

## Supporting Information

### Metal-free radical oxidative decarboxylation/cyclization of acylperoxides and 2-isocyanobiphenyls

Changduo Pan, Honglin Zhang, Jie Han, Yixiang Cheng and Chengjian Zhu\*  
State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical  
Engineering, Nanjing University, Nanjing, 210093, China  
*E-mail: cjzhu@nju.edu.cn*

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## 1. General experimental details

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured on 400 MHz spectrometer, using CDCl<sub>3</sub> as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts ( $\delta$ ) are given in ppm relative to TMS, the coupling constants *J* are given in Hz. HRMS were recorded on a TOF LC/MS equipped with electrospray ionization (ESI) probe operating in positive or negative ion mode.

### Starting Materials:

2-Isocyanobiaryl compounds were prepared according to the reported procedure.<sup>1</sup> Acylperoxides were synthesized<sup>2</sup> except benzoyl peroxide (**2a**) and lauroyl peroxide (**2l**).

**Typical procedure for the decarboxylatively arylation cyclization of 2-isocyanobiaryls with benzoyl peroxide:** the mixture of 2-isocyanobiaryl **1** (0.2 mmol), benzoyl peroxide **2a** (0.6 mmol, 145.2 mg) and PhCF<sub>3</sub> (2 mL) were added into the sealed tube. The sealed tube was evacuated and backfilled with N<sub>2</sub>. The reaction mixture was vigorously stirred at 100 °C for 12 h. After the completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the desired products.

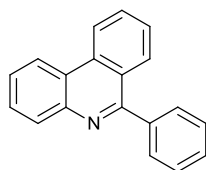
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<sup>1</sup> (a) M. Tobisu, K. Koh, T. Furukawa and N. Chatani, *Angew. Chem., Int. Ed.*, 2012, **51**, 11363; (b) Z. Liang, J. Zhang, Z. Liu, K. Wang and Y. Zhang, *Tetrahedron* 2013, **69**, 6519.

<sup>2</sup> W. Y. Yu, W. N. Sit, Z. Zhou and A. S. C. Chan, *Org. Lett.*, 2009, **11**, 3174.

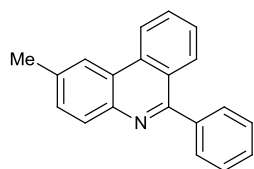
## 2. Experimental characterization data for compounds

### 6-phenylphenanthridine (3aa)<sup>3</sup>



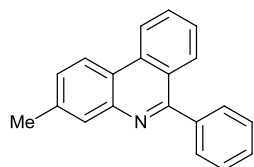
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.59 (d, *J* = 8.3 Hz, 1H), 8.51 (d, *J* = 8.1 Hz, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.77-7.75 (m, 1H), 7.68-7.63 (m, 3H), 7.61-7.56 (m, 1H), 7.53-7.41 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 161.3, 143.8, 139.8, 133.5, 130.6, 130.4, 129.7, 128.9, 128.8, 128.7, 128.4, 127.1, 126.9, 125.2, 123.7, 122.2, 121.9.

### 2-methyl-6-phenylphenanthridine (3ba)<sup>3</sup>



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.56 (d, *J* = 8.3 Hz, 1H), 8.28 (s, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.73-7.69 (m, 1H), 7.65-7.62 (m, 2H), 7.50-7.41 (m, 5H), 2.54 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 160.3, 142.1, 139.9, 136.8, 133.2, 130.6, 130.3, 130.1, 129.8, 128.8, 128.6, 128.4, 126.9, 125.3, 123.6, 122.2, 121.6, 22.0.

### 3-methyl-6-phenylphenanthridine (3ca)<sup>4</sup>

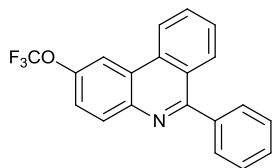


<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.53 (d, *J* = 8.3 Hz, 1H), 8.37 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.95 (s, 1H), 7.73-7.68 (m, 1H), 7.64-7.62 (m, 2H), 7.48-7.39 (m, 5H), 2.49 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 160.1, 143.7, 139.1, 133.1, 131.8, 131.1, 130.5, 129.7, 129.2, 129.0, 128.7, 127.9, 127.4, 126.2, 124.0, 123.1, 121.8.

### 6-phenyl-2-(trifluoromethoxy)phenanthridine (3da)

<sup>3</sup> Z. Xia, J. Huang, Y. He, J. Zhao, J. Lei and Q. Zhu, *Org. Lett.*, 2014, **16**, 2546.

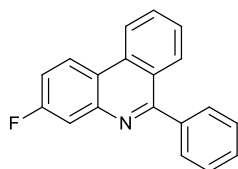
<sup>4</sup> J. Peng, T. Chen, C. Chen and B. Li, *J. Org. Chem.*, 2011, **76**, 9507.



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.60 (d,  $J = 8.3$  Hz, 1H), 8.40 (s, 1H), 8.26 (d,  $J = 8.9$  Hz, 1H), 8.12 (d,  $J = 8.2$  Hz, 1H), 7.90-7.86 (m, 1H), 7.73-7.52 (m, 7H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  161.8, 147.6, 142.1, 139.4, 132.9, 132.3, 130.9, 129.7, 129.1, 128.9, 128.5, 127.9, 125.3, 124.6, 122.3, 122.2, 113.7.

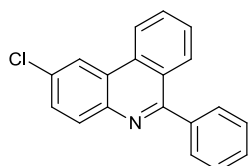
HRMS (ESI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{13}\text{F}_3\text{NO}(\text{M}+\text{H})^+$  340.0944, found 340.0948.

### **3-fluoro-6-phenylphenanthridine (3ea)**<sup>5</sup>



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.59-8.53 (m, 2H), 8.09 (d,  $J = 8.2$  Hz, 1H), 7.89-7.81 (m, 2H), 7.73-7.70 (m, 2H), 7.60-7.52 (m, 4H), 7.44-7.39 (m, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  162.8 (d,  $J_{\text{C-F}} = 246.5$  Hz), 162.6, 145.1 (d,  $J_{\text{C-F}} = 11.8$  Hz), 139.5, 133.3, 130.9, 129.7, 129.1, 128.9, 128.5, 126.9, 124.8 (d,  $J_{\text{C-F}} = 1.0$  Hz), 123.9 (d,  $J_{\text{C-F}} = 9.5$  Hz), 122.0, 120.4 (d,  $J_{\text{C-F}} = 2.0$  Hz), 116.0 (d,  $J_{\text{C-F}} = 23.7$  Hz), 114.8 (d,  $J_{\text{C-F}} = 20.4$  Hz).

### **2-chloro-6-phenylphenanthridine (3fa)**<sup>3</sup>

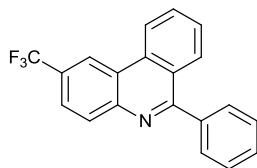


$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.47 (d,  $J = 8.3$  Hz, 1H), 8.44 (d,  $J = 2.2$  Hz, 1H), 8.06 (d,  $J = 8.7$  Hz, 1H), 8.01 (d,  $J = 8.2$  Hz, 1H), 7.77-7.73 (m, 1H), 7.64-7.61 (m, 2H), 7.59-7.51 (m, 2H), 7.49-7.43 (m, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  161.5, 142.2, 139.4, 132.8, 132.4, 131.8, 130.8, 129.7, 129.4, 129.0, 128.9, 128.5, 127.8, 125.3, 124.8, 122.2, 121.6.

### **6-phenyl-2-(trifluoromethyl)phenanthridine (3ga)**<sup>6</sup>

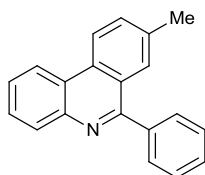
<sup>5</sup> J. Li, H. Wang, J. Sun, Y. Yang and L. Liu, *Org. Biomol. Chem.*, 2014, **12**, 7904.

<sup>6</sup> T. Xiao, L. Li, G. Lin, Q. Wang, P. Zhang, Z.-W. Mao and L. Zhou, *Green Chem.*, 2014, **16**, 2418.



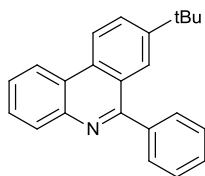
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.86 (s, 1H), 8.68 (d,  $J = 8.2$  Hz, 1H), 8.32 (d,  $J = 8.5$  Hz, 1H), 8.13 (d,  $J = 8.2$  Hz, 1H), 7.94-7.86 (m, 2H), 7.74-7.72 (m, 2H), 7.65 (d,  $J = 7.6$  Hz, 1H), 7.59-7.54 (m, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  163.5, 145.2, 139.3, 133.2, 131.2, 129.7, 129.2, 129.1, 128.7, 128.6, 128.5 (q,  $J_{\text{C-F}} = 32.1$  Hz), 128.0, 125.5, 124.8 (q,  $J_{\text{C-F}} = 3.2$  Hz), 124.5 (q,  $J_{\text{C-F}} = 270.2$  Hz), 123.4, 122.2, 119.8 (q,  $J_{\text{C-F}} = 4.2$  Hz).

**8-methyl-6-phenylphenanthridine (3ha)**<sup>7</sup>



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.58-8.55 (m, 2H), 8.23 (d,  $J = 8.1$  Hz, 1H), 7.85 (s, 1H), 7.73-7.63 (m, 5H), 7.58-7.52 (m, 3H), 2.49 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  161.0, 143.5, 140.0, 137.1, 132.3, 131.3, 130.3, 129.7, 128.6, 128.5, 128.4, 128.2, 126.8, 125.4, 123.8, 122.1, 121.7, 21.8.

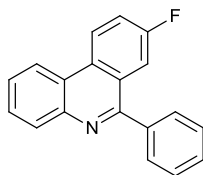
**8-(tert-butyl)-6-phenylphenanthridine (3ia)**<sup>5</sup>



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.62 (d,  $J = 8.7$  Hz, 1H), 8.58 (d,  $J = 8.1$  Hz, 1H), 8.23 (d,  $J = 8.1$  Hz, 1H), 8.10 (s, 1H), 7.94-7.91 (m, 1H), 7.78-7.63 (m, 4H), 7.59-7.51 (m, 3H), 1.36 (s, 9H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  161.3, 150.2, 143.6, 139.9, 131.3, 130.3, 129.8, 128.9, 128.7, 128.42, 128.40, 126.8, 125.1, 124.5, 123.7, 122.0, 121.8, 35.0, 31.2.

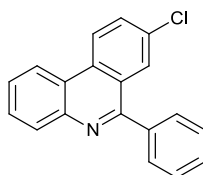
**8-fluoro-6-phenylphenanthridine (3ja)**<sup>5</sup>

<sup>7</sup> S. W. Youn, J. H. Bihn, *Tetrahedron Lett.*, 2009, **50**, 4598.



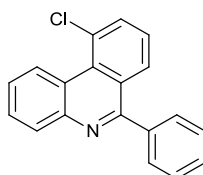
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.67-8.63 (m, 1H), 8.52 (d,  $J = 8.1$  Hz, 1H), 8.24 (d,  $J = 8.1$  Hz, 1H), 7.76-7.65 (m, 5H), 7.59-7.51 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  161.2 (d,  $J_{\text{C-F}} = 246.4$  Hz), 160.4 (d,  $J_{\text{C-F}} = 3.8$  Hz), 143.5, 139.3, 130.5, 130.1 (d,  $J_{\text{C-F}} = 1.8$  Hz), 129.6, 129.0, 128.7, 128.6, 127.3, 126.5 (d,  $J_{\text{C-F}} = 7.8$  Hz), 124.8 (d,  $J_{\text{C-F}} = 8.3$  Hz), 123.3, 121.7, 119.8 (d,  $J_{\text{C-F}} = 23.8$  Hz), 113.3 (d,  $J_{\text{C-F}} = 21.9$  Hz).

### **8-chloro-6-phenylphenanthridine (3ka)**<sup>3</sup>



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.55 (d,  $J = 8.8$  Hz, 1H), 8.49 (d,  $J = 8.2$  Hz, 1H), 8.22 (d,  $J = 8.1$  Hz, 1H), 8.04 (s, 1H), 7.76-7.63 (m, 5H), 7.59-7.51 (m, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  160.1, 143.7, 139.1, 133.1, 131.8, 131.1, 130.5, 129.6, 129.2, 129.0, 128.7, 127.9, 127.4, 126.1, 124.0, 123.1, 121.8..

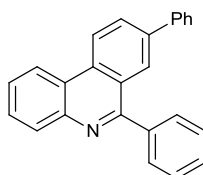
### **10-chloro-6-phenylphenanthridine (3la)**



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  9.83 (d,  $J = 8.5$  Hz, 1H), 8.26 (d,  $J = 8.1$  Hz, 1H), 8.03 (d,  $J = 8.1$  Hz, 1H), 7.90 (d,  $J = 7.6$  Hz, 1H), 7.81-7.77 (m, 1H), 7.71-7.65 (m, 3H), 7.57-7.45 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  161.1, 144.8, 139.9, 134.3, 131.4, 130.6, 130.4, 129.7, 129.2, 128.8, 128.6, 128.5, 128.0, 126.8, 126.5, 126.3, 122.9.

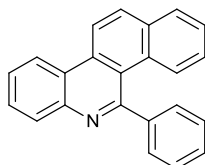
HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{13}\text{ClN}$  ( $\text{M}+\text{H}$ )<sup>+</sup> 290.0731, found 290.0733.

### **6,8-diphenylphenanthridine (3ma)**<sup>6</sup>



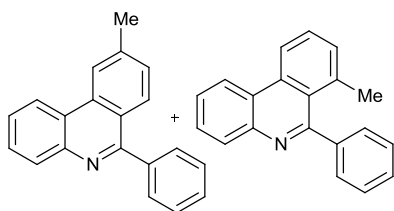
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.75 (d,  $J = 8.6$  Hz, 1H), 8.62 (d,  $J = 7.8$  Hz, 1H), 8.31 (s, 1H), 8.26 (d,  $J = 7.4$  Hz, 1H), 8.10 (d,  $J = 8.5$  Hz, 1H), 7.79-7.74 (m, 4H), 7.71-7.67 (m, 1H), 7.63-7.50 (m, 5H), 7.47-7.43 (m, 1H), 7.39-7.35 (m, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  161.4, 143.8, 140.3, 139.9, 139.8, 132.5, 130.4, 129.8, 129.7, 129.0, 128.9, 128.8, 128.5, 127.8, 127.4, 127.0, 126.8, 125.6, 123.6, 122.9, 122.0.

**5-phenylbenzo[i]phenanthridine (3na)**<sup>1a</sup>



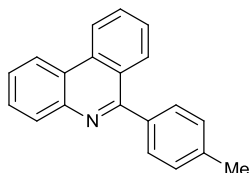
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.64 (d,  $J = 8.8$  Hz, 2H), 8.27 (d,  $J = 8.2$  Hz, 1H), 8.15 (d,  $J = 8.9$  Hz, 1H), 7.91 (d,  $J = 7.8$  Hz, 1H), 7.79-7.75 (m, 2H), 7.71-7.66 (m, 1H), 7.63-7.61 (m, 2H), 7.51-7.46 (m, 4H), 7.21-7.17 (m, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  159.3, 144.6, 144.0, 134.4, 133.2, 132.3, 130.3, 129.9, 129.1, 129.0, 128.9, 128.5, 128.4, 128.3, 126.8, 126.4, 125.8, 123.6, 122.5, 121.5, 119.9.

**9-methyl-6-phenylphenanthridine and 7-methyl-6-phenylphenanthridine (3oa and 3oa')**<sup>6</sup>



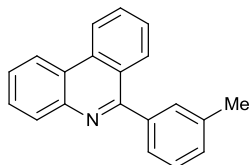
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.58 (d,  $J = 8.1$  Hz, 2.55H), 8.46 (s, 0.53H), 8.24-8.18 (m, 1.6H), 7.97 (d,  $J = 8.4$  Hz, 0.65H), 7.73-7.69 (m, 3.73H), 7.67-7.62 (m, 1.96H), 7.54-7.44 (m, 6.04H), 7.42-7.40 (m, 1.96), 2.63 (s, 1.5H), 2.07 (s, 3H).

**6-(*p*-tolyl)phenanthridine (3ab)**<sup>5</sup>



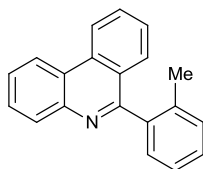
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.67 (d,  $J = 8.3$  Hz, 1H), 8.59 (d,  $J = 8.2$  Hz, 1H), 8.23 (d,  $J = 8.1$  Hz, 1H), 8.13 (d,  $J = 8.1$  Hz, 1H), 7.84-7.80 (m, 1H), 7.76-7.72 (m, 1H), 7.68-7.57 (m, 4H), 7.36 (d,  $J = 7.8$  Hz, 2H), 2.47 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  161.3, 143.9, 138.6, 136.9, 133.5, 130.5, 130.3, 129.7, 129.1, 128.9, 128.8, 126.8, 125.3, 123.7, 122.2, 121.9, 21.4.

**6-(*m*-tolyl)phenanthridine (3ac)<sup>4</sup>**



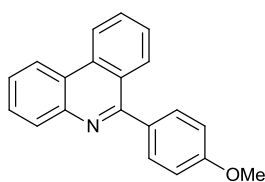
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.67 (d, *J* = 8.3 Hz, 1H), 8.59 (d, *J* = 7.8 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 7.82 (t, *J* = 8.1 Hz, 1H), 7.76-7.62 (m, 1H), 7.68-7.64 (m, 1H), 7.61-7.55 (m, 2H), 7.51-7.49 (m, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 2.47 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 161.5, 143.8, 139.7, 138.2, 133.4, 130.5, 130.4, 130.3, 129.4, 129.0, 128.8, 128.2, 127.1, 126.9, 125.3, 123.7, 122.2, 121.9, 21.6.

**6-(*o*-tolyl)phenanthridine (3ad)<sup>4</sup>**



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.69 (d, *J* = 8.3 Hz, 1H), 8.63 (d, *J* = 8.1 Hz, 1H), 8.25 (d, *J* = 8.1 Hz, 1H), 7.85-7.81 (m, 1H), 7.78-7.74 (m, 1H), 7.72-7.67 (m, 2H), 7.58-7.54 (m, 1H), 7.43-7.33 (m, 4H), 2.11 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 161.9, 143.8, 139.2, 136.4, 133.0, 130.7, 130.4, 130.3, 129.3, 128.8, 128.7, 128.6, 127.3, 126.9, 125.8, 123.8, 122.1, 122.0, 19.8.

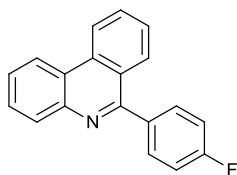
**6-(4-methoxyphenyl)phenanthridine (3ae)<sup>5</sup>**



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.67 (d, *J* = 8.3 Hz, 1H), 8.59 (d, *J* = 8.1 Hz, 1H), 8.23 (d, *J* = 8.1 Hz, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.85-7.81 (m, 1H), 7.76-7.58 (m, 5H), 7.11-7.07 (m, 2H), 3.90 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 160.9, 160.1, 143.9, 133.5, 132.3, 131.2, 130.5, 130.3, 128.9, 128.8, 127.0, 126.7, 123.6, 122.2, 121.9, 113.9, 55.5.

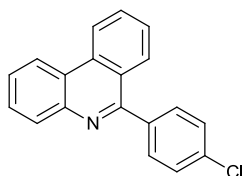
**6-(4-fluorophenyl)phenanthridine (3af)<sup>6</sup>**





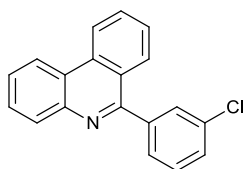
$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.68 (d,  $J = 8.4$  Hz, 1H), 8.60 (d,  $J = 8.1$  Hz, 1H), 8.22 (d,  $J = 8.2$  Hz, 1H), 8.06 (d,  $J = 8.2$  Hz, 1H), 7.87-7.82 (m, 1H), 7.77-7.66 (m, 4H), 7.63-7.59 (m, 1H), 7.27-7.22 (m, 2H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  163.2 (d,  $J_{\text{C-F}} = 246.6$  Hz), 160.1, 143.7, 135.8 (d,  $J_{\text{C-F}} = 3.3$  Hz), 133.5, 131.7, 131.6, 130.7, 130.3, 128.8 (d,  $J_{\text{C-F}} = 32.9$  Hz), 127.2, 127.0, 125.1, 123.7, 122.3, 121.9, 115.5 (d,  $J_{\text{C-F}} = 21.4$  Hz).

**6-(4-chlorophenyl)phenanthridine (3ag)**<sup>5</sup>



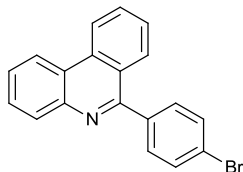
$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.68 (d,  $J = 8.3$  Hz, 1H), 8.59 (d,  $J = 8.1$  Hz, 1H), 8.22 (d,  $J = 8.1$  Hz, 1H), 8.04 (d,  $J = 8.2$  Hz, 1H), 7.87-7.82 (m, 1H), 7.77-7.73 (m, 1H), 7.70-7.66 (m, 3H), 7.63-7.59 (m, 1H), 7.55-7.51 (m, 2H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  159.9, 143.7, 138.2, 134.9, 133.5, 131.2, 130.7, 130.3, 128.9, 128.7, 128.5, 127.3, 127.2, 125.0, 123.8, 122.3, 120.0.

