

Electronic Supplementary Information (ESI) for

## **Diamine-mediated N<sup>2</sup>-selective $\beta$ -selenoalkylation of triazoles with alkenes**

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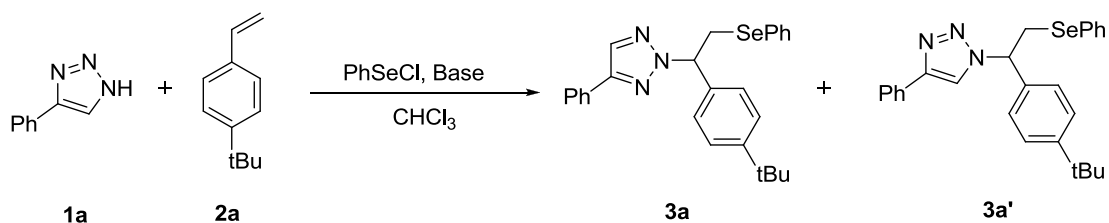
## 1. General Conditions

All reactions were run under air atmosphere. All reagents were purchased from commercial sources and used as received. Column chromatography was performed using 200-300 mesh silica with the proper solvent system according to TLC analysis by staining with an ethanolic solution of phosphomolybdic acid and UV light to visualize the reaction components. Unless otherwise noted, nuclear magnetic resonance spectra were recorded on 400 MHz spectrometer. NMR data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and brs = broad singlet), coupling constant in Hz and integration. Chemical shifts for  $^{13}\text{C}$  NMR spectra were recorded in parts per million from tetramethylsilane using the central peak of deuteriochloroform (77.0 ppm) as the internal standard. HRMS data were obtained using ESI ionization. The isolated yields of  $N^2$ -fuctionalized products were reported in the part of 'Analytical Data'. The total yield of each reaction (on the main text) was calculated based on the isolated yield of  $N^2$ -fuctionalized product and the ratio of  $N^2/N^1$  on the crude  $^1\text{H}$  NMR.

## 2. Typical Experimental Procedure

A mixture of 1,2,3-triazole (0.5 mmol), N,N'-dimethylpiperazine (0.25 mmol) and alkene (1.0 mmol) in  $\text{CHCl}_3$  (3 mL) was stirred 5 min under an air atmosphere at 30 °C, which was added to a suspension of PhSeCl (0.5 mmol) in  $\text{CHCl}_3$ (2 mL). When the reaction completed, the solution was diluted with 50 mL EtOAc and washed with water (3  $\times$ 10 mL) and brine (10 mL). The organic phase was dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated *in vacuo*. Purification of the crude product through chromatography on silica gel with a gradient eluant of petroleum ether and ethyl acetate afforded  $\beta$ -selenoalkylated product.

### Table S1. Screening of Optimal Reaction Conditions.<sup>a</sup>

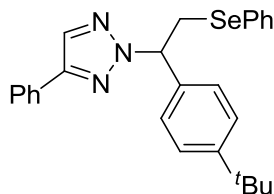


Entry	Base(eq.)	Additive(mol%)	Yield <sup>b</sup> (%)	<b>3a/3a'</b> <sup>c</sup>
1	-	-	90	2/1
2	Et <sub>3</sub> N (1.0)	-	65	5/1
3	DABCO (1.0)	-	35	3/1
4	DBU (1.0.)	-	42	3/1
5	TMEDA (1.0)	-	63	6/1
6	TMEDA (0.5)	-	90	9/1
7	TMEDA (0.25)	-	85	6/1
8	TMEDA (0.1)	-	82	5/1
9	TMEDA(2.0)	-	32	2/1
10	TMEDA (0.5)	Zn(OTf) <sub>2</sub> (10)	28	1/1
11	TMEDA (0.5)	CuCl <sub>2</sub> (10)	21	1/1
12	1,8-Bis(dimethylamino)- Naphthalene (0.5)	-	49	6/1
13	5,10-Dimethyldihydro- phenazine (0.5)	-	56	6/1
14	TMPDA (0.5)	-	84	4/1
15	TMMDA(0.5)	-	68	2/1
16	N,N'-DiMethylpiperazine (0.5)	-	99	8/1
17 <sup>d</sup>	N,N'-DiMethylpiperazine (0.5)	-	99	10/1

<sup>a</sup> Reaction conditions unless specified otherwise: **1a** (0.5 mmol), **2a** (1.0 mmol), PhSeCl (1.0 mmol), base, CHCl<sub>3</sub> (5 ml), under air atmosphere, 70 °C, 2 h. <sup>b</sup> Isolated yield of N<sup>2</sup> and N<sup>1</sup> product. <sup>c</sup> The ratio of N<sup>2</sup> and N<sup>1</sup> isomer was determined by <sup>1</sup>H NMR analysis of crude product. <sup>d</sup>The reaction temperature was 30 °C.

### 3. Product Characterization

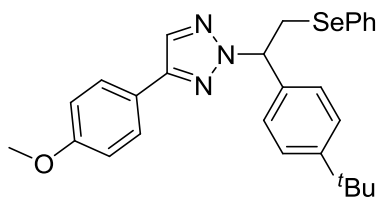
#### 2-(1-(4-*tert*-butylphenyl)-2-(phenylselanyl)ethyl)-4-phenyl-2*H*-1,2,3-triazole (**3a**)



4-phenyl-1,2,3-triazole (72.6 mg, 0.5 mmol) was reacted with 4-*t*-butylstyrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 200:1) to afford the title compound as a white solid (m. p. 48 – 50 °C) in 90% yield (207.4 mg, 99% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 91% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.6; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.83 (s, 1H), 7.77 (d,  $J = 7.1$  Hz, 2H), 7.53 – 7.47 (m, 2H), 7.41 (t,  $J = 7.4$  Hz, 2H), 7.36 – 7.27 (m, 5H), 7.27 – 7.21 (m, 3H), 5.82 (dd,  $J = 10.0, 5.3$  Hz, 1H), 4.05 (dd,  $J = 13.0, 10.1$  Hz, 1H), 3.61 (dd,  $J = 13.0, 5.3$  Hz, 1H), 1.27 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  151.5, 147.6, 135.9, 133.8, 131.1, 130.5, 129.3, 129.2, 128.8, 128.4, 127.6, 126.6, 126.0, 125.7, 69.1, 34.6, 33.0, 31.3; **HRMS** (ESI) calcd for C<sub>26</sub>H<sub>27</sub>N<sub>3</sub>NaSe [M+Na]<sup>+</sup>: 484.1262, found: 484.1267.

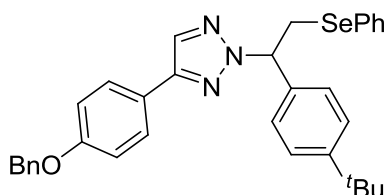
#### 2-(1-(4-*tert*-butylphenyl)-2-(phenylselanyl)ethyl)-4-(4-methoxyphenyl)-2*H*-1,2,3-triazole (**3b**)



4-(4-methoxyphenyl)-1,2,3-triazole (87.6 mg, 0.5 mmol) was reacted with 4-*t*-butylstyrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 50:1) to afford the title compound as a white solid (m. p. 68 – 70 °C) in 86% yield (211.7 mg, 97% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 89% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 10:1): 0.7; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.81 (s, 1H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.59 – 7.51 (m, 2H), 7.39 – 7.31 (m, 4H), 7.29 (dd, *J* = 3.8, 2.4 Hz, 3H), 6.99 (d, *J* = 8.6 Hz, 2H), 5.93 – 5.77 (m, 1H), 4.09 (ddd, *J* = 12.0, 10.1, 1.8 Hz, 1H), 3.87 (s, 3H), 3.65 (dd, *J* = 13.0, 5.3 Hz, 1H), 1.31 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 159.8, 151.4, 147.5, 136.0, 133.8, 130.5, 129.3, 129.2, 127.5, 127.3, 126.6, 125.7, 123.2, 114.2, 69.0, 55.4, 34.6, 33.0, 31.3; **HRMS** (ESI) calcd for C<sub>27</sub>H<sub>30</sub>N<sub>3</sub>OSe [M+H]<sup>+</sup>: 492.1549, found: 492.1539.

#### 4-(4-(benzyloxy)phenyl)-2-(1-(4-*tert*-butylphenyl)-2-(phenylselanyl)ethyl)-2*H*-1,2,3-triazole (3c)

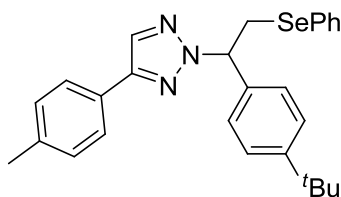


4-(4-(benzyloxy)phenyl)-1,2,3-triazole (125.6 mg, 0.5 mmol) was reacted with 4-*t*-butylstyrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 100:1) to afford the title compound as a white solid (m. p. 64 – 66 °C) in 77% yield (219.3 mg, 88% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 88% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.4; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.76 (s, 1H), 7.70 (d, *J* = 8.7 Hz, 2H), 7.53 – 7.49 (m, 2H), 7.45 (d, *J* = 6.9 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.36 – 7.32 (m, 3H), 7.29 (d, *J* = 8.6 Hz, 2H), 7.26 – 7.23 (m, 3H), 7.02 (d, *J* = 8.8 Hz, 2H), 5.81 (dd, *J* = 10.0, 5.3 Hz, 1H), 5.11 (s,

2H), 4.05 (dd,  $J = 13.0, 10.0$  Hz, 1H), 3.61 (dd,  $J = 13.0, 5.4$  Hz, 1H), 1.28 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.0, 151.5, 147.5, 136.9, 136.0, 133.9, 130.6, 129.4, 129.3, 128.7, 128.1, 127.6, 127.4, 126.7, 125.8, 123.6, 115.3, 70.2, 69.1, 34.7, 33.0, 31.4; HRMS (ESI) calcd for  $\text{C}_{33}\text{H}_{34}\text{N}_3\text{OSe}$   $[\text{M}+\text{H}]^+$ : 568.1862, found: 568.1861.

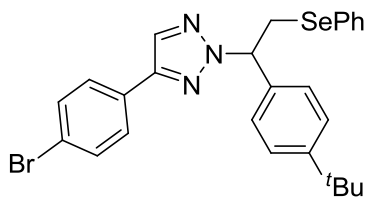
**2-(1-(4-*tert*-butylphenyl)-2-(phenylselanyl)ethyl)-4-*p*-tolyl-2H-1,2,3-triazole (3d)**



4-*p*-tolyl-1,2,3-triazole (79.6 mg, 0.5 mmol) was reacted with 4-*t*-butylstyrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 100:1) to afford the title compound as a white solid (m. p. 42 – 44 °C) in 86% yield (204.6 mg, 98% yield in total of  $\text{N}^2$  and  $\text{N}^1$  isomers) and 88%  $\text{N}^2$ -selectivity.

Rf (petroleum ether: EtOAc = 20:1): 0.4;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.80 (s, 1H), 7.67 (d,  $J = 8.2$  Hz, 2H), 7.52 – 7.50 (m, 2H), 7.33 (d,  $J = 8.6$  Hz, 2H), 7.30 (d,  $J = 8.5$  Hz, 2H), 7.26 – 7.20 (m, 5H), 5.82 (dd,  $J = 10.0, 5.4$  Hz, 1H), 4.05 (dd,  $J = 13.0, 10.0$  Hz, 1H), 3.62 (dd,  $J = 13.0, 5.4$  Hz, 1H), 2.38 (s, 3H), 1.28 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  151.5, 147.8, 138.3, 136.0, 133.9, 131.0, 129.6, 129.4, 129.3, 127.8, 127.6, 126.7, 126.0, 125.8, 69.1, 34.7, 33.0, 31.4, 21.4; HRMS (ESI) calcd for  $\text{C}_{27}\text{H}_{30}\text{N}_3\text{Se}$   $[\text{M}+\text{H}]^+$ : 476.1599, found: 476.1603.

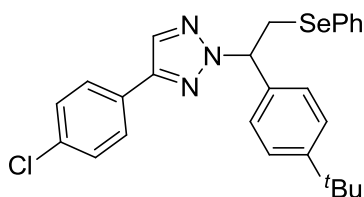
**4-(4-bromophenyl)-2-(1-(4-*tert*-butylphenyl)-2-(phenylselanyl)ethyl)-2H-1,2,3-triazole (3e)**



4-(4-bromophenyl)-1,2,3-triazole (112.0 mg, 0.5 mmol) was reacted with 4-*t*-butylstyrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 100:1) to afford the title compound as a white solid (m. p. 60 – 62 °C) in 77% yield (208.7 mg, 90% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 86% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.4; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.80 (s, 1H), 7.63 (d, *J* = 8.7 Hz, 2H), 7.55 – 7.51 (m, 2H), 7.51 – 7.47 (m, 2H), 7.36 – 7.27 (m, 4H), 7.26 – 7.21 (m, 3H), 5.81 (dd, *J* = 10.1, 5.2 Hz, 1H), 4.04 (dd, *J* = 13.1, 10.1 Hz, 1H), 3.60 (dd, *J* = 13.1, 5.2 Hz, 1H), 1.27 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 151.7, 146.7, 135.8, 133.9, 132.0, 131.1, 129.6, 129.3, 129.2, 127.7, 127.6, 126.6, 125.8, 122.4, 69.4, 34.7, 33.0, 31.3; **HRMS** (ESI) calcd for C<sub>26</sub>H<sub>27</sub>BrN<sub>3</sub>Se [M+H]<sup>+</sup>: 540.0548, found: 540.0547.

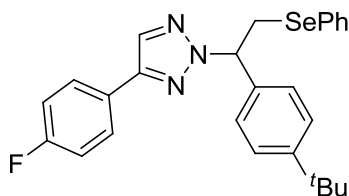
**2-(1-(4-*tert*-butylphenyl)-2-(phenylselanyl)ethyl)-4-(4-chlorophenyl)-2H-1,2,3-triazole (3f)**



4-(4-chlorophenyl)-1,2,3-triazole (89.8 mg, 0.5 mmol) was reacted with 4-*t*-butylstyrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 200:1) to afford the title compound as a white solid (m. p. 50 – 52 °C) in 81% yield (199.3 mg, 97% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 83% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.5; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.80 (s, 1H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.53 – 7.47 (m, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 7.26 – 7.21 (m, 3H), 5.81 (dd, *J* = 10.1, 5.2 Hz, 1H), 4.04 (dd, *J* = 13.1, 10.1 Hz, 1H), 3.60 (dd, *J* = 13.1, 5.2 Hz, 1H), 1.27 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 151.7, 146.7, 135.8, 134.2, 133.9, 131.1, 129.3, 129.2, 129.1, 129.0, 127.7, 127.3, 126.6, 69.4, 34.7, 33.0, 31.3; **HRMS** (ESI) calcd for C<sub>26</sub>H<sub>27</sub>ClN<sub>3</sub>Se [M+H]<sup>+</sup>: 496.1053, found: 496.1048.

**2-(1-(4-*tert*-butylphenyl)-2-(phenylselanyl)ethyl)-4-(4-fluorophenyl)-2H-1,2,3-triazole (3g)**

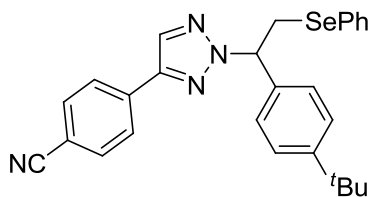


4-(4-fluorophenyl)-1,2,3-triazole (81.6 mg, 0.5 mmol) was reacted with 4-*t*-butylstyrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 200:1) to afford the title compound as a white solid (m. p. 46 – 48 °C) in 77% yield (183.2 mg, 88% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 87% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.5; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.79 (s, 1H), 7.78 – 7.71 (m, 2H), 7.52 – 7.50 (m, 2H), 7.36 – 7.28 (m, 4H), 7.27 – 7.22 (m, 3H), 7.11 (t, *J* = 8.8 Hz, 2H), 5.83 (dd, *J* = 10.1, 5.2 Hz, 1H), 4.06 (dd, *J* = 13.0, 10.1 Hz, 1H), 3.62 (dd, *J* = 13.0, 5.3 Hz, 1H), 1.28 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 162.9 (d, *J*<sub>C-F</sub> = 246.3 Hz), 151.6, 146.9, 135.9, 133.9, 130.9, 129.3, 127.8 (d, *J*<sub>C-F</sub> = 8.1 Hz), 127.7, 126.7, 125.8, 115.8 (d, *J*<sub>C-F</sub> = 21.6 Hz), 69.3, 34.7, 33.0, 31.4; **HRMS** (ESI) calcd for C<sub>26</sub>H<sub>27</sub>FN<sub>3</sub>Se [M+H]<sup>+</sup>: 480.1349, found: 480.1349.

**4-(2-(1-(4-*tert*-butylphenyl)-2-(phenylselanyl)ethyl)-2H-1,2,3-triazol-4-yl)benzotrile (3h)**

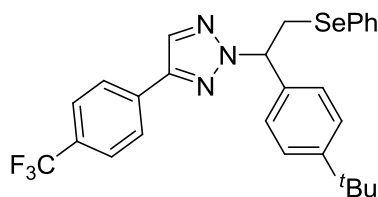




4-(4-cyano-2-((4-*t*-butylphenyl)ethyl)amino)phenyl-1,2,3-triazole (85.1 mg, 0.5 mmol) was reacted with 4-*t*-butylstyrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 30:1) to afford the title compound as a pale yellow oil in 81% yield (196.9 mg, 92% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 88% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 10:1): 0.3; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.88(s, 1H); 7.86 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.50 – 7.47 (m, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.25 – 7.22 (m, 3H), 5.82 (dd, *J* = 10.3, 5.1 Hz, 1H), 4.04 (dd, *J* = 13.1, 10.3 Hz, 1H), 3.60 (dd, *J* = 13.2, 5.0 Hz, 1H), 1.27 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 151.8, 145.9, 135.5, 135.0, 134.0, 132.7, 131.8, 129.3, 129.0, 127.7, 126.6, 126.5, 125.9, 118.9, 111.8, 69.7, 34.7, 32.9, 31.3; **HRMS** (ESI) calcd for C<sub>27</sub>H<sub>27</sub>N<sub>4</sub>Se [M+H]<sup>+</sup>: 487.1395, found: 487.1388.

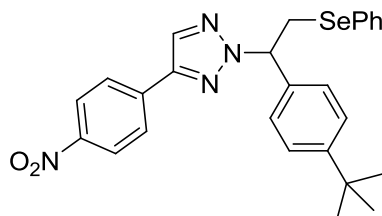
**2-(1-(4-*tert*-butylphenyl)-2-(phenylselanyl)ethyl)-4-(4-(trifluoromethyl)phenyl)-2H-1,2,3-triazole (3i)**



4-(4-(trifluoromethyl)-2-((4-*t*-butylphenyl)ethyl)amino)phenyl-1,2,3-triazole (106.6 mg, 0.5 mmol) was reacted with 4-*t*-butylstyrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 150:1) to afford the title compound as a colorless oil in 76% yield (199.6 mg, 91% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 83% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.3; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.89(s, 1H), 7.88 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.53 – 7.49 (m, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.27 – 7.22 (m, 3H), 5.85 (dd, *J* = 10.2, 5.2 Hz, 1H), 4.07 (dd, *J* = 13.1, 10.2 Hz, 1H), 3.62 (dd, *J* = 13.1, 5.2 Hz, 1H), 1.28 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 151.8, 146.4, 135.7, 134.0, 131.6, 130.2 (q, *J*<sub>C-F</sub> = 32.4 Hz), 129.3, 129.1, 127.7, 126.7, 126.3, 125.9, 124.2 (q, *J*<sub>C-F</sub> = 270.4 Hz), 69.5, 34.6, 32.9, 31.3; **HRMS** (ESI) calcd for C<sub>27</sub>H<sub>27</sub>F<sub>3</sub>N<sub>3</sub>Se [M+H]<sup>+</sup>: 530.1317, found: 530.1319.

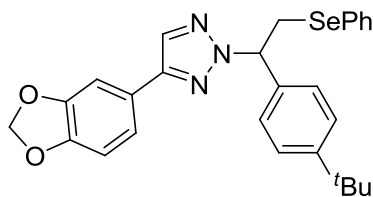
**2-(1-(4-*tert*-butylphenyl)-2-(phenylselanyl)ethyl)-4-(4-nitrophenyl)-2H-1,2,3-triazole (3j)**



4-(4-nitrophenyl)-1,2,3-triazole (95.0 mg, 0.5 mmol) was reacted with 4-*t*-butylstyrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 100:1) to afford the title compound as a pale yellow oil in 80% yield (202.4 mg, 91% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 88% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 10:1): 0.6; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.27 (d, *J* = 9.0 Hz, 2H), 7.92 (s, 1H), 7.91 (d, *J* = 8.8 Hz, 2H), 7.52 – 7.47 (m, 2H), 7.37 – 7.30 (m, 4H), 7.26 – 7.22 (m, 3H), 5.85 (dd, *J* = 10.3, 5.0 Hz, 1H), 4.06 (dd, *J* = 13.1, 10.3 Hz, 1H), 3.62 (dd, *J* = 13.2, 5.1 Hz, 1H), 1.28 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 151.9, 147.5, 145.5, 136.8, 135.5, 134.0, 132.1, 129.3, 129.0, 127.8, 126.7, 126.6, 125.9, 124.3, 69.8, 34.7, 32.9, 31.3; **HRMS** (ESI) calcd for C<sub>26</sub>H<sub>27</sub>N<sub>4</sub>O<sub>2</sub>Se [M+H]<sup>+</sup>: 507.1294, found: 507.1295.

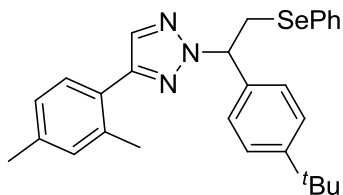
**4-(benzo[*d*][1,3]dioxol-5-yl)-2-(1-(4-*tert*-butylphenyl)-2-(phenylselanyl)ethyl)-2*H*-1,2,3-triazole (3k)**



4-(benzo[*d*][1,3]dioxol-5-yl)-1,2,3-triazole (94.5 mg, 0.5 mmol) was reacted with 4-*t*-butylstyrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 30:1) to afford the title compound as a white solid (m. p. 67 – 69 °C) in 82% yield (206.1 mg, 95% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 86% N<sup>2</sup>-selectivity.

**R<sub>f</sub>** (petroleum ether: EtOAc = 10:1): 0.5; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.72 (s, 1H), 7.52 – 7.47 (m, 2H), 7.34 – 7.21 (m, 9H), 6.84 (d, *J* = 8.0 Hz, 1H), 5.98 (s, 2H), 5.78 (dd, *J* = 10.0, 5.3 Hz, 1H), 4.02 (dd, *J* = 13.0, 10.0 Hz, 1H), 3.59 (dd, *J* = 13.0, 5.3 Hz, 1H), 1.26 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 151.5, 148.2, 147.8, 147.5, 135.9, 133.9, 130.7, 129.3, 129.2, 127.6, 126.6, 125.8, 124.8, 119.8, 108.7, 106.7, 101.3, 69.1, 34.6, 33.0, 31.3; **HRMS** (ESI) calcd for C<sub>27</sub>H<sub>28</sub>N<sub>3</sub>O<sub>2</sub>Se [M+H]<sup>+</sup>: 506.1341, found: 506.1344.

**2-(1-(4-*tert*-butylphenyl)-2-(phenylselanyl)ethyl)-4-(2,4-dimethylphenyl)-2*H*-1,2,3-triazole (3l)**

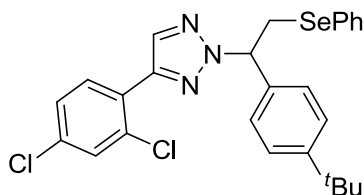


4-(2,4-dimethylphenyl)-1,2,3-triazole (86.6 mg, 0.5 mmol) was reacted with 4-*t*-butylstyrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc

= 150:1) to afford the title compound as a colorless oil in 70% yield (172.0 mg, 80% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 88% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.6; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.72 (s, 1H), 7.63 – 7.46 (m, 3H), 7.45 – 7.29 (m, 4H), 7.29 – 7.18 (m, 3H), 7.14 – 6.99 (m, 2H), 5.84 (dd, *J* = 10.3, 5.5 Hz, 1H), 4.06 (dd, *J* = 13.1, 10.0 Hz, 1H), 3.62 (dd, *J* = 13.1, 5.4 Hz, 1H), 2.47 (s, 3H), 2.36 (s, 3H), 1.29 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 151.5, 147.6, 138.2, 136.0, 133.9, 133.2, 131.9, 129.4, 129.3, 129.1, 127.6, 127.1, 126.7, 125.8, 69.0, 34.7, 33.2, 31.4, 21.4, 21.3; **HRMS** (ESI) calcd for C<sub>28</sub>H<sub>32</sub>N<sub>3</sub>Se [M+H]<sup>+</sup>: 490.1756, found: 490.1758.

**2-(1-(4-*tert*-butylphenyl)-2-(phenylselanyl)ethyl)-4-(2,4-dichlorophenyl)-2H-1,2,3-triazole (3m)**

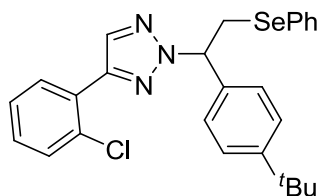


4-(2,4-dichlorophenyl)-1,2,3-triazole (106.0 mg, 0.5 mmol) was reacted with 4-*t*-butylstyrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 200:1) to afford the title compound as a white solid (m. p. 39 – 41 °C) in 68% yield (180.1 mg, 84% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 81% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.7; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.13 (s, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.50 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.47 (d, *J* = 2.1 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.32 – 7.28 (m, 3H), 7.26 – 7.22 (m, 3H), 5.84 (dd, *J* = 10.1, 5.3 Hz, 1H), 4.05 (dd, *J* = 13.1, 10.1 Hz, 1H), 3.62 (dd, *J* = 13.1, 5.3 Hz, 1H), 1.28 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 151.7, 144.0, 135.7, 134.5, 134.2, 133.9, 132.7,

131.3, 130.2, 129.3, 129.2, 128.1, 127.7, 127.5, 126.7, 125.9, 69.5, 34.7, 33.0, 31.4; **HRMS** (ESI) calcd for  $C_{26}H_{26}Cl_2N_3Se$   $[M+H]^+$ : 530.0664, found: 530.0648.

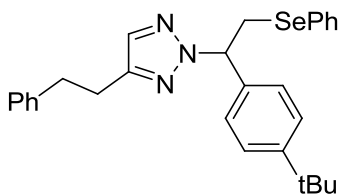
**2-(1-(4-*tert*-butylphenyl)-2-(phenylselanyl)ethyl)-4-(2-chlorophenyl)-2*H*-1,2,3-triazole (3n)**



4-(2-chlorophenyl)-1,2,3-triazole (89.9 mg, 0.5 mmol) was reacted with 4-*t*-butylstyrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 150:1) to afford the title compound as a colorless oil in 71% yield (176.8 mg, 85% yield in total of  $N^2$  and  $N^1$  isomers) and 84%  $N^2$ -selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.4;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ ):  $\delta$  8.15 (s, 1H), 7.88 (dd,  $J = 7.7$ , 1.9 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.45 (dd,  $J = 7.7$ , 1.5 Hz, 1H), 7.35 (d,  $J = 8.8$  Hz, 2H), 7.33 – 7.29 (m, 3H), 7.28 – 7.23 (m, 4H), 5.85 (dd,  $J = 10.0$ , 5.4 Hz, 1H), 4.06 (dd,  $J = 13.0$ , 10.0 Hz, 1H), 3.63 (dd,  $J = 13.0$ , 5.4 Hz, 1H), 1.28 (s, 9H);  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ ):  $\delta$  151.6, 144.9, 135.8, 134.3, 133.9, 132.2, 130.6, 130.5, 129.4, 129.4, 129.3, 129.3, 127.7, 127.1, 126.7, 125.8, 69.3, 34.7, 33.0, 31.4; **HRMS** (ESI) calcd for  $C_{26}H_{26}ClN_3Se$   $[M+H]^+$ : 496.1053, found: 496.1059.

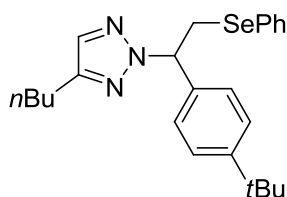
**2-(1-(4-*tert*-butylphenyl)-2-(phenylselanyl)ethyl)-4-phenethyl-2*H*-1,2,3-triazole (3o)**



4-phenethyl-1,2,3-triazole (89.9 mg, 0.5 mmol) was reacted with 4-*t*-butylstyrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 100:1) to afford the title compound as a colorless oil in 83% yield (202.2 mg, 89% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 93% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.4; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.52 (dd, *J* = 6.3, 3.0 Hz, 2H), 7.36 – 7.18 (m, 13H), 5.75 (dd, *J* = 10.1, 5.3 Hz, 1H), 4.00 (dd, *J* = 12.9, 10.1 Hz, 1H), 3.57 (dd, *J* = 13.0, 5.3 Hz, 1H), 2.99 (s, 4H), 1.30 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 151.4, 147.73, 141.2, 136.2, 133.8, 132.9, 129.5, 129.2, 128.6, 128.5, 127.6, 126.6, 126.2, 125.7, 68.7, 35.6, 34.7, 33.0, 31.4, 27.6; **HRMS** (ESI) calcd for C<sub>28</sub>H<sub>32</sub>N<sub>3</sub>Se [M+H]<sup>+</sup>: 490.1756, found: 490.1766.

#### 4-butyl-2-(1-(4-*tert*-butylphenyl)-2-(phenylselanyl)ethyl)-2*H*-1,2,3-triazole (3p)

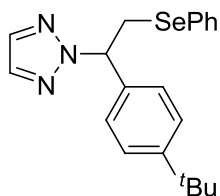


4-butyl-1,2,3-triazole (62.6 mg, 0.5 mmol) was reacted with 4-*t*-butylstyrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 150:1) to afford the title compound as a colorless oil in 62% yield (137.2 mg, 67% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 93% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.5; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.53 – 7.45 (m, 2H), 7.36 (s, 1H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.27 – 7.19 (m, 5H), 5.73 (dd, *J* = 9.9, 5.5 Hz, 1H), 3.97 (dd, *J* = 12.9, 9.9 Hz, 1H), 3.55 (dd, *J* = 12.9, 5.5 Hz, 1H), 2.76 – 2.54 (m, 2H), 1.66 – 1.59 (m, 2H), 1.42 – 1.33 (m, 2H), 1.27 (s, 9H), 0.93 (t, *J* = 7.3 Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 151.3, 148.7, 136.1, 133.7, 132.6, 129.4,

129.1, 127.5, 126.5, 125.6, 68.6, 34.6, 33.0, 31.4, 31.3, 25.3, 22.4, 13.9; **HRMS** (ESI) calcd for  $C_{24}H_{32}N_3Se$   $[M+H]^+$ : 442.1756, found: 442.1758.

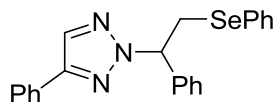
**2-(1-(4-*tert*-butylphenyl)-2-(phenylselanyl)ethyl)-2*H*-1,2,3-triazole (3q)**



1,2,3-triazole (59.6mg, 0.5 mmol) was reacted with 4-*t*-butylstyrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 100:1) to afford the title compound as a white solid (51 – 53 °C) in 77% yield (147.3 mg, 97% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 79% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.5; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.65 (s, 2H), 7.53 (dd,  $J$  = 6.4, 3.1 Hz, 2H), 7.35 (d,  $J$  = 8.4 Hz, 2H), 7.30 – 7.28 (m, 5H), 5.84 (dd,  $J$  = 10.0, 5.4 Hz, 1H), 4.03 (dd,  $J$  = 13.0, 10.0 Hz, 1H), 3.62 (dd,  $J$  = 13.0, 5.4 Hz, 1H), 1.30 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  151.6, 135.8, 134.3, 133.9, 129.3, 129.3, 127.7, 126.6, 125.8, 68.9, 34.7, 32.9, 31.3; **HRMS** (ESI) calcd for  $C_{20}H_{24}N_3Se$   $[M+H]^+$ : 386.1130, found: 386.1130.

**4-phenyl-2-(1-phenyl-2-(phenylselanyl)ethyl)-2*H*-1,2,3-triazole (3r)**

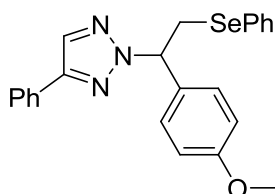


4-phenyl-1,2,3-triazole (72.6 mg, 0.5 mmol) was reacted with styrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 100:1) to afford

the title compound as a white solid (m. p. 60 – 62 °C) in 78% yield (157.7 mg, 92% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 85% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.4; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.83 (s, 1H), 7.76 (d, *J* = 7.1 Hz, 2H), 7.53 – 7.48 (m, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.37 – 7.19 (m, 9H), 5.83 (dd, *J* = 9.9, 5.5 Hz, 1H), 4.05 (dd, *J* = 13.0, 9.9 Hz, 1H), 3.61 (dd, *J* = 13.0, 5.5 Hz, 1H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 147.8, 138.9, 133.9, 131.2, 130.5, 129.3, 129.2, 128.9, 128.8, 128.6, 128.5, 127.7, 126.9, 126.1, 69.4, 33.0; **HRMS** (ESI) calcd for C<sub>22</sub>H<sub>20</sub>N<sub>3</sub>Se [M+H]<sup>+</sup>: 406.0817, found: 406.0822.

### 2-(1-(4-methoxyphenyl)-2-(phenylselanyl)ethyl)-4-phenyl-2H-1,2,3-triazole (3s)

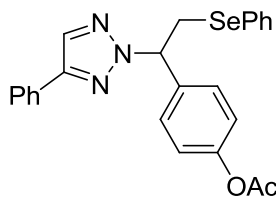


4-phenyl-1,2,3-triazole (72.6 mg, 0.5 mmol) was reacted with 4-methoxystyrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 100:1) to afford the title compound as a colorless oil in 82% yield (177.9 mg, 91% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 90% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.3; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.82 (s, 1H), 7.76 (d, *J* = 7.1 Hz, 2H), 7.55 – 7.47 (m, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.36 – 7.29 (m, 3H), 7.27 – 7.22 (m, 3H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.78 (dd, *J* = 9.5, 5.9 Hz, 1H), 4.01 (dd, *J* = 12.9, 9.6 Hz, 1H), 3.76 (s, 3H), 3.62 (dd, *J* = 12.9, 5.9 Hz, 1H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 159.7, 147.6, 133.8, 131.0, 130.9, 130.5, 129.2, 128.8, 128.4, 128.3, 127.6, 126.0, 114.1, 68.8, 55.3, 32.9; **HRMS** (ESI) calcd for C<sub>23</sub>H<sub>22</sub>N<sub>3</sub>OSe [M+H]<sup>+</sup>: 436.0923, found: 436.0931.



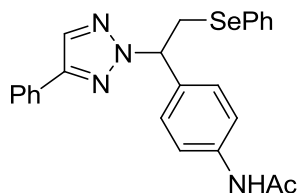
#### 4-(1-(4-phenyl-2H-1,2,3-triazol-2-yl)-2-(phenylselanyl)ethyl)phenyl acetate (3t)



4-phenyl-1,2,3-triazole (72.6 mg, 0.5 mmol) was reacted with 4-vinylphenyl acetate according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 50:1) to afford the title compound as a colorless oil in 82% yield (189.1 mg, 94% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 87% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 5:1): 0.5; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.83 (s, 1H), 7.76 (d,  $J$  = 7.1 Hz, 2H), 7.54 – 7.46 (m, 2H), 7.43 – 7.36 (m, 4H), 7.36 – 7.30 (m, 1H), 7.27 – 7.21 (m, 3H), 7.03 (d,  $J$  = 8.6 Hz, 2H), 5.82 (dd,  $J$  = 9.9, 5.4 Hz, 1H), 4.03 (dd,  $J$  = 13.1, 9.9 Hz, 1H), 3.58 (dd,  $J$  = 13.1, 5.4 Hz, 1H), 2.25 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  169.3, 150.7, 147.9, 136.4, 133.9, 131.2, 130.4, 129.2, 129.0, 128.8, 128.5, 128.2, 127.7, 126.1, 121.9, 68.8, 32.9, 21.1; **HRMS** (ESI) calcd for C<sub>24</sub>H<sub>22</sub>N<sub>3</sub>O<sub>2</sub>Se [M+H]<sup>+</sup>: 464.0872, found: 464.0873.

#### N-(4-(1-(4-phenyl-2H-1,2,3-triazol-2-yl)-2-(phenylselanyl)ethyl)phenyl)acetamide (3u)

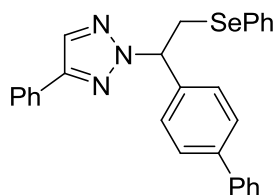


4-phenyl-1,2,3-triazole (72.6 mg, 0.5 mmol) was reacted with N-(4-vinylphenyl)acetamide according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc

= 3:1) to afford the title compound as a pale yellow oil in 61% yield (139.8mg, 73% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 83% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 3:1): 0.2; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.82 (s, 1H), 7.76 (d, *J* = 7.1 Hz, 2H), 7.53 – 7.48 (m, 2H), 7.43 – 7.39 (m, 4H), 7.38 – 7.28 (m, 4H), 7.24 – 7.23 (m, 2H), 5.78 (dd, *J* = 9.6, 5.8 Hz, 1H), 4.01 (dd, *J* = 13.0, 9.7 Hz, 1H), 3.59 (dd, *J* = 13.0, 5.8 Hz, 1H), 2.63 (br, 1H), 2.13 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 168.3, 147.8, 138.1, 134.6, 133.8, 131.1, 130.4, 129.2, 129.1, 128.8, 128.4, 127.7, 127.6, 126.0, 120.0, 68.8, 32.8, 24.6; **HRMS** (ESI) calcd for C<sub>24</sub>H<sub>23</sub>N<sub>4</sub>OSe [M+H]<sup>+</sup>: 463.1032, found: 463.1032.

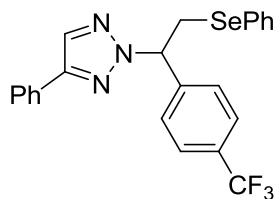
### 2-(1-(biphenyl-4-yl)-2-(phenylselanyl)ethyl)-4-phenyl-2H-1,2,3-triazole (3v)



4-phenyl-1,2,3-triazole (72.6 mg, 0.5 mmol) was reacted with 4-phenylstyrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 100:1) to afford the title compound as a white solid (m. p. 95 – 97 °C) in 77% yield (184.0 mg, 83% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 93% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.4; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.84 (s, 1H), 7.78 (d, *J* = 7.1 Hz, 2H), 7.55 – 7.48 (m, 6H), 7.46 – 7.35 (m, 6H), 7.35 – 7.26 (m, 2H), 7.26 – 7.20 (m, 3H), 5.88 (dd, *J* = 9.6, 5.7 Hz, 1H), 4.07 (dd, *J* = 13.0, 9.7 Hz, 1H), 3.66 (dd, *J* = 13.0, 5.7 Hz, 1H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 147.9, 141.5, 140.5, 137.8, 133.9, 131.3, 130.5, 129.3, 129.2, 128.9, 128.8, 128.5, 127.7, 127.6, 127.5, 127.2, 126.1, 69.2, 32.9; **HRMS** (ESI) calcd for C<sub>28</sub>H<sub>24</sub>N<sub>3</sub>Se [M+H]<sup>+</sup>: 482.1130, found: 482.1120.

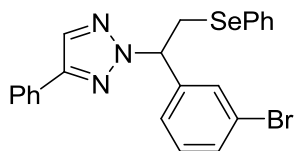
#### 4-phenyl-2-(2-(phenylselanyl)-1-(4-(trifluoromethyl)phenyl)ethyl)-2H-1,2,3-triazole (3w)



4-phenyl-1,2,3-triazole (72.6 mg, 0.5 mmol) was reacted with 4-trifluoromethylstyrene at 70 °C according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 150:1) to afford the title compound as a white solid (m. p. 60 – 62 °C) in 70% yield (166.3 mg, 80% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 88% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 10:1): 0.6; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.85 (s, 1H), 7.76 (d, *J* = 7.1 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.51 – 7.38 (m, 6H), 7.36 – 7.32 (m, 1H), 7.28 – 7.20 (m, 3H), 5.87 (dd, *J* = 9.2, 6.2 Hz, 1H), 4.01 (dd, *J* = 13.1, 9.2 Hz, 1H), 3.62 (dd, *J* = 13.1, 6.1 Hz, 1H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 148.1, 142.5, 134.0, 131.4, 130.73 (q, *J*<sub>C-F</sub> = 32.4 Hz), 130.2, 129.3, 128.9, 128.8, 128.6, 127.9, 127.5, 126.1, 125.8 (q, *J*<sub>C-F</sub> = 3.7 Hz), 123.9 (q, *J*<sub>C-F</sub> = 270.6 Hz), 68.83, 32.52; **HRMS** (ESI) calcd for C<sub>23</sub>H<sub>19</sub>F<sub>3</sub>N<sub>3</sub>Se [M+H]<sup>+</sup>: 474.0691, found: 474.0699.

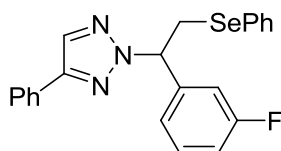
#### 2-(1-(3-bromophenyl)-2-(phenylselanyl)ethyl)-4-phenyl-2H-1,2,3-triazole (3x)



4-phenyl-1,2,3-triazole (72.6 mg, 0.5 mmol) was reacted with 3-bromostyrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 100:1) to afford the title compound as a white solid (m. p. 44 – 46 °C) in 79% yield (191.4 mg, 91% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 87% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.3; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.84 (s, 1H), 7.76 (d, *J* = 7.1 Hz, 2H), 7.50 – 7.48 (m, 3H), 7.44 – 7.37 (m, 3H), 7.36 – 7.31 (m, 1H), 7.27 – 7.21 (m, 4H), 7.15 (t, *J* = 7.9 Hz, 1H), 5.76 (dd, *J* = 9.6, 5.8 Hz, 1H), 3.99 (dd, *J* = 13.1, 9.6 Hz, 1H), 3.58 (dd, *J* = 13.1, 5.8 Hz, 1H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 148.0, 140.9, 134.0, 131.7, 131.4, 130.4, 130.3, 130.1, 129.3, 128.9, 128.8, 128.6, 127.8, 126.1, 125.7, 122.8, 68.7, 32.6; **HRMS** (ESI) calcd for C<sub>22</sub>H<sub>19</sub>BrN<sub>3</sub>Se [M+H]<sup>+</sup>: 483.9922, found: 483.9925.

