

*Supporting Information*

**Hypervalent Iodine(III)-Mediated Benzannulation of Enamines with Alkynes for  
the Synthesis of Polysubstituted Naphthalene Derivatives**

Peng Gao, Jinjian Liu, Yunyang Wei\*

School of Chemical Engineering, Nanjing University of Science and Technology,

Nanjing 210094, P. R. China

ywei@mail.njust.edu.cn

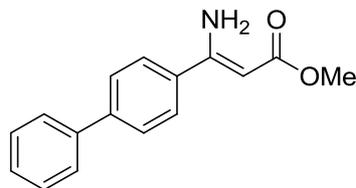
**Contents**

1. General Information and Materials	S2
2. Experimental Procedures	S2
3. Characterization Data for the Products	S3
4. <sup>1</sup> H NMR and <sup>13</sup> C NMR Spectra	S9
5. X Ray Structure Report of <b>3aa</b>	S39

## 1. General and materials

All solvents and reagents were obtained from commercial sources and used without further purification.  $^1\text{H-NMR}$  spectra obtained with tetramethylsilane (TMS,  $\delta = 0$  ppm) as internal standard in  $\text{CDCl}_3$  or  $\text{DMSO-}d_6$  using a Bruker Avance 500 spectrometer (500 MHz). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad), coupling constant ( $J$ ) and integration.  $^{13}\text{C}$  NMR spectra were recorded on Bruker Avance 500 spectrometer (125 MHz). The chemical shifts were determined in the  $\delta$ -scale relative to  $\text{CDCl}_3$  ( $\delta = 77.0$  ppm) or  $\text{DMSO-}d_6$  ( $\delta = 39.6$  ppm). Infrared (IR) spectra drawn at regular intervals were recorded on a Nicolet-10 FTIR instrument. HR-MS were recorded on an Agilent 6200 TOF LC/MS equipped with an electrospray ionization (ESI) probe operating in positive ion mode. Melting points were determined on Yamato melting point apparatus Model MP-21. Silica gel (200–300 mesh) was used for column chromatographic separations and purifications. Petroleum ether (PE) refers to the fraction boiling at 60–90°C.

Enamine compounds **1a-i** were prepared following the literatures<sup>1</sup> and conformed by  $^1\text{H}$  NMR spectra. **1i** is a new compound and the characterization data are given as follows:



**(Z)-Methyl 3-([1,1'-biphenyl]-4-yl)-3-aminoacrylate (1i)**: yellow solid. m. p. 162-164 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.60-7.66 (m, 6H), 7.47 (t,  $J = 7.6$  Hz, 2H), 7.39 (t,  $J = 7.4$  Hz, 1H), 5.04 (s, 1H), 3.74 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 170.8, 160.2, 143.2, 140.0, 135.3, 129.0, 127.9, 127.6, 127.1, 126.8, 84.3, 50.5. HR-MS ( $m/z$ ) Calcd for  $\text{C}_{16}\text{H}_{15}\text{NO}_2$   $[\text{M} + \text{H}]^+$ : 254.1175. Found: 254.1176.

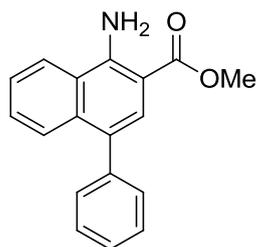
## 2. Experimental Procedures

To a solution of enamine **1** (0.5 mmol) in TFE (5 mL) was added  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (0.6 mmol) at 0 °C, followed by addition of  $(\text{PhIO})_n$  in one portion. Alkyne **2** was added to the mixture when most of  $\text{PhIO}$  was dissolved in the solution. Then the whole was slowly warmed to room temperature for 5 hours. The reaction mixture was quenched with saturated aqueous  $\text{NaHCO}_3$  (10 mL) and extracted with  $\text{EtOAc}$  (10 mL  $\times$  3). The organic layers were combined and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After removal of the solvent under reduced pressure, product **3** was isolated by column chromatography on silica gel ( $\text{EtOAc/PE} = 1/30$ ).

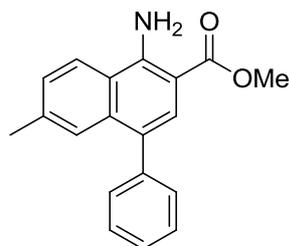
---

1 (a) Hou, G.; Li, W.; Ma, M.; Zhang, X.; Zhang, X. *J. Am. Chem. Soc.* **2010**, *132*, 12844. (b) Zheng, Y.; Li, X.; Ren, C.; Zhang-Negerie, D.; Du, Y.; Zhao, K. *J. Org. Chem.* **2012**, *77*, 10353.

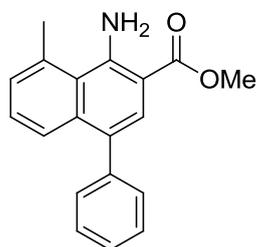
### 3. Characterization data for the Products



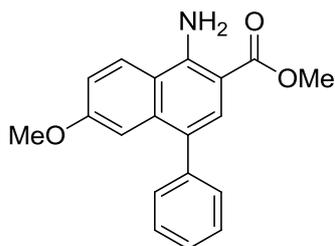
**Methyl 1-amino-4-phenyl-2-naphthoate (3aa):** yellow solid (85% yield), m. p. 155-157 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 8.43 (d, *J* = 8.2 Hz, 1H), 7.88 (b, 2H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.64 (s, 1H), 7.52-7.59 (m, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.38-7.41 (m, 3H), 3.82 (s, 3H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 169.0, 150.1, 140.7, 134.6, 130.3, 129.5, 128.9, 127.5, 127.3, 126.6, 126.0, 125.6, 124.4, 123.7, 101.8, 52.0. FTIR: 3469, 3359, 1669, 1613, 1438, 1232. GC-MS (EI): 269.98. Structure of **3aa** was clearly determined by X-ray crystallographic analysis of its single crystal.



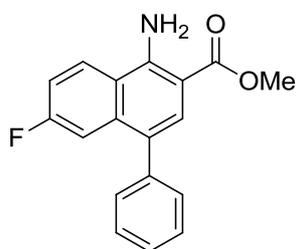
**Methyl 1-amino-6-methyl-4-phenyl-2-naphthoate (3ba):** yellow solid (85% yield), m. p. 166-168 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 8.31 (d, *J* = 8.5 Hz, 1H), 7.83 (b, 2H), 7.58 (s, 1H), 7.44-7.47 (m, 3H), 7.35-7.39 (m, 4H), 3.79 (s, 3H), 2.35 (s, 3H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 169.0, 150.1, 140.8, 139.2, 134.8, 130.3, 128.9, 127.7, 127.3, 126.2, 125.1, 124.4, 121.8, 101.3, 51.9, 21.9. FTIR: 3465, 3351, 1667, 1617, 1436, 1235. HR-MS (m/z): Calcd for C<sub>19</sub>H<sub>17</sub>NNaO<sub>2</sub> [M + Na]<sup>+</sup>: 314.1151. Found: 314.1161.



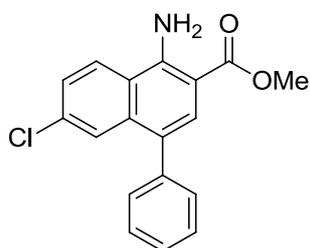
**Methyl 1-amino-8-methyl-4-phenyl-2-naphthoate (3ca):** yellow solid (86% yield), m. p. 118-120 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 7.58-7.60 (b, 3H), 7.43-7.47 (m, 3H), 7.32-7.38 (m, 4H), 7.23 (d, *J* = 7 Hz, 1H), 3.79 (s, 3H), 2.98 (s, 3H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 169.3, 152.5, 141.4, 136.9, 136.6, 130.3, 129.7, 128.9, 128.8, 127.5, 127.4, 127.3, 124.5, 124.4, 103.0, 52.5, 25.4. FTIR: 3504, 3311, 1671, 1591, 1433, 1235. HR-MS (m/z): Calcd for C<sub>19</sub>H<sub>18</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 292.1332. Found: 292.1331.



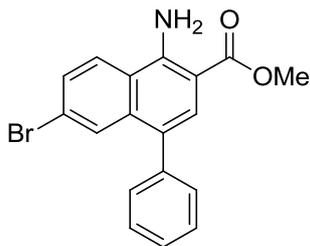
**Methyl 1-amino-6-methoxy-4-phenyl-2-naphthoate (3da):** yellow solid (91% yield), m. p. 147-149 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 8.35 (d, *J* = 9.3 Hz, 1H), 7.81 (b, 2H), 7.59 (s, 1H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.36-7.42 (m, 3H), 7.17 (dd, *J*<sub>1</sub> = 9.2 Hz, *J*<sub>2</sub> = 2.3 Hz, 1H), 7.07 (d, *J* = 2.3 Hz, 1H), 3.78 (s, 3H), 3.70 (s, 3H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 169.0, 160.0, 150.2, 140.8, 136.5, 130.1, 129.0, 128.4, 127.3, 126.5, 125.8, 118.3, 116.0, 106.0, 100.6, 55.5, 51.8. FTIR: 3478, 3392, 1678, 1609, 1435, 1216. HR-MS (m/z): Calcd for C<sub>19</sub>H<sub>18</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 308.1281. Found: 308.1288.



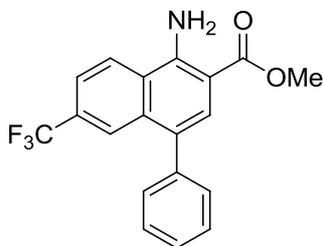
**Methyl 1-amino-6-fluoro-4-phenyl-2-naphthoate (3ea):** yellow solid (75% yield), m. p. 175-176 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 8.51-8.54 (m, 1H), 7.95 (b, 2H), 7.68 (s, 1H), 7.37-7.50 (m, 6H), 7.28 (dd, *J*<sub>1</sub> = 11.2 Hz, *J*<sub>2</sub> = 2.6 Hz, 1H), 3.81 (s, 3H), 3.33 (s, 3H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 168.8, 162.7 (d, *J*<sub>C-F</sub> = 245.6 Hz), 150.1, 140.1, 136.4 (d, *J*<sub>C-F</sub> = 7.5 Hz), 130.2, 129.1, 128.9, 128.0 (d, *J*<sub>C-F</sub> = 9.3 Hz), 127.6, 125.9, 120.3, 114.8 (d, *J*<sub>C-F</sub> = 24.3 Hz), 109.6 (d, *J*<sub>C-F</sub> = 21.5 Hz), 101.7, 52.0. FTIR: 3450, 3348, 1668, 1611, 1436, 1240. HR-MS (m/z): Calcd for C<sub>18</sub>H<sub>15</sub>FNO<sub>2</sub> [M +H]<sup>+</sup>: 296.1081. Found: 296.1086.



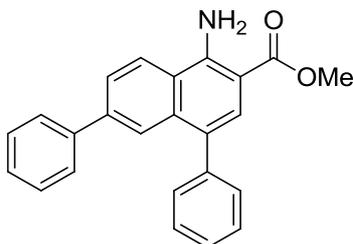
**Methyl 1-amino-6-chloro-4-phenyl-2-naphthoate (3fa):** yellow solid (81% yield), m. p. 181-183 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 8.47 (d, *J* = 8.1 Hz, 1H), 7.95 (b, 2H), 7.68 (s, 1H), 7.55-7.59 (m, 2H), 7.48-7.51 (m, 2H), 7.38-7.43 (m, 3H), 3.81 (s, 3H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 168.7, 150.0, 140.0, 135.7, 134.6, 130.2, 129.2, 129.0, 127.7, 127.0, 125.7, 125.6, 124.5, 122.2, 102.3, 52.1. FTIR: 3447, 3347, 1671, 1611, 1439, 1236. HR-MS (m/z): Calcd for C<sub>18</sub>H<sub>15</sub>ClNO<sub>2</sub> [M +H]<sup>+</sup>: 312.0785. Found: 312.0789.



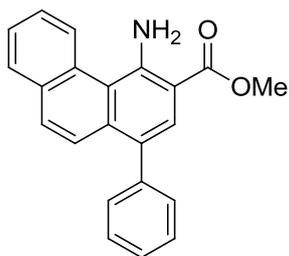
**Methyl 1-amino-6-bromo-4-phenyl-2-naphthoate (3ga):** yellow solid (78% yield), m. p. 195-197 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  (ppm) 8.39 (d,  $J = 9.1$  Hz, 1H), 7.94 (b, 2H), 7.75 (d,  $J = 1.9$  Hz, 1H), 7.66-7.68 (m, 2H), 7.48 (t,  $J = 7.5$  Hz, 2H), 7.35-7.42 (m, 3H), 3.80 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ )  $\delta$  (ppm) 168.7, 150.0, 139.9, 136.0, 130.2, 129.2, 129.0, 128.3, 127.8, 127.7, 127.1, 125.6, 123.6, 122.4, 102.4, 52.1. FTIR: 3503, 3350, 1683, 1605, 1435, 1230. HR-MS (m/z): Calcd for  $\text{C}_{18}\text{H}_{15}\text{BrNO}_2$   $[\text{M}+\text{H}]^+$ : 356.0281. Found: 356.0280.



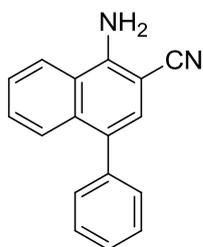
**Methyl 1-amino-4-phenyl-6-(trifluoromethyl)-2-naphthoate (3ha):** yellow solid (81% yield), m. p. 178- 182 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  (ppm) 8.66 (d,  $J = 8.9$  Hz, 1H), 8.01 (b, 2H), 7.95 (s, 1H), 7.90 (dd,  $J_1 = 8.9$  Hz,  $J_2 = 1.3$  Hz, 1H ), 7.76 (s, 1H), 7.49 (t,  $J_1 = 7.3$  Hz, 2H), 7.39-7.44(m, 3H), 3.83 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ )  $\delta$  (ppm) 168.6, 149.6, 139.7, 133.8, 130.3, 129.2 (m), 127.8, 126.9, 126.4, 125.5, 123.0, 120.7, 103.7, 52.2. FTIR: 3504, 3355, 1684, 1613, 1440, 1236. HR-MS (m/z): Calcd for  $\text{C}_{19}\text{H}_{15}\text{F}_3\text{NO}_2$   $[\text{M} +\text{H}]^+$ : 346.1049. Found: 346.1048.



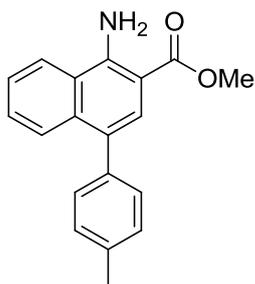
**Methyl 1-amino-4,6-diphenyl-2-naphthoate (3ia):** yellow solid (84% yield), m. p. 188-190 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  (ppm) 8.53 (d,  $J = 8.8$  Hz, 1H), 7.91-7.92 (m, 3H), 7.84 (dd,  $J_1 = 8.8$  Hz,  $J_2 = 1.4$  Hz, 1H), 7.67 (s, 1H), 7.61 (d,  $J = 7.5$  Hz, 2H), 7.35-7.51 (m, 8H), 3.82 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ )  $\delta$  (ppm) 168.9, 150.0, 141.0, 140.6, 140.1, 134.9, 130.3, 129.6, 129.1, 128.5, 128.1, 127.5, 126.8, 125.4, 124.6, 123.5, 122.8, 102.0, 52.0. FTIR: 3497, 3366, 1671, 1606, 1438, 1234. HR-MS (m/z): Calcd for  $\text{C}_{24}\text{H}_{20}\text{NO}_2$   $[\text{M} +\text{H}]^+$ : 354.1489. Found: 354.1488.



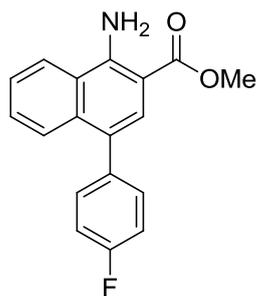
**Methyl 4-amino-1-phenylphenanthrene-3-carboxylate (3ja):** red solid (71% yield), m. p. 179-180 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 9.30 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 7.7 Hz, 1H), 7.84 (t, *J* = 4.3 Hz, 2H), 7.55-7.68 (m, 5H), 7.49 (t, *J* = 7.3 Hz, 2H), 7.39-7.43 (m, 3H), 3.85 (s, 3H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 169.2, 151.1, 140.8, 134.8, 132.5, 131.0, 130.5, 130.4, 129.3, 129.1, 129.0, 128.1, 127.5, 127.2, 126.6, 125.7, 124.3, 119.5, 106.8, 52.3. FTIR: 3467, 3329, 1682, 1586, 1421, 1227. HR-MS (m/z): Calcd for C<sub>22</sub>H<sub>18</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 328.1332. Found: 328.1334.



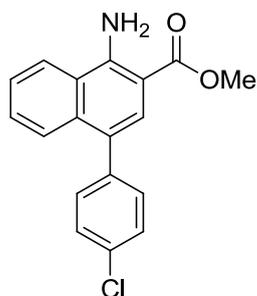
**1-Amino-4-phenyl-2-naphthonitrile (3la):** yellow solid (53% yield), m. p. 215-217 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 8.40 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.51-7.58 (m, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.37-7.40 (m, 3H), 7.20 (s, 1H), 6.98 (b, 2H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 150.3, 139.7, 134.1, 130.4, 129.7, 129.0, 128.2, 127.8, 127.6, 126.2, 126.1, 124.1, 122.5, 119.5, 86.4. FTIR: 3409, 3342, 2900, 2210, 1617, 1394, 1241. HR-MS (m/z): Calcd for C<sub>17</sub>H<sub>13</sub>N<sub>2</sub> [M +H]<sup>+</sup>: 245.1073. Found: 245.1098.



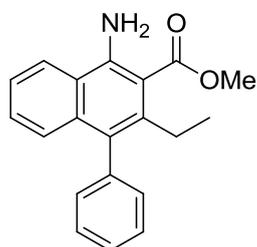
**Methyl 1-amino-4-(p-tolyl)-2-naphthoate (3ab):** yellow solid (87% yield), m. p. 188-190 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 8.40 (d, *J* = 8.2 Hz, 1H), 7.84 (b, 2H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.68 (s, 1H), 7.50-7.56 (m, 2H), 7.27 (s, 4H), 3.81 (s, 3H), 2.36 (s, 3H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 169.0, 150.0, 137.7, 136.5, 134.7, 130.2, 129.5, 129.4, 127.3, 126.6, 126.1, 125.5, 124.4, 123.7, 101.8, 52.0, 21.3. FTIR: 3474, 3357, 2988, 2359, 1670, 1611, 1437, 1231. HR-MS (m/z): Calcd for C<sub>19</sub>H<sub>18</sub>NO<sub>2</sub> [M +H]<sup>+</sup>: 292.1332. Found: 292.1339.



**Methyl 1-amino-4-(4-fluorophenyl)-2-naphthoate (3ac):** yellow solid (86% yield), m. p. 197-199 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  (ppm) 8.42 (d,  $J = 8.2$  Hz, 1H), 7.89 (b, 2H), 7.61-7.66 (m, 2H), 7.51-7.58 (m, 2H), 7.39-7.42 (m, 2H), 7.28 (t,  $J = 8.7$  Hz, 1H), 3.81 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ )  $\delta$  (ppm) 168.9, 161.8 (d,  $J_{\text{C-F}} = 241.3$  Hz) 150.2, 137.0, 134.6, 132.2 (d,  $J_{\text{C-F}} = 7.7$  Hz), 129.6, 127.6, 125.8, 125.6, 125.4, 124.5, 123.7, 115.7 (d,  $J_{\text{C-F}} = 21.0$  Hz), 101.7, 52.0. FTIR: 3468, 3357, 1670, 1614, 1498, 1217. HR-MS (m/z): Calcd for  $\text{C}_{18}\text{H}_{15}\text{FNO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 296.1081. Found: 296.1113.

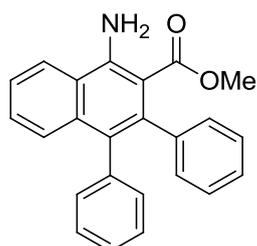


**Methyl 1-amino-4-(4-chlorophenyl)-2-naphthoate (3ad):** yellow solid (86% yield), m. p. 152-154 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  (ppm) 8.42 (d,  $J = 8.2$  Hz, 1H), 7.91 (b, 2H), 7.62-7.65 (m, 2H), 7.50-7.58 (m, 4H), 7.40 (d,  $J = 8.2$  Hz, 2H), 3.81 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ )  $\delta$  (ppm) 168.9, 150.3, 139.5, 134.4, 132.1, 129.7, 129.0, 127.7, 125.8, 125.7, 125.2, 124.5, 123.7, 101.8, 52.0. FTIR: 3447, 3346, 1668, 1615, 1438, 1238. HR-MS (m/z): Calcd for  $\text{C}_{18}\text{H}_{15}\text{ClNO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 312.0785. Found: 312.0804.

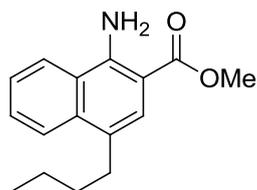


**Methyl 1-amino-3-ethyl-4-phenyl-2-naphthoate (3ae)** yellow solid (82 % yield), m. p. 138-139 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  (ppm) 8.24 (d,  $J = 8.3$  Hz, 1H), 7.47 (t,  $J = 7.4$  Hz, 2H), 7.31-7.41 (m, 3H), 7.18 (d,  $J = 7.4$  Hz, 2H), 7.00 (d,  $J = 8.3$  Hz, 1H), 6.19 (b, 2H), 3.86 (s, 3H), 2.45 (m, 2H), 0.88(t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ )  $\delta$  (ppm) 170.4, 143.9, 140.0, 137.1, 134.4, 131.2, 128.9, 127.8, 127.4, 127.0, 126.5, 124.5, 123.4, 121.8, 110.4, 52.4, 25.2, 16.0. FTIR: 3504, 3392, 2900, 2359, 1686, 1599, 1428, 1240. HR-MS (m/z): Calcd for

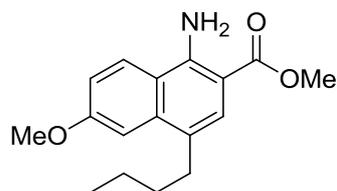
$C_{20}H_{20}NO_2$   $[M+H]^+$ : 306.1489. Found: 306.1482.



