

**NaH-Promoted One-Pot Oxidation/Aromatization and C-3H
Chalcogenation of Indoline: Atmospheric Control-Based Selective
Intermediates**

Suman Majee,^{a,b†} Km. Anjali,^{a,b†} Shailly Agarwal,^b Vishnu Poonia,^c Alok Kumar Singh,^b
Biswajit Guchhait,^c Devalina Ray^{a,b*}

Table of contents		
1.	General Information	S3
1.1	Reagent Information	S3
1.2	Analytical Information	S3
2.	Experimental Section	S3
2.1	General Method for Procedure A	S3
2.2	General Method for Procedure B	S3
2.3	General procedure for synthesis of sulfoxide	S4
2.4	Optimizing Table	S4
2.5	Procedure for the synthesis of <i>N</i> -methyldoline	S5
2.6	Detection of intermediate from crude mixture in procedure A	S5
2.7	Fate of reaction in presence of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy)	S9
2.8	Fate of reaction in presence of BHT (3,5-di- <i>tert</i> -4-butylhydroxytoluene)	S9
2.9	Procedure for Intermolecular competition experiment	S12
2.10	EPR analysis	S12
2.11	General procedure for gram scale synthesis	S16
2.12	Synthesis of 3-((4-chlorophenyl)sulfinyl)-1H-indole	S17
3	Anti-bacterial studies	S17
4	Spectral Data	S18
5	References	S24
6	NMR Spectrums	S25

1. General Informations

1.1. Reagent information

All the reactions are carried out in presence of air unless stated otherwise and all the glass wares were oven dried at 100 °C. The commercially available reagents were used without further purification. The solvents were dried before use following procedures. The thin layer chromatography (TLC) was done using TLC Silica gel F254 plates purchased by Merck. For column chromatography, silica gel (100-200 mesh) from Merck was used. All the products were purified by column chromatography using either silica gel (mesh 100-200) or thin layer chromatography. 90% dry NaH was purchased from Sigma Aldrich. All the dialkyl/diaryl diselenides and dialkyl/diaryl disulphides were mostly purchased from Sigma Aldrich, Merck and Alfa-Aesar. Indoline derivatives were purchased from Sigma Aldrich and used without further purification. *N*-methylindoline was synthesized from literature report. The spectroscopic data (¹H NMR) was matched with the literature report and found the same.

1.2. Analytical information

The NMR spectra of products were recorded on Bruker spectrometer (600 MHz, 500 MHz, 400 MHz). The Chemical shifts of ¹H are given in ppm relative to internal standards CDCl₃ at 7.26 ppm. The chemical shifts for ¹³C are given in ppm relative to internal standards CDCl₃ at 77.00 ppm. HPLC (Agilent, 1220 Infinity LC Gradient System VL, reverse phase chromatography, C18 column, gradient system water: acetonitrile, UV absorbance 250 nm) was used for the analysis of purity for substrates and products as well as conversion in controlled experiments.

2. Experimental Section

2.1 General Method for Procedure A: To a 10 mL round bottom flask 90% dry NaH (0.1 mmol, 0.5 equiv.) was taken in nitrogen atmosphere. Indoline derivative (0.2 mmol, 1 equiv.) in DMF (0.5 mL) was added into flask dropwise and stir at ice cold condition for 30 mins. After 30 minutes, diarylselenides (0.1 mmol, 0.5 equiv.)/diarylsulphides (0.14 mmol, 0.7 equiv.) in DMF (0.5 mL) was added into flask and stirred at 70-120 °C for completion of the reaction monitored by TLC. After completion of the reaction, crude mixture was diluted by water and the aqueous layer was extracted by 20 ml dichloromethane for three times. The organic layer was collected and washed with brine solution, dried over sodium sulfate and was evaporated. The crude reaction mixture was further purified using column chromatography (dichloromethane: hexane) to afford **3** or **5**.

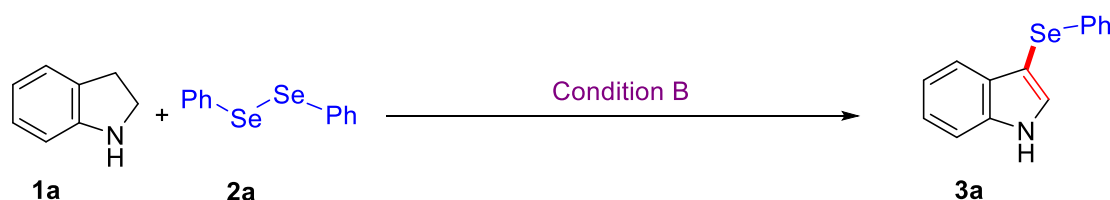
2.2. General Method for Procedure B: To a 10 mL round bottom flask indoline derivative (0.2 mmol, 1.0 equiv.), 90% dry NaH (0.12 mmol, 0.6 equiv.) in DMF (1 mL) were taken and stirred for 10 mins in air at room temperature (25 °C). After 10 minutes diarylselenides (0.1 mmol, 0.5 equiv.) /diarylsulphides (0.14 mmol, 0.7 equiv.) was added to the stirred solution. The reaction mixture was stirred at room temperature (25 °C) in air until completion and monitored by TLC. After completion of the reaction, the crude reaction mixture was diluted by water and aqueous layer was extracted by 20 ml dichloromethane for three times. The organic

layer was collected and washed by brine solution, dried over sodium sulfate and was evaporated. The reaction mixture was further purified using column chromatography (dichloromethane: hexane) to afford **3** or **5**.

2.3. General procedure for synthesis of sulfoxide: To a 50 mL round bottom flask compound **5e** (1 mmol) in 8 mL acetic acid was taken. 30% H₂O₂ (4 mmol) was added dropwise and stir for 1 hour at room temperature until consumption of the starting material, as monitored by TLC. The reaction mixture was then neutralized by sodium bicarbonate solution and aqueous layer was then extracted by 50 ml dichloromethane for three times. The organic layer was collected and washed by brine solution, dried over sodium sulfate and was evaporated. The reaction mixture was further purified using column chromatography (CH₂Cl₂: hexane = 1: 1) to afford **5e'** with 81% yield.

2.4. Optimizing Table:

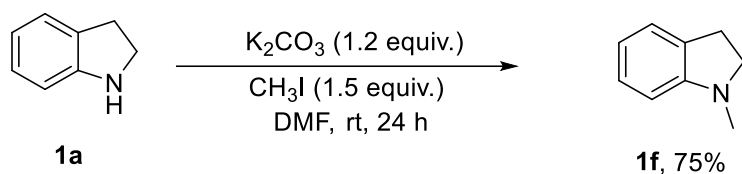
Table 2. Optimization of C-3 chalcogenation of indolines under air



Entry	Base	Solvent	Time (h)	Yield of 3a ^[b] [%]
1	-	DMF	24	0
2	K ₂ CO ₃	DMF	24	35
3	90% dry	DMF	24	20
4	NaOH	DMF	24	40
5	KOH	DMF	24	37
6	^t BuOLi	DMF	24	10
7	^t BuONa	DMF	24	20
8	^t BuOK	DMF	24	25
9	Cs ₂ CO ₃	DMF	24	11
10	DBU	DMF	24	0
11	Et ₃ N	DMF	24	0
12	Pyridine	DMF	24	0
13	LiH	DMF	24	23
14	CaH ₂	DMF	24	0
15	90% dry NaH	DMF	24	90
16	90% dry NaH	DMF	24	81 ^c

[a] Conditions: **1a** (0.2 mmol) and base (0.12 mmol) in solvent (1 mL), stirred for 15 mins at in open air, then **2a** (0.1 mmol) was added. And stir at rt. [b] Isolated yields. [c] 0.5 equiv. 90% dry NaH used.

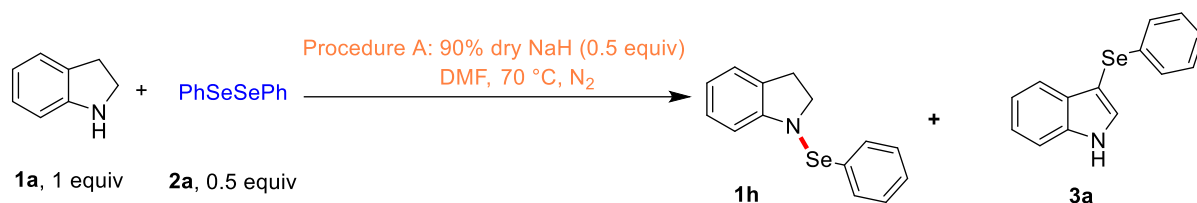
2.5. Procedure for the synthesis of *N*-methylindoline (**1f**)



Scheme 1: *N*-methylation of indoline (**1a**).

N-methylation was done the known literature method.¹ Indoline (224 μ L, 2 mmol, 1 equiv) and K_2CO_3 (280 mg, 2 mmol, 1.2 equiv) in 10 mL of DMF was taken in 50 mL of round bottom flask and stirred it at rt for 30 minutes. To this reaction mixture, methyl iodide (496 mg, 3.5 mmol, 1.5 equiv) was added dropwise and stirred it at room temperature for overnight. After completion of reaction the reaction was quenched with water and extracted the organic layer with ethyl acetate. The organic layer was washed with brine solution three times and dried with anhydrous sodium sulfate. The solvent was evaporated and the crude product purified with silica gel chromatography (ethyl acetate/hexane 1:4) to obtain *N*-methylindoline (**1f**) in 75% yield (**Scheme 1**).

2.6. Detection of intermediate from crude mixture in procedure A



Scheme 2: Chalcogenation of indoline (**1a**) in procedure A.

To a 10 mL round bottom flask 90% dry NaH (0.1 mmol, 0.5 equiv.) was taken in nitrogen atmosphere. Indoline (**1a**) (0.2 mmol, 1 equiv.) in DMF (0.5 mL) was added into flask dropwise and stir at ice cold condition for 30 mins. After 30 minutes, diphenyldiselenide (0.1 mmol, 0.5 equiv.) in DMF (0.5 mL) was added into flask and stir at 70 °C (**Scheme 2**). Following TLC detection, aliquot from the reaction mixture was taken for LCMS and HRMS (**Figure 1a-b**).

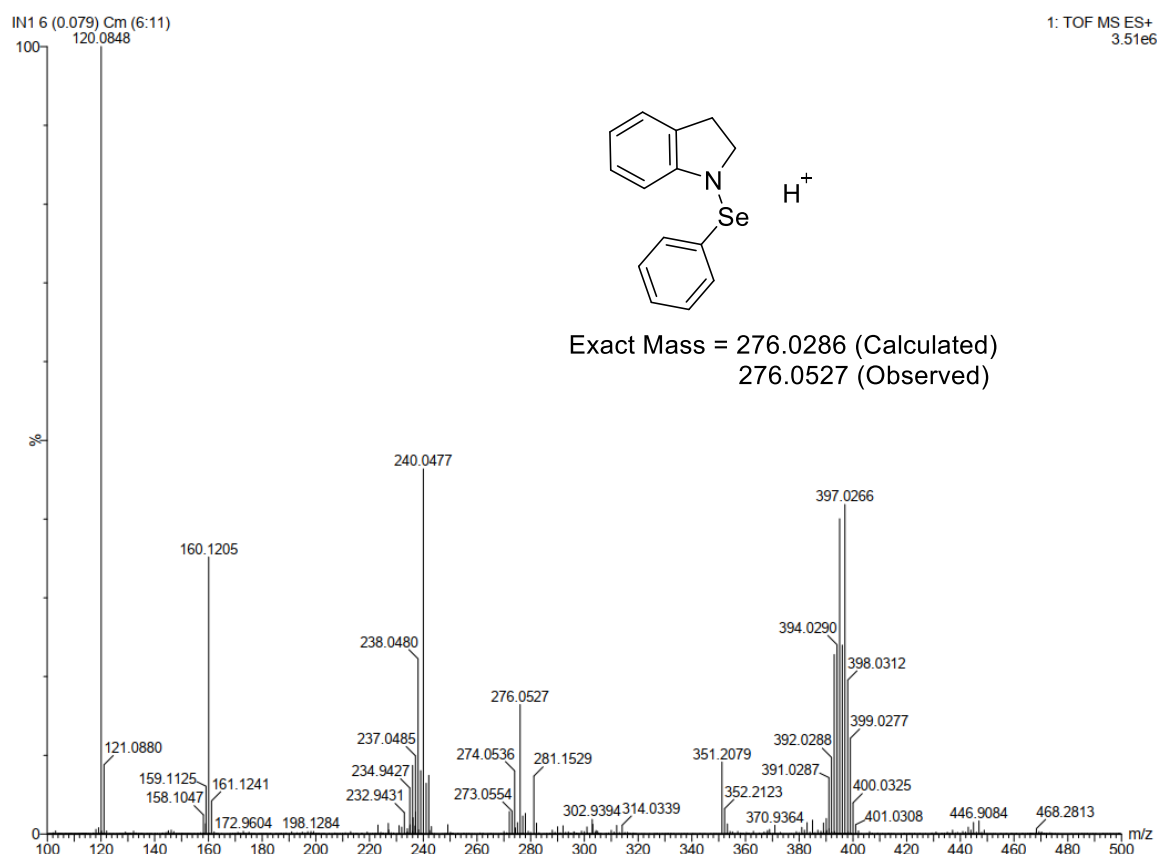


Figure 1a: LCMS analysis of crude mixture of indoline, 90% dry NaH, Ph_2Se_2 and DMF at 2 h.

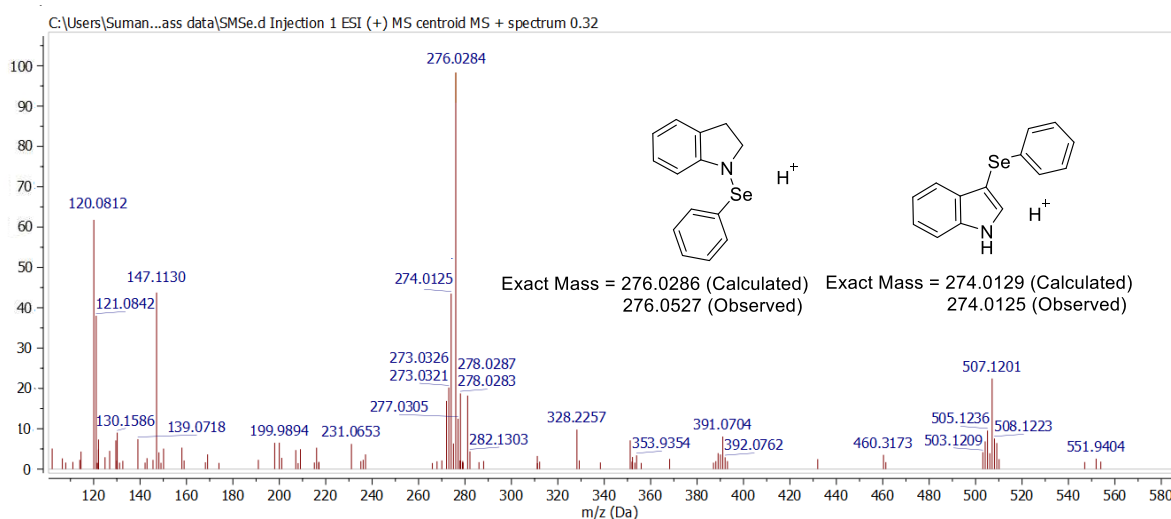
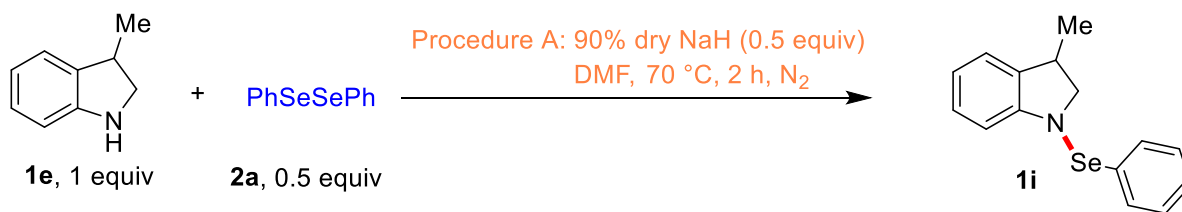


Figure 1b: LCMS analysis of crude mixture of indoline, 90% dry NaH, Ph_2Se_2 and DMF at 12 h.



Scheme 3: Chalcogenation of 3-methylindoline (1e)

To a 10 mL round bottom flask 90% dry NaH (0.1 mmol, 0.5 equiv.) was taken in nitrogen atmosphere. 3-methylindoline (**1e**) (0.2 mmol, 1 equiv.) in DMF (0.5 mL) was added into flask dropwise and stir at ice cold condition for 30 mins. After 30 minutes, diphenyldiselenide (0.1 mmol, 0.5 equiv.) in DMF (0.5 mL) was added into flask and stir at 70 °C for 2 h (**Scheme 3**). Following TLC detection, aliquot from the reaction mixture was taken for HRMS (**Figure 2**).

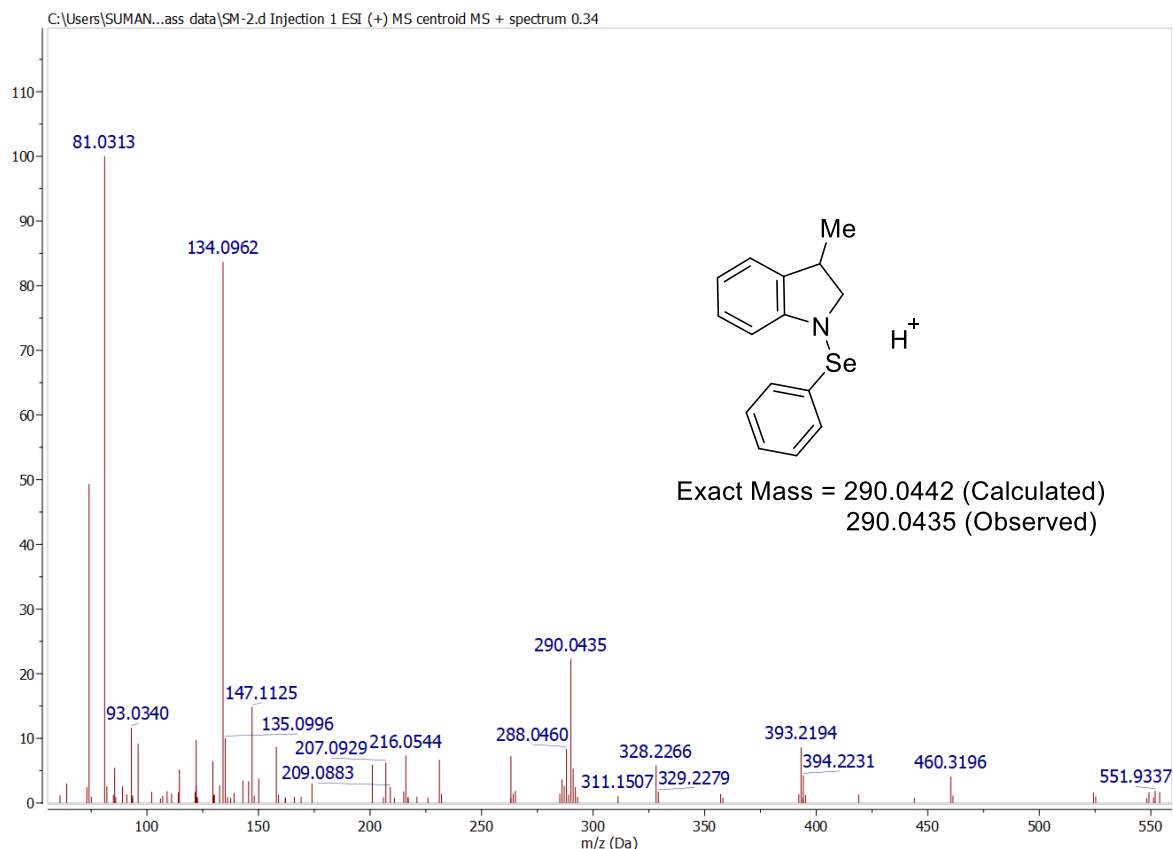
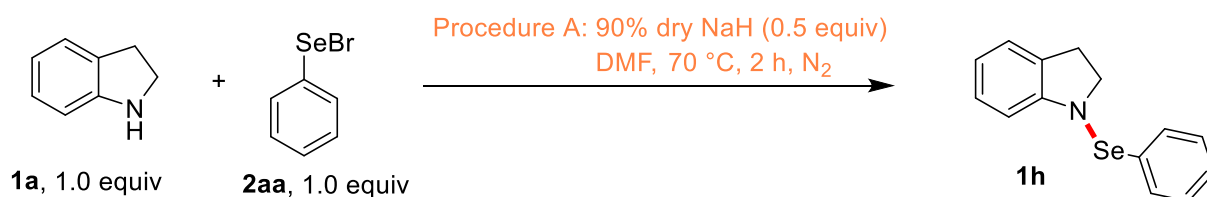


Figure 2: HRMS analysis of crude mixture of 3-methylindoline, 90% dry NaH, Ph_2Se_2 and DMF at 2 h.



Scheme 4: Chalcogenation of indoline with phenylselenenyl bromide.

To a 10 mL round bottom flask 90% dry NaH (0.1 mmol, 0.5 equiv.) was taken in nitrogen atmosphere. Indoline (**1a**) (0.2 mmol, 1 equiv.) in DMF (0.5 mL) was added into flask dropwise and stir at ice cold condition for 30 mins. After 30 minutes, phenylselenenyl bromide (0.1 mmol, 0.5 equiv.) in DMF (0.5 mL) was added into flask and stir at 70 °C for 2 h (**Scheme 4**). Following TLC detection, aliquot from the reaction mixture was taken for HRMS at 2 h (**Figure 3**).

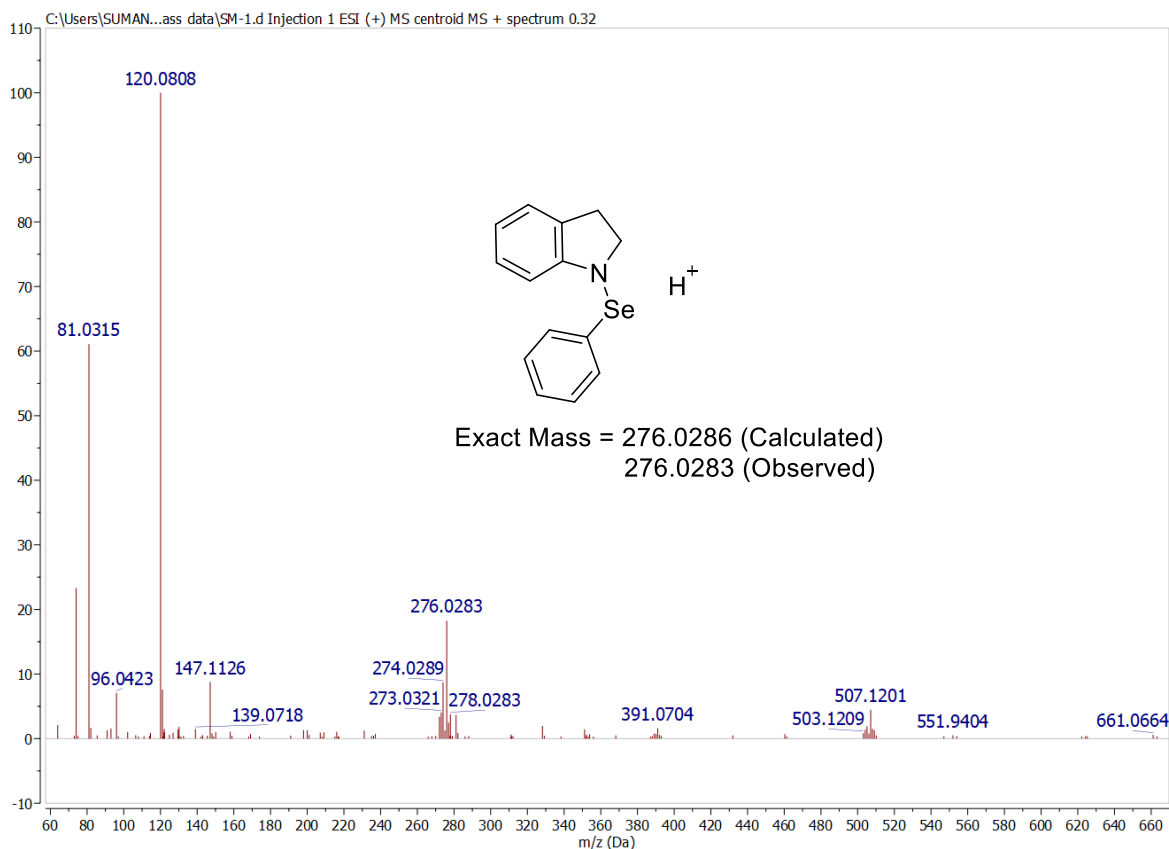
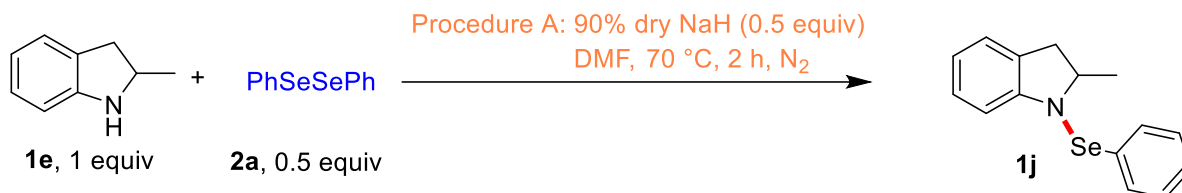


Figure 3: HRMS analysis of crude mixture of indoline, 90% dry NaH, Ph₂Se₂ and DMF after 2h.



Scheme 5: Chalcogenation of 2-methylindoline (**1g**)

To a 10 mL round bottom flask 90% dry NaH (0.1 mmol, 0.5 equiv.) was taken in nitrogen atmosphere. 2-methylindoline (**1g**) (0.2 mmol, 1 equiv.) in DMF (0.5 mL) was added into flask dropwise and stir at ice cold condition for 30 mins. After 30 minutes, diphenyldiselenide (0.1 mmol, 0.5 equiv.) in DMF (0.5 mL) was added into flask and stir at 70 °C for 2 h (**Scheme 5**). Following TLC detection, aliquot from the reaction mixture was taken for HRMS at 2 h (**Figure 4**).

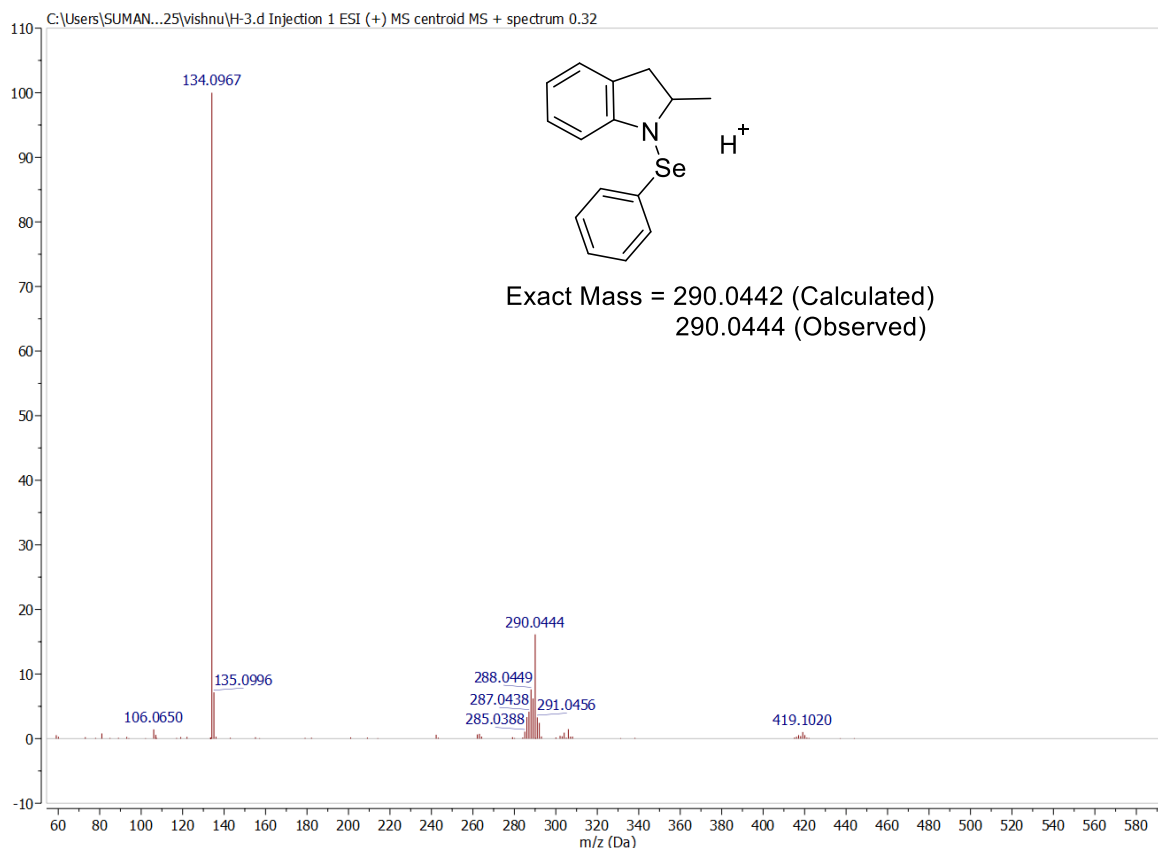


Figure 4: HRMS analysis of crude mixture of 2-methylindoline, 90% dry NaH, Ph₂Se₂ and DMF after 2h.

2.7. Fate of reaction in presence of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy)

Procedure A: In a 10 mL round bottom flask, 90% dry NaH (0.1 mmol, 0.5 equiv.) was taken in nitrogen atmosphere. Indoline derivative (0.2 mmol, 1 equiv.) in DMF (0.5 mL) was added into flask dropwise and stir at ice cold condition for 30 mins. After 30 minutes, diphenyldiselenide (0.1 mmol, 0.5 equiv.) and TEMPO (0.4 mmol, 2 equiv.) in DMF (0.5 mL) was added into flask and stir at 70 °C for 12 h. Following TLC detection, the starting materials were decomposed, and no trace of products was found.

Procedure B: In a 10 mL round bottom flask, indoline derivative (0.2 mmol, 1.0 equiv.), 90% dry NaH (0.12 mmol, 0.6 equiv.) in DMF (1 mL) were taken and stirred for 10 mins in air at room temperature (25 °C). After 10 minutes diphenyldiselenide (0.1 mmol, 0.5 equiv.) and TEMPO (0.4 mmol, 2 equiv.) was added to the stirred solution. The reaction mixture was stirred at room temperature (25 °C) in air for 12 h. Following TLC detection, the starting materials were decomposed and no trace of products was found.

2.8. Fate of reaction in presence of BHT (3,5-di-*tert*-4-butylhydroxytoluene)

Condition A: In a 10 mL round bottom flask, 90% dry NaH (0.1 mmol, 0.5 equiv.) was taken in nitrogen atmosphere. Indoline derivative (0.2 mmol, 1 equiv.) in DMF (0.5 mL) was added into flask dropwise and stir at ice cold condition for 30 mins. After 30 minutes, diphenyldiselenide (0.1 mmol, 0.5 equiv.) and BHT (0.4 mmol, 2 equiv.) in DMF (0.5 mL)

was added into flask and stir at 70 °C for 2 h. Taking aliquot from the reaction mixture LCMS taken, one BHT trapped intermediate and no trace of **3a** were found (**Figure 5**).

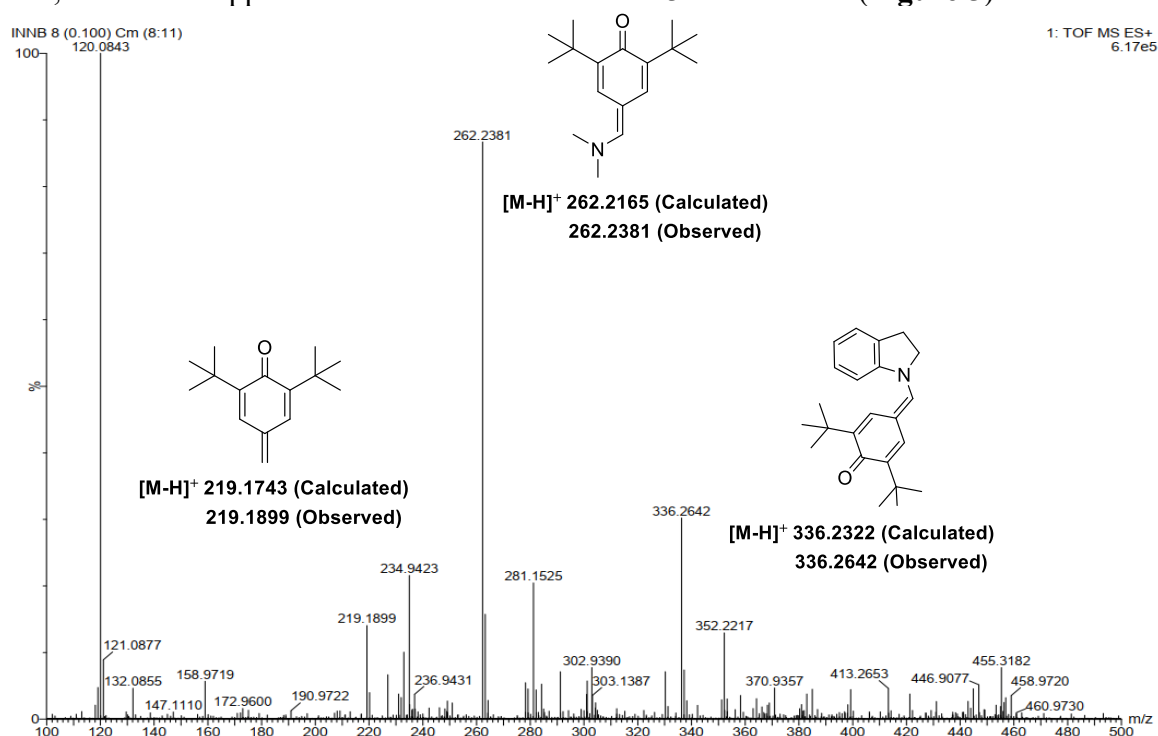


Figure 5: LCMS analysis of crude mixture of indoline, 90% dry NaH, Ph₂Se₂, BHT and DMF under N₂ atmosphere at 2 h.

Procedure B: In a 10 mL round bottom flask, indoline derivative (0.2 mmol, 1.0 equiv.), 90% dry NaH (0.12 mmol, 0.6 equiv.) in DMF (1 mL) were taken and stirred for 10 mins in air at room temperature (25 °C). After 10 minutes diphenyldiselenide (0.1 mmol, 0.5 equiv.) and BHT (0.4 mmol, 2 equiv.) was added to the stirred solution. The reaction mixture was stirred at room temperature (25 °C) in air for 1 h. Taking aliquot from the reaction mixture LCMS taken, one BHT trapped intermediate and no trace of **3a** was found (**Figure 6**).

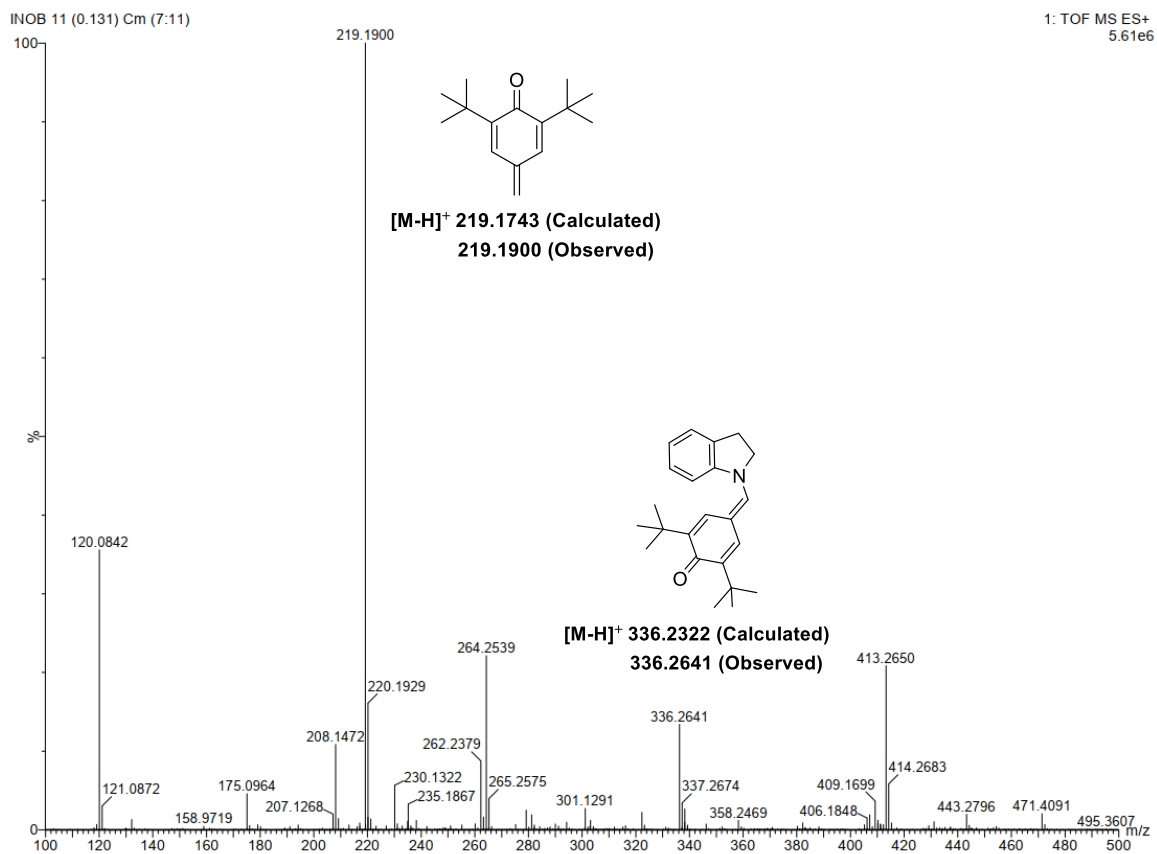
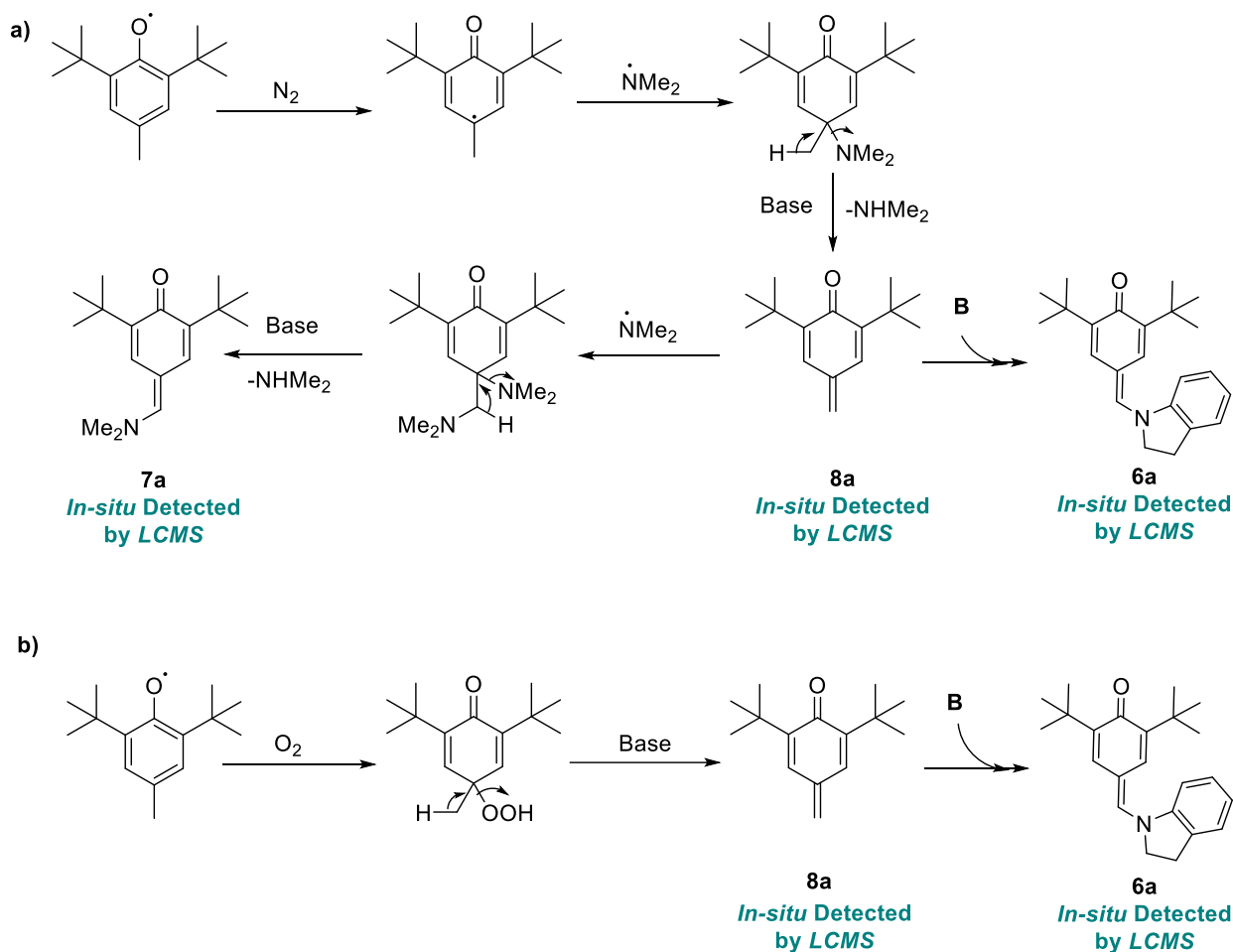


Figure 6: LCMS analysis of crude mixture of indoline, 90% dry NaH, Ph₂Se₂, BHT and DMF under air atmosphere at 2 h.



Scheme 6: Mechanism of radical quenching by BHT.

2.9. Procedure for Intermolecular competition experiment

Procedure B: In a 10 mL round bottom flask, indoline (0.2 mmol, 1.0 equiv.), 90% dry NaH (0.12 mmol, 0.6 equiv.) in DMF (1 mL) were taken and stirred for 10 mins in air at room temperature (25 °C). After 10 minutes 1,2-di-*p*-tolyl diselenide (**2b**, 0.05 mmol, 0.25 equiv) and 1,2-bis(4-(trifluoromethyl)phenyl)diselenide (**2d**, 0.05 mmol, 0.25 equiv) were added to the stirred solution. The reaction mixture was stirred at room temperature (25 °C) in air for 24 h monitored by TLC. Reaction mixture was then diluted by water and aqueous layer extracted by 20 ml dichloromethane for three times. The organic layer was collected and washed by brine solution, dried over sodium sulfate and was evaporated. The crude mixture was purified by column chromatography and products were isolated.

2.10. EPR analysis

The presence of free radicals was confirmed by an EPR experiment conducted on a frozen aliquot of an incomplete reaction between indoline (**1a**) and catalytic quantity of NaH in DMF solvent under both N₂ and air atmosphere (**Figure 7,9**). Our calculations revealed that the peak's cross-over point had a g-factor of 2.00802 and 2.00801 for the reactions under N₂ and air respectively, which is indicative of an unpaired electron's free-radical nature. Subsequent addition of diphenyl diselenide led to the quenching and broadening of the peak in case of NaH-catalyzed reaction at N₂ atmosphere (**Figure 8**) but no broadening was visible in case of air atmosphere (**Figure 10**). However, a peak

around $g = 2.007001$ was observed after addition of diselenide in the reaction under N_2 atmosphere indicating the probable existence of PhSe radical under the reaction conditions.

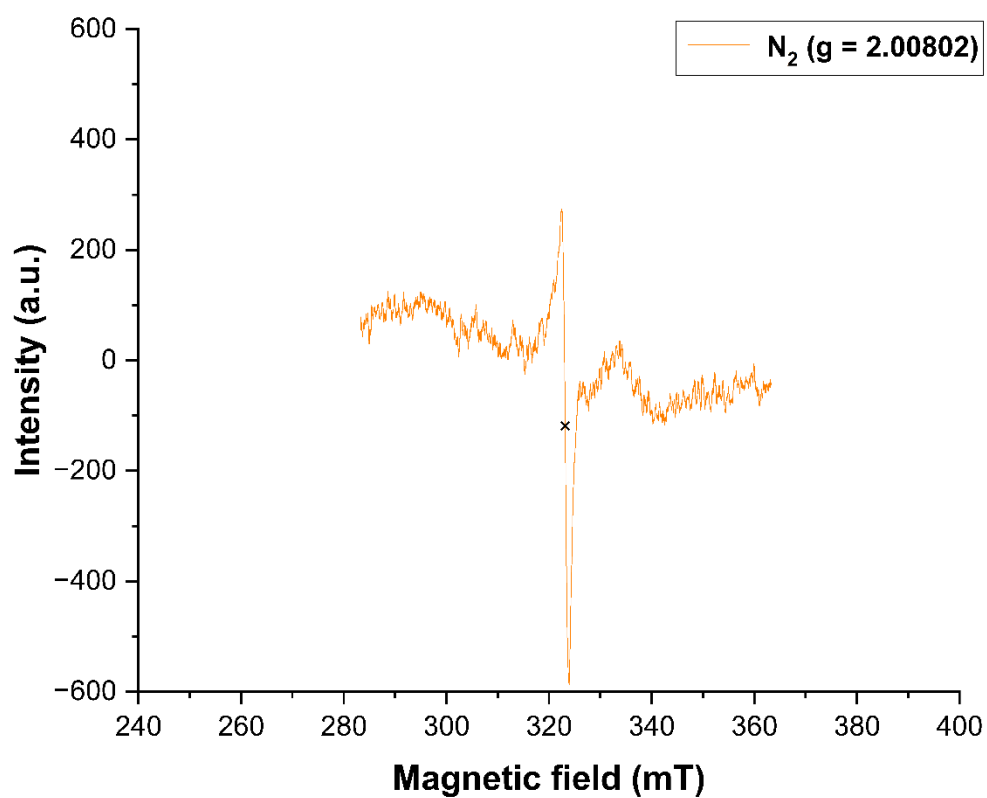


Figure 7: EPR spectrum of reaction between indoline and 90% dry NaH in DMF under nitrogen atmosphere at 77 K ($g=2.00802$ at [A] 323.153 mT).

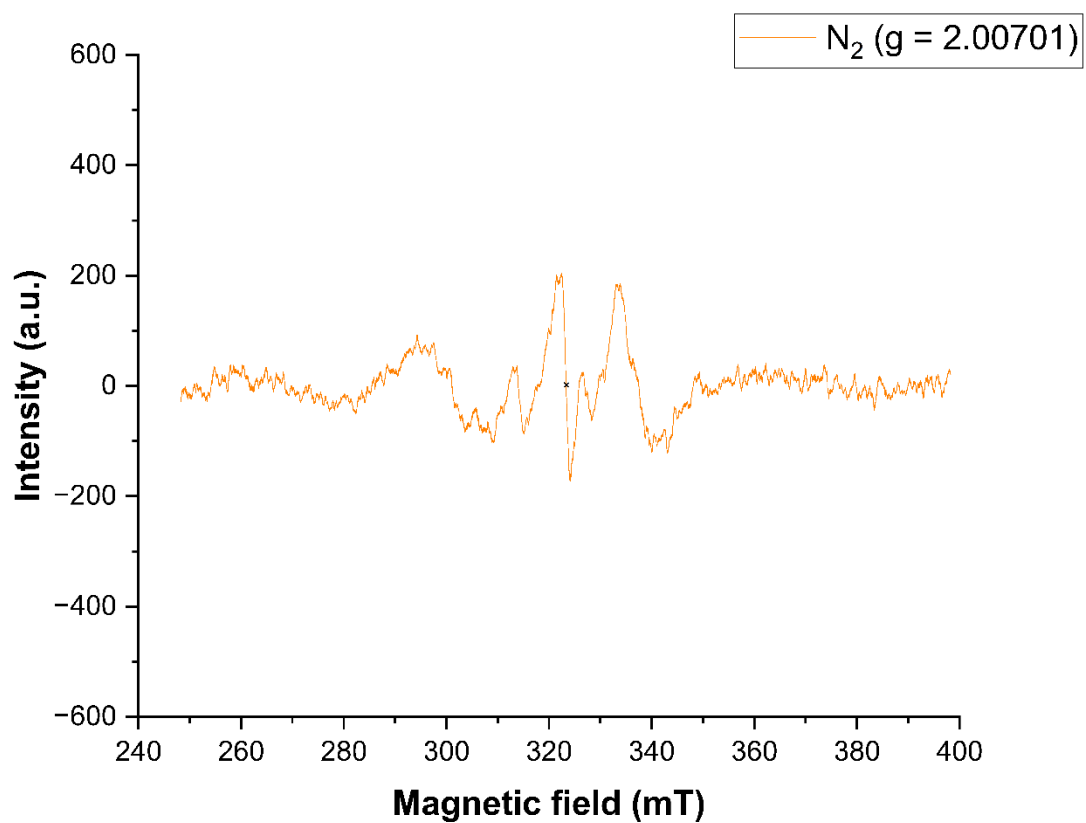


Figure 8: EPR spectrum of reaction between indoline, diphenyl diselenide and 90% dry NaH in DMF under nitrogen atmosphere at 77 K ($g=2.00701$ at [A] 323.321 mT).

