Rose Bengal Catalysed Photo-Induced Selenylation of Indoles, Imidazoles and Arenes: A Metal Free Approach

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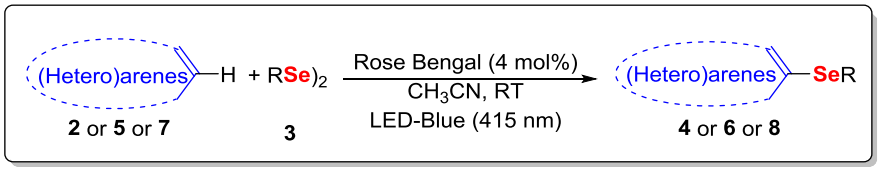
Table of Contents

I. Materials and Methods

Proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained at 200 MHz on a Bruker AC-200 NMR spectrometer or at 400 MHz on a Varian AS-400 NMR spectrometer. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$ or tetramethylsilane (TMS) as the external reference. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant (J) in Hertz and integrated intensity. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained either at 50 MHz on a Bruker AC-200 NMR spectrometer or at 100 MHz on a Varian AS-400 NMR spectrometer. Spectra were recorded in $CDCl_3$/, acetone-d_6 or DMSO-d_6 solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$. Abbreviations to denote the multiplicity of a particular signal are: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet) and m (multiplet). High resolution mass spectra were recorded on a Bruker microTOF-Q II APPI/APCI mass spectrometer equipped with an automatic syringe pump for sample injection. The melting points were determined in a Microquimica MQRPF-301 digital model equipment with heating plate. Column chromatography was performed using Silica Gel (230-400 mesh). Thin layer chromatography (TLC) was performed using Merck Silica Gel GF_{254}, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapor and acidic vanillin. Most reactions were monitored by TLC for disappearance of starting material.

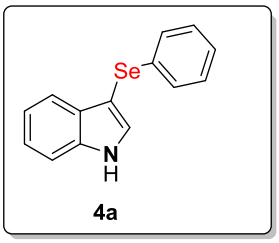
Unless otherwise stated, all reactions were carried out in Schlenk tube; all reagents and solvents were obtained from commercial sources and used without any further purification. Reactions under inert atmosphere were conducted in flame-dried or oven dried glassware equipped with tightly fitted rubber septa and under a positive atmosphere of dry argon. Reagents and solvents were handled using standard syringe techniques. The yields are based on isolated compounds after purification.

II. General procedure for the Rose Bengal-catalyzed selenylation

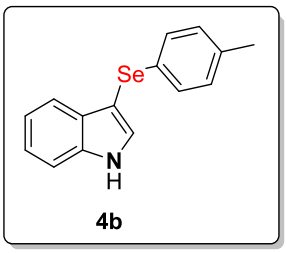


A mixture of appropriate substrate **2** or **5** or **7** (0.25 mmol), diorganyl diselenide **3** (0.125 mmol), Rose Bengal (4 mol %, 10.11 mg), and CH_3CN (2 mL) were charged in a Schlenck tube. The reaction was irradiated under LED-Blue (415 nm) for 6 h, at room temperature. After this, the reaction mixture was dissolved in ethyl acetate (10 mL), and washed with 2 x 5 mL of brine. The organic phase was separated, dried over $MgSO_4$, and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel using hexane or a mixture of hexane/ ethyl acetate (95:5) as the eluent.

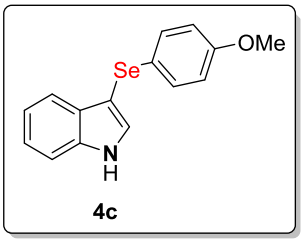
III. Characterization data of the synthesized compounds



3-(Phenylselanyl)-1*H*-indole (4a): Yield: 93% (63.4 mg); white solid; mp: 134-135 °C (134-137 °C);[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 2.0 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.05 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 133.8, 131.2, 129.9, 128.9, 128.6, 125.6, 122.9, 120.8, 120.3, 111.3, 98.1.

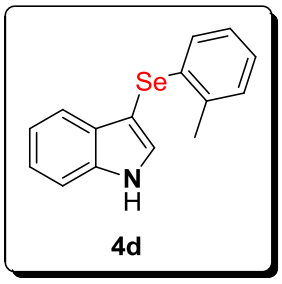


3-(*p*-Tolylselanyl)-1*H*-indole (4b): Yield: 88% (63mg); white solid; mp: 105-106 °C (104-106 °C);[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.13 (m, 6H), 6.92 (d, *J* = 7.9 Hz, 2H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 135.6, 131.1, 130.0, 129.9, 129.2, 122.9, 120.8, 120.4, 111.4, 98.5, 21.0.



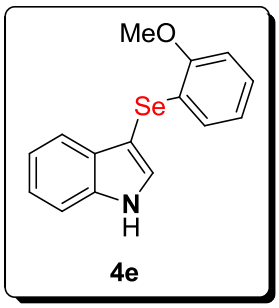
4c

3-((4-Methoxyphenyl)selanyl)-1*H*-indole (4c): Yield: 92% (70 mg); white solid; mp: 113−115ºC (113−115);[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.23 – 7,15 (m, 4H), 6.65 (d, *J* = 8.8 Hz, 2H), 3.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 136.4, 131.3, 130.8, 129.9, 123.5, 122.8, 120.8, 120.3, 114.8, 111.5, 99.2, 55.3.



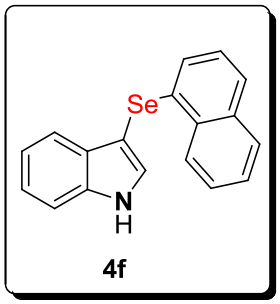
4d

3-(*o*-Tolylselanyl)-1*H*-indole (4d): Yield: 82% (59 mg); white solid; mp: 117−120 ºC (117−120);[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.40 – 6.94 (m, 6H), 6.82 (d, J = 3.6 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 136.2, 134.6, 131.6, 130.2, 129.9, 128.1, 126.6, 125.5, 123.1, 120.9, 120.5, 111.5, 97.3, 21.4.



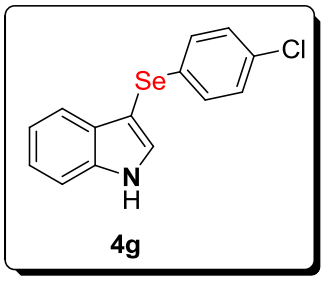
4e

3-((2-Methoxyphenyl)selanyl)-1*H*-indole (4e): Yield: 70% (53 mg); dark red solid; mp: 117−119 ºC (117.5−118.3 ºC);[1] ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.34 (m, 2H), 7.30 – 7.01 (m, 3H), 6.79 (d, J = 7.9 Hz, 1H), 6.70 – 6.55 (m, 2H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 136.6, 132.1, 130.3, 128.1, 126.4, 123.2, 122.9, 121.6, 120.8, 120.4, 111.6, 110.1, 95.8, 55.9.



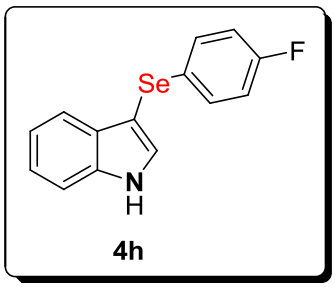
4f

3-(Naphthalen-1-ylselanyl)-1*H*-indole (4f): Yield: 92% (74 mg); white solid; mp: 117-118 ºC; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.9 Hz, 1H), 8.23 (s, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.62 – 7.06 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 133.9, 132.7, 132.4, 131.7, 130.0, 128.7, 126.9, 126.4, 126.3, 126.2, 126.1, 125.7, 123.0, 120.9, 120.4, 111.58, 97.2.



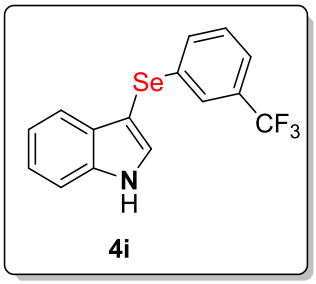
4g

3-((4-Chlorophenyl)selanyl)-1*H*-indole (4g): Yield: 87% (67 mg); white solid; mp: 117−120 ºC (117−120 ºC);[1] ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.45 – 7.36 (m, 3H), 7.30 – 7.04 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 132.2, 131.8, 131.4, 130.1, 129.8, 129.1, 123.2, 121.1, 120.3, 111.6, 98,0.



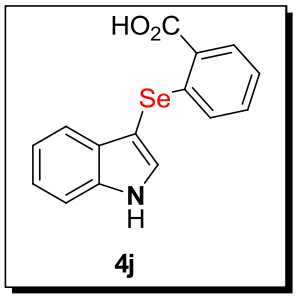
4h

3-((4-Fluorophenyl)selanyl)-1*H*-indole (4h): Yield: 79% (57 mg); brown solid; mp: 134−137ºC (135−136 ºC);[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 2.5 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.29 – 7.13 (m, 4H), 6.87 – 6.78 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161,7 (d, J_F = 244.6 Hz), 136.5, 131.1, 130,8 (d, J_F = 7.5 Hz), 129.8, 128.0 (d, J_F = 2.5 Hz), 123.1, 121.1, 120.3, 116.2 (d, J_F = 21.7 Hz), 111.5, 98.7.



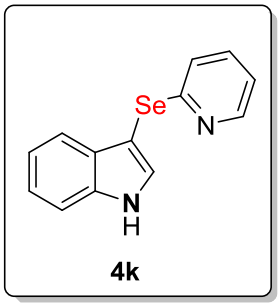
4i

3-((3-(Trifluoromethyl)phenyl)selanyl)-1*H*-indole (4i): Yield: 72% (61 mg); yellow solid; mp: 76−78 ºC (75.8−77.0 ºC);[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.53 (s, 1H), 7.41 (d, *J* = 2.5 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.33 – 7.11 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 135.4, 131.9, 131.6, 131.2 (d, J_F = 32.1 Hz), 129.7, 129.3, 125.2 (d, J_F = 3.6 Hz), 123.9 (q, J_F = 272.0 Hz) 123.3, 122.5, 122.5 (d, J_F = 4.4 Hz) , 121.2, 120.2, 199.9, 111.7, 97.3.



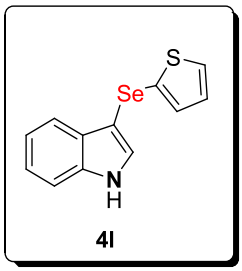
4j

2-((1*H*-indol-3-yl)selanyl)benzoic acid: Yield: 79% (63 mg); red solid; mp: 152−154 ºC ;[1]H NMR (400 MHz, Acetone) δ 10.85 (s, 1H), 8.12 (d, *J* = 9.1 Hz, 1H), 7.66 (d, *J* = 2.3 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.26 – 7.04 (m, 5H), 6.95 (dd, *J* = 7.8, 1.0 Hz, 1H);^{13}C NMR (101 MHz, Acetone) δ 168.4, 141.9, 138.3, 133.8, 133.6, 133.2, 132.4, 131.2, 129.3, 128.2, 123.2, 121.1, 120.4, 112.8, 98.7.



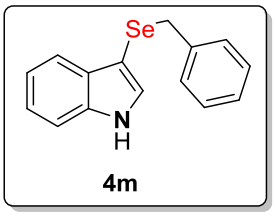
4k

3-(Pyridin-2-ylselanyl)-1*H*-indole (4k): Yield: 79% (54 mg); white solid; mp: 102-104 ºC (103−104);[2] ^{1}H NMR (200 MHz, DMSO-d_6) δ = 11.77 (s, 1H), 8.40 – 8.37 (m, 1H), 7.78 – 7.77 (m, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.38 (m, 2H), 7.25 – 7.16 (m, 1H), 7.14 – 7.03 (m, 2H), 6.74 – 6.67 (m, 1H); ^{13}C NMR (50 MHz, DMSO-d_6) δ = 159.1, 149.4, 136.8, 136.6, 133.0, 129.2, 122.0, 121.8, 120.1, 118.8, 112.1, 94.4.



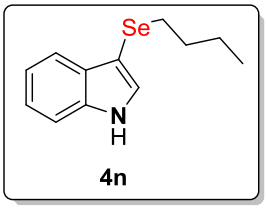
4l

3-(Thiophen-2-ylselanyl)-1*H*-indole (4l): Yield: 73% (51 mg); yellow solid; mp: 109−111 ºC; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.12 (s, 1H), 7.80 – 7.76 (m, 1H), 7.34 – 7.17 (m, 6H), 6.86 – 6.81 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 136.1, 132.7, 130.1, 129.5, 129.2, 127.8, 127.6, 122.9, 120.8, 120.2, 111.4, 101.1; HRMS (APCI+) *m/z* calculated for $C_{12}H_9NSSe$ [M]+ 278.9615, found 278.9618.



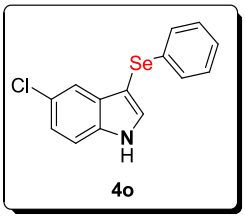
4m

3-(Benzylselanyl)-1*H*-indole (4m): Yield: 57% (41 mg); yellow oil;[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.26 – 7.13 (m, 5H), 7.02 (dd, *J* = 7.4, 1.8 Hz, 2H), 6.97 (d, *J* = 2.5 Hz, 1H), 3.86 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 136.2, 130.7, 130.2, 128.8, 128.3, 126.5, 122.6, 120.5, 120.2, 111.4, 98.9, 31.9.



4n

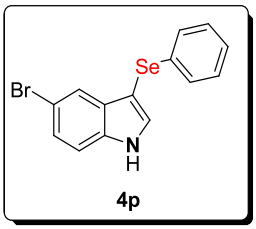
3-(Butylselanyl)-1*H*-indole (4n): Yield: 72% (46 mg); yellow oil;[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.75 (d, *J* = 8.9 Hz, 1H), 7.32 – 7.16 (m, 4H), 2.67 (m, 2H), 1.58 (dt, *J* = 15.0, 7.4 Hz, 2H), 1.42 – 1.31 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3, 130.4, 130.2, 122.6, 120.4, 120.3, 111.4, 98.8, 32.7, 28.6, 22.8, 13.7.



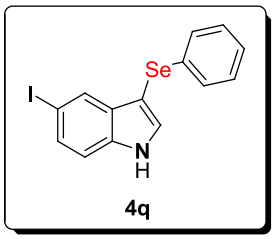
4o

5-Chloro-3-(phenylselanyl)-1*H*-indole (4o): Yield: 92% (71 mg); yellow solid; mp: 112−115ºC; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.60 (d, *J* = 1.5 Hz, 1H), 7.44 (d, *J* = 2.5 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 1H), 7.24 – 7.08 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 134.9, 133.5, 132.7, 131.4,

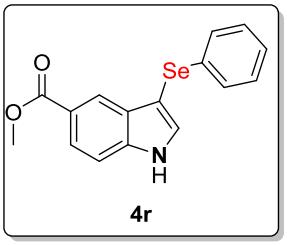
129.2, 128.9, 126.9, 125.9, 123.5, 119.9, 112.6, 98.2. HRMS (APCI$^+$) *m/z* calculated for $C_{14}H_{10}NClSe$ $[M]^+$ 306.9659, found 306.9659.



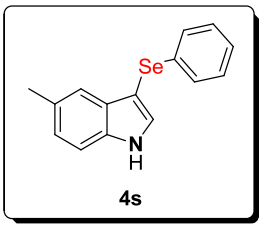
5-Bromo-3-(phenylselanyl)-1*H*-indole (4p): Yield: 99 % (87 mg); white solid; mp: 135-138ºC (136-138 ºC);[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.75 (s, 1H), 7.35 – 7.03 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.1, 133.5, 132.6, 131.9, 129.2, 128.8, 126.0, 125.9, 122.9, 114.4, 113.1, 97.8.



5-Iodo-3-(phenylselanyl)-1*H*-indole (4q): Yield: 99% (99 mg); white solid; mp: 125-128 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.97 (s, 1H), 7.48 (d, *J* = 9.7 Hz, 1H), 7.37 (d, *J* = 2.4 Hz, 1H), 7.23 – 7.07 (m, 6H). ^{3}C NMR (101 MHz, $CDCl_3$) δ 135.6, 133.5, 132.6, 132.1, 131.5, 129.3, 129.2, 128.8, 125.9, 113.5, 97.6, 84.8. HRMS (APCI$^+$) *m/z* calculated for $C_{14}H_{10}NISe$ $[M]^+$ 398.9018, found 398.9019.

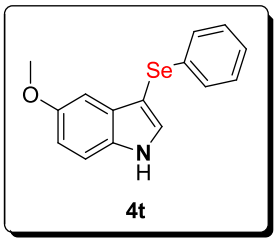


Methyl 3-(phenylselanyl)-1*H*-indole-5-carboxylate (4r): Yield: 94% (78 mg); white solid; mp: 164-165 ºC (164.6–165.2 ºC);[1] ^{1}H NMR (400 MHz, DMSO) δ 11.95 (s, 1H), 7.99 (s, 1H), 7.75 (s, 1H), 7.67 (dd, *J* = 8.6, 1.3 Hz, 1H), 7.45 (d, *J* = 8.6 Hz, 1H), 7.08 – 6.84 (m, 5H), 3.64 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 166.9, 139.5, 134.9, 133.4, 129.3, 129.2, 128.1, 125.7, 123.1, 121.7, 121.5, 112.3, 96.7, 51.4.



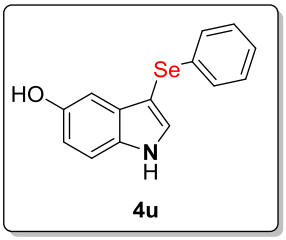
4s

5-Methyl-3-(phenylselanyl)-1*H*-indole (4s): Yield: 83% (60 mg); black liquid;[1] ^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.24 (s, 1H), 7.42 (s, 1H), 7.36 (d, *J* = 2.6 Hz, 1H), 7.30 – 7.19 (m, 3H), 7.14 – 7.04 (m, 4H), 2.41 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 134.8, 134.1, 131.5, 130.4, 130.3, 129.0, 128.6, 125.6, 124.7, 119.9, 111.1, 97.5, 21.5.



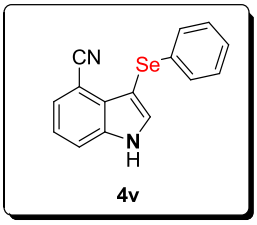
4t

5-Methoxy-3-(phenylselanyl)-1*H*-indole (4t): Yield: 77% (58 mg); yellow viscous liquid;[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.31 (d, *J* = 2.6 Hz, 1H), 7.24 – 7.19 (m, 3H), 7.13 – 7.03 (m, 4H), 6.91 – 6.86 (m, 1H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 134.0, 132.1, 131.4, 130.8, 129.1, 128.5, 125.7, 113.4, 112.4, 101.6, 97.5, 55.9.



4u

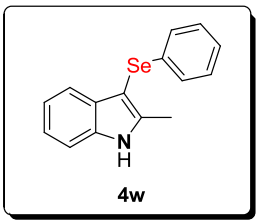
5-Hydroxy-3-(phenylselanyl)-1*H*-indole (4u): Yield: 79% (57 mg); red solid; mp: 151-154 ºC (164.6–165.2 ºC);[1] ^{1}H NMR (400 MHz, DMSO) δ 11.45 (s, 1H), 8.90 (s, 1H), 7.65 (d, *J* = 2.4 Hz, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 7.22 – 7.02 (m, 5H), 6.81 (s, 1H), 6.74 (dd, *J* = 8.6, 2.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 151.7, 134.0, 133.0, 131.1, 130.6, 129.1, 127.9, 125.5, 112.7, 112.5, 103.0, 93.9; HRMS (APPI^{+}) *m/z* calculated for $C_{14}H_{12}NOSe$ $[M+H]^{+}$ 290.0081, found 290.0079.



4v

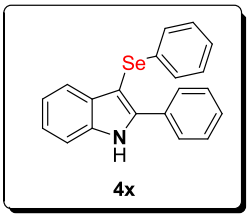
3-(Phenylselanyl)-1*H*-indole-4-carbonitrile (4v): Yield: 79% (59 mg); yellow solid; mp: 166-168 ºC (166.2-167.8 ºC);[2] ^{1}H NMR (400 MHz, DMSO) δ 12.34 (s, 1H), 8.03 (d, *J* = 2.4 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.59 (d, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.25 – 7.11 (m, 5H).

^{13}C NMR (101 MHz, DMSO) δ 137.5, 137.4, 134.7, 129.6, 128.9, 128.4, 128.0, 126.3, 122.4, 118.2, 118.0, 102.1, 94.9.



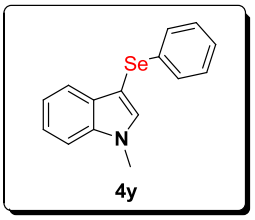
4w

2-Methyl-3-(phenylselanyl)-1*H*-indole (4w): Yield: 92% (66 mg); white solid; mp: 98-99 ºC (97-98 ºC);[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.54 (d, *J* = 6.9 Hz, 1H), 7.18 – 6.96 (m, 8H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 135.8, 133.9, 131.2, 129.0, 128.4, 125.5, 122.1, 120.7, 119.7, 110.7, 96.1, 13.0.



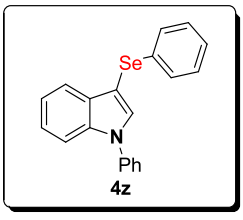
4x

2-Phenyl-3-(phenylselenyl)-1*H*-indole (4x): Yield: 99% (86 mg); pink viscous oil;[1] ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.72 – 7.62 (m, 3H), 7.43 – 7.34 (m, 4H), 7.28 – 7.06 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 136.2, 134.1, 132.1, 131.9, 129.1, 128.6, 128.6, 128.3, 125.6, 123.2, 121.1, 120.8, 111.2, 95.6.



4y

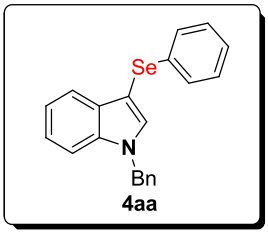
1-Methyl-3-(phenylselanyl)-1*H*-indole (4y): Yield: 90% (65 mg); white solid; mp: 65-67 ºC (65-68 ºC);[1] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.7 Hz, 1H), 7.38 – 7.02 (m, 9H), 3.77 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.6, 135.7, 134.3, 130.8, 129.0, 128.7, 125.6, 122.5, 120.5, 109.6, 96.1, 33.1.



4z

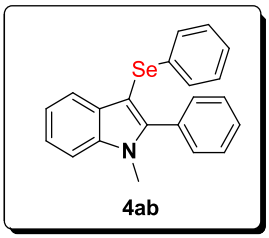
1-Phenyl-3-(phenylselanyl)-1*H*-indole (4z): Yield: 87% (76 mg); yellow viscous oil;[1] ^{1}H NMR (200 MHz, $CDCl_3$) *δ* = 7.68 (dd, *J* = 6.8, 1.7 Hz, 1H), 7.62 – 7.51 (m, 6H), 7.44 – 7.278 (m, 4H),

7.25 – 7.10 (m, 4H); ^{13}C NMR (50 Hz, $CDCl_3$) δ = 139.2, 136.8, 134.5, 133.6, 131.3, 129.9, 129.2, 129.1, 127.2, 125.9, 124.6, 123.3, 121.4, 120.9, 110.9, 99.5.



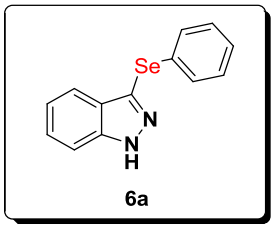
4aa

1-benzyl-3-(phenylselanyl)-1*H*-indole (4aa): Yield: 99% (90 mg); white solid; mp: 77-78 ºC (77-78 ºC);[4] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 6.8, 1.7 Hz, 1H), 7.36 – 7.02 (m, 14H), 5.27 (s, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.2, 136.7, 135.1, 134.2, 131.0 129.1, 129.0, 128.7, 128,0, 127.1, 125.6, 122.8, 120.8, 120.7, 110.2, 97.0, 50.5.



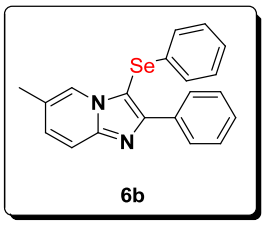
4ab

1-Methyl-2-phenyl-3-(phenylselanyl)-1*H*-indole (4ab): Yield: 99% (90 mg); yellow viscous oil;[1] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.43 – 7.34 (m, 6H), 7.32 – 7.00 (m, 7H), 3.66 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 145.9, 137.9, 134.7, 131.4, 130.9, 130.8, 128.9, 128.7, 128.6, 128.2, 125.4, 122.8, 120.9, 120.8, 109.8, 96.6, 31.8.



6a

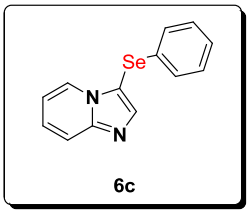
3-(phenylselanyl)-1*H*-indazole (6a): Yield: 81% (55mg); yellow solid; mp: 91-93 ºC (91-92 ºC);[5] ^{1}H NMR (200 MHz, $CDCl_3$) δ 12.84 (s, 1H), 7.74 – 7.62 (m, 2H), 7.48 – 7.30 (m, 3H), 7.21 – 7.09 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 141.5, 133.3, 131.2, 130.8, 129.4, 127.5, 127.0, 126.5, 121.8, 121.2, 111.0.



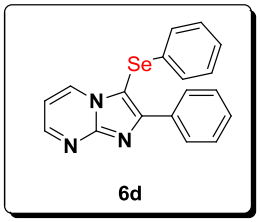
6b

6-methyl-2-phenyl-3-(phenylselanyl)imidazo[1,2-*a*]pyridine (6b): Yield: 54% (49 mg); yellow solid; mp: 110-111 ºC (109-111 ºC);[5] ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.16 – 8.11 (m, 3H), 7.61 (d,

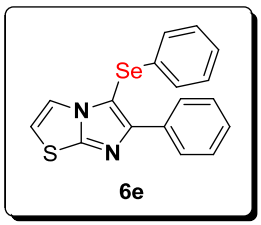
J = 9.1 Hz, 1H), 7.49 – 7.29 (m, 3H), 7.21 – 7.01 (m, 6H), 2.29 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 151.7, 146.9, 134.0, 131.4, 129.7, 129.6, 128.7, 128.3, 128.1, 126.6, 123.4, 122.9, 116.9, 102.4, 18.5.



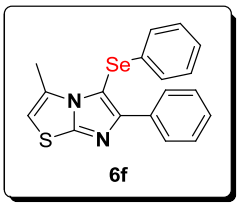
3-(phenylselanyl)imidazo[1,2-*a*]pyridine (6c): Yield: 47% (32 mg); yellow liquid;[5] ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.23 (dt, *J* = 6.8, 1.1 Hz, 1H), 7.97 (s, 1H), 7.66 (dt, *J* = 9.0, 1.1 Hz, 1H), 7.22 (ddd, *J* = 9.0, 6.8, 1.3 Hz, 1H), 7.13 (s, 5H), 6.79 (td, *J* = 6.8, 1.1 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.1, 142.9, 130.5, 129.4, 128.8, 126.7, 125.6, 125.1, 118.0, 112.9, 106.4.



2-phenyl-3-(phenylselanyl)imidazo[1,2-*a*]pyrimidine (6d): Yield: 48% (42 mg); yellow solid; mp: 114-116 ºC (116-117 ºC);[5] ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.60 (dt, *J* = 7.4, 1.9 Hz, 2H), 8.29 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.52 – 7.32 (m, 3H), 7.14 (m, 5H), 6.91 (dd, *J* = 6.7, 4.2 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 153.2, 151.5, 150.8, 133.2, 130.1, 129.9, 129.1, 129.0, 128.6, 128.5, 127.2, 109.5, 101.7.

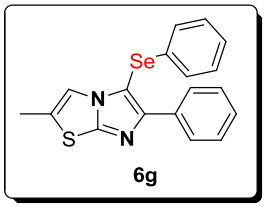


6-phenyl-5-(phenylselanyl)imidazo[2,1-*b*]thiazole (6e): Yield: 55% (49 mg); yellow solid; mp: 132-134 ºC (109-111 ºC); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.46 – 7.28 (m, 4H), 7.17 (s, 5H), 6.77 (d, *J* = 4.5 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 152.9, 151.6, 133.9, 131.5, 129.7, 128.6, 128.4, 128.1, 127.8, 126.8, 118.8, 112.6, 102.6; HRMS (APPI): m/z calcd for $C_{17}H_{13}N_2SSe$: 356.9956 $[M+H]^+$; found: 356.9956.



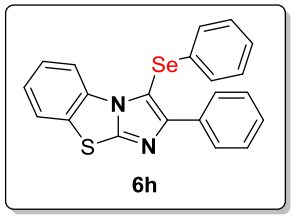
3-Methyl-6-phenyl-5-(phenylselanyl)imidazo[2,1-*b*]thiazole (6f): Yield: 59% (55 mg); yellow solid; mp: 145-146 ºC; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.97 (d, *J* = 6.5 Hz, 3H), 7.37 (m, 3H), 7.18

(m, 5H), 6.35 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 154.5, 153.7, 134.5, 134.0, 131.5, 129.7, 128.4, 128.1, 127.9, 127.6, 107.6, 102.7, 77.1, 15.0; HRMS (APPI): m/z calcd for $C_{18}H_{15}N_2SSe$: 371.0116 $[M+H]^+$; found: 371.0113.



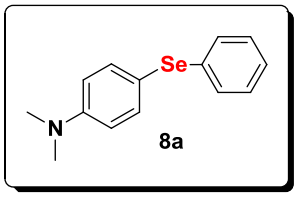
6g

2-Methyl-6-phenyl-5-(phenylselanyl)imidazo[2,1-*b*]thiazole (6g): Yield: 56% (52 mg); yellow solid; mp: 141-143 ºC; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.6 Hz, 2H), 7.32 (dt, *J* = 15.1, 7.3 Hz, 3H) 7.16 (s, 6H), 2.34 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 151.7, 151.0, 134.1, 131.7, 129.7, 128.4, 128.3, 127.8, 127.7, 126.7, 115.4, 102.0, 14.2 HRMS (APPI): m/z calcd for $C_{18}H_{15}N_2SSe$: 371.0116 $[M+H]^+$; found: 371.0114.



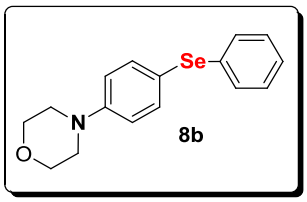
6h

2-Phenyl-3-(phenylthio)benzo[*d*]imidazo[2,1-*b*]thiazole (6h): Yield: 40% (41 mg); yellow solid; mp: 140-143 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.55 – 8.44 (m, 1H), 8.03 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.68 – 7.57 (m, 1H), 7.46 – 7.10 (m, 10H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 154.2, 151.5, 133.9, 133.7, 132.5, 130.3, 129.8, 128.3, 126.8, 126.2, 124.9, 124.1, 114.6, 104.2; HRMS (APPI, *m/z*) calculated for $C_{21}H_{15}N_2SSe$ $[M+H]^+$: 407.0116, found: 407.0115.



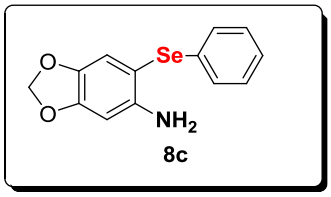
8a

***N,N*-Dimethyl-4-(phenylselanyl)aniline (8a):** Yield: 59% (41 mg); yellow oil;[6] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.6 Hz, 2H), 7.37 – 7.07 (m, 5H), 6.66 (d, *J* = 8.8 Hz, 2H), 2.96 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 150.7, 137.2, 134.7, 130.0, 129.1, 125.9, 113.9, 113.3, 40.4.

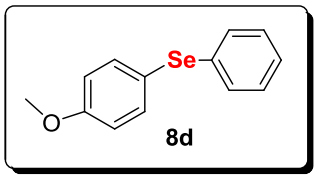


8b

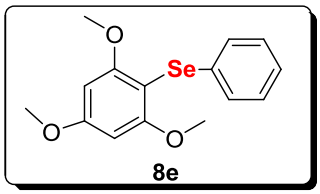
4-(4-(Phenylselanyl)phenyl)morpholine (8b): Yield: 64% (51 mg); white solid; mp: 70-71 ºC (69-71 ºC);[6] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.9 Hz, 2H), 7.37 – 7.26 (m, 2H), 7.26 – 7.12 (m, 3H), 6.84 (d, *J* = 8.9 Hz, 2H), 3.90 – 3.78 (m, 4H), 3.24 – 3.10 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 151.3, 136.5, 133.6, 130.8, 129.2, 126.4, 118.7, 116.3, 66.9, 48.8.



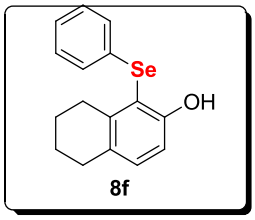
6-(Phenylselanyl)benzo[*d*][1,3]dioxol-5-aminedioxole (8c): Yield: 61% (45 mg); brown solid; mp: 66-68 ºC (68-70 ºC);[6] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.30 – 7.08 (m, 5H), 7.04 (s, 1H), 6.39 (s, 1H), 5.89 (s, 2H), 4.14 (s, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 150.4, 144.7, 140.5, 132.5, 129.4, 129.0, 126.2, 117.2, 102.5, 101.2, 97.1.



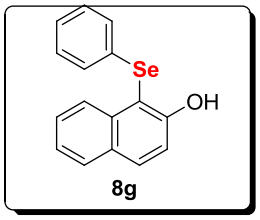
(4-Methoxyphenyl)(phenyl)selane (8d): Yield: 40% (27 mg); yellow oil;[6] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.8 Hz, 2H), 7.38 – 7.27 (m, 2H), 7.27 – 7.15 (m, 3H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.9, 135.6, 132.3, 130.1, 128.3, 125.6, 119.1, 114.3, 54.4.



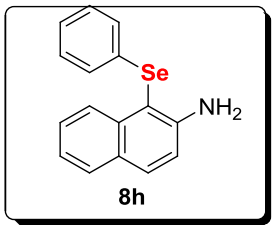
Phenyl(2,4,6-trimethoxyphenyl)selane (8e): Yield: 85% (69 mg); yellow oil;[6] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.32 – 6.94 (m, 5H), 6.21 (s, 2H), 3.86 (s, 3H), 3.78 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 162.1, 161.1, 132.7, 128.0, 127.8, 124.4, 96.5, 90.4, 55.4, 54.5.



1-(Phenylselanyl)-5,6,7,8-tetrahydronaphthalen-2-ol (8f): Yield: 62% (47 mg); yellow oil;[7] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.33 – 7.05 (m, 6H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.67 (s, 1H), 2.87 – 2.77 (m, 2H), 2.77 – 2.63 (m, 2H), 1.83 – 1.64 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 155.1, 142.0, 132.9, 130.7, 130.2, 129.6, 128.9, 126.6, 115.9, 112.2, 30.9, 29.5, 23.5, 22.9.



1-(Phenylselanyl)naphthalen-2-ol (8g): Yield: 55% (41 mg); white solid; mp: 76-77 ºC (77-78 ºC);[7] ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.9 Hz, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.51 – 7.38 (m, 1H), 7.32 (d, *J* = 8.7 Hz, 2H), 7.17 – 7.02 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 156.3, 135.9, 132.8, 130.7, 129.5, 129.2, 128.6, 128.0, 127.0, 126.7, 123.8, 116.7, 109.1.



1-(Phenylselanyl)naphthalen-2-amine (8h): Yield: 43% (33 mg); white solid; mp: 73-75 ºC (75-76 ºC);[7] ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.4 Hz, 1H), 7.70 (t, *J* = 7.8 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.14 - 7.07(m, 5H), 7.03 (d, *J* = 8.9 Hz, 1H), 4.71 (s, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.2, 137.1, 131.9, 131.8, 129.3, 128.7, 128.4, 127.8, 126.7, 125.9, 122.6, 117.5, 105.6.