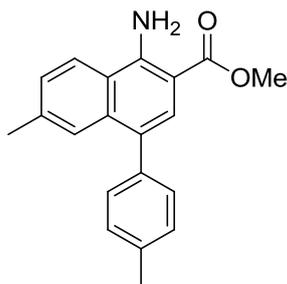
**Methyl 1-amino-3,4-diphenyl-2-naphthoate (3af)**: yellow solid (65% yield), m. p. 189-191 °C.  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 8.35 (d,  $J = 7.8$  Hz, 1H), 7.42-7.50 (m, 2H), 7.26 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 0.94$  Hz, 1H), 7.13-7.21 (m, 3H), 7.00-7.05 (m, 5H), 6.94-6.96 (m, 2H), 6.50 (b, 2H), 3.23 (s, 3H).  $^{13}C$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 170.0, 144.7, 141.8, 139.4, 137.5, 134.1, 132.1, 130.0, 128.5, 128.1, 127.3, 127.1, 126.9, 126.7, 126.3, 125.3, 123.7, 122.5, 109.9, 51.6. FTIR: 3431, 3330, 1657, 1608, 1430, 1255. HR-MS (m/z): Calcd for  $C_{24}H_{20}NO_2$   $[M+H]^+$ : 354.1488. Found: 354.1484.



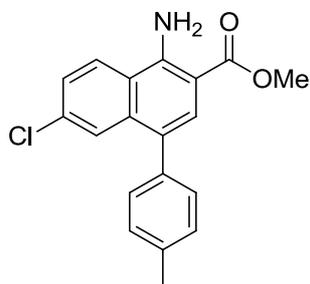
**Methyl 1-amino-4-butyl-2-naphthoate (3ah)** yellow solid (75% yield), m. p. 88-89 °C.  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 8.34 (d,  $J = 8.4$  Hz, 1H), 7.89 (d,  $J = 8.4$  Hz, 1H), 7.60-7.64 (m, 3H), 7.56 (s, 1H), 7.46-7.49 (t,  $J = 7.5$  Hz, 1H), 3.81 (s, 3H), 2.81 (t,  $J = 7.6$  Hz, 2H), 1.52-1.57 (m, 2H), 1.33-1.37 (m, 2H), 0.89 (t,  $J = 7.4$  Hz, 3H).  $^{13}C$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 169.1, 149.4, 135.2, 129.2, 125.8, 125.1, 124.5, 124.1, 101.7, 51.8, 33.0, 32.1, 22.7, 14.4. FTIR: 3477, 3370, 2953, 2358, 1683, 1617, 1436, 1232. HR-MS (m/z): Calcd for  $C_{16}H_{19}NNaO_2$   $[M+Na]^+$ : 280.1308. Found: 280.1336.



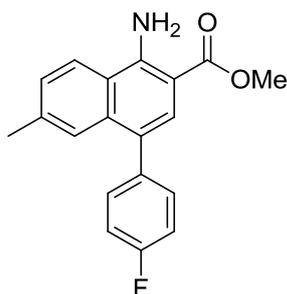
**Methyl 1-amino-4-butyl-6-methoxy-2-naphthoate (3dh)** yellow solid (77% yield), m. p. 89-91 °C.  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 8.26 (d,  $J = 9.2$  Hz, 1H), 7.57 (b, 2H), 7.53 (s, 2H), 7.17 (d,  $J = 2.0$  Hz, 1H), 7.12 (dd,  $J_1 = 9.0$  Hz,  $J_2 = 2.0$  Hz, 1H), 3.88 (s, 3H), 3.79 (s, 3H), 2.78 (t,  $J = 7.6$  Hz, 2H), 1.55-1.58 (m, 2H), 1.34-1.38 (m, 2H), 0.91 (t,  $J = 7.3$  Hz, 2H).  $^{13}C$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 169.0, 159.9, 149.5, 137.1, 126.5, 123.6, 118.6, 115.7, 104.5, 100.4, 55.6, 51.7, 32.5, 32.0, 22.6, 14.4. FTIR: 3460, 3353, 2910, 2359, 1661, 1604, 1438, 1238. HR-MS (m/z):  $C_{17}H_{21}NNaO_3$   $[M+Na]^+$ : 310.1414. Found: 310.1421.



**Methyl 1-amino-6-methyl-4-(p-tolyl)-2-naphthoate (3bb)** yellow solid (88% yield), m. p. 161-163 °C.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 8.30 (d,  $J = 8.6$  Hz, 1H), 7.78 (b, 2H), 7.56 (s, 1H), 7.46 (s, 1H), 7.35 (d,  $J = 8.6$  Hz, 1H), 7.23-7.27 (m, 4H), 3.79 (s, 3H), 2.34 (s, 3H), 2.34 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 150.0, 139.0, 137.9, 136.4, 135.0, 130.1, 129.5, 127.5, 127.4, 126.2, 125.2, 124.4, 121.8, 101.3, 51.9, 21.9, 21.3. FTIR: 3465, 3357, 1659, 1617, 1437, 1234. HR-MS (m/z): Calcd for  $\text{C}_{20}\text{H}_{19}\text{NNaO}_2$  [ $\text{M} + \text{Na}$ ] $^+$ : 328.1308. Found: 328.1338.

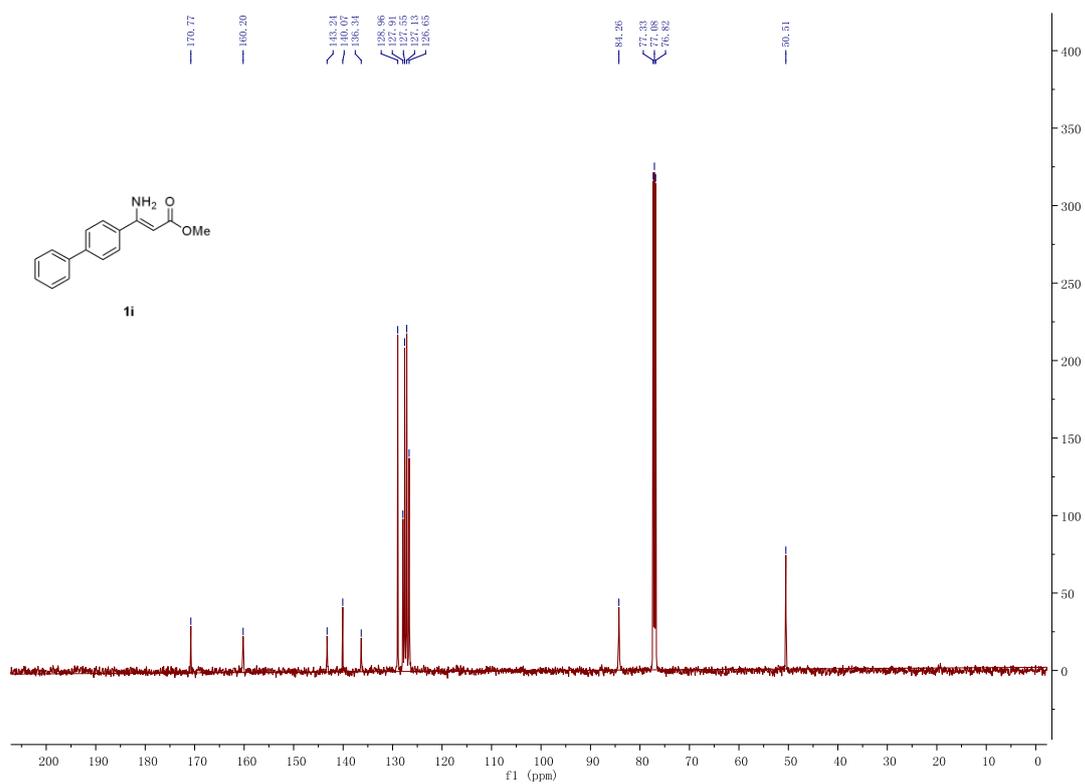
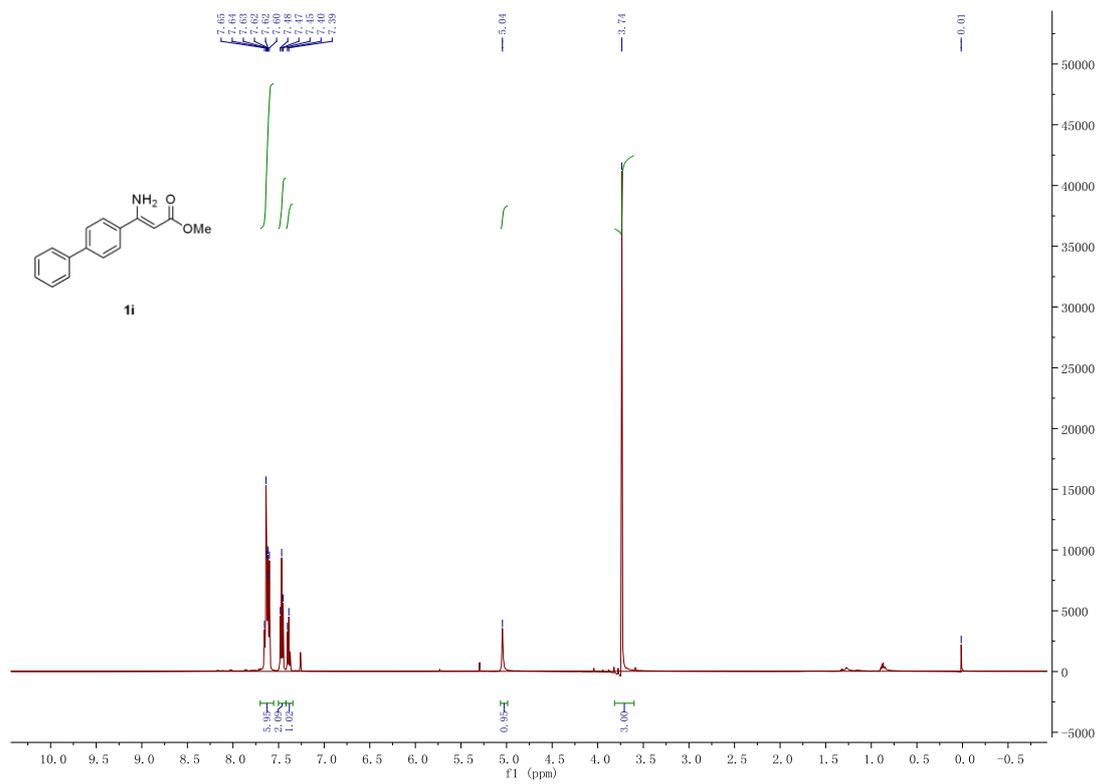


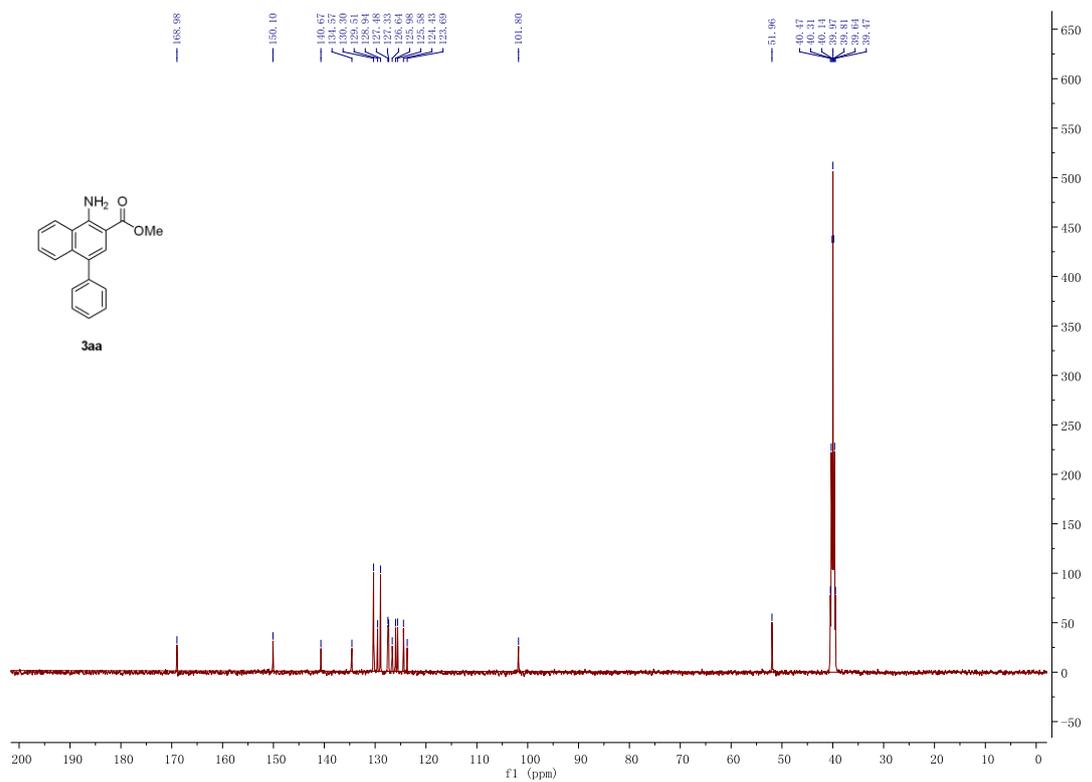
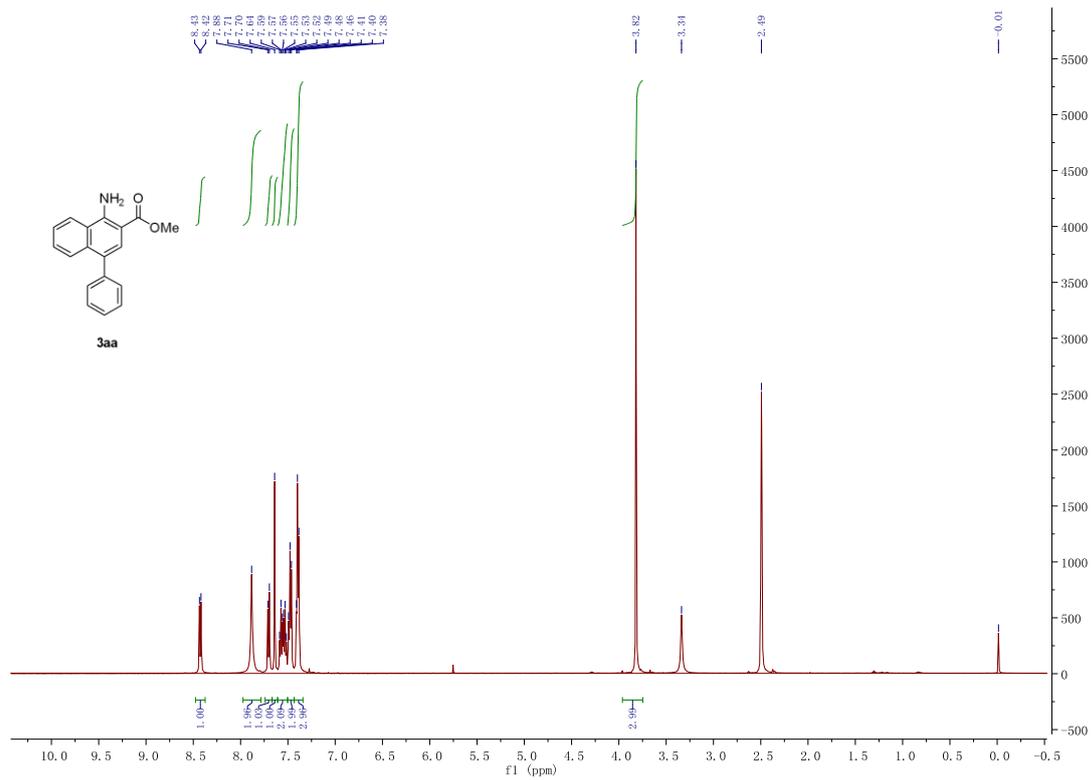
**Methyl 1-amino-6-chloro-4-(p-tolyl)-2-naphthoate (3fb)**: yellow solid (85% yield), m. p. 195-197 °C.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 8.45 (d,  $J = 8.6$  Hz, 1H), 7.91 (b, 2H), 7.66 (s, 1H), 7.59 (d,  $J = 2.1$  Hz, 1H), 7.53 (dd,  $J_1 = 9.0$  Hz,  $J_2 = 2.0$  Hz, 1H), 7.22-7.27 (m, 4H), 3.80 (s, 3H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 168.7, 149.8, 137.0, 136.8, 135.9, 134.5, 130.1, 129.7, 128.8, 127.0, 125.6, 124.6, 122.2, 102.4, 52.1, 21.3. FTIR: 3468, 3363, 2966, 1661, 1611, 1438, 1229. HR-MS (m/z): Calcd for  $\text{C}_{19}\text{H}_{17}\text{ClNO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 326.0947. Found: 326.0945.

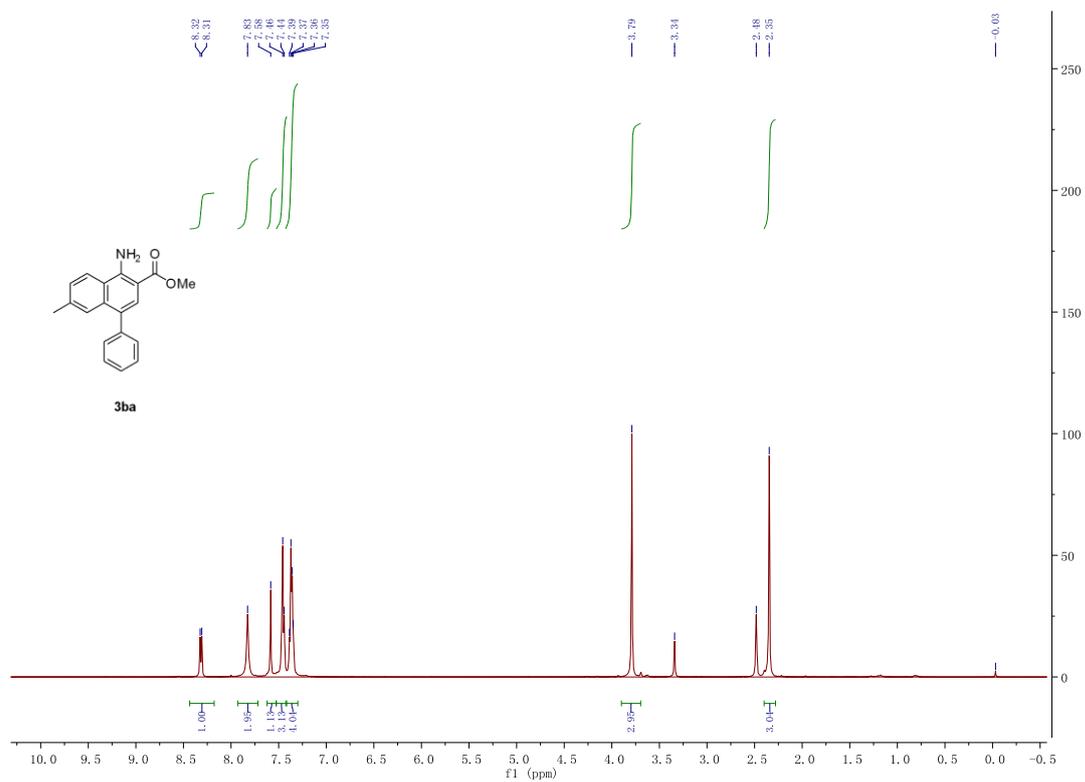
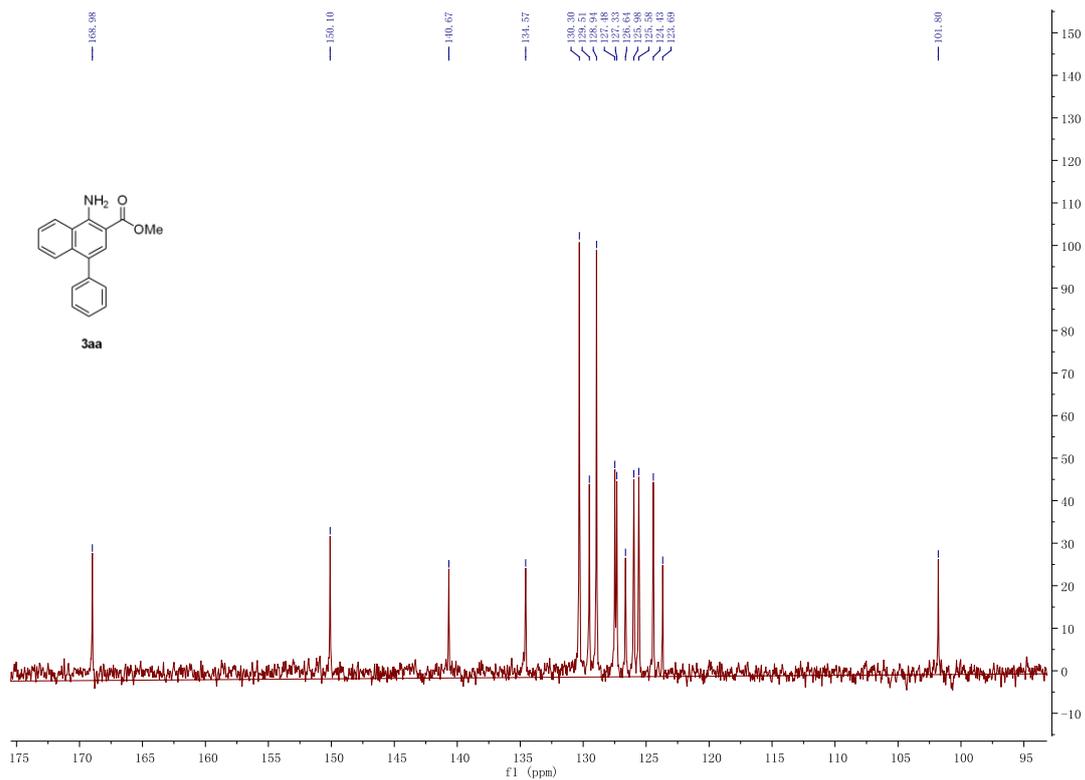


