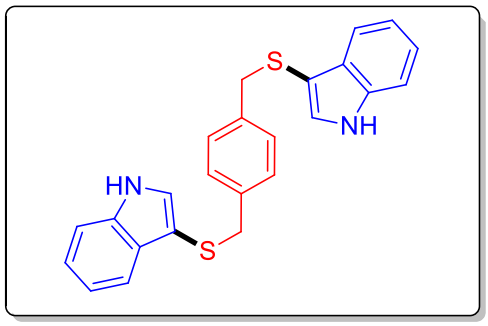
***tert*-Butyl 2-((1-methyl-1*H*-indol-3-yl)thio)acetate (5l)**

Yellow oil.
IR (neat, *v*, cm^{-1}): 2977, 2929, 1720, 1123, 740 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.28 (dd, *J* = 6.9, 1.0 Hz, 1H), 7.25 (s, 1H), 7.23 – 7.17 (m, 1H), 3.78 (s, 3H), 3.31 (s, 2H), 1.37 (s, 9H),ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 137.4, 134.8, 129.9, 122.5, 120.4, 119.6, 109.8, 103.1, 81.4, 40.4, 33.2, 28.1.ppm;
HRMS (ESI) *m/z*: calcd for $C_{15}H_{19}NNaO_2S$: $(M+Na)^+$300.1029, found: 300.1040.



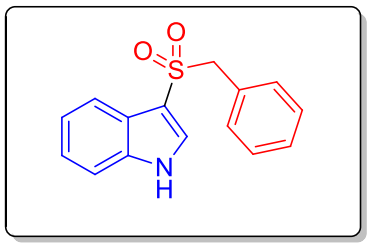
2-((1*H*-Indol-3-yl)thio)acetonitrile (5m)

Grown solid, mp: 49.6-51.2 ℃
IR (neat, *v*, cm^{-1}): 3379, 3305, 2973, 2926, 2854, 2244, 1234, 745 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.76 (d, *J* = 7.3 Hz, 1H), 7.54 (d, *J* = 2.5 Hz, 1H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.31 – 7.23 (m, 2H), 3.38 (s, 2H).ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 131.8, 128.7, 123.5, 121.4, 119.0, 117.5, 112.1, 102.4, 22.71.ppm;
HRMS (ESI) *m/z*: calcd for $C_{10}H_8N_2NaS$: $(M+Na)^+$ 211.0300, found: 211.0300.



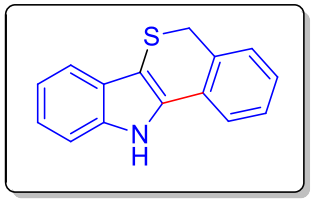
1, 4-Bis(((1*H*-indol-3-yl)thio)methyl)benzene (7)

White solid, mp: 145-146 ℃
IR (neat, *v*, cm^{-1}): 3386, 2365, 2160, 1453, 741 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 2H), 7.71 (d, *J* = 7.6 Hz, 3H), 7.35 (d, *J* = 7.9 Hz, 3H), 7.24 – 7.16 (m, 6H), 6.96 – 6.79 (m, 6H), 3.80 (s, 4H).ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 136.3, 130.2, 129.5, 129.0, 122.8, 120.7, 119.5, 111.6, 105.2, 40.7.ppm;
HRMS (ESI) *m/z*: calcd for $C_{24}H_{20}N_2NaS_2$: $(M+Na)^+$ 423.0960, found: 423.0961.



3-(Benzylsulfonyl)-1*H*-indole (8)

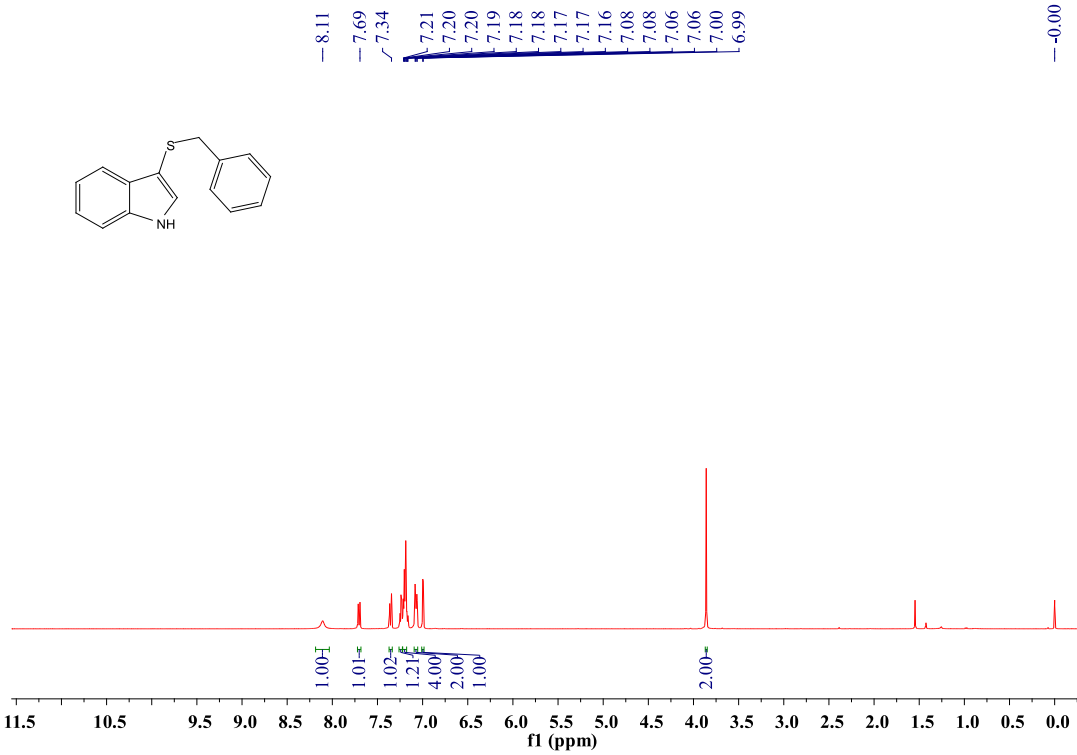
Yellow solid, mp: 49.6-51.2 ℃
IR (neat, *v*, cm^{-1}): 3256, 2969, 2919, 2363, 1689, 1289, 719 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.17 – 7.94 (m, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 6.9 Hz, 1H), 7.37 (d, *J* = 3.1 Hz, 1H), 7.31 – 7.16 (m, 5H), 7.09 – 7.01 (m, 2H), 4.41 (s, 2H).ppm;
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 136.1, 131.3, 131.0, 129.1, 128.8, 128.6, 124.2, 122.8, 119.6, 113.2, 112.4, 63.4.ppm;
HRMS (ESI) *m/z*: calcd for $C_{15}H_{13}NNaO_2S$: $(M+Na)^+$ 294.0559, found: 294.0556.

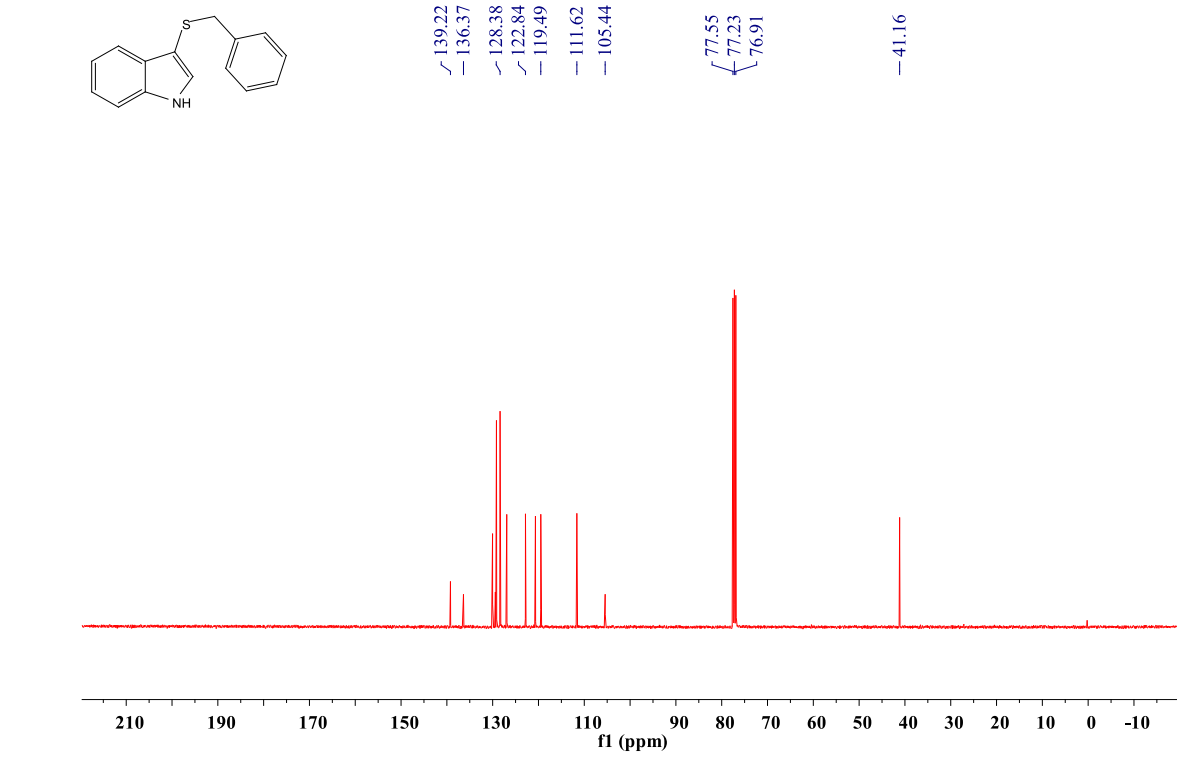


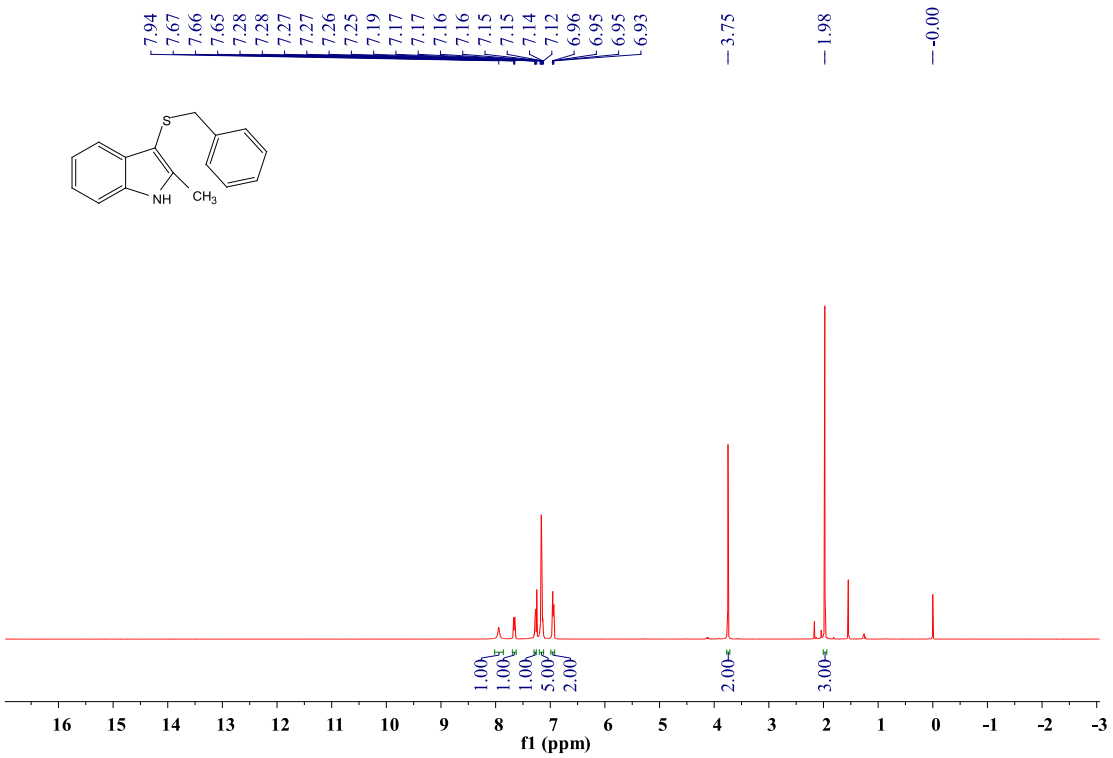
5, 11-Dihydroisothiochromeno[4,3-*b*]indole (9)

White solid, mp: 145-146 ℃.
IR (neat, *v*, cm^{-1}): 3272, 1651, 1595, 1474 cm^{-1}.
^{1}H NMR (400 MHz, CDCl3) *δ* 8.35 (s, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.46 – 7.33 (m, 3H), 7.29 (dd, J = 12.7, 5.1 Hz, 2H), 7.24 – 7.18 (m, 1H), 7.14 (t, J = 7.5 Hz, 1H), 4.02 (s, 2H).ppm;
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 136.8, 132.3, 130.9, 128.2, 128.1, 127.9, 126.9, 123.7, 121.7, 120.5, 119.7, 111.5, 107.0, 32.9.ppm;
HRMS (ESI) *m/z*: calcd for $C_{15}H_{11}NNaS$: $(M+Na)^+$ 260.0504, found: 260.0509.

Copies of ^{1}H and ^{13}C NMR Spectra for Compounds



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7.65
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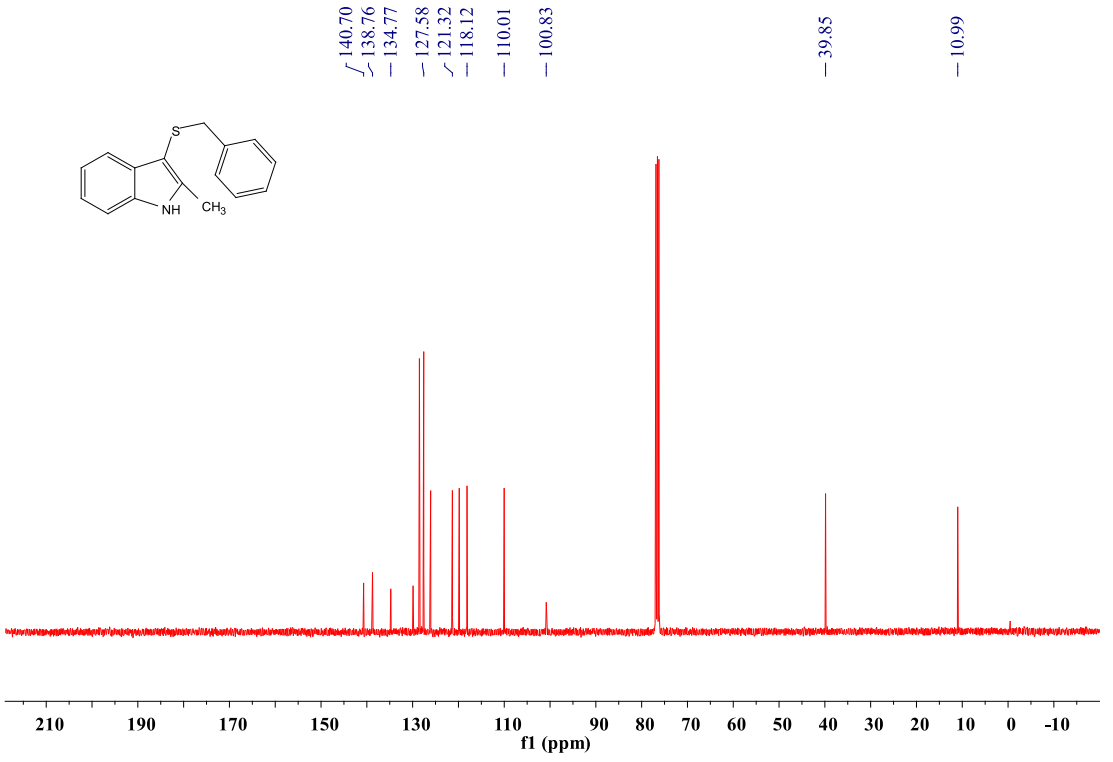
7.27
7.27
7.26
7.25
7.19
7.17
7.17
7.16
7.16
7.15
7.15
7.14
7.12
6.96
6.95
6.95
6.93
3.75
1.98
0.00
S
NH
CH3
1.00
1.00
1.00
5.00
2.00
2.00
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


140.70
138.76
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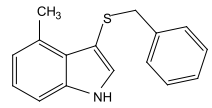
127.58
121.32
118.12
110.01
100.83
39.85
10.99
S
NH
CH3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CH3
S
NH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7.10
7.06
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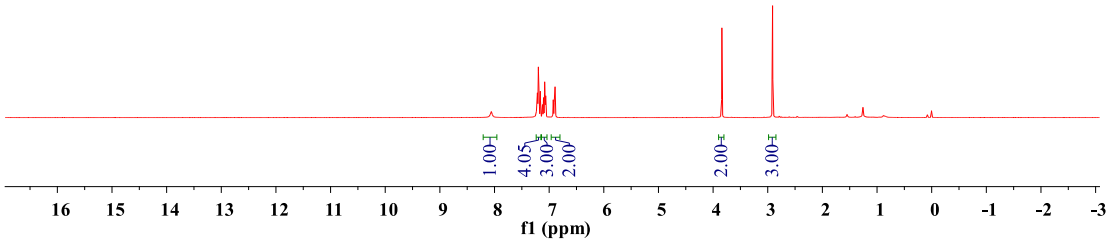
6.91
6.89
3.84
2.91
0.00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3.00
2.00
2.00
3.00
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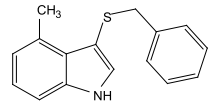
f1 (ppm)


