

**Transition-Metal-Free C-C Bond Cleavage and Formation: An  
Efficient Synthesis of 2,3-Disubstituted Imidazo[1,2- $\alpha$ ]pyridines  
from 2-Aminopyridines and Alkynoates**

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## **Supporting Information**

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## A. General method

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on a 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, chloroform is solvent with TMS as the internal standard unless otherwise noted. Mass spectra were recorded on a GC-MS spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). Elemental analyses were performed with a Vario EL elemental analyzer. High-resolution mass spectra (HRMS) were obtained from a JEOL JMS-700 instrument (EI). Silica gel (300-400 mesh) was used for flash column chromatograph, eluting (unless otherwise stated) with ethyl acetate/petroleum ether (PE) (60-90 °C) mixture.

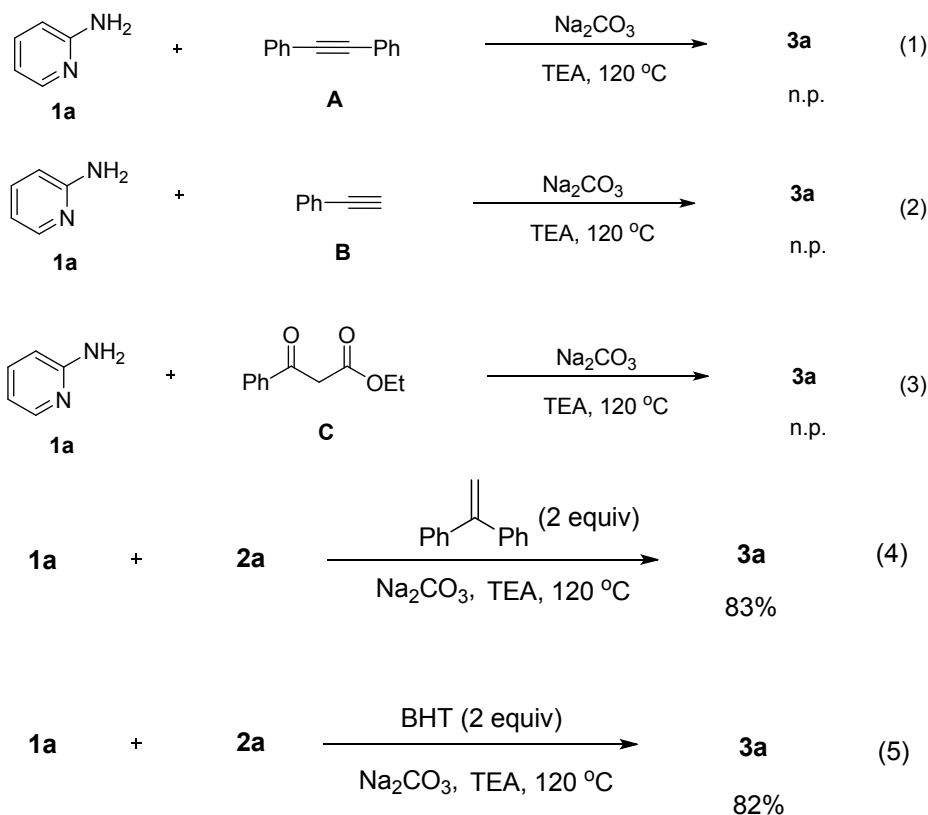
## B. General procedure for the synthesis of alkynoate derivatives

To the mixture of aryl halide (0.25 mmol),  $\text{Pd}(\text{OAc})_2$  (5 mol %) and  $\text{PPh}_3$  (10 mol %) in DMF (1.5 mL) solvent,  $\text{K}_2\text{CO}_3$  (1 mmol) and  $\text{CuI}$  (5 mol %) were added successively, stirred for ten minutes at the room temperature, then slowly added ethyl propiolate (0.375 mmol). Finally, the reaction was stirred at 80 °C about 20 minutes. The solution was extracted with ethyl acetate (3×15 mL), and the combined extract was dried with anhydrous  $\text{MgSO}_4$ . Solvent was removed, and the residue was separated by column chromatography to give the pure sample.

## C. General procedure for the synthesis of Imidazo[1,2- $\alpha$ ]pyridines

A mixture of 2-aminopyridine (0.3 mmol), alkynoate (0.2 mmol) and  $\text{Na}_2\text{CO}_3$  (0.5 equiv) in TEA (1 mL) was placed in a test tube (10 mL) equipped with a magnetic stirring bar. The mixture was stirred at 120 or 140 °C for 20 h. After the reaction was finished, water (5 mL) was added and the solution was extracted with ethyl acetate (3×5 mL), the combined extract was dried with anhydrous  $\text{MgSO}_4$ . Solvent was removed, and the residue was separated by column chromatography to give the pure sample.

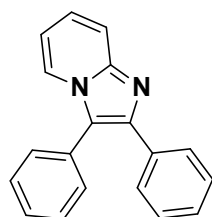
## D. Controlled experiments



Scheme 1. Controlled experiments

## E. Analytical data

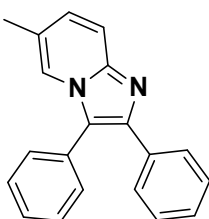
### 2,3-diphenylimidazo[1,2-a]pyridine (3a)<sup>[1]</sup>



Yellow solid; 85 %; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.95 (d, *J* = 5.6 Hz, 1H), 7.68–7.66 (m, 3H), 7.53–7.50 (m, 2H), 7.48–7.44 (m, 3H), 7.29–7.22 (m, 3H), 7.20–7.17 (m, 1H), 6.73–6.70 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 144.8, 142.4, 134.2, 130.7, 129.9, 129.5, 128.8, 128.2, 128.1, 127.4, 124.6, 123.2, 121.0, 117.5, 112.2. MS (EI) *m/z*: 270, 241, 207, 190, 165, 134, 121, 78, 28.

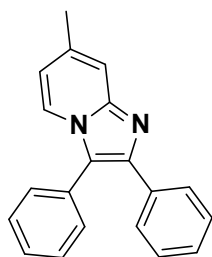
HRMS (ESI): calcd. for C<sub>19</sub>H<sub>15</sub>N<sub>2</sub> [M+H]<sup>+</sup> 271.1235; found 271.1227.

### 6-methyl-2,3-diphenylimidazo[1,2-a]pyridine (3b)<sup>[1]</sup>



Yellow solid; 83 %; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.71 (s, 1H), 7.66–7.64 (m, 2H), 7.58 (d, *J* = 9.2 Hz, 1H), 7.55–7.48 (m, 3H), 7.46–7.44 (m, 2H), 7.29–7.20 (m, 3H), 7.06–7.04 (m, 1H), 2.26 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 143.8, 142.2, 134.3, 130.7, 130.1, 129.5, 128.7, 128.2, 127.9, 127.8, 127.3,

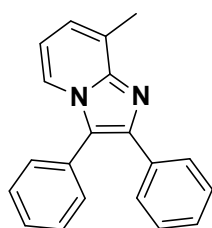
121.9, 120.8, 120.8, 116.8, 18.3. MS (EI) m/z: 284, 268, 220, 207, 165, 142, 91, 77, 28. HRMS (ESI): calcd. for C<sub>20</sub>H<sub>17</sub>N<sub>2</sub> [M+H]<sup>+</sup> 285.1392; found 285.1384.



**7-methyl-2,3-diphenylimidazo[1,2-a]pyridine (3c)<sup>[1]</sup>**

Yellow solid; 84 %; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.83 (d, *J* = 6.8 Hz, 1H), 7.66–7.64 (m, 2H), 7.52–7.46 (m, 3H), 7.44–7.41 (m, 3H), 7.29–7.20 (m, 3H), 6.56–6.54 (m, 1H), 2.40 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 145.2, 142.0, 135.6, 134.3, 130.7, 130.0, 129.4, 128.7, 128.2, 128.0, 127.3, 122.5, 120.5, 115.8, 114.8, 21.3.

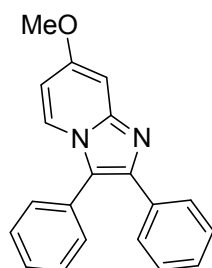
MS (EI) m/z: 284, 268, 220, 207, 165, 142, 91, 77, 28. HRMS (ESI): calcd. for C<sub>20</sub>H<sub>17</sub>N<sub>2</sub> [M+H]<sup>+</sup> 285.1392; found 285.1389.



**8-methyl-2,3-diphenylimidazo[1,2-a]pyridine (3d)<sup>[2]</sup>**

White solid; 61 %; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.85 (d, *J* = 6.8 Hz, 1H), 7.64–7.67 (m, 2H), 7.43–7.52 (m, 6H), 7.21–7.30 (m, 3H), 6.59 (d, *J* = 6.0 Hz, 1H), 2.42 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 144.9, 136.1, 133.8, 130.7, 129.8, 129.5, 128.8, 128.2, 128.0, 127.5, 127.1, 122.5, 120.5, 115.7, 115., 21.3.

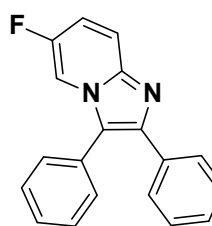
MS (EI) m/z: 284, 268, 220, 207, 165, 142, 91, 77, 28. HRMS (ESI): calcd. for C<sub>20</sub>H<sub>17</sub>N<sub>2</sub> [M+H]<sup>+</sup> 285.1389; found 285.1386.



**7-methoxy-2,3-diphenylimidazo[1,2-a]pyridine (3e)**

White solid; 49 %; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.77 (s, 1H), 7.61–7.63 (m, 2H), 7.41–7.50 (m, 5H), 7.25–7.27 (m, 3H), 6.48 (s, 1H), 7.03 (s, 1H), 3.89 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 158.3, 146.0, 141.0, 133.7, 130.7, 129.6, 129.5, 128.8, 128.2, 127.8, 127.4, 123.8, 120.0, 107.5, 94.4, 55.6.

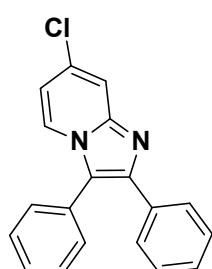
MS (EI) m/z: 300, 269, 220, 207, 190, 165, 134, 121, 78, 28. Anal. Calcd for C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O: C, 79.98; H, 5.37; N, 9.33. Found: C, 74.64; H, 5.28; N, 9.47.



**6-fluoro-2,3-diphenylimidazo[1,2-a]pyridine (3f)**

Yellow solid; 75 %; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.89–7.87 (m, 1H), 7.68–7.63 (m, 3H), 7.56–7.50 (m, 3H), 7.45–7.43 (m, 2H), 7.30–7.25 (m, 3H), 7.15–7.10 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 153.4 (d, *J* = 236 Hz), 143.7, 142.4, 133.7, 130.4, 129.7, 129.3, 129.2, 128.3, 128.0, 127.7, 122.4, 118.0 (d, *J* = 9.0 Hz), 116.7 (d, *J* = 26.0 Hz), 109.9 (d, *J* = 42.0 Hz).

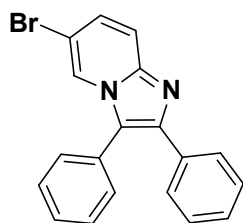
MS (EI) m/z: 288, 190, 165, 143, 130, 96, 76, 63. Anal. Calcd for C<sub>19</sub>H<sub>13</sub>FN<sub>2</sub>: C, 79.15; H, 4.54; N, 9.72. Found: C, 78.96; H, 4.47; N, 9.90.



**7-chloro-2,3-diphenylimidazo[1,2-a]pyridine (3g)<sup>[1]</sup>**

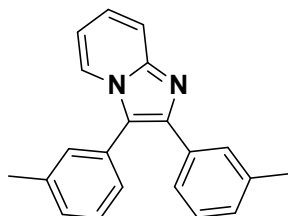
Yellow solid; 50 %; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.86 (d, *J* = 7.2 Hz, 1H), 7.68–7.62 (m, 3H), 7.56–7.49 (m, 3H), 7.44–7.42 (m, 2H), 7.30–7.23 (m, 3H), 6.73–6.71 (m, 1H). <sup>13</sup>C NMR (100 MHz,

CDCl<sub>3</sub>)  $\delta$  = 144.4, 143.1, 133.6, 131.1, 130.6, 129.6, 129.2, 129.1, 128.3, 128.0, 127.7, 123.6, 121.2, 116.2, 113.8. MS (EI) *m/z*: 304, 281, 268, 207, 165, 152, 133, 91, 43, 28. Anal. Calcd for C<sub>19</sub>H<sub>13</sub>ClN<sub>2</sub>: C, 74.88; H, 4.30; N, 9.19. Found: C, 74.71; H, 4.22; N, 9.34.



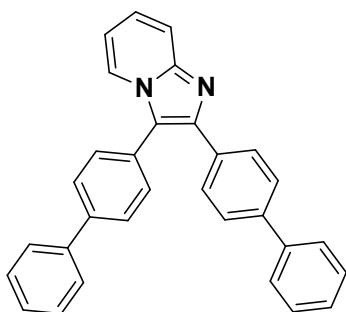
### 6-bromo-2,3-diphenylimidazo[1,2-a]pyridine (3h)<sup>[3]</sup>

Yellow solid; 38 %; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.05 (t, *J* = 0.8 Hz, 1H), 7.65–7.63 (m, 2H), 7.61–7.52 (m, 4H), 7.45–7.43 (m, 2H), 7.29–7.25 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 143.1, 143.0, 133.4, 130.6, 129.7, 129.3, 129.1, 128.3, 128.1, 128.0, 127.8, 123.3, 121.4, 118.1, 107.2. MS (EI) *m/z*: 348, 267, 220, 207, 191, 165, 134, 91, 63, 28. Anal. Calcd for C<sub>19</sub>H<sub>13</sub>BrN<sub>2</sub>: C, 65.35; H, 3.75; N, 8.02. Found: C, 65.19; H, 3.68; N, 8.20.



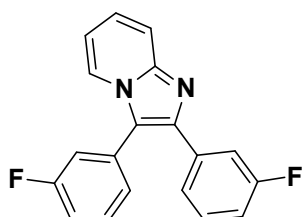
### 2,3-di-*m*-tolylimidazo[1,2-a]pyridine (3i)

Yellow solid; 79 %; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.93 (d, *J* = 6.8 Hz, 1H), 7.67 (d, *J* = 9.2 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.33–7.23 (m, 4H), 7.20–7.16 (m, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.71 (t, *J* = 6.4 Hz, 1H), 2.40 (s, 3H), 2.32 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 144.6, 142.2, 139.2, 137.9, 134.0, 131.1, 129.8, 129.6, 129.3, 128.7, 128.2, 128.0, 127.8, 125.0, 124.5, 123.3, 121.2, 117.4, 112.1, 21.4, 21.4. MS (EI) *m/z*: 298, 282, 207, 190, 178, 141, 128, 91, 28. HRMS (ESI): calcd. for C<sub>21</sub>H<sub>19</sub>N<sub>2</sub> [M+H]<sup>+</sup> 299.1548; found 299.1540.



### 2,3-di([1,1'-biphenyl]-4-yl)imidazo[1,2-a]pyridine (3j)

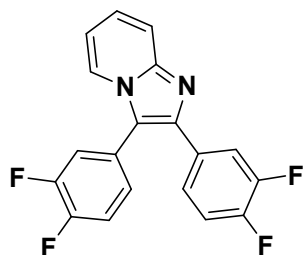
Yellow solid; 82 %; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.04 (d, *J* = 6.8 Hz, 1H), 7.82–7.77 (m, 4H), 7.73–7.69 (m, 3H), 7.62–7.56 (m, 6H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.44–7.39 (m, 3H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.26–7.21 (m, 1H), 6.76 (t, *J* = 6.8 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 144.9, 142.1, 141.6, 140.7, 140.2, 140.1, 133.1, 131.1, 128.9, 128.7, 128.4, 128.2, 127.8, 127.2, 127.1, 127.0, 126.9, 124.8, 123.3, 120.8, 117.5, 112.4, 99.9. HRMS (ESI): calcd. for C<sub>31</sub>H<sub>23</sub>N<sub>2</sub> [M+H]<sup>+</sup> 423.1861; found 423.1848.



### 2,3-bis(3-fluorophenyl)imidazo[1,2-a]pyridine (3k)

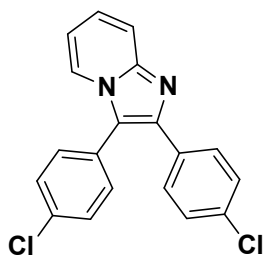
Yellow solid; 81 %; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.95 (d, *J* = 6.8 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.55–7.50 (m, 1H), 7.41–7.38 (m, 2H), 7.28–7.16 (m, 5H), 6.98–6.93 (m, 1H), 6.79 (t, *J* = 6.8 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 163.3 (d, *J* = 247.0 Hz), 162.8 (d, *J* = 243.0 Hz), 144.9, 141.5, 136.1 (d, *J* = 8.0 Hz), 131.5 (d, *J* = 8.0 Hz), 131.3 (d, *J* = 8.0 Hz), 129.8 (d, *J* = 8.0 Hz), 126.5 (d, *J* = 3.0 Hz), 125.3, 123.68 (d, *J* = 2 Hz), 123.2, 120.0, 117.7, 117.5

(d,  $J = 21.6$  Hz), 116.2 (d,  $J = 21.0$  Hz), 114.8 (d,  $J = 22$  Hz), 114.5 (d,  $J = 21$  Hz), 112.8. MS (EI)  $m/z$ : 306, 284, 201, 143, 133, 78, 28. Anal. Calcd for  $C_{19}H_{12}F_2N_2$ : C, 74.50; H, 3.95; N, 9.15. Found: C, 74.28; H, 3.87; N, 9.31.



