

## Supporting Information

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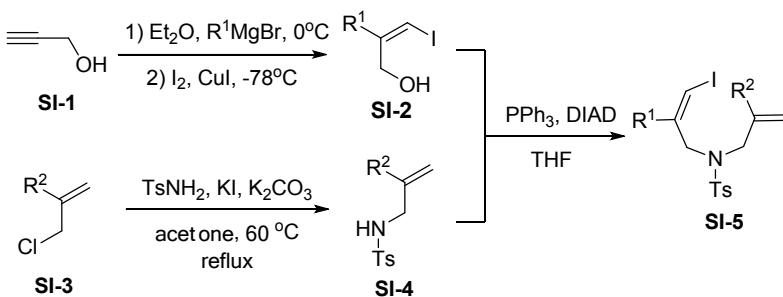
## I. General Information

Organic solvents (Aldrich) were used without further purification. Purifications of reactions products were carried out by flash chromatography using Merck silica gel (40-63  $\mu\text{m}$ ).  $^1\text{H}$  NMR (400 MHz),  $^{13}\text{C}$  NMR (100 MHz) were measured on a Brucker Avance 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm,  $\delta$ ) downfield from residual solvents peaks and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), doublet (d), triplet (t). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). Unless otherwise noted, all other commercially available reagents and solvents were used without further purification.

## II. The General Synthetic Procedure for substrates Vinyl Iodide **SI-5** and **SI-6**, N-Tosyl Hydrazones **SI-8**

### General Procedure:

Vinyl iodides **SI-5** were prepared through Mitsunobu reaction from vinyl iodiel alcohols **SI-2** and allyl amine **SI-4**.

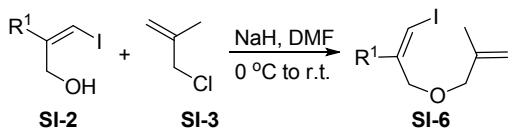


**Preparation of SI-2:** Compounds **SI-2** were prepared as described in the literature<sup>1</sup>. To a stirred solution of propargyl alcohol **SI-1** (50 mmol, 1.0 equiv) in anhydrous THF (100 mL) under  $\text{N}_2$  atmosphere was added CuI (5 mmol, 10 mol%) and the mixture was cooled to  $-78^\circ\text{C}$ . Grignard reagent **SI-2** (125 mmol, 2.5 equiv), which had been freshly prepared in THF, was then added via constant pressure funnel maintain the temperature below  $-60^\circ\text{C}$  for 1h. Then, the mixture was allowed to warm up to room temperture and vigorously stirred overnight. The reaction was cooled again to  $-78^\circ\text{C}$  and treated with  $\text{I}_2$  (55 mmol, 1.1 equiv) in anhydrous THF (100 mL). After warming up to room temperature and stirring at r.t. for additional 1h, the reaction mixture was kept in refrigerator at about  $0\text{-}3^\circ\text{C}$  overnight. The mixture was cooled to  $0^\circ\text{C}$  and was quenched with saturated aqueous  $\text{NH}_4\text{Cl}$  (50 mL). The two phase mixture was poured through a separatory funnel and combined organic layers were washed extracted with saturated aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  (2 x 50 mL) and saturated aqueous  $\text{NaCl}$  (100 mL), and dried over  $\text{Na}_2\text{SO}_4$ . It was purified by column chromatography to give **SI-2**.

**Preparation of SI-4:** Compounds **SI-4** were prepared as described in the literature.<sup>2</sup> Dropwise adding 3-Chloro-2-methylpropene **SI-3**(10 mmol, 1.0 equiv) to the mixture of Tosylamide (30 mmol, 3.0 equiv),  $\text{K}_2\text{CO}_3$  (25 mmol, 2.5 equiv), KI (5 mmol, 0.5

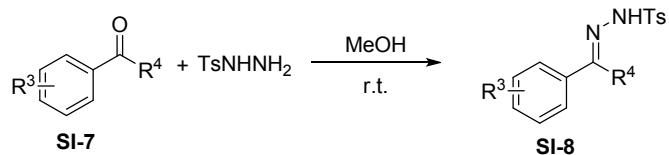
equiv) and acetone (50 mL). The mixture was stirred with reflux at 60 °C for 5 h. The precipitate that had formed was filtered off and then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The crude product was purified by column chromatography (PE:EA, 15:1) to give the **SI-4** as a white solid.

**Preparation of SI-5:** Compounds **SI-5** were prepared as described in the literature.<sup>3</sup> To a solution of **SI-4** (6.0 mmol, 1.2 equiv) in THF (15 mL) at room temperature was added PPh<sub>3</sub> (6.0 mmol, 1.2 equiv) and DIAD (6.0 mmol, 1.2 equiv). Then a solution of **SI-2** (5.0 mmol, 1.0 equiv) in 10 mL THF was added by constant pressure funnel under moderate stirring. Then the mixture was stirred overnight. After washed with water (50 mL x 3) and 1N HCl (20 mL), then the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and purification by column chromatography to give **SI-5**.



**Preparation of SI-6:** Compounds **SI-6** were prepared through the way described in the literature.<sup>4</sup> To a solution of **SI-2** (10.0 mmol, 1.0 equiv) in DMF (15 mL) at 0 °C was added NaH (12 mmol, 1.2 equiv) for 50 min. Then a solution of **SI-3** (12 mmol, 1.2 equiv) in 5 mL DMF was added dropwise by constant pressure funnel under vigorous stirring. Then the mixture was stirred and refluxed at r.t. for 1 h. After washed with water (50 mL x 3) and then the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and purification by column chromatography (PE:EA, 5:1) to give **SI-6**.

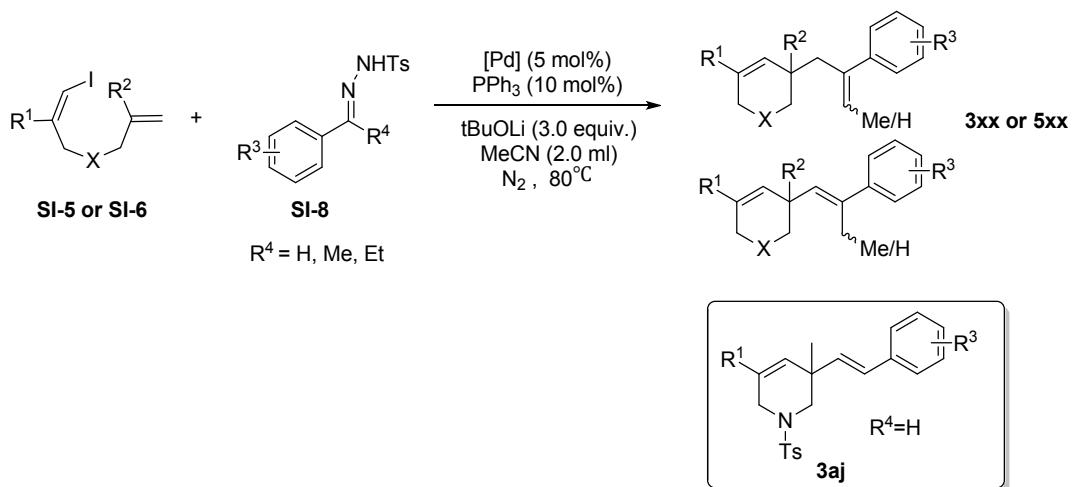
### Preparation of SI-8:



<sup>5</sup>To a solution of p-Toluenesulfonyl hydrazide (5.0 mmol) in 12mL MeOH, **SI-7** (5.0 mmol) was added dropwise. The solution was stirred in room temperature for 3 hours, and then cooled to 0 °C. The solid in solution was filtrated and washed by a little cooled MeOH. Then N-Tosyl Hydrazones **SI-8** was synthesized.

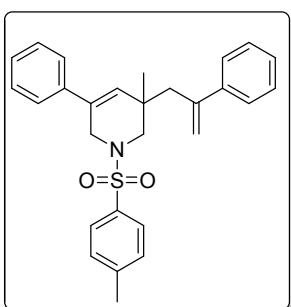
### III. The General Synthetic Procedure and Analytical Data for products

#### General Procedure:



To the solution of vinyl iodide **SI-5** or **SI-6** (0.2 mmol, 1.0 equiv.), N-Tosyl Hydrazones **SI-8** (0.24 mmol, 1.2 equiv.), Pd(dba)<sub>2</sub> (0.01 mmol, 5 mol%), PPh<sub>3</sub> (0.02 mmol, 10 mol%) and tBuOLi (0.6 mmol, 3.0 equiv.) in 2.0 mL MeCN under N<sub>2</sub> atmosphere. The reactions were operated in sealed tube at 80 °C. After stirring for 3 hours, the mixture was evaporated and purified by flash chromatography to give product **3 or 5**.

### Analytical Data:



**3aa**

C<sub>28</sub>H<sub>29</sub>NO<sub>2</sub>S

**MW:** 443.60 g.mol<sup>-1</sup>

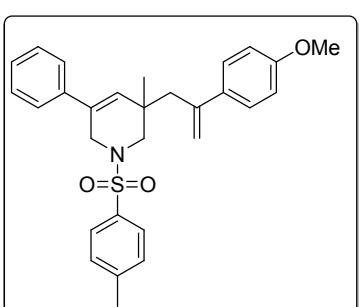
**Yellow liquid**

**Yield:** 88%

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm):** δ 7.73 (d, *J* = 8.0 Hz, 0.58H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.38 – 7.29 (m, 9H), 7.22-7.20 (m, 3H), 6.96 – 6.94 (m, 2H), 6.18(s, 0.14H), 5.78(s, 0.14H), 5.61 (s, 1H), 5.34 (d, *J* = 1.2 Hz, 1H), 5.18 (s, 1H), 3.75 (dd, *J* = 51.6, 15.6 Hz, 2.4H), 2.97 – 2.87 (m, 2.4H), 2.68 (dd, *J* = 14.0, 11.6 Hz, 2H), 2.42 (s, 3.86H), 2.06 (s, 0.7H), 1.43 (s, 0.7H), 1.03 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm):** 145.5, 143.6, 143.0, 138.4, 133.1, 132.2, 130.7, 129.7, 128.5, 128.5, 128.3, 127.7, 127.2, 126.6, 125.2, 118.0, 53.7, 46.5, 45.5, 37.4, 24.7, 21.6.

**HRMS (ESI):** Calcd for C<sub>28</sub>H<sub>29</sub>NO<sub>2</sub>S+H 444.1977, found 444.1980.



**3ab**

C<sub>29</sub>H<sub>31</sub>NO<sub>3</sub>S

**MW:** 473.63 g.mol<sup>-1</sup>

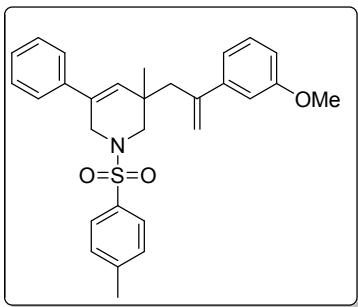
**Brown liquid**

**Yield:** 86%

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm):** 7.5 (d, *J* = 8.4 Hz, 0.5H ), 7.52 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 4.0 Hz, 1H) 7.23 – 7.21 (m, 5H), 7.15-7.14 (m, 2H), 6.92 -6.90 (m, 2H), 6.78 -6.75 (m, 2.5H), 6.10(s, 0.21H), 5.65(s, 0.21H), 5.54 (s, 1H), 5.20 (d, *J* = 1.6 Hz, 1H), 5.02 (d, *J*=0.8Hz, 1H), 3.80 – 3.76 (m, 1H), 3.73 (s, 3.7H), 3.62 – 3.58 (m, 1.3H), 2.81 (dd, *J* = 27.3, 12.3 Hz, 2.39H), 2.59 (dd, *J* = 37.1, 12.3 Hz, 2H), 2.35 (s, 3.6H), 1.95 (s, 0.62H), 1.35 (s, 0.65H), 0.96 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm):** 159.0, 144.8, 143.5, 138.4, 135.4, 132.9, 132.3, 130.5, 129.7, 128.3, 127.7, 127.6, 125.2, 116.4, 113.8, 55.3, 53.7, 46.4, 45.6, 37.4, 24.7, 21.5.

**HRMS (ESI):** Calcd for C<sub>29</sub>H<sub>31</sub>NO<sub>3</sub>S+H 474.2103, found 474.2106



**3ac**

C<sub>29</sub>H<sub>31</sub>NO<sub>3</sub>S

**MW:** 473.63 g.mol<sup>-1</sup>

Brown liquid

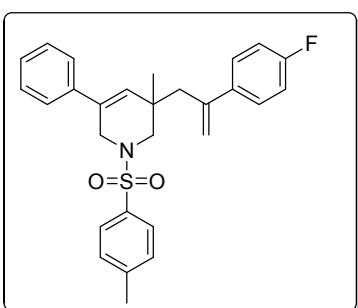
**Yield:** 77%

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm):** 7.72 (d, *J* = 7.6 Hz, 0.5H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.34 – 7.20 (m, 8H), 7.00 – 6.95 (m, 3H), 6.9 (s, 1H), 6.80 (d, *J* = 7.6 Hz, 1H ), 6.18 (s, 0.19H), 5.79 (s, 0.19H), 5.63 (s, 1H), 5.35 (s, 1H), 5.17 (s, 1H), 3.81 (t, *J* = 7.7 Hz, 1.63H), 3.76 (s, 3H), 3.70 (d, *J* = 15.4 Hz, 1H), 2.91 (dd, *J* = 44.5, 12.3 Hz, 2.52H), 2.68 (dd, *J* = 28.0, 12.3 Hz, 2H), 2.42 (s, 3.83H), 2.04 (s, 0.72H), 1.43 (s, 0.76H), 1.03 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm):** 159.6, 145.4, 144.5, 143.6, 138.4, 132.8, 132.2, 130.7, 129.7, 129.4, 128.6, 128.3, 127.7, 125.2, 119.2, 118.0, 112.7, 112.4, 55.3, 53.6, 46.5, 45.5, 37.4, 24.7, 21.6.

**HRMS (ESI):** Calcd for C<sub>29</sub>H<sub>31</sub>NO<sub>3</sub>S+H 474.2103, found 474.2106

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**3ad**

C<sub>28</sub>H<sub>28</sub>FNO<sub>2</sub>S

**MW:** 416.59 g.mol<sup>-1</sup>

Brown liquid

**Yield:** 73%

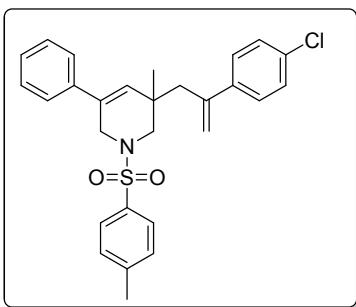
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm):** 7.72 (d, *J* = 7.6Hz, 0.5H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.34 – 7.30 (m, 6H), 7.25 – 7.23(m, 3H), 6.99 (d, *J* = 7.3 Hz, 4H), 6.17 (s, 0.19H), 5.73 (s, 0.19H), 5.59 (s, 1H), 5.30 (s, 1H), 5.17 (s, 1H), 3.85 - 3.70 (m, 2.65H), 3.08 – 2.79 (m, 2.47H), 2.64 (dd, *J* = 11.8, 7.2 Hz, 2H), 2.42 (s, 3.83H), 2.04 (s, 0.75H), 1.42 (s, 0.73H), 1.02 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm):** 162.2 (d, *J* = 197), 144.4, 143.7, 139.1, 138.3, 132.7, 132.0, 130.8, 129.7, 128.7, 128.4, 128.2, 127.7(d, *J* = 4Hz), 125.2, 118.0, 115.2 (d, *J* = 17Hz)), 53.6, 46.5, 45.7, 37.4, 24.8, 21.6, 21.6.

**<sup>19</sup>F{<sup>1</sup>H} NMR (376 MHz, CDCl<sub>3</sub>, δ ppm):** 110.0.

**HRMS(ESI):** Calcd for C<sub>28</sub>H<sub>28</sub>FNO<sub>2</sub>S+H 462.1903, found 412.1900.

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**3ae**

C<sub>28</sub>H<sub>28</sub>ClNO<sub>2</sub>S

**MW:** 478.05 g.mol<sup>-1</sup>

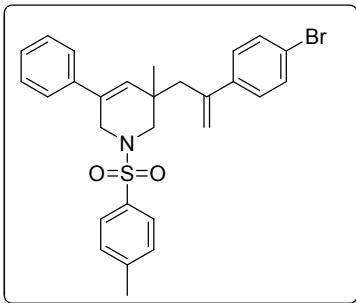
Brown liquid

**Yield:** 76%

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm):** 7.72 (d, *J* = 7.6 Hz, 0.5H), 7.60 (d, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 3.6H), 7.28 - 7.23 (m, 7H), 6.95 (d, *J* = 6.6 Hz, 2H), 6.17 (s, 0.18H), 5.77 (s, 0.18), 5.56 (s, 1H), 5.33 (s, 1H), 5.20 (s, 1H), 3.85 - 3.68 (m, 2.52H), 3.23-2.84 (m, 2.5H), 2.64 (dd, *J* = 12.0, 6.1 Hz, 2H), 2.43 (s, 3.65H), 2.04 (s, 0.84H), 1.41 (s, 0.72H), 1.02 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm):** 144.4, 143.7, 141.5, 138.2, 133.1, 132.7, 132.0, 130.9, 129.7, 128.6, 128.4, 128.0, 127.7, 127.7, 125.2, 118.5, 53.6, 46.5, 45.6, 37.4, 24.7, 21.6.

**HRMS(ESI):** Calcd for C<sub>28</sub>H<sub>28</sub>ClNO<sub>2</sub>S+H 478.1608, found 478.1605.



**3af**

C<sub>28</sub>H<sub>28</sub>BrNO<sub>2</sub>S

**MW:** 522.50 g.mol<sup>-1</sup>

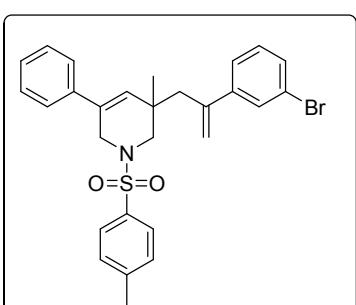
Brown liquid

**Yield:** 53%

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm):** 7.73 (t, *J* = 5.6Hz, 0.7H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.42 (d, *J* = 7.7 Hz, 3H), 7.32 (d, *J* = 7.9 Hz, 4H), 7.26 – 7.21 (m, 5H), 6.94 (d, *J* = 6.6 Hz, 2H), 6.16 (s, 0.21H), 5.83 (s, 0.21H), 5.55 (s, 1H), 5.34 (s, 1H), 5.20 (s, 1H), 3.74 (q, *J* = 15.5 Hz, 2.58H), 3.00 – 2.85 (m, 2.52H), 2.67 – 2.61 (m, 2H), 2.43 (s, 3.89H), 2.04 (s, 0.76H), 1.41 (s, 0.86H), 1.03 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm):** 144.4, 143.7, 141.9, 138.2, 132.7, 132.0, 131.5, 129.8, 128.4, 128.3, 127.7, 127.7, 125.2, 121.3, 118.5, 53.6, 46.5, 45.6, 37.4, 24.7, 21.6.

