

# **K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/I<sub>2</sub>-Promoted Electrophilic Selenylative Cyclization to Access Seleno-Benzob[*b*]azepines**

Zhen Zhang\*, Shilong Wang, Pengpeng Tan, Xiaowen Gu, Wenjie Sun, Chang Liu, Jinchun Chen, Jiazhu Li, and Kai Sun\*

College of Chemistry and Chemical Engineering, Yantai University, Yantai, 264005, P. R. China.

*E-mail:* zhangz@ytu.edu.cn; sunk468@nenu.edu.cn

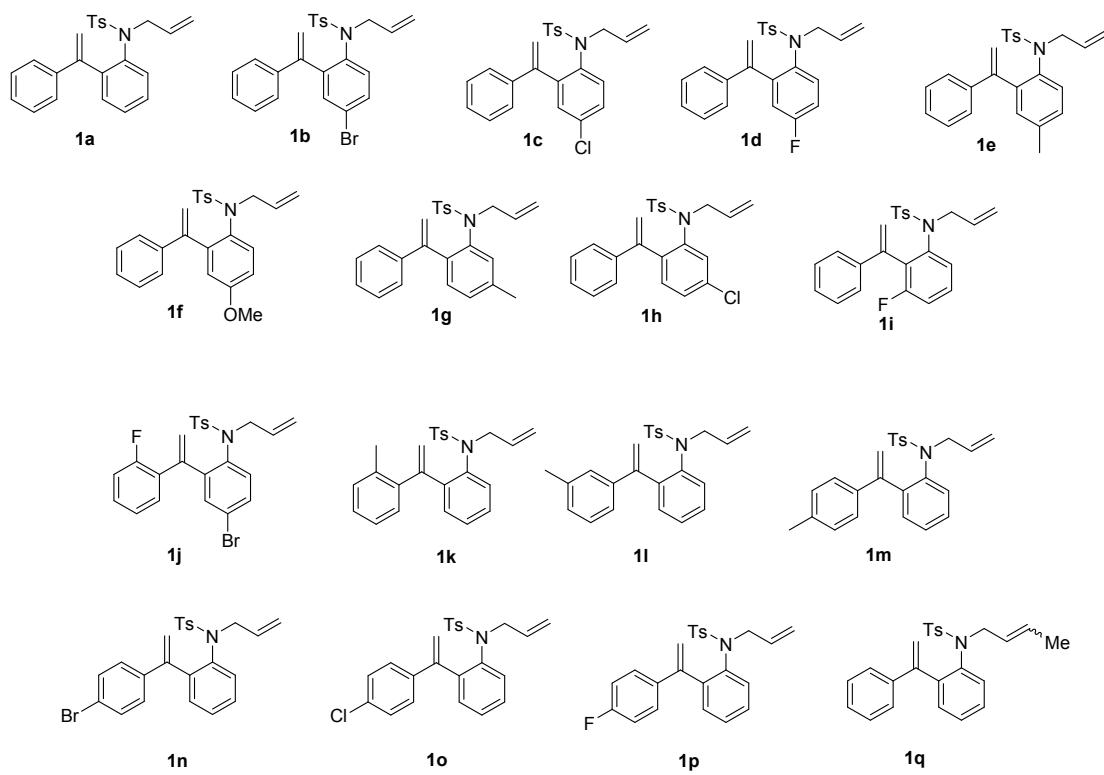
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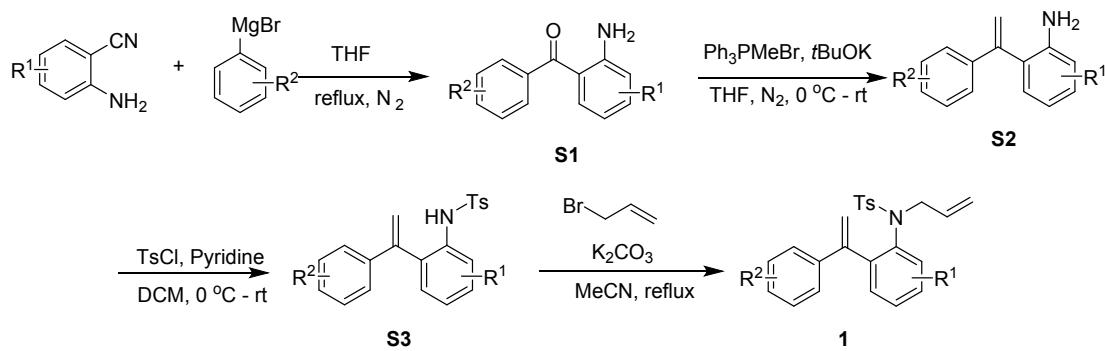
## 1. General

All reactions were performed in a glass vial under atmosphere. The boiling point of petroleum ether is between 60 °C and 90 °C. For chromatography, 200-300 neutral alumina powder and mesh silica gel (Qingdao, China) was employed. <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra were recorded on Ascend 400, Bruker Biospin GmbH 500 spectrometer; <sup>77</sup>Se spectra were recorded on Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm relative to CDCl<sub>3</sub> (<sup>1</sup>H, TMS δ 0; <sup>13</sup>C, δ 77.16), DMSO-d<sub>6</sub> (<sup>1</sup>H, δ 2.50; <sup>13</sup>C, δ 39.52). HMRS were obtained on a Bruker SolanX 70 FT-MS or Waters Xevo G2-XS QT spectrometer. The X-ray diffraction data were collected at room temperature on a Bruker D8 QUEST ECO diffractometer with graphite-monochromated MoKα radiation ( $\lambda = 0.71073 \text{ \AA}$ ) for product 6m. All reagents and solvents were obtained from commercial sources and used as supplied unless otherwise noted. All diselenides **2** were synthesized following reported procedure.<sup>1</sup>

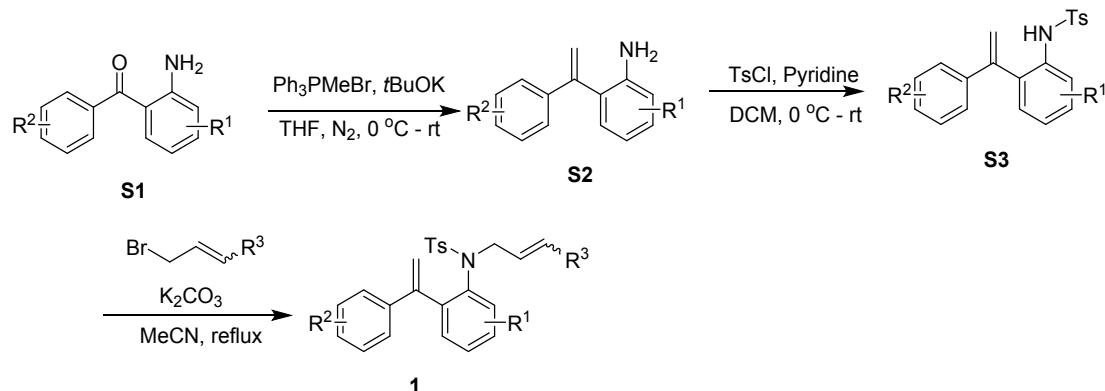
## 2. Preparation of material 1



**1d, 1e, 1f, 1g, 1i, 1k, 1l, 1m** were prepared from 2-aminobenzonitrile.<sup>2,3</sup>



**1a<sup>3</sup>, 1b, 1c, 1h, 1j, 1n, 1o, 1p, 1q** were prepared from (2-aminophenyl)(phenyl)methanone **S1**.<sup>3</sup>



## General Procedure for the synthesis of S1

To a round-bottomed flask charged with the 2-aminobenzonitrile (10 mmol, 1.0 equiv.) in dry THF (20 mL), arylmagnesium bromide (30 mmol, 3.0 equiv., 2.8 M in THF) was added dropwise *via* syringe at 0 °C in a nitrogen atmosphere. The reaction mixture was heated to oil bath 65 °C for 4 hours. Upon the reaction completed, the suspension was cooled to 0 °C, the reaction mixture was quenched by 3 M HCl, extracted with EtOAc (3 x 40 mL). The separated organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 25:1-15:1) to afford S1.

## General Procedure for the synthesis of S2

To a round-bottom flask of tetrahydrofuran (20 mL) solution containing Ph<sub>3</sub>PMeBr (10.0 mmol, 2.0 equiv.), potassium *tert*-butanol (7.5 mmol, 2.5 equiv.) was added in batches at 0 °C in a nitrogen atmosphere. **S1** (5.0 mmol, 1.0 equiv.) was added dropwise at 0 °C. The reaction mixture was warmed to room temperature and stirred for overnight under N<sub>2</sub>. Upon the reaction completed, the desired product **S2** was purified on silica gel column by flash column chromatography (eluent: petroleum ether/EtOAc = 15:1-8:1).

## General Procedure for the synthesis of S3

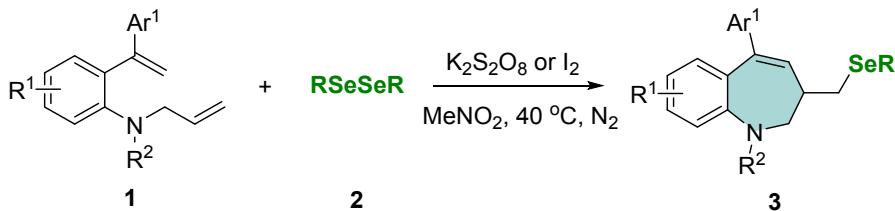
To a round-bottomed flask of dichloromethane (15 mL) solution dissolved with TsCl (2.4 mmol, 1.2 equiv.), product **S2** (2.0 mmol, 1.0 equiv.) was added and then pyridine (3.0 mmol, 1.5 equiv.) was dropped at 0 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. Upon the reaction completed, the reaction mixture was extracted with EtOAc (3 x 15 mL). The separated organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent:

petroleum ether/EtOAc = 20:1-15:1) to afford **S3**.

#### General Procedure for the synthesis of **1**

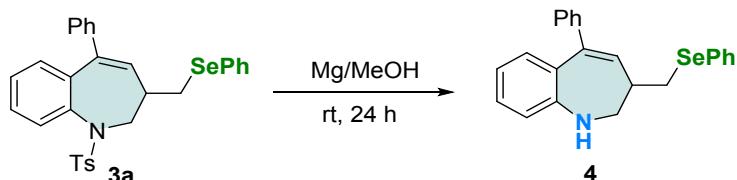
To a round bottom flask containing potassium carbonate (1.44 mmol, 1.2 equiv.) and product **5** (1.2 mmol, 1.0 equiv.), the acetonitrile (10 mL) and propylene bromide (2.4 mmol, 2.0 equiv.) were added. The reaction mixture was stirred at oil bath 80 °C for 4 h. Upon the reaction completed, the reaction mixture was concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1-10:1) to afford **1**.

#### 3. General procedure for the synthesis of **3**



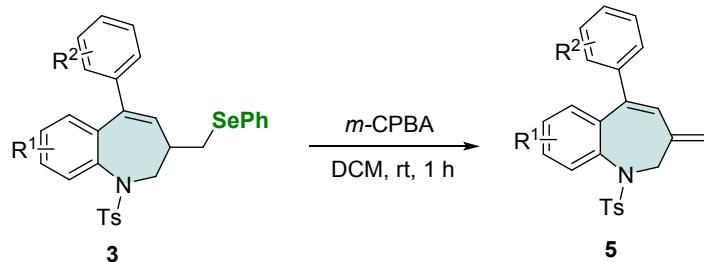
To a 10 mL dry thick walled tube equipped with a magnetic stir bar, was added **1a** (0.3 mmol, 116.74 mg) and  $\text{MeNO}_2$  (3 mL). Then, the diaryl diselenide **2** (0.3 mmol, 93.6 mg) and  $\text{K}_2\text{S}_2\text{O}_8$  (0.9 mmol, 162.2 mg) or  $\text{I}_2$  (0.15 mmol, 38.1 mg) was added. The tube was sealed and the reaction mixture was stirred at oil bath 40 °C for 10 h under  $\text{N}_2$ . Upon the reaction completed, the mixture was concentrated under reduced pressure. The resulting crude residue was purified via flash column chromatography (petroleum ether/EtOAc = 10:1-5:1) on neutral alumina to afford the desired product **3a** (145.4 mg, 89%).

#### 4. General procedure for the synthesis of 5-phenyl-3-((phenylselanyl)methyl)-2,3-dihydro-1H-benzo[b]azepine (**4**)



To a 10 mL dry thick walled tube equipped with a magnetic stir bar, was added **3a** (0.3 mmol, 163.4 mg) and  $\text{MeOH}$  (3 mL). Then, the  $\text{Mg}$  (3.5 mmol, 78.3 mg) was added. The tube was sealed and the reaction mixture was stirred at room temperature for 24 h. Upon the reaction completed,  $\text{H}_2\text{O}$  was added to mixture and extracted with ethyl acetate. The combined organic layer was dried (anhydrous  $\text{Na}_2\text{SO}_4$ ), filtered, and evaporated followed by a silica gel column chromatography (petroleum ether/ethyl acetate = 30:1) to afford desired product **4** (107.8 mg, 92%).

#### 5. General procedure for the synthesis of **5**



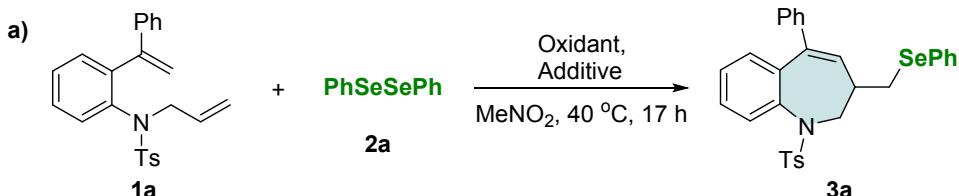
To a 10 mL dry thick walled tube equipped with a magnetic stir bar, was added **3a** (0.3 mmol, 163.4 mg) and DCM (1.5 mL). Then, the *m*-CPBA (0.45 mmol, 77.6 mg) was dissolved in 1.5 mL of DCM was added. The tube was sealed and the reaction mixture was stirred at rt for 1 h. Upon the reaction completed, the mixture was concentrated under reduced pressure. The resulting crude residue was purified via flash column chromatography (petroleum ether/ethyl acetate = 30:1) on silica gel to afford the desired product **5a** (91.8 mg, 79%).

## 6. The gram-scale synthesis of compound **3a**



To a 100 mL dry thick walled tube equipped with a magnetic stir bar, was added **1a** (2.6 mmol, 1.01 g) and  $\text{MeNO}_2$  (25 mL). Then, the diaryl diselenide **2** (2.6 mmol, 0.81 g) and  $\text{K}_2\text{S}_2\text{O}_8$  (5.2 mmol, 0.94 g) were added. The reaction mixture was stirred at oil bath  $40^\circ\text{C}$  for 24 h under  $\text{N}_2$ . Upon the reaction completed, the mixture was concentrated under reduced pressure. The resulting crude residue was purified *via* flash column chromatography (petroleum ether/EtOAc = 10:1-5:1) on neutral alumina to afford the desired product **3a** (1.22 g, 86%).

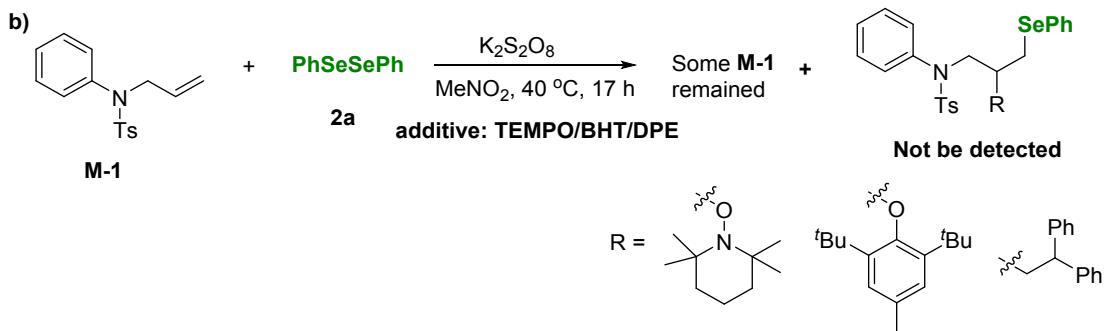
## 7. Control experiments



Oxidant	Additives	Yield of <b>3a</b>
$\text{K}_2\text{S}_2\text{O}_8$ (2 equiv.)	TEMPO (3 equiv.)	66%
	BHT (3 equiv.)	75%
	$\text{Ph}_2\text{C}=\text{CH}_2$ (3 equiv.)	74%
$\text{I}_2$ (0.5 equiv.)	TEMPO (3 equiv.)	64%
	BHT (3 equiv.)	72%
	$\text{Ph}_2\text{C}=\text{CH}_2$ (3 equiv.)	69%

To a 10 mL dry thick walled tube equipped with a magnetic stir bar, was added **1a** (0.3 mmol, 116.7 mg), additive and  $\text{MeNO}_2$  (3 mL). Then, the **2a** (0.3 mmol, 93.6 mg) and  $\text{K}_2\text{S}_2\text{O}_8$  (0.6 mmol, 162.2 mg) or  $\text{I}_2$  (0.15 mmol, 38.1 mg) were added. The tube was sealed and the reaction mixture was stirred at oil bath  $40^\circ\text{C}$  for 17 h under  $\text{N}_2$ . Upon the reaction completed, the mixture was concentrated under reduced pressure. The resulting crude residue was purified *via* flash column

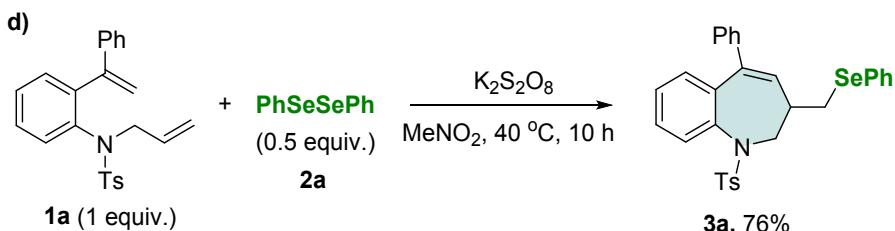
chromatography (petroleum ether/ EtOAc = 10:1-5:1) on neutral alumina to afford the desired product **3a**.



To a 10 mL dry thick walled tube equipped with a magnetic stir bar, was added **M-1** (0.15 mmol, 43.1 mg), additive (0.30 mmol) and MeNO<sub>2</sub> (2 mL). Then, the **2a** (0.15 mmol, 46.8 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.3 mmol, 81.1 mg) were added. The tube was sealed and the reaction mixture was stirred at oil bath 40 °C for 17 h under N<sub>2</sub>.



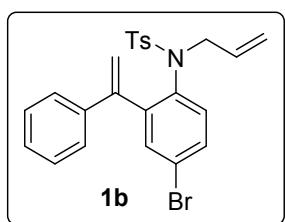
To a 10 mL dry thick walled tube equipped with a magnetic stir bar, was added **1a** (0.3 mmol, 116.7 mg), PhSeBr (0.6 mmol, 141.5 mg) and MeNO<sub>2</sub> (3 mL). The tube was sealed and the reaction mixture was stirred at oil bath 40 °C for 17 h under N<sub>2</sub>. Upon the reaction completed, the mixture was concentrated under reduced pressure. The resulting crude residue was purified *via* flash column chromatography (petroleum ether/ EtOAc = 10:1-5:1) on neutral alumina to afford the desired product **3a** in 21% yield.



To a 10 mL dry thick walled tube equipped with a magnetic stir bar, was added **1a** (0.3 mmol, 116.7 mg) and MeNO<sub>2</sub> (3 mL). Then, the **2a** (0.15 mmol, 46.8 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.2 mg) were added. The tube was sealed and the reaction mixture was stirred at oil bath 40 °C for 10 h under N<sub>2</sub>. Upon the reaction completed, the mixture was concentrated under reduced pressure. The resulting crude residue was purified *via* flash column chromatography (petroleum ether/ EtOAc = 10:1-5:1) on neutral alumina to afford the desired product **3a** in 76% yield.

## 8. Characteristic Data

**N-allyl-N-(4-bromo-2-(1-phenylvinyl)phenyl)-4-methylbenzenesulfonamide (1b)**



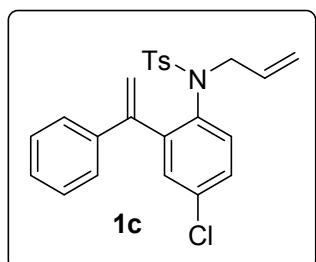
White solid; yield 85 % (477.6 mg); mp 101-103 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.53 – 7.49 (m, 3H), 7.38 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.32 – 7.27 (m, 3H), 7.24 (dd, *J* = 7.8, 4.1 Hz, 4H), 6.82 (d, *J* = 8.5 Hz, 1H), 5.72 (d, *J* = 1.0 Hz, 1H), 5.38 (d, *J* = 0.9 Hz, 1H), 5.27 (ddd, *J* = 17.0, 10.1, 6.7 Hz, 1H), 4.85 (d, *J* = 11.5 Hz, 1H), 4.79 – 4.74 (m, 1H), 3.63 (s, 2H), 2.43 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 145.8, 145.1, 143.7, 140.7, 136.6, 134.7, 132.6, 131.5, 131.1, 129.6, 128.4, 128.3, 128.0, 127.3, 122.2, 119.4, 118.4, 54.0, 21.7.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>23</sub>BrNO<sub>2</sub>S<sup>+</sup>, 468.0627; found, 468.0620

**N-allyl-N-(4-chloro-2-(1-phenylvinyl)phenyl)-4-methylbenzenesulfonamide (1c)**



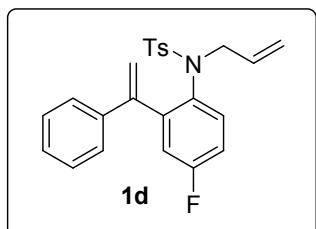
White solid; yield 88 % (446.4 mg); mp 100-102 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 2.5 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 3H), 7.26 – 7.22 (m, 5H), 6.89 (d, *J* = 8.5 Hz, 1H), 5.77 – 5.68 (m, 1H), 5.38 (s, 1H), 5.34 – 5.22 (m, 1H), 4.85 (d, *J* = 10.1 Hz, 1H), 4.77 (d, *J* = 17.0 Hz, 1H), 3.64 (s, 2H), 2.43 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 145.9, 144.8, 143.7, 136.7, 136.3, 134.0, 132.7, 131.9, 131.2, 129.6, 128.4, 128.3, 128.1, 128.0, 127.3, 119.4, 118.3, 54.0, 21.7.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>23</sub>ClNO<sub>2</sub>S<sup>+</sup>, 424.1133; found, 424.1146

**N-allyl-N-(4-fluoro-2-(1-phenylvinyl)phenyl)-4-methylbenzenesulfonamide (1d)**



White solid; yield 93 % (454.1 mg); mp 93-95 °C;

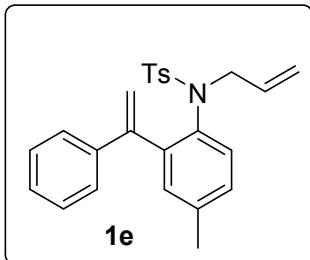
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.1 Hz, 3H), 7.25 (d, *J* = 7.6 Hz, 4H), 7.04 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.99 – 6.84 (m, 2H), 5.73 (s, 1H), 5.39 (s, 1H), 5.35 – 5.23 (m, 1H), 4.85 (d, *J* = 10.0 Hz, 1H), 4.77 (d, *J* = 17.0 Hz, 1H), 3.77 (s, 1H), 3.51 (s, 1H), 2.43 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 161.8 (d, *J* = 249.1 Hz), 145.4 (d, *J* = 8.3 Hz), 143.7, 140.8, 136.8,

133.6 (d,  $J = 2.9$  Hz), 132.8, 131.6 (d,  $J = 8.8$  Hz), 129.6, 128.4, 128.3, 128.0, 127.3, 119.3, 118.7 (d,  $J = 22.6$  Hz), 118.2, 114.8 (d,  $J = 22.3$  Hz), 54.1, 21.7.

HRMS (ESI)  $m/z$ : [M + H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>23</sub>FNO<sub>2</sub>S<sup>+</sup>, 408.1428; found, 408.1427

**N-allyl-4-methyl-N-(4-methyl-2-(1-phenylvinyl)phenyl)benzenesulfonamide (1e)**



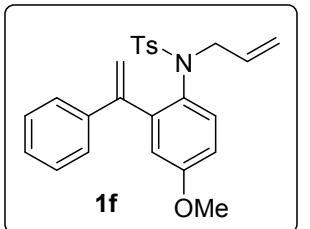
White solid; yield 89 % (430.4 mg); mp 147–148 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.54 (d,  $J = 8.0$  Hz, 2H), 7.30 – 7.26 (m, 4H), 7.24 (t,  $J = 8.5$  Hz, 3H), 7.13 (s, 1H), 7.05 (d,  $J = 8.1$  Hz, 1H), 6.83 (d,  $J = 8.0$  Hz, 1H), 5.70 (s, 1H), 5.38 (s, 1H), 5.35 – 5.27 (m, 1H), 4.83 (d,  $J = 10.1$  Hz, 1H), 4.76 (d,  $J = 17.0$  Hz, 1H), 3.66 (s, 2H), 2.42 (s, 3H), 2.35 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 146.9, 143.3, 141.5, 138.2, 135.0, 133.1, 132.6, 129.6, 129.4, 128.7, 128.3, 128.2, 127.6, 127.3, 118.8, 117.4, 54.1, 21.6, 21.2.

HRMS (ESI)  $m/z$ : [M + H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>26</sub>NO<sub>2</sub>S<sup>+</sup>, 404.1679; found, 404.1680

**N-allyl-N-(4-methoxy-2-(1-phenylvinyl)phenyl)-4-methylbenzenesulfonamide (1f)**



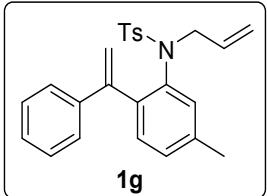
White solid; yield 85 % (427.2 mg); mp 83–84 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.54 (d,  $J = 8.0$  Hz, 2H), 7.28 (d,  $J = 7.2$  Hz, 4H), 7.25 (d,  $J = 6.0$  Hz, 2H), 7.23 (s, 1H), 6.87 – 6.81 (m, 2H), 6.80 – 6.73 (m, 1H), 5.70 (d,  $J = 1.2$  Hz, 1H), 5.38 (d,  $J = 1.2$  Hz, 1H), 5.35 – 5.27 (m, 1H), 4.83 (d,  $J = 8.7$  Hz, 1H), 4.76 (d,  $J = 17.1$  Hz, 1H), 3.79 (s, 3H), 3.43 (s, 2H), 2.42 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 159.0, 146.8, 143.3, 137.1, 133.1, 131.0, 130.2, 129.4, 128.2, 127.7, 127.3, 118.8, 117.5, 117.0, 113.3, 55.5, 54.2, 21.6.

HRMS (ESI)  $m/z$ : [M + H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>26</sub>NO<sub>3</sub>S<sup>+</sup>, 420.1628; found, 420.1628

**N-allyl-4-methyl-N-(5-methyl-2-(1-phenylvinyl)phenyl)benzenesulfonamide (1g)**



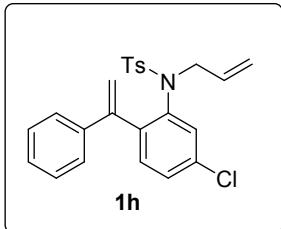
White solid; yield 93 % (449.6 mg); mp 107–109 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.22 (m, 7H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 6.80 (s, 1H), 5.69 (s, 1H), 5.41 – 5.26 (m, 2H), 4.84 (d, *J* = 10.0 Hz, 1H), 4.78 (d, *J* = 17.0 Hz, 1H), 3.69 (s, 2H), 2.43 (s, 3H), 2.30 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 146.8, 143.4, 141.6, 139.8, 138.0, 137.5, 137.1, 133.2, 131.8, 130.5, 129.4, 129.0, 128.4, 128.3, 127.7, 127.3, 118.7, 117.3, 54.1, 21.7, 21.1.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>26</sub>NO<sub>2</sub>S<sup>+</sup>, 404.1679; found, 404.1677

#### *N*-allyl-*N*-(5-chloro-2-(1-phenylvinyl)phenyl)-4-methylbenzenesulfonamide (**1h**)



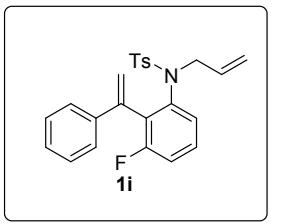
White solid; yield 82 % (416.4 mg); mp 99-101 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.22 (m, 9H), 6.95 (d, *J* = 1.9 Hz, 1H), 5.73 (s, 1H), 5.40 (s, 1H), 5.33 – 5.22 (m, 1H), 4.87 (d, *J* = 10.0 Hz, 1H), 4.79 (d, *J* = 17.0 Hz, 1H), 3.67 (s, 2H), 2.43 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 145.9, 143.9, 141.6, 140.9, 138.9, 136.4, 133.1, 132.9, 132.5, 130.0, 129.6, 128.5, 128.3, 128.2, 127.9, 127.2, 119.4, 118.1, 54.0, 21.7.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>23</sub>ClNO<sub>2</sub>S<sup>+</sup>, 424.1133; found, 424.1143

#### *N*-allyl-*N*-(3-fluoro-2-(1-phenylvinyl)phenyl)-4-methylbenzenesulfonamide (**1i**)



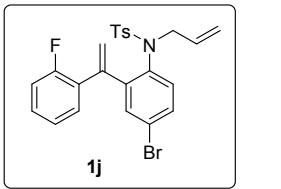
White solid; yield 90 % (439.6 mg); mp 92-94 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.23 (m, 8H), 7.13 (t, *J* = 8.5 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.01 (s, 1H), 5.43 (s, 1H), 5.30 (dd, *J* = 16.6, 9.5 Hz, 1H), 4.82 (d, *J* = 10.1 Hz, 1H), 4.73 (d, *J* = 17.0 Hz, 1H), 3.73 (s, 2H), 2.43 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 160.8 (d, *J* = 246.9 Hz), 143.7, 139.4 (d, *J* = 5.2 Hz), 137.0, 132.6, 130.9 (d, *J* = 17.4 Hz), 129.6, 128.5, 128.4, 128.2, 127.9, 126.4, 125.9 (d, *J* = 3.3 Hz), 119.5, 119.3, 115.9 (d, *J* = 23.1 Hz), 54.2, 21.7.

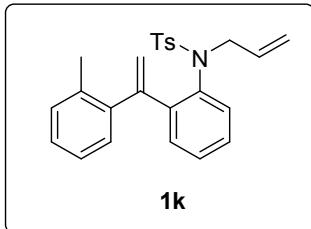
HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>23</sub>FNO<sub>2</sub>S<sup>+</sup>, 408.1428; found, 408.1427

#### *N*-allyl-*N*-(4-bromo-2-(1-(2-fluorophenyl)vinyl)phenyl)-4-methylbenzenesulfonamide (**1j**)



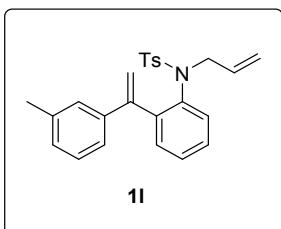
White solid; yield 93 % (541.2 mg); mp 102-104 °C;  
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.61 – 7.49 (m, 3H), 7.32 (dq, *J* = 7.5, 2.6 Hz, 2H), 7.26 (d, *J* = 5.7 Hz, 3H), 7.18 – 7.11 (m, 1H), 7.04 – 6.96 (m, 1H), 6.63 (d, *J* = 8.5 Hz, 1H), 5.70 (s, 1H), 5.62 (s, 1H), 5.14 (s, 1H), 4.84 (d, *J* = 10.0 Hz, 1H), 4.81 – 4.75 (m, 1H), 3.69 (s, 2H), 2.43 (s, 3H).  
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 160.2 (d, *J* = 249.1 Hz), 145.2, 143.8, 141.5, 136.4 (d, *J* = 7.0 Hz), 134.5, 132.1, 131.4 (d, *J* = 3.0 Hz), 131.1, 130.7, 129.6, 129.5 (d, *J* = 8.2 Hz), 128.3, 124.2 (d, *J* = 3.5 Hz), 122.8 (d, *J* = 2.9 Hz), 122.3, 119.6, 115.8 (d, *J* = 22.1 Hz), 54.0, 21.7.  
HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>22</sub>BrFNO<sub>2</sub>S<sup>+</sup>, 486.0533; found, 486.0539

***N*-allyl-4-methyl-*N*-(2-(*o*-tolyl)vinyl)phenyl)benzenesulfonamide (**1k**)**



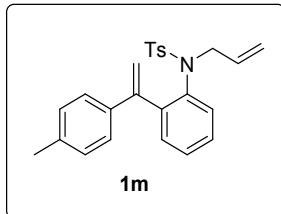
White solid; yield 74 % (358.3 mg); mp 150-152 °C;  
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.42 – 7.38 (m, 3H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.12 – 7.09 (m, 2H), 7.05 (dd, *J* = 8.2, 5.0 Hz, 2H), 6.50 (d, *J* = 7.9 Hz, 1H), 5.57 (s, 1H), 5.33 (s, 1H), 4.93 – 4.82 (m, 1H), 4.69 – 4.60 (m, 2H), 3.55 (s, 1H), 3.34 – 3.20 (m, 1H), 2.35 (s, 3H), 2.09 (s, 3H).  
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 148.7, 143.4, 137.2, 136.3, 135.9, 132.5, 132.3, 130.6, 130.3, 129.4, 129.2, 128.5, 128.4, 127.6, 127.4, 125.7, 120.9, 119.1, 53.9, 21.7, 21.0.  
HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>26</sub>NO<sub>2</sub>S<sup>+</sup>, 404.1679; found, 404.1673

***N*-allyl-4-methyl-*N*-(2-(*m*-tolyl)vinyl)phenyl)benzenesulfonamide (**1l**)**



White solid; yield 79 % (382.2 mg); mp 87-89 °C;  
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 3.9 Hz, 2H), 7.28 – 7.19 (m, 3H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.13 – 7.01 (m, 3H), 6.99 (d, *J* = 7.9 Hz, 1H), 5.71 (s, 1H), 5.47 – 5.21 (m, 2H), 4.83 (d, *J* = 10.0 Hz, 1H), 4.76 (d, *J* = 17.1 Hz, 1H), 3.69 (s, 2H), 2.41 (s, 3H), 2.29 (s, 3H).  
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 146.9, 143.4, 143.0, 141.2, 137.7, 137.6, 137.0, 133.1, 132.1, 130.0, 129.4, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 124.4, 118.7, 117.3, 54.0, 21.6, 21.5.  
HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>26</sub>NO<sub>2</sub>S<sup>+</sup>, 404.1679; found, 404.1676

***N*-allyl-4-methyl-*N*-(2-(*p*-tolyl)vinyl)phenyl)benzenesulfonamide (**1m**)**



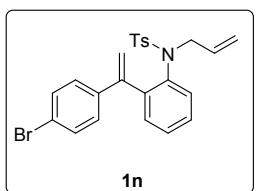
Yellow liquid; yield 71 % (343.3 mg);

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.27 – 7.21 (m, 3H), 7.16 – 7.04 (m, 4H), 6.99 (d, *J* = 7.9 Hz, 1H), 5.70 (s, 1H), 5.32 (s, 1H), 4.85 (d, *J* = 10.1 Hz, 1H), 4.82 – 4.68 (m, 1H), 3.74 (s, 2H), 2.42 (s, 3H), 2.34 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 146.48, 143.43, 138.48, 137.70, 137.54, 137.18, 133.13, 132.10, 130.05, 129.46, 128.96, 128.31, 128.20, 127.94, 127.14, 118.85, 116.68, 54.09, 21.67, 21.28.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>26</sub>NO<sub>2</sub>S<sup>+</sup>, 404.1679; found, 404.1676

#### *N*-allyl-*N*-(2-(1-(4-bromophenyl)vinyl)phenyl)-4-methylbenzenesulfonamide (**1n**)



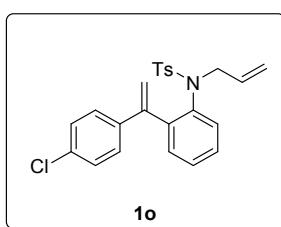
Yellow liquid; yield 85% (476.4 mg);

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.23 (m, 5H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 7.9 Hz, 1H), 5.73 (s, 1H), 5.44 (s, 1H), 5.40 – 5.28 (m, 1H), 4.85 (d, *J* = 10.1 Hz, 1H), 4.80 (d, *J* = 17.1 Hz, 1H), 3.73 (s, 2H), 2.42 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 145.9, 143.6, 142.4, 140.4, 137.8, 136.6, 132.7, 131.9, 131.3, 129.6, 129.5, 128.9, 128.3, 128.2, 121.7, 119.1, 118.2, 54.2, 21.6.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>23</sub>BrNO<sub>2</sub>S<sup>+</sup>, 468.0627; found, 468.0623

#### *N*-allyl-*N*-(2-(1-(4-chlorophenyl)vinyl)phenyl)-4-methylbenzenesulfonamide (**1o**)



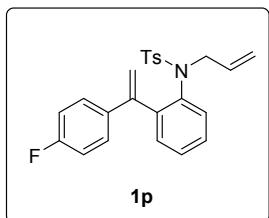
White solid; yield 84 % (426.4 mg); mp 69–71 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.25 (ddd, *J* = 7.8, 5.1, 3.2 Hz, 5H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 7.8 Hz, 1H), 5.72 (s, 1H), 5.43 (s, 1H), 5.40 – 5.26 (m, 1H), 4.85 (d, *J* = 10.0 Hz, 1H), 4.80 (d, *J* = 17.1 Hz, 1H), 3.73 (s, 2H), 2.41 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 145.8, 143.6, 139.9, 137.8, 136.6, 133.5, 132.7, 131.9, 129.6, 129.5, 128.6, 128.3, 128.2, 119.1, 118.1, 54.2, 21.6.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>23</sub>ClNO<sub>2</sub>S<sup>+</sup>, 424.1133; found, 424.1135

#### *N*-allyl-*N*-(2-(1-(4-fluorophenyl)vinyl)phenyl)-4-methylbenzenesulfonamide (**1p**)



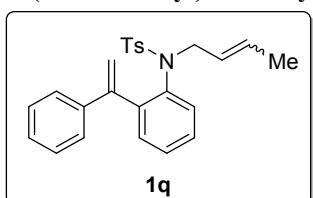
White solid; yield 85 % (415.2 mg); mp 68-70 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.26 – 7.21 (m, 5H), 7.00 – 6.92 (m, 3H), 5.67 (s, 1H), 5.40 – 5.29 (m, 2H), 4.85 (d, *J* = 10.1 Hz, 1H), 4.79 (d, *J* = 17.0 Hz, 1H), 3.72 (s, 2H), 2.42 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 163.5, 161.6, 145.9, 143.6, 142.9, 137.8, 137.6, 137.6, 136.8, 132.8, 131.9, 129.7, 129.5, 129.0, 128.9, 128.3, 128.2, 128.2, 119.0, 117.5, 115.1, 114.9, 54.2, 21.6.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>23</sub>FNO<sub>2</sub>S<sup>+</sup>, 408.1428; found, 408.1435

#### *N*-(but-2-en-1-yl)-4-methyl-*N*-(2-(1-phenylvinyl)phenyl)benzenesulfonamide (1q)



White solid; yield 77 % (372.4 mg); mp 76-78 °C;

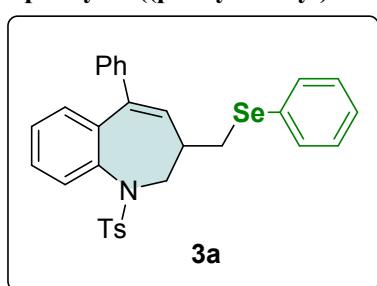
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.32 (t, *J* = 4.3 Hz, 2H), 7.30 – 7.19 (m, 8H), 6.99 (dd, *J* = 42.1, 7.8 Hz, 1H), 5.72 (d, *J* = 1.1 Hz, 1H), 5.41 (d, *J* = 1.0 Hz, 1H), 5.35 – 5.10 (m, 1H), 5.05 – 4.87 (m, 1H), 3.63 (s, 2H), 2.40 (s, 3H), 1.33 (ddd, *J* = 74.1, 6.7, 1.6 Hz, 3H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 147.0, 146.9, 143.3, 143.3, 143.1, 143.0, 141.5, 141.4, 137.9, 137.8, 137.2, 137.0, 132.0, 130.3, 129.8, 129.4, 129.3, 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 127.6, 127.6, 127.3, 127.2, 125.5, 124.7, 117.5, 117.5, 53.5, 47.7, 21.6, 17.6, 12.6.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>26</sub>NO<sub>2</sub>S<sup>+</sup>, 404.1679; found, 404.1680

For the <sup>13</sup>C NMR of seleno-benzo[b]azepines 3, many carbon singles are weak. We speculate that this may be due to the unique structural features of compound (e.g., stacking of multiple aromatic rings), leading to the prolonged relaxation time for some carbon atoms. A similar situation can be found in a reported reference (*Adv. Synth. Catal.* **2021**, 363, 3491–3495, compound 3ra).

#### 5-phenyl-3-((phenylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-benzo[b]azepine (3a)



White solid; yield 86 % (140.5 mg); mp 77-79 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.51 – 7.42 (m, 4H), 7.29 (t, *J* = 7.6 Hz,

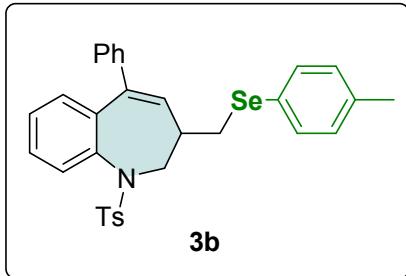
1H), 7.26 – 7.19 (m, 5H), 7.16 (t,  $J$  = 7.4 Hz, 2H), 6.92 (d,  $J$  = 7.8 Hz, 3H), 6.84 (d,  $J$  = 7.3 Hz, 2H), 6.00 (s, 1H), 4.35 (s, 1H), 4.07 (s, 1H), 2.99 (qd,  $J$  = 12.1, 6.6 Hz, 2H), 2.72 (s, 1H), 2.19 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  143.0, 141.9, 139.7, 137.8, 133.4, 131.2, 130.6, 129.8, 129.3, 129.3, 128.4, 128.1, 128.0, 127.9, 127.5, 127.4, 63.3, 38.5, 29.9, 21.5.

$^{77}\text{Se}$  NMR (76 MHz, Chloroform-*d*)  $\delta$  280.1.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>30</sub>H<sub>28</sub>NO<sub>2</sub>SSe<sup>+</sup>, 546.1001; found, 546.1003

### 5-phenyl-3-((p-tolylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3b)



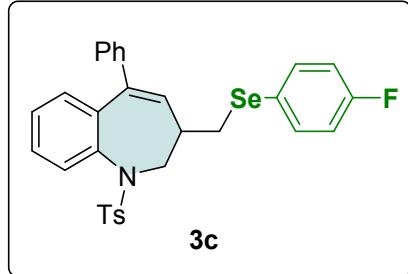
White solid; yield 95 % (159.2 mg); mp 79–80 °C;

$^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.47 (d,  $J$  = 7.9 Hz, 1H), 7.39 (d,  $J$  = 8.5 Hz, 2H), 7.30 (d,  $J$  = 8.1 Hz, 2H), 7.22 (t,  $J$  = 7.5 Hz, 1H), 7.15 (q,  $J$  = 7.2, 6.4 Hz, 2H), 7.09 (t,  $J$  = 7.5 Hz, 2H), 6.96 (d,  $J$  = 8.1 Hz, 2H), 6.85 (d,  $J$  = 8.2 Hz, 3H), 6.76 (d,  $J$  = 7.5 Hz, 2H), 5.91 (s, 1H), 4.25 (s, 1H), 3.98 (s, 1H), 2.86 (qd,  $J$  = 12.1, 6.7 Hz, 2H), 2.63 (s, 1H), 2.23 (s, 3H), 2.12 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  143.0, 141.7, 139.7, 137.8, 137.6, 133.9, 133.4, 131.4, 130.6, 130.1, 129.4, 128.4, 128.1, 128.01, 127.9, 127.5, 125.9, 63.3, 38.6, 30.2, 21.5, 21.2.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>31</sub>H<sub>30</sub>NO<sub>2</sub>SSe<sup>+</sup>, 560.1157; found, 560.1161

### 3-(((4-fluorophenyl)selanyl)methyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3c)



Yellow liquid; yield 62 % (104.6 mg);

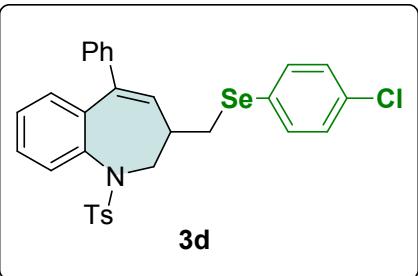
$^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.54 (d,  $J$  = 7.9 Hz, 1H), 7.52 – 7.40 (m, 4H), 7.29 (t,  $J$  = 7.2 Hz, 1H), 7.26 – 7.13 (m, 5H), 6.95 – 6.83 (m, 6H), 5.99 (s, 1H), 4.34 (s, 1H), 4.04 (s, 1H), 3.02 – 2.86 (m, 2H), 2.65 (s, 1H), 2.20 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  162.6 (d,  $J$  = 247.3 Hz), 143.0, 141.9, 139.7, 137.8, 136.1 (d,  $J$  = 7.4 Hz), 131.2, 130.5, 130.5, 129.3, 128.5, 128.1, 127.9, 127.5, 127.4, 123.9 (d,  $J$  = 3.7 Hz), 116.4 (d,  $J$  = 22.1 Hz), 63.1, 38.3, 30.6, 21.4.

$^{19}\text{F}$  NMR (471 MHz, Chloroform-*d*)  $\delta$  -113.82.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>30</sub>H<sub>27</sub>FNO<sub>2</sub>SSe<sup>+</sup>, 564.0906; found, 564.0907

### 3-(((4-chlorophenyl)selanyl)methyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3d)



White solid; yield 72 % (125.1 mg); mp 97-99 °C;

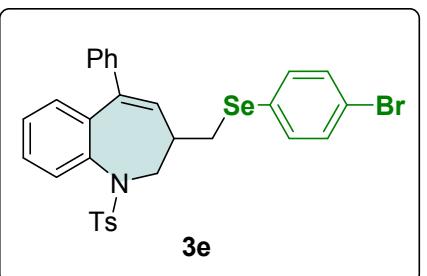
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.21 (ddd, *J* = 19.0, 9.8, 5.1 Hz, 6H), 6.92 (t, *J* = 9.2 Hz, 3H), 6.82 (d, *J* = 7.1 Hz, 2H), 5.96 (s, 1H), 4.33 (s, 1H), 4.06 (s, 1H), 2.97 (qd, *J* = 12.0, 6.6 Hz, 2H), 2.70 (s, 1H), 2.21 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 143.1, 142.0, 139.7, 137.8, 134.9, 133.8, 131.2, 130.6, 129.5, 129.4, 128.6, 128.2, 128.0, 127.9, 127.6, 127.4, 63.1, 38.5, 30.2, 21.5.

<sup>77</sup>Se NMR (76 MHz, Chloroform-*d*) δ 280.5.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>30</sub>H<sub>27</sub>ClNO<sub>2</sub>SSe<sup>+</sup>, 580.0611; found, 580.0612

### 3-(((4-bromophenyl)selanyl)methyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3e)



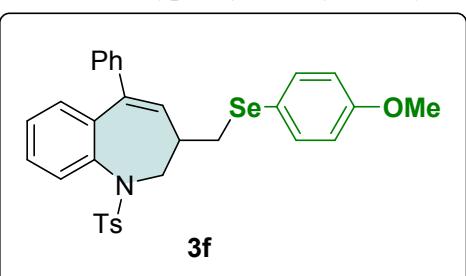
White solid; yield 85 % (158.9 mg); mp 113-115 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.33 (dd, *J* = 12.8, 4.6 Hz, 5H), 7.24 (dd, *J* = 13.8, 6.7 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 2H), 7.00 – 6.86 (m, 3H), 6.82 (d, *J* = 7.0 Hz, 2H), 5.95 (s, 1H), 4.32 (s, 1H), 4.06 (s, 1H), 3.04 – 2.86 (m, 2H), 2.70 (s, 1H), 2.21 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 143.1, 142.4, 139.7, 137.8, 135.1, 132.4, 131.2, 130.6, 129.4, 128.6, 128.2, 128.0, 127.6, 127.5, 121.9, 63.1, 38.6, 30.2, 21.5.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>30</sub>H<sub>27</sub>BrNO<sub>2</sub>SSe<sup>+</sup>, 624.0106; found, 624.0107

### 3-(((4-methoxyphenyl)selanyl)methyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3f)



White solid; yield 96 % (165.8 mg); mp 79-81 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.68 – 7.37 (m, 5H), 7.32 – 7.16 (m, 5H), 6.89 (dd, *J* = 39.3, 7.0

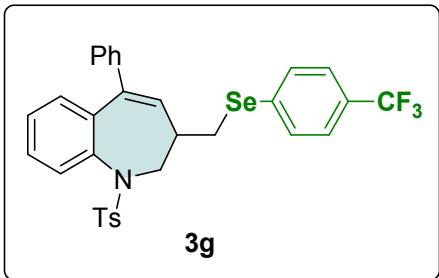
Hz, 5H), 6.76 (d,  $J$  = 8.3 Hz, 2H), 6.00 (s, 1H), 4.32 (s, 1H), 4.04 (s, 1H), 3.77 (s, 3H), 2.97 – 2.82 (m, 2H), 2.66 (s, 1H), 2.20 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  159.7, 143.0, 141.6, 139.8, 137.8, 136.3, 131.3, 130.6, 129.4, 128.4, 128.1, 128.0, 127.9, 127.5, 119.4, 115.0, 63.3, 55.4, 38.5, 30.8, 21.5.

$^{77}\text{Se}$  NMR (76 MHz, Chloroform-*d*)  $\delta$  270.5.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>31</sub>H<sub>30</sub>NO<sub>3</sub>SSe<sup>+</sup>, 576.1106; found, 576.1107

**5-phenyl-1-tosyl-3-(((4-(trifluoromethyl)phenyl)selanyl)methyl)-2,3-dihydro-1*H*-benzo[*b*]azepine (3g)**



White solid; yield 49 % (90.1 mg); mp 78–79 °C;

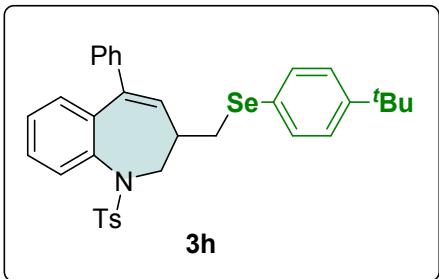
$^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.55 (dd,  $J$  = 7.5, 4.7 Hz, 3H), 7.47 (d,  $J$  = 8.2 Hz, 4H), 7.31 (t,  $J$  = 7.1 Hz, 1H), 7.23 (dd,  $J$  = 13.2, 7.1 Hz, 2H), 7.17 (t,  $J$  = 7.5 Hz, 2H), 6.93 (dd,  $J$  = 13.3, 8.0 Hz, 3H), 6.81 (d,  $J$  = 7.2 Hz, 2H), 5.96 (s, 1H), 4.36 (s, 1H), 4.10 (s, 1H), 3.06 (qd,  $J$  = 12.0, 6.6 Hz, 2H), 2.74 (s, 1H), 2.21 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  143.1, 142.1, 139.7, 137.8, 135.4, 132.4, 131.2, 130.7, 129.4, 129.2, 128.6, 128.3, 128.0, 127.7, 127.5, 126.0 (q,  $J$  = 3.7 Hz), 124.1 (q,  $J$  = 272.1 Hz), 63.1, 38.5, 29.5, 21.5.

$^{77}\text{Se}$  NMR (76 MHz, Chloroform-*d*)  $\delta$  288.6.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>31</sub>H<sub>27</sub>F<sub>3</sub>NO<sub>2</sub>SSe<sup>+</sup>, 614.0874; found, 614.0869

**3-(((4-(tert-butyl)phenyl)selanyl)methyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3h)**



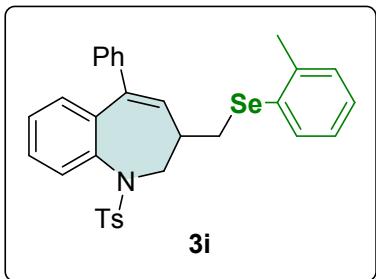
White solid; yield 76 % (136.9 mg); mp 100–101 °C;

$^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.47 (d,  $J$  = 7.9 Hz, 1H), 7.40 (d,  $J$  = 8.1 Hz, 2H), 7.33 (d,  $J$  = 8.2 Hz, 2H), 7.25 – 7.01 (m, 7H), 6.81 (dd,  $J$  = 37.4, 7.5 Hz, 5H), 5.93 (s, 1H), 4.27 (s, 1H), 3.98 (s, 1H), 2.94 – 2.81 (m, 2H), 2.60 (s, 1H), 2.12 (s, 3H), 1.21 (s, 9H).