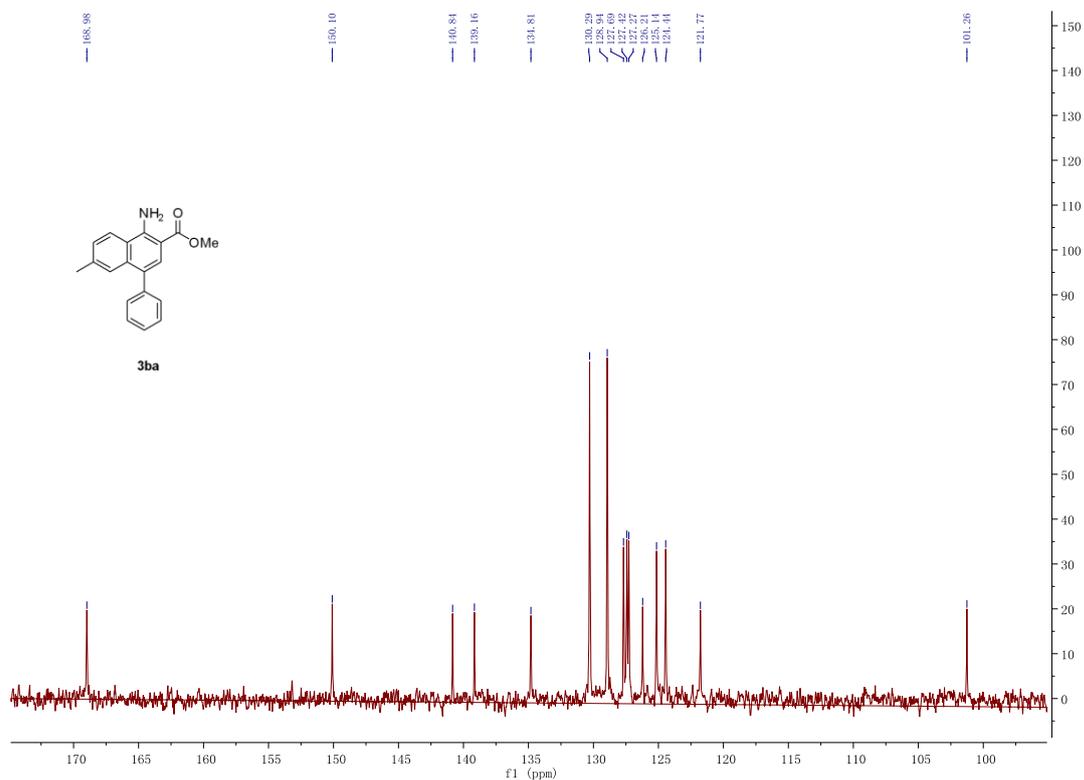
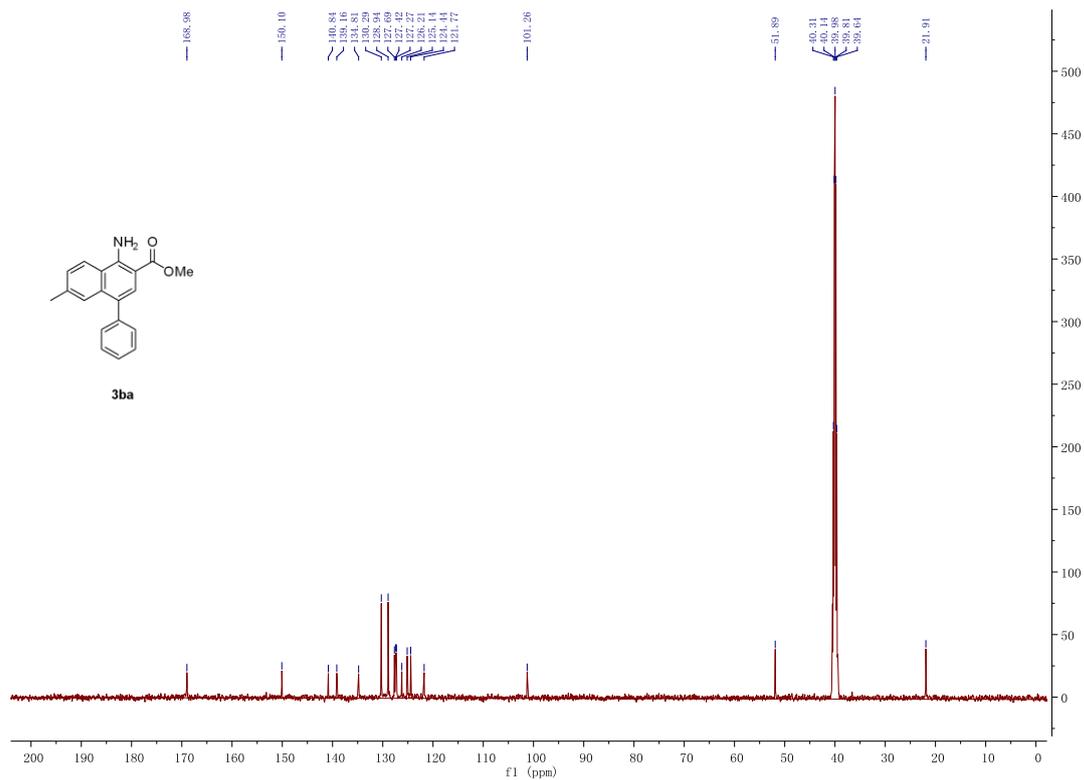
**Methyl 1-amino-4-(4-fluorophenyl)-6-methyl-2-naphthoate (3bc)**: yellow solid (82% yield), m. p. 152-154 °C.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 8.31 (d,  $J = 8.4$  Hz, 1H), 7.82 (b, 2H), 7.57 (s, 1H), 7.36-7.40 (m, 4H), 7.28 (t,  $J = 8.7$  Hz, 1H), 3.79 (s, 3H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 168.9, 161.7 (d,  $J_{\text{C-F}} = 242.5$  Hz), 150.2, 139.3, 137.1, 134.9, 132.2 (d,  $J_{\text{C-F}} = 7.5$  Hz), 127.8, 127.5, 125.0 (d,  $J_{\text{C-F}} = 4.8$  Hz), 124.5, 121.8, 115.7 (d,  $J_{\text{C-F}} = 20.9$  Hz), 101.3, 51.9, 21.9. FTIR: 3480, 3327, 1678, 1600, 1437, 1217. HR-MS (m/z): Calcd for  $\text{C}_{19}\text{H}_{17}\text{FNO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 310.1239. Found: 310.1263.

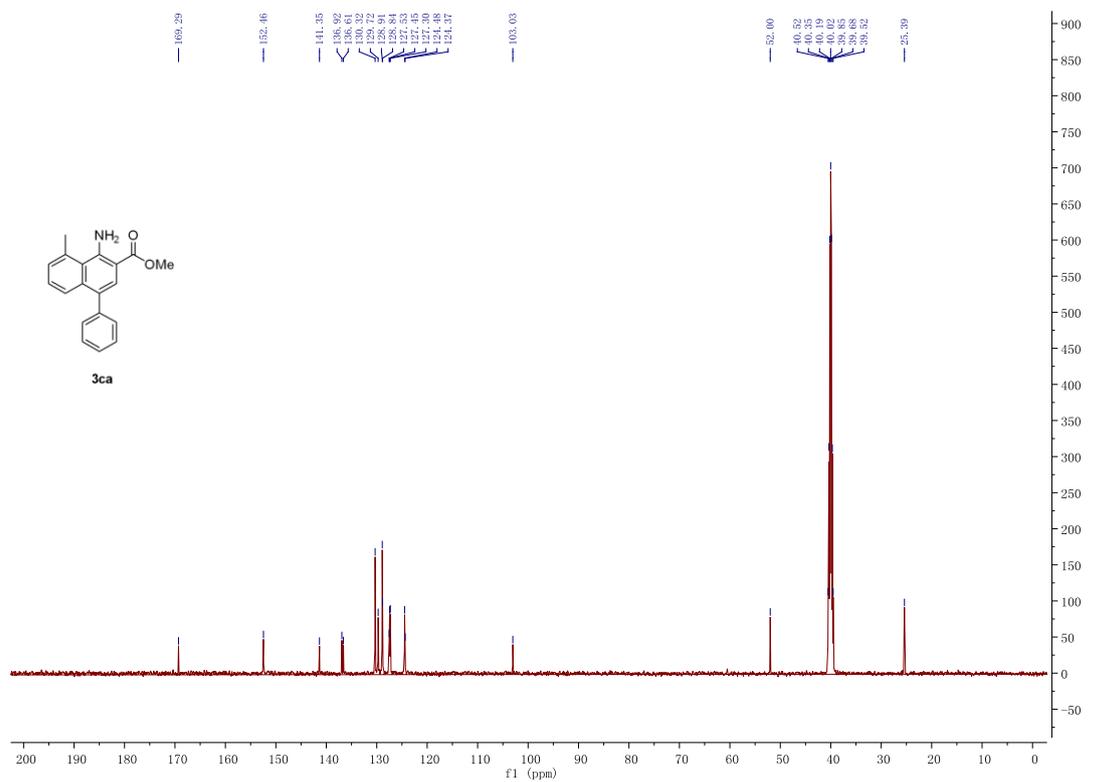
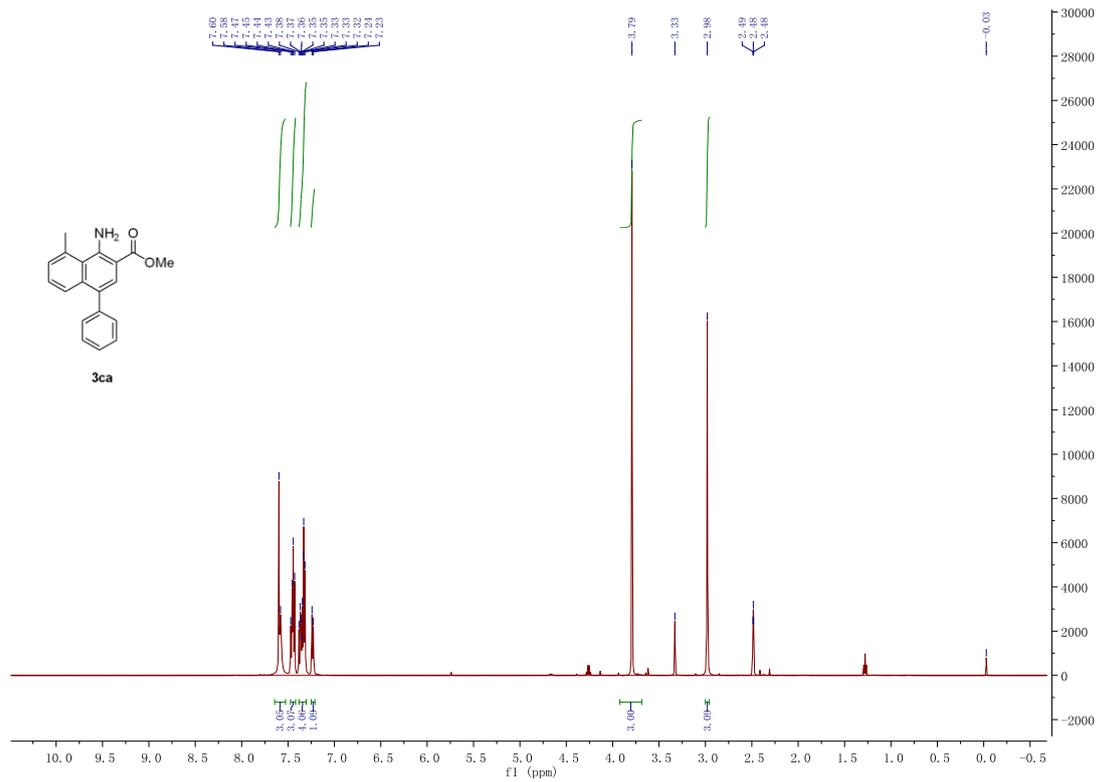
#### 4. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra

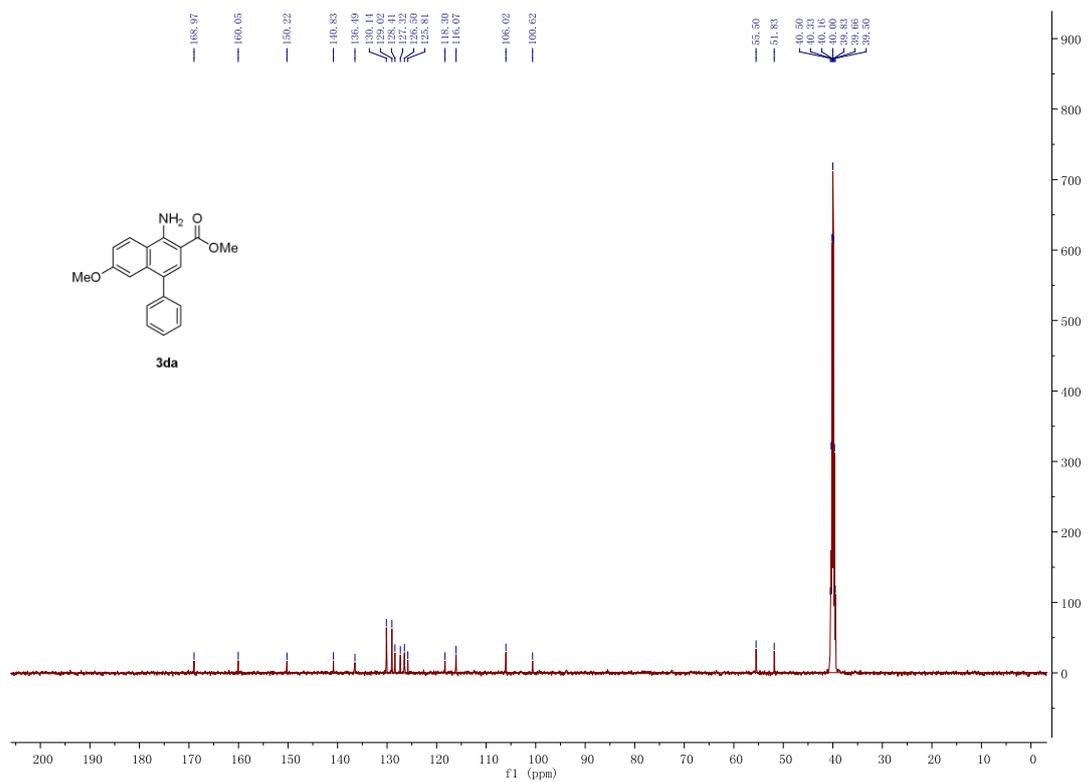
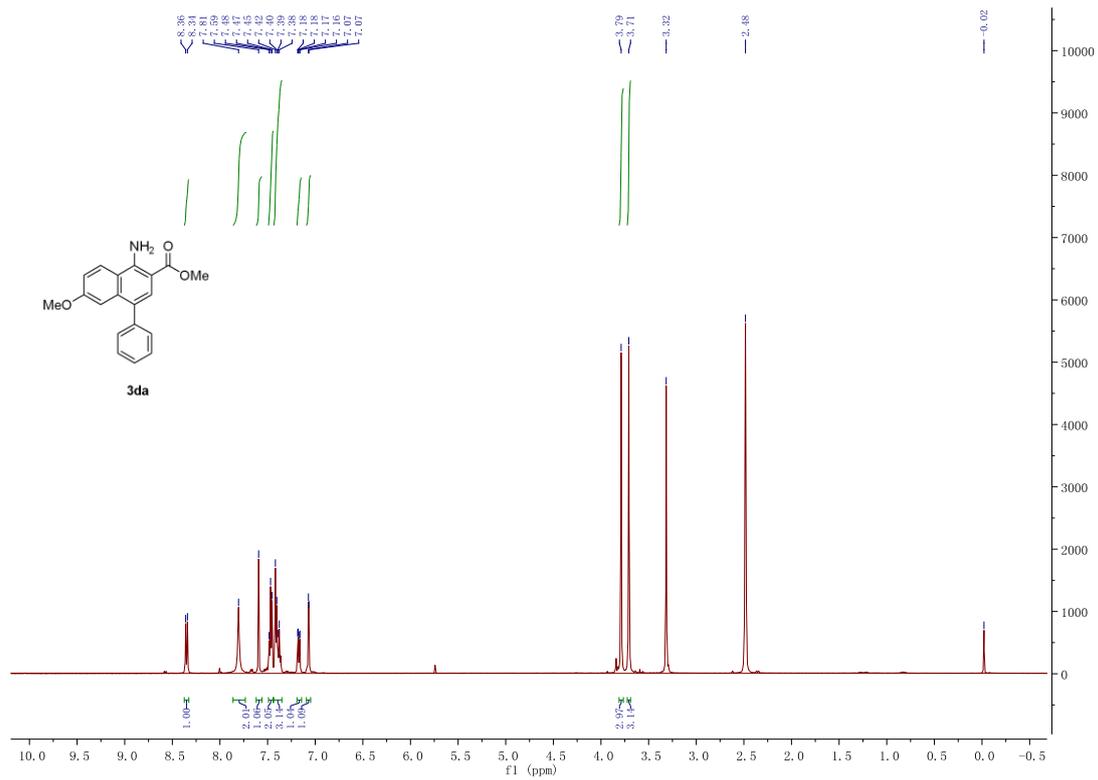


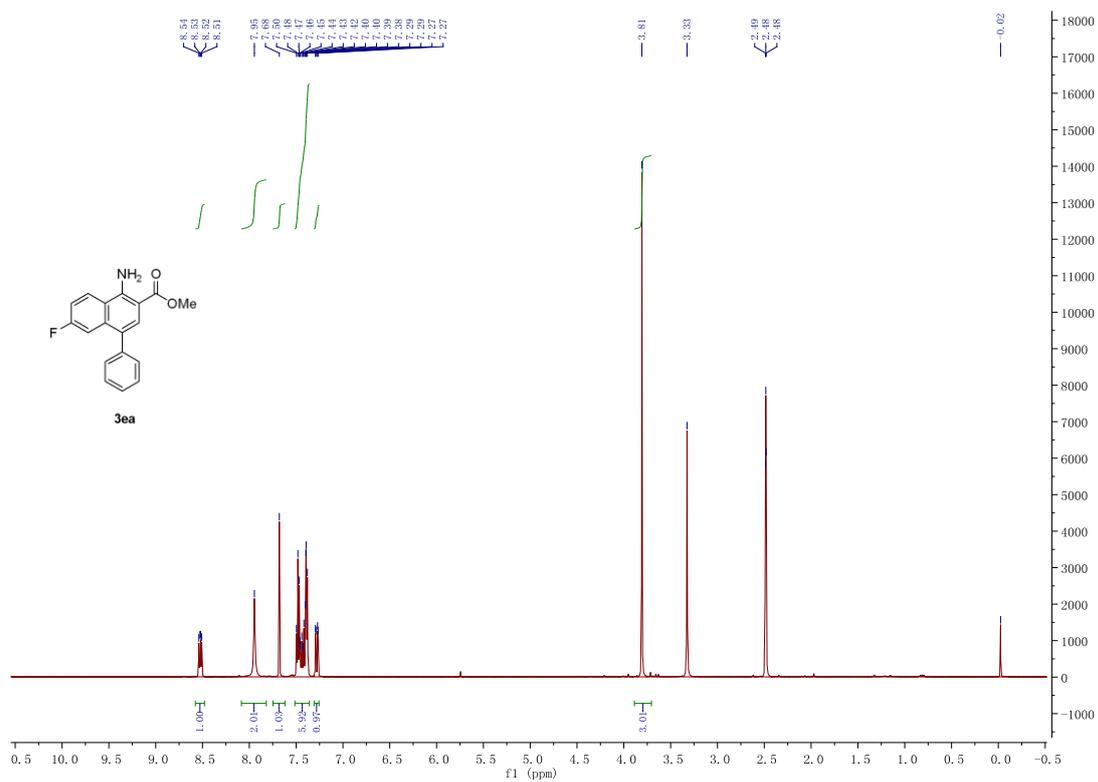
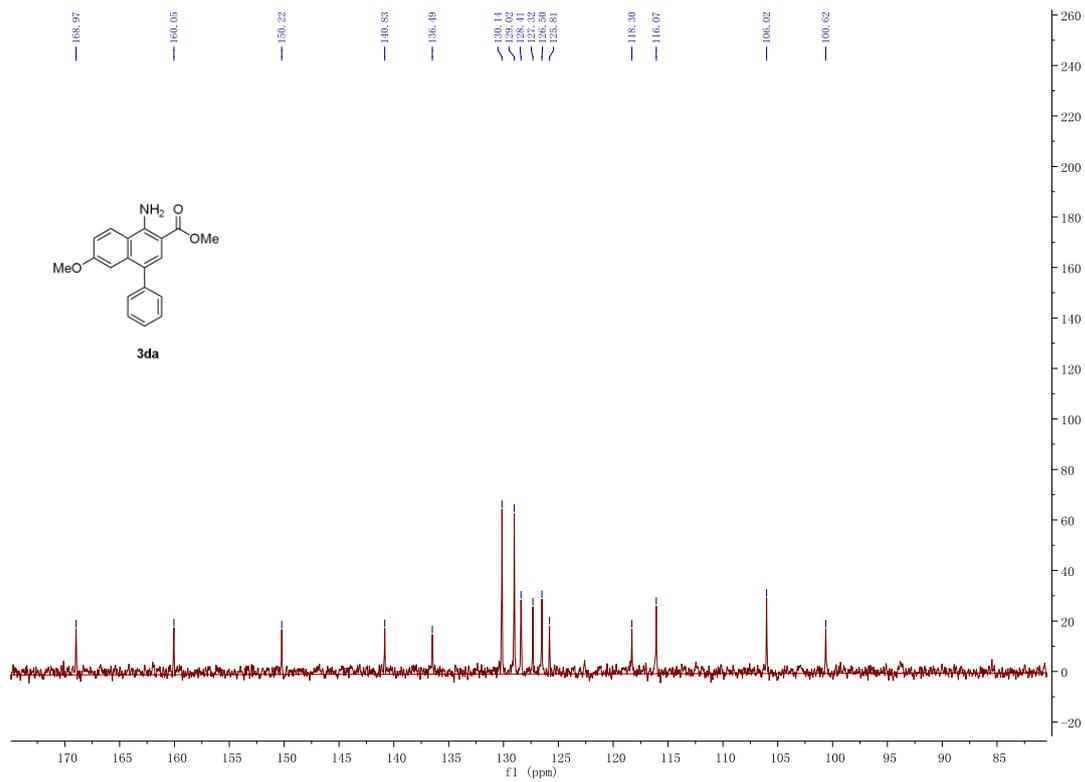


