

## Supporting Information

### **Additive Controlled Switchable Mono- vs. Di-Selenylation of Primary Arylamides *via* Ru(II) Catalyzed C-H activation**

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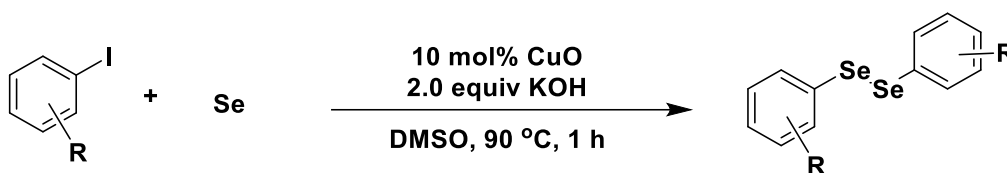
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## 1. General Considerations

Unless otherwise noted, all reagents were purchased from a commercial supplier and used without further purification. All arylamides derivatives were prepared by following the reported procedure in literature<sup>1</sup> and diaryl diselenide derivatives were prepared by following the reported procedure in literature.<sup>2</sup> All the reactions were run in sealed tubes, and the indicated temperature was that of an oil bath. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>19</sup>F{<sup>1</sup>H} NMR spectra were recorded at Bruker 400 MHz and JEOL 500 MHz spectrometers in CDCl<sub>3</sub> or DMSO-D<sub>6</sub> as a solvent. Chemical shifts are reported in (δ) ppm referenced to CDCl<sub>3</sub> (δ 7.26) or DMSO-D<sub>6</sub> (δ 2.50) for <sup>1</sup>H NMR and CDCl<sub>3</sub> (δ 77.16) or DMSO-D<sub>6</sub> (δ 39.52) for <sup>13</sup>C NMR. The following abbreviations explain multiplicities: (s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hertz). Infrared spectra were recorded by PerkinElmer Spectrum 400 FTIR spectrophotometer. High-resolution mass (HRMS) spectra were obtained over an ESI-TOF (electron spray ionization-time of flight) spectrometer, and acetonitrile was used to dissolve the sample. Melting points were recorded with an automated melting point apparatus without correction. Column chromatography was performed on silica gel (100–200) mesh using ethyl acetate and hexanes as eluents in different ratios.

## 2. General procedure for the preparation of diaryl diselenides<sup>2</sup>



To a stirred solution of Se (0) metal (4.0 mmol) and aryl iodides (2.0 mmol) in dry DMSO (3.0 mL), CuO (10 mol %) was added, followed by KOH (2.0 equiv) under a nitrogen atmosphere at 90 °C. The progress of the reaction was monitored by TLC. After the reaction was complete, Et<sub>2</sub>O (10 mL) was added and the mixture was washed successively with water (2×20mL). The organic layer was separated and dried by adding anhydrous Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent under reduced pressure gave almost pure product. Further purification was achieved by column chromatography on silica gel (ethylacetate: hexane (1:50)) to give the pure product.

## 3. Optimization of reaction conditions for the Ru(II) catalyzed C-H selenylation

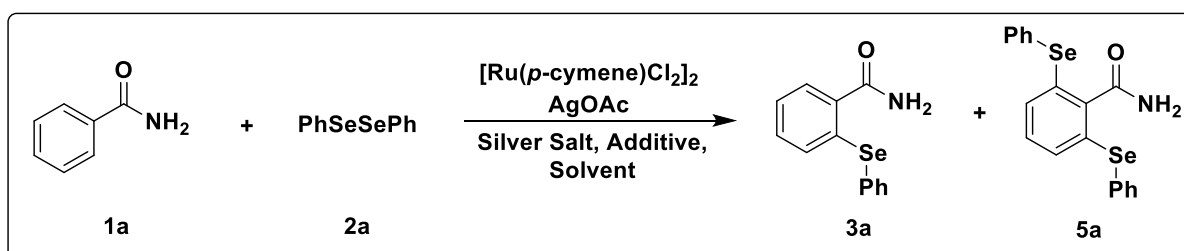


Table S1. Optimization of additives<sup>a</sup>

s.no.	solvent	additive (20 mol %)	silver salt (20 mol %)	yield <sup>b</sup> (%) 3a/5a
1	TFE	AgOTf	AgSbF <sub>6</sub>	9/77 <sup>c</sup>
2	TFE	Zn(OTf) <sub>2</sub>	AgSbF <sub>6</sub>	40/25
3	TFE	Sc(OTf) <sub>3</sub>	AgSbF <sub>6</sub>	33/35
4	TFE	Cu(OTf) <sub>2</sub>	AgSbF <sub>6</sub>	50/26
5	TFE	Fe(OTf) <sub>3</sub>	AgSbF <sub>6</sub>	81/7
6	TFE	Ni(OTf) <sub>2</sub>	AgSbF <sub>6</sub>	51/13
7	TFE	AgNO <sub>3</sub>	AgSbF <sub>6</sub>	5/2
8	TFE	–	AgSbF <sub>6</sub>	22/18

<sup>a</sup>Reaction Condition: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2.0 equiv), [Ru(*p*-cymene)Cl<sub>2</sub>]<sub>2</sub> (5 mol %), AgSbF<sub>6</sub> (20 mol %), AgOAc (2.0 equiv), additive, solvent (2.0 mL) for 36 h at 100 °C. <sup>b</sup>Isolated yield.

**Table S2. Optimization of solvents<sup>a</sup>**

s.no.	solvent	silver salt (20 mol %)	additive (20 mol %)	yield <sup>b</sup> (%) 3a/5a
1	TFE	AgSbF <sub>6</sub>	AgOTf	14/60
2	DCE	AgSbF <sub>6</sub>	AgOTf	29/35
3	1,4-dioxane	AgSbF <sub>6</sub>	AgOTf	trace
4	DMSO	AgSbF <sub>6</sub>	AgOTf	Nr
5	DMF	AgSbF <sub>6</sub>	AgOTf	trace
6	Toluene	AgSbF <sub>6</sub>	AgOTf	7/9
7	THF	AgSbF <sub>6</sub>	AgOTf	5/10
8	ACN	AgSbF <sub>6</sub>	AgOTf	trace
9	TFE	AgSbF <sub>6</sub>	AgOTf	9/77 <sup>c</sup>
10	DCE	AgSbF <sub>6</sub>	Fe(OTf) <sub>3</sub>	42/trace <sup>c</sup>
11	TFE	AgSbF <sub>6</sub>	Fe(OTf) <sub>3</sub>	67/5

<sup>a</sup>Reaction Condition: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2.0 equiv), [Ru(*p*-cymene)Cl<sub>2</sub>]<sub>2</sub> (5 mol %), AgSbF<sub>6</sub> (20 mol %), AgOAc (2.0 equiv), additive (20 mol %), solvent (1.0 mL) for 36 h at 100 °C. <sup>b</sup>Isolated yield. <sup>c</sup>2 mL of solvent was used.

**Table S3. Optimization of substrates stoichiometry and silver salt<sup>a</sup>**

s.no.	benzamide (1a) (equiv)	diphenyl diselenide (2a) (equiv)	silver salt (20 mol%)	yield <sup>b</sup> (%) 3a/5a
1	1.0	1.2	AgSbF <sub>6</sub>	18/10
2	1.0	1.2	AgSbF <sub>6</sub>	65/11 <sup>c</sup>
3	2.0	1.0	AgSbF <sub>6</sub>	16/3
4	1.0	2.0	AgBF <sub>4</sub>	15/38
5	1.0	2.0	–	15/16

<sup>a</sup>Reaction Condition: [Ru(*p*-cymene)Cl<sub>2</sub>]<sub>2</sub> (5 mol %), silver salt (20 mol %), AgOAc (2.0 equiv), additive (AgOTf 20 mol %), TFE (0.05 M) for 36 h at 100 °C. <sup>b</sup>Isolated yield. <sup>c</sup>Fe(OTf)<sub>3</sub> (20 mol %) was used as an additive.

**Table S4. Optimization of reaction time/temperature and catalyst loading<sup>a</sup>**

s.no.	time (h)	temperature (°C)	[Ru( <i>p</i> -cymene)Cl <sub>2</sub> ] <sub>2</sub> (mol %)	additive (20 mol %)	yield <sup>b</sup> (%) 3a/5a
1	36	120	5 mol %	AgOTf	29/51
2	36	120	5 mol %	Fe(OTf) <sub>3</sub>	73/13
3	36	70	5 mol %	AgOTf	15/26
4	36	70	5 mol %	Fe(OTf) <sub>3</sub>	30/trace

<b>5</b>	<b>24</b>	100	5 mol %	AgOTf	33/46
<b>6</b>	<b>48</b>	100	5 mol %	AgOTf	13/75
<b>7</b>	<b>24</b>	100	5 mol %	Fe(OTf) <sub>3</sub>	65/5
<b>8</b>	<b>48</b>	100	5 mol %	Fe(OTf) <sub>3</sub>	72/14
<b>9</b>	36	100	<b>2.5 mol %</b>	AgOTf	51/14
<b>10</b>	36	100	–	AgOTf	nr

<sup>a</sup>Reaction Condition: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2.0 equiv), AgOAc (2.0 equiv), AgSbF<sub>6</sub> (20 mol %), additive (20 mol %), TFE (2.0 mL). <sup>b</sup>Isolated yield.

#### 4. General procedure for the synthesis of *ortho*-mono-selenylated arylamides (GP-A)

To a clean oven-dried 15 mL seal tube equipped with a magnetic stir bar was sequentially added arylamides (0.1 mmol, 1.0 equiv), 1,2-diaryldiselane (0.2 mmol, 2.0 equiv), [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (5.0 mol %), Fe(OTf)<sub>3</sub> (20 mol %) and AgOAc (2.0 equiv.) in CF<sub>3</sub>CH<sub>2</sub>OH (2.0 mL). Subsequently, AgSbF<sub>6</sub> (20 mol %) was added under an argon atmosphere and the reaction tube was flushed with argon. The tube was tightly closed, placed in a preheated oil bath at 100 °C and stirred for 36 h according to the conversion estimated by TLC. At ambient temperature, the reaction mixture was quenched with H<sub>2</sub>O (10 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel (100-200 mesh) using ethyl acetate/hexane as eluent.

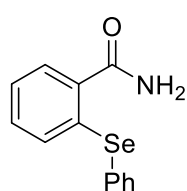
#### 5. General procedure for the synthesis of *ortho*-di-selenylated arylamides (GP-B)

To a clean oven-dried 15 mL seal tube equipped with a magnetic stir bar was sequentially added arylamides (0.1 mmol, 1.0 equiv), 1,2-diaryldiselane (0.2 mmol, 2.0 equiv), [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (5.0 mol %), AgOTf (20 mol %) and AgOAc (2.0 equiv.) in CF<sub>3</sub>CH<sub>2</sub>OH (2.0 mL). Subsequently, AgSbF<sub>6</sub> (20 mol %) was added under an argon atmosphere, and the reaction tube was flushed with argon. The tube was tightly closed, placed in a preheated oil bath at 100 °C and stirred for 36 h according to the conversion estimated by TLC. At ambient temperature,

the reaction mixture was quenched with H<sub>2</sub>O (10 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel (100-200 mesh) using ethyl acetate/hexane as eluent.

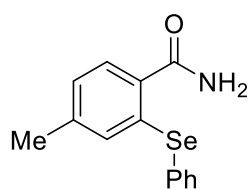
## 6. Characterisation of products

### 2-(phenylselanyl)benzamide (3a)



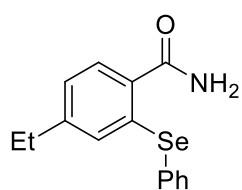
Following **GP-A**, **3a** was isolated as a white solid (22 mg, 81% yield); R<sub>f</sub> (1:1 hexane/ethyl acetate) = 0.5; mp 202-204 °C; IR (ATR): 3413, 3198, 1608, 1466, 1430, 1380, 739, 689 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.67 – 7.62 (m, 2H), 7.62 – 7.56 (m, 1H), 7.42 – 7.34 (m, 3H), 7.23 – 7.16 (m, 2H), 7.14 – 7.07 (m, 1H), 5.93 (s, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 170.2, 136.6, 132.6, 131.7, 131.1, 129.9, 129.8, 128.9, 128.0, 125.7. HRMS (ESI-TOF) m/z: [M + H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>12</sub>NOS<sub>e</sub>, 278.0079; found, 278.0088.

### 4-methyl-2-(phenylselanyl)benzamide (3b)



Following **GP-A**, **3b** was isolated as a white solid (23 mg, 79% yield); R<sub>f</sub> (1:1 hexane/ethyl acetate) = 0.5; mp 187-189 °C; IR (ATR): 3407, 3202, 2921, 1611, 1557, 1379, 742 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.65 – 7.62 (m, 2H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.43 – 7.31 (m, 3H), 7.00 (dd, *J* = 7.8, 0.9 Hz, 1H), 6.88 (s, 1H), 5.98 (bs, 2H), 2.18 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 170.2, 142.2, 136.4, 136.3, 131.7, 130.1, 129.9, 129.7, 128.7, 128.1, 126.7, 21.5. HRMS (ESI-TOF) m/z: [M + H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>14</sub>NOS<sub>e</sub>, 292.0235; found, 292.0237.

### 4-ethyl-2-(phenylselanyl)benzamide (3c)



Following **GP-A**, **3c** was isolated as a white solid (25 mg, 82% yield);  $R_f$

(1:1 hexane/ethyl acetate) = 0.5; mp 197-199 °C; IR (ATR): 3401, 3176,

2965, 1640, 1605, 1385, 745  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 –

7.60 (m, 2H), 7.52 (d,  $J = 7.8$  Hz, 1H), 7.43 – 7.32 (m, 3H), 7.02 (dd,  $J = 7.9, 1.7$  Hz, 1H), 6.91

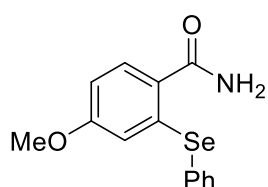
(d,  $J = 1.7$  Hz, 1H), 5.92 (bs, 2H), 2.47 (q,  $J = 7.6$  Hz, 2H), 1.05 (t,  $J = 7.6$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$

NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.2, 148.3, 136.3, 130.7, 130.2, 130.1, 129.7, 128.7, 128.2, 125.5,

28.7, 15.0. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_{16}\text{NOSe}$ , 306.0392; found,

306.0391.

#### **4-methoxy-2-(phenylselanyl)benzamide (3d)**



Following **GP-A**, **3d** was isolated as a white solid (24 mg, 78% yield);

$R_f$  (1:1 hexane/ethyl acetate) = 0.4; mp 209-211 °C; IR (ATR): 3389,

3176, 2924, 1637, 1605, 1593, 1554, 1394, 1296, 1276, 1228, 1030 793

$\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 – 7.66 (m, 2H), 7.54 (d,  $J = 8.6$  Hz, 1H), 7.46 – 7.34

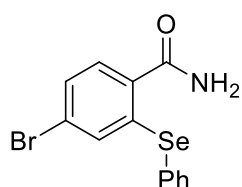
(m, 3H), 6.68 (dd,  $J = 8.6, 2.5$  Hz, 1H), 6.51 (d,  $J = 2.5$  Hz, 1H), 5.85 (bs, 2H), 3.57 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.8, 162.0, 140.1, 137.1, 129.9, 129.8, 129.6, 129.1,

124.1, 115.7, 111.2, 55.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{14}\text{NO}_2\text{Se}$ , 308.0184;

found, 308.0182.

#### **4-bromo-2-(phenylselanyl)benzamide (3e)**



Following **GP-A**, **3e** was isolated as a white solid (25 mg, 71% yield);  $R_f$

(1:1 hexane/ethyl acetate) = 0.5; mp 216-218 °C; IR (ATR): 3383, 3182,

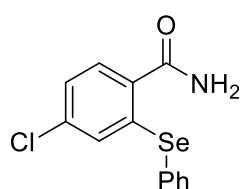
2915, 1643, 1607, 1569, 1388  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69

– 7.60 (m, 2H), 7.49 – 7.36 (m, 4H), 7.31 (dd,  $J = 8.2, 1.9$  Hz, 1H), 7.12 (d,  $J = 1.9$  Hz, 1H),

5.92 (bs, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.4, 139.6, 136.8, 133.2, 130.9, 130.1,

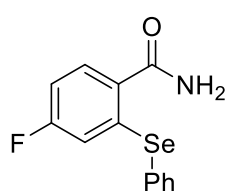
129.4, 129.1, 129.0, 128.6, 126.8. HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  calcd for  $C_{13}H_{11}BrNOSe$ , 355.9184; found, 355.9181.

#### **4-chloro-2-(phenylselanyl)benzamide (3f)**



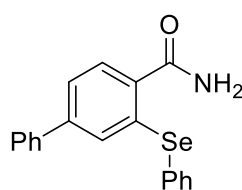
Following **GP-A**, **3f** was isolated as a white solid (20 mg, 63% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.5; mp 204-206 °C; IR (ATR): 3389, 3181, 2924, 1640, 1610, 1572, 1394, 1101  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.70 – 7.60 (m, 2H), 7.53 – 7.37 (m, 4H), 7.15 (dd,  $J = 8.2, 2.0$  Hz, 1H), 6.95 (d,  $J = 2.0$  Hz, 1H), 5.97 (s, 2H).  $^{13}C\{^1H\}$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  169.4, 139.6, 138.2, 136.9, 130.3, 130.2, 130.1, 129.5, 129.0, 128.9, 125.6. HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  calcd for  $C_{13}H_{12}ClNOSe$ , 311.9689; found, 311.9685.

#### **4-fluoro-2-(phenylselanyl)benzamide (3g)**



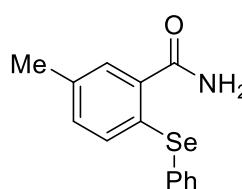
Following **GP-A**, **3g** was isolated as a white solid (17 mg, 58% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.4; mp 185-187 °C; IR (ATR): 3390, 3173, 2922, 1642, 1612, 1574, 1476, 1397, 1260, 1207  $cm^{-1}$ .  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.71 – 7.64 (m, 2H), 7.57 (dd,  $J = 8.5, 5.6$  Hz, 1H), 7.49 – 7.38 (m, 3H), 6.88 – 6.82 (m, 1H), 6.67 (dd,  $J = 9.7, 2.5$  Hz, 1H), 5.98 (bs, 2H).  $^{13}C\{^1H\}$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  169.4, 164.6 (d,  $J_{C-F} = 254.5$  Hz), 141.2 (d,  $J_{C-F} = 7.9$  Hz), 137.2, 130.1, 129.8 (d,  $J_{C-F} = 9.1$  Hz), 129.5, 129.1, 127.8, 117.3 (d,  $J_{C-F} = 24.8$  Hz), 112.5 (d,  $J_{C-F} = 22.5$  Hz).  $^{19}F\{^1H\}$  NMR (471 MHz,  $CDCl_3$ )  $\delta$  -107.38. HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  calcd for  $C_{13}H_{11}FNOSe$ , 295.9984; found, 295.9982.

#### **3-(phenylselanyl)-[1,1'-biphenyl]-4-carboxamide (3h)**



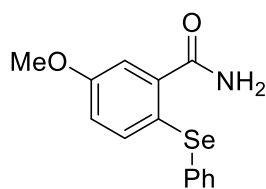
Following **GP-A**, **3h** was isolated as a white solid (26 mg, 72% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.5; mp 255-257 °C; IR (ATR): 3416, 3192, 2924, 1607, 1590, 1468, 1369, 742  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz, DMSO- $\text{D}_6$ )  $\delta$  8.13 (s, 1H), 7.86 (d,  $J$  = 8.1 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.57 (s, 1H), 7.53 – 7.43 (m, 4H), 7.39 – 7.35 (m, 2H), 7.34 – 7.29 (m, 3H), 7.05 (d,  $J$  = 1.8 Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, DMSO- $\text{D}_6$ )  $\delta$  169.1, 142.4, 138.9, 137.4, 136.8, 131.3, 129.9, 129.1, 129.0, 128.2, 127.0, 126.5, 123.5. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{16}\text{NOSe}$ , 354.0392; found, 354.0416.

### 5-methyl-2-(phenylselanyl)benzamide (**3i**)



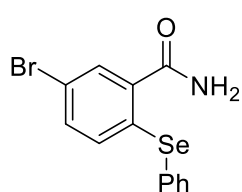
Following **GP-A**, **3i** was isolated as a white solid (23 mg, 79% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.4; mp 188-190 °C; IR (ATR): 3392, 3175, 2918, 1639, 1610, 1462, 1409, 1376  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 – 7.57 (m, 2H), 7.43 (s, 1H), 7.40 – 7.30 (m, 3H), 7.07 – 6.97 (m, 2H), 6.09 (bs, 2H), 2.31 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.5, 136.0, 135.9, 133.3, 132.6, 131.8, 131.7, 130.4, 129.7, 128.9, 128.5, 20.9. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{14}\text{NOSe}$ , 292.0235; found, 292.0249.

### 5-methoxy-2-(phenylselanyl)benzamide (**3j**)



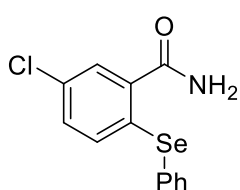
Following **GP-A**, **3j** was isolated as a white solid (19 mg, 62% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.5; mp 158-160 °C; IR (ATR): 3321, 3149, 2924, 1658, 1617, 1447, 1427, 1394, 1261  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 – 7.35 (t,  $J$  = 8.0 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.23 – 7.14 (m, 4H), 6.98 (dd,  $J$  = 8.3, 1.2 Hz, 1H), 6.04 (s, 1H), 5.88 (s, 1H), 3.76 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.9, 160.0, 142.9, 132.5, 130.8, 130.7, 129.2, 126.6, 120.7, 115.8, 113.0, 56.4. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{14}\text{NO}_2\text{Se}$ , 308.0184; found, 308.0193.

### 5-bromo-2-(phenylselanyl)benzamide (3k)



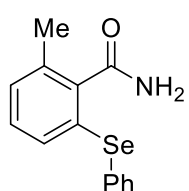
Following **GP-A**, **3k** was isolated as a white solid (22 mg, 62% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.5; mp 163-165 °C; IR (ATR): 3368, 3167, 2921, 1648, 1622, 1460, 1403, 742  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}D_6$ )  $\delta$  8.18 (s, 1H), 7.93 (d,  $J = 2.2$  Hz, 1H), 7.66 (s, 1H), 7.64 – 7.61 (m, 2H), 7.48 – 7.42 (m, 4H), 6.76 (d,  $J = 8.6$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}D_6$ )  $\delta$  168.0, 136.6, 135.9, 134.4, 133.7, 131.0, 130.8, 130.0, 129.4, 129.2, 118.1. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_{11}\text{BrNOSe}$ , 355.9184; found, 355.9180.

### 5-chloro-2-(phenylselanyl)benzamide (3l)



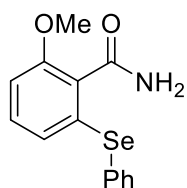
Following **GP-A**, **3l** was isolated as a white solid (21 mg, 68% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.5; mp 141-143 °C; IR (ATR): 3383, 3182, 2915, 1643, 1460, 1400, 1107, 1021  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 – 7.61 (m, 2H), 7.56 (d,  $J = 2.3$  Hz, 1H), 7.46 – 7.34 (m, 3H), 7.15 (dd,  $J = 8.6, 2.3$  Hz, 1H), 6.97 (d,  $J = 8.6$  Hz, 1H), 6.04 (bs, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.0, 136.5, 134.9, 134.0, 132.4, 131.7, 131.6, 129.9, 129.4, 129.1, 127.9. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_{12}\text{ClNOSe}$ , 311.9689; found, 311.9692.

### 2-methyl-6-(phenylselanyl)benzamide (3m)



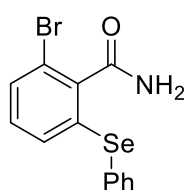
Following **GP-A**, **3m** was isolated as a white solid (22 mg, 75% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.4; mp 160-162 °C; IR (ATR): 3398, 3164, 2921, 1639, 1605, 1433, 1375, 772, 742  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 – 7.46 (m, 2H), 7.29 – 7.26 (m, 3H), 7.22 – 7.19 (m, 1H), 7.15 – 7.11 (m, 2H), 5.91 (s, 1H), 5.61 (s, 1H), 2.42 (s, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  171.1, 139.7, 135.7, 133.5, 131.8, 131.2, 129.9, 129.7, 129.6, 128.3, 127.8, 19.8. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{14}\text{H}_{13}\text{NNaOSe}$ , 314.0055; found, 314.0048.

### 2-methoxy-6-(phenylselanyl)benzamide (3n)



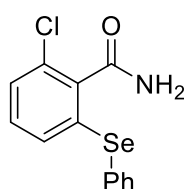
Following **GP-A**, **3n** was isolated as a white solid (28 mg, 91% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.4; mp 222-224 °C; IR (ATR): 3419, 3164, 2918, 1640, 1560, 1433, 1391, 1261, 1033  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 – 7.63 (m, 2H), 7.43 – 7.32 (m, 3H), 7.27 (bs, 1H), 7.08 (t,  $J$  = 8.2 Hz, 1H), 6.76 (dd,  $J$  = 8.3, 1.0 Hz, 1H), 6.66 (dd,  $J$  = 8.1, 0.9 Hz, 1H), 5.90 (bs, 1H), 3.92 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  168.5, 158.7, 141.4, 137.0, 131.5, 131.4, 129.6, 128.8, 123.5, 120.8, 108.4, 56.4. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{14}\text{NO}_2\text{Se}$ , 308.0184; found, 308.0180.

### 2-bromo-6-(phenylselanyl)benzamide (3o)



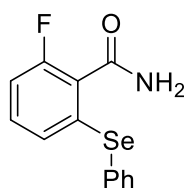
Following **GP-A**, **3o** was isolated as a white solid (25 mg, 70% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.5; mp 171-173 °C; IR (ATR): 3366, 3155, 2921, 1646, 1613, 1546, 1421, 1382, 733  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 – 7.51 (m, 2H), 7.44 (dd,  $J$  = 8.0, 1.0 Hz, 1H), 7.38 – 7.28 (m, 3H), 7.20 (dd,  $J$  = 7.9, 1.1 Hz, 1H), 7.04 (t,  $J$  = 7.9 Hz, 1H), 6.04 (s, 1H), 5.77 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.0, 139.3, 134.8, 132.6, 132.0, 131.4, 131.1, 129.9, 129.8, 128.6, 119.6. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{13}\text{H}_{10}\text{BrNNaOSe}$ , 377.9003; found, 377.9000.

### 2-chloro-6-(phenylselanyl)benzamide (3p)



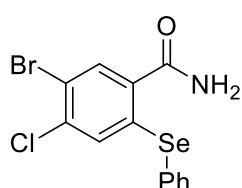
Following **GP-A**, **3p** was isolated as a white solid (20 mg, 65% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.5; mp 192-194 °C; IR (ATR): 3395, 3167, 2924, 1640, 1604, 1424, 1382, 742  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 – 7.52 (m, 2H), 7.36 – 7.31 (m, 3H), 7.30 – 7.22 (m, 1H), 7.16 – 7.08 (m, 2H), 6.00 (bs, 1H), 5.81 (bs, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  168.1, 136.9, 135.1, 133.2, 131.2, 130.8, 129.9, 129.8, 128.7, 128.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{13}\text{H}_{10}\text{ClNNaOSe}$ , 333.9508; found, 333.9509.

### 2-fluoro-6-(phenylselanyl)benzamide (3q)



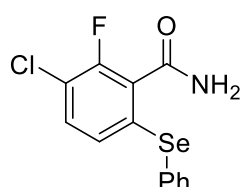
Following **GP-A**, **3q** was isolated as a white solid (21 mg, 71% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.5; mp 220-222 °C; IR (ATR): 302, 3157, 2919, 1643, 1599, 1439, 1391, 1234, 804  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 – 7.64 (m, 2H), 7.47 – 7.35 (m, 3H), 7.14 – 7.07 (m, 1H), 6.93 – 6.87 (m, 1H), 6.81 (d,  $J$  = 8.1 Hz, 1H), 6.49 (bs, 1H), 5.92 (bs, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.1, 161.6 (d,  $J$  = 249.7 Hz), 141.7, 137.2, 132.0 (d,  $J$  = 10.2 Hz), 130.1, 129.9, 129.2, 126.4 (d,  $J$  = 2.4 Hz), 119.7 (d,  $J$  = 14.3 Hz), 112.7 (d,  $J$  = 25.3 Hz).  $^{19}\text{F}\{^1\text{H}\}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -111.71. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_{11}\text{FNOSe}$ , 295.9984; found, 295.9995.

### 5-bromo-4-chloro-2-(phenylselanyl)benzamide (3r)



Following **GP-A**, **3r** was isolated as a white solid (20 mg, 52% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.5; mp 205-207 °C; IR (ATR): 3377, 3176, 2918, 1649, 1613, 1456, 1376  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (s, 1H), 7.67 – 7.59 (m, 2H), 7.50 – 7.38 (m, 3H), 7.03 (s, 1H), 5.93 (bs, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  168.0, 138.4, 138.1, 136.8, 132.6, 131.9, 130.2, 129.6, 128.6, 119.0. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_{10}\text{BrClNOSe}$ , 389.8794; found, 389.8789.

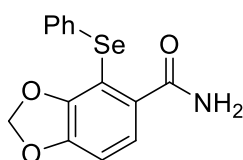
### 3-chloro-2-fluoro-6-(phenylselanyl)benzamide (3s)



Following **GP-A**, **3s** was isolated as a white solid (26 mg, 79% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.5; mp 205-207 °C; IR (ATR): 3398, 3173, 2921, 1646, 1616, 1447, 1382, 745  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 – 7.61 (m, 2H), 7.47 – 7.36 (m, 3H), 7.16 (dd,  $J$  = 8.7, 7.6 Hz, 1H), 6.75 (dd,  $J$  = 8.7, 1.3 Hz, 1H), 6.39 (bs, 1H), 5.99 (bs, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  165.1, 156.6 (d,  $J$  = 251.6 Hz), 139.3, 137.0, 132.4, 130.0, 129.5, 129.4, 126.8 (d,  $J$  = 4.2 Hz), 121.6 (d,  $J$  = 15.3

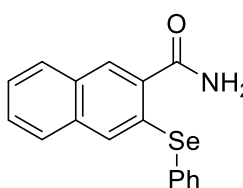
Hz), 118.4 (d,  $J = 20.2$  Hz).  $^{19}\text{F}\{^1\text{H}\}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.13. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_{10}\text{ClFNOSe}$ , 329.9595; found, 329.9592.

### 6-(phenylselanyl)benzo[d][1,3]dioxole-5-carboxamide (3t)



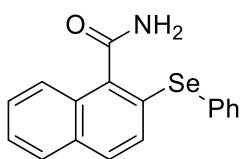
Following **GP-A**, **3t** was isolated as a white solid (28 mg, 88% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.4; mp 187-189 °C; IR (ATR): 3356, 3173, 2922, 1640, 1376, 1243, 927,  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 – 7.35 (m, 3H), 7.24 – 7.18 (m, 3H), 6.82 (d,  $J = 8.1$  Hz, 1H), 6.56 (bs, 1H), 5.94 (s, 2H), 5.82 (bs, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.4, 150.3, 149.1, 132.1, 131.4, 131.0, 129.4, 127.3, 124.2, 108.5, 107.8, 101.6. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{12}\text{NO}_3\text{Se}$ , 321.9977; found, 321.9982.

### 3-(phenylselanyl)-2-naphthamide (3u)



Following **GP-A**, **3u** was isolated as a white solid (28 mg, 86% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.5; mp 243-245 °C; IR (ATR): 3380, 3173, 2054, 1643, 1610, 1388, 976, 742  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}D_6$ )  $\delta$  8.29 (s, 1H), 8.23 (s, 1H), 7.95 – 7.87 (m, 1H), 7.70 – 7.64 (m, 2H), 7.64 (s, 1H), 7.52 – 7.44 (m, 6H), 7.32 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}D_6$ )  $\delta$  = 169.7, 136.2, 133.9, 132.4, 131.9, 130.2, 130.2, 129.9, 128.9, 128.3, 128.1, 128.0, 127.7, 126.5, 126.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{14}\text{NOSe}$ , 328.0235; found, 328.0244.

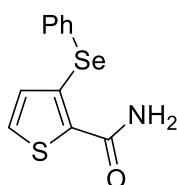
### 2-(phenylselanyl)-1-naphthamide (3v)



Following **GP-A**, **3v** was isolated as a white solid (13 mg, 40% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.4; mp 240-242 °C; IR (ATR): 3386, 3155, 2921, 1640, 1607, 1462, 1261, 1021  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J = 8.3$  Hz, 1H), 7.80 (d,  $J = 8.1$  Hz, 1H), 7.69 (d,  $J = 8.7$  Hz, 1H), 7.60 – 7.47 (m, 4H), 7.39 (d,  $J = 8.6$  Hz, 1H), 7.34 – 7.26 (m, 3H), 6.20 (bs, 1H), 5.88 (bs, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR

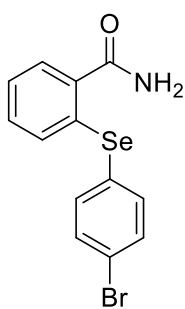
(125 MHz, CDCl<sub>3</sub>)  $\delta$  170.7, 136.6, 134.0, 132.5, 130.7, 130.4, 130.3, 130.1, 129.7, 128.3, 128.1, 127.8, 127.2, 126.7, 125.1. HRMS (ESI-TOF)  $m/z$ : [M + H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>OSe, 328.0235; found, 328.0227.

### 3-(phenylselanyl)thiophene-2-carboxamide (3w)



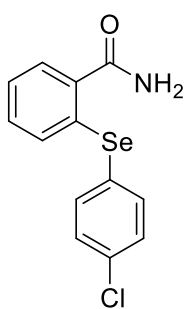
Following **GP-A**, **3w** was isolated as a white solid (20 mg, 71% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.5; mp 131-133 °C; IR (ATR): 3395, 3164, 2921, 1643, 1599, 1400, 1364, 730 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.53 – 7.48 (m, 2H), 7.38 (d,  $J$  = 5.1 Hz, 1H), 7.34 – 7.28 (m, 3H), 6.79 (d,  $J$  = 5.1 Hz, 1H), 6.53 (bs, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  163.8, 133.7, 133.6, 133.5, 130.1, 130.0, 129.8, 129.7, 128.4. HRMS (ESI-TOF)  $m/z$ : [M + H]<sup>+</sup> calcd for C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>OSe, 283.9643; found, 283.9640.

### 2-((4-fluorophenyl)selanyl)benzamide (4b)



Following **GP-A**, **4b** was isolated as a white solid (27 mg, 76% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.4; mp 192-194 °C; IR (ATR): 3430, 3300, 3175, 1652, 1602, 1409, 1377, 742 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.62 – 7.54 (m, 1H), 7.56 – 7.45 (m, 4H), 7.29 – 7.16 (m, 2H), 7.07 – 6.99 (m, 1H), 5.97 (bs, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  170.1, 138.3, 136.6, 133.0, 132.3, 131.9, 130.9, 128.9, 128.0, 125.8, 123.6. HRMS (ESI-TOF)  $m/z$ : [M + Na]<sup>+</sup> calcd for C<sub>13</sub>H<sub>11</sub>BrNOSe, 355.9184; found, 355.9180.

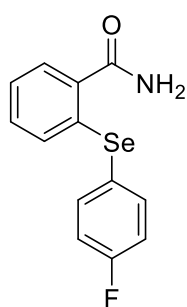
### 2-((4-chlorophenyl)selanyl)benzamide (4c)



Following **GP-A**, **4c** was isolated as a white solid (27 mg, 87% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.4; mp 191-193 °C; IR (ATR): 3436, 3187, 2924, 1611, 1466, 1374, 1089, 812 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 – 7.56 (m, 3H), 7.37 – 7.32 (m, 2H), 7.25 – 7.17 (m, 2H), 7.05 – 7.00 (m, 1H), 6.00 (bs, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  170.1, 138.1, 136.7, 135.4,

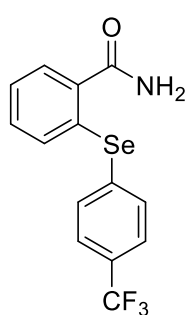
132.3, 131.9, 130.8, 130.0, 128.2, 128.0, 125.8. HRMS (ESI-TOF) m/z: [M + H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>11</sub>ClNOSe, 311.9689; found, 311.9687.

#### 2-((4-fluorophenyl)selanyl)benzamide (4d)



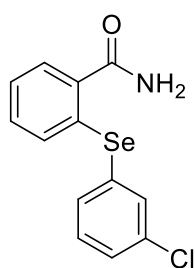
Following **GP-A**, **4d** was isolated as a white solid (22 mg, 75% yield); R<sub>f</sub> (1:1 hexane/ethyl acetate) = 0.4; mp 197-199 °C; IR (ATR): 3433, 3194, 2918, 1610, 1581, 1379, 1222, 739 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.68 – 7.61 (m, 2H), 7.60 – 7.56 (m, 1H), 7.23 – 7.16 (m, 2H), 7.11 – 7.05 (m, 2H), 7.00 – 6.96 (m, 1H), 6.06 (bs, 2H). <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 170.1, 163.5 (d, J<sub>C-F</sub> = 248.9 Hz), 139.1 (d, J<sub>C-F</sub> = 8.1 Hz), 137.4, 131.9, 131.8, 130.4, 127.9, 125.6, 124.6 (d, J<sub>C-F</sub> = 2.8 Hz), 117.1 (d, J<sub>C-F</sub> = 21.6 Hz). <sup>19</sup>F {<sup>1</sup>H} NMR (471 MHz, CDCl<sub>3</sub>) δ -111.97. HRMS (ESI-TOF) m/z: [M + H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>11</sub>FNOSe, 295.9984; found, 295.9981.

#### 2-((4-(trifluoromethyl)phenyl)selanyl)benzamide (4e)



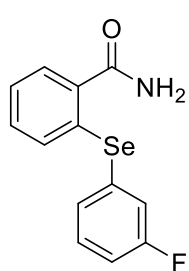
Following **GP-A**, **4e** was isolated as a white solid (28 mg, 82% yield); R<sub>f</sub> (1:1 hexane/ethyl acetate) = 0.4; mp 162-164 °C; IR (ATR): 3431, 3191, 2930, 1620, 1602, 1326, 1119, 742 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.74 (d, J = 7.6 Hz, 2H), 7.65 – 7.56 (m, 3H), 7.29 – 7.23 (m, 2H), 7.12 – 7.06 (m, 1H), 6.10 (bs, 2H). <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 170.2, 136.1, 135.4, 135.2, 133.2, 131.9, 131.7, 130.7 (d, J<sub>C-F</sub> = 32.5 Hz), 128.1, 126.5 (d, J<sub>C-F</sub> = 3.3 Hz), 126.3, 125.2, 123.1. <sup>19</sup>F {<sup>1</sup>H} NMR (471 MHz, CDCl<sub>3</sub>) δ -62.63. HRMS (ESI-TOF) m/z: [M + H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>11</sub>F<sub>3</sub>NOSe, 345.9952; found, 345.9947.

#### 2-((3-chlorophenyl)selanyl)benzamide (4f)



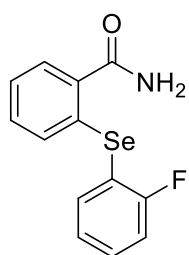
Following **GP-A**, **4f** was isolated as a white solid (25 mg, 80% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.4; mp 179-181 °C; IR (ATR): 3425, 3197, 2921, 1610, 1468, 1377, 1211, 742  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (s, 1H), 7.59 (d,  $J = 7.0$  Hz, 1H), 7.53 (d,  $J = 7.6$  Hz, 1H), 7.38 (d,  $J = 8.1$  Hz, 1H), 7.30 (t,  $J = 7.7$  Hz, 1H), 7.25 – 7.17 (m, 2H), 7.06 (d,  $J = 7.2$  Hz, 1H), 5.99 (bs, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.2, 136.4, 136.2, 135.3, 134.7, 132.6, 132.0, 131.8, 131.2, 130.9, 129.2, 128.1, 126.0. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_{11}\text{ClNOSe}$ , 311.9689; found, 311.9695.

#### 2-((3-fluorophenyl)selanyl)benzamide (**4g**)



Following **GP-A**, **4g** was isolated as a white solid (25 mg, 85% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.4; mp 170-172 °C; IR (ATR): 3380, 3170, 2924, 1637, 1611, 1560, 1391  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 – 7.57 (m, 1H), 7.45 – 7.40 (m, 1H), 7.38 – 7.31 (m, 2H), 7.25 – 7.19 (m, 2H), 7.12 – 7.05 (m, 2H), 5.97 (bs, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.1, 163.0 (d,  $J_{\text{C-F}} = 251.0$  Hz), 136.1, 132.6, 132.1 (d,  $J_{\text{C-F}} = 2.8$  Hz), 131.9, 131.8 (d,  $J_{\text{C-F}} = 6.4$  Hz), 131.2, 131.0 (d,  $J_{\text{C-F}} = 7.8$  Hz), 128.0, 126.0, 123.1 (d,  $J_{\text{C-F}} = 21.2$  Hz), 116.0 (d,  $J_{\text{C-F}} = 21.0$  Hz).  $^{19}\text{F}\{^1\text{H}\}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -111.31. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_{11}\text{FNOSe}$ , 295.9984; found, 295.9998.

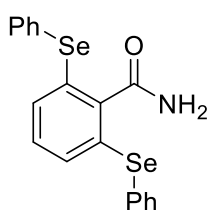
#### 2-((2-fluorophenyl)selanyl)benzamide (**4h**)



Following **GP-A**, **4h** was isolated as a white solid (25 mg, 85% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.4; mp 187-189 °C; IR (ATR): 3445, 3158, 2924, 1664, 1462, 1382, 733  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 – 7.62 (m, 1H), 7.64 – 7.56 (m, 1H), 7.46 – 7.40 (m, 1H), 7.25 – 7.17 (m, 2H), 7.21 – 7.12 (m, 2H), 7.06 – 6.98 (m, 1H), 6.01 (bs, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.1,

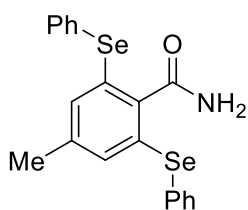
163.3 (d,  $J_{C-F} = 245.6$  Hz), 138.7, 135.7, 132.1, 131.9, 131.7 (d,  $J_{C-F} = 7.8$  Hz), 130.6, 128.0, 125.8, 125.3 (d,  $J_{C-F} = 4.0$  Hz), 117.0 (d,  $J_{C-F} = 23.3$  Hz), 116.1 (d,  $J_{C-F} = 24.1$  Hz).  $^{19}\text{F}\{^1\text{H}\}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -100.65. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_{11}\text{FNOSe}$ , 295.9984; found, 299.9986.

### **2,6-bis(phenylselanyl)benzamide (5a)**



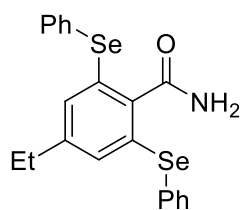
Following **GP-B**, **5a** was isolated as a white solid (33 mg, 77% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.7; mp 211-213 °C; IR (ATR): 3377, 3155, 1631, 1605, 1546, 1424, 1365, 742  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 – 7.51 (m, 4H), 7.37 – 7.28 (m, 6H), 7.10 (d,  $J = 8.1$  Hz, 2H), 7.00 (dd,  $J = 8.5, 7.1$  Hz, 1H), 5.97 (bs, 1H), 5.82 (bs, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.7, 134.7, 131.7, 131.3, 130.6, 130.4, 130.2, 129.8, 128.4. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{16}\text{NOSe}_2$ , 433.9557; found, 433.9552.

### **4-methyl-2,6-bis(phenylselanyl)benzamide (5b)**



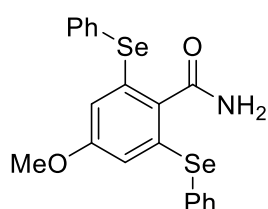
Following **GP-B**, **5b** was isolated as a white solid (31 mg, 70% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.8; mp 142-144 °C; IR (ATR): 3383, 3048, 2918, 1643, 1607, 1437, 1367, 745  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 – 7.48 (m, 4H), 7.36 – 7.27 (m, 6H), 7.00 (s, 2H), 5.82 (bs, 1H), 5.76 (bs, 1H), 2.11 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.0, 140.9, 137.7, 134.2, 133.1, 130.6, 130.5, 129.7, 128.2, 21.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{18}\text{NOSe}_2$ , 447.9713; found, 447.9712.

### **4-ethyl-2,6-bis(phenylselanyl)benzamide (5c)**



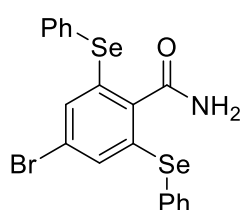
Following **GP-B**, **5c** was isolated as a white solid (29 mg, 64% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.7; mp 159-161 °C; IR (ATR): 3404, 3173, 2921, 1637, 1599, 1436, 1376, 736  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 – 7.47 (m, 4H), 7.34 – 7.28 (m, 6H), 7.01 (s, 2H), 6.01 (bs, 1H), 5.81 (bs, 1H), 2.39 (q,  $J = 7.6$  Hz, 2H), 0.99 (t,  $J = 7.6$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.1, 147.1, 137.7, 134.1, 131.9, 130.7, 130.6, 129.7, 128.2, 28.4, 15.1. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{20}\text{NOSe}_2$ , 461.9870; found, 461.9865.

#### **4-methoxy-2,6-bis(phenylselanyl)benzamide (5d)**



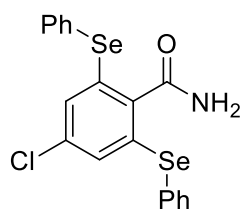
Following **GP-B**, **5d** was isolated as a white solid (33 mg, 72% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.8; mp 171-173 °C; IR (ATR): 3374, 3176, 2921, 1572, 1536, 1379, 1237, 739  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 – 7.51 (m, 4H), 7.39 – 7.26 (m, 6H), 6.55 (s, 2H), 5.97 (s, 2H), 3.46 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.8, 160.4, 135.1, 133.4, 130.9, 129.9, 129.8, 128.7, 116.4, 55.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{18}\text{NO}_2\text{Se}_2$ , 463.9662; found, 462.9657.

#### **4-bromo-2,6-bis(phenylselanyl)benzamide (5e)**



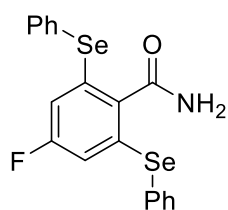
Following **GP-B**, **5e** was isolated as a white solid (31 mg, 60% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.7; mp 202-204 °C; IR (ATR): 3362, 3149, 2918, 1637, 1613, 1542, 1436, 1376, 728  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 – 7.53 (m, 4H), 7.39 – 7.31 (m, 6H), 7.12 (s, 2H), 6.06 (bs, 1H), 5.88 (bs, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.1, 137.1, 135.2, 133.7, 132.9, 130.1, 129.1, 129.0, 124.8. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{15}\text{BrNOSe}_2$ , 511.8662; found, 511.8637.

#### **4-chloro-2,6-bis(phenylselanyl)benzamide (5f)**



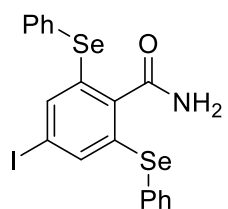
Following **GP-B**, **5f** was isolated as a white solid (25 mg, 55% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.7; mp 192-194 °C; IR (ATR): 3365, 3143, 2927, 1637, 1613, 1551, 1438, 1373, 727  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (dd,  $J = 7.6, 1.9$  Hz, 4H), 7.42 – 7.31 (m, 6H), 6.94 (s, 2H), 6.11 (bs, 1H), 5.91 (bs, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.0, 136.5, 135.4, 135.3, 133.6, 130.1, 129.9, 129.1, 128.9. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{19}\text{H}_{14}\text{ClNaOSe}_2$ , 489.8987; found, 489.8986.

#### 4-fluoro-2,6-bis(phenylselanyl)benzamide (**5g**)



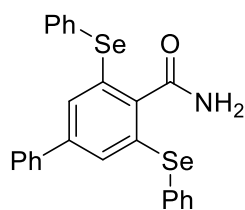
Following **GP-B**, **5g** was isolated as a white solid (23 mg, 51% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.7; mp 215-217 °C; IR (ATR): 3380, 3187, 2921, 1602, 1572, 1361, 1219, 742  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 – 7.57 (m, 4H), 7.43 – 7.33 (m, 6H), 6.61 (d,  $J = 8.6$  Hz, 2H), 5.95 (bs, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.0, 163.0 (d,  $J_{\text{C-F}} = 254.8$  Hz), 135.8, 135.0 (d,  $J_{\text{C-F}} = 7.3$  Hz), 130.1, 129.3, 128.7, 116.6 (d,  $J_{\text{C-F}} = 24.0$  Hz).  $^{19}\text{F}\{^1\text{H}\}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -109.98. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{19}\text{H}_{14}\text{FNaOSe}_2$ , 473.9282; found, 473.9288.

#### 4-iodo-2,6-bis(phenylselanyl)benzamide (**5h**)



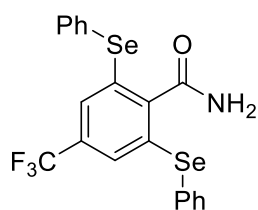
Following **GP-B**, **5h** was isolated as a white solid (34 mg, 61% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.7; mp 217-219 °C; IR (ATR): 3359, 3162, 2921, 1637, 1613, 1513, 1436, 730  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 – 7.51 (m, 4H), 7.41 – 7.30 (m, 8H), 5.95 (bs, 1H), 5.82 (bs, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.1, 139.1, 138.2, 134.9, 133.3, 130.0, 129.3, 129.0, 97.0. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{15}\text{INOSe}_2$ , 559.8523; found, 559.8509.

#### 3,5-bis(phenylselanyl)-[1,1'-biphenyl]-4-carboxamide (**5i**)



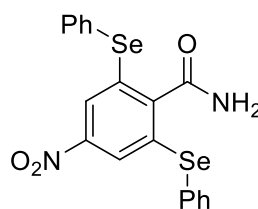
Following **GP-B**, **5i** was isolated as a white solid (34 mg, 68% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.7; mp 205-207 °C; IR (ATR): 3368, 3179, 2924, 1596, 1581, 1434, 1379, 690  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 – 7.54 (m, 4H), 7.37 (s, 2H), 7.35 – 7.28 (m, 9H), 7.22 (dd,  $J$  = 7.7, 1.9 Hz, 2H), 6.01 (bs, 1H), 5.89 (bs, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.8, 143.3, 139.1, 138.5, 134.5, 131.6, 130.6, 130.3, 129.8, 129.0, 128.4, 128.2, 127.1. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{25}\text{H}_{20}\text{NOSe}_2$ , 509.9870; found, 509.9875.

### 2,6-bis(phenylselanyl)-4-(trifluoromethyl)benzamide (**5j**)



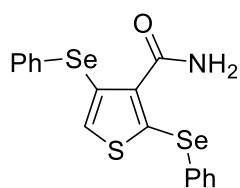
Following **GP-B**, **5j** was isolated as a white solid (21 mg, 42% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.8; mp 223-225 °C; IR (ATR): 3371, 3170, 2924, 1634, 1599, 1302, 1123, 733  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 – 7.53 (m, 4H), 7.44 – 7.31 (m, 6H), 7.23 (s, 2H), 6.08 (bs, 1H), 5.87 (bs, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  168.7, 141.4, 135.2, 133.2, 132.6, 132.4, 130.1, 129.2, 128.7, 127.1 (q,  $J_{\text{C-F}}$  = 3.6 Hz). 124.0, 121.8.  $^{19}\text{F}\{^1\text{H}\}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.29. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{15}\text{F}_3\text{NOSe}_2$ , 501.9431; found, 501.9440.

### 4-nitro-2,6-bis(phenylselanyl)benzamide (**5k**)



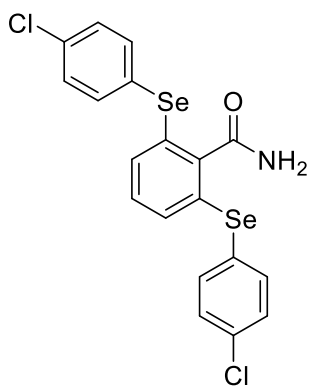
Following **GP-B**, **5k** was isolated as a white solid (17 mg, 36% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.8; mp 211-213 °C; IR (ATR): 3448, 3300, 2924, 1667, 1516, 1332, 1281, 733  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (s, 2H), 7.66 – 7.58 (m, 4H), 7.49 – 7.35 (m, 6H), 6.23 (bs, 1H), 5.97 (bs, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  168.2, 148.7, 142.1, 135.8, 134.8, 130.4, 129.8, 127.9, 123.9. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{19}\text{H}_{14}\text{N}_2\text{NaO}_3\text{Se}_2$ , 500.9227; found, 500.9225.

### 2,4-bis(phenylselanyl)thiophene-3-carboxamide (**5l**)



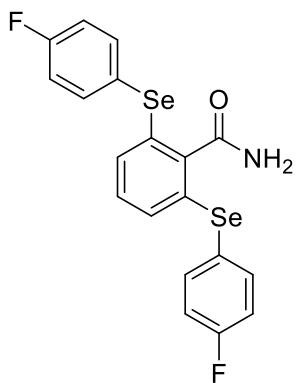
Following **GP-B**, **5l** was isolated as a white solid (31 mg, 71% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.6; mp 168-170 °C; IR (ATR): 3407, 3184, 2924, 1631, 1599, 1421, 1296, 733  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 – 7.66 (m, 2H), 7.47 (s, 1H), 7.42 – 7.34 (m, 3H), 7.32 – 7.29 (m, 2H), 7.25 – 7.20 (m, 3H), 6.00 (bs, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  164.7, 146.1, 136.6, 135.5, 132.9, 132.6, 130.4, 130.0, 129.6, 129.5, 129.3, 127.3, 124.4. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{14}\text{NOSSe}_2$ , 439.9121; found, 439.9117.

### 2,6-bis((4-chlorophenyl)selanyl)benzamide (**5m**)



Following **GP-B**, **5m** was isolated as a white solid (30 mg, 60% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.7; mp 193-195 °C; IR (ATR): 3404, 3303, 2924, 1625, 1607, 1424, 1089, 819  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 – 7.43 (m, 4H), 7.32 – 7.24 (m, 4H), 7.18 – 7.08 (m, 2H), 7.05– 7.01 (m, 1H), 5.93 (bs, 1H), 5.81 (bs, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.5, 139.7, 136.0, 134.9, 131.9, 131.1, 130.9, 130.0, 128.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{14}\text{Cl}_2\text{NOSe}_2$ , 501.8777; found, 501.8779.

