

## **Supporting Information**

### **Ni(II)-Catalyzed Nucleophilic Substitution for the Synthesis of Allenylselenide**

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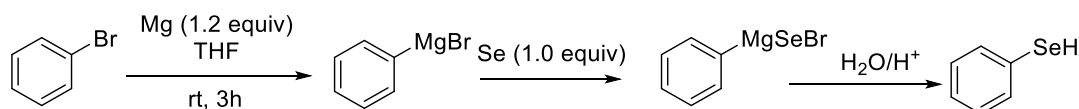
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## 1. General information

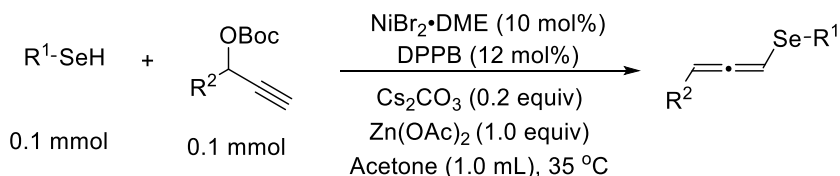
Unless otherwise noted, all reactions were performed in a glovebox filled with N<sub>2</sub>, reagents and solvents obtained from commercial suppliers were used directly. All reactions were monitored by thin-layer chromatography (TLC) on gel F254 plates. The silica gel (200-300 or 300-400 meshes) was used for column chromatography. All NMR analysis was recorded on a Bruker Aescend TM 500 MHz instrument and Bruker Aescend TM 400 MHz instruments. The residual solvent peak or TMS is used as an internal reference. <sup>1</sup>H NMR chemical shifts were recorded relative to SiMe<sub>4</sub> (δ 0.00). <sup>13</sup>C NMR chemical shifts were recorded relative to solvent resonance (CDCl<sub>3</sub>: δ 77.0). High-resolution mass spectral analysis (HRMS) data were measured by means of ESI and EI technique. Enantiomer excess was determined by HPLC analysis using Darcel Chiracel columns (IB N-3) and *n*-hexane/*i*-PrOH as eluents.

## 2. General methods for synthesis Selenol



Selenol were prepared according to references<sup>1,2</sup>. Under a nitrogen atmosphere, magnesium (0.29 g, 12 mmol) were added to a 250 mL round-bottom flask equipped with a magnetic stirrer, followed by the addition of 80 mL of THF. To the flask, bromobenzene (1.6 g, 10 mmol) was introduced, and the mixture was stirred at room temperature for 3 hours to generate the Grignard reagent, ArMgBr. Selenium powder (0.79 g, 10 mmol) was then added in portions, and the reaction was allowed to continue for an additional 3 hours. Upon completion of the reaction, the mixture was quenched with aqueous hydrochloric acid, and the PH was adjusted to an acidic value. The organic phase was then extracted with diethyl ether (30 mL × 3), and the combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on a short silica gel column, using petroleum ether as the eluent. The desired product, yellow liquid PhSeH, was obtained in 0.94 g (60% yield). The product exhibited a strong characteristic odor.

## 3. General methods for synthesis Allenylselenide

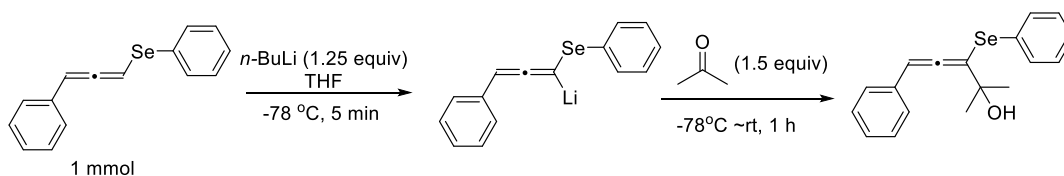


To a 4mL vial were added NiBr<sub>2</sub>·DME (0.01 mmol, 3.0 mg), DPPB (0.012 mmol, 5.0 mg) and Cs<sub>2</sub>CO<sub>3</sub> (0.02 mmol, 6.5 mg) in acetone. The mixture was stirred at room temperature for 15 minutes. Zn(OAc)<sub>2</sub> (0.1 mmol, 18.3 mg), selenol (0.1 mmol, 13 uL, 15.6mg) and propargyl carbonate (0.12

mmol, 30 $\mu$ L, 27.8 mg) were added subsequently. The vial was capped and taken out of the glovebox. The reaction was kept stirring at 35 °C for 2 days. The mixture was purified by thin-layer chromatography to afford the desired product.

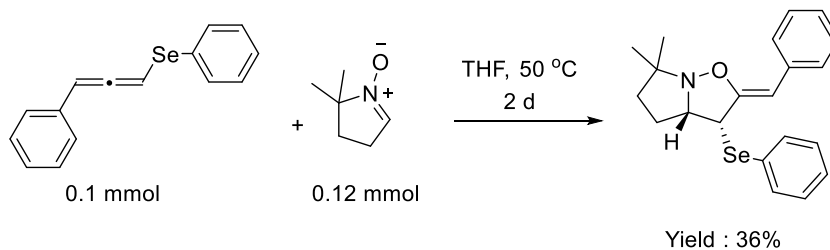
## 4. General methods for synthesis applications

### 4.1 synthesis of 4aa, 5aa and 6aa



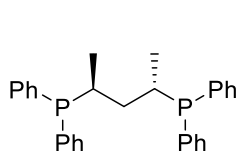
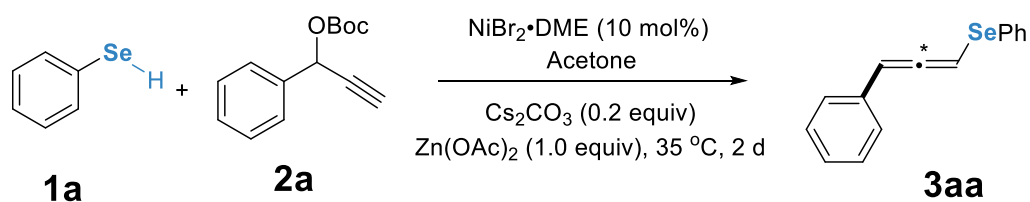
To a 50 mL round-bottom flask were added phenyl(3-phenylpropa-1,2-dien-1-yl)selane (0.27 g, 1 mmol) and THF (10 mL) under N<sub>2</sub> atmosphere. After being cooled to -78 °C, the flask was added *n*-BuLi (0.5 mL, 1.25 mmol, 2.5 M). When the mixture was stirred for 5 mins, acetone (0.1 mL, 1.5 mmol) was added to the flask, kept for 1h. After the completion of the reaction, the mixture was quenched with water (5 mL), extracted with EtOAc. The organic layer was concentrated at reduced pressure and purified by column chromatography.

### 4.2 synthesis of 7aa

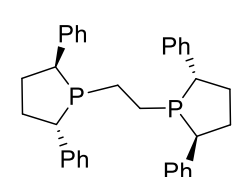


To a 4 mL vial were add phenyl(3-phenylpropa-1,2-dien-1-yl)selane (27.2 mg, 0.1 mmol), 2,2-dimethyl-3,4-dihydro-2H-pyrrole-1-oxide (13.6 mg 0.12mmol) and THF (1 mL). The vial was capped and taken out of the glovebox. The reaction was kept stirring at 50 °C for 2 days. The mixture was purified directly by thin-layer chromatography to afford the desired product in 13.9 mg, 36% yield.

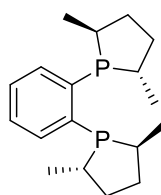
## 5. Screening of chiral ligands



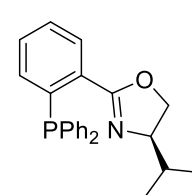
Yield: 11%, ee: 9%



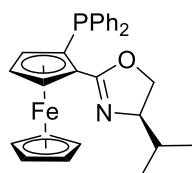
Yield: 57%, ee: 10%



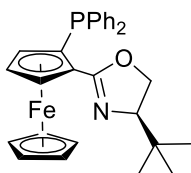
Yield: 44%, ee: 17%



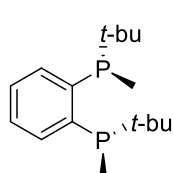
Yield: 24%, ee: 54%



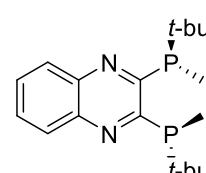
Yield: 25%, ee: 55%



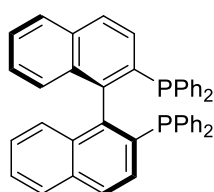
Yield: 23%, ee: 24%



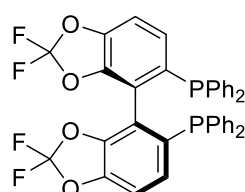
Yield: 22%, ee: 69%



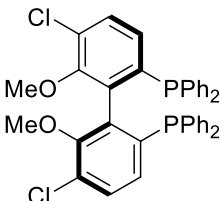
Yield: 15%, ee: 10%



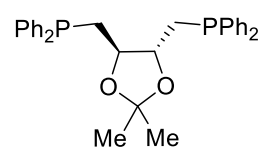
Yield: 17%, ee: 52%



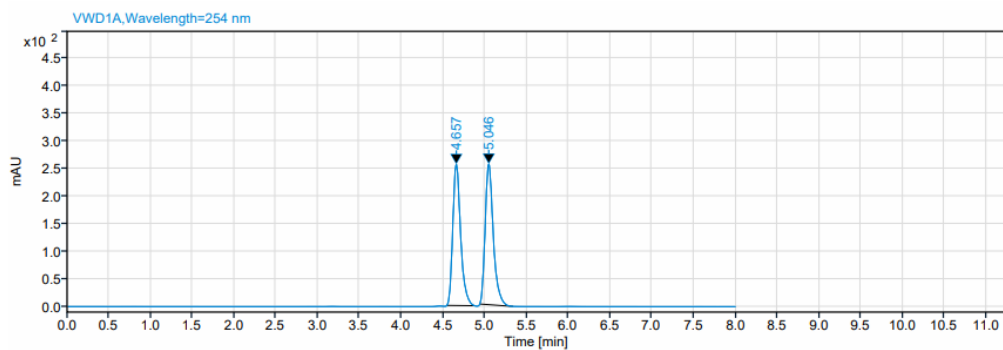
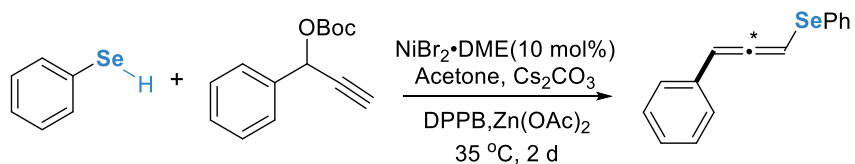
Yield: 72%, ee: 0%



Yield: 43%, ee: 5%

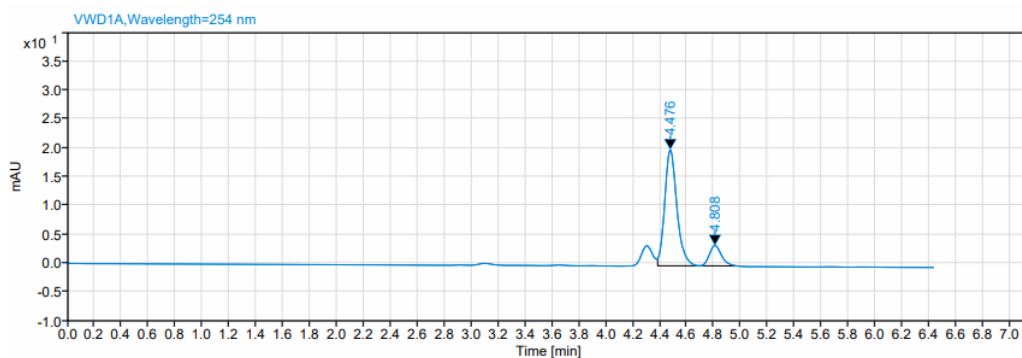
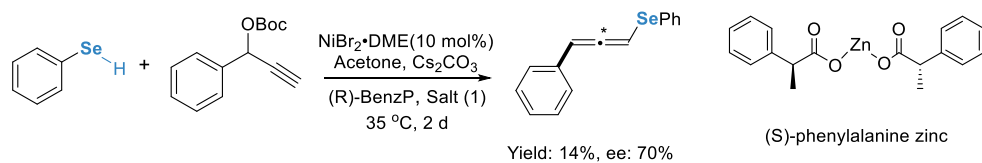


Yield: 86%, ee: 0%



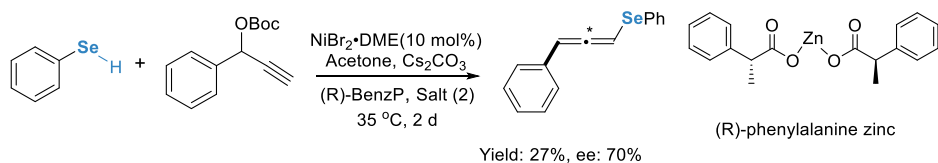
Signal: VWD1A,Wavelength=254 nm

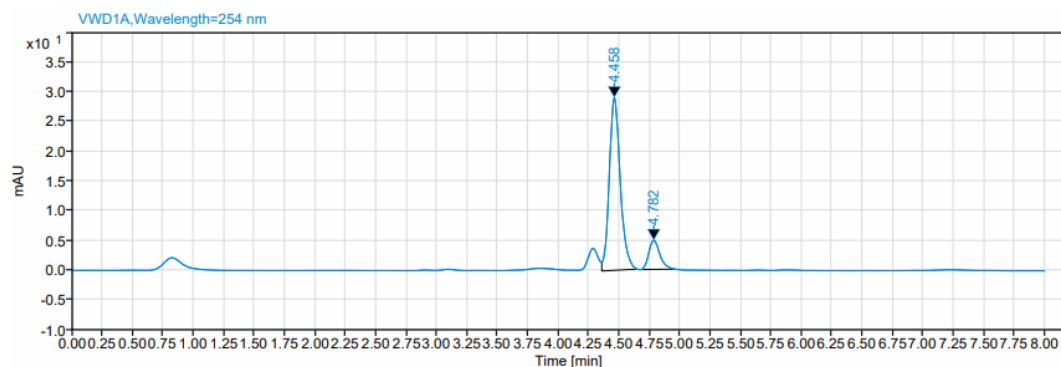
RT [min]	Type	Width [min]	Area	Height	Area%	Name
4.657	MM M	0.33	1674.78	256.33	49.24	
5.046	MM M	0.40	1726.48	255.48	50.76	
<b>Sum</b>			<b>3401.26</b>			



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
4.476	MM m	0.32	126.44	20.14	85.24	
4.808	MM m	0.27	21.89	3.53	14.76	
<b>Sum</b>			<b>148.32</b>			



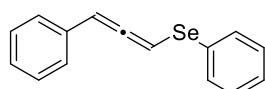


Signal: VWD1A,Wavelength=254 nm

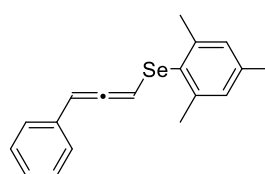
RT [min]	Type	Width [min]	Area	Height	Area%	Name
4.458	MM m	0.29	183.12	29.08	85.55	
4.782	MM m	0.28	30.92	4.91	14.45	
Sum			214.05			

The enantiomeric excess was determined by Daicel Chiralcel IB N-3 (70% ee), *n*-Hexanes/*i*-PrOH = 95/5, 1 mL/min,  $\lambda$  = 254 nm, *t* (major) = 4.54 min, *t* (minor) = 4.87 min.

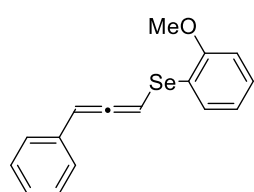
## 6. Spectroscopic data of products



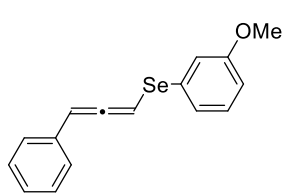
**(3aa)** : 22.9 mg, 84 % yield, yellow solid,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 – 7.54 (m, 2H), 7.33 – 7.17 (m, 8H), 6.48 (d,  $J$  = 6.0 Hz, 1H), 6.18 (d,  $J$  = 6.0 Hz, 1H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  203.7, 133.1, 132.9, 130.0, 129.2, 128.6, 127.5, 127.5, 127.2, 97.5, 82.4.  $^{77}\text{Se}$  NMR (76 MHz,  $\text{CDCl}_3$ )  $\delta$  363.71. HRMS (EI-MS)  $m/z$  calculated for  $\text{C}_{15}\text{H}_{12}\text{Se}^+$ ,  $M^+$ : 272.0099, found: 272.0099.



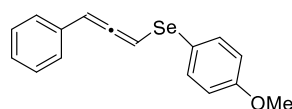
**(3ba)** : 15.4 mg, 54 % yield, yellow oil,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 (t,  $J$  = 7.5 Hz, 2H), 7.17 (t,  $J$  = 7.3 Hz, 1H), 7.15 (d,  $J$  = 7.1 Hz, 2H), 6.87 (s, 2H), 6.21 (d,  $J$  = 6.1 Hz, 1H), 5.99 (d,  $J$  = 6.1 Hz, 1H), 2.52 (s, 6H), 2.21 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  201.3, 143.2, 138.8, 133.7, 128.5, 128.4, 127.2, 127.0, 97.9, 83.3, 24.4, 20.9. HRMS (EI-MS)  $m/z$  calculated for  $\text{C}_{18}\text{H}_{18}\text{Se}^+$ ,  $M^+$ : 314.0568, found: 314.0564



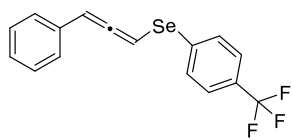
**(3ca)** : 24.0 mg, 79 % yield, yellow oil,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (dd,  $J$  = 7.6, 1.4 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.26 – 7.18 (m, 3H), 6.93 (td,  $J$  = 7.5, 1.1 Hz, 1H), 6.83 (d,  $J$  = 8.2 Hz, 1H), 6.47 (d,  $J$  = 6.0 Hz, 1H), 6.21 (d,  $J$  = 6.0 Hz, 1H), 3.85 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  205.2, 157.3, 133.2, 131.6, 128.6, 128.3, 127.5, 127.3, 121.6, 120.0, 110.5, 96.5, 80.0, 55.8. HRMS (ESI-MS)  $m/z$  calculated for  $\text{C}_{16}\text{H}_{14}\text{OSeNa}^+$ ,  $[\text{M}+\text{Na}]^+$ : 325.0102, found: 325.0129.



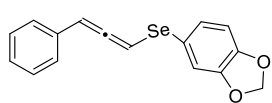
**(3da)** : 19.6 mg, 65 % yield, yellow oil,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 – 7.26 (m, 4H), 7.21 (t,  $J = 7.3$  Hz, 1H), 7.18 (d,  $J = 7.9$  Hz, 1H), 7.15 (d,  $J = 7.6$  Hz, 1H), 7.10 (d,  $J = 2.4$  Hz, 1H), 6.80 (dq,  $J = 8.0, 1.2$  Hz, 1H), 6.50 (d,  $J = 6.0$  Hz, 1H), 6.20 (d,  $J = 6.0$  Hz, 1H), 3.74 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  203.9, 159.8, 133.1, 131.0, 129.9, 128.7, 127.6, 127.2, 124.9, 117.9, 113.6, 97.5, 82.2, 55.3. HRMS (ESI-MS)  $m/z$  calculated for  $\text{C}_{16}\text{H}_{14}\text{OSeNa}^+$ ,  $[\text{M}+\text{Na}]^+$ : 325.0102, found: 325.0122.



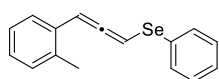
**(3ea)** : 20.5 mg, 68 % yield, yellow oil,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (d,  $J = 8.7$  Hz, 2H), 7.29 (t,  $J = 7.4$  Hz, 2H), 7.23 (d,  $J = 7.3$  Hz, 2H), 7.19 (d,  $J = 7.2$  Hz, 1H), 6.78 (d,  $J = 8.7$  Hz, 2H), 6.42 (d,  $J = 6.0$  Hz, 1H), 6.12 (d,  $J = 6.1$  Hz, 1H), 3.76 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  202.4, 159.7, 136.0, 134.0, 128.6, 127.4, 127.1, 119.5, 114.8, 97.9, 83.9, 55.3. HRMS (ESI-MS)  $m/z$  calculated for  $\text{C}_{16}\text{H}_{14}\text{OSeNa}^+$ ,  $[\text{M}+\text{Na}]^+$ : 325.0102, found: 325.0134.



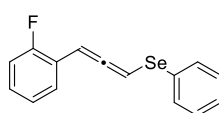
**(3fa)** : 31.0 mg, 91 % yield, white solid,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (d,  $J = 8.1$  Hz, 2H), 7.49 (d,  $J = 8.1$  Hz, 2H), 7.34 – 7.30 (m, 2H), 7.28 – 7.20 (m, 3H), 6.49 (d,  $J = 6.0$  Hz, 1H), 6.25 (d,  $J = 6.0$  Hz, 1H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  205.0, 135.7, 132.6, 131.9, 129.4 (q,  $J = 32.7$  Hz), 128.7, 127.9, 127.3, 125.9 (q,  $J = 3.8$  Hz), 124.0 (q,  $J = 274.6$  Hz), 97.6, 80.8. (EI-MS)  $m/z$  calculated for  $\text{C}_{16}\text{H}_{11}\text{F}_3\text{Se}^+$ ,  $\text{M}^+$ : 339.9973, found: 339.9970.



**(3ga)** : 24.2 mg, 77 % yield, yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 7.10 – 7.05 (m, 2H), 6.70 (d,  $J = 8.5$  Hz, 1H), 6.43 (d,  $J = 6.1$  Hz, 1H), 6.15 (d,  $J = 6.1$  Hz, 1H), 5.93 (d,  $J = 1.4$  Hz, 1H), 5.90 (d,  $J = 1.4$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  202.7, 148.0, 147.9, 133.2, 128.6, 128.2, 127.5, 127.1, 120.6, 114.7, 109.0, 101.2, 97.9, 83.7. HRMS (ESI-MS)  $m/z$  calculated for  $\text{C}_{16}\text{H}_{12}\text{O}_2\text{SeNa}^+$ ,  $[\text{M}+\text{Na}]^+$ : 338.9895, found: 338.9889

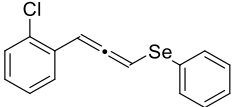


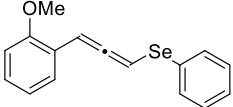
**(3ab)** : 22.0 mg, 77 % yield, yellow oil,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 – 7.52 (m, 2H), 7.31 (d,  $J = 7.2$  Hz, 1H), 7.30 – 7.22 (m, 3H), 7.19 – 7.09 (m, 3H), 6.44 (d,  $J = 6.1$  Hz, 1H), 6.38 (d,  $J = 6.1$  Hz, 1H), 2.32 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  204.5, 135.6, 132.8, 131.4, 130.5, 130.2, 129.2, 127.9, 127.5, 127.4, 126.2, 94.8, 81.4, 19.9. HRMS (EI-MS)  $m/z$  calculated for  $\text{C}_{16}\text{H}_{14}\text{Se}^+$ ,  $\text{M}^+$ : 286.0258, found: 286.0255.

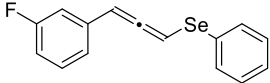


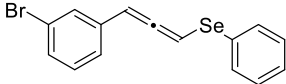
**(3ac)** : 24.0 mg, 83 % yield, yellow oil,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 – 7.51 (m, 2H), 7.32 (td,  $J = 7.7, 1.7$  Hz, 1H), 7.28 – 7.22 (m, 3H), 7.17 (ddd,  $J = 13.7, 5.5, 2.6$  Hz, 1H), 7.07 (td,  $J = 7.6, 1.0$  Hz, 1H), 7.01 (ddd,  $J = 9.4, 8.2, 1.0$  Hz, 1H), 6.49 (d,  $J = 6.1$  Hz, 1H), 6.39 (d,  $J = 6.1$  Hz, 1H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  204.1 (d,  $J = 1.9$  Hz), 159.8 (d,  $J = 250.4$  Hz), 133.0, 129.8, 129.2, 128.9 (d,  $J = 8.2$  Hz), 128.6 (d,  $J = 3.2$  Hz), 127.6, 124.2 (d,  $J = 3.6$  Hz), 120.8 (d,  $J = 12.0$  Hz), 115.6 (d,  $J = 21.3$  Hz), 89.9 (d,  $J = 6.4$  Hz), 82.5.

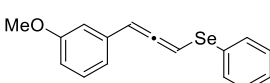


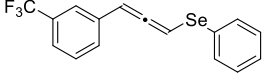
 **(3ad)** : 24.2 mg, 79 % yield, yellow oil, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.56 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.38 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.32 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.28 – 7.23 (m, 3H), 7.19 (td, *J* = 7.5, 1.4 Hz, 1H), 7.13 (td, *J* = 7.6, 1.7 Hz, 1H), 6.62 (d, *J* = 6.1 Hz, 1H), 6.51 (d, *J* = 6.1 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 204.2, 133.1, 132.3, 131.0, 129.7, 129.7, 129.2, 128.7, 128.5, 127.7, 126.8, 93.8, 82.8. HRMS (EI-MS) *m/z* calculated for C<sub>15</sub>H<sub>11</sub>ClSe<sup>+</sup>, M<sup>+</sup>: 305.9709, found: 305.9703.

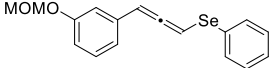
 **(3ae)** : 22.1 mg, 73 % yield, yellow oil, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.59 – 7.53 (m, 2H), 7.32 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.29 – 7.23 (m, 3H), 7.21 – 7.17 (m, 1H), 6.91 (td, *J* = 7.5, 0.8 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.61 (d, *J* = 6.1 Hz, 1H), 6.44 (d, *J* = 6.1 Hz, 1H), 3.83 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 204.85, 156.31, 132.47, 130.57, 129.13, 128.70, 128.41, 127.25, 121.55, 120.76, 110.95, 91.31, 80.94, 55.57. HRMS (ESI-MS) *m/z* calculated for C<sub>16</sub>H<sub>14</sub>OSeNa<sup>+</sup>, [M+Na]<sup>+</sup>: 325.0102, found: 325.0133. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 204.8, 156.3, 132.5, 130.6, 129.1, 128.7, 128.4, 127.2, 121.5, 120.8, 111.0, 91.3, 80.9, 55.6.

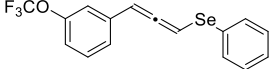
 **(3af)** : 19.9 mg, 69 % yield, yellow oil, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.59 – 7.54 (m, 2H), 7.29 – 7.22 (m, 4H), 7.01 (d, *J* = 7.7 Hz, 1H), 6.95 (dt, *J* = 9.7, 2.0 Hz, 1H), 6.90 (td, *J* = 8.4, 2.4 Hz, 1H), 6.51 (d, *J* = 6.0 Hz, 1H), 6.12 (d, *J* = 6.0 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 203.5, 163.1 (d, *J* = 245.6 Hz), 135.7 (d, *J* = 7.8 Hz), 133.3, 130.0 (d, *J* = 8.4 Hz), 129.5, 129.2, 127.8, 122.9 (d, *J* = 2.8 Hz), 114.4 (d, *J* = 21.5 Hz), 113.6 (d, *J* = 22.3 Hz), 96.9 (d, *J* = 2.8 Hz), 83.3. HRMS (EI-MS) *m/z* calculated for C<sub>15</sub>H<sub>11</sub>FSe<sup>+</sup>, M<sup>+</sup>: 290.0005, found: 290.0006.

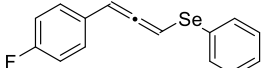
 **(3ag)** : 21.5 mg, 61 % yield, yellow oil, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.56 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.37 (s, 1H), 7.34 – 7.31 (m, 1H), 7.30 – 7.24 (m, 3H), 7.15 (d, *J* = 5.4 Hz, 2H), 6.53 (d, *J* = 6.0 Hz, 1H), 6.08 (d, *J* = 6.0 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 203.5, 135.5, 133.4, 130.4, 130.0, 129.9, 129.5, 129.2, 127.8, 125.7, 122.8, 96.5, 83.4. HRMS (EI-MS) *m/z* calculated for C<sub>15</sub>H<sub>11</sub>BrSe<sup>+</sup>, M<sup>+</sup>: 349.9204, found: 349.9193.

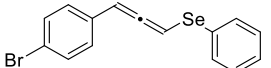
 **(3ah)** : 16.6 mg, 55 % yield, yellow oil, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.63 – 7.53 (m, 2H), 7.30 – 7.24 (m, 3H), 7.21 (t, *J* = 7.9 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.81 (s, 1H), 6.77 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.49 (d, *J* = 6.0 Hz, 1H), 6.16 (d, *J* = 6.1 Hz, 1H), 3.79 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 203.8, 159.8, 134.6, 132.9, 130.0, 129.6, 129.2, 127.0, 119.9, 113.5, 112.2, 97.5, 82.5, 55.2. HRMS (ESI-MS) *m/z* calculated for C<sub>16</sub>H<sub>14</sub>OSeNa<sup>+</sup>, [M+Na]<sup>+</sup>: 325.0102, found: 325.0098.