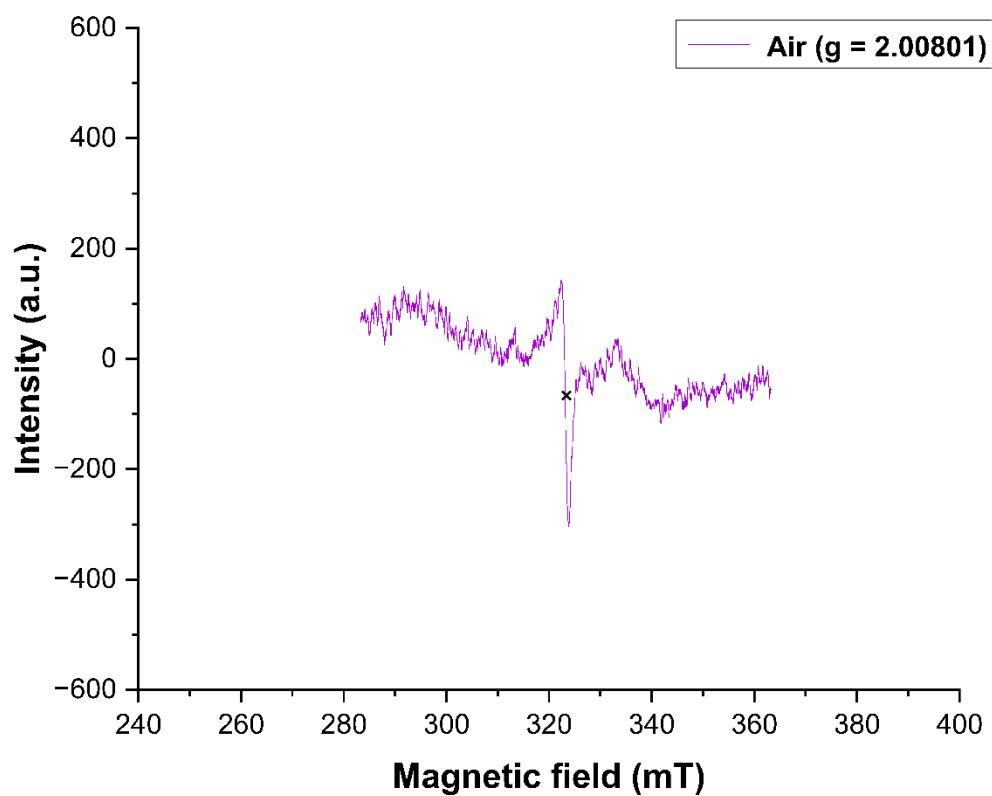


Figure 9: EPR spectrum of reaction between indoline and 90% dry NaH in DMF under air atmosphere at 77 K ($g=2.00801$ at [A] 323.153 mT).

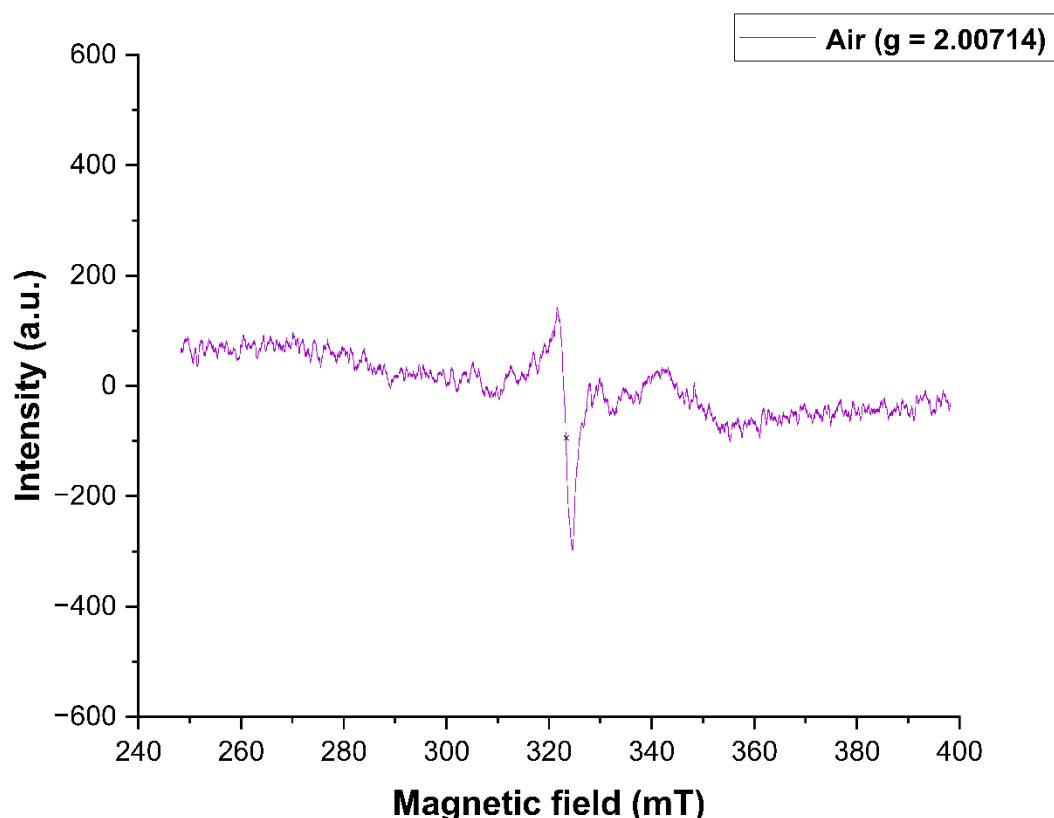
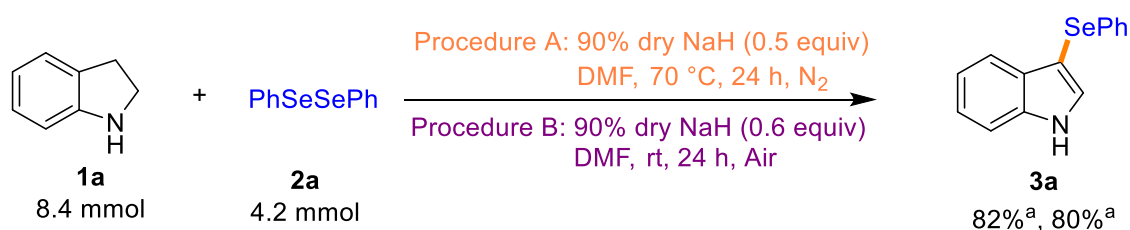


Figure 10: EPR spectrum of reaction between indoline, diphenyl diselenide and 90% dry NaH in DMF under air atmosphere at 77 K ($g=2.00714$ at $[A]$ 323.300 mT).

2.11. General procedure for gram scale synthesis:



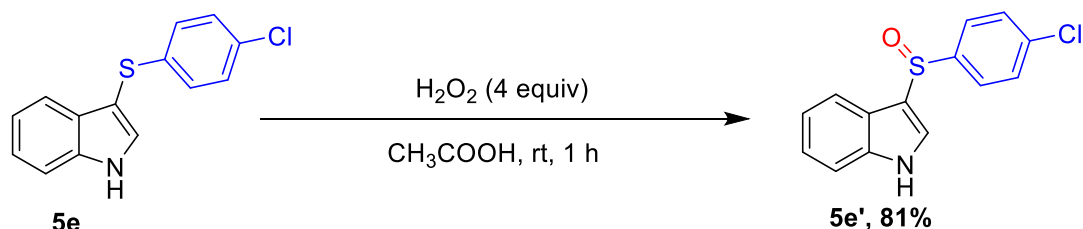
Scheme 7: Gram scale synthesis of 3-(phenylselanyl)-1*H*-indole.

Procedure A: To a 100 mL round bottom flask 90% dry NaH (4.2 mmol, 101 mg) was taken in nitrogen atmosphere. Indoline derivative (8.4 mmol, 1000 mg) in DMF (20 mL) was added into flask dropwise and stir at ice cold condition for 30 mins. After 30 minutes, diphenyldiselenide (4.2 mmol, 1312 mg) in DMF (5 mL) was added into flask and stir at 70 °C for 24 h monitored by TLC. After completion of the reaction, reaction mixture was diluted by water and aqueous layer extracted by 50 ml dichloromethane for three times. The organic layer collected and washed by brine solution (70 ml, 3 times). The organic layer was separated and

dried over sodium sulfate. The solvent was evaporated and the reaction mixture was further purified using column chromatography (dichloromethane: hexane = 1: 5) to afford **3a** with 82% yield (**Scheme 7**).

Procedure B: To a 10 mL round bottom flask indoline derivative (8.4 mmol, 1000 mg), 90% dry NaH (5.04 mmol, 121 mg) in DMF (25 mL) were taken and stirred for 10 mins in air at room temperature (25 °C). After 10 minutes diphenyldiselenide (4.2 mmol, 1312 mg) was added to the stirred solution. The reaction mixture was stirred at room temperature (25 °C) in air for 24 h. After completion of the reaction, reaction mixture was diluted by water and aqueous layer extracted by 50 ml dichloromethane for three times. The organic layer collected and washed by brine solution (70 ml, 3 times). The organic layer was separated and dried over sodium sulfate. The solvent was evaporated and the reaction mixture was further purified using column chromatography (dichloromethane: hexane = 1:5) to afford **3a** with 80% yield (**Scheme 7**).

2.12. Synthesis of 3-((4-chlorophenyl)sulfinyl)-1H-indole



Scheme 8: Synthesis of 3-((4-chlorophenyl)sulfinyl)-1H-indole.

To a 50 mL round bottom flask compound **5e** (1 mmol) in 8 mL acetic acid was taken. 30% H_2O_2 (4 mmol) was added dropwise and stir for 1 hour at room temperature until consumption of the starting material, as monitored by TLC. The reaction mixture was then neutralized by sodium bicarbonate solution and aqueous layer was then extracted by 50 ml dichloromethane for three times. The organic layer collected and washed by brine solution. The organic layer was separated and dried over sodium sulfate. The solvent was evaporated and the reaction mixture was further purified using column chromatography (ethylacetate: hexane = 1 : 1) to afford **5e'** with 81% yield (**Scheme 8**).

3. Anti-bacterial studies:

Materials & methods-

Growth media & reagents- All bacterial media, supplements and antibiotics including: Middlebrook 7H9 broth; Middlebrook 7H11 Agar; albumin, dextrose and catalase supplement; oleic acid, albumin, dextrose and catalase (OADC) supplement were purchased from HiMedia.

Bacterial strains- The bacterial strains utilized were *Mycobacterium fortuitum* ATCC 6841, *Mycobacterium chelonae* ATCC 35752 and *Mycobacterium abscessus* ATCC 19977. The

mycobacteria were propagated in Middlebrook 7H9 broth supplemented with glycerol, oleic acid, albumin, dextrose and catalase and 0.05% Tween-80 at 37°C.

Minimal inhibitory concentration (MIC) assays—Broth microdilution assay was performed to determine the minimum inhibitory concentration (MIC) following CLSI guidelines. Stock solutions (10 mg/ml) of all test and control compounds were prepared in DMSO and stored at -20°C. Bacterial cultures were inoculated in suitable media and incubated overnight at 37°C. The optical density (OD_{600nm}) of the cultures was measured, and the cultures were diluted to obtain an approximate concentration of 10⁵ colony-forming units (CFU)/ml. The compounds were tested in a two-fold serial dilution ranging from 64 to 0.5 µg/ml. A volume of 2.5 µl of each compound was added to individual wells of a 96-well round-bottom microtiter plate, followed by the addition of 97.5 µl of the diluted bacterial culture (~10⁵ CFU/ml) into each well. The plates were then incubated at 37°C for 48 hours. The MIC was determined as the lowest compound concentration that completely inhibited visible bacterial growth. Each MIC determination was conducted three times independently, with duplicate measurements for each compound.

4. Spectral data

1-(phenylselanyl)indoline (1h). White solid, ¹H NMR (600 MHz, CDCl₃) δ 8.21 (d, *J* = 9.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.29 – 7.13 (m, 5H), 6.93 (t, *J* = 7.4 Hz, 1H), 4.06 (t, *J* = 8.2 Hz, 2H), 3.21 (t, *J* = 8.3 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 149.26, 144.38, 139.73, 132.61, 127.42, 125.94, 125.75, 121.81, 114.88, 110.67, 52.20, 28.14. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₄H₁₄NSe⁺ 276.0286; found 276.0286.

3-(phenylselanyl)-1*H*-indole² (3a). White solid, mp 134-136 °C (lit.¹ 134-137 °C), ¹H NMR (500 MHz, CDCl₃) δ 8.51 (s, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.57 (d, *J* = 2.6 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.32 (d, *J* = 1.4 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.21 (t, *J* = 7.0 Hz, 2H), 7.20 – 7.16 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 136.50, 133.92, 131.37, 130.08, 129.08, 128.74, 125.71, 123.06, 120.99, 120.50, 111.49, 98.23.

3-(*p*-tolylselanyl)-1*H*-indole² (3b). White solid, mp 104-106 °C (lit.¹ 104-106 °C), ¹H NMR (600 MHz, CDCl₃) δ 8.33 (s, 1H), 7.45 (d, *J* = 2.5 Hz, 1H), 7.33 (d, *J* = 8.9 Hz, 1H), 7.18 – 7.15 (m, 2H), 7.10 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.07 – 7.04 (m, 2H), 6.92 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.78 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 136.51, 135.62, 131.08, 130.13, 129.90, 129.22, 123.01, 120.93, 120.55, 111.43, 98.86, 21.06.

3-(*o*-tolylselanyl)-1*H*-indole³ (3c). White solid, mp 117-118 °C (lit.³ 117-120 °C), ¹H NMR (600 MHz, CDCl₃) δ 8.47 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.25 (m, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 7.3 Hz, 1H), 6.85 (q, *J* = 7.3 Hz, 2H), 2.48 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 136.64, 136.25, 134.61, 131.62, 130.25, 129.93, 128.13, 126.59, 125.51, 123.10, 121.01, 120.54, 111.52, 97.44, 21.42. ⁷⁷Se NMR (114 MHz, CDCl₃) δ 180.89.

3-((4-(trifluoromethyl)phenyl)selanyl)-1*H*-indole⁴ (3d). Black solid, mp 105-107 °C, ¹H NMR (600 MHz, CDCl₃) δ 8.54 (s, 1H), 7.59 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.52 (d, *J* = 2.5 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.28 (m, 2H), 7.27 (s, 1H), 7.20 (ddd, *J* = 8.2, 7.1, 1.0 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 139.71, 136.61, 131.69, 129.81, 128.28, 127.92, 127.70, 125.75, 125.72, 125.30, 123.40, 121.32, 120.28, 111.67, 97.17. ⁷⁷Se

NMR (114 MHz, CHLOROFORM-*D*) δ 226.11. ^{19}F NMR (565 MHz, CHLOROFORM-*D*) δ -60.51.

3-((2-methoxyphenyl)selanyl)-1*H*-indole⁴ (3e). White solid, mp 117-118 °C (lit.³ 117-119 °C). ^1H NMR (600 MHz, CDCl_3) δ 8.48 (s, 1H), 7.63 (d, $J = 7.9$ Hz, 1H), 7.47 (d, $J = 8.6$ Hz, 2H), 7.28 (d, $J = 7.6$ Hz, 1H), 7.18 (t, $J = 7.6$ Hz, 1H), 7.08 (t, $J = 7.8$ Hz, 1H), 6.82 (d, $J = 8.0$ Hz, 1H), 6.67 (d, $J = 7.9$ Hz, 1H), 6.64 (t, $J = 7.5$ Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 156.14, 136.72, 132.00, 130.46, 128.24, 126.38, 123.40, 123.07, 121.70, 120.99, 120.67, 111.50, 110.11, 96.32, 55.99.

3-(phenethylselanyl)-1*H*-indole (3f)⁴. Liquid, ^1H NMR (600 MHz, CDCl_3) δ 8.23 (s, 1H), 7.71 (d, $J = 8.0$ Hz, 1H), 7.34 (d, $J = 8.0$ Hz, 1H), 7.26 (d, $J = 2.3$ Hz, 1H), 7.20 – 7.13 (m, 5H), 7.07 (d, $J = 7.5$ Hz, 2H), 2.88 (s, 4H). ^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 141.44, 136.39, 130.43, 130.37, 128.66, 128.62, 128.53, 128.49, 126.29, 122.76, 120.60, 120.35, 111.40, 98.77, 37.25, 29.34.

3-((4-nitrophenyl)selanyl)-1*H*-indole⁶ (3g). Yellow liquid, ^1H NMR (600 MHz, CDCl_3) δ 8.44 (s, 1H), 7.64 (d, $J = 7.9$ Hz, 1H), 7.49 (d, $J = 2.4$ Hz, 1H), 7.45 (d, $J = 8.1$ Hz, 1H), 7.28 (d, $J = 7.4$ Hz, 1H), 7.24 (d, $J = 7.5$ Hz, 1H), 7.20 – 7.16 (m, 1H), 7.13 (t, $J = 7.3$ Hz, 2H), 7.10 (d, $J = 7.2$ Hz, 1H). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_2\text{Se}^+$ 318.9980; found 318.9985.

5-fluoro-3-(phenylselanyl)-1*H*-indole⁷ (3h). White solid, mp 116-117 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.49 (s, 1H), 7.56 (d, $J = 2.6$ Hz, 1H), 7.40 (dd, $J = 8.9, 4.3$ Hz, 1H), 7.34 – 7.26 (m, 3H), 7.21 – 7.13 (m, 3H), 7.04 (t, $J = 9.0$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 159.60, 158.03, 133.50, 132.98, 131.06, 129.17, 128.91, 125.94, 112.31, 112.24, 111.77, 111.60, 105.65, 105.49, 98.56. ^{77}Se NMR (114 MHz, CHLOROFORM-*D*) δ 212.72.

5-fluoro-3-(*p*-tolylselanyl)-1*H*-indole (3i)⁵. White Solid, mp 117-118 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.41 (s, 1H), 7.50 (d, $J = 2.6$ Hz, 1H), 7.34 (dd, $J = 8.9, 4.3$ Hz, 1H), 7.28 (dd, $J = 9.3, 2.6$ Hz, 1H), 7.16 (s, 1H), 7.15 (s, 1H), 7.00 (dd, $J = 9.0, 2.6$ Hz, 1H), 6.97 (d, $J = 7.9$ Hz, 2H), 2.25 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 159.56, 157.99, 135.89, 132.72, 129.98, 129.38, 112.25, 112.18, 111.66, 111.49, 105.66, 105.49, 99.03, 21.05.

5-fluoro-3-(*o*-tolylselanyl)-1*H*-indole (3j)⁵. White solid, mp 110-112 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.59 (s, 1H), 7.61 (d, $J = 2.6$ Hz, 1H), 7.51 – 7.45 (m, 1H), 7.39 – 7.35 (m, 1H), 7.25 (d, $J = 7.5$ Hz, 1H), 7.18 – 7.11 (m, 2H), 6.99 (t, $J = 7.6$ Hz, 1H), 6.93 (d, $J = 7.8$ Hz, 1H), 2.59 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 159.61, 158.05, 136.37, 134.21, 133.29, 130.05, 128.08, 126.64, 125.70, 112.35, 112.28, 111.79, 111.61, 105.68, 97.58, 21.42. ^{77}Se NMR (114 MHz, CDCl_3) δ 181.31. ^{19}F NMR (565 MHz, CDCl_3) δ -122.58.

5-bromo-3-(phenylselanyl)-1*H*-indole¹ (3k)⁵. White solid, mp 107-109 °C (lit.¹ 107-110 °C), ^1H NMR (600 MHz, CDCl_3) δ 8.47 (s, 1H), 7.76 (d, $J = 1.8$ Hz, 1H), 7.49 (d, $J = 2.5$ Hz, 1H), 7.35 (dd, $J = 8.7, 1.9$ Hz, 1H), 7.32 (s, 1H), 7.19 – 7.16 (m, 2H), 7.10 – 7.06 (m, 3H). ^{13}C NMR (50 MHz, CDCl_3) δ 135.08, 133.46, 132.55, 131.90, 129.19, 128.77, 126.00, 125.95, 122.94, 114.42, 113.03, 97.81.

5-bromo-3-(*p*-tolylselanyl)-1*H*-indole² (3l). White solid, mp 119-121 °C (lit.¹ 119-123 °C), ^1H NMR (600 MHz, CHLOROFORM-*D*) δ 8.51 (s, 1H), 7.85 (d, $J = 1.9$ Hz, 1H), 7.58 (d, $J = 2.6$ Hz, 1H),

7.44 (dd, $J = 8.6, 1.8$ Hz, 1H), 7.40 (d, $J = 8.6$ Hz, 1H), 7.13 – 7.07 (m, 4H), 2.36 (s, 3H). HRMS (ESI) m/z : $[M+H]^+$ calcd for $C_{15}H_{13}BrNSe^+$ 365.9391; found 365.9395.

5-bromo-3-(*o*-tolylselanyl)-1*H*-indole⁸ (3m). Yellow viscous liquid, 1H NMR (600 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.75 – 7.73 (m, 1H), 7.48 (d, $J = 2.5$ Hz, 1H), 7.36 (dd, $J = 8.6, 1.8$ Hz, 1H), 7.33 (d, $J = 8.6$ Hz, 1H), 7.13 (dd, $J = 7.5, 1.7$ Hz, 1H), 7.03 (td, $J = 7.5, 1.4$ Hz, 1H), 6.88 (td, $J = 7.6, 1.7$ Hz, 1H), 6.78 (dd, $J = 8.0, 1.4$ Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.27, 135.27, 134.21, 132.83, 132.12, 130.07, 127.93, 126.70, 126.11, 125.71, 123.07, 114.51, 113.04, 97.02, 21.39.

5-bromo-3-((4-(trifluoromethyl)phenyl)selanyl)-1*H*-indole (3n)⁶. White solid, mp 95-96 °C, 1H NMR (500 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.75 (d, $J = 1.8$ Hz, 1H), 7.53 (d, $J = 2.5$ Hz, 1H), 7.38 (dd, $J = 7.9, 6.1$ Hz, 4H), 7.28 (s, 1H), 7.26 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.22, 135.26, 132.93, 131.73, 128.26, 126.44, 125.91, 125.88, 125.85, 125.82, 122.88, 114.83, 113.19, 96.79. ^{77}Se NMR (95 MHz, $CDCl_3$) δ 224.37. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.12.

5-methoxy-3-(phenylselanyl)-1*H*-indole⁷ (3o). liquid, 1H NMR (600 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.46 (d, $J = 2.5$ Hz, 1H), 7.33 (d, $J = 8.9$ Hz, 1H), 7.19 – 7.15 (m, 2H), 7.11 (d, $J = 1.4$ Hz, 1H), 7.09 (d, $J = 1.1$ Hz, 1H), 7.07 – 7.04 (m, 2H), 6.92 (dd, $J = 8.8, 2.5$ Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.25, 139.45, 131.48, 130.09, 128.84, 125.79, 124.85, 113.71, 112.57, 102.25, 100.93, 55.91.

5-methoxy-3-(*p*-tolylselanyl)-1*H*-indole⁷ (3p). Liquid, 1H NMR (600 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.43 (d, $J = 2.9$ Hz, 1H), 7.31 (d, $J = 8.6$ Hz, 1H), 7.05 (d, $J = 2.3$ Hz, 1H), 7.04 – 7.01 (m, 2H), 7.00 – 6.97 (m, 2H), 6.91 (dd, $J = 8.9, 2.6$ Hz, 1H), 3.79 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.11, 135.74, 134.67, 131.48, 131.35, 130.07, 129.86, 129.61, 126.11, 125.13, 113.53, 112.55, 102.68, 100.91, 55.88, 20.93.

5-methoxy-3-(*o*-tolylselanyl)-1*H*-indole⁹ (3q). Yellow viscous liquid, 1H NMR (600 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.43 (d, $J = 2.9$ Hz, 1H), 7.35 (d, $J = 8.9$ Hz, 1H), 7.12 (d, $J = 7.5$ Hz, 1H), 7.03 (d, $J = 2.0$ Hz, 1H), 7.01 (dd, $J = 7.2, 1.7$ Hz, 1H), 6.92 (dd, $J = 8.8, 2.4$ Hz, 1H), 6.87 (ddd, $J = 8.6, 7.3, 1.4$ Hz, 1H), 6.83 (dd, $J = 7.9, 1.5$ Hz, 1H), 3.80 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.19, 136.11, 134.71, 132.25, 131.52, 131.02, 129.94, 127.89, 126.61, 125.45, 113.60, 112.42, 101.63, 96.69, 55.90, 21.33.

5-methoxy-3-((4-(trifluoromethyl)phenyl)selanyl)-1*H*-indole⁸ (3r). Brown solid, mp 110-112 °C, 1H NMR (600 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.48 (d, $J = 2.6$ Hz, 1H), 7.37 (d, $J = 2.2$ Hz, 1H), 7.35 (d, $J = 1.8$ Hz, 2H), 7.27 (d, $J = 8.5$ Hz, 2H), 7.01 (d, $J = 2.5$ Hz, 1H), 6.94 (dd, $J = 8.8, 2.5$ Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.44, 139.81, 132.34, 131.51, 130.62, 128.14, 127.86, 127.65, 125.74, 125.71, 125.30, 123.50, 113.83, 112.56, 101.51, 96.58, 55.94. ^{77}Se NMR (114 MHz, $CDCl_3$) δ 223.13. ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.25.

3-(phenylthio)-1*H*-indole² (5a). White solid, mp 150-151 °C (lit.¹ 150-151 °C), 1H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.61 (d, $J = 8.1$ Hz, 1H), 7.48 (d, $J = 2.6$ Hz, 1H), 7.43 (d, $J = 8.2$ Hz, 1H), 7.28 – 7.25 (m, 1H), 7.18 – 7.13 (m, 3H), 7.10 (d, $J = 7.0$ Hz, 2H), 7.04 (t, $J = 7.0$ Hz,

1H). ¹³C NMR (101 MHz, CDCl₃) δ 139.20, 135.61, 132.41, 132.39, 131.46, 129.30, 126.54, 126.33, 125.51, 122.66, 114.91, 113.60, 103.08.

3-(*o*-tolylthio)-1*H*-indole² (5b). White Solid, mp 119-121 °C, ¹H NMR (600 MHz, CDCl₃) δ 8.44 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 2.4 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.28 (td, *J* = 7.6, 1.2 Hz, 1H), 7.17 (td, *J* = 7.4, 1.0 Hz, 1H), 7.15 – 7.12 (m, 1H), 6.98 (td, *J* = 7.4, 1.4 Hz, 1H), 6.90 (td, *J* = 7.6, 1.4 Hz, 1H), 6.73 (dd, *J* = 8.0, 1.3 Hz, 1H), 2.50 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 138.40, 136.70, 134.50, 130.90, 129.95, 129.37, 126.39, 125.41, 124.59, 123.18, 121.01, 119.84, 111.73, 102.49, 20.03.

3-(*p*-tolylthio)-1*H*-indole¹⁰ (5c). Brown solid, mp 121-122 °C (lit.¹⁰ 122-125 °C), ¹H NMR (600 MHz, CDCl₃) δ 8.38 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.40 (m, 2H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 2.23 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 136.56, 135.58, 134.78, 130.59, 129.61, 129.19, 126.36, 123.06, 120.92, 119.75, 111.68, 103.45, 20.96.

3-((4-fluorophenyl)thio)-1*H*-indole¹⁰ (5d). White solid, mp 139-140 °C (lit.¹¹ 141-142 °C), ¹H NMR (600 MHz, CDCl₃) δ 8.41 (s, 1H), 7.60 (d, *J* = 6.9 Hz, 1H), 7.49 (d, *J* = 2.6 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.28 (dd, *J* = 7.2, 1.1 Hz, 1H), 7.17 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 7.12 – 7.07 (m, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 161.85, 160.24, 136.64, 134.14, 130.60, 129.01, 128.07, 128.01, 123.28, 121.12, 119.67, 115.95, 115.80, 111.75, 103.59. ¹⁹F NMR (565 MHz, CDCl₃) δ -118.13.

3-((4-chlorophenyl)thio)-1*H*-indole¹⁰ (5e). White solid. mp 134-135 °C (lit.¹¹ 135-136 °C), ¹H NMR (600 MHz, CDCl₃) δ 8.43 (s, 1H), 7.58 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.50 (d, *J* = 2.6 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.28 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 7.18 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 1H), 7.13 (d, *J* = 2.0 Hz, 1H), 7.12 (d, *J* = 2.0 Hz, 1H), 7.03 (d, *J* = 2.1 Hz, 1H), 7.02 (d, *J* = 2.0 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 137.95, 136.64, 130.84, 130.69, 128.94, 128.89, 127.25, 123.36, 121.21, 119.65, 111.80, 102.60.

3-((4-methoxyphenyl)thio)-1*H*-indole¹⁰ (5f). White solid, mp 109-111 °C (lit.¹¹ 110-111 °C). ¹H NMR (600 MHz, CDCl₃) δ 8.38 (s, 1H), 7.63 (d, *J* = 8.3 Hz, 1H), 7.46 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 6.9 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.14 (s, 1H), 7.13 (s, 1H), 6.74 (d, *J* = 9.2 Hz, 2H), 3.73 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 155.23, 139.50, 131.51, 130.09, 128.82, 125.77, 124.81, 113.67, 112.58, 102.16, 100.89, 55.90.

5-bromo-3-(phenylthio)-1*H*-indole² (5g). White solid, mp 120-122 °C (lit.¹ 120-122 °C), ¹H NMR (600 MHz, CDCl₃) δ 8.47 (s, 1H), 7.76 (d, *J* = 2.3 Hz, 1H), 7.49 (d, *J* = 2.6 Hz, 1H), 7.35 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 1H), 7.20 – 7.15 (m, 2H), 7.10 – 7.05 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 138.85, 135.26, 132.05, 132.04, 131.10, 128.94, 126.18, 125.98, 125.15, 122.30, 114.55, 113.24, 102.73.

5-bromo-3-(*o*-tolylthio)-1*H*-indole² (5h). White Solid, mp 102-104 °C, ¹H NMR (600 MHz, CDCl₃) δ 8.41 (s, 1H), 7.65 – 7.63 (m, 1H), 7.37 (d, *J* = 2.5 Hz, 1H), 7.26 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 1H), 7.03 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.93 (td, *J* = 7.5, 1.4 Hz, 1H), 6.78 (td, *J* = 7.6, 1.7 Hz, 1H), 6.68 (dd, *J* = 8.0, 1.4 Hz, 1H), 2.37 (s, 3H). ¹³C NMR (101 MHz,

CDCl₃) δ 135.50, 135.40, 134.41, 132.52, 130.87, 129.87, 129.29, 125.83, 125.05, 123.36, 121.47, 113.52, 113.43, 101.35, 20.62.

5-bromo-3-(*p*-tolylthio)-1*H*-indole¹¹ (5i). Pale brown solid, mp 121-122 °C (lit.¹⁰ 123-125 °C), ¹H NMR (600 MHz, CDCl₃) δ 8.41 (s, 1H), 7.75 (d, *J* = 2.0 Hz, 1H), 7.48 (d, *J* = 2.6 Hz, 1H), 7.34 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.30 (d, *J* = 8.6 Hz, 1H), 7.00 (d, *J* = 3.0 Hz, 4H), 2.26 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 135.50, 135.40, 134.41, 132.52, 130.87, 129.87, 129.29, 125.83, 125.05, 123.36, 121.47, 113.52, 113.43, 101.35, 20.62.

5-methoxy-3-(phenylthio)-1*H*-indole¹⁰ (5j). White solid, mp 79-80 °C (lit.¹¹ 76-79 °C), ¹H NMR (600 MHz, CDCl₃) δ 8.39 (s, 1H), 7.45 (d, *J* = 2.6 Hz, 1H), 7.32 (d, *J* = 8.6 Hz, 1H), 7.19 – 7.15 (m, 2H), 7.12 – 7.09 (m, 2H), 7.06 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.05 (d, *J* = 2.3 Hz, 1H), 6.92 (dd, *J* = 8.9, 2.6 Hz, 1H), 3.79 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 155.23, 139.50, 131.51, 130.09, 128.82, 125.77, 124.81, 113.67, 112.58, 102.16, 100.89, 55.90.

5-methoxy-3-(*p*-tolylthio)-1*H*-indole¹⁰ (5k). White solid, mp 77-78 °C, ¹H NMR (600 MHz, CHLOROFORM-*D*) δ 8.41 (s, 1H), 7.43 (d, *J* = 2.9 Hz, 1H), 7.35 (d, *J* = 8.9 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 2.0 Hz, 1H), 7.01 (dd, *J* = 7.2, 1.7 Hz, 1H), 6.92 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.87 (ddd, *J* = 8.6, 7.3, 1.4 Hz, 1H), 6.83 (dd, *J* = 7.9, 1.5 Hz, 1H), 3.80 (s, 3H), 2.47 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 155.11, 135.74, 134.67, 131.48, 131.35, 130.07, 129.86, 129.61, 126.11, 125.13, 113.53, 112.55, 102.68, 100.91, 55.88, 20.93.

5-methoxy-3-(*o*-tolylthio)-1*H*-indole¹⁰ (5l). White Solid, mp 90-92 °C, ¹H NMR (600 MHz, CHLOROFORM-*D*) δ 8.36 (s, 1H), 7.43 (d, *J* = 2.9 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 1H), 7.05 (d, *J* = 2.3 Hz, 1H), 7.04 – 7.01 (m, 2H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.91 (dd, *J* = 8.9, 2.6 Hz, 1H), 3.79 (s, 3H), 2.26 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 155.11, 135.74, 134.67, 131.48, 131.35, 130.07, 129.86, 129.61, 126.11, 125.13, 113.53, 112.55, 102.68, 100.91, 55.88, 20.93.

5-methoxy-3-((4-fluorophenyl)thio)-1*H*-indole⁸ (5m). White solid, mp 118-120 °C, ¹H NMR (600 MHz, CDCl₃) δ 8.37 (s, 1H), 7.45 (d, *J* = 2.6 Hz, 1H), 7.32 (d, *J* = 8.7 Hz, 1H), 7.10 – 7.06 (m, 2H), 7.02 (d, *J* = 2.6 Hz, 1H), 6.92 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.90 – 6.86 (m, 2H), 3.80 (s, 3H). HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₅H₁₃FNOS⁺ 274.0696; found 274.0690.

5-methoxy-3-((4-chlorophenyl)thio)-1*H*-indole¹³ (5n). White solid. mp 103-105 °C, ¹H NMR (600 MHz, CDCl₃) δ 8.36 (s, 1H), 7.45 (d, *J* = 2.5 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.13 (d, *J* = 2.0 Hz, 1H), 7.12 (d, *J* = 2.0 Hz, 1H), 7.03 – 7.00 (m, 3H), 6.93 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.80 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 155.38, 138.07, 131.50, 130.60, 129.83, 128.89, 127.04, 113.84, 112.66, 101.90, 100.82, 55.93.

5-methoxy-3-((4-methoxyphenyl)thio)-1*H*-indole¹¹ (5o). White solid, mp 57-59 °C, ¹H NMR (600 MHz, CDCl₃) δ 8.29 (s, 1H), 7.42 (d, *J* = 2.6 Hz, 1H), 7.30 (d, *J* = 8.6 Hz, 1H), 7.13 – 7.12 (m, 1H), 7.11 (d, *J* = 3.2 Hz, 1H), 7.06 (d, *J* = 2.6 Hz, 1H), 6.90 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.75 (d, *J* = 2.3 Hz, 1H), 6.74 (d, *J* = 2.2 Hz, 1H), 3.80 (s, 3H), 3.73 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 157.84, 155.17, 133.72, 131.49, 130.89, 129.99, 129.82, 129.10, 128.37, 115.24, 114.63, 113.55, 112.48, 111.87, 104.02, 101.01, 55.93, 55.48.

Indole¹⁵ (1a'). Brown solid, ¹H NMR (500 MHz, CDCl₃) δ 7.85 (d, *J* = 7.9 Hz, 2H), 7.44 – 7.36 (m, 2H), 7.33 (td, *J* = 7.3, 1.6 Hz, 1H), 7.18 – 7.15 (m, 1H), 6.72 – 6.69 (m, 1H). ¹³C NMR

(126 MHz, CDCl₃) δ 135.74, 127.82, 124.36, 121.98, 120.76, 119.85, 111.12, 102.41, 77.42, 77.16, 76.90.

5-fluoroindole¹⁴ (1b'). White solid, ¹H NMR (400 MHz, DMSO) δ 11.17 (s, 1H), 7.42 – 7.39 (m, 1H), 7.39 – 7.35 (m, 1H), 7.28 (ddt, J = 10.0, 2.6, 0.6 Hz, 1H), 6.95 – 6.87 (m, 1H), 6.41 (ddd, J = 3.0, 2.0, 0.9 Hz, 1H).

5-bromoindole¹⁵ (1c'). Brown solid, ¹H NMR (400 MHz, DMSO) δ 11.28 (s, 1H), 7.72 (d, J = 2.0 Hz, 1H), 7.40 (t, J = 2.8 Hz, 1H), 7.37 (dt, J = 8.6, 0.7 Hz, 1H), 7.18 (dd, J = 8.6, 2.0 Hz, 1H), 6.42 (ddd, J = 3.0, 1.9, 0.9 Hz, 1H).

5-methoxyindole¹⁶ (1d'). White solid, ¹H NMR (400 MHz, DMSO) δ 10.90 (s, 1H), 7.30 – 7.26 (m, 2H), 7.04 (d, J = 2.5 Hz, 1H), 6.73 (dd, J = 8.7, 2.5 Hz, 1H), 6.34 (ddd, J = 3.0, 2.0, 0.9 Hz, 1H), 3.75 (s, 3H).

3-methylindole¹⁶ (1e'). White solid, ¹H NMR (500 MHz, CDCl₃) δ 7.60 (d, J = 7.9 Hz, 1H), 7.27 (d, J = 8.1 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.17 – 7.13 (m, 1H), 6.88 – 6.85 (m, 1H), 2.34 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 136.31, 128.33, 121.93, 121.74, 119.19, 118.91, 111.67, 111.08, 77.42, 77.16, 76.90, 9.94.

2-methylindole¹⁵ (1g'). White solid, ¹H NMR (400 MHz, CDCl₃) δ 7.86 (s, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.30 (t, J = 7.3 Hz, 1H), 7.12 (dt, J = 18.1, 7.1 Hz, 2H), 6.25 (s, 1H), 2.47 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 136.18, 135.15, 129.20, 121.04, 119.74, 110.31, 100.52, 13.84.

3-((4-chlorophenyl)sulfinyl)-1H-indole (5e')¹⁷. White Solid, m.p. 128-129 °C¹⁶, ¹H NMR (500 MHz, CDCl₃) δ 10.38 (s, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 7.9 Hz, 1H), 7.25 (d, J = 8.1 Hz, 2H), 7.13 (t, J = 7.6 Hz, 1H), 7.01 (t, J = 7.6 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 141.83, 137.30, 136.65, 130.63, 129.38, 128.22, 126.55, 123.80, 123.28, 121.81, 119.25, 115.36, 112.80.

N-methylindoline¹⁴ (1f). Yield 75%, Brown liquid, ¹H NMR (600 MHz, CDCl₃) δ 7.93 – 7.90 (m, 1H), 7.51 – 7.48 (m, 2H), 7.45 – 7.42 (m, 1H), 4.52 (t, J = 7.3 Hz, 2H), 3.86 (s, 3H), 3.45 (t, J = 7.2 Hz, 2H).

Sodium benzeneselenolate (2a'). White solid, ¹H NMR (400 MHz, D₂O) δ 7.66 – 7.56 (m, 2H), 7.44 (m, , 3H).

2-methyl-3-(phenylselanyl)-1H-indole (3s). White solid, ¹H NMR (400 MHz, CDCl₃) δ 8.30 (s, 1H), 7.57 (d, J = 7.7 Hz, 1H), 7.34 (d, J = 7.9 Hz, 1H), 7.21 – 7.15 (m, 3H), 7.15 – 7.06 (m, 4H), 2.56 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 140.97, 135.91, 134.07, 131.37, 129.06, 128.51, 128.44, 128.38, 125.47, 122.23, 120.76, 119.91, 110.59, 96.38, 13.32.

5. References

1. V. Kumar, K. Banert, D. Ray, B. Saha, *Org. Biomol. Chem.*, 2019, **17**, 10245–10250
2. C. C. Silveira, S. R. Mendes, L. Wolf, G. M. Martins and L. Von Mühlen, *Tetrahedron*, 2012, **68**, 10464–10469.
3. B. M. Vieira, S. Thurow, M. da Costa, A. M. Casaril, M. Domingues, R. F. Schumacher, G. Perin, D. Alves, L. Savegnago and E. J. Lenardão, *Asian J. Org. Chem.*, 2017, **6**, 1635–1646.
4. S. Saba, J. Rafique, M. S. Franco, A. R. Schneider, L. Espíndola, D. O. Silva and A. L. Braga, *Org. Biomol. Chem.*, 2018, **16**, 880–885.
5. I. D. Lemir, W. D. Castro-Godoy, A. A. Heredia, L. C. Schmidt and J. E. Argüello, *RSC Adv.*, 2019, **9**, 22685–22694.
6. J. Rafique, S. Saba, M. S. Franco, L. Bettanin, A. R. Schneider, L. T. Silva and A. L. Braga, *Chem. - A Eur. J.*, 2018, **24**, 4173–4180.
7. H. Li, J. Wang, X. Wang and J. Yan, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2018, **193**, 394–399.
8. V. Rathore and S. Kumar, *Green Chem.*, 2019, **21**, 2670–2676.
9. N. L. Ferreira, J. B. Azeredo, B. L. Fiorentin and A. L. Braga, *European J. Org. Chem.*, 2015, **2015**, 5070–5074.
10. S.-Q. Chen, Q.-M. Wang, P.-C. Xu, S.-P. Ge, P. Zhong and X.-H. Zhang, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2016, **191**, 100–103.
11. C. D. Prasad, S. Kumar, M. Sattar, A. Adhikary and S. Kumar, *Org. Biomol. Chem.*, 2013, **11**, 8036–8040.
12. S. Q. Chen, Q. M. Wang, P. C. Xu, S. P. Ge, P. Zhong and X. H. Zhang, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2016, **191**, 100–103.
13. C. Liu, X. Peng, D. Hu, F. Shi, P. Huang, J. Luo, Q. Liu and L. Liu, *New J. Chem.*, 2020, **44**, 17245–17251.
14. M. Tan and Y. Zhang, *Tetrahedron Lett.*, 2009, **50**, 4912–4915.
15. R. Yang, S. Yue, W. Tan, Y. Xie and H. Cai, *J. Org. Chem.*, 2020, **85**, 7501–7509.

16. T. Liu, K. Wu, L. Wang and Z. Yu, *Adv. Synth. Catal.*, 2019, **361**, 3958–3964.
17. Y.-Z. Ji, J.-Y. Zhang, H.-J. Li, C. Han, Y.-K. Yang and Y.-C. Wu, *Org. Biomol. Chem.*, 2019, **17**, 4789–4800.

2. NMR Spectrums

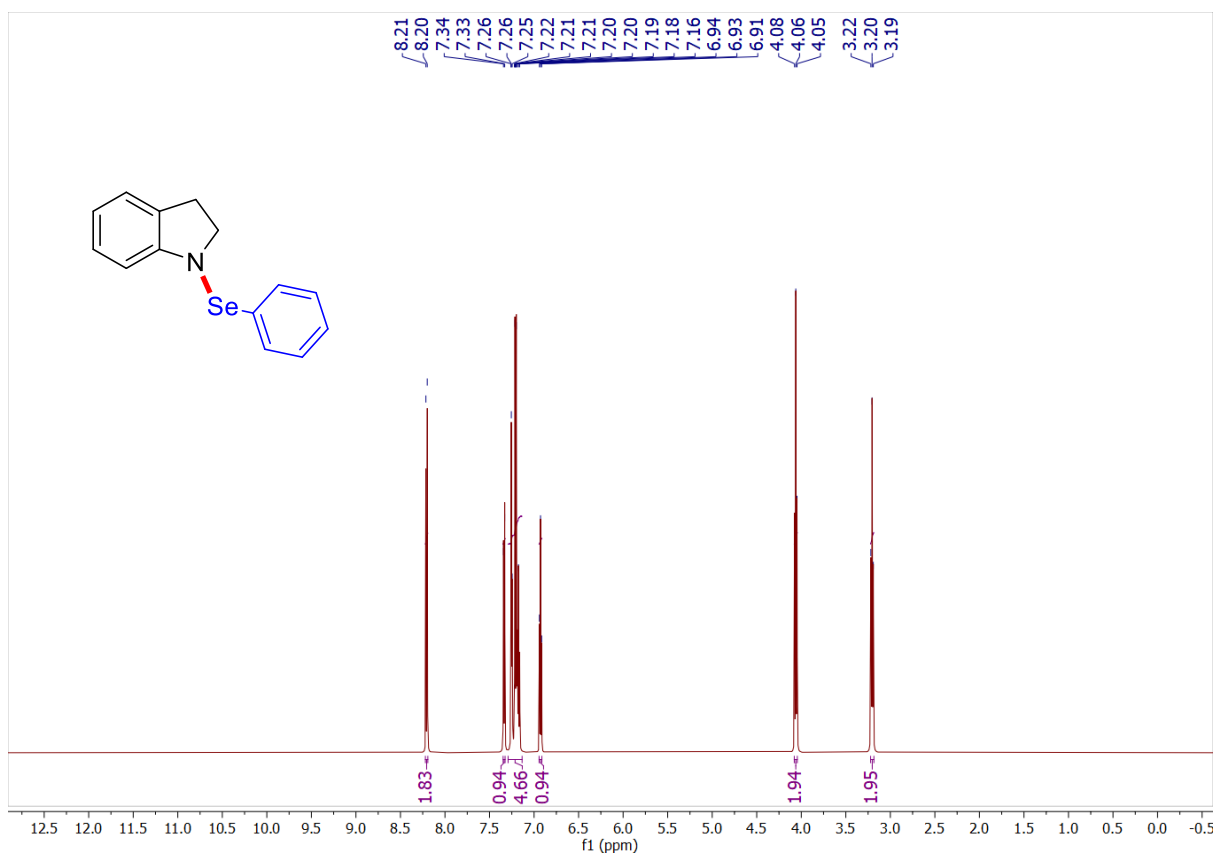


Figure 11: ¹H NMR (600 MHz, CDCl₃) spectrum of 1-(phenylselanyl)indoline (**1h**).

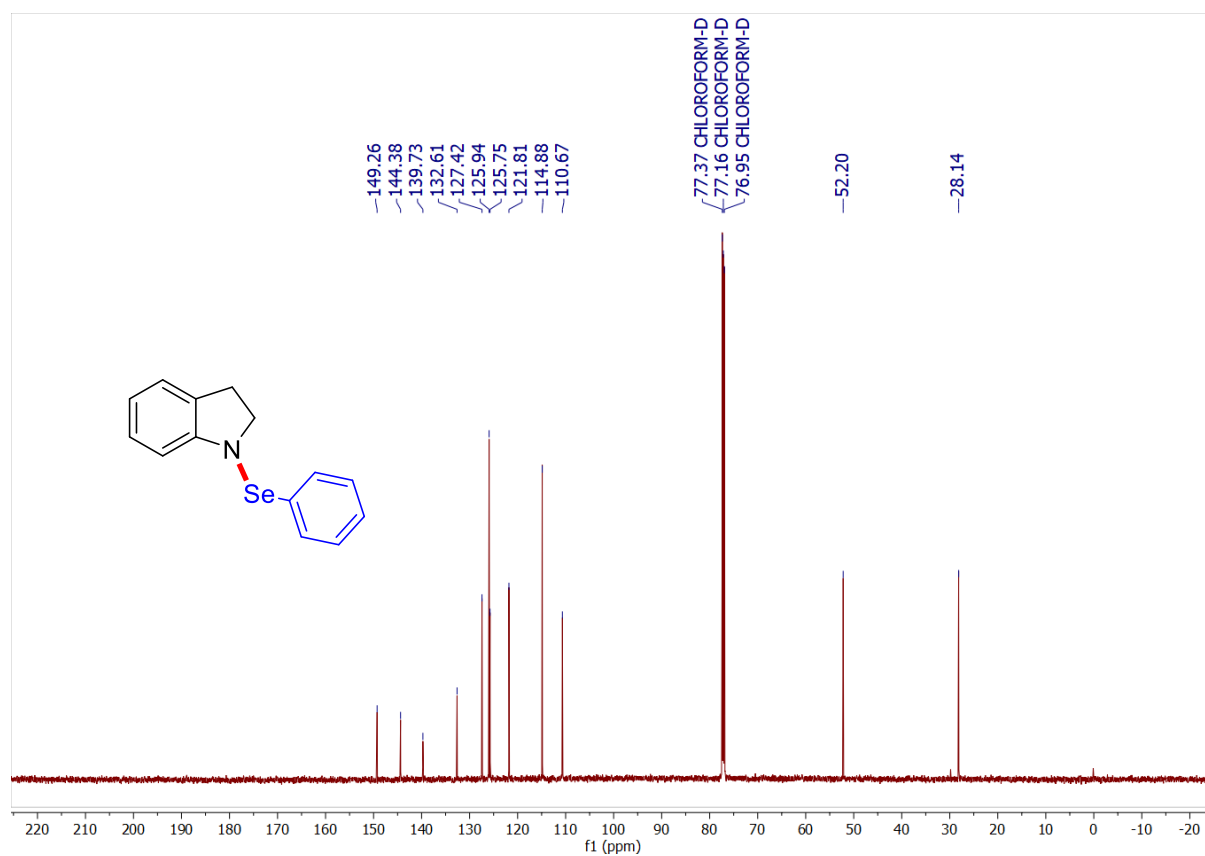


Figure 12: ^{13}C NMR (600 MHz, CDCl_3) spectrum of 1-(phenylselanyl)indoline (**1h**).