**6-(3-chlorophenyl)phenanthridine (3ah)**<sup>5</sup>



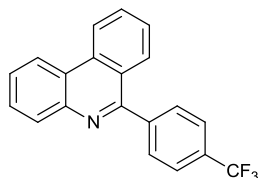
$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.70 (d,  $J = 8.3$  Hz, 1H), 8.61 (d,  $J = 8.1$  Hz, 1H), 8.23 (d,  $J = 8.1$  Hz, 1H), 8.05 (d,  $J = 8.2$  Hz, 1H), 7.88-7.84 (m, 1H), 7.79-7.68 (m, 3H), 7.65-7.59 (m, 2H), 7.52-7.46 (m, 2H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  159.7, 143.7, 141.5, 134.5, 133.5, 130.8, 130.4, 129.9, 129.7, 129.0, 128.9, 128.5, 127.9, 127.3, 127.2, 124.9, 123.8, 122.3, 122.0.

**6-(4-bromophenyl)phenanthridine (3ai)**<sup>5</sup>



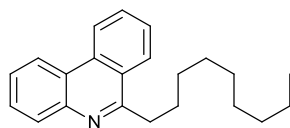
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.69 (d,  $J = 8.3$  Hz, 1H), 8.60 (d,  $J = 8.1$  Hz, 1H), 8.22 (d,  $J = 8.2$  Hz, 1H), 8.05 (d,  $J = 8.2$  Hz, 1H), 7.87-7.83 (m, 1H), 7.78-7.73 (m, 1H), 7.70-7.66 (m, 3H), 7.64-7.59 (m, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  159.9, 143.7, 138.7, 133.5, 131.6, 131.4, 130.7, 130.4, 128.9, 128.5, 127.3, 127.2, 124.9, 123.8, 123.2, 122.3, 122.0.

**6-(4-(trifluoromethyl)phenyl)phenanthridine (3aj)**<sup>6</sup>



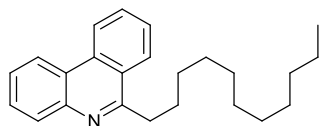
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.70 (d,  $J = 8.3$  Hz, 1H), 8.62 (d,  $J = 8.1$  Hz, 1H), 8.23 (d,  $J = 8.0$  Hz, 1H), 8.01 (d,  $J = 8.3$  Hz, 1H), 7.89-7.81 (m, 5H), 7.79-7.75 (m, 1H), 7.72-7.68 (m, 1H), 7.64-7.60 (m, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  159.7, 143.7, 143.3, 133.5, 130.86, 130.83 (q,  $J_{\text{C-F}} = 33.2$  Hz), 130.4, 130.2, 129.1, 128.3, 127.4, 125.4 (q,  $J_{\text{C-F}} = 3.7$  Hz), 124.8, 123.8, 122.4, 122.0.

**6-nonylphenanthridine (3ak)**



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.63 (d,  $J = 8.2$  Hz, 1H), 8.53 (d,  $J = 8.1$  Hz, 1H), 8.25 (d,  $J = 8.1$  Hz, 1H), 8.12 (d,  $J = 8.1$  Hz, 1H), 7.84-7.80 (m, 1H), 7.72-7.63 (m, 2H), 7.63-7.59 (m, 1H), 3.36 (t,  $J = 8.0$  Hz, 2H), 1.95-1.87 (m, 2H), 1.57-1.49 (m, 2H), 1.38-1.26 (m, 10H), 0.87 (t,  $J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  162.5, 143.8, 132.9, 130.2, 129.6, 128.5, 127.2, 126.4, 126.2, 125.2, 123.6, 122.5, 121.9, 36.5, 31.9, 30.0, 29.7, 29.5, 29.3, 22.7, 14.1. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{28}\text{N}$  ( $\text{M}+\text{H}$ )<sup>+</sup> 306.2216, found 306.2219.

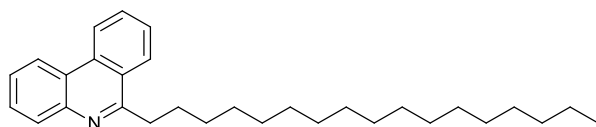
**6-undecylphenanthridine (3al)**



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.63 (d,  $J = 8.2$  Hz, 1H), 8.53 (d,  $J = 7.6$  Hz, 1H), 8.24 (d,  $J = 8.1$  Hz, 1H), 8.12 (d,  $J = 8.1$  Hz, 1H), 7.84-7.79 (m, 1H), 7.72-7.66 (m, 2H), 7.62-7.58 (m, 1H), 3.36 (t,  $J = 8.0$  Hz, 2H), 1.95-1.87 (m, 2H), 1.53-1.49 (m, 2H), 1.40-1.25 (m, 14H), 0.87 (t,  $J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  162.5, 143.8, 132.9, 130.2, 129.6, 128.5, 127.2, 126.4, 126.2, 125.2, 123.6, 122.5, 121.9, 36.5, 31.9, 30.0, 29.7, 29.68, 29.65, 29.63, 29.5, 29.3, 22.7, 14.1.

HRMS (ESI)  $m/z$  calcd for  $C_{24}H_{32}N(M+H)^+$  334.2529, found 334.2533.

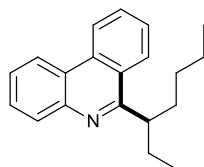
**6-heptadecylphenanthridine (3am)**



$^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  8.62 (d,  $J = 8.2$  Hz, 1H), 8.52 (d,  $J = 8.0$  Hz, 1H), 8.24 (d,  $J = 8.1$  Hz, 1H), 8.12 (d,  $J = 8.1$  Hz, 1H), 7.81 (t,  $J = 7.5$  Hz, 1H), 7.72-7.65 (m, 2H), 7.60 (t,  $J = 7.5$  Hz, 1H), 3.35 (t,  $J = 7.9$  Hz, 2H), 1.95-1.87 (m, 2H), 1.56-1.49 (m, 2H), 1.38-1.25 (m, 26H), 0.87 (t,  $J = 6.8$  Hz, 3H).  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  162.5, 143.8, 132.9, 130.2, 129.6, 128.5, 127.2, 126.4, 126.2, 125.2, 123.6, 122.5, 121.9, 36.5, 31.9, 30.0, 29.73, 29.70, 29.69, 29.64, 29.6, 29.4, 22.7, 14.1.

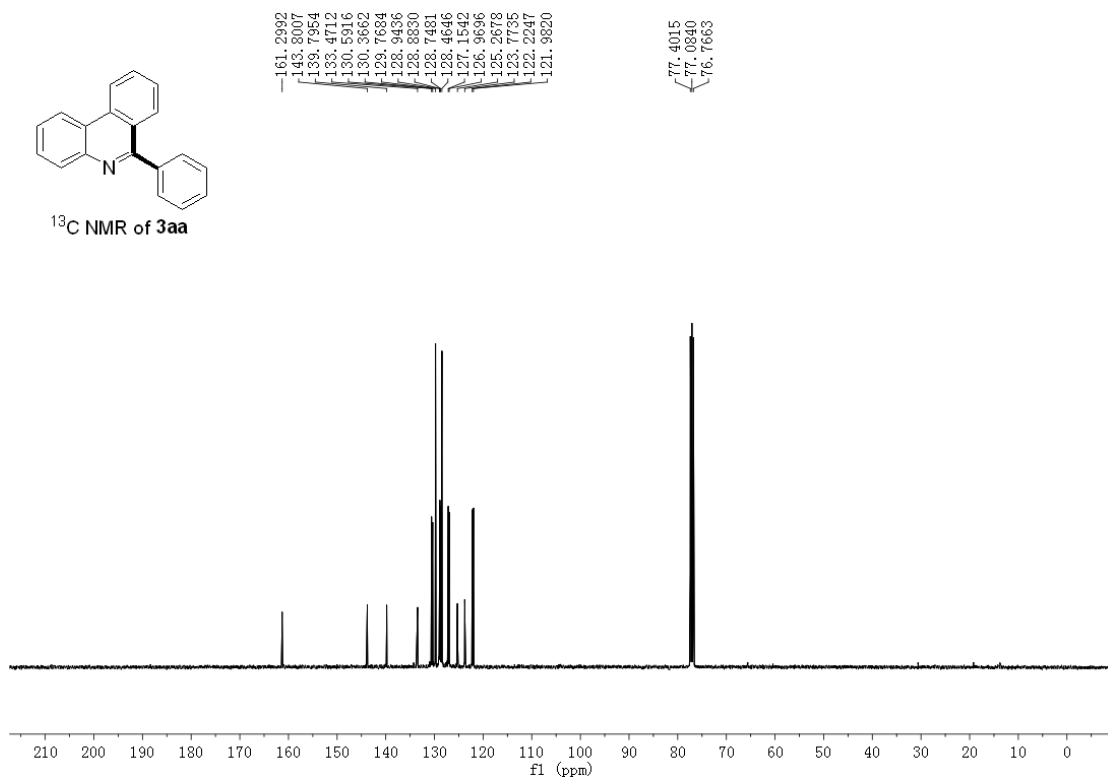
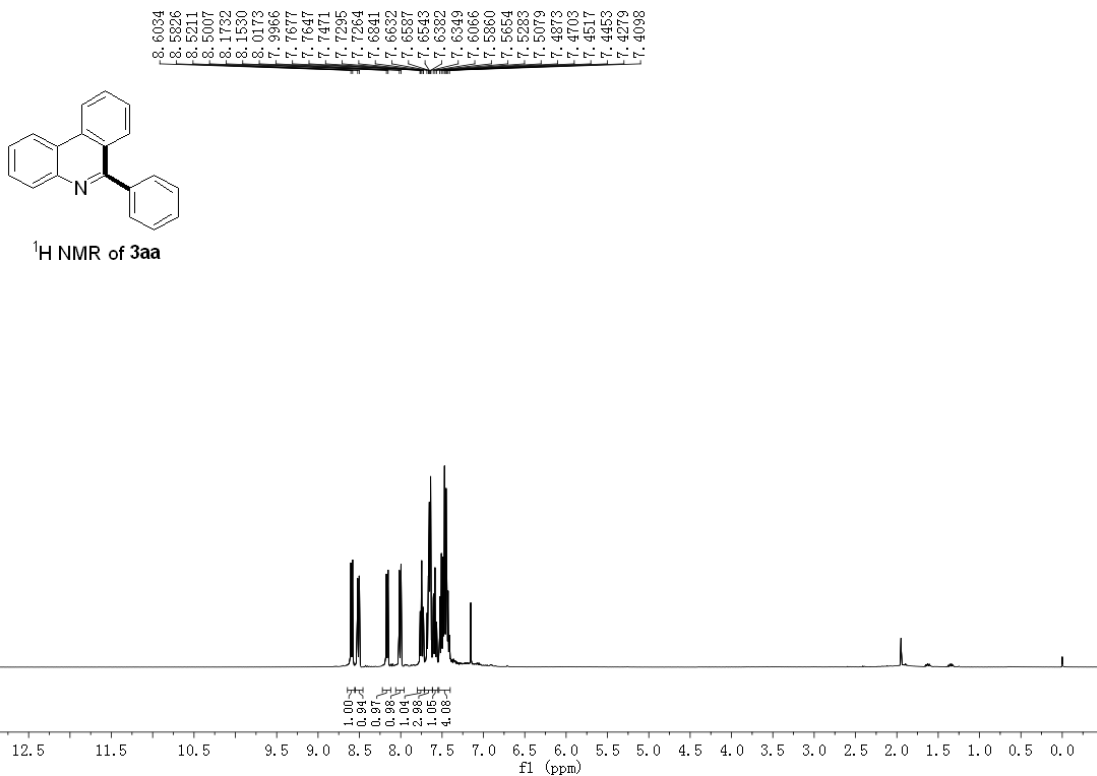
HRMS (ESI)  $m/z$  calcd for  $C_{30}H_{44}N(M+H)^+$  418.3468, found 418.3473.

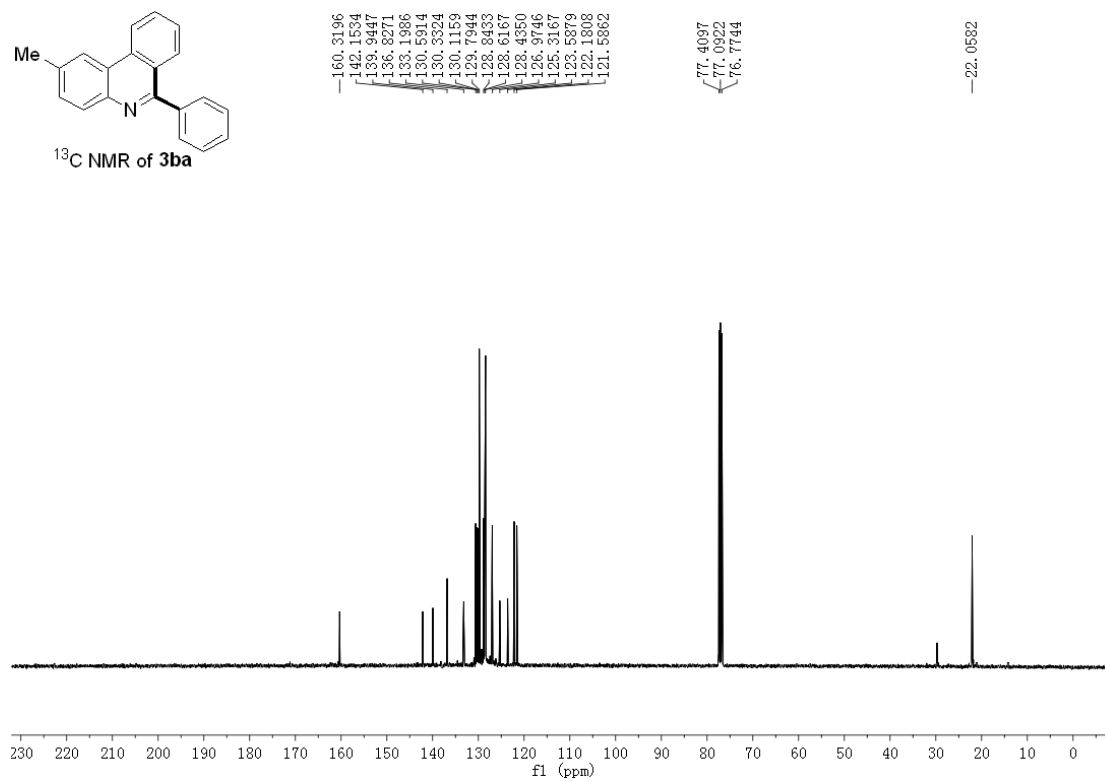
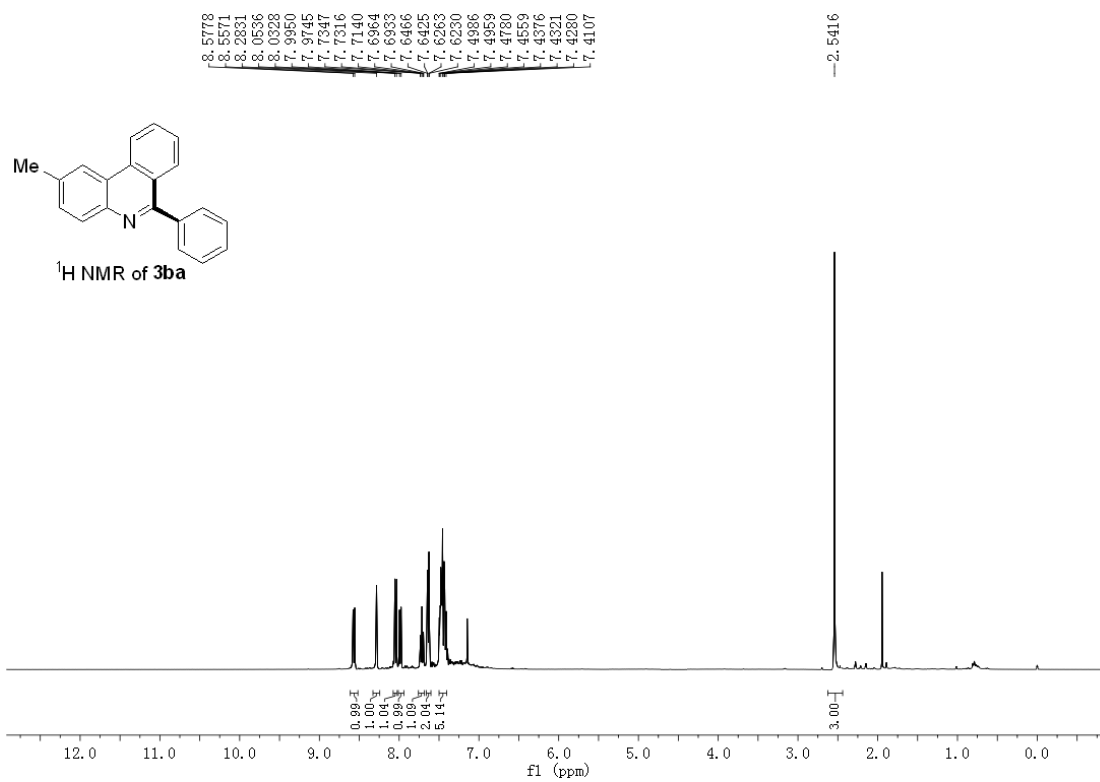
**6-(heptan-3-yl)phenanthridine (3an)**

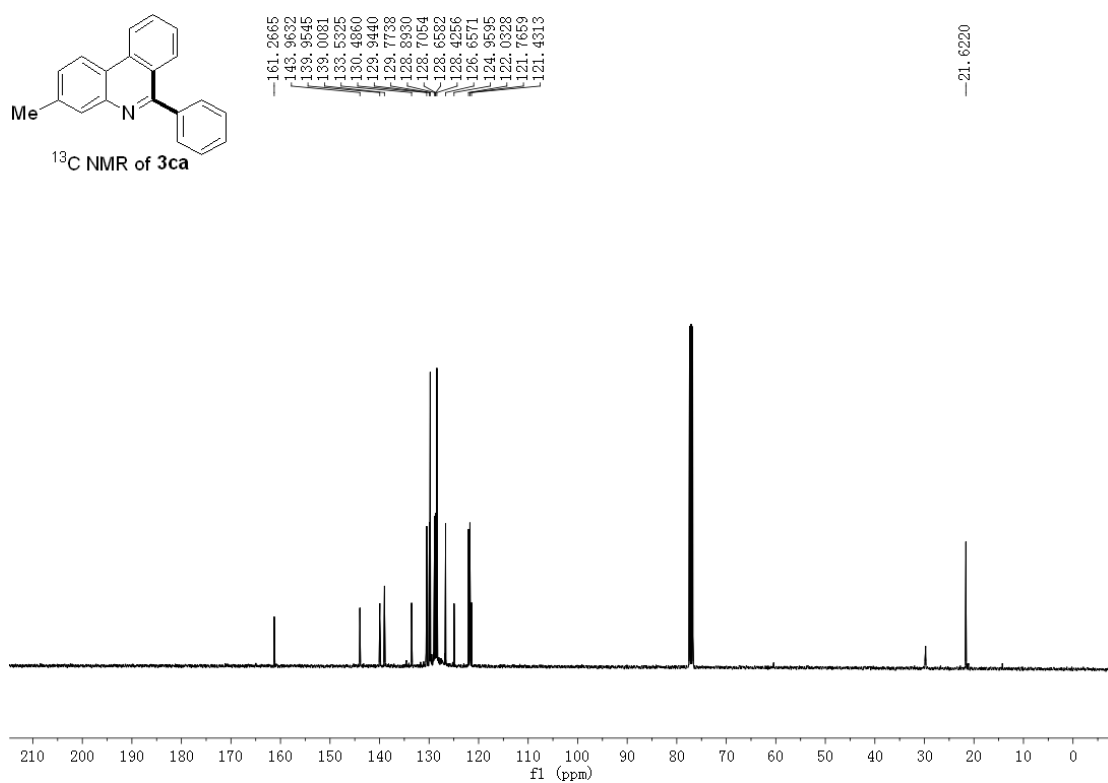
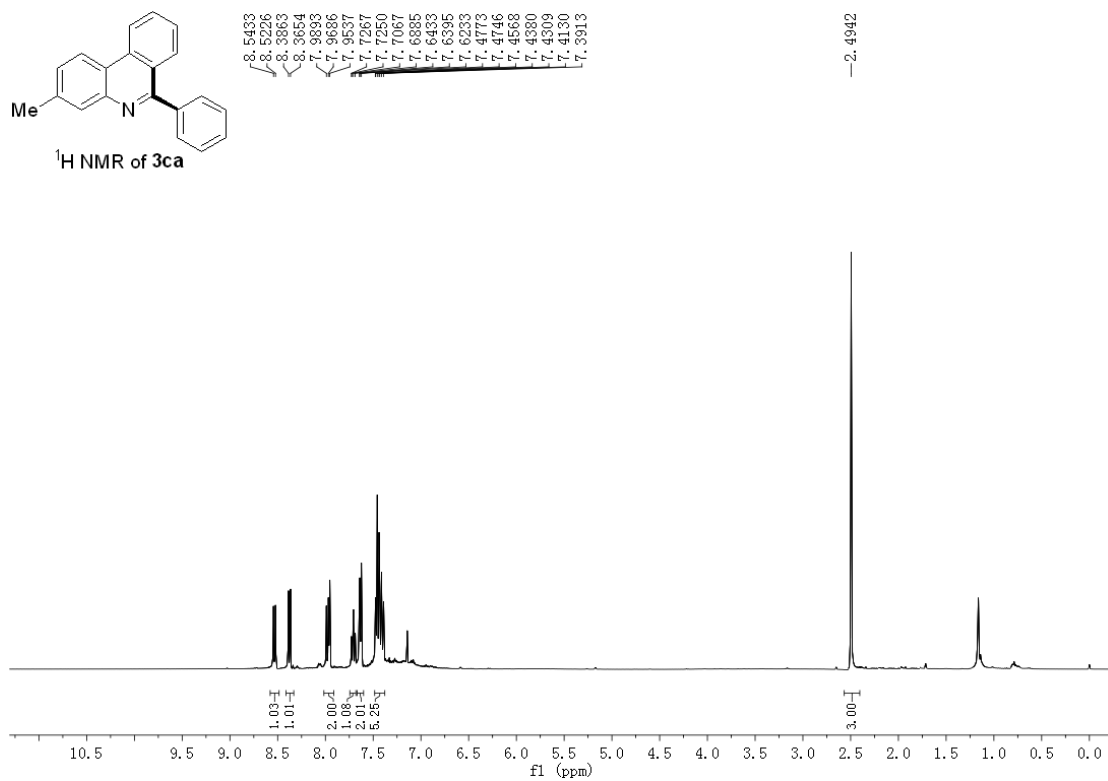