CH3
S
NH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131.03
129.28
128.38
128.30
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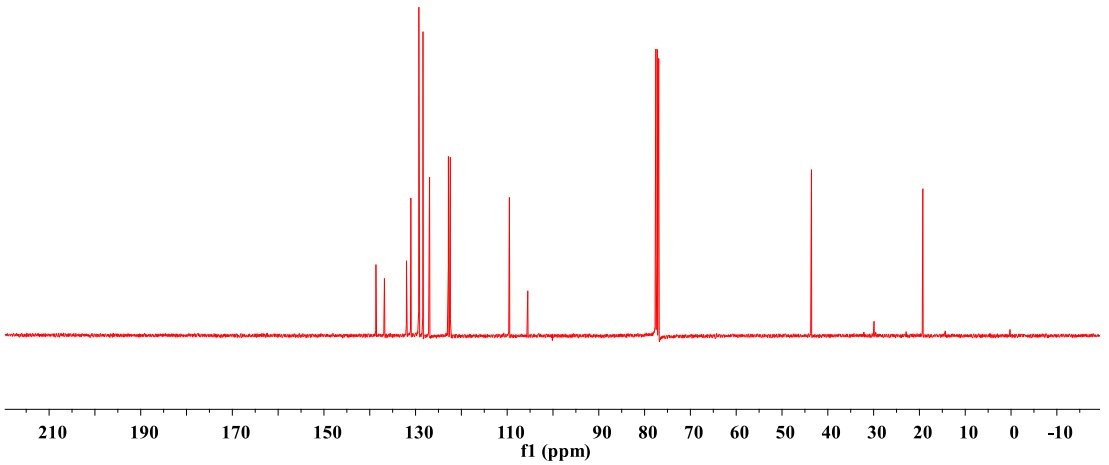
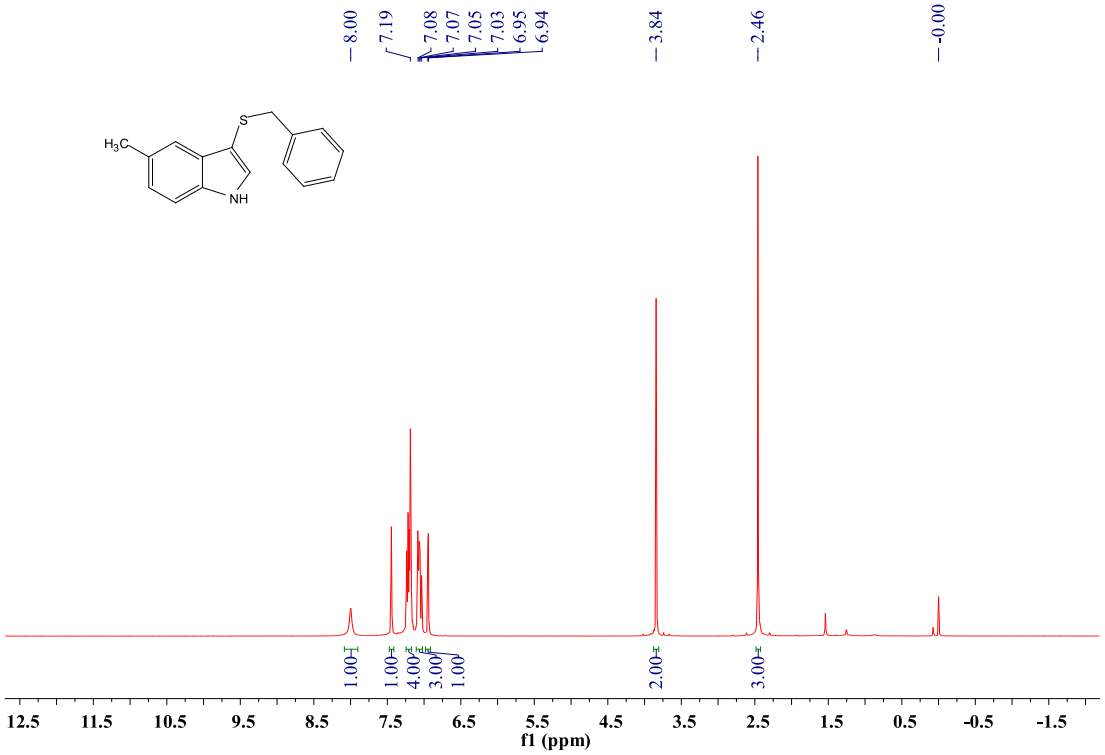
122.83
122.41
109.51
105.50
100.13
77.55
77.23
76.91
43.57
19.26


210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.19
7.08
7.07
7.05
7.03
6.95
6.94
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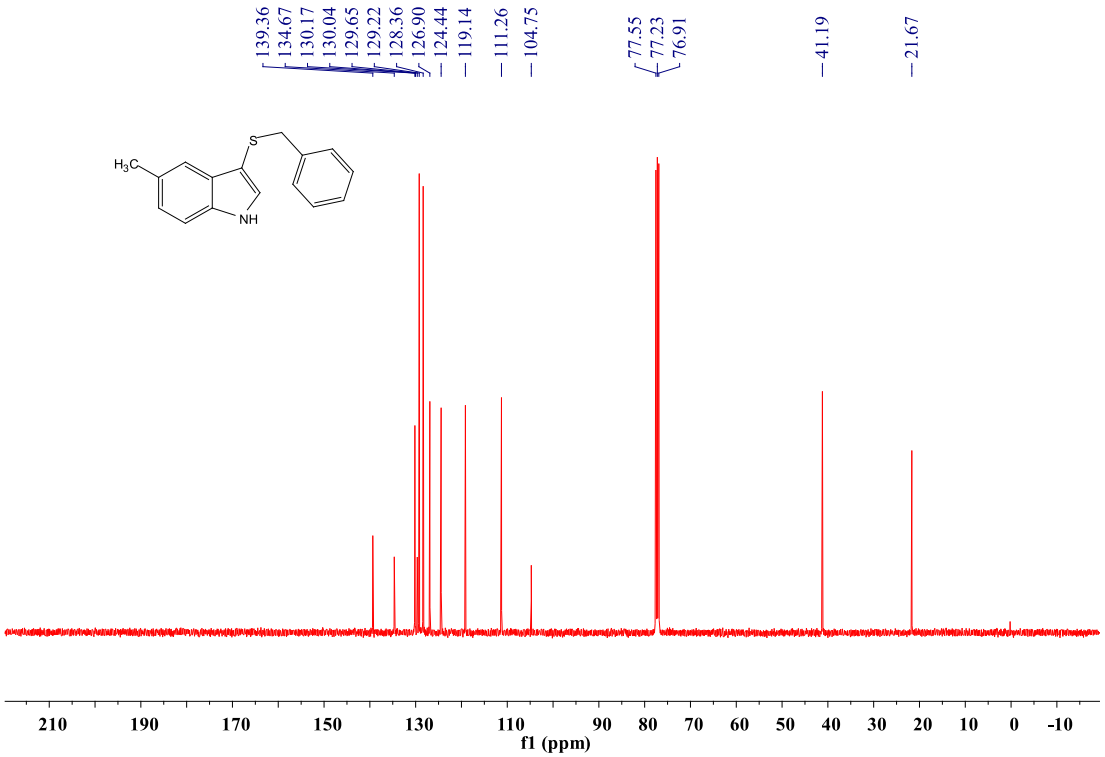
1.00
4.00
3.00
1.00
2.00
3.00
S
H3C
NH
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)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119.14
111.26
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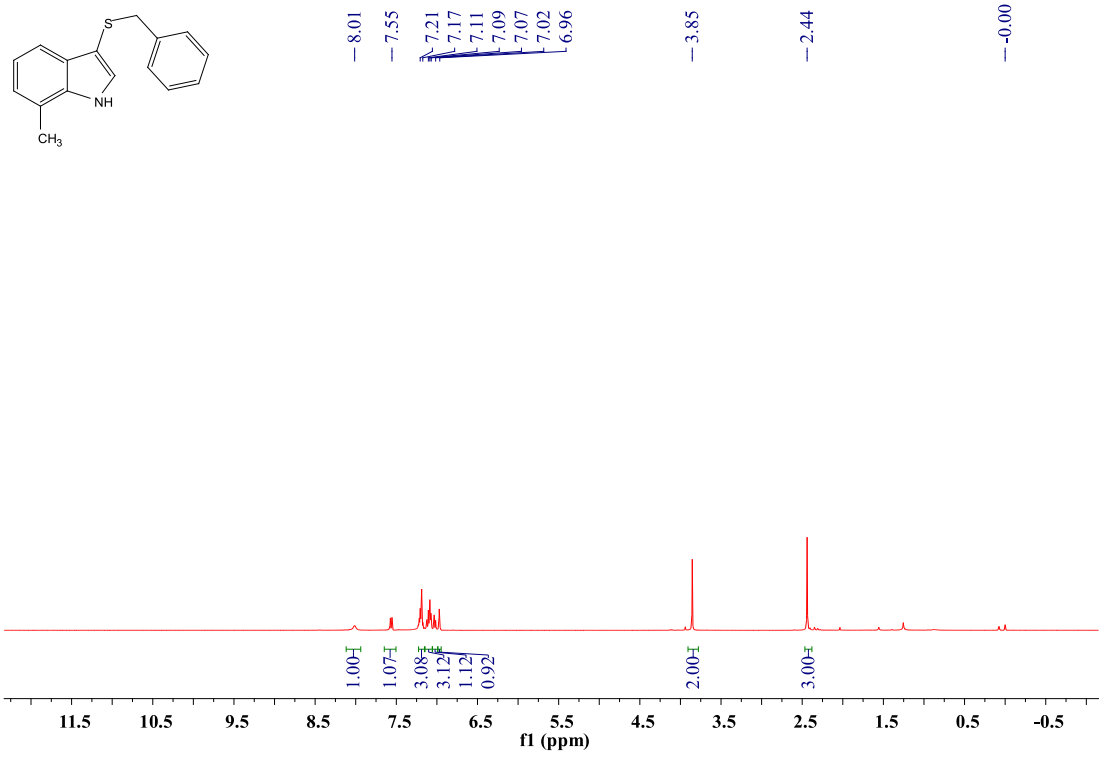
77.55
77.23
76.91
41.19
21.67
S
H3C
NH
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

S
NH
CH3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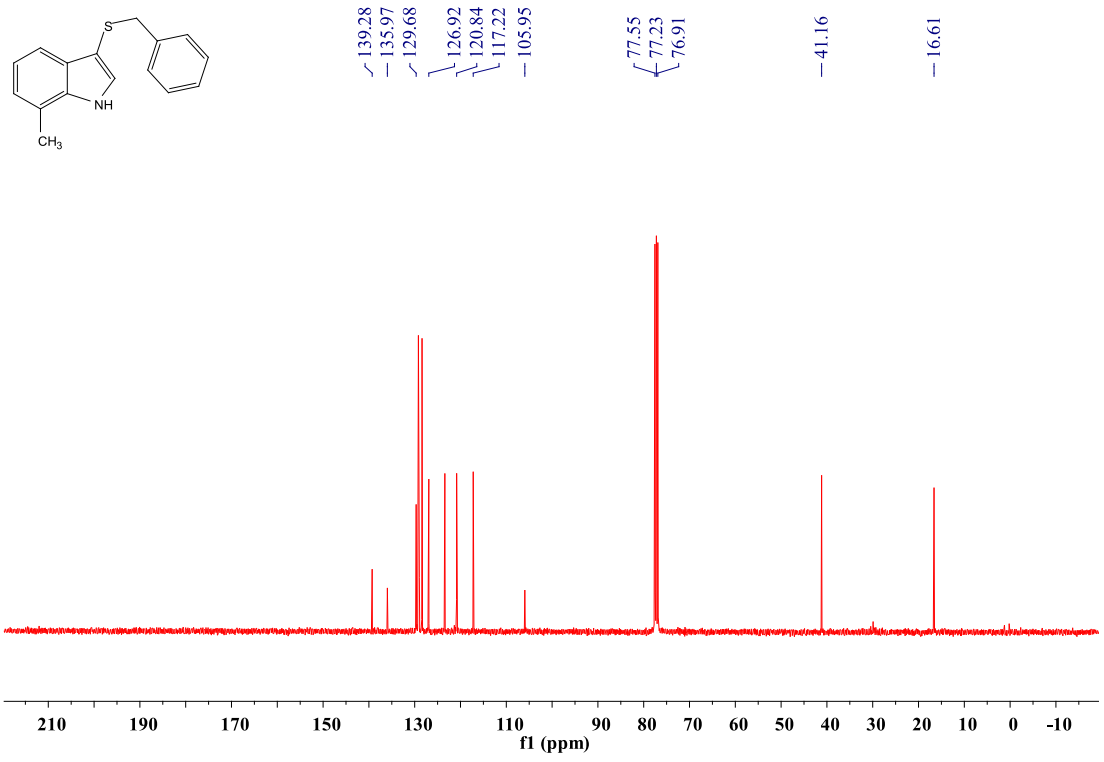
7.17
7.11
7.09
7.07
7.02
6.96
3.85
2.44
-0.00
1.00
1.07
3.08
3.12
1.12
0.92
2.00
3.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