**HRMS(ESI):** Calcd for C<sub>28</sub>H<sub>28</sub>BrNO<sub>2</sub>S+H 522.1102, found 522.1105.



**3ag**

C<sub>28</sub>H<sub>28</sub>BrNO<sub>2</sub>S

**MW:** 522.50 g.mol<sup>-1</sup>

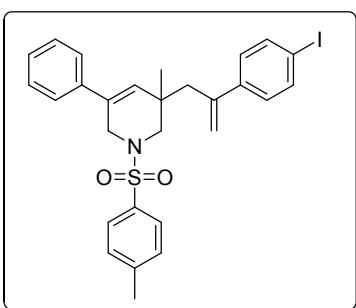
Brown liquid

**Yield:** 57%

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm):** 7.73 (d, *J* = 7.6 Hz, 0.5H), 7.62 (d, *J* = 7.7 Hz, 2H), 7.50 (s, 1H), 7.30 (m, 10H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 6.2 Hz, 2H), 6.15 (s, 0.19H), 5.76 (s, 0.19H), 5.60 (s, 1H), 5.35 (s, 1H), 5.23 (s, 1H), 3.76-3.71 (s, 2.34H), 2.93 (dd, *J* = 62.2, 12.3 Hz, 2.35H), 2.64 (dd, *J* = 11.9, 5.2 Hz, 2H), 2.43 (s, 3.76H), 2.04 (s, 0.82H), 1.42 (s, 0.61H), 1.01 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm):** 145.2, 144.2, 143.6, 138.2, 132.7, 131.8, 131.0, 130.2, 130.0, 129.8, 129.6, 128.4, 127.7, 127.6, 125.3, 125.2, 122.6, 119.1, 53.5, 46.5, 45.3, 37.4, 24.8, 21.6.

**HRMS(ESI):** Calcd for C<sub>28</sub>H<sub>28</sub>BrNO<sub>2</sub>S+H 522.1102, found 522.1105.



**3ah**

C<sub>28</sub>H<sub>28</sub>INO<sub>2</sub>S

**MW:** 569.50 g.mol<sup>-1</sup>

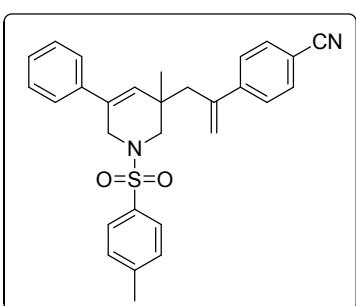
Brown liquid

**Yield:** 42%

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm):** 7.73 (dd, *J* = 8.4 Hz, *J* = 6.0 Hz, 0.8H), 7.61 (t, *J* = 8.4 Hz, 4.5H), 7.34 – 7.31 (m, 5H), 7.25 - 7.23 (m, 2H), 7.10 (dt, *J* = 8.4 Hz, *J* = 2.4 Hz, 2H), 6.91 (dt, *J* = 6.4, *J* = 1.6 Hz, 2H), 6.16 (s, 0.2 H), 5.77 (s, 0.2H), 5.53 (s, 1H), 5.34 (d, *J* = 1.6 Hz, 1H), 5.20 (s, 1H), 3.74 (q, *J* = 16.0 Hz, 2.6H), 2.52 (dd, *J* = 28.0, 9.6 Hz, 0.45H), 2.92 (dd, *J* = 38.4, 11.2 Hz, 2 H), 2.63 (t, *J* = 12.4 Hz, 2H), 2.44 (s, 3H), 2.42 (s, 0.8H), 2.03 (d, *J* = 1.2 Hz, 0.62H), 1.41 (s, 0.61H), 1.02 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm):** 144.5, 143.7, 142.6, 138.3, 137.5, 132.7, 131.9, 130.9, 129.8, 128.6, 128.5, 127.8, 127.7, 125.1, 118.4, 92.73, 53.60, 46.5, 45.5, 37.4, 24.7, 21.6.

**HRMS(ESI):** Calcd for C<sub>28</sub>H<sub>28</sub>INO<sub>2</sub>S+H 570.0964, found 570.0961



**3ai**

C<sub>29</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>S

**MW:** 468.61 g.mol<sup>-1</sup>

Brown liquid

**Yield:** 45%

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm):** 7.72 (d, *J* = 8.0Hz, 0.5H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.31 (m, 4H), 7.26 –

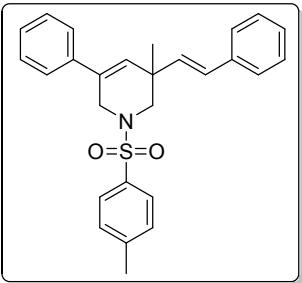
7.20 (m, 3H), 6.91 (dd,  $J = 6.4, 3.1$  Hz, 2H), 6.18 (s, 0.18), 5.67 (s, 0.18), 5.49 (s, 1H), 5.45 (s, 1H), 5.36 (s, 1H), 3.92 – 3.86 (m, 1.56H), 3.61 (dd,  $J = 15.6, 1.7$  Hz, 1H), 3.19 (d,  $J = 11.3$  Hz, 1H), 3.10 (q,  $J = 11.3$  Hz, 0.63H), 2.96 (d,  $J = 13.5$  Hz, 1H), 2.67 – 2.50 (m, 2H), 2.44 (s, 3.76H), 2.09 (s, 0.61H), 1.42 (s, 0.61H), 0.98 (s, 3H).

**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm):** 147.6, 144.2, 143.8, 138.0, 132.8, 131.56, 131.3, 129.8, 128.4, 127.9, 127.7, 127.3, 125.0, 120.6, 118.8, 110.7, 53.3, 46.4, 45.1, 37.4, 24.8, 21.6.

**HRMS(ESI):** Calcd for  $\text{C}_{29}\text{H}_{28}\text{N}_2\text{O}_2\text{S} + \text{H}$  469.1950, found 469.1953

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**3aj**



$\text{C}_{27}\text{H}_{27}\text{NO}_2\text{S}$

**MW:** 429.57 g.mol<sup>-1</sup>

Brown liquid

**Yield:** 87%

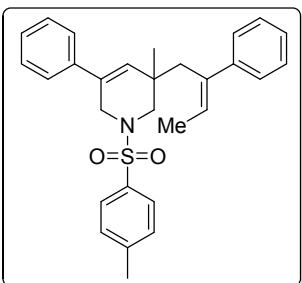
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm):** 7.71 (d,  $J = 8.2$  Hz, 2H), 7.34 (d,  $J = 3.6$  Hz, 4H), 7.32 – 7.27 (m, 6H), 7.02 (dd,  $J = 8.6, 2.9$  Hz, 2H), 6.42 (d,  $J = 16.2$  Hz, 1H), 6.24 (d,  $J = 16.2$  Hz, 1H), 5.93 (s, 1H), 3.94 (dd,  $J = 5.6, 1.9$  Hz, 2H), 3.09 (dd,  $J = 74.2, 11.3$  Hz, 2H), 2.40 (s, 3H), 1.35 (s, 3H).

**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm):** 143.7, 138.2, 137.1, 134.8, 133.2, 132.4, 130.2, 129.8, 129.2, 128.6, 128.5, 128.0, 127.8, 127.5, 126.4, 125.4, 53.5, 46.3, 39.4, 24.7, 21.6.

**HRMS(ESI):** Calcd for  $\text{C}_{27}\text{H}_{27}\text{NO}_2\text{S} + \text{H}$  430.1841, found 430.1844.

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**3ak**



$\text{C}_{29}\text{H}_{31}\text{NO}_2\text{S}$

**MW:** 457.62 g.mol<sup>-1</sup>

Brown liquid

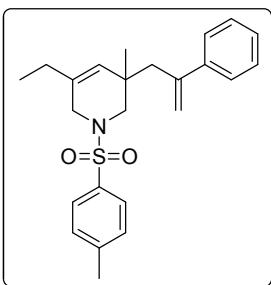
**Yield:** 83%

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm):** 7.73 (t,  $J = 6.8$  Hz, 0.35H), 7.57 (d,  $J = 7.6$  Hz, 2H), 7.30 – 7.19 (m, 11H), 6.89 (d,  $J = 5.1$  Hz, 2H), 5.79 (q,  $J = 7.4$  Hz, 1H), 5.59 (d,  $J = 2.4$  Hz, 1H), 5.59 (s, 0.09H), 3.73 (dd,  $J = 138.1, 15.4$  Hz, 2.4H), 2.79 (dd,  $J = 30.4, 11.2$  Hz, 2.2H), 2.79 (dd,  $J = 112.8, 13.6$  Hz, 2H), 2.42 (s, 3.4H), 2.03 (s, 0.46H), 1.80 (d,  $J = 6.8$  Hz, 3H), 1.59 (s, 0.30H), 1.05 (s, 3H).

**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm):** 145.5, 143.5, 138.4, 137.9, 132.9, 132.5, 132.3, 130.4, 129.7, 129.6, 128.4, 127.7, 126.7, 125.3, 125.1, 54.3, 46.3, 39.4, 38.5, 25.0, 21.5, 15.2.

**HRMS(ESI):** Calcd for  $\text{C}_{29}\text{H}_{31}\text{NO}_2\text{S}+\text{H}$  458.2154, found 458.2151.

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**3ba**

$\text{C}_{24}\text{H}_{29}\text{NO}_2\text{S}$

**MW:** 395.56 g.mol<sup>-1</sup>

Yellow liquid

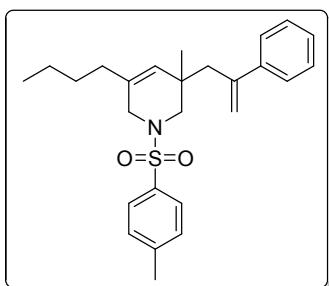
**Yield:** 91%

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm):** 7.69 (d,  $J = 7.6$  Hz, 0.5H), 7.55 (d,  $J = 7.8$  Hz, 2H), 7.34 – 7.26 (m, 9H), 5.70 (s, 0.20H), 5.55 (s, 0.19H), 5.30 (s, 1H), 5.13 (s, 1H), 4.96 (s, 1H), 3.33 – 3.12 (m, 2.54H), 2.81 (dd,  $J = 42.4, 12.2$  Hz, 2.46H), 2.58 – 2.50 (m, 2H), 2.43 (s, 3.8H), 2.01 (s, 0.76H), 1.74 (p,  $J = 7.2$  Hz, 2H), 1.56 (s, 0.78H), 0.89 (s, 3H), 0.76 (t,  $J = 7.4$  Hz, 3H).

**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm):** 145.7, 143.3, 143.1, 132.9, 132.6, 129.6, 129.5, 128.2, 127.8, 127.7, 126.6, 117.5, 53.9, 47.4, 45.4, 36.7, 26.9, 24.8, 21.5, 11.7.

**HRMS(ESI):** Calcd for  $\text{C}_{24}\text{H}_{29}\text{NO}_2\text{S}+\text{H}$  396.1997, found 396.1994.

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**3ca**

$\text{C}_{26}\text{H}_{33}\text{NO}_2\text{S}$

**MW:** 423.61 g.mol<sup>-1</sup>

Yellow liquid

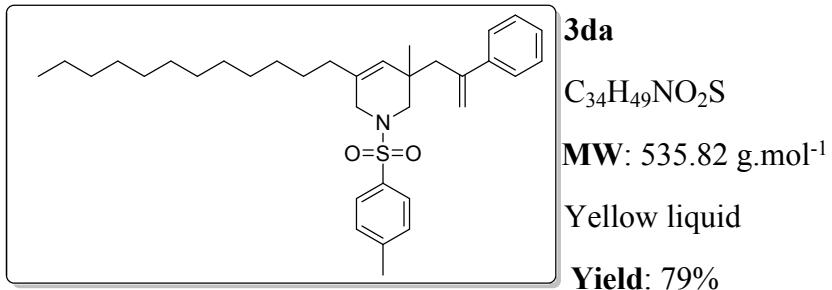
**Yield:** 82%

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm):** 7.67 – 7.59 (m, 1H), 7.47 (d,  $J = 8.2$  Hz, 2H), 7.26 – 7.19 (m, 8H), 5.63 (s,  $J = 1.2$  H, 0.17H), 5.48 (s, 0.18H), 5.23 (d,  $J = 1.8$  Hz, 1H), 5.06 (d,  $J = 1.7$  Hz, 1H), 4.92 (s, 1H), 3.23 – 3.09 (m, 2.42H), 2.78 – 2.65 (m, 2.41H), 2.47 (dd,  $J = 12.2, 8.0$  Hz, 2H), 2.36 (s, 3.9H), 1.94 (d,  $J = 1.1$  Hz, 0.66H), 1.64 (dd,  $J = 12.4, 6.6$  Hz, 2.2H), 1.54 (s, 0.45H) 1.24 – 1.21 (m, 2.3H), 1.10 – 1.06 (m, 22H), 0.81 (s, 3H), 0.76 (t,  $J = 6.9$  Hz, 3.2H).

**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm):** 145.7, 143.3, 143.2, 132.9, 131.4, 129.6, 128.2, 127.7, 127.1, 126.6, 125.9, 117.6, 53.9, 47.4, 45.3, 36.8, 34.0, 29.5, 24.7, 22.3, 21.5, 13.9.

**HRMS(ESI):** Calcd for  $\text{C}_{26}\text{H}_{33}\text{NO}_2\text{S}+\text{H}$  424.2310, found 424.2313.

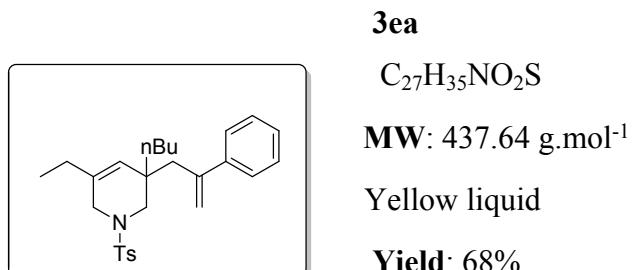
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**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm):** 7.68 (d, *J* = 7.6 Hz, 0.38H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.29 (m, 9H), 5.70(s, 0.12H), 5.55 (s, 0.13H), 5.29 (s, 1H), 5.12 (s, 1H), 4.99 (s, 1H), 3.32 – 3.11 (m, 2.32H), 2.79 (dd, *J* = 42.0, 12.2 Hz, 2.30H), 2.54 (dd, *J* = 11.8, 5.4 Hz, 2H), 2.42 (s, 3.41H), 2.01 (s, 0.39H), 1.71(d, *J* = 4.8Hz, 2H), 1.58 (s, 0.40H), 1.24 (d, *J* = 17.1 Hz, 20H), 1.14 (s, 3H), 0.88 (s, 3.3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm):** 145.6, 143.3, 143.2, 132.7, 131.4, 129.6, 128.9, 128.2, 127.7, 127.1, 126.6, 117.7, 53.9, 47.4, 45.3, 36.8, 34.3, 32.0, 29.7, 29.6, 29.4, 29.4, 29.3, 27.3, 24.7, 22.8, 21.6, 14.2.

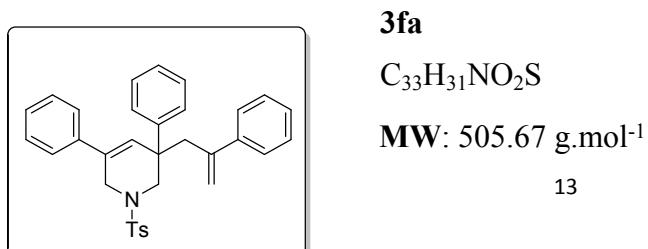
**HRMS(ESI):** Calcd for C<sub>34</sub>H<sub>49</sub>NO<sub>2</sub>S+H 536.3562, found 536.3565.



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm):** 7.68 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.31 (m, 2H), 7.29 – 7.24 (m, 7.2H), 5.67 (s, 0.24H), 5.60 (s, 0.24H), 5.24 (d, *J* = 2.0 Hz, 1H), 5.08 (d, *J* = 1.6 Hz, 1H), 4.93 (s, 1H), 3.26 – 3.23 (m, 2.75H), 2.86 – 2.70 (m, 2.55H), 2.66 – 2.53 (m, 2H), 2.42 (s, 4.2H), 1.98 (d, *J* = 1.2 Hz, 2H), 1.78 – 1.66 (m, 2.78H), 1.30 – 1.23 (m, 2.7H), 1.14 – 1.11 (m, 2.77H), 1.03 (t, *J* = 7.6 Hz, 1H), 0.91 – 0.87 (m, 2.3H), 0.81 (t, *J* = 6.4 Hz, 3H), 0.74 (t, *J* = 7.6 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm):** 146.0, 143.3, 143.2, 138.1, 132.9, 129.6, 128.1, 127.7, 127.0, 126.7, 125.9, 117.5, 52.4, 47.4, 42.9, 41.5, 39.3, 37.1, 27.0, 25.9, 23.3, 21.6, 14.1, 11.7.

**HRMS(ESI):** Calcd for C<sub>27</sub>H<sub>35</sub>NO<sub>2</sub>S+H 438.2467, found 438.2470.



Yellow liquid

**Yield:** 24%

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm):** 7.51 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.16 (m, 16.6H), 6.96 (dd, *J* = 6.4, 2.8Hz, 2H), 6.14 (s, 1H), 5.29 (s, 0.13H), 5.14 (d, *J* = 1.2 Hz, 1H), 4.86 (s, 1H), 3.80 (t, *J* = 2.4 Hz, 2.16H), 3.26 (s, 2H), 3.26 (dd, *J* = 52.8, 14Hz, 2H), 2.39 (s, 3.25H), 1.57 (s, 0.87H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm):** 144.9, 143.9, 143.5, 143.0 138.4, 132.9, 132.4, 129.8, 129.7, 128.4, 128.4, 128.3, 127.8, 127.7, 127.1, 126.9, 126.6, 126.5, 125.3, 118.1, 53.5, 46.4, 45.8, 45.0, 21.5.