IV. References

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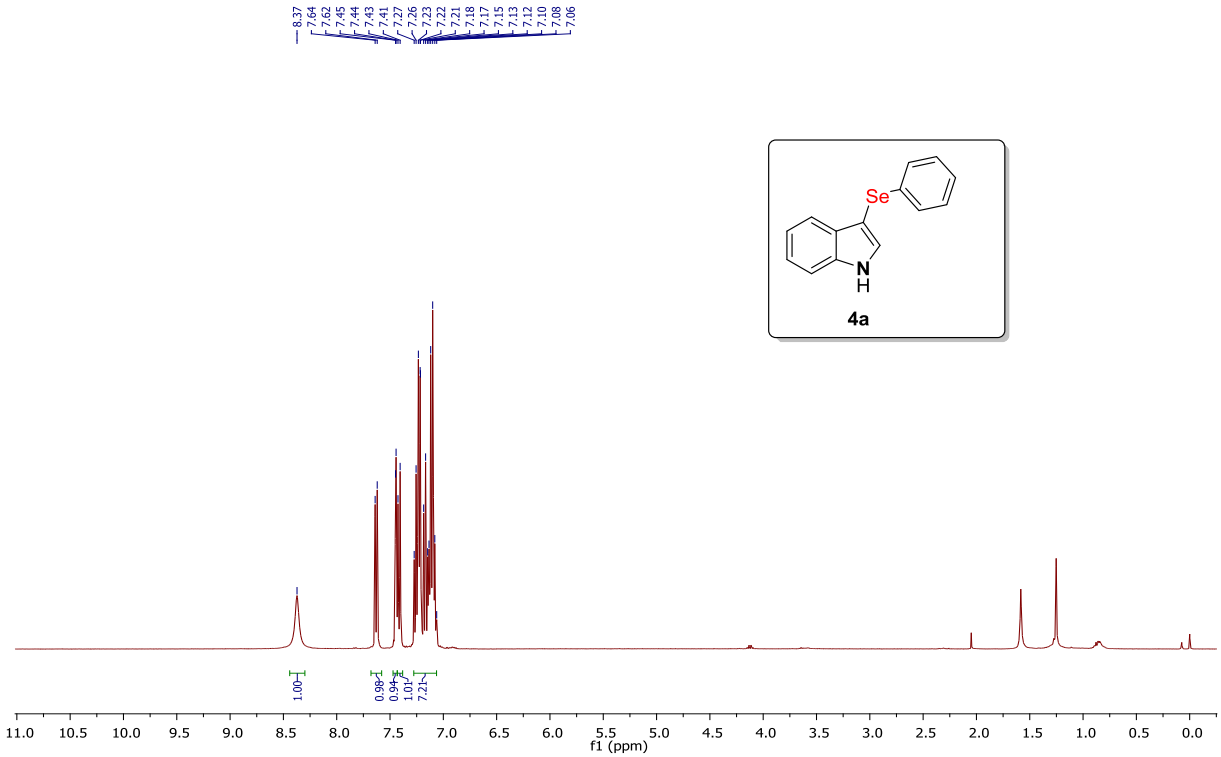
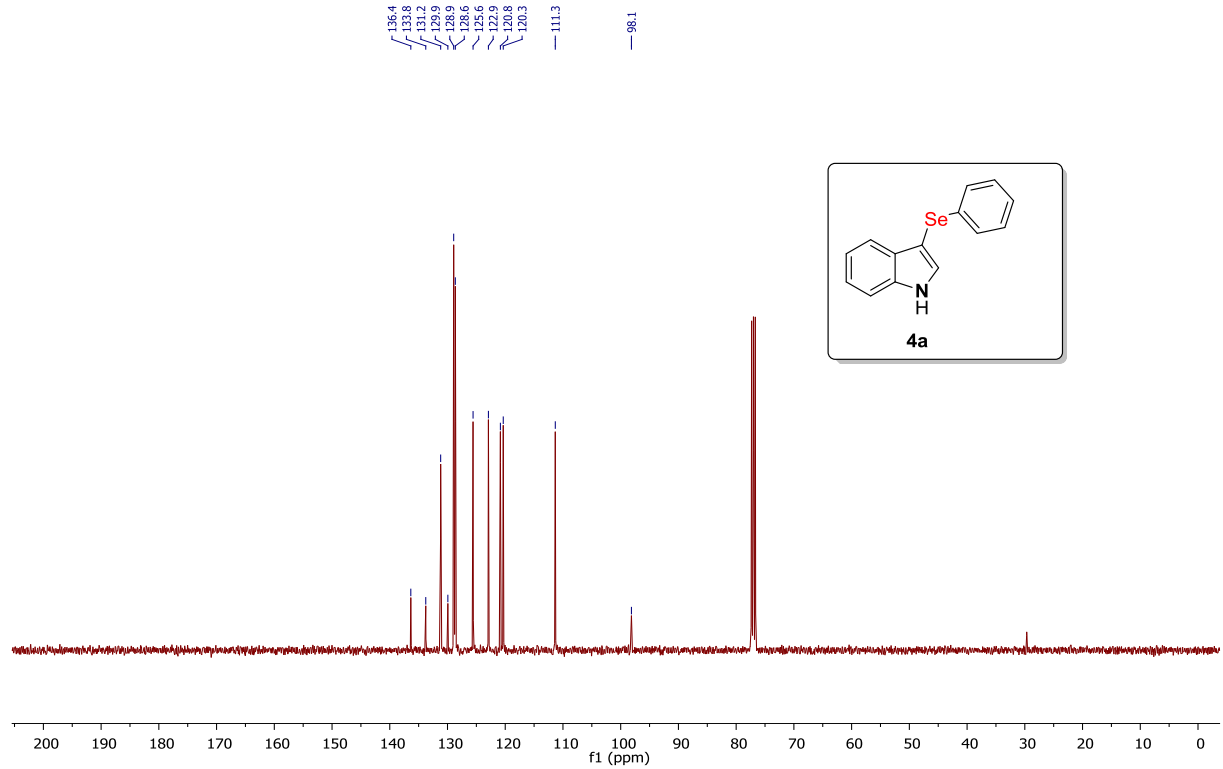
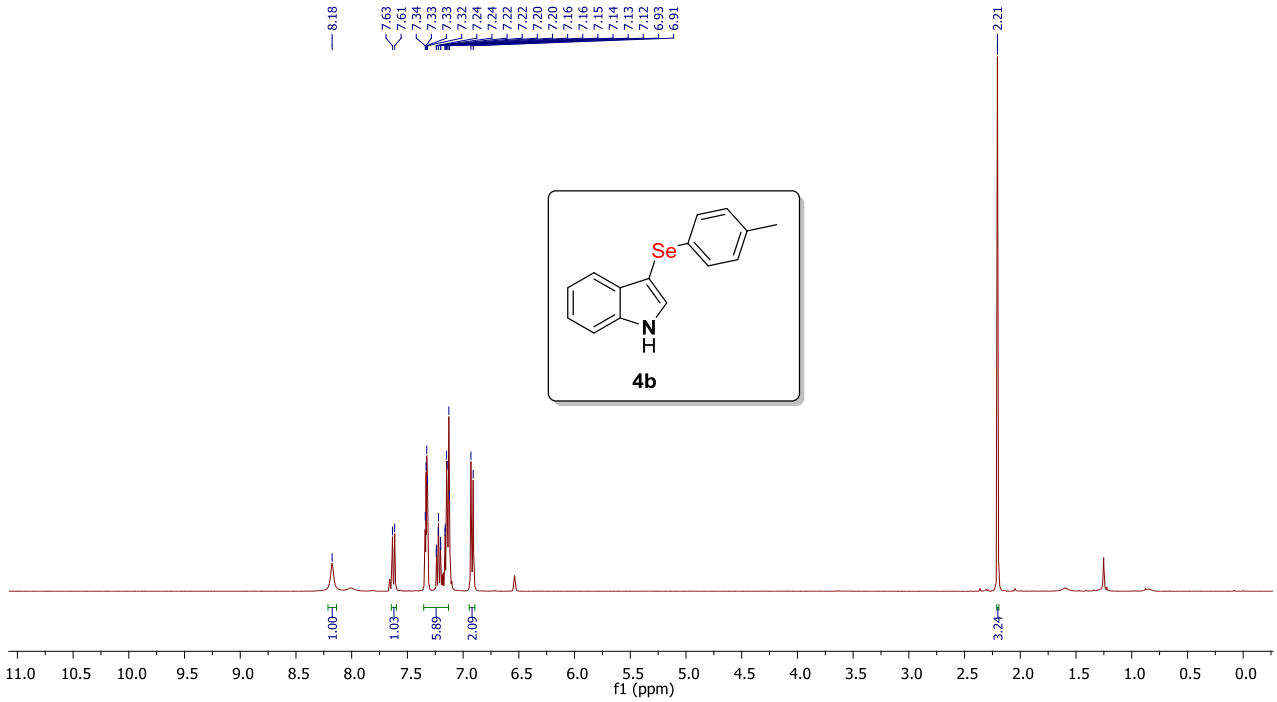
V. NMR Spectra



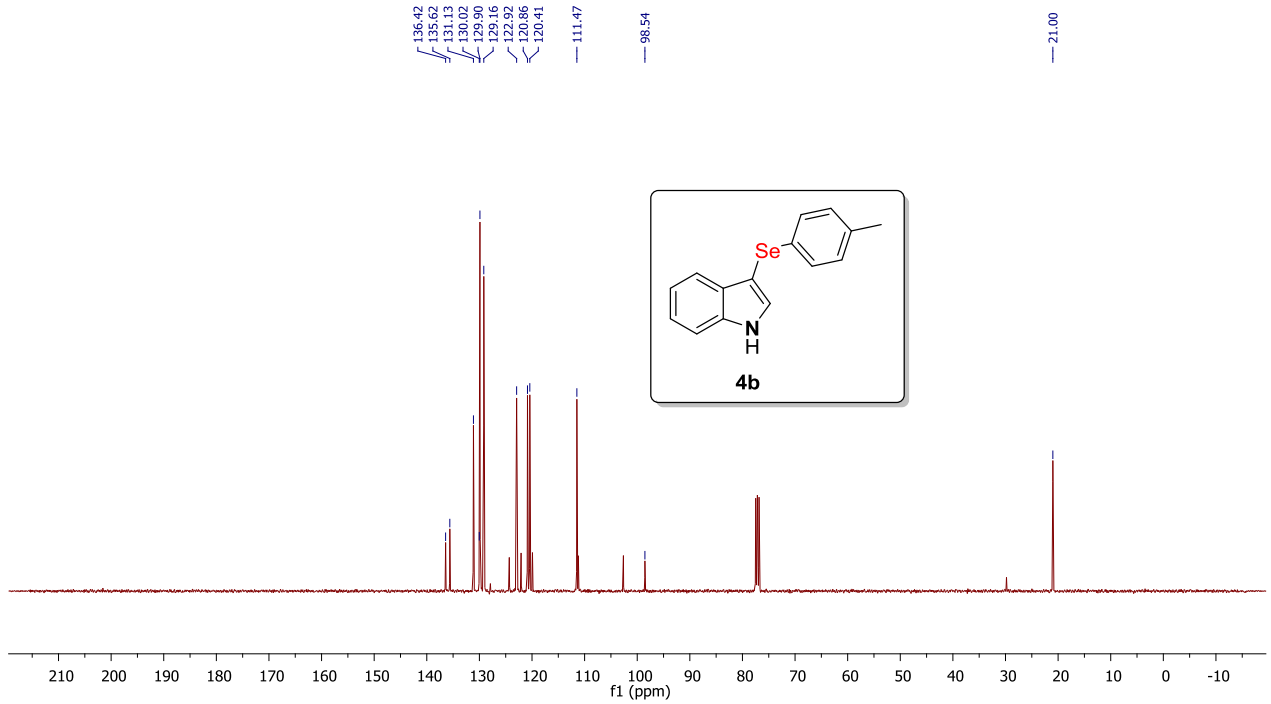
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4a**



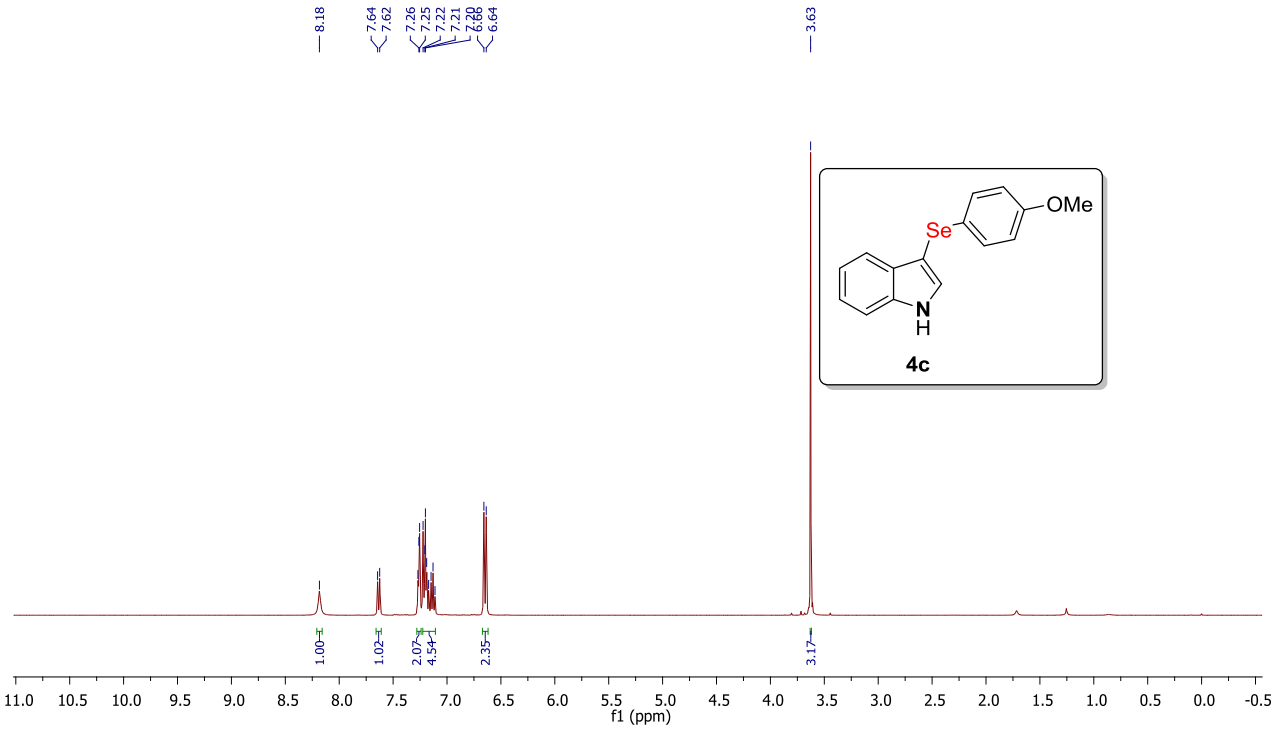
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4a**



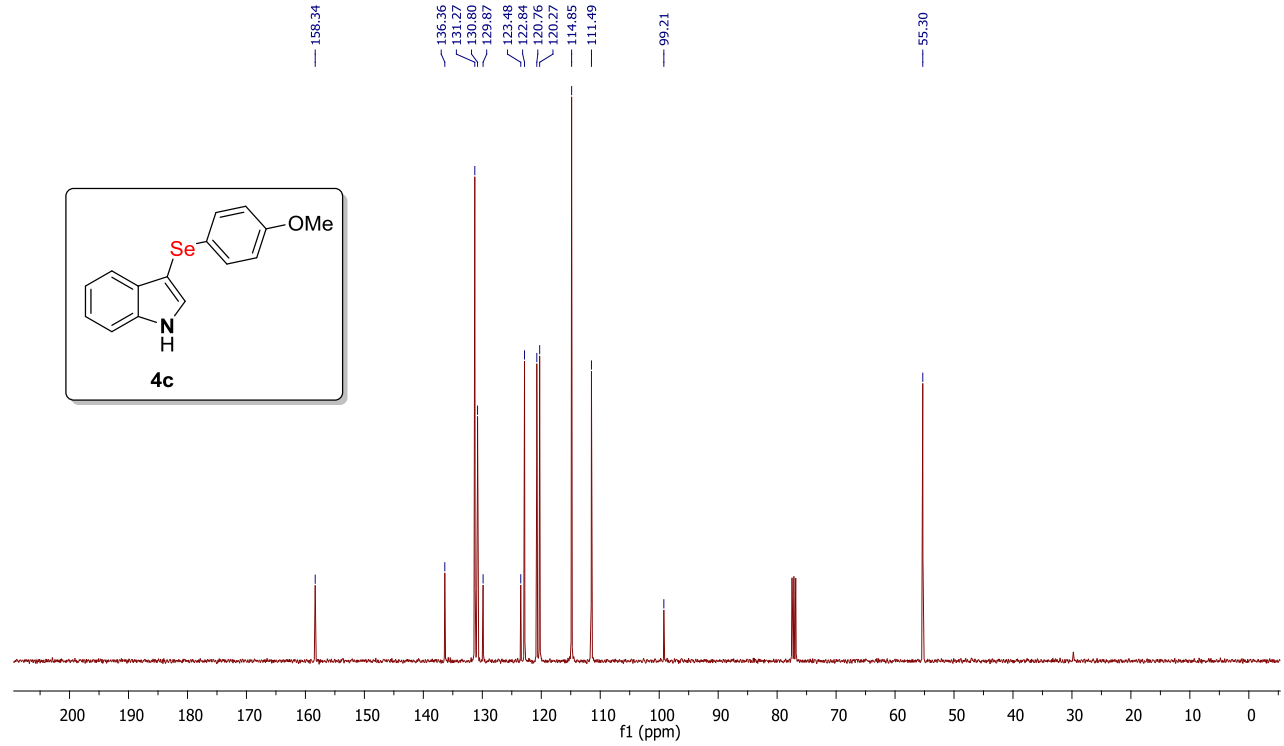
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4b**



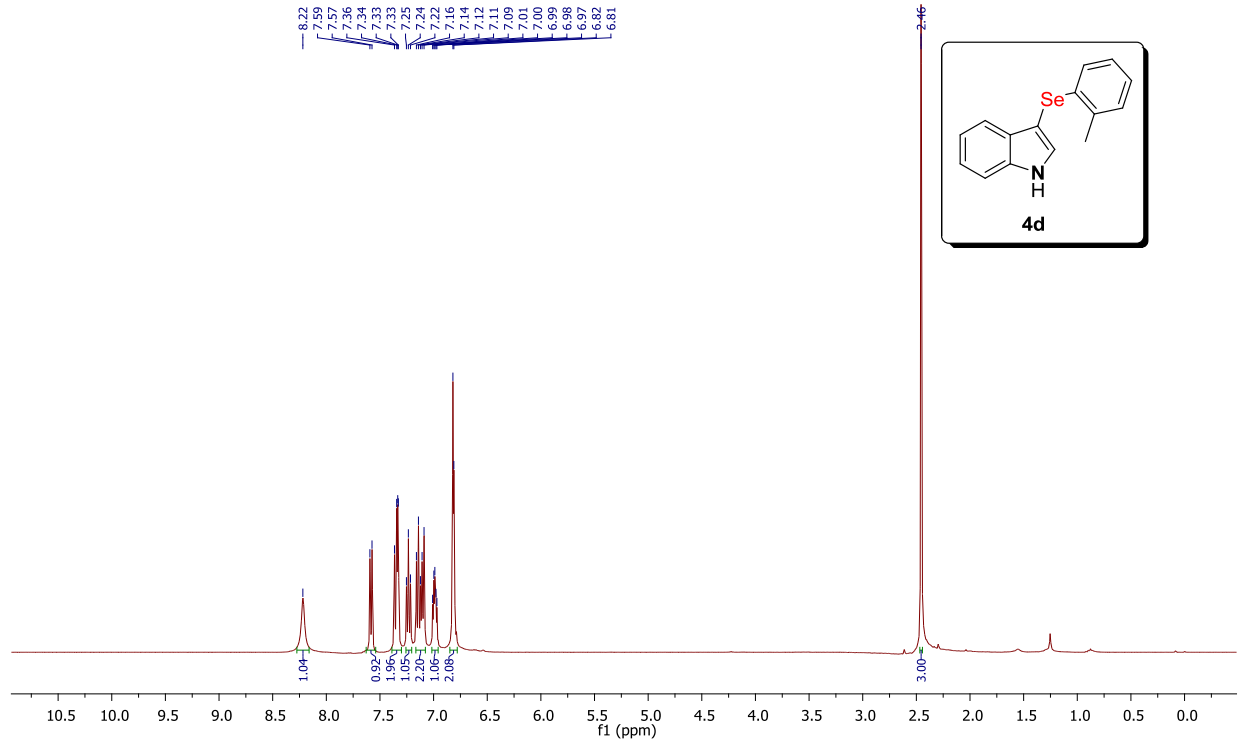
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4b**



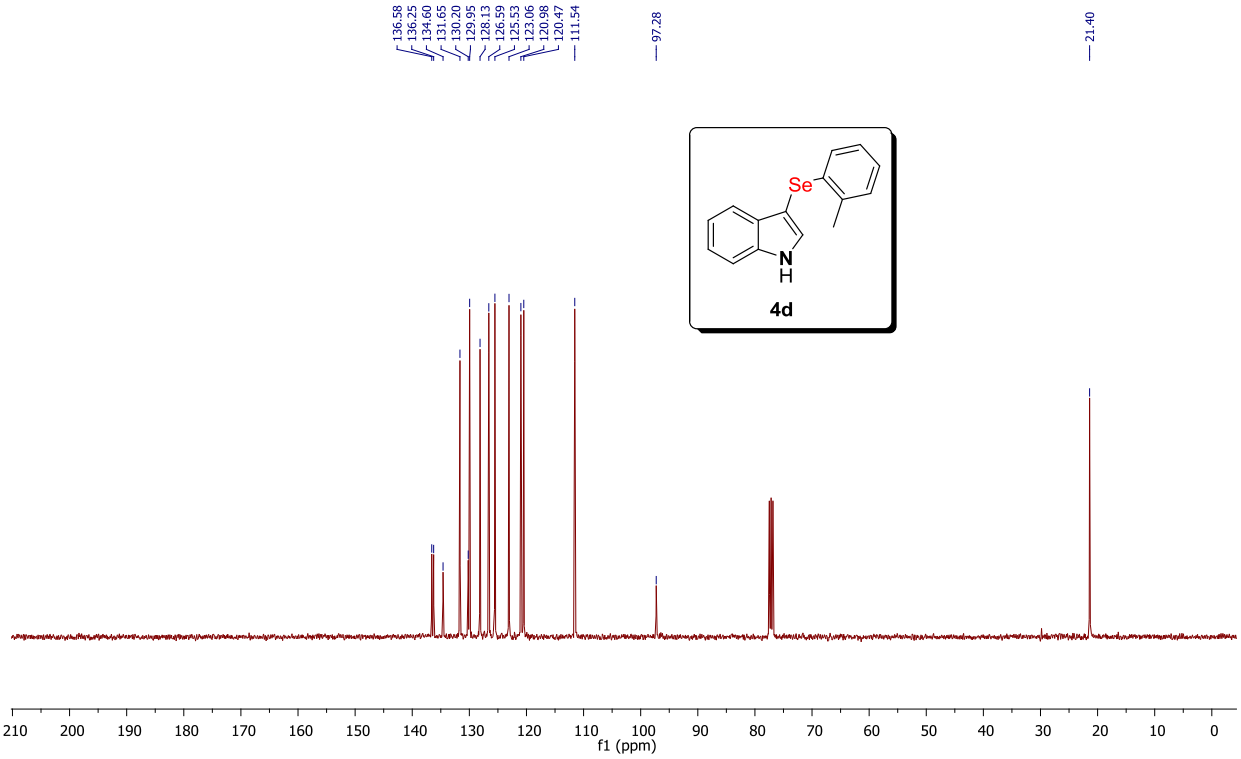
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4c**



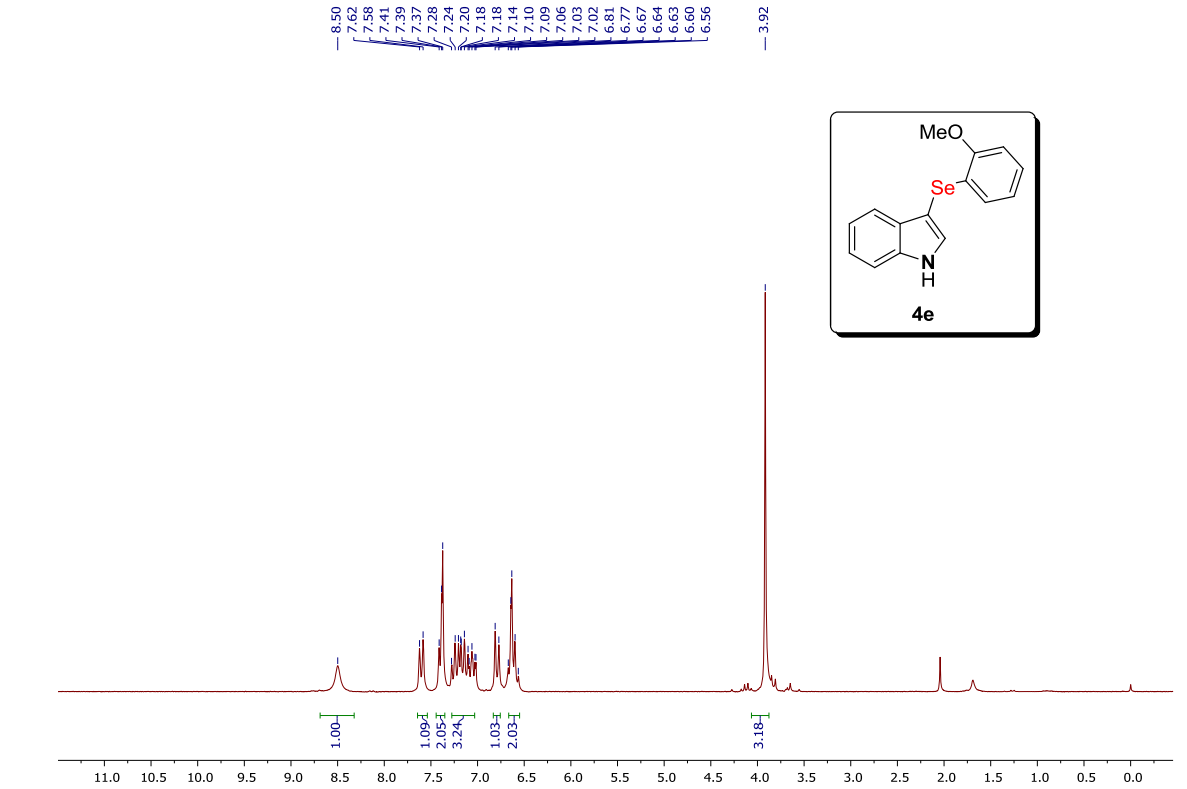
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4c**



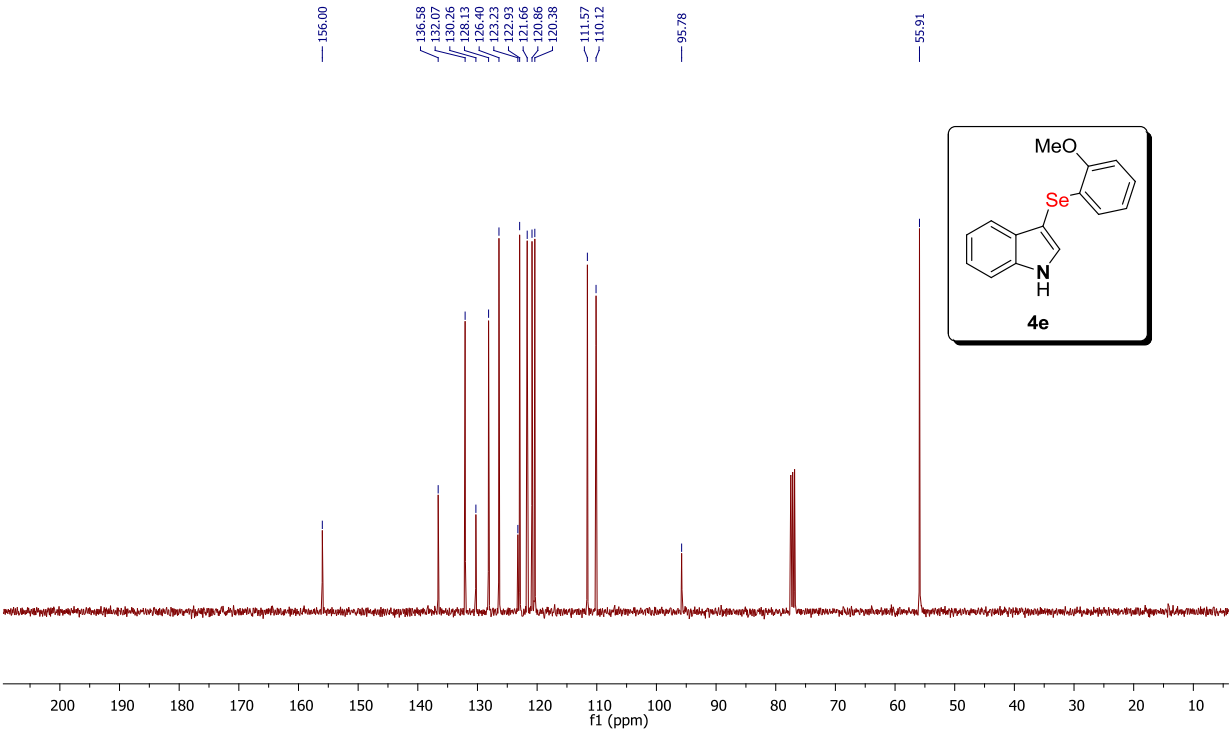
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4d**



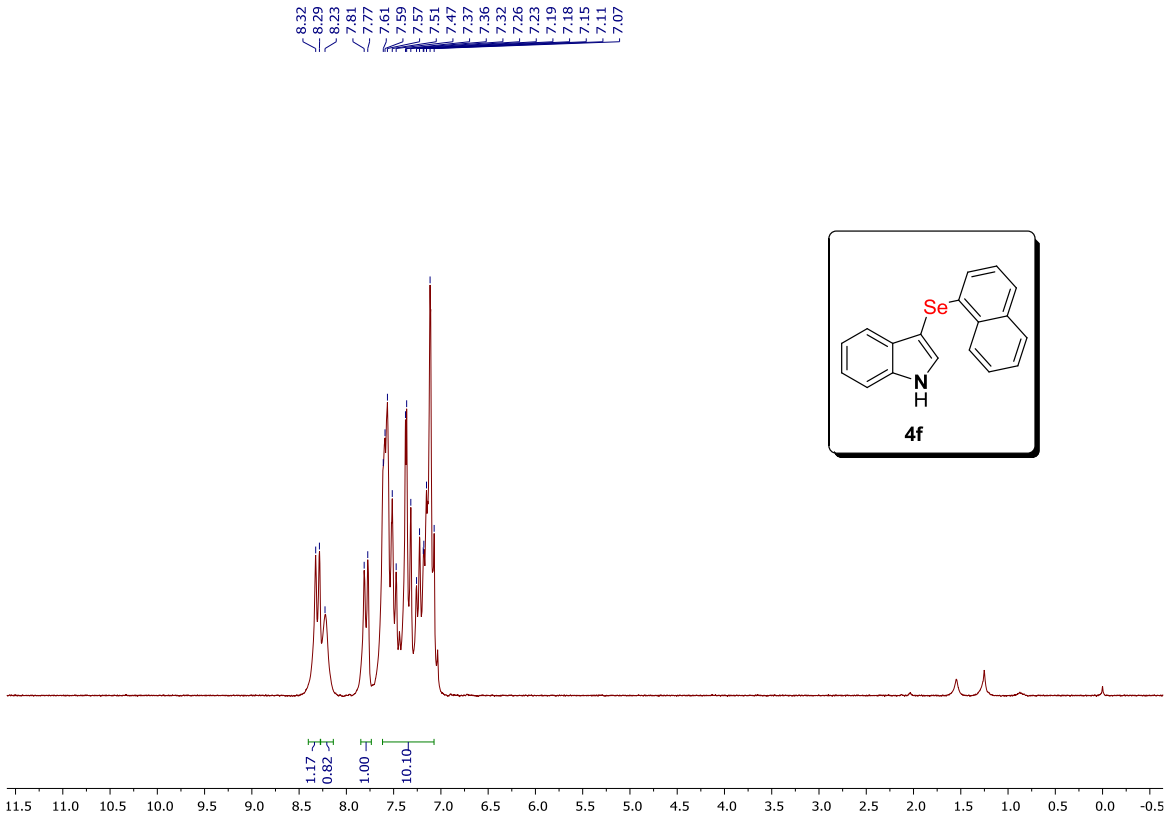
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4d**



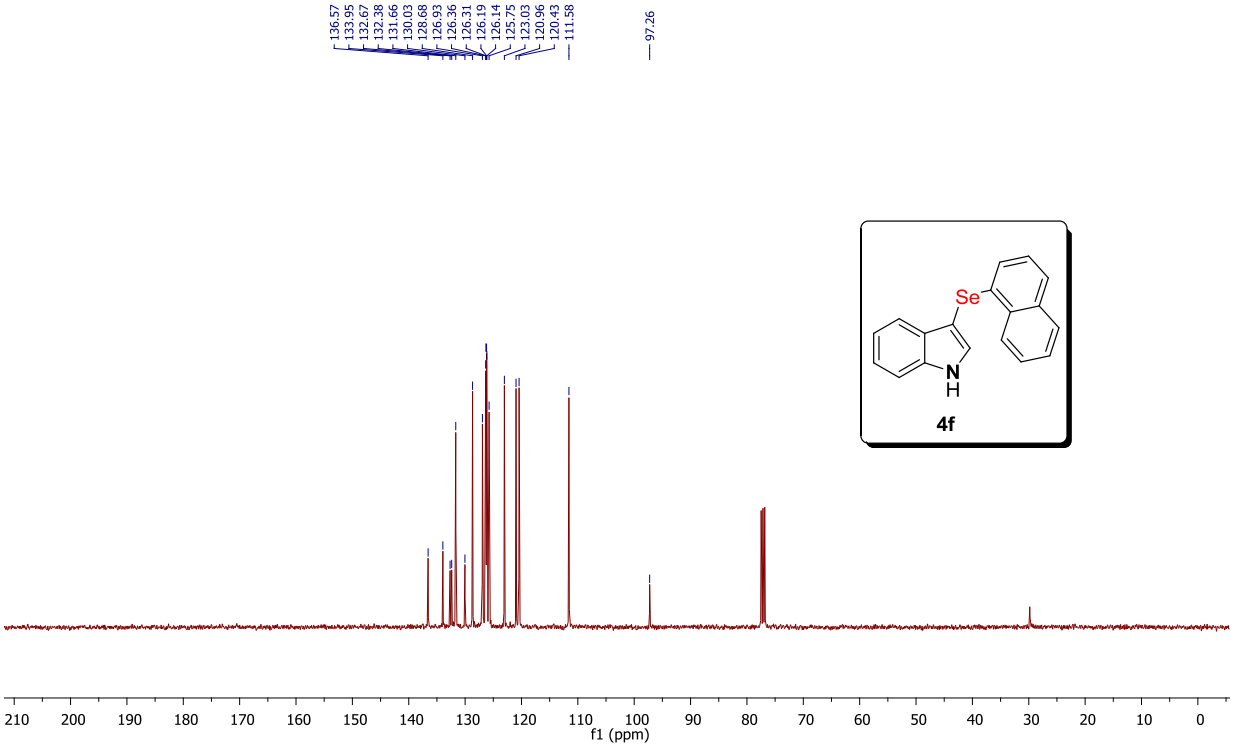
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **4e**



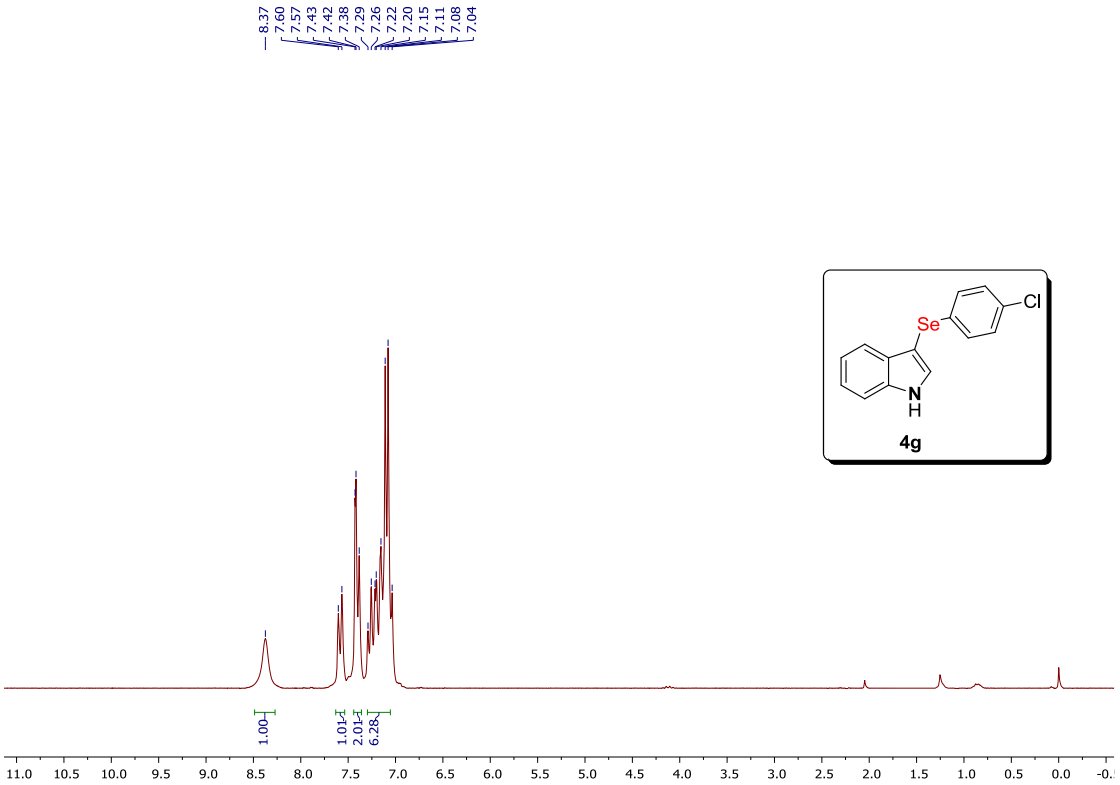
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4e**