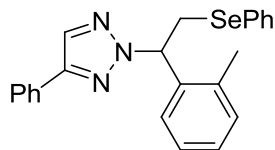
### 2-(1-(3-fluorophenyl)-2-(phenylselanyl)ethyl)-4-phenyl-1,2,3-triazole (3y)



4-phenyl-1,2,3-triazole (72.6 mg, 0.5 mmol) was reacted with 3-fluorostyrene at 70 °C according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 100:1) to afford the title compound as a white solid (m. p. 43 – 45 °C) in 77% yield (163.5 mg, 90% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 86% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.3; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.84 (s, 1H), 7.76 (d, *J* = 7.1 Hz, 2H), 7.50 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.40 (t, *J* = 8.1 Hz, 2H), 7.36 – 7.29 (m, 1H), 7.30 – 7.19 (m, 4H), 7.14 – 7.04 (m, 2H), 7.00 – 6.91 (m, 1H), 5.81 (dd, *J* = 9.6, 5.7 Hz, 1H), 4.00 (dd, *J* = 13.1, 9.7 Hz, 1H), 3.59 (dd, *J* = 13.1, 5.7 Hz, 1H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 162.9 (d, *J*<sub>C-F</sub> = 245.6 Hz), 148.0, 141.2 (d, *J*<sub>C-F</sub> = 7.0 Hz), 134.0, 131.3, 130.4, 130.3, 129.3, 128.9, 128.8, 128.6, 127.8, 126.1, 122.7 (d, *J*<sub>C-F</sub> = 3.0 Hz), 115.5 (d, *J*<sub>C-F</sub> = 21.0 Hz), 114.1 (d, *J*<sub>C-F</sub> = 22.4 Hz), 68.8, 32.7; **HRMS** (ESI) calcd for C<sub>22</sub>H<sub>19</sub>FN<sub>3</sub>Se [M+H]<sup>+</sup>: 424.0723, found: 424.0715.

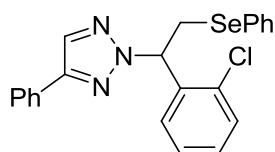
#### 4-phenyl-2-(2-(phenylselanyl)-1-*o*-tolylethyl)-2*H*-1,2,3-triazole (3z)



4-phenyl-1,2,3-triazole (72.6 mg, 0.5 mmol) was reacted with 2-methylstyrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 100:1) to afford the title compound as a colorless oil in 70% yield (147.4 mg, 87% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 81% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.4; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84 (s, 1H), 7.78 (d, *J* = 7.1 Hz, 2H), 7.61 – 7.51 (m, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.38 – 7.30 (m, 2H), 7.28 – 7.23 (m, 3H), 7.18 – 7.07 (m, 3H), 6.10 (dd, *J* = 10.2, 4.9 Hz, 1H), 4.03 (dd, *J* = 13.1, 10.2 Hz, 1H), 3.49 (dd, *J* = 13.1, 4.9 Hz, 1H), 2.24 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 147.7, 137.2, 135.3, 134.4, 131.1, 130.7, 130.6, 129.2, 129.2, 128.8, 128.4, 128.3, 127.8, 126.6, 126.1, 65.2, 32.6, 19.1; **HRMS** (ESI) calcd for C<sub>23</sub>H<sub>22</sub>N<sub>3</sub>Se [M+H]<sup>+</sup>: 420.0973, found: 420.0982.

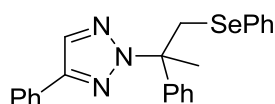
#### 2-(1-(2-chlorophenyl)-2-(phenylselanyl)ethyl)-4-phenyl-2*H*-1,2,3-triazole (3aa)



4-phenyl-1,2,3-triazole (72.6 mg, 0.5 mmol) was reacted with 2-chlorostyrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 100:1) to afford the title compound as a colorless oil in 73% yield (159.9 mg, 90% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 81% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.4; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.89 (s, 1H), 7.80 (d, *J* = 7.1 Hz, 2H), 7.62 – 7.51 (m, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.24 (m, 4H), 7.21 – 7.14 (m, 2H), 6.39 (dd, *J* = 10.5, 4.4 Hz, 1H), 3.94 (dd, *J* = 13.1, 10.5 Hz, 1H), 3.58 (dd, *J* = 13.2, 4.4 Hz, 1H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 148.0, 136.8, 134.4, 132.5, 131.3, 130.4, 129.8, 129.5, 129.1, 129.0, 128.9, 128.5, 127.8, 127.7, 127.4, 126.1, 65.7, 32.0; **HRMS** (ESI) calcd for C<sub>22</sub>H<sub>19</sub>ClN<sub>3</sub>Se [M+H]<sup>+</sup>: 440.0427, found: 440.0429.

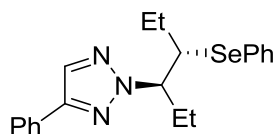
#### 4-phenyl-2-(2-phenyl-1-(phenylselanyl)propan-2-yl)-2*H*-1,2,3-triazole (3ab)



4-phenyl-1,2,3-triazole (72.6 mg, 0.5 mmol) was reacted with prop-1-en-2-ylbenzene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 100:1) to afford the title compound as a colorless oil in 66% yield (137.4 mg, 73% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 90% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.4; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.90 (s, 1H), 7.80 (d, *J* = 7.1 Hz, 2H), 7.50 – 7.45 (m, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.29 – 7.22 (m, 3H), 7.22 – 7.17 (m, 3H), 6.98 (dd, *J* = 8.0, 1.6 Hz, 2H), 4.29 (d, *J* = 12.7 Hz, 1H), 3.76 (d, *J* = 12.7 Hz, 1H), 2.25 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 147.3, 144.5, 133.6, 131.2, 130.9, 130.6, 129.0, 128.8, 128.5, 128.4, 127.7, 127.2, 126.1, 125.1, 71.2, 41.5, 26.4; **HRMS** (ESI) calcd for C<sub>23</sub>H<sub>22</sub>N<sub>3</sub>Se [M+H]<sup>+</sup>: 420.0973, found: 420.0969.

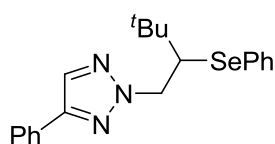
#### 4-phenyl-2-((3*R*\*,4*S*\*)-4-(phenylselanyl)hexan-3-yl)-2*H*-1,2,3-triazole (3ac)



4-phenyl-1,2,3-triazole (72.6 mg, 0.5 mmol) was reacted with (*E*)-hex-3-ene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 150:1) to afford the title compound as a colorless oil in 76% yield (145.2 mg, 83% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 91% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.6; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.81 (s, 1H), 7.77 (d, *J* = 7.1 Hz, 2H), 7.61 – 7.54 (m, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.29 – 7.24 (m, 3H), 4.56 (ddd, *J* = 11.1, 9.6, 3.2 Hz, 1H), 3.51 (ddd, *J* = 9.4, 7.9, 4.6 Hz, 1H), 2.55 – 2.45 (m, 1H), 2.23 – 2.12 (m, 1H), 1.40 – 1.26 (m, 2H), 1.04 (t, *J* = 7.2 Hz, 3H), 0.75 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 147.3, 135.0, 130.6, 130.5, 129.1, 128.8, 128.7, 128.3, 127.8, 126.0, 71.5, 52.8, 26.9, 25.0, 12.1, 10.8; **HRMS** (ESI) Calcd for C<sub>20</sub>H<sub>24</sub>N<sub>3</sub>Se [M+H]<sup>+</sup>: 386.1130, found: 386.1120.

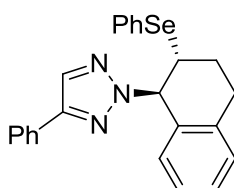
### 2-(3,3-dimethyl-2-(phenylselanyl)butyl)-4-phenyl-2*H*-1,2,3-triazole (3ad)



4-phenyl-1,2,3-triazole (72.6 mg, 0.5 mmol) was reacted with 3,3-dimethylbut-1-ene at 70 °C according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 100:1) to afford the title compound as a white solid (m. p. 85 – 87 °C) in 66% yield (126.9 mg, 71% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 93% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.4; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.76 – 7.61 (m, 3H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.34 – 7.31 (m, 3H), 7.13 – 7.01 (m, 3H), 4.97 (dd, *J* = 14.0, 4.8 Hz, 1H), 4.66 (dd, *J* = 14.0, 10.0 Hz, 1H), 3.81 (dd, *J* = 10.0, 4.8 Hz, 1H), 1.17 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 147.5, 134.0, 130.7, 130.5, 130.2, 128.8, 128.7, 128.3, 127.1, 126.0, 60.1, 57.7, 35.2, 28.5; **HRMS** (ESI) Calcd for C<sub>20</sub>H<sub>24</sub>N<sub>3</sub>Se [M+H]<sup>+</sup>: 386.1130, found: 386.1131.

**4-phenyl-2-((1*R*\*,2*R*\*)-2-(phenylselanyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-2*H*-1,2,3-triazole (3ae)**

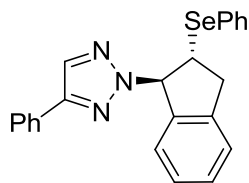


4-phenyl-1,2,3-triazole (72.6 mg, 0.5 mmol) was reacted with 1,2-dihydronaphthalene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 100:1) to afford the title compound as a colorless oil in 77% yield (164.6 mg, 85% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 90% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.3; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.84 (s, 1H), 7.79 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.70 – 7.55 (m, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.31 – 7.21 (m, 3H), 7.22 – 7.07 (m, 2H), 7.08 – 7.00 (m, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 5.93 (d, *J* = 9.7 Hz, 1H), 4.19 (ddd, *J* = 11.3, 9.2, 3.3 Hz, 1H), 3.44 – 3.03 (m, 1H), 2.96 (dt, *J* = 17.3, 5.3 Hz, 1H), 2.68 – 2.46 (m, 1H), 2.18 – 1.88 (m, 1H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 147.8, 136.2, 136.1, 133.9, 131.2, 130.6, 129.1, 129.1, 128.9, 128.5, 128.3, 128.1, 127.8, 126.7, 126.6, 126.1, 68.8, 44.2, 29.4, 29.3; **HRMS** (ESI) Calcd for C<sub>24</sub>H<sub>22</sub>N<sub>3</sub>Se [M+H]<sup>+</sup>: 432.0973, found: 432.0966.

**4-phenyl-2-((1*R*\*,2*R*\*)-2-(phenylselanyl)-2,3-dihydro-1*H*-inden-1-yl)-2*H*-1,2,3-triazole (3af)**

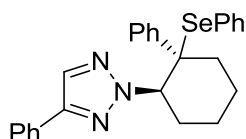




4-phenyl-1,2,3-triazole (72.6 mg, 0.5 mmol) was reacted with 1*H*-indene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 100:1) to afford the title compound as a pale pink solid (m. p. 62 – 64 °C) in 78% yield (163.0 mg, 87% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 90% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 10:1): 0.4; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.80 (s, 1H), 7.73 (d, *J* = 7.1 Hz, 2H), 7.59 – 7.50 (m, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.29 – 7.23 (m, 2H), 7.22 – 7.12 (m, 4H), 7.02 (d, *J* = 7.7 Hz, 1H), 6.18 (d, *J* = 7.1 Hz, 1H), 4.60 (dd, *J* = 15.2, 7.9 Hz, 1H), 3.67 (dd, *J* = 16.2, 8.0 Hz, 1H), 3.14 (dd, *J* = 16.2, 7.9 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 148.0, 141.5, 139.9, 135.3, 131.5, 130.4, 129.1, 129.1, 128.8, 128.4, 128.0, 127.6, 127.4, 126.0, 124.8, 124.3, 75.6, 45.3, 38.4; **HRMS** (ESI) Calcd for C<sub>23</sub>H<sub>20</sub>N<sub>3</sub>Se [M+H]<sup>+</sup>: 418.0817, found: 418.0822.

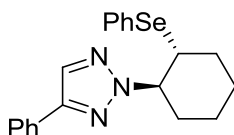
#### 4-phenyl-2-((1*R*\*,2*R*\*)-2-phenyl-2-(phenylselanyl)cyclohexyl)-2*H*-1,2,3-triazole (**3ag**)



4-phenyl-1,2,3-triazole (72.6 mg, 0.5 mmol) was reacted with cyclohexenylbenzene at 70 °C according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 200:1) to afford the title compound as a white solid (m. p. 82 – 83 °C) in 44% yield (101.9 mg, 63% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 70% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.5;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.85 (s, 1H), 7.79 (dd,  $J = 8.5$ , 1.5 Hz, 2H), 7.54 – 7.37 (m, 2H), 7.34 – 7.32 (m, 1H), 7.31 – 7.27 (m, 2H), 7.24 – 7.15 (m, 3H), 7.17 – 7.02 (m, 5H), 4.88 (d,  $J = 3.3$  Hz, 1H), 3.28 (d,  $J = 17.9$  Hz, 1H), 2.75 (td,  $J = 13.3$ , 4.1 Hz, 1H), 2.44 – 2.23 (m, 1H), 2.16 (dd,  $J = 16.6$ , 2.1 Hz, 1H), 2.00 – 1.80 (m, 1H), 1.81 – 1.58 (m, 1H), 1.53 (dd,  $J = 8.9$ , 7.7 Hz, 1H), 1.37 – 1.22 (m, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.3, 143.4, 135.0, 130.9, 130.8, 130.3, 128.9, 128.8, 128.4, 128.1, 127.7, 127.6, 126.1, 125.6, 72.1, 53.1, 30.3, 29.7, 21.6, 20.8; **HRMS** (ESI) Calcd for  $\text{C}_{26}\text{H}_{26}\text{N}_3\text{Se}$   $[\text{M}+\text{H}]^+$ : 460.1286, found: 460.1283.

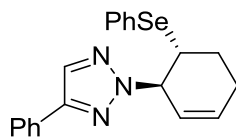
#### 4-phenyl-2-((1*R*\*,2*R*\*)-2-(phenylselanyl)cyclohexyl)-2H-1,2,3-triazole (3ah)



4-phenyl-1,2,3-triazole (72.6 mg, 0.5 mmol) was reacted with cyclohexene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 100:1) to afford the title compound as a colorless oil in 76% yield (146.1 mg, 84% yield in total of  $\text{N}^2$  and  $\text{N}^1$  isomers) and 91%  $\text{N}^2$ -selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.5;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.75 (d,  $J = 7.1$  Hz, 2H), 7.74 (s, 1H), 7.48 (dd,  $J = 8.0$ , 1.5 Hz, 2H), 7.41 (t,  $J = 7.5$  Hz, 2H), 7.32 (t,  $J = 7.4$  Hz, 1H), 7.23 – 7.13 (m, 3H), 4.51 (td,  $J = 11.4$ , 4.2 Hz, 1H), 3.78 – 3.66 (m, 1H), 2.37 – 2.32 (m, 1H), 2.22 – 2.17 (m, 1H), 2.03 (qd,  $J = 12.8$ , 3.8 Hz, 1H), 1.91 – 1.82 (m, 1H), 1.81 – 1.72 (m, 1H), 1.61 – 1.51 (m, 1H), 1.50 – 1.32 (m, 2H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.1, 136.3, 130.8, 130.4, 128.8, 128.7, 128.2, 127.9, 126.9, 126.0, 68.6, 46.9, 34.2, 34.1, 26.6, 24.9; **HRMS** (ESI) Calcd for  $\text{C}_{20}\text{H}_{22}\text{N}_3\text{Se}$   $[\text{M}+\text{H}]^+$ : 384.0973, found: 384.0982.

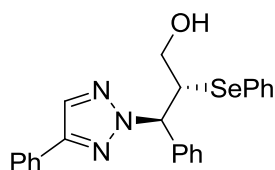
#### 4-phenyl-2-((1*R*\*,6*R*\*)-6-(phenylselanyl)cyclohex-2-enyl)-2*H*-1,2,3-triazole (3ai)



4-phenyl-1,2,3-triazole (72.6 mg, 0.5 mmol) was reacted with cyclohexa-1,3-diene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 200:1) to afford the title compound as a colorless oil in 83% yield (157.5 mg, 92% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 90% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 20:1): 0.4; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.79 (s, 1H), 7.77 (d, *J* = 7.1 Hz, 2H), 7.55 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.26 – 7.18 (m, 3H), 6.07 – 5.96 (m, 1H), 5.73 (dd, *J* = 10.0, 1.9 Hz, 1H), 5.39 – 5.24 (m, 1H), 3.94 (ddd, *J* = 11.2, 8.3, 3.0 Hz, 1H), 2.39 – 2.22 (m, 3H), 2.03 – 1.79 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 147.7, 135.7, 131.0, 130.9, 130.6, 128.9, 128.8, 128.3, 128.0, 127.1, 126.0, 125.0, 66.0, 43.6, 28.4, 25.1.

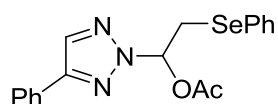
#### (2*R*\*,3*R*\*)-3-phenyl-3-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-2-(phenylselanyl)propan-1-ol (3aj)



4-phenyl-1,2,3-triazole (72.6 mg, 0.5 mmol) was reacted with cinnamic alcohol according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 10:1) to afford the title compound as a white solid (m. p. 43 – 45 °C) in 59% yield (127.1 mg, 65% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 90% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 3:1): 0.4; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.85 (s, 1H), 7.76 (d, *J* = 7.1 Hz, 2H), 7.45 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.41 (dt, *J* = 10.9, 4.3 Hz, 4H), 7.35 – 7.27 (m, 5H), 7.25 – 7.20 (m, 2H), 5.97 (d, *J* = 10.2 Hz, 1H), 4.25 (dt, *J* = 10.1, 4.1 Hz, 1H), 3.70 – 3.64 (m, 1H), 3.62 – 3.57 (m, 1H), 2.98 (dd, *J* = 7.7, 5.6 Hz, 1H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 148.0, 137.0, 135.7, 131.2, 130.1, 129.2, 128.9, 128.7, 128.6, 128.4, 128.1, 127.6, 126.1, 70.2, 61.5, 53.1; **HRMS** (ESI) calcd for C<sub>23</sub>H<sub>22</sub>N<sub>3</sub>OSe [M+H]<sup>+</sup>: 436.0923, found: 436.0918.

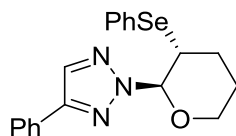
#### 1-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-2-(phenylselanyl)ethyl acetate (**3ak**)



4-phenyl-1,2,3-triazole (72.6 mg, 0.5 mmol) was reacted with vinyl acetate at 70 °C according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 20:1) to afford the title compound as a colorless oil in 63% yield (121.7 mg, 70% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 90% N<sup>2</sup>-selectivity.

**Rf** (petroleum ether: EtOAc = 3:1): 0.6; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.87 (s, 1H), 7.77 (d, *J* = 7.0 Hz, 2H), 7.58 – 7.51 (m, 2H), 7.43 (t, *J* = 7.3 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.29 – 7.23 (m, 3H), 7.13 (dd, *J* = 7.7, 6.2 Hz, 1H), 3.75 (dd, *J* = 13.3, 7.7 Hz, 1H), 3.64 (dd, *J* = 13.3, 6.2 Hz, 1H), 2.04 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 169.0, 148.8, 133.9, 132.3, 129.7, 129.3, 128.9, 128.9, 128.2, 127.9, 126.2, 83.9, 29.4, 20.7; **HRMS** (ESI) calcd for C<sub>18</sub>H<sub>18</sub>N<sub>3</sub>O<sub>2</sub>Se [M+H]<sup>+</sup>: 388.0559, found: 388.0552.

#### 4-phenyl-2-((2*R*\*,3*R*\*)-3-(phenylselanyl)tetrahydro-2*H*-pyran-2-yl)-2*H*-1,2,3-triazole (**3al**)

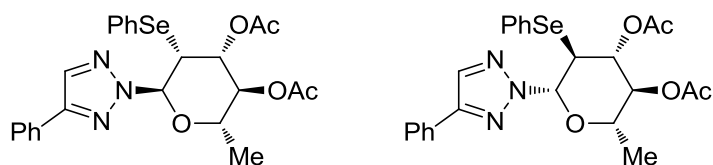


4-phenyl-1,2,3-triazole (72.6 mg, 0.5 mmol) was reacted with 3,4-dihydro-2*H*-pyran according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 80:1) to afford the title compound as a white solid (m. p. 58 – 60 °C) in 77% yield (148.8 mg, 88% yield in total of  $N^2$  and  $N^1$  isomers) and 88%  $N^2$ -selectivity.

**Rf** (petroleum ether: EtOAc = 10:1): 0.4;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.77 (s, 1H), 7.73 (dd,  $J = 8.5$ , 1.5 Hz, 2H), 7.46 (dd,  $J = 8.3$ , 1.5 Hz, 2H), 7.44 – 7.27 (m, 3H), 7.23 – 7.09 (m, 3H), 5.66 (d,  $J = 9.9$  Hz, 1H), 4.12 (ddd,  $J = 6.9$ , 4.4, 2.1 Hz, 1H), 4.06 – 3.91 (m, 1H), 3.65 (td,  $J = 11.9$ , 2.5 Hz, 1H), 2.55 – 2.42 (m, 1H), 2.13 – 1.86 (m, 1H), 1.80 – 1.66 (m, 2H);  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.3, 136.6, 131.8, 130.2, 128.9, 128.8, 128.7, 128.4, 126.3, 125.9, 93.2, 68.1, 42.3, 30.8, 26.6; **HRMS** (ESI) calcd for  $\text{C}_{19}\text{H}_{20}\text{N}_3\text{OSe}$  [ $\text{M}+\text{H}$ ] $^+$ : 386.0766, found: 386.0759.

**(2*S*\*,3*R*\*,4*R*\*,5*R*\*,6*R*\*)-4-methyl-6-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-5-(phenylselanyl)tetrahydro-2*H*-pyran-2,3-diyl diacetate (3am)**

**(2*S*\*,3*R*\*,4*R*\*,5*R*\*,6*R*\*)-4-methyl-6-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-5-(phenylselanyl)tetrahydro-2*H*-pyran-2,3-diyl diacetate (3an)**



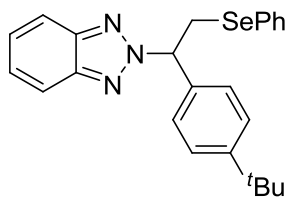
**3am, 3an**, 66% (dr = 1:1.2,  $N^2/N^1 > 95/5$ )

4-phenyl-1,2,3-triazole (108.8 mg, 0.75 mmol) was reacted with diacetyl-L-rhamnal (107.1 mg, 0.5 mmol) according at 70 °C to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 20:1) to afford the title compound as a pale yellow oil in 66% yield (76 mg of **3am**; 93 mg of **3an**) and N<sup>1</sup> isomers have not been found on crude <sup>1</sup>H NMR.

**3am: Rf** (petroleum ether: EtOAc = 3:1): 0.5; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.89 (s, 1H), 7.79 (d, *J* = 7.0 Hz, 2H), 7.54 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.27 – 7.20 (m, 3H), 6.35 (d, *J* = 3.9 Hz, 1H), 5.98 (dd, *J* = 7.4, 4.6 Hz, 1H), 5.16 (dd, *J* = 8.3, 7.7 Hz, 1H), 4.66 – 4.56 (m, 1H), 3.94 – 3.87 (m, 1H), 2.09 (s, 3H), 1.97 (s, 3H), 1.25 (d, *J* = 6.3 Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 170.0, 169.8, 148.4, 135.2, 132.0, 129.8, 129.3, 128.9, 128.9, 128.4, 127.7, 126.2, 89.0, 72.2, 71.7, 70.0, 45.0, 20.9, 20.7, 17.6; **HRMS** (ESI) calcd for C<sub>24</sub>H<sub>26</sub>N<sub>3</sub>O<sub>5</sub>Se [M+H]<sup>+</sup>: 516.1032, found: 516.1033.

**3an: Rf** (petroleum ether: EtOAc = 3:1): 0.4; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.88 (s, 1H), 7.74 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.48 – 7.45 (m, 2H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.22 (t, *J* = 7.2 Hz, 2H), 5.67 (d, *J* = 10.6 Hz, 1H), 5.25 (dd, *J* = 11.4, 9.0 Hz, 1H), 4.97 (t, *J* = 9.4 Hz, 1H), 4.19 – 4.08 (m, 1H), 3.70 – 3.63 (m, 1H), 2.12 (s, 3H), 2.06 (s, 3H), 1.22 (d, *J* = 6.2 Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 170.2, 169.9, 148.7, 136.9, 132.2, 129.8, 129.1, 128.9, 128.8, 128.8, 126.2, 124.6, 90.2, 74.3, 72.7, 72.4, 46.1, 20.9, 20.8, 17.3; **HRMS** calcd for C<sub>24</sub>H<sub>26</sub>N<sub>3</sub>O<sub>5</sub>Se [M+H]<sup>+</sup>: 516.1032, found: 516.1039.

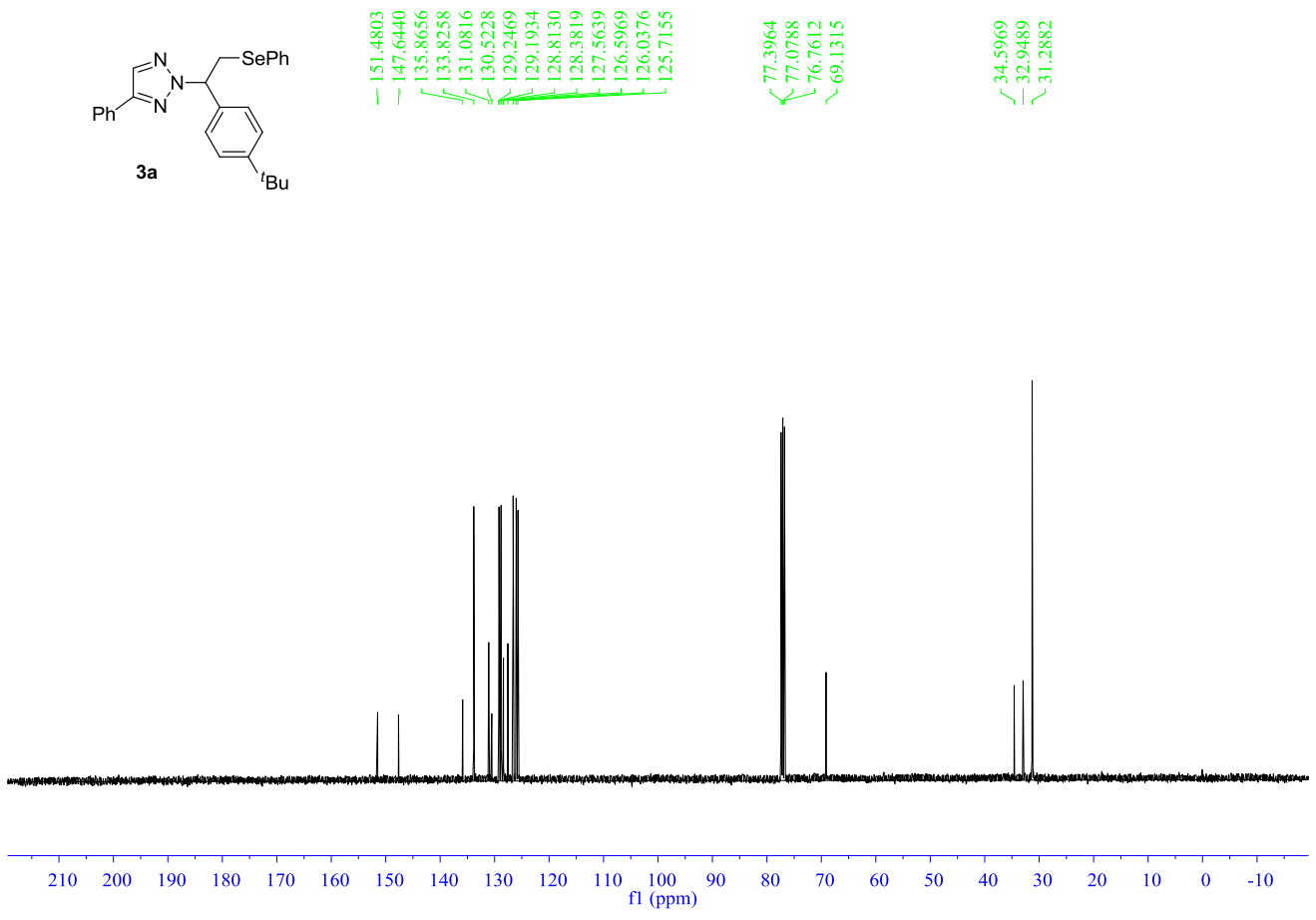
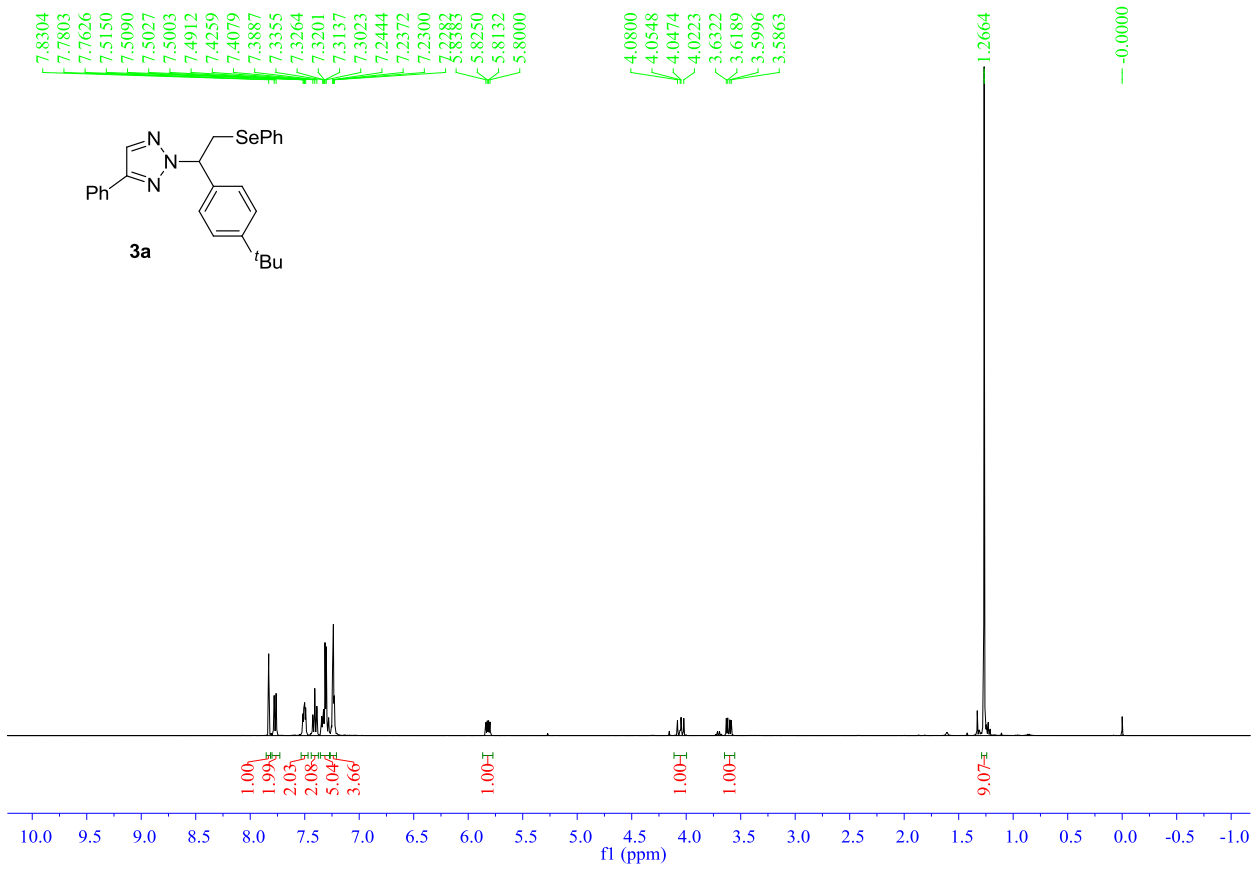
## **2-(1-(4-tert-butylphenyl)-2-(phenylselanyl)ethyl)-2H-benzo[d][1,2,3]triazole (5)**



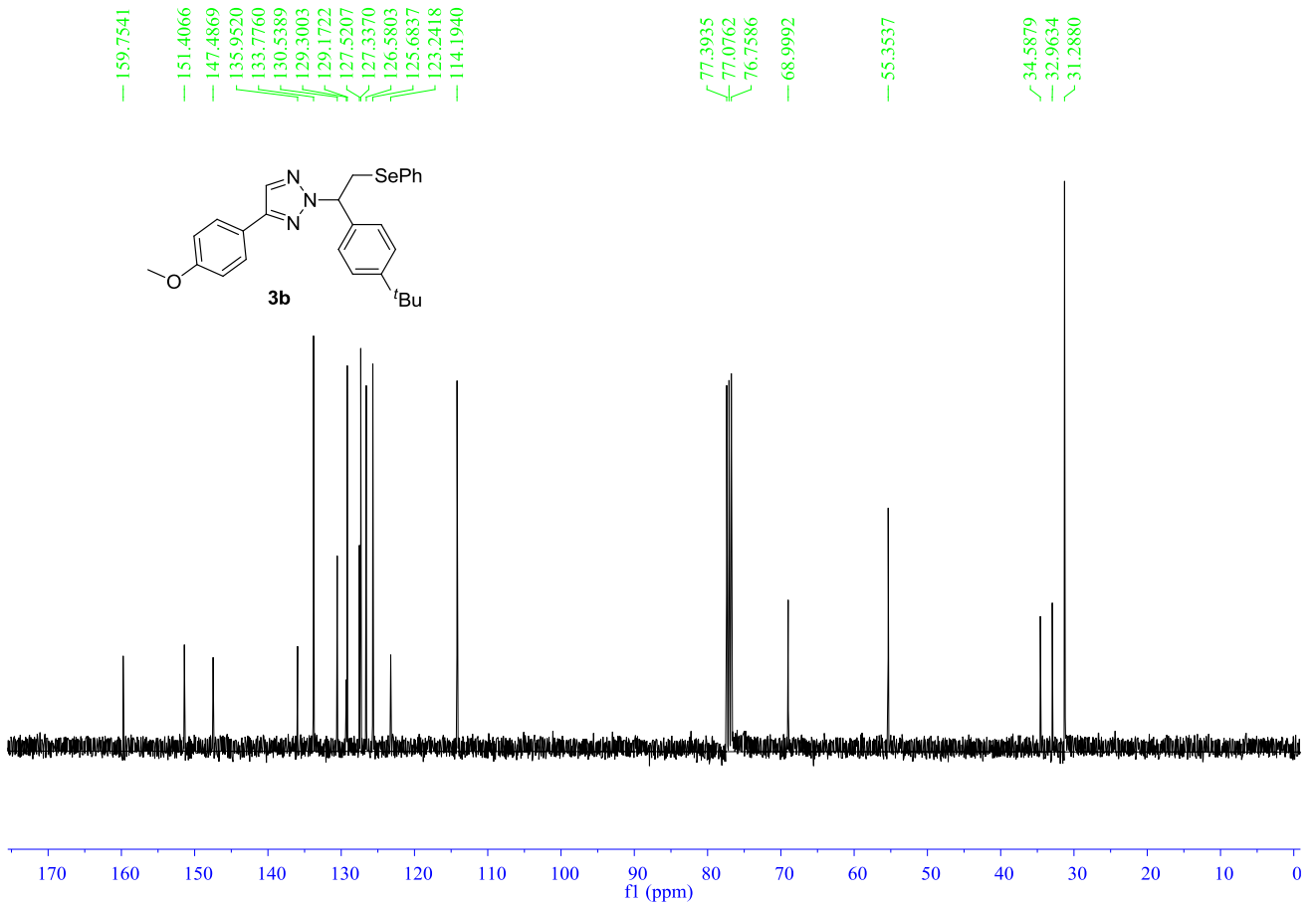
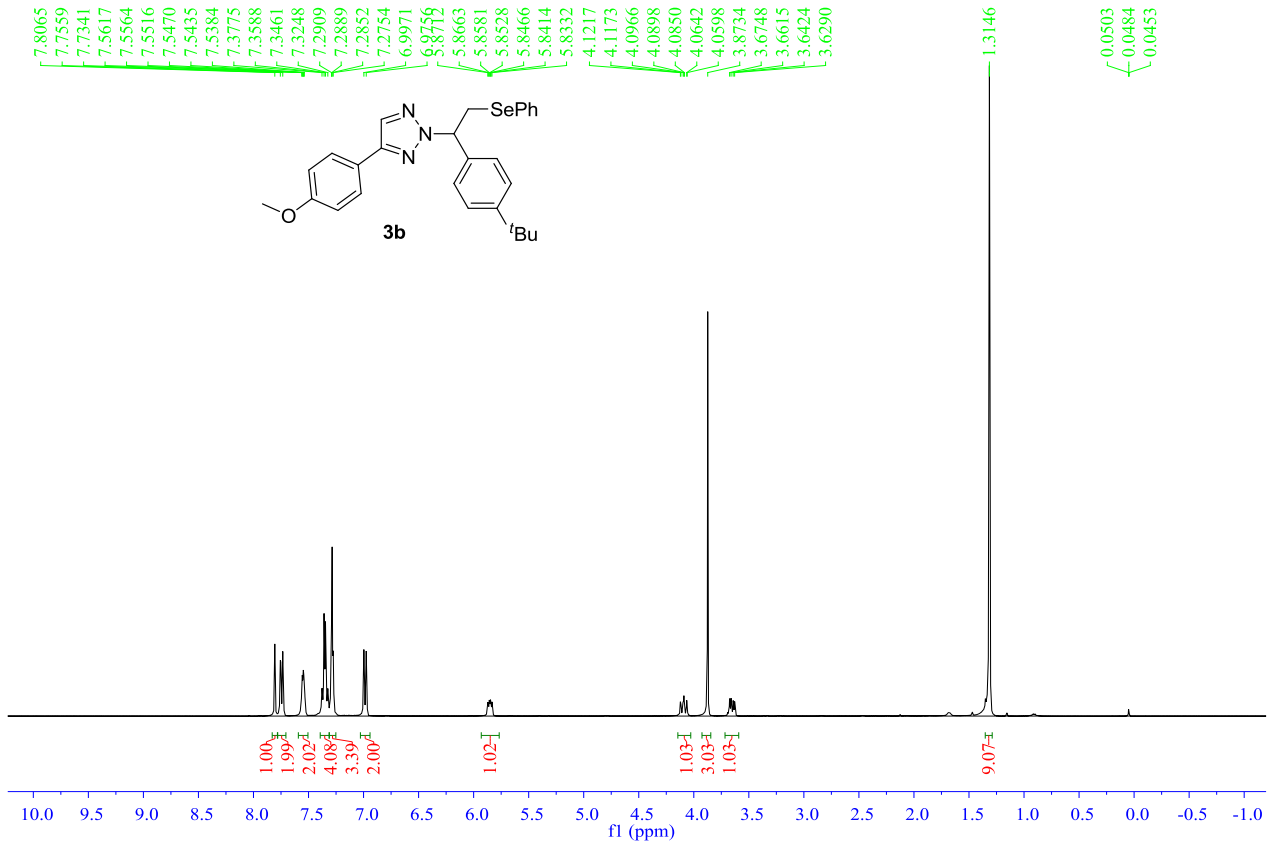
Benzotriazole (59.6mg, 0.5 mmol) was reacted with 4-*t*-butylstyrene according to General Procedure. The crude product was purified by column chromatography (petroleum ether: EtOAc = 200:1) to afford the title compound as a white solid (65 – 67 °C) in 69% yield (148.9 mg, 98% yield in total of N<sup>2</sup> and N<sup>1</sup> isomers) and 70% N<sup>2</sup>-selectivity.

