

## *Supporting Information*

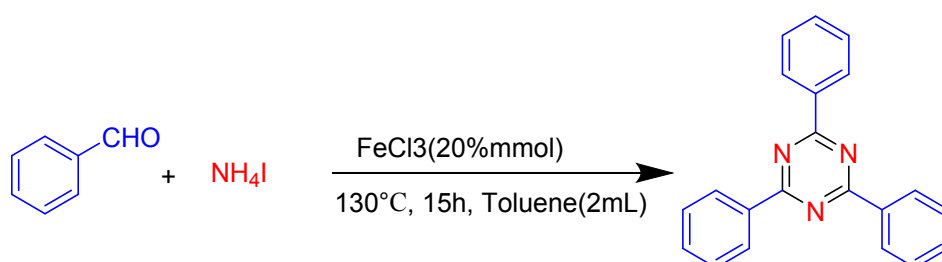
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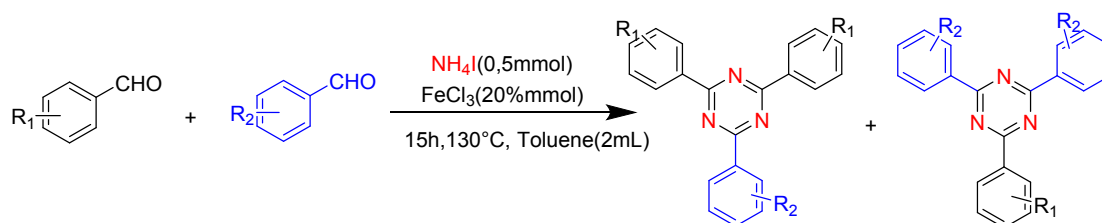
## 1. General information

Unless otherwise noted, all reactions were carried out in Schlenk tubes. Reagents and solvents were obtained from commercial sources and used without further purification. The  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^9\text{F}$  spectra were recorded on a Bruker ADVANCE III spectrometer at 400 MHz, 100 MHz and 376 MHz, and chemical shifts were reported in parts per million (ppm). Column chromatography was performed using silica gel of 300-400  $\mu\text{m}$ . The GC-MS results were recorded on a GC-MS QP2010 equipment. The electron ionization (EI) method was used for HRMS measurement, and the mass analyzer type is TOF for EI. The HRMS (EI) was recorded on an Esquire 3000 plus instrument.

## 2. General Procedures



General procedure for the synthesis of symmetrical 2,4,6-trisubstituted 1,3,5-triazin: In a Schlenk tube of 25 mL, benzaldehyde 1a (0.5 mmol, 1.0 equiv.),  $\text{NH}_4\text{I}$  2a (0.5 mmol, 1.0 equiv.),  $\text{FeCl}_3$  (0.1 mmol, 0.2 equiv.), were dissolved in Toluene (2 mL). The mixture was stirred at  $130^\circ\text{C}$  for 15 h under air atmosphere. After completion of the reaction, the resulting solution was cooled to room temperature; the solution was diluted with ethyl acetate (10 mL), washed with water (5 mL), extracted with ethyl acetate (3 $\times$ 5 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (petroleum ether /diethyl ether) to afford the product in order to analyze NMR.



General procedure for the synthesis of unsymmetrical 2,4,6-trisubstituted 1,3,5-triazin: In a Schlenk tube of 25 mL, benzaldehyde 1a (0.3 mmol.), 4-methylbenzaldehyde 1b (0.2 mmol.)  $\text{NH}_4\text{I}$  2a (0.5 mmol.),  $\text{FeCl}_3$  (0.1 mmol, 0.2 equiv.), were dissolved in Toluene (2 mL). The mixture was stirred at  $130^\circ\text{C}$  for 15 h under air atmosphere. After completion of the reaction, the resulting solution was cooled to room temperature; the solution was diluted with ethyl acetate (10 mL), washed with water (5

mL), extracted with ethyl acetate (3×5 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (petroleum ether /diethyl ether) to afford the product in order to analyze NMR.

### 3. GC-MS detection of reaction

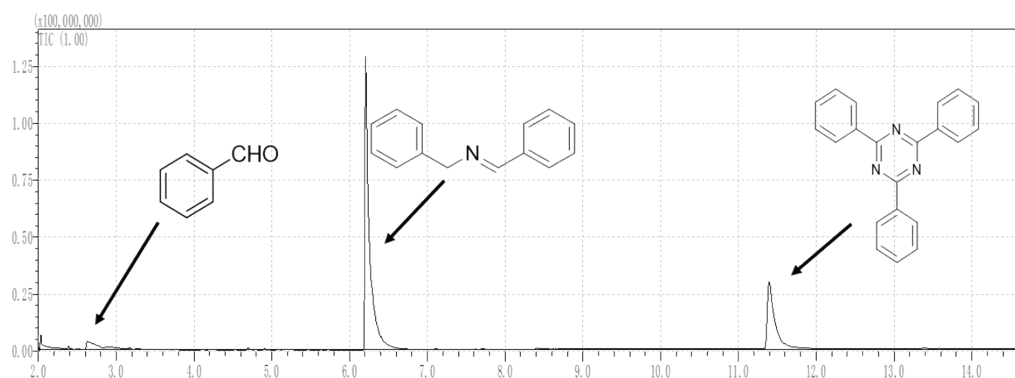
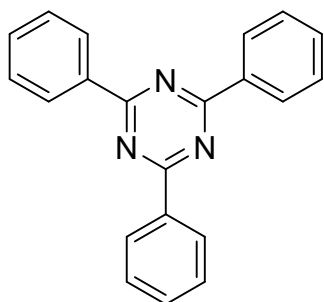


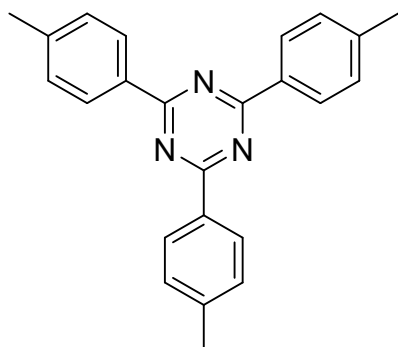
Figure.1 GC-MS detection of aldehyde and N-benzyl-1-phenylmethanimine reacted