SM1_230315155251 #17-34 RT: 0.14-0.27 AV: 18 SB: 1 0.33 NL: 9.79E5
T: FTMS + c ESI Full ms [100.00-750.00]

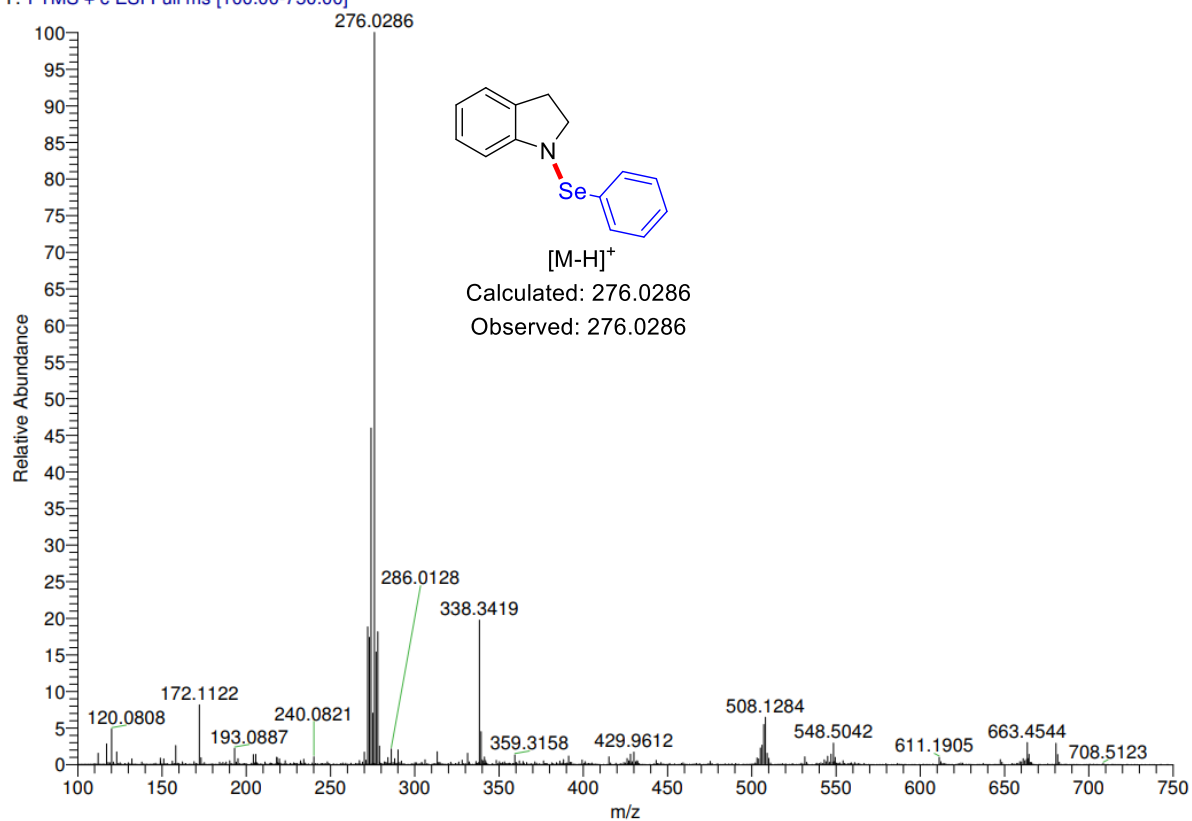


Figure 13: HRMS of 1-(phenylselanyl)indoline (**1h**).

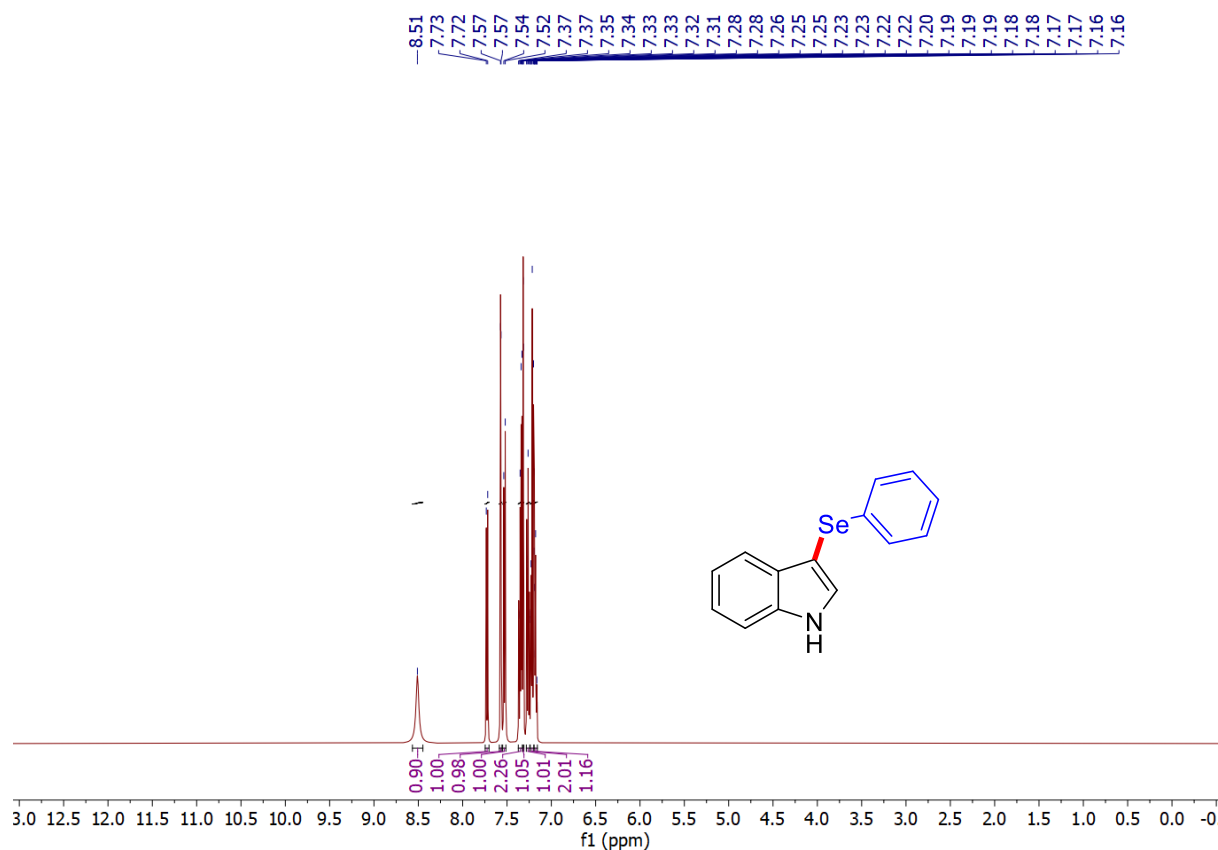


Figure 14: ¹H NMR (500 MHz, CDCl₃) spectrum of 3-(phenylselanyl)-1H-indole (**3a**).

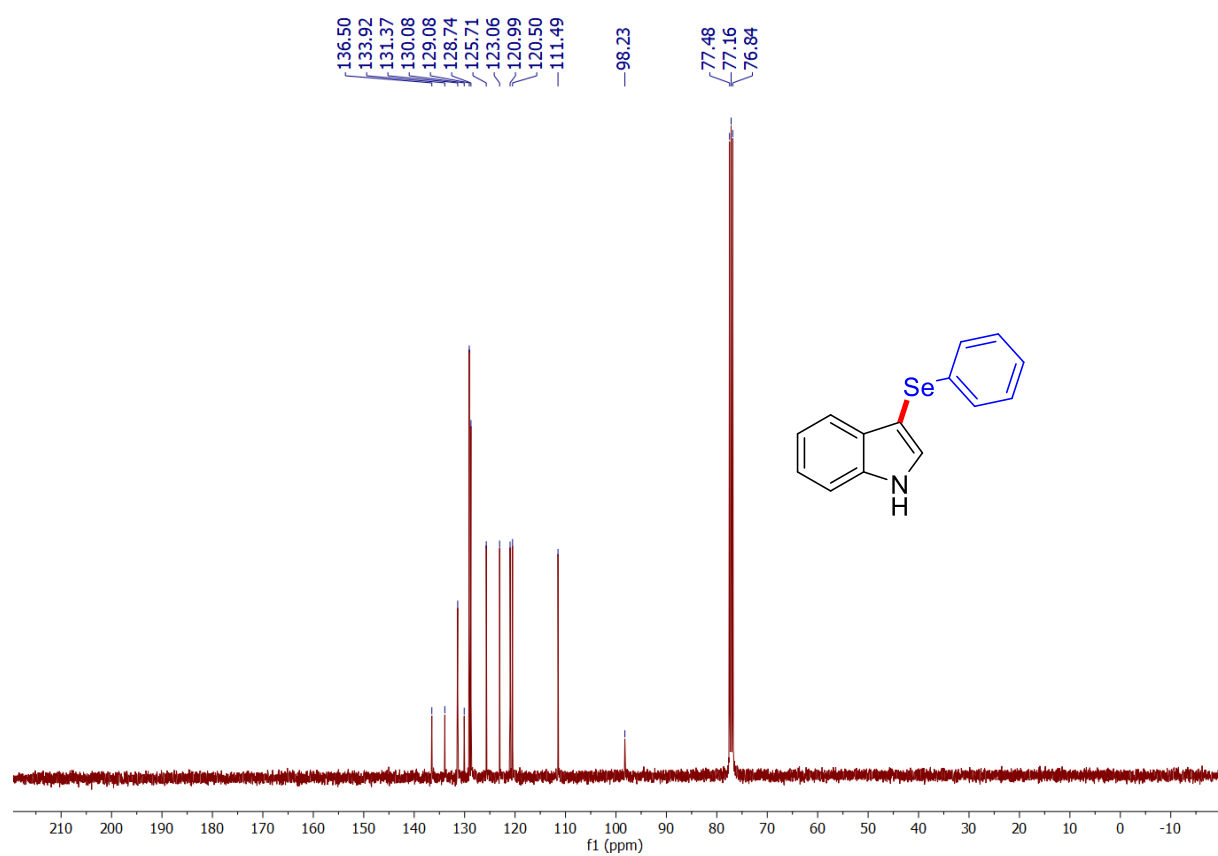


Figure 15: ¹³C NMR (500 MHz, CDCl₃) spectrum of 3-(phenylselanyl)-1H-indole (**3a**).

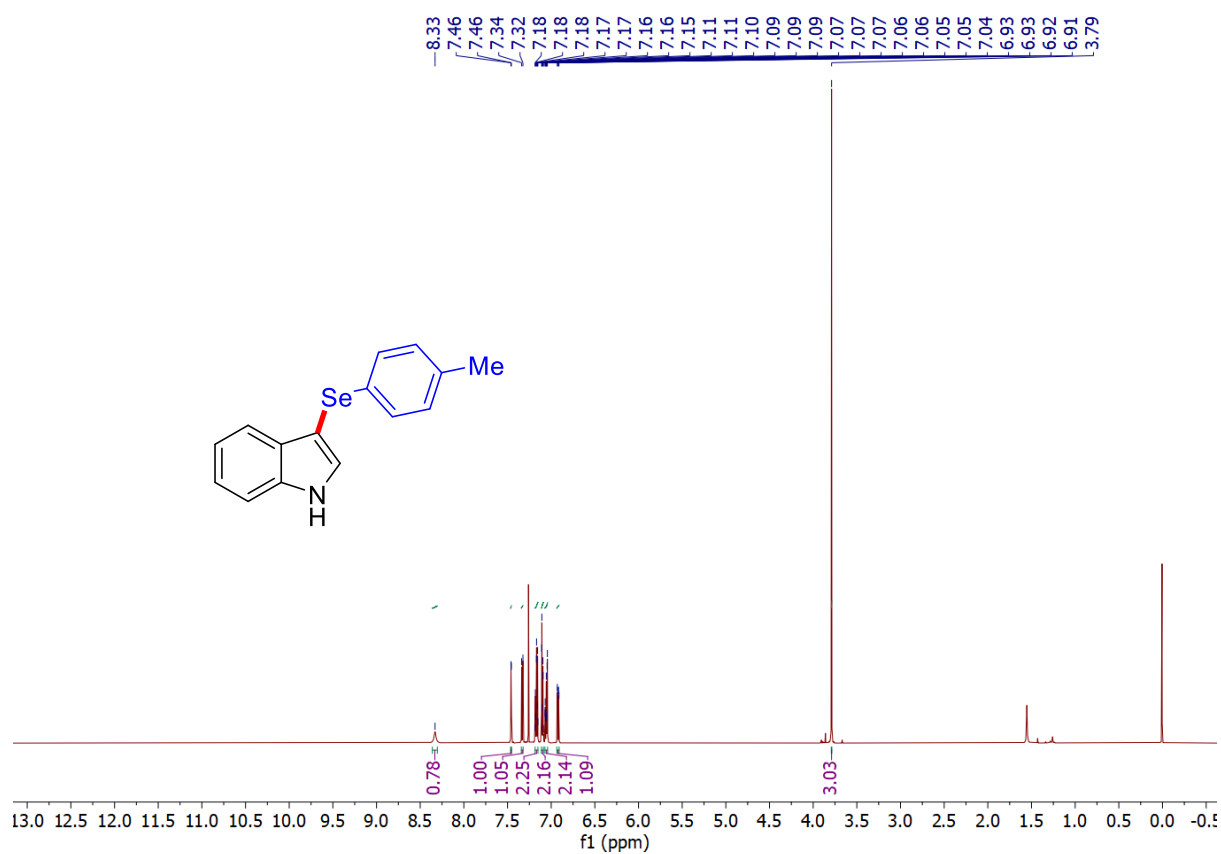


Figure 16: ¹H NMR (600 MHz, CDCl₃) spectrum of 3-(*p*-tolylselanyl)-1*H*-indole (**3b**).

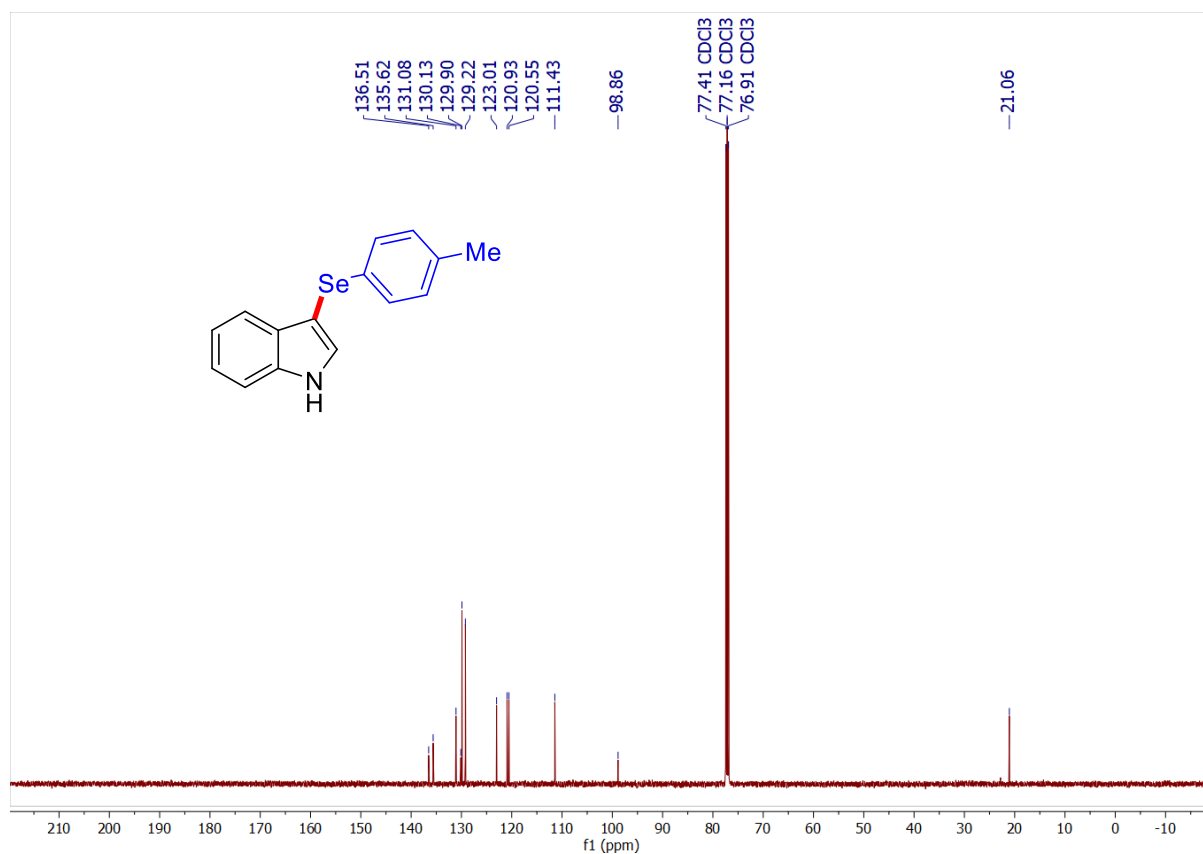


Figure 17: ¹³C NMR (126 MHz, CDCl₃) spectrum of 3-(*p*-tolylselanyl)-1*H*-indole (**3b**).

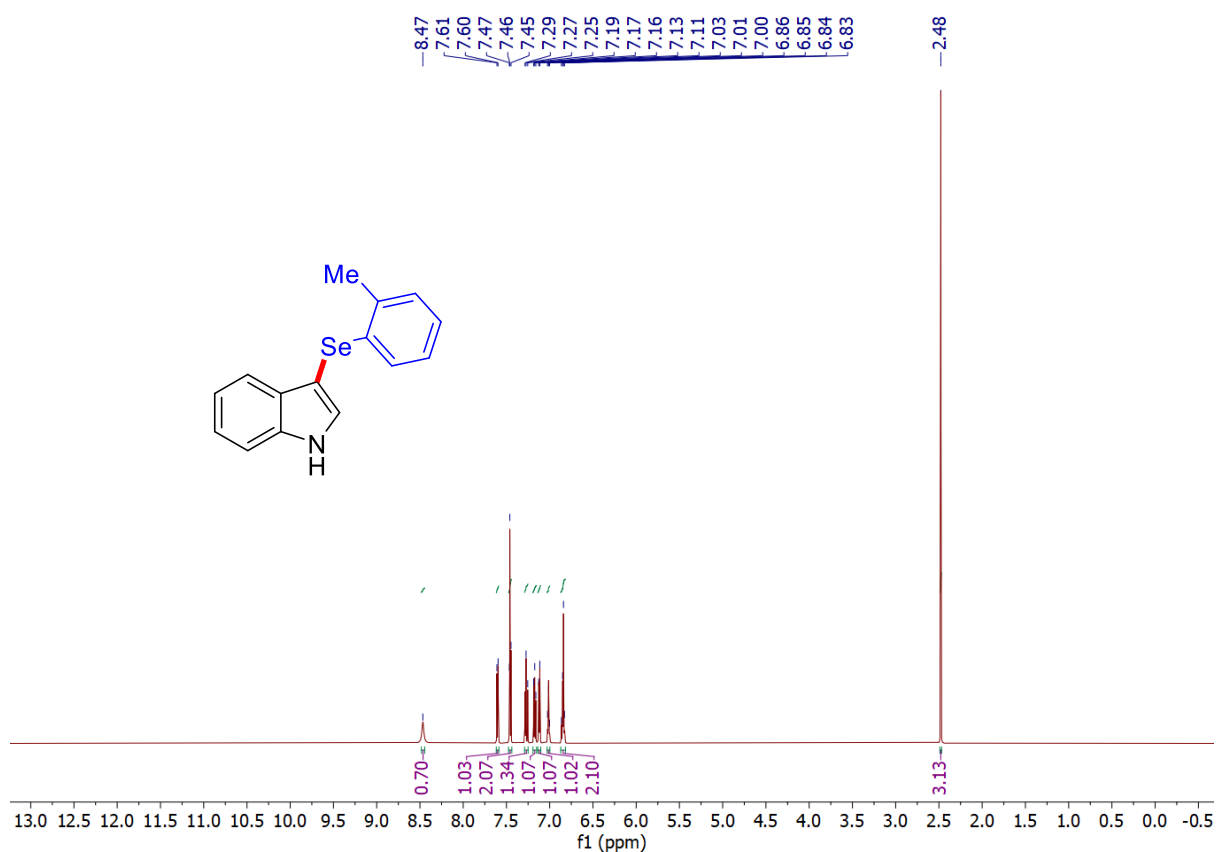


Figure 18: ¹H NMR (500 MHz, CDCl₃) spectrum of 3-(*o*-tolylselanyl)-1*H*-indole (3c).

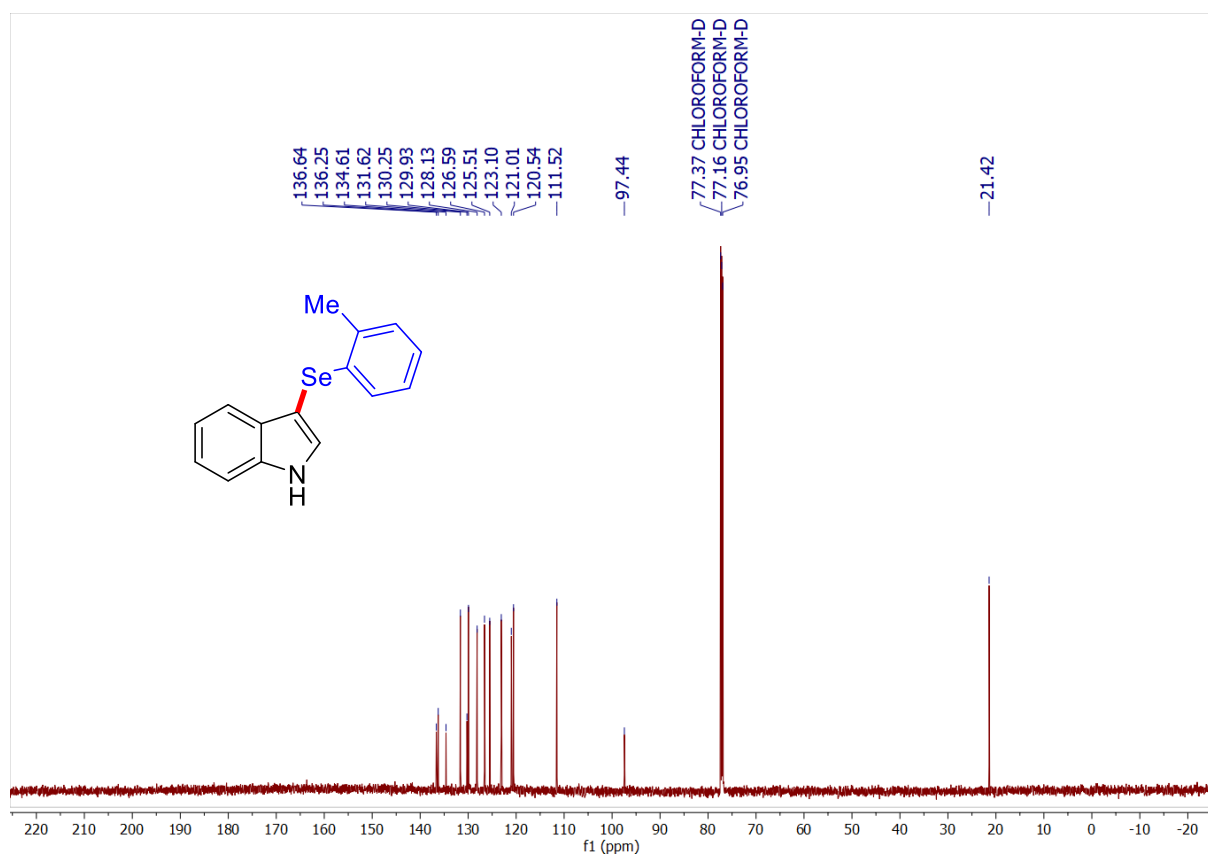


Figure 19: ¹³C NMR (151 MHz, CDCl₃) spectrum of 3-(*o*-tolylselanyl)-1*H*-indole (3c).

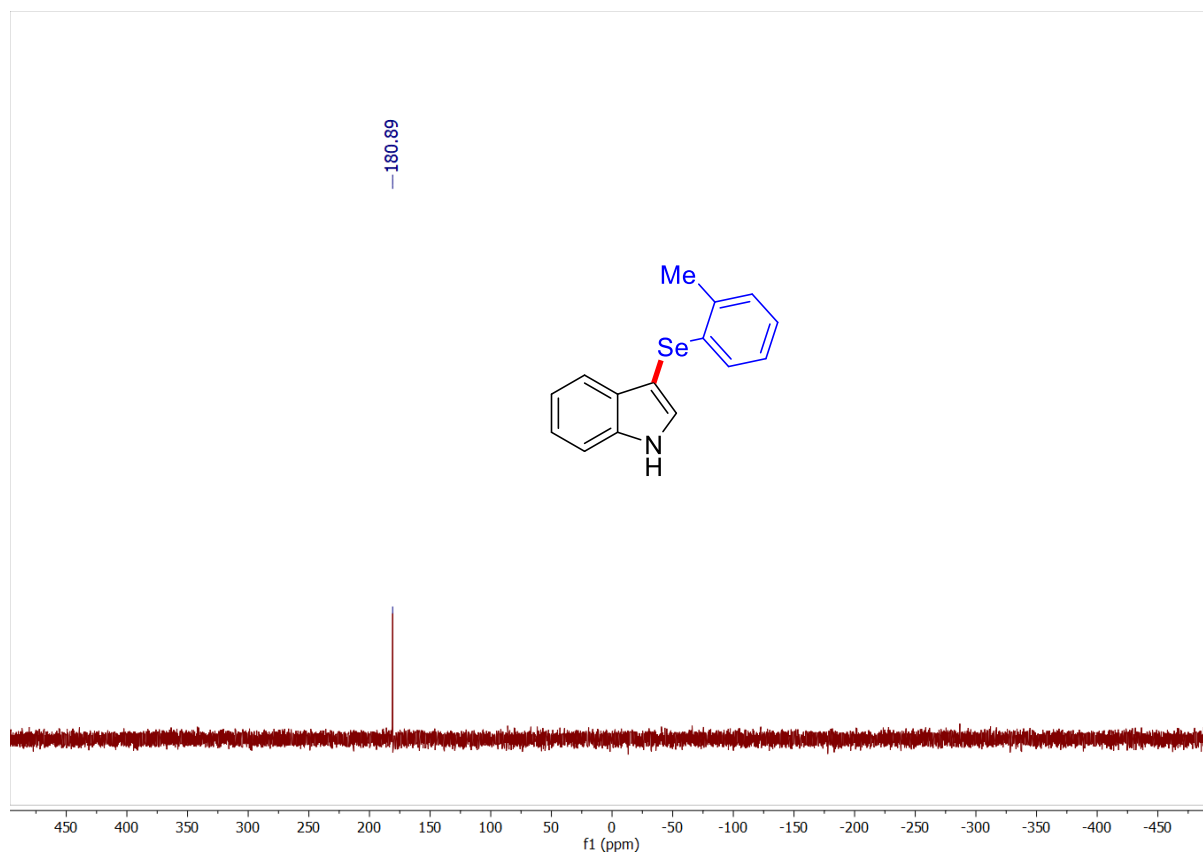


Figure 20: ⁷⁷Se NMR (114 MHz, CDCl₃) spectrum of 3-(*o*-tolylselanyl)-1*H*-indole (3c)

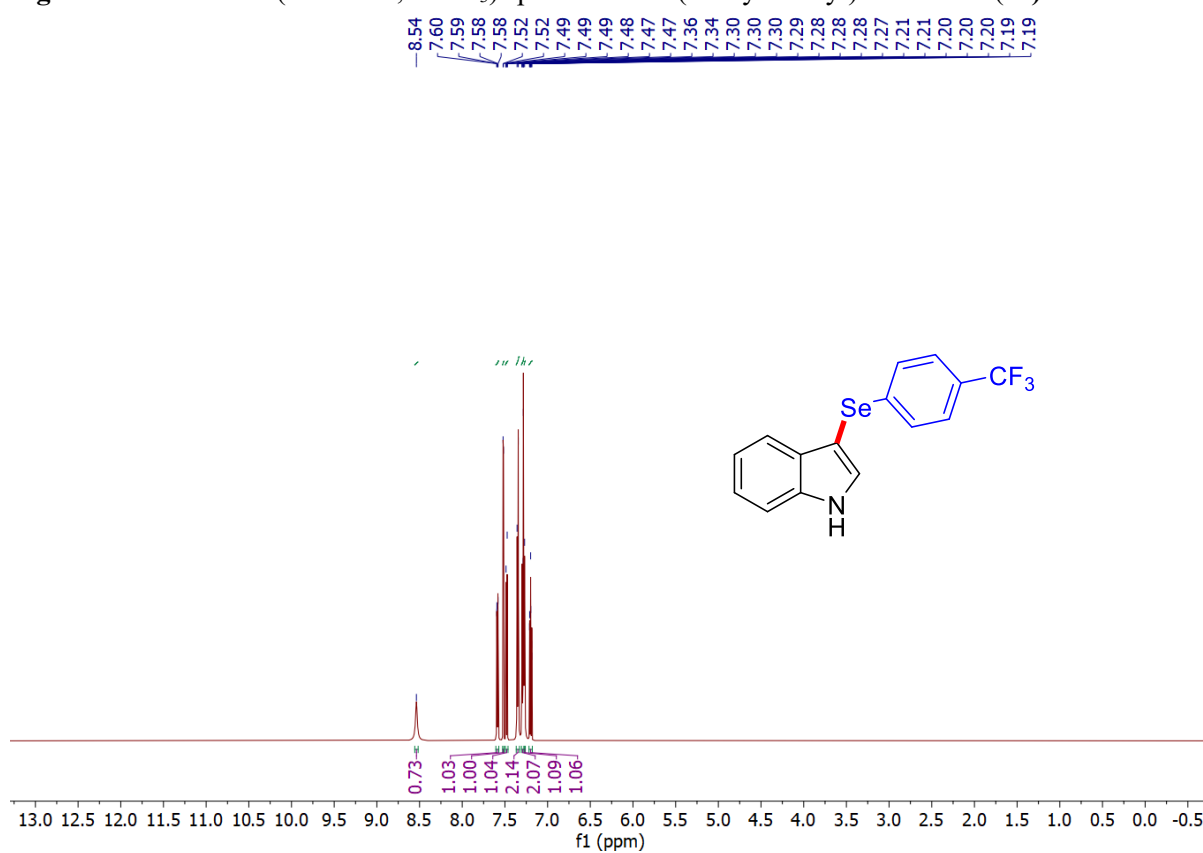


Figure 21: ¹H NMR (600 MHz, CDCl₃) spectrum of 3-((4-(trifluoromethyl)phenyl)selanyl)-1*H*-indole (3d).

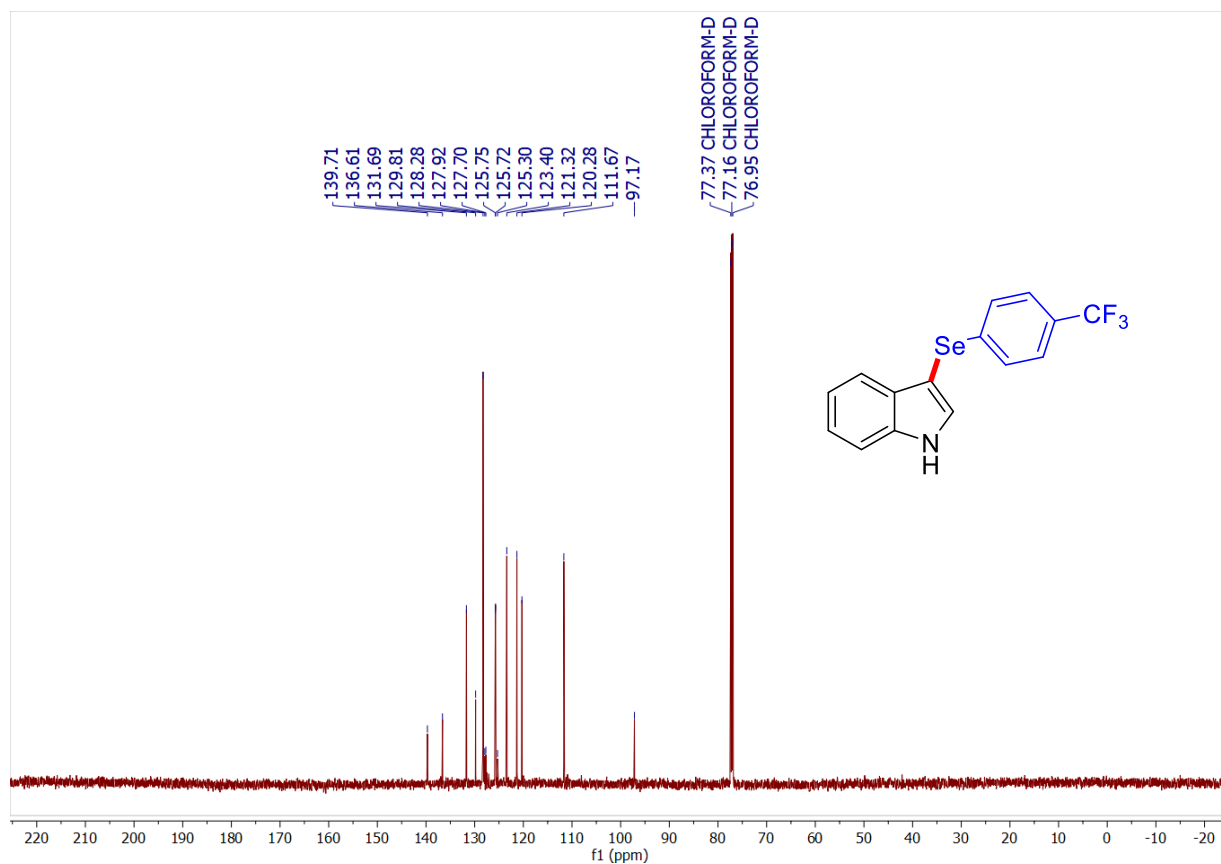


Figure 22: ¹³C NMR (151 MHz, CDCl₃) spectrum of 3-((4-(trifluoromethyl)phenyl)selenanyl)-1H-indole (3d)

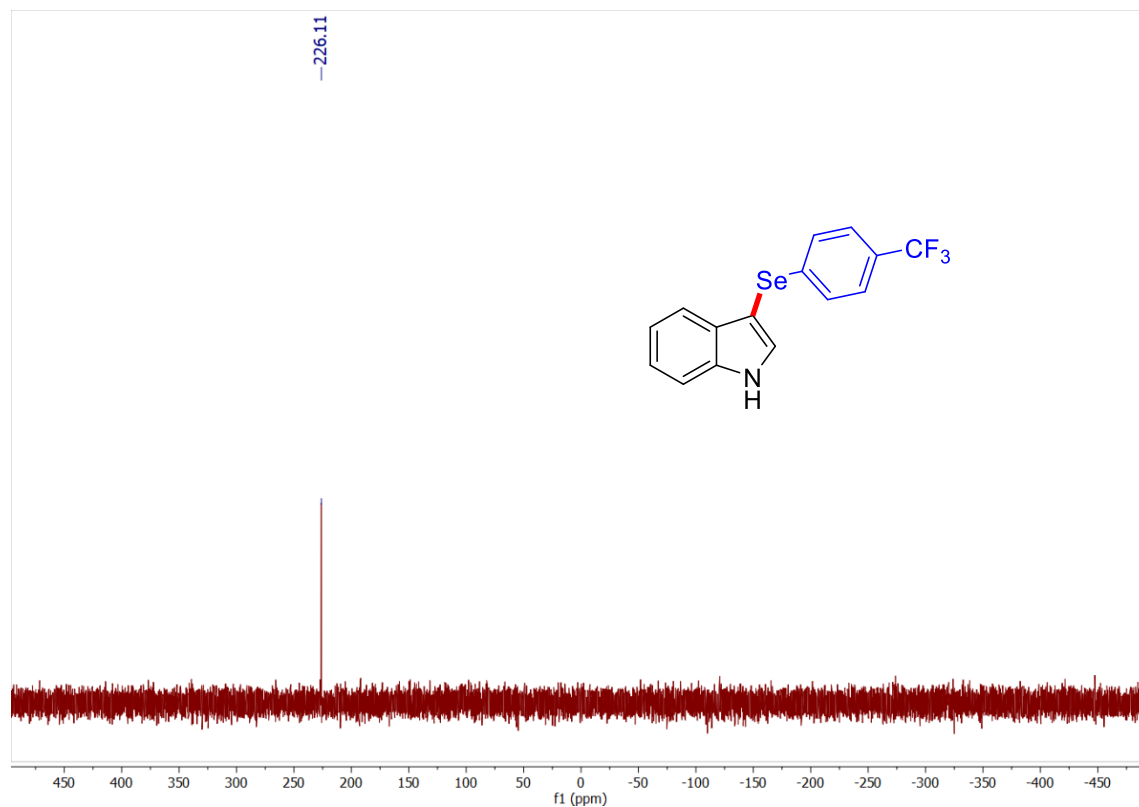


Figure 23: ⁷⁷Se NMR (114 MHz, CDCl₃) spectrum of 3-((4-(trifluoromethyl)phenyl)selenanyl)-1H-indole (3d).

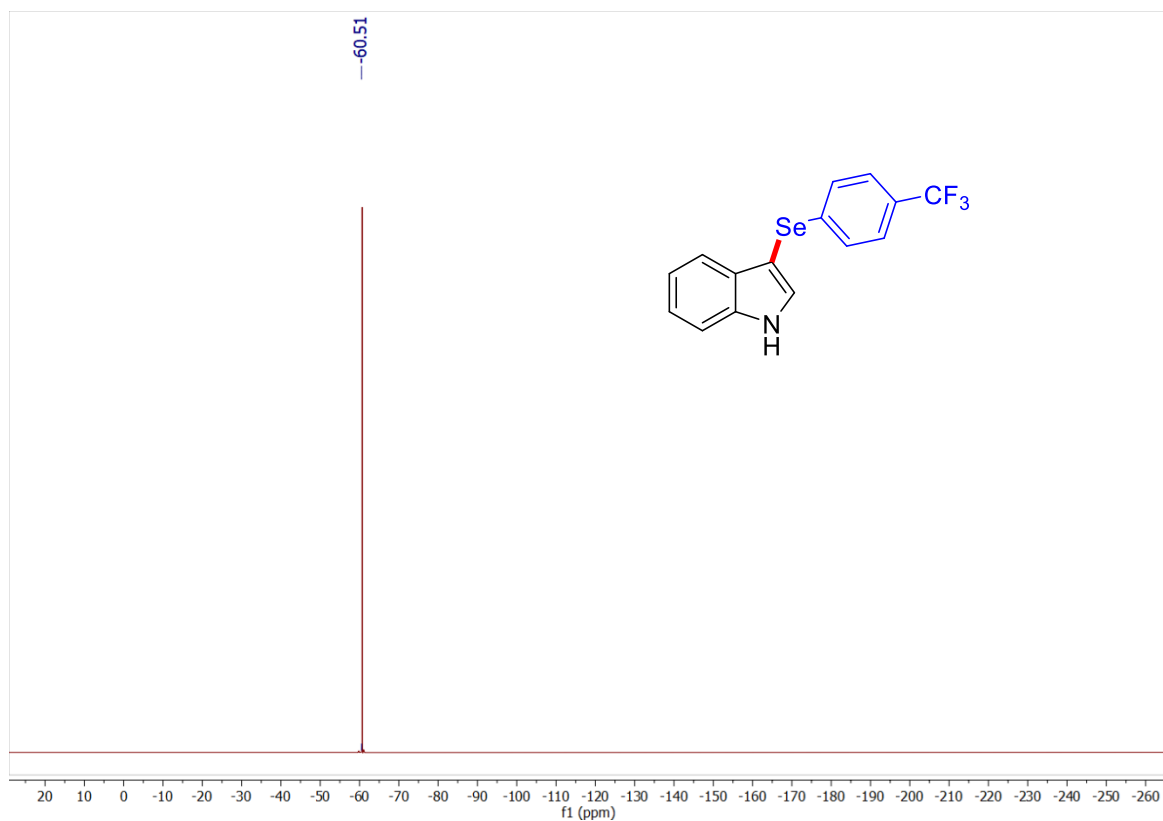


Figure 24: ¹⁹F NMR (565 MHz, CDCl₃) spectrum of 3-((4-(trifluoromethyl)phenyl)selanyl)-1H-indole (3d).

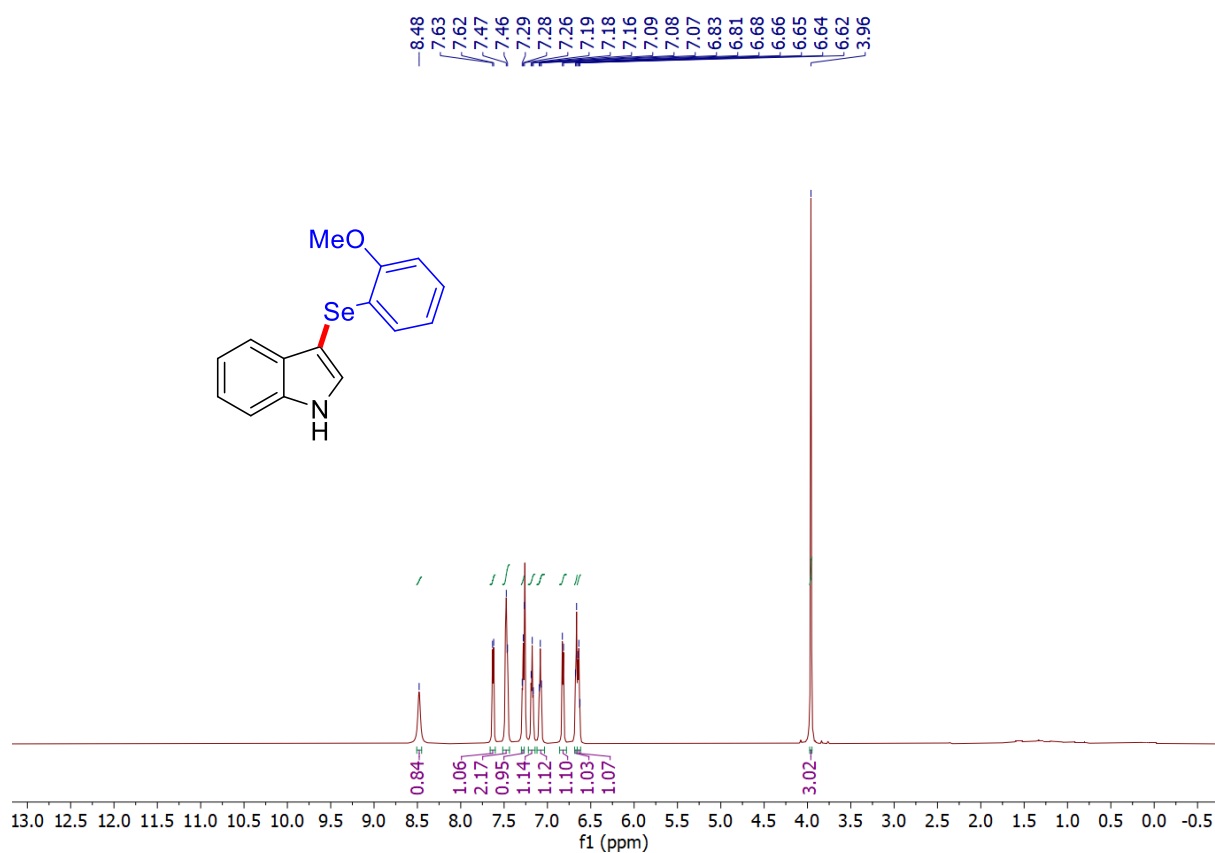


Figure 25: ¹H NMR (600 MHz, CDCl₃) spectrum of 3-((2-methoxyphenyl)selanyl)-1H-indole (3e).

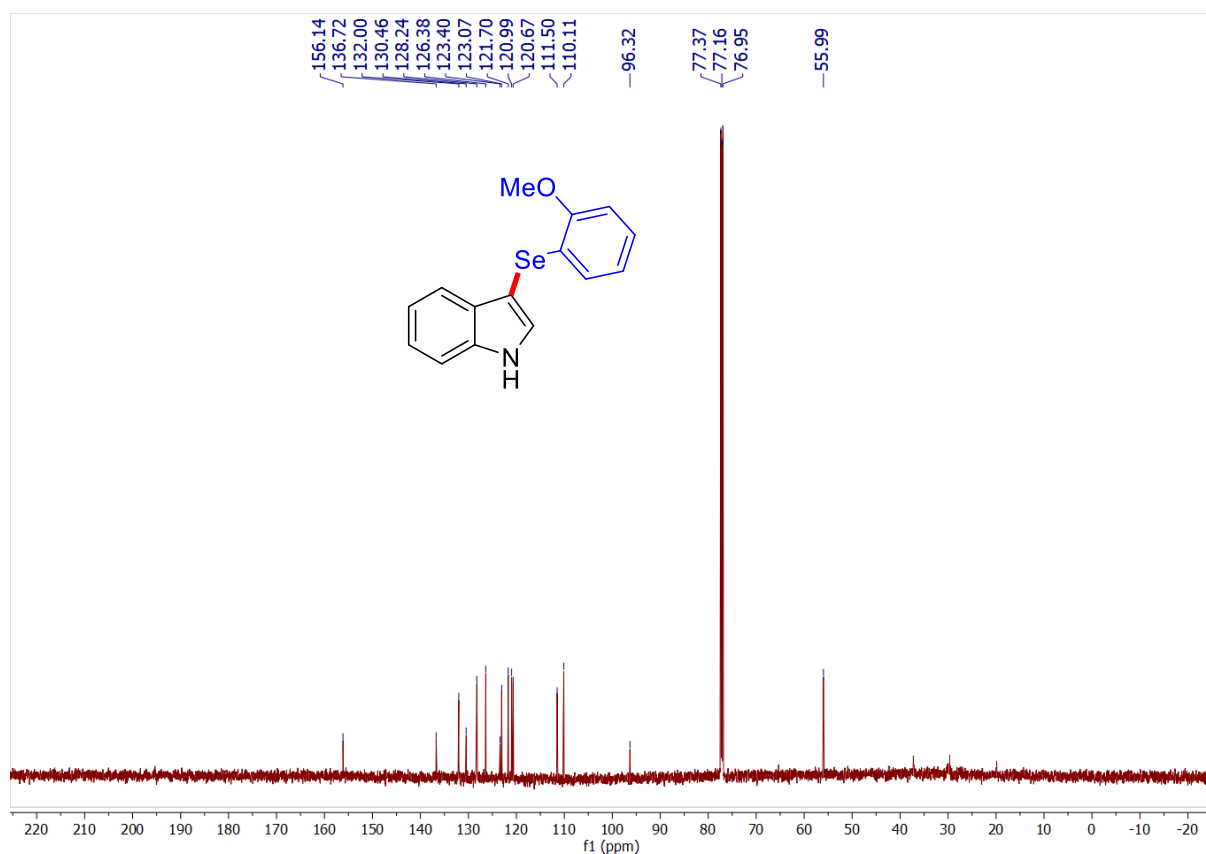


Figure 26: ¹³C NMR (151 MHz, CDCl₃) spectrum of 3-((2-methoxyphenyl)selanyl)-1H-indole (**3e**).