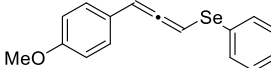
 **(3ai)** : 23.3 mg, 69 % yield, yellow oil, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.64 – 7.55 (m, 2H), 7.51 – 7.45 (m, 2H), 7.42 (d, *J* = 4.3 Hz, 2H), 7.31 – 7.25 (m, 3H), 6.58 (d, *J* = 6.0 Hz, 1H), 6.19 (d, *J* = 6.1 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 203.5, 134.3, 133.5, 131.1 (q, *J* = 32.3 Hz), 130.2, 129.3, 129.2, 129.0, 127.9, 124.1 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.4 Hz), 123.7 (q, *J* = 3.9 Hz), 96.7, 83.8. HRMS (EI-MS) *m/z* calculated for C<sub>16</sub>H<sub>11</sub>F<sub>3</sub>Se<sup>+</sup>, M<sup>+</sup>: 339.9973, found: 339.9968.

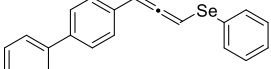
 **(3aj)** : 28.8 mg, 87 % yield, yellow solid,  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (dd,  $J = 7.7, 1.8$  Hz, 2H), 7.35 (dd,  $J = 7.7, 1.7$  Hz, 1H), 7.30 – 7.23 (m, 3H), 7.22 – 7.14 (m, 1H), 7.08 (d,  $J = 8.4$  Hz, 1H), 6.97 (t,  $J = 8.1$  Hz, 1H), 6.62 (d,  $J = 6.1$  Hz, 1H), 6.45 (d,  $J = 6.1$  Hz, 1H), 5.19 (s, 2H), 3.47 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  204.6, 153.9, 132.5, 130.4, 129.1, 128.7, 128.4, 127.3, 122.3, 122.0, 114.7, 94.6, 91.4, 81.2, 56.2. HRMS (ESI-MS)  $m/z$  calculated for  $\text{C}_{17}\text{H}_{16}\text{O}_2\text{SeNa}^+$ ,  $[\text{M}+\text{Na}]^+$ : 355.0205, found: 355.0205.

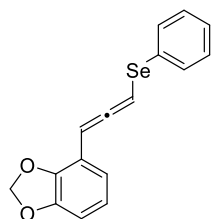
 **(3ak)** : 26.3 mg, 74 % yield, yellow oil,  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (dd,  $J = 7.6, 1.9$  Hz, 1H), 7.56 (dd,  $J = 6.6, 3.0$  Hz, 2H), 7.30 (t,  $J = 7.9$  Hz, 1H), 7.26 (d,  $J = 4.7$  Hz, 2H), 7.15 (d,  $J = 7.7$  Hz, 1H), 7.10 – 7.02 (m, 2H), 6.53 (d,  $J = 6.0$  Hz, 1H), 6.12 (d,  $J = 6.1$  Hz, 1H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  203.4, 149.5, 135.5, 133.4, 131.4, 129.9, 129.3, 129.2, 128.5 (q,  $J = 199.5$  Hz), 127.8, 125.4, 119.8, 119.3, 96.7, 83.6. HRMS (ESI-MS)  $m/z$  calculated for  $\text{C}_{16}\text{H}_{11}\text{F}_3\text{OSeH}^+$ ,  $[\text{M}+\text{H}]^+$ : 357.0000, found: 357.0035.

 **(3al)** : 17.0 mg, 54 % yield, with solid,  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 – 7.49 (m, 2H), 7.33 – 7.23 (m, 3H), 7.24 – 7.15 (m, 2H), 6.99 (t,  $J = 8.7$  Hz, 2H), 6.49 (d,  $J = 6.1$  Hz, 1H), 6.14 (d,  $J = 6.1$  Hz, 1H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  203.3, 162.2 (d,  $J = 247.1$  Hz), 133.1, 129.8, 129.2, 129.1 (d,  $J = 3.5$  Hz), 128.7 (d,  $J = 8.1$  Hz), 127.6, 115.6 (d,  $J = 21.8$  Hz), 96.7, 82.9. HRMS (EI-MS)  $m/z$  calculated for  $\text{C}_{15}\text{H}_{11}\text{FSe}^+$ ,  $\text{M}^+$ : 290.0005, found: 290.0001.

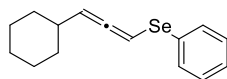
 **(3am)** : 18.3 mg, 52 % yield, white solid,  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (dd,  $J = 6.8, 2.8$  Hz, 2H), 7.41 (d,  $J = 8.5$  Hz, 2H), 7.29 – 7.24 (m, 3H), 7.10 (d,  $J = 8.5$  Hz, 2H), 6.48 (d,  $J = 6.0$  Hz, 1H), 6.10 (s, 1H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  203.3, 133.3, 132.2, 131.7, 129.6, 129.2, 128.6, 127.7, 121.3, 96.8, 83.3. HRMS (EI-MS)  $m/z$  calculated for  $\text{C}_{15}\text{H}_{11}\text{BrSe}^+$ ,  $\text{M}^+$ : 349.9204, found: 349.9196.

 **(3an)** : 10.0 mg, 33 % yield, yellow oil,  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (dd,  $J = 7.3, 2.1$  Hz, 2H), 7.36 – 7.23 (m, 3H), 7.19 (d,  $J = 8.7$  Hz, 2H), 6.85 (d,  $J = 8.8$  Hz, 2H), 6.46 (d,  $J = 6.0$  Hz, 1H), 6.16 (d,  $J = 6.0$  Hz, 1H), 3.81 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  202.2, 160.2, 132.9, 130.1, 129.1, 128.4, 127.4, 125.3, 114.2, 97.2, 82.3, 55.3. HRMS (ESI-MS)  $m/z$  calculated for  $\text{C}_{16}\text{H}_{14}\text{OSeNa}^+$ ,  $[\text{M}+\text{Na}]^+$ : 325.0102, found: 325.0128.

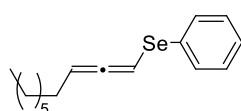
 **(3ao)** : 22.0 mg, 63 % yield, yellow solid,  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 – 7.57 (m, 4H), 7.55 (d,  $J = 8.3$  Hz, 2H), 7.44 (t,  $J = 7.7$  Hz, 2H), 7.34 (t,  $J = 8.1$  Hz, 3H), 7.31 – 7.25 (m, 3H), 6.52 (d,  $J = 6.0$  Hz, 1H), 6.23 (d,  $J = 6.0$  Hz, 1H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  203.9, 140.6, 140.4, 133.0, 132.2, 130.0, 129.2, 128.8, 127.6, 127.6, 127.4, 127.3, 126.9, 97.2, 82.6. HRMS (EI-MS)  $m/z$  calculated for  $\text{C}_{21}\text{H}_{16}\text{Se}^+$ ,  $\text{M}^+$ : 348.0412, found: 348.0415.



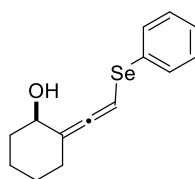
**(3ap)** : 23.2 mg, 74 % yield, yellow solid,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 – 7.46 (m, 2H), 7.22 – 7.16 (m, 3H), 6.70 (d,  $J = 4.5$  Hz, 2H), 6.61 (t,  $J = 4.4$  Hz, 1H), 6.40 (d,  $J = 6.1$  Hz, 1H), 6.18 (d,  $J = 6.1$  Hz, 1H), 5.89 (d,  $J = 2.1$  Hz, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  204.5, 147.5, 144.8, 132.7, 130.1, 129.1, 127.5, 121.6, 120.4, 115.2, 107.4, 101.0, 90.8, 82.0. HRMS (ESI-MS)  $m/z$  calculated for  $\text{C}_{16}\text{H}_{12}\text{O}_2\text{SeNa}^+$ ,  $[\text{M}+\text{Na}]^+$ : 338.9895, found: 338.9917.



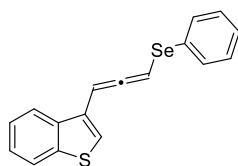
**(3aq)** : 12.8 mg, 46 % yield, yellow oil,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 – 7.42 (m, 2H), 7.32 – 7.22 (m, 3H), 6.06 (dd,  $J = 5.9, 2.8$  Hz, 1H), 5.21 (t,  $J = 5.9$  Hz, 1H), 2.02 (tt,  $J = 11.0, 5.5$  Hz, 1H), 1.78 – 1.65 (m, 4H), 1.64 – 1.58 (m, 1H), 1.33 – 1.21 (m, 2H), 1.16 (tt,  $J = 12.2, 2.9$  Hz, 1H), 1.09 – 0.99 (m, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  202.7, 132.3, 130.8, 129.1, 127.0, 100.2, 78.7, 36.9, 32.7, 32.6, 26.0, 25.8. HRMS (EI-MS)  $m/z$  calculated for  $\text{C}_{15}\text{H}_{18}\text{Se}^+$ ,  $\text{M}^+$ : 278.0547, found: 278.0569.



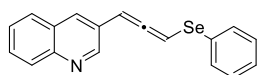
**(3ar)** : 20.1 mg, 68 % yield, yellow oil,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (d,  $J = 7.3$  Hz, 2H), 7.36 – 7.07 (m, 3H), 6.03 (dt,  $J = 5.9, 2.9$  Hz, 1H), 5.23 (q,  $J = 6.5$  Hz, 1H), 2.08 – 1.97 (m, 2H), 1.36 (q,  $J = 7.0$  Hz, 2H), 1.32 – 1.21 (m, 8H), 0.88 (t,  $J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  203.9, 132.0, 130.9, 129.1, 127.0, 94.3, 77.9, 31.8, 29.1, 29.0, 28.8, 28.2, 22.6, 14.1. HRMS (EI-MS)  $m/z$  calculated for  $\text{C}_{16}\text{H}_{22}\text{Se}^+$ ,  $\text{M}^+$ : 294.0881, found: 294.0882.



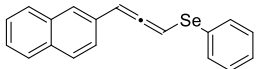
**(3as)** : 16.8 mg, 60 % yield for 1:1 dr, yellow oil,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 – 7.50 (m, 2H), 7.35 – 7.27 (m, 3H), 6.35 – 6.13 (m, 1H), 4.06 – 3.85 (m, 1H), 2.43 – 2.28 (m, 1H), 2.07 – 1.86 (m, 2H), 1.72 – 1.63 (m, 1H), 1.63 – 1.54 (m, 1H), 1.42 (dd,  $J = 18.2, 4.0$  Hz, 1H), 1.39 – 1.32 (m, 1H), 1.32 – 1.24 (m, 1H), 1.21 – 1.04 (m, 1H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  194.7, 193.9, 134.6, 133.5, 130.0, 129.3, 129.3, 129.1, 128.0, 127.6, 112.8, 112.3, 83.5, 82.7, 68.8, 68.7, 35.6, 35.4, 29.2, 29.2, 26.3, 26.2, 23.3, 23.2. HRMS (ESI-MS)  $m/z$  calculated for  $\text{C}_{14}\text{H}_{16}\text{OSeNa}^+$ ,  $[\text{M}+\text{Na}]^+$ : 303.0259, found: 303.0262.

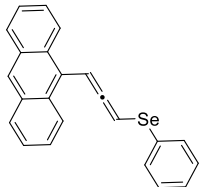


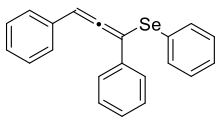
**(3at)** : 26.8 mg, 82 % yield, yellow oil,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 – 8.08 (m, 1H), 7.87 – 7.84 (m, 1H), 7.61 – 7.56 (m, 2H), 7.38 (dd,  $J = 6.4, 2.6$  Hz, 2H), 7.31 – 7.22 (m, 4H), 6.54 (d,  $J = 6.2$  Hz, 1H), 6.52 (d,  $J = 6.2$  Hz, 1H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  203.8, 140.5, 137.0, 133.2, 131.5, 129.7, 129.2, 129.2, 127.8, 127.7, 124.8, 124.6, 124.4, 122.8, 122.7, 90.9, 82.3. HRMS (ESI-MS)  $m/z$  calculated for  $\text{C}_{17}\text{H}_{18}\text{SSe}^+$ ,  $\text{M}^+$ : 327.9819, found: 327.9818.

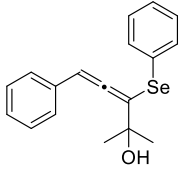


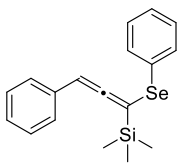
**(3au)** : 22.2 mg, 66 % yield, yellow solid,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.83 (s, 1H), 8.07 (d,  $J = 8.4$  Hz, 1H), 7.88 (d,  $J = 2.2$  Hz, 1H), 7.75 (d,  $J = 6.8$  Hz, 1H), 7.71 – 7.66 (m, 1H), 7.64 – 7.59 (m, 2H), 7.56 – 7.48 (m, 1H), 7.29 – 7.16 (m, 3H), 6.63 (d,  $J = 6.1$  Hz, 1H), 6.29 (d,  $J = 6.1$  Hz, 1H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  203.6, 149.8, 147.3, 133.7, 132.8, 129.3, 129.2, 129.2, 128.0, 128.0, 127.6, 127.0, 126.4, 94.9, 84.1. HRMS (ESI-MS)  $m/z$  calculated for  $\text{C}_{18}\text{H}_{13}\text{NSeH}^+$ ,  $[\text{M}+\text{H}]^+$ : 324.0286, found: 324.0294.

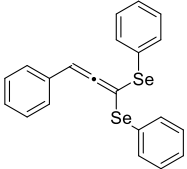

**(3av)**: 23.1 mg, 78 % yield, yellow solid,  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 – 7.78 (m, 1H), 7.76 (d,  $J = 8.6$  Hz, 2H), 7.62 (s, 1H), 7.60 (dd,  $J = 7.3, 2.1$  Hz, 2H), 7.49 – 7.40 (m, 3H), 7.30 – 7.21 (m, 3H), 6.56 (d,  $J = 6.0$  Hz, 1H), 6.35 (d,  $J = 6.0$  Hz, 1H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  204.0, 133.6, 133.2, 132.9, 131.5, 130.7, 129.8, 129.2, 128.3, 127.8, 127.7, 127.6, 126.3, 126.3, 125.9, 124.8, 98.0, 82.8. HRMS (EI-MS)  $m/z$  calculated for  $\text{C}_{19}\text{H}_{14}\text{Se}^+$ ,  $\text{M}^+$ : 322.0255, found: 322.0256

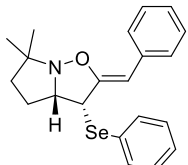

**(3aw)**: 26.4 mg, 71 % yield, yellow solid,  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.41 (s, 1H), 8.38 – 8.33 (m, 2H), 8.04 – 7.97 (m, 2H), 7.54 (dd,  $J = 5.8, 2.8$  Hz, 2H), 7.50 – 7.46 (m, 4H), 7.27 – 7.25 (m, 1H), 7.24 – 7.20 (m, 2H), 7.14 (d,  $J = 6.2$  Hz, 1H), 6.43 (d,  $J = 6.2$  Hz, 1H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  206.3, 132.5, 131.5, 131.0, 130.3, 129.6, 129.2, 128.8, 127.4, 125.9, 125.8, 125.5, 125.2, 91.0, 79.8. HRMS (EI-MS)  $m/z$  calculated for  $\text{C}_{23}\text{H}_{16}\text{Se}^+$ ,  $\text{M}^+$ : 322.0255, found: 322.0256


**(3ax)**: 26.4 mg, 71 % yield, yellow solid,  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 7.4$  Hz, 2H), 7.53 (dd,  $J = 6.5, 3.0$  Hz, 2H), 7.35 – 7.20 (m, 8H), 7.19 – 7.16 (m, 3H), 6.38 (s, 1H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  206.1, 134.5, 133.1, 133.1, 130.4, 129.0, 128.7, 128.6, 127.9, 127.6, 127.6, 127.4, 127.3, 100.2, 97.2. HRMS (EI-MS)  $m/z$  calculated for  $\text{C}_{21}\text{H}_{16}\text{Se}^+$ ,  $\text{M}^+$ : 348.0417, found: 348.0405


**(4aa)**: 281.1 mg, 85 % yield, brown solid,  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (dd,  $J = 7.9, 1.5$  Hz, 2H), 7.23 (d,  $J = 7.5$  Hz, 2H), 7.19 – 7.14 (m, 4H), 7.14 – 7.09 (m, 2H), 6.09 (s, 1H), 1.55 (s, 3H), 1.52 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  199.7, 134.4, 133.5, 130.1, 128.9, 128.6, 127.8, 127.4, 126.9, 110.1, 98.1, 72.8, 29.7, 29.7. HRMS (ESI-MS)  $m/z$  calculated for  $\text{C}_{18}\text{H}_{18}\text{OSeNa}^+$ ,  $[\text{M}+\text{Na}]^+$ : 353.0415, found: 353.0405.

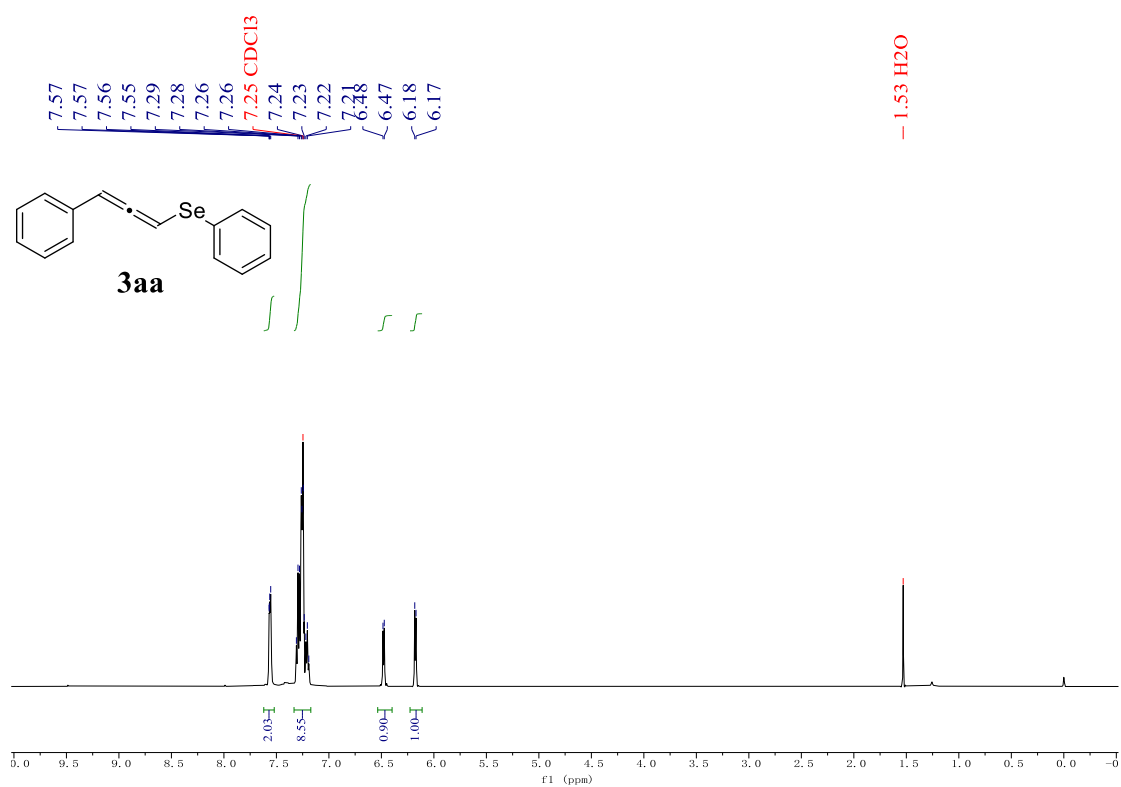

**(5aa)**: 245.7 mg, 72 % yield, yellow solid,  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (dd,  $J = 7.9, 1.6$  Hz, 2H), 7.24 (d,  $J = 7.6$  Hz, 2H), 7.20 – 7.09 (m, 6H), 5.80 (s, 1H), 0.21 (s, 9H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  204.5, 134.7, 134.3, 129.7, 128.7, 128.5, 127.7, 126.6, 126.3, 92.5, 91.5, -1.0. (EI-MS)  $m/z$  calculated for  $\text{C}_{18}\text{H}_{20}\text{SiSe}^+$ ,  $\text{M}^+$ : 344.0494, found: 344.0491.

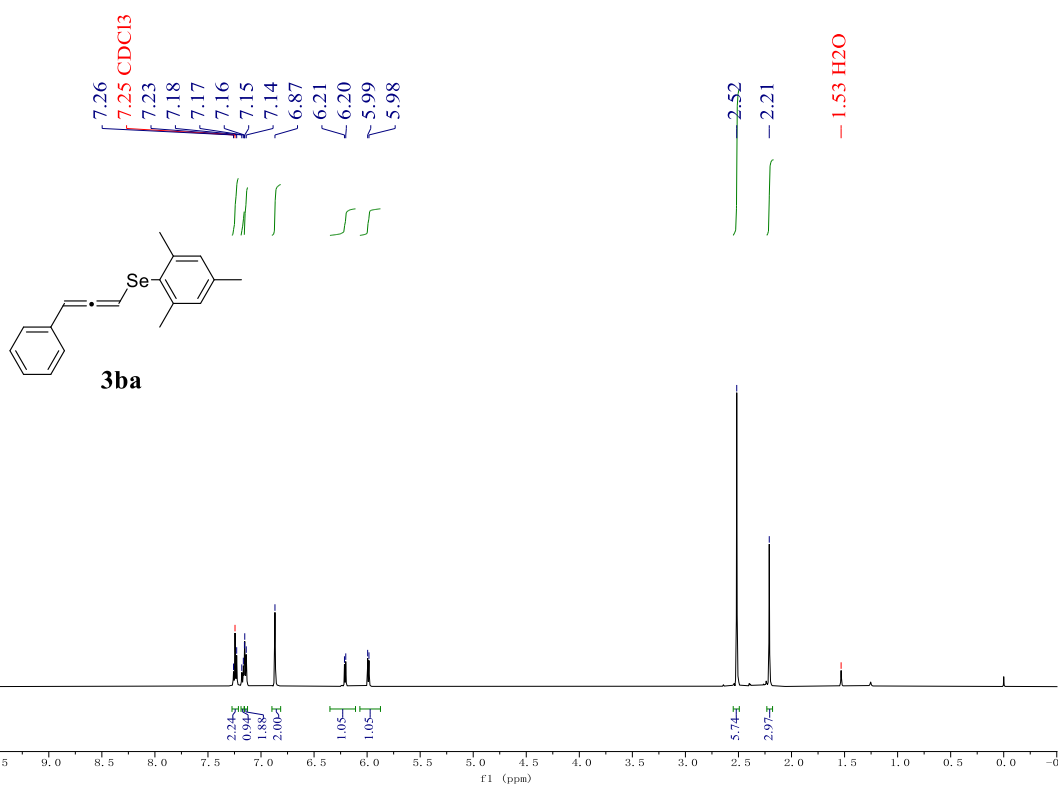
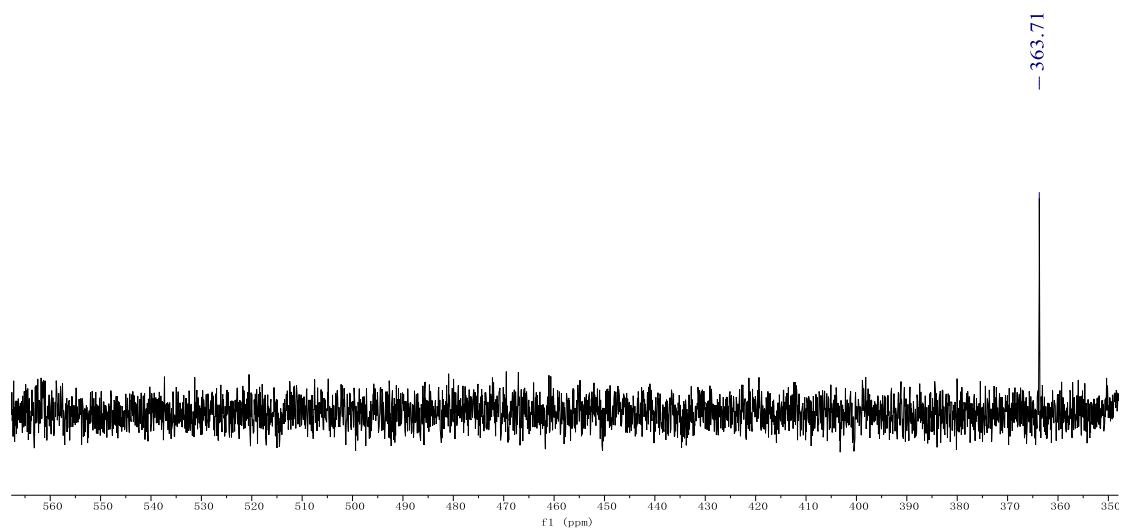
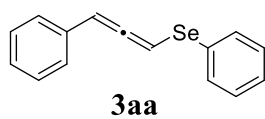

**(6aa)**: 282.5 mg, 66 % yield, yellow solid,  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (dd,  $J = 7.9, 1.5$  Hz, 4H), 7.28 – 7.21 (m, 8H), 7.20 – 7.17 (m, 1H), 7.10 – 7.07 (m, 2H), 5.97 (s, 1H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  203.9, 134.2, 132.8, 130.5, 129.0, 128.5, 128.2, 127.7, 127.4, 96.7, 81.6. (EI-MS)  $m/z$  calculated for  $\text{C}_{21}\text{H}_{16}\text{Se}_2^+$ ,  $\text{M}^+$ : 427.9577, found: 427.9548.

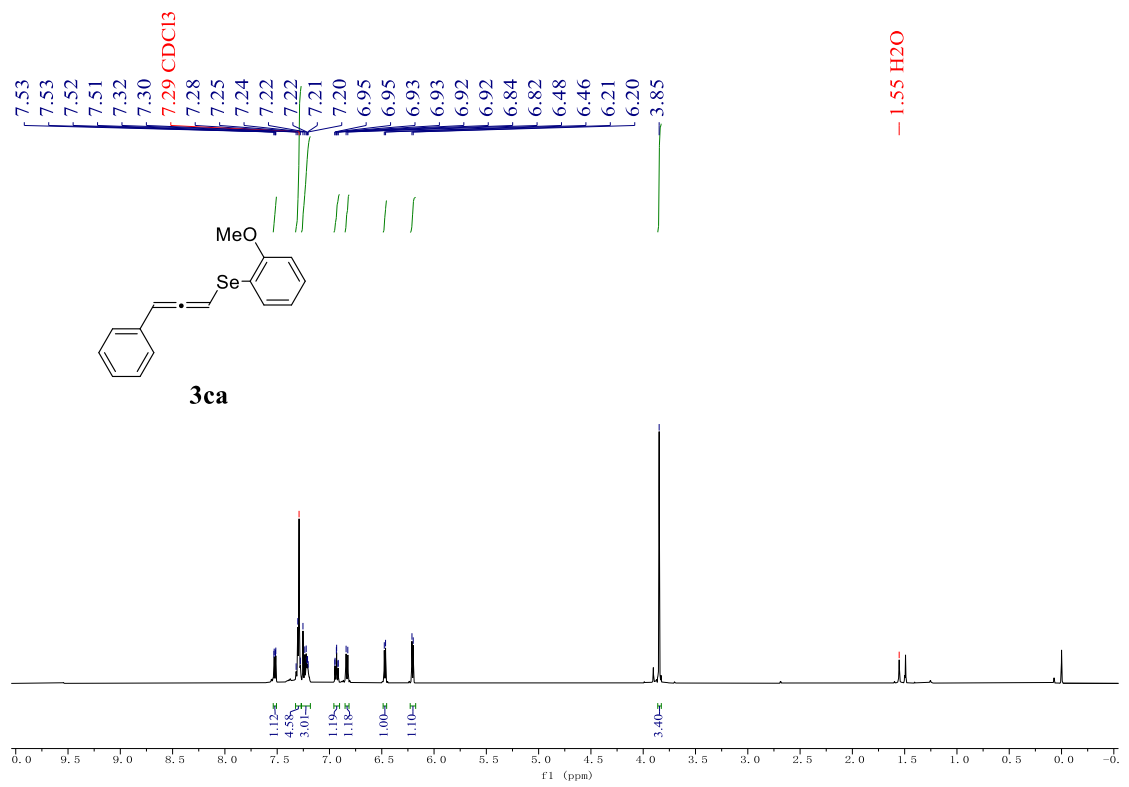
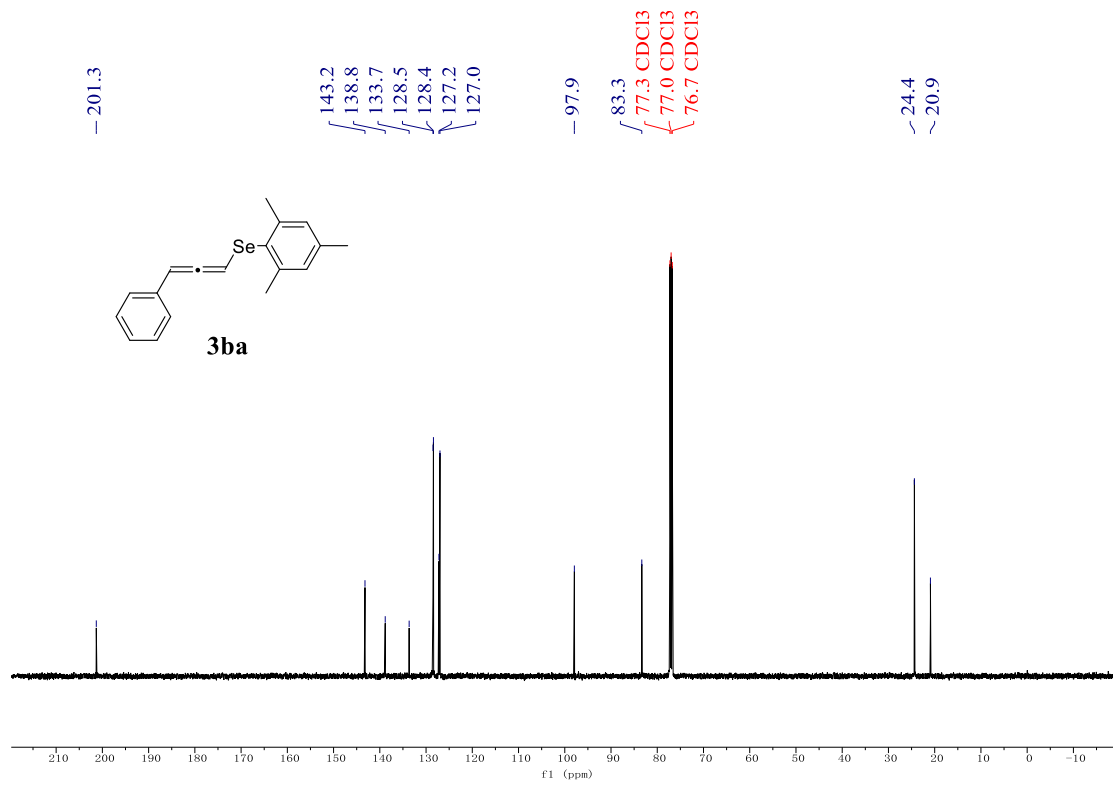

**(7aa)**: 13.9 mg, 36 % yield, white solid,  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.32 (m, 4H), 7.30 (d,  $J = 7.3$  Hz, 1H), 7.28 – 7.23 (m, 3H), 6.43 (t,  $J = 1.9$  Hz, 2H), 5.55 (s, 1H), 4.48 – 4.40 (m, 1H), 2.44 – 2.19 (m, 1H), 1.98 – 1.87 (m, 2H), 1.74 – 1.65 (m, 1H), 1.29 (s, 3H), 1.15 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.9, 139.9,

131.8, 131.3, 129.2, 128.4, 128.2, 128.1, 127.2, 110.7, 84.4, 69.3, 67.1, 36.2, 30.7, 27.5, 22.8. HRMS (ESI-MS)  $m/z$  calculated for  $C_{21}H_{23}NOSeH^+$ ,  $[M+H]^+$ : 386.1018, found:386.1010.