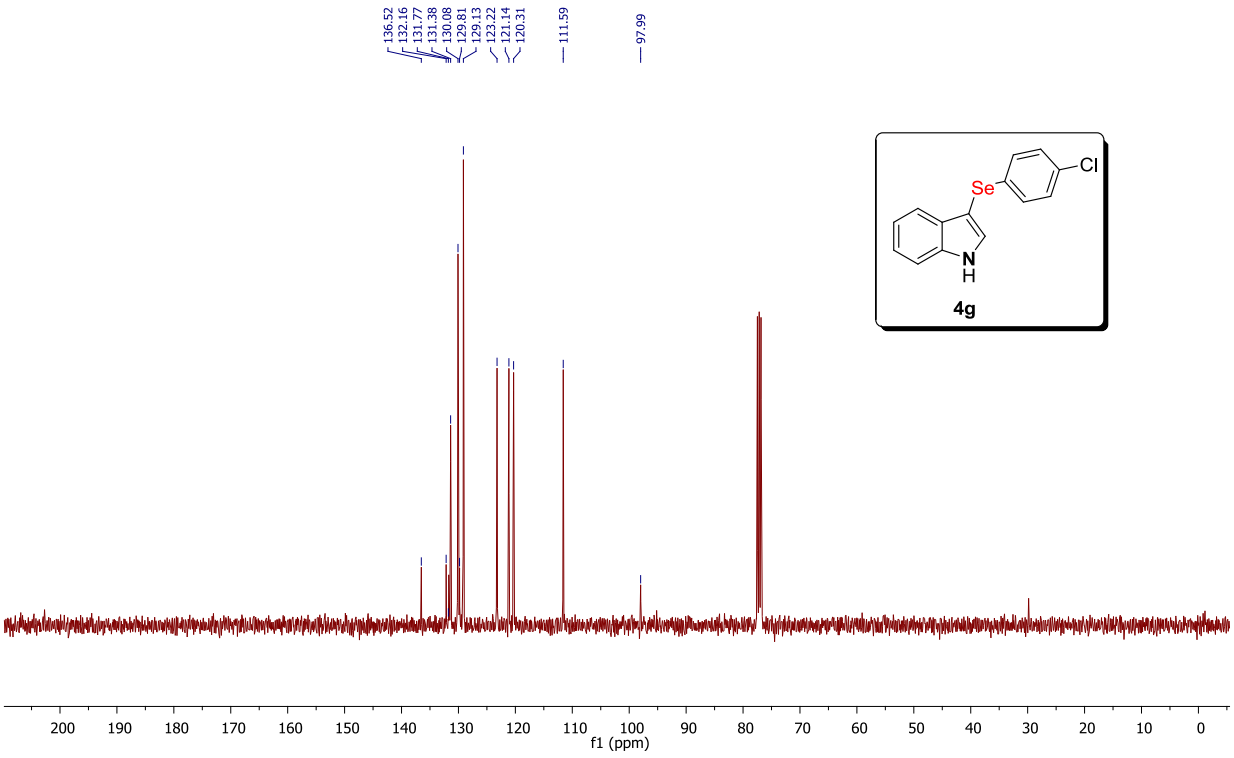
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **4f**



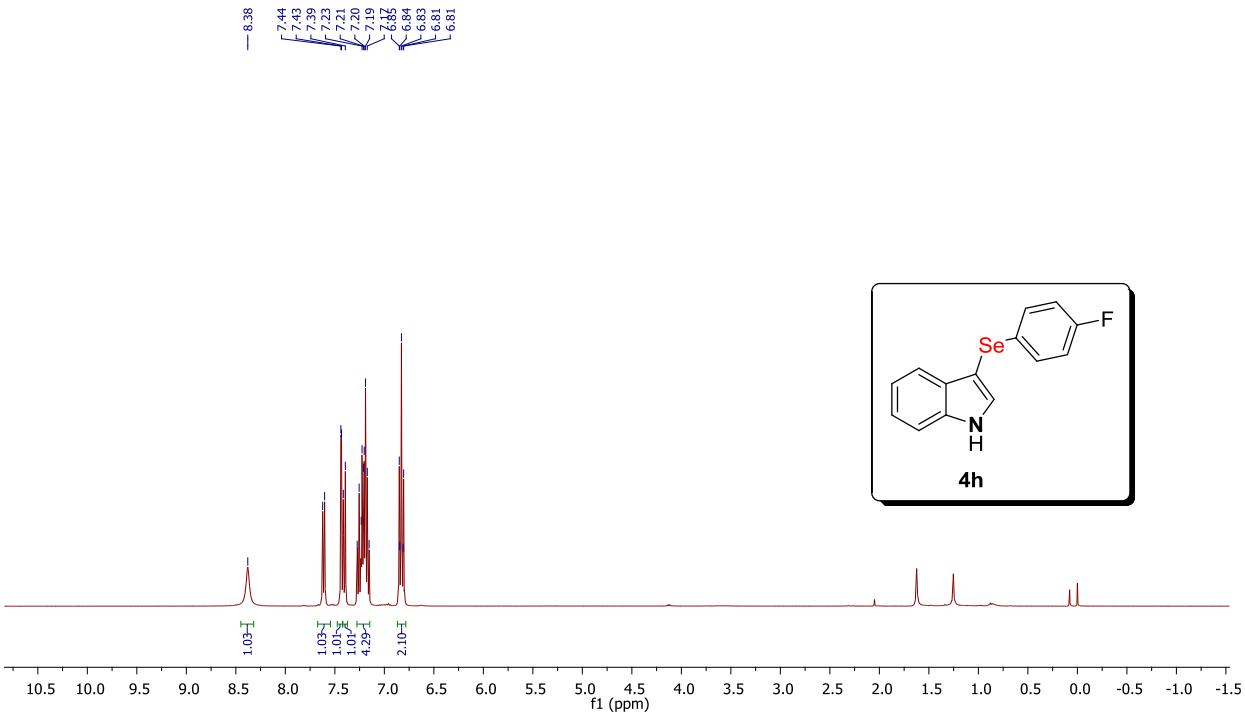
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4f**



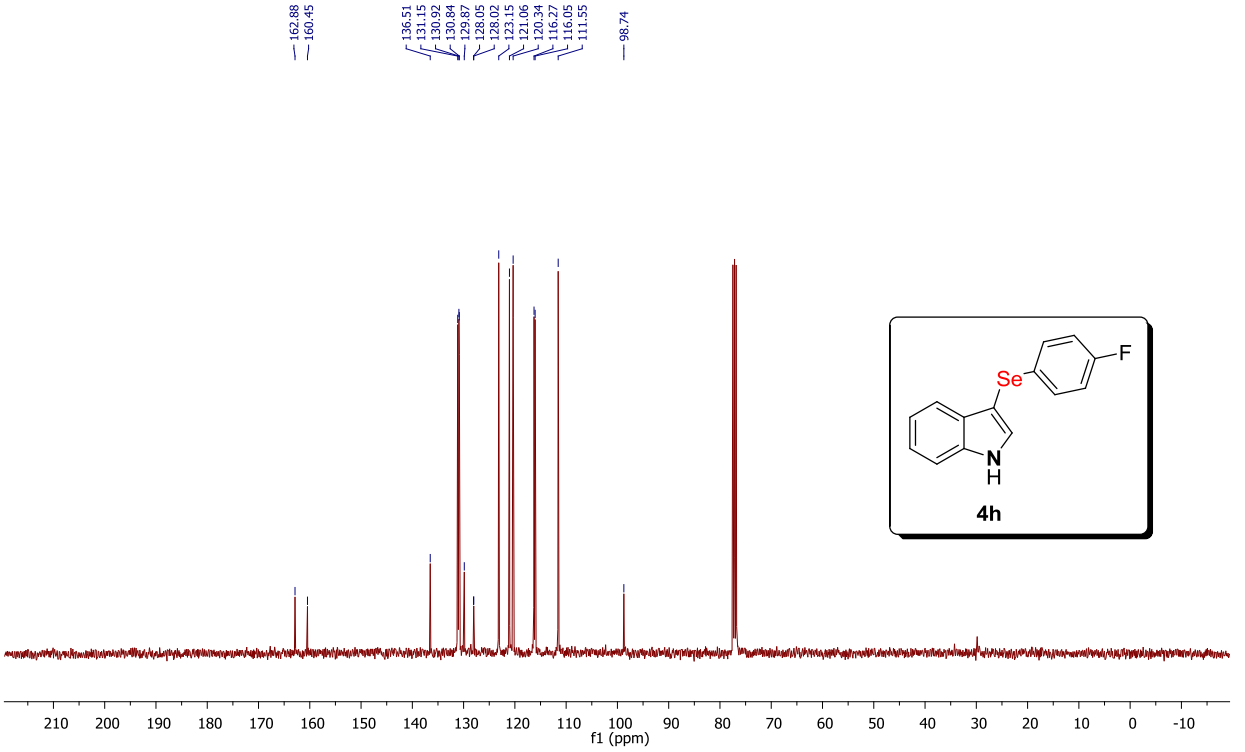
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **4g**



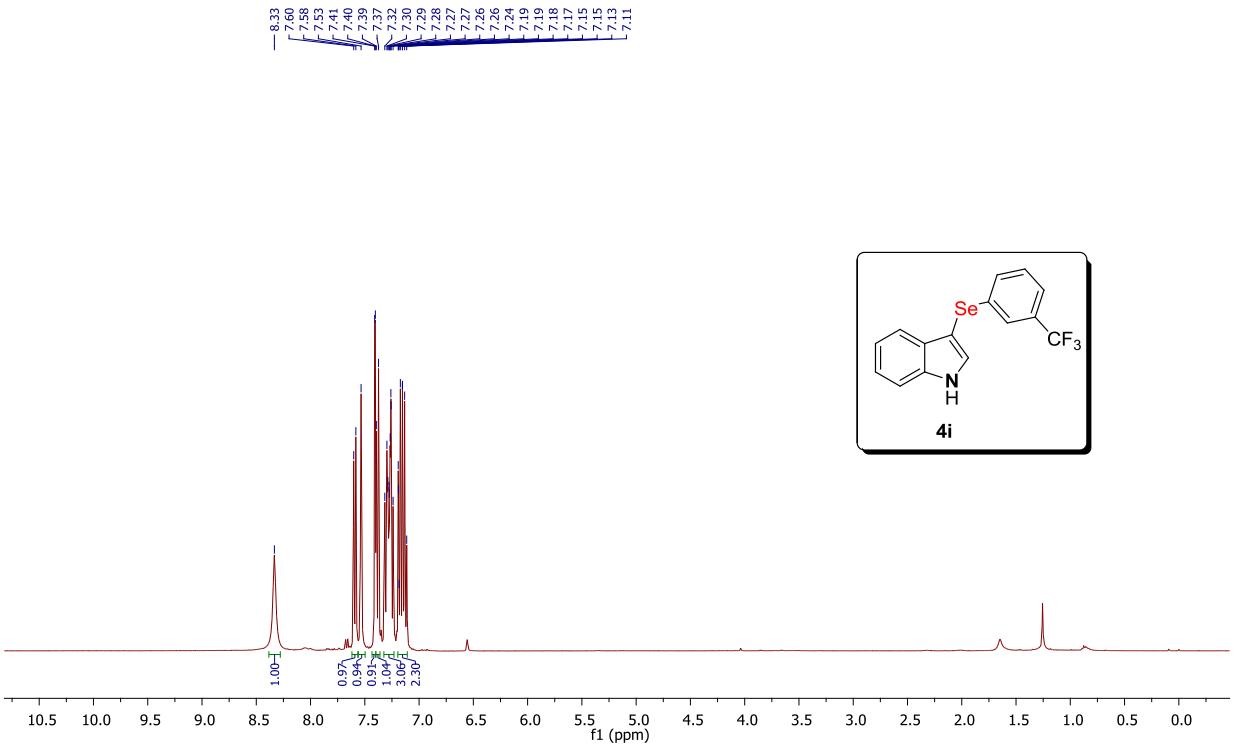
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4g**



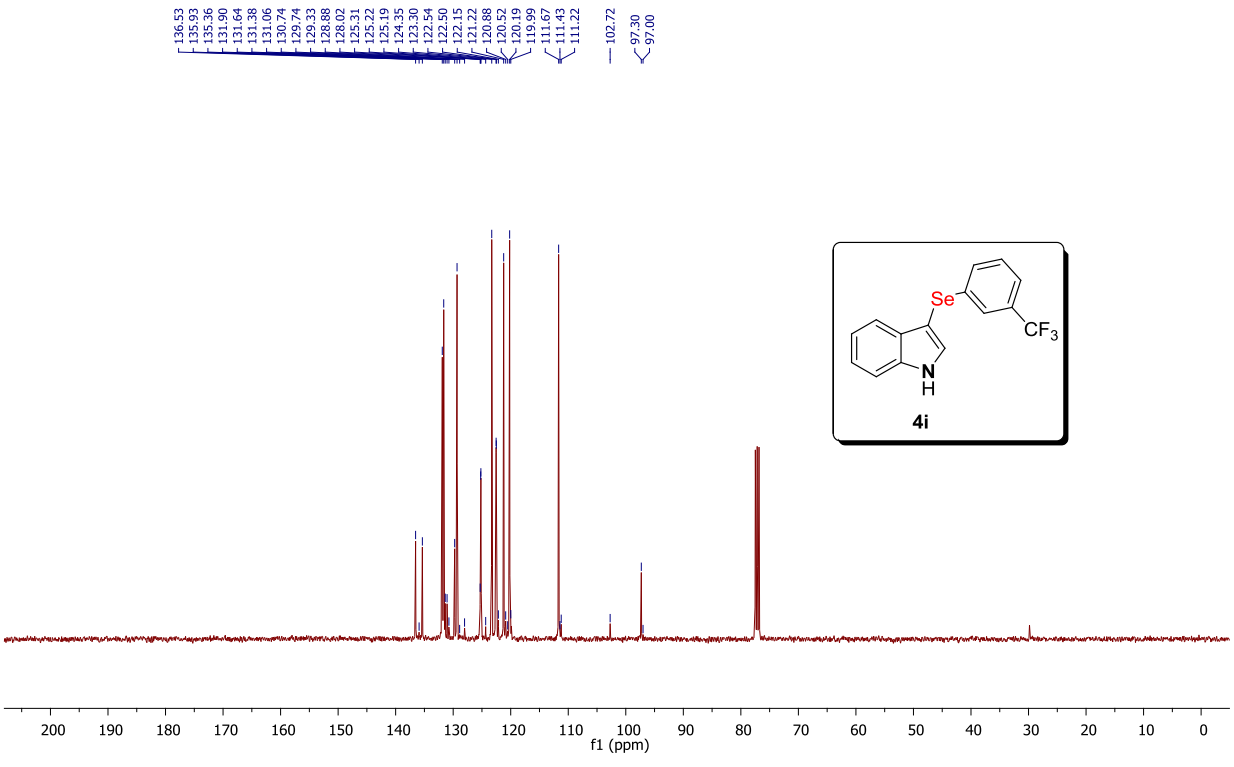
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4h**



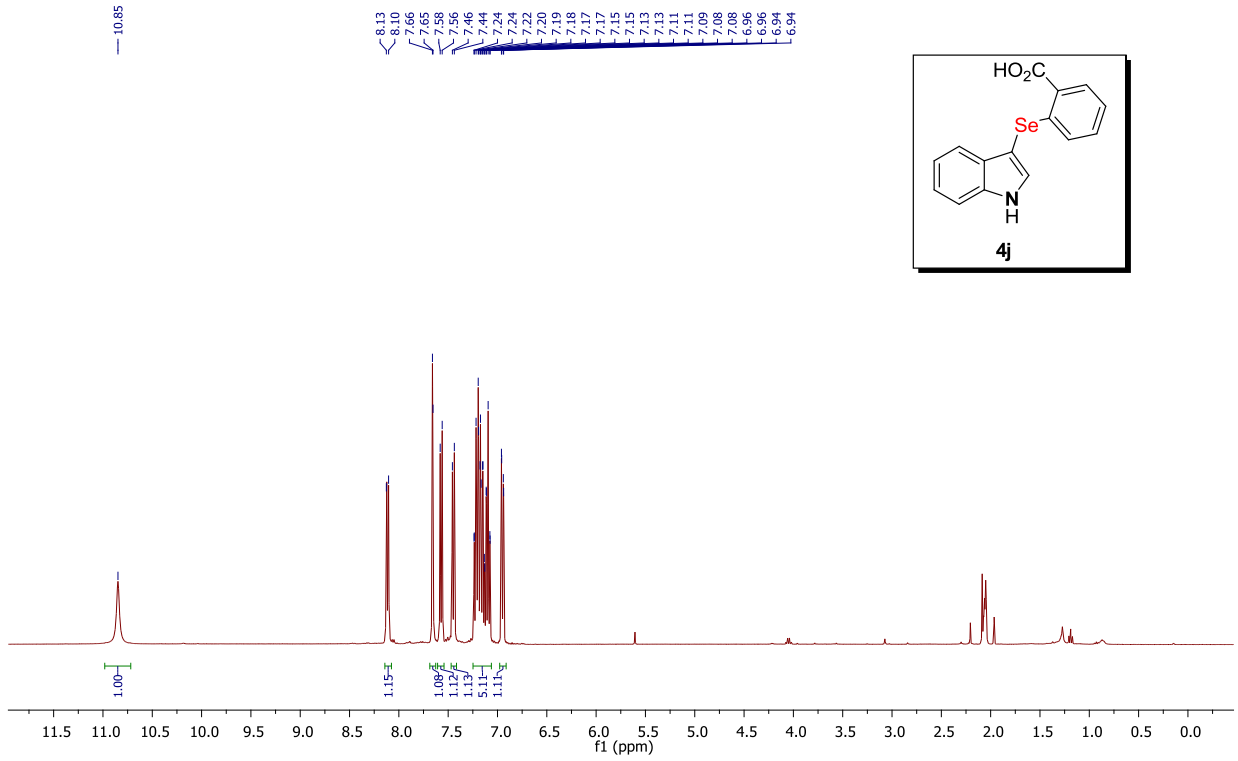
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4h**



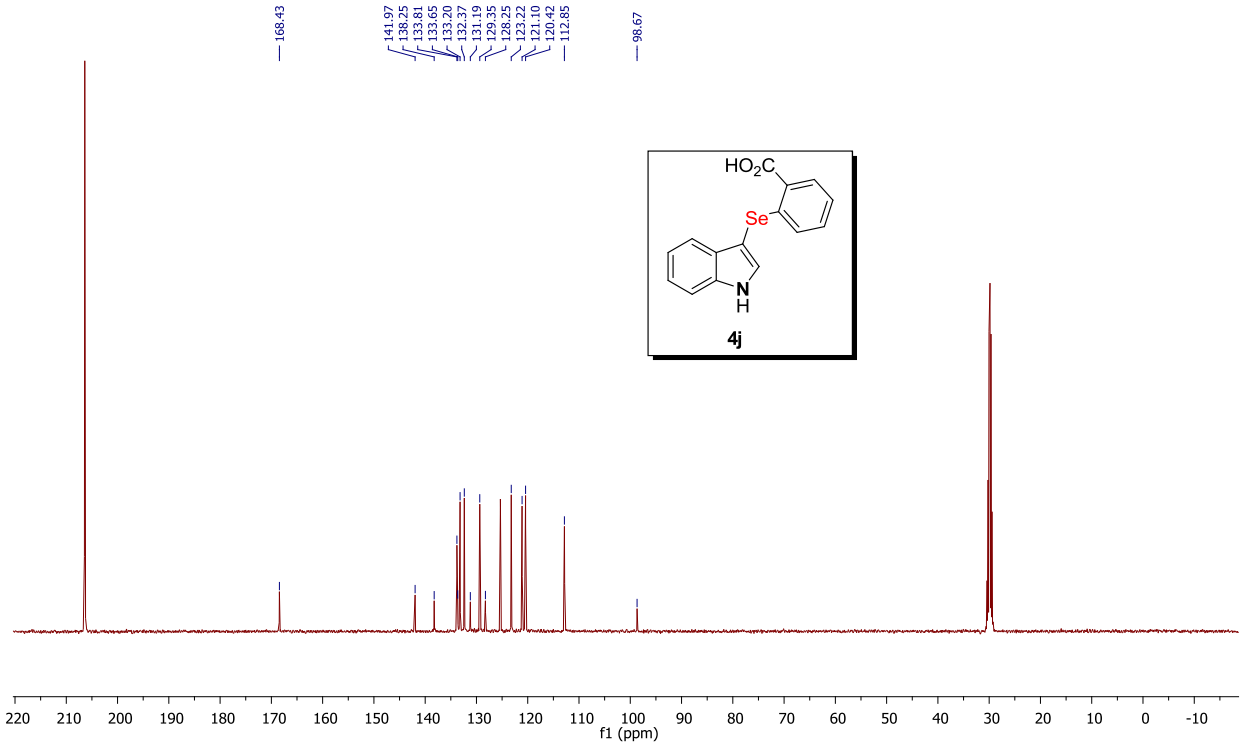
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4i**



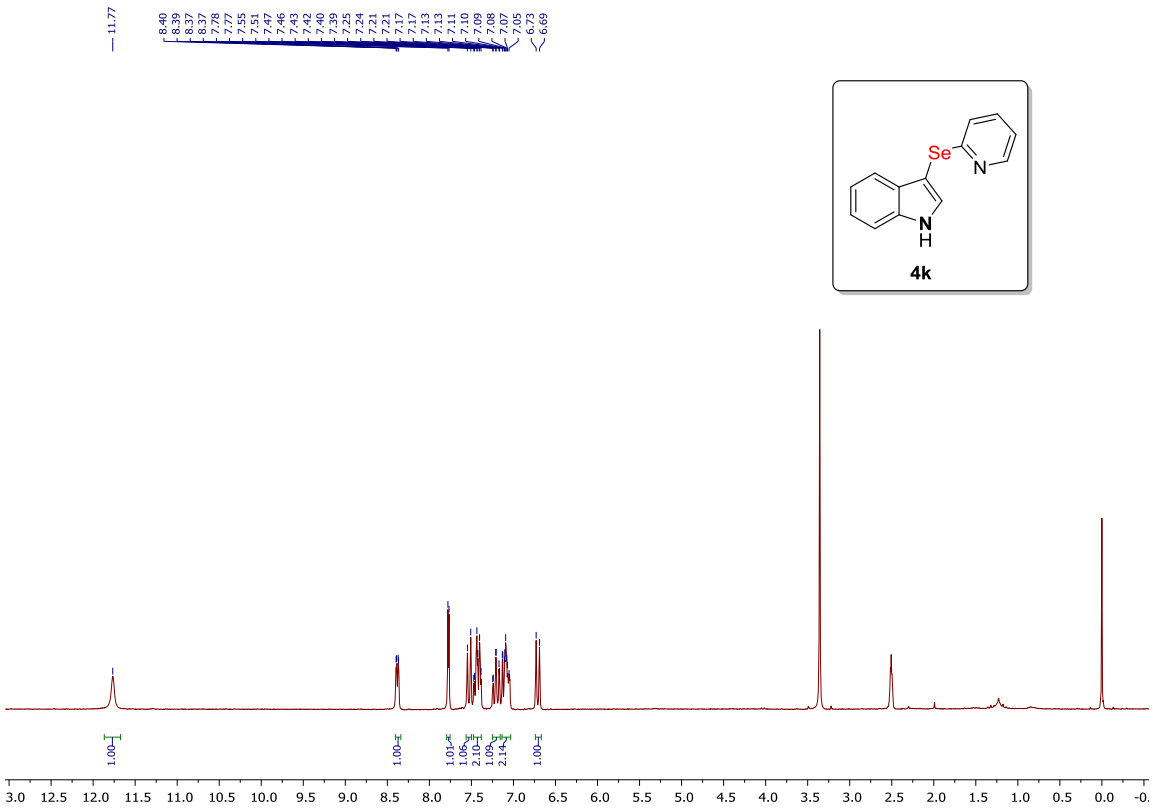
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4i**



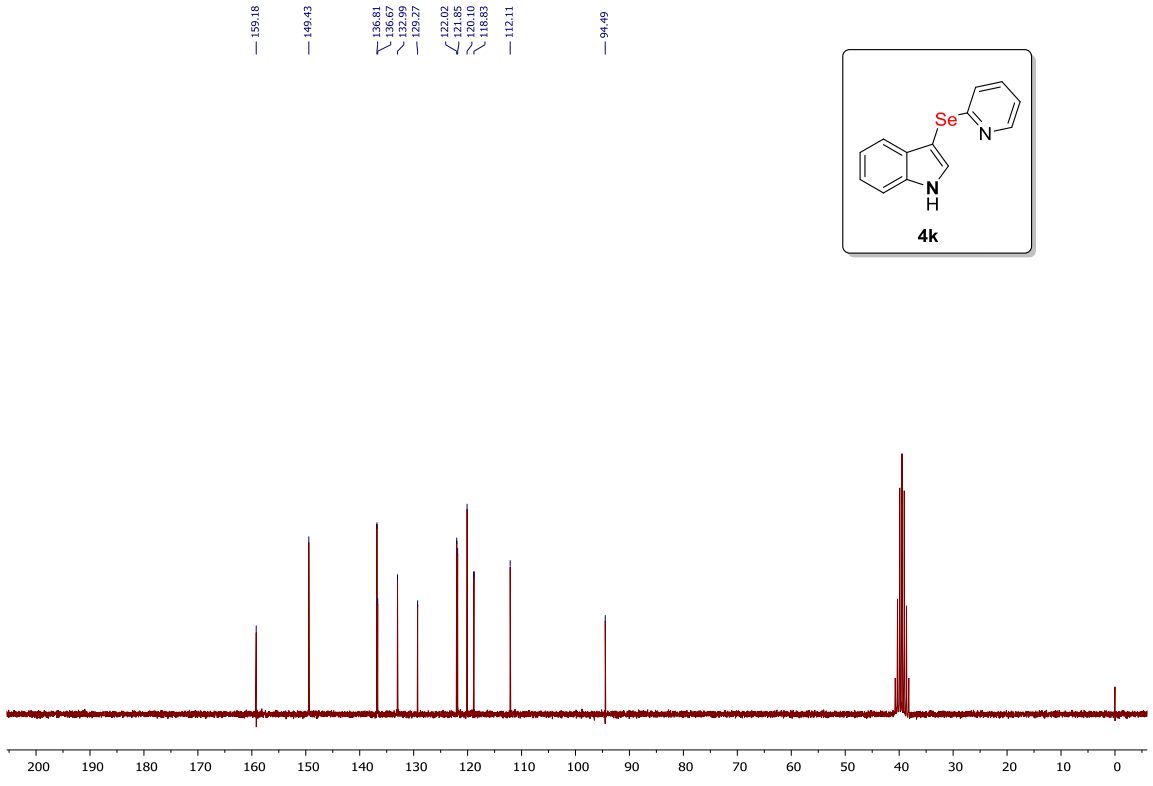
^{1}H NMR (400 MHz, Acetone-d_6) spectrum of **4j**



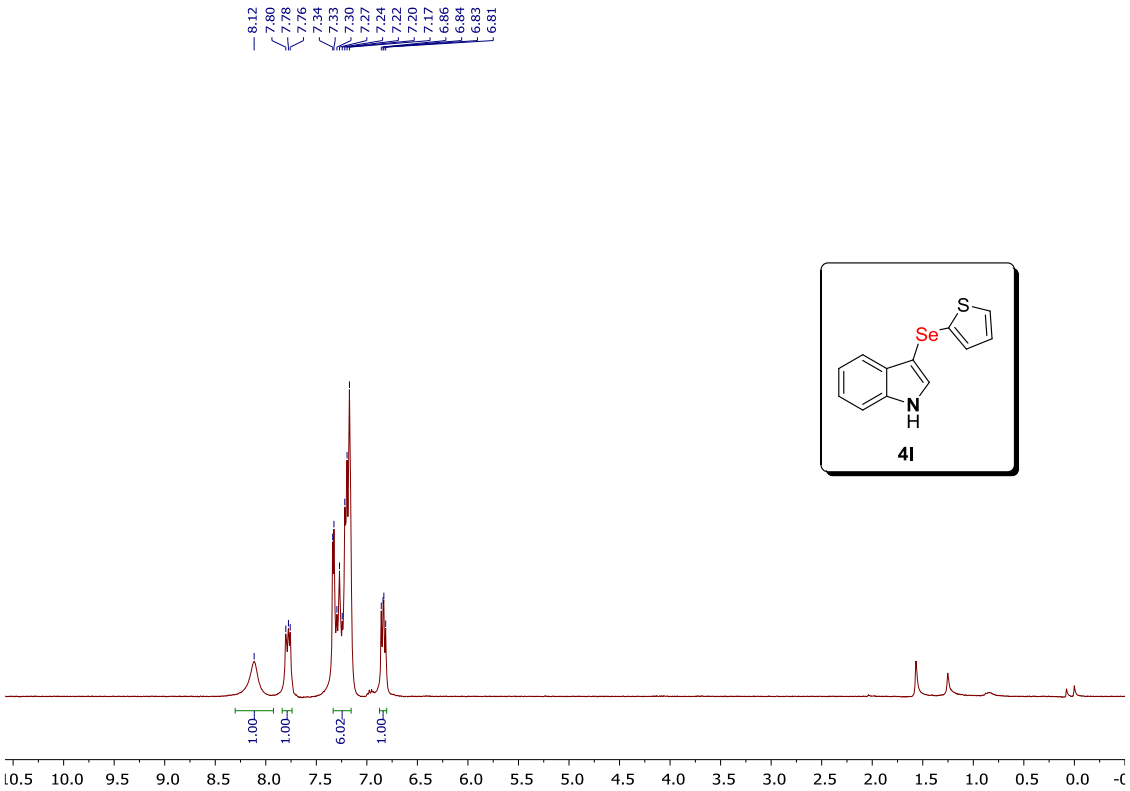
^{13}C NMR (101 MHz, Acetone-d_6) spectrum of **4j**



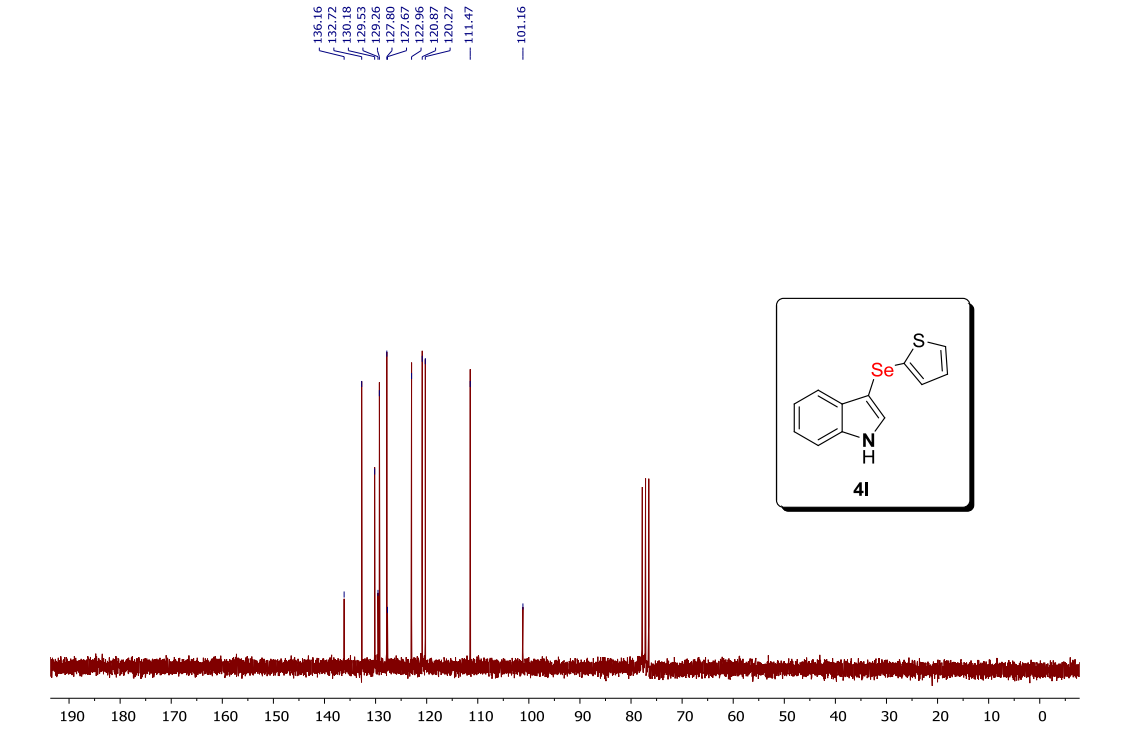
^{1}H NMR (200 MHz, DMSO-d_6) spectrum of **4k**



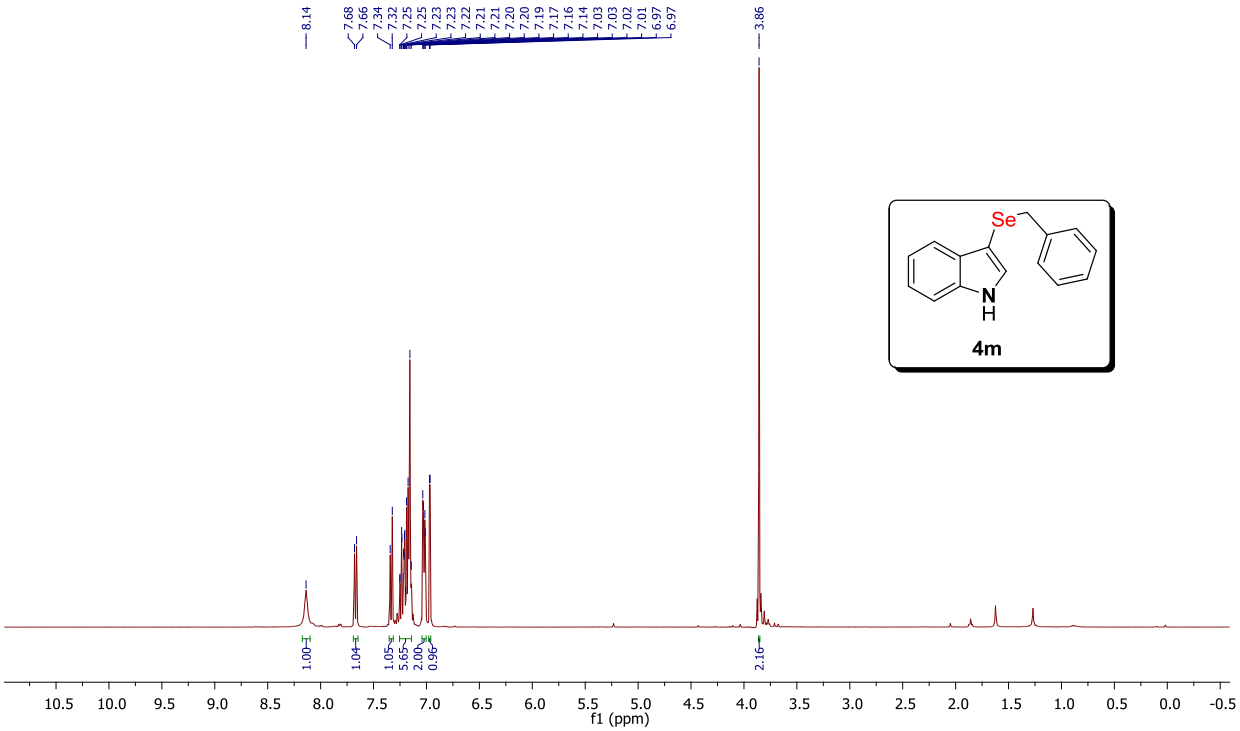
^{13}C NMR (50 MHz, DMSO-d_6) spectrum of **4k**



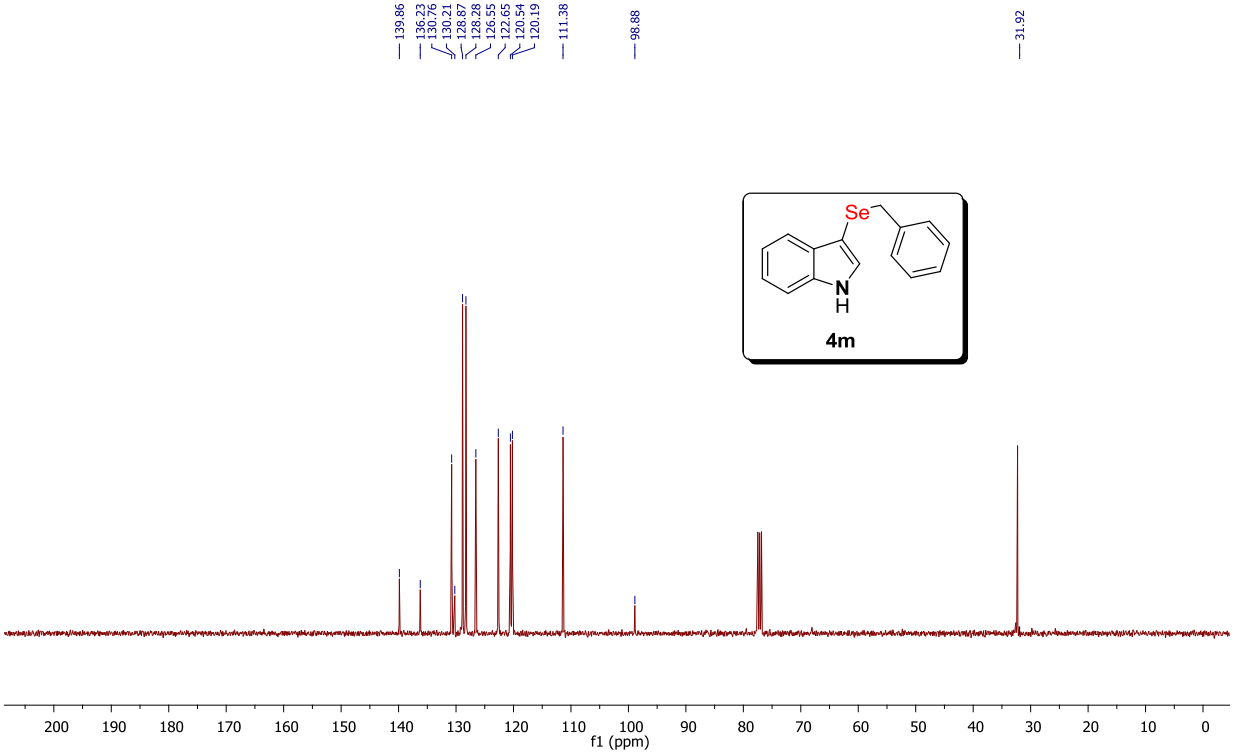
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **4l**