### 4. Spectra Data of the Products



#### 2,4,6-triphenyl-1,3,5-triazine(2a)

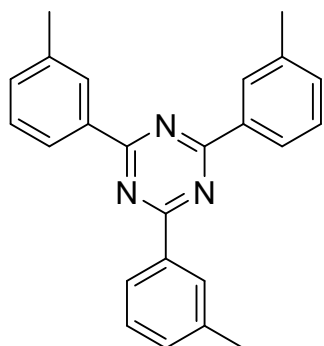
White solid; mp: 238.2-239.1 °C; Lit.mp: 237-239 °C <sup>[1]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.80-8.78 (dd, J = 8.0 Hz, 6H), 8.17- 7.42 (m, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 171.66, 136.26, 132.49, 128.96, 128.63. HRMS (EI): calcd for C<sub>21</sub>H<sub>15</sub>N<sub>3</sub>: 309.1266; found: 309.1272



#### 2,4,6-tri-p-tolyl-1,3,5-triazine(2b)

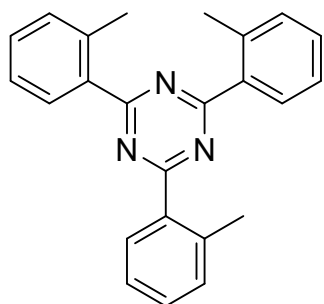
White solid; mp: 292.1-294.4 °C; Lit.mp: 297-298 °C [1]

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.66-8.64 (d, J = 8.0 Hz, 6H), 7.37-7.35 (d, J = 8.0 Hz, 6H), 2.48 (s, 9H) **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 171.37, 142.82, 133.76, 129.30, 128.90, 21.70. **HRMS (EI)**: calcd for C<sub>24</sub>H<sub>21</sub>N<sub>3</sub>: 351.17335; found: 351.1738



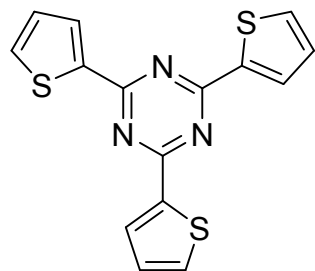
#### 2,4,6-tri-m-tolyl-1,3,5-triazine(2c)

White solid; mp: 145.1-147.6 °C; Lit.mp: 146-147 °C [2] **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.60-8.58 (d, J = 9.2 Hz, 6H), 7.96 – 6.85 (m, 6H), 2.54 (s, 9H) **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 171.68, 138.25, 136.27, 133.22, 129.38, 128.50, 126.20, 77.32, 77.00, 76.68, 21.55. **HRMS (EI)**: calcd for C<sub>24</sub>H<sub>21</sub>N<sub>3</sub>: 351.1735; found: 351.1742



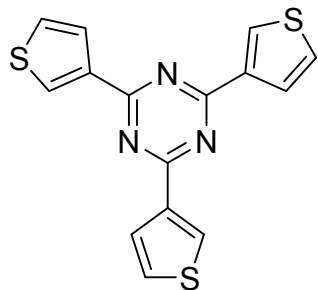
#### 2,4,6-tri-o-tolyl-1,3,5-triazine(2d)

White solid; mp: 112.3-114.7 °C; Lit.mp: 110-111 °C [2] **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.25-8.23 (d, J = 7.6 Hz, 3H), 7.71 – 7.23 (m, 9H), 2.80 (d, J = 13.6 Hz, 9H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 173.81, 138.91, 136.16, 131.79, 131.28, 130.84, 126.03, 22.26. **HRMS (EI)**: calcd for C<sub>24</sub>H<sub>21</sub>N<sub>3</sub>: 351.1735; found: 351.1731



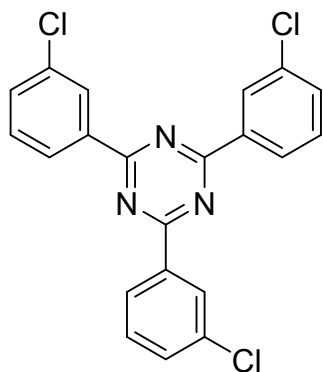
#### 2,4,6-tri(thiophen-2-yl)-1,3,5-triazine(2e)

White solid; mp: 183.6-185.4 °C; Lit.mp: 187 °C [3] **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.28-8.27 (d, J = 3.6 Hz, 3H), 7.63-7.61 (d, J = 4.8 Hz, 3H), 7.22-7.20 (t, J = 4.4 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 167.69, 141.43, 132.28, 131.66, 128.38. **HRMS (EI)**: calcd for C<sub>15</sub>H<sub>9</sub>N<sub>3</sub>S<sub>3</sub>: 326.9959.1263; found: 326.9965



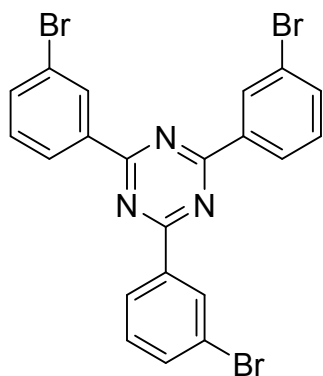
**2,4,6-tri(thiophen-3-yl)-1,3,5-triazine(2f)**

White solid; mp: 176.4-178.8 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.61-8.60 (dd, J = 3.0, 1.0 Hz, 3H), 8.07-8.05 (dd, J = 4.8, 1.2 Hz, 3H), 7.44-7.42 (dd, J = 5.2, 3.2 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 168.34, 140.40, 131.00, 127.62, 126.21. **HRMS (EI)**: calcd for C<sub>15</sub>H<sub>9</sub>N<sub>3</sub>S<sub>3</sub>: 326.9959; found: 326.9963



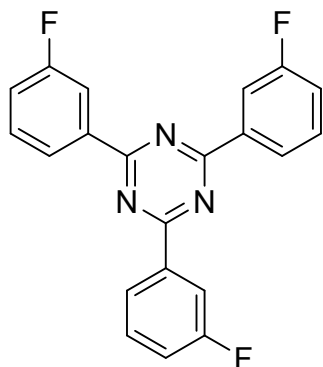
**2,4,6-tris(3-chlorophenyl)-1,3,5-triazine(2k)**

White solid; mp: 226.2-228.7 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.61 (s, 3H), 8.57-8.55 (d, J = 8.0 Hz, 3H), 7.58-7.56 (d, J = 8.0 Hz, 3H), 7.51-7.47 (t, J = 7.8 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.67, 137.39, 134.92, 132.76, 129.93, 128.85, 127.09. **HRMS (EI)**: calcd for C<sub>21</sub>H<sub>12</sub>N<sub>3</sub>Cl<sub>3</sub>: 411.0097; found: 411.0092



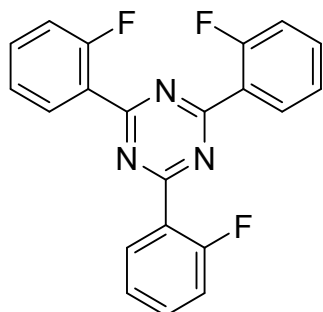
### 2,4,6-tris(3-bromophenyl)-1,3,5-triazine(2j)