$^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  150.9, 143.0, 141.7, 139.8, 138.0, 137.8, 133.6, 131.3, 130.6, 129.3, 128.4, 128.1, 128.0, 127.9, 127.5, 126.4, 126.0, 63.4, 38.5, 34.7, 31.4, 30.0, 21.5.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>34</sub>H<sub>36</sub>NO<sub>2</sub>SSe<sup>+</sup>, 602.1626; found, 602.1622

**5-phenyl-3-((*o*-tolylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3i)**



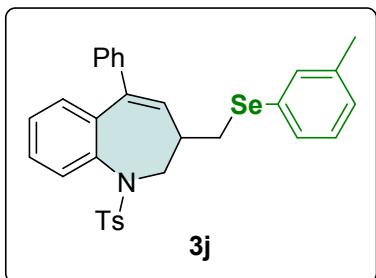
White solid; yield 83 % (139.1 mg); mp 98–100 °C;

$^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.48 (d,  $J = 7.8$  Hz, 1H), 7.40 (d,  $J = 8.5$  Hz, 2H), 7.33 (d,  $J = 7.6$  Hz, 1H), 7.24 – 7.13 (m, 3H), 7.12 – 7.04 (m, 4H), 6.99 (t,  $J = 6.5$  Hz, 1H), 6.85 (d,  $J = 8.2$  Hz, 3H), 6.77 (d,  $J = 7.5$  Hz, 2H), 5.94 (s, 1H), 4.29 (s, 1H), 4.02 (s, 1H), 2.92 – 2.83 (m, 2H), 2.64 (s, 1H), 2.31 (s, 3H), 2.13 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  143.0, 141.9, 140.0, 139.8, 137.8, 132.7, 131.3, 131.0, 130.6, 130.2, 129.4, 128.5, 128.2, 128.0, 127.9, 127.5, 127.5, 127.4, 126.7, 63.4, 38.4, 29.1, 22.6, 21.5.

HRMS (ESI)  $m/z$ : [M + H]<sup>+</sup> calcd for C<sub>31</sub>H<sub>30</sub>NO<sub>2</sub>SSe<sup>+</sup>, 560.1157; found, 560.1162

**5-phenyl-3-((*m*-tolylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3j)**



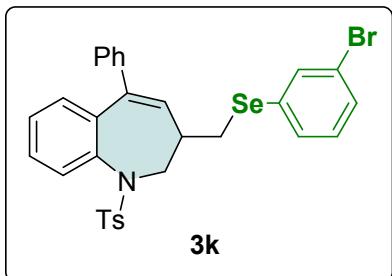
White solid; yield 79 % (132.3 mg); mp 77–79 °C;

$^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.48 (d,  $J = 7.9$  Hz, 1H), 7.40 (d,  $J = 8.2$  Hz, 2H), 7.28 – 7.03 (m, 8H), 6.98 (d,  $J = 7.5$  Hz, 1H), 6.85 (d,  $J = 7.8$  Hz, 3H), 6.77 (d,  $J = 7.3$  Hz, 2H), 5.93 (s, 1H), 4.27 (s, 1H), 3.99 (s, 1H), 2.96 – 2.84 (m, 2H), 2.65 (s, 1H), 2.21 (s, 3H), 2.13 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  143.0, 141.8, 139.9, 139.1, 137.8, 134.2, 131.3, 130.6, 130.5, 129.6, 129.4, 129.1, 128.5, 128.4, 128.1, 128.0, 127.9, 127.5, 127.5, 63.3, 38.5, 29.9, 21.5, 21.4.

HRMS (ESI)  $m/z$ : [M + H]<sup>+</sup> calcd for C<sub>31</sub>H<sub>30</sub>NO<sub>2</sub>SSe<sup>+</sup>, 560.1157; found, 560.1152

**3-((3-bromophenylselanyl)methyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3k)**



White solid; yield 69 % (129.1 mg); mp 84–86 °C;

$^1\text{H}$  NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.67 (t,  $J = 1.8$  Hz, 1H), 7.47 (dd,  $J = 15.8, 8.0$  Hz, 4H), 7.35 (tt,  $J = 17.1, 8.8$  Hz, 3H), 7.23 (p,  $J = 6.7$  Hz, 4H), 7.07 (d,  $J = 8.1$  Hz, 2H), 6.81 (dd,  $J = 35.1, 7.2$  Hz, 3H), 6.05

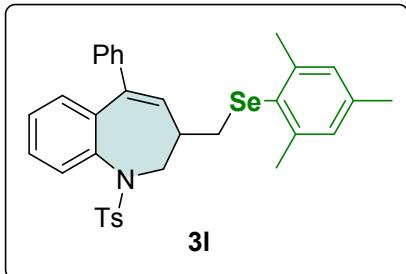
(s, 1H), 4.36 (s, 1H), 4.00 (s, 1H), 3.21 (d,  $J = 6.3$  Hz, 2H), 2.18 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  142.9, 140.6, 139.5, 139.2, 137.6, 137.3, 133.6, 132.5, 131.1, 130.9,

130.6, 129.7, 129.5, 128.4, 128.3, 127.9, 127.4, 126.8, 122.3, 62.6, 38.2, 28.2, 20.9.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>30</sub>H<sub>27</sub>BrNO<sub>2</sub>SSe<sup>+</sup>, 624.0106; found, 624.0103

**3-((mesitylselanyl)methyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3l)**



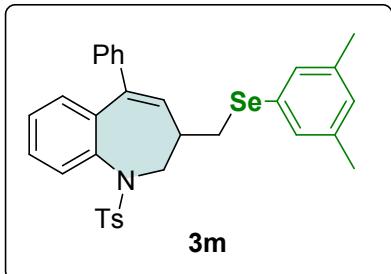
White solid; yield 86 % (176.0 mg); mp 122–123 °C;

$^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.47 (d,  $J = 7.9$  Hz, 1H), 7.39 (d,  $J = 8.0$  Hz, 2H), 7.22 (t,  $J = 7.5$  Hz, 1H), 7.15 (dd,  $J = 15.1, 6.8$  Hz, 2H), 7.08 (t,  $J = 7.5$  Hz, 2H), 6.91 – 6.77 (m, 5H), 6.74 (d,  $J = 7.6$  Hz, 2H), 5.89 (s, 1H), 4.21 (s, 1H), 3.93 (s, 1H), 2.66 – 2.60 (m, 2H), 2.53 (s, 1H), 2.38 (s, 6H), 2.16 (s, 3H), 2.12 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  143.2, 143.2, 143.0, 141.6, 139.7, 138.5, 137.8, 131.3, 130.9, 130.4, 129.4, 128.7, 128.4, 128.1, 127.9, 127.5, 127.3, 63.4, 39.1, 29.3, 24.4, 21.5, 21.0.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>33</sub>H<sub>34</sub>NO<sub>2</sub>SSe<sup>+</sup>, 588.1470; found, 588.1467

**3-(((3,5-dimethylphenyl)selanyl)methyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3m)**



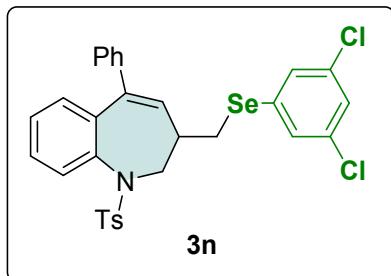
White solid; yield 75 % (128.8 mg); mp 69–71 °C;

$^1\text{H}$  NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.45 (d,  $J = 8.1$  Hz, 2H), 7.35 (dt,  $J = 17.3, 8.7$  Hz, 3H), 7.22 (q,  $J = 8.6, 7.4$  Hz, 3H), 7.14 – 7.03 (m, 4H), 6.86 (d,  $J = 18.1$  Hz, 2H), 6.77 (d,  $J = 7.8$  Hz, 2H), 6.05 (s, 1H), 4.35 (s, 1H), 4.00 (s, 1H), 3.10 (d,  $J = 7.1$  Hz, 2H), 2.19 (d,  $J = 8.1$  Hz, 9H).

$^{13}\text{C}$  NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  142.8, 139.4, 138.4, 137.6, 131.2, 130.8, 129.9, 129.4, 129.1, 128.6, 128.3, 128.2, 127.9, 127.3, 126.8, 62.7, 40.1, 39.9, 39.7, 39.5, 39.3, 39.1, 38.9, 38.3, 28.2, 20.8, 20.7.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>32</sub>H<sub>32</sub>NO<sub>2</sub>SSe<sup>+</sup>, 574.1313; found, 574.1316

**3-(((3,5-dichlorophenyl)selanyl)methyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3n)**



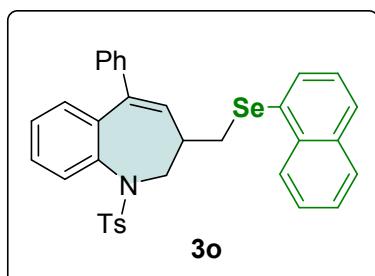
White solid; yield 77 % (141.7 mg); mp 78-80 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.28 (m, 3H), 7.27 – 7.22 (m, 3H), 7.19 (t, *J* = 7.4 Hz, 2H), 6.95 (d, *J* = 7.4 Hz, 3H), 6.86 (d, *J* = 7.2 Hz, 2H), 5.96 (s, 1H), 4.35 (s, 1H), 4.08 (s, 1H), 3.11 – 2.94 (m, 2H), 2.72 (s, 1H), 2.22 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 143.2, 142.4, 139.8, 137.8, 135.4, 132.8, 131.3, 130.8, 129.4, 128.7, 128.3, 128.0, 127.7, 127.6, 127.5, 63.0, 38.3, 30.2, 21.5.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>30</sub>H<sub>26</sub>Cl<sub>2</sub>NO<sub>2</sub>SSe<sup>+</sup>, 614.0221; found, 614.0214

### 3-((naphthalen-1-ylselanyl)methyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3o)



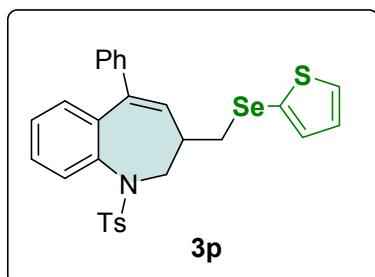
White solid; yield 66 % (117.7 mg); mp 47-49 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 8.0 Hz, 1H), 7.79 (dd, *J* = 18.6, 8.1 Hz, 3H), 7.61 – 7.42 (m, 5H), 7.35 – 7.25 (m, 2H), 7.21 (t, *J* = 6.8 Hz, 2H), 7.14 (t, *J* = 7.5 Hz, 2H), 6.88 (dd, *J* = 15.6, 7.7 Hz, 3H), 6.78 (d, *J* = 7.5 Hz, 2H), 5.99 (s, 1H), 4.33 (s, 1H), 4.03 (s, 1H), 3.06 – 2.92 (m, 2H), 2.66 (s, 1H), 2.18 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 144.2, 143.0, 141.8, 139.8, 137.8, 134.5, 134.1, 133.7, 131.2, 130.6, 129.3, 129.0, 128.8, 128.4, 128.1, 127.9, 127.8, 127.5, 127.4, 127.0, 126.4, 125.9, 63.4, 53.6, 38.6, 30.2, 21.5.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>34</sub>H<sub>30</sub>NO<sub>2</sub>SSe<sup>+</sup>, 596.1157; found, 596.1164

### 5-phenyl-3-((thiophen-2-ylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3p)



Yellow liquid; yield 71 % (117.3 mg);

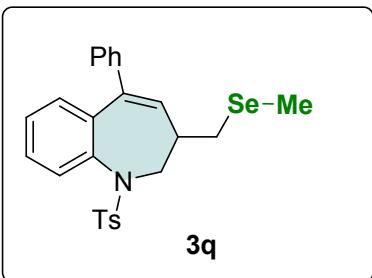
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.47 (t, *J* = 6.8 Hz, 4H), 7.42 (s, 2H), 7.28 – 7.22 (m, 4H), 7.19 (t, *J* = 7.5 Hz, 2H), 7.04 (s, 1H), 6.95 (d, *J* = 7.9 Hz, 2H), 6.80 (d, *J* = 7.4 Hz, 2H), 6.03 (s, 1H), 4.32 (s,

1H), 4.03 (s, 1H), 3.01 (dd,  $J = 12.1, 5.3$  Hz, 1H), 2.95 (dd,  $J = 12.2, 8.1$  Hz, 1H), 2.67 (s, 1H), 2.21 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  143.1, 142.0, 139.9, 137.8, 136.2, 134.8, 133.4, 131.3, 130.6, 129.4, 128.5, 128.2, 128.1, 127.9, 127.6, 127.5, 122.9, 63.1, 38.3, 33.1, 21.5.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>28</sub>H<sub>26</sub>NO<sub>2</sub>S<sub>2</sub>Se<sup>+</sup>, 552.0565; found, 552.0568

### 3-((methylselanyl)methyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3q)



White solid; yield 57 % (82.5 mg); mp 95-97 °C;

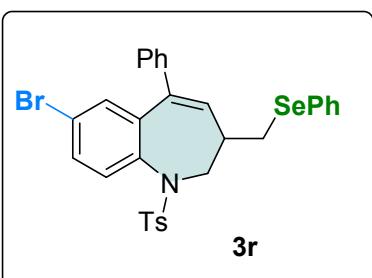
$^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.59 (d,  $J = 7.9$  Hz, 1H), 7.50 (d,  $J = 7.9$  Hz, 2H), 7.32 (t,  $J = 7.6$  Hz, 1H), 7.28 – 7.16 (m, 4H), 6.92 (dd,  $J = 20.9, 6.9$  Hz, 5H), 6.02 (s, 1H), 4.32 (s, 1H), 4.12 (s, 1H), 2.66 (t,  $J = 5.5$  Hz, 3H), 2.21 (s, 3H), 1.99 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  143.0, 141.7, 139.8, 137.8, 131.3, 130.7, 129.4, 128.5, 128.2, 128.0, 127.9, 127.5, 127.5, 63.4, 38.3, 27.4, 21.5, 5.4.

$^{77}\text{Se}$  NMR (76 MHz, Chloroform-*d*)  $\delta$  273.4.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>26</sub>NO<sub>2</sub>S<sub>2</sub>Se<sup>+</sup>, 484.0844; found, 484.0846

### 7-bromo-5-phenyl-3-((phenylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3r)



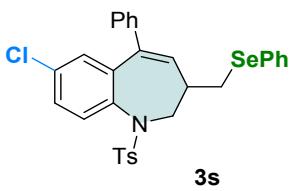
White solid; yield 78 % (146.1 mg); mp 92-94 °C;

$^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.63 – 7.37 (m, 6H), 7.28 – 7.13 (m, 6H), 7.04 (s, 1H), 6.95 (d,  $J = 7.8$  Hz, 2H), 6.80 (d,  $J = 7.5$  Hz, 2H), 6.03 (s, 1H), 4.31 (s, 1H), 4.03 (s, 1H), 3.05 – 2.91 (m, 2H), 2.67 (s, 1H), 2.21 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  143.3, 141.8, 140.9, 139.1, 137.5, 136.9, 133.5, 133.3, 132.8, 131.6, 129.6, 129.5, 129.4, 128.1, 127.9, 127.8, 127.6, 127.5, 122.3, 63.2, 38.5, 29.7, 21.5.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>30</sub>H<sub>27</sub>BrNO<sub>2</sub>S<sub>2</sub>Se<sup>+</sup>, 624.0106; found, 624.0110

### 7-chloro-5-phenyl-3-((phenylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3s)



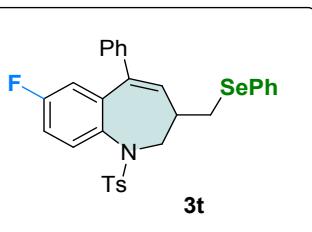
White solid; yield 83 % (144.2 mg); mp 88-89 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.48 (q, *J* = 8.2 Hz, 5H), 7.22 (d, *J* = 33.7 Hz, 7H), 7.02 – 6.86 (m, 3H), 6.80 (d, *J* = 7.3 Hz, 2H), 6.03 (s, 1H), 4.33 (s, 1H), 4.05 (s, 1H), 3.09 – 2.88 (m, 2H), 2.68 (s, 1H), 2.22 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 143.2, 141.3, 139.0, 137.4, 136.3, 134.1, 133.4, 132.4, 131.5, 130.2, 129.5, 129.4, 129.3, 128.5, 128.0, 127.8, 127.7, 127.5, 127.4, 63.1, 38.3, 29.6, 21.4.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>30</sub>H<sub>27</sub>ClNO<sub>2</sub>SSe<sup>+</sup>, 580.0611; found, 580.0613

#### 7-fluoro-5-phenyl-3-((phenylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3t)



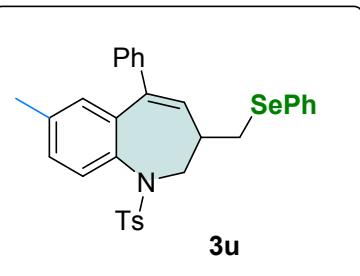
White solid; yield 79 % (133.3 mg); mp 103-105 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.58 – 7.41 (m, 5H), 7.31 – 7.21 (m, 4H), 7.17 (t, *J* = 7.5 Hz, 2H), 7.05 – 6.89 (m, 3H), 6.81 (d, *J* = 6.5 Hz, 2H), 6.67 – 6.55 (m, 1H), 6.05 (s, 1H), 4.38 (s, 1H), 4.02 (s, 1H), 3.05 – 2.92 (m, 2H), 2.66 (s, 1H), 2.20 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 162.0 (d, *J* = 247.3 Hz), 143.2, 142.0, 141.4, 138.8, 137.6, 135.7, 133.5, 133.4, 133.1, 131.3, 130.1, 129.6, 129.4, 129.3, 128.0, 127.9, 127.8, 127.6, 127.5, 117.1, 115.5 (d, *J* = 23.0 Hz), 63.4, 38.4, 29.8, 21.5.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>30</sub>H<sub>27</sub>FNO<sub>2</sub>SSe<sup>+</sup>, 564.0906; found, 564.0899

#### 7-methyl-5-phenyl-3-((phenylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3u)



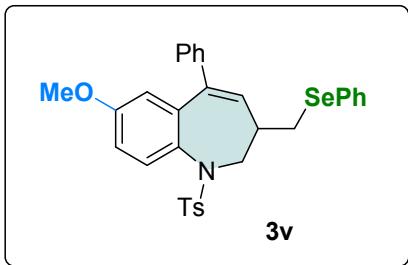
White solid; yield 83 % (155.9 mg); mp 112-114 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.44 (dd, *J* = 30.5, 7.7 Hz, 5H), 7.32 – 7.14 (m, 6H), 7.09 (d, *J* = 8.2 Hz, 1H), 6.88 (dd, *J* = 34.1, 7.7 Hz, 4H), 6.72 (s, 1H), 5.97 (s, 1H), 4.34 (s, 1H), 4.03 (s, 1H), 3.08 – 2.88 (m, 2H), 2.70 (s, 1H), 2.21 (d, *J* = 20.0 Hz, 6H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 142.9, 142.1, 139.9, 139.5, 138.1, 137.9, 135.2, 133.3, 131.0, 130.4, 130.0, 129.3, 129.3, 128.0, 127.9, 127.5, 127.4, 63.2, 38.6, 30.0, 21.5, 21.2.

HRMS (ESI)  $m/z$ : [M + H]<sup>+</sup> calcd for C<sub>31</sub>H<sub>30</sub>NO<sub>2</sub>SSe<sup>+</sup>, 560.1157; found, 560.1156

**7-methoxy-5-phenyl-3-((phenylselanyl)methyl)-1-tosyl-2,3-dihydro-1H-benzo[b]azepine (3v)**



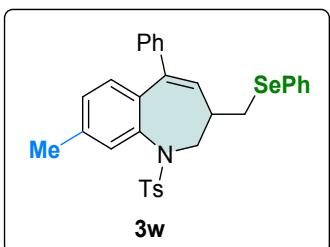
White solid; yield 91 % (156.9 mg); mp 100-102 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.47 (dd, *J* = 11.8, 6.7 Hz, 5H), 7.37 – 7.09 (m, 6H), 6.87 (dd, *J* = 34.4, 8.2 Hz, 5H), 6.43 (s, 1H), 6.01 (s, 1H), 4.37 (s, 1H), 4.01 (s, 1H), 3.67 (s, 3H), 3.12 – 2.92 (m, 2H), 2.69 (s, 1H), 2.18 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 159.1, 142.9, 142.0, 141.1, 139.4, 137.8, 133.3, 133.3, 132.5, 130.5, 130.3, 129.9, 129.3, 127.9, 127.8, 127.5, 127.5, 127.4, 115.4, 113.9, 63.2, 55.5, 38.5, 29.9, 21.4.

HRMS (ESI)  $m/z$ : [M + H]<sup>+</sup> calcd for C<sub>31</sub>H<sub>30</sub>NO<sub>3</sub>SSe<sup>+</sup>, 576.1106; found, 576.1102

**8-methyl-5-phenyl-3-((phenylselanyl)methyl)-1-tosyl-2,3-dihydro-1H-benzo[b]azepine (3w)**



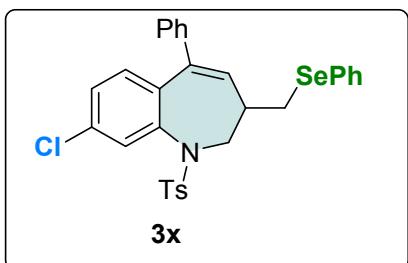
White solid; yield 83 % (139.1 mg); mp 103-105 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.55 – 7.43 (m, 4H), 7.38 (s, 1H), 7.28 – 7.19 (m, 4H), 7.16 (t, *J* = 7.4 Hz, 2H), 7.04 (d, *J* = 8.1 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 2H), 6.82 (dd, *J* = 19.6, 7.7 Hz, 3H), 5.93 (s, 1H), 4.31 (s, 1H), 4.06 (s, 1H), 2.98 (qd, *J* = 12.1, 6.8 Hz, 2H), 2.74 (s, 1H), 2.36 (s, 3H), 2.19 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 142.9, 141.8, 140.0, 138.6, 137.9, 136.4, 133.3, 131.9, 130.4, 130.0, 129.3, 129.0, 128.0, 127.9, 127.5, 127.4, 63.1, 38.6, 30.1, 21.5, 21.3.

HRMS (ESI)  $m/z$ : [M + H]<sup>+</sup> calcd for C<sub>31</sub>H<sub>30</sub>NO<sub>2</sub>SSe<sup>+</sup>, 560.1157; found, 560.1157

**8-chloro-5-phenyl-3-((phenylselanyl)methyl)-1-tosyl-2,3-dihydro-1H-benzo[b]azepine (3x)**



White solid; yield 78 % (135.5 mg); mp 82-84 °C;

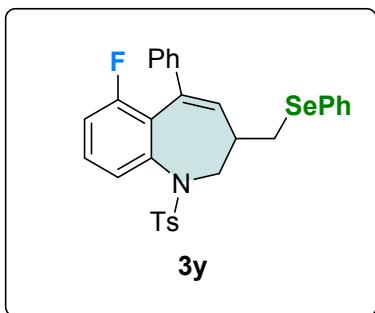
<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.69 – 7.36 (m, 6H), 7.36 – 7.16 (m, 6H), 7.07 (d, *J* = 8.1 Hz, 2H),

6.78 (dd,  $J = 60.4$ , 8.2 Hz, 3H), 6.08 (s, 1H), 4.34 (s, 1H), 4.06 (s, 1H), 3.26 – 3.04 (m, 2H), 2.17 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  143.1, 140.7, 139.4, 137.9, 133.4, 133.3, 131.4, 131.0, 130.3, 129.8, 129.3, 129.1, 128.7, 128.3, 128.1, 127.5, 127.4, 63.3, 38.7, 29.8, 21.4.

HRMS (ESI)  $m/z$ : [M + H] $^+$  calcd for  $\text{C}_{30}\text{H}_{27}\text{ClNO}_2\text{SSe}^+$ , 580.0611; found, 580.0618

**6-fluoro-5-phenyl-3-((phenylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3y)**



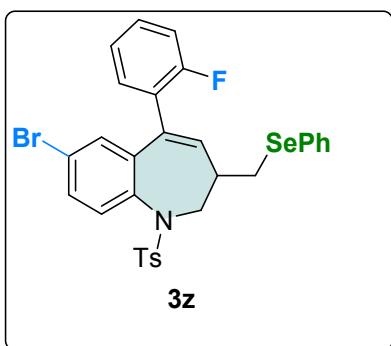
White solid; yield 68 % (114.8 mg); mp 101-103 °C;

$^1\text{H}$  NMR (500 MHz, Chloroform- $d$ )  $\delta$  7.48 – 7.34 (m, 5H), 7.21 – 7.13 (m, 4H), 7.10 (t,  $J = 7.5$  Hz, 2H), 6.96 – 6.82 (m, 3H), 6.73 (d,  $J = 7.8$  Hz, 2H), 6.60 – 6.50 (m, 1H), 5.97 (s, 1H), 4.31 (s, 1H), 3.94 (s, 1H), 2.97 – 2.85 (m, 2H), 2.59 (s, 1H), 2.13 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz, Chloroform- $d$ )  $\delta$  162.0 (d,  $J = 249.3$  Hz), 143.2, 142.1, 141.4, 139.0, 137.6, 133.5, 133.1, 131.2, 129.6, 129.4, 129.3, 128.0, 127.9, 127.8, 127.6, 127.5, 117.1, 115.5 (d,  $J = 23.0$  Hz), 63.4, 38.4, 29.8, 21.5.

HRMS (ESI)  $m/z$ : [M + H] $^+$  calcd for  $\text{C}_{30}\text{H}_{27}\text{FNO}_2\text{SSe}^+$ , 564.0906; found, 564.0903

**7-bromo-5-(2-fluorophenyl)-3-((phenylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3z)**



White solid; yield 72 % (138.6 mg); mp 85-87 °C;

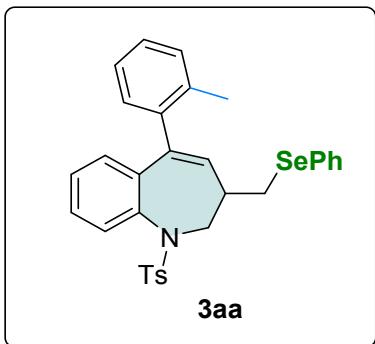
$^1\text{H}$  NMR (500 MHz, Chloroform- $d$ )  $\delta$  7.46 (d,  $J = 8.2$  Hz, 2H), 7.44 – 7.38 (m, 2H), 7.34 – 7.27 (m, 2H), 7.20 – 7.16 (m, 4H), 7.00 (d,  $J = 8.4$  Hz, 2H), 6.97 – 6.85 (m, 3H), 6.60 (t,  $J = 7.0$  Hz, 1H), 5.99 (s, 1H), 4.07 (s, 1H), 2.94 – 2.84 (m, 2H), 2.76 (s, 1H), 2.22 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz, Chloroform- $d$ )  $\delta$  161.1, 143.4, 137.8, 137.3, 136.3, 133.5, 133.4, 132.9, 131.8, 131.5, 131.5, 131.4, 129.6, 129.6, 129.5, 129.4, 129.4, 128.1, 127.6, 127.5, 124.0, 122.0, 116.1, 115.9, 63.0, 39.1, 29.7, 21.6.

$^{19}\text{F}$  NMR (471 MHz, Chloroform- $d$ )  $\delta$  -113.33.

HRMS (ESI)  $m/z$ : [M + H] $^+$  calcd for  $\text{C}_{30}\text{H}_{26}\text{BrFNO}_2\text{SSe}^+$ , 642.0011; found, 642.0007

**3-((phenylselanyl)methyl)-5-(*o*-tolyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3aa)**



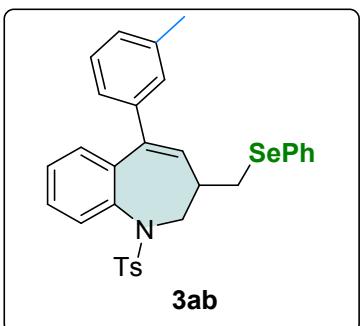
Colorless liquid; yield 76% (112.5 mg);

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 7.9 Hz, 2H), 7.49 (dd, *J* = 6.5, 3.1 Hz, 3H), 7.30 – 7.22 (m, 4H), 7.20 – 7.11 (m, 5H), 7.07 (t, *J* = 7.7 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 2H), 5.76 (s, 1H), 4.35 (s, 1H), 3.71 (s, 1H), 3.13 (s, 1H), 2.98 (dt, *J* = 9.3, 4.5 Hz, 2H), 2.38 (s, 3H), 1.99 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 143.4, 138.9, 138.3, 136.4, 134.2, 133.2, 130.8, 130.2, 130.0, 129.7, 129.3, 128.4, 127.9, 127.5, 127.4, 127.4, 127.4, 125.6, 56.4, 40.2, 30.3, 21.6, 20.2.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>31</sub>H<sub>30</sub>NO<sub>2</sub>SSe<sup>+</sup>, 560.1157; found, 560.1159

**3-((phenylselanyl)methyl)-5-(*m*-tolyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3ab)**



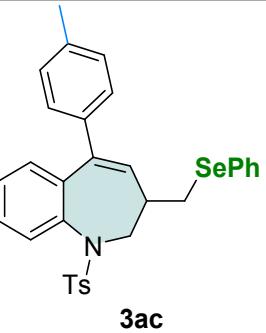
White solid; yield 79 % (167.6 mg); mp 112–114 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.9 Hz, 1H), 7.52 – 7.42 (m, 4H), 7.34 – 7.17 (m, 5H), 7.05 (q, *J* = 8.7, 8.1 Hz, 2H), 6.93 (t, *J* = 8.6 Hz, 3H), 6.66 (s, 1H), 6.62 (d, *J* = 6.6 Hz, 1H), 5.97 (s, 1H), 4.34 (s, 1H), 4.07 (s, 1H), 2.99 (qd, *J* = 12.1, 6.6 Hz, 2H), 2.73 (s, 1H), 2.27 (s, 3H), 2.20 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 142.9, 141.9, 139.8, 137.9, 137.4, 135.9, 133.4, 131.2, 130.7, 130.2, 129.9, 129.3, 129.3, 128.6, 128.4, 128.3, 128.1, 127.8, 127.5, 127.5, 125.3, 63.5, 38.7, 30.0, 21.5, 21.5.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>31</sub>H<sub>30</sub>NO<sub>2</sub>SSe<sup>+</sup>, 560.1157; found, 560.1159

**3-((phenylselanyl)methyl)-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3ac)**



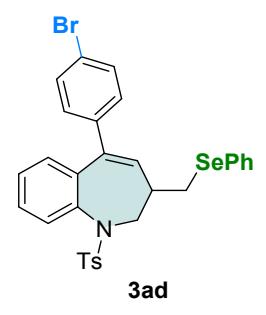
White solid; yield 73 % (122.4 mg); mp 81–83 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 4H), 7.35 – 7.15 (m, 5H), 6.95 (dd, *J* = 24.2, 7.7 Hz, 5H), 6.72 (d, *J* = 7.5 Hz, 2H), 5.96 (s, 1H), 4.34 (s, 1H), 4.06 (s, 1H), 3.06 – 2.90 (m, 2H), 2.71 (s, 1H), 2.33 (s, 3H), 2.20 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 143.0, 141.7, 139.9, 137.8, 137.3, 137.0, 133.4, 133.4, 131.3, 130.6, 129.9, 129.3, 128.6, 128.4, 128.1, 127.9, 127.5, 127.4, 63.4, 38.5, 30.0, 21.5, 21.2.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>31</sub>H<sub>30</sub>NO<sub>2</sub>SSe<sup>+</sup>, 560.1157; found, 560.1149

#### 5-(4-bromophenyl)-3-((phenylselanyl)methyl)-1-tosyl-2,3-dihydro-1H-benzo[b]azepine (3ad)



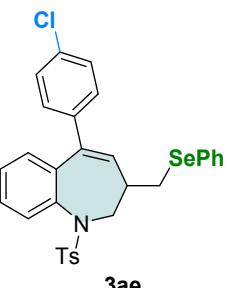
White solid; yield 76 % (142.1 mg); mp 109–111 °C;

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.47 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.45 – 7.35 (m, 6H), 7.35 – 7.22 (m, 4H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.86 (d, *J* = 5.9 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 2H), 6.12 (s, 1H), 4.41 (s, 1H), 4.02 (s, 1H), 3.23 – 3.09 (m, 2H), 2.16 (s, 3H).

<sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>) δ 142.8, 139.2, 138.9, 137.9, 137.5, 137.1, 131.9, 131.4, 130.8, 129.7, 129.4, 129.3, 129.1, 128.7, 128.5, 126.9, 126.9, 120.6, 62.8, 38.4, 28.0, 20.8.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>30</sub>H<sub>27</sub>BrNO<sub>2</sub>SSe<sup>+</sup>, 624.0106; found, 624.0106

#### 5-(4-chlorophenyl)-3-((phenylselanyl)methyl)-1-tosyl-2,3-dihydro-1H-benzo[b]azepine (3ae)



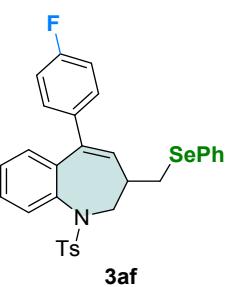
White solid; yield 80% (173.7 mg); mp 86-88 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 7.9 Hz, 1H), 7.42 – 7.35 (m, 4H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.16 (dt, *J* = 5.2, 2.7 Hz, 4H), 7.04 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.1 Hz, 2H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.67 (d, *J* = 8.5 Hz, 2H), 5.93 (s, 1H), 4.33 (s, 1H), 3.97 (s, 1H), 2.91 (qd, *J* = 12.1, 6.7 Hz, 2H), 2.63 (s, 1H), 2.14 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 143.1, 139.3, 138.5, 137.1, 131.9, 131.9, 131.4, 130.8, 129.7, 129.5, 129.3, 128.4, 128.0, 127.5, 127.3, 126.9, 126.8, 62.8, 38.1, 28.0, 20.8.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>30</sub>H<sub>27</sub>ClNO<sub>2</sub>SSe<sup>+</sup>, 580.0611; found, 580.0610

#### 5-(4-fluorophenyl)-3-((phenylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3af)



White solid; yield 67 % (113.1 mg); mp 83-85 °C;

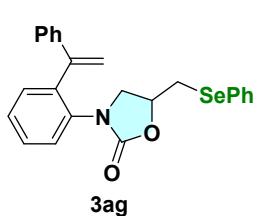
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.50 (dd, *J* = 21.9, 8.1 Hz, 5H), 7.30 (t, *J* = 7.1 Hz, 1H), 7.26 – 7.21 (m, 4H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.85 (td, *J* = 19.6, 18.8, 8.1 Hz, 5H), 5.96 (s, 1H), 4.38 (s, 1H), 4.06 (s, 1H), 2.99 (qd, *J* = 12.1, 6.7 Hz, 2H), 2.71 (s, 1H), 2.24 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 162.4 (d, *J* = 247.3 Hz), 143.1, 140.9, 139.7, 138.0, 133.4, 131.3, 130.4, 129.8, 129.6, 129.4, 129.3, 128.6, 128.3, 127.5, 127.5, 114.8 (d, *J* = 22.1 Hz), 63.2, 38.6, 29.9, 21.5.

<sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -114.87.

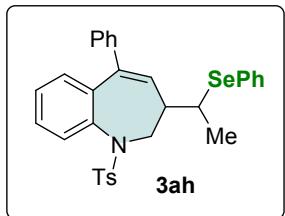
HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>30</sub>H<sub>27</sub>FNO<sub>2</sub>SSe<sup>+</sup>, 564.0906; found, 564.0911

#### 5-((phenylselanyl)methyl)-3-(2-(1-phenylvinyl)phenyl)oxazolidin-2-one (3ag)



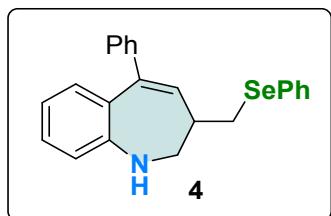
White solid; yield 73 % (95.1 mg); mp 76-78 °C;  
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.40 (ddd, *J* = 31.4, 16.1, 8.2 Hz, 5H), 7.33 – 7.19 (m, 9H), 5.69 (s, 1H), 5.42 (s, 1H), 4.07 (ddq, *J* = 8.2, 4.3, 2.1 Hz, 1H), 3.63 (t, *J* = 8.7 Hz, 1H), 3.40 (dd, *J* = 9.0, 6.4 Hz, 1H), 2.99 (dd, *J* = 12.7, 4.4 Hz, 1H), 2.29 (dd, *J* = 12.7, 9.8 Hz, 1H).  
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 155.4, 147.5, 140.0, 139.2, 135.3, 133.6, 131.9, 129.5, 129.1, 128.6, 128.3, 128.1, 128.0, 127.9, 127.3, 126.5, 117.1, 72.2, 51.9, 30.2.  
HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>22</sub>NO<sub>2</sub>Se<sup>+</sup>, 436.0810; found, 436.0808

### 5-phenyl-3-(1-(phenylselanyl)ethyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3ah)



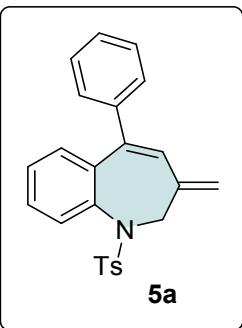
White solid; yield 59 % (98.9 mg); mp 112-114 °C;  
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.60 – 7.42 (m, 5H), 7.24 (ddq, *J* = 24.5, 14.4, 7.1 Hz, 8H), 6.91 (dd, *J* = 22.2, 6.8 Hz, 5H), 6.12 (s, 1H), 4.44 (s, 1H), 4.11 (s, 1H), 3.50 – 3.31 (m, 1H), 2.67 (s, 1H), 2.20 (d, *J* = 6.3 Hz, 3H), 1.47 (d, *J* = 7.1 Hz, 3H).  
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 143.0, 141.8, 139.8, 137.9, 135.5, 135.4, 131.3, 130.6, 129.4, 129.2, 128.8, 128.4, 128.1, 128.0, 128.0, 127.5, 127.5, 62.1, 42.9, 40.4, 21.5, 19.2.  
HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>30</sub>NO<sub>2</sub>SSe<sup>+</sup>, 560.1157; found, 560.1157.

### 5-phenyl-3-((phenylselanyl)methyl)-2,3-dihydro-1*H*-benzo[*b*]azepine (4)



White solid; yield 92 % (107.8 mg); mp 58-60 °C;  
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.46 (m, 2H), 7.34 – 7.19 (m, 8H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 6.77 – 6.63 (m, 2H), 5.96 (d, *J* = 5.4 Hz, 1H), 3.55 (s, 1H), 3.55 – 3.29 (m, 2H), 3.19 – 2.98 (m, 2H), 2.92 – 2.76 (m, 1H).  
<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 149.5, 145.4, 140.9, 133.7, 132.9, 132.7, 130.5, 129.3, 129.3, 128.1, 127.9, 127.0, 126.8, 126.6, 119.6, 118.9, 52.5, 42.5, 31.7.  
HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>23</sub>H<sub>22</sub>NSe<sup>+</sup>, 392.0912; found, 392.0911

### 3-methylene-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (5a)



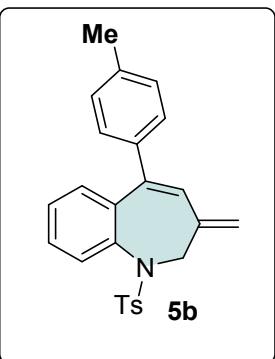
White solid; yield 79 % (91.8 mg); mp 127-129 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.1 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.17 (m, 4H), 7.10 (t, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.89 – 6.67 (m, 3H), 6.06 (s, 1H), 5.22 (d, *J* = 38.9 Hz, 2H), 4.97 (d, *J* = 16.2 Hz, 1H), 3.95 (d, *J* = 15.3 Hz, 1H), 2.21 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 145.1, 143.2, 142.4, 139.8, 138.7, 137.1, 136.1, 133.3, 132.7, 130.5, 129.2, 129.0, 128.5, 127.9, 127.5, 127.4, 127.2, 119.5, 55.4, 21.4.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>22</sub>NO<sub>2</sub>S<sup>+</sup>, 388.1366; found, 388.1369

### 3-methylene-5-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (**5b**)



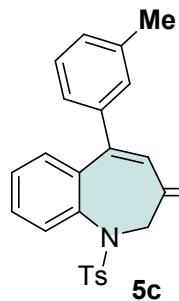
White solid; yield 74 % (89.2 mg); mp 193-194 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.10 (t, *J* = 8.1 Hz, 1H), 7.02 (dd, *J* = 12.0, 8.0 Hz, 4H), 6.82 (d, *J* = 7.9 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 2H), 6.04 (s, 1H), 5.24 (s, 1H), 5.16 (s, 1H), 4.96 (d, *J* = 16.2 Hz, 1H), 3.94 (d, *J* = 16.2 Hz, 1H), 2.34 (s, 3H), 2.22 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 143.2, 142.4, 142.3, 139.8, 138.7, 137.2, 136.9, 136.2, 133.0, 132.7, 130.5, 129.1, 129.0, 128.6, 128.5, 127.5, 127.4, 119.2, 55.4, 21.5, 21.2.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>24</sub>NO<sub>2</sub>S<sup>+</sup>, 402.1522; found, 402.1522

### 3-methylene-5-(*m*-tolyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (**5c**)



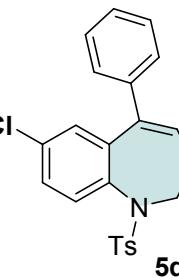
White solid; yield 71 % (85.5 mg); mp 161-163 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.25 (m, 1H), 7.11 (q, *J* = 6.9 Hz, 2H), 7.08 – 6.99 (m, 3H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.57 (s, 2H), 6.05 (s, 1H), 5.26 (s, 1H), 5.18 (s, 1H), 4.97 (d, *J* = 16.1 Hz, 1H), 3.94 (d, *J* = 16.1 Hz, 1H), 2.30 (s, 3H), 2.22 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 145.2, 143.1, 142.4, 139.7, 138.9, 137.5, 137.2, 136.2, 133.1, 132.7, 130.5, 129.9, 129.0, 128.5, 127.9, 127.8, 127.6, 127.4, 126.3, 119.4, 55.4, 21.5, 21.5.

HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>24</sub>NO<sub>2</sub>S<sup>+</sup>, 402.1522; found, 402.1524

#### 7-chloro-3-methylene-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (5d)



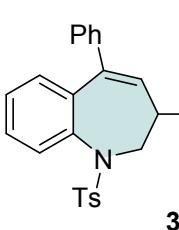
White solid; yield 84 % (106.3 mg); mp 166-168 °C;

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.5 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 6.0 Hz, 4H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.76 (d, *J* = 6.9 Hz, 3H), 6.09 (s, 1H), 5.30 (s, 1H), 5.22 (s, 1H), 4.96 (d, *J* = 16.2 Hz, 1H), 3.90 (d, *J* = 16.2 Hz, 1H), 2.22 (s, 3H).

<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 144.3, 143.5, 142.0, 138.3, 137.7, 137.6, 136.9, 134.5, 133.3, 132.1, 131.9, 129.1, 129.0, 128.4, 128.2, 127.5, 127.5, 120.5, 55.3, 21.4.

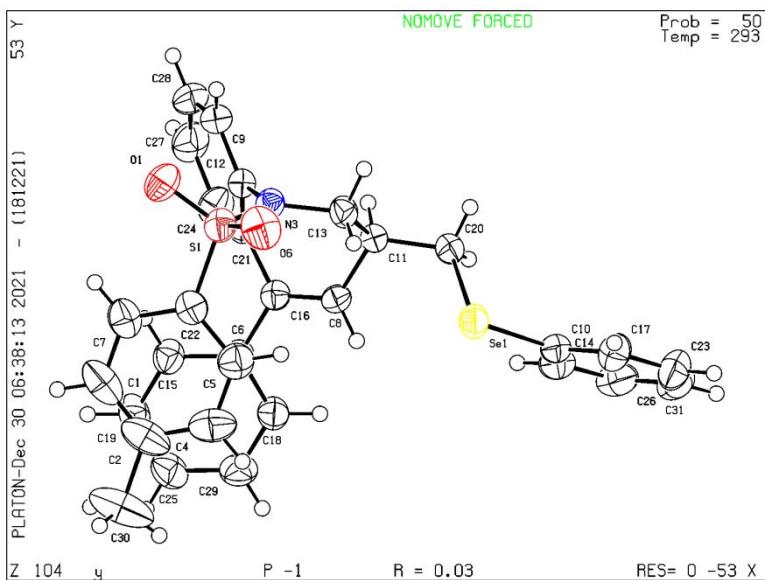
HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>21</sub>ClNO<sub>2</sub>S<sup>+</sup>, 422.0976; found, 422.0977

#### 9. Crystal data and structure refinement for 3a



**Method for crystal growth of 3a:** Single crystals of product 3a was obtained through slow evaporation

at room temperature of a solution in diethyl ether (0.3 M) for 2 days.



**3a** (ellipsoid contour at 50% probability level)

Bond precision: C-C = 0.0035 Å Wavelength=0.71073

Cell:  $a=9.7669(13)$   $b=11.4145(16)$   $c=12.6055(17)$   
 $\alpha=98.935(5)$   $\beta=111.149(5)$   $\gamma=94.771(5)$

Temperature: 293 K

	Calculated	Reported
Volume	1279.9(3)	1279.9(3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C <sub>30</sub> H <sub>27</sub> N O <sub>2</sub> S Se	C <sub>30</sub> H <sub>27</sub> N O <sub>2</sub> S Se
Sum formula	C <sub>30</sub> H <sub>27</sub> N O <sub>2</sub> S Se	C <sub>30</sub> H <sub>27</sub> N O <sub>2</sub> S Se
Mr	544.55	544.54
Dx, g cm <sup>-3</sup>	1.413	1.413
Z	2	2
Mu (mm <sup>-1</sup> )	1.576	1.576
F000	560.0	560.0
F000'	560.25	
h, k, lmax	12, 14, 15	12, 14, 15
Nref	5311	5251
Tmin, Tmax	0.797, 0.854	0.515, 0.745
Tmin'	0.730	

Correction method= # Reported T Limits: Tmin=0.515 Tmax=0.745  
AbsCorr = NONE

Data completeness= 0.989 Theta(max)= 26.511

R(reflections)= 0.0320( 4369) wR2 (reflections)=  
0.0787( 5251)

S = 1.036 Npar= 317

For more details, please see the CIF file attached with ESI. The crystal data of **3a** has already been

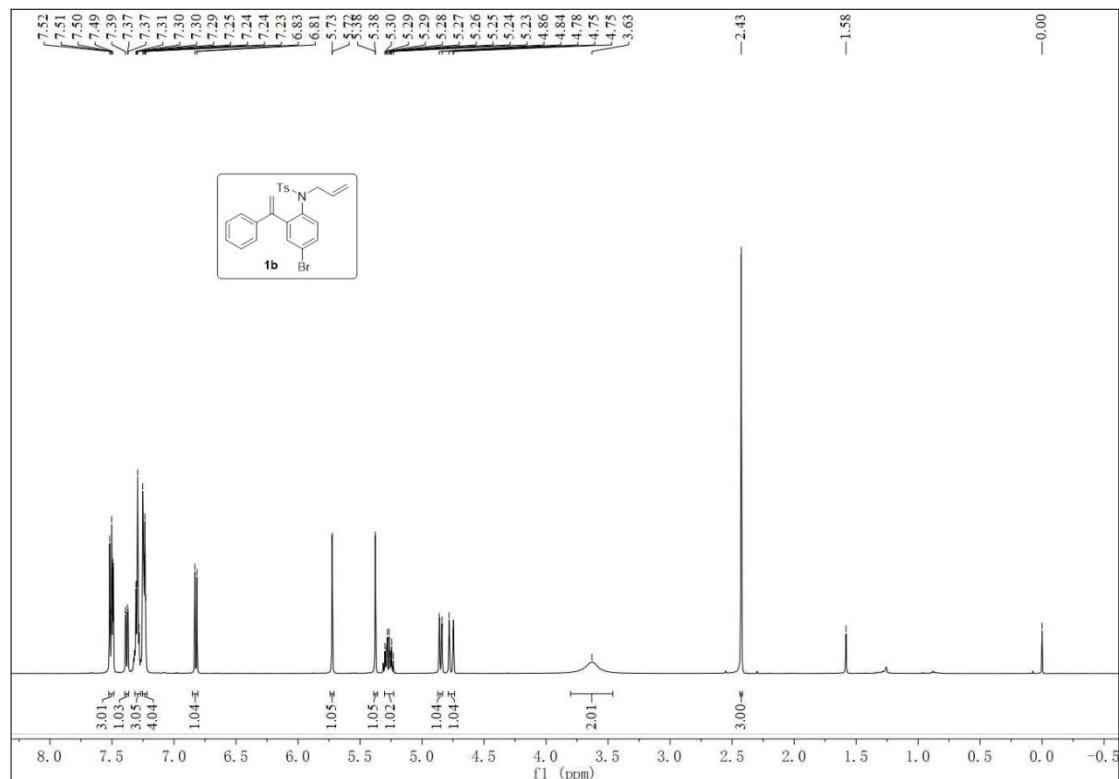
deposited at Cambridge Crystallographic Data Center, UK, and the CCDC reference number is 2141440.

## References:

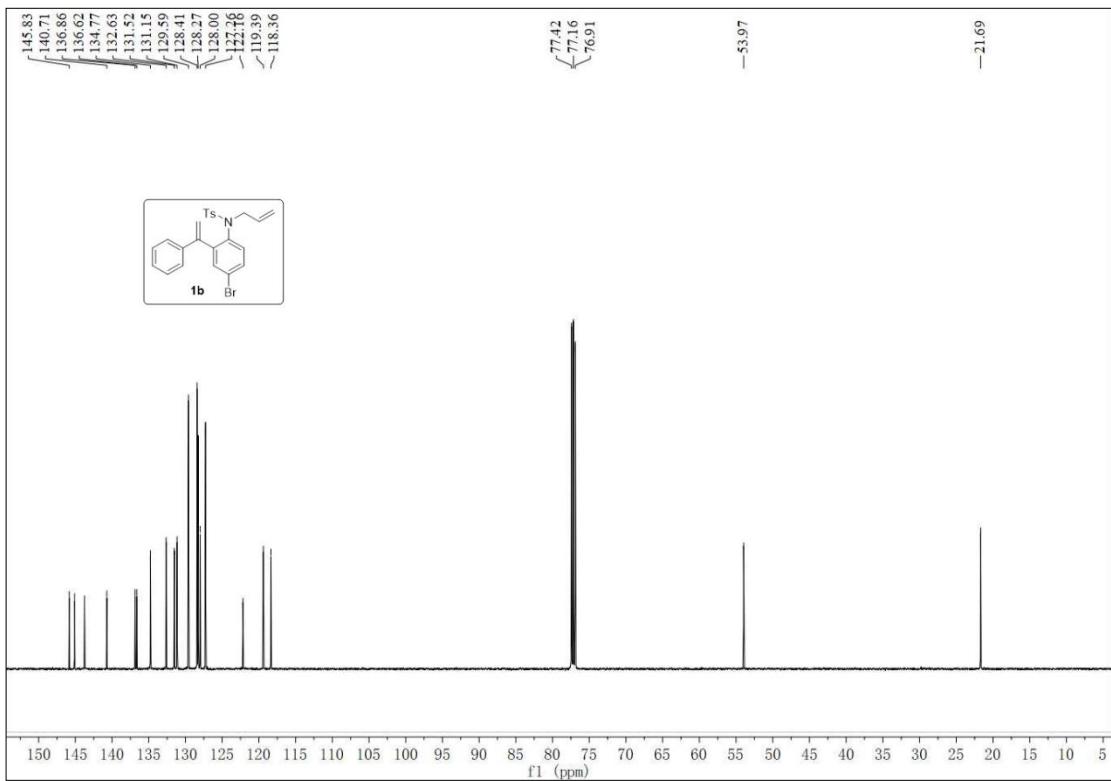
- (1) (a) Ren, Y.; Xu, B.; Zhong, Z.; Pittman, C. U.; Zhou, A., Using SeO<sub>2</sub> as a selenium source to make RSe-substituted aniline and imidazo[1,2-a]pyridine derivatives. *Org. Chem. Front.* **2019**, *6*, 2023-2027; (b) Liu, H. Y.; Zhang, J. R.; Huang, G. B.; Zhou, Y. H.; Chen, Y. Y.; Xu, Y. L., Visible Light-Promoted Selenylation/Cyclization of Enaminones toward the Formation of 3-Selanyl-4H-Chromen-4-Ones. *Adv. Synth. Catal.* **2021**, *363*, 1656-1661.
- (2) (a) Boelke, A.; Caspers, L. D.; Nachtsheim, B. J., NH<sub>2</sub>-Directed C-H Alkenylation of 2-Vinylanilines with Vinylbenziodoxolones. *Org. Lett.* **2017**, *19*, 5344-5347; (b) Wu, X.; Tang, Z.; Zhang, C.; Wang, C.; Wu, L.; Qu, J.; Chen, Y., Pd-Catalyzed Regiodivergent Synthesis of Diverse Oxindoles Enabled by the Versatile Heck Reaction of Carbamoyl Chlorides. *Org. Lett.* **2020**, *22*, 3915-3921.
- (3) Zhou, N.; Kuang, K.; Wu, M.; Wu, S.; Xu, Q.; Xia, Z.; Zhang, M., tert-Butyl Hydroperoxide - Initiated Radical Cyclization of 1-(Allyloxy)-2-(1-Arylvinyl)Benzenes with Sulfenic Acids to Access Sulfonated Benzoxepines. *Adv. Synth. Catal.* **2021**, *363*, 3491-3495.