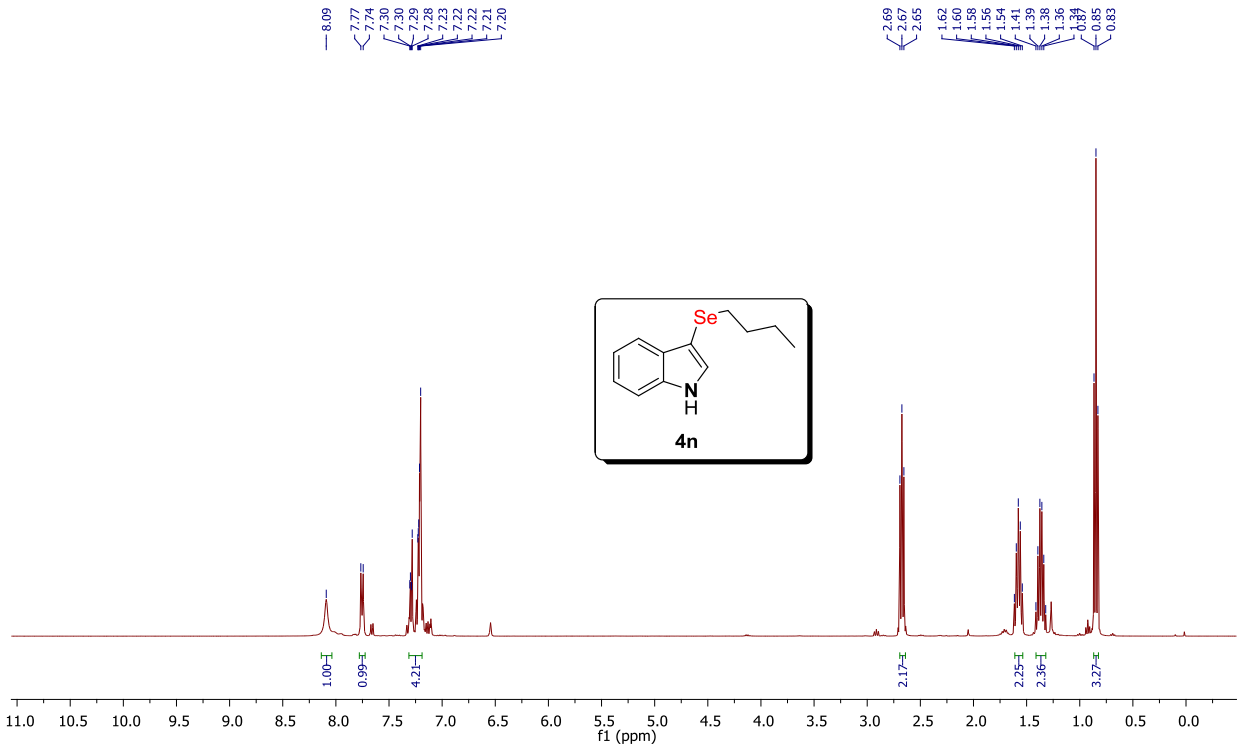
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **4l**



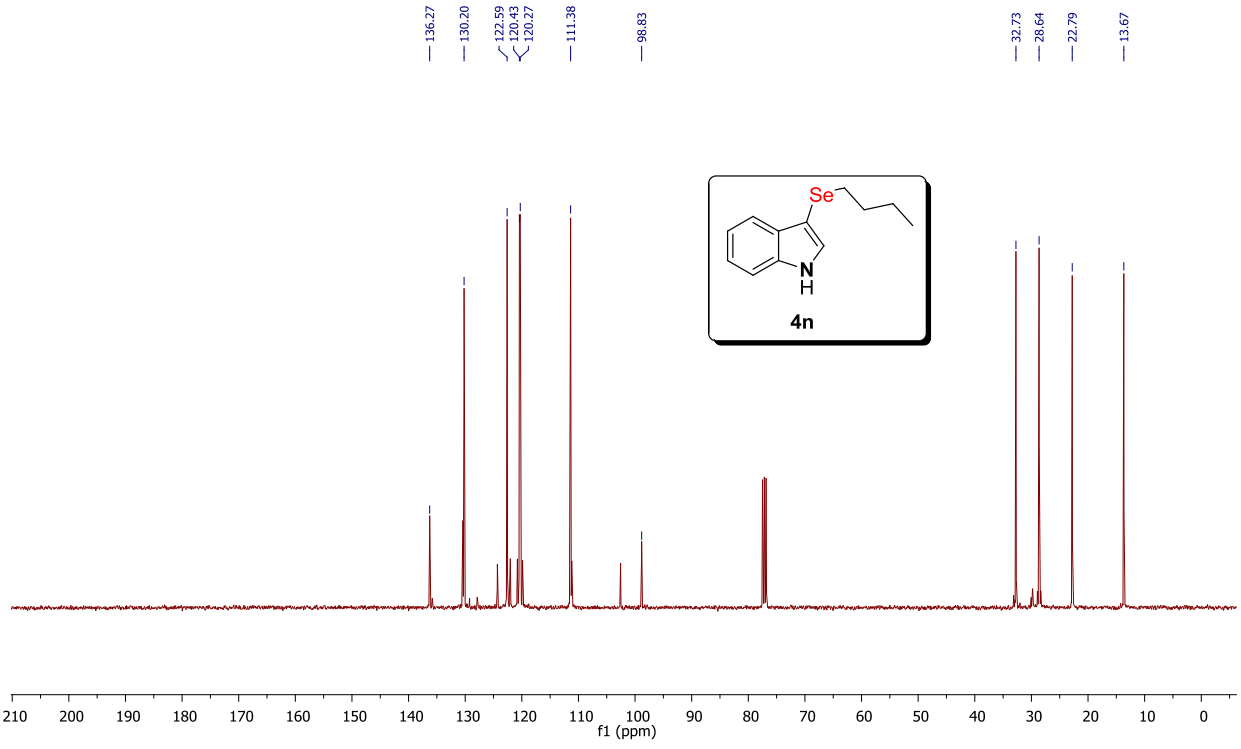
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4m**



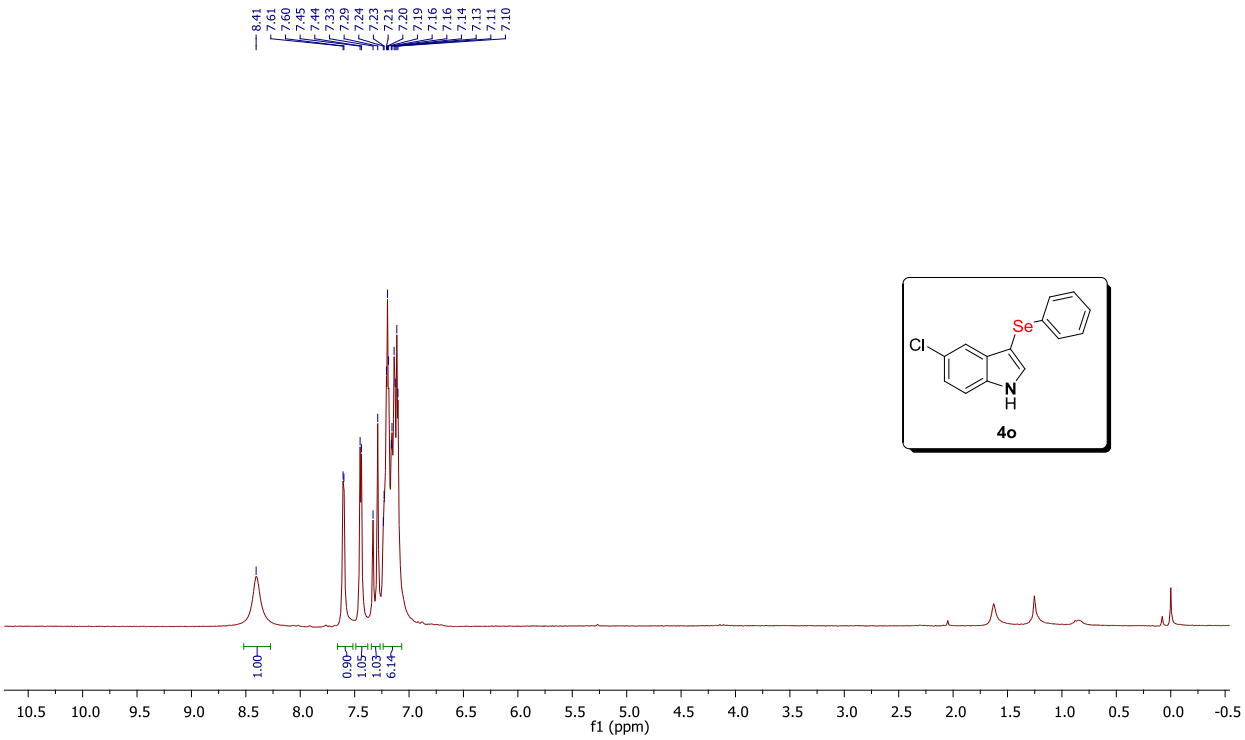
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4m**



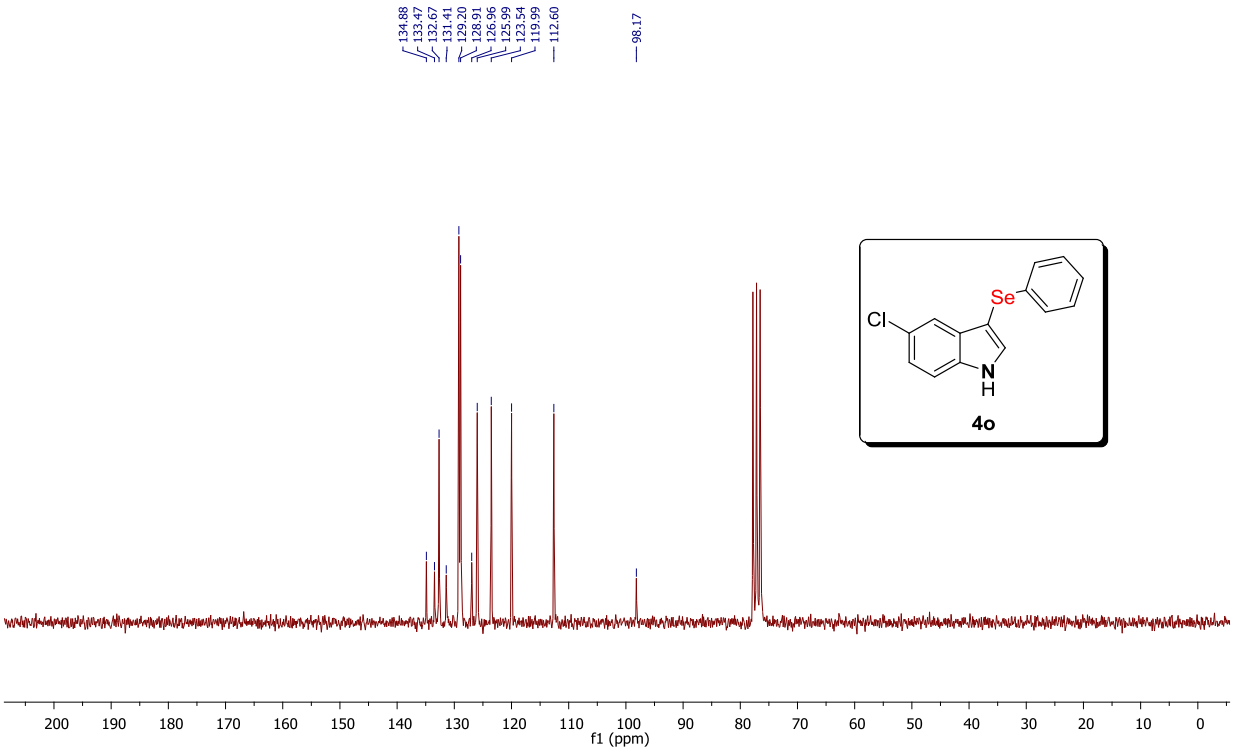
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4n**



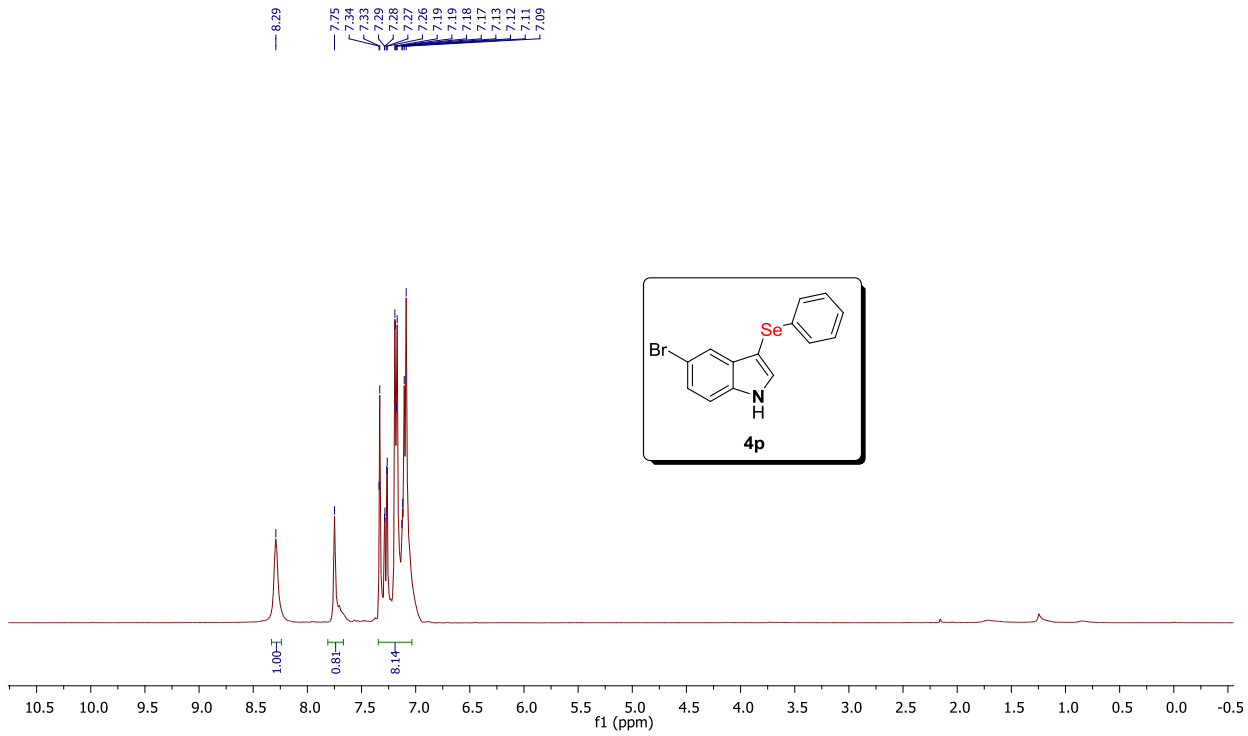
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4n**



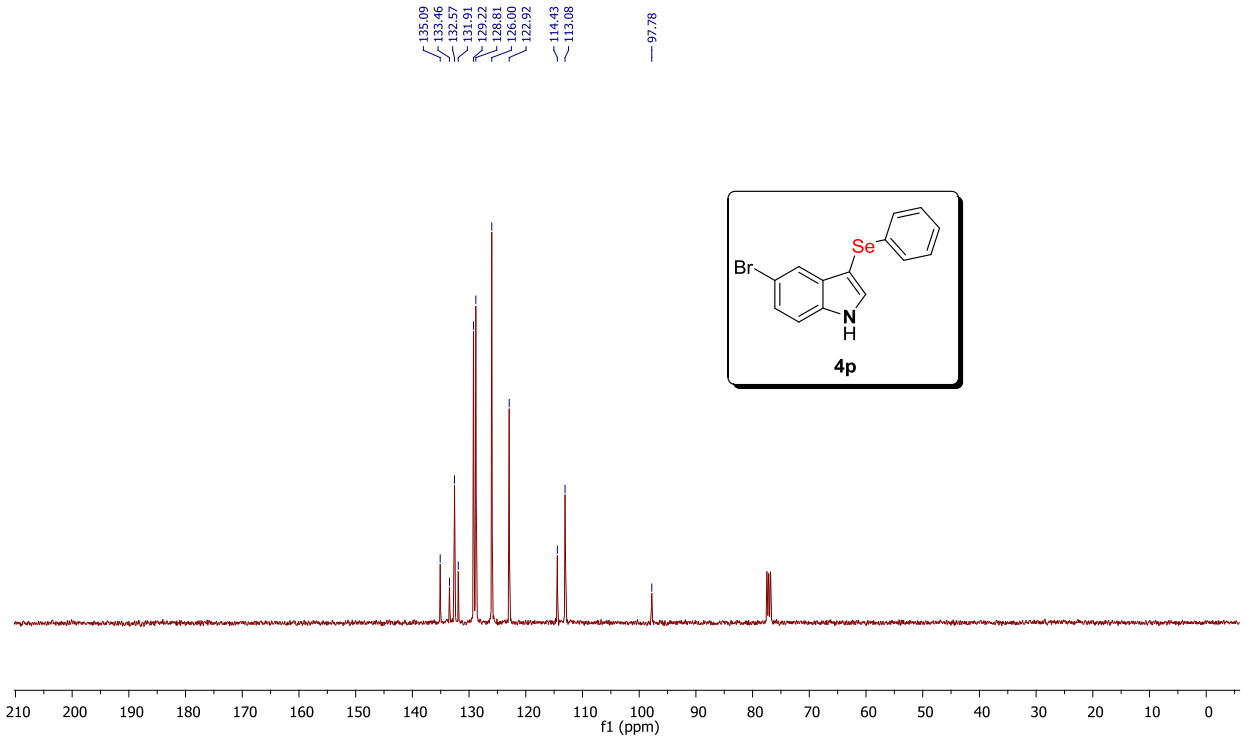
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **4o**



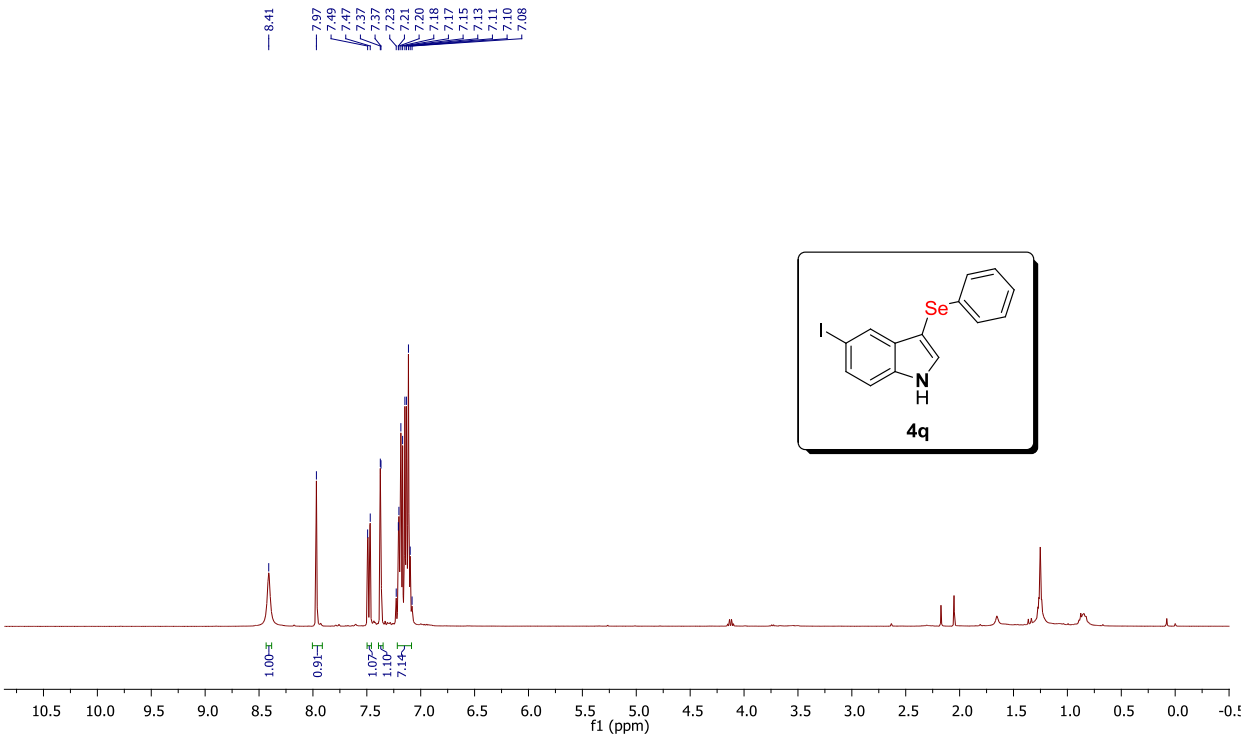
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **4o**



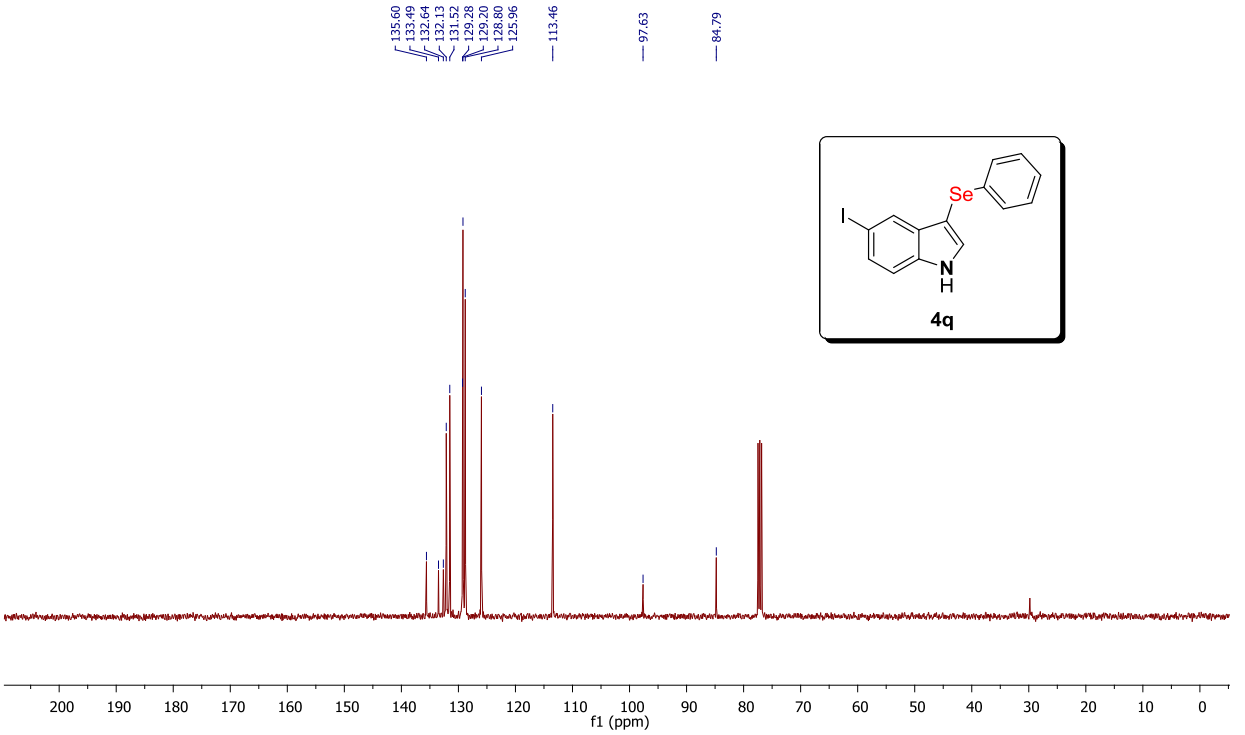
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4p**



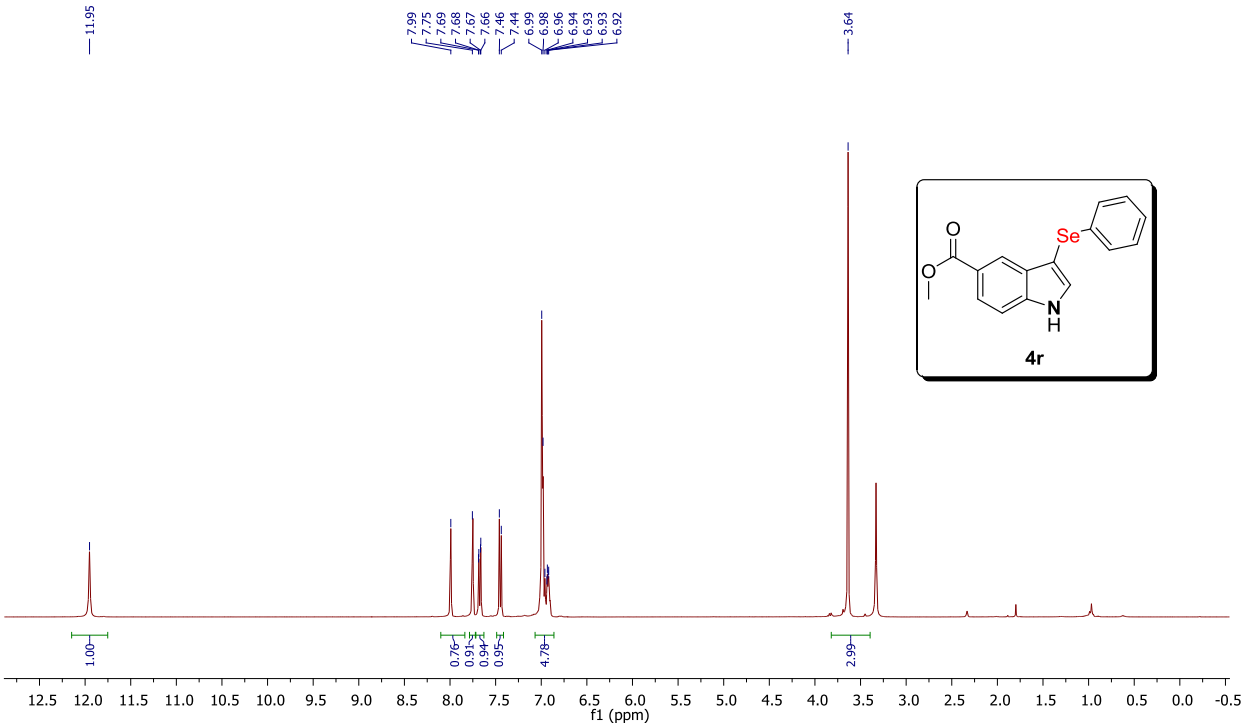
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4p**



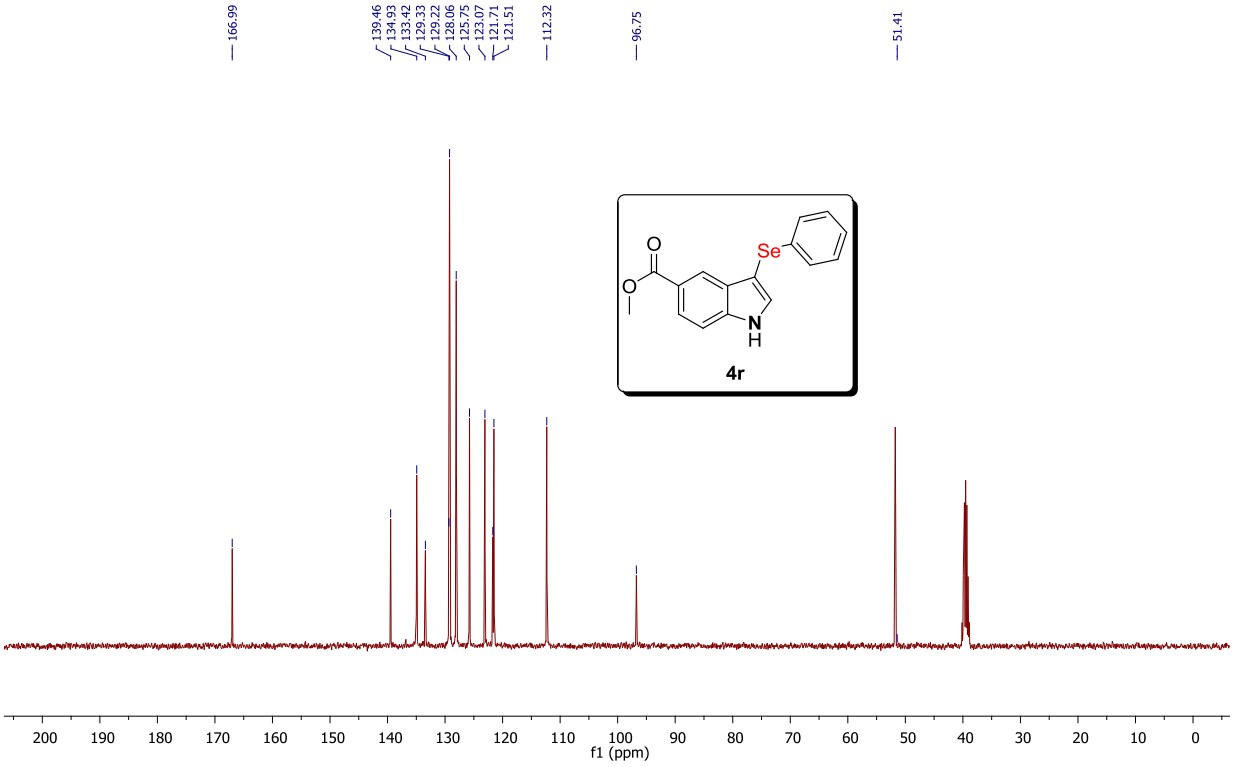
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4q**



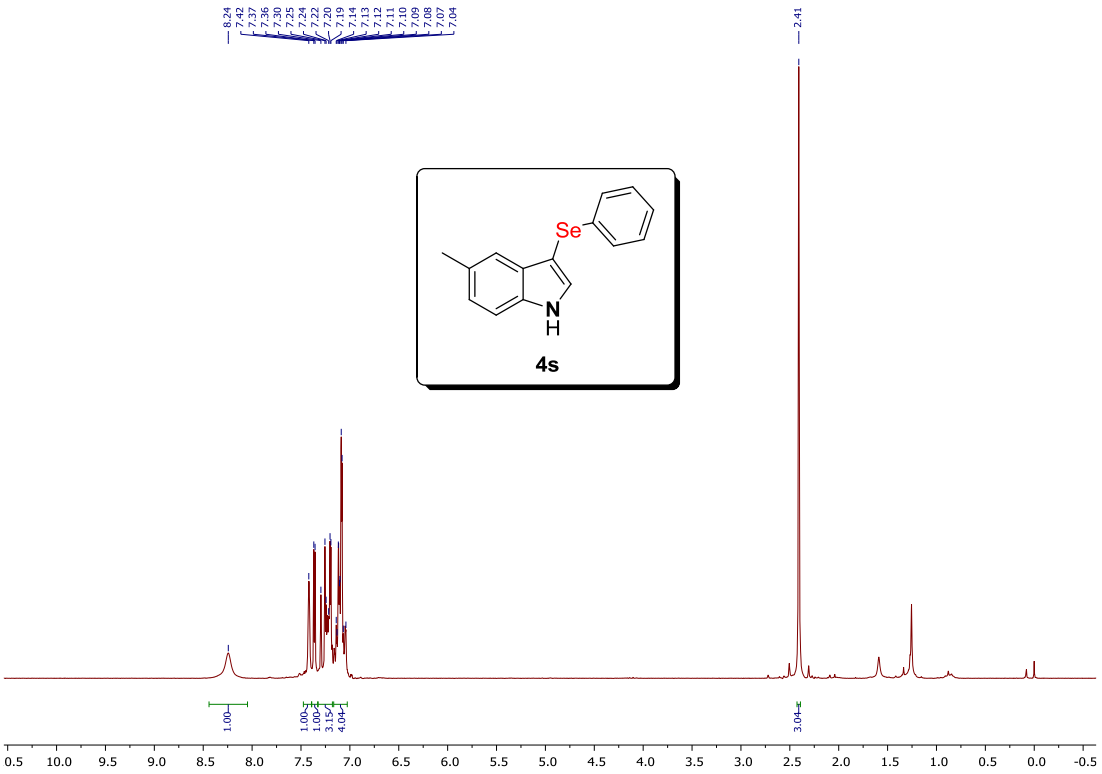
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4q**



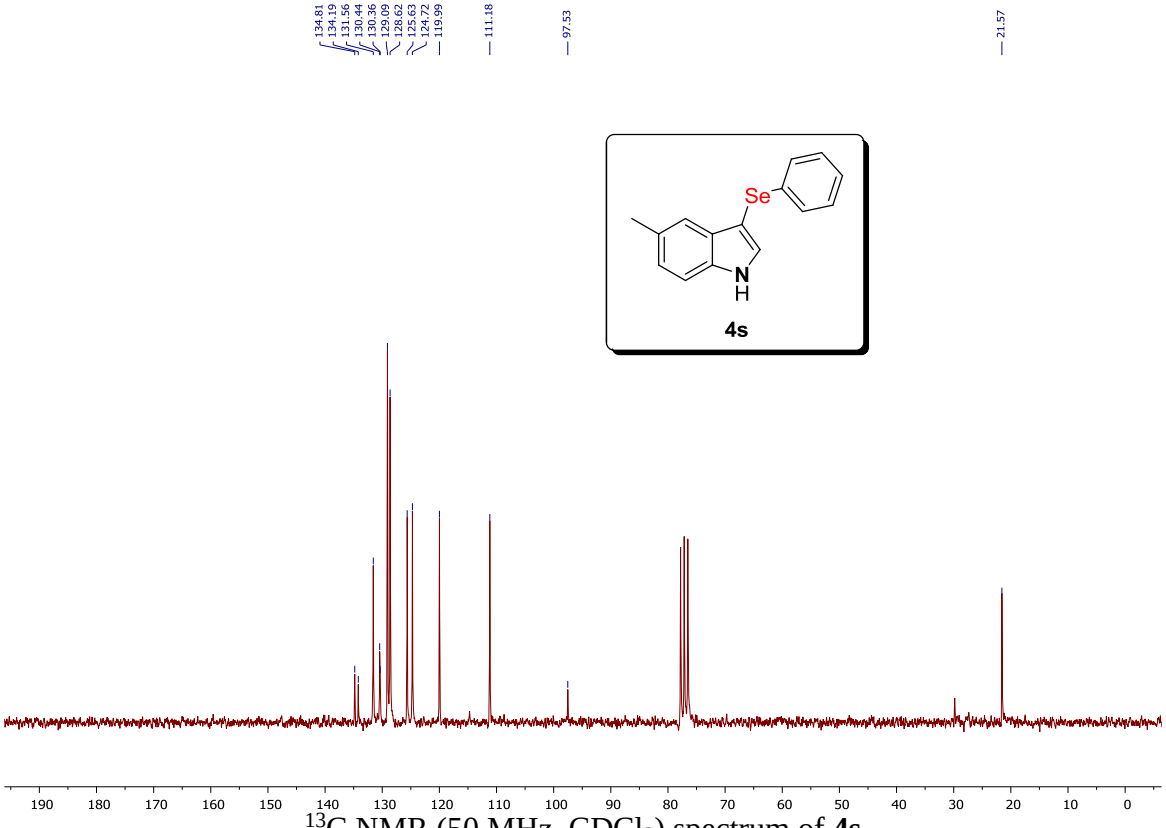
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **4r**