**HRMS(ESI):** Calcd for C<sub>33</sub>H<sub>31</sub>NO<sub>2</sub>S+H 506.2154, found 506.2151.

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**5aa**

C<sub>21</sub>H<sub>22</sub>O

**MW:** 290.40 g.mol<sup>-1</sup>

Yellow liquid

**Yield:** 90%

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm):** 7.93 - 7.90 (m, 0.35H), 7.42 – 7.39 (m, 2H), 7.36 – 7.27 (m, 5H), 7.22 (d, *J* = 7.6 Hz, 3H), 6.96 (dd, *J* = 7.7, 1.7 Hz, 2H), 6.26 (s, 0.29H), 5.74 (d, *J*= 0.8Hz, 0.29H), 5.70 (s, 1H), 5.33 (d, *J* = 1.8 Hz, 1H), 5.12 (s, 1H), 4.54 (dd, *J* = 24.0, 1.2 Hz, 0.43H), 4.49 – 4.30 (m, 2.0H), 3.70 (dd, *J* = 44.4, 10.8 Hz, 0.65H), 3.46 (dd, *J* = 104.8, 10.8 Hz, 2H), 2.74 (dd, *J* = 70.8, 13.2 Hz, 2H), 2.17 (dd, *J* = 1.2 Hz, 0.88H), 1.38 (s, 0.86H), 0.95 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm):** 146.1, 143.0, 138.1, 133.3, 131.2, 128.3, 128.2, 127.3, 126.6, 125.9, 124.8, 117.1, 74.3, 66.9, 44.8, 35.6, 23.7.

**HRMS(ESI):** Calcd for C<sub>21</sub>H<sub>22</sub>O+H 291.1749, found 291.1752.

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**5ba**

C<sub>22</sub>H<sub>24</sub>O<sub>2</sub>

**MW:** 320.42 g.mol<sup>-1</sup>

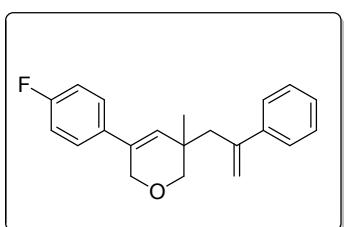
Yellow liquid

**Yield:** 80%

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm):** 7.41 – 7.36 (m, 3H), 7.32 – 7.25 (m, 5H), 6.90 (d, *J* = 6.9 Hz, 2H), 6.76 (d, *J* = 7.8 Hz, 2H), 6.16 (s, 0.31H), 5.74 (s, 0.31H), 5.60 (s, 1H), 5.32 (s, 1H), 5.11 (s, 1H), 4.36 (dd, *J* = 44.0, 16.0Hz, 2.4H), 3.81 (s, 0.86H), 3.78 (s, 3H), 3.63 (d, *J* = 10.8 Hz, 0.53H), 3.57 (d, *J* = 12Hz, 1H), 3.31 (d, *J* = 12 Hz, 1H), 2.72 (dd, *J* = 64, 16 Hz, 2H), 2.16 (s, 0.86H), 1.37 (s, 0.86H), 0.94 (s, 3H).

**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm):** 158.9, 146.1, 143.1, 132.7, 130.7, 129.8, 129.6, 128.4, 126.6, 12.6, 117.1, 113.8, 74.3, 67.0, 55.2, 44.9, 35.6, 23.9.

**HRMS:** Calcd for  $\text{C}_{22}\text{H}_{24}\text{O}_2\text{+H}$  321.1855, found 321.1852.



**5ca**

$\text{C}_{21}\text{H}_{21}\text{FO}$

**MW:** 308.39 g.mol<sup>-1</sup>

Yellow liquid

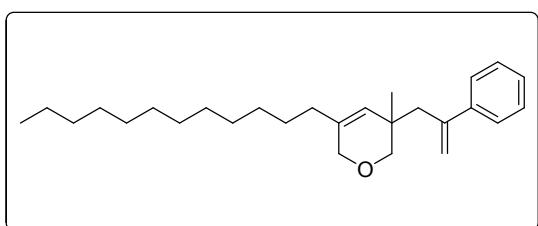
**Yield:** 89%

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm):** 7.40 (d,  $J$  = 7.6 Hz, 2H), 7.30 (t,  $J$  = 7.4 Hz, 2H), 7.26 (s, 1.5H), 6.92 - 6.88 (m, 4H), 6.19 (s, 0.09H), 5.73 (s, 0.09H), 5.60 (s, 1H), 5.32 (s, 1H), 5.11 (s, 1H), 4.34 (dd,  $J$  = 48.0, 16.0 Hz, 2.2H), 3.46 (dd,  $J$  = 104.0, 12.0 Hz, 2.2H), 2.74 (dd,  $J$  = 80.0, 12.0 Hz, 2H), 2.16 (s, 0.21H), 1.55 (s, 0.44H), 0.95 (s, 3H).

**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm):** 163.1, 161.1, 146.0, 143.0, 132.4, 131.2, 128.4, 127.2, 126.5 (d,  $J$  = 22.0 Hz), 126.3, 117.2, 115.1 (d,  $J$  = 17.0 Hz), 74.3, 66.9, 44.9, 35.6, 23.7.

**$^{19}\text{F}\{\text{H}\}$  NMR (376 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm):** 115.7.

**HRMS(ESI):** Calcd for  $\text{C}_{21}\text{H}_{21}\text{FO+H}$  309.1655, found 309.1658.



**5da**

$\text{C}_{27}\text{H}_{42}\text{O}$

**MW:** 382.6218 g.mol<sup>-1</sup>

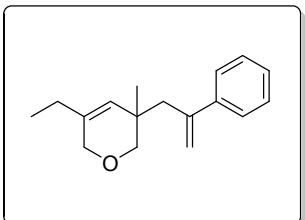
Yellow liquid

**Yield:** 82%

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm):** 7.37 - 7.26 (m, 5H), 7.23 (d,  $J$  = 6.3 Hz, 1H), 5.67 (s, 0.19H), 5.59 (s, 0.19H), 5.27 (s, 1H), 5.06 (s, 1H), 5.05 (s, 1H), 4.04 (s, 0.39H), 3.89 (s, 2H), 3.58 (dd,  $J$  = 50.4, 10.9 Hz, 0.52H), 3.31 (dd,  $J$  = 115.6, 10.8 Hz, 2H), 2.61 (dd,  $J$  = 37.2, 13.2 Hz, 2H), 2.13 (s, 0.63H), 1.93 (t,  $J$  = 8.0 Hz, 0.43H), 1.70 (d,  $J$  = 4.0 Hz, 2H), 1.42 (s, 0.66H), 1.26 (s, 20H), 0.88 (t,  $J$  = 6.0 Hz, 3.7H), 0.81 (s, 3H).

**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm):** 146.3, 143.2, 134.6, 128.1, 127.1, 126.6, 125.9, 116.8, 74.3, 68.0, 44.6, 35.2, 32.7, 32.0, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4, 27.3, 23.8, 22.8, 14.2.

**HRMS(ESI):** Calcd for  $\text{C}_{27}\text{H}_{42}\text{O+H}$  383.3314, found 383.3311.

**5ea**C<sub>17</sub>H<sub>22</sub>OMW: 242.36 g.mol<sup>-1</sup>

Yellow liquid

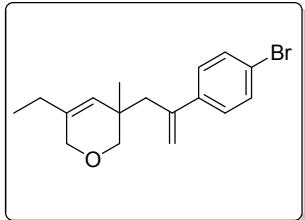
Yield: 86%

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm):** 7.91 (d, *J* = 6.0 Hz, 0.45H), 7.36 (d, *J* = 7.3 Hz, 2H), 7.30 – 7.22 (m, 4H), 5.67 (s, 0.23H), 5.59 (s, 0.23H), 5.27 (s, 1H), 5.06 (s, 1H), 5.04 (s, 1H), 4.05 (s, 0.5H), 3.89 (s, 2H), 3.66 – 3.50 (m, 0.66H), 3.33 (dd, *J* = 115.4, 10.8 Hz, 2H), 2.73 – 2.51 (m, 2H), 2.12 (s, 0.76H), 1.96 – 1.93 (m, 0.64H), 1.71 (p, *J* = 7.2 Hz, 2H), 1.33 (s, 0.59H), 1.05 (t, *J* = 7.2 Hz, 0.86H), 0.82 (s, 3H), 0.79 (t, *J* = 7.4 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm):** 146.4, 143.2, 135.8, 128.1, 127.0, 126.6, 116.7, 74.4, 68.0, 44.7, 35.0, 25.2, 23.7, 11.5.

**HRMS(ESI):** Calcd for C<sub>17</sub>H<sub>22</sub>O+H 243.1749, found 243.1746.

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**5eb**C<sub>17</sub>H<sub>21</sub>BrOMW: 321.25 g.mol<sup>-1</sup>

Yellow liquid

Yield: 75%

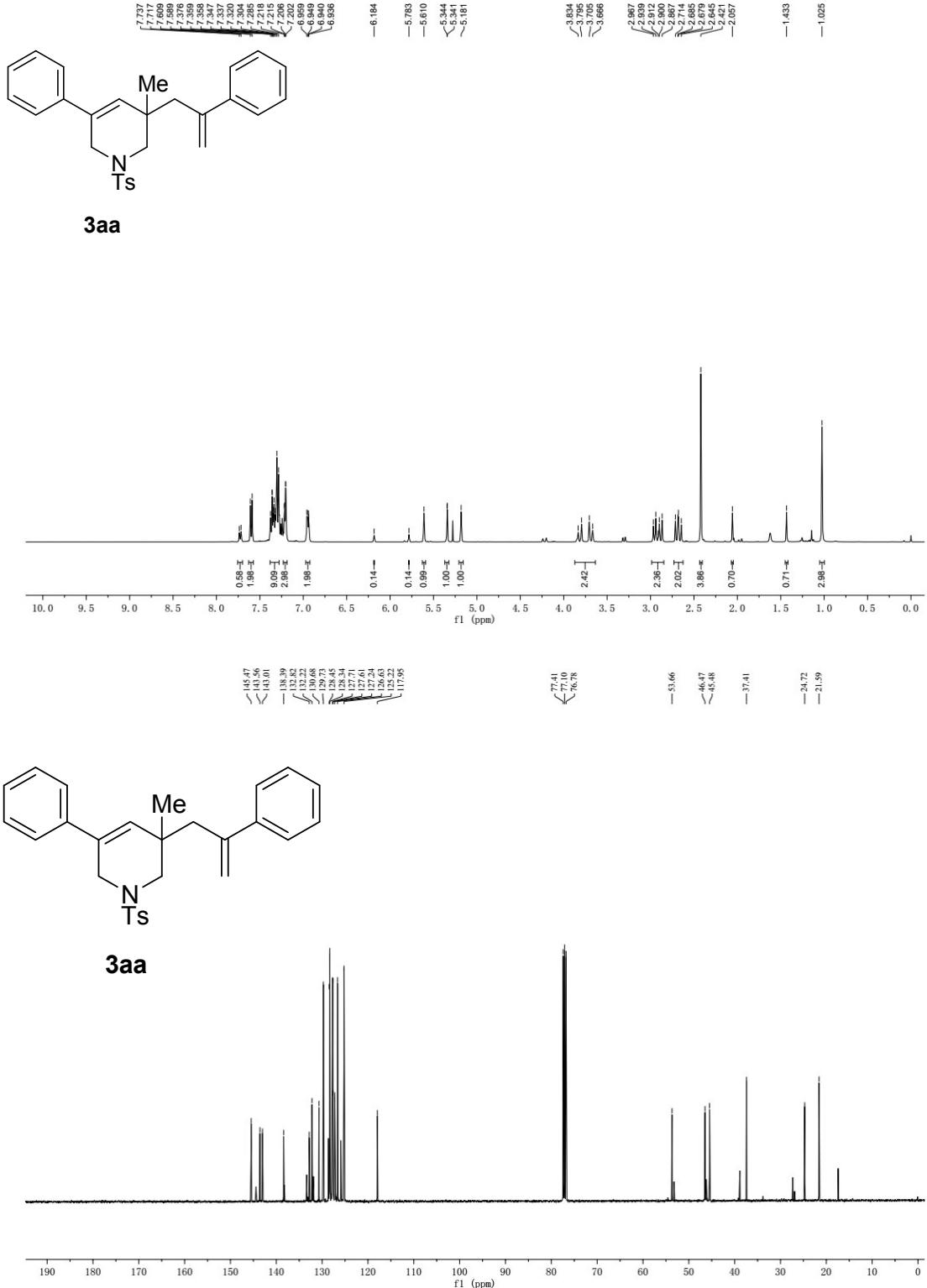
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm):** 7.91 (d, *J* = 5.2 Hz, 0.41H), 7.36 (d, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 1H), 5.67(s, 0.25H), 5.59(s, 0.25H), 5.27 (s, 1H), 5.05 (s, 1H), 5.04 (s, 1H), 4.05 (s, 0.52H), 3.89 (s, 2H), 3.67 – 3.50 (m, 0.71H), 3.33 (dd, *J* = 115.8, 10.8 Hz, 2H), 2.62 (dd, *J* = 48.4, 13.2 Hz, 2H), 2.12 (s, 0.83H), 2.00 – 1.92 (m, 0.56H), 1.71 (p, *J* = 7.3 Hz, 2H), 1.35 (s, 0.46H), 1.05 (t, *J* = 7.4 Hz, 0.87H), 0.82 (s, 3H), 0.78 (t, *J* = 7.4 Hz, 3H).

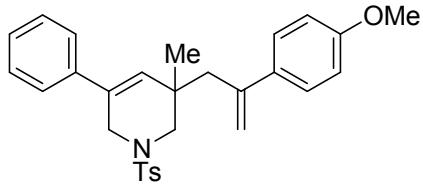
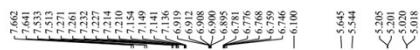
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm):** 146.4, 143.2, 135.8, 128.1, 127.0, 126.6, 116.7, 74.4, 68.0, 44.7, 35.0, 25.2, 23.9, 11.6.

**HRMS(ESI):** Calcd for C<sub>17</sub>H<sub>21</sub>BrO+H 321.0854, found 321.0851.

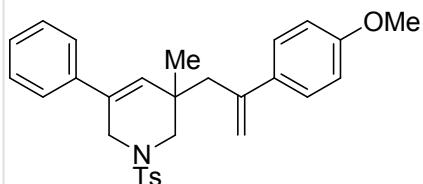
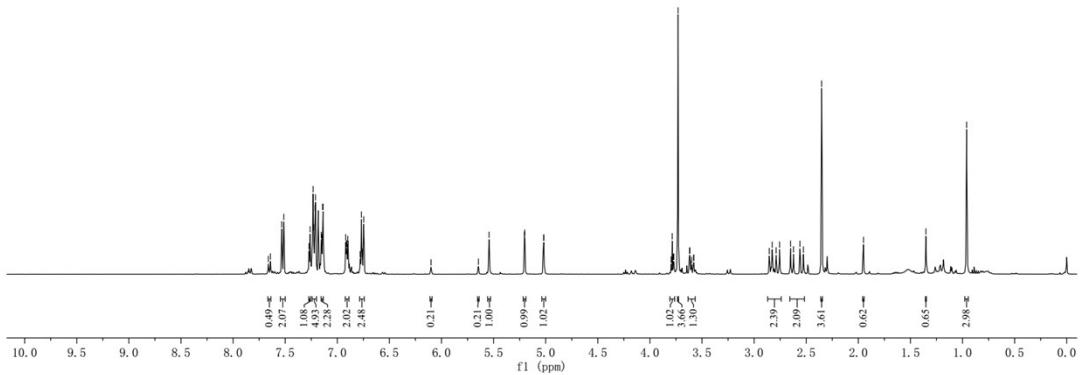
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#### IV Copies of the $^1\text{H}$ NMR, $^{13}\text{C}$ NMR