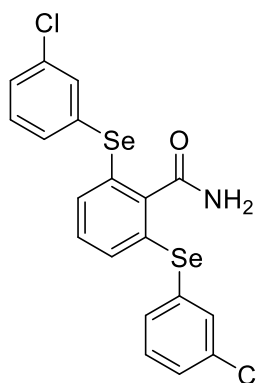
### 2,6-bis((4-fluorophenyl)selanyl)benzamide (**5n**)



Following **GP-B**, **5n** was isolated as a white solid (26 mg, 56% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.7; mp 177-179 °C; IR (ATR): 3401, 3301, 2925, 1621, 1580, 1485, 1426, 1222, 831  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 – 7.52 (m, 4H), 7.05 – 6.95 (m, 7H), 6.12 (bs, 1H), 5.90 (bs, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.6, 163.3 (d,  $J_{\text{C-F}} = 249.0$  Hz), 138.4, 137.5 (d,  $J_{\text{C-F}} = 8.0$  Hz), 132.0,

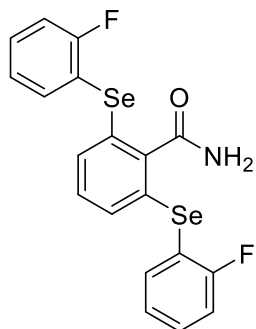
130.7, 130.6, 124.3 (d,  $J_{C-F} = 3.4$  Hz), 117.1 (d,  $J_{C-F} = 21.7$  Hz).  $^{19}\text{F}\{^1\text{H}\}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -112.15. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{14}\text{F}_2\text{NOSe}_2$ , 469.9368; found, 469.9369.

### 2,6-bis((3-chlorophenyl)selanyl)benzamide (5o)



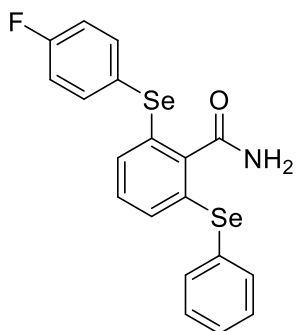
Following **GP-B**, **5o** was isolated as a white solid (24 mg, 49% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.7; mp 172-174 °C; IR (ATR): 3395, 3297, 2921, 1628, 1604, 1541, 1424, 1358  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (t,  $J = 1.8$  Hz, 2H), 7.42 – 7.32 (m, 2H), 7.37 – 7.28 (m, 2H), 7.27 – 7.20 (m, 4H), 7.12 – 7.08 (m, 1H), 5.92 (bs, 1H), 5.78 (bs, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.4, 140.7, 135.3, 133.7, 132.9, 132.2, 132.0, 131.0, 130.8, 130.3, 128.6. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{14}\text{Cl}_2\text{NOSe}_2$ , 501.8777; found, 501.8775.

### 2,6-bis((2-fluorophenyl)selanyl)benzamide (5p)



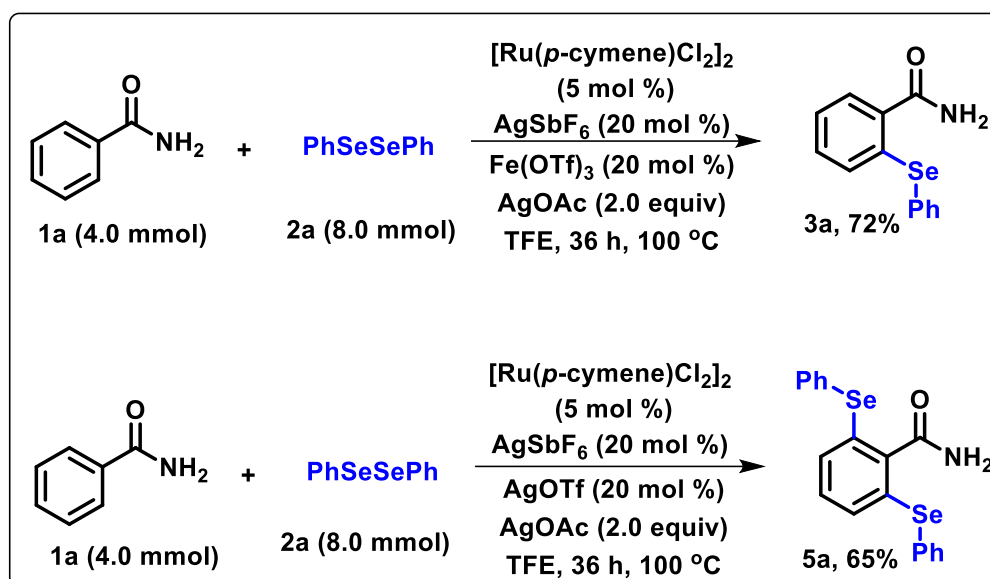
Following **GP-B**, **5p** was isolated as a white solid (27 mg, 58% yield);  $R_f$  (1:1 hexane/ethyl acetate) = 0.7; mp 138-140 °C; IR (ATR): 3407, 3253, 2928, 1625, 1592, 1491, 1235, 829  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.11 (s, 1H), 7.86 (s, 1H), 7.51 – 7.40 (m, 4H), 7.31 (td,  $J = 8.8, 1.3$  Hz, 2H), 7.20 (td,  $J = 7.6, 1.3$  Hz, 2H), 7.13 (dd,  $J = 8.3, 7.3$  Hz, 1H), 7.02 (d,  $J = 7.8$  Hz, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{DMSO-}d_6$ )  $\delta$  168.8, 161.11 (d,  $J_{C-F} = 249.0$  Hz), 141.8, 136.2, 131.2 (d,  $J_{C-F} = 7.8$  Hz), 131.0, 130.5, 128.8, 125.8 (d,  $J_{C-F} = 3.5$  Hz), 116.6 (d,  $J_{C-F} = 22.2$  Hz), 116.0 (d,  $J_{C-F} = 23.3$  Hz).  $^{19}\text{F}\{^1\text{H}\}$  NMR (471 MHz,  $\text{DMSO-}d_6$ )  $\delta$  -102.89. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{14}\text{F}_2\text{NOSe}_2$ , 469.9368; found, 469.9392.

### 2-((4-fluorophenyl)selanyl)-6-(phenylselanyl)benzamide (5q)



To a clean oven-dried seal tube equipped with a magnetic stir bar was sequentially added **3a** (0.1 mmol, 1.0 equiv), 1,2-bis(4-fluorophenyl)diselane (2.0 equiv) (**2d**),  $[\text{RuCl}_2(p\text{-cymene})]_2$  (5.0 mol %), AgOTf (20 mol %) and AgOAc (2.0 equiv.) in  $\text{CF}_3\text{CH}_2\text{OH}$  (2.0 mL). Subsequently,  $\text{AgSbF}_6$  (20 mol %) was added under an argon atmosphere, and the reaction tube was flushed with argon. The tube was tightly closed, placed in a preheated oil bath at 100 °C and stirred for 24 h according to the conversion estimated by TLC. At ambient temperature, the reaction mixture was quenched with  $\text{H}_2\text{O}$  (10 mL) and extracted with EtOAc ( $3 \times 15$  mL). The combined organic layer was washed with brine and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After filtration and evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel (100-200 mesh) using ethyl acetate/hexane as eluent to give the desired product **5q** (white solid, 22 mg, 49% yield).  $R_f$  (50% Ethyl acetate in Hexane) = 0.8; mp 196-198 °C; IR (ATR): 3393, 3301, 2921, 1622, 1580, 1425, 1220, 830  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 – 7.52 (m, 4H), 7.37 – 7.28 (m, 3H), 7.10 (dd,  $J = 7.4, 1.4$  Hz, 1H), 7.05 – 6.94 (m, 4H), 5.99 (bs, 1H), 5.85 (bs, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.6, 163.3 (d,  $J_{\text{C-F}} = 249.3$  Hz), 139.0, 137.5 (d,  $J_{\text{C-F}} = 8.1$  Hz), 134.7, 132.0, 131.5, 131.3, 130.8, 130.7, 130.0, 129.8, 128.5, 124.4 (d,  $J_{\text{C-F}} = 3.5$  Hz), 117.1 (d,  $J_{\text{C-F}} = 21.3$  Hz).  $^{19}\text{F}\{^1\text{H}\}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -112.28. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{15}\text{FNOSe}_2$ , 451.9463; found, 451.9457.

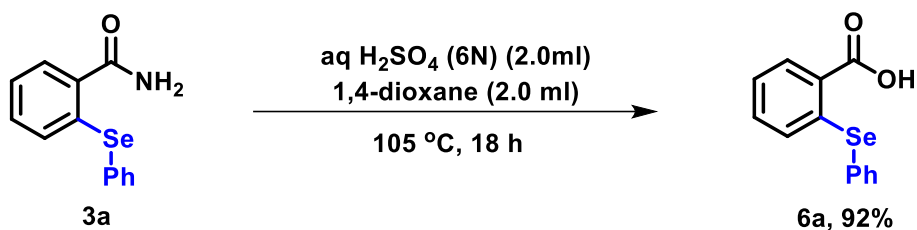
## 7. Procedure for scale-up synthesis



To a clean oven-dried seal tube equipped with a magnetic stir bar was sequentially added benzamide (**1a**) (4.0 mmol, 1.0 equiv), 1,2-diphenyldiselenane (2.0 equiv) (**2a**), [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (5.0 mol %), Fe(OTf)<sub>3</sub>/AgOTf (20 mol %) and AgOAc (2.0 equiv.) in CF<sub>3</sub>CH<sub>2</sub>OH (2.0 mL). Subsequently, AgSbF<sub>6</sub> (20 mol %) was added under an argon atmosphere, and the reaction tube was flushed with argon. The tube was tightly closed, placed in a preheated oil bath at 100 °C and stirred for 36 h according to the conversion estimated by TLC. At ambient temperature, the reaction mixture was quenched with H<sub>2</sub>O (10 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel (100-200 mesh) using ethyl acetate/hexane as eluent to give the desired products **3a** and **5a** in 72% and 65% yield.

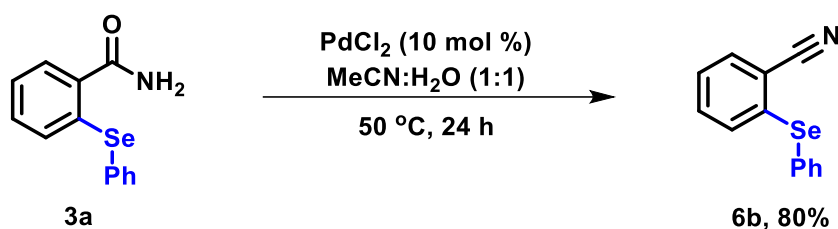
## 8. Procedures for synthesis of synthetic derivatives

### *Synthesis of 2-(phenylselanyl)benzoic acid (6a)*



By following a reported procedure,<sup>3</sup> **3a** (55 mg, 0.2 mmol) dissolved in a mixture of 1,4-dioxane (2 mL) and 6 N aqueous H<sub>2</sub>SO<sub>4</sub> (2 mL). The reaction mixture was then heated at 105 °C. After 18 hours, heating was stopped, and the solution was cooled to room temperature. H<sub>2</sub>O (10 mL) was added to precipitate the product. The solid was extracted with ethyl acetate, dried in vacuo and purified by column chromatography to give **6a** (white solid, 51 mg, 92% yield). *R<sub>f</sub>* (50% Ethyl acetate in Hexane) = 0.5; mp 185-187 °C; IR (ATR): 2924, 1667, 1415, 1258, 733 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 8.19 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.75 – 7.71 (m, 2H), 7.50 – 7.41 (m, 3H), 7.29 – 7.17 (m, 2H), 6.94 (dd, *J* = 8.0, 1.3 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 171.7, 141.7, 137.8, 133.6, 132.6, 130.0, 129.4, 129.2, 128.8, 126.2, 125.0. The NMR data of **6a** are in accordance with previous literature.<sup>4</sup>

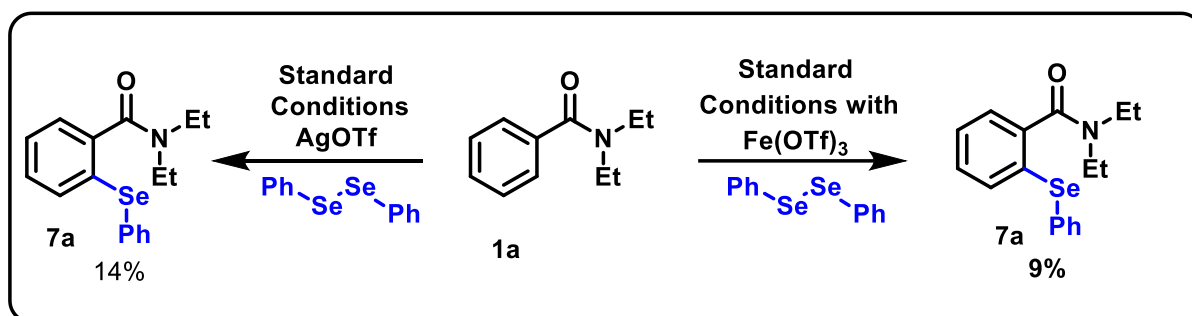
#### Synthesis of 2-(phenylselanyl)benzonitrile (**6b**)



By following a reported procedure,<sup>5</sup> **3a** (0.2 mmol, 55 mg) and PdCl<sub>2</sub> (10 mol %, 3.5 mg) in CH<sub>3</sub>CN/H<sub>2</sub>O (1:1) (6 mL) were stirred at 50 °C for 24 h in a round-bottom flask. After completion, the reaction mixture was quenched with water and extracted with ethyl acetate (10 mL × 3). The solvent was removed in a vacuum, and the crude product was purified by column chromatography to afford **6b** (yellow oil, 41 mg, 80% yield). *R<sub>f</sub>* (30% Ethyl acetate in Hexane) = 0.7; IR (ATR): 2922, 2223, 1577, 1463, 1439, 1428, 763, 735 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz,

CDCl<sub>3</sub>) 7.67 – 7.56 (m, 3H), 7.44 – 7.31 (m, 4H), 7.30 – 7.27 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 137.7, 135.4, 133.9, 133.1, 132.5, 130.0, 129.1, 128.2, 127.1, 117.7, 115.0. HRMS (ESI-TOF) m/z: [M + H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>10</sub>NSe, 259.9973; found, 259.9979.

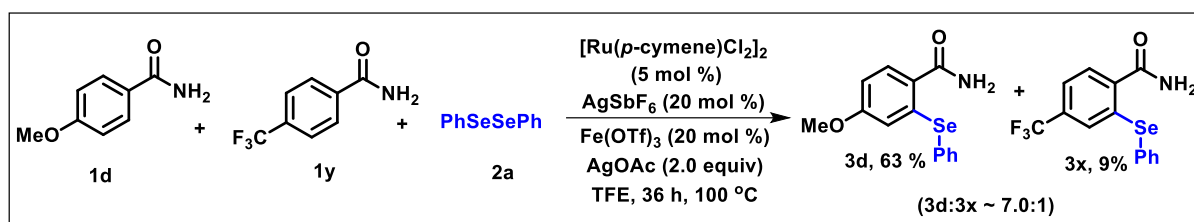
### 9. Procedure for Control Experiments supporting N-directed cyclometallation



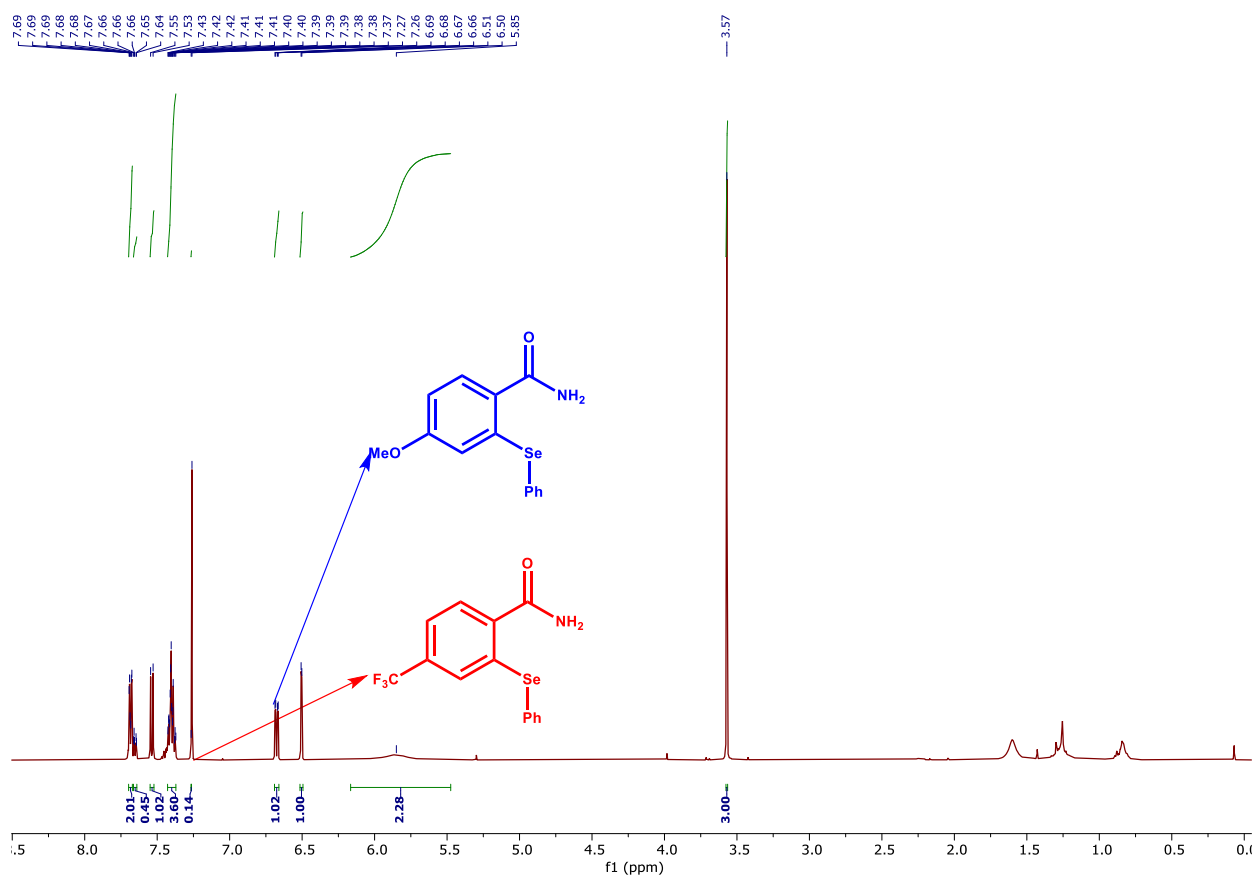
To a clean oven-dried seal tube equipped with a magnetic stir bar was sequentially added *N,N*-diethyl benzamide (0.1 mmol, 1.0 equiv), 1,2-diphenyldiselenane (2.0 equiv) (**2a**), [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (5.0 mol %), Fe(OTf)<sub>3</sub>/AgOTf (20 mol %) and AgOAc (2.0 equiv.) in CF<sub>3</sub>CH<sub>2</sub>OH (2.0 mL). Subsequently, AgSbF<sub>6</sub> (20 mol %) was added under an argon atmosphere, and the reaction tube was flushed with argon. The tube was tightly closed, placed in a preheated oil bath at 100 °C and stirred for 36 h. The reaction was then brought to an ambient temperature, quenched with H<sub>2</sub>O (10 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel (100-200 mesh) using ethyl acetate/hexane as eluent to give the desired products **7a** in 9% and 14% yield respectively in the presence of Fe(OTf)<sub>3</sub> and AgOTf as an additive. *N,N*-diethyl-2-(phenylselanyl)benzamide (**7a**): Isolated as colourless liquid; *R<sub>f</sub>* (30% Ethyl acetate in Hexane) = 0.5; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.56 – 7.53 (m, 2H), 7.31 – 7.26 (m, 4H), 7.25 – 7.23 (m, 2H), 7.21 – 7.16 (m, 1H), 3.58 (q, *J* = 7.1 Hz, 2H), 3.16 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 4H), 1.07 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 169.9, 139.7, 134.5, 133.4, 130.1, 129.7, 129.6, 129.4, 128.0, 127.2, 126.5, 43.0, 39.1, 14.2, 12.8.

## 10. Procedure for Intermolecular Competition Experiments

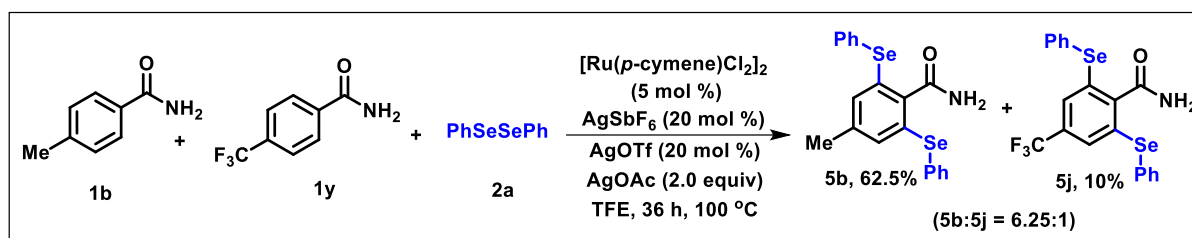
### Intermolecular Competition Experiment between **1d** and **1y**



To a clean oven-dried seal tube equipped with a magnetic stir bar was sequentially added arylamide (**1d** and **1y**) (0.1 mmol, 1.0 equiv), 1,2-diphenyldiselenane (**2a**) (2.0 equiv),  $[\text{RuCl}_2(p\text{-cymene})]_2$  (5.0 mol %),  $\text{AgOTf}$  (20 mol %) and  $\text{AgOAc}$  (2.0 equiv.) in  $\text{CF}_3\text{CH}_2\text{OH}$  (2.0 mL). Subsequently,  $\text{AgSbF}_6$  (20 mol %) was added under an argon atmosphere, and the reaction tube was flushed with argon. The tube was tightly closed, placed in a preheated oil bath at 100 °C and stirred for 36 h. At ambient temperature, the reaction mixture was quenched with  $\text{H}_2\text{O}$  (10 mL) and extracted with  $\text{EtOAc}$  ( $3 \times 15$  mL). The combined organic layer was washed with brine and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After filtration and evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel (100-200 mesh) using ethyl acetate/hexane as eluent to give a mixture of products **3d** and **3x** in a combined yield of 72% in the ratio of  $\sim 7:1$  as determined by  $^1\text{H}$  NMR.

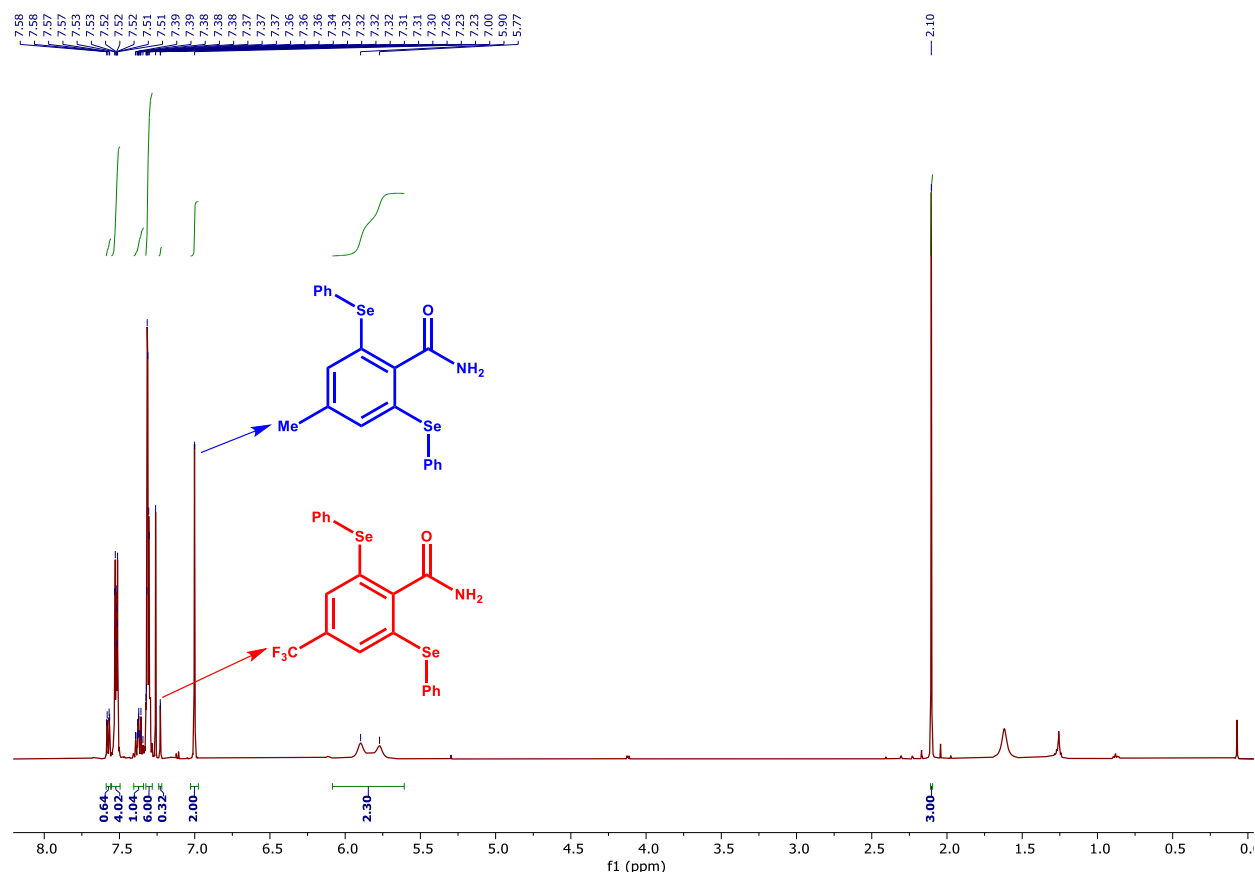


### Intermolecular Competition Experiment between **1b** and **1y**

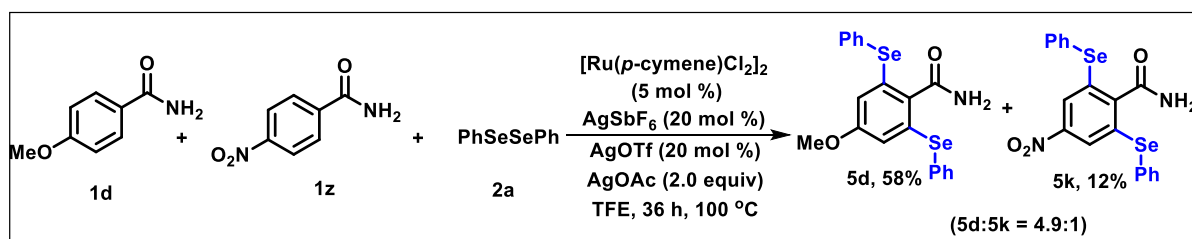


To a clean oven-dried seal tube equipped with a magnetic stir bar was sequentially added arylamide (**1b** and **1y**) (0.1 mmol, 1.0 equiv), 1,2-diphenyldiselenane (**2a**) (2.0 equiv), [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (5.0 mol %), AgOTf (20 mol %) and AgOAc (2.0 equiv.) in CF<sub>3</sub>CH<sub>2</sub>OH (2.0 mL). Subsequently, AgSbF<sub>6</sub> (20 mol %) was added under an argon atmosphere, and the reaction tube was flushed with argon. The tube was tightly closed, placed in a preheated oil bath at 100 °C and stirred for 36 h. At ambient temperature, the reaction mixture was quenched with H<sub>2</sub>O (10 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layer was washed with

brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel (100-200 mesh) using ethyl acetate/hexane as eluent to give a mixture of products **5b** and **5j** in a combined yield of 62.5% in the ratio of 6.25:1 as determined by <sup>1</sup>H NMR.

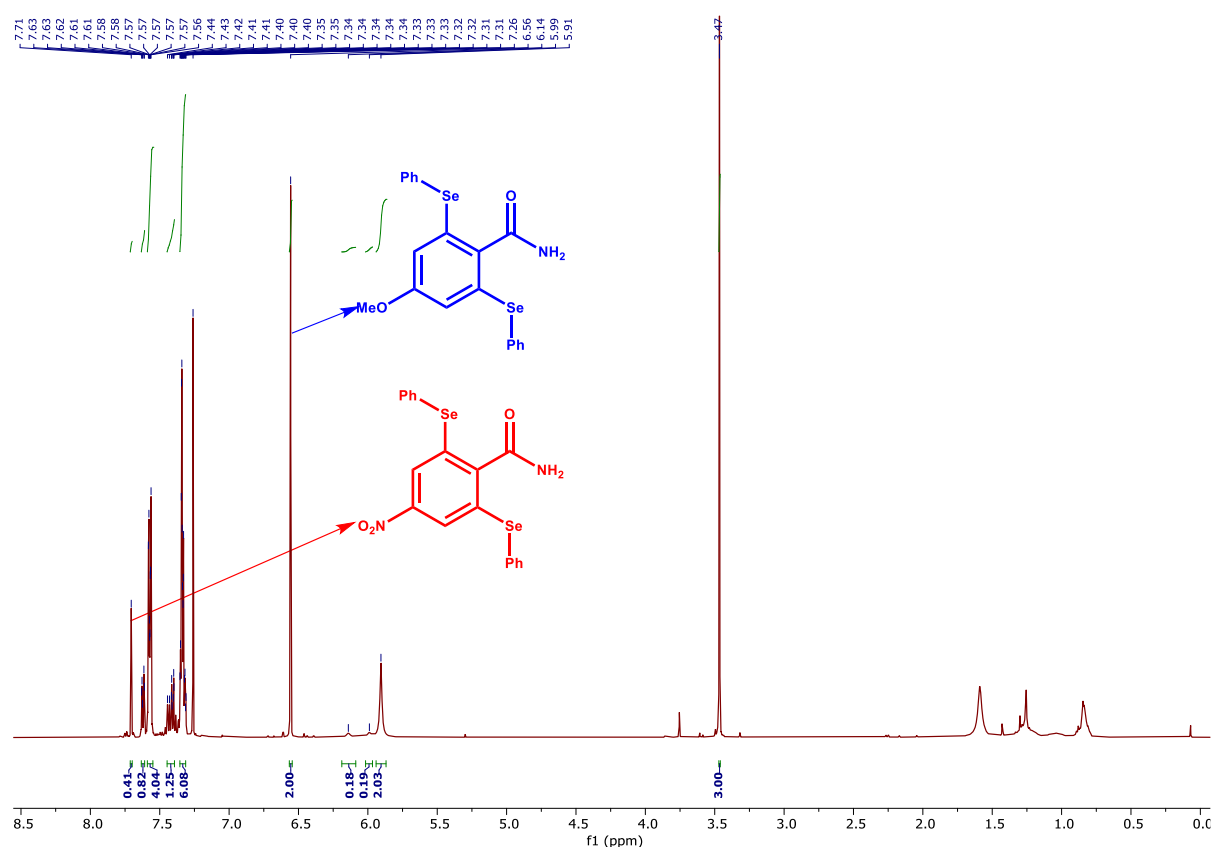


### Intermolecular Competition Experiment between **1d** and **1z**



To a clean oven-dried seal tube equipped with a magnetic stir bar was sequentially added arylamide (**1d** and **1z**) (0.1 mmol, 1.0 equiv), 1,2-diphenyldiselenane (**2a**) (2.0 equiv), [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (5.0 mol %), AgOTf (20 mol %) and AgOAc (2.0 equiv.) in CF<sub>3</sub>CH<sub>2</sub>OH (2.0 mL).

Subsequently, AgSbF<sub>6</sub> (20 mol %) was added under an argon atmosphere, and the reaction tube was flushed with argon. The tube was tightly closed, placed in a preheated oil bath at 100 °C and stirred for 36 h. At ambient temperature, the reaction mixture was quenched with H<sub>2</sub>O (10 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel (100-200 mesh) using ethyl acetate/hexane as eluent to give a mixture of products **5d** and **5k** in a combined yield of 70% in the ratio of 4.9:1 as determined by <sup>1</sup>H NMR.

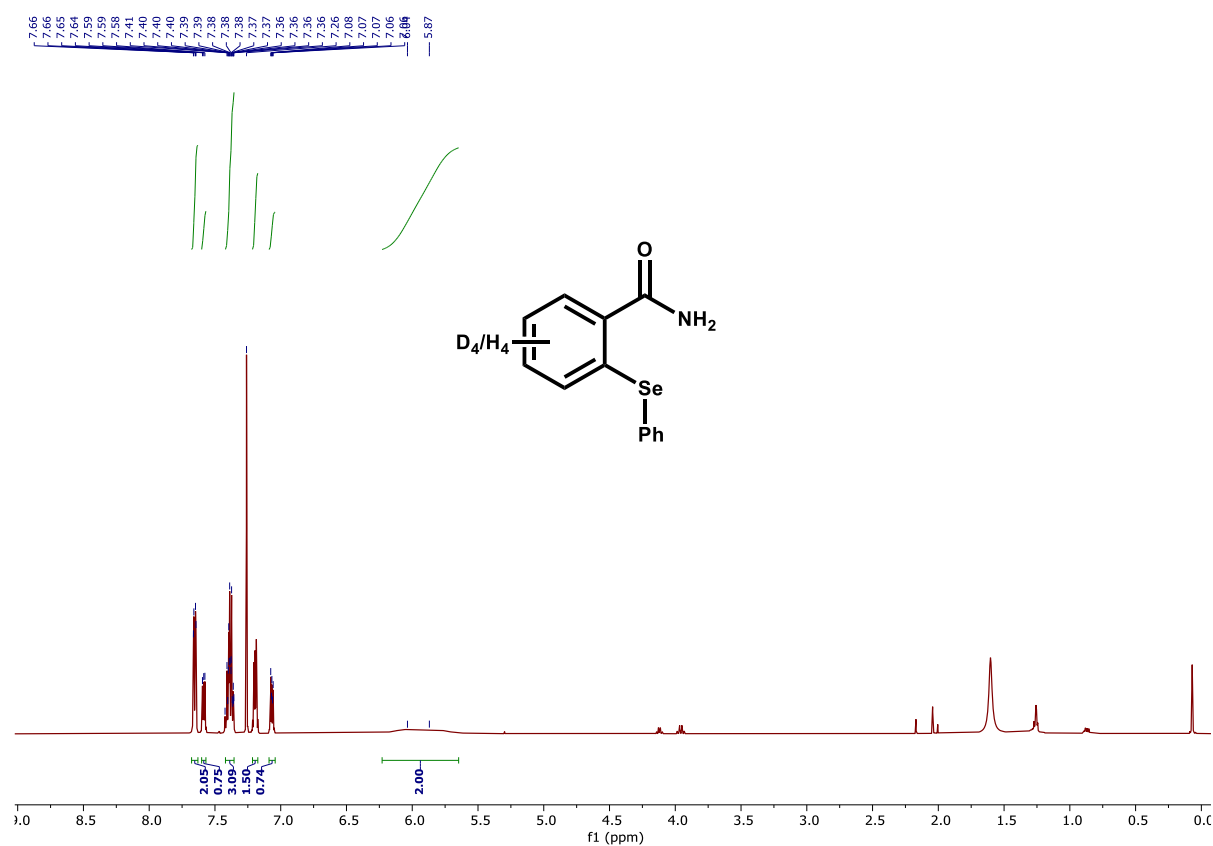


## 11. Procedure for KIE (Kinetic Isotopic Effect) Experiment between **1a** and **1a-D<sub>5</sub>**

### (i) *Competitive KIE*

To a clean oven-dried seal tube equipped with a magnetic stir bar was sequentially added benzamide **1a** (0.1 mmol, 1.0 equiv), deuterated benzamide **1a-D<sub>5</sub>** (0.1 mmol, 1.0 equiv), 1,2-

diphenyldiselenane **2a** (2.0 equiv), [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (5.0 mol %), Fe(OTf)<sub>3</sub> (20 mol %) and AgOAc (2.0 equiv.) in CF<sub>3</sub>CH<sub>2</sub>OH (2.0 mL). Subsequently, AgSbF<sub>6</sub> (20 mol %) was added under an argon atmosphere, and the reaction tube was flushed with argon. The tube was tightly closed, placed in a preheated oil bath at 100 °C and stirred for 3 h. At ambient temperature, the reaction mixture was quenched with H<sub>2</sub>O (10 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel (100-200 mesh) using ethyl acetate/hexane as eluent to give 21% of the product in combined yield. The ratio of **3a** and **3a-D<sub>4</sub>** was determined by <sup>1</sup>H NMR analysis and found to be  $k_H/k_D \approx 3:1$ .



**(ii) Parallel KIE**

**Reaction A.** To a clean oven-dried seal tube equipped with a magnetic stir bar was sequentially added benzamide **1a** (0.1 mmol, 1.0 equiv), 1,2-diphenyldisilane **2a** (2.0 equiv), [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (5.0 mol %), Fe(OTf)<sub>3</sub> (20 mol %) and AgOAc (2.0 equiv.) in CF<sub>3</sub>CH<sub>2</sub>OH (2.0 mL). Subsequently, AgSbF<sub>6</sub> (20 mol %) was added under an argon atmosphere, and the reaction tube was flushed with argon. The tube was tightly closed, placed in a preheated oil bath at 100 °C and stirred for 3 h.

**Reaction B.** To a clean oven-dried seal tube equipped with a magnetic stir bar was sequentially added deuterated benzamide **1a-D<sub>5</sub>** (0.1 mmol, 1.0 equiv), 1,2-diphenyldisilane **2a** (2.0 equiv), [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (5.0 mol %), Fe(OTf)<sub>3</sub> (20 mol %) and AgOAc (2.0 equiv.) in CF<sub>3</sub>CH<sub>2</sub>OH (2.0 mL). Subsequently, AgSbF<sub>6</sub> (20 mol %) was added under an argon atmosphere, and the reaction tube was flushed with argon. The tube was tightly closed, placed in a preheated oil bath at 100 °C and stirred for 3 h.

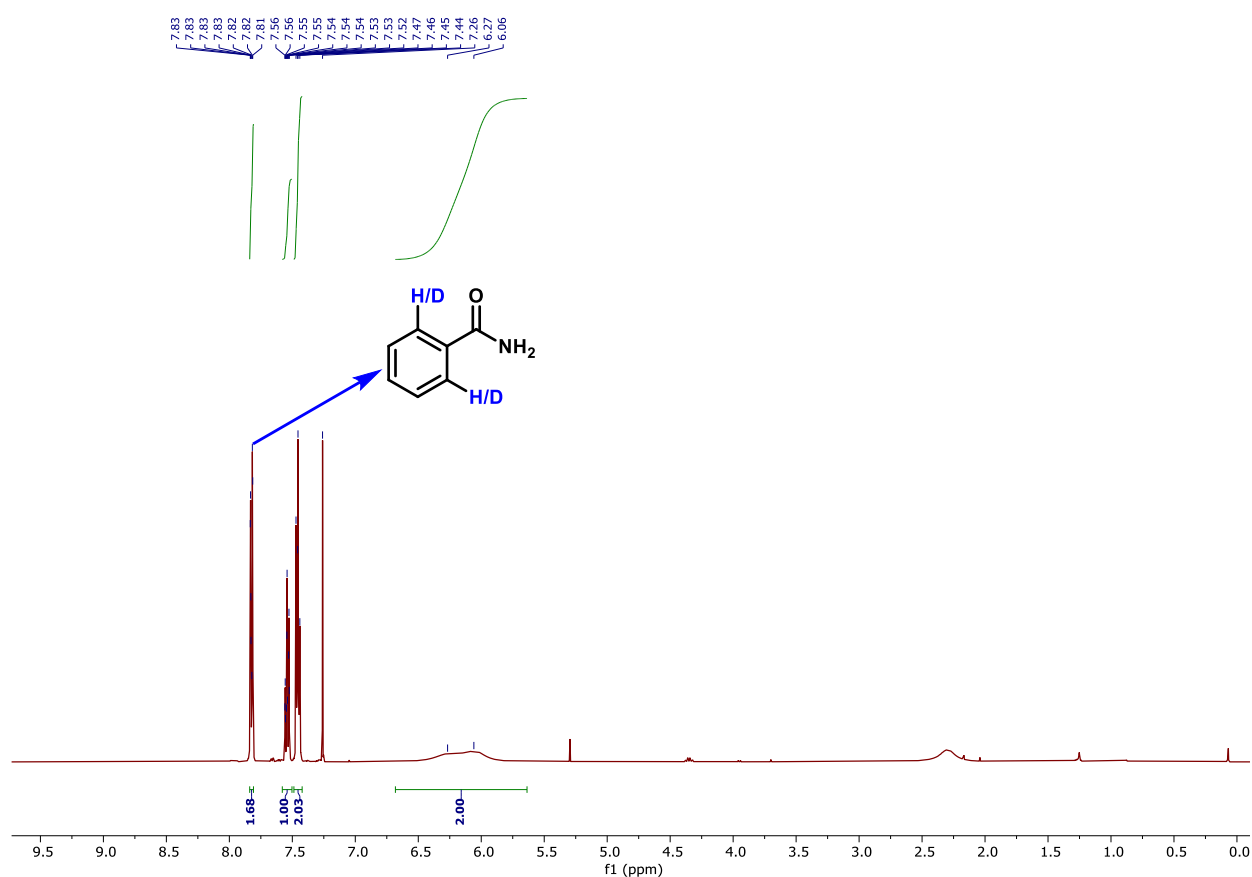
After that, both reactions A & B were cooled to ambient temperature. The reaction mixtures were quenched with H<sub>2</sub>O (10 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvent in vacuo, the crude products were purified by column chromatography on silica gel (100-200 mesh) using a 1:1 ethyl acetate/hexane mixture as the eluent to yield **3a** and **3a-D<sub>4</sub>** in 20% and 6% yield, respectively. The kinetic isotopic effect (KIE) was found to be  $k_H/k_D \approx 3:33$  through the independent parallel experiments.

## 12. Procedure for H/D exchange experiment with/without 1,2-diphenyldisilane

### ***H/D* exchange experiment without 1,2-diphenyldisilane [with Fe(OTf)<sub>3</sub> as additive]**

To a clean oven-dried seal tube equipped with a magnetic stir bar was sequentially added benzamide **1a** (0.1 mmol, 1.0 equiv), [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (5.0 mol %), Fe(OTf)<sub>3</sub> (20 mol %), AgOAc (2.0 equiv) and MeOD (0.2mL) in CF<sub>3</sub>CH<sub>2</sub>OH (2.0 mL) . Subsequently, AgSbF<sub>6</sub> (20

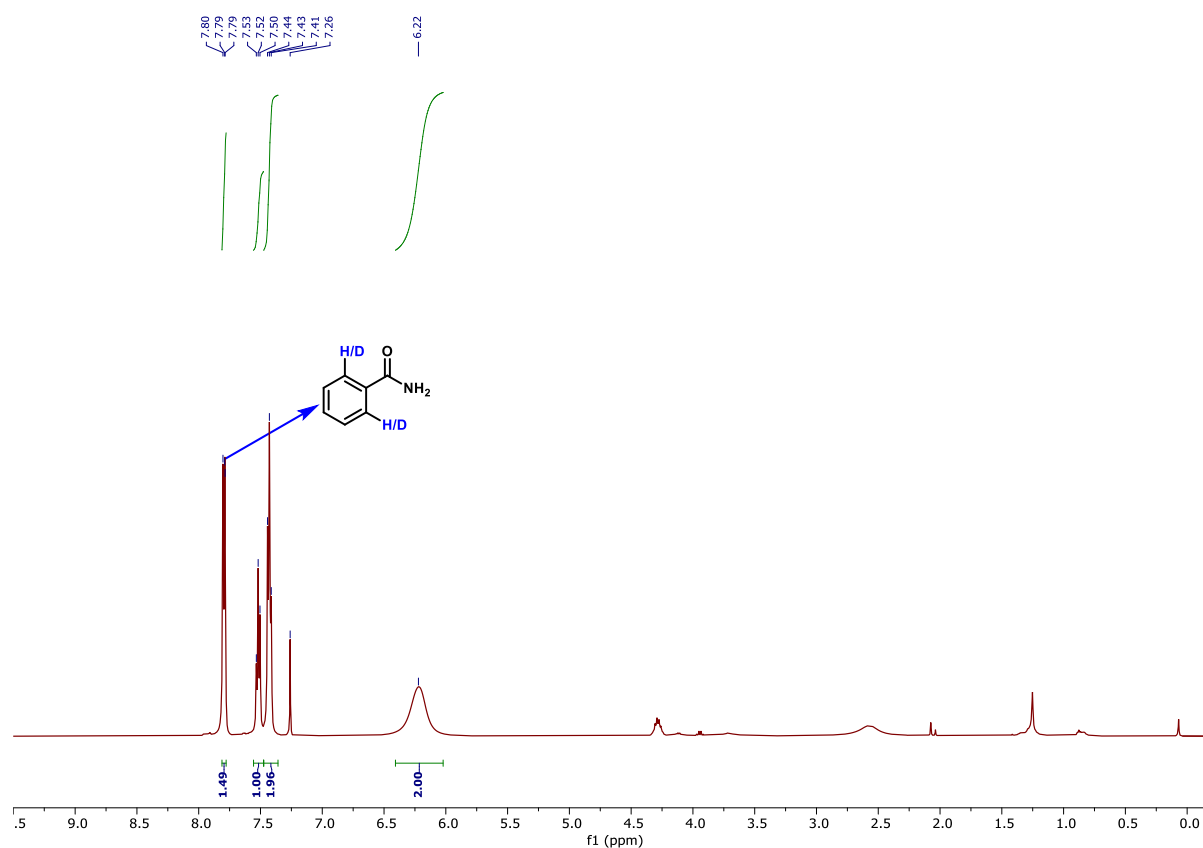
mol %) was added under an argon atmosphere, and the reaction tube was flushed with argon. The tube was tightly closed, placed in a preheated oil bath at 100 °C and stirred for 36 h. At ambient temperature, the reaction mixture was quenched with H<sub>2</sub>O (10 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel (100-200 mesh) using ethyl acetate/hexane as eluent. The desired product was obtained in 98% yield and the amount of deuteration, as determined by <sup>1</sup>H NMR analysis, was found to be 16% at the *ortho*-position.



### ***H/D* exchange experiment without 1,2-diphenyldisilane [with AgOTf as additive]**

To a clean oven-dried seal tube equipped with a magnetic stir bar was sequentially added benzamide **1a** (0.1 mmol, 1.0 equiv), [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (5.0 mol %), AgOTf (20 mol %), AgOAc (2.0 equiv) and MeOD (0.2 mL) in CF<sub>3</sub>CH<sub>2</sub>OH (2.0 mL). Subsequently, AgSbF<sub>6</sub> (20

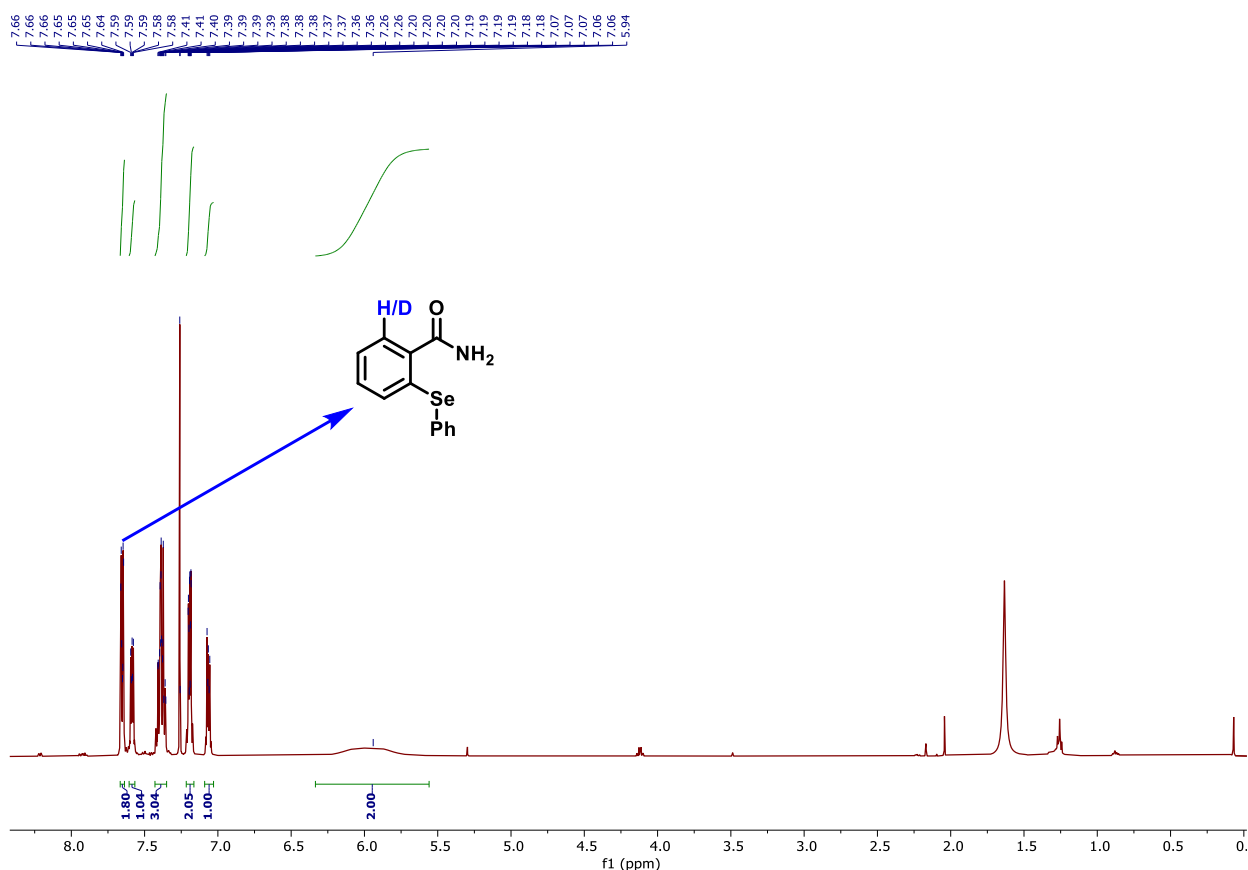
mol %) was added under an argon atmosphere, and the reaction tube was flushed with argon. The tube was tightly closed, placed in a preheated oil bath at 100 °C and stirred for 36 h. At ambient temperature, the reaction mixture was quenched with H<sub>2</sub>O (10 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel (100-200 mesh) using ethyl acetate/hexane as eluent. The desired product was obtained in 96% yield and the amount of deuteration, as determined by <sup>1</sup>H NMR analysis, was found to be 26% at the *ortho*-position.



### *H/D exchange experiment with 1,2-diphenyldisilane*

To a clean oven-dried seal tube equipped with a magnetic stir bar was sequentially added benzamide **1a** (0.1 mmol, 1.0 equiv), 1,2-diphenyldisilane **2a** (2.0 equiv), [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (5.0 mol %), Fe(OTf)<sub>3</sub> (20 mol %), AgOAc (2.0 equiv) and MeOD (0.2 mL) in CF<sub>3</sub>CH<sub>2</sub>OH (2.0

mL) . Subsequently, AgSbF<sub>6</sub> (20 mol %) was added under an argon atmosphere, and the reaction tube was flushed with argon. The tube was tightly closed, placed in a preheated oil bath at 100 °C and stirred for 36 h. At ambient temperature, the reaction mixture was quenched with H<sub>2</sub>O (10 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel (100-200 mesh) using ethyl acetate/hexane as eluent. The desired product was obtained in 72% yield and the amount of deuteration, as determined by <sup>1</sup>H NMR analysis, was found to be 20% at the *ortho*-position.



### 13. Procedure for radical inhibition experiment.

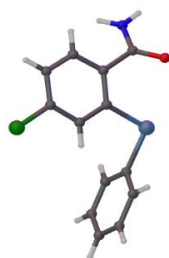
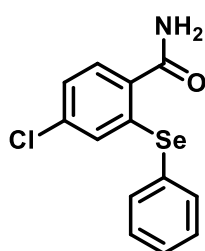
To a clean oven-dried seal tube equipped with a magnetic stir bar was sequentially added benzamide **1a** (0.1 mmol, 1.0 equiv), 1,2-diphenyldisilane **2a** (2.0 equiv), [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub>

(5.0 mol %), Fe(OTf)<sub>3</sub> (20 mol %), AgOAc (2.0 equiv) and TEMPO (1.5 equiv) in CF<sub>3</sub>CH<sub>2</sub>OH (2.0 mL). Subsequently, AgSbF<sub>6</sub> (20 mol %) was added under an argon atmosphere, and the reaction tube was flushed with argon. The tube was tightly closed, placed in a preheated oil bath at 100 °C and stirred for 36 h. At ambient temperature, the reaction mixture was quenched with H<sub>2</sub>O (10 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel (100-200 mesh) using ethyl acetate/hexane as eluent to give desired product (**3a**) in 62% yield.

#### 14. Crystal data for products

A suitable single crystal of compounds (**3f** /**3t**) were carefully selected under a polarizing microscope and mounted at the tip of the thin glass fiber using cyanoacrylate (super glue) adhesive. Single crystals were grown in a test tube at room temperature using MeOH as a solvent over a period of 3-4 weeks by slow evaporation of solvent. Single crystal XRD patterns were recorded using a Bruker AXS (D8 Quest system) X-ray diffractometer equipped with Photon 100 CMOS detector at 293 K. The X-ray generator was operated at 50 kV and 30 mA using Mo-K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation.