## 10. Copy of <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F and <sup>77</sup>Se NMR

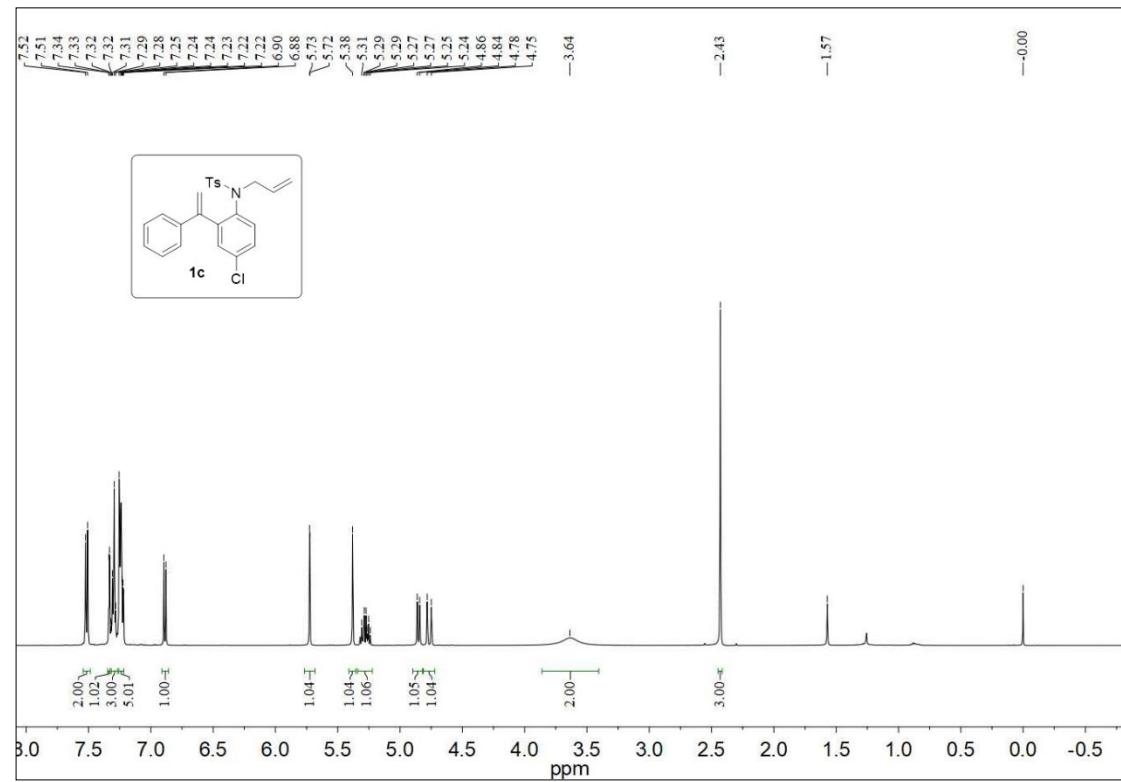
<sup>1</sup>H NMR (500 MHz, Chloroform-d)



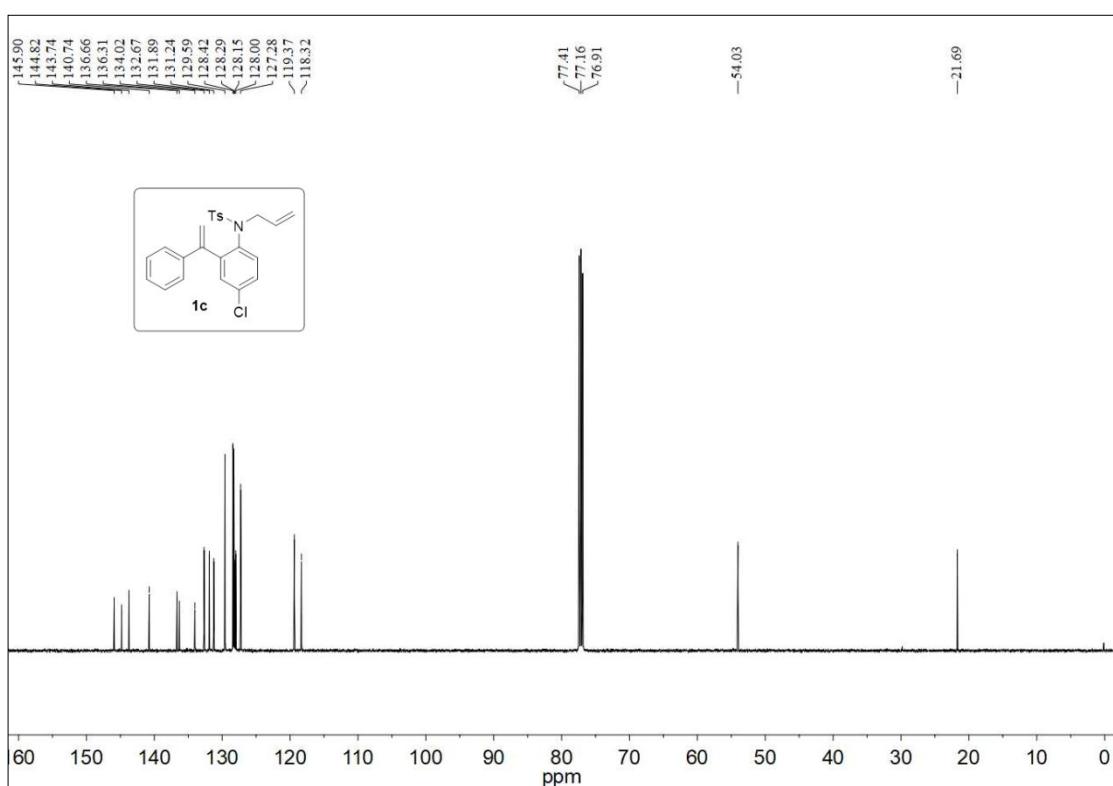
<sup>13</sup>C NMR (126 MHz, Chloroform-d)



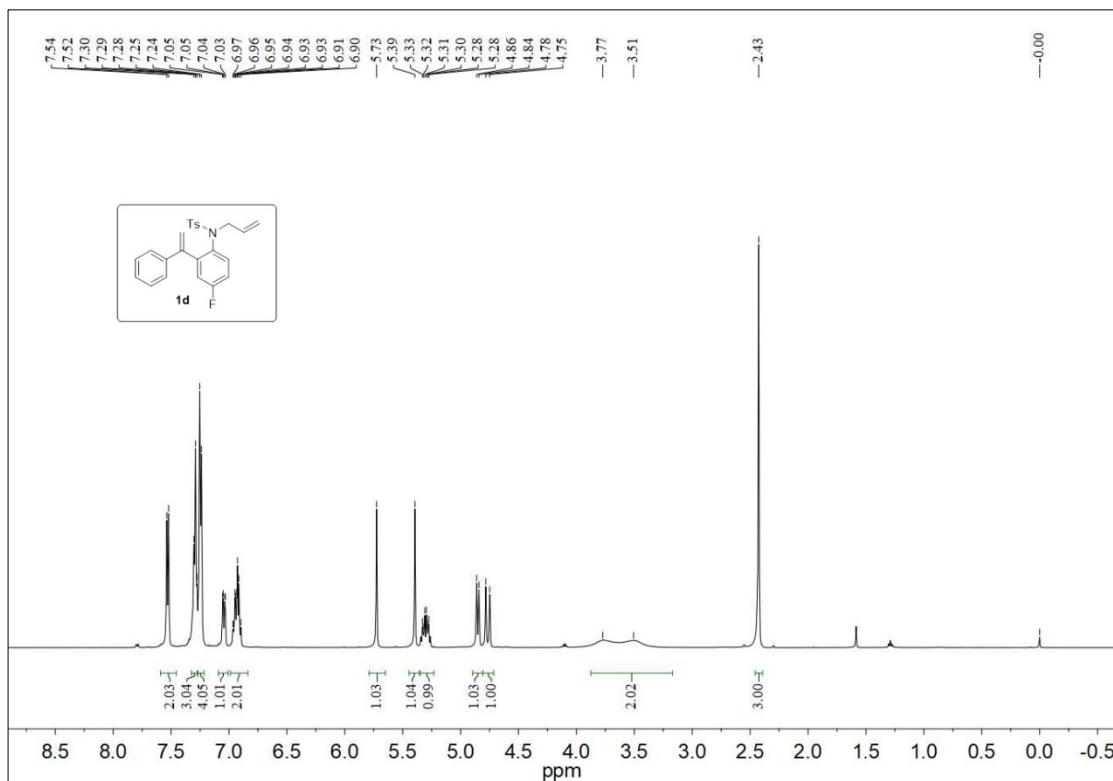
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



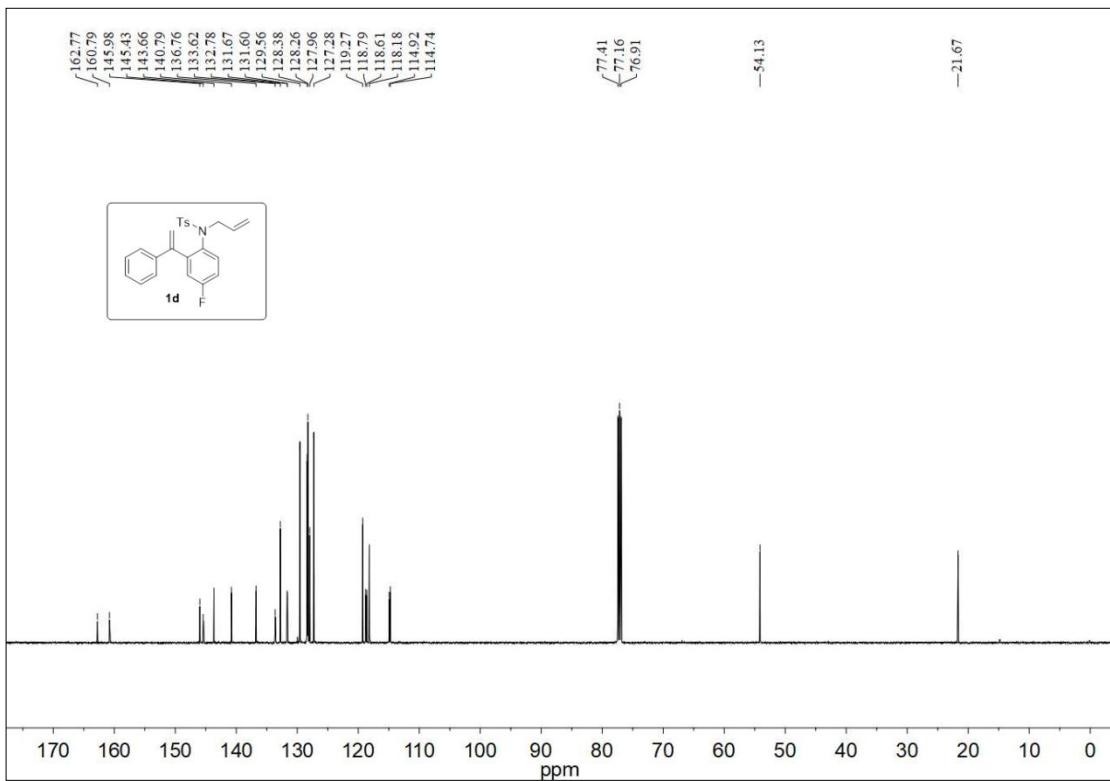
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



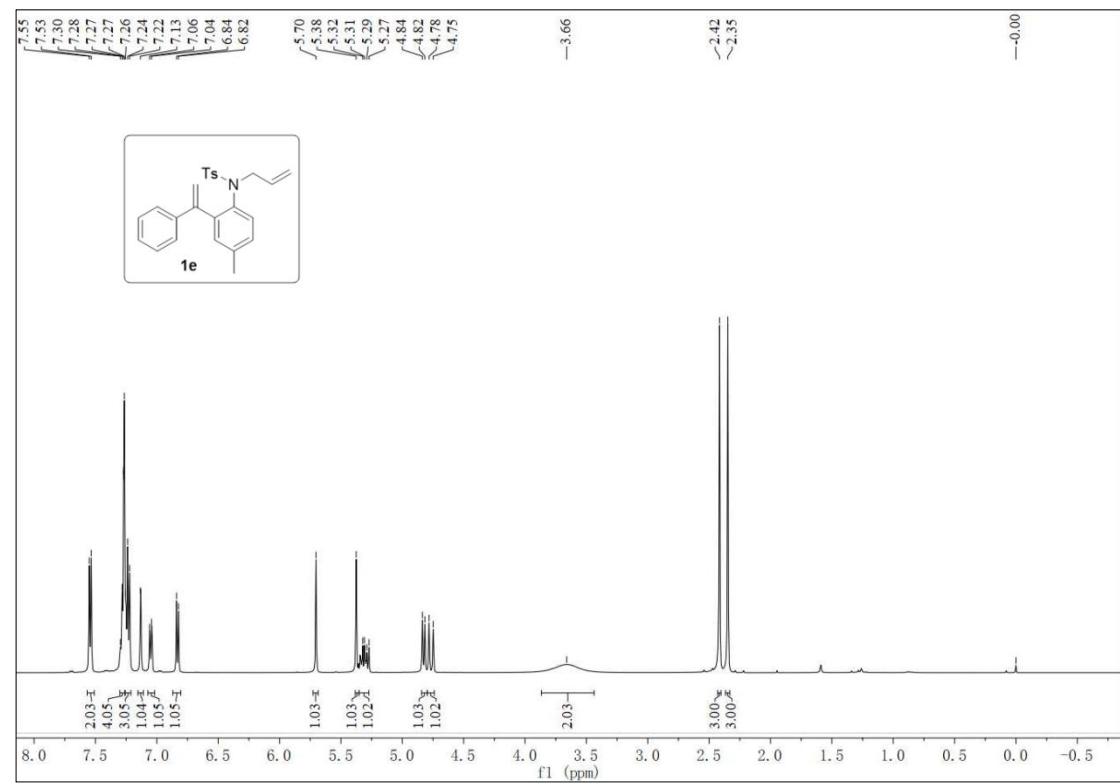
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



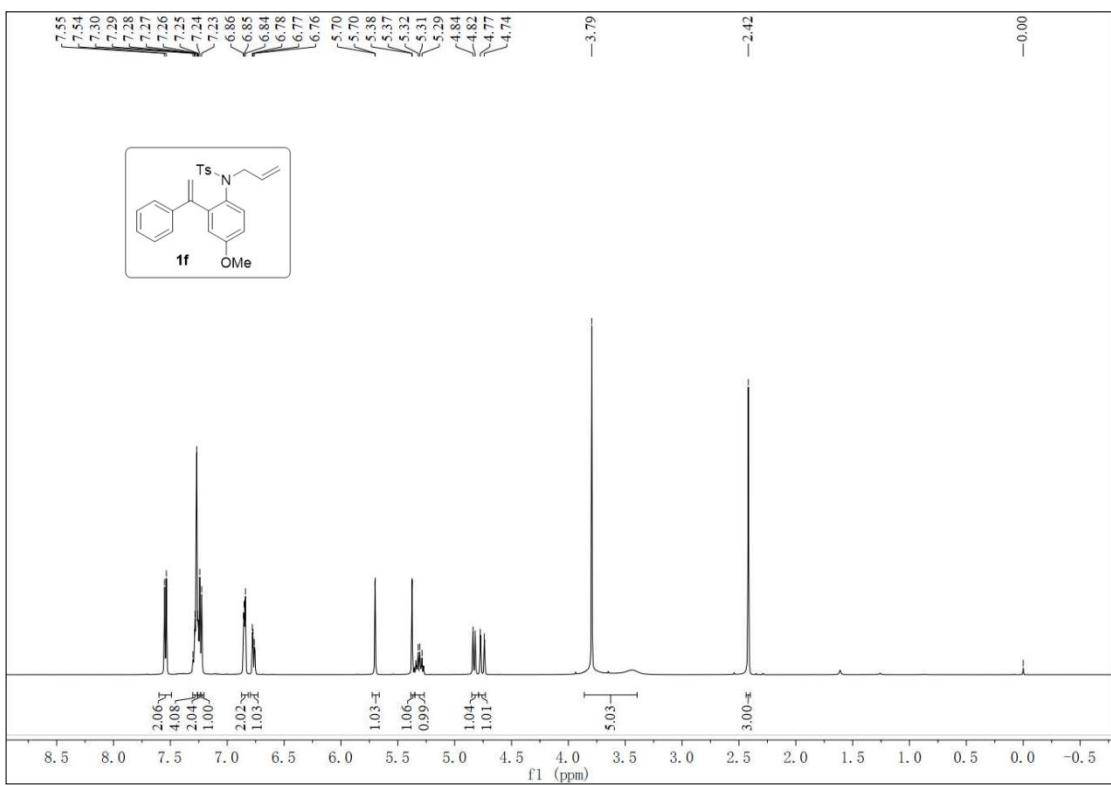
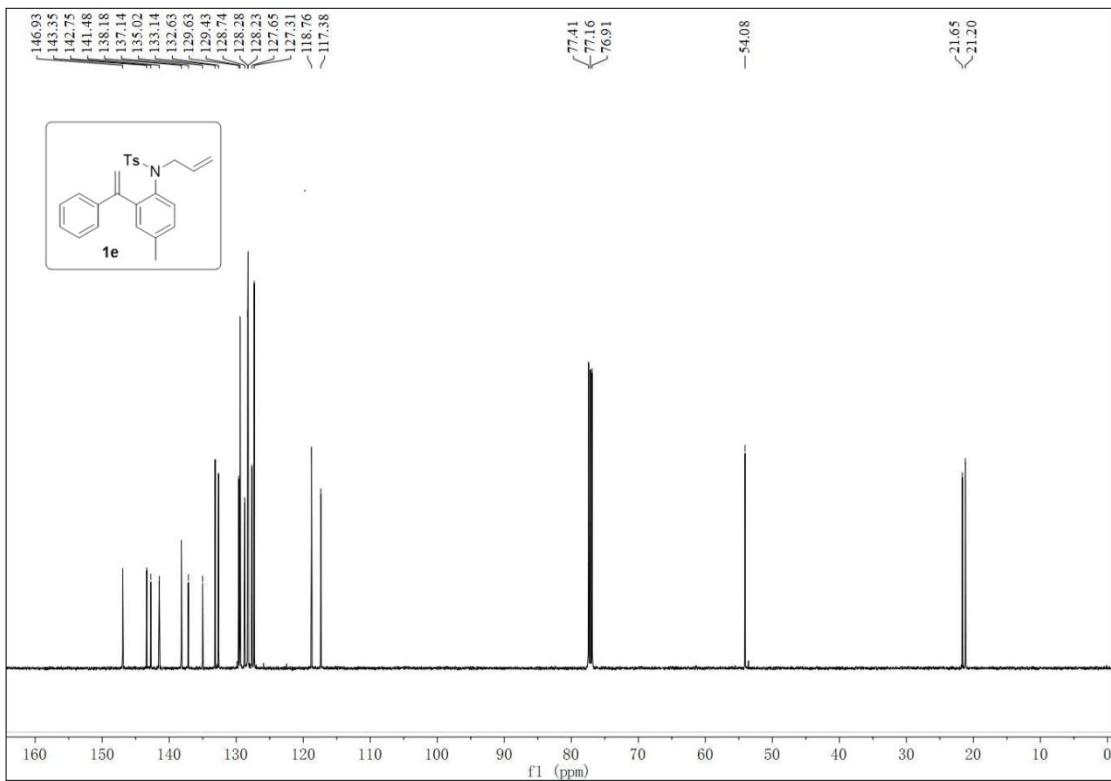
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



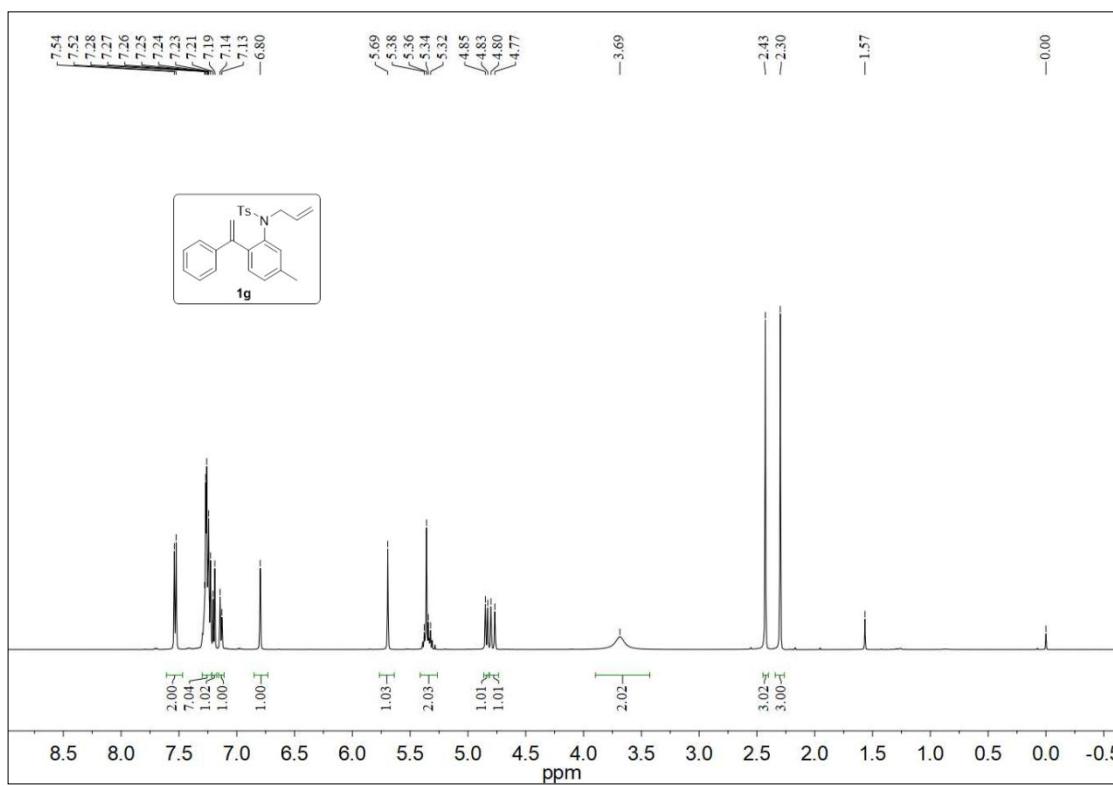
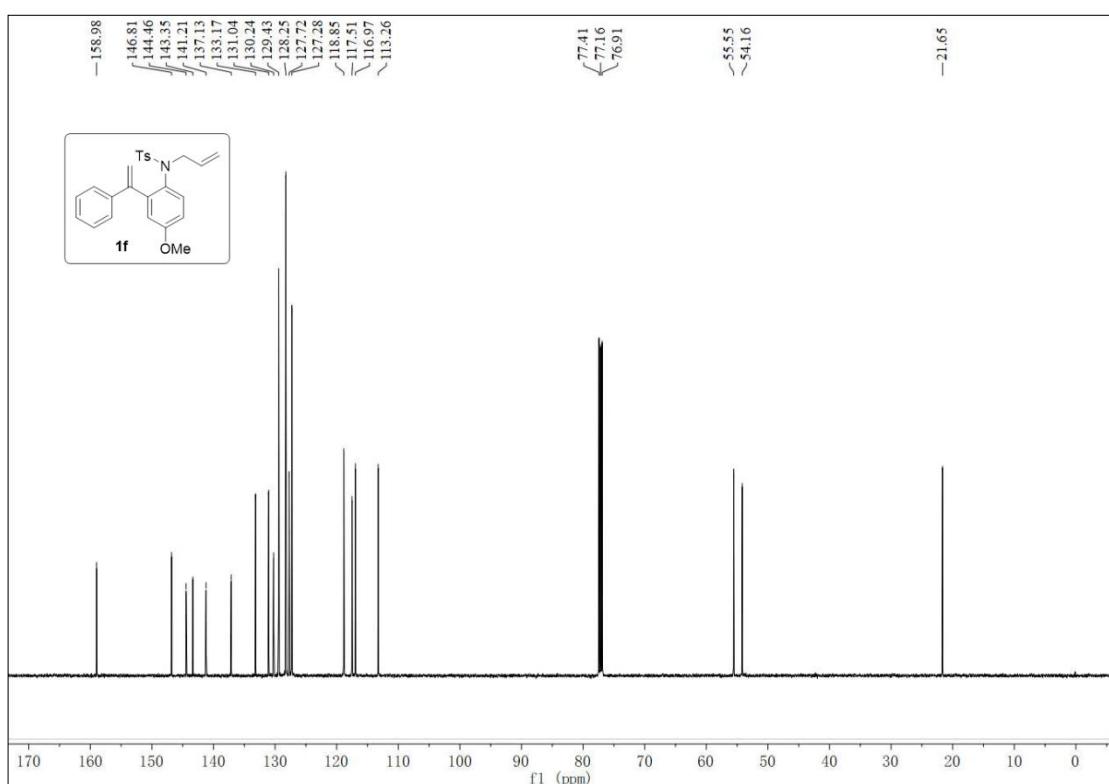
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



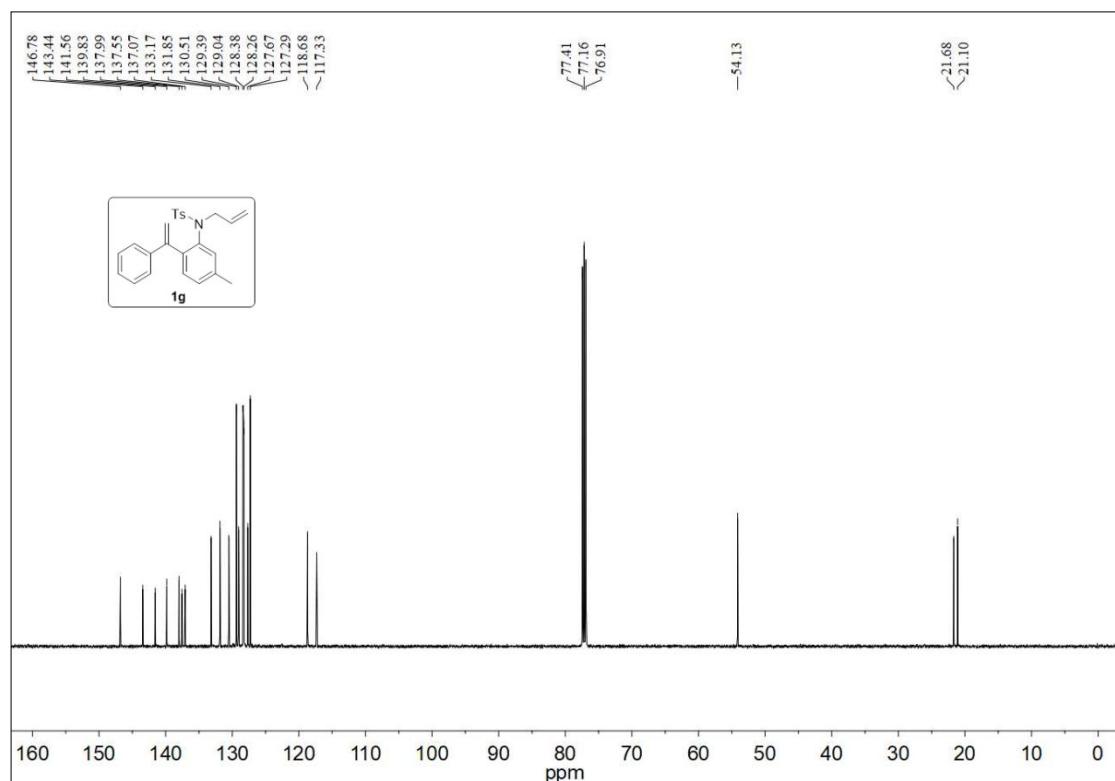
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



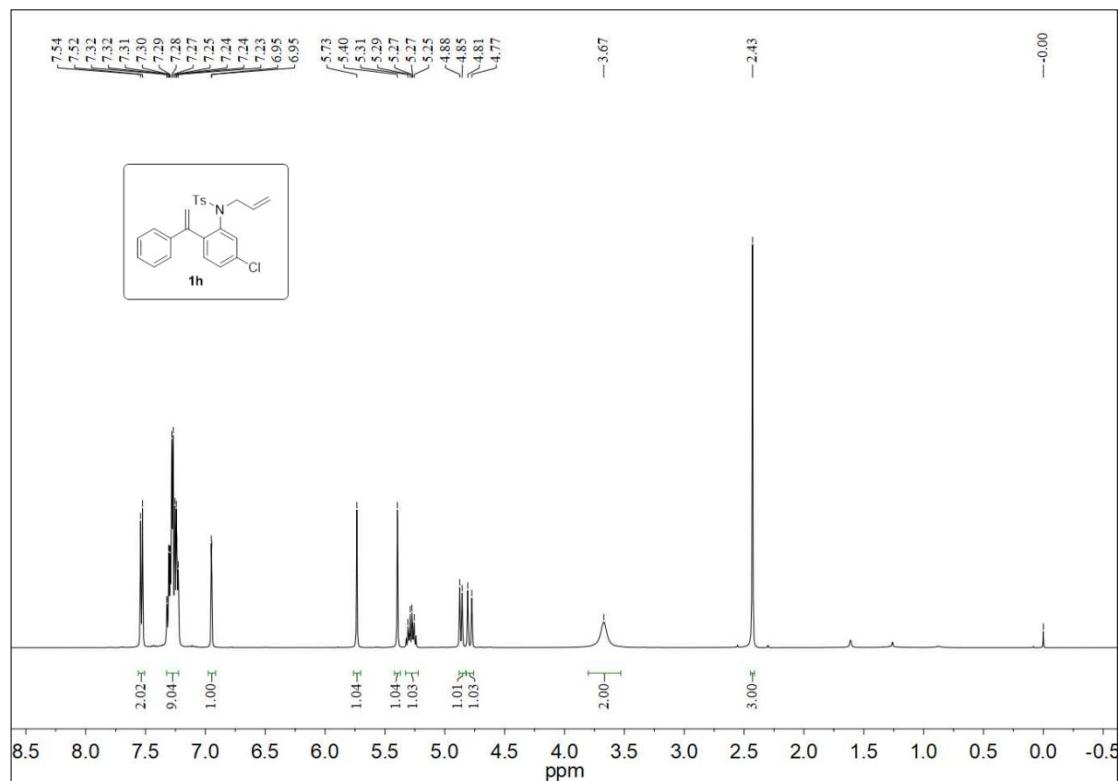
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



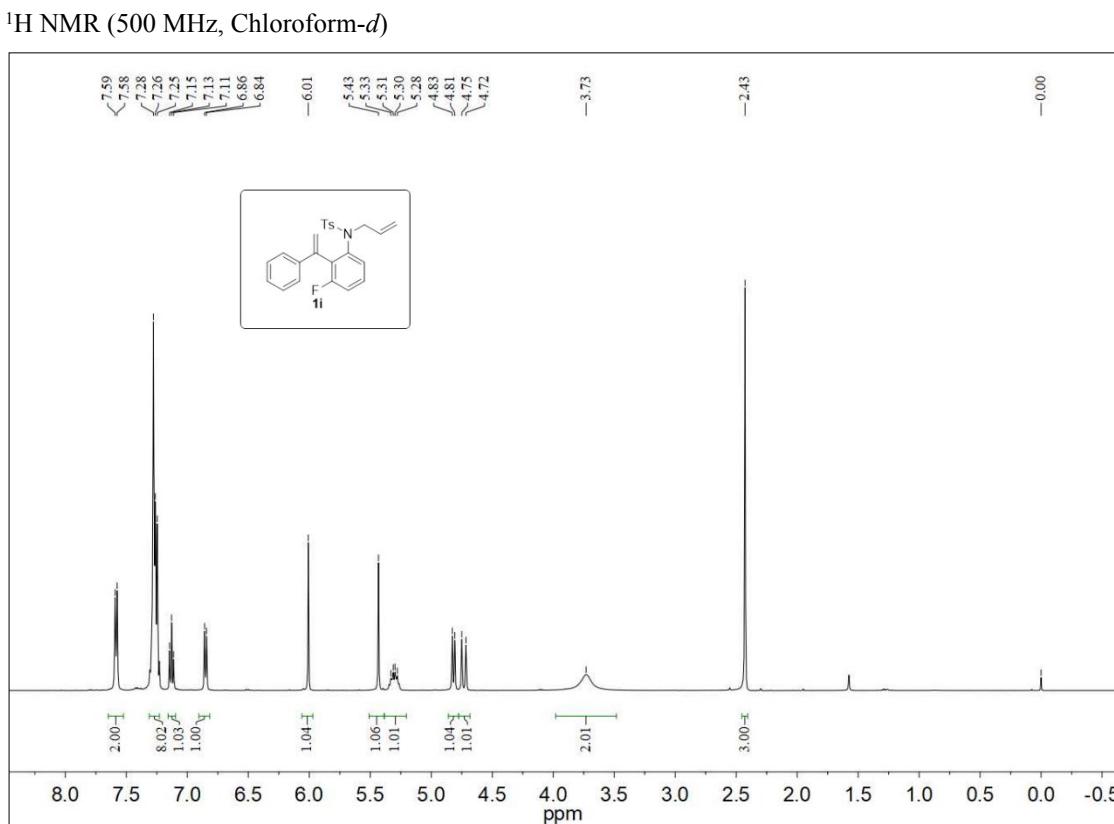
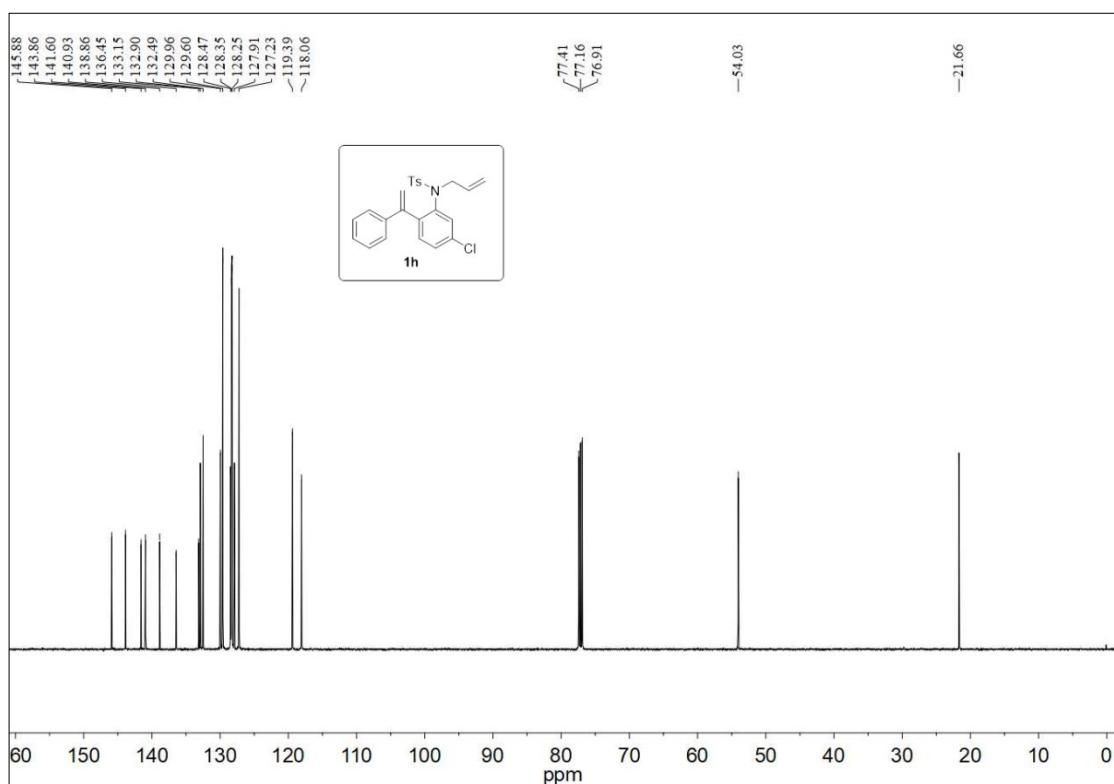
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



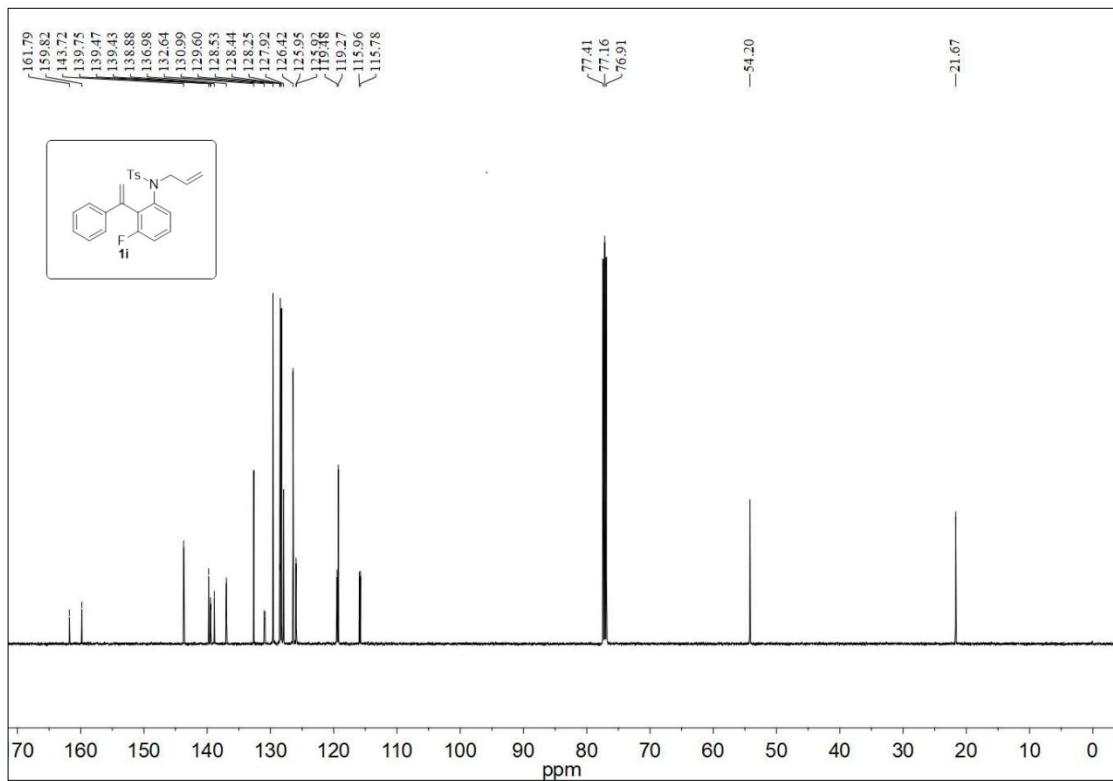
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



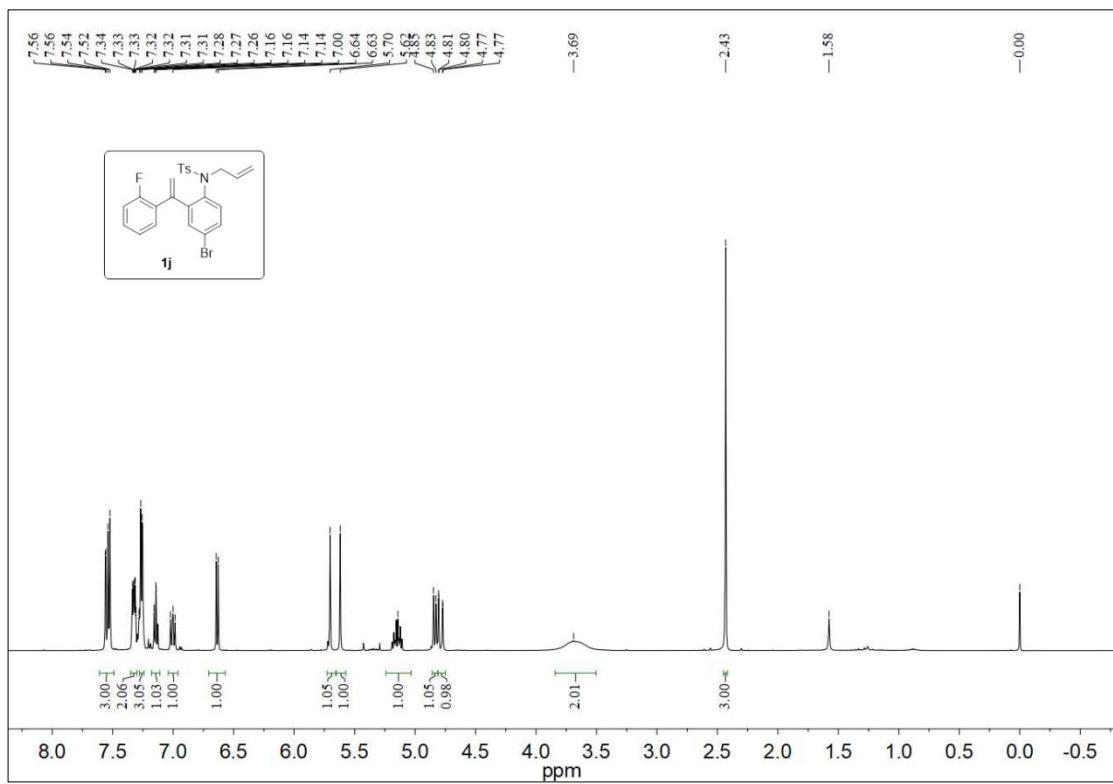
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



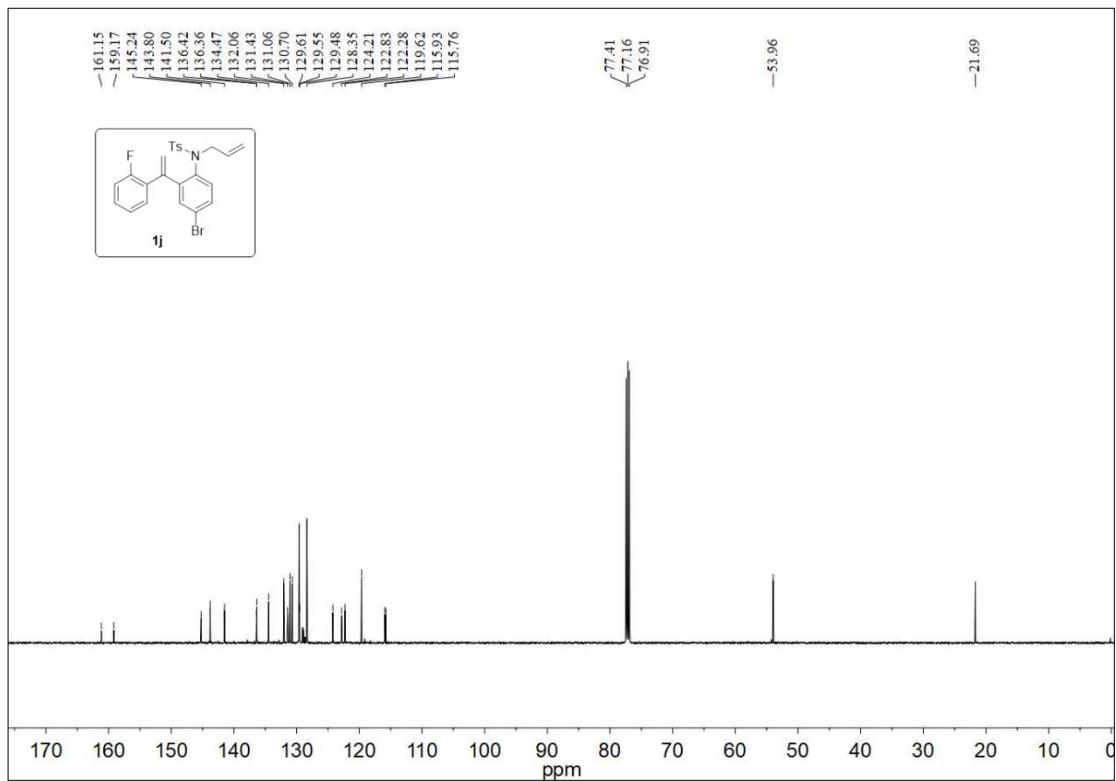
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



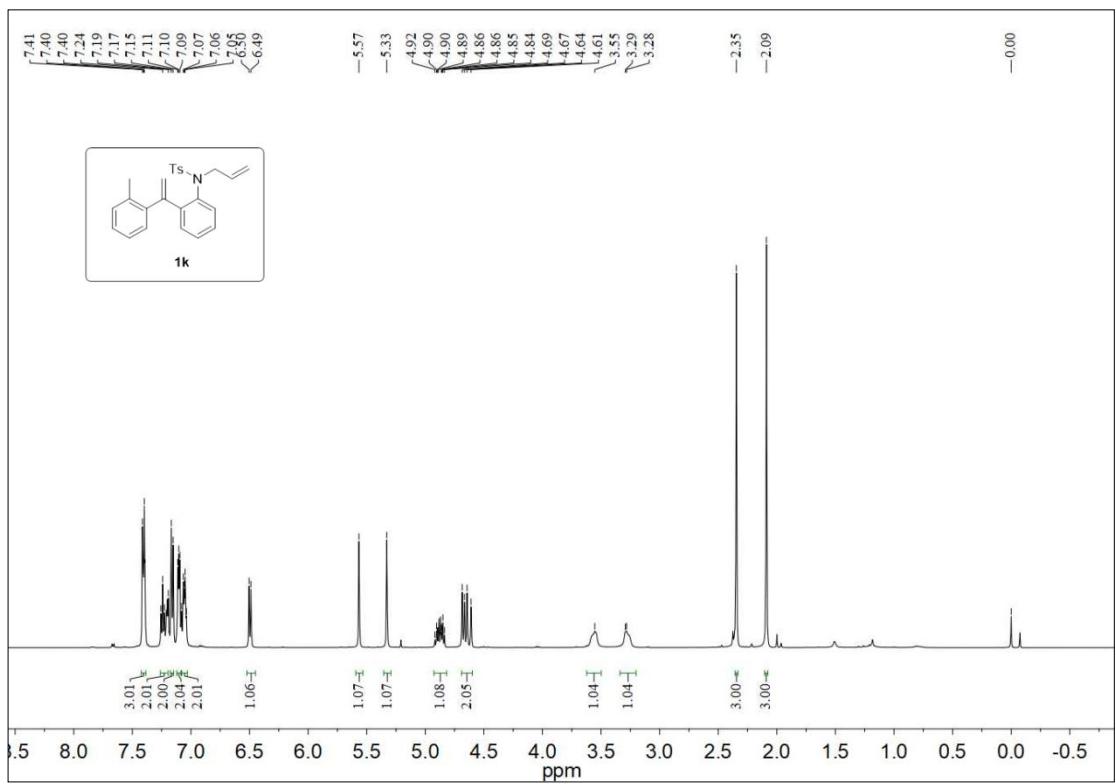
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



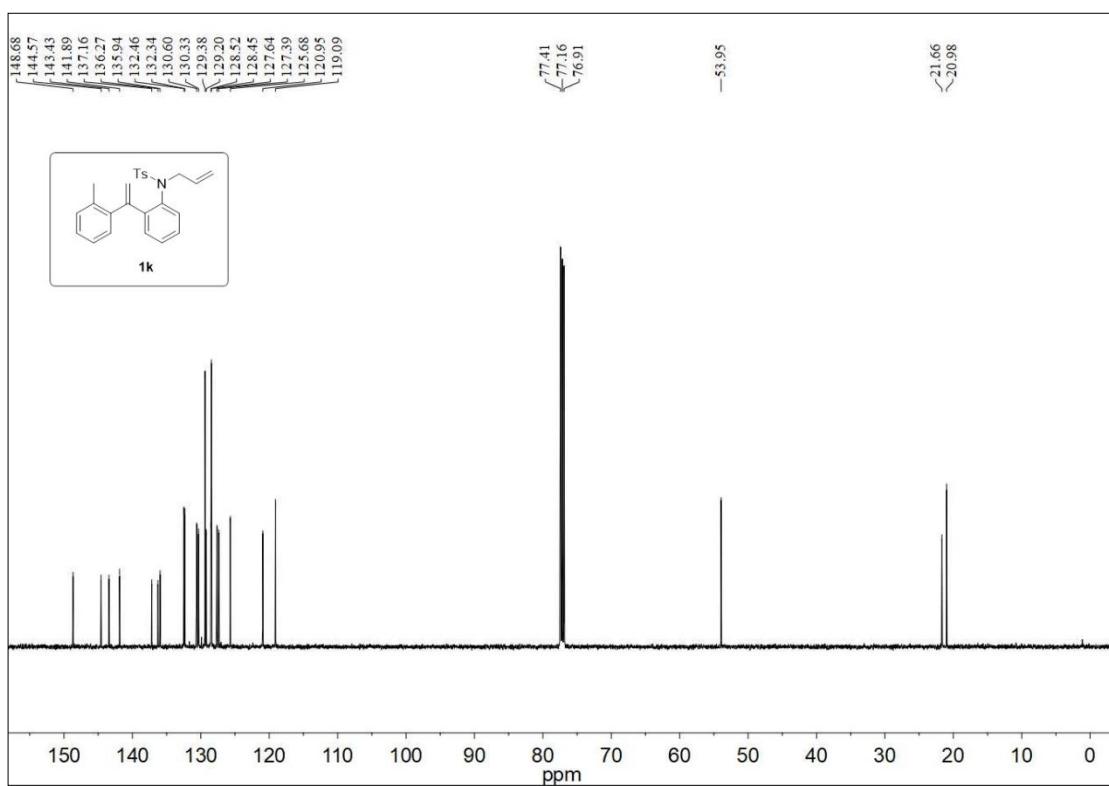
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



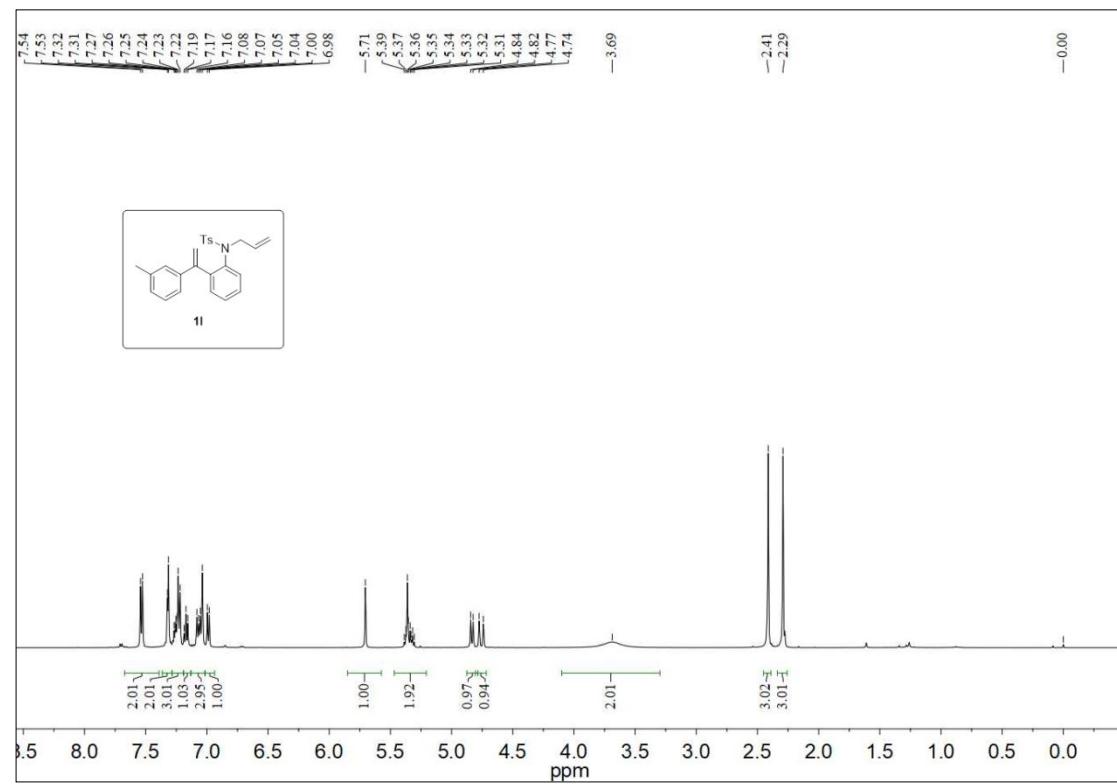
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