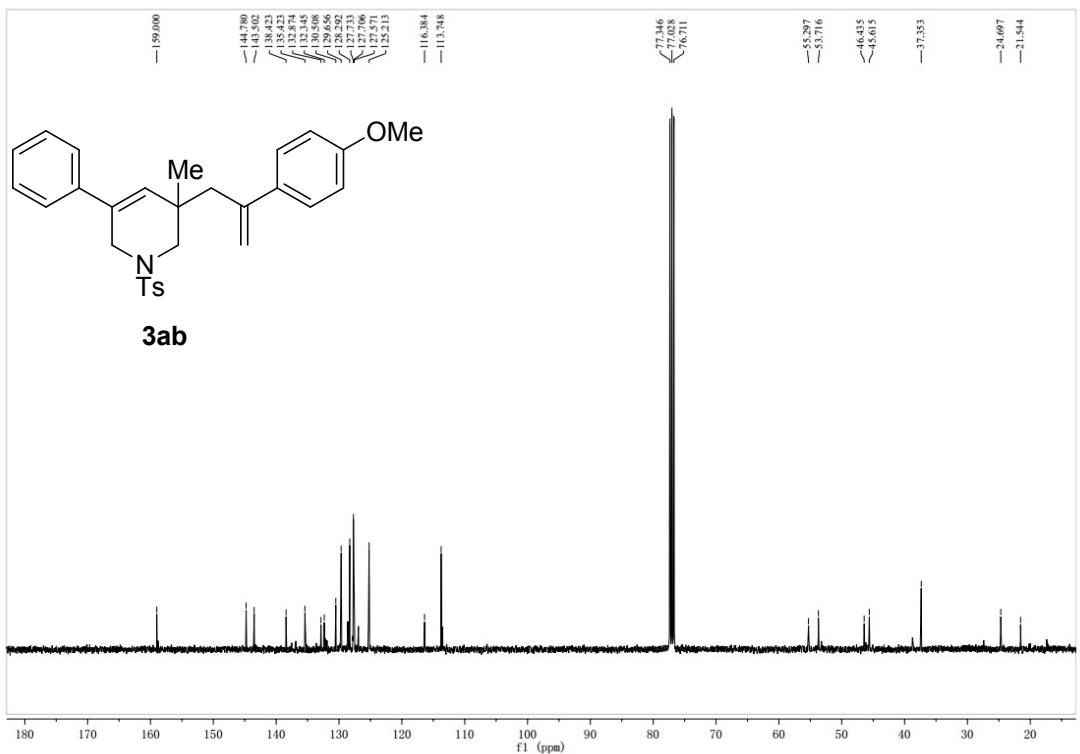


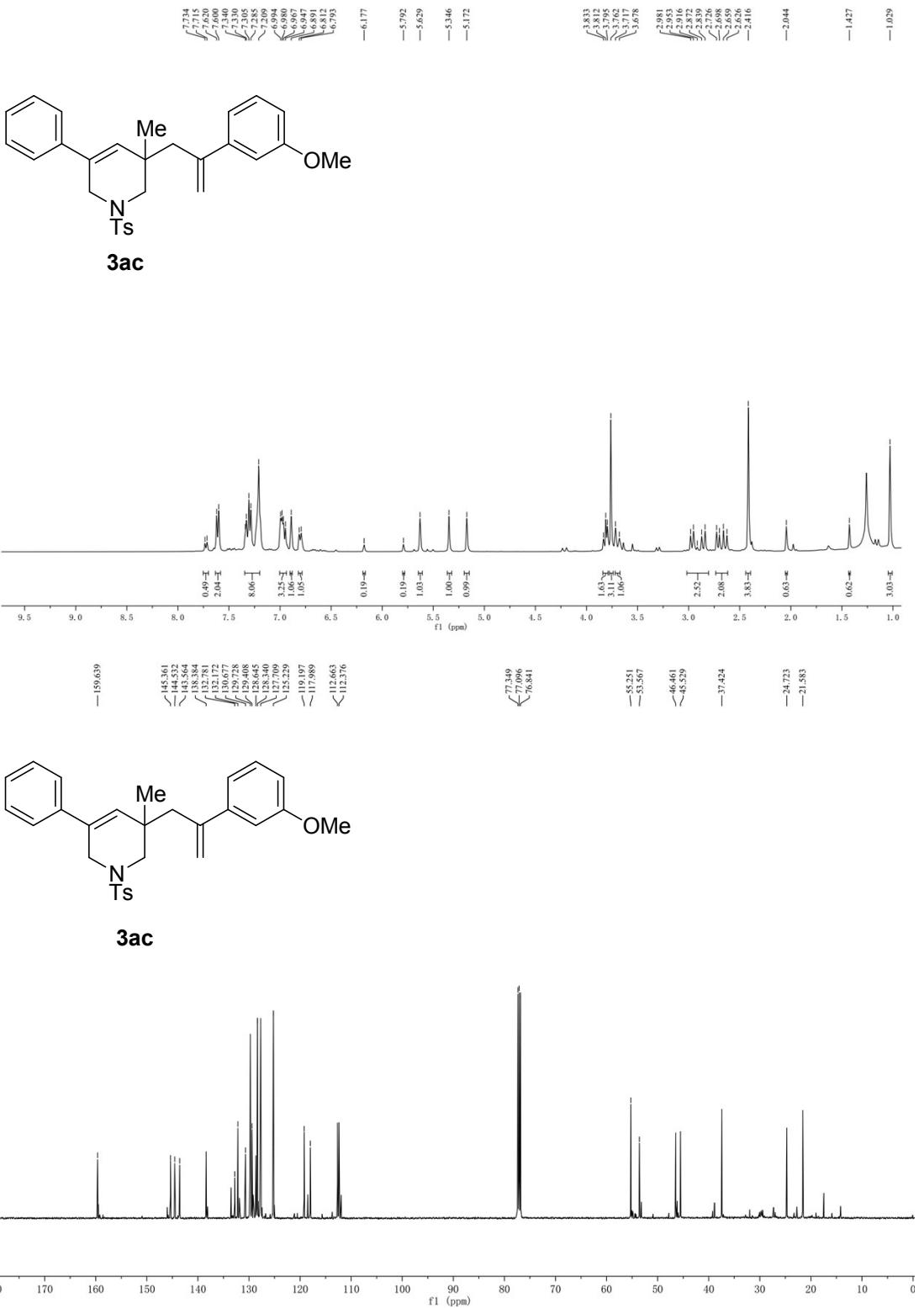


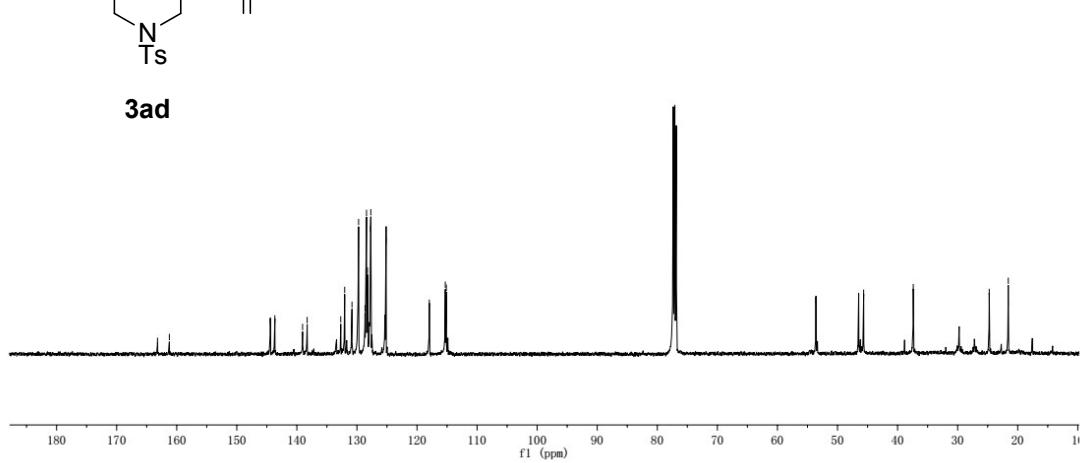
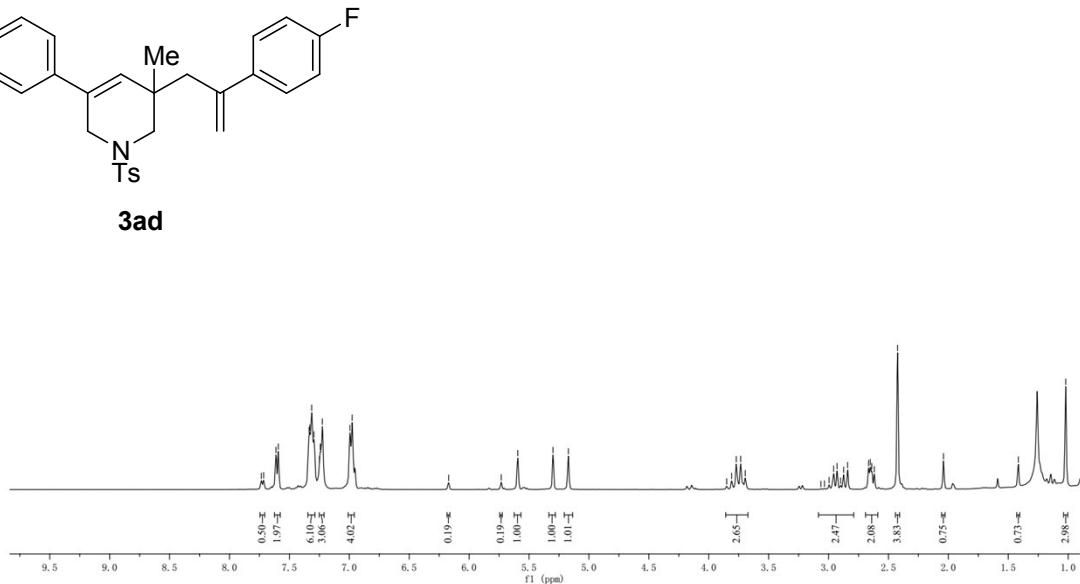
3ab

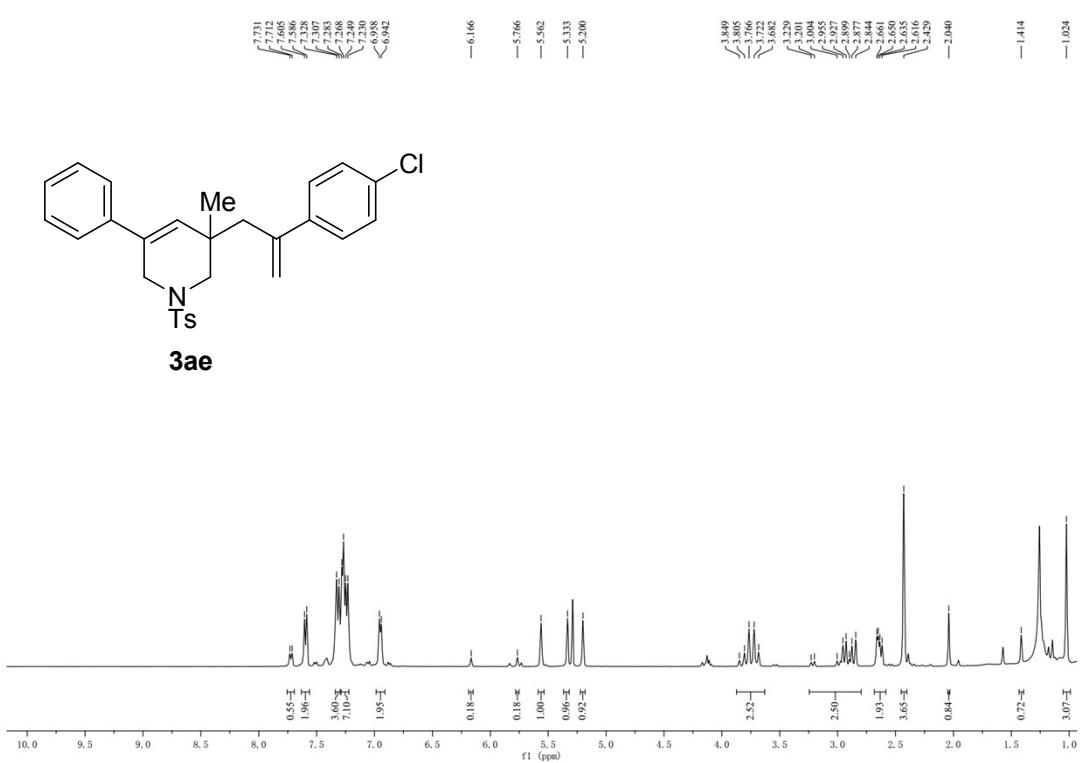
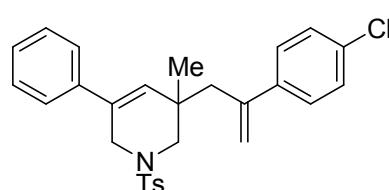
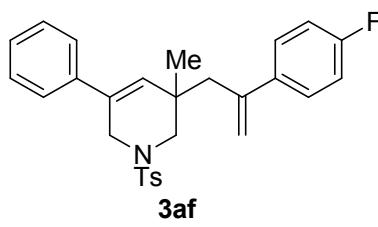


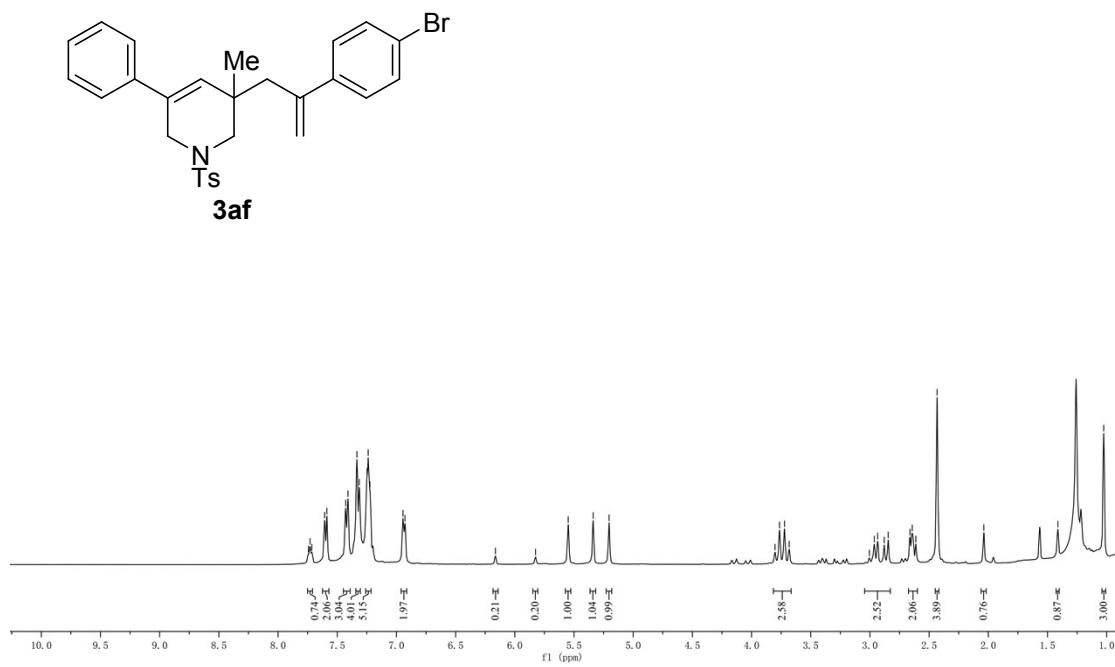
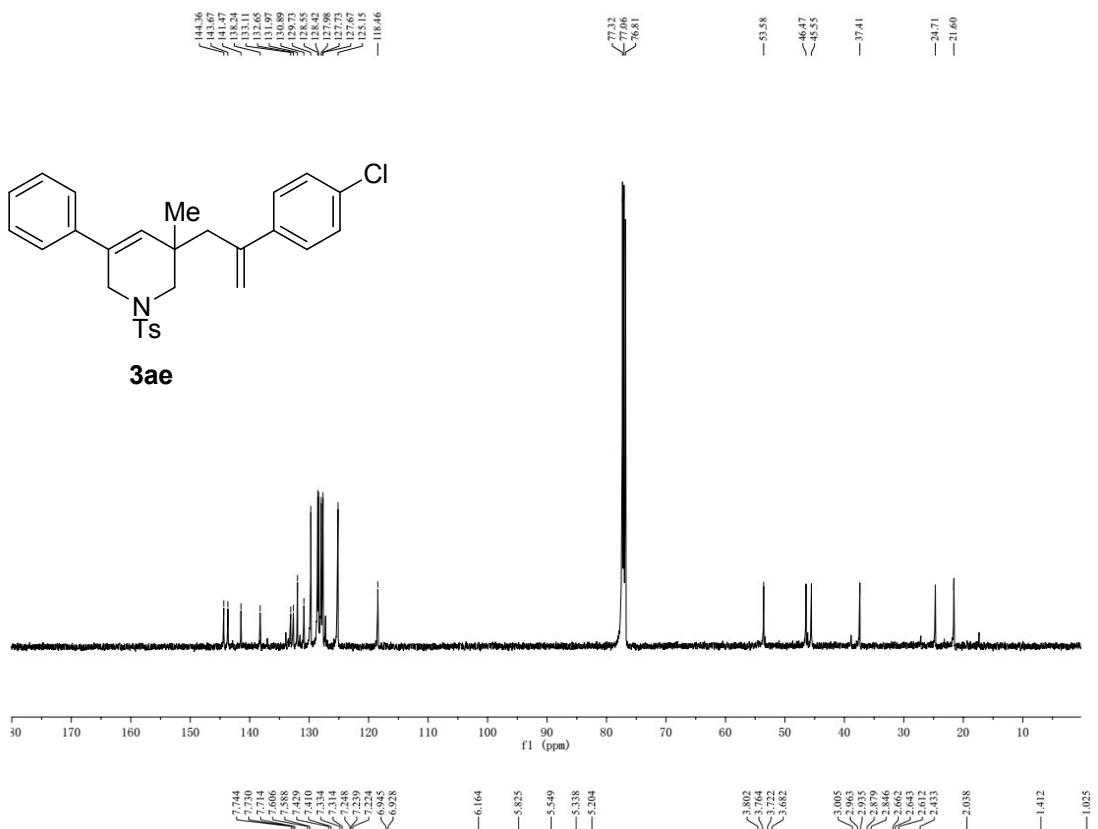
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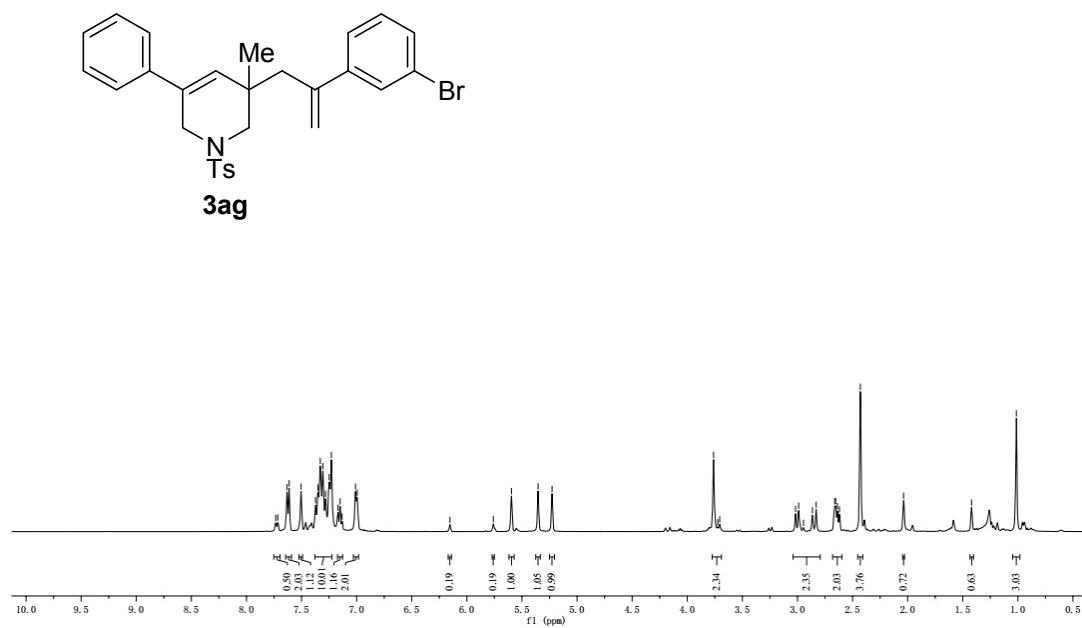
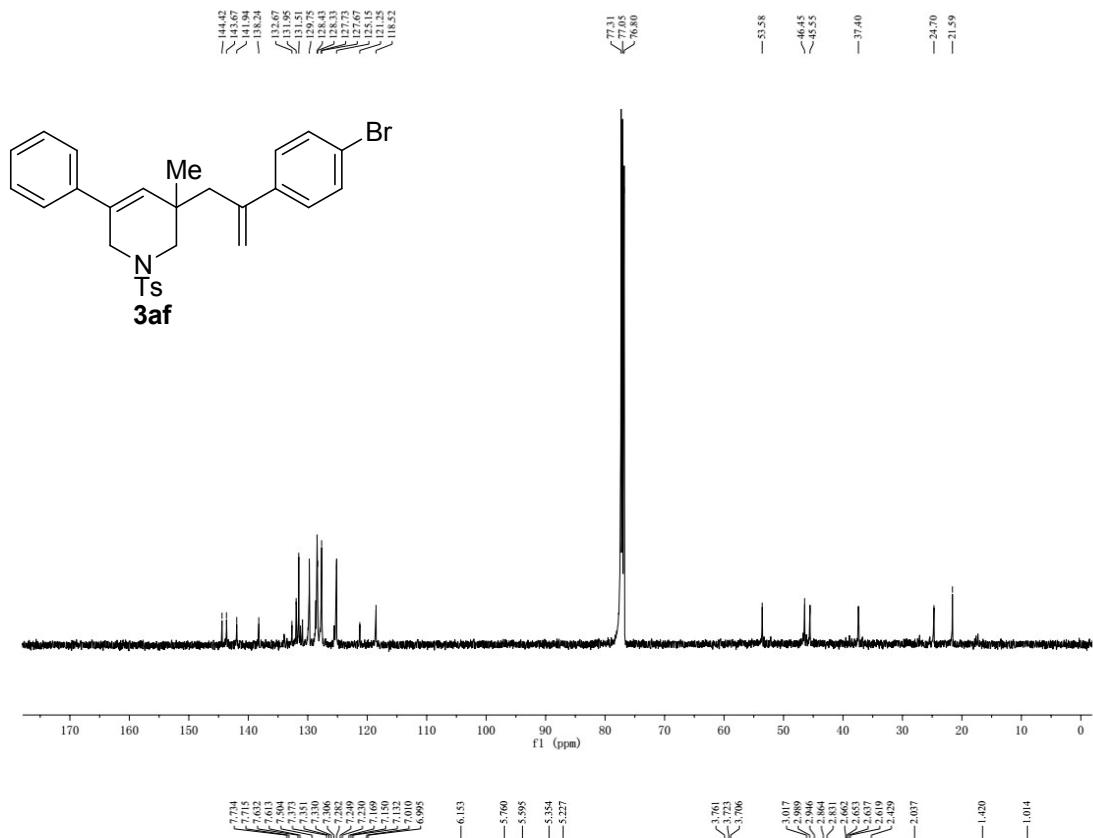


