

***Supporting Information For***  
**HOTf-Catalyzed Sustainable One-Pot Synthesis of Benzene  
and Pyridine Derivatives under Solvent-free Conditions**

Xu Zhang,<sup>a</sup> Zhiqiang Wang,<sup>a</sup> Kun Xu,<sup>a</sup> Yuquan Feng,<sup>a</sup> Wei Zhao,<sup>a</sup> Xuefeng Xu,<sup>a</sup>  
Yanlei Yan<sup>a</sup> and Wei Yi<sup>b\*</sup>

*<sup>a</sup>School of Chemistry and Pharmacony Engineering, Nanyang Normal University,  
Nanyang 473061, P.R. China*

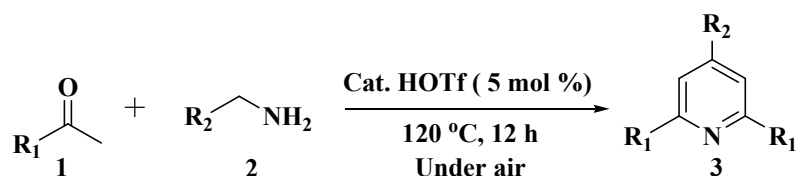
*<sup>b</sup>VARI/SIMM Center, Center for Structure and Function of Drug Targets, CAS-Key  
Laboratory of Receptor Research, Shanghai Institute of Materia Medica, Chinese  
Academy of Sciences, Shanghai 201203, P.R. China*

*E-mail: [yiwei.simm@simm.ac.cn](mailto:yiwei.simm@simm.ac.cn).*

## General Methods:

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  or  $\text{DMSO}-d_6$  solutions on a Bruker AVANCE 400 MHz spectrometer. High resolution mass spectra were obtained on a Waters Micromass GCT facility. HOTf was purchased from Adamas-beta. All other reagents and solvents were used as is from commercial sources. Unless noted below, all other compounds have been reported in the literature or are commercially available.

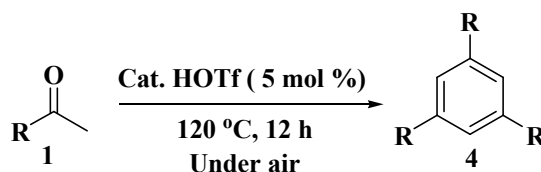
### General procedure for the synthesis of pyridine derivatives from ketones **1** and amine **2**:



A reaction kettle (10 mL) was charged with ketone (1.0 mmol, 1.0 equiv), amine (0.75 mmol, 1.5 equiv), and the HOTf (0.025 mmol) was added. The mixture was stirred at 120 °C for 12 hours, the mixture was quenched by sat. aq.  $\text{NaHCO}_3$ , and diluted with 20 mL of dichloromethane and washed with 10 mL of  $\text{H}_2\text{O}$ . The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over  $\text{Na}_2\text{SO}_4$ . After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/ $\text{AcOEt}$  = 30: 1) to afford pyridine derivatives. All other compounds are synthesized in a similar manner, with the yields listed in the main text calculated from the isolated, pure products.

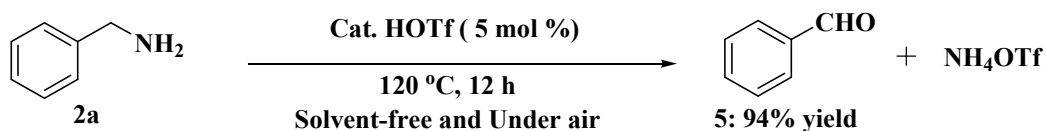
### Mechanistic studies:

a)



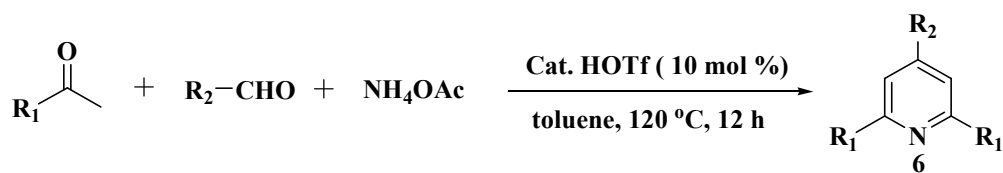
A reaction kettle (15 mL) was charged with ketone (0.5 mmol, 1.0 equiv), and HOTf (0.025 mmol) were added. The mixture was stirred at 120 °C for 12 hours, the reaction was cooled down to room temperature, and diluted with 10 mL of dichloromethane and washed with 10 mL of H<sub>2</sub>O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 50: 1) to afford benzene derivatives. All other compounds are synthesized in a similar manner, with the yields listed in the main text calculated from the isolated, pure products.

b)



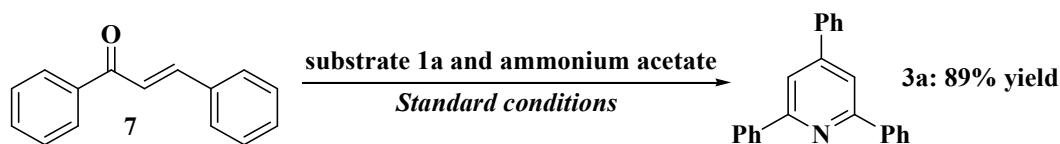
A reaction kettle (15 mL) was charged with benzylamine (1.0 mmol, 1.0 equiv), and HOTf (0.05 mmol) were added. The mixture was stirred at 120 °C for 12 hours, the reaction was cooled down to room temperature, and diluted with 10 mL of dichloromethane and washed with 10 mL of H<sub>2</sub>O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 20: 1) to afford the desired product.

c)



A reaction tube (15 mL) was charged with ketone (1.0 mmol, 2.0 equiv), aldehyde (0.5 mmol, 1.0 equiv), ammonium acetate (3.0 mmol, 6.0 equiv), HOTf (0.05 mmol) and toluene (0.5 mL) were added. The mixture was stirred at 120 °C for 12 hours, the reaction was cooled down to room temperature, and diluted with 10 mL of dichloromethane and washed with 10 mL of H<sub>2</sub>O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 30:1) to afford the desired product.

d)



A reaction kettle (15 mL) was charged with chalcone (0.5 mmol, 1.0 equiv), and acetophenone (**1a**, 0.5 mmol, 1.0 equiv), ammonium acetate (3.0 mmol, 6.0 equiv) and HOTf (0.025 mmol) were added. The mixture was stirred at 120 °C for 12 hours, the reaction was cooled down to room temperature, and diluted with 10 mL of dichloromethane and washed with 10 mL of H<sub>2</sub>O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 30: 1) to afford the desired product.

### Characterizations of products 3a-3t, 4a-d and 6a-f:

2,4,6-Triphenylpyridine (**3a**):  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  ppm:  $\delta$  8.34 (d,  $J$  = 7.2 Hz, 4H), 8.19 (s, 2H), 8.04 (d,  $J$  = 6.8 Hz, 2H), 7.49 - 7.59 (m, 9H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  ppm:  $\delta$  157.0, 150.1, 139.3, 138.2, 129.8, 129.7, 129.6, 129.2, 127.8, 127.4, 117.1; HRMS (EI) Calcd. for  $\text{C}_{23}\text{H}_{17}\text{N}$ :  $[\text{M}^+]$ , 307.1361. Found:  $m/z$  307.1364.

2,6-Diphenyl-4-*p*-tolyl-pyridine (**3b**):  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  ppm:  $\delta$  8.33 (d,  $J$  = 7.2 Hz, 4H), 8.18 (s, 2H), 7.96 (d,  $J$  = 8.4 Hz, 2H), 7.49 - 7.58 (m, 6H), 7.38 (d,  $J$  = 8.0 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  ppm:  $\delta$  156.4, 149.9, 139.5, 139.3, 135.2, 130.2, 129.7, 129.2, 127.6, 127.4, 116.7, 21.3; HRMS (EI) Calcd. for  $\text{C}_{24}\text{H}_{19}\text{N}$ :  $[\text{M}^+]$ , 321.1517. Found:  $m/z$  321.1521.

4-(4-Fluorophenyl)-2,6-diphenylpyridine (**3c**):  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  ppm:  $\delta$  8.36 (d,  $J$  = 7.6 Hz, 4H), 8.21 (s, 2H), 8.15 (q, 2H), 7.49 - 7.60 (m, 6H), 7.43 (t, 2H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  ppm:  $\delta$  164.7, 162.2, 157.0, 148.9, 139.2, 134.6, 130.1, 129.7, 129.2, 127.4, 116.5; HRMS (EI) Calcd. for  $\text{C}_{23}\text{H}_{16}\text{NF}$ :  $[\text{M}^+]$ , 325.1267. Found:  $m/z$  325.1268.

2,6-Diphenyl-4-*m*-tolyl-pyridine (**3d**):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  8.22 (d,  $J$  = 7.6 Hz, 4H), 7.87 (q, 2H), 7.41 - 7.55 (m, 9H), 7.29 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  157.5, 150.4, 139.7, 139.1, 138.9, 129.8, 129.1, 128.8, 128.0, 127.2, 127.2, 124.4, 117.2, 21.6; HRMS (EI) Calcd. for  $\text{C}_{24}\text{H}_{19}\text{N}$ :  $[\text{M}^+]$ , 321.1517. Found:  $m/z$  321.1519.

4-(3-Fluoro-phenyl)-2,6-diphenylpyridine (**3e**):  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  ppm:  $\delta$  8.35 (d,  $J$  = 7.6 Hz, 4H), 8.24 (s, 2H), 7.91 - 8.00 (m, 2H), 7.47 - 7.58 (m, 8H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  ppm:  $\delta$  164.5, 162.0, 157.1, 148.6, 139.1, 131.5, 129.8, 129.2, 129.1, 128.4, 128.1, 127.5, 117.1; HRMS (EI) Calcd. for  $\text{C}_{23}\text{H}_{16}\text{NF}$ :  $[\text{M}^+]$ , 325.1267. Found:  $m/z$  325.1270.

2,6-Diphenyl-4-thiophen-2-yl-pyridine (**3f**):  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  ppm:  $\delta$  8.29 (d,  $J = 7.2$  Hz, 4H), 8.12 (s, 2H), 8.09 - 8.11 (q, 1H), 7.91 - 8.00 (m, 2H), 7.78 - 7.80 (m, 2H), 7.48 - 7.58 (m, 6H), 7.28 - 7.30 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  ppm:  $\delta$  157.2, 143.5, 141.2, 138.9, 129.9, 129.3, 129.3, 128.8, 127.6, 127.3, 115.1; HRMS (EI) Calcd. for  $\text{C}_{21}\text{H}_{15}\text{NS}$ :  $[\text{M}^+]$ , 313.0925. Found:  $m/z$  313.0926.

4-Benzyl-2,6-diphenylpyridine (**3g**):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  8.09 (d,  $J = 7.2$  Hz, 4H), 7.42 - 7.48 (m, 6H), 7.35 - 7.39 (m, 2H), 7.19 - 7.31 (m, 5H), 4.01 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  157.2, 151.4, 139.3, 139.3, 129.2, 129.1, 128.9, 128.8, 127.2, 126.8, 119.5, 41.8; HRMS (EI) Calcd. for  $\text{C}_{24}\text{H}_{19}\text{N}$ :  $[\text{M}^+]$ , 321.1517. Found:  $m/z$  321.1519.

4-Pentyl-2,6-diphenylpyridine (**3h**):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  8.14 (d,  $J = 7.2$  Hz, 4H), 7.39 - 7.51 (m, 8H), 2.69 - 2.73 (q, 2H), 1.68 - 1.73 (m, 2H), 1.32 - 1.37 (m, 4H), 0.89 - 0.92 (q, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  156.9, 153.2, 139.8, 128.8, 128.7, 127.1, 119.1, 35.8, 31.5, 30.3, 22.6, 14.1; HRMS (EI) Calcd. for  $\text{C}_{22}\text{H}_{23}\text{N}$ :  $[\text{M}^+]$ , 301.1830. Found:  $m/z$  301.1833.

4-Pentyl-2,6-di-*p*-tolyl-pyridine (**3i**):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  7.96 (d,  $J = 8.0$  Hz, 4H), 7.78 (s, 2H), 7.20 (d,  $J = 8.0$  Hz, 4H), 2.59 - 2.63 (q, 2H), 2.33 (s, 6H), 1.61 - 1.65 (m, 2H), 1.28 - 1.29 (m, 4H), 0.81 - 0.84 (q, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  156.8, 153.0, 138.7, 137.1, 129.3, 126.9, 118.5, 35.8, 31.5, 30.3, 22.6, 21.3, 14.0; HRMS (EI) Calcd. for  $\text{C}_{24}\text{H}_{27}\text{N}$ :  $[\text{M}^+]$ , 329.2143. Found:  $m/z$  329.2145.

4-Pentyl-2,6-di-*m*-tolyl-pyridine (**3j**):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  7.72 - 7.93 (m, 4H), 7.39 (s, 2H), 7.26 - 7.33 (m, 2H), 7.13 (d,  $J = 6.8$  Hz, 2H), 2.59 - 2.63 (q, 2H), 2.37 (s, 6H), 1.61 - 1.64 (m, 2H), 1.27 - 1.33 (m, 4H), 0.81 - 0.85 (q, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  157.1, 153.1, 139.9, 138.2, 129.6, 128.6, 127.8, 124.3, 119.2, 35.8, 31.6, 30.4, 22.6, 21.7, 14.1; HRMS (EI) Calcd. for  $\text{C}_{24}\text{H}_{27}\text{N}$ :  $[\text{M}^+]$ ,

329.2143. Found: m/z 329.2144.

4-Phenyl-2,6-di-thiophen-2-yl-pyridine (**3k**):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  7.62 - 7.66 (m, 6H), 7.38 - 7.49 (m, 5H), 7.08 - 7.11 (t, 2H), ;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 152.7, 150.2, 144.9, 138.6, 129.2, 129.2, 128.0, 127.9, 127.1, 124.9, 115.1; HRMS (EI) Calcd. for  $\text{C}_{19}\text{H}_{13}\text{NS}_2$ :  $[\text{M}^+]$ , 319.0489. Found: m/z 319.0484.

2,6-Bis-benzofuran-2-yl-4-phenyl-pyridine (**3l**):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  8.08 (s, 2H), 7.84 (d,  $J = 7.2$  Hz, 2H), 7.69 (d,  $J = 7.6$  Hz, 2H), 7.64 (s, 2H), 7.48 - 7.60 (m, 5H), 7.34 (t, 2H), 7.29 (t, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  155.4, 155.2, 150.1, 149.9, 138.1, 129.4, 129.2, 128.9, 127.2, 125.3, 123.3, 121.8, 116.8, 111.6, 105.5; HRMS (EI) Calcd. for  $\text{C}_{27}\text{H}_{17}\text{NO}_2$ :  $[\text{M}^+]$ , 387.1259. Found: m/z 387.1265.

2,6-Bis-(4-chloro-phenyl)-4-phenylpyridine (**3m**):  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  ppm:  $\delta$  8.16 (d,  $J = 7.6$  Hz, 4H), 7.90 (s, 2H), 7.76 (d,  $J = 6.4$  Hz, 2H), 7.47 - 7.55 (m, 7H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ )  $\delta$  ppm:  $\delta$  160.9, 155.3, 143.2, 142.5, 139.8, 134.0, 134.0, 133.6, 133.1, 131.9, 121.8; HRMS (EI) Calcd. for  $\text{C}_{23}\text{H}_{15}\text{NCl}_2$ :  $[\text{M}^+]$ , 375.0582. Found: m/z 375.0786.

2,6-Di-naphthalen-2-yl-4-p-tolyl-pyridine (**3n**):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  8.64 (s, 2H), 8.37 (d,  $J = 8.4$  Hz, 2H), 7.95 - 7.98 (m, 6H), 7.87 (d,  $J = 8.4$  Hz, 2H), 7.66 (d,  $J = 7.6$  Hz, 2H), 7.50 (m, 4H), 7.31 (d,  $J = 7.6$  Hz, 2H), 2.41 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  157.5, 150.2, 139.2, 137.1, 136.1, 133.9, 133.6, 129.9, 128.9, 128.5, 127.8, 127.1, 126.6, 126.3, 125.1, 117.3, 21.4; HRMS (EI) Calcd. for  $\text{C}_{32}\text{H}_{23}\text{N}$ :  $[\text{M}^+]$ , 421.1830. Found: m/z 421.1832.

4-(4-Fluoro-phenyl)-2,6-di-naphthalen-2-yl-pyridine (**3o**):  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  ppm:  $\delta$  8.96 (s, 2H), 8.59 (dd,  $J = 8.4, 0.8$  Hz, 2H), 8.41 (s, 2H), 8.20 - 8.22 (m, 2H), 8.10 - 8.15 (m, 4H), 8.00 - 8.02 (m, 2H), 7.57 - 7.63 (m, 4H), 7.44 -

7.57 (t, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  ppm:  $\delta$  150.7, 149.1, 136.6, 134.6, 133.9, 133.6, 130.2, 130.1, 129.2, 128.7, 128.1, 127.3, 127.0, 126.8, 125.3, 116.4; HRMS (EI) Calcd. for  $\text{C}_{31}\text{H}_{20}\text{NF}$ :  $[\text{M}^+]$ , 425.1580. Found:  $m/z$  425.1583.

4-Phenyl-2,6-di-*p*-tolyl-pyridine (**3p**):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  8.08 (d,  $J = 8.0$  Hz, 4H), 7.81 (s, 2H), 7.71 (d,  $J = 7.2$  Hz, 2H), 7.44 - 7.51 (m, 3H), 7.29 (d,  $J = 8.0$  Hz, 4H), 2.40 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  152.7, 145.3, 134.6, 134.2, 132.2, 124.7, 124.4, 124.1, 122.5, 122.3, 111.8, 16.6; HRMS (EI) Calcd. for  $\text{C}_{25}\text{H}_{21}\text{N}$ :  $[\text{M}^+]$ , 335.1674. Found:  $m/z$  335.1679.

2,4,6-Tri-*p*-tolyl-pyridine (**3q**):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  8.09 (d,  $J = 7.6$  Hz, 4H), 7.81 (s, 2H), 7.63 (d,  $J = 7.2$  Hz, 2H), 7.30 (d,  $J = 6.4$  Hz, 6H), 2.42 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  157.4, 149.9, 138.9, 137.0, 129.8, 129.4, 127.0, 116.3, 21.3; HRMS (EI) Calcd. for  $\text{C}_{26}\text{H}_{23}\text{N}$ :  $[\text{M}^+]$ , 349.1834. Found:  $m/z$  349.1830.

4-(4-Fluoro-phenyl)-2,6-di-*p*-tolyl-pyridine (**3r**):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  8.08 (d,  $J = 8.0$  Hz, 4H), 7.78 (s, 2H), 7.69 - 7.73 (t, 2H), 7.31 (d,  $J = 8.0$  Hz, 2H), 7.19 - 7.25 (m, 4H), 2.43 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  164.6, 162.1, 157.5, 149.0, 139.1, 136.8, 129.4, 129.0, 128.9, 127.0, 116.0, 21.4; HRMS (EI) Calcd. for  $\text{C}_{25}\text{H}_{20}\text{NF}$ :  $[\text{M}^+]$ , 353.1580. Found:  $m/z$  353.1582.

2,4,6-Tri-*m*-tolyl-pyridine(**3s**):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  7.79 – 8.01 (m, 4H), 7.85 (s, 2H), 7.56 (s, 2H), 7.39 - 7.43 (m, 3H), 7.25 - 7.29 (m, 3H), 2.48 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  157.7, 150.2, 139.7, 139.1, 138.8, 138.3, 129.8, 129.7, 129.0, 128.6, 127.9, 127.9, 124.4, 117.3, 21.7, 21.6; HRMS (EI) Calcd. for  $\text{C}_{26}\text{H}_{23}\text{N}$ :  $[\text{M}^+]$ , 349.1830. Found:  $m/z$  349.1833.

4-(3-Fluoro-phenyl)-2,6-di-*m*-tolyl-pyridine (**3t**):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  7.97 (m, 4H), 7.80 (s, 2H), 7.38 = 7.52 (m, 5H), 7.26 (d,  $J = 7.6$  Hz, 2H), 7.13 - 7.17 (t, 1H), 2.47 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  164.5, 162.1, 157.9, 148.8, 139.4, 138.4, 130.7, 130.0, 128.7, 127.9, 124.4, 122.9, 116.6, 21.7; HRMS (EI)



Calcd. for  $C_{25}H_{20}NF$ :  $[M^+]$ , 353.1580. Found:  $m/z$  353.1581.

1,3,5-Triphenylbenzene (**4a**):  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  ppm:  $\delta$  7.78 (s, 3H), 7.70 (d,  $J = 7.6$  Hz, 6H), 7.46 - 7.49 (t,  $J = 7.6$  Hz, 6H), 7.37 - 7.40 (t,  $J = 7.2$  Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  ppm:  $\delta$  142.4, 141.2, 128.9, 127.6, 127.4, 125.2; HRMS (EI) Calcd. for  $C_{24}H_{19}$ :  $[M^+]$ , 306.1409. Found:  $m/z$  306.1406.

1,3,5-Tri-*m*-tolyl-benzene (**4b**):  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  ppm:  $\delta$  7.75 (s, 3H), 7.48-7.50 (m, 6H), 7.34 (m, 3H), 7.18 (m, 3H), 2.43 (s, 9H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  ppm:  $\delta$  142.4, 141.3, 138.5, 128.8, 128.3, 128.2, 125.2, 124.6, 21.7; HRMS (EI) Calcd. for  $C_{27}H_{24}$ :  $[M^+]$ , 348.1878. Found:  $m/z$  348.1481.

1,3,5-Tri-*p*-tolyl-benzene (**4c**):  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  ppm:  $\delta$  7.73 (s, 3H), 7.59 (d,  $J = 7.6$  Hz, 6H), 7.28 (d,  $J = 8.0$  Hz, 6H), 2.41 (s, 9H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  142.2, 138.5, 137.3, 129.6, 127.2, 124.6, 21.2; HRMS (EI) Calcd. for  $C_{27}H_{24}$ :  $[M^+]$ , 348.1878. Found:  $m/z$  348.1481.