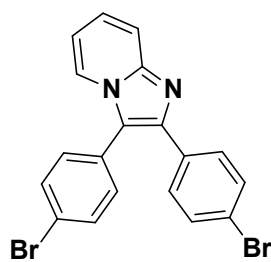
### 2,3-bis(3,4-difluorophenyl)imidazo[1,2-a]pyridine (3l)

Yellow solid; 80 %;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta = 7.88$  (d,  $J = 6.8$  Hz, 1H), 7.67–7.64 (m, 2H), 7.29–7.21 (m, 5H), 6.97 (t,  $J = 4.4$  Hz, 1H), 6.77 (t,  $J = 6.8$  Hz, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta = 150.7$  (dd,  $J = 249.0, 74.0$  Hz), 150.6 (dd,  $J = 249.0, 74.0$  Hz), 150.5 (dd,  $J = 249.0, 74.0$  Hz), 150.4 (dd,  $J = 249.0, 74.0$  Hz), 144.9, 140.9, 130.89 (dd,  $J = 7.0, 3.0$  Hz), 127.35 (dd,  $J = 7.0, 3.0$  Hz), 126.2 (dd,  $J = 7.0, 3.0$  Hz), 125.4, 123.97 (dd,  $J = 7.0, 3.0$  Hz), 123.0, 119.8 (d,  $J = 18.0$  Hz), 119.0, 118.8, 117.7, 117.2 (d,  $J = 17.0$  Hz), 116.9 (d,  $J = 18.0$  Hz), 112.97. MS (EI)  $m/z$ : 342, 320, 237, 161, 146, 78, 51, 28. HRMS (ESI): calcd. for  $C_{19}H_{11}F_4N_2$   $[M+H]^+$  343.0858; found 343.0852.



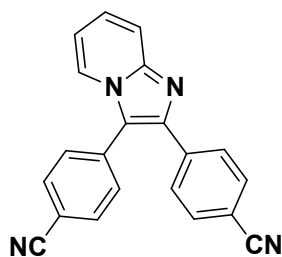
### 2,3-bis(4-chlorophenyl)imidazo[1,2-a]pyridine (3m)

Yellow solid; 78 %;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta = 7.93$  (d,  $J = 7.2$  Hz, 1H), 7.71 (d,  $J = 9.2$  Hz, 1H), 7.59–7.52 (m, 4H), 7.38 (d,  $J = 8.0$  Hz, 2H), 7.29–7.23 (m, 3H), 6.79 (t,  $J = 6.8$  Hz, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta = 145.0, 141.6, 135.1, 133.6, 132.3, 131.9, 130.0, 129.3, 128.6, 127.9, 125.2, 123.0, 119.8, 117.6, 112.7$ . MS (EI)  $m/z$ : 338, 302, 266, 220, 207, 151, 134, 91, 43, 28. HRMS (ESI): calcd. for  $C_{19}H_{13}Cl_2N_2$   $[M+H]^+$  339.0456; found 339.0444.



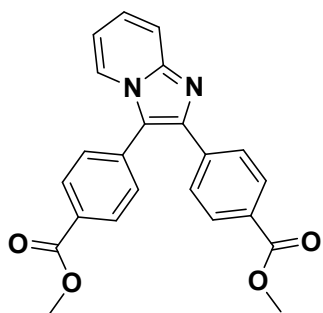
### 2,3-bis(4-bromophenyl)imidazo[1,2-a]pyridine (3n)

Yellow solid; 72 %;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta = 7.93$  (d,  $J = 6.9$  Hz, 1H), 7.72–7.67 (m, 3H), 7.51 (d,  $J = 8.4$  Hz, 2H), 7.43 (d,  $J = 8.4$  Hz, 2H), 7.32 (d,  $J = 8.4$  Hz, 2H), 7.28–7.24 (m, 1H), 6.80 (t,  $J = 6.7$  Hz, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta = 144.9, 141.5, 133.0, 132.7, 132.2, 131.5, 129.6, 128.4, 125.3, 123.4, 123.0, 121.9, 119.9, 117.6, 112.8$ . HRMS (ESI): calcd. for  $C_{19}H_{13}Br_2N_2$   $[M+H]^+$  426.9445; found 426.9435.



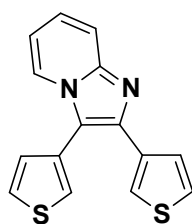
### 4,4'-(imidazo[1,2-a]pyridine-2,3-diyl)dibenzonitrile (3o)

Yellow solid; 75 %;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta = 7.98$  (d,  $J = 6.8$  Hz, 1H), 7.84 (d,  $J = 8.3$  Hz, 2H), 7.72–7.68 (m, 3H), 7.58 (d,  $J = 8.4$  Hz, 4H), 7.33–7.29 (m, 1H), 6.87–6.84 (m, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta = 145.6, 141.6, 138.2, 133.9, 133.5, 132.3, 131.1, 128.6, 126.2, 122.9, 120.2, 118.7, 118.1, 118.1, 113.6, 113.0, 111.4$ . HRMS (ESI): calcd. for  $C_{21}H_{13}N_4$   $[M+H]^+$  321.1140; found 321.1123.



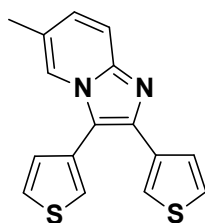
**dimethyl 4,4'-(imidazo[1,2-a]pyridine-2,3-diyl)dibenzoate (3p)**

Yellow solid; 65 %;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.20 (d,  $J$  = 8.0 Hz, 2H), 8.03–7.95 (m, 3H), 7.71 (t,  $J$  = 8.4 Hz, 3H), 7.54 (d,  $J$  = 8.4 Hz, 2H), 7.28 (t,  $J$  = 6.8 Hz, 1H), 6.82 (t,  $J$  = 6.8 Hz, 1H), 3.98 (s, 3H), 3.90 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 166.9, 166.4, 145.3, 142.0, 138.3, 134.0, 130.8, 130.5, 130.4, 129.7, 129.1, 128.0, 125.5, 123.2, 120.9, 117.9, 113.0, 52.4, 52.1. MS (EI)  $m/z$ : 386, 371, 356, 312, 268, 240, 207, 134, 77, 55. Anal. Calcd for  $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_4$ : C, 71.49; H, 4.70; N, 7.25. Found: C, 71.28; H, 4.65; N, 7.42.



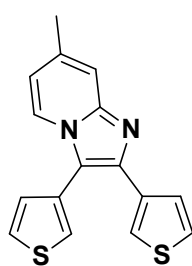
**2,3-di(thiophen-3-yl)imidazo[1,2-a]pyridine (3q)**

Yellow solid; 83 %;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.88 (d,  $J$  = 6.8 Hz, 1H), 7.68–7.65 (m, 2H), 7.31–7.22 (m, 5H), 6.99–6.97 (m, 1H), 6.80–6.77 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 145.2, 140.0, 137.0, 131.2, 129.5, 128.7, 128.2, 127.4, 125.7, 125.4, 125.1, 123.8, 117.1, 112.6, 112.0. MS (EI)  $m/z$ : 282, 237, 207, 177, 140, 119, 78, 28. HRMS (ESI): calcd. for  $\text{C}_{15}\text{H}_{11}\text{N}_2\text{S}_2$   $[\text{M}+\text{H}]^+$  283.0364; found 283.0355.



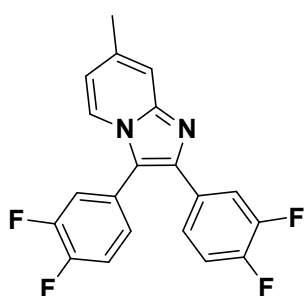
**6-methyl-2,3-di(thiophen-3-yl)imidazo[1,2-a]pyridine (3r)**

Yellow solid; 80 %;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.66–7.63 (m, 2H), 7.54 (d,  $J$  = 9.2 Hz, 1H), 7.30–7.26 (m, 2H), 7.23 (d,  $J$  = 5.2 Hz, 1H), 7.18 (d,  $J$  = 3.6 Hz, 1H), 7.07–7.05 (m, 1H), 6.96–6.94 (m, 1H), 2.26 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 144.3, 139.8, 137.3, 131.1, 129.5, 129.0, 128.5, 128.2, 127.4, 125.4, 124.7, 122.4, 121.5, 116.4, 111.6, 18.2. MS (EI)  $m/z$ : 296, 281, 251, 207, 177, 147, 126, 69, 28. HRMS (ESI): calcd. for  $\text{C}_{16}\text{H}_{13}\text{N}_2\text{S}_2$   $[\text{M}+\text{H}]^+$  297.0520; found 297.0509.



**7-methyl-2,3-di(thiophen-3-yl)imidazo[1,2-a]pyridine (3s)**

Yellow solid; 81 %;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.74 (d,  $J$  = 7.2 Hz, 1H), 7.64–7.62 (m, 1H), 7.39 (s, 1H), 7.27–7.21 (m, 4H), 6.96–6.94 (m, 1H), 6.60–6.58 (m, 1H), 2.39 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 145.6, 139.6, 137.2, 136.5, 131.1, 129.4, 128.9, 128.2, 127.4, 125.5, 124.9, 123.0, 115.5, 115.2, 111.4, 21.3. MS (EI)  $m/z$ : 296, 281, 251, 220, 207, 148, 126, 91, 69, 28. HRMS (ESI): calcd. for  $\text{C}_{16}\text{H}_{13}\text{N}_2\text{S}_2$   $[\text{M}+\text{H}]^+$  297.0520; found 297.0512.



**2,3-bis(3,4-difluorophenyl)-7-methylimidazo[1,2-a]pyridine (3t)**

Yellow solid; 84 %;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.78 (d,  $J$  = 7.2 Hz, 1H), 7.50–7.43 (m, 2H), 7.39–7.24 (m, 3H), 7.19–7.16 (m, 1H), 7.11–7.04 (m, 1H), 6.65 (d,  $J$  = 6.8 Hz, 1H), 2.43 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 150.7

(dd,  $J = 250.0, 74.0$  Hz), 150.5 (dd,  $J = 250.0, 74.0$  Hz), 150.4 (dd,  $J = 250.0, 74.0$  Hz), 150.3 (dd,  $J = 250.0, 74.0$  Hz), 145.3, 140.4, 136.7, 130.9 (d,  $J = 3$  Hz), 127.3 (dd,  $J = 7.0, 3.0$  Hz), 126.2 (dd,  $J = 7.0, 3.0$  Hz), 123.94 (dd,  $J = 7.0, 3.0$  Hz), 122.2, 119.7 (d,  $J = 17.0$  Hz), 118.9 (d,  $J = 18.0$  Hz), 118.3, 117.2 (d,  $J = 18.0$  Hz), 116.8 (d,  $J = 19.0$  Hz), 115.9, 115.7, 21.3. MS (EI)  $m/z$ : 356, 340, 237, 178, 168, 153, 65, 28. Anal. Calcd for  $C_{20}H_{12}F_4N_2$ : C, 67.42; H, 3.39; N, 7.86. Found: C, 67.25; H, 3.32; N, 7.98.

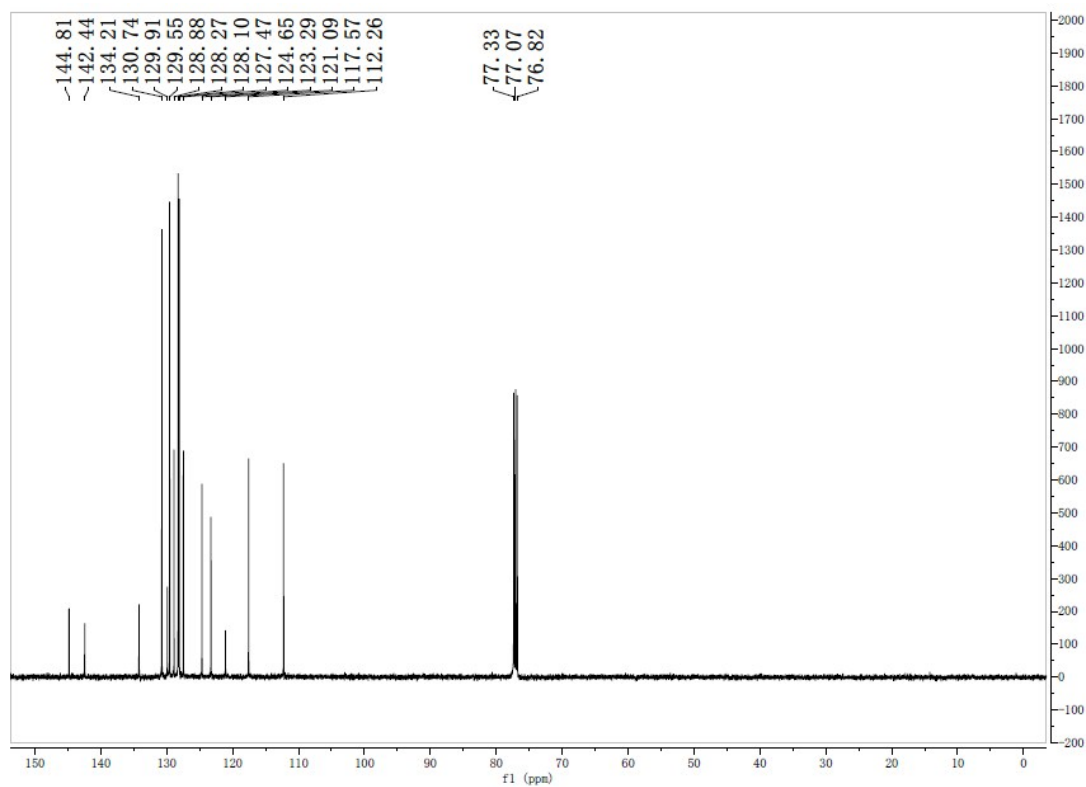
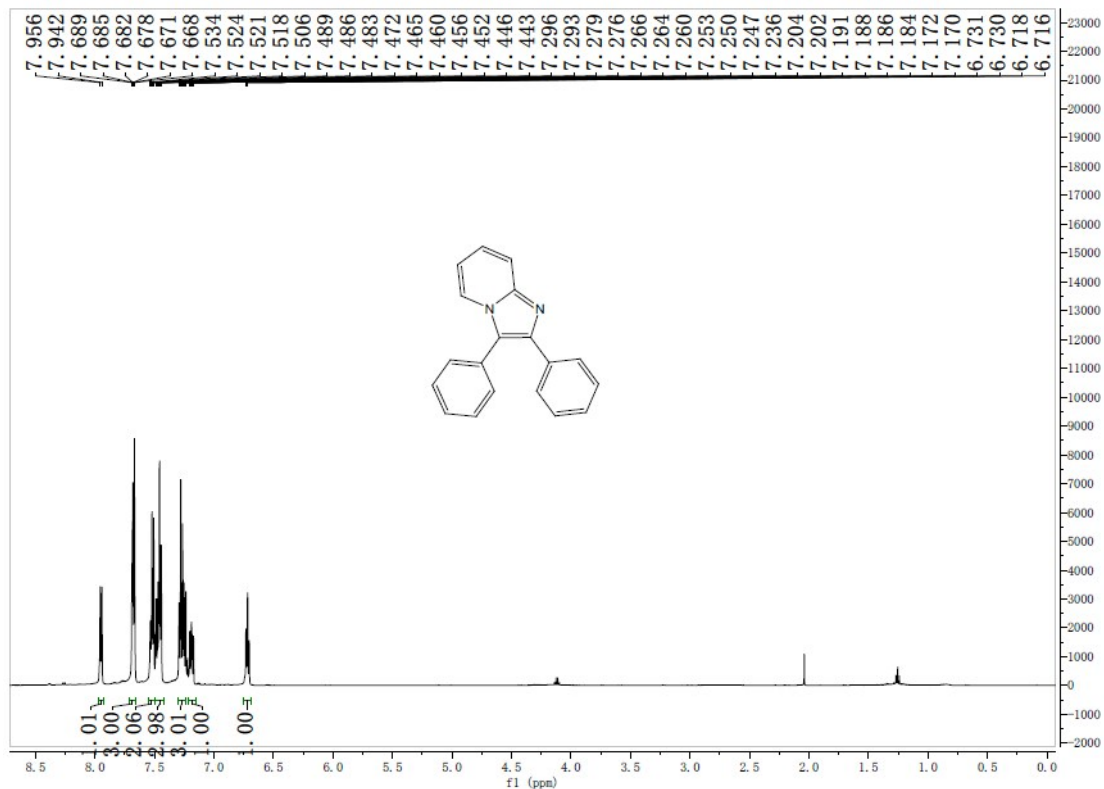
## F. Reference

- [1] Hiebel, M.-A.; Fall, Y.; Scherrmann, M.-C.; Berteina-Raboin, S. *Eur. J. Org. Chem.* **2014**, 4643-4650.
- [2] Samanta, S.; Jana, S.; Mondal, S.; Monir, K.; Chandra, S. K.; Hajra, A. *Org. Biomol. Chem.* **2016**, *14*, 5073.
- [3] Yin, L.; Erdmann, F.; Liebscher, J. *J. Heterocyclic Chem.* **2005**, *42*, 1369-1379.