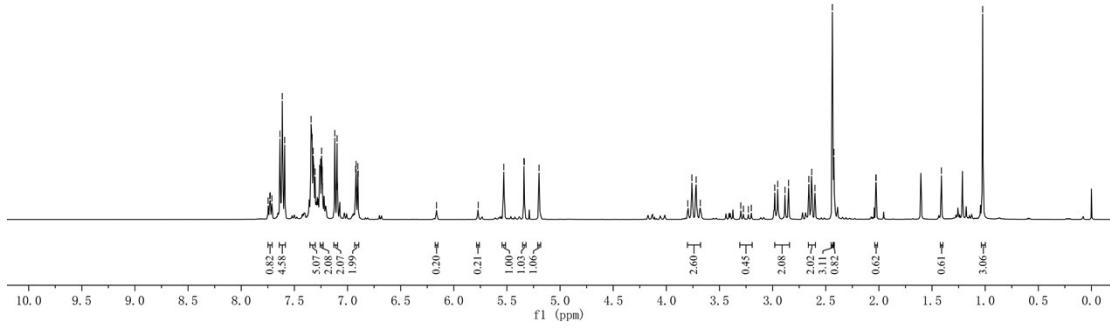
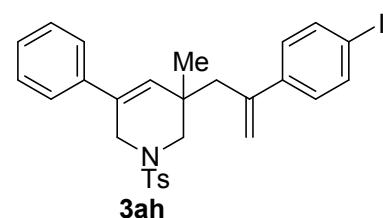
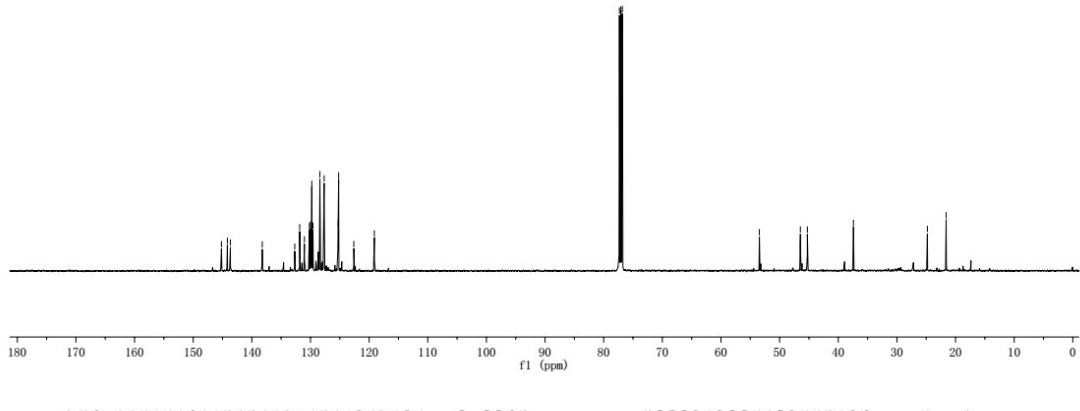
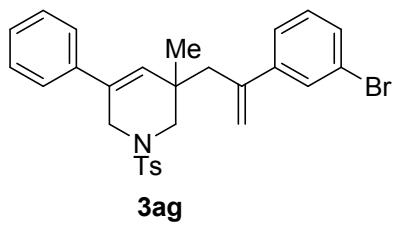


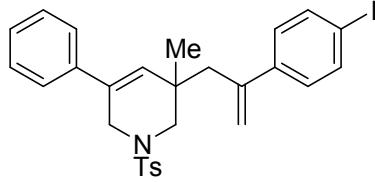
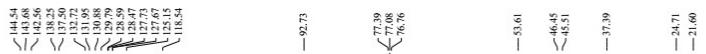




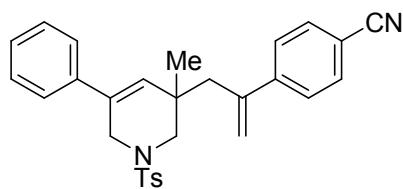
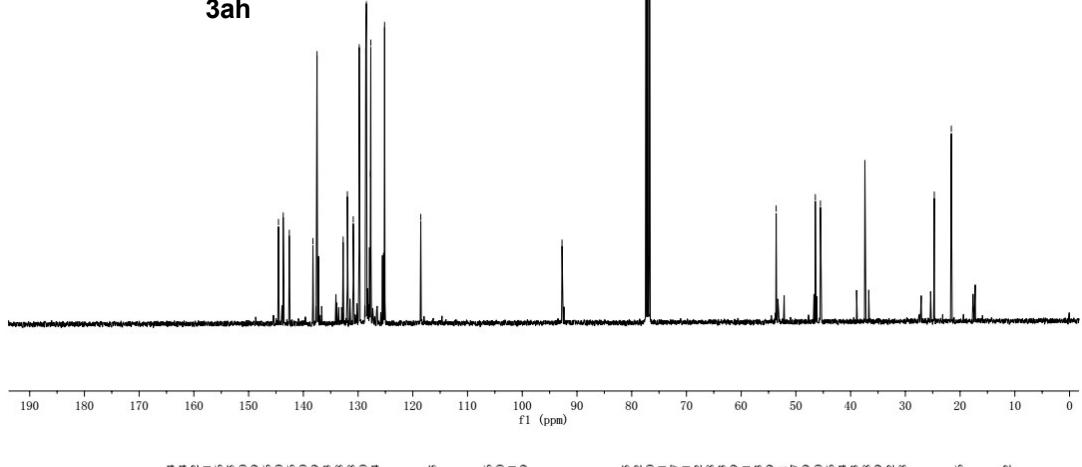




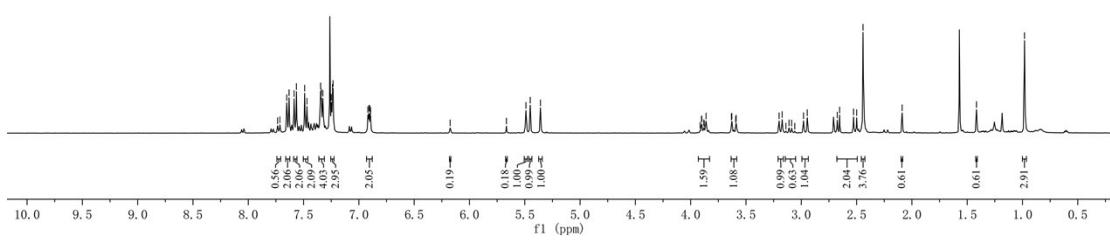


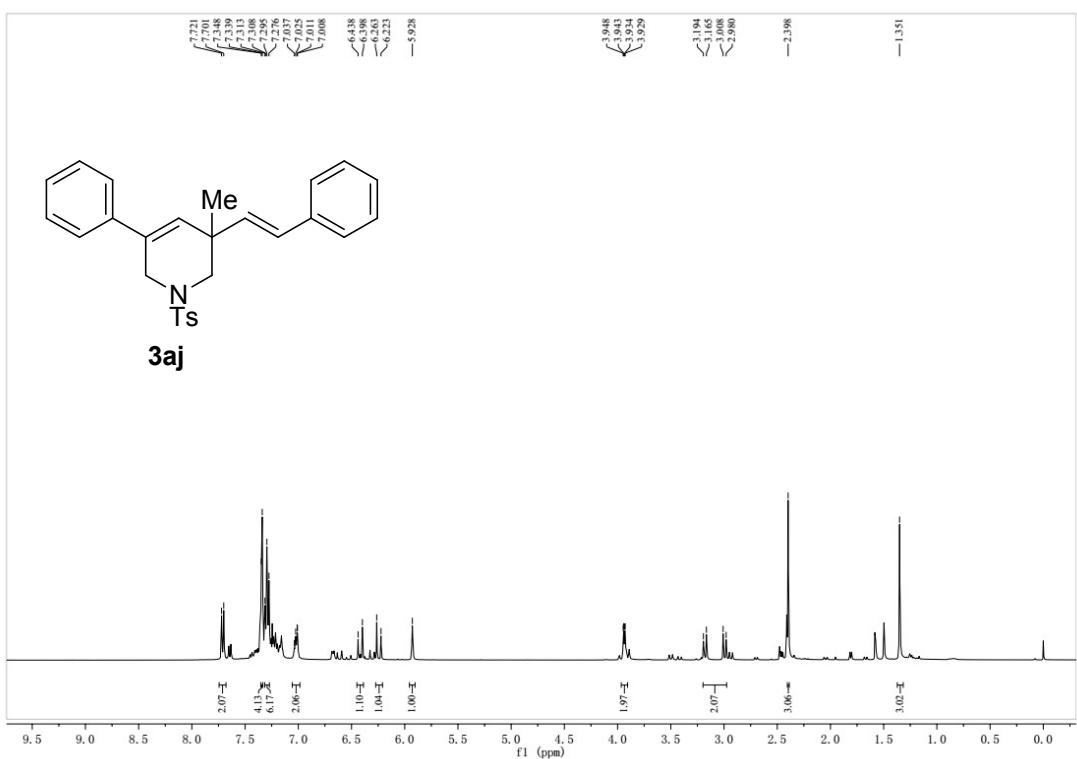
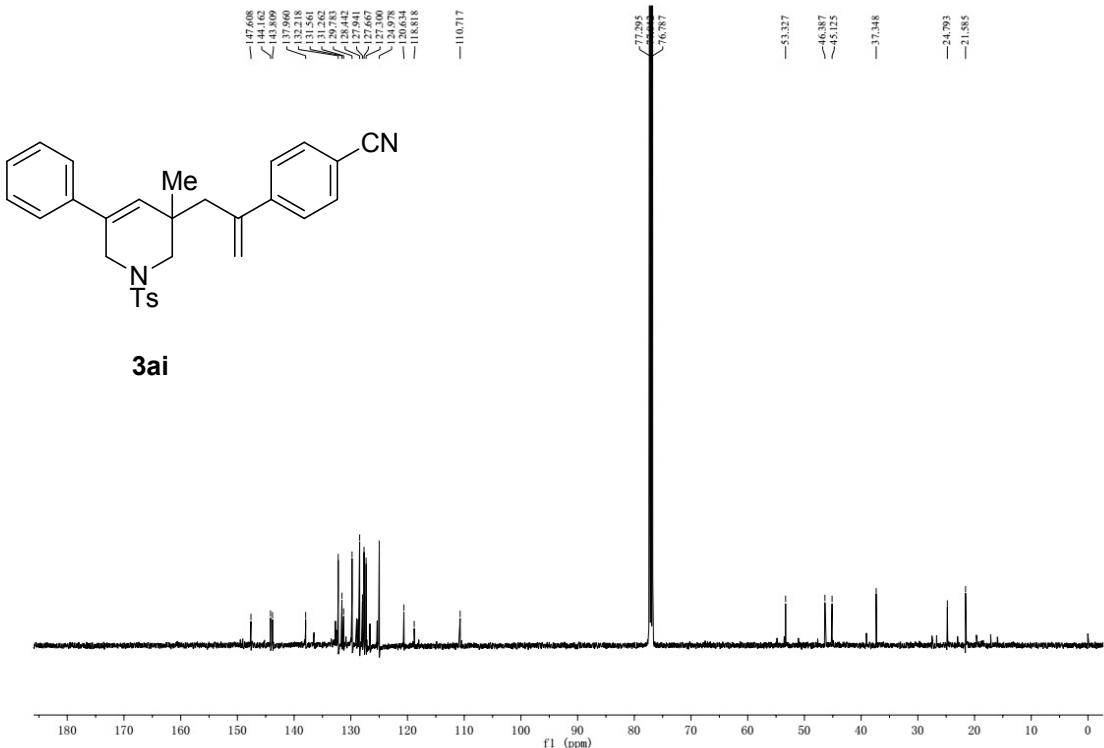


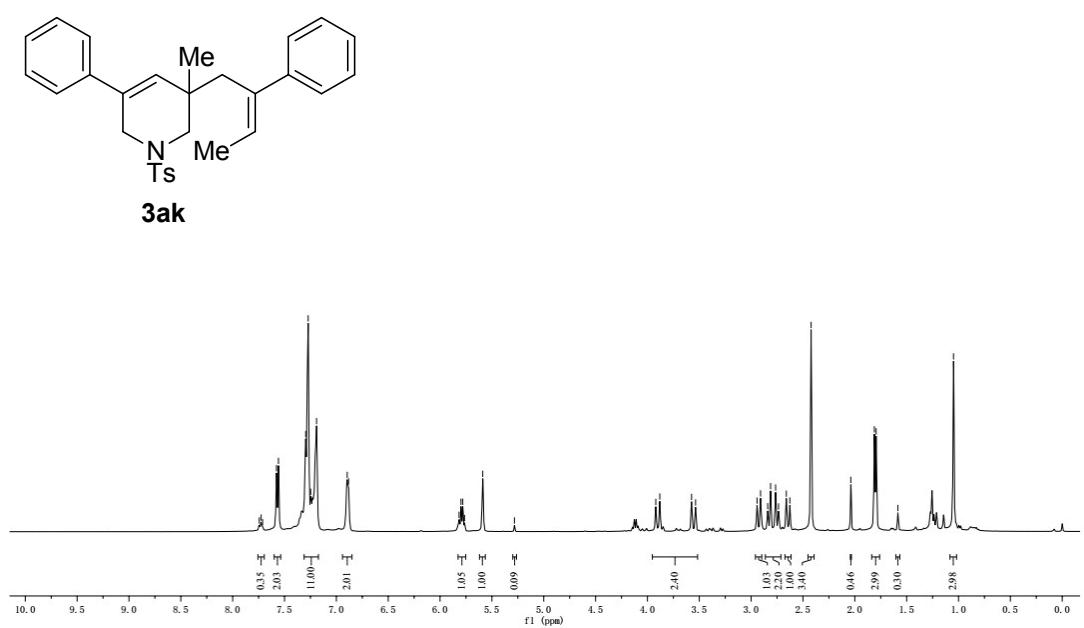
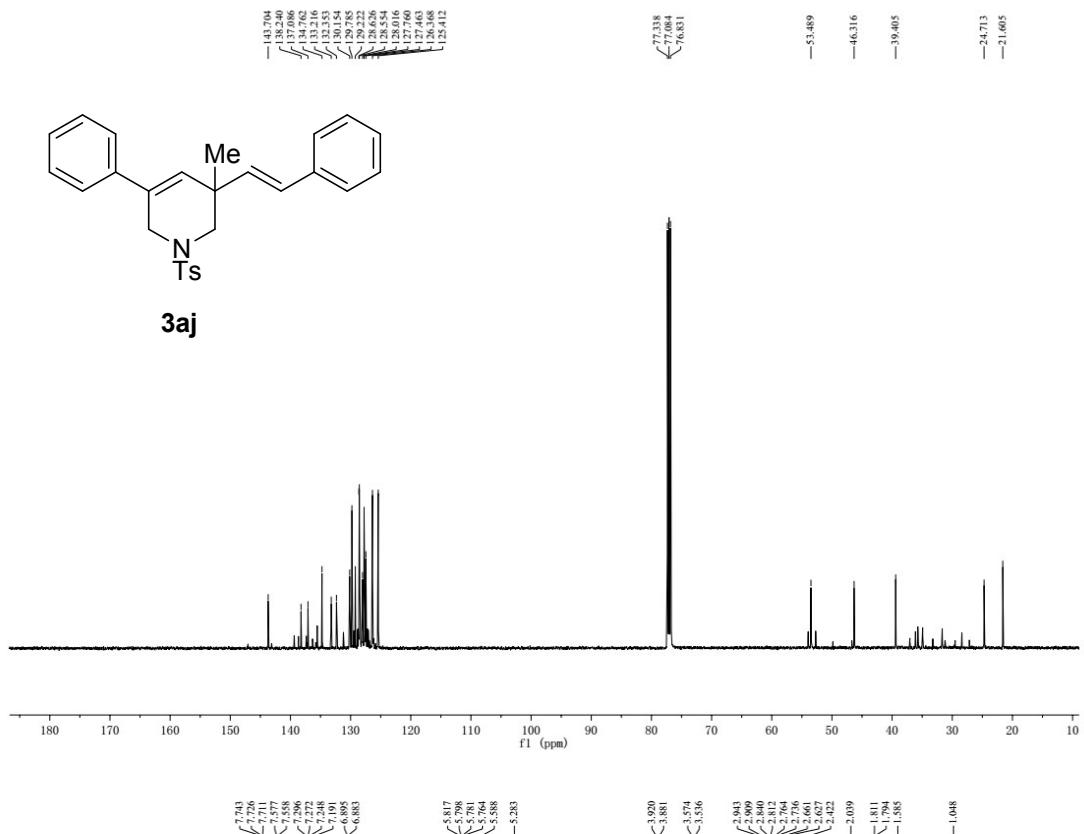
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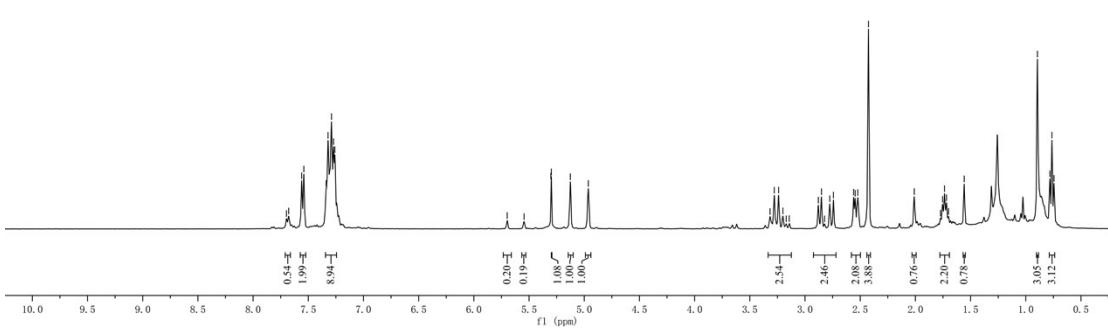
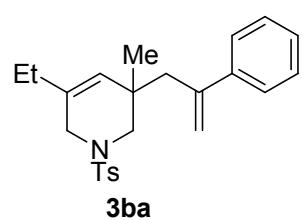
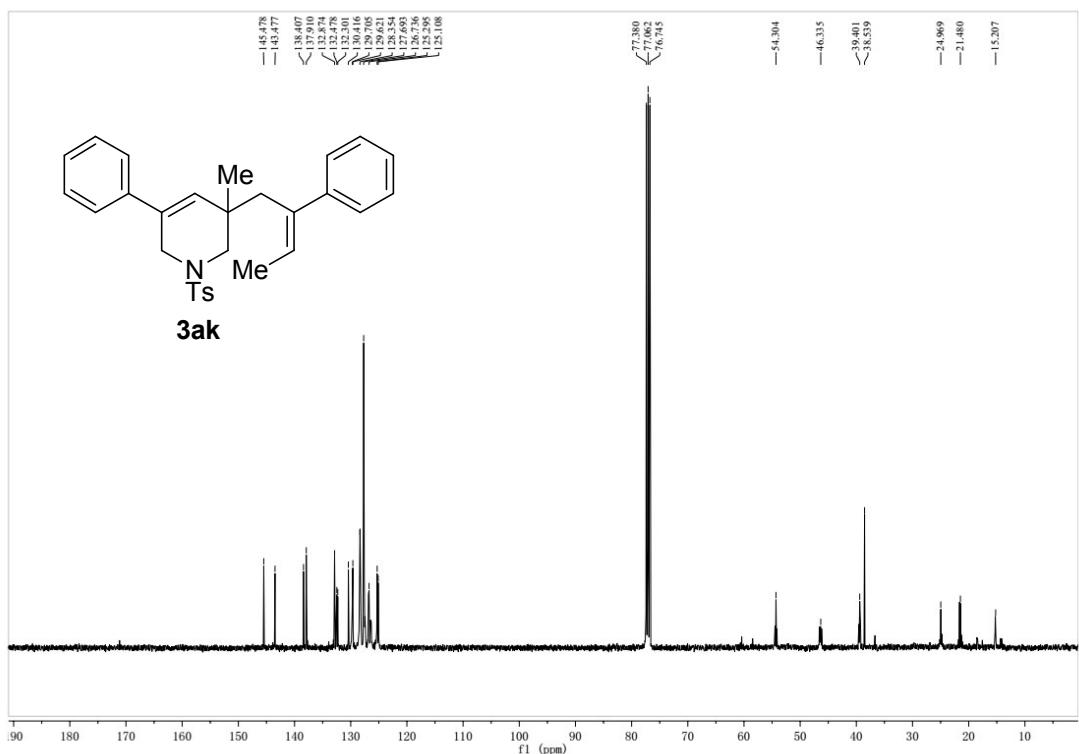