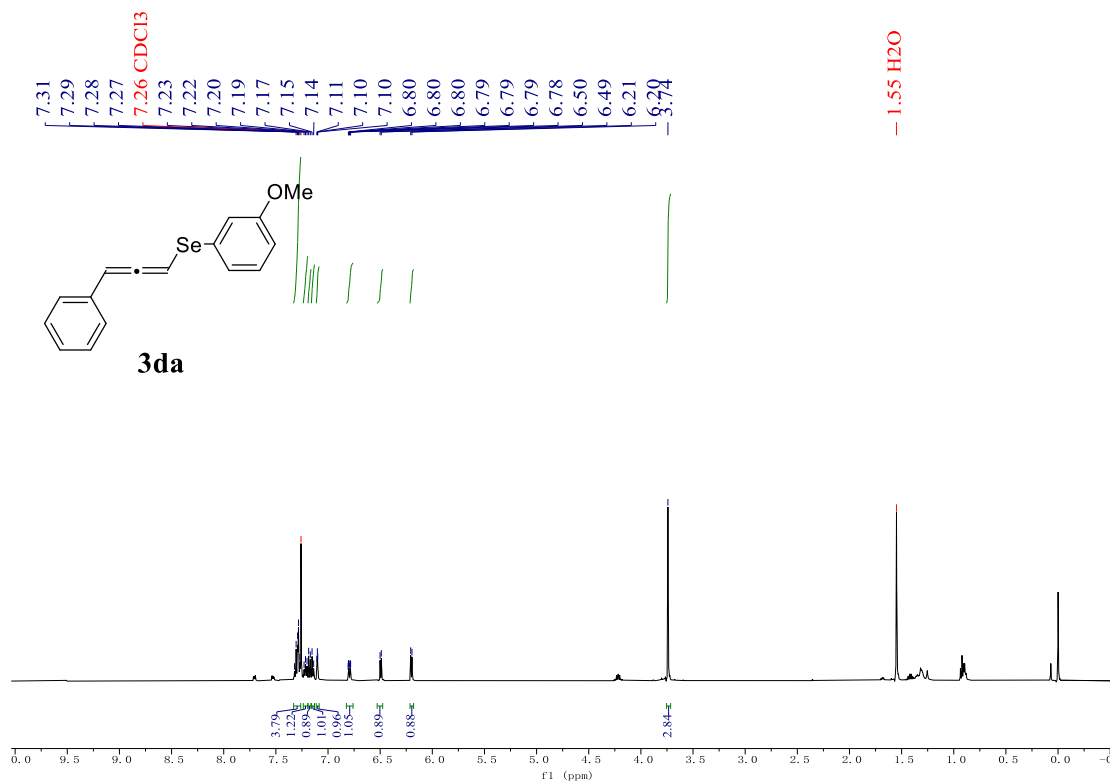
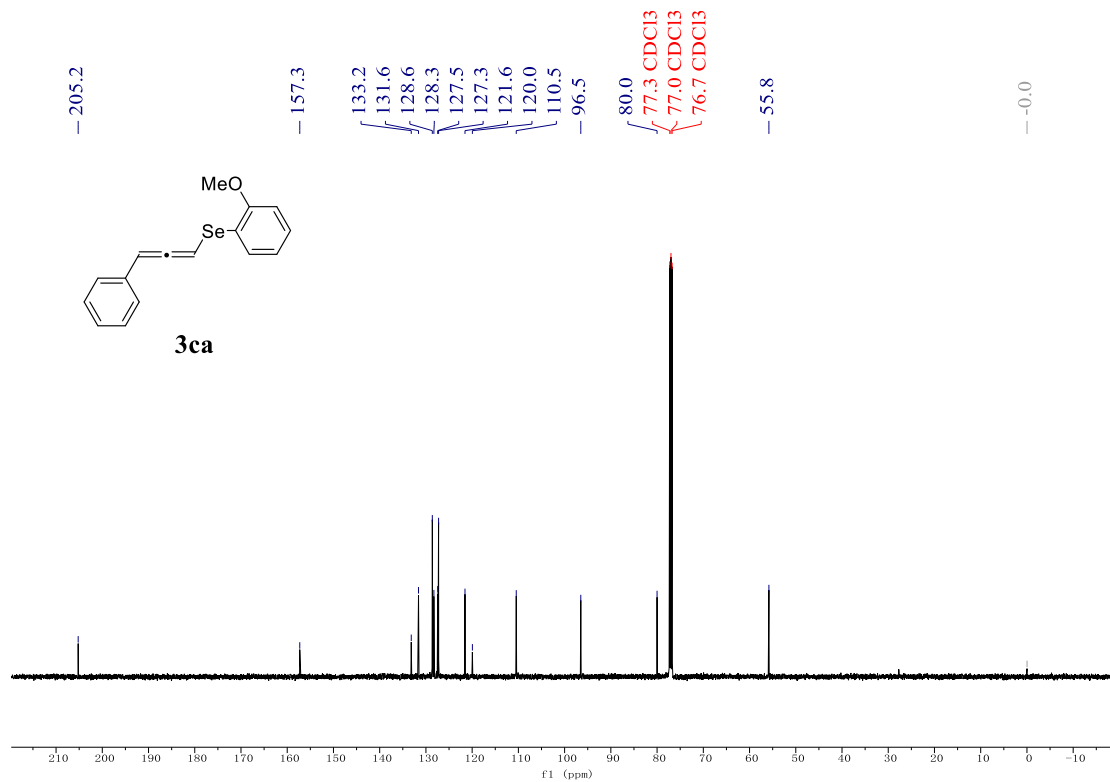
## 7. Copies of NMR Spectroscopic data

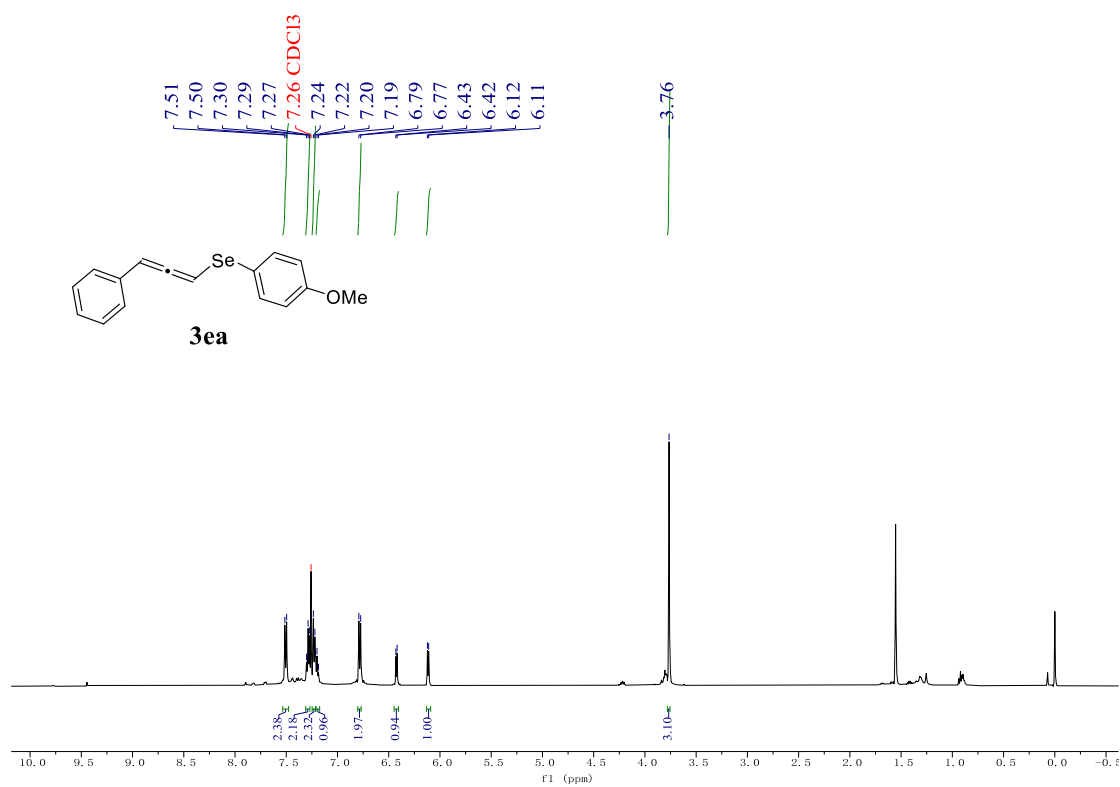
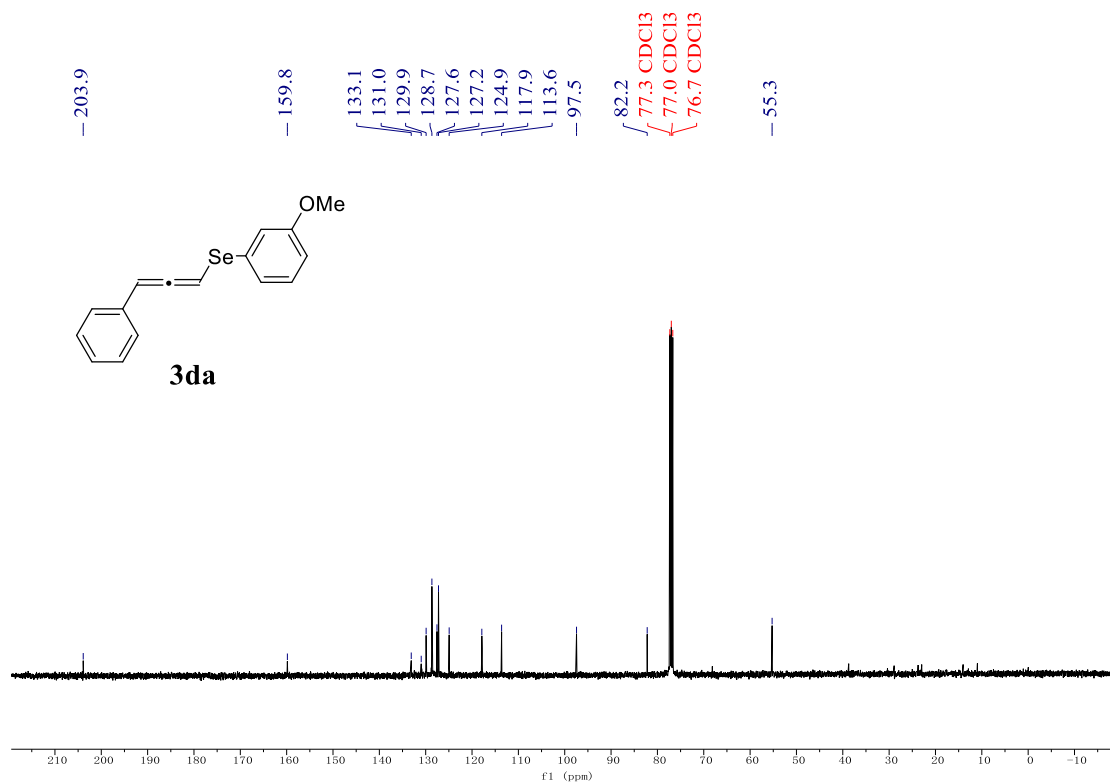


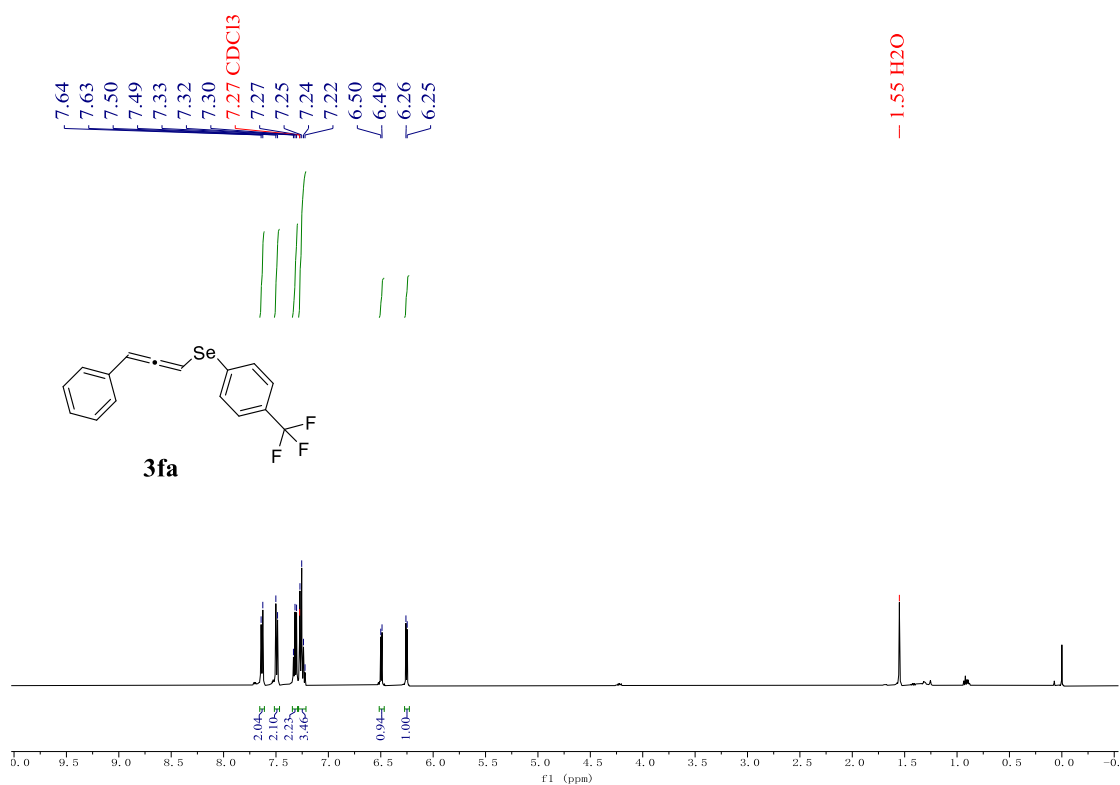
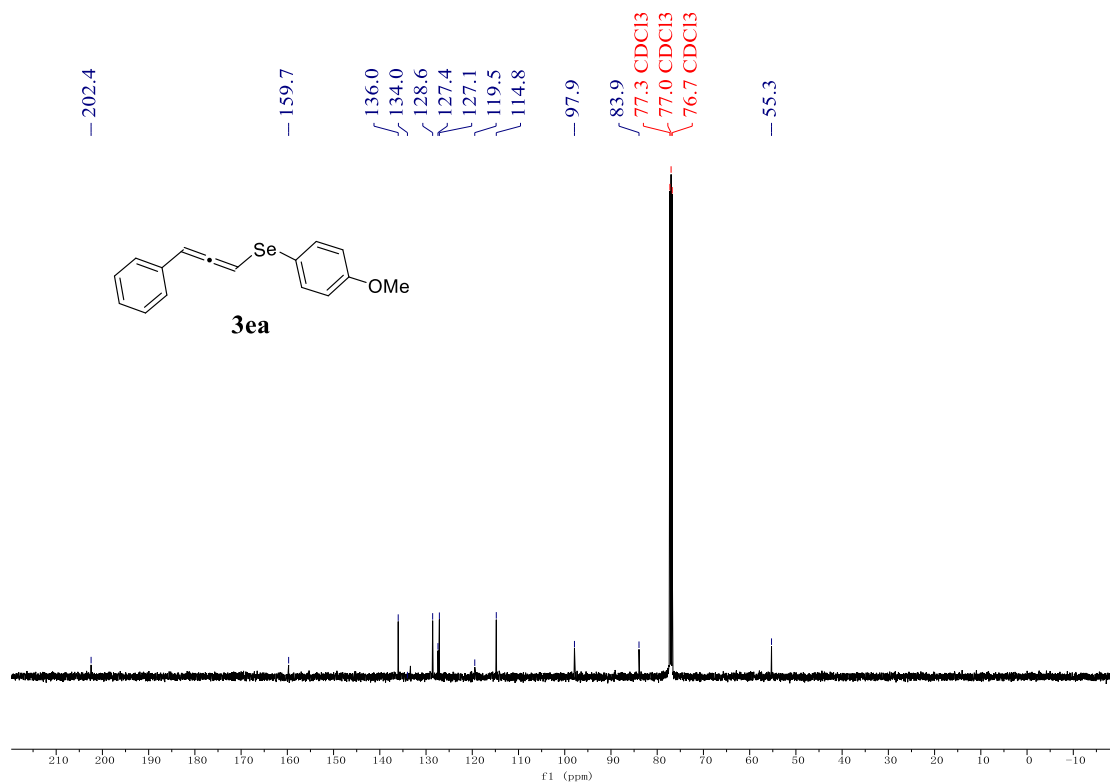


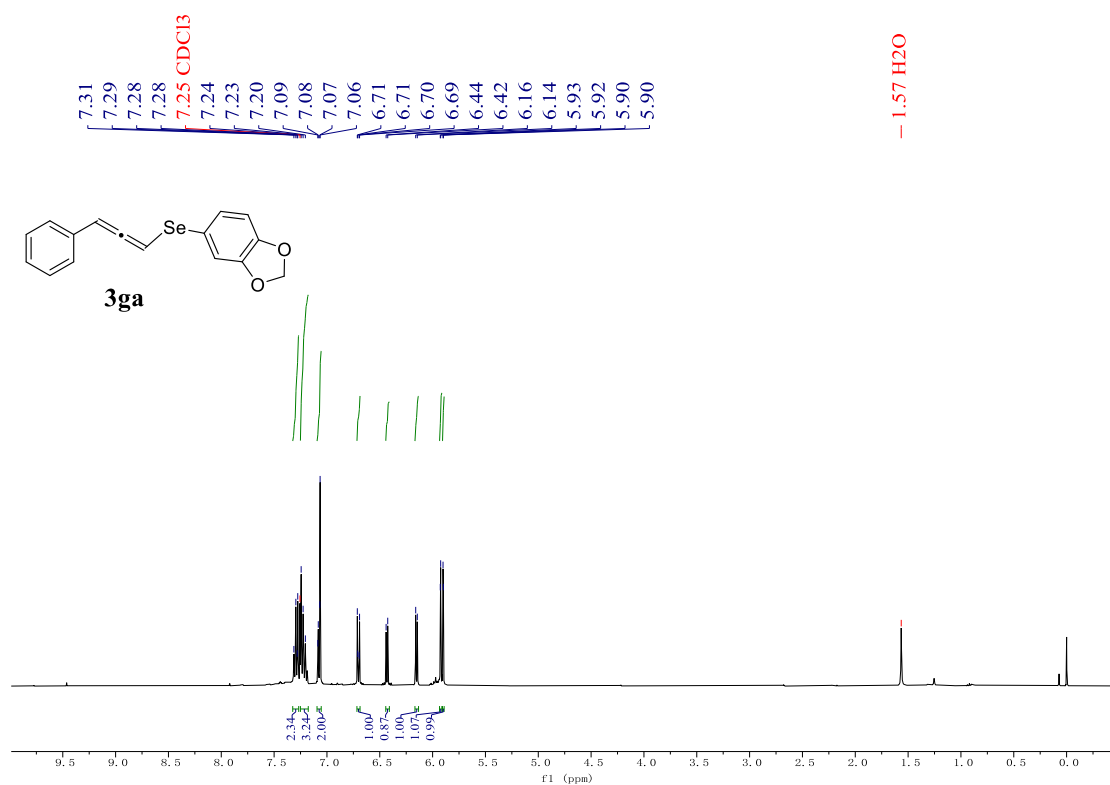
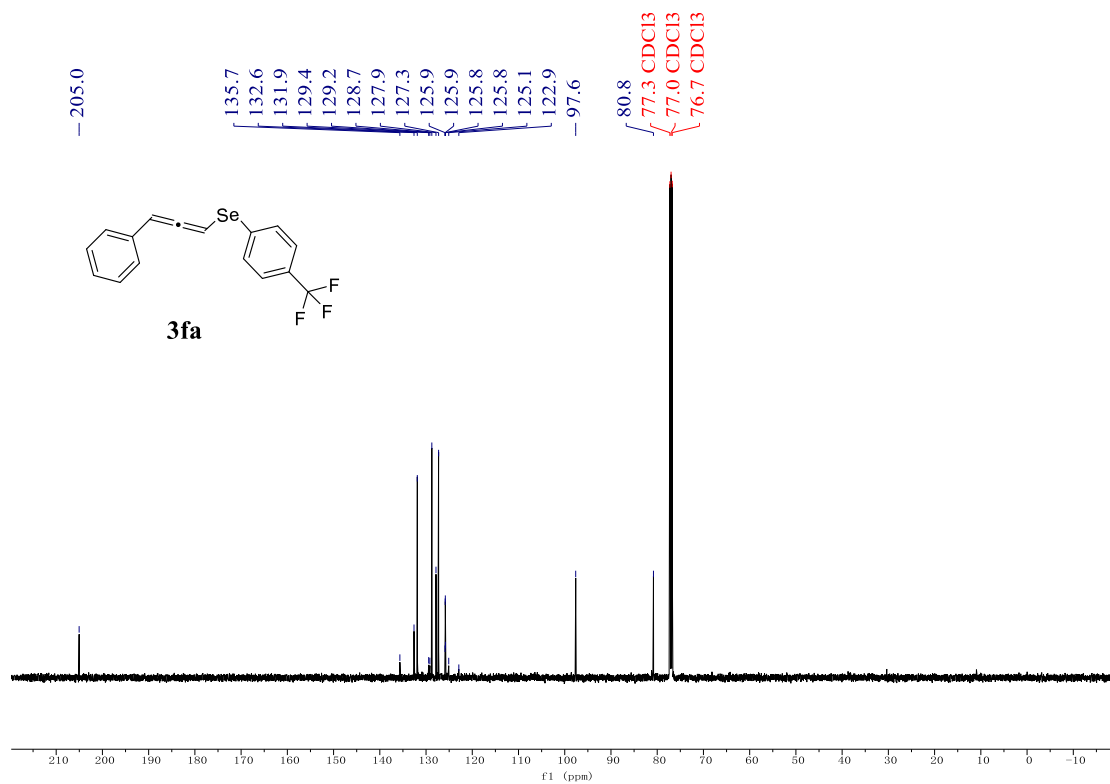


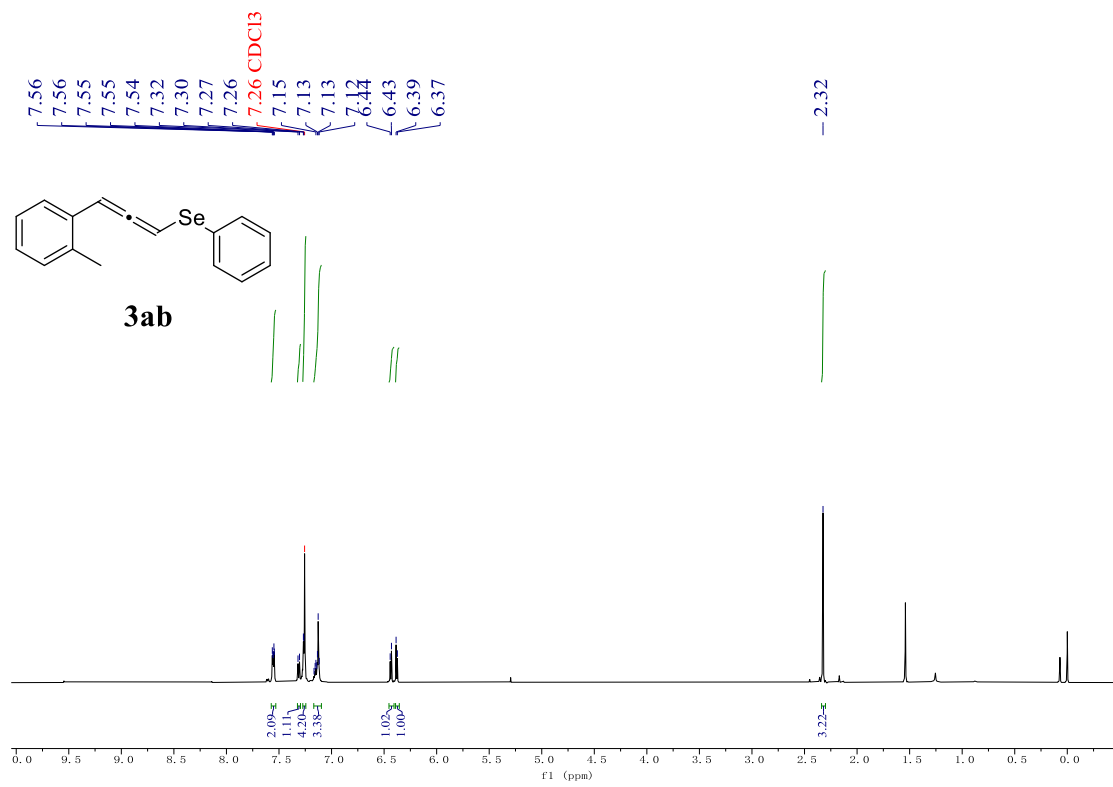
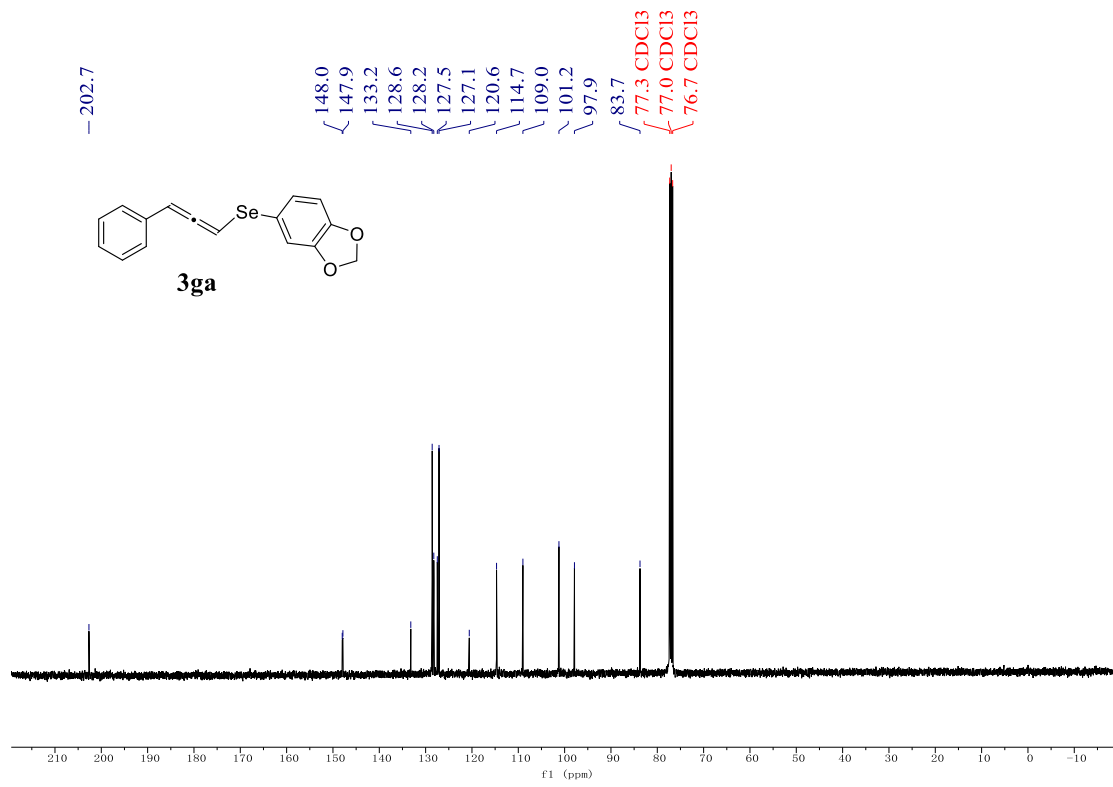


