Supporting Information

Content

1. General Considerations

All glassware was oven dried at 85 °C for hours and cooled down for use. Acetonitrile (CH_3CN) was dried and distilled using calcium hydride under argon. Analytical grade solvents and commercially available reagents were used to conduct the reactions. Reactions were monitored by thin layer chromatography (TLC), and the products were obtained by column chromatography on silica gel (200-300 mesh). Unless otherwise stated, all reactions were set up in a four-necked flask and were stirred with a Teflon-coated magnetic stir bar. The instruments for electrochemical studies are Metrohm Autolab PGSTAT204 (made in The Netherlands) and dual display potentiostat (DJS-292B) (made in China). The anode is graphite plate electrode (1.5×1.5 cm^2) and cathode is platinum plate electrode (1.5×1.5 cm^2). ^{1}H and ^{13}C NMR data were recorded with Bruker AVANCE III (600 MHz) spectrometers with tetramethylsilane (TMS) as the internal standard. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$ = δ 7.26; DMSO = δ 2.50). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.16; DMSO = δ 39.60). Gas chromatographic (GC) analyses were recorded on an Agilent GC-7820A gas chromatography instrument with FID detector. GC-MS spectra were recorded on Thermo GC MS TRACE 1300.

2. Optimization of conditions for the electrochemical C-H selenation of 1*H*-indole

In an oven-dried undivided four-necked flask (25 mL) equipped with a stir bar (**Figure S1**), 1*H*-indole (0.3 mmol, 1 equiv), diphenyle diselenide (0.15 mmol, 0.5 equiv), and electrolyte salt (additives) were added to 10 mL CH_3CN. The flask was equipped with a graphite plate (1.5×1.5 cm^2) as the anode and a platinum plate (1.5×1.5 cm^2) as the cathode. The reaction mixture was stirred and electrolyzed under constant current mode at room temperature. After the completion of reaction, the resulted solution was analyzed by gas chromatography with 1*H*-indole itself as the internal standard.

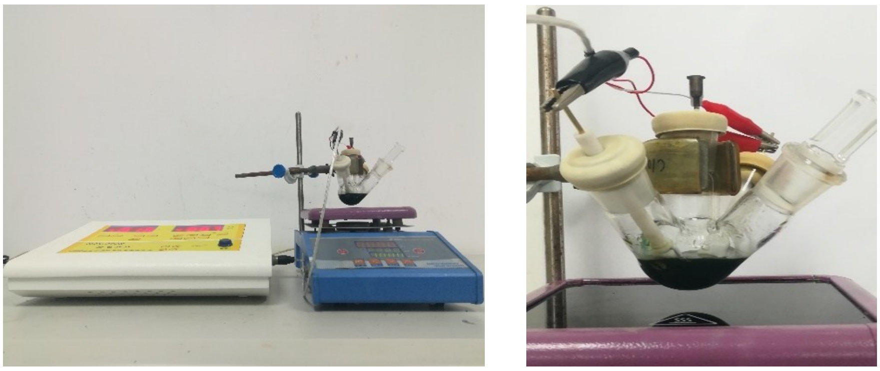
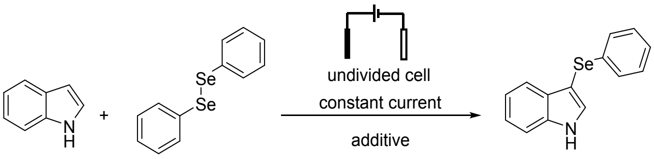


Fig. S1 Electrosynthetic installation

Table S1: Optimization of reaction conditions[a]



1a 1eq **2a** 0.5eq **3a**

Entry	Electrode	Current	Time of electrolysis	Additive	Solvent	Yield[b]
1	C(+)|C(-)	12mA	60min	KI (0.5eq.)	MeCN	95%
2	C(+)|Pt(-)	12mA	60min	KI(0.5eq.)	MeCN	95%
3	Pt(+)|Pt(-)	12mA	60min	KI(0.5eq.)	MeCN	94%
4	Pt(+)|C(-)	12mA	60min	KI(0.5eq.)	MeCN	85%
5	C(+)|Pt(-)	18mA	40min	KI(0.5eq.)	MeCN	98%
6	C(+)|Pt(-)	0	40min	KI(0.5eq.)	MeCN	0
7	C(+)|Pt(-)	18mA	40min	$LiClO_4$(0.5eq.)	MeCN	21%
8	C(+)|Pt(-)	18mA	40min	*n*Bu_4NPF_6(0.5eq.)	MeCN	40%
9	C(+)|Pt(-)	18mA	40min	*n*Bu_4NPF_6(0.5eq.) +KI(0.05eq.)	MeCN	73%
10	C(+)|Pt(-)	18mA	40min	*n*Bu_4NPF_6(0.5eq.) +KI(0.1eq.)	MeCN	69%

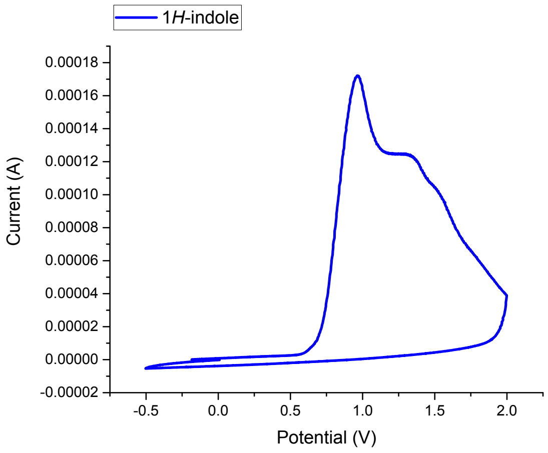
11	C(+)|Pt(-)	18mA	40min	nBu$_4$NPF$_6$(0.5eq.) +KI(0.25eq.)	MeCN	96%
12	C(+)|Pt(-)	18mA	40min	KI(0.5eq.)	MeOH	93%
13	C(+)|Pt(-)	18mA	40min	KI(0.5eq.)	MeCN:H_2O =9:1	89%
14[c]	C(+)|Pt(-)	18mA	40min	KI(0.5eq.)	MeCN	90%
15	C(+)|Pt(-)	18mA	40min	NaI(0.5eq.)	MeCN	91%
16	C(+)|Pt(-)	18mA	40min	LiI(0.5eq.)	MeCN	57%
17	C(+)|Pt(-)	18mA	40min	NH_4I(0.5eq.)	MeCN	60%

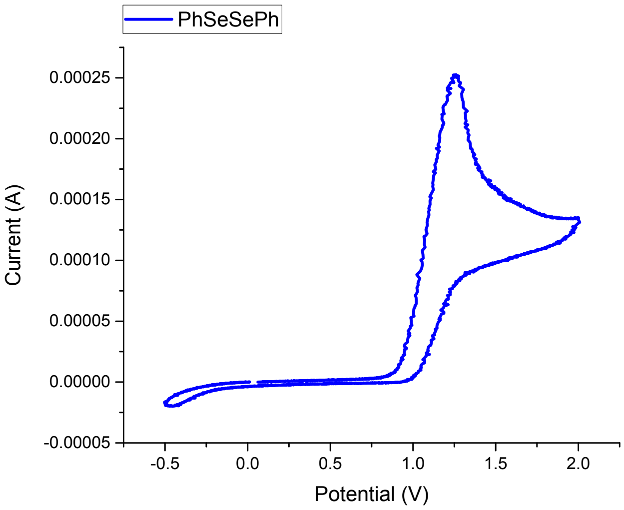
[a] Standard reaction conditions: carbon or platinum plate electrode, constant current mode (12 mA or 18mA), solvent (10.0 mL), **1a** (0.3 mmol, 1 equiv), **2a** (0.15 mmol, 0.5 equiv), RT, open to air. [b] The yield of **3a** was determined by gas chromatography. [c] Under argon.

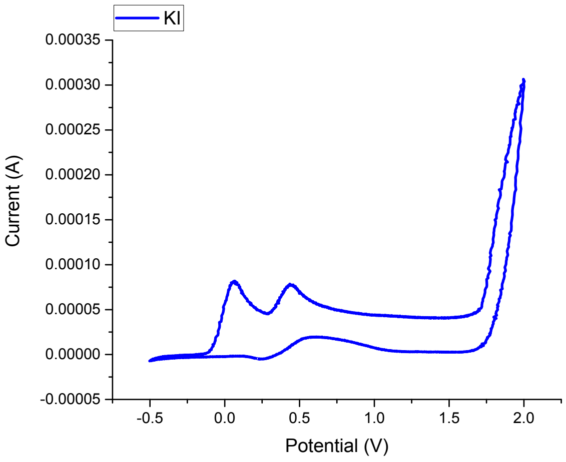
3. General procedure for cyclic voltammetry

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

4. Cyclic voltammograms







5. General procedure for selenlation of indole and imidazopyridine derivatives

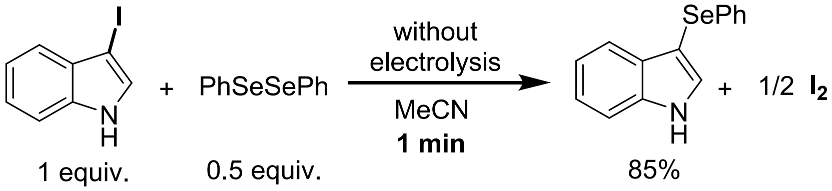
In an oven-dried undivided four-necked flask (25 mL) equipped with a stir bar, Diselenide (0.15 mmol, 0.5 equiv.), indole or imidazopyridine derivatives (0.3 mmol, 1 equiv.) and KI (0.15 mmol, 0.5 equiv.) were added to 10 mL CH_3CN. The flask was equipped with graphite plate electrode (1.5×1.5 cm^2) as the anode and platinum plate electrode (1.5×1.5 cm^2) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 18 mA at room temperature for 40 min open to air. When the reaction was finished, the solvent was removed with a rotary evaporator. The pure product was obtained by column chromatography on silica gel.

6. Mechanism reactions

6.1 Synthesis of 3-iodo-indole

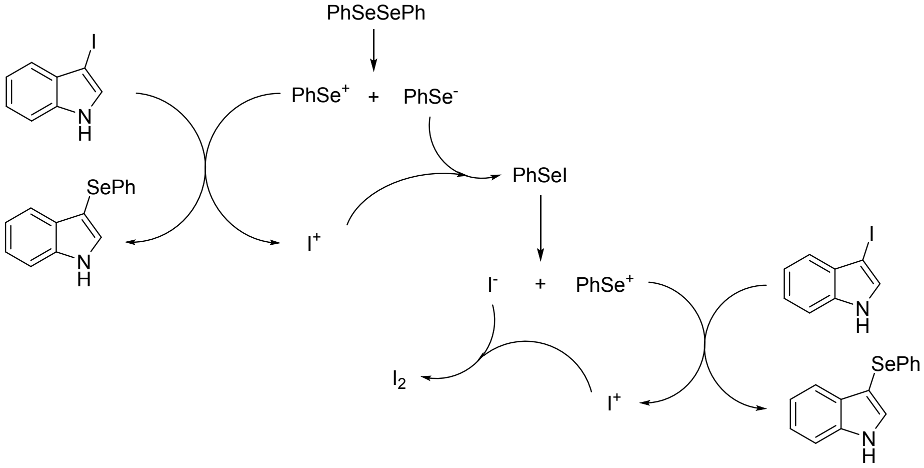
3-iodo-1H-indole: According to a procedure by Sun *et al.*,[1] in an oven-dried undivided four-necked flask (25 mL) equipped with a stir bar. KI (2 mmol, 1equiv.) and 1H-indole (2 mmol, 1equiv.) were added to 10 mL CH_3CN. The flask was equipped with platinum electrode (1.5×1.5 cm^2) as both anode and cathode. The reaction mixture was stirred and electrolyzed at a constant current of 12 mA at room temperature for 12 h in the argon. When the reaction was finished, the solvent was removed with a rotary evaporator. The pure product was obtained by column chromatography on silica gel.

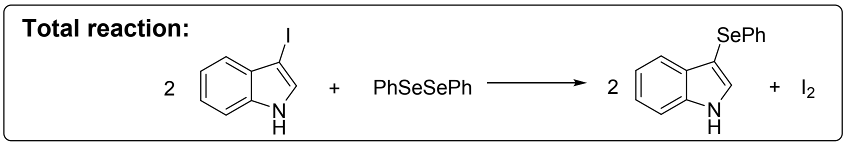
6.2 Control reactions



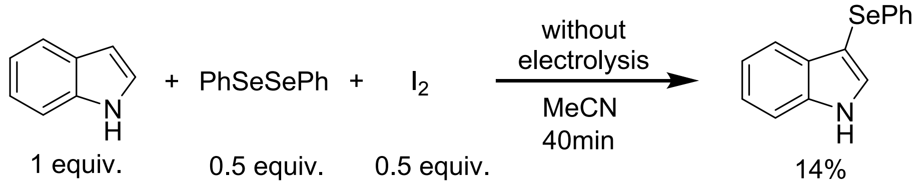
In an oven-dried undivided four-necked flask (25 mL) equipped with a stir bar. Diphenyldiselane (0.15 mmol, 0.5 eq.), and 3-iodo-1H-indole (0.3 mmol, 1eq.) were added to 10 mL CH_3CN. The reaction mixture was stirred at room temperature for 1 min in the air. When the reaction was finished, the yield was determined by Gas Chromatography. (yield: 85%, conversion of 3-iodo-indole: 85%) The quantity of I_2 was titrated by sodium thiosulfate solution.

Proposed mechanism

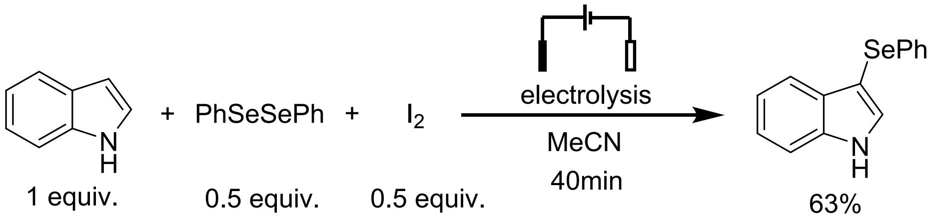




We have also proposed a putative mechanism for this chemical selenation process. As illustrated in the scheme above, PhSeSePh firstly undergoes heterolysis to afford $PhSe^+$ and $PhSe^-$. The strong electrophile $PhSe^+$ will attack the first molecule of 3-iodoindole at the C3 position to form 3-selenyl-indole and I^+. I^+ will interact with $PhSe^-$ to produce PhSeI. PhSeI is actually an in situ intermediate which next undergoes heterolysis to afford $PhSe^+$ and I^-. A second molecule of 3-iodoindole will be selenated by $PhSe^+$ and release I^+. In the last step, I_2 is formed by the interaction between I+ and I- in the solution.

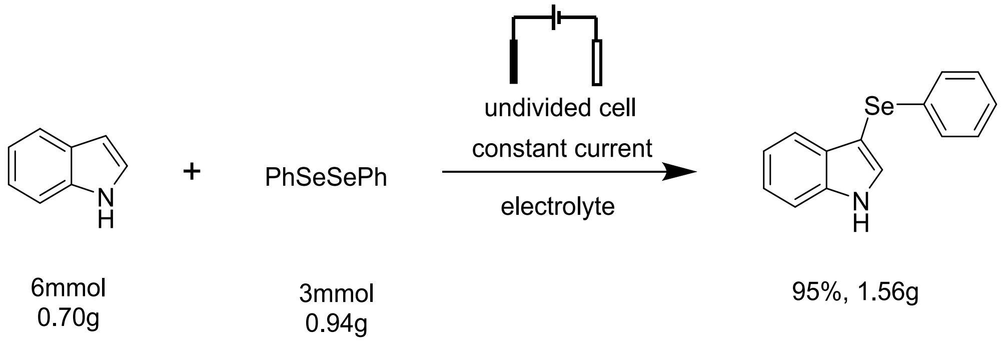


In an oven-dried undivided four-necked flask (25 mL) equipped with a stir bar. Diphenyldiselane (0.15 mmol, 0.5 eq.), 1H-indole (0.3 mmol, 1eq.) and I_2 (0.15 mmol, 0.5 eq.) were added to 10 mL CH_3CN. The reaction mixture was stirred at room temperature for 40 min in the air. When the reaction was finished, the yield was determined by Gas Chromatography. (yield: 14%, conversion of indole: 23%)



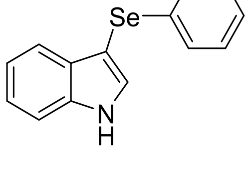
In an oven-dried undivided four-necked flask (25 mL) equipped with a stir bar. Diphenyldiselane (0.15 mmol, 0.5 eq.), 1H-indole (0.3 mmol, 1eq.) and I_2 (0.15 mmol, 0.5 eq.) were added to 10 mL CH_3CN. The flask was equipped with graphite plate electrode (1.5×1.5 cm^2) as the anode and platinum plate electrode (1.5×1.5 cm^2) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 18 mA at room temperature for 40 min open to air. When the reaction was finished, the yield was determined by Gas Chromatography. (yield: 63%, conversion of indole: 63%)

7. Gram-Scale Selenation



In an oven-dried undivided glass cell (100 mL) equipped with a stir bar. Diphenyldiselane (3 mmol, 0.5 eq.), KI (3 mmol, 0.5 eq.) and 1H-indole (6 mmol, 1eq.) were added to 70 mL CH_3CN. The flask was equipped with graphite plate electrode (1.5×1.5 cm^2) as the anode and platinum plate electrode (1.5×1.5 cm^2) as the cathode. The reaction mixture was stirred and electrolyzed at room temperature for 800 min in the air at constant current (18 mA). When the reaction was finished, the solvent was removed with a rotary evaporator. The pure product was obtained by column chromatography on silica gel. (1.56g, Yield: 95%)

8. Characterization Data

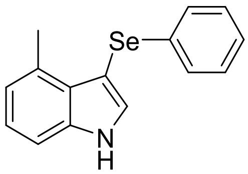


3-(phenylselanyl)-1*H*-indole(3aa)[2]: Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=50:1 as the eluent to give the title compound as a white solid; Yield - (80.0mg, 96%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.38 (brs, 1H), 7.64 (d, J=7.8Hz, 1H), 7.46-7.42 (m, 2H), 7.27-7.21 (m, 3H), 7.18-7.07 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 136.52, 133.93, 131.34, 130.10, 129.09, 128.79, 125.73, 123.09, 121.01, 120.52, 111.48, 98.32.

GC-MS: m/z 271.97.

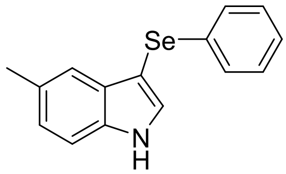


4-methyl-3-(phenylselanyl)-1*H*-indole(3ba)[3]: Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=10:1 as the eluent to give the title compound as a yellow solid; Yield - (76.4mg, 89%).

^{1}H NMR (600 MHz, DMSO-d_6): δ 11.66 (brs, 1H), 7.66 (d, J=2.8Hz, 1H), 7.34 (d, J=8.5Hz, 1H), 7.19-7.08 (m, 5H), 7.04 (t, J=7.3Hz, 1H), 6.77 (d, J=7.0Hz, 1H), 2.58 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6): δ=137.25, 136.29, 133.96, 130.29, 129.26, 127.61, 126.89, 125.47, 122.12, 121.67, 110.30, 93.92, 18.57.

GC-MS: m/z 286.98.

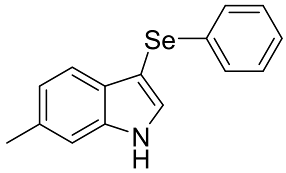


5-methyl-3-(phenylselanyl)-1*H*-indole(3ca)[3]: Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=10:1 as the eluent to give the title compound as a white solid; Yield - (82.4mg, 96%).

^{1}H NMR (600 MHz, DMSO-d_6): δ 11.56 (brs, 1H), 7.67 (s, 1H), 7.37 (d, J=7.7Hz, 1H), 7.20-7.10 (m, 6H), 7.00 (d, J=8.2Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 135.04, 134.07, 133.01, 129.87, 129.17, 128.81, 127.94, 125.57, 123.74, 118.57, 111.93, 94.31, 21.25.

GC-MS: m/z 286.98.

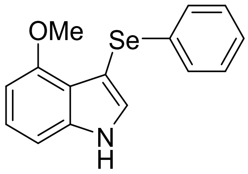


6-methyl-3-(phenylselanyl)-1*H*-indole(3da)[3]: Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=10:1 as the eluent to give the title compound as a pale yellow solid; Yield - (79.9mg, 93%).

^{1}H NMR (600 MHz, DMSO-d_6): δ 11.52 (brs, 1H), 7.63 (d, J=2.5Hz, 1H), 7.27 (t, J=4.5Hz, 2H), 7.17-7.08 (m, 5H), 6.89 (d, J=8.2Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 137.15, 133.96, 132.20, 131.33, 129.15, 128.08, 127.51, 125.60, 121.92, 118.81, 111.96, 94.82, 21.38.

GC-MS: m/z 286.98.

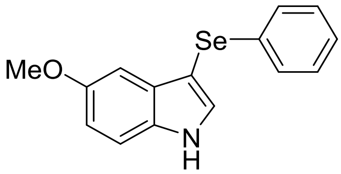


4-methoxy-3-(phenylselanyl)-1*H*-indole(3ea): Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=10:1 as the eluent to give the title compound as a white solid; Yield - (84.3mg, 93%).

^{1}H NMR (600 MHz, DMSO-d_6): δ 11.55 (brs, 1H), 7.42 (d, J=2.4Hz, 1H), 7.24-7.23 (m, 2H), 7.17 (t, J=7.6Hz, 2H), 7.12-7.06 (m, 3H), 6.51 (dd, J=6.0, 2.7Hz, 1H), 3.66 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 153.95, 138.63, 135.44, 131.30, 128.94, 128.87, 125.52, 122.94, 118.60, 105.34, 100.73, 93.59, 55.23.

GC-MS: m/z 302.95.

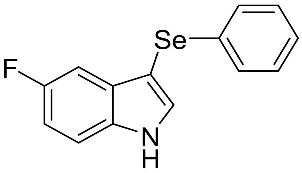


5-methoxy-3-(phenylselanyl)-1*H*-indole(3fa)[3]: Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=10:1 as the eluent to give the title compound as a pale yellow solid; Yield - (86.1mg, 95%).