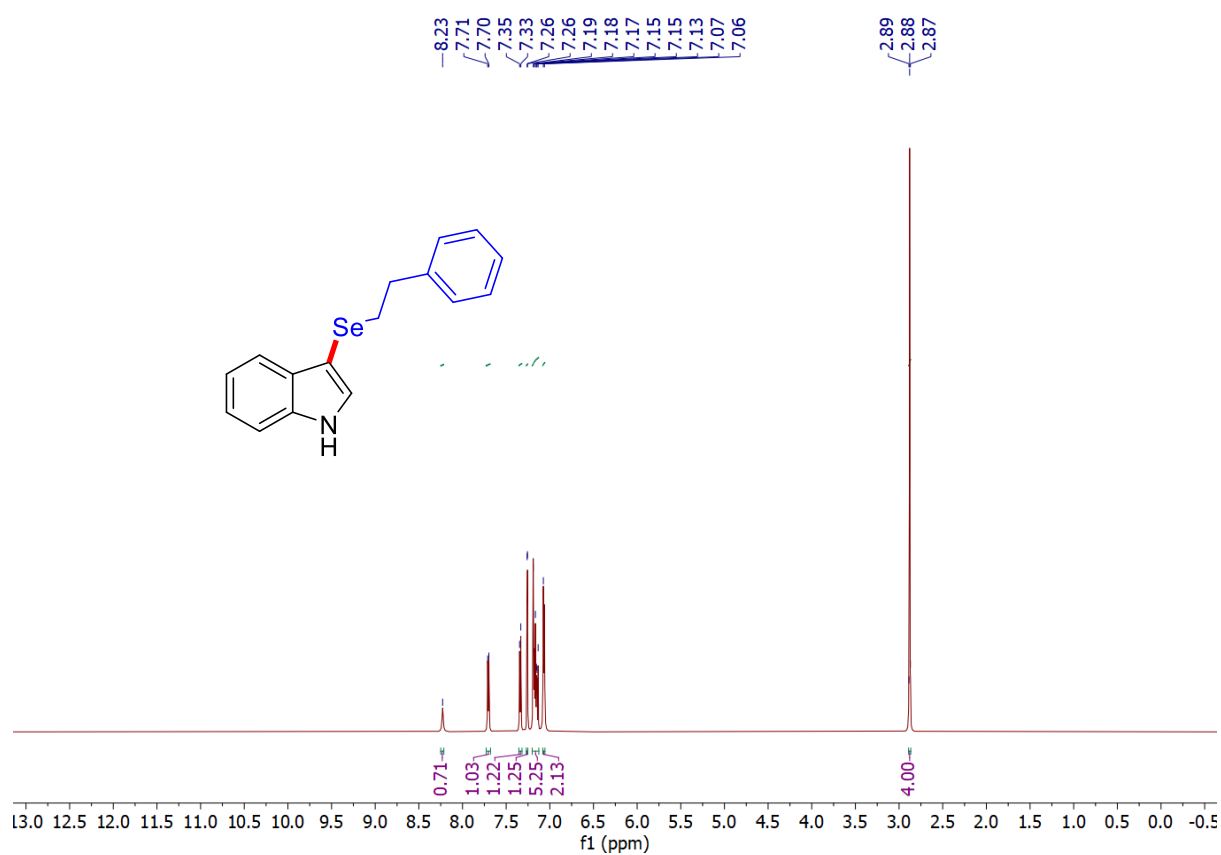


Figure 27: ¹H NMR (600 MHz, CDCl₃) spectrum of 3-(phenethylselanyl)-1H-indole (**3f**).

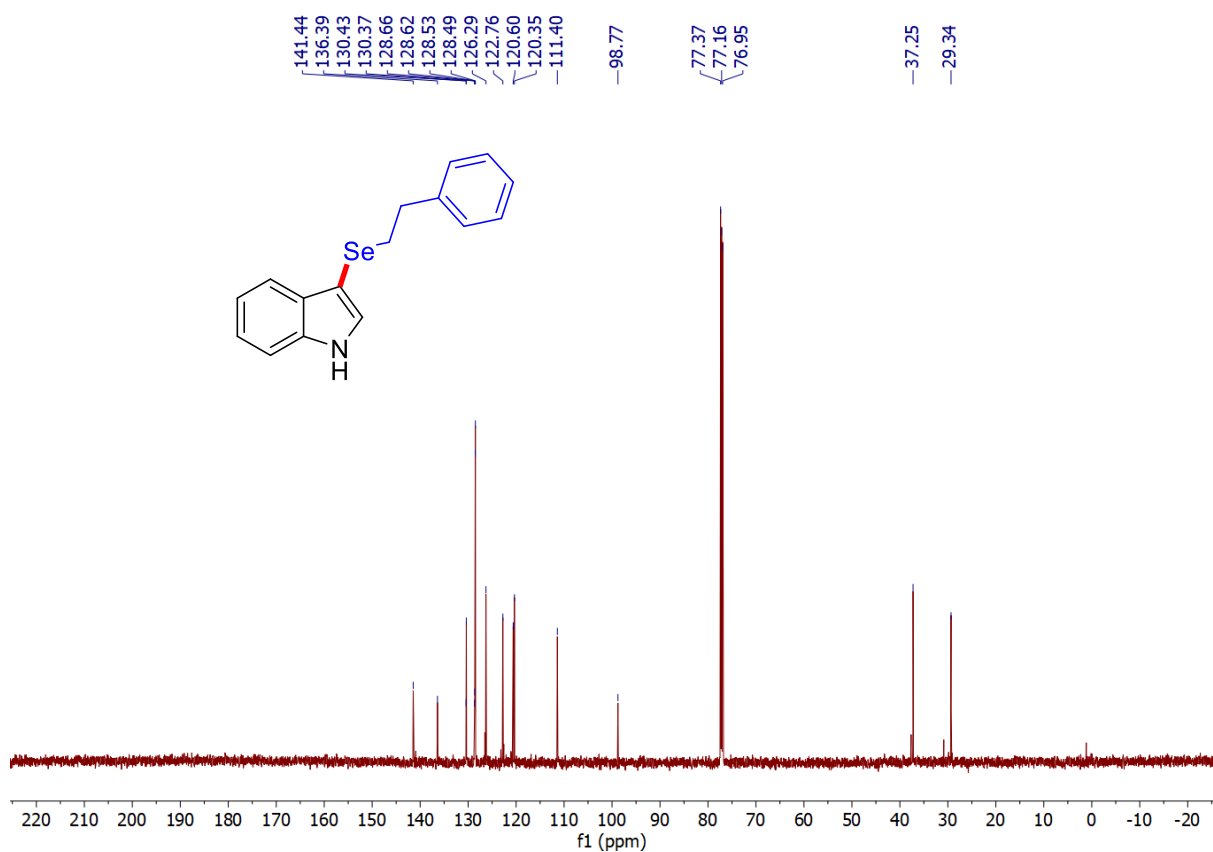


Figure 28: ¹³C NMR (151 MHz, CDCl₃) spectrum of 3-(phenethylselanyl)-1H-indole(3f).

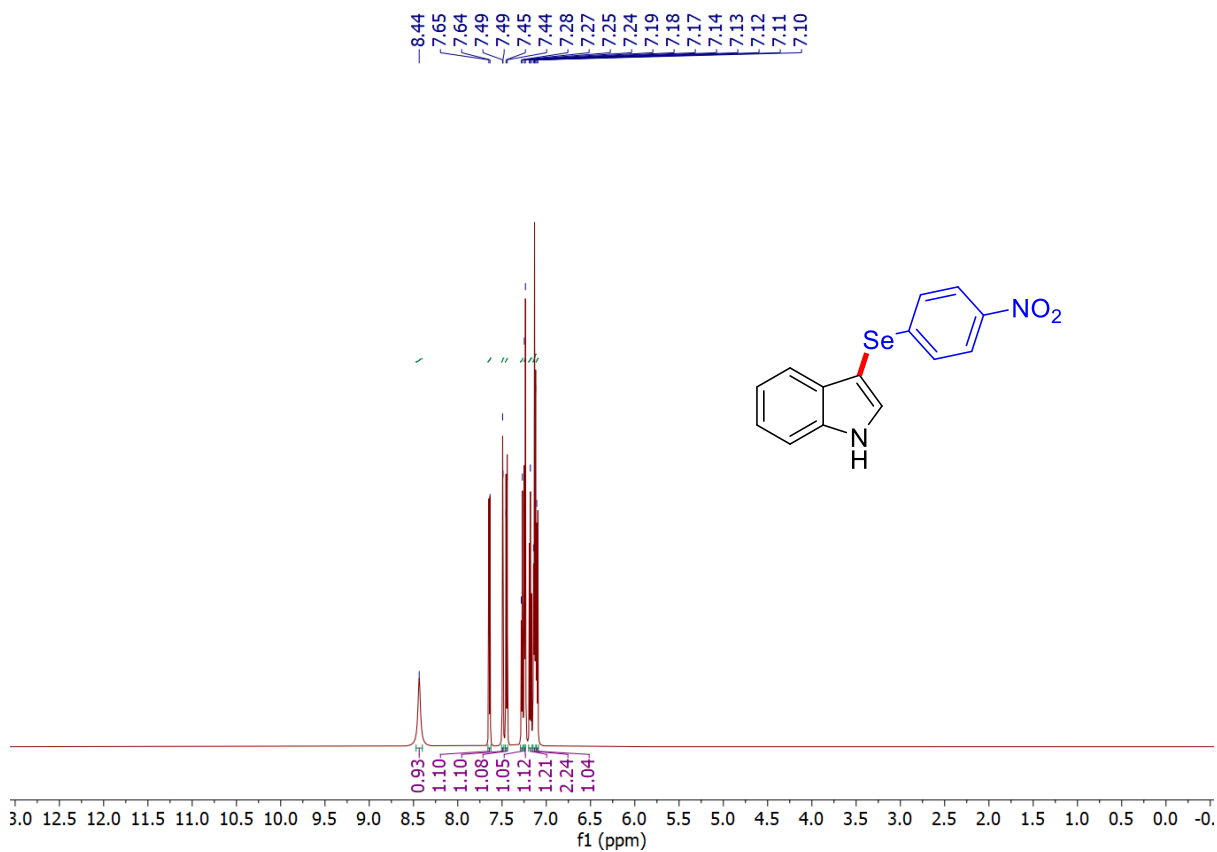


Figure 29: ¹H NMR (600 MHz, CDCl₃) spectrum of 3-((4-nitrophenyl)selanyl)-1H-indole (3g).

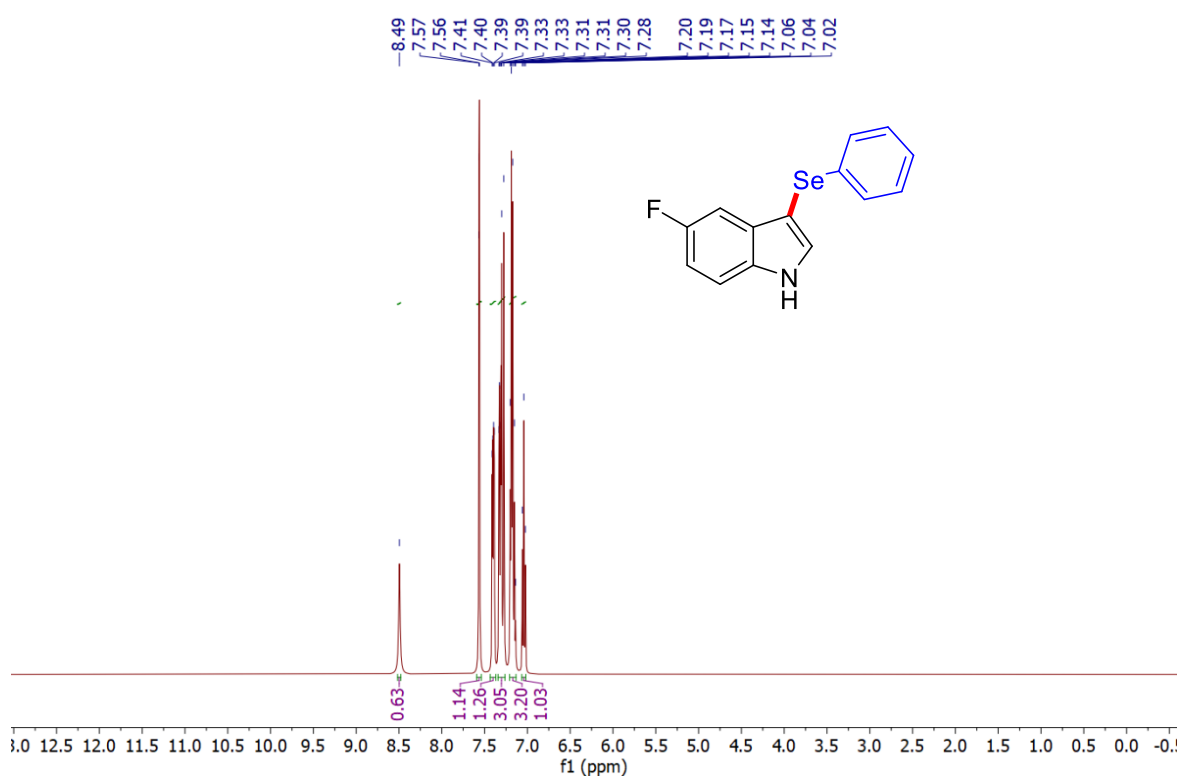


Figure 30: ¹H NMR (500 MHz, CDCl₃) spectrum of 5-fluoro-3-(phenylselanyl)-1*H*-indole (**3h**).

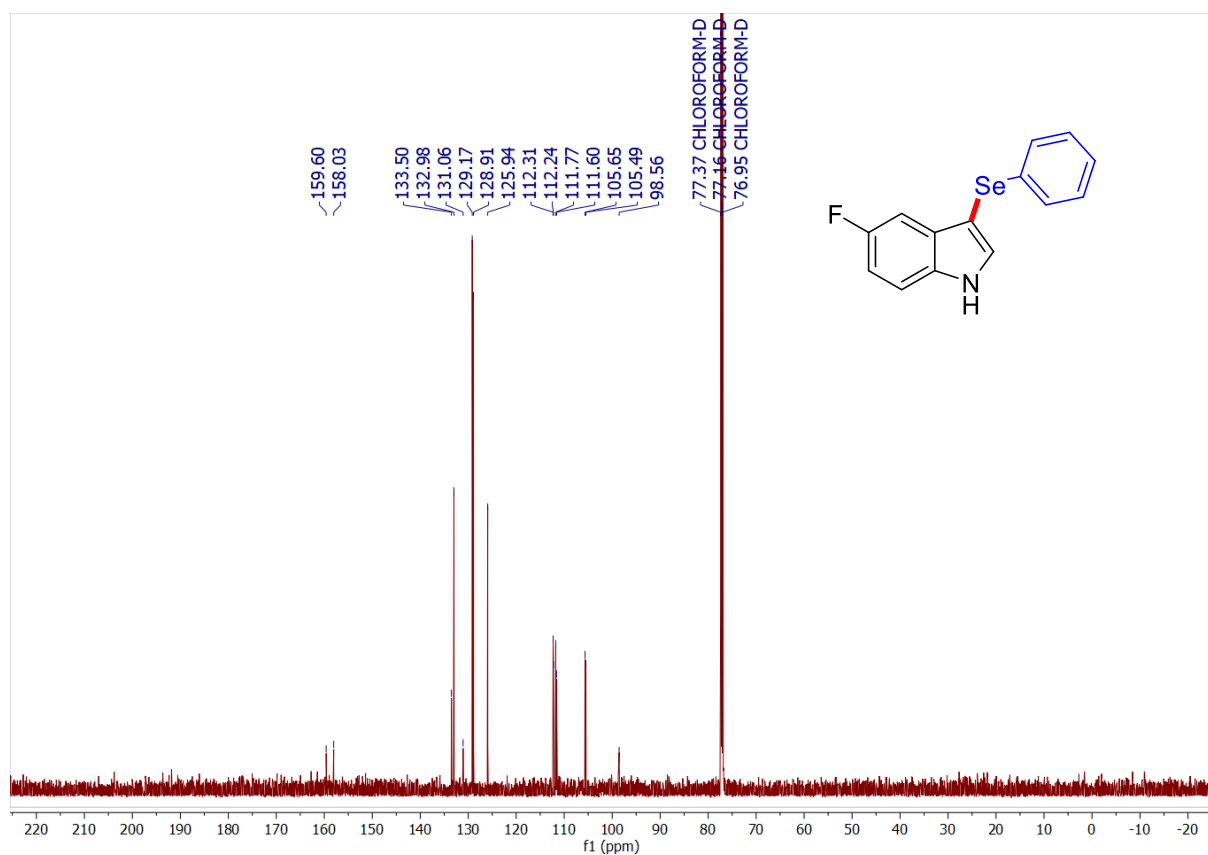


Figure 31: ¹³C NMR (151 MHz, CDCl₃) spectrum of 5-fluoro-3-(phenylselanyl)-1*H*-indole (**3h**).

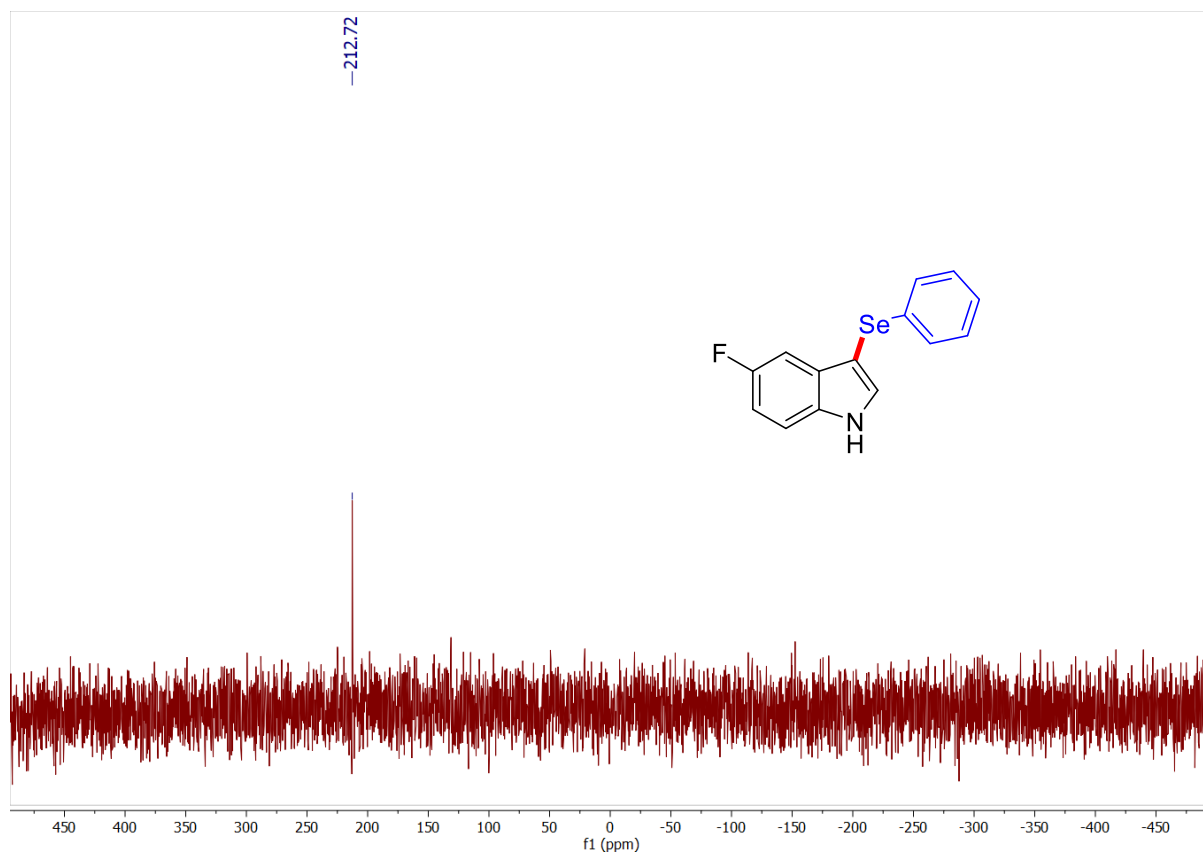


Figure 32: ⁷⁷Se NMR (114 MHz, CDCl₃) spectrum of 5-fluoro-3-(phenylselanyl)-1H-indole (3h).

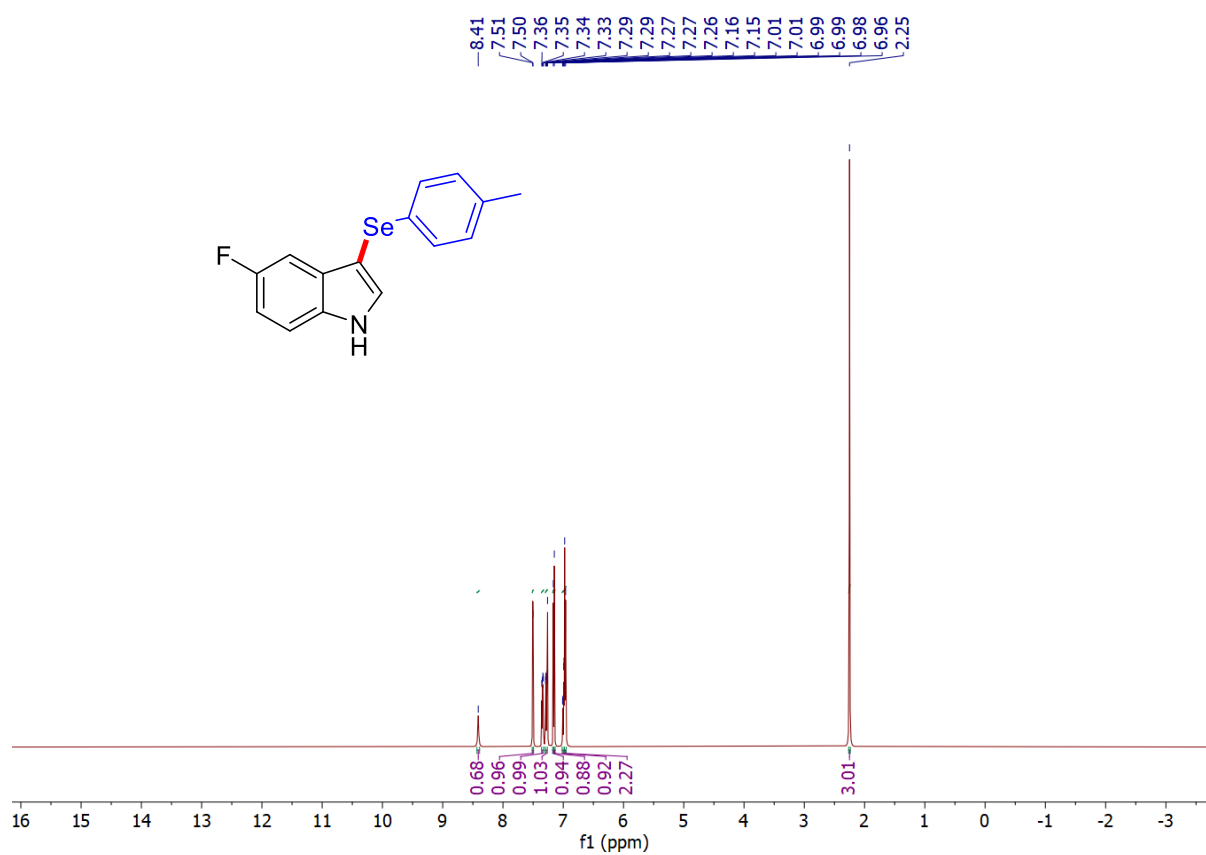


Figure 33: ¹H NMR (500 MHz, CDCl₃) spectrum of 5-fluoro-3-(p-tolylselanyl)-1H-indole (3i).

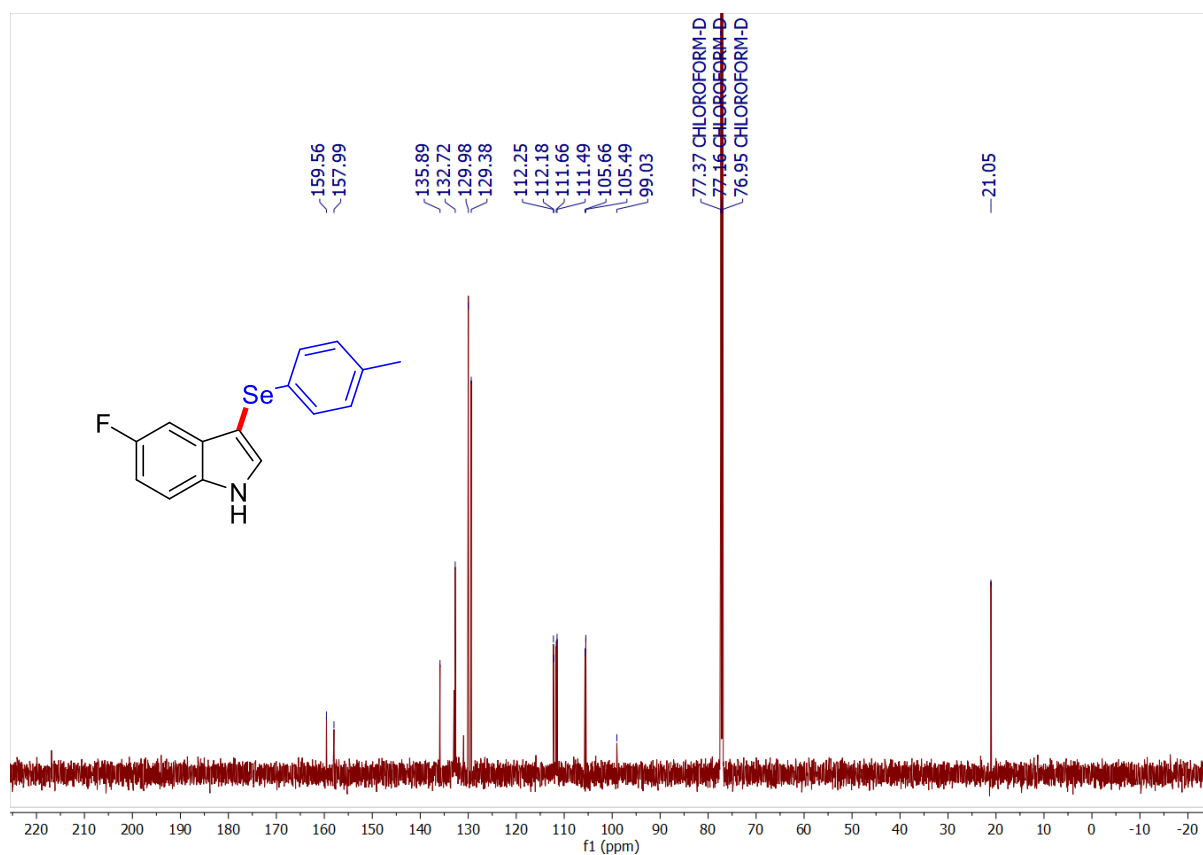


Figure 34: ¹³C NMR (151 MHz, CDCl₃) spectrum of 5-fluoro-3-(*p*-tolylselanyl)-1*H*-indole (**3i**).

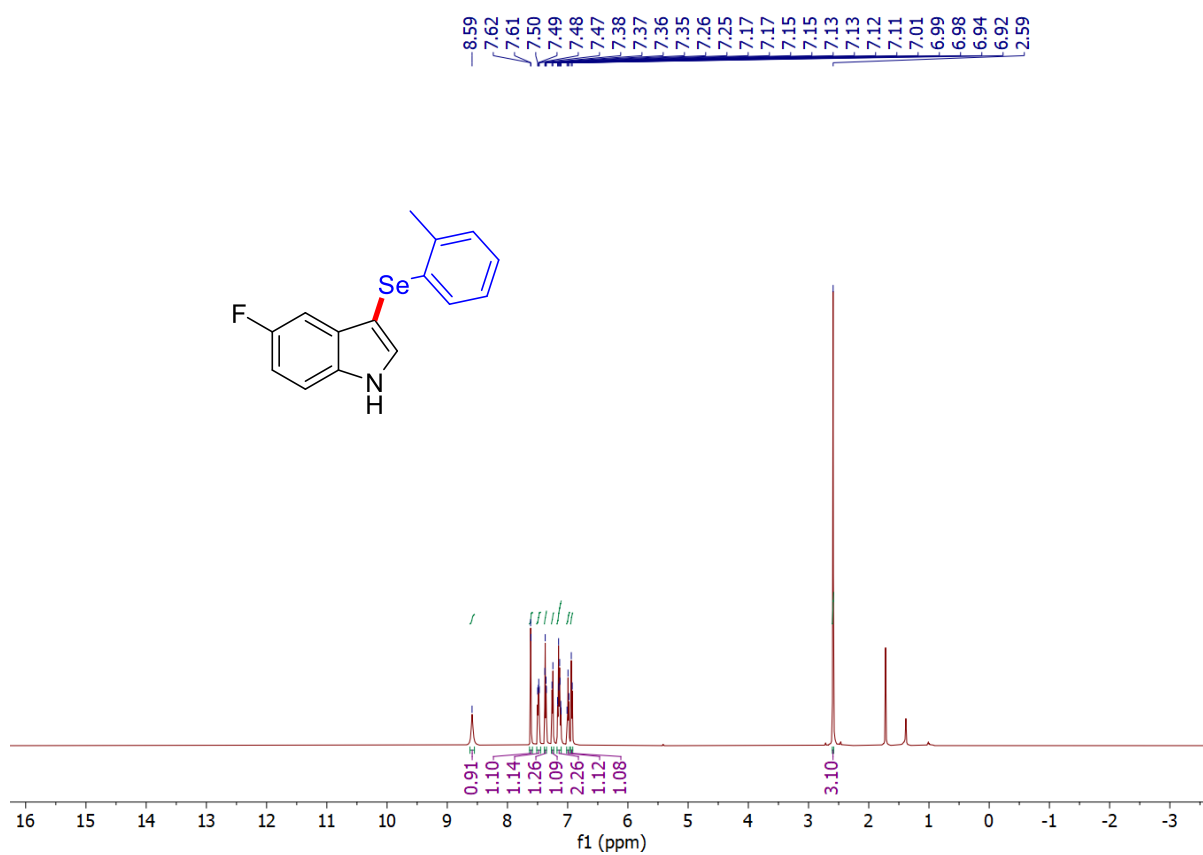


Figure 35: ¹H NMR (500 MHz, CDCl₃) spectrum of 5-fluoro-3-(*o*-tolylselanyl)-1*H*-indole (**3j**).

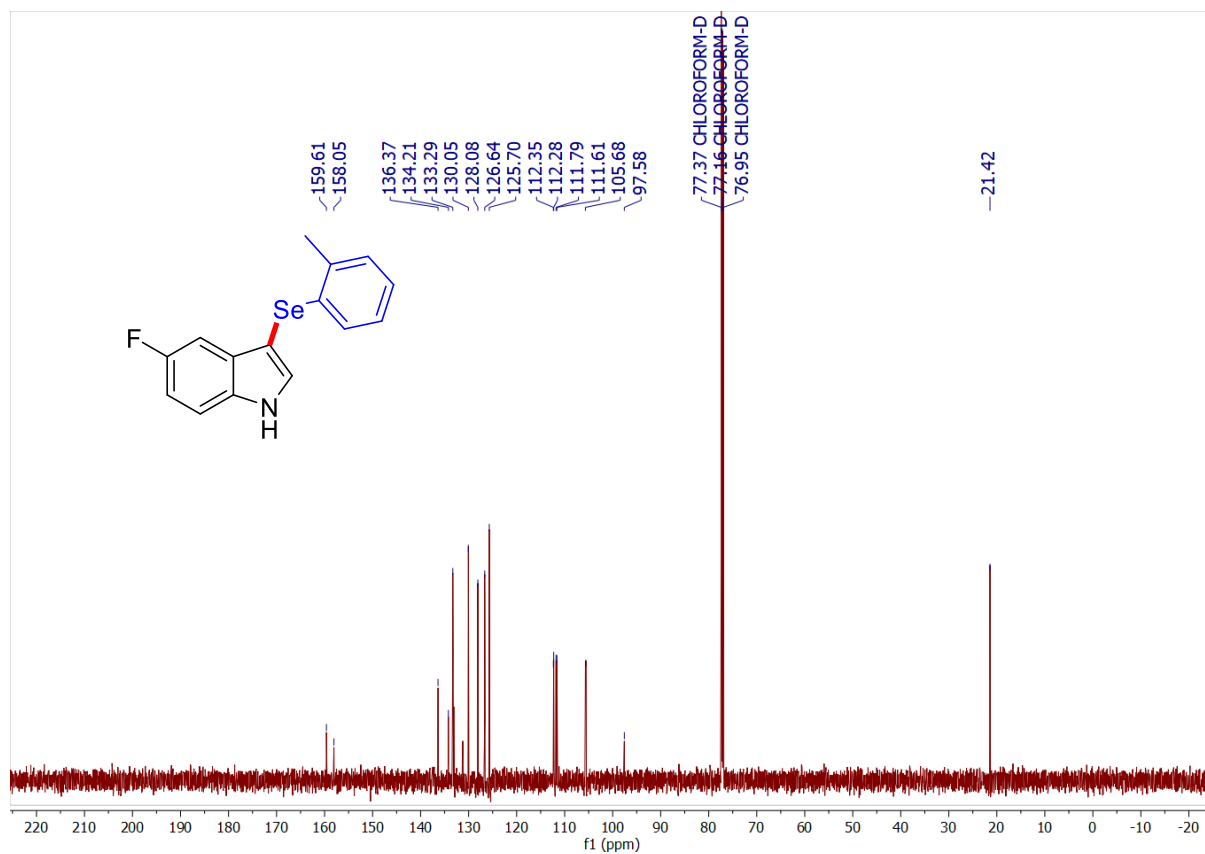


Figure 36: ¹³C NMR (151 MHz, CDCl₃) spectrum of 5-fluoro-3-(*o*-tolylselanyl)-1*H*-indole (3j).

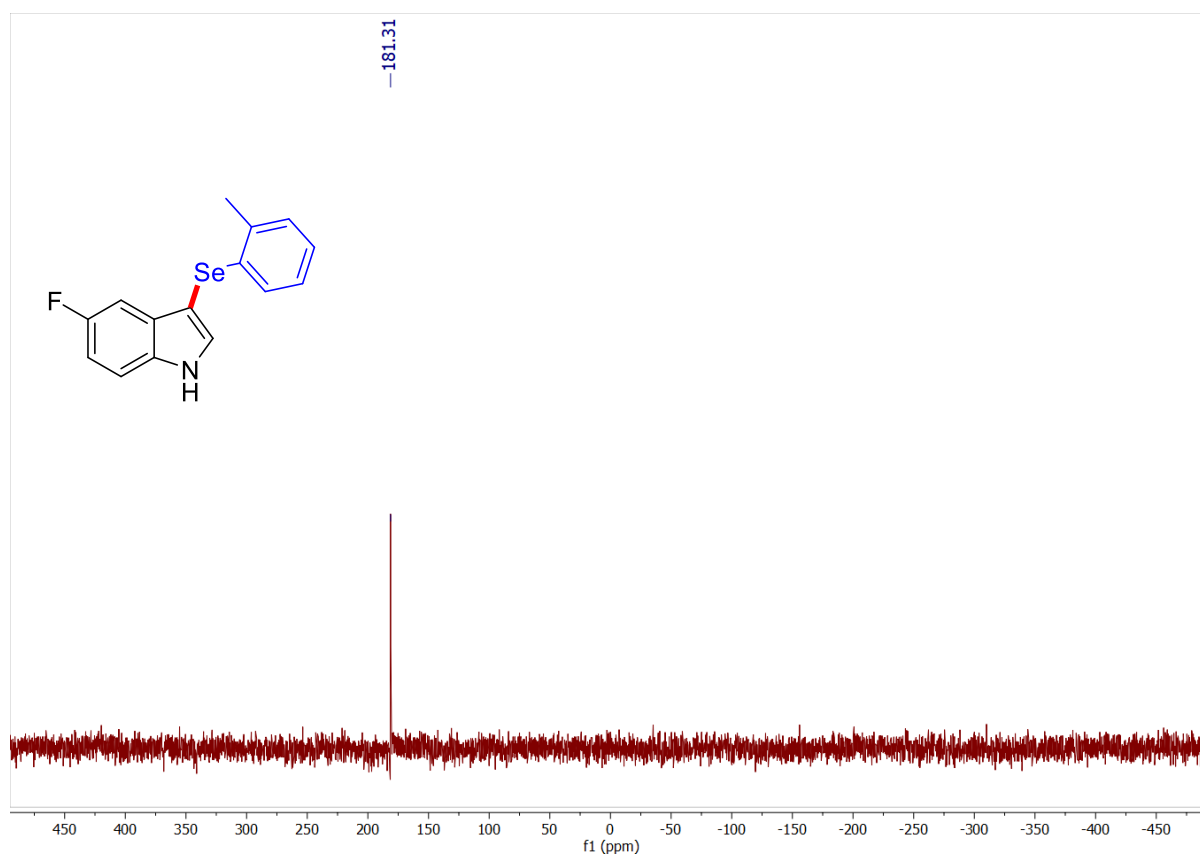


Figure 37: ⁷⁷Se NMR (114 MHz, CDCl₃) spectrum of 5-fluoro-3-(*o*-tolylselanyl)-1*H*-indole (3j).

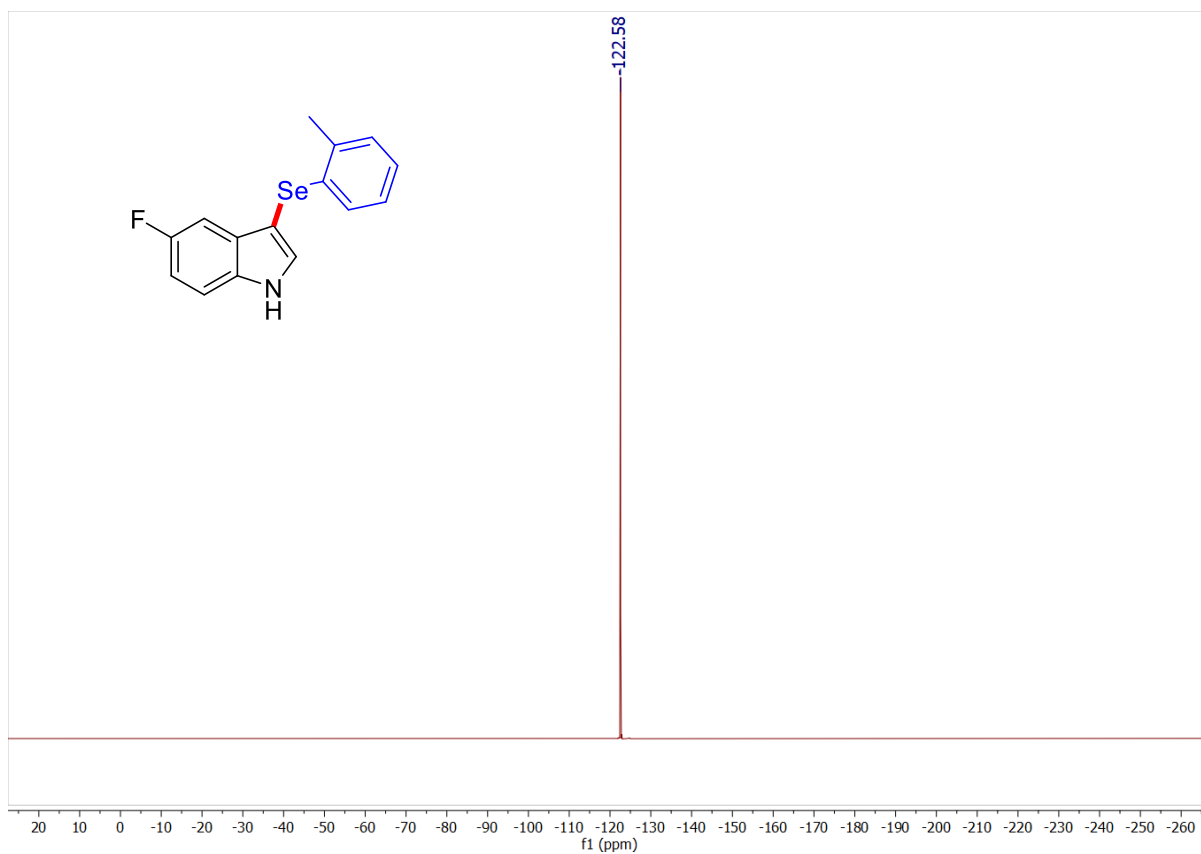


Figure 38: ¹⁹F NMR (565 MHz, CDCl₃) spectrum of 5-fluoro-3-(*o*-tolylselanyl)-1*H*-indole (3j).

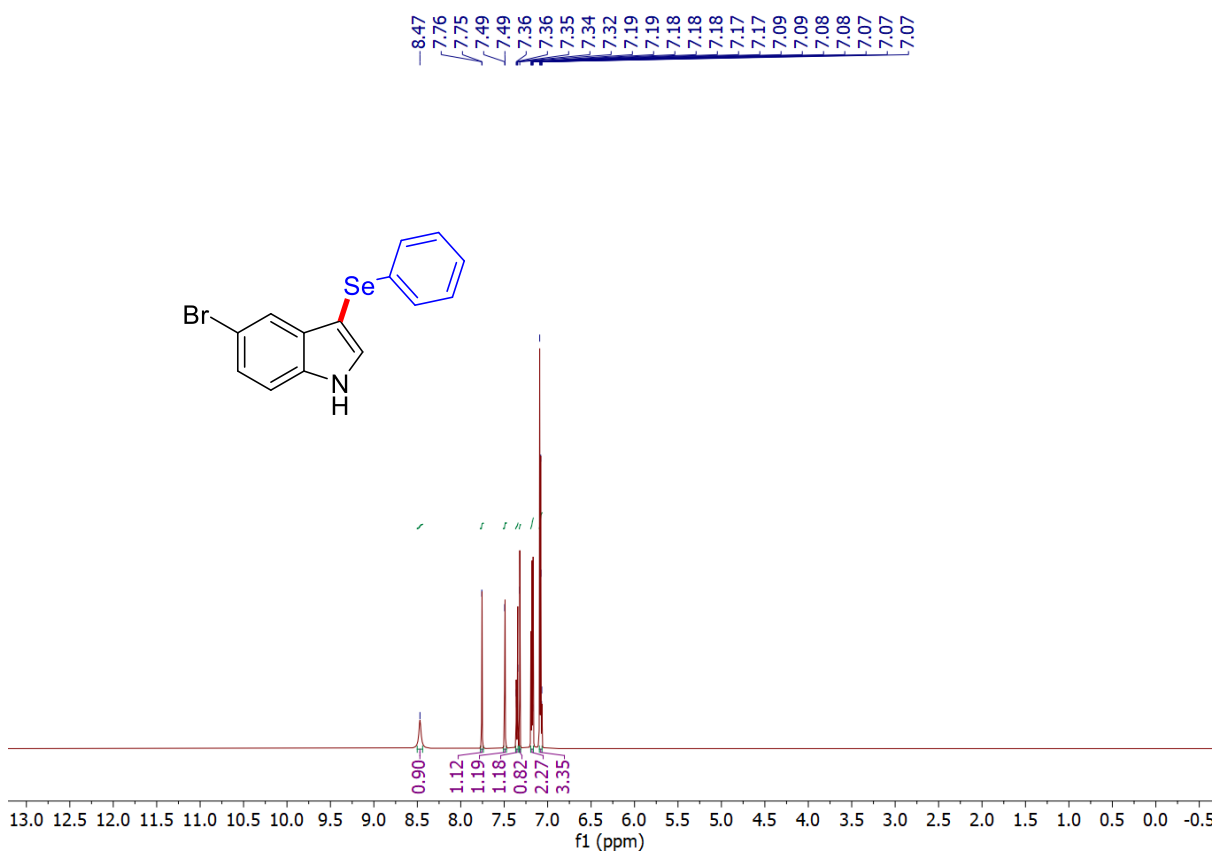


Figure 39: ¹H NMR (600 MHz, CDCl₃) spectrum of 5-bromo-3-(phenylselanyl)-1*H*-indole (3k).

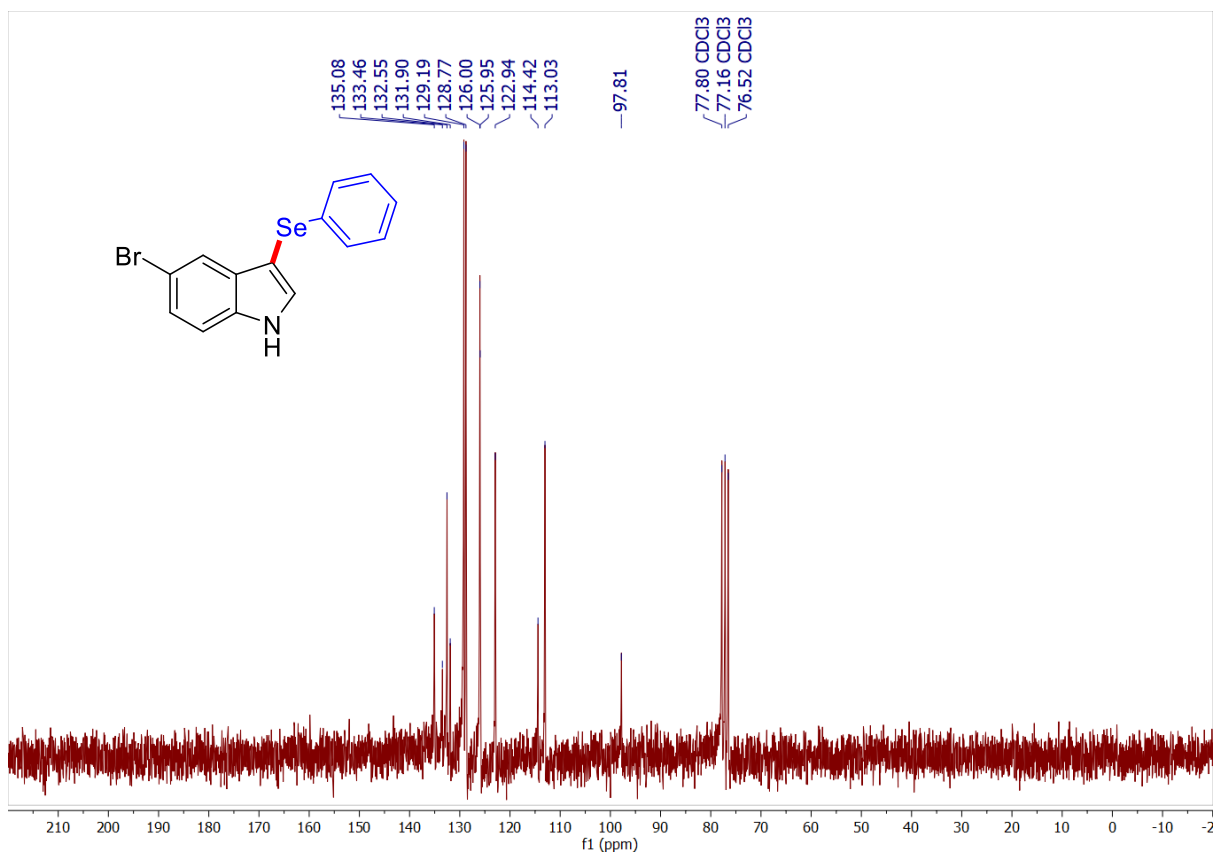


Figure 40: ¹³C NMR (50 MHz, CDCl₃) spectrum of 5-bromo-3-(phenylselanyl)-1H-indole (3k).

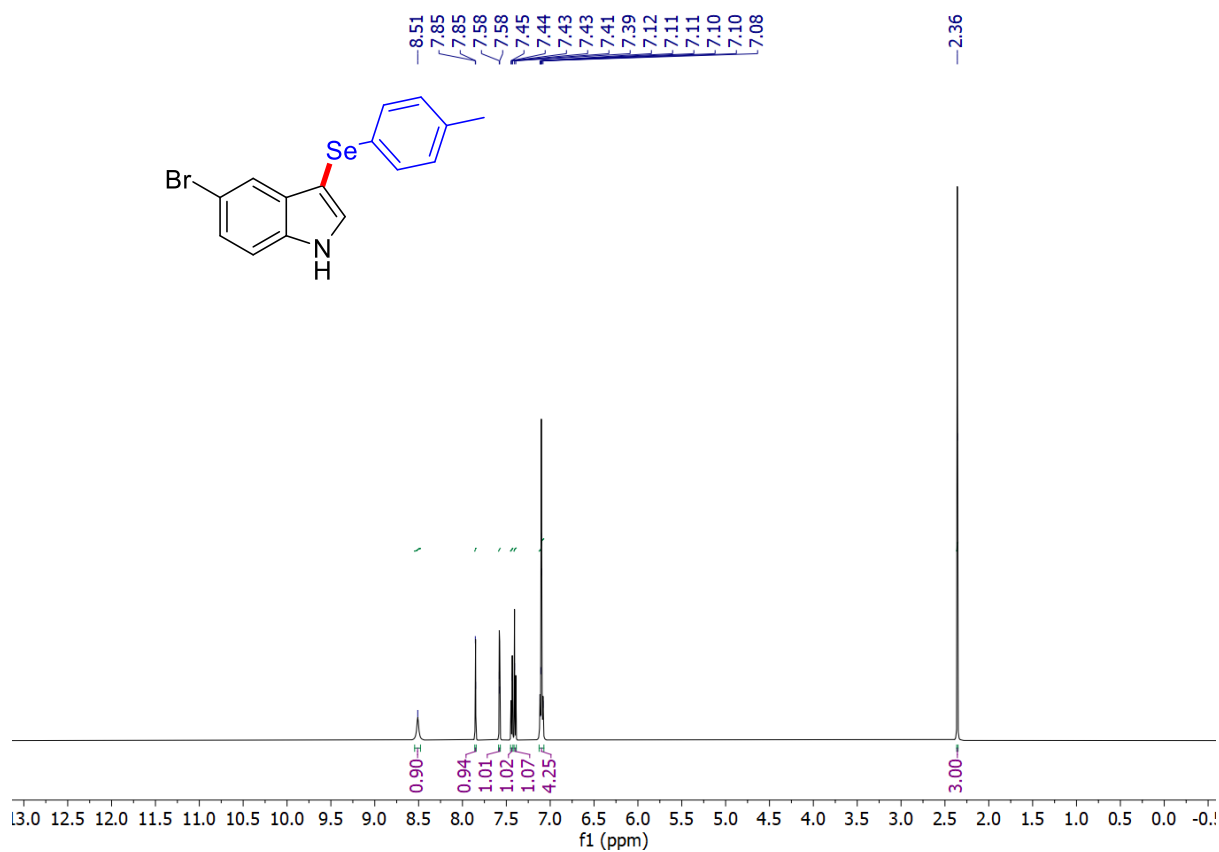


Figure 41: ¹H NMR (600 MHz, CDCl₃) spectrum of 5-bromo-3-(p-tolylselanyl)-1H-indole (3l).