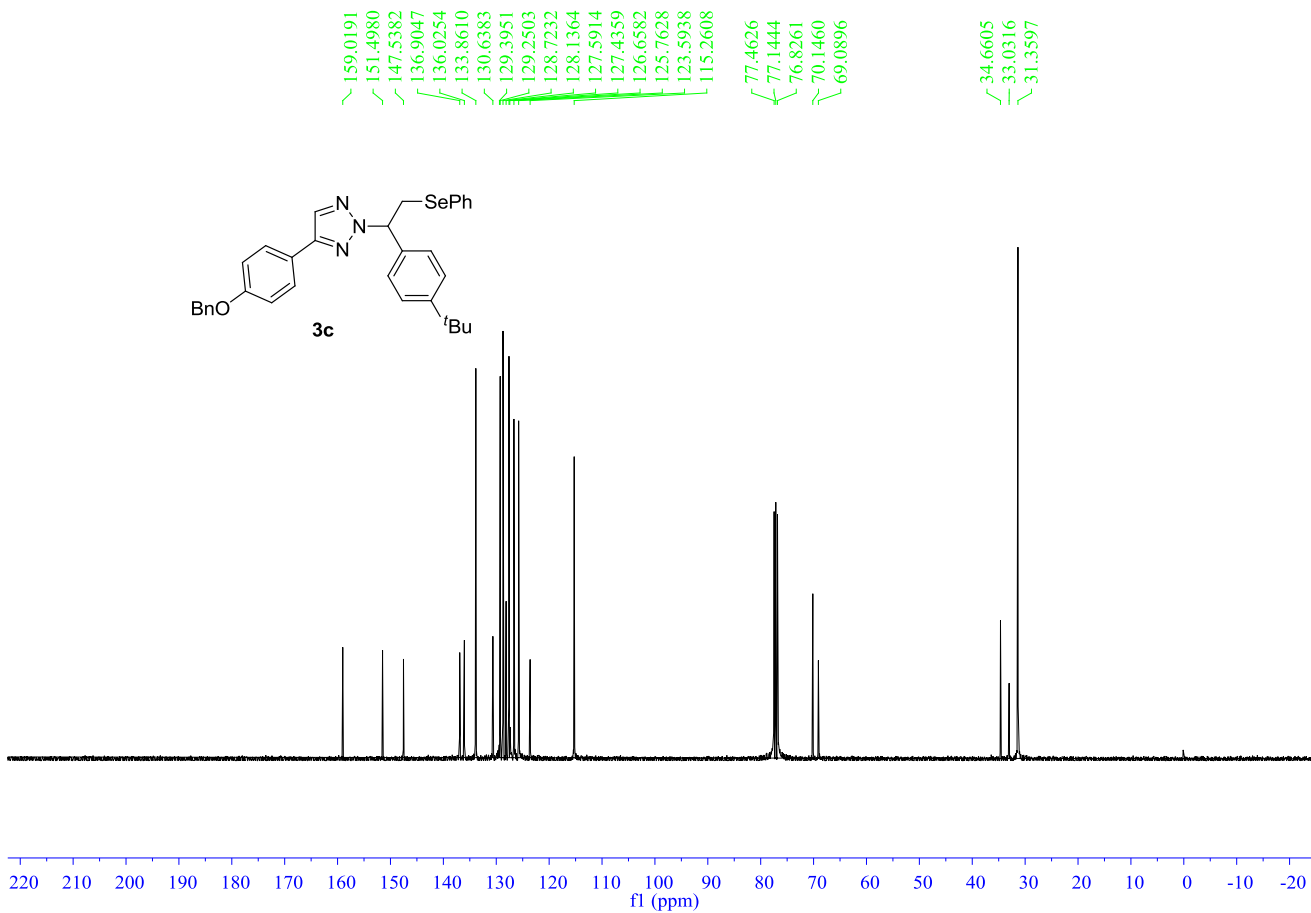
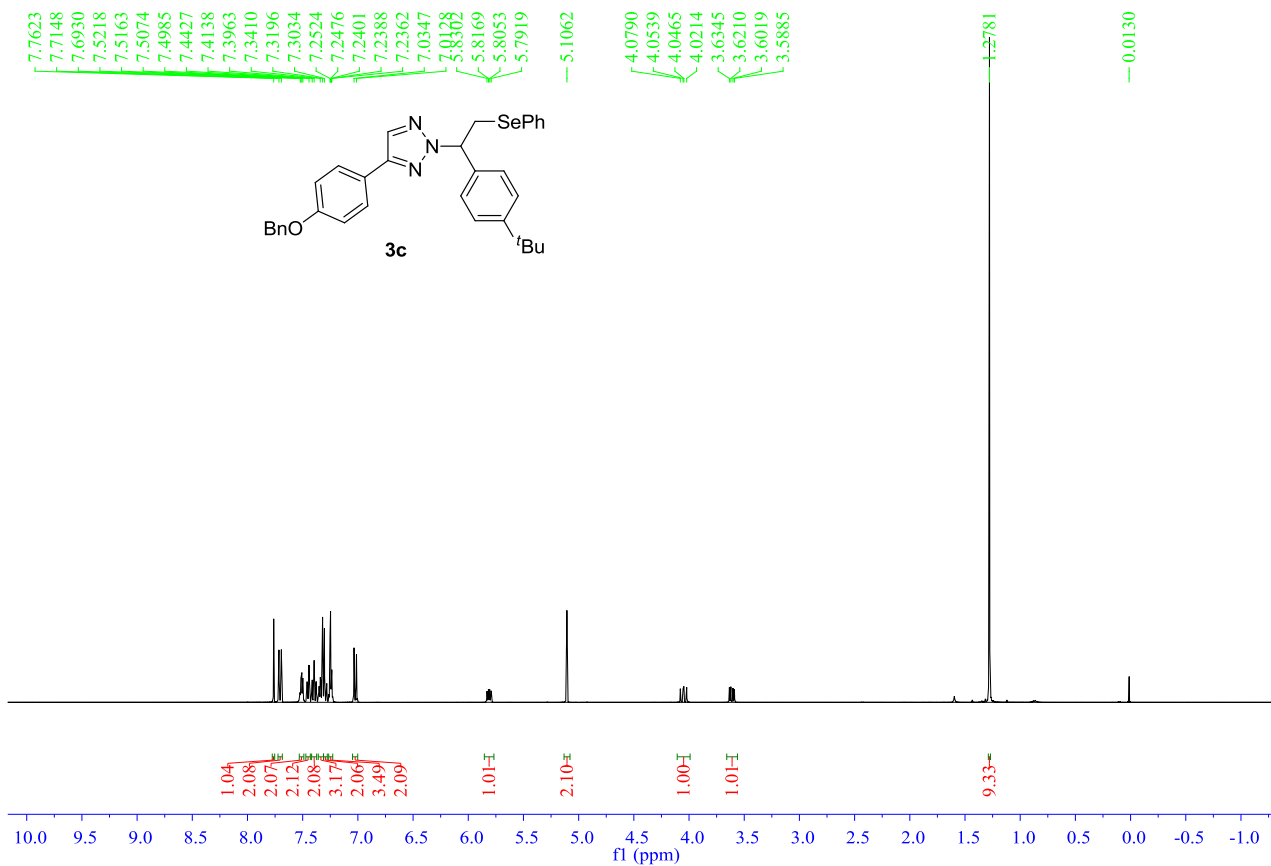
**Rf** (petroleum ether: EtOAc = 10:1): 0.6; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.87 – 7.79 (m, 2H), 7.51 – 7.44 (m, 2H), 7.38 – 7.30 (m, 6H), 7.23 – 7.16 (m, 3H), 6.08 (dd, *J* = 9.9, 5.4 Hz, 1H), 4.20 (dd, *J* = 13.1, 9.9 Hz, 1H), 3.71 (dd, *J* = 13.1, 5.4 Hz, 1H), 1.25 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 151.8, 144.2, 135.4, 134.0, 129.2, 128.9, 127.7, 126.8, 126.3, 125.8, 118.3, 70.8, 34.6, 32.7, 31.3; **HRMS** (ESI) calcd for C<sub>24</sub>H<sub>26</sub>N<sub>3</sub>Se [M+H]<sup>+</sup>: 436.1286, found: 436.1294.

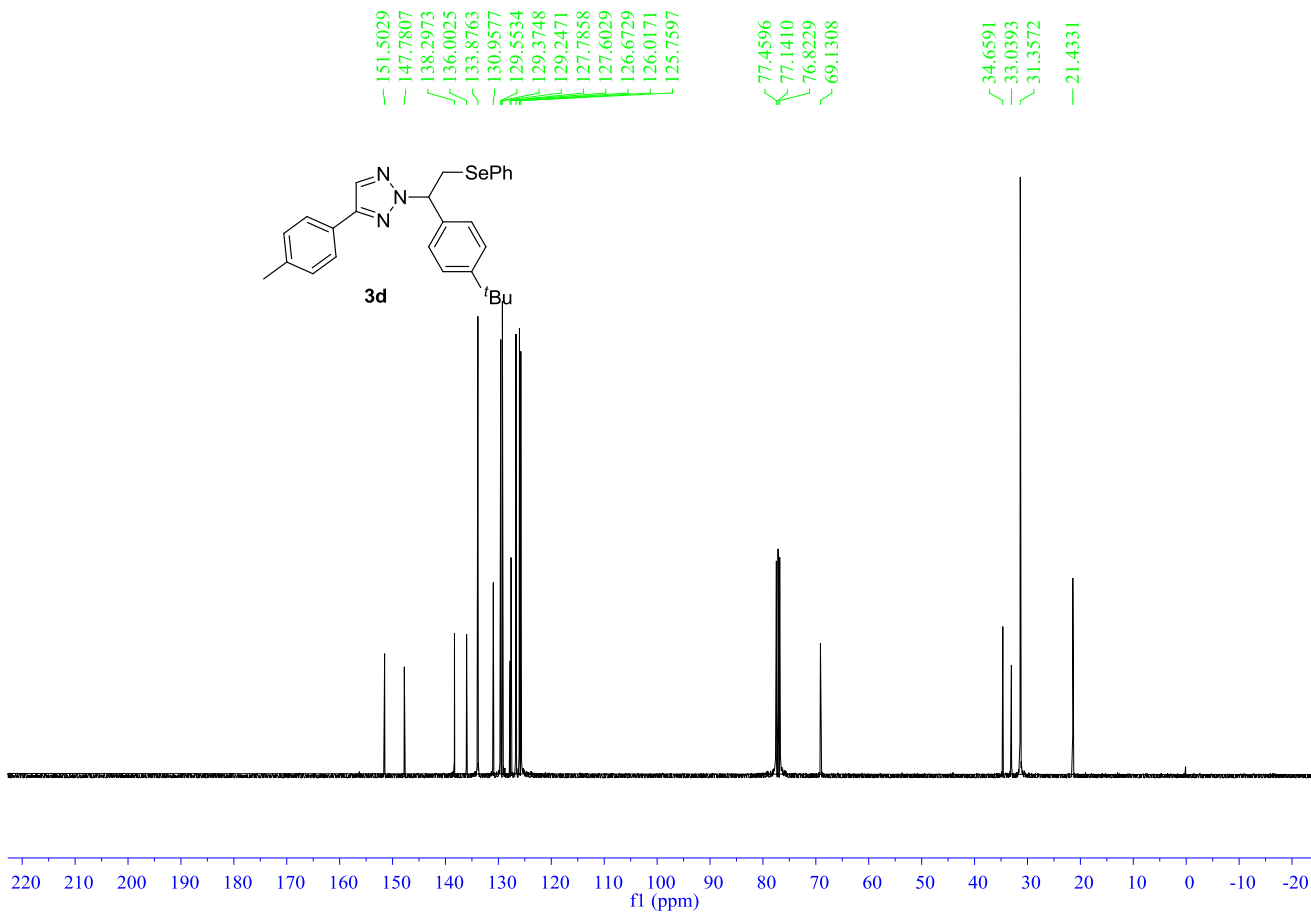
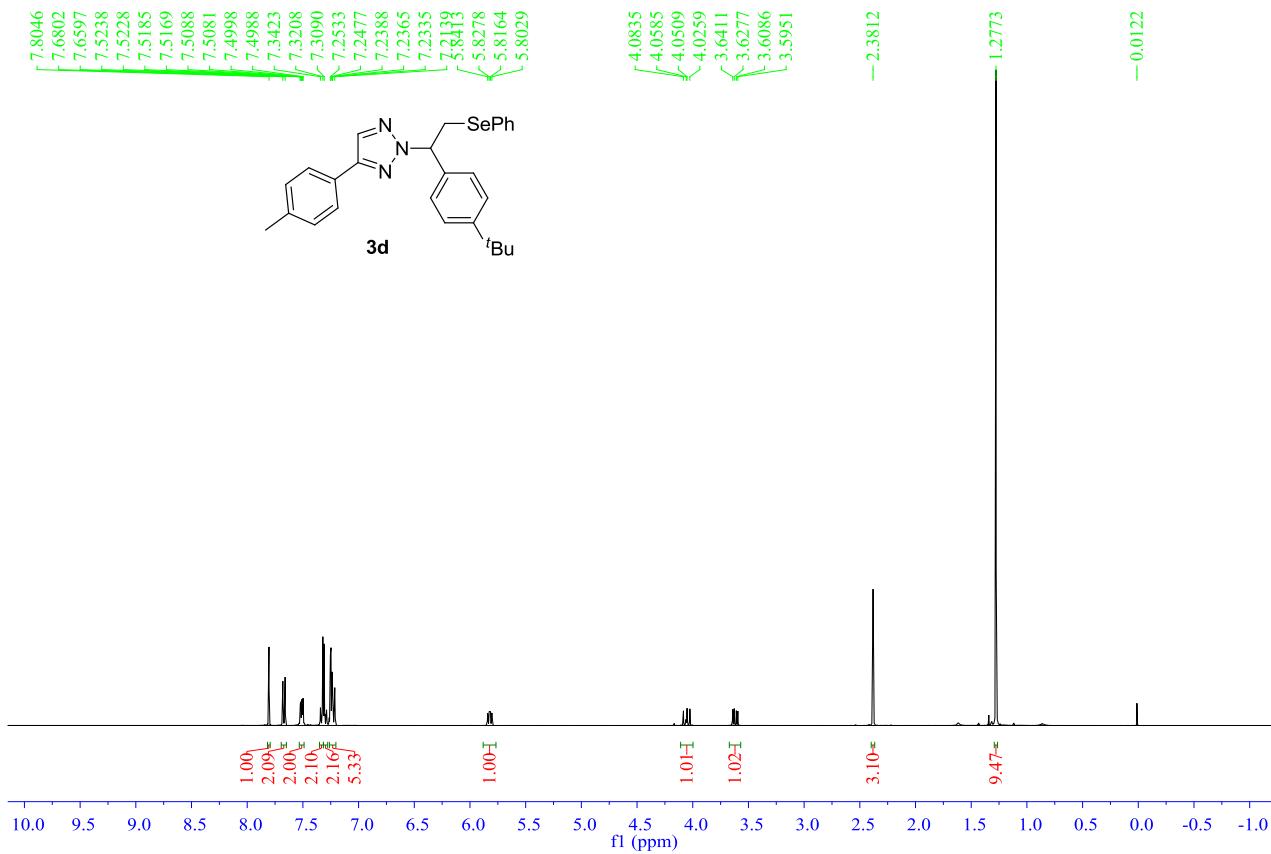
#### 4. <sup>1</sup>H and <sup>13</sup>C NMR Spectra

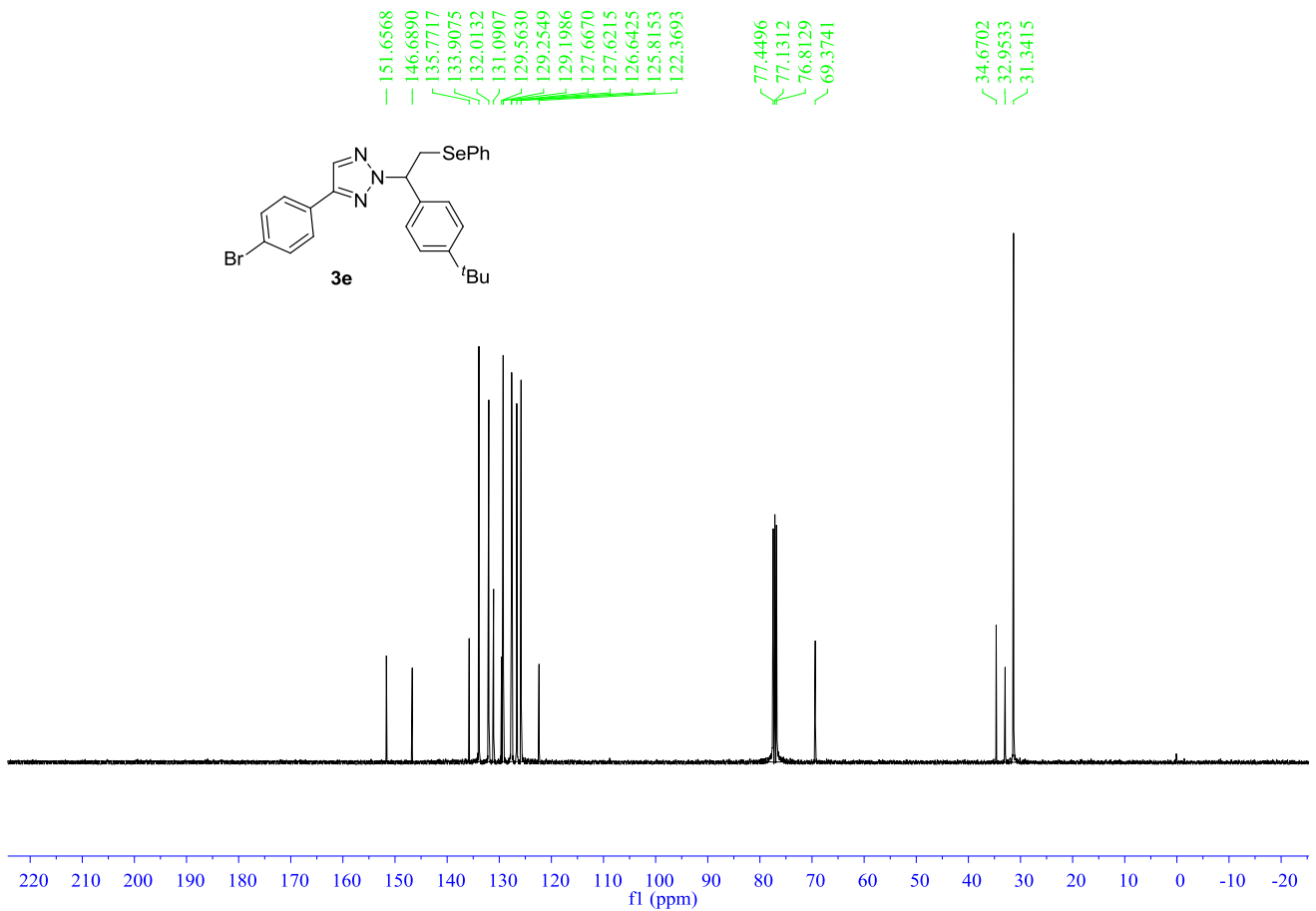
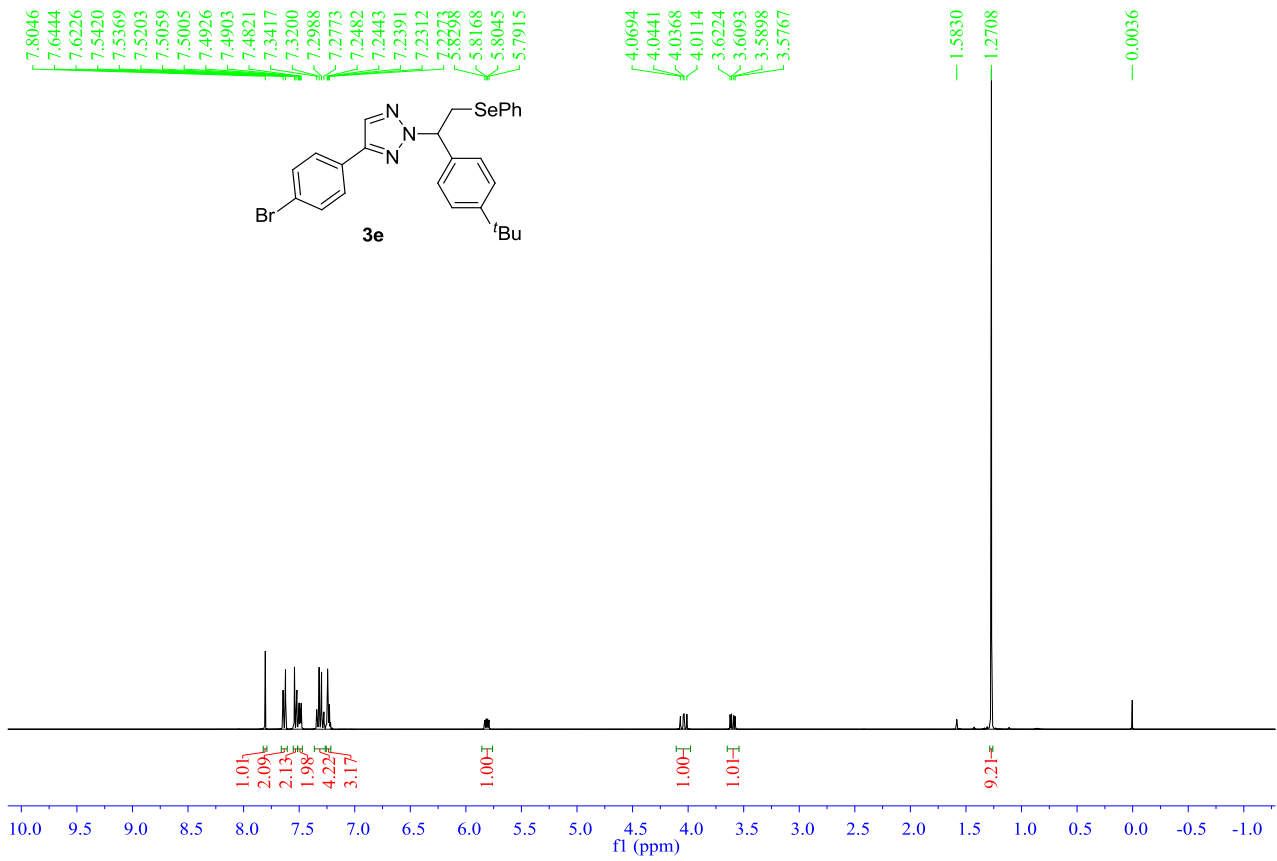


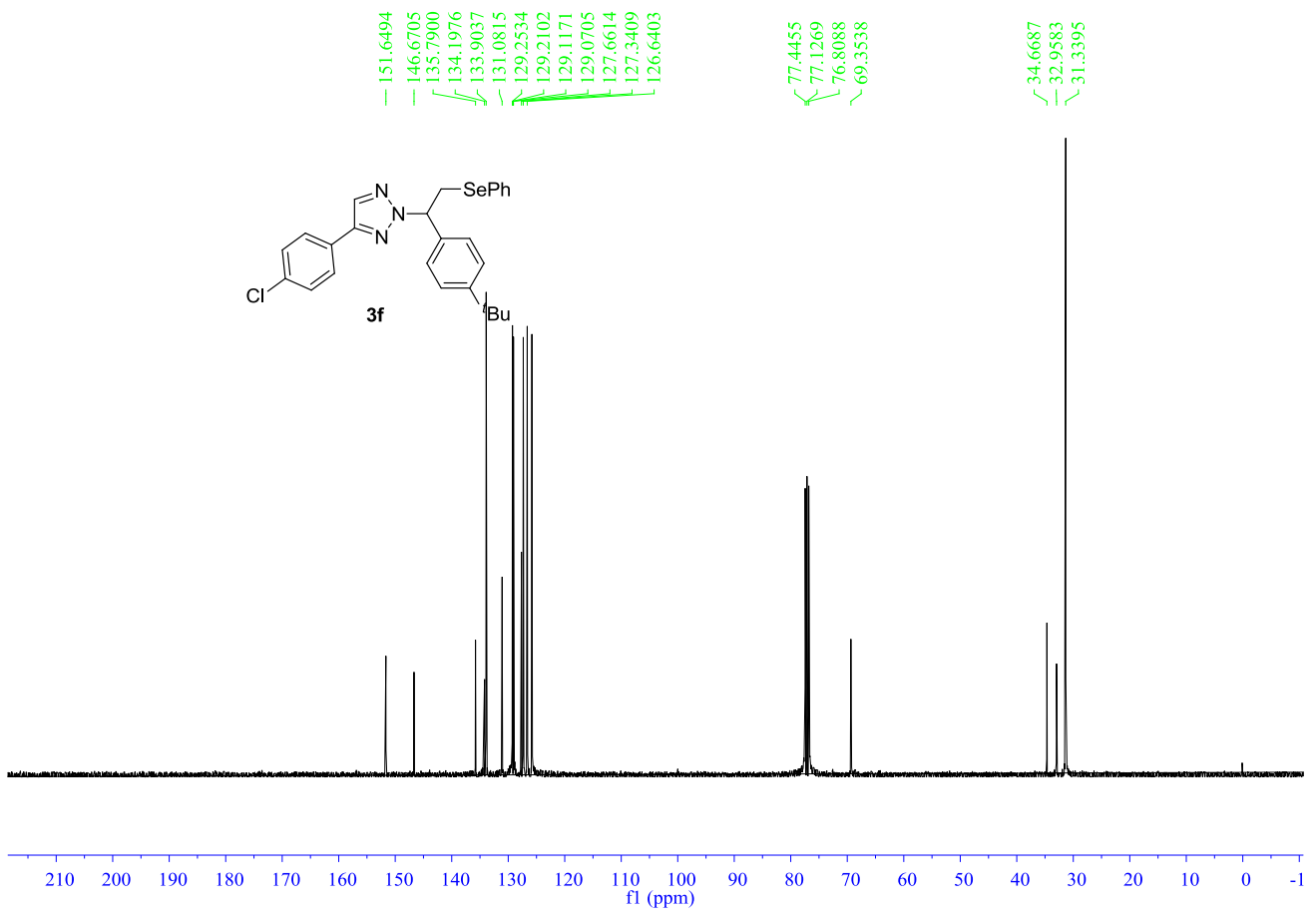
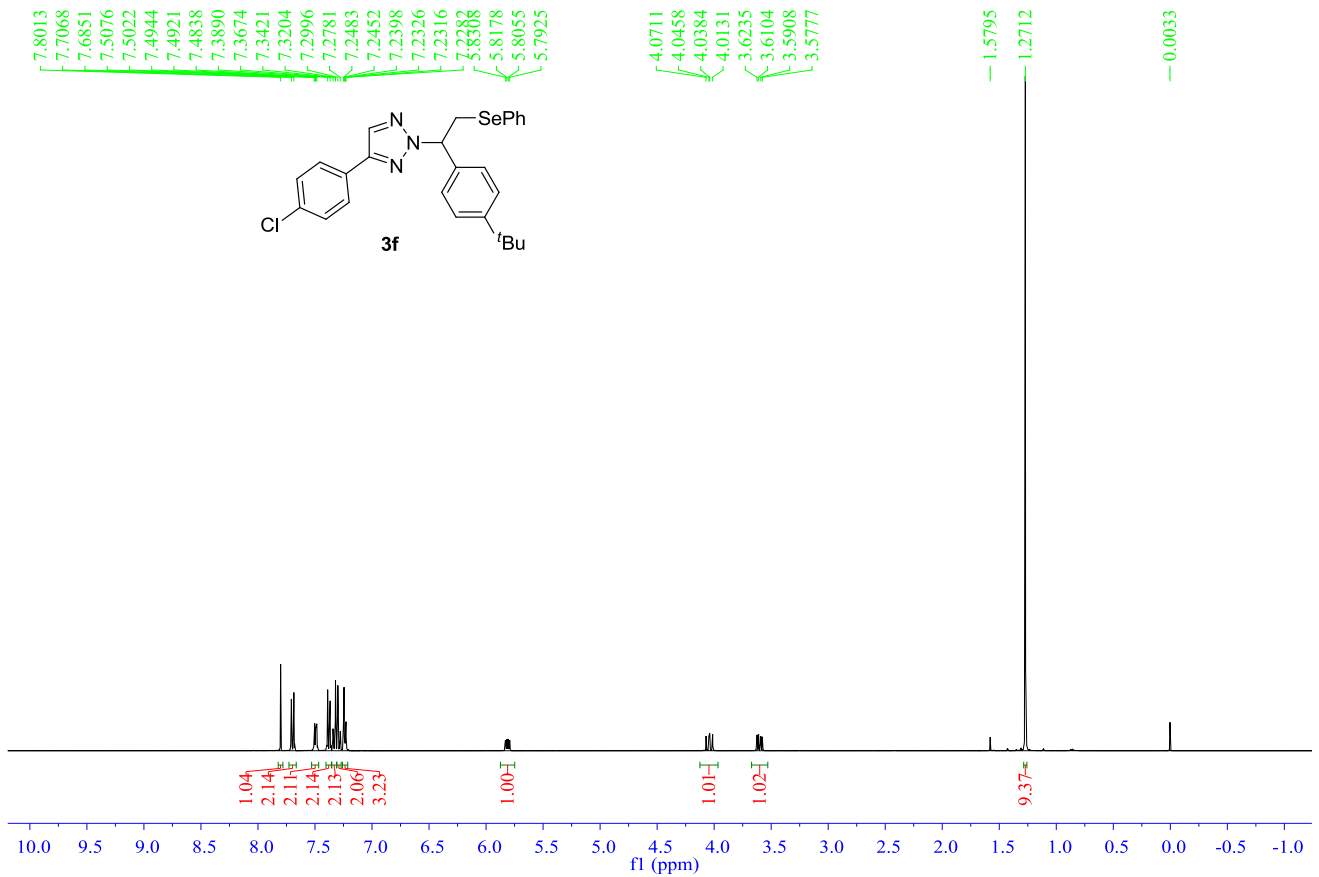


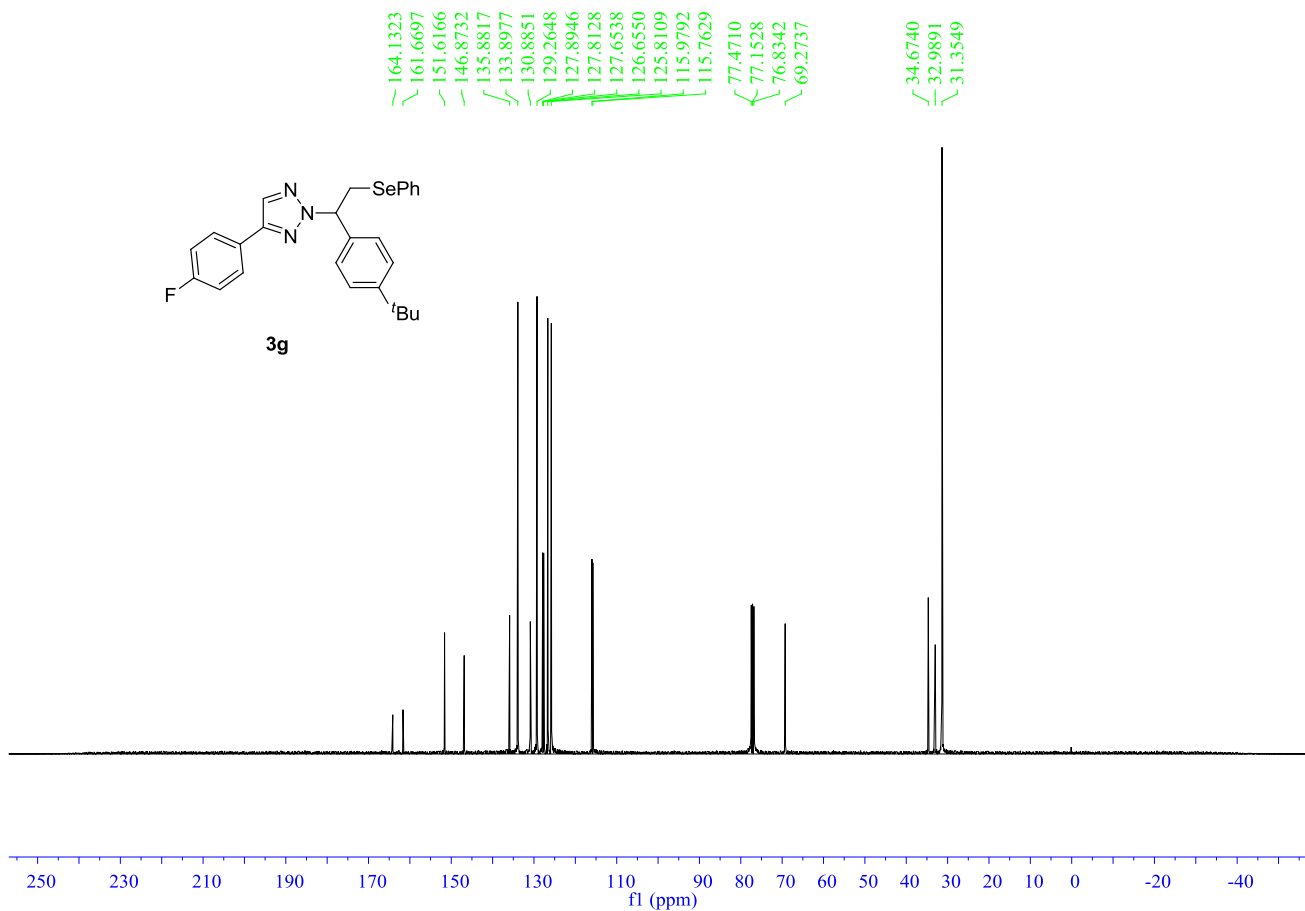
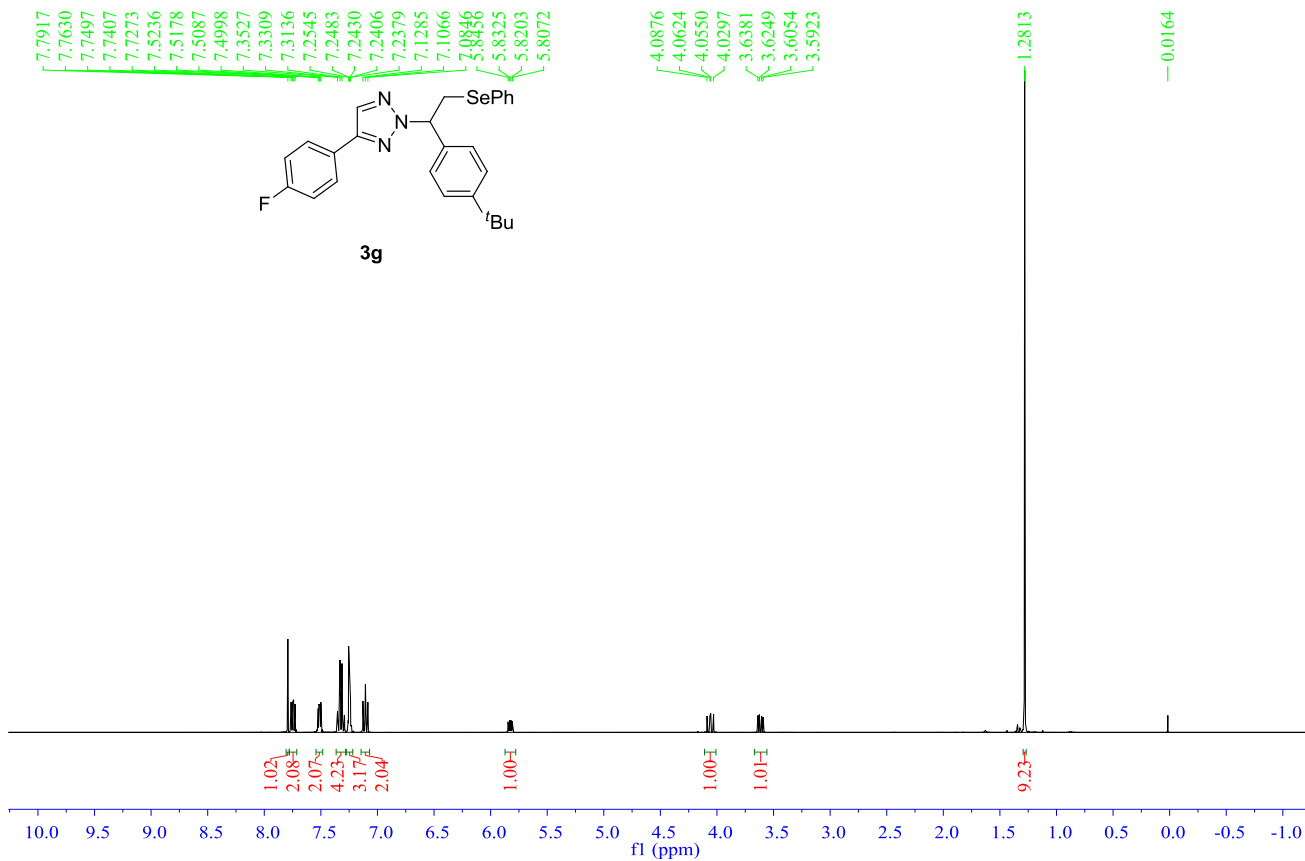


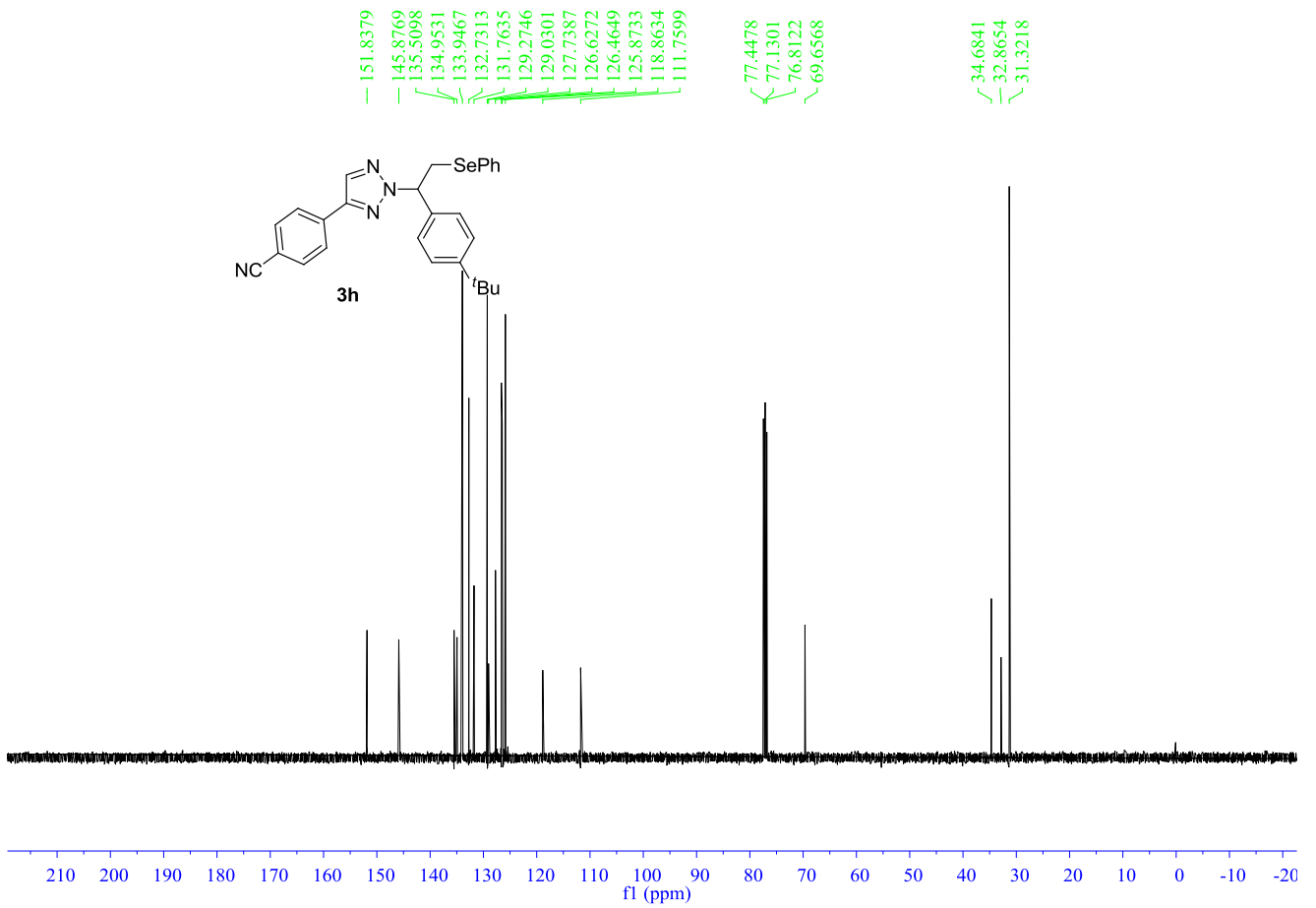
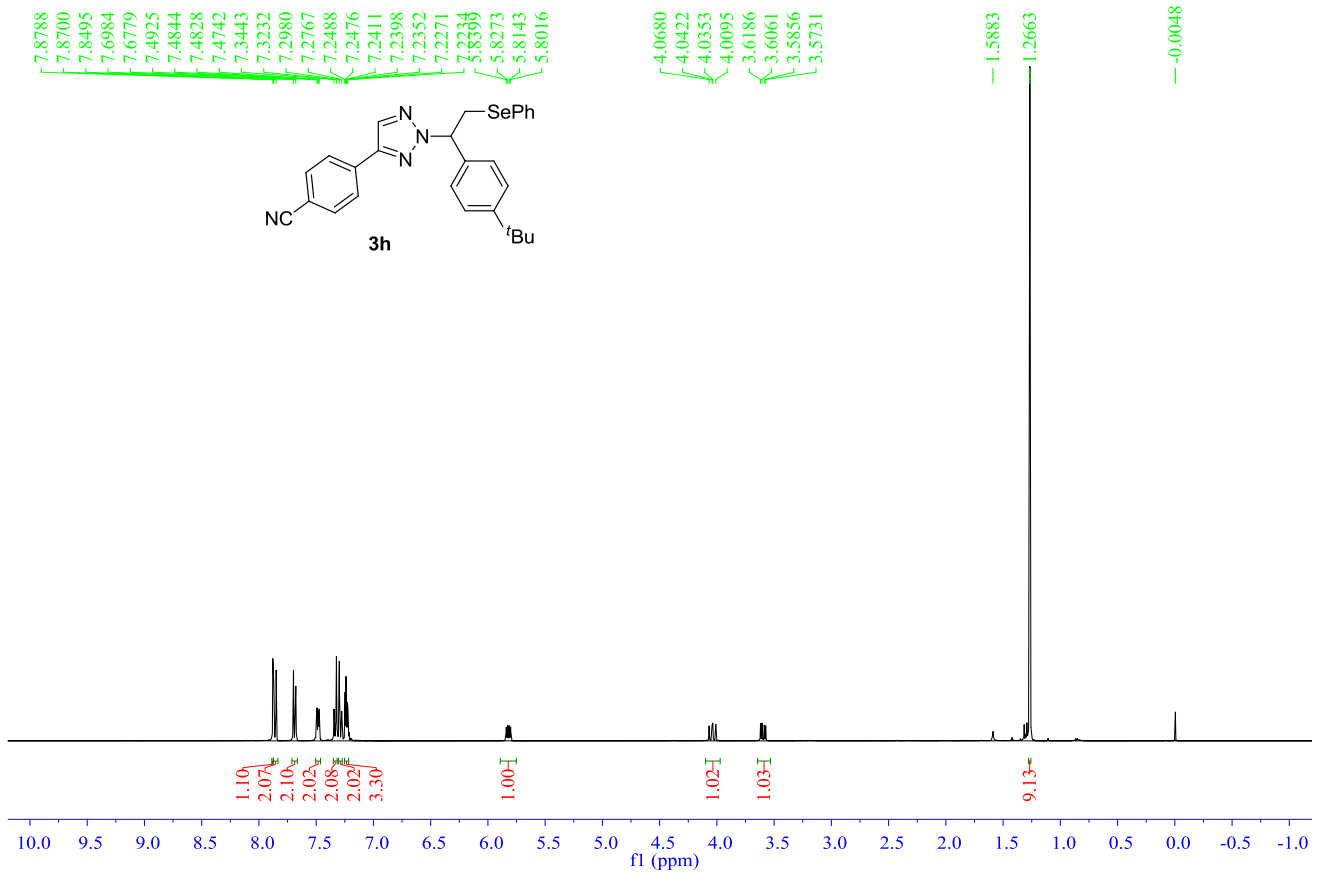