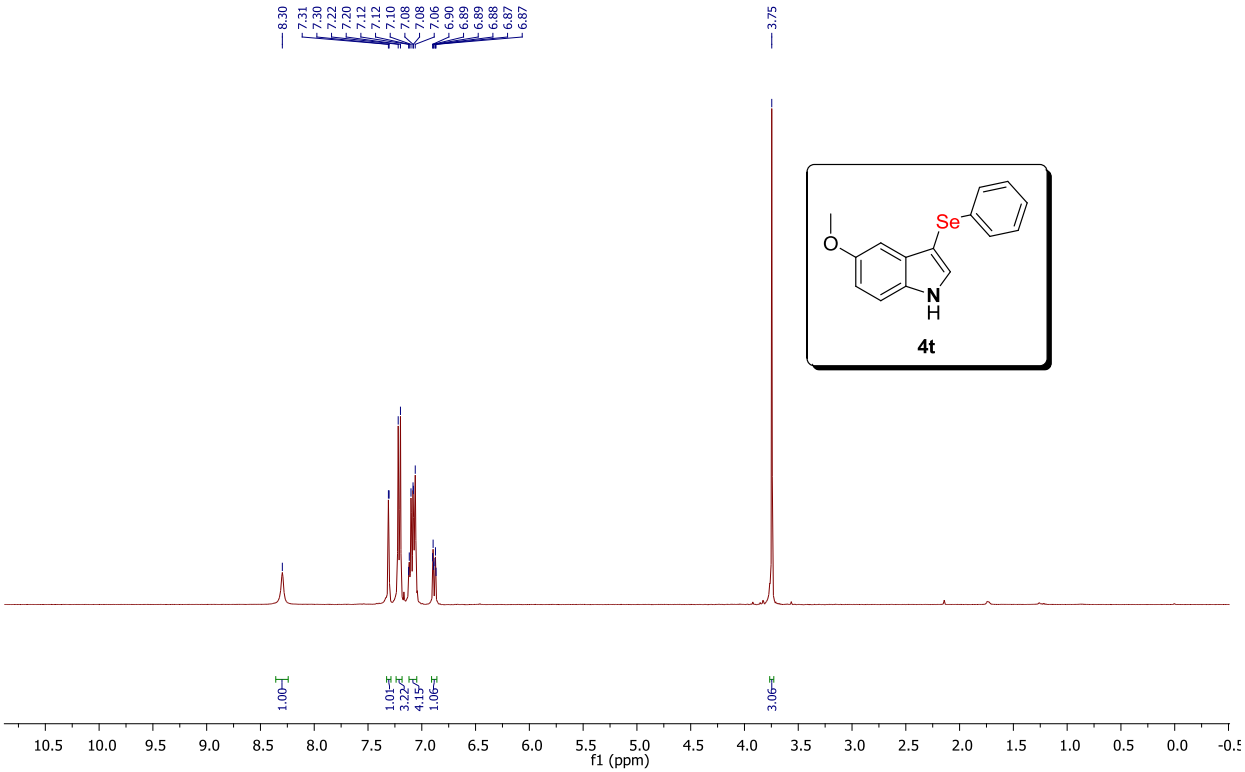
^{13}C NMR (101 MHz, DMSO-d_6) spectrum of **4r**



^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **4s**



^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **4s**



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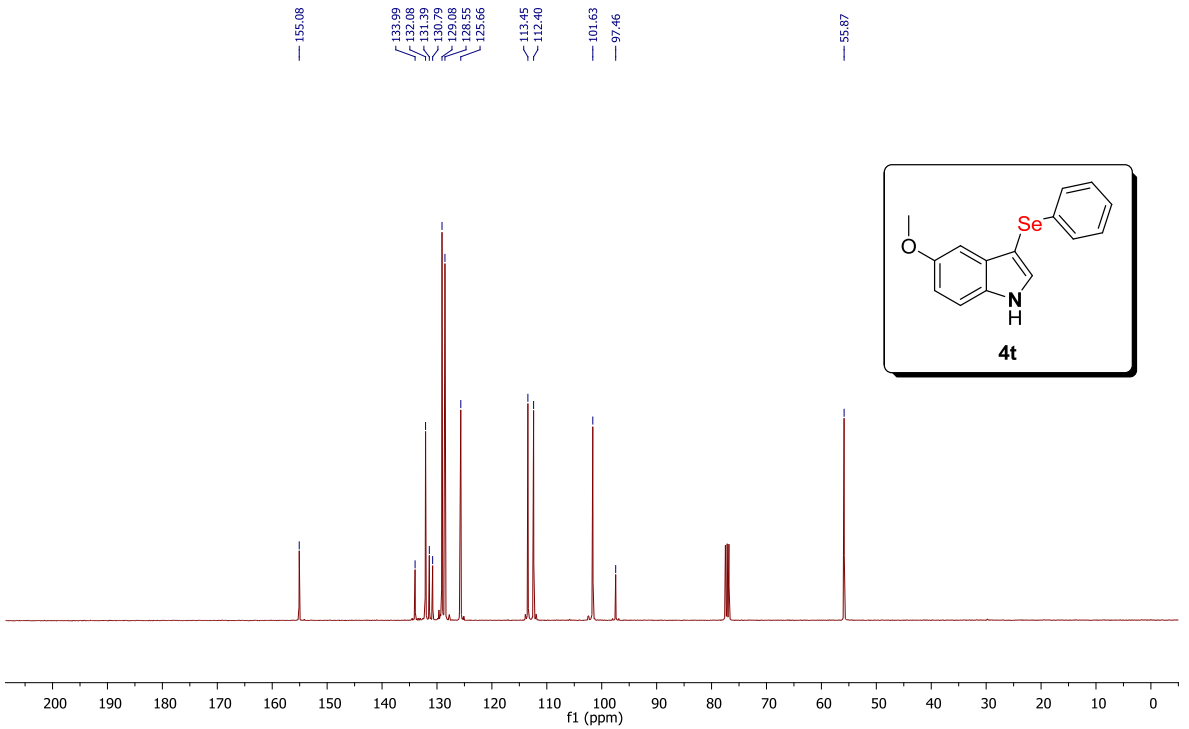
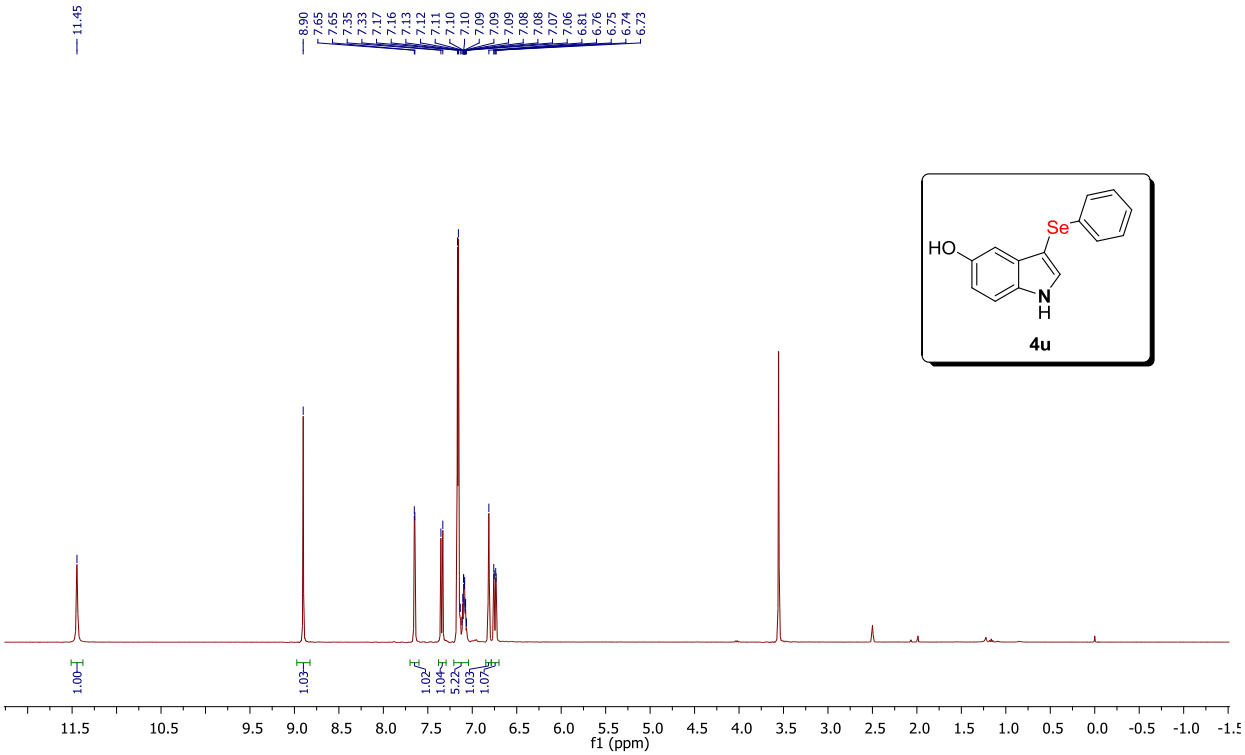
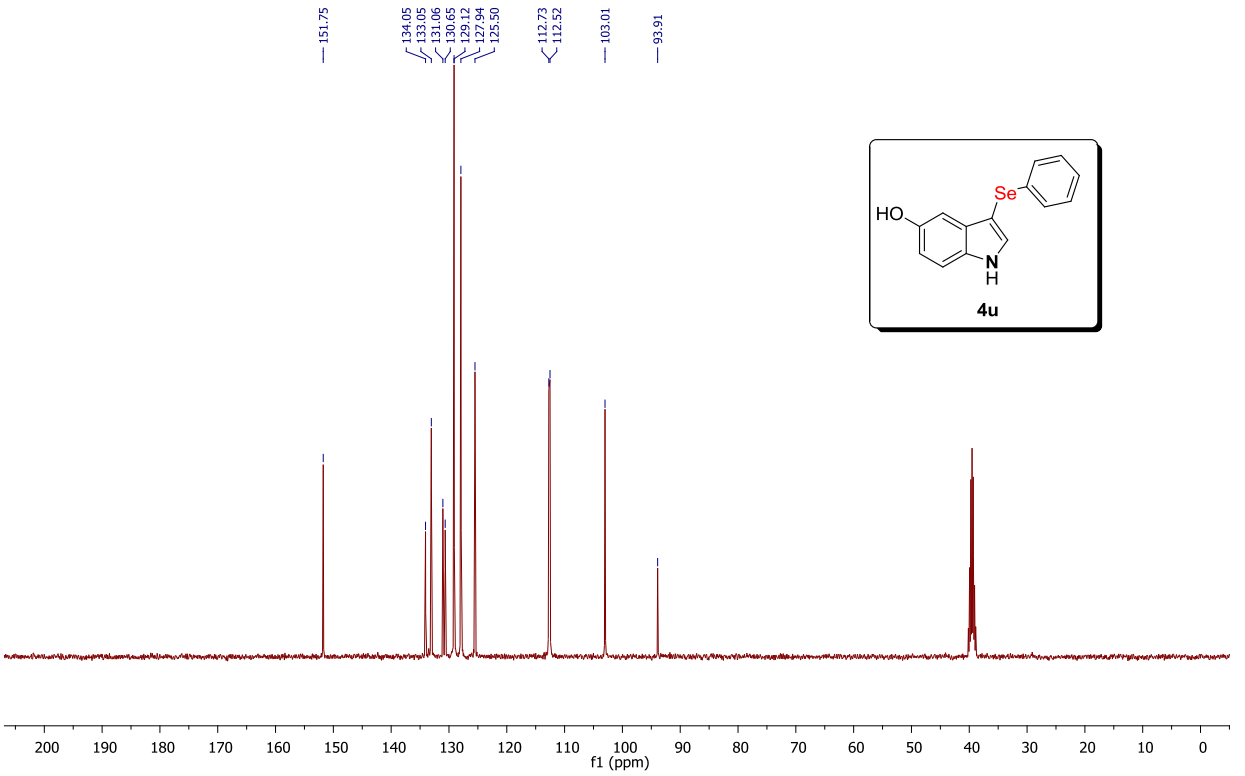


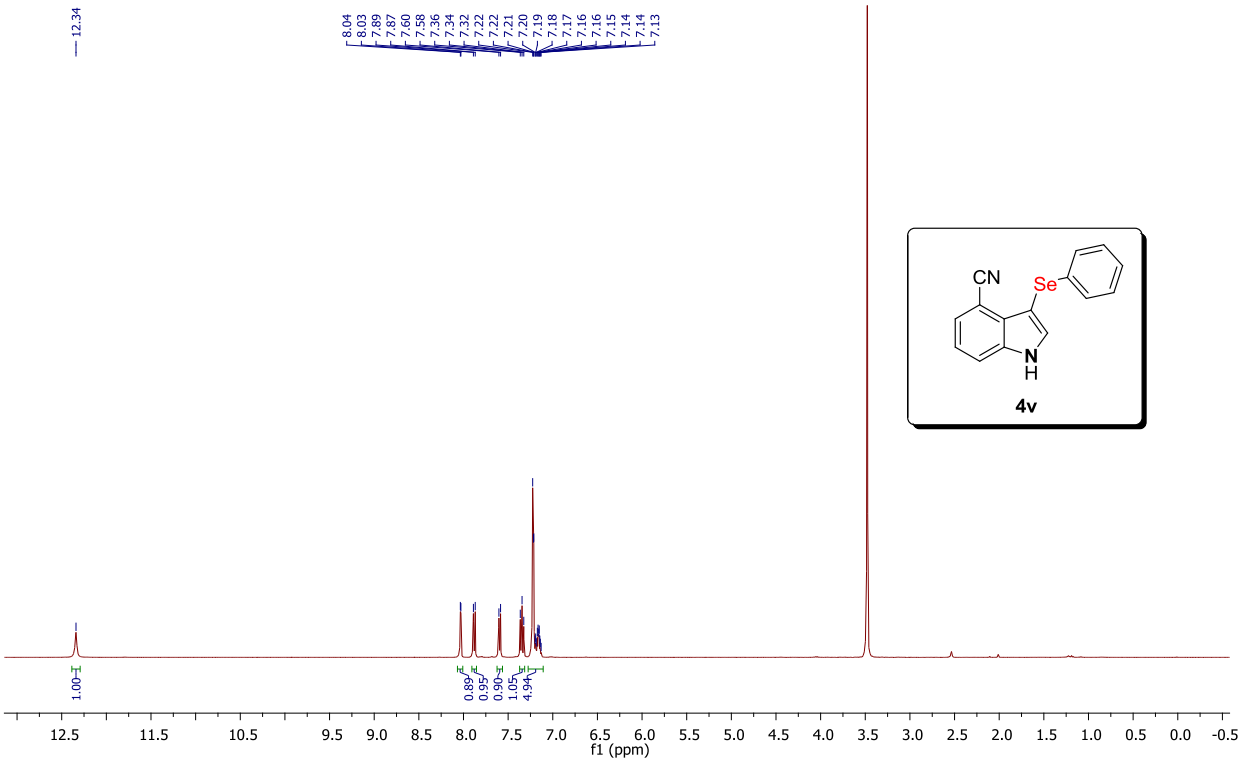
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4t**



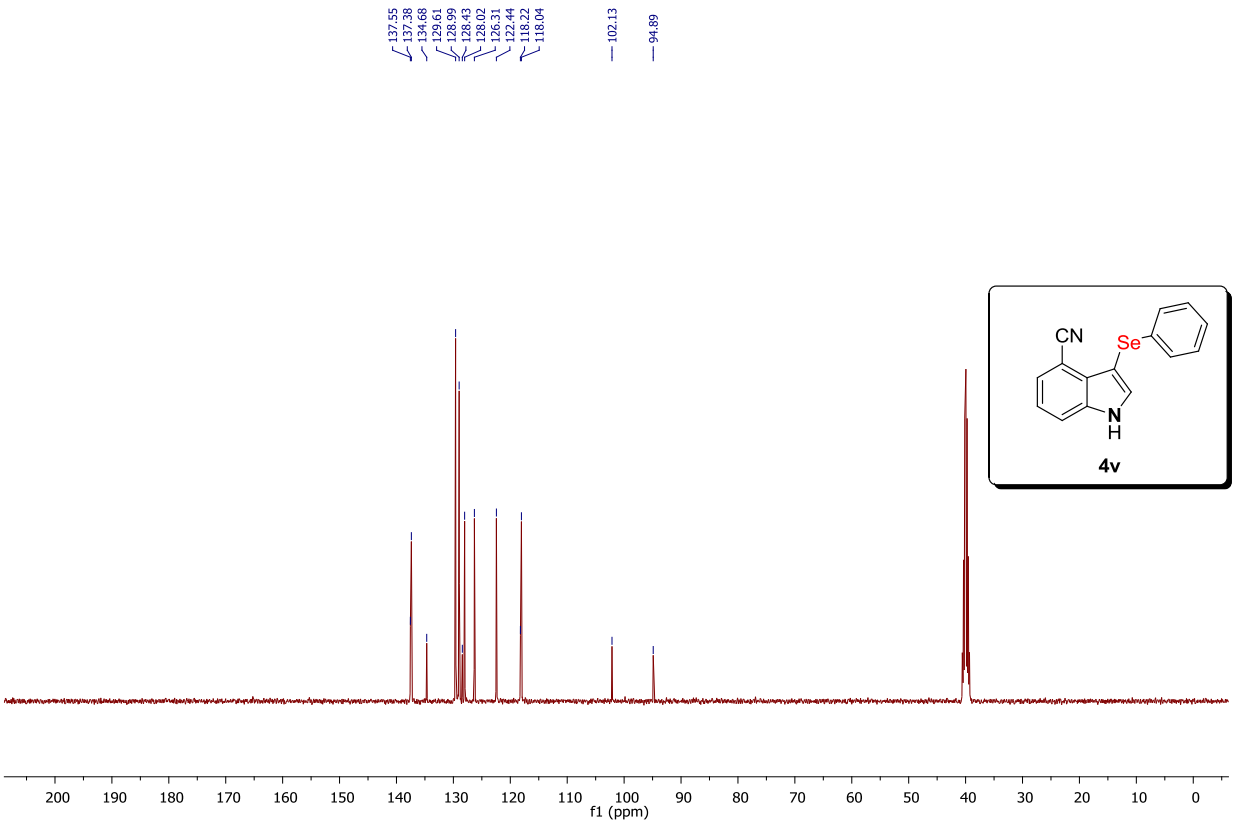
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **4u**



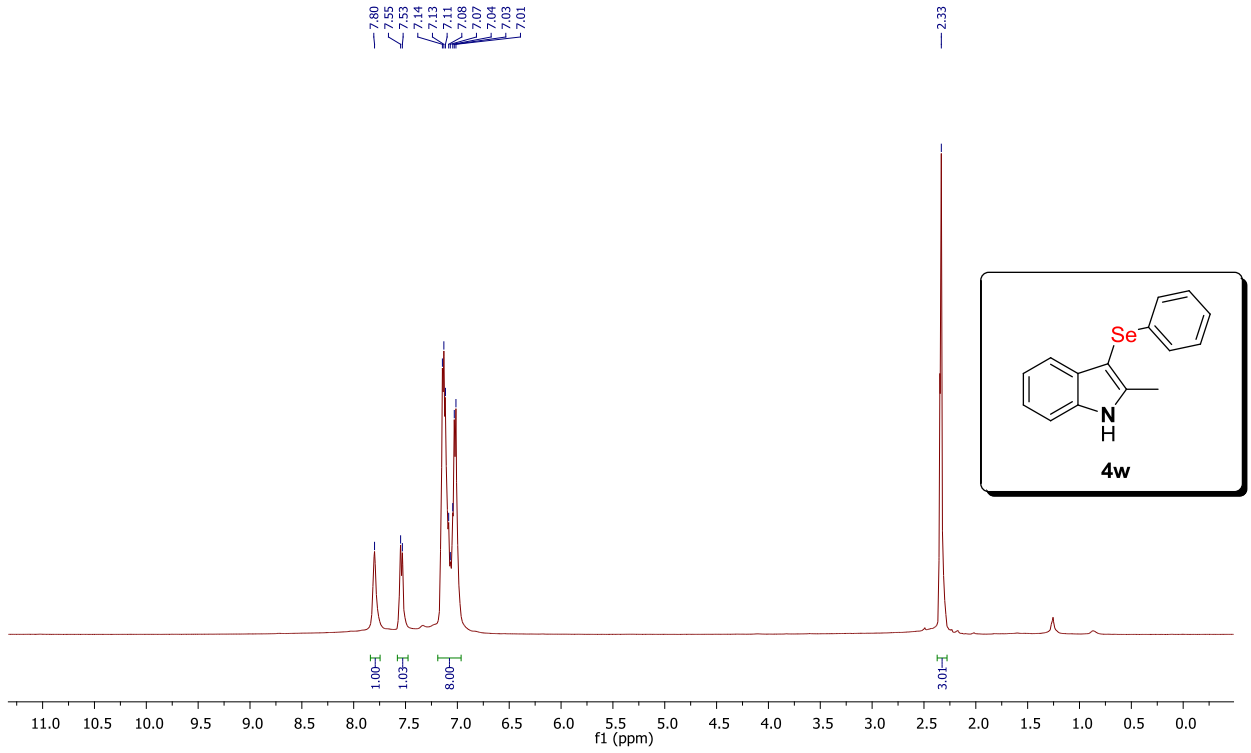
^{13}C NMR (101 MHz, DMSO-d_6) spectrum of **4u**



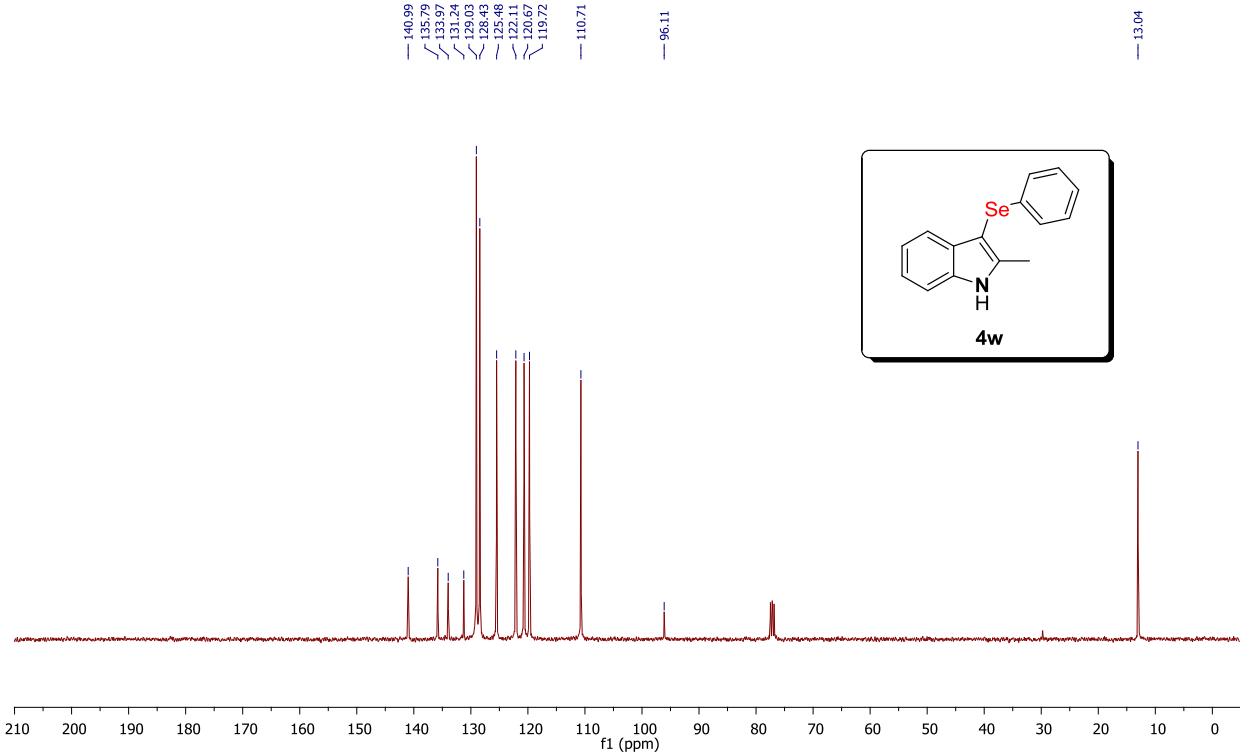
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **4v**



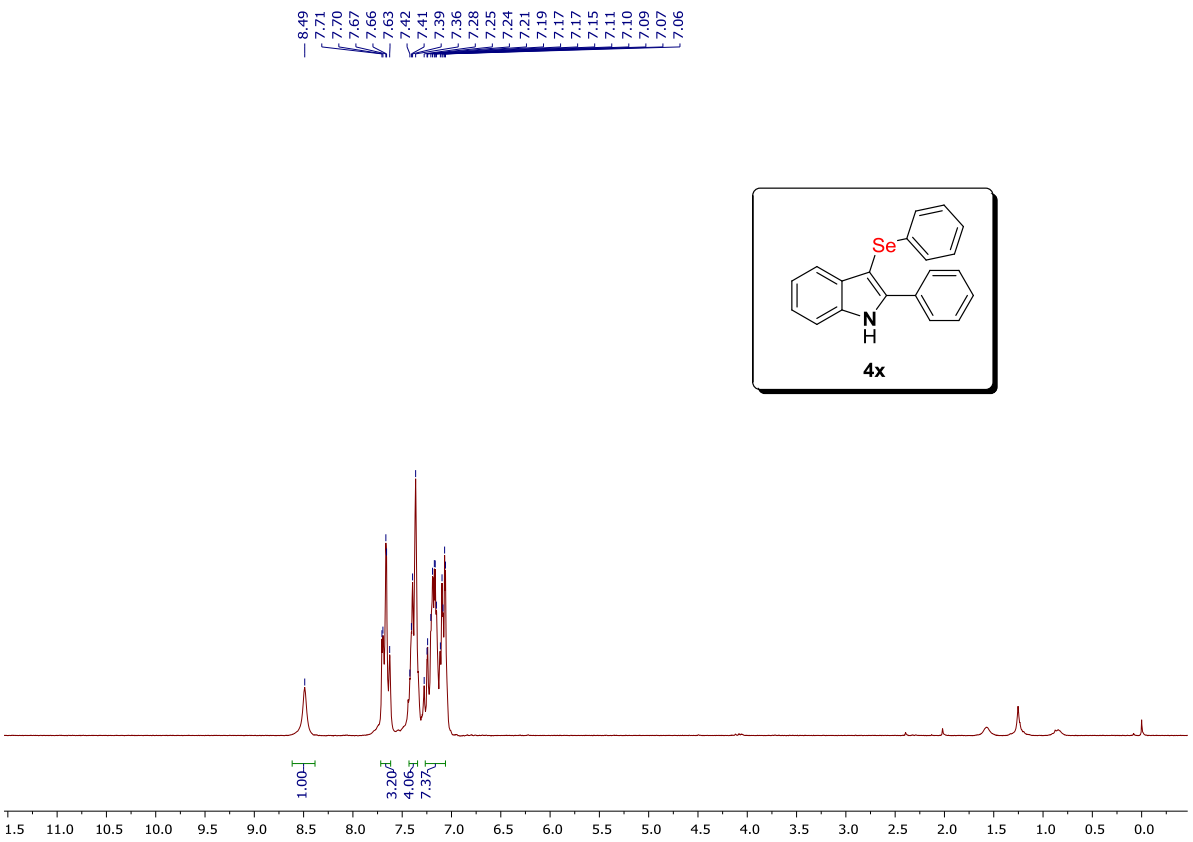
^{13}C NMR (101 MHz, DMSO-d_6) spectrum of **4v**



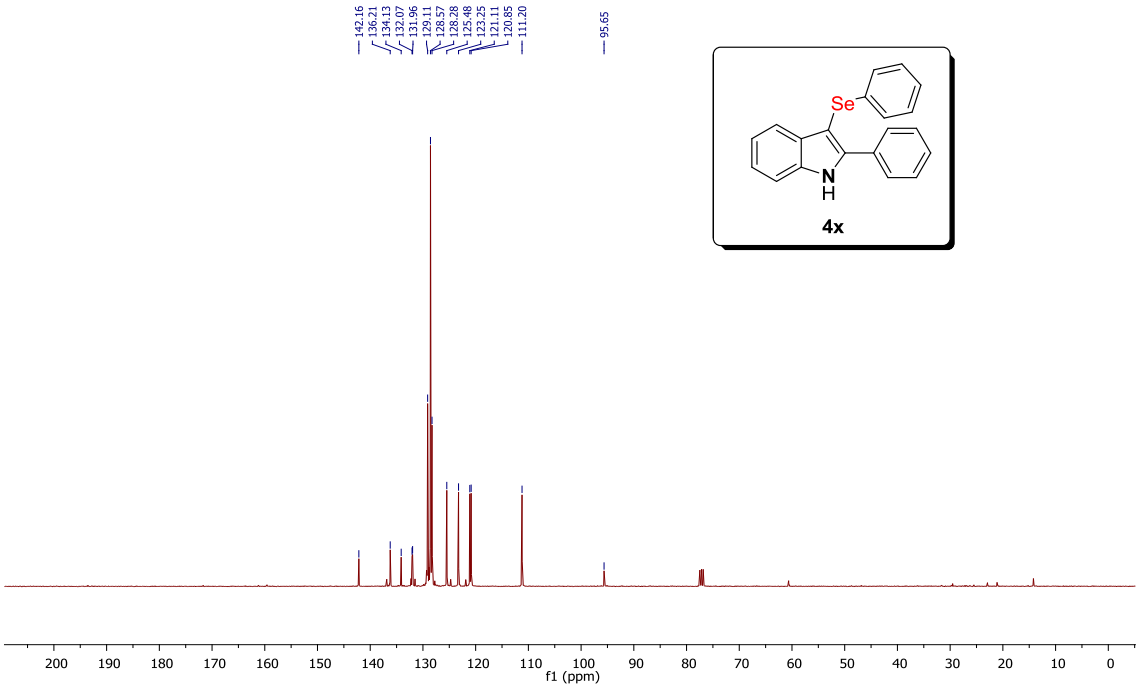
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4w**



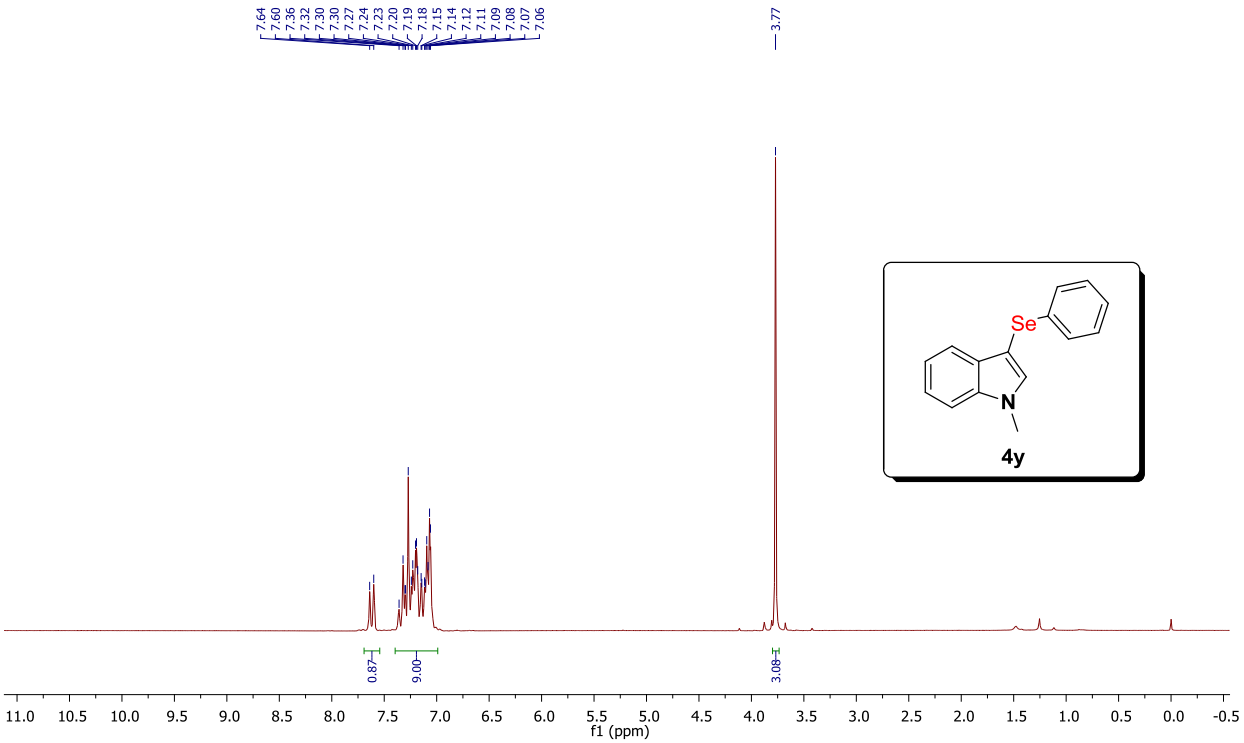
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4w**



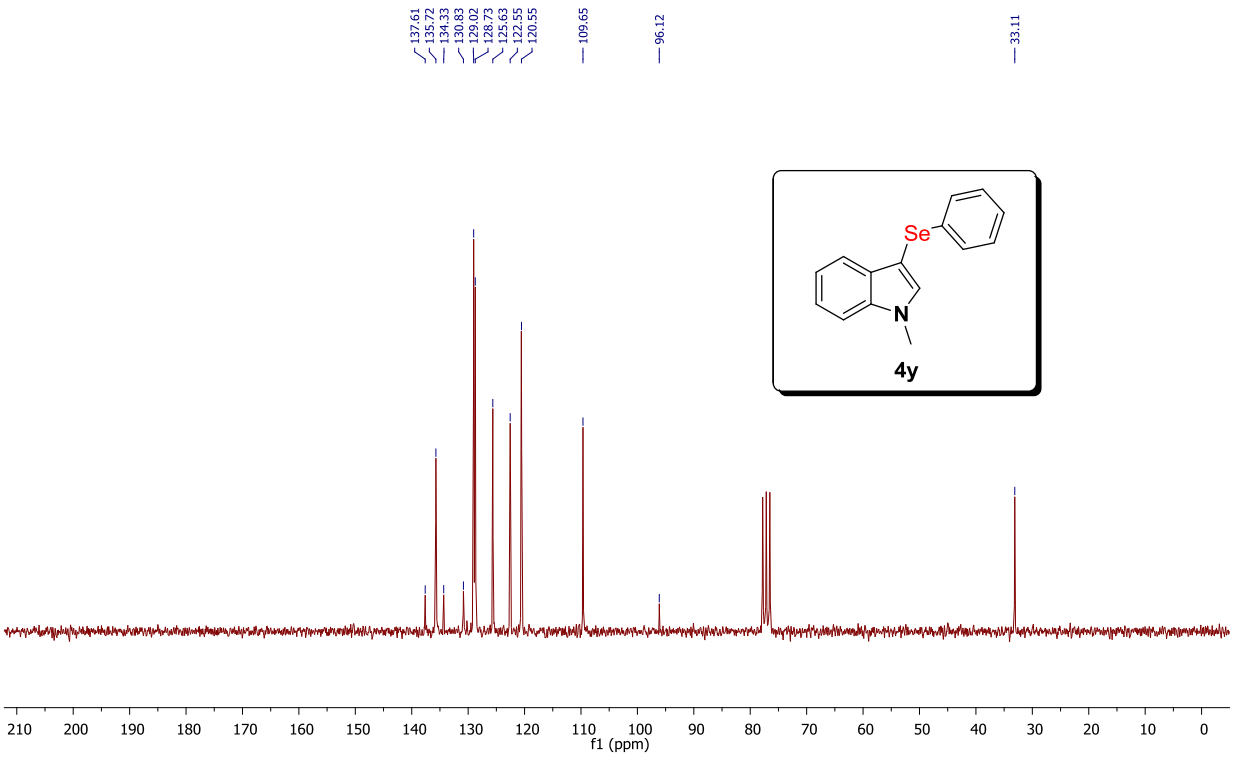
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **4x**



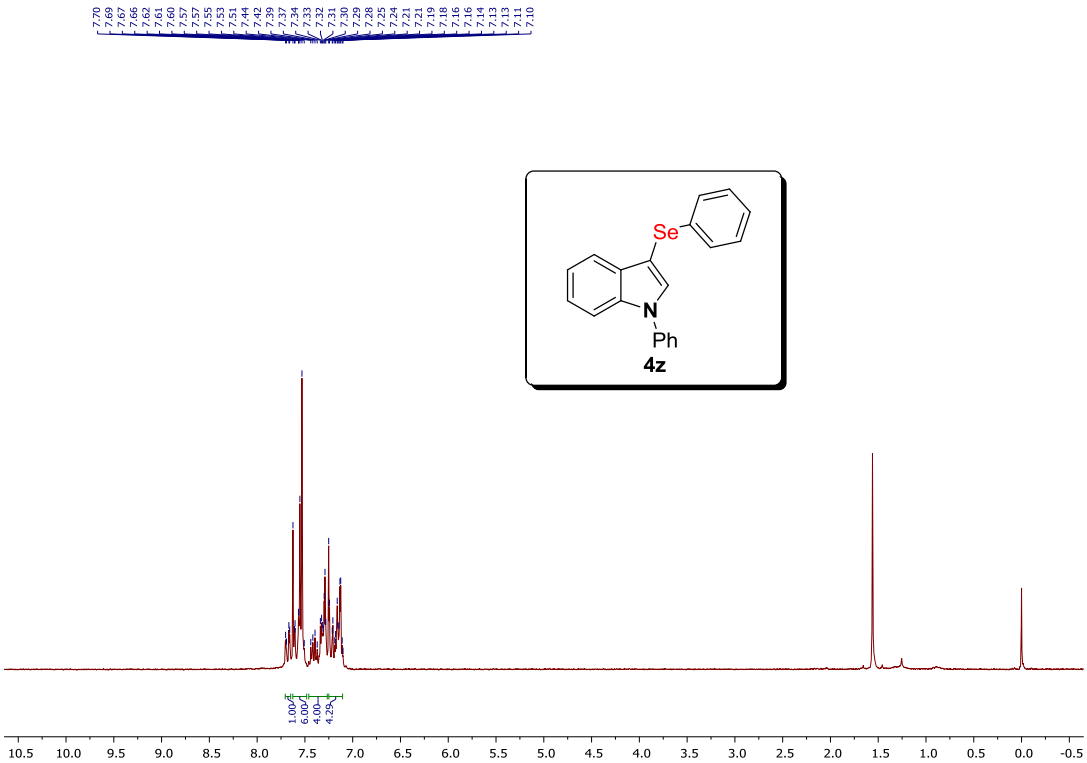
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4x**