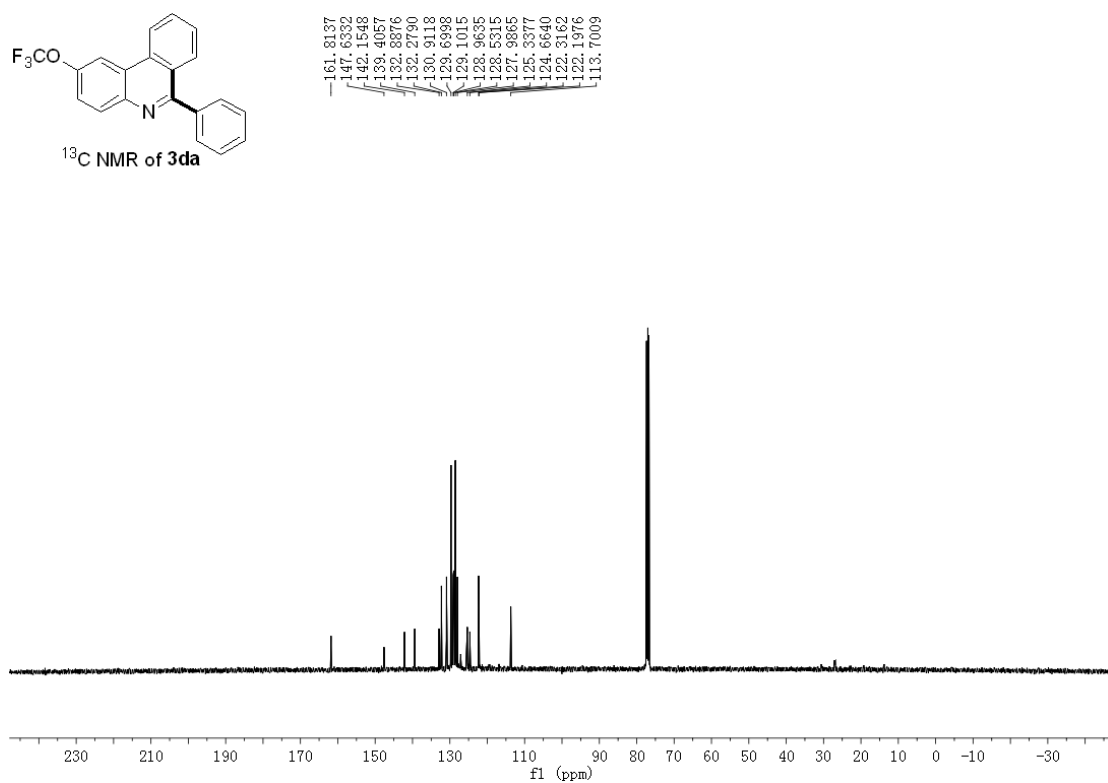
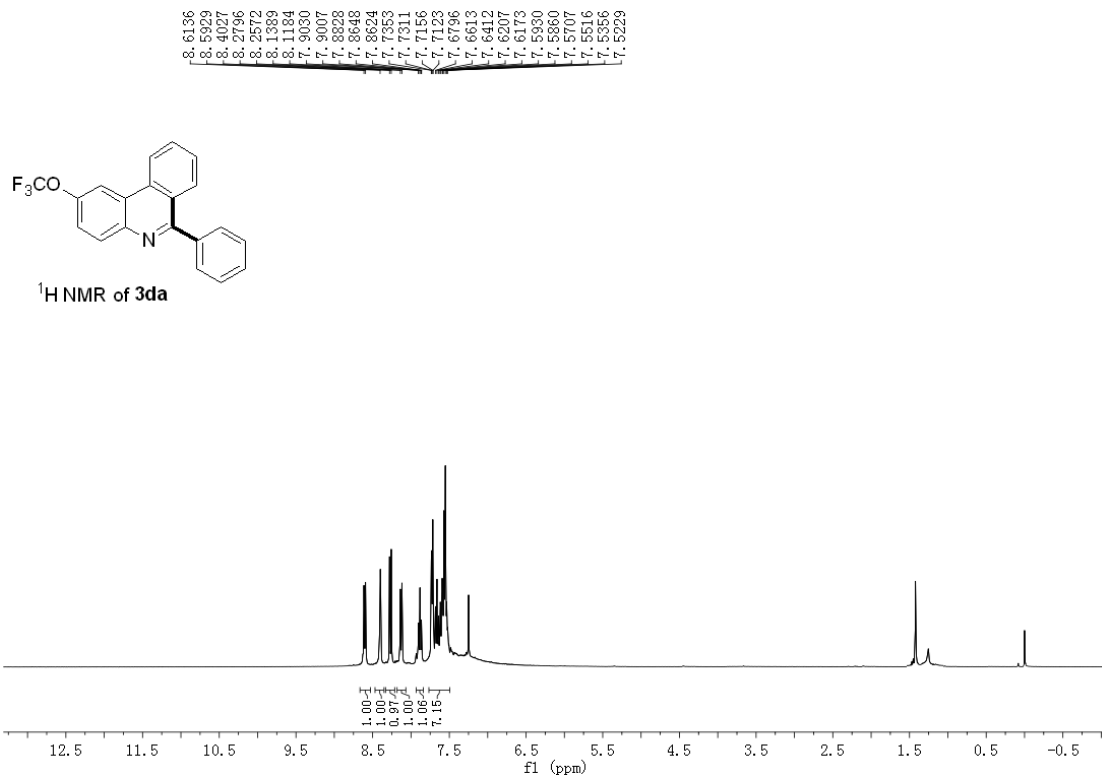
$^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  8.66 (d,  $J = 8.2$  Hz, 1H), 8.55 (d,  $J = 8.1$  Hz, 1H), 8.34 (d,  $J = 8.2$  Hz, 1H), 8.13 (d,  $J = 8.1$  Hz, 1H), 7.84-7.97 (m, 1H), 7.72-7.66 (m, 2H), 7.62-7.58 (m, 1H), 3.69-3.62 (m, 1H), 2.14-2.05 (m, 2H), 1.91-1.77 (m, 2H), 1.32-1.25 (m, 4H), 0.87-0.79 (m, 6H).  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  164.9, 143.9, 132.8, 129.9, 129.8, 127.0, 126.2, 126.0, 125.7, 123.2, 122.5, 121.8, 34.5, 30.9, 30.1, 28.0, 23.0, 14.0, 12.4.

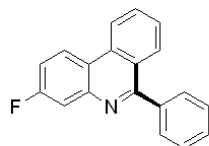
HRMS (ESI)  $m/z$  calcd for  $C_{20}H_{24}N(M+H)^+$  278.1903, found 278.1905.



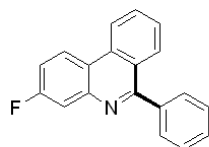
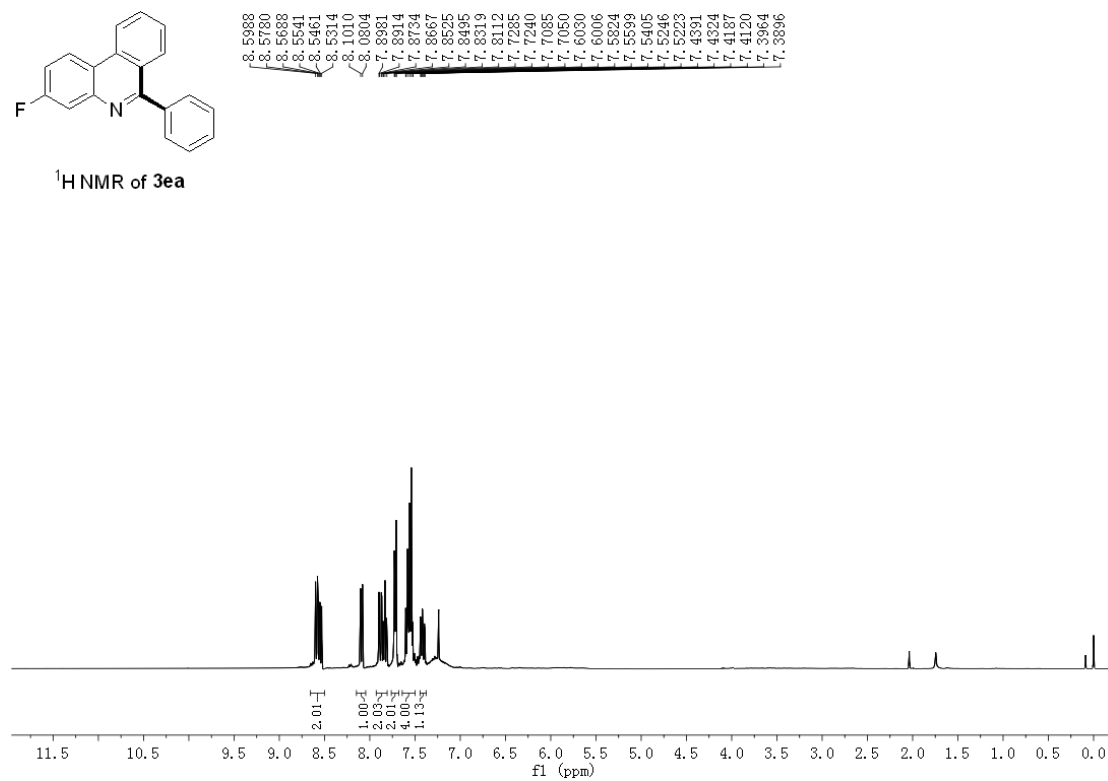




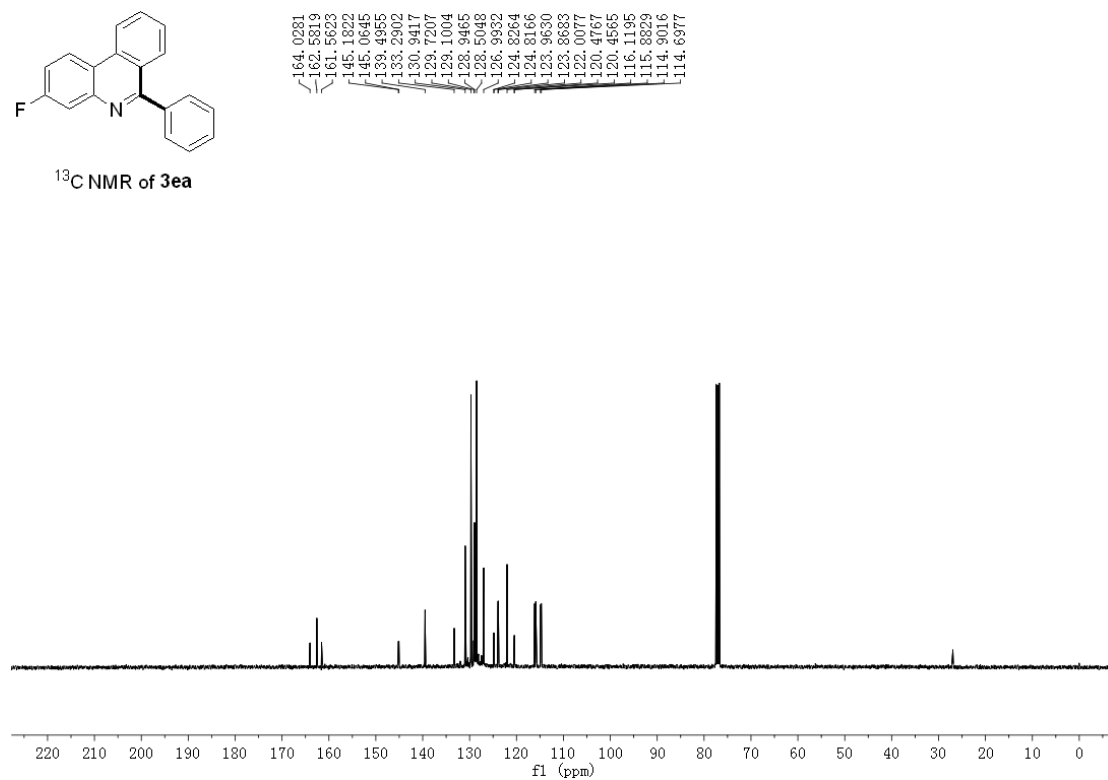




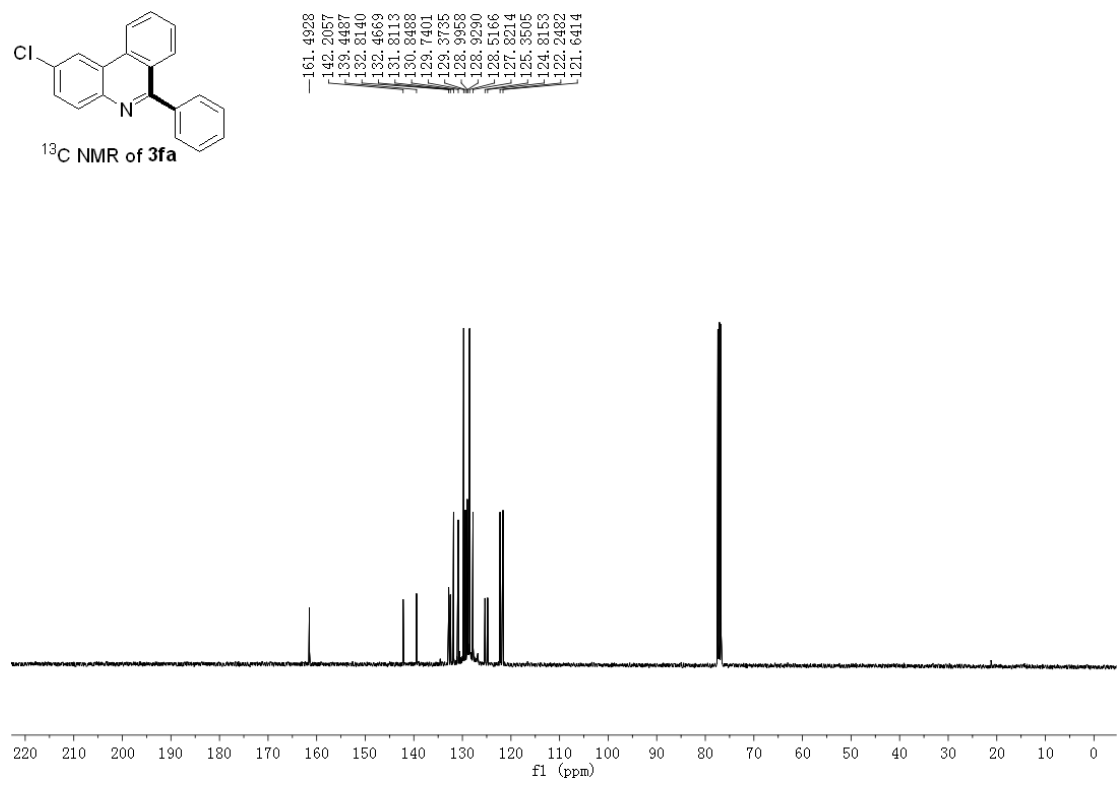
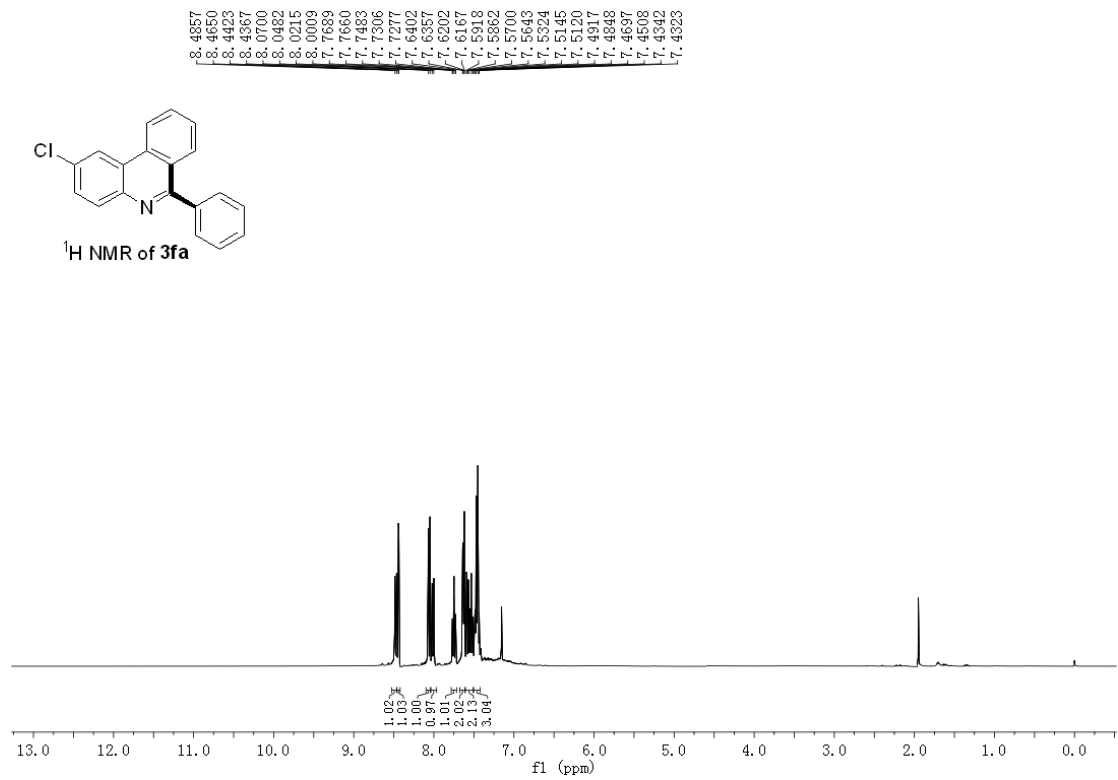
<sup>1</sup>H NMR of 3a

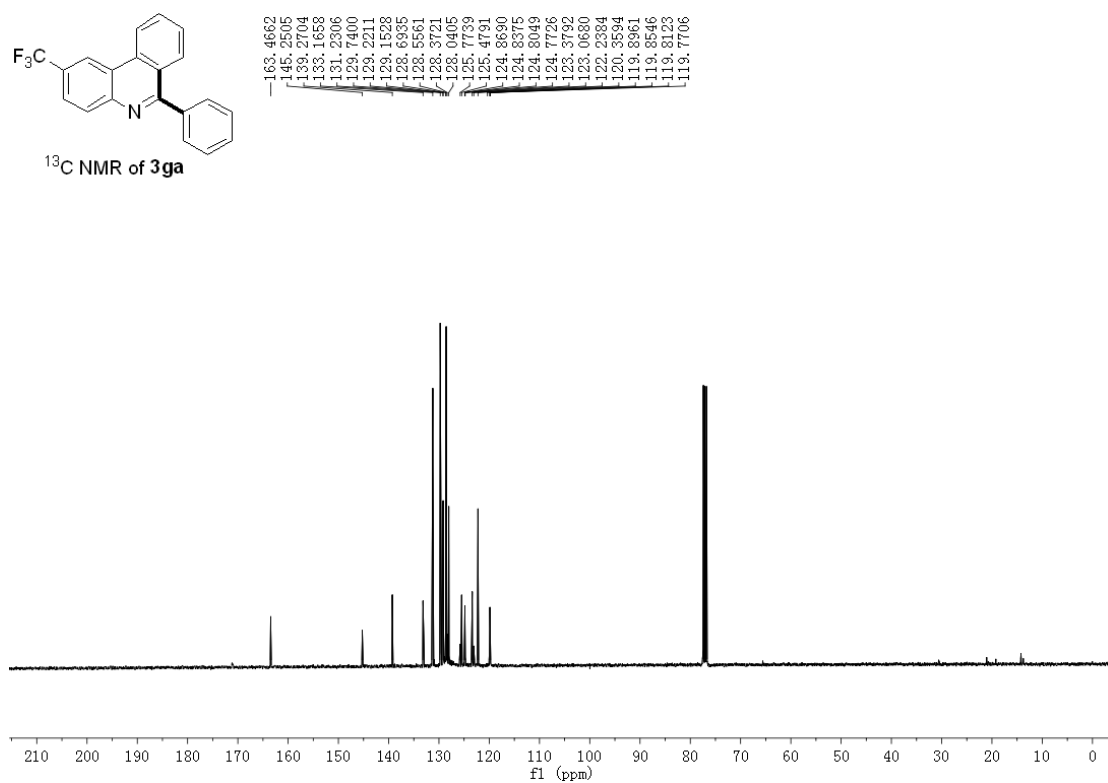
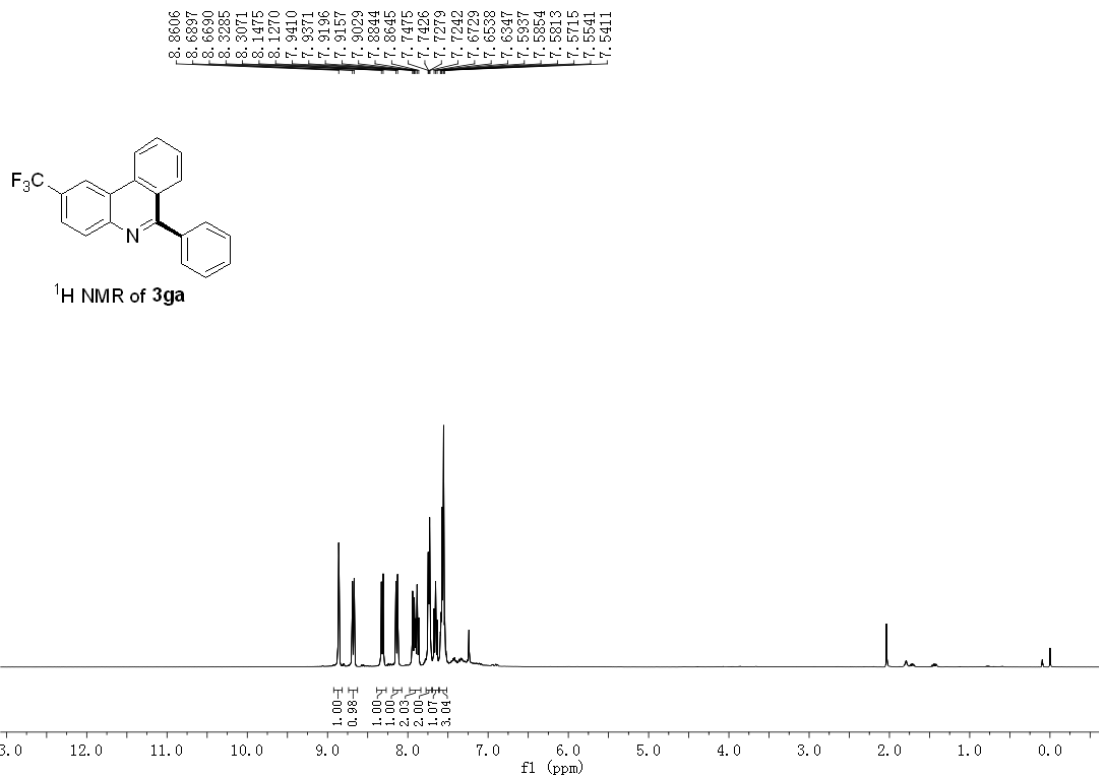