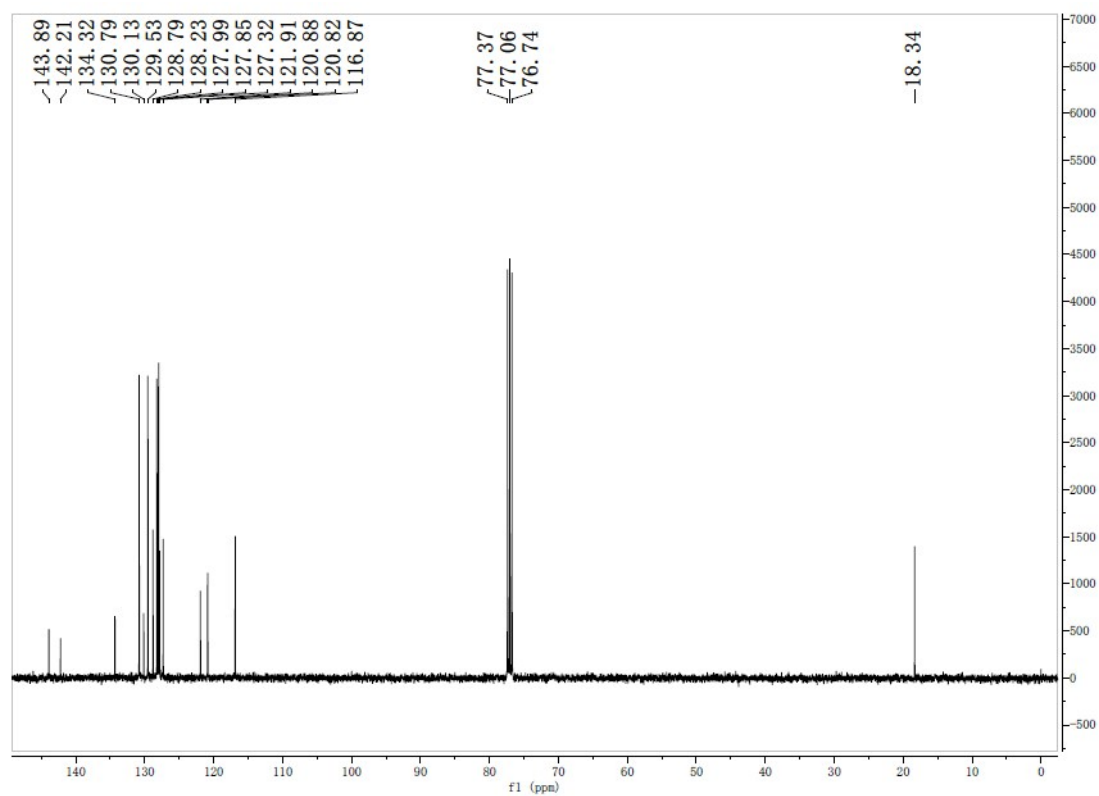
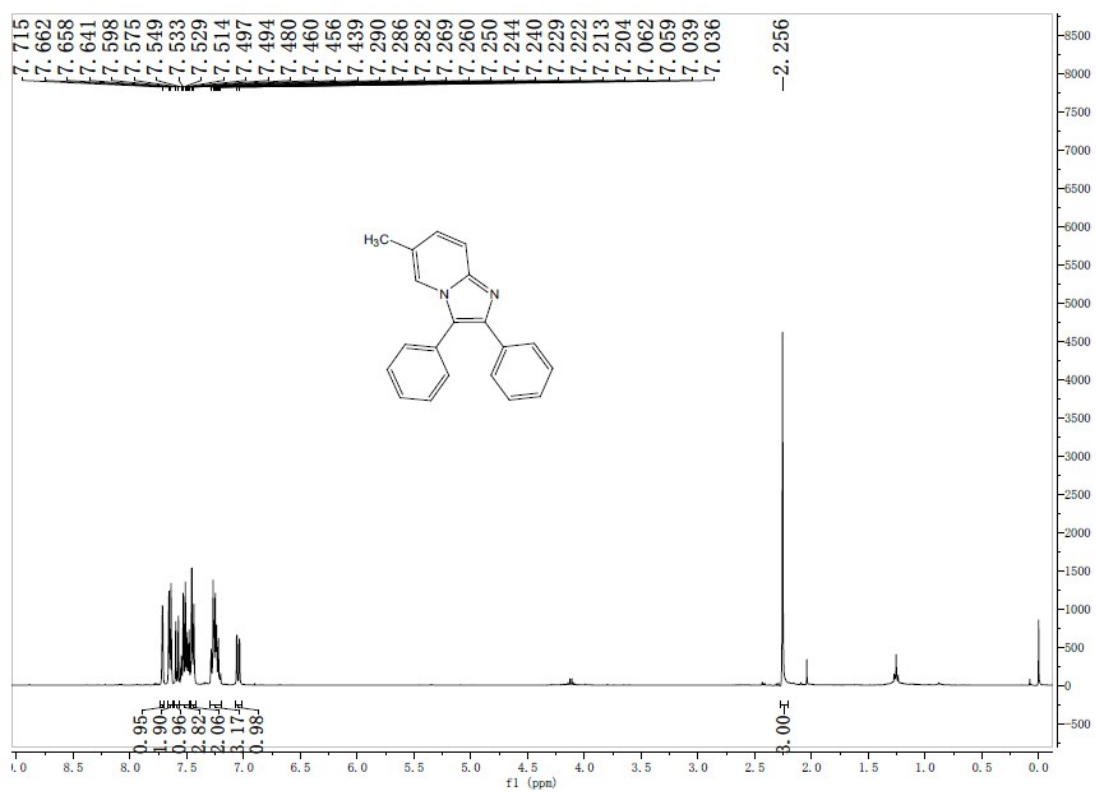


## G. NMR Spectra

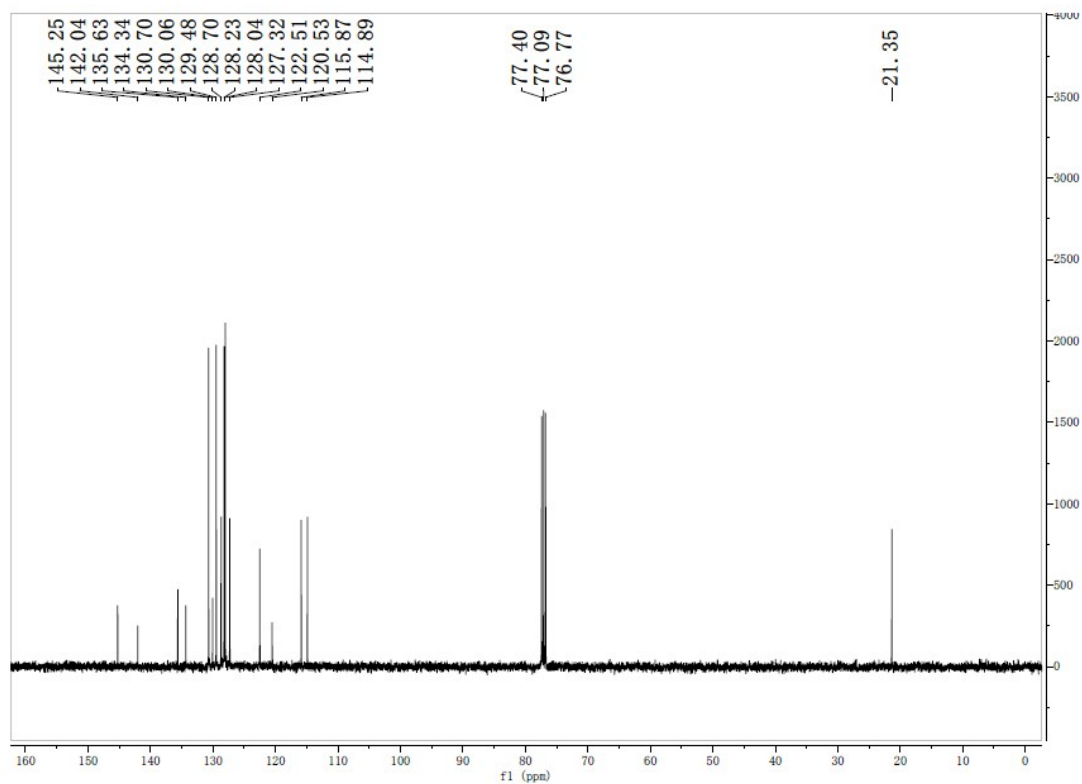
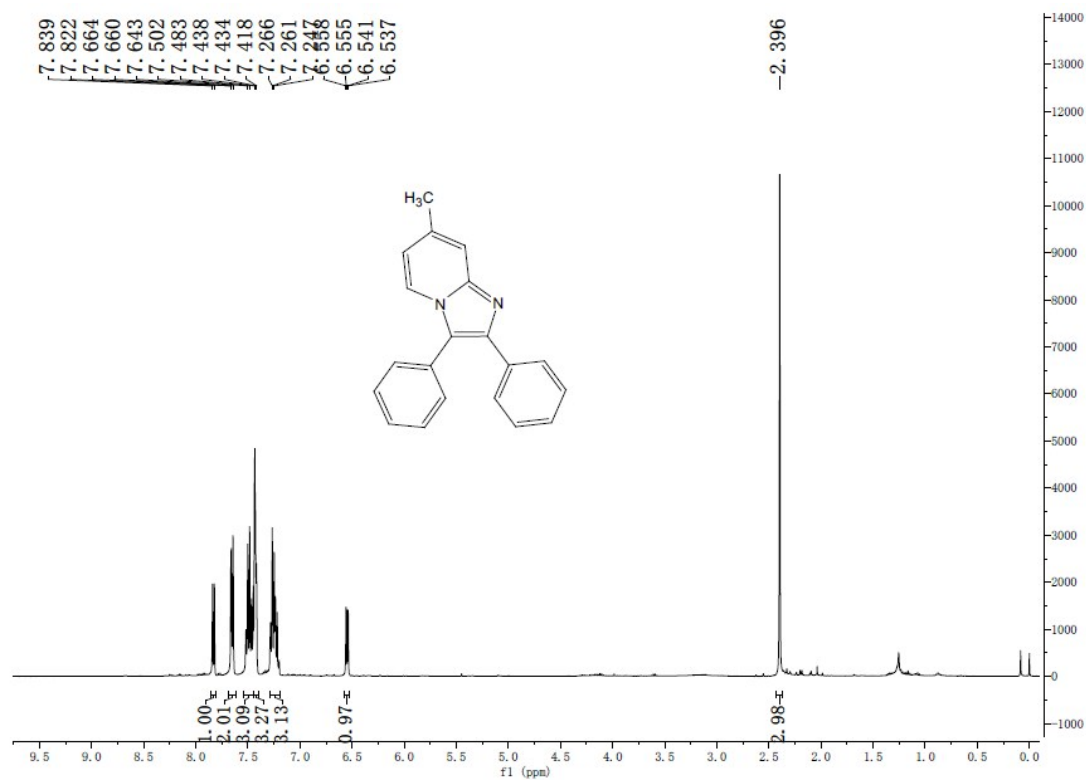
### $^1\text{H}$ NMR and $^{13}\text{C}$ NMR of 2,3-diphenylimidazo[1,2-a]pyridine



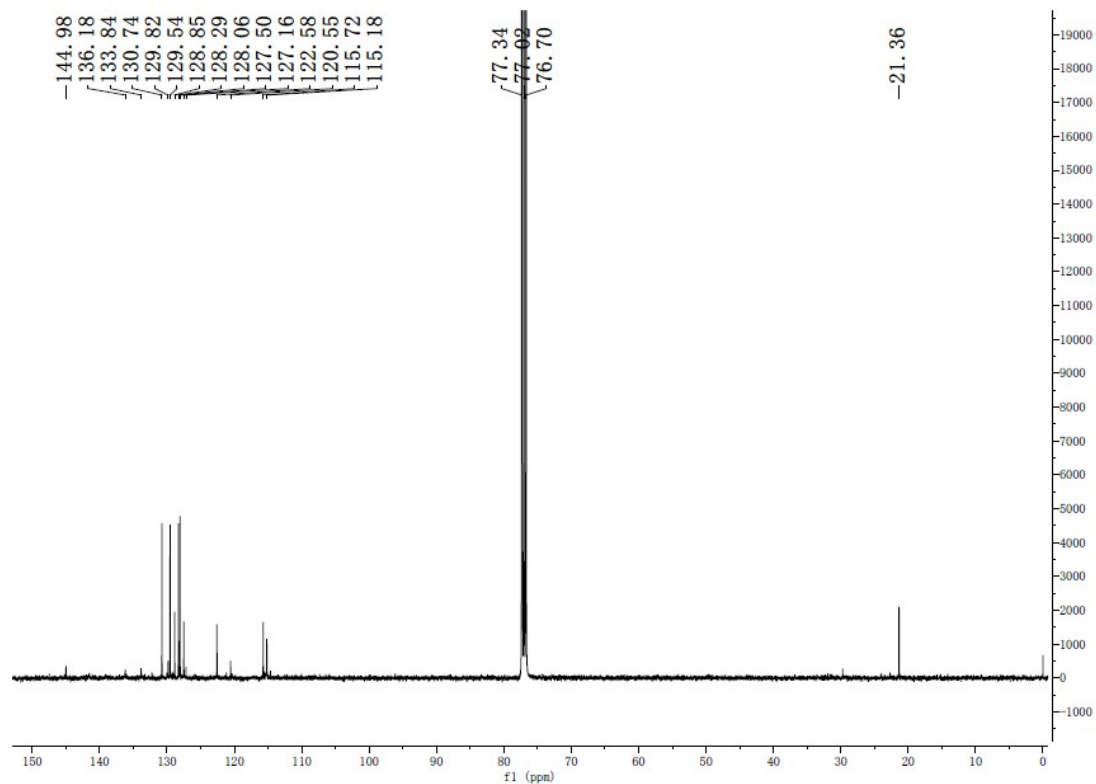
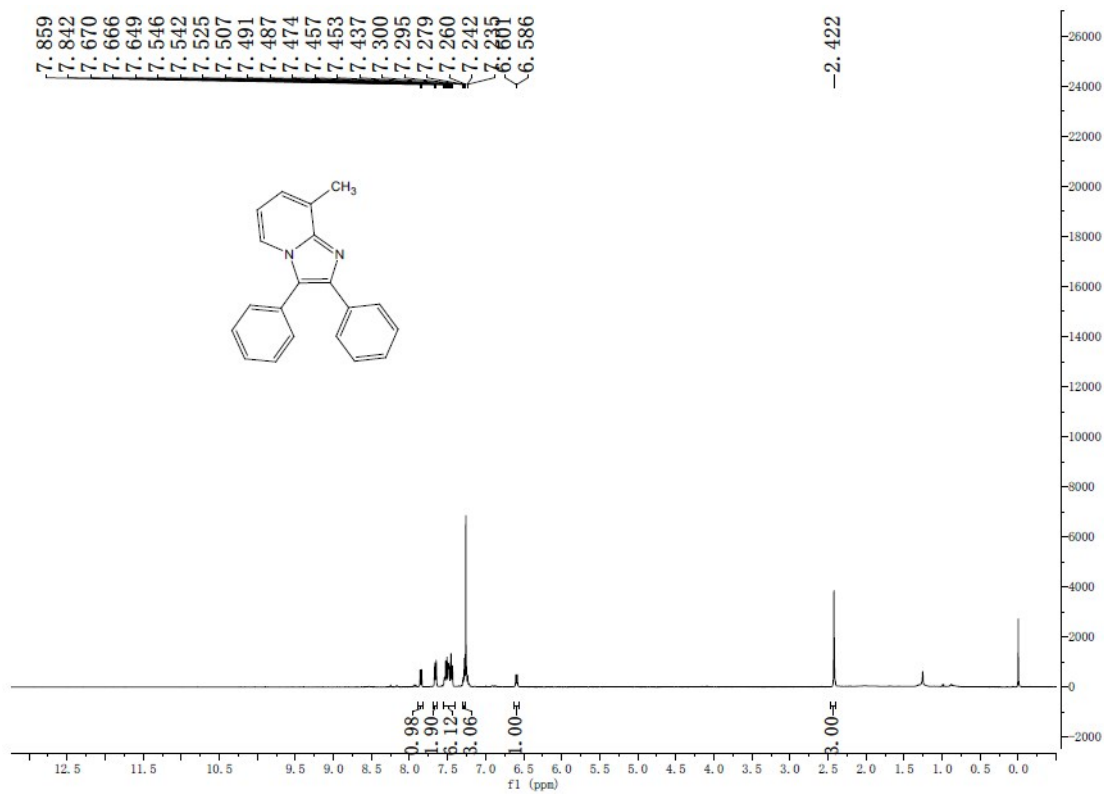
# <sup>1</sup>H NMR and <sup>13</sup>C NMR of 6-methyl-2,3-diphenylimidazo[1,2-a]pyridine