^{1}H NMR (600 MHz, DMSO-d_6): δ 11.56 (brs, 1H), 7.69 (d, J=2.7Hz, 1H), 7.40 (d, J=9.0Hz, 1H), 7.18-7.15 (m, 4H), 7.11-7.09 (m, 1H), 6.87 (d, J=2.5Hz, 1H), 6.83 (dd, J=8.8, 2.5Hz, 1H), 3.69 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 154.36, 133.98, 133.41, 131.68, 130.38, 129.18, 128.09, 125.63, 113.07, 112.27, 100.58, 94.65, 55.34.

GC-MS: m/z 302.95.

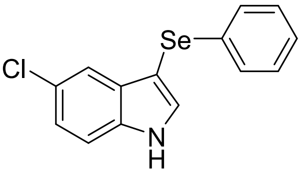


5-fluoro-3-(phenylselanyl)-1*H*-indole(3ga)[3]: Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=10:1 as the eluent to give the title compound as a pale yellow solid; Yield - (83.6mg, 96%).

^{1}H NMR (600 MHz, DMSO-d_6): δ 11.80 (brs, 1H), 7.82 (d, J=2.6Hz, 1H), 7.50 (dd, J=8.8, 4.7Hz, 1H), 7.19-7.02 (m, 7H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 158.51 (d, J=233Hz), 134.93, 133.44, 133.36, 130.36 (d, J=13Hz), 129.25, 128.28, 125.83, 113.54 (d, J=10Hz), 110.50 (d, J=25Hz), 103.74 (d, J=23Hz), 95.18 (d, J=5Hz).

GC-MS: m/z 290.93.

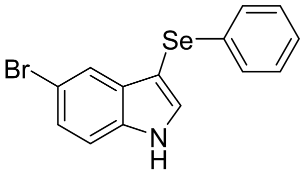


5-chloro-3-(phenylselanyl)-1*H*-indole(3ha)[3]: Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=10:1 as the eluent to give the title compound as a pale yellow solid; Yield - (87.4mg, 95%).

^{1}H NMR (600 MHz, DMSO-d_6): δ 11.89 (brs, 1H), 7.84 (d, J=2.8Hz, 1H), 7.52 (d, J=8.6Hz, 1H), 7.35 (d, J=2.2Hz, 1H), 7.20-7.12 (m, 6H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 135.27, 134.75, 133.32, 130.94, 129.30, 128.26, 125.89, 124.92, 122.19, 118.11, 113.97, 94.85.

GC-MS: m/z 306.88.

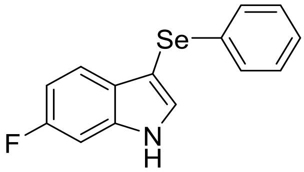


5-bromo-3-(phenylselanyl)-1*H*-indole(3ia)[3]: Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=10:1 as the eluent to give the title compound as a pale yellow solid; Yield - (100.0mg, 95%).

^{1}H NMR (600 MHz, DMSO-d_6): δ 11.90 (brs, 1H), 7.82 (d, J=2.4Hz, 1H), 7.49 (d, J=1.8Hz, 1H), 7.47 (d, J=9Hz, 1H),7.30 (dd, J=8.7, 2.0Hz, 1H), 7.20-7.11 (m, 5H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 135.51, 134.59, 133.32, 131.58, 129.31, 128.23, 125.89, 124.72, 121.15, 114.40, 112.85, 94.71.

GC-MS: (m+H$^+$)/z 352.85.

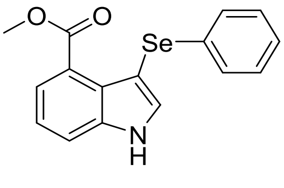


6-fluoro-3-(phenylselanyl)-1*H*-indole(3ja)[4]: Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=10:1 as the eluent to give the title compound as a white solid; Yield - (82.7mg, 95%).

^{1}H NMR (600 MHz, DMSO-d_6): δ 11.74 (brs, 1H), 7.74 (d, J=2.8Hz, 1H), 7.37 (dd, J=8.6, 5.3Hz, 1H), 7.27 (dd, J=10.0, 2.3Hz, 1H), 7.19-7.10 (m, 5H), 6.95-6.91 (m, 1H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 159.35 (d, J=234Hz), 136.58 (d, J=13Hz), 133.55 (d, J=19Hz), 129.23, 128.26, 126.32, 125.80, 120.27 (d, J=10Hz), 108.71 (d, J=25Hz) 98.24 (d, J=26Hz), 95.34.

GC-MS: m/z 290.93.

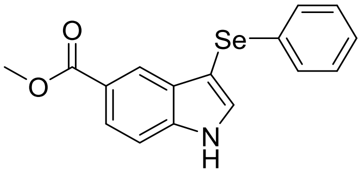


methyl 3-(phenylselanyl)-1*H*-indole-4-carboxylate(3ka): Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=10:1 as the eluent to give the title compound as a yellow liquid; Yield - (51.5mg, 52%).

^{1}H NMR (600 MHz, DMSO-d_6): δ 12.00 (brs, 1H), 7.69 (dd, J=10.0, 2.7Hz, 2H), 7.32 (dd, J=7.3, 1.0Hz, 1H), 7.24 (t, J=7.8Hz, 1H), 7.20-7.11 (m, 5H), 3.58 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 168.80, 137.66, 135.23, 134.71, 129.05, 128.78, 125.75, 125.71, 124.82, 121.27, 121.00, 115.43, 94.85, 51.47.

GC-MS: m/z 330.94.

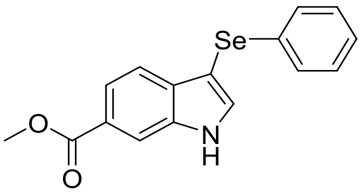


methyl 3-(phenylselanyl)-1*H*-indole-5-carboxylate(3la)[3]: Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=5:1 as the eluent to give the title compound as a white solid; Yield - (90.2mg, 91%).

^{1}H NMR (600 MHz, DMSO-d_6): δ 12.08 (brs, 1H), 8.10 (s, 1H), 7.91 (d, J=2.7Hz, 1H), 7.81 (dd, J=8.6, 1.6Hz, 1H), 7.59 (d, J=8.6Hz, 1H), 7.20-7.11 (m, 5H), 3.81 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 167.00, 139.47, 135.07, 133.40, 129.35, 128.07, 125.87, 123.08, 121.70, 121.45, 112.41, 96.65, 51.88.

GC-MS: m/z 330.94.

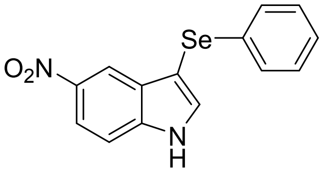


methyl 3-(phenylselanyl)-1*H*-indole-6-carboxylate(3ma)[4]: Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=5:1 as the eluent to give the title compound as a white solid; Yield - (94.1mg, 95%).

^{1}H NMR (600 MHz, DMSO-d_6): δ 12.08 (brs, 1H), 8.15 (s, 1H), 8.00 (d, J=2.5Hz, 1H), 7.70 (dd, J=8.3, 1.3Hz, 1H), 7.50 (d, J=8.3Hz, 1H), 7.17-7.11 (m, 5H), 3.86 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 167.04, 136.60, 136.06, 133.34, 129.28, 128.31, 125.89, 123.31, 120.80, 119.09, 114.16, 95.79, 52.00.

GC-MS: m/z 330.94.

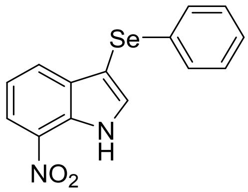


5-nitro-3-(phenylselanyl)-1*H*-indole(3na)[4]: Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=4:1 as the eluent to give the title compound as a white solid; Yield - (87.5mg, 92%).

^{1}H NMR (600 MHz, DMSO-d_6): δ 12.39 (brs, 1H), 8.28 (d, J=2.3Hz, 1H), 8.08-8.06 (m, 2H), 7.68 (d, J=9.0Hz, 1H), 7.21-7.15 (m, 5H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 141.64, 140.08, 136.96, 132.77, 129.44, 129.22, 128.55, 126.19, 117.56, 115.72, 113.08, 98.15.

GC-MS: m/z 317.94.

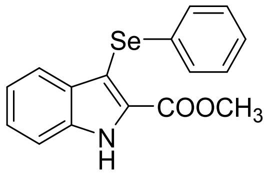


7-nitro-3-(phenylselanyl)-1*H*-indole(3oa): Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=20:1 as the eluent to give the title compound as a yellow solid; Yield - (60.0mg, 63%).

^{1}H NMR (600 MHz, DMSO-d_6): δ 12.42 (brs, 1H), 8.19 (d, J=8.0Hz, 1H), 7.90 (t, J=2.6Hz, 2H), 7.31 (t, J=7.9Hz, 1H), 7.21-7.14 (m, 5H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 135.90, 133.61, 133.27, 132.69, 129.38, 129.03, 128.69, 127.76, 126.18, 120.02, 119.61, 97.95.

GC-MS: m/z 317.94.

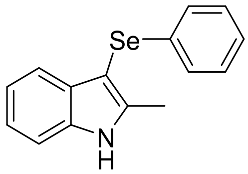


methyl 3-(phenylselanyl)-1*H*-indole-2-carboxylate(3pa): Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=10:1 as the eluent to give the title compound as a white solid; Yield - (83.2mg, 84%).

^{1}H NMR (600 MHz, DMSO-d_6): δ 12.38 (brs, 1H), 7.51 (d, J=8.2Hz, 1H), 7.31-7.16 (m, 7H), 7.05 (t, J=7.5Hz, 1H), 3.88 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 161.06, 136.93, 132.15, 129.92, 129.59, 129.28, 128.60, 126.35, 125.43, 121.39, 120.97, 113.19, 103.73, 52.02.

GC-MS: m/z 330.94.

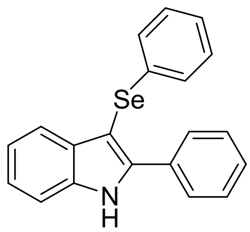


2-methyl-3-(phenylselanyl)-1*H*-indole(3qa)[3]: Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=20:1 as the eluent to give the title compound as an orange liquid; Yield - (78.1mg, 91%).

^{1}H NMR (600 MHz, DMSO-d_6): δ 11.63 (brs, 1H), 7.39 (d, J=7.5Hz, 1H), 7.34 (d, J=8.0Hz, 1H), 7.17-7.08 (m, 6H), 7.03-7.00 (m, 1H), 2.50 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 141.86, 136.08, 133.79, 130.68, 129.19, 127.90, 125.51, 121.38, 119.89, 118.51, 111.24, 93.65, 12.77.

GC-MS: m/z 286.98.

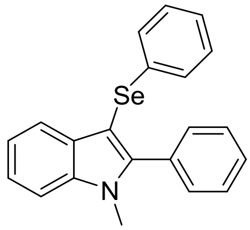


2-phenyl-3-(phenylselanyl)-1*H*-indole(3ra)[3]: Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=20:1 as the eluent to give the title compound as an orange oil; Yield - (97.2mg, 93%).

^{1}H NMR (600 MHz, DMSO-d_6): δ 12.09 (brs, 1H), 7.84 (dd, J=8.3, 1.4Hz, 2H), 7.53-7.46 (m, 4H), 7.41-7.39 (m, 1H), 7.23-7.20 (m, 1H), 7.17-7.08 (m, 6H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 142.26, 136.66, 133.89, 131.85, 131.47, 129.35, 128.66, 128.50, 127.67, 125.60, 122.72, 120.50, 119.68, 111.96, 93.24.

GC-MS: m/z 348.97.

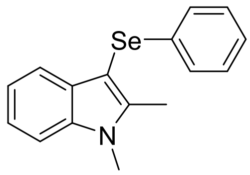


1-methyl-2-phenyl-3-(phenylselanyl)-1H-indole(3sa)[2]: Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=50:1 as the eluent to give the title compound as a colorless liquid; Yield - (93.5mg, 86%).

^{1}H NMR (600 MHz, DMSO-d_6): δ 7.61 (d, J=8.1Hz, 1H), 7.51-7.46 (m, 6H), 7.30-7.28 (m, 1H), 7.16-7.13 (m, 3H), 7.09-7.06 (m, 3H), 3.73 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 145.79, 137.55, 133.93, 130.74, 129.86, 129.24, 128.84, 128.27, 127.82, 125.57, 122.66, 120.81, 119.64, 110.84, 94.90, 31.81.

GC-MS: m/z 362.99.

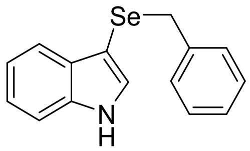


1,2-dimethyl-3-(phenylselanyl)-1H-indole(3ta)[3]: Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=10:1 as the eluent to give the title compound as an red solid; Yield - (77.5mg, 86%).

^{1}H NMR (600 MHz, DMSO-d_6): δ 7.50 (d, J=8.2Hz, 1H), 7.37 (d, J=7.7Hz, 1H), 7.17-7.06 (m, 7H), 3.80 (s, 3H), 2.54 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 143.21, 137.18, 133.73, 129.85, 129.23, 127.95, 125.62, 121.46, 120.17, 118.69, 109.95, 93.54, 30.49, 11.72.

GC-MS: m/z 300.98.

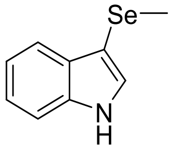


3-(benzylselanyl)-1H-indole(3ab)[5]: Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=10:1 as the eluent to give the title compound as a reddish-brown solid; Yield - (74.7mg, 87%).

^{1}H NMR (600 MHz, CDCl$_3$): δ 8.17 (brs, 1H), 7.66 (d, J=7.8Hz, 1H), 7.37 (d, J=8.2Hz, 1H), 7.24 (t, J=7.6Hz, 1H), 7.22-7.13 (m, 4H), 7.03-7.02 (m, 3H), 3.86 (s, 2H).

^{13}C NMR (151 MHz, CDCl$_3$): δ 139.91, 136.29, 130.76, 130.29, 128.91, 128.30, 126.58, 122.72, 120.61, 120.28, 111.35, 99.07, 32.29.

GC-MS: m/z 286.98.

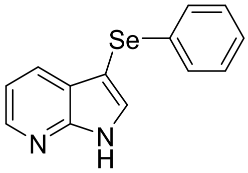


3-(methylselanyl)-1H-indole(3ac): Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=10:1 as the eluent to give the title compound as a reddish-brown liquid; Yield - (52.3mg, 83%).

^{1}H NMR (600 MHz, CDCl$_3$): δ 8.20 (brs, 1H), 7.74 (d, J=7.8Hz, 1H), 7.37 (d, J=7.8Hz, 1H), 7.30 (d, J=2.4Hz, 1H), 7.25-7.19 (m, 2H), 2.19 (s, 3H).

^{13}C NMR (151 MHz, CDCl$_3$): δ 136.37, 129.85, 129.23, 122.78, 120.52, 120.18, 111.45, 100.29, 9.44.

GC-MS: m/z 210.96.

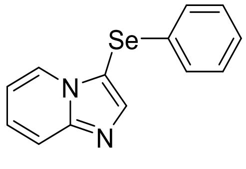


3-(phenylselanyl)-1*H*-pyrrolo[2,3-b]pyridine(3xa)[3]: Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=3:1 as the eluent to give the title compound as a white solid; Yield - (68.8mg, 84%).

^{1}H NMR (600 MHz, DMSO-d_6): δ 12.26 (brs, 1H), 8.29 (dd, J=4.6, 1.6Hz, 1H), 7.89 (d, J=2.2Hz, 1H), 7.78 (dd, J=7.8, 1.5Hz, 1H), 7.18-7.12 (m, 6H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 148.98, 143.65, 133.61, 133.28, 129.29, 128.40, 127.38, 125.93, 121.94, 116.67, 94.05.

GC-MS: m/z 273.95.



3-(phenylselanyl)imidazo[1,2-a]pyridine(3ya): Purified by column chromatography on a silica gel column using petroleum ether: ethyl acetate=2:1 as the eluent to give the title compound as a pale yellow solid; Yield - (45.9mg, 56%).

^{1}H NMR (600 MHz, CDCl$_3$): δ 8.27 (d, J=7.0Hz, 1H), 7.98 (s, 1H), 7.69 (d, J=9.2Hz, 1H), 7.30-7.27 (m, 1H), 7.19-7.14 (m, 5H), 6.86 (t, J=6.6Hz, 1H).
^{13}C NMR (151 MHz, CDCl$_3$): δ 148.41, 143.17, 130.67, 129.64, 129.10, 126.99, 125.90, 125.36, 118.05, 113.20, 106.58.
GC-MS: m/z 273.95.

9. References

[1] Sun Linhao, Zhang Xing, Li Zilong, Ma Jimei, Zeng Zhen, Jiang Hong, *Eur. J. Org. Chem.*, **2018**. DOI: 10.1002/ejoc.201800267

[2] Juliano B. Azeredo, Marcelo Godoi, Guilherme M. Martins, Claudio C. Silveira, and Antonio L. Braga, *J. Org. Chem.,* **2014**, 79, 4125−4130.

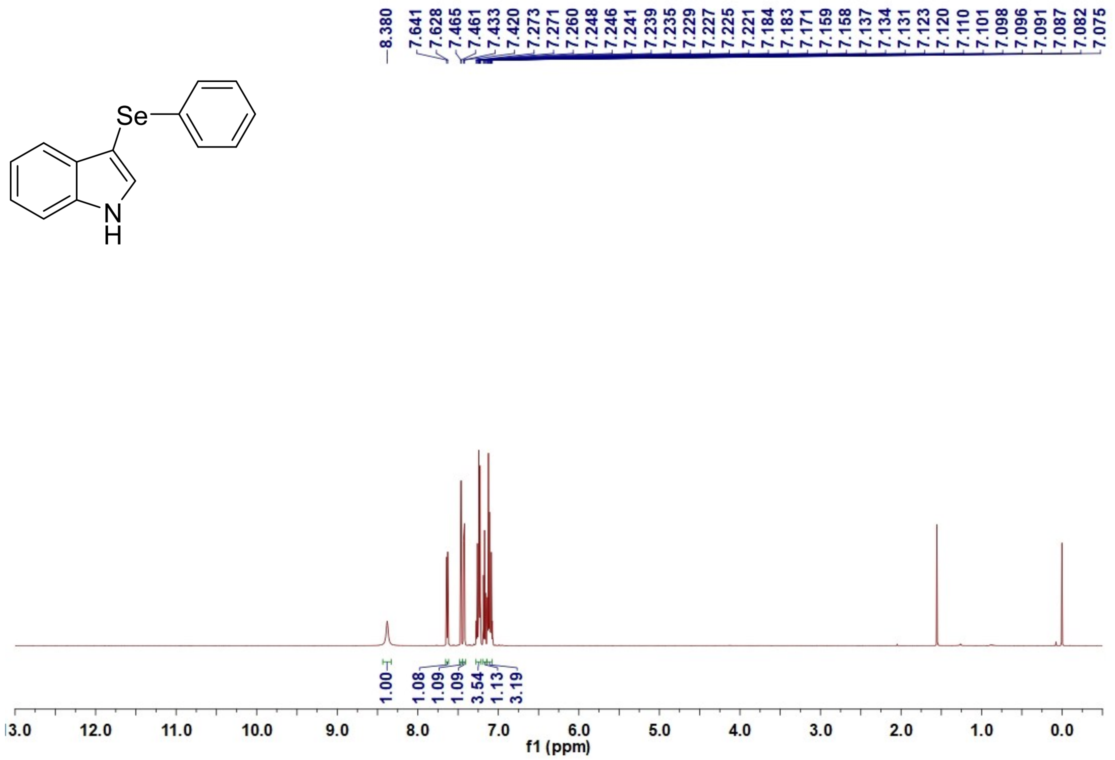
[3] Qing-Bao Zhang, Yong-Liang Ban, Pan-Feng Yuan, Shou-Jiao Peng, Jian-Guo Fang, Li-Zhu Wu and Qiang Liu, *Green Chem.*, **2017**, 19, 5559–5563.

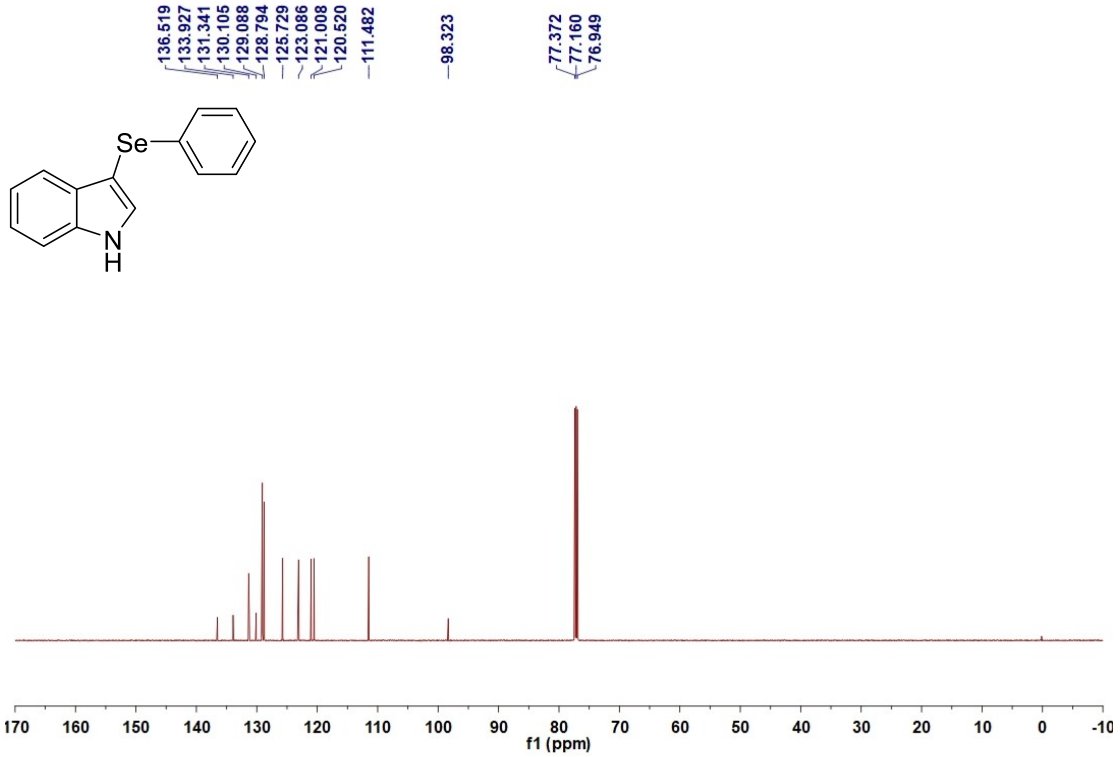
[4] Dongping Luo, Ge Wu, Hang Yang, Miaochang Liu, Wenxia Gao, Xiaobo Huang, Jiuxi Chen, and Huayue Wu, *J. Org. Chem.,* **2016**, 81, 4485−4493.