S
NH
CH3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126.92
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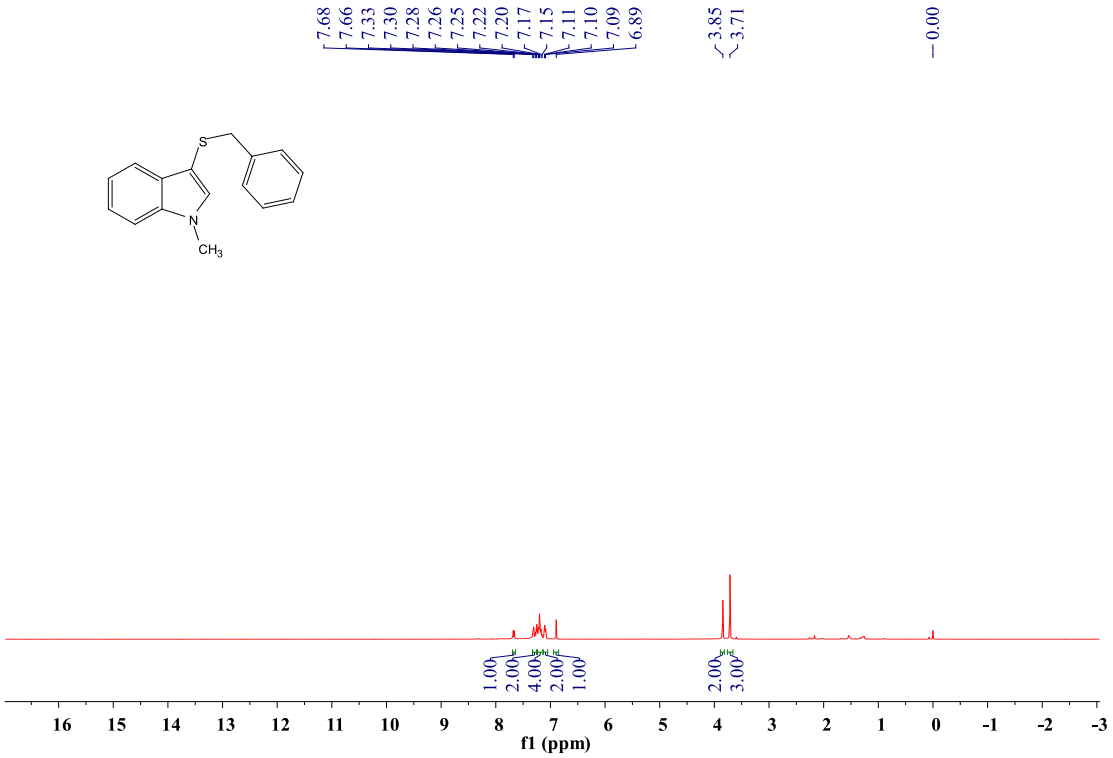
117.22
105.95
77.55
77.23
76.91
41.16
16.61
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.22
7.20
7.17
7.15
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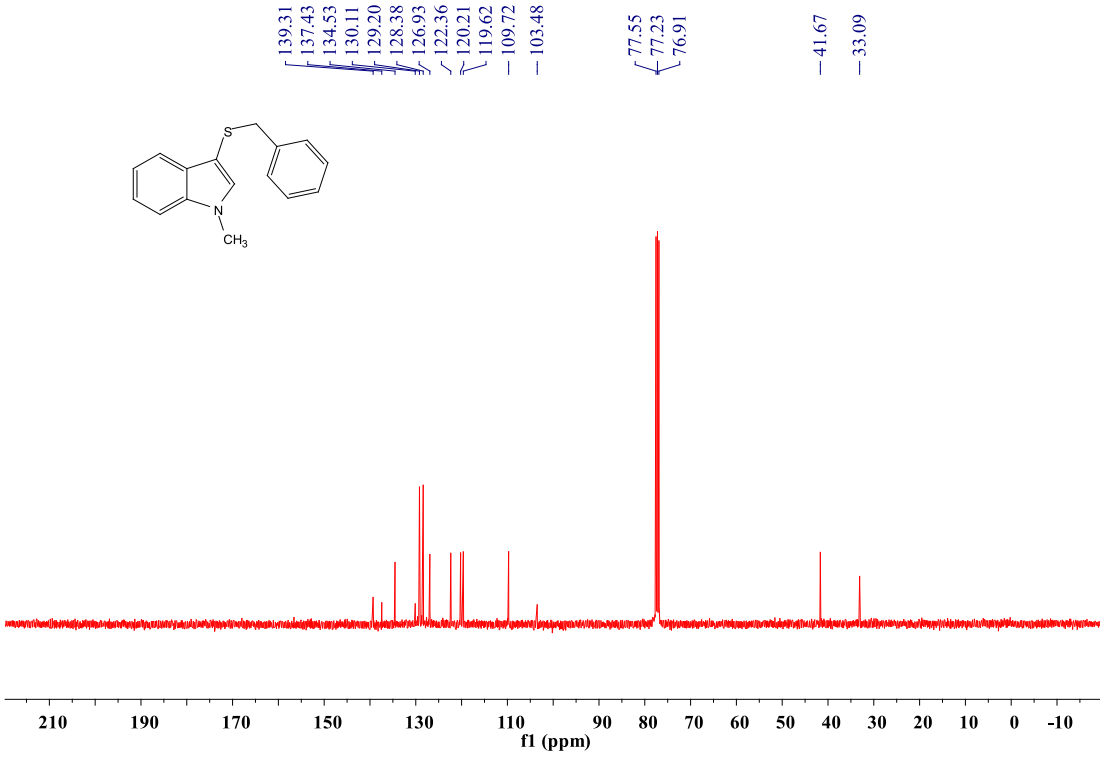
7.10
7.09
6.89
3.85
3.71
0.00
S
N
CH3
1.00
2.00
4.00
2.00
1.00
2.00
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)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122.36
120.21
119.62
109.72
103.48
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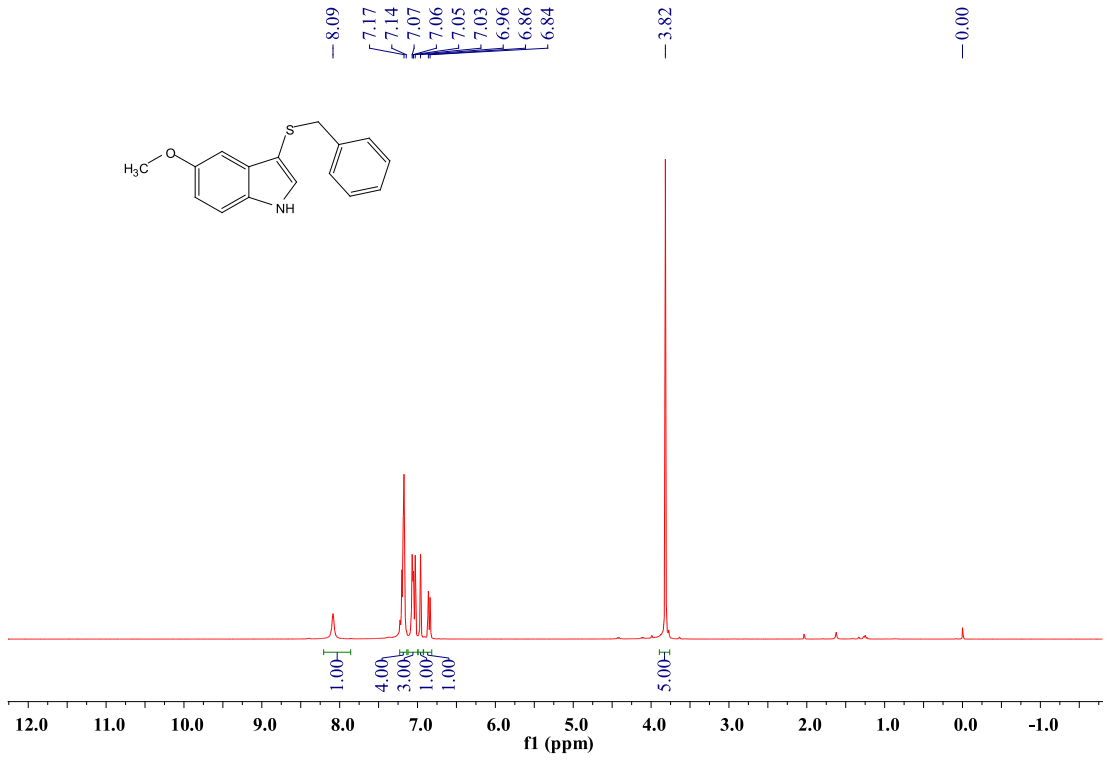
77.23
76.91
41.67
33.09
S
N
CH3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.09
7.17
7.14
7.07
7.06
7.05
7.03
6.96
6.86
6.84
3.82
0.00
1.00
4.00
3.00
1.00
1.00
5.00
12.0
11.0
10.0
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5.0
4.0
3.0
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1.0
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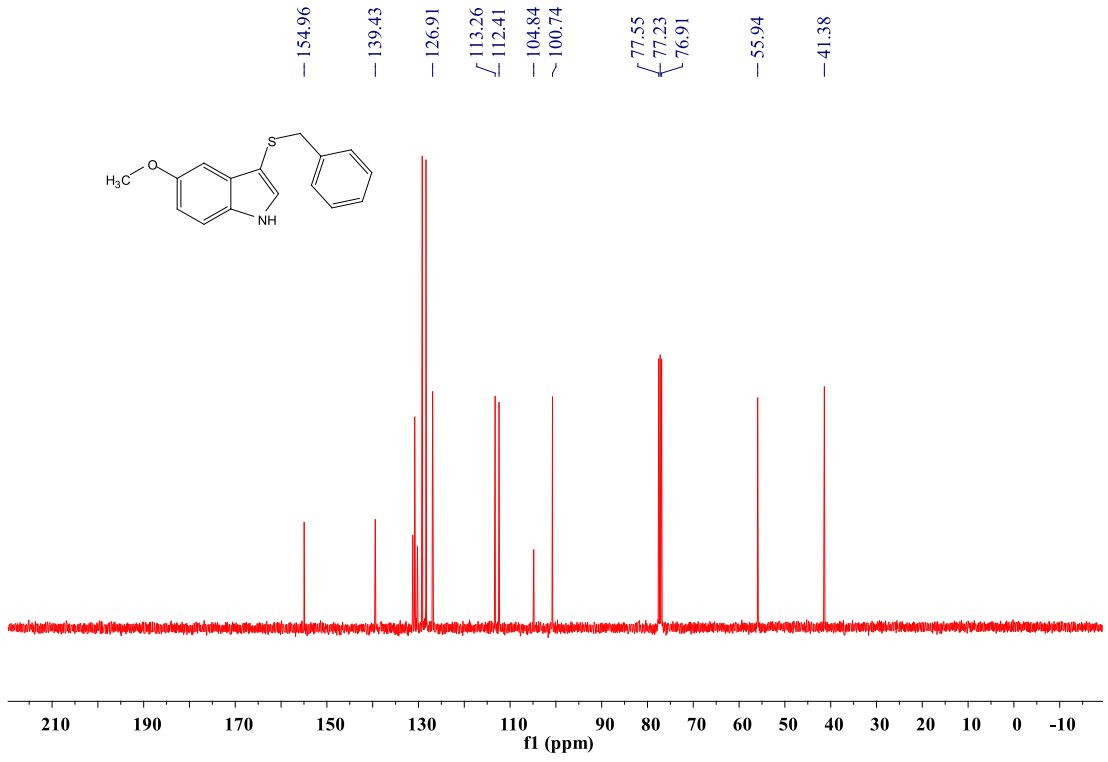
-1.0
f1 (ppm)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113.26
112.41
104.84
100.74
77.55
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76.91
55.94
41.38
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110
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80
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60
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40
30
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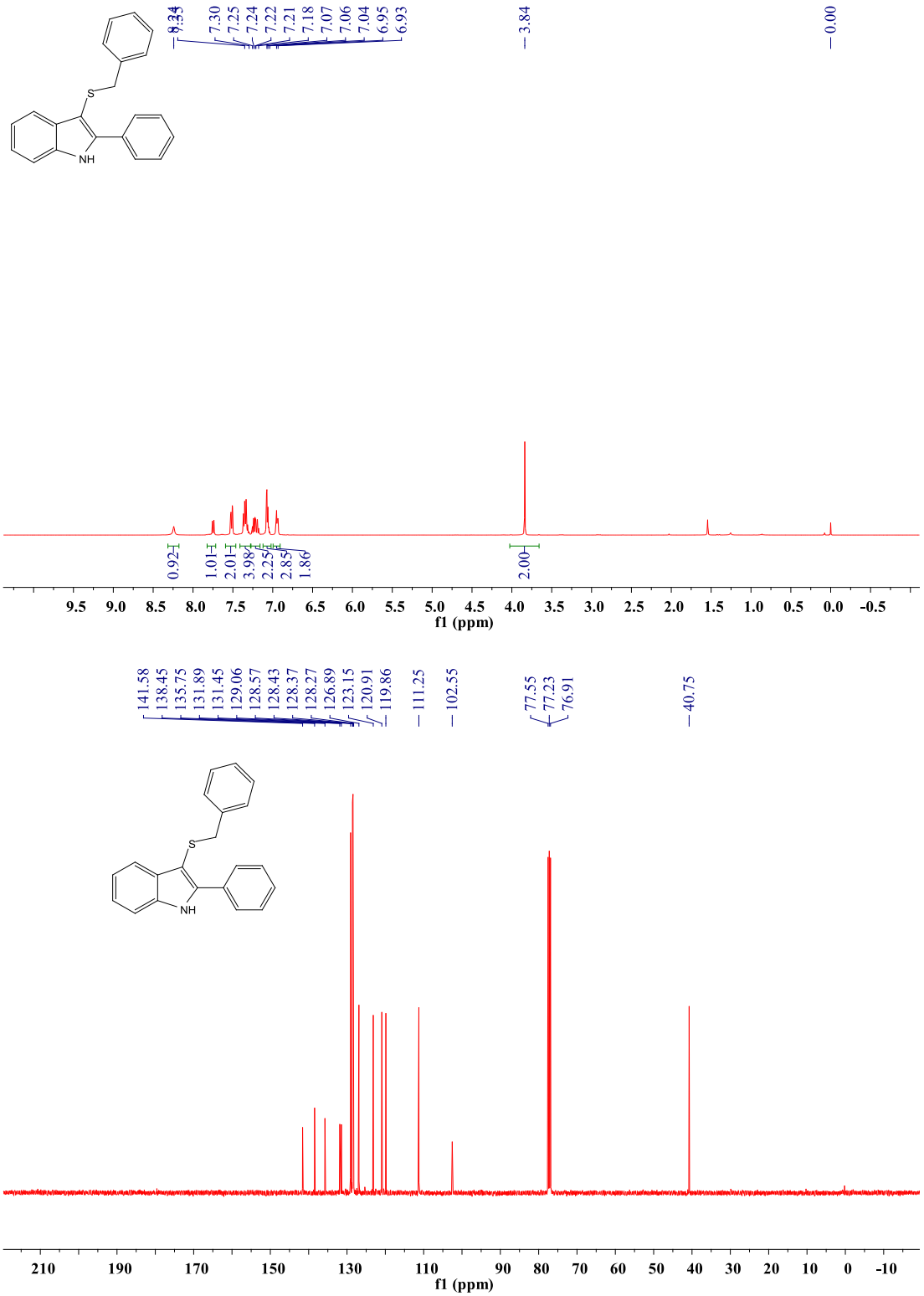
-10
f1 (ppm)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7.18
7.07
7.06
7.04
6.95
6.93
3.84
0.00
S
NH
0.92
1.01
2.01
3.98
2.25
2.85
1.86
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
141.58
138.45
135.75
131.89
131.45
129.06
128.57
128.43
128.37
128.27
126.89
123.15
120.91
119.86
111.25
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77.23
76.91
40.75
S
NH
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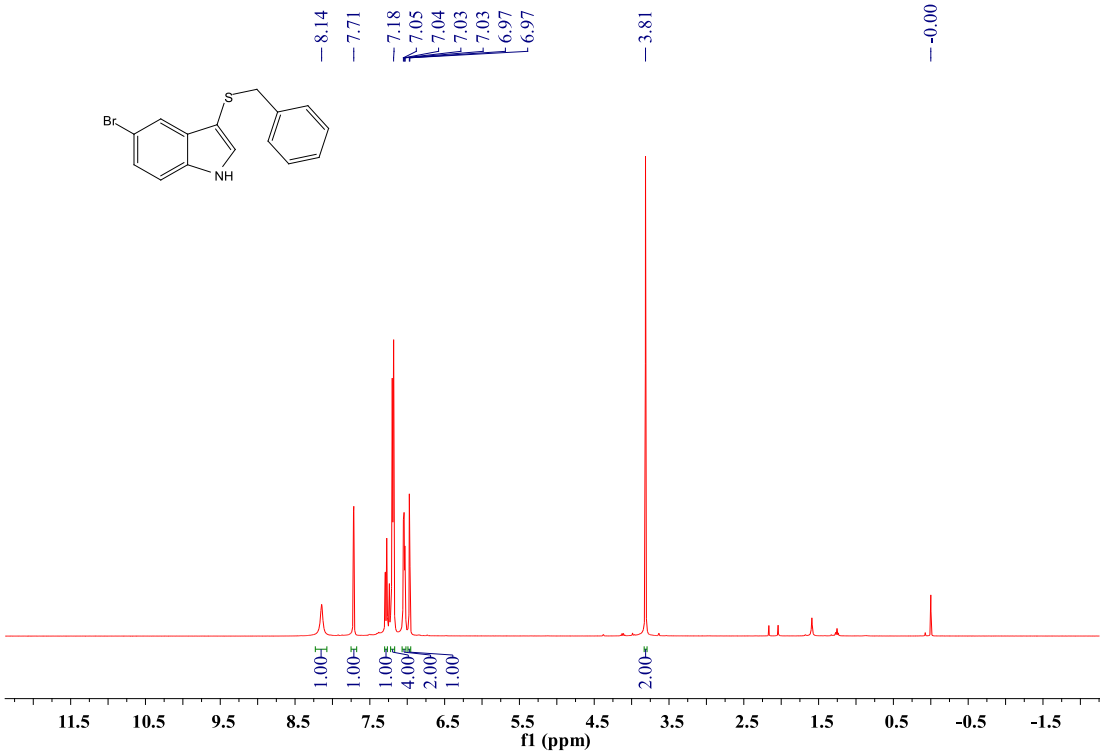
f1 (ppm)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7.04
7.03
7.03
6.97
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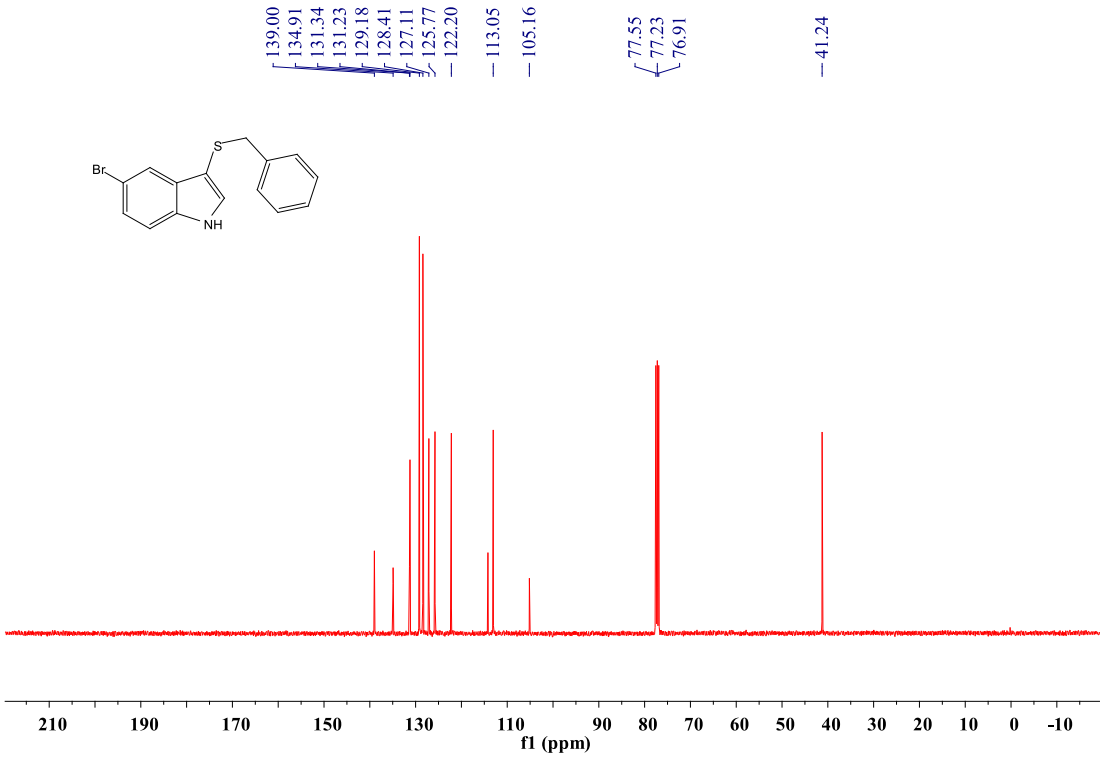
Br
S
NH
1.00
1.00
1.00
4.00
2.00
1.00
2.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)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122.20
113.05
105.16
77.55
77.23
76.91
41.24
Br
S
NH
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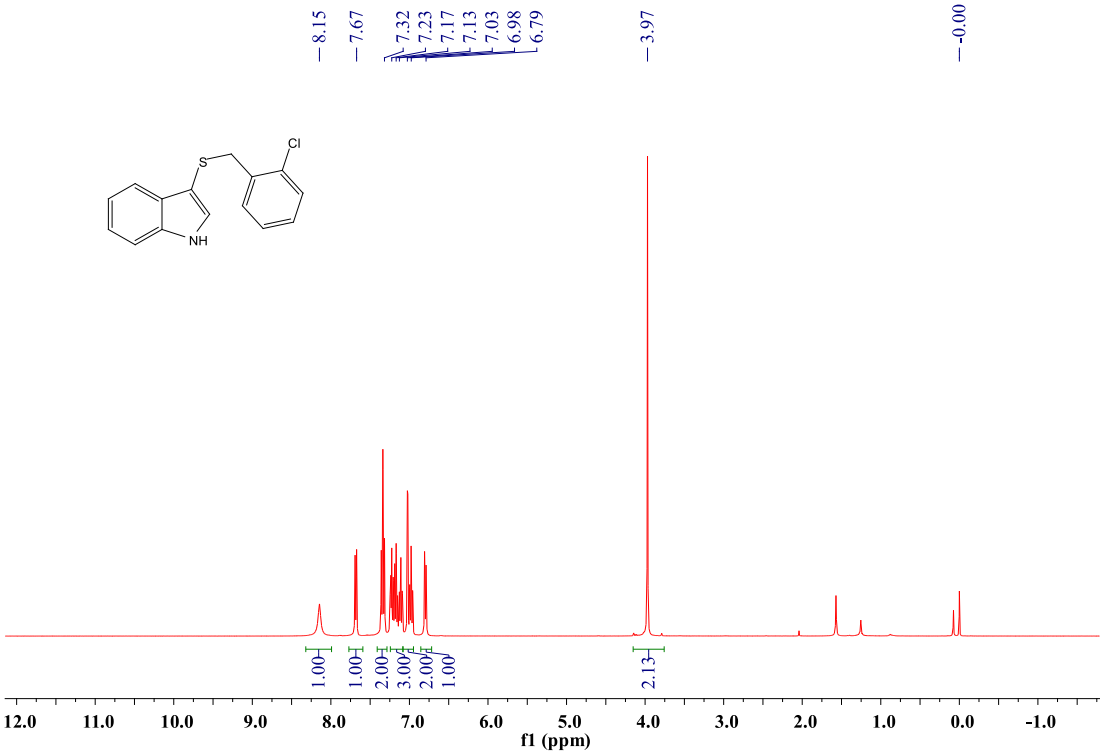
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.67
7.32
7.23
7.17
7.13
7.03
6.98