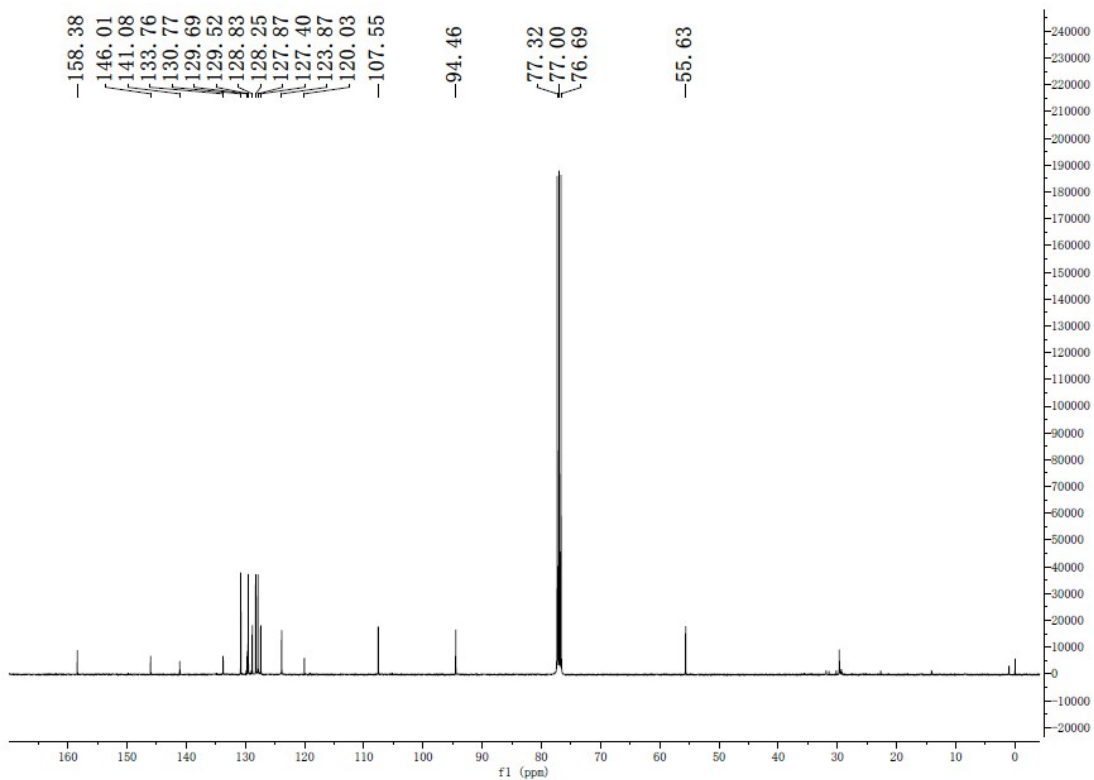
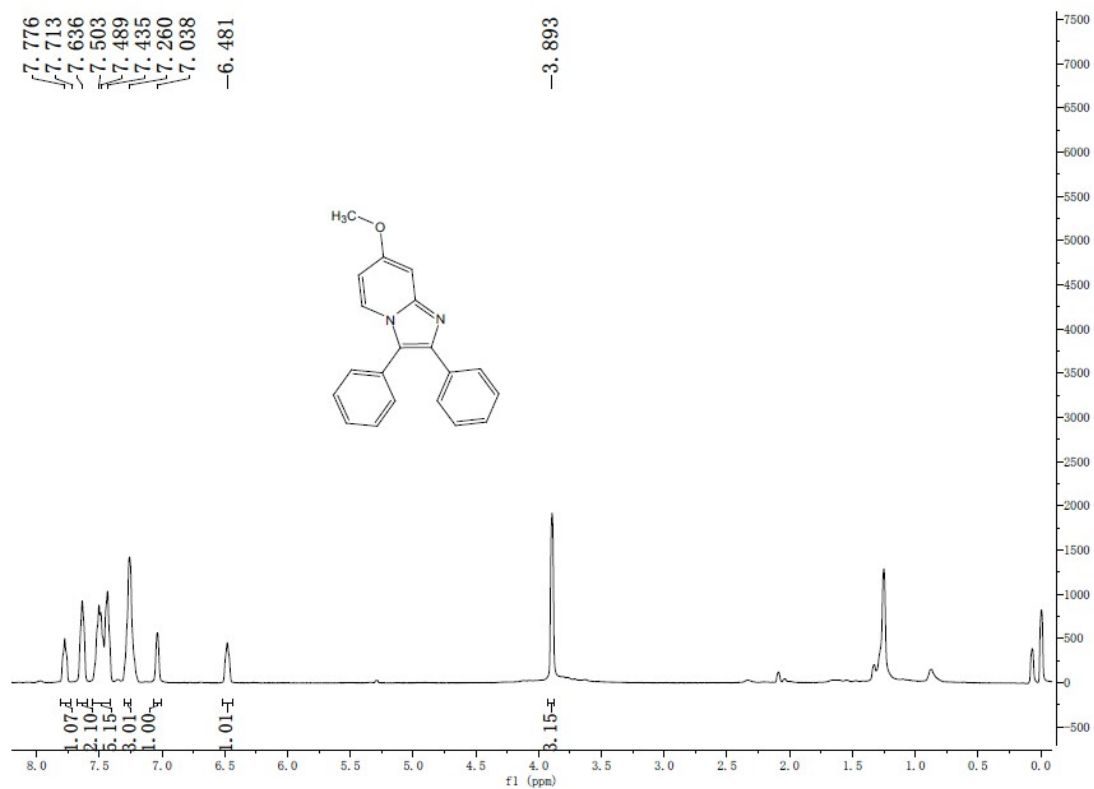
# <sup>1</sup>H NMR and <sup>13</sup>C NMR of 7-methyl-2,3-diphenylimidazo[1,2-a]pyridine



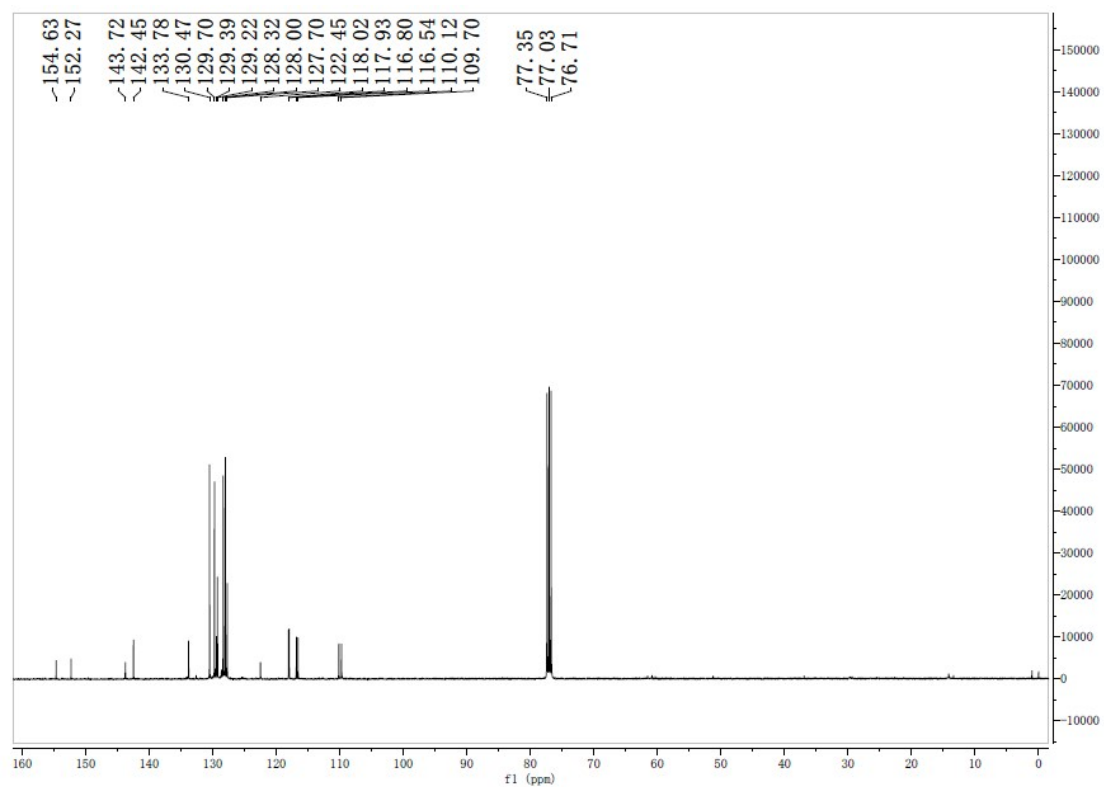
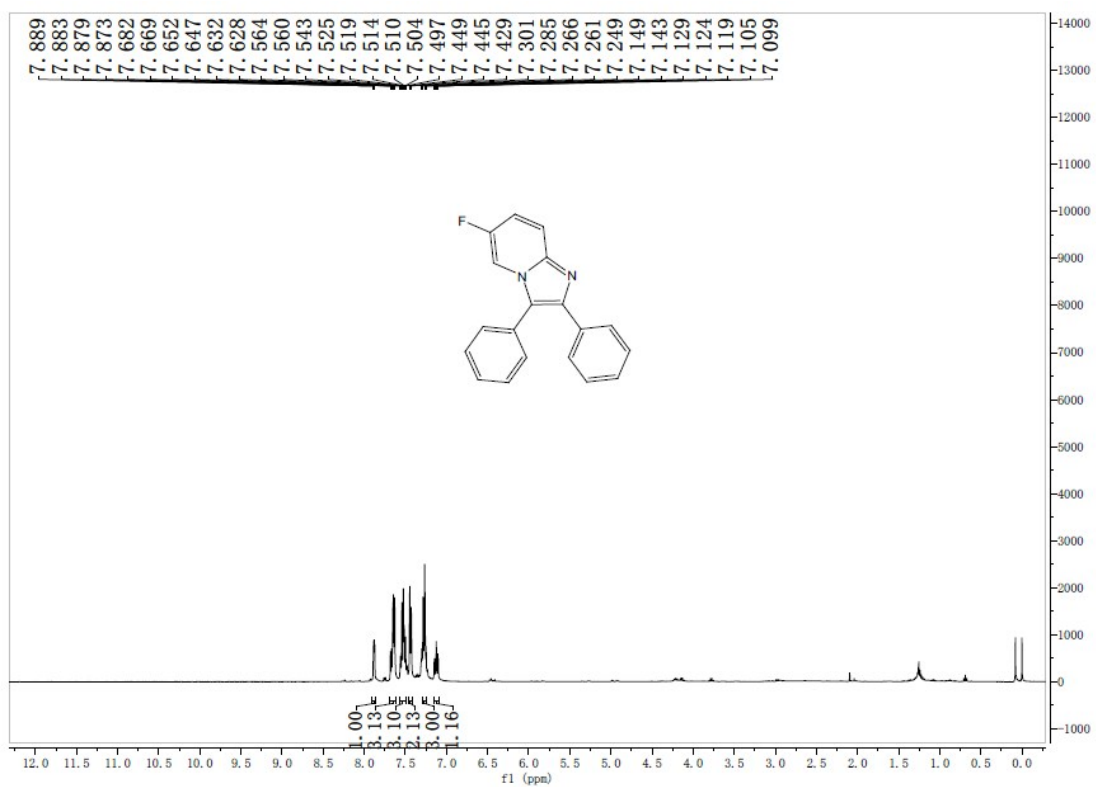
# <sup>1</sup>H NMR and <sup>13</sup>C NMR of 8-methyl-2,3-diphenylimidazo[1,2-a]pyridine



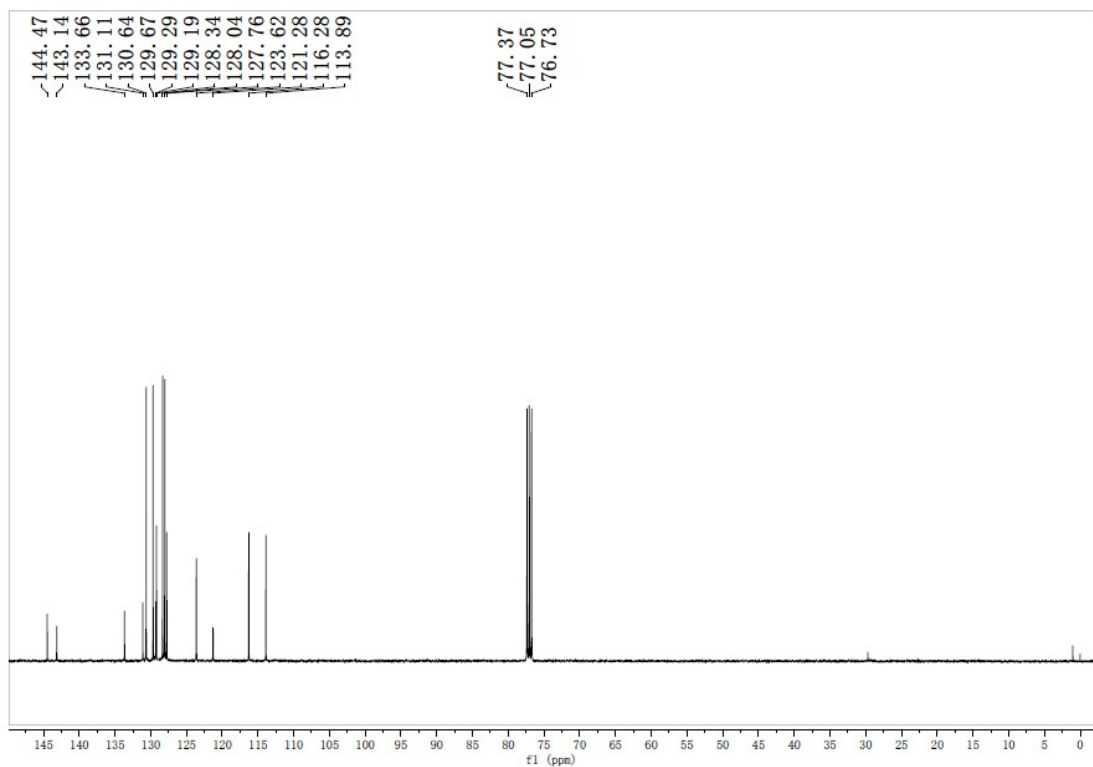
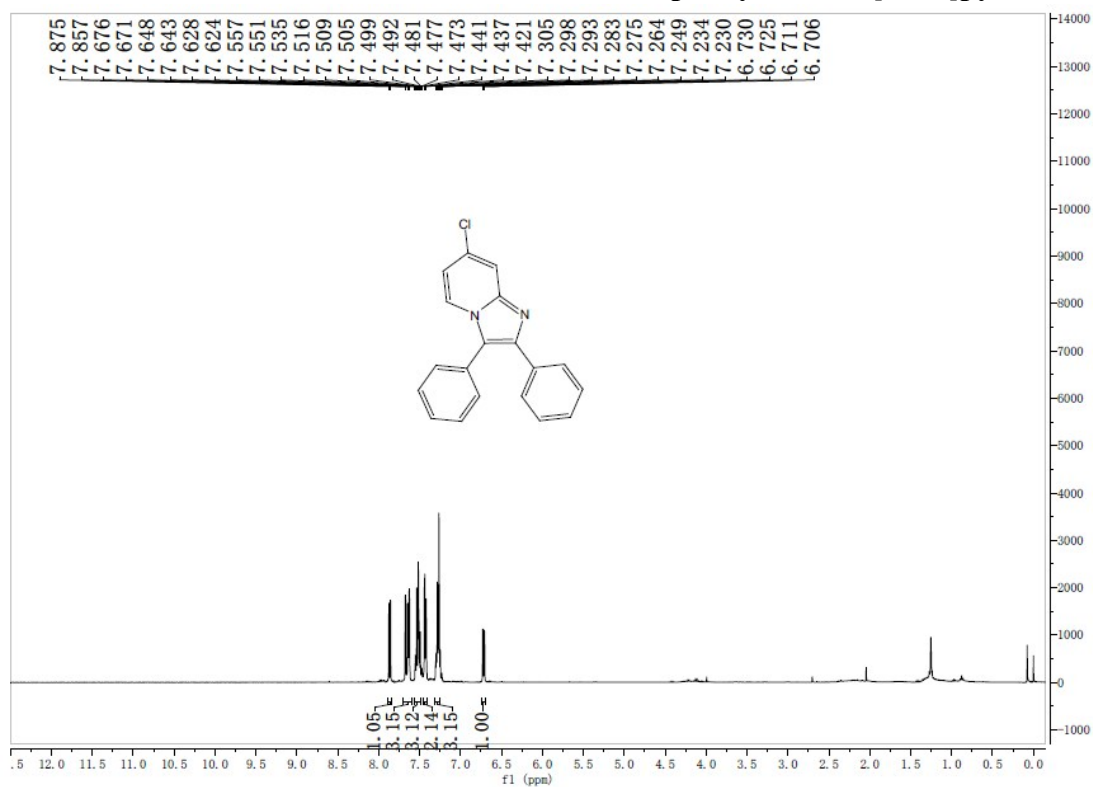
# <sup>1</sup>H NMR and <sup>13</sup>C NMR of 7-methoxy-2,3-diphenylimidazo[1,2-a]pyridine