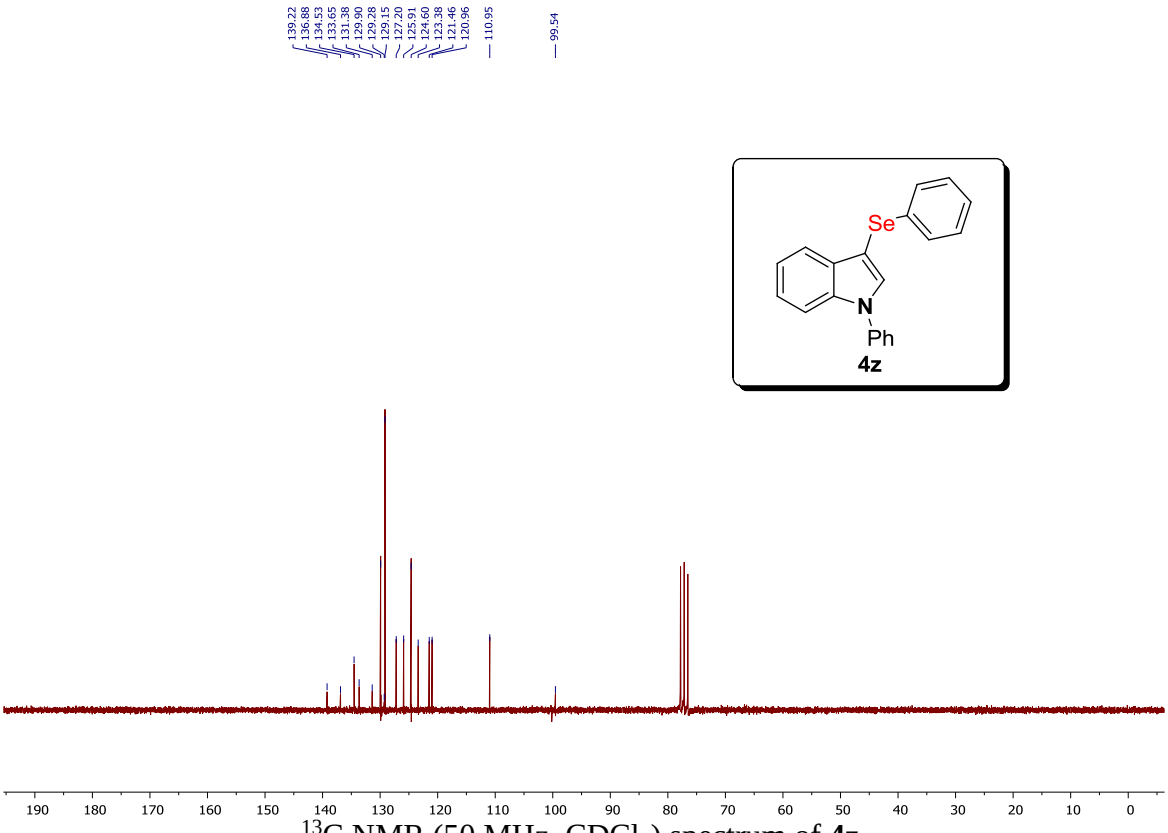
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **4y**



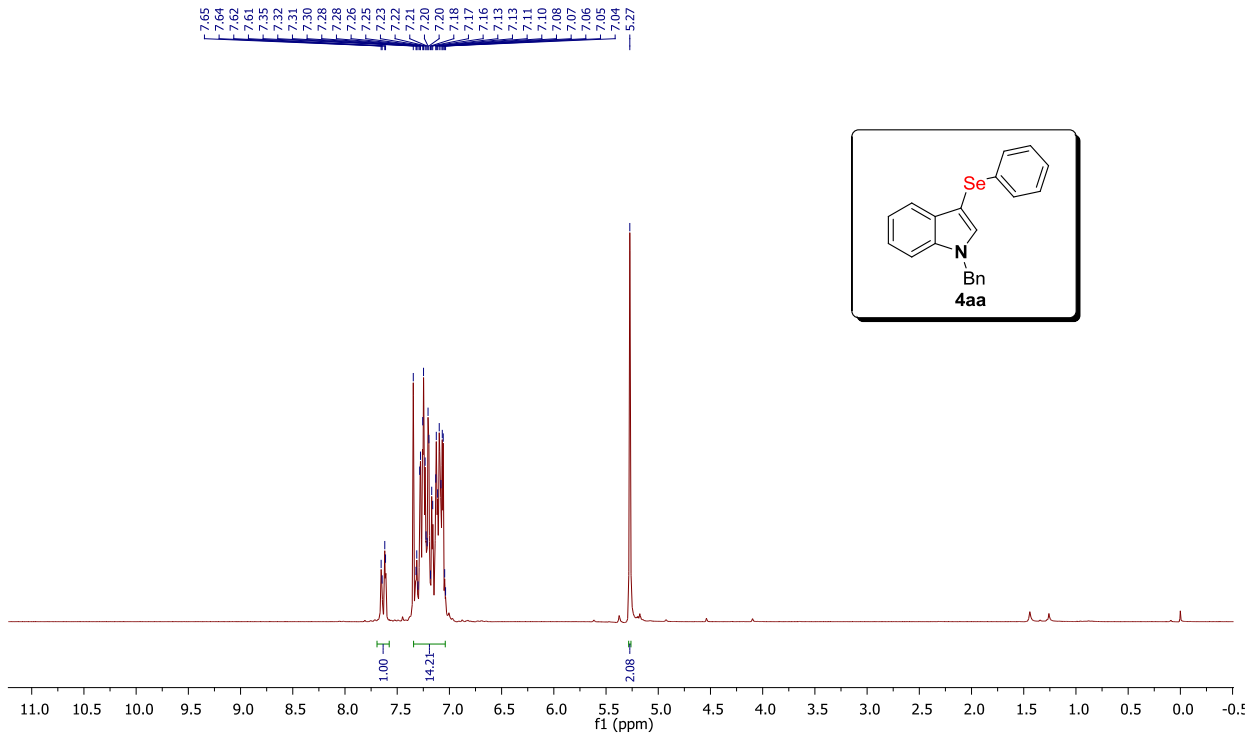
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **4y**



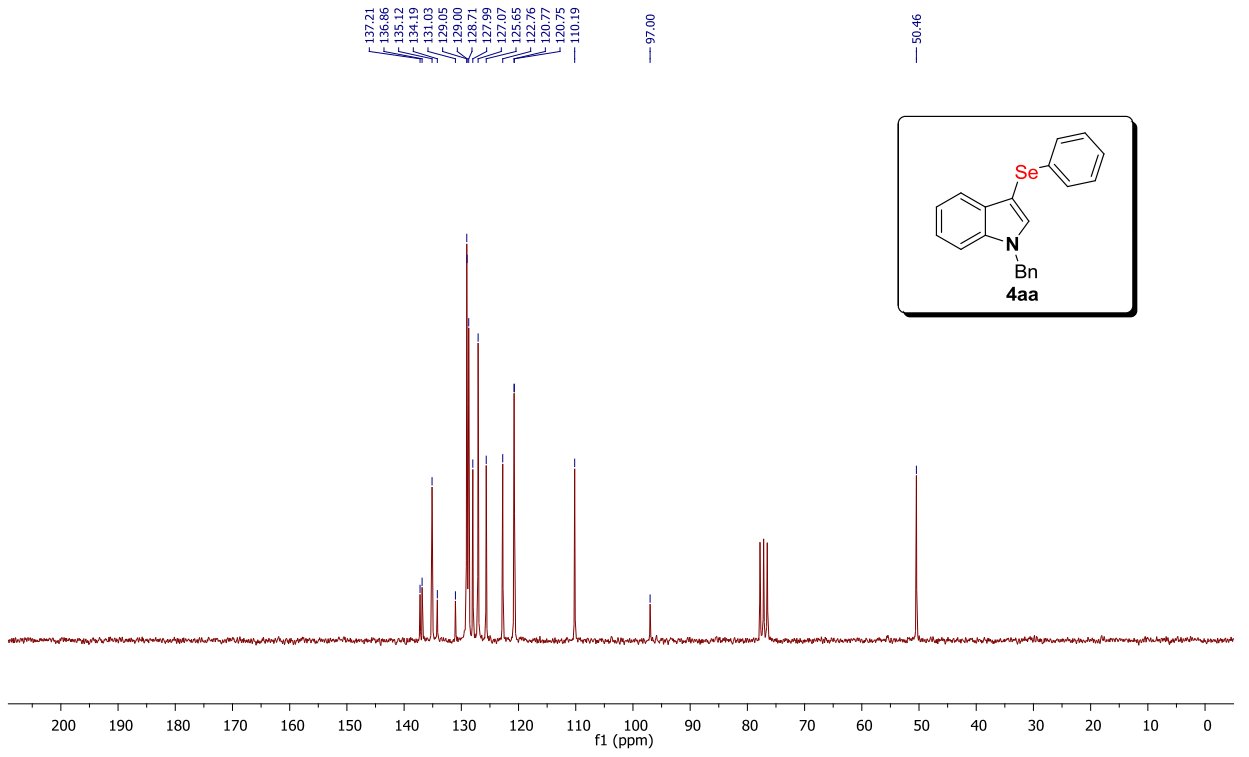
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **4z**



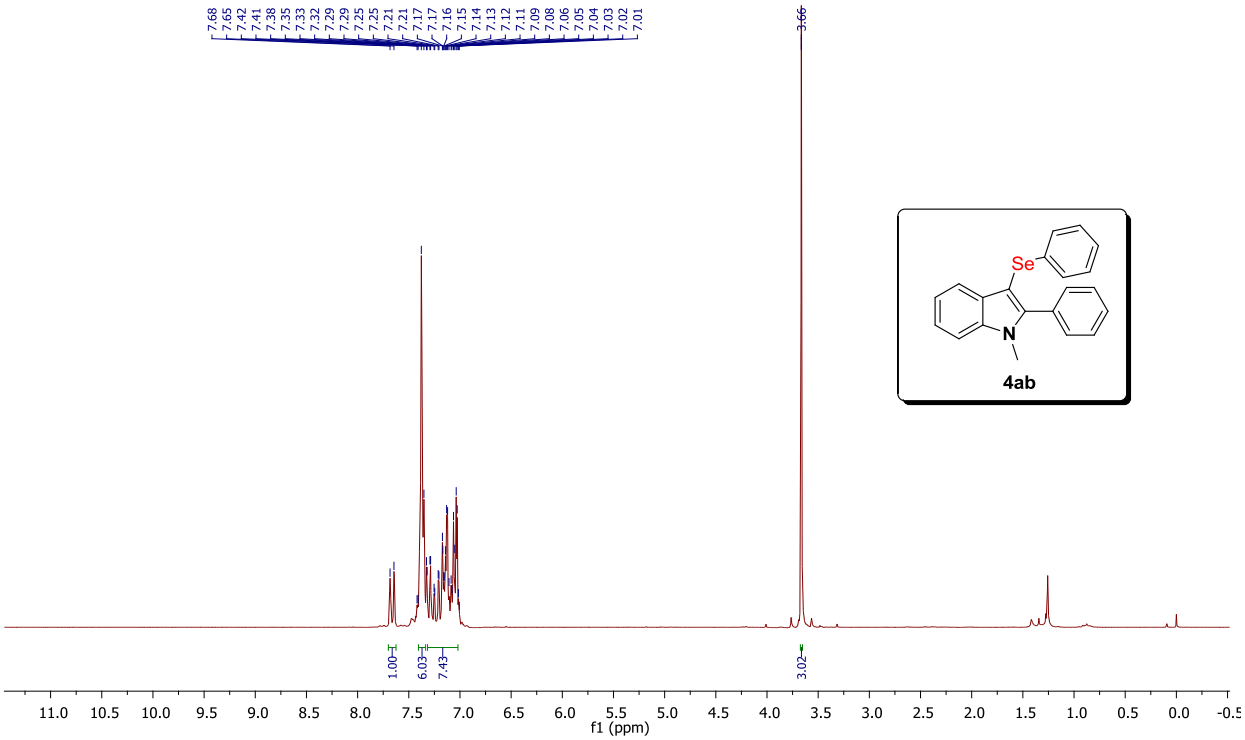
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **4z**



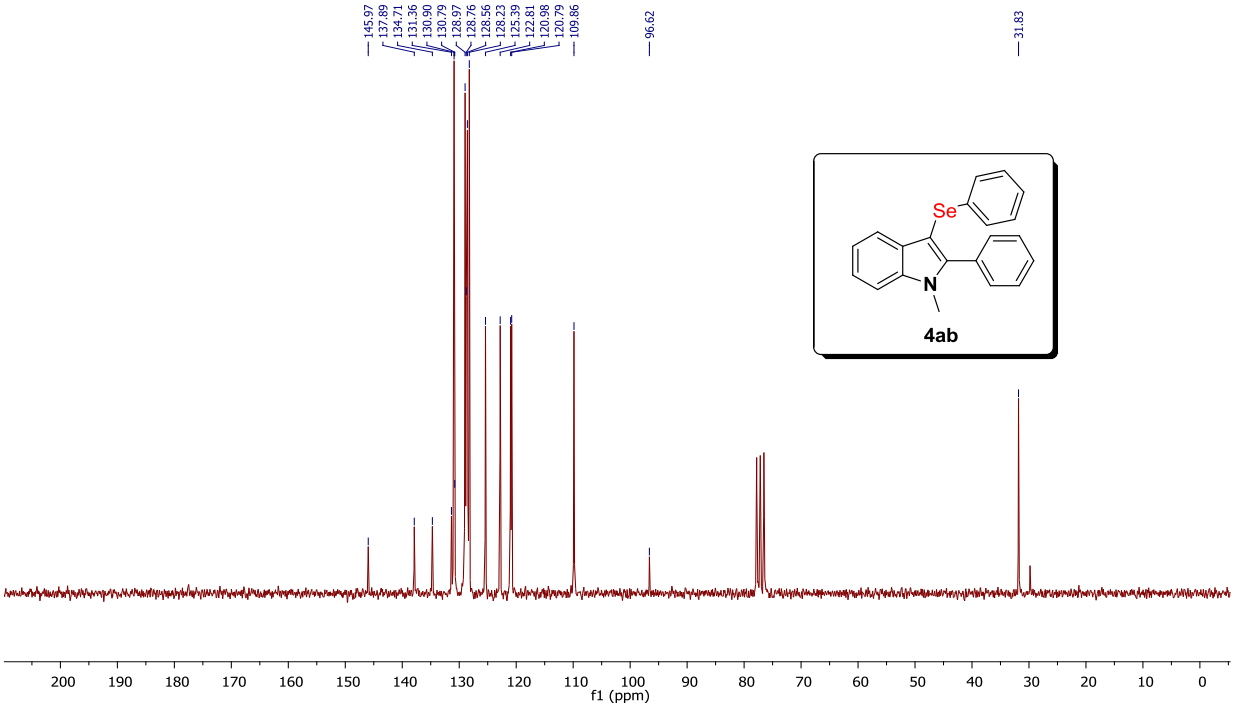
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **4aa**



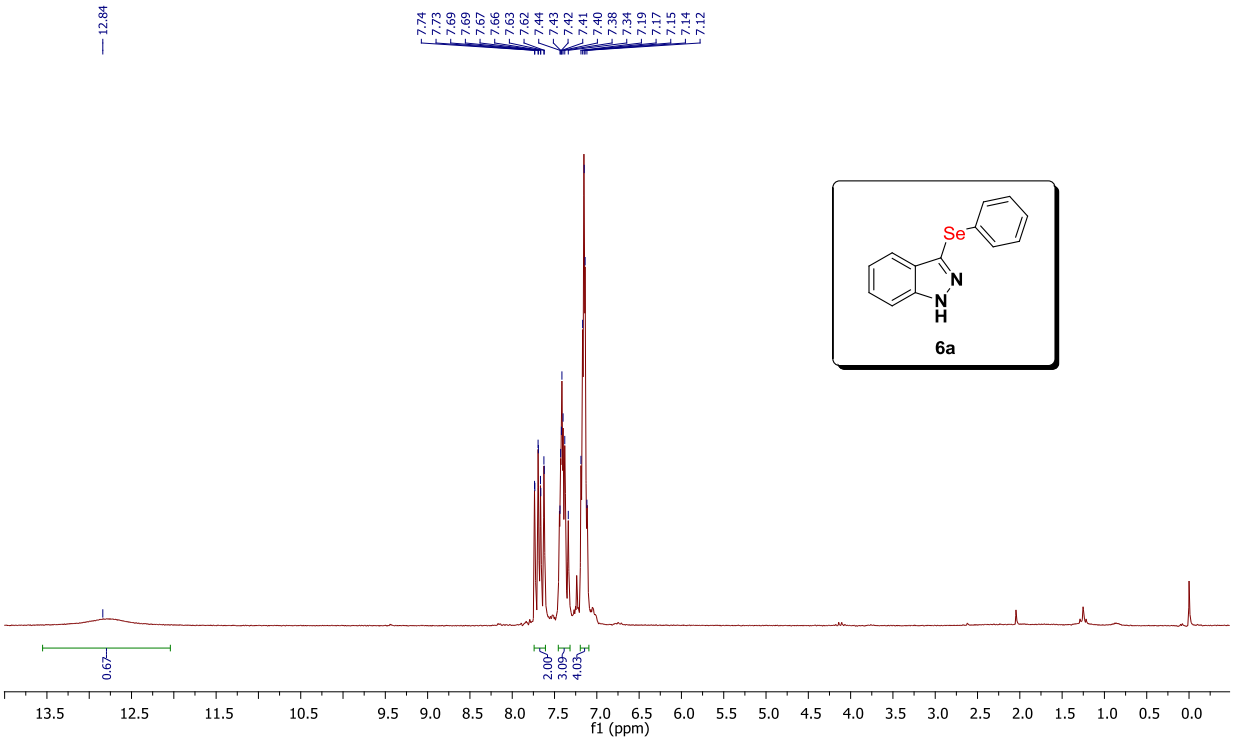
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **4aa**



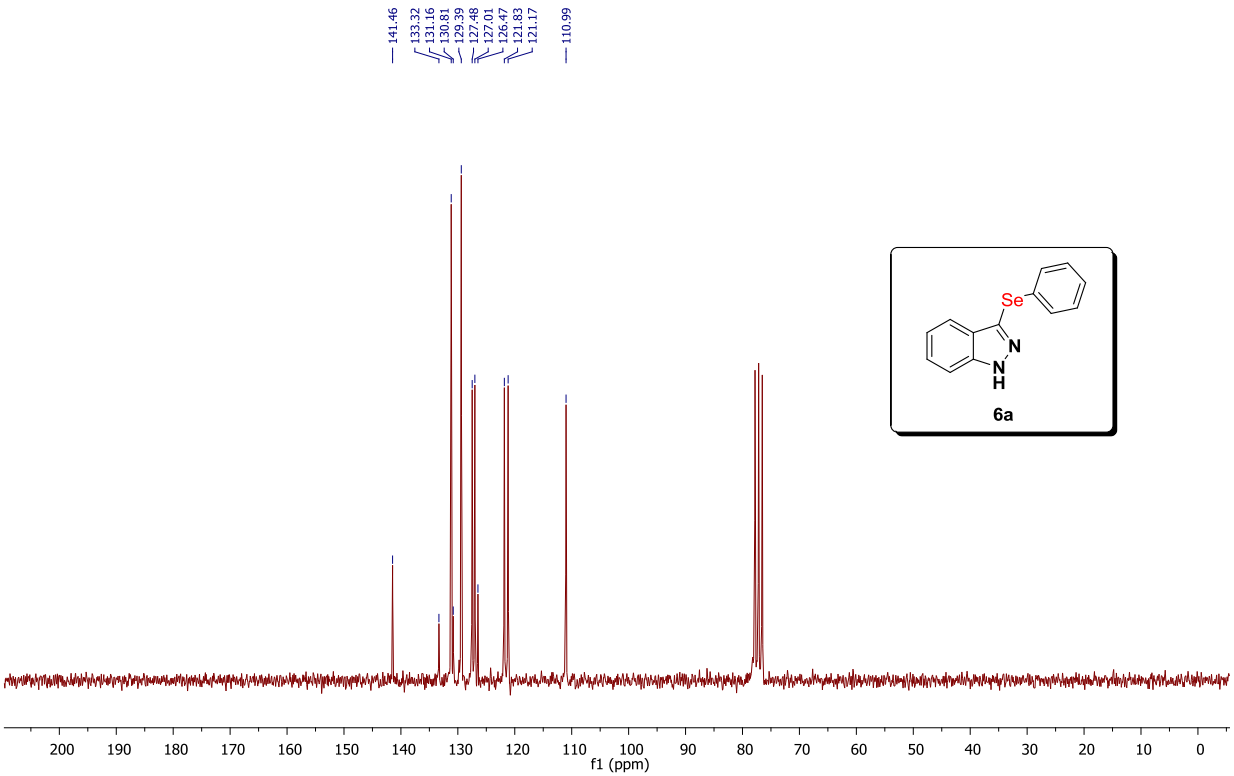
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **4ab**



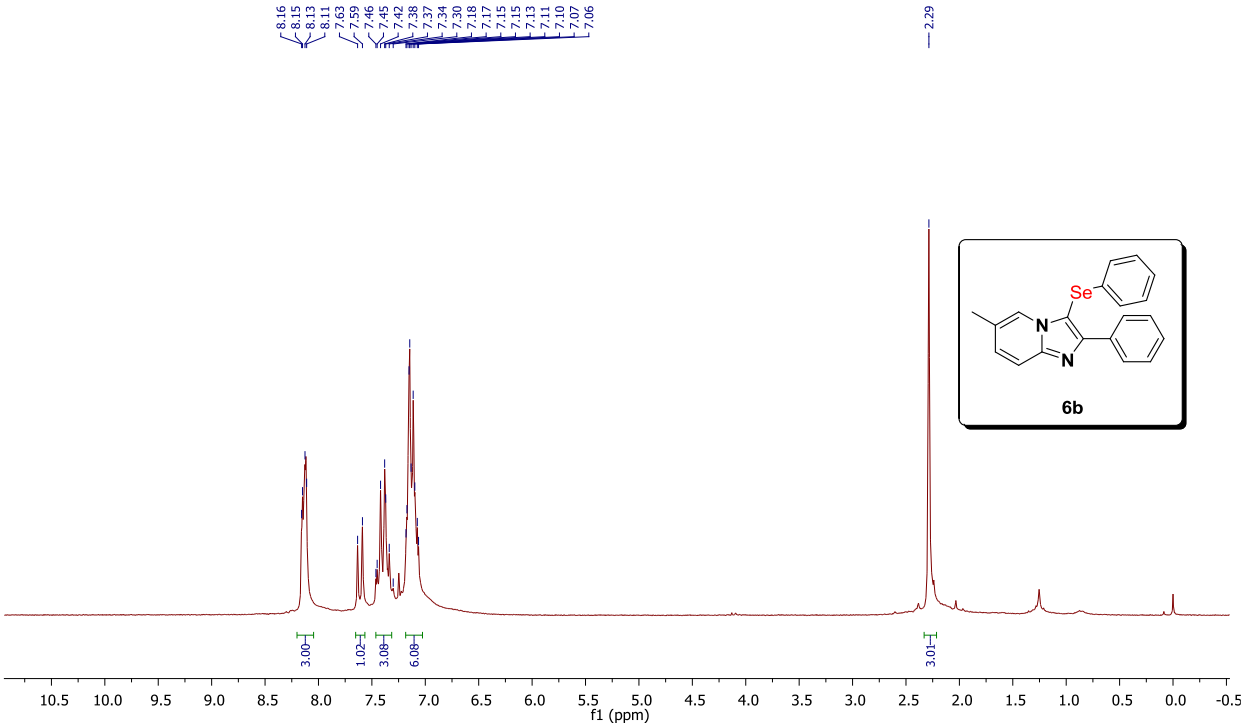
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **4ab**



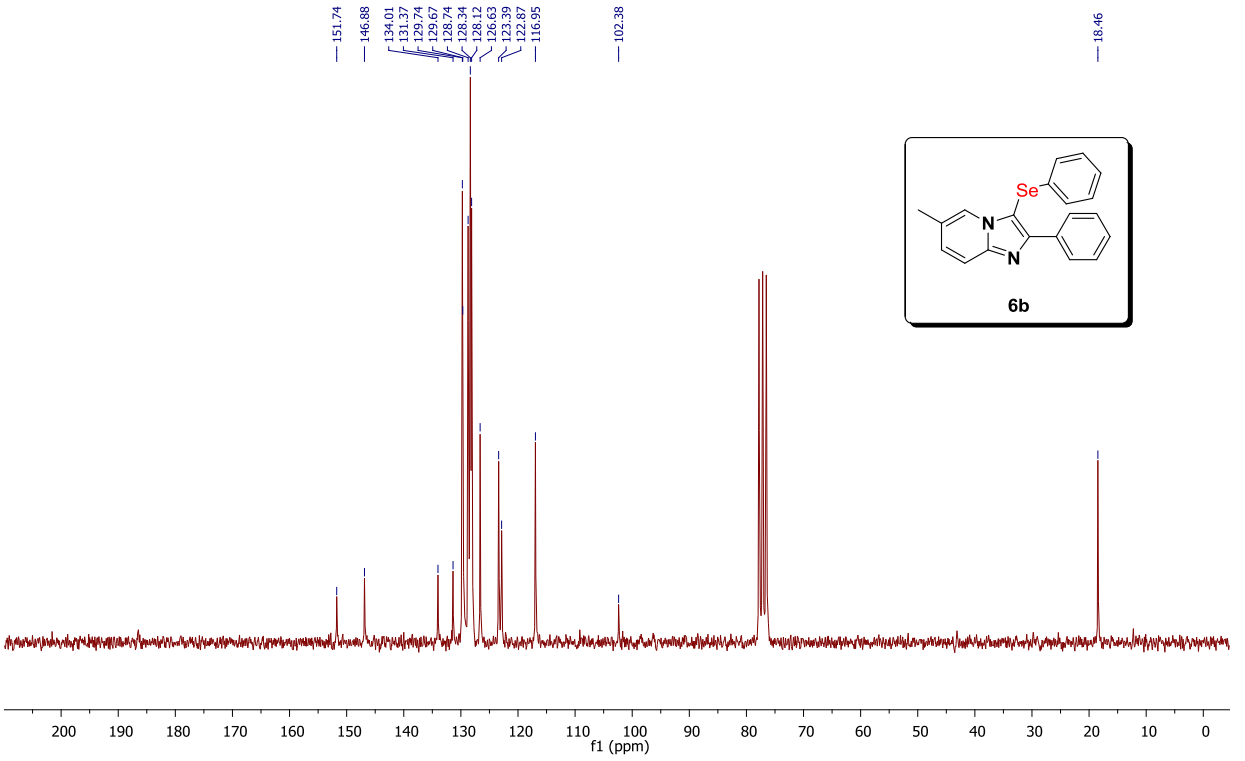
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **6a**



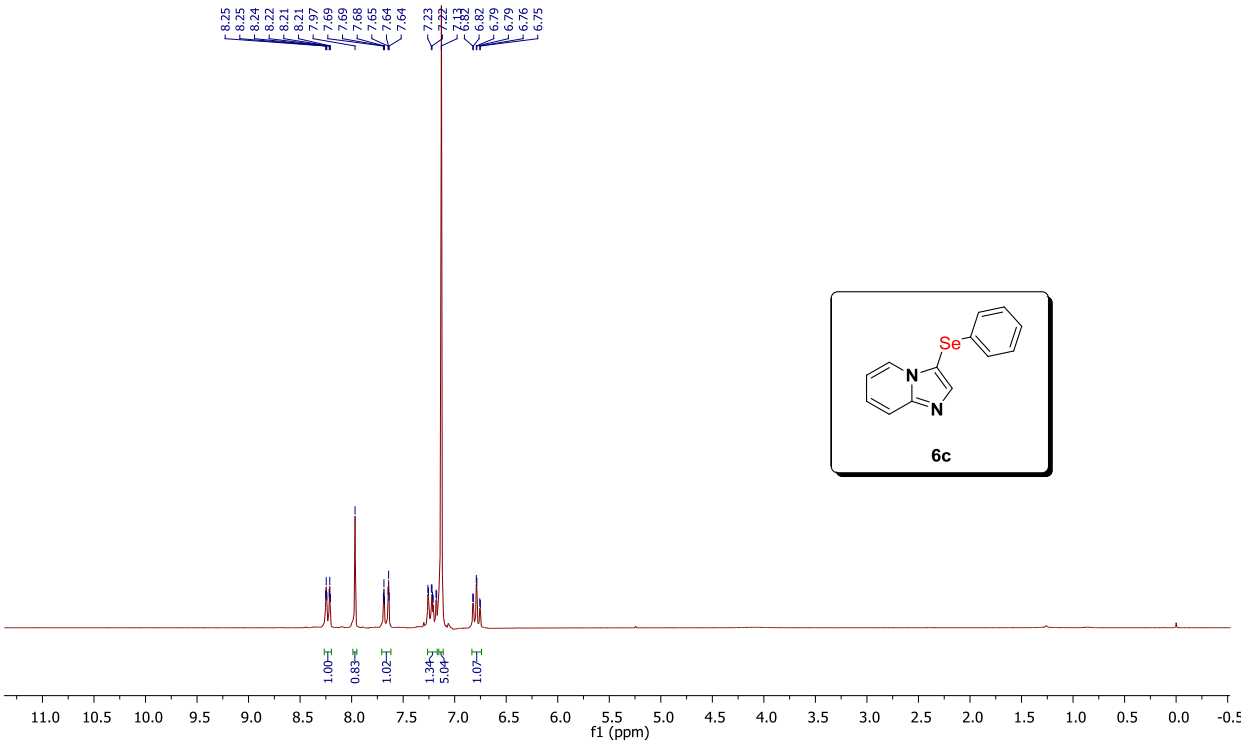
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **6a**



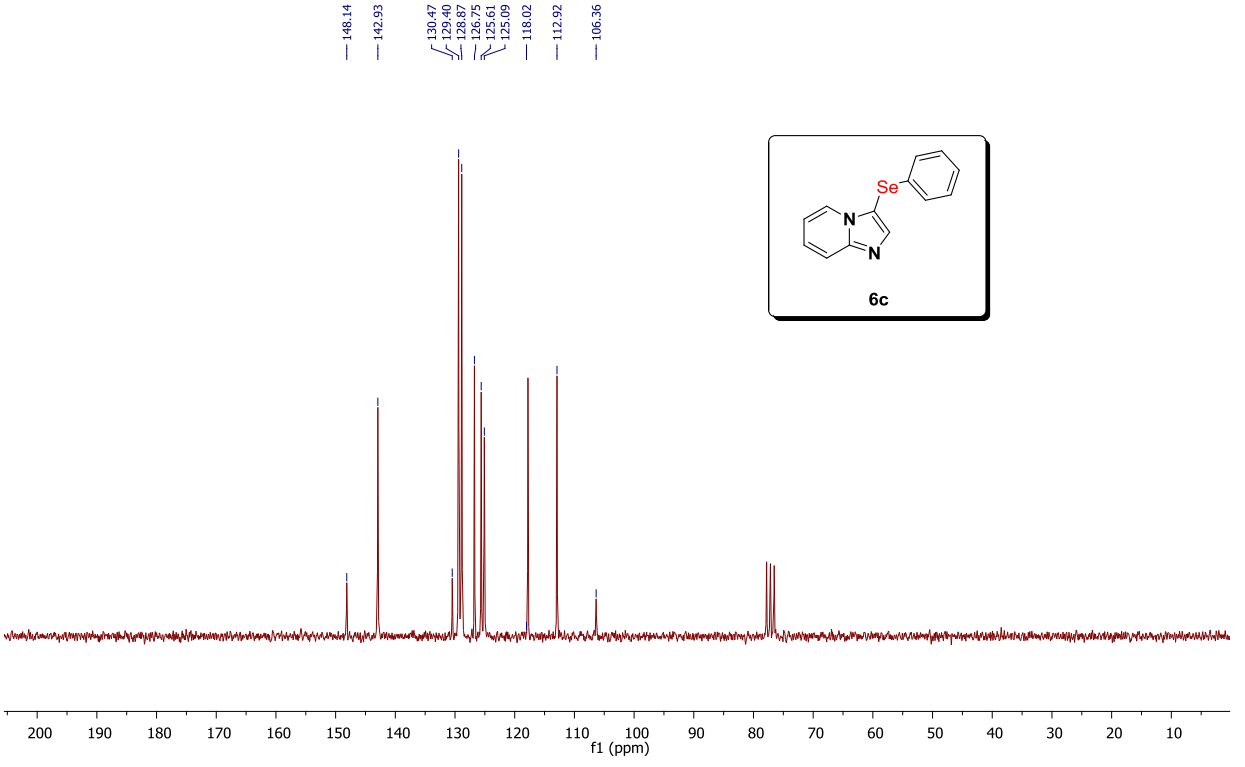
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **6b**



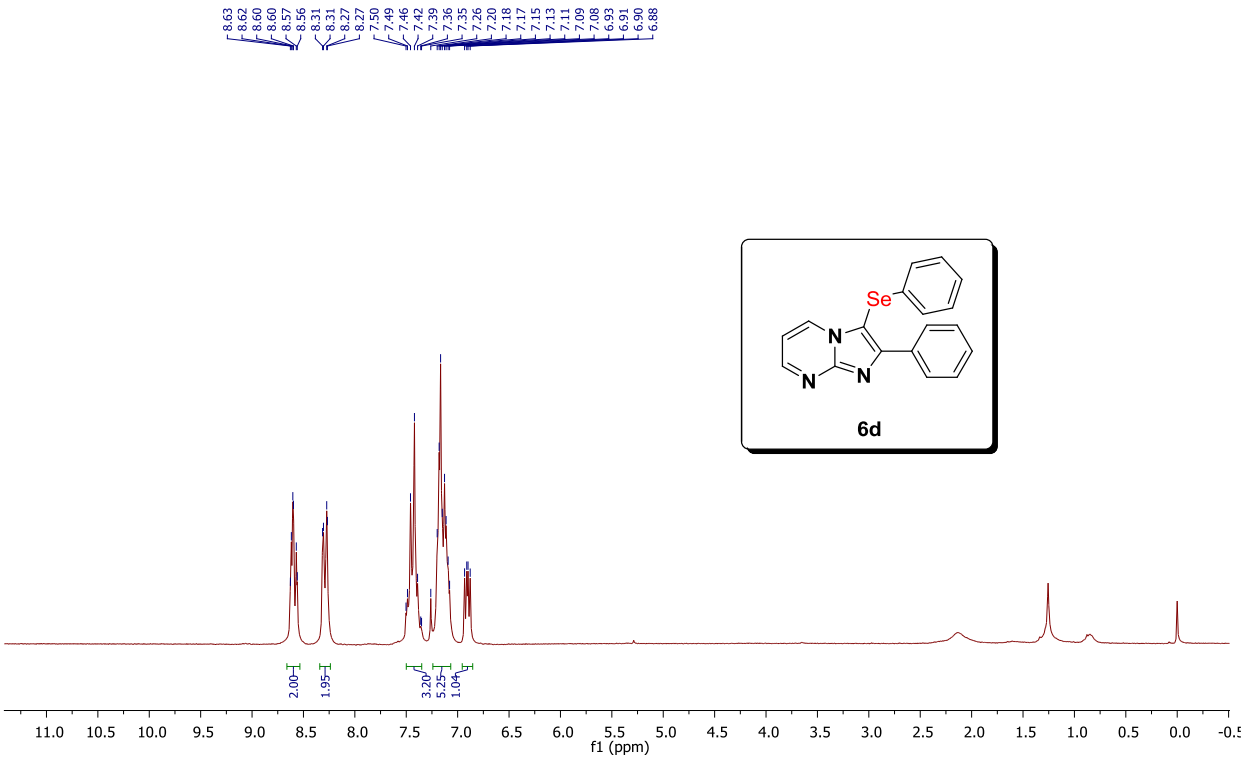
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **6b**