6.79
3.97
-0.00
Cl
S
NH
1.00
1.00
2.00
3.00
2.00
1.00
2.13
12.0
11.0
10.0
9.0
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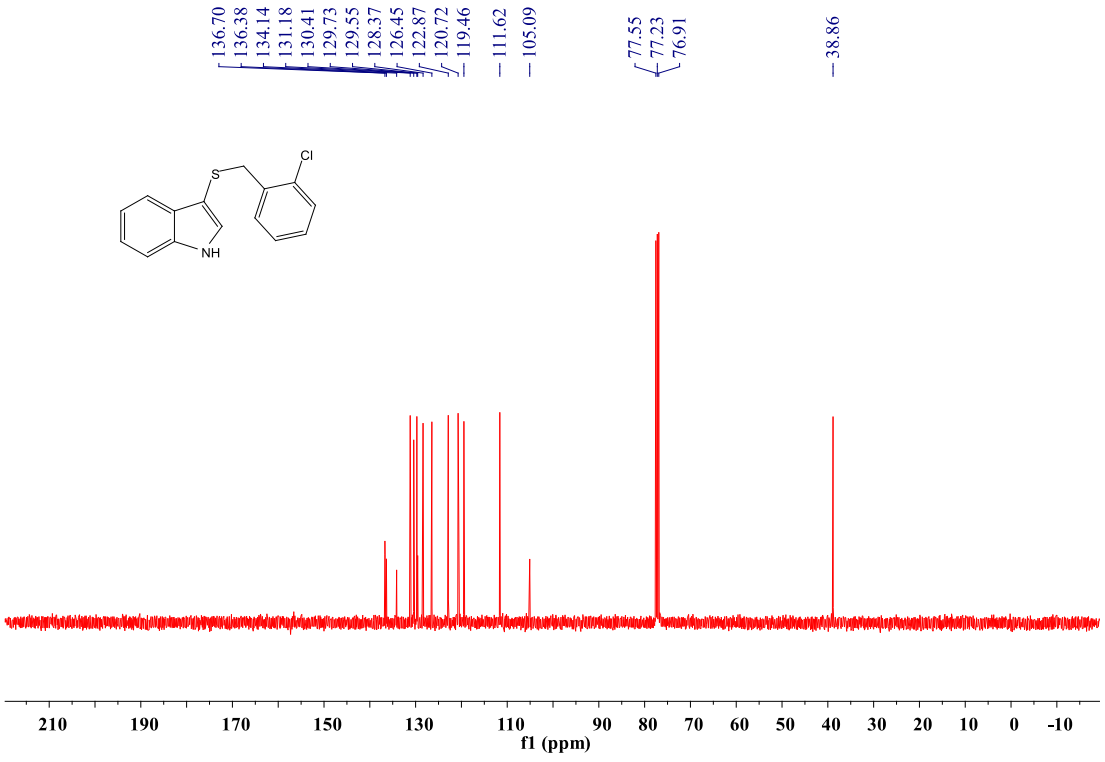
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)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129.73
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126.45
122.87
120.72
119.46
111.62
105.09
77.55
77.23
76.91
38.86
Cl
S
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110
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80
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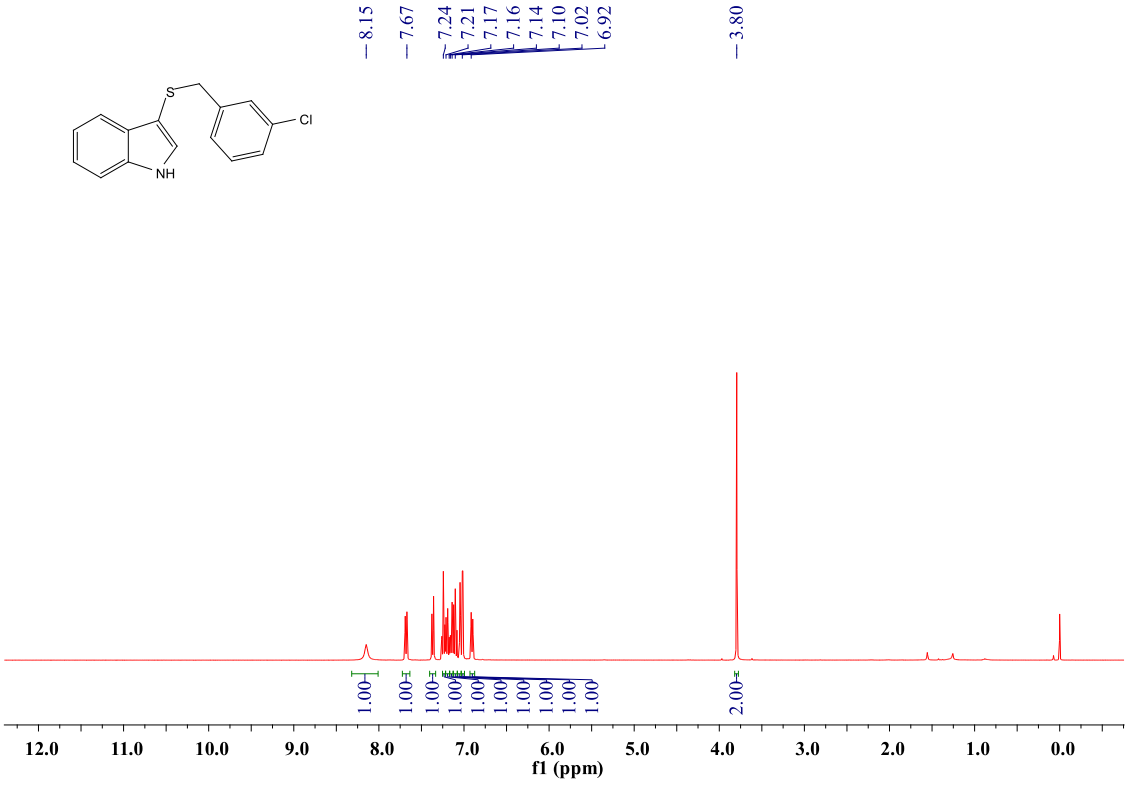
f1 (ppm)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7.21
7.17
7.16
7.14
7.10
7.02
6.92
3.80
S
Cl
NH
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
2.00
12.0
11.0
10.0
9.0
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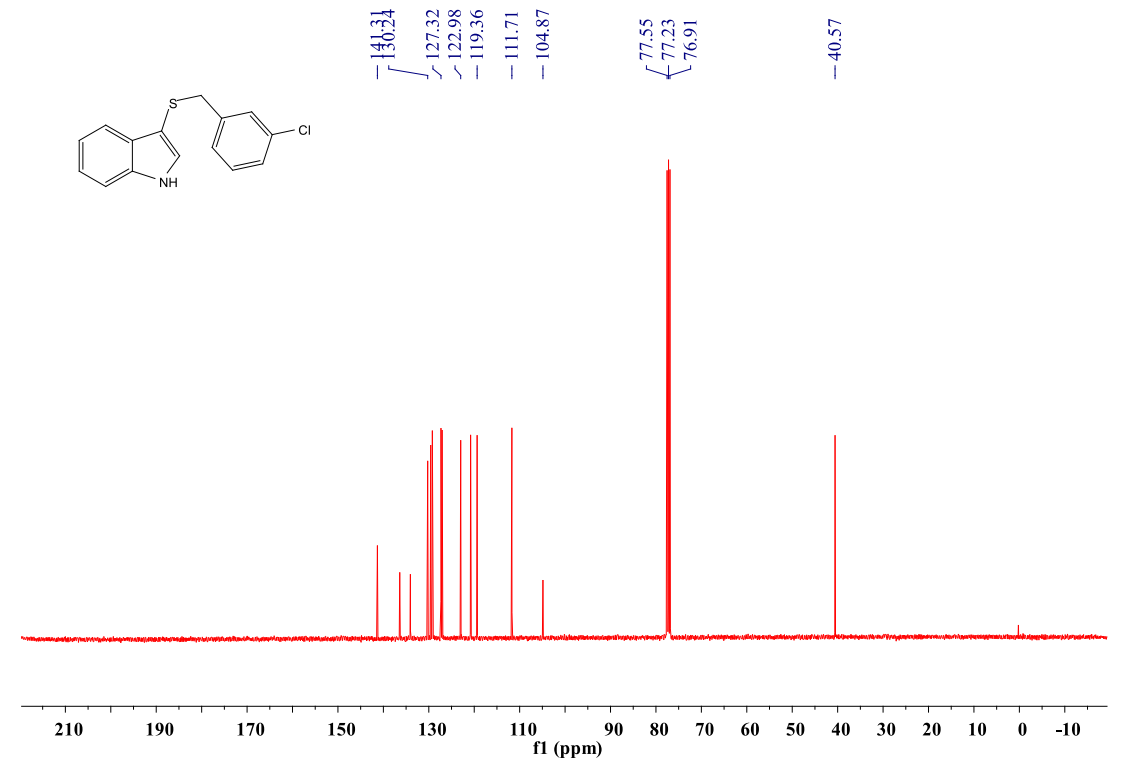
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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119.36
111.71
104.87
77.55
77.23
76.91
40.57
S
Cl
NH
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150
130
110
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80
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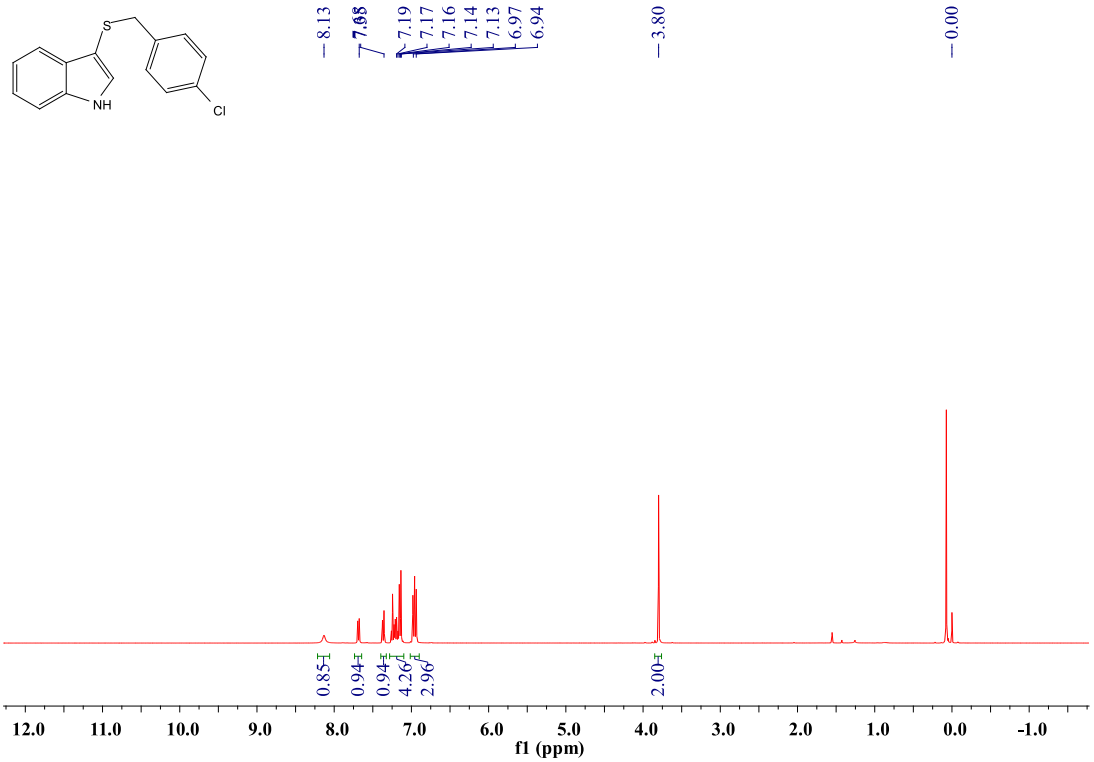
60
50
40
30
20
10
0
-10
f1 (ppm)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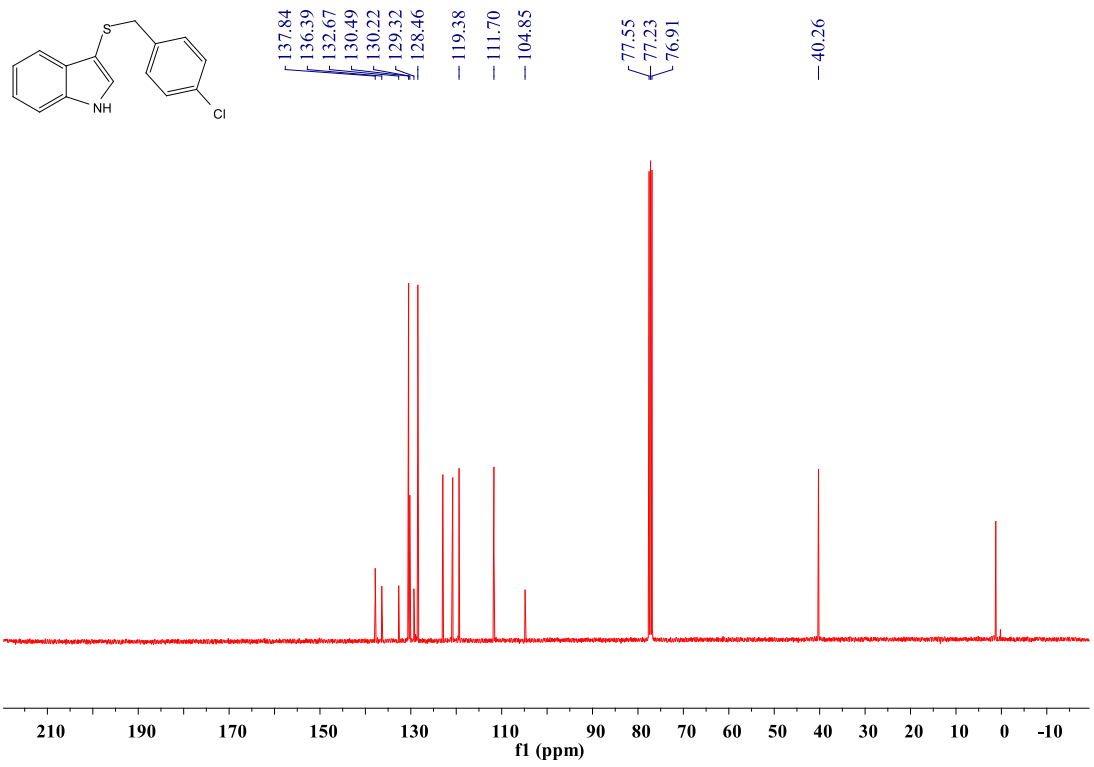
7.68
7.19
7.17
7.16
7.14
7.13
6.97
6.94
3.80
0.00
S
NH
Cl
0.85
0.94
0.94
4.26
2.96
2.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)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129.32
128.46
119.38
111.70
104.85
77.55
77.23
76.91
40.26
S
NH
Cl
210
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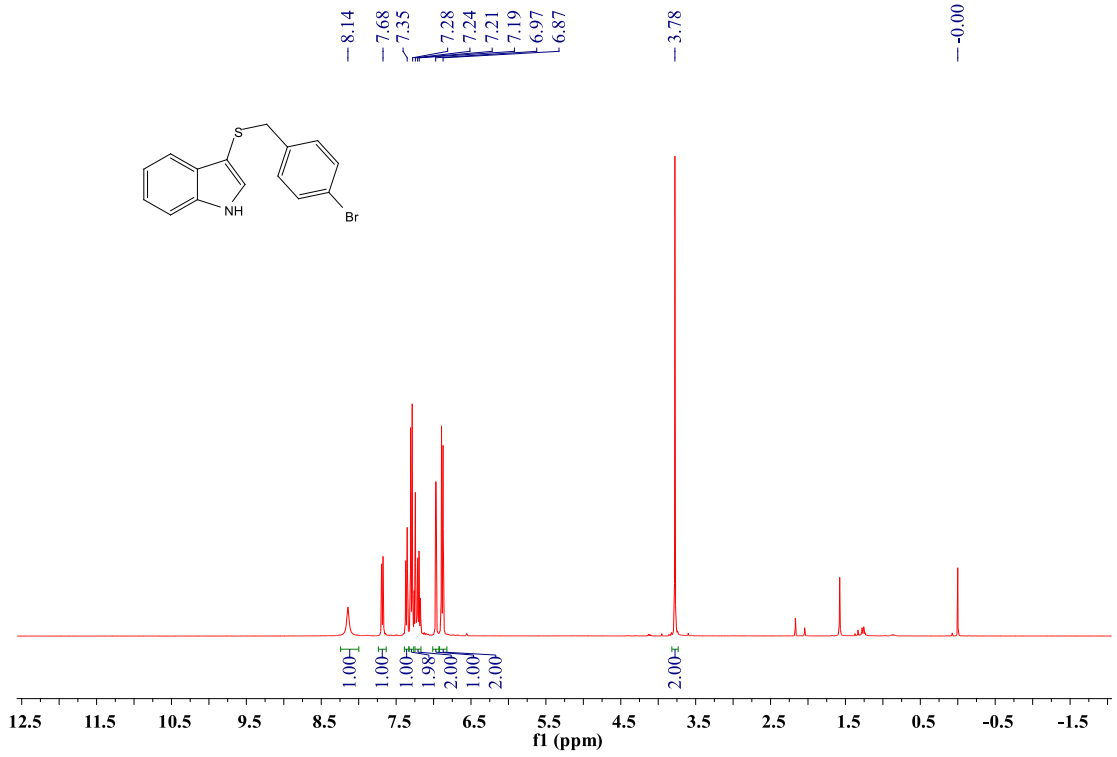
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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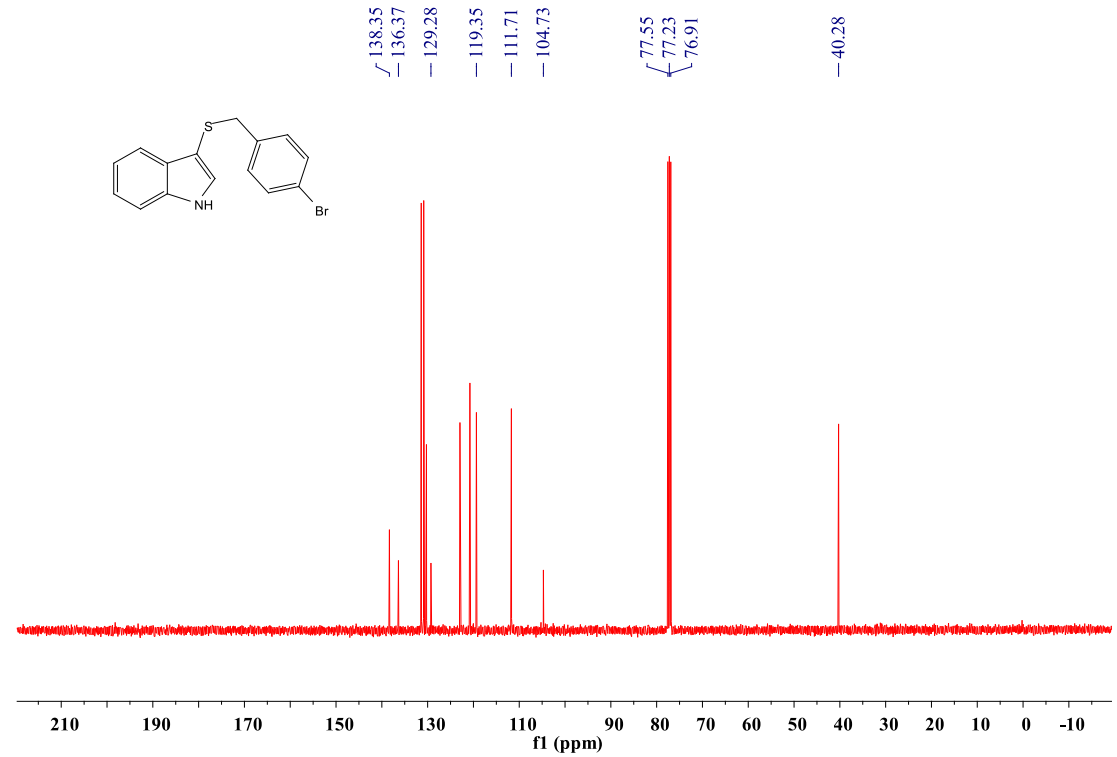
7.68
7.35
7.28
7.24
7.21
7.19
6.97
6.87
3.78
-0.00
S
NH
Br
1.00
1.00
1.00
1.98
2.00
1.00
2.00
2.00
12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5
f1 (ppm)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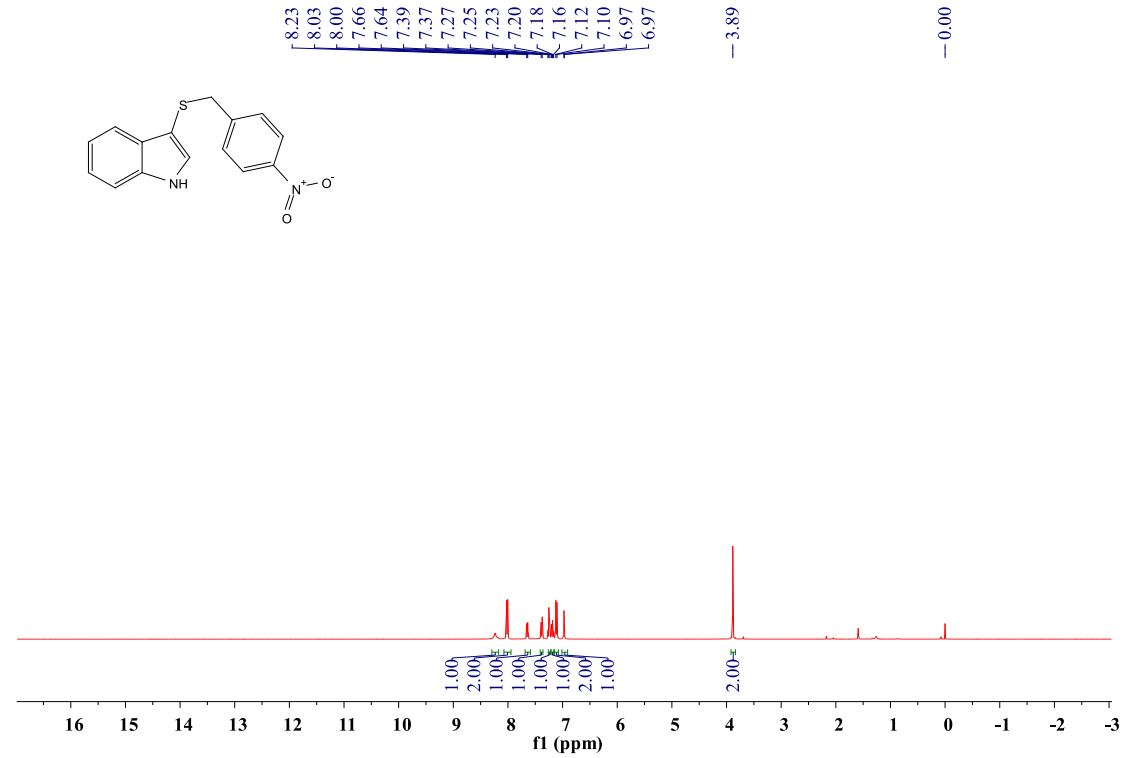
136.37
129.28
119.35
111.71
104.73
77.55
77.23
76.91
40.28
S
NH
Br
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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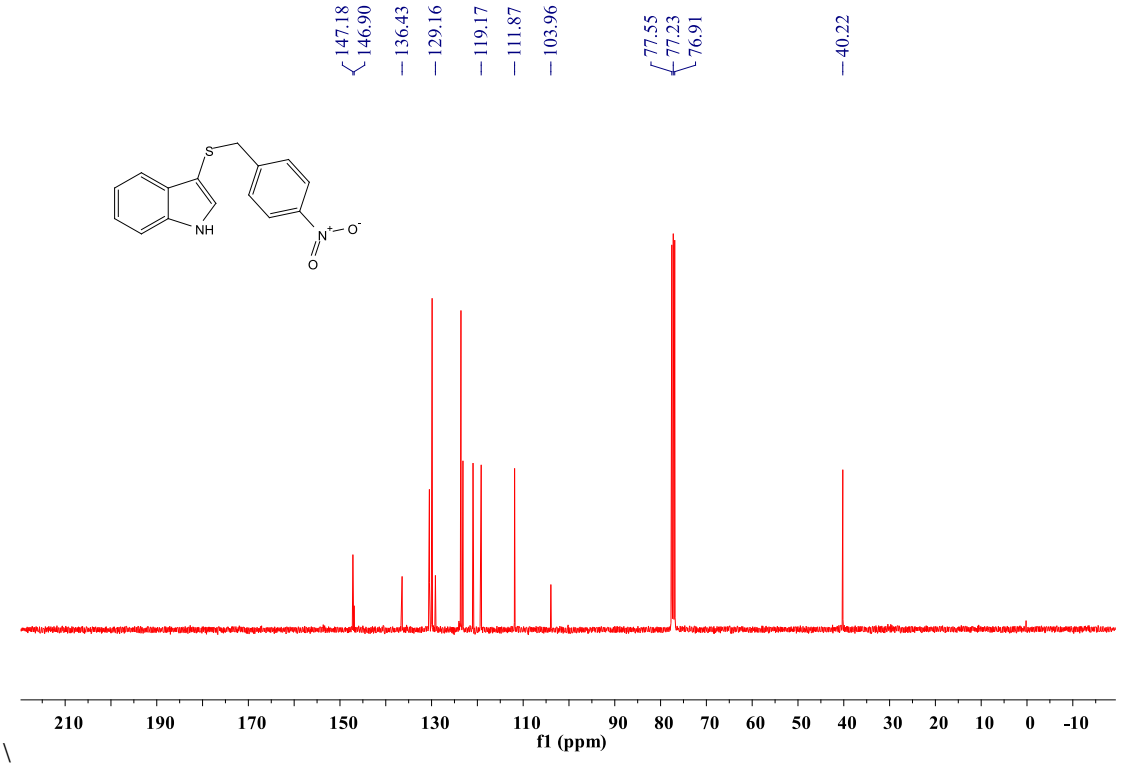
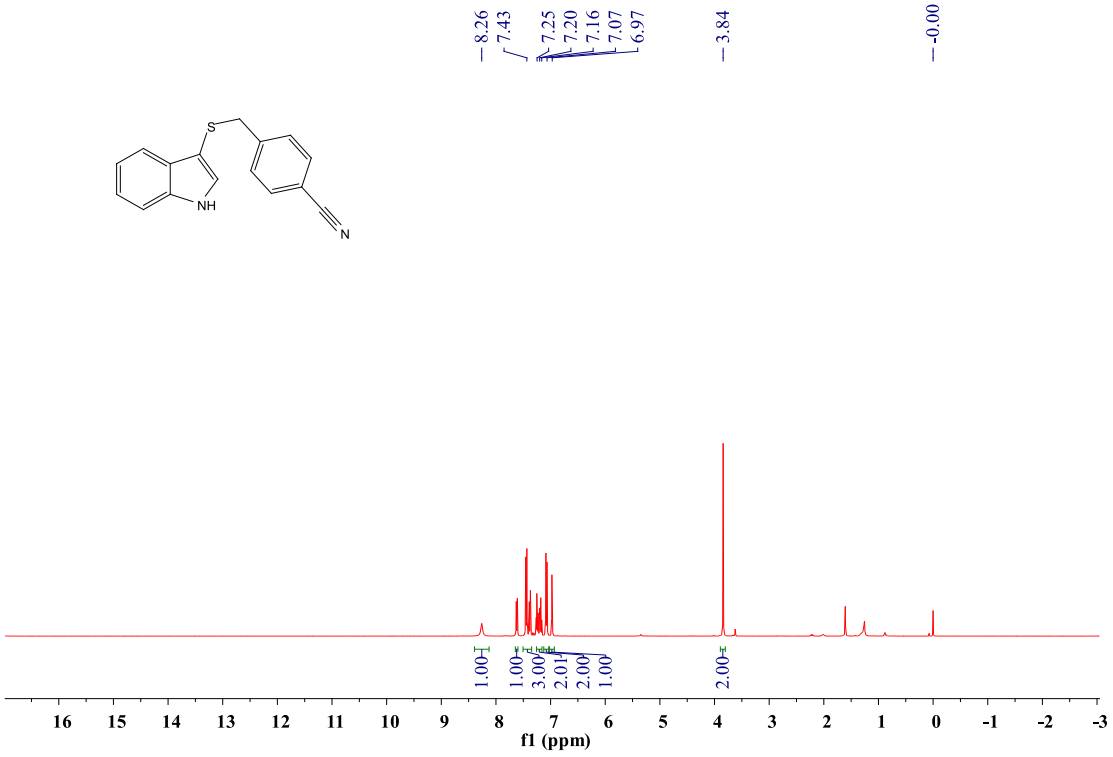
7.64
7.39
7.37
7.27
7.25
7.23
7.20
7.18
7.16
7.12
7.10
6.97
6.97
3.89
0.00
S
NH
N+
O-
O
1.00
2.00
1.00
1.00
1.00
1.00
2.00
1.00
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