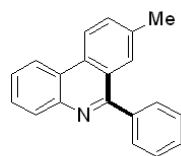
<sup>13</sup>C NMR of 3a



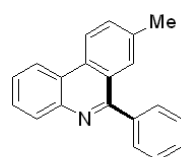
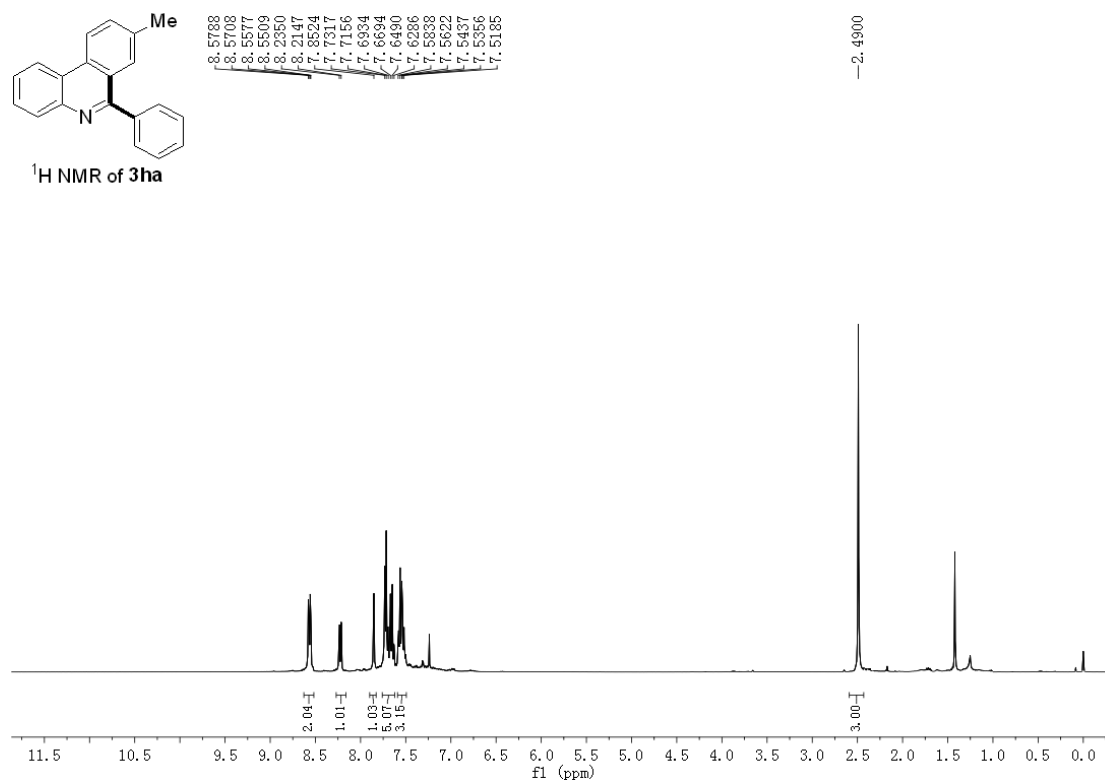




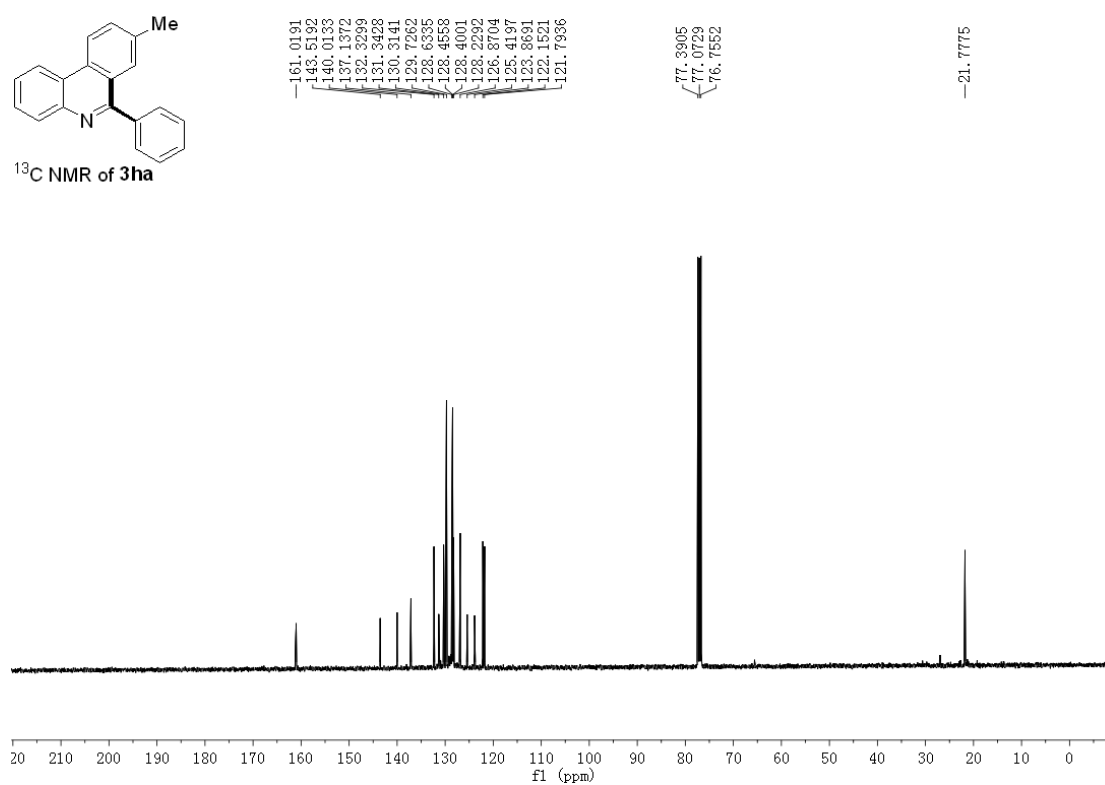


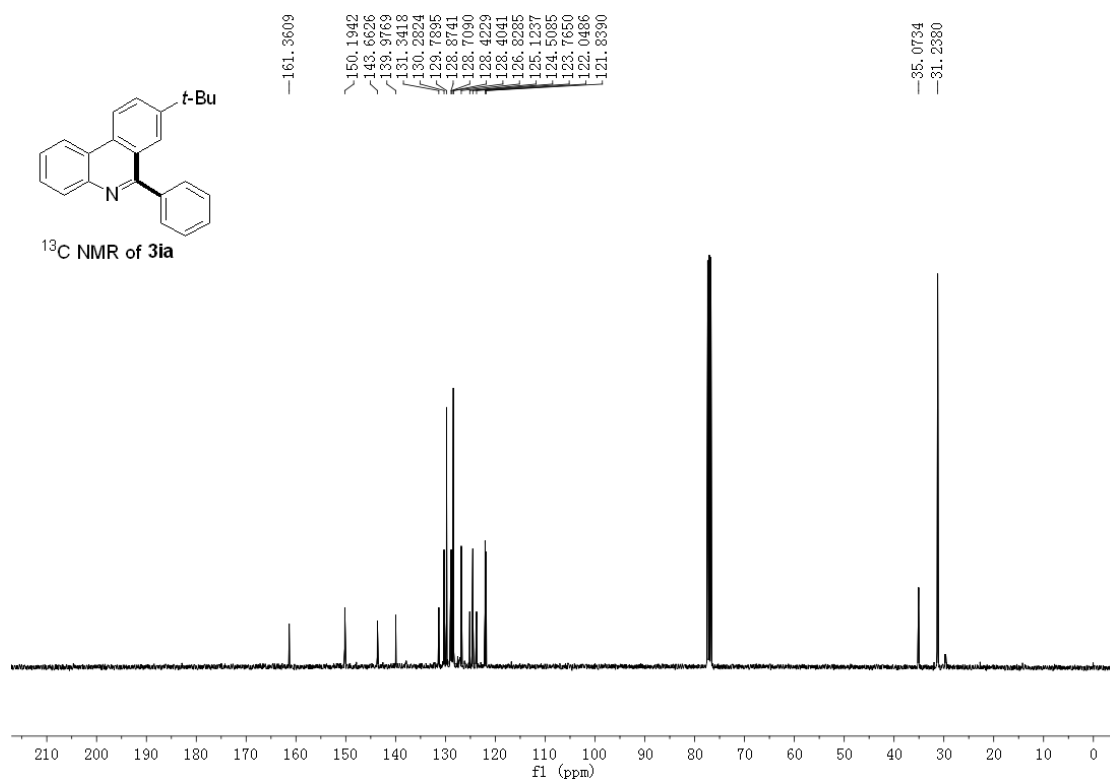
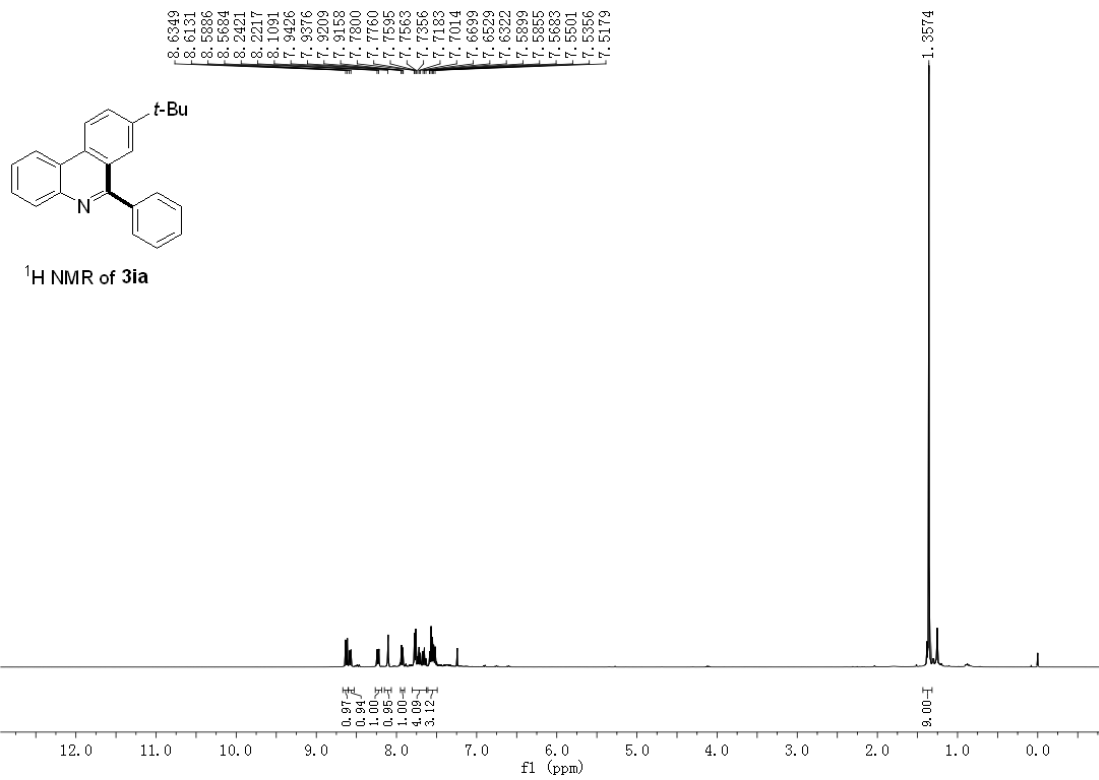


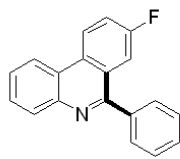
<sup>1</sup>H NMR of 3ha



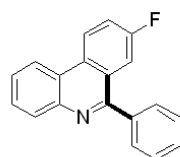
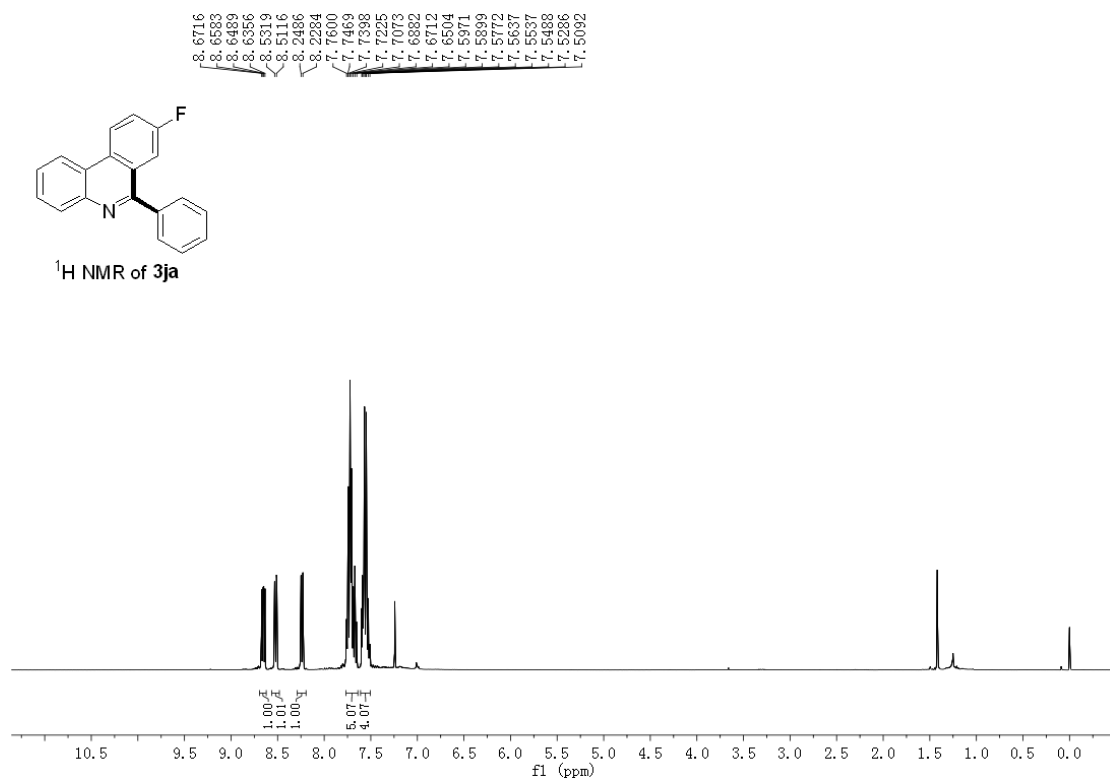
<sup>13</sup>C NMR of 3ha



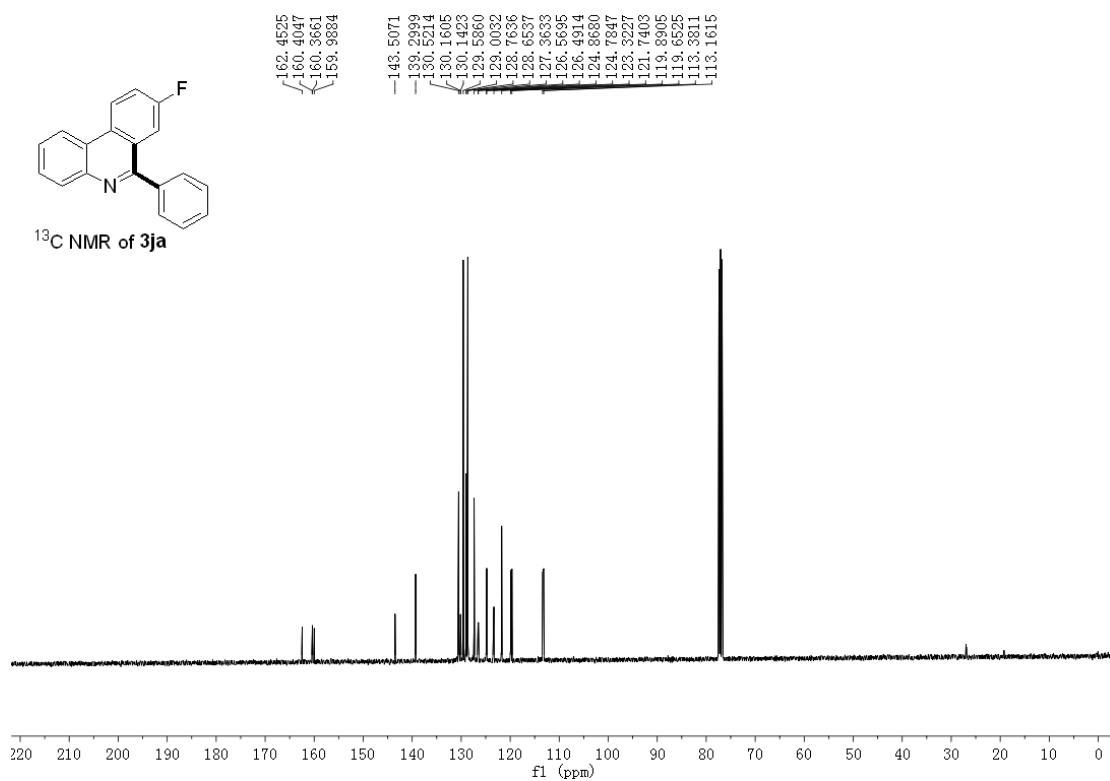


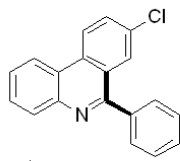


<sup>1</sup>H NMR of 3ja

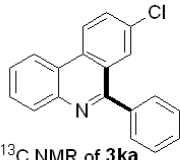
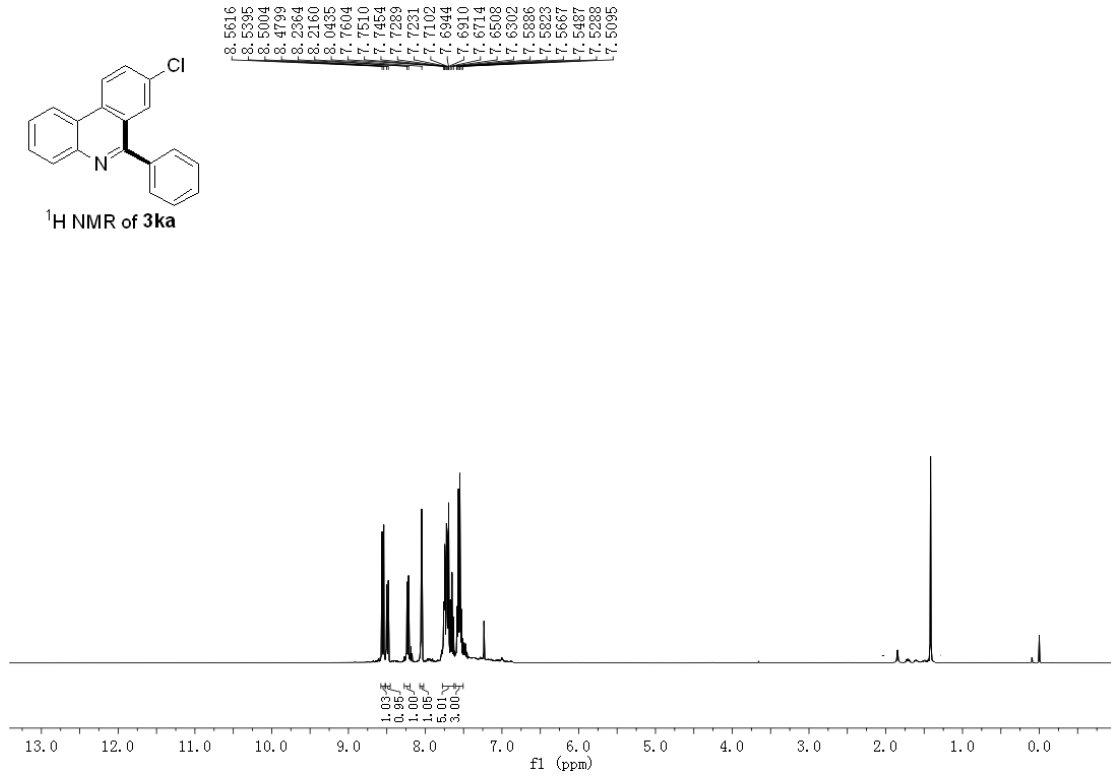