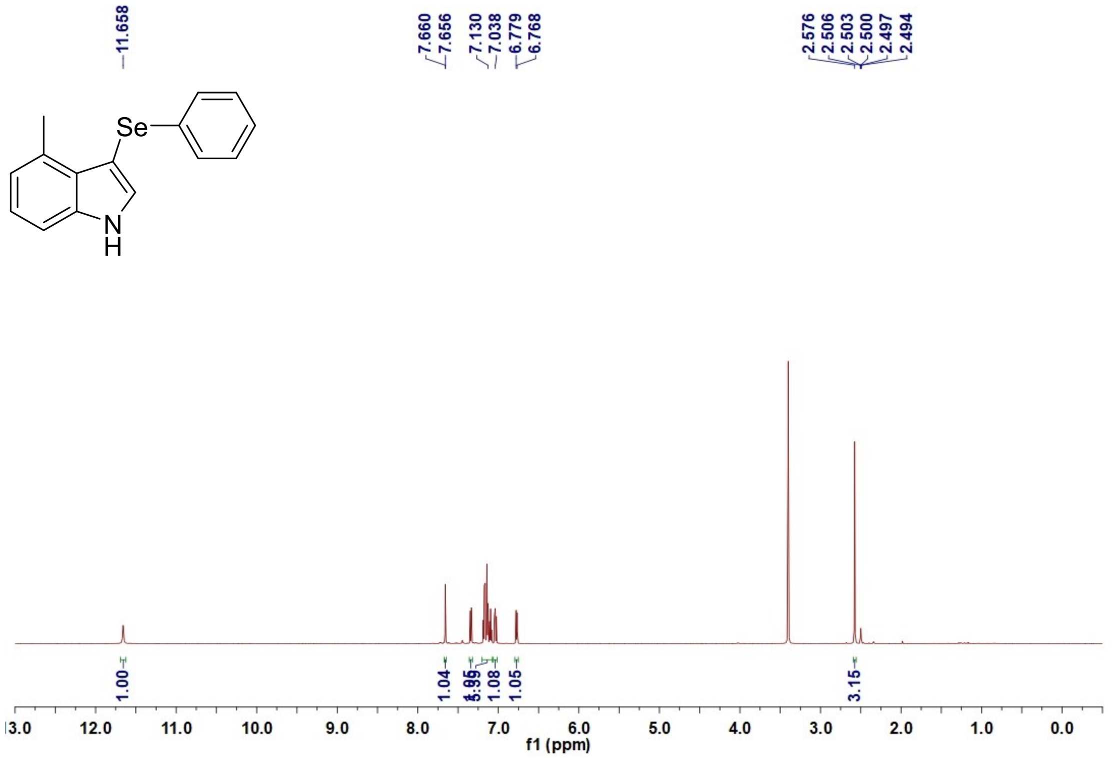
[5] Sumbal Saba, Jamal Rafique, Marcelo S. Franco, Alex R. Schneider, Leandro Espíndola, Dagoberto O. Silva and Antonio L. Braga, *Org. Biomol. Chem.,* **2018**, 16, 880–885.

[6] Ryoma Ohkado, Tatsuro Ishikawa and Hiroki Iida, *Green Chem.,* **2018**, 20, 984-988.

10.NMR Spectra



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H
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1.04
5.96
1.08
1.05
3.15
13.0
12.0
11.0
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6.0
5.0
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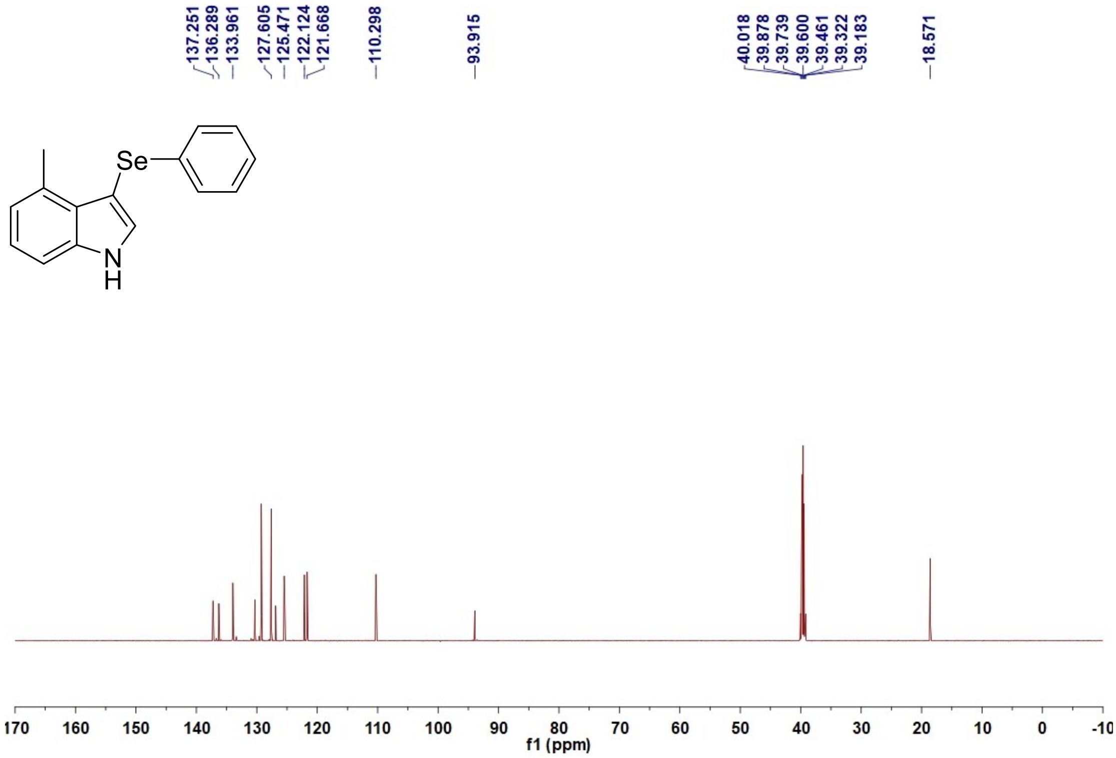
f1 (ppm)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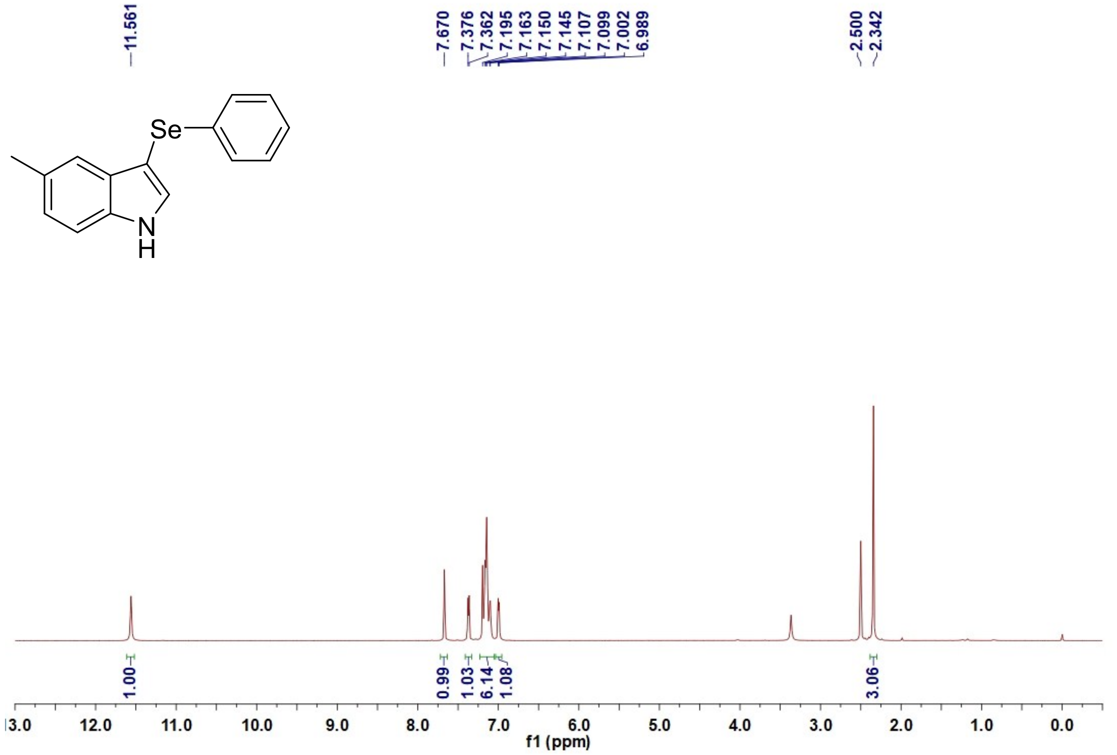
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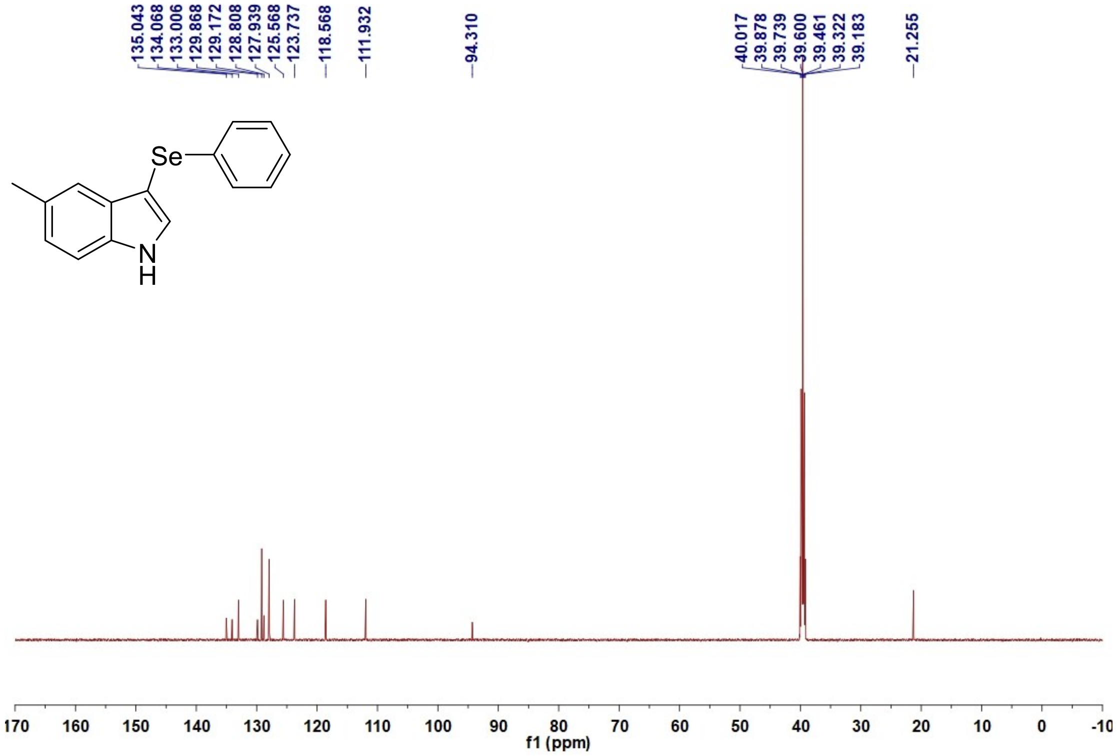
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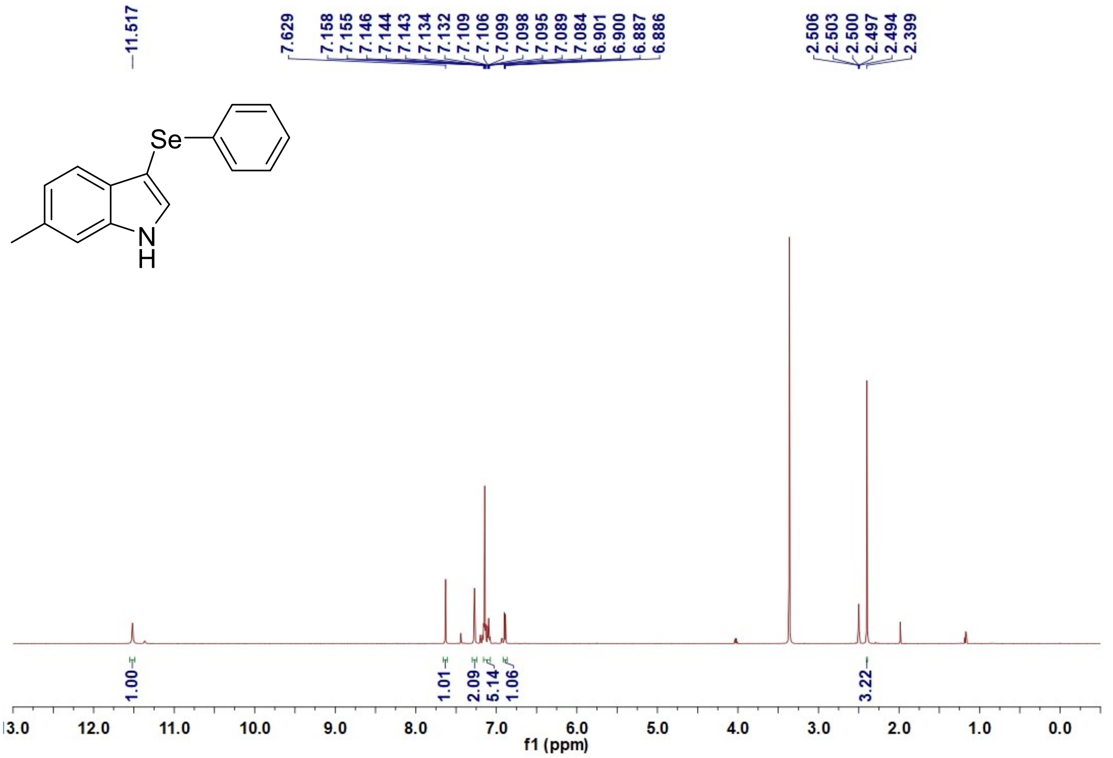
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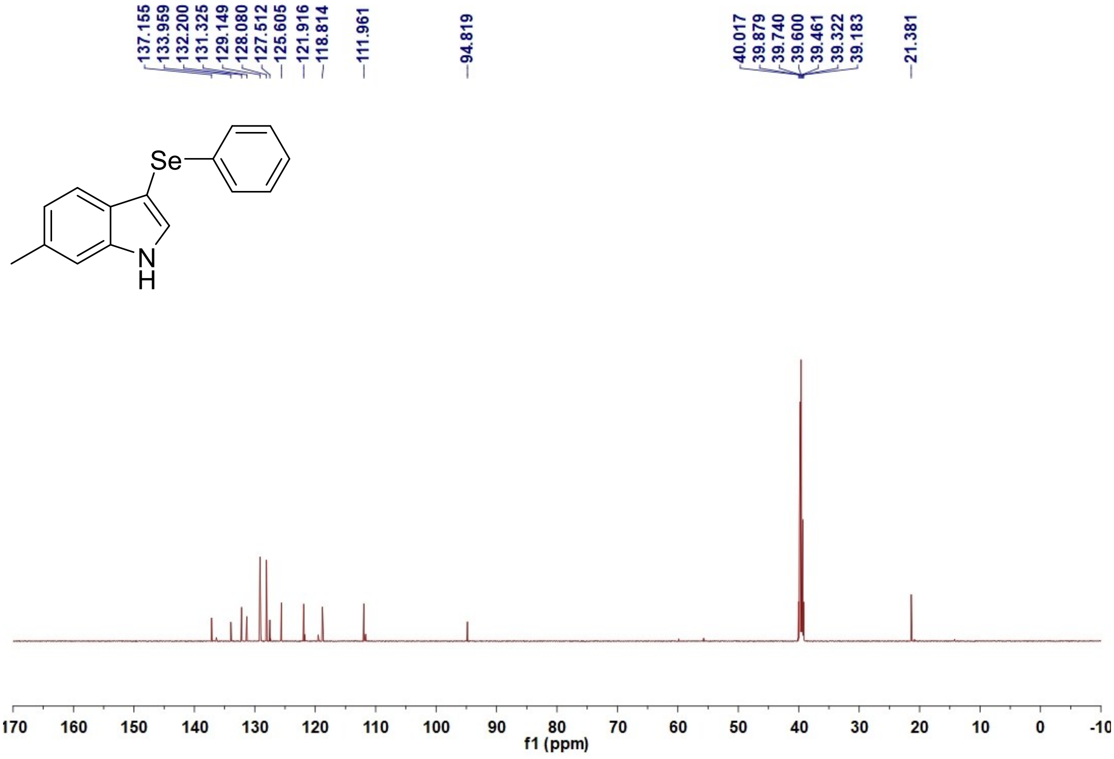
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H
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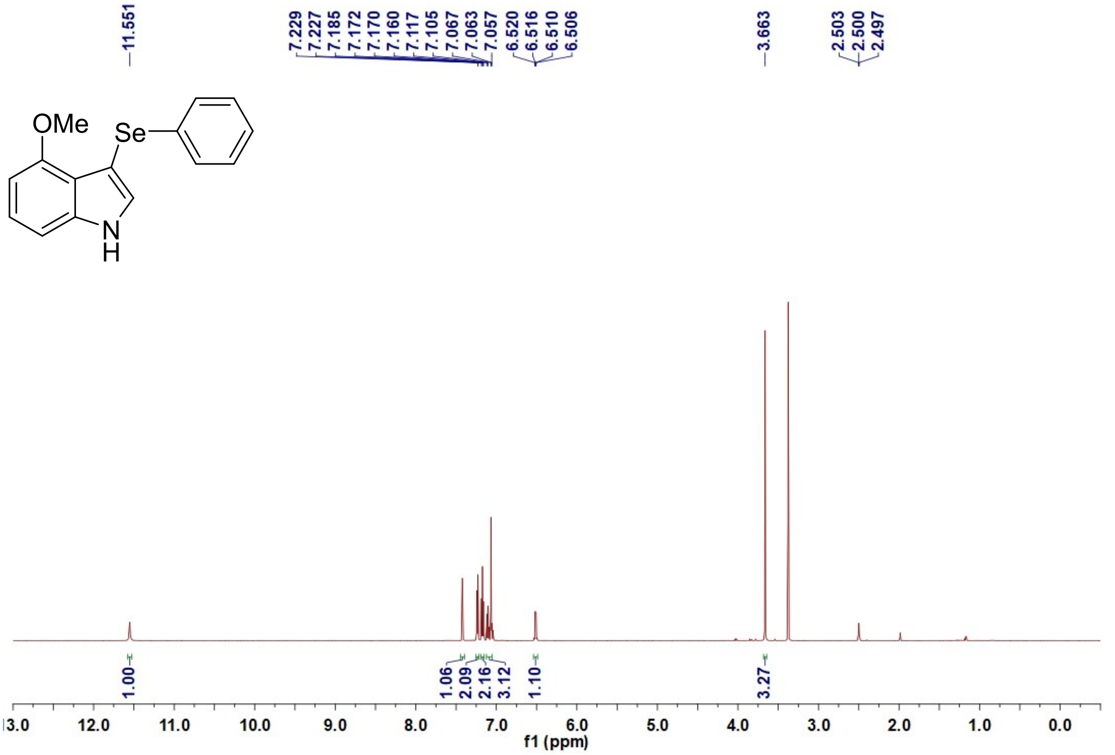

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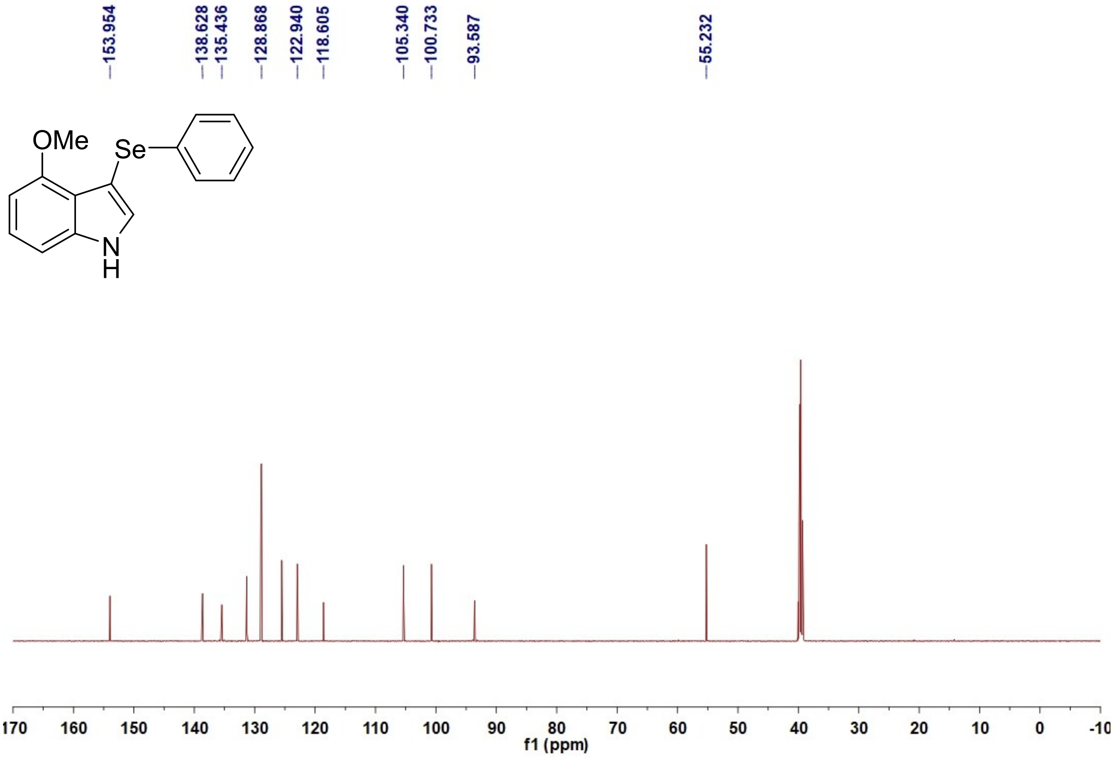