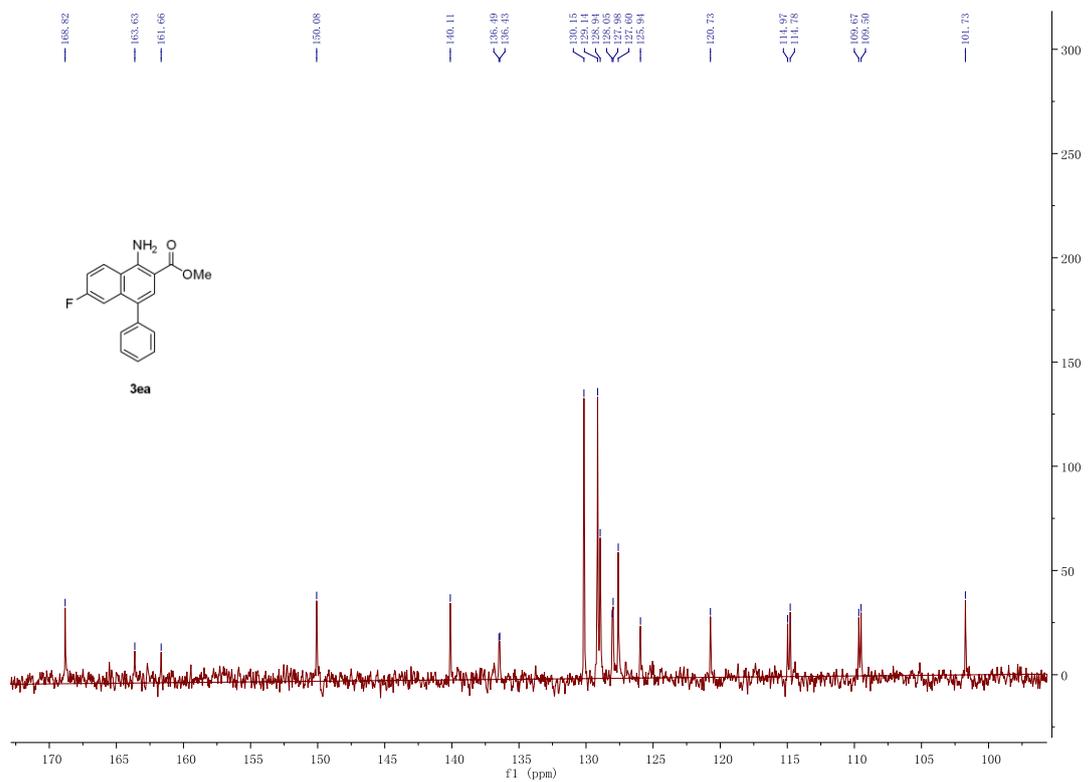
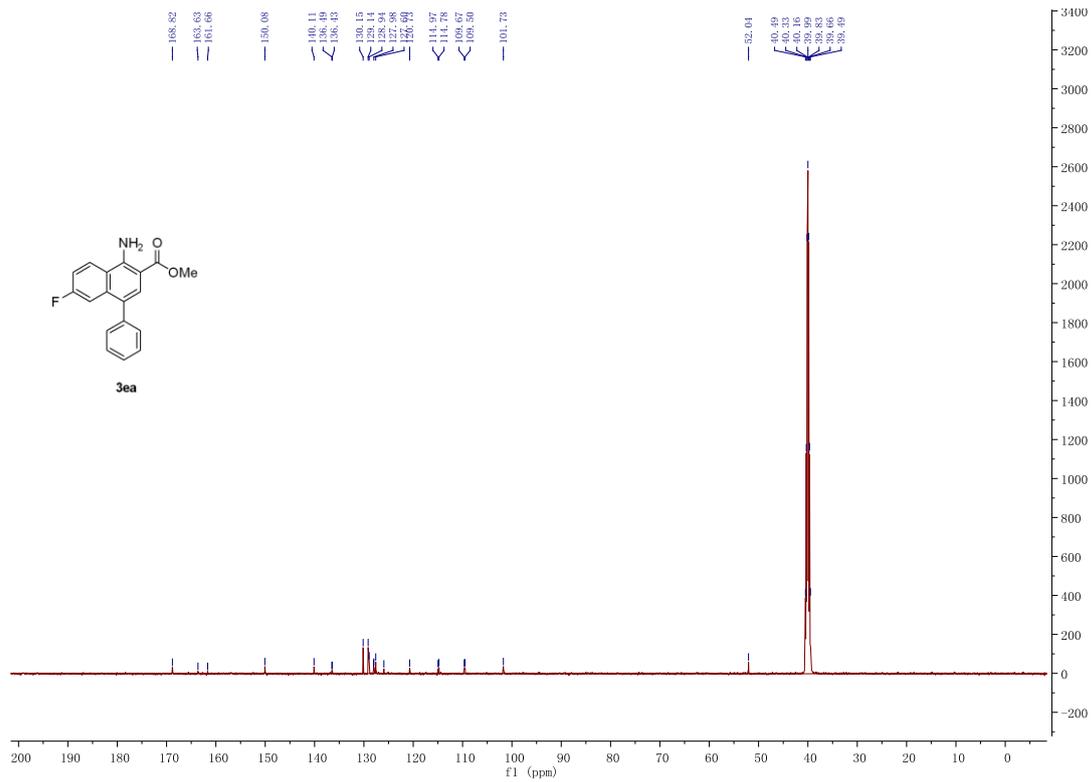




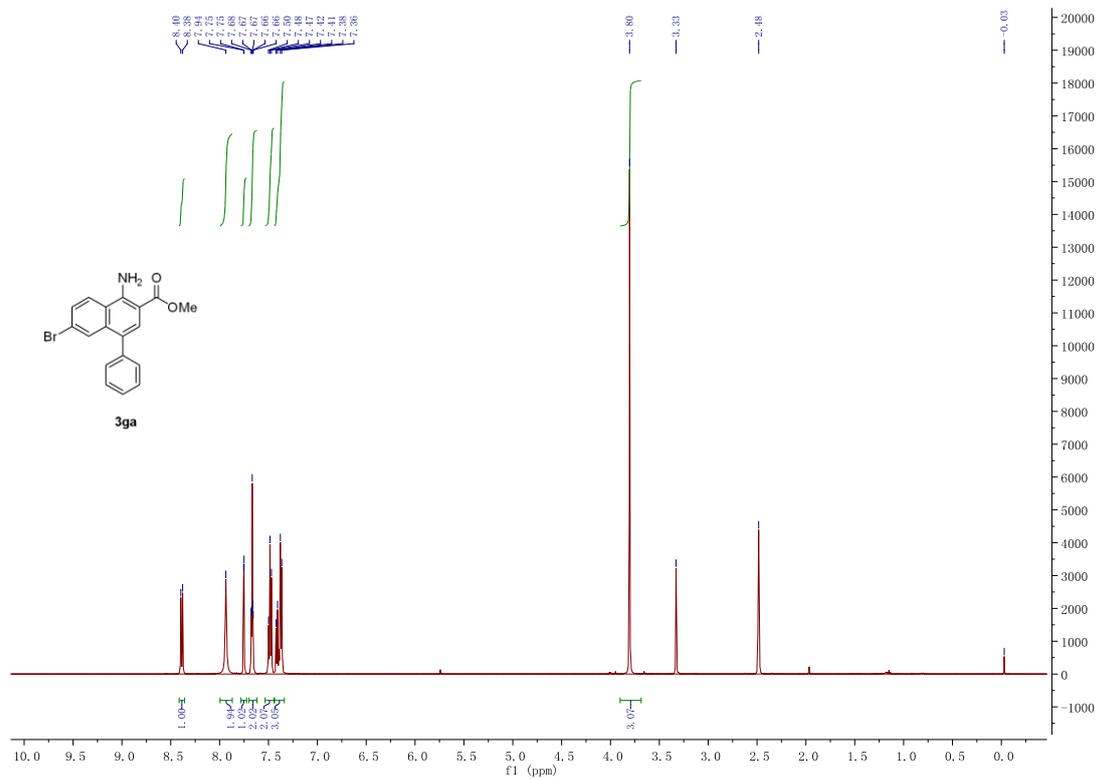
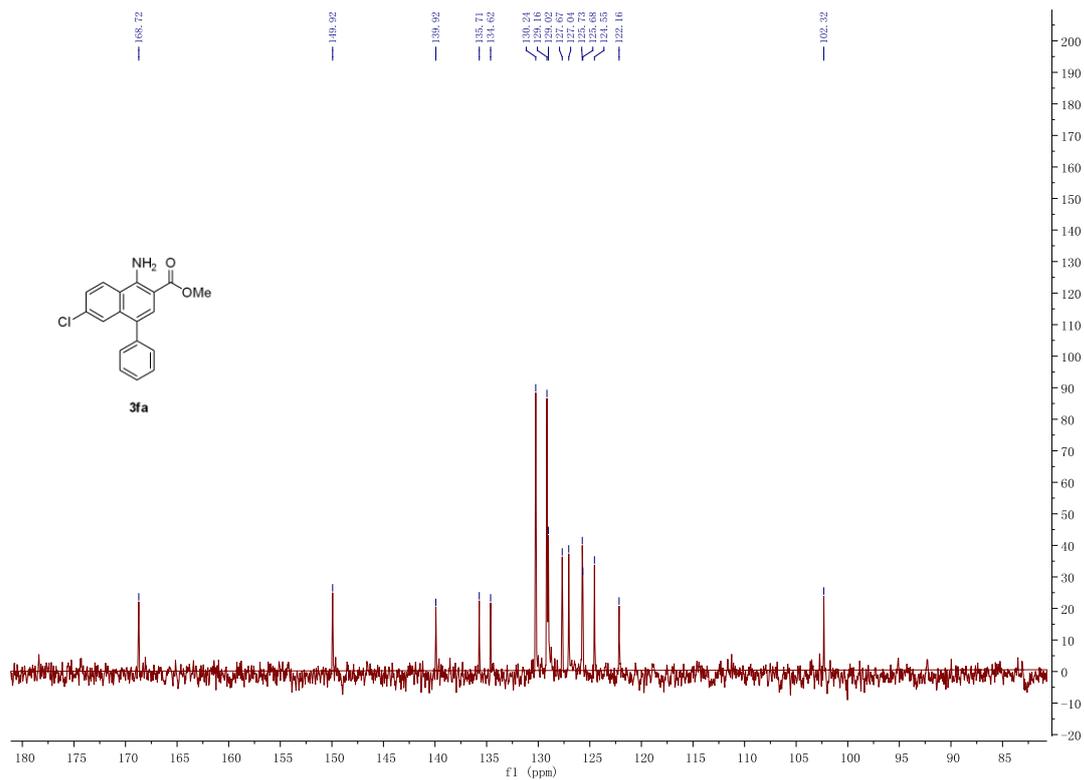


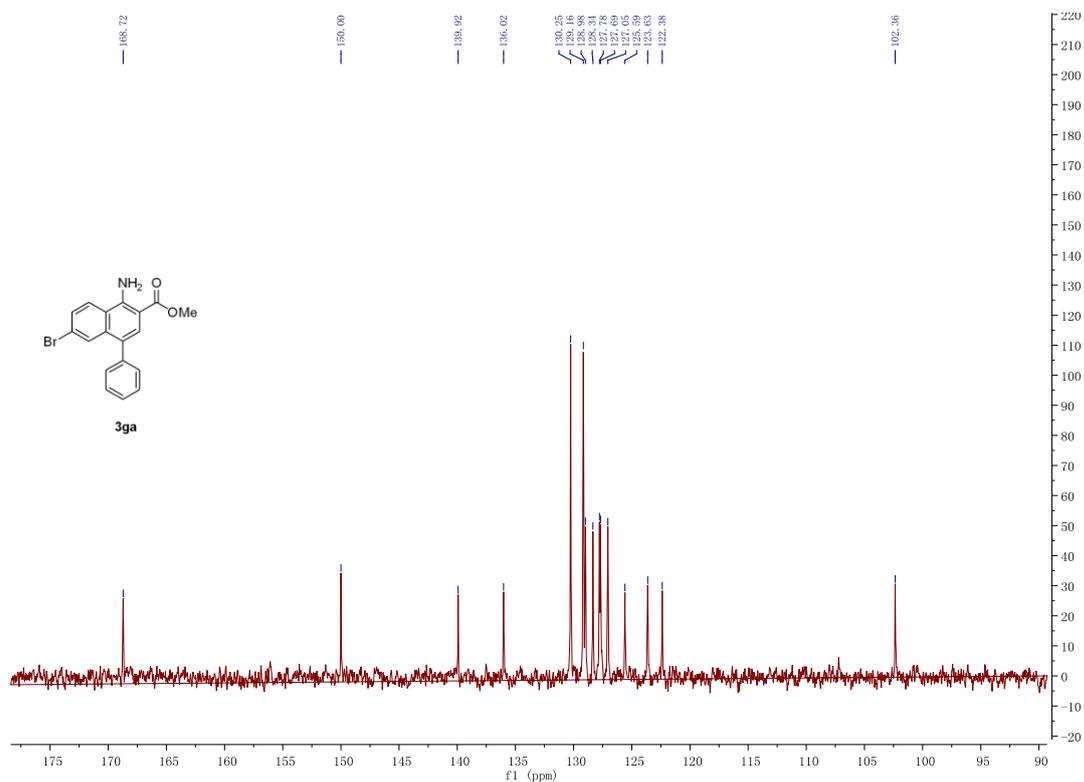
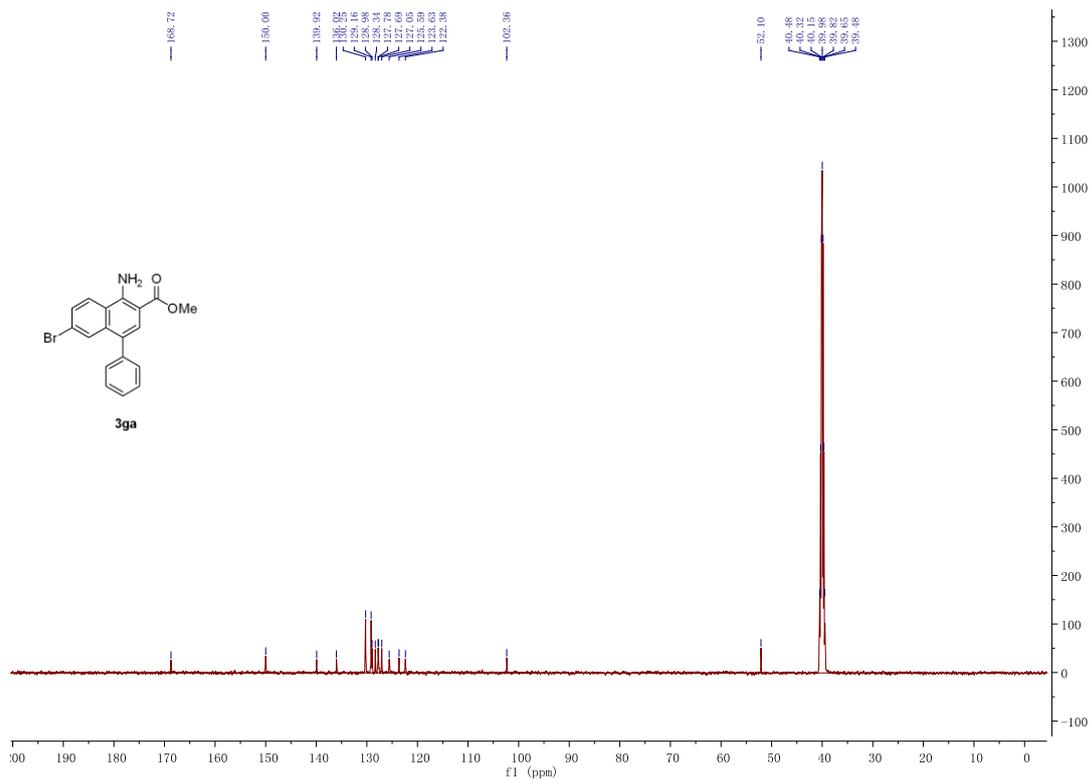


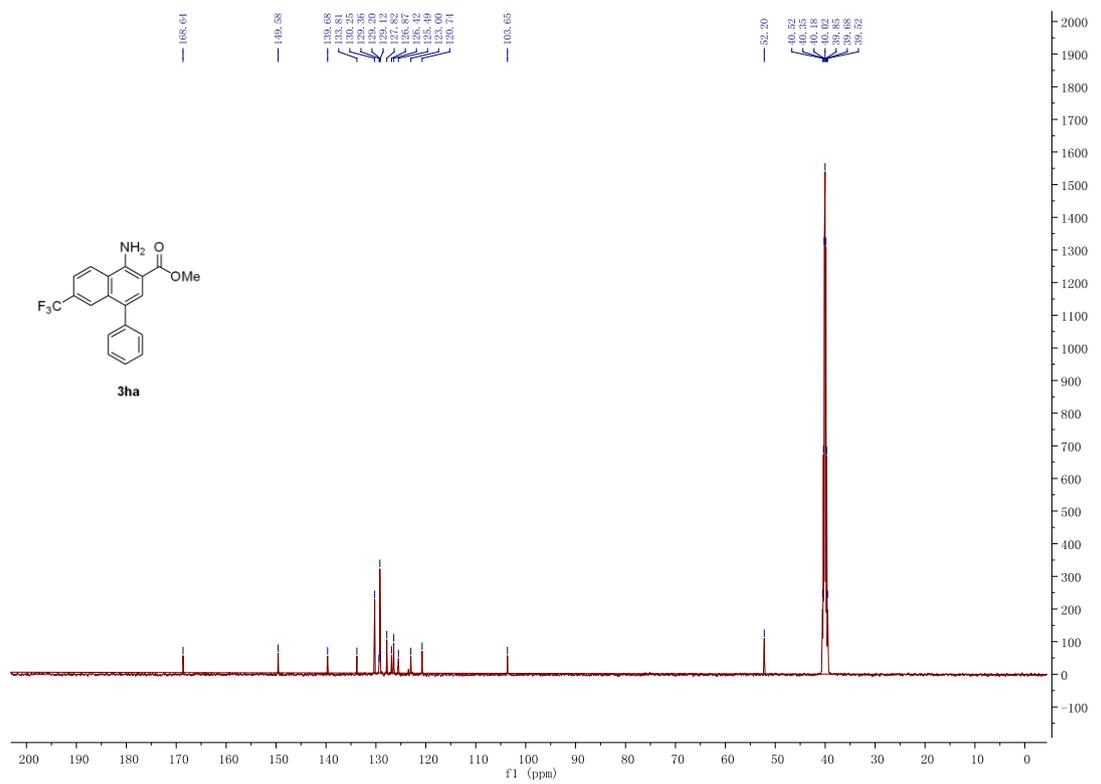
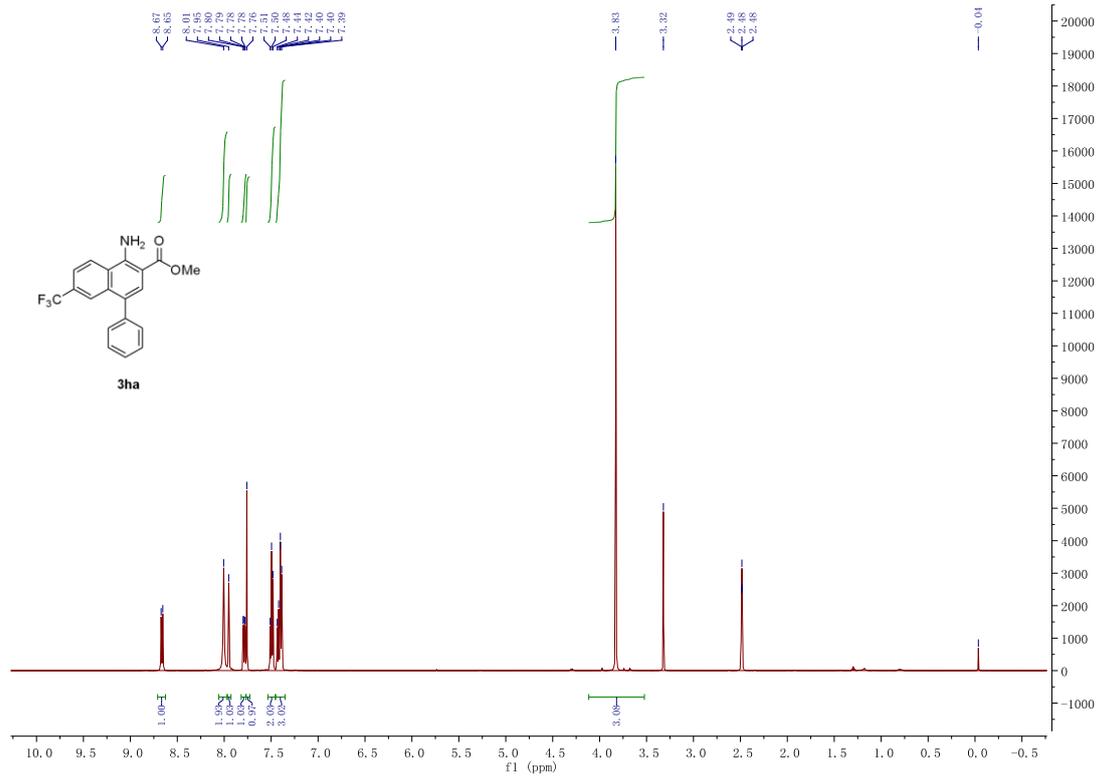