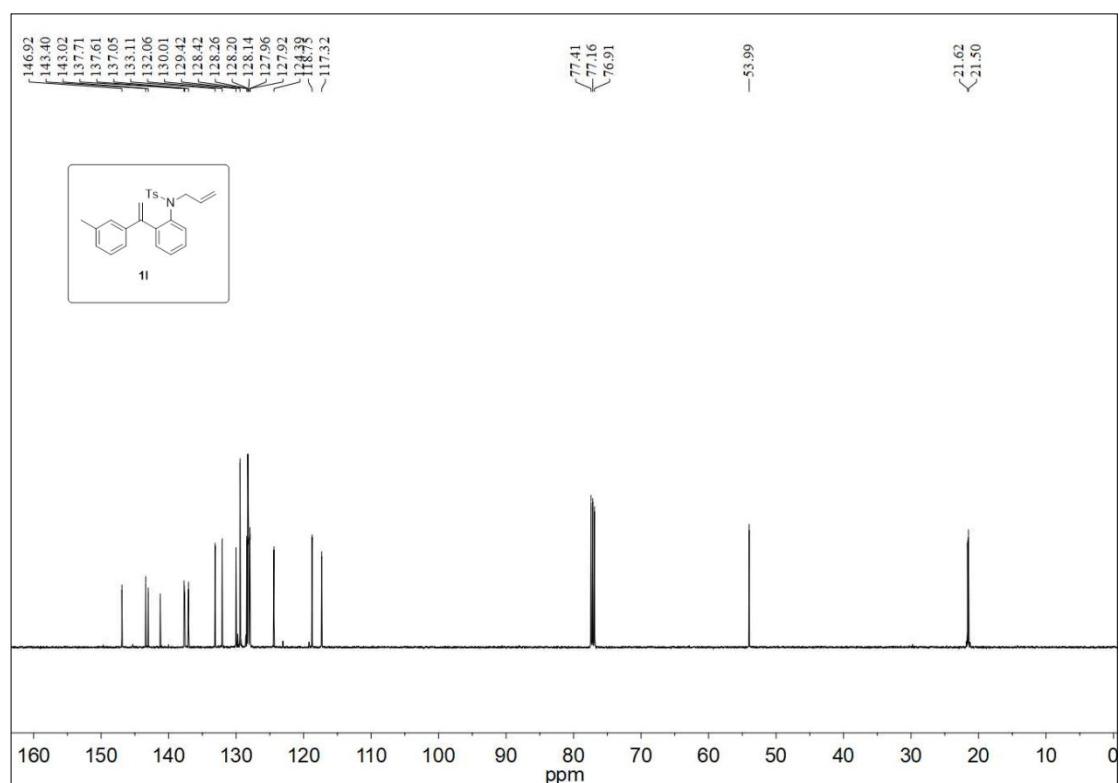
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



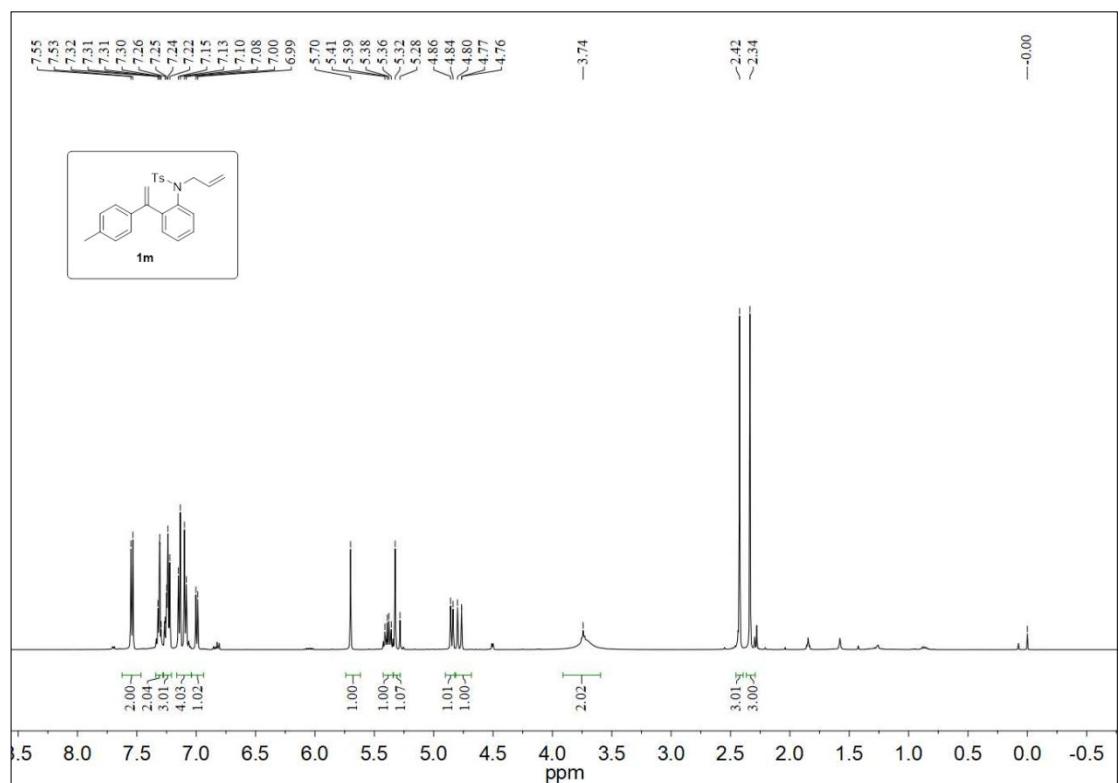
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



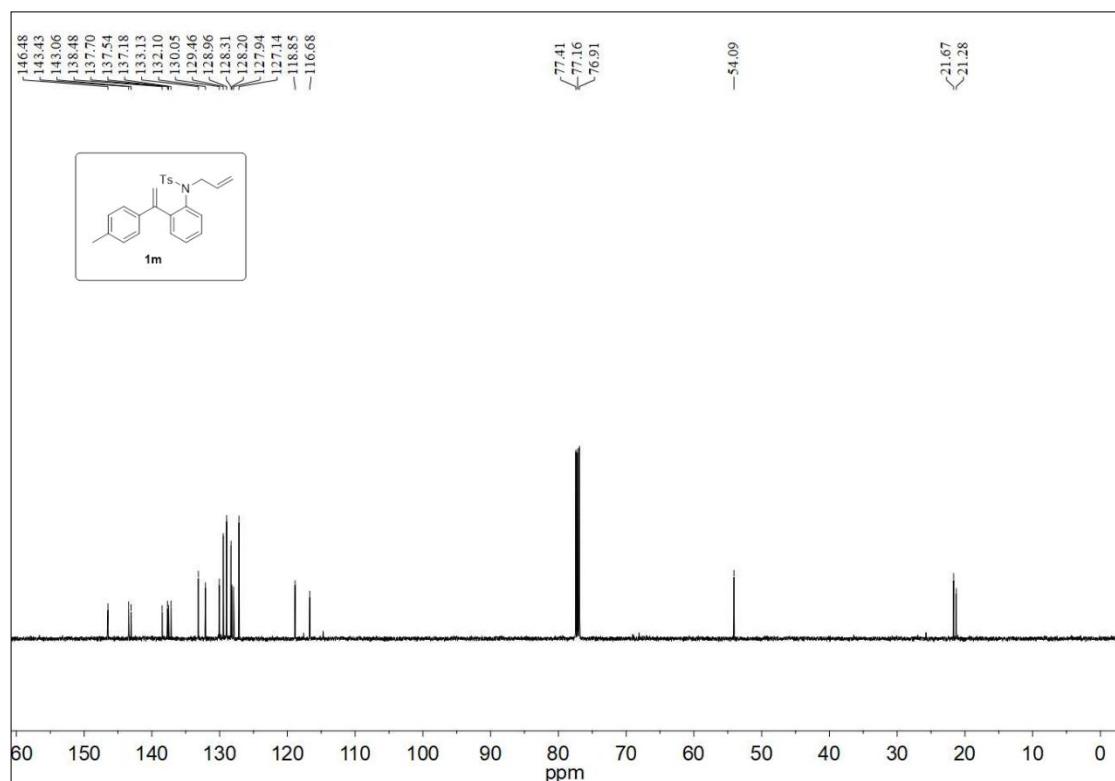
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



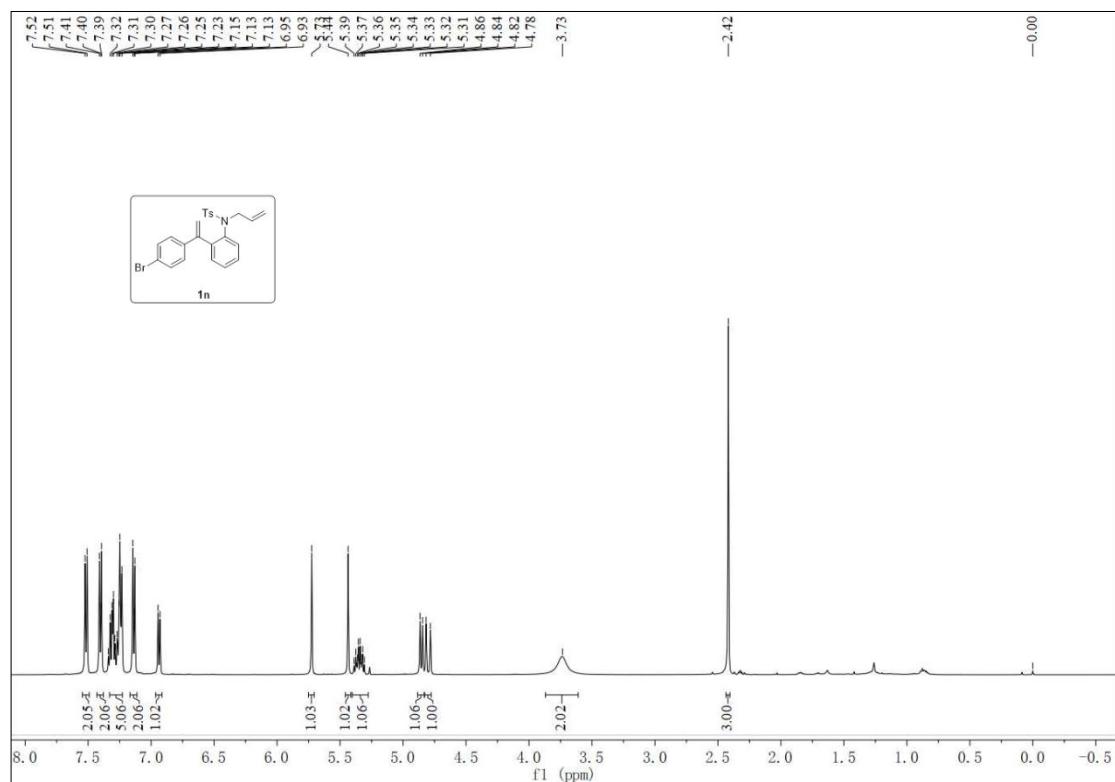
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



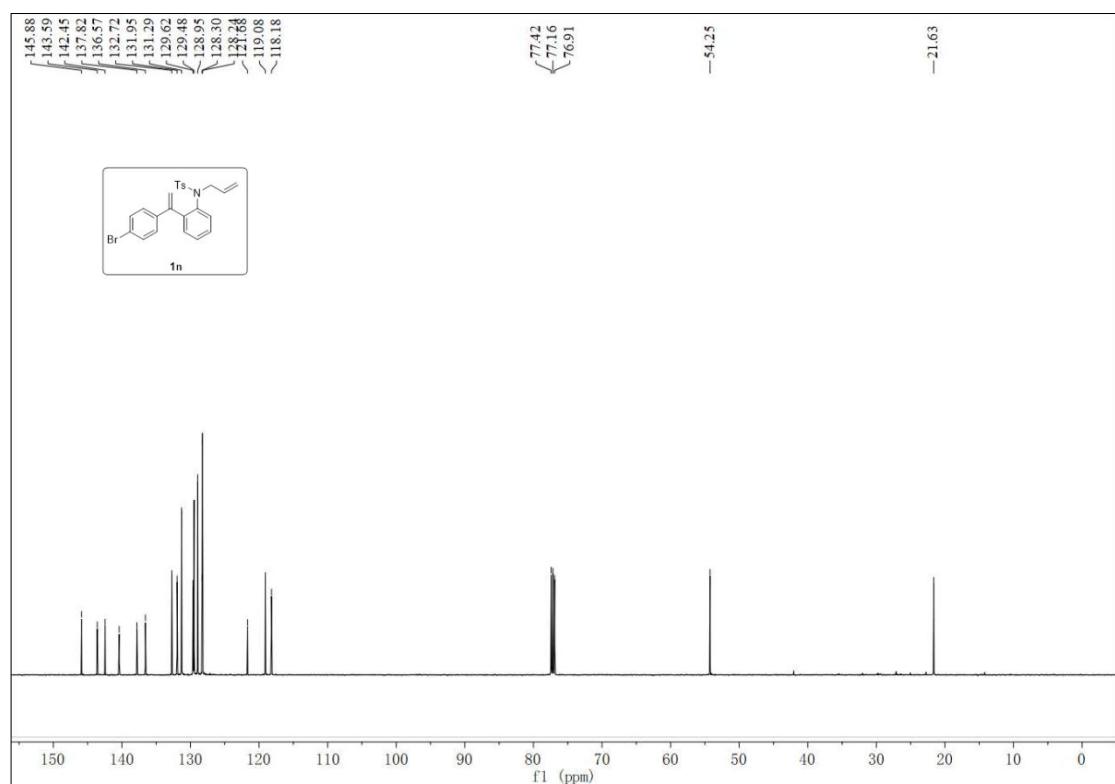
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



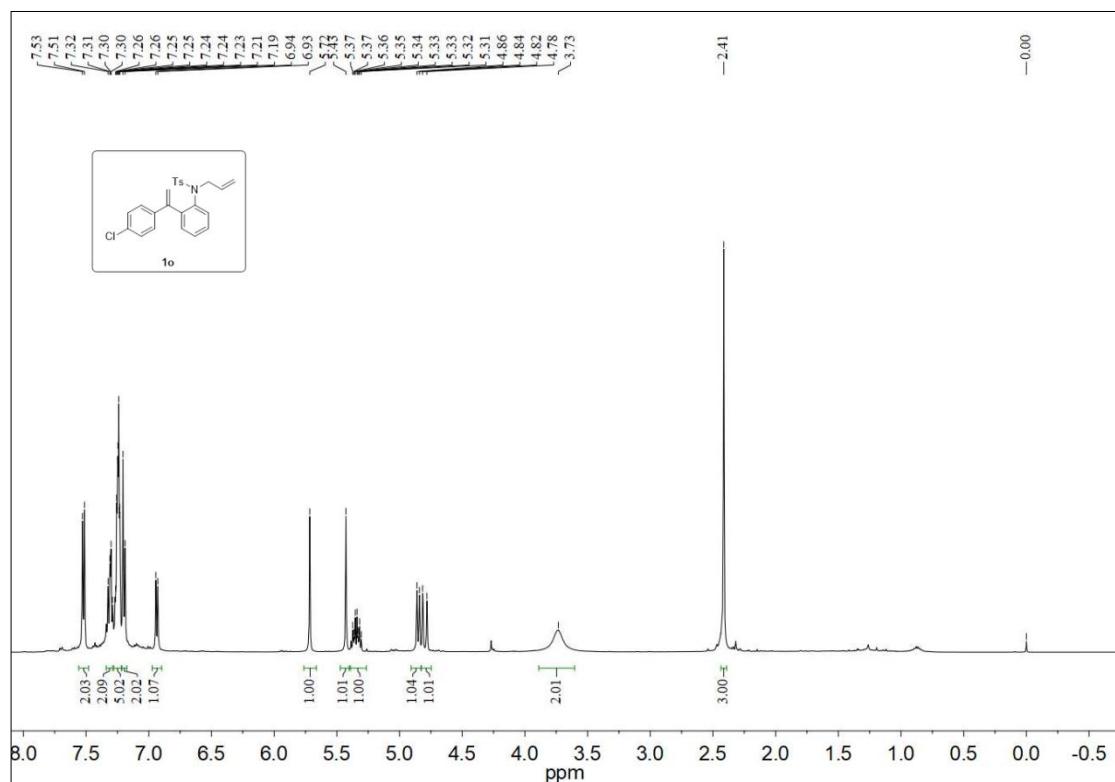
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



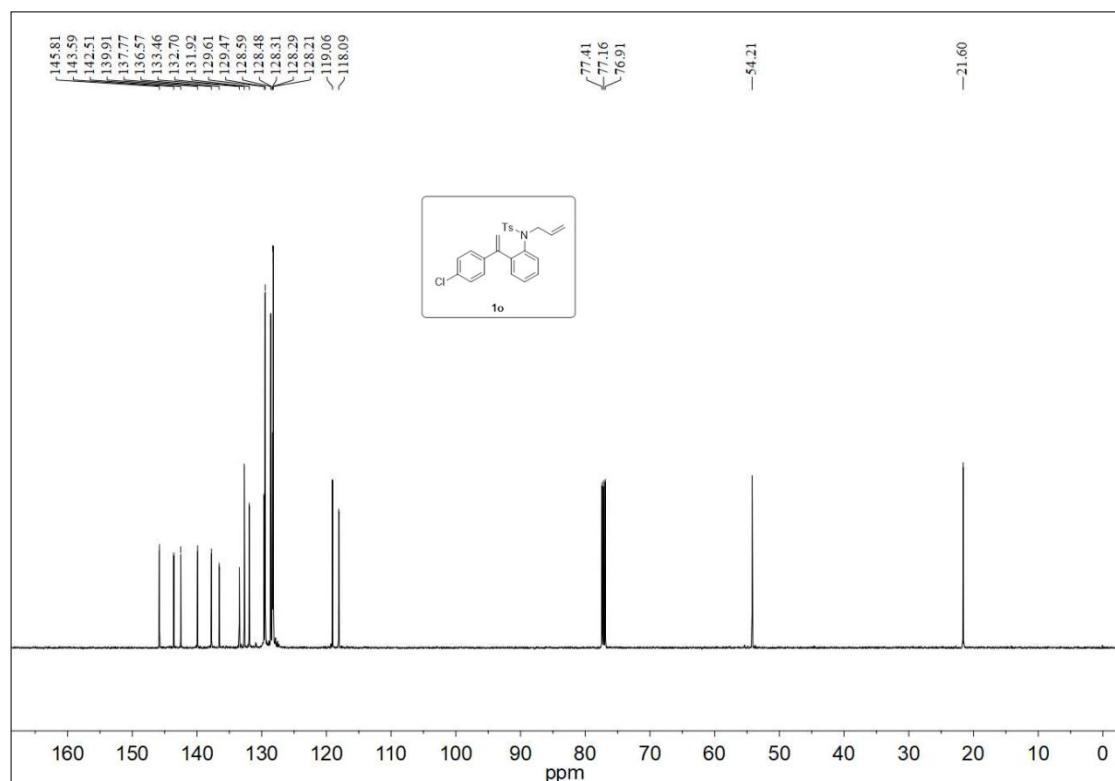
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



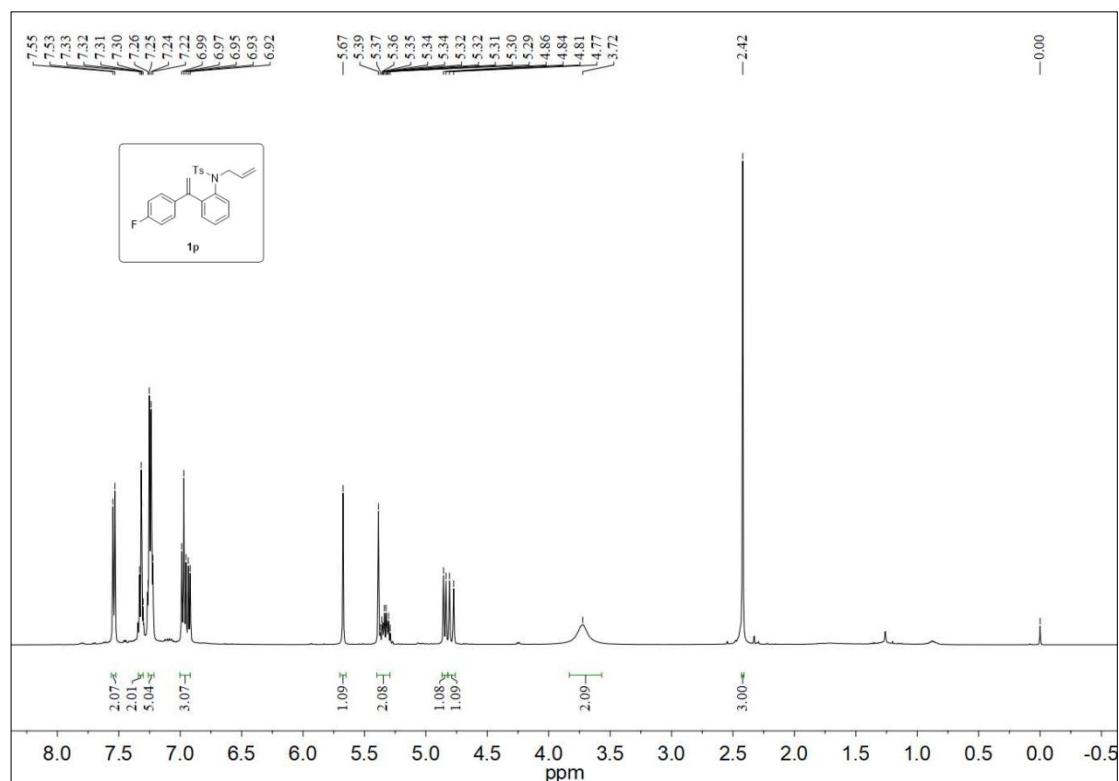
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



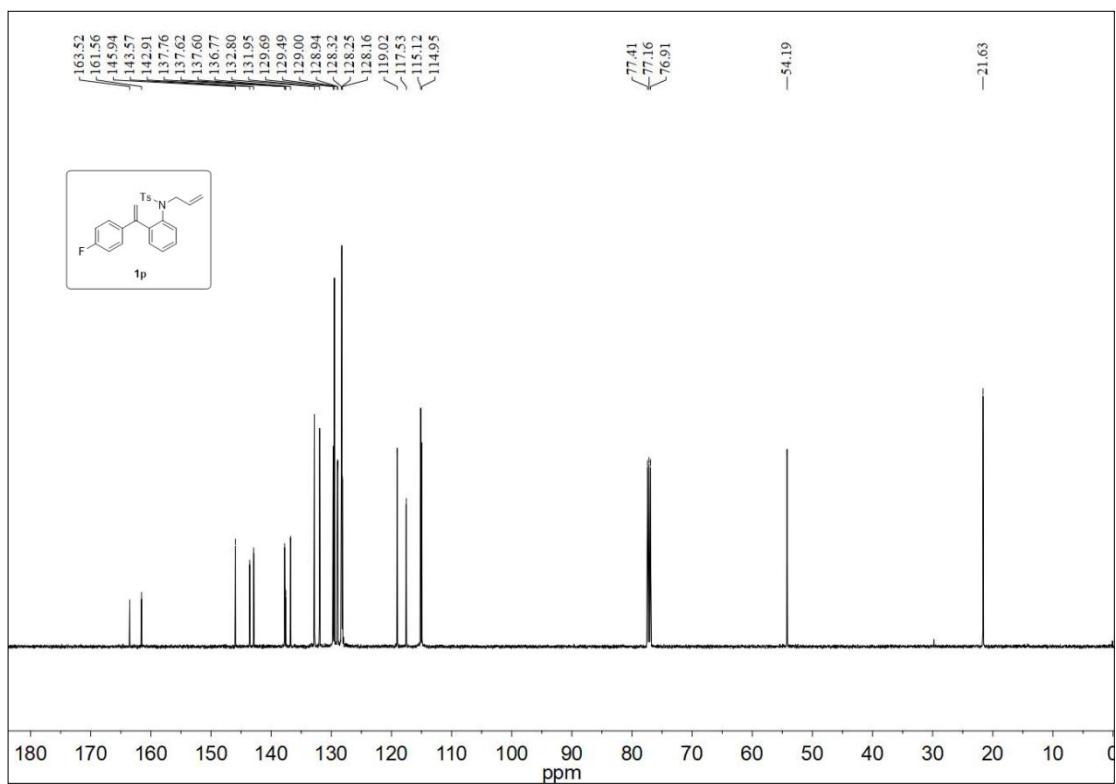
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



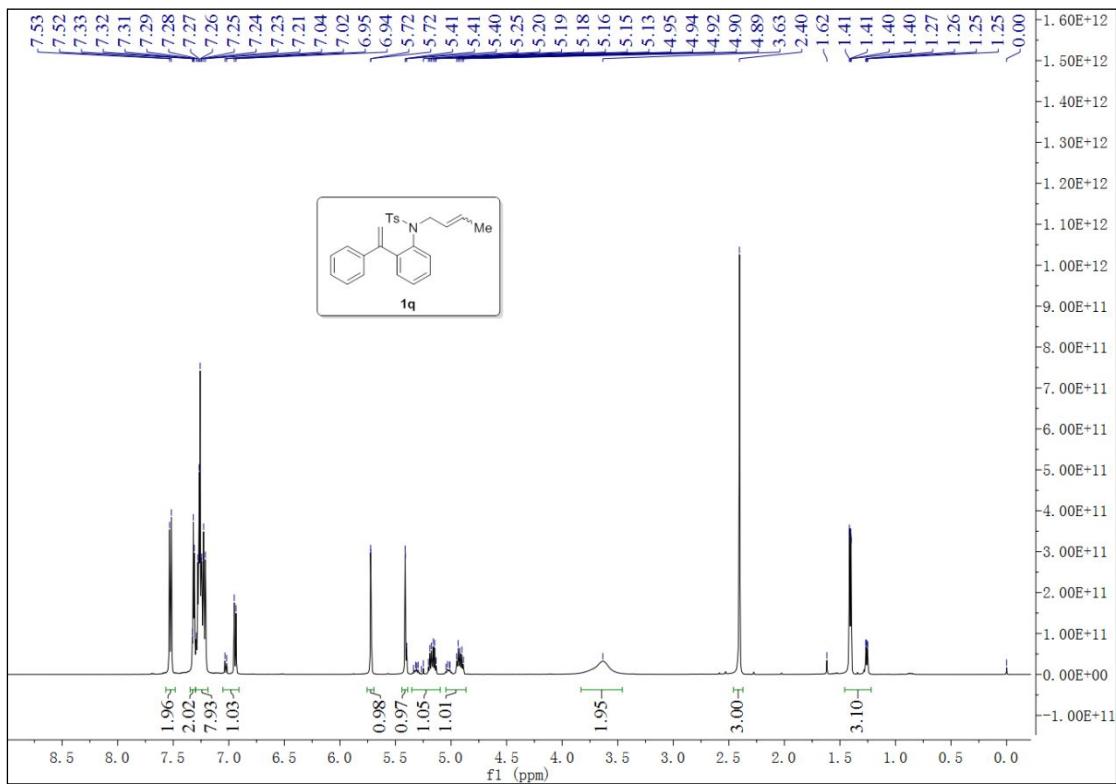
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



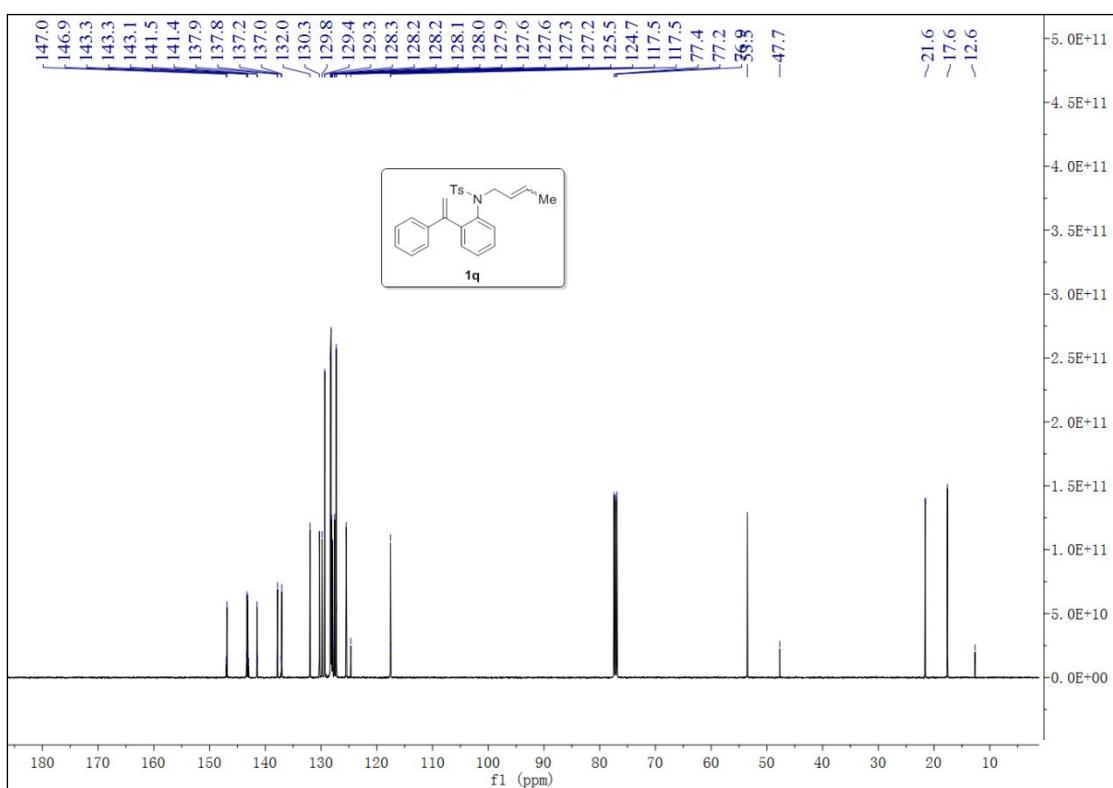
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



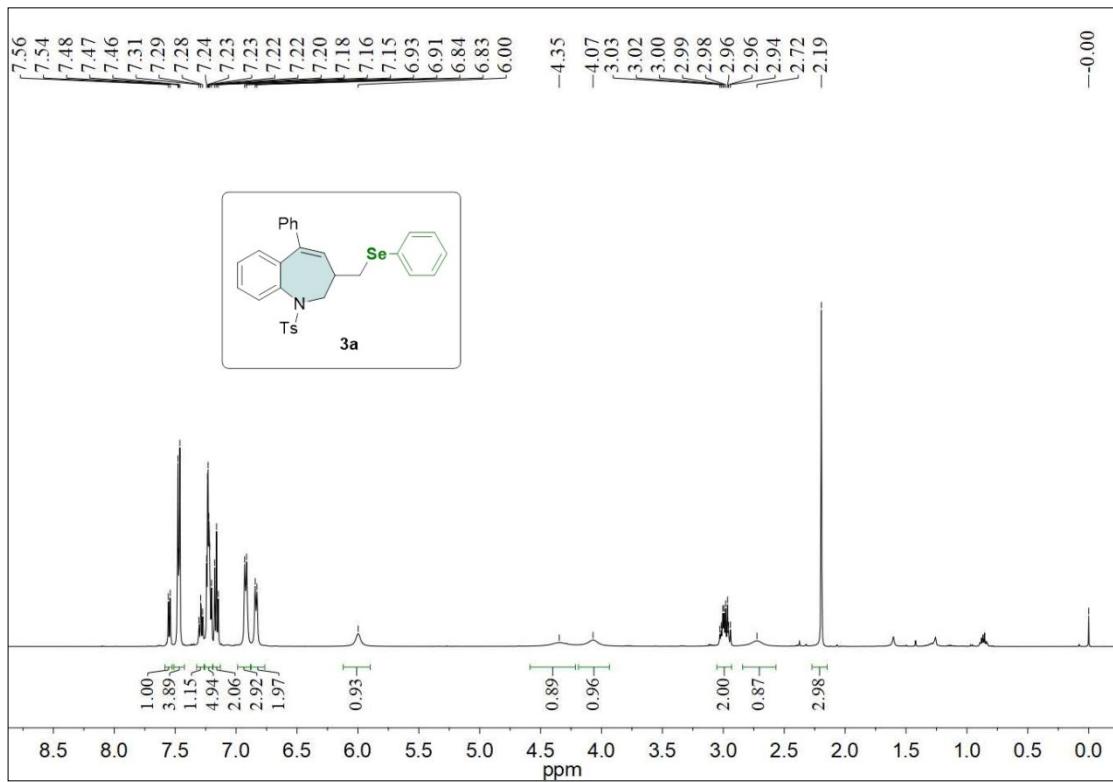
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



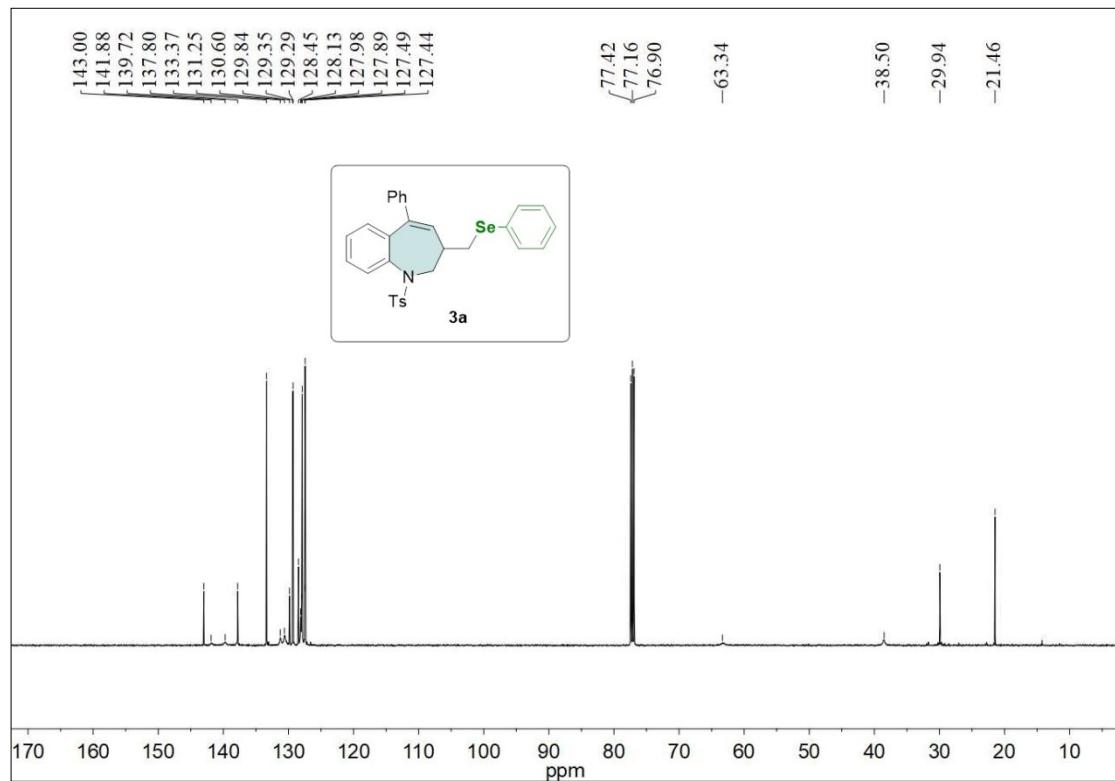
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



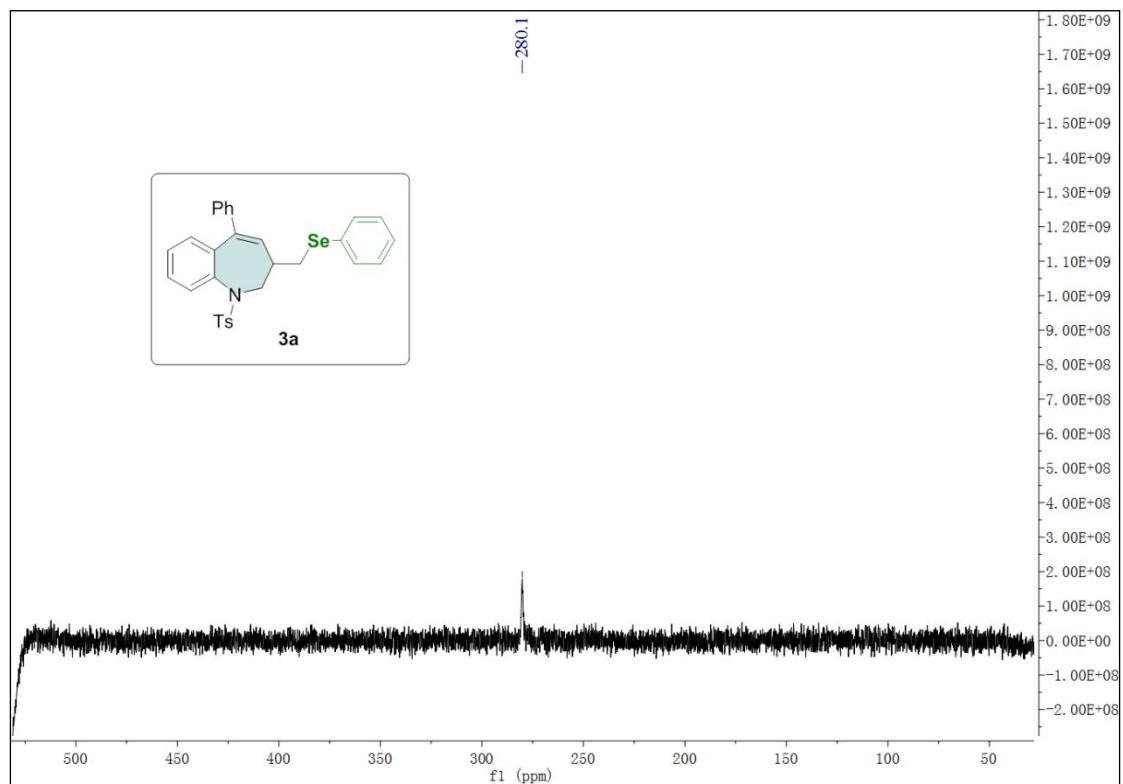
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



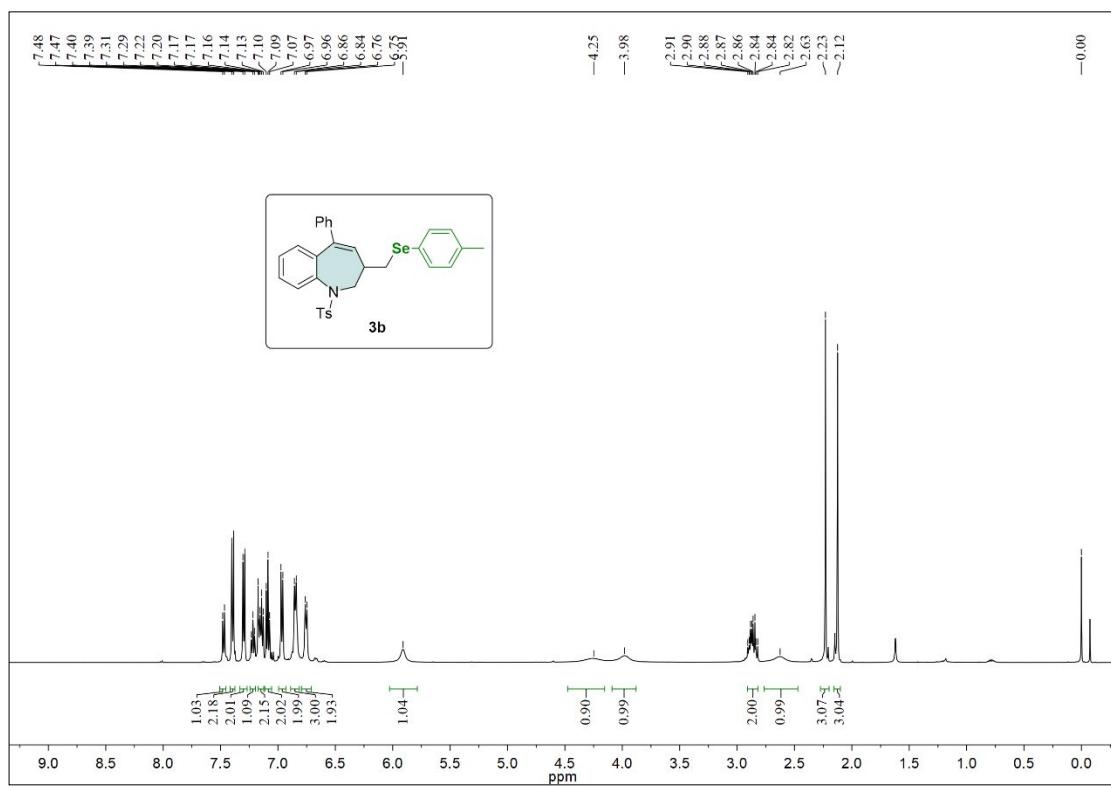
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



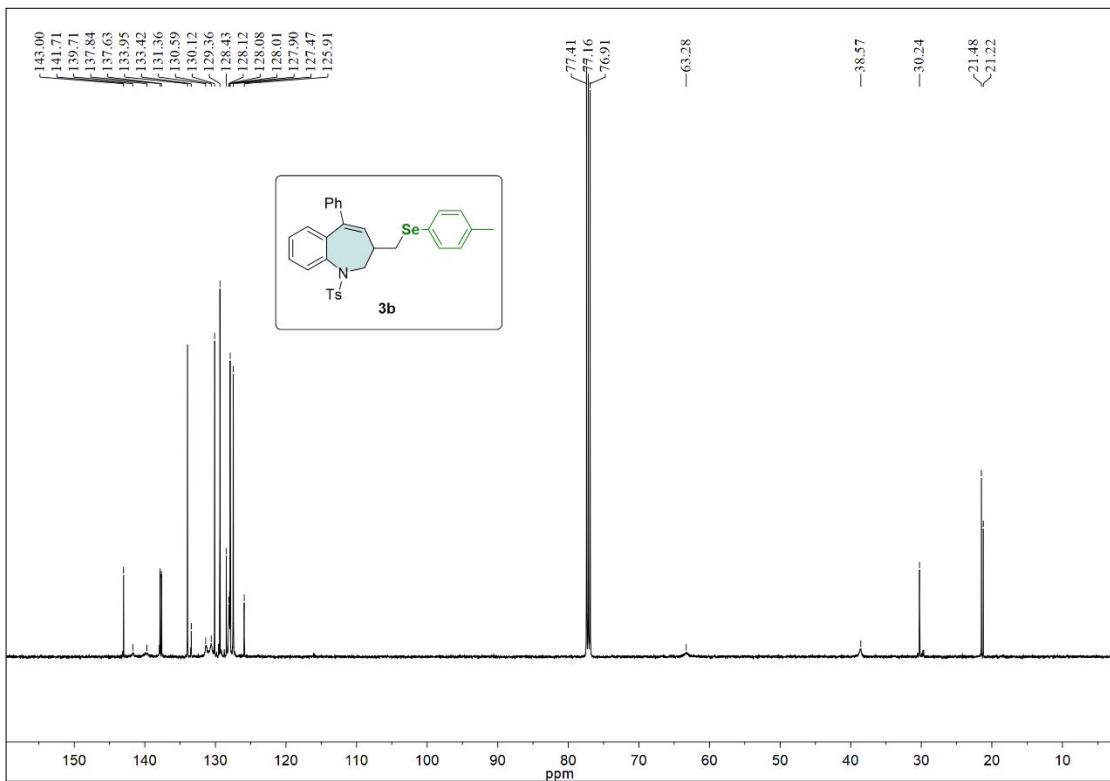
<sup>77</sup>Se NMR (76 MHz, Chloroform-*d*)



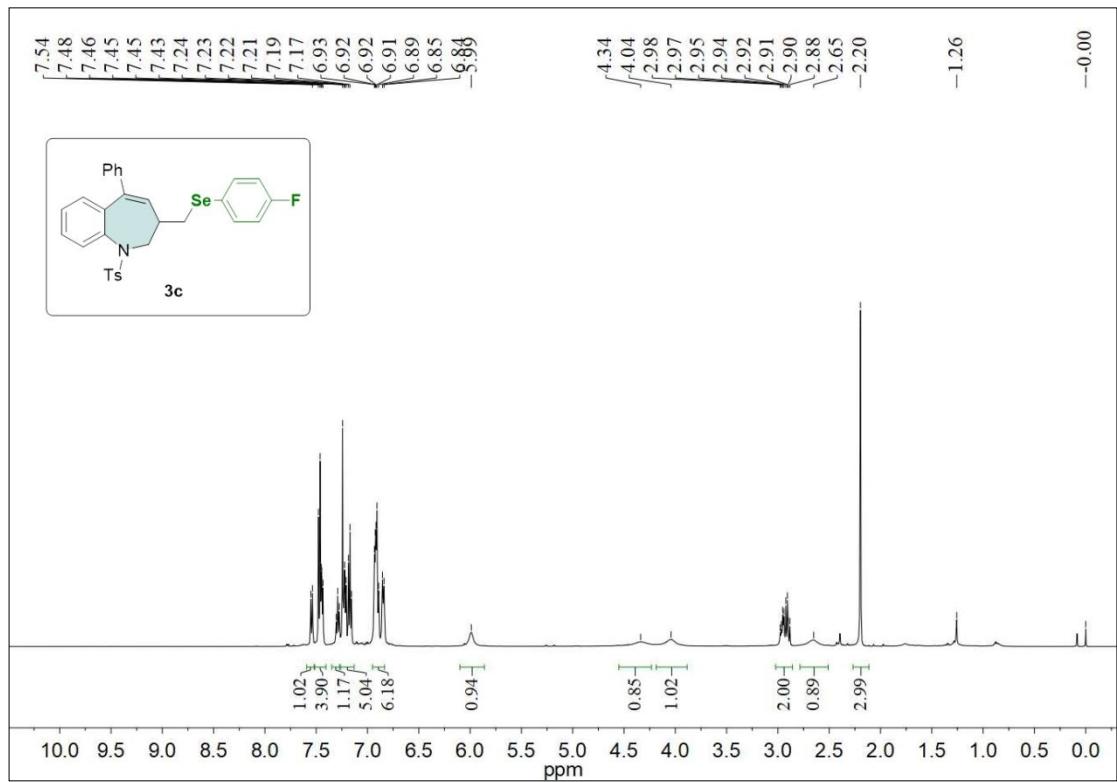
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



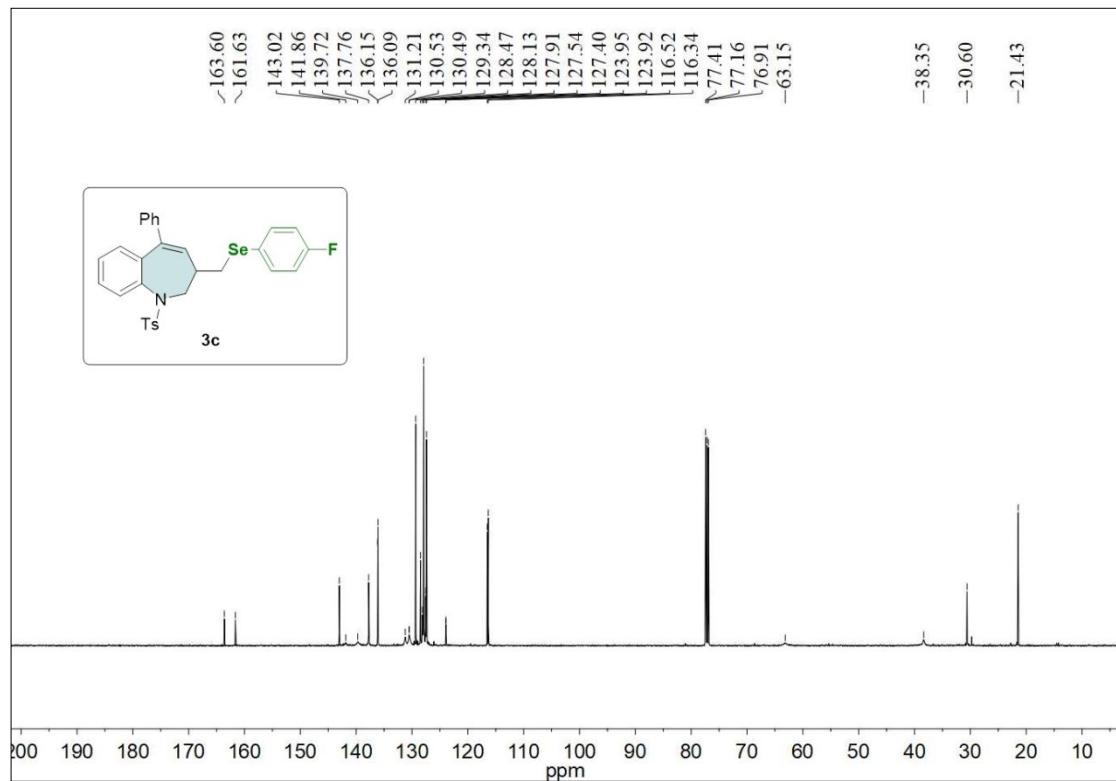
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



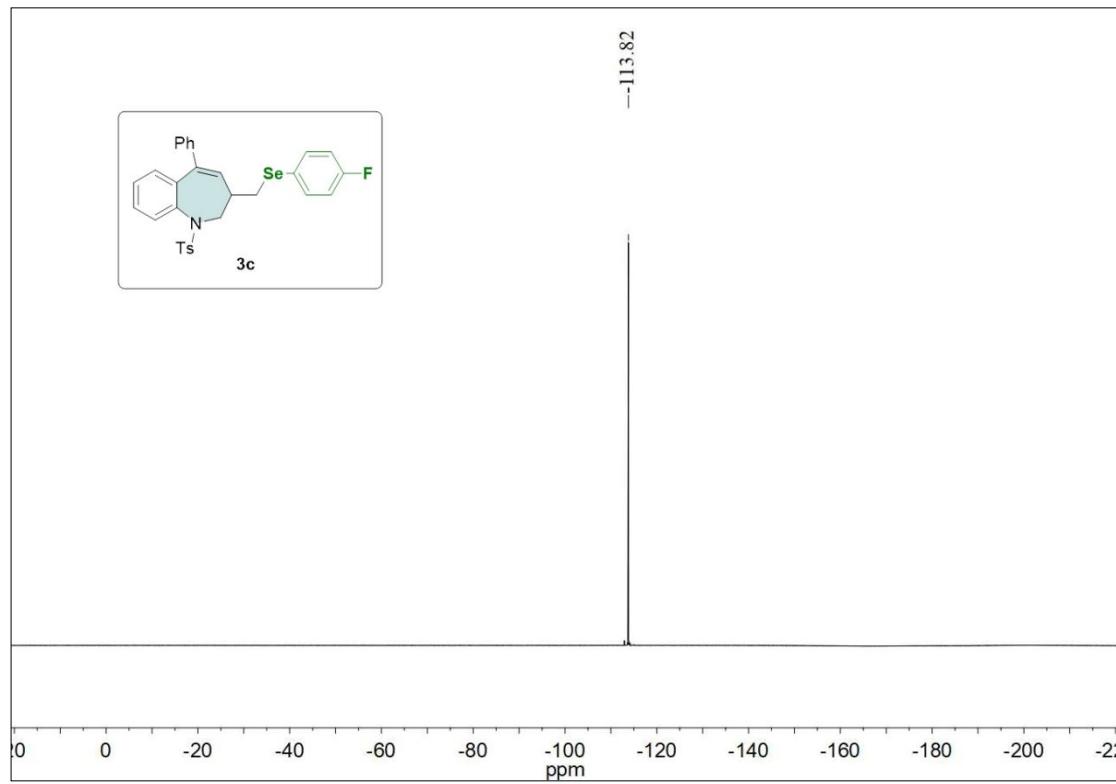
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