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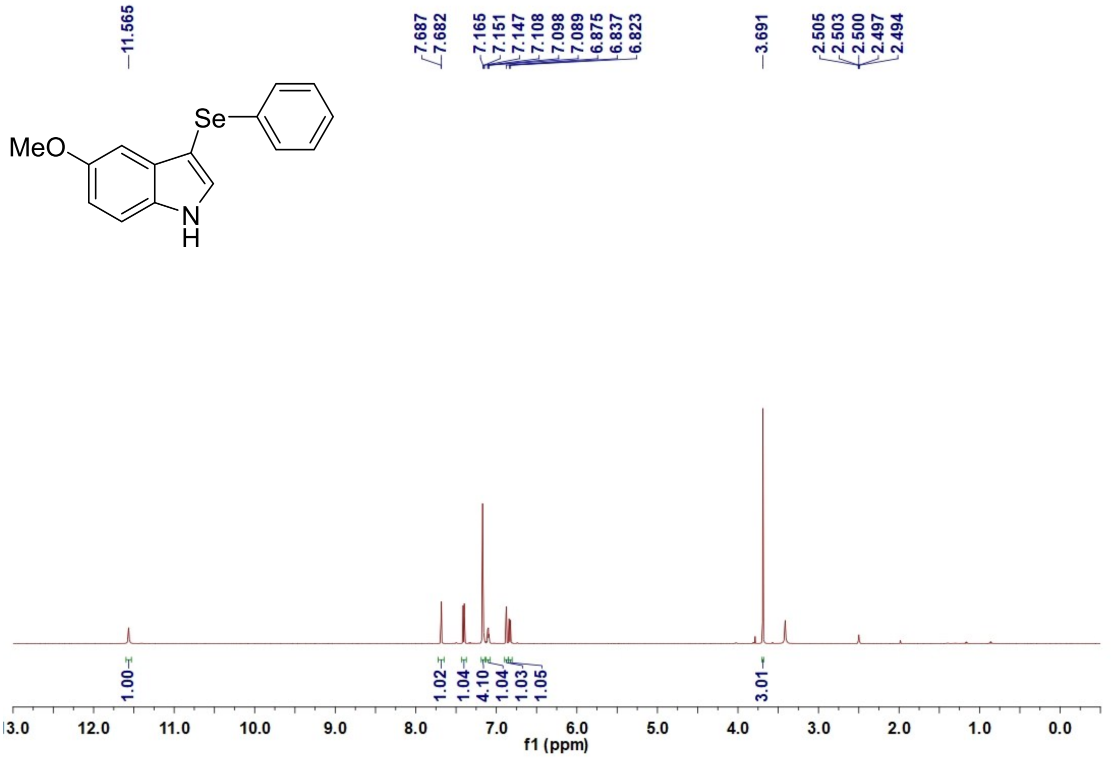
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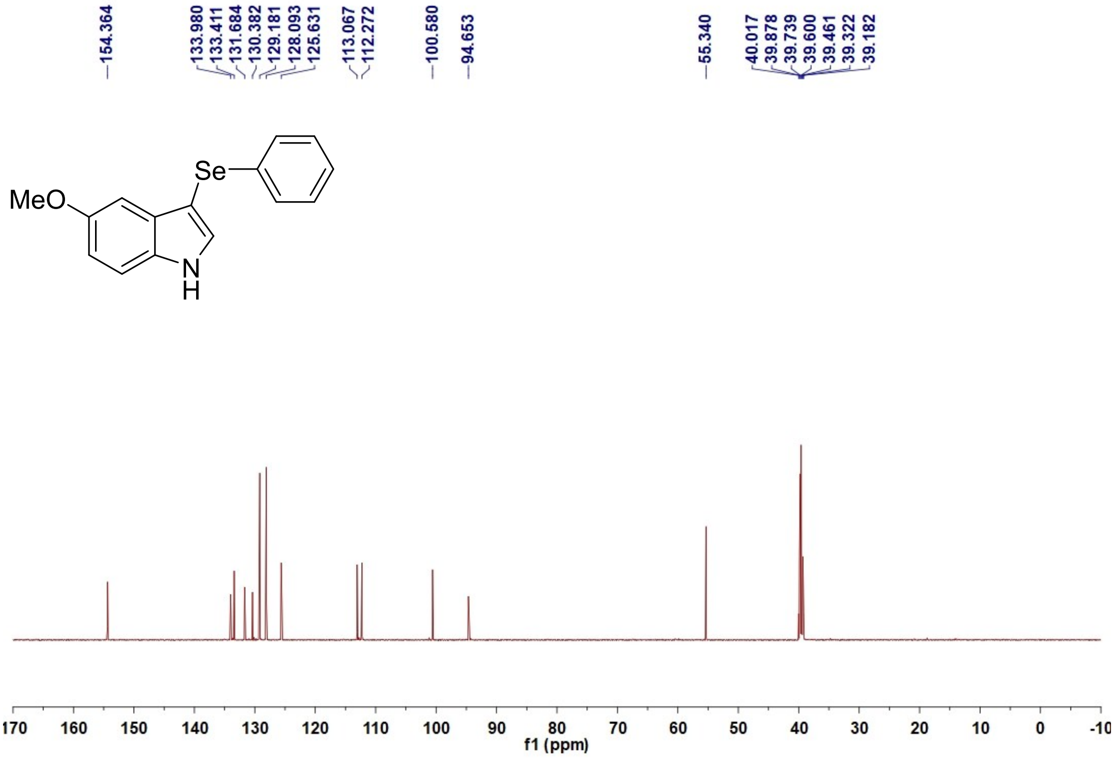
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H
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100
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30
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0
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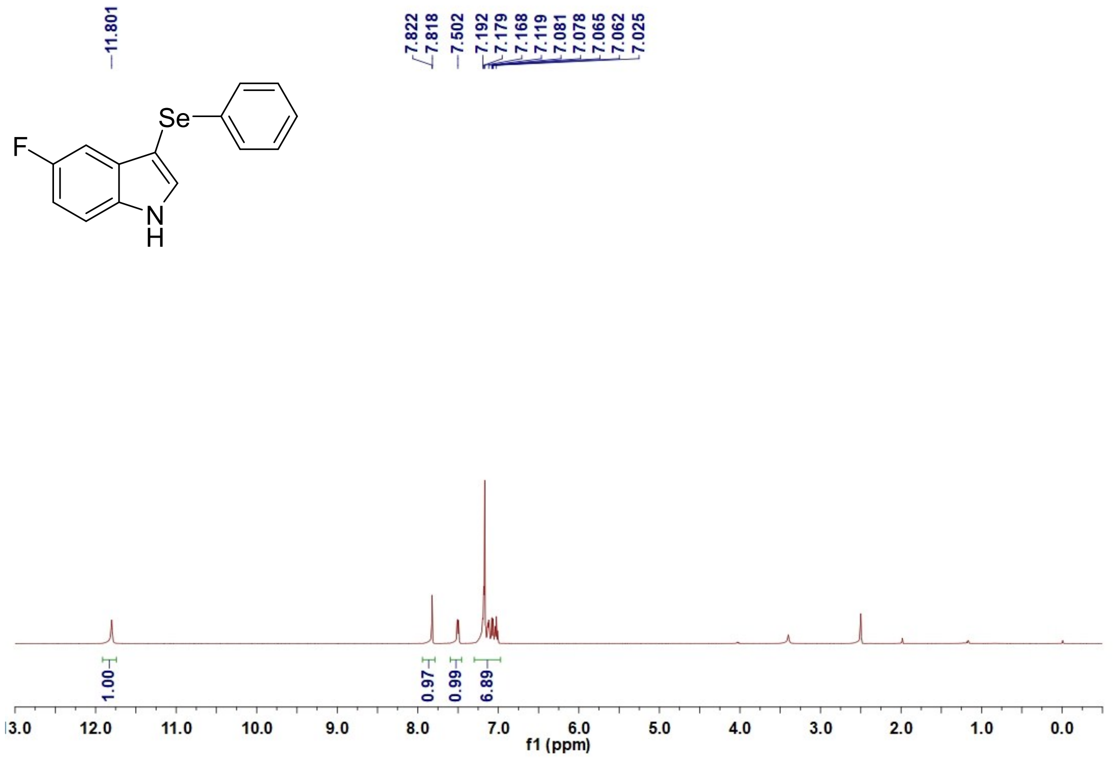
f1 (ppm)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7.818
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7.119
7.081
7.078
7.065
7.062
7.025
Se
F
N
H
1.00
0.97
0.99
6.89
13.0
12.0
11.0
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7.0
6.0
5.0
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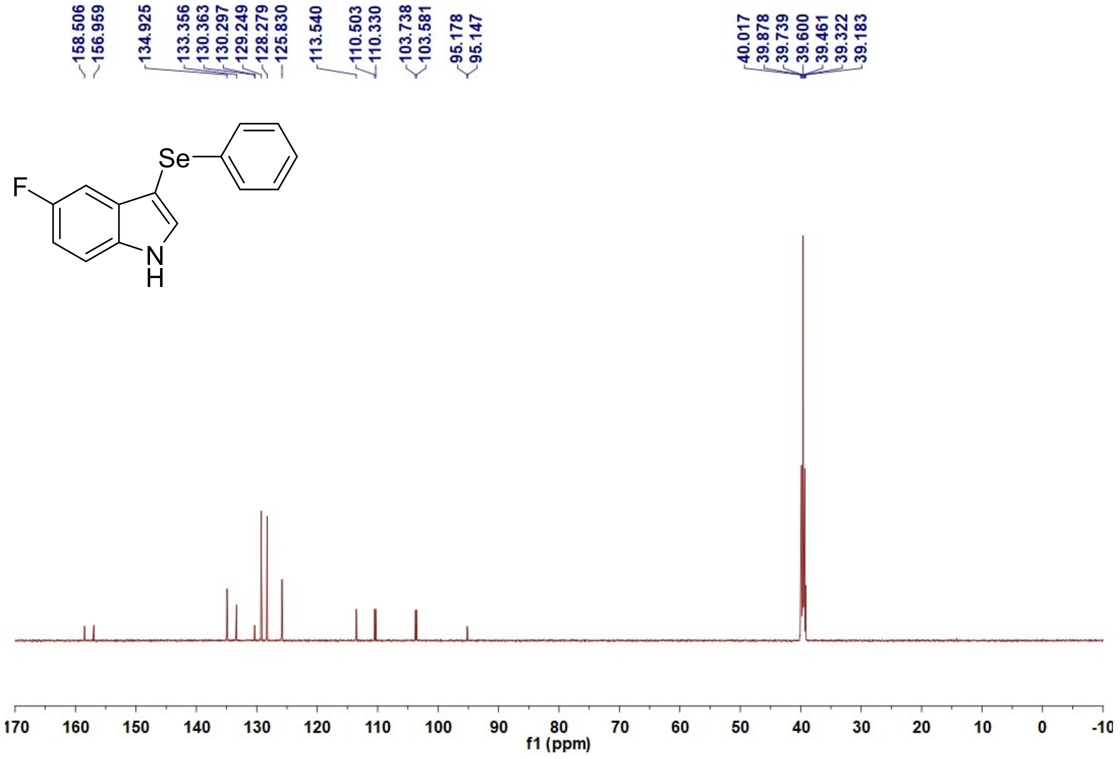
3.0
2.0
1.0
0.0
f1 (ppm)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110.503
110.330
103.738
103.581
95.178
95.147
40.017
39.878
39.739
39.600
39.461
39.322
39.183
Se
F
N
H
170
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40
30
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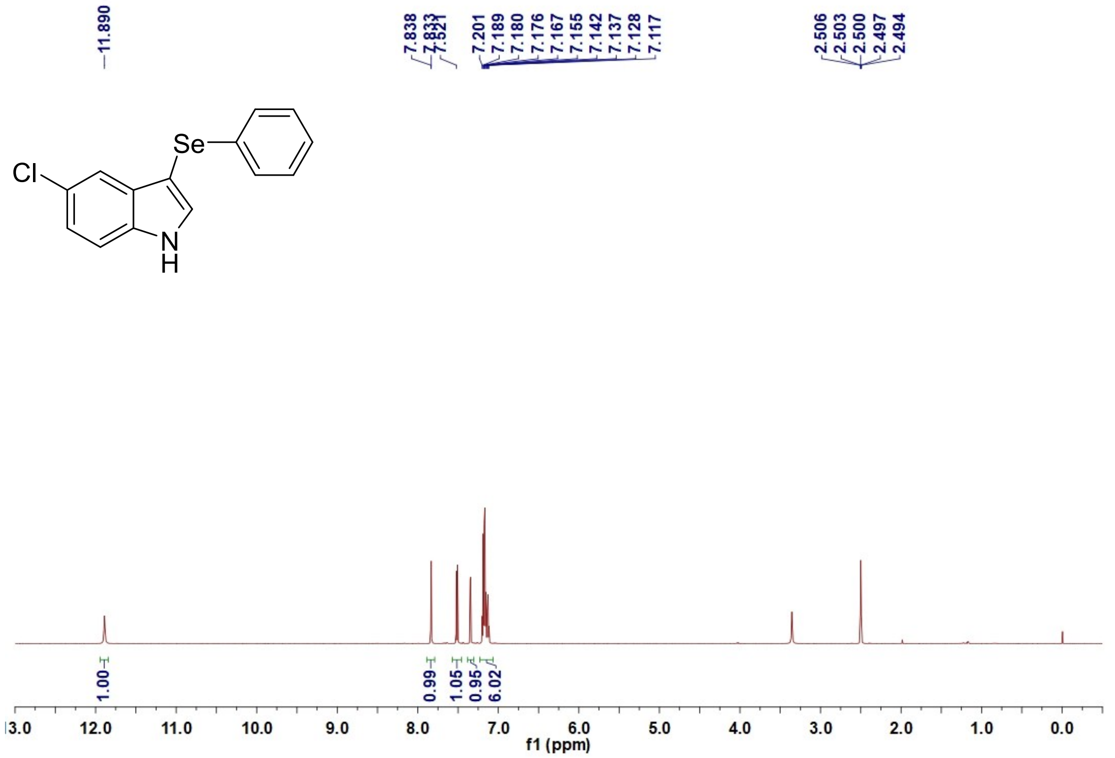
-10
f1 (ppm)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7.176
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7.155
7.142
7.137
7.128
7.117
2.506
2.503
2.500
2.497
2.494
Cl
Se
N
H
1.00
0.99
1.05
0.95
6.02
13.0
12.0
11.0
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5.0
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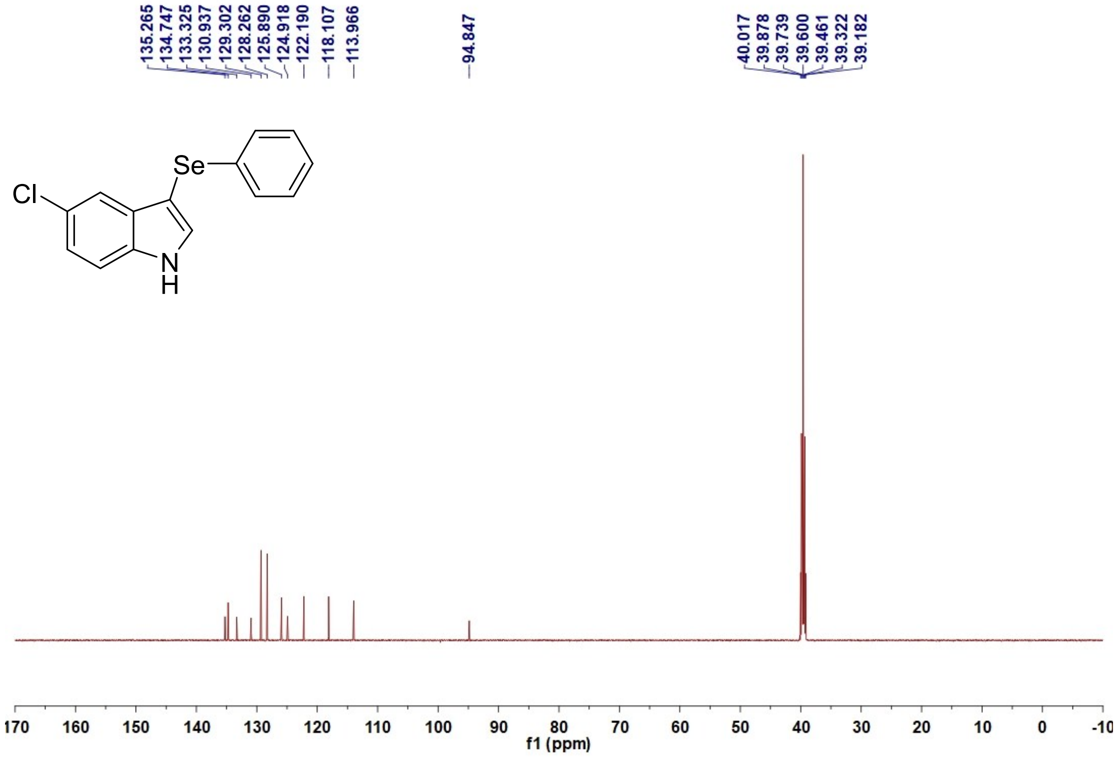
f1 (ppm)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130.937
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125.890
124.918
122.190
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94.847
40.017
39.878
39.739
39.600
39.461
39.322
39.182
Cl
Se
N
H
170
160
150
140
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120
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100
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30
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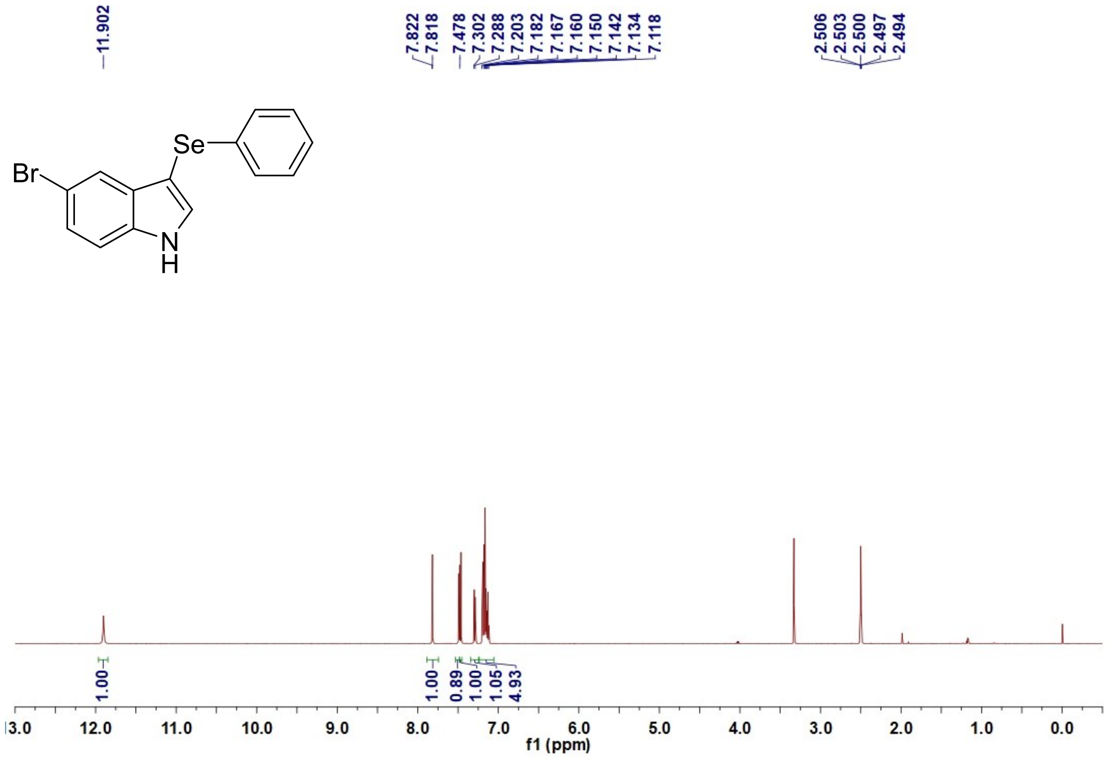
f1 (ppm)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7.182
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7.160
7.150
7.142
7.134
7.118
2.506
2.503
2.500
2.497
2.494
Br
Se
N
H
1.00
1.00
0.89
1.00
1.05
4.93
13.0
12.0
11.0
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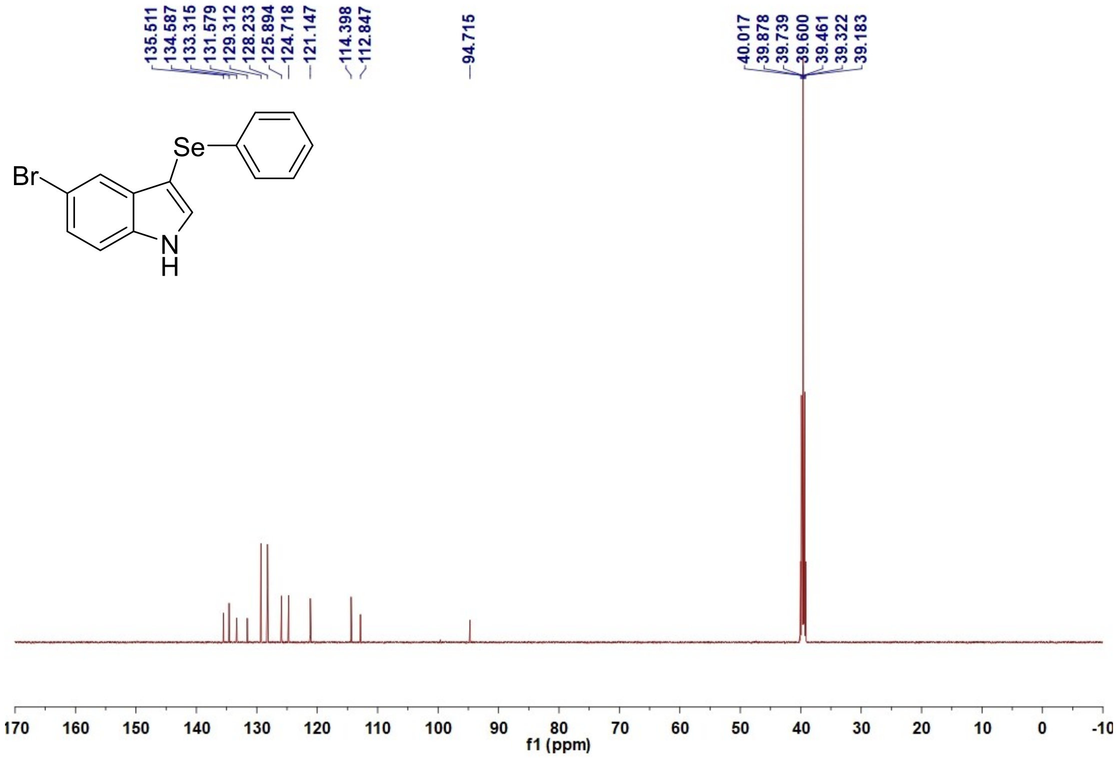
f1 (ppm)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94.715
40.017
39.878
39.739
39.600
39.461
39.322
39.183
Br
Se
N
H
170
160
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100
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80
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30
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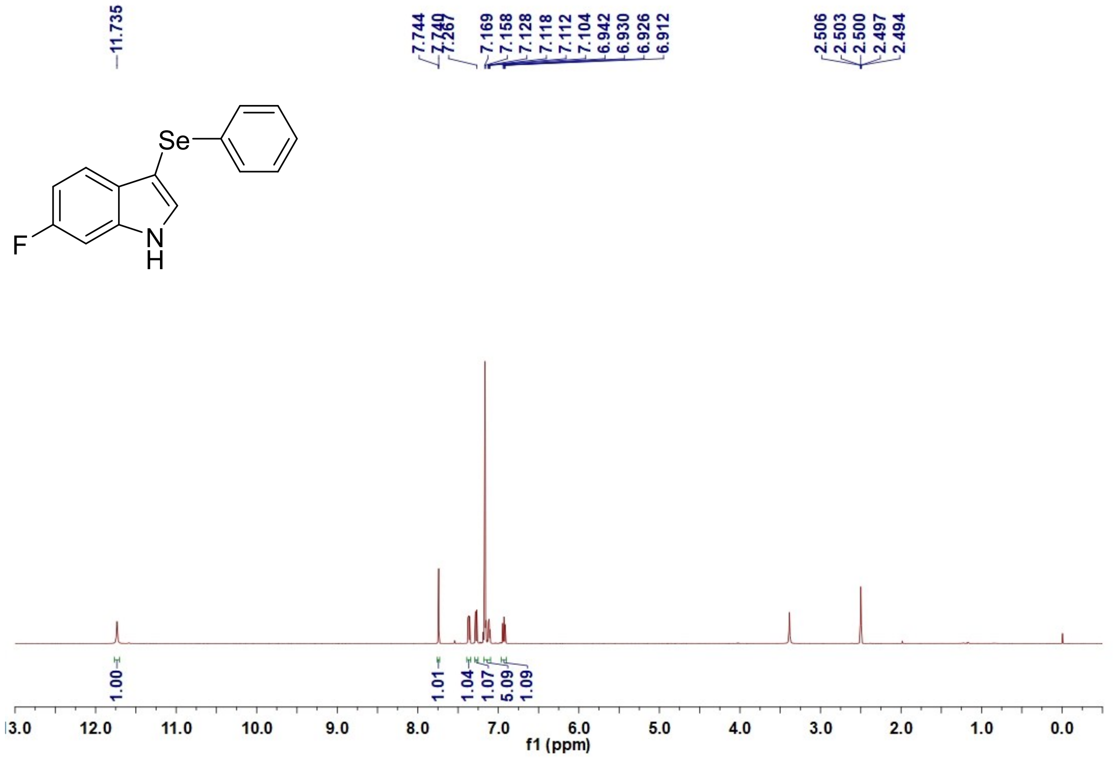
0
-10
f1 (ppm)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7.118
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7.104
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6.930
6.926
6.912
2.506
2.503
2.500
2.497
2.494
Se
F
N
H
1.00
1.01
1.04
1.07
5.09
1.09
13.0
12.0
11.0
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6.0
5.0
4.0
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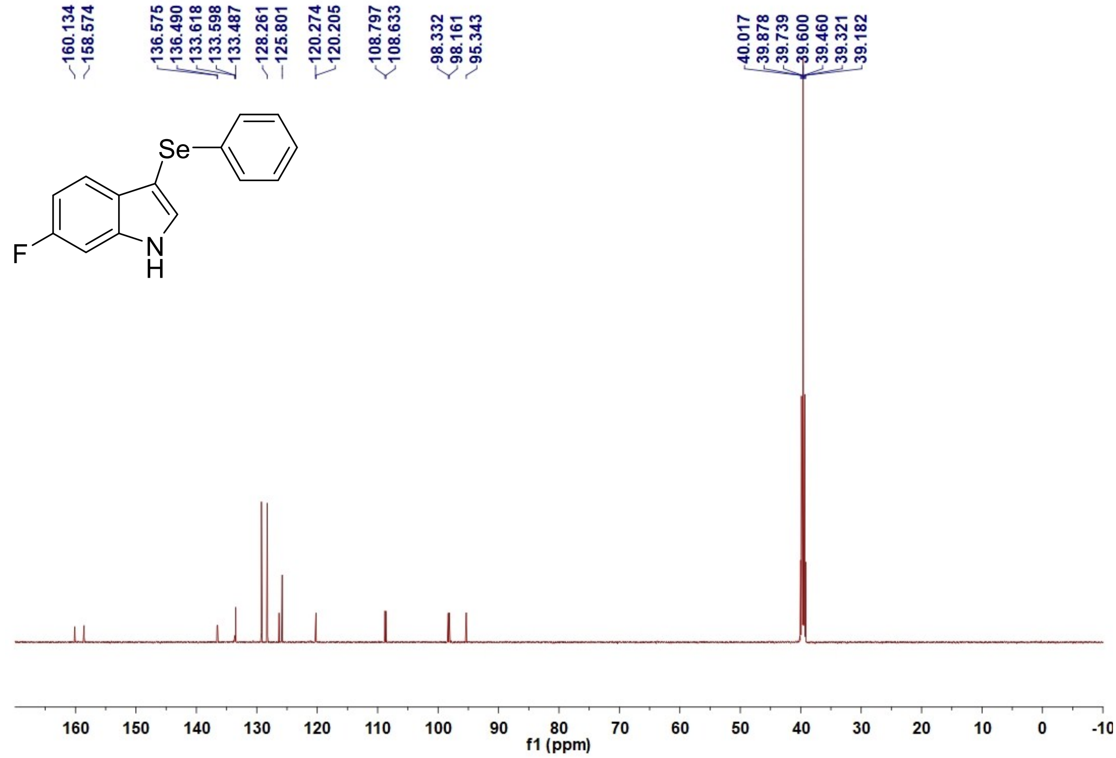
1.0
0.0
f1 (ppm)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133.618
133.598
133.487
128.261
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120.274
120.205
108.797
108.633
98.332
98.161
95.343
40.017
39.878
39.739
39.600
39.460
39.321
39.182
Se
F
N
H
160
150
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120
110
100
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80
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30
20
10
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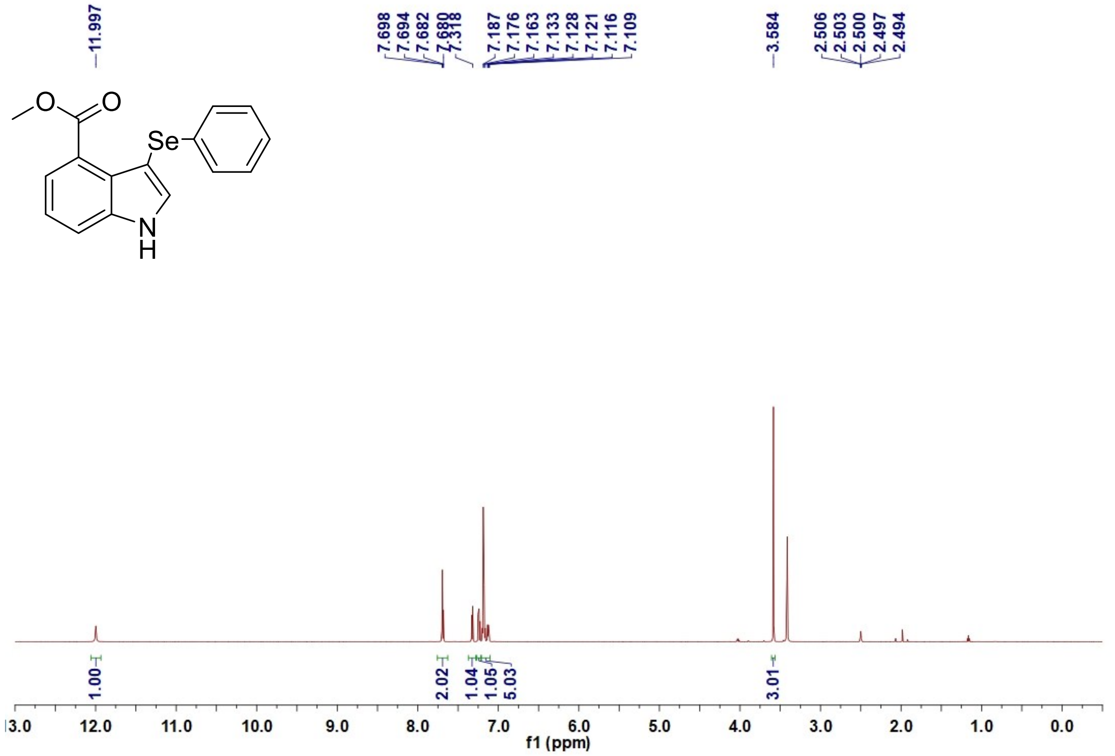
f1 (ppm)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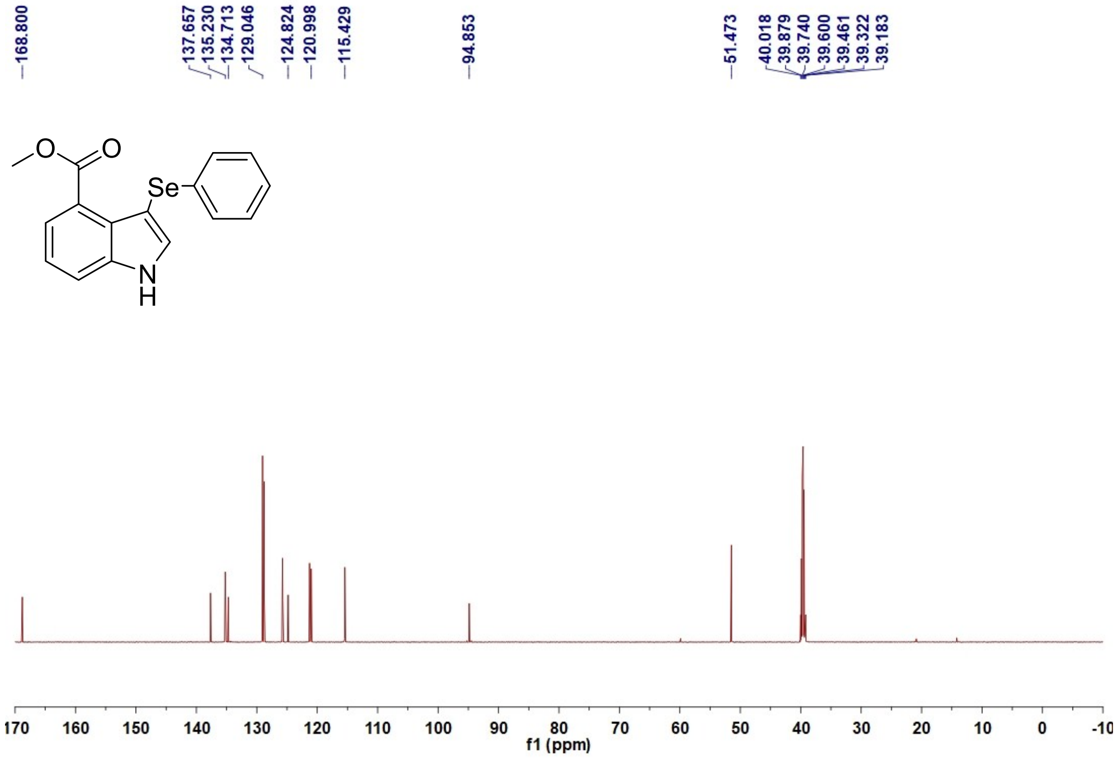
7.680
7.318
7.187
7.176
7.163
7.133
7.128
7.121
7.116
7.109
3.584
2.506
2.503
2.500
2.497
2.494
Se
O
O
N
H
1.00
2.02
1.04
1.05
5.03
3.01
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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137.657
135.230
134.713
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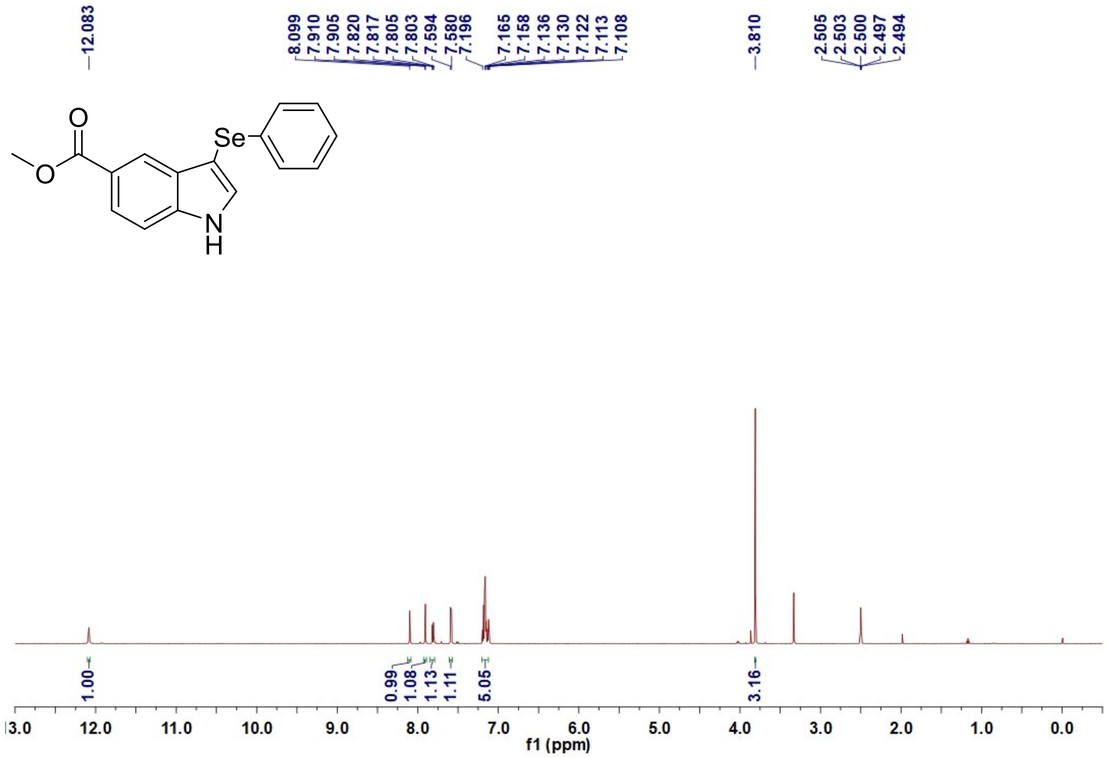
124.824
120.998
115.429
94.853
51.473
40.018
39.879
39.740
39.600
39.461
39.322
39.183
Se
O
O
N
H
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