1,3,5-Tri-2-naphthylbenzene (**4d**):  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  ppm:  $\delta$  8.21 (m, 3H), 7.87 - 7.93 (m, 6H), 7.76 (s, 3H), 7.62 (d,  $J = 6.8$  Hz, 3H), 7.49 - 7.57 (m, 9H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  140.8, 139.8, 133.9, 131.6, 130.7, 128.4, 127.9, 127.3, 126.3, 126.0, 125.9, 125.5; HRMS (EI) Calcd. for  $C_{36}H_{24}$ :  $[M^+]$ , 456.1878. Found:  $m/z$  456.1871.

2,6-Bis-(4-fluoro-phenyl)-4-*p*-tolyl-pyridine (**6a**):  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  ppm:  $\delta$  7.61 (d,  $J = 8.0$  Hz, 2H), 7.57 (s, 2H), 7.50 (t, 2H), 7.25 - 7.29 (m, 8H), 2.40 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  ppm:  $\delta$  160.1, 148.8, 140.9, 139.2, 136.0, 130.8, 129.9, 128.3, 127.0, 125.9, 120.0, 21.3; HRMS (EI) Calcd. for  $C_{24}H_{17}NF_2$ :  $[M^+]$ , 357.1329. Found:  $m/z$  357.1332.

2,4,6-Tris-(4-fluoro-phenyl)-pyridine (**6b**):  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  ppm:  $\delta$  8.18 (d,  $J = 8.0$  Hz, 4H), 7.79 (s, 2H), 7.69 - 7.74 (t, 2H), 7.18 - 7.27 (m, 6H);  $^{13}C$

NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm:  $\delta$  164.9, 162.5, 156.6, 149.4, 135.5, 134.9, 128.9, 116.5, 116.3, 116.1, 115.8; HRMS (EI) Calcd. for C<sub>23</sub>H<sub>14</sub>NF<sub>3</sub>: [M<sup>+</sup>], 361.1078. Found: m/z 361.1082.

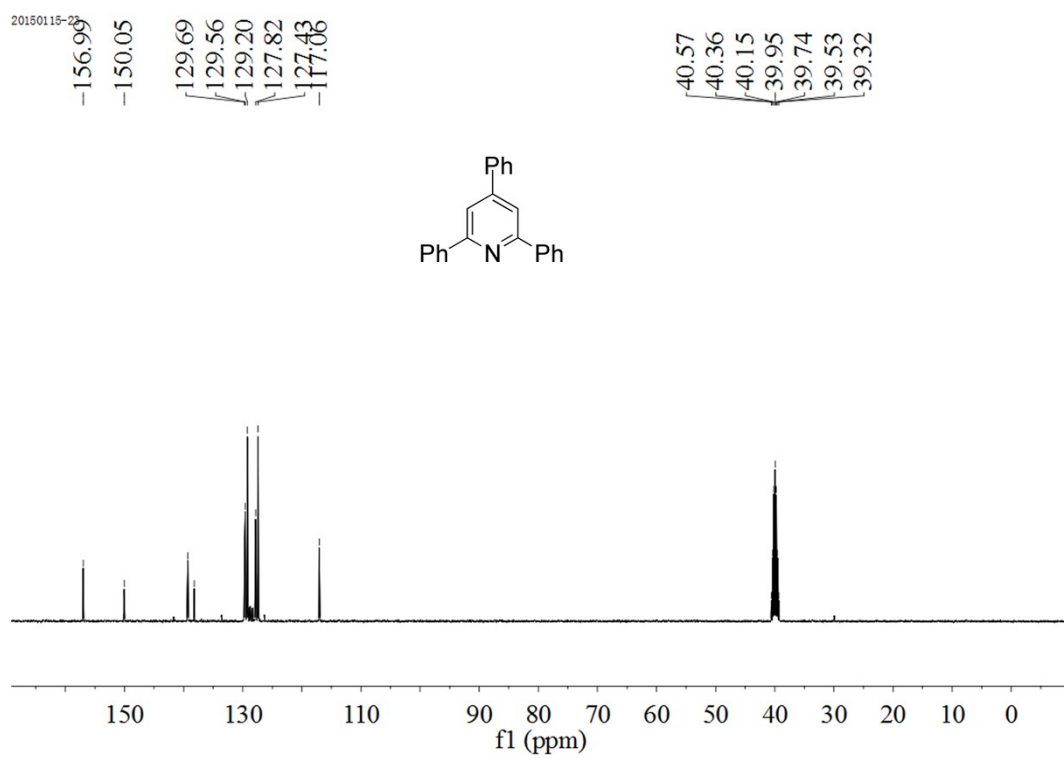
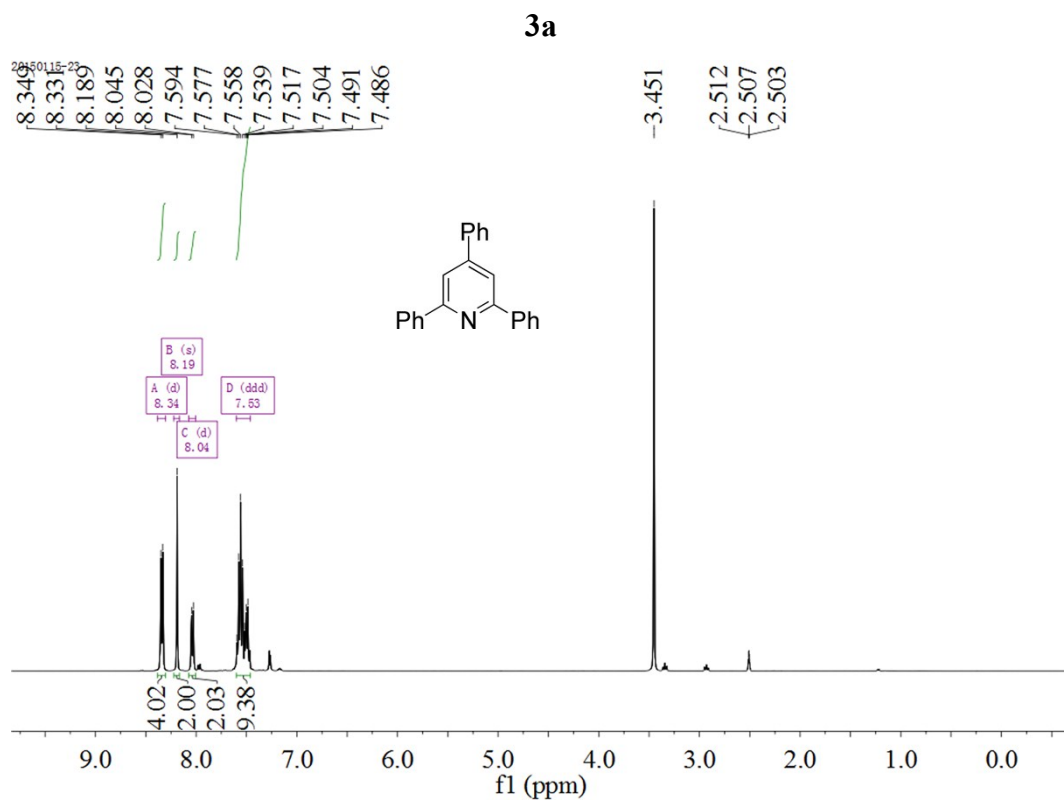
2,6-Bis-(3-fluoro-phenyl)-4-*p*-tolyl-pyridine (**6c**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm:  $\delta$  8.07 (t, 4H), 7.67 (s, 2H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.09 - 7.16 (m, 4H), 2.37 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm:  $\delta$  164.9, 162.4, 156.3, 150.2, 139.3, 129.9, 129.0, 128.9, 127.0, 116.4, 115.7, 21.3; HRMS (EI) Calcd. for C<sub>24</sub>H<sub>17</sub>NF<sub>2</sub>: [M<sup>+</sup>], 357.1329. Found: m/z 357.1333.

4-(4-Fluoro-phenyl)-2,6-bis-(3-fluoro-phenyl)-pyridine (**6d**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm:  $\delta$  7.95 (t, 4H), 7.85 (s, 2H), 7.42 - 7.52 (m, 5H), 7.13 - 7.22 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm:  $\delta$  164.6, 162.2, 156.3, 149.3, 141.3, 130.8, 130.3, 122.9, 122.6, 117.5, 116.2; HRMS (EI) Calcd. for C<sub>23</sub>H<sub>14</sub>NF<sub>3</sub>: [M<sup>+</sup>], 361.1078. Found: m/z 361.1079.

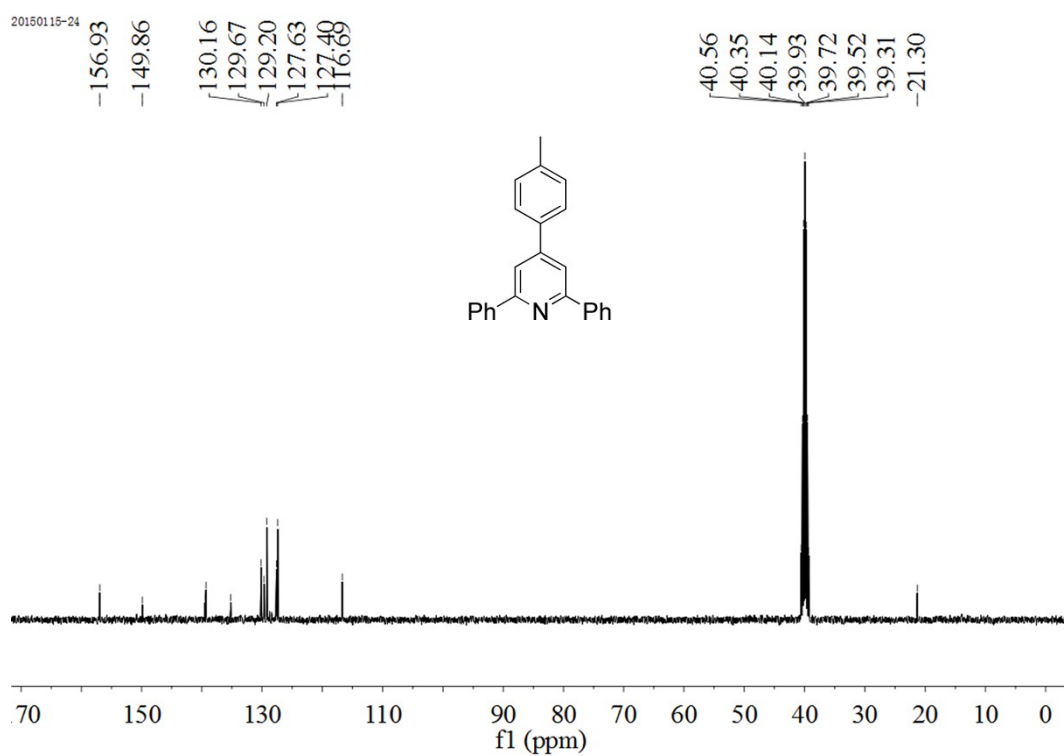
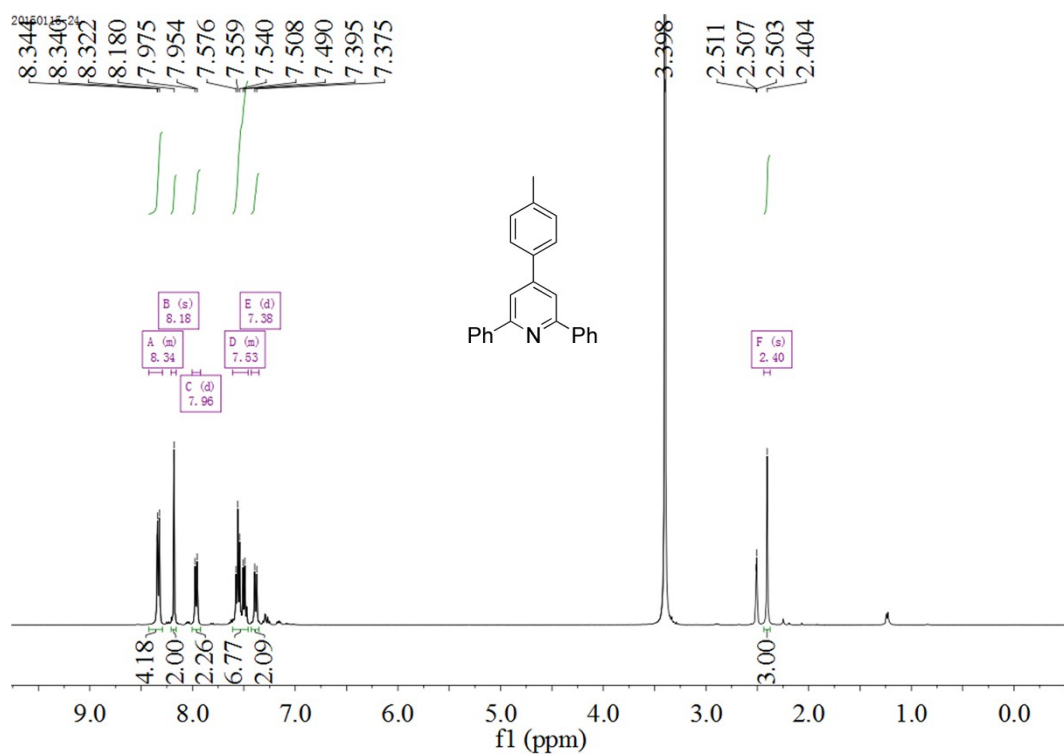
2,6-Bis-(2-fluoro-phenyl)-4-*p*-tolyl-pyridine (**6e**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm:  $\delta$  7.92 (m, 4H), 7.85 (s, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.43 - 7.49 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.11 - 7.15 (m, 2H), 2.43 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm:  $\delta$  164.6, 162.2, 156.1, 150.5, 141.7, 139.4, 135.6, 130.2, 130.0, 127.0, 122.6, 117.4, 116.0, 114.2, 21.3; HRMS (EI) Calcd. for C<sub>24</sub>H<sub>17</sub>NF<sub>2</sub>: [M<sup>+</sup>], 357.1329. Found: m/z 357.1330.

4-(4-Fluoro-phenyl)-2,6-bis-(2-fluoro-phenyl)-pyridine (**6f**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm:  $\delta$  8.16 (t, 2H), 7.93 (s, 2H), 7.69 (m, 2H), 7.36 (m, 2H), 7.29 (t, 2H), 7.16 - 7.20 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm:  $\delta$  164.7, 162.3, 162.0, 159.5, 153.7, 148.1, 134.7, 131.3, 130.6, 129.1, 127.5, 124.6, 121.2, 116.4; HRMS (EI) Calcd. for C<sub>23</sub>H<sub>14</sub>NF<sub>3</sub>: [M<sup>+</sup>], 361.1078. Found: m/z 361.1080.

**<sup>1</sup>H and <sup>13</sup>C spectra of products 3a-3t, 4a-d and 6a-f:**

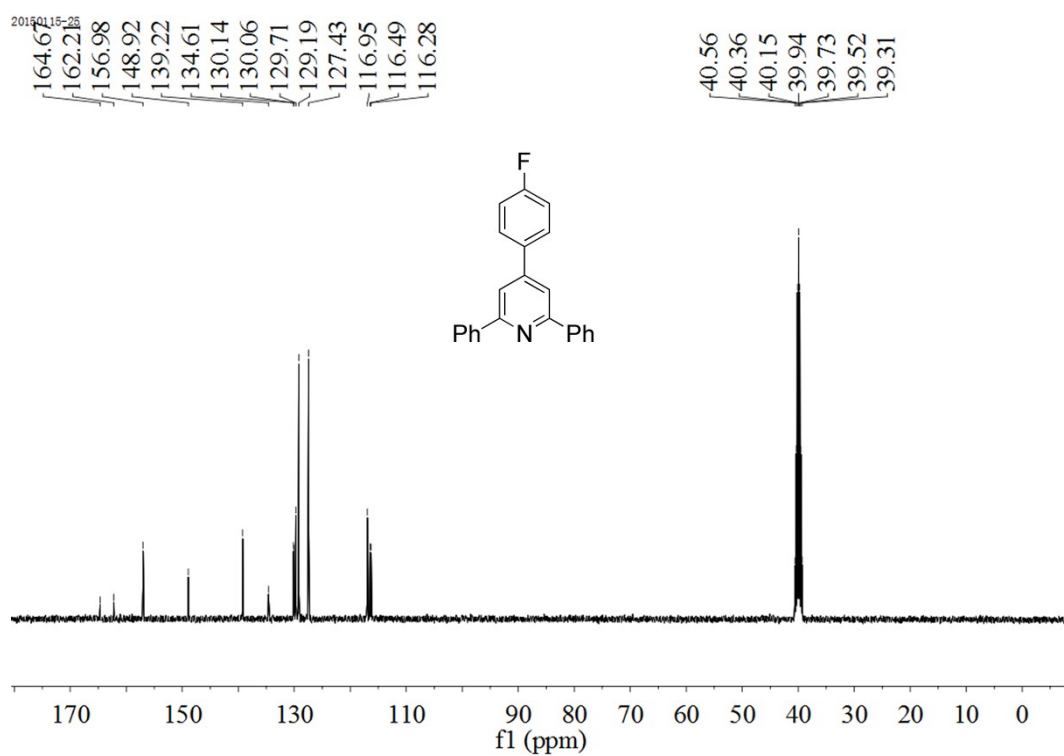
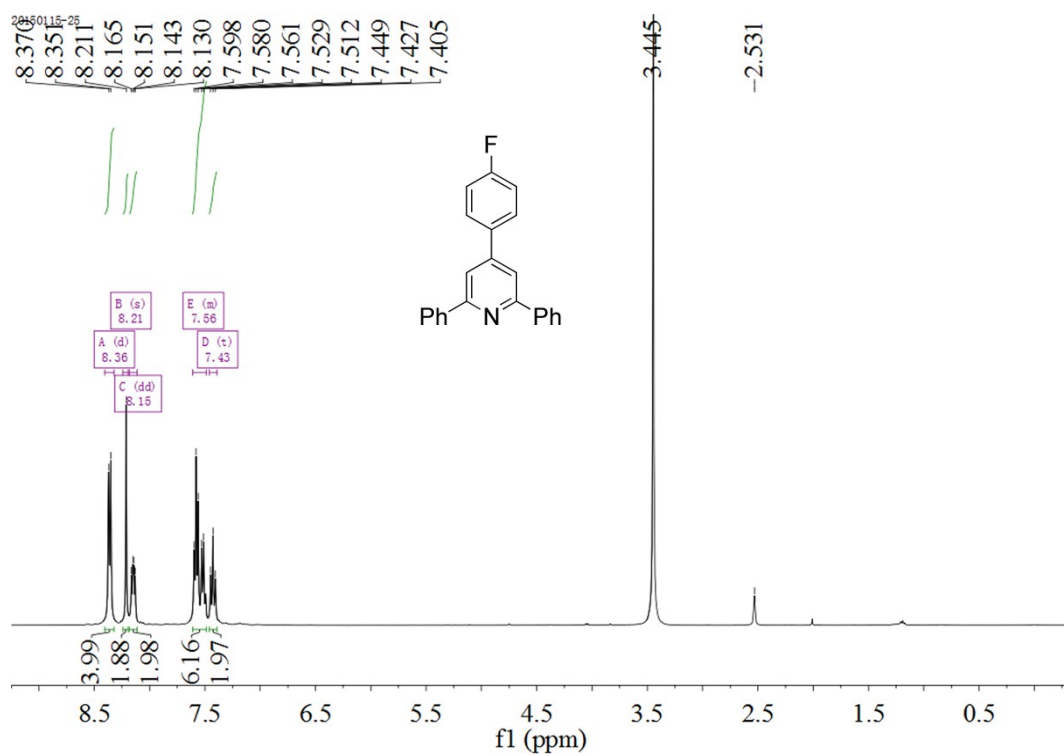