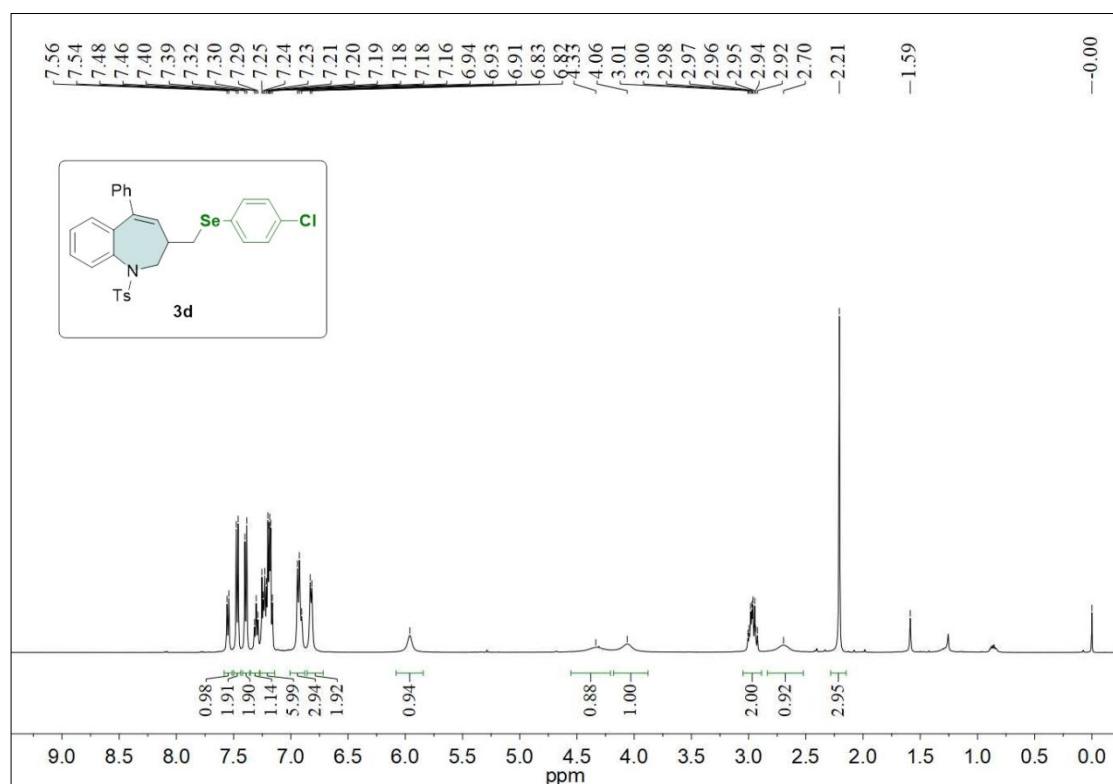
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



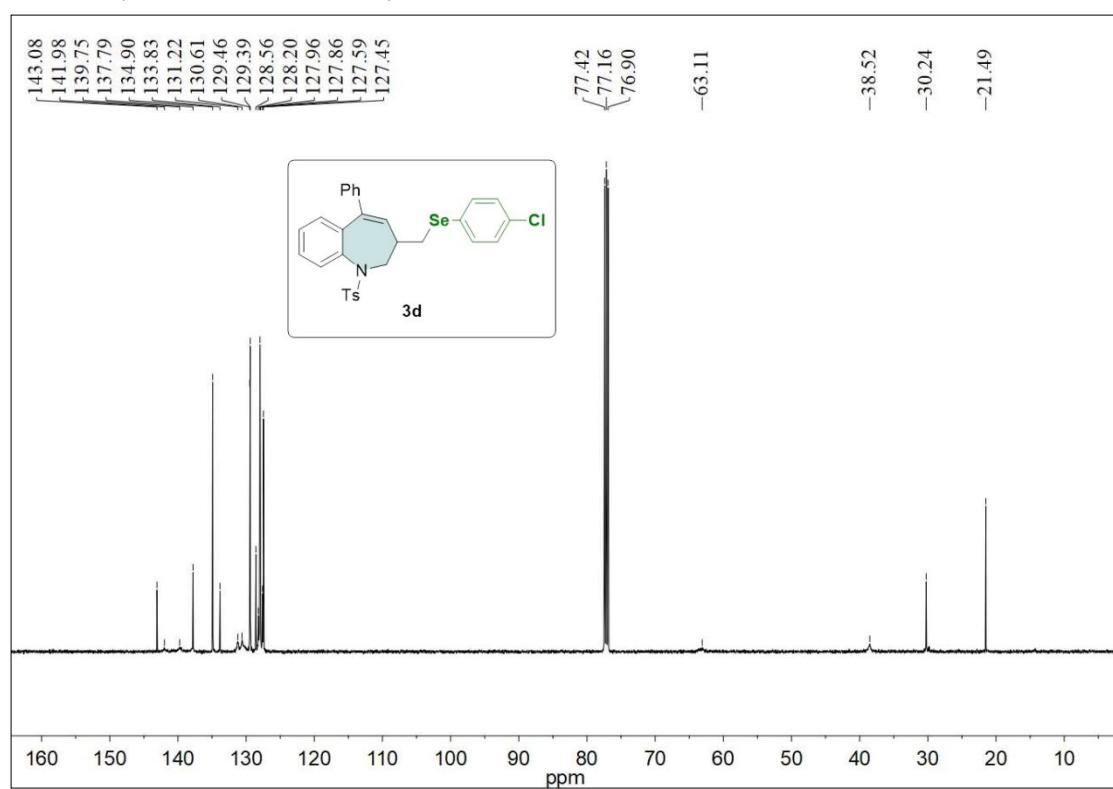
<sup>19</sup>F NMR (471 MHz, Chloroform-*d*)



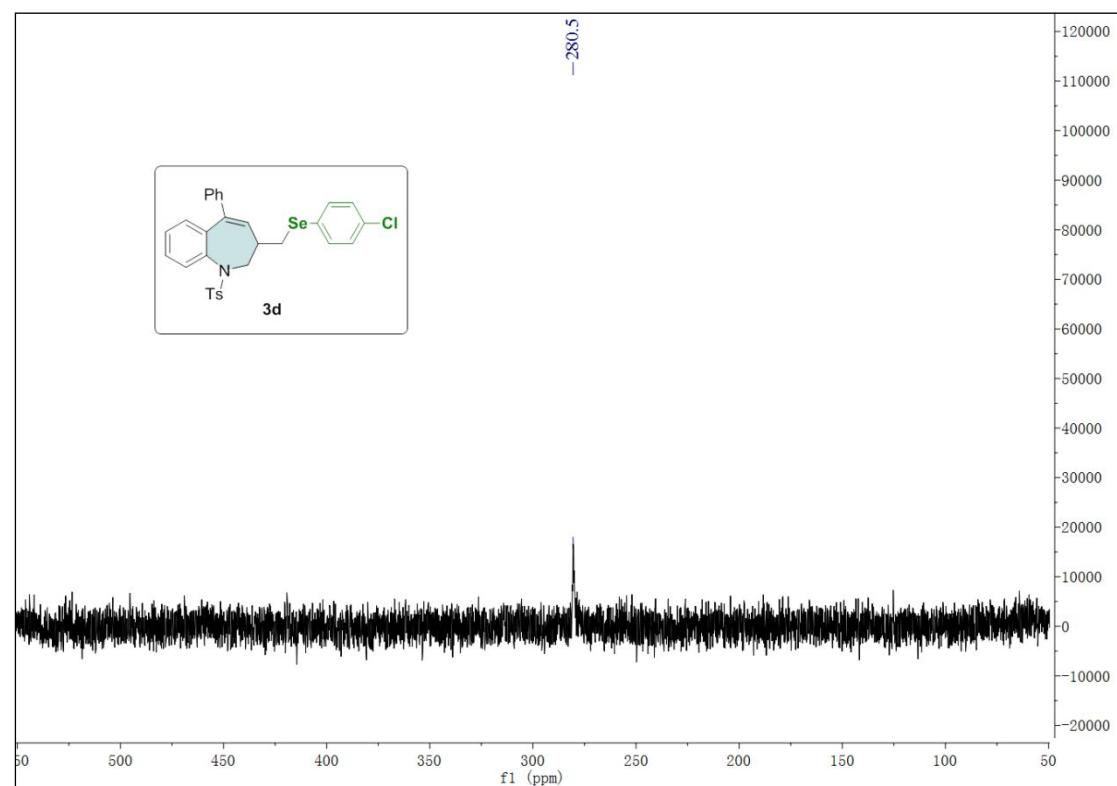
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



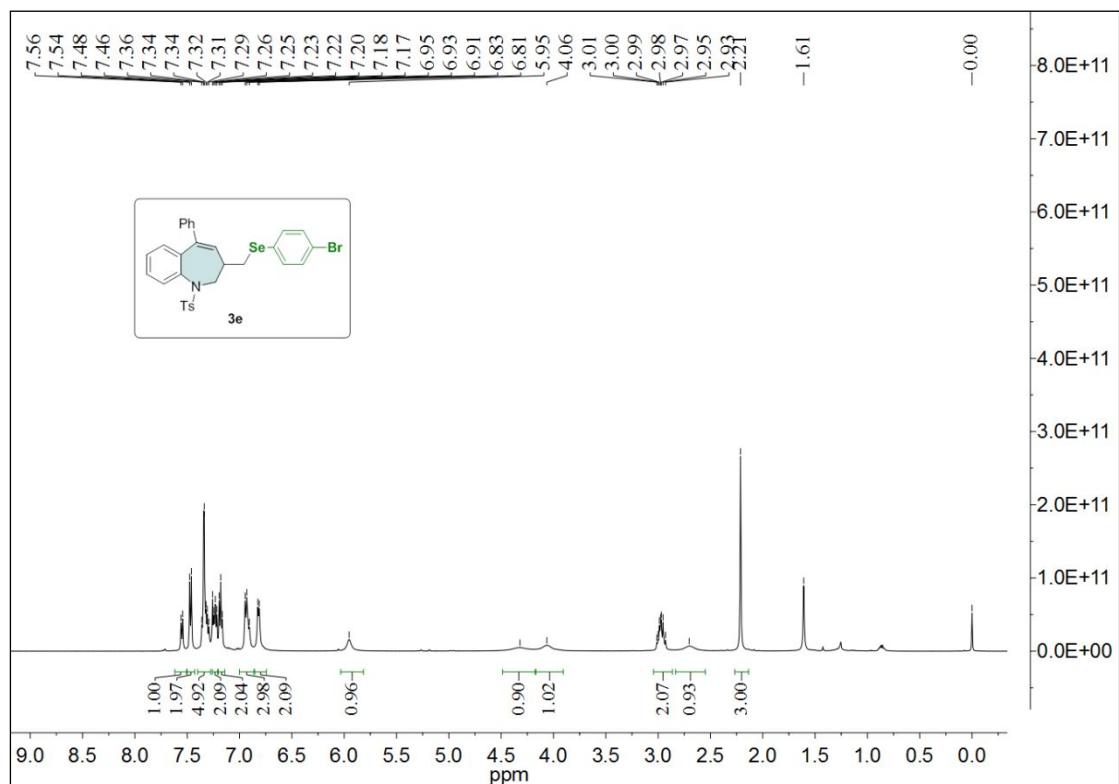
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



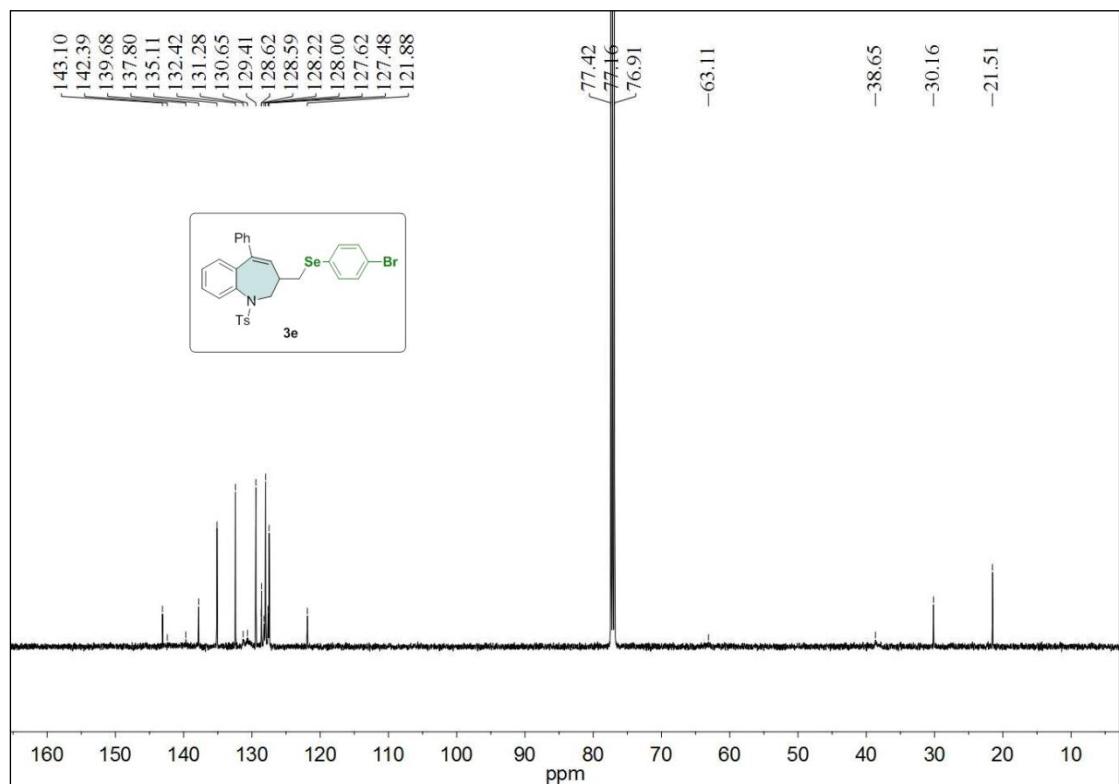
<sup>77</sup>Se NMR (76 MHz, Chloroform-*d*)



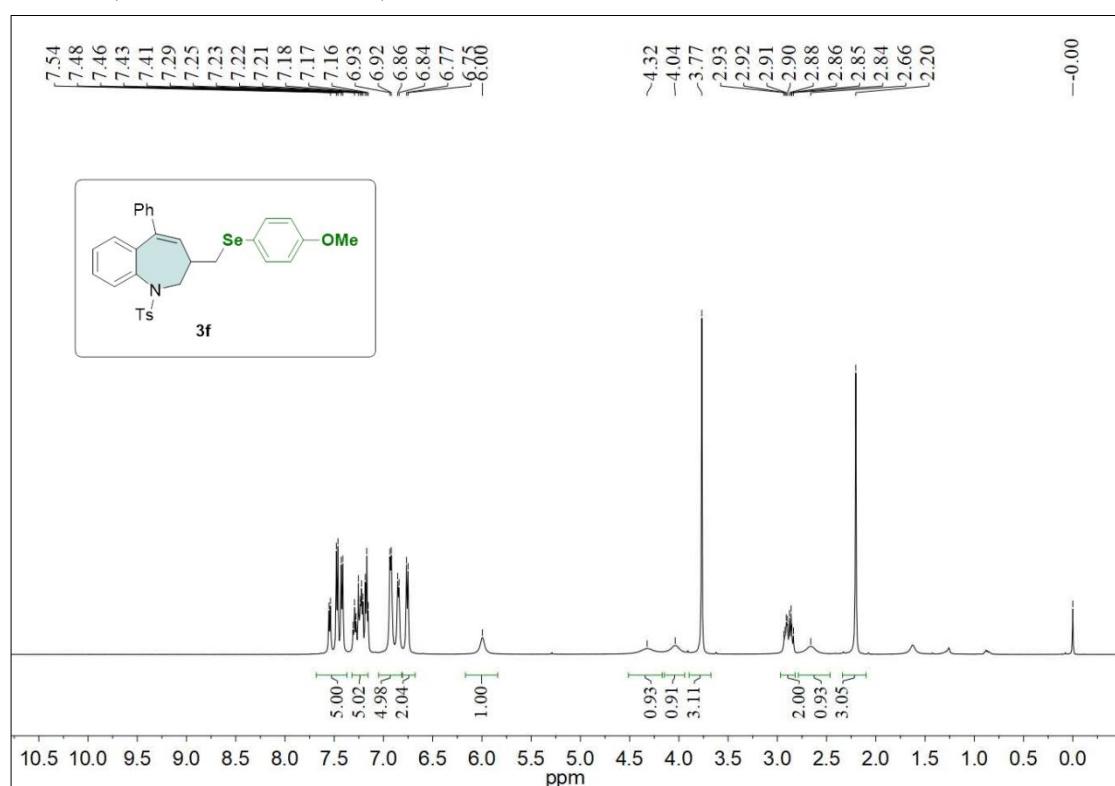
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



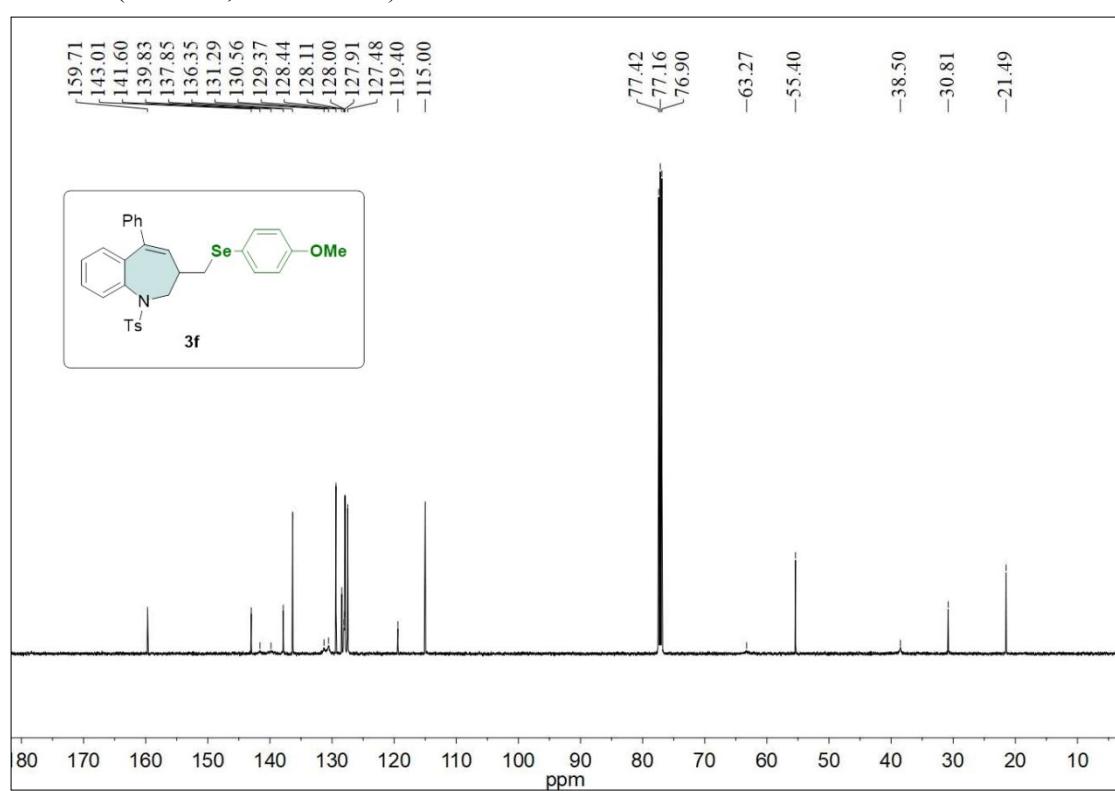
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



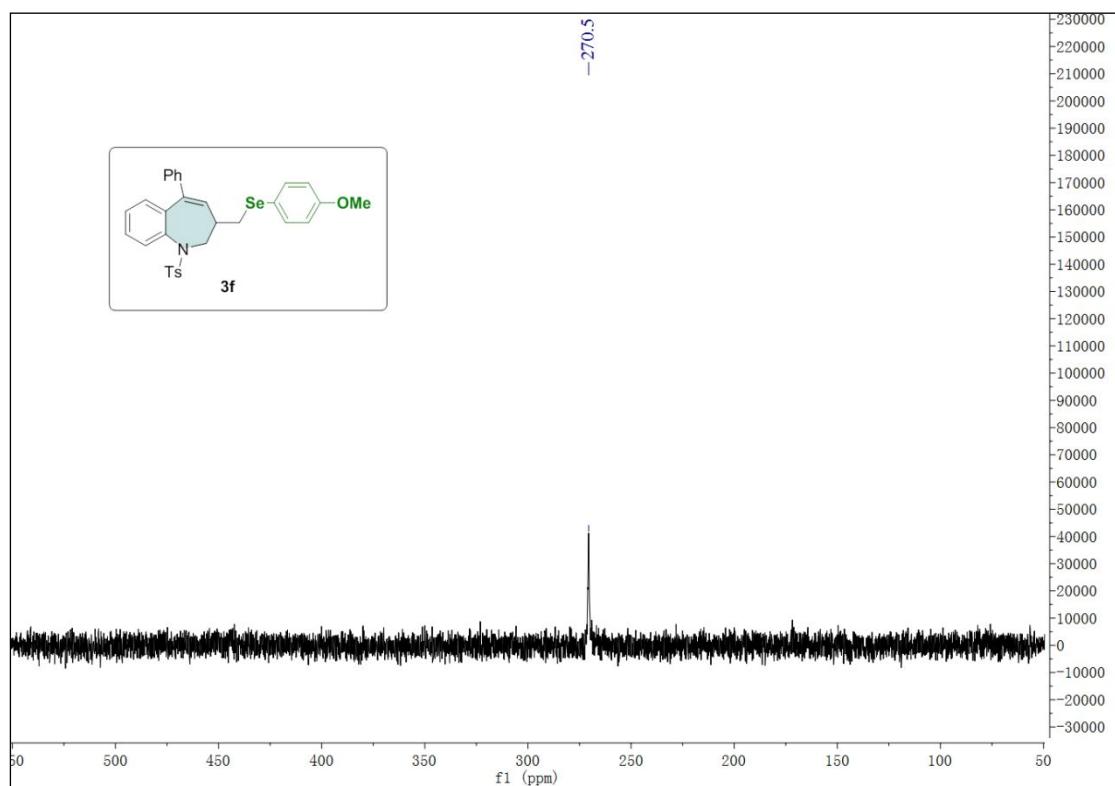
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



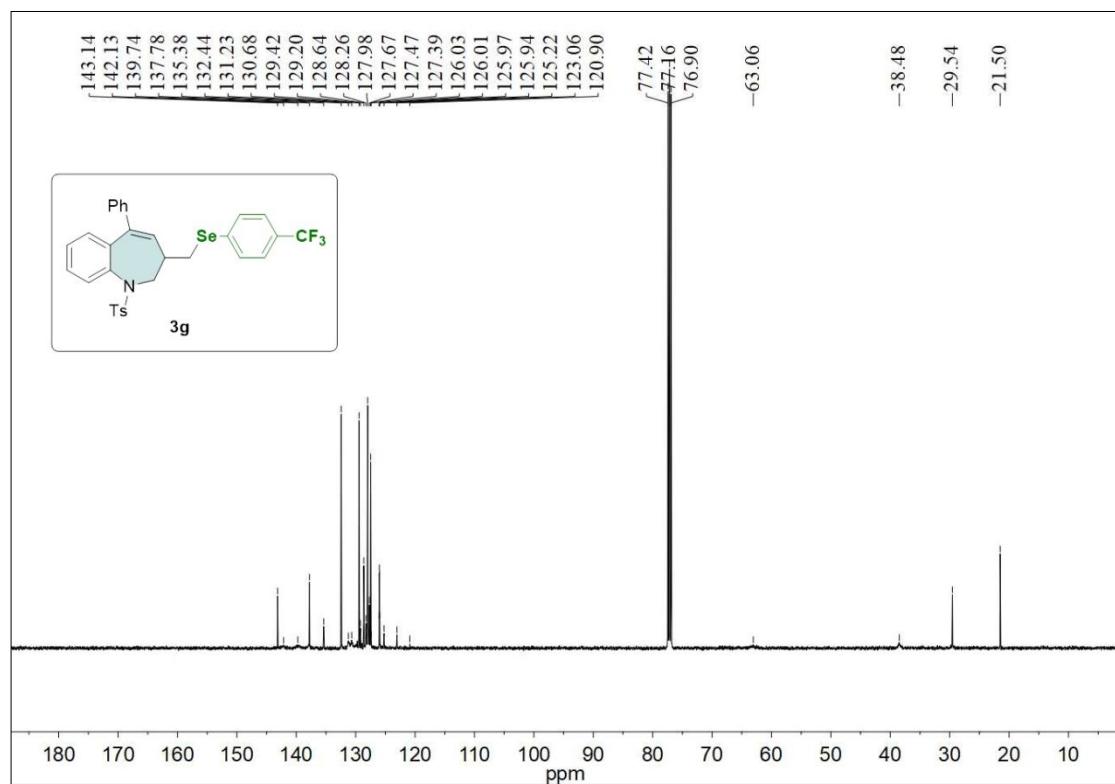
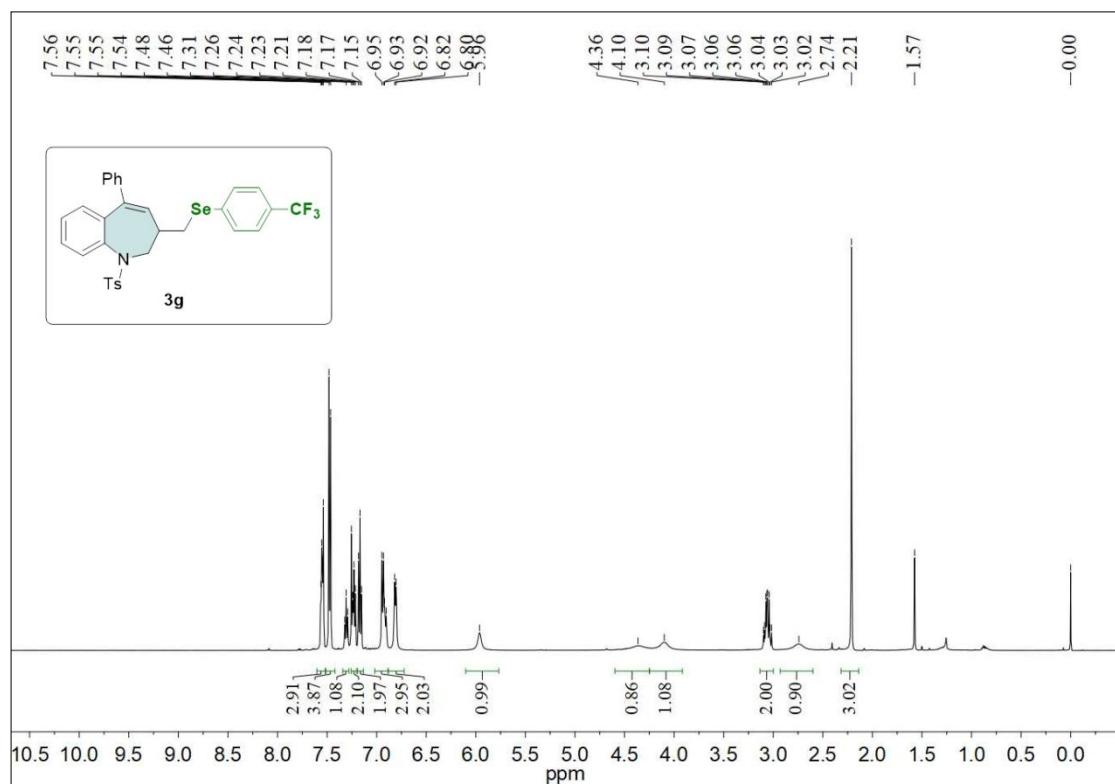
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



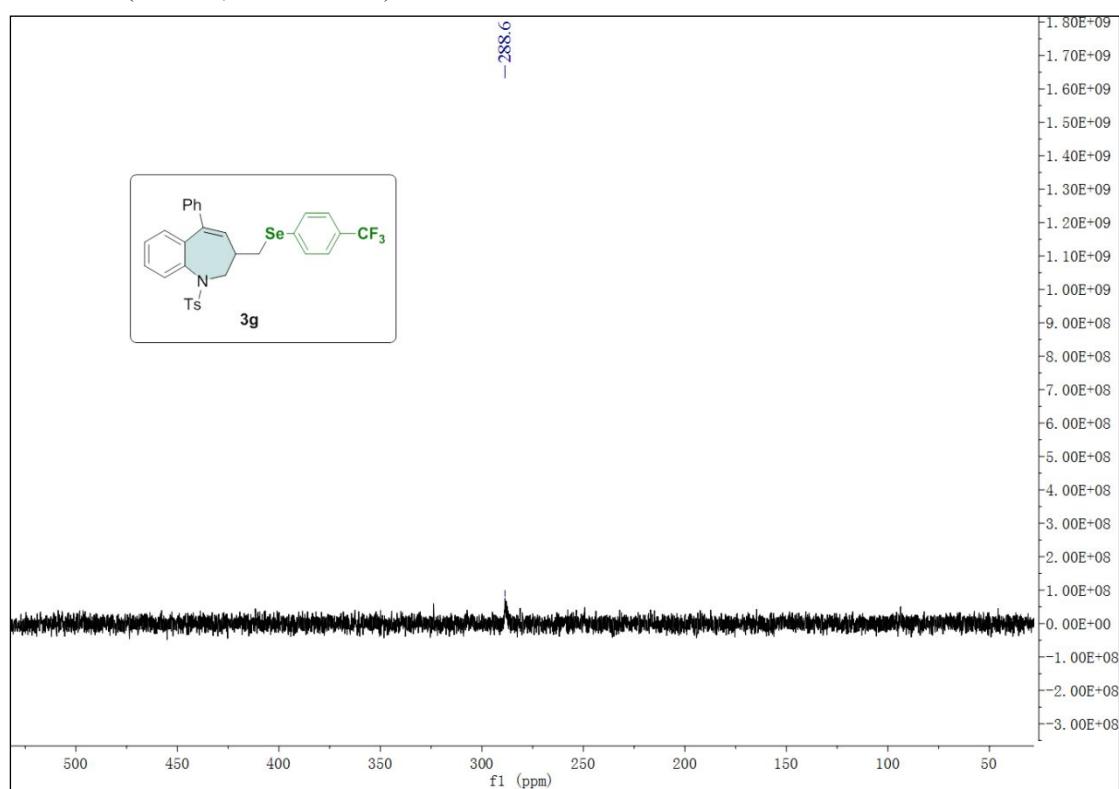
<sup>77</sup>Se NMR (76 MHz, Chloroform-*d*)



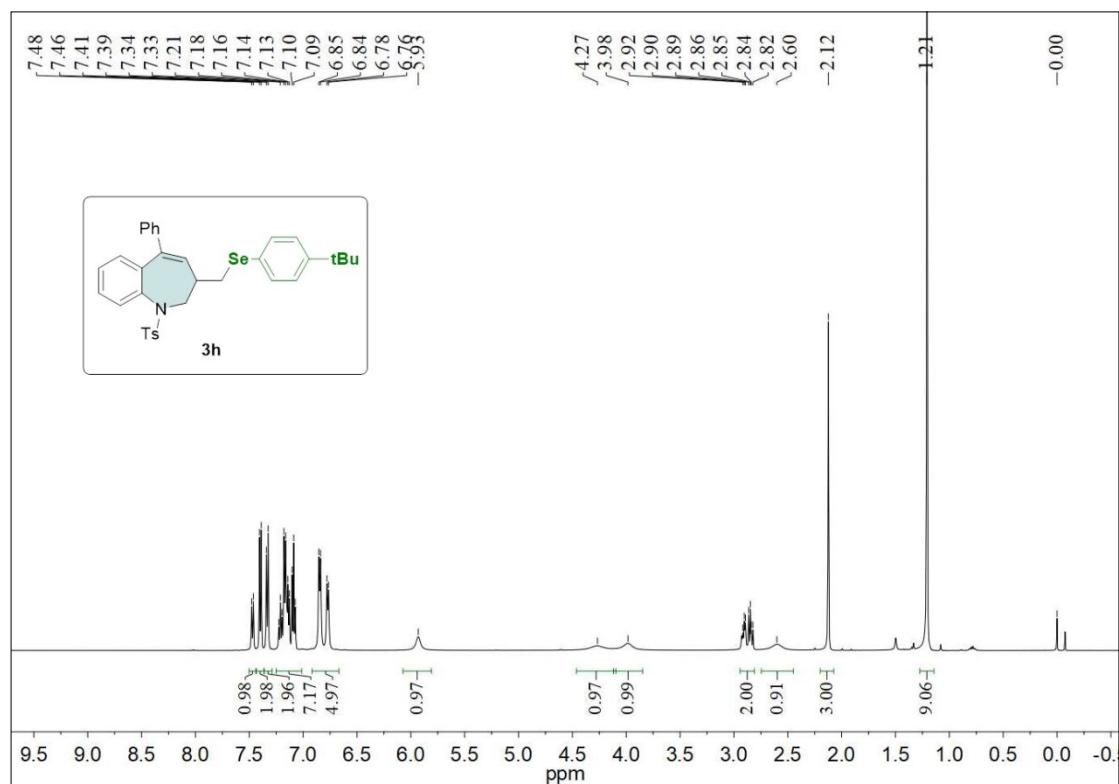
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



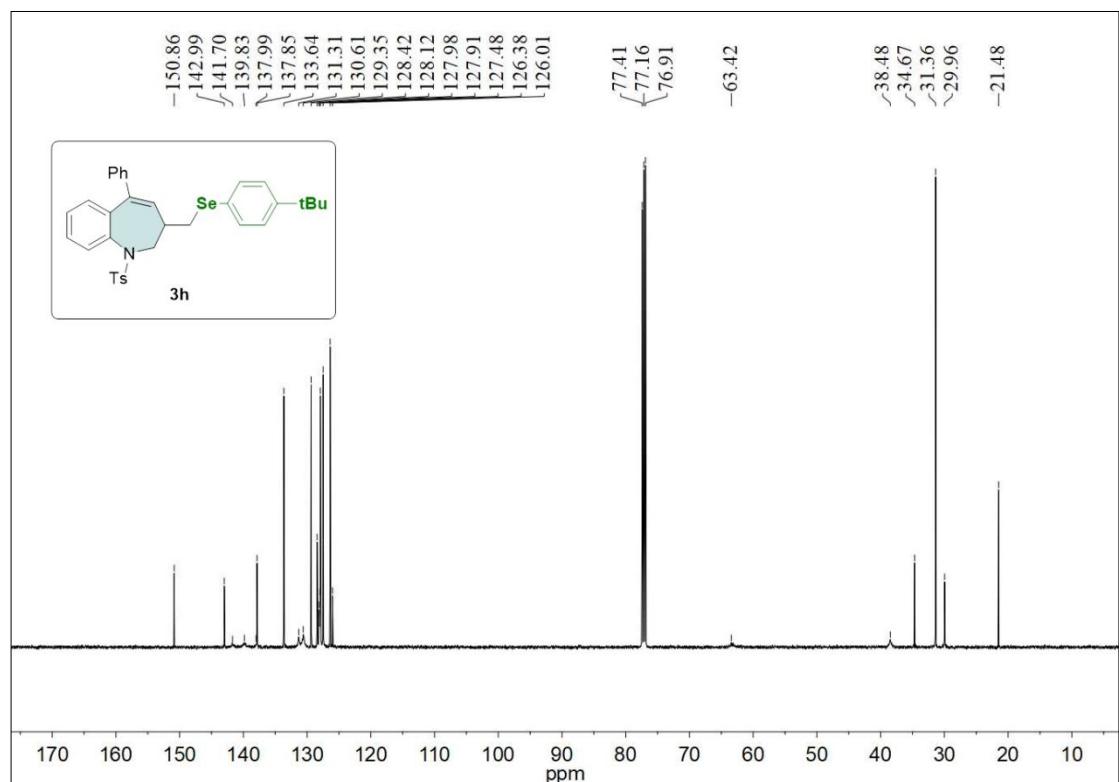
<sup>77</sup>Se NMR (76 MHz, Chloroform-*d*)



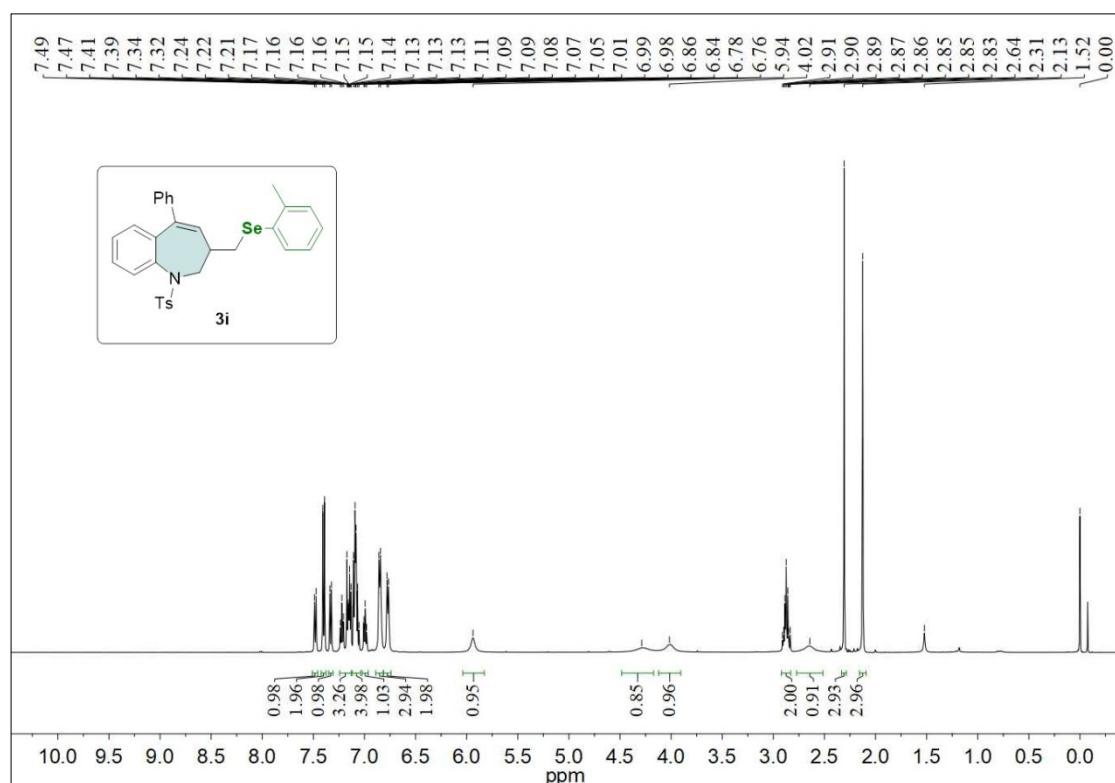
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



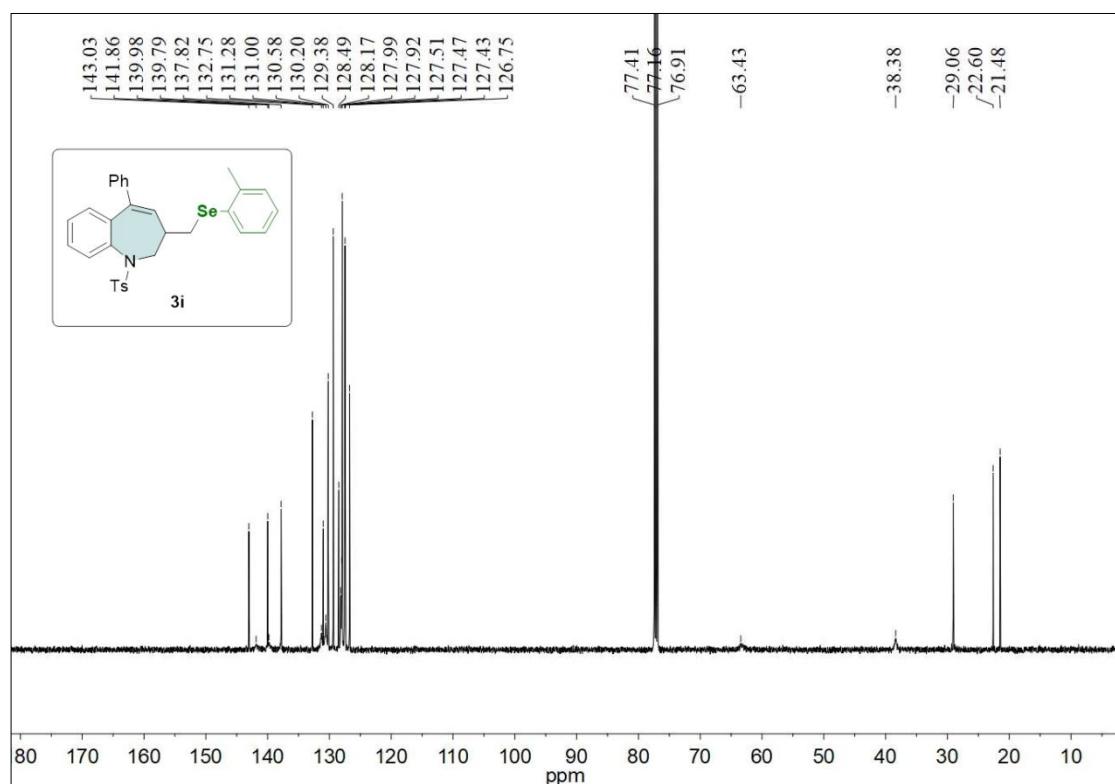
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



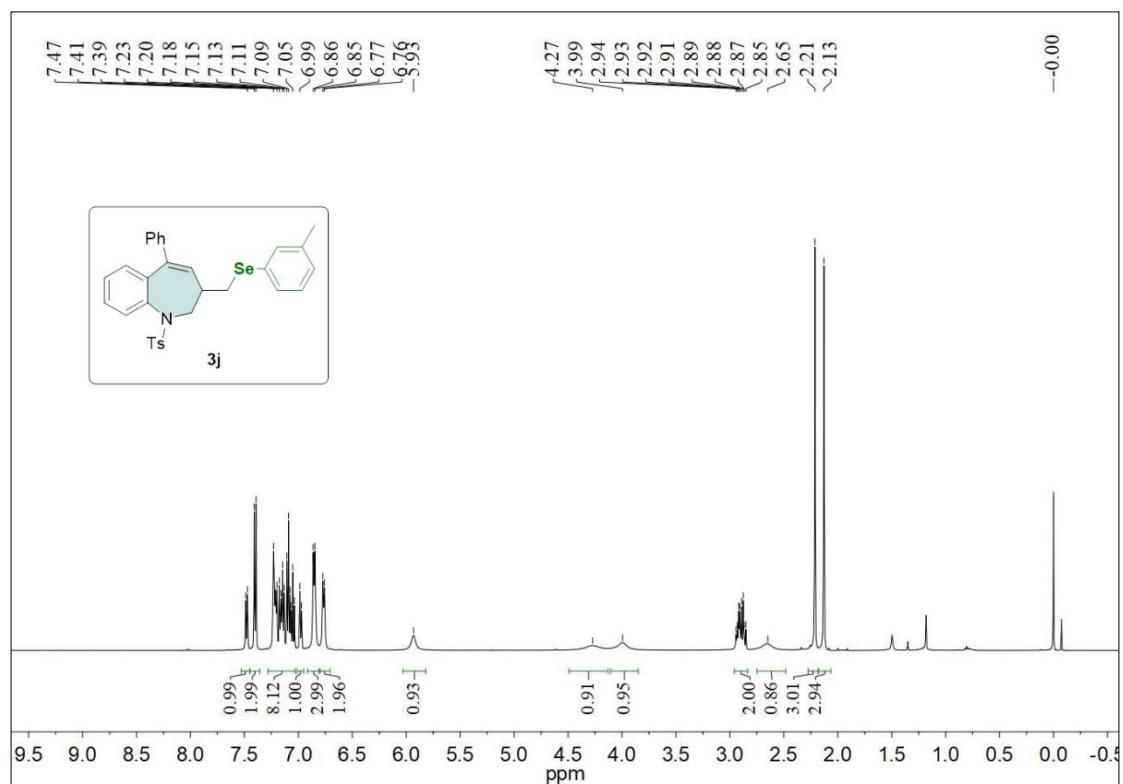
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



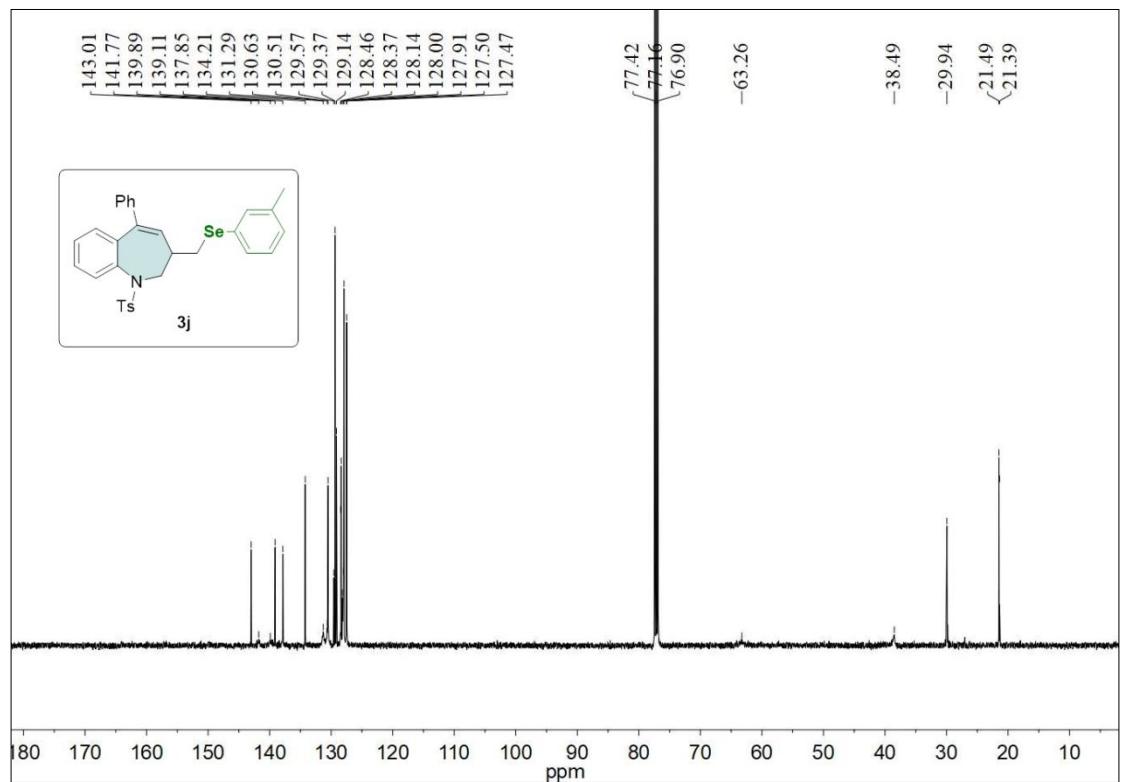
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



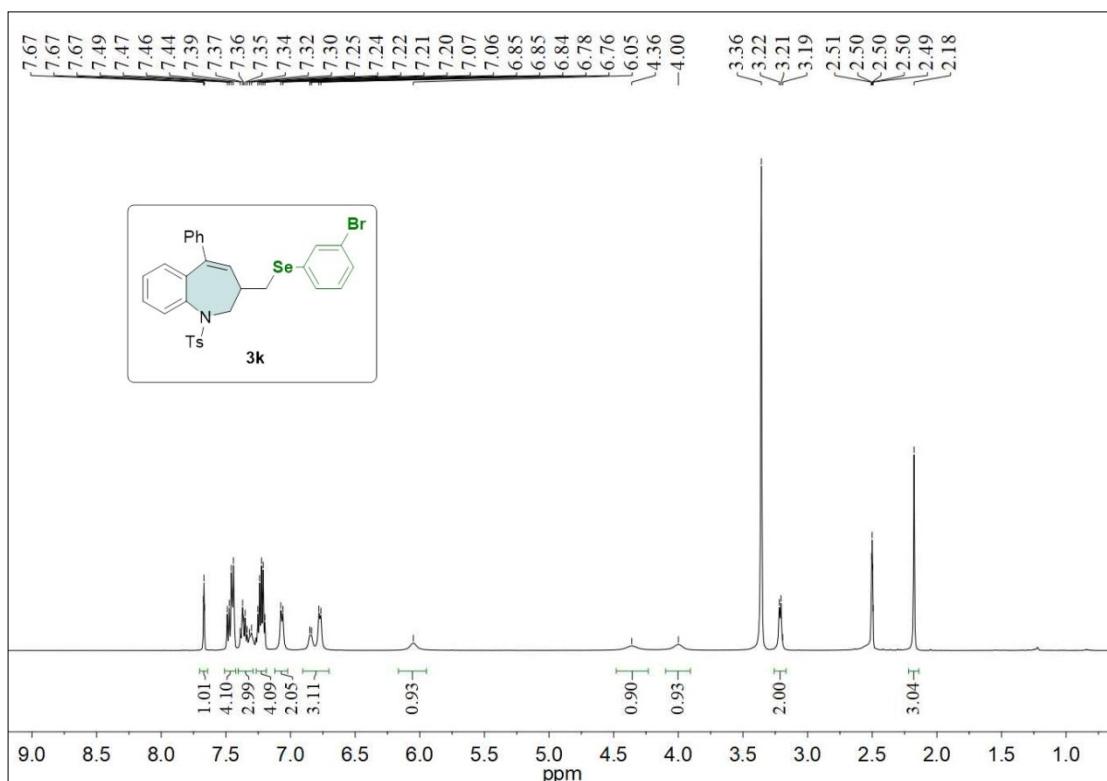
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



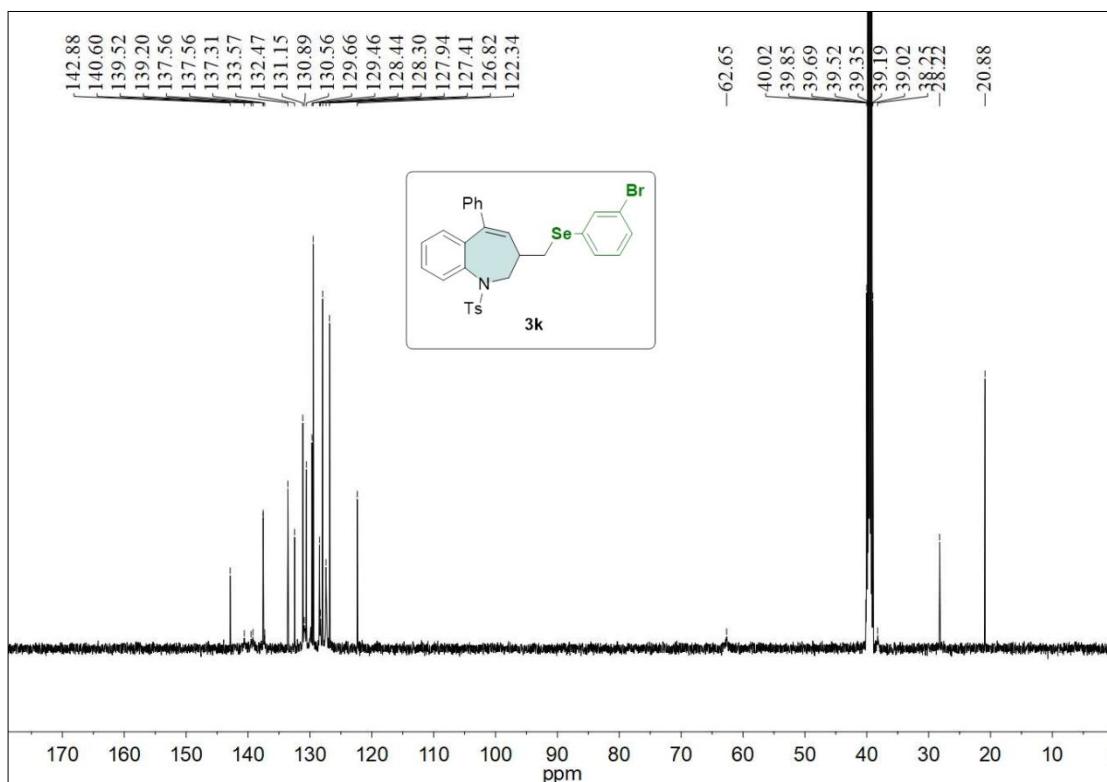
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