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7.905
7.820
7.817
7.805
7.803
7.594
7.580
7.196
7.165
7.158
7.136
7.130
7.122
7.113
7.108
3.810
2.505
2.503
2.500
2.497
2.494
O
O
Se
N
H
1.00
0.99
1.08
1.13
1.11
5.05
3.16
13.0
12.0
11.0
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9.0
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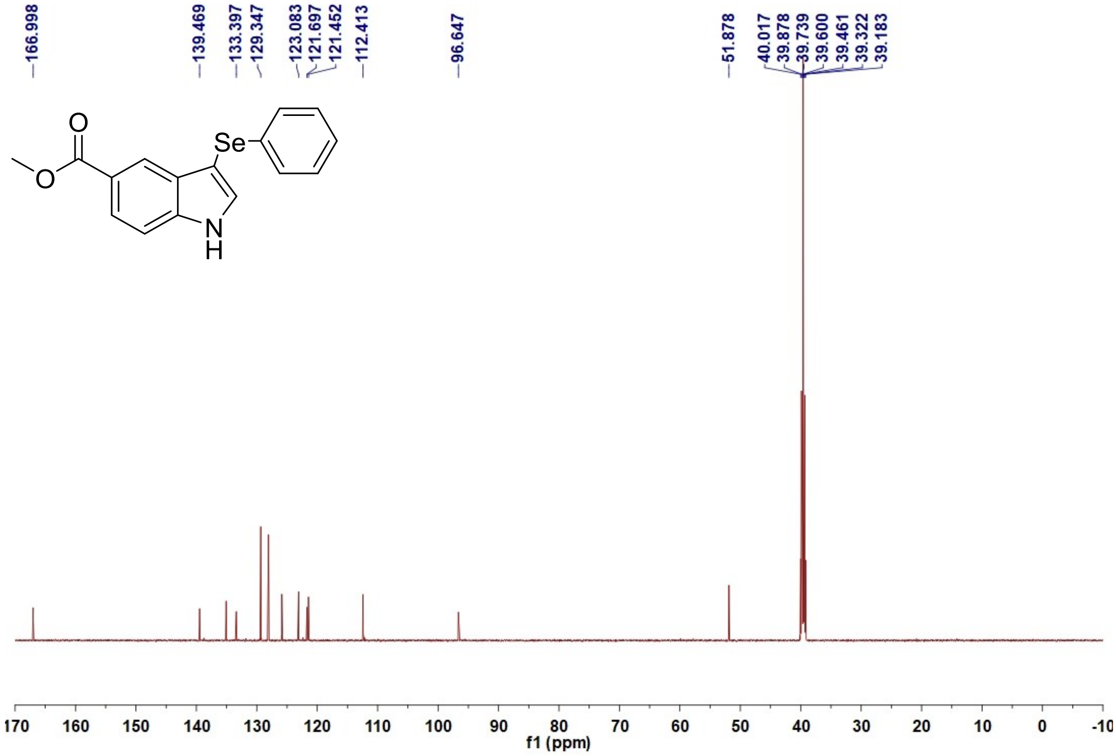
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)