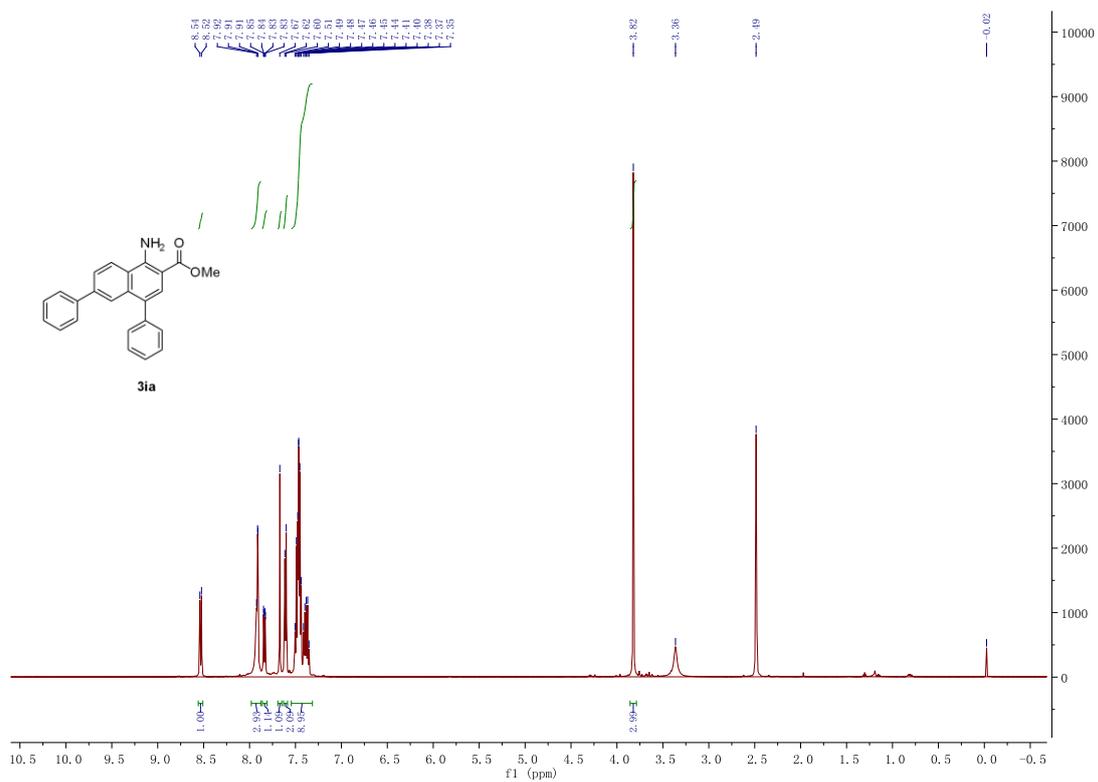
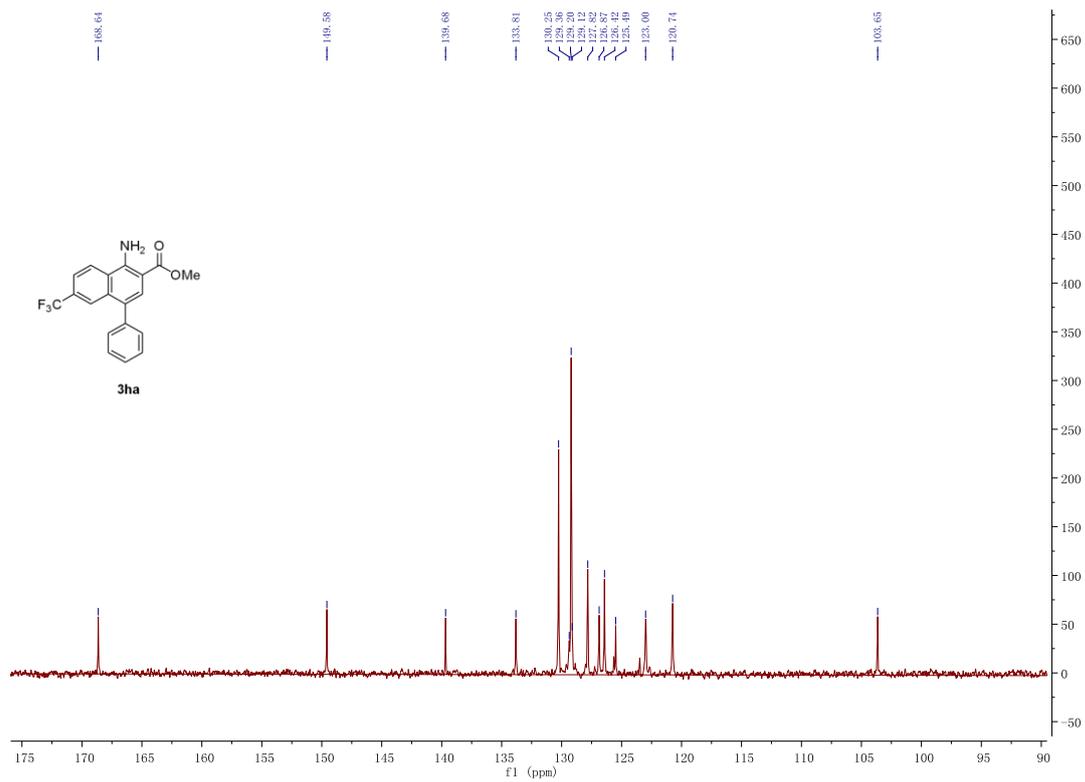


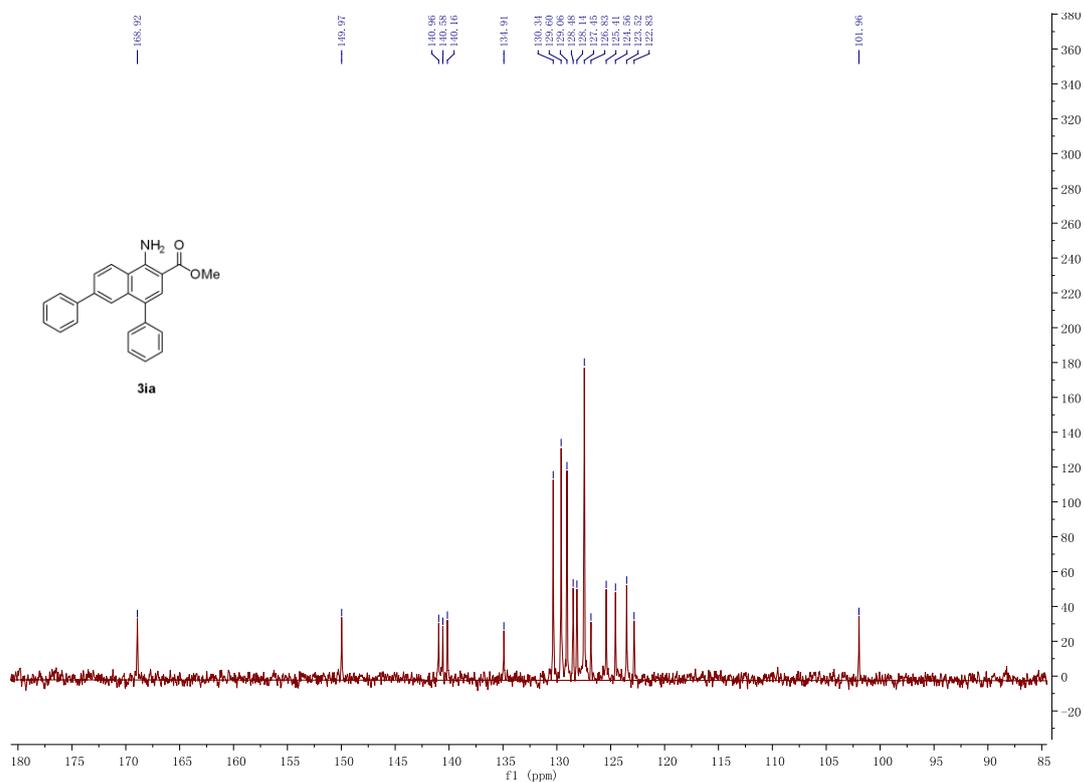
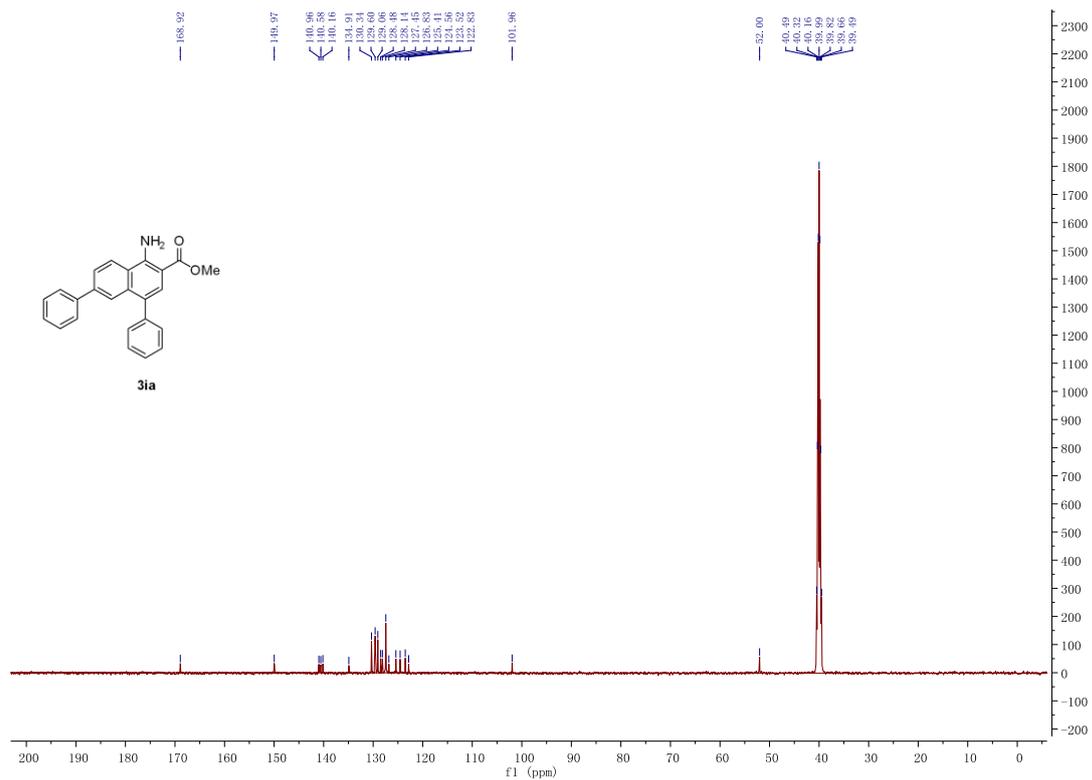


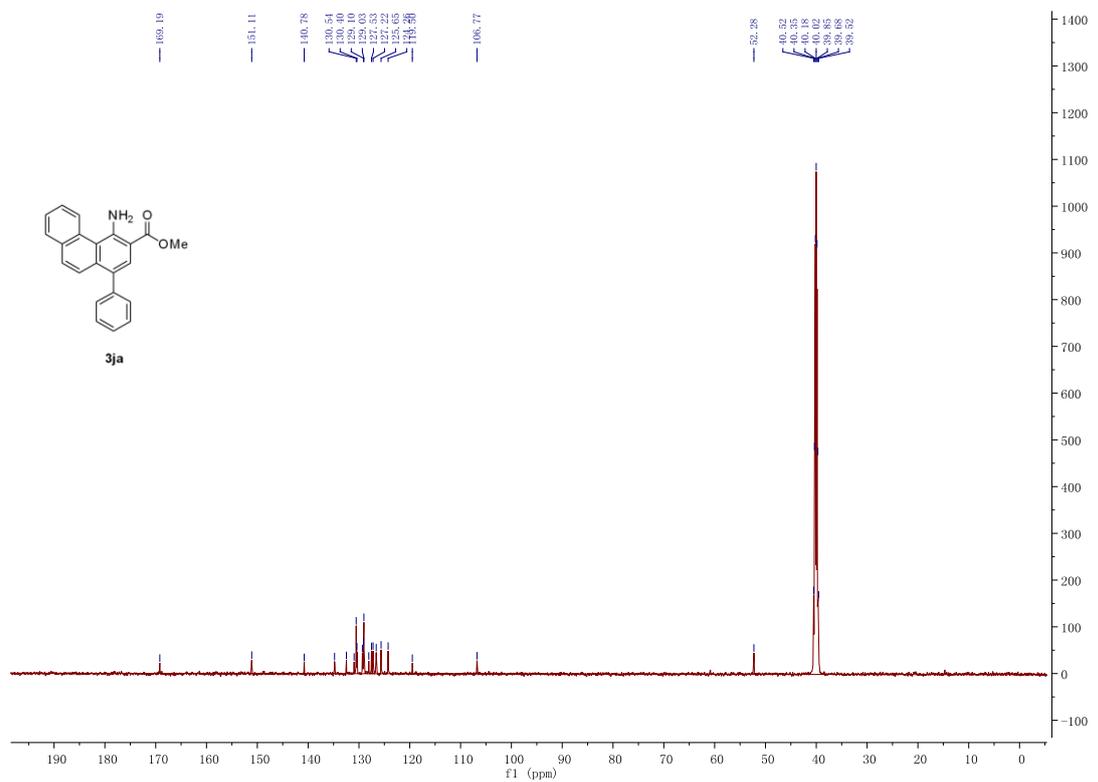
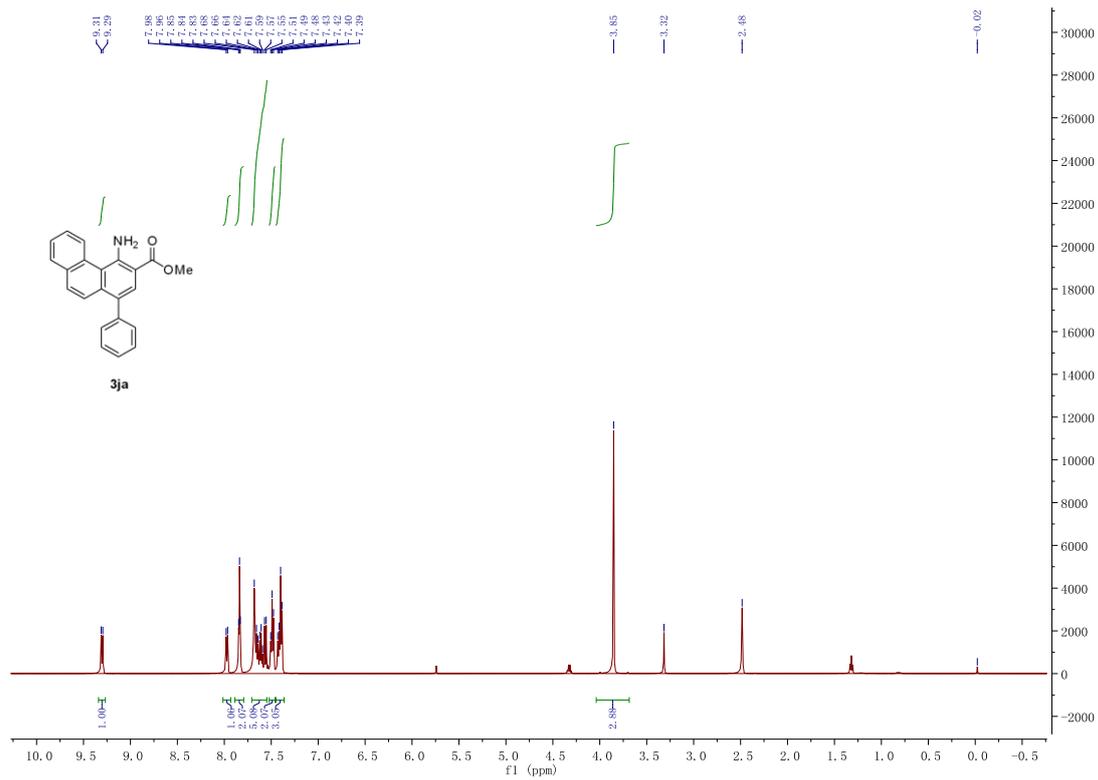


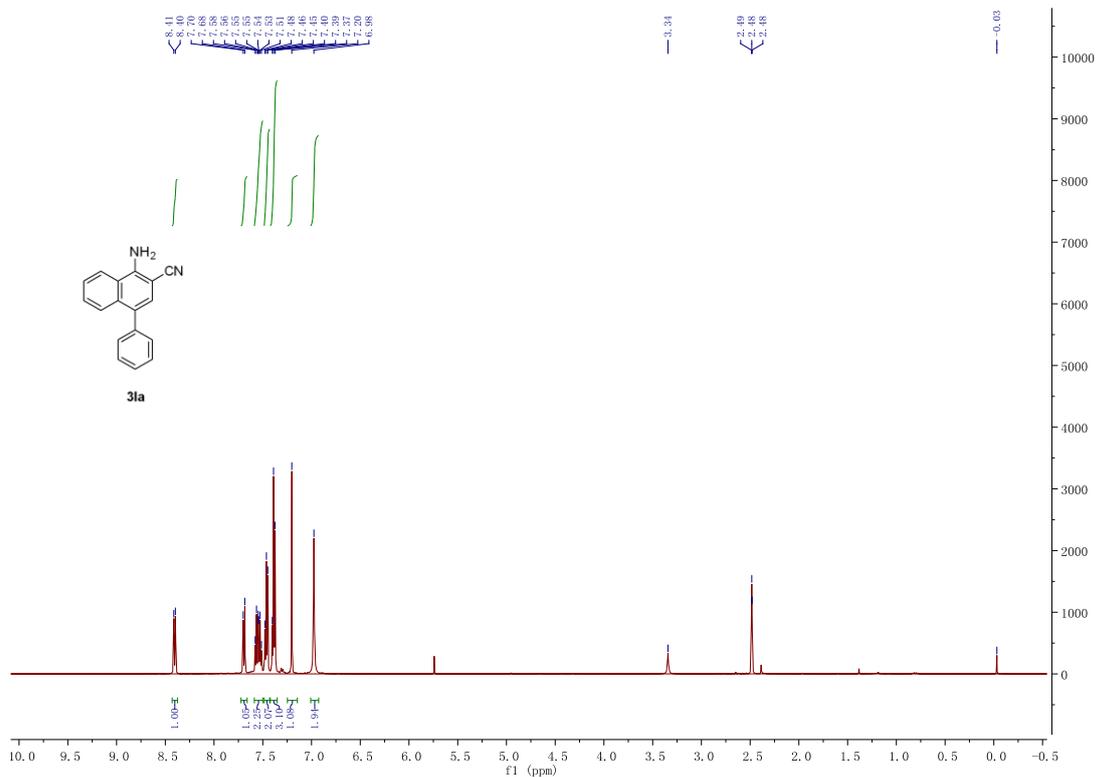
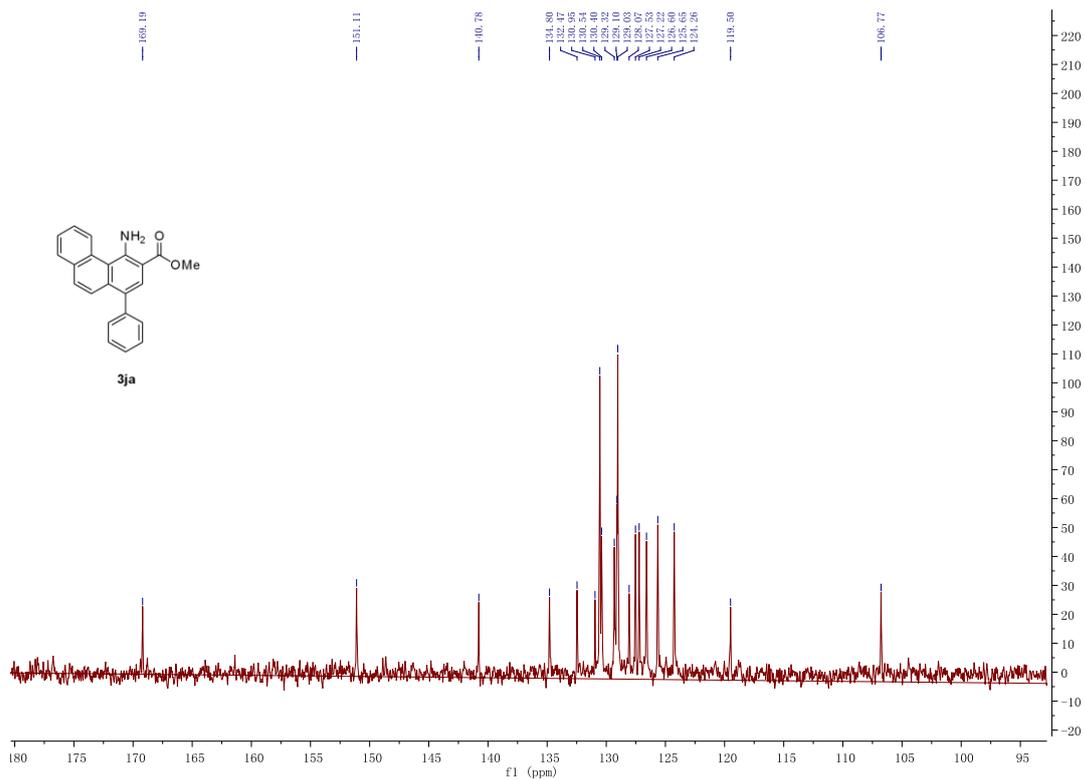