147.18
146.90
136.43
129.16
119.17
111.87
103.96
77.55
77.23
76.91
40.22
S
NH
N+
O-
O
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

\


8.26
7.43
7.25
7.20
7.16
7.07
6.97
3.84
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NH
N
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1.00
3.00
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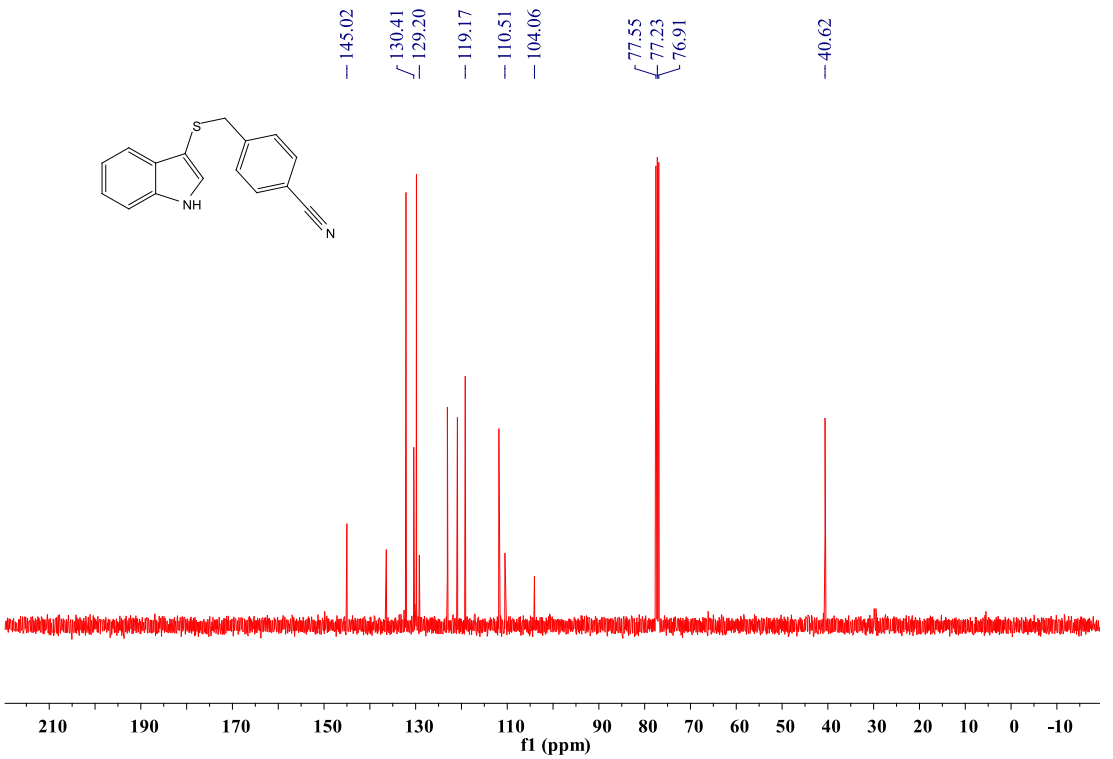
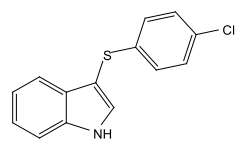
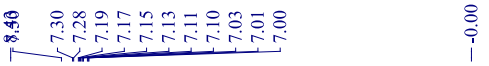
2.00
1.00
2.00
f1 (ppm)


145.02
130.41
129.20
119.17
110.51
104.06
77.55
77.23
76.91
40.62
S
NH
N
f1 (ppm)


Cl
S
NH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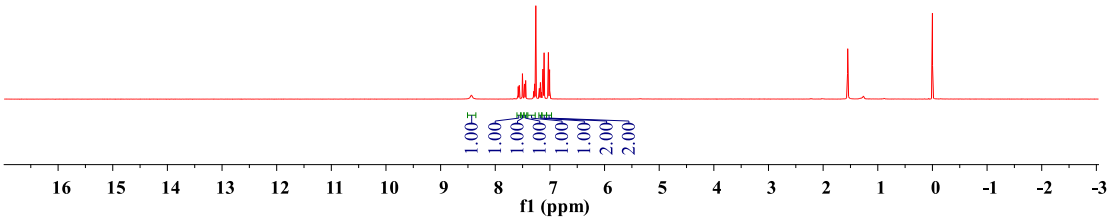
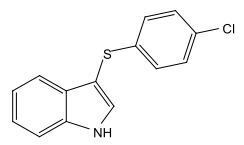
7.13
7.11
7.10
7.03
7.01
7.00
-0.00


1.00
1.00
1.00
1.00
1.00
2.00
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