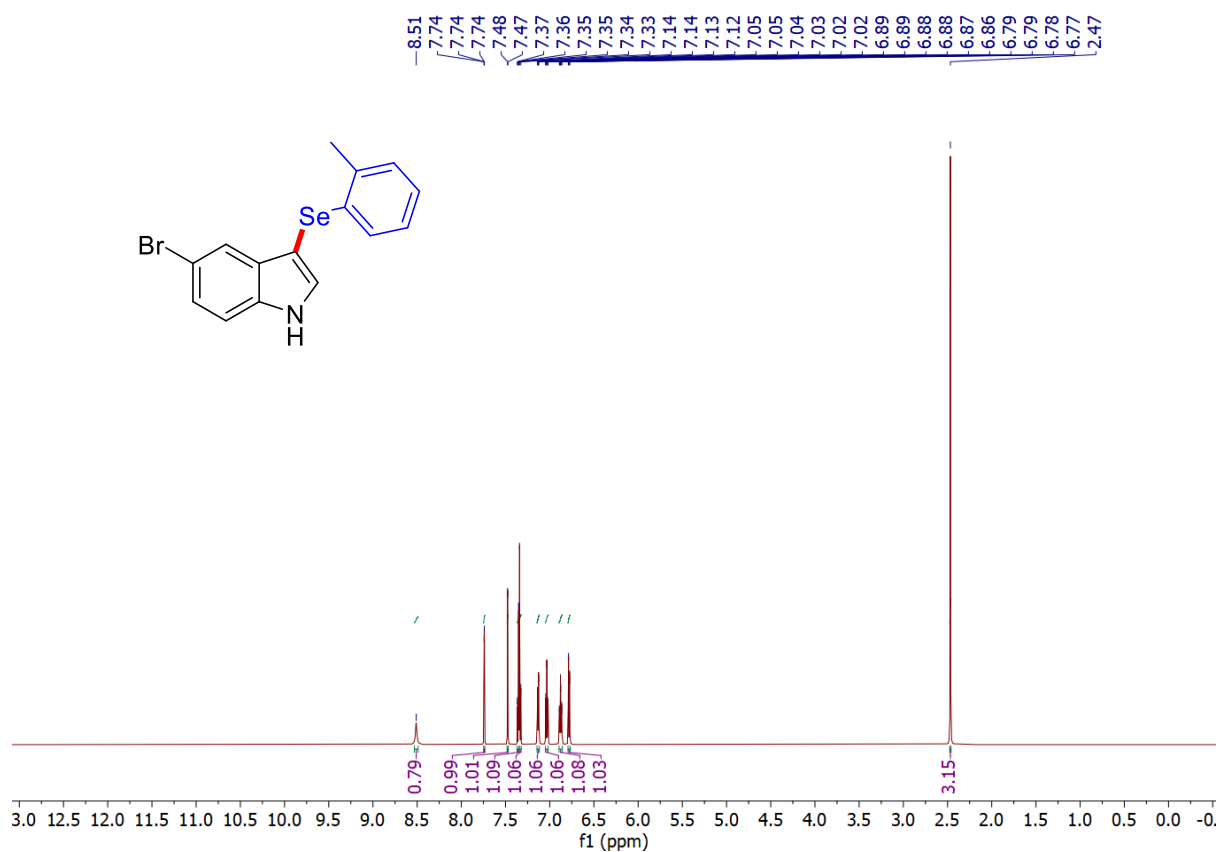


Figure 42: ¹H NMR (600 MHz, CDCl₃) spectrum of 5-bromo-3-(*o*-tolylselanyl)-1*H*-indole (**3m**)

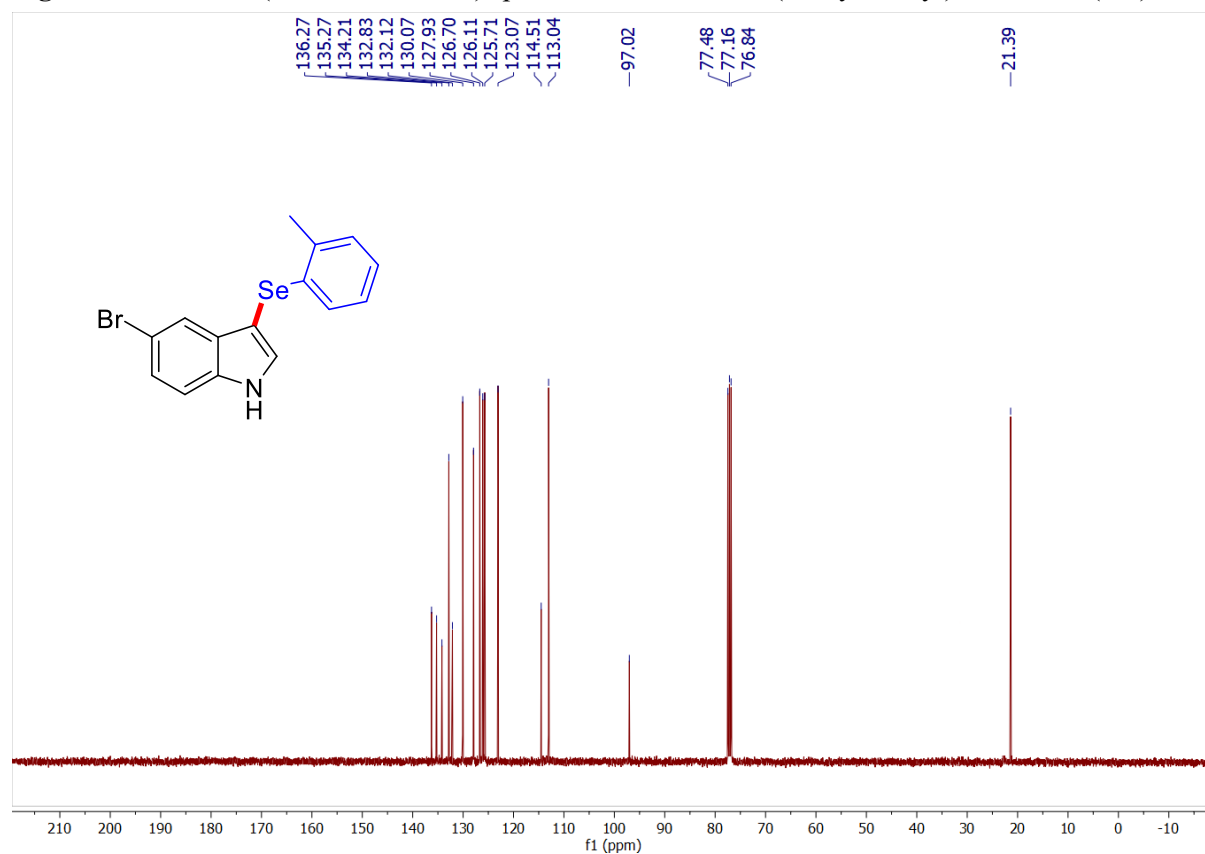


Figure 43: ¹³C NMR (400 MHz, CDCl₃) spectrum of 5-bromo-3-(*o*-tolylselanyl)-1*H*-indole (**3m**)

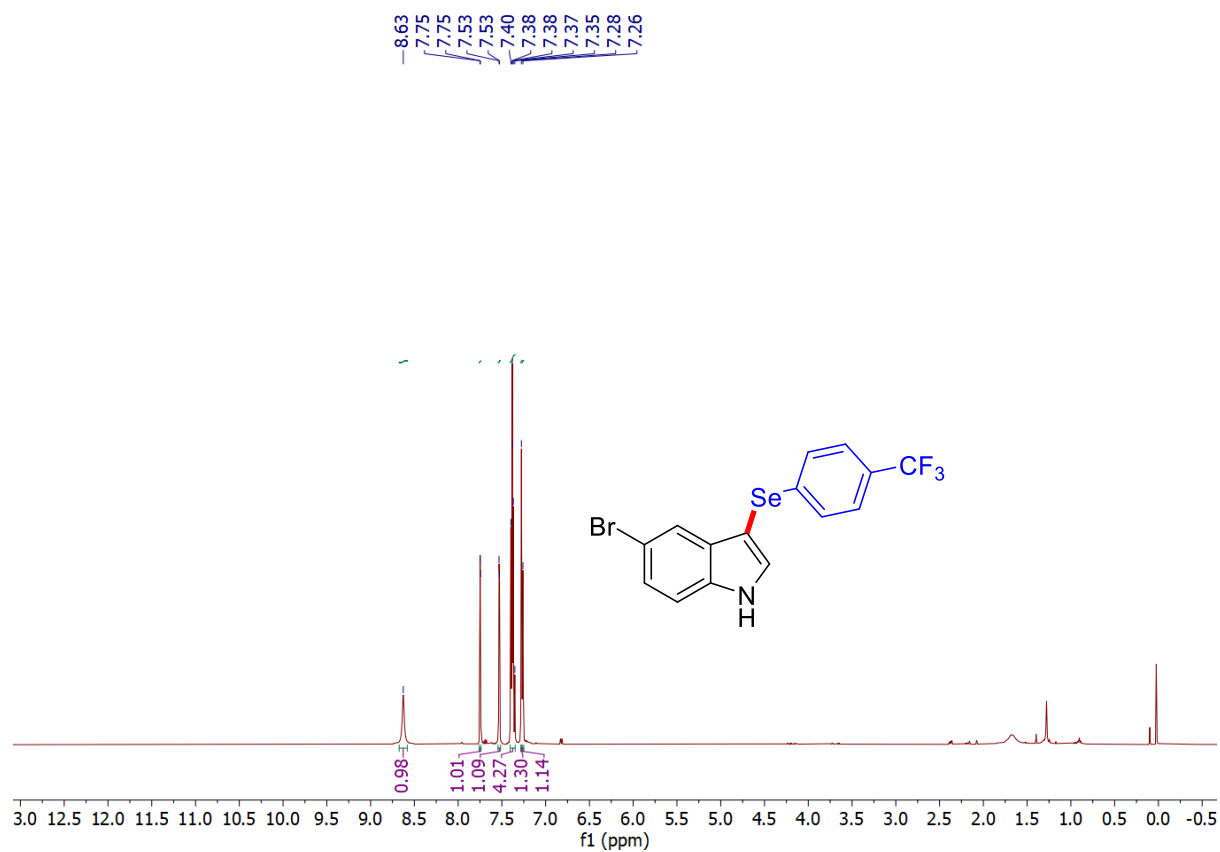


Figure 44: ¹H NMR (500 MHz, CDCl₃) spectrum of 5-bromo-3-((4-(trifluoromethyl)phenyl)selanyl)-1H-indole (**3n**).

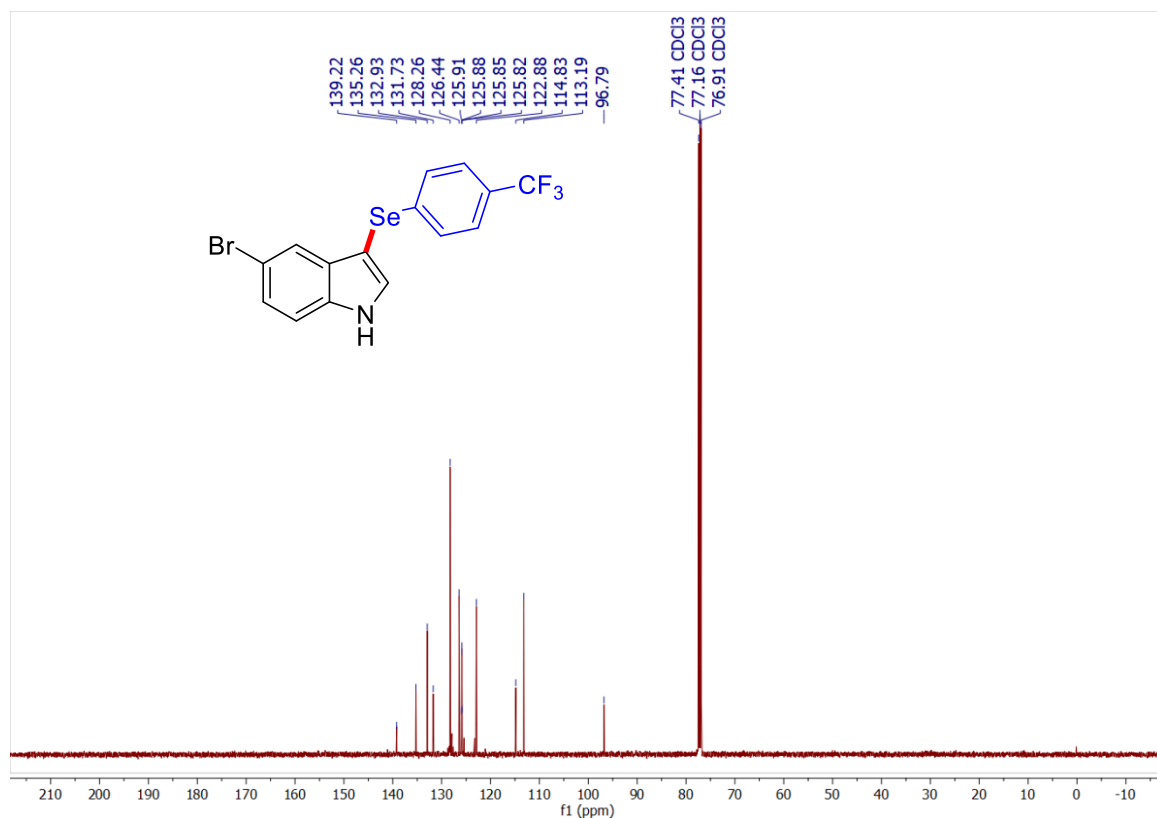


Figure 45: ¹³C NMR (126 MHz, CDCl₃) spectrum of 5-bromo-3-((4-(trifluoromethyl)phenyl)selanyl)-1H-indole (3n).

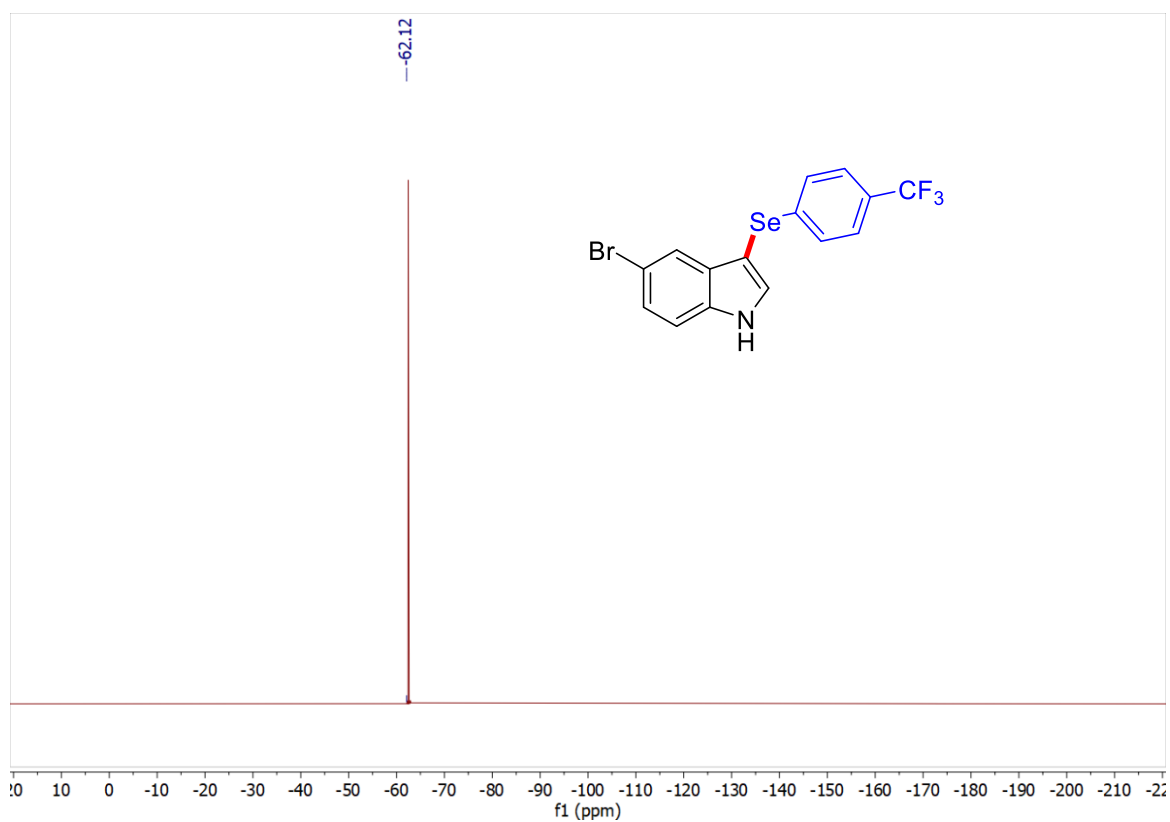


Figure 46: ¹⁹F NMR (471 MHz, CDCl₃) spectrum of 5-bromo-3-((4-(trifluoromethyl)phenyl)selanyl)-1H-indole (3n).

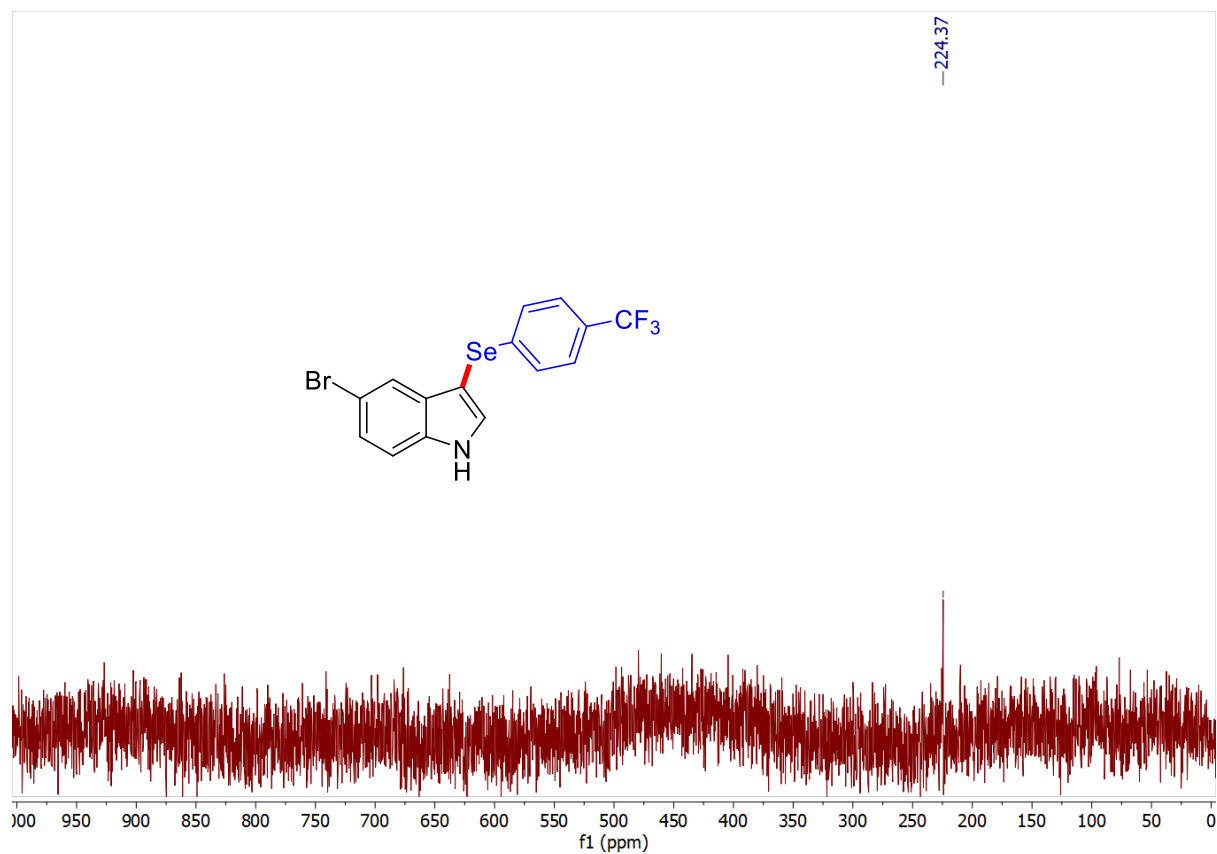


Figure 47: ^{77}Se NMR (95 MHz, CDCl_3) spectrum of 5-bromo-3-((4-(trifluoromethyl)phenyl)selanyl)-1H-indole (**3n**).

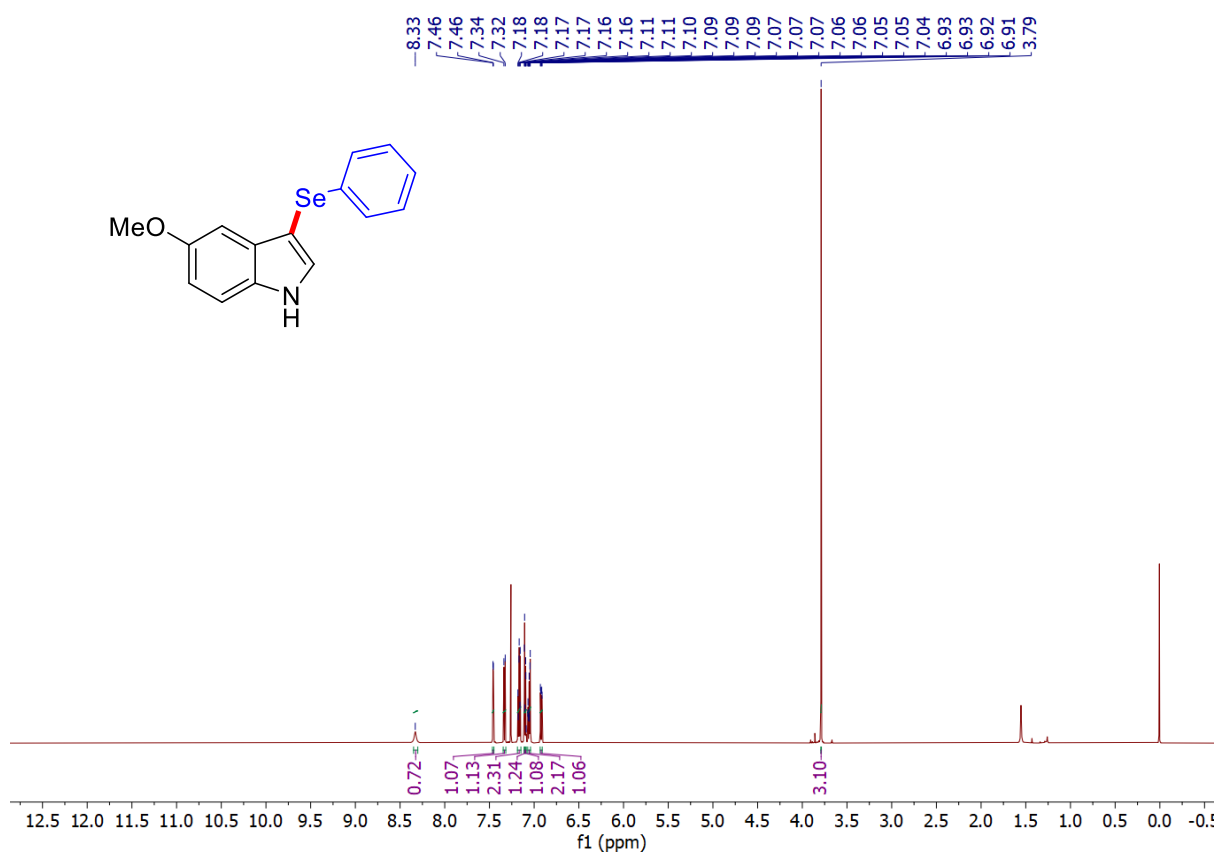


Figure 48: ^1H NMR (600 MHz, CDCl_3) spectrum of 5-methoxy-3-(phenylselanyl)-1H-indole (30).

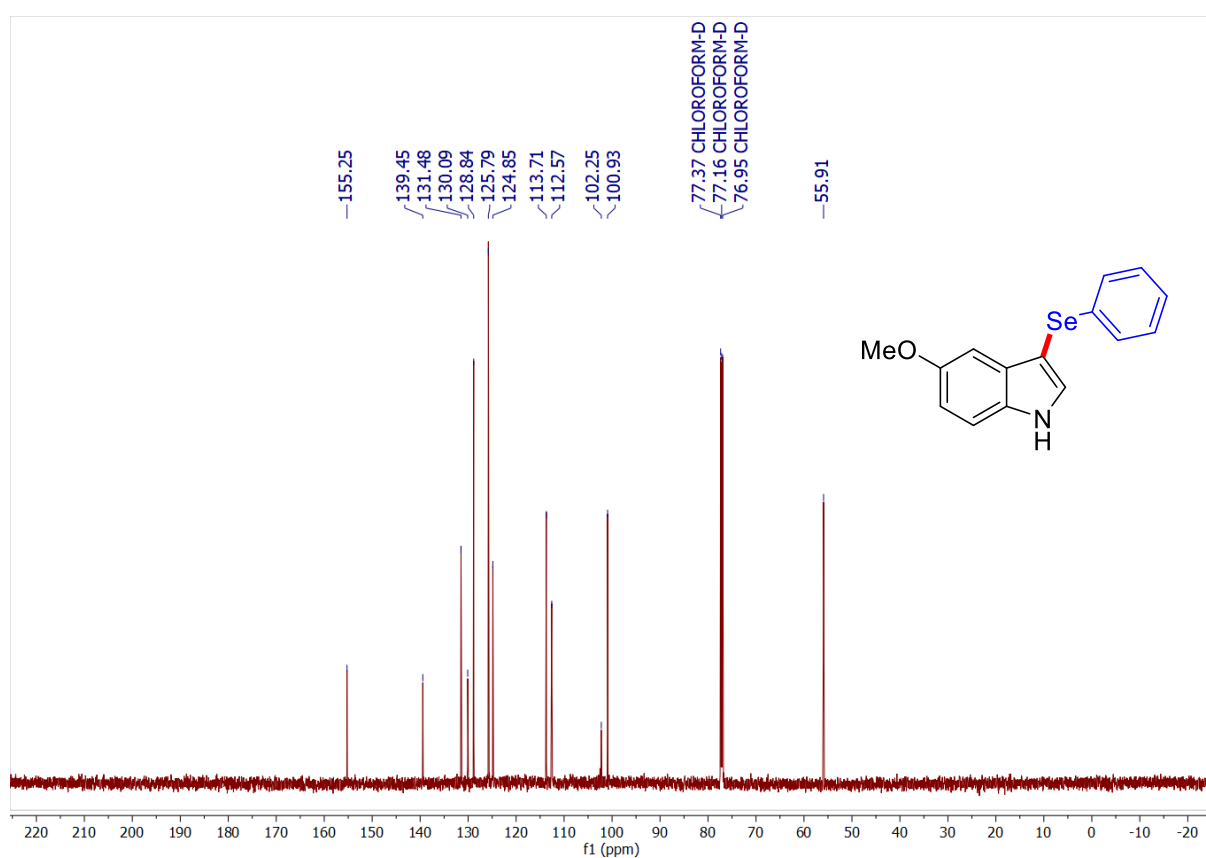


Figure 49: ^{13}C NMR (151 MHz, CDCl_3) spectrum of 5-methoxy-3-(phenylselanyl)-1H-indole (30).

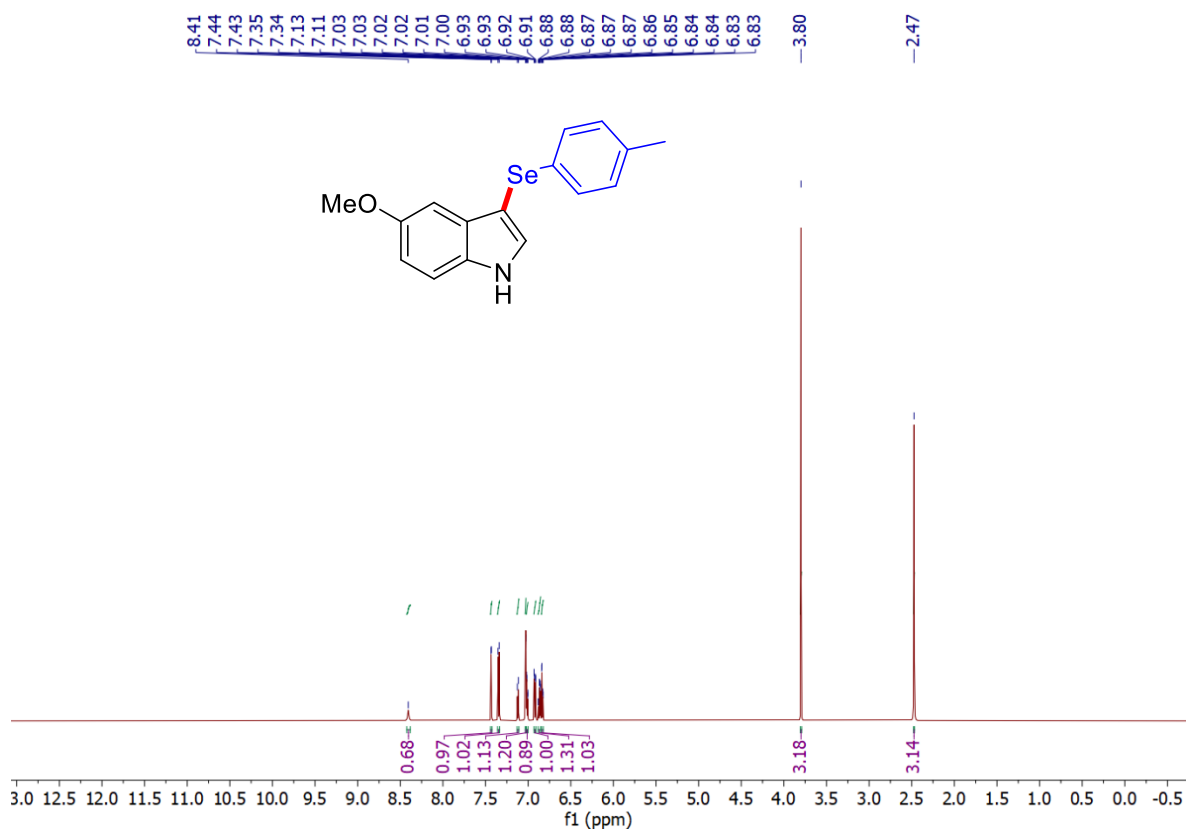


Figure 50: ¹H NMR (600 MHz, CDCl₃) spectrum of 5-methoxy-3-(*p*-tolylselanyl)-1*H*-indole (**3p**).

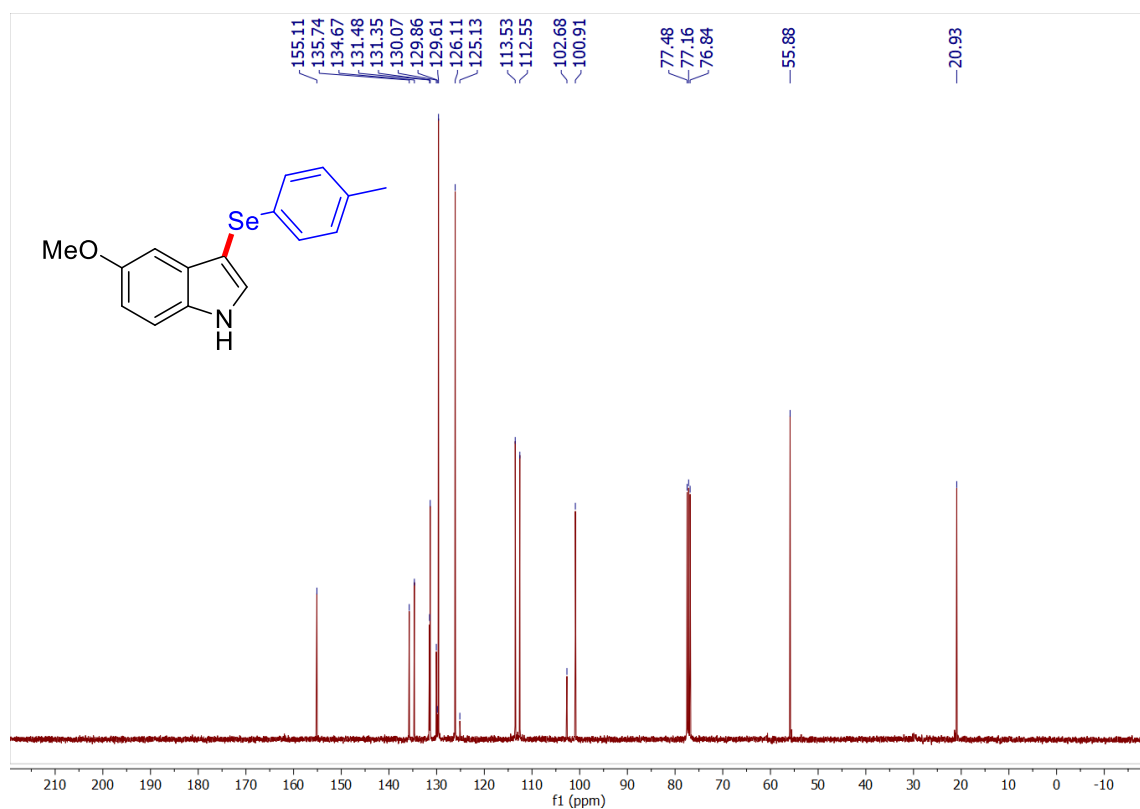


Figure 51: ¹³C NMR (101 MHz, CDCl₃) spectrum of 5-methoxy-3-(*p*-tolylselanyl)-1*H*-indole (**3p**).

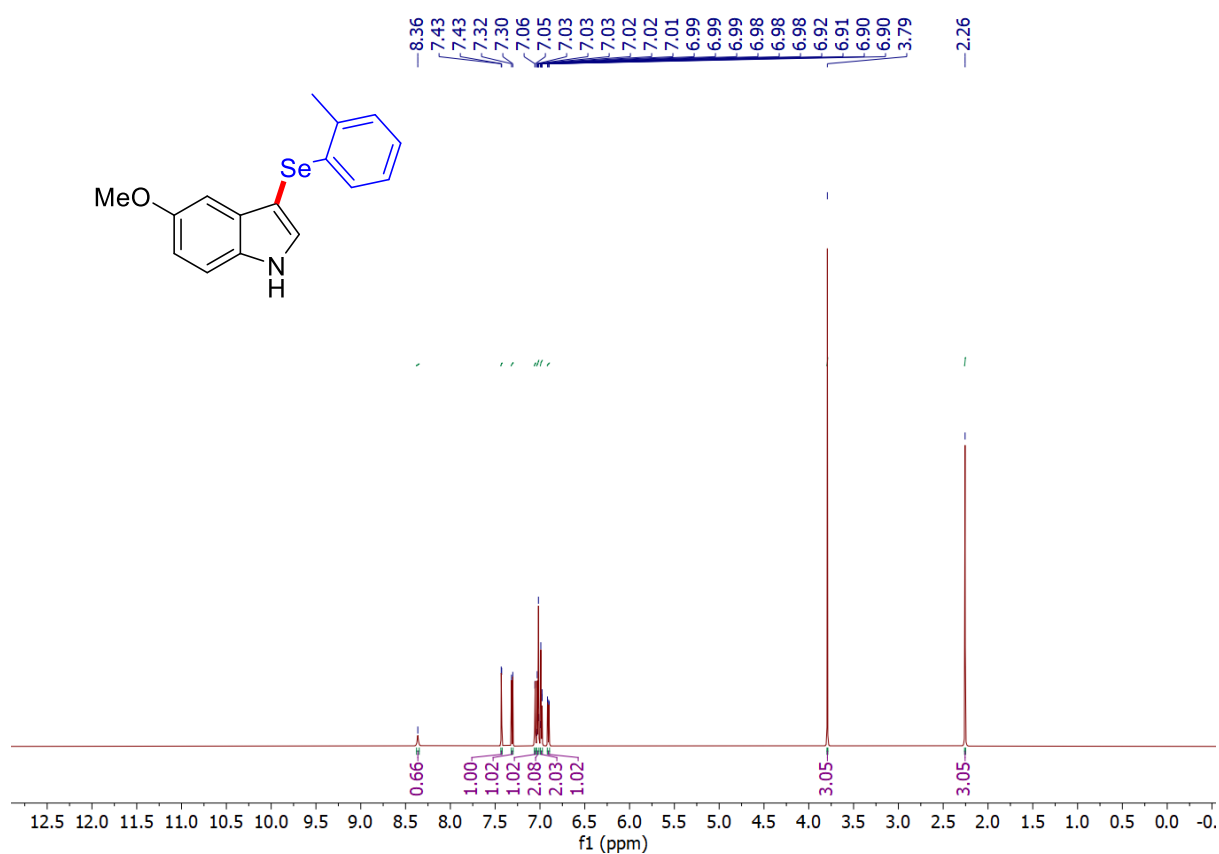


Figure 52: ¹H NMR (600 MHz, CDCl₃) spectrum of 5-methoxy-3-(*o*-tolylselanyl)-1*H*-indole (**3q**).

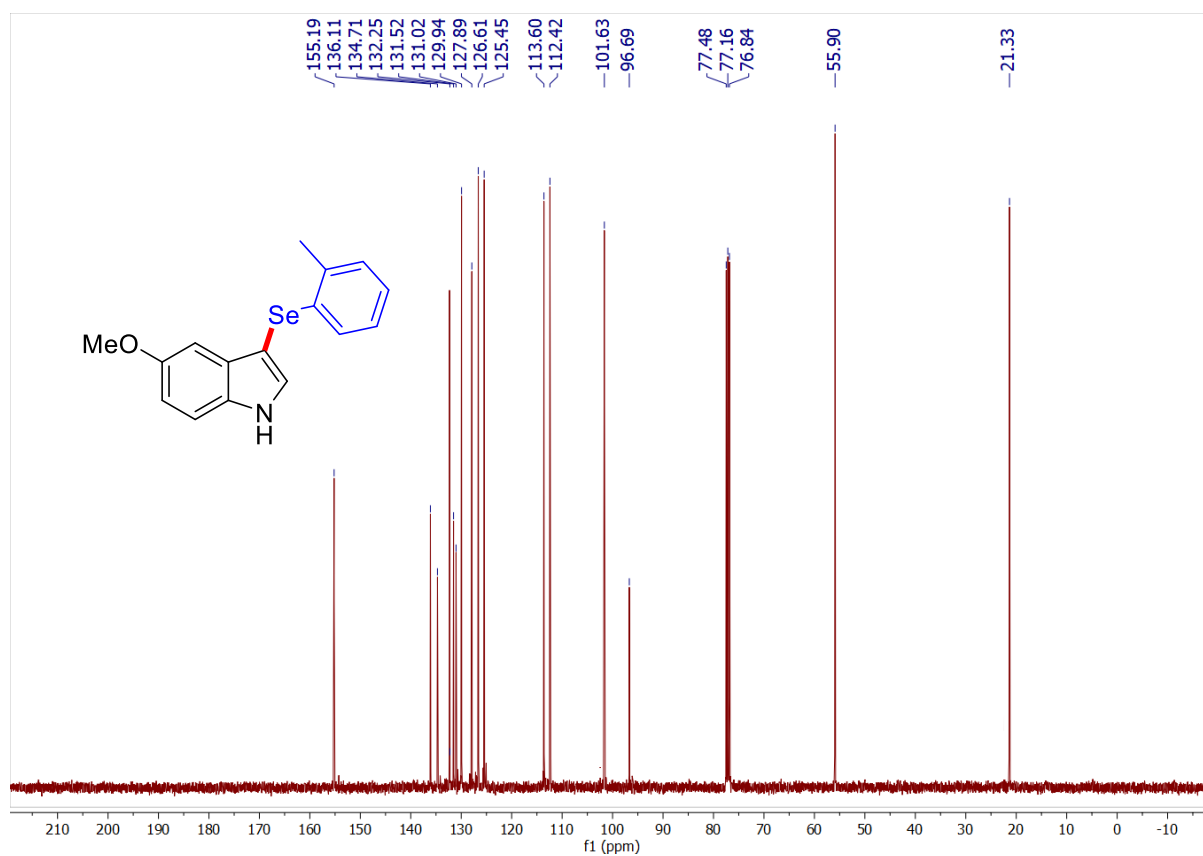


Figure 53: ^{13}C NMR (400 MHz, CDCl_3) spectrum of 5-methoxy-3-(*o*-tolylselanyl)-1*H*-indole (**3q**).

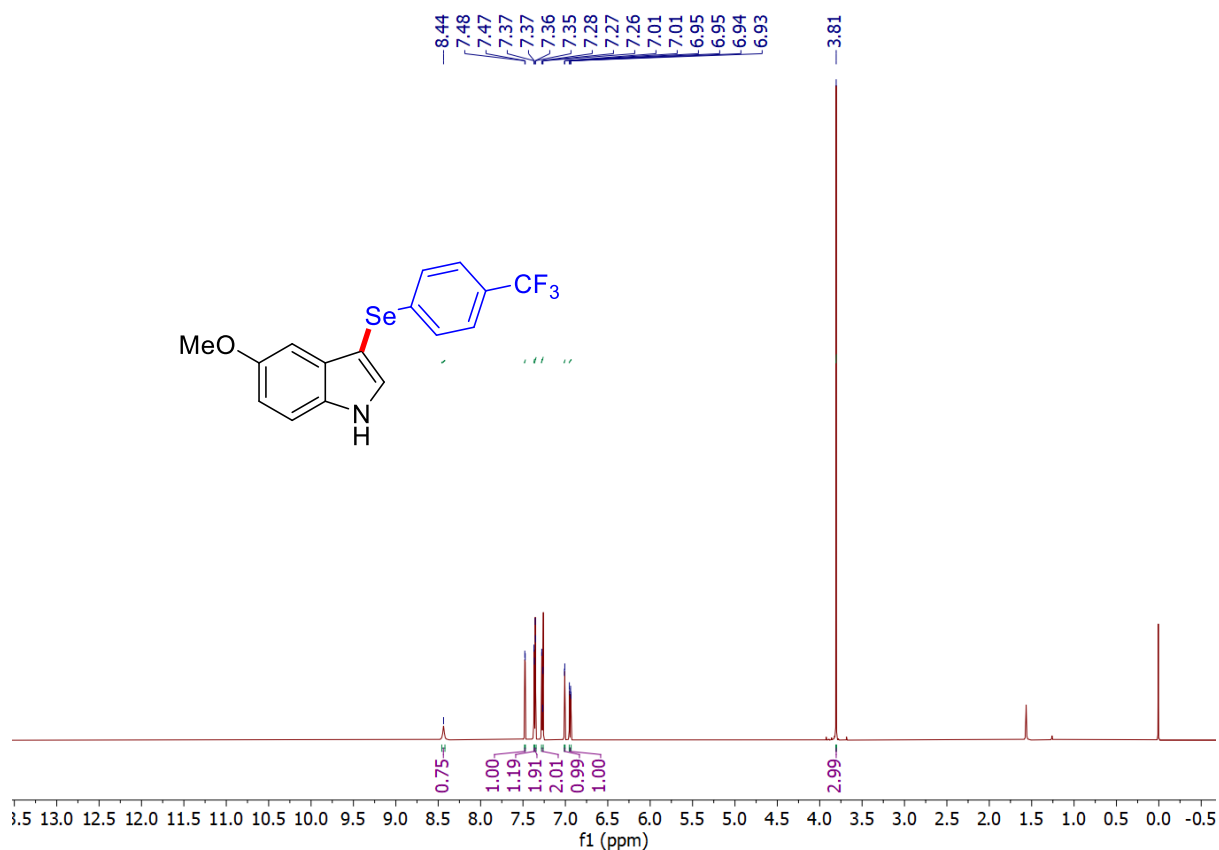


Figure 54: ¹H NMR (600 MHz, CDCl₃) spectrum of 5-methoxy-3-((4-(trifluoromethyl)phenyl)selanyl)-1H-indole (3r).

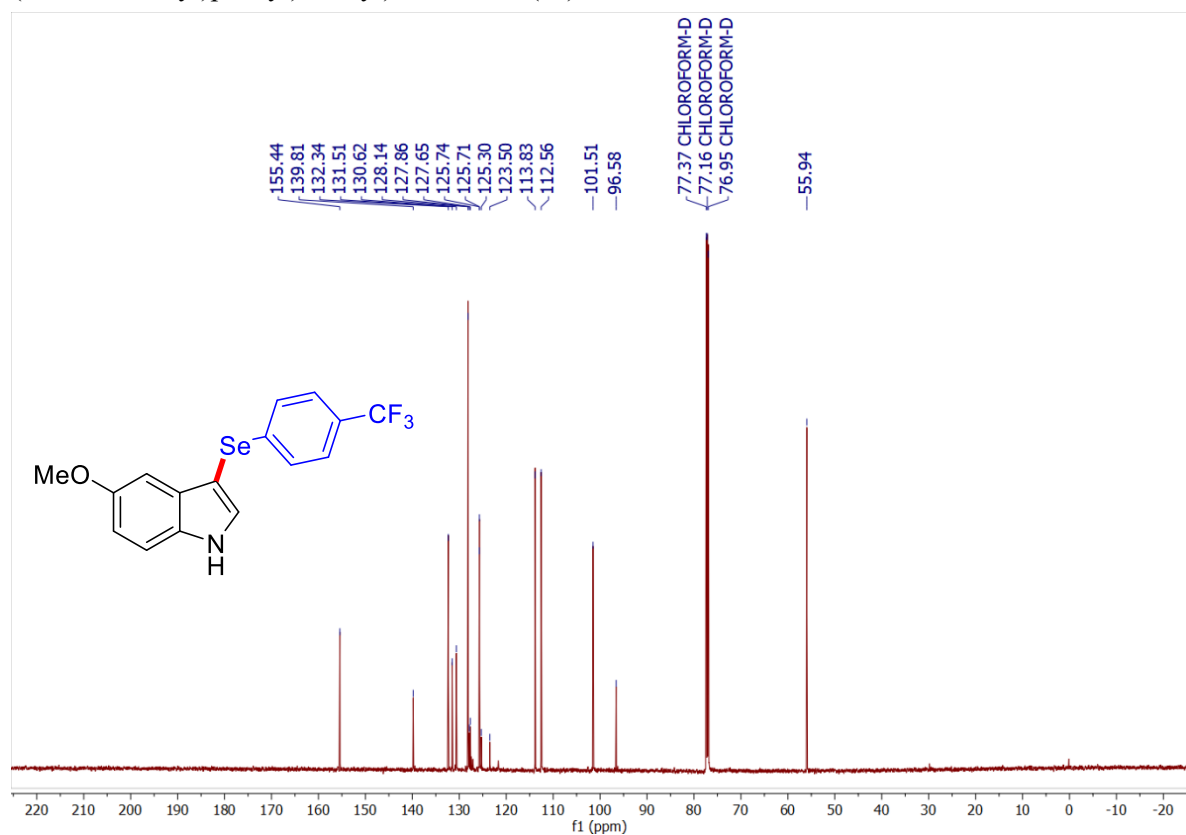


Figure 55: ¹³C NMR (151 MHz, CDCl₃) spectrum of 5-methoxy-3-((4-(trifluoromethyl)phenyl)selanyl)-1H-indole (3r).