White solid; mp: 192.2-194.5 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.76 (s, 3H), 8.61-8.59 (d, J = 8.0 Hz, 3H), 7.74-7.72 (d, J = 7.8 Hz, 3H), 7.44-7.41 (t, J = 8.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.58, 137.59, 135.72, 131.79, 130.21, 127.58, 122.98. HRMS (EI): calcd for C<sub>21</sub>H<sub>12</sub>N<sub>3</sub>Br<sub>3</sub>: 544.8561; found: 544.8566



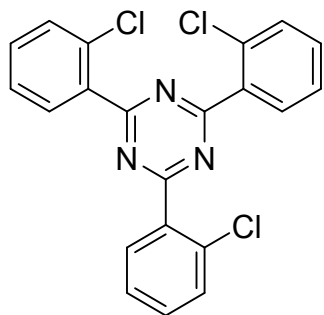
### 2,4,6-tris(3-fluorophenyl)-1,3,5-triazine(2l)

White solid; mp: 257.4-259.6 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.56-8.54 (d, J = 8.0 Hz, 3H), 8.50 – 8.33 (m, 3H), 7.56 (q, J = 7.8 Hz, 3H), 7.46 – 7.27 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.96, 164.39, 161.94, 138.16, 138.08, 130.33, 130.25, 124.70, 124.67, 119.87, 119.66, 115.86, 115.62. HRMS (EI): calcd for C<sub>21</sub>H<sub>12</sub>N<sub>3</sub>F<sub>3</sub>: 363.0983; found: 363.0988



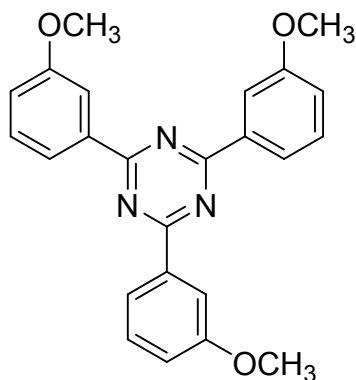
### 2,4,6-tris(2-fluorophenyl)-1,3,5-triazine(2g)

White solid; mp: 167.8-171.4 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.49-8.46 (t, J = 7.8 Hz, 3H), 7.61-7.56 (q, J = 6.8 Hz, 3H), 7.38-7.34 (t, J = 7.6 Hz, 3H), 7.31 – 7.28 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.80, 170.75, 163.70, 161.12, 133.74, 133.65, 132.38, 124.61, 124.53, 124.30, 124.26, 117.37, 117.15. HRMS (EI): calcd for C<sub>21</sub>H<sub>12</sub>N<sub>3</sub>F<sub>3</sub>: 363.0983; found: 363.0976



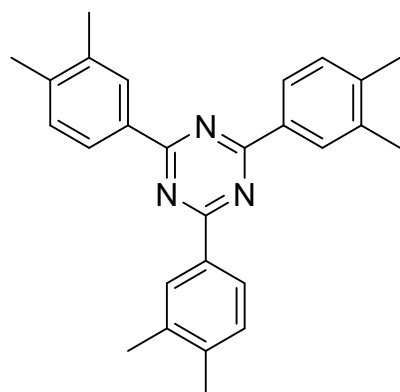
**2,4,6-tris(2-chlorophenyl)-1,3,5-triazine(2h)**

Yellow solid; mp: 201.5-203.7°C; Lit.mp: 202-203°C<sup>[10]</sup> **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.12-8.10 (m, 3H), 7.58-7.55 (m, 1H), 7.49-7.42 (m, Hz, 6H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 172.73, 135.35, 133.63, 132.66, 131.91, 131.13, 126.99. **HRMS (EI)**: calcd for C<sub>21</sub>H<sub>12</sub>N<sub>3</sub>Cl<sub>3</sub>: 411.0097; found: 411.0103



**2,4,6-tris(3-methoxyphenyl)-1,3,5-triazine(2n)**

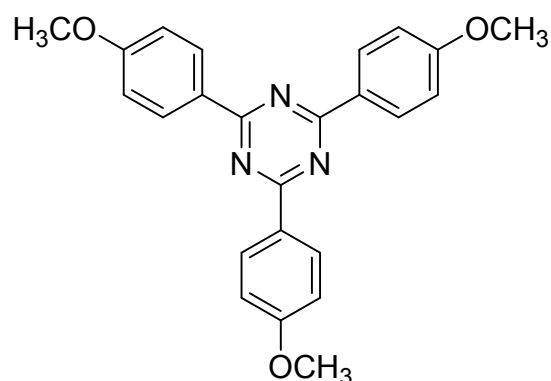
White solid; mp: 172.3-176.4 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.37-8.35 (d, J = 8.0 Hz, 3H), 8.30-8.29 (m, 3H), 7.50-7.46 (t, J = 8.0 Hz, 3H), 7.17 – 7.14 (m, 3H), 3.96 (s, 9H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 171.42, 159.91, 137.61, 129.63, 121.52, 118.44, 113.88, 55.44. **HRMS (EI)**: calcd for C<sub>24</sub>H<sub>21</sub>N<sub>3</sub>O<sub>3</sub>: 399.1583; found: 399.1589



**2,4,6-tris(3,4-dimethylphenyl)-1,3,5-triazine(2o)**

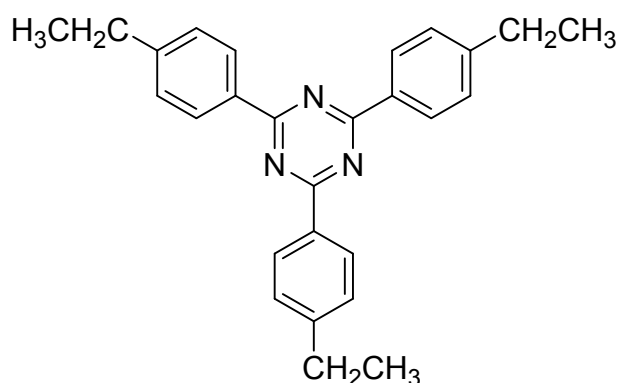
White solid; mp: 212.8-214.4 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.51-8.49 (d, J = 9.2 Hz, 6H), 7.34-7.32 (d, J = 7.6 Hz, 3H), 2.44-2.39 (d, J = 20.8 Hz, 18H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 171.50, 141.50, 136.79, 134.17, 129.94, 129.87, 126.58, 20.06, 19.94.