Cl
S
NH


138.02
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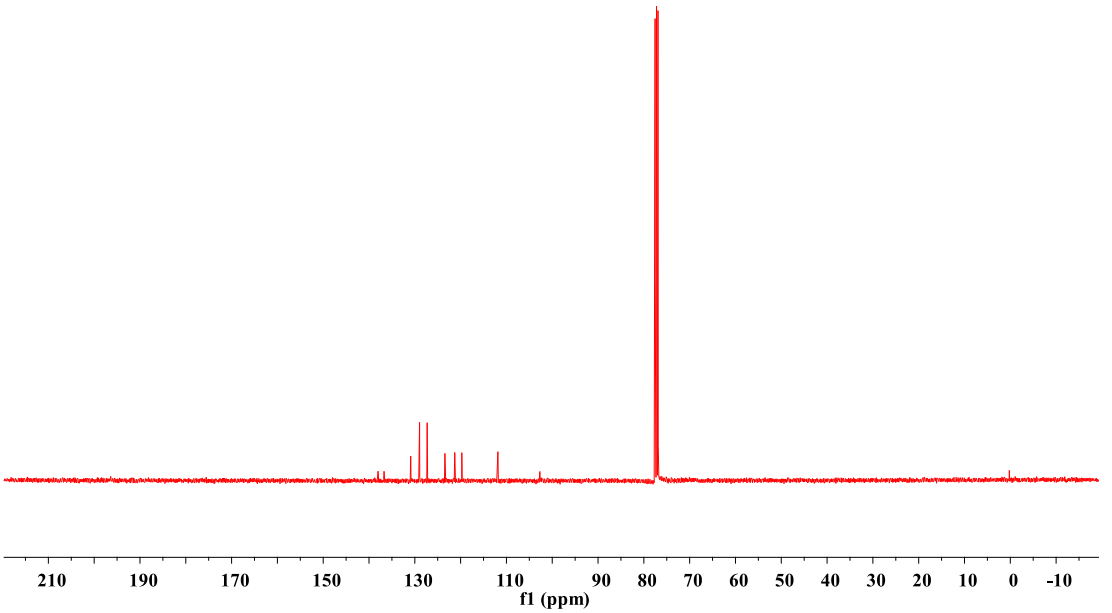
128.96
123.43
119.74
111.86
77.55
77.23
76.91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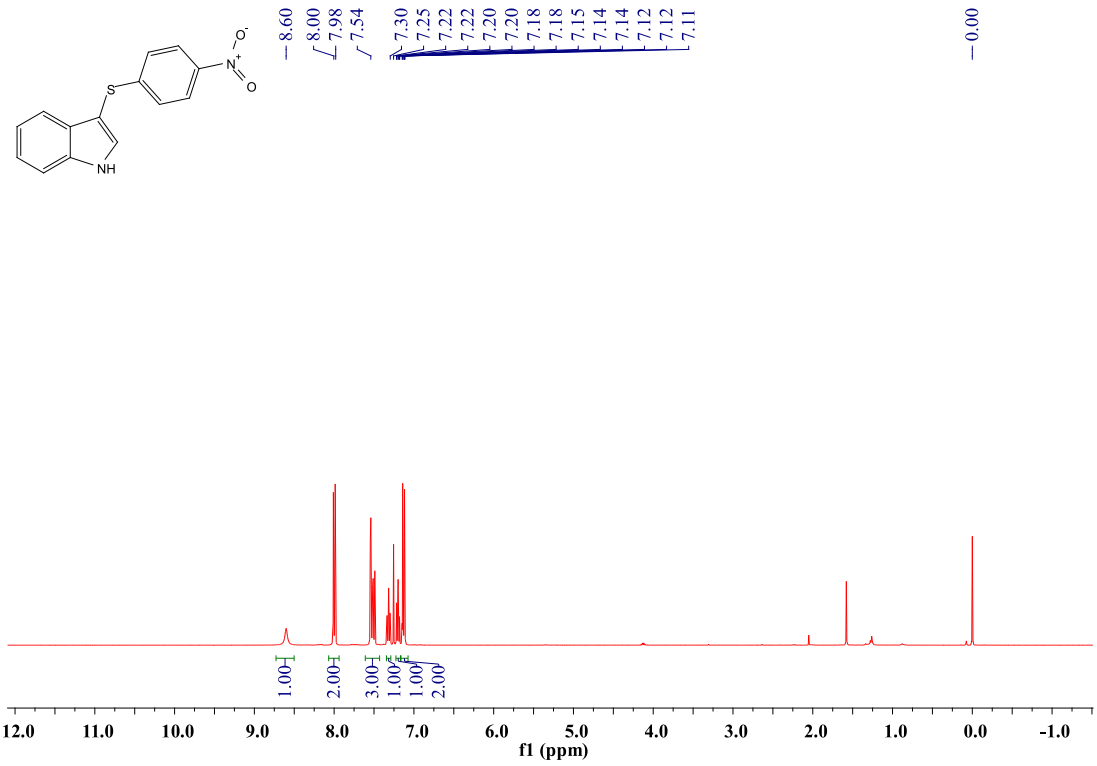
f1 (ppm)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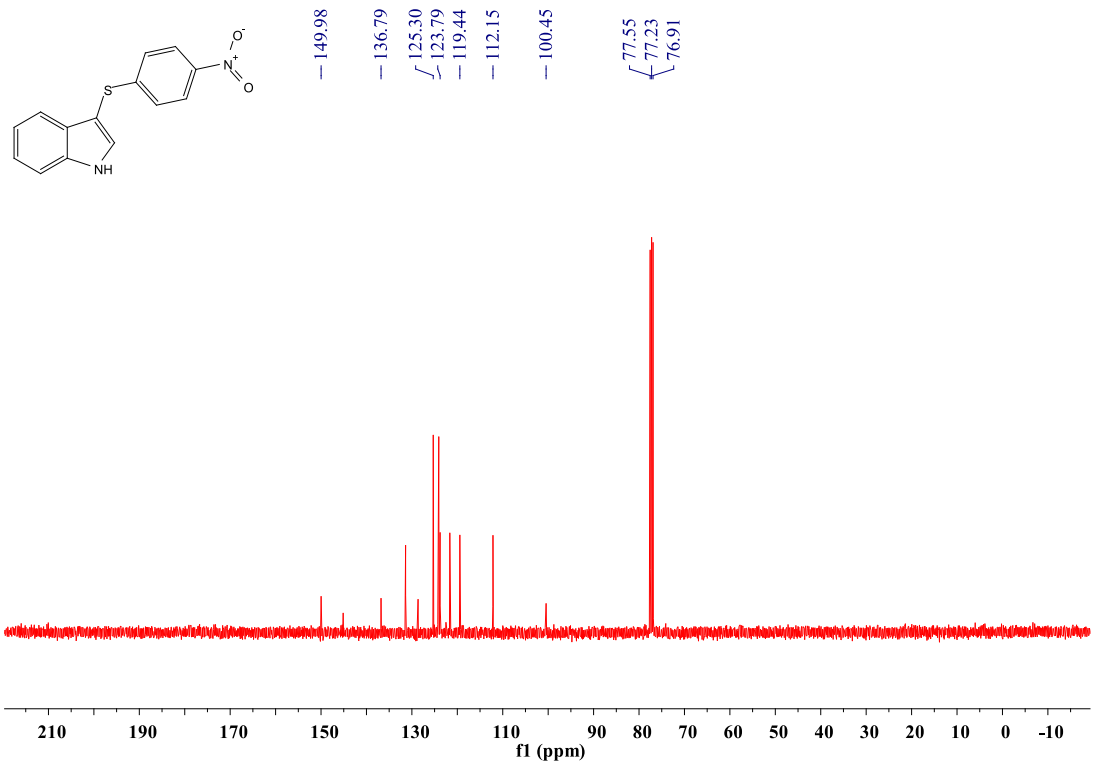
7.20
7.18
7.18
7.15
7.14
7.14
7.12
7.12
7.11
0.00
1.00
2.00
3.00
1.00
1.00
2.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)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112.15
100.45
77.55
77.23
76.91
210
190
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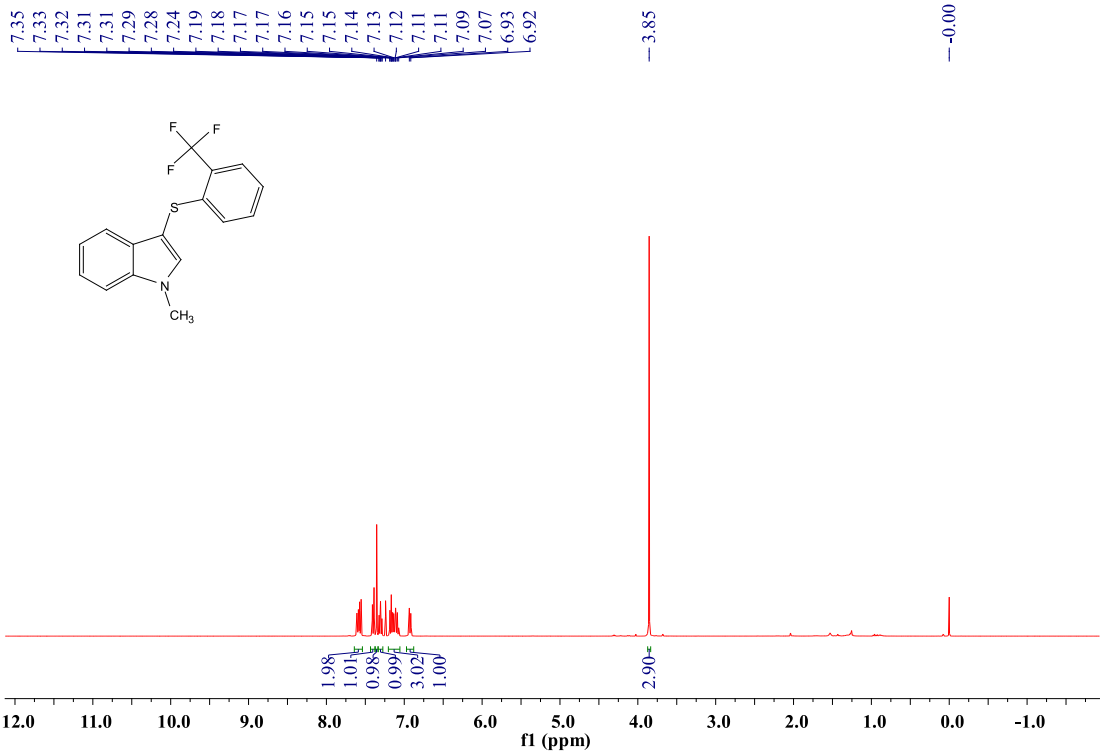
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.35
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7.29
7.28
7.24
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7.18
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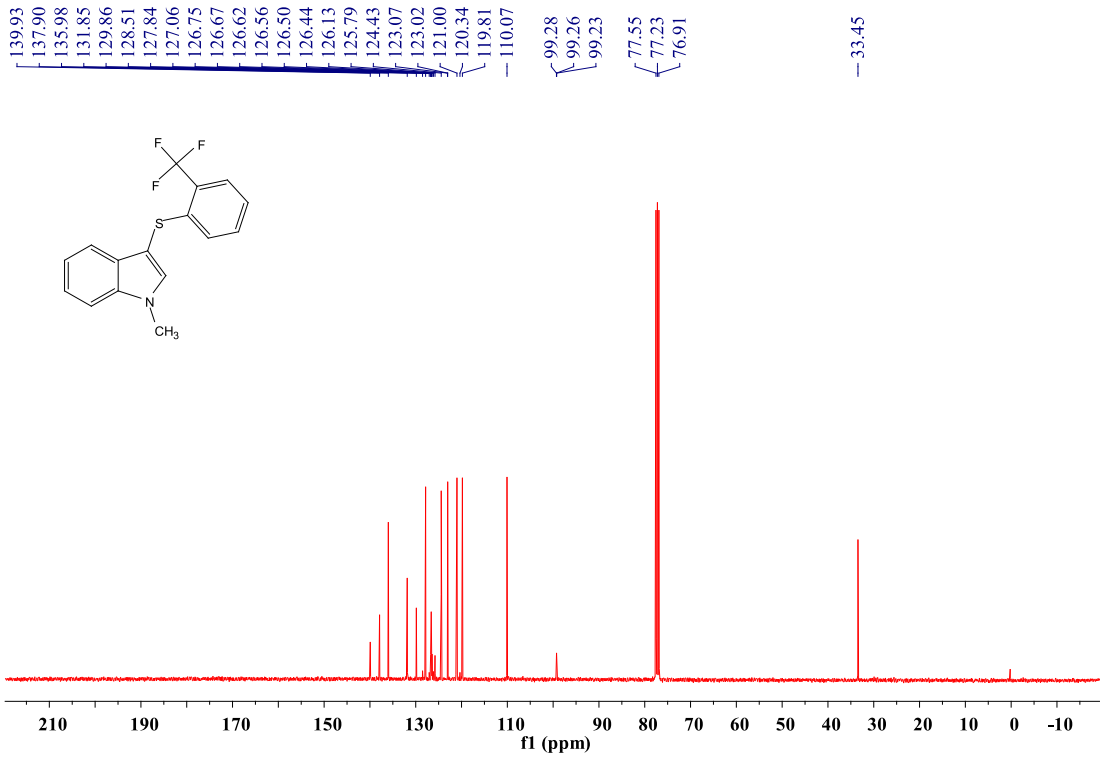
7.17
7.16
7.15
7.15
7.14
7.13
7.12
7.11
7.11
7.09
7.07
6.93
6.92
3.85
-0.00
F
F
F
S
N
CH3
1.98
1.01
0.98
0.99
3.02
1.00
2.90
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)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126.62
126.56
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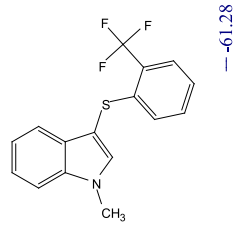
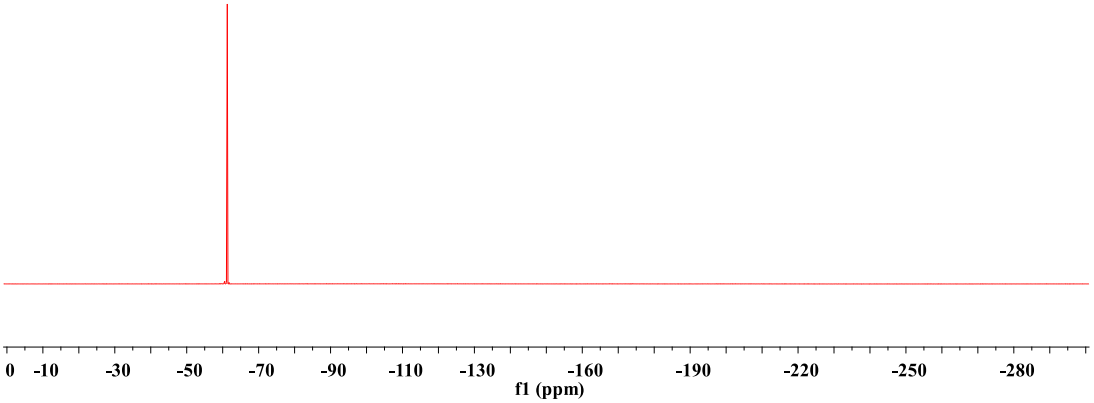
126.44
126.13
125.79
124.43
123.07
123.02
121.00
120.34
119.81
110.07
99.28
99.26
99.23
77.55
77.23
76.91
33.45
F
F
F
S
N
CH3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


F
F
F
S
N
CH3

-61.28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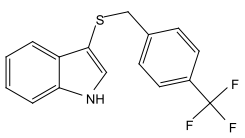
-110
-130
-160
-190
-220
-250
-280
f1 (ppm)


S
NH
F
F
F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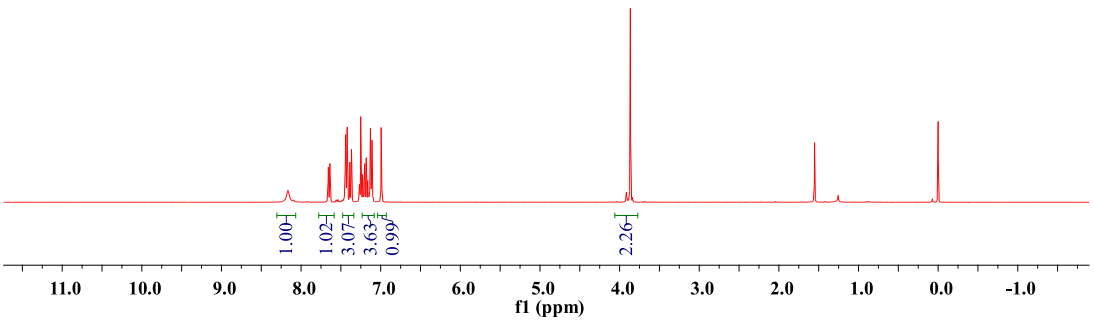
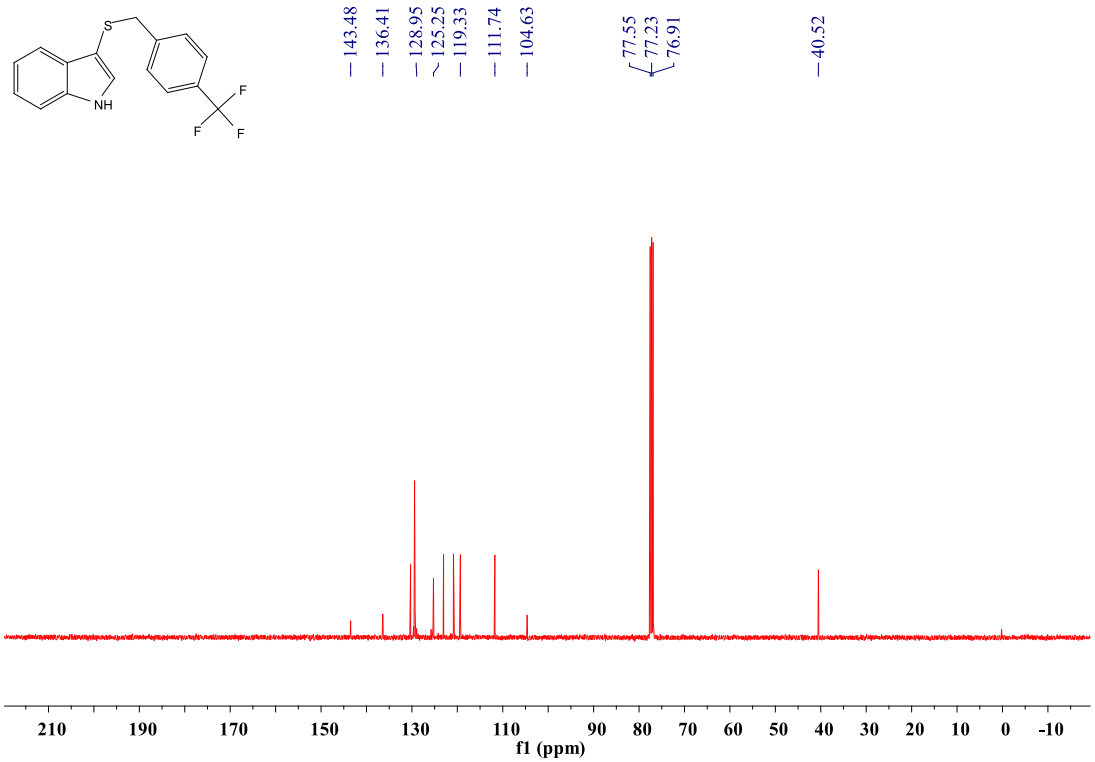
7.24
7.22
7.20
7.18
7.16
7.11
6.99
3.87
-0.00