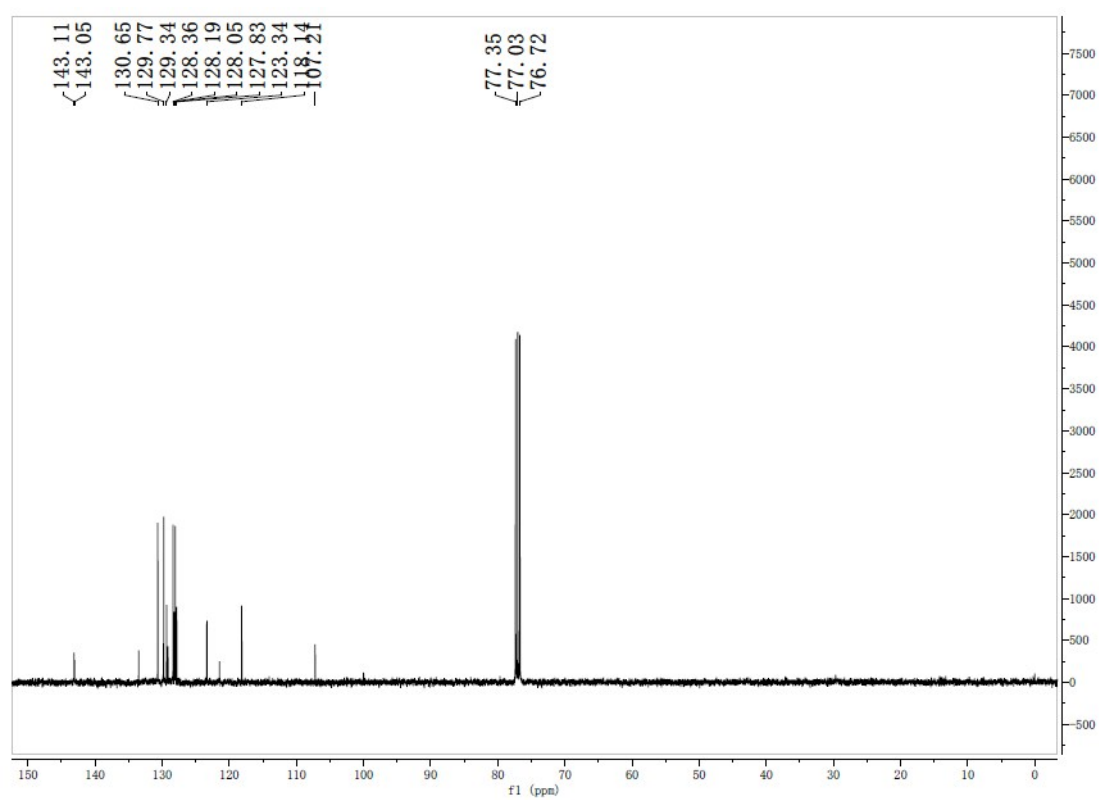
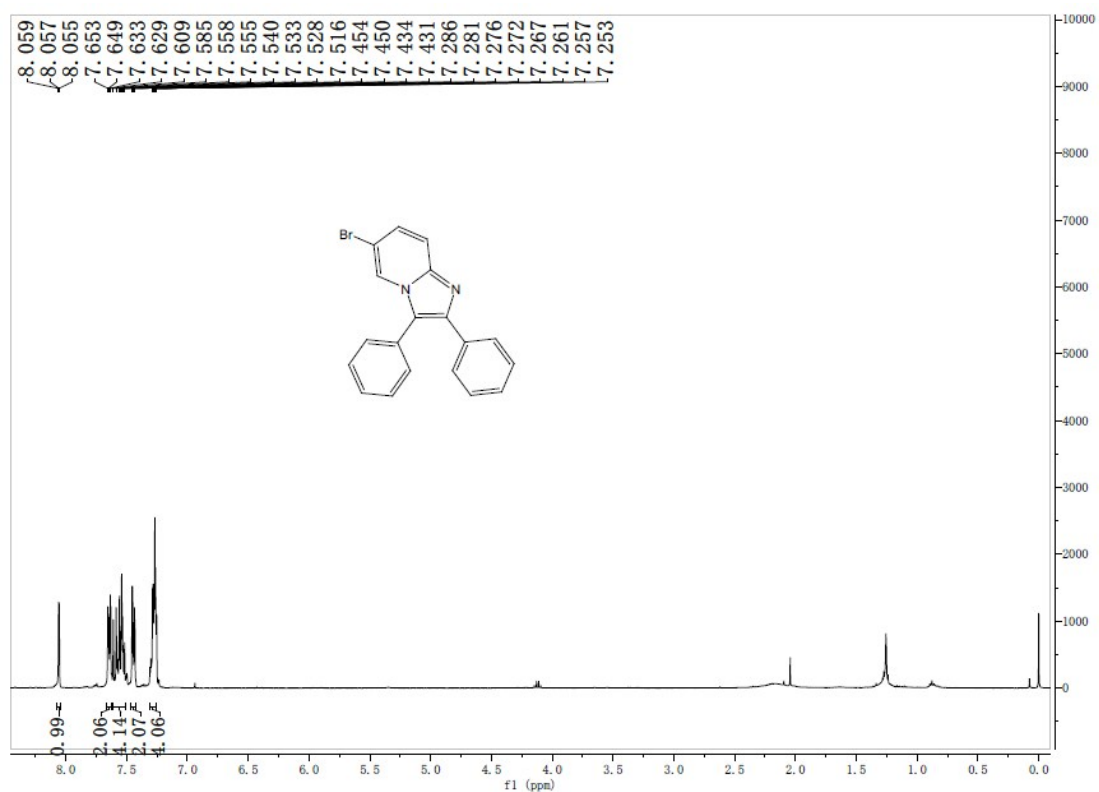
# <sup>1</sup>H NMR and <sup>13</sup>C NMR of 6-fluoro-2,3-diphenylimidazo[1,2-a]pyridine



# <sup>1</sup>H NMR and <sup>13</sup>C NMR of 7-chloro-2,3-diphenylimidazo[1,2-a]pyridine

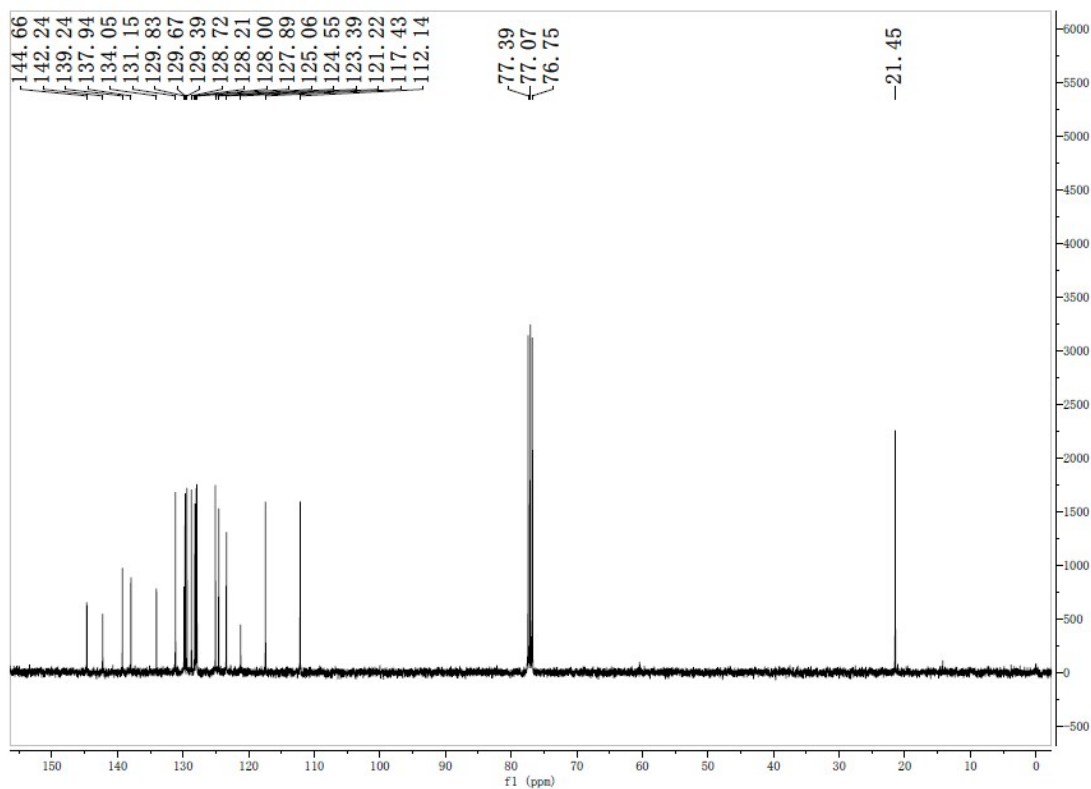
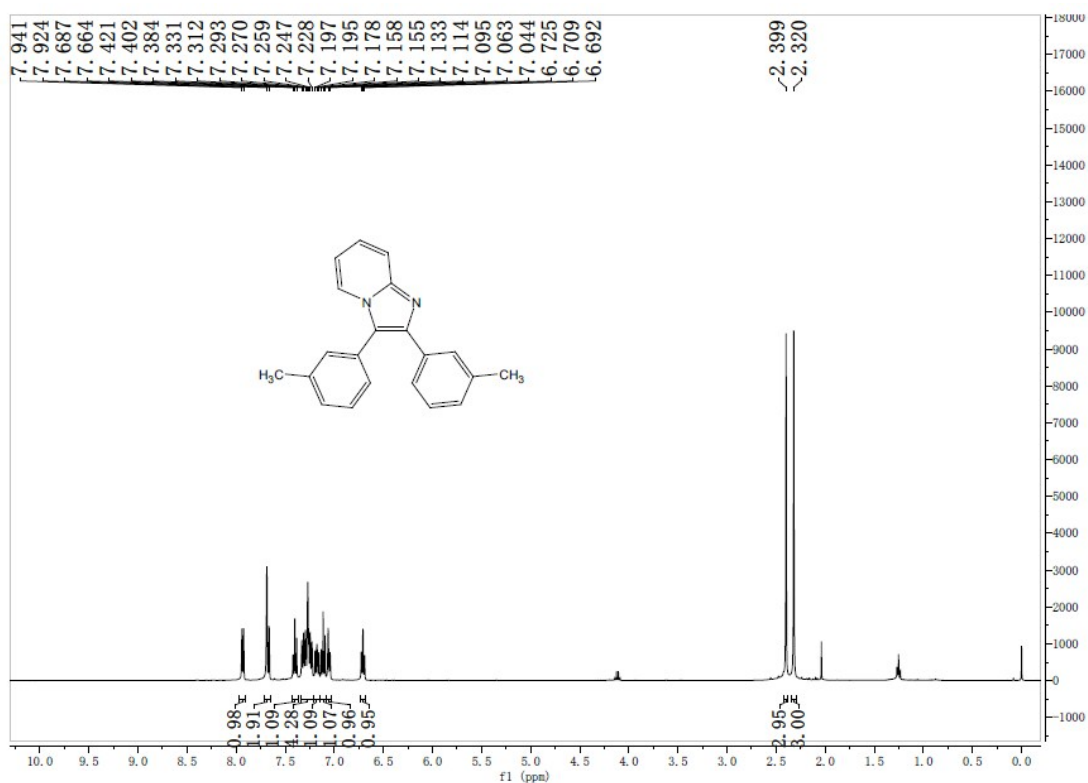


# <sup>1</sup>H NMR and <sup>13</sup>C NMR of 6-bromo-2,3-diphenylimidazo[1,2-a]pyridine

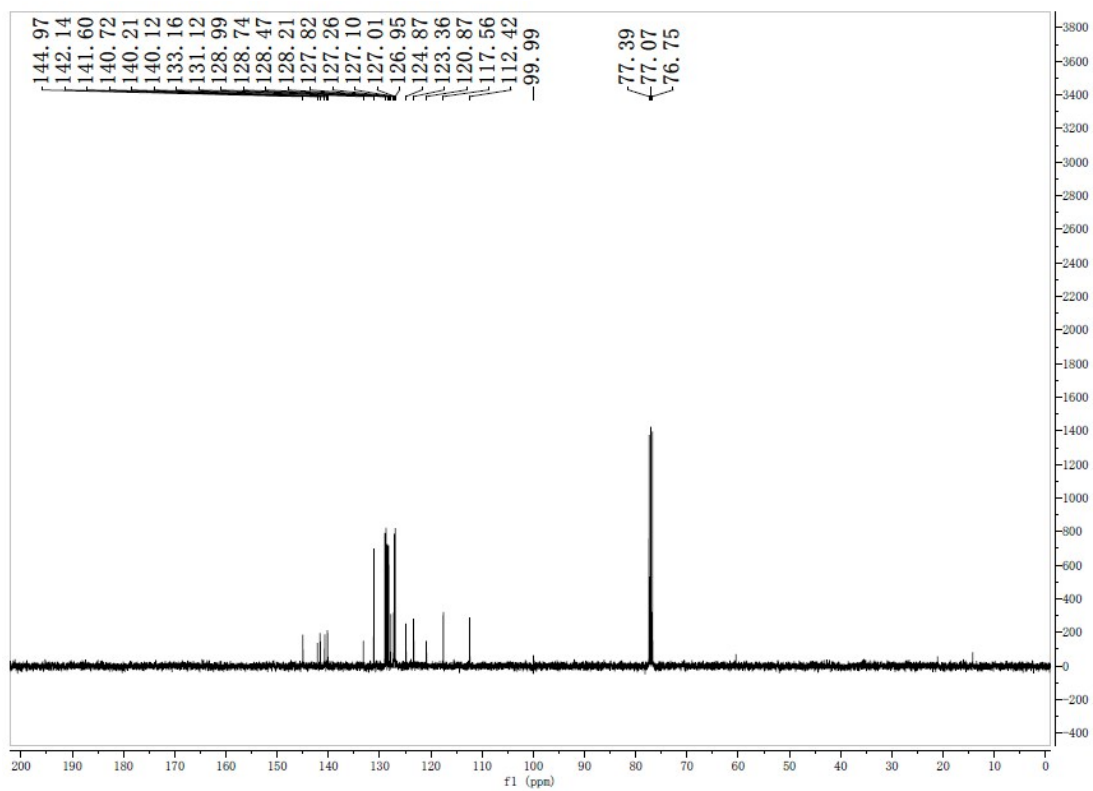
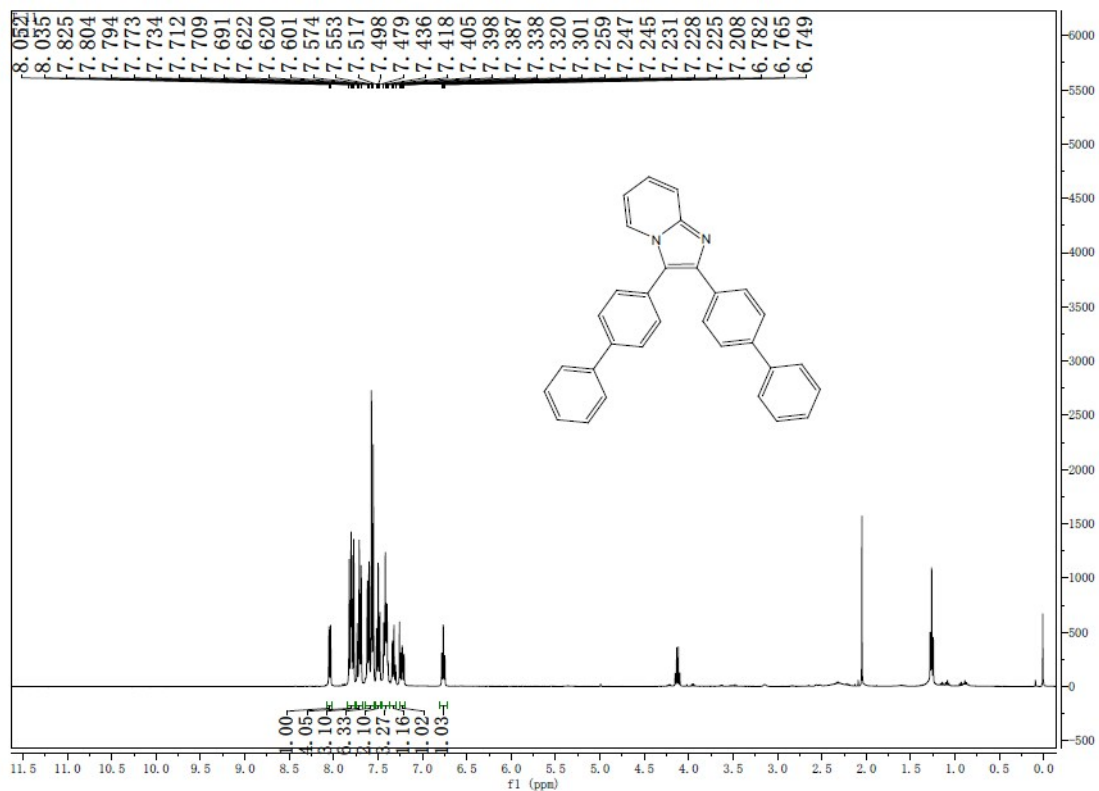