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121.697
121.452
112.413
96.647
51.878
40.017
39.878
39.739
39.600
39.461
39.322
39.183
O
O
Se
N
H
170
160
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140
130
120
110
100
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80
70
60
50
40
30
20
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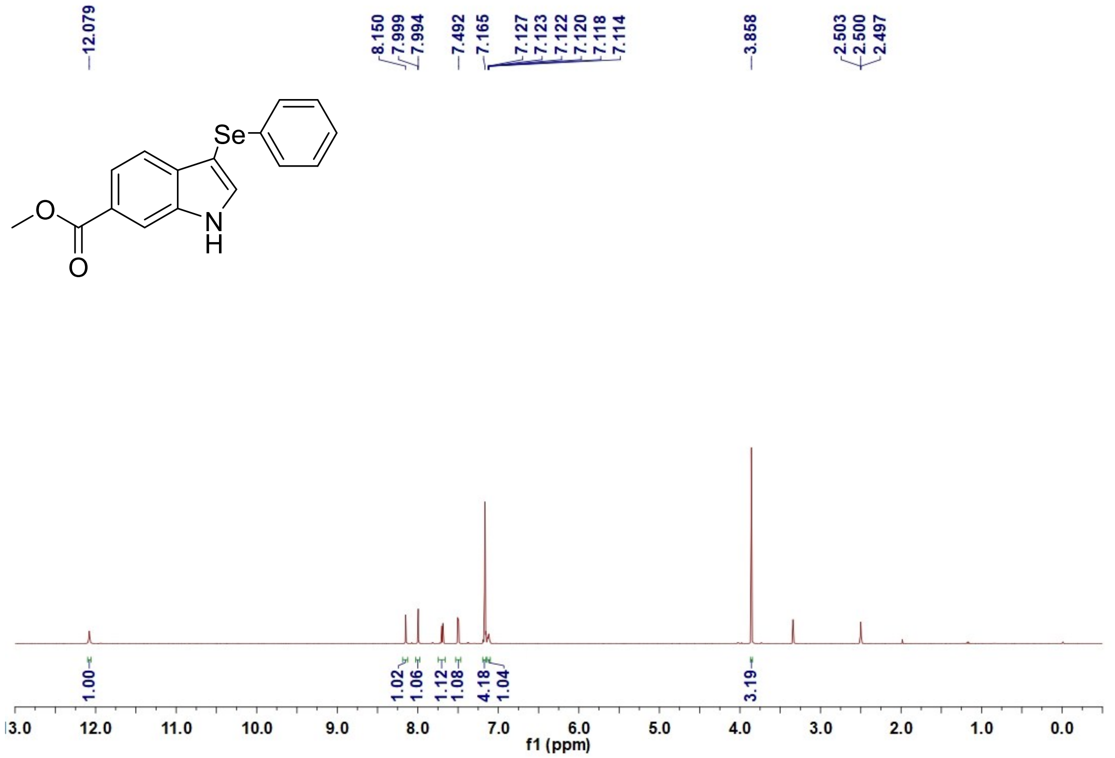
0
-10
f1 (ppm)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7.123
7.122
7.120
7.118
7.114
3.858
2.503
2.500
2.497
Se
O
O
N
H
1.00
1.02
1.06
1.12
1.08
4.18
1.04
3.19
13.0
12.0
11.0
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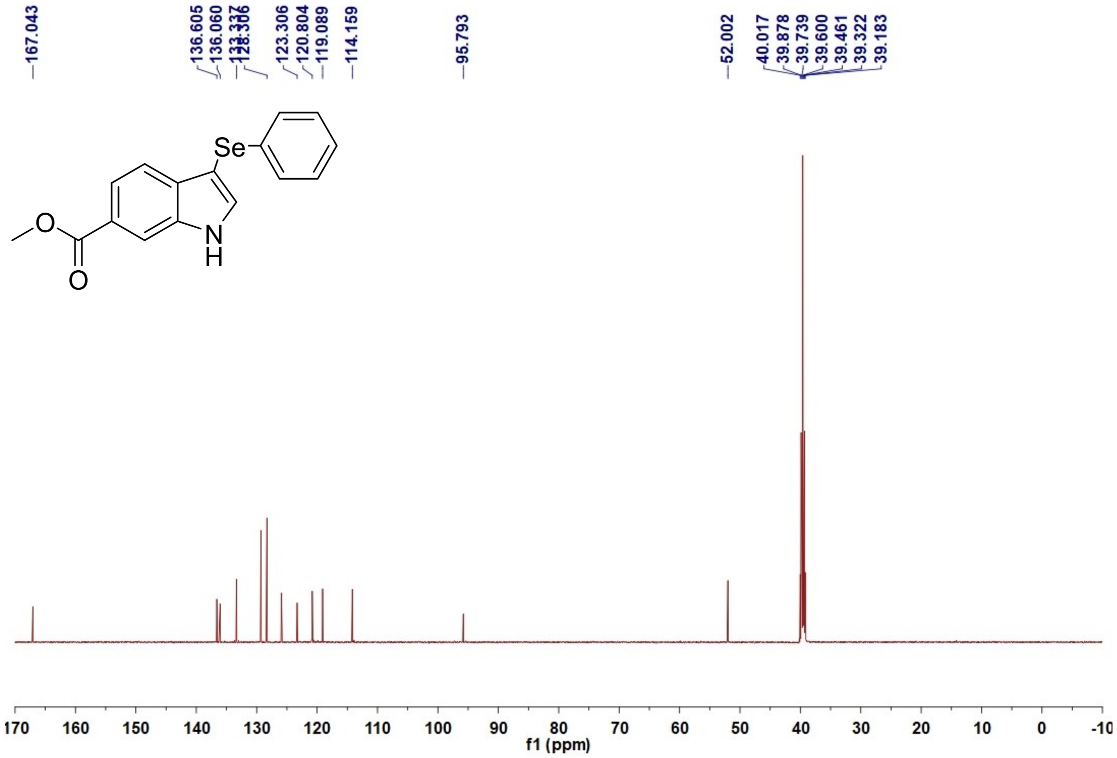
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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39.878
39.739
39.600
39.461
39.322
39.183
Se
O
O
N
H
170
160
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140
130
120
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100
90
80
70
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50
40
30
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10
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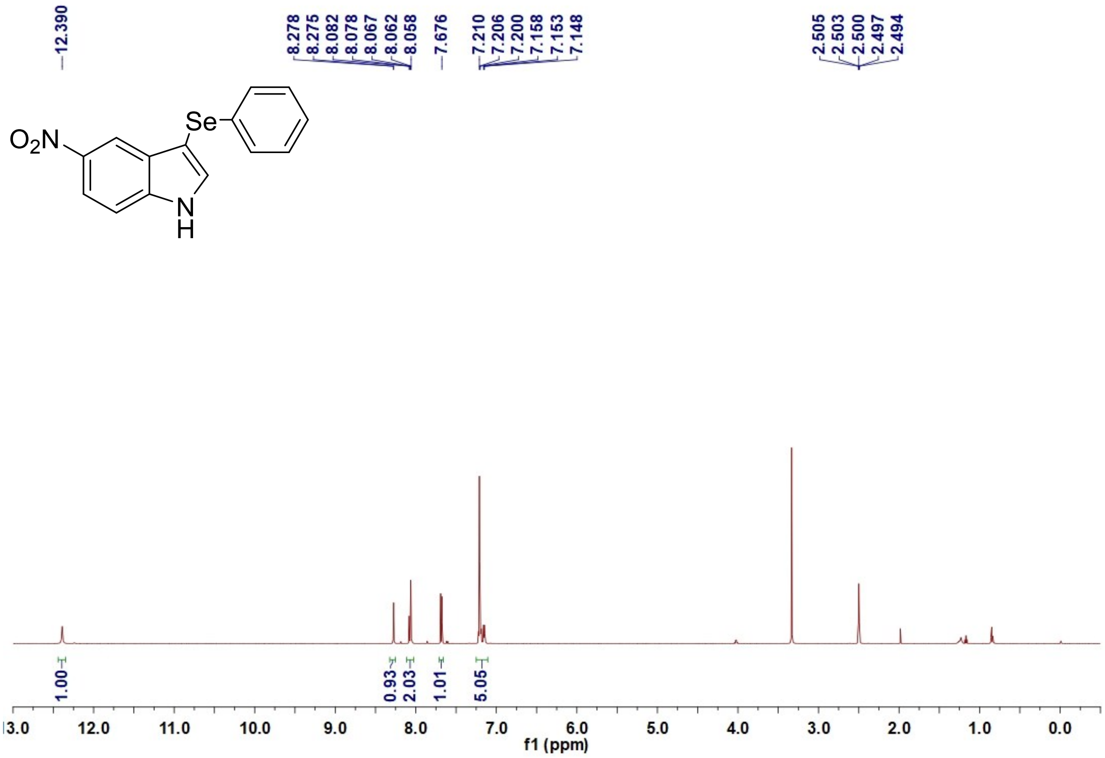
-10
f1 (ppm)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8.067
8.062
8.058
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7.206
7.200
7.158
7.153
7.148
2.505
2.503
2.500
2.497
2.494
O2N
Se
N
H
1.00
0.93
2.03
1.01
5.05
3.0
12.0
11.0
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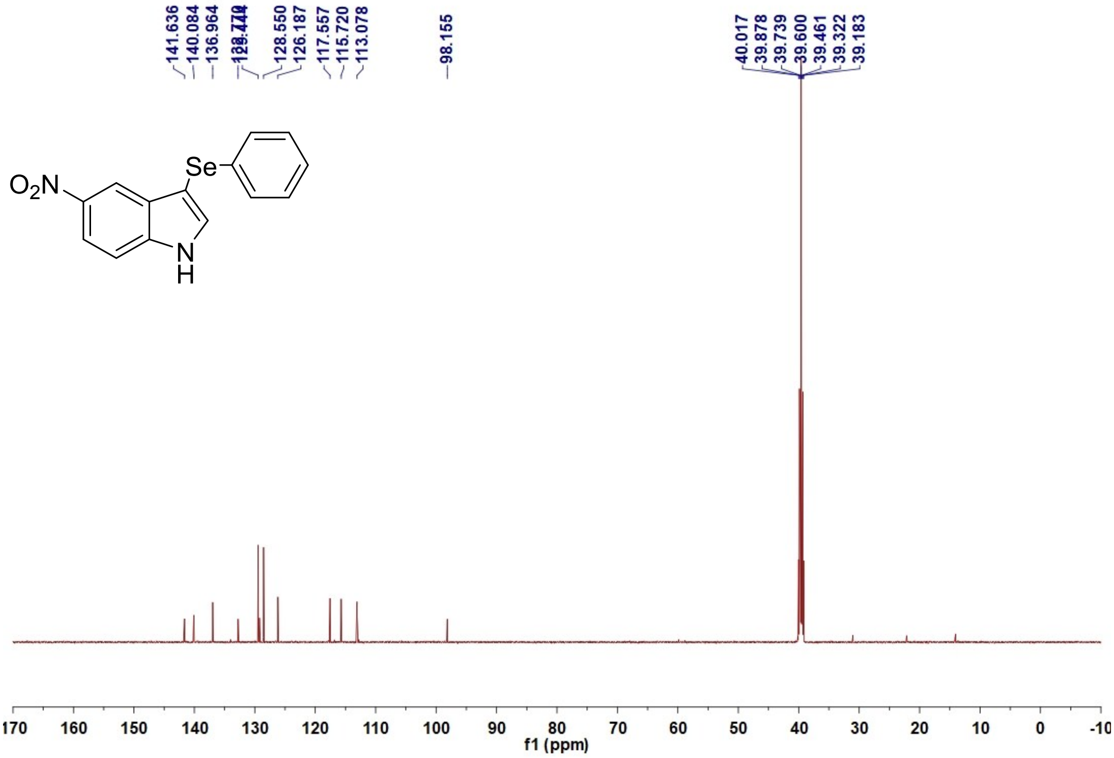
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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39.461
39.322
39.183
O2N
Se
N
H
170
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140
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120
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100
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80
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60
50
40
30
20
10
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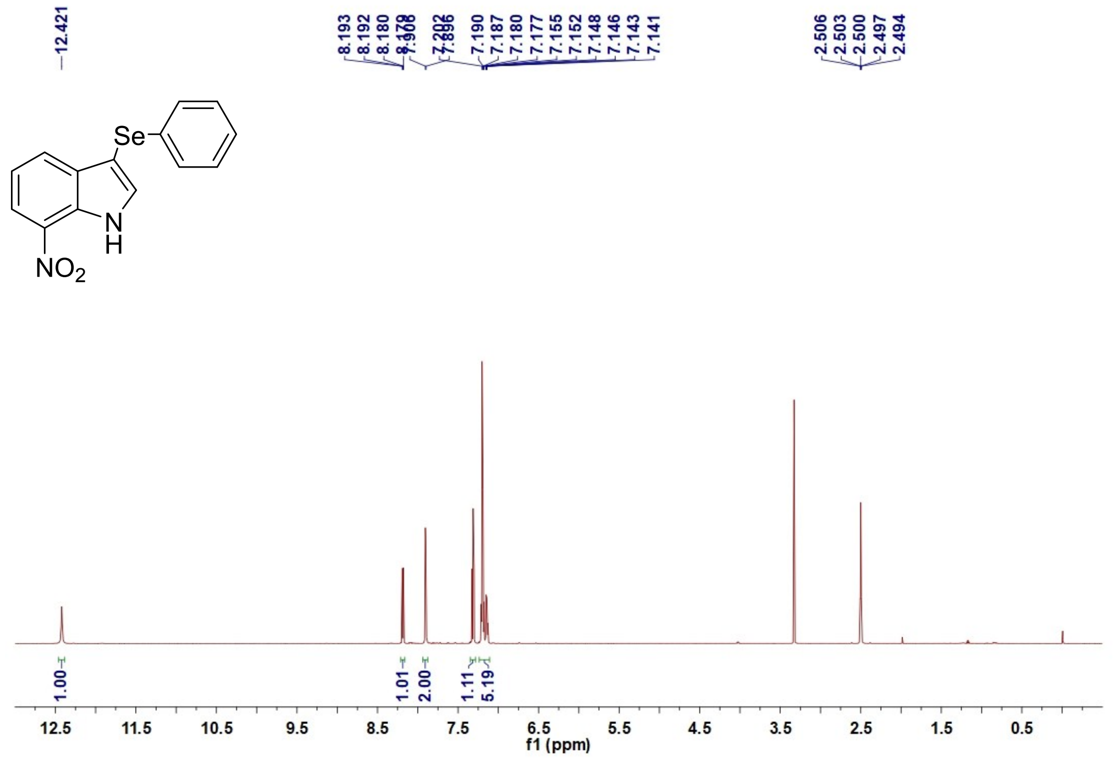
-10
f1 (ppm)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7.177
7.155
7.152
7.148
7.146
7.143
7.141
2.506
2.503
2.500
2.497
2.494
Se
N
H
NO2
1.00
1.01
2.00
1.11
5.19
12.5
11.5
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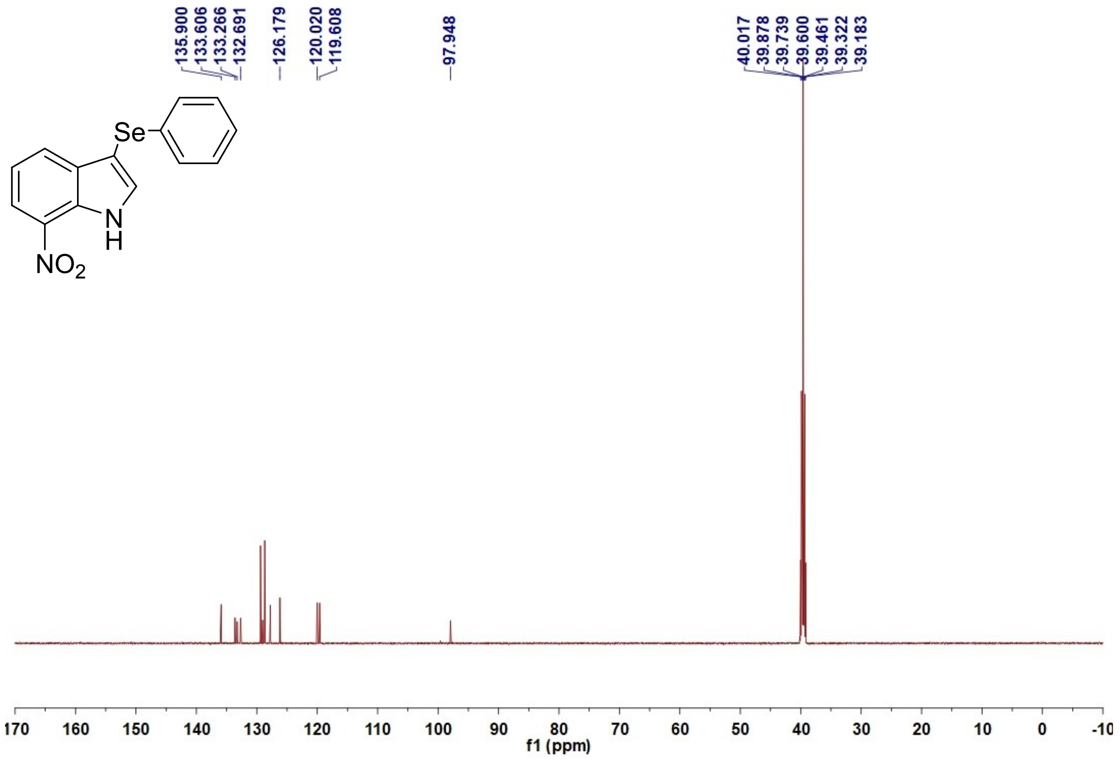
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39.322
39.183
Se
N
H
NO2
170
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120
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100
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80
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30
20
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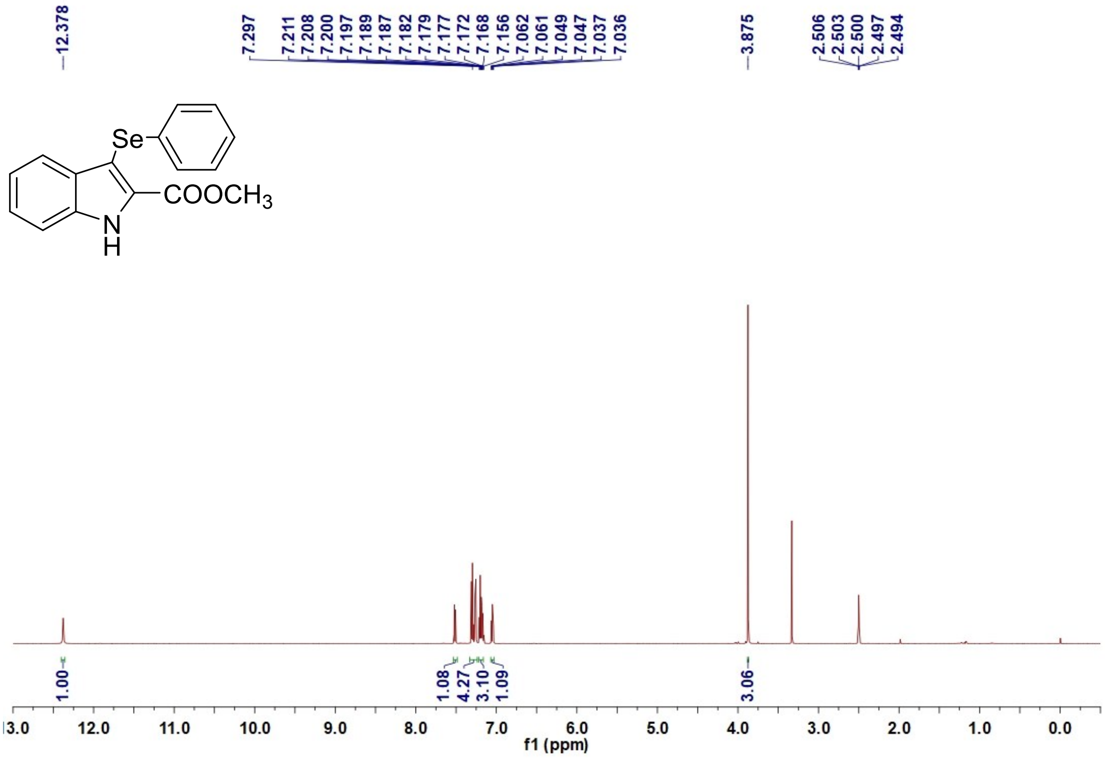
-10
f1 (ppm)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7.177
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7.156
7.062
7.061
7.049
7.047
7.037
7.036
3.875
2.506
2.503
2.500
2.497
2.494
Se
COOCH3
N
H
1.00
1.08
4.27
3.10
1.09
3.06
3.0
12.0
11.0
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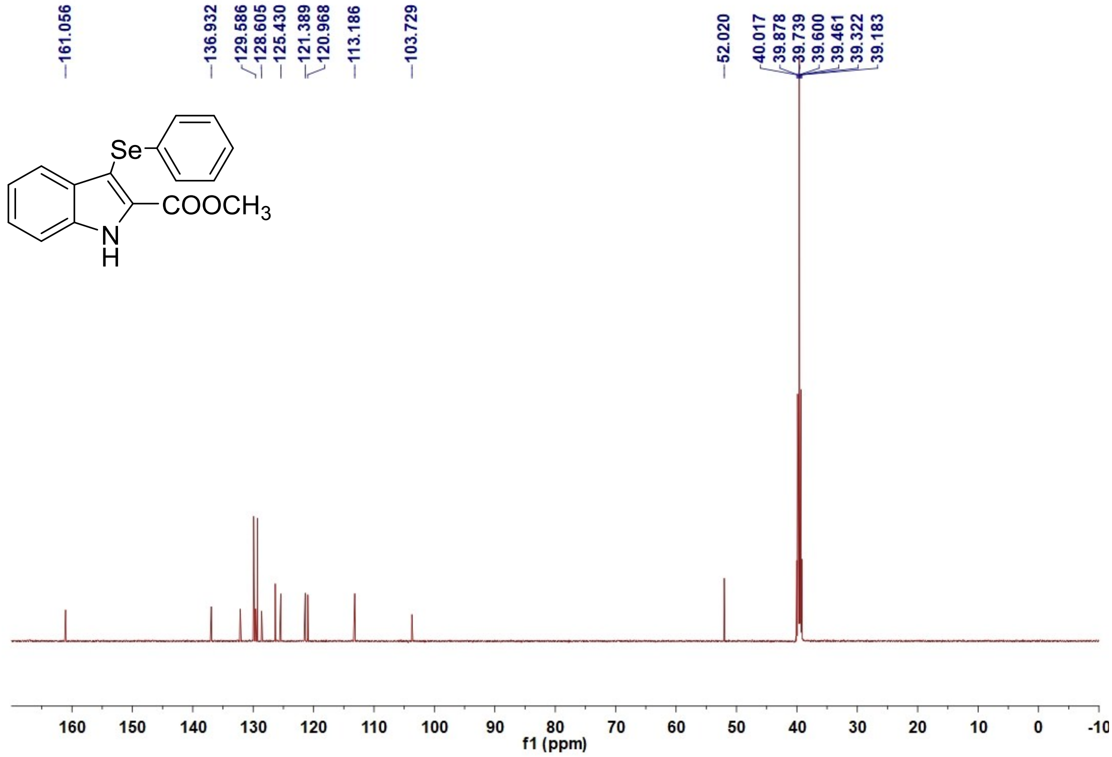
f1 (ppm)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39.739
39.600
39.461
39.322
39.183
Se
COOCH3
N
H
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80
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30
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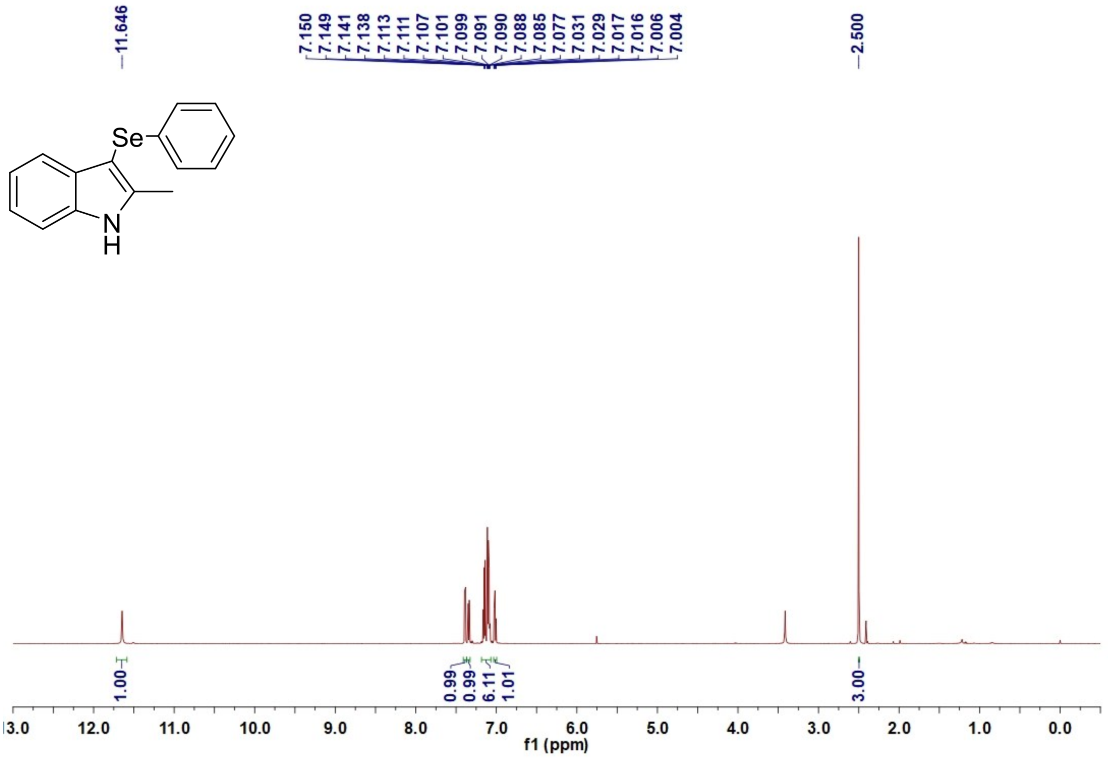
-10
f1 (ppm)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7.099