1.00
1.02
3.07
3.63
0.99
2.26
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)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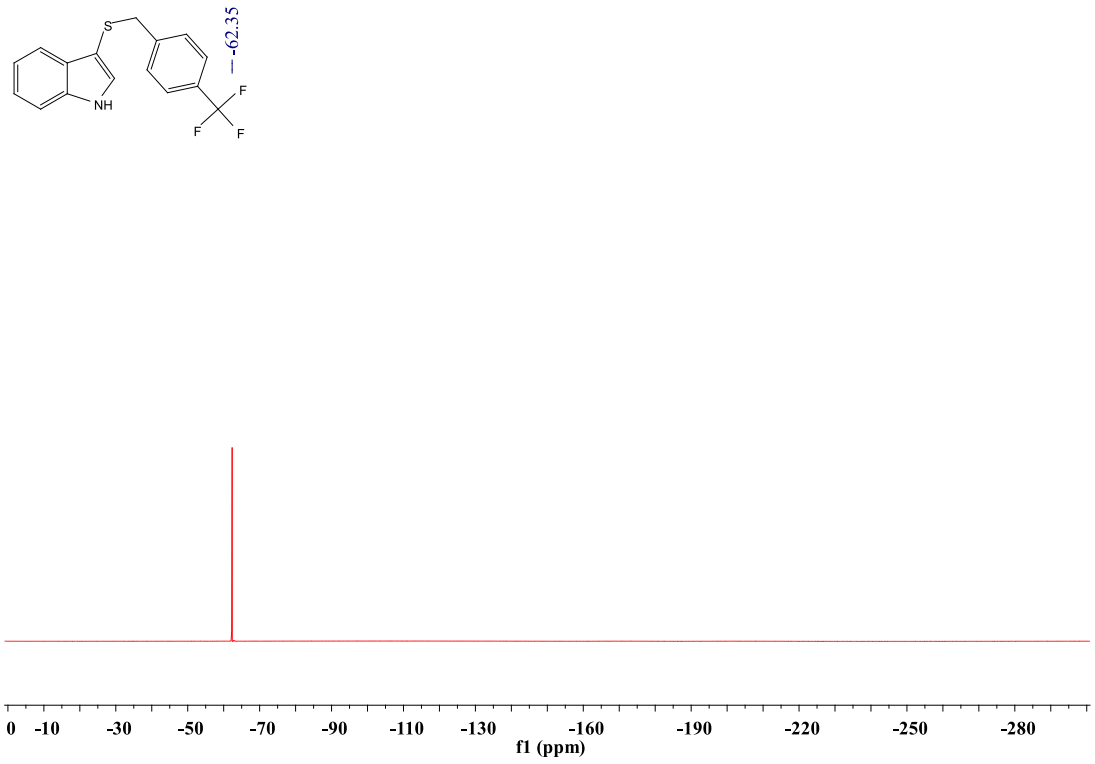
125.25
119.33
111.74
104.63
77.55
77.23
76.91
40.52
S
NH
F
F
F
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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S
NH
F
F
F
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-50
-70
-90
-110
-130
-160
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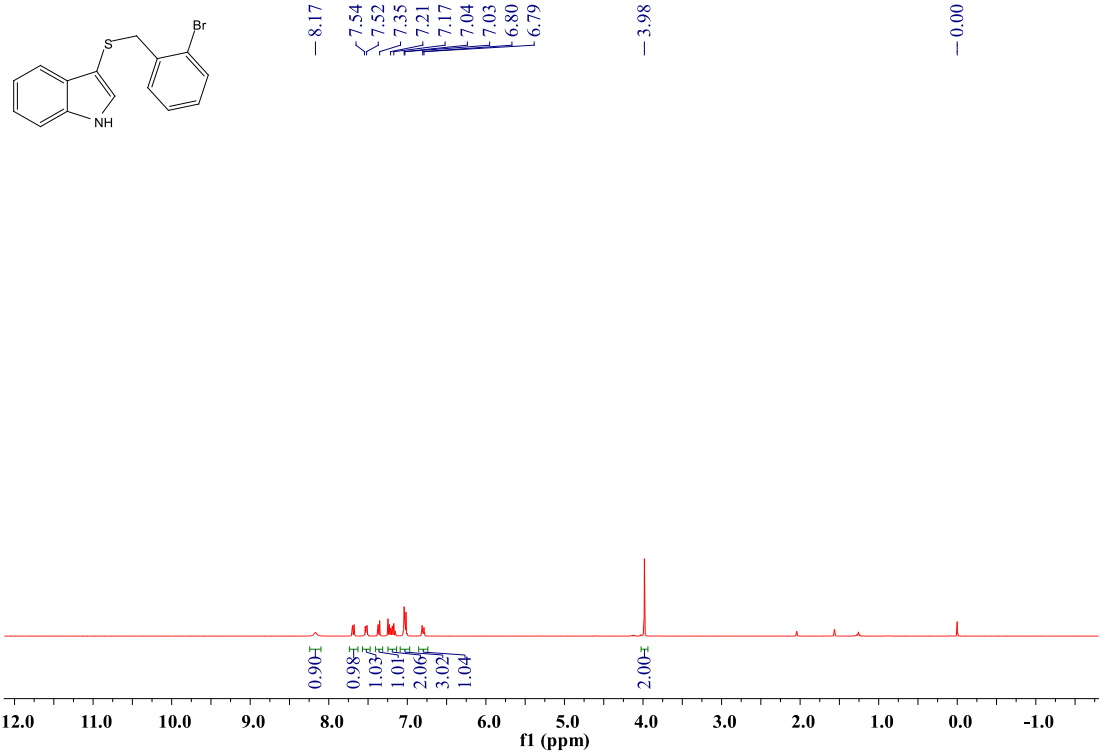
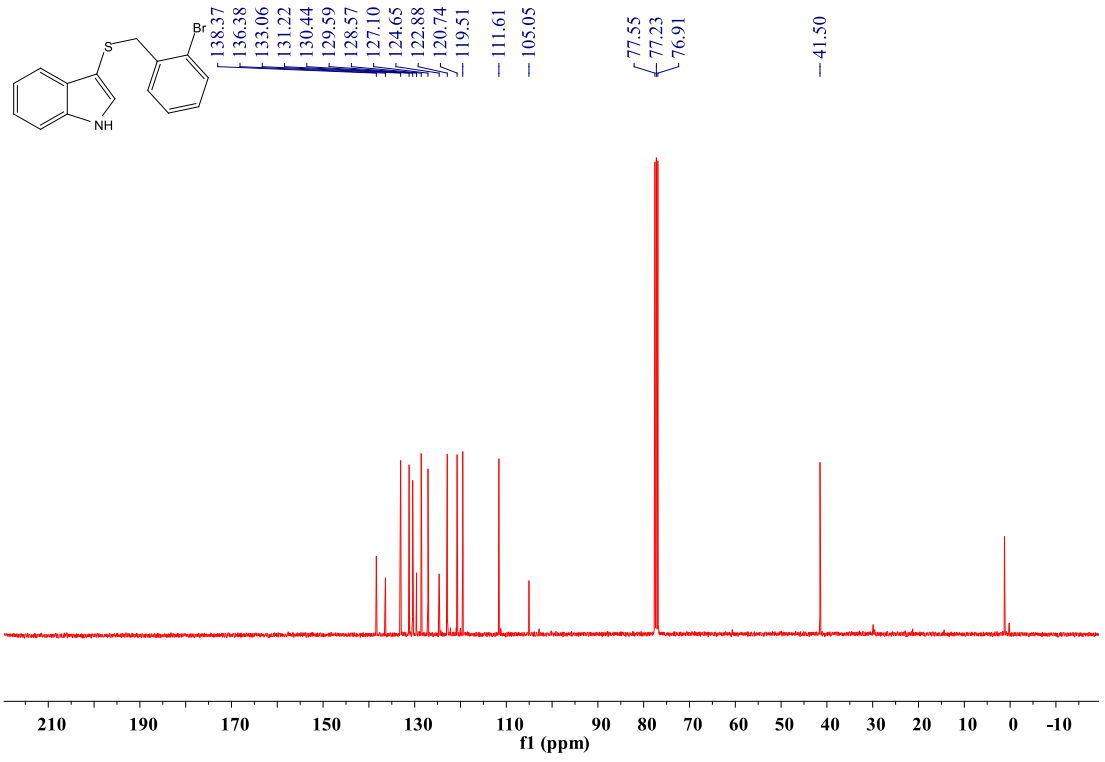
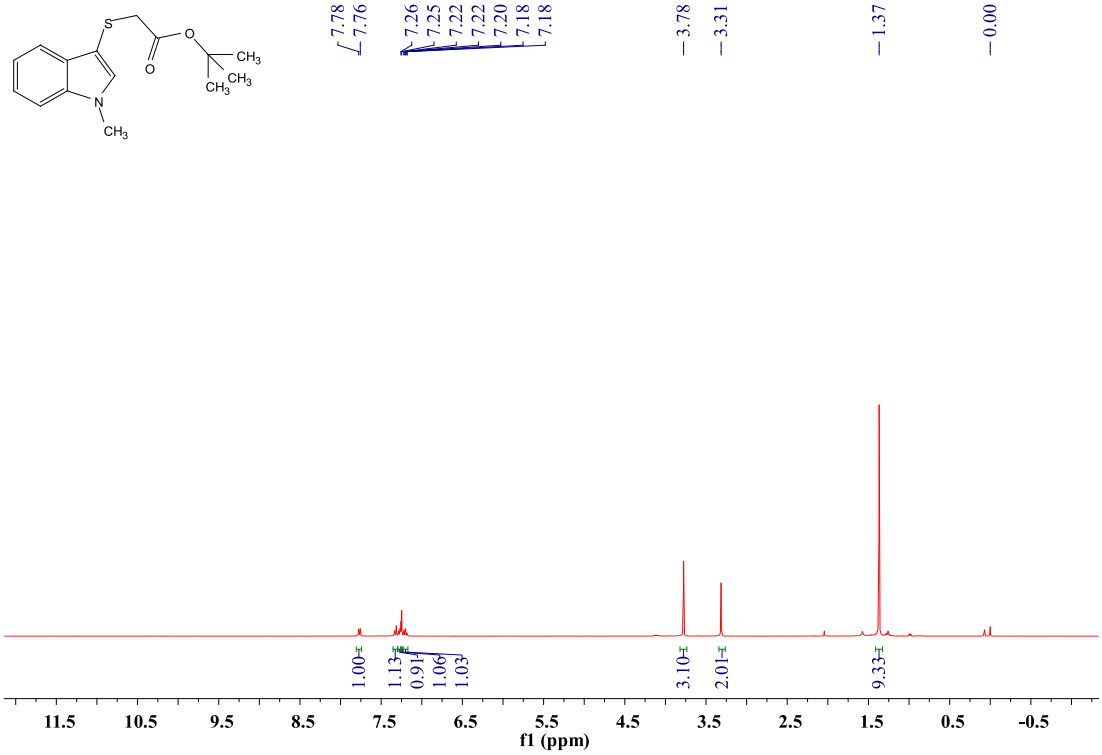
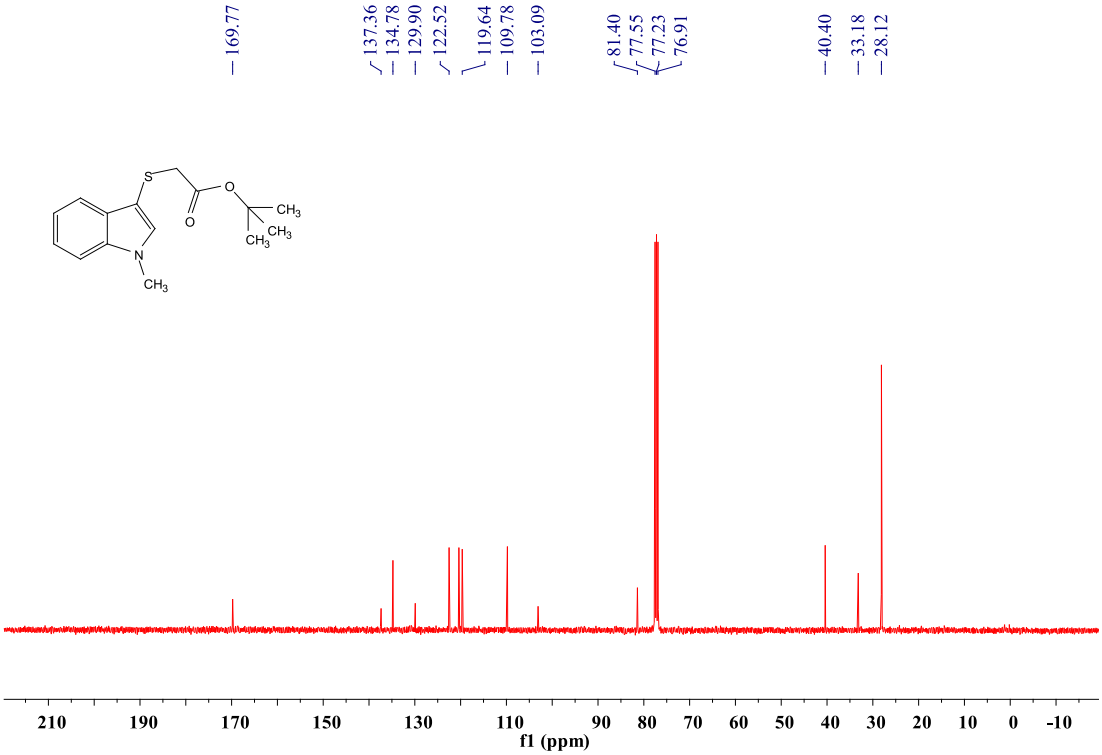
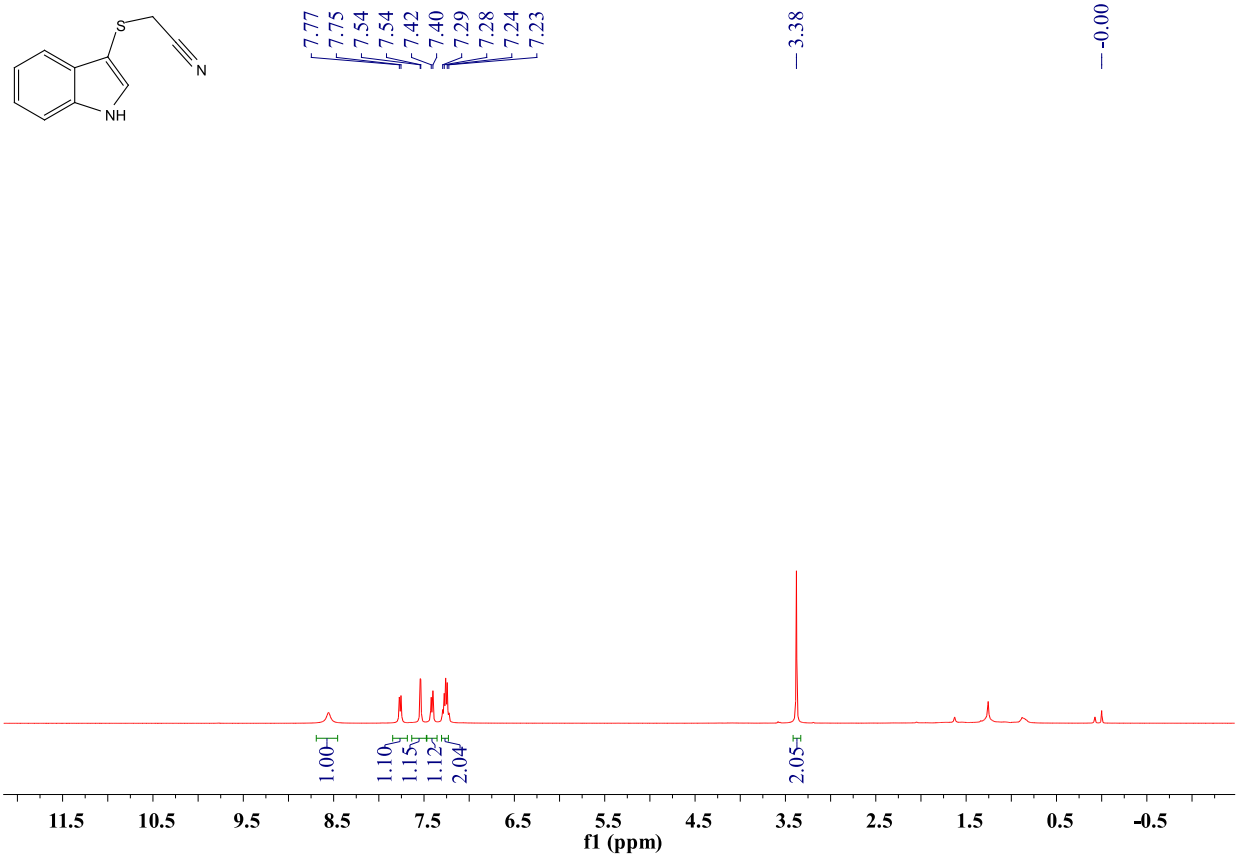
-220
-250
-280
f1 (ppm)

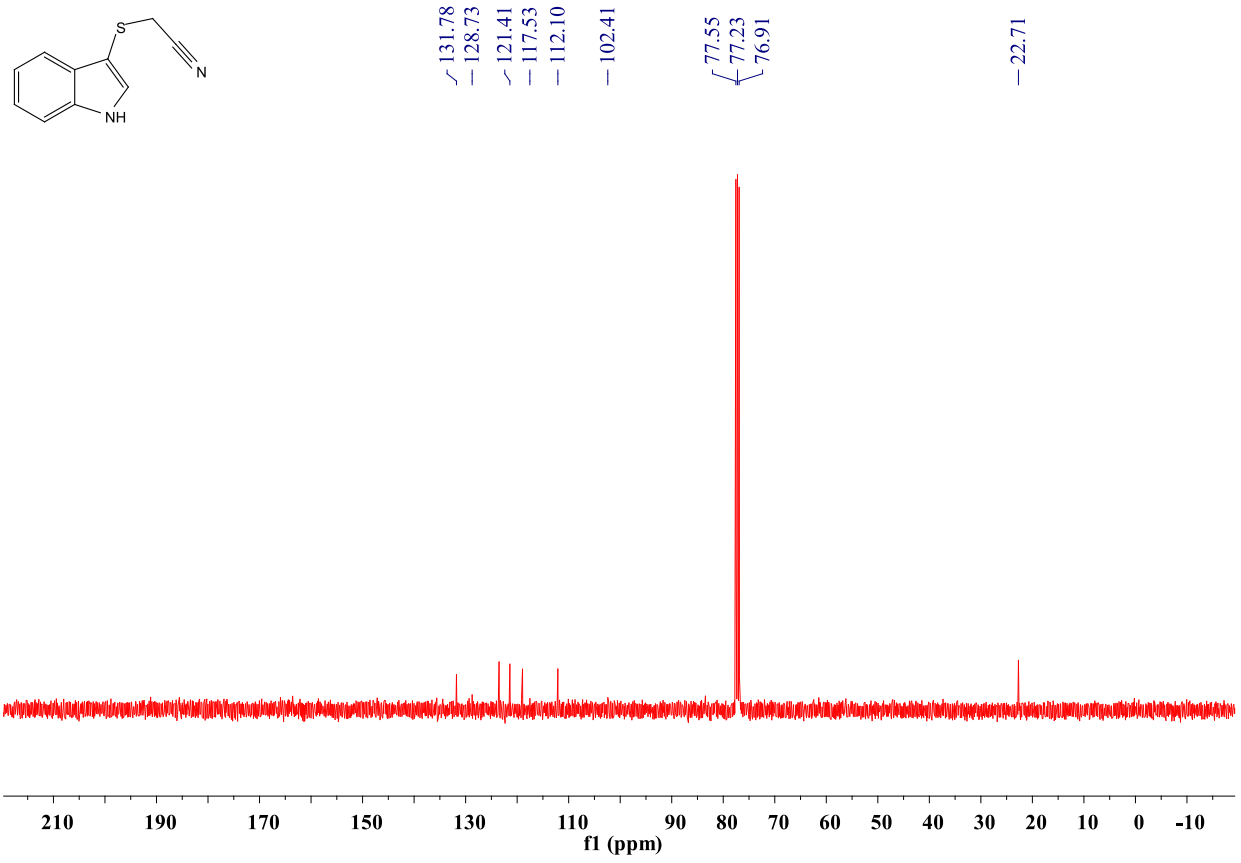

Br
S
NH
8.17
7.54
7.52
7.35
7.21
7.17
7.04
7.03
6.80
6.79
3.98
0.00
0.90
0.98
1.03
1.01
2.06
3.02
1.04
2.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