**HRMS (EI):** calcd for C<sub>27</sub>H<sub>27</sub>N<sub>3</sub>:393.2205; found: 393.2201



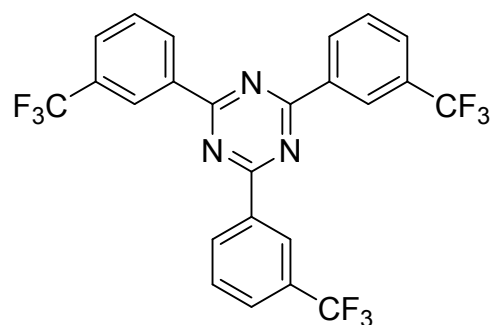
**2,4,6-tris(4-methoxyphenyl)-1,3,5-triazine(2m)**

White solid; mp: 220.4-222.6 °C; Lit.mp: 219-220°C [4] **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.71-8.69 (d, J = 9.2 Hz, 6H), 7.06-7.04 (d, J = 9.6 Hz, 6H), 3.91 (s, 9H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.68, 163.08, 130.68, 129.13, 113.82, 55.41. **HRMS (EI):** calcd for C<sub>24</sub>H<sub>21</sub>N<sub>3</sub>O<sub>3</sub>: 399.1583; found: 399.1576



**2,4,6-tris(4-ethylphenyl)-1,3,5-triazine(2i)**

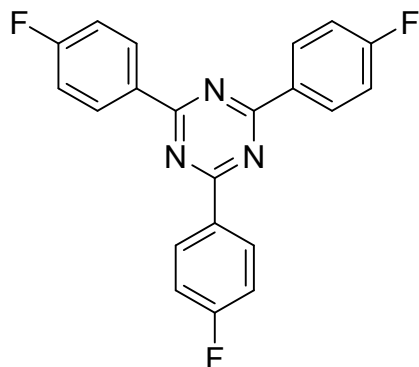
White solid; mp: 112.8-114.6 °C; Lit.mp: 114-115 °C [9] **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.70-8.68 (d, J = 7.6 Hz, 6H), 7.41-7.39 (d, J = 7.6 Hz, 6H), 2.81-2.76 (q, J = 7.4 Hz, 6H), 1.35-1.31 (t, J = 7.6 Hz, 9H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 171.43, 149.09, 134.03, 129.01, 128.11, 29.02, 15.37. **HRMS (EI):** calcd for C<sub>27</sub>H<sub>27</sub>N<sub>3</sub>: 393.2205; found: 393.2213





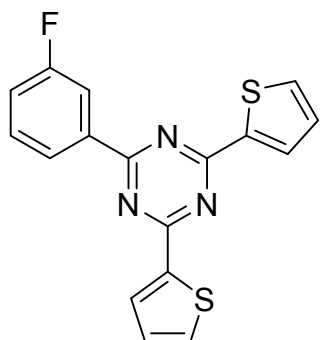
### 2,4,6-tris(3-(trifluoromethyl)phenyl)-1,3,5-triazine(2q)

White solid; mp: 210.1-211.6 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.97 – 8.92 (m, 6H), 7.91-7.89 (d,  $J = 7.8$  Hz, 3H), 7.76-7.72 (t,  $J = 7.8$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.98, 136.32, 132.21, 131.63, 131.30, 129.43, 125.82, 125.79, 125.29, 122.58. **HRMS (EI)**: calcd for  $\text{C}_{24}\text{H}_{12}\text{N}_3\text{F}_9$ : 513.0888; found: 513.0883



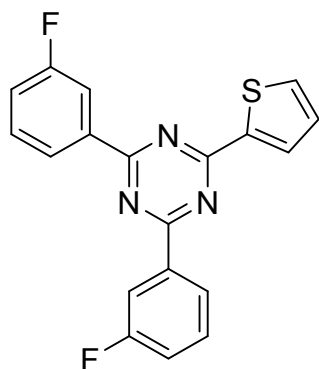
### 2,4,6-tris(4-fluorophenyl)-1,3,5-triazine(2p)

White solid; mp: 260.3-261.5 °C; Lit.mp: 261.2-262°C [5]  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.81-8.78 (dd,  $J = 8.7, 5.6$  Hz, 6H), 7.30-7.28 (m, 6H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.71, 167.16, 132.21, 131.35, 131.26, 115.88, 115.67. **HRMS (EI)**: calcd for  $\text{C}_{21}\text{H}_{12}\text{N}_3\text{F}_3$ : 363.0983; found: 363.0991



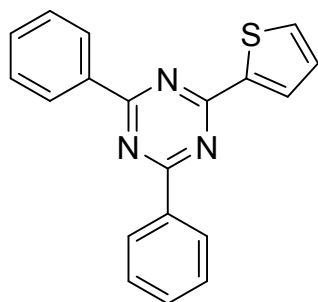
### 2-(3-fluorophenyl)-4,6-di(thiophen-2-yl)-1,3,5-triazine(3a)

White solid; mp: 218.3-219.7 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.46-8.44 (d,  $J = 8.0$  Hz, 1H), 8.34 – 8.31 (m, 3H), 7.65-7.64 (d,  $J = 5.2$  Hz, 2H), 7.54 – 7.49 (m, 1H), 7.31-7.28 (m, 1H) 7.24-7.22 (t,  $J = 4.4$  Hz, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.34, 170.31, 168.00, 164.28, 161.84, 141.51, 132.49, 131.80, 130.12, 130.04, 128.49, 124.57, 124.54, 119.55, 119.34, 115.74, 115.50.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -112.50 – -112.91 (m). **HRMS (EI)**: calcd for  $\text{C}_{17}\text{H}_{10}\text{N}_3\text{S}_2\text{F}$ : 339.0300; found: 339.0305



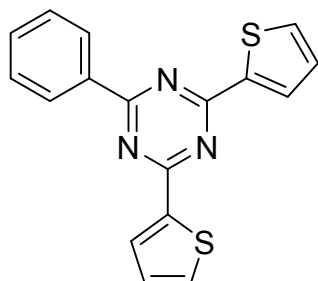
**2,4-bis(3-fluorophenyl)-6-(thiophen-2-yl)-1,3,5-triazine(4a)**

White solid; mp: 190.3-192.7 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.51-8.49 (d,  $J = 8.0$  Hz, 2H), 8.39 – 8.36 (m, 3H), 7.68-7.66 (dd,  $J = 4.8, 1.2$  Hz, 1H), 7.57-7.51 (m, 2H), 7.33-7.29 (td,  $J = 8.2, 2.4$  Hz, 2H), 7.25-7.24 (m, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.62, 168.31, 164.33, 161.89, 141.56, 138.13, 138.05, 132.71, 131.95, 130.22, 130.14, 128.60, 124.63, 124.60, 119.71, 119.49, 115.80, 115.56.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -102.32 – -116.72 (m, 2F). **HRMS (EI)**: calcd for  $\text{C}_{19}\text{H}_{11}\text{N}_3\text{SF}_2$ : 351.0642; found: 351.0646