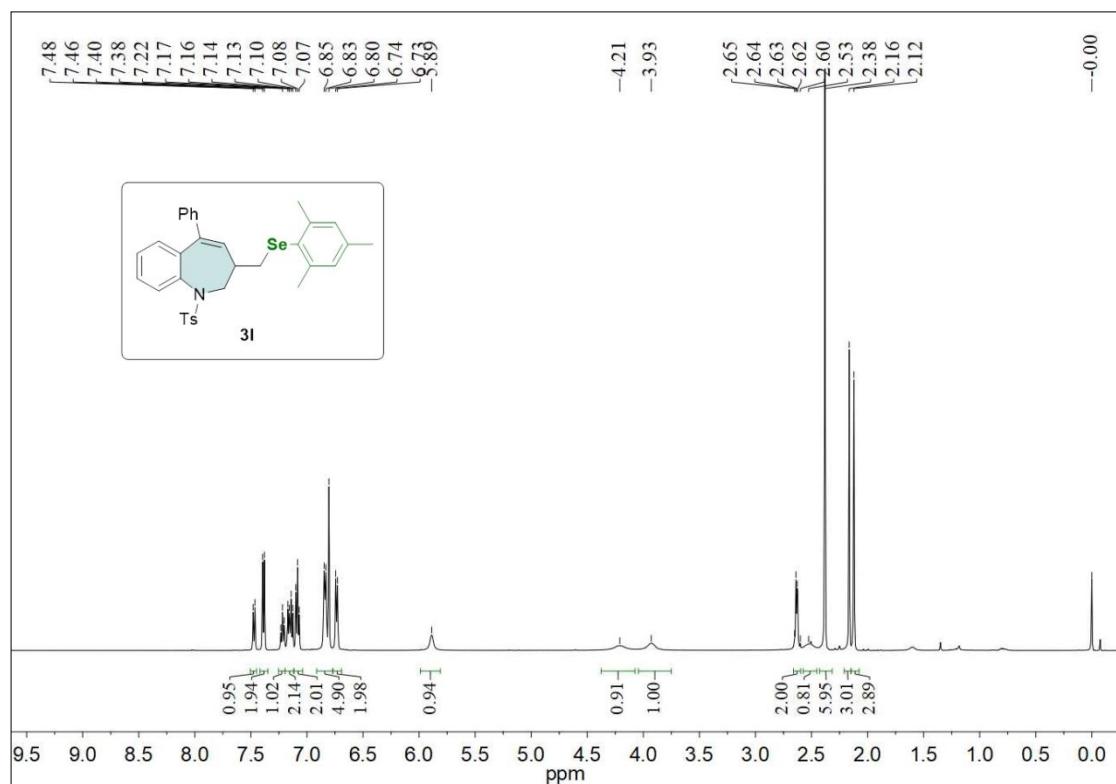
<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)



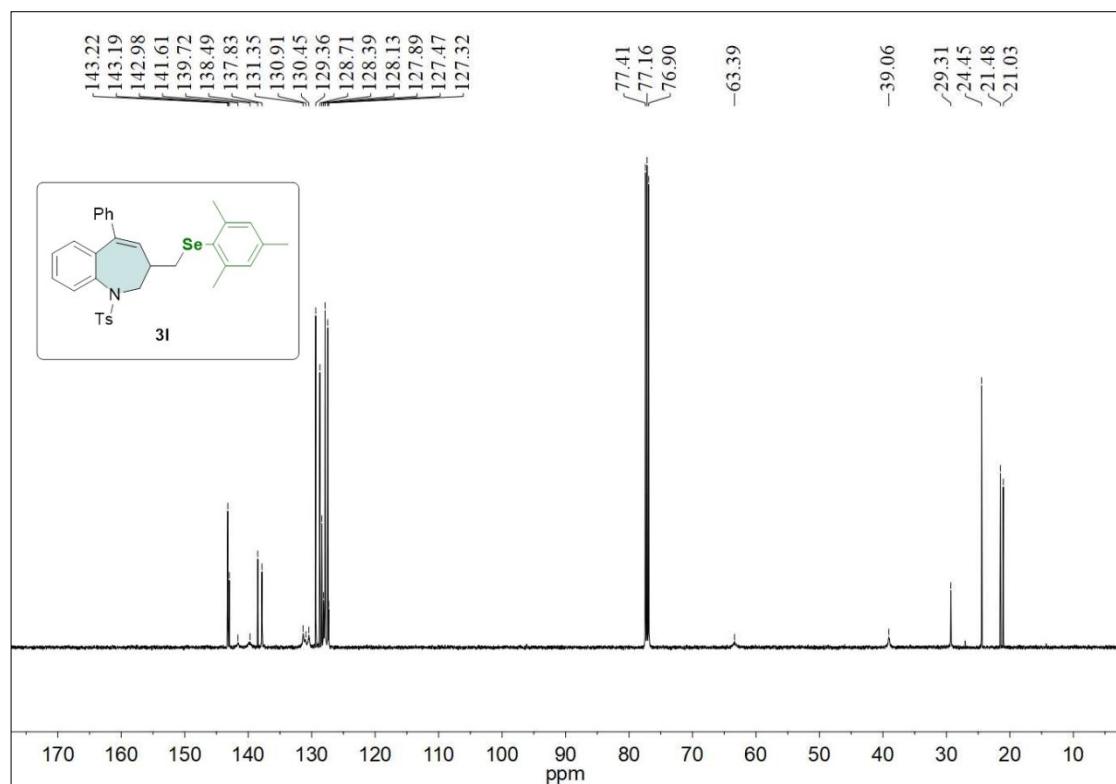
<sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)



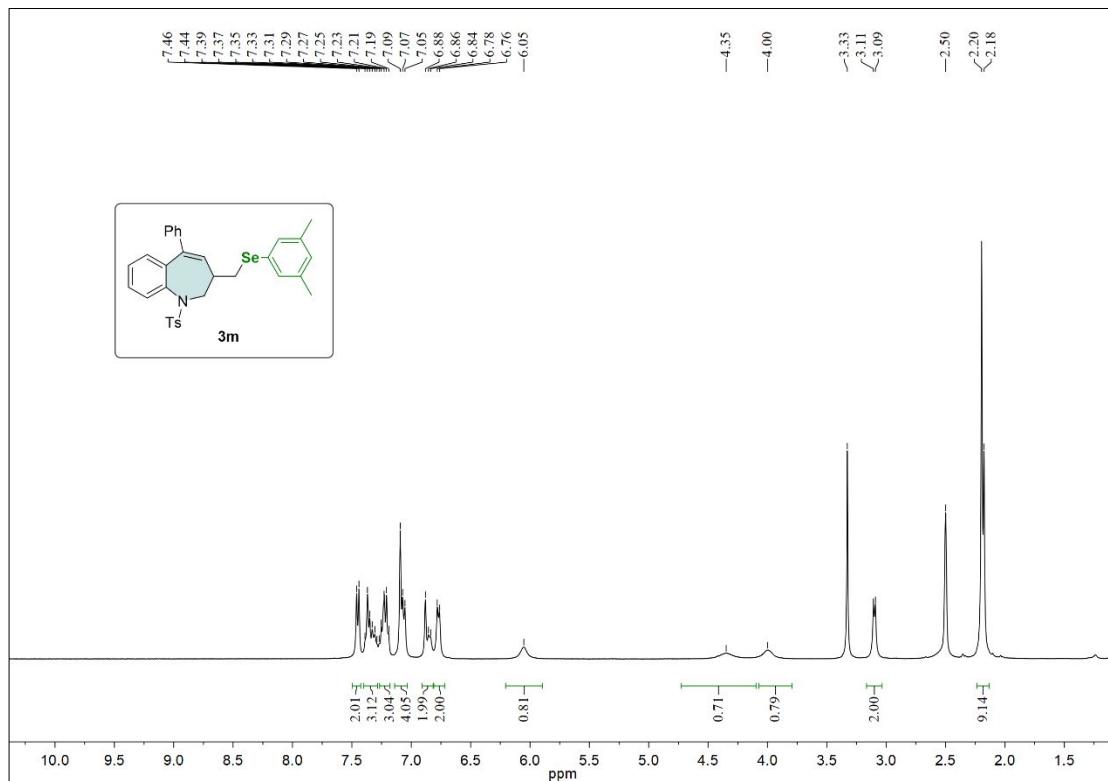
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



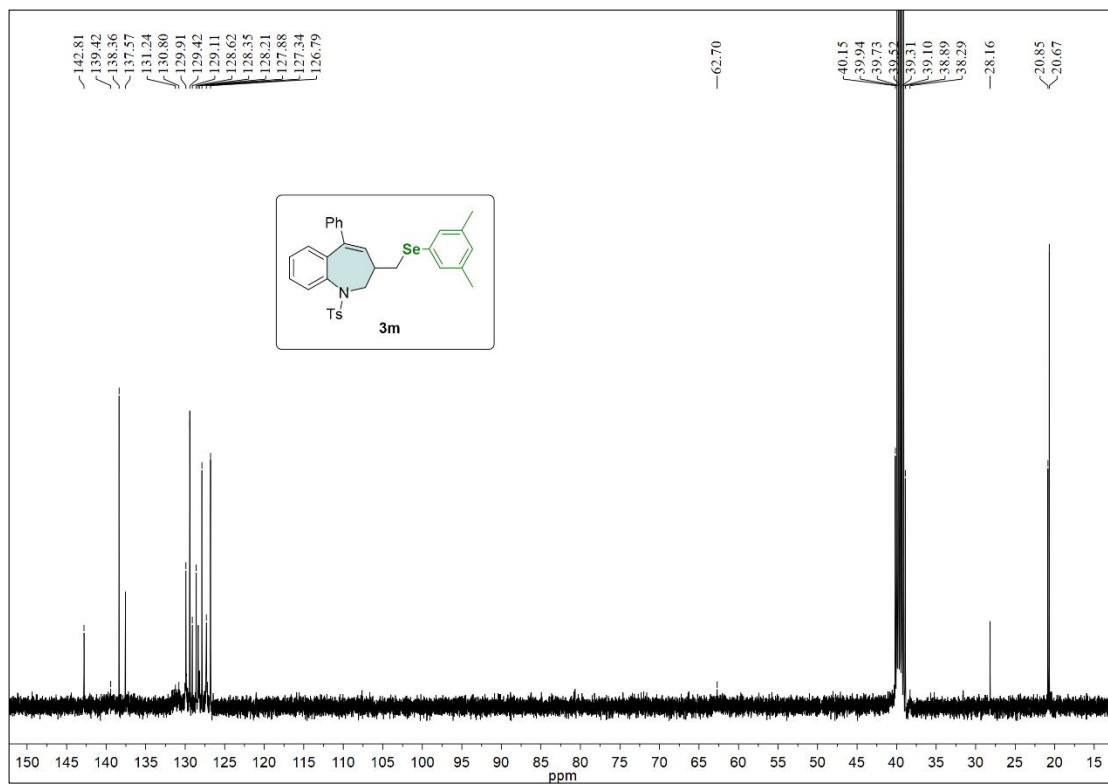
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



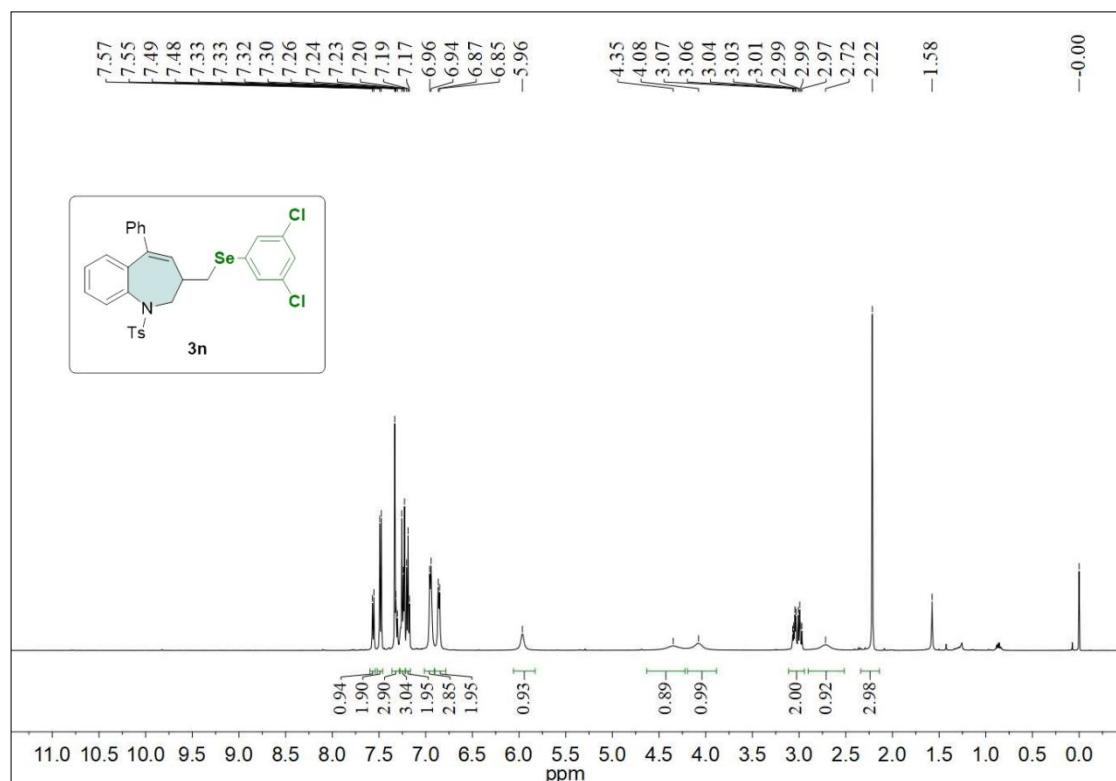
<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)



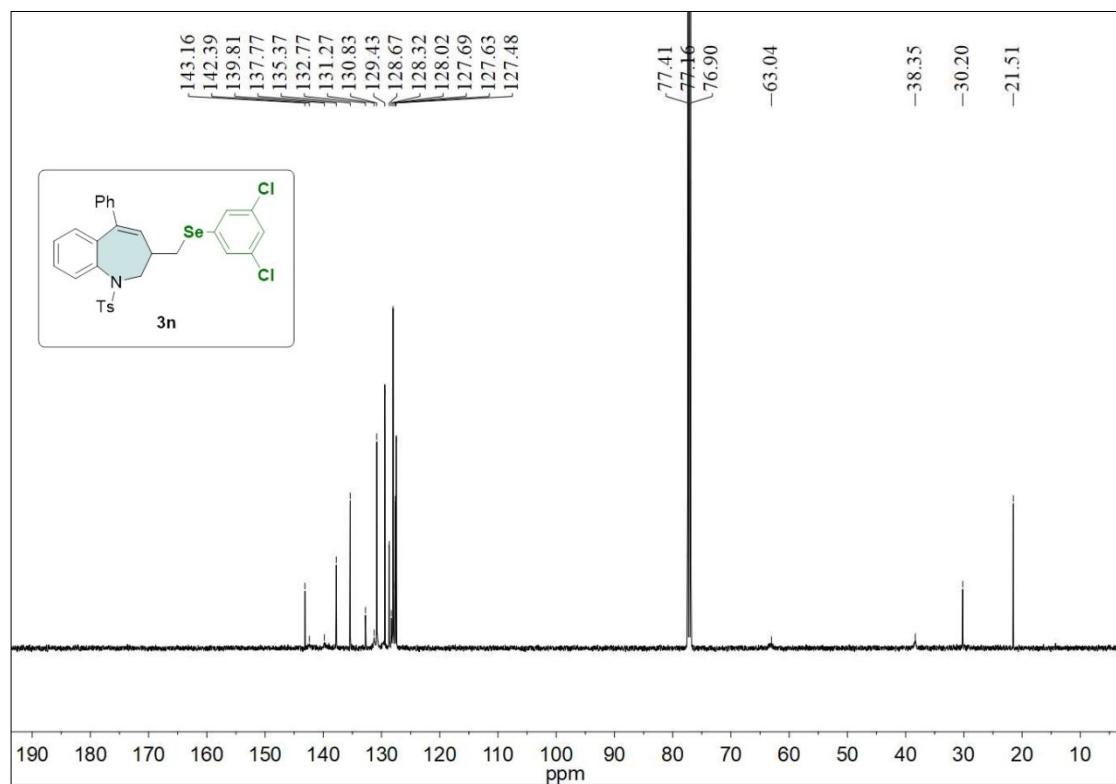
<sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)



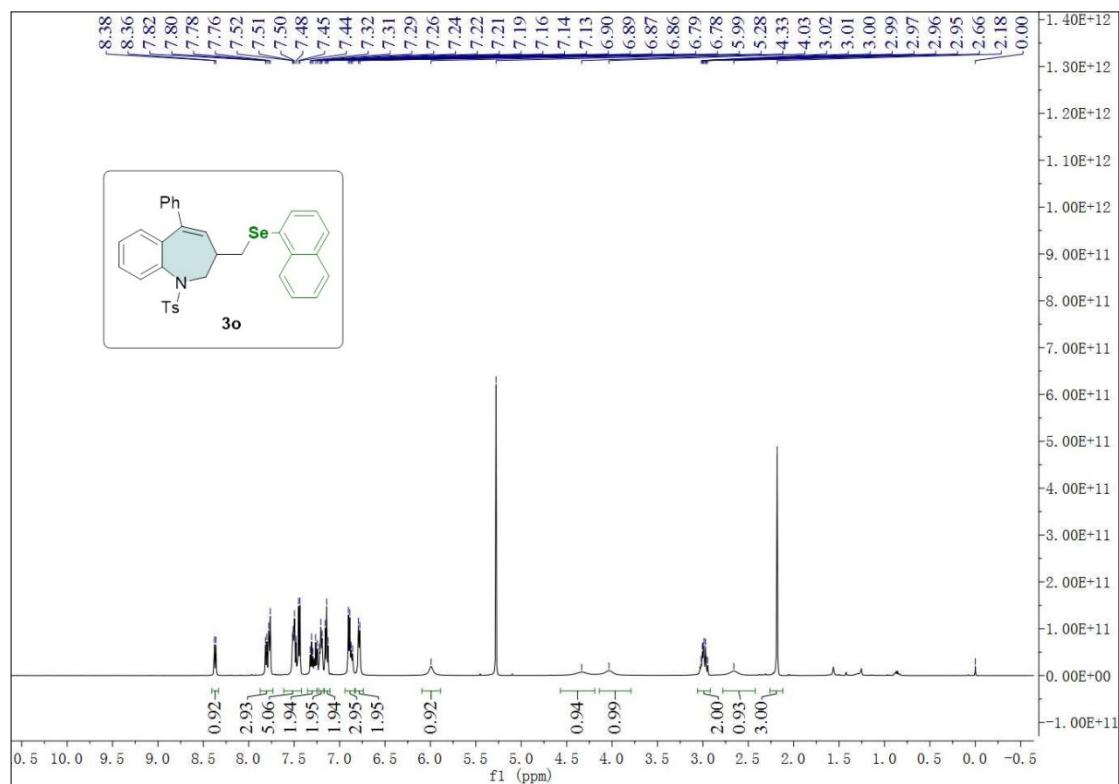
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



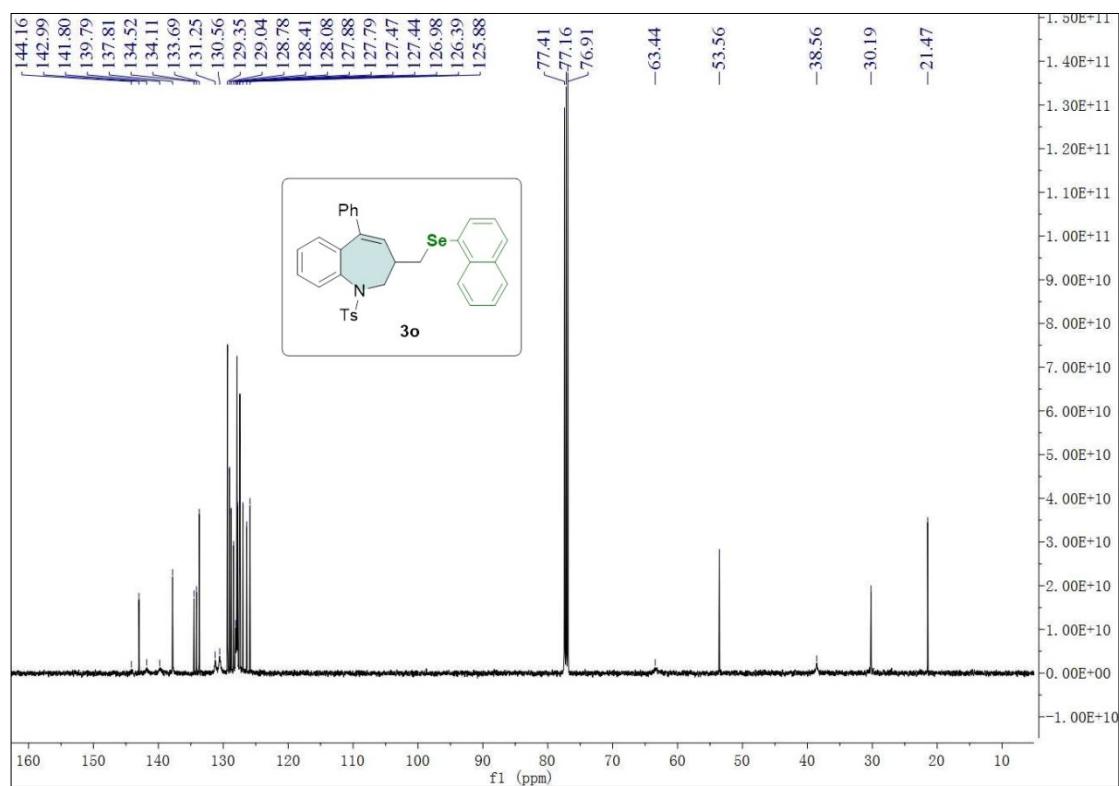
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



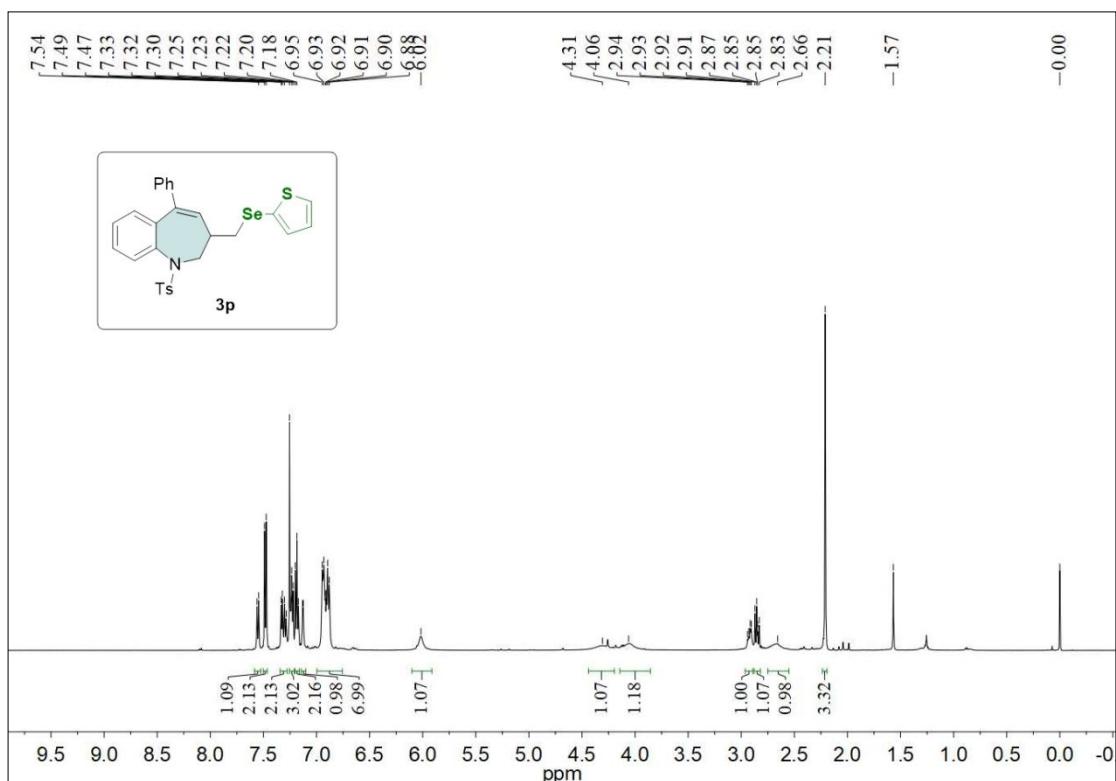
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



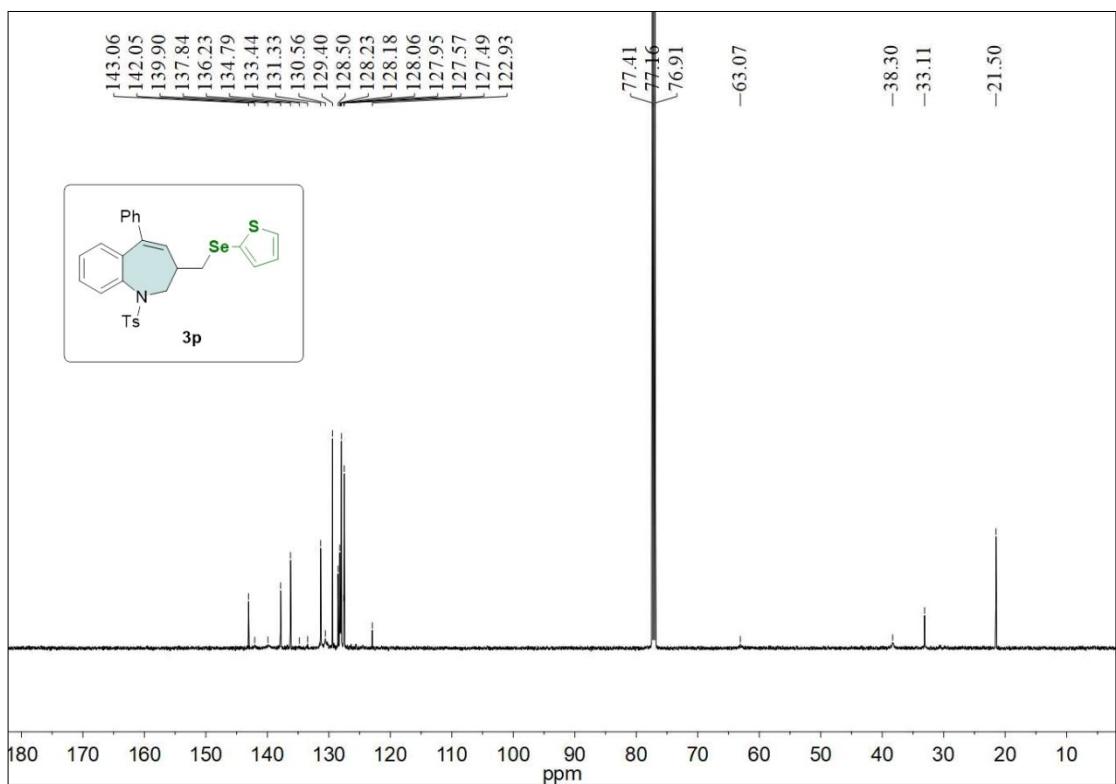
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



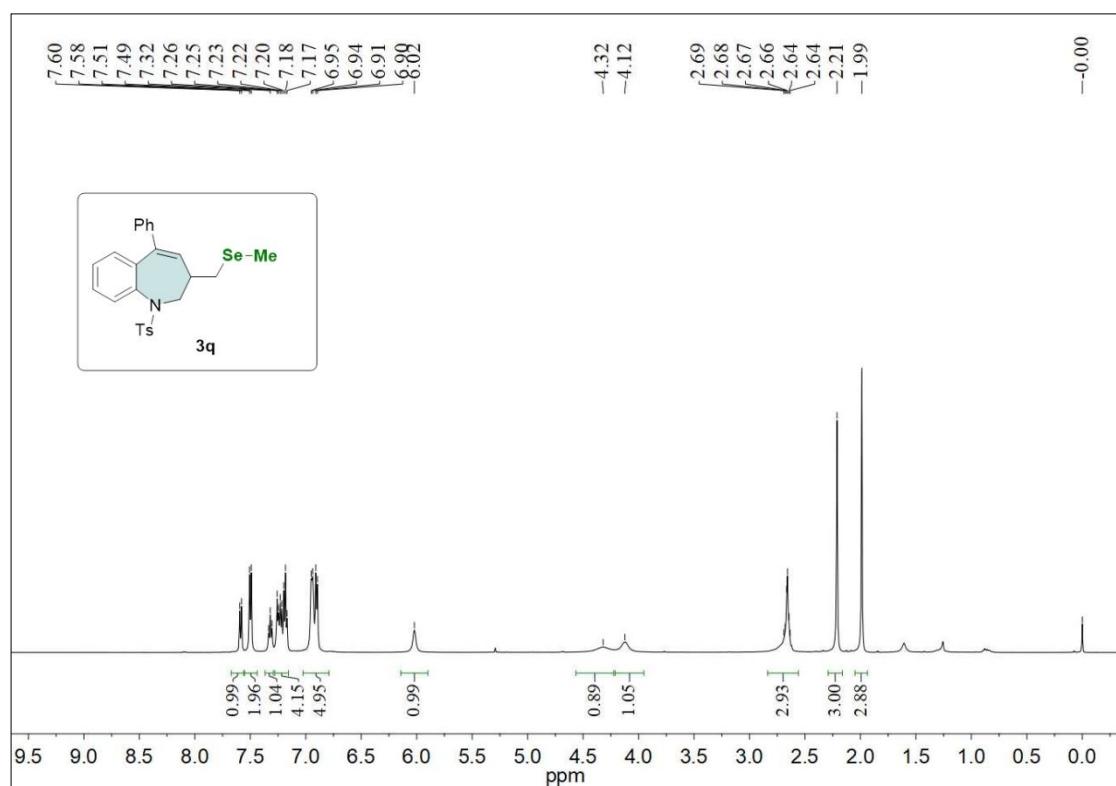
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



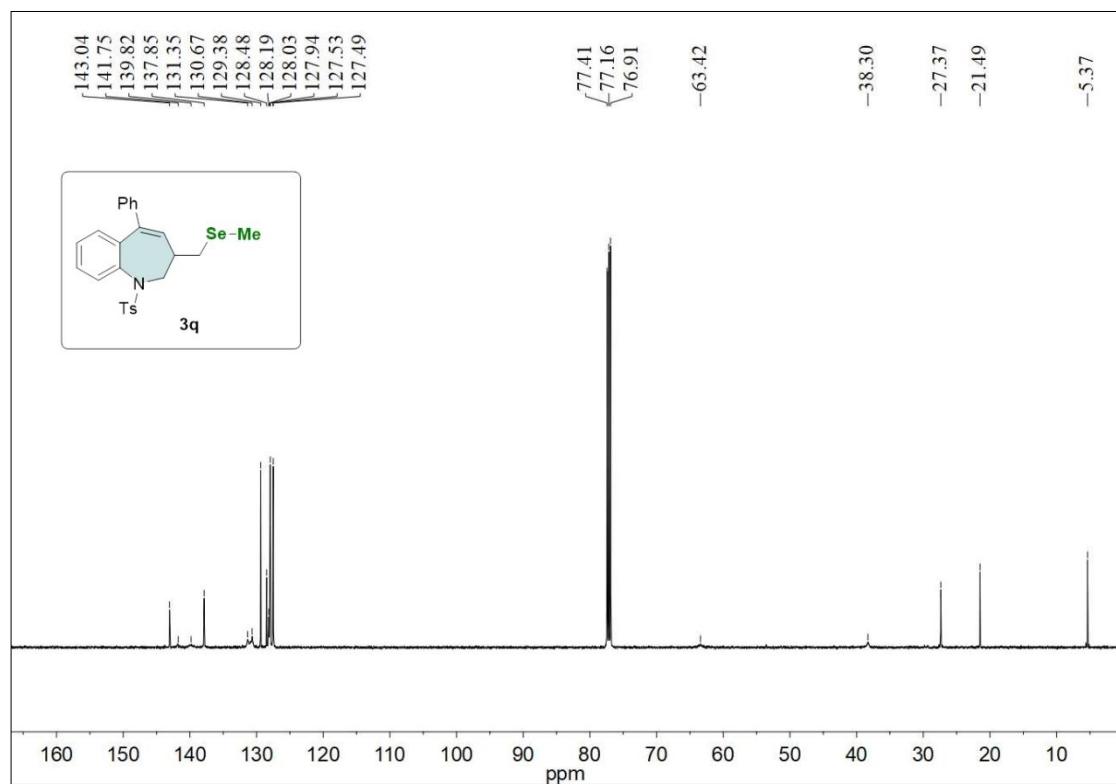
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



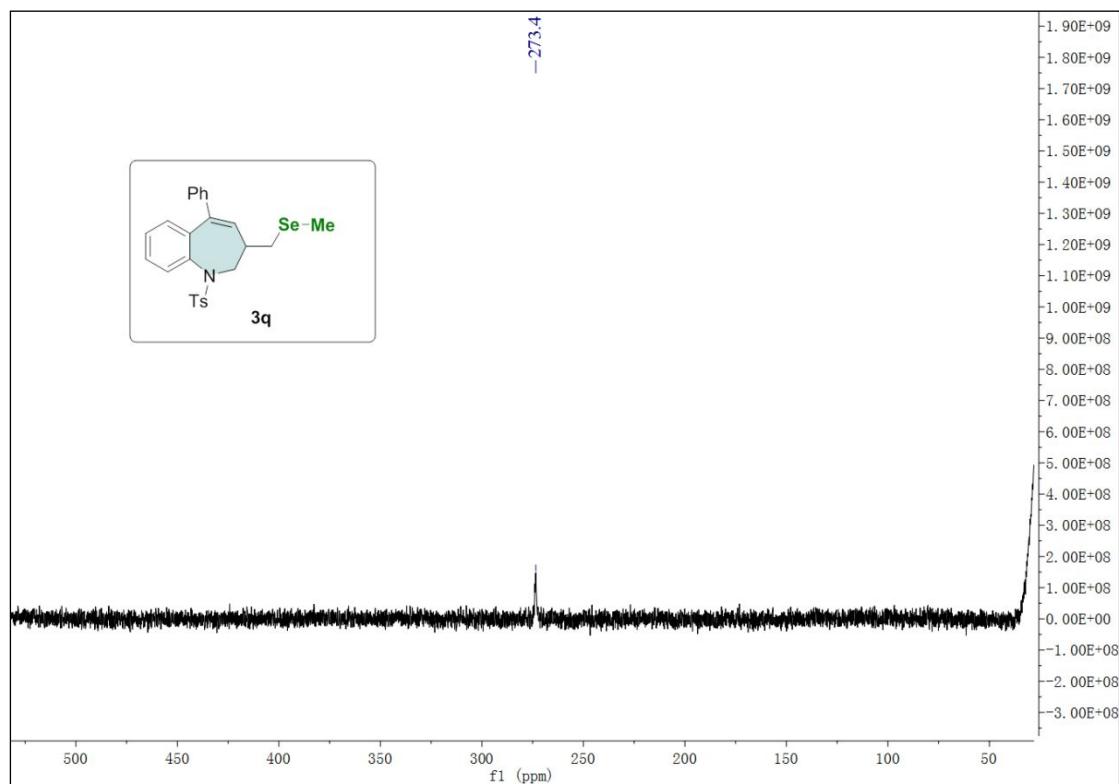
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



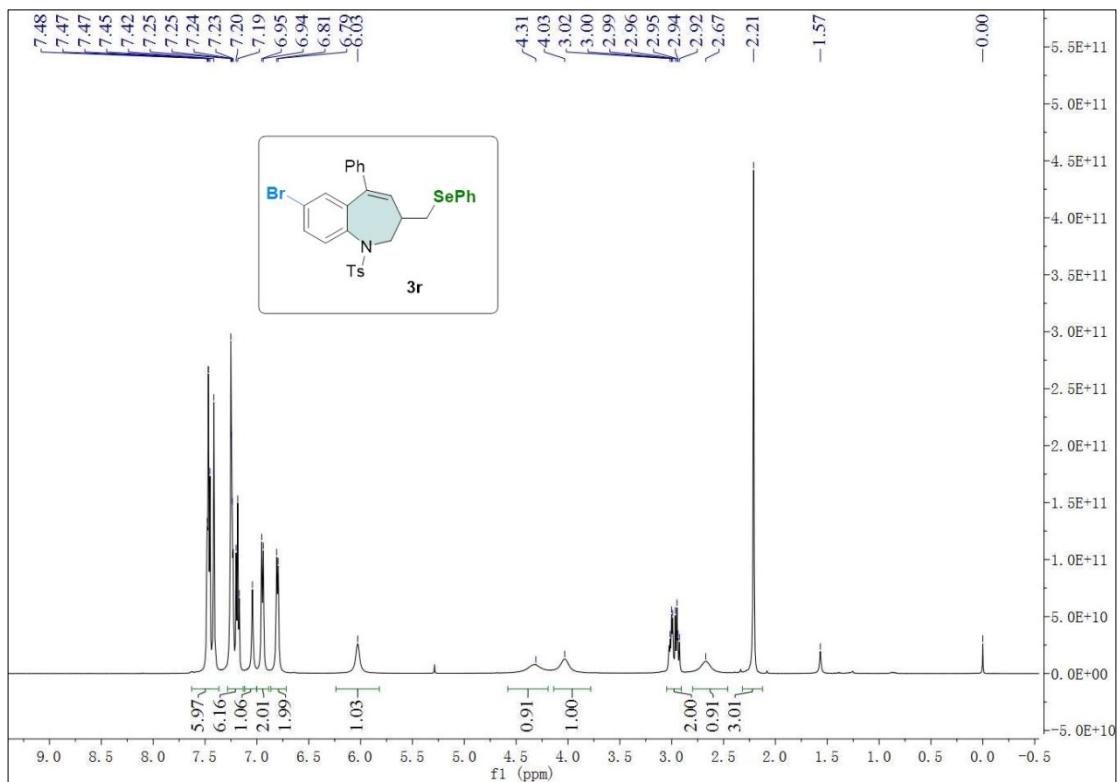
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



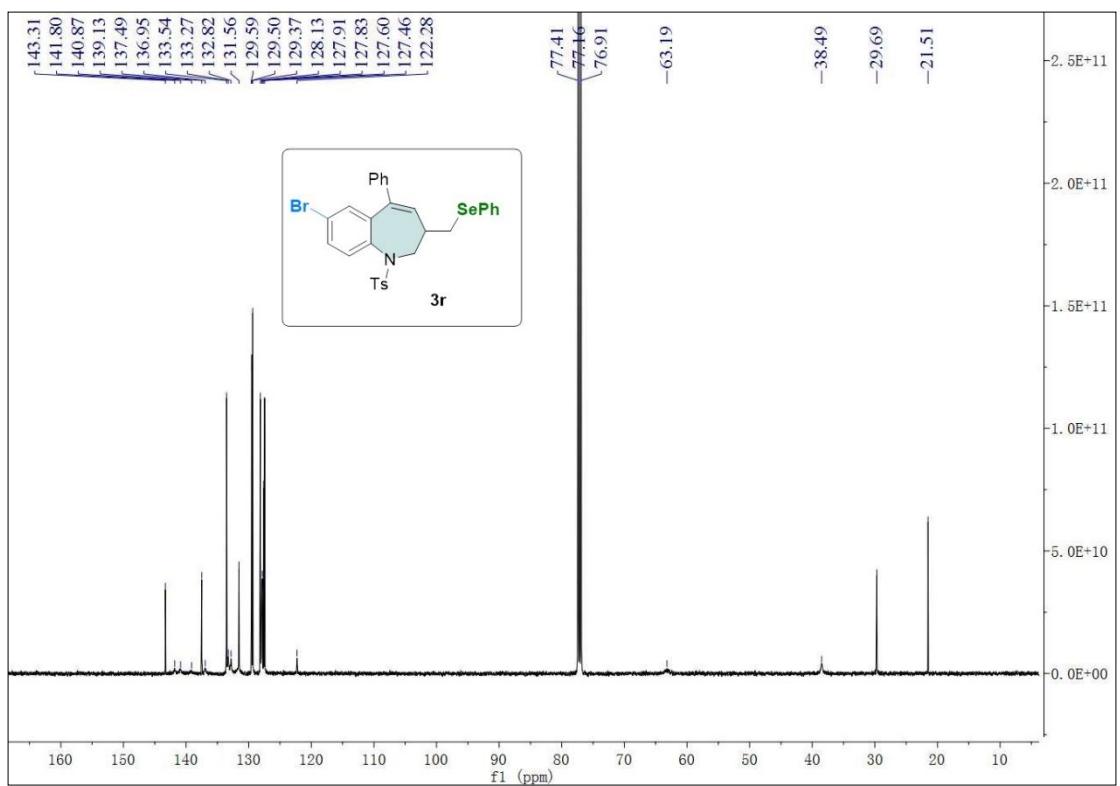
<sup>77</sup>Se NMR (76 MHz, Chloroform-*d*)



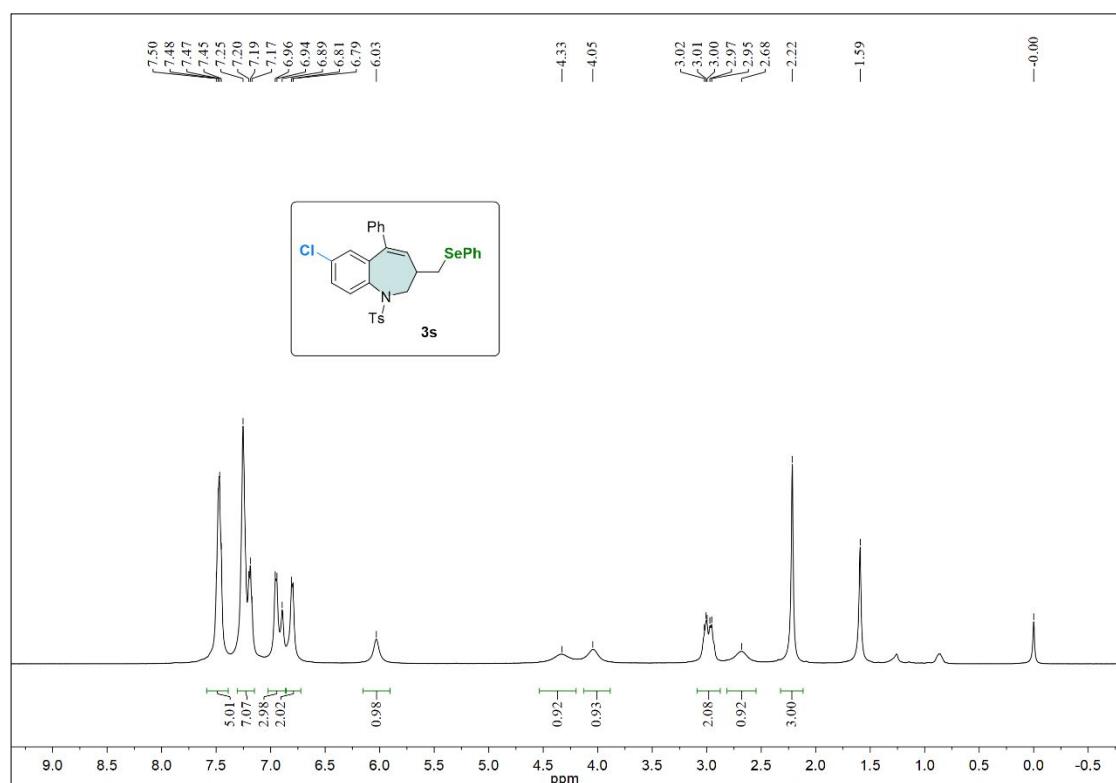
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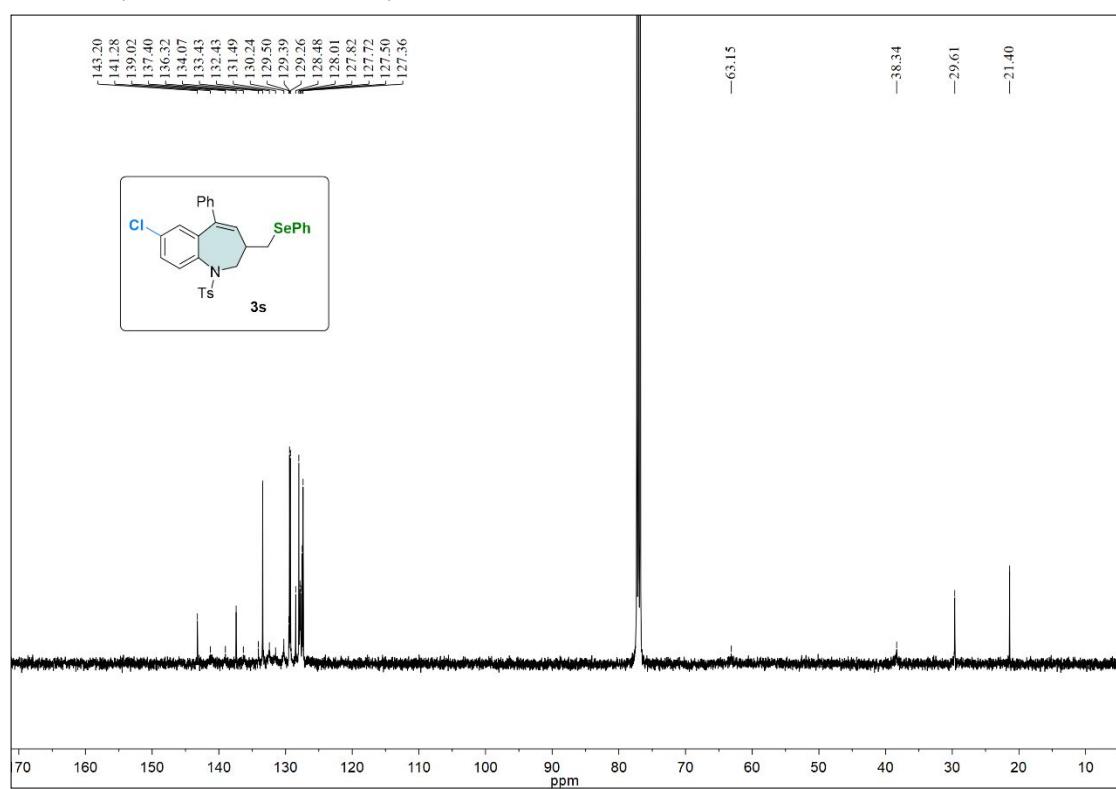
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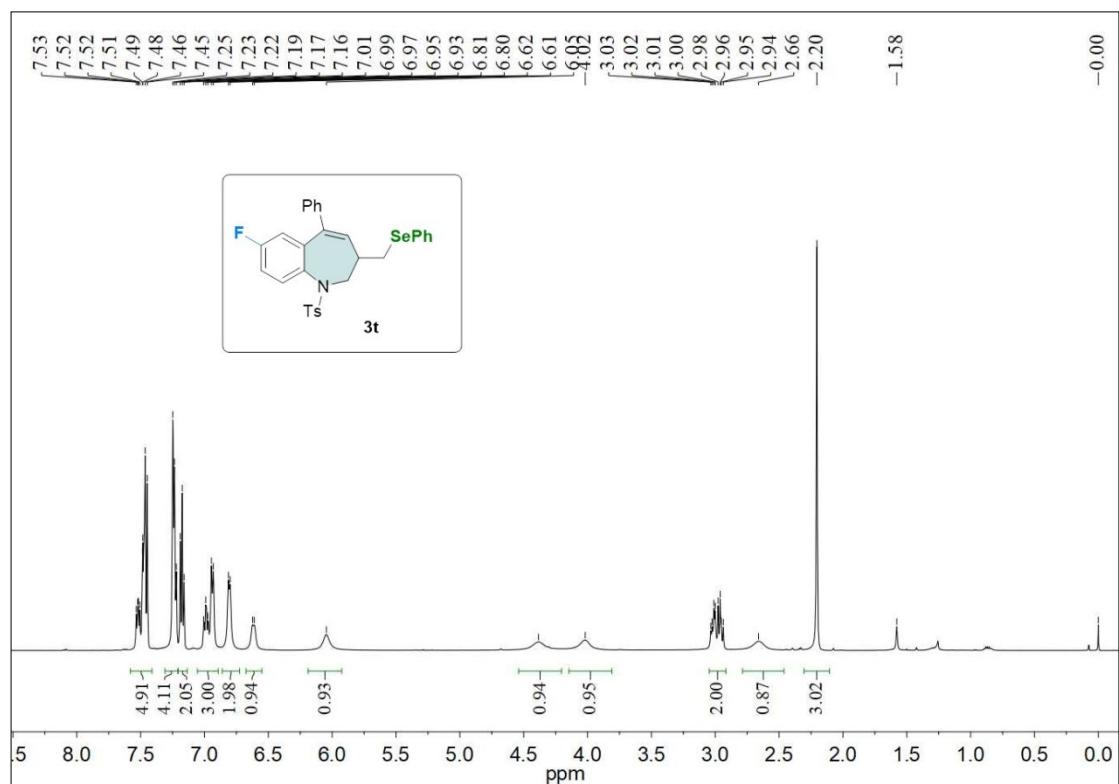
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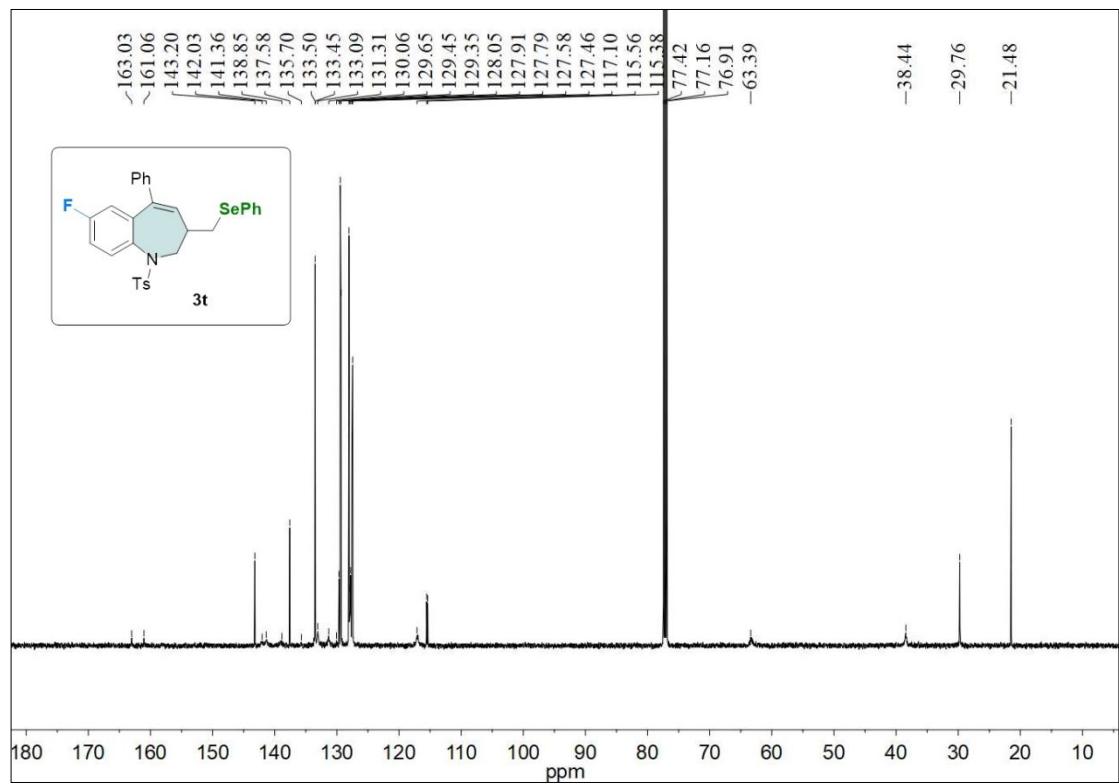
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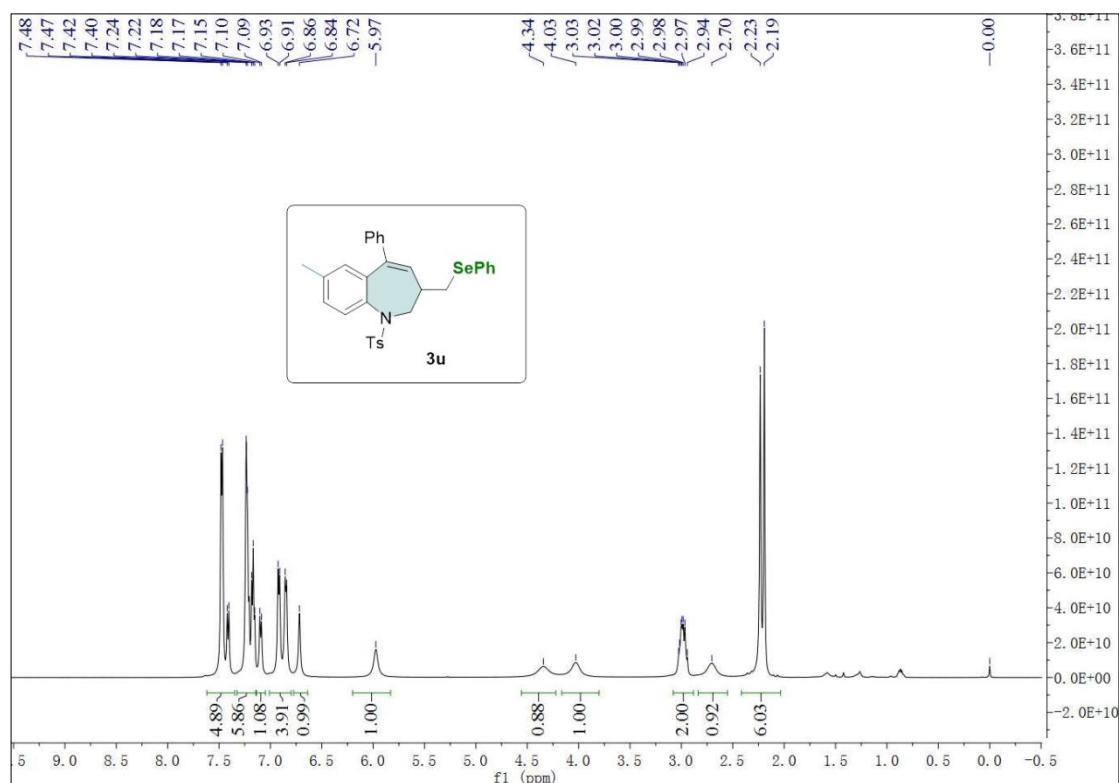
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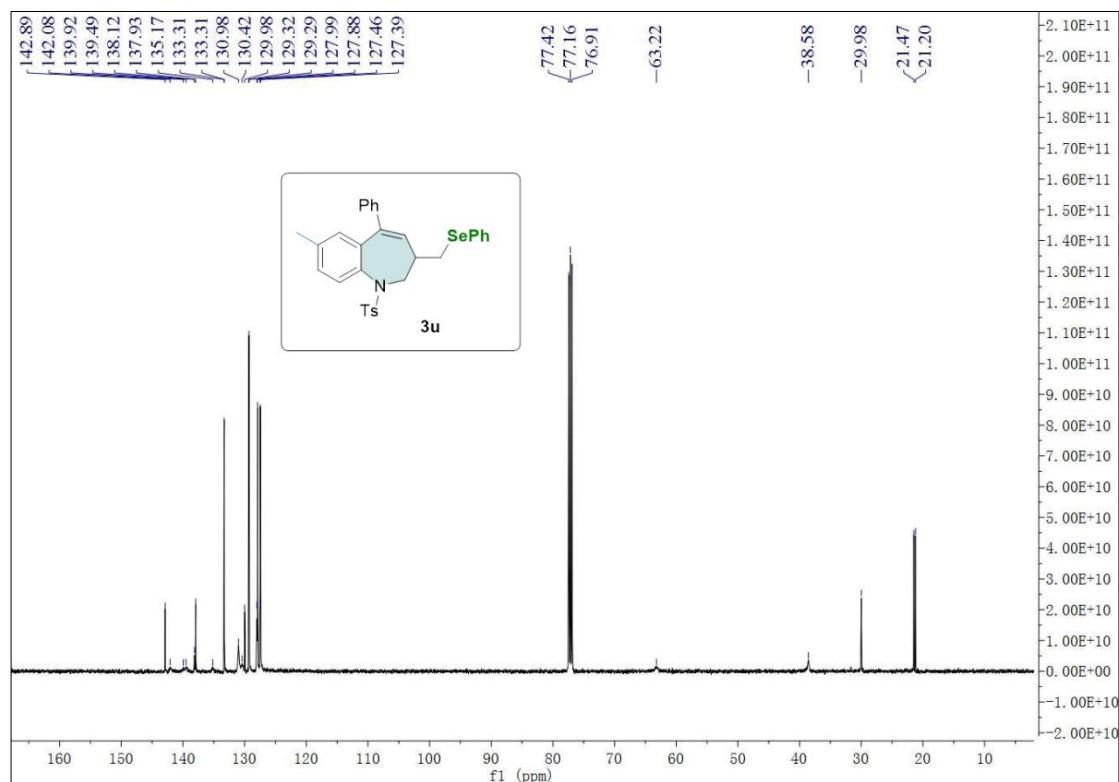
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