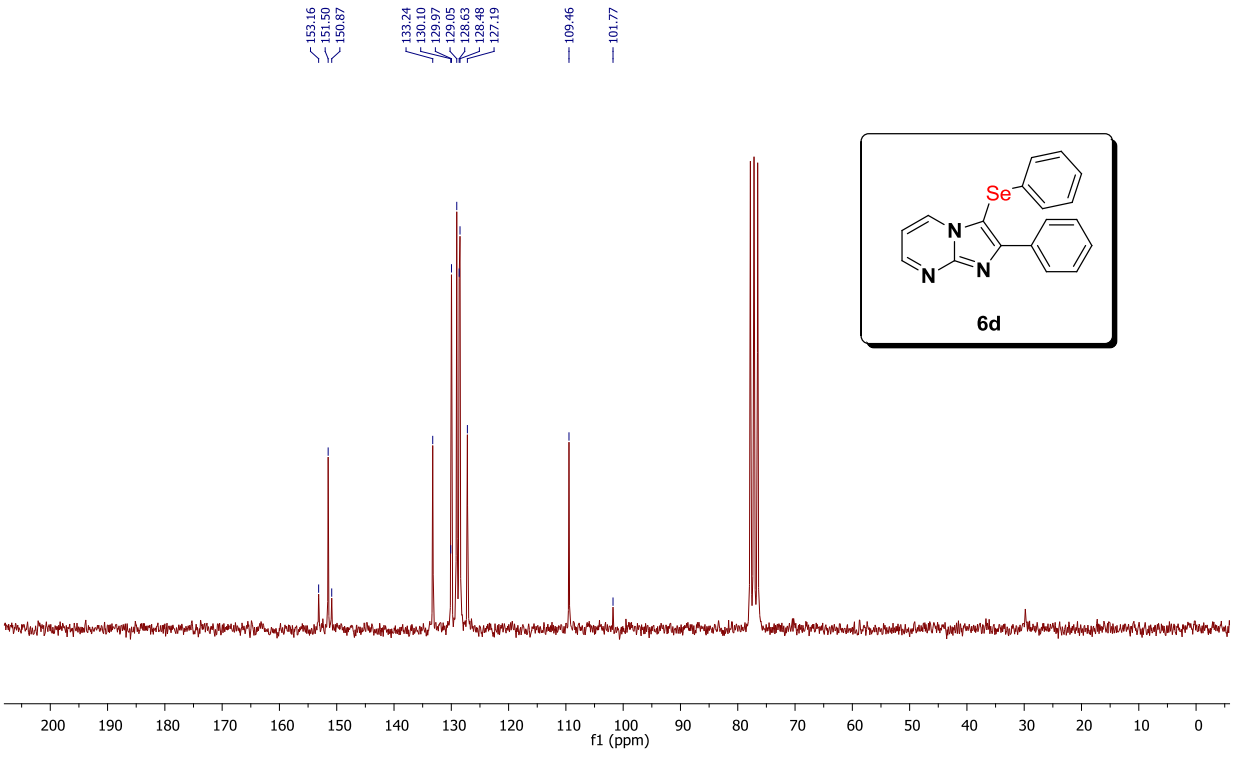
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **6c**



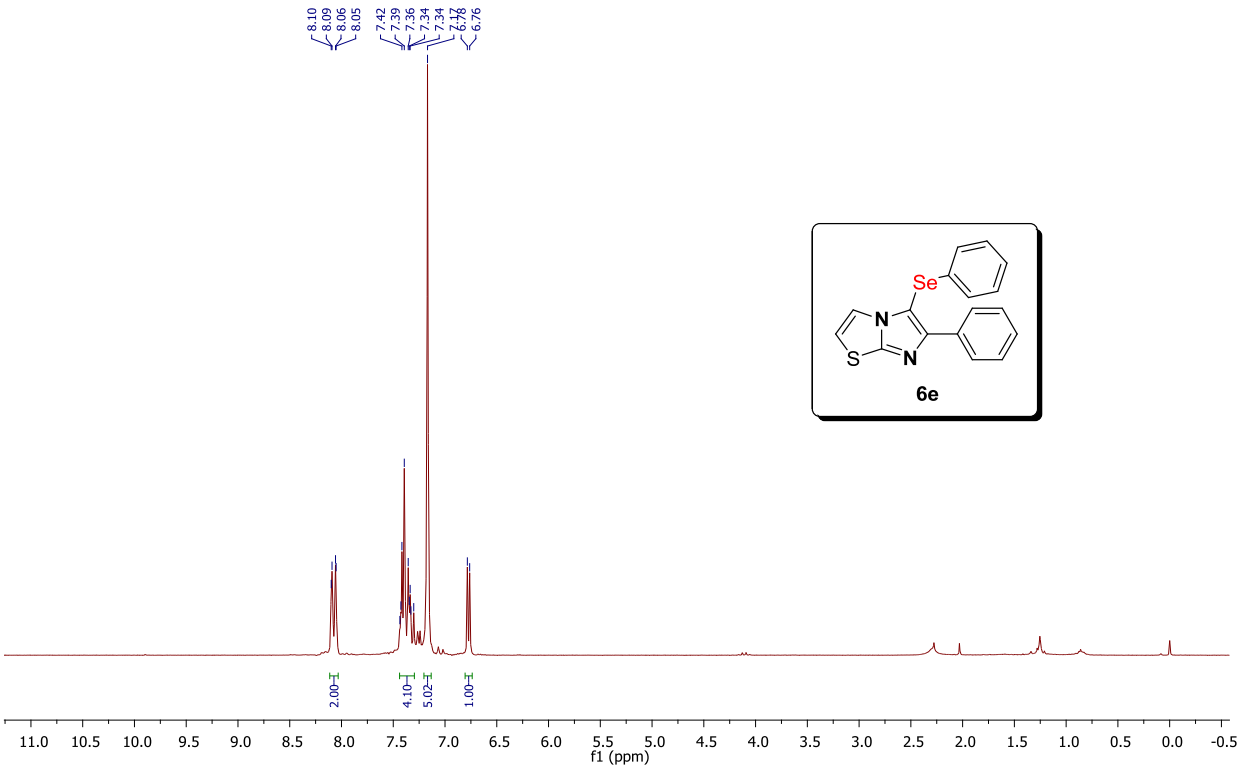
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **6c**



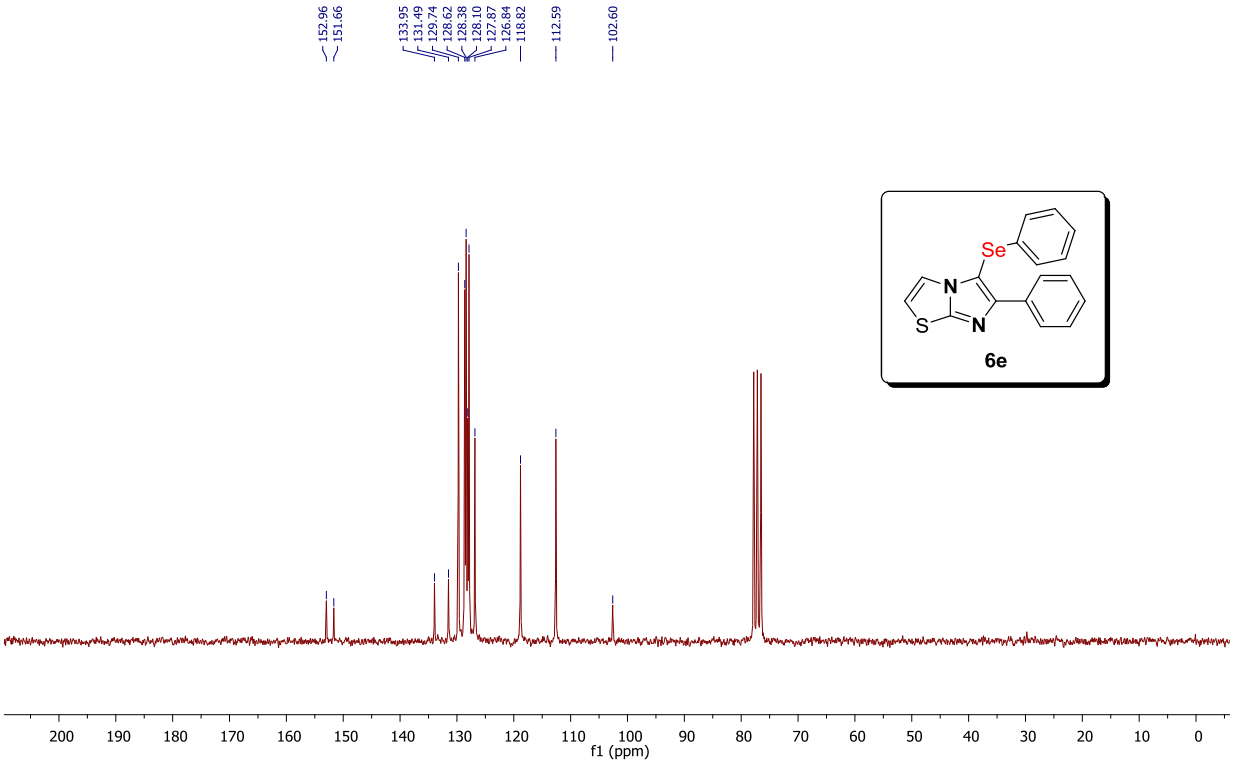
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **6d**



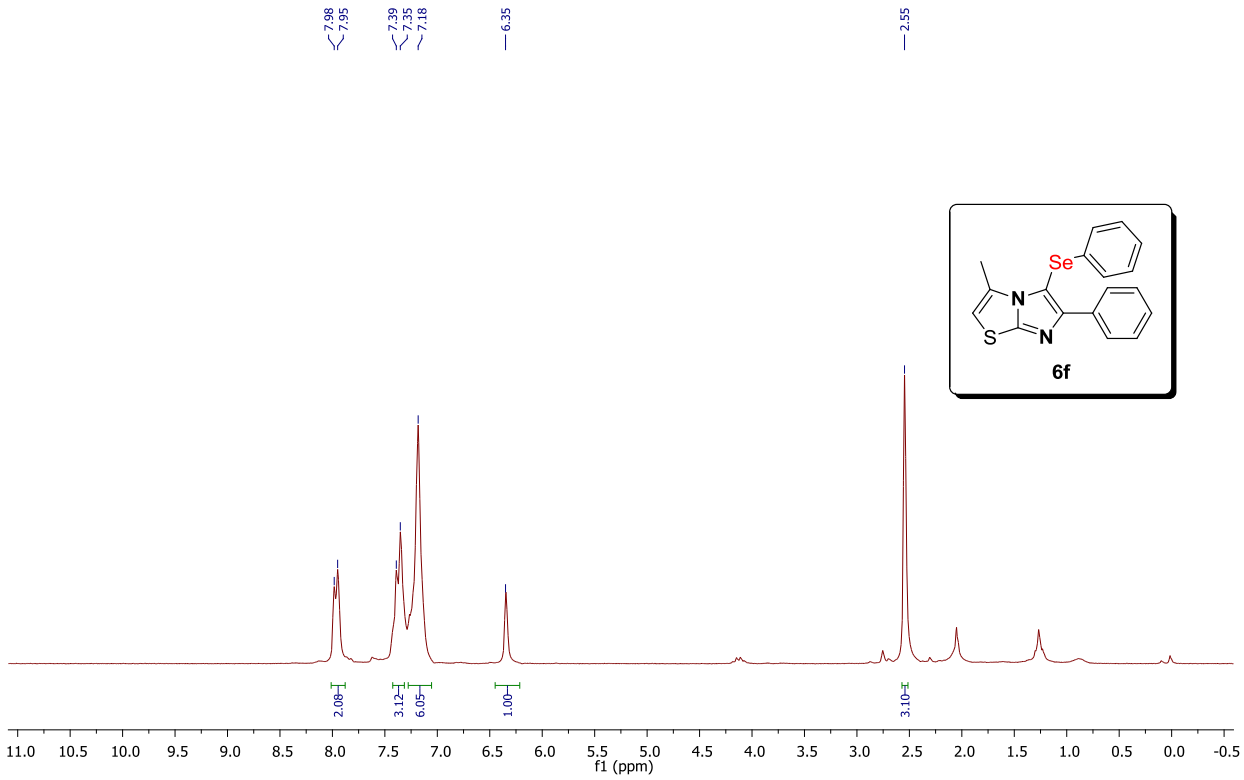
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **6d**



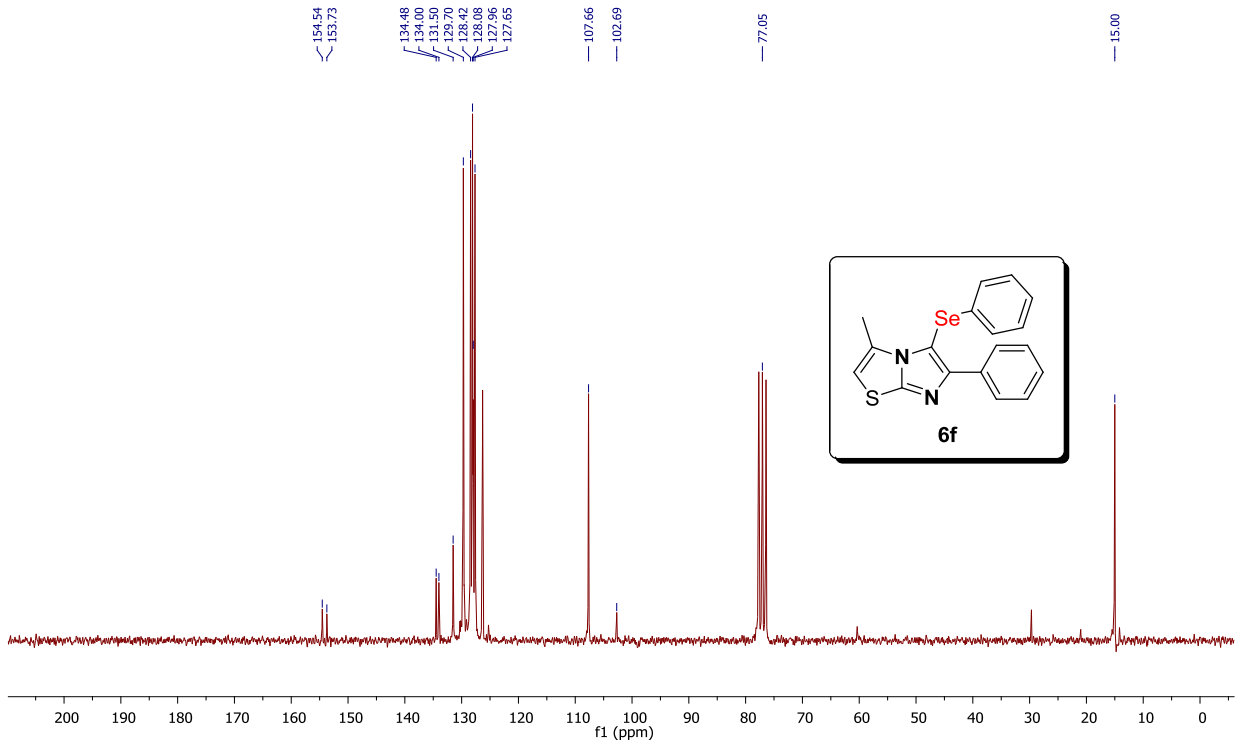
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **6e**



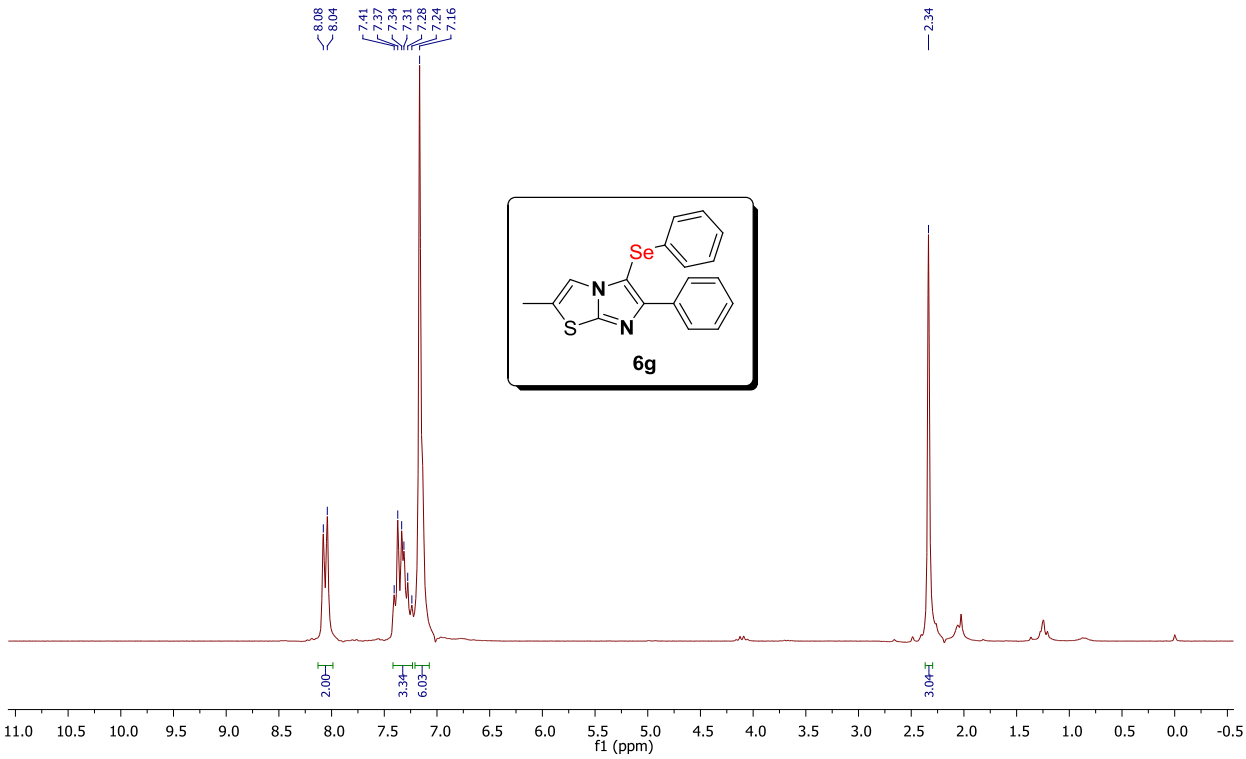
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **6e**



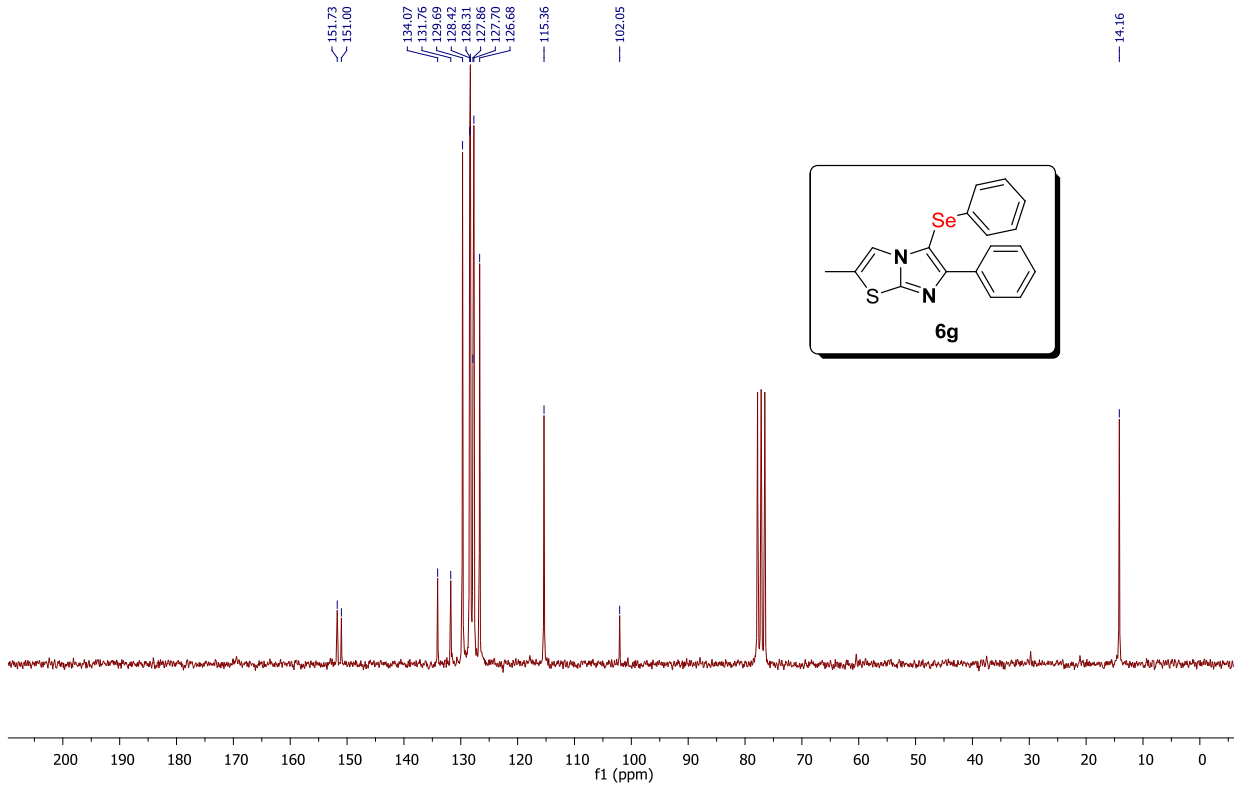
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **6f**



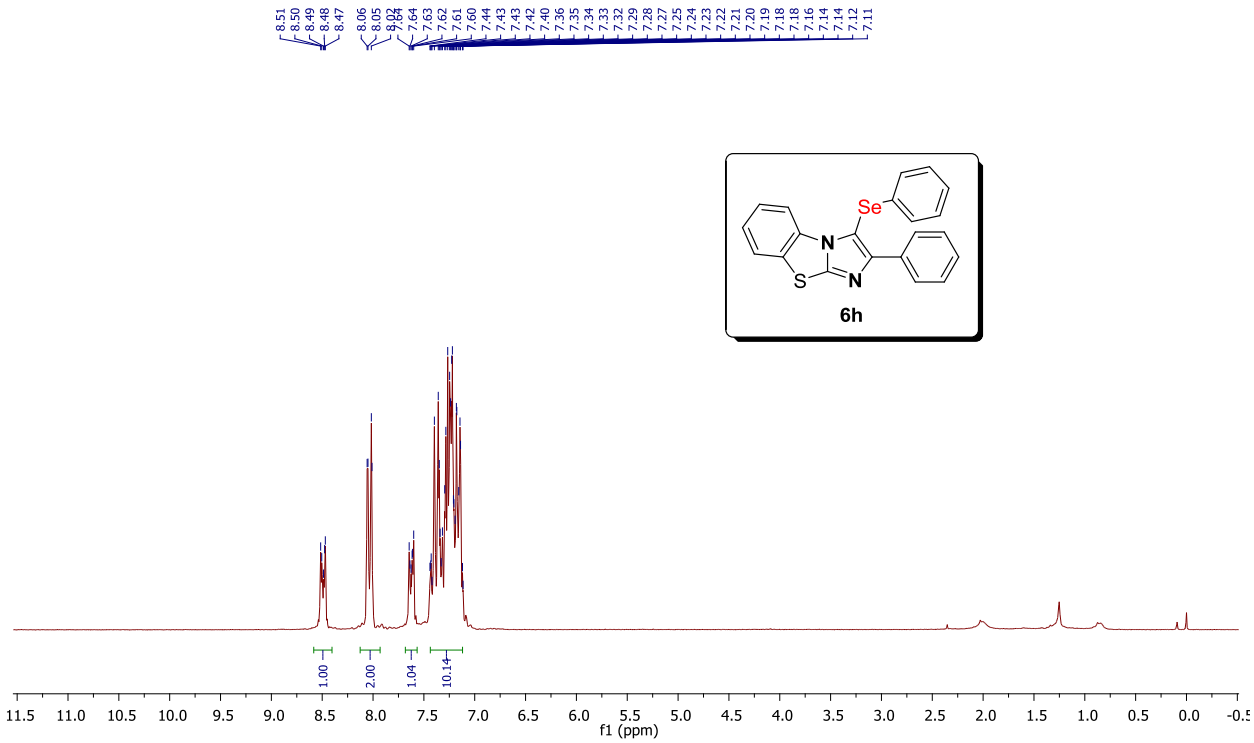
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **6f**



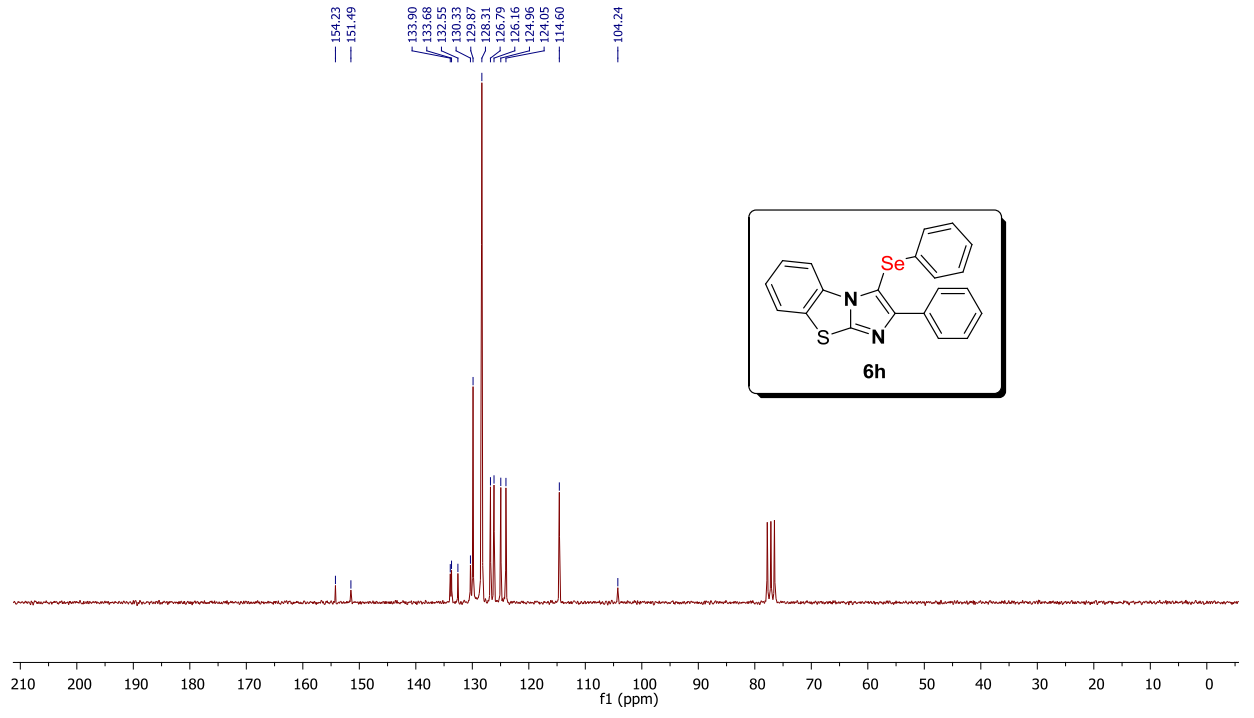
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **6g**



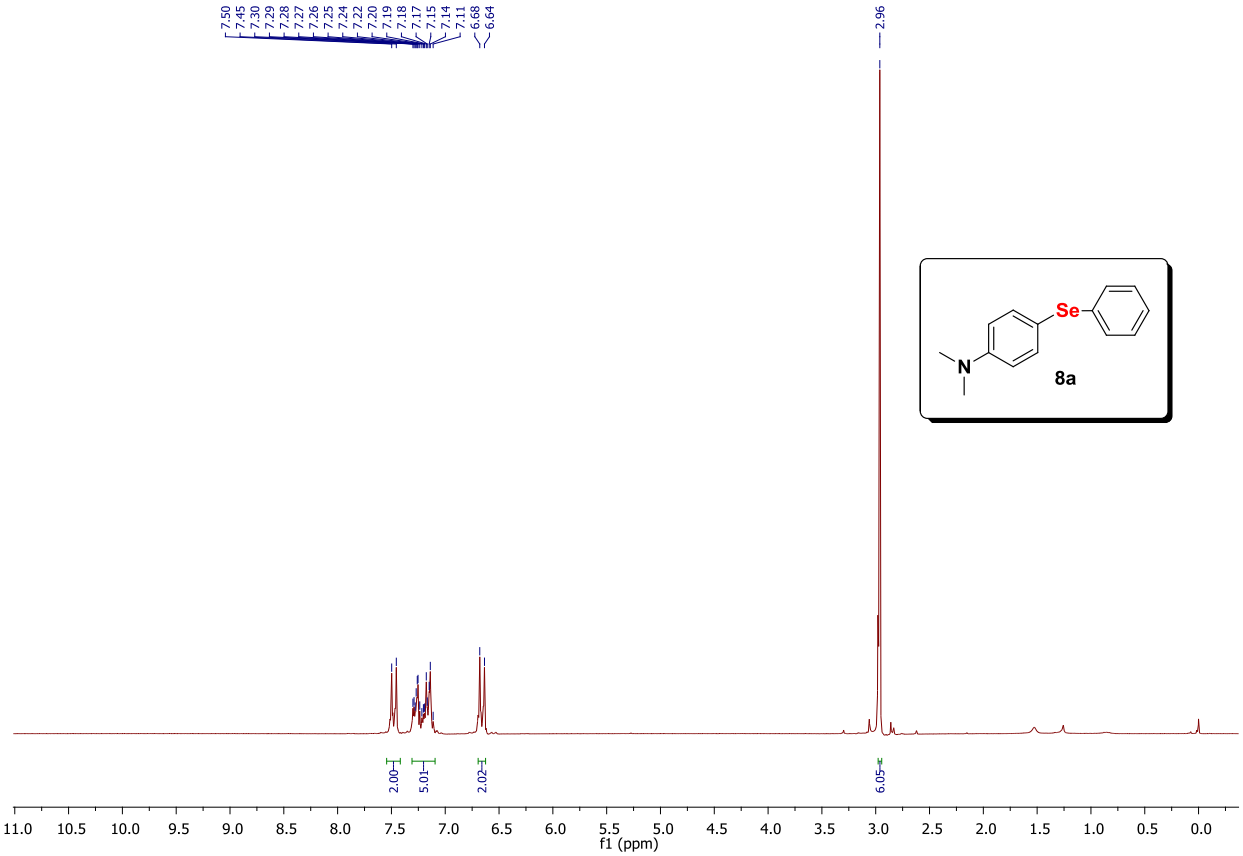
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **6g**



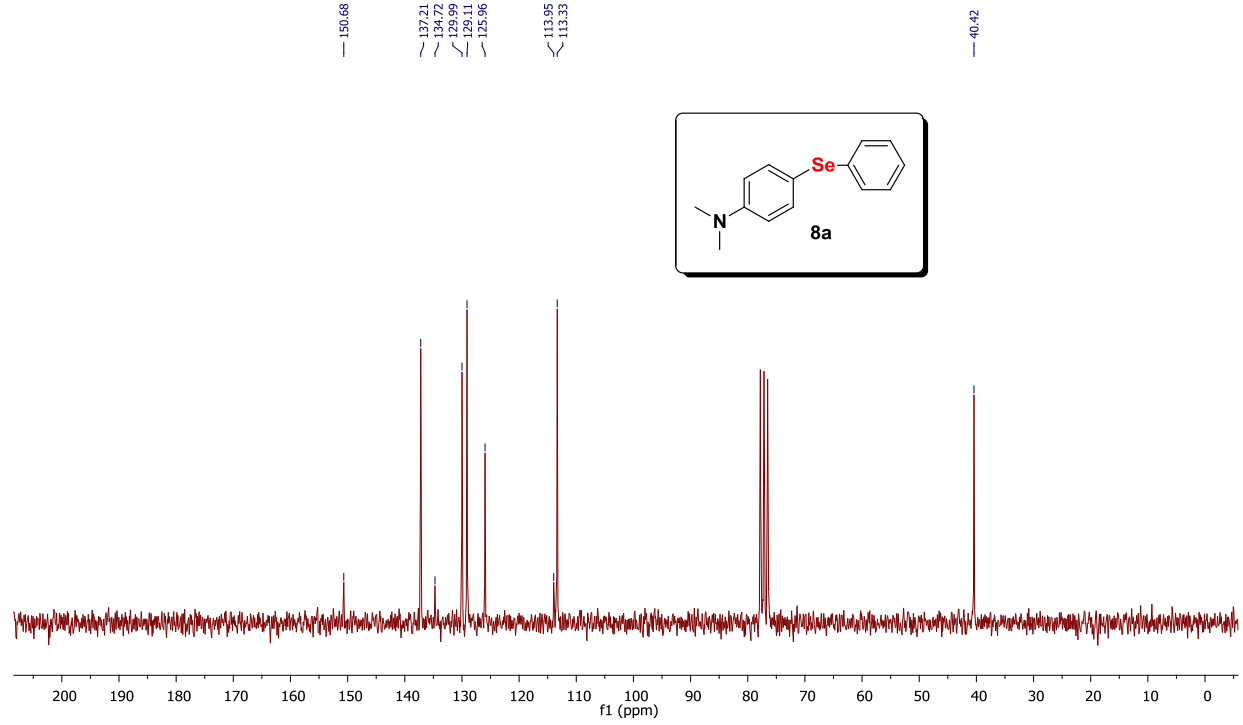
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **6h**



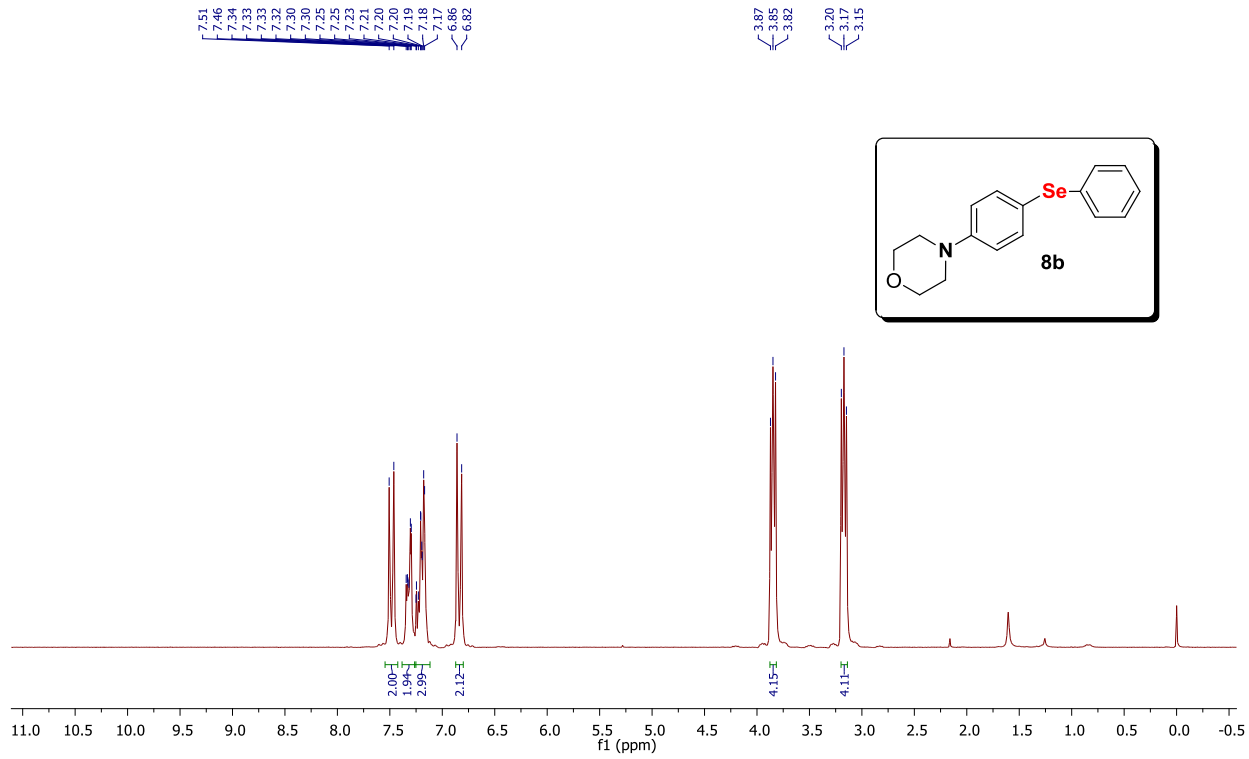
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **6h**