**3b**

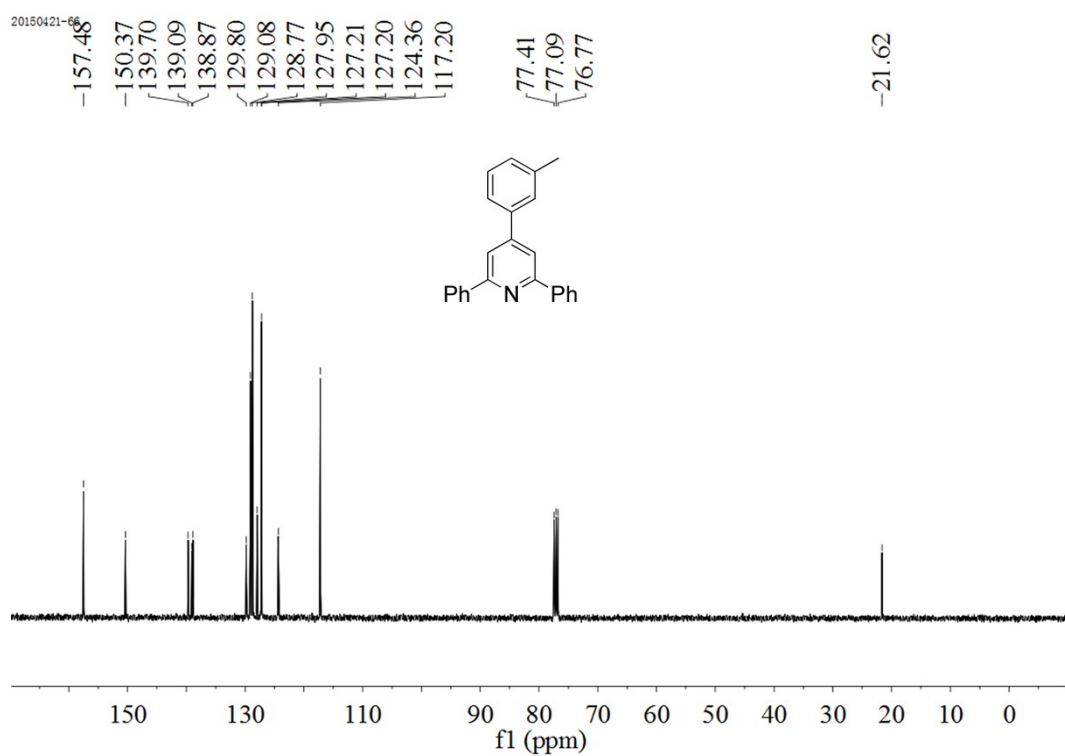
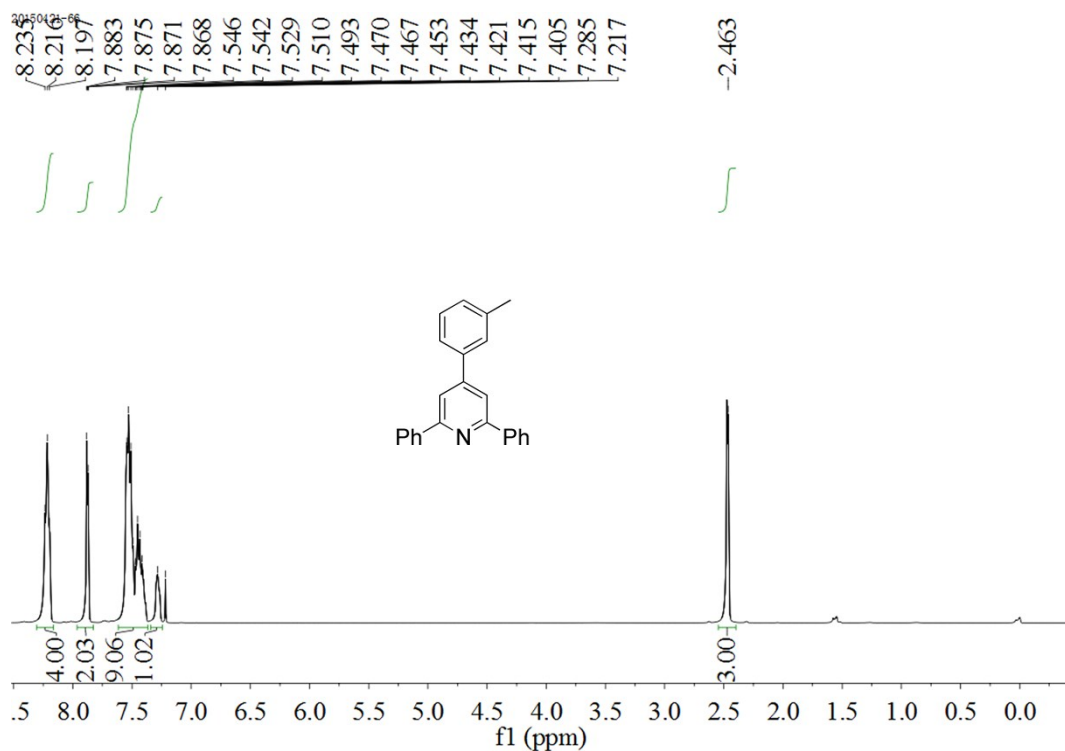


**3c**

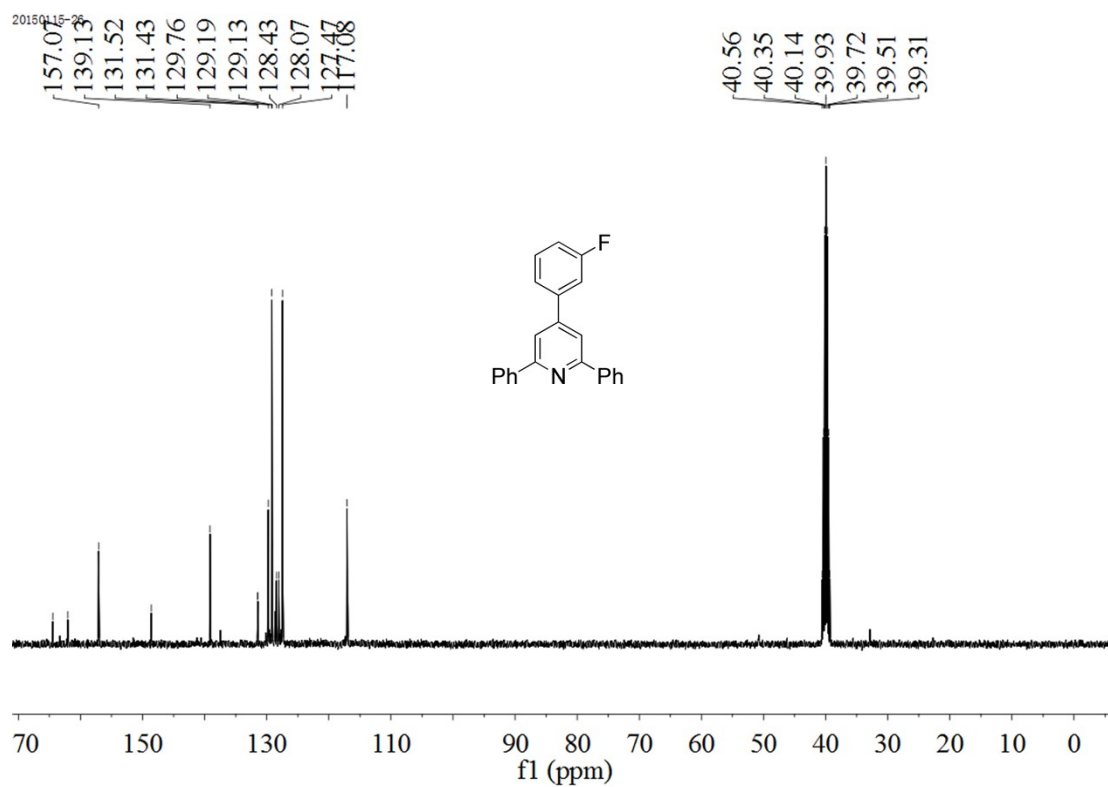
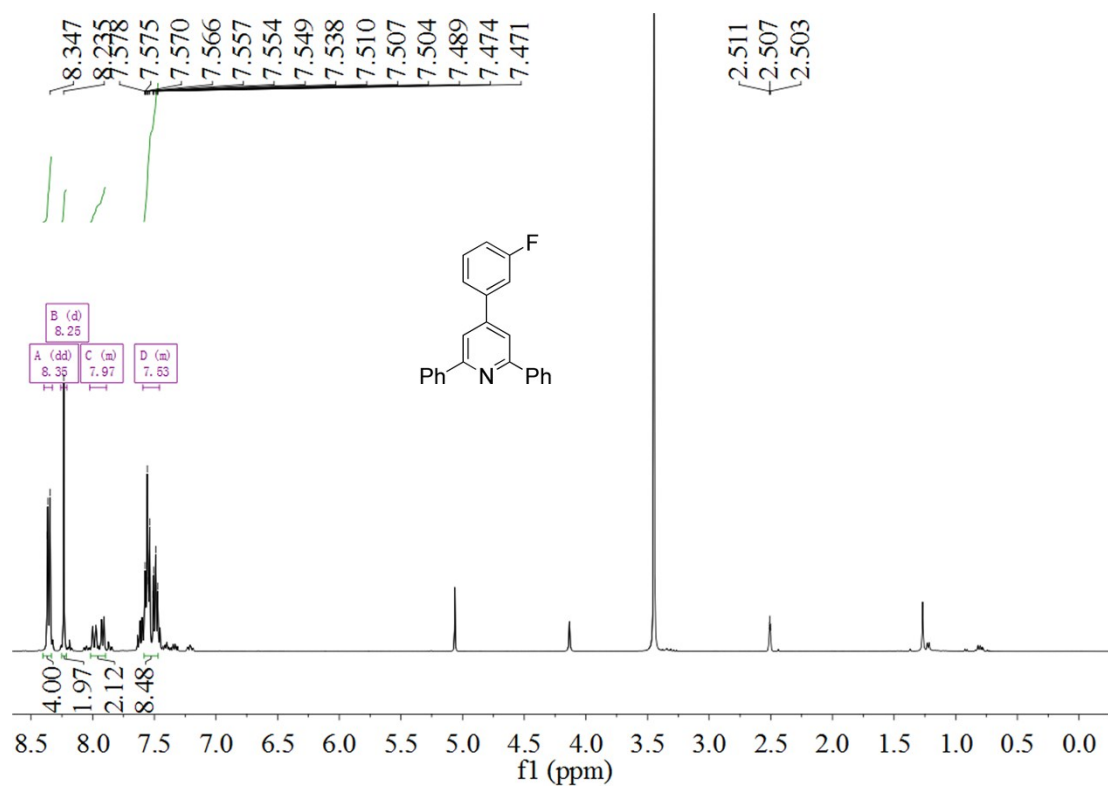
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**3d**

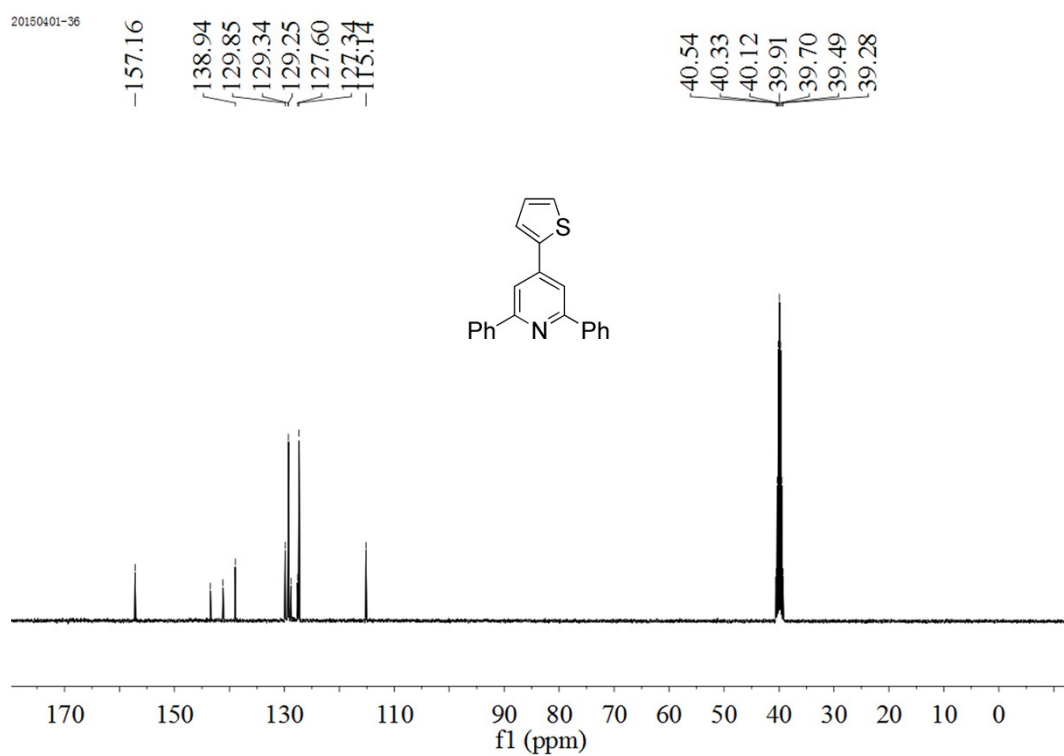
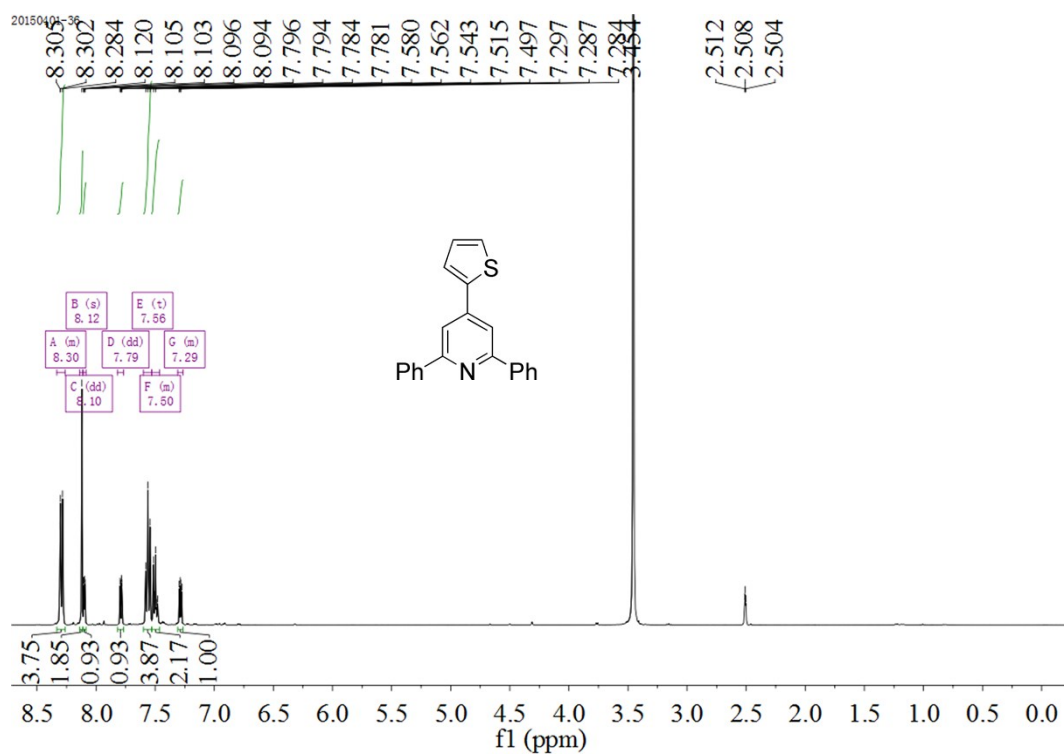


**3e**



**3f**

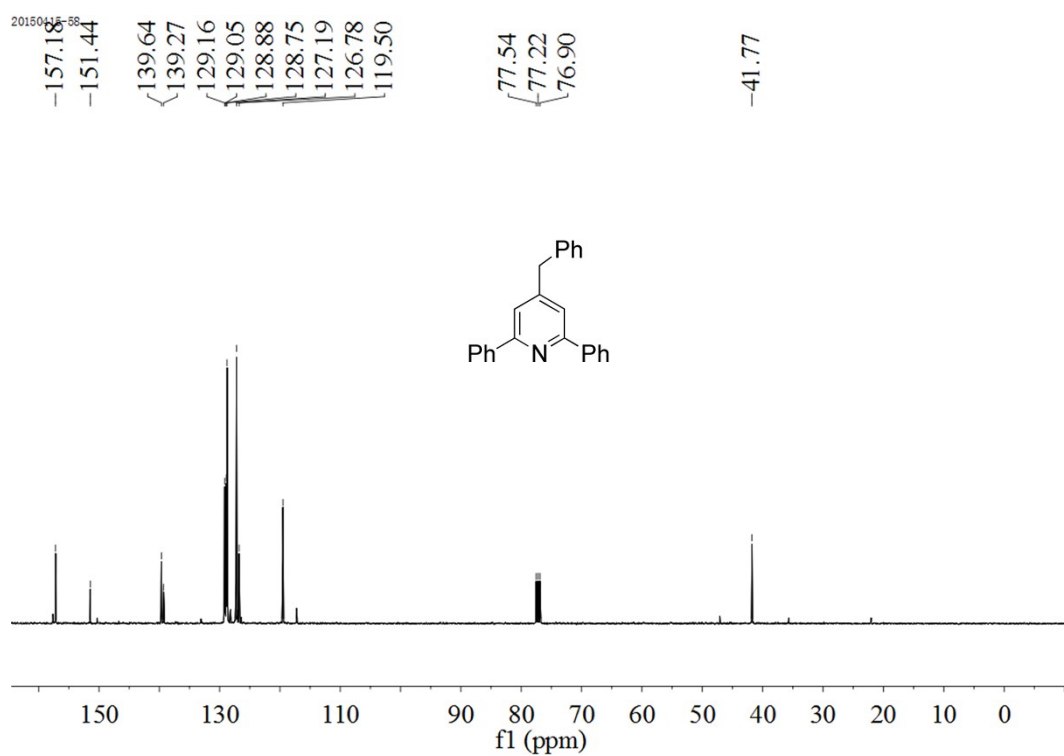
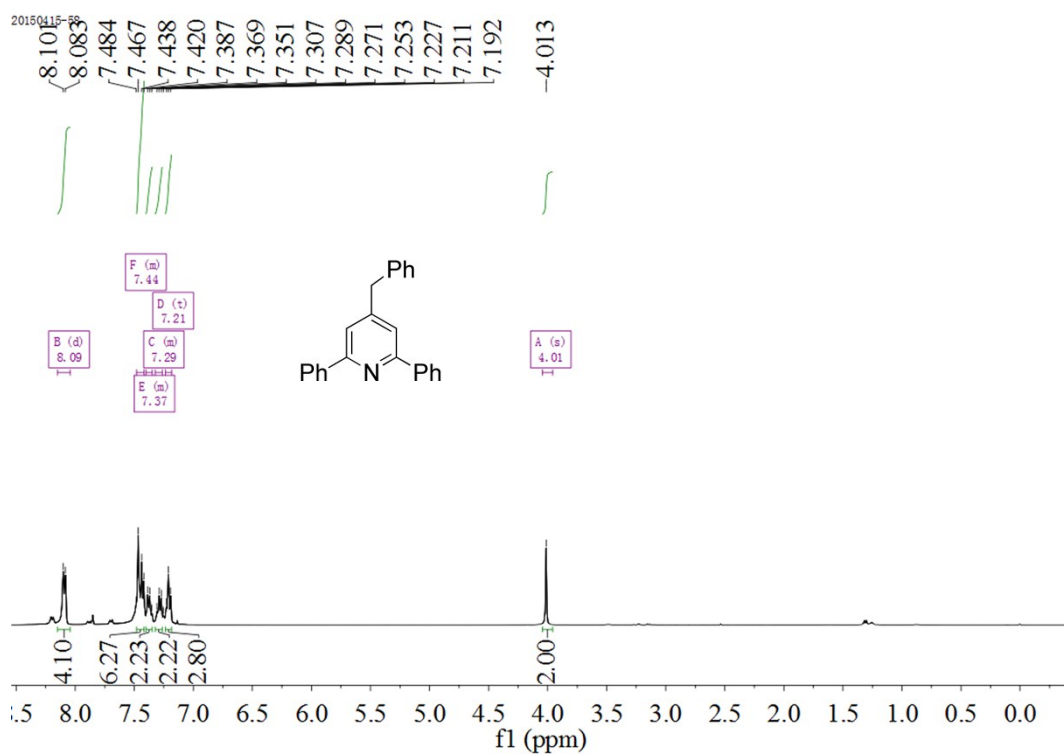
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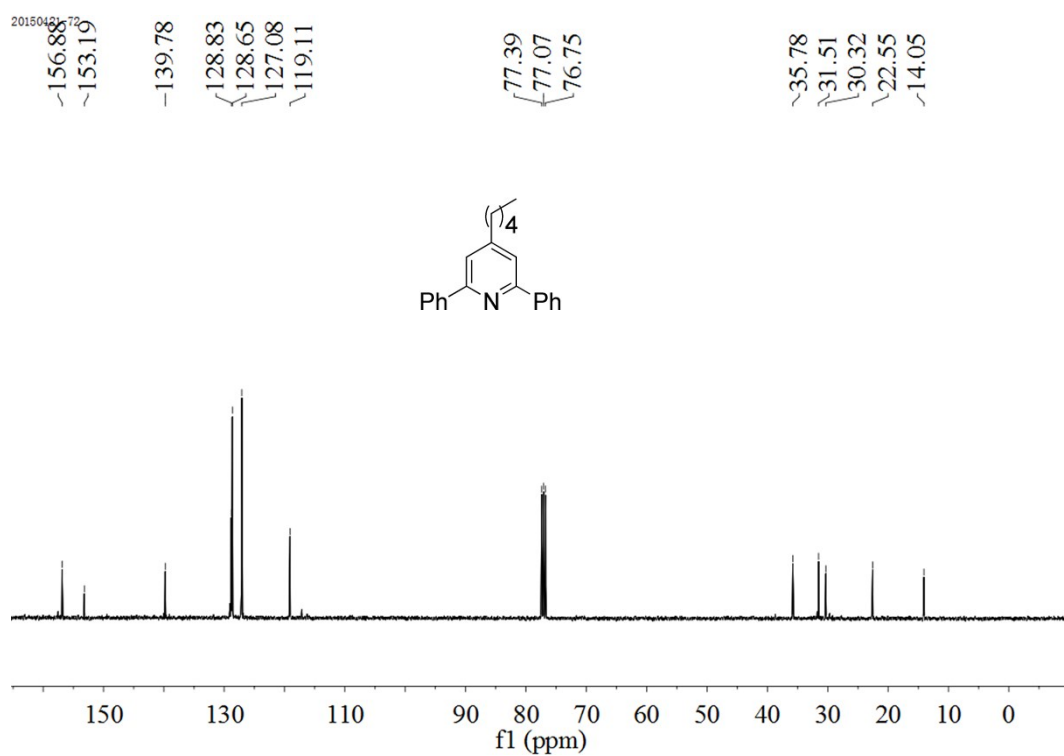
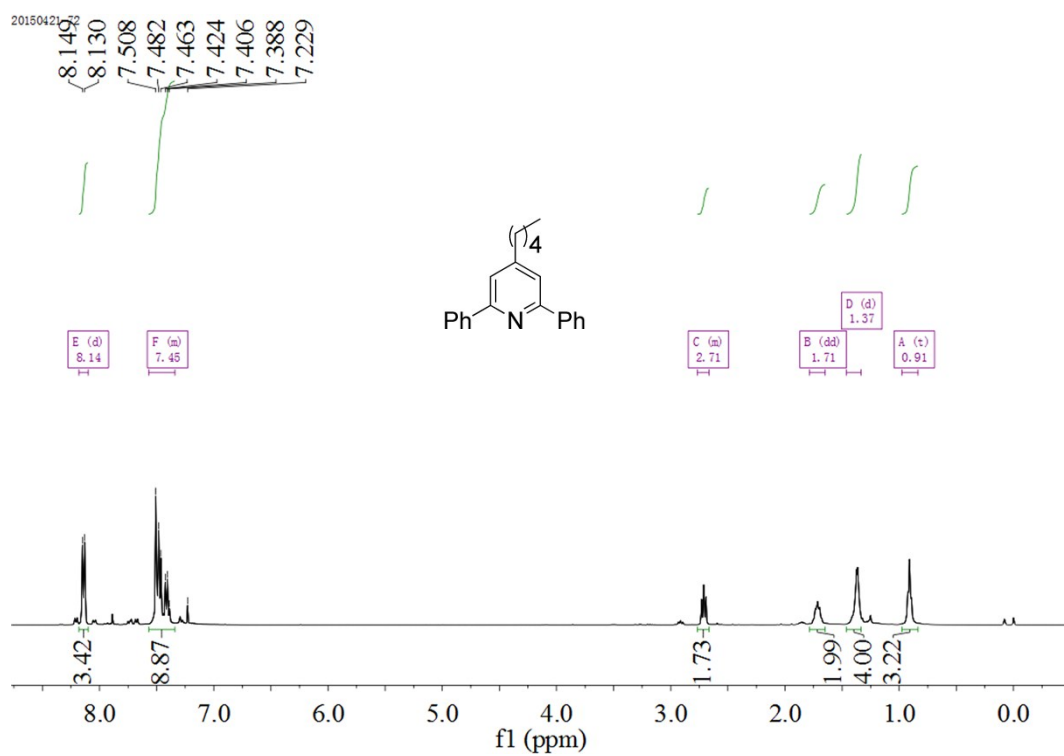
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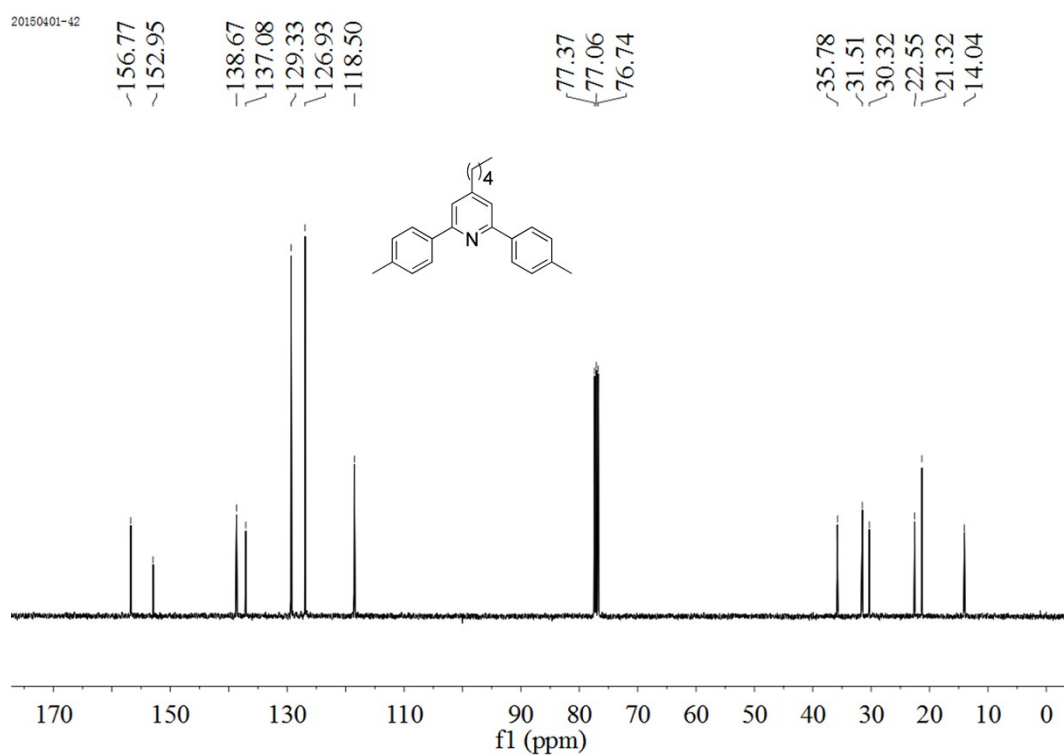
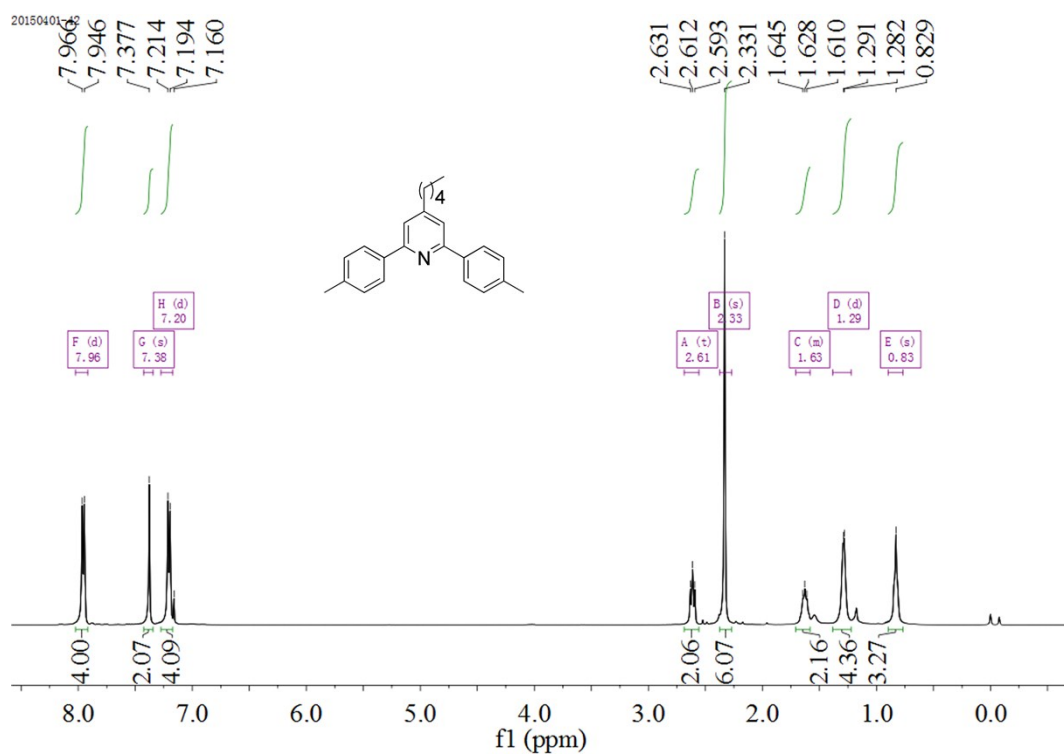