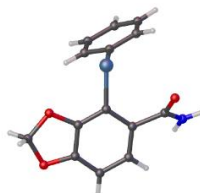
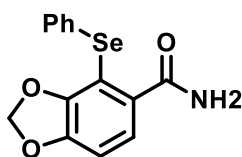
XRD data of **3f** (CCDC Number: 2518317)



<b>Empirical formula</b>	<b>C<sub>13</sub>H<sub>10</sub>ClNOSe</b>
<b>Formula weight</b>	<b>310.63</b>
<b>Temperature/K</b>	<b>273.15</b>
<b>Crystal system</b>	<b>monoclinic</b>
<b>Space group</b>	<b>P2<sub>1</sub>/C</b>
<b>a/Å</b>	<b>5.2679(2)</b>
<b>b/Å</b>	<b>10.7453(5)</b>

<b>c/Å</b>	<b>22.8596(10)</b>
<b>α/°</b>	<b>90</b>
<b>β/°</b>	<b>93.002(2)</b>
<b>γ/°</b>	<b>90</b>
<b>Volume/Å<sup>3</sup></b>	<b>1292.20(10)</b>
<b>Z</b>	<b>4</b>
<b>ρ<sub>calc</sub> g/cm<sup>3</sup></b>	<b>1.597</b>
<b>μ/mm<sup>-1</sup></b>	<b>3.094</b>
<b>F(000)</b>	<b>616.0</b>
<b>Radiation</b>	<b>MoKα (λ = 0.71073)</b>
<b>2θ range for data collection/°</b>	<b>4.19 to 56.518</b>
<b>Index ranges</b>	<b>-7 ≤ h ≤ 6, -14 ≤ k ≤ 14, -30 ≤ l ≤ 30</b>
<b>Reflections collected</b>	<b>18995</b>
<b>Independent reflections</b>	<b>3185 [R<sub>int</sub> = 0.0511, R<sub>sigma</sub> = 0.0371]</b>
<b>Data/restraints/parameters</b>	<b>3185/0/154</b>
<b>Goodness-of-fit on F<sup>2</sup></b>	<b>1.086</b>
<b>Final R indexes [I ≥ 2σ (I)]</b>	<b>R<sub>1</sub> = 0.0436, wR<sub>2</sub> = 0.1293</b>
<b>Final R indexes [all data]</b>	<b>R<sub>1</sub> = 0.0862, wR<sub>2</sub> = 0.1759</b>
<b>Largest diff. peak/hole /e Å<sup>-3</sup></b>	<b>0.59/-0.69</b>

XRD data of **3t** (CCDC Number: 2537738)



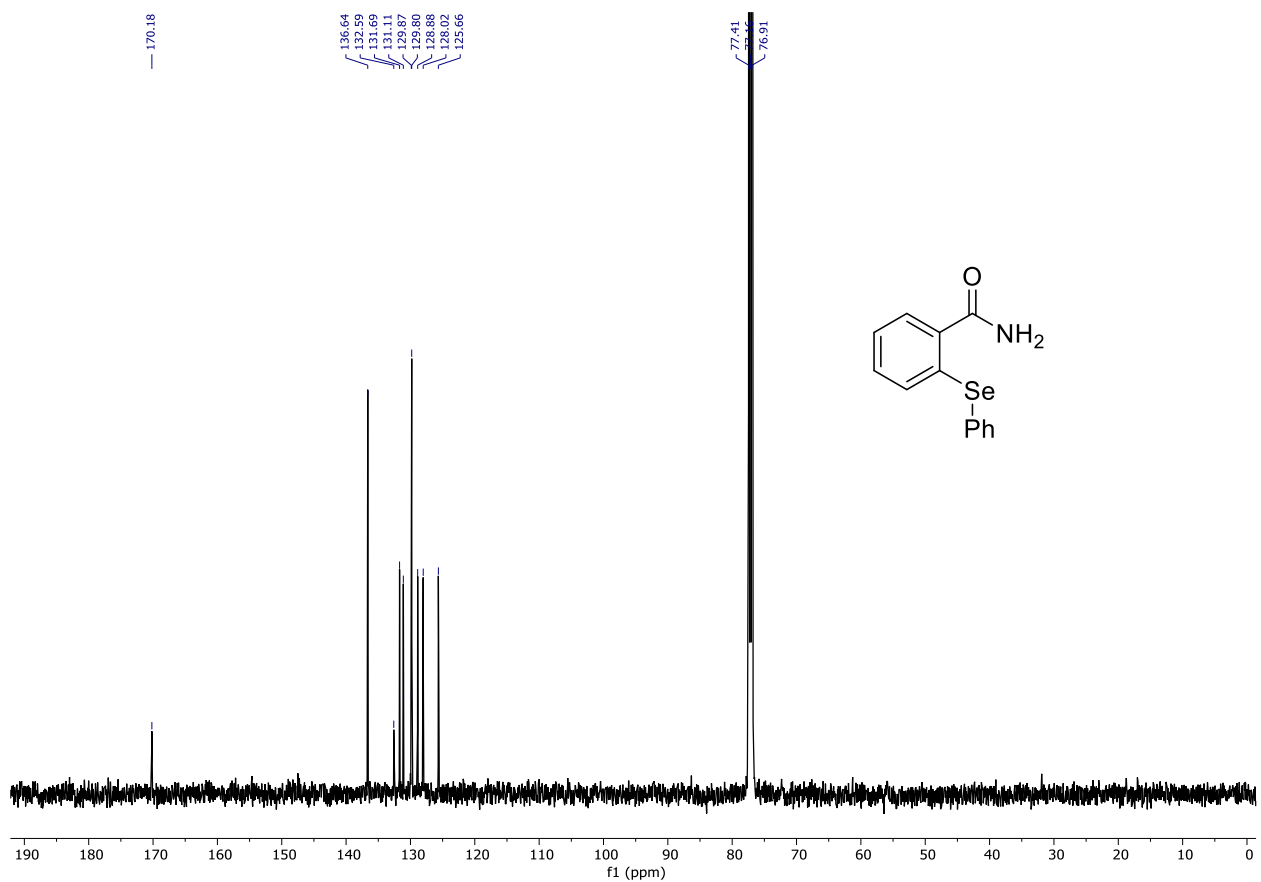
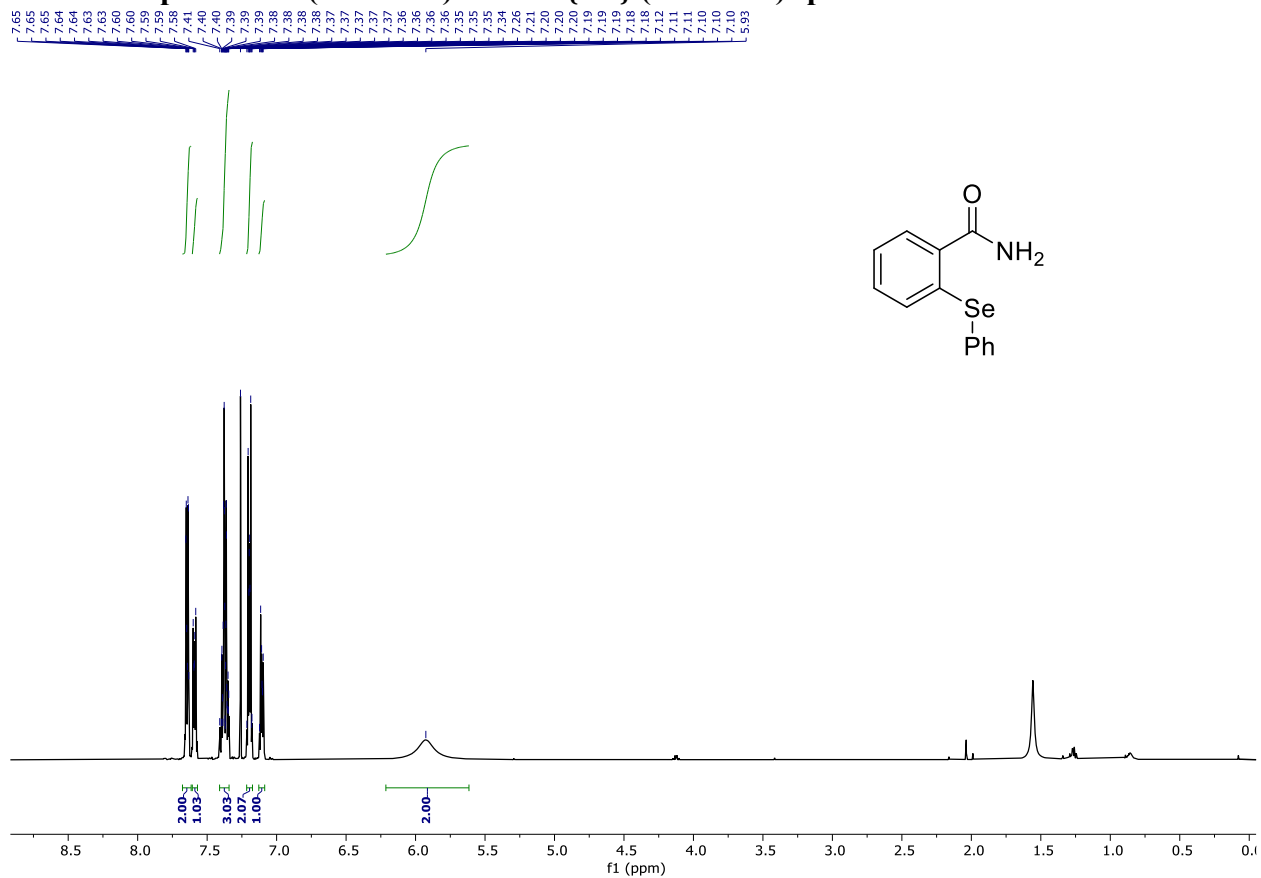
<b>Empirical formula</b>	<b>C<sub>14</sub>H<sub>13</sub>NO<sub>3</sub>Se</b>
<b>Formula weight</b>	<b>320.20</b>
<b>Temperature/K</b>	<b>293(2)</b>
<b>Crystal system</b>	<b>triclinic</b>
<b>Space group</b>	<b>P-1</b>
<b>a/Å</b>	<b>5.0631(13)</b>
<b>b/Å</b>	<b>8.940(2)</b>
<b>c/Å</b>	<b>15.051(4)</b>
<b>α/°</b>	<b>97.607(12)</b>
<b>β/°</b>	<b>91.807(12)</b>
<b>γ/°</b>	<b>105.462(12)</b>
<b>Volume/Å<sup>3</sup></b>	<b>649.3(3)</b>
<b>Z</b>	<b>1</b>
<b>ρ<sub>calc</sub> g/cm<sup>3</sup></b>	<b>1.638</b>
<b>μ/mm<sup>-1</sup></b>	<b>2.894</b>
<b>F(000)</b>	<b>320.0</b>
<b>Radiation</b>	<b>MoKα (λ = 0.71073)</b>
<b>2θ range for data collection/°</b>	<b>5.844 to 57.15</b>
<b>Index ranges</b>	<b>-6 ≤ h ≤ 6, -11 ≤ k ≤ 11, -19 ≤ l ≤ 20</b>

<b>Reflections collected</b>	<b>9617</b>
<b>Independent reflections</b>	<b>3311 [R<sub>int</sub> = 0.0679, R<sub>sigma</sub> = 0.0756]</b>
<b>Data/restraints/parameters</b>	<b>3311/0/173</b>
<b>Goodness-of-fit on F<sup>2</sup></b>	<b>1.261</b>
<b>Final R indexes [I ≥ 2σ (I)]</b>	<b>R<sub>1</sub> = 0.0709, wR<sub>2</sub> = 0.1827</b>
<b>Final R indexes [all data]</b>	<b>R<sub>1</sub> = 0.1040, wR<sub>2</sub> = 0.2127</b>
<b>Largest diff. peak/hole /e Å<sup>-3</sup></b>	<b>1.14/-1.58</b>

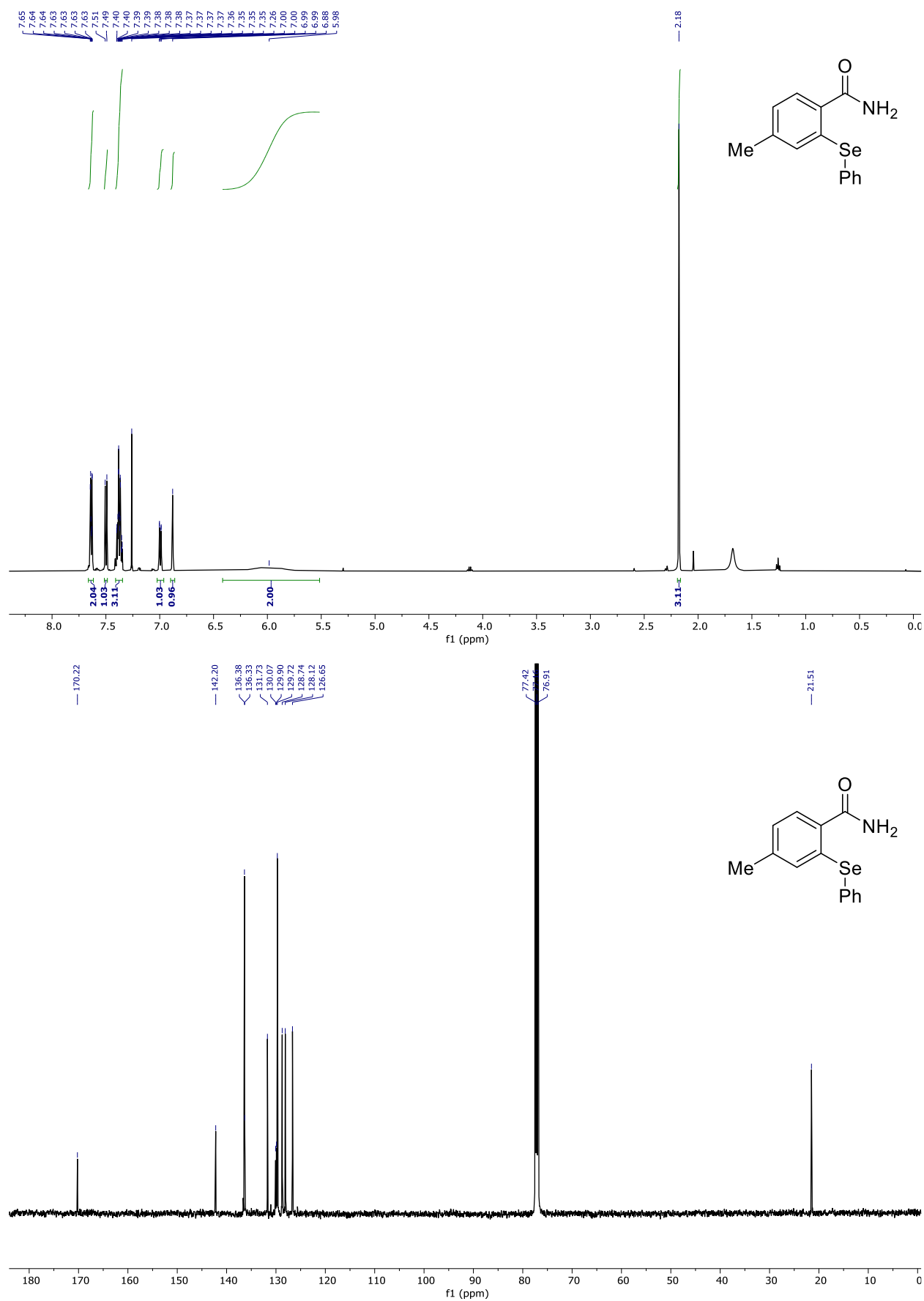
## 15. References.

1. (a) H. Veisi, B. Maleki, M. Hamelian, S. S. Ashrafi, "Chemoselective hydration of nitriles to amides using hydrated ionic liquid (IL) tetrabutylammonium hydroxide (TBAH) as a green catalyst" *RSC Adv.*, **2015**, 5, 6365–6371; (b) J. N. Moorthy, N. Singhal, "Facile and highly selective conversion of nitriles to amides via indirect acid-catalyzed hydration using TFA or AcOH–H<sub>2</sub>SO<sub>4</sub>" *J. Org. Chem.*, **2005**, 70, 1926–1929.
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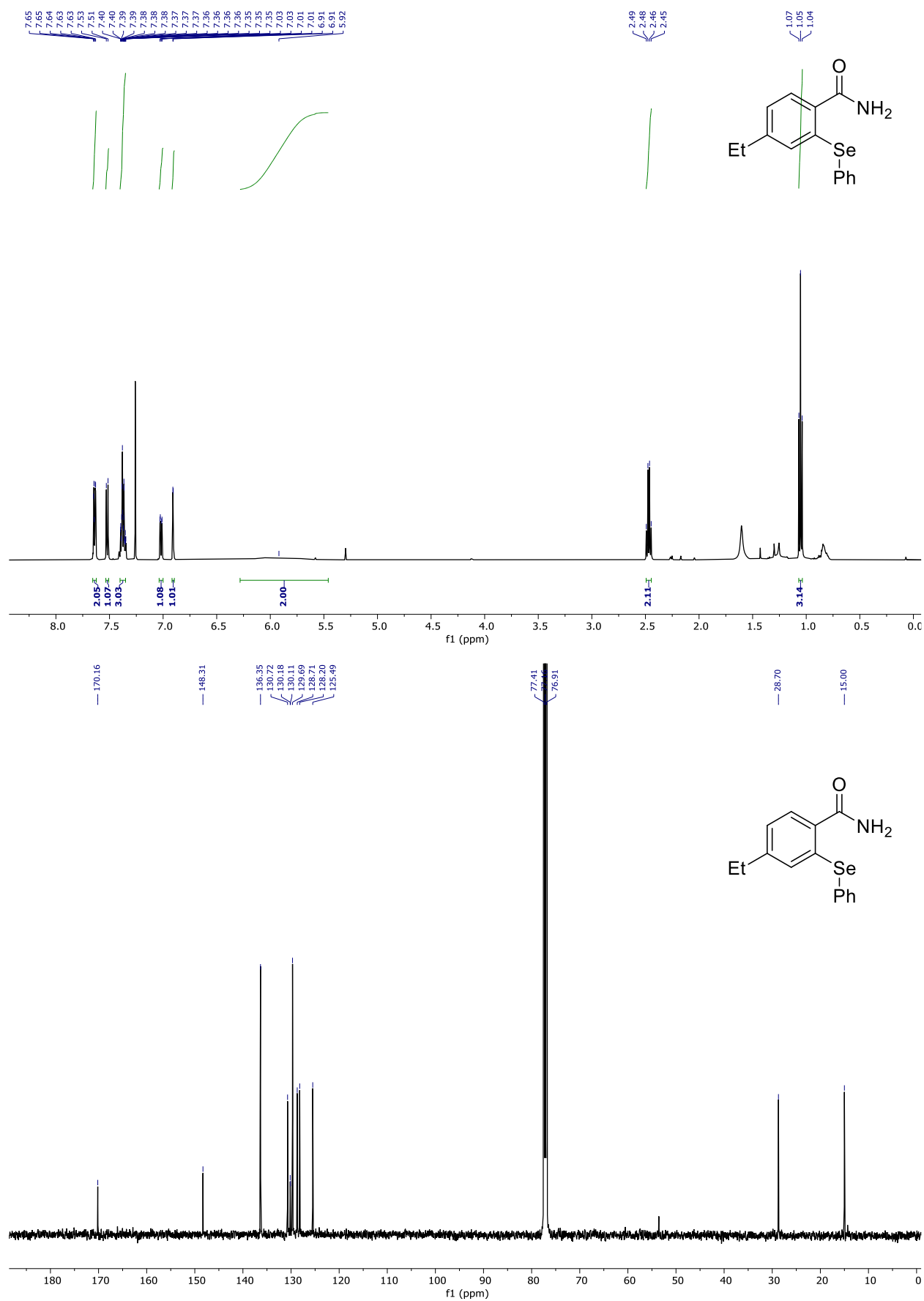
16. NMR Spectra.  $^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 3a in  $\text{CDCl}_3$



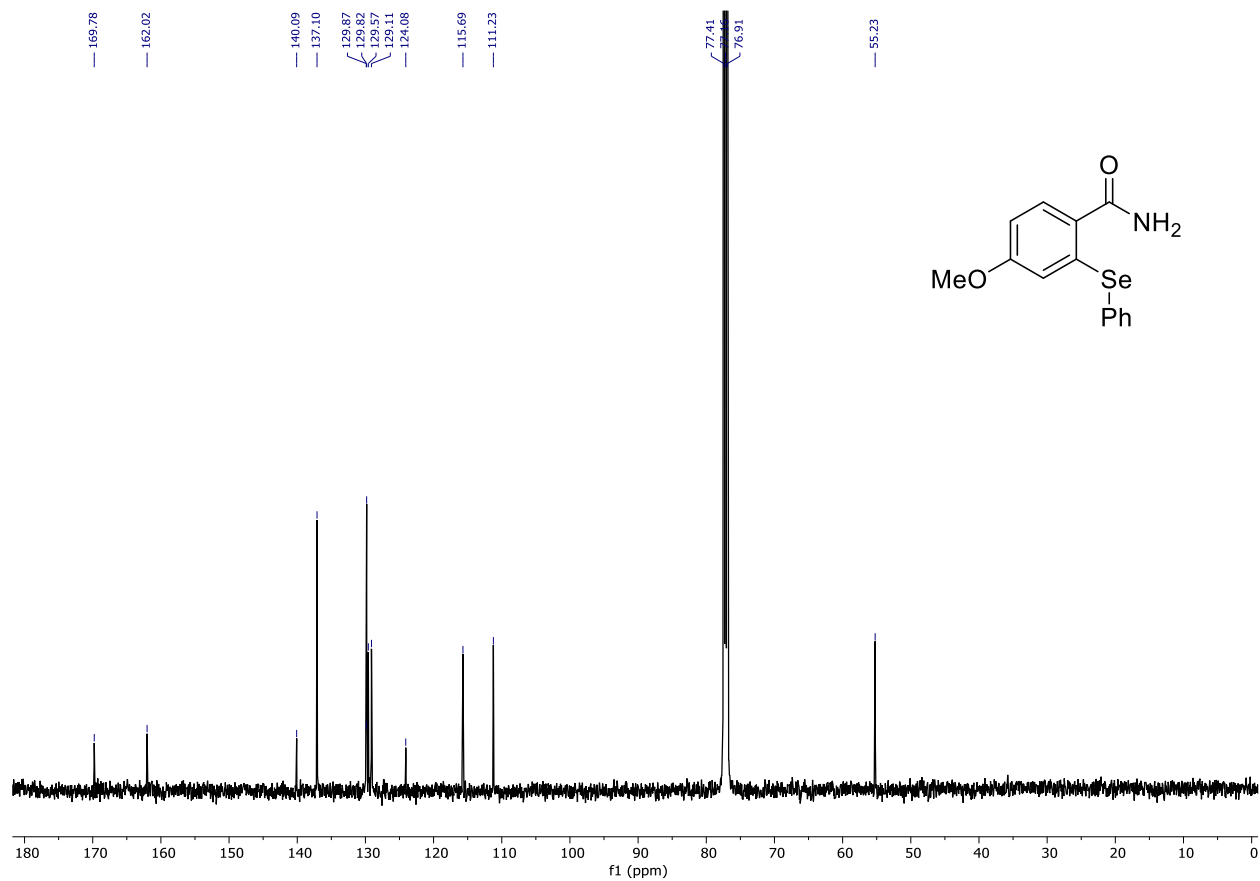
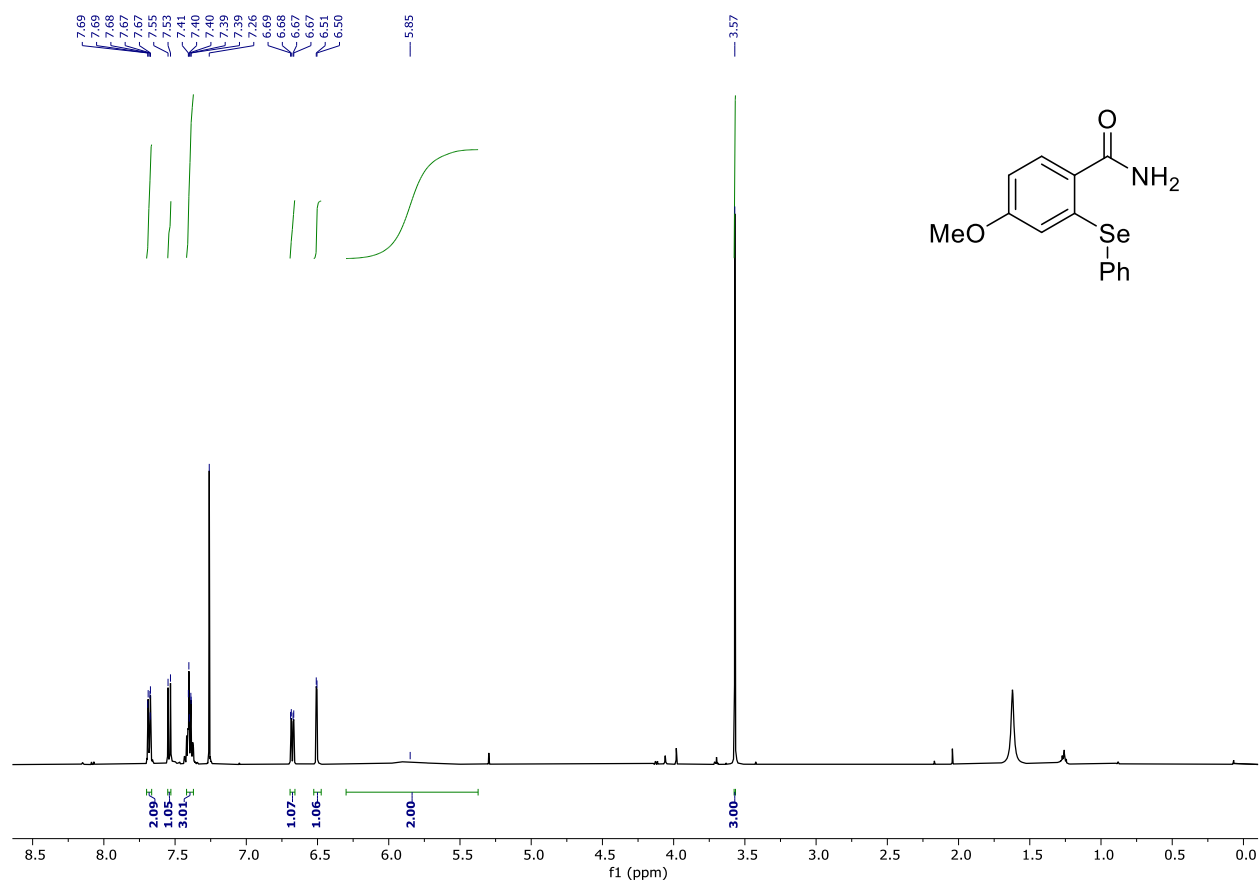
$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 3b in  $\text{CDCl}_3$



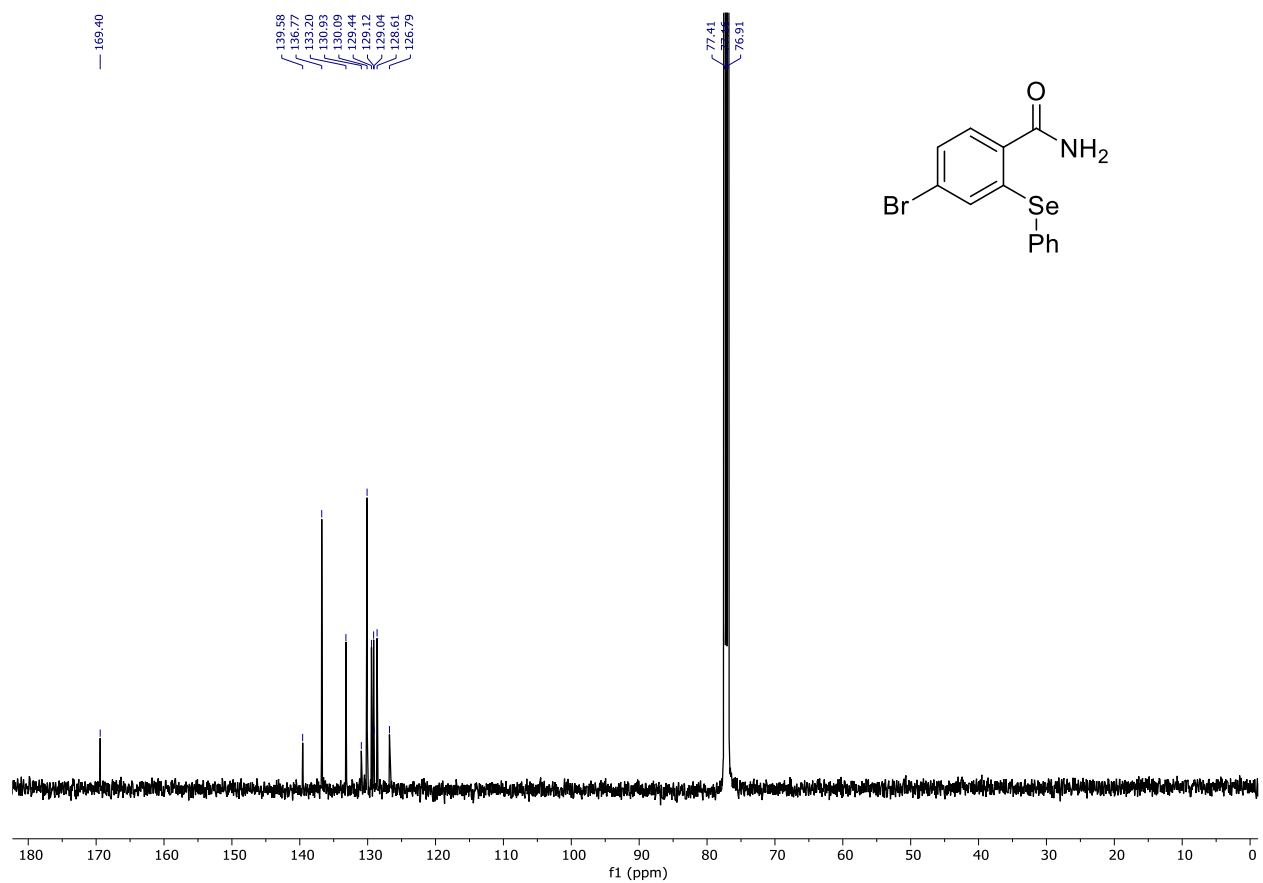
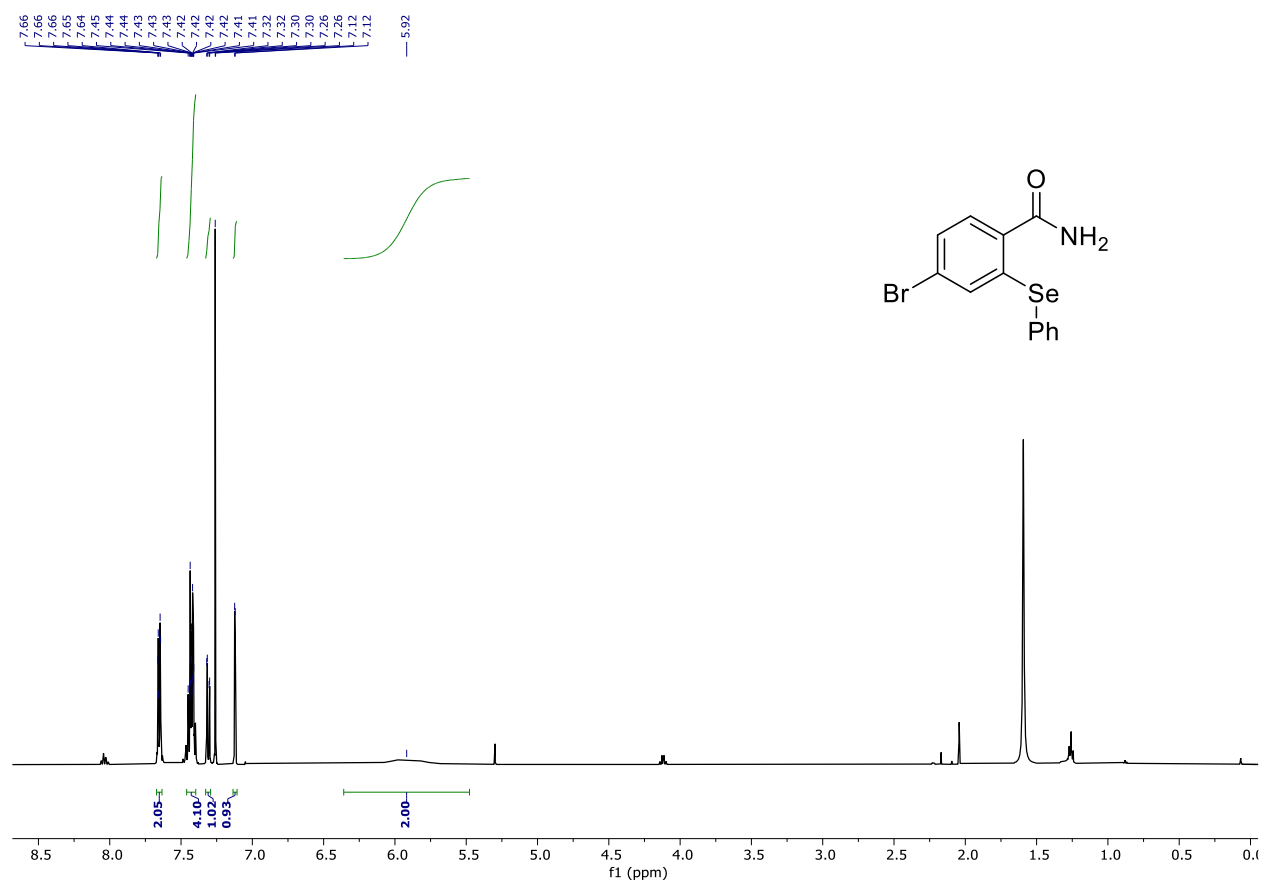
**$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 3c in  $\text{CDCl}_3$**



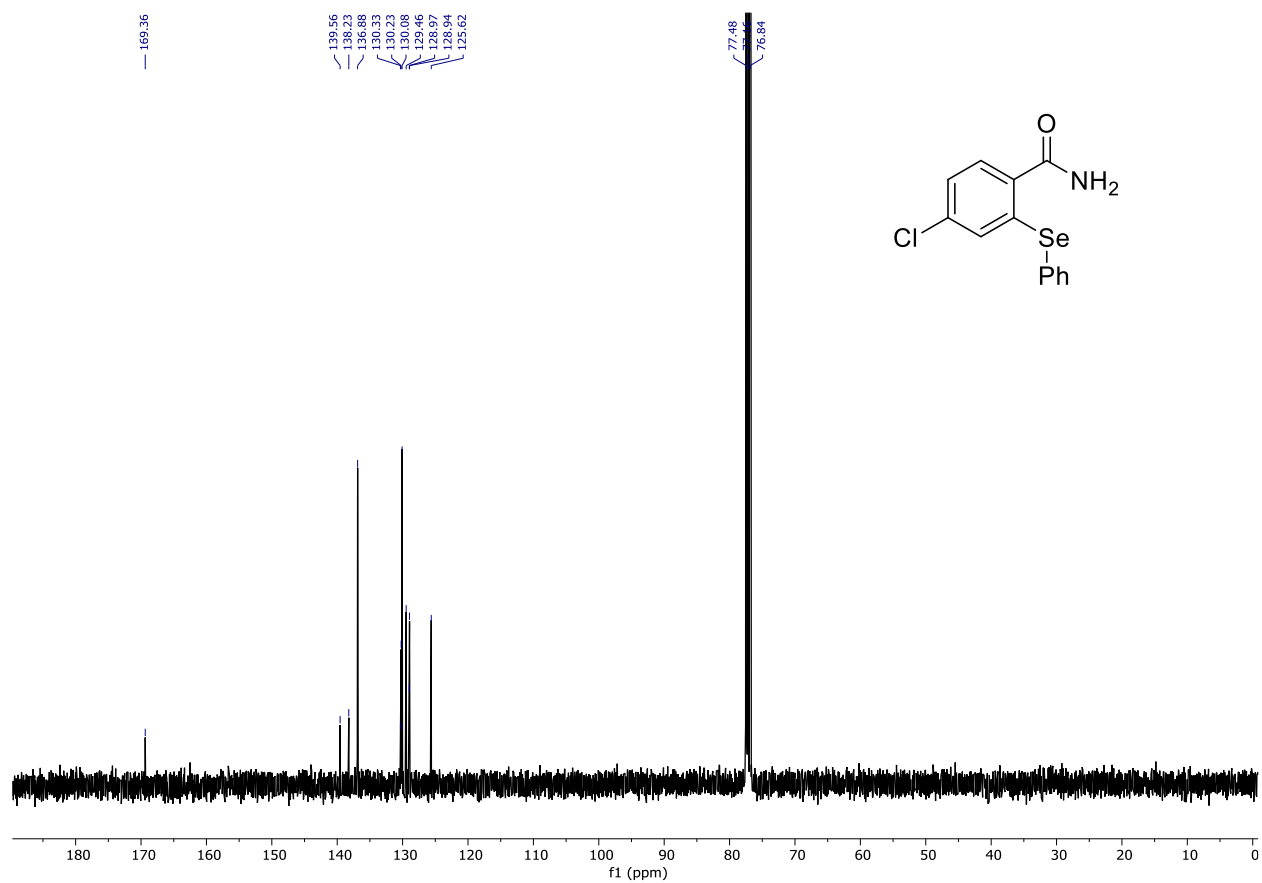
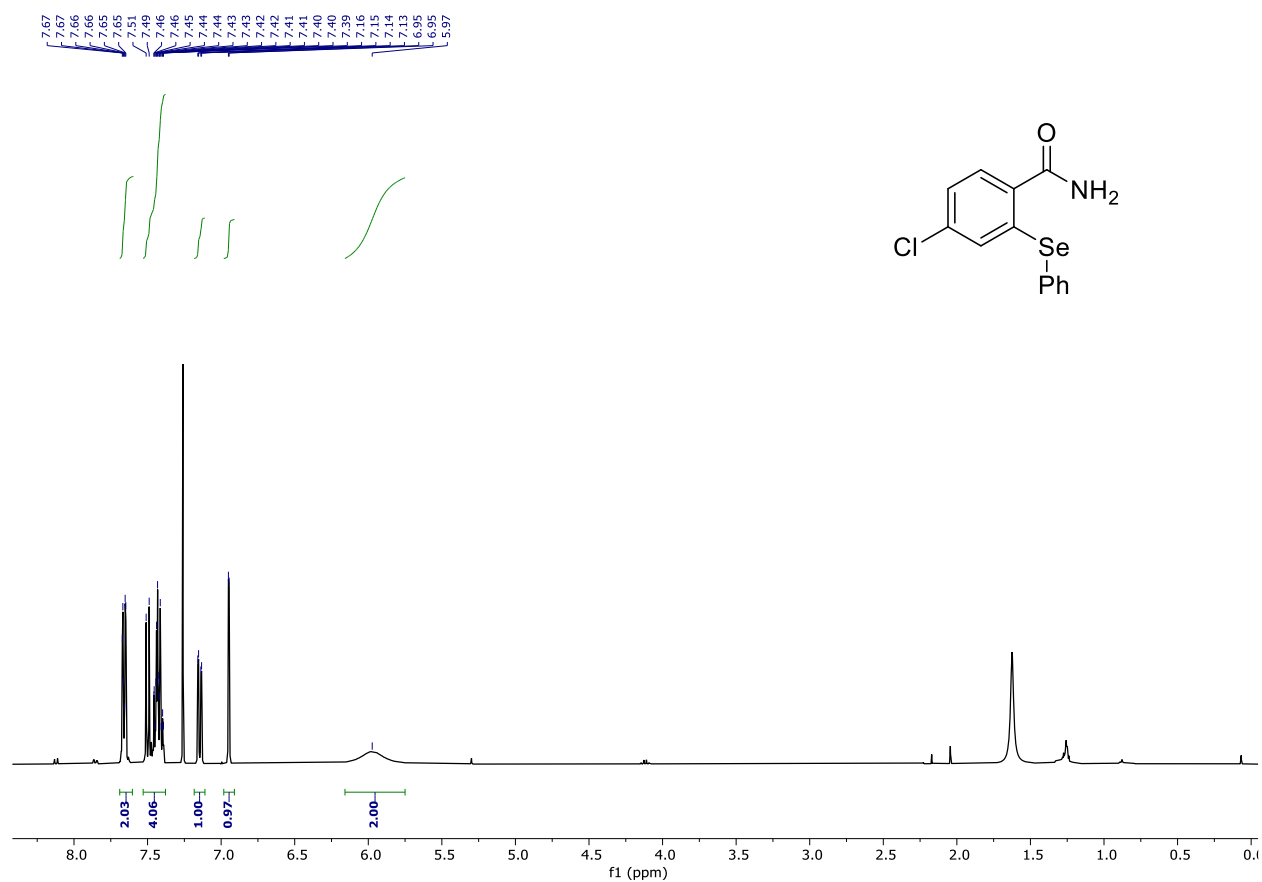
$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 3d in  $\text{CDCl}_3$



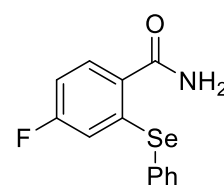
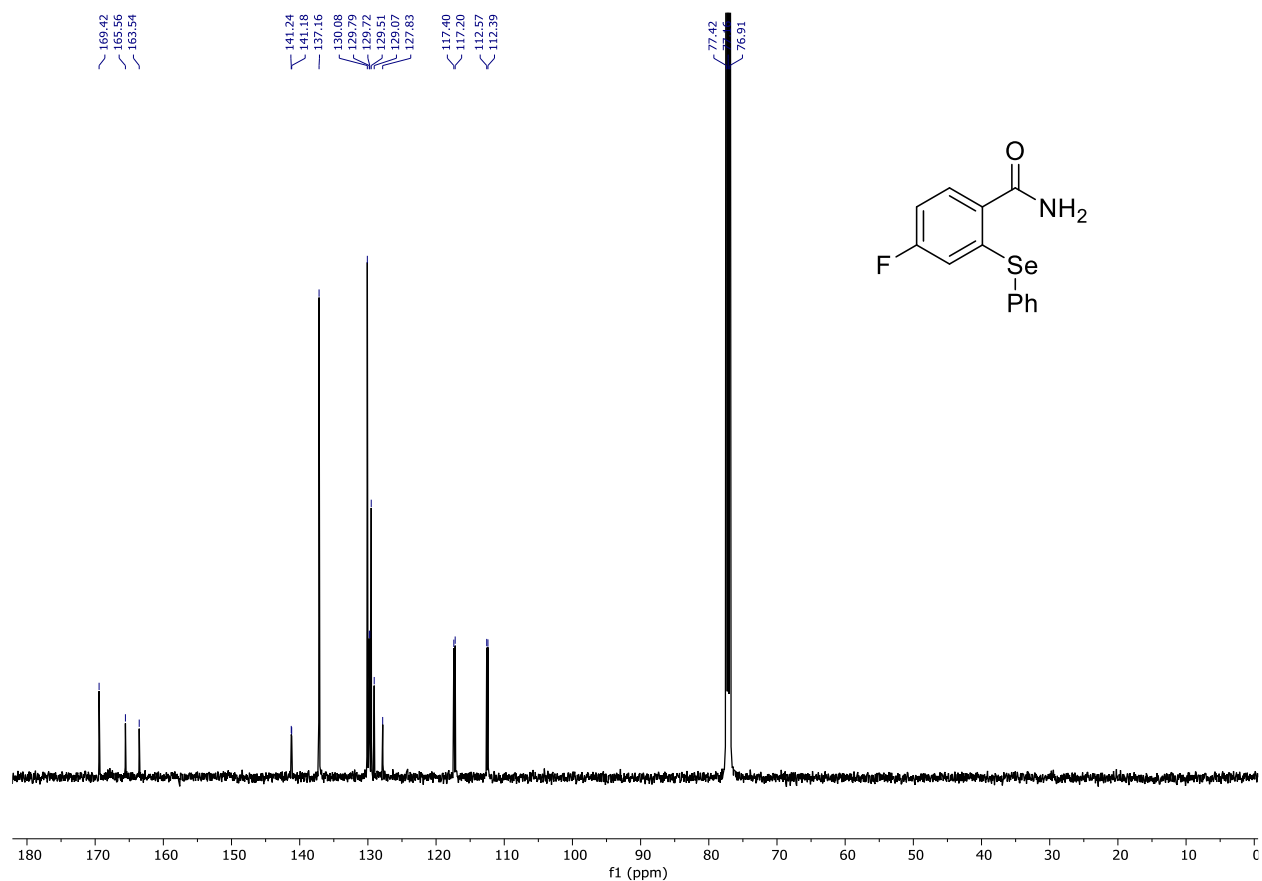
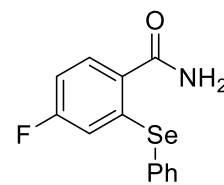
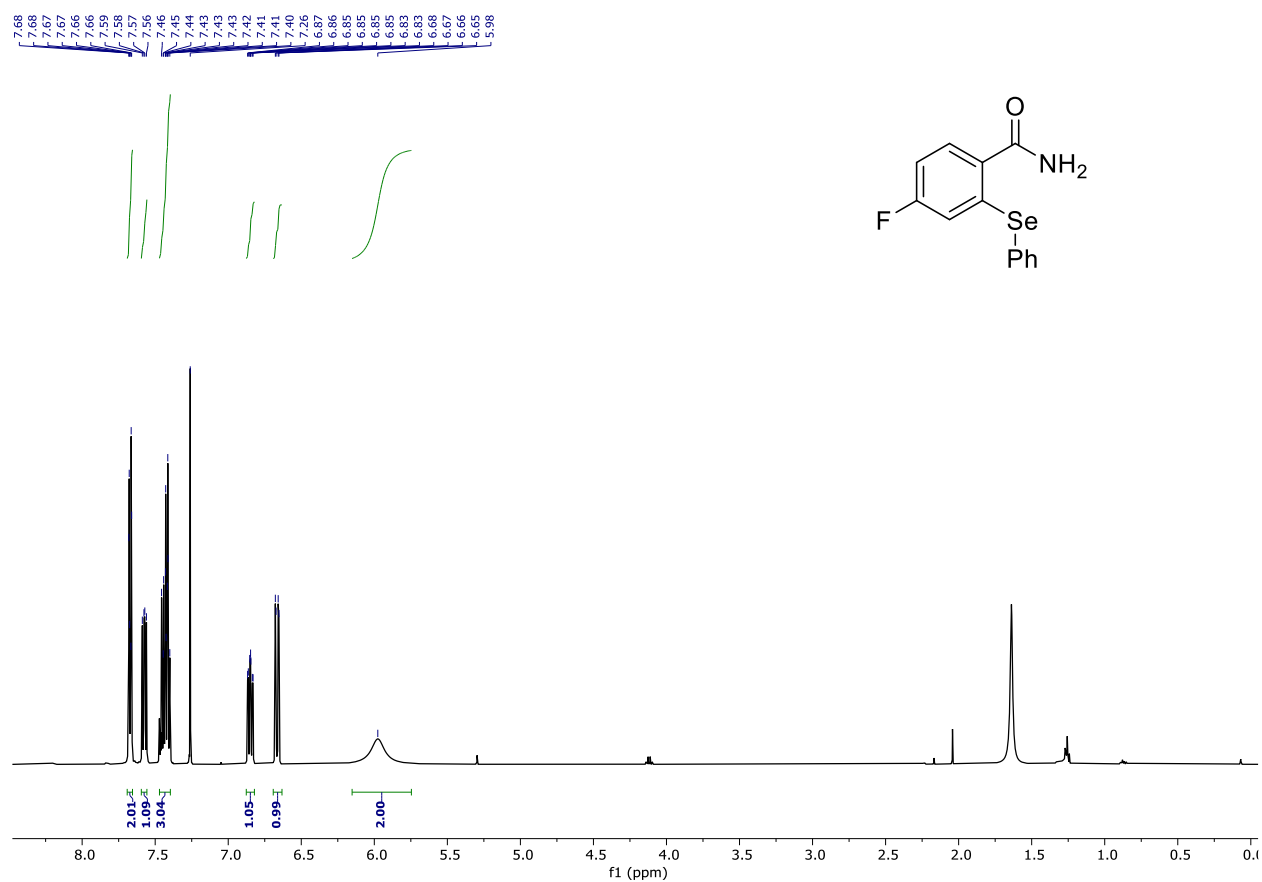
**$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 3e in  $\text{CDCl}_3$**



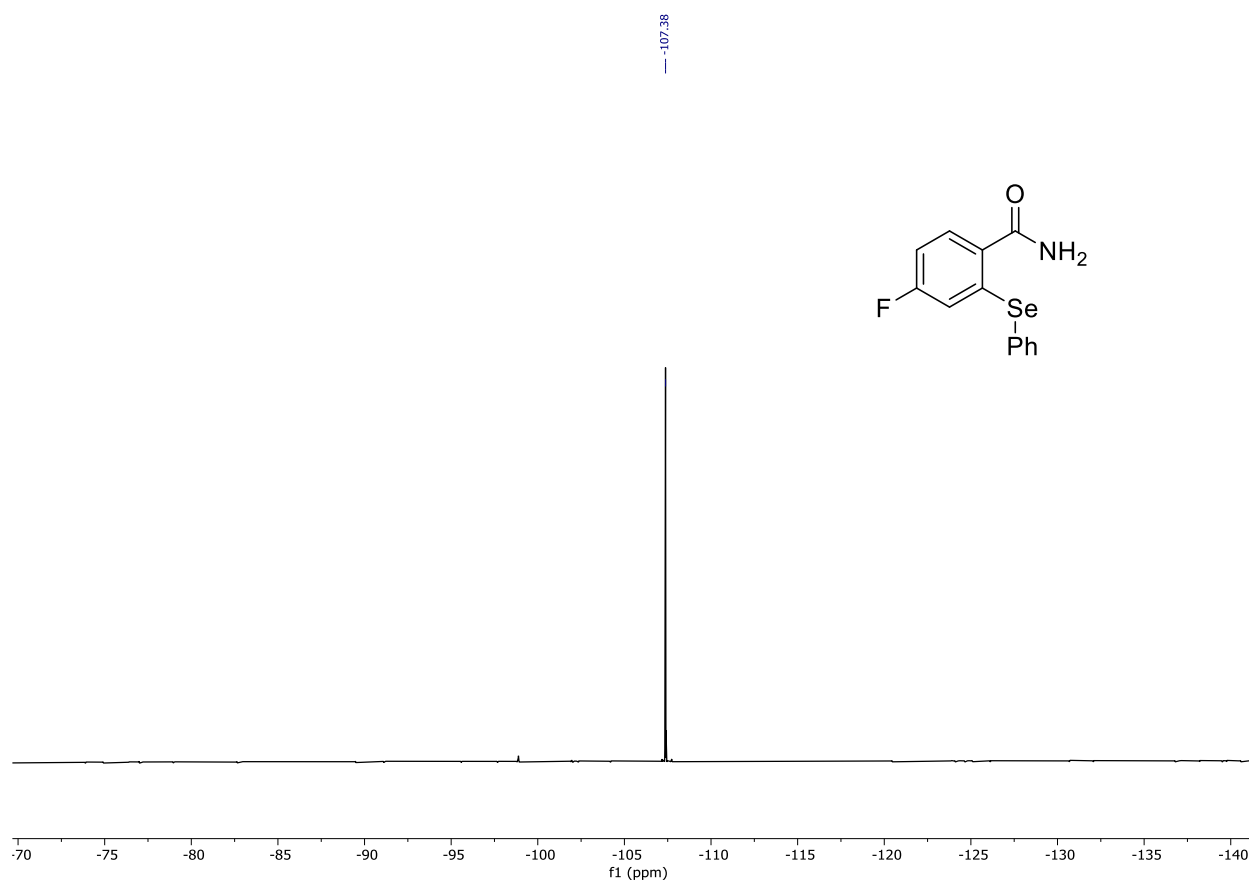
$^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (100 MHz) spectra of 3f in  $\text{CDCl}_3$



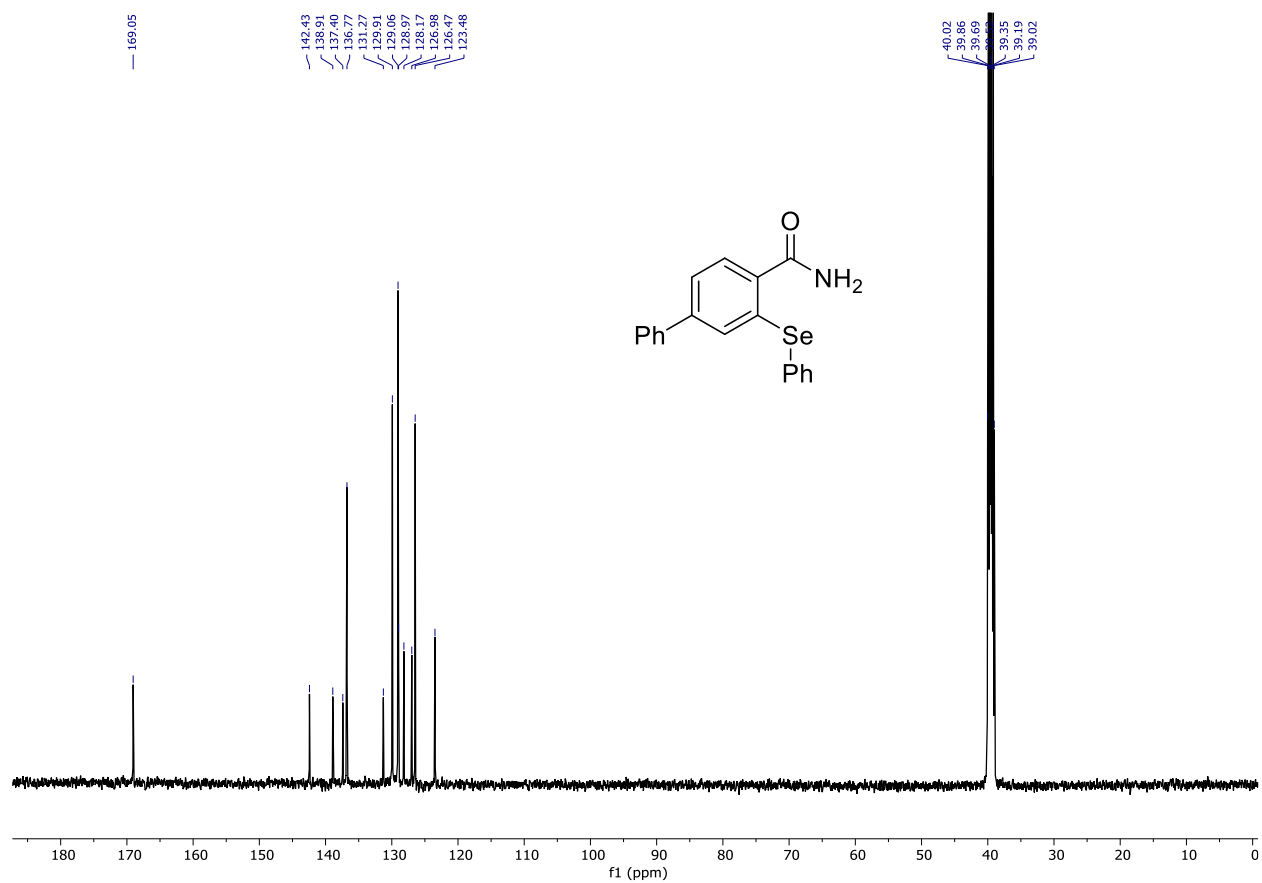
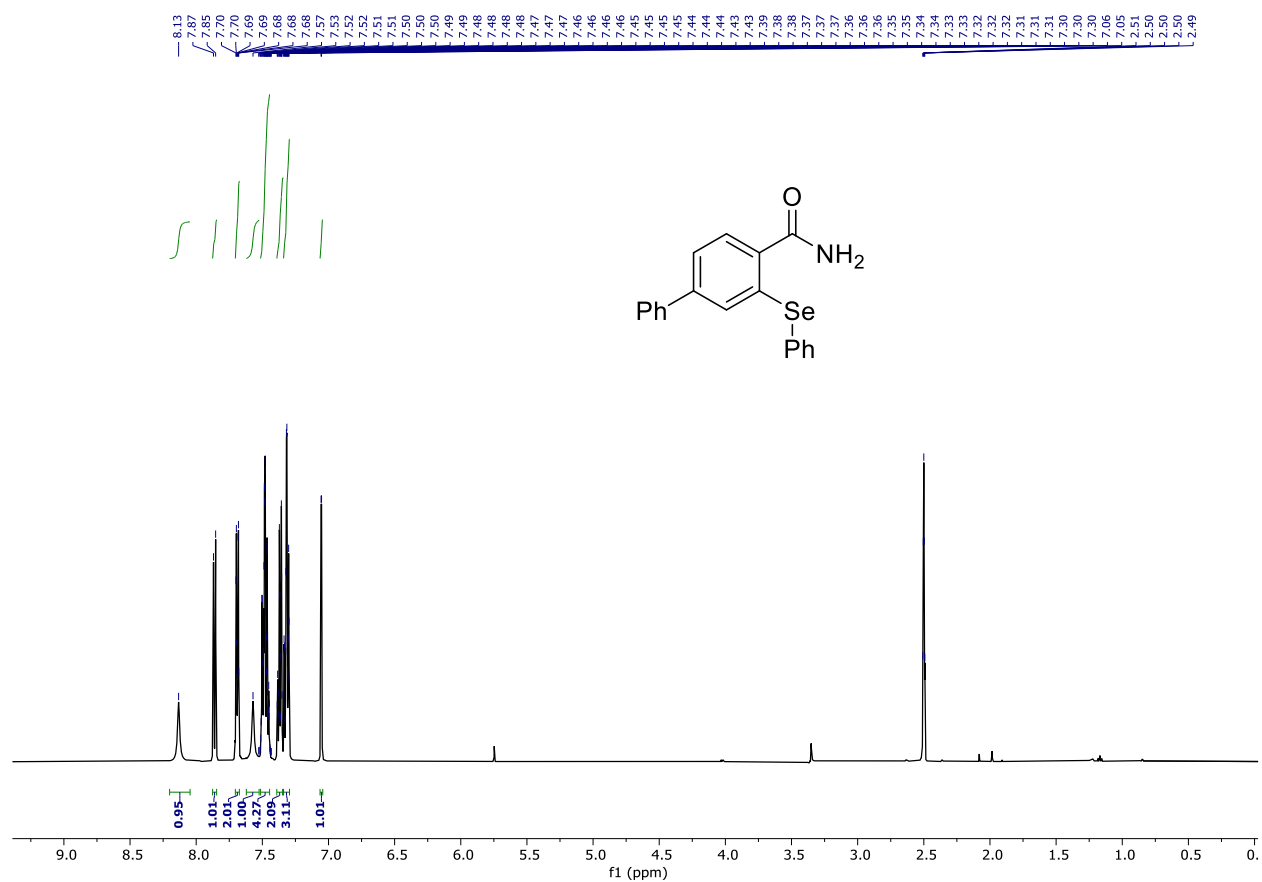
**$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 3g in  $\text{CDCl}_3$**