**2,4-diphenyl-6-(thiophen-2-yl)-1,3,5-triazine(3b)**

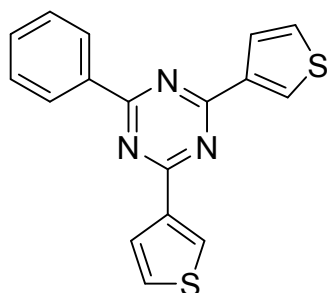
White solid; mp: 254.6-256.2 °C; Lit.mp: 255.2-257°C [6]  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.74-8.71 (dd,  $J = 8.0, 1.6$  Hz, 4H), 8.38-8.37 (dd,  $J = 4.0, 1.4$  Hz, 1H), 7.65 – 7.55 (m, 7H), 7.25 – 7.24 (m, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.55, 168.09, 142.15, 135.93, 132.55, 132.15, 131.49, 128.94, 128.60, 128.46. **HRMS (EI)**: calcd for  $\text{C}_{19}\text{H}_{13}\text{N}_3\text{S}$ : 315.0830; found: 315.0837



**2-phenyl-4,6-di(thiophen-2-yl)-1,3,5-triazine(4b)**

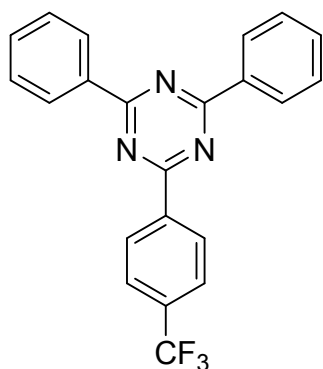
White solid; mp: 181.5-183.7 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.67-8.66 (d,  $J = 6.8$  Hz, 2H), 8.33-8.32 (d,  $J = 3.6$  Hz, 2H), 7.64-7.63 (d,  $J = 4.8$  Hz, 2H), 7.60-7.54 (m, 3H), 7.24 – 7.22 (t,  $J=4.0$ , 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.41, 167.91, 141.80,

135.60, 132.59, 132.23, 131.59, 128.91, 128.57, 128.44. **HRMS (EI)**: calcd for  $C_{17}H_{11}N_3S_2$ : 321.0394; found: 321.0399



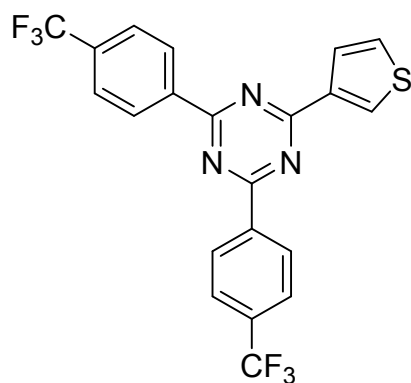
**2-phenyl-4,6-di(thiophen-3-yl)-1,3,5-triazine(4c)**

White solid; mp: 196.2-198.8 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.70 – 8.68 (m, 2H), 8.65-8.64 (dd,  $J = 3.0, 1.0$  Hz, 2H), 8.11-8.10 (d,  $J = 5.2$  Hz, 2H), 7.62-7.54 (m, 3H), 7.45-7.43 (dd,  $J = 5.0, 2.4$  Hz, 2H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  171.68, 168.34, 140.53, 136.07, 132.43, 131.02, 128.82, 128.56, 127.67, 126.22. **HRMS (EI)**: calcd for  $C_{17}H_{11}N_3S_2$ : 321.0394; found: 321.0390



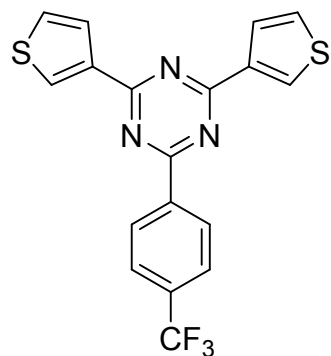
**2,4-diphenyl-6-(4-(trifluoromethyl)phenyl)-1,3,5-triazine(3d)**

White solid; mp: 183.3.2-185.2 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.89-8.87 (d,  $J = 8.2$  Hz, 2H), 8.79-8.76 (m, 4H), 7.84-8.72 (d,  $J = 8.0$  Hz, 2H), 7.66 – 7.57 (m, 6H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  171.94, 170.47, 139.59, 135.89, 132.79, 129.23, 129.02, 128.72, 125.57, 125.53. **HRMS (EI)**: calcd for  $C_{22}H_{14}N_3F_3$ : 377.1140; found: 377.1133



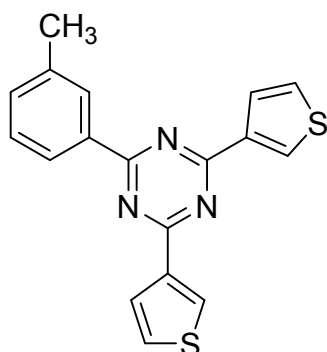
**2-(thiophen-3-yl)-4,6-bis(4-(trifluoromethyl)phenyl)-1,3,5-triazine(4e)**

White solid; mp: 149.1-152.3 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.78-8.76 (d,  $J = 8.0$  Hz, 4H), 8.67 (d,  $J = 2.0$  Hz, 1H), 8.09-8.08 (d,  $J = 4.8$  Hz, 1H), 7.81-7.79 (d,  $J = 8.0$  Hz, 4H), 7.47-7.45 (dd,  $J = 5.0, 2.4$  Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.66, 168.65, 139.85, 139.04, 134.23, 133.91, 131.93, 129.16, 127.57, 126.63, 125.63, 125.59, 125.55, 125.51, 125.25, 122.54.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.92. **HRMS (EI)**: calcd for  $\text{C}_{21}\text{H}_{11}\text{N}_3\text{F}_6\text{S}$ : 451.0578; found: 451.0572



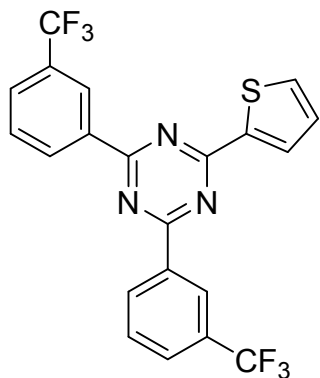
**2,4-di(thiophen-3-yl)-6-(4-(trifluoromethyl)phenyl)-1,3,5-triazine(3e)**