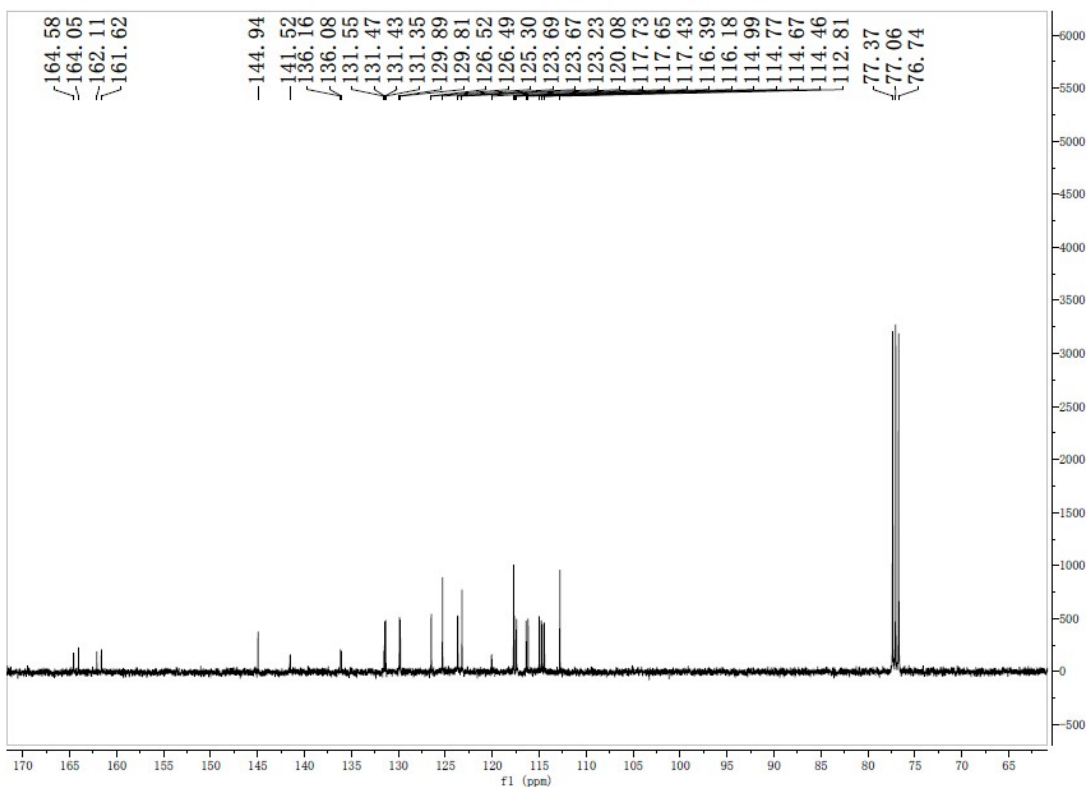
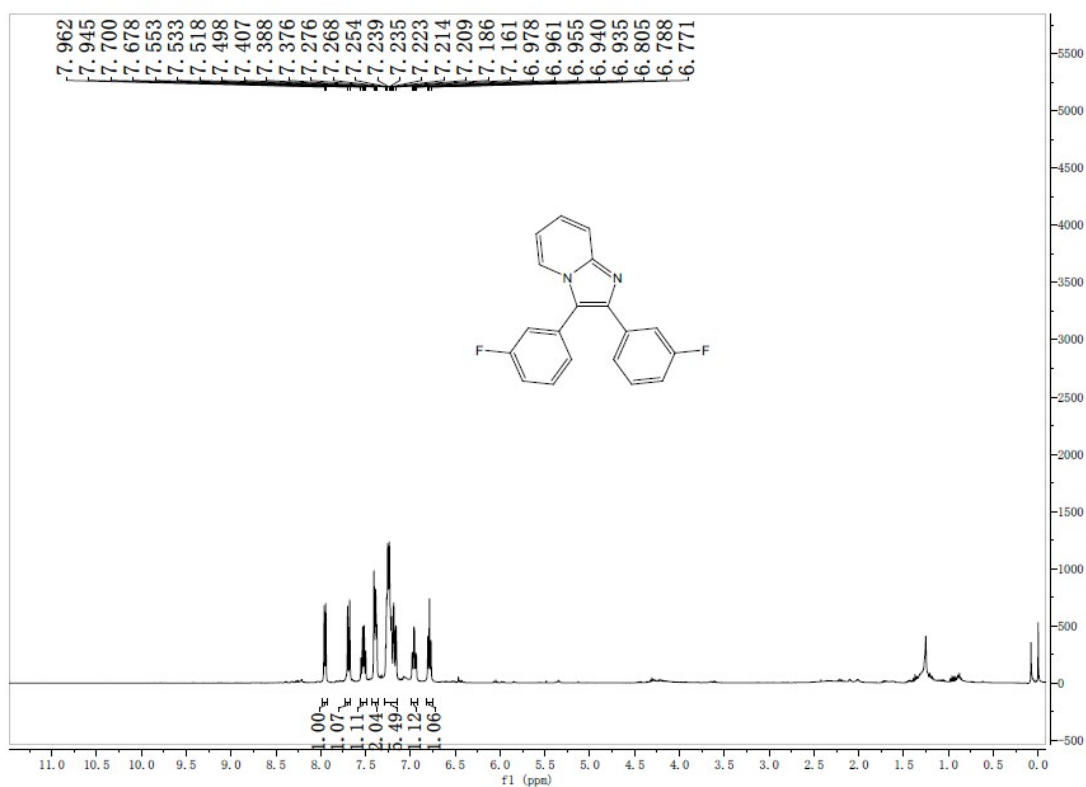
# <sup>1</sup>H NMR and <sup>13</sup>C NMR of 2,3-di-m-tolylimidazo[1,2-a]pyridine



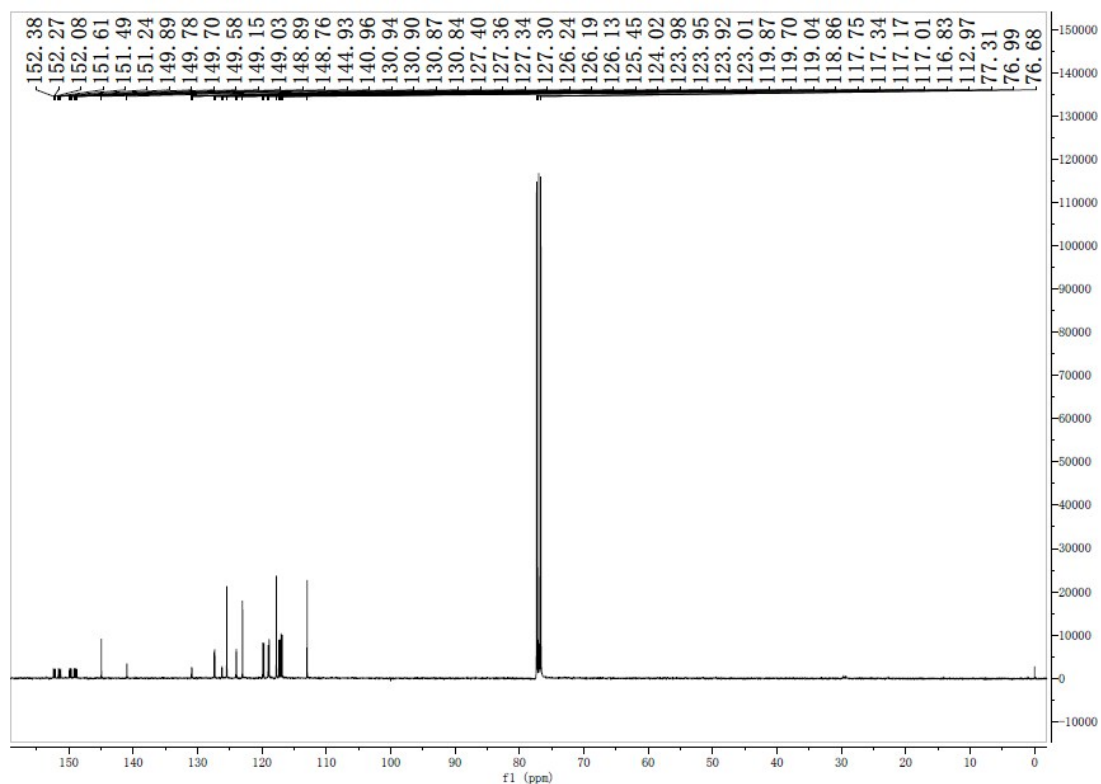
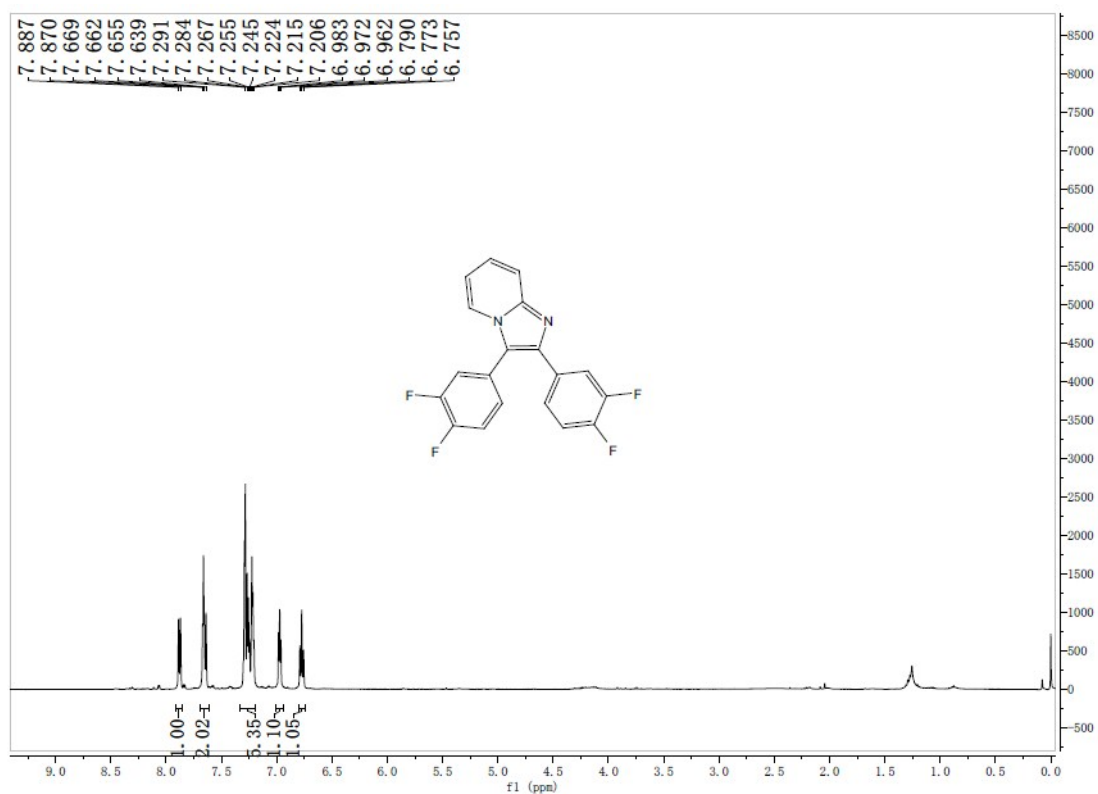
# <sup>1</sup>H NMR and <sup>13</sup>C NMR of 2,3-di([1,1'-biphenyl]-4-yl)imidazo[1,2-a]pyridine



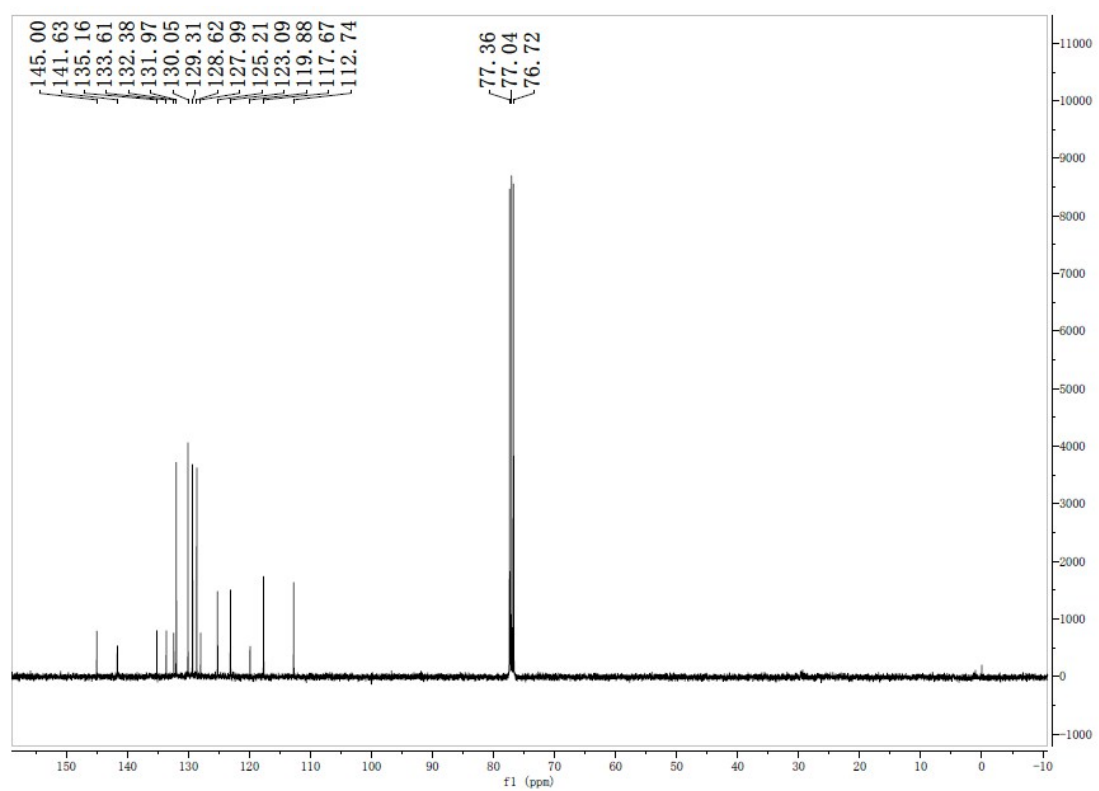
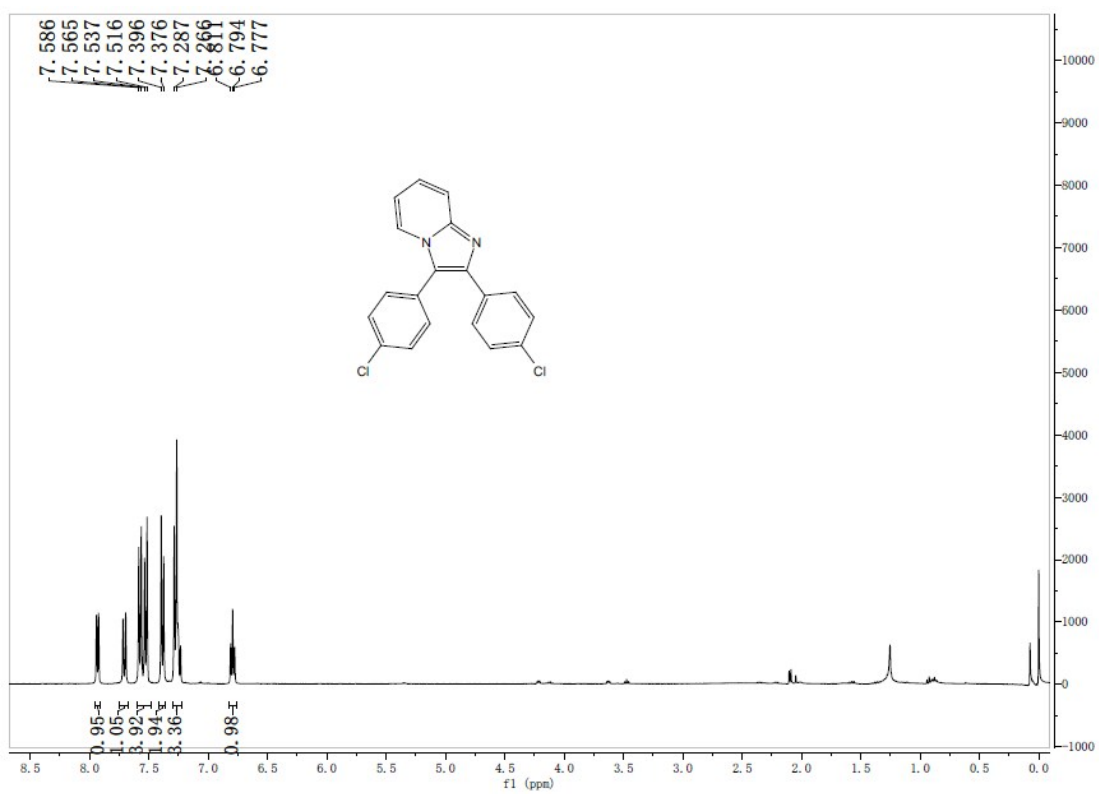
# <sup>1</sup>H NMR and <sup>13</sup>C NMR of 2,3-bis(3-fluorophenyl)imidazo[1,2-a]pyridine