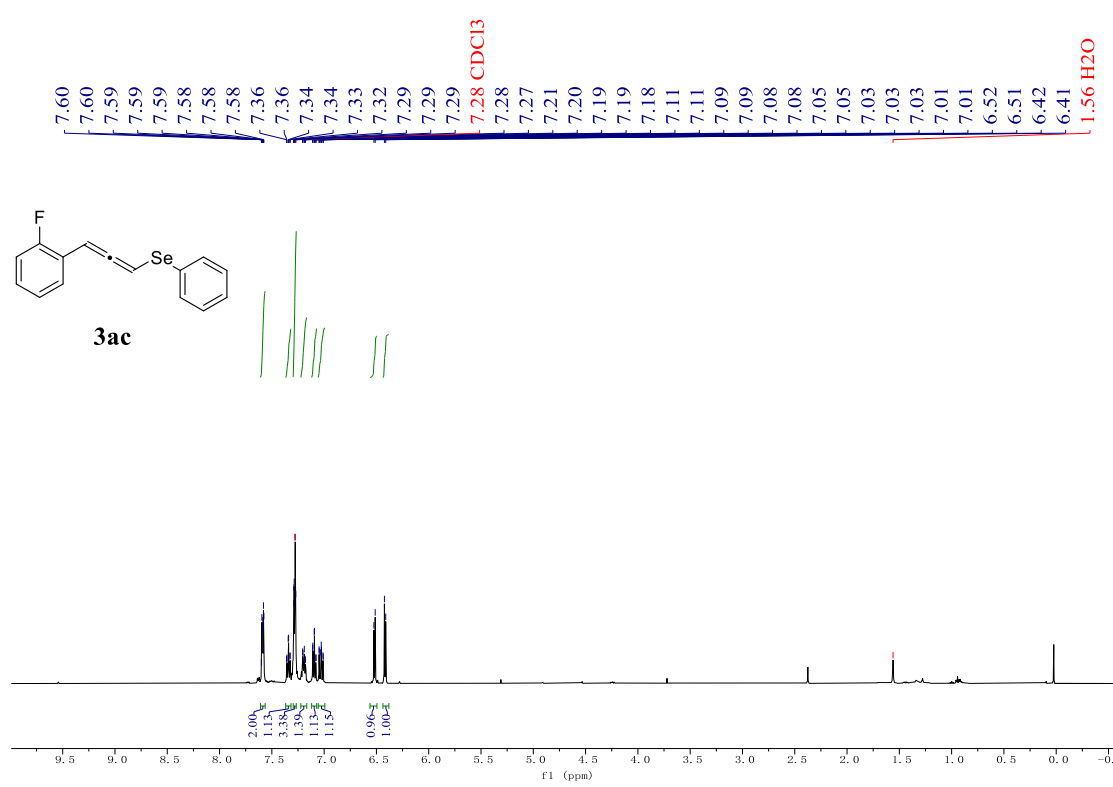
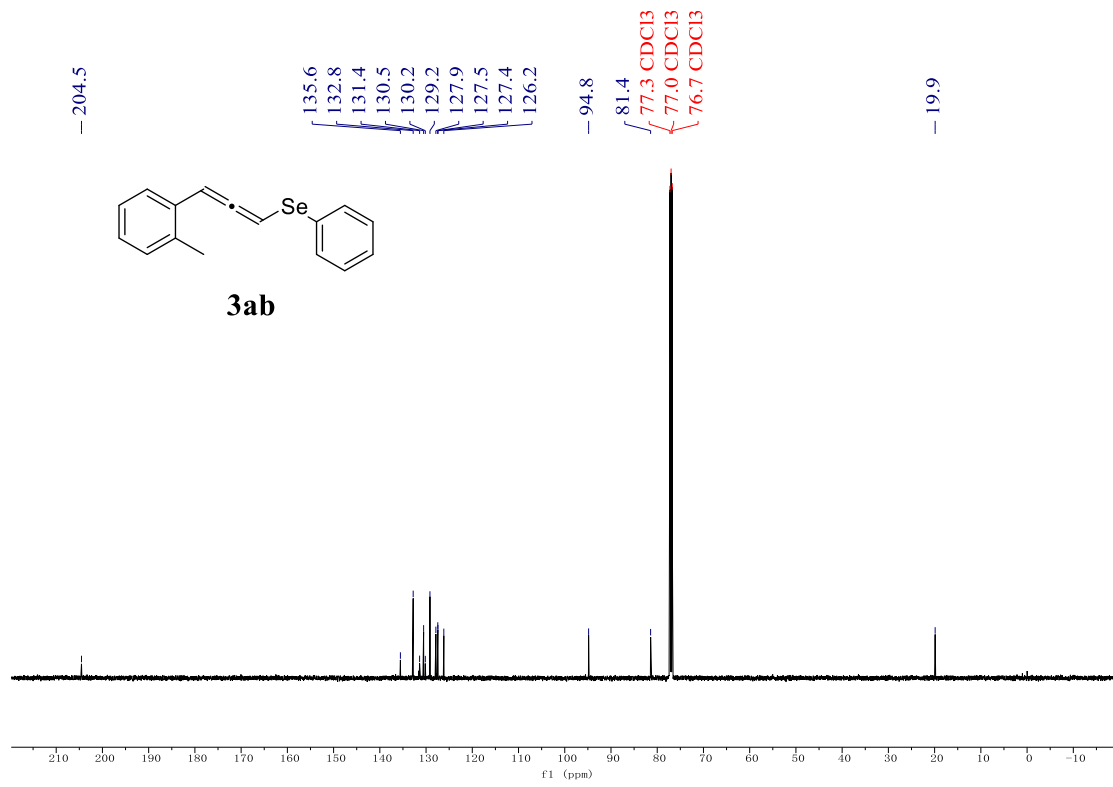


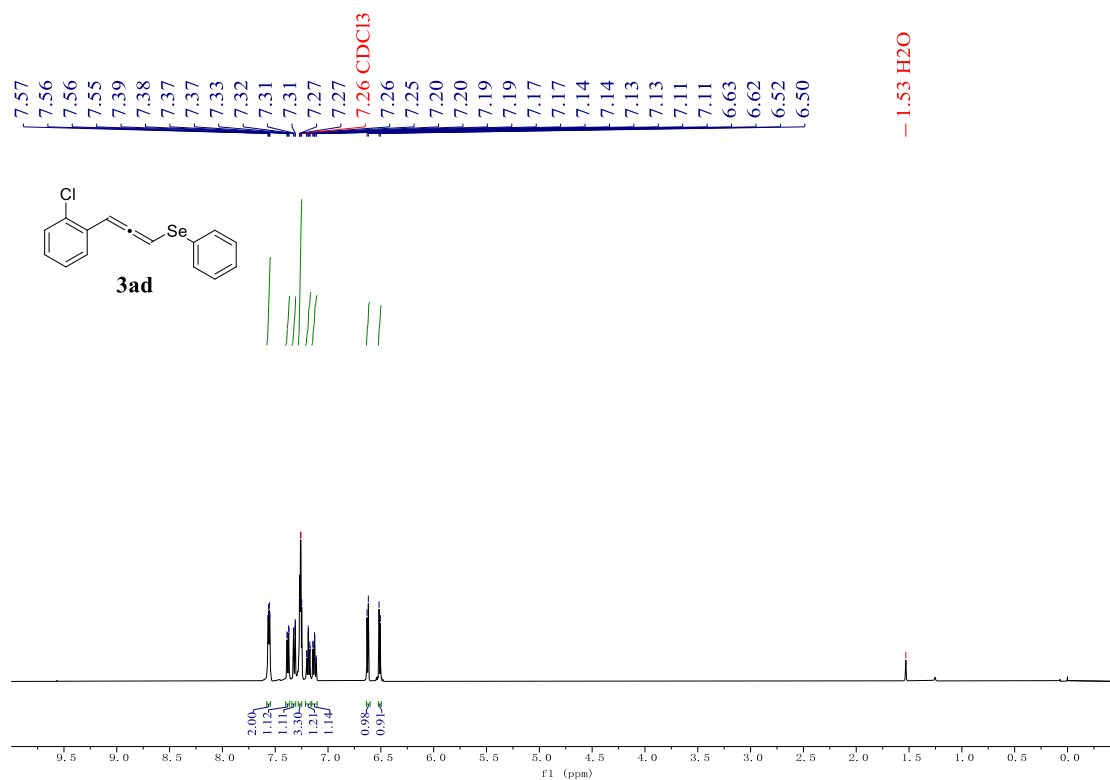
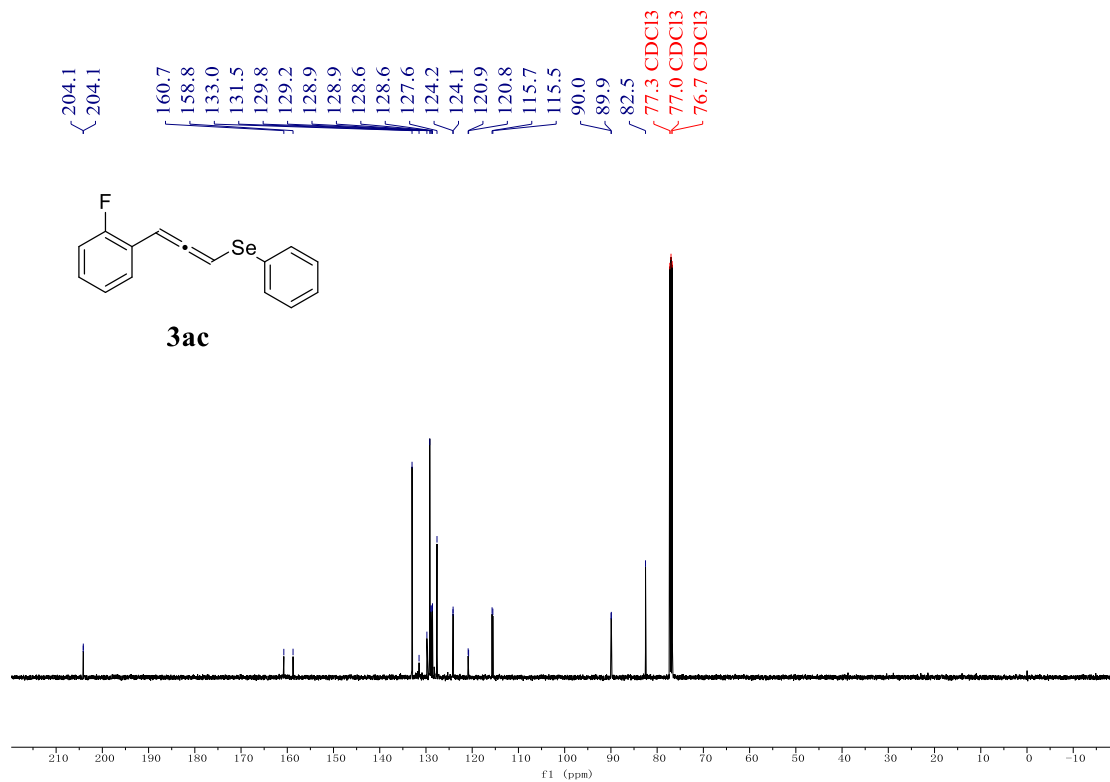


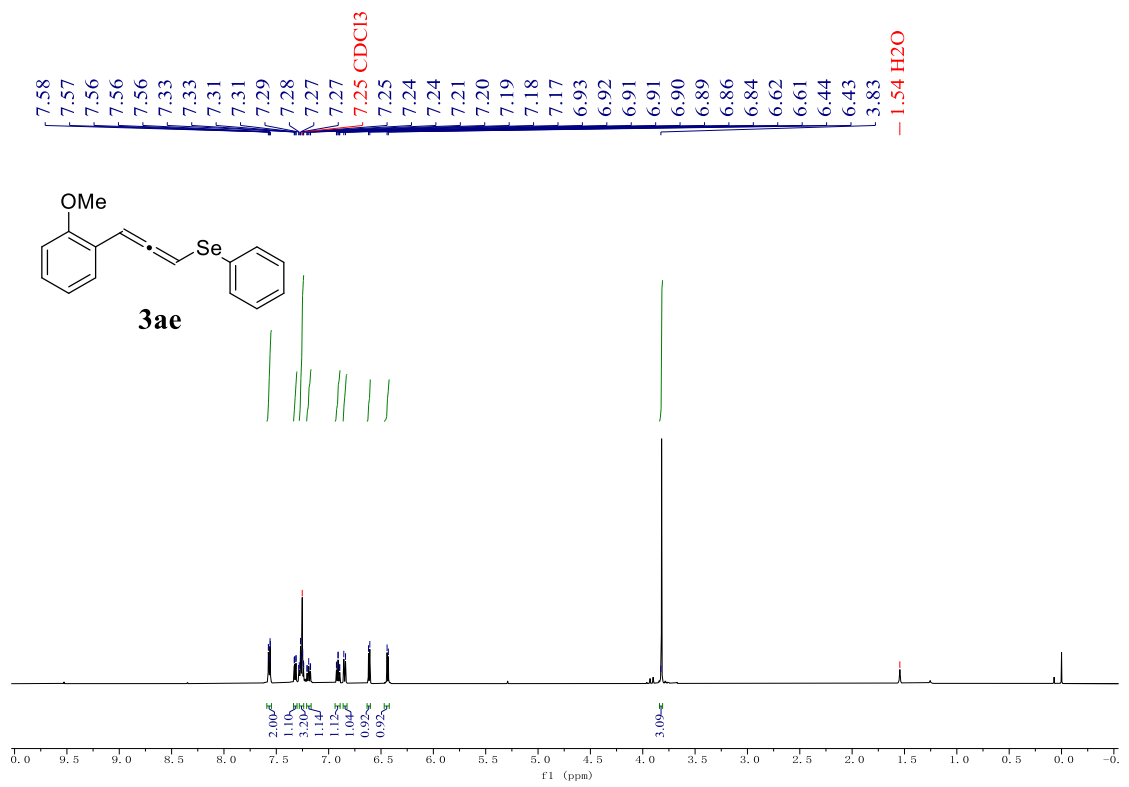
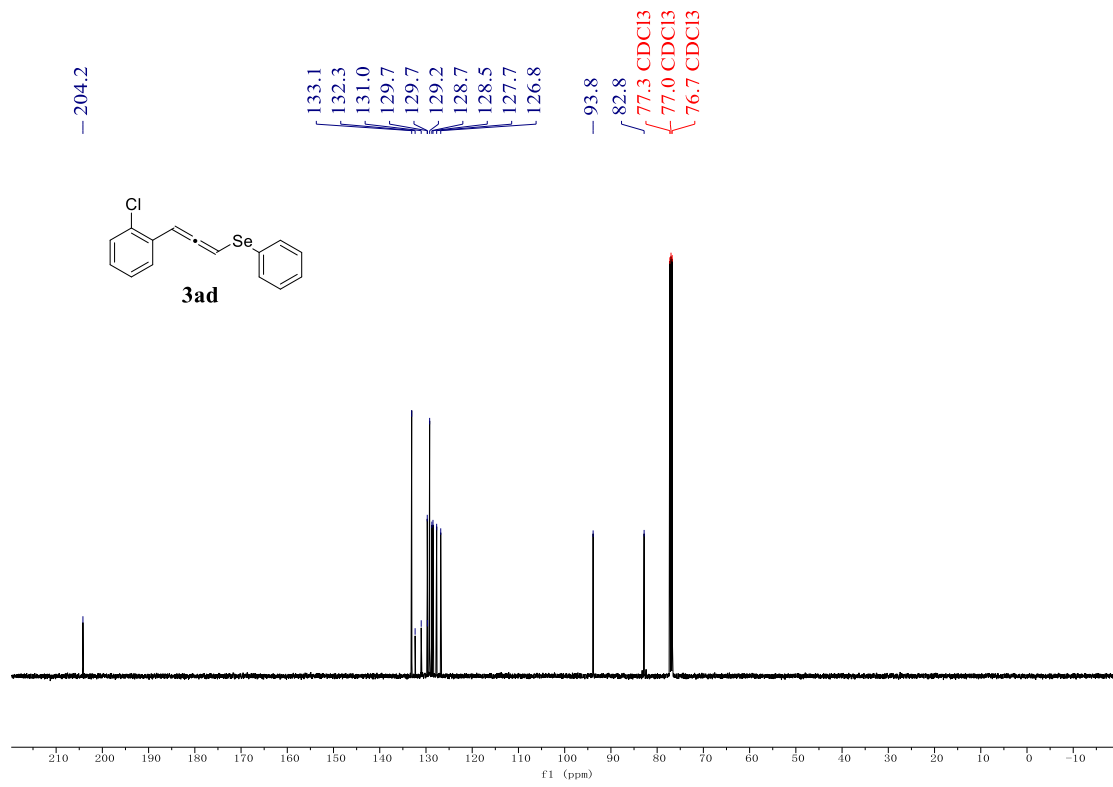




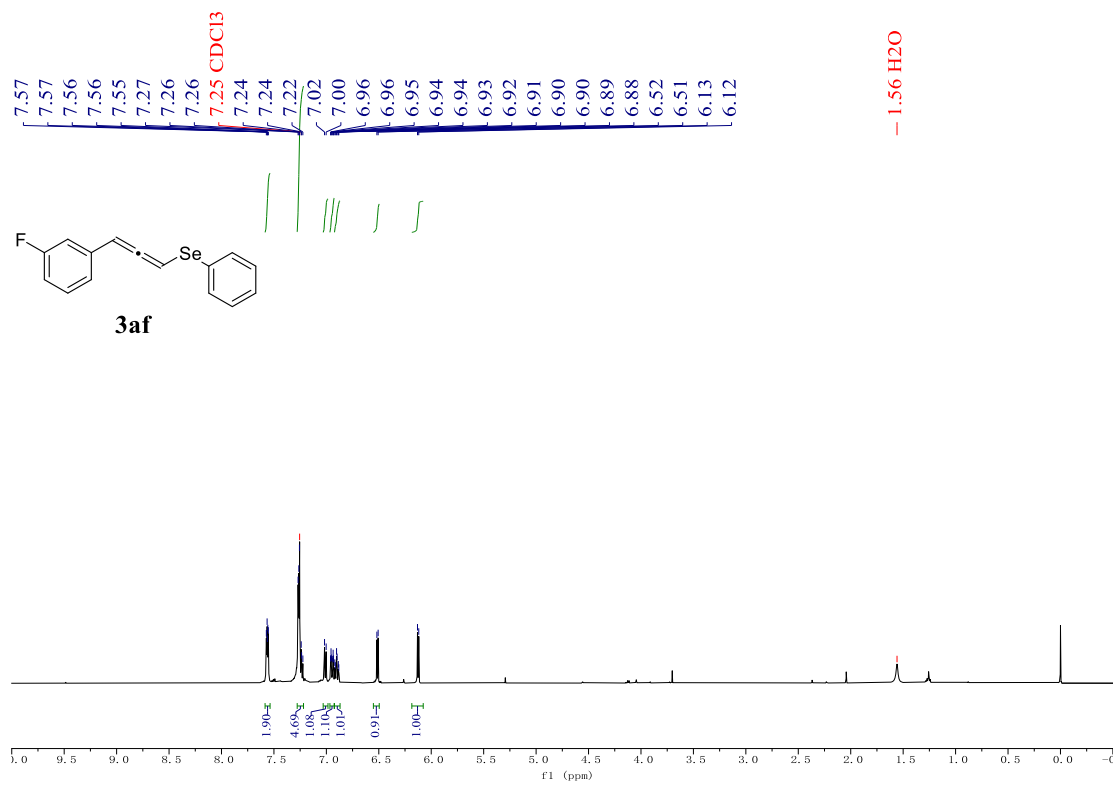
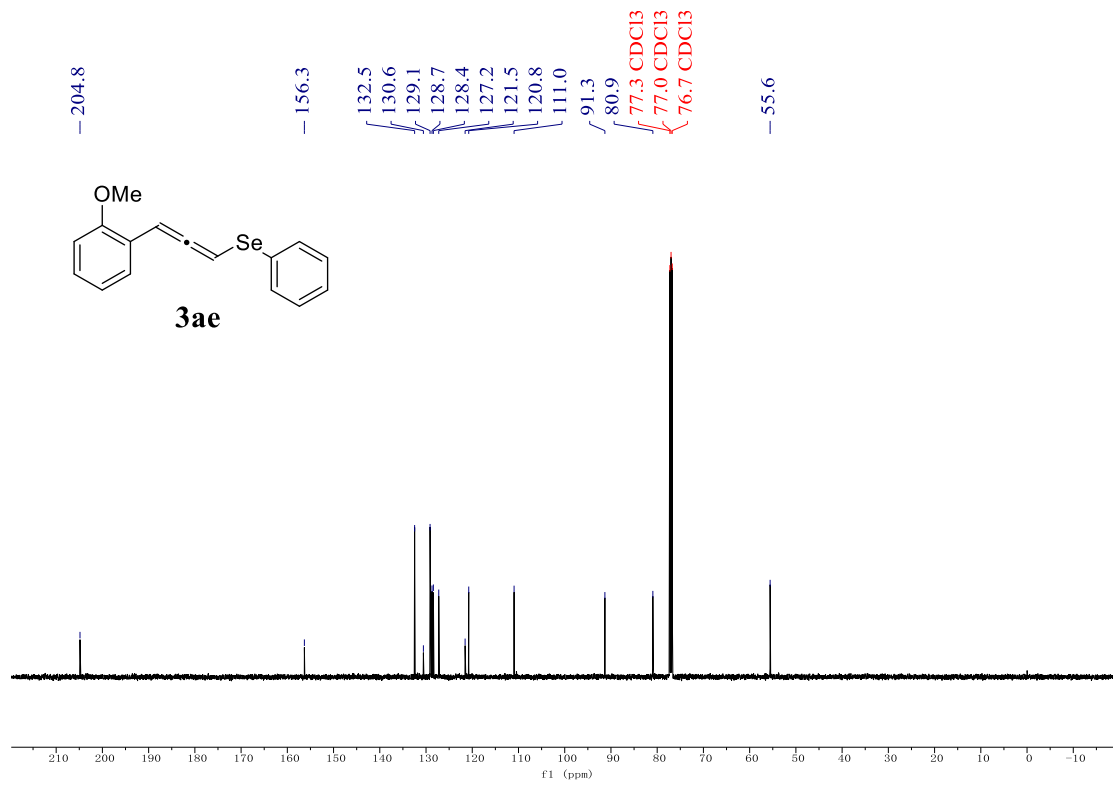


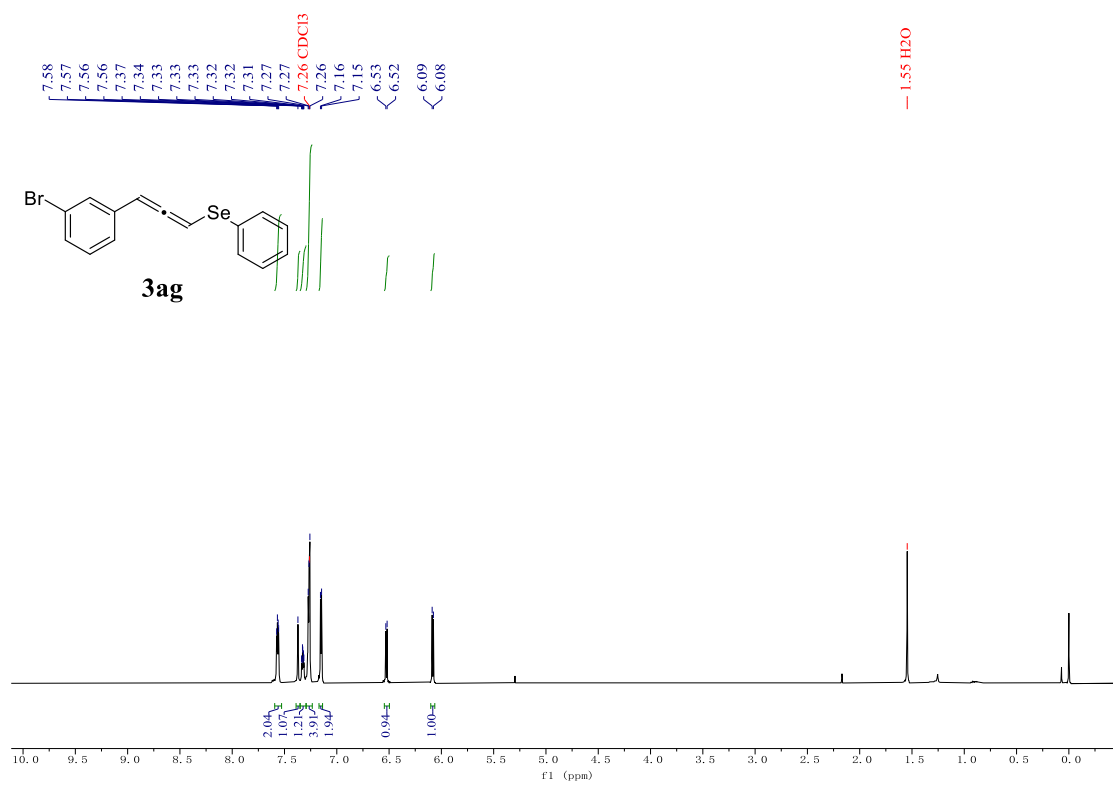
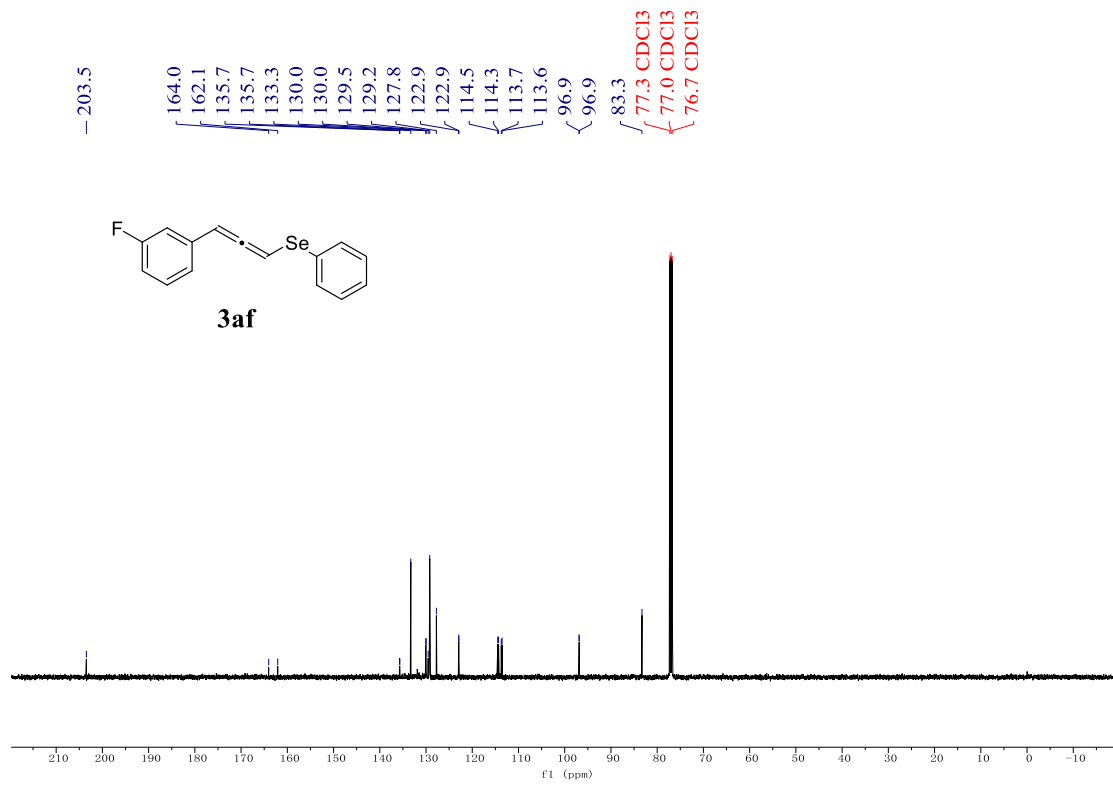