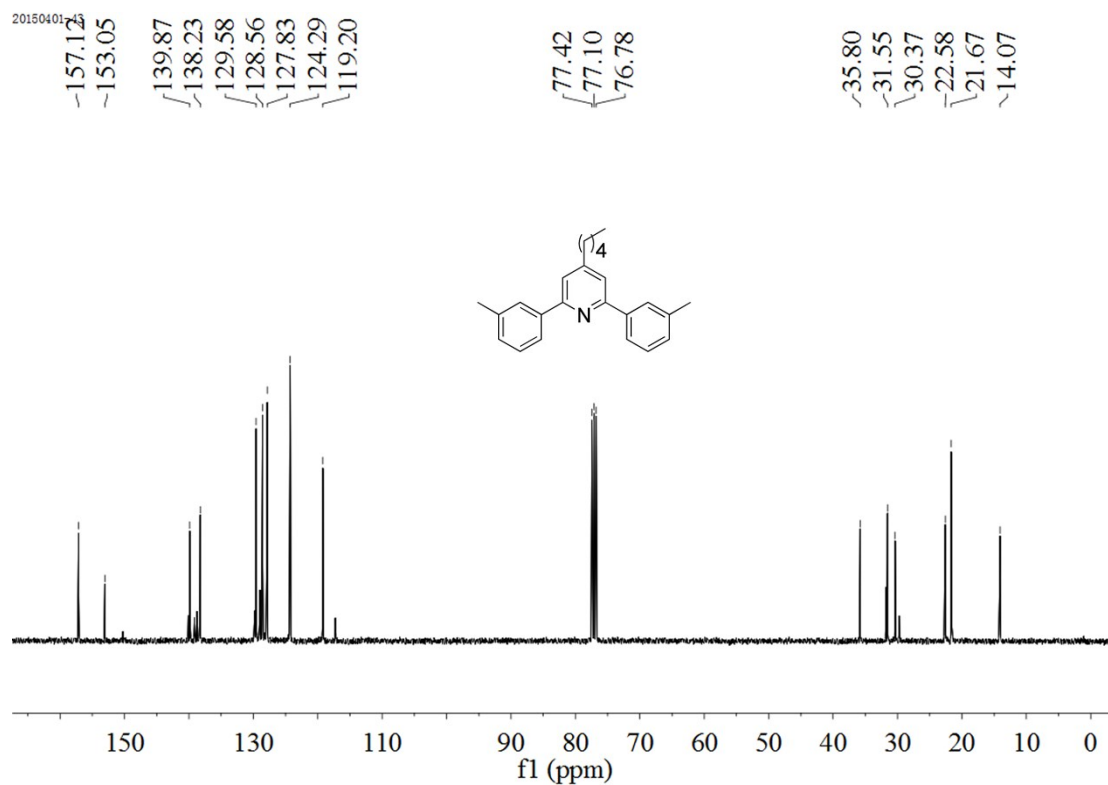
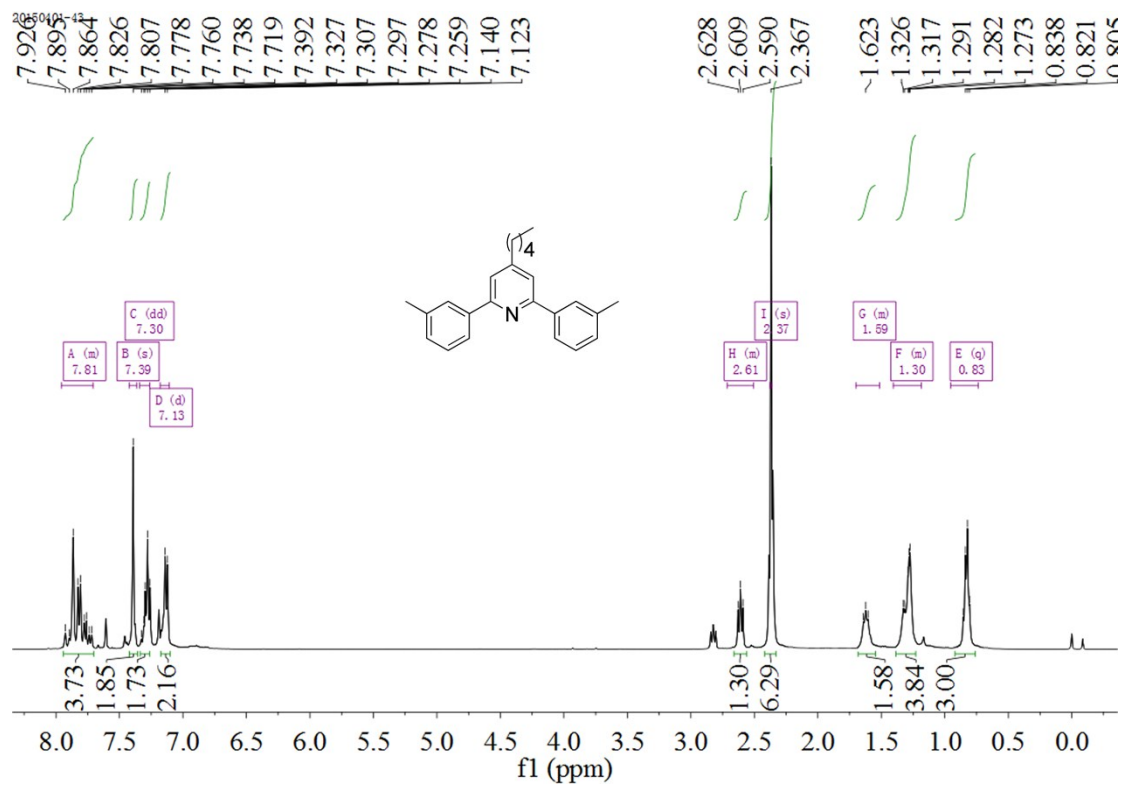
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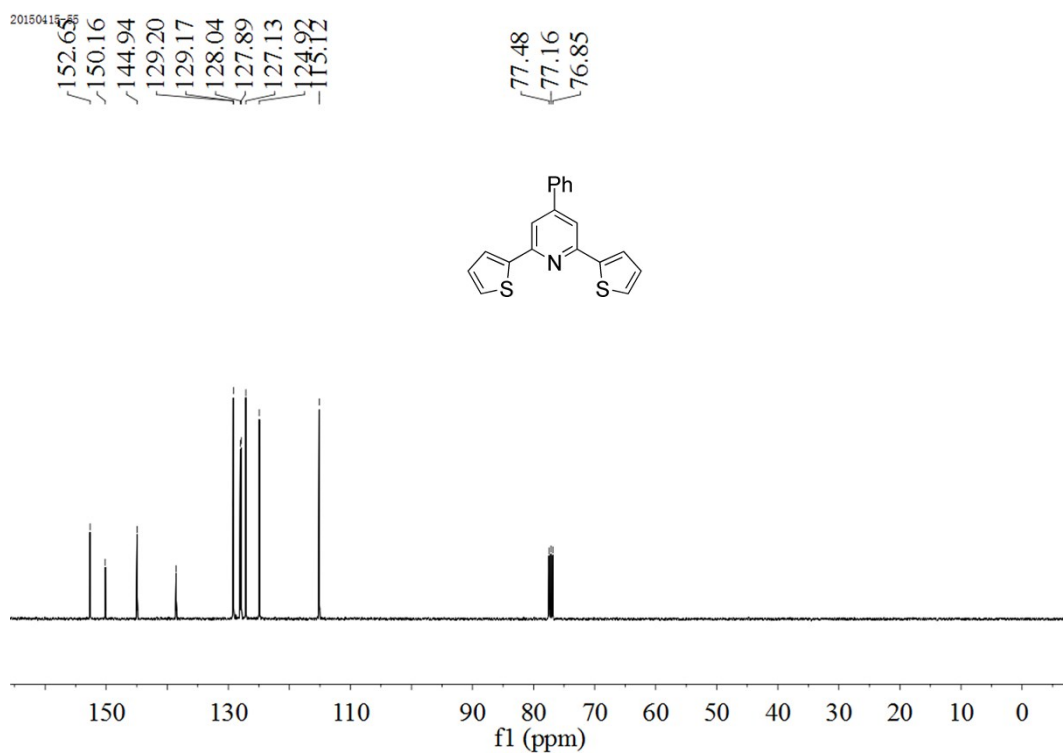
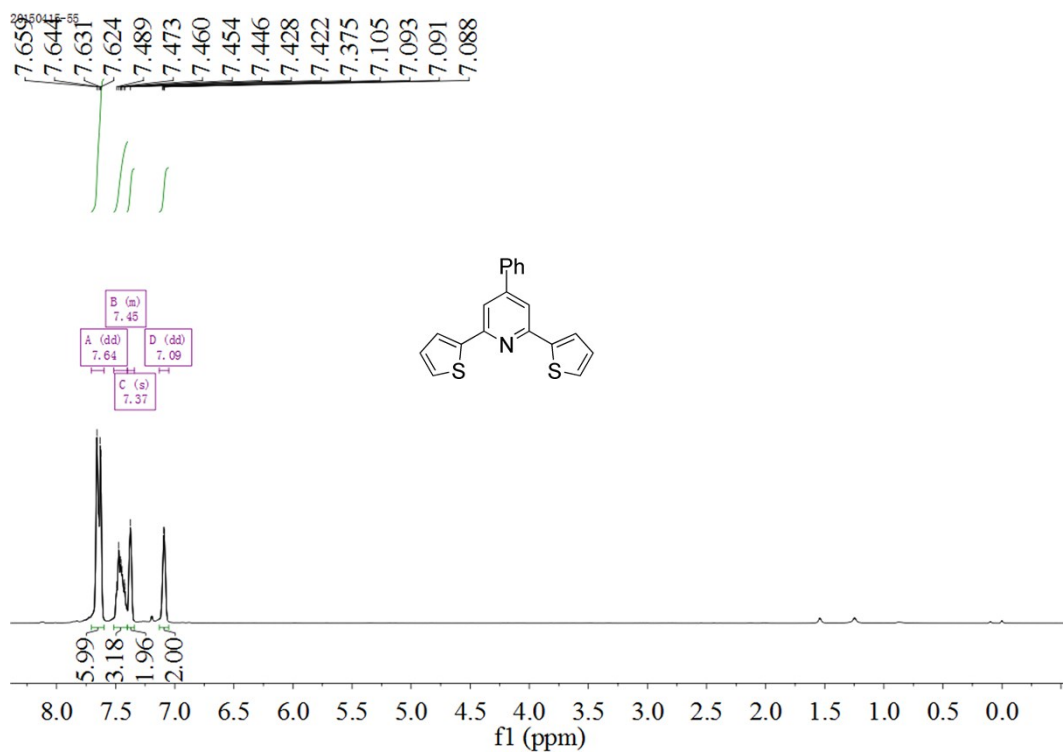
**3i**



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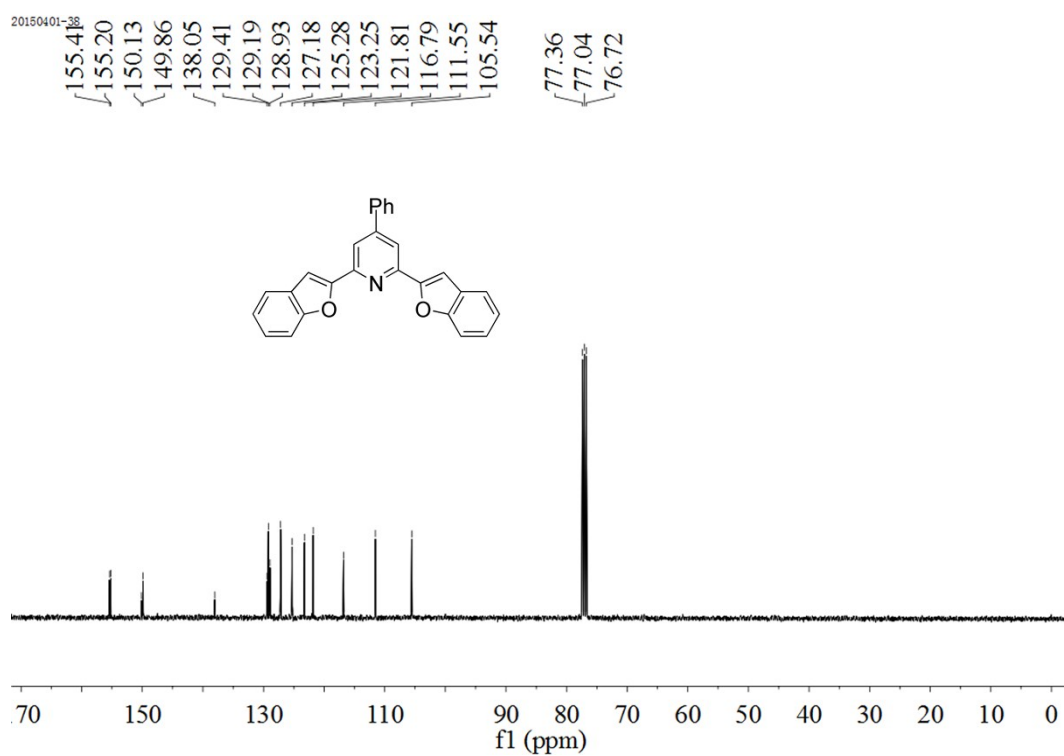
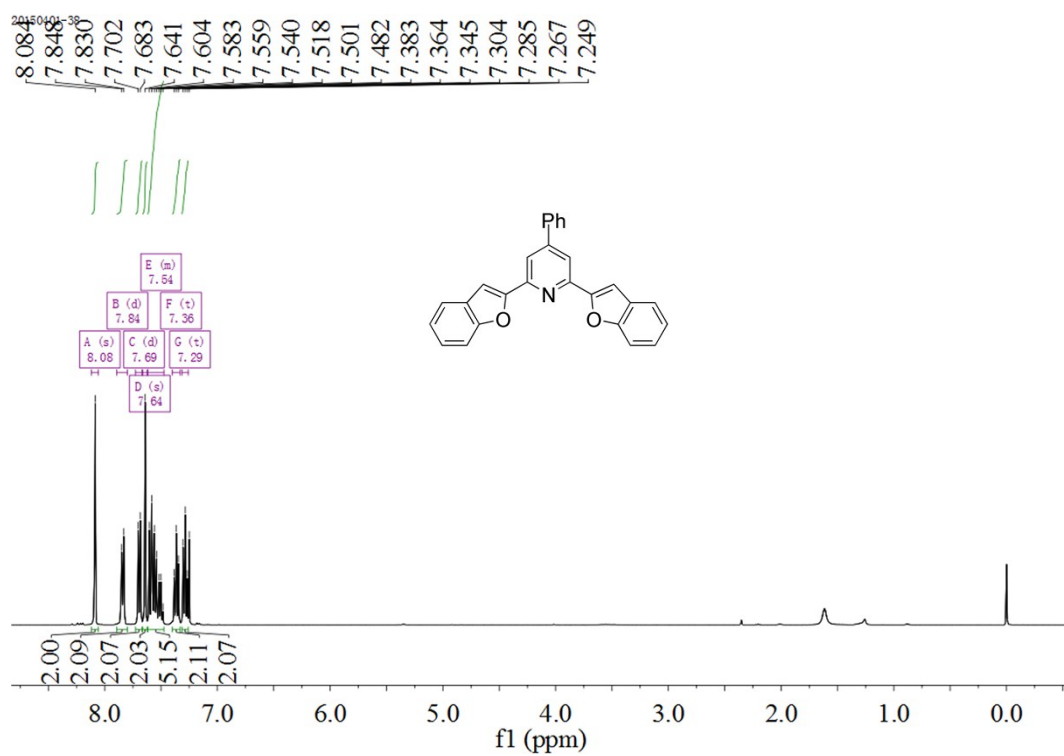