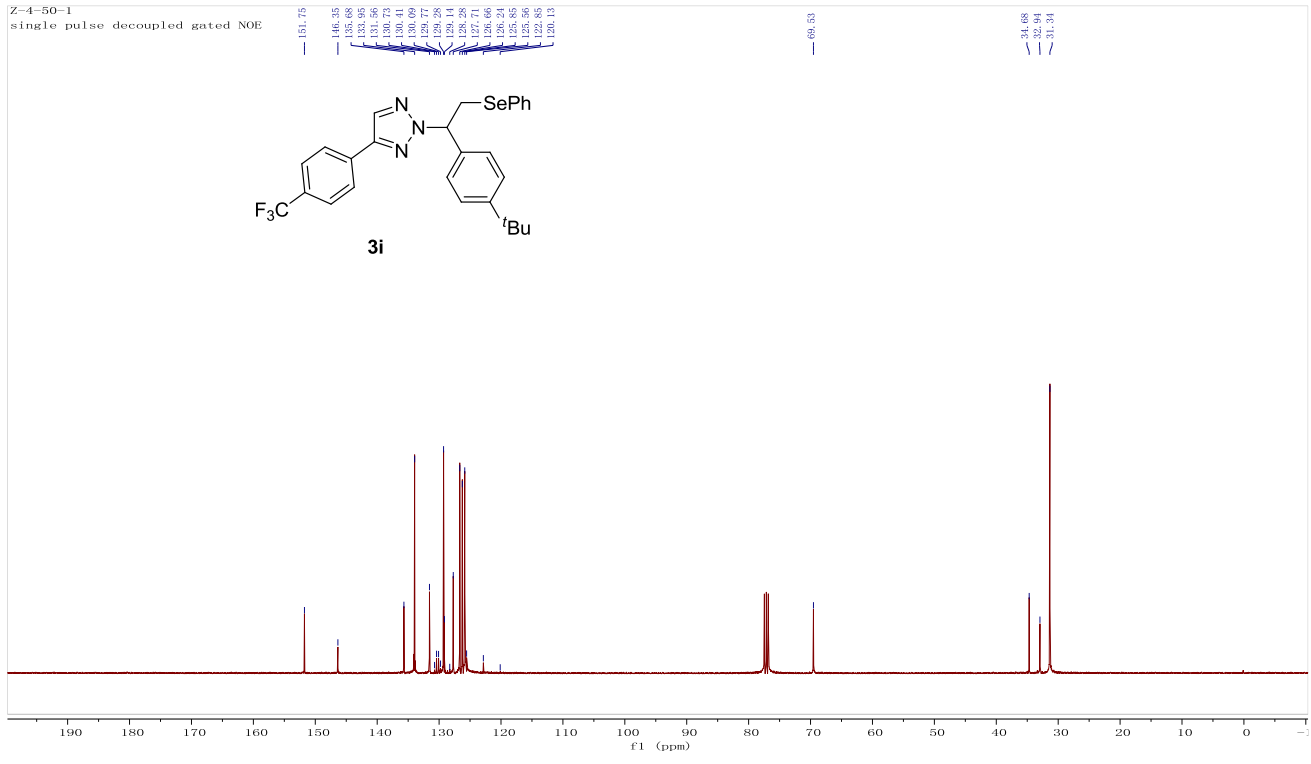
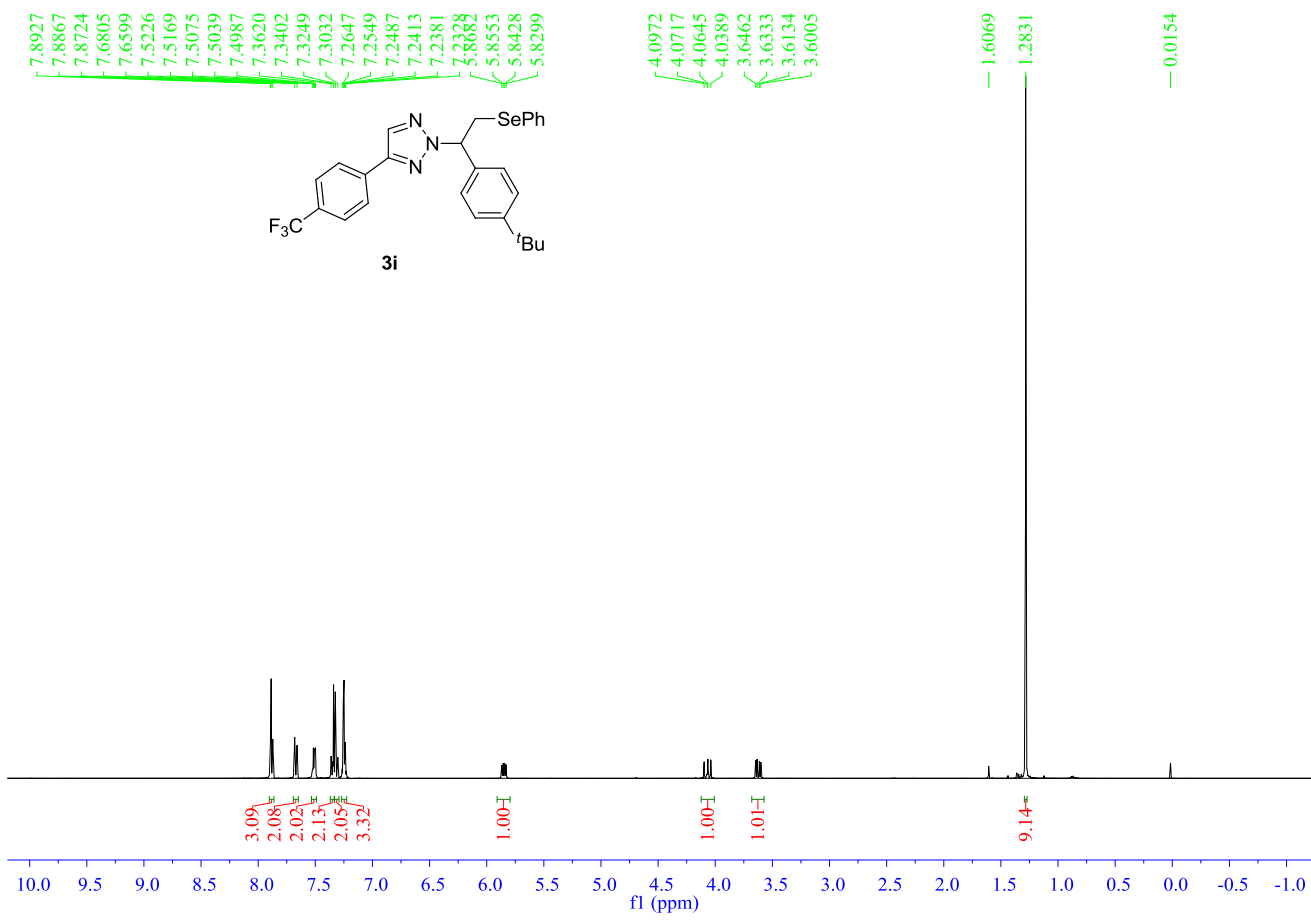




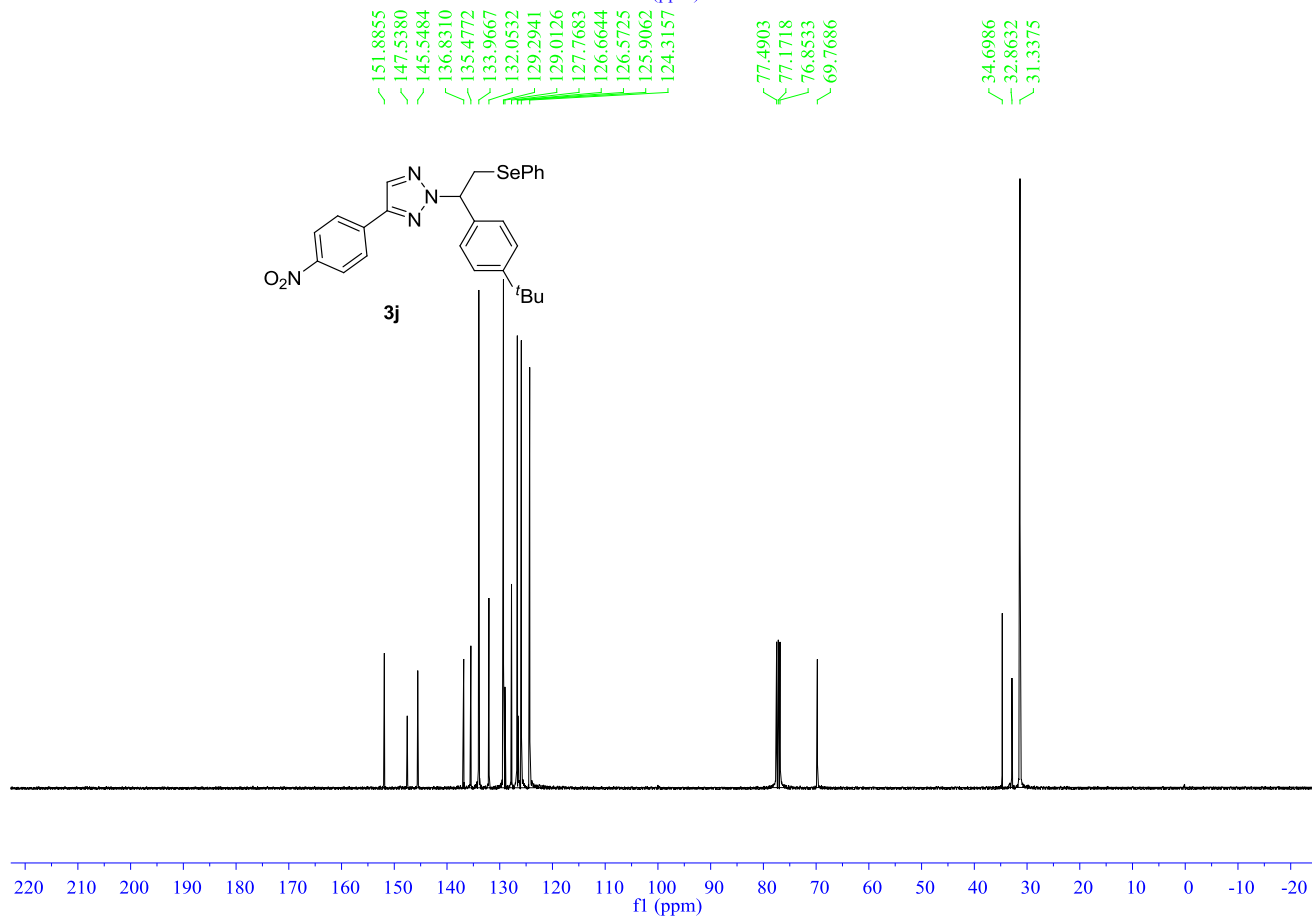
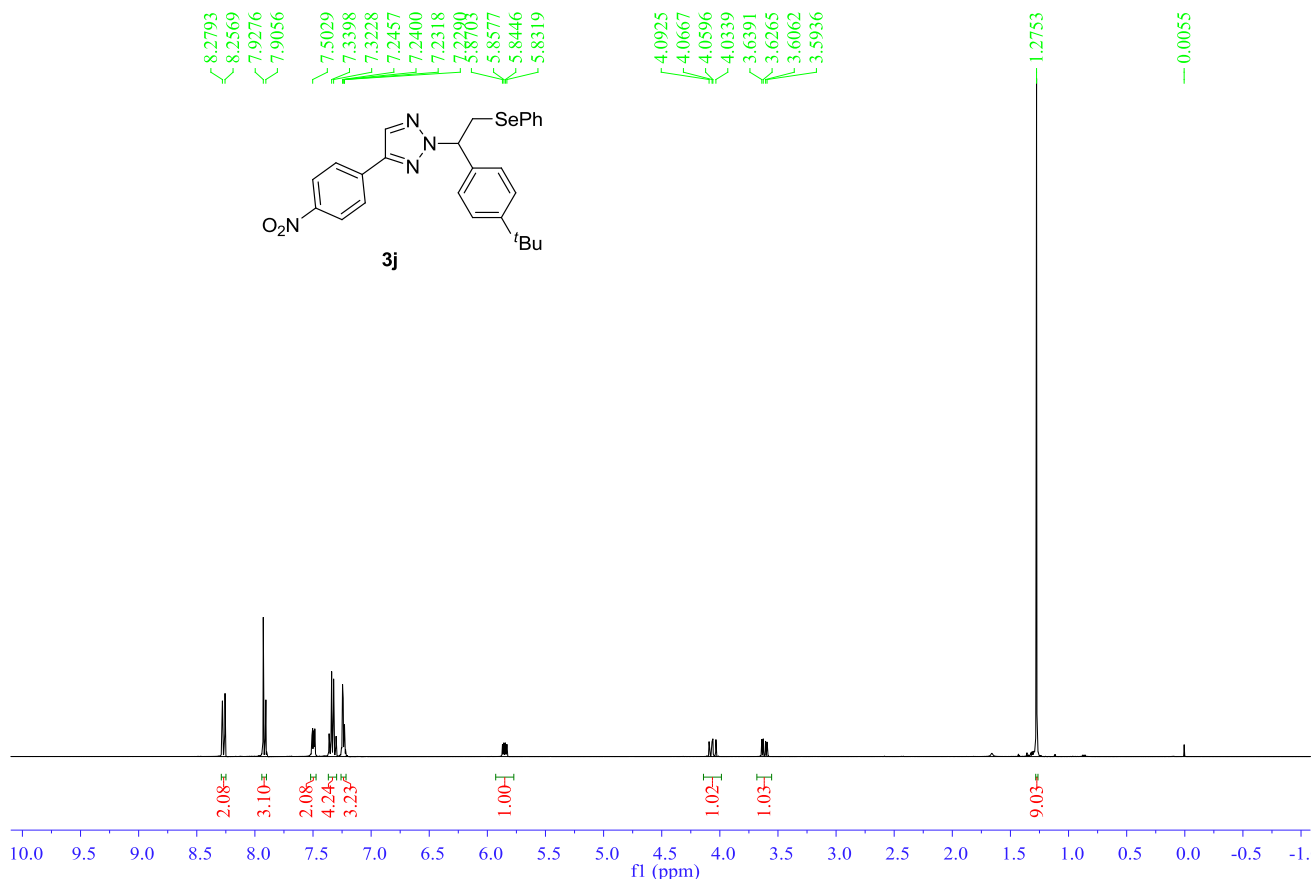


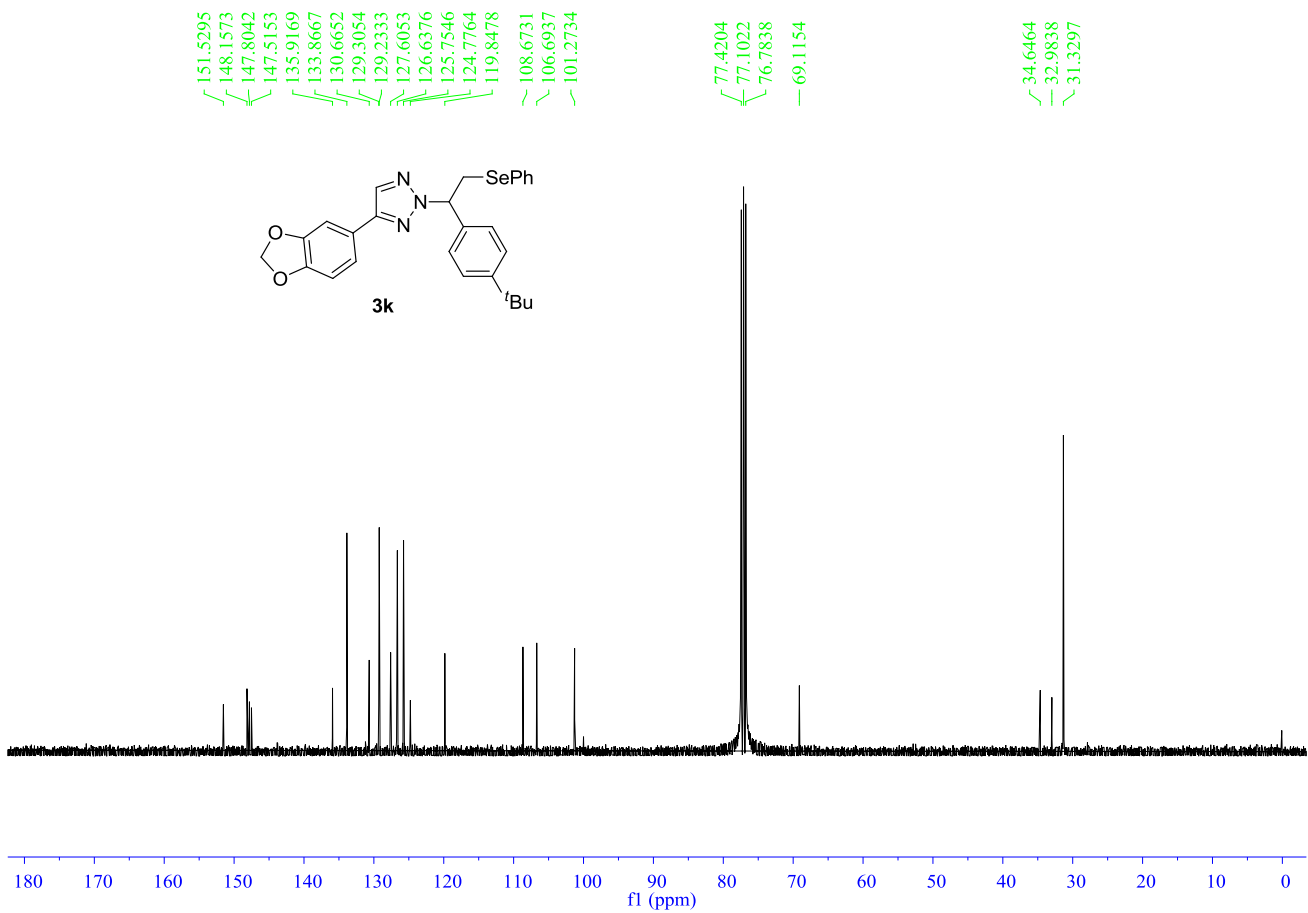
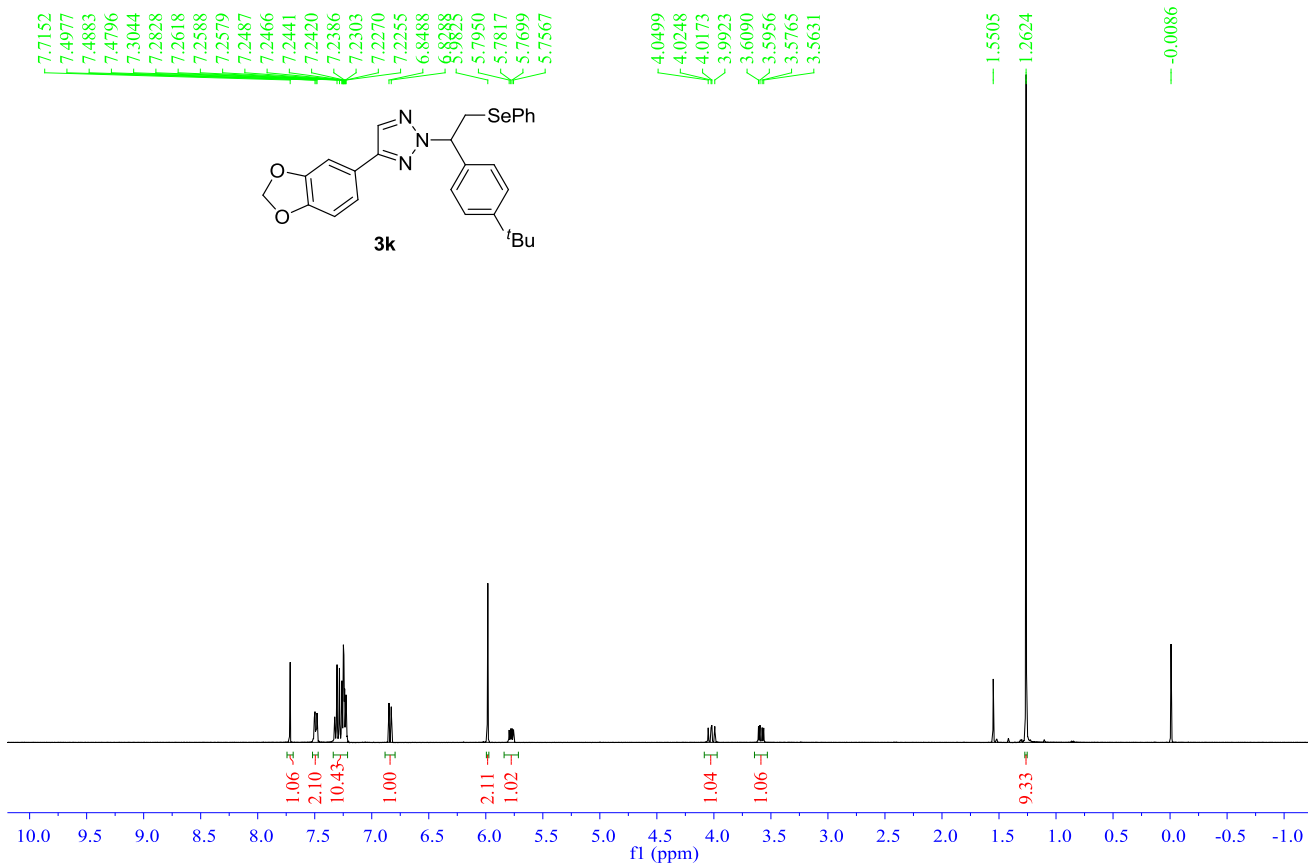




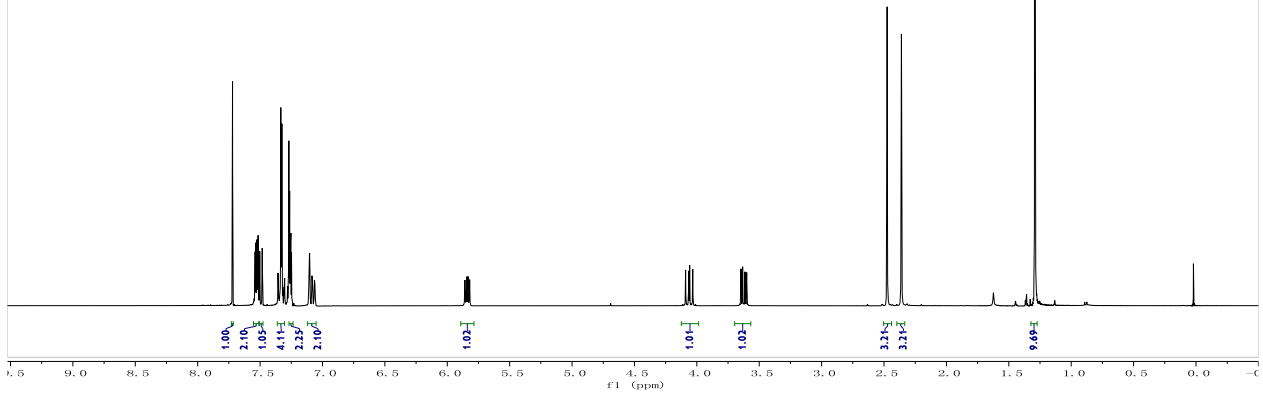
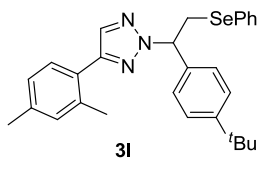




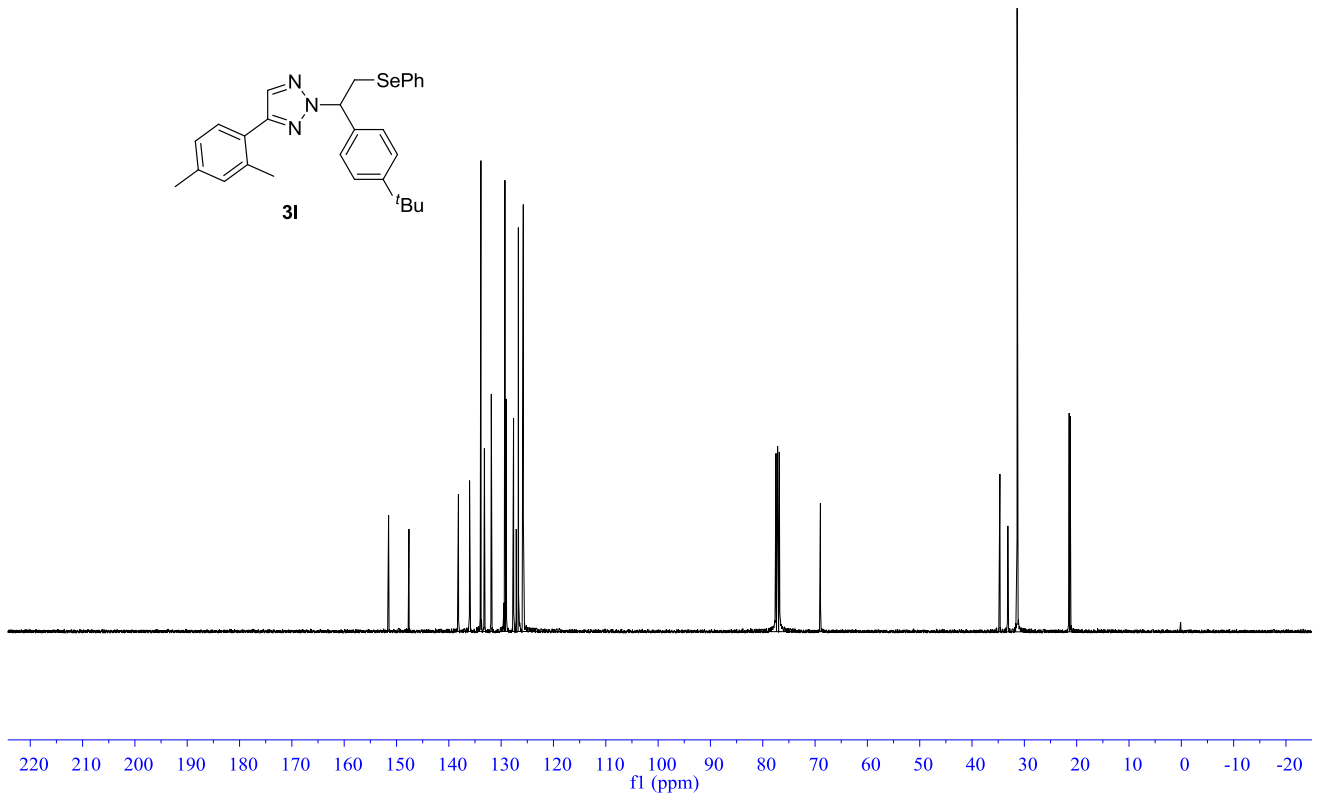
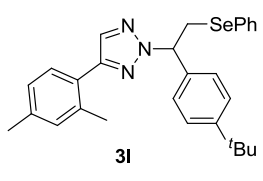


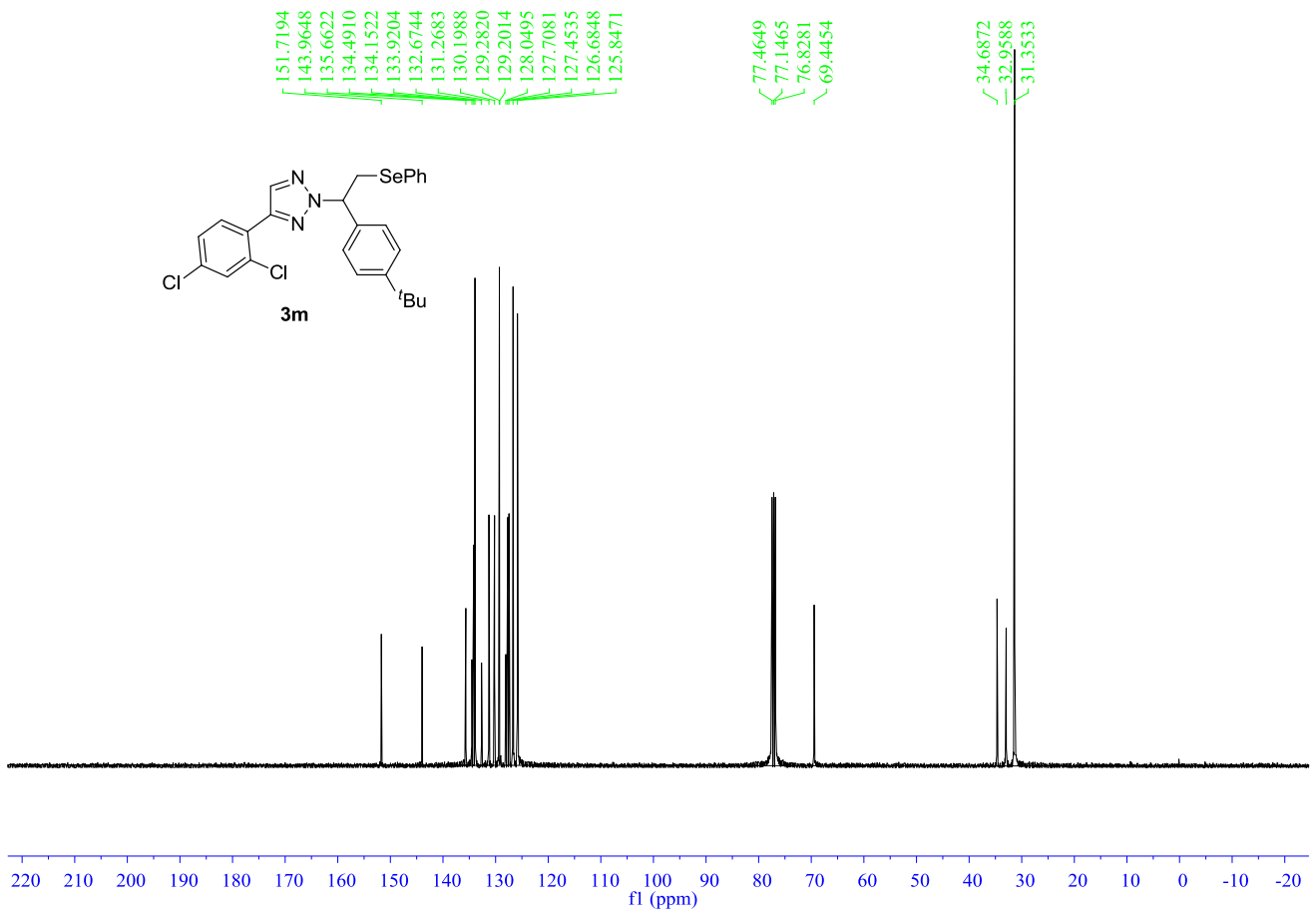
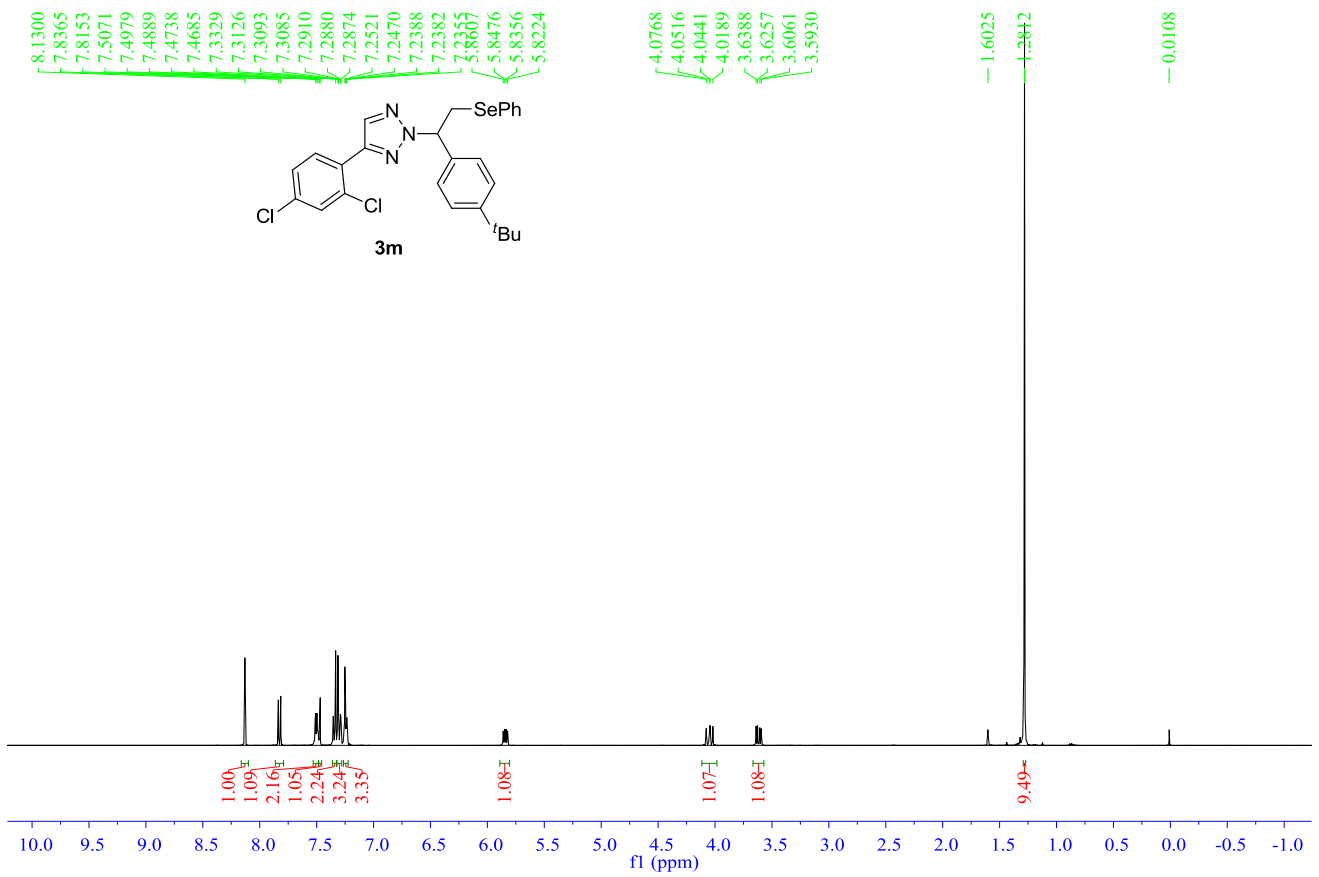


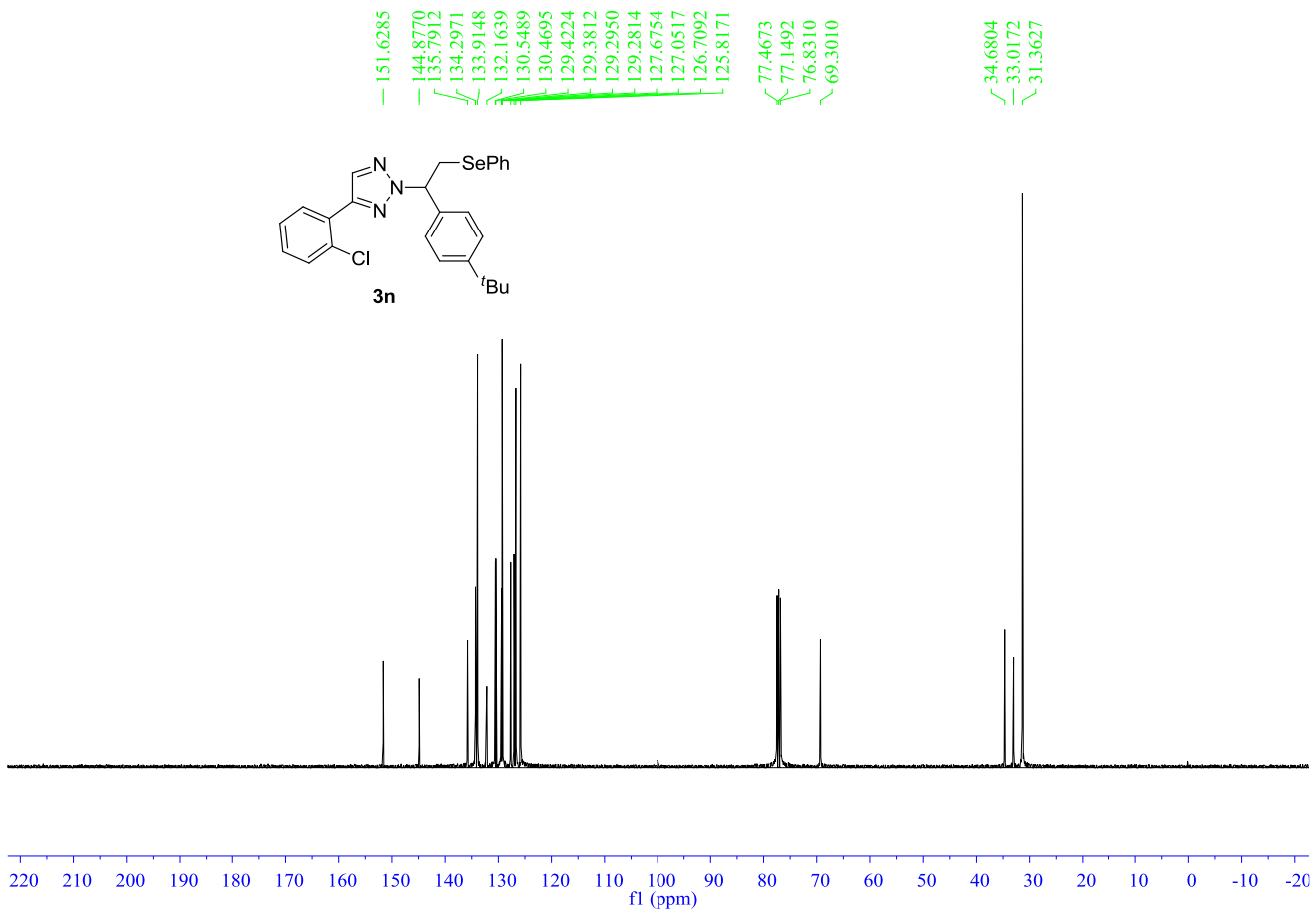
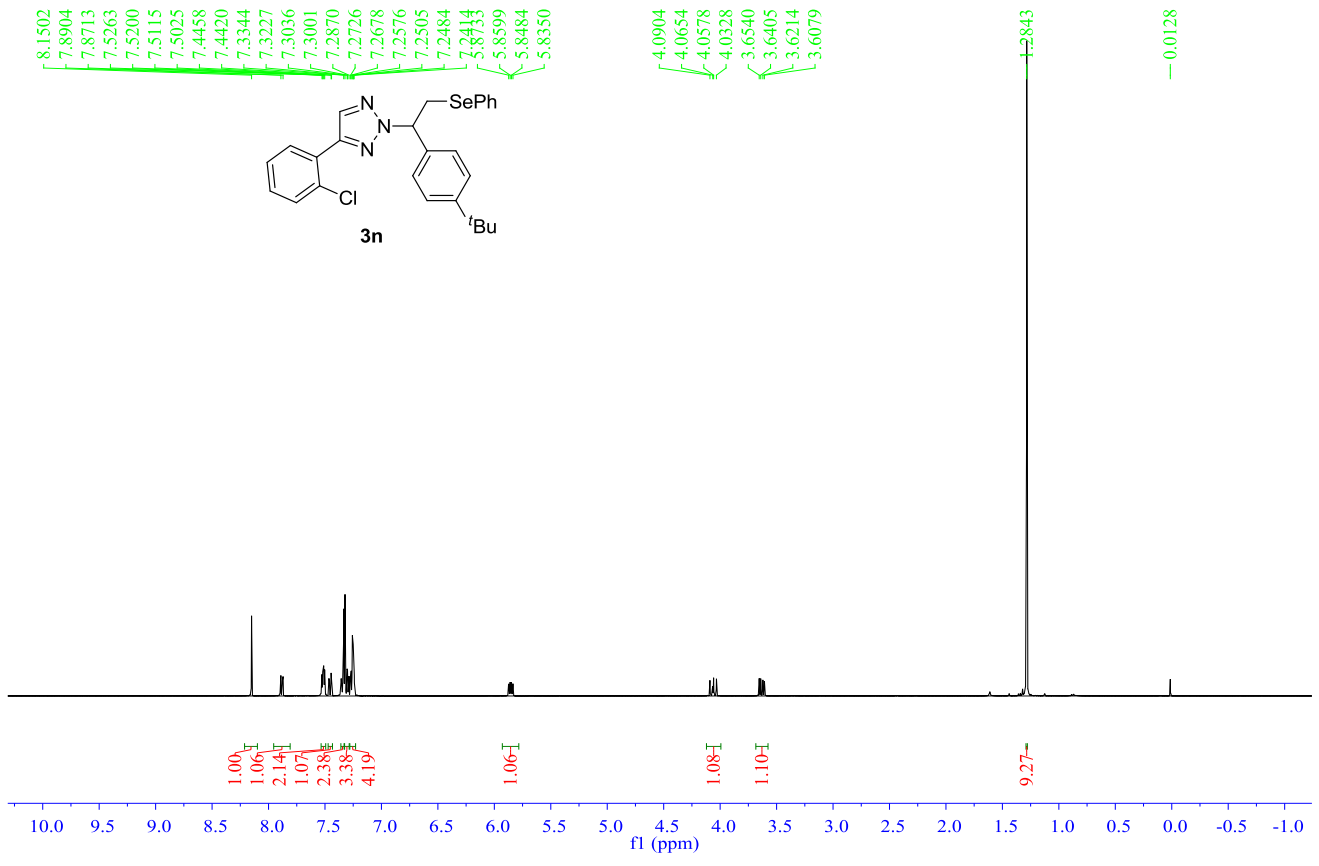
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single\_pulse