7.091
7.090
7.088
7.085
7.077
7.031
7.029
7.017
7.006
7.004
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Se
N
H
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0.99
6.11
1.01
3.00
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12.0
11.0
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5.0
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2.0
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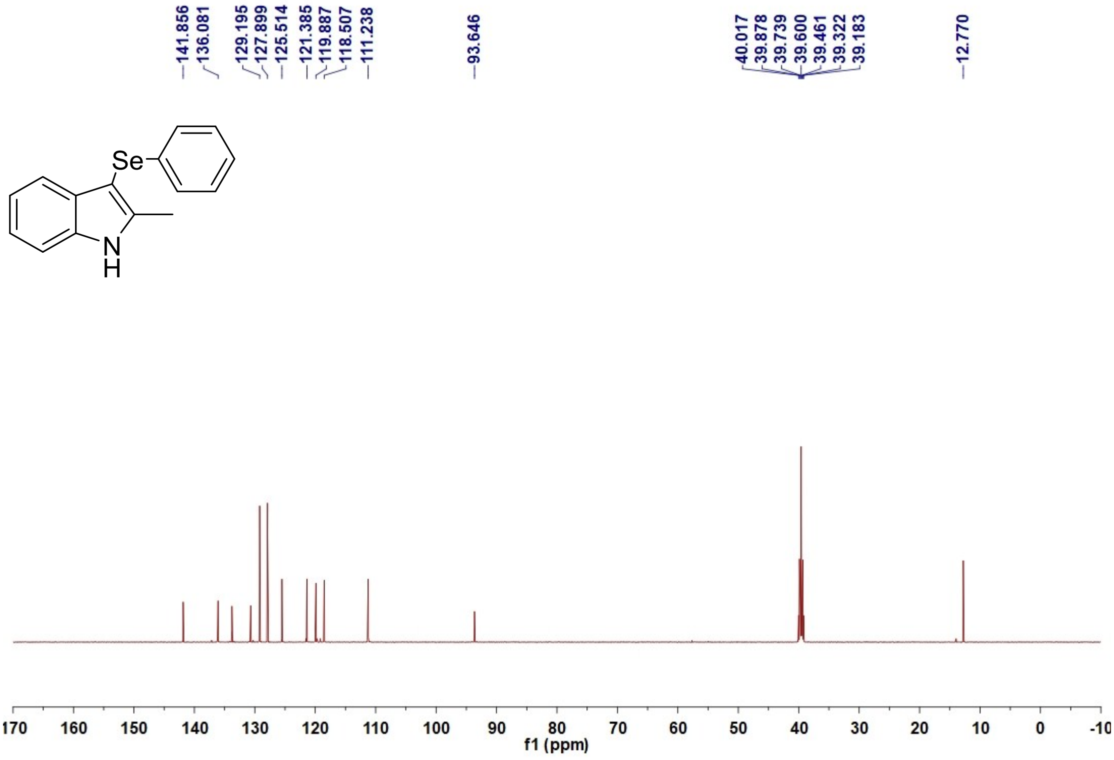
f1 (ppm)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39.878
39.739
39.600
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39.322
39.183
12.770
Se
N
H
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100
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30
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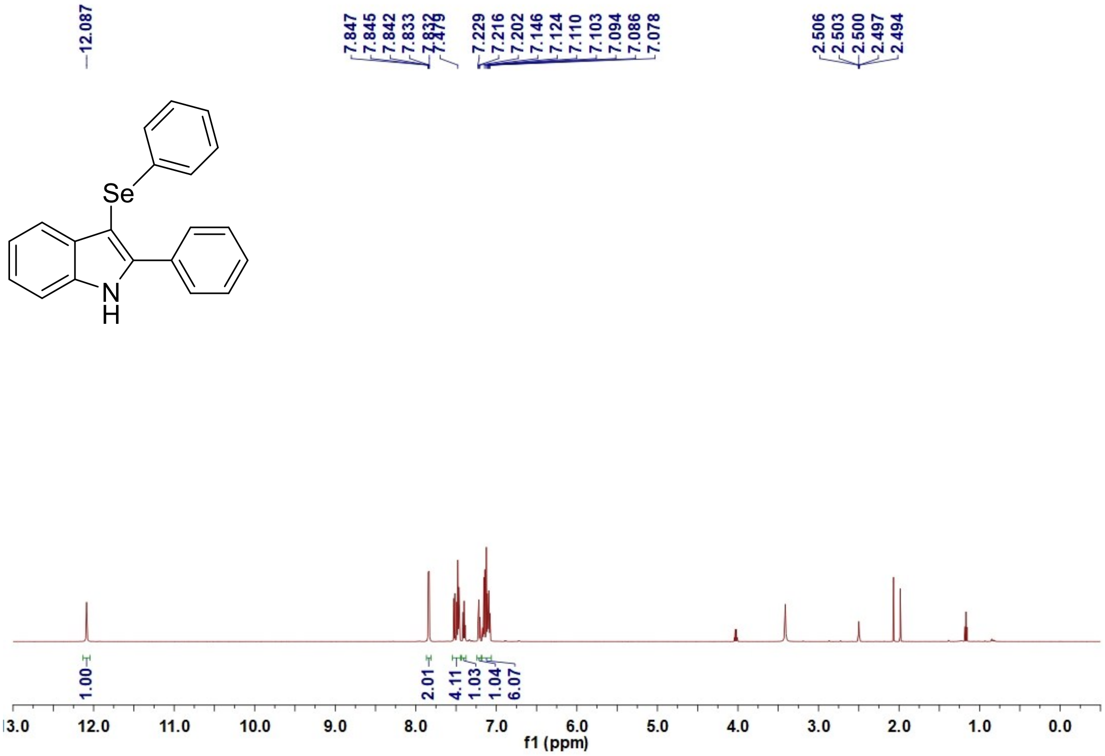
-10
f1 (ppm)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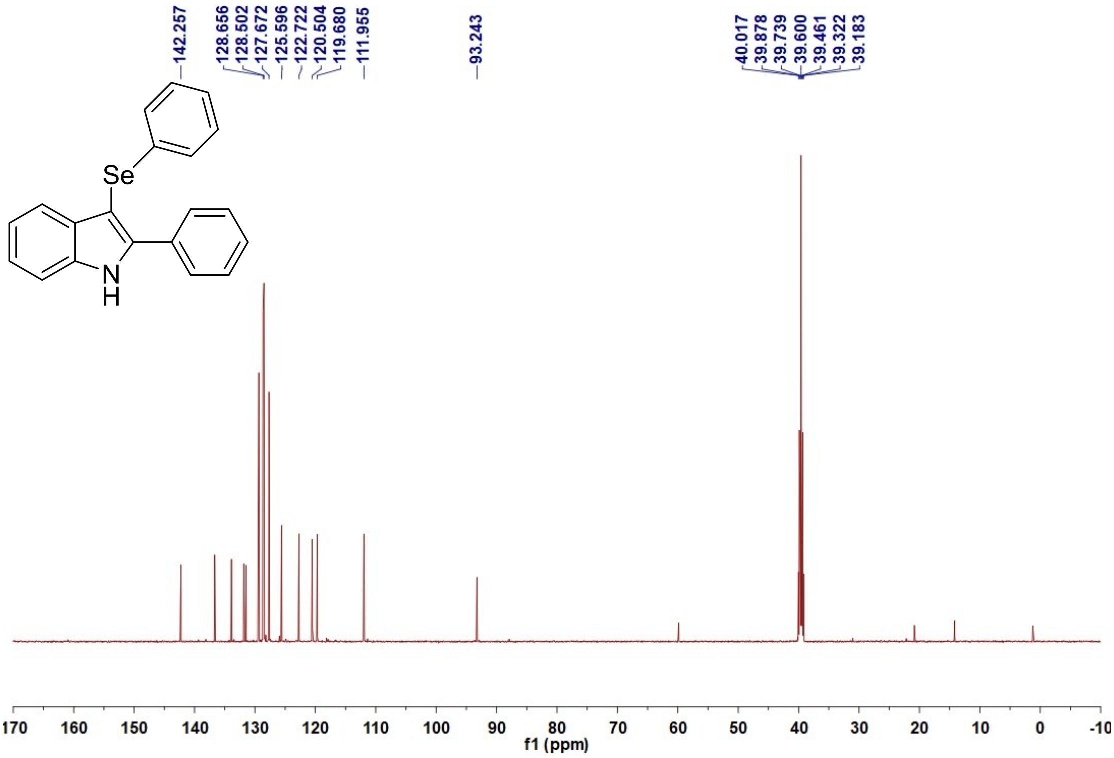
7.110
7.103
7.094
7.086
7.078
2.506
2.503
2.500
2.497
2.494
Se
N
H
1.00
2.01
4.11
1.03
1.04
6.07
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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119.680
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39.878
39.739
39.600
39.461
39.322
39.183
Se
N
H
170
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120
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100
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80
70
60
50
40
30
20
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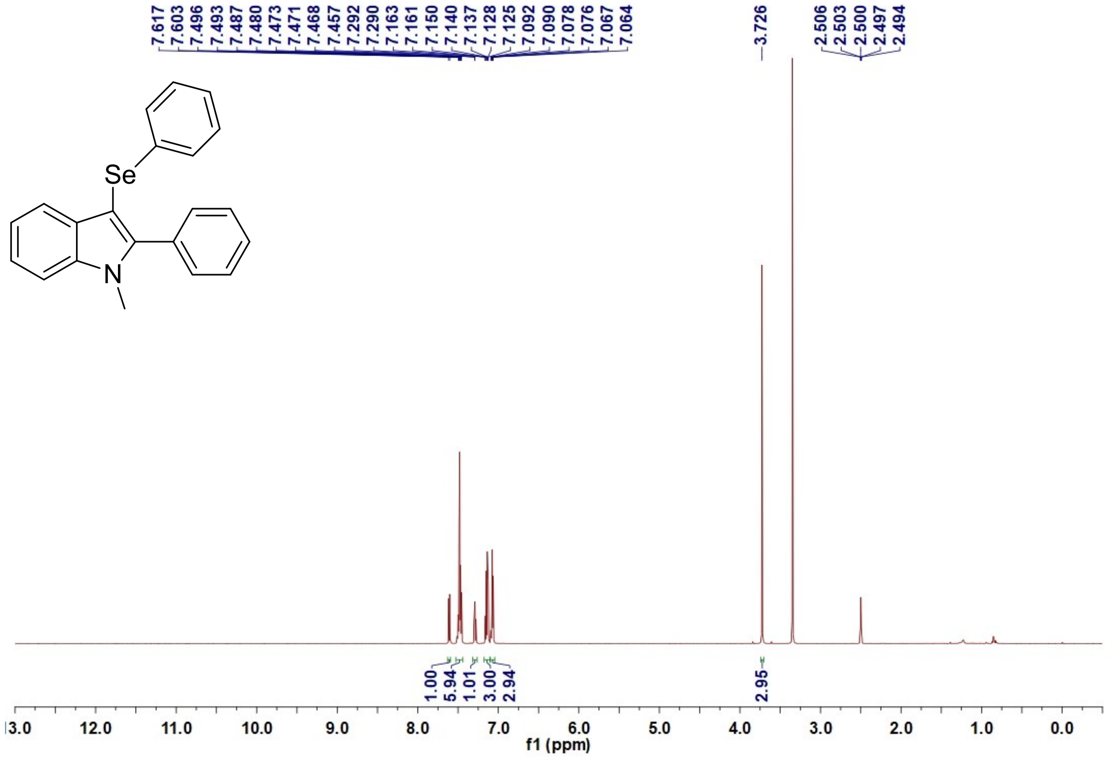
0
-10
f1 (ppm)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7.163
7.161
7.150
7.140
7.137
7.128
7.125
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7.090
7.078
7.076
7.067
7.064
3.726
2.506
2.503
2.500
2.497
2.494
Se
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1.01
3.00
2.94
2.95
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12.0
11.0
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4.0
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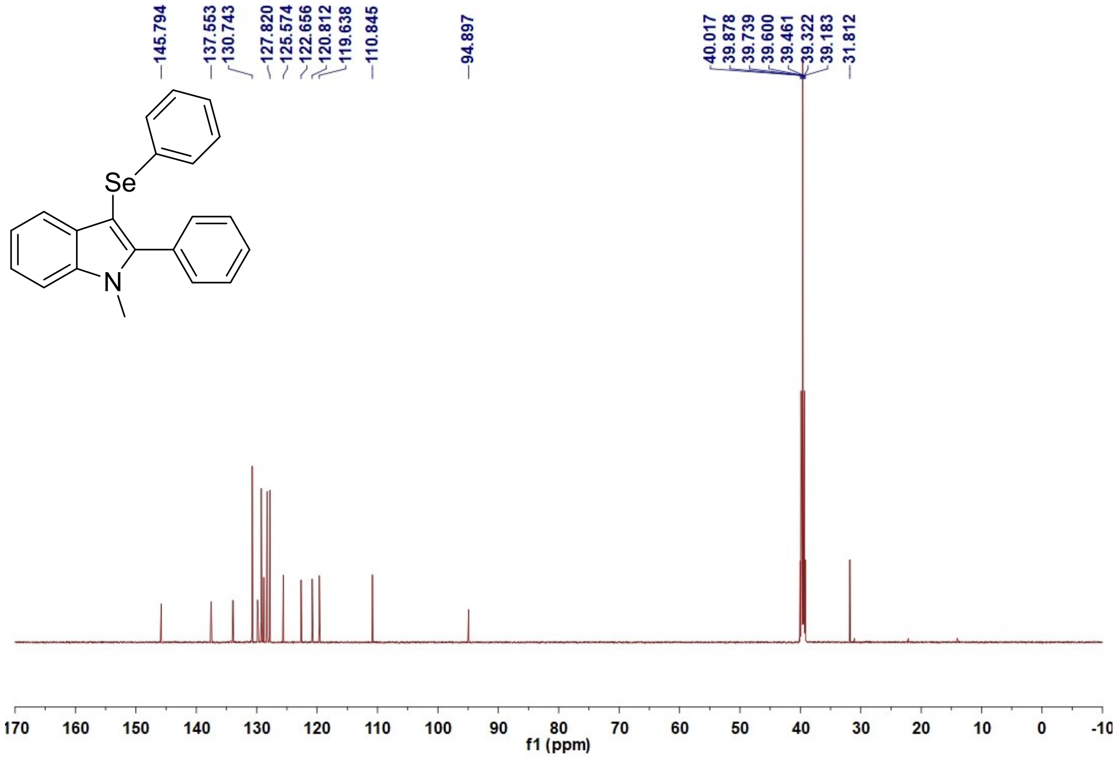
0.0
f1 (ppm)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39.739
39.600
39.461
39.322
39.183
31.812
Se
N
170
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100
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60
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30
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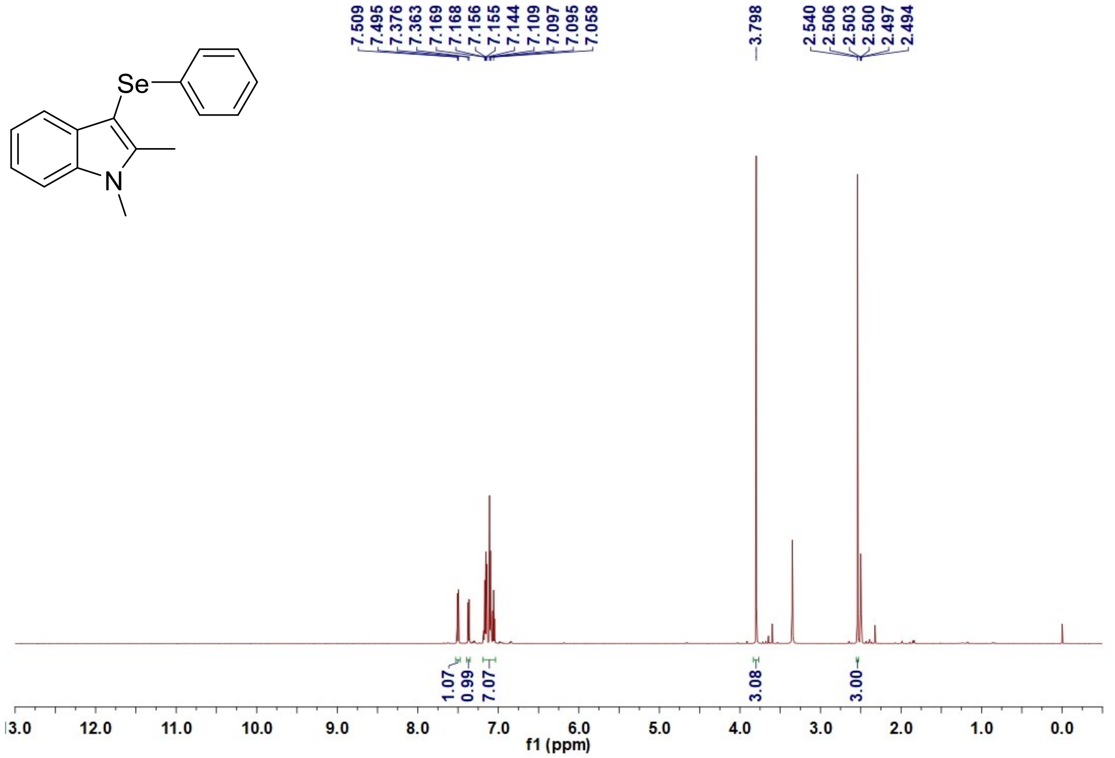
10
0
-10
f1 (ppm)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7.058
3.798
2.540
2.506
2.503
2.500
2.497
2.494
Se
N
1.07
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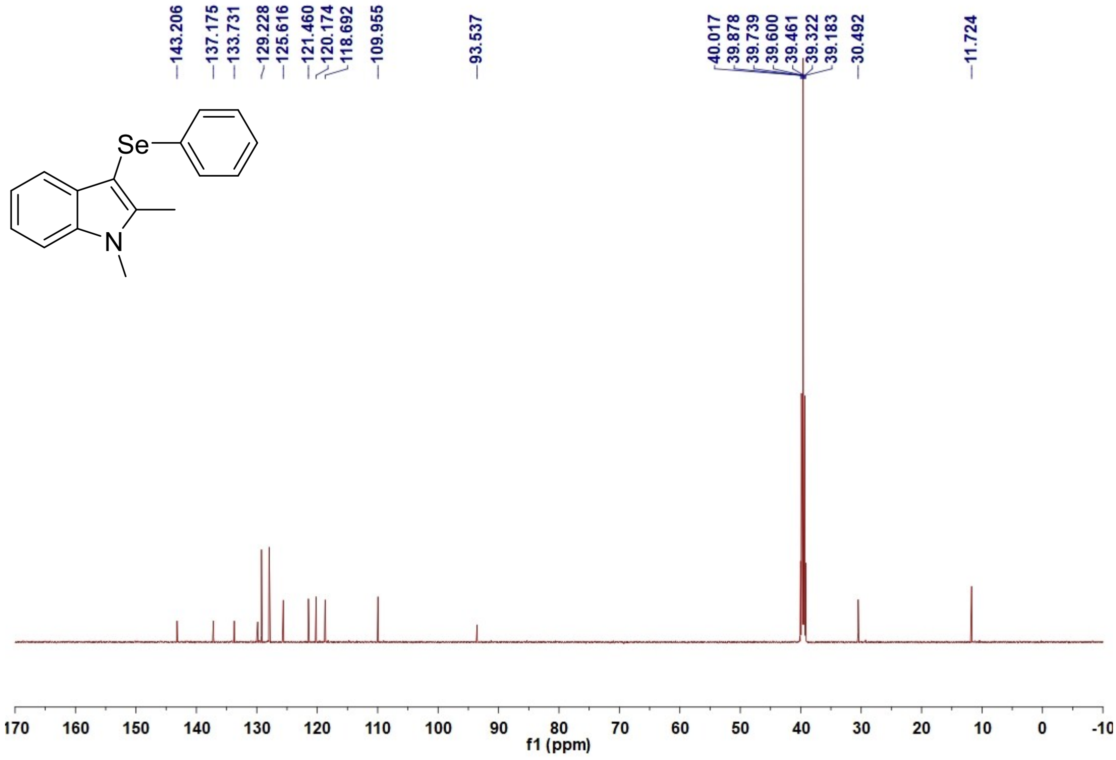
3.08
3.00
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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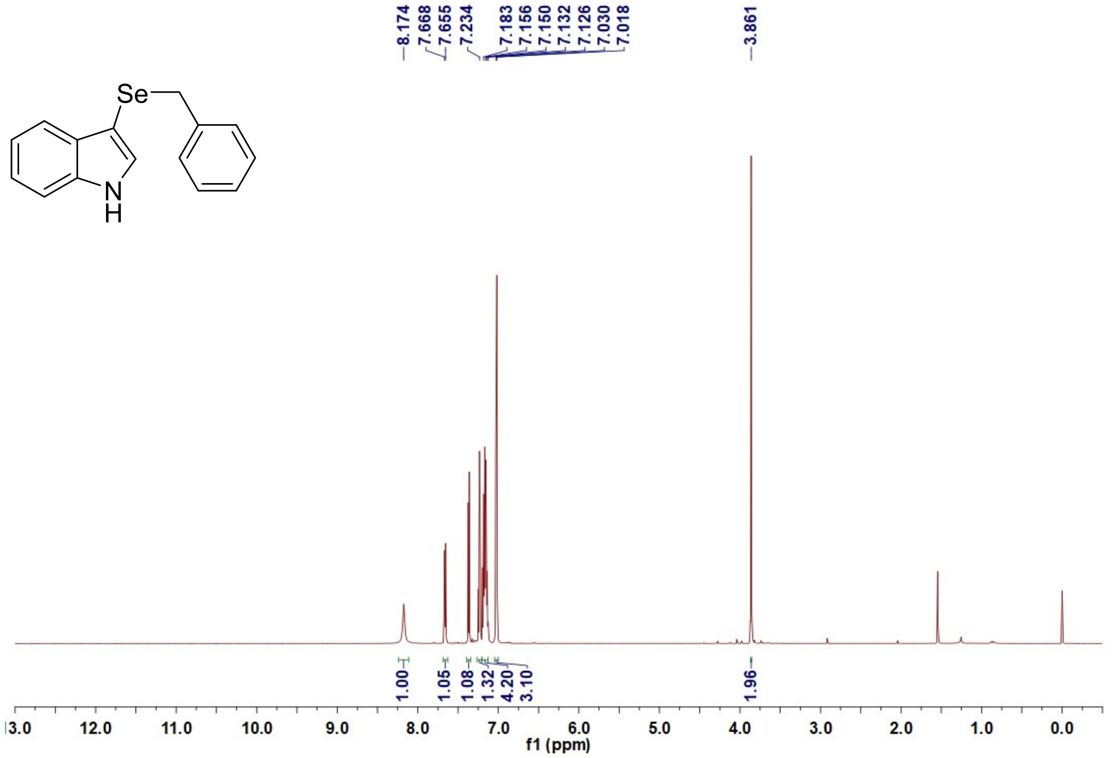
137.175
133.731
129.228
125.616
121.460
120.174
118.692
109.955
93.537
40.017
39.878
39.739
39.600
39.461
39.322
39.183
30.492
11.724
Se
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Se
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H
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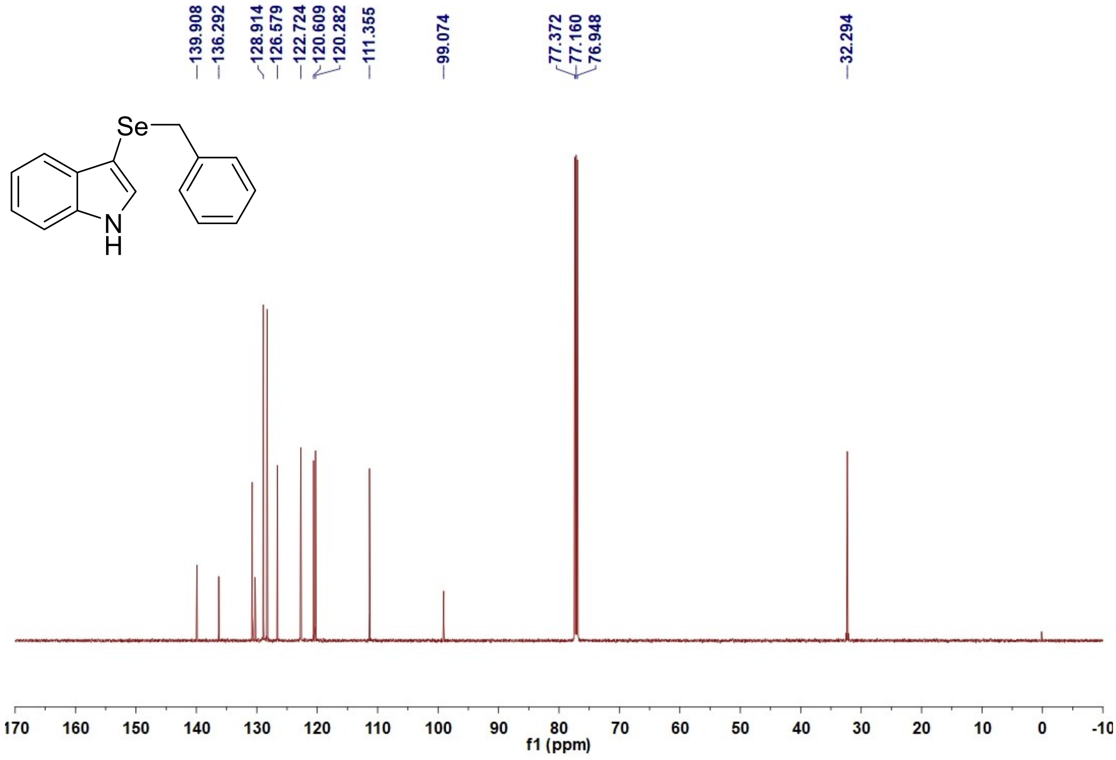
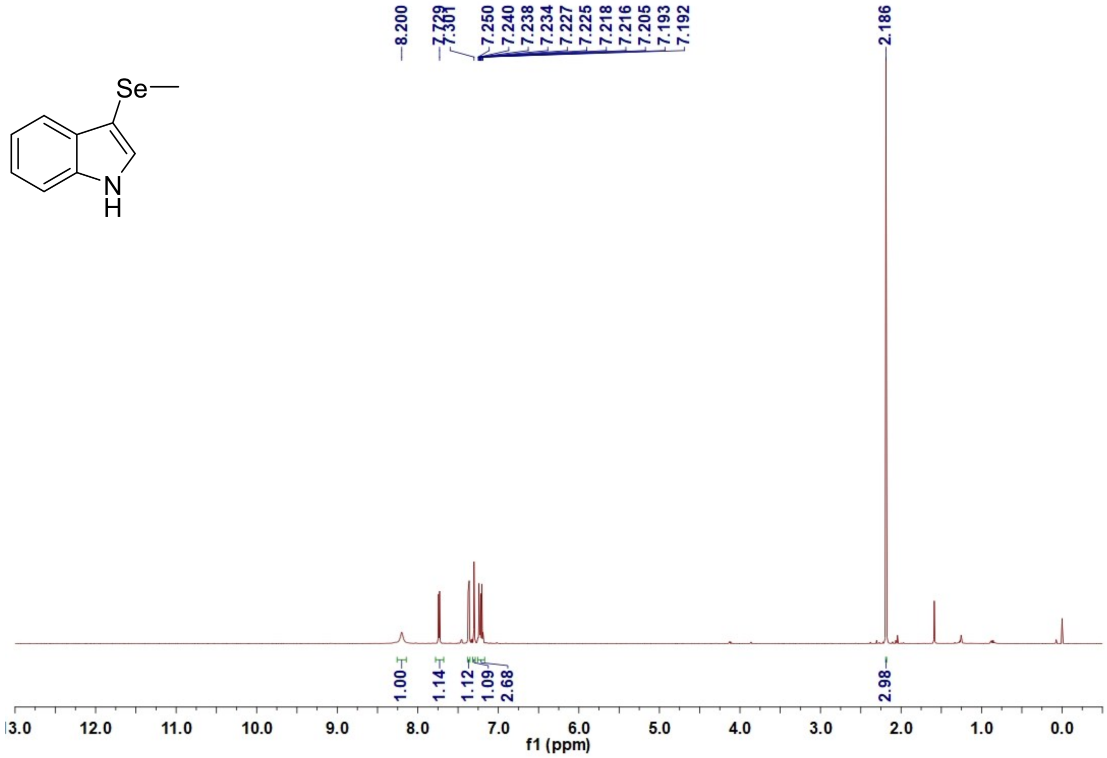
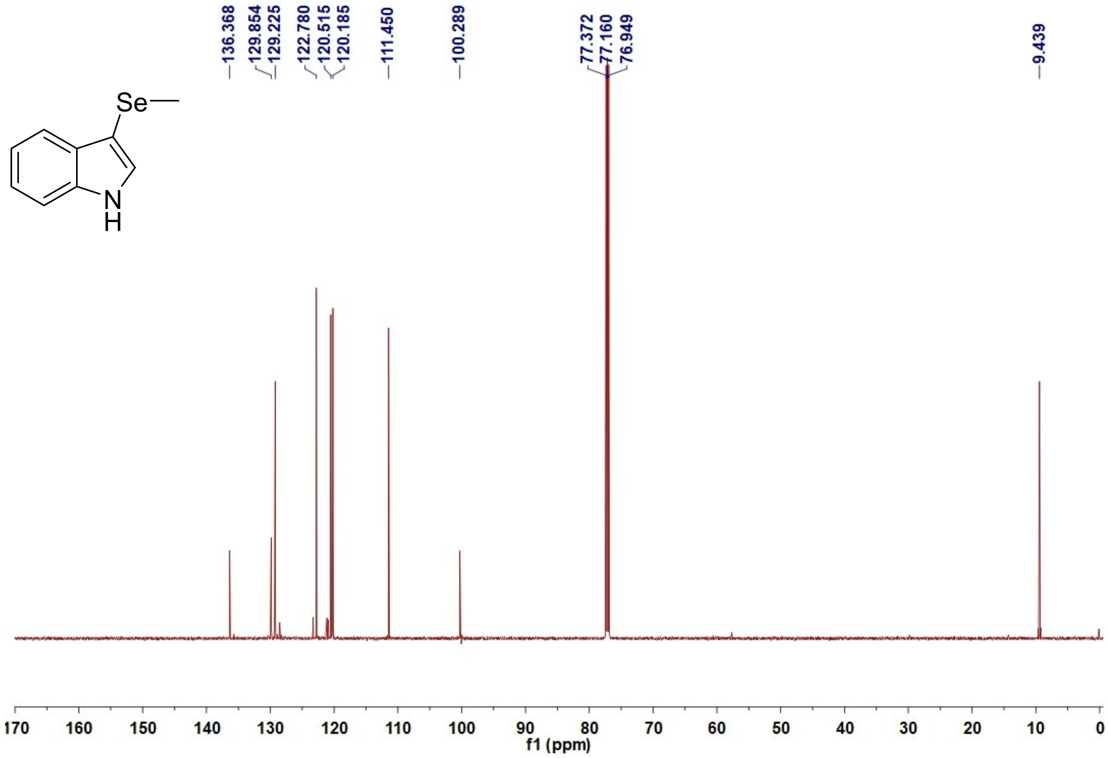
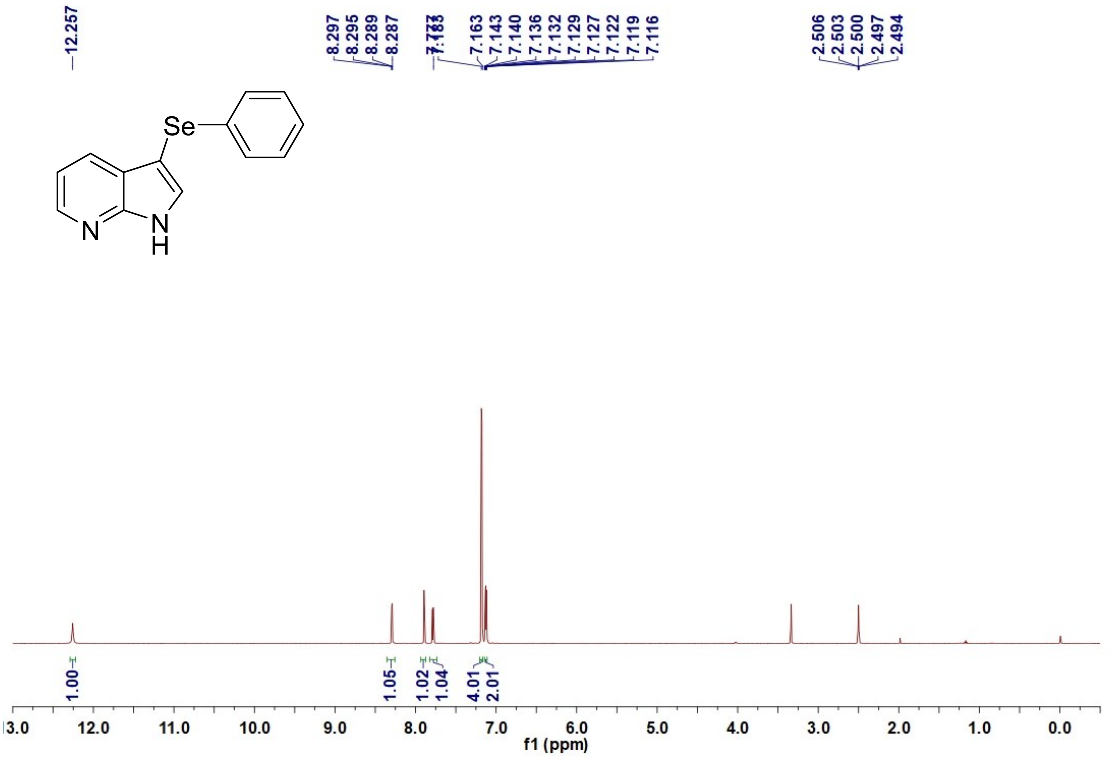
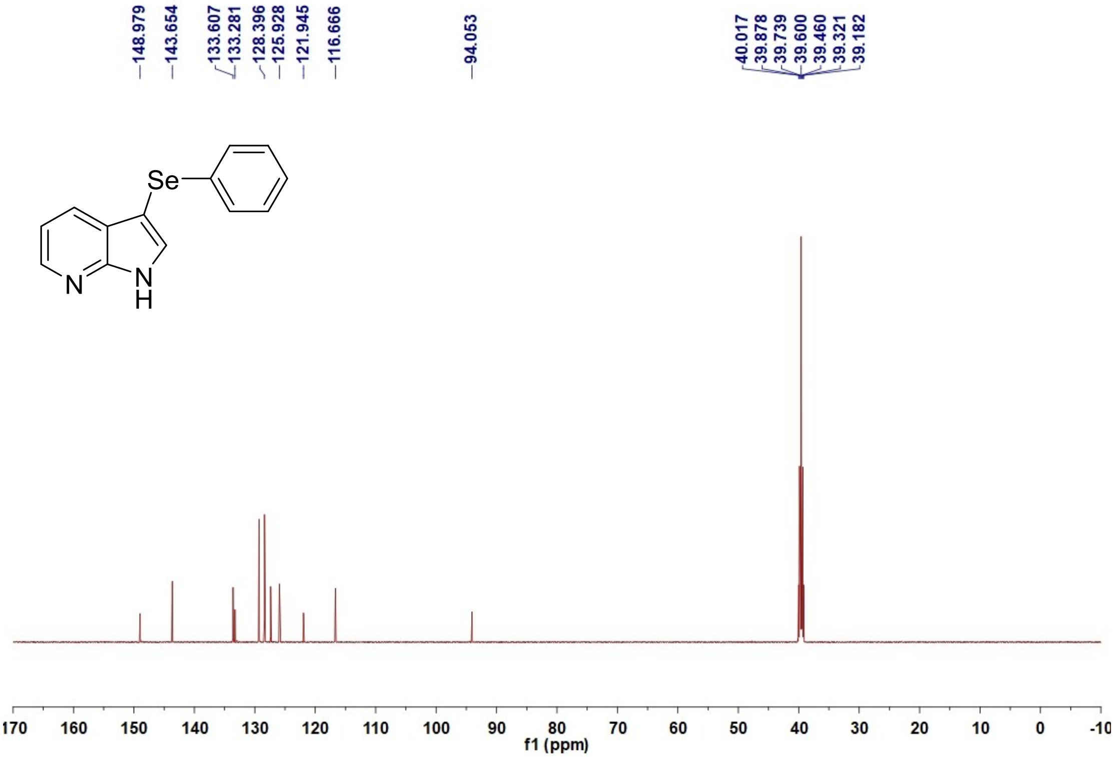
7.668
7.655
7.234
7.183
7.156
7.150
7.132
7.126
7.030
7.018
3.861
1.00
1.05
1.08
1.32
4.20
3.10
1.96
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