White solid; mp: 175.9-177.2 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.77-8.75 (d,  $J = 8.4$  Hz, 2H), 8.64-8.63 (d,  $J = 2.4$  Hz, 2H), 8.08 – 8.06 (m, 2H), 7.80-7.78 (d,  $J = 7.2$  Hz, 2H), 7.45-7.43 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.42, 168.48, 140.16, 139.38, 133.92, 133.59, 131.40, 129.06, 127.59, 126.38, 125.50, 125.47, 125.43, 125.40.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.85. **HRMS (EI)**: calcd for  $\text{C}_{18}\text{H}_{10}\text{N}_3\text{F}_3\text{S}_2$ : 389.0268; found: 389.0274



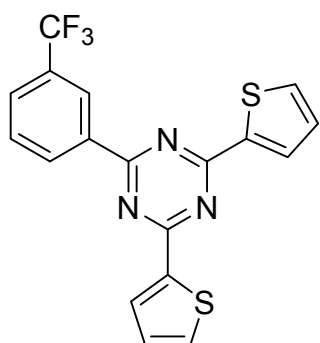
**2,4-di(thiophen-2-yl)-6-(m-tolyl)-1,3,5-triazine(3f)**

White solid; mp: 142.7-145.6 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.47-7.46 (d,  $J = 7.2$  Hz, 2H), 8.33-8.32 (d,  $J = 3.6$  Hz, 2H), 7.64-7.63 (d,  $J = 4.8$  Hz, 2H), 7.46 – 7.40 (m, 2H), 7.24 – 7.22 (t,  $J = 4.4$  Hz, 2H), 2.50 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.55, 167.86, 141.84, 138.24, 135.53, 133.43, 132.16, 131.55, 129.36, 128.49, 128.41, 126.16, 21.52. **HRMS (EI)**: calcd for  $\text{C}_{18}\text{H}_{13}\text{N}_3\text{S}_2$ : 335.0551; found: 335.0558



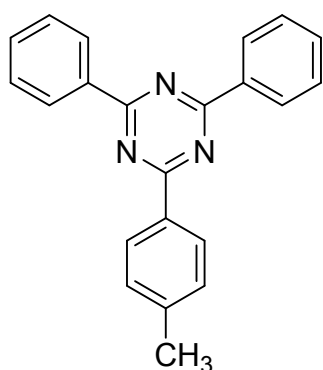
**2-(thiophen-2-yl)-4,6-bis(3-(trifluoromethyl)phenyl)-1,3,5-triazine(4g)**

White solid; mp: 145.2-147.3 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.97– 8.91 (m, 4H), 8.42-8.41 (d,  $J = 4.0$  Hz, 1H), 7.92-7.90 (d,  $J = 7.6$  Hz, 2H), 7.77-7.73 (dd,  $J = 9.4, 6.4$  Hz, 3H), 7.31 – 7.29 (t,  $J = 4.4$  Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.51, 168.45, 141.26, 136.42, 133.07, 132.28, 132.10, 131.45, 131.12, 129.25, 129.20, 129.16, 128.71, 125.75, 125.71. **HRMS (EI)**: calcd for  $\text{C}_{21}\text{H}_{11}\text{N}_3\text{F}_6\text{S}$ : 451.0578; found: 451.0570



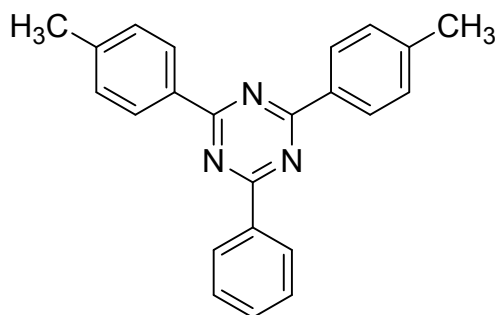
**2,4-di(thiophen-2-yl)-6-(3-(trifluoromethyl)phenyl)-1,3,5-triazine(3g)**

White solid; mp: 170.1-171.9 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.89 (s, 1H), 8.84-8.82 (d,  $J = 7.6$  Hz, 1H), 8.33-8.31 (dd,  $J = 3.6, 0.8$  Hz, 2H), 7.85-7.83 (d,  $J = 8.0$  Hz, 1H), 7.69 – 7.64 (m, 3H), 7.24 – 7.22 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.07, 168.07, 141.36, 136.48, 132.64, 132.01, 131.95, 131.29, 130.96, 129.10, 128.95, 128.91, 128.54, 125.68, 125.64. **HRMS (EI)**: calcd for  $\text{C}_{18}\text{H}_{10}\text{N}_3\text{F}_3\text{S}_2$ : 389.0268; found: 389.0271



### 2,4-diphenyl-6-(p-tolyl)-1,3,5-triazine(3h)

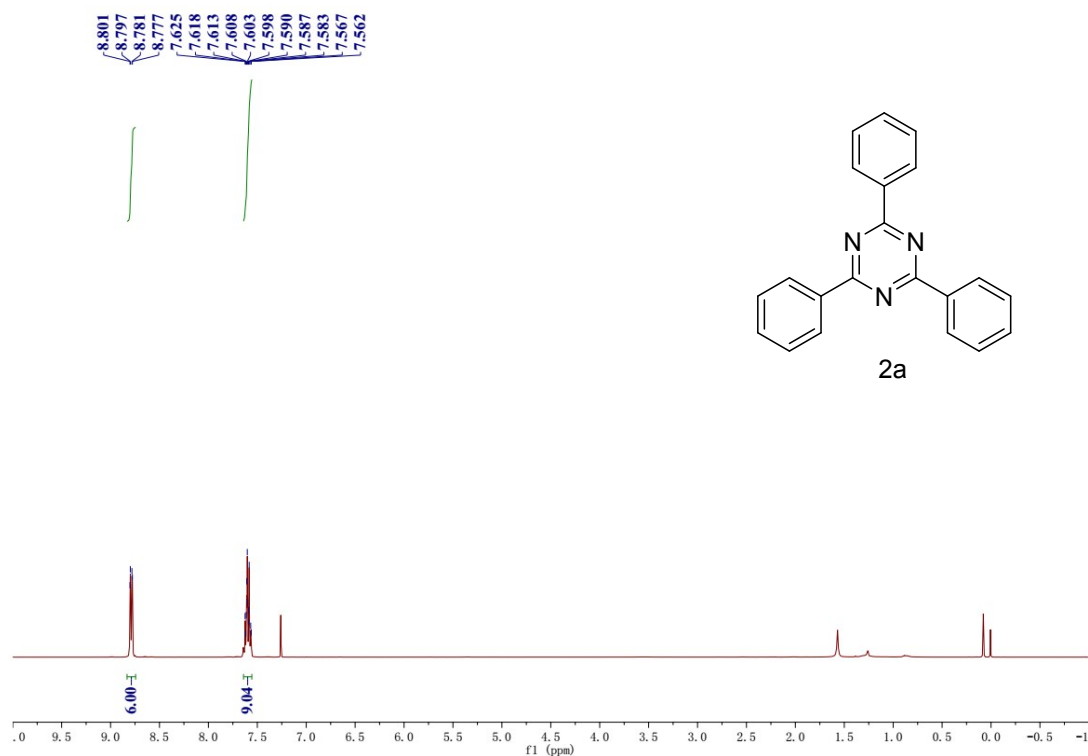
White solid; mp: 196.1-198.5 °C; Lit.mp: 197-199°C [7] **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.79-8.77 (d, J = 7.6 Hz, 4H), 8.67-8.68 (d, J = 8.0 Hz, 2H), 7.62 – 7.56 (m, 6H), 7.39-7.37 (d, J = 8.0 Hz, 2H), 2.49 (s, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 171.66, 171.56, 143.12, 136.37, 133.56, 132.40, 129.40, 128.98, 128.94, 128.60, 21.73. **HRMS (EI)**: calcd for C<sub>22</sub>H<sub>17</sub>N<sub>3</sub>: 323.1422; found: 323.1426