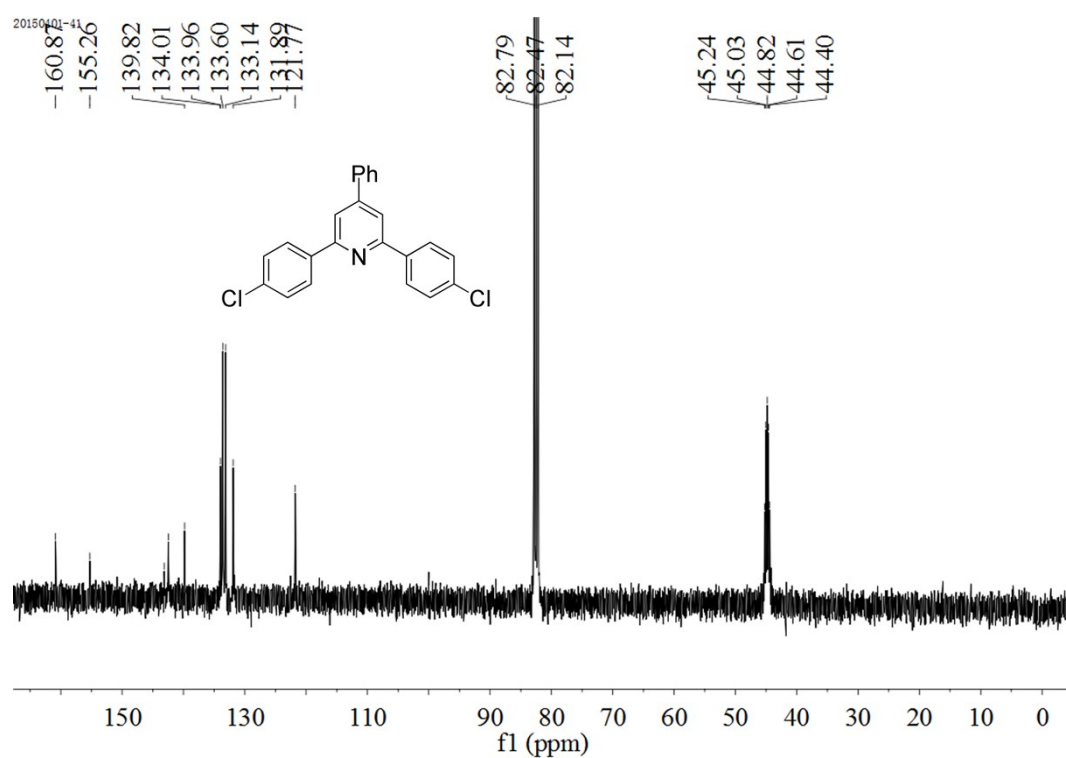
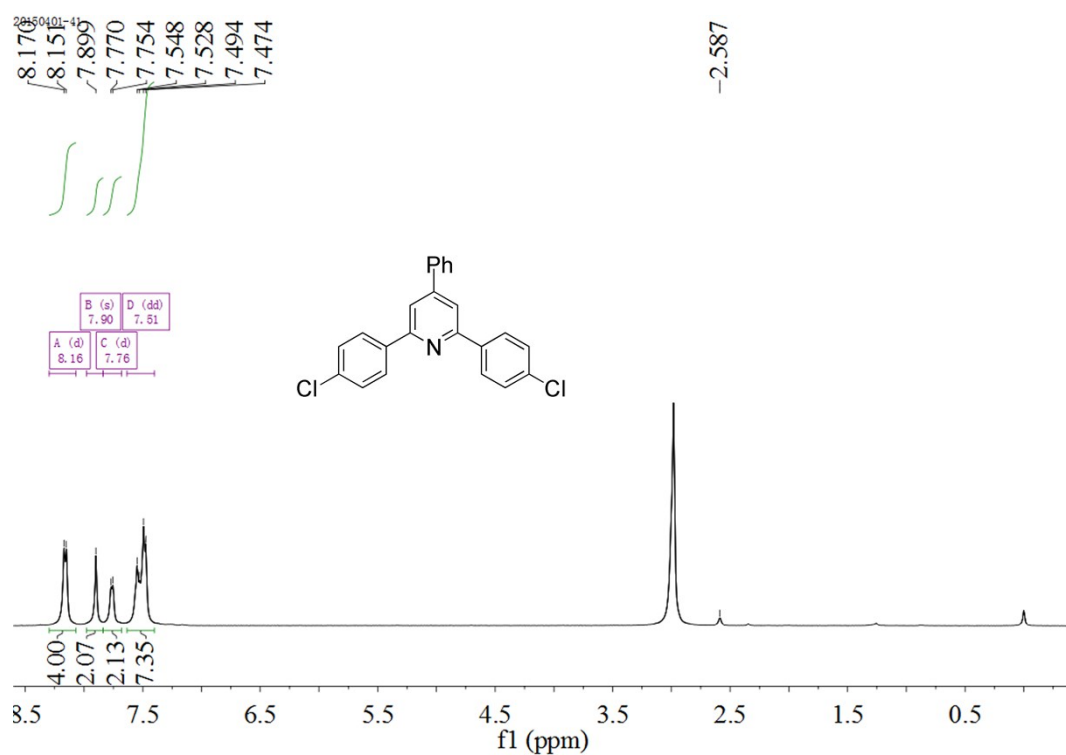
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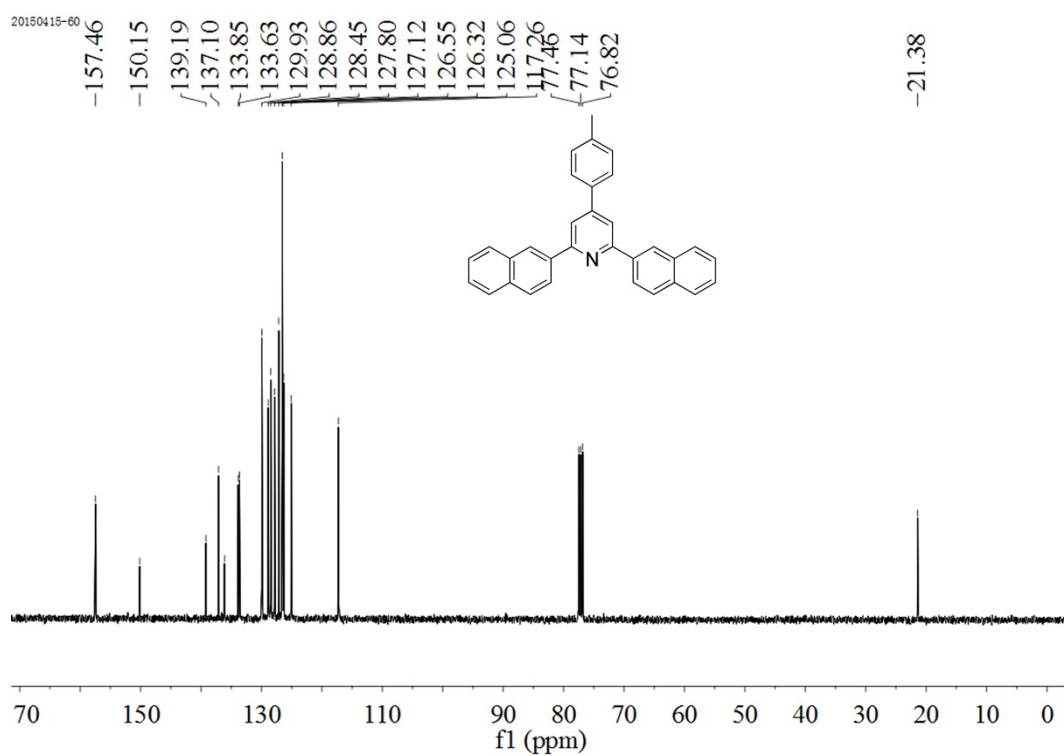
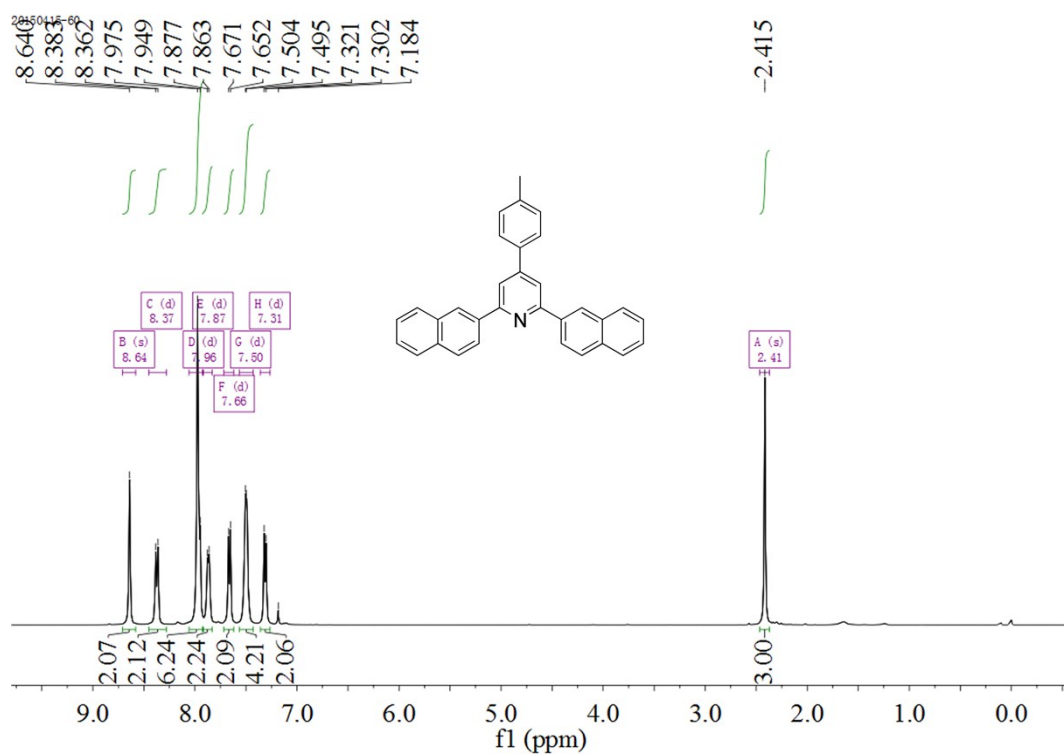
**3I**

21



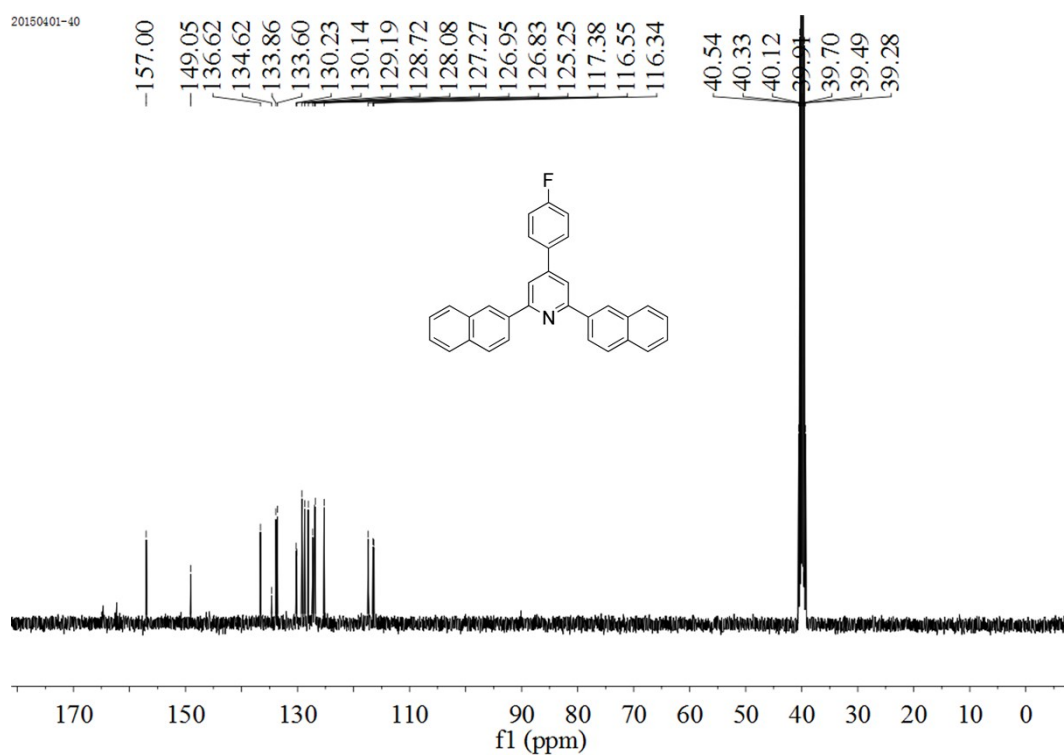
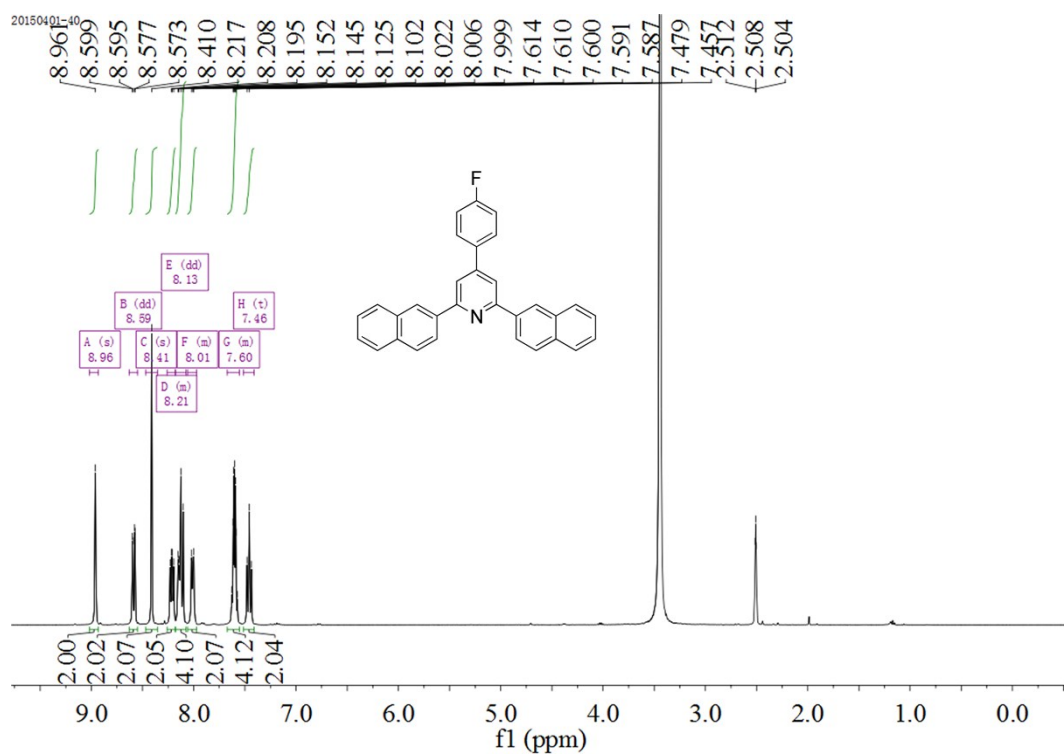


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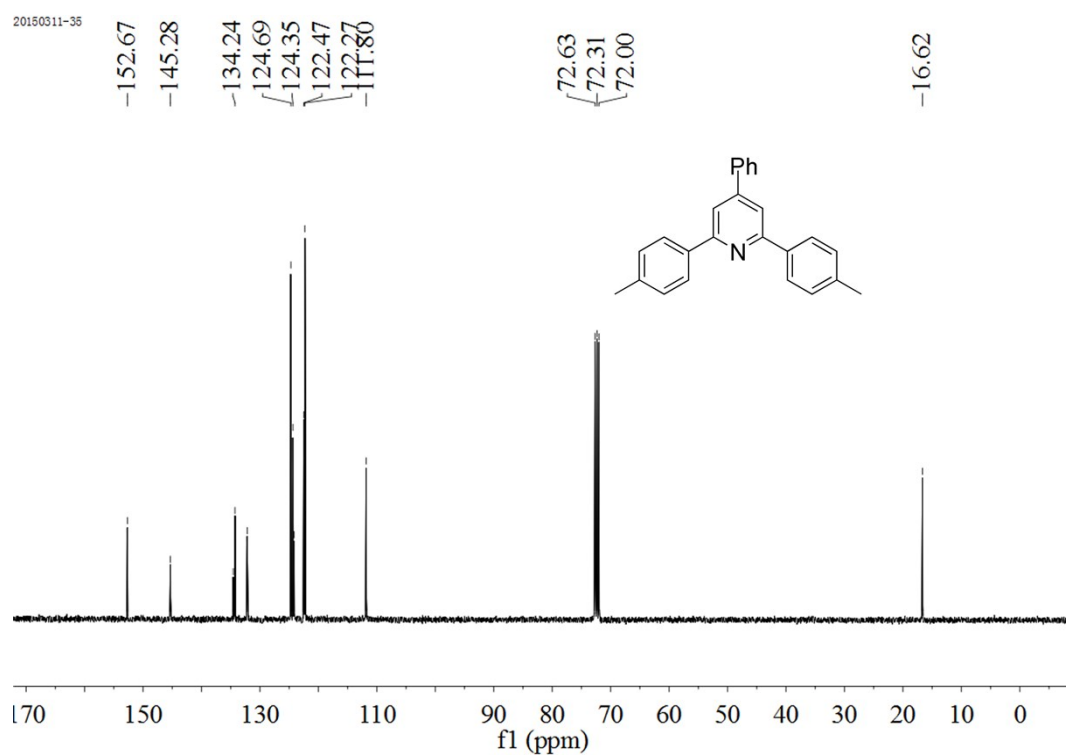
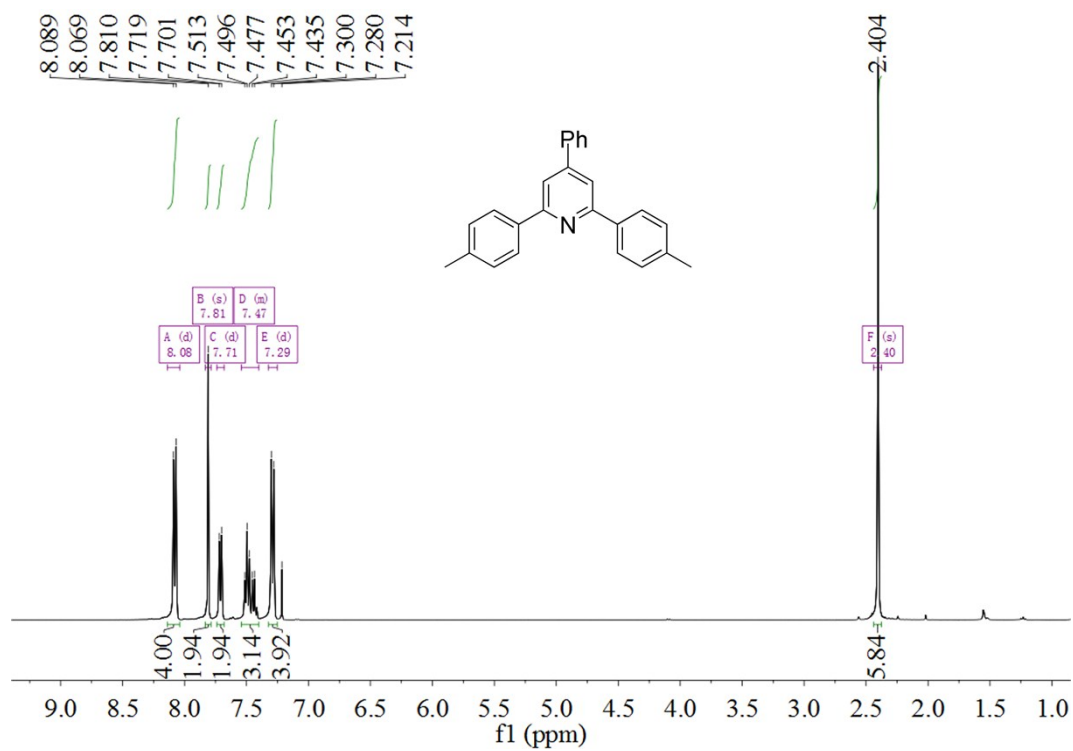