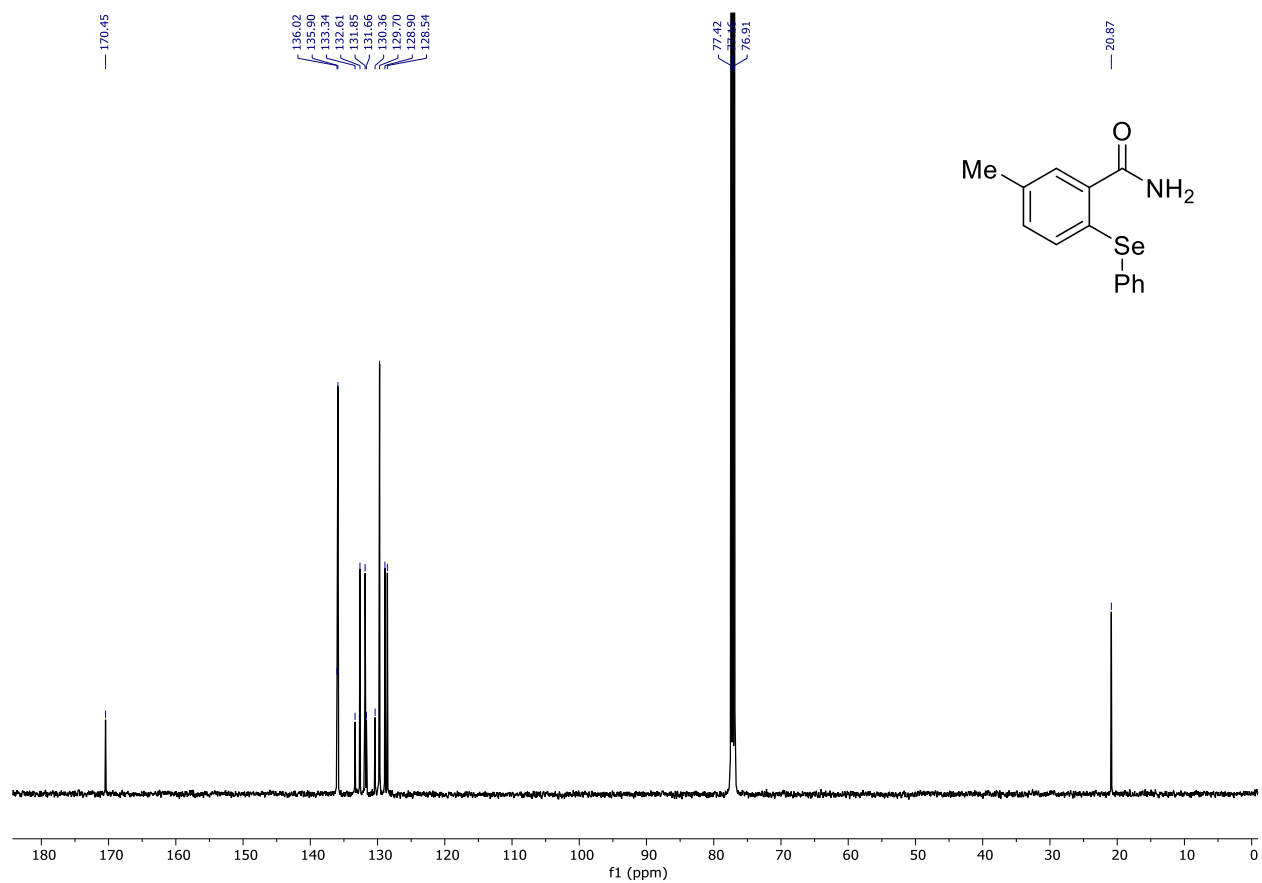
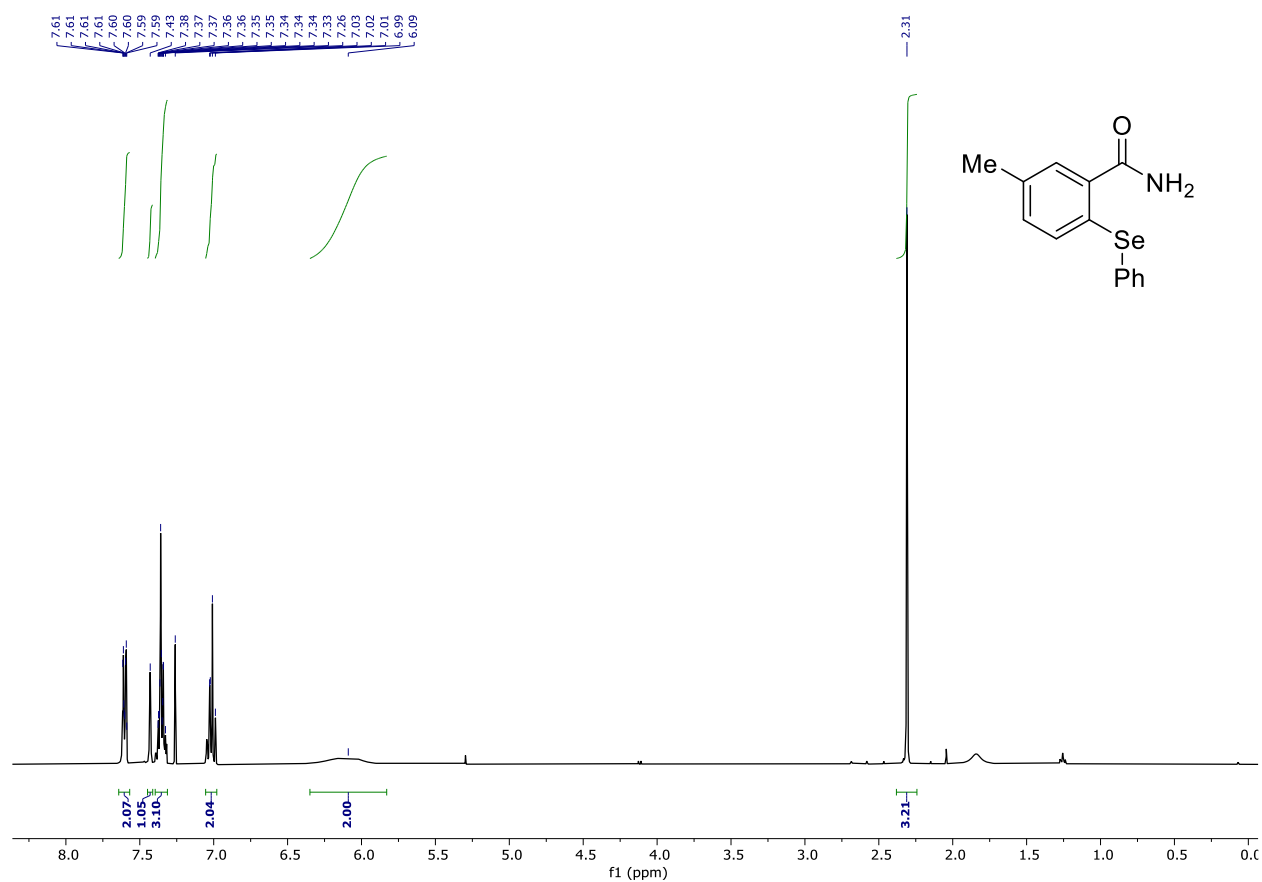
**$^{19}\text{F}\{^1\text{H}\}$  (471 MHz) NMR spectra of 3g in  $\text{CDCl}_3$**



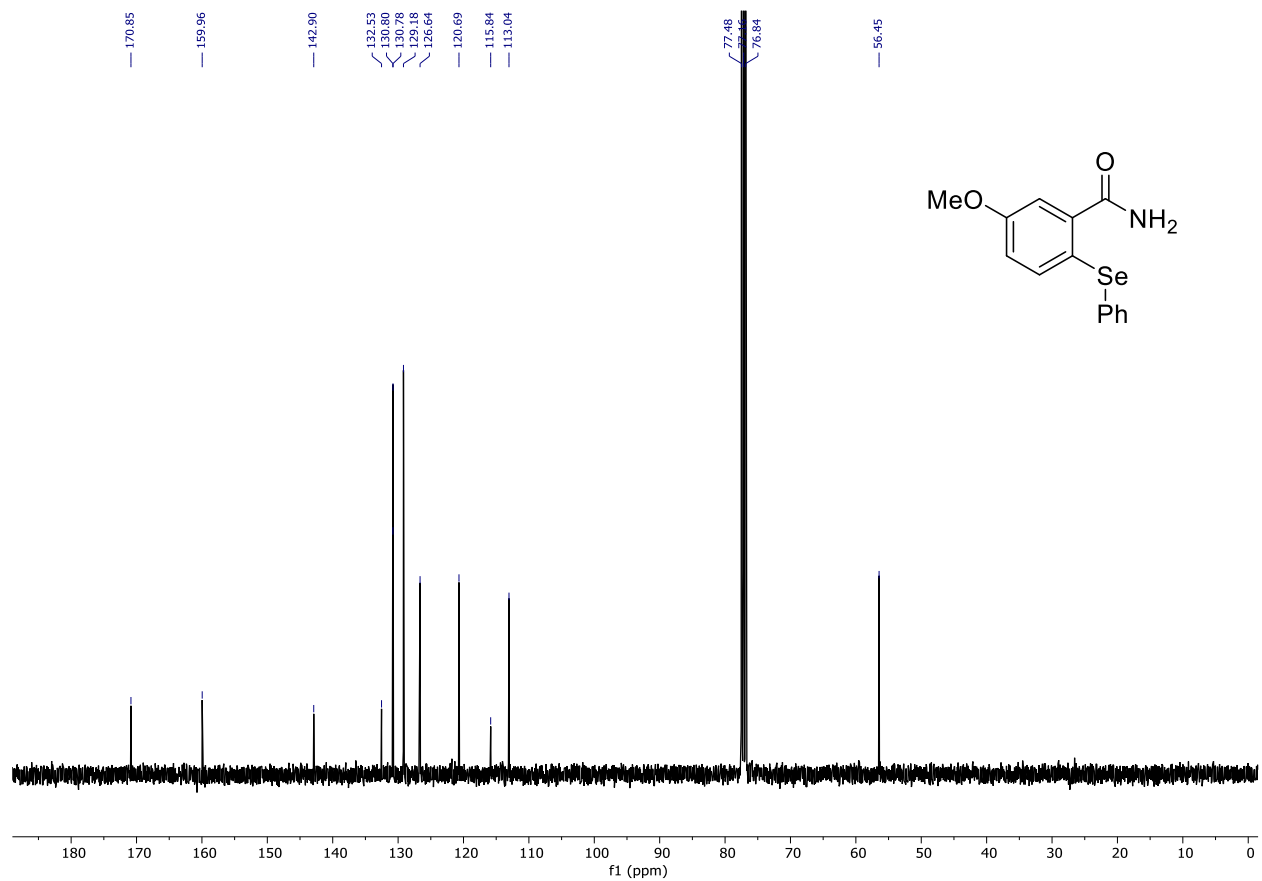
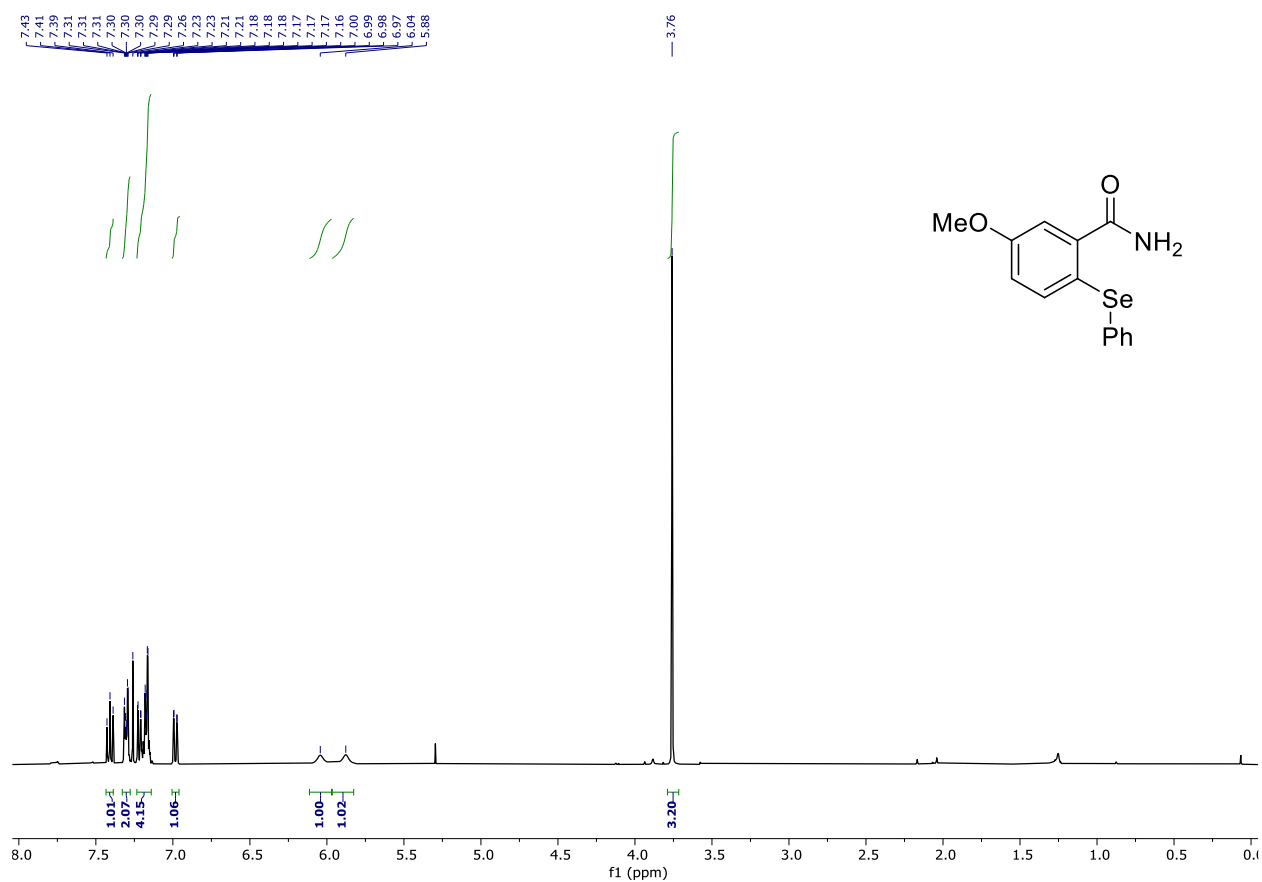
**$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 3h in DMSO- $\text{D}_6$**



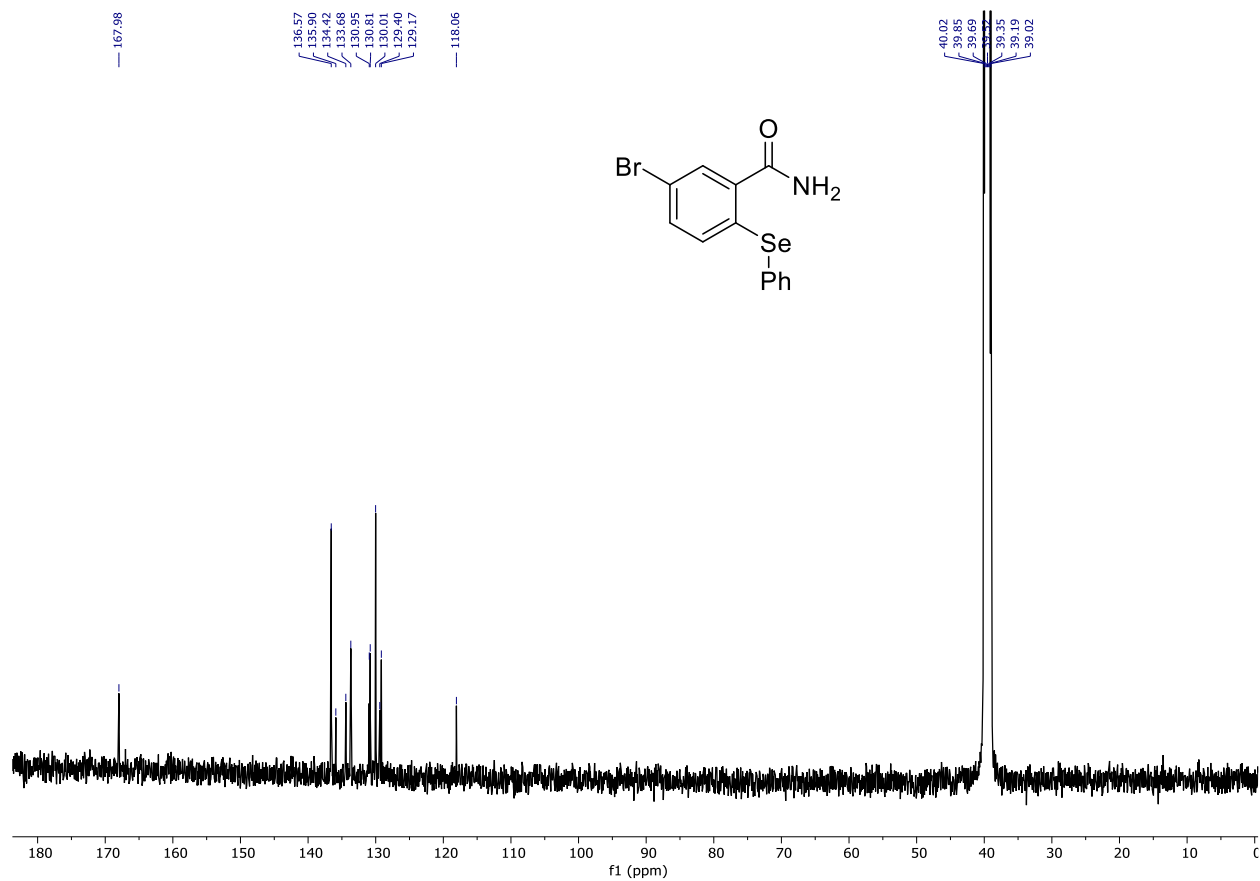
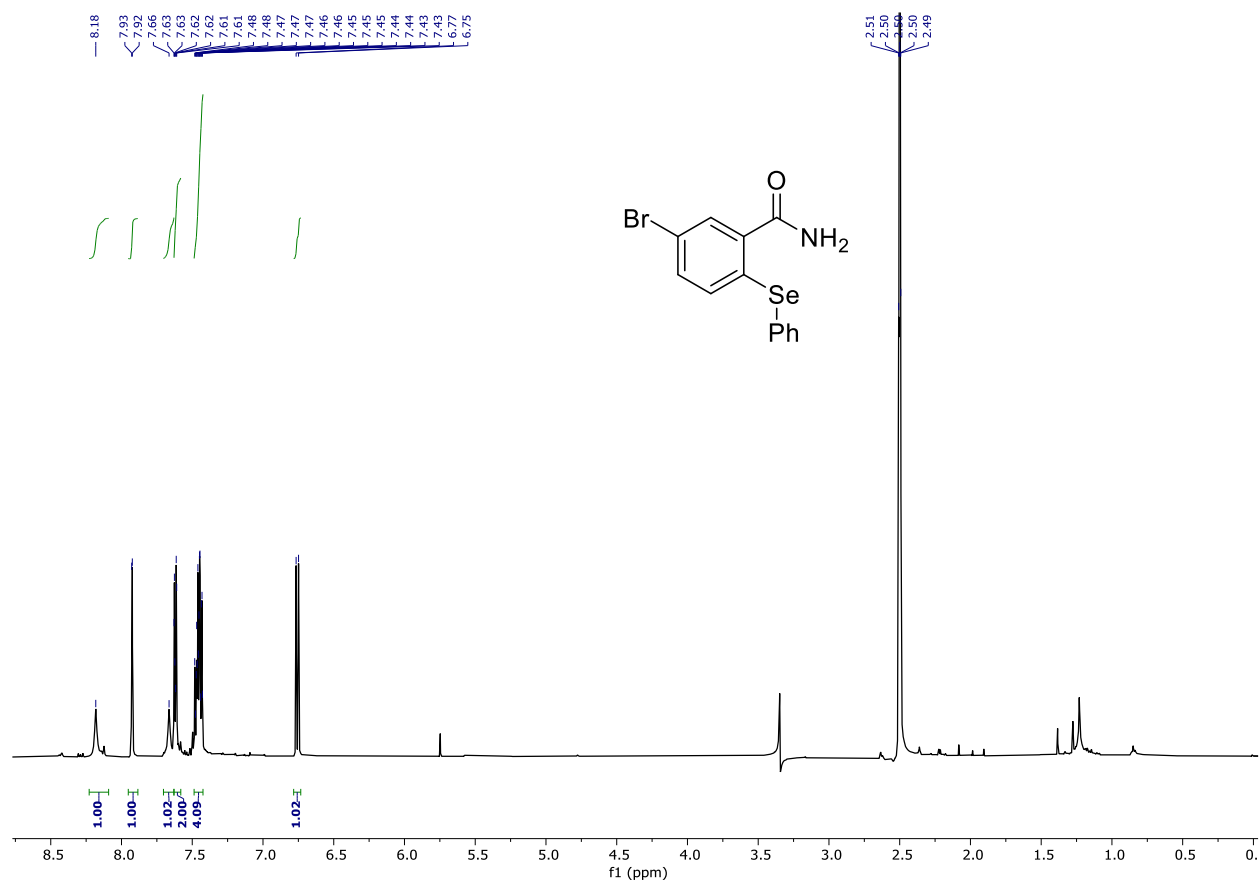
$^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 3i in  $\text{CDCl}_3$



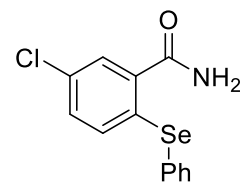
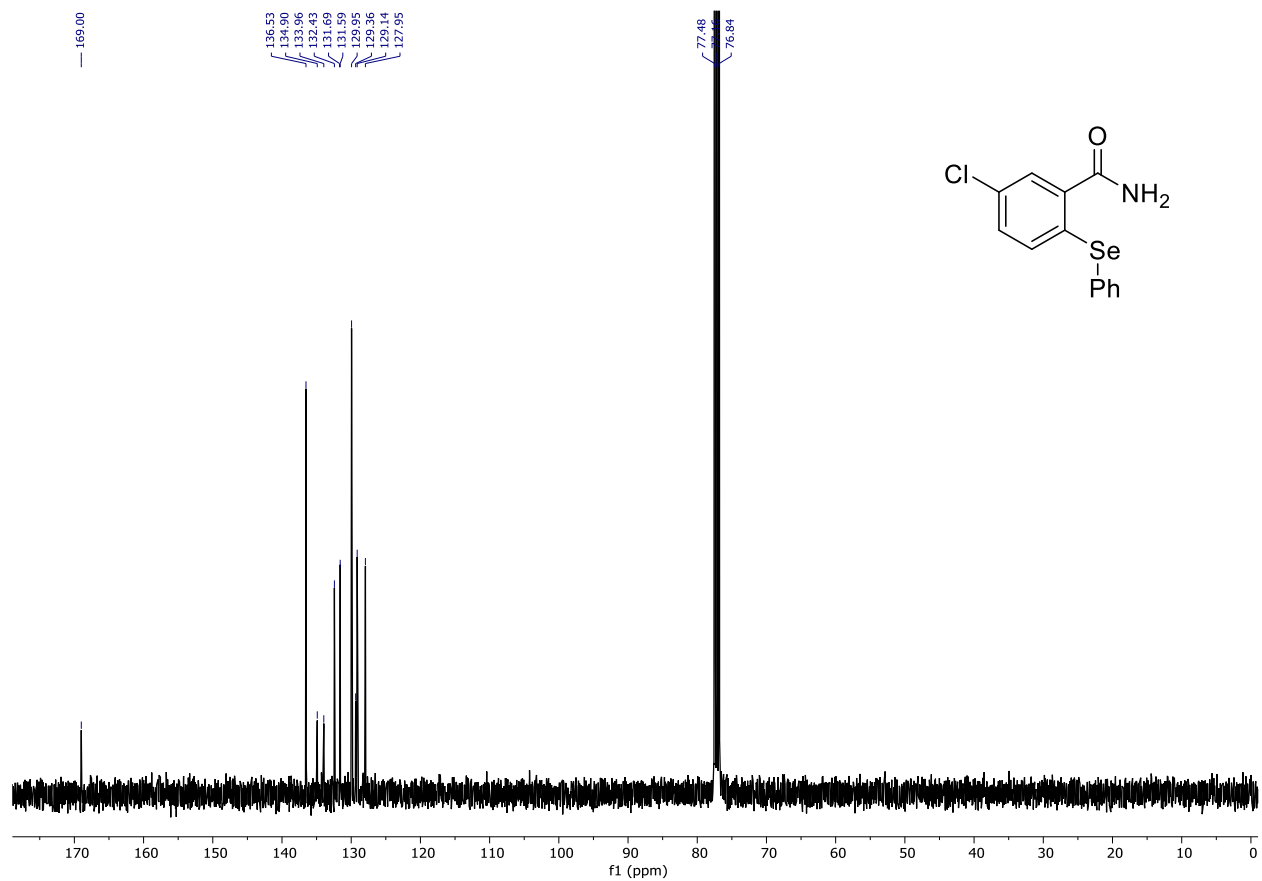
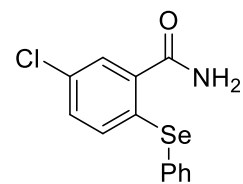
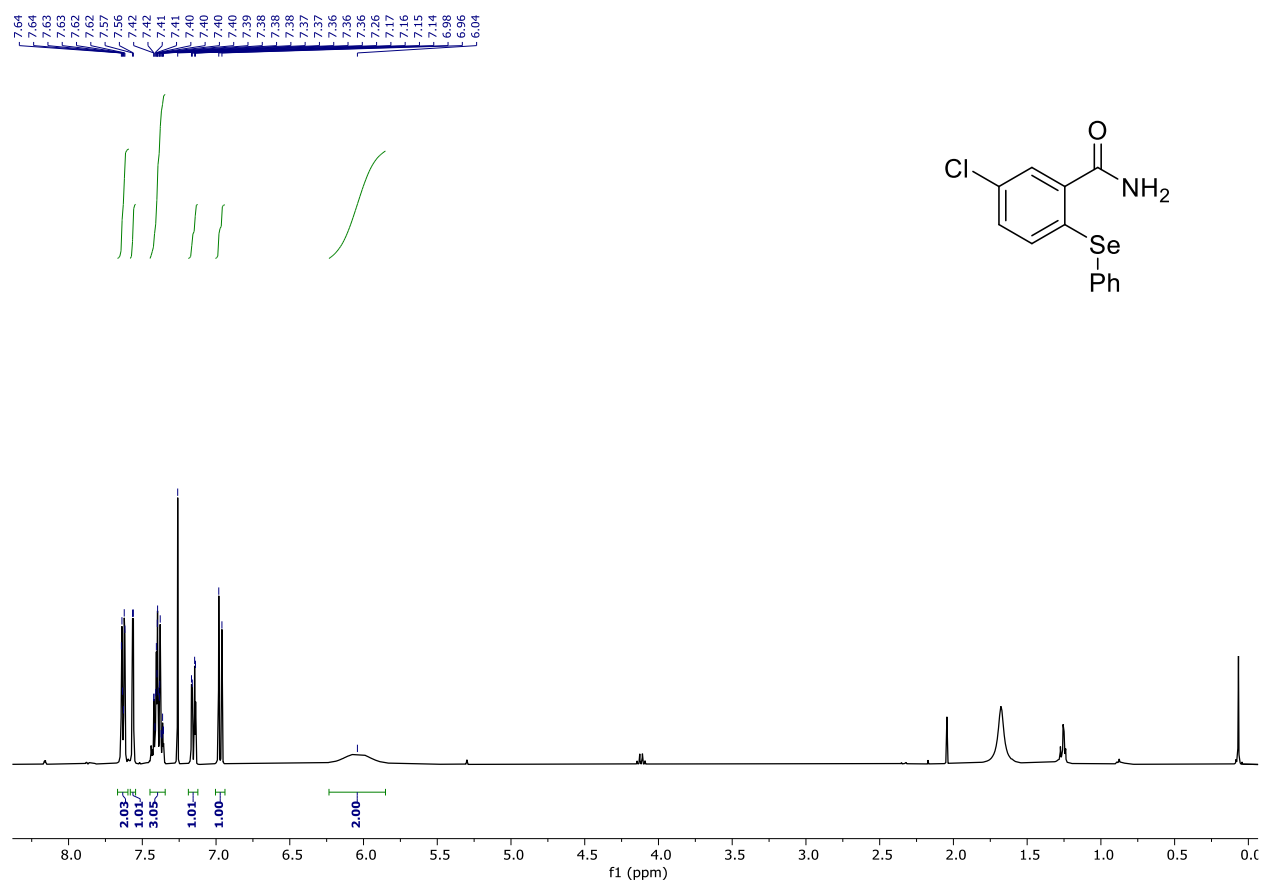
**$^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (100 MHz) spectra of 3j in  $\text{CDCl}_3$**



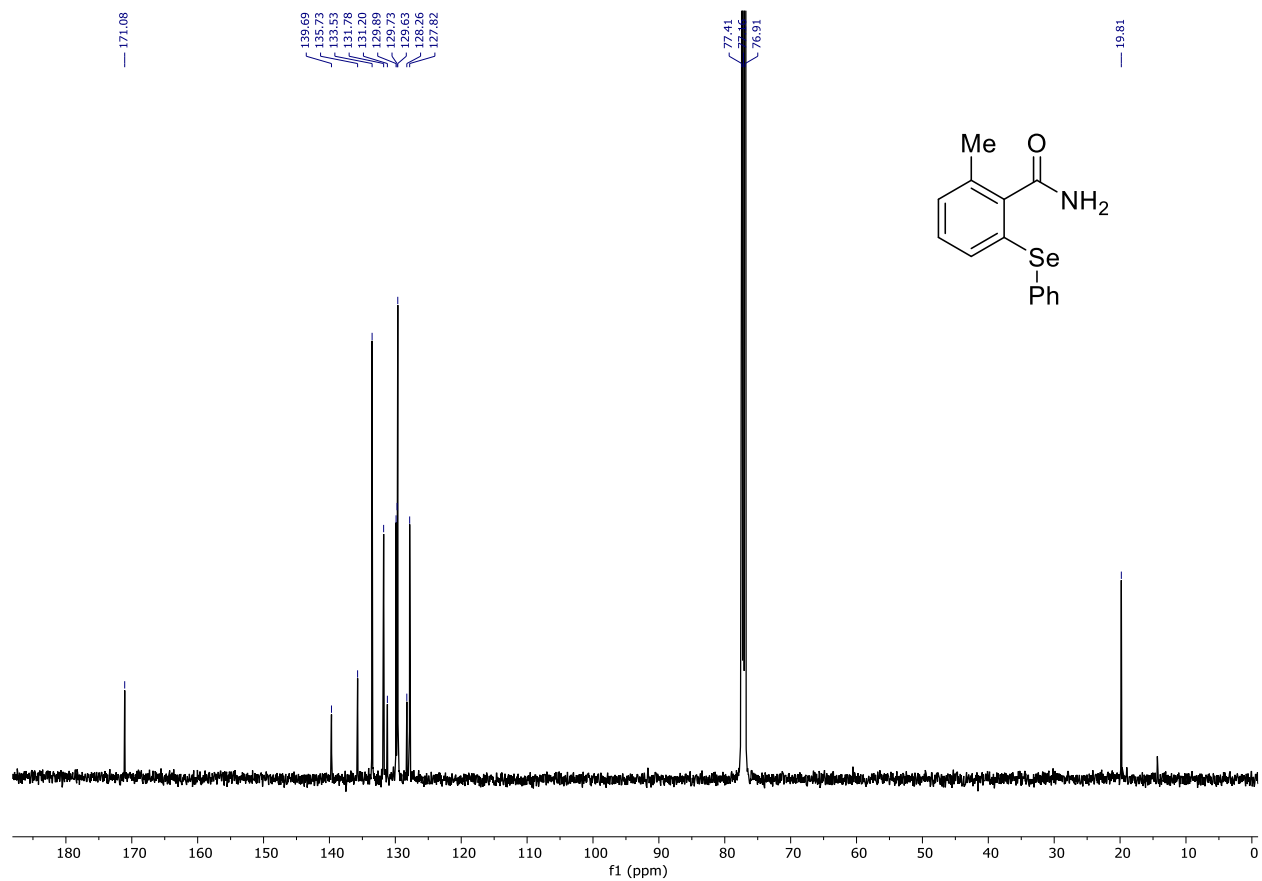
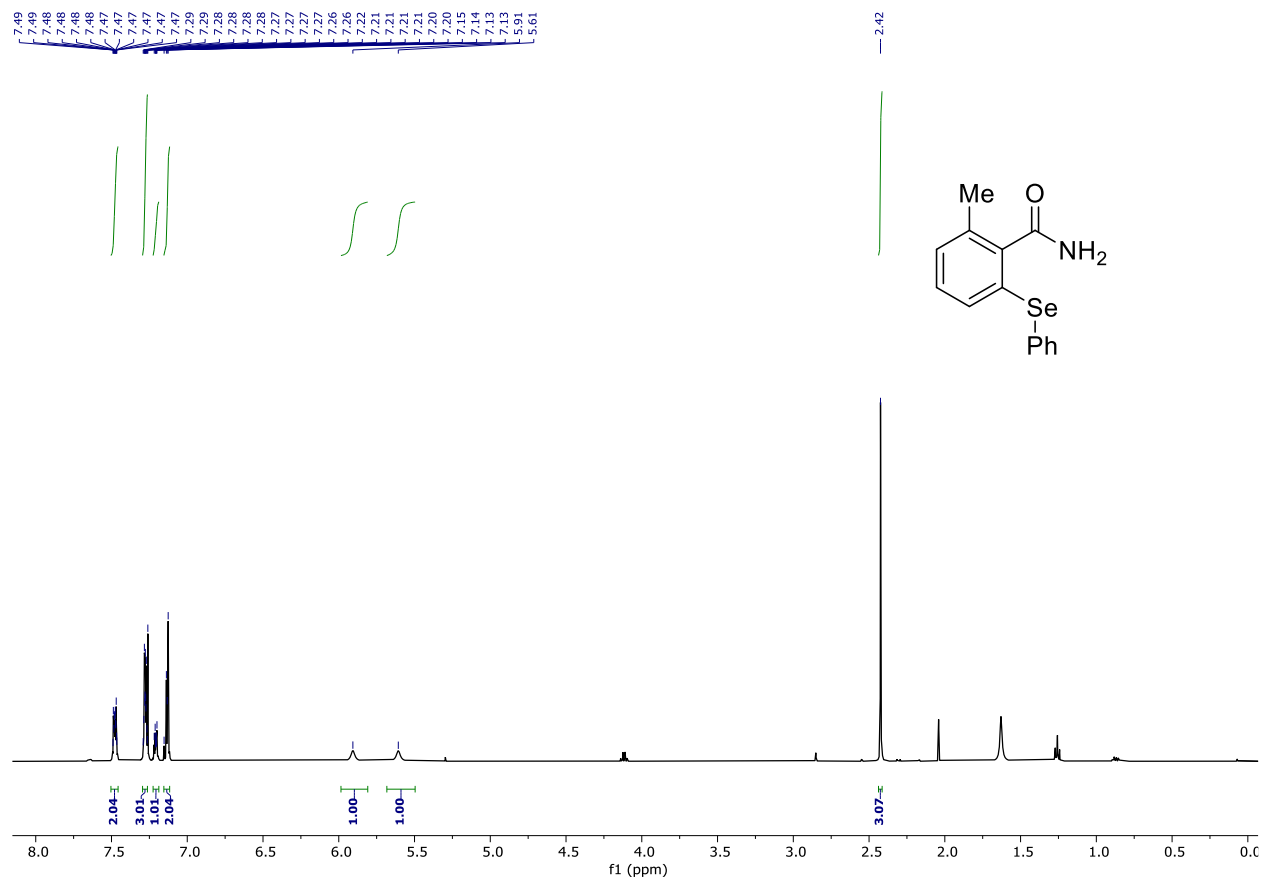
$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 3k in DMSO- $\text{D}_6$



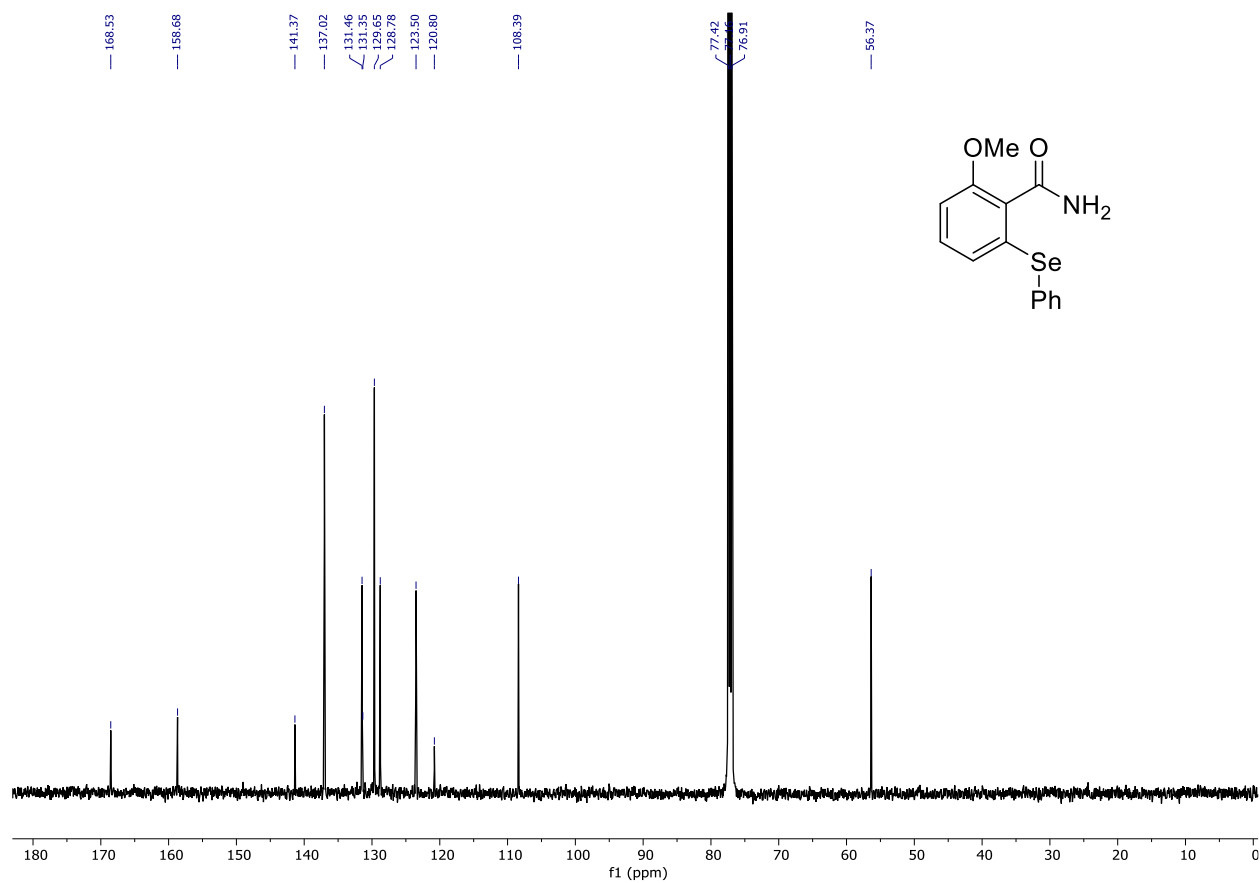
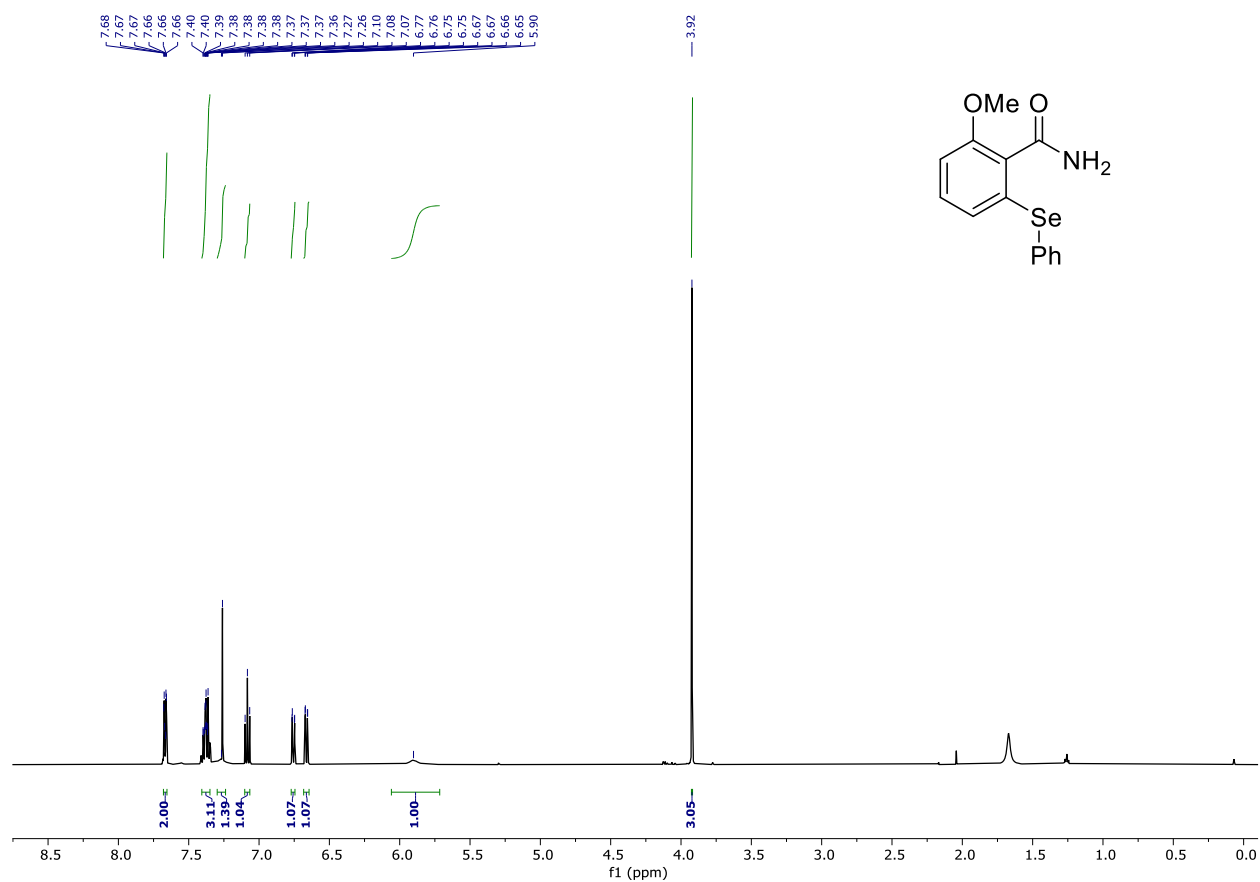
**$^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (100 MHz) spectra of 3l in  $\text{CDCl}_3$**



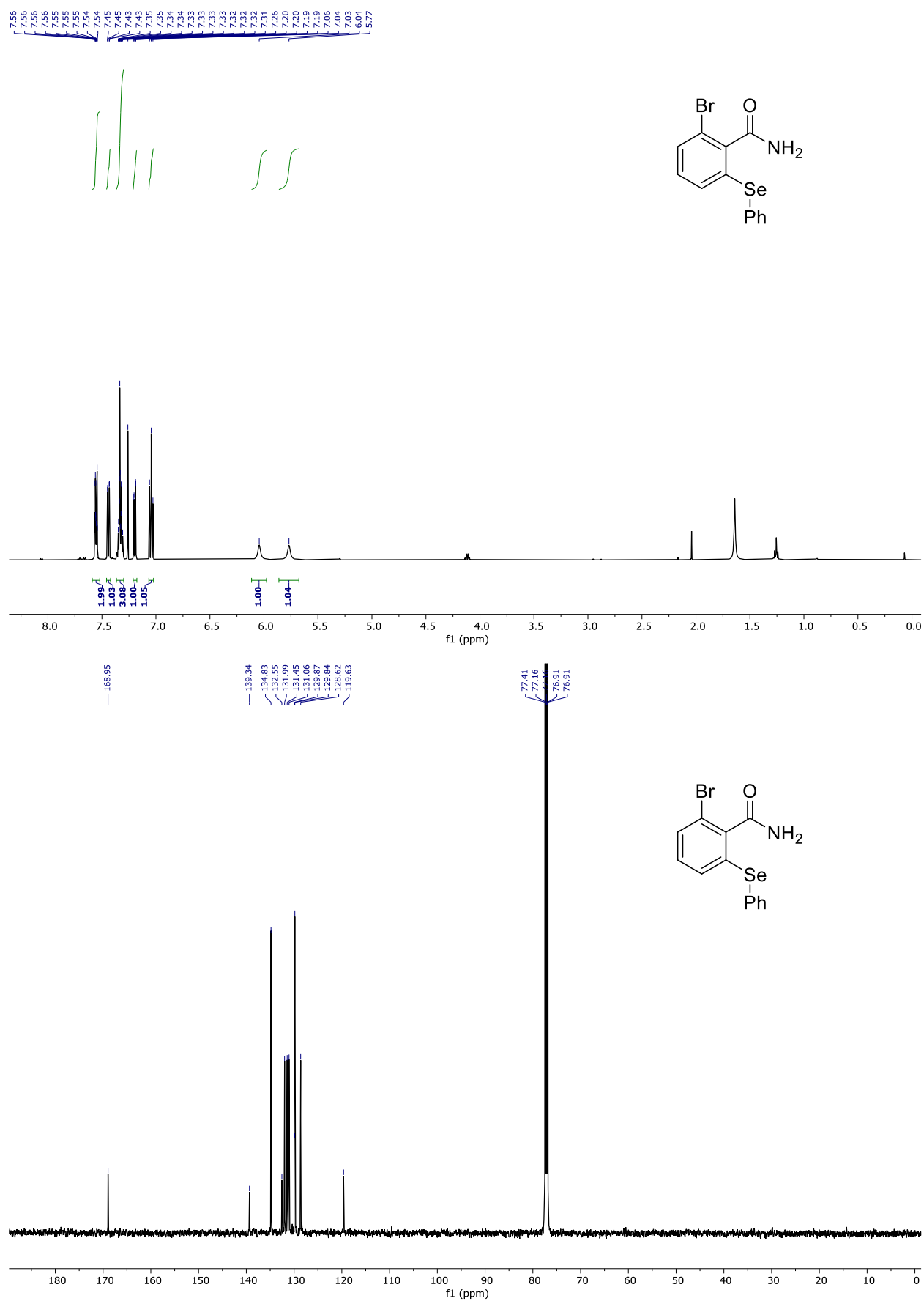
**$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 3m in  $\text{CDCl}_3$**



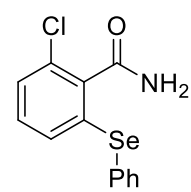
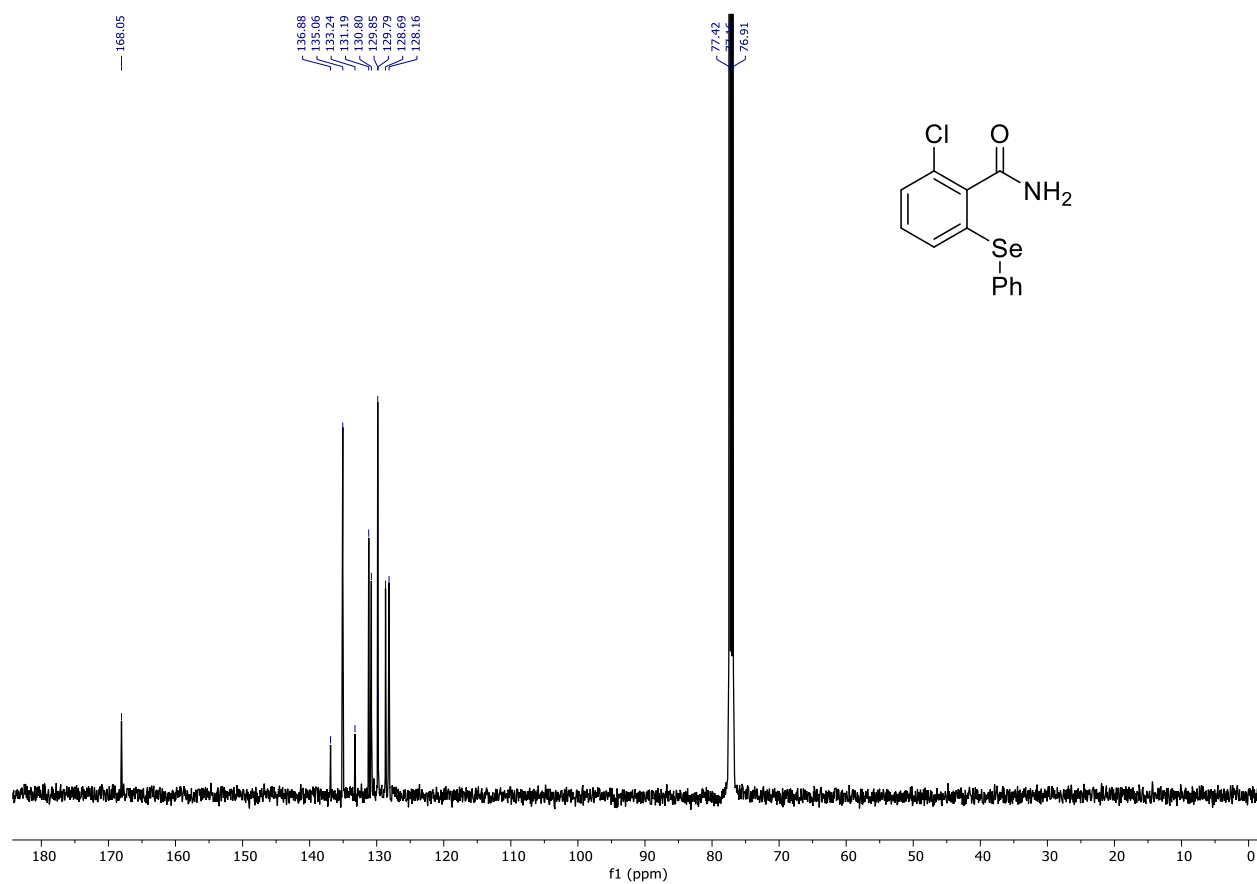
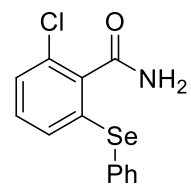
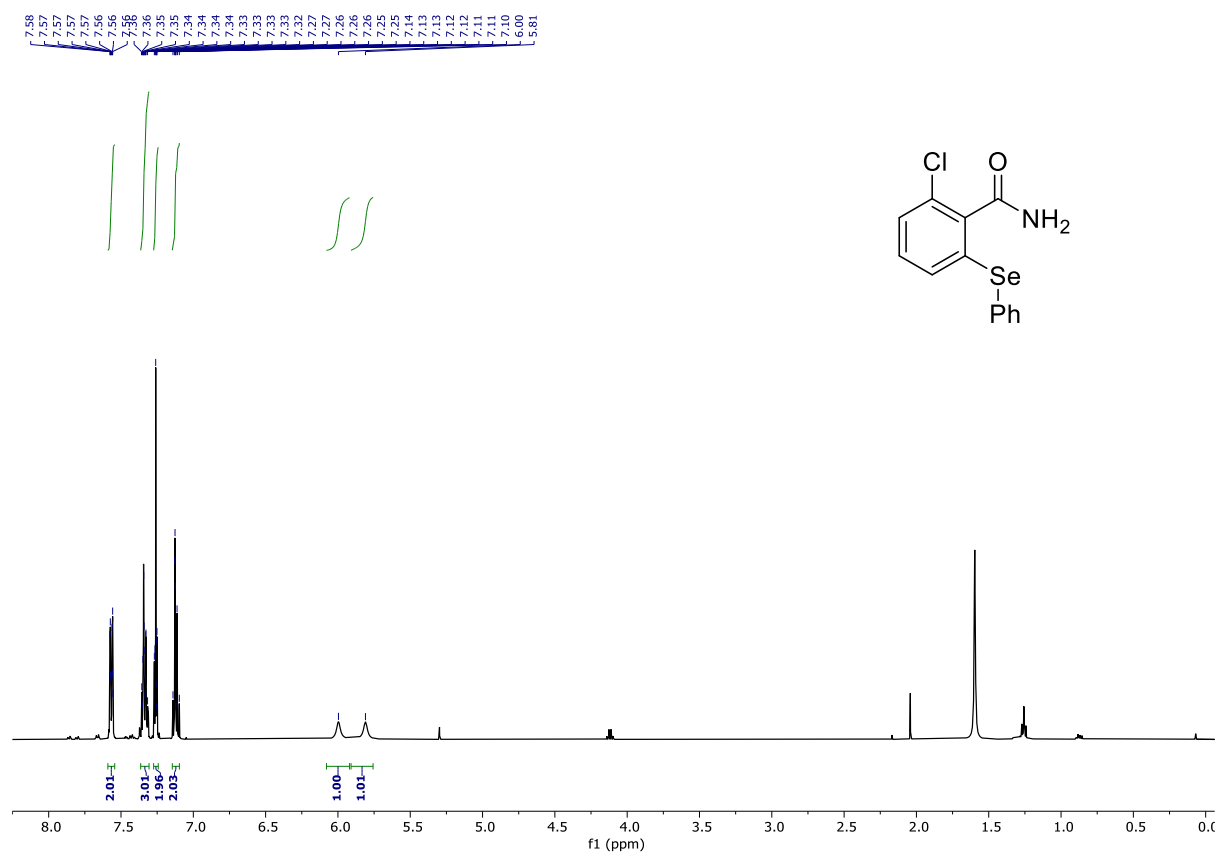
$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of **3n** in  $\text{CDCl}_3$