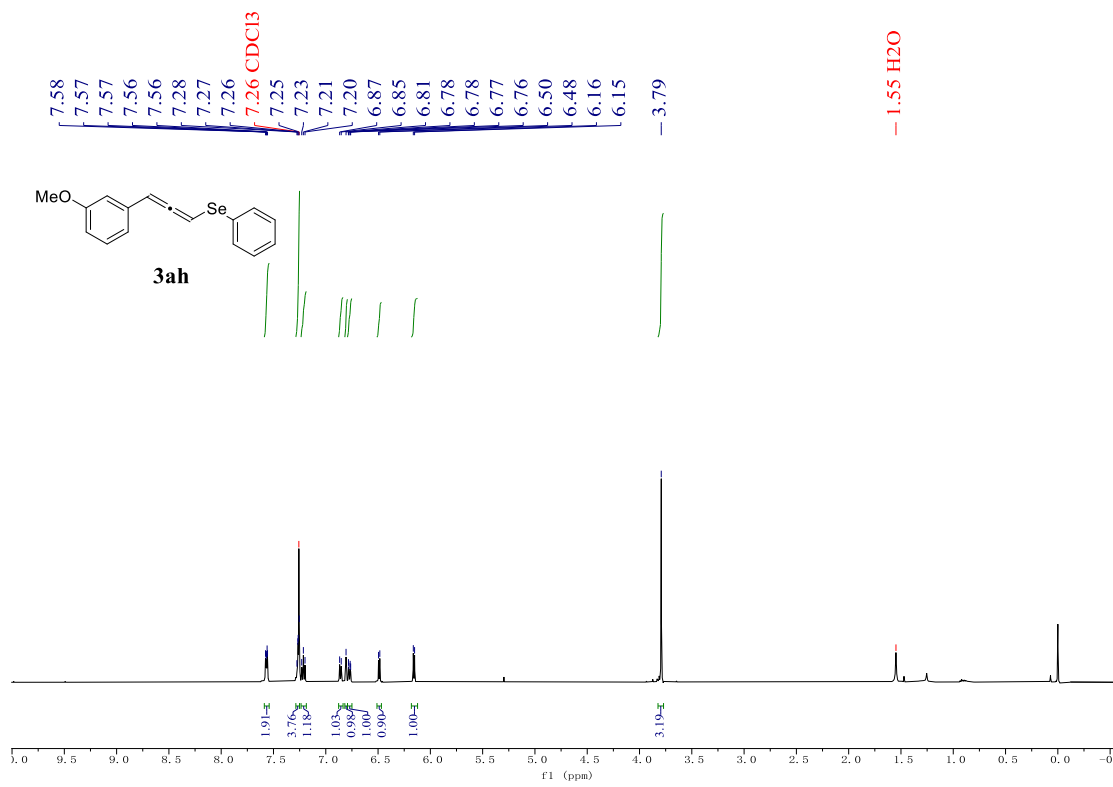
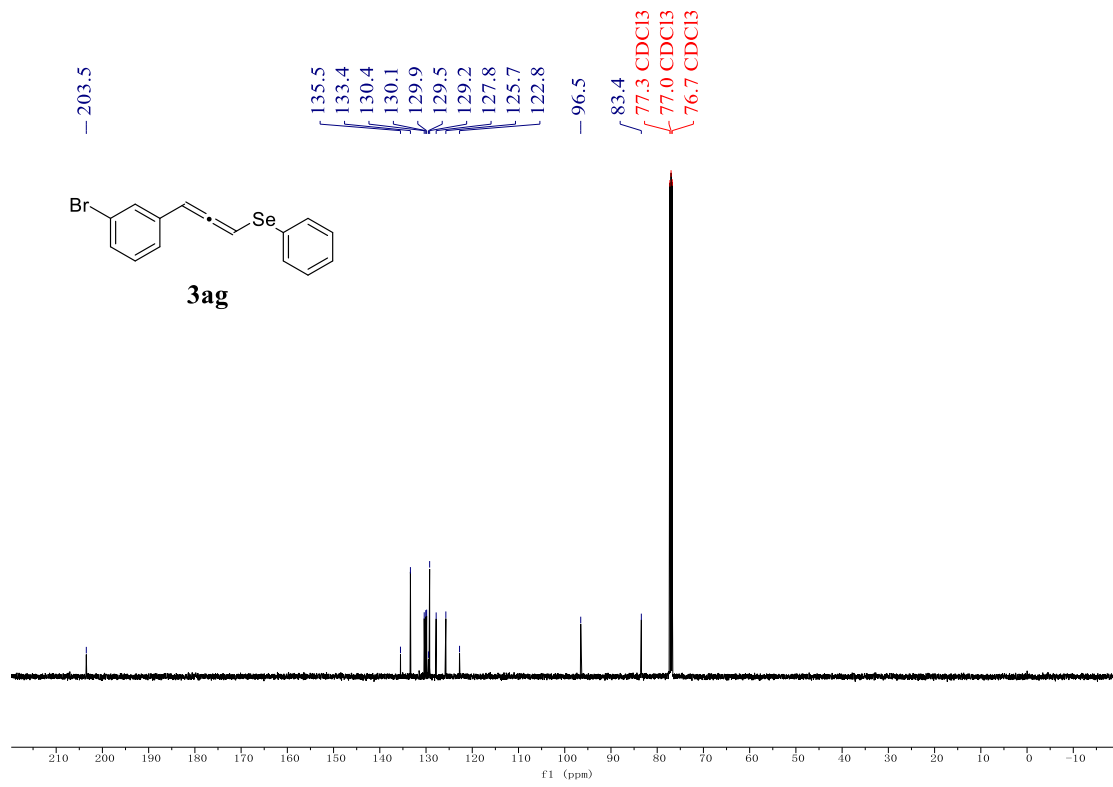


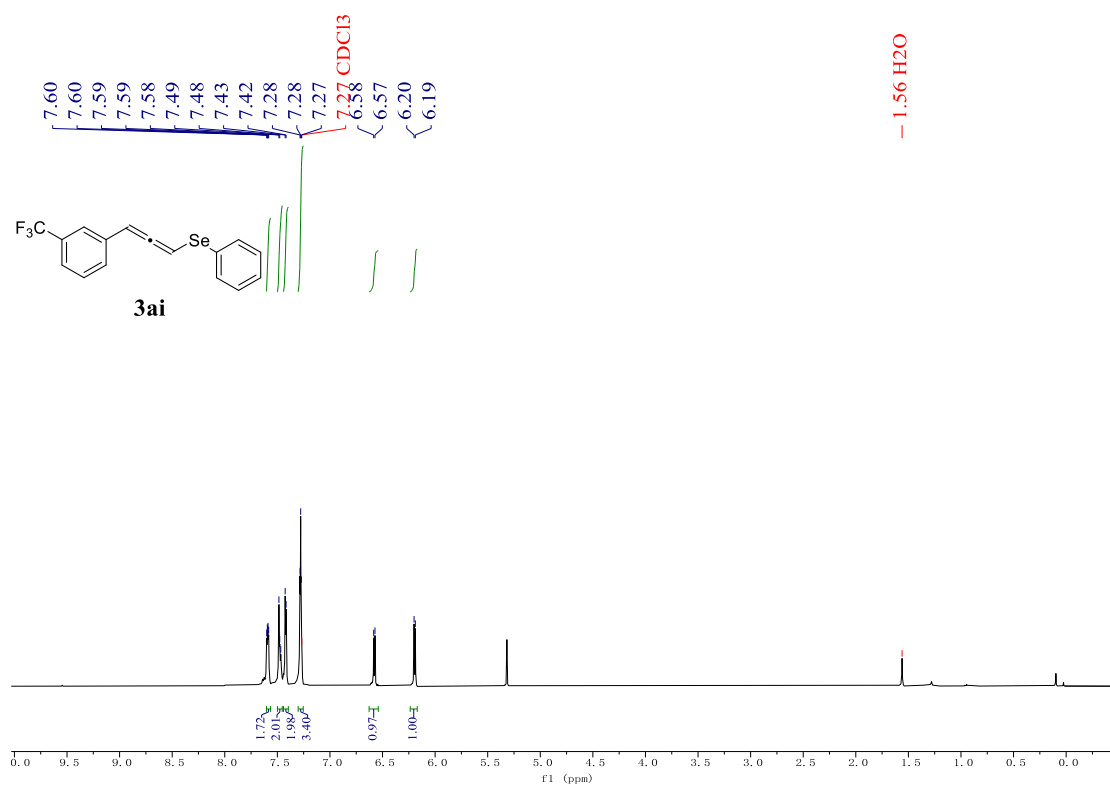
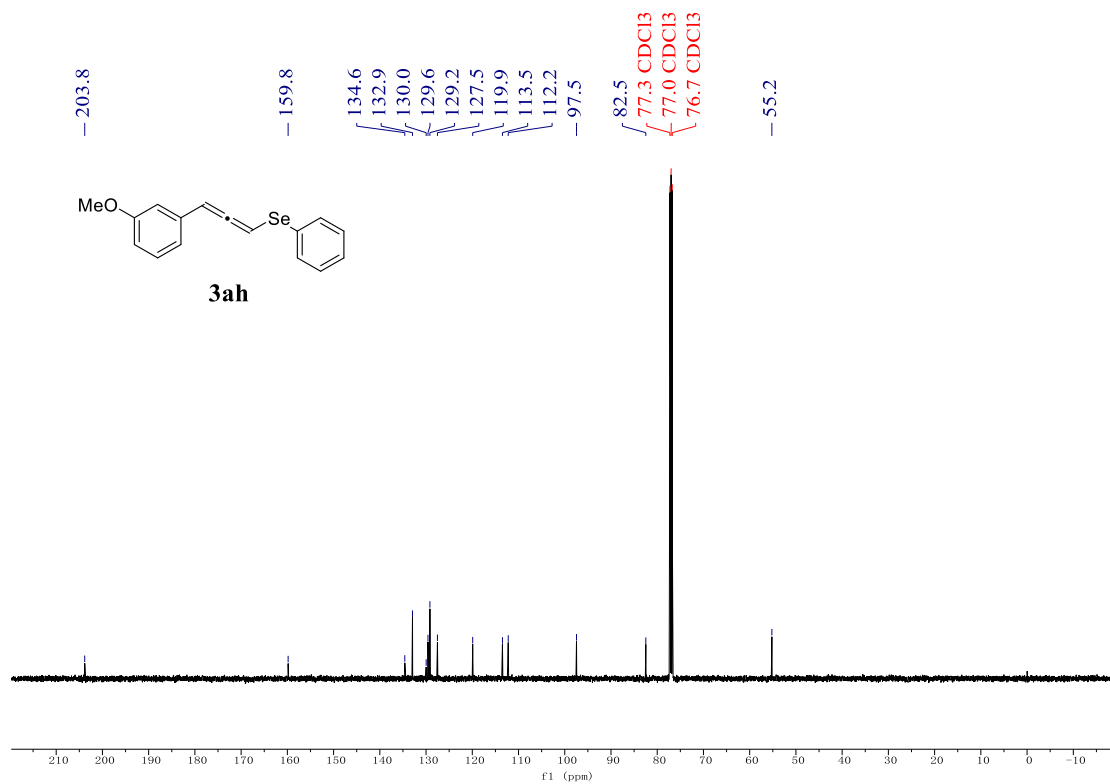


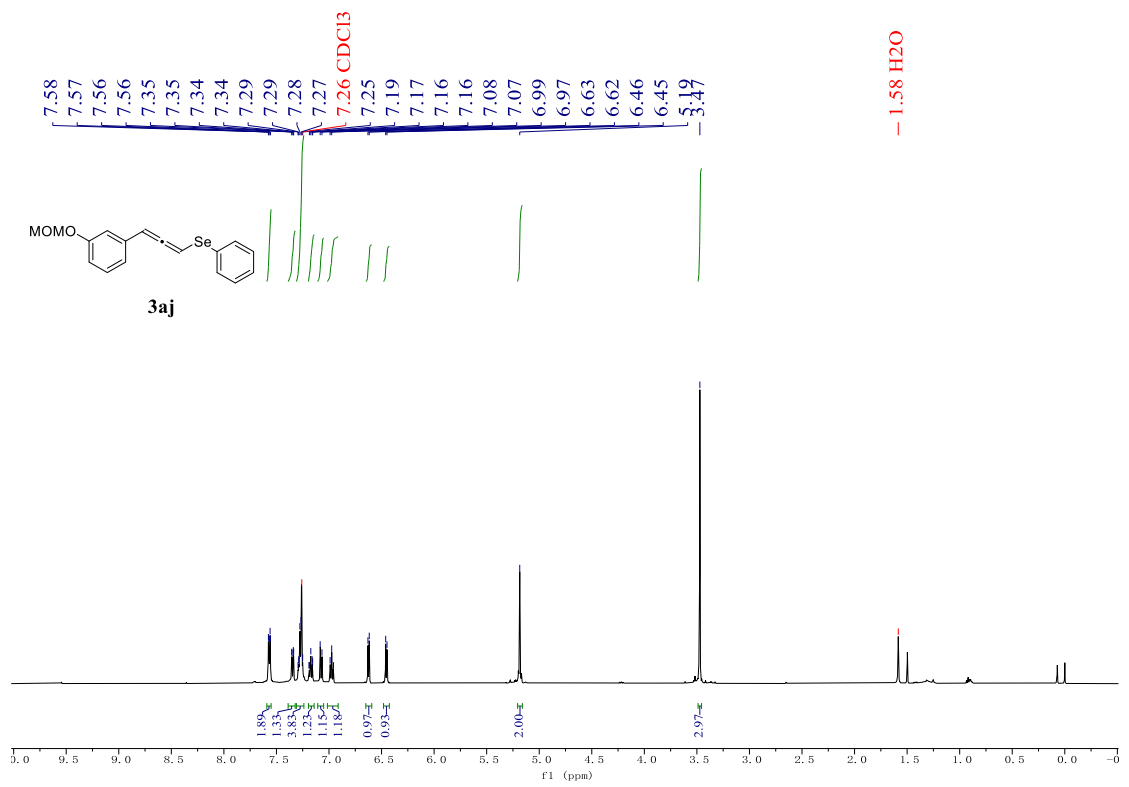
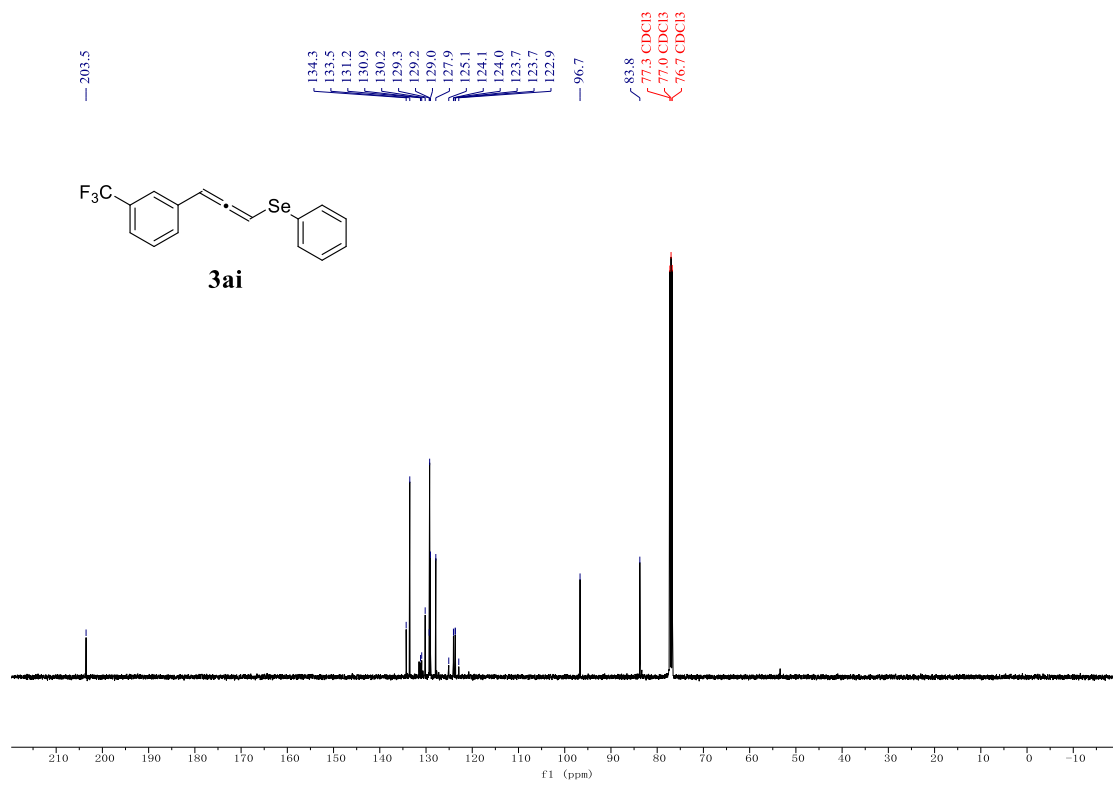


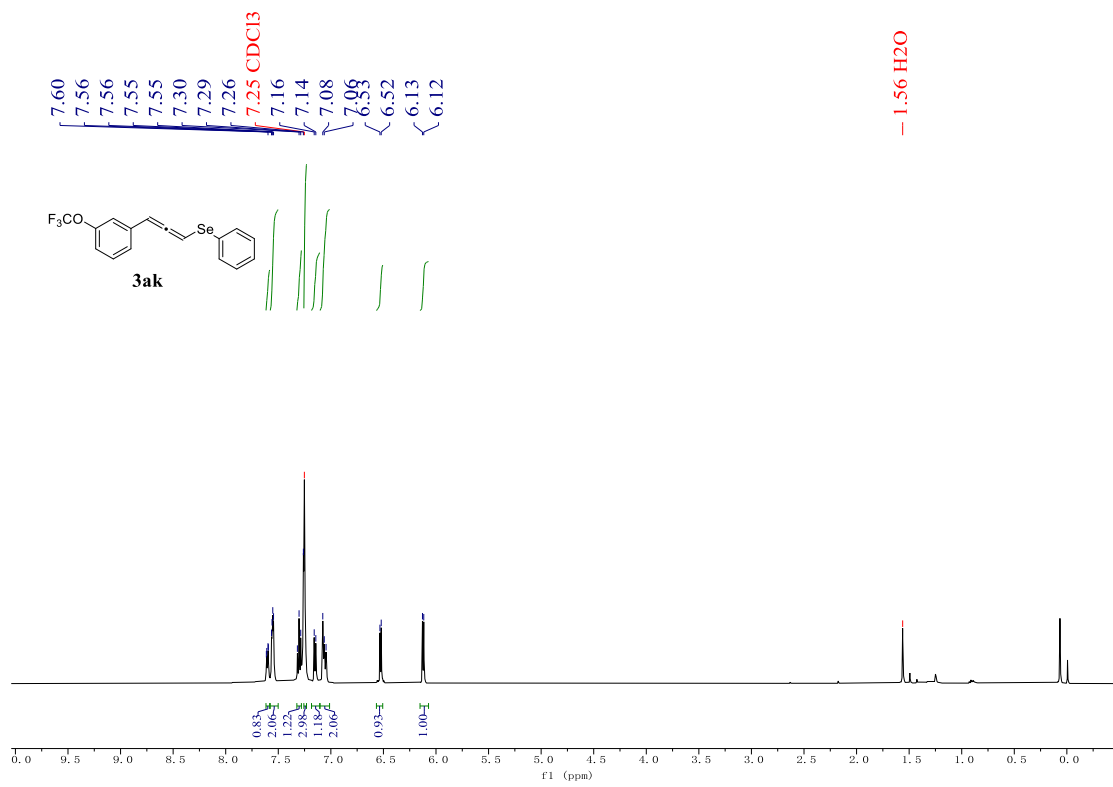
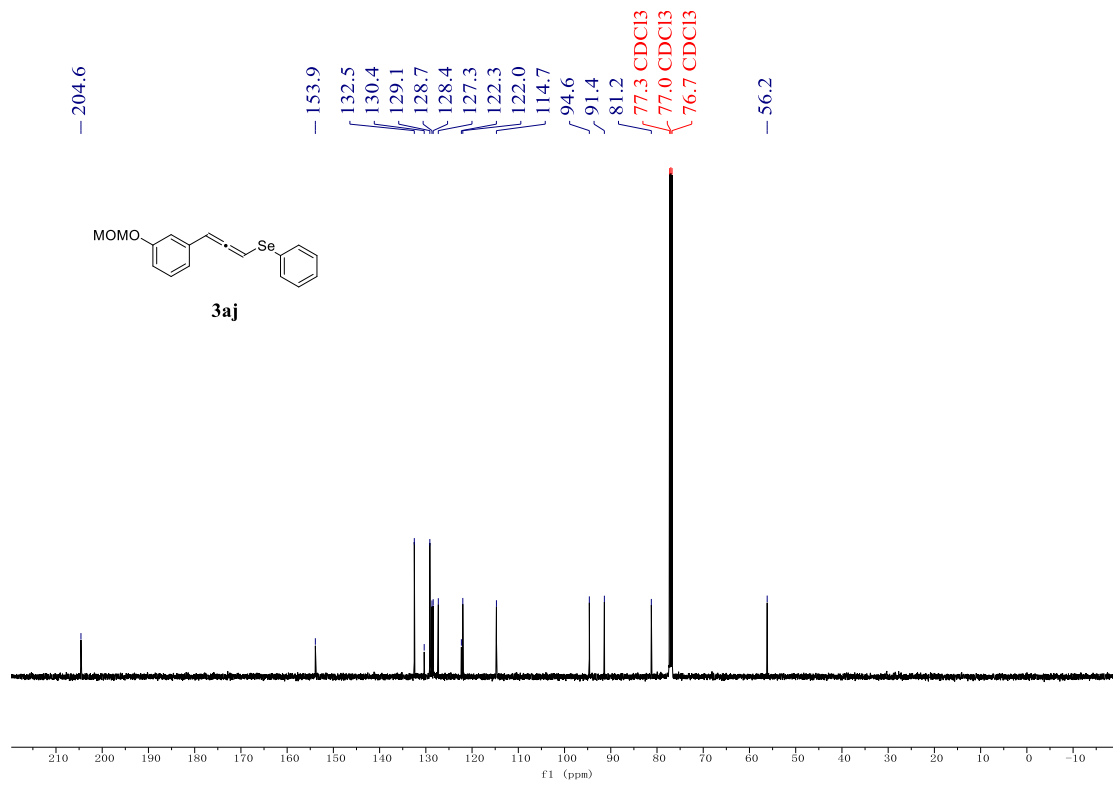


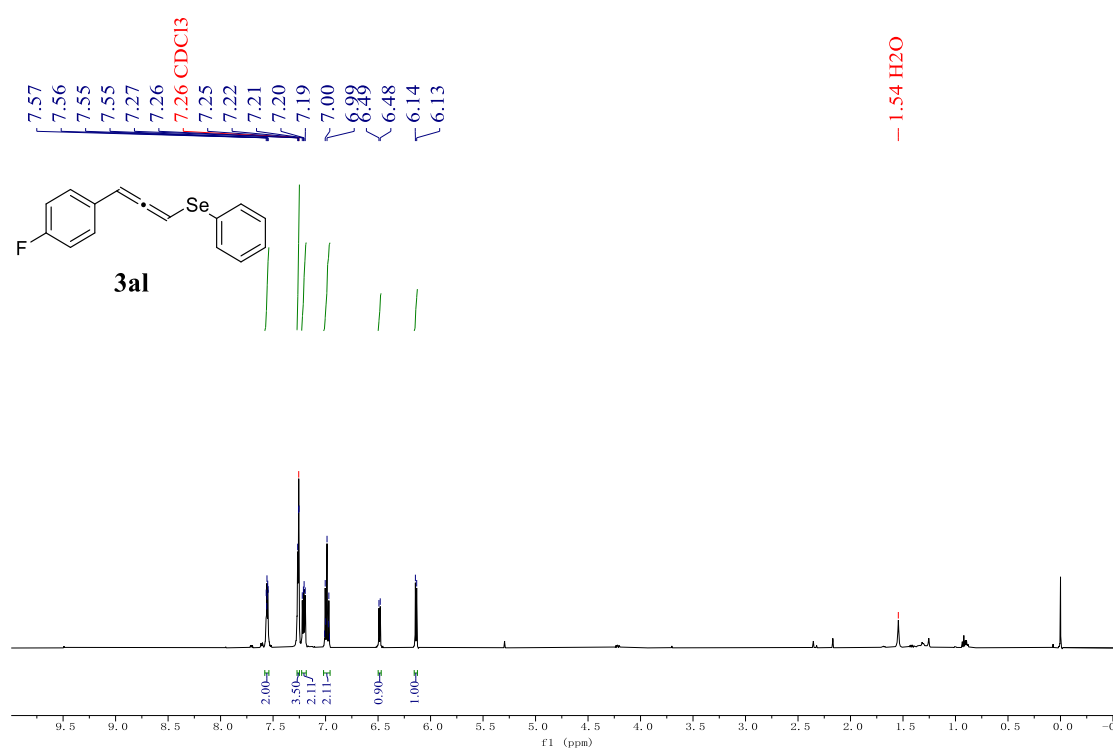
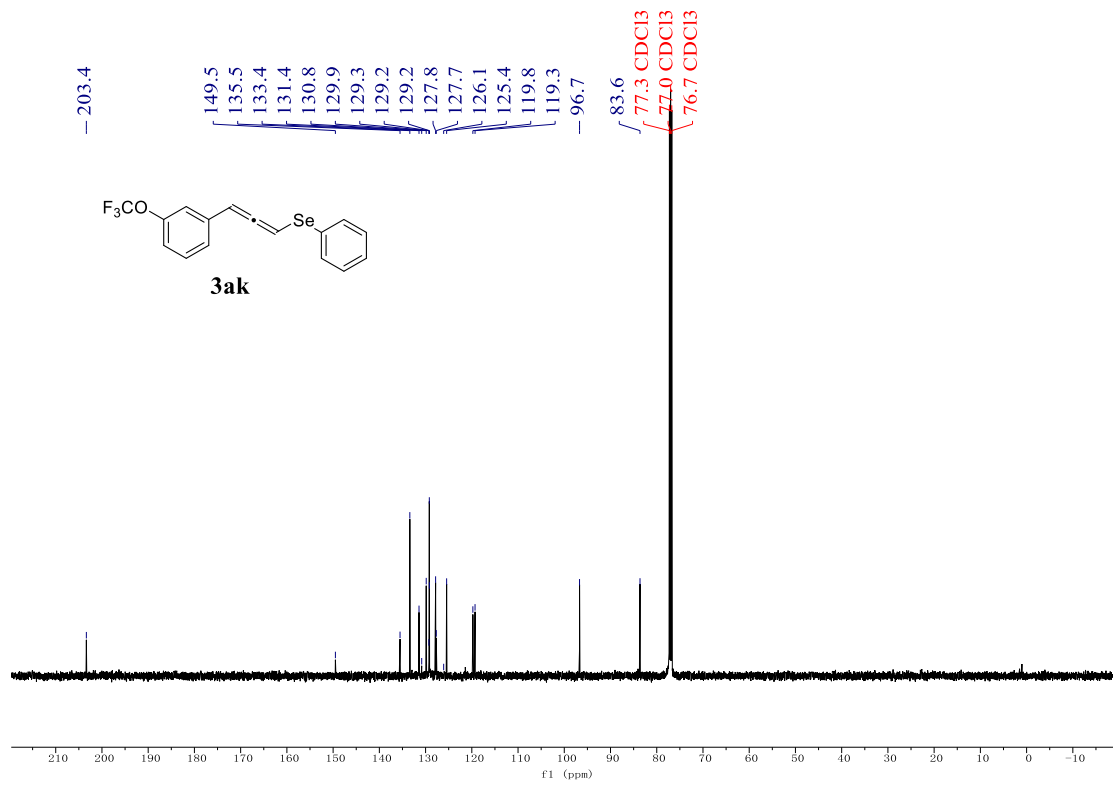


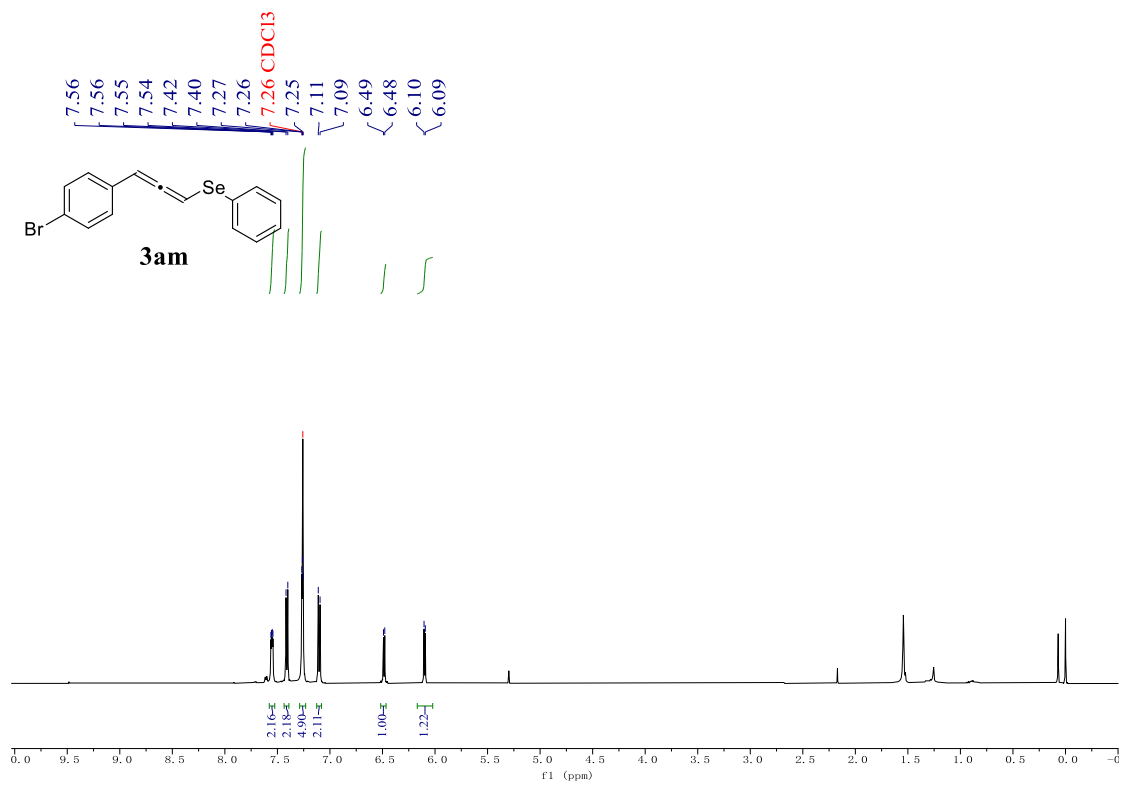
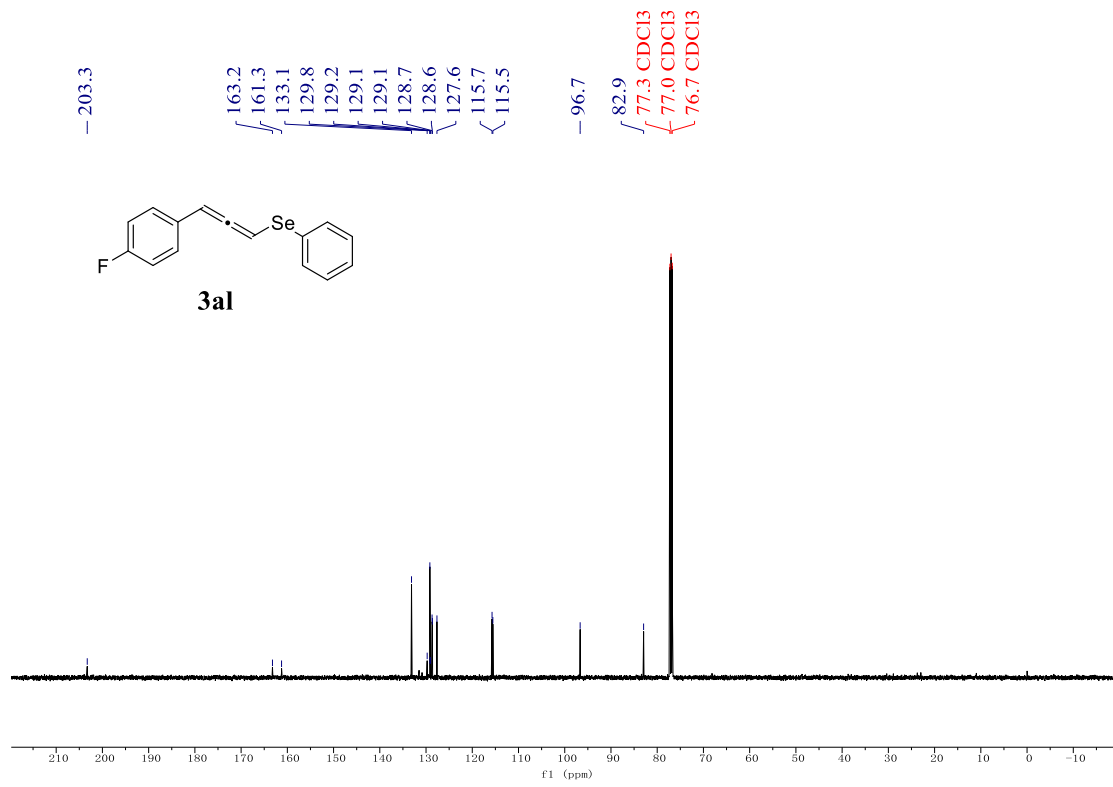