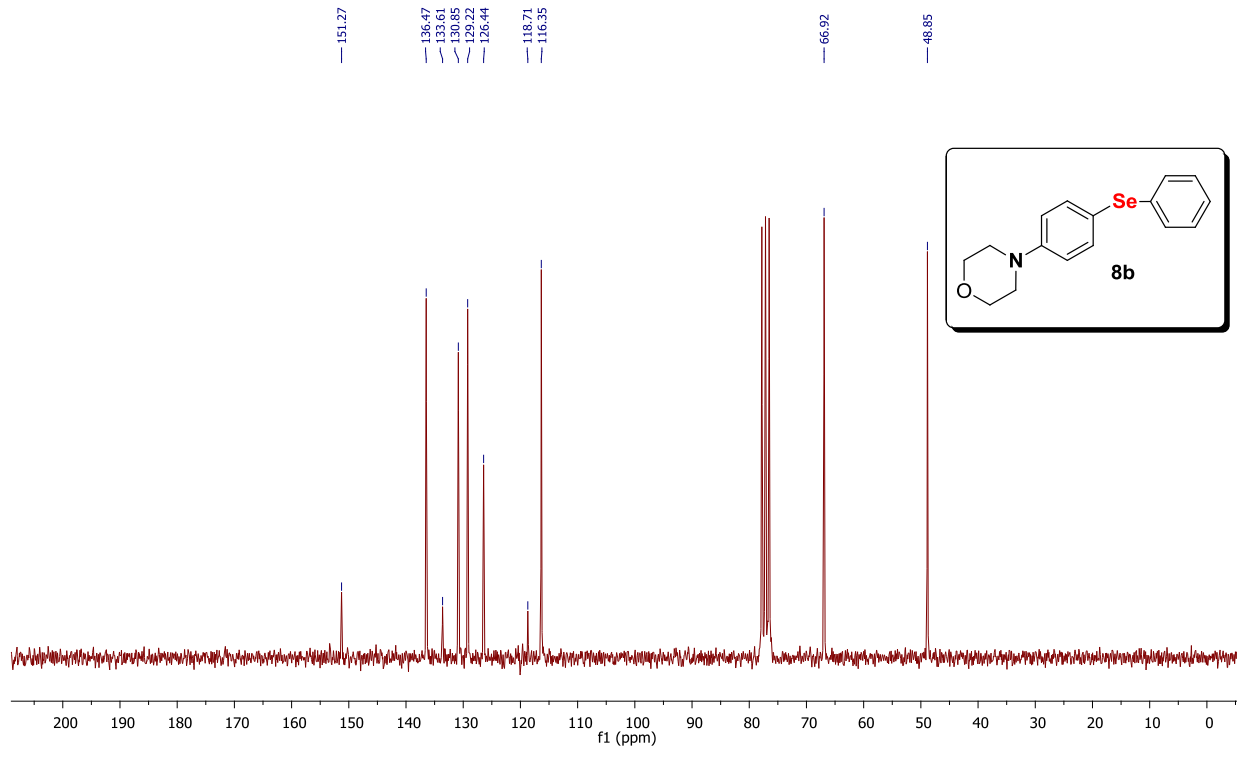
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **8a**



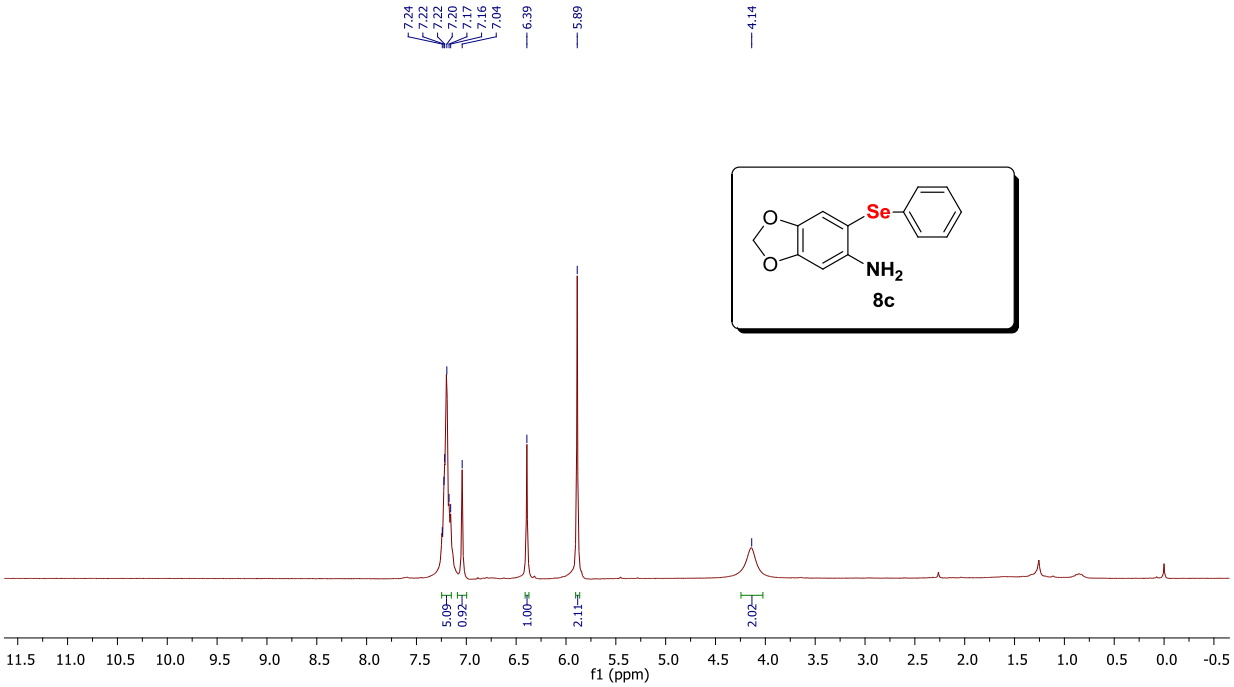
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **8a**



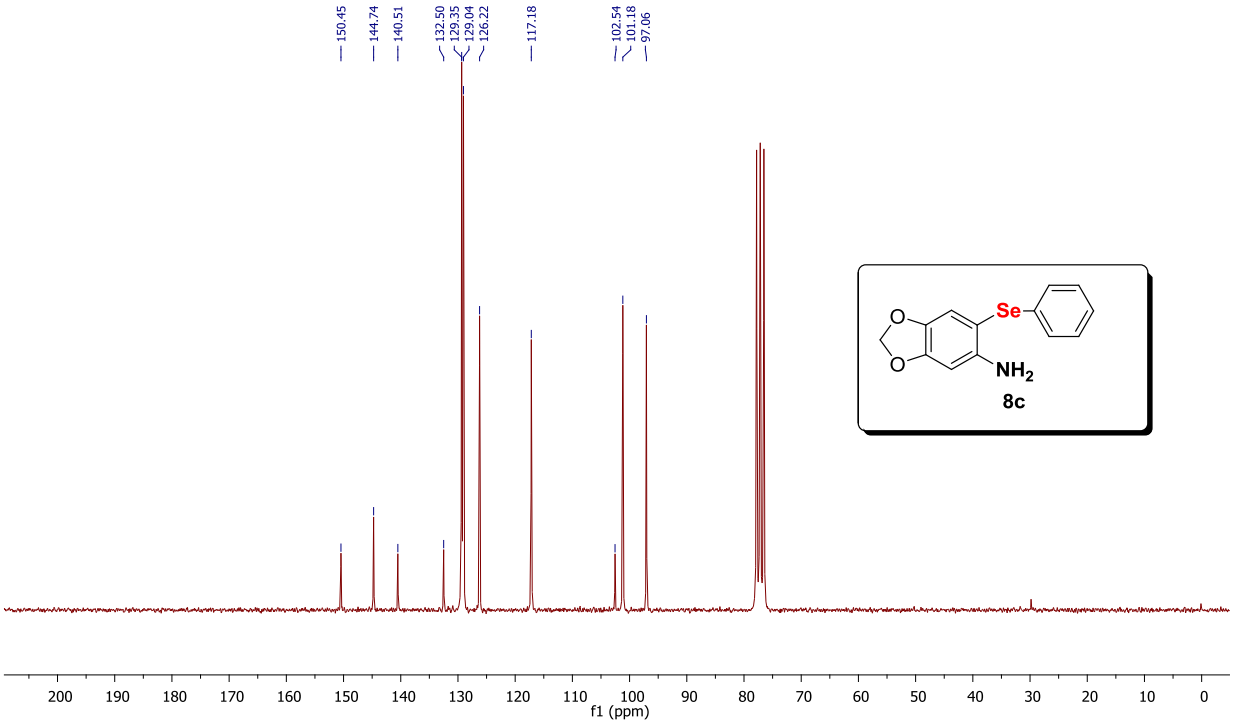
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **8b**



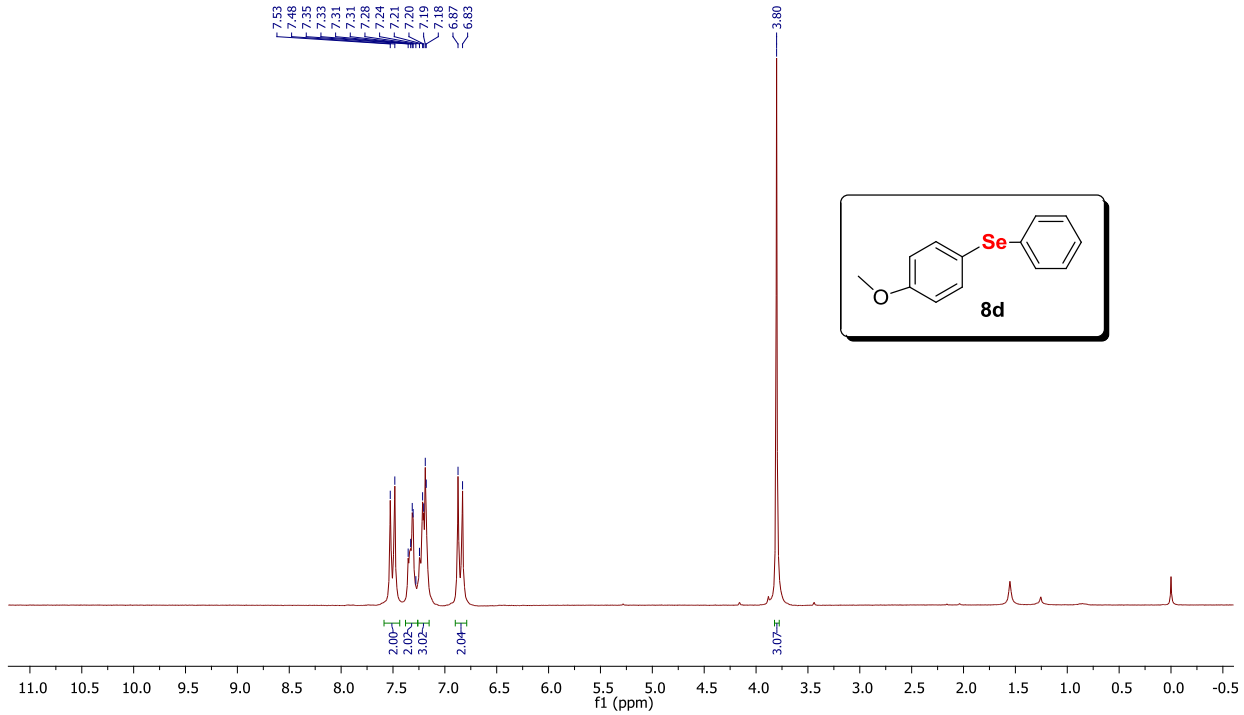
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **8b**



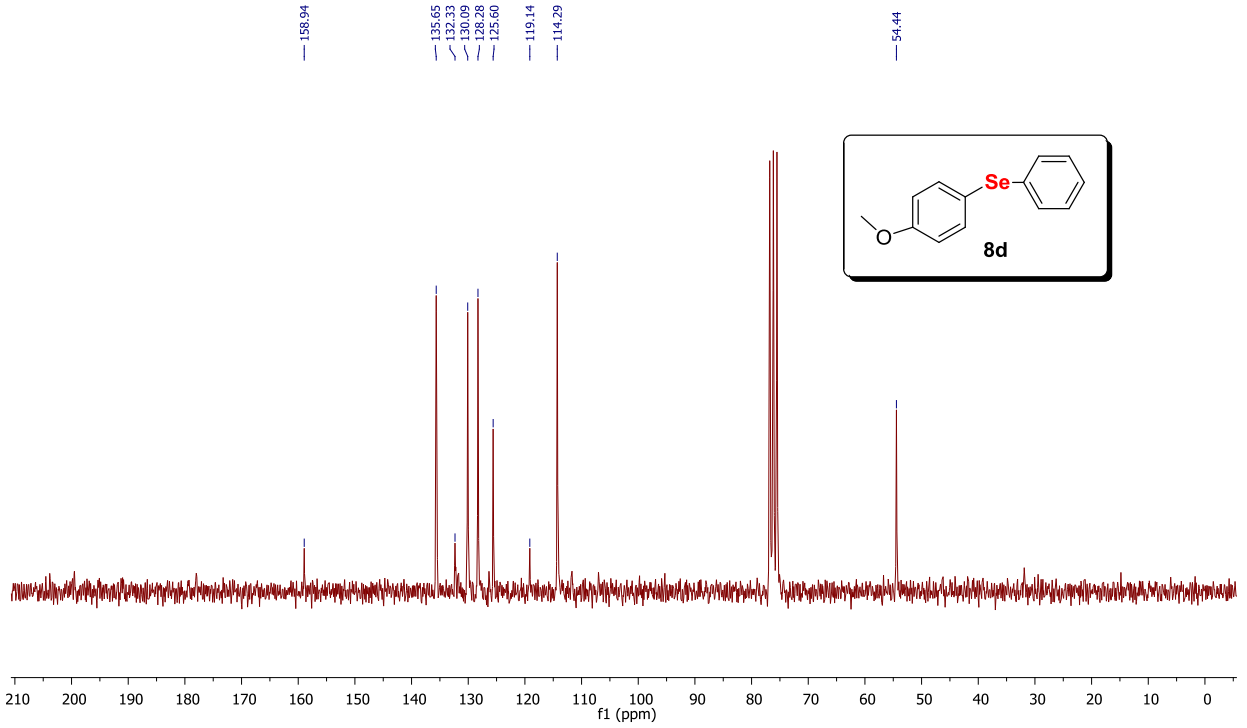
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **8c**



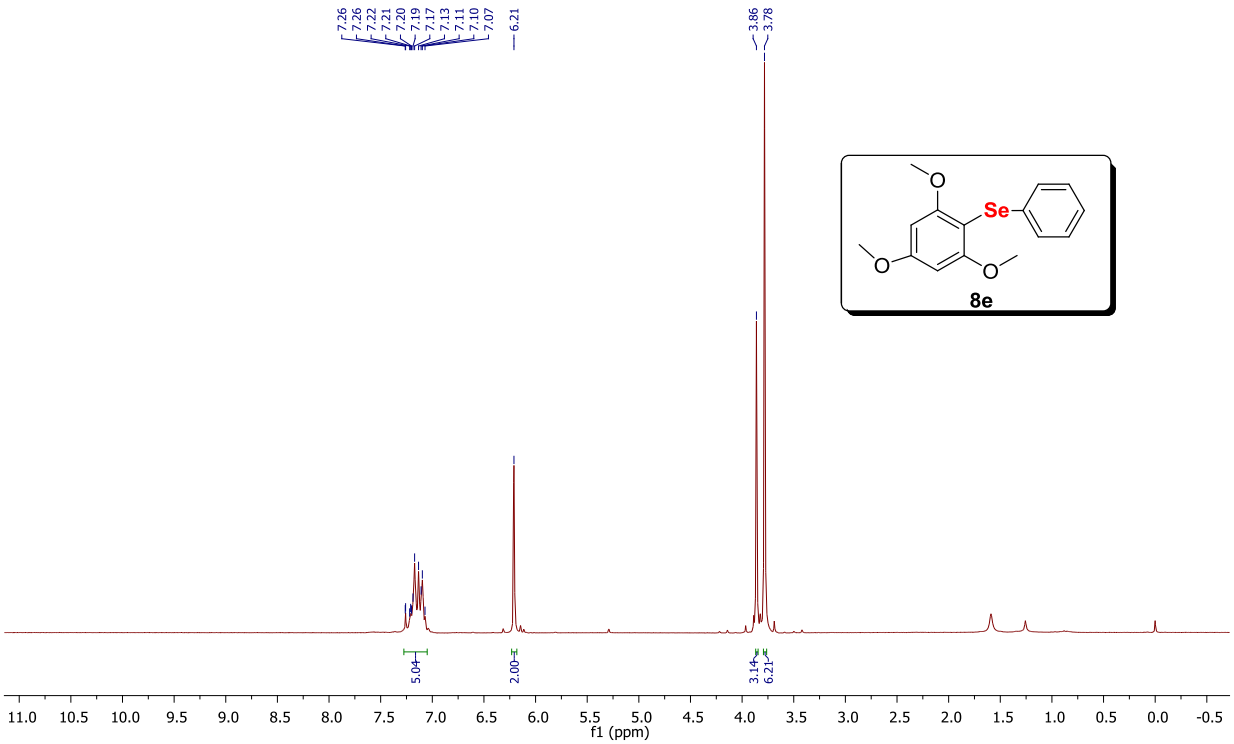
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **8c**



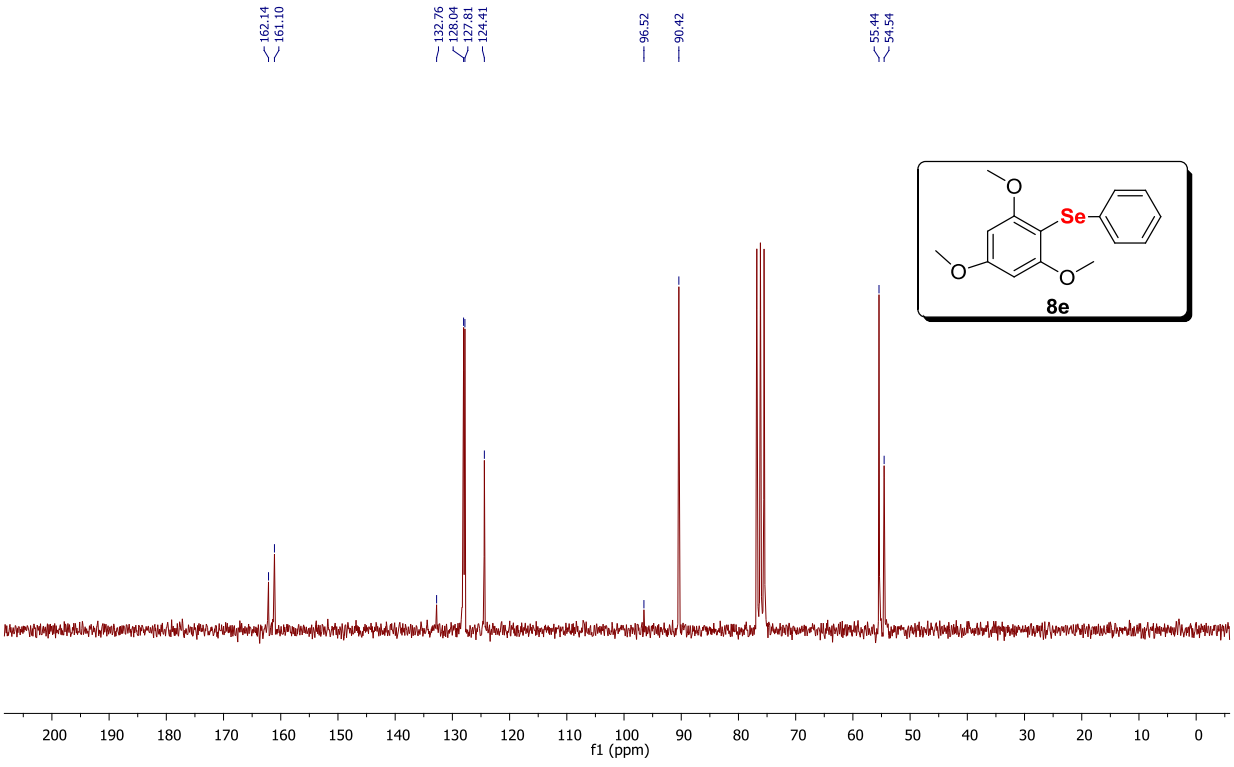
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **8d**



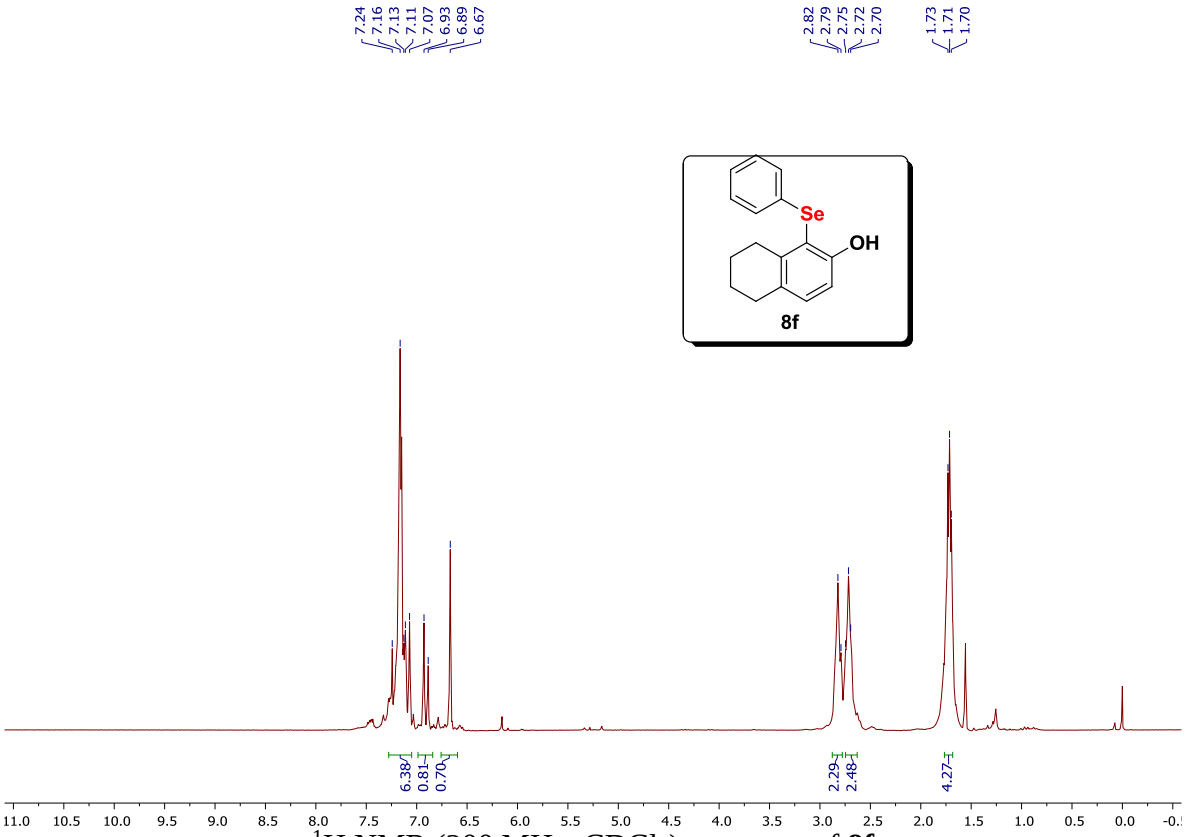
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **8d**



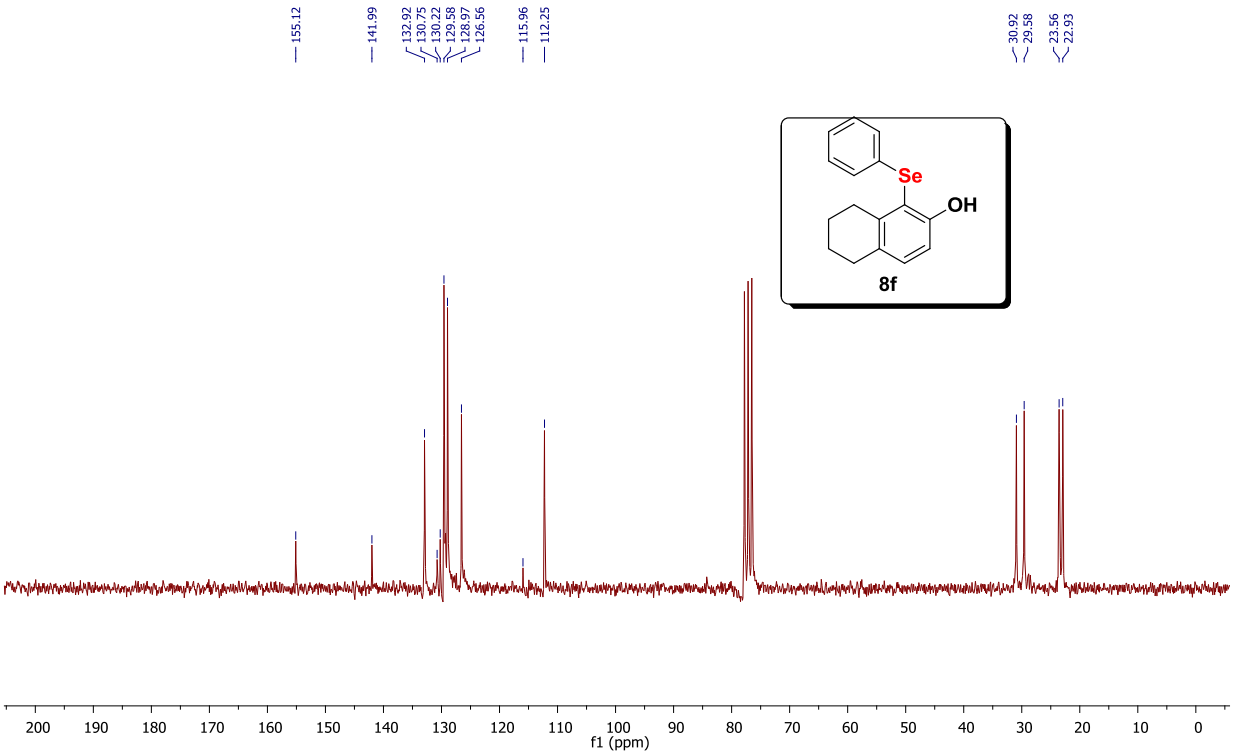
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **8e**



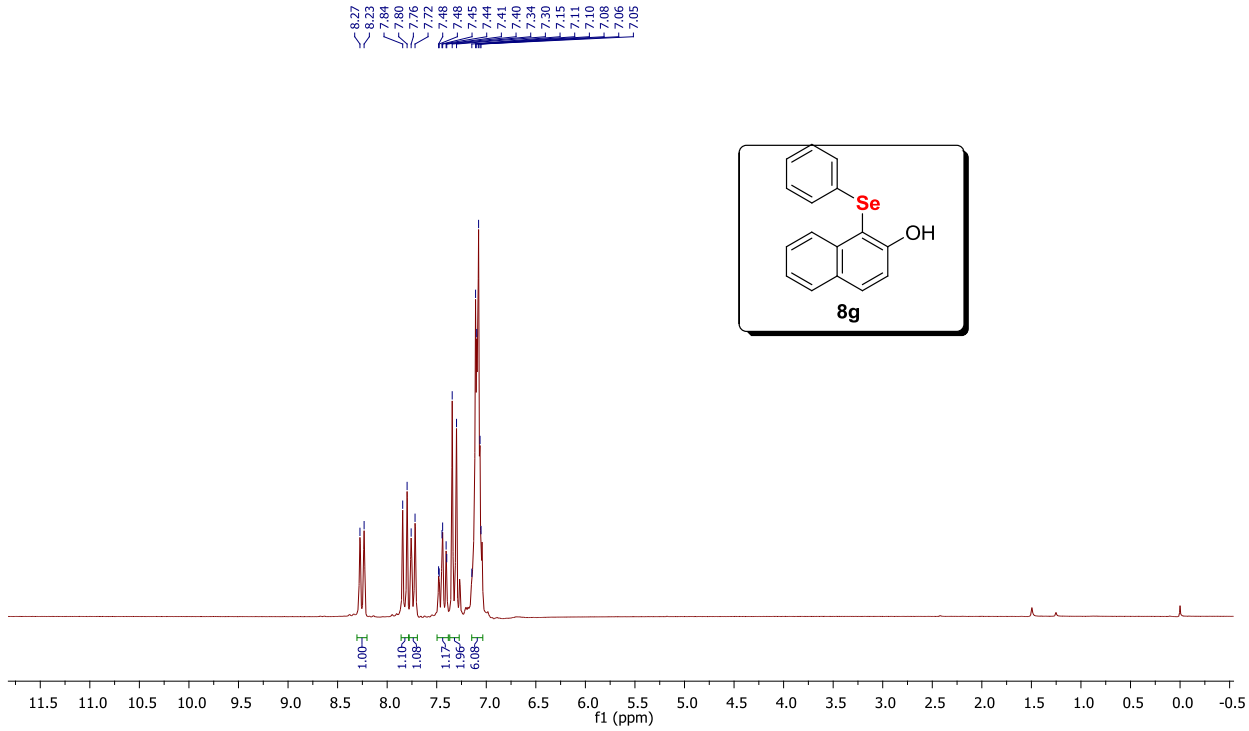
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **8e**



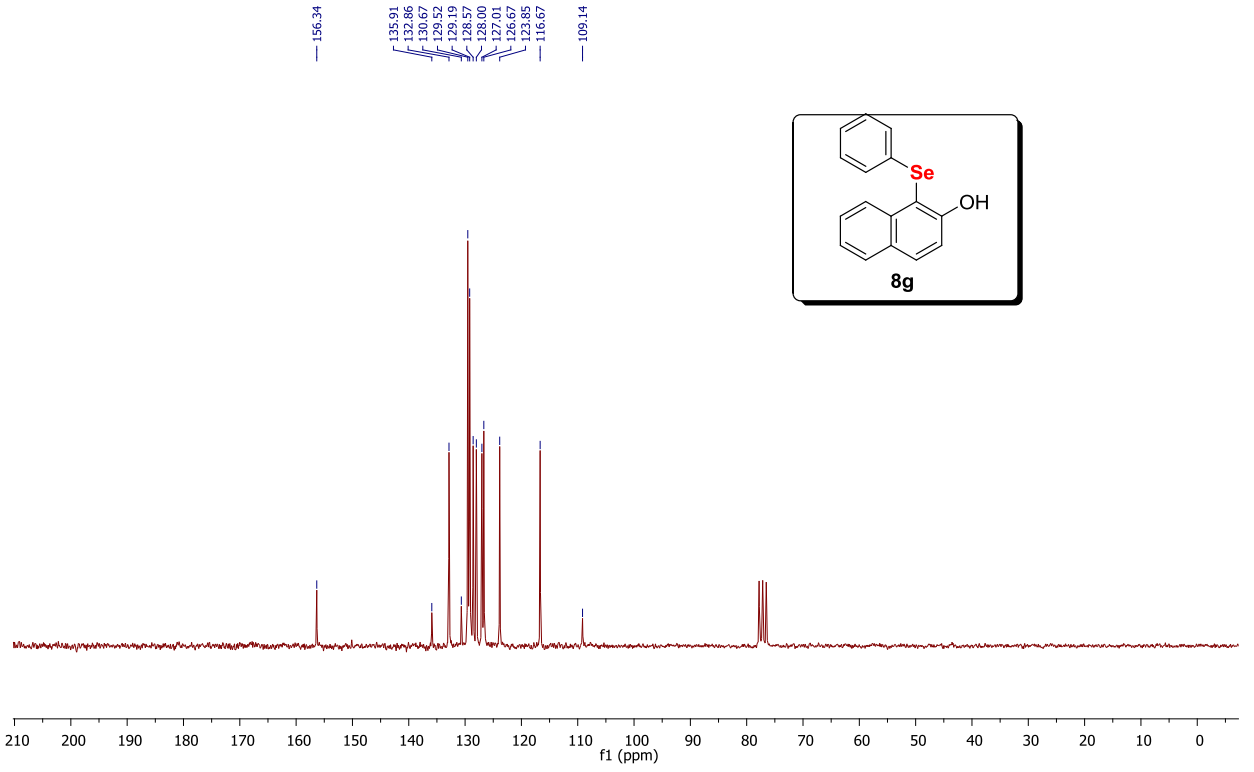
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **8f**



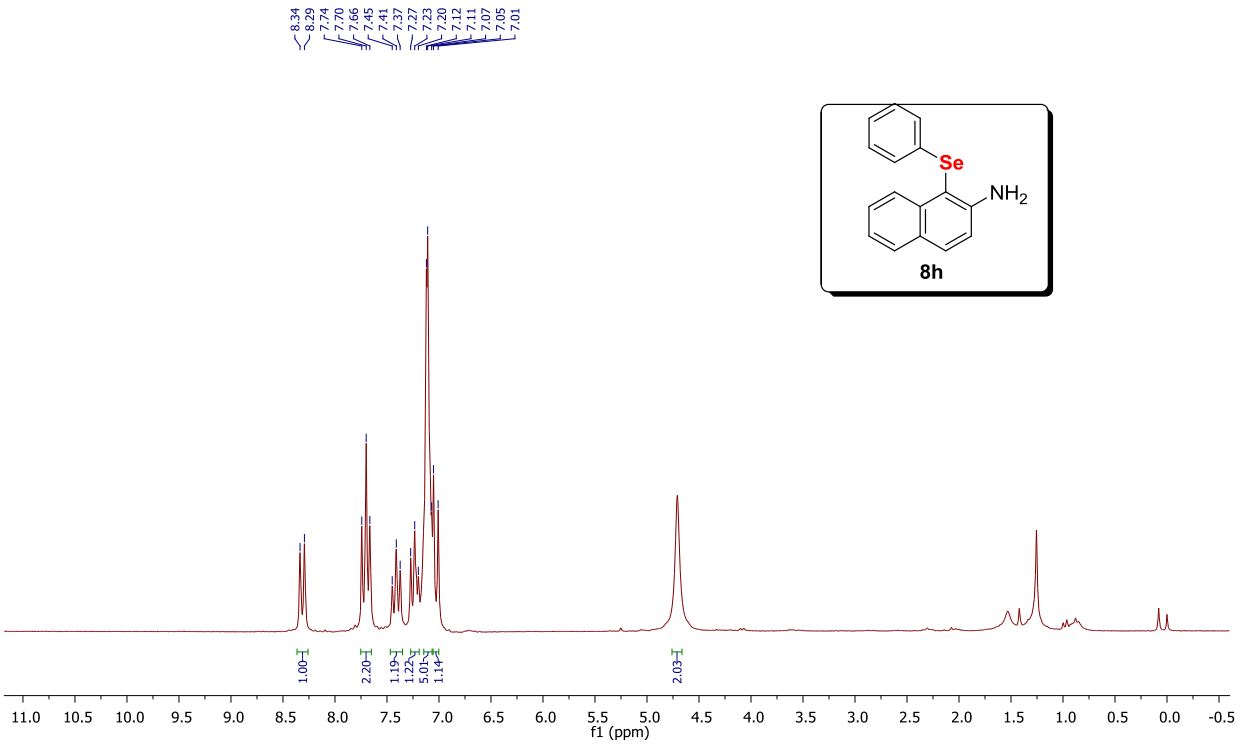
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **8f**



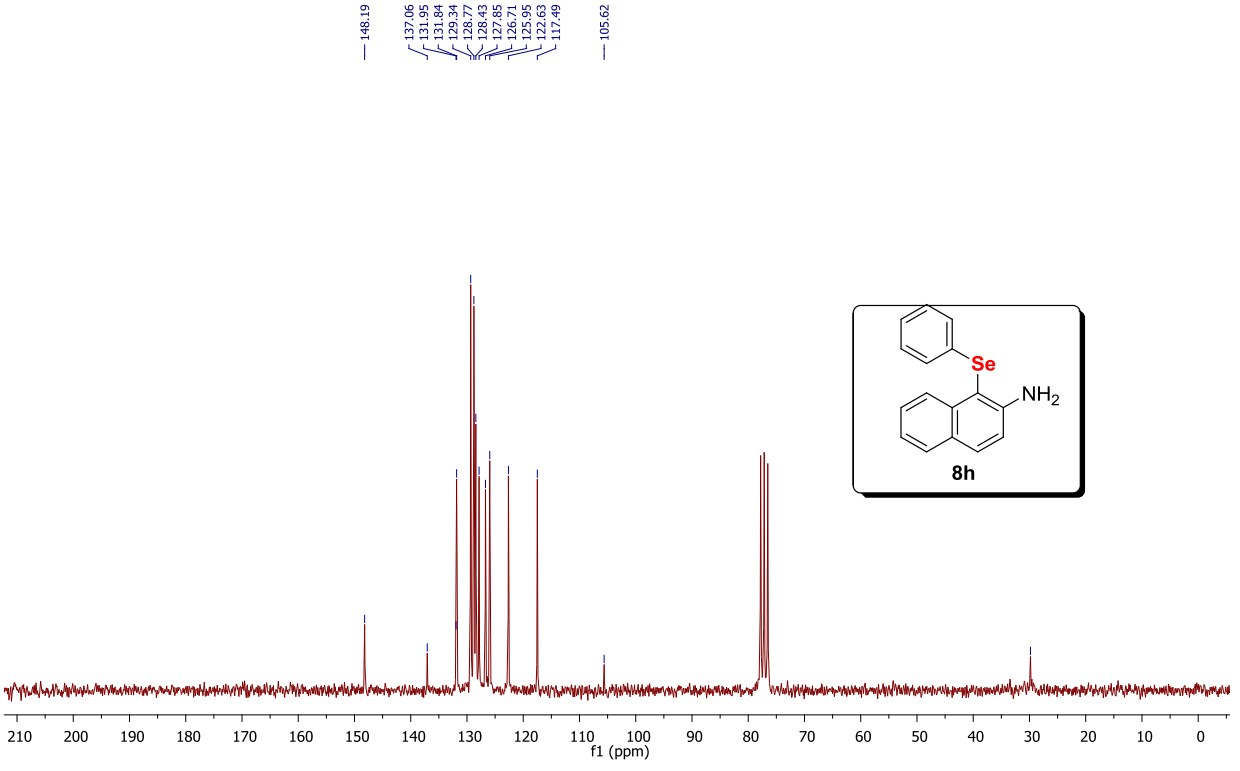
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **8g**



^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **8g**



^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **8h**



^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **8h**