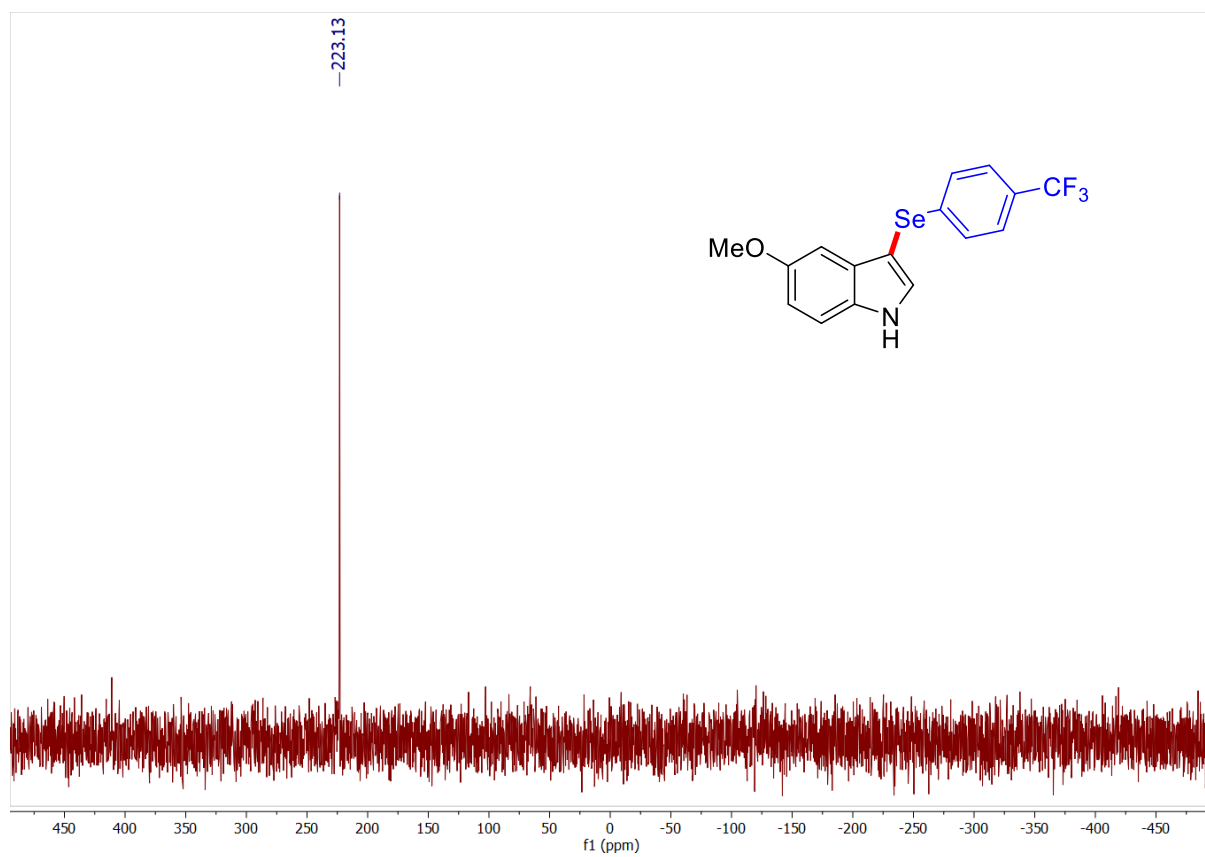


Figure 56: ^{77}Se NMR (114 MHz, CDCl_3) spectrum of 5-methoxy-3-((4-(trifluoromethyl)phenyl)selanyl)-1H-indole (**3r**).

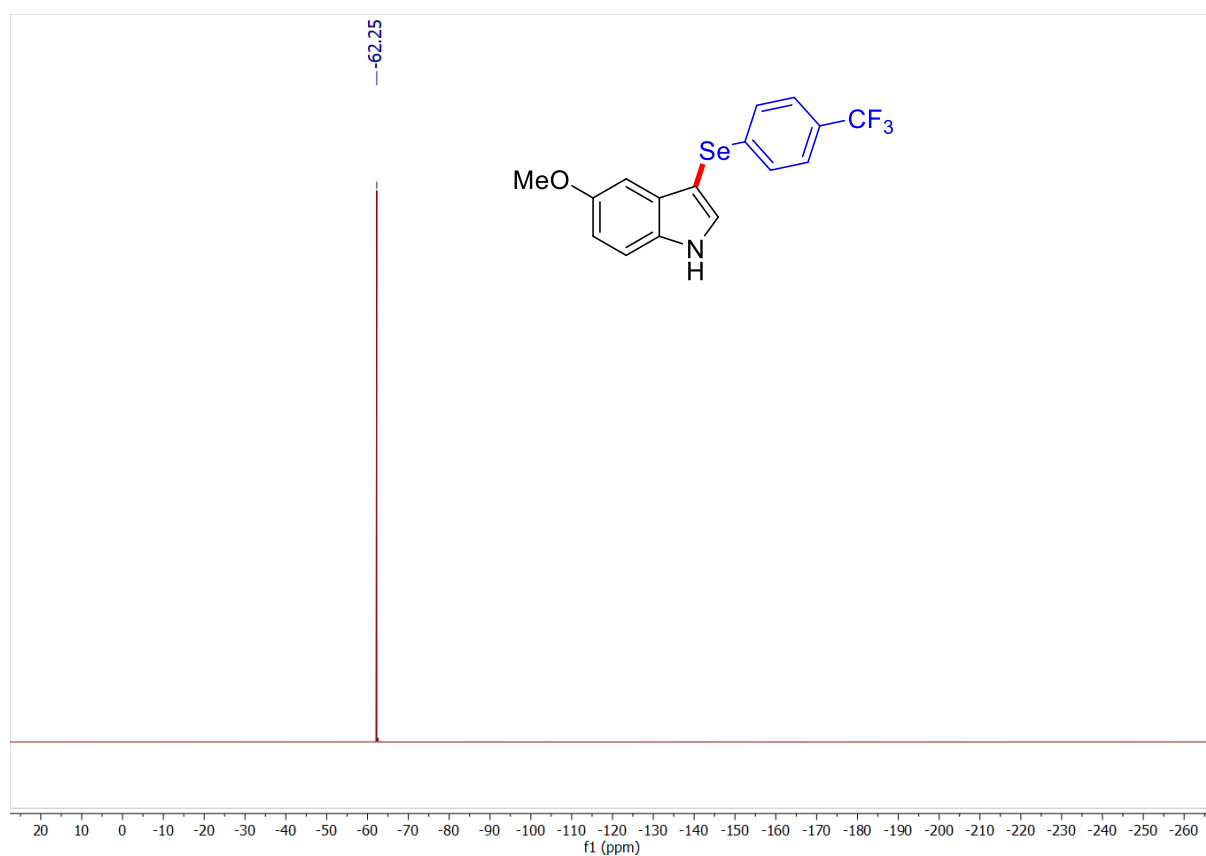


Figure 57: ^{19}F NMR (565 MHz, CDCl_3) spectrum of 5-methoxy-3-((4-(trifluoromethyl)phenyl)selanyl)-1H-indole (**3r**).

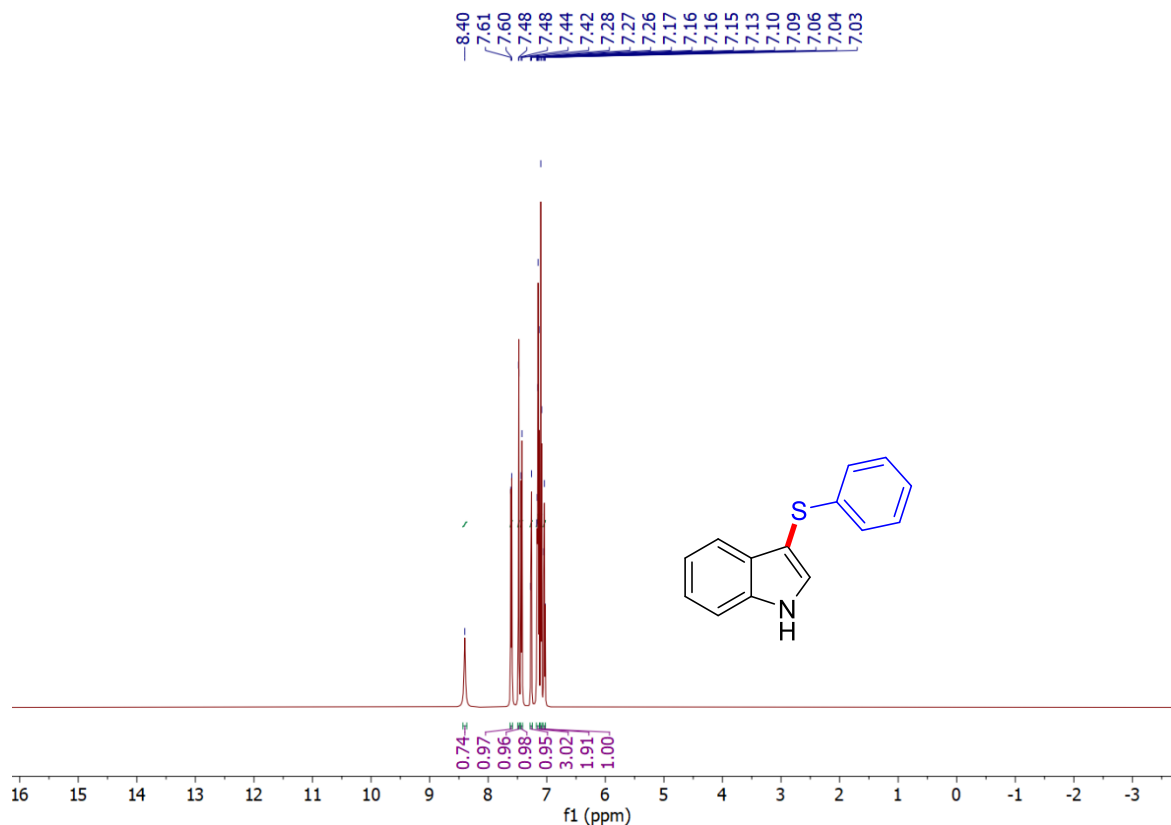


Figure 58: ¹H NMR (500 MHz, CDCl₃) spectrum of 3-(phenylthio)-1H-indole (5a).

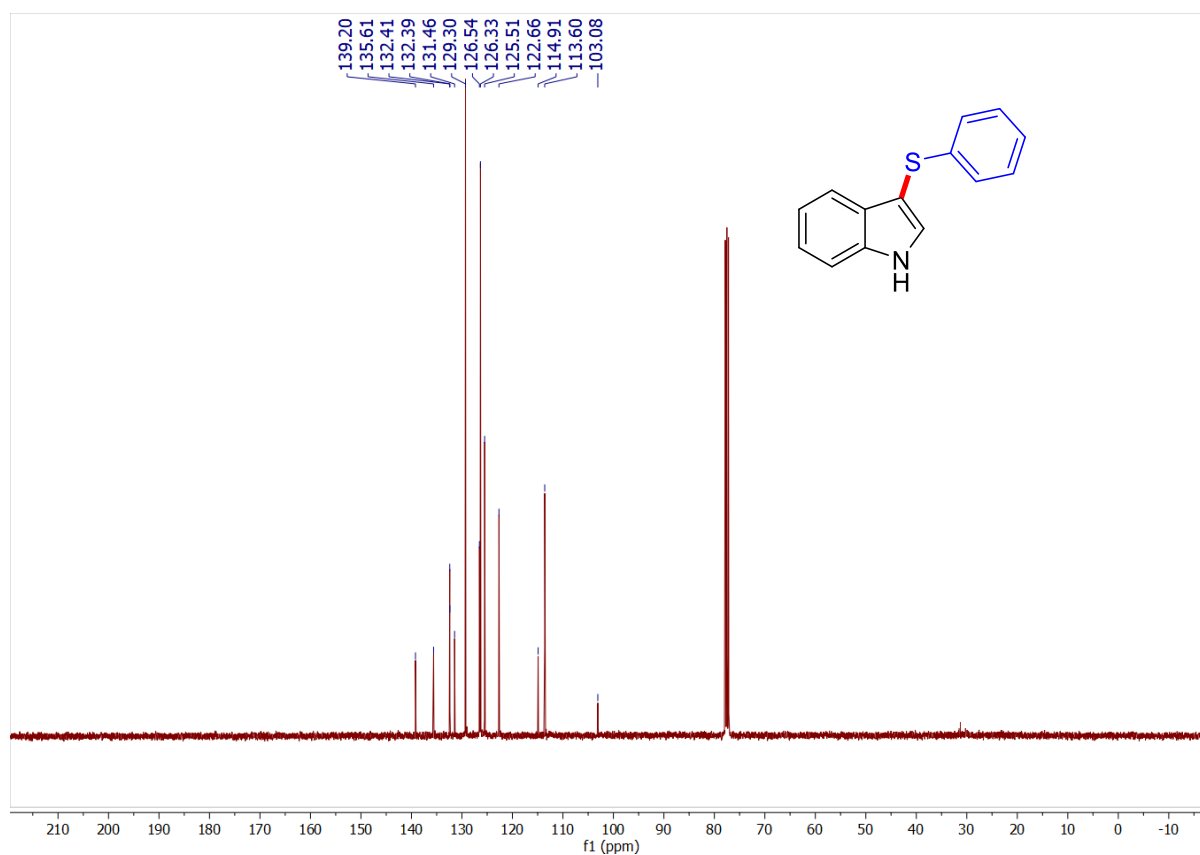


Figure 59: ¹³C NMR (101 MHz, CDCl₃) spectrum of 3-(phenylthio)-1H-indole (5a).

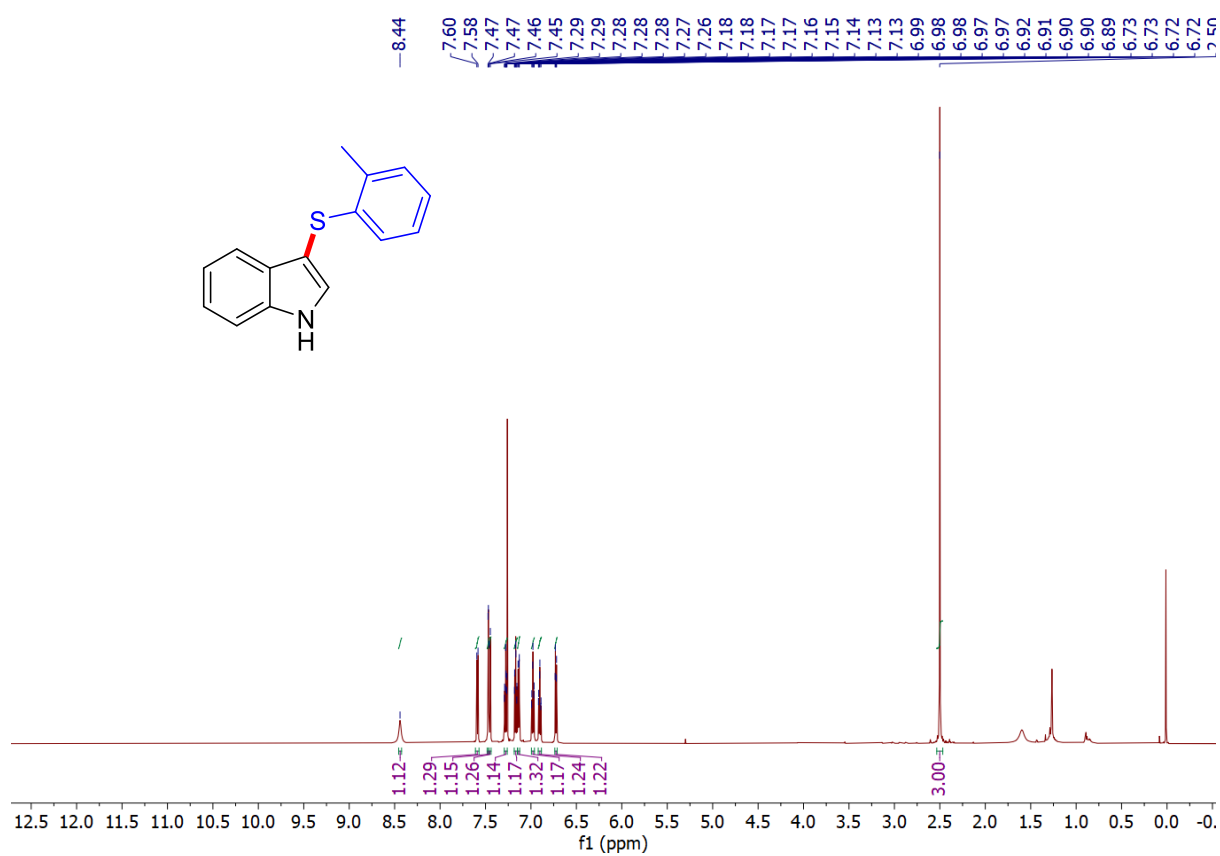


Figure 60: ¹H NMR (600 MHz, CDCl₃) spectrum of 3-(*o*-tolylthio)-1*H*-indole (**5b**).

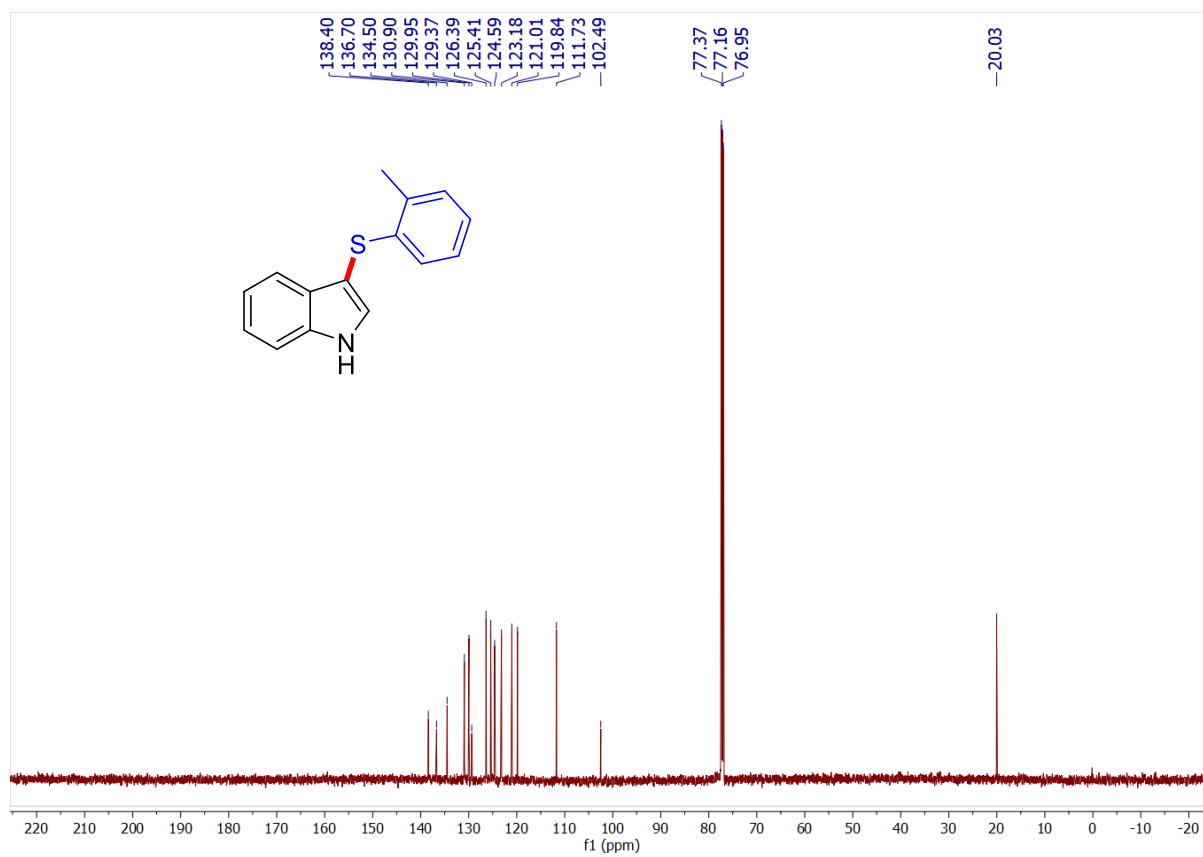


Figure 61: ¹³C NMR (151 MHz, CDCl₃) spectrum of 3-(*o*-tolylthio)-1*H*-indole (**5b**).

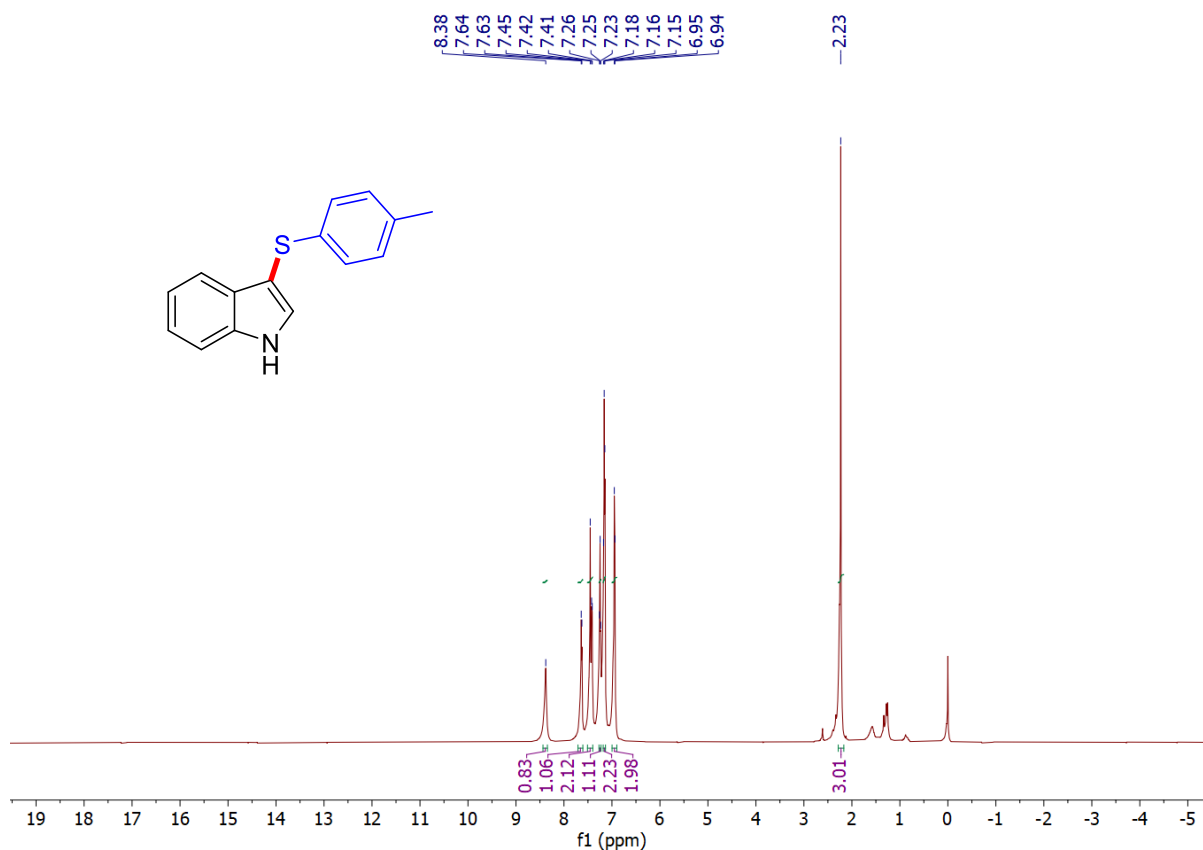


Figure 62: ¹H NMR (600 MHz, CDCl₃) spectrum of 3-(*p*-tolylthio)-1*H*-indole (**5c**).

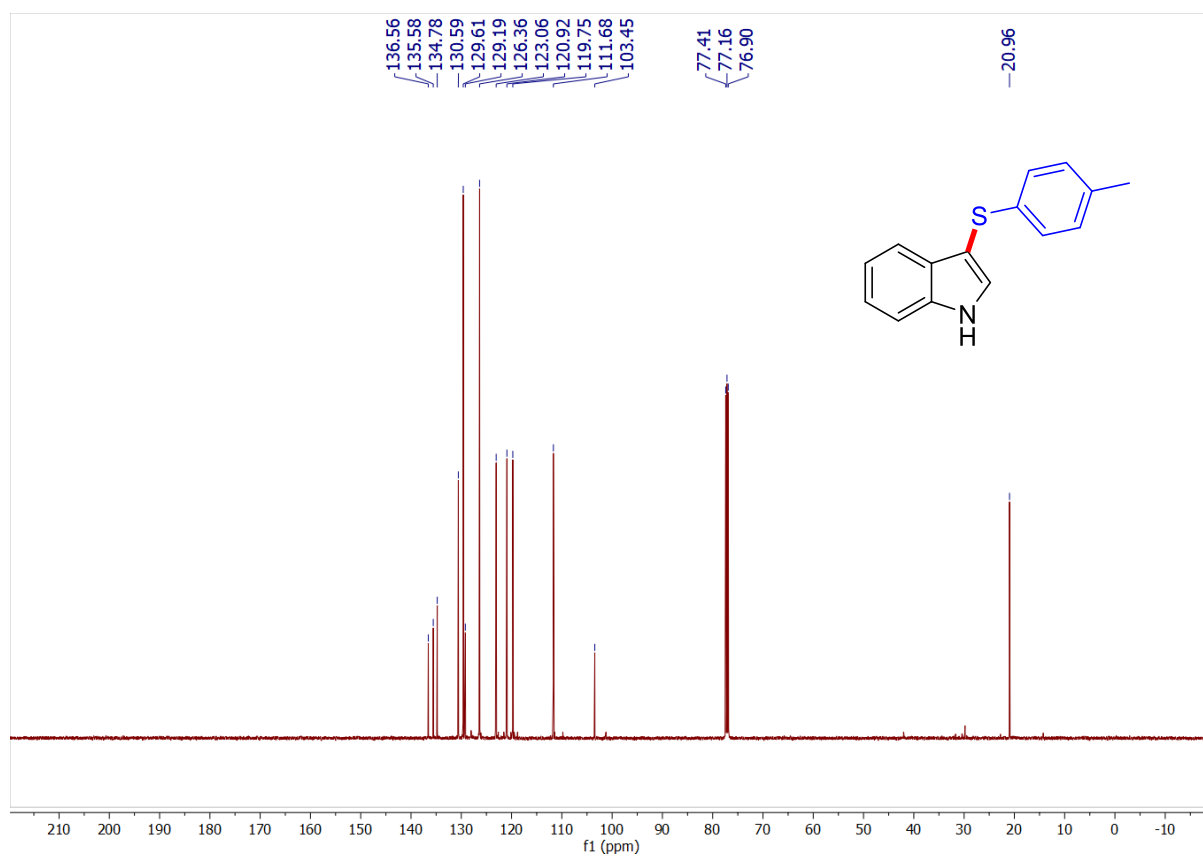


Figure 63: ¹³C NMR (126 MHz, CDCl₃) spectrum of 3-(*p*-tolylthio)-1*H*-indole (**5c**).

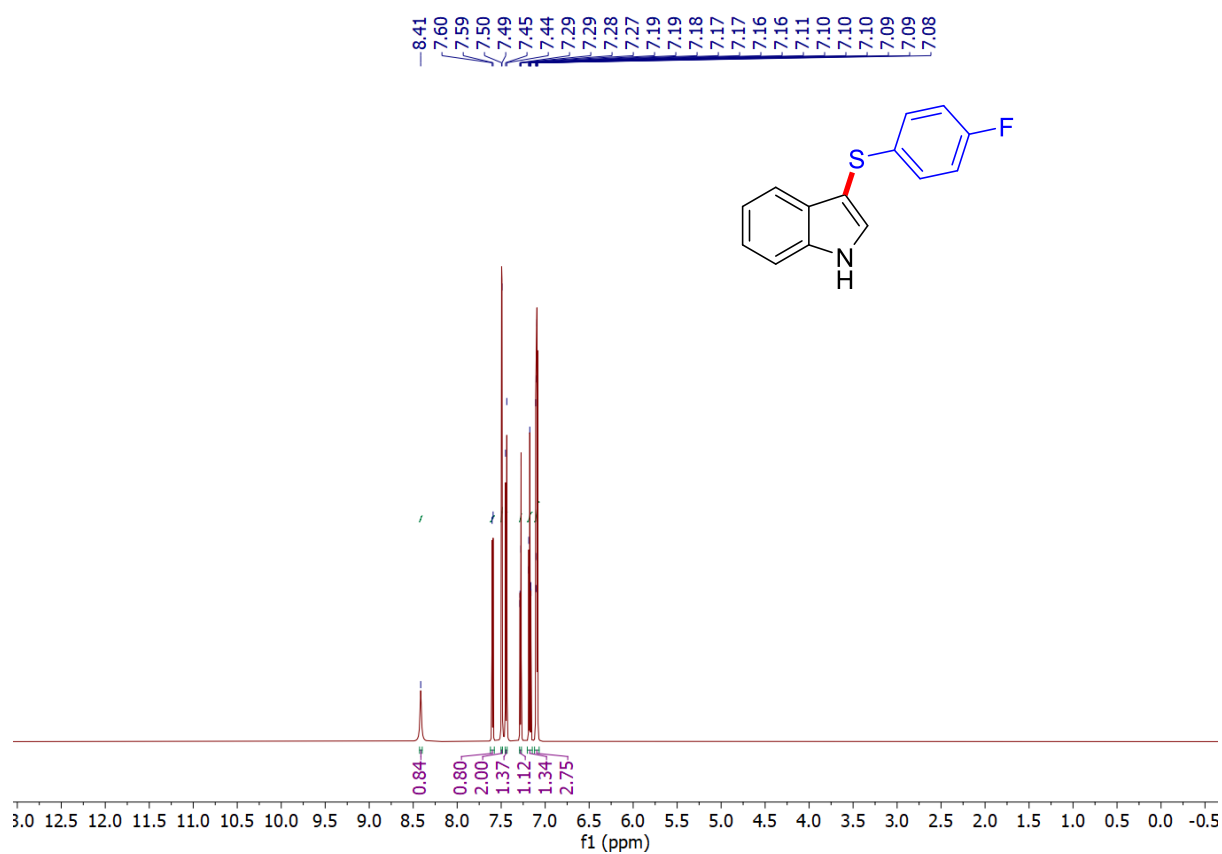


Figure 64: ¹H NMR (600 MHz, CDCl₃) spectrum of 3-((4-fluorophenyl)thio)-1*H*-indole (**5d**).

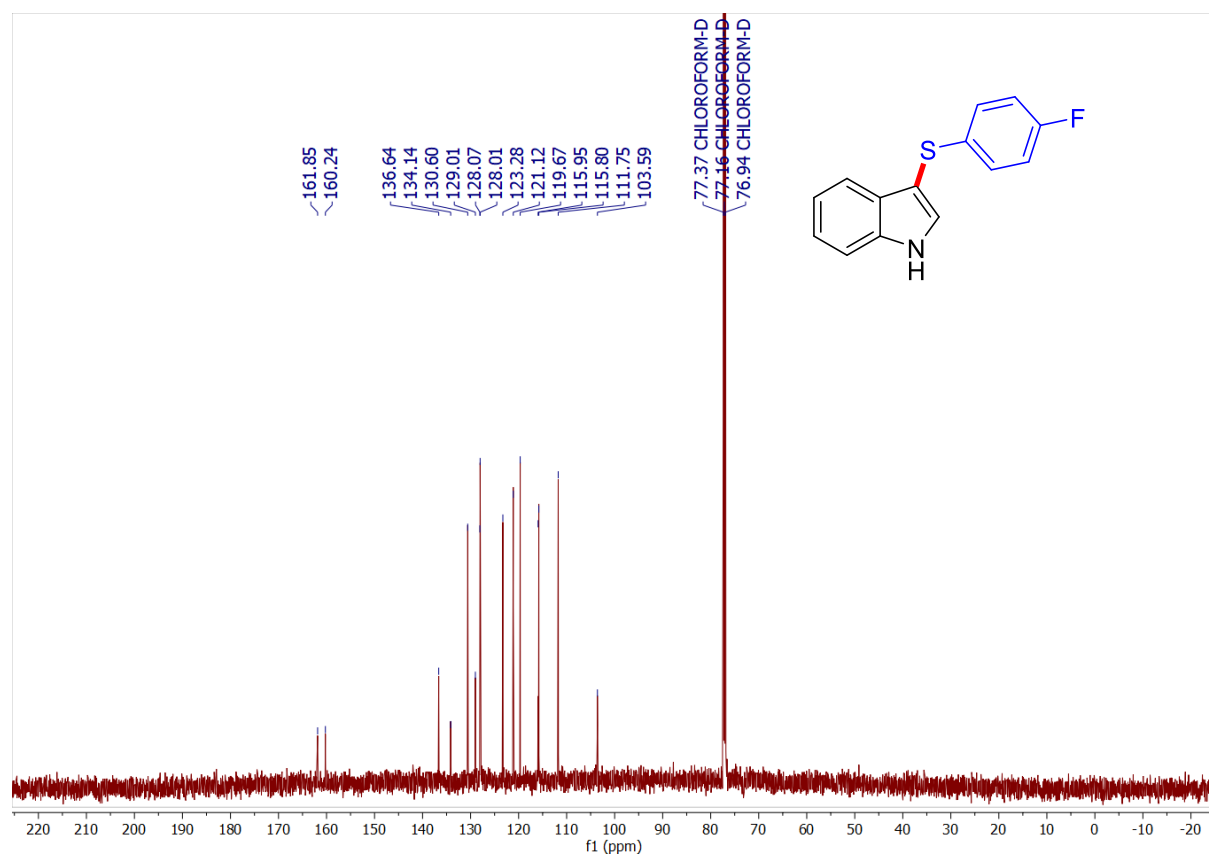


Figure 65: ¹³C NMR (151 MHz, CDCl₃) spectrum of 3-((4-fluorophenyl)thio)-1*H*-indole (**5d**).

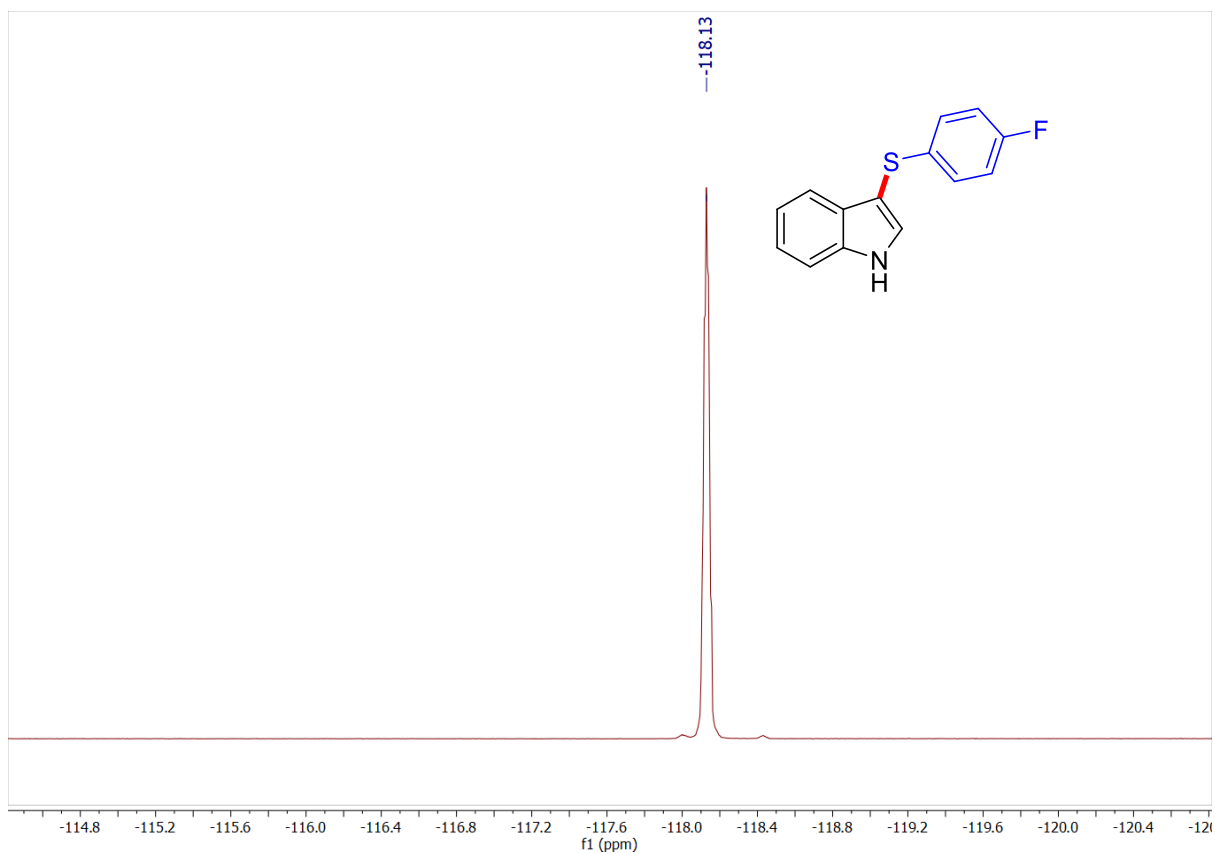


Figure 66: ¹⁹F NMR (565 MHz, CDCl₃) spectrum of 3-((4-fluorophenyl)thio)-1H-indole (5d).

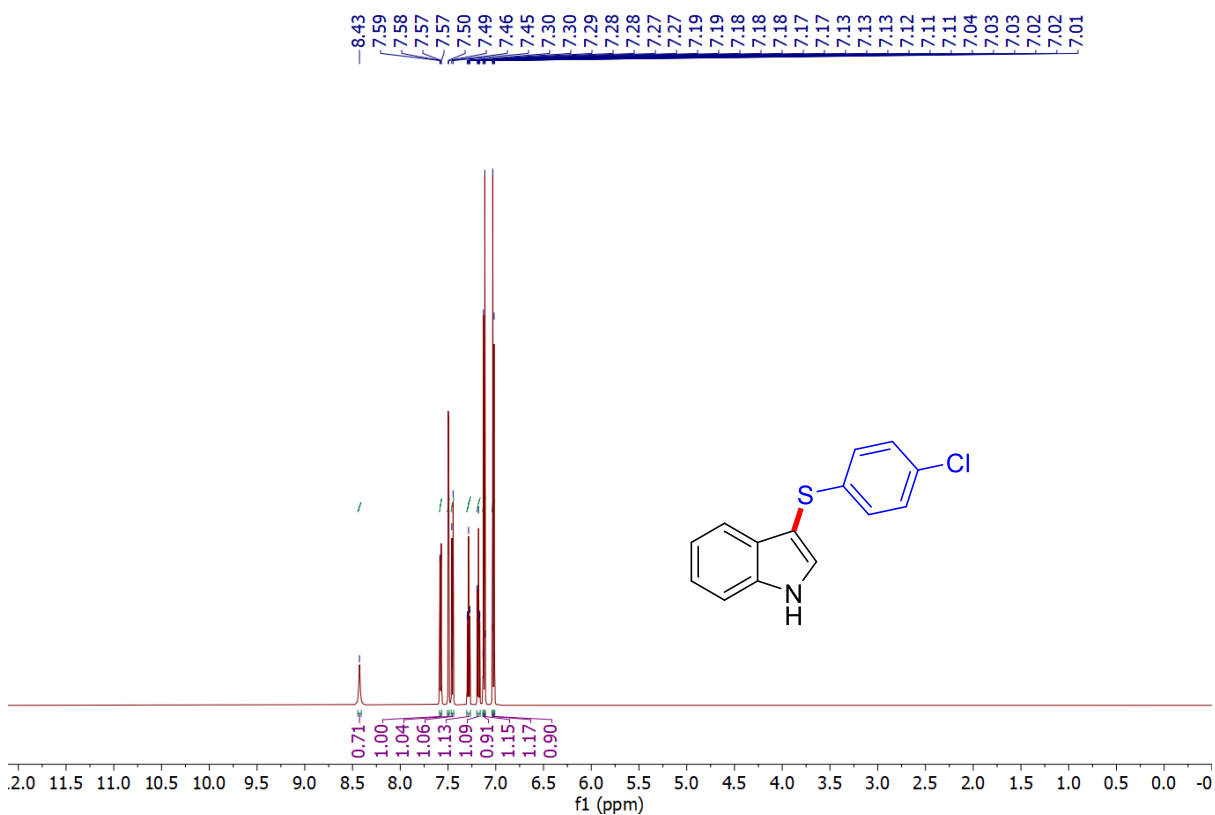


Figure 67: ¹H NMR (600 MHz, CDCl₃) spectrum of 3-((4-chlorophenyl)thio)-1H-indole (5e).

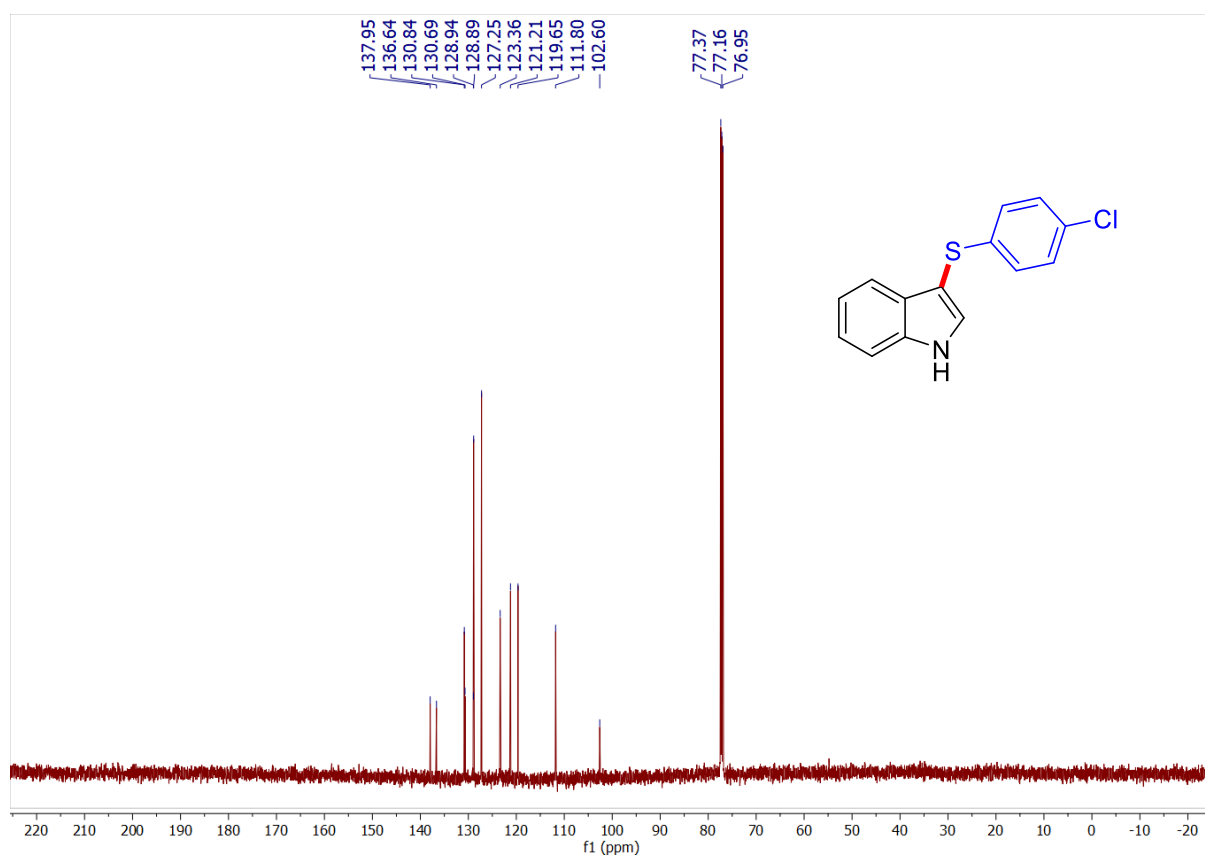


Figure 68: ¹³C NMR (151 MHz, CDCl₃) spectrum of 3-((4-chlorophenyl)thio)-1*H*-indole (**5e**).

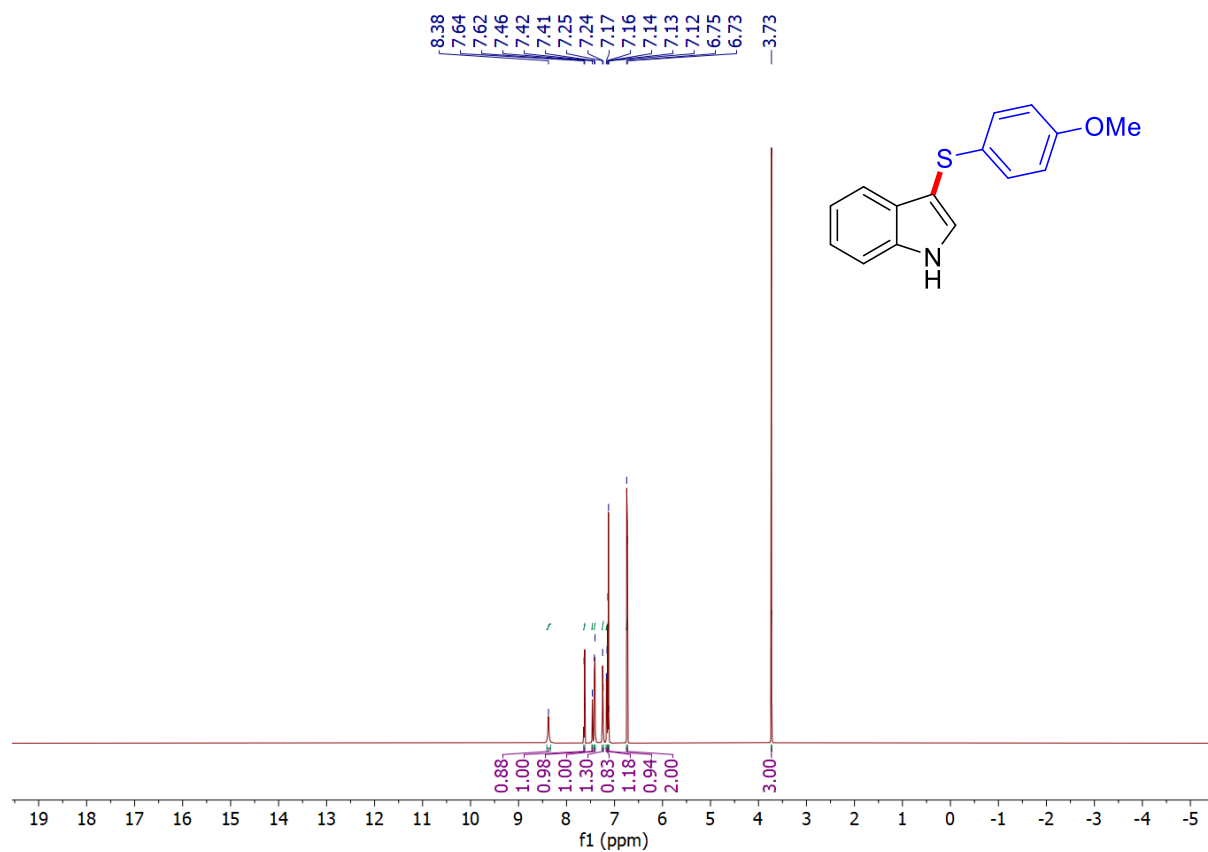


Figure 69: ¹H NMR (600 MHz, CDCl₃) spectrum of 3-((4-methoxyphenyl)thio)-1*H*-indole (**5f**).

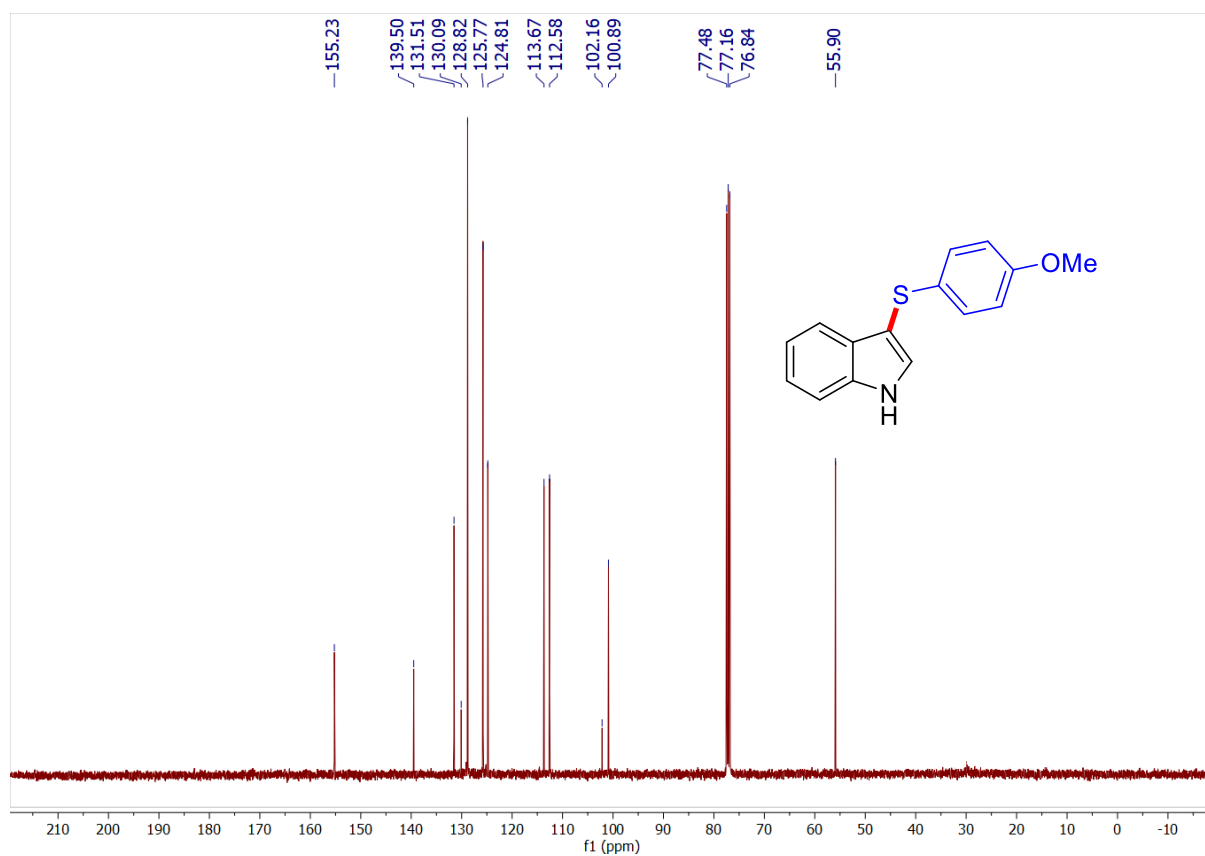


Figure 70: ^{13}C NMR (101 MHz, CDCl_3) spectrum of 3-((4-methoxyphenyl)thio)-1H-indole (**5f**).