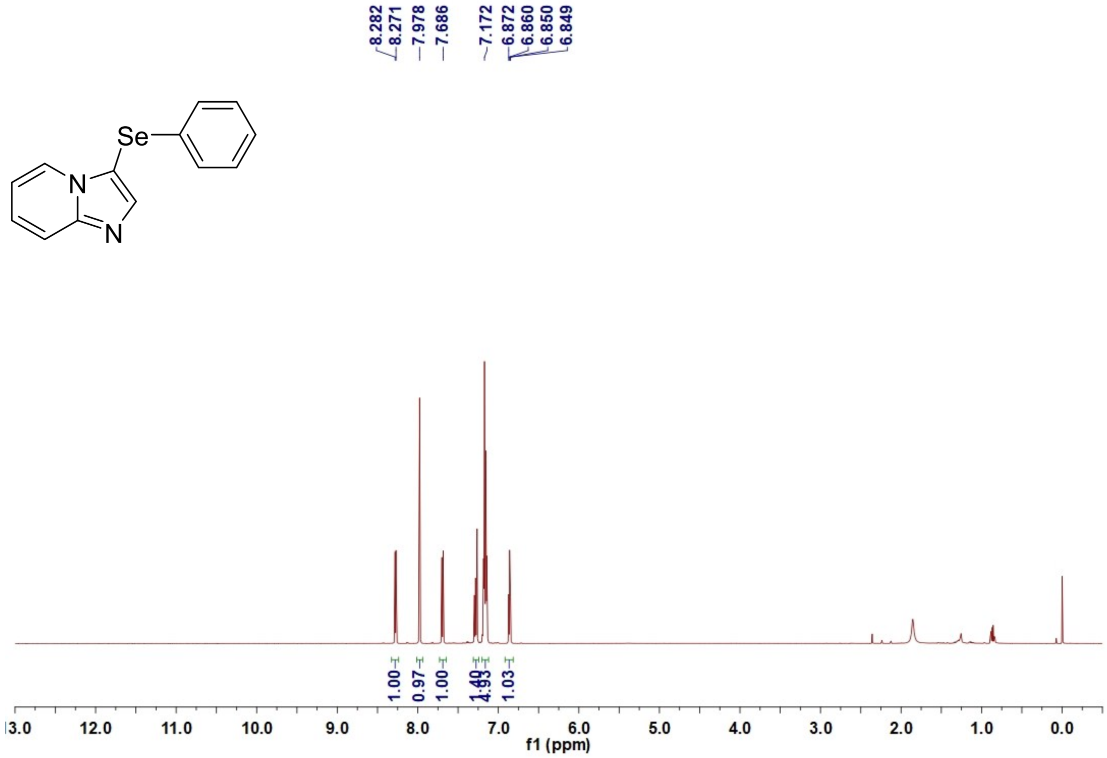

Se
N
H
139.908
136.292
128.914
126.579
122.724
120.609
120.282
111.355
99.074
77.372
77.160
76.948
32.294
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

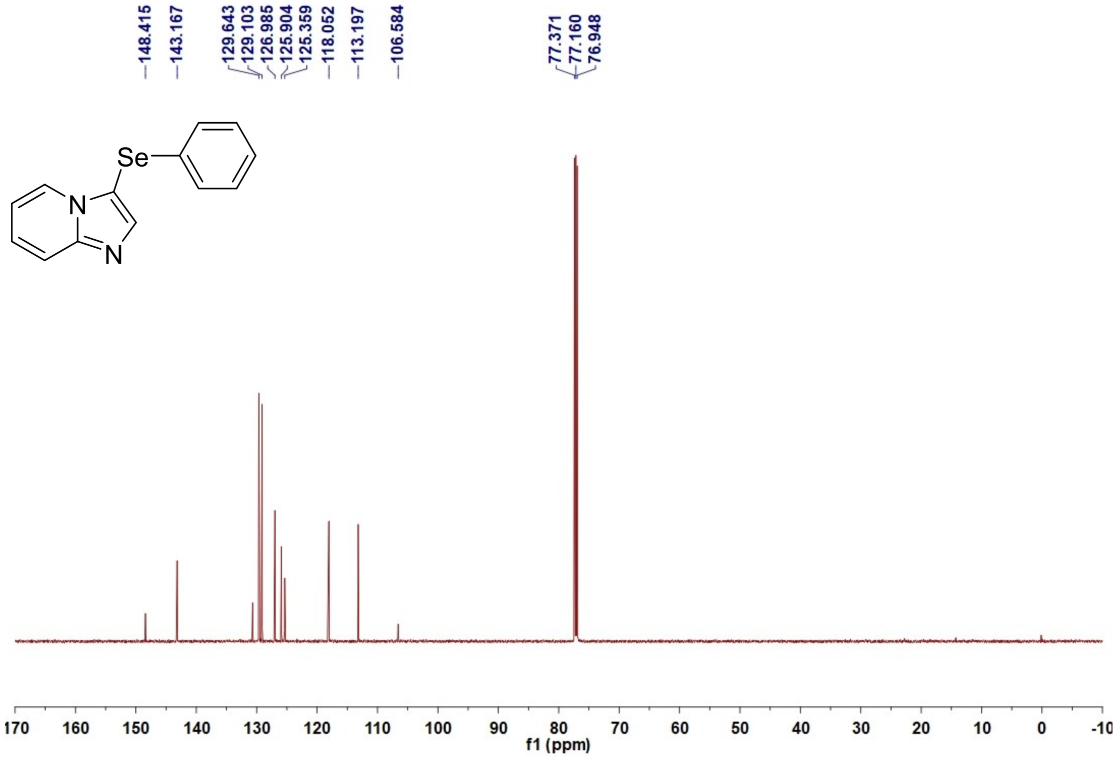

Se
N
H
8.200
7.729
7.301
7.250
7.240
7.238
7.234
7.227
7.225
7.218
7.216
7.205
7.193
7.192
2.186
1.00
1.14
1.12
1.09
2.68
2.98
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


Se
N
H
136.368
129.854
129.225
122.780
120.515
120.185
111.450
100.289
77.372
77.160
76.949
9.439
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


12.257
8.297
8.295
8.289
8.287
7.773
7.183
7.163
7.143
7.140
7.136
7.132
7.129
7.127
7.122
7.119
7.116
2.506
2.503
2.500
2.497
2.494
Se
N
N
H
1.00
1.05
1.02
1.04
4.01
2.01
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)


148.979
143.654
133.607
133.281
128.396
125.928
121.945
116.666
94.053
40.017
39.878
39.739
39.600
39.460
39.321
39.182
Se
N
N
H
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.282
8.271
7.978
7.686
7.172
6.872
6.860
6.850
6.849
Se
N
N
1.00
0.97
1.00
1.40
4.93
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)


148.415
143.167
129.643
129.103
126.985
125.904
125.359
118.052
113.197
106.584
77.371
77.160
76.948
Se
N
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)