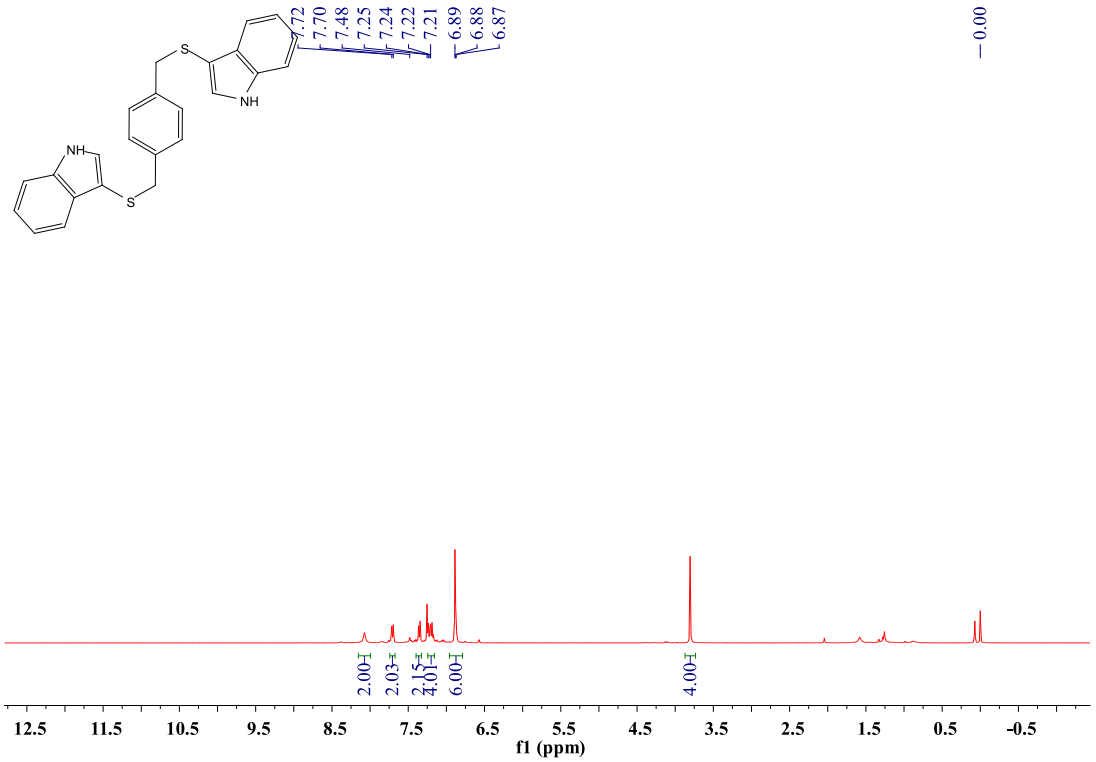

Br
S
NH
138.37
136.38
133.06
131.22
130.44
129.59
128.57
127.10
124.65
122.88
120.74
119.51
111.61
105.05
77.55
77.23
76.91
41.50
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

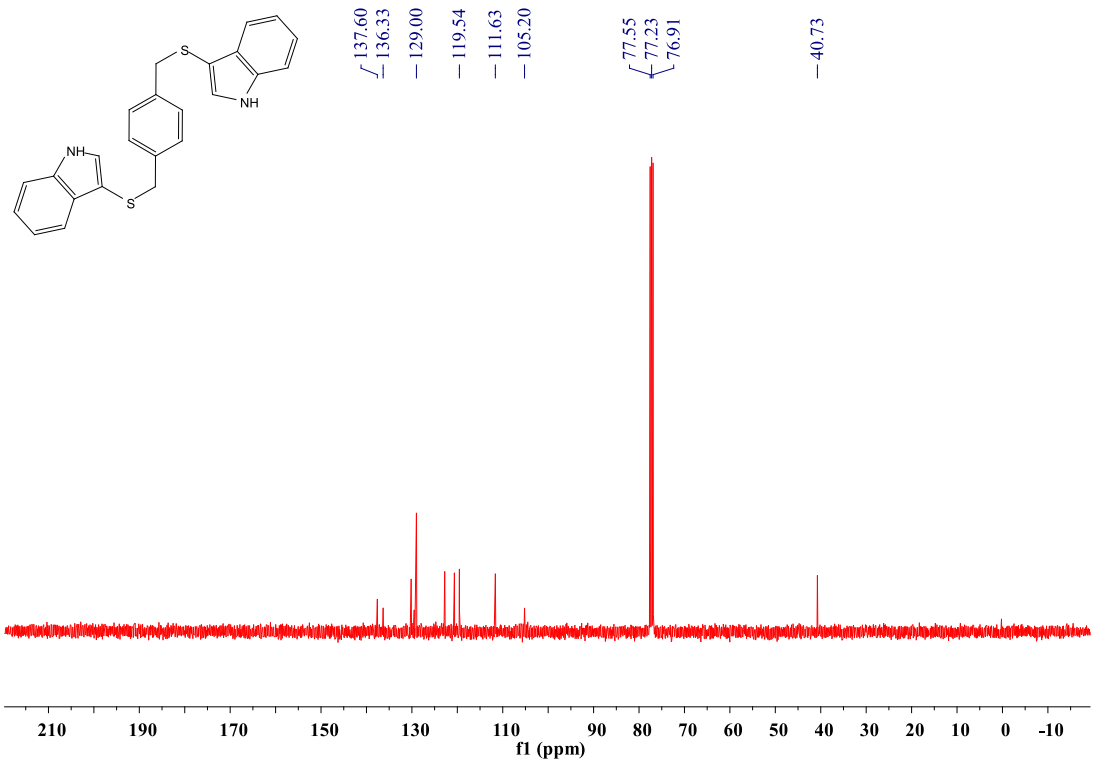

7.78
7.76
7.26
7.25
7.22
7.22
7.20
7.18
7.18
3.78
3.31
1.37
0.00
1.00
1.13
0.91
1.06
1.03
3.10
2.01
9.33
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

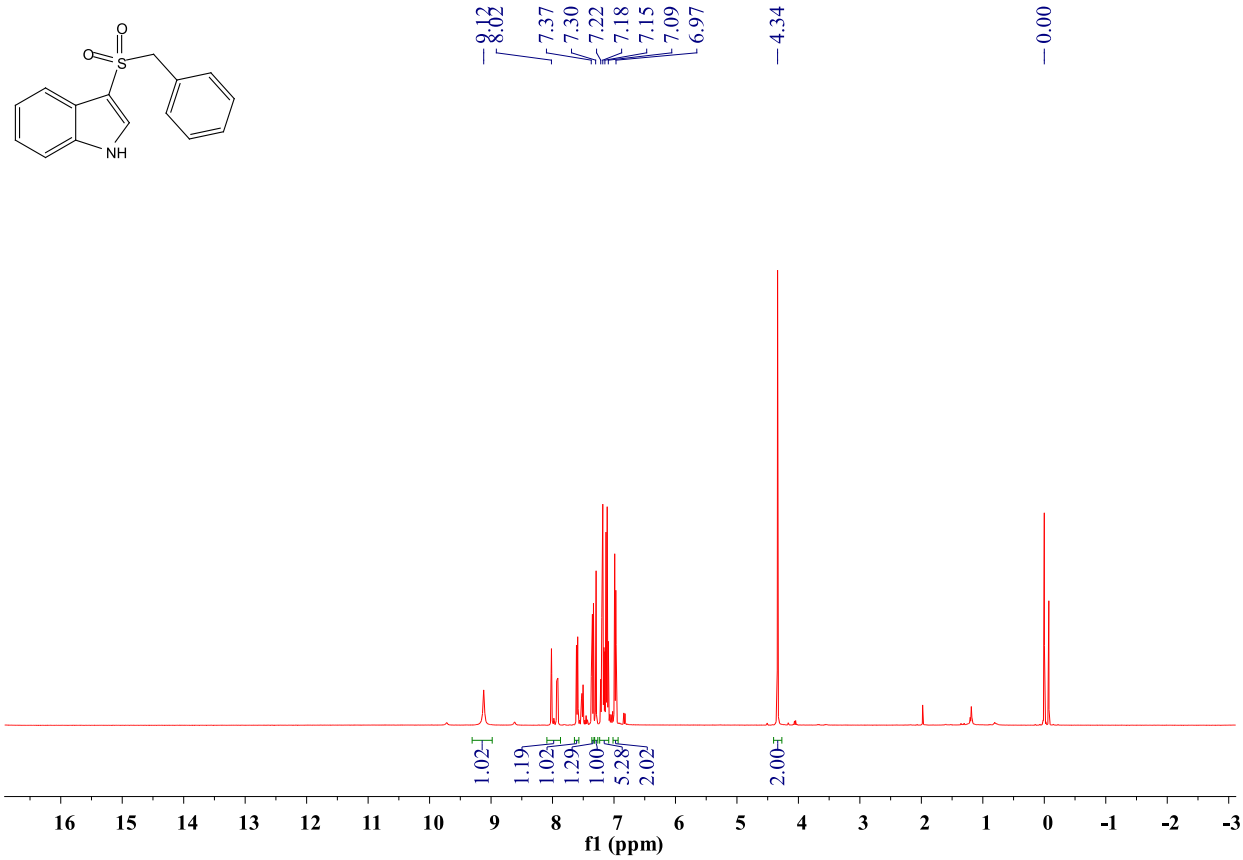

169.77
137.36
134.78
129.90
122.52
119.64
109.78
103.09
81.40
77.55
77.23
76.91
40.40
33.18
28.12
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

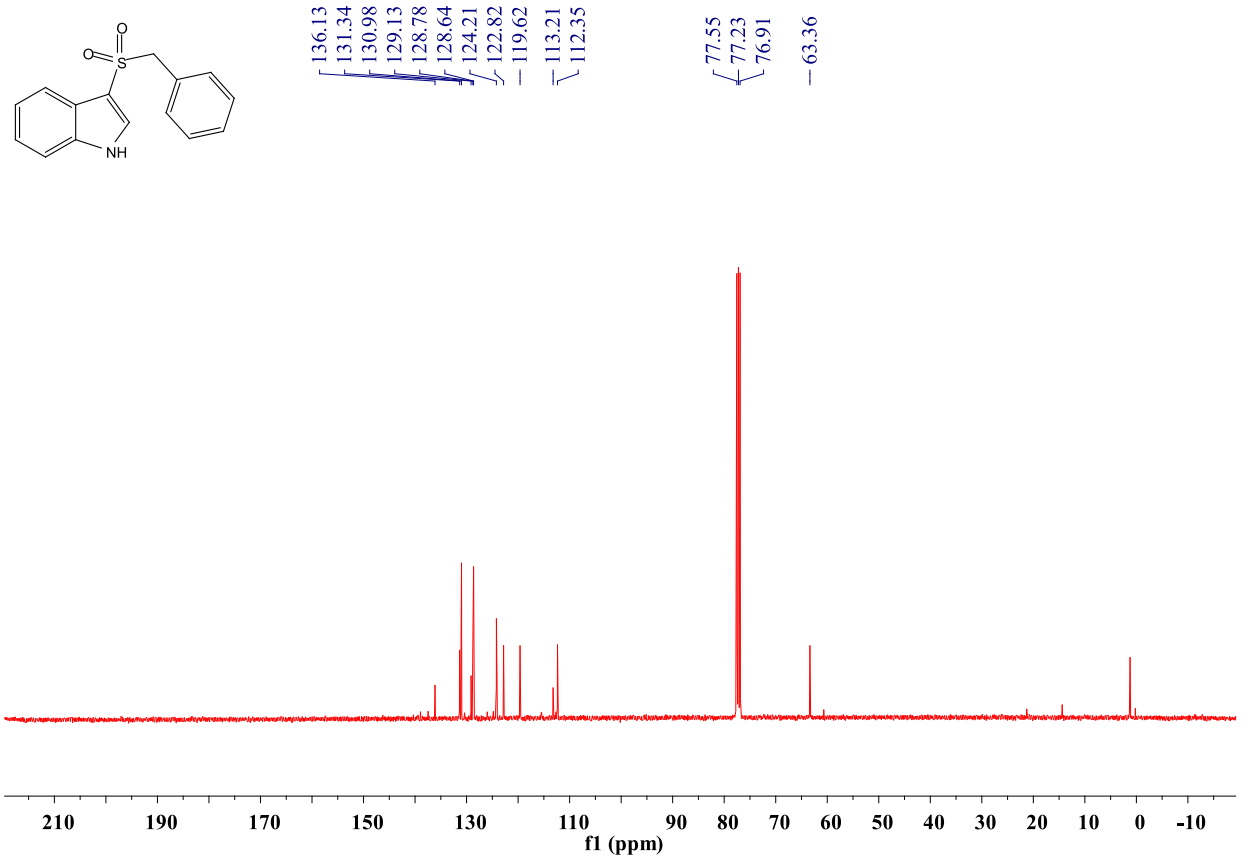

7.77
7.75
7.54
7.54
7.42
7.40
7.29
7.28
7.24
7.23
3.38
0.00
1.00
1.10
1.15
1.12
2.04
2.05
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)
S
N
NH


131.78
128.73
121.41
117.53
112.10
102.41
77.55
77.23
76.91
22.71
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
S
N
NH

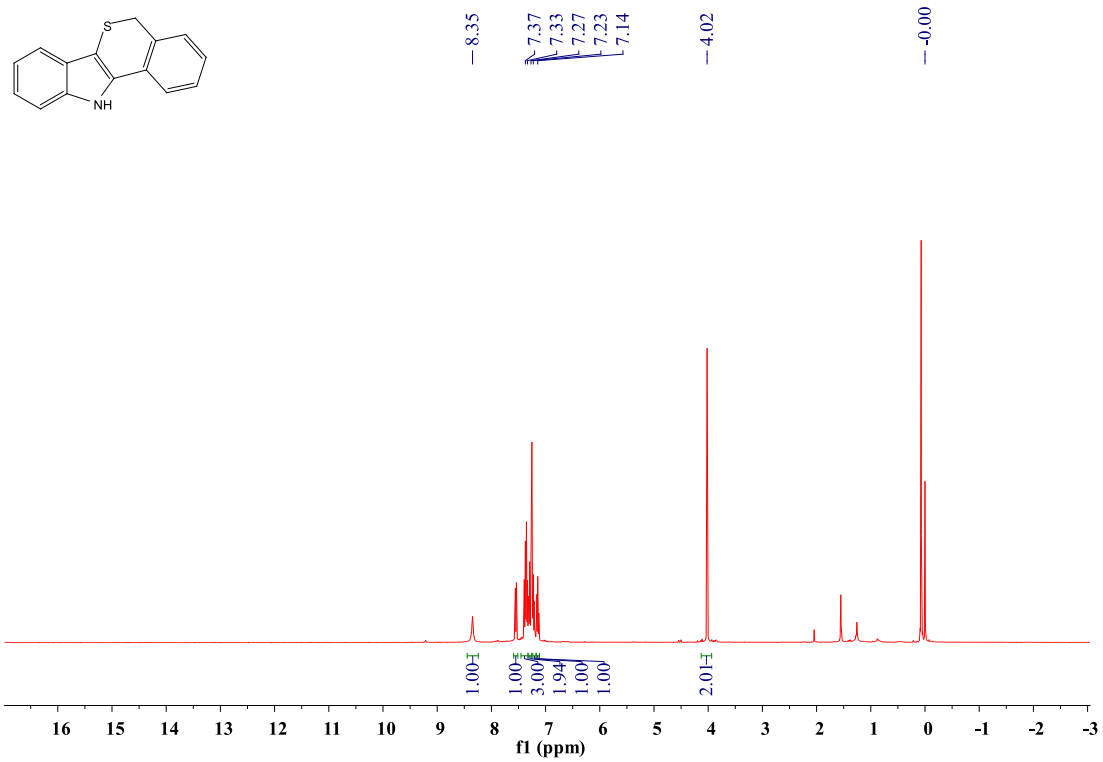

7.72
7.70
7.48
7.25
7.24
7.22
7.21
6.89
6.88
6.87
0.00
NH
S
NH
S
2.00
2.03
2.15
4.01
6.00
4.00
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


137.60
136.33
129.00
119.54
111.63
105.20
77.55
77.23
76.91
40.73
NH
S
NH
S
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

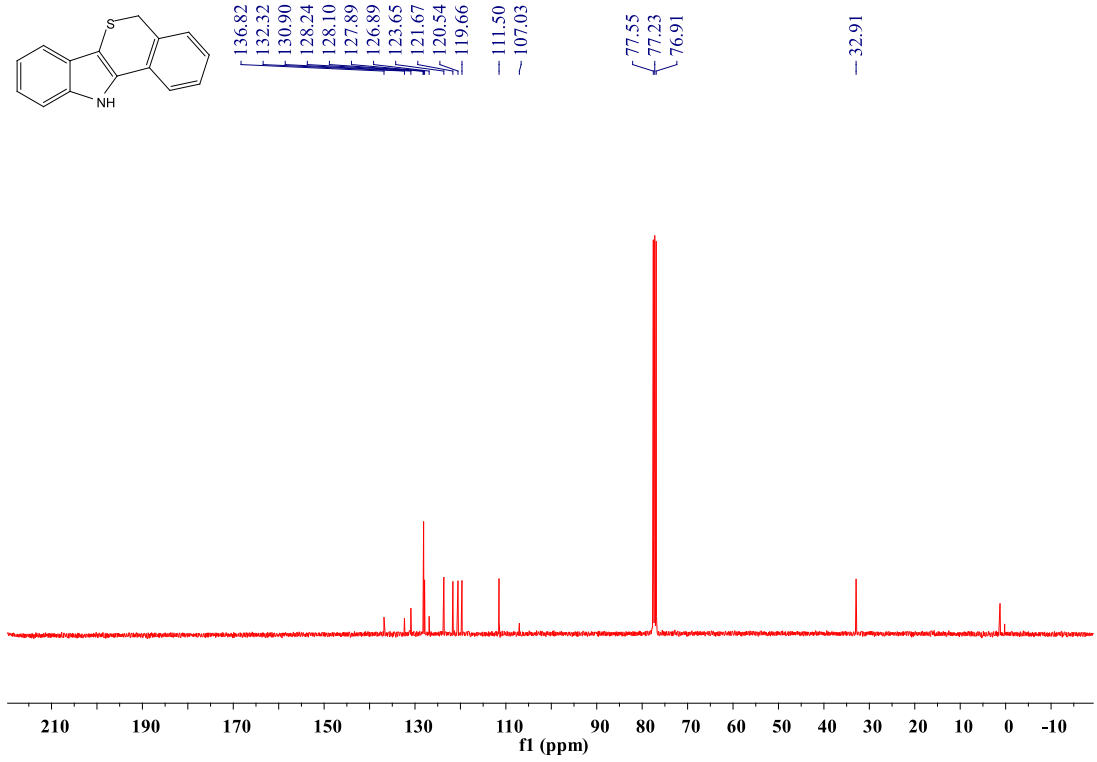

9.12
8.02
7.37
7.30
7.22
7.18
7.15
7.09
6.97
4.34
0.00
1.02
1.19
1.02
1.29
1.00
5.28
2.02
2.00
f1 (ppm)


136.13
131.34
130.98
129.13
128.78
128.64
124.21
122.82
119.62
113.21
112.35
77.55
77.23
76.91
63.36
f1 (ppm)

S
NH


8.35
7.37
7.33
7.27
7.23
7.14
4.02
-0.00
1.00
1.00
3.00
1.94
1.00
1.00
2.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

S
NH


136.82
132.32
130.90
128.24
128.10
127.89
126.89
123.65
121.67
120.54
119.66
111.50
107.03
77.55
77.23
76.91
32.91
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)