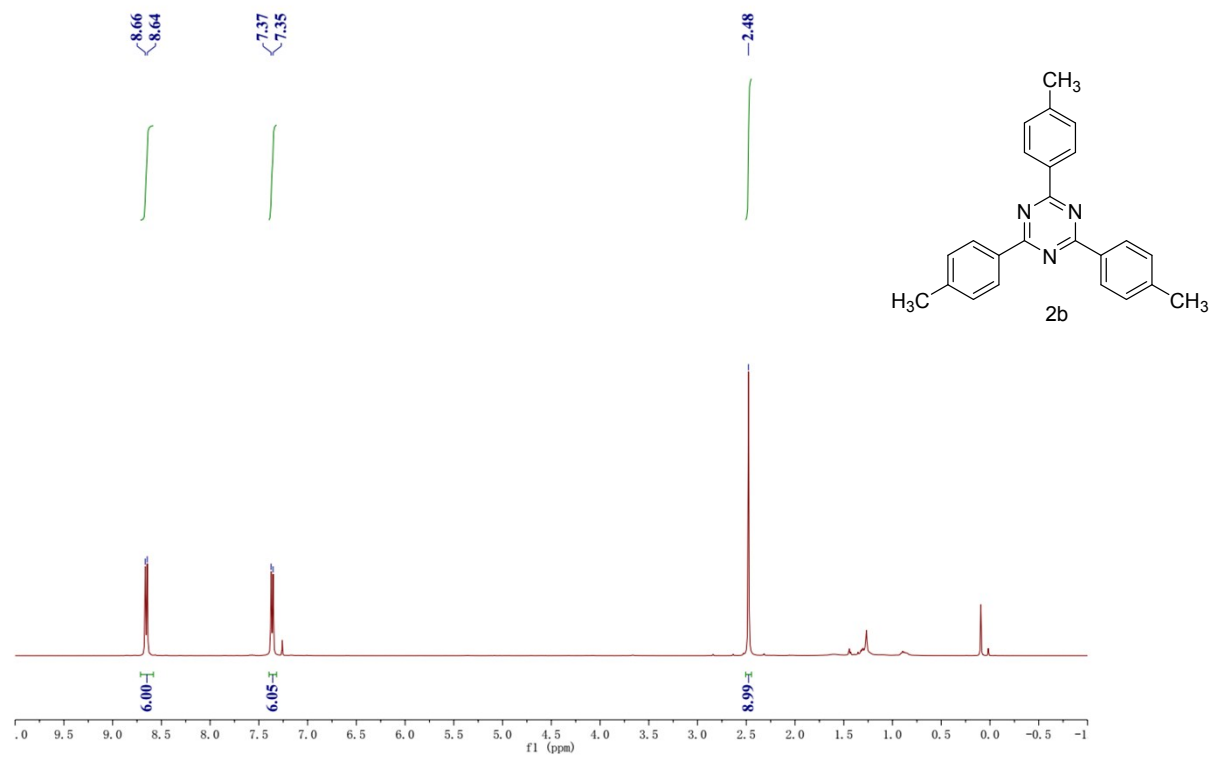
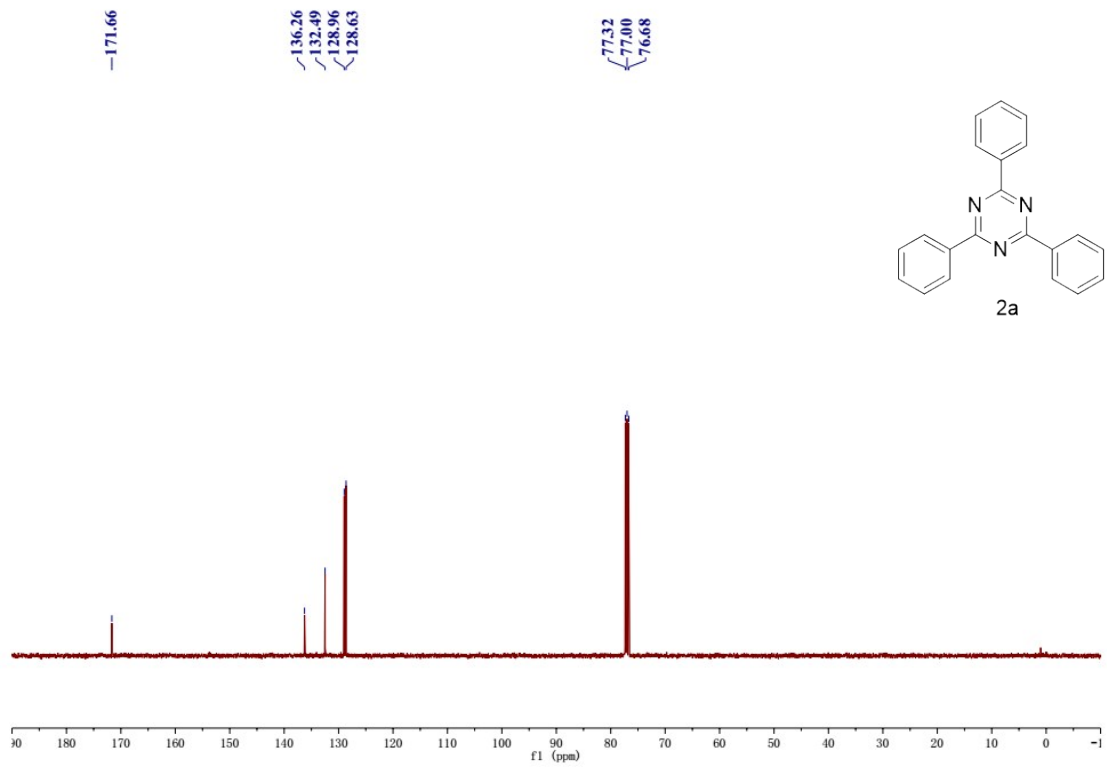