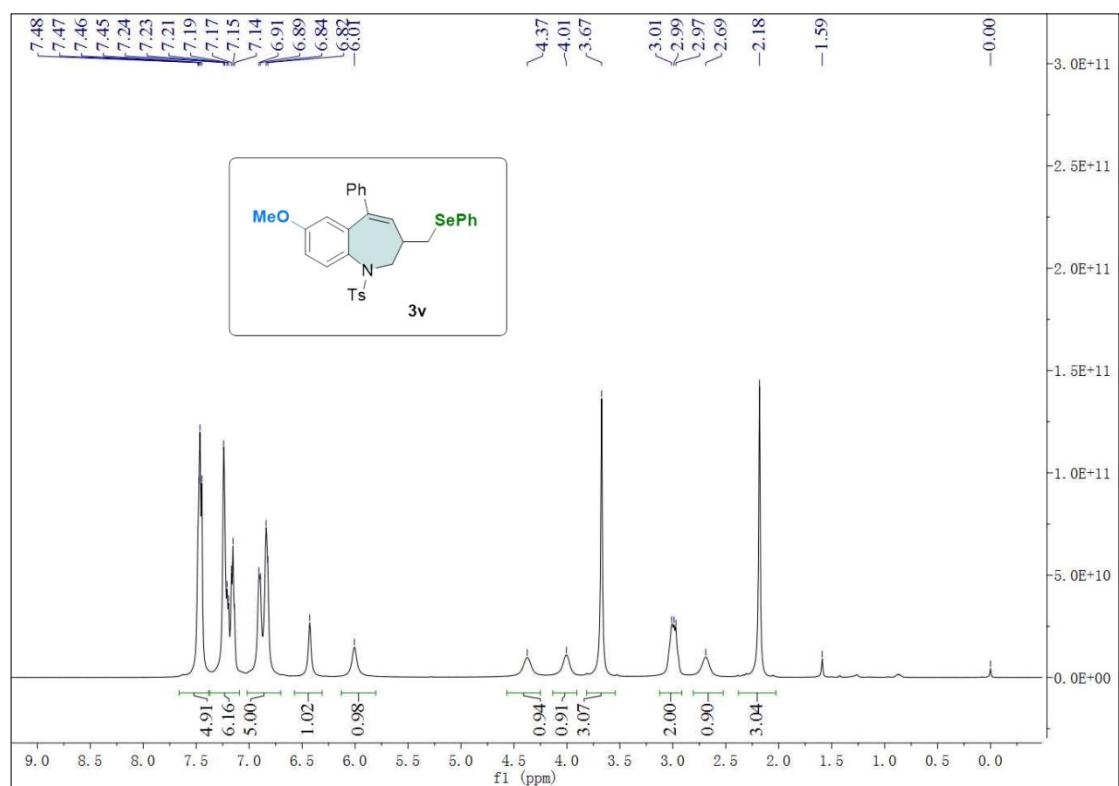
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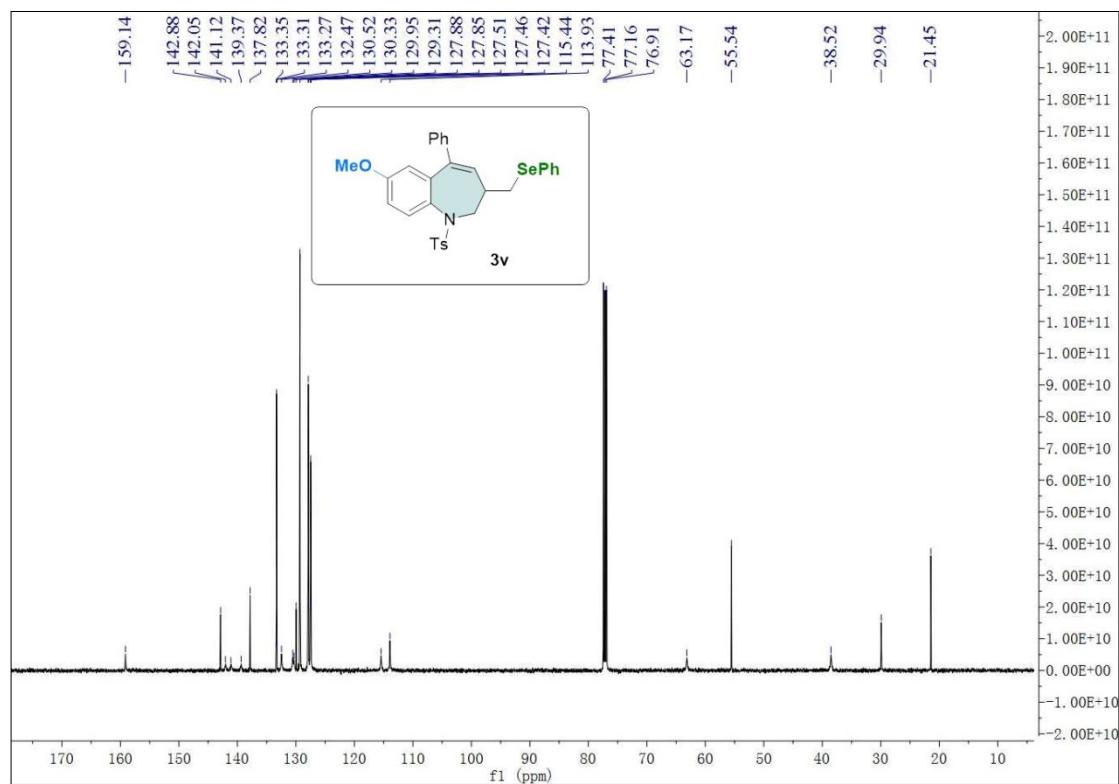
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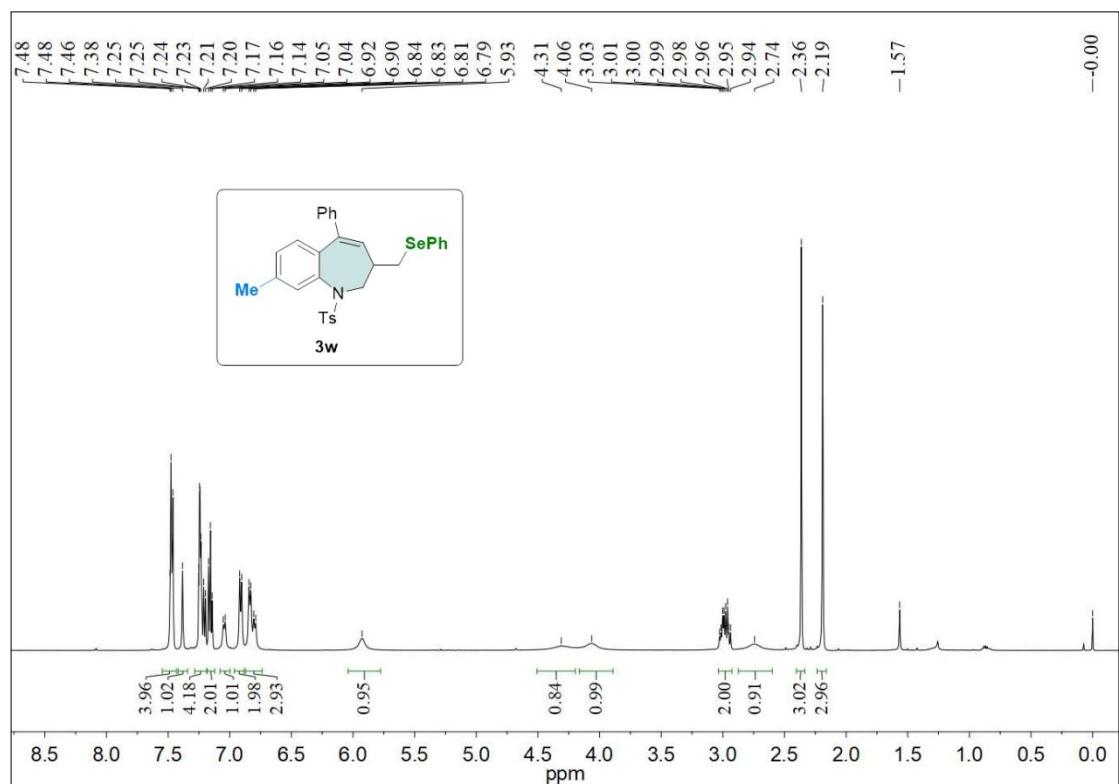
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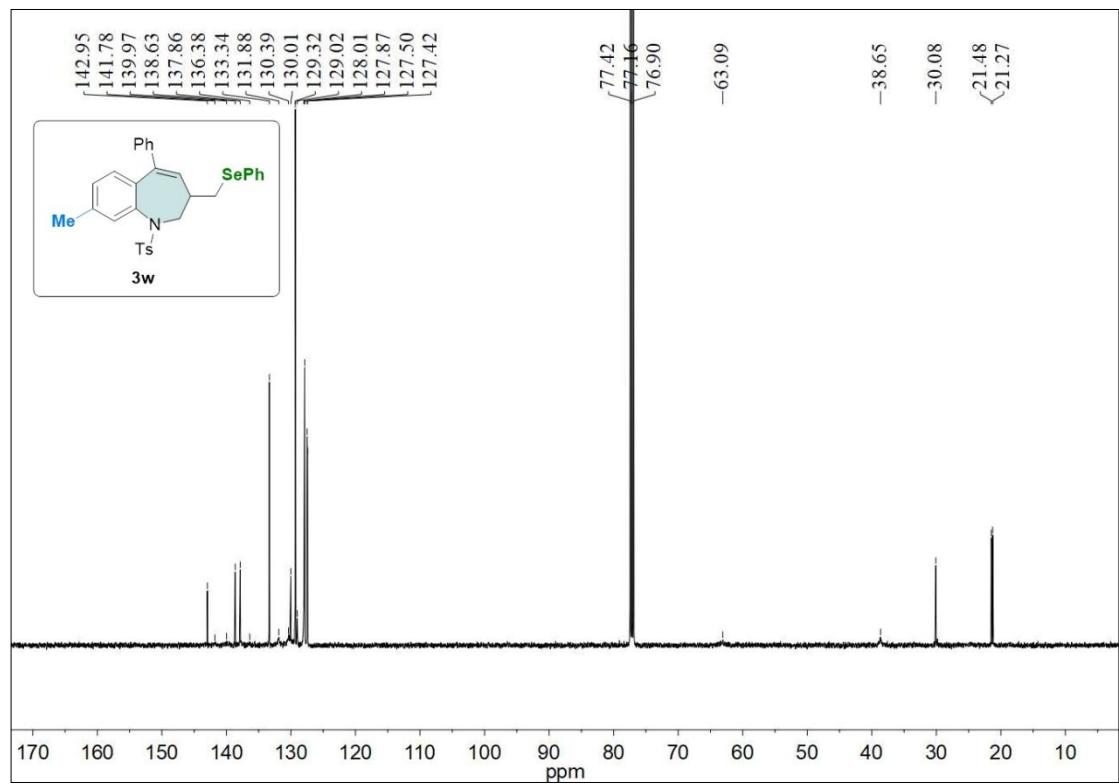
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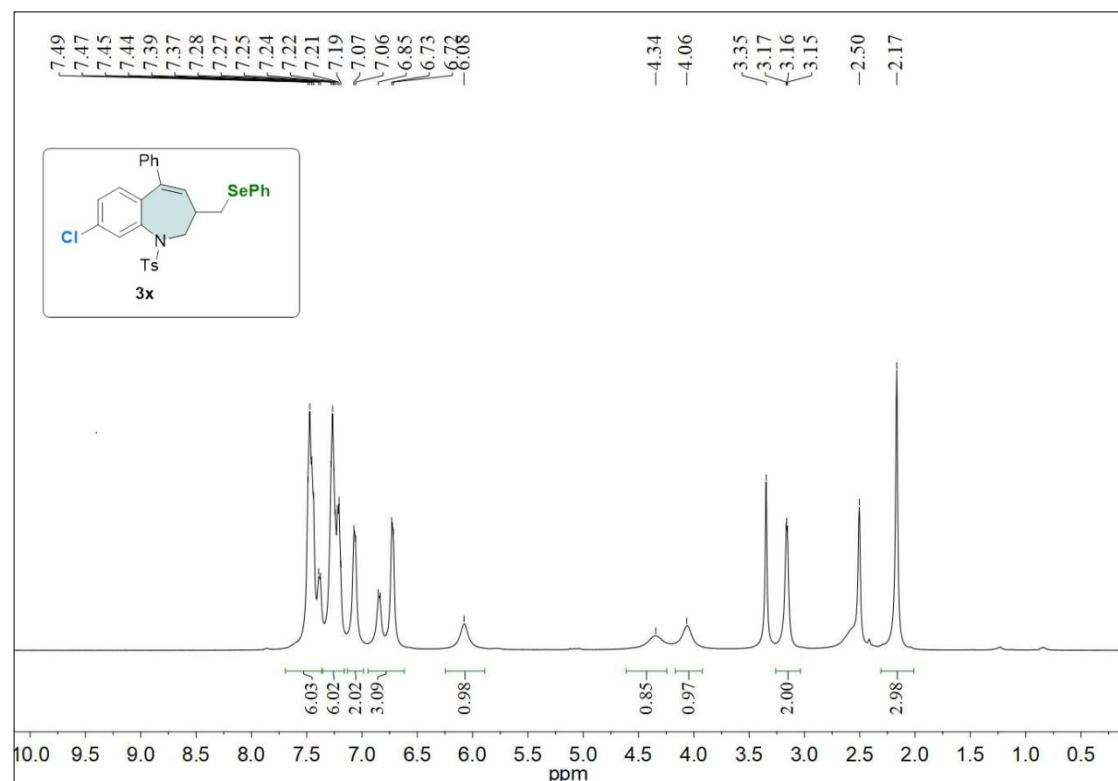
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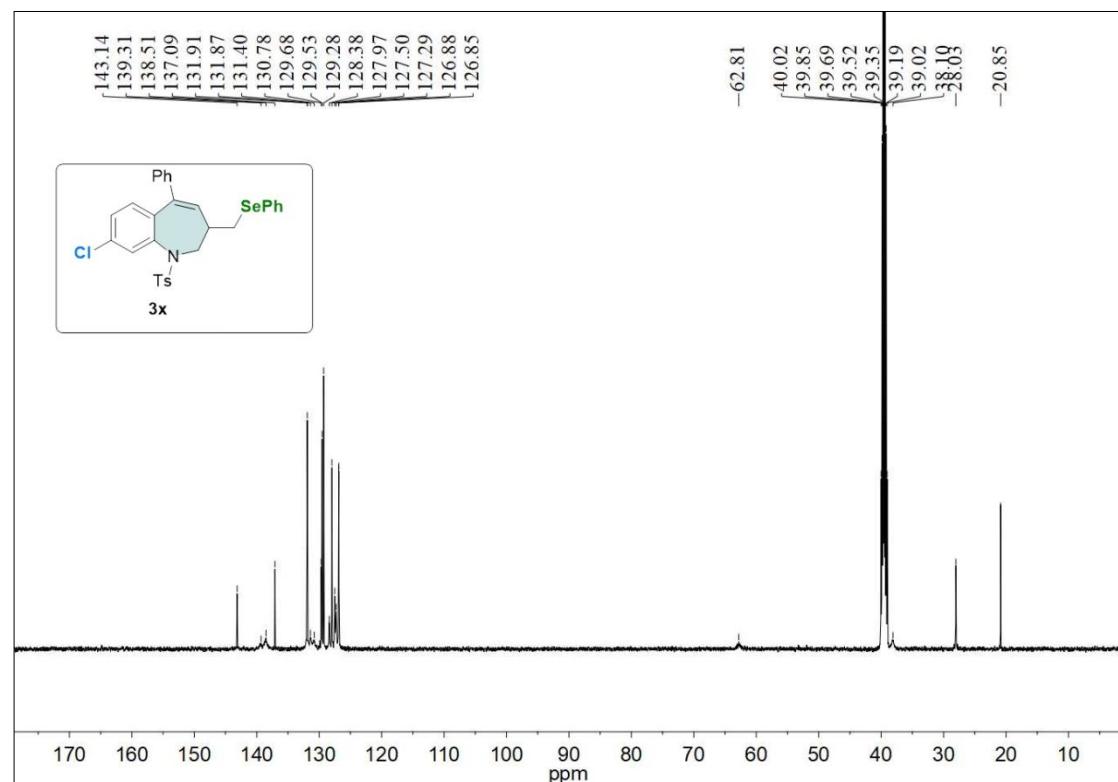
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



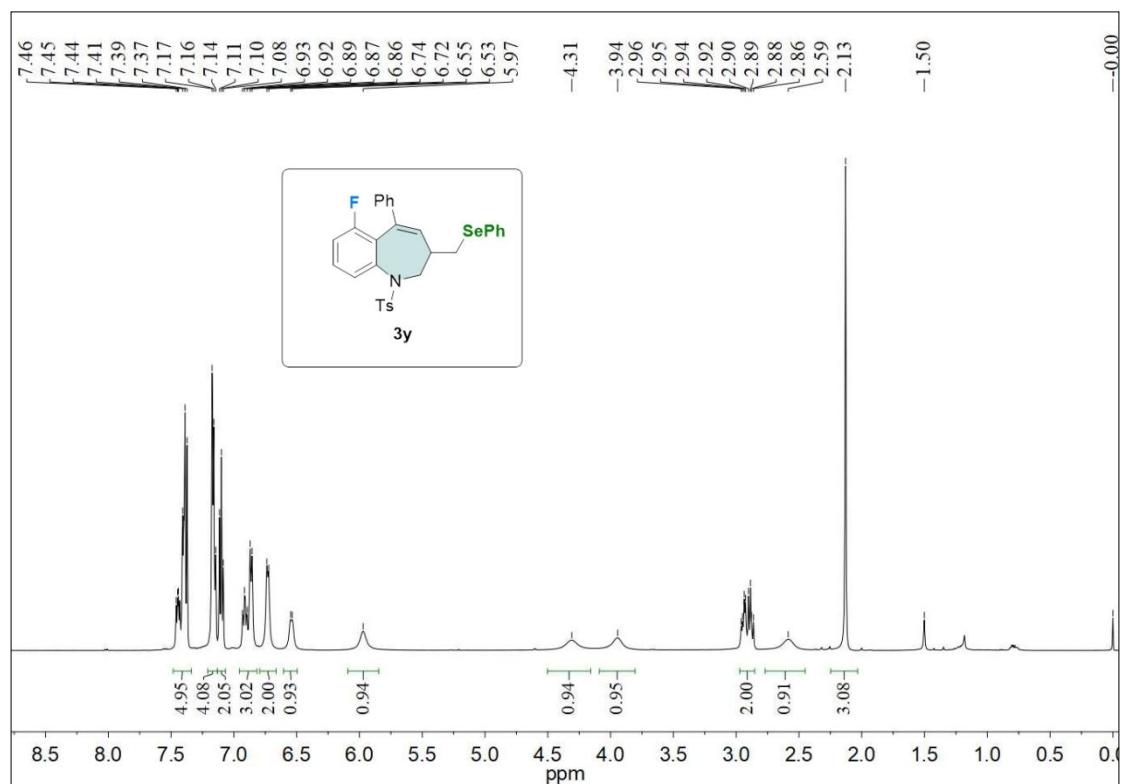
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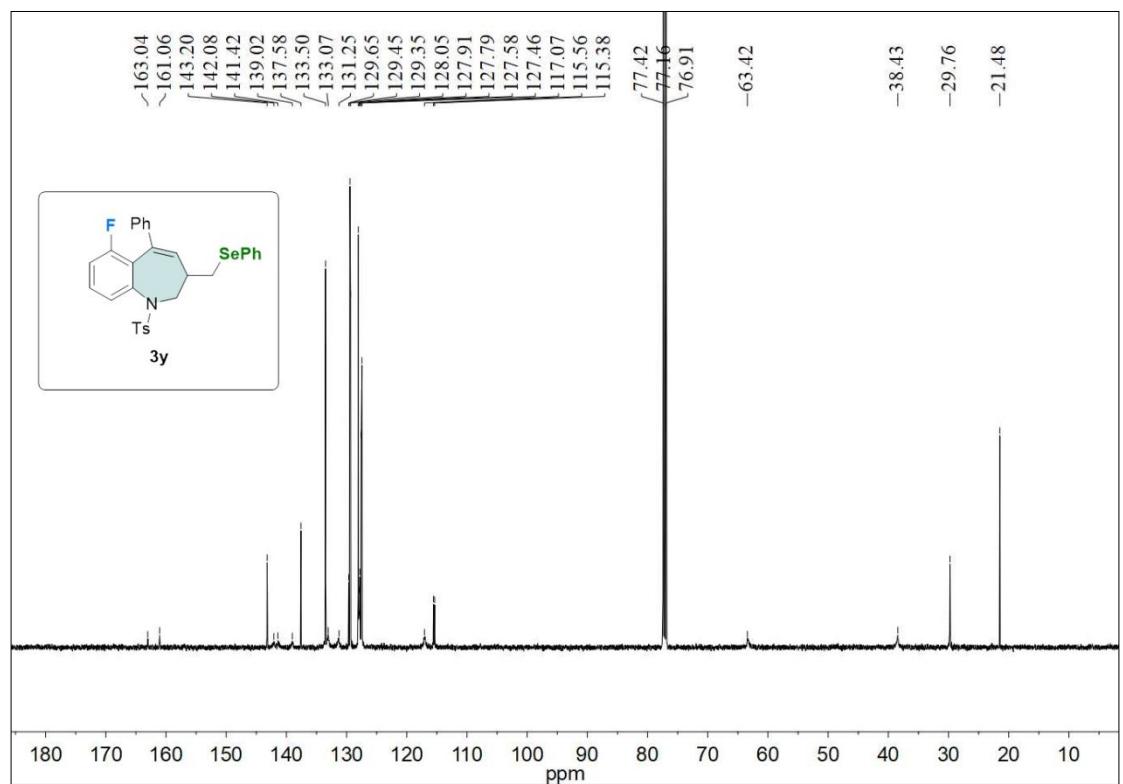
<sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)



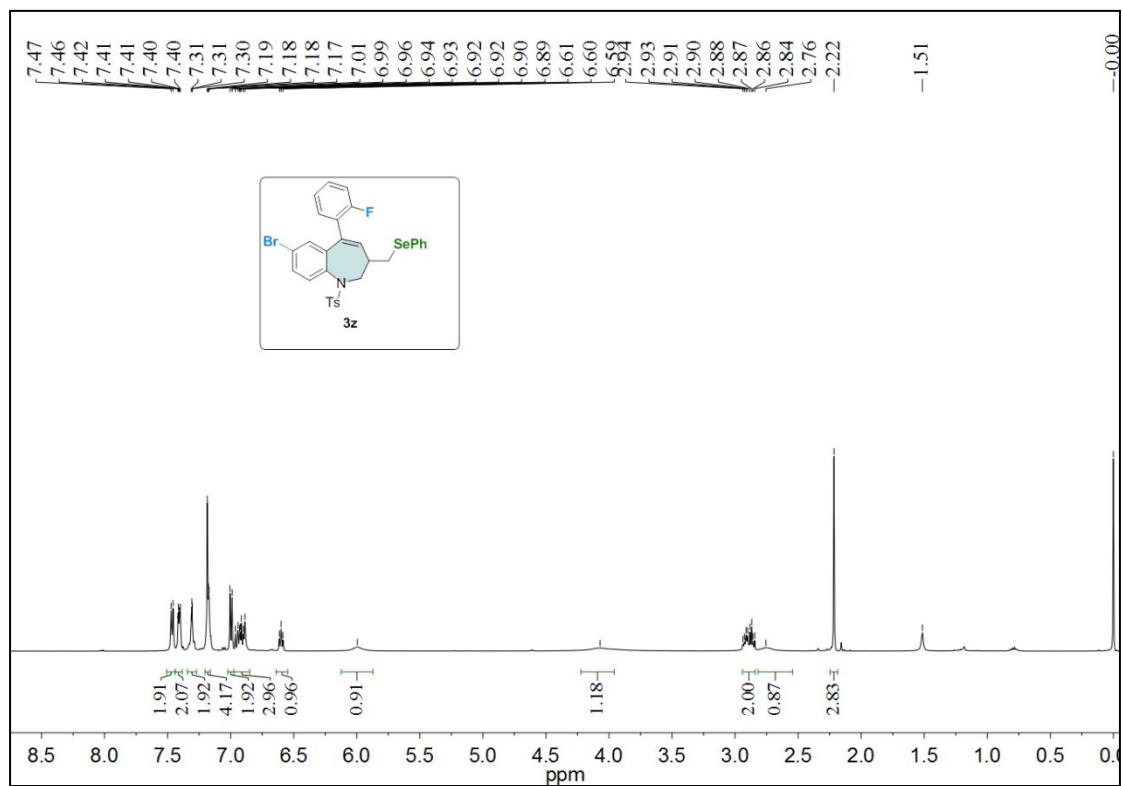
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



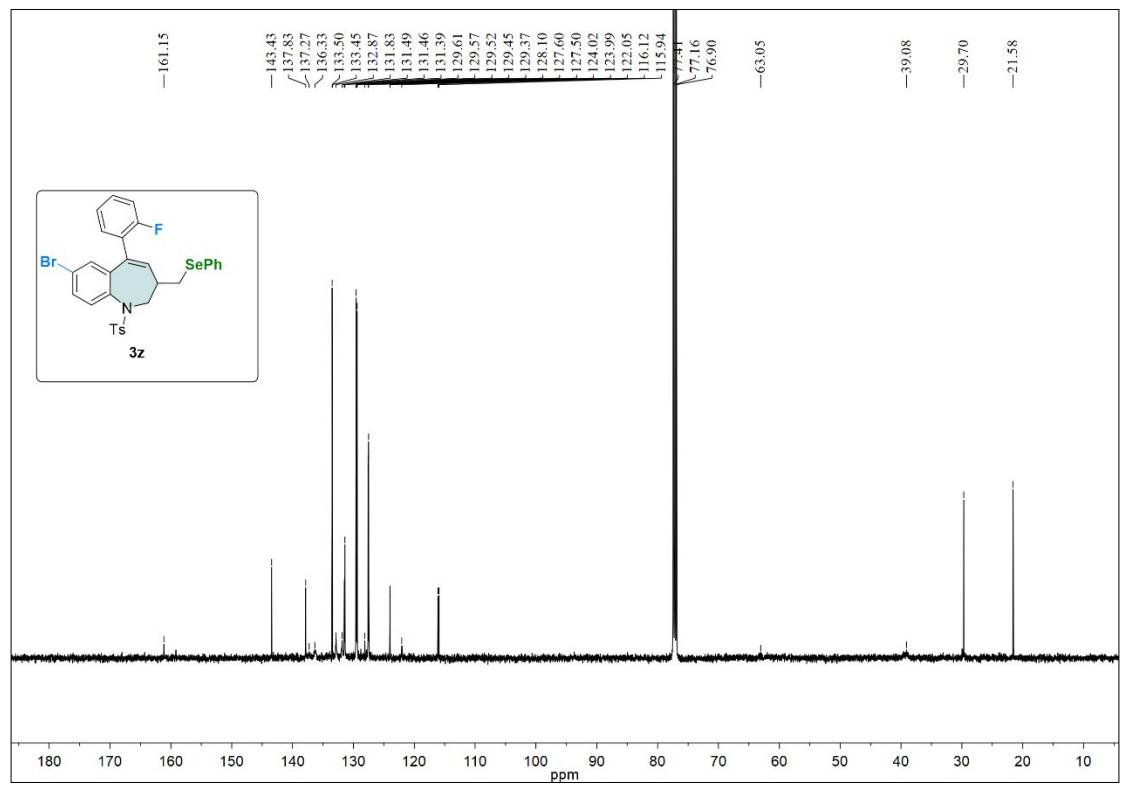
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



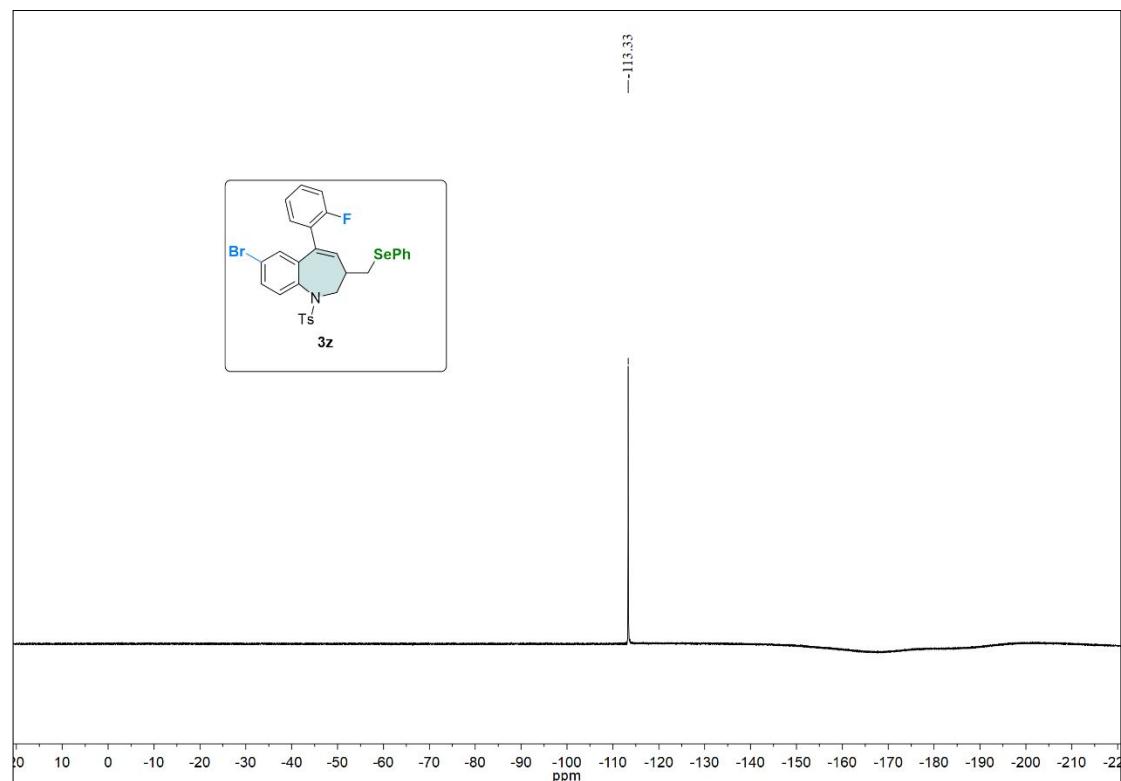
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



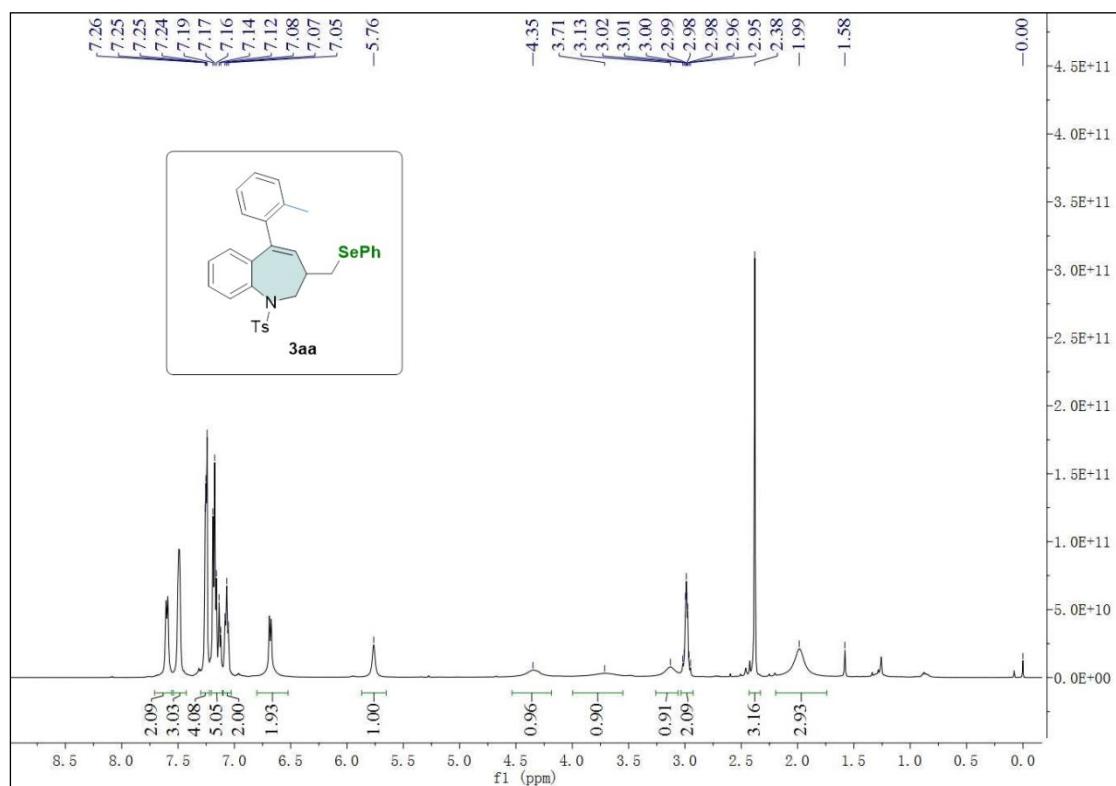
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



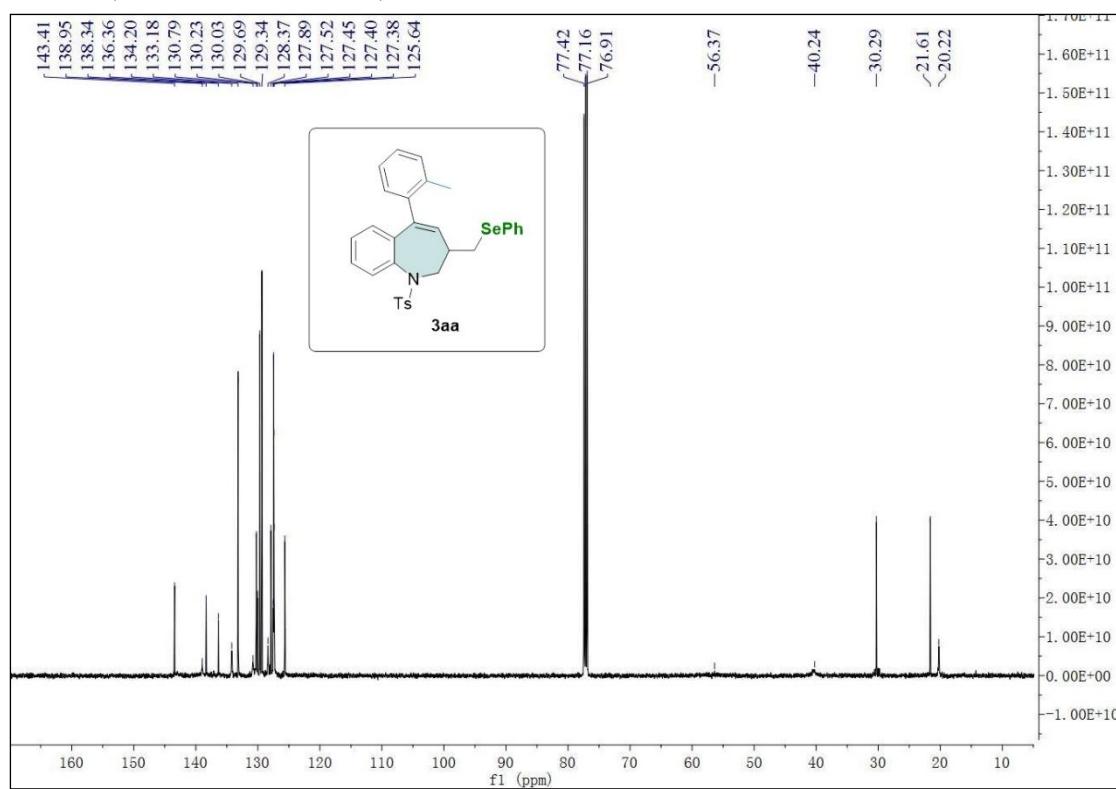
<sup>19</sup>F NMR (471 MHz, Chloroform-*d*)



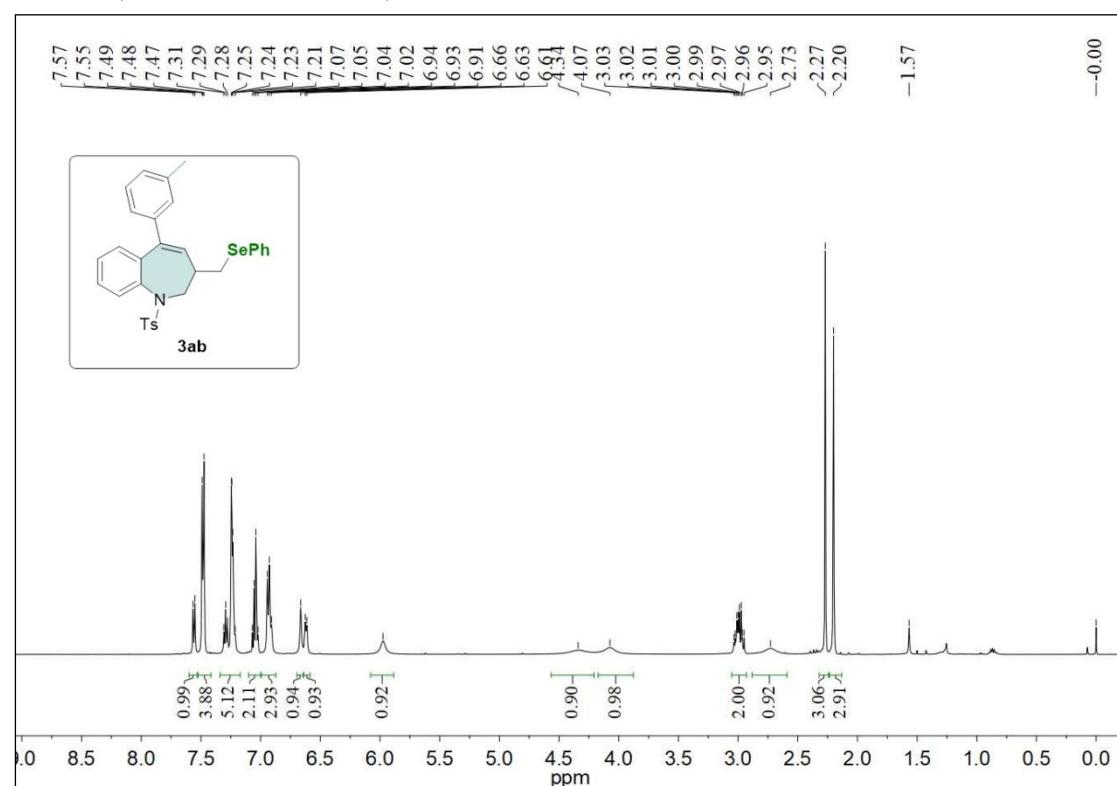
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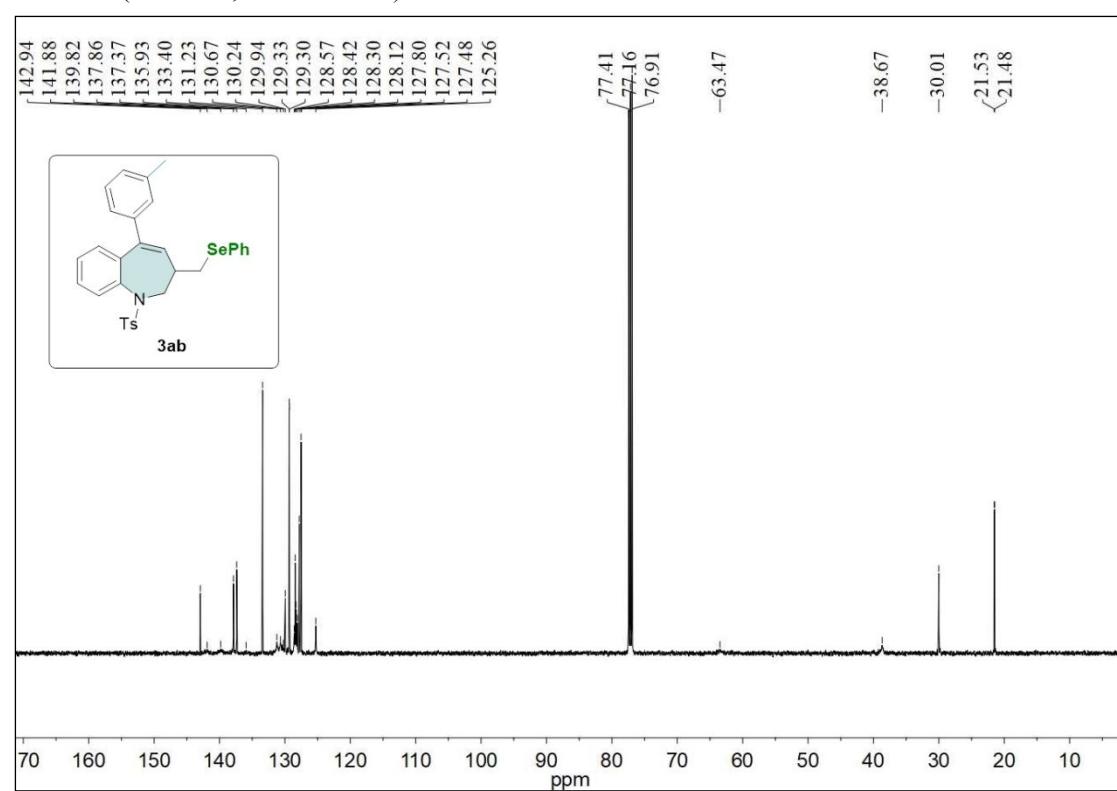
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



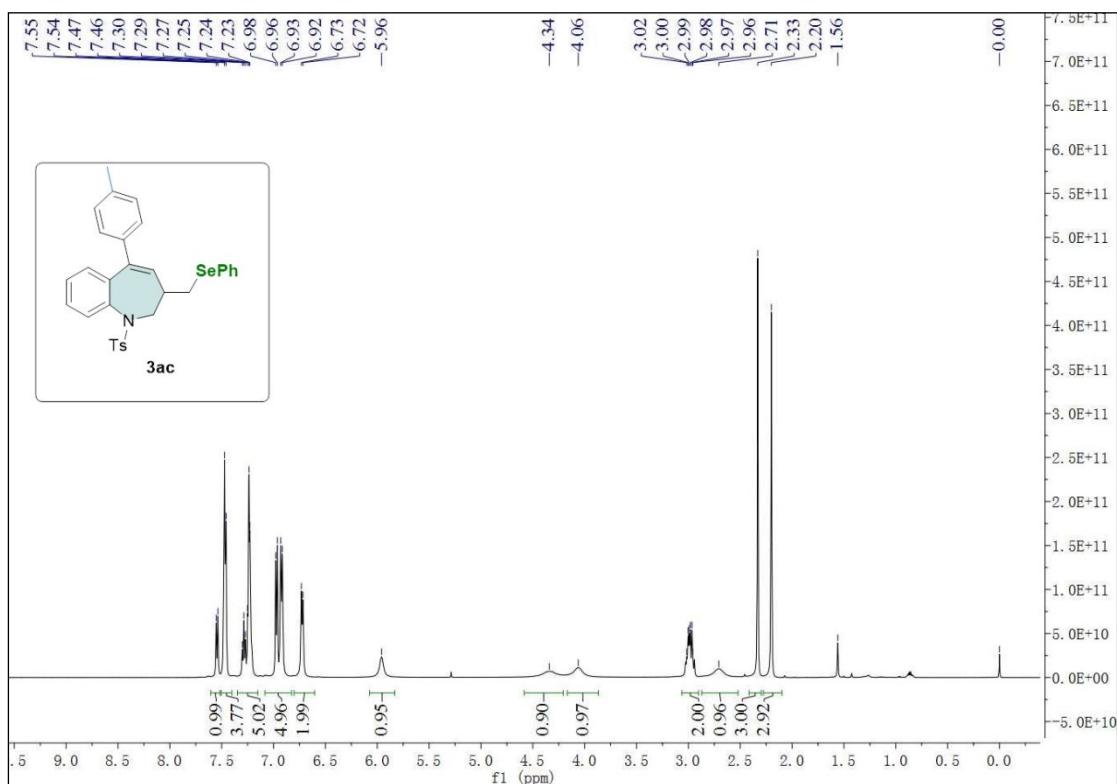
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



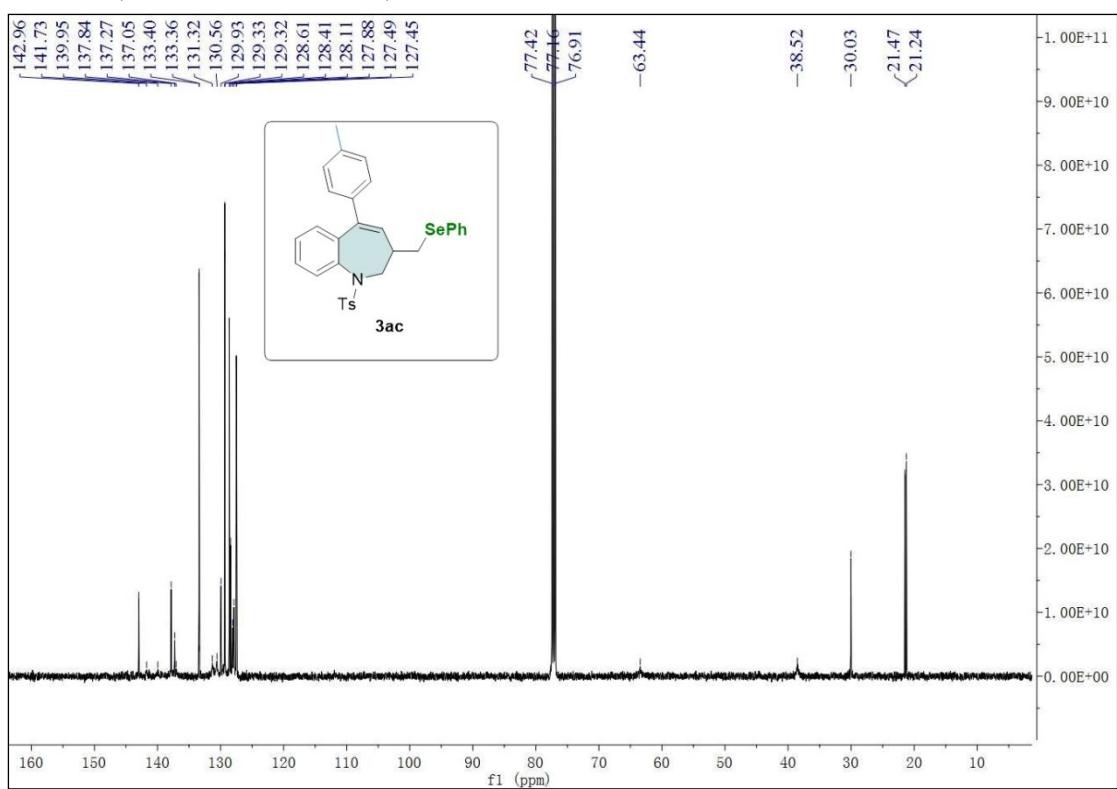
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