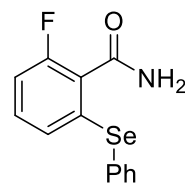
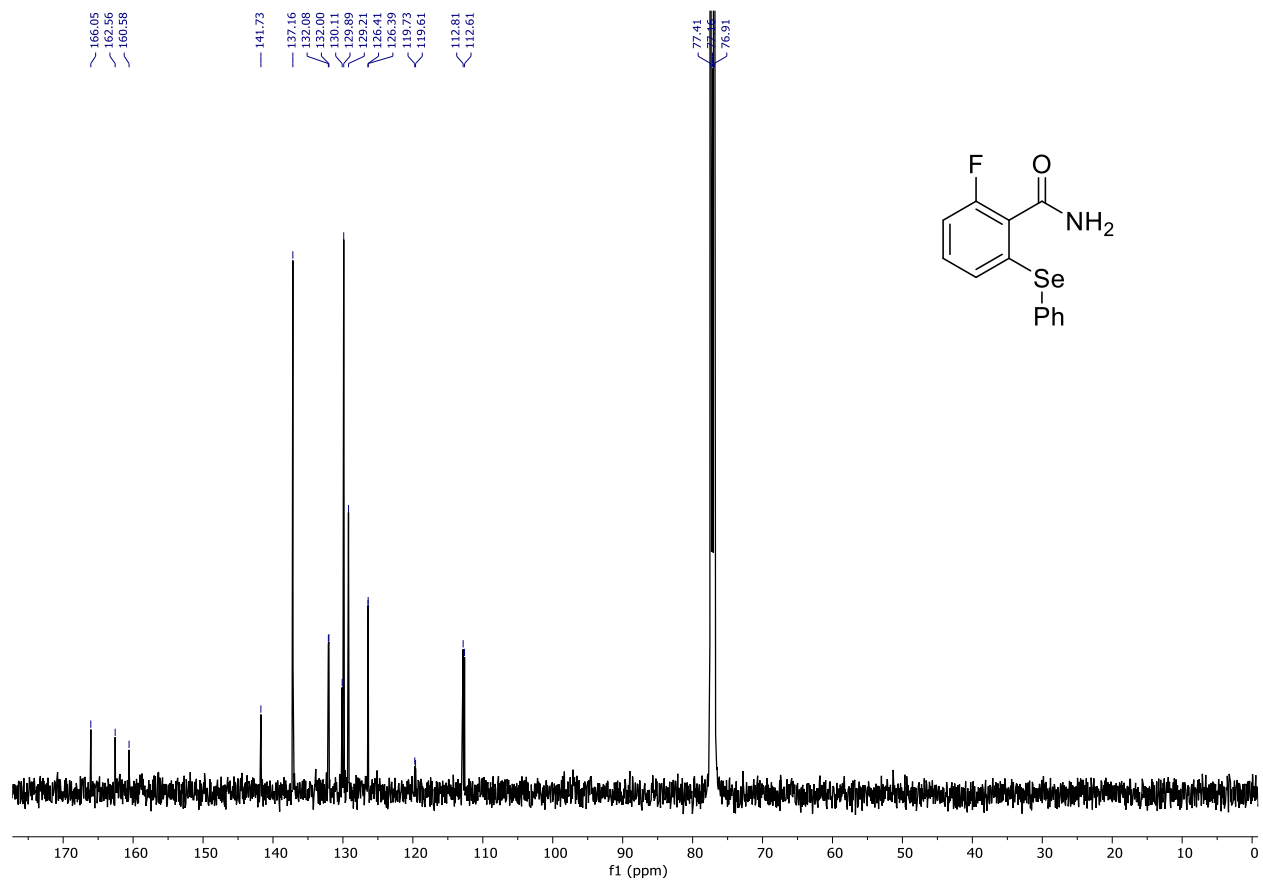
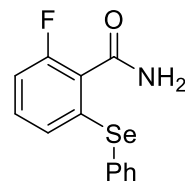
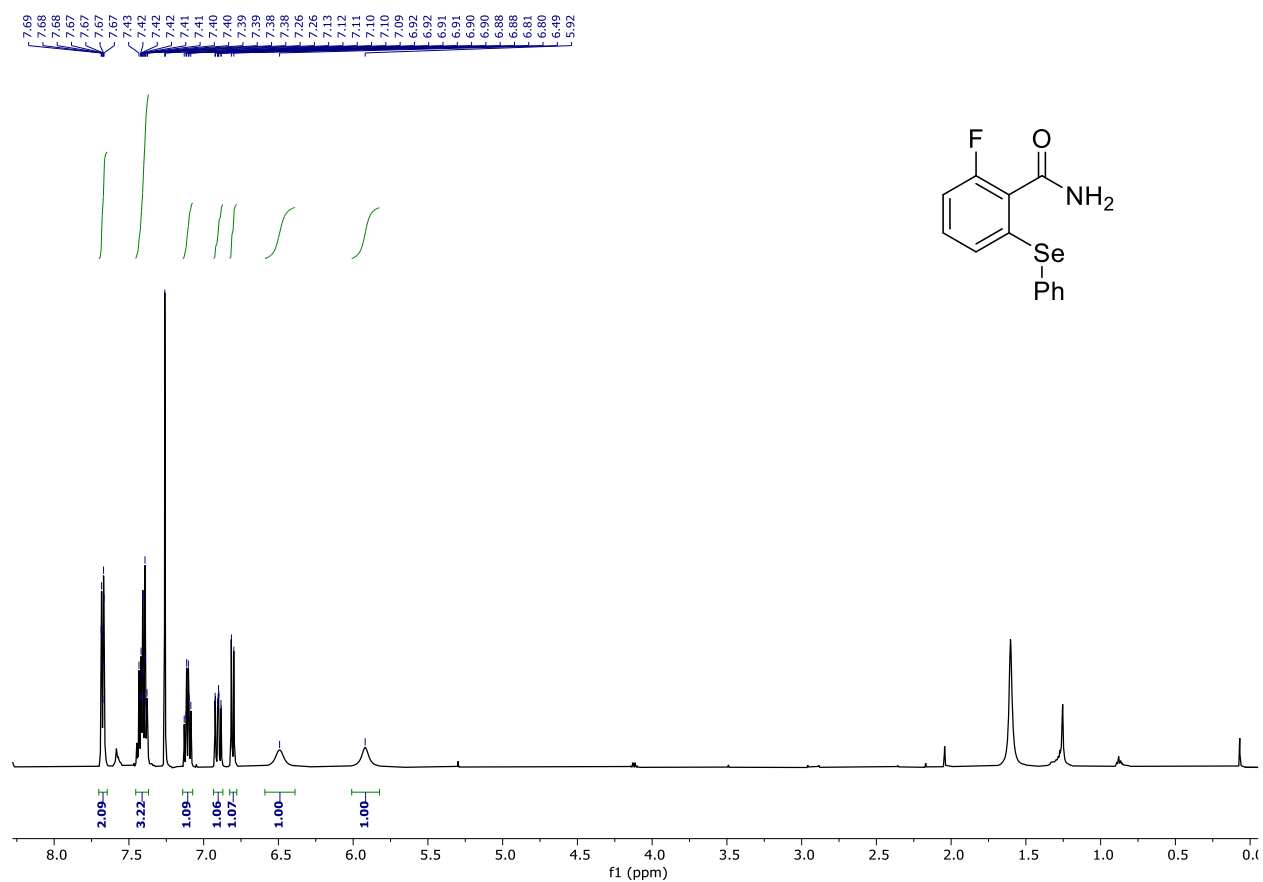
**$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 3o in  $\text{CDCl}_3$**



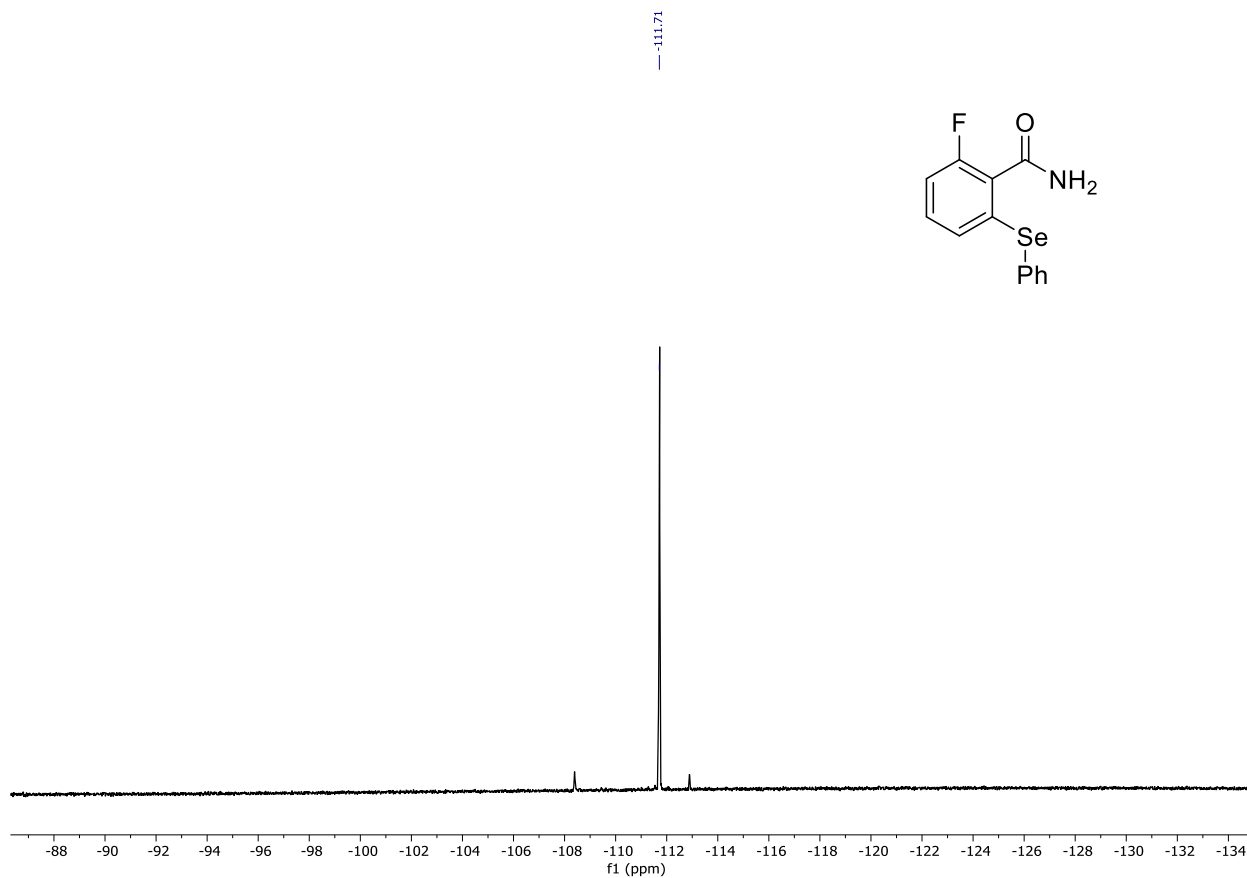
**$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 3p in  $\text{CDCl}_3$**



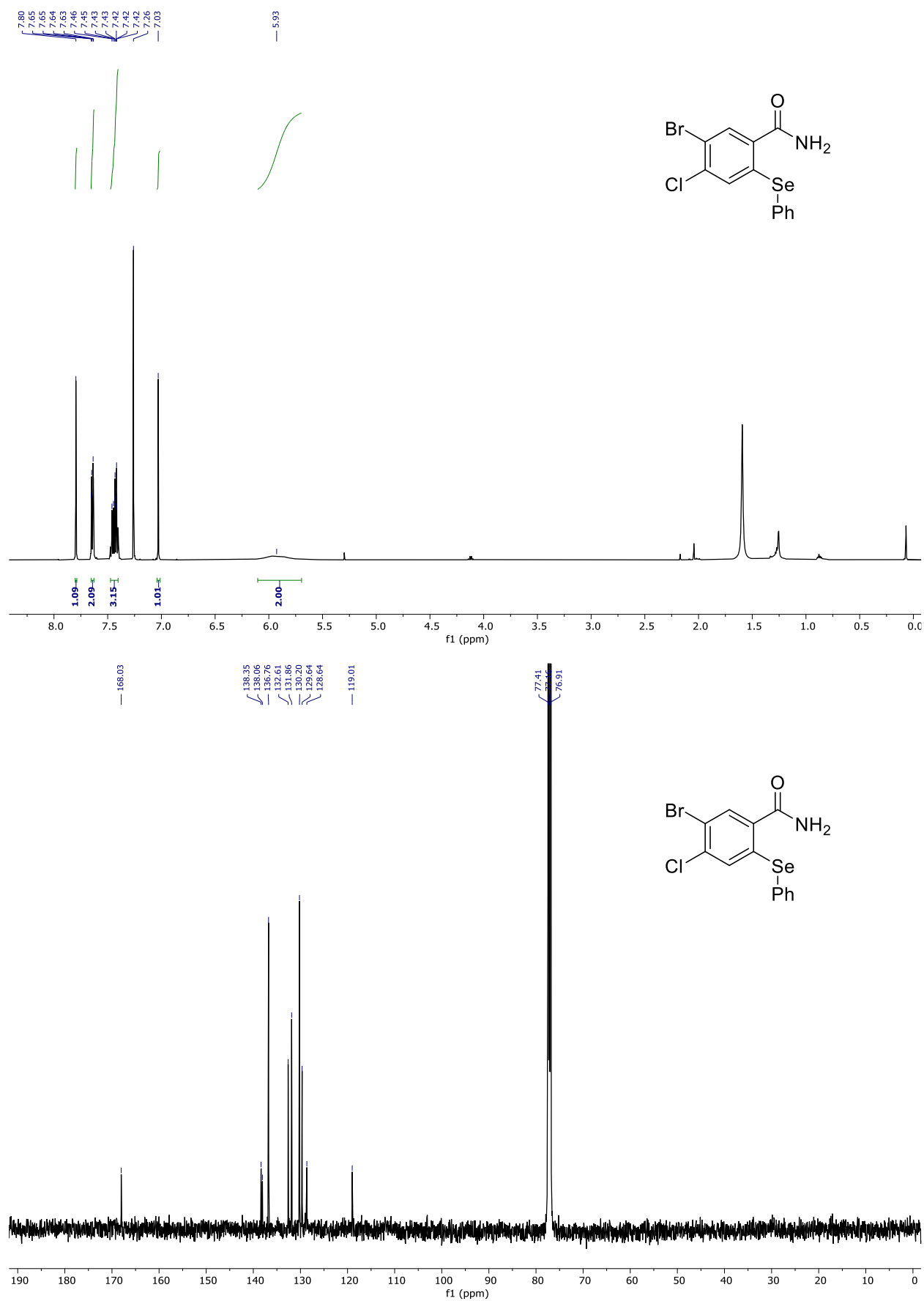
**$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 3q in  $\text{CDCl}_3$**



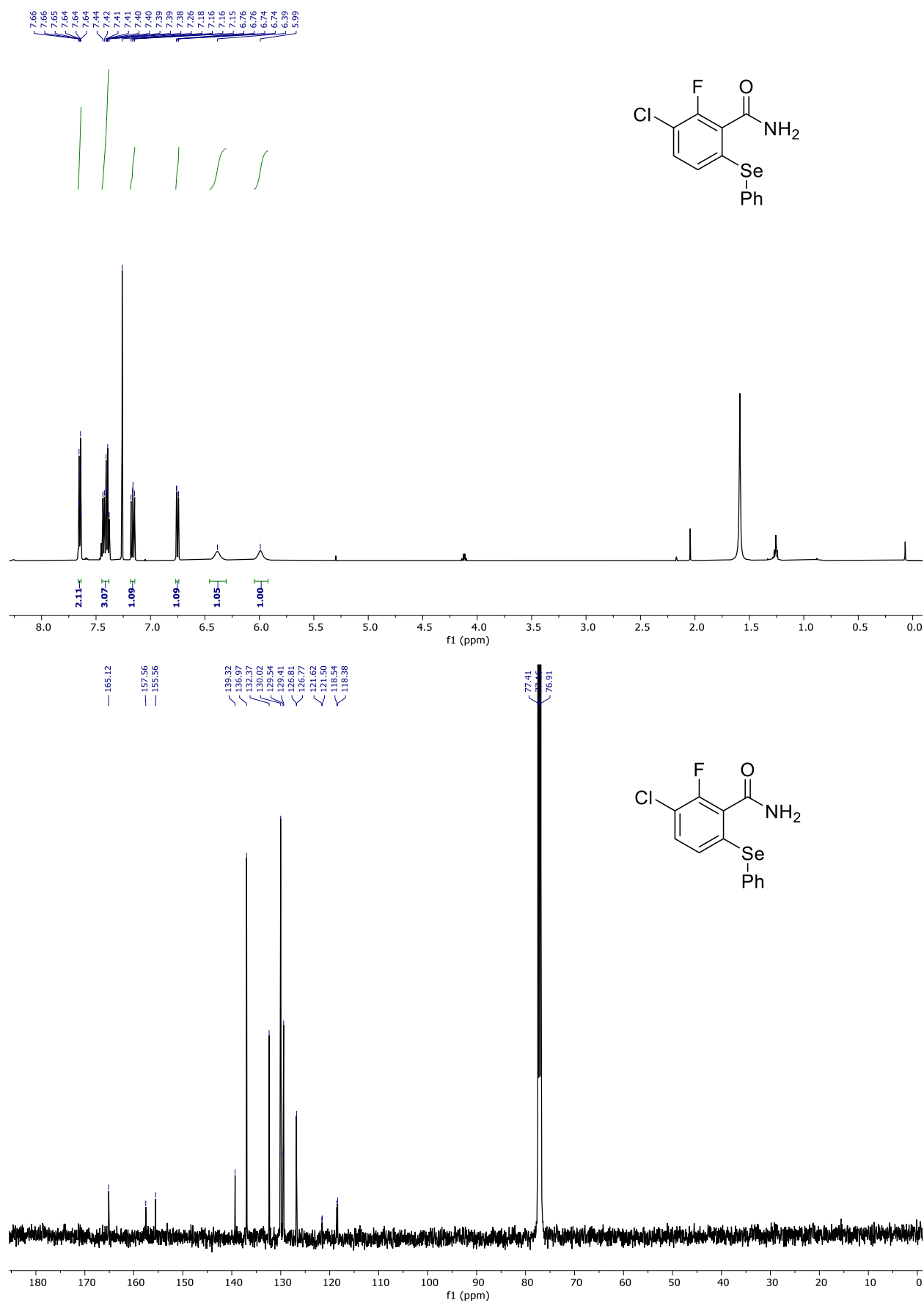
**$^{19}\text{F}\{^1\text{H}\}$  (471 MHz) NMR spectra of 3q in  $\text{CDCl}_3$**



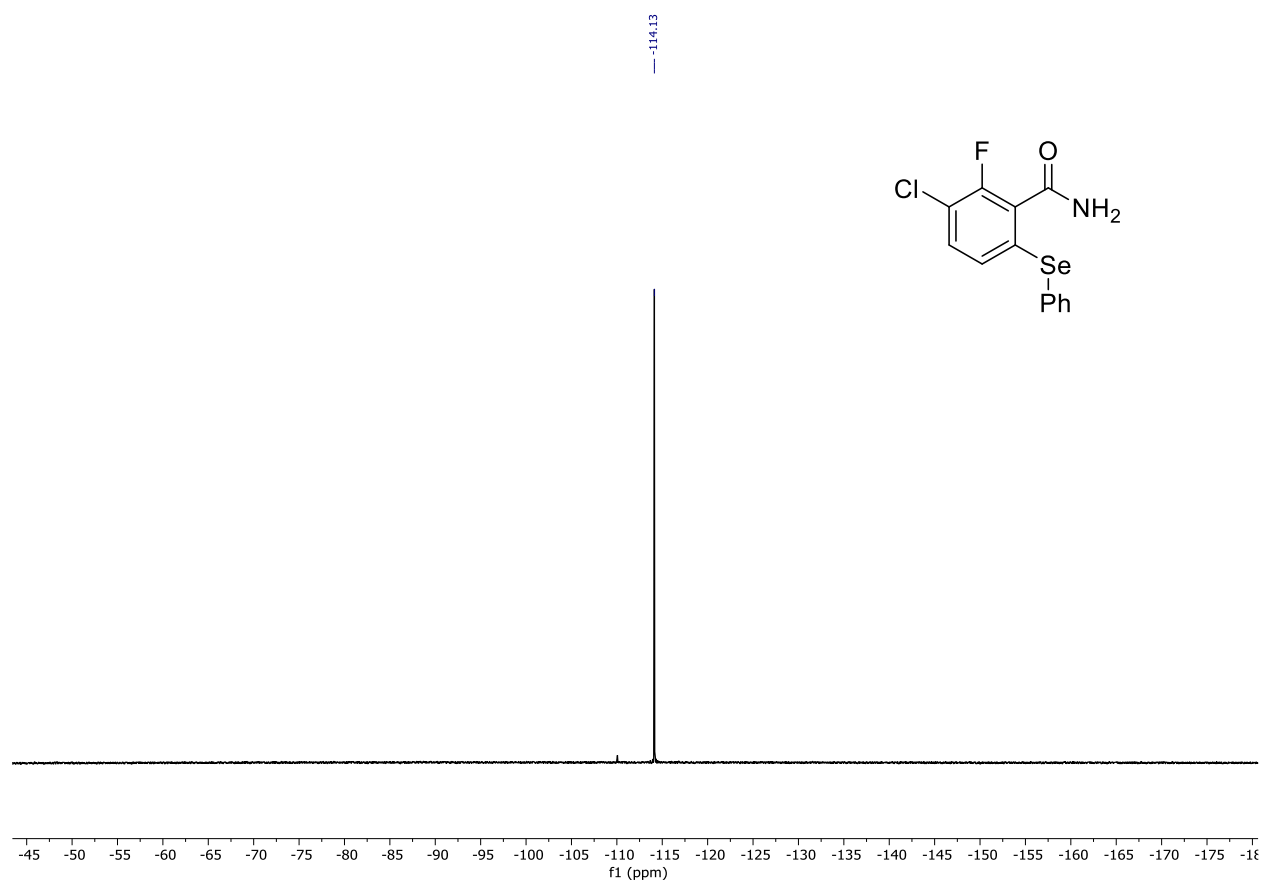
$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 3r in  $\text{CDCl}_3$



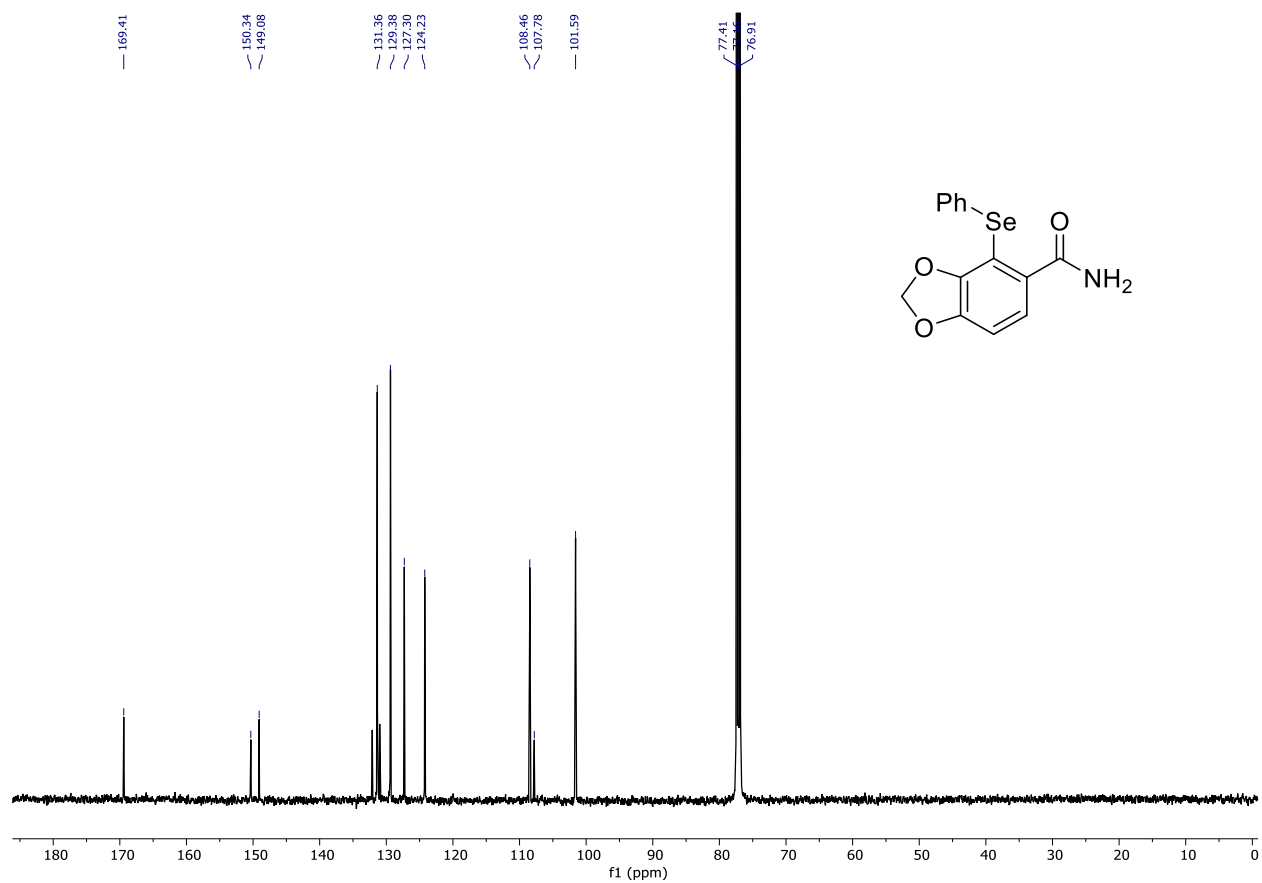
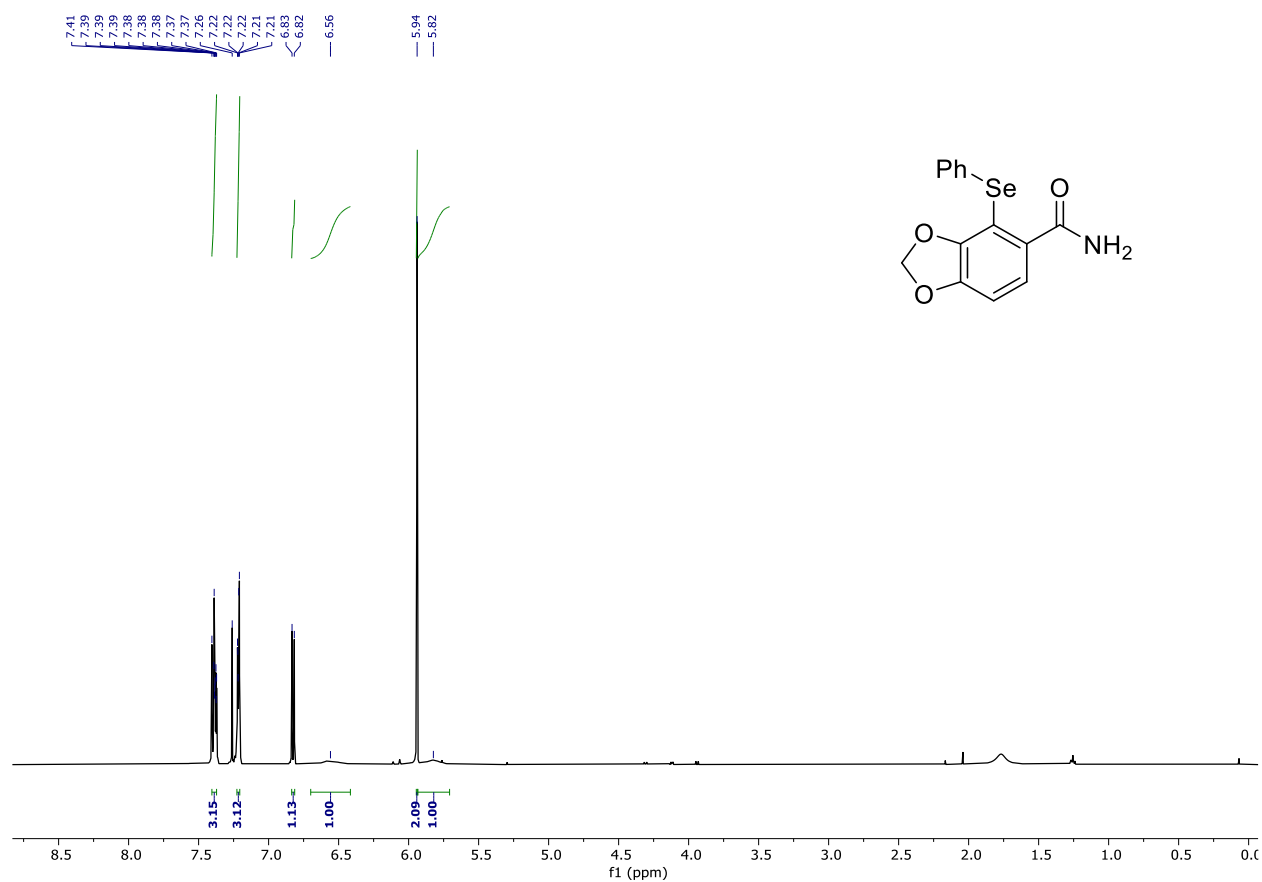
$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 3s in  $\text{CDCl}_3$



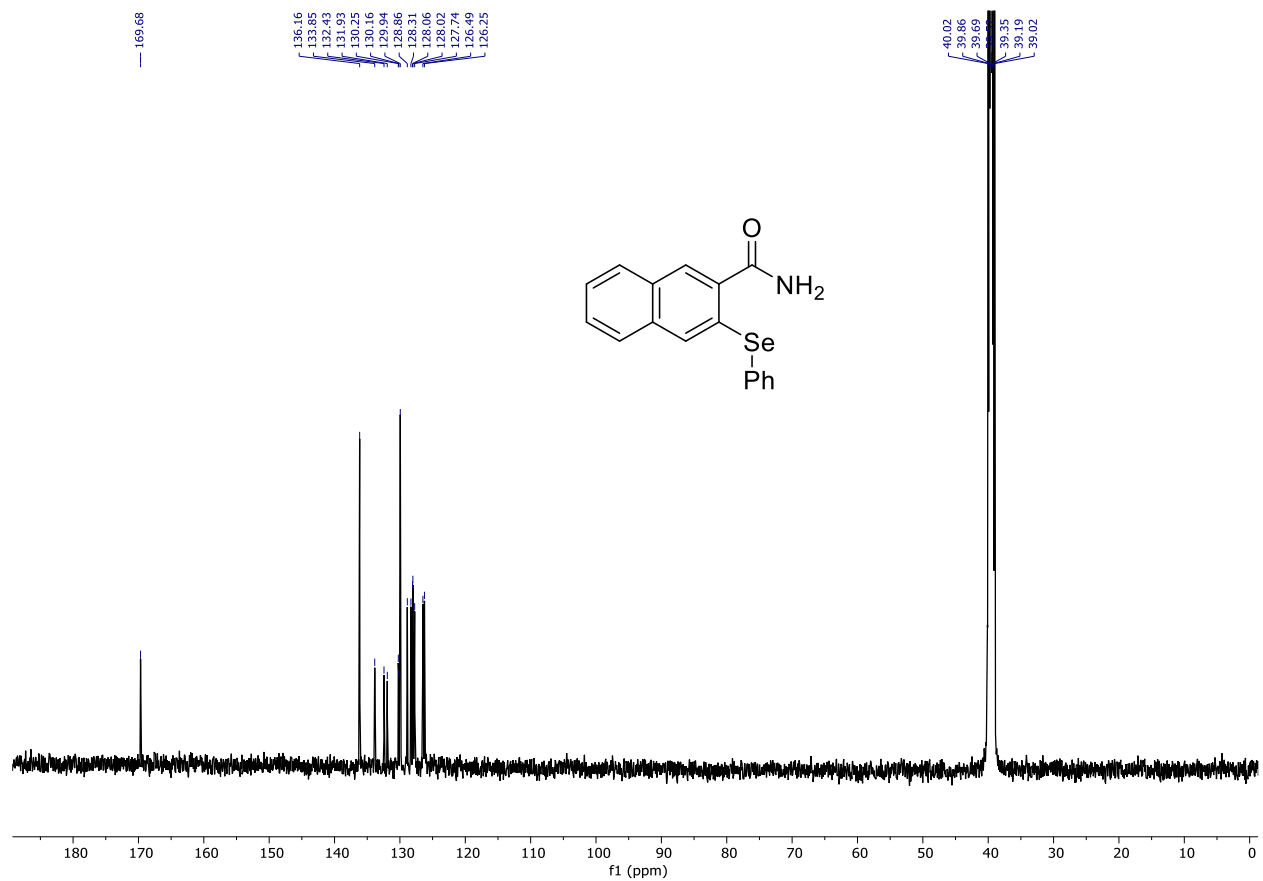
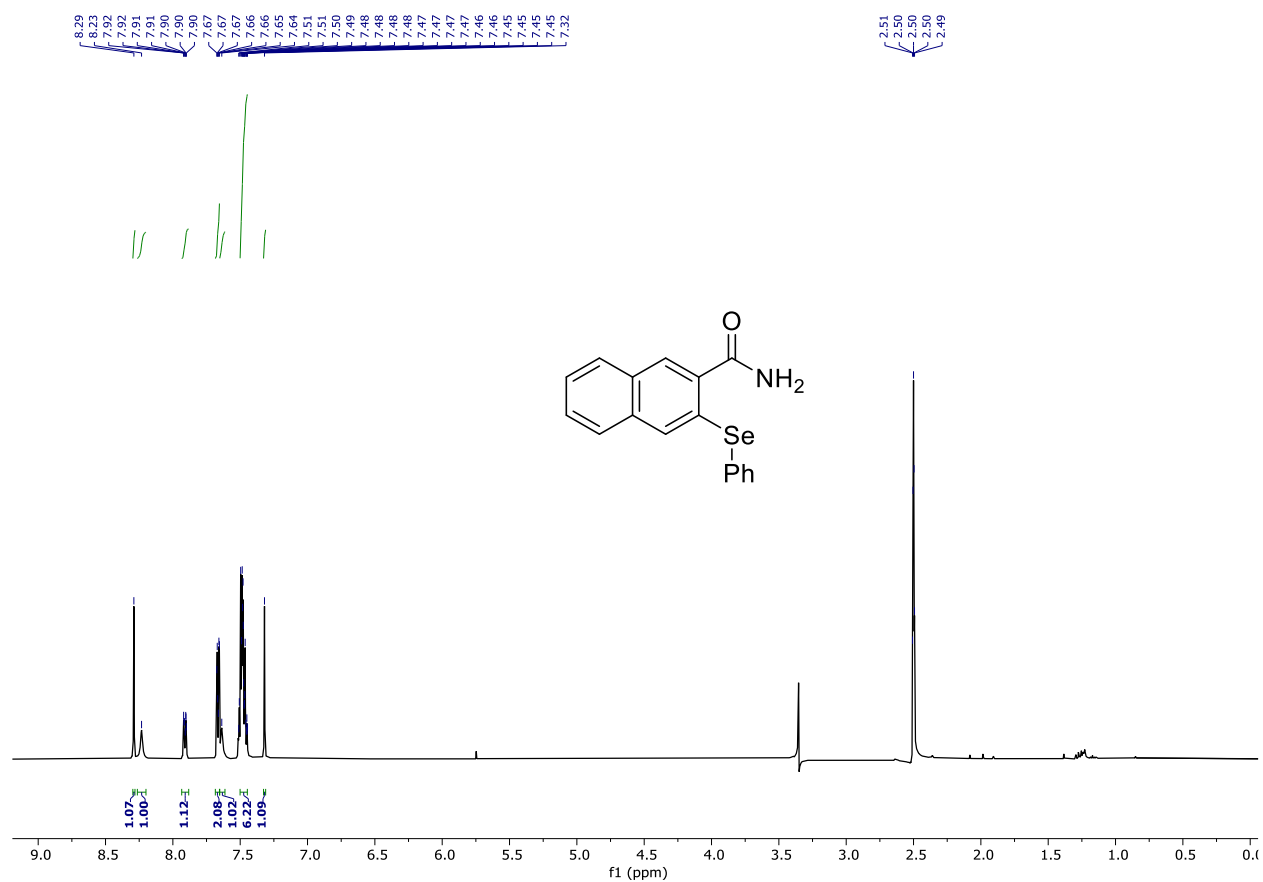
**$^{19}\text{F}\{^1\text{H}\}$  (471 MHz) NMR spectra of 3s in  $\text{CDCl}_3$**



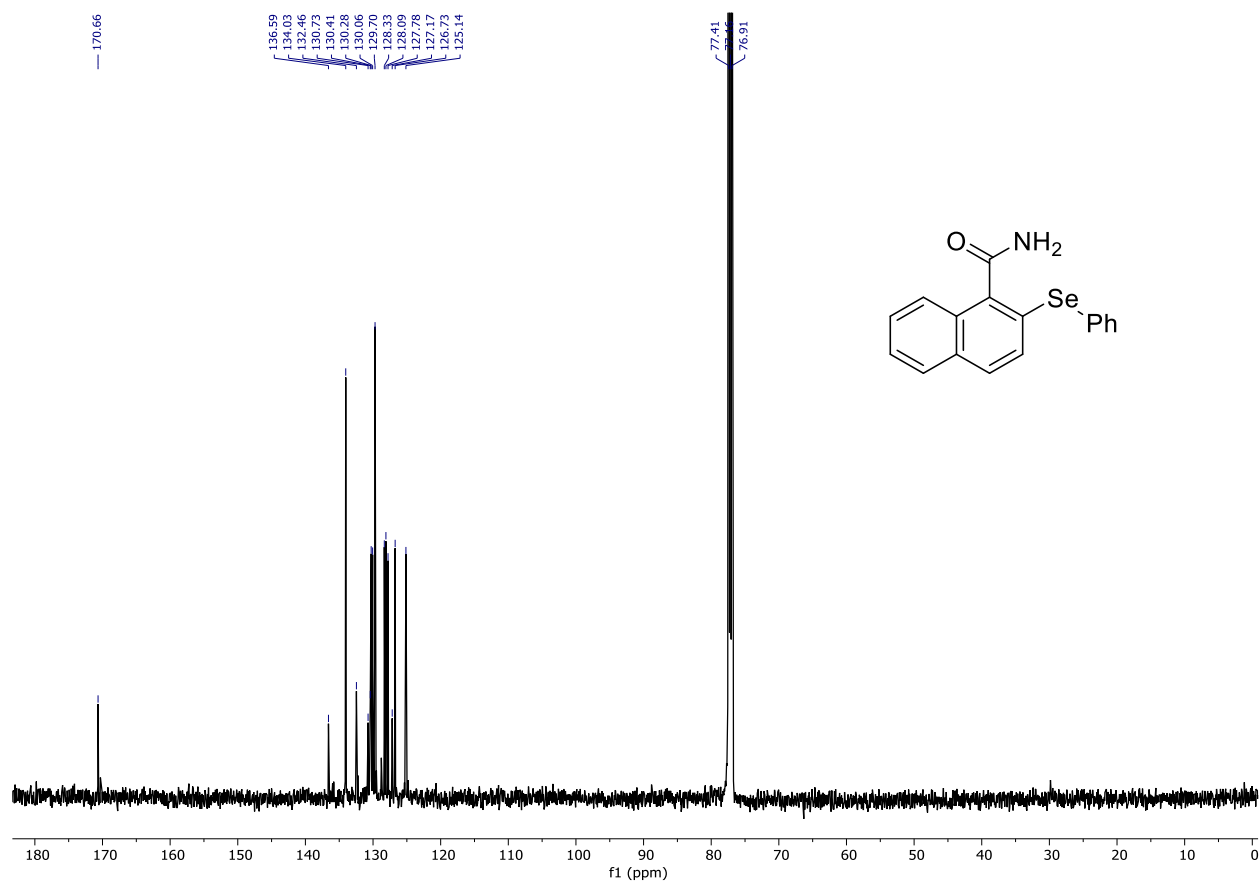
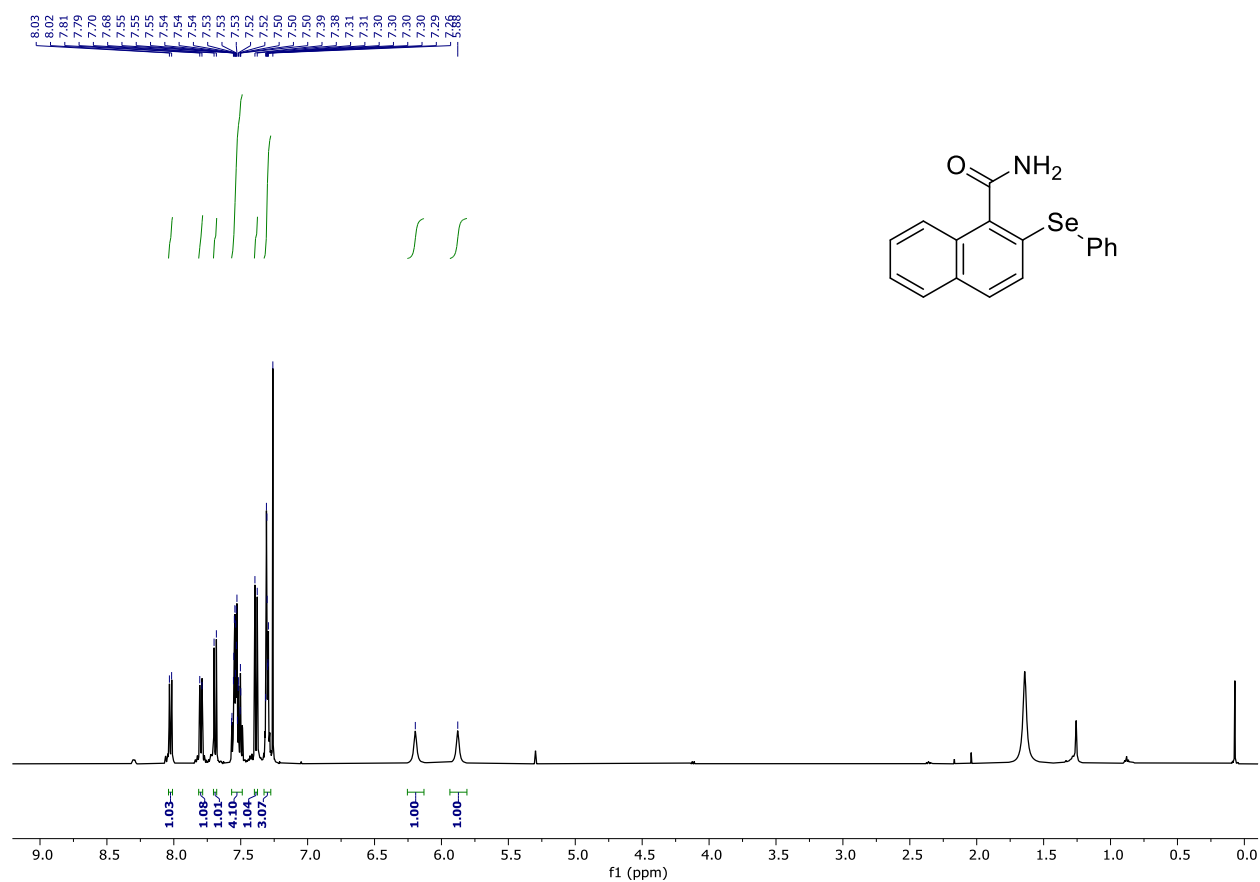
**$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 3t in  $\text{CDCl}_3$**



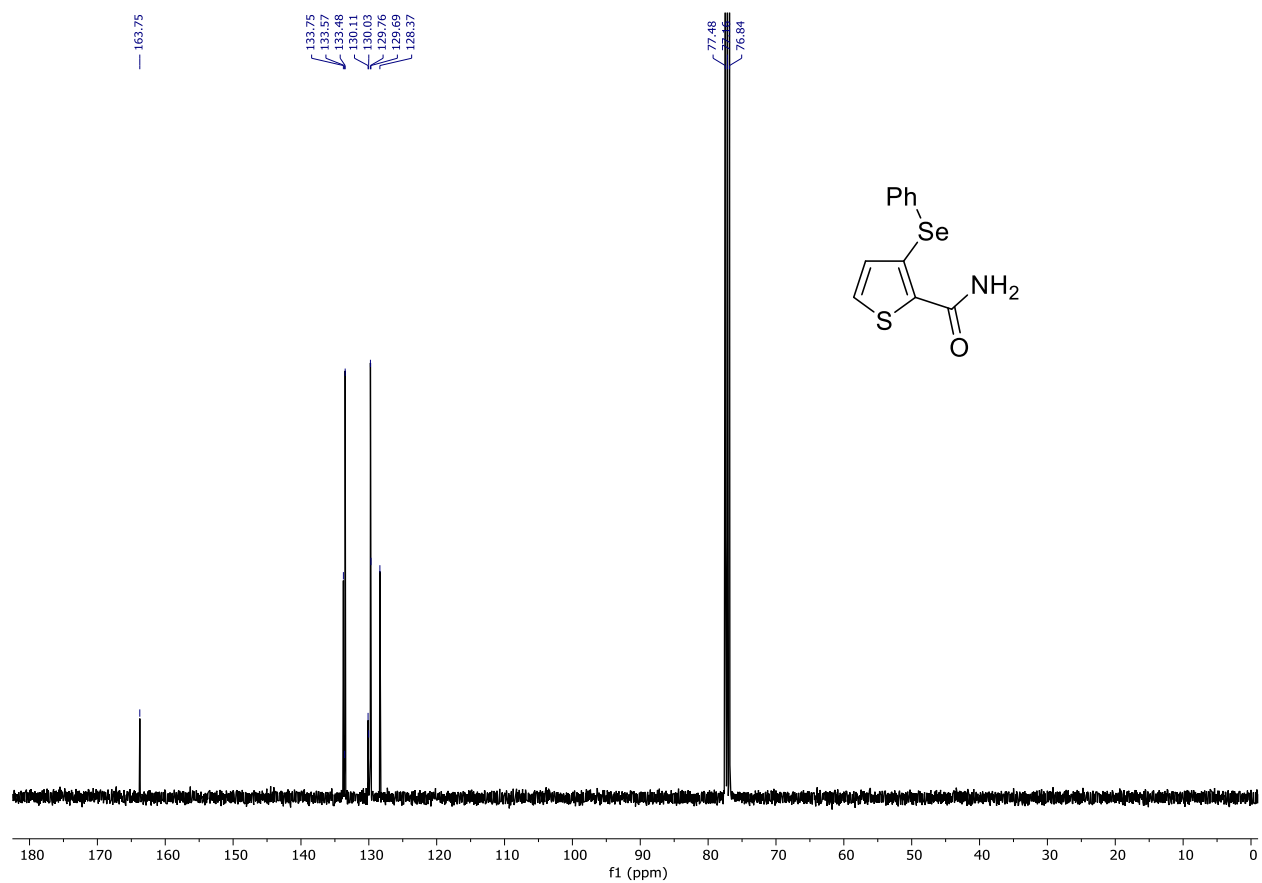
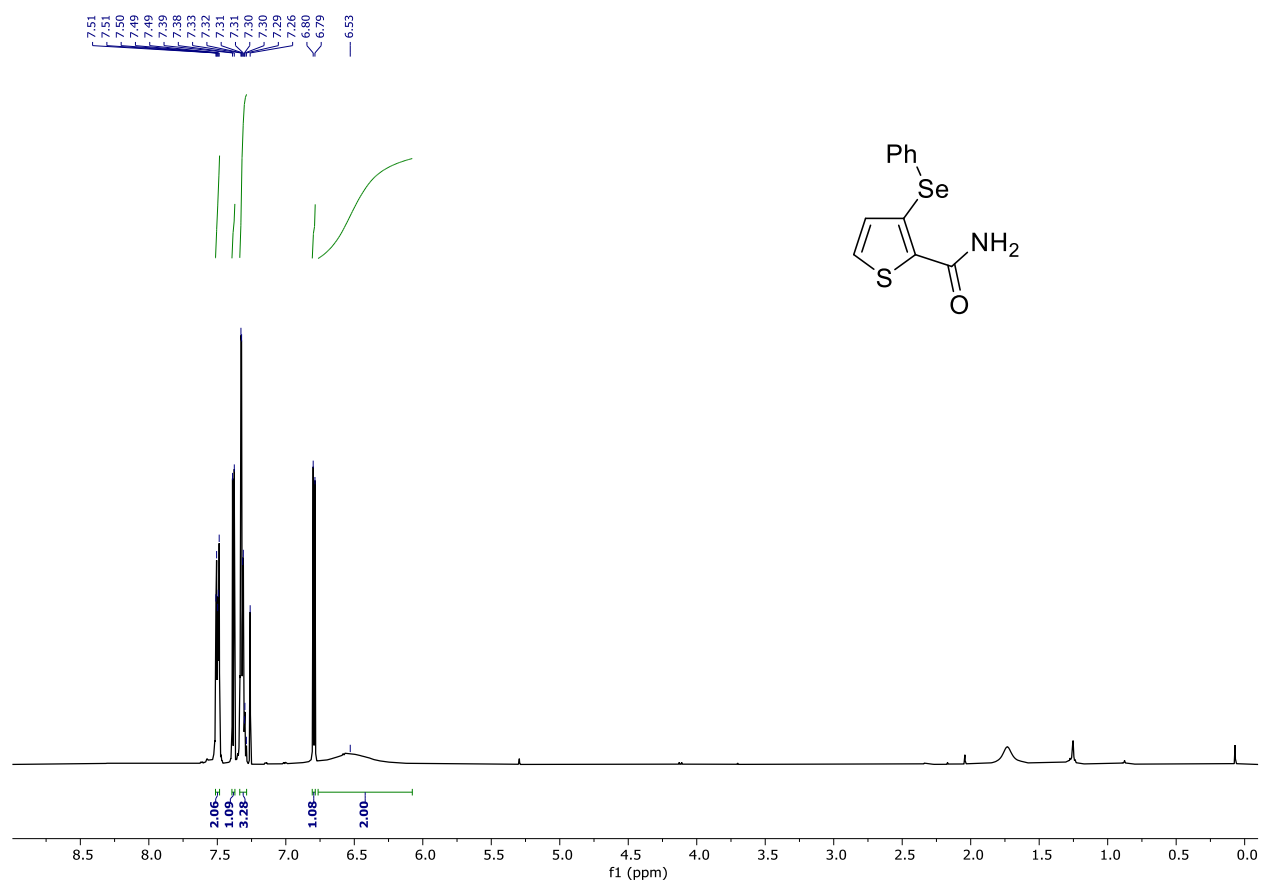
$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 3u in  $\text{DMSO-}D_6$



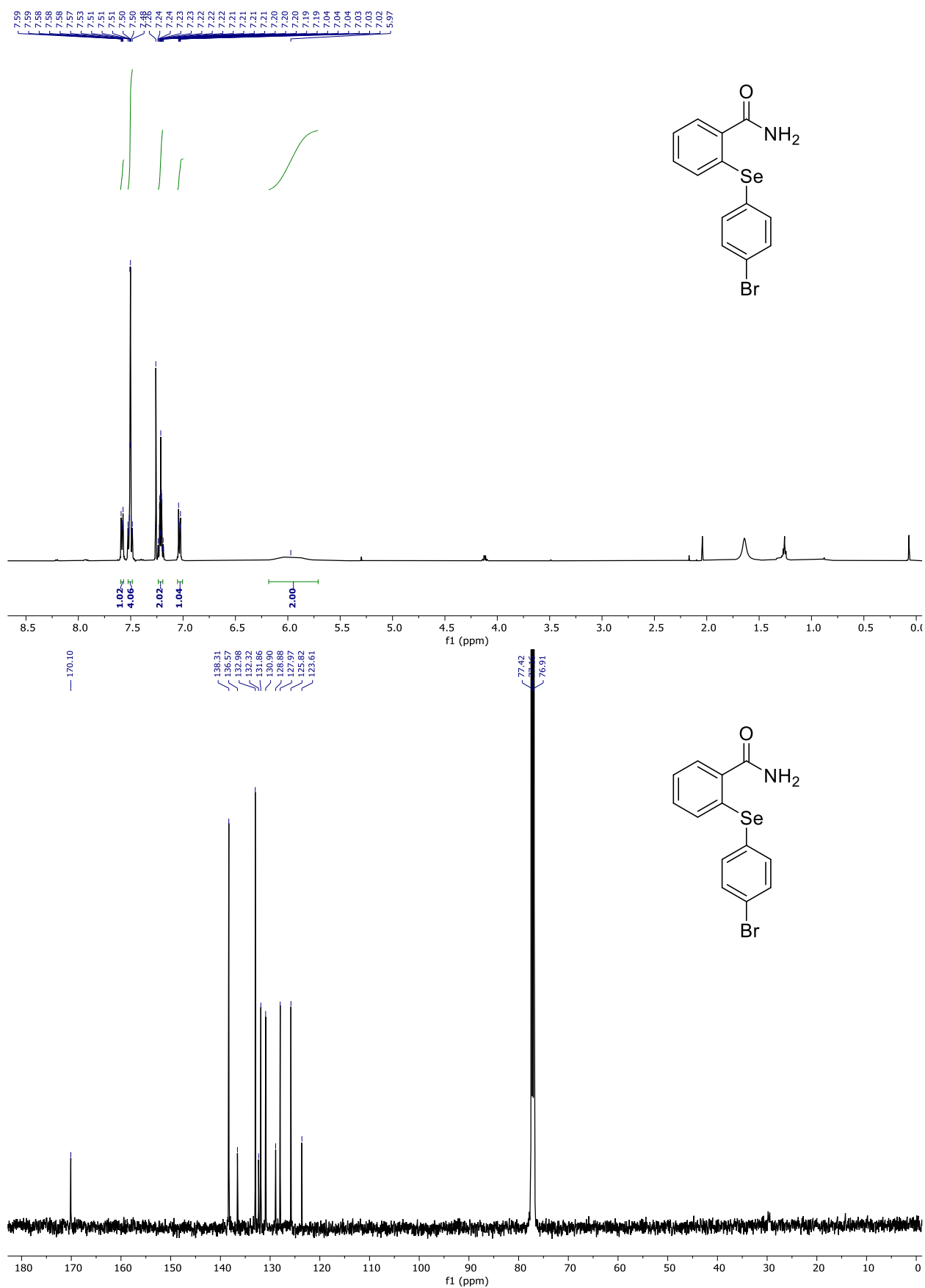
$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 3v in  $\text{CDCl}_3$