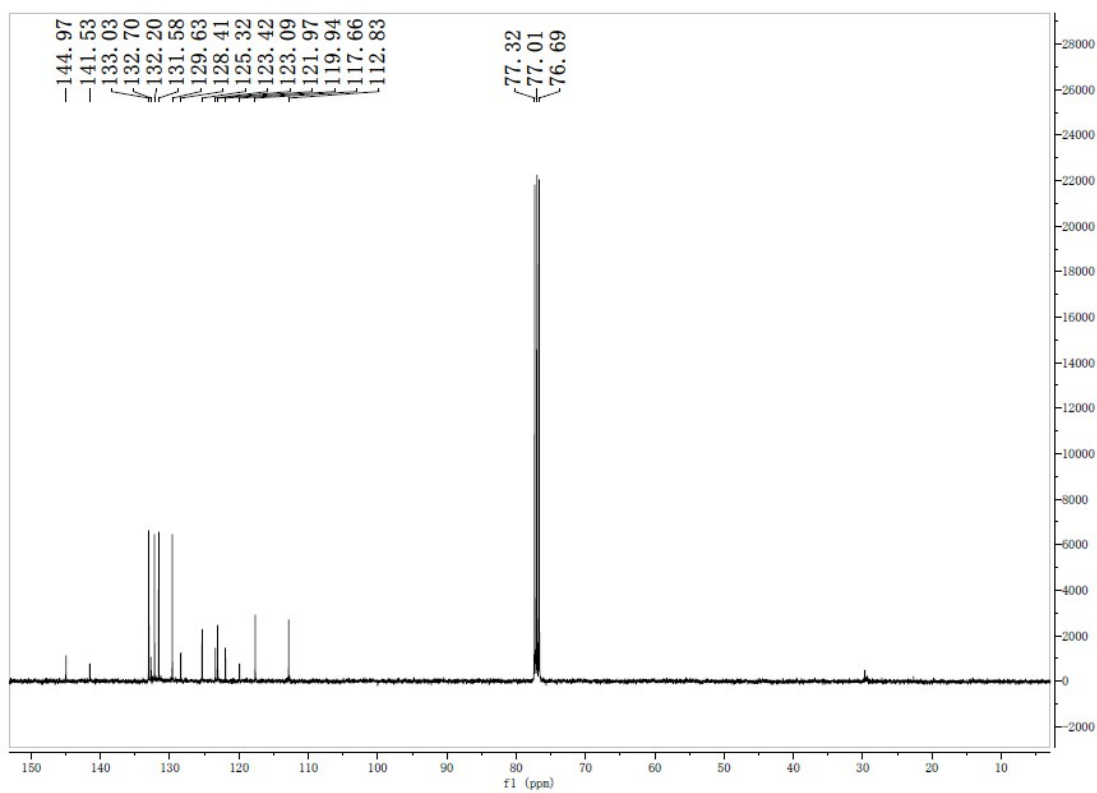
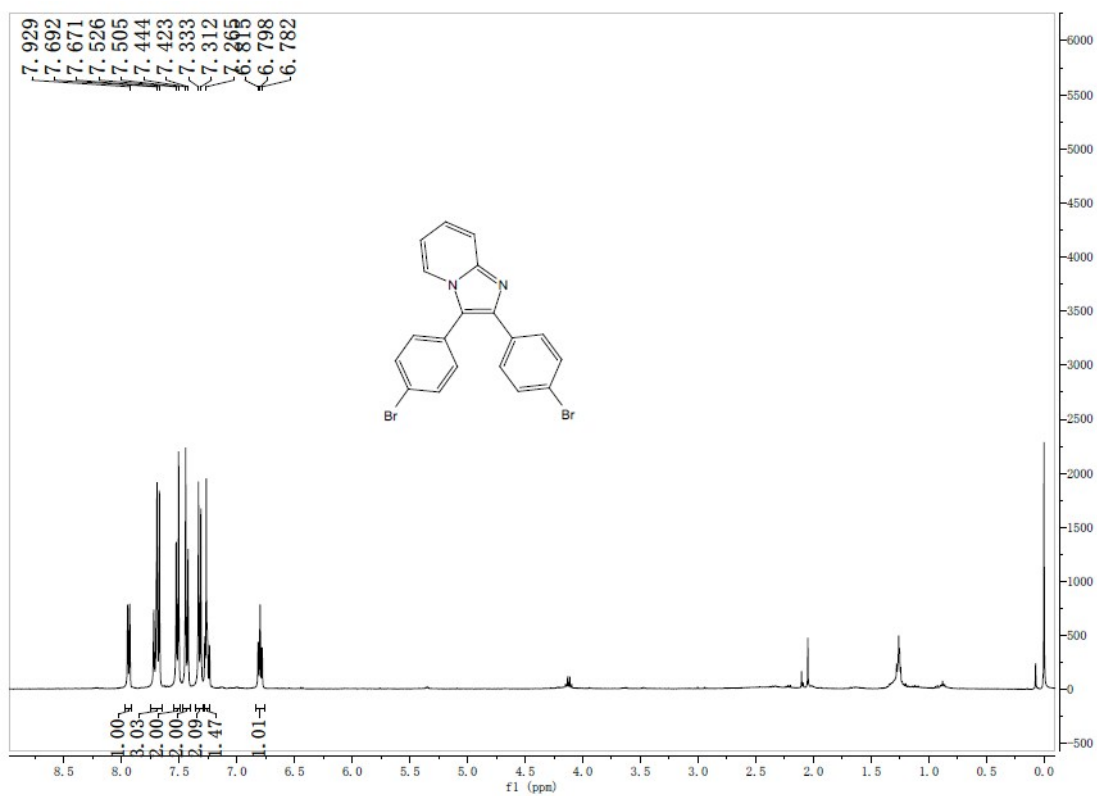
# <sup>1</sup>H NMR and <sup>13</sup>C NMR of 2,3-bis(3,4-difluorophenyl)imidazo[1,2-a]pyridine



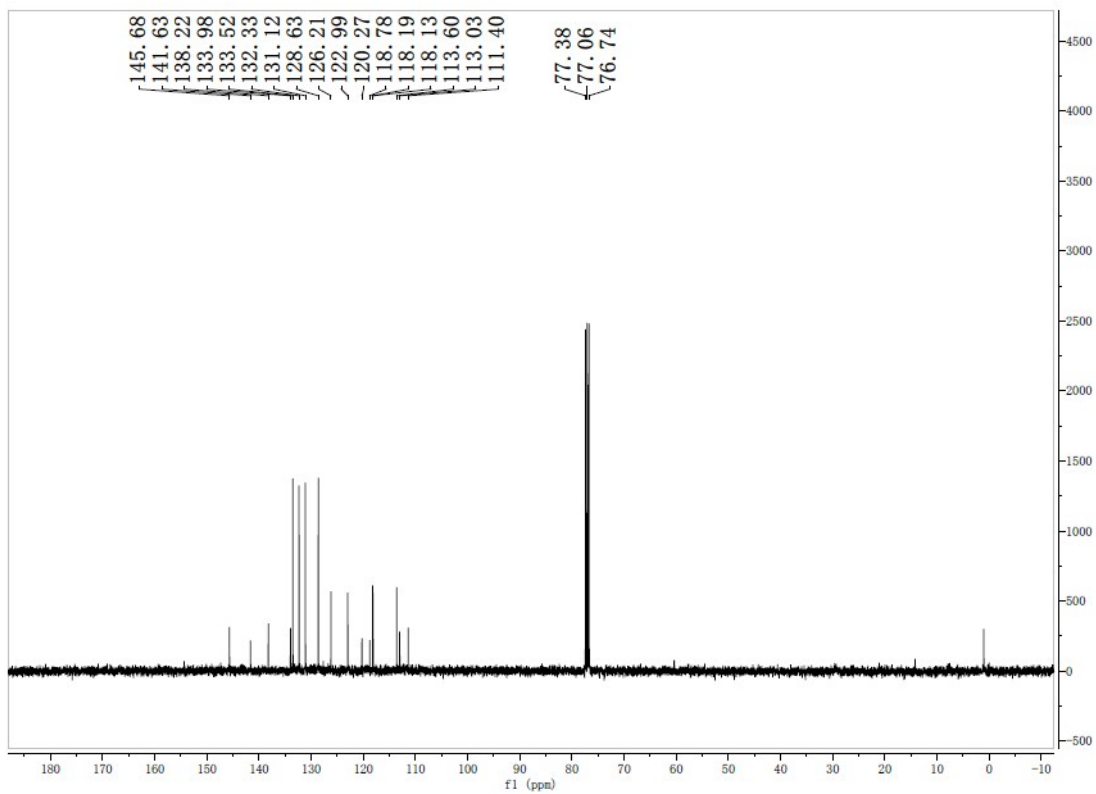
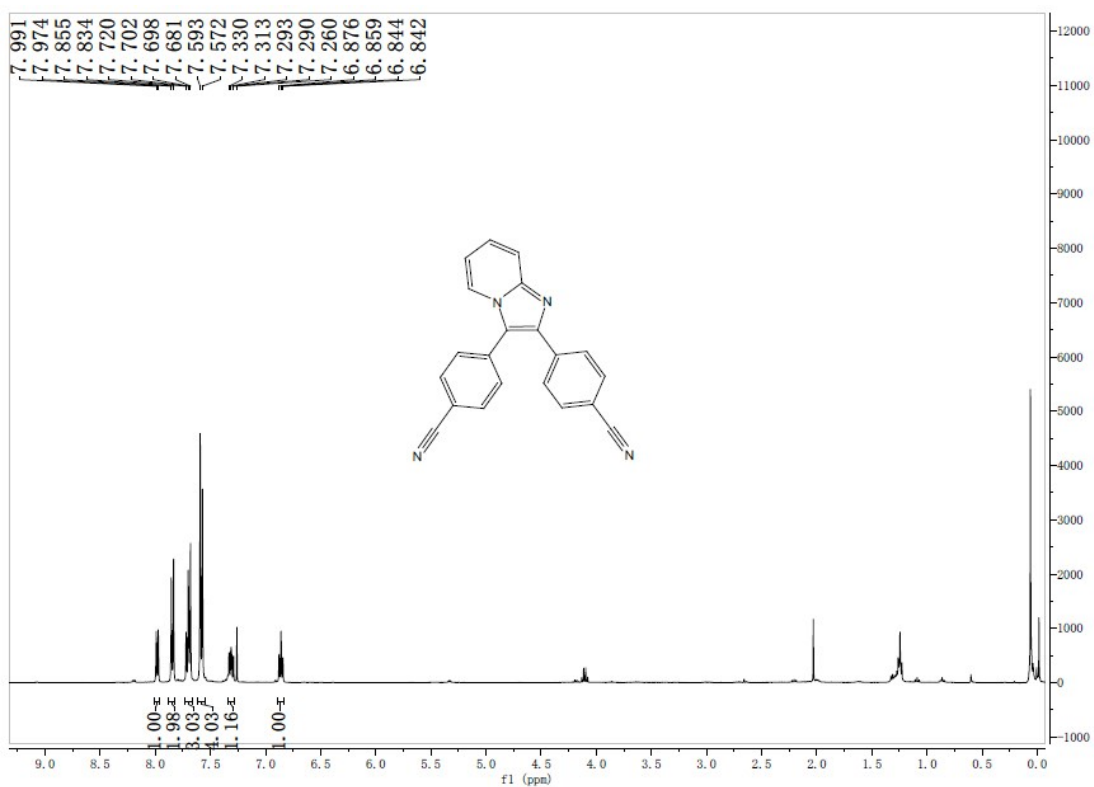
# <sup>1</sup>H NMR and <sup>13</sup>C NMR of 2,3-bis(4-chlorophenyl)imidazo[1,2-a]pyridine



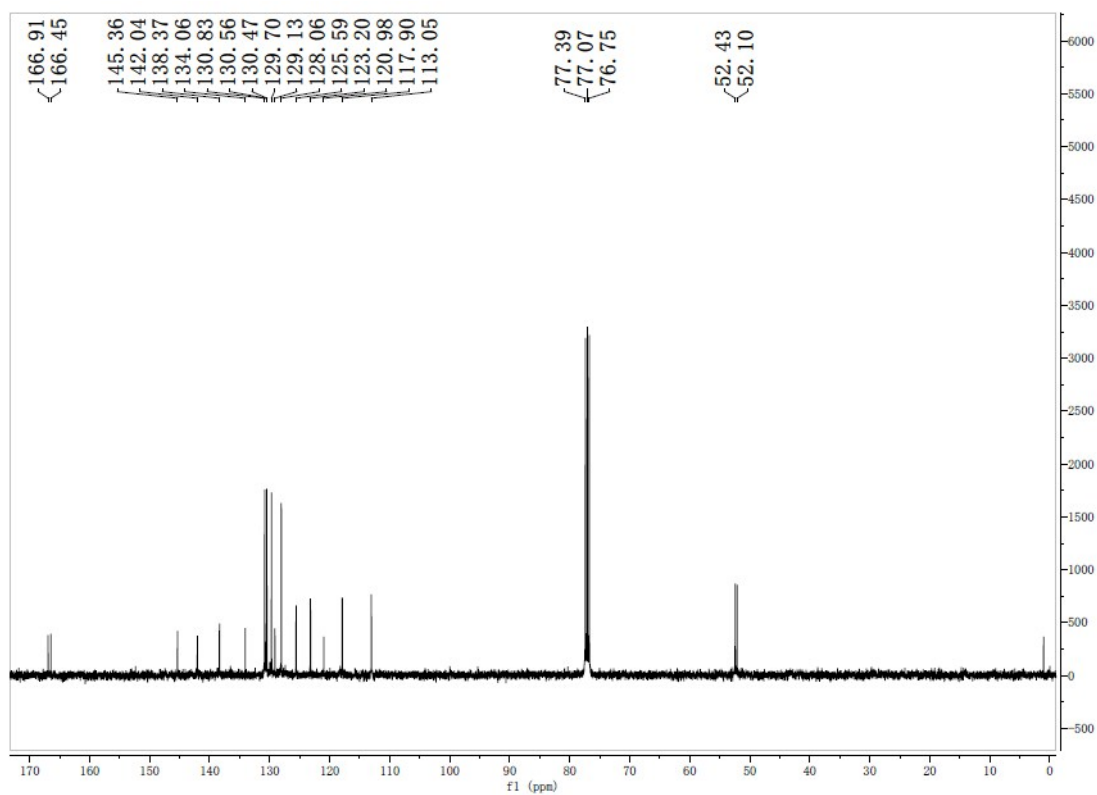
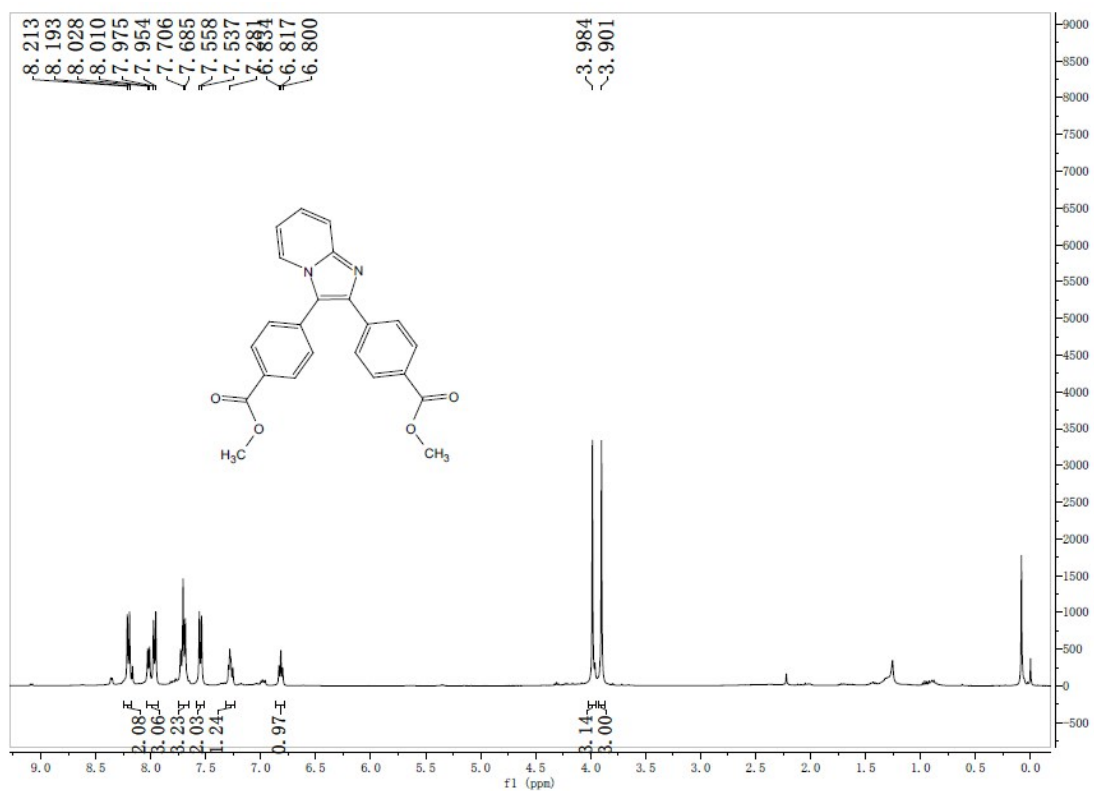
# <sup>1</sup>H NMR and <sup>13</sup>C NMR of 2,3-bis(4-bromophenyl)imidazo[1,2-a]pyridine