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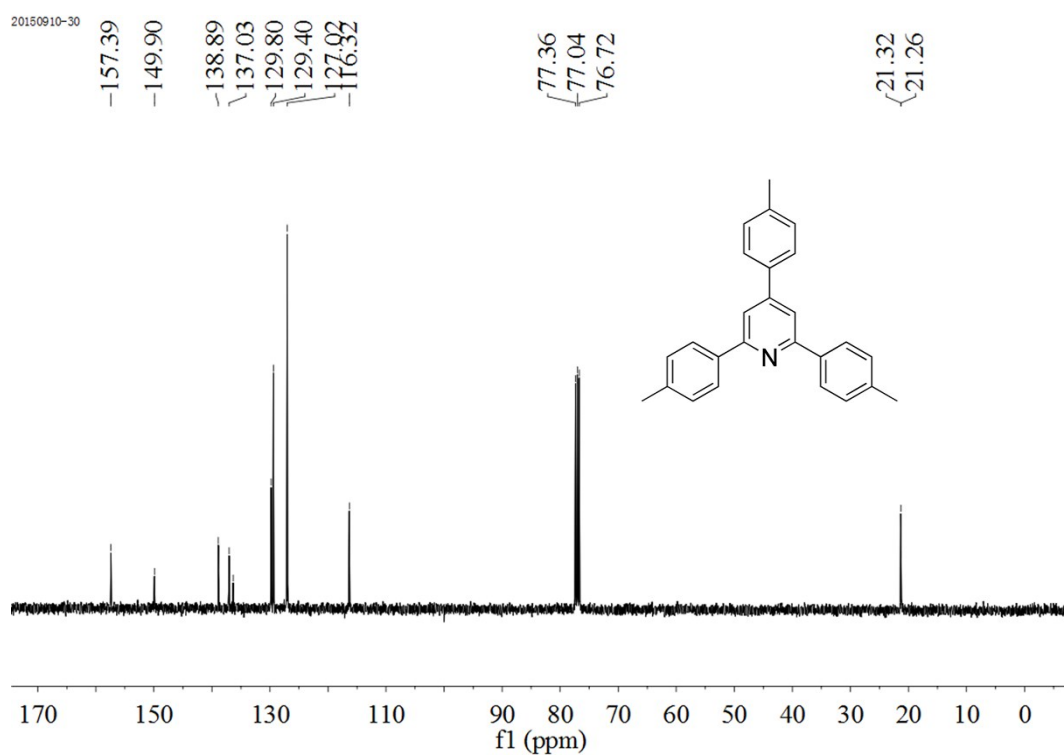
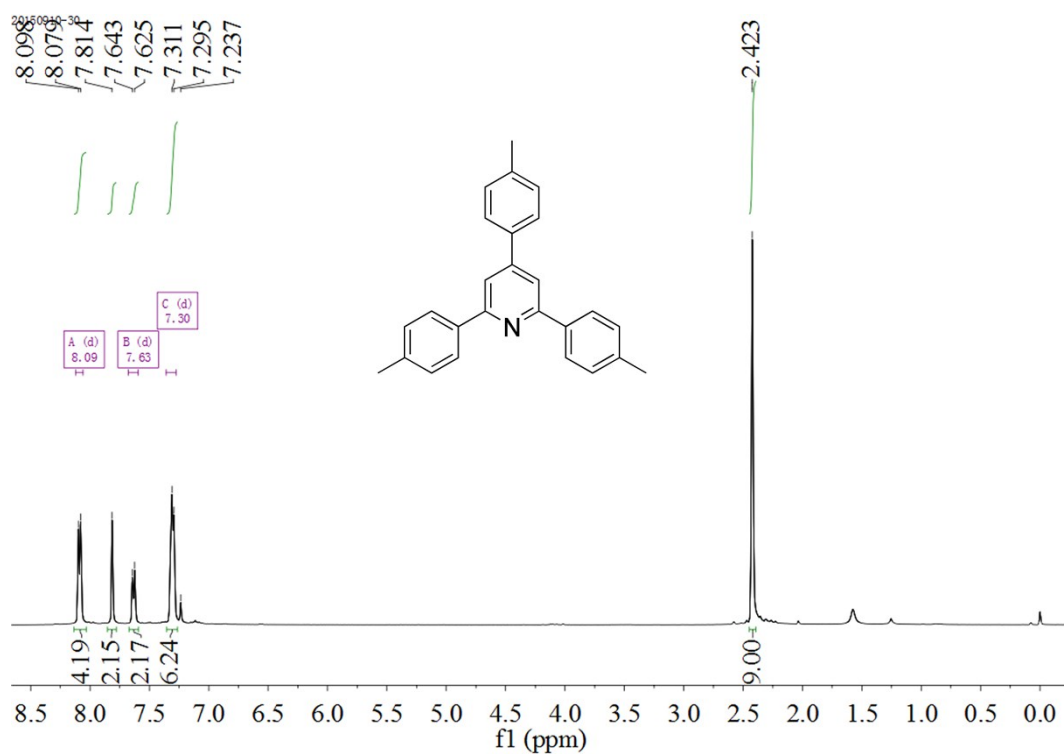




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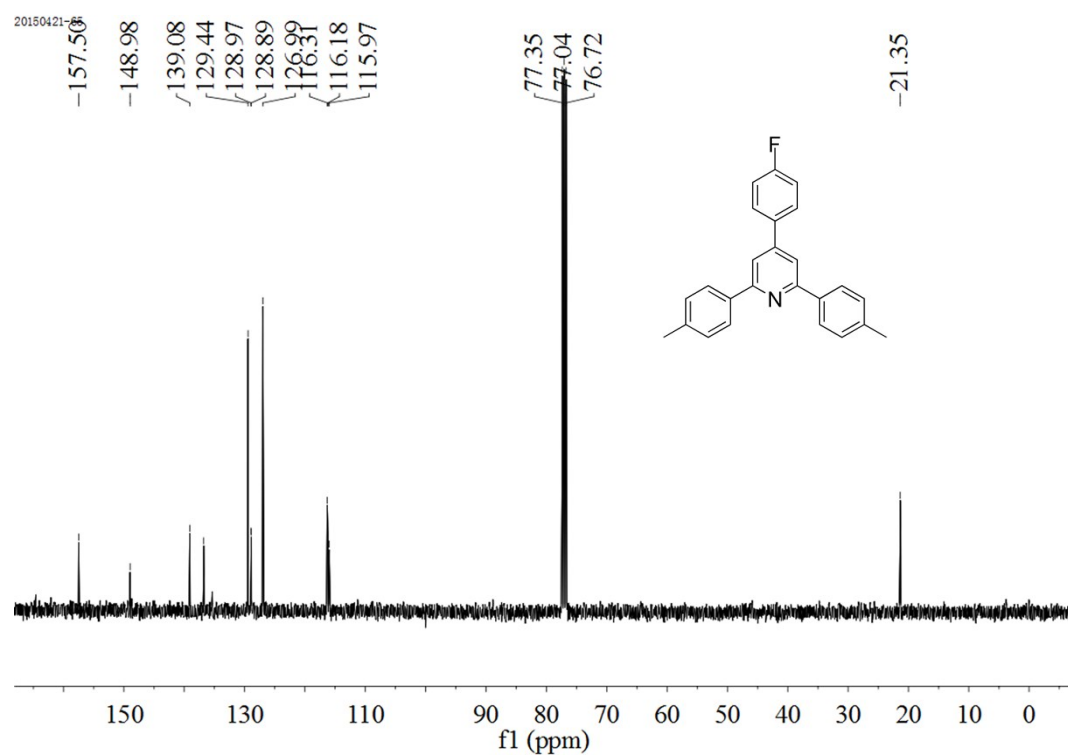
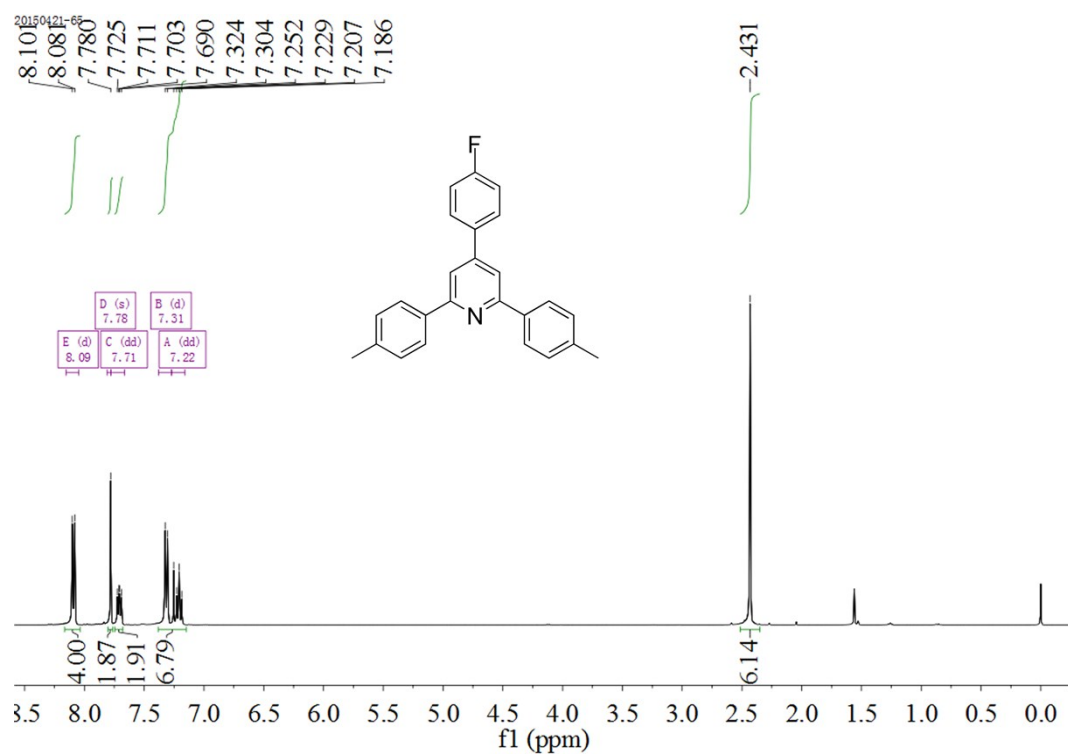


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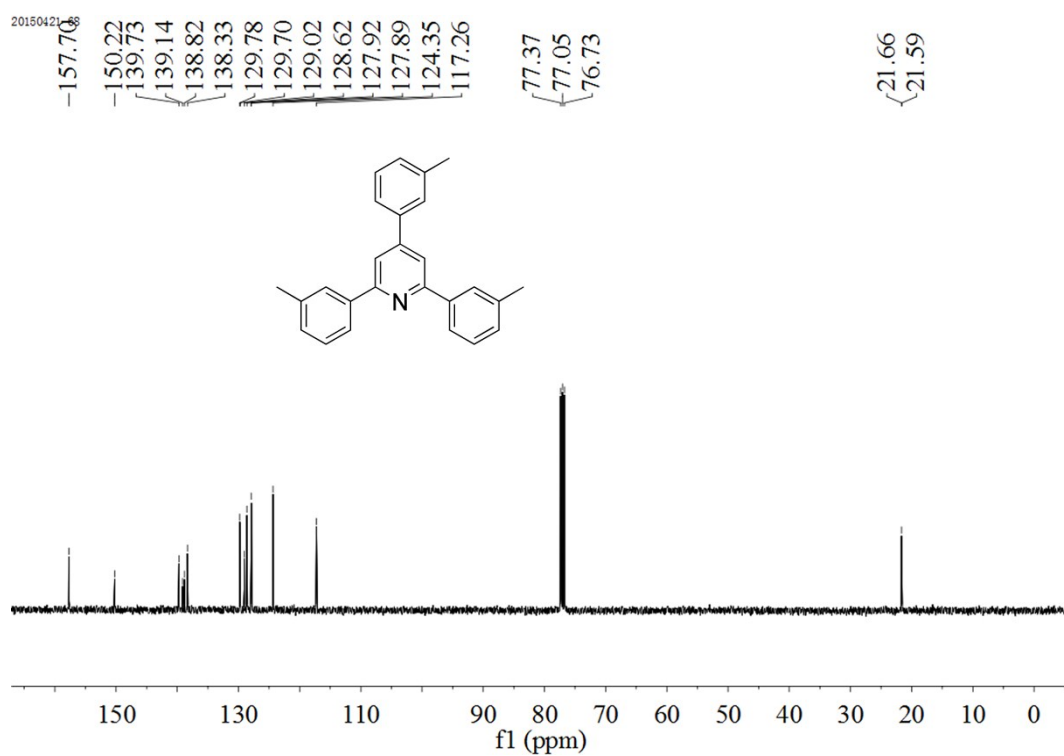
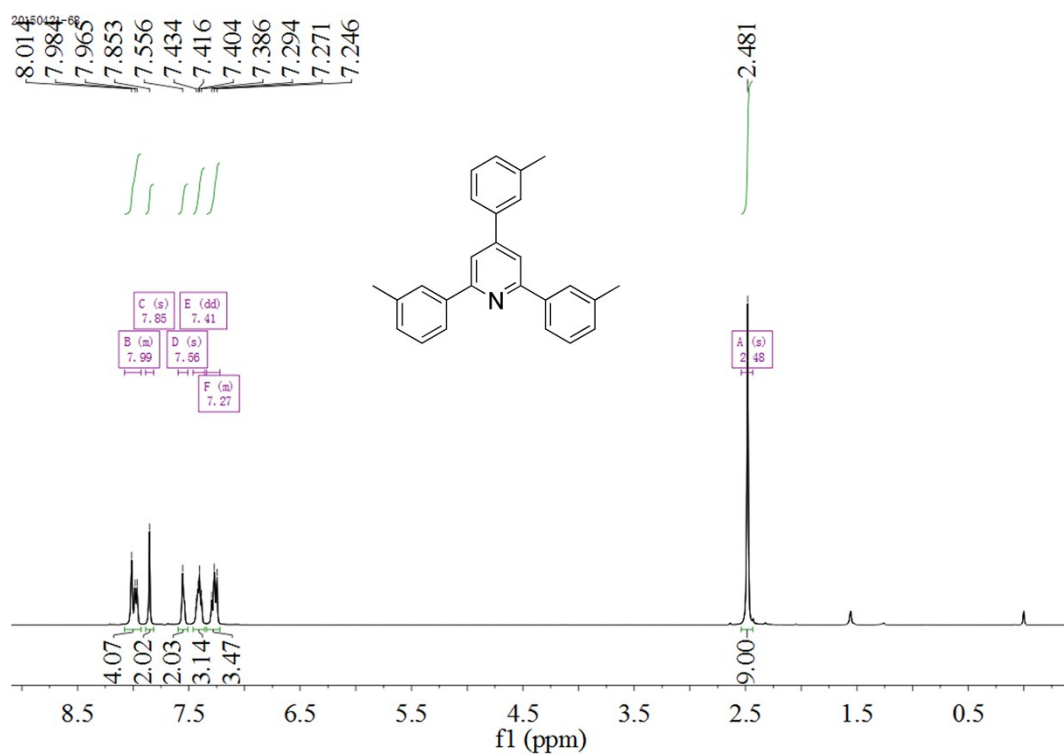


**3r**

27

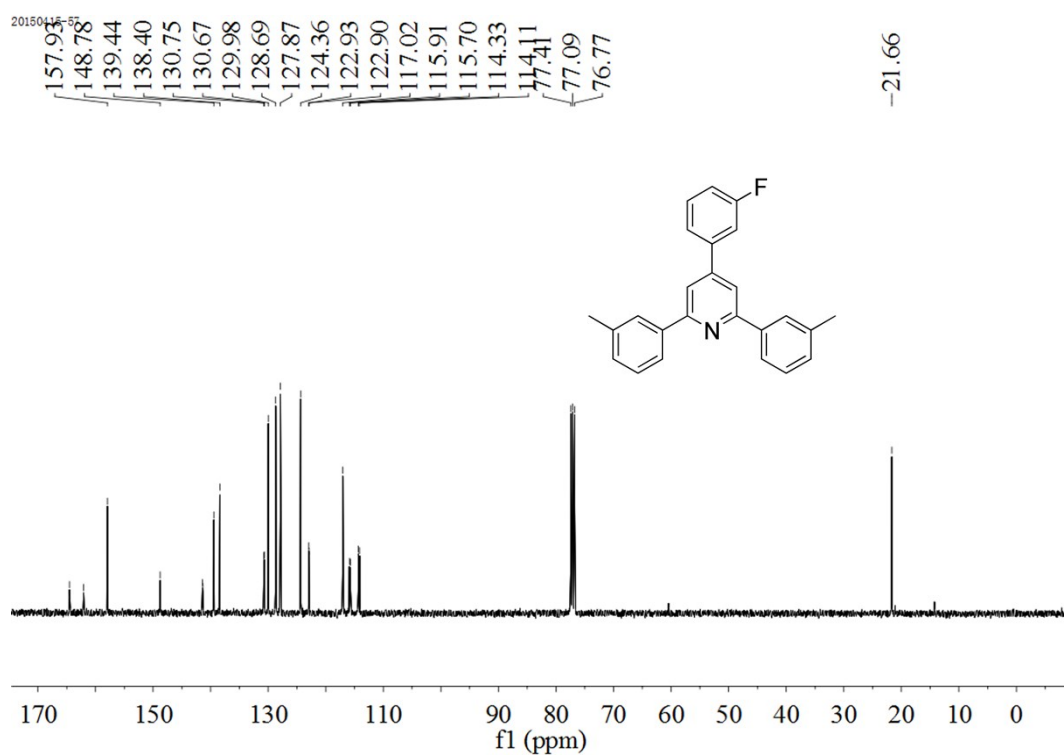
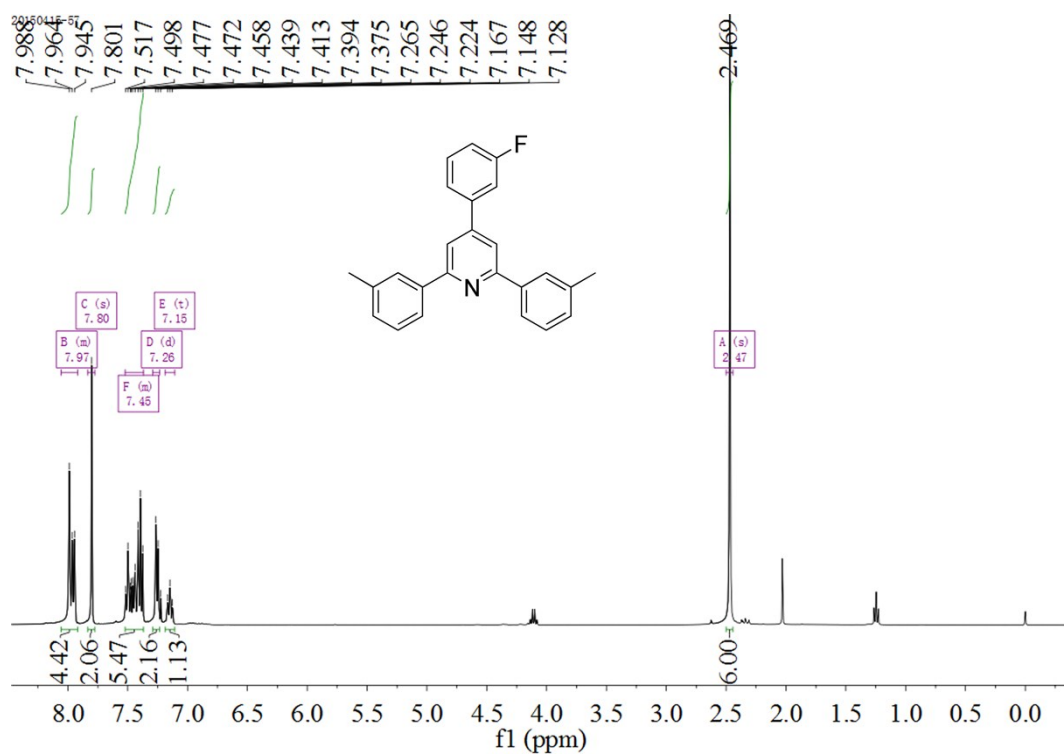


**3s**

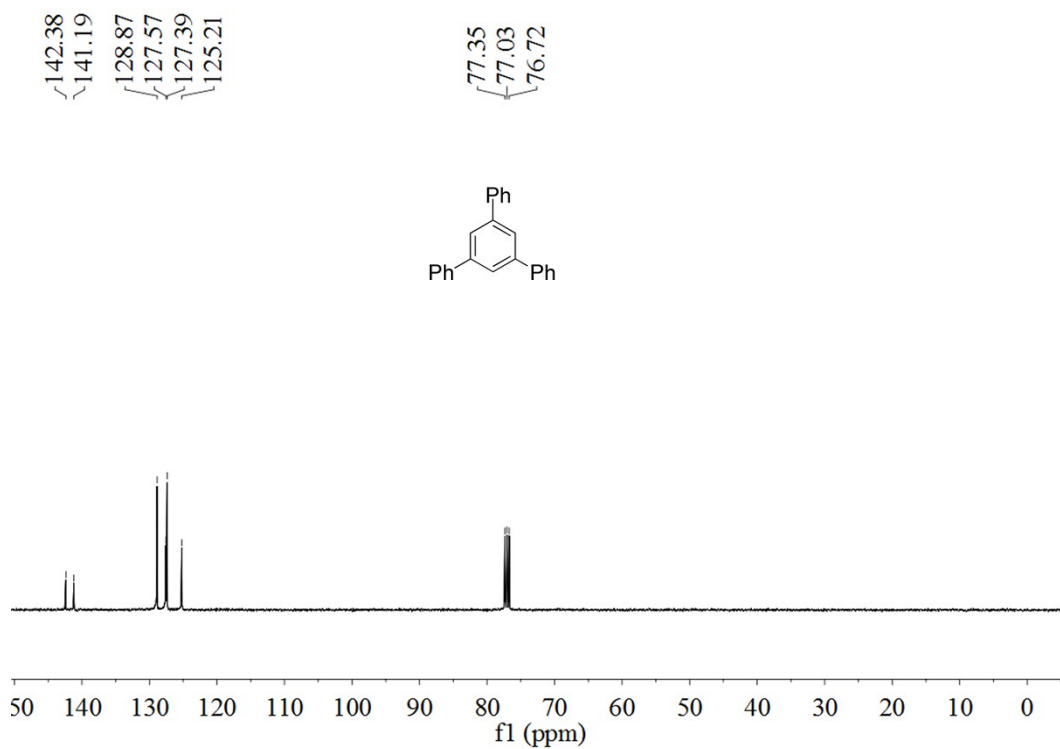
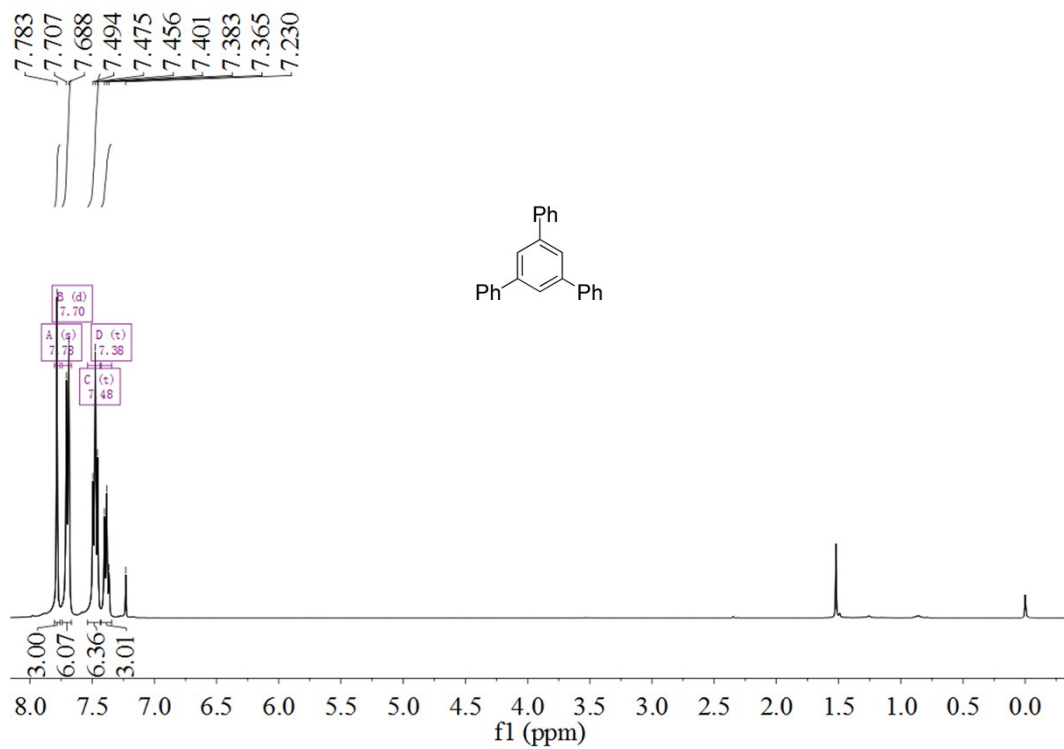