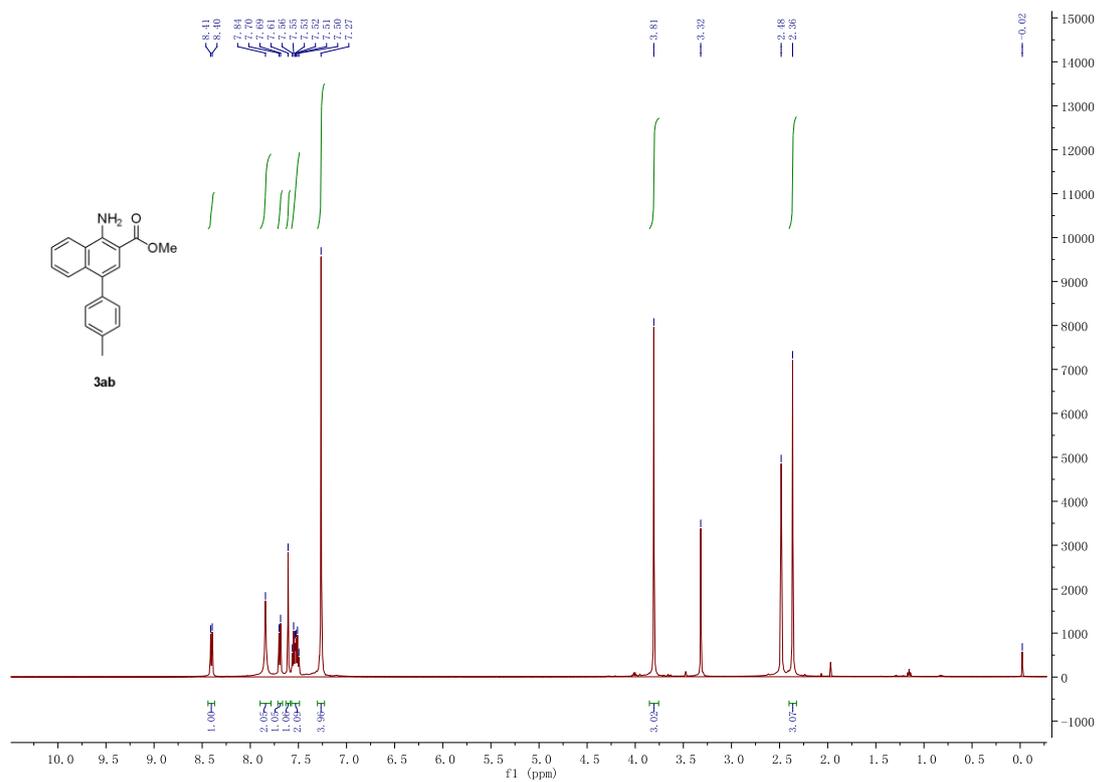
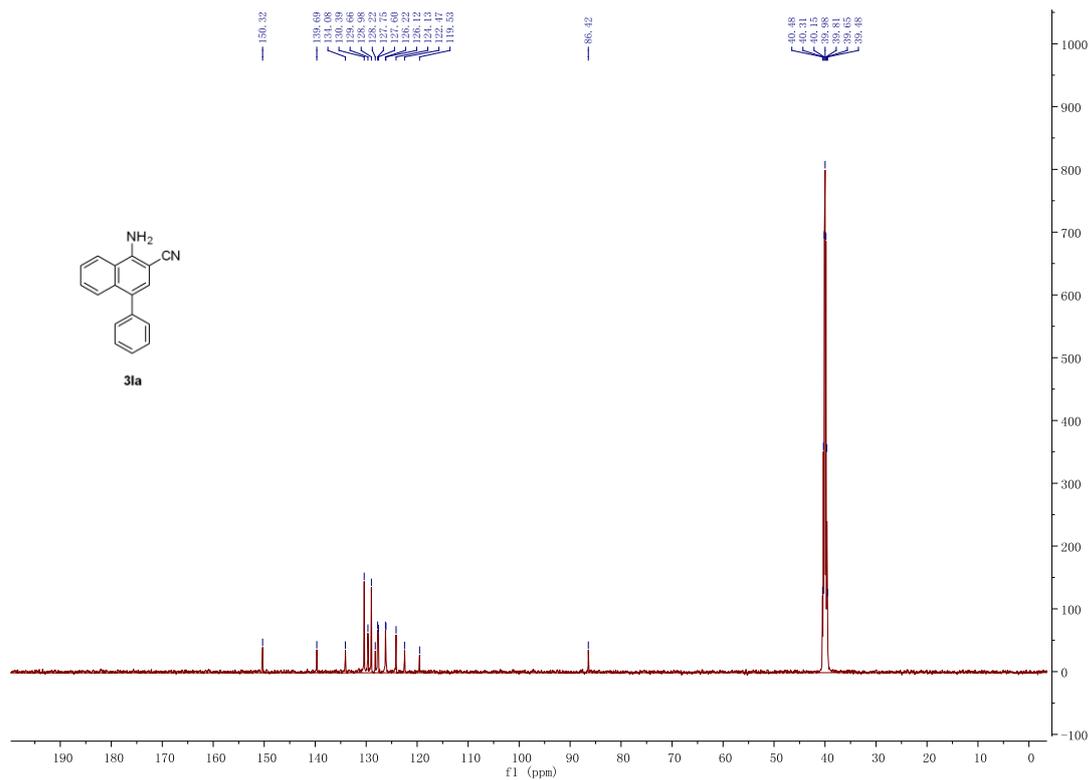




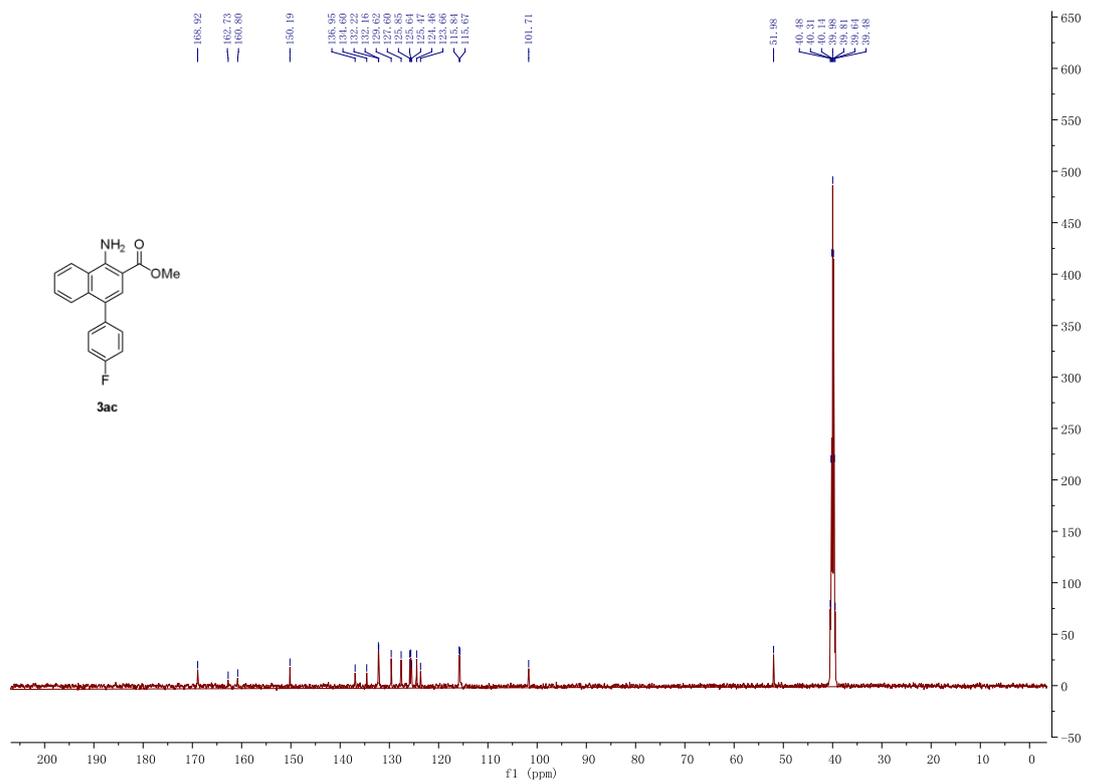
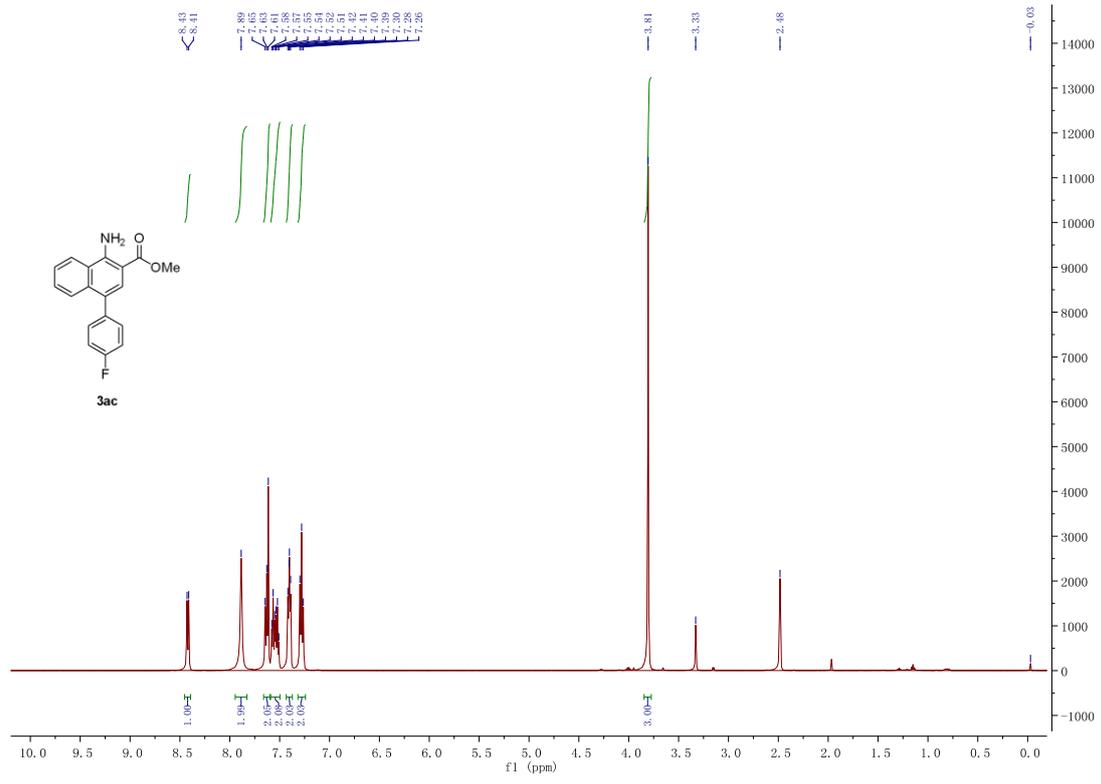


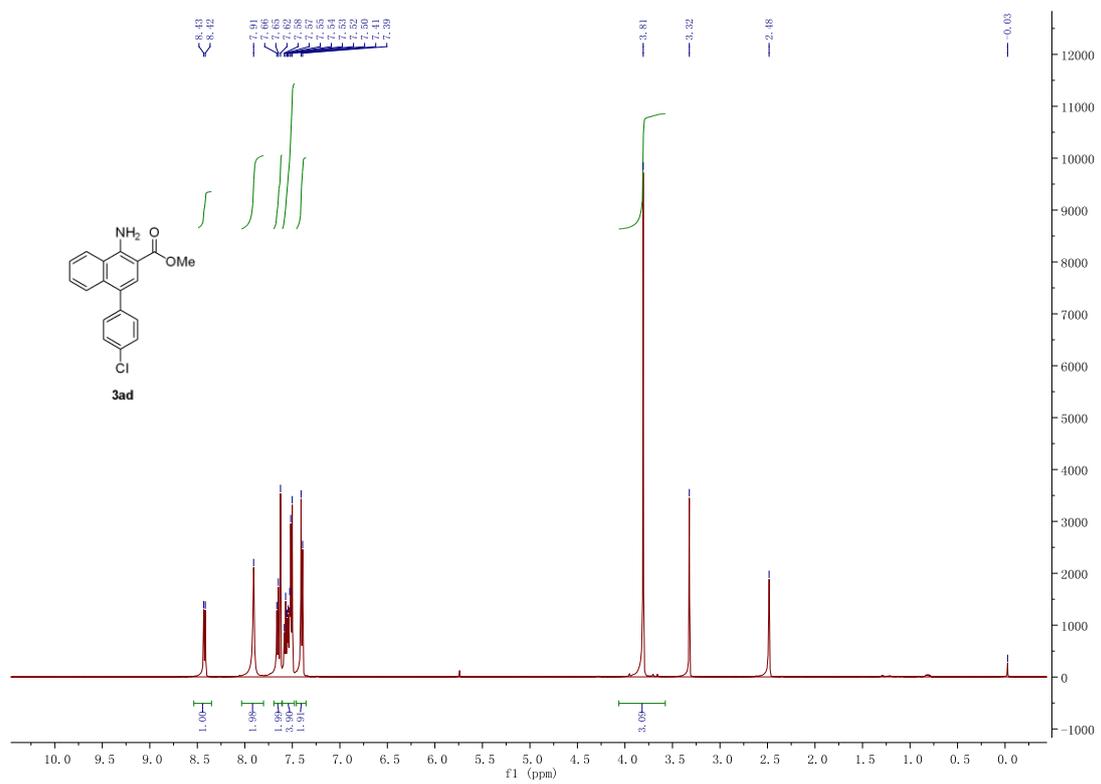
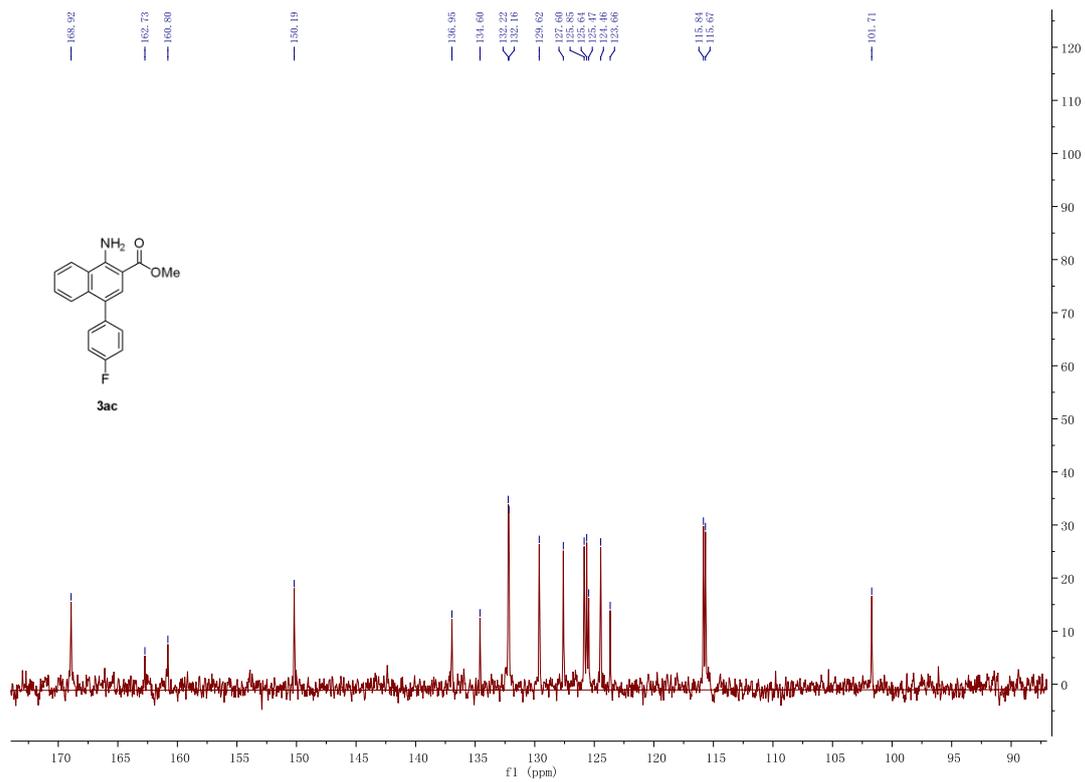


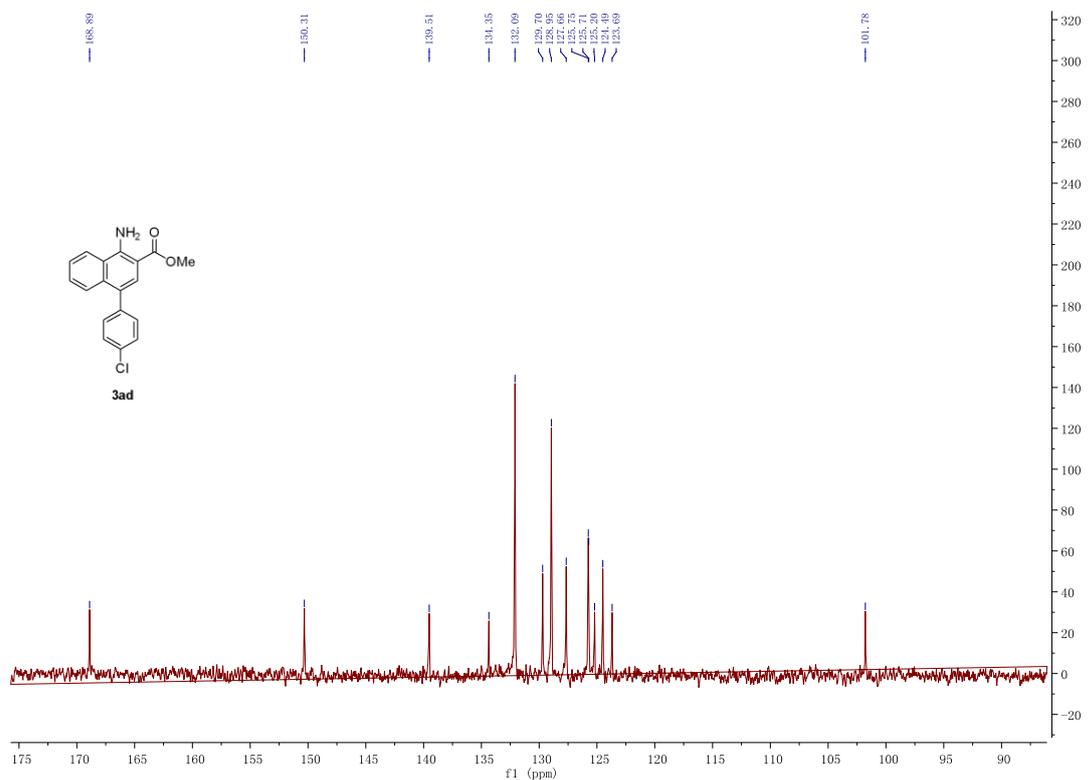
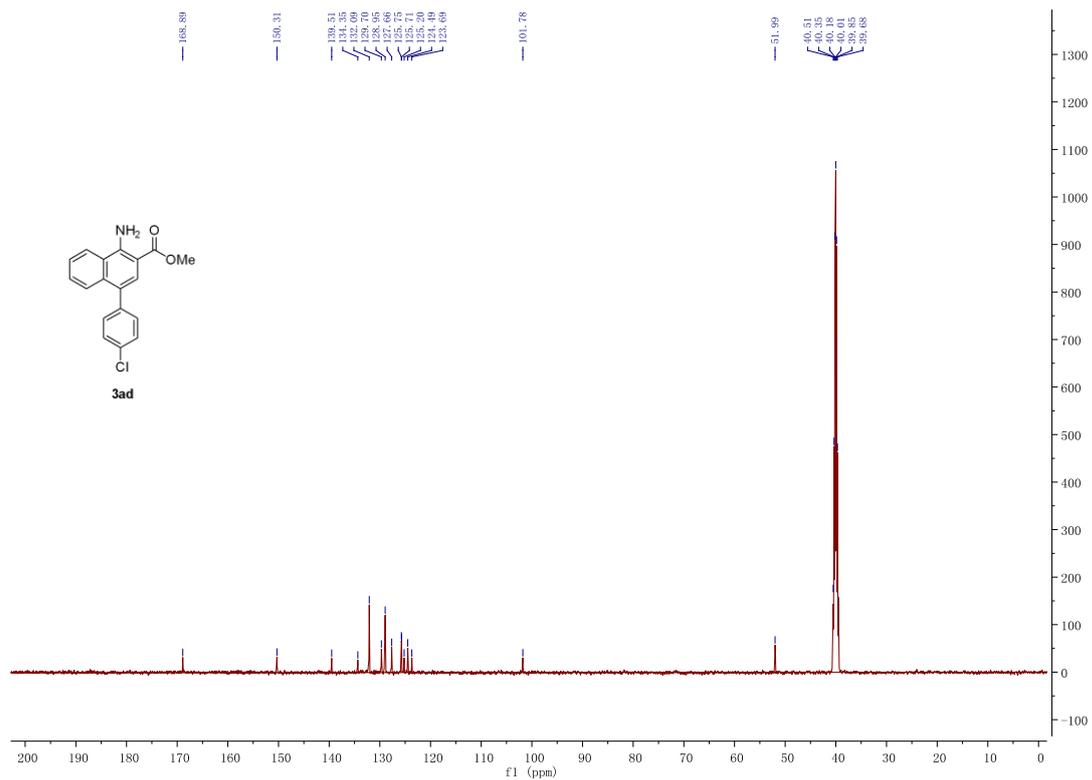