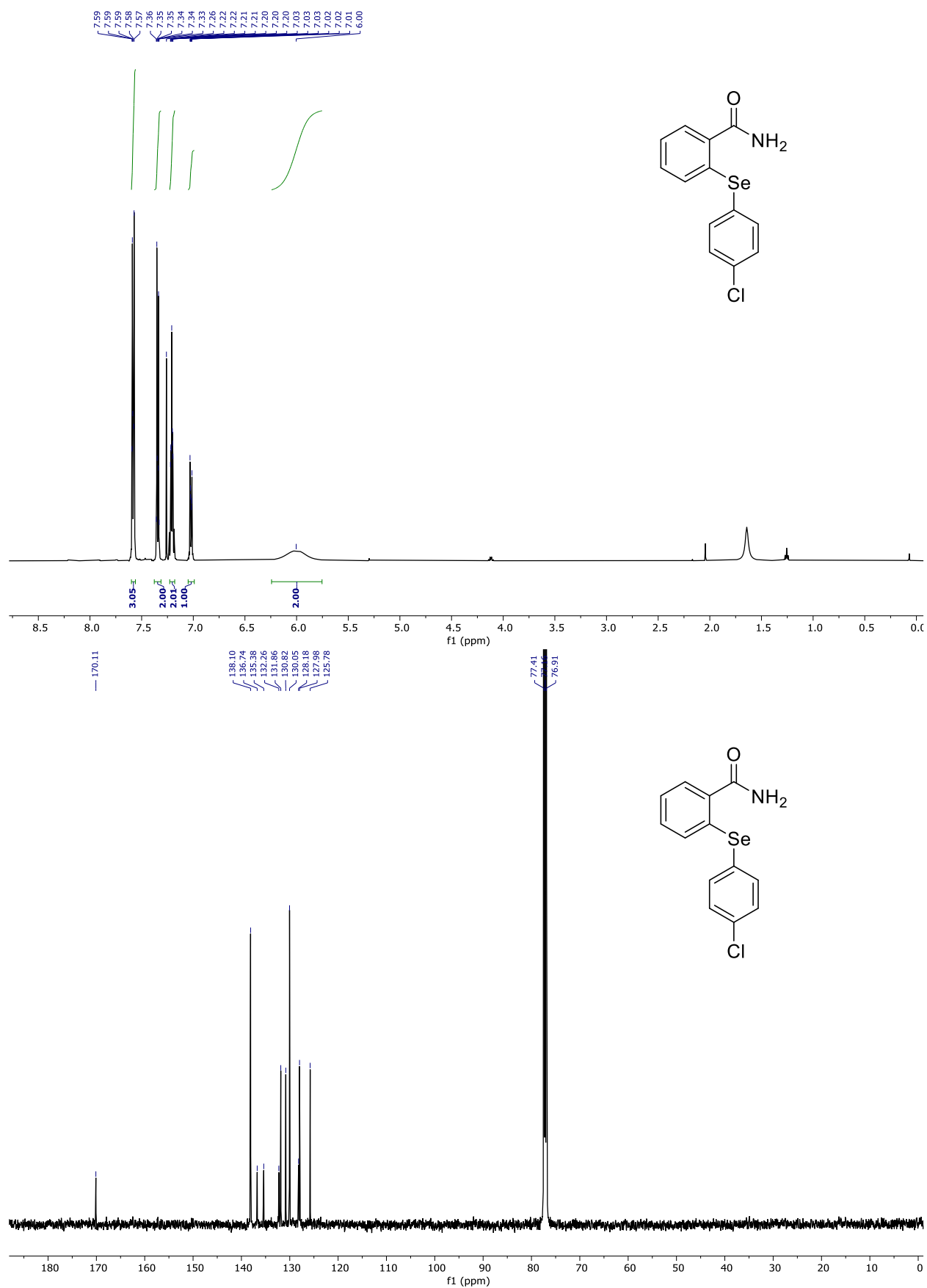
$^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (100 MHz) spectra of 3w in  $\text{CDCl}_3$



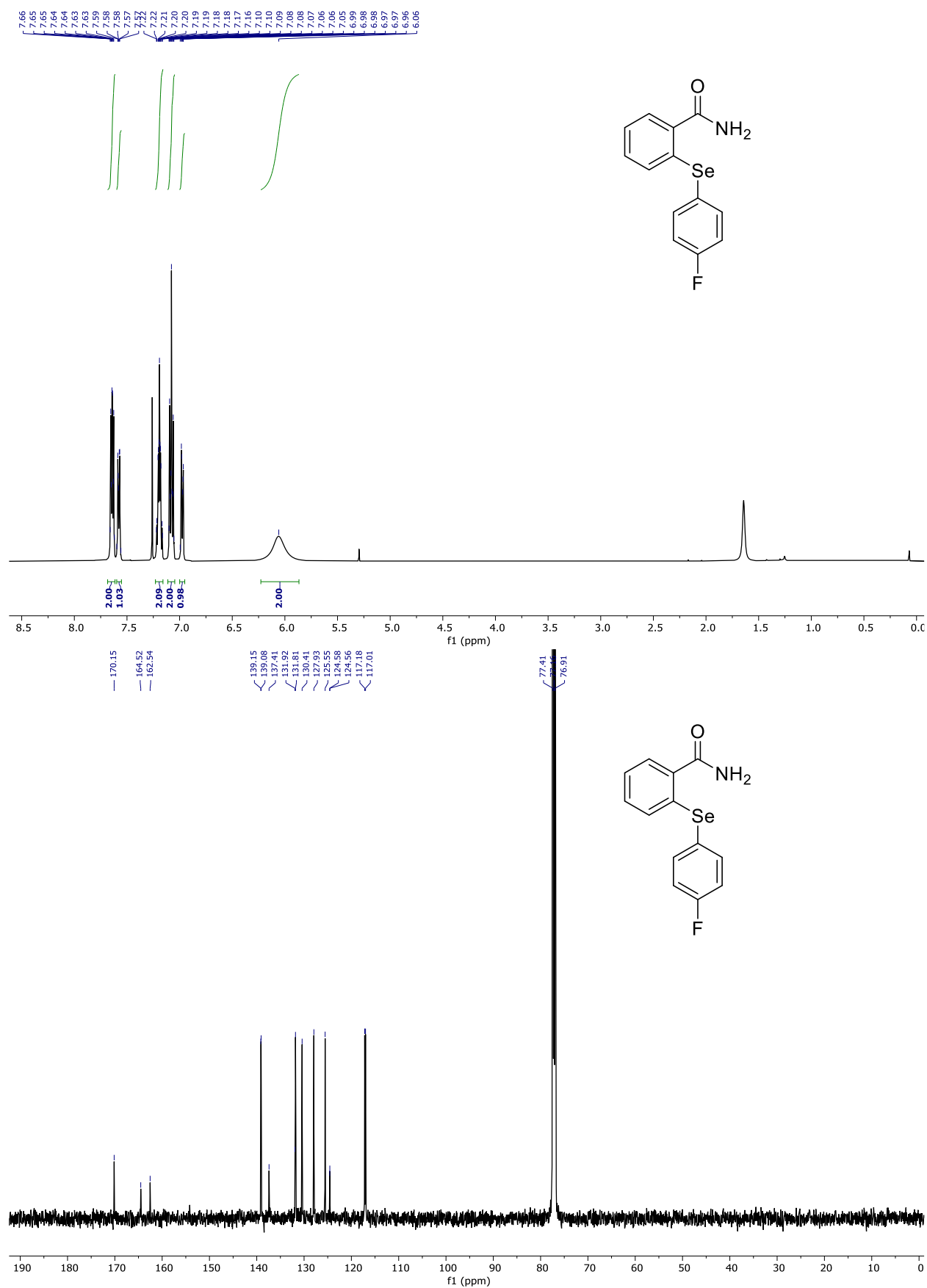
**$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 4b in  $\text{CDCl}_3$**



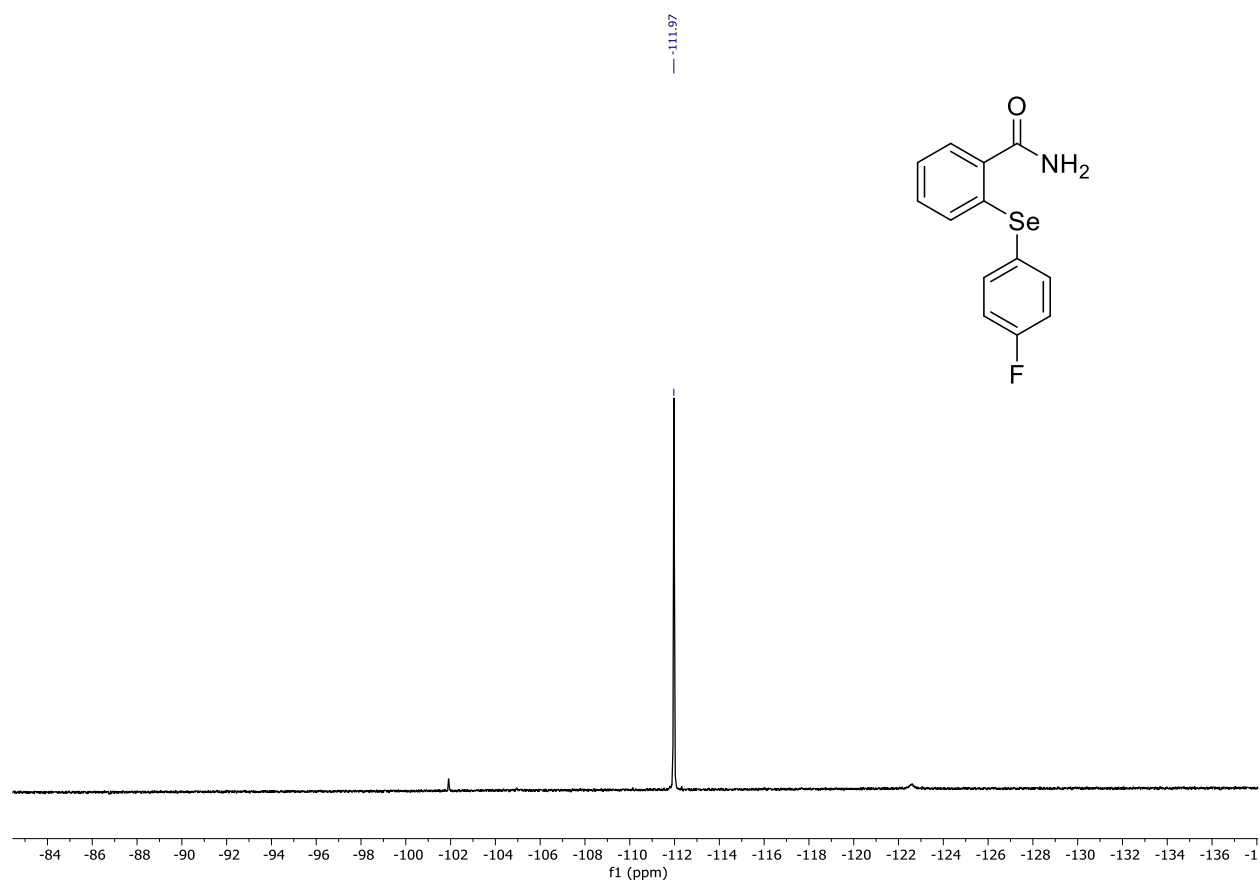
$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 4c in  $\text{CDCl}_3$



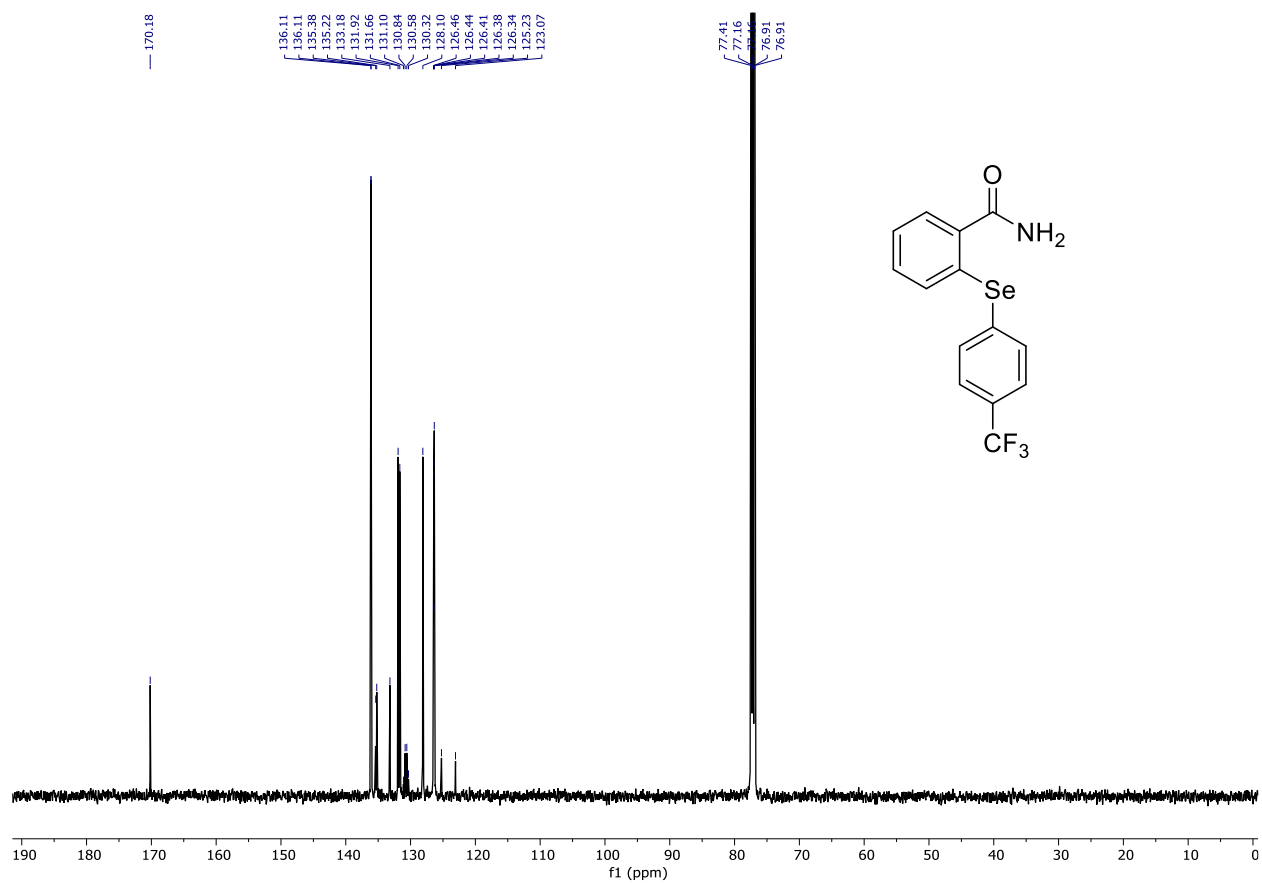
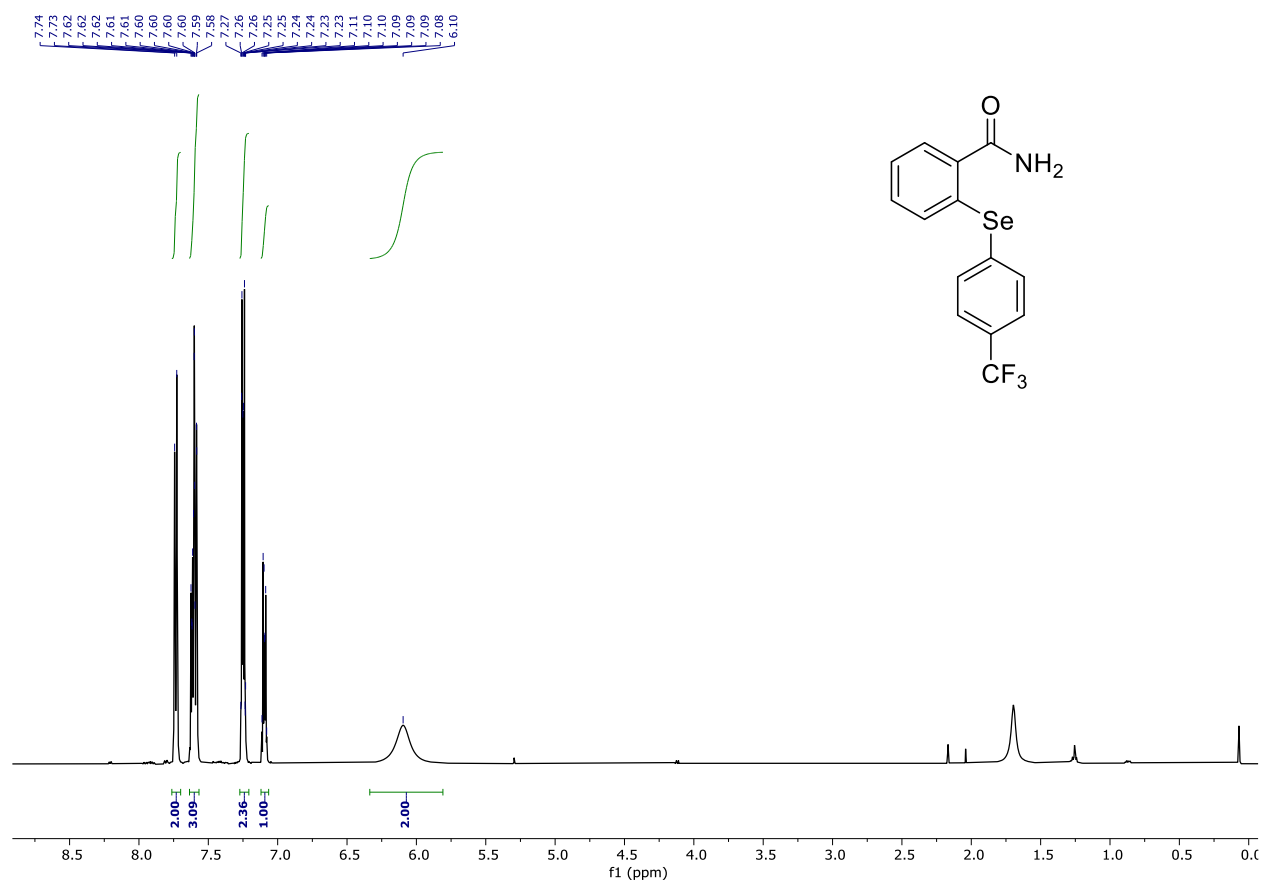
**$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 4d in  $\text{CDCl}_3$**



**$^{19}\text{F}\{^1\text{H}\}$  (471 MHz) NMR spectra of 4d in  $\text{CDCl}_3$**



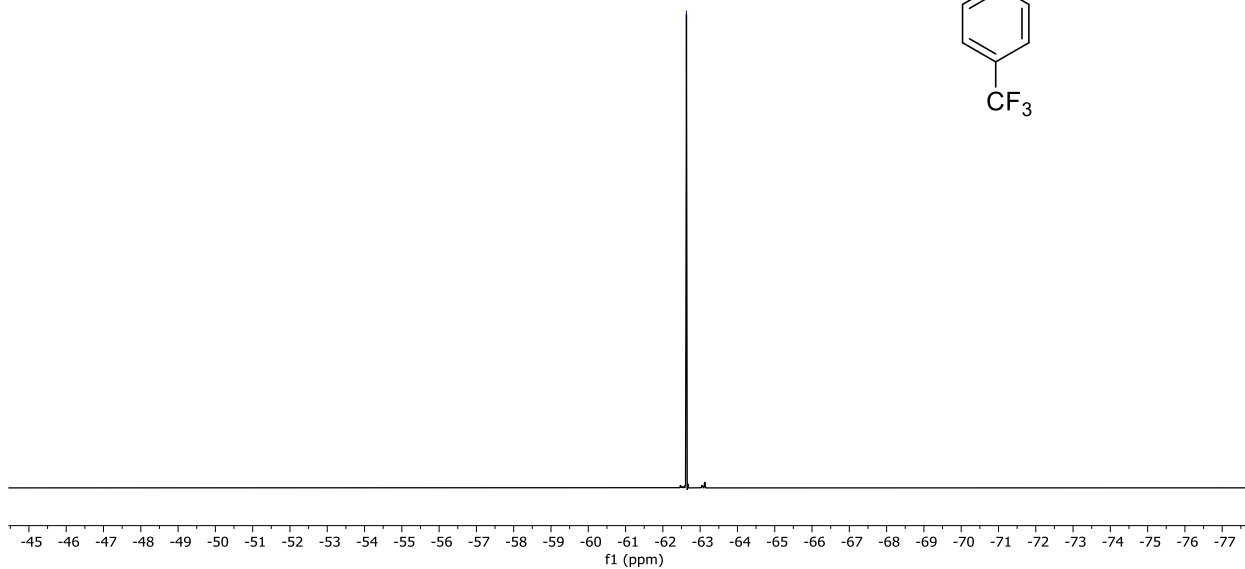
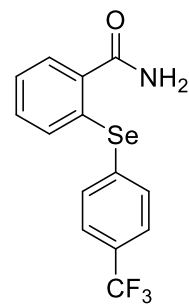
$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 4e in  $\text{CDCl}_3$



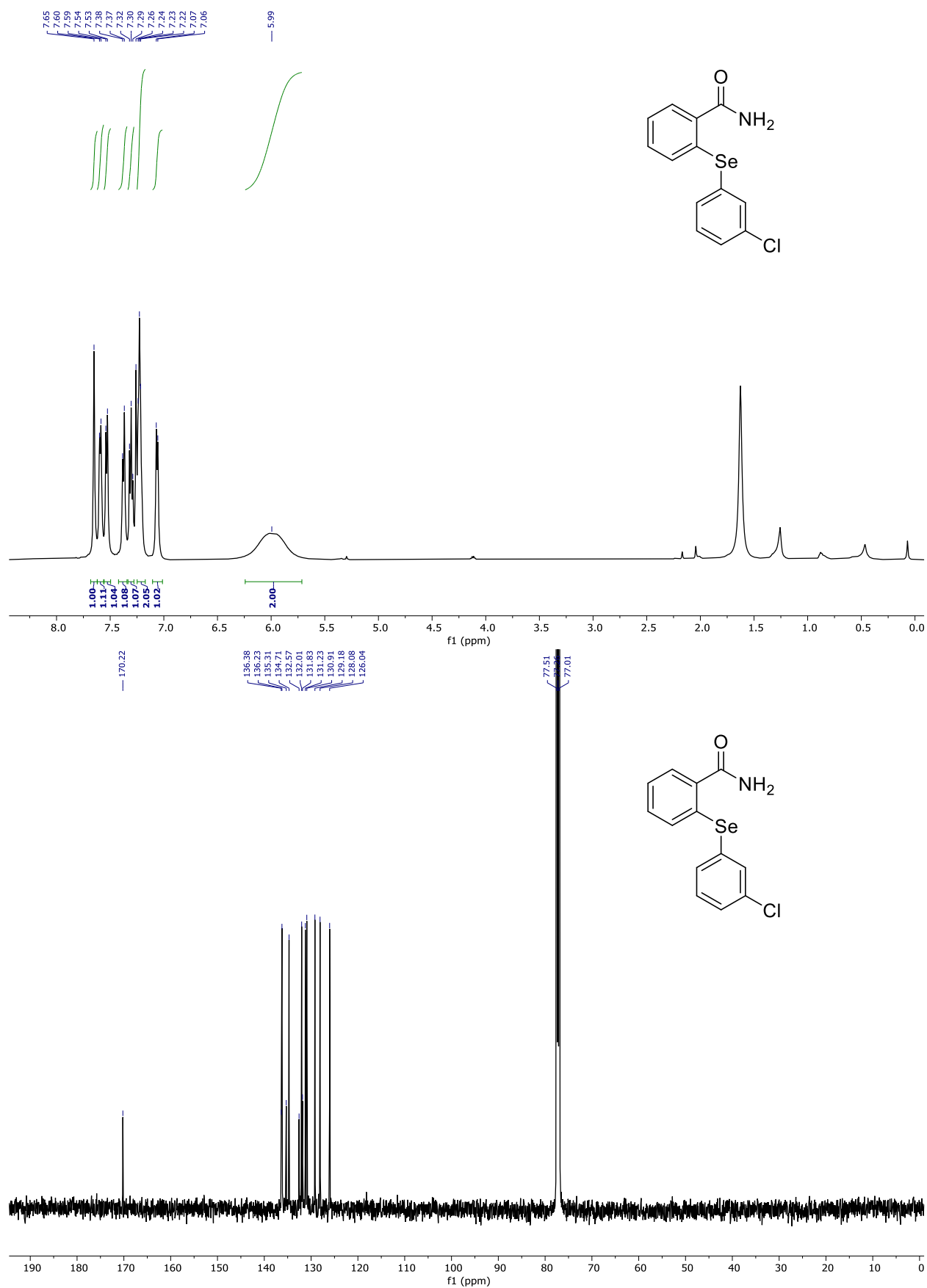
**$^{19}\text{F}\{^1\text{H}\}$  (471 MHz) NMR spectra of 4e in  $\text{CDCl}_3$**

SM-811  
-19F

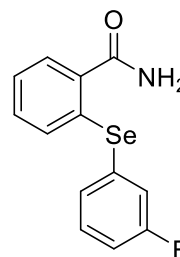
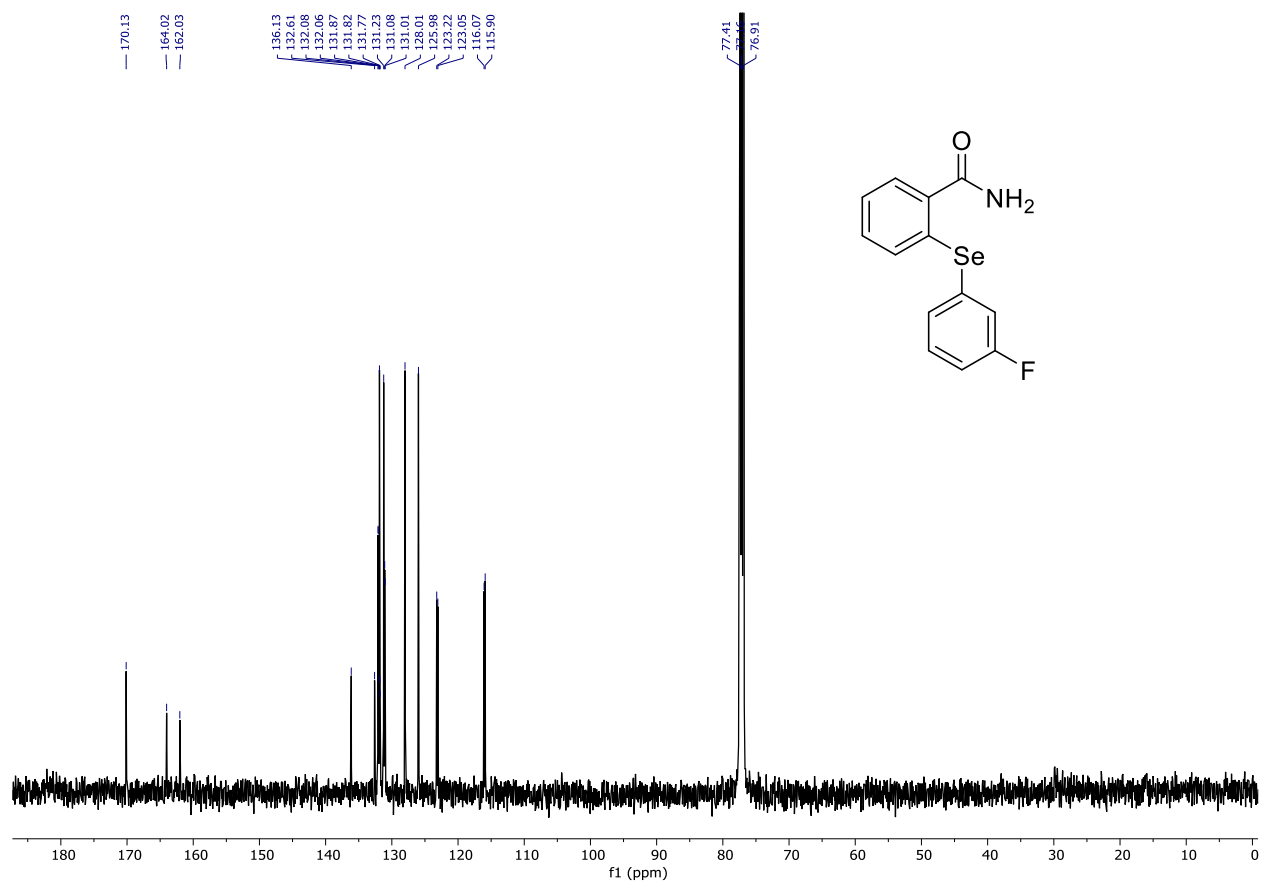
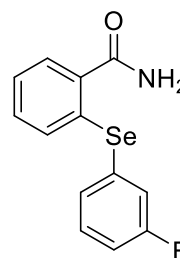
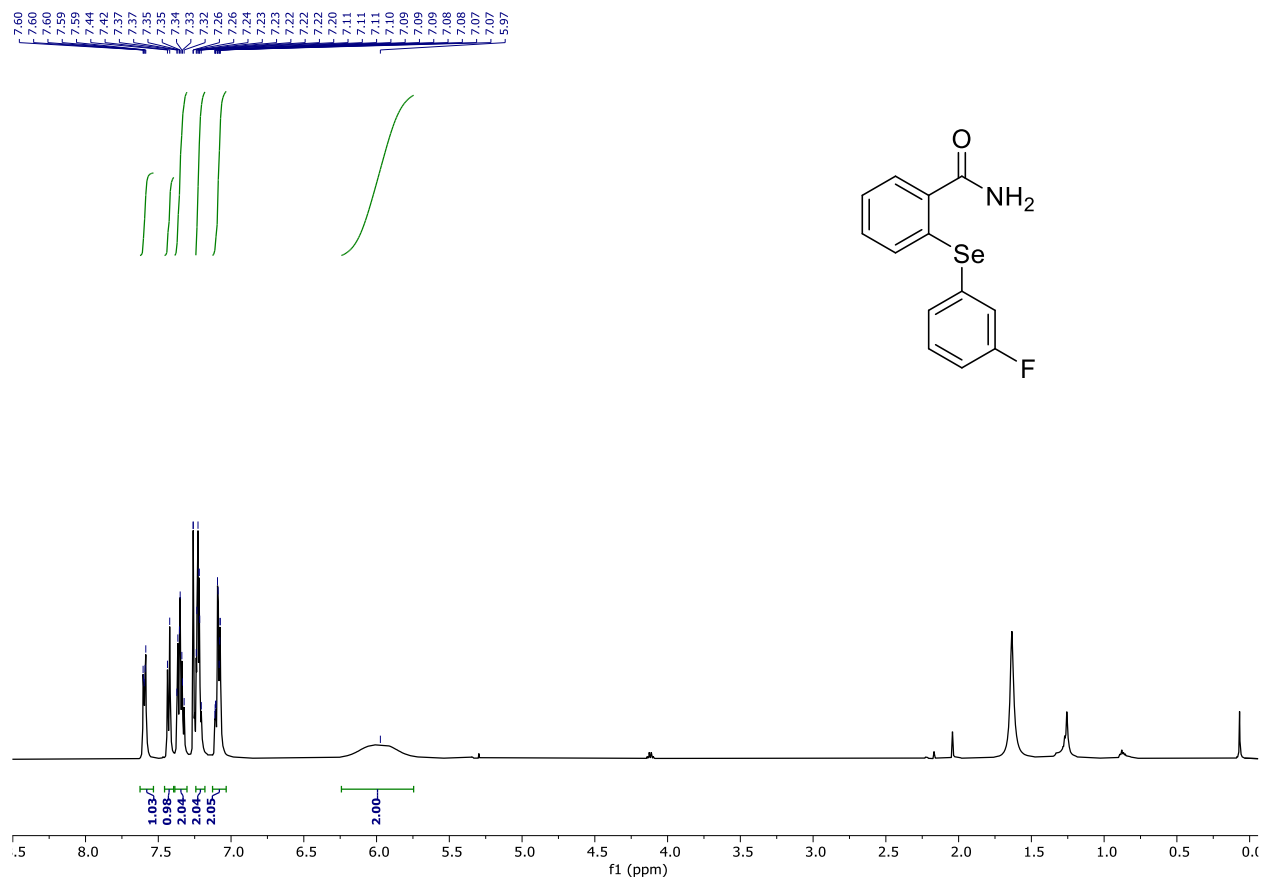
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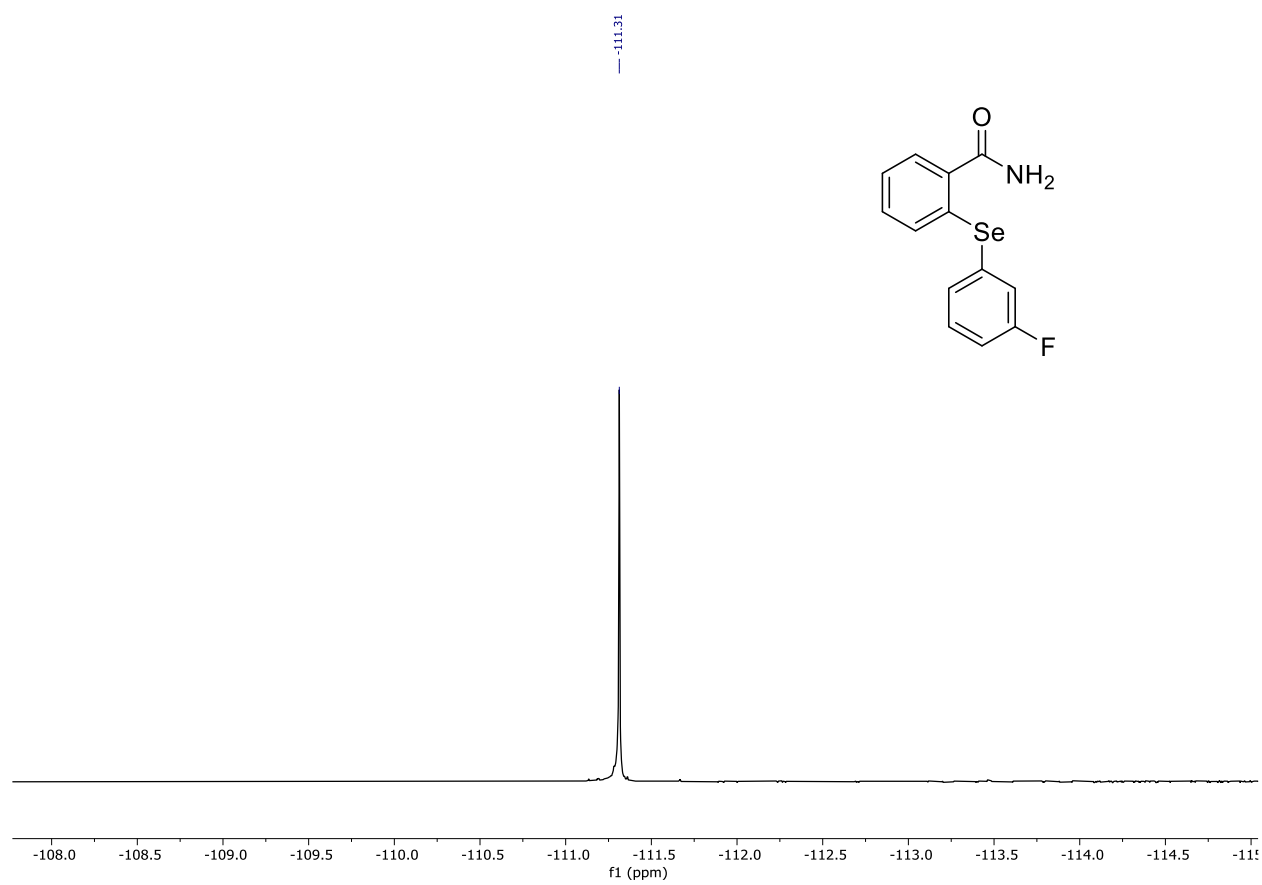
$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 4f in  $\text{CDCl}_3$



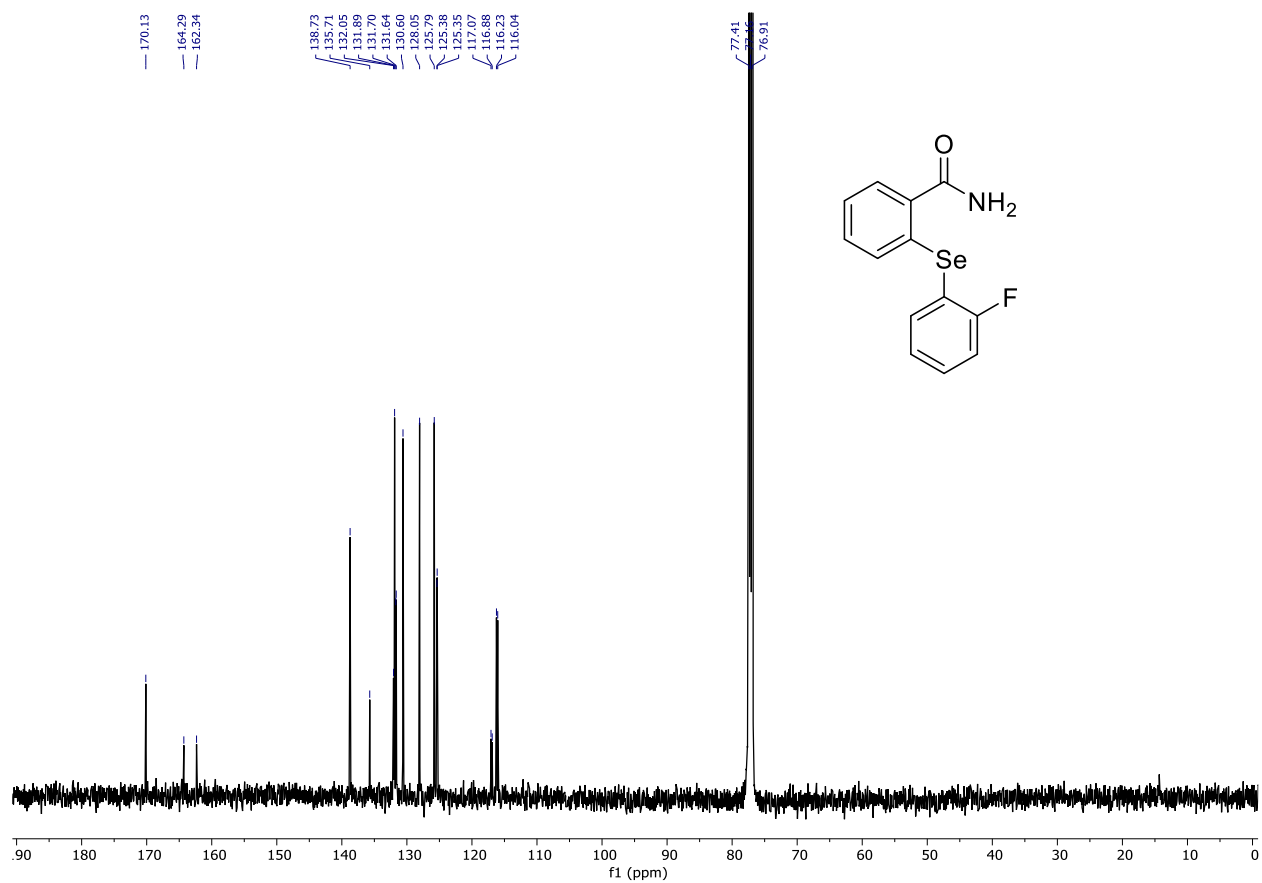
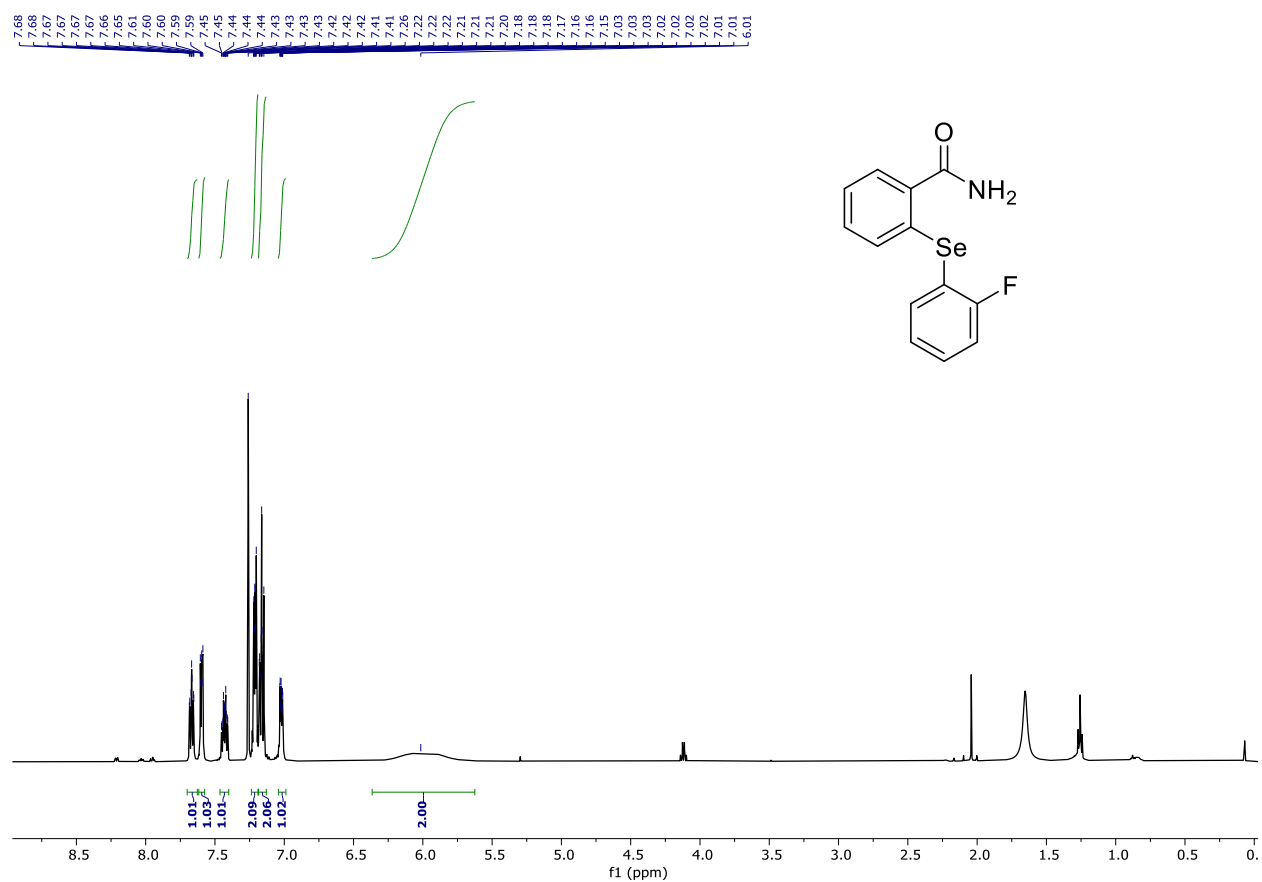
**$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 4g in  $\text{CDCl}_3$**



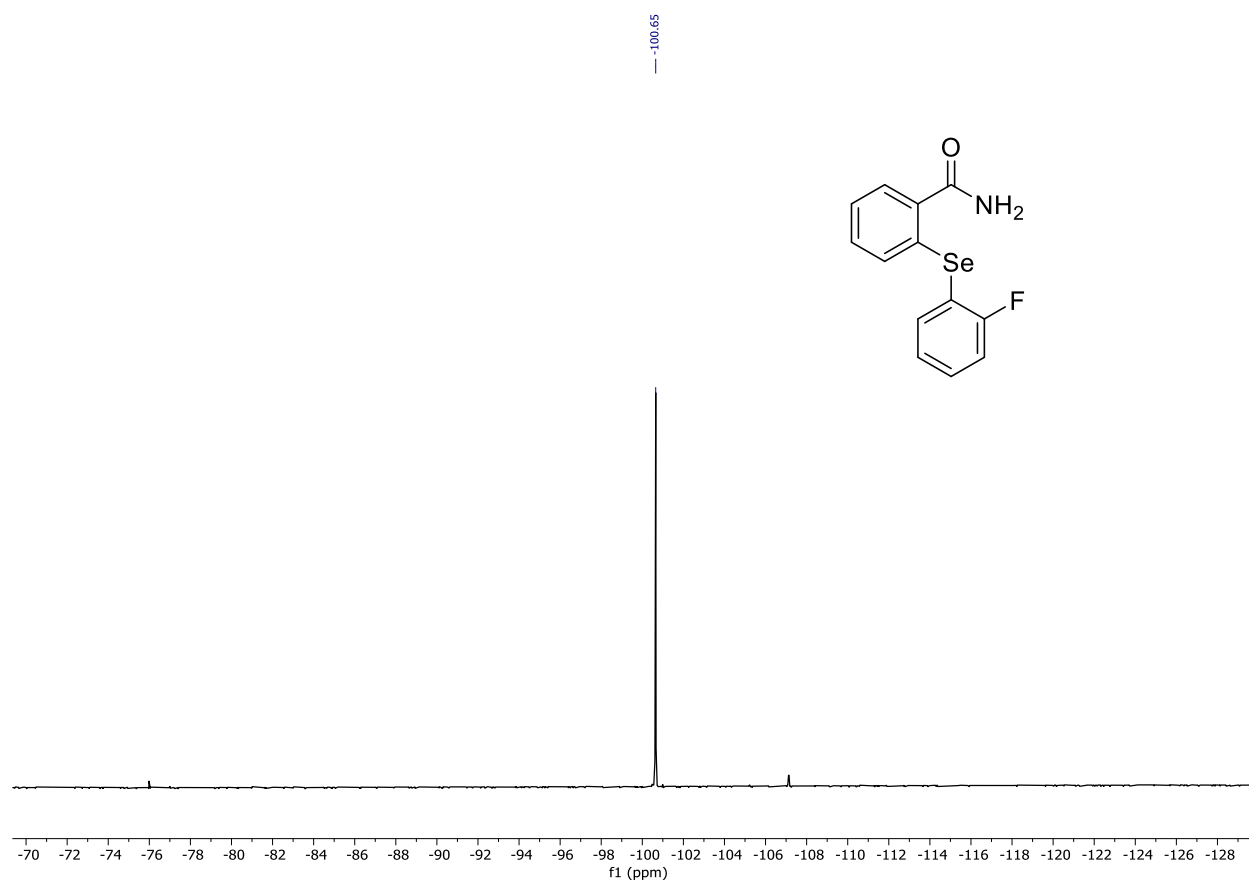
**$^{19}\text{F}\{^1\text{H}\}$  (471 MHz) NMR spectra of 4g in  $\text{CDCl}_3$**



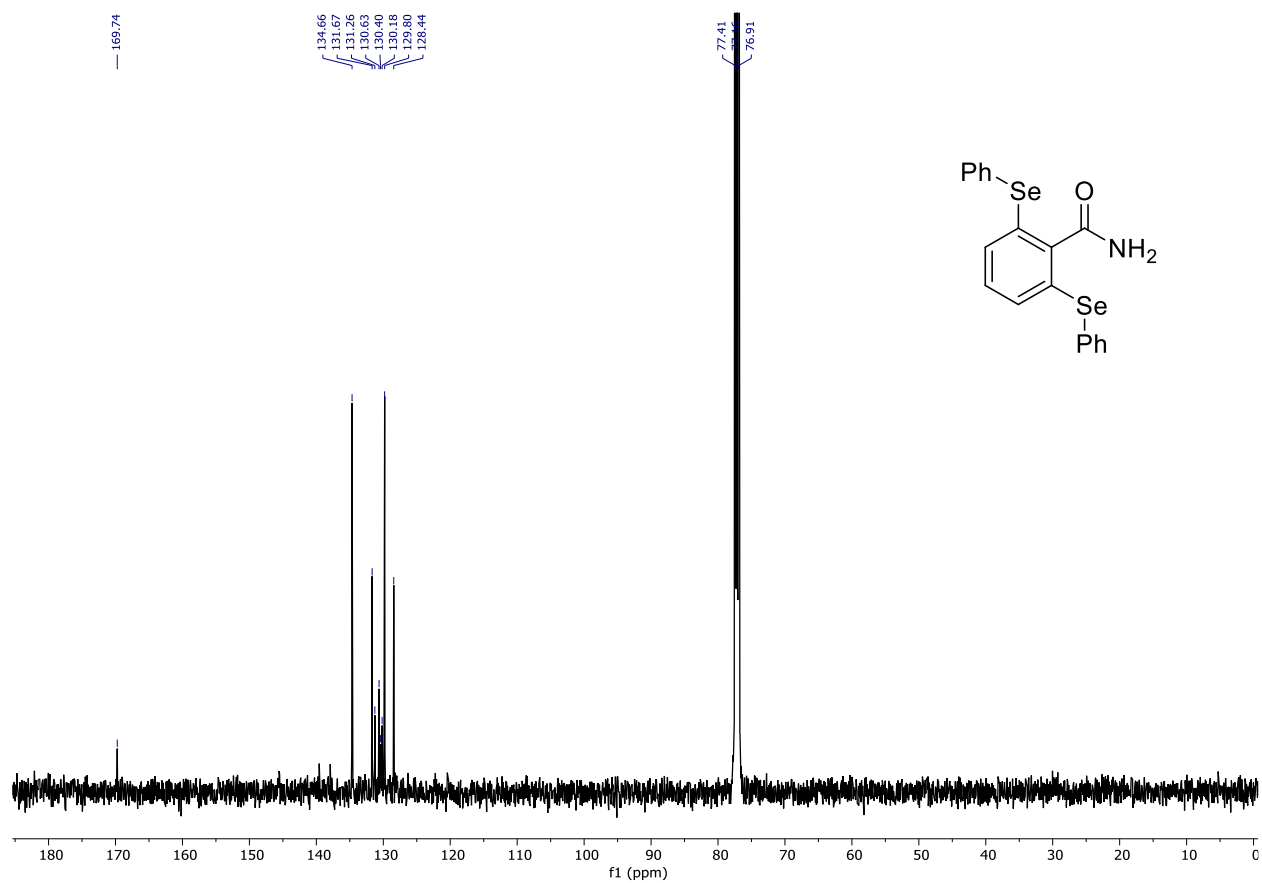
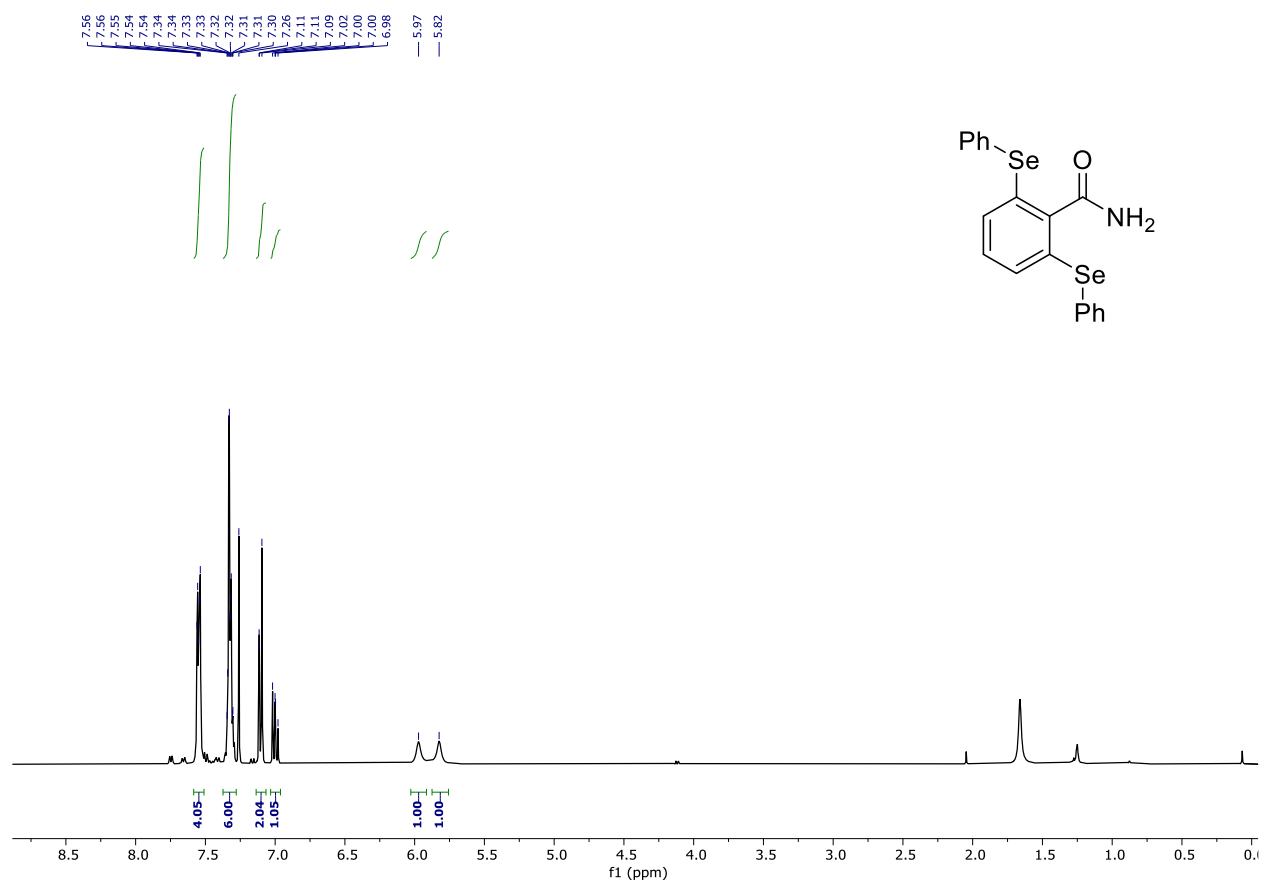
# $^1\text{H}$ (500 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (125 MHz) spectra of 4h in $\text{CDCl}_3$