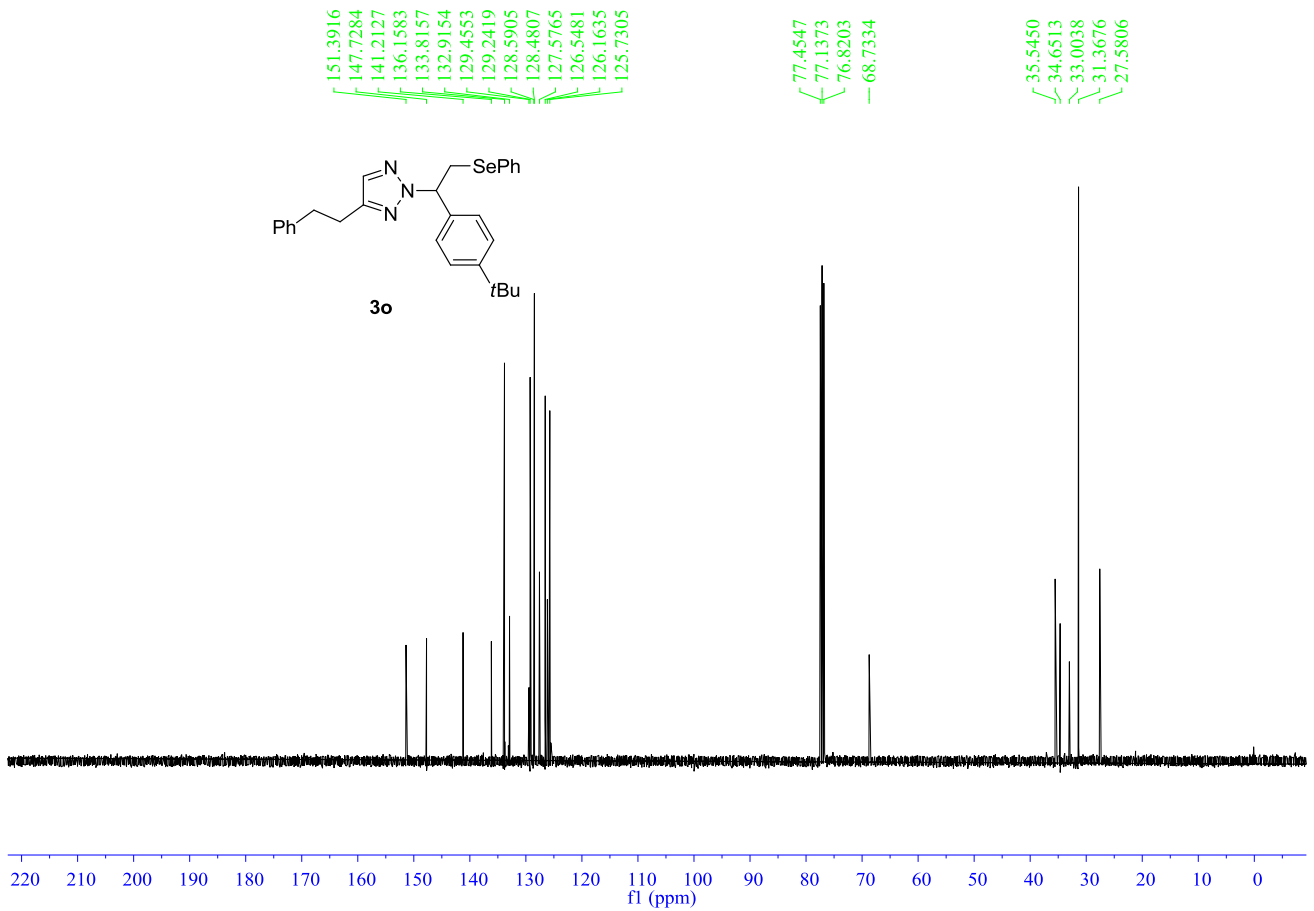
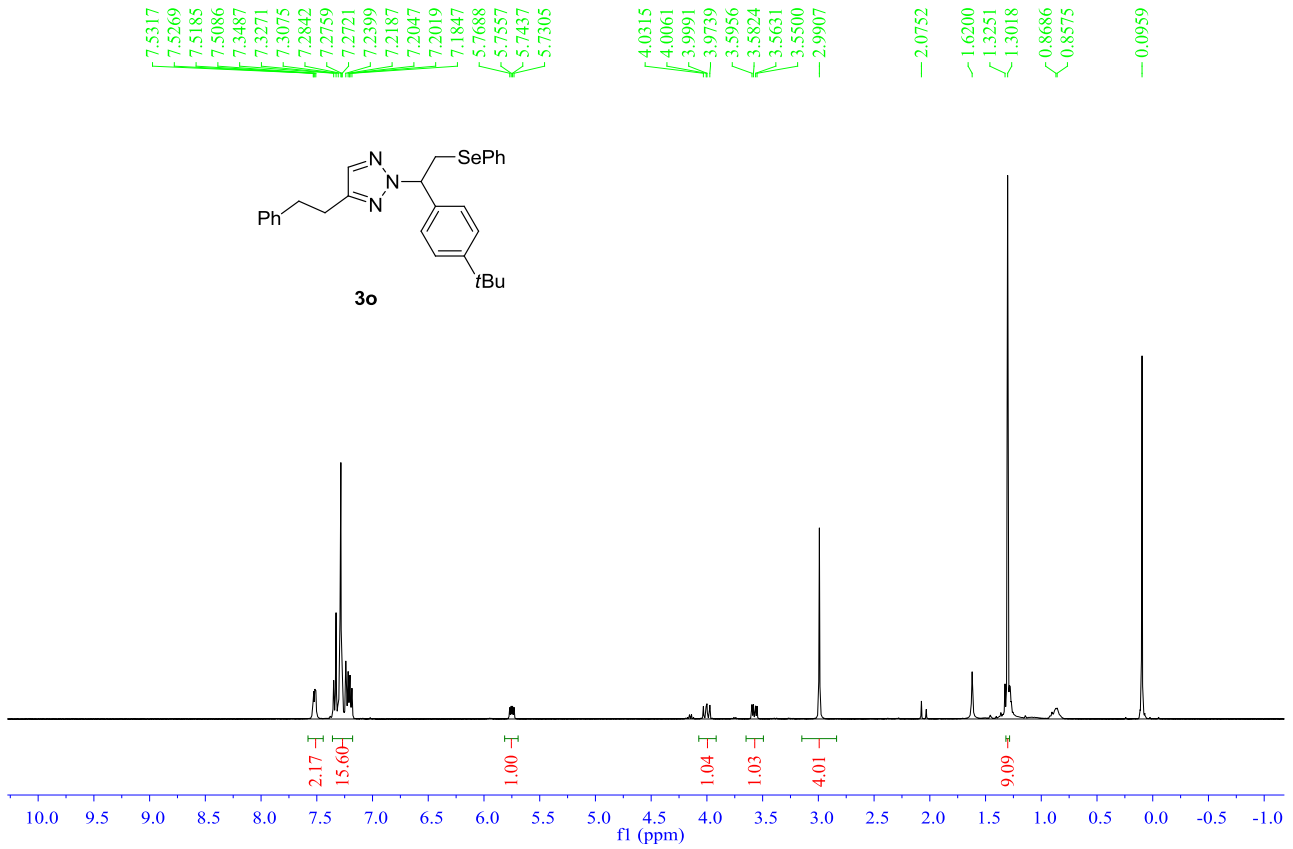


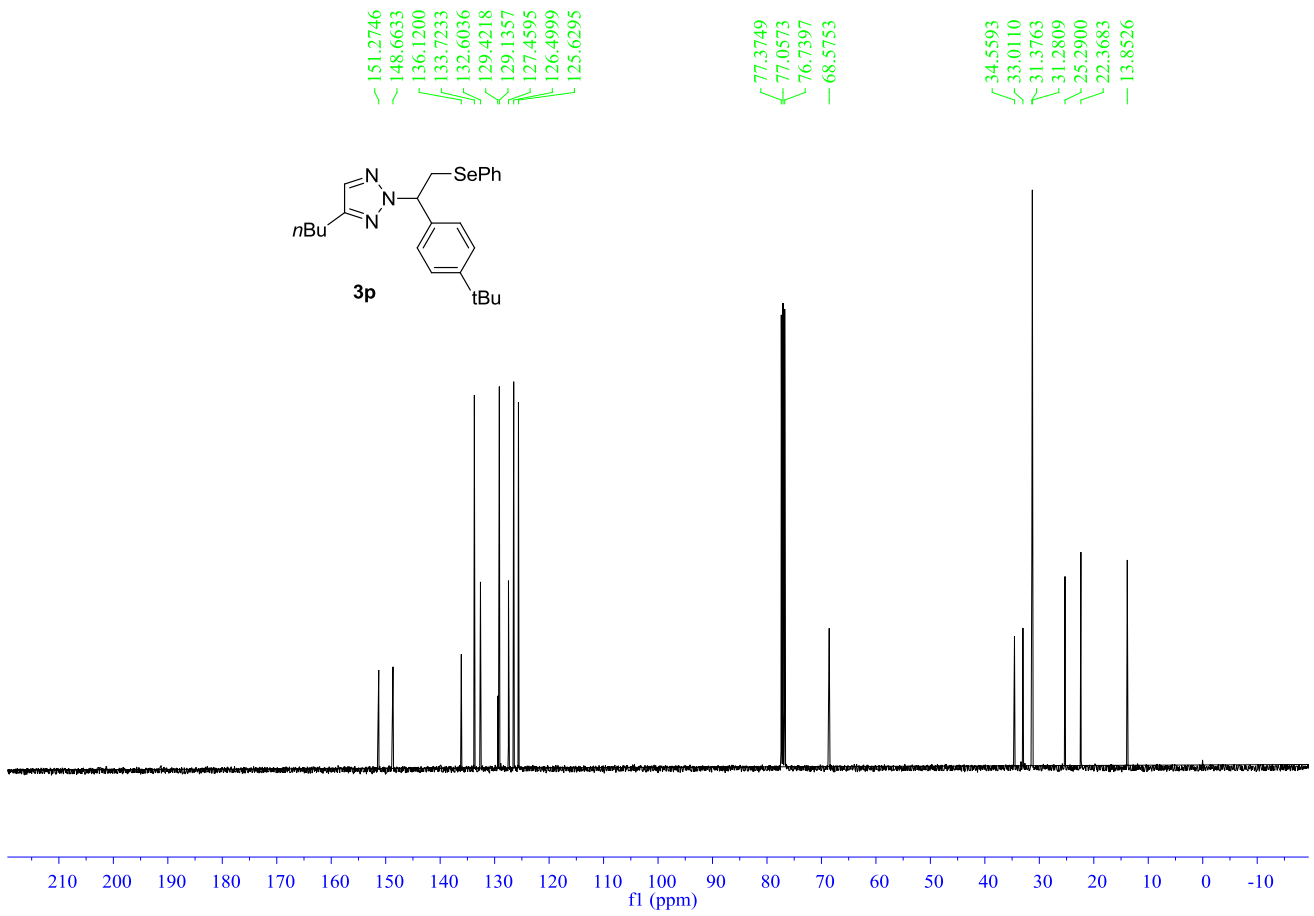
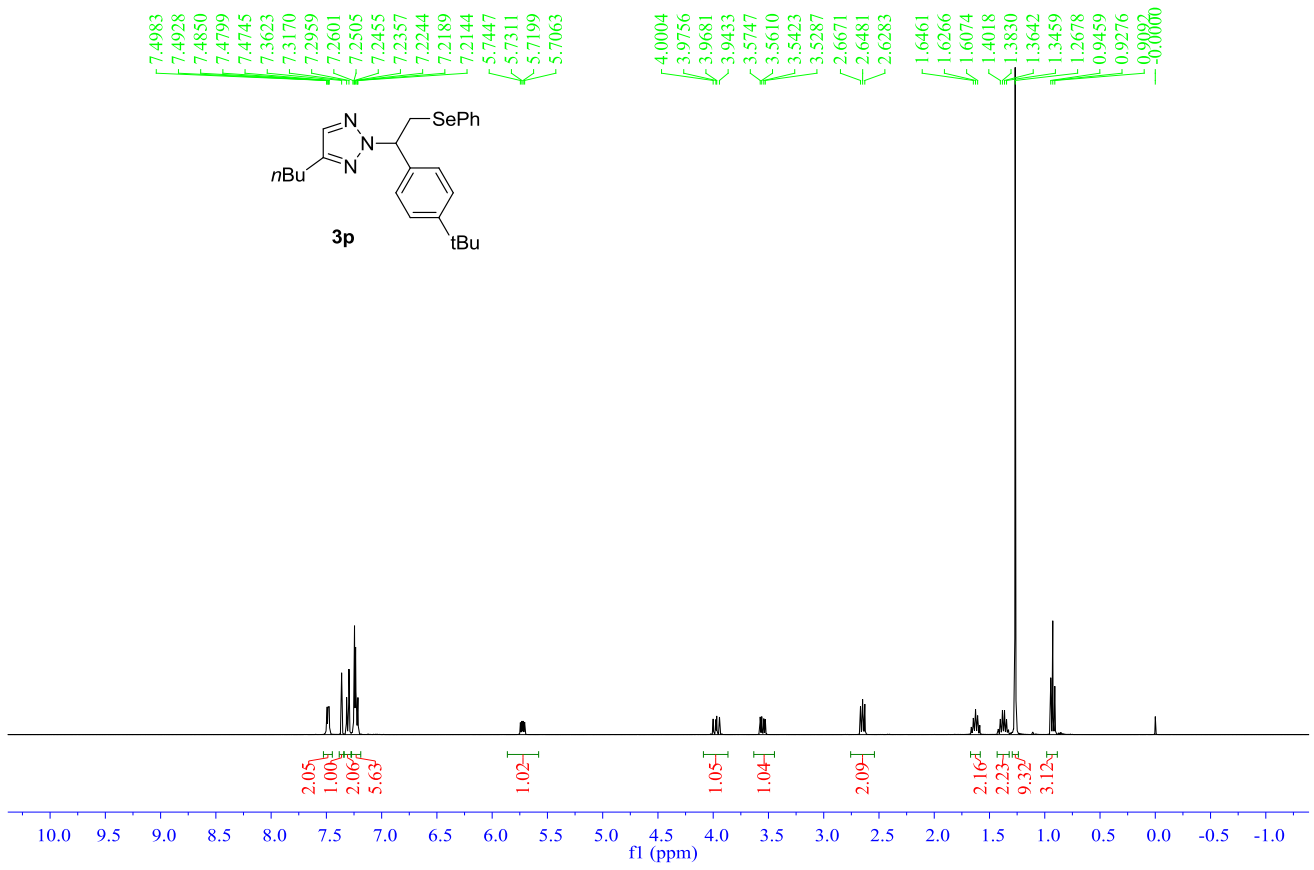
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- 147.6219
- 138.1645
- 136.0361
- 133.8695
- 133.1976
- 131.8830
- 129.4203
- 129.2784
- 129.0549
- 127.6280
- 127.1091
- 126.7092
- 125.7673
- 77.4723
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- 76.8353
- 68.9774
- 34.6740
- 33.1574
- 31.3725
- 21.4341
- 21.2637

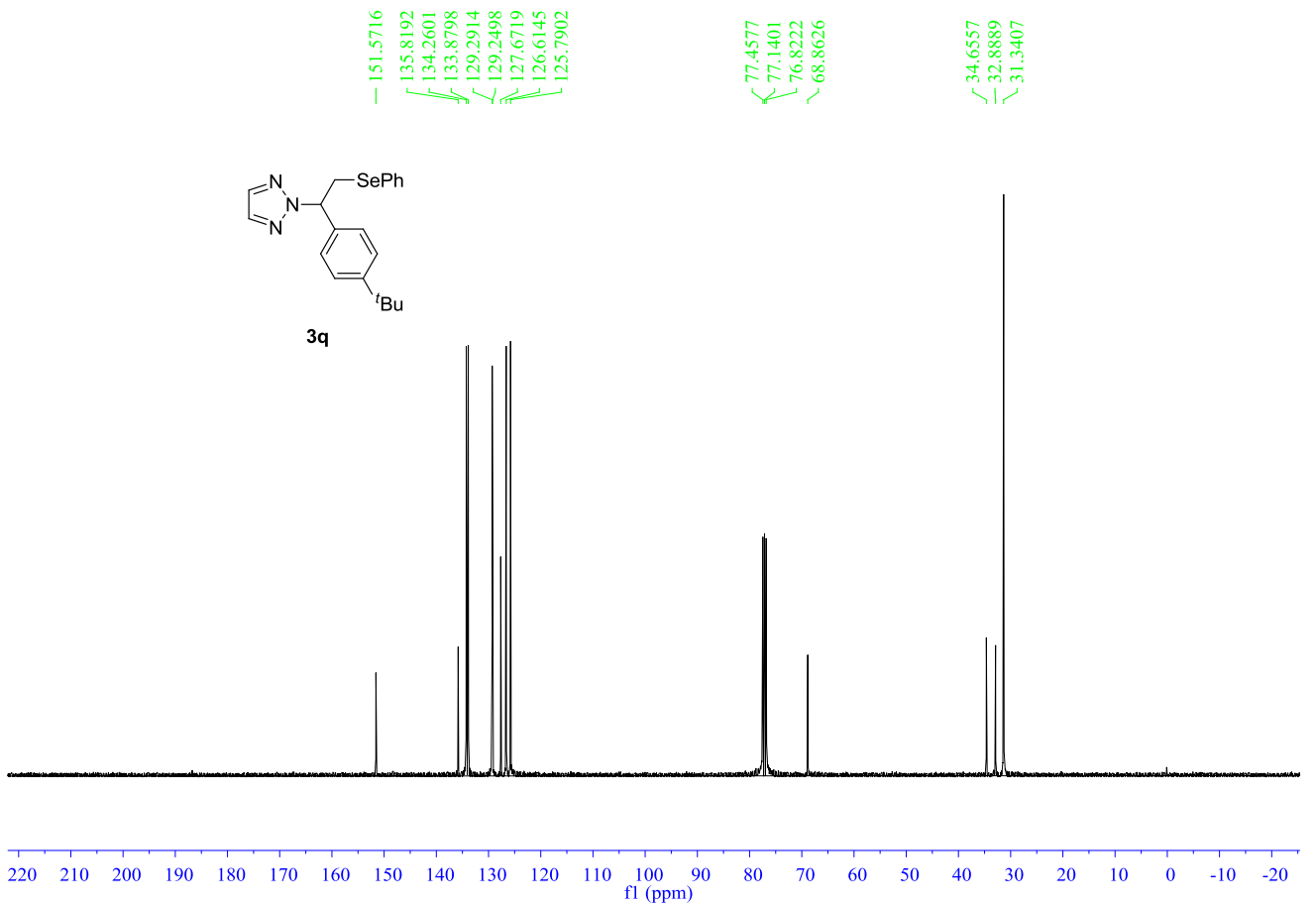
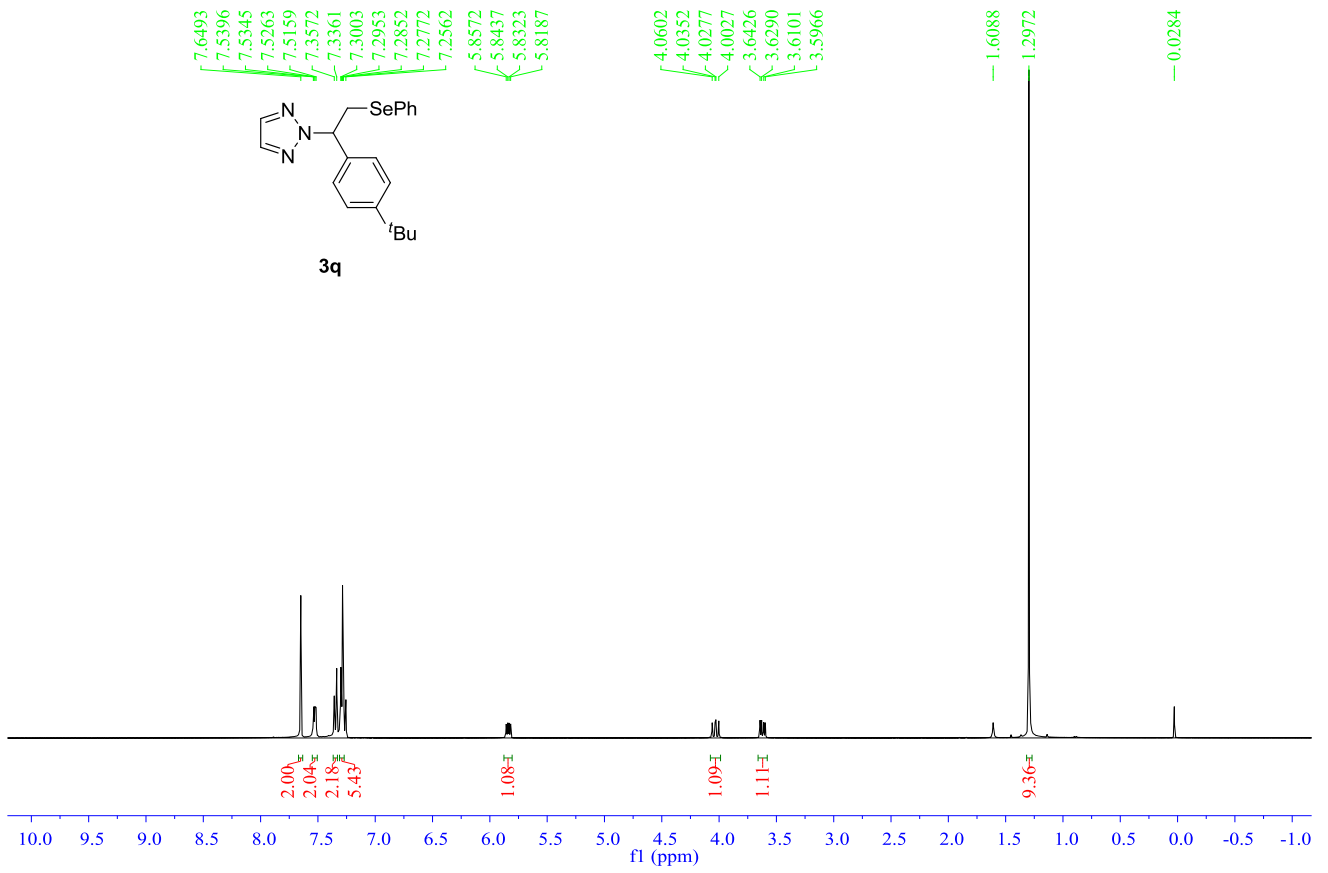




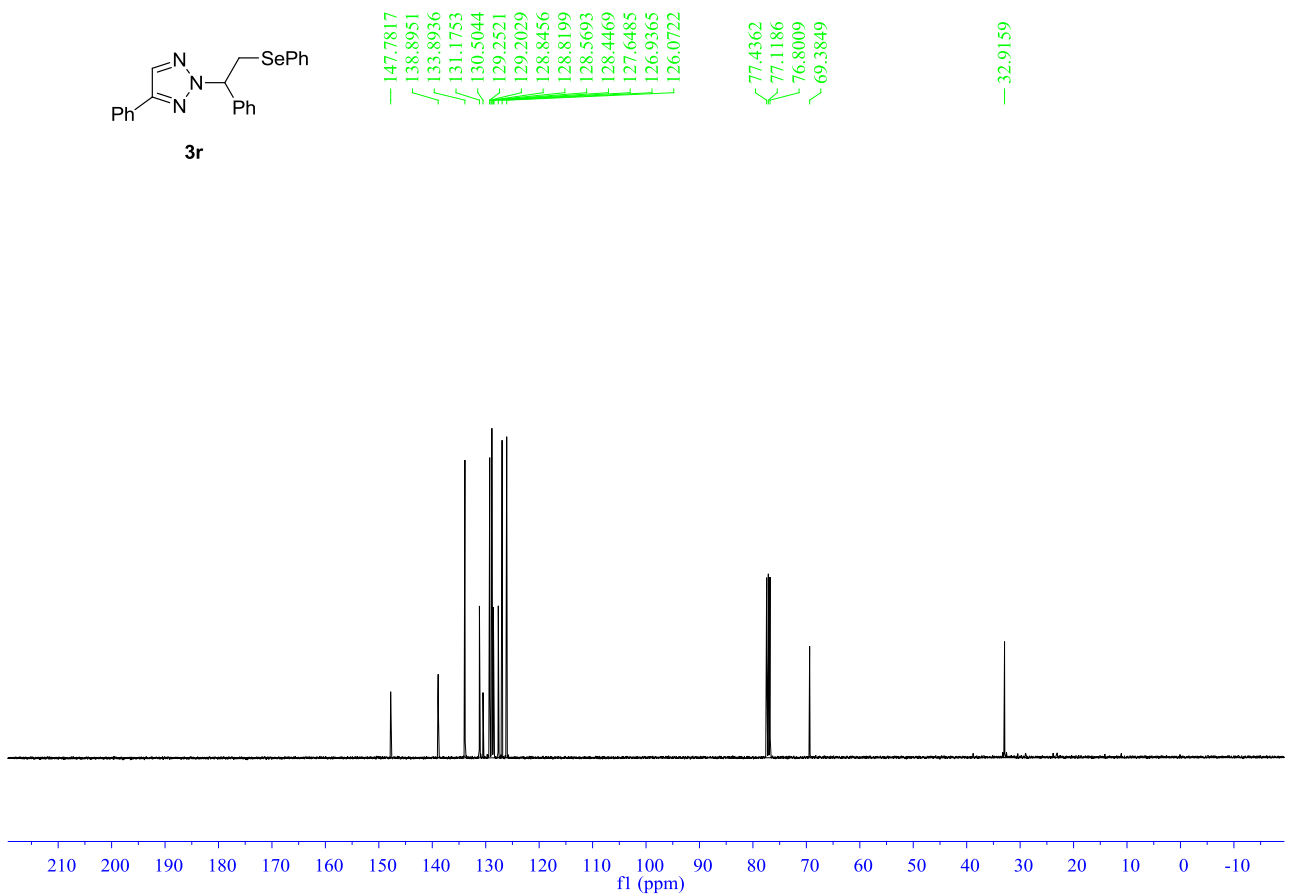
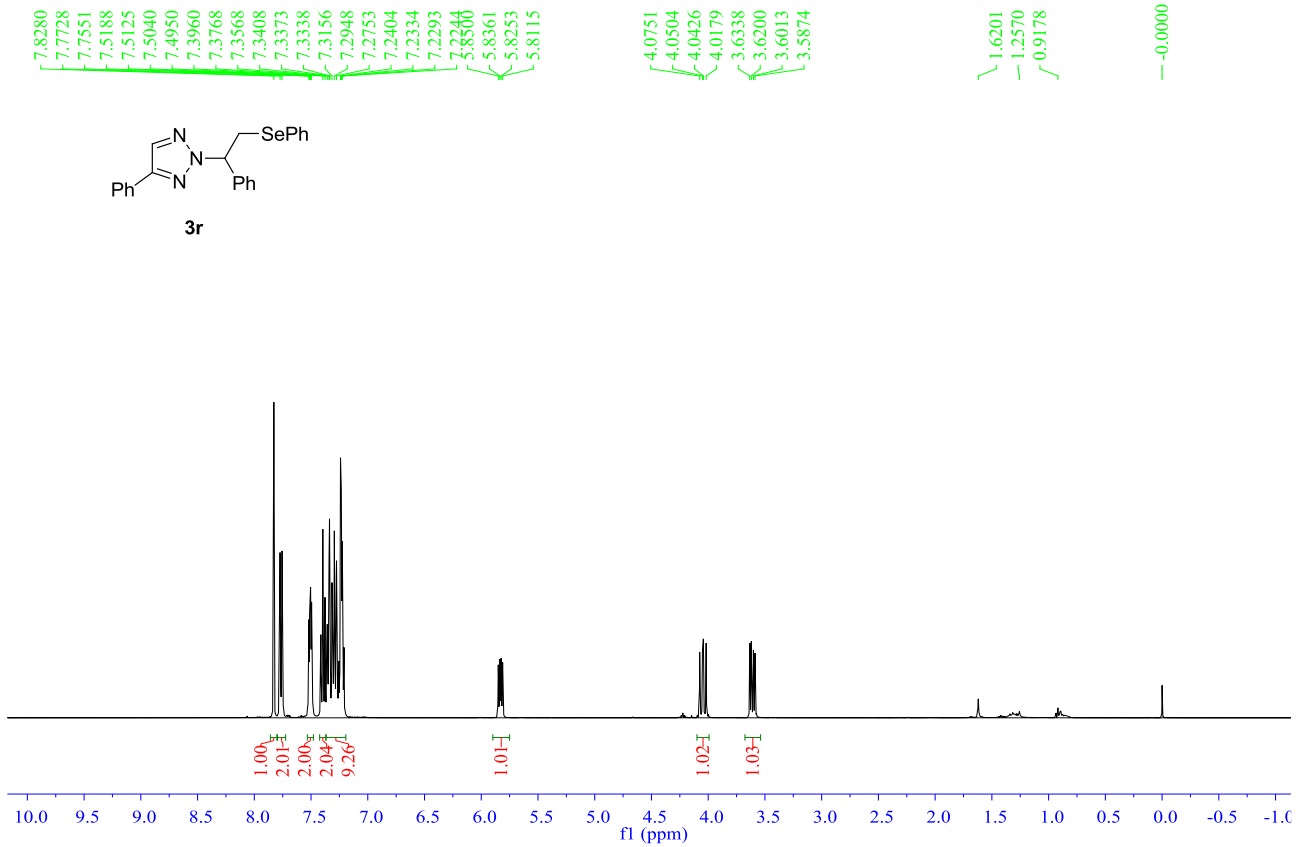


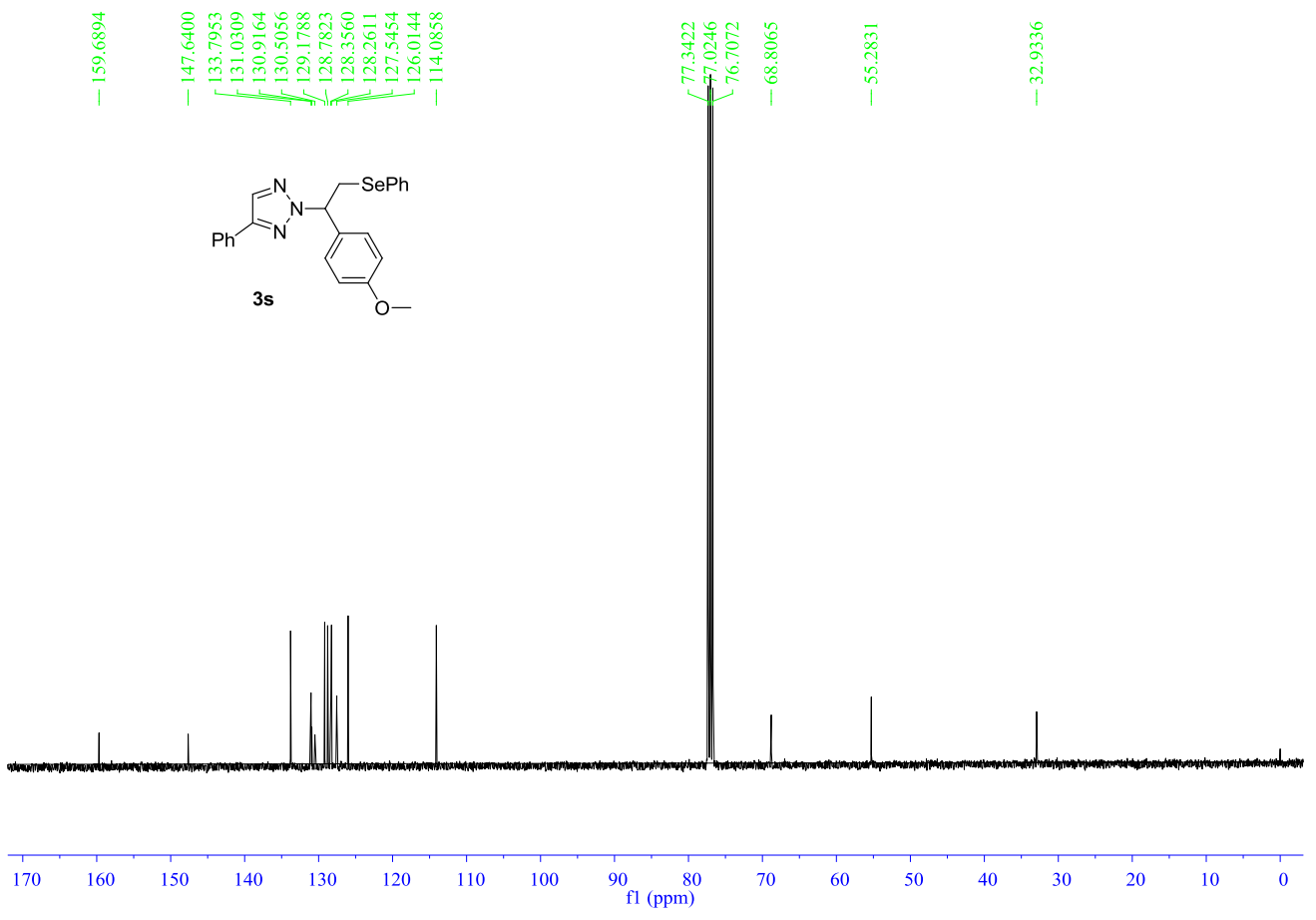
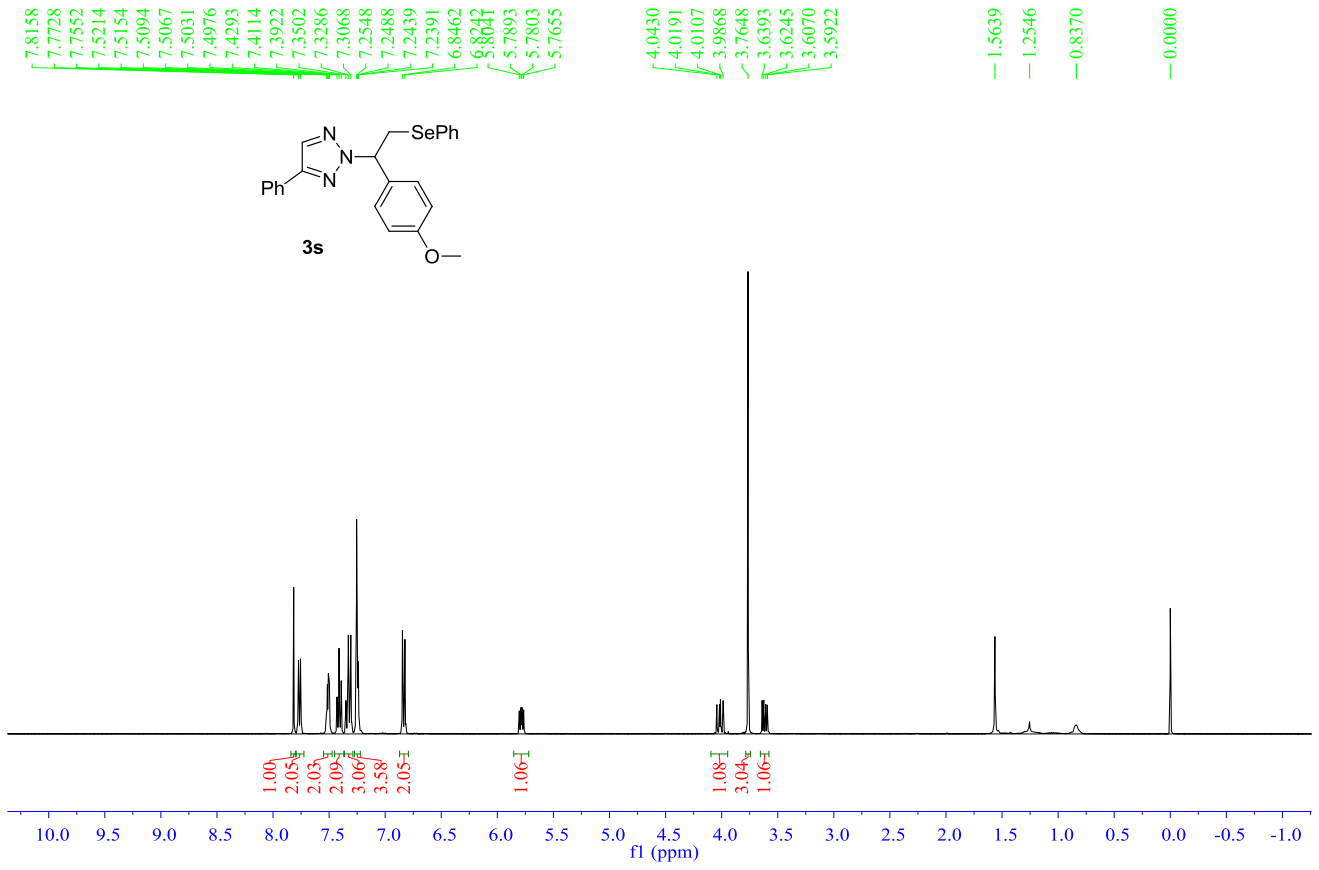


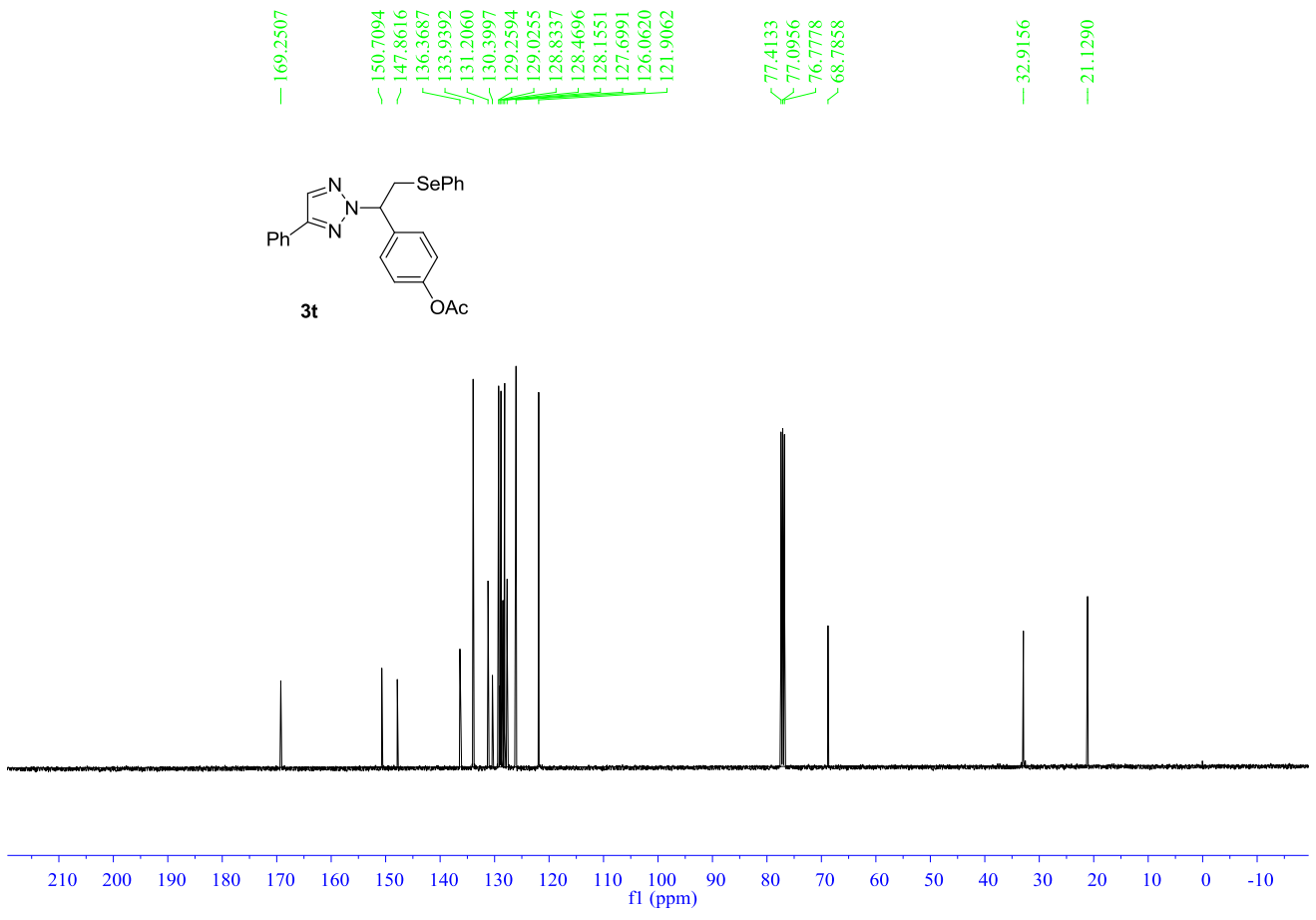
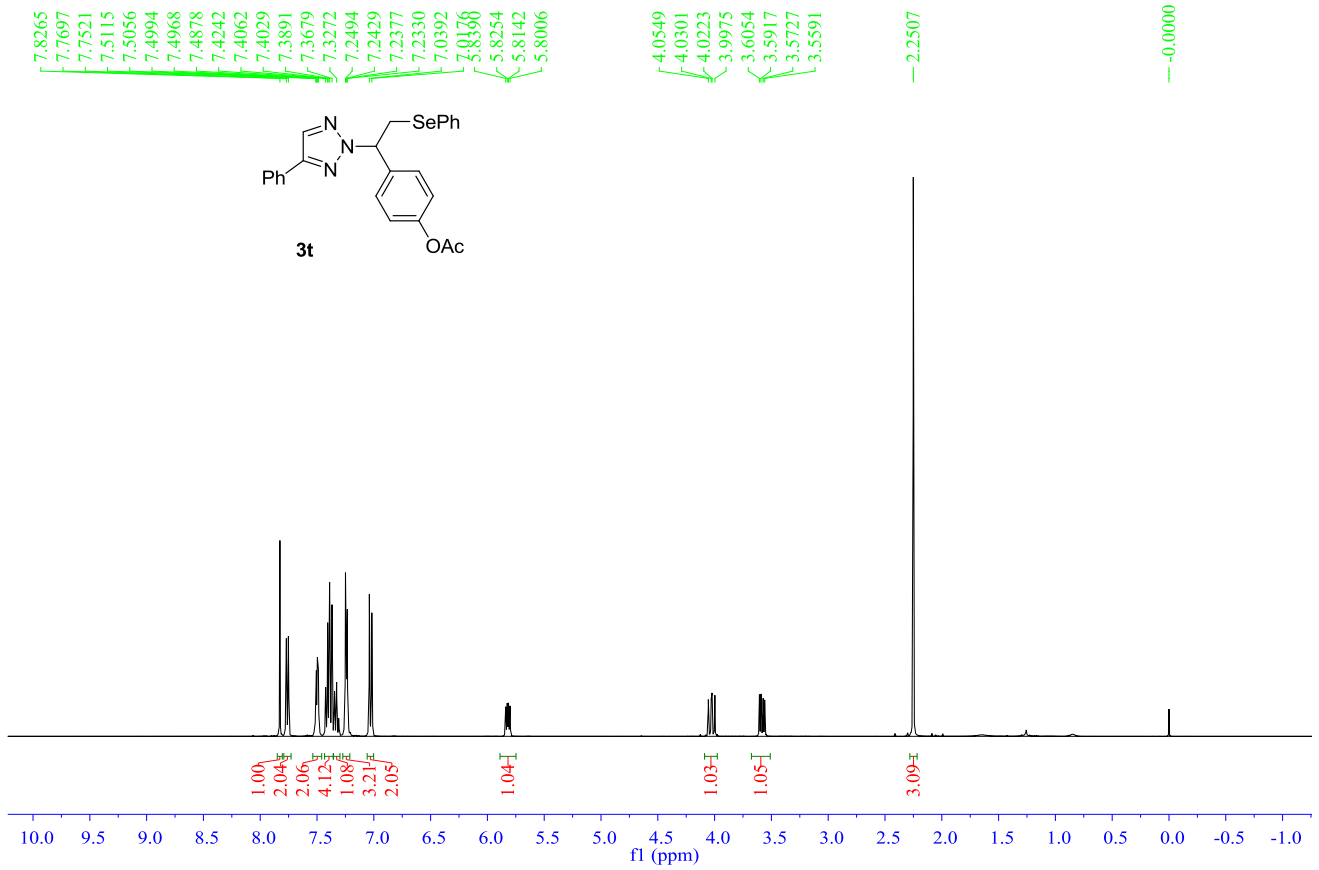