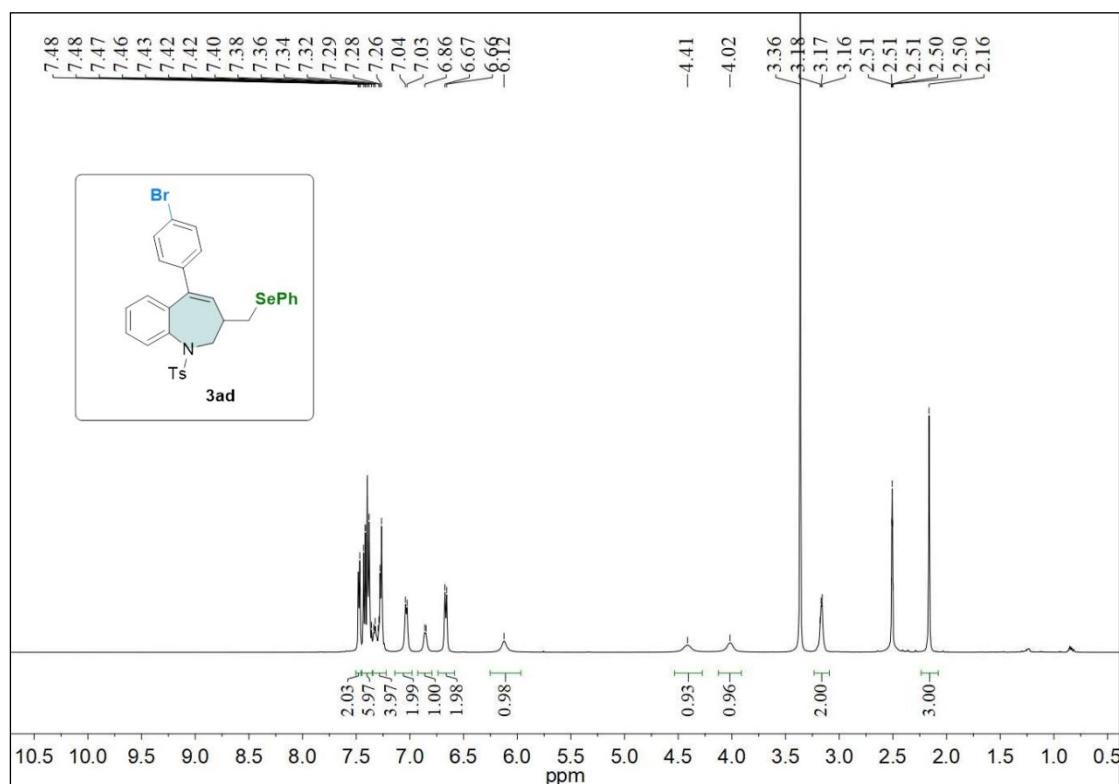
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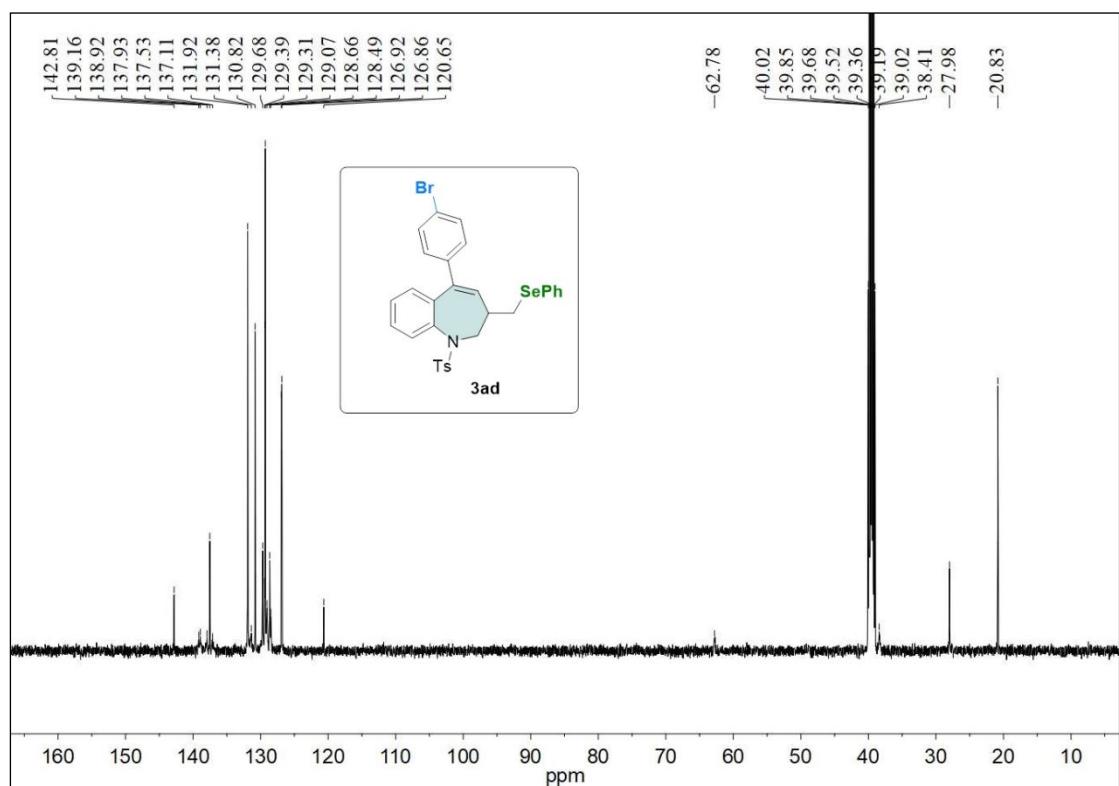
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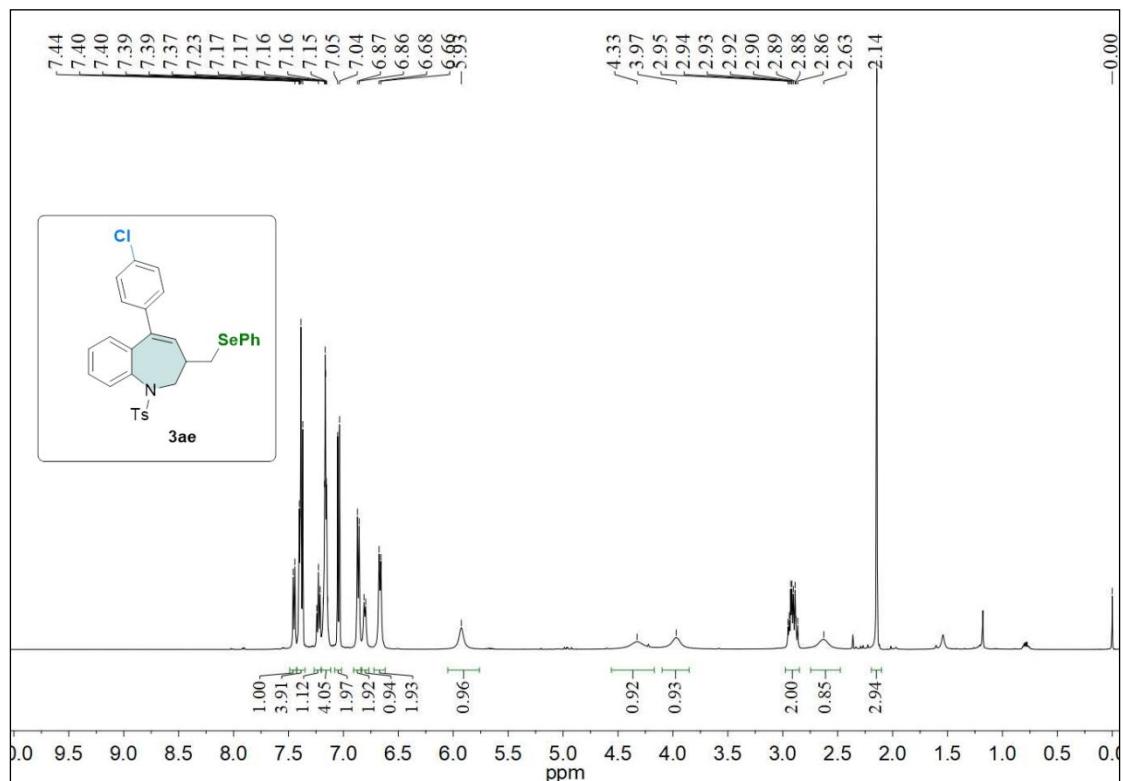
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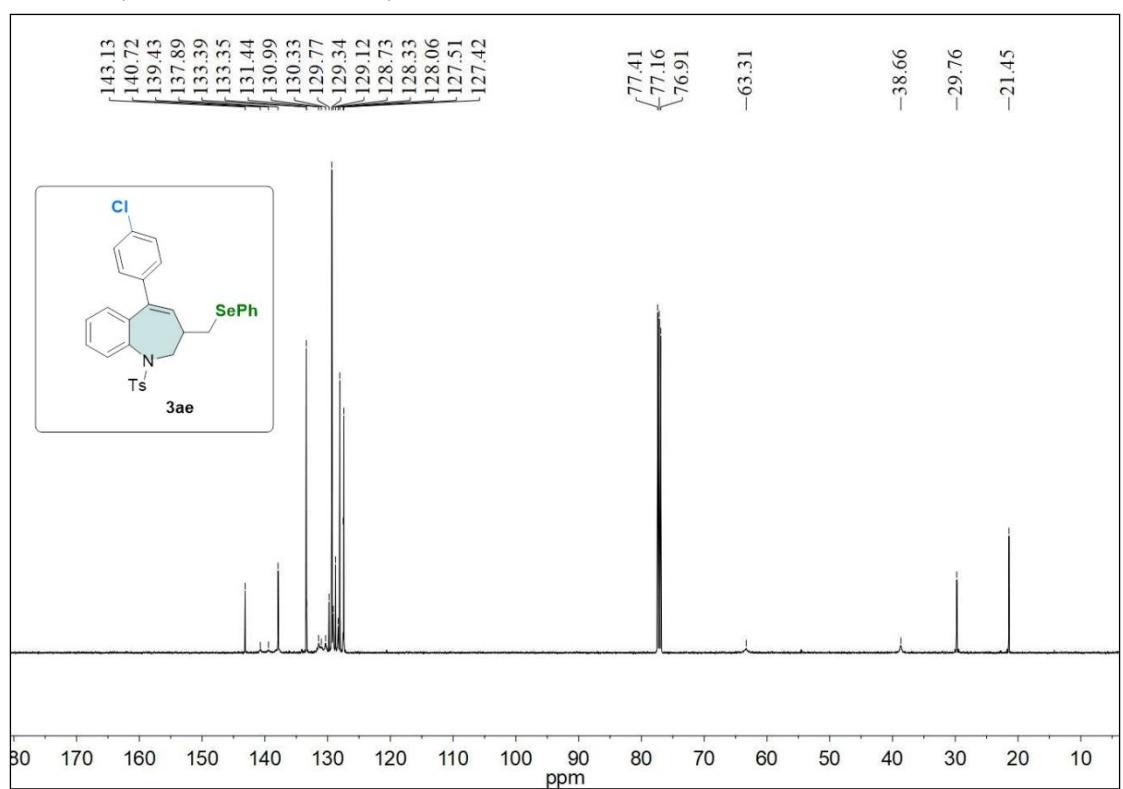
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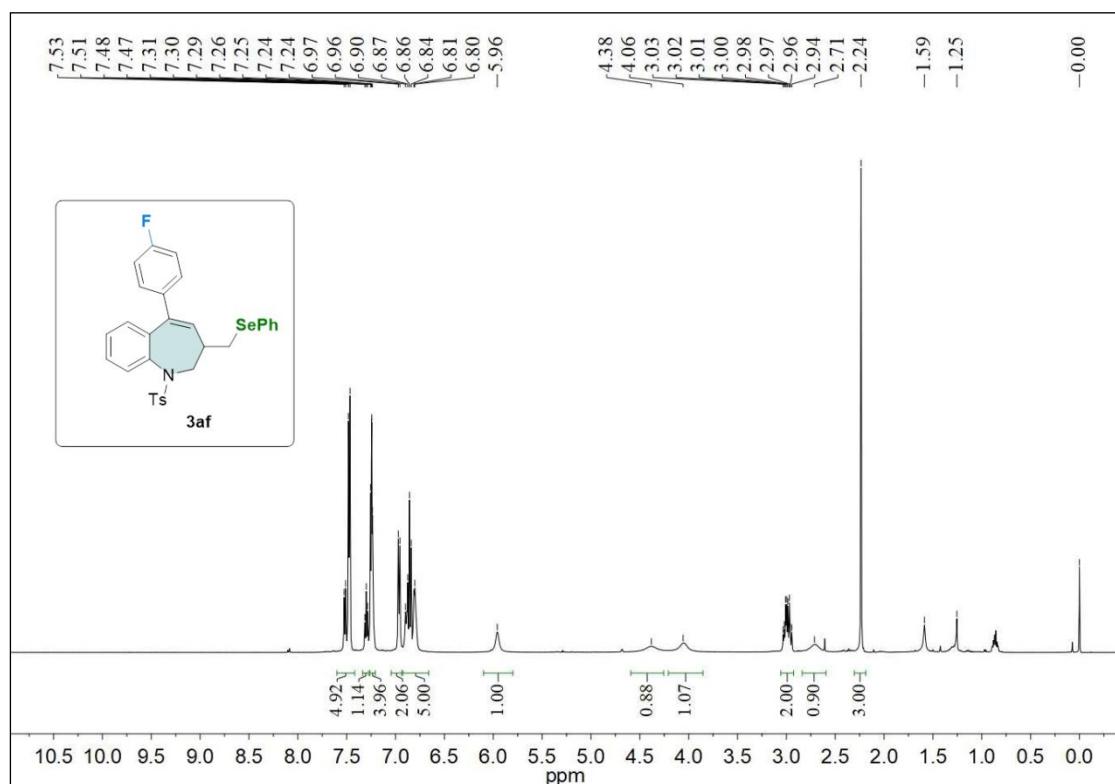
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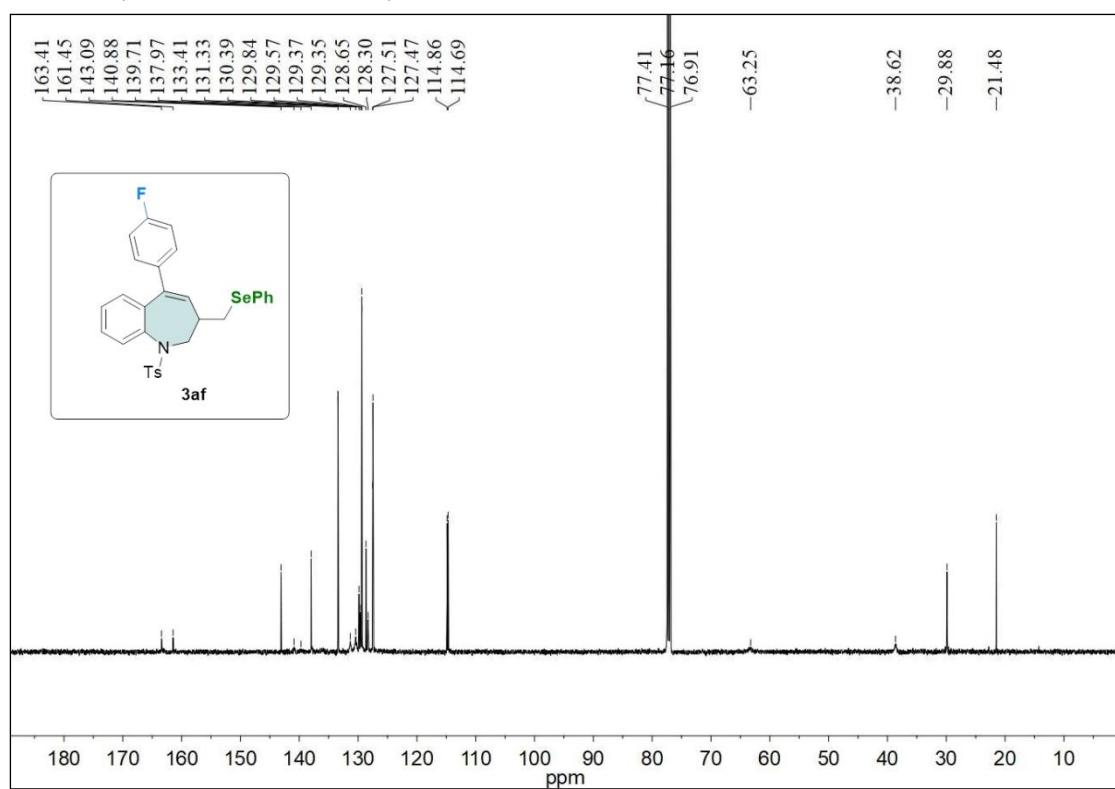
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



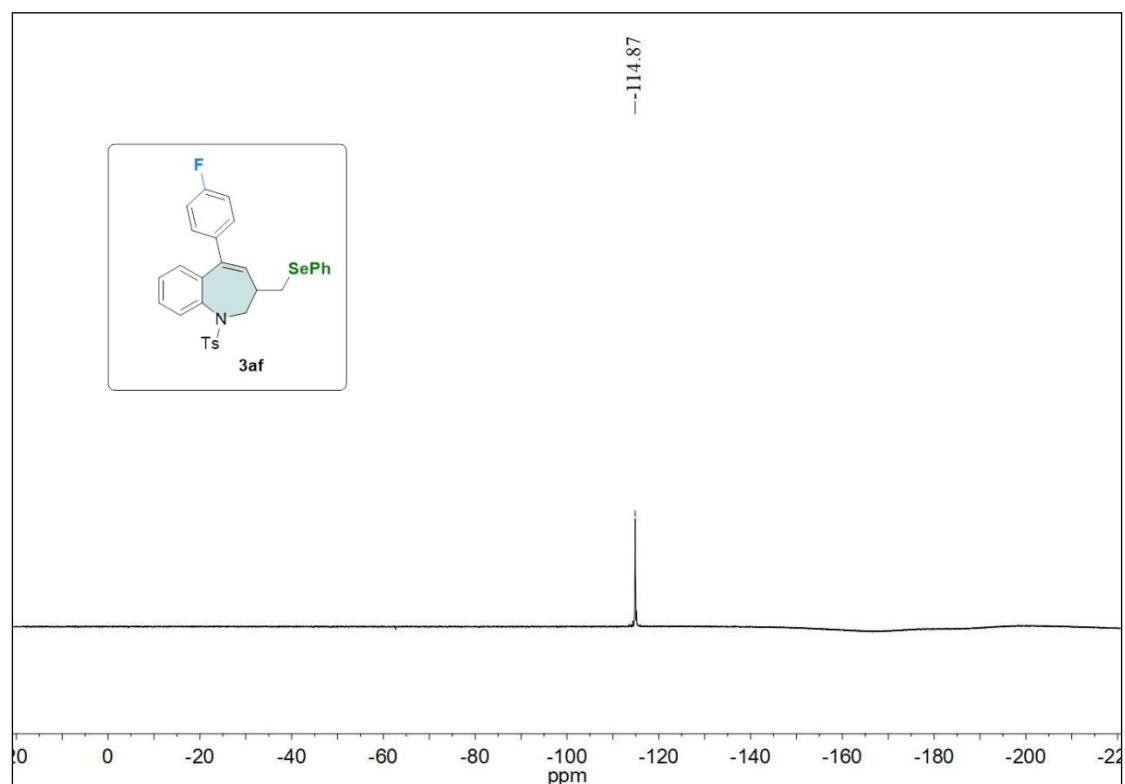
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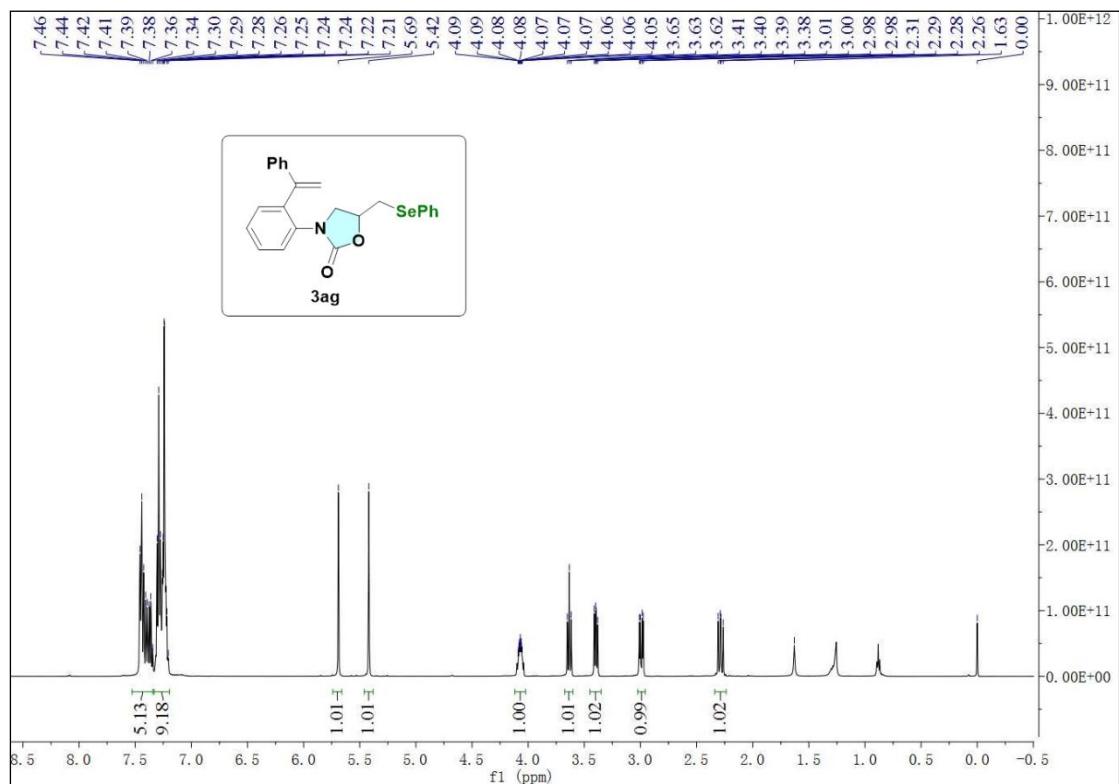
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



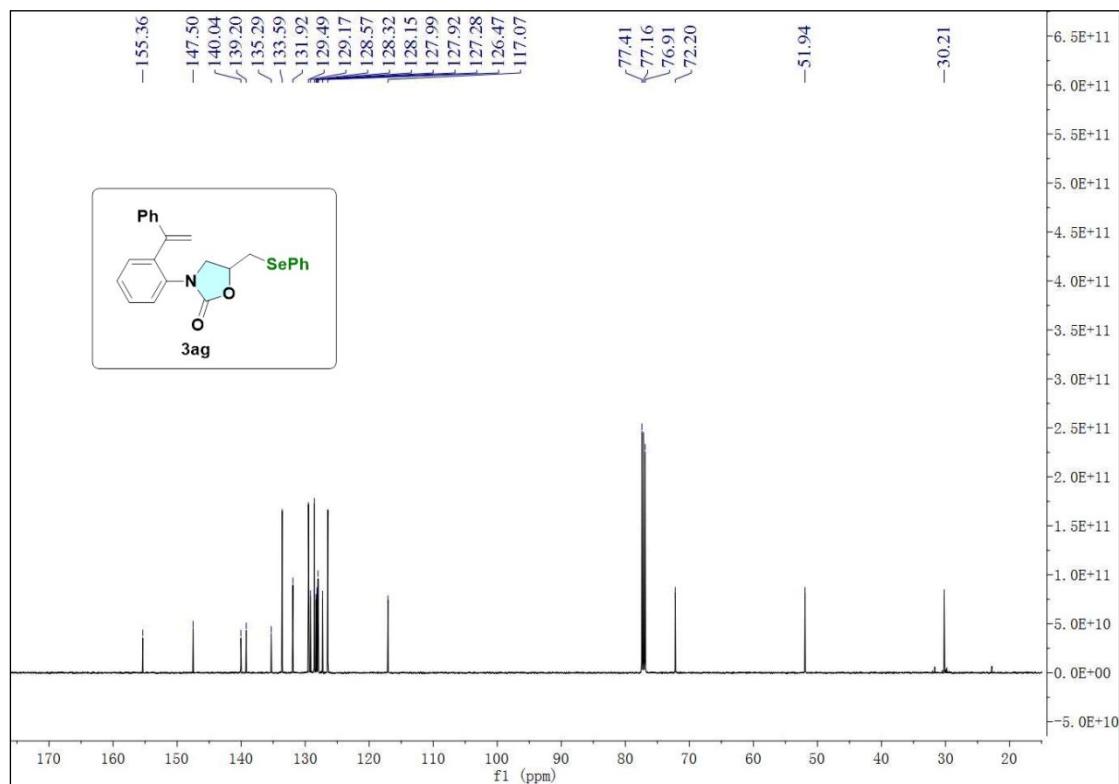
<sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)



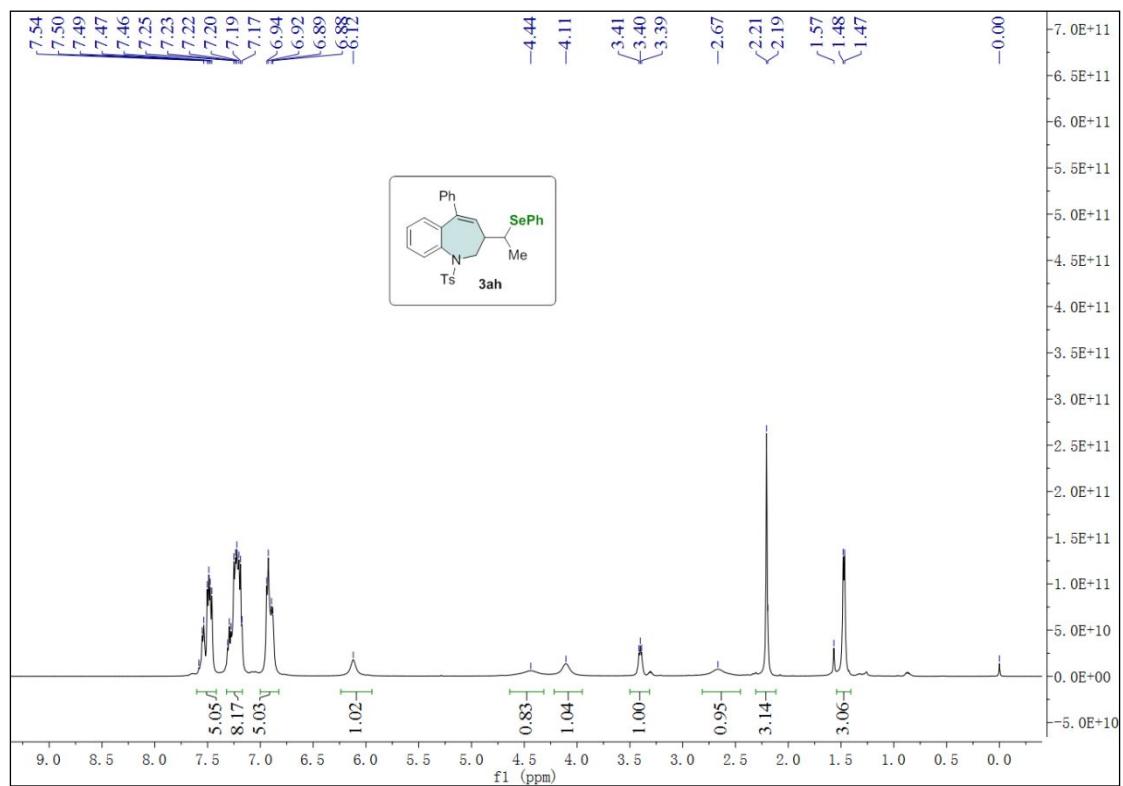
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



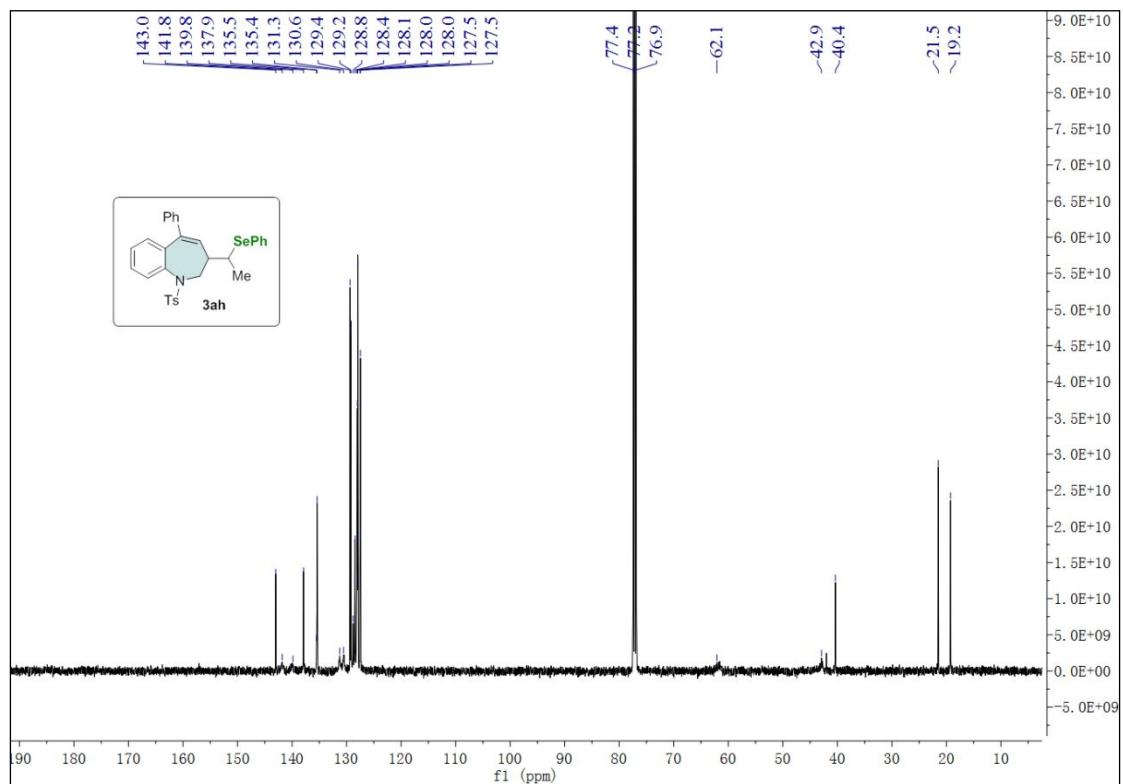
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



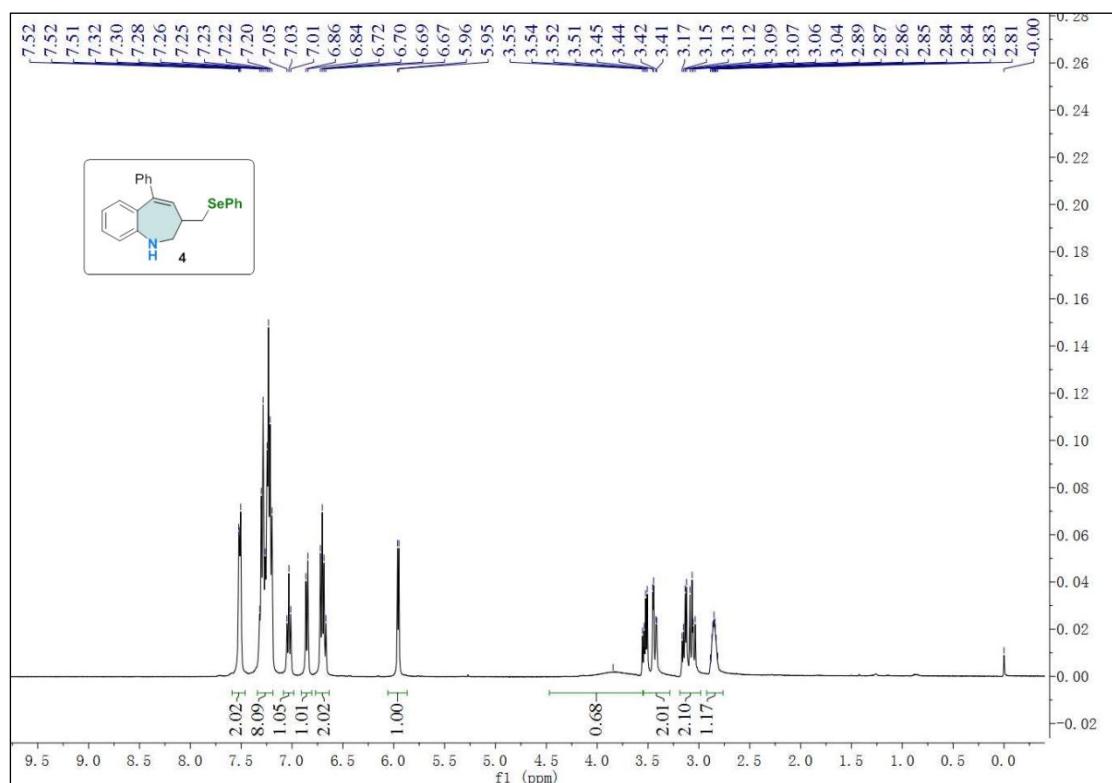
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



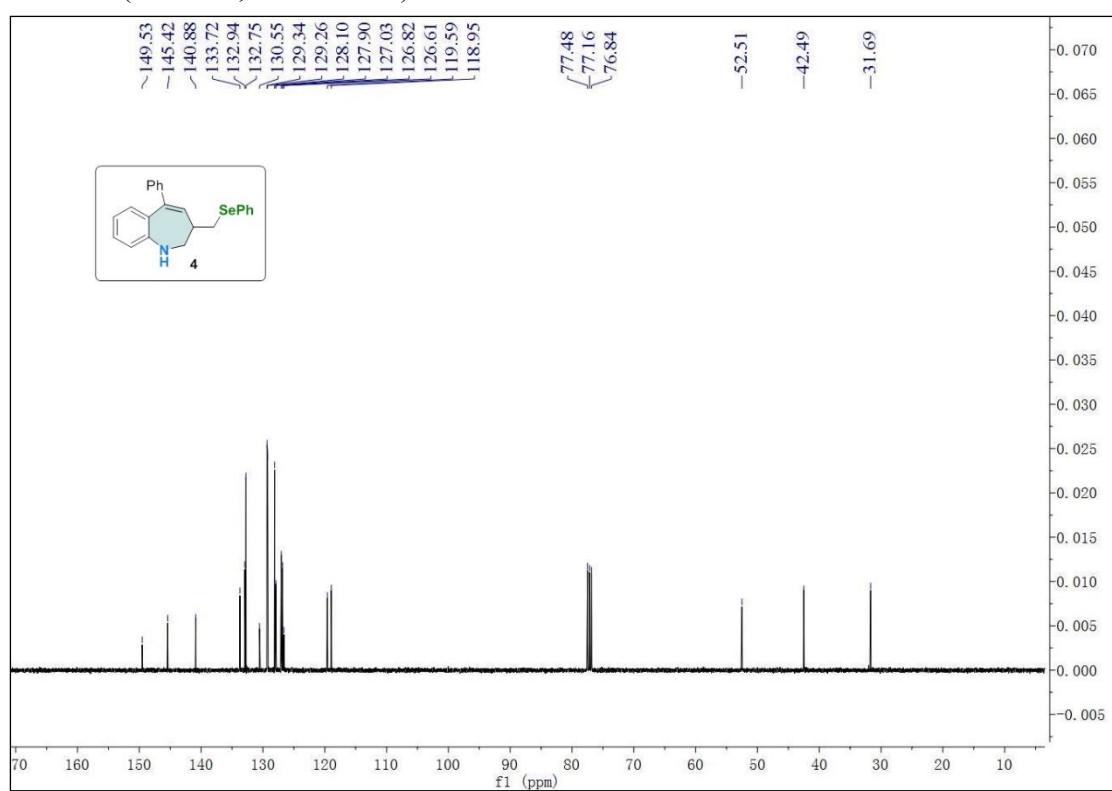
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



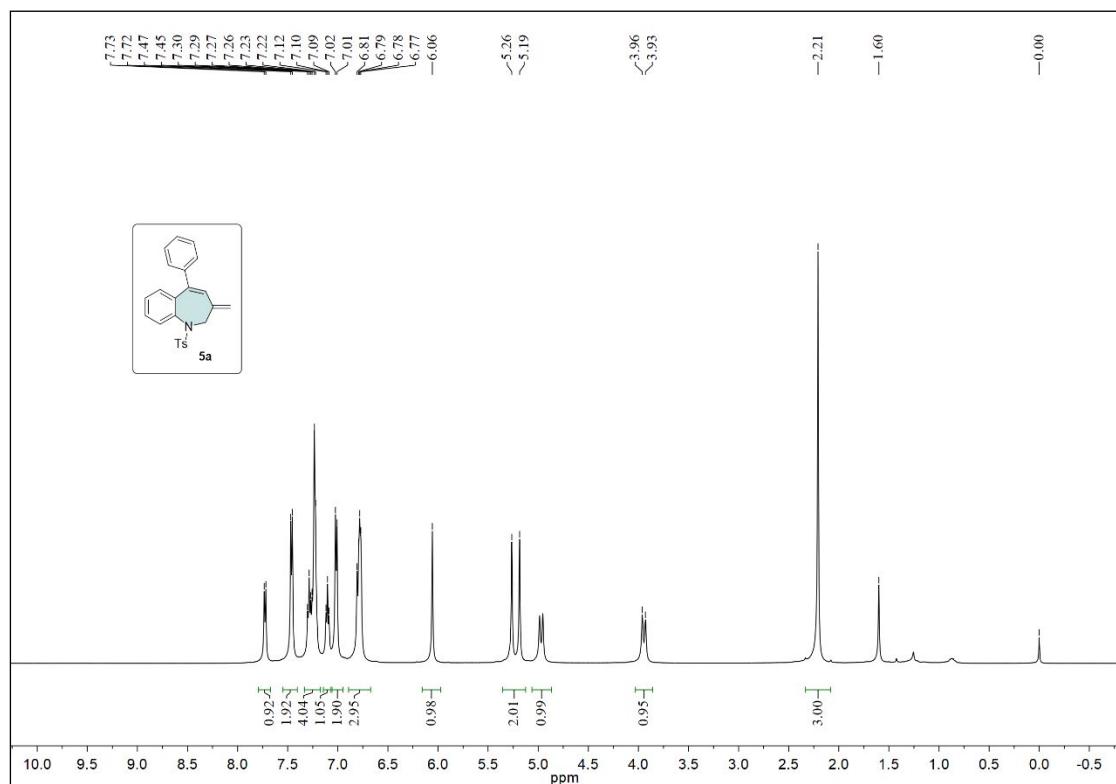
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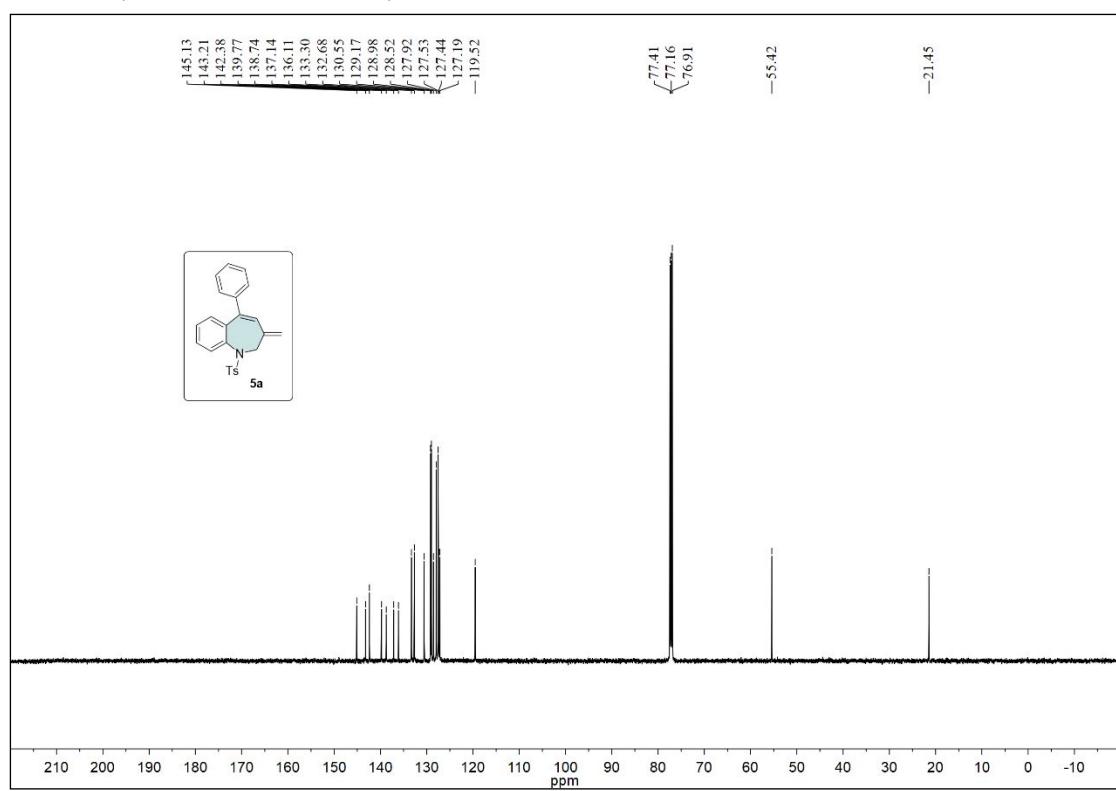
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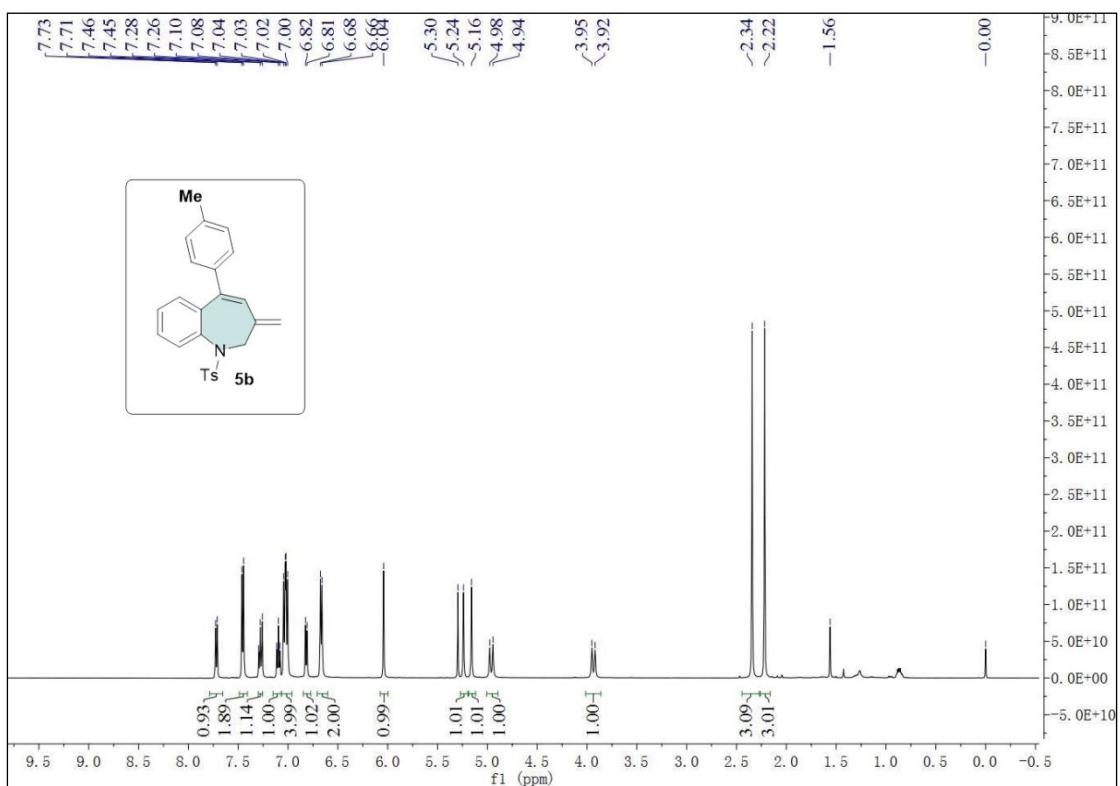
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



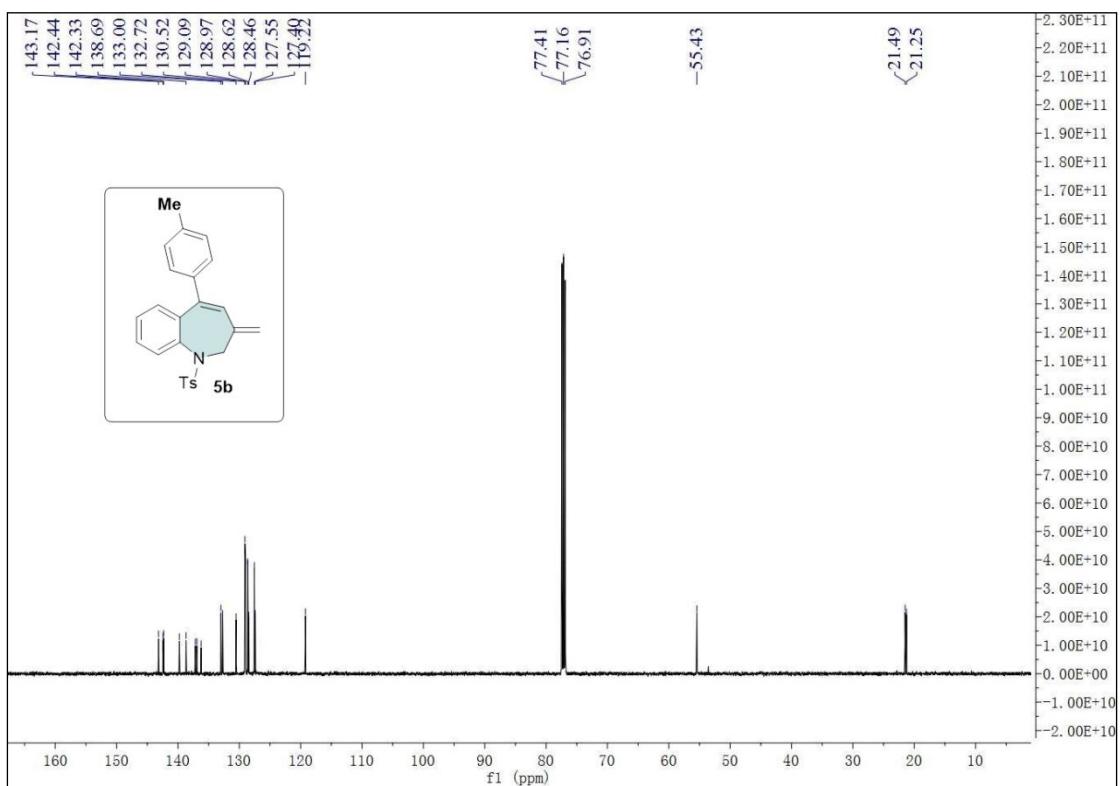
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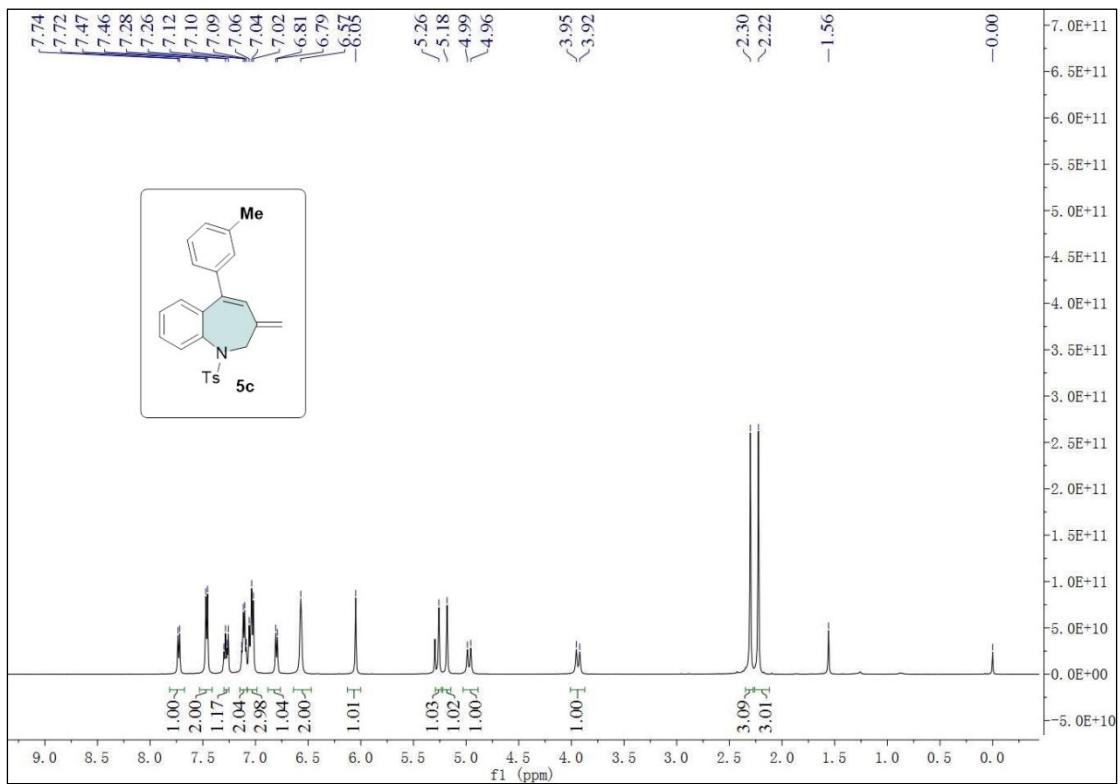
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



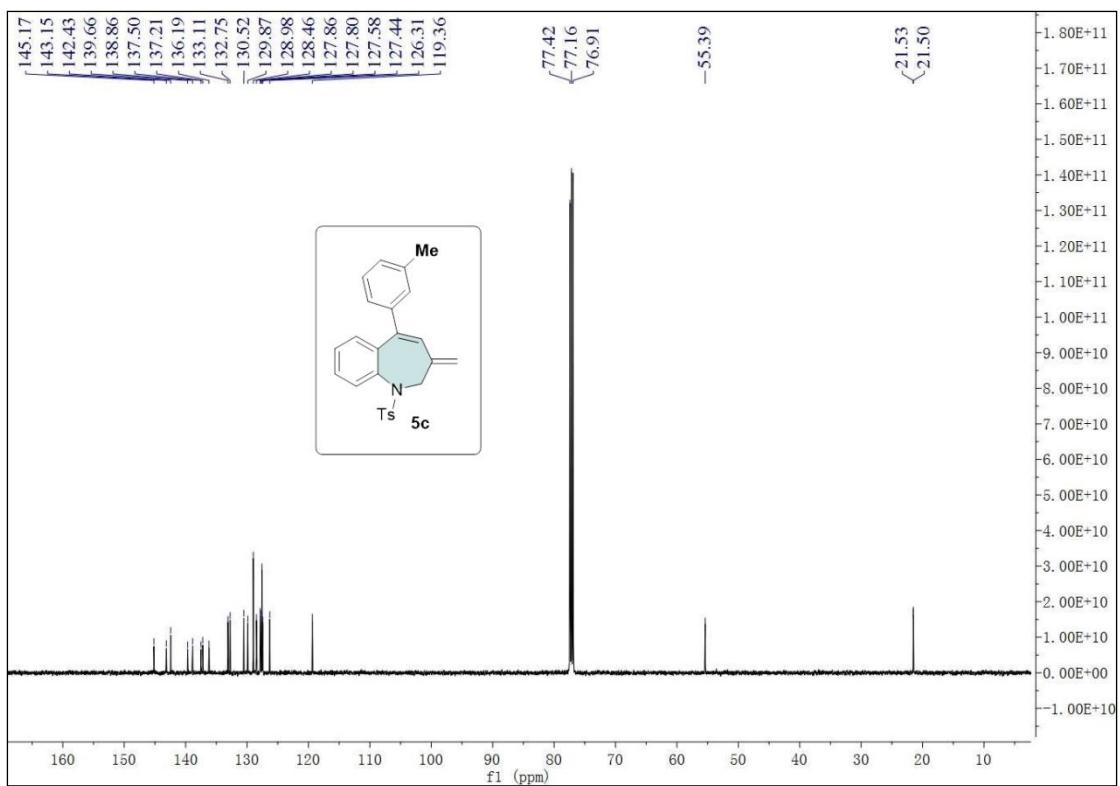
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



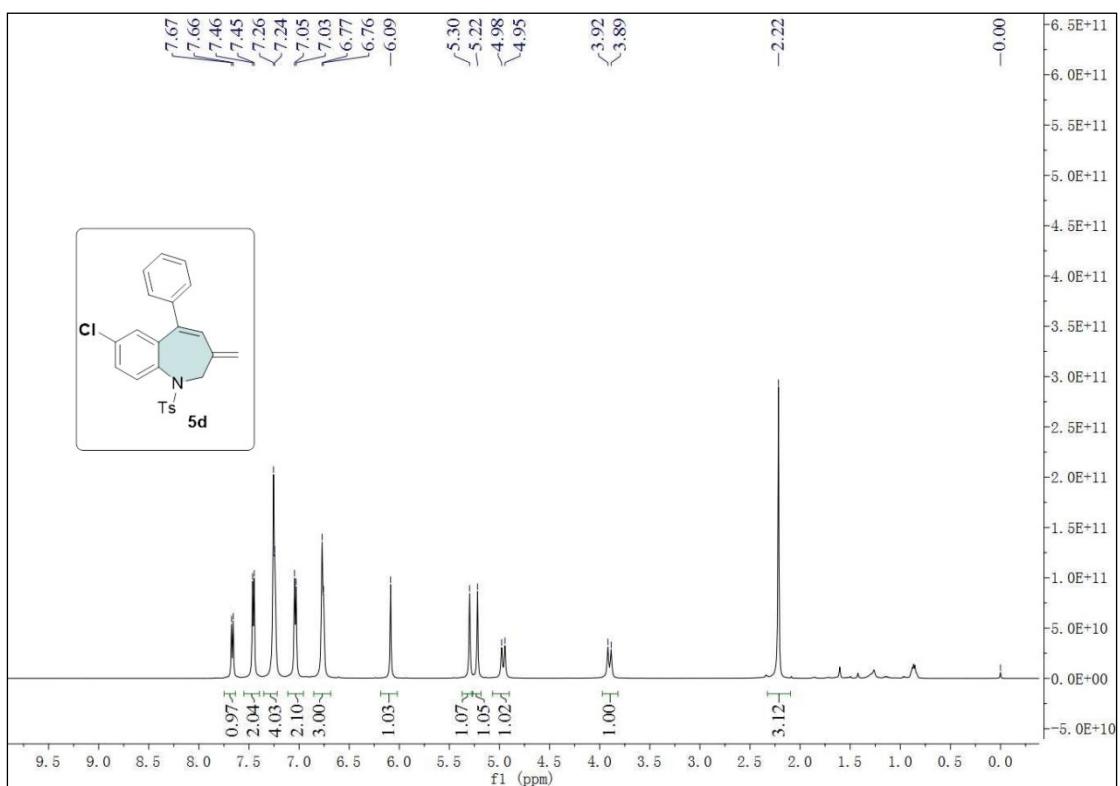
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)



<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)



<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)