# <sup>1</sup>H NMR and <sup>13</sup>C NMR of 4,4'-(imidazo[1,2-a]pyridine-2,3-diyl)dibenzonitrile

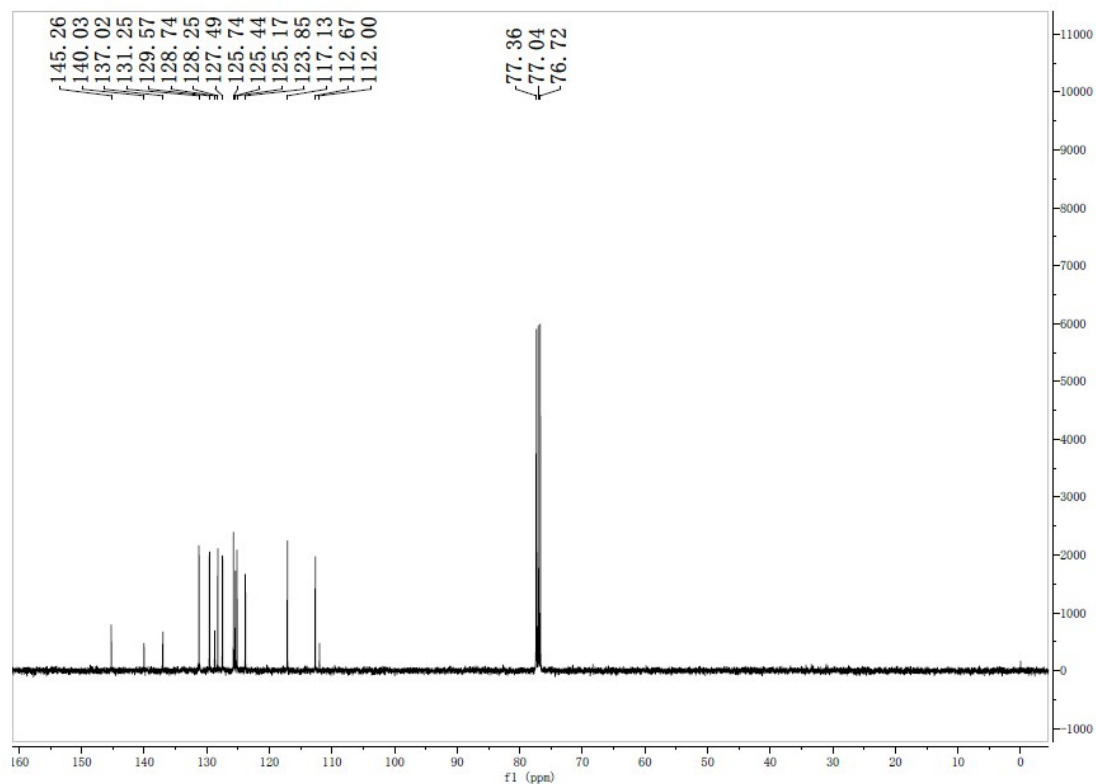
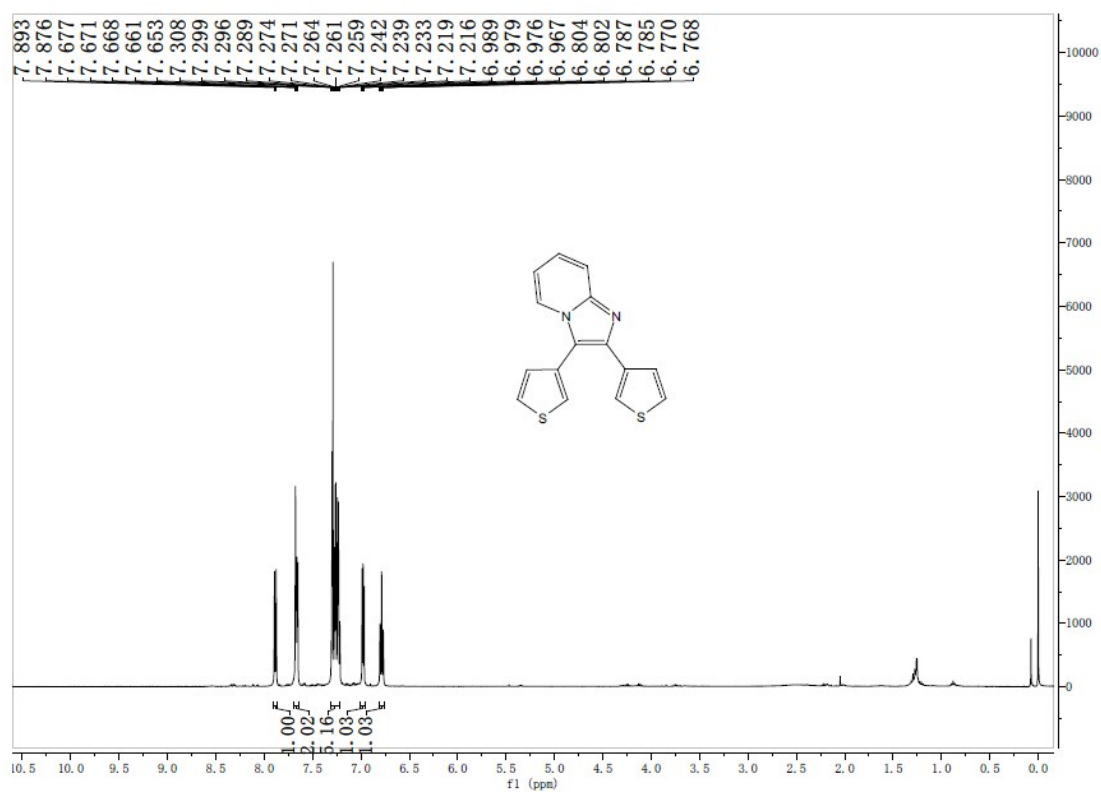


**<sup>1</sup>H NMR and <sup>13</sup>C NMR of  
dimethyl 4,4'-(imidazo[1,2-a]pyridine-2,3-diyl)dibenzoate**

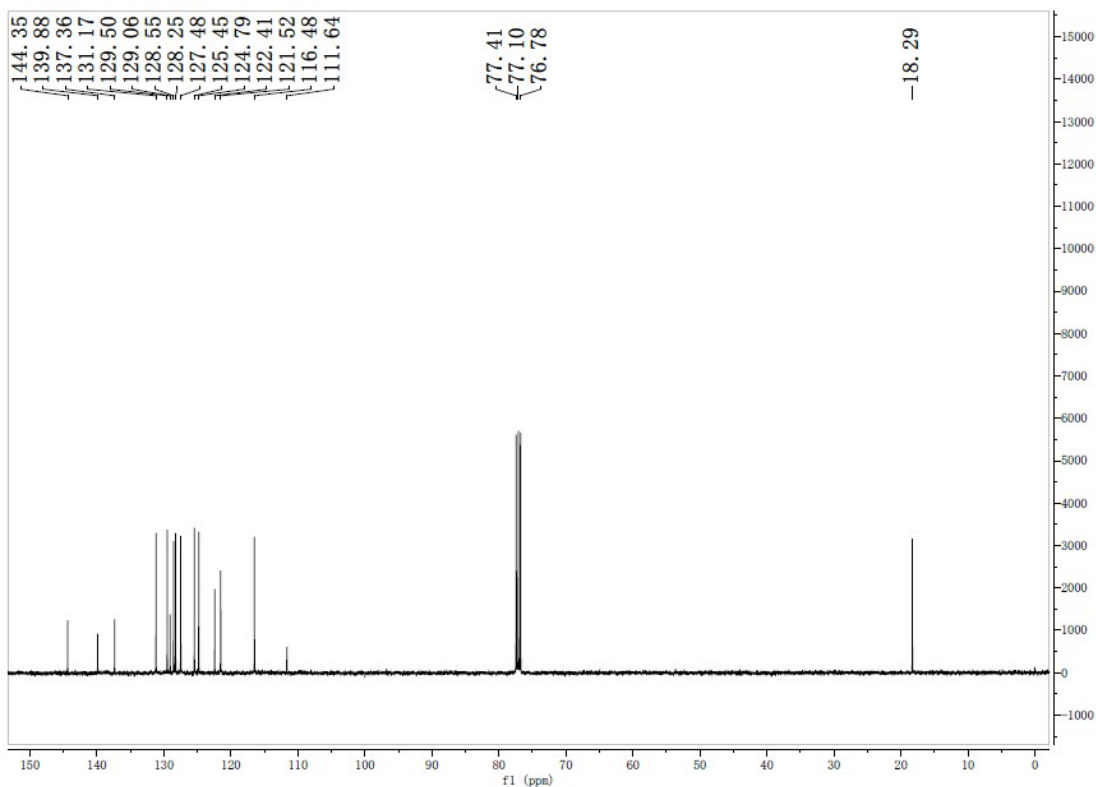
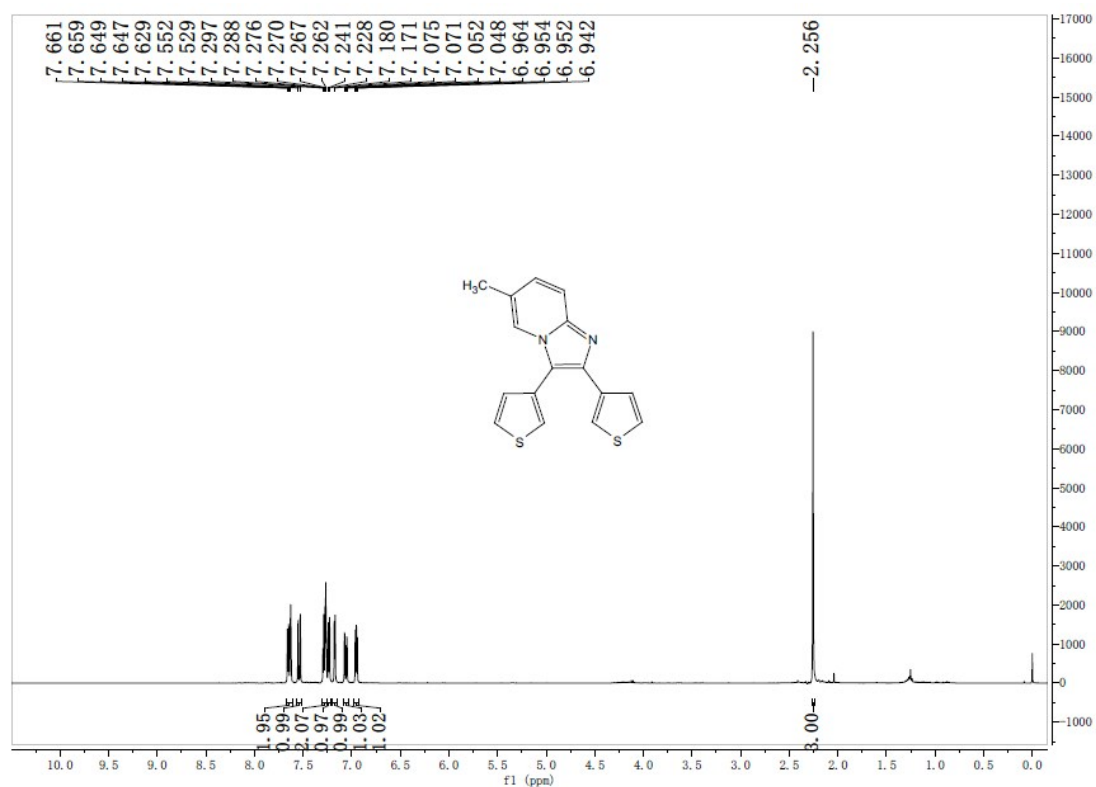




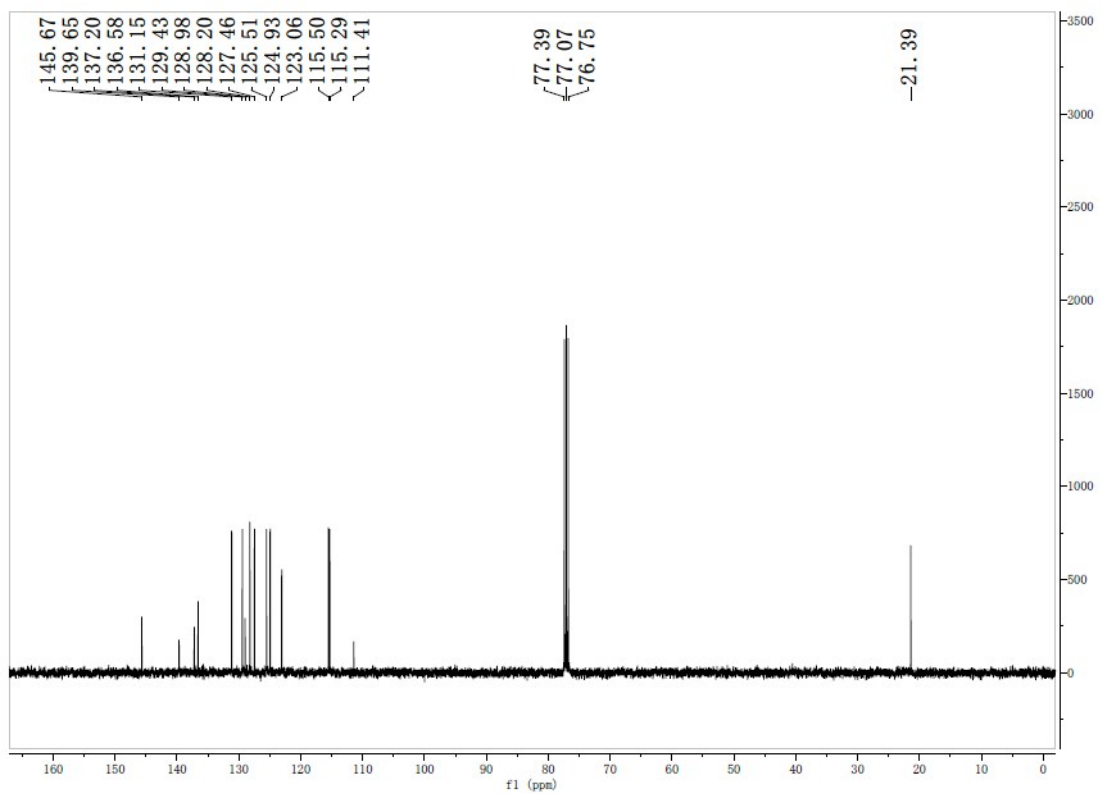
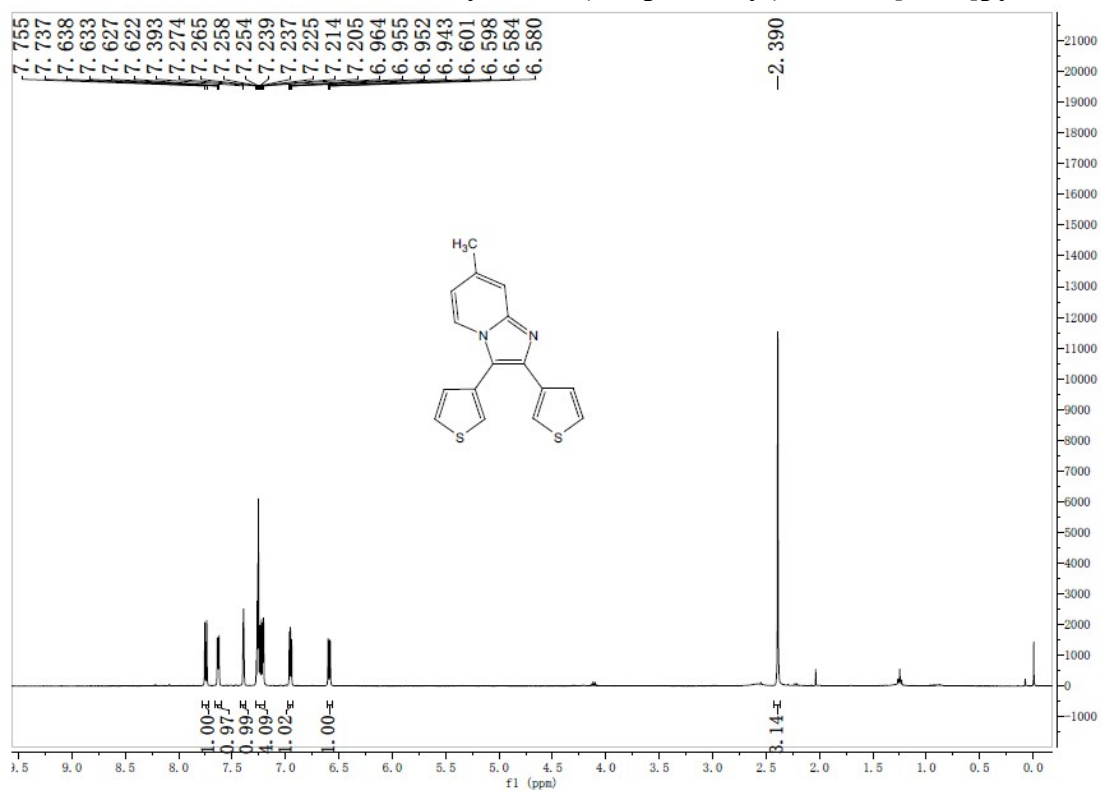
# <sup>1</sup>H NMR and <sup>13</sup>C NMR of 2,3-di(thiophen-3-yl)imidazo[1,2-a]pyridine



# <sup>1</sup>H NMR and <sup>13</sup>C NMR of 6-methyl-2,3-di(thiophen-3-yl)imidazo[1,2-a]pyridine



# <sup>1</sup>H NMR and <sup>13</sup>C NMR of 7-methyl-2,3-di(thiophen-3-yl)imidazo[1,2-a]pyridine



**<sup>1</sup>H NMR and <sup>13</sup>C NMR of  
2, 3-bis(3,4-difluorophenyl)-7-methylimidazo[1,2-a]pyridine**