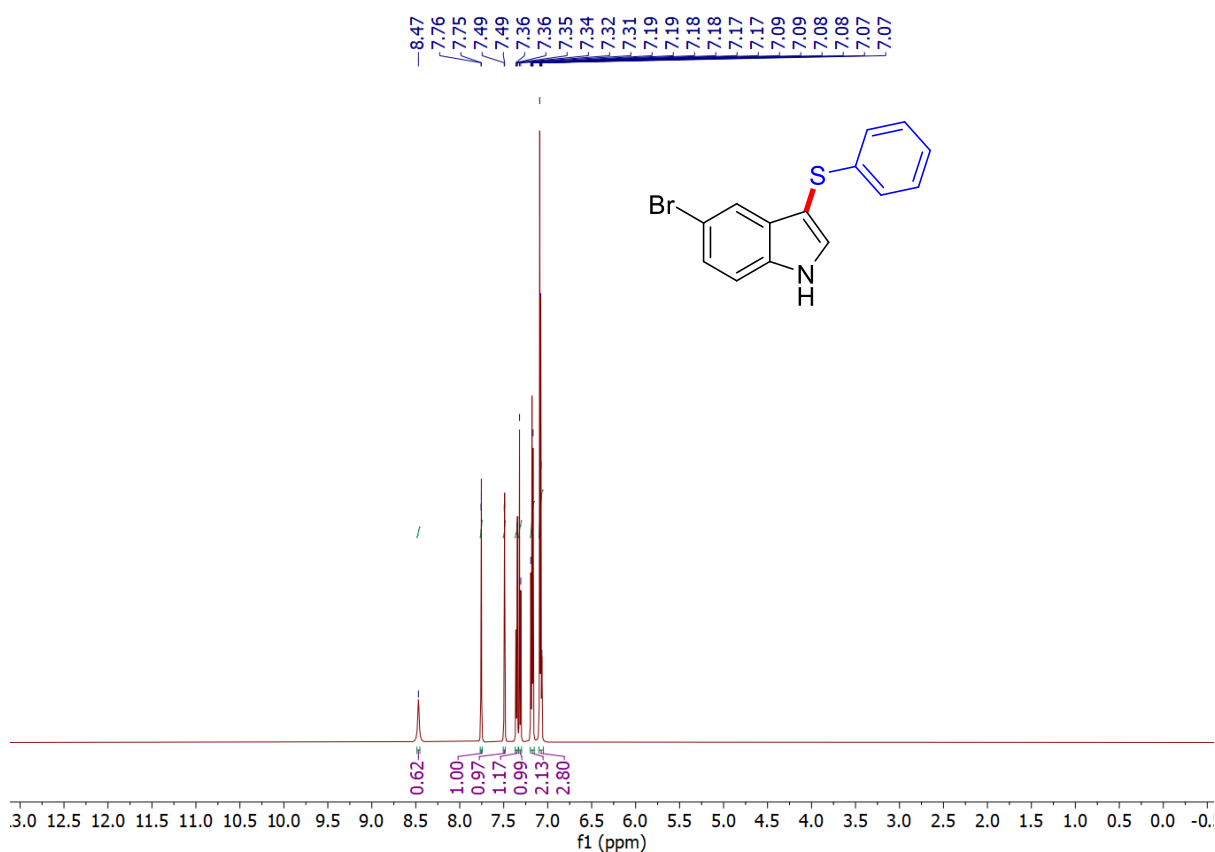


Figure 71: ¹H NMR (600 MHz, CDCl₃) spectrum of 5-bromo-3-(phenylthio)-1H-indole (**5g**).

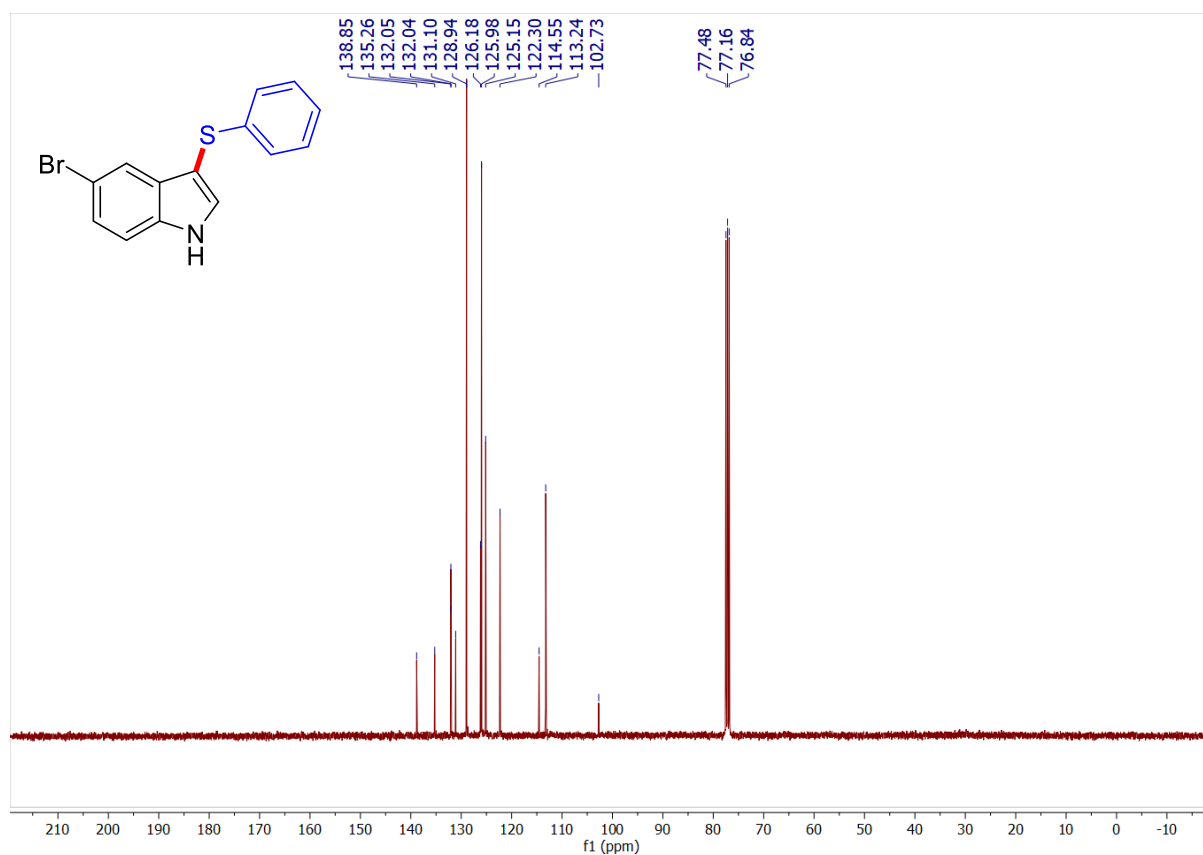


Figure 72: ¹³C NMR (101 MHz, CDCl₃) spectrum of 5-bromo-3-(phenylthio)-1H-indole (**5g**).

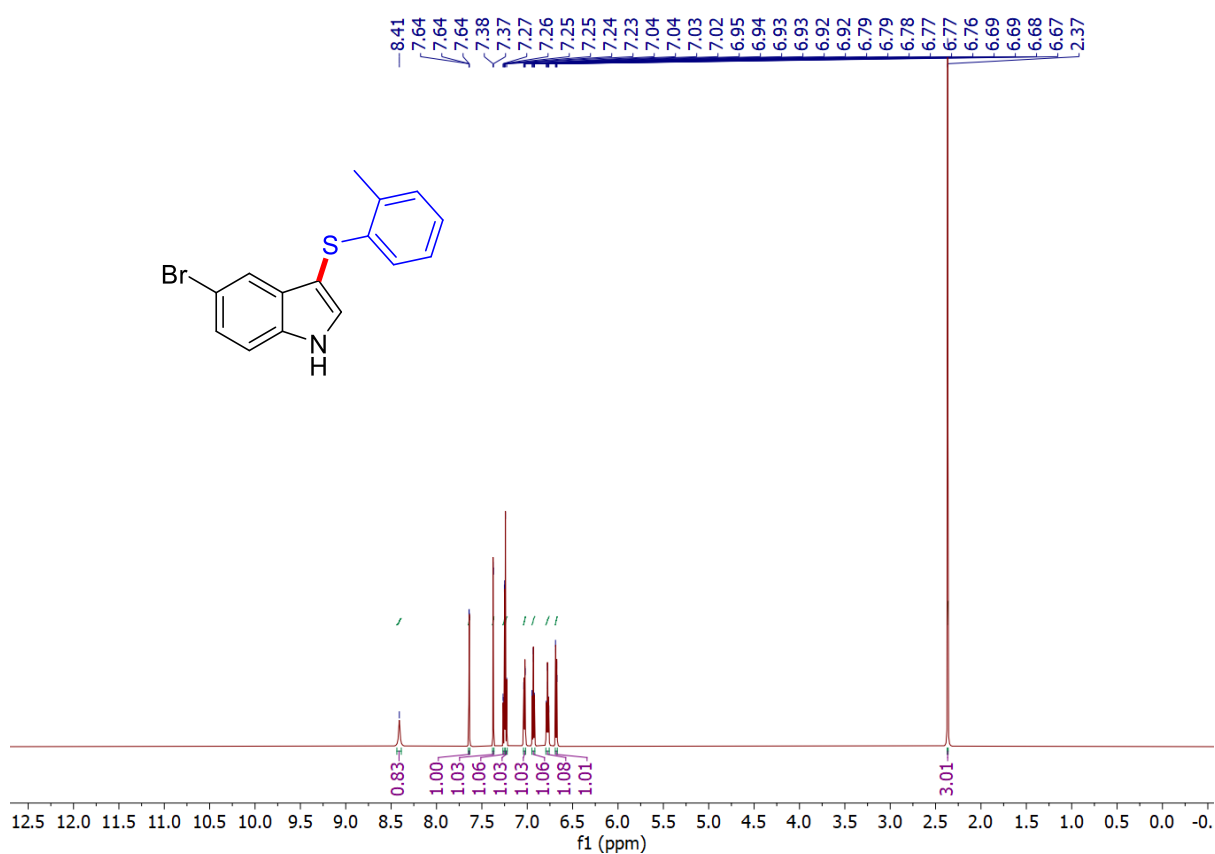


Figure 73: ¹H NMR (600 MHz, CDCl₃) spectrum of 5-bromo-3-(*o*-tolylthio)-1*H*-indole (**5h**).

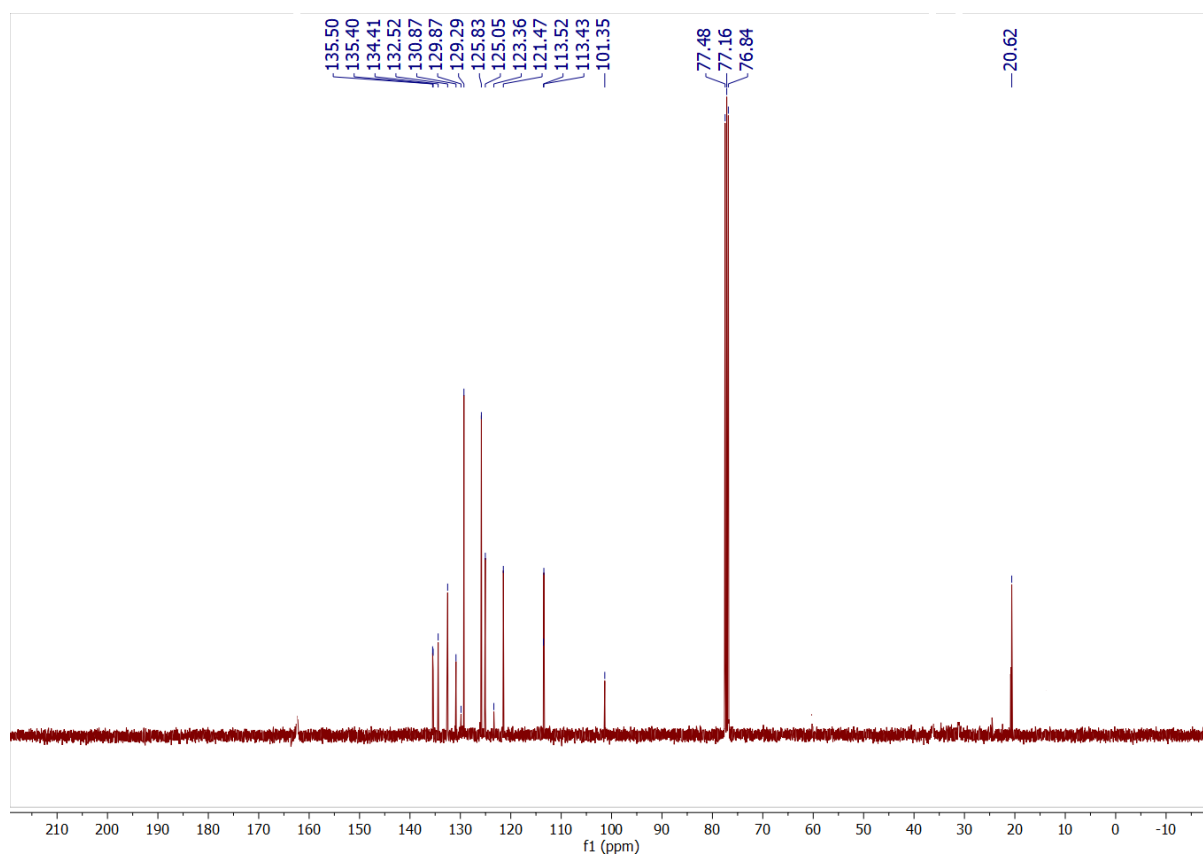


Figure 74: ¹³C NMR (101 MHz, CDCl₃) spectrum of 5-bromo-3-(*o*-tolylthio)-1*H*-indole (**5h**).

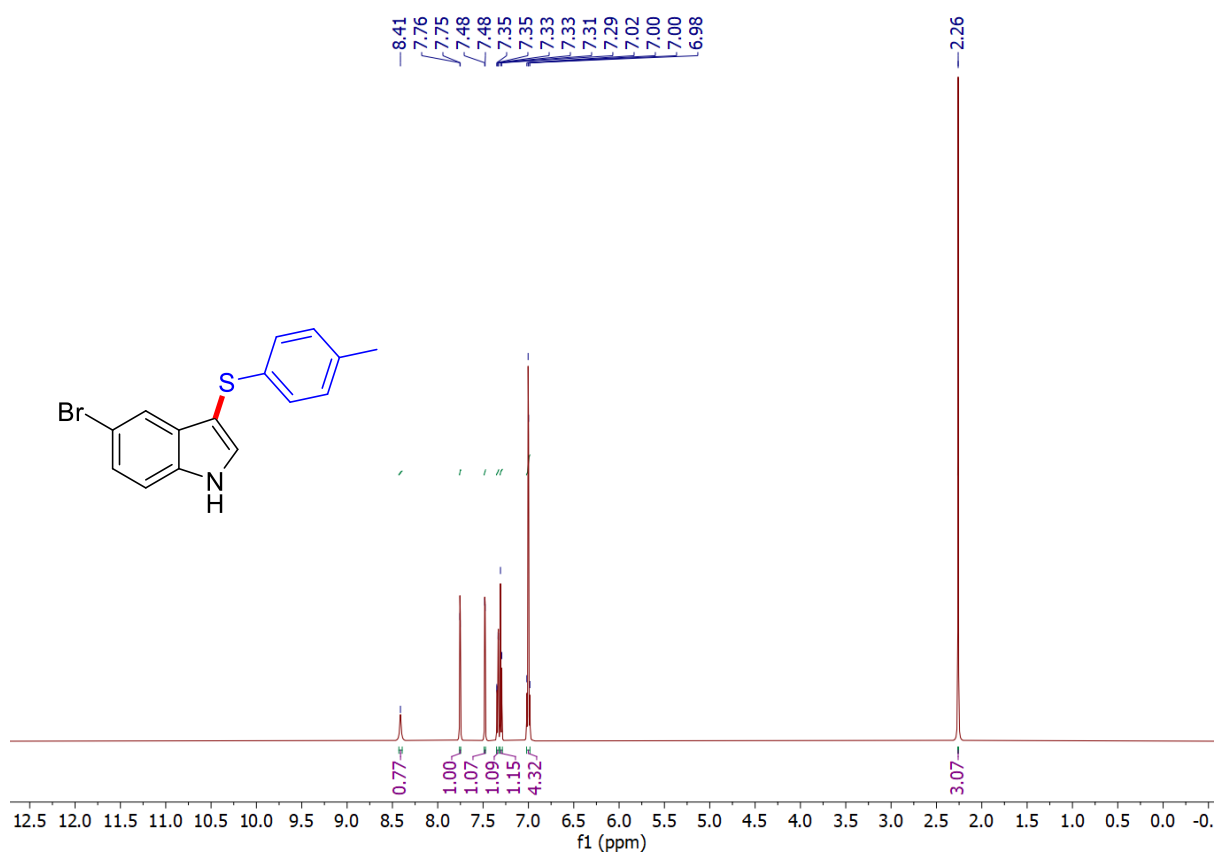


Figure 75: ¹H NMR (600 MHz, CDCl₃) spectrum of 5-bromo-3-(p-tolylthio)-1H-indole (**5i**).

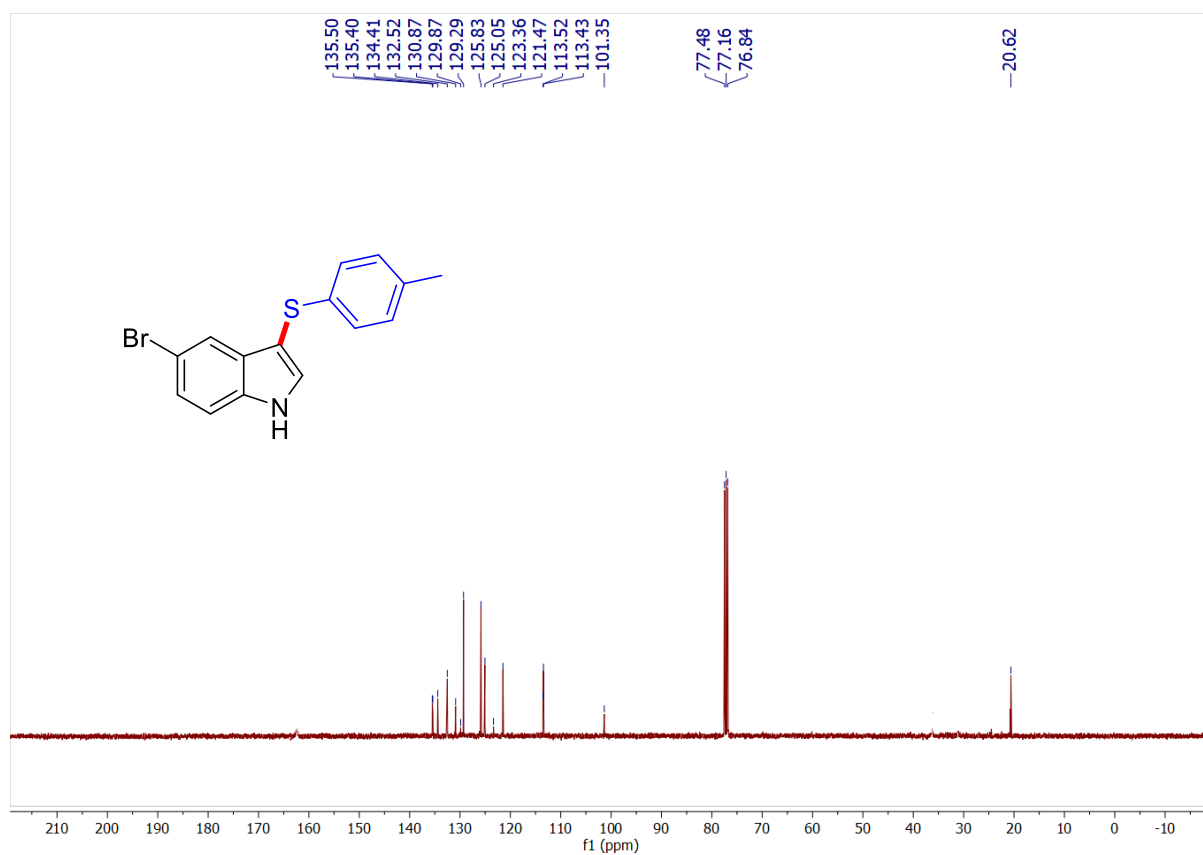


Figure 76: ¹³C NMR (101 MHz, CDCl₃) spectrum of 5-bromo-3-(p-tolylthio)-1H-indole (**5i**).

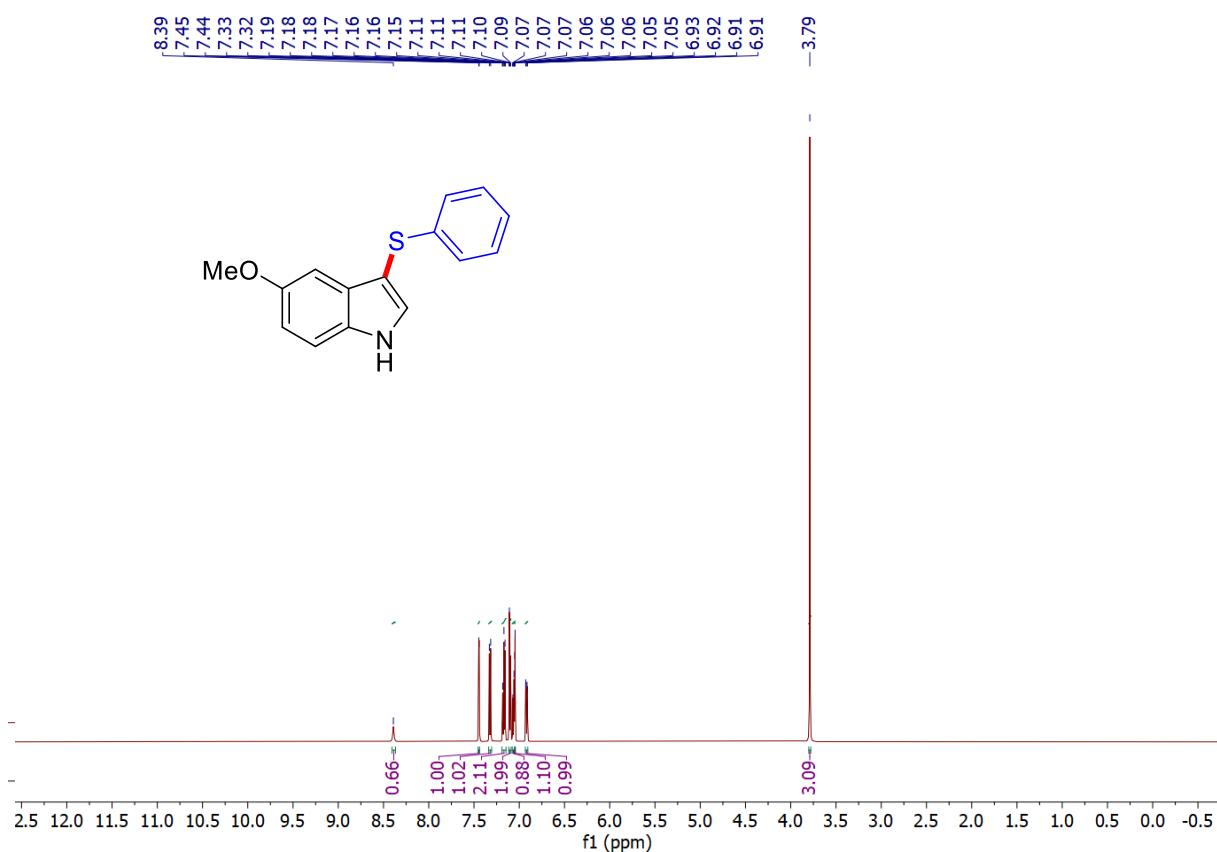


Figure 77: ¹H NMR (600 MHz, CDCl₃) spectrum of 5-methoxy-3-(phenylthio)-1H-indole (5j).

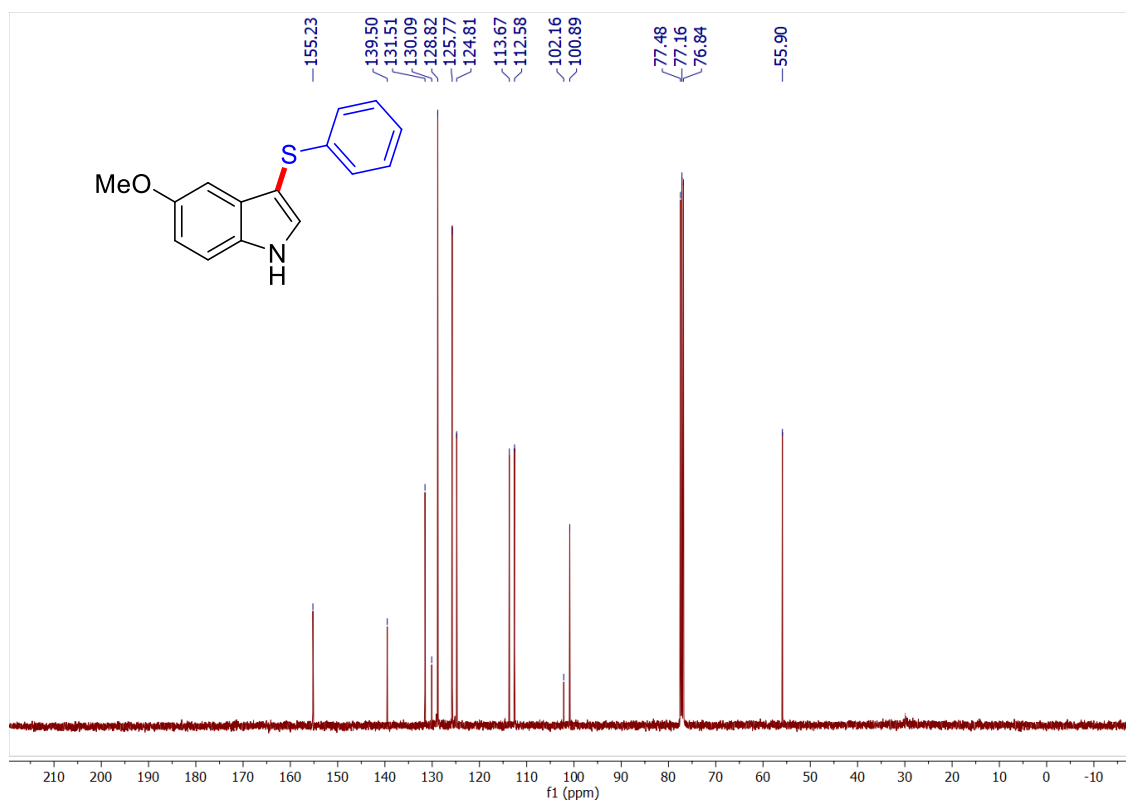


Figure 78: ¹³C NMR (101 MHz, CDCl₃) spectrum of 5-methoxy-3-(phenylthio)-1H-indole (5j).

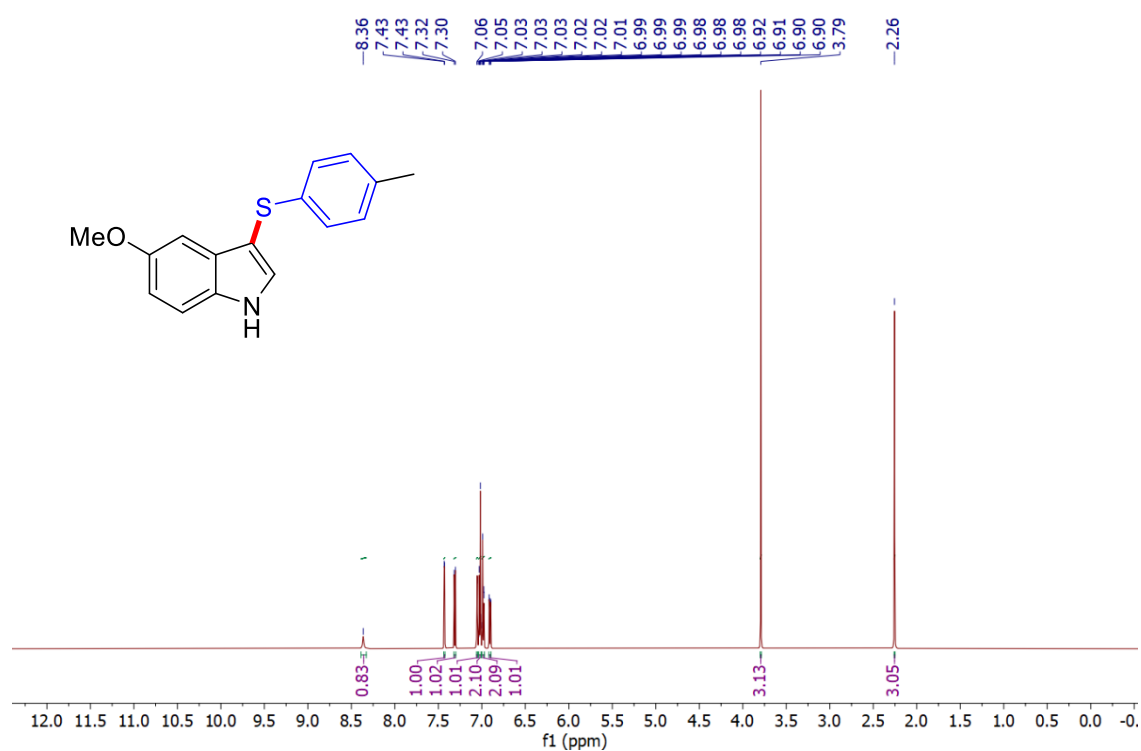


Figure 79: ¹H NMR (600 MHz, CDCl₃) spectrum of 5-methoxy-3-(*p*-tolylthio)-1*H*-indole (**5k**).

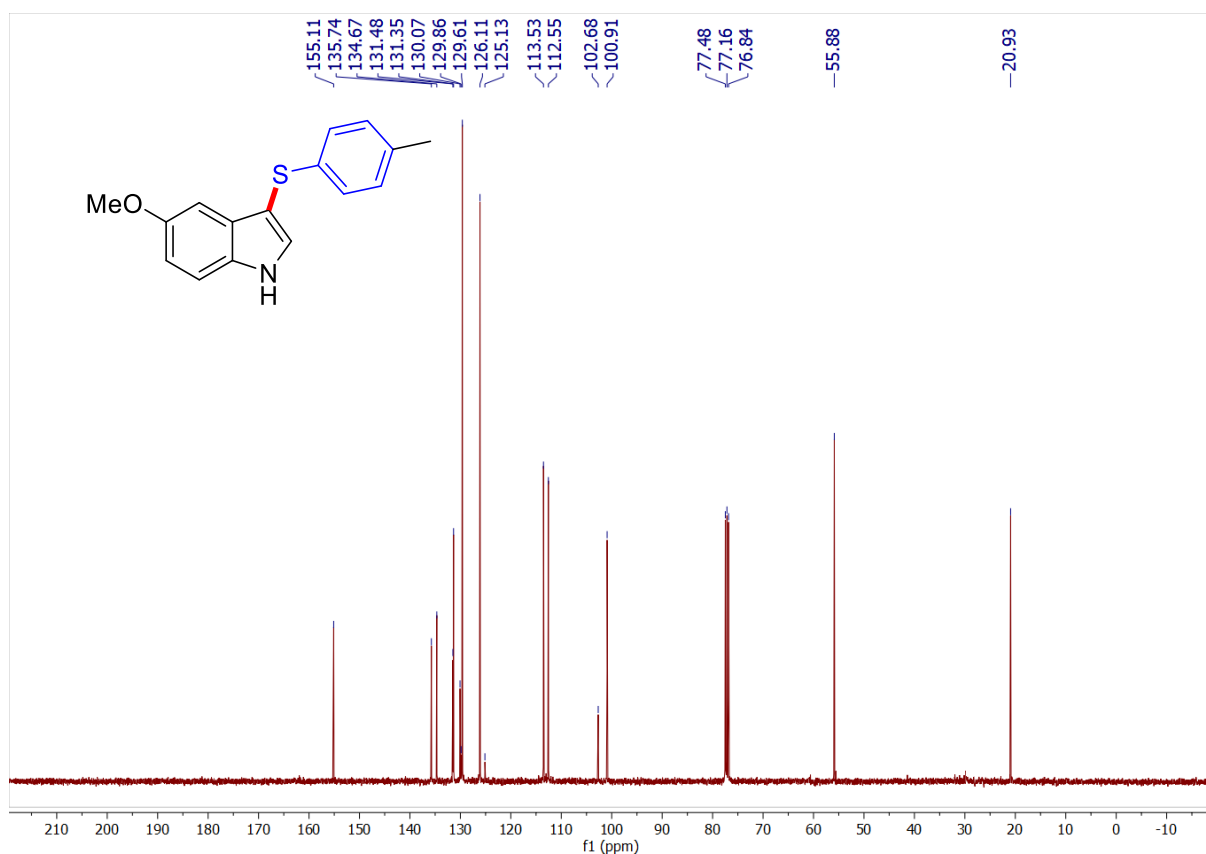


Figure 80: ¹³C NMR (101 MHz, CDCl₃) spectrum of 5-methoxy-3-(*p*-tolylthio)-1*H*-indole (**5k**).

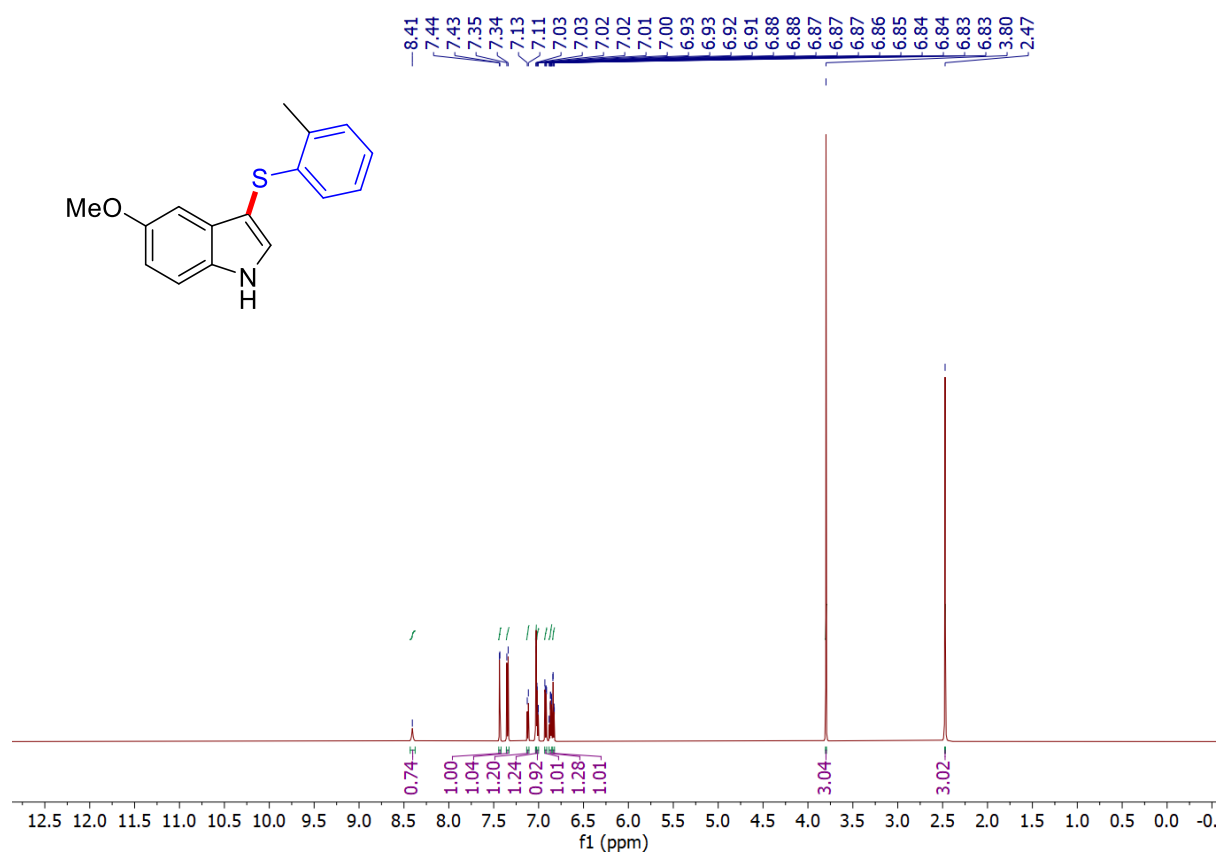


Figure 81: ¹H NMR (600 MHz, CDCl₃) spectrum of 5-methoxy-3-(*o*-tolylthio)-1*H*-indole (**5l**).

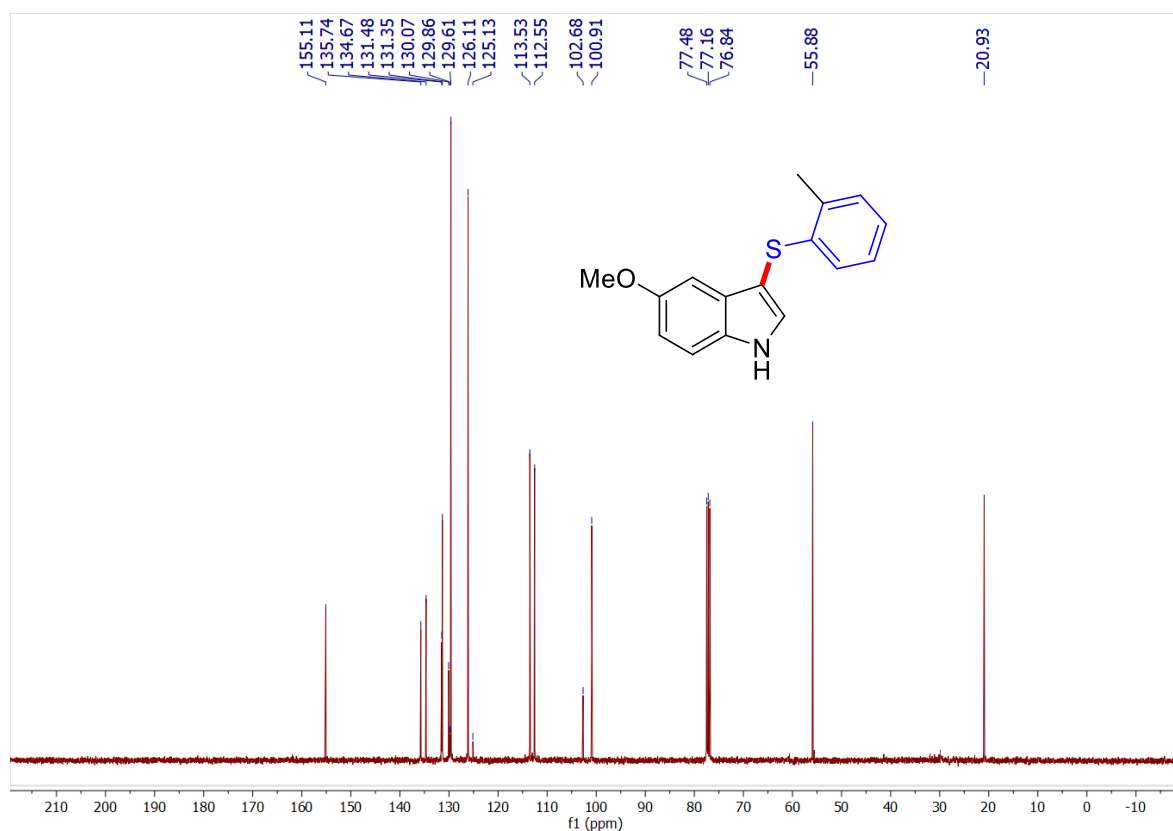


Figure 82: ¹³C NMR (101 MHz, CDCl₃) spectrum of 5-methoxy-3-(*o*-tolylthio)-1*H*-indole (**5l**).

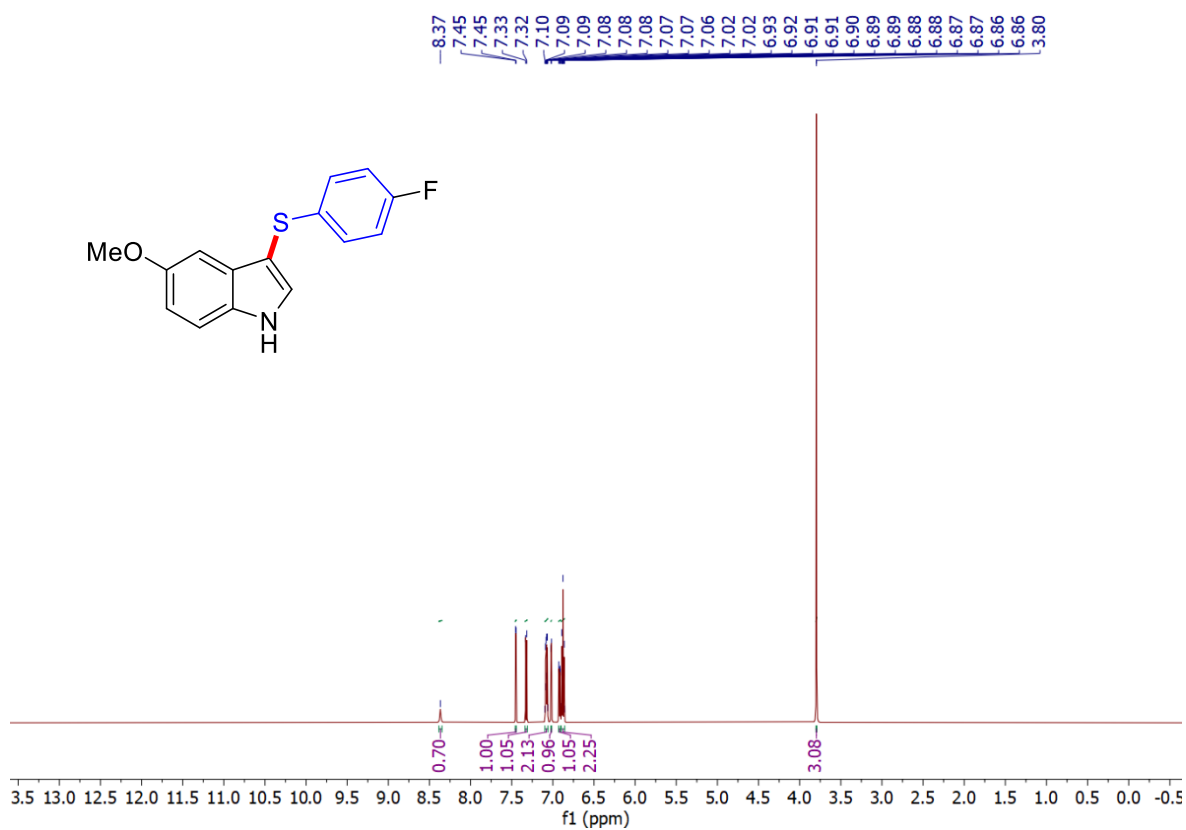


Figure 83: ¹H NMR (600 MHz, CDCl₃) spectrum of 5-methoxy-3-((4-fluorophenyl)thio)-1*H*-indole (**5m**).

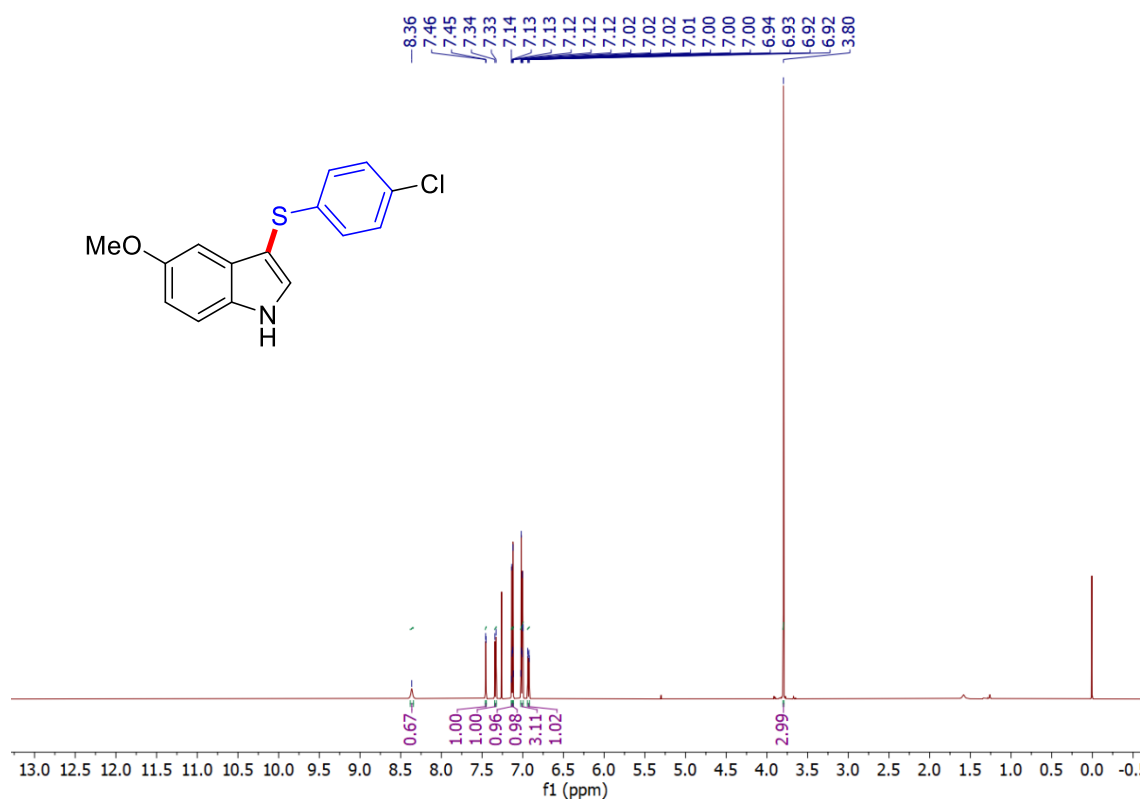


Figure 84: ¹H NMR (600 MHz, CDCl₃) spectrum of 5-methoxy-3-((4-chlorophenyl)thio)-1H-indole (**5n**).

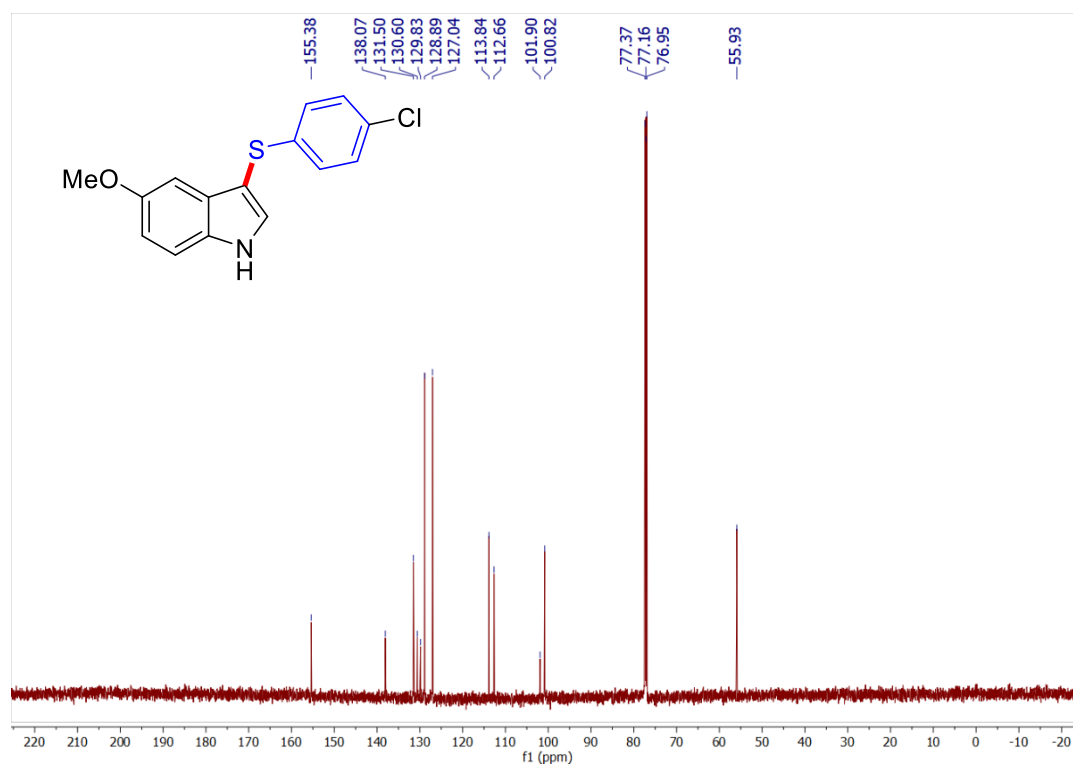


Figure 85: ¹³C NMR (151 MHz, CDCl₃) spectrum of 5-methoxy-3-((4-chlorophenyl)thio)-1H-indole (**5n**).