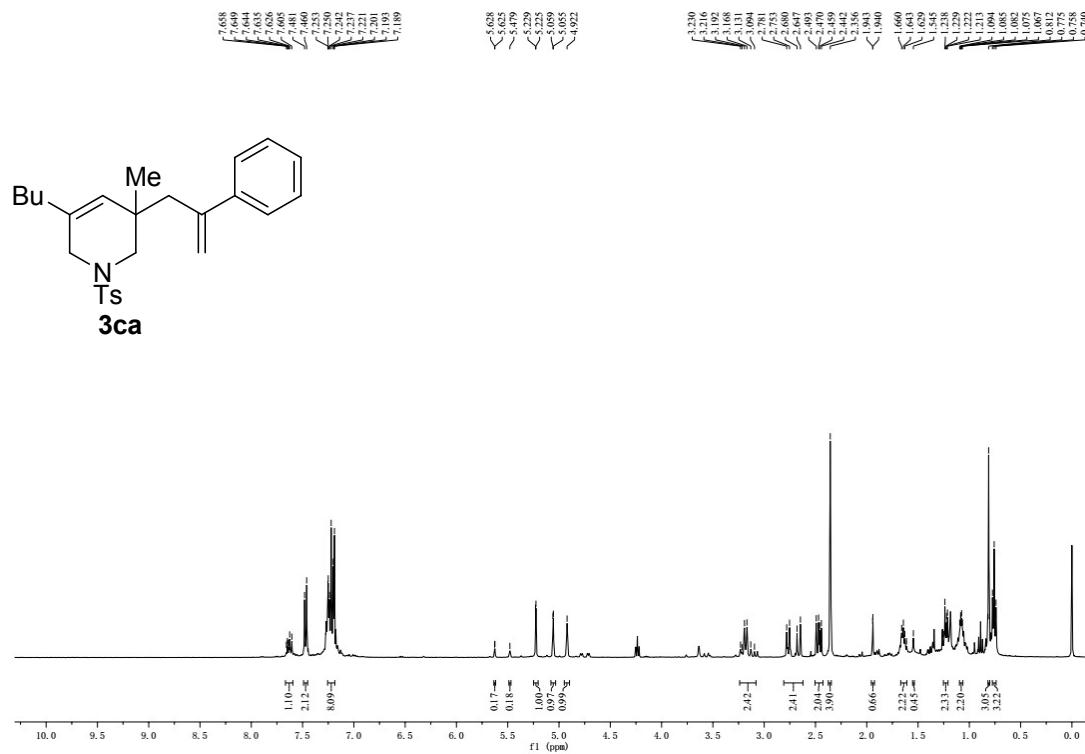
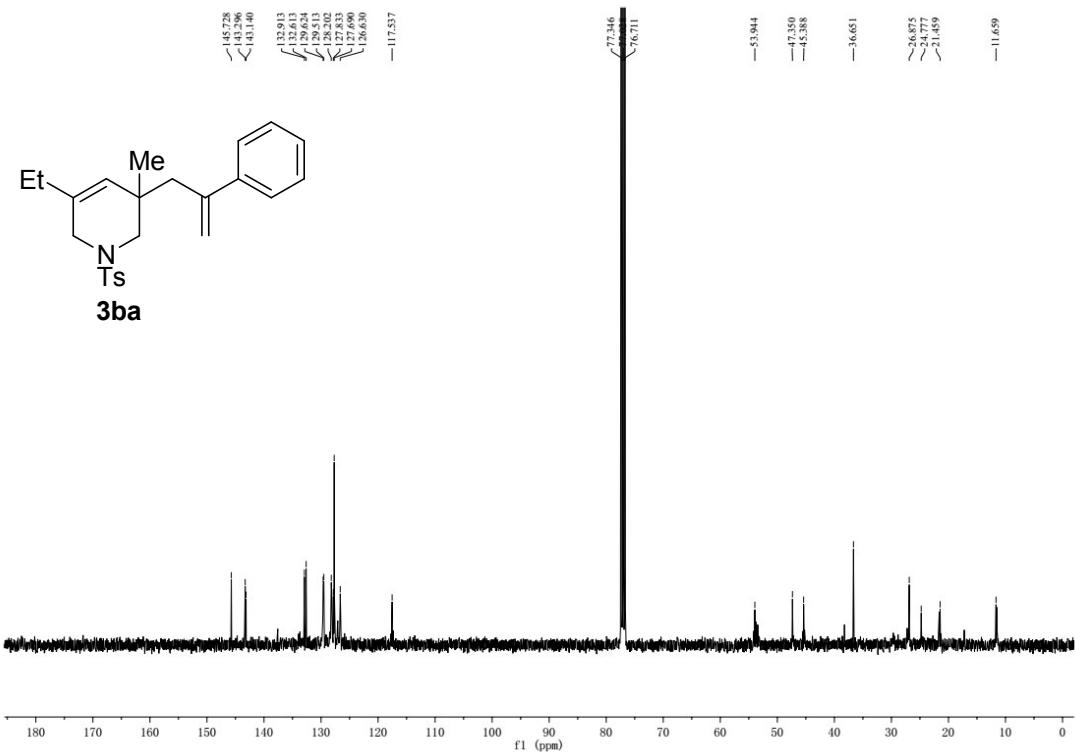
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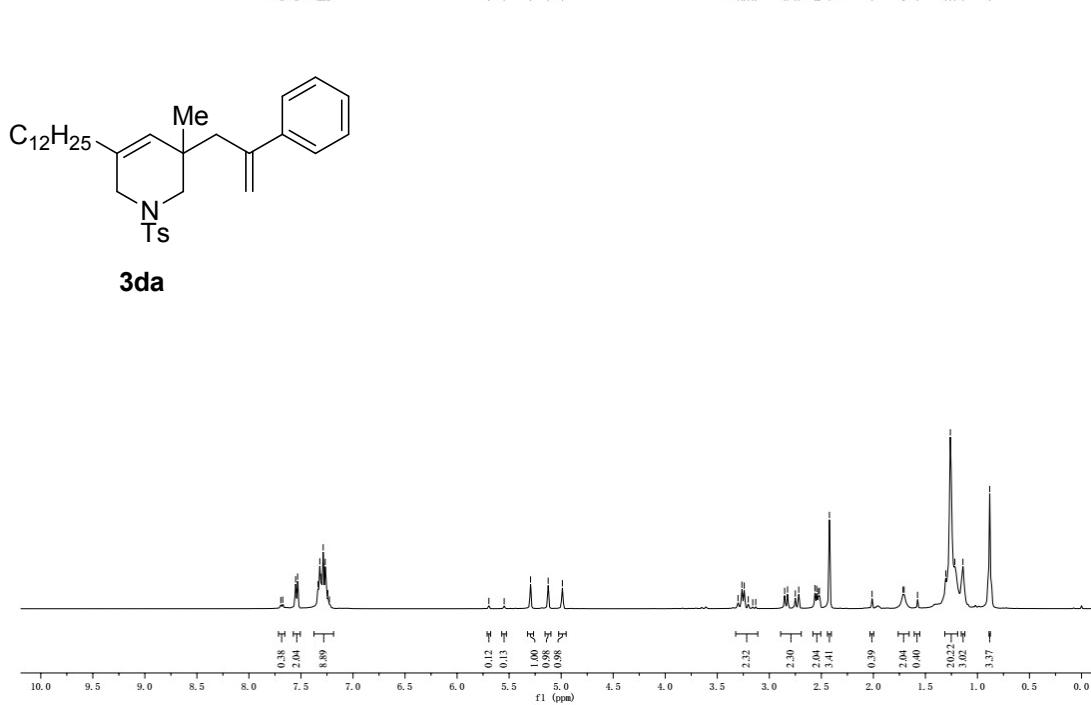
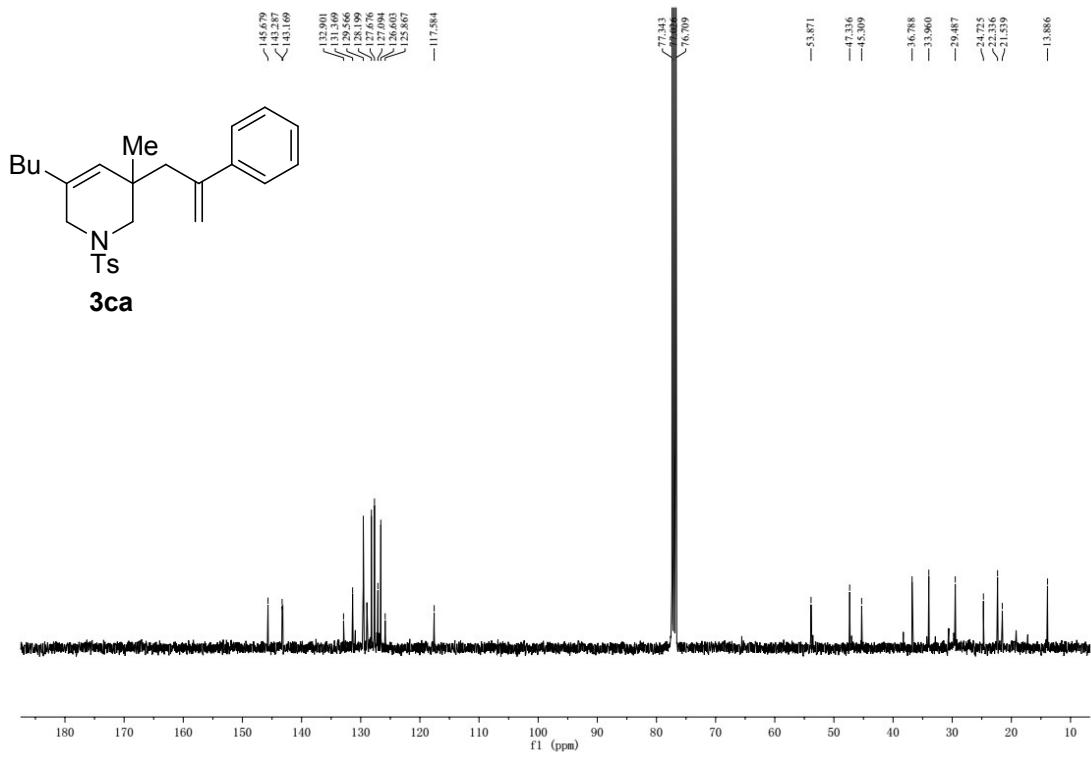


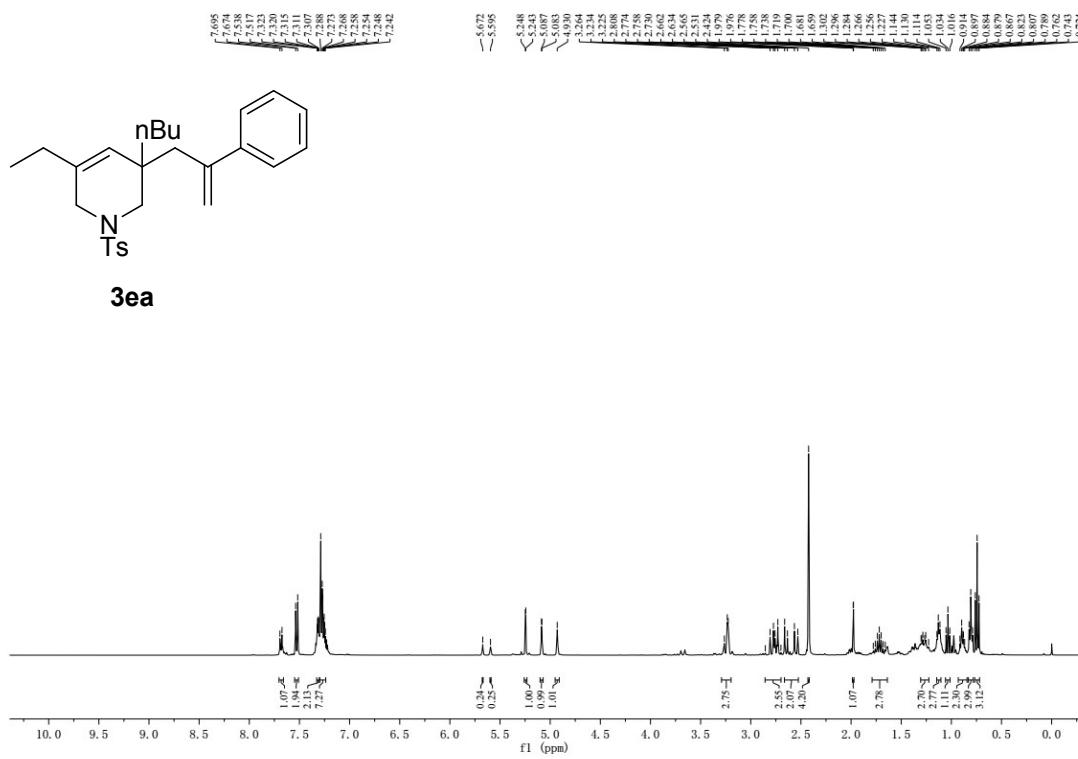
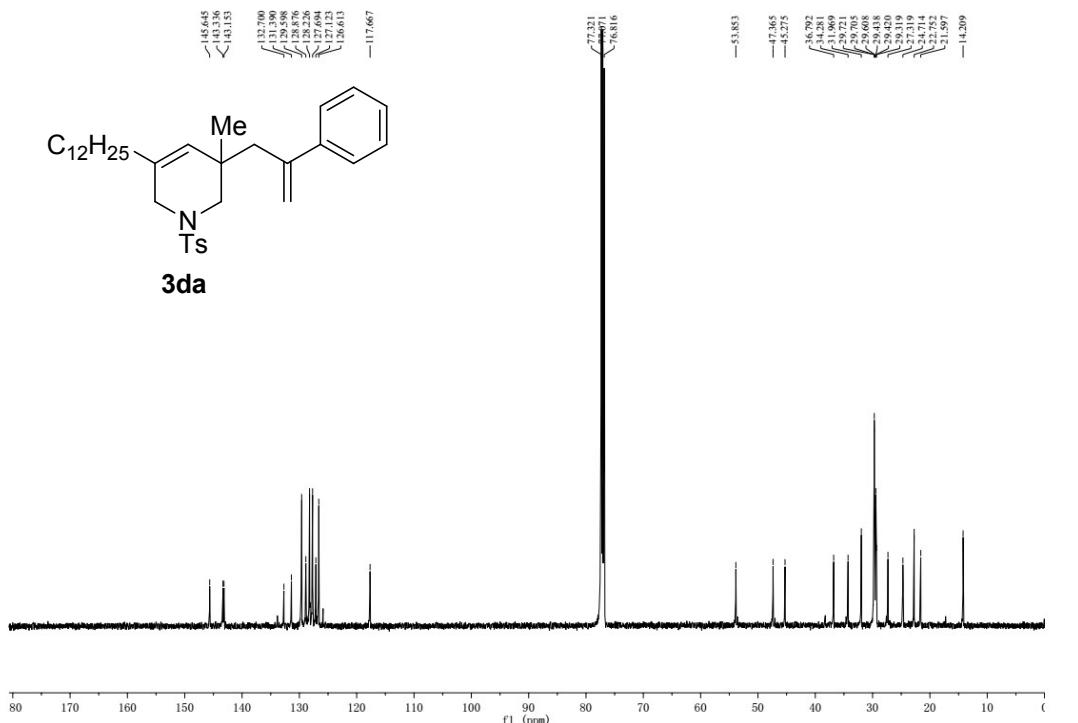