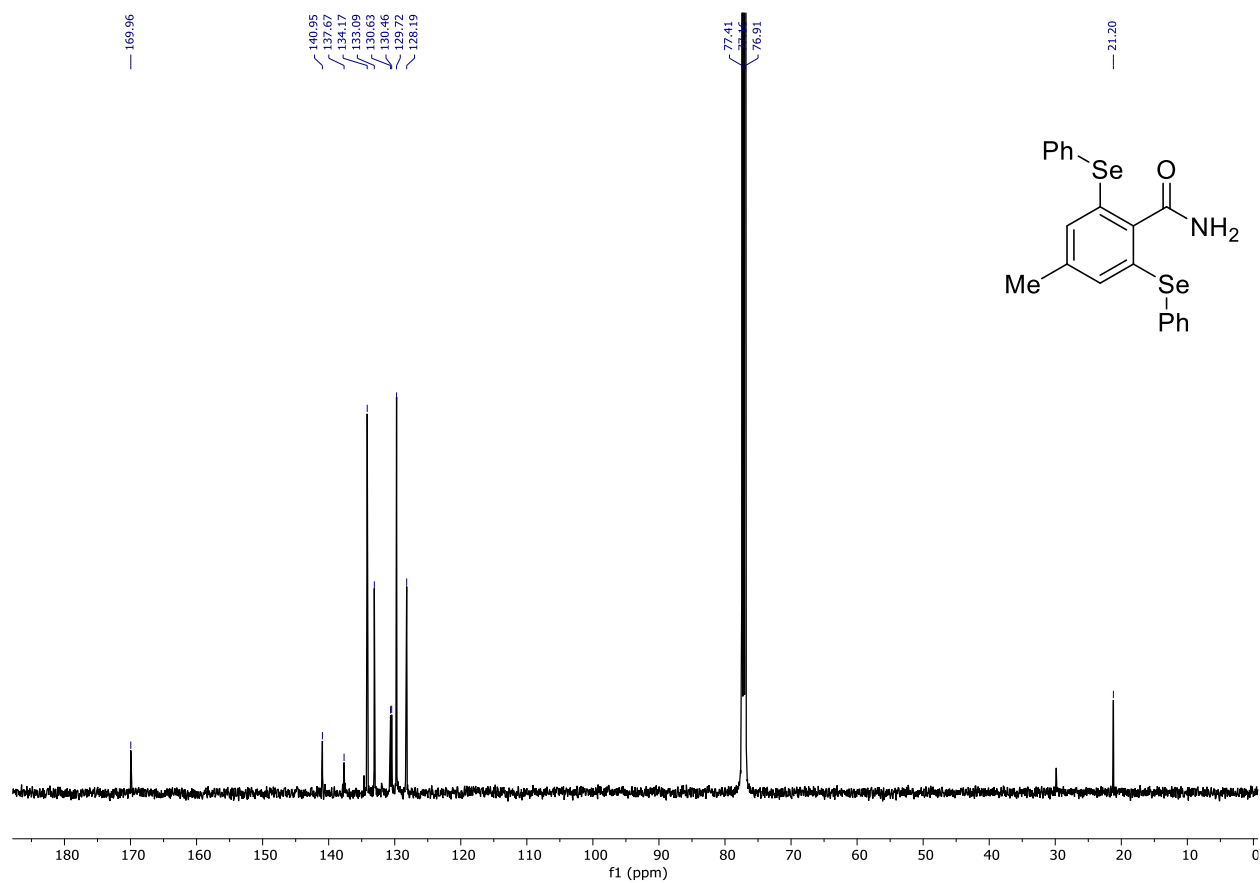
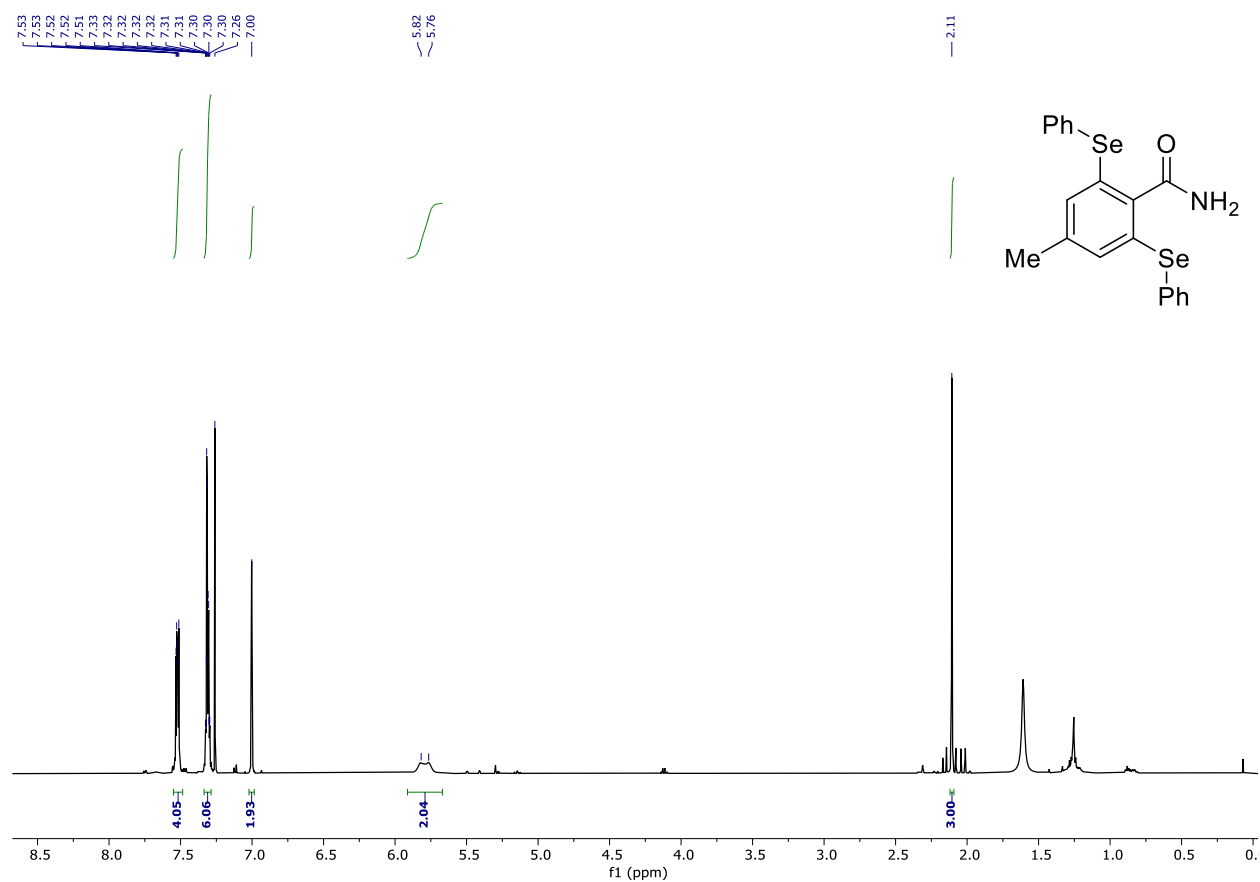
**$^{19}\text{F}\{^1\text{H}\}$  (471 MHz) NMR spectra of 4h in  $\text{CDCl}_3$**



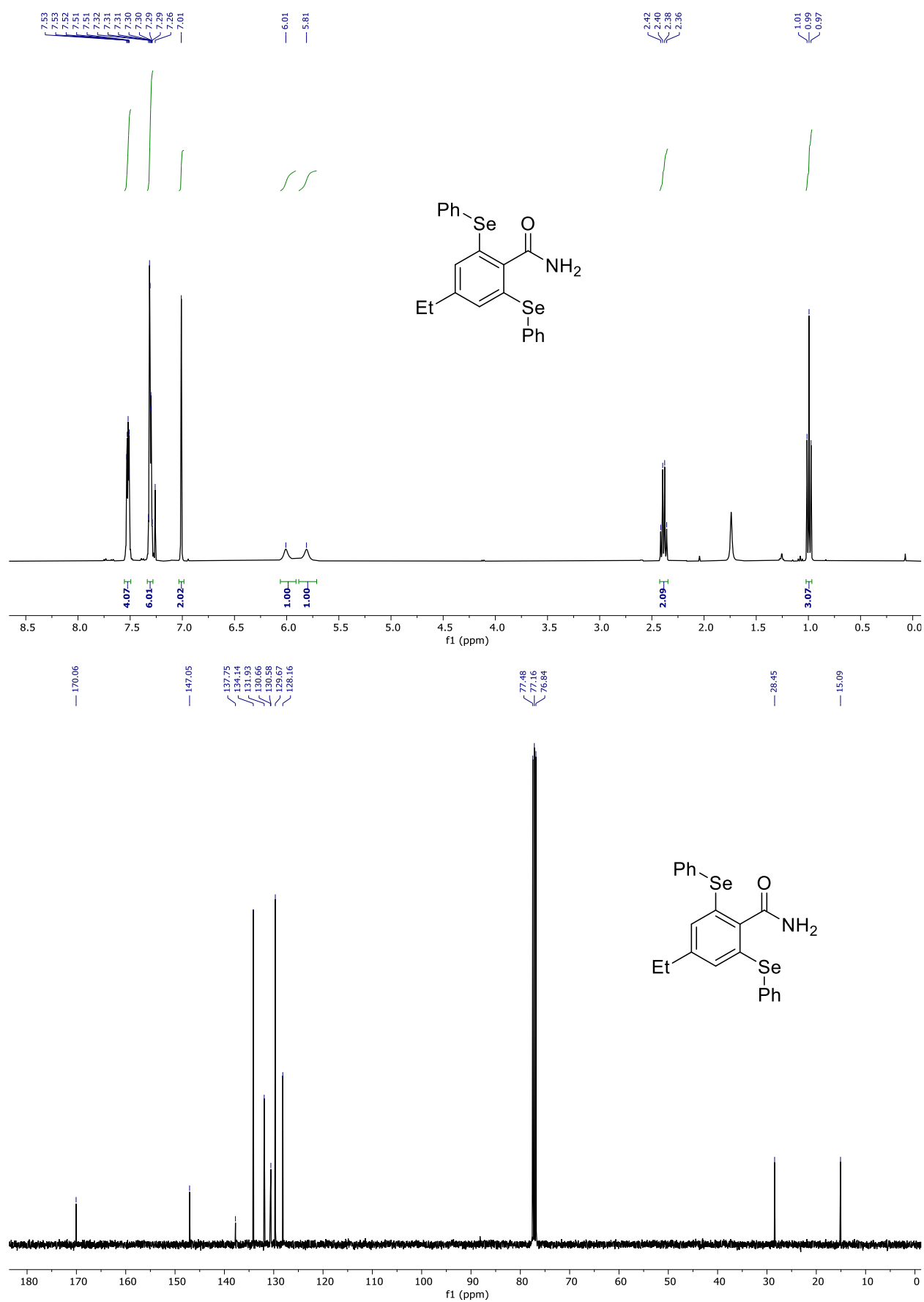
$^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 5a in  $\text{CDCl}_3$



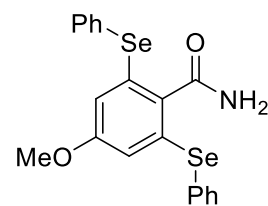
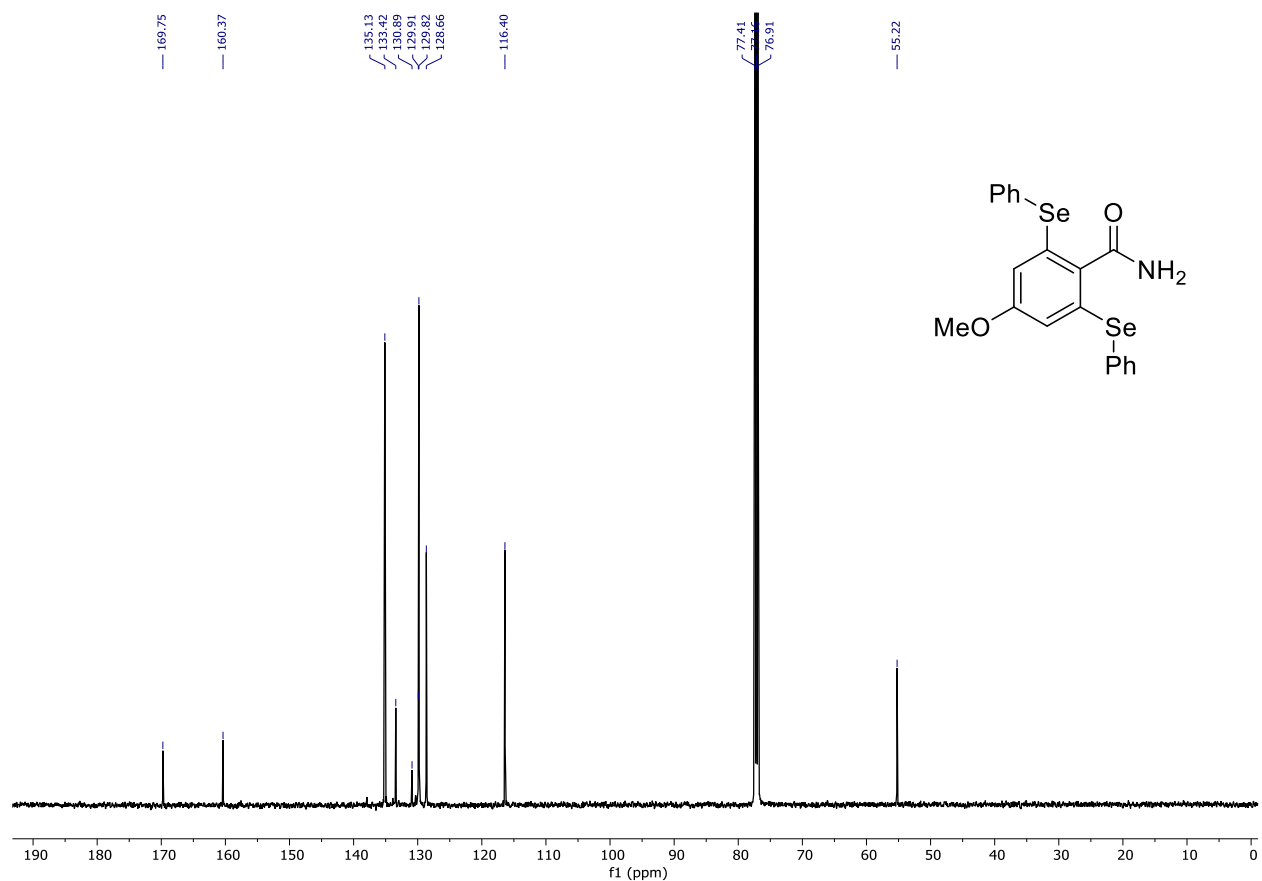
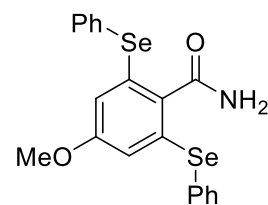
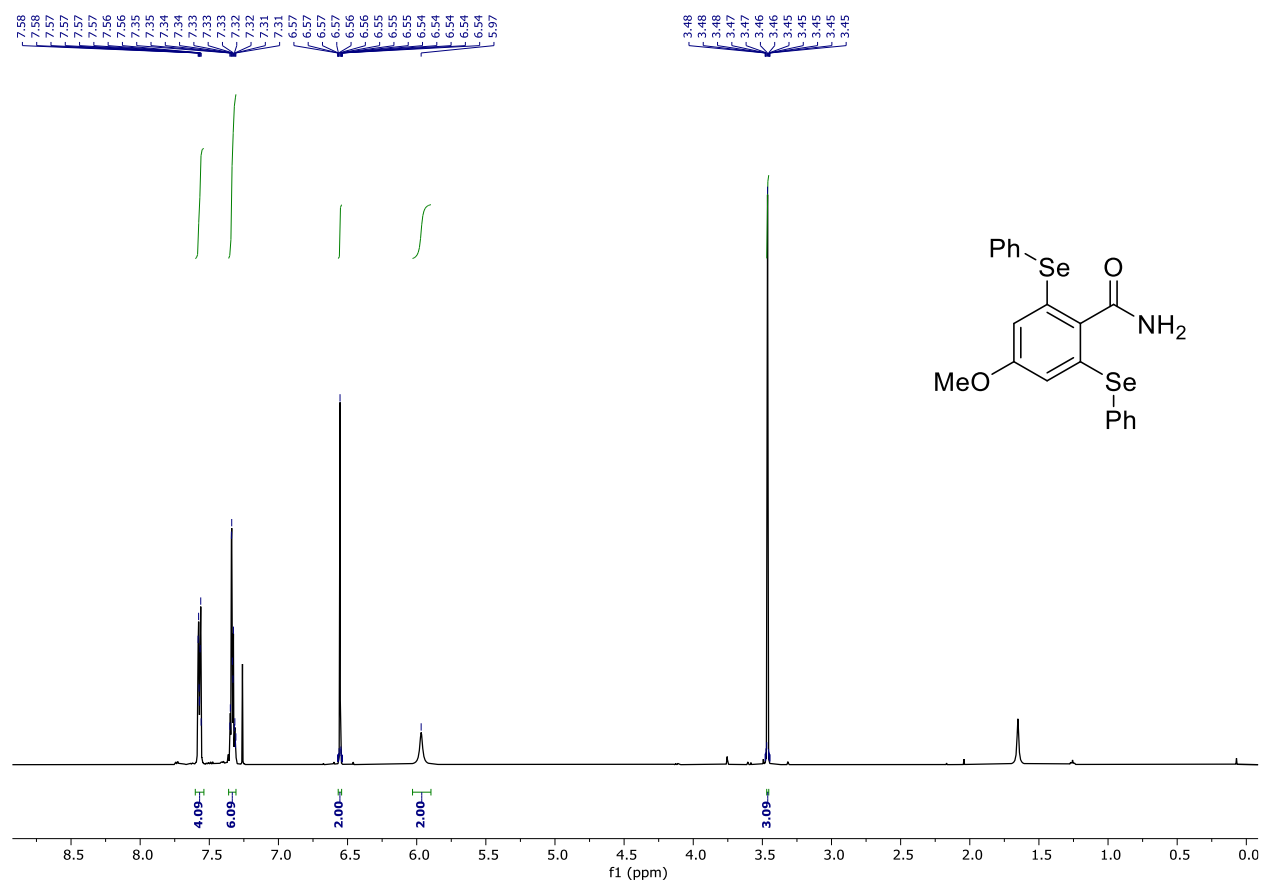
**$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 5b in  $\text{CDCl}_3$**



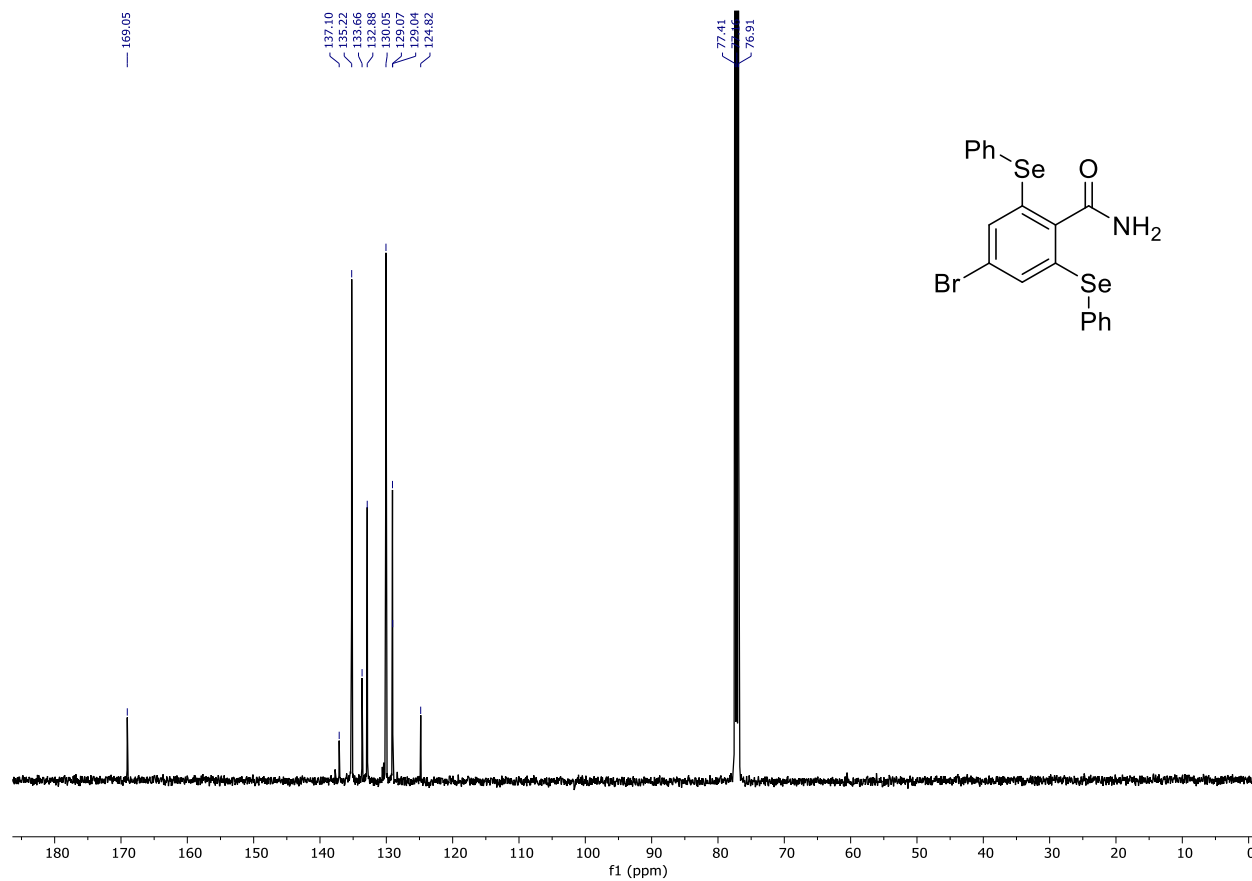
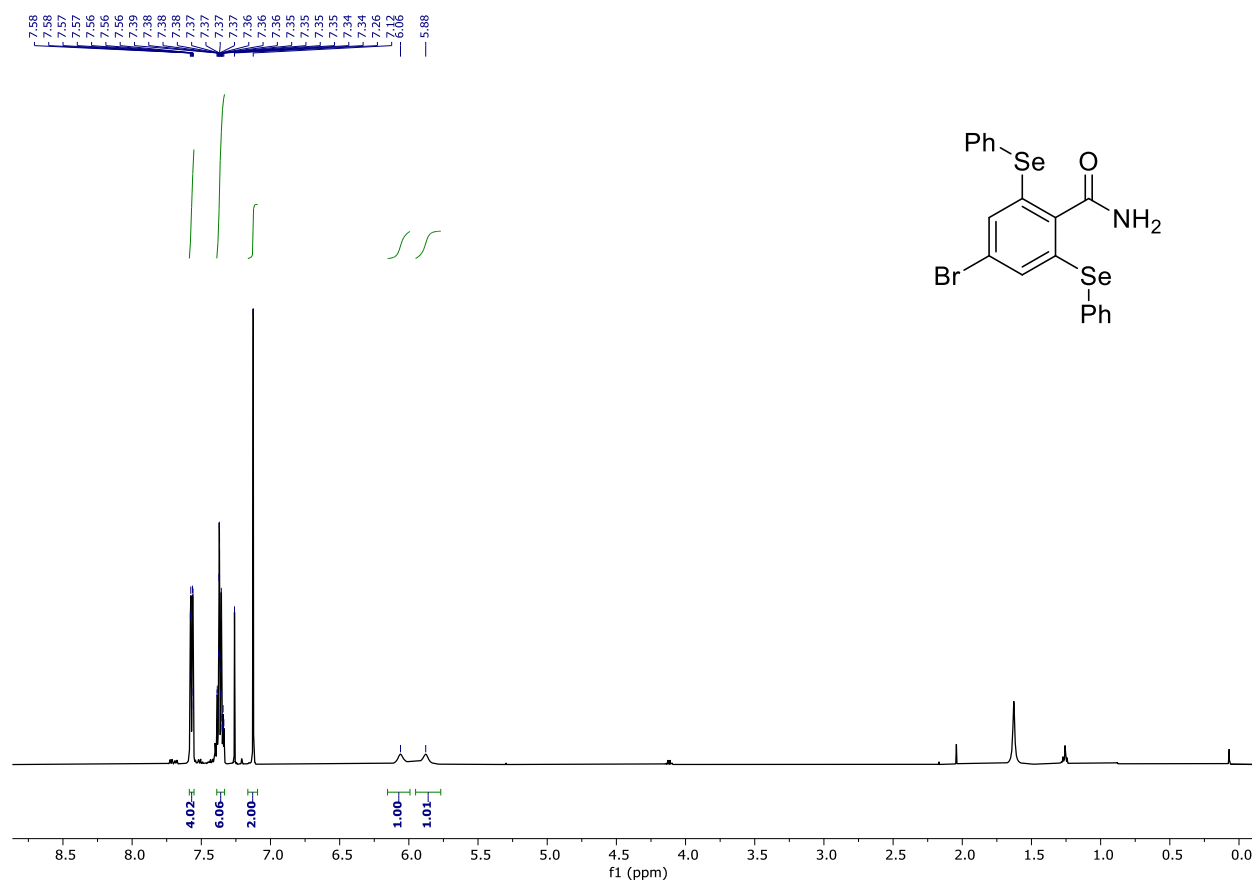
$^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (100 MHz) spectra of 5c in  $\text{CDCl}_3$



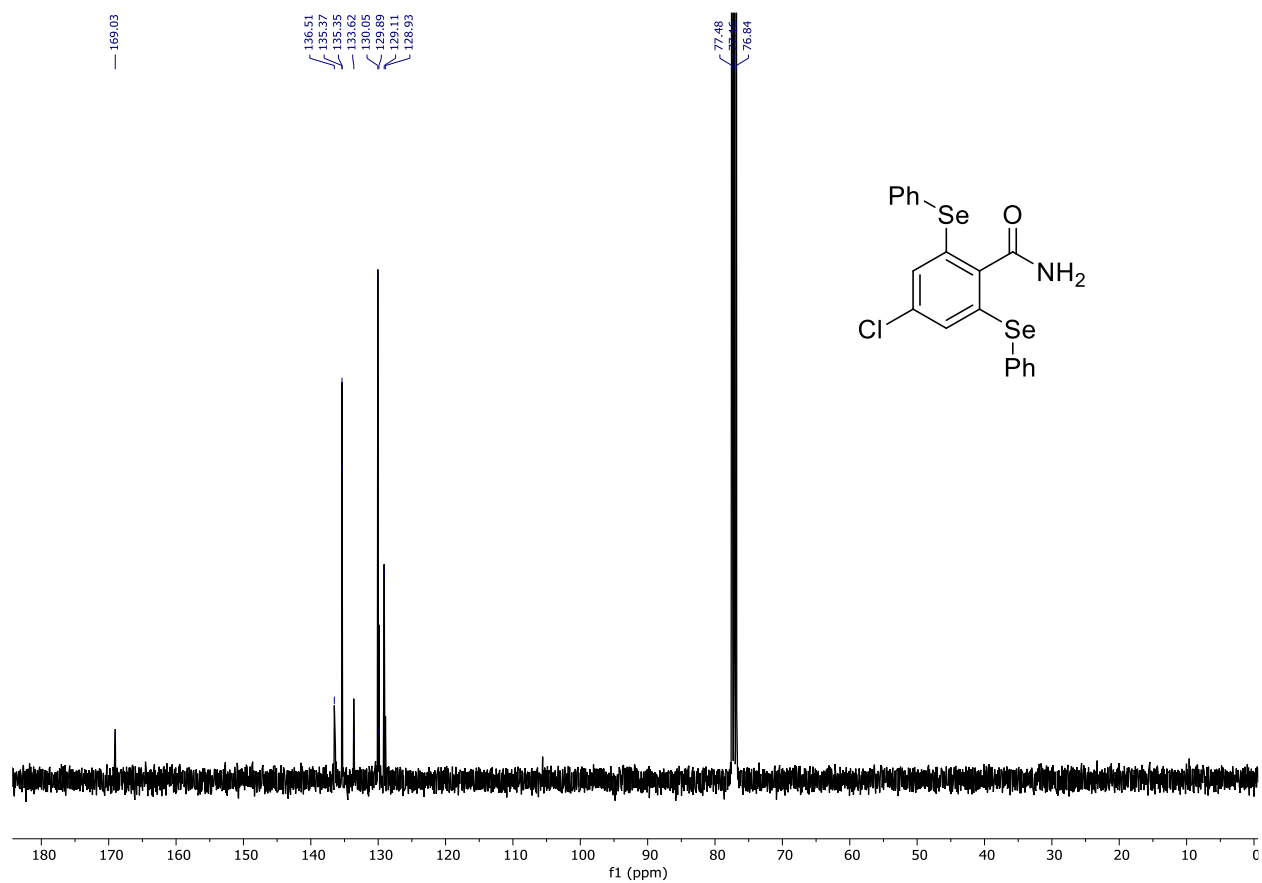
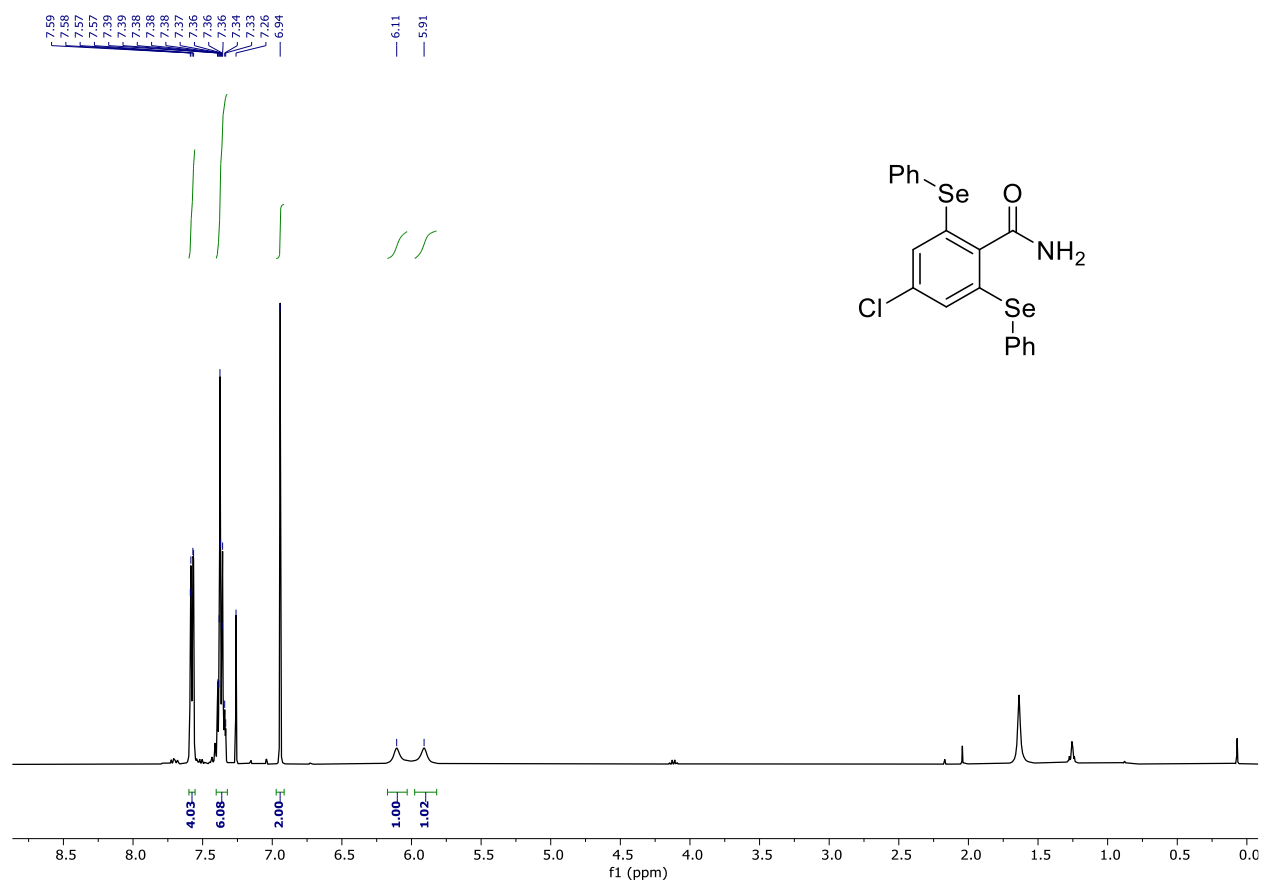
**$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 5d in  $\text{CDCl}_3$**



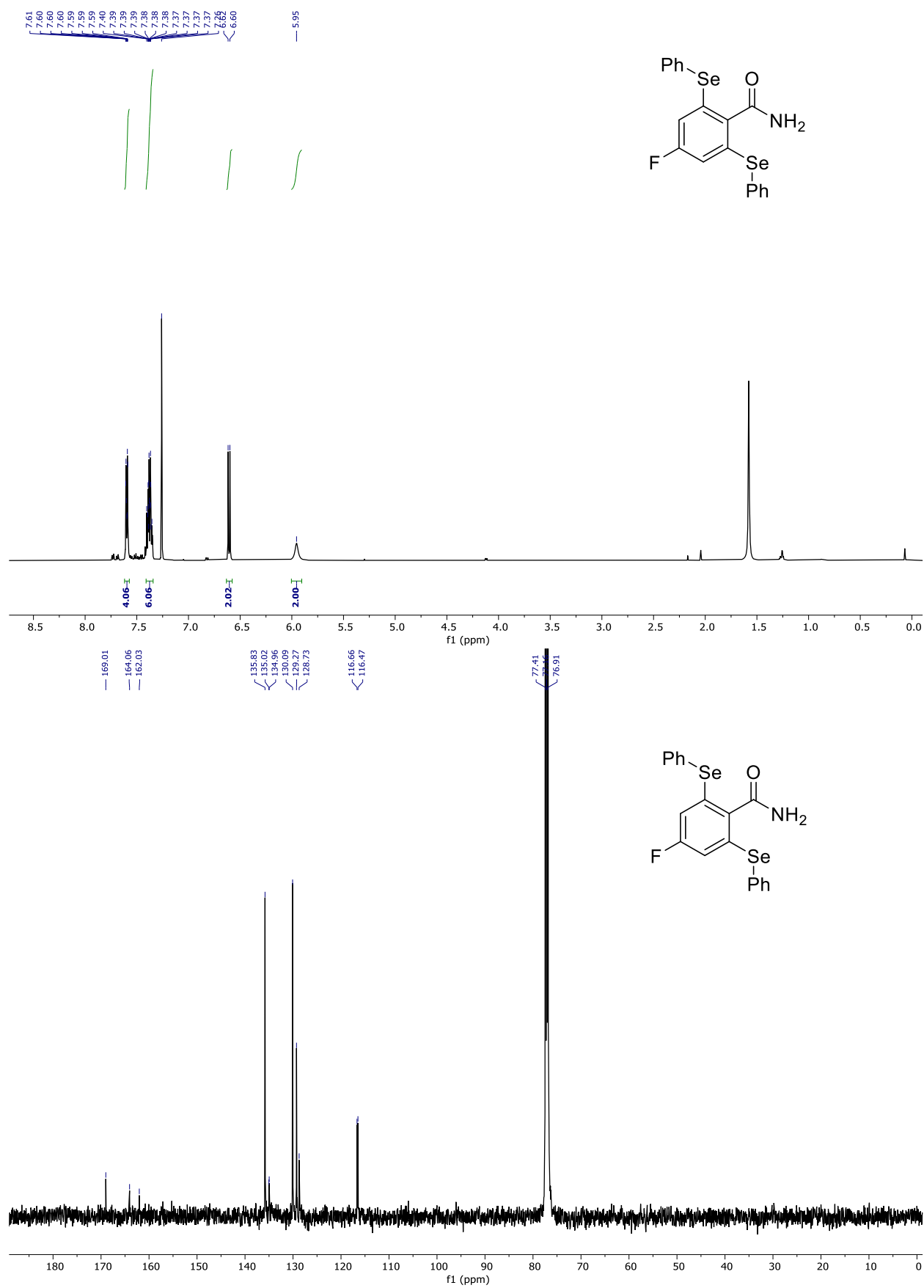
$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 5e in  $\text{CDCl}_3$



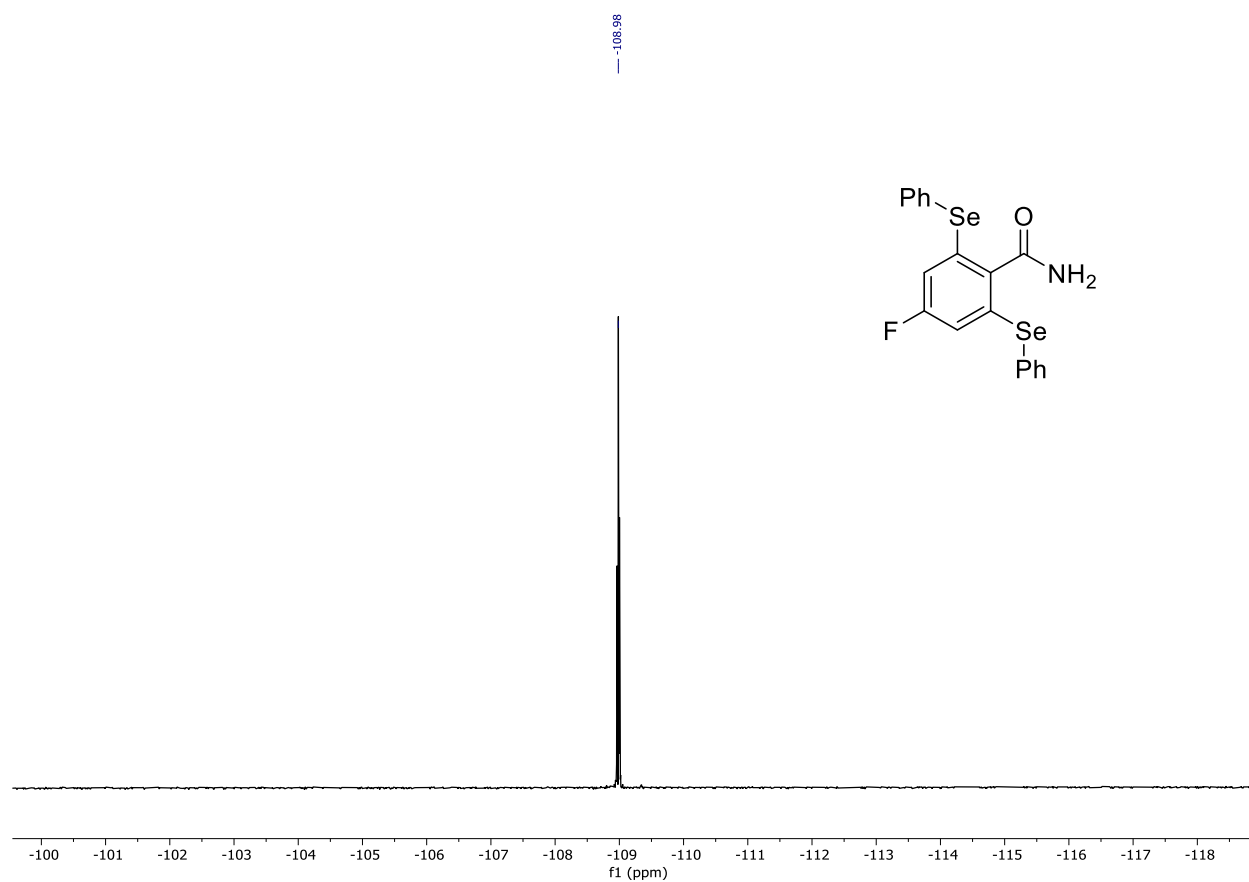
$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 5f in  $\text{CDCl}_3$



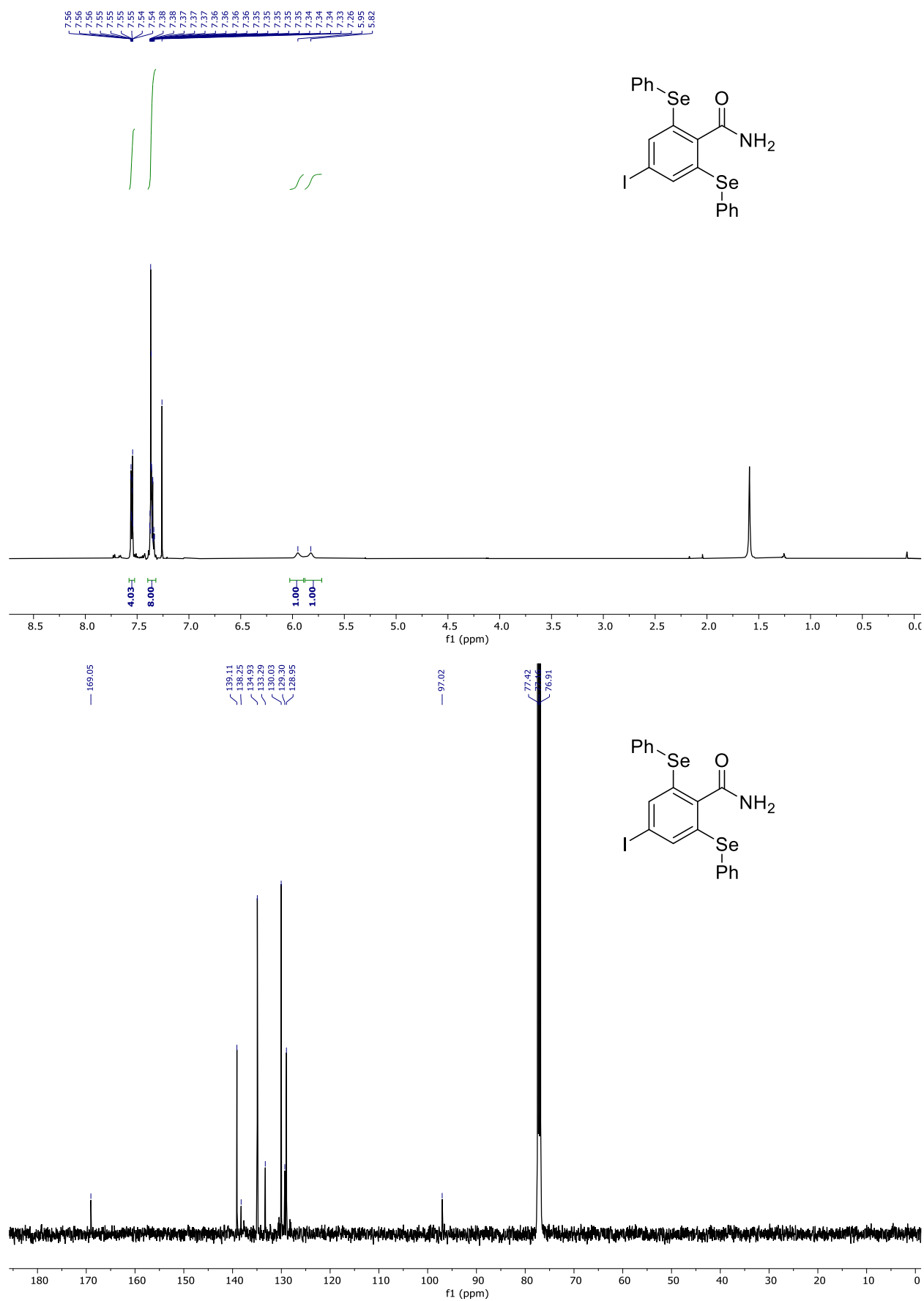
$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 5g in  $\text{CDCl}_3$



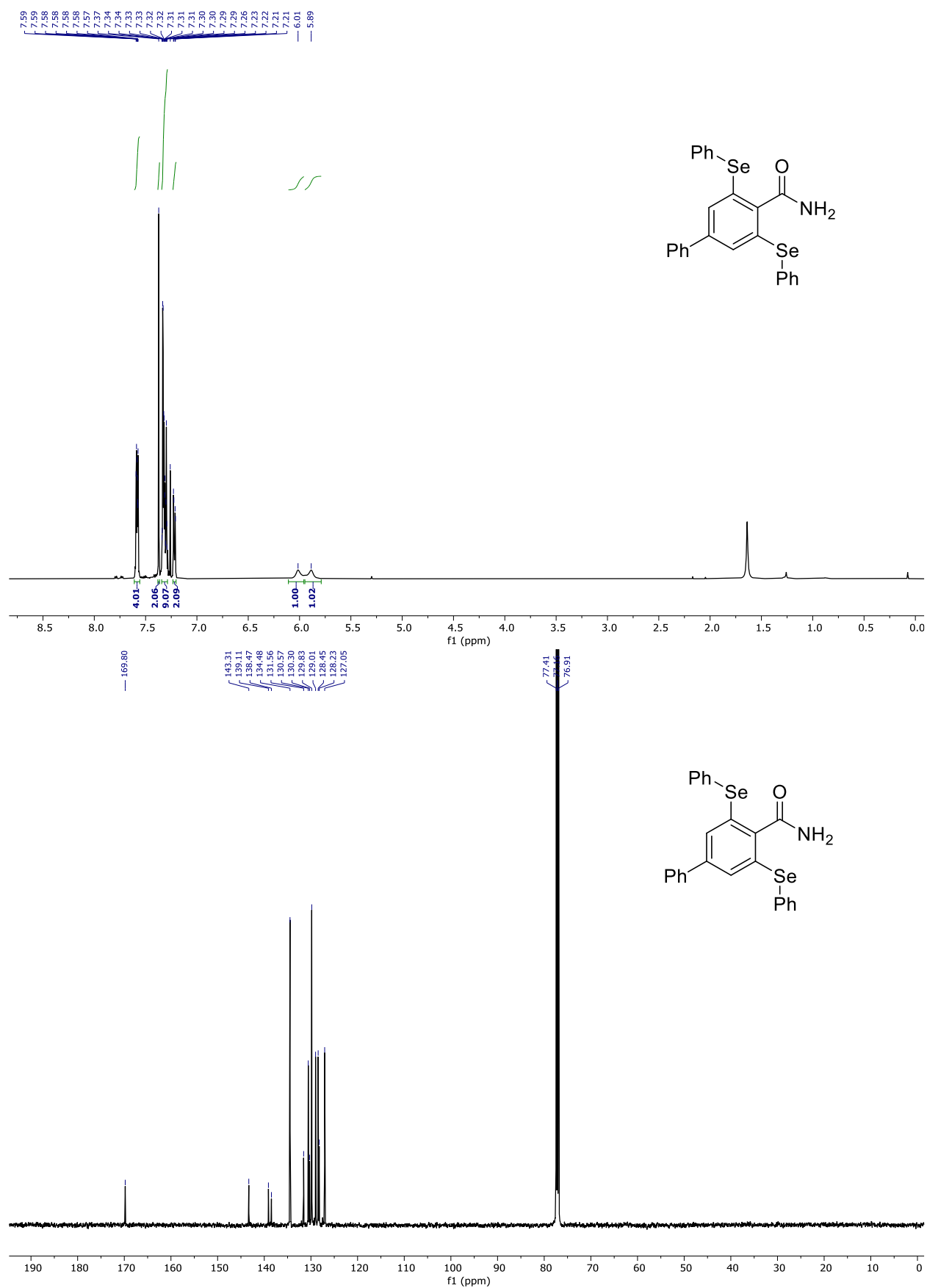
**$^{19}\text{F}\{^1\text{H}\}$  (471 MHz) NMR spectra of 5g in  $\text{CDCl}_3$**



**$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 5h in  $\text{CDCl}_3$**



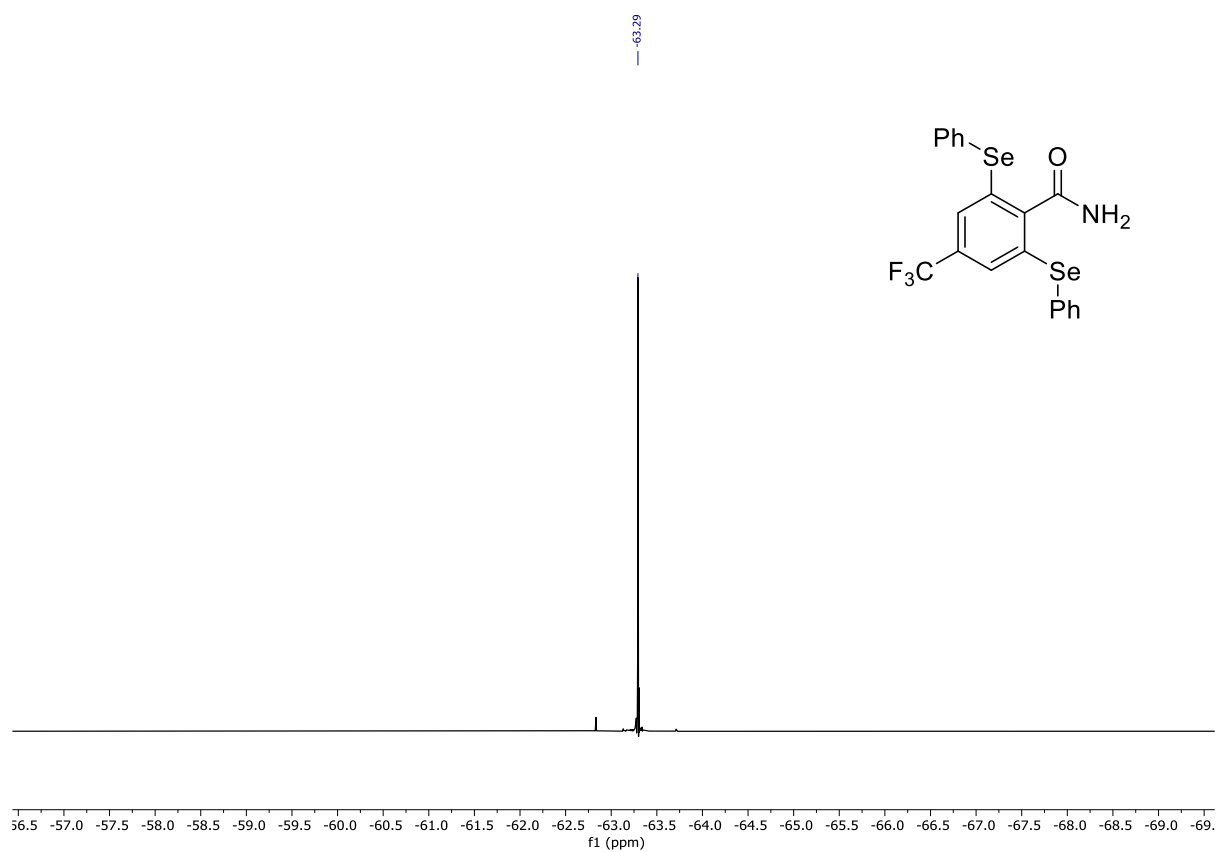
$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 5i in  $\text{CDCl}_3$



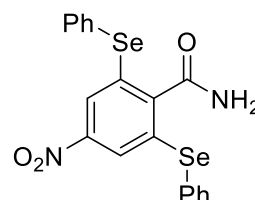
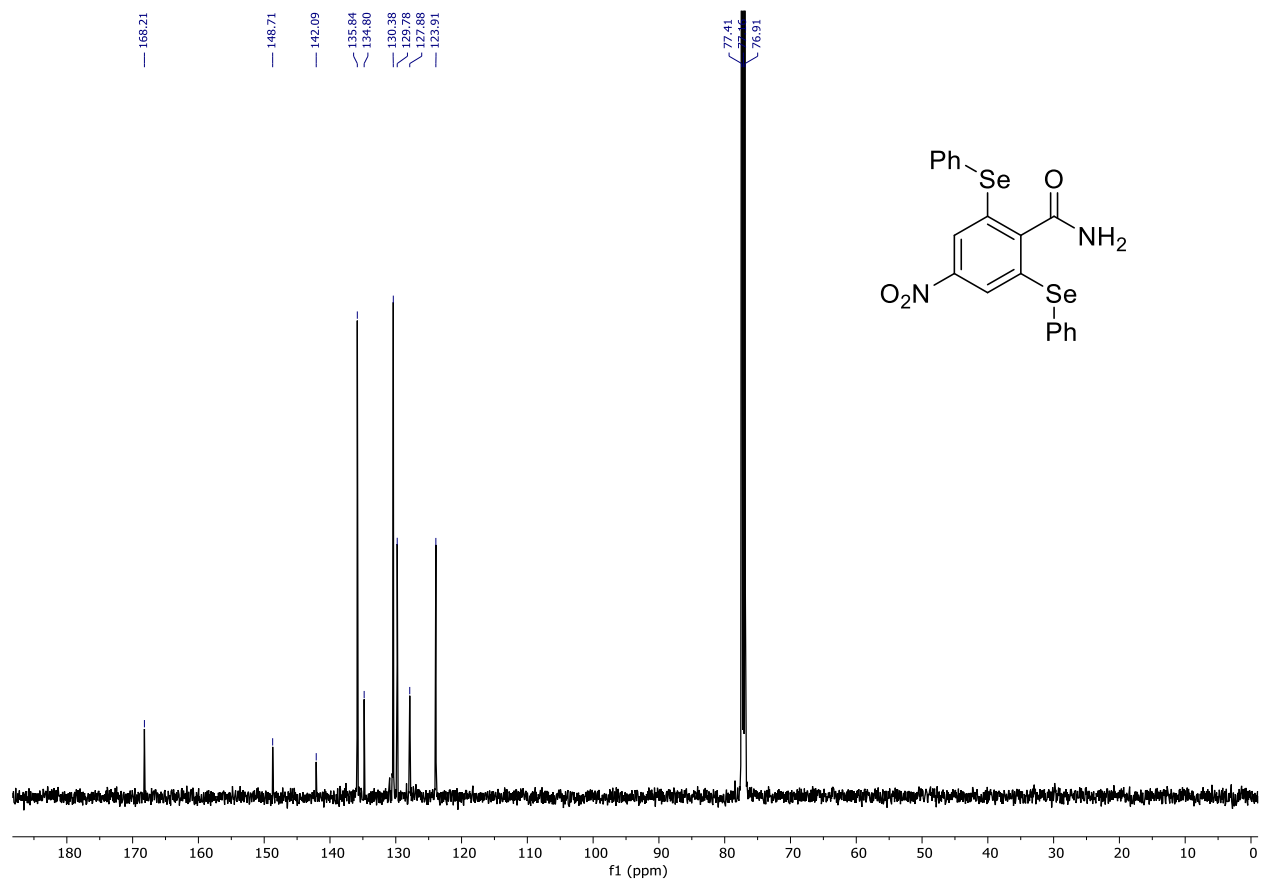
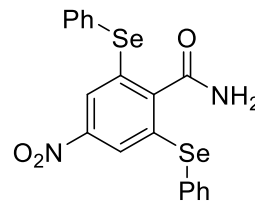
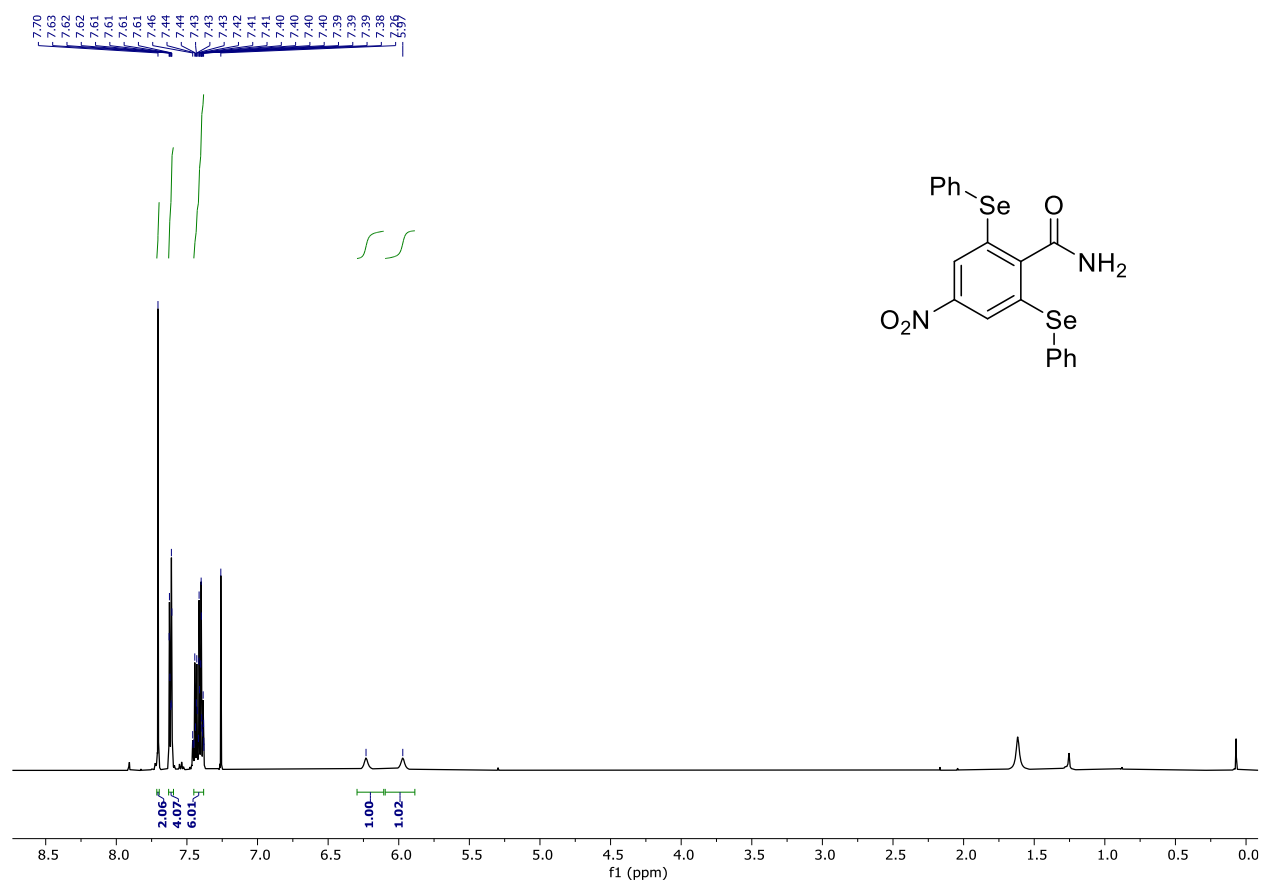
**$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 5j in  $\text{CDCl}_3$**