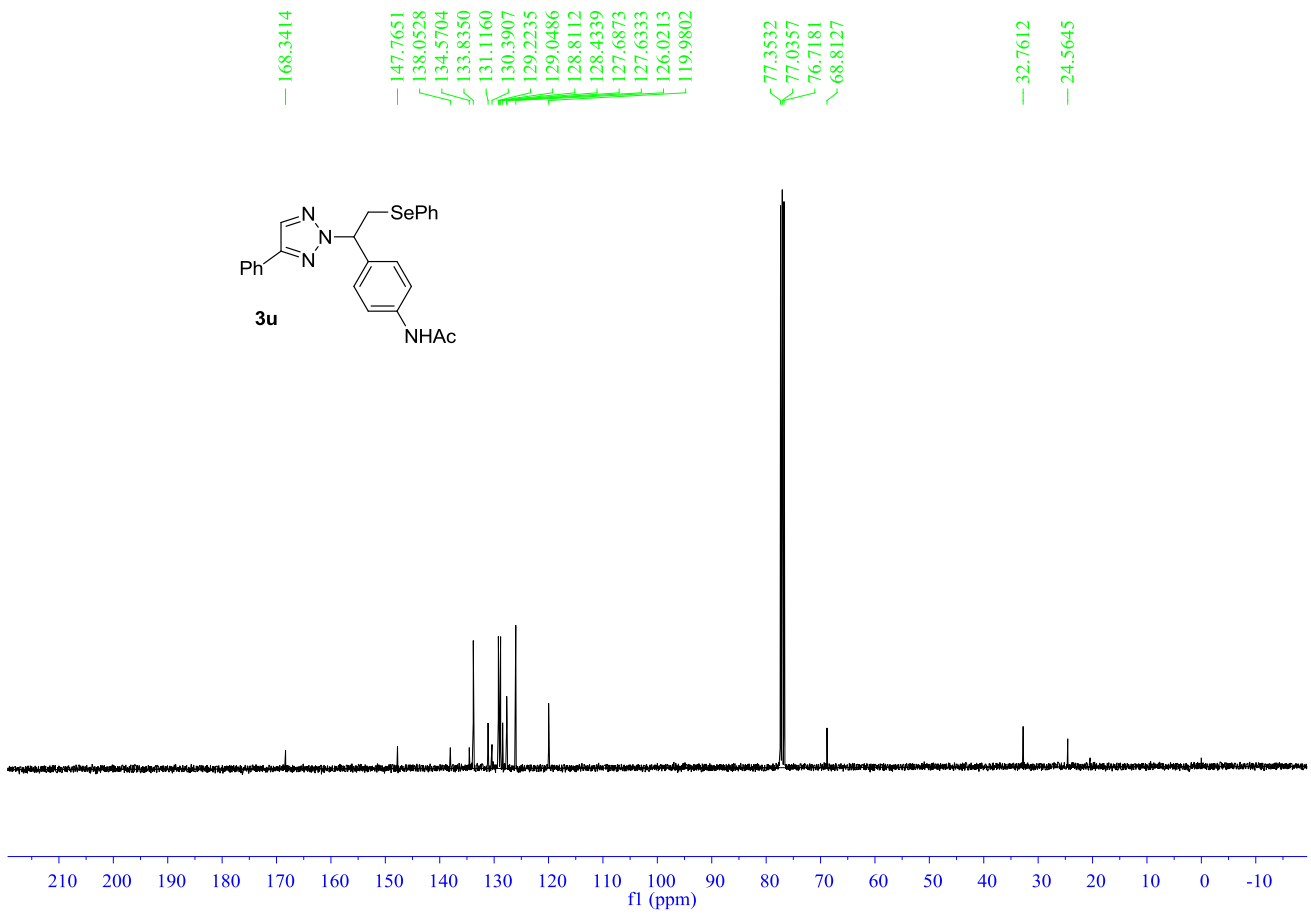
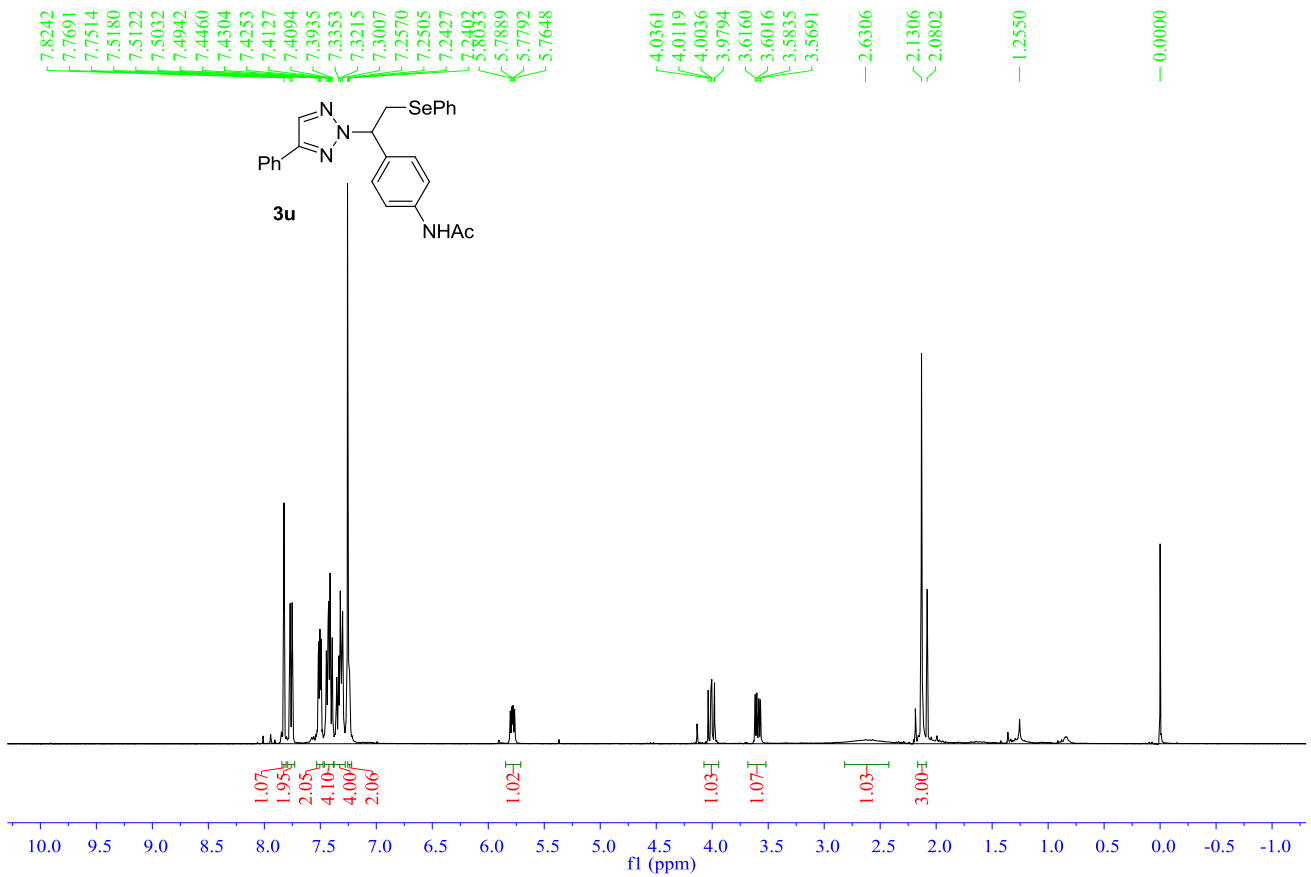


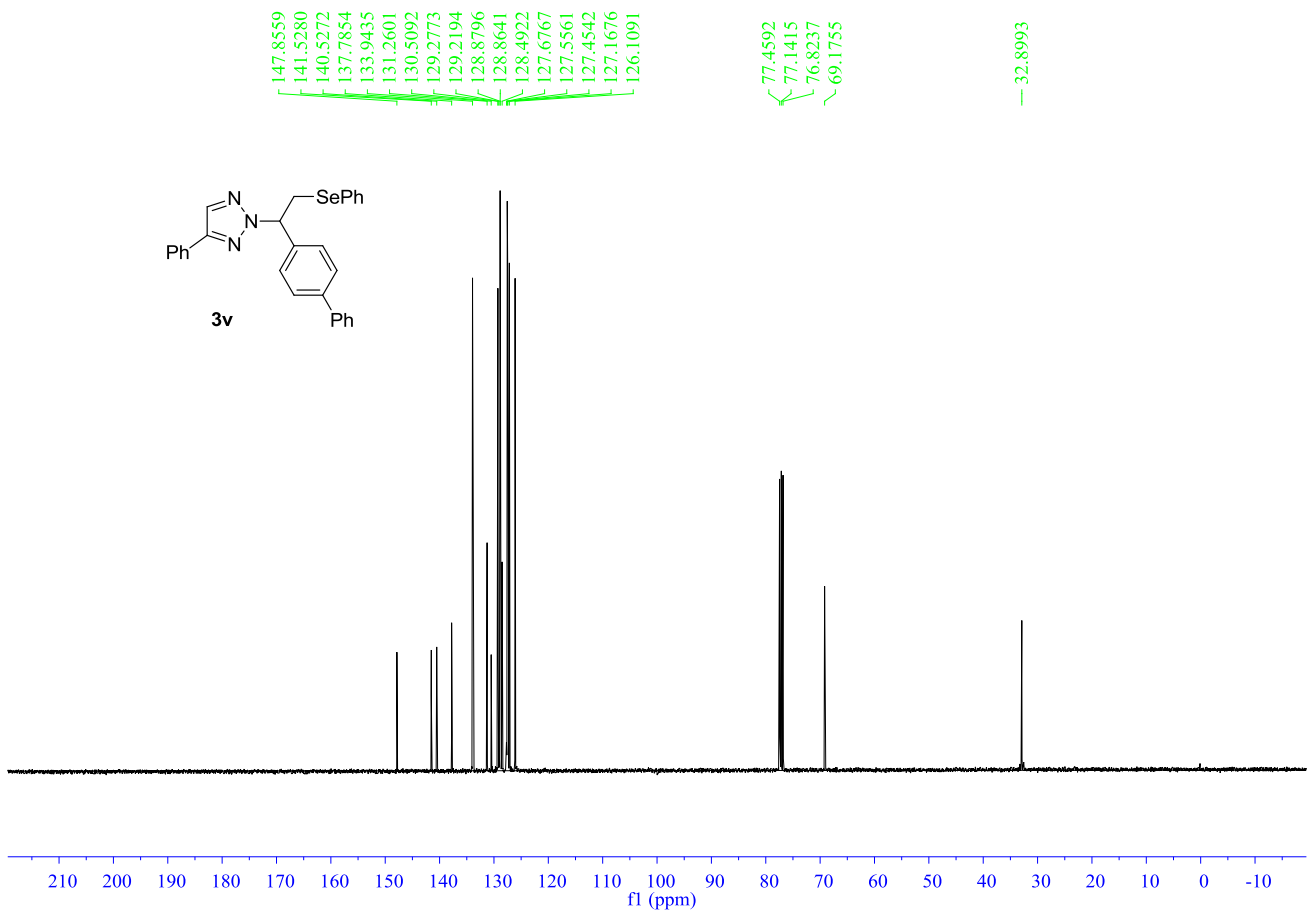
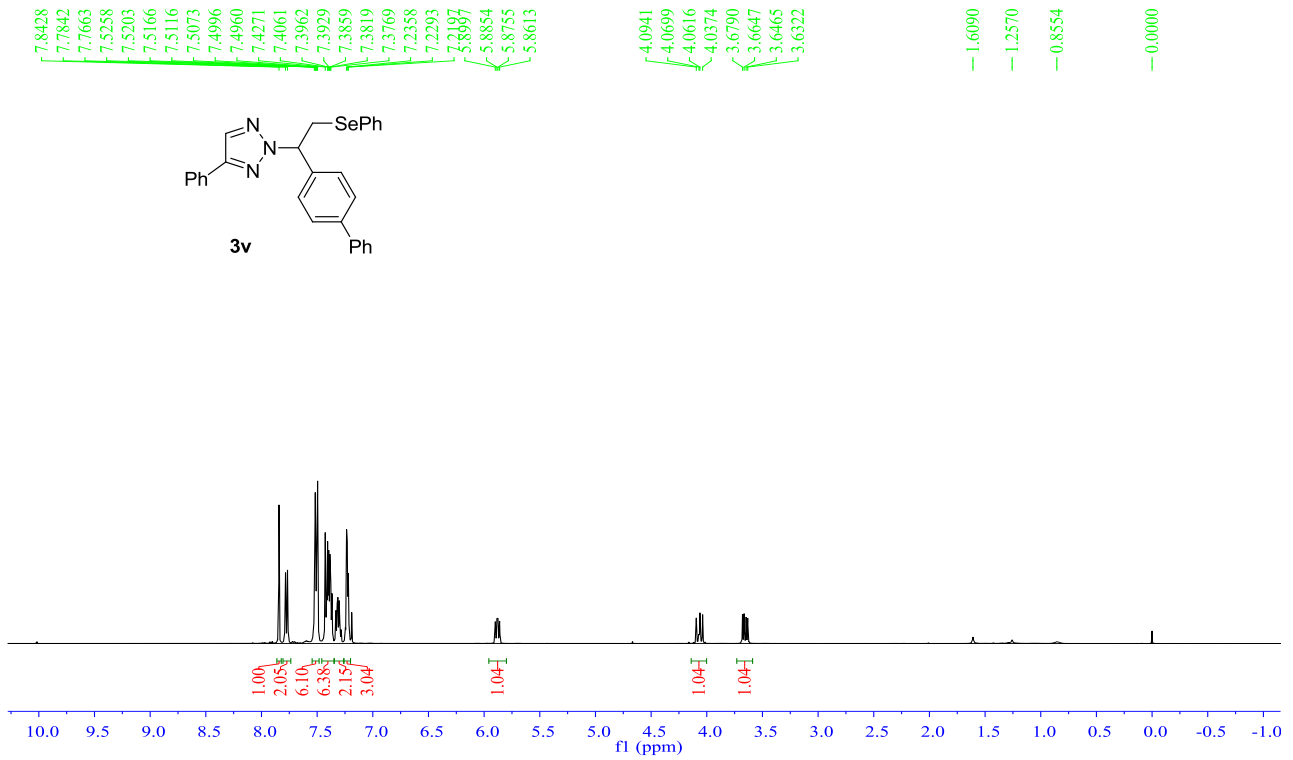


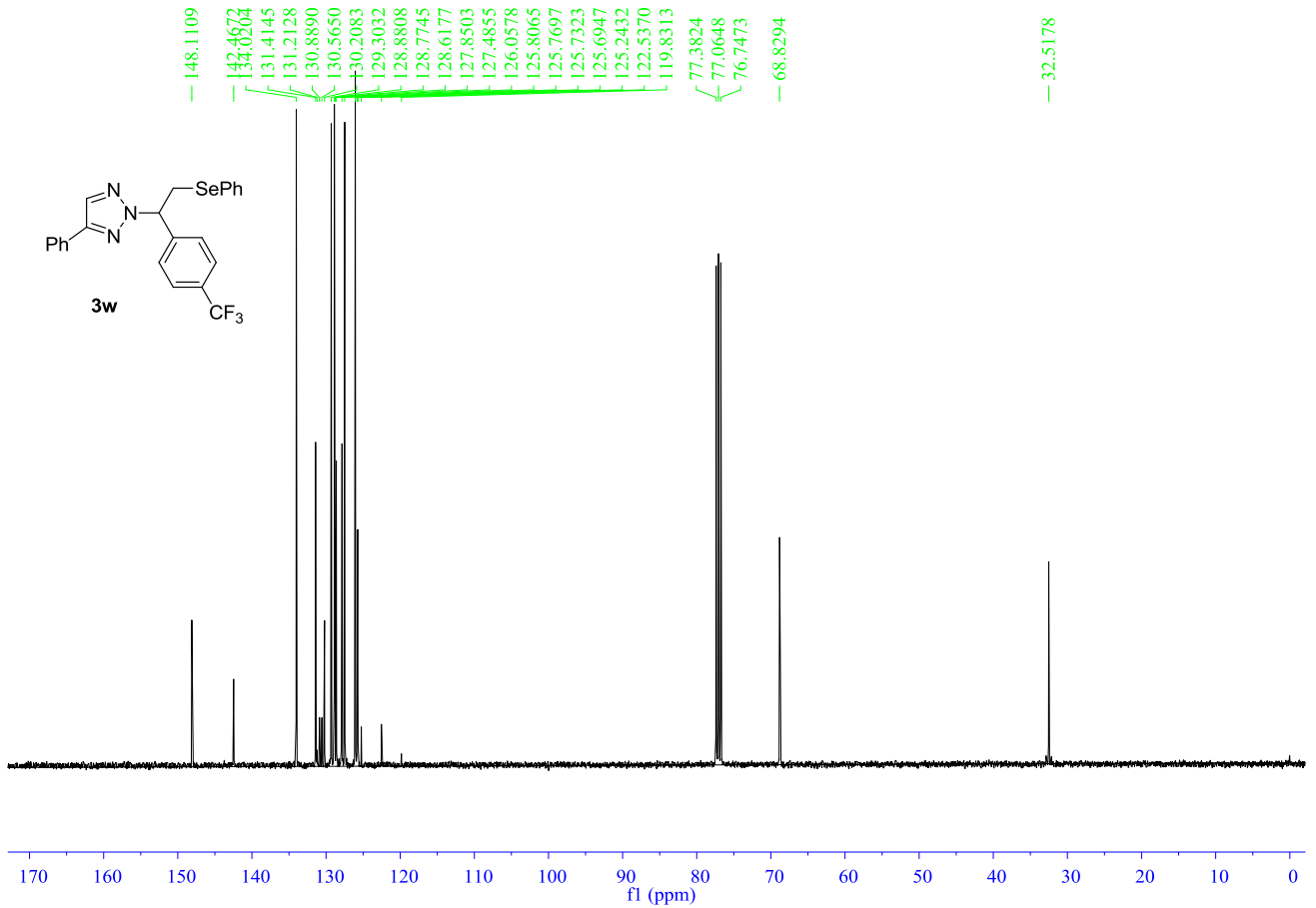
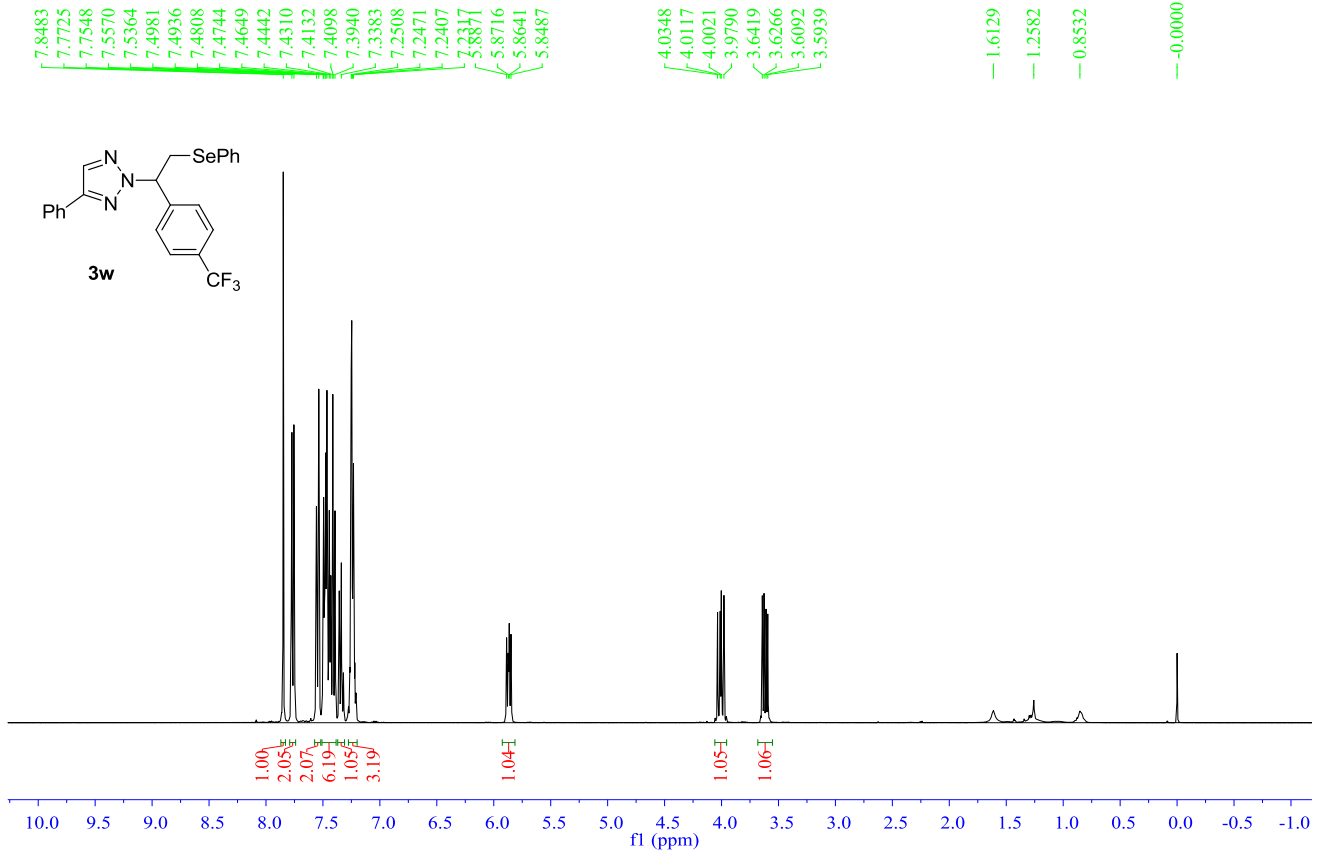


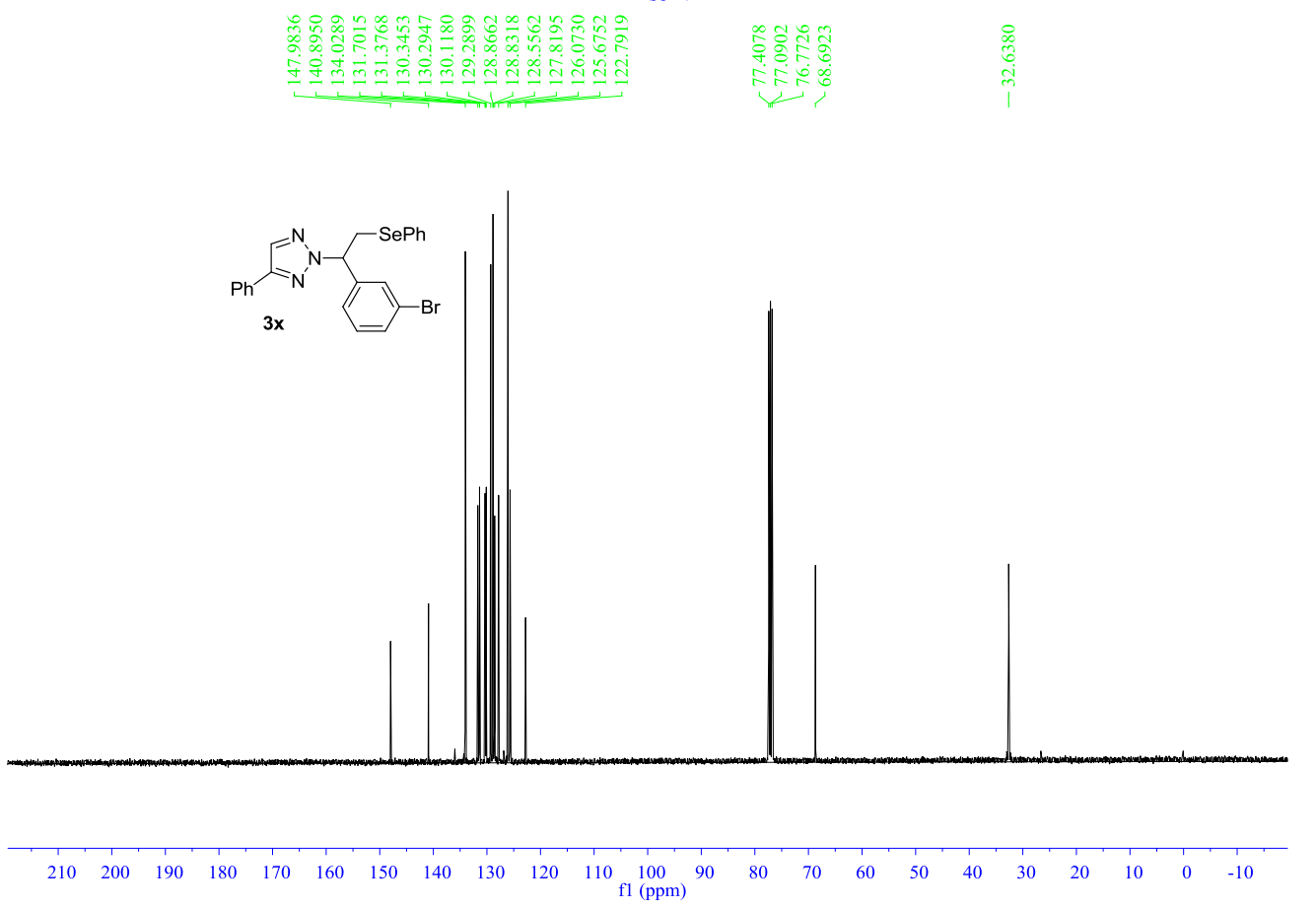
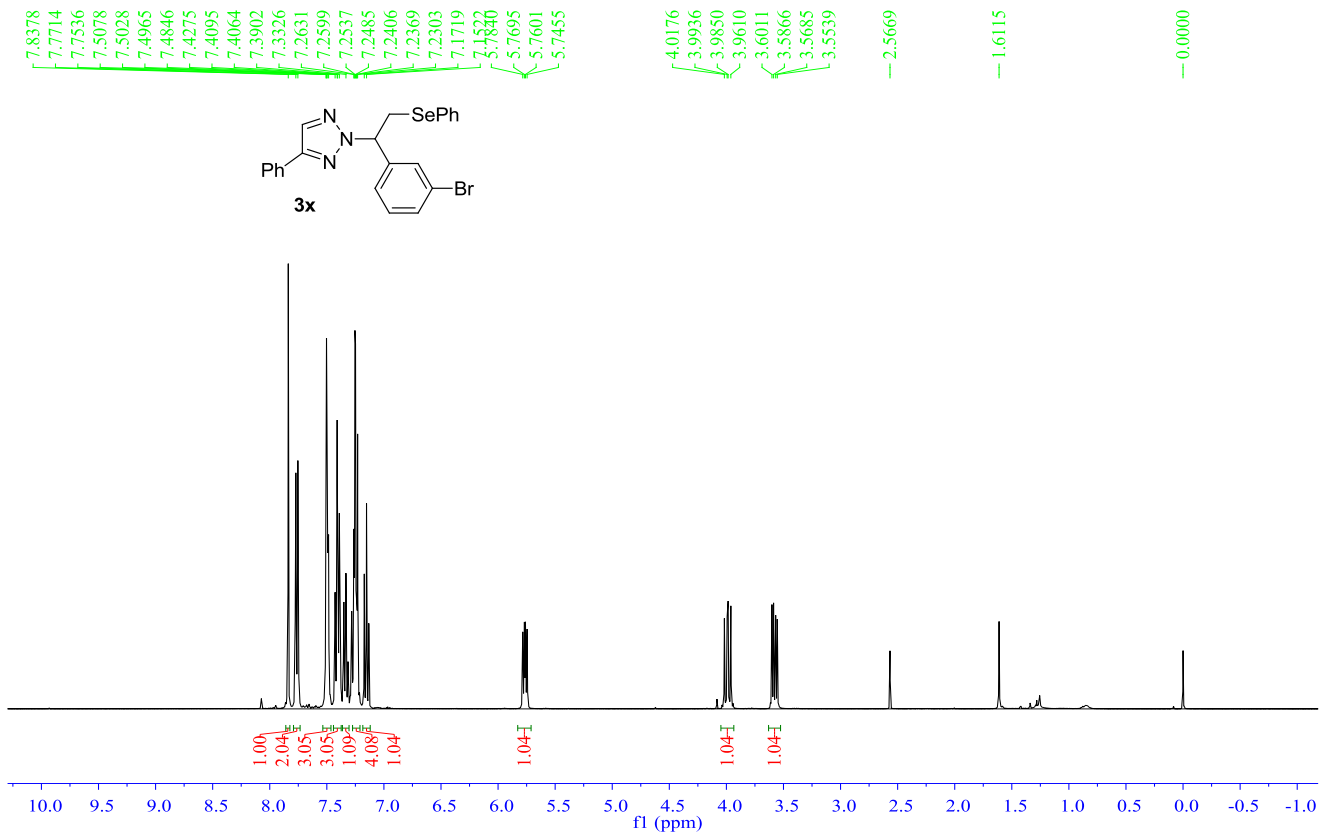


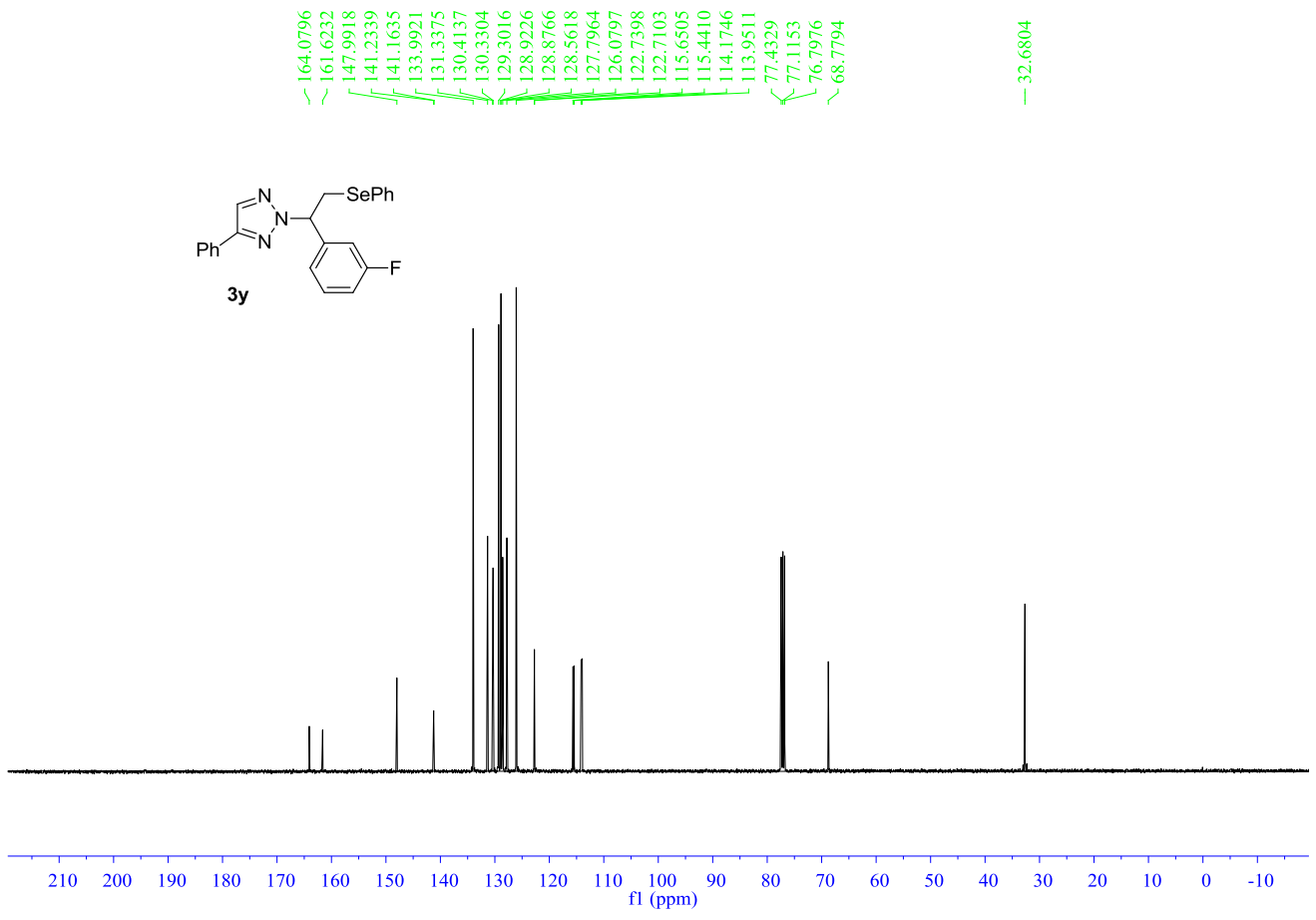
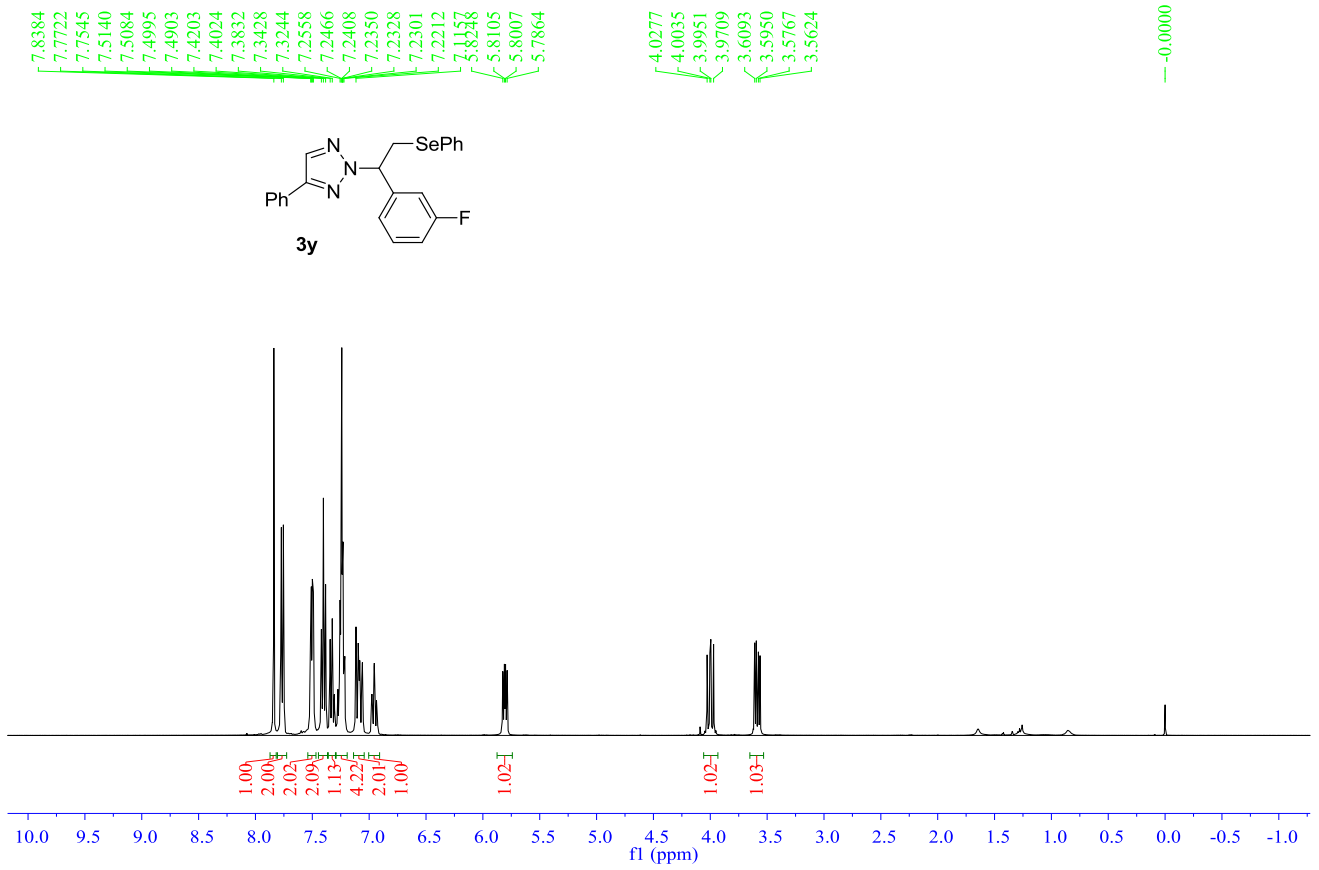