<sup>13</sup>C NMR of 3ja

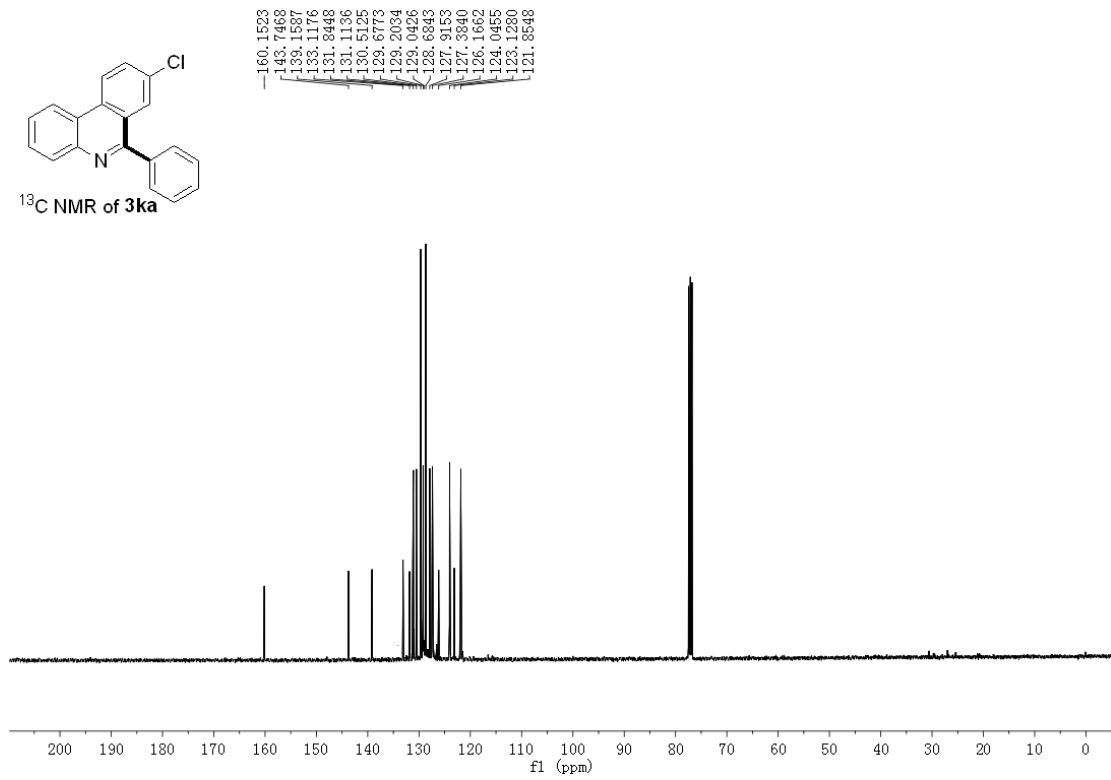


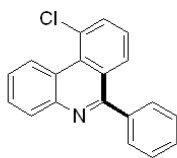


<sup>1</sup>H NMR of 3ka

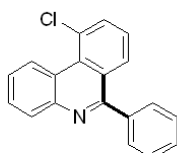
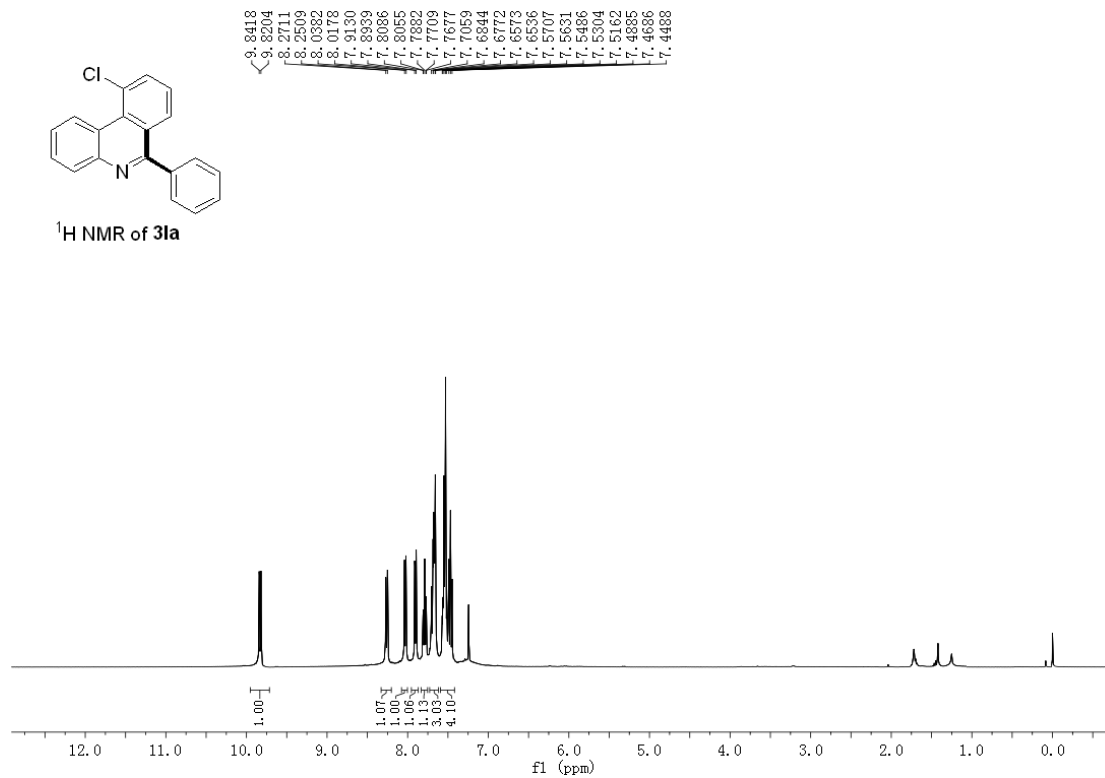


<sup>13</sup>C NMR of 3ka

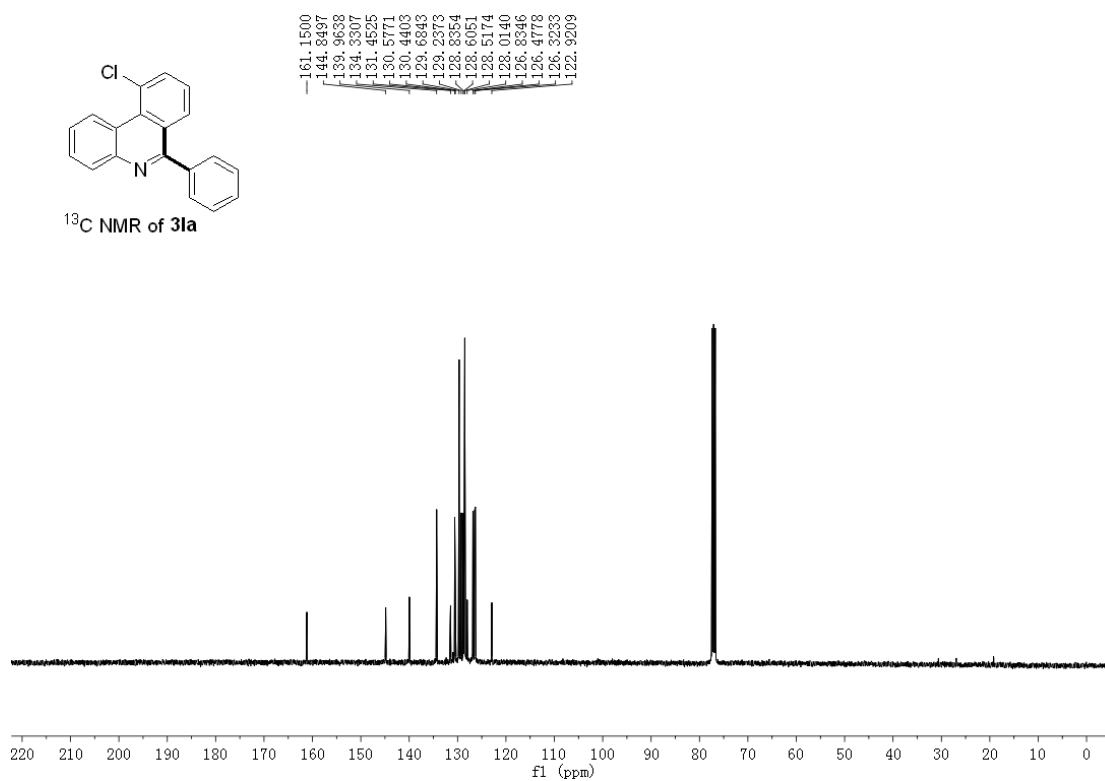


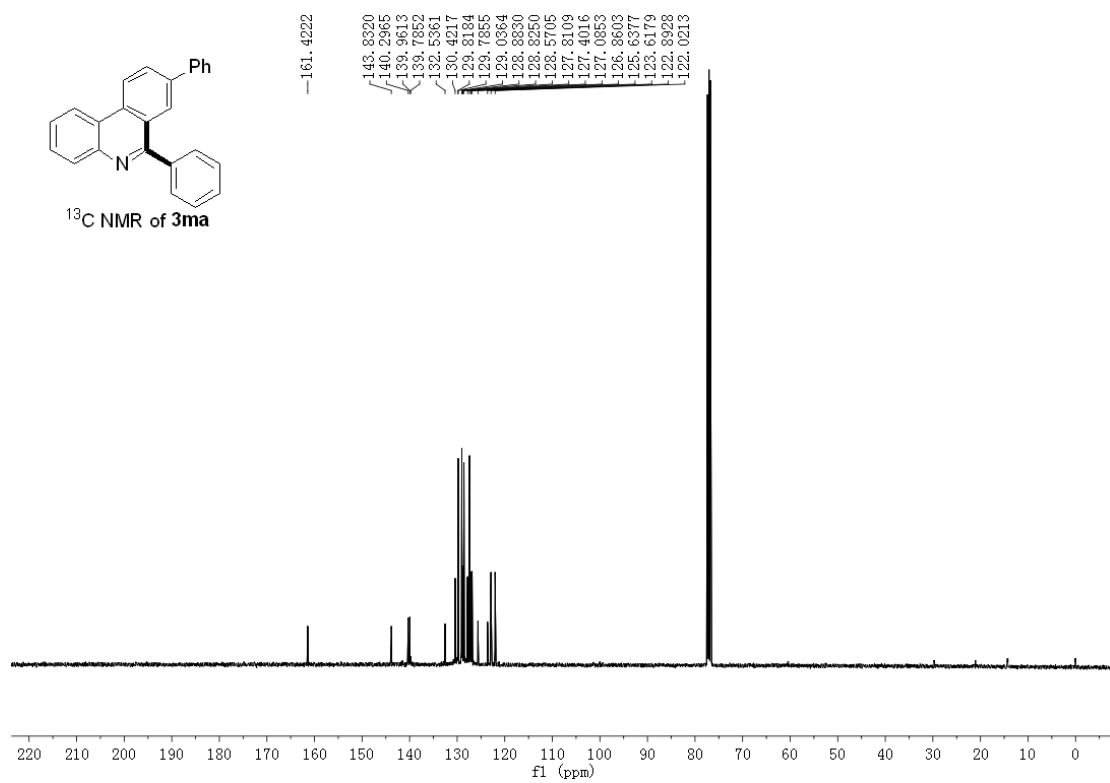
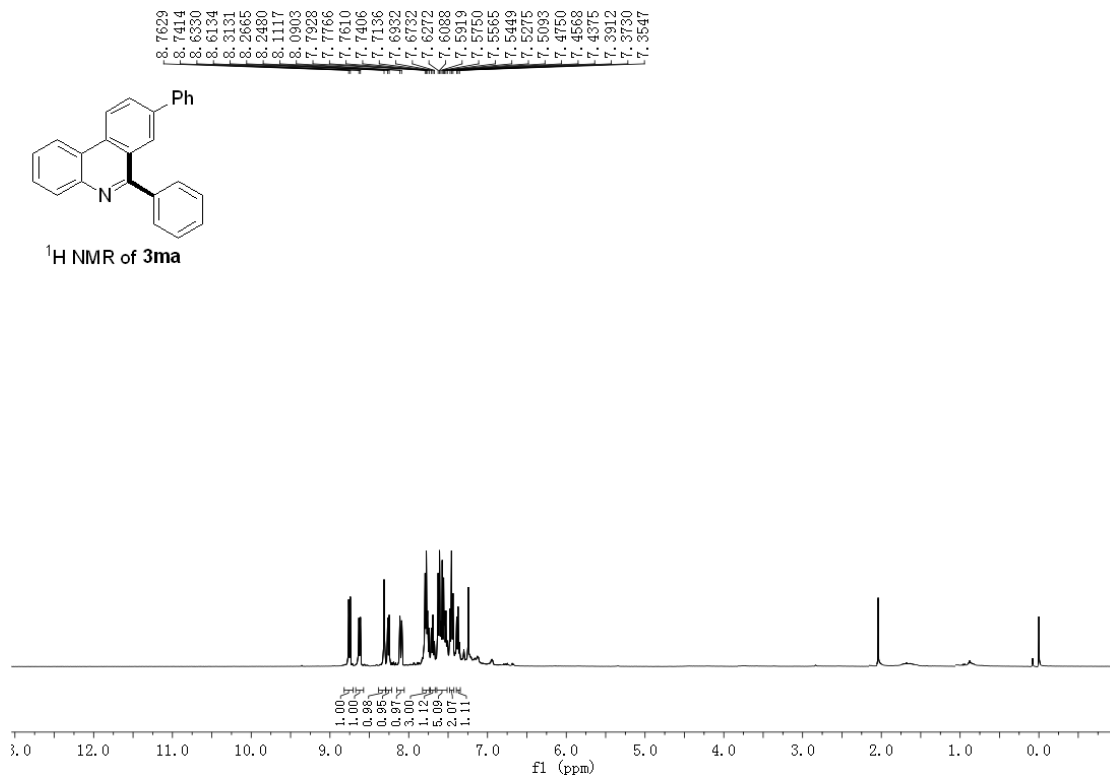


<sup>1</sup>H NMR of 3a

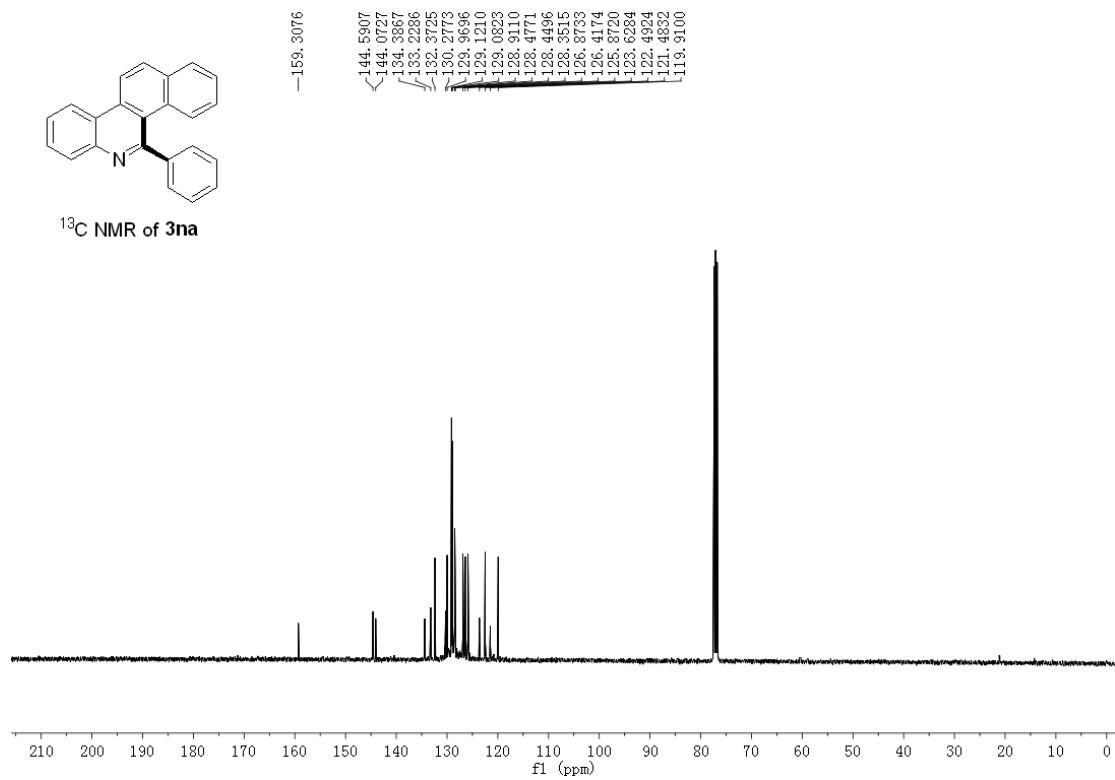
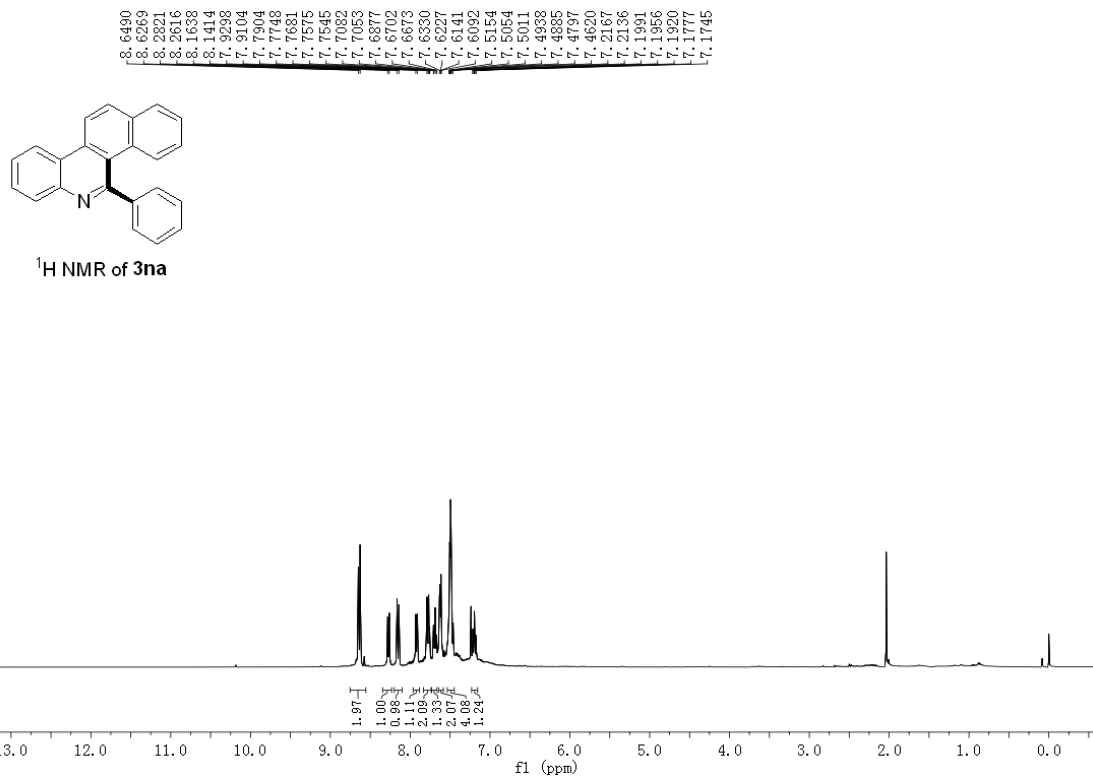