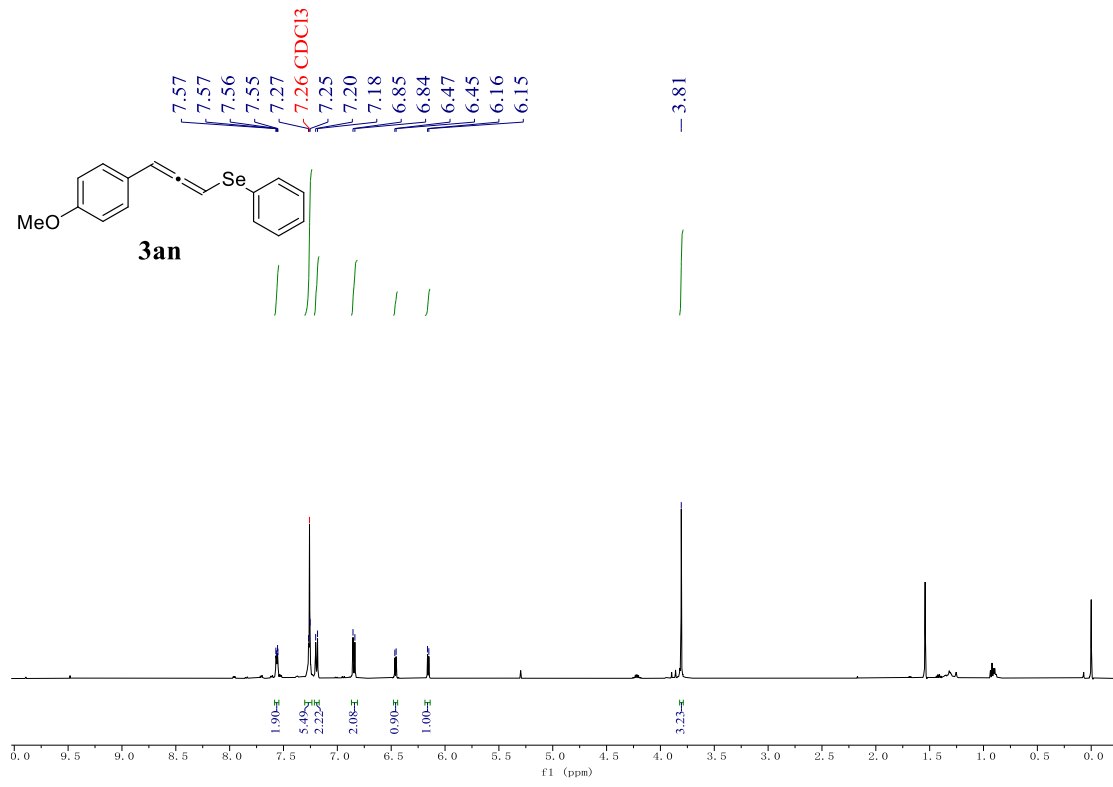
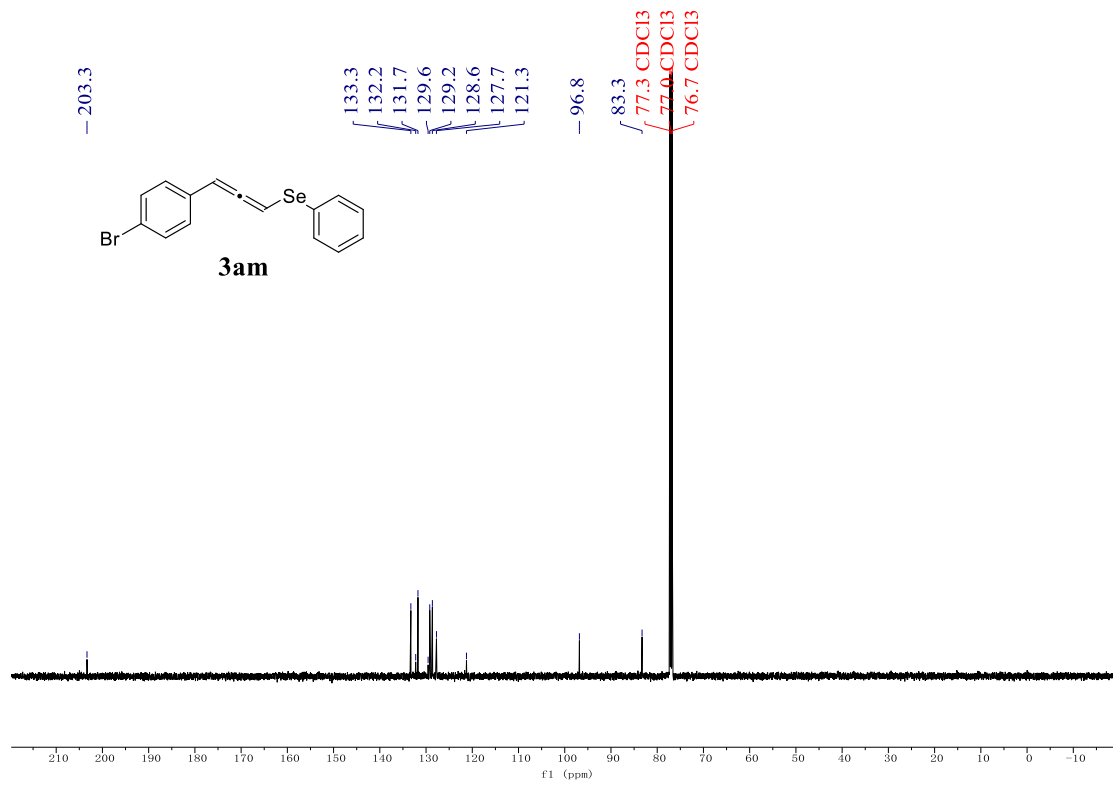


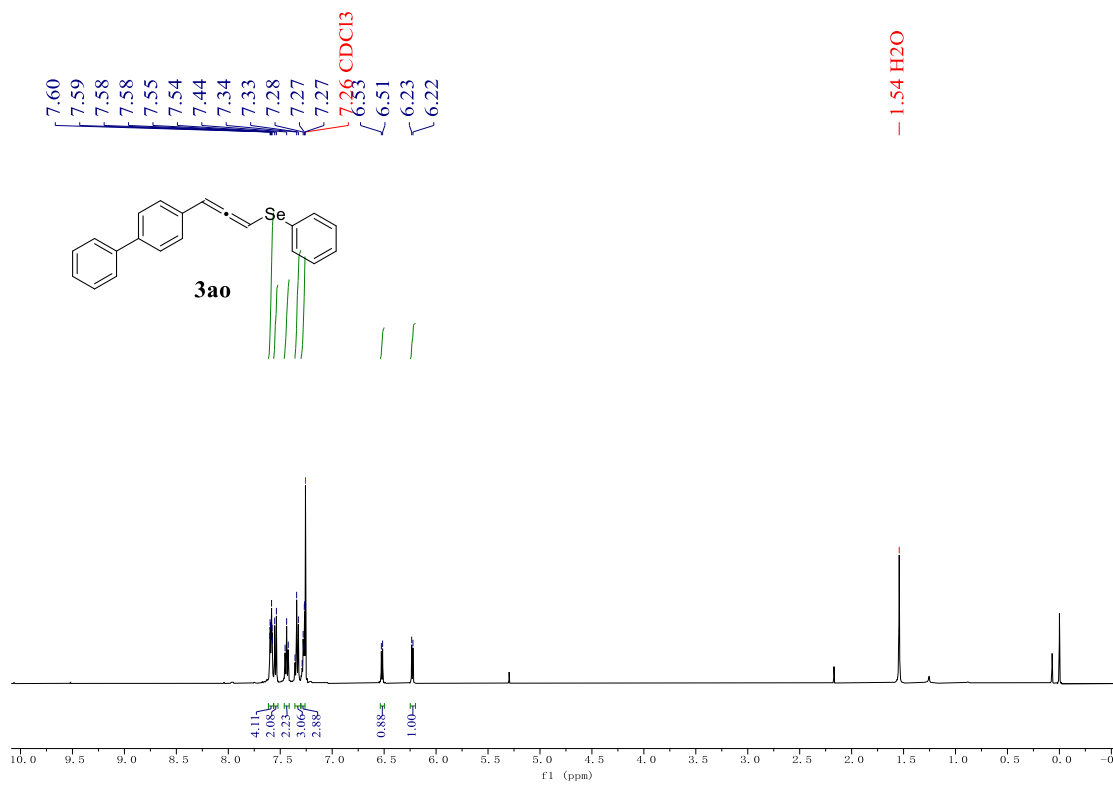
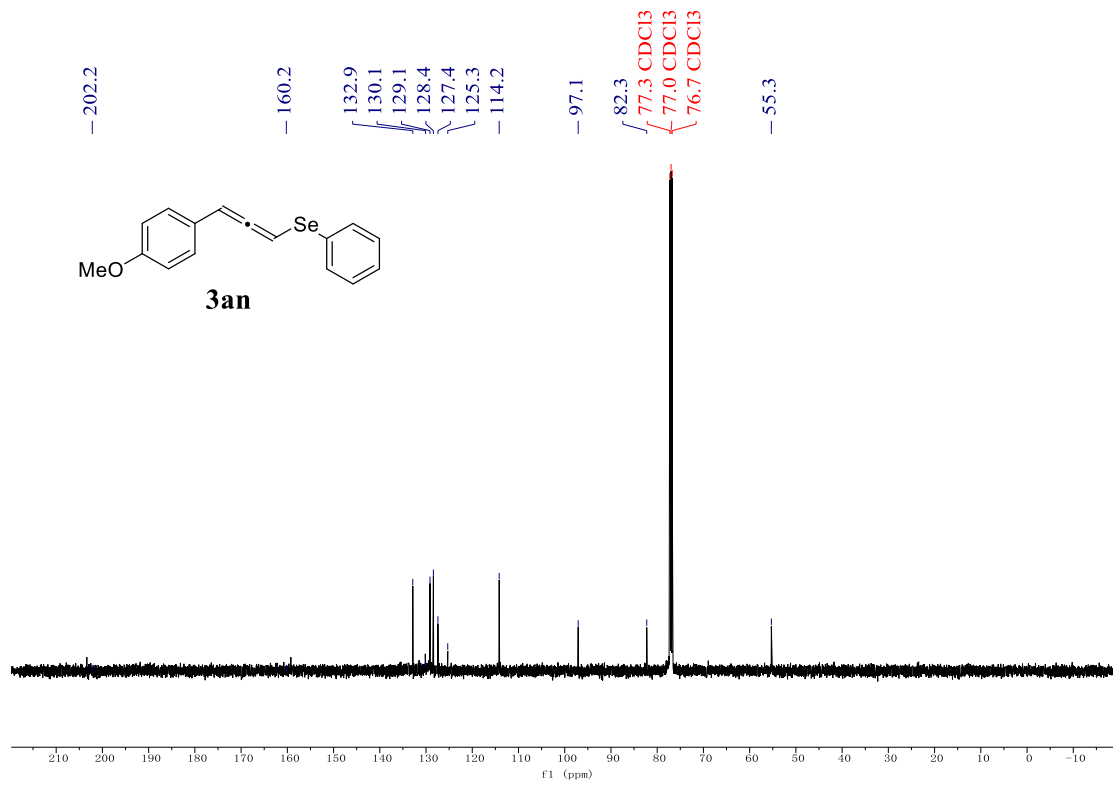


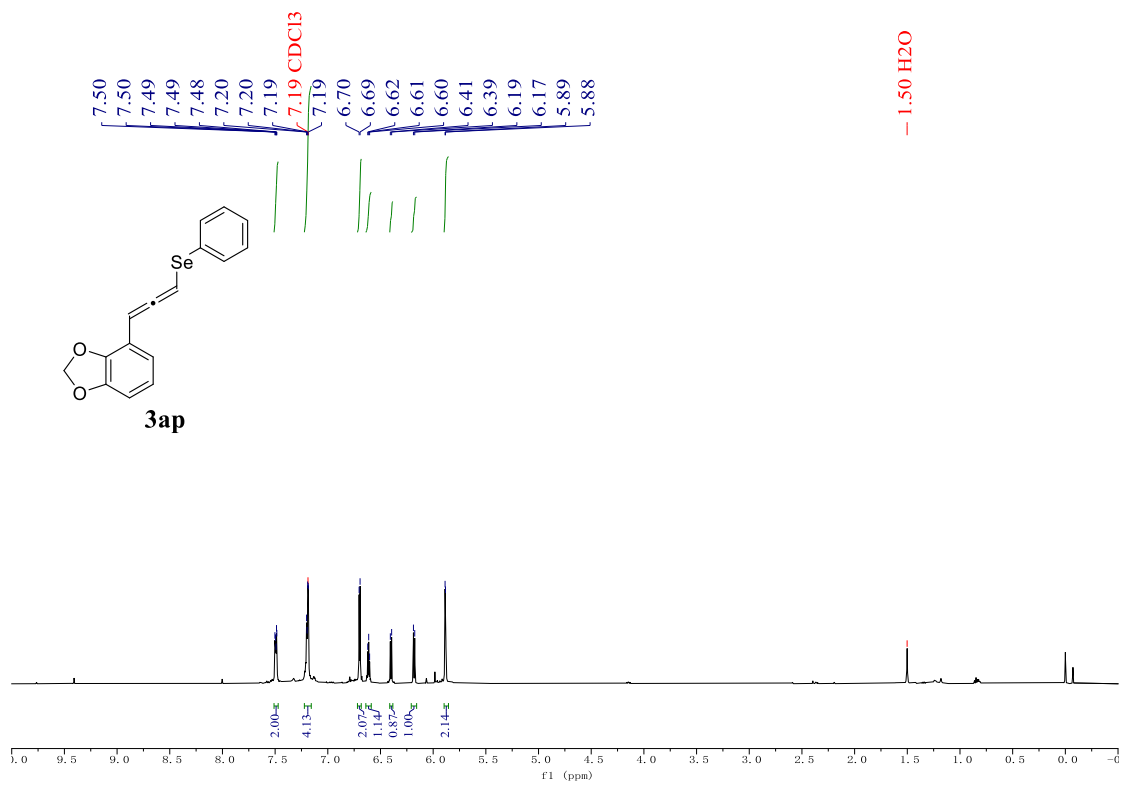
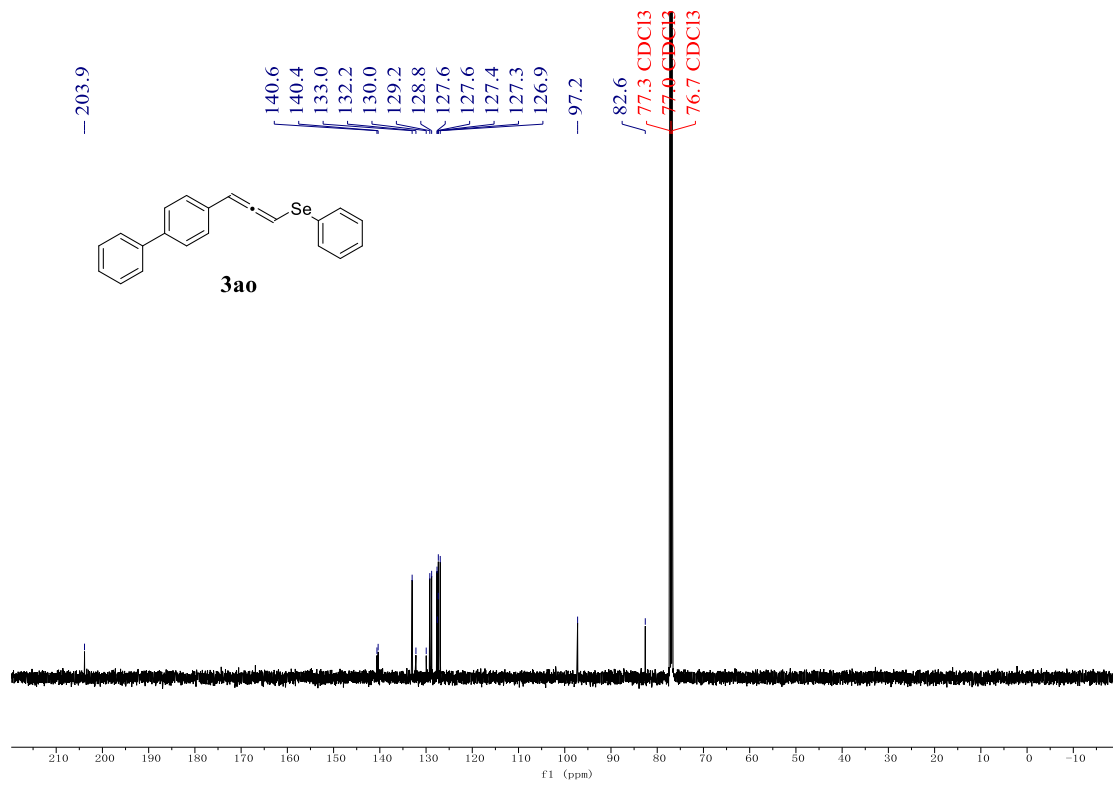


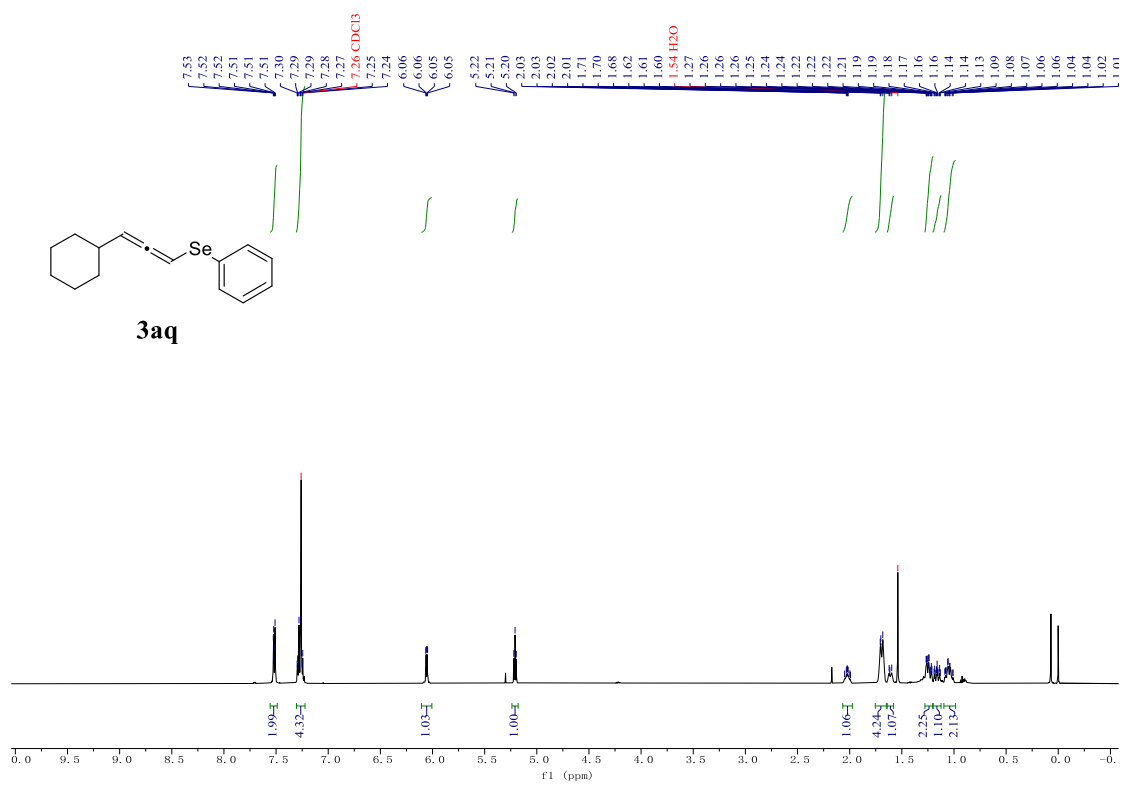
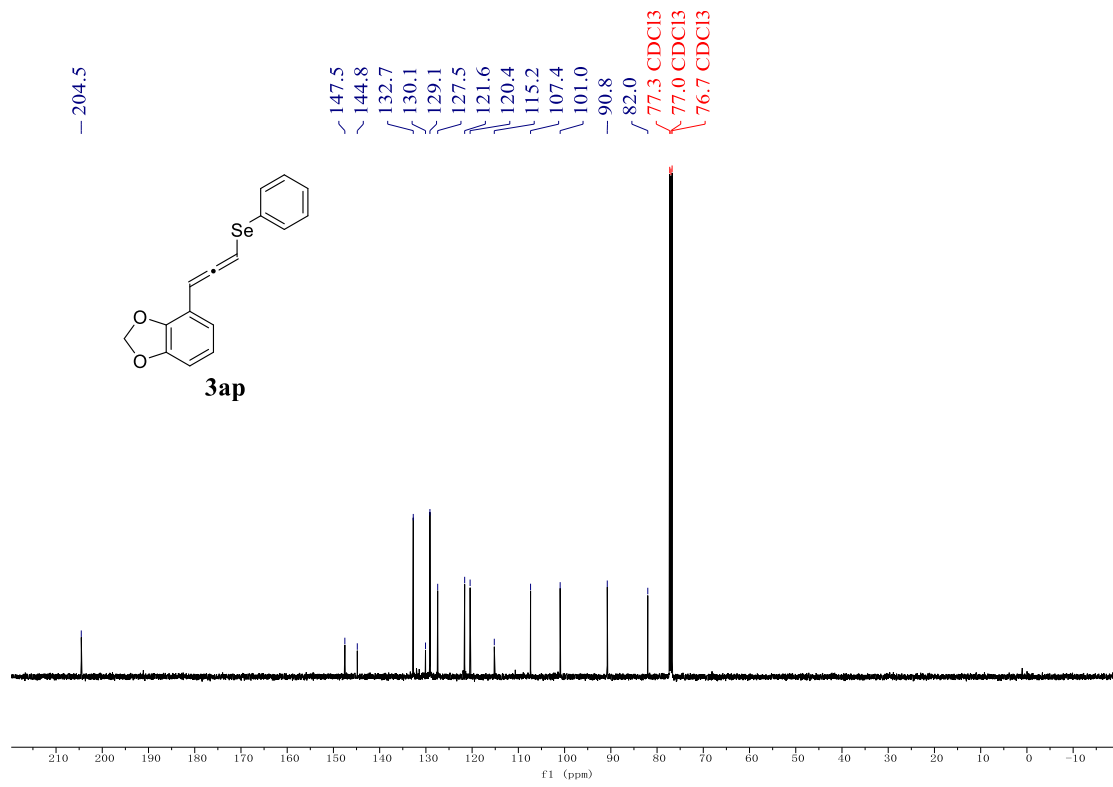


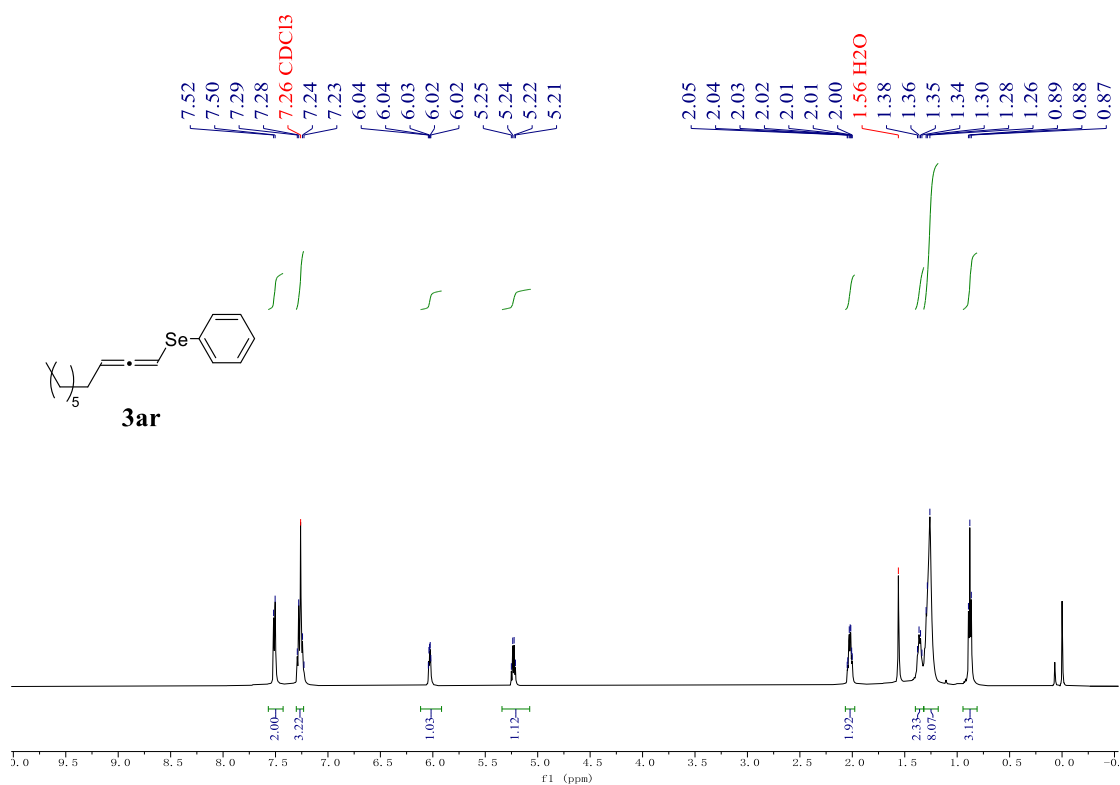
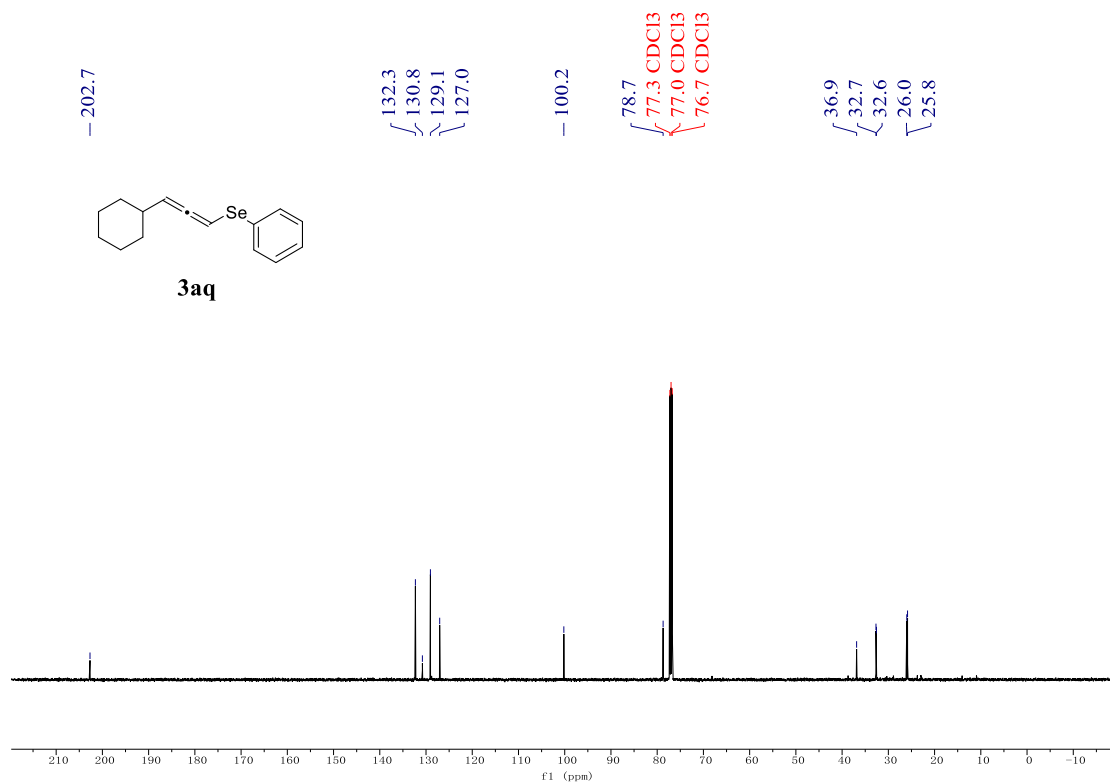