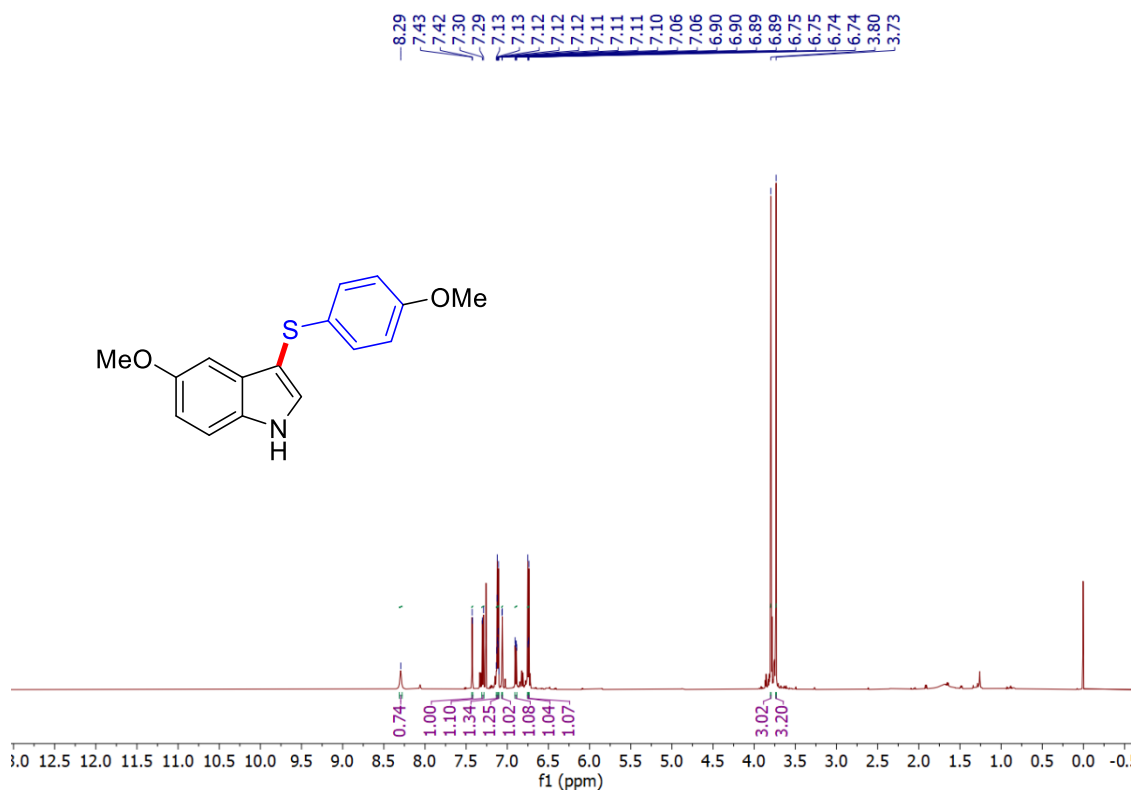


Figure 86: ¹H NMR (600 MHz, CDCl₃) spectrum of 5-methoxy-3-((4-methoxyphenyl)thio)-1H-indole (50).

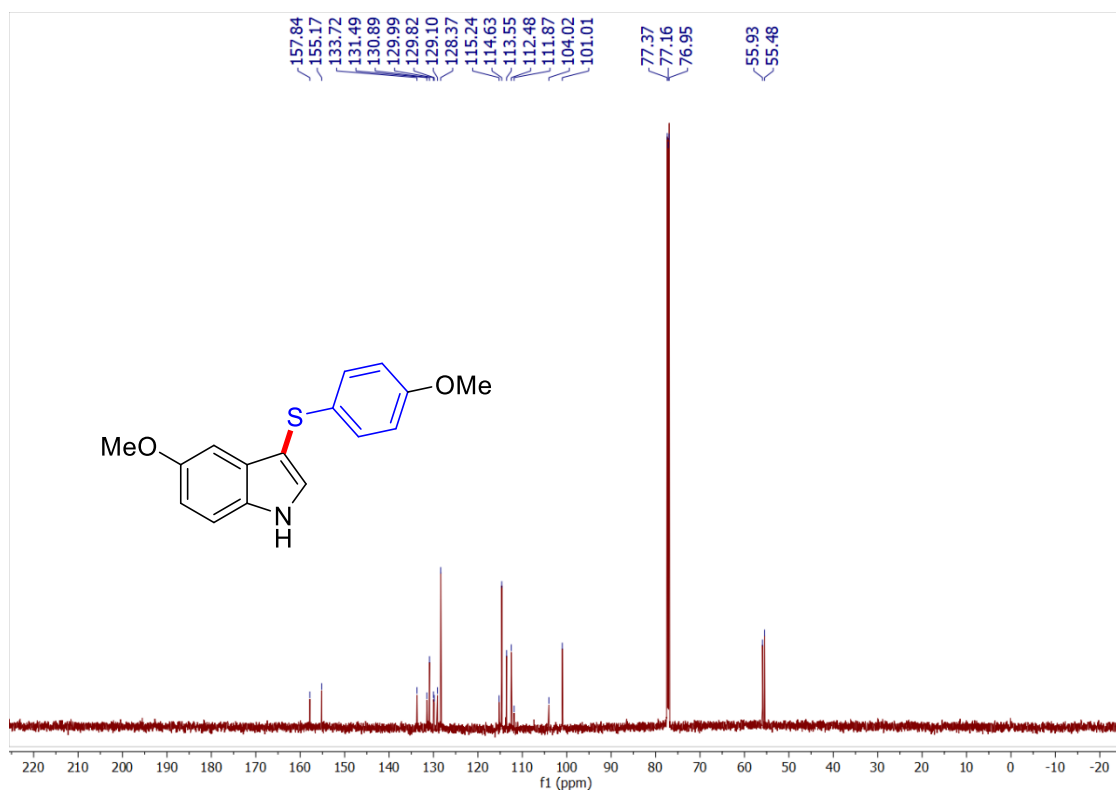


Figure 87: ¹³C NMR (151 MHz, CDCl₃) spectrum of 5-methoxy-3-((4-methoxyphenyl)thio)-1H-indole (50).

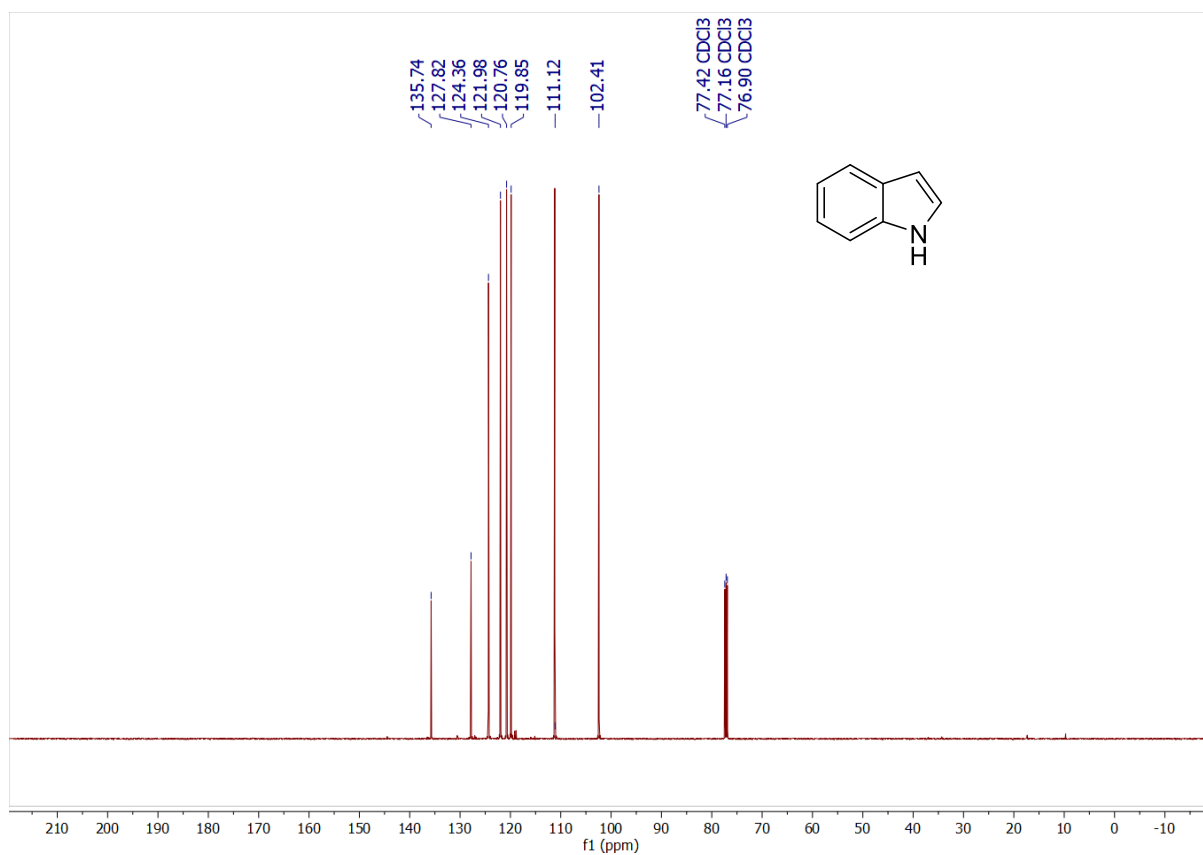


Figure 89: ¹³C NMR (500 MHz, CDCl₃) spectrum of Indole(**1a'**).

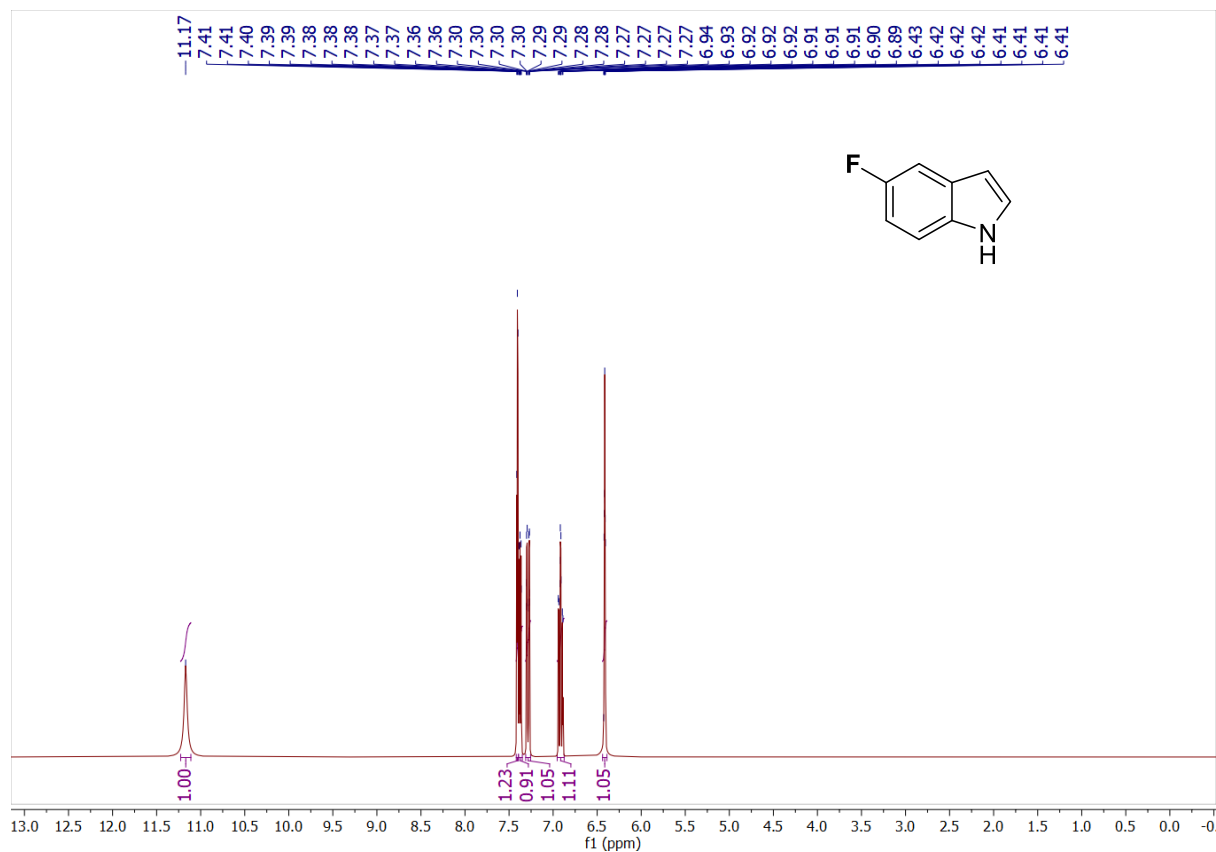


Figure 90: ¹H NMR (400 MHz, DMSO-d₆) spectrum of 5-fluorindole (**1b'**).



Figure 91: ^1H NMR (400 MHz, DMSO-d_6) spectrum of 5-bromoindole (**1c'**) .

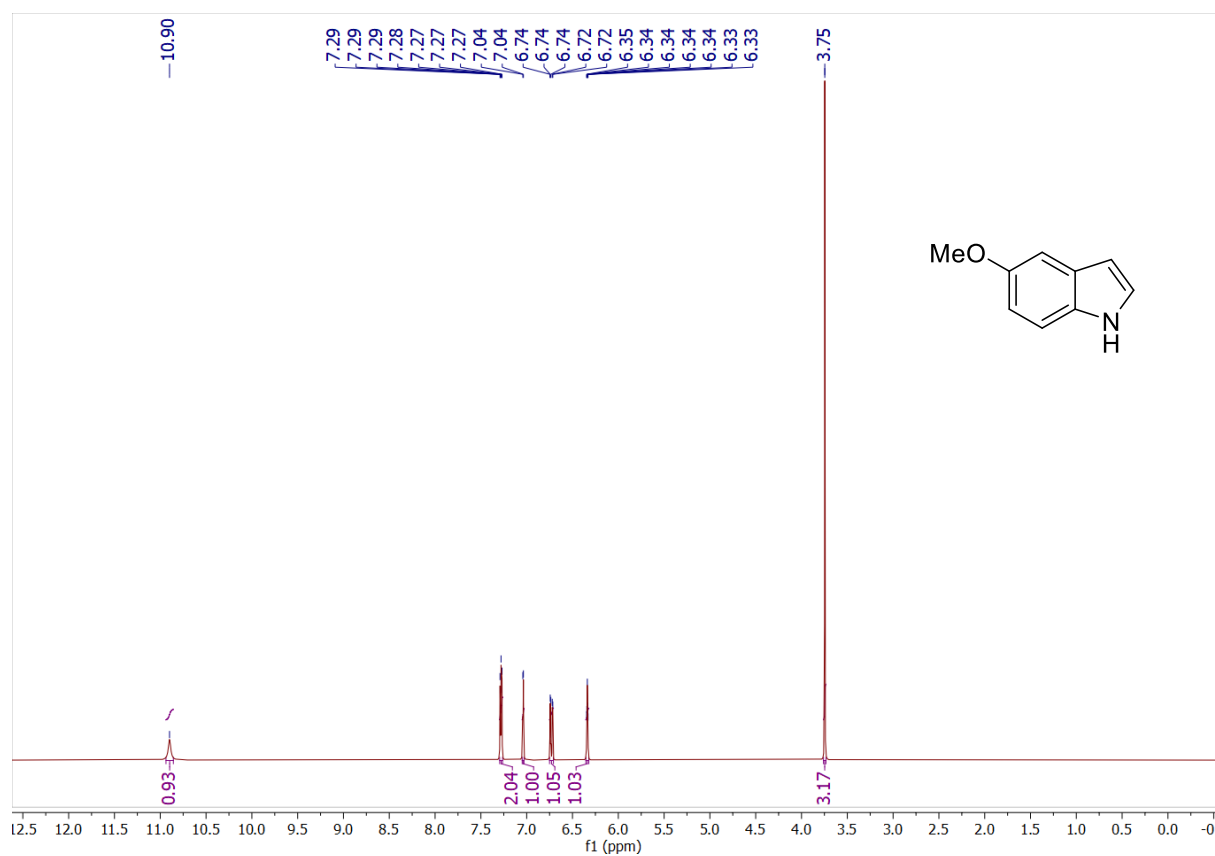


Figure 92: ^1H NMR (400 MHz, DMSO-d_6) spectrum of 5-methoxyindole (**1d'**) .

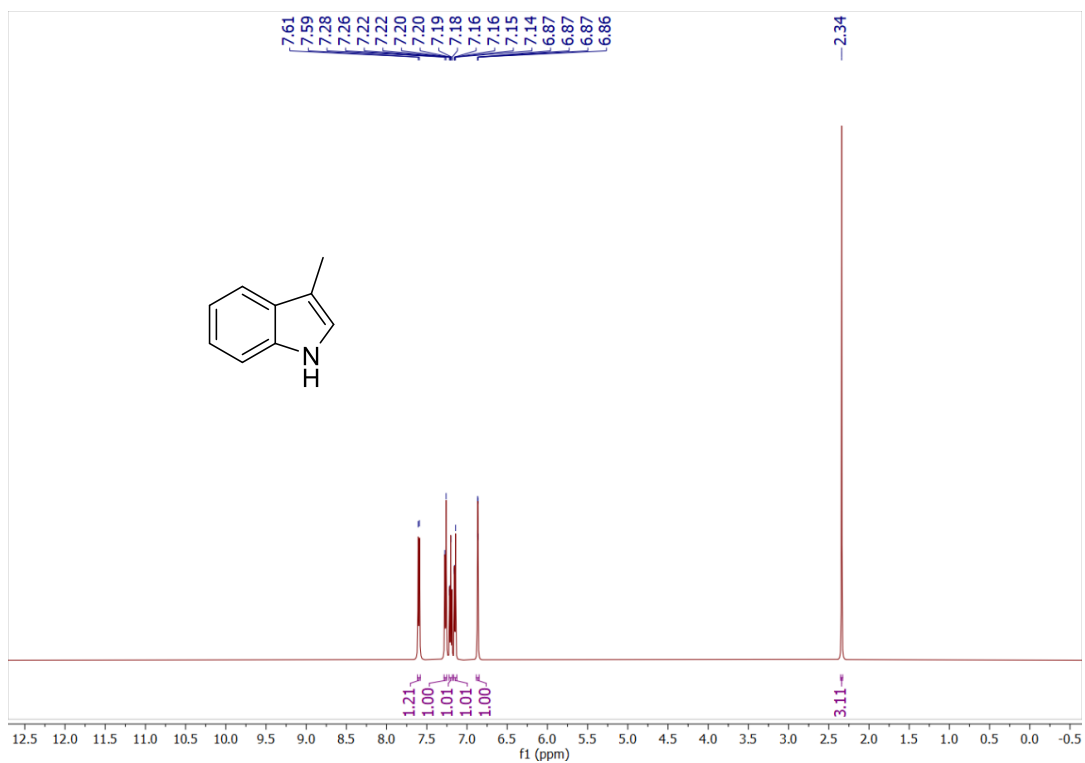


Figure 93: ^1H NMR (400 MHz, CDCl_3) spectrum of 3-methylindole (**1e'**) .

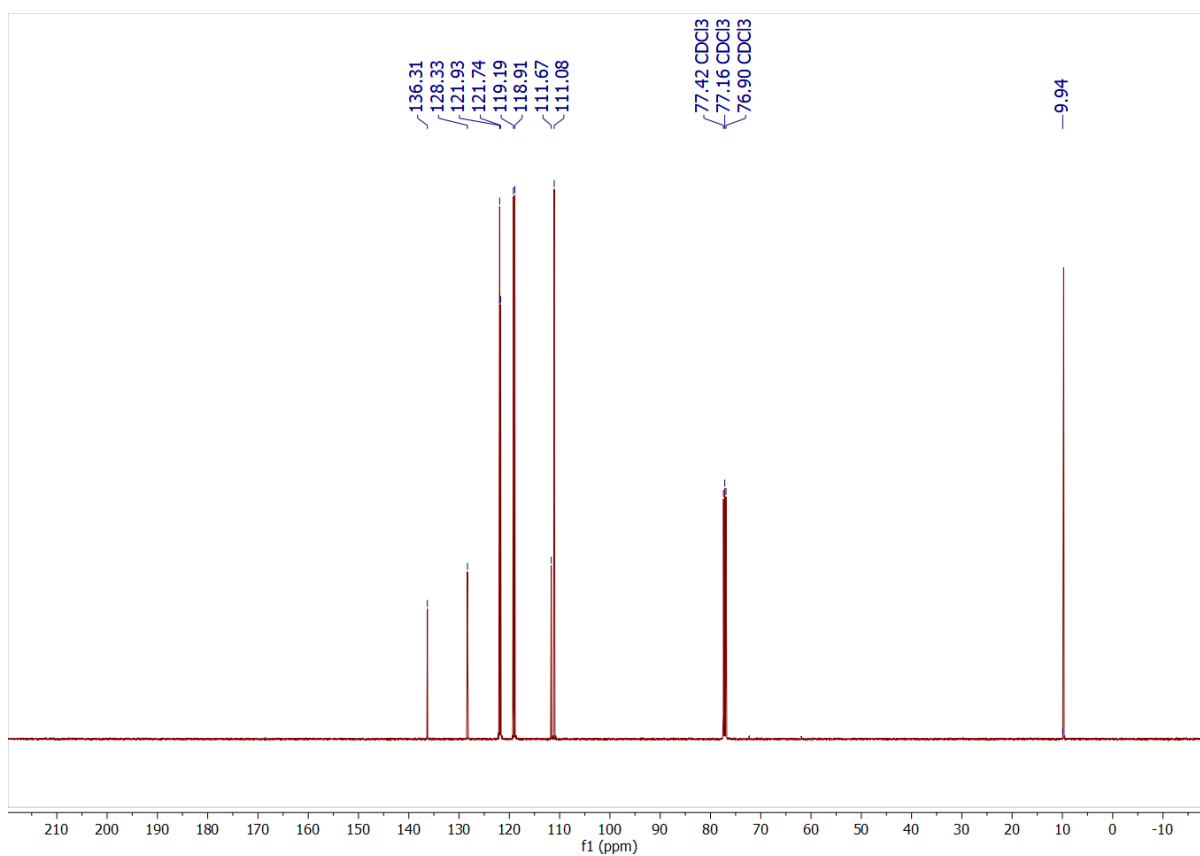


Figure 94: ¹³C NMR (400 MHz, CDCl₃) spectrum of 3-methylindole (**1e'**) .

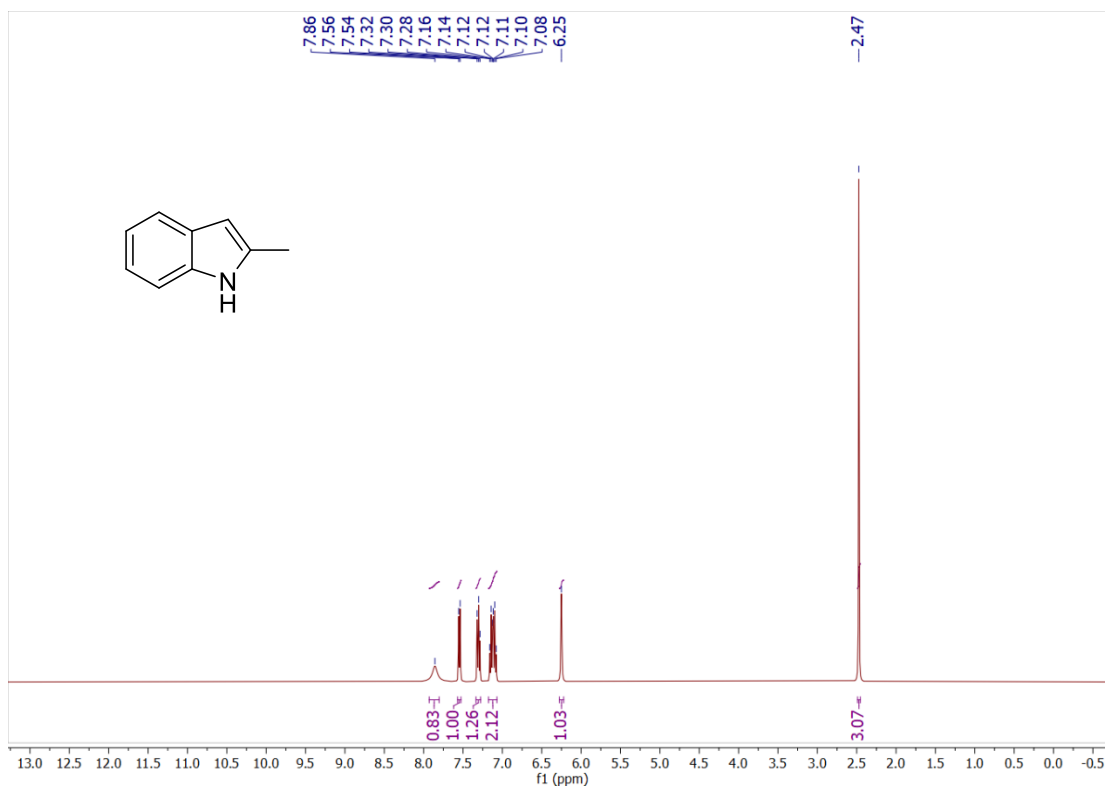


Figure 95: ¹H NMR (400 MHz, CDCl₃) spectrum of 2-methylindole (**1g'**)

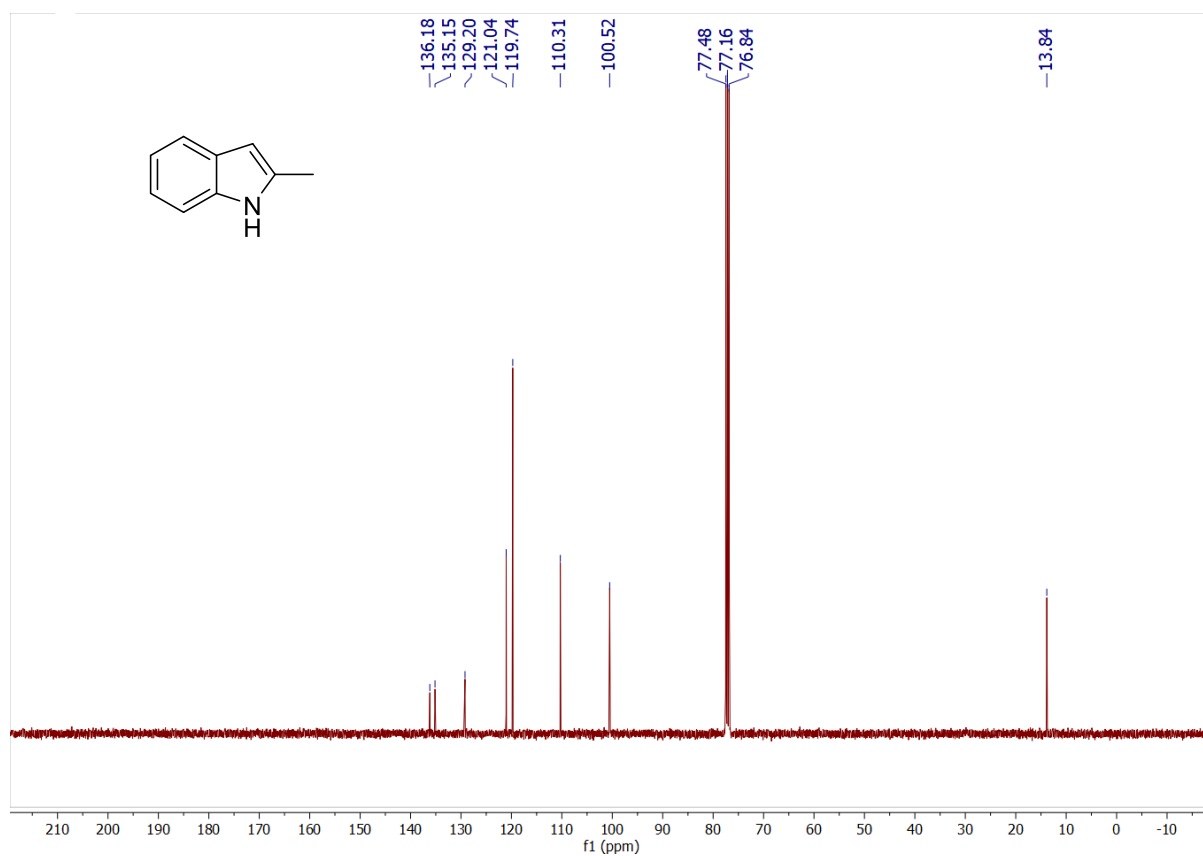


Figure 96: ^{13}C NMR (400 MHz, CDCl_3) spectrum of 2-methylindole (**1g'**) .

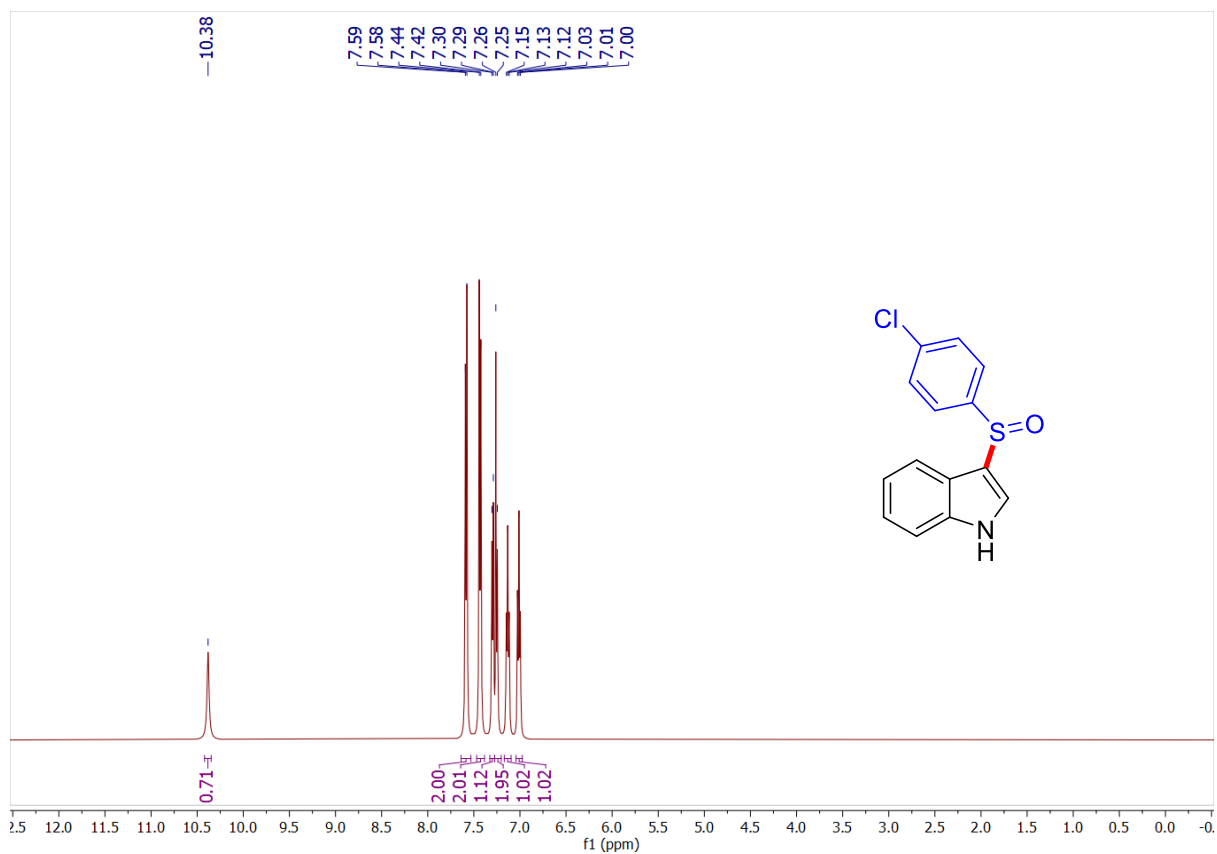


Figure 97: ¹H NMR (500 MHz, CDCl₃) spectrum of 3-((4-chlorophenyl)sulfinyl)-1H-indole (**5e'**).

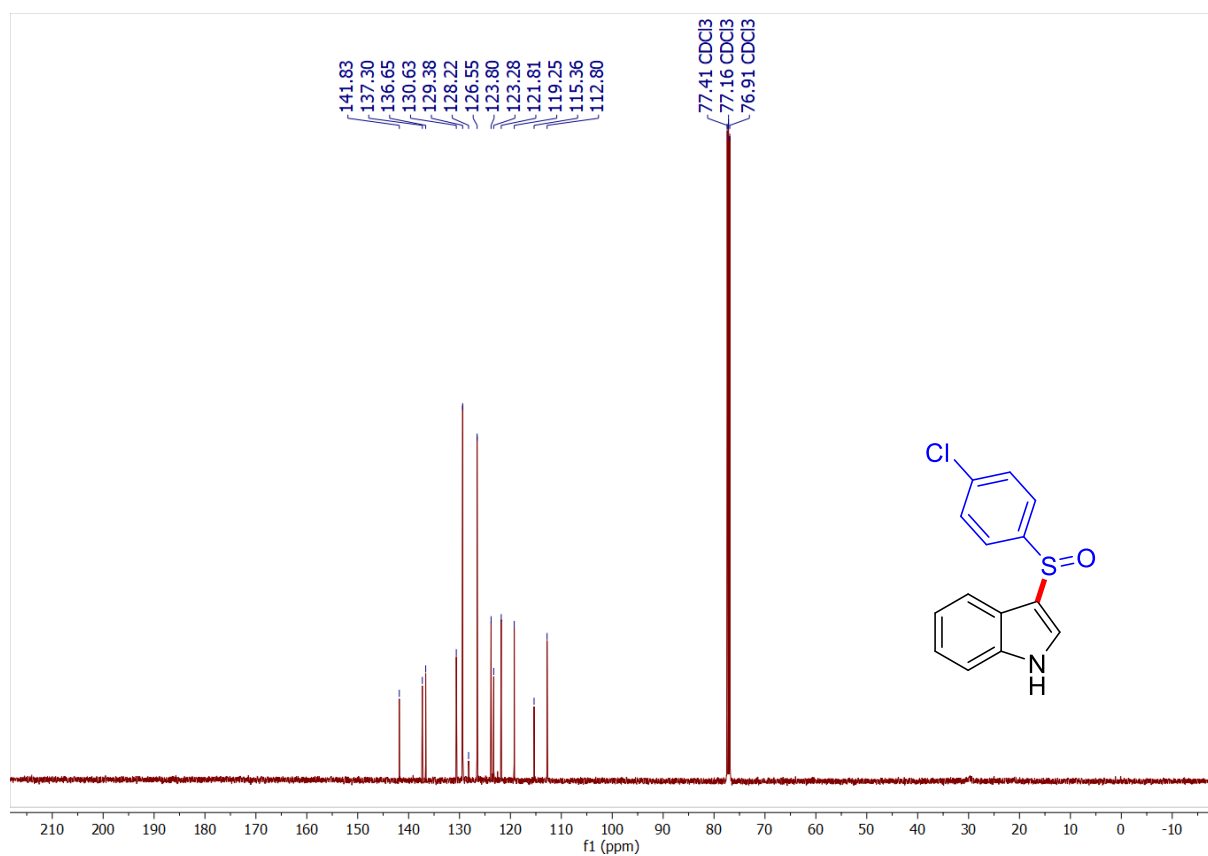


Figure 98: ¹³C NMR (126 MHz, CDCl₃) spectrum of 3-((4-chlorophenyl)sulfinyl)-1H-indole (**5e'**).

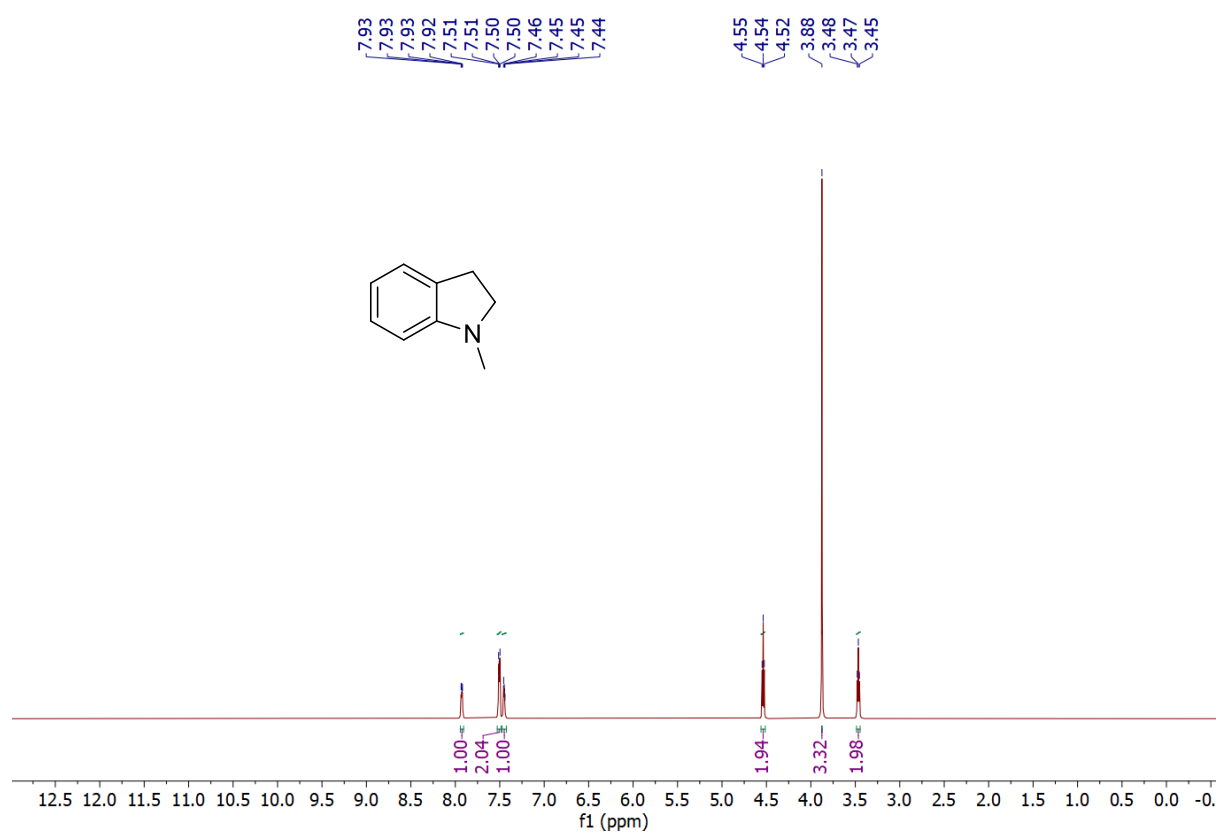


Figure 99: ¹H NMR (600 MHz, CDCl₃) spectrum of *N*-methylindoline (**1f**).

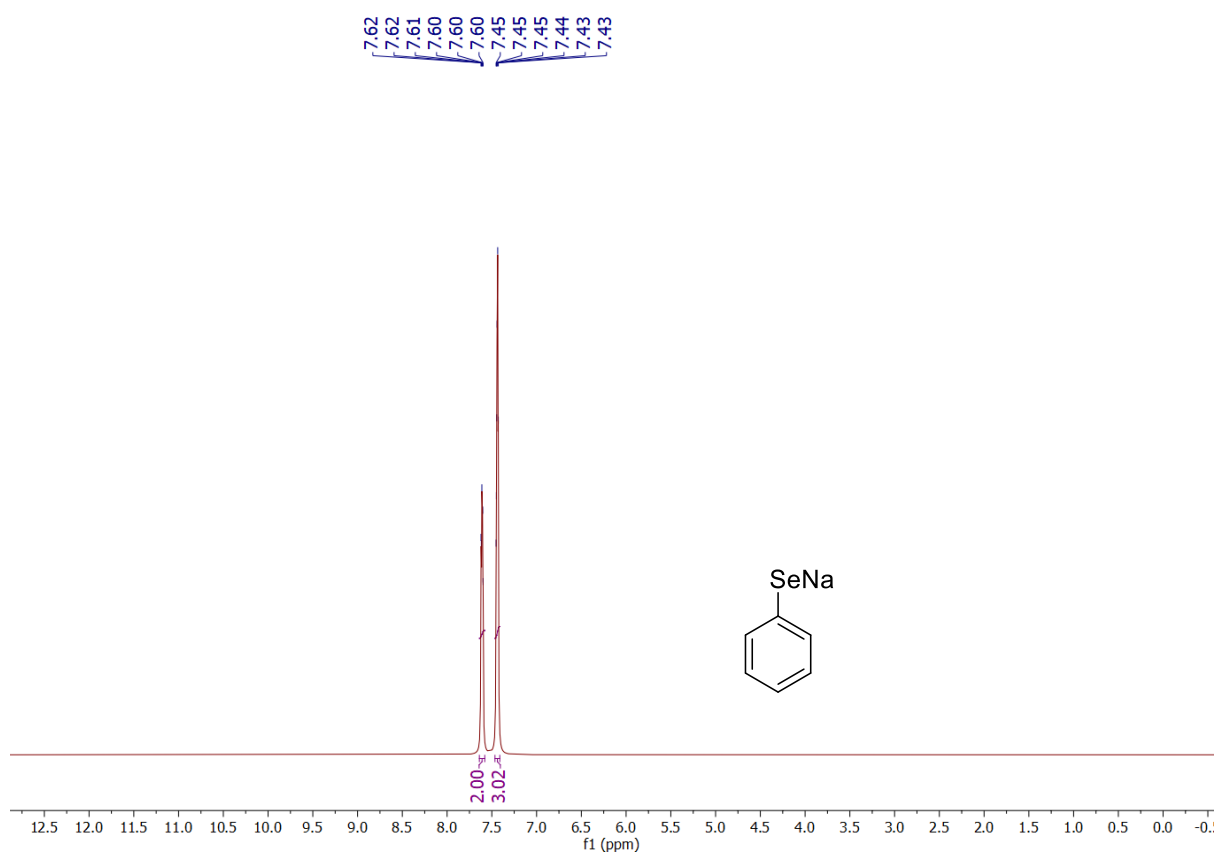


Figure 100: ¹H NMR (400 MHz, CDCl₃) spectrum sodium benzeneselenolate (**2a'**)

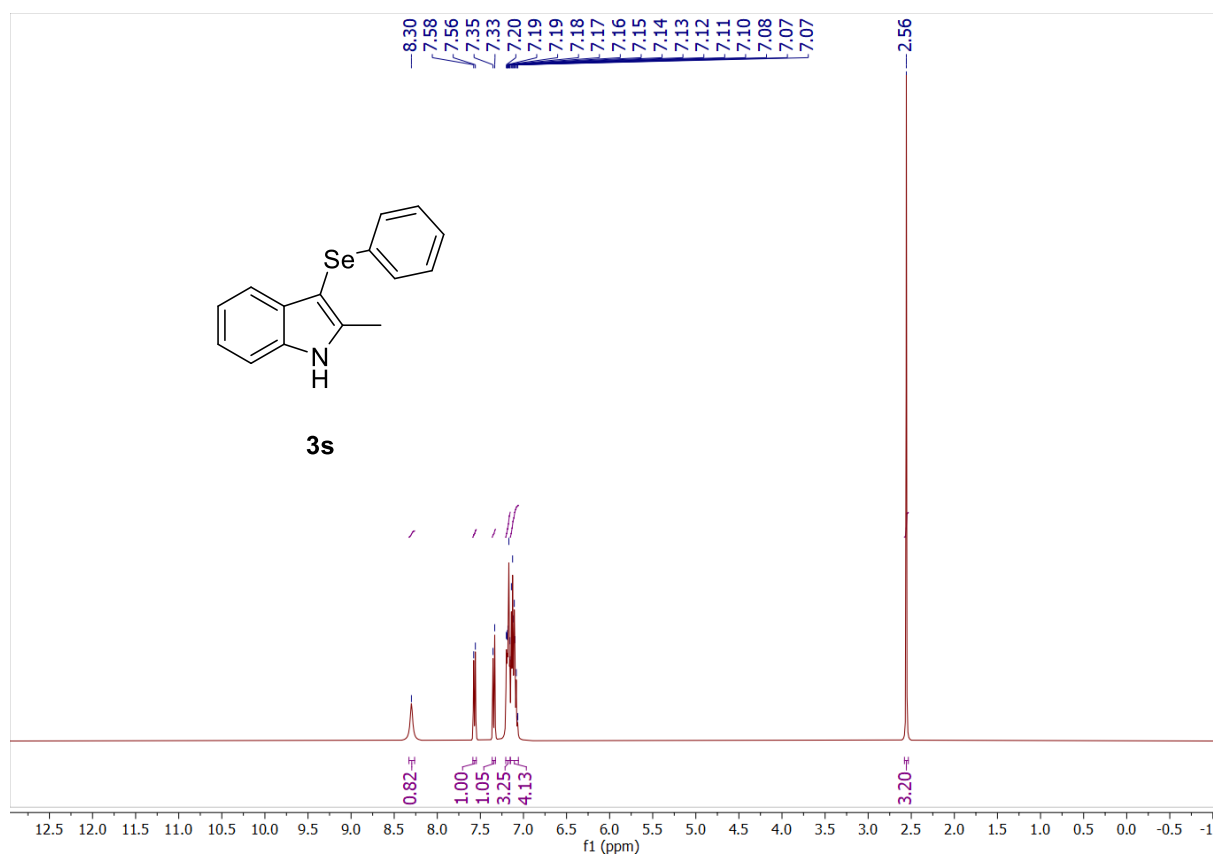


Figure 101: ¹H NMR (400 MHz, CDCl₃) spectrum of 2-methyl-3-(phenylselanyl)-1H-indole (**3s**).

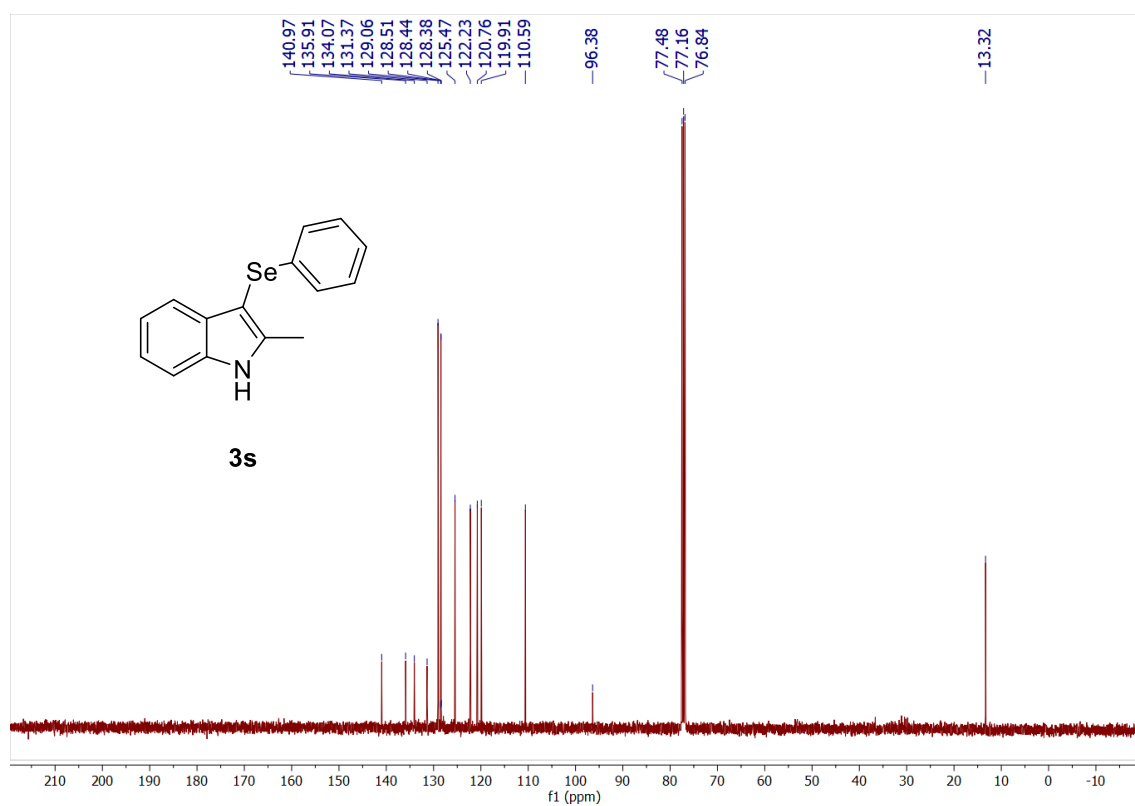


Figure 102: ¹³C NMR (400 MHz, CDCl₃) spectrum of 2-methyl-3-(phenylselanyl)-1H-indole (**3s**).