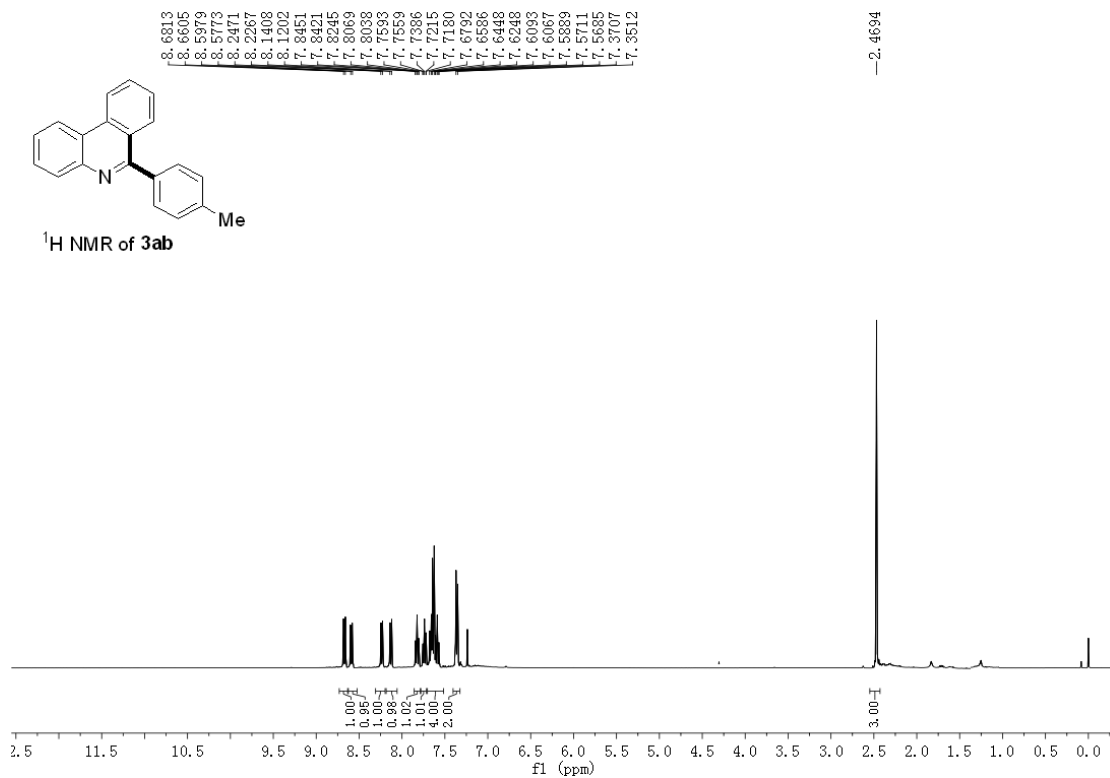
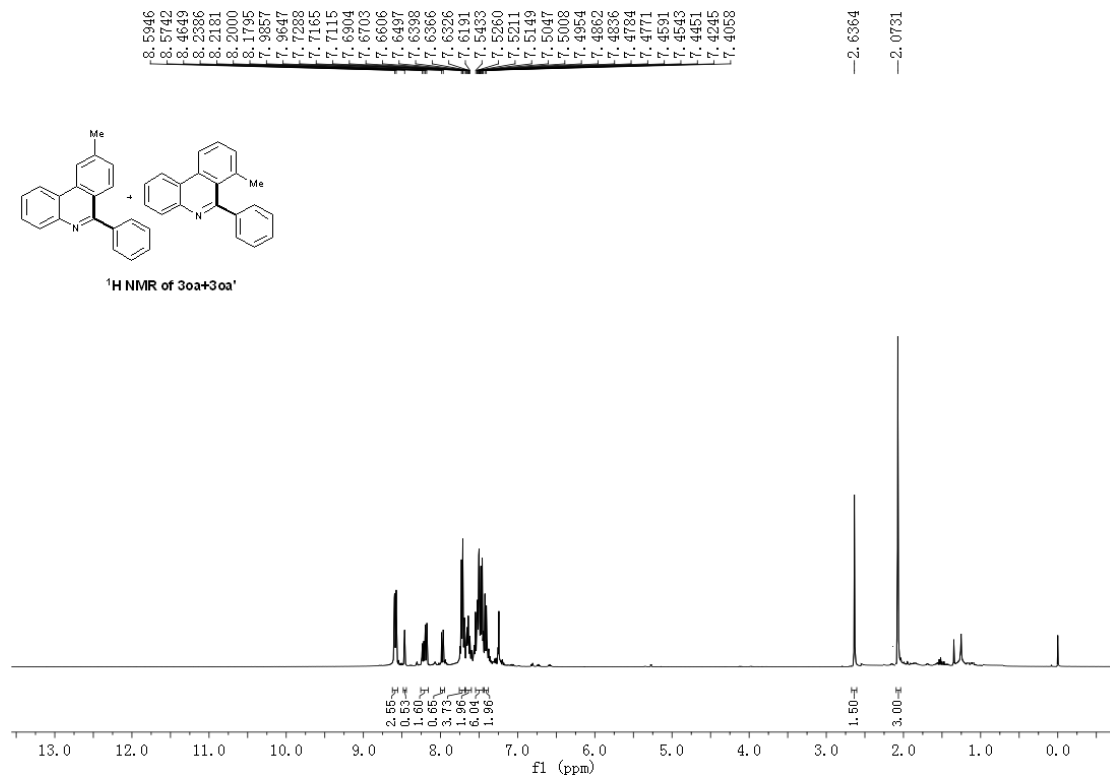
<sup>13</sup>C NMR of 3a

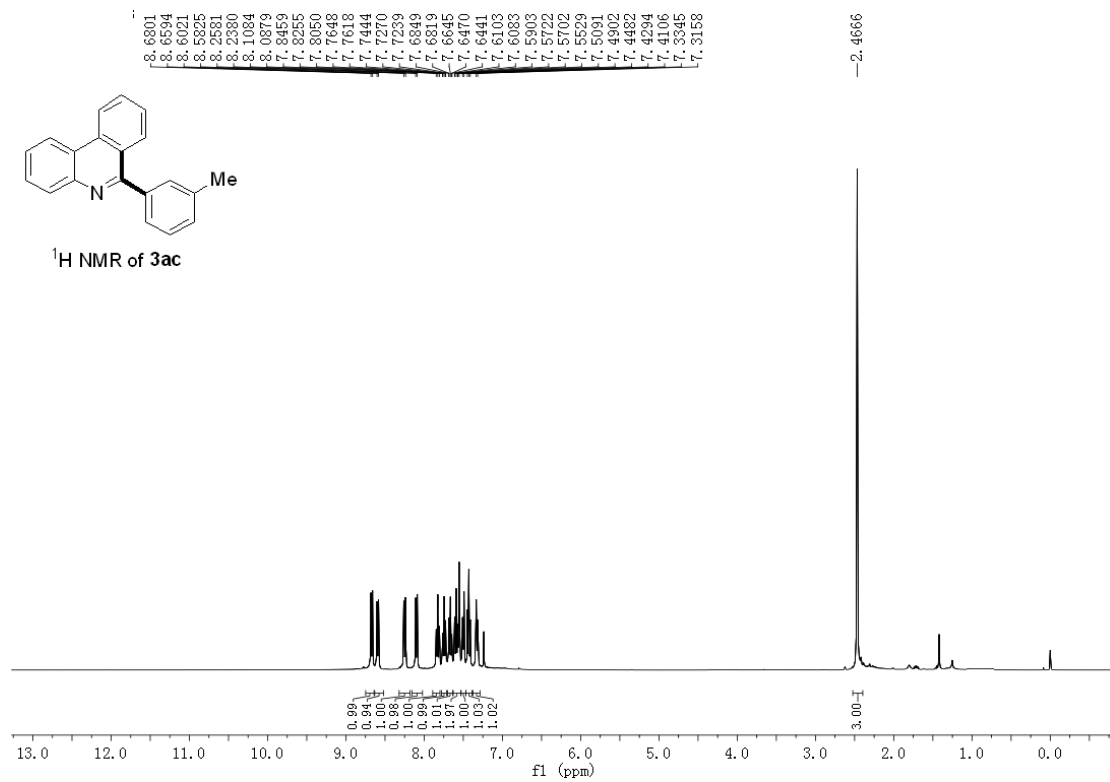
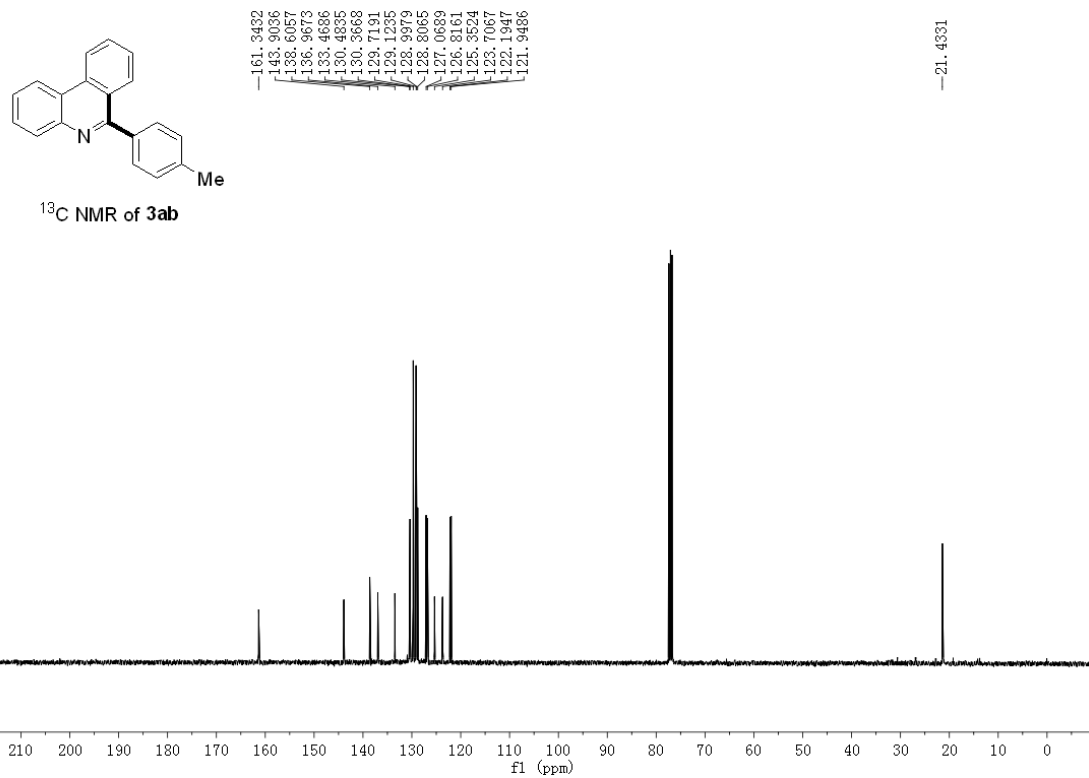


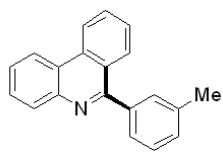




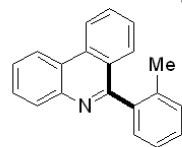
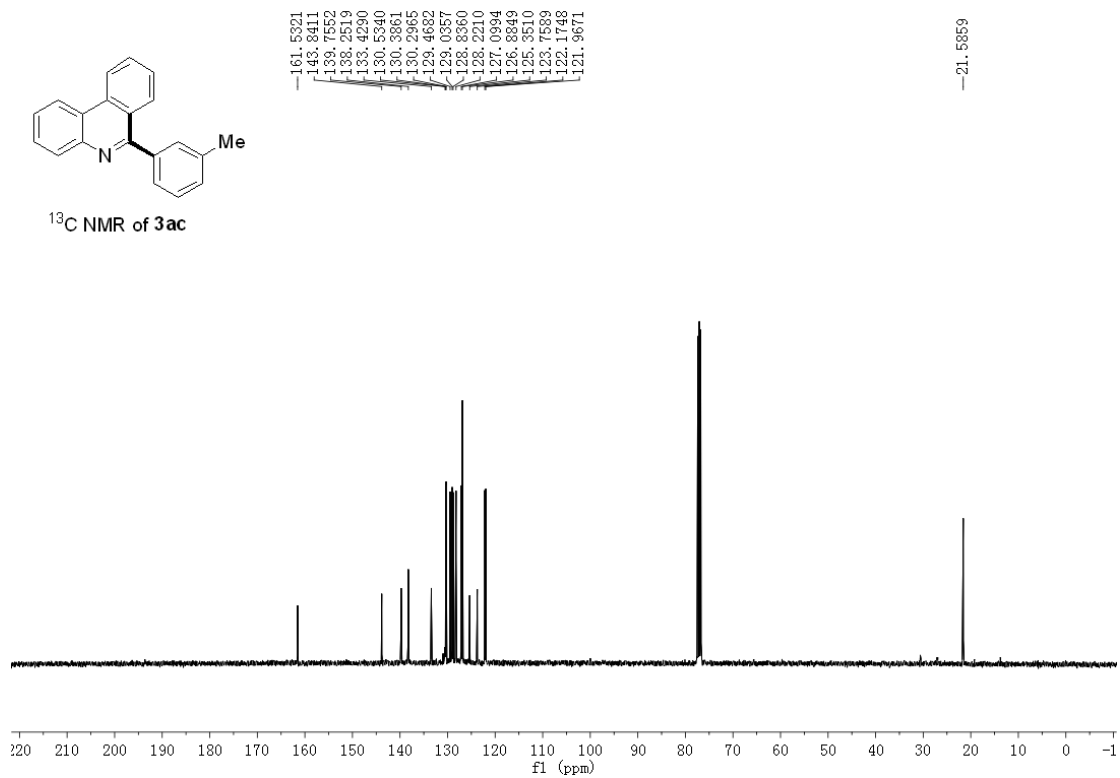




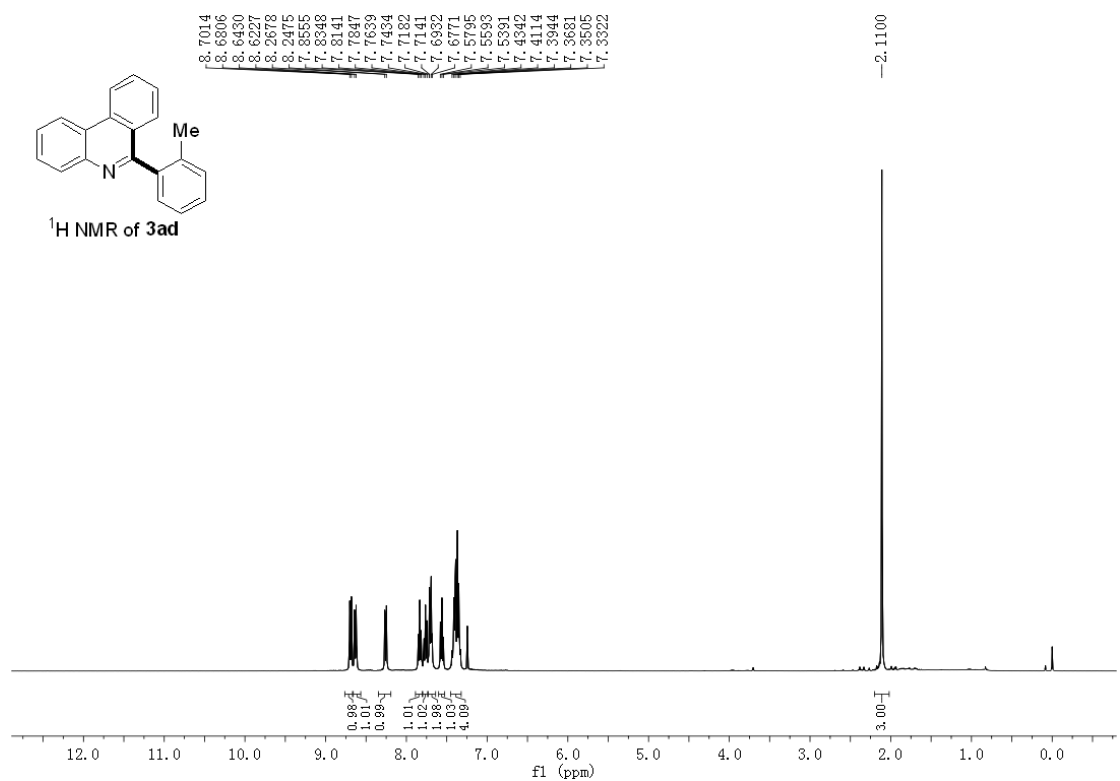


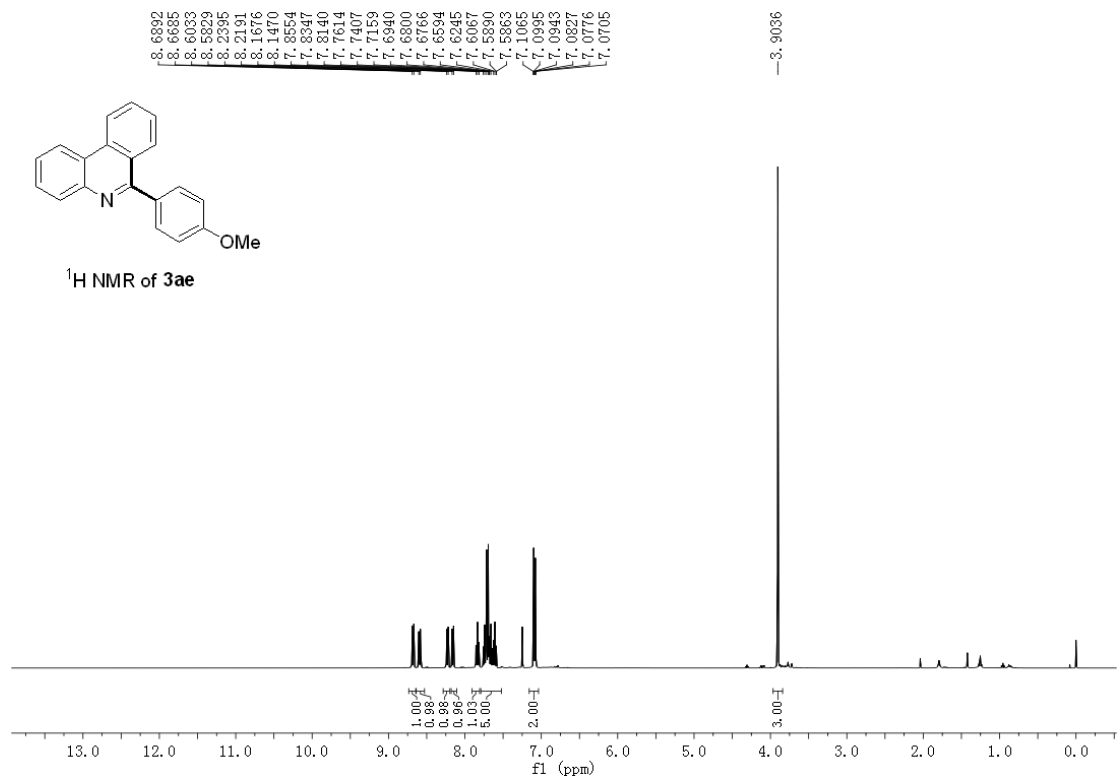
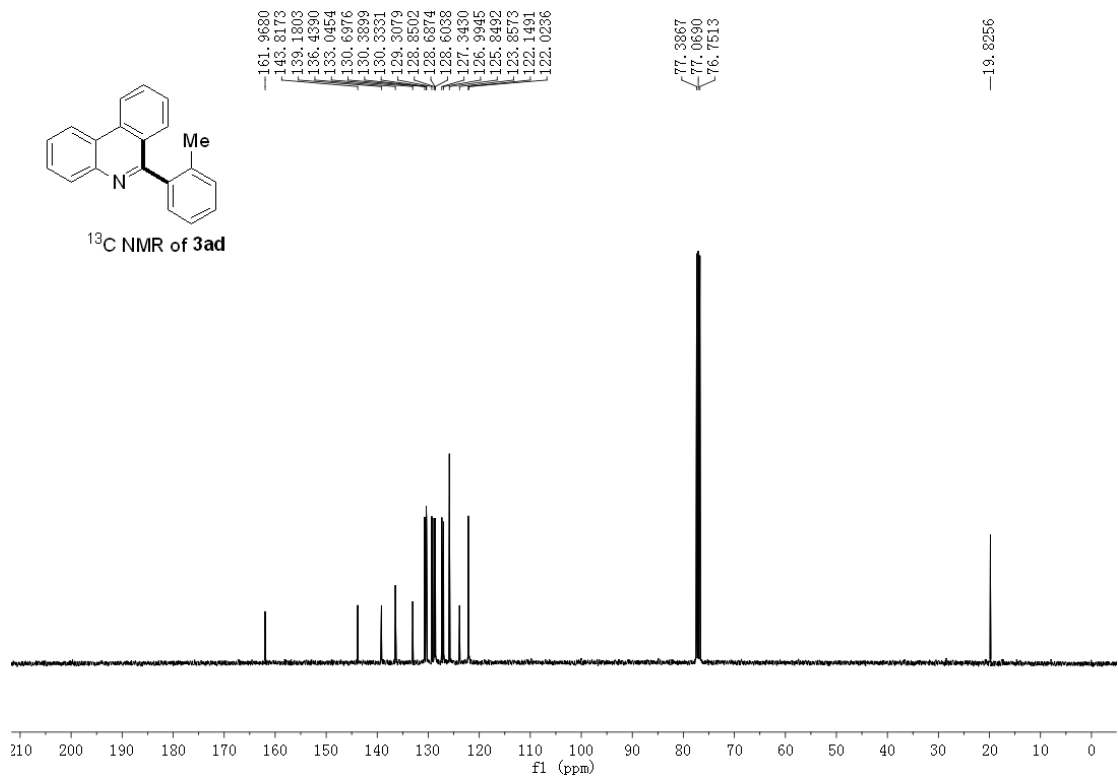