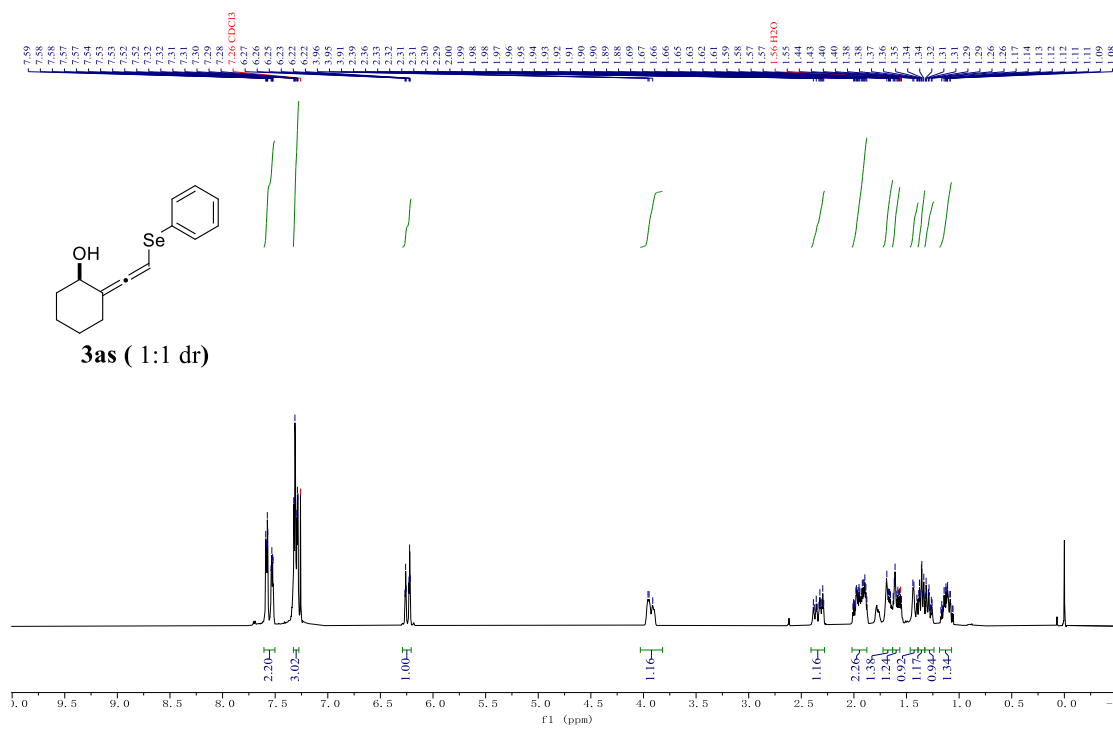
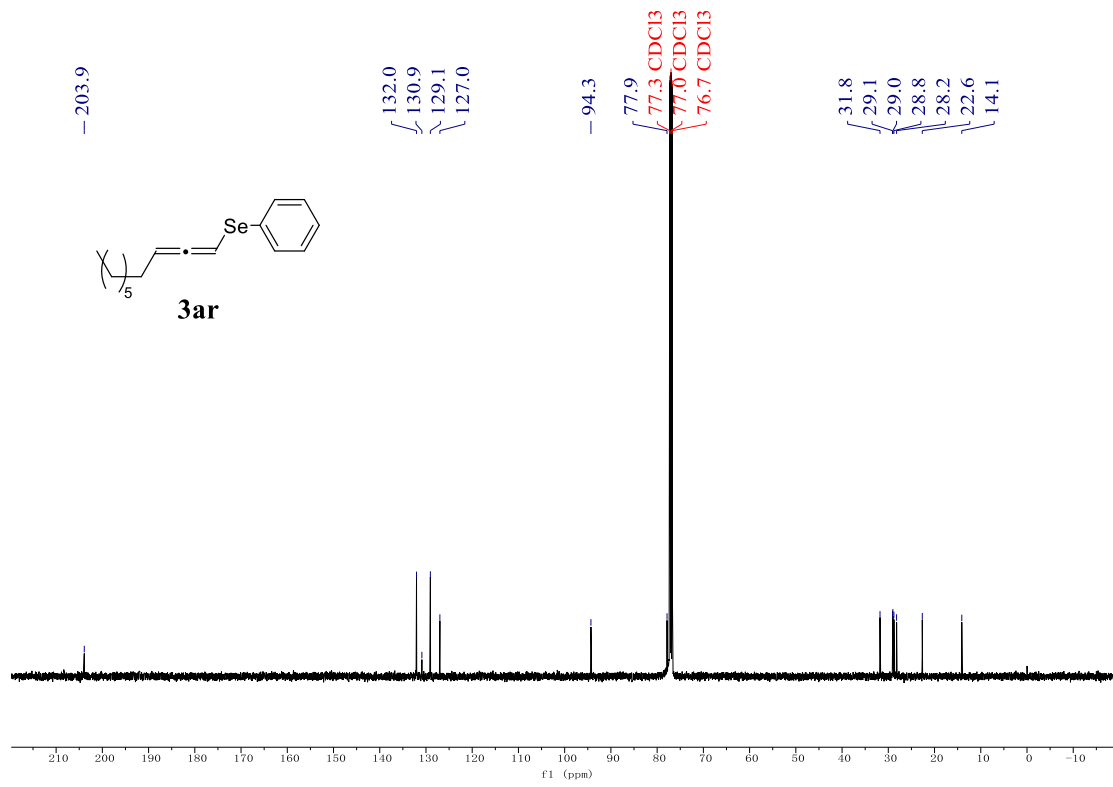


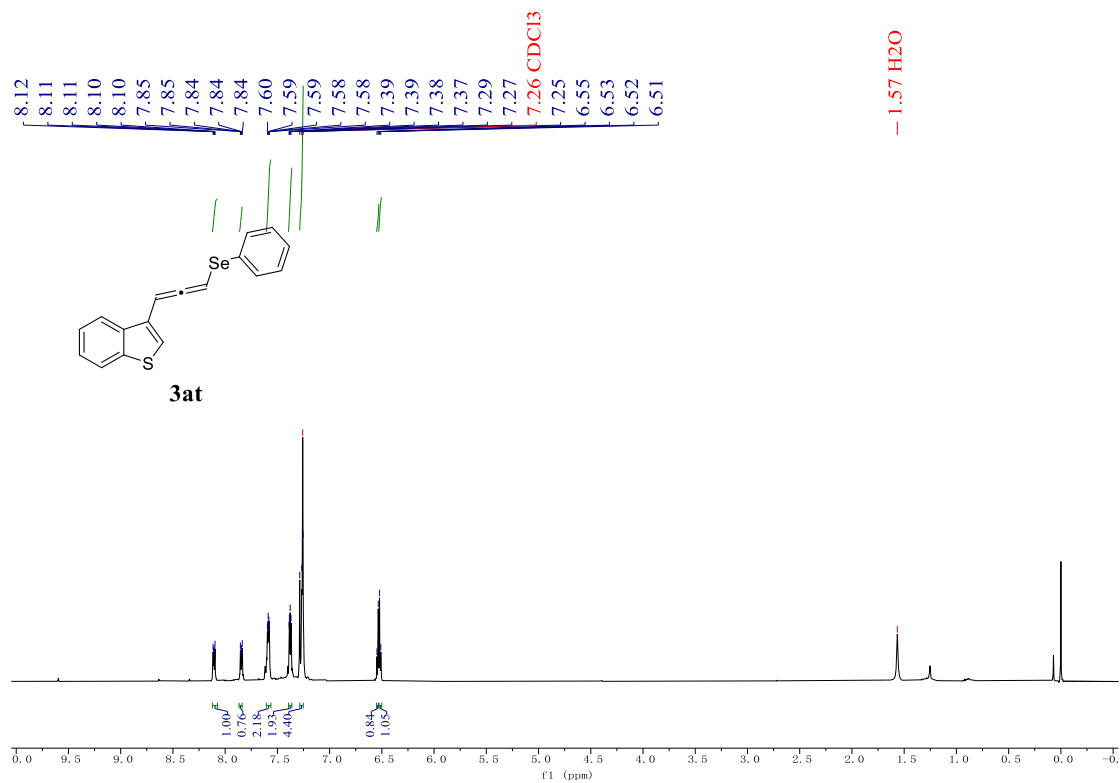
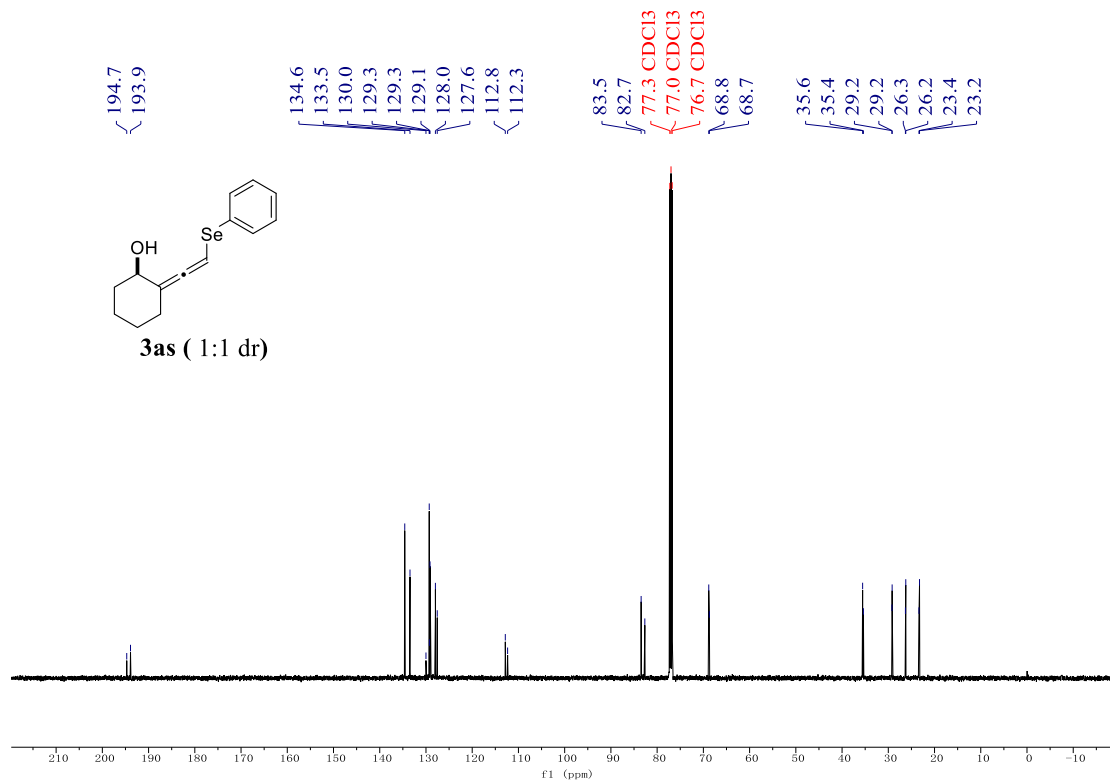


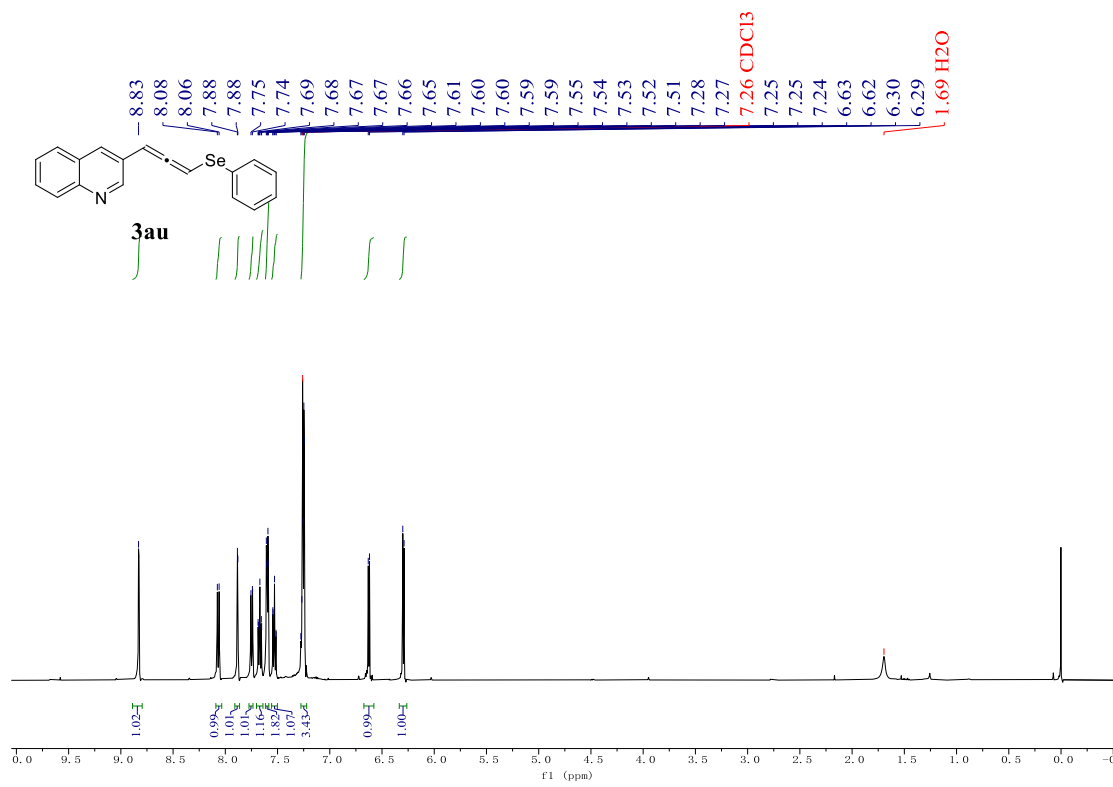
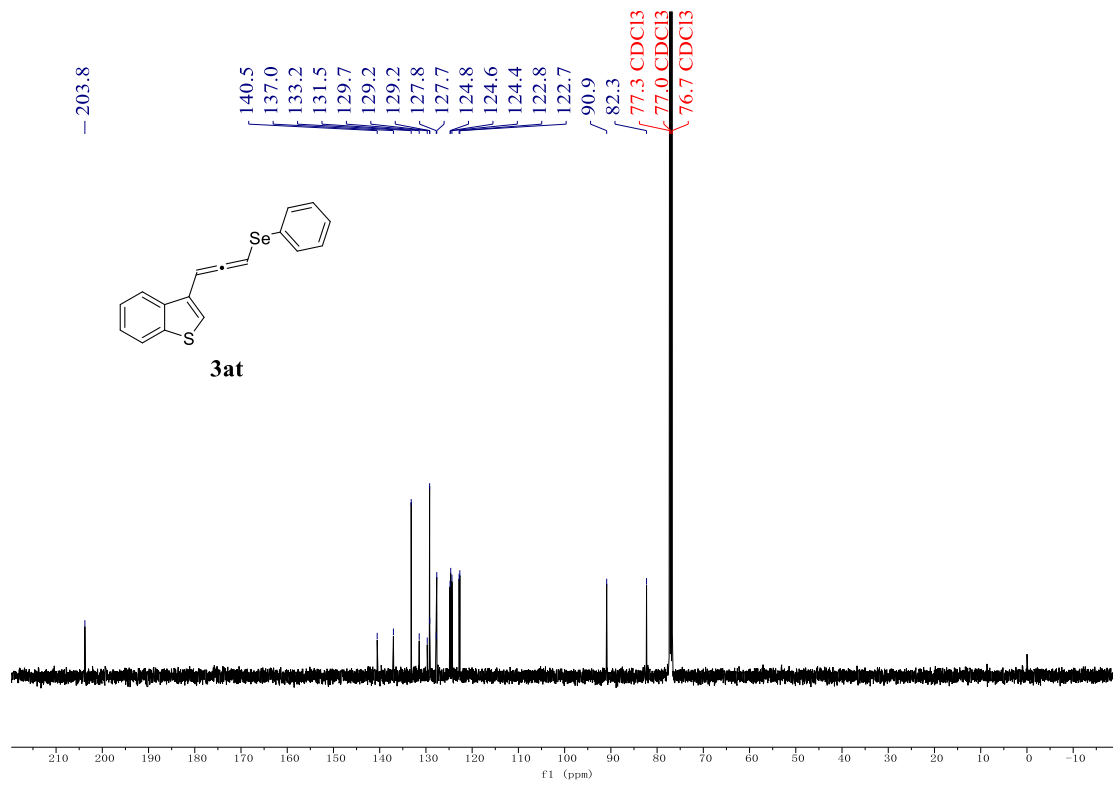




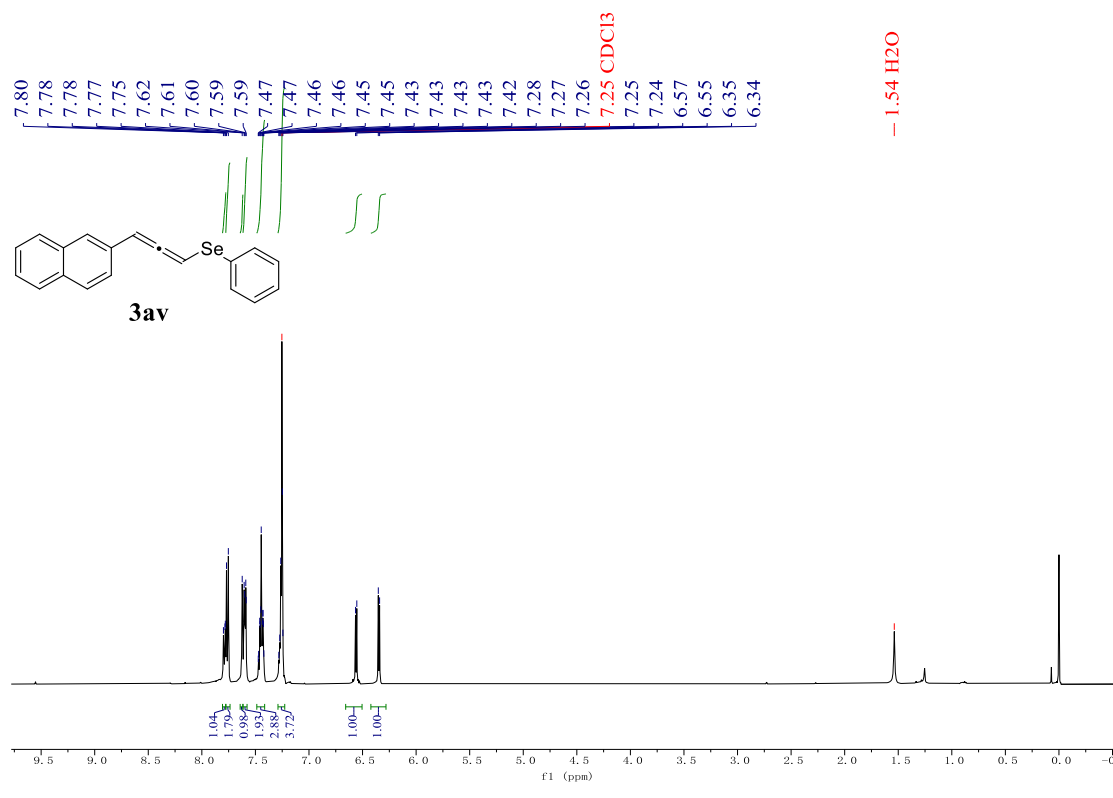
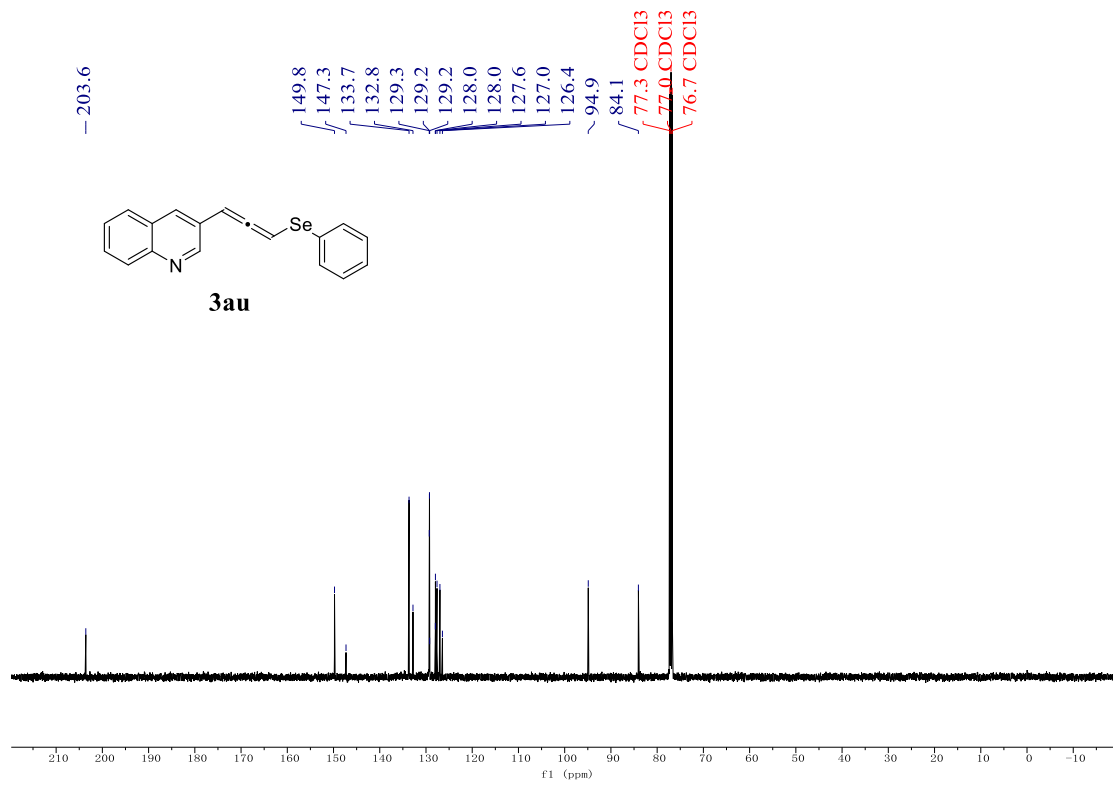


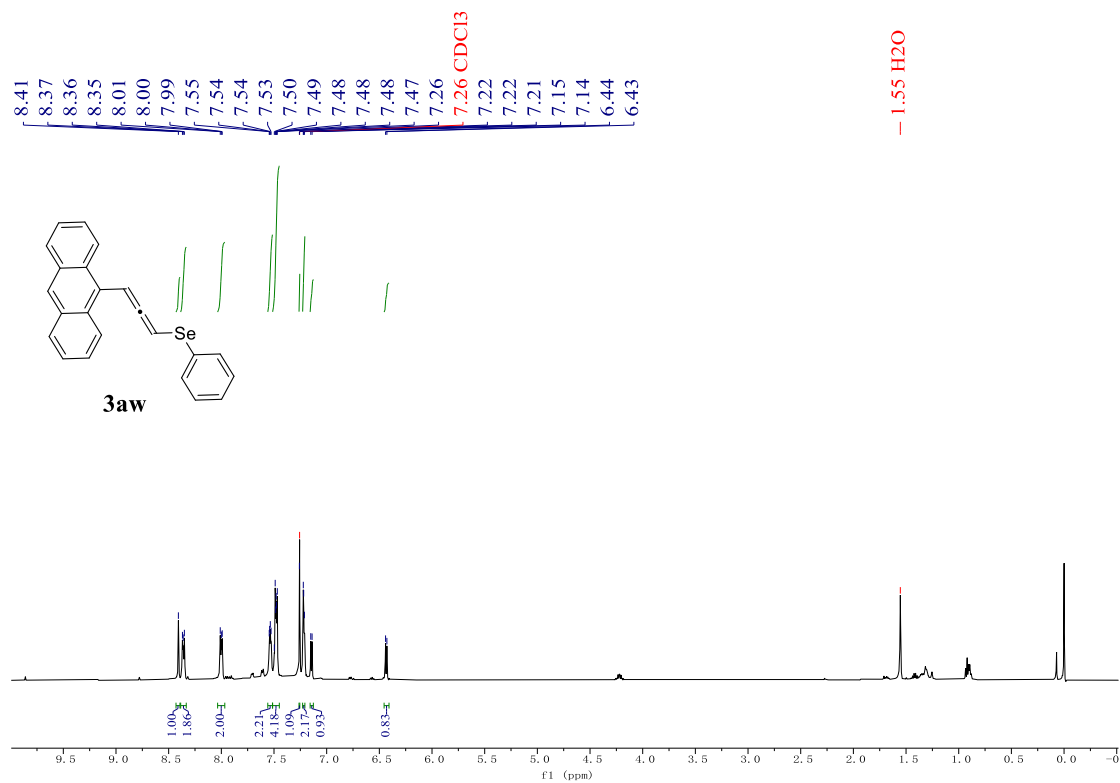
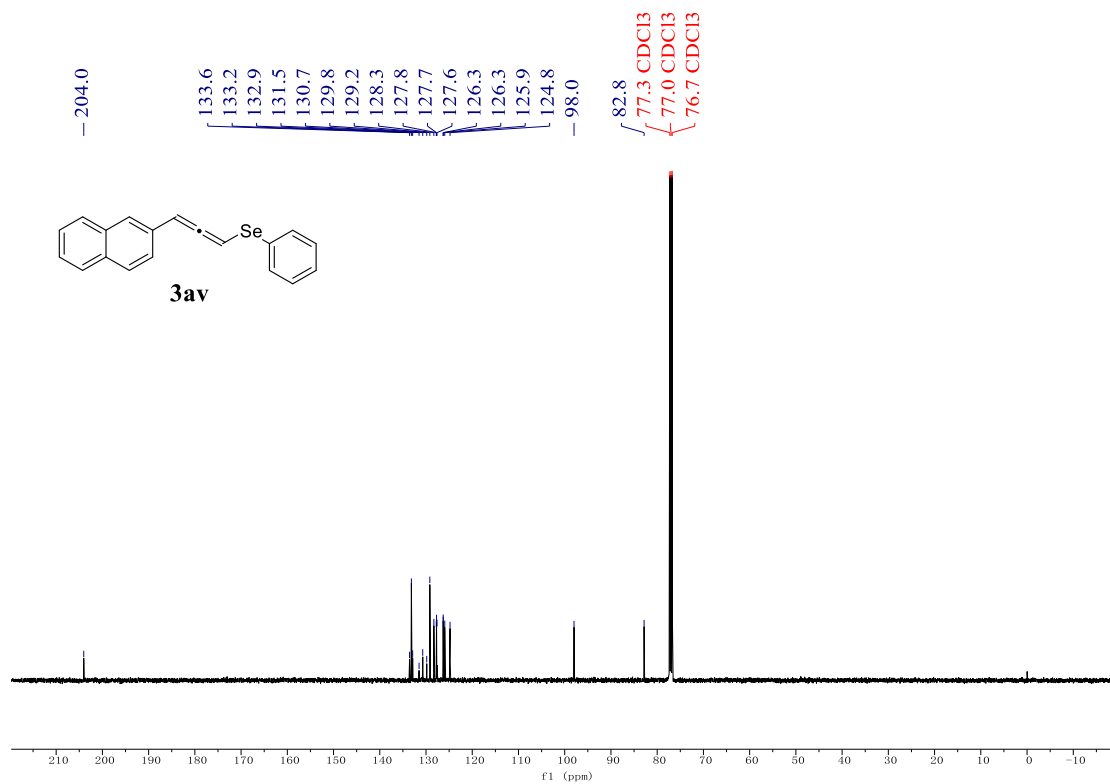