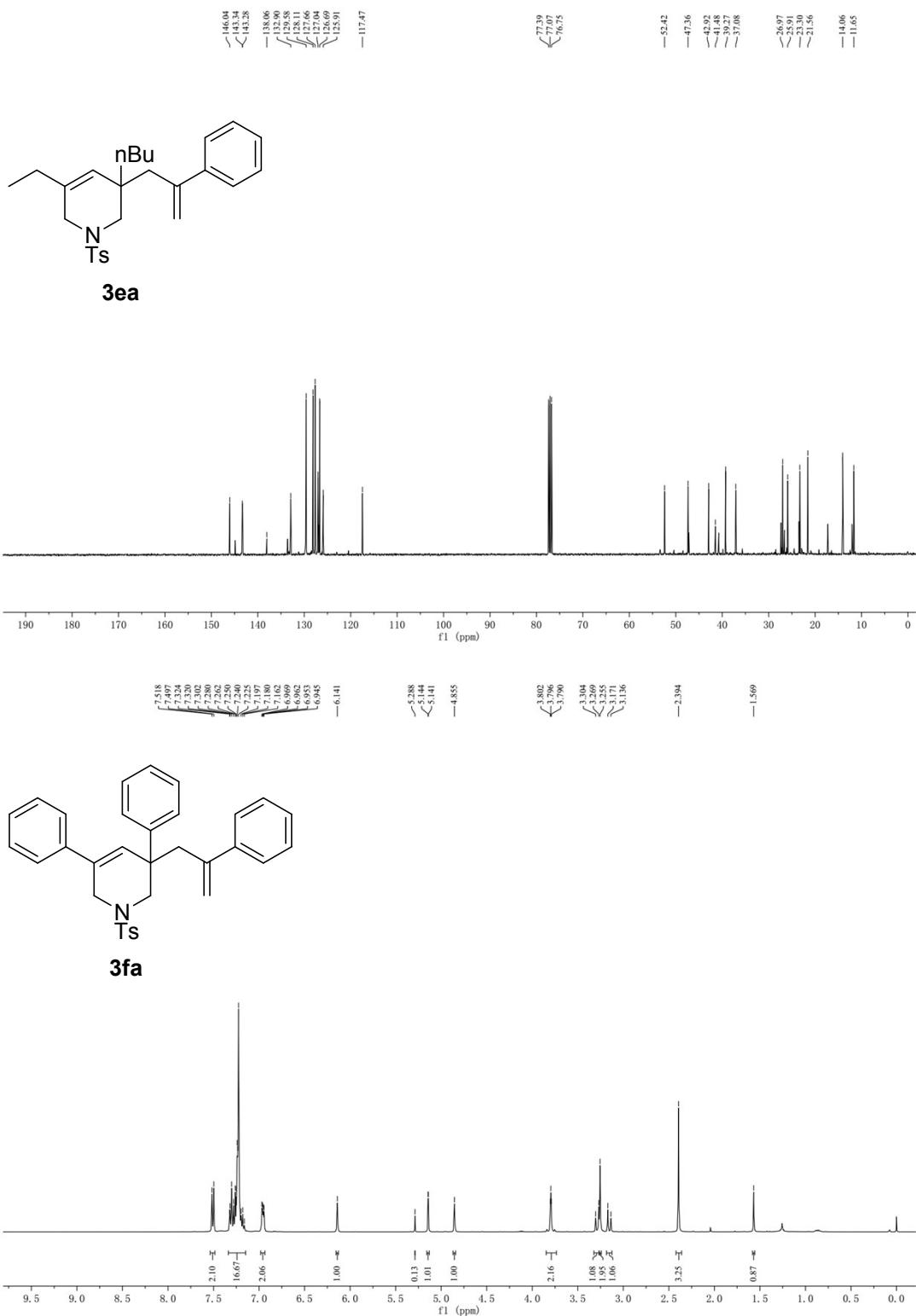


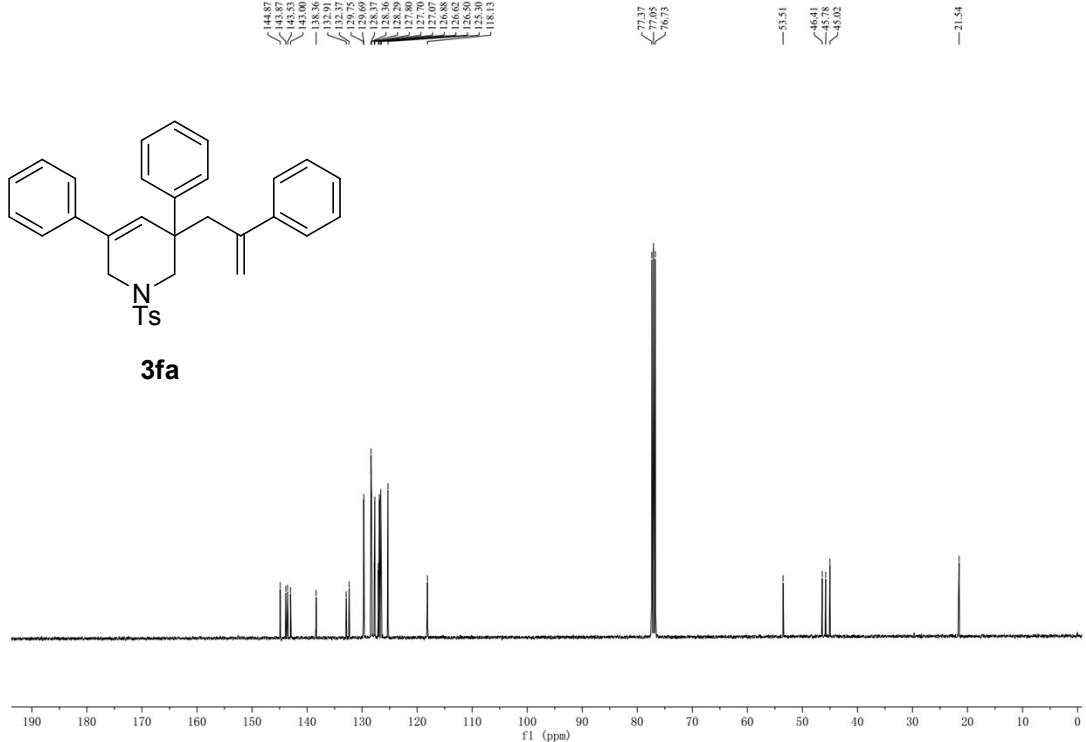


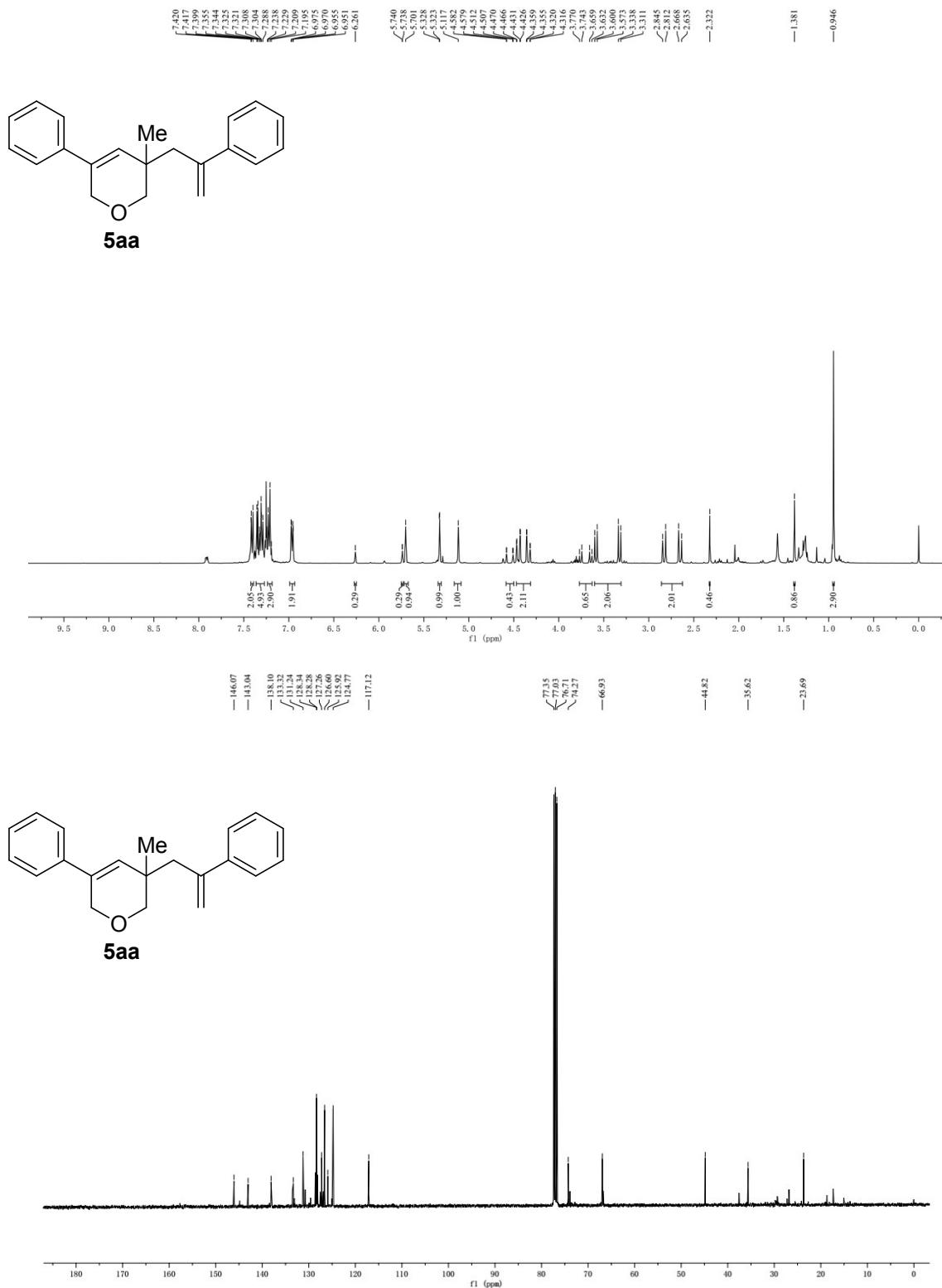




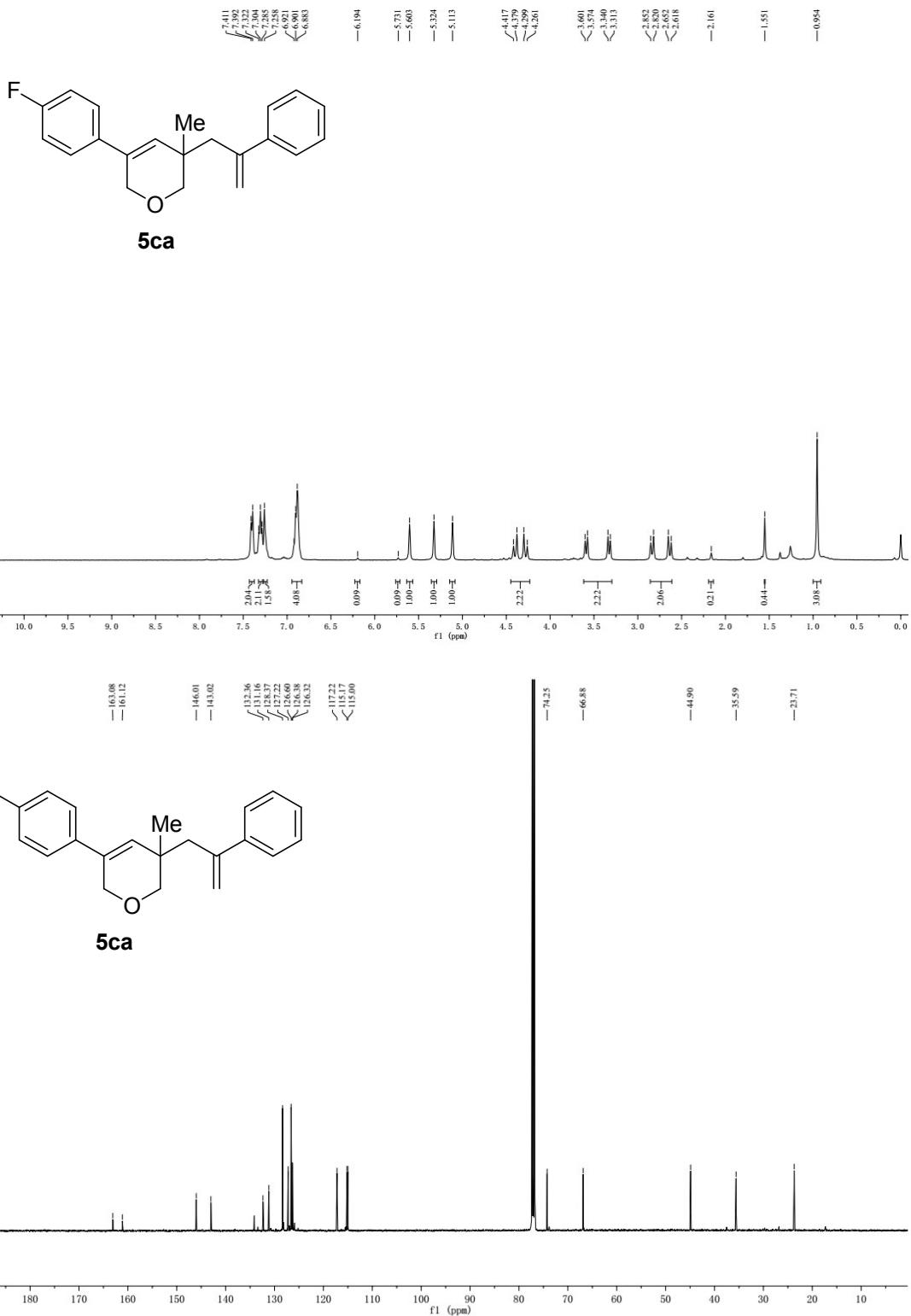


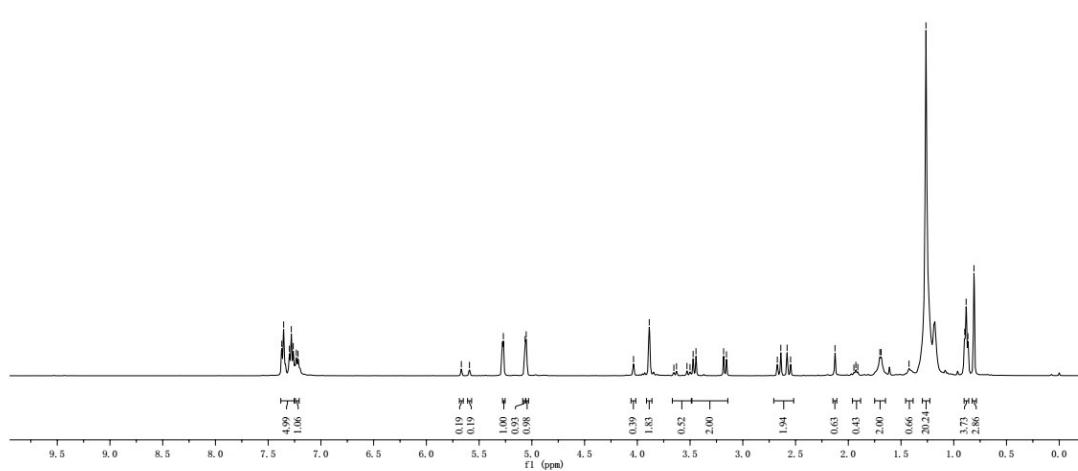
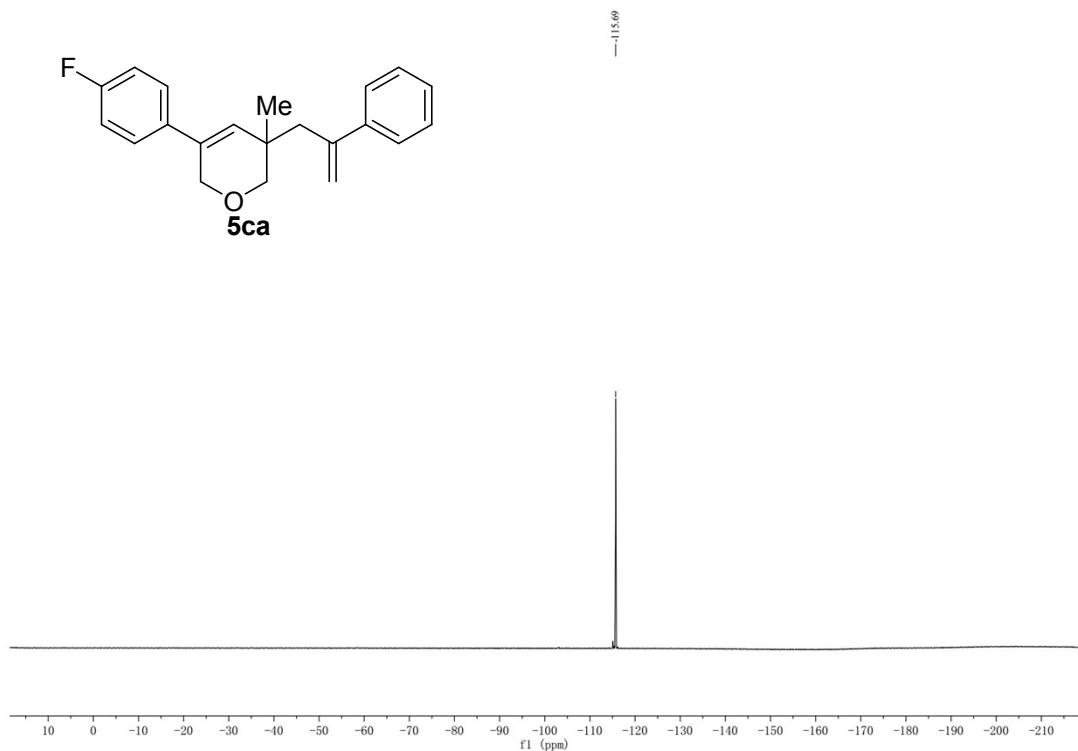
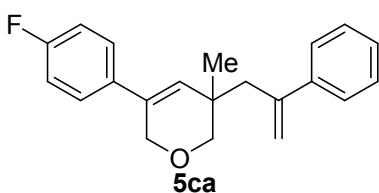