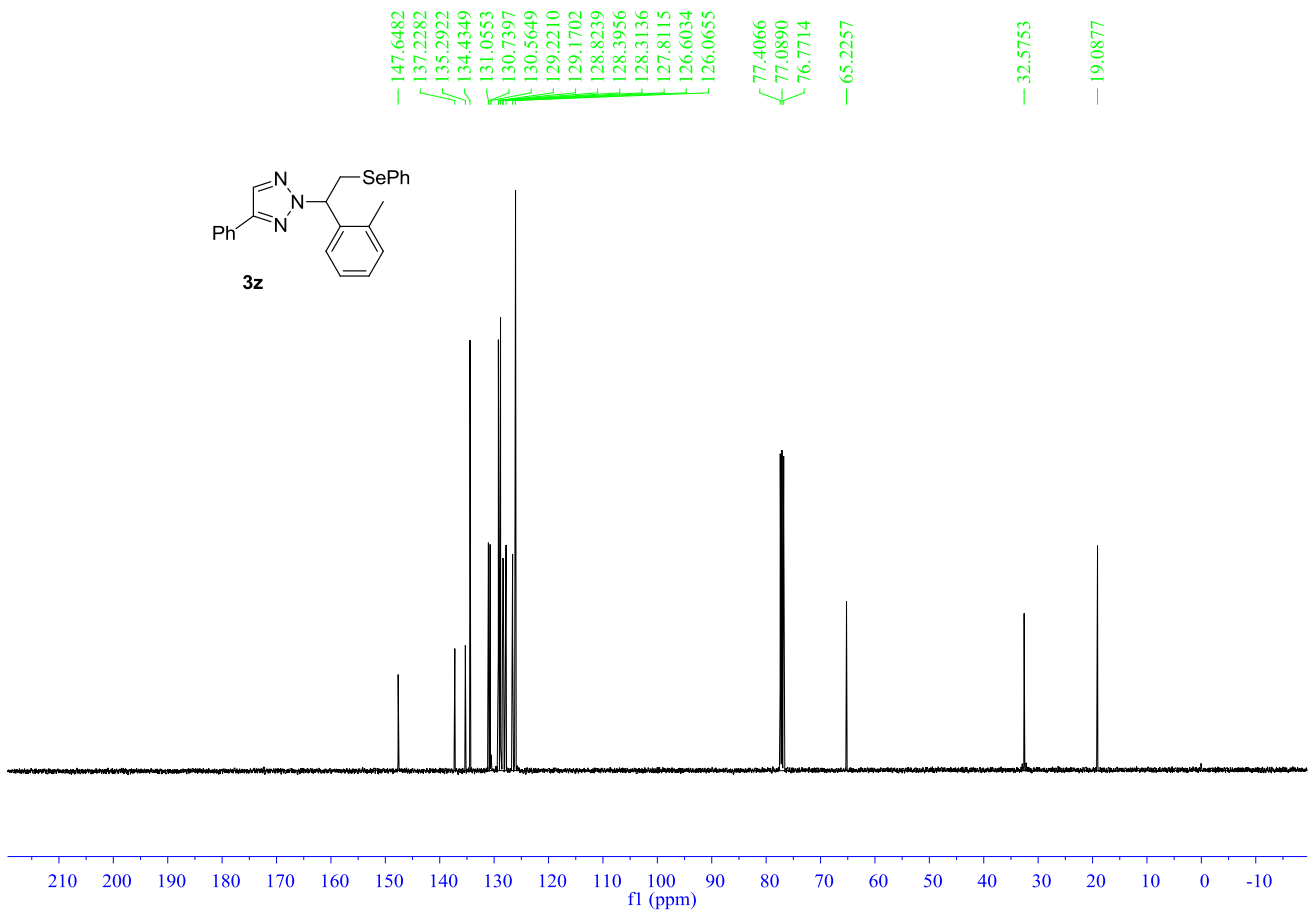
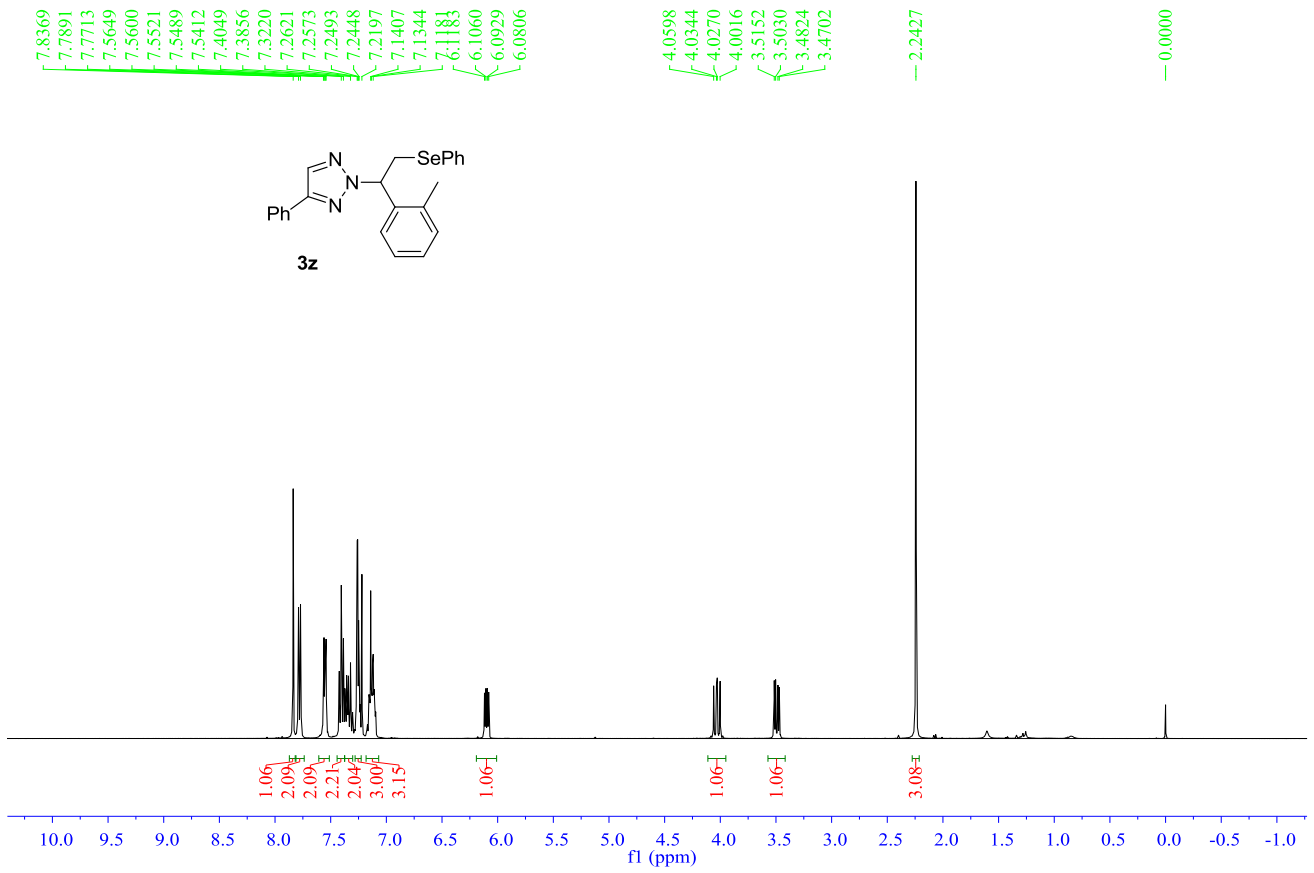


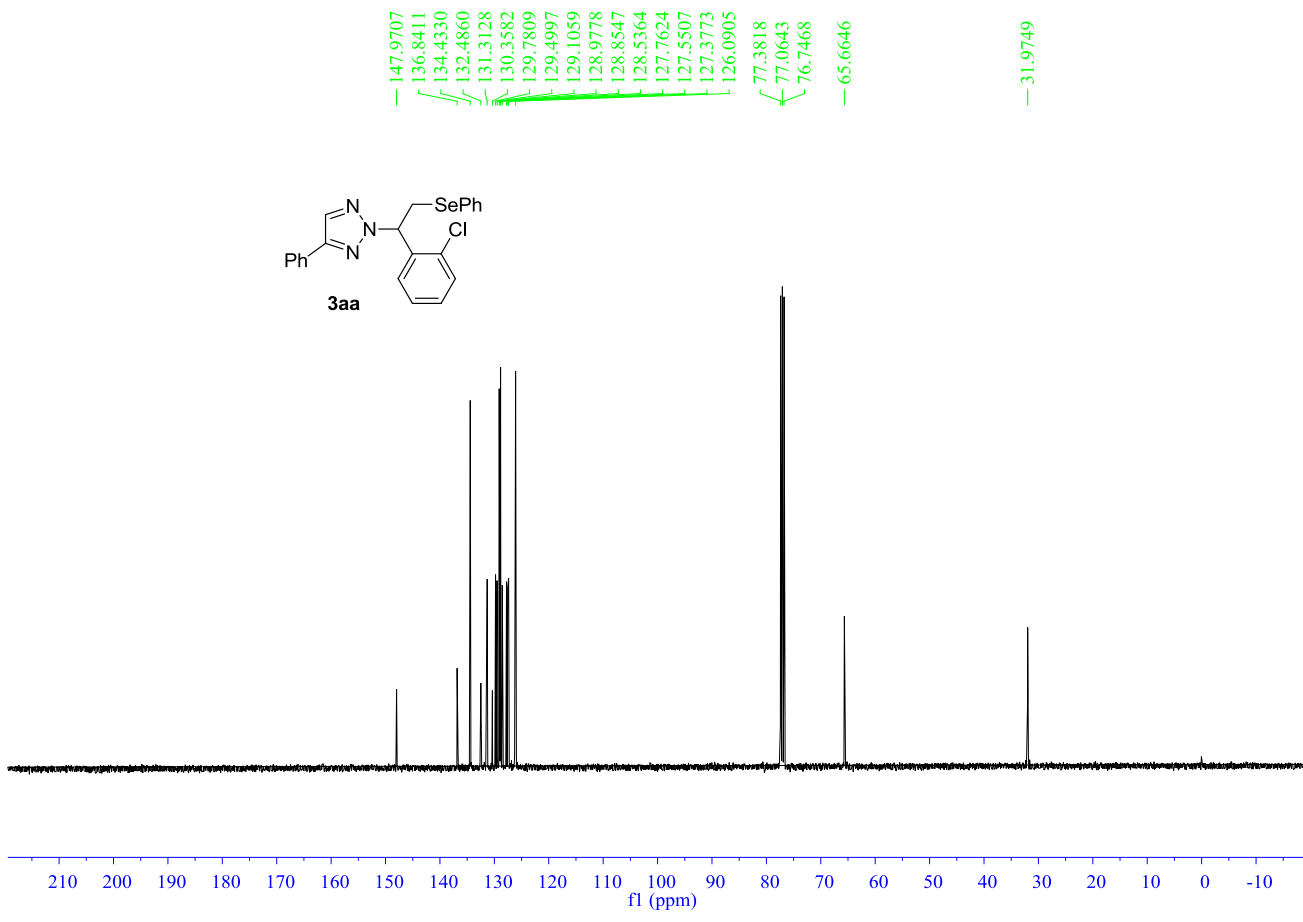
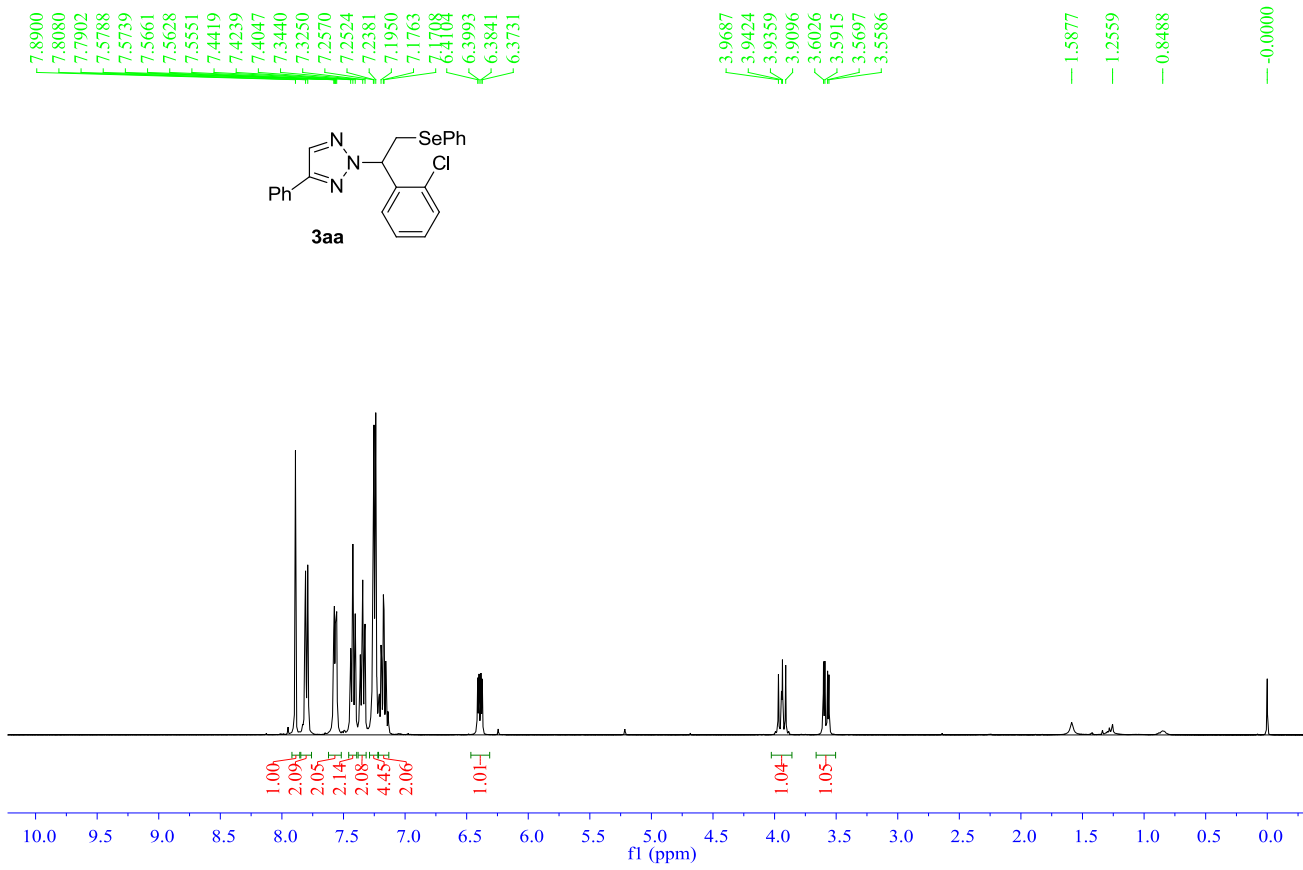


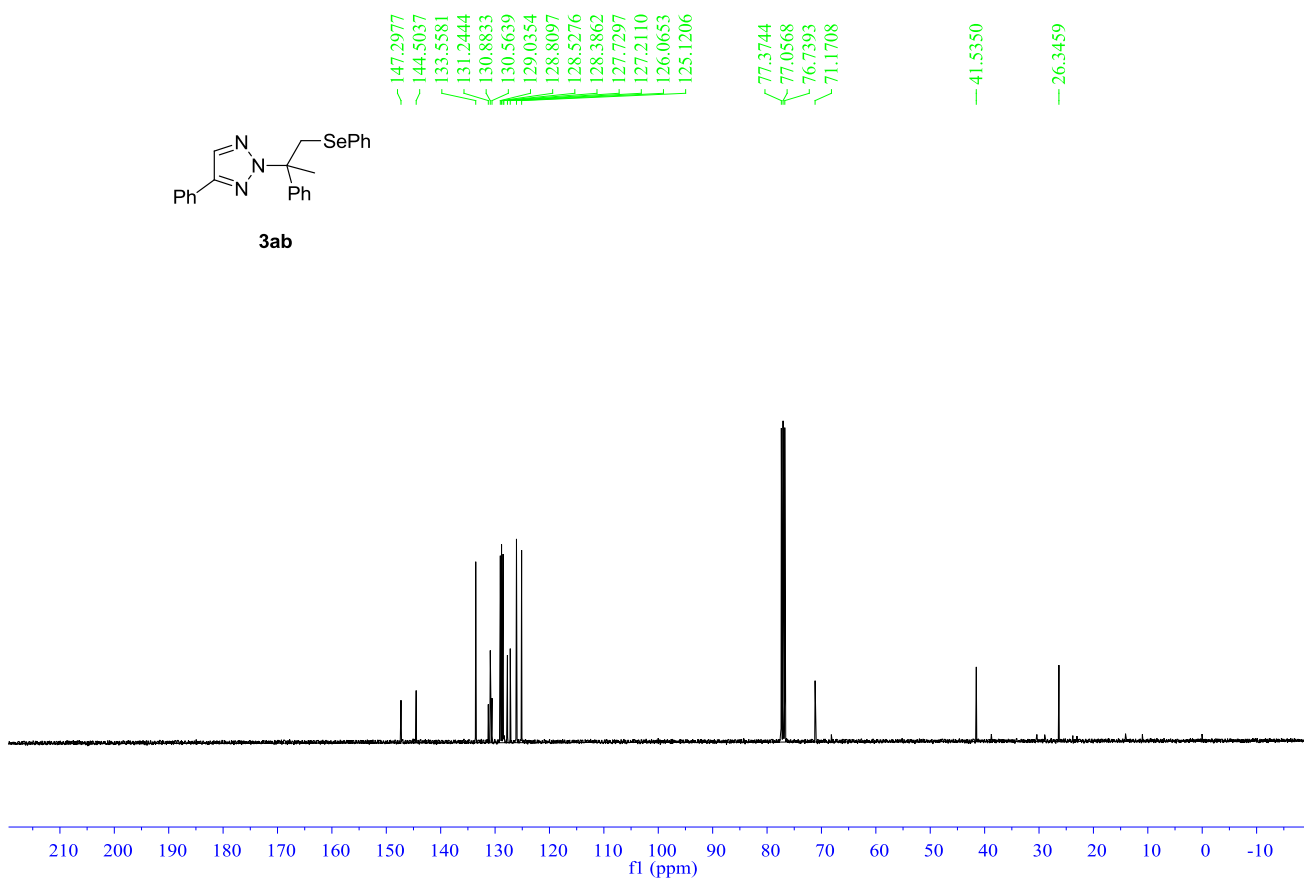
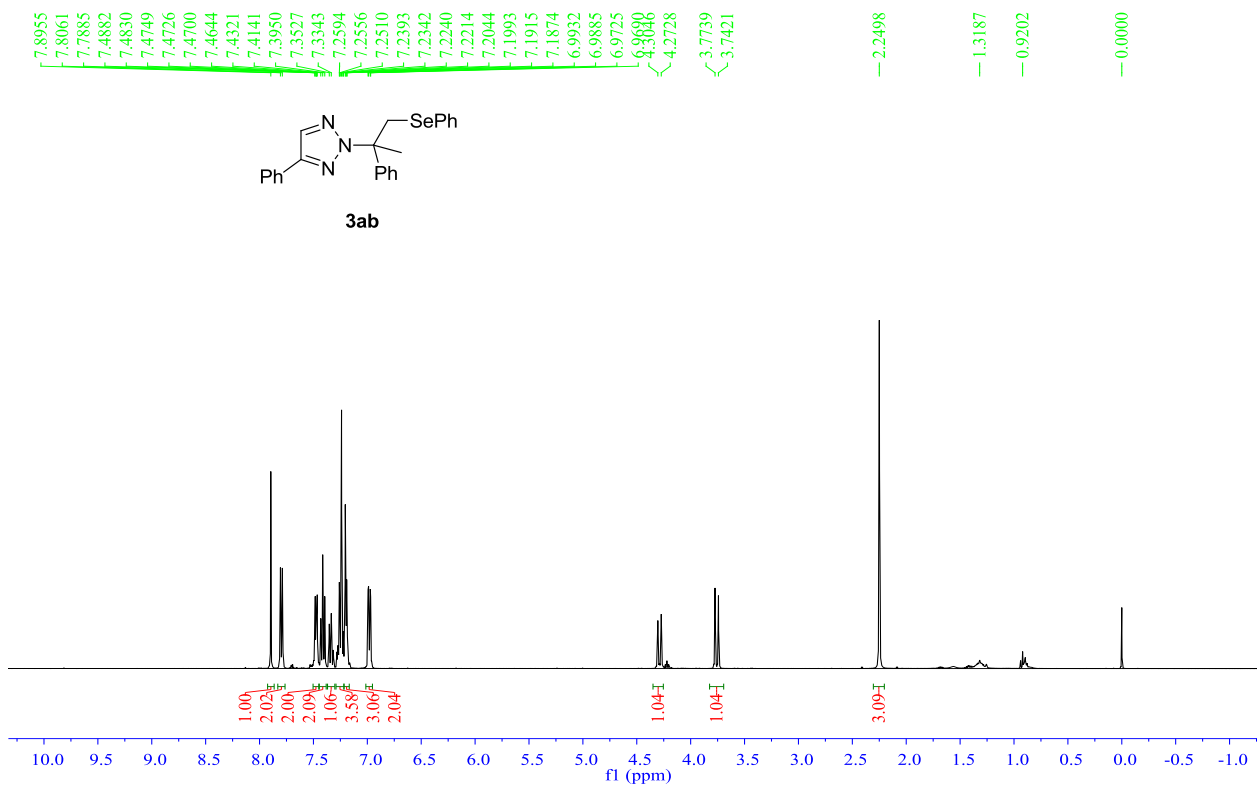


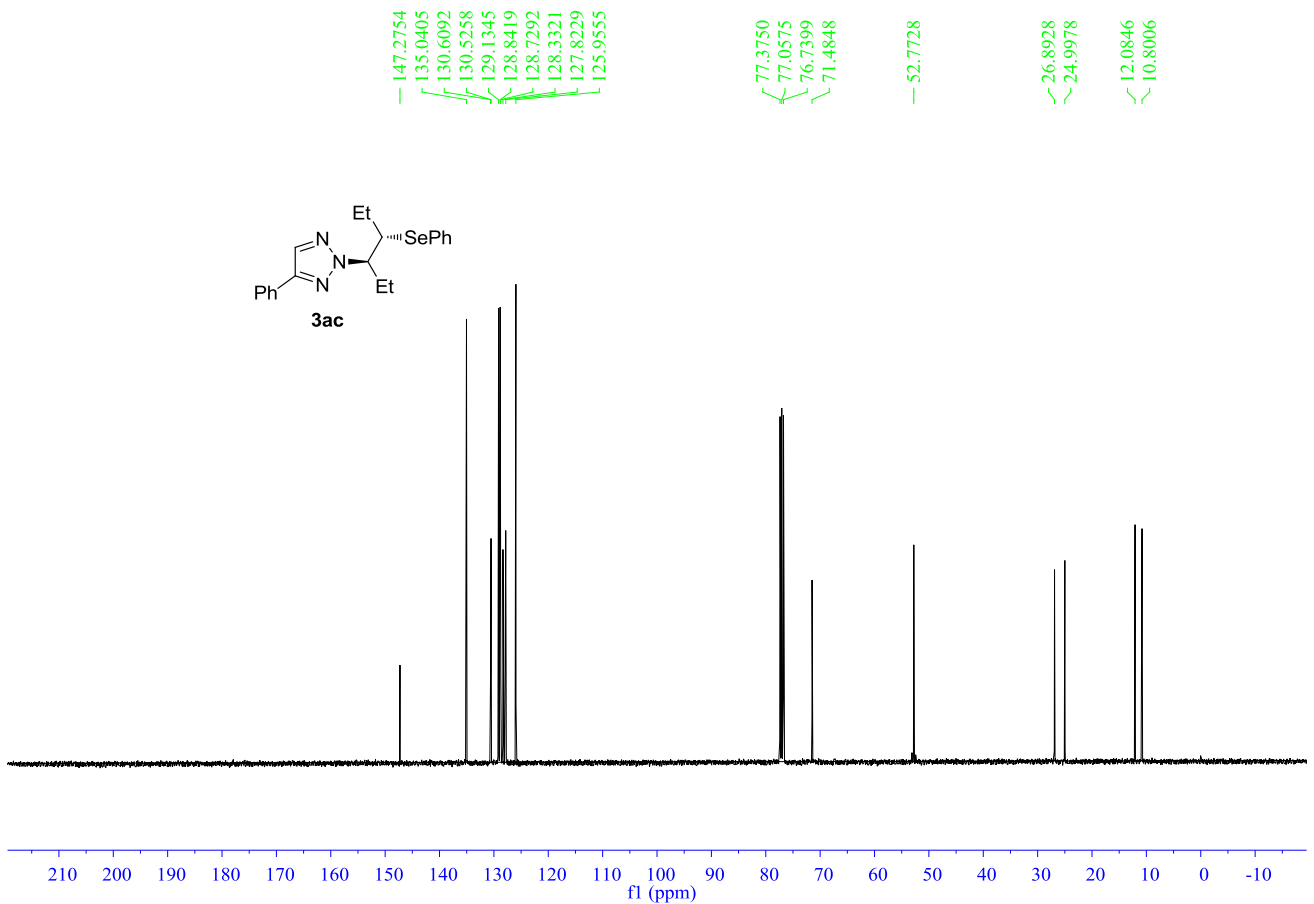
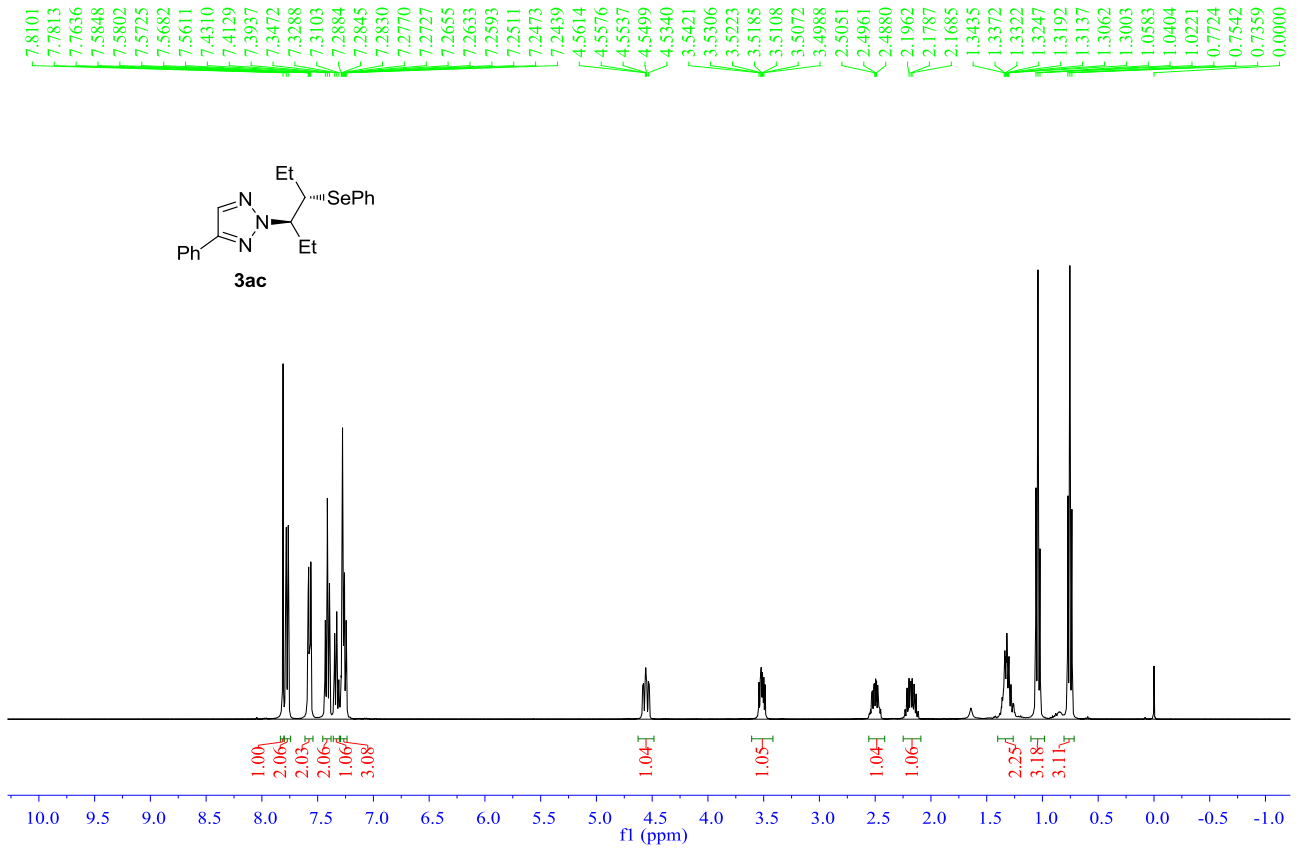


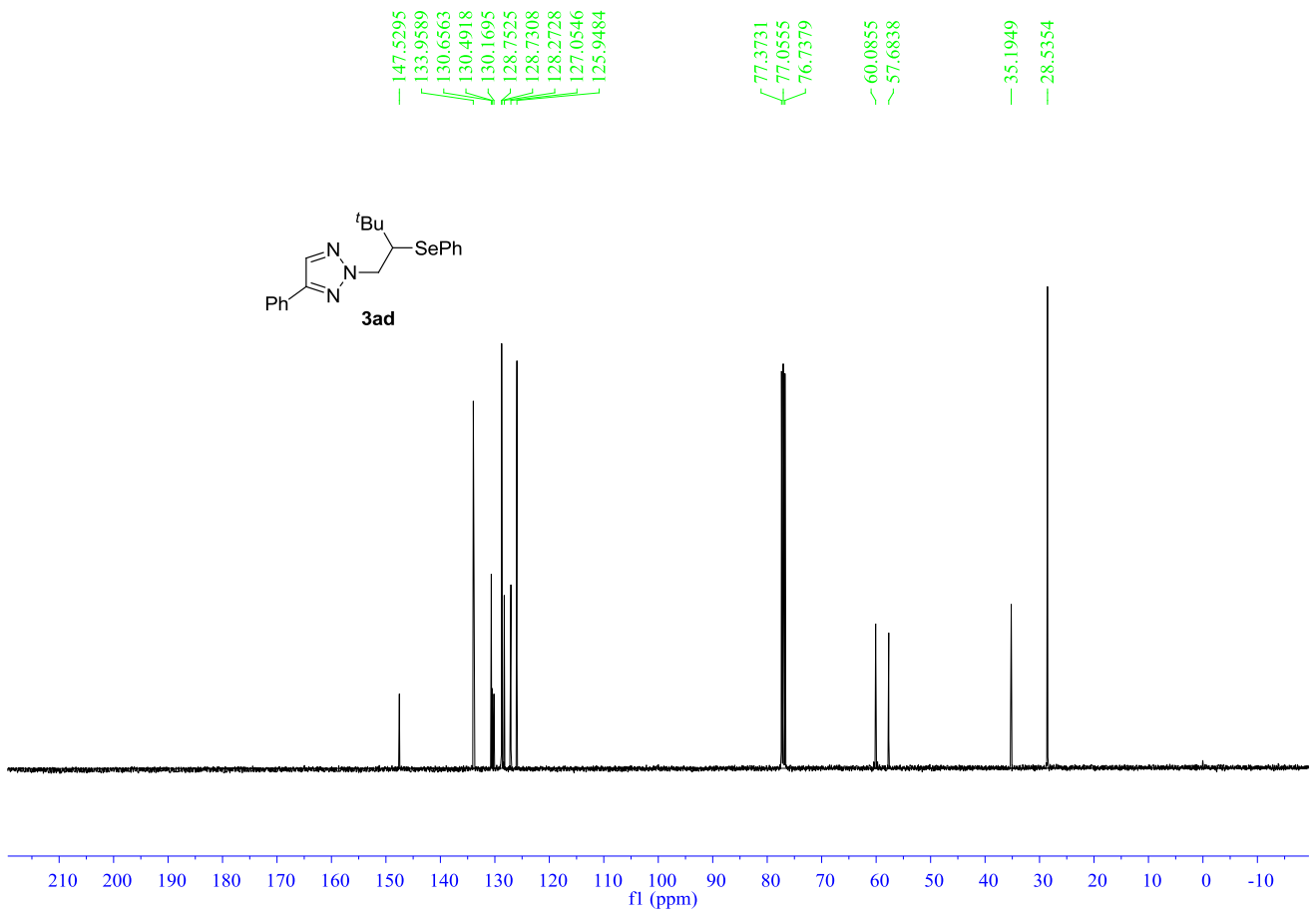
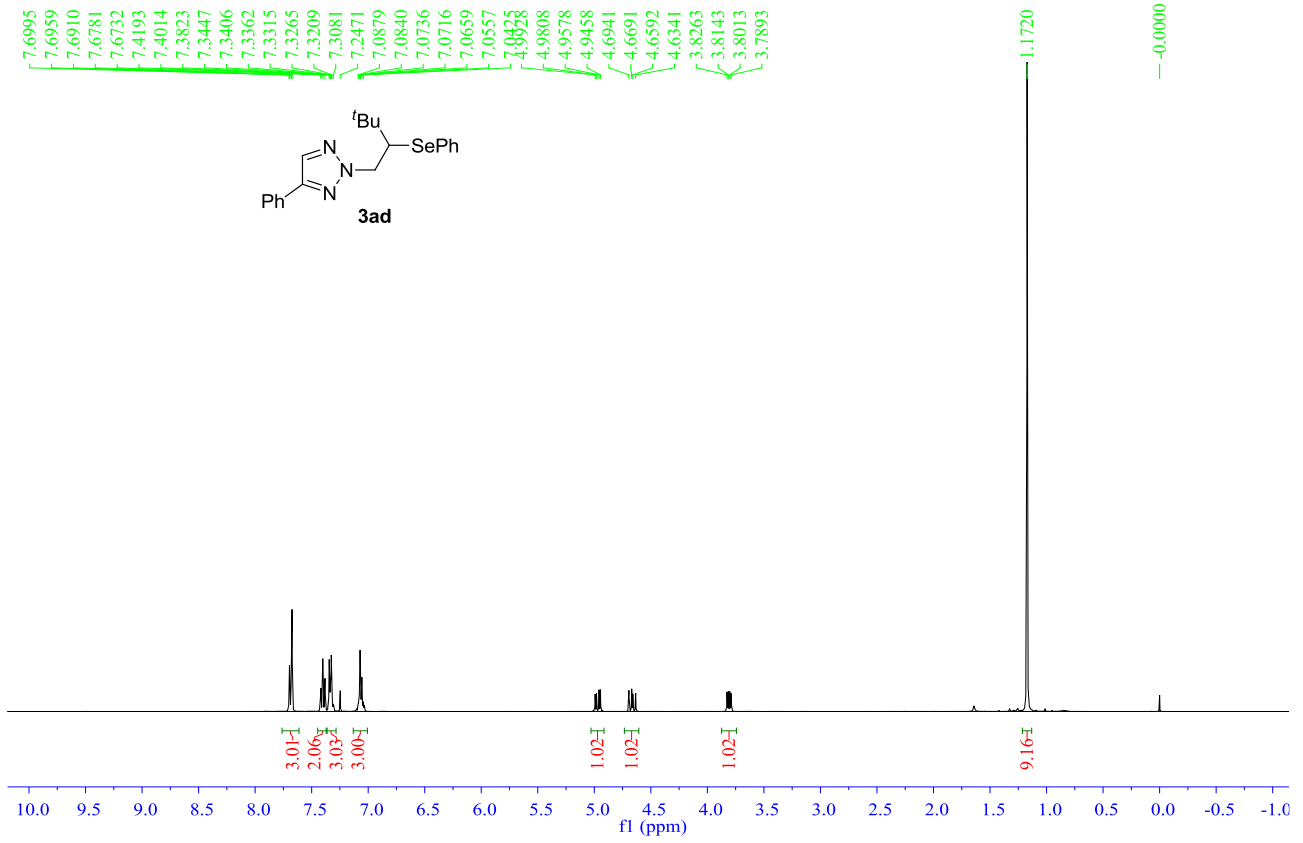


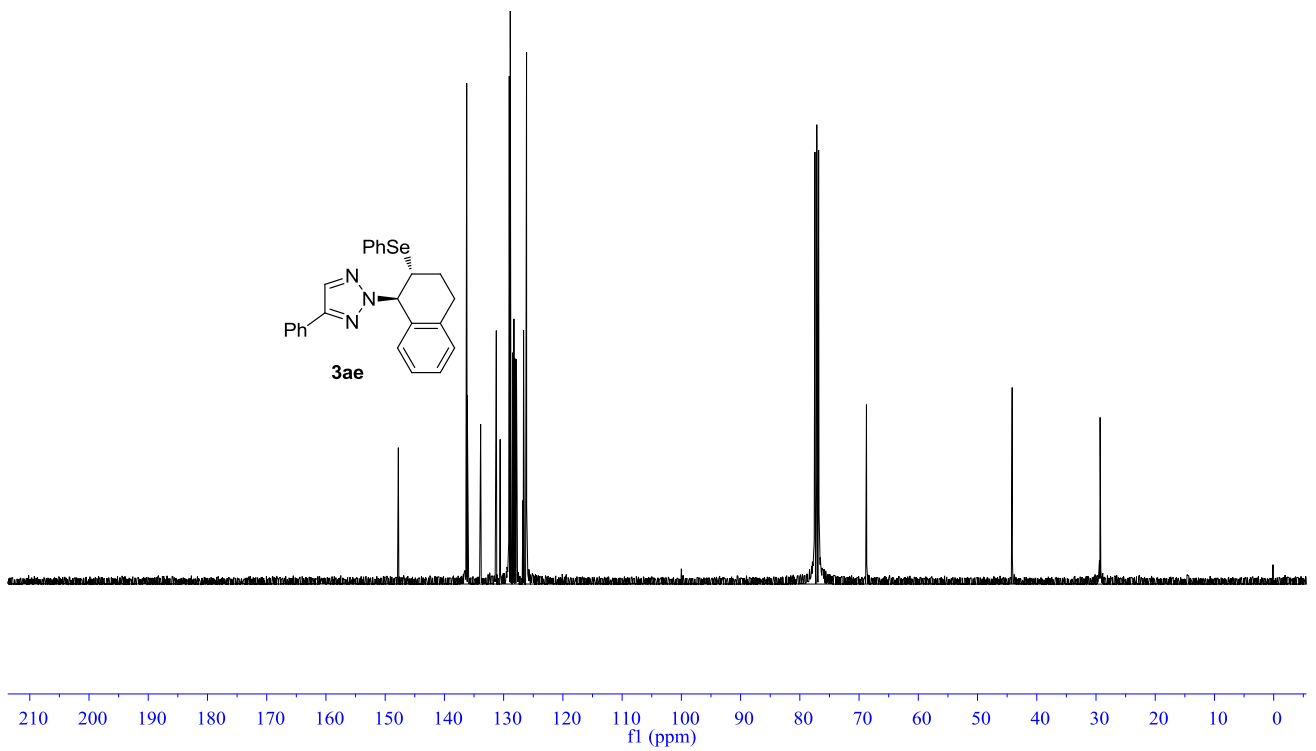
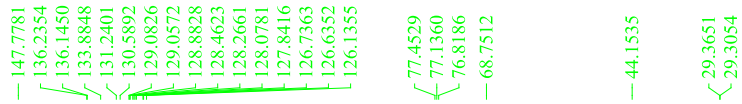
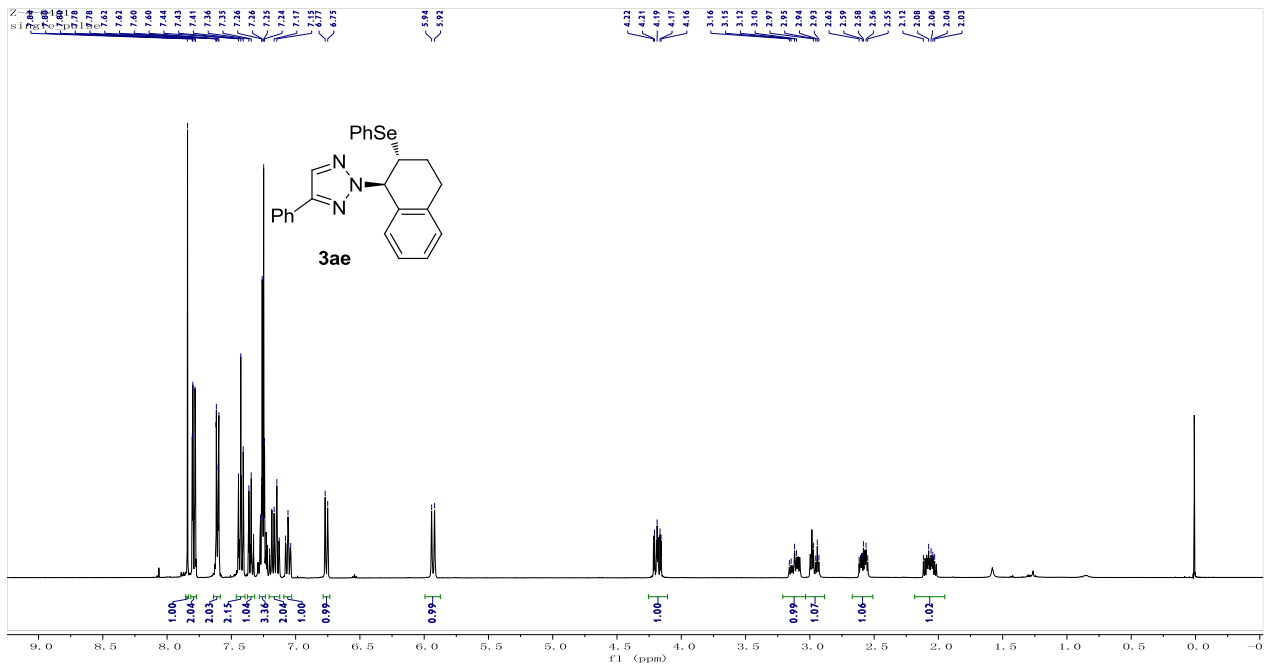