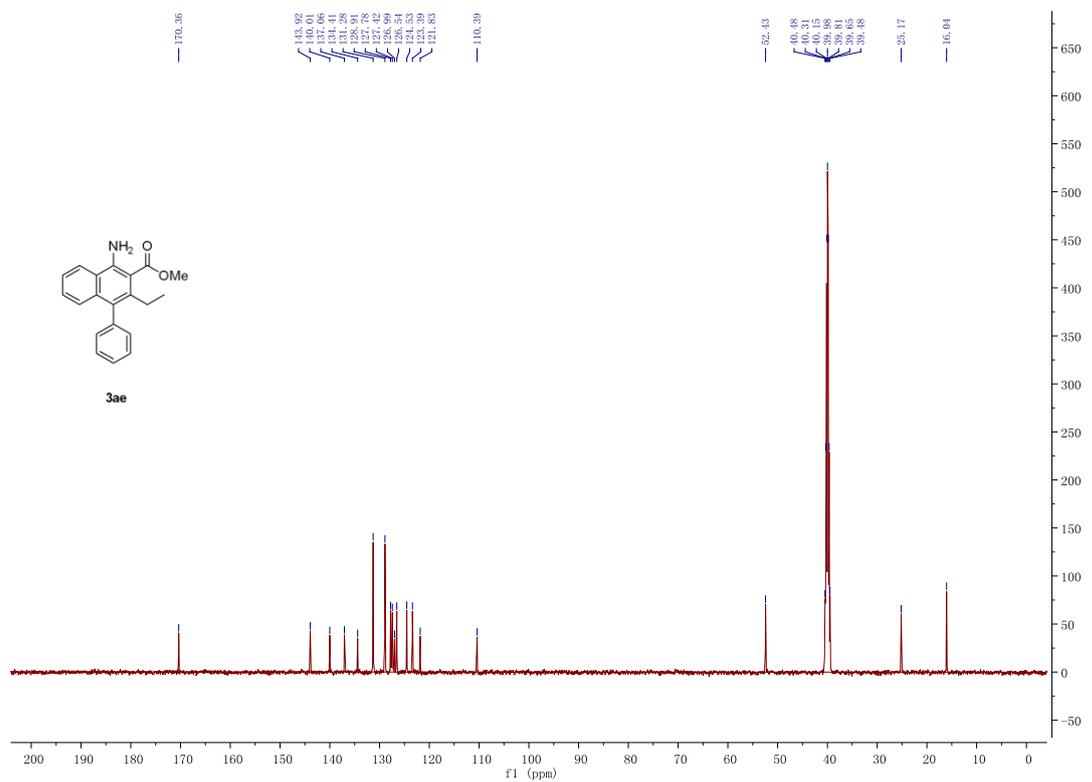
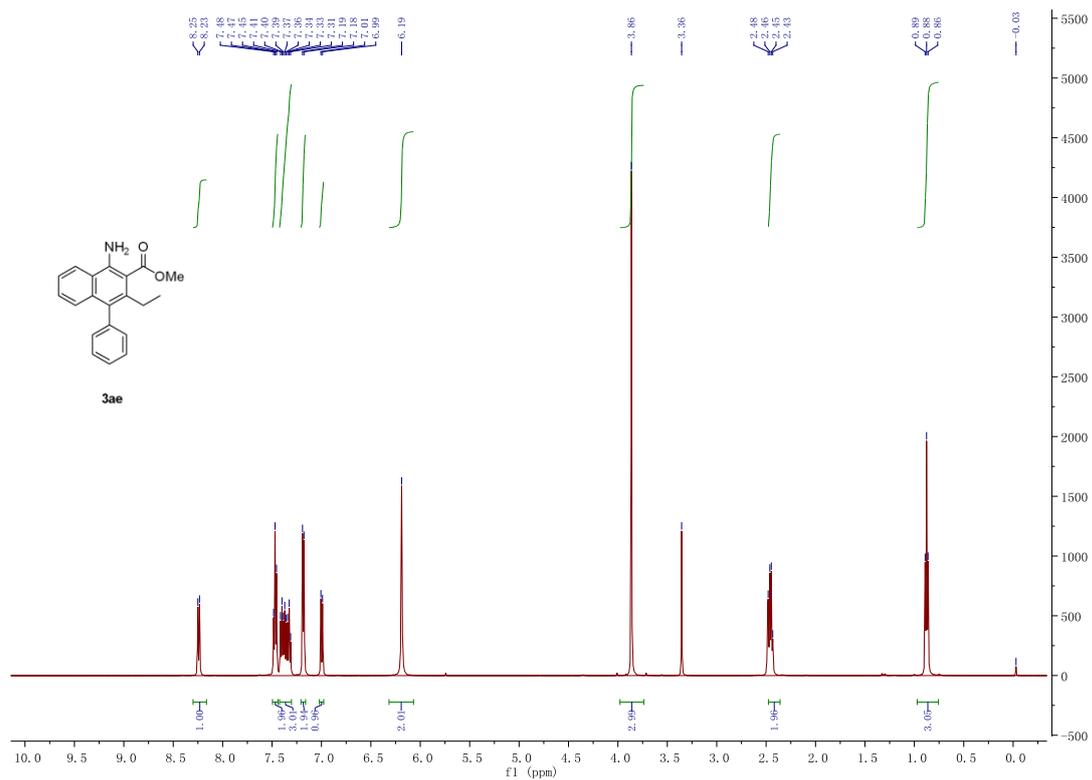


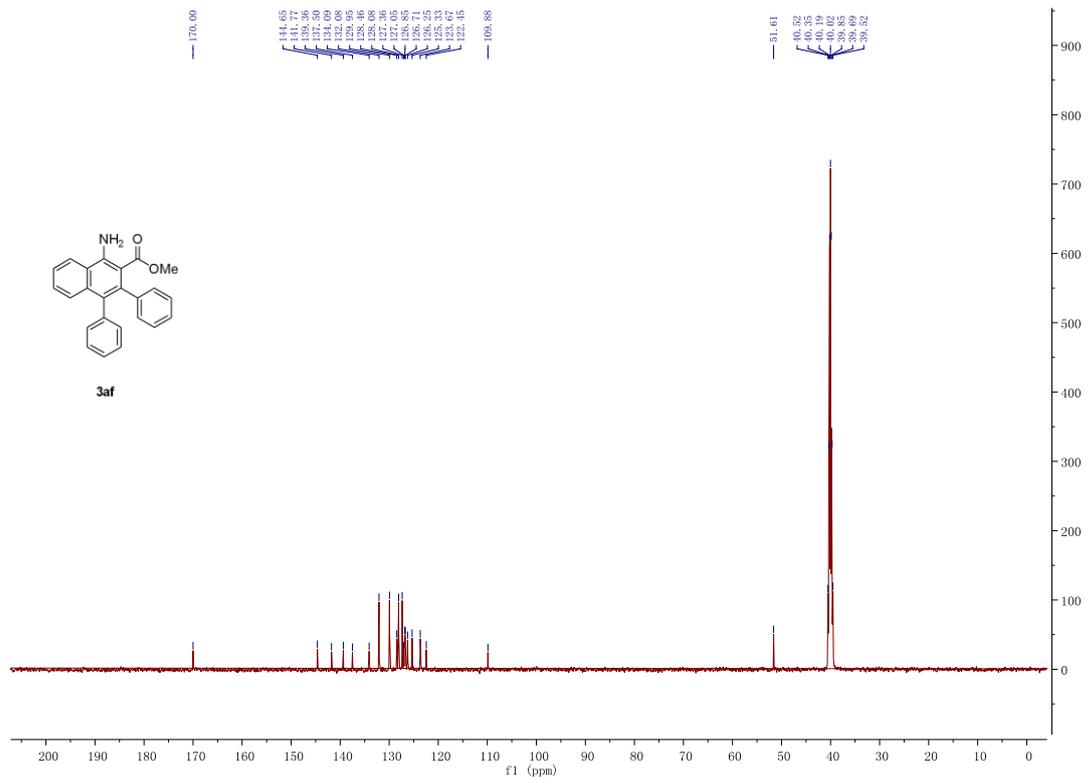
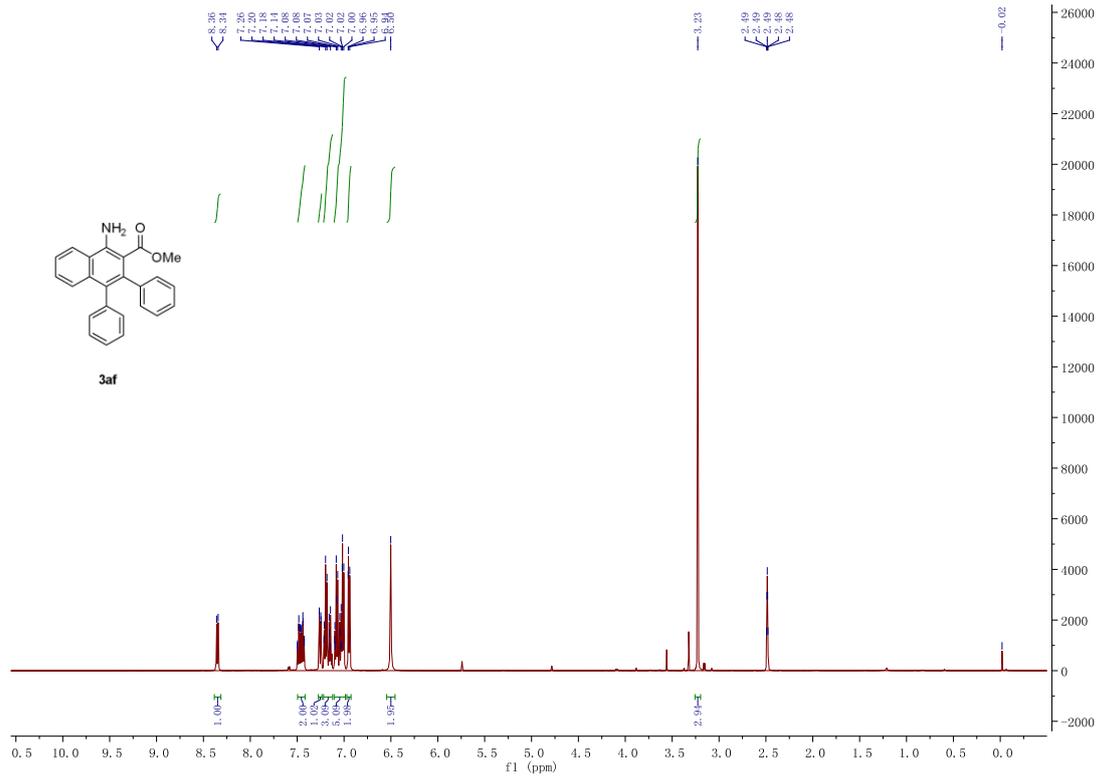


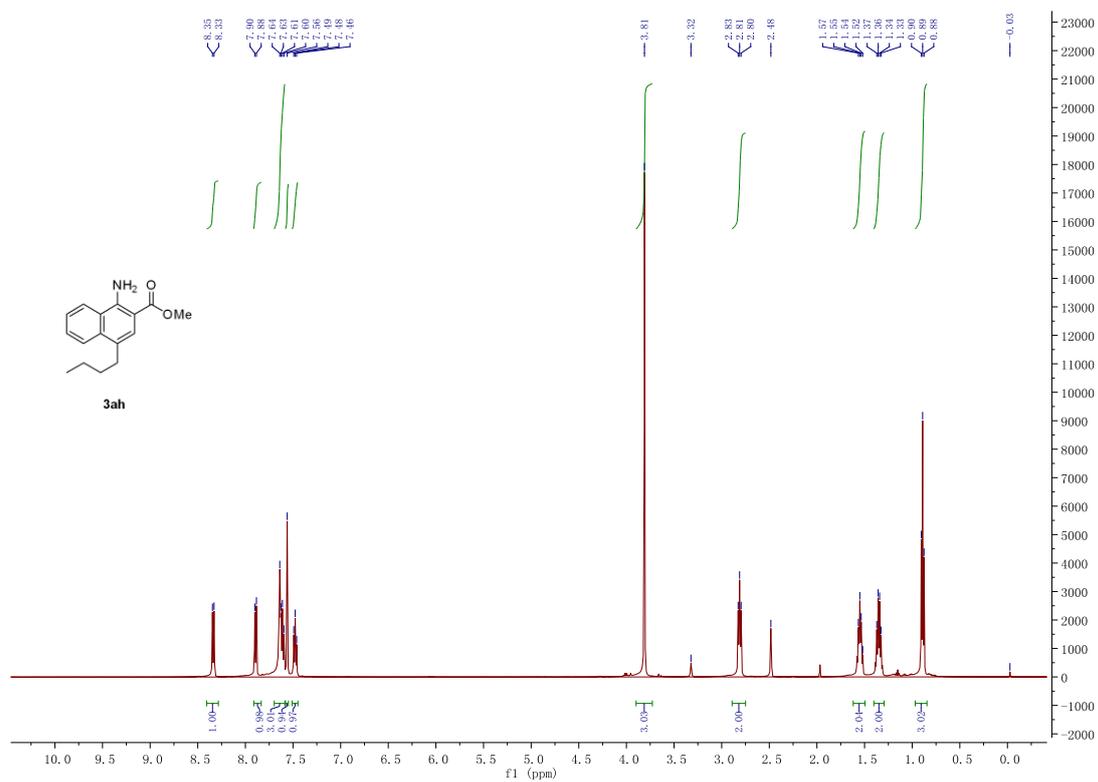
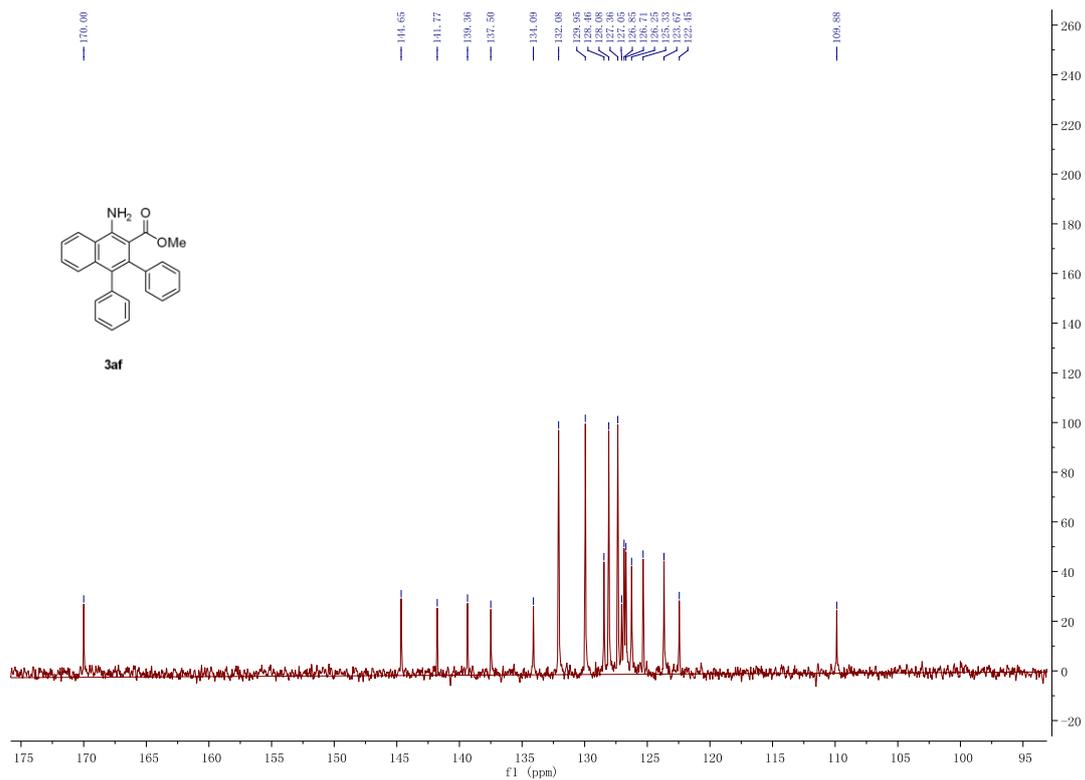


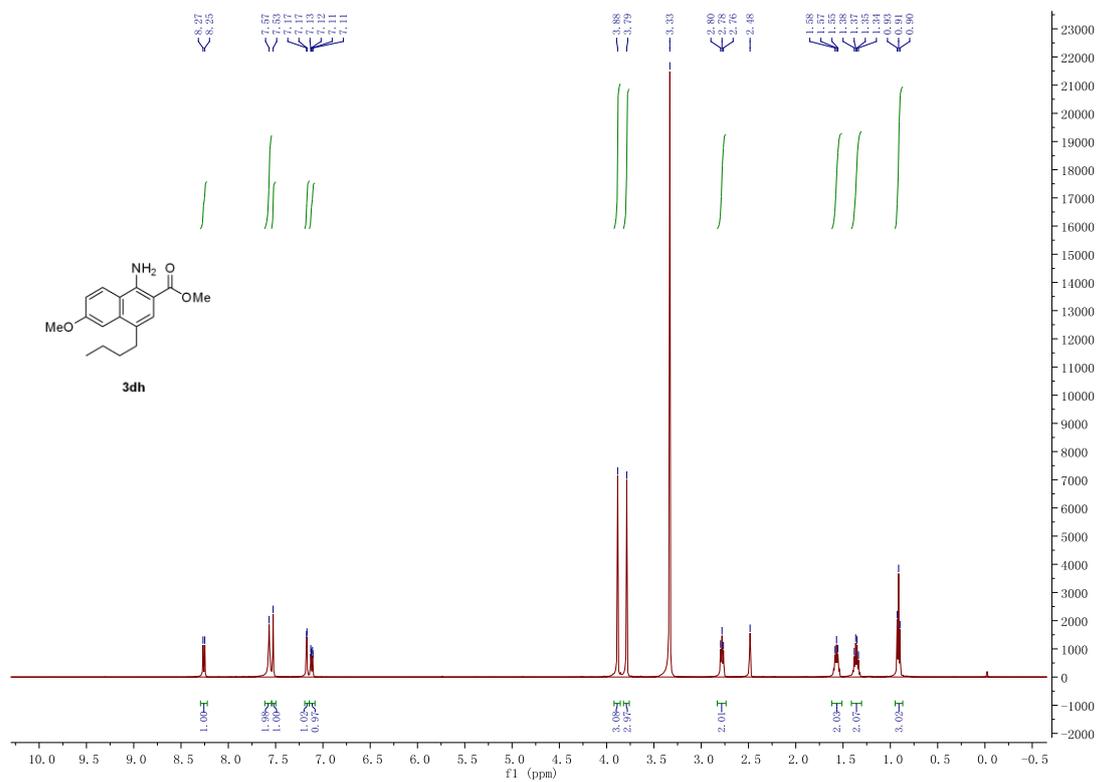
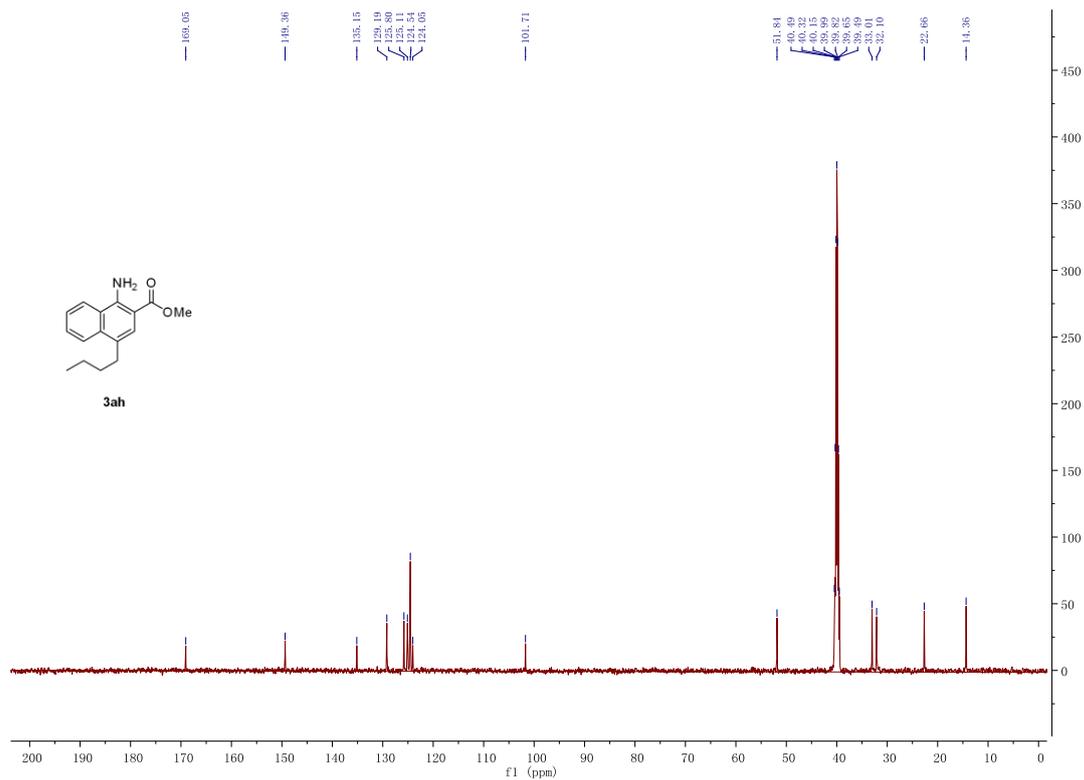