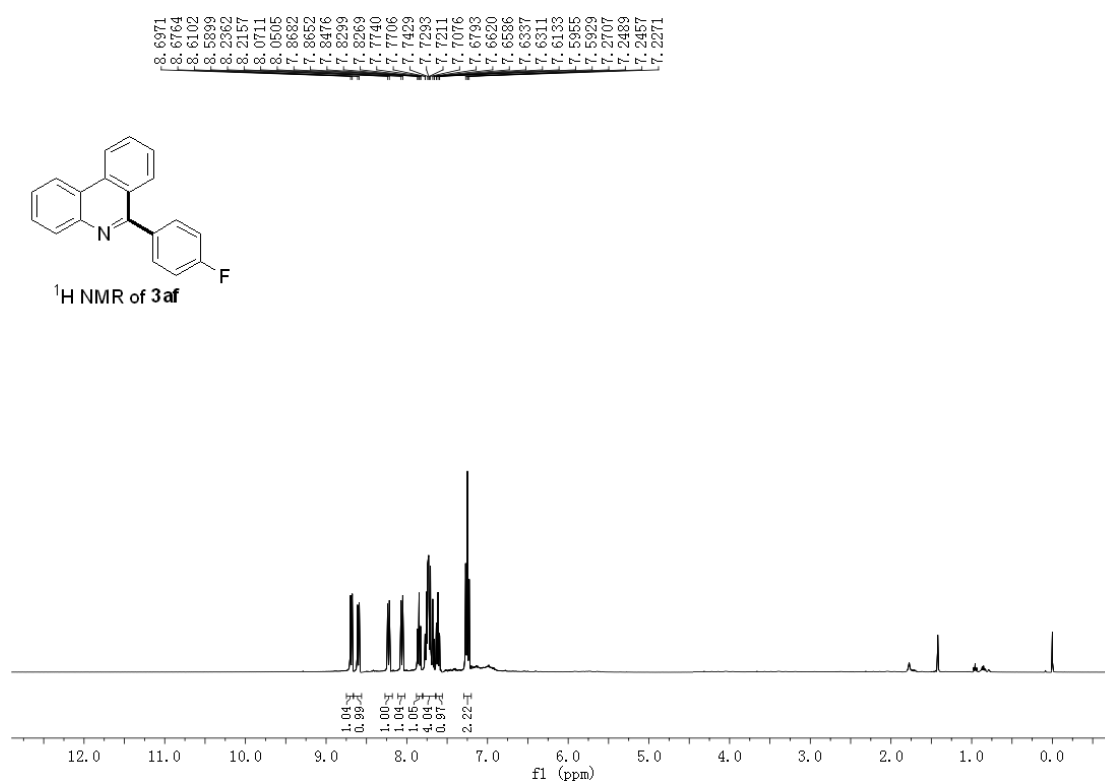
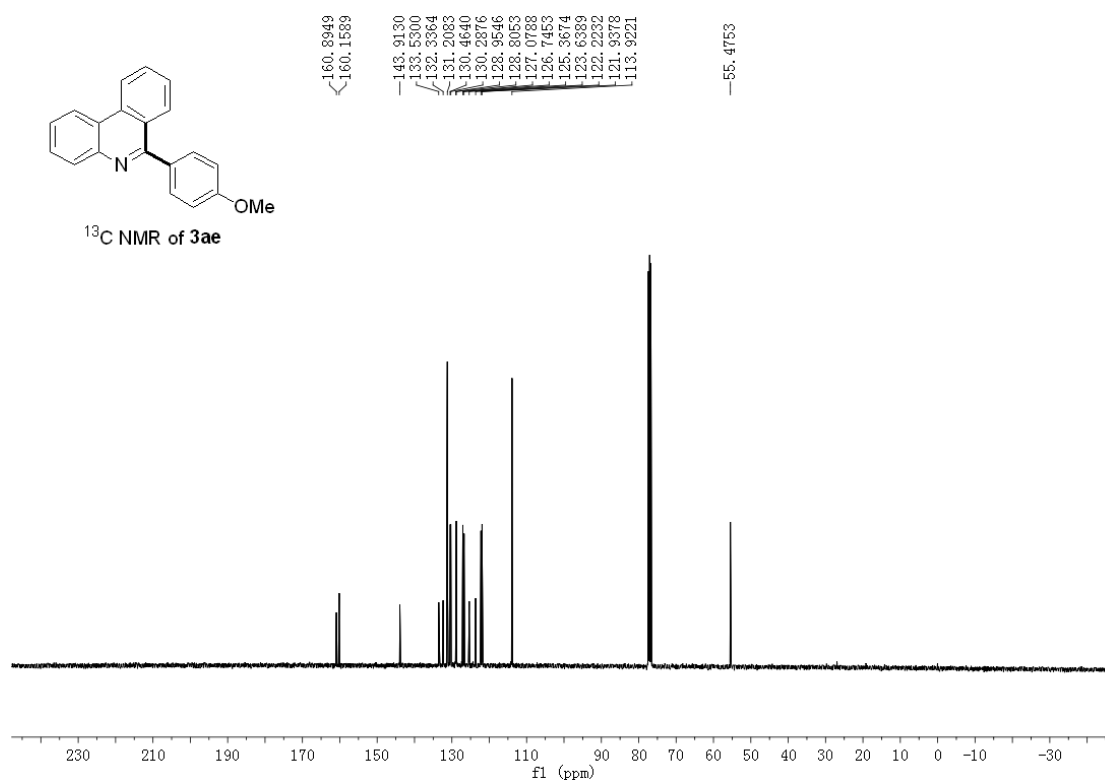
<sup>13</sup>C NMR of 3ac

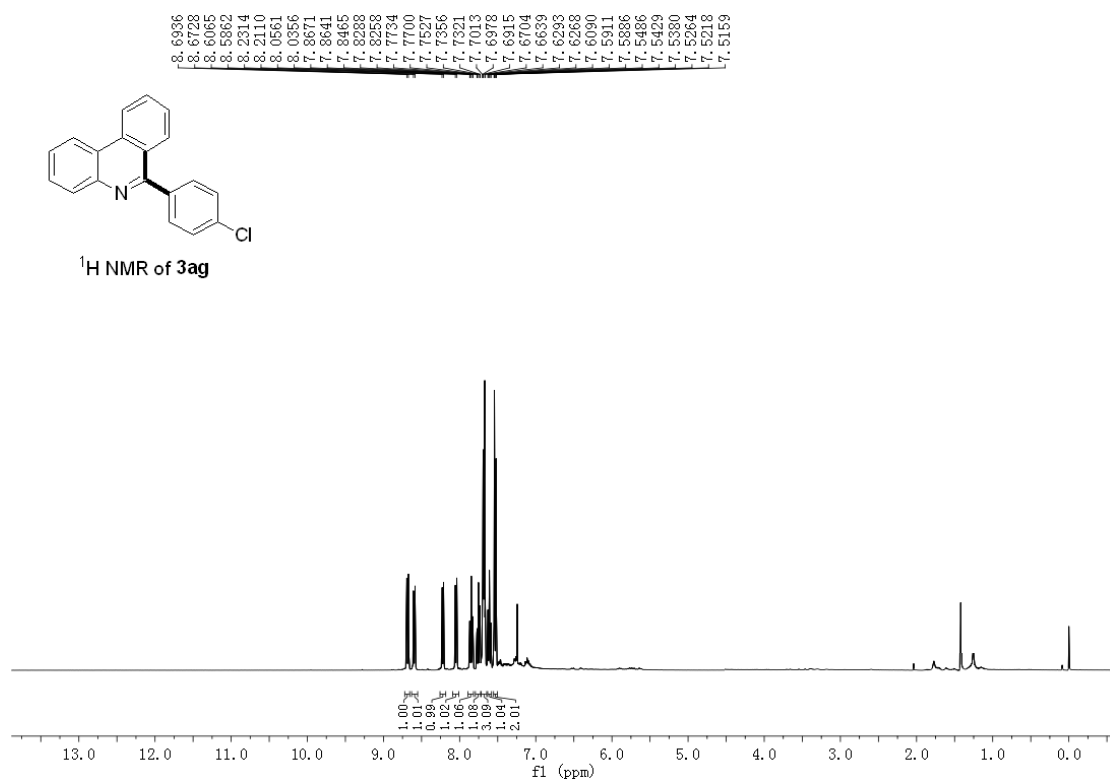
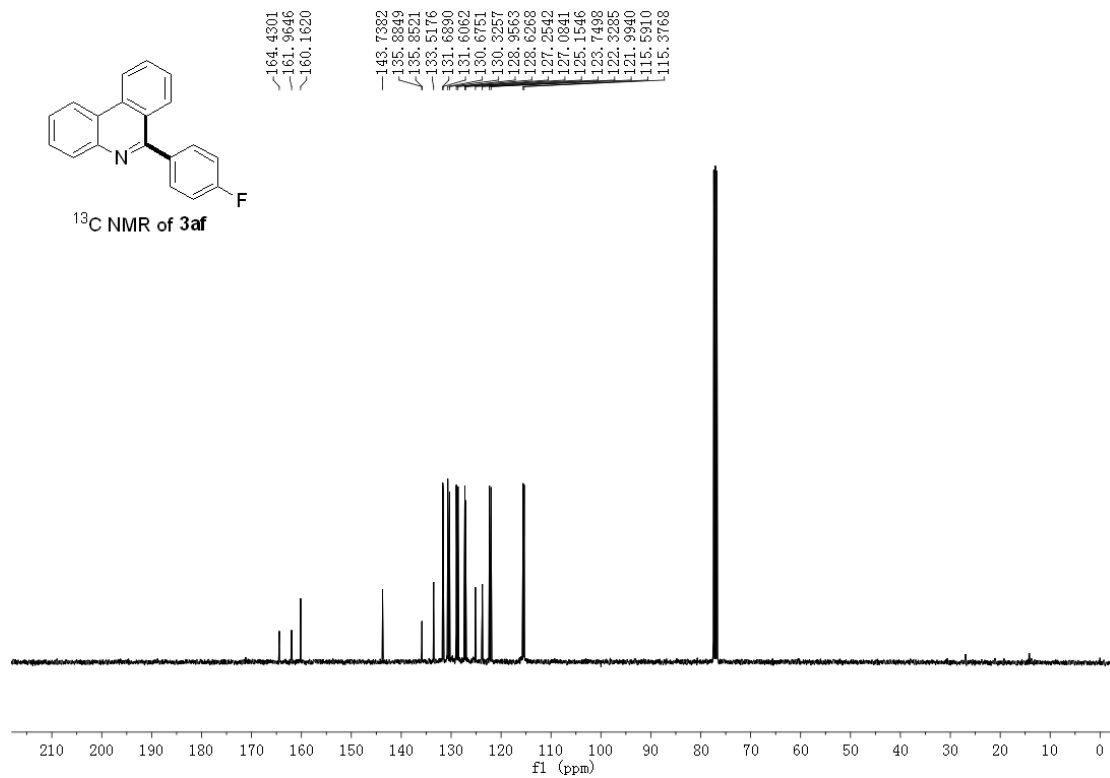


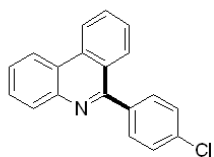
<sup>1</sup>H NMR of 3ad



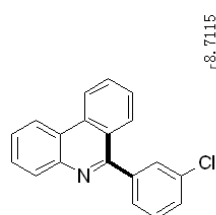
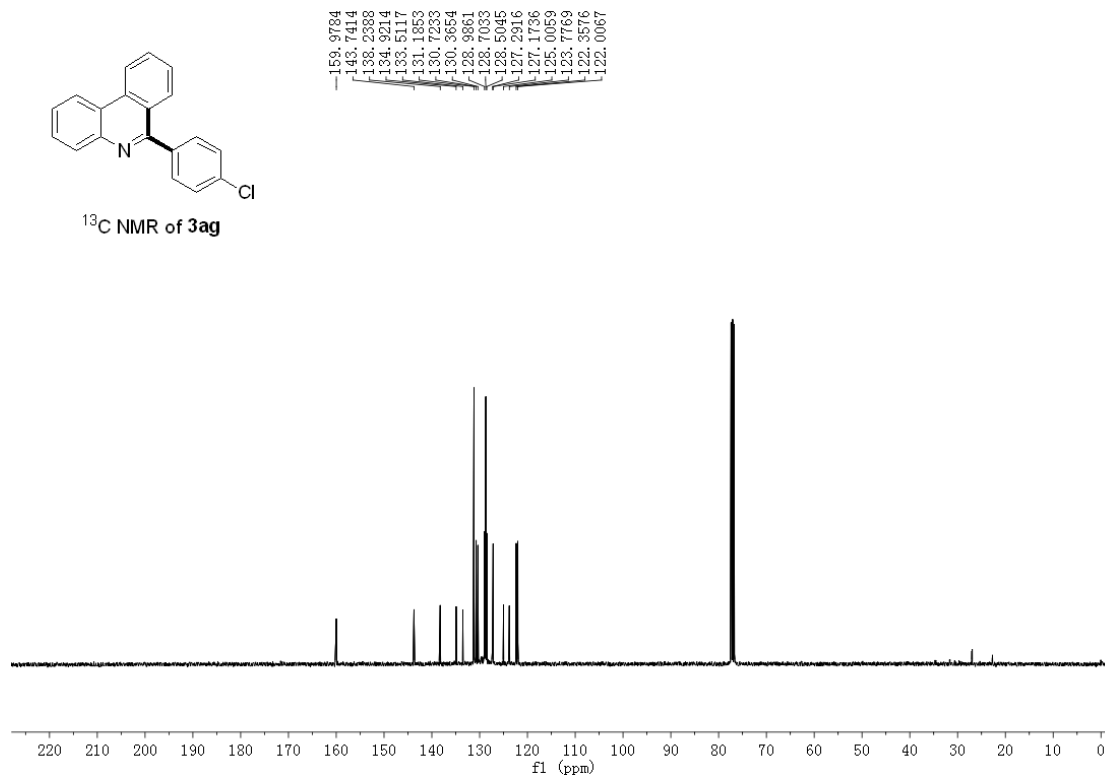




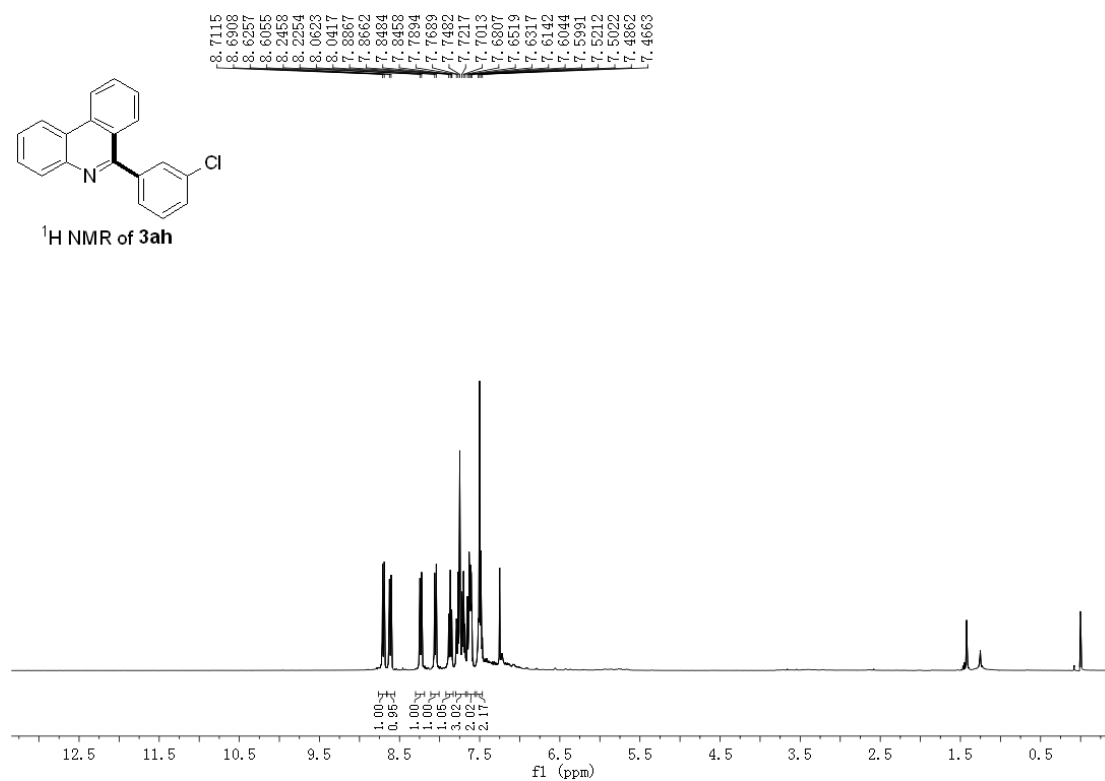




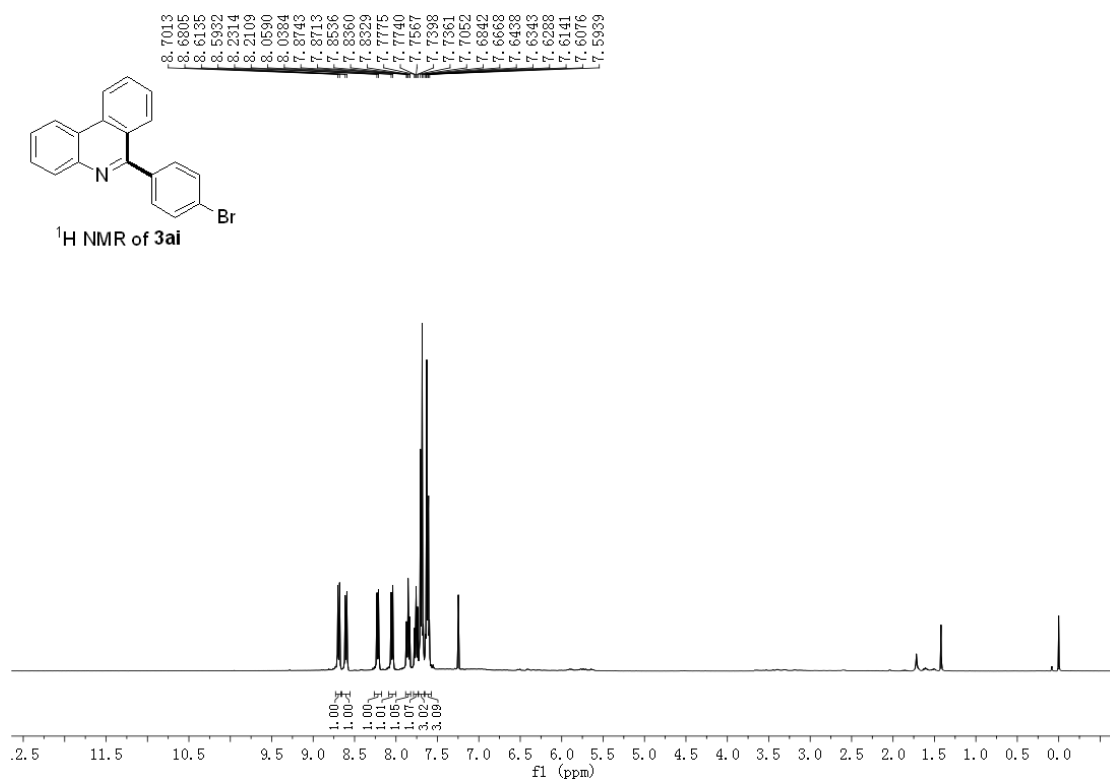
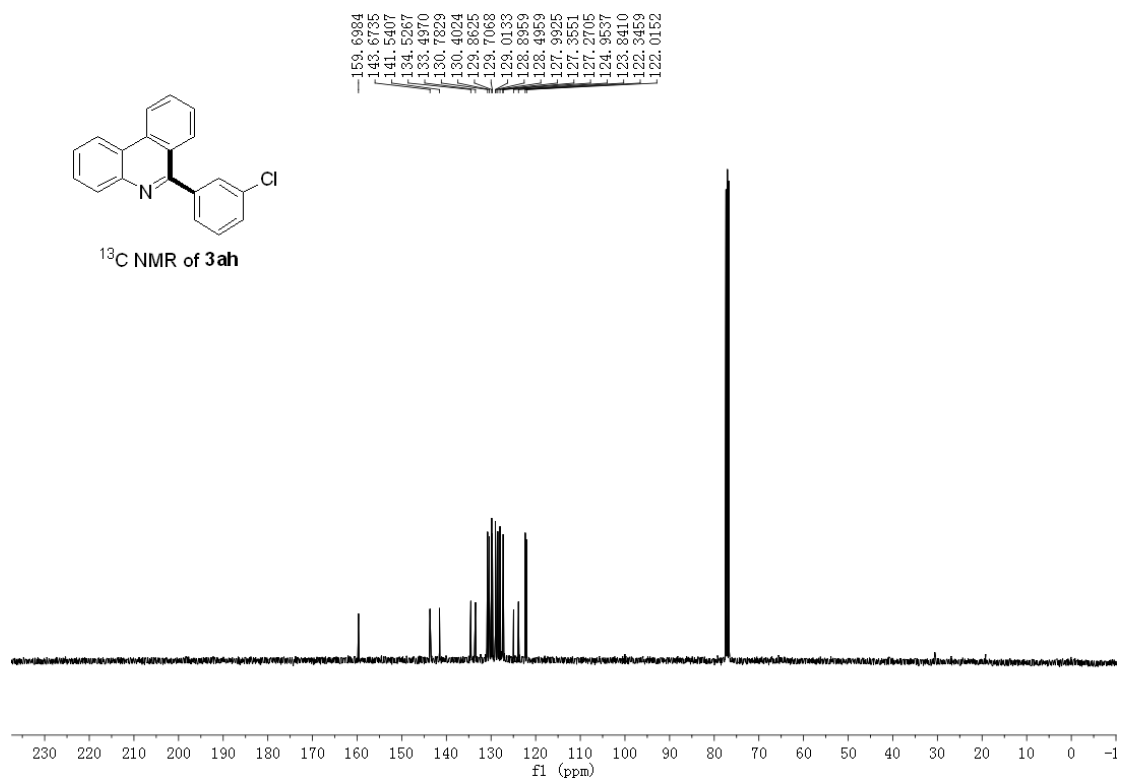
<sup>13</sup>C NMR of 3ag