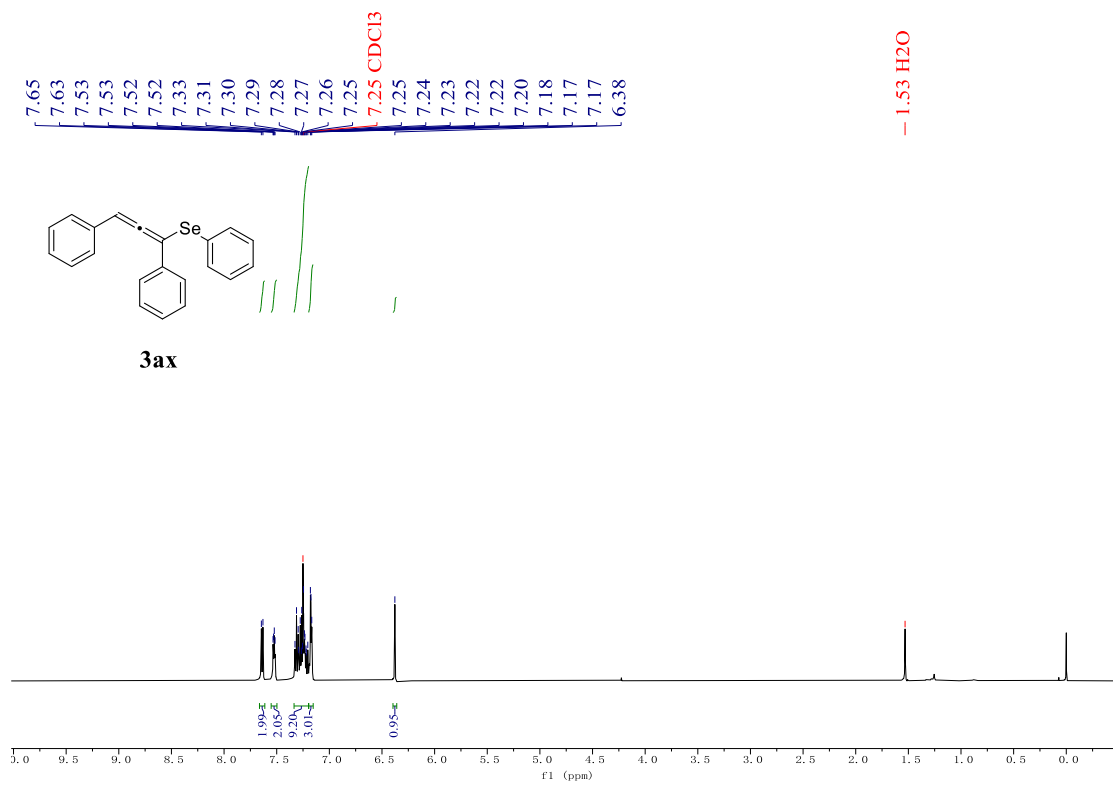
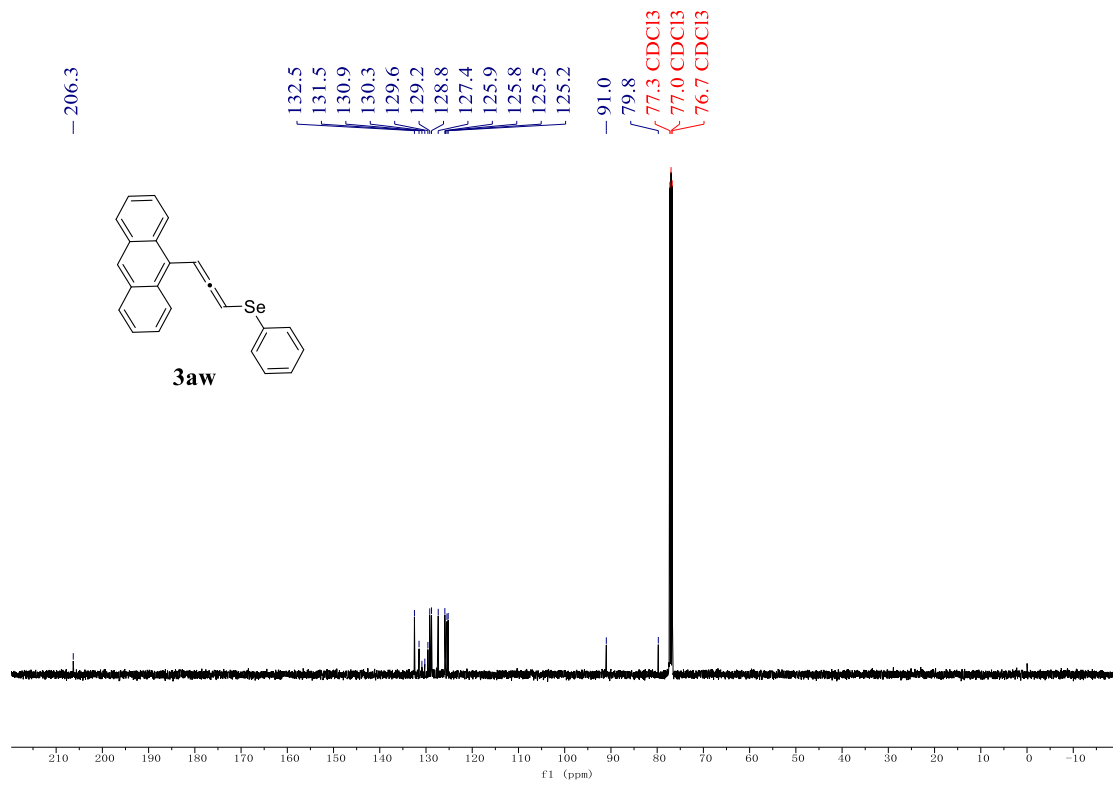


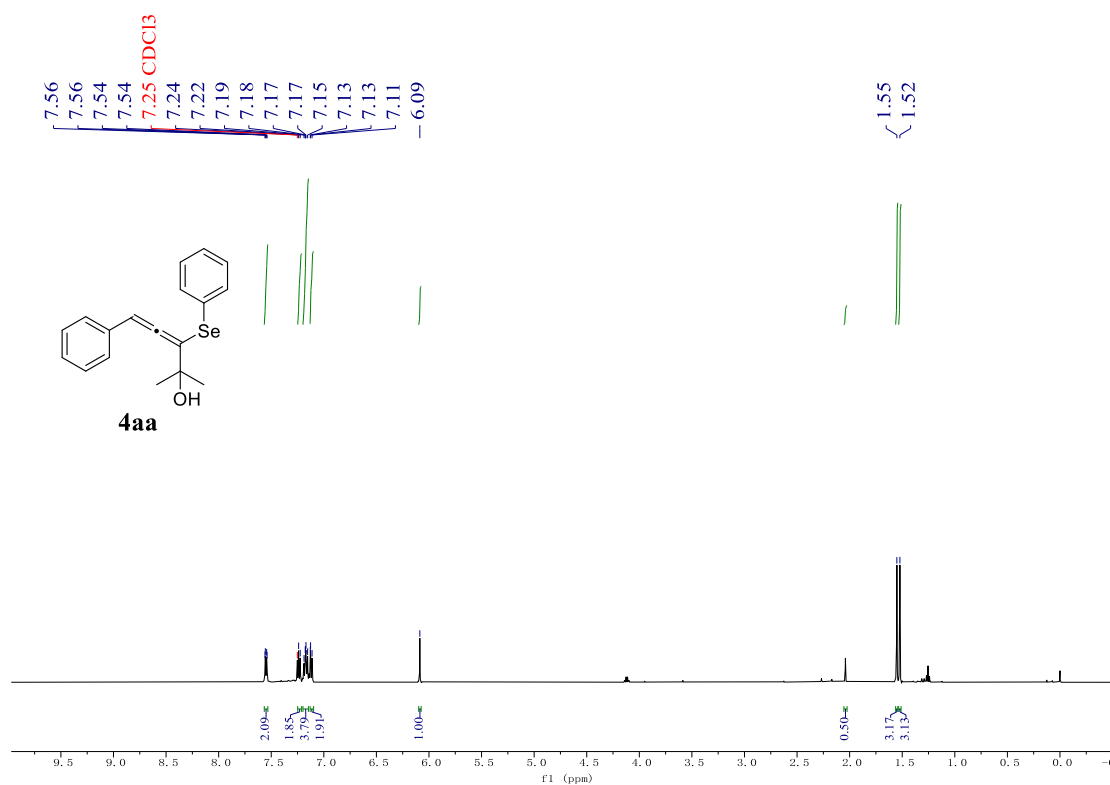
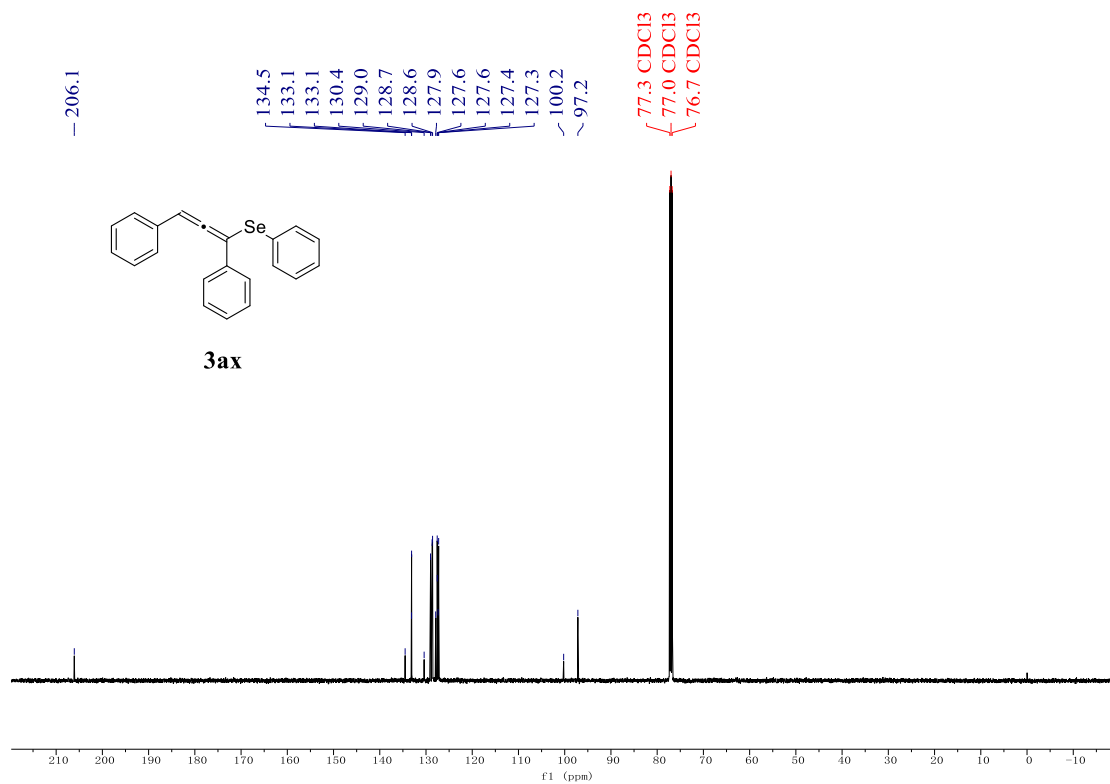


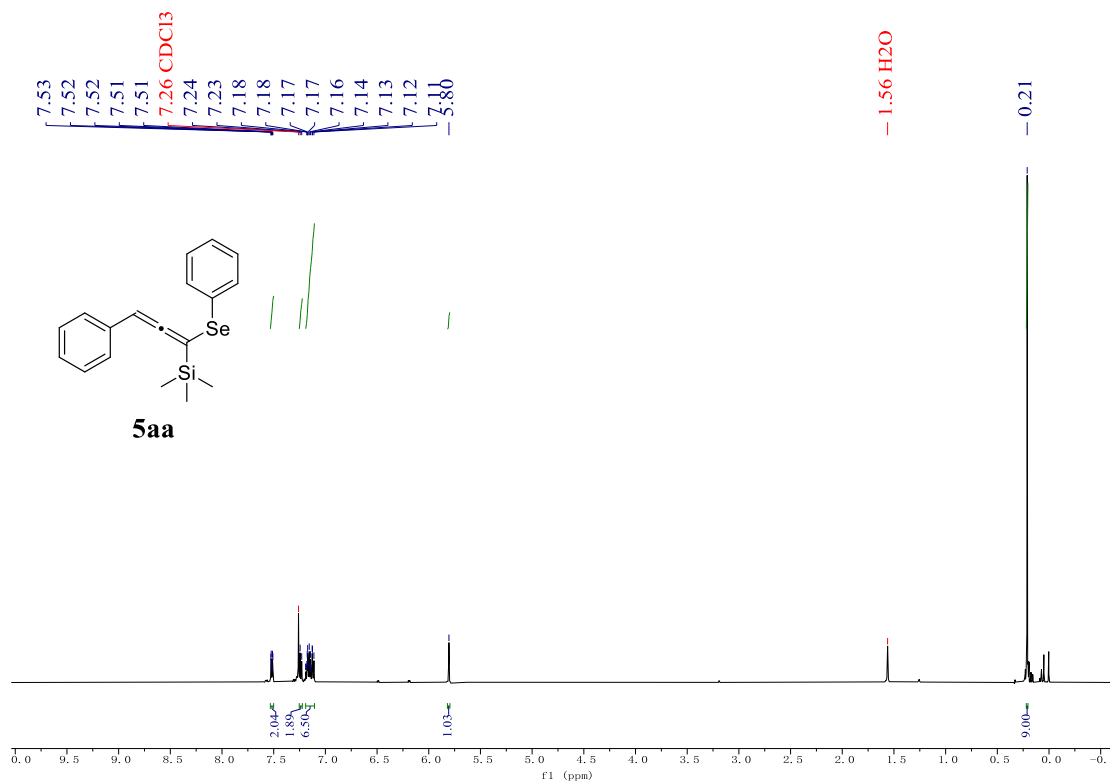
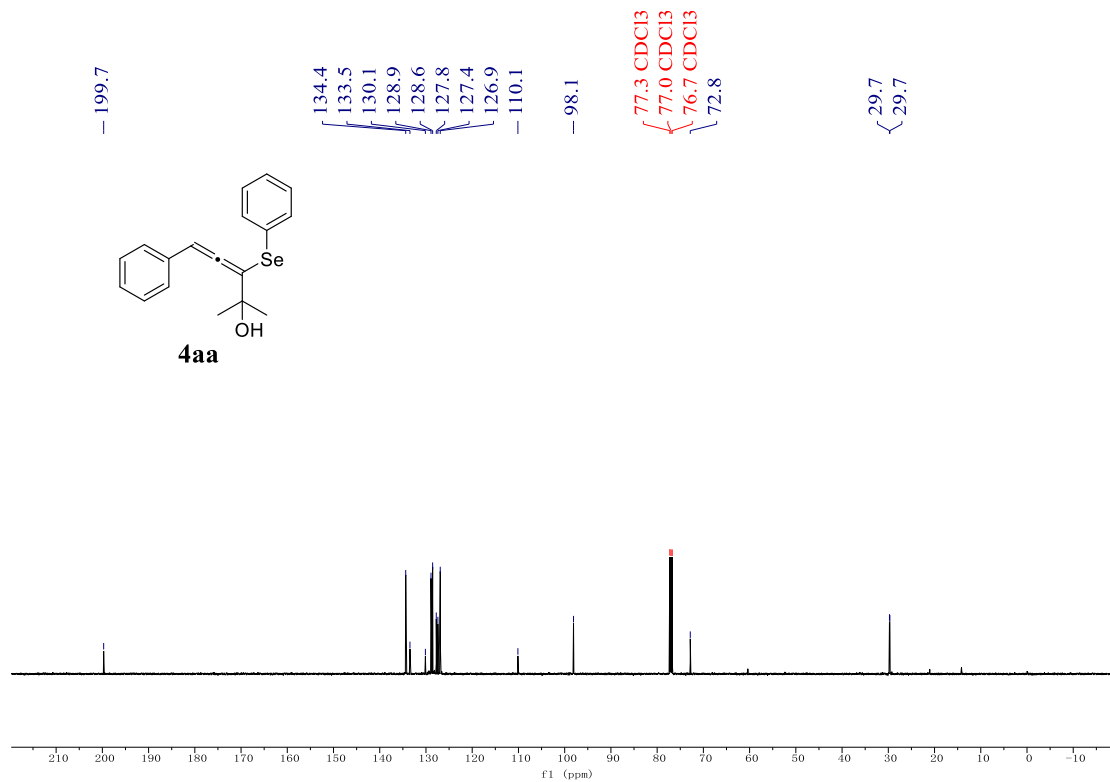


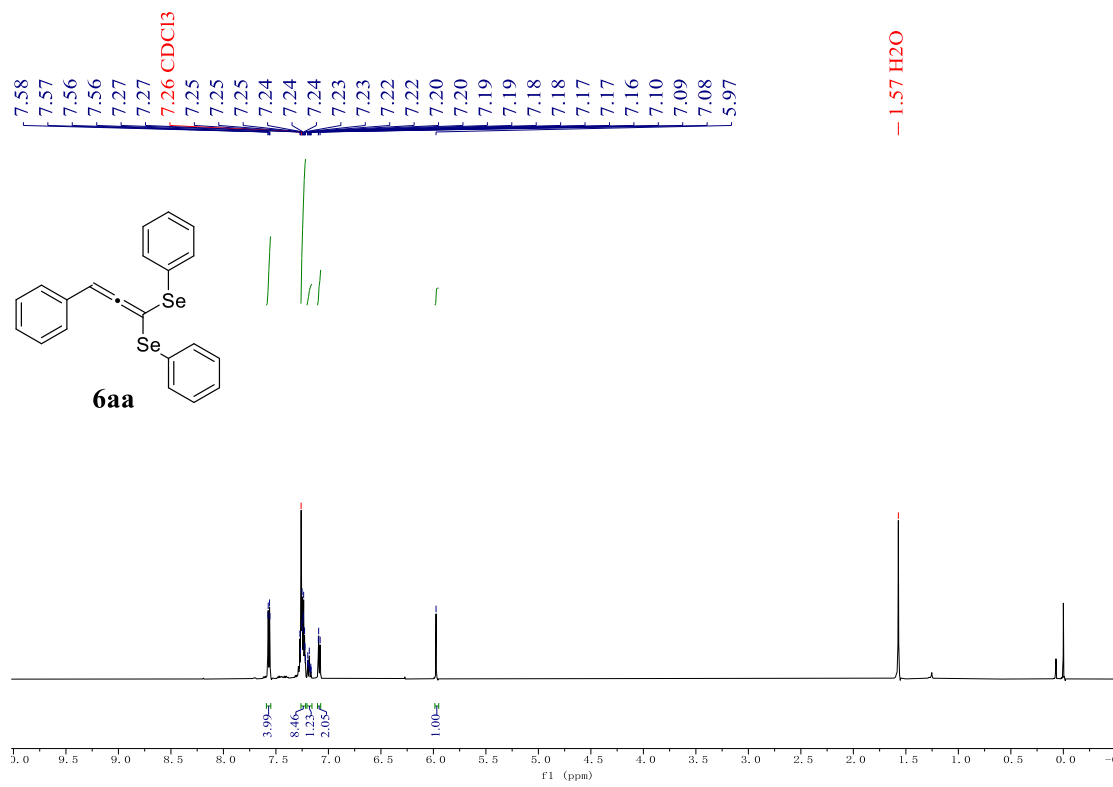
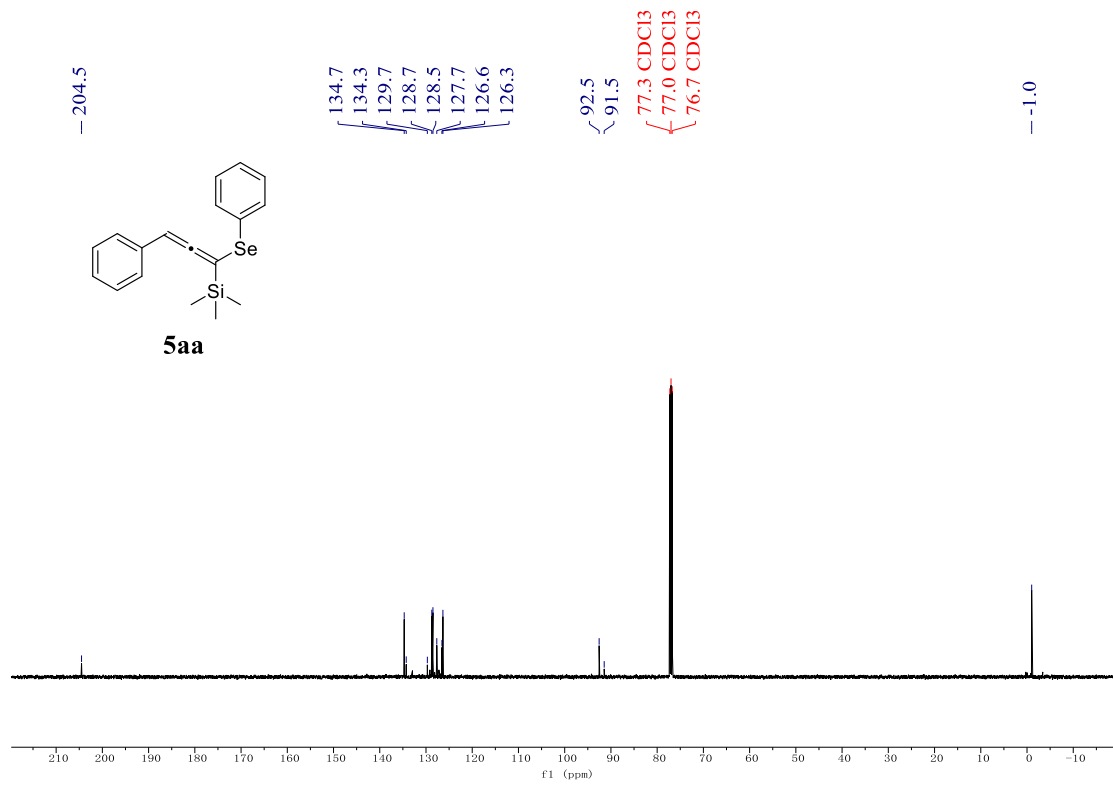


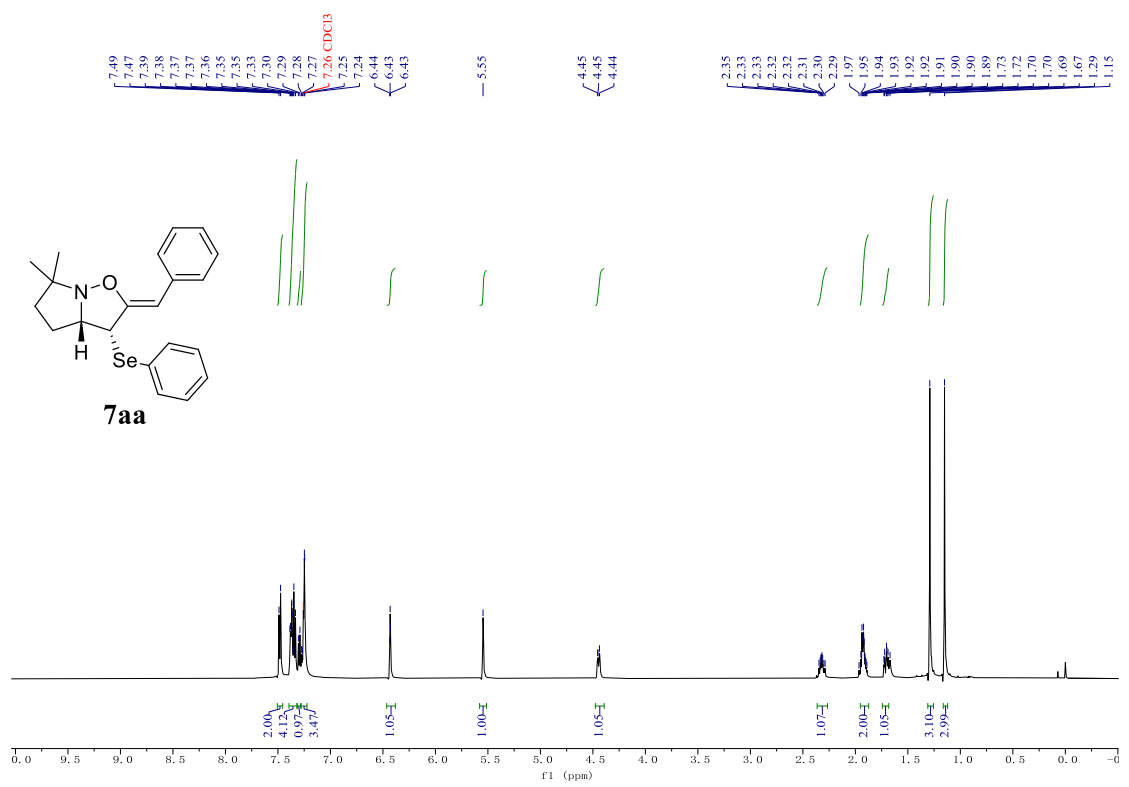
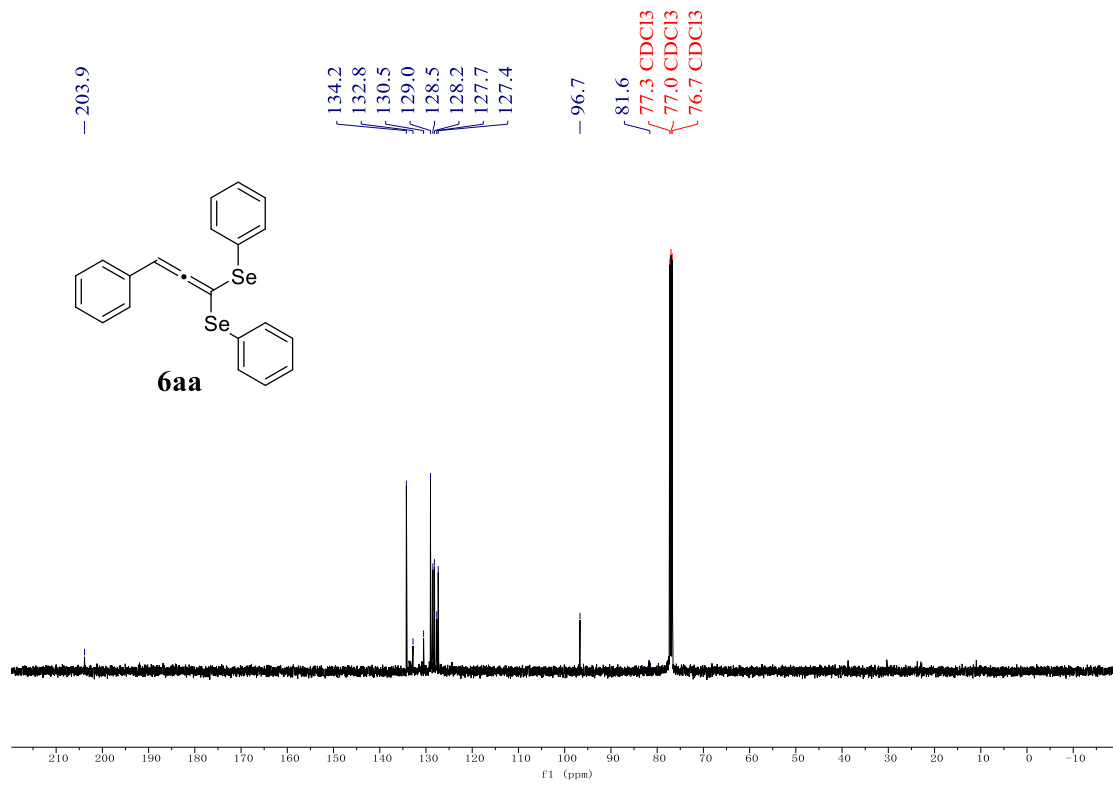


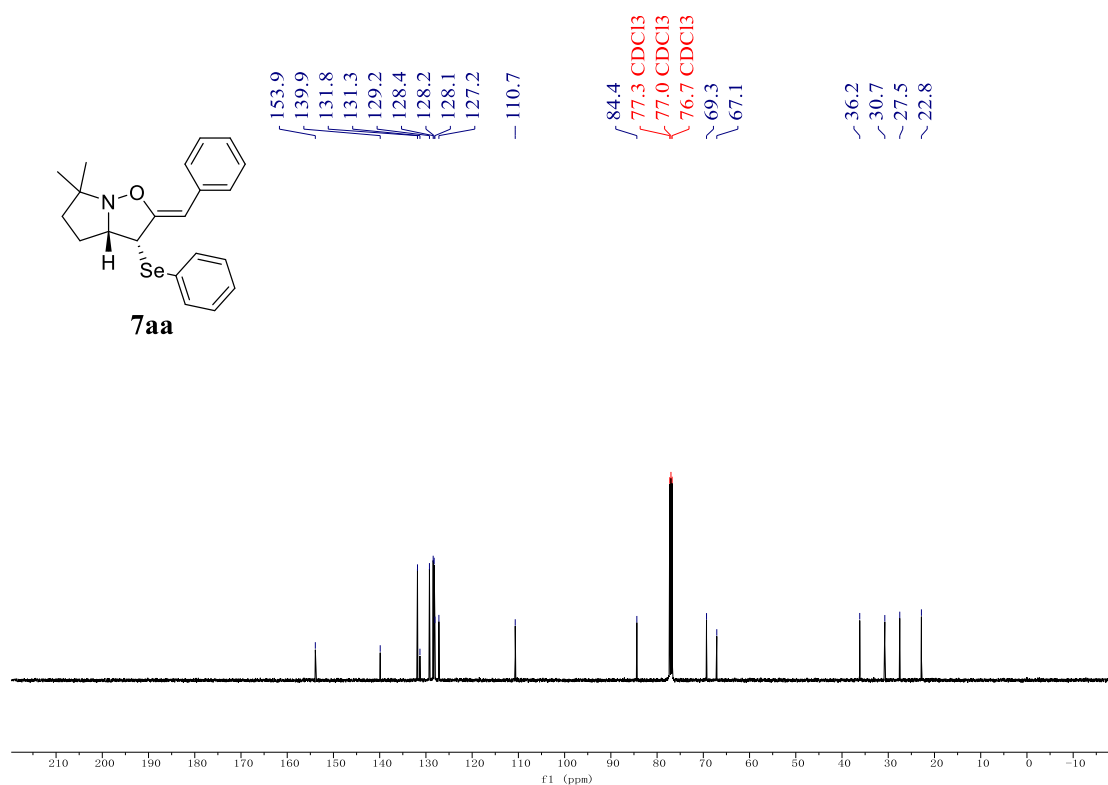












## 8. References

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