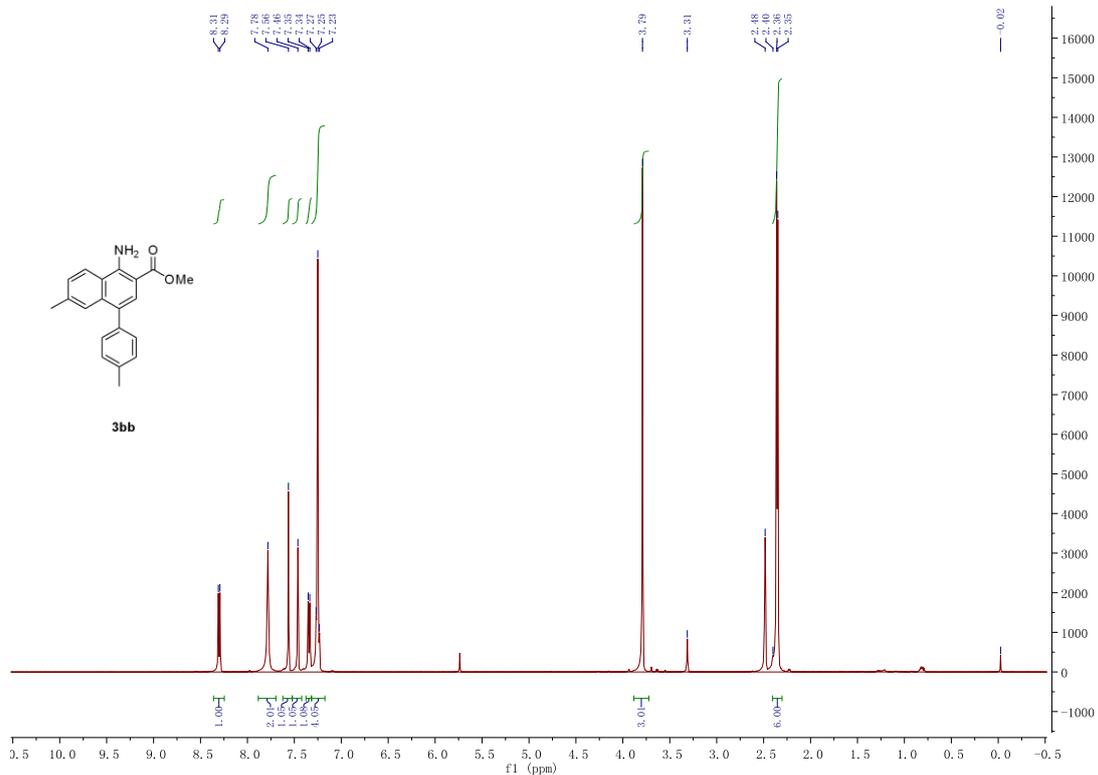
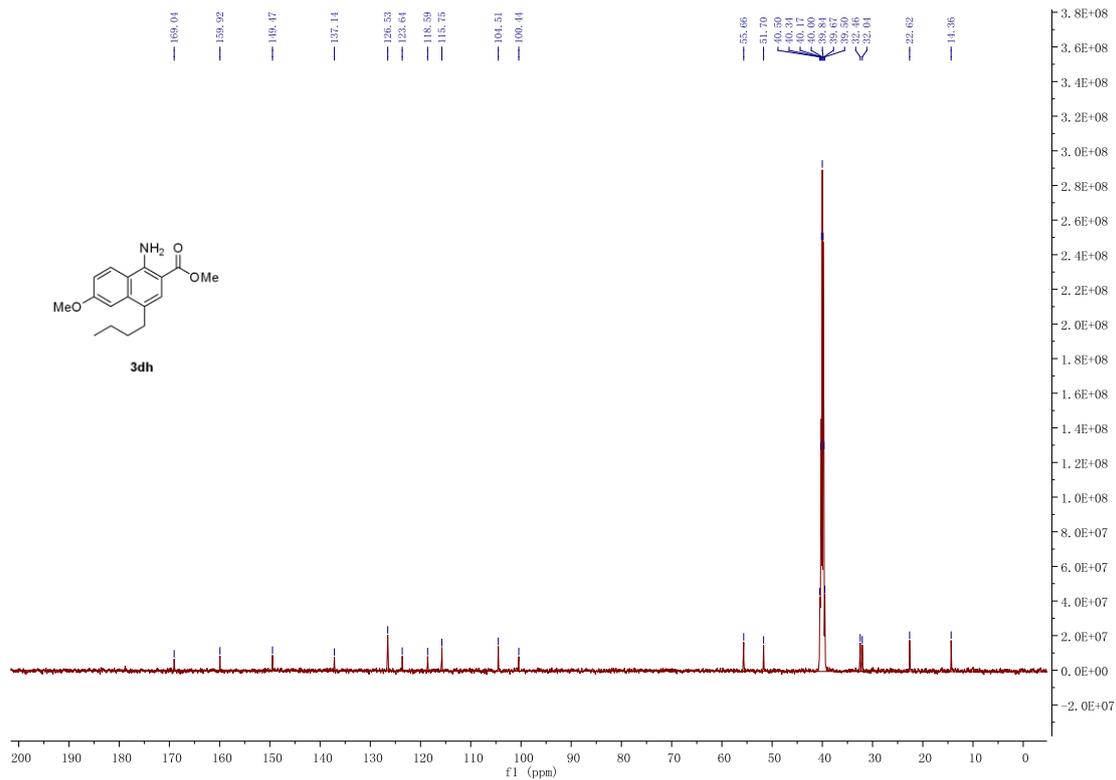


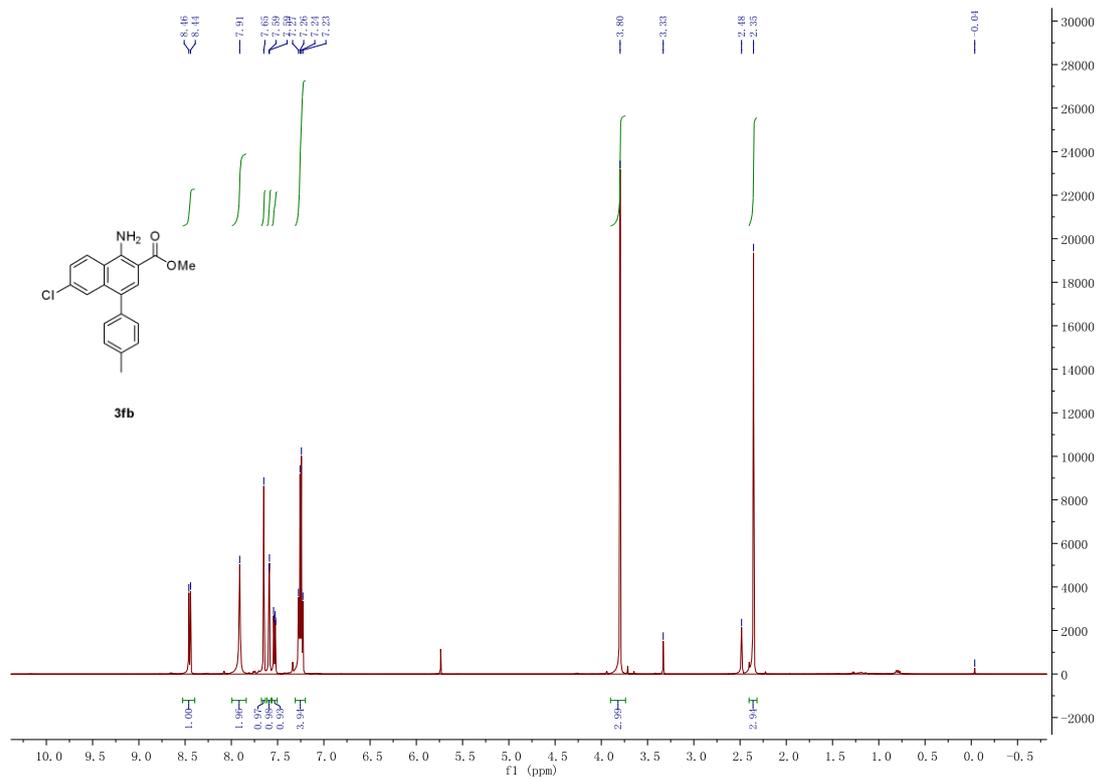
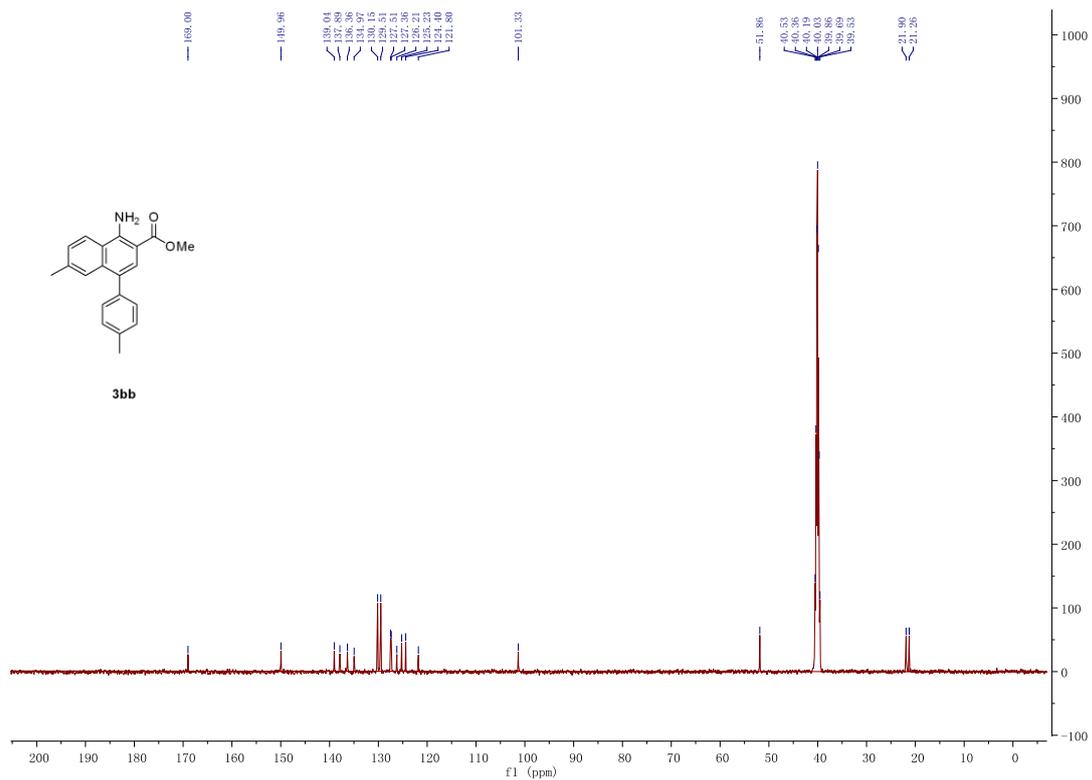


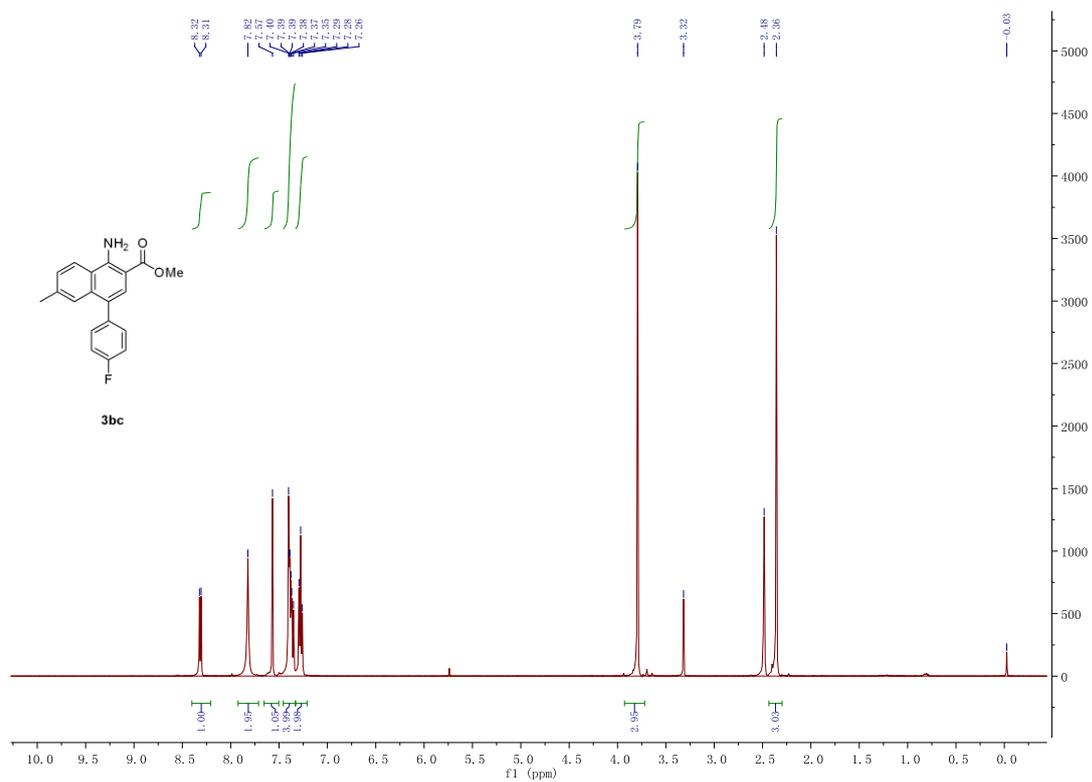
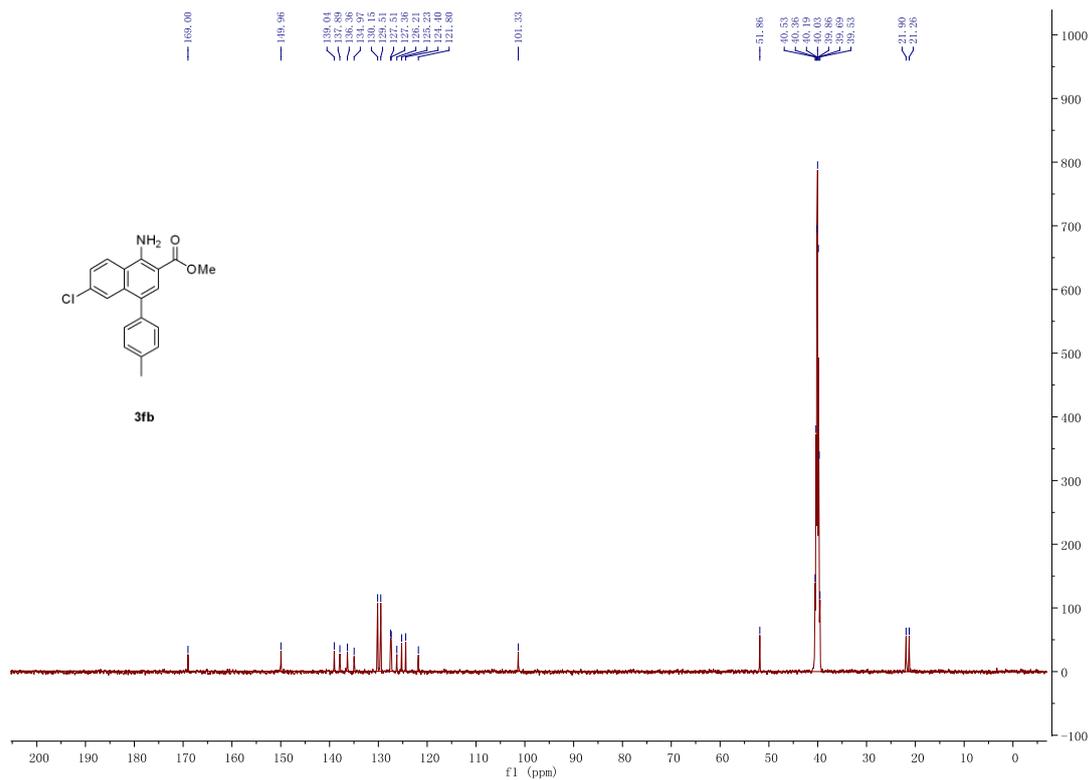


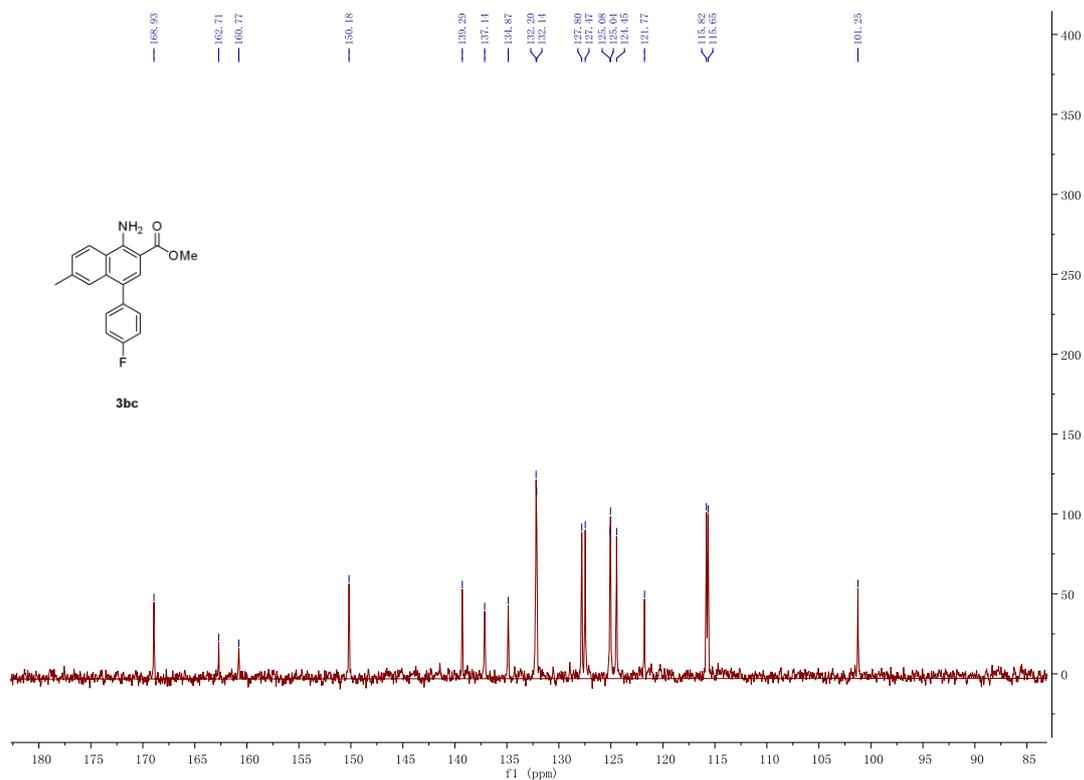
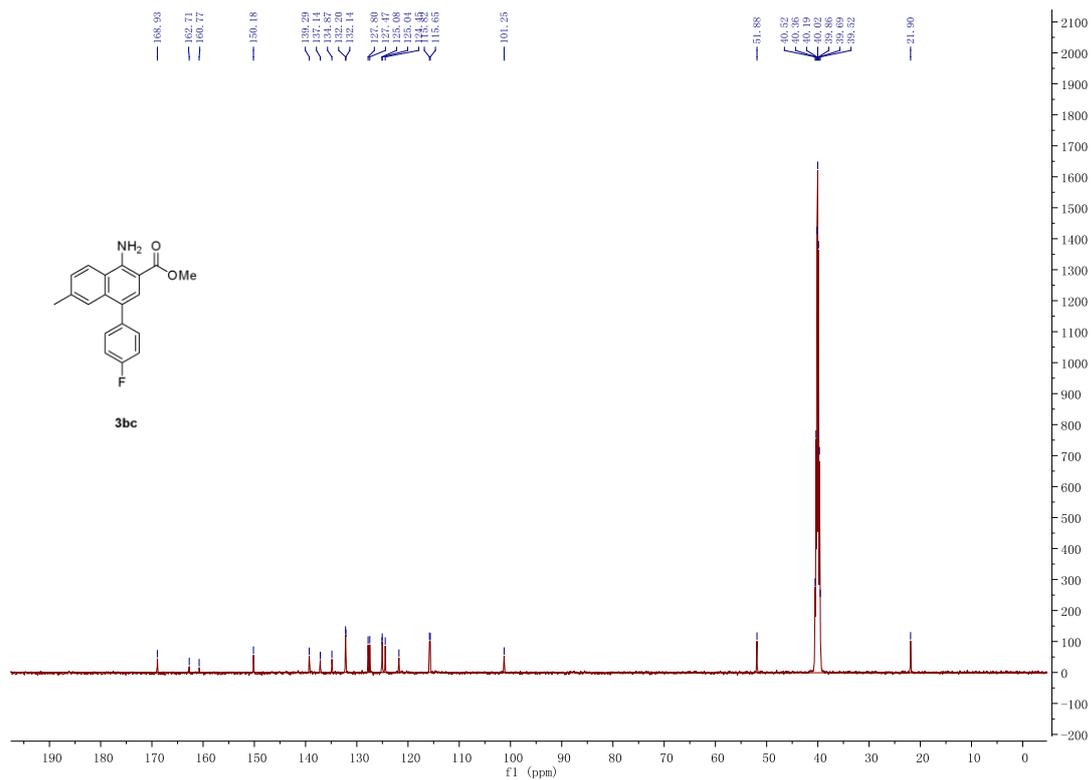




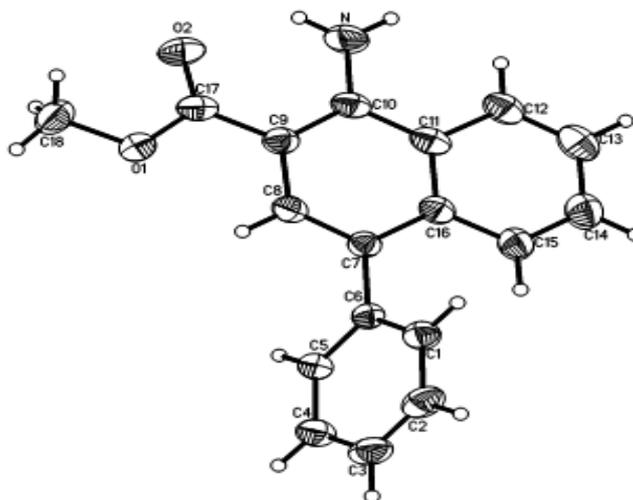








## 5. X-ray structures of compound of 3aa



---

Bond precision: C-C = 0.0047 Å

Wave length=0.71073 Å

Cell: a=14.488(3)Å, b=7.5150(15)Å, c=13.547(3)Å, alpha=90, beta=105.95(3), gamma=90

Temperature: 293 K

Volume: 1418.2(5) Å<sup>3</sup>

Space group: P21/c

Empirical formula: C<sub>18</sub>H<sub>15</sub>NO<sub>2</sub>

Formula weight: 277.31

D<sub>x</sub>,g cm<sup>-3</sup> :1.299

Z : 4

Mu (mm<sup>-1</sup>) 0.085

F<sub>000</sub>: 584.0

h, k, lmax: 17,9,16

Nref : 2596

Tmin,Tmax: 0.975,0.992

Tmin' 0.975

Correction method= PSI-SCAN

Data completeness= 0.997

Theta(max)= 25.370

R(reflections)= 0.0694( 1358)

wR2(reflections)= 0.1847( 2596)

S = 1.008

Npar= 190

---