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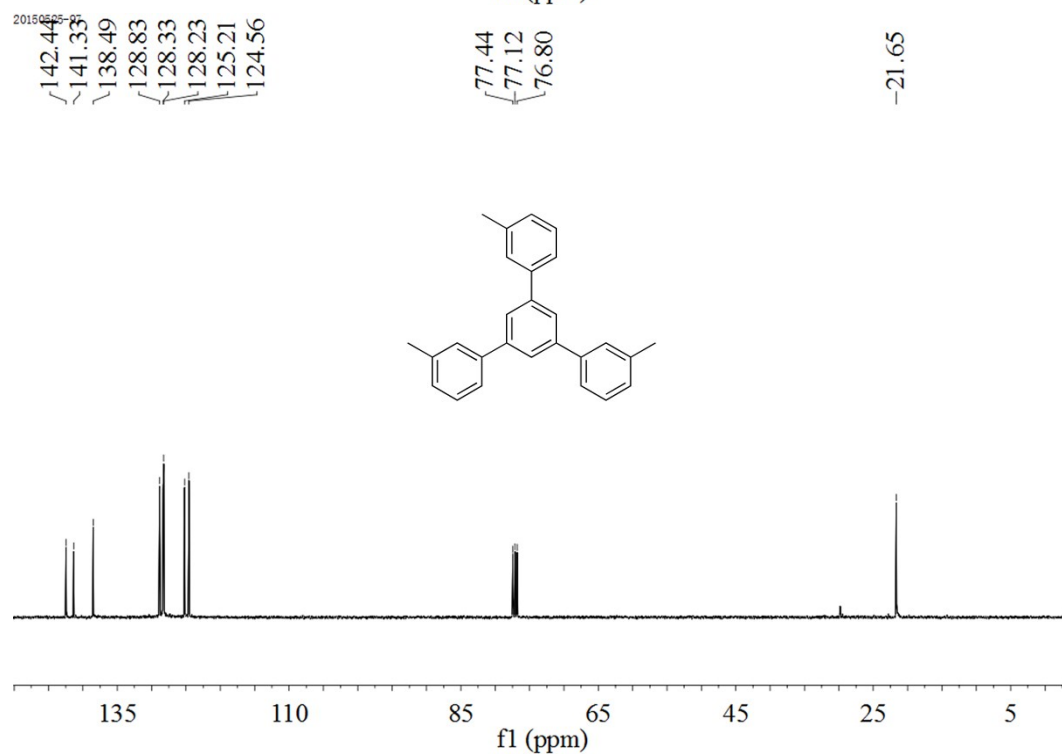
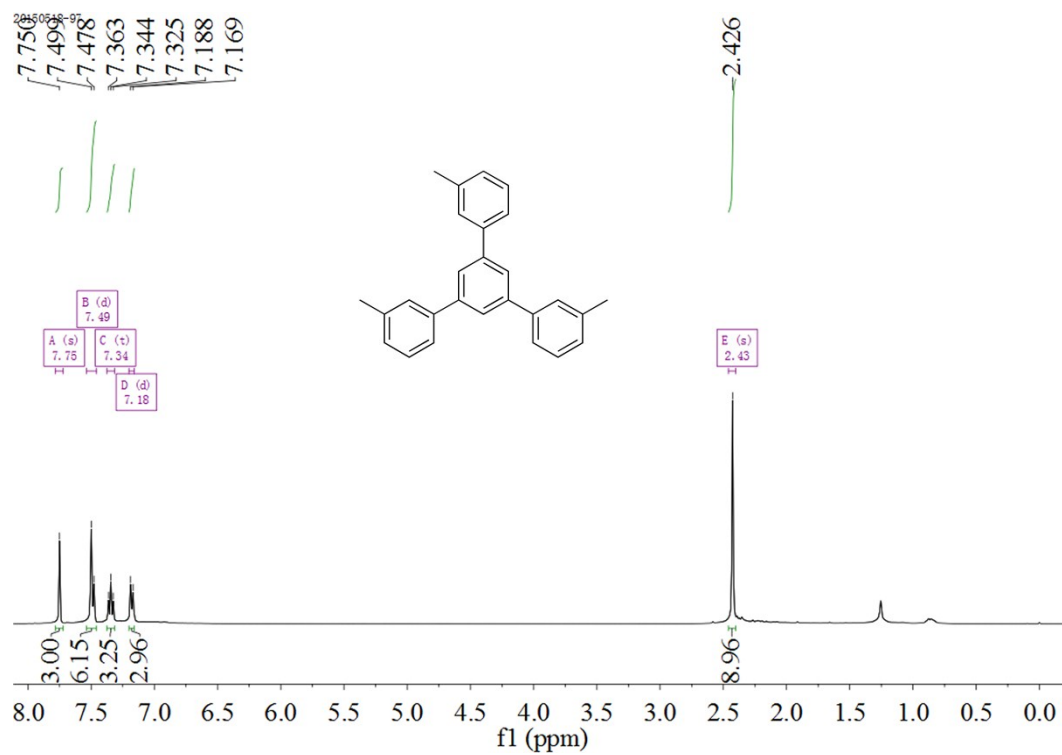
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4a

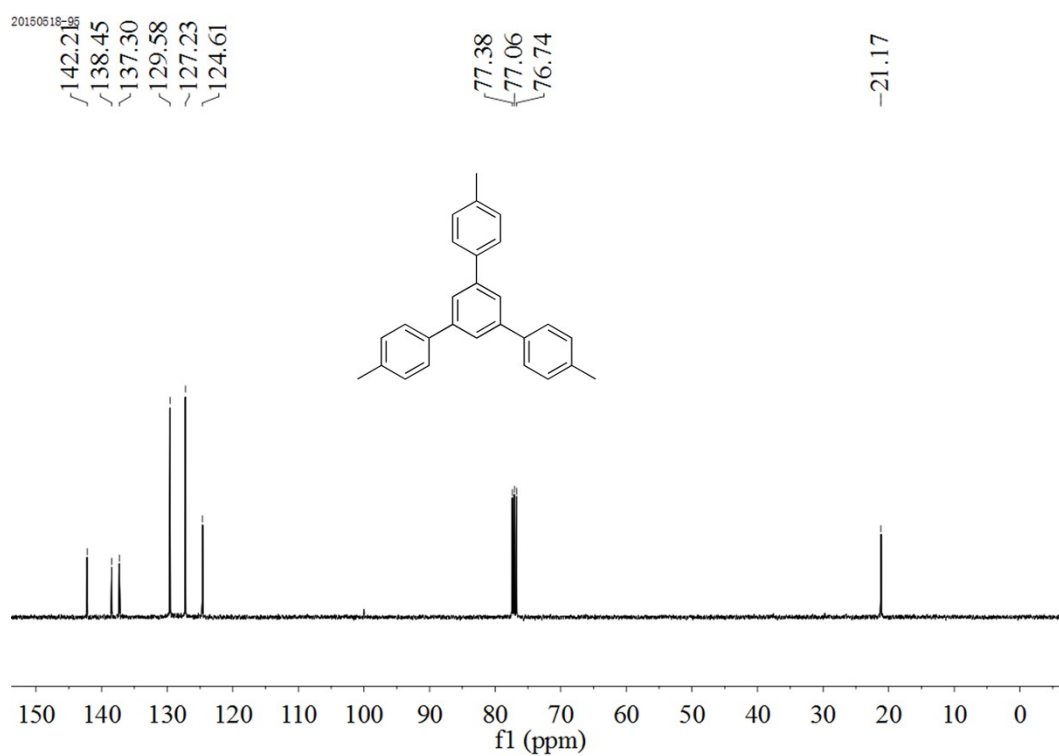
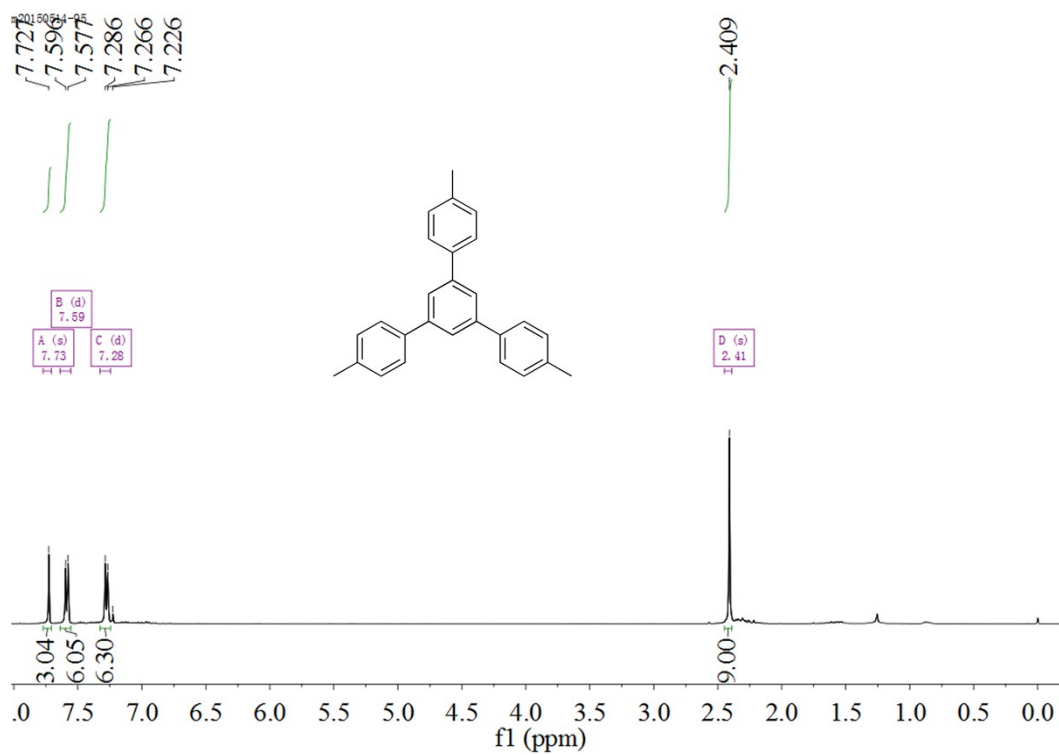


**4b**

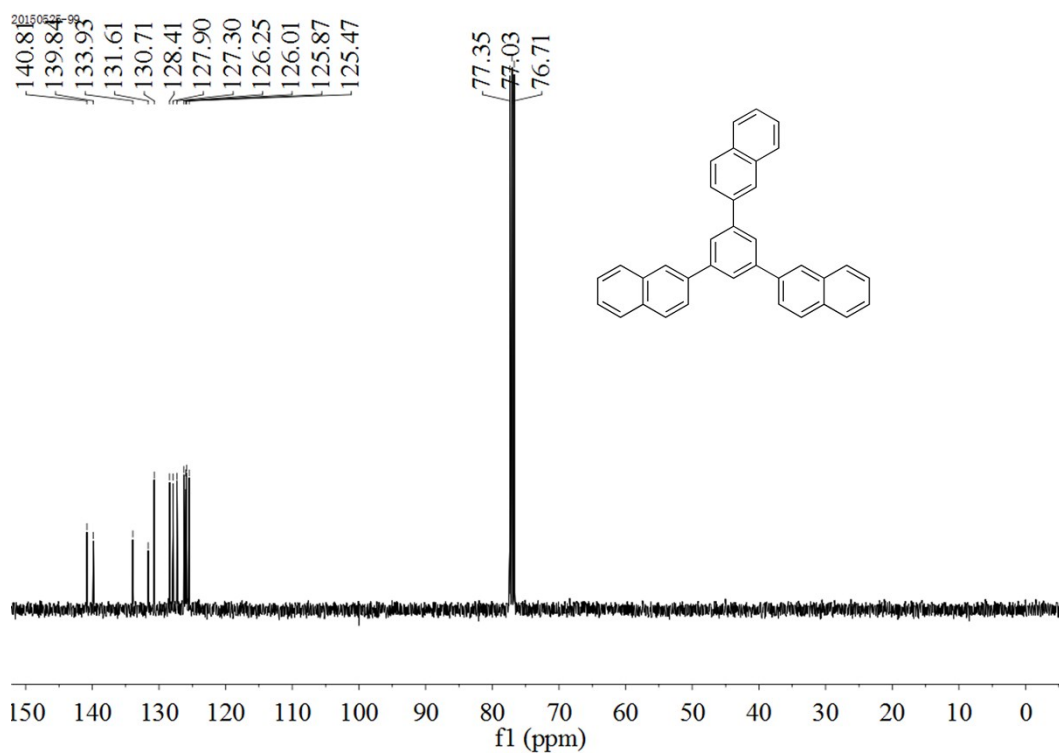
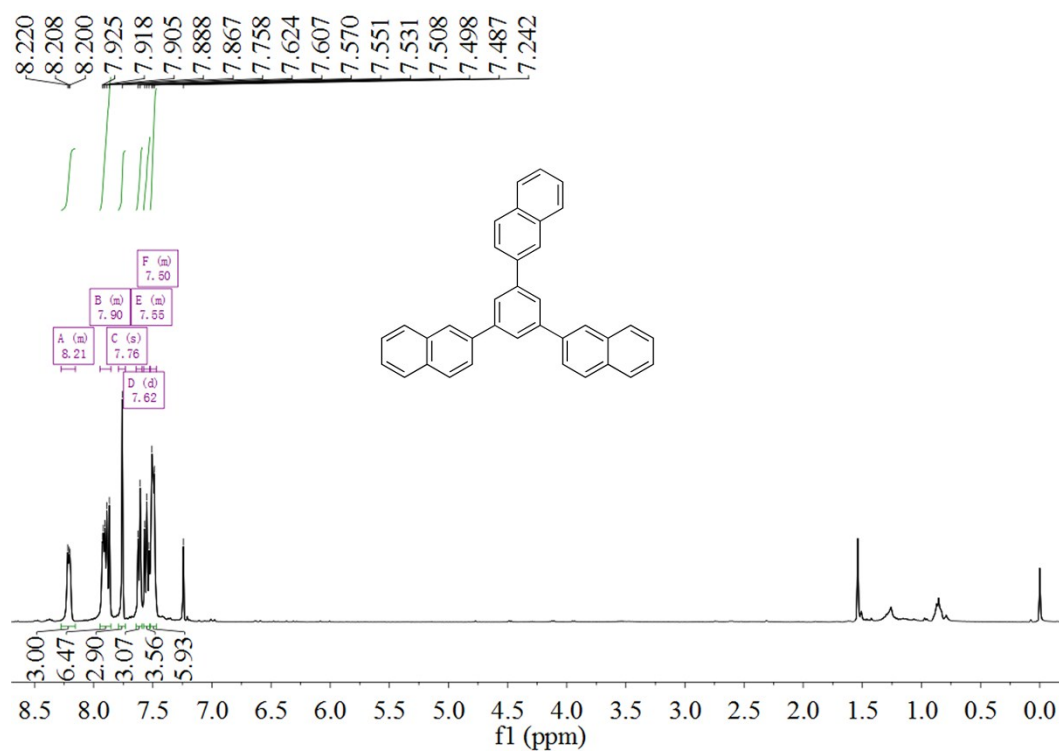


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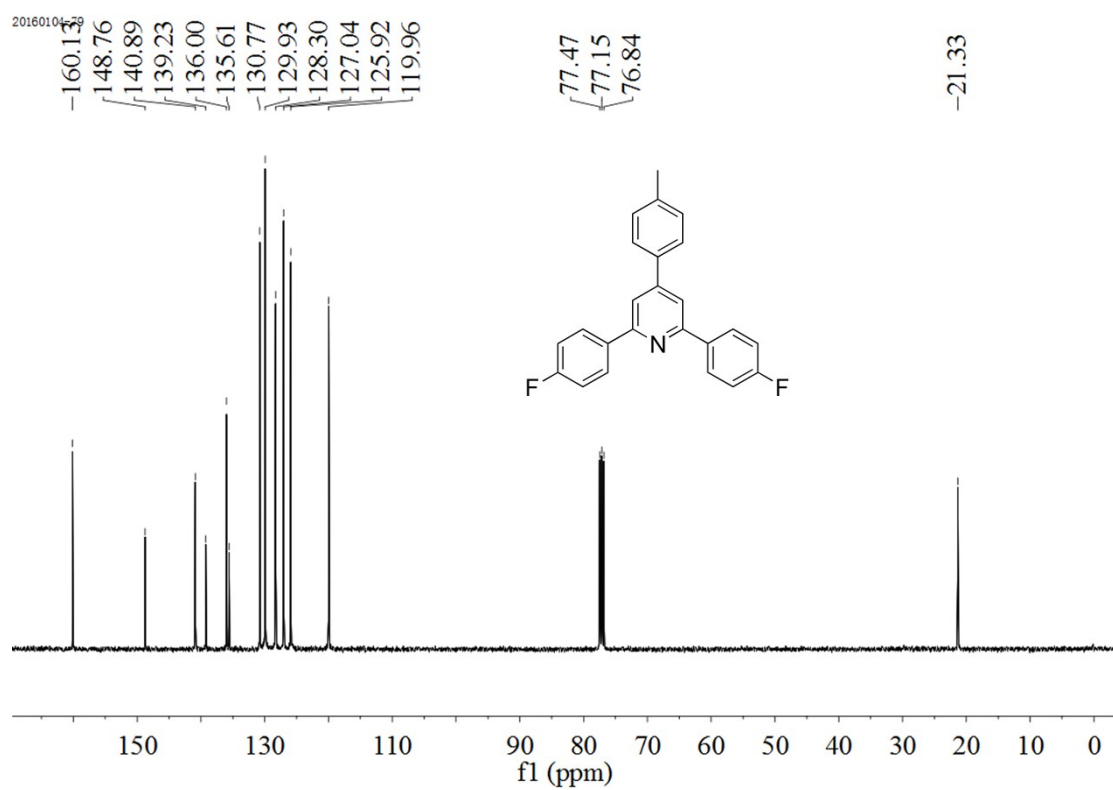
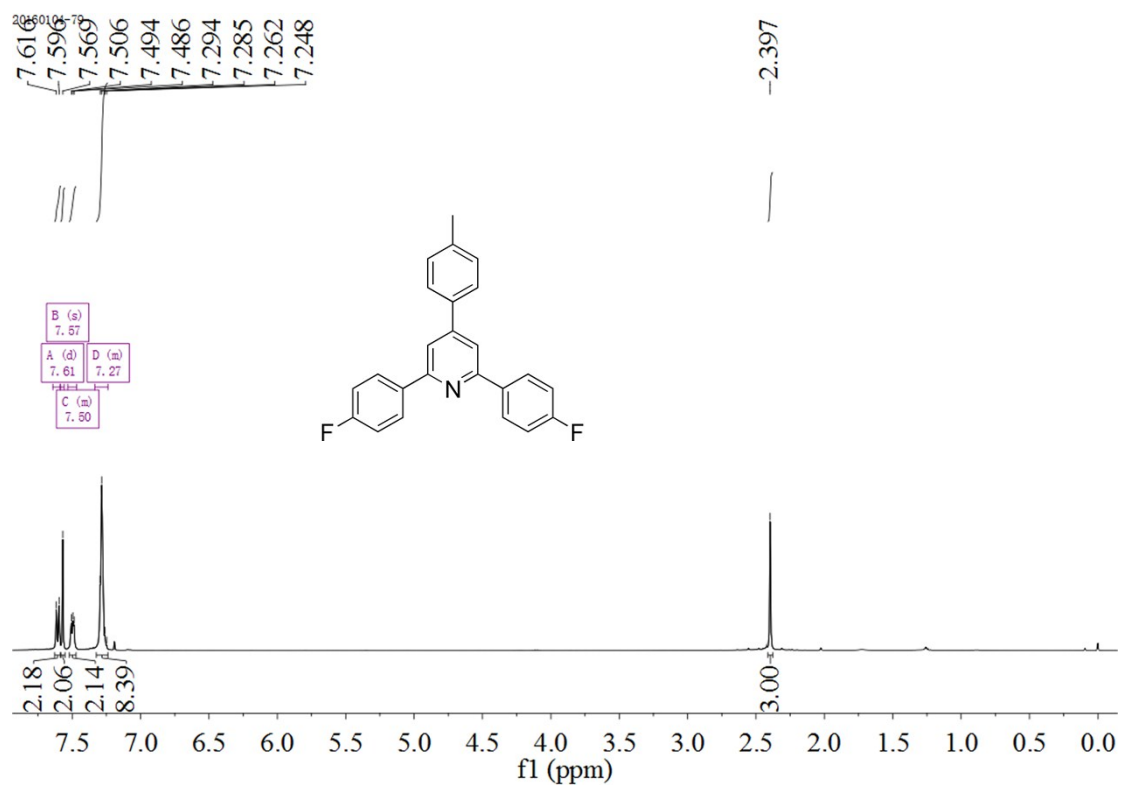