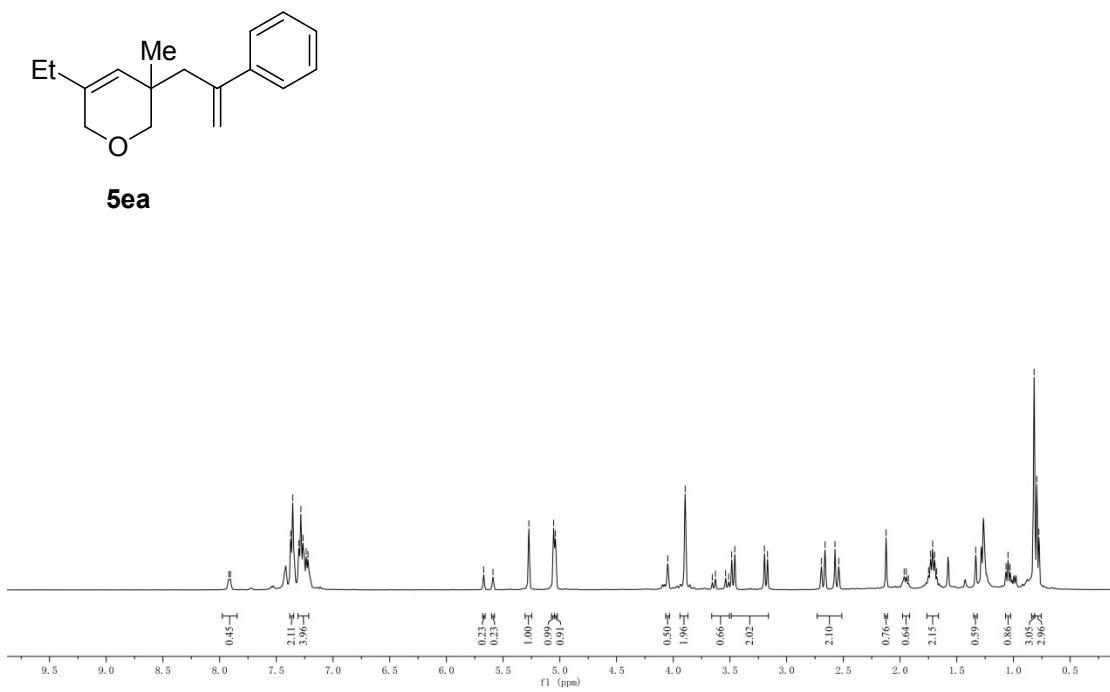
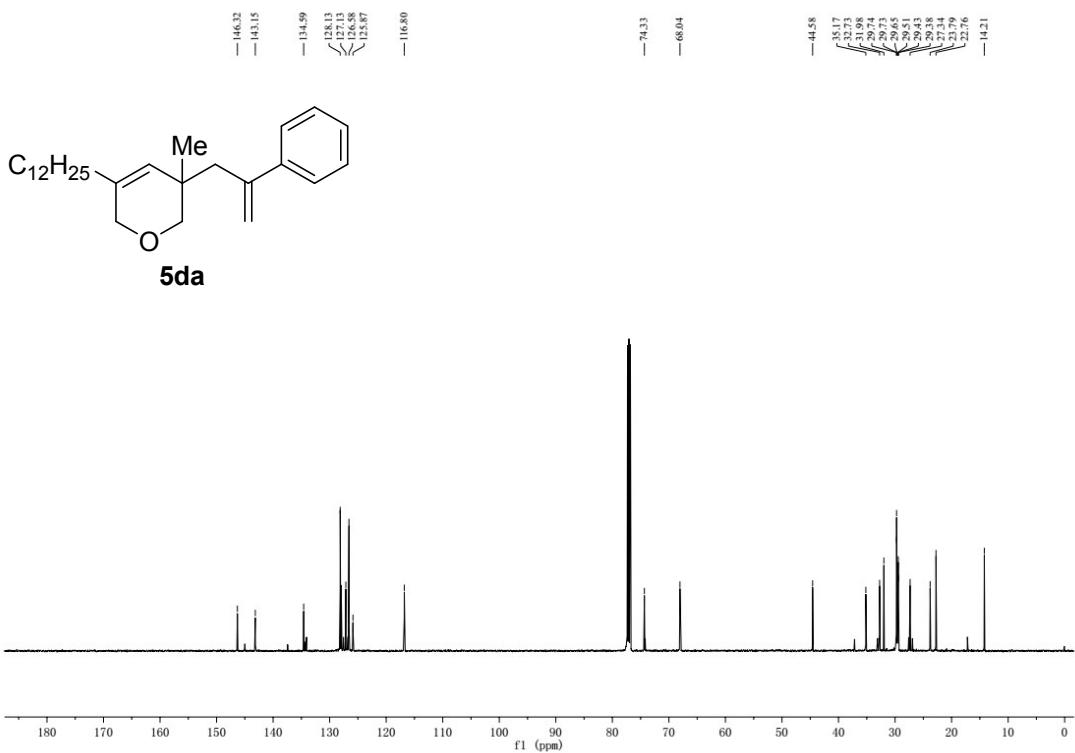


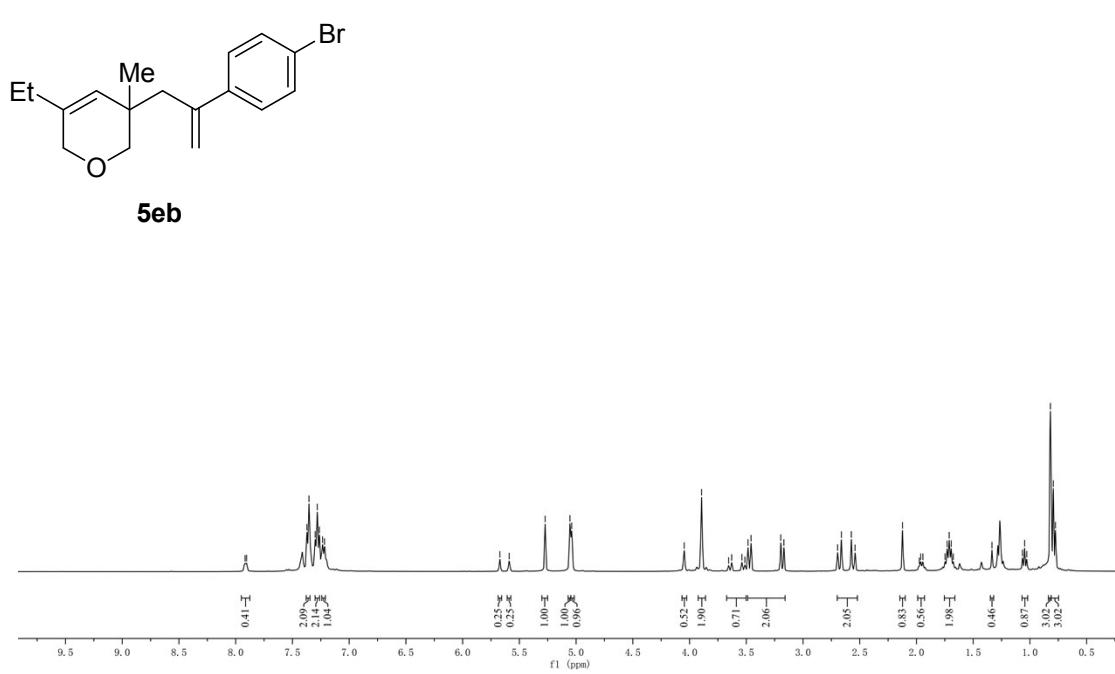
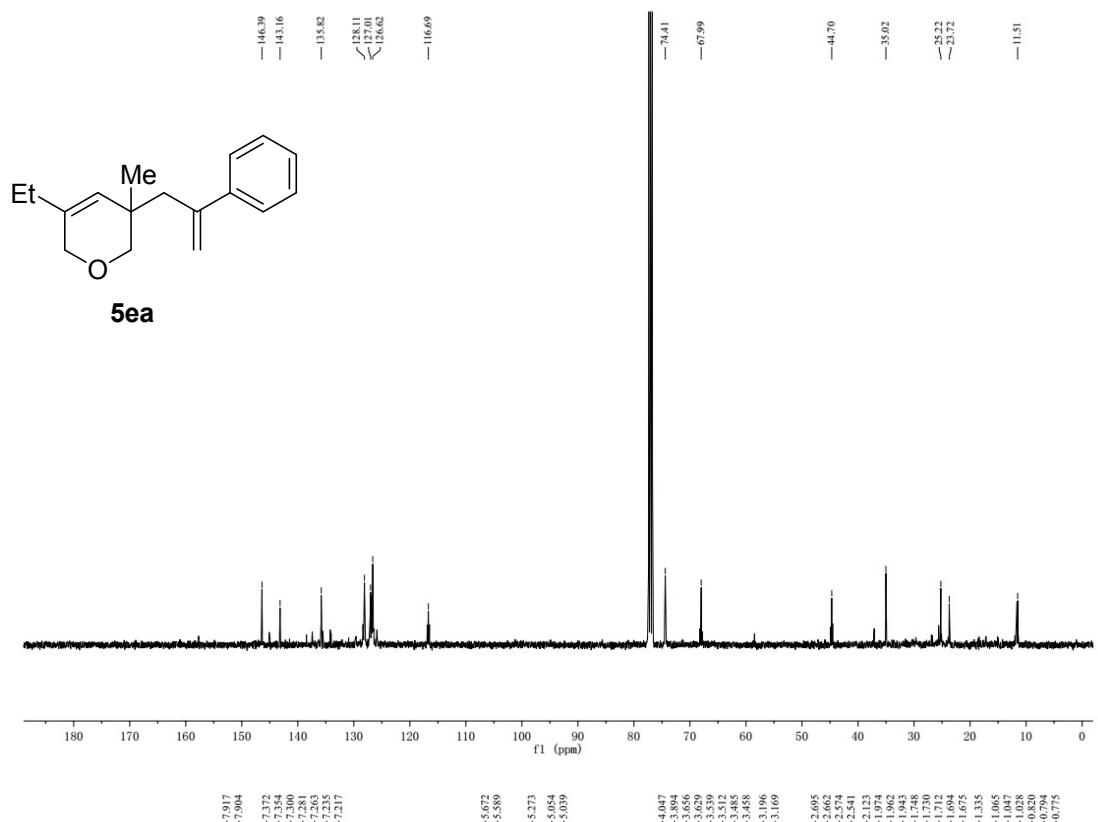


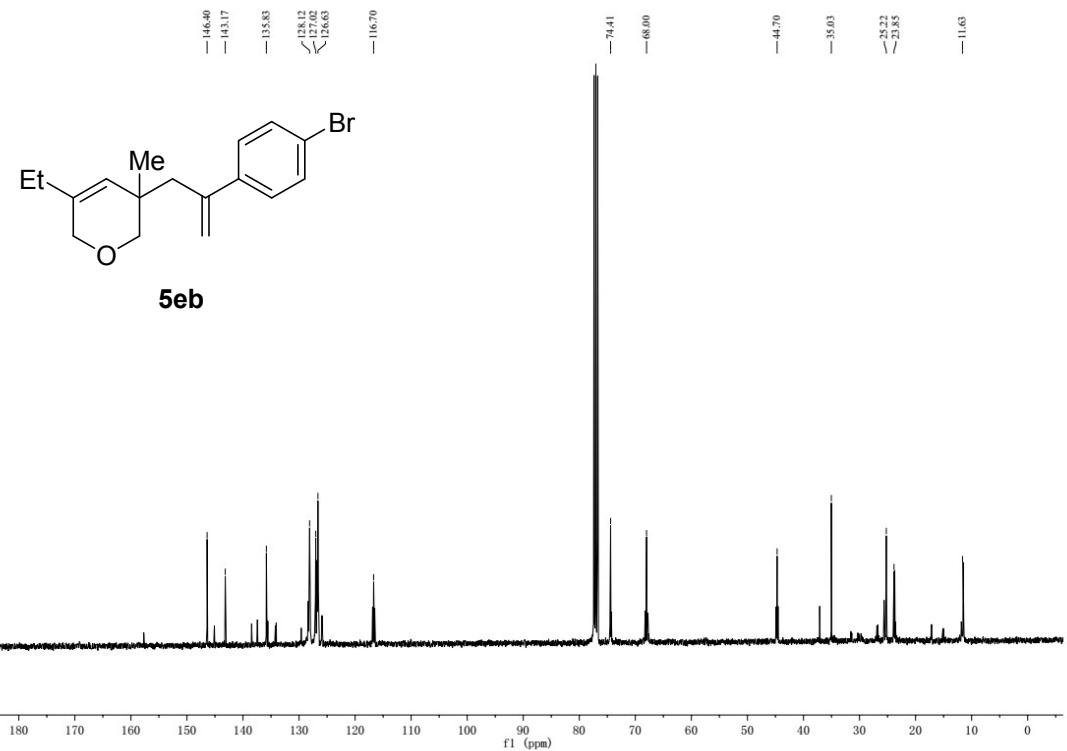




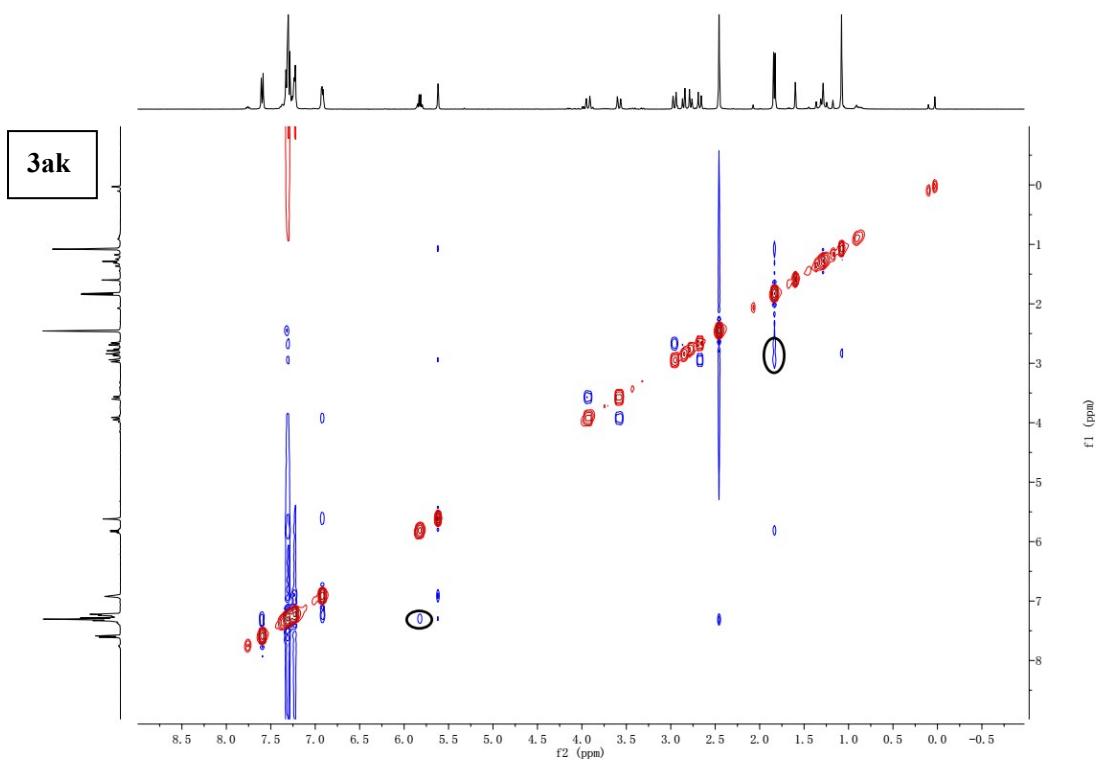




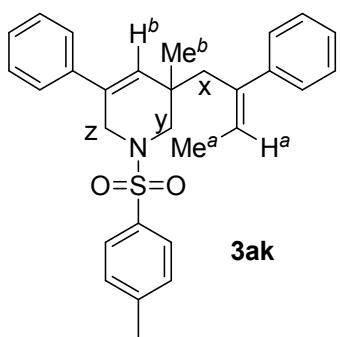




## V. Copies of the NOESY for Product 3ak



From the view of the spectrum **3ak**, there was signal between protons of the allyl ( $H^a$ , 5.79) and phenyl (7.30). There were signals between protons of methyl ( $Me^a$ , 1.80) and methylene (x, dd, 2.96 and 2.68). On the contrast, there were no signals between  $H^a$  and methylene hydrogen (x), or methyl hydrogen ( $Me^a$ ) and phenyl. So, the isomer of product **3ak** should be in E configuration as below.



<sup>1</sup> Richard C. Larock, Mark J. Doty, and Xiaojun Han *J. Org. Chem.*, 1999, 64(24), 8770-8779.

<sup>2</sup> Zhenjie Ni, Laurent Giordano, Alphonse Tenaglia, *Chemistry - A European Journal*, 2014, 20, 11703-11706.

<sup>3</sup> Hui Liu, Chaolong Li, Dong Qiu, Xiaofeng Tong, *Journal of the American Chemical Society*, 2011, 133, 6187 – 6193.

<sup>4</sup> Adele Casaschi, Ronald Grigg, Jose M. Sansano, *Tetrahedron*, 2000, 56, 38, 7553 – 7560.

<sup>5</sup> Abadh Kishor Jha, Nidhi Jain, *Chemical Communications*, 2016, 52, 1831 – 1834.