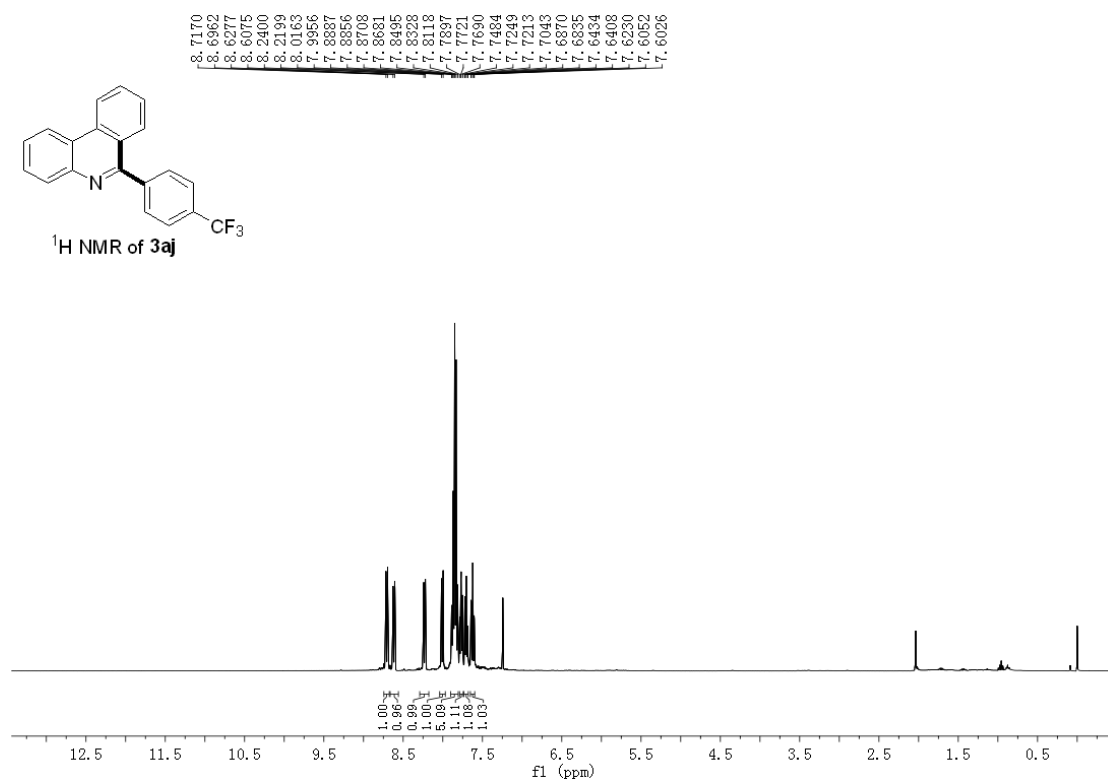
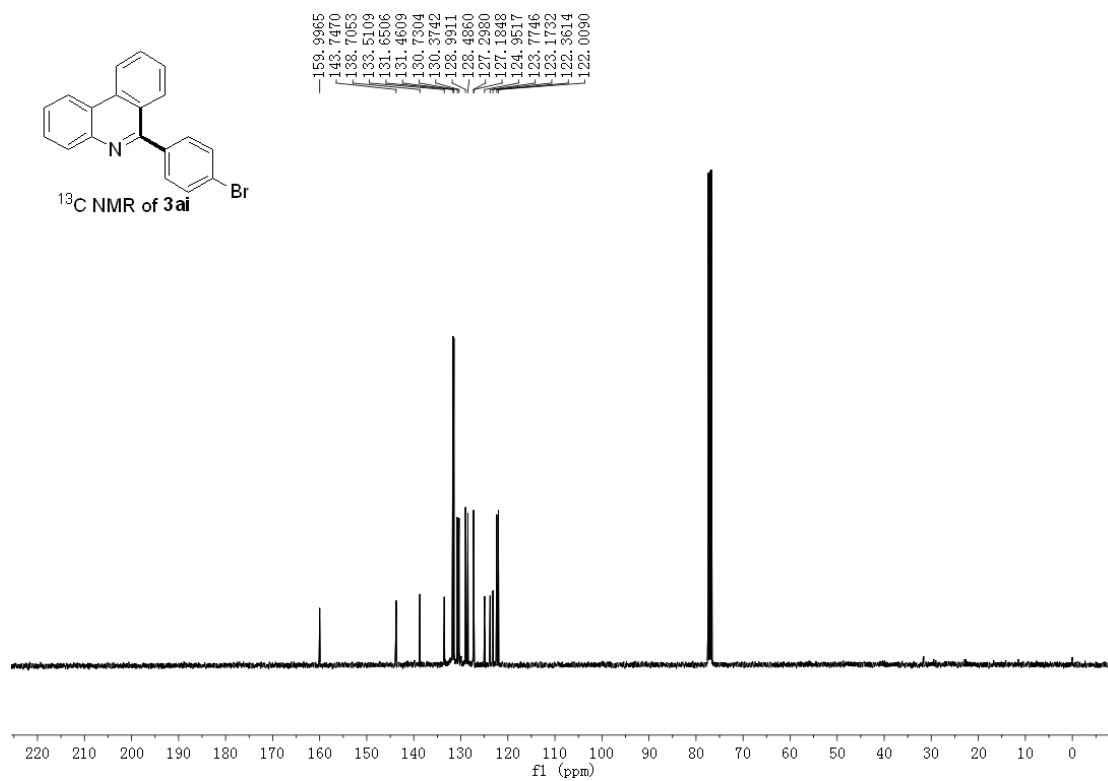


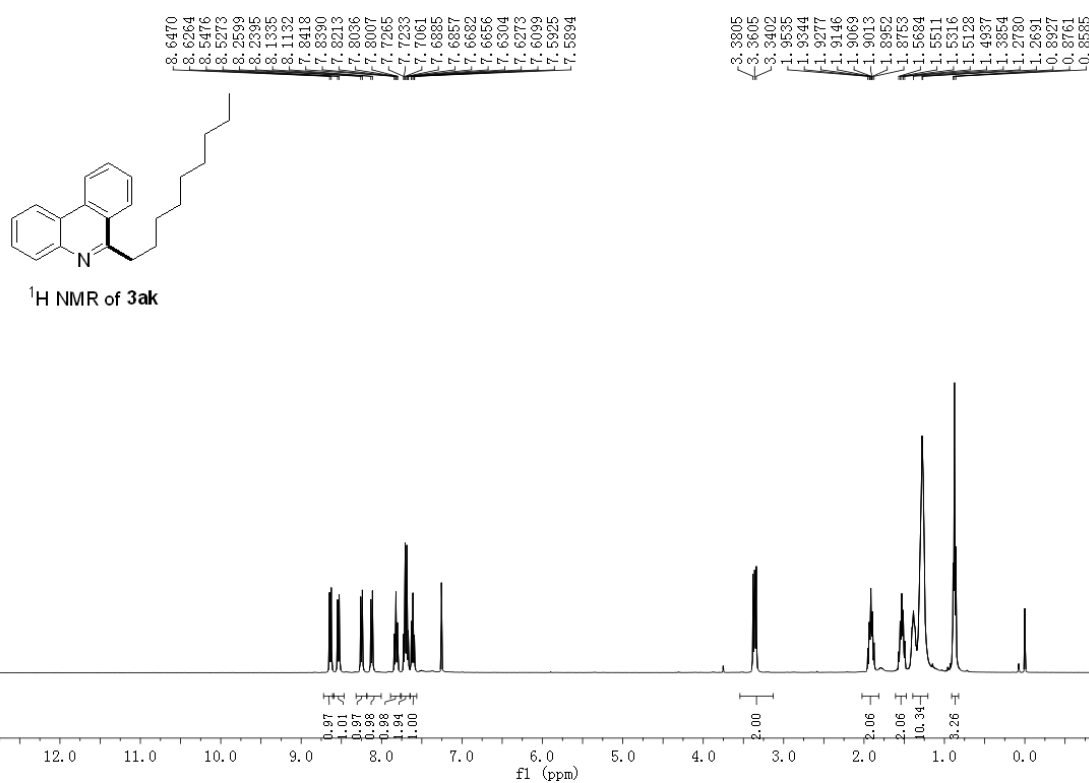
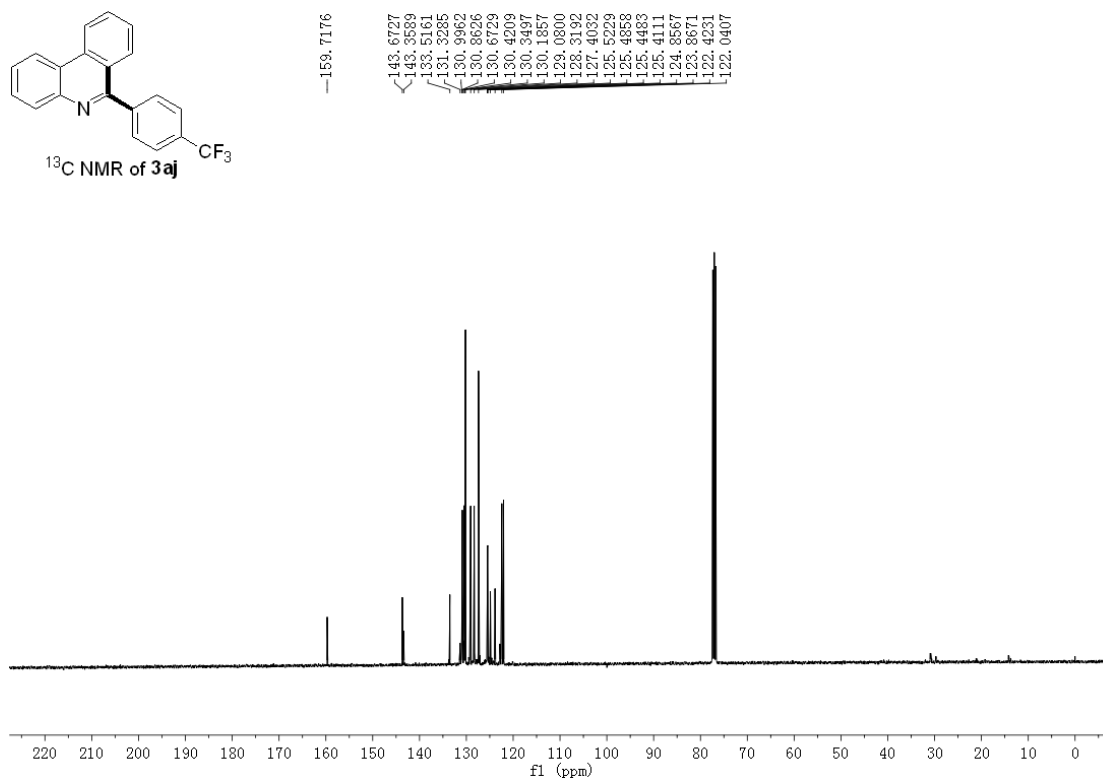
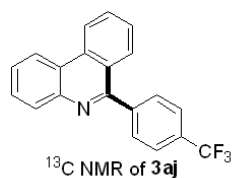
<sup>1</sup>H NMR of 3ah

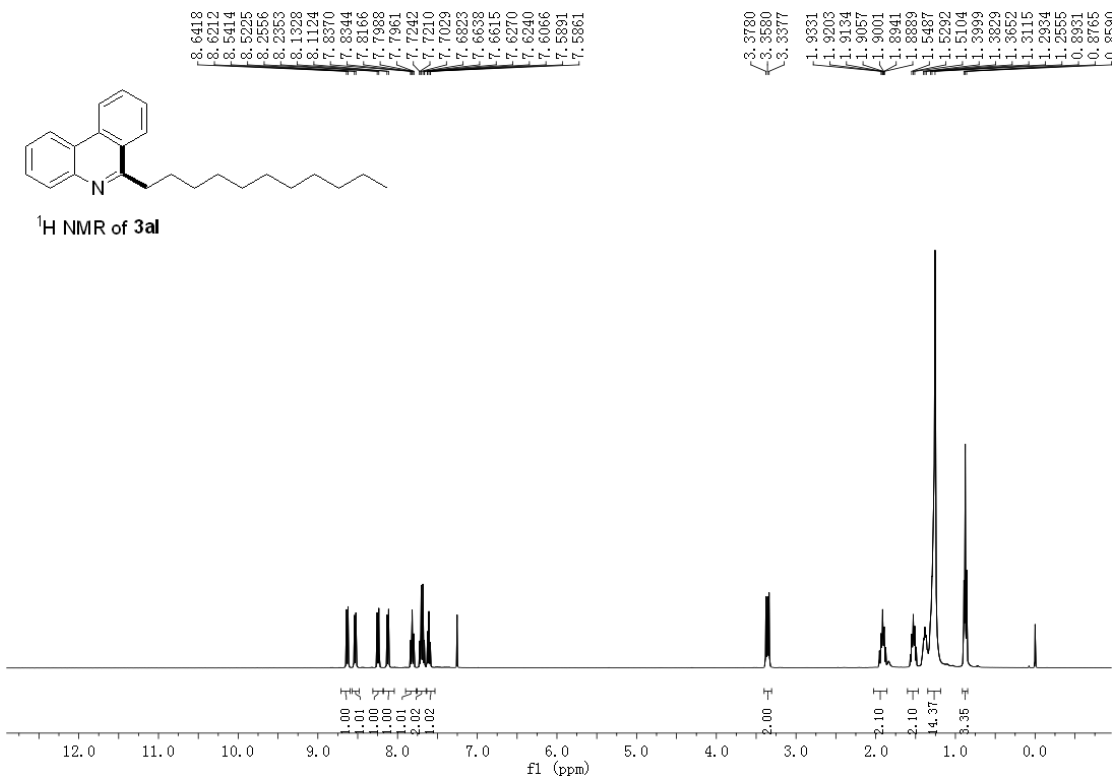
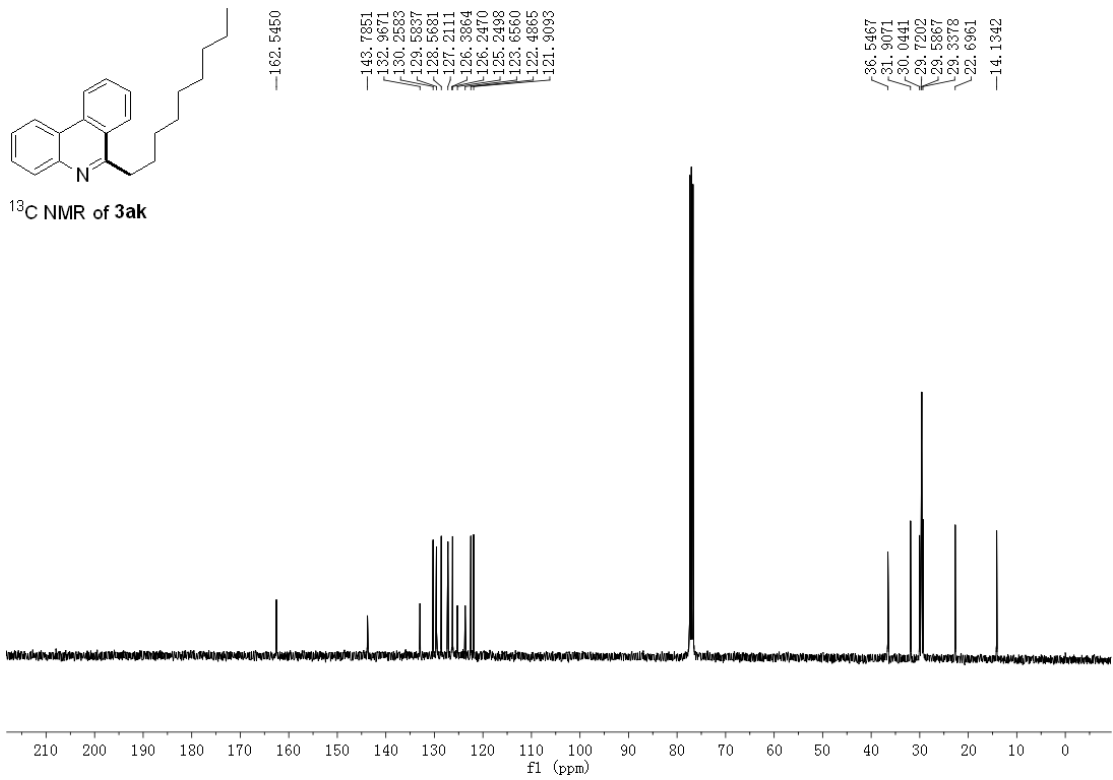


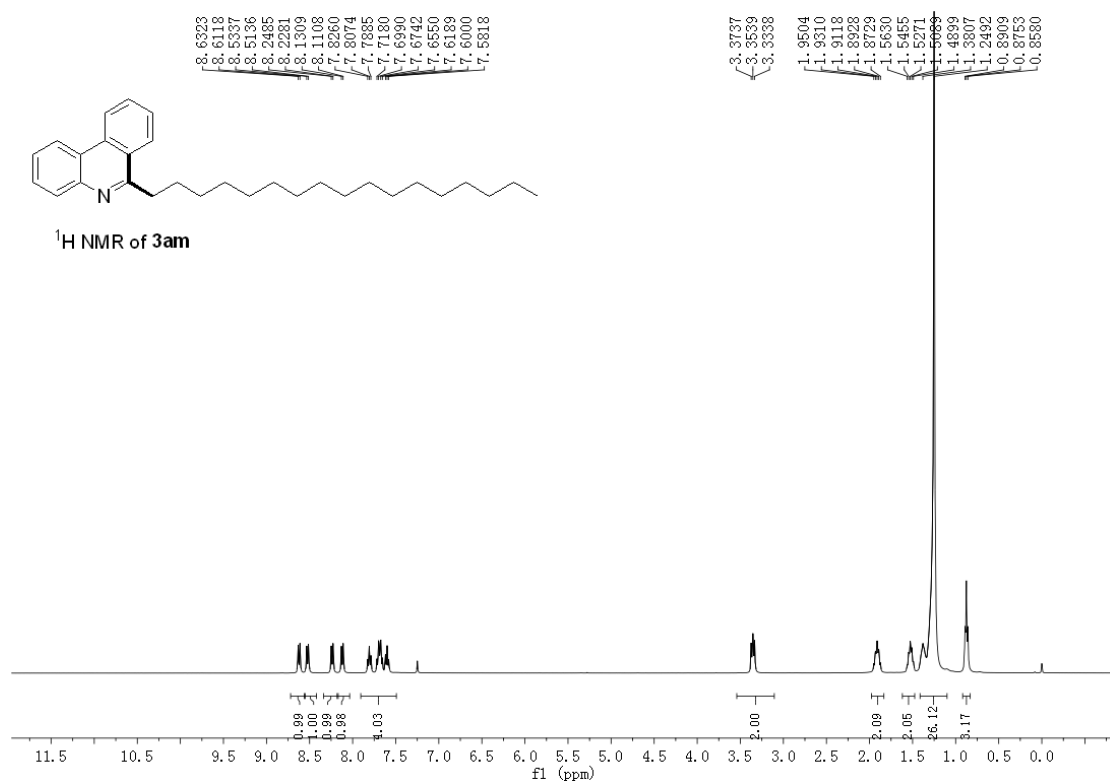
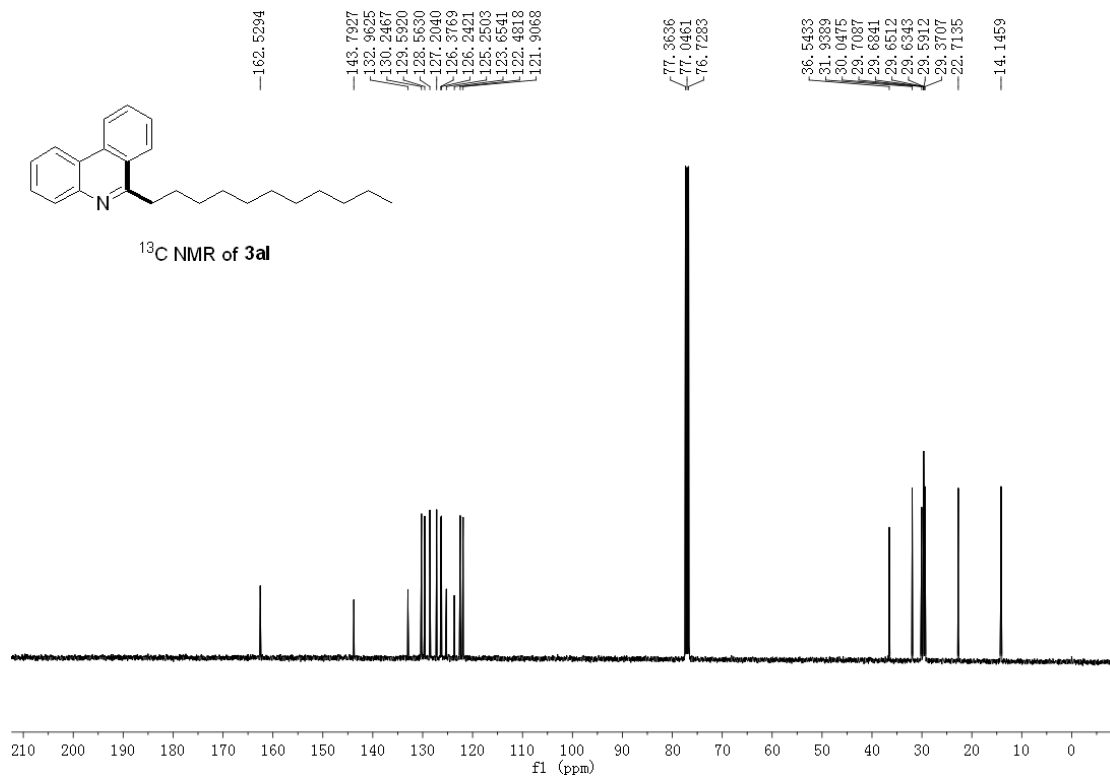




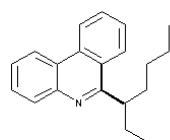












<sup>13</sup>C NMR of 3an