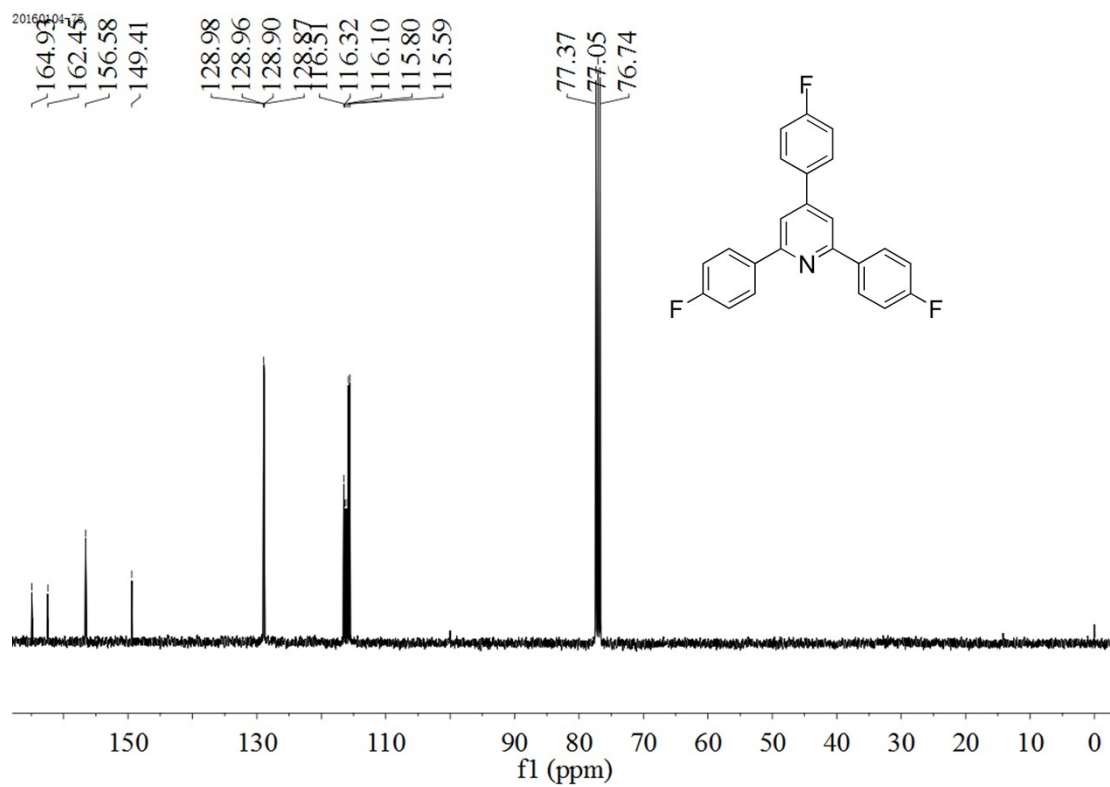
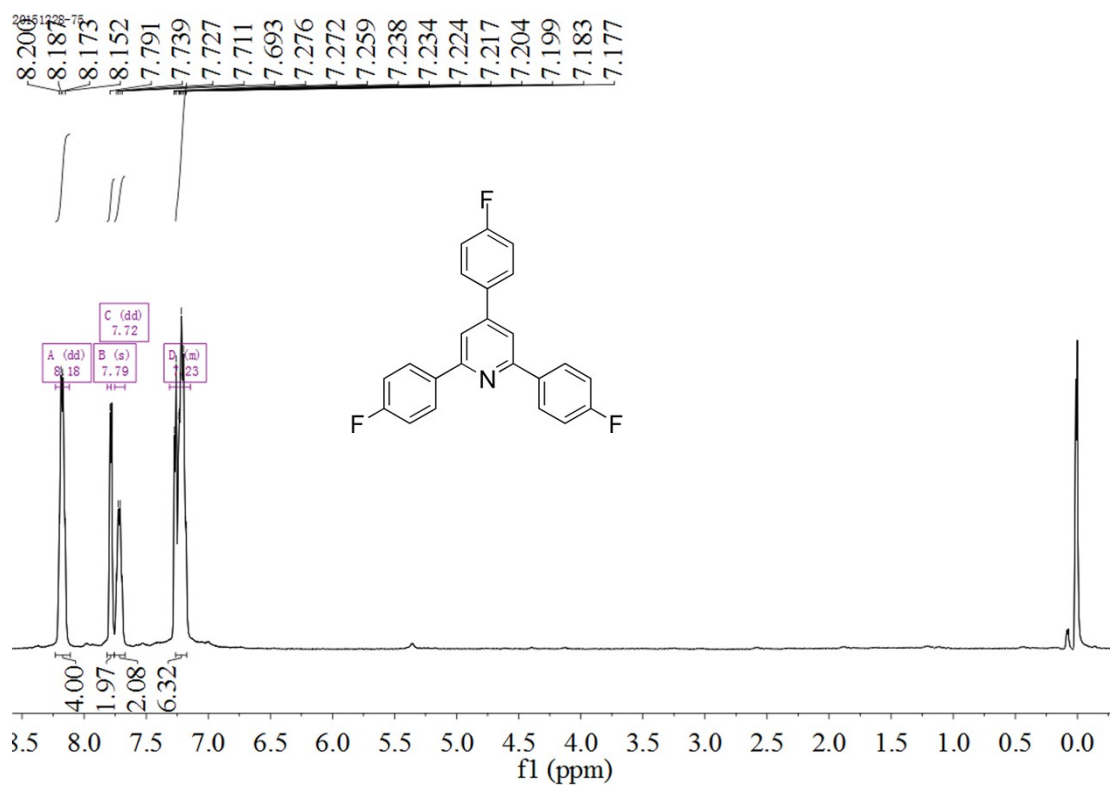
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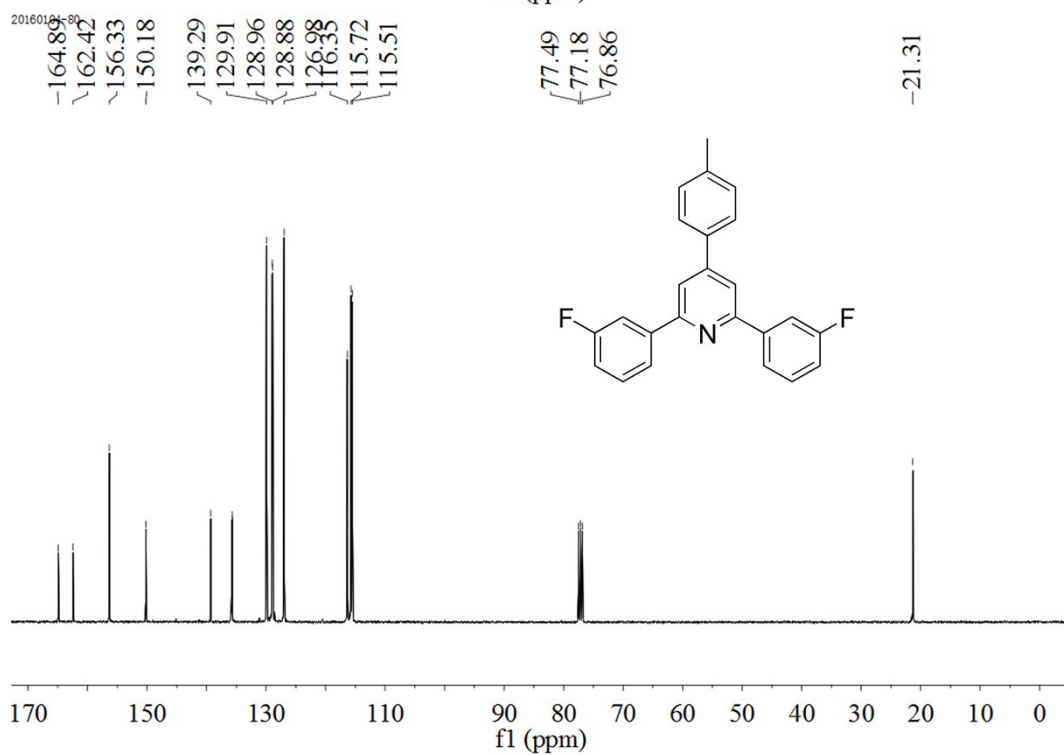
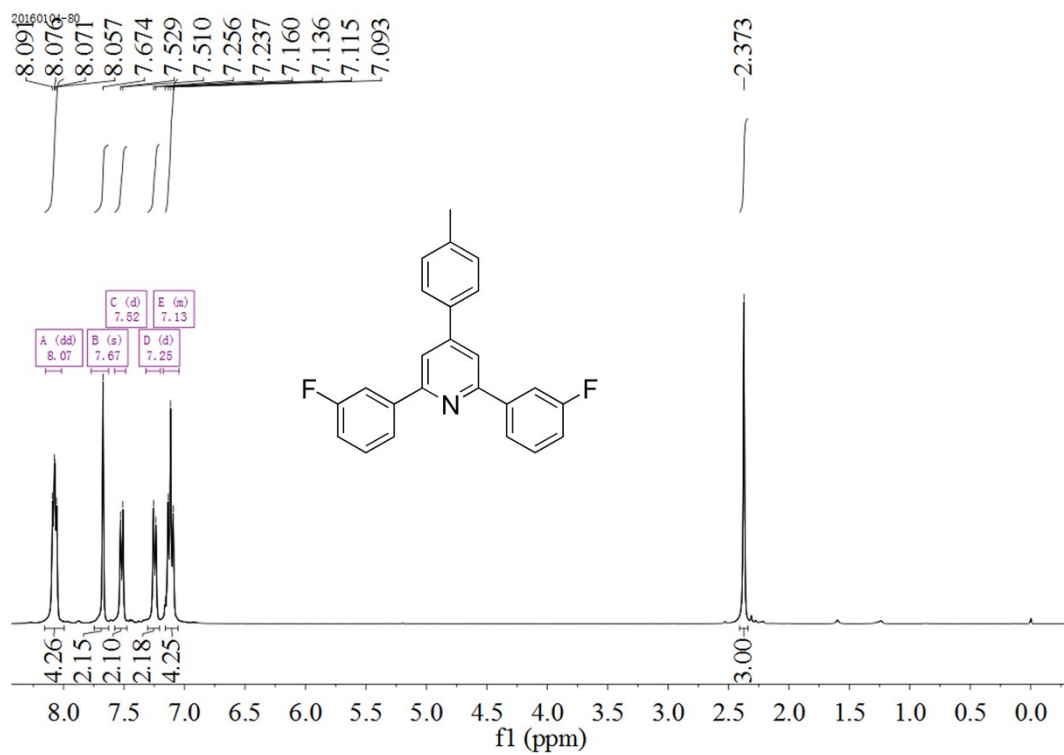
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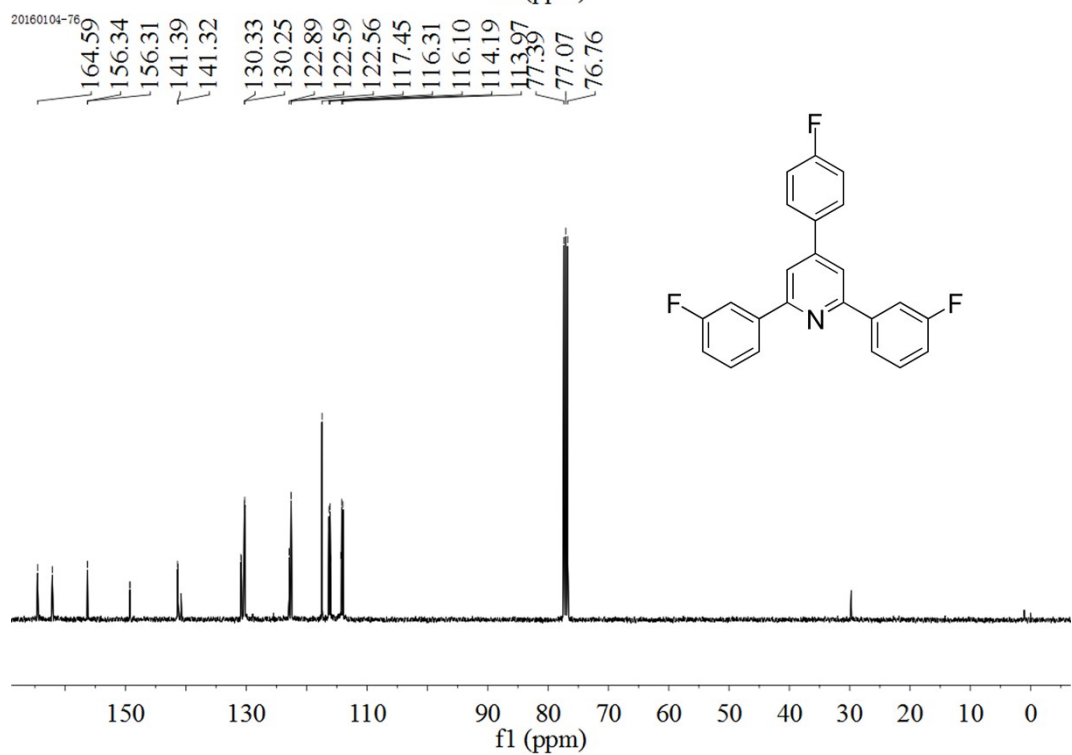
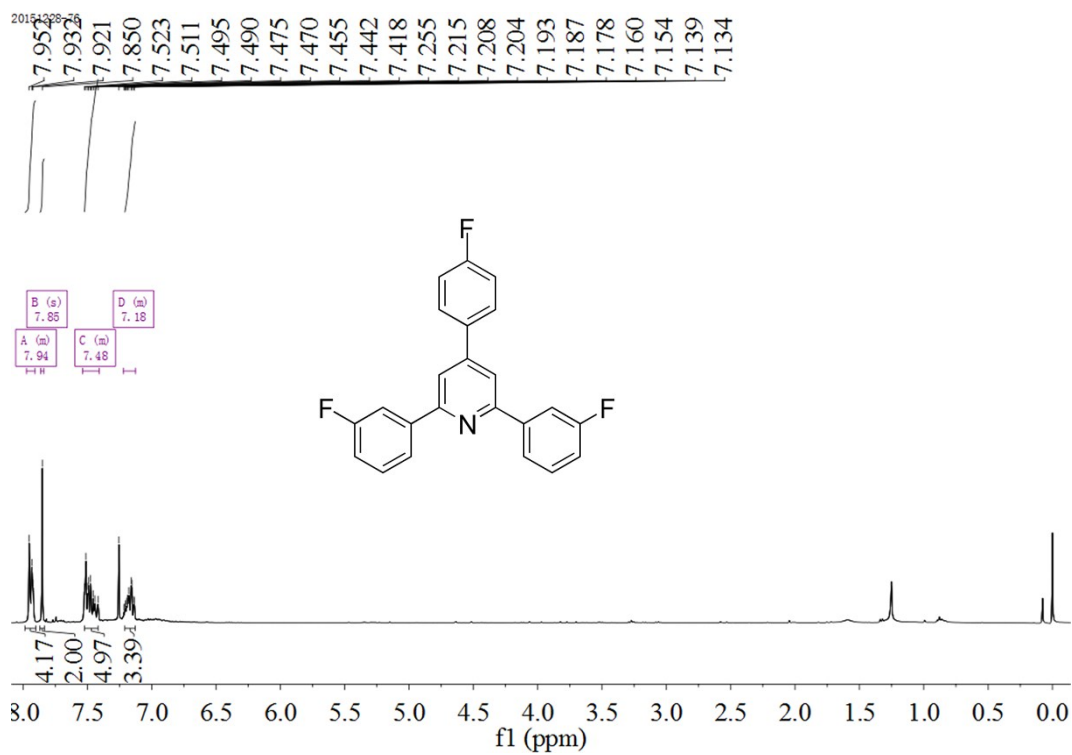
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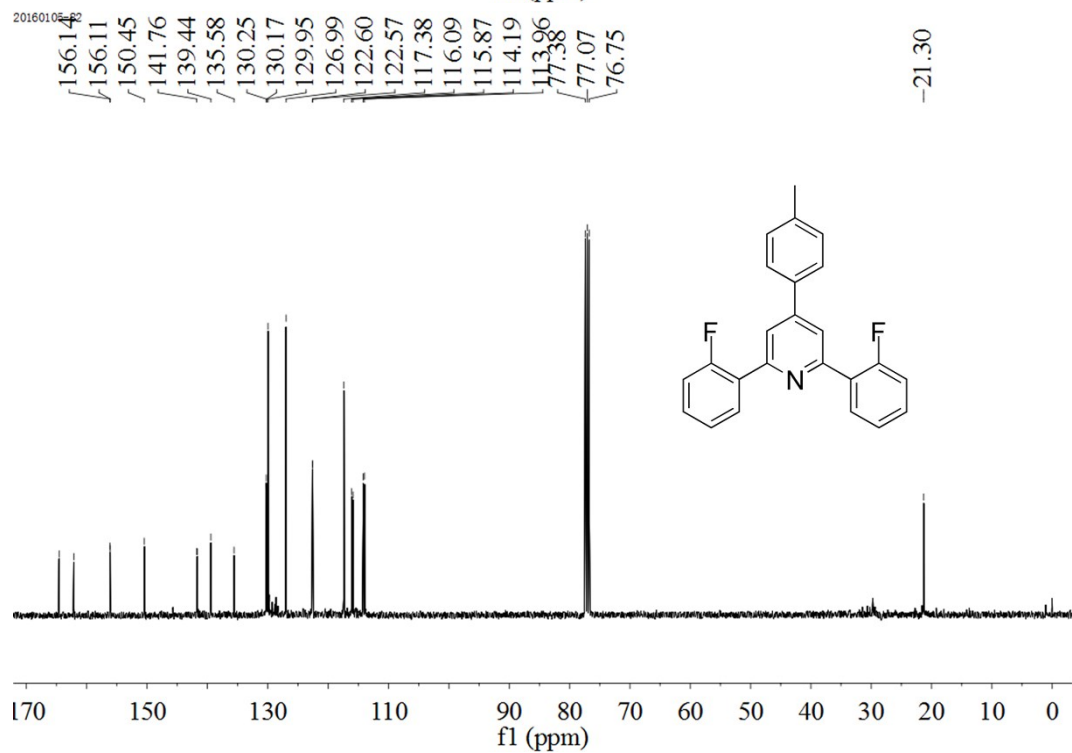
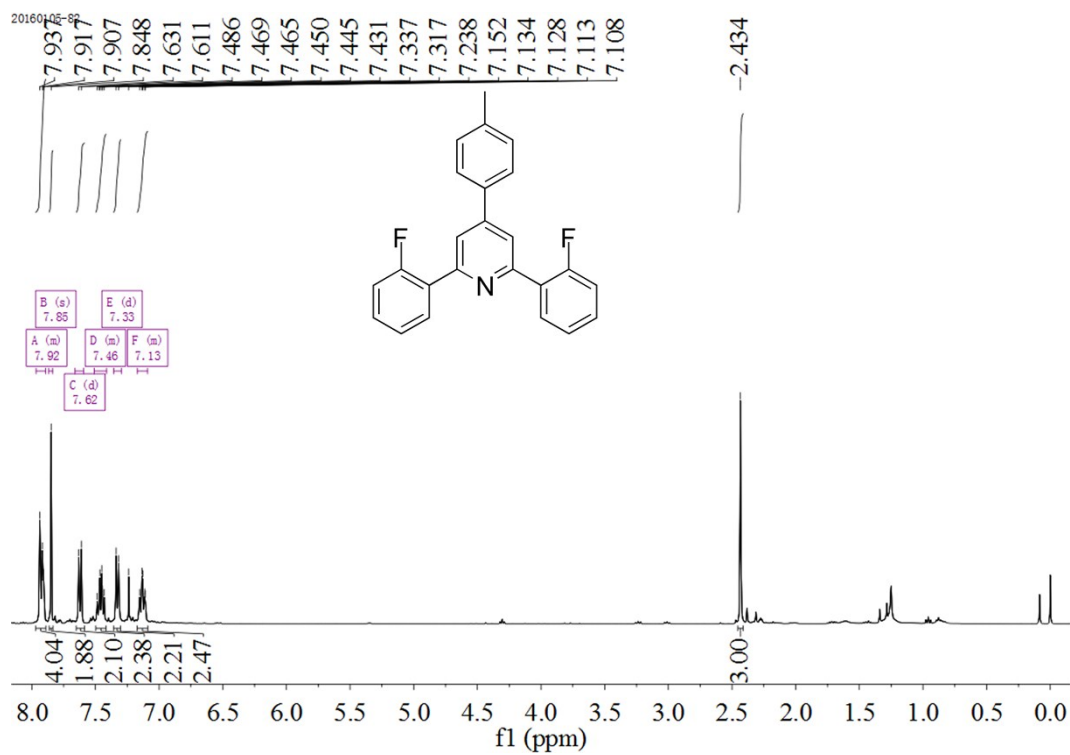
**6c**



6d



6e



6f