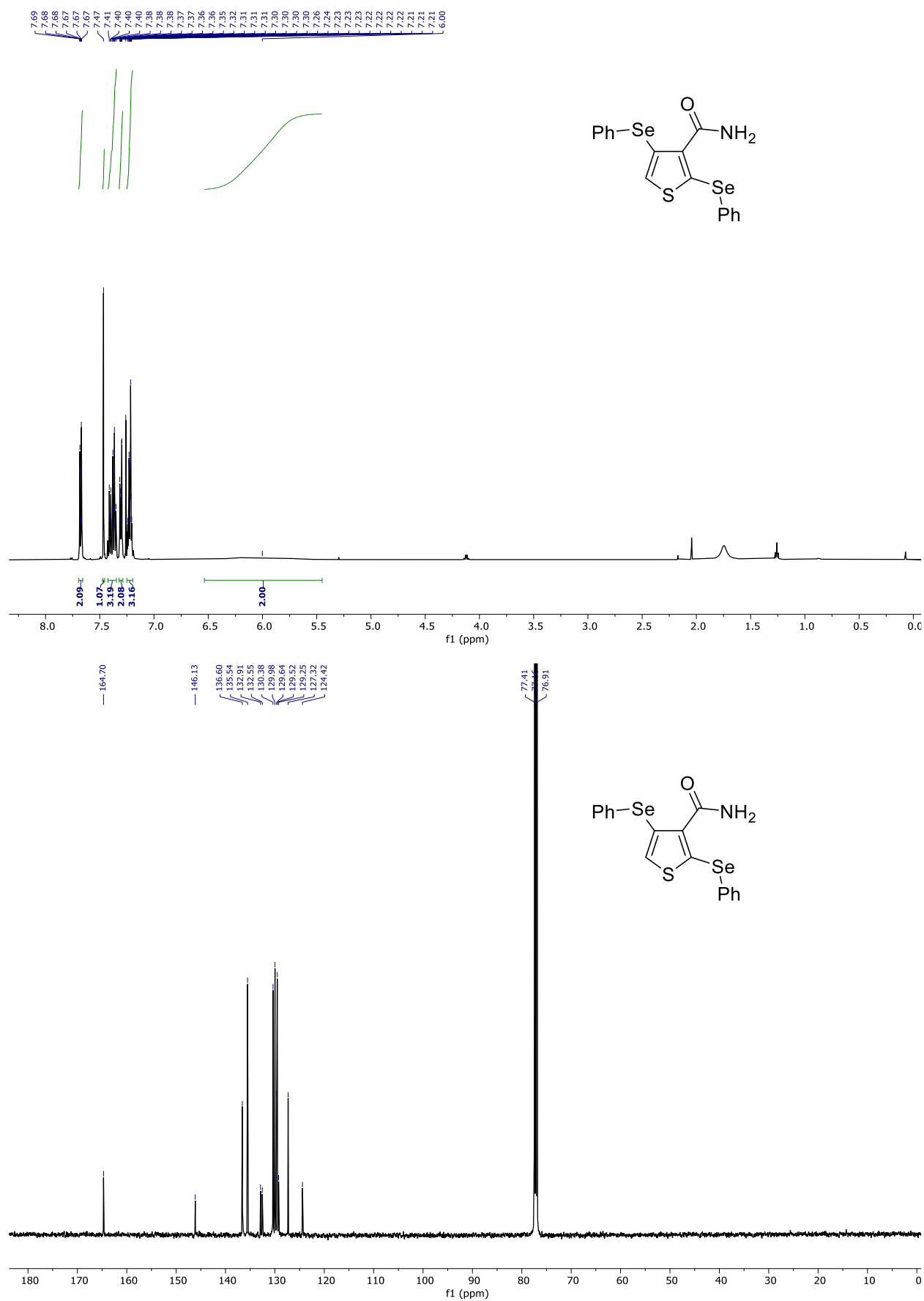
**$^{19}\text{F}\{^1\text{H}\}$  (471 MHz) NMR spectra of 5j in  $\text{CDCl}_3$**



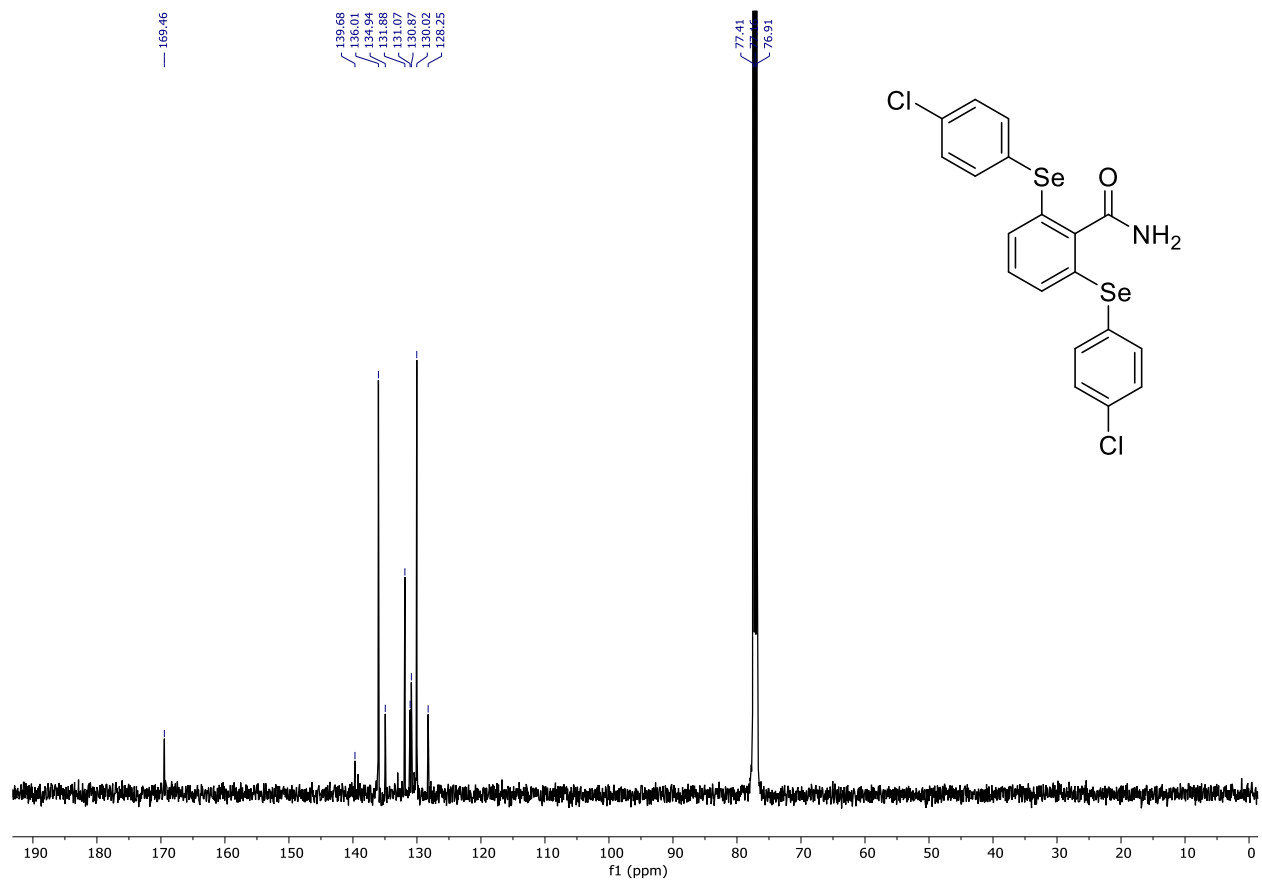
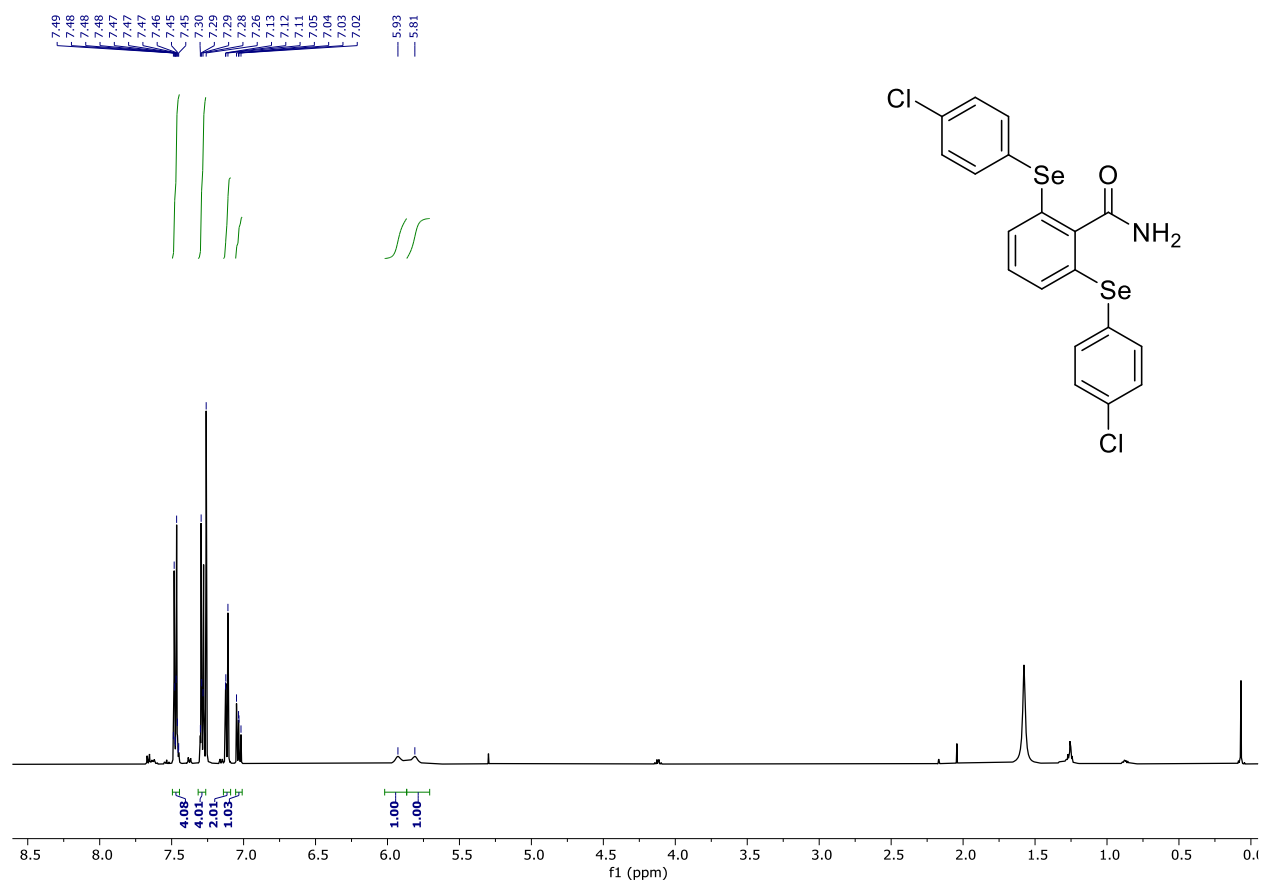
$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 5k in  $\text{CDCl}_3$



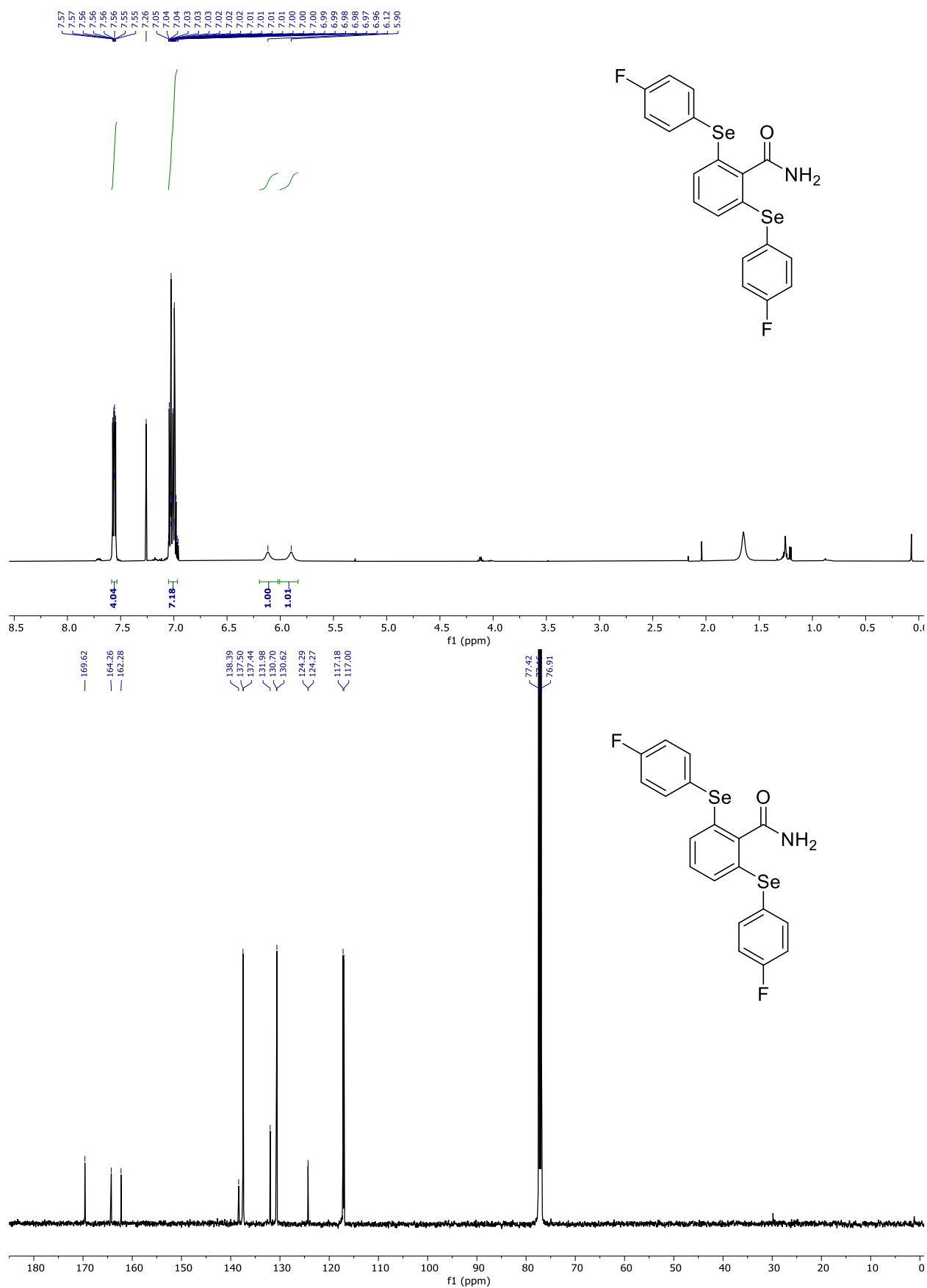
**$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 5l in  $\text{CDCl}_3$**



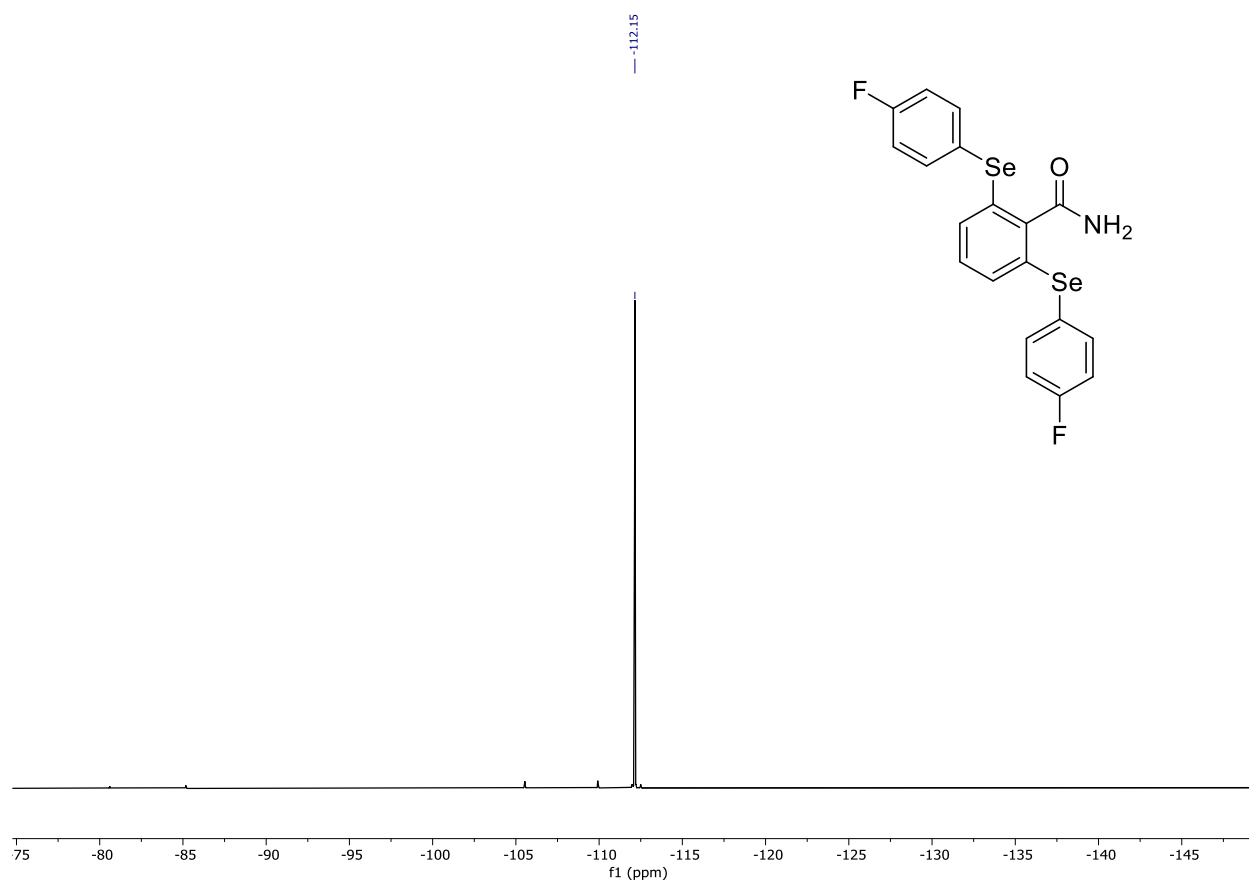
$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 5m in  $\text{CDCl}_3$



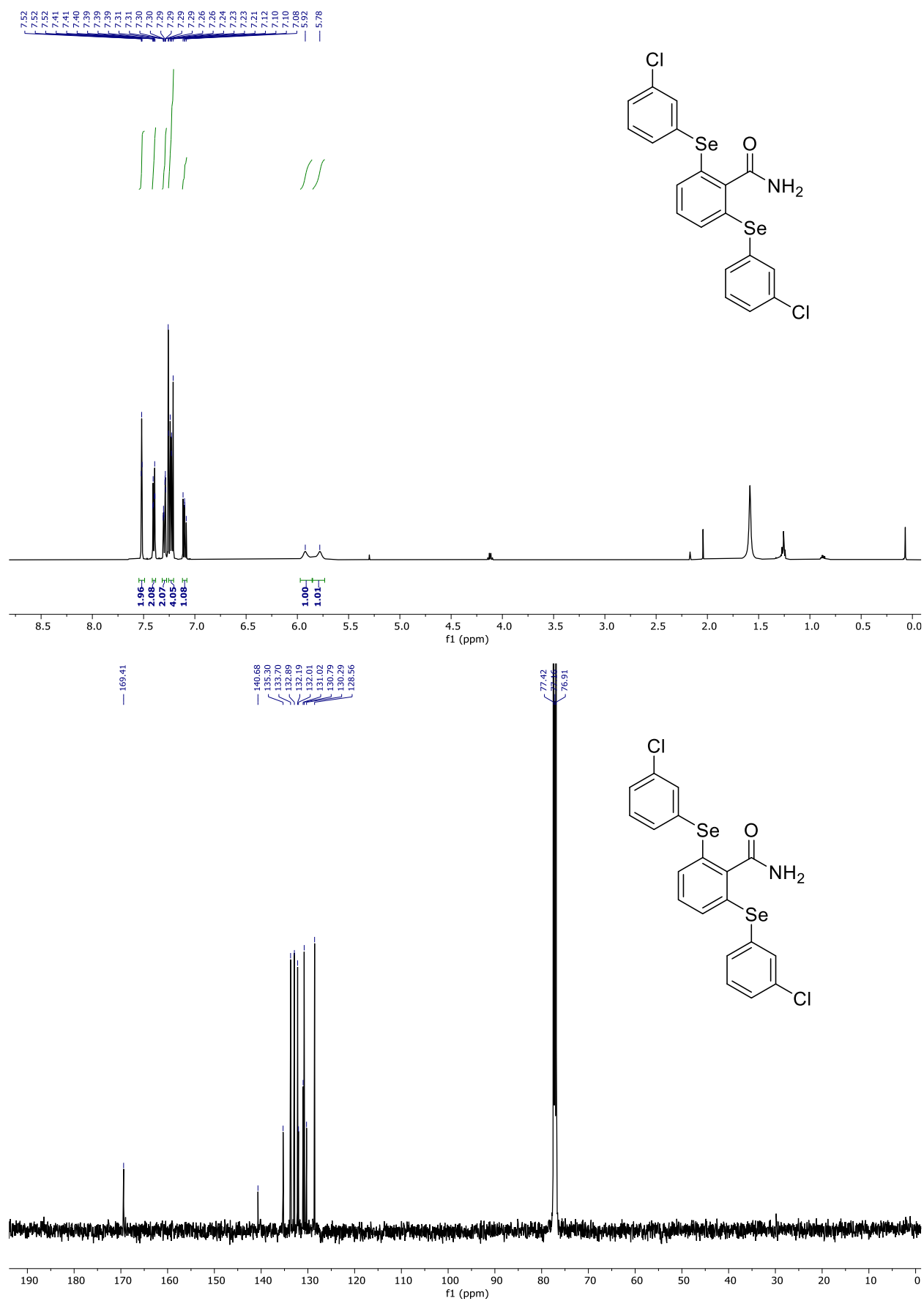
**$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 5n in  $\text{CDCl}_3$**



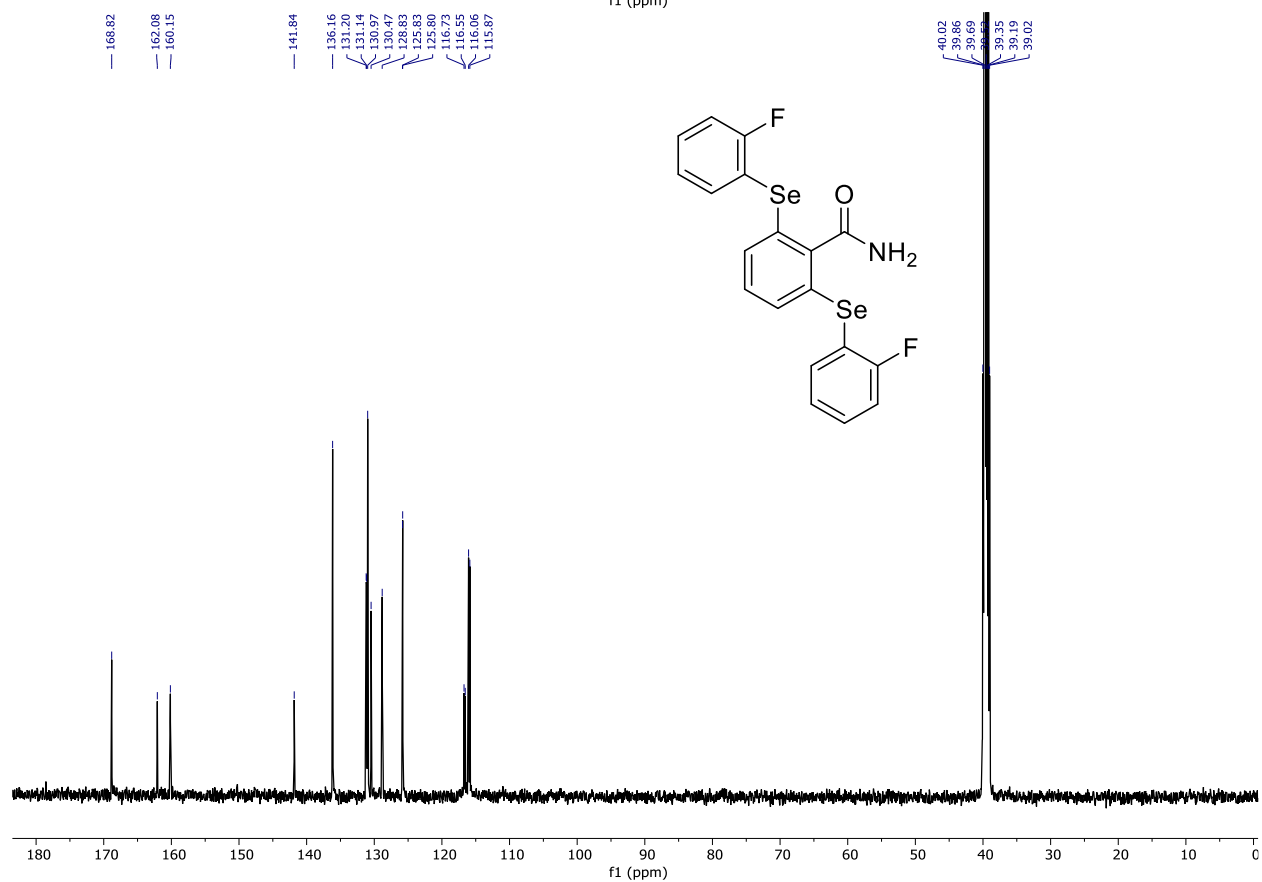
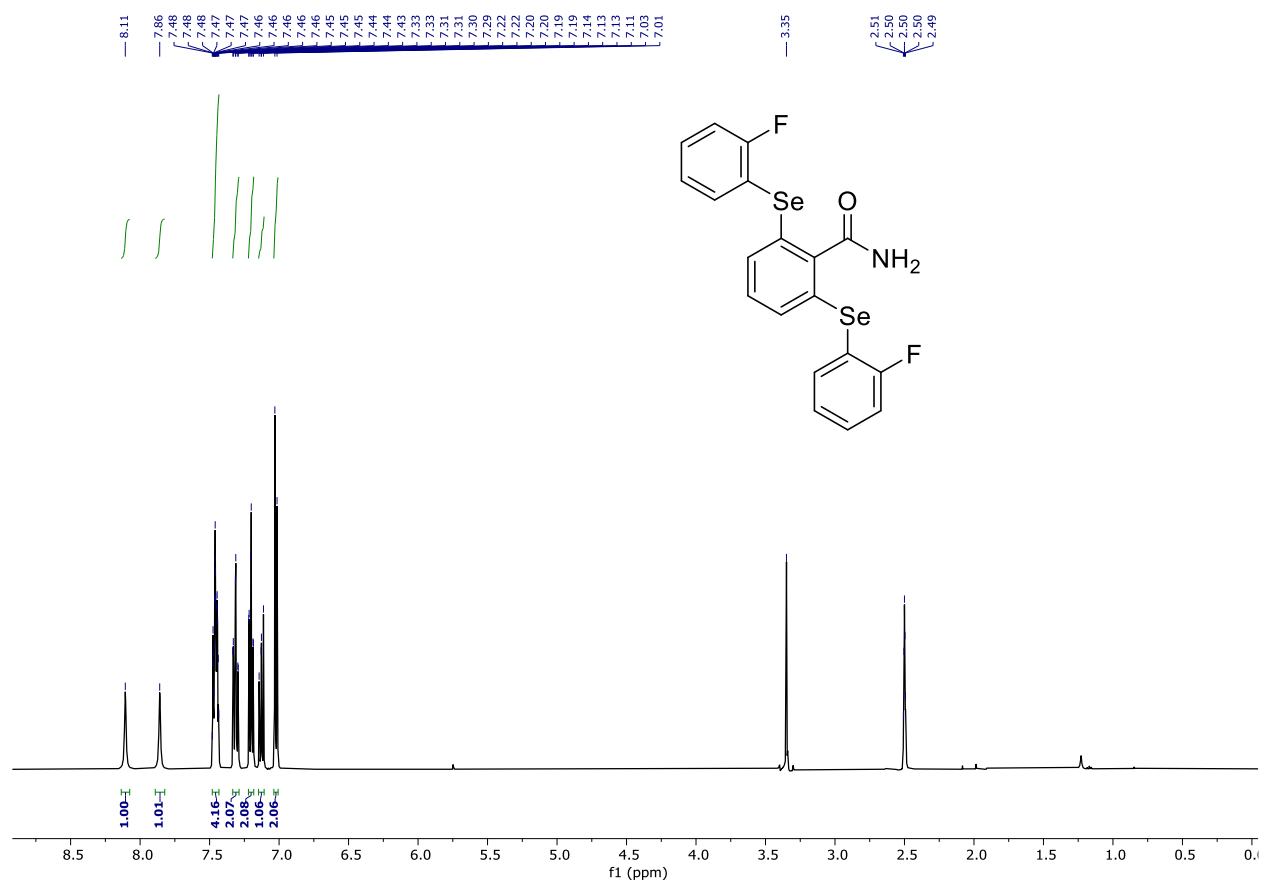
**$^{19}\text{F}\{^1\text{H}\}$  (471 MHz) NMR spectra of 5n in  $\text{CDCl}_3$**



**$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 5o in  $\text{CDCl}_3$**



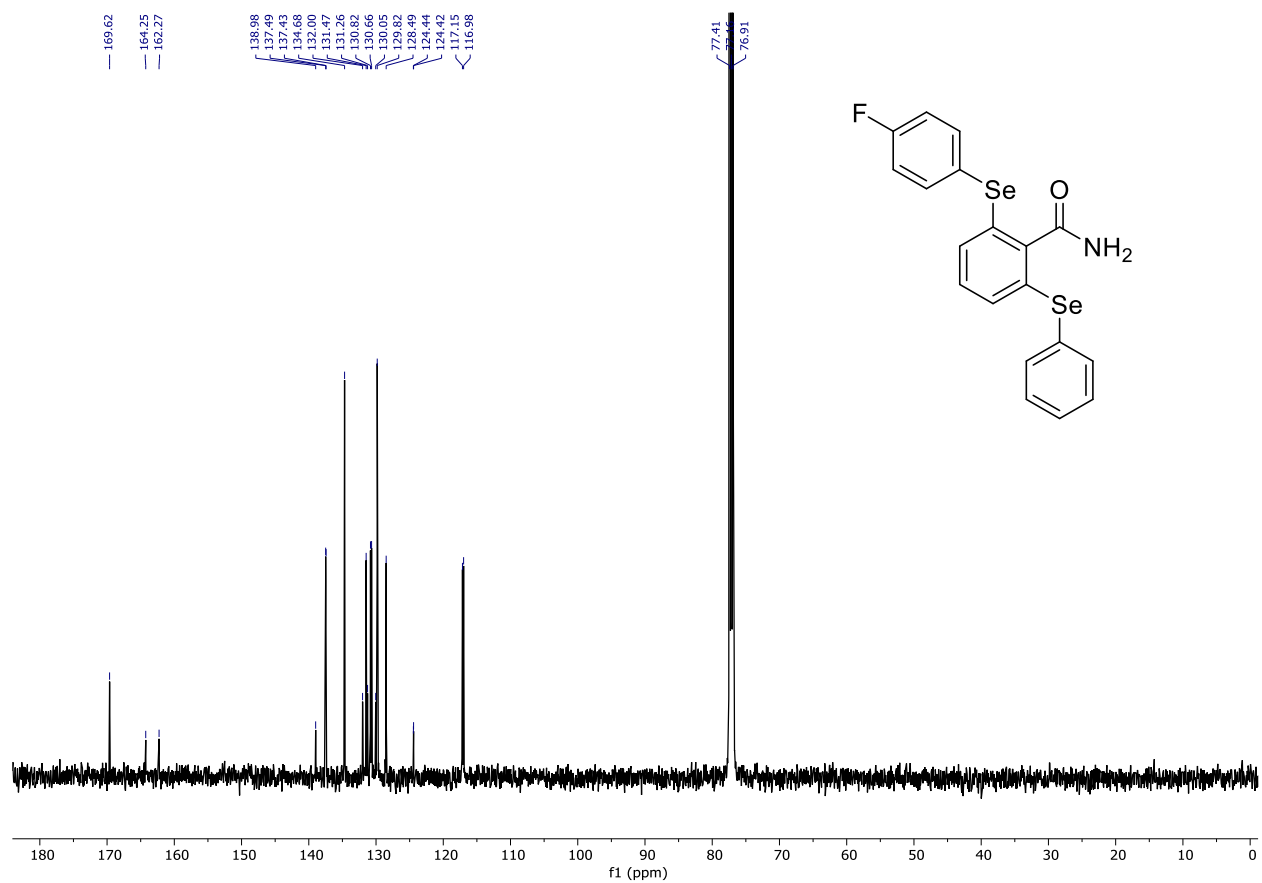
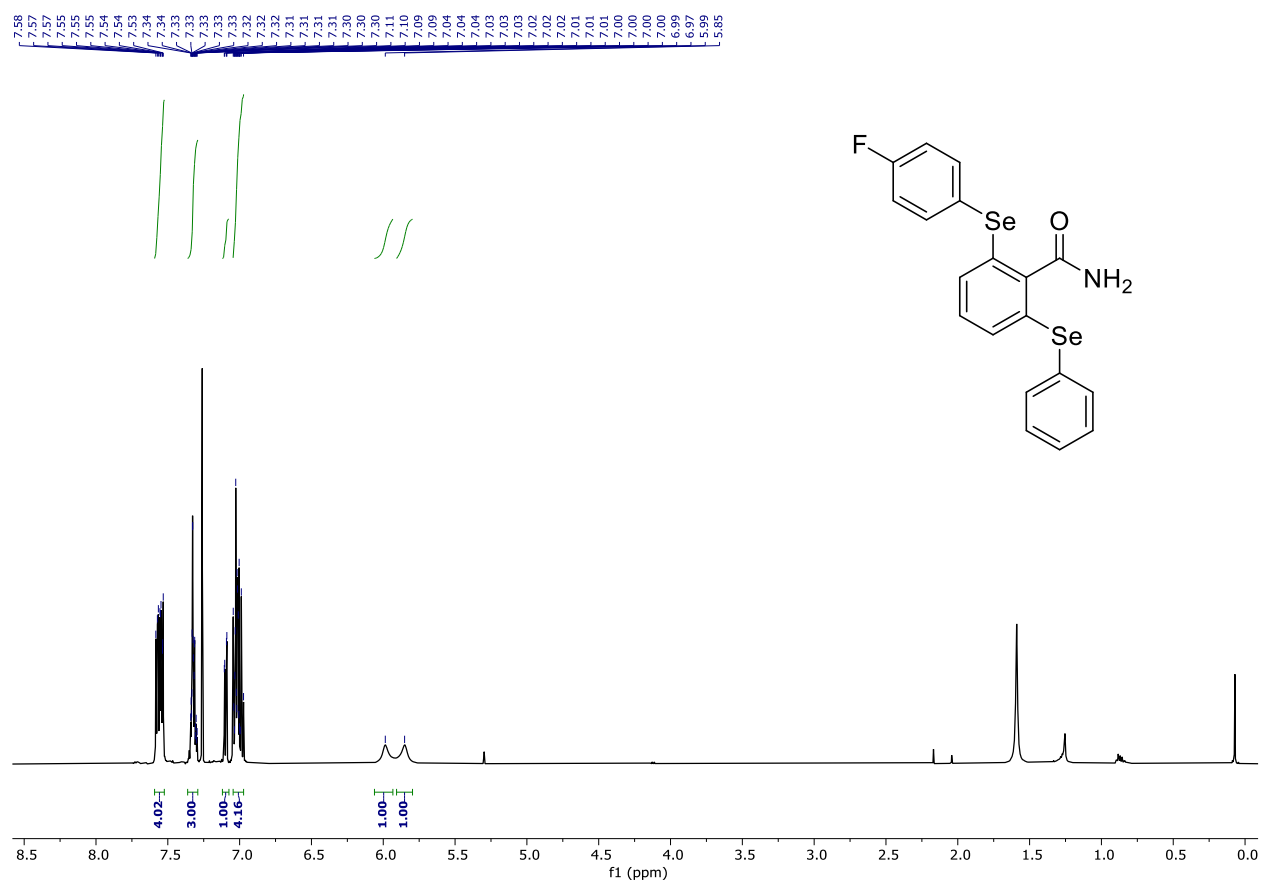
$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 5p in DMSO- $\text{D}_6$



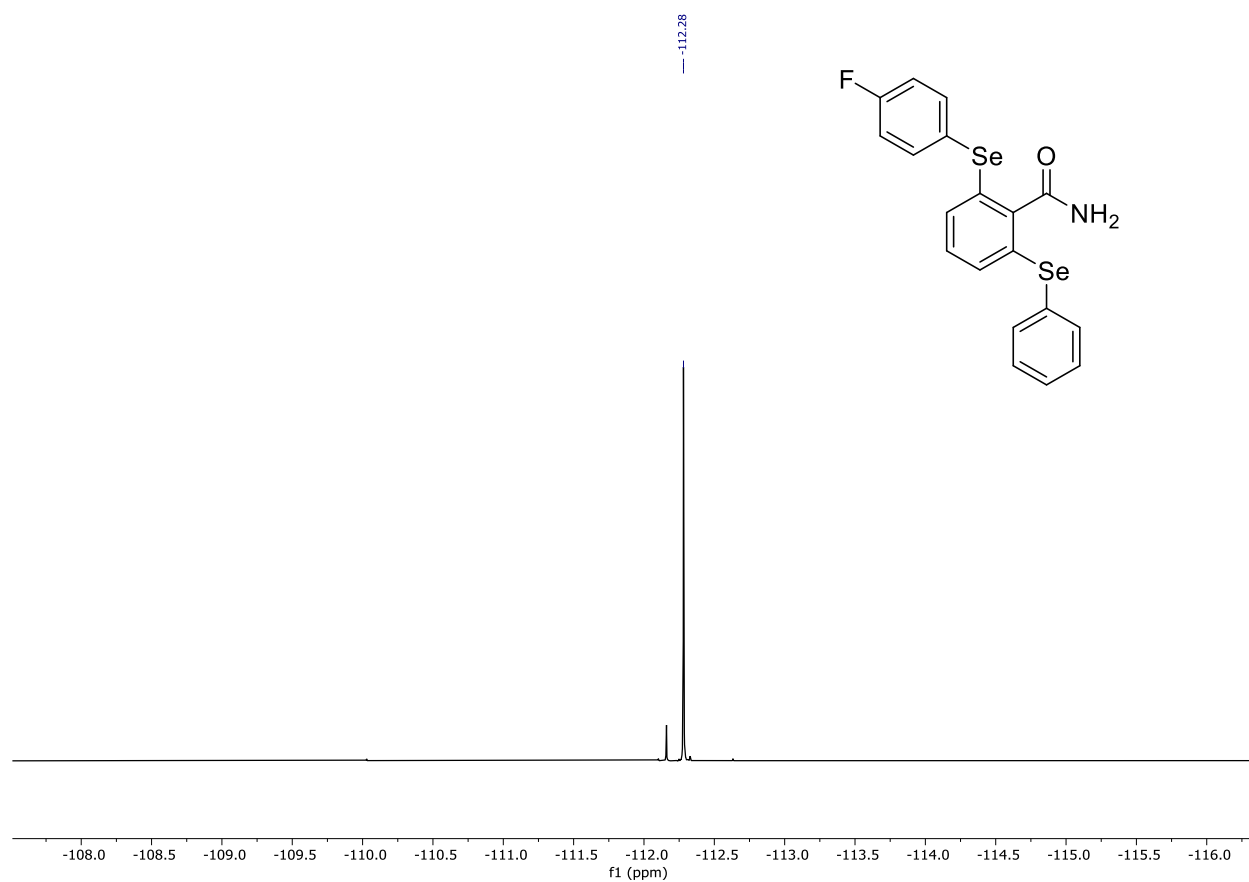
**$^{19}\text{F}\{^1\text{H}\}$  (471 MHz) NMR spectra of 5p in DMSO- $\text{D}_6$**



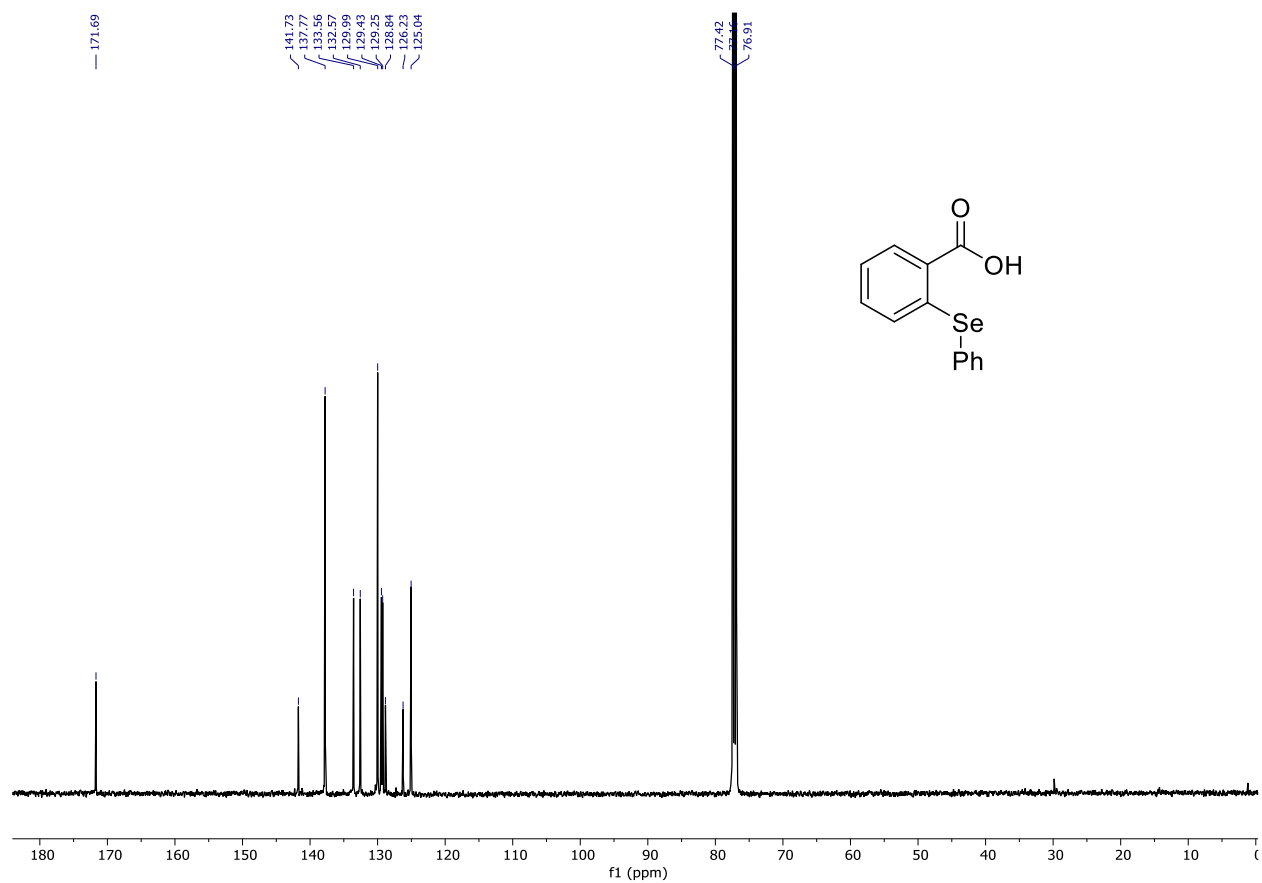
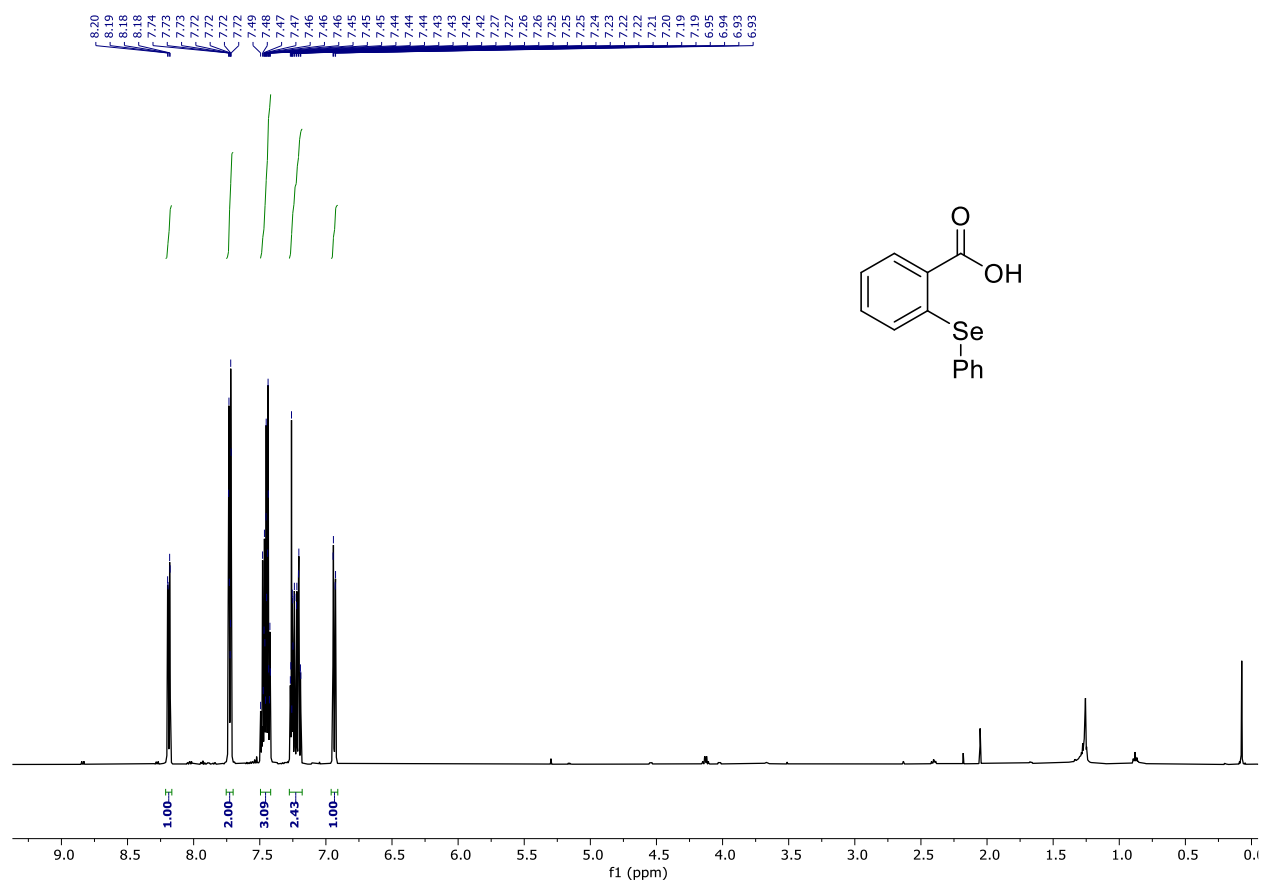
# $^1\text{H}$ (500 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (125 MHz) spectra of 5q in $\text{CDCl}_3$



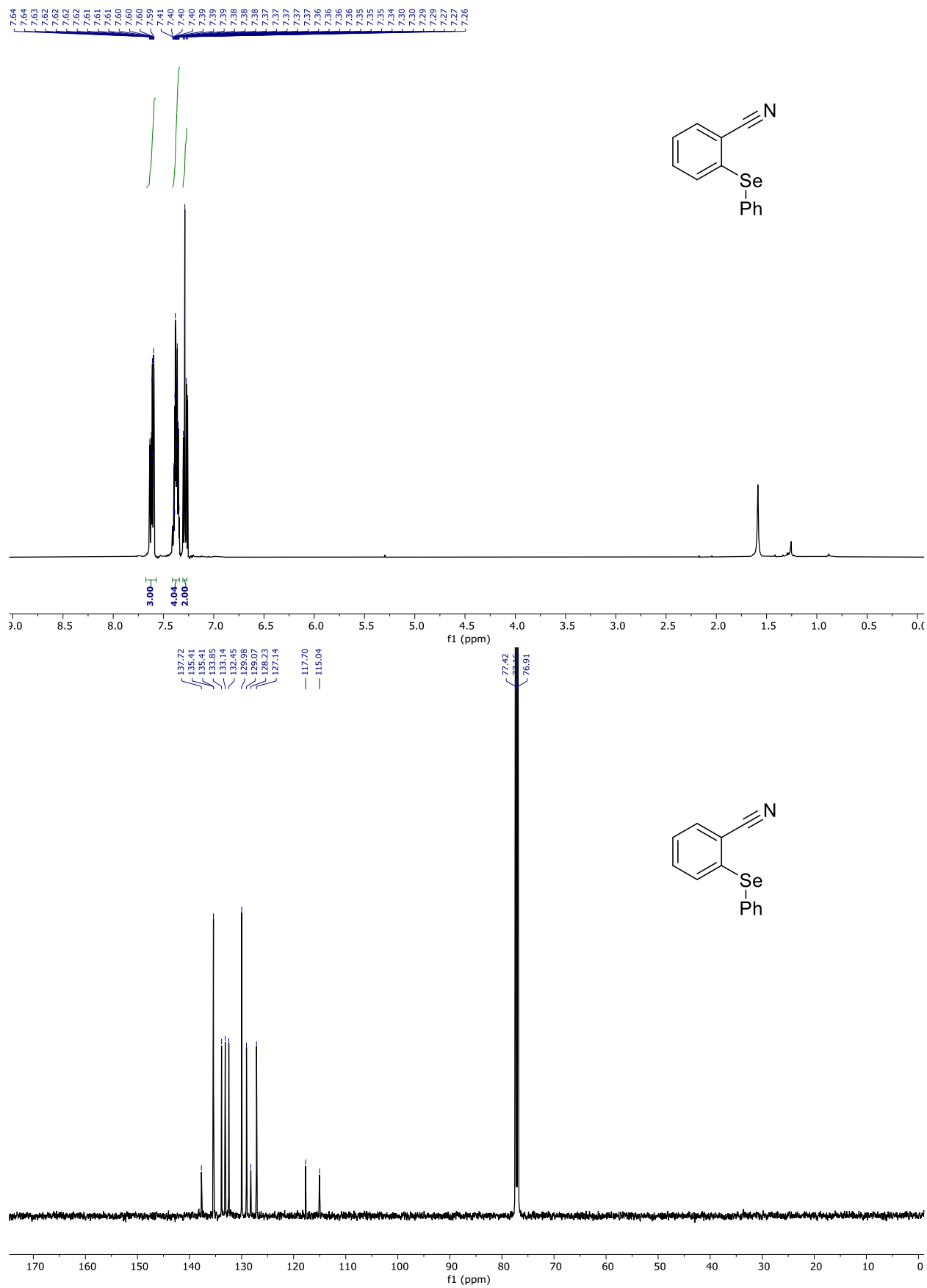
**$^{19}\text{F}\{^1\text{H}\}$  (471 MHz) NMR spectra of 5q in  $\text{CDCl}_3$**



$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 6a in  $\text{CDCl}_3$



**$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 6b in  $\text{CDCl}_3$**



**$^1\text{H}$  (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz) spectra of 6b in  $\text{CDCl}_3$**