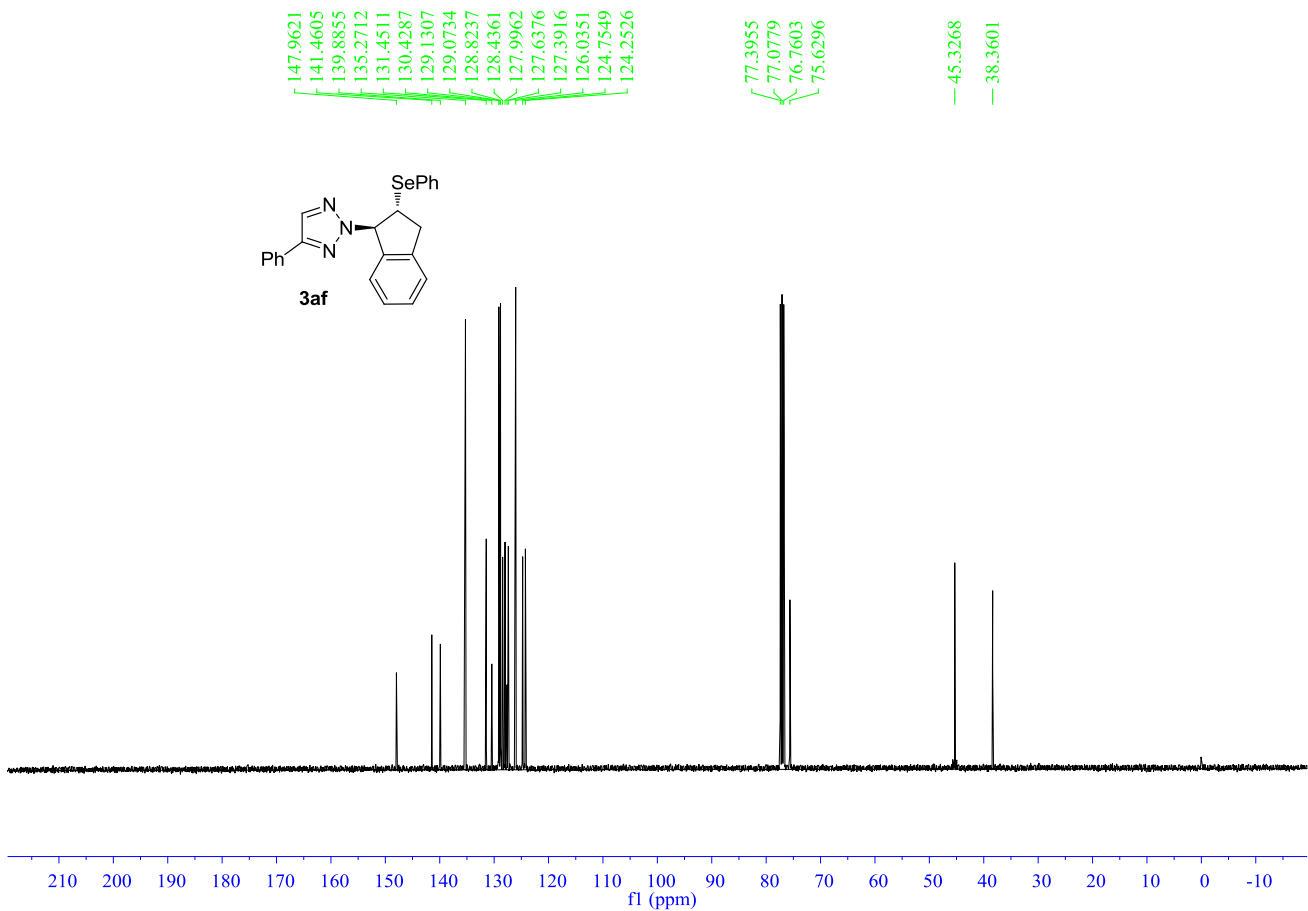
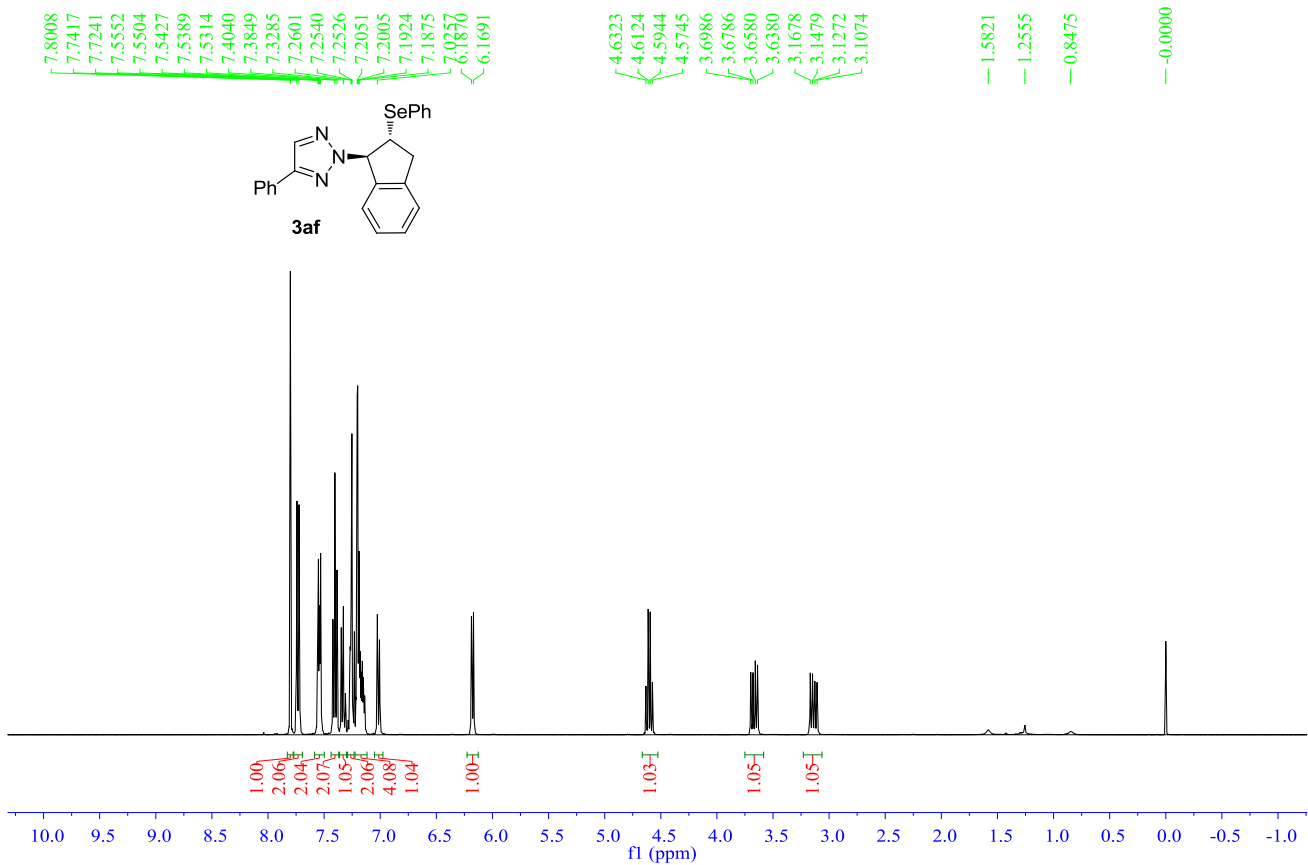


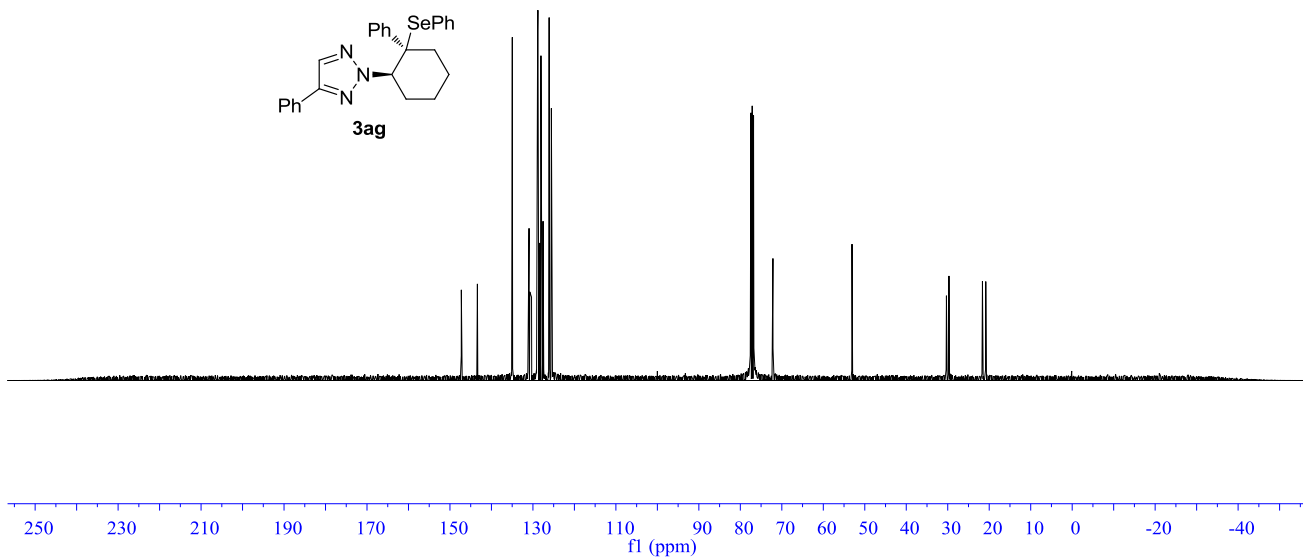
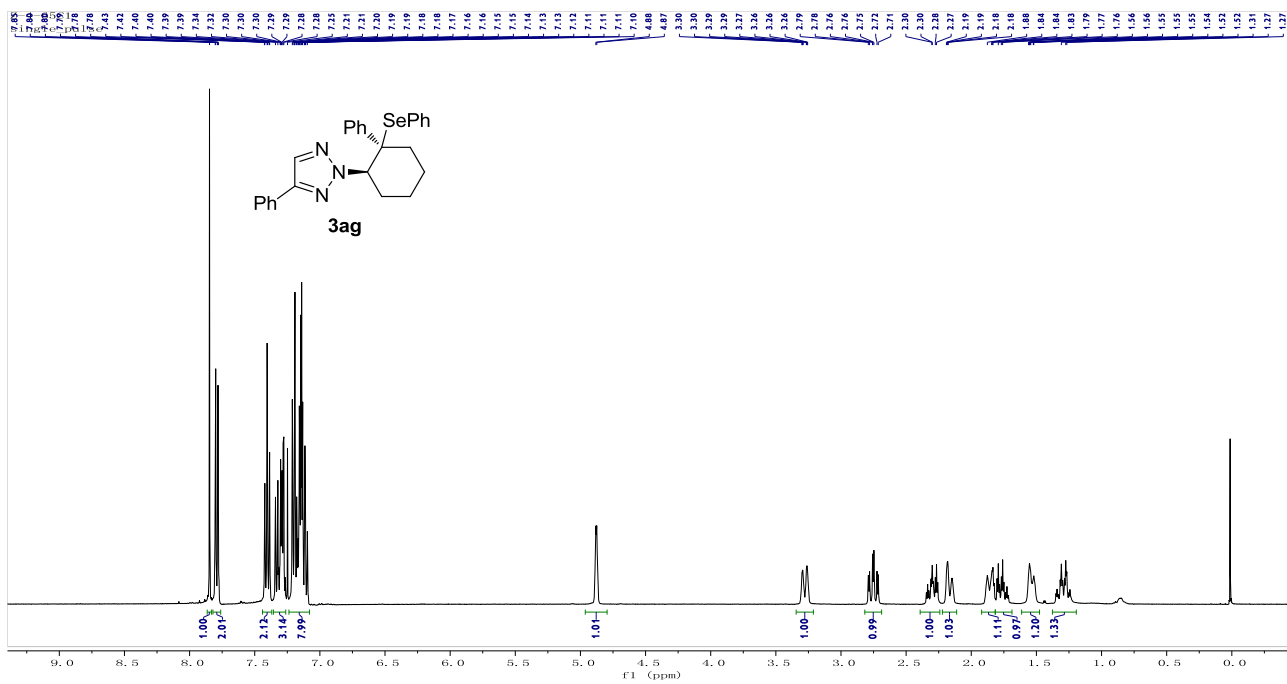




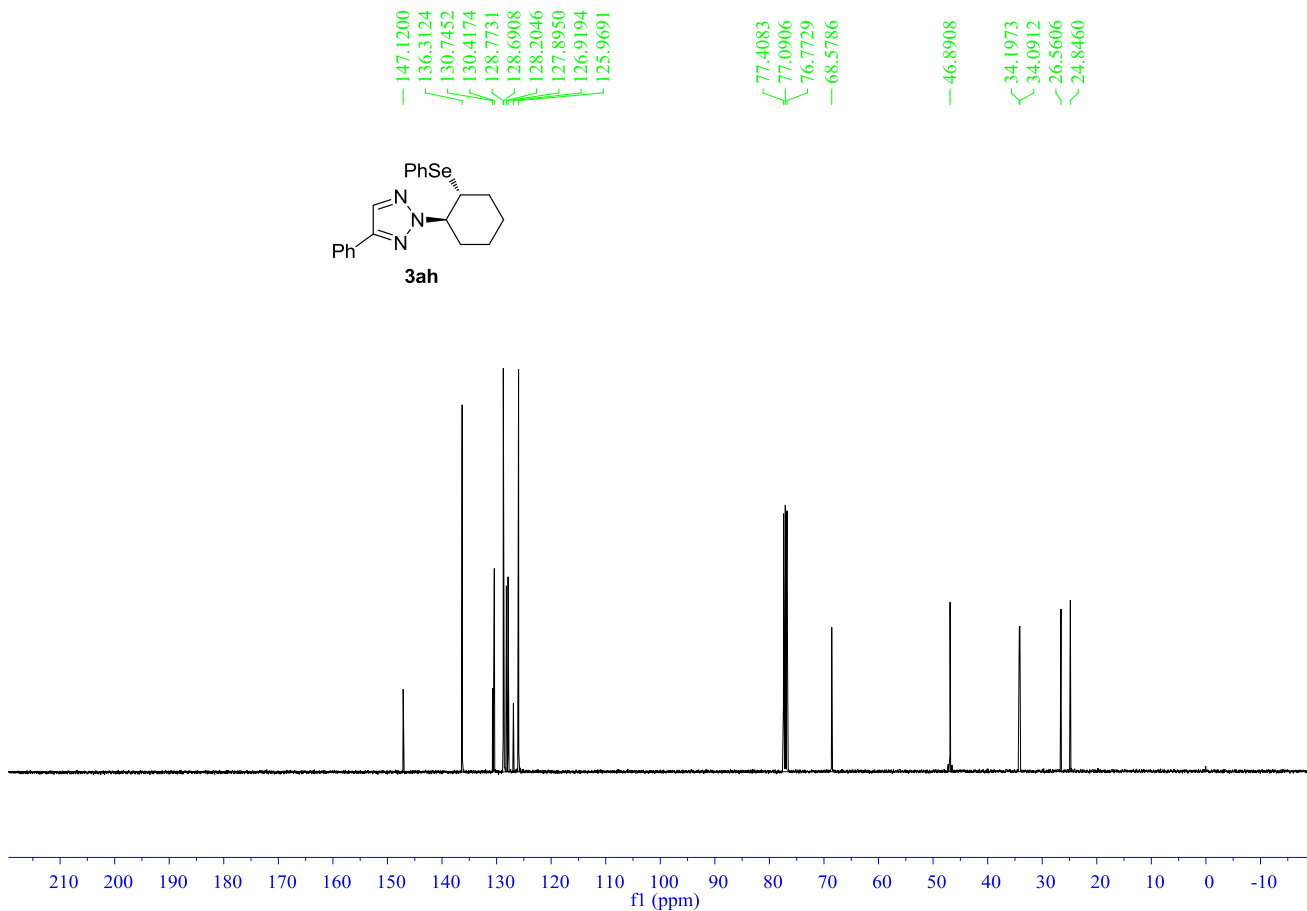
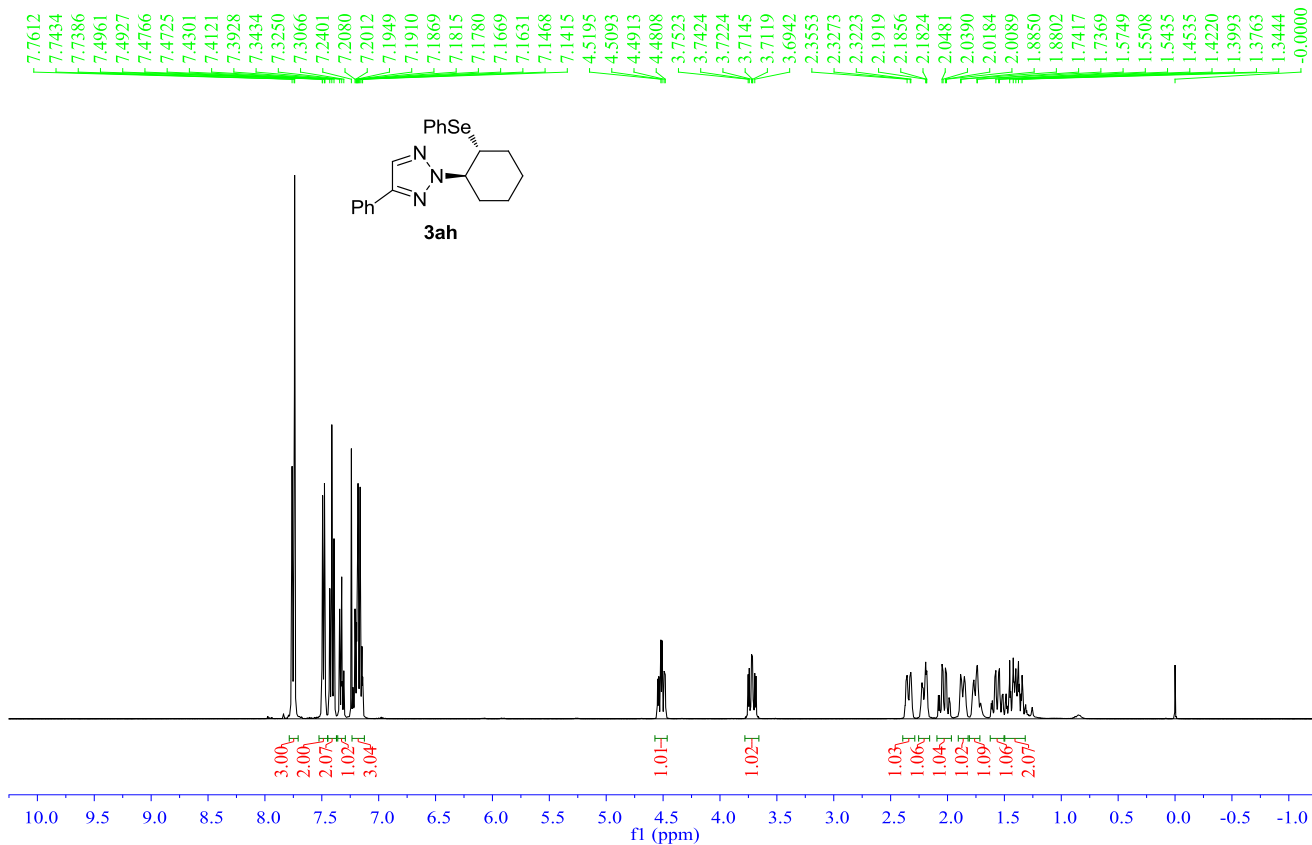




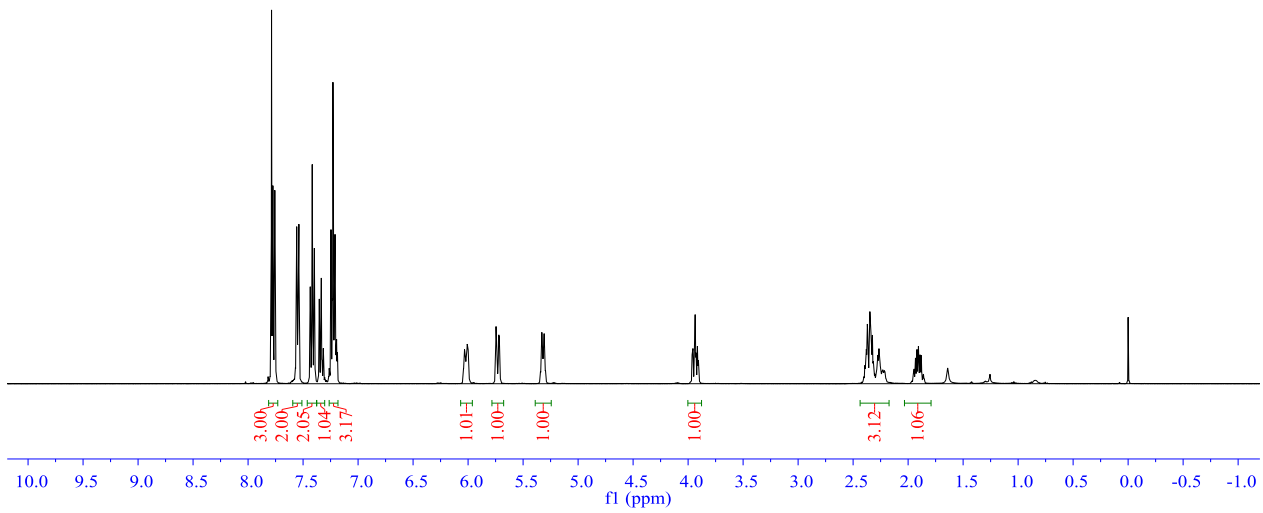
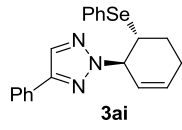




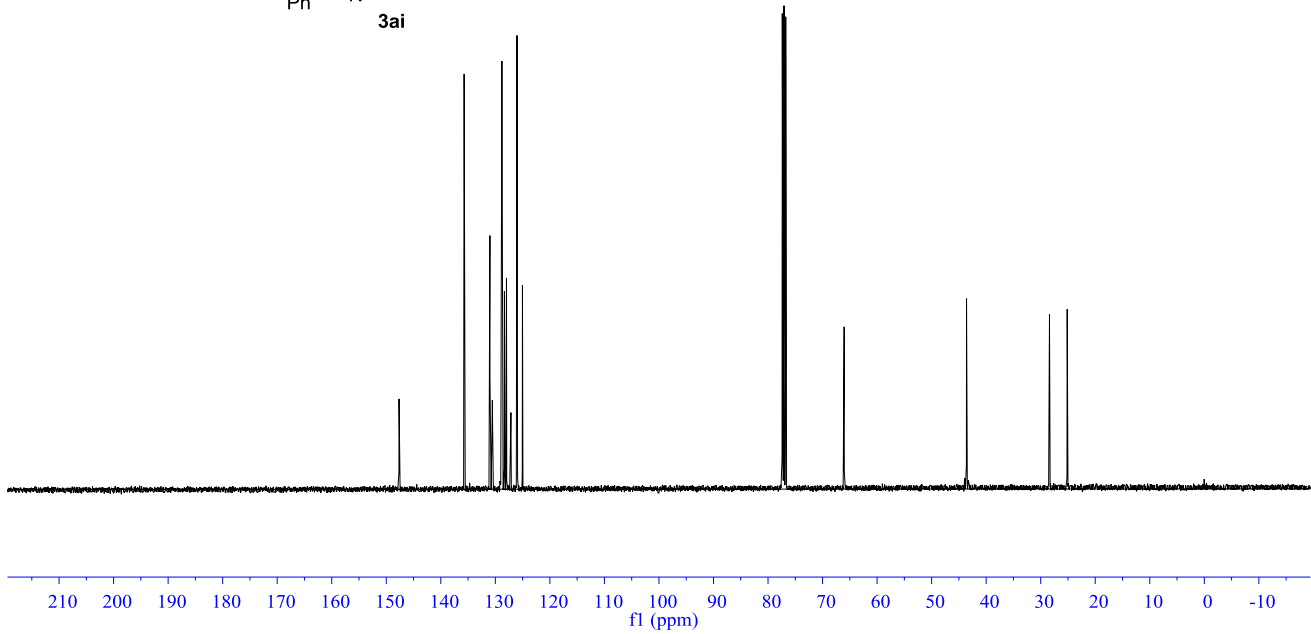
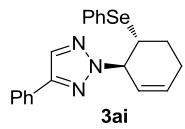




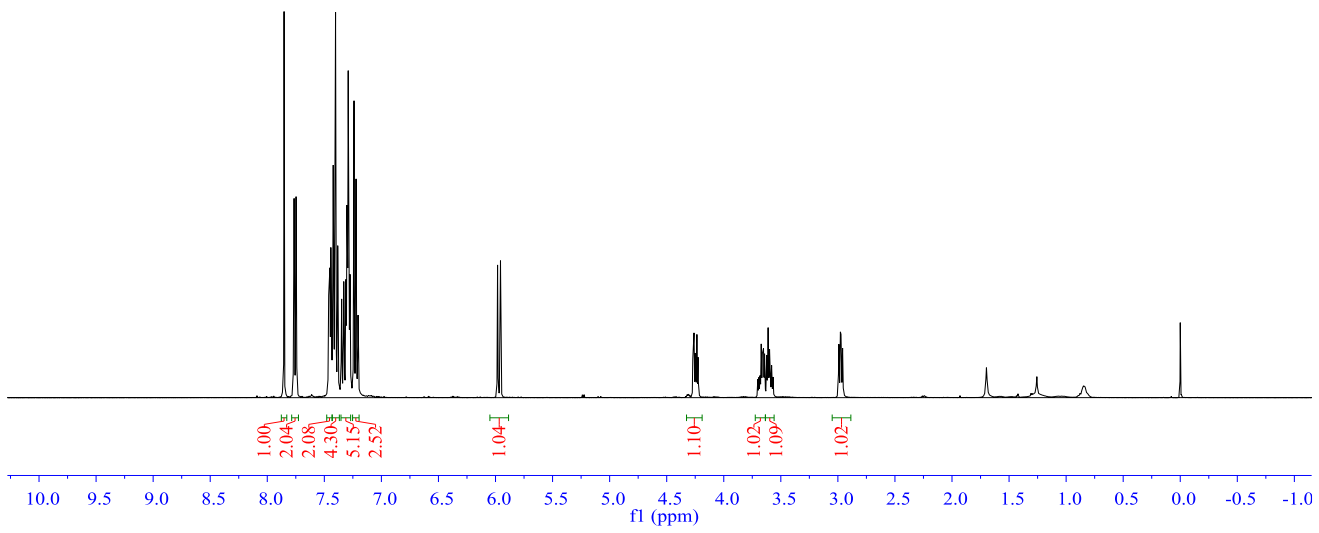
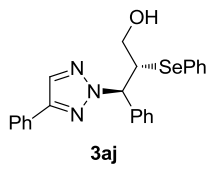
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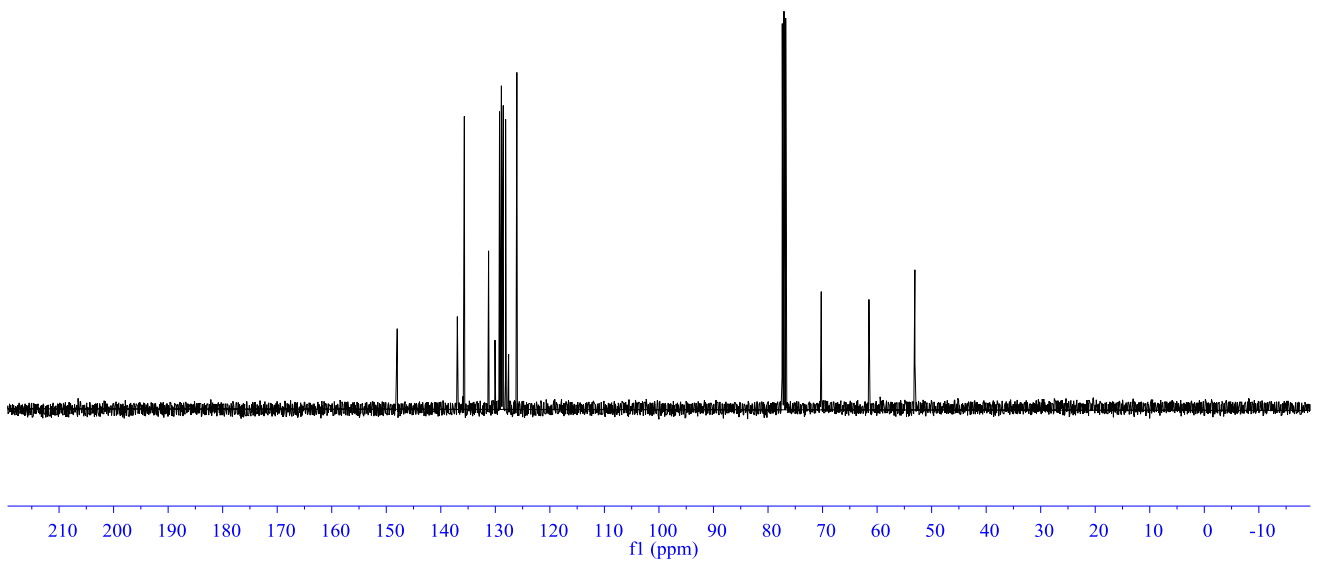
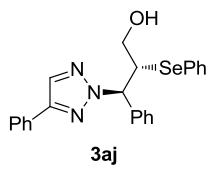
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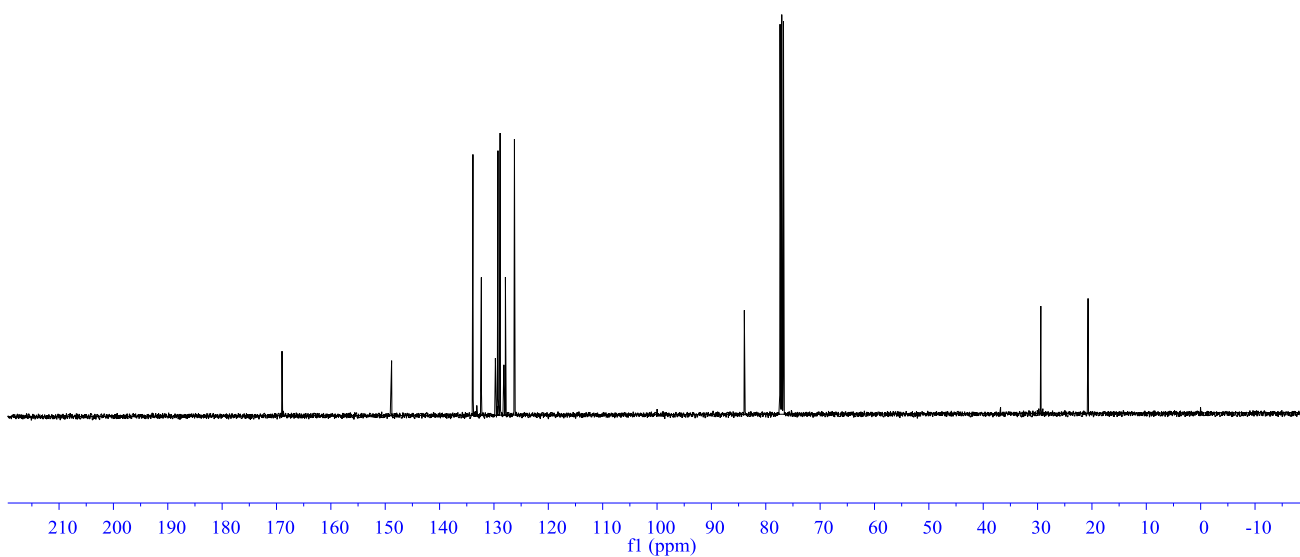
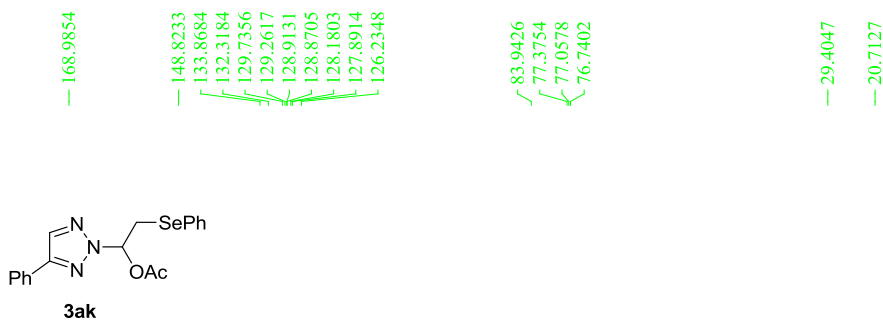
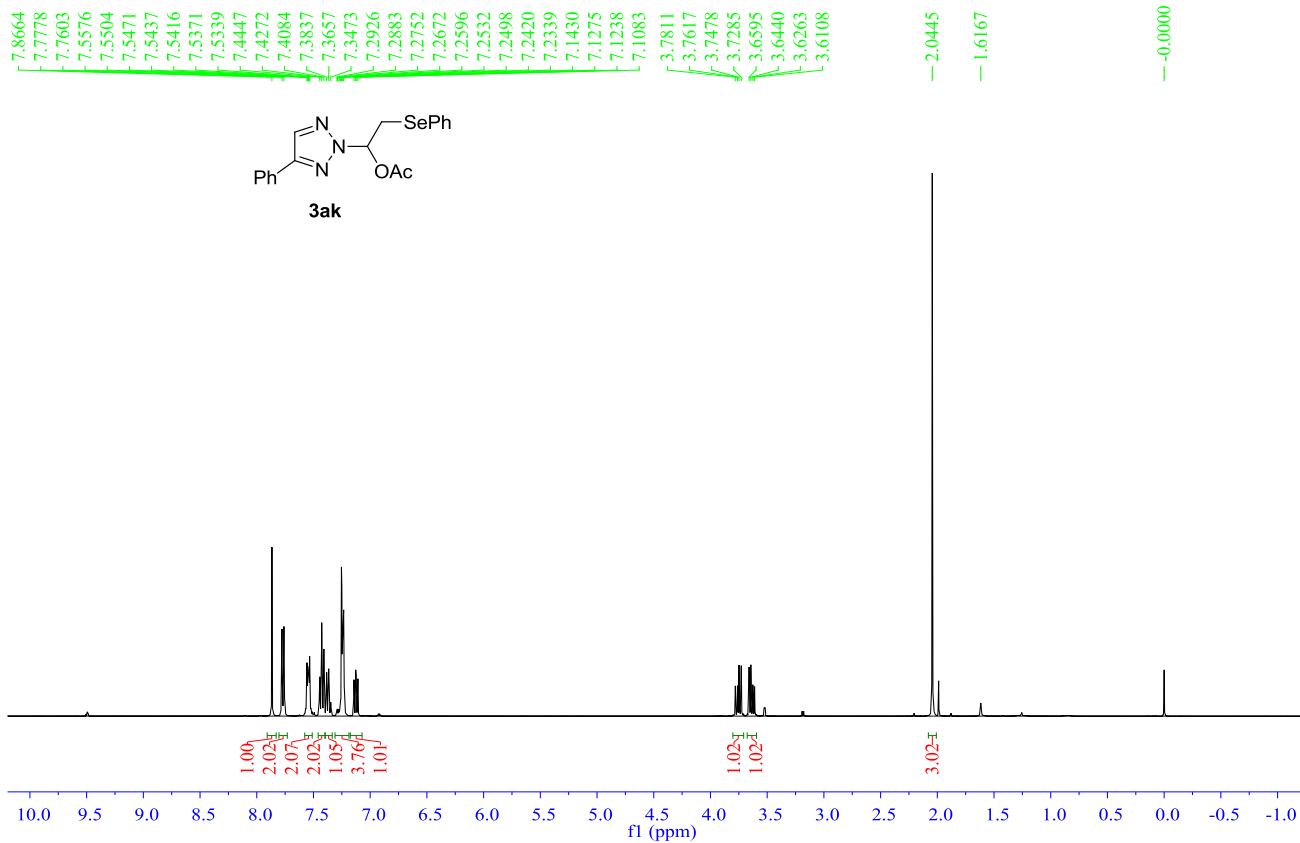


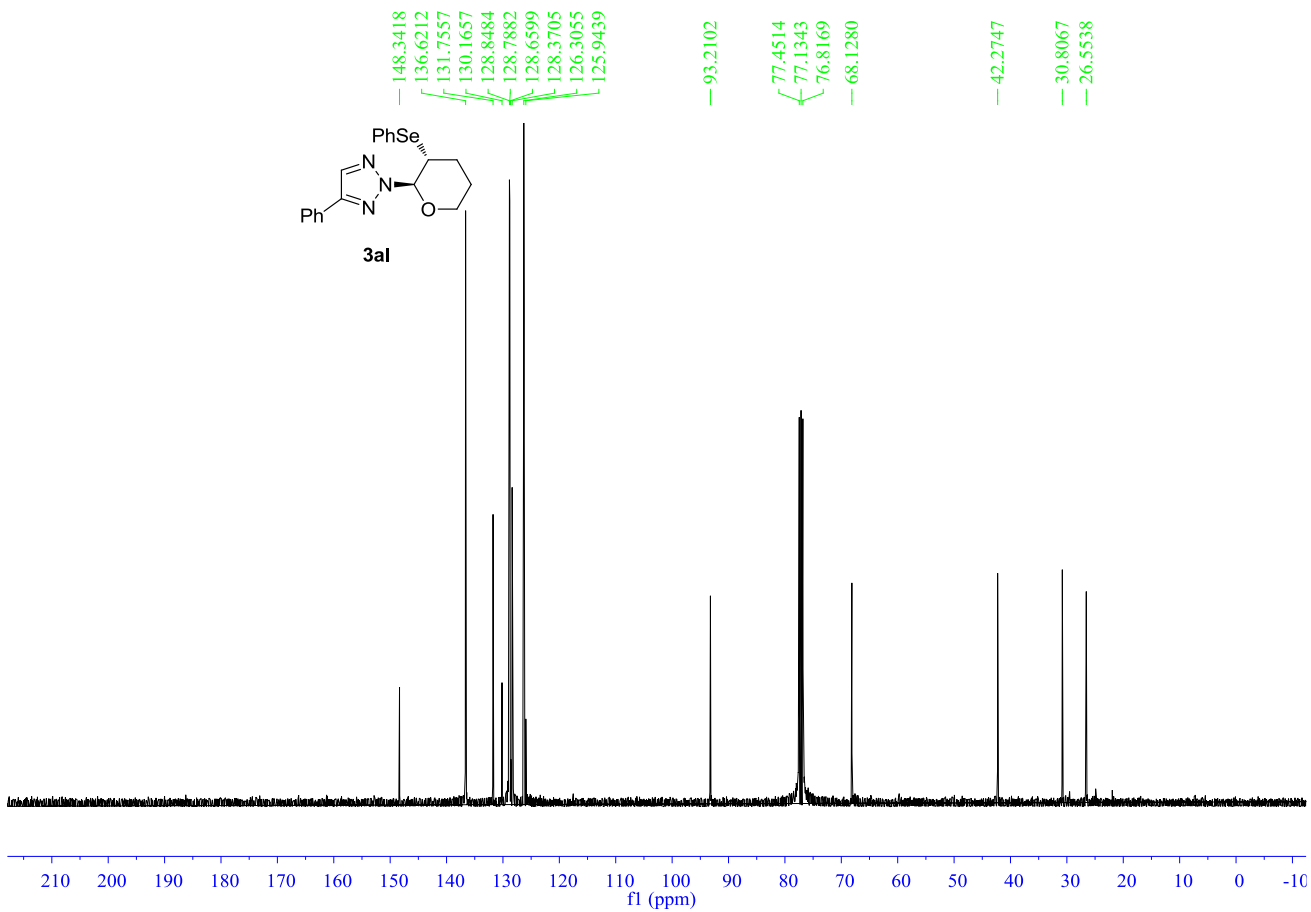
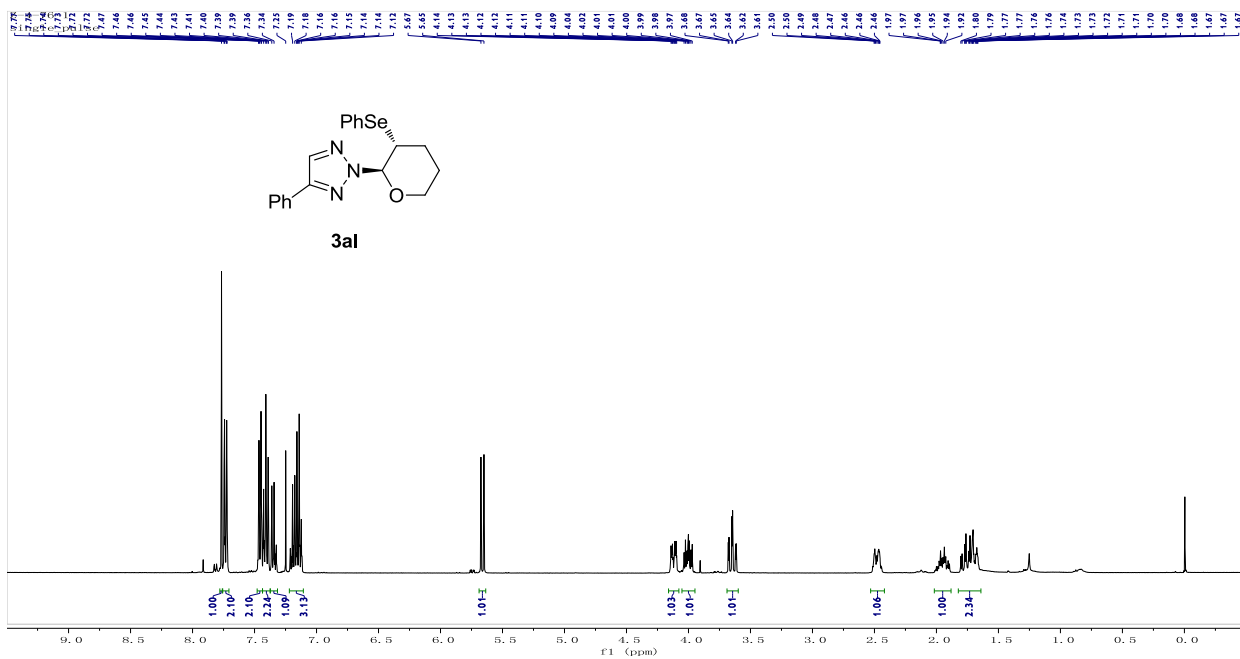
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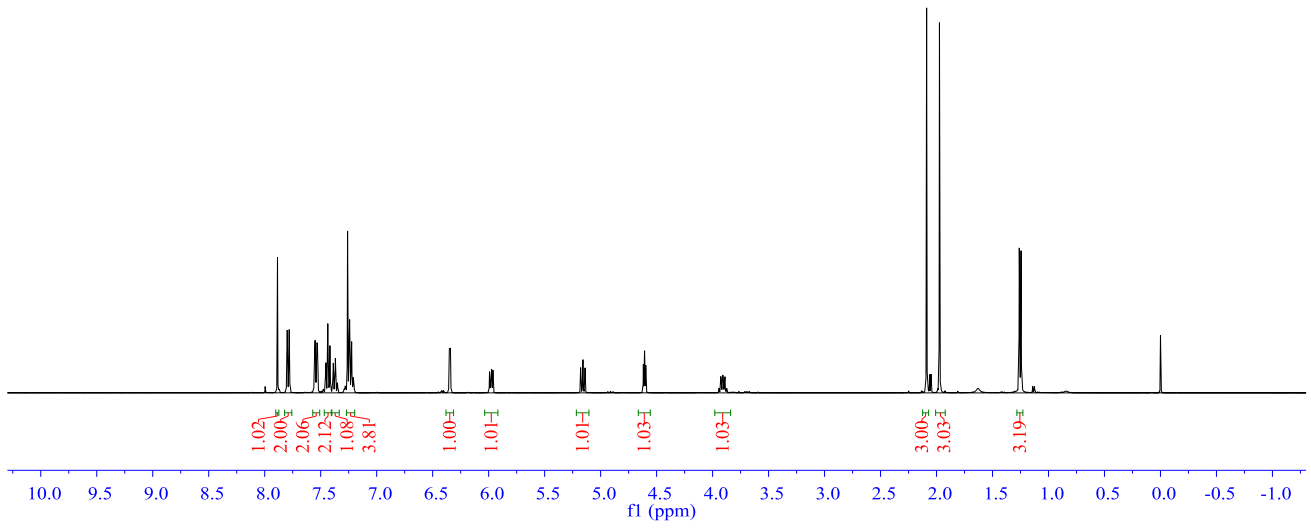
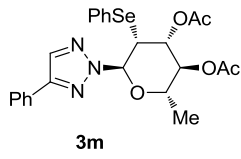
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