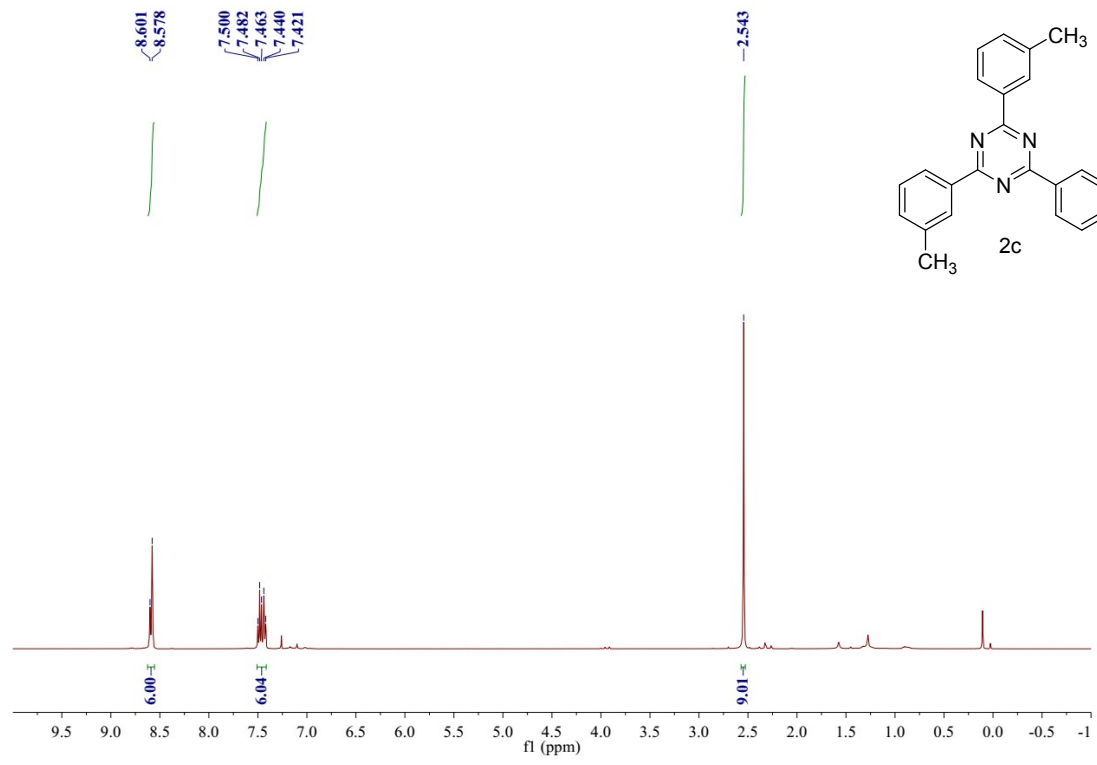
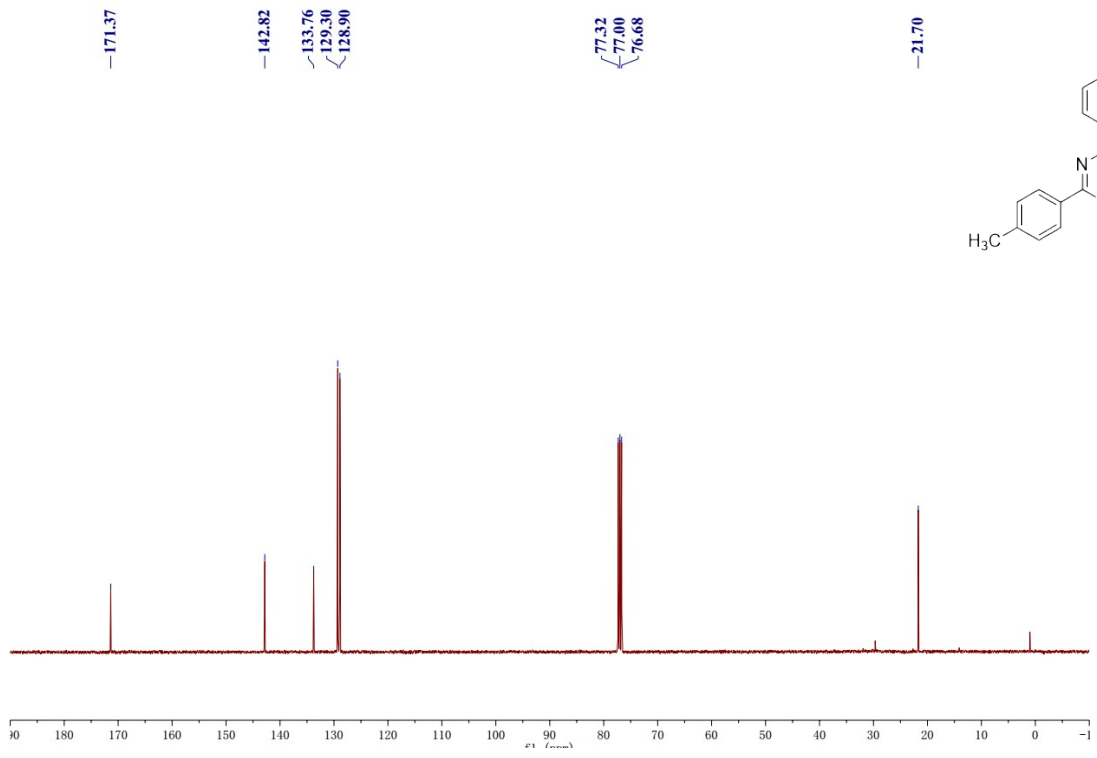
### 2-phenyl-4,6-di-p-tolyl-1,3,5-triazine(4h)

White solid; mp: 235.7-237.5 °C; Lit.mp: 236-238°C [8] **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.78-8.76 (d, J = 7.6 Hz, 2H), 8.68-8.66 (d, J = 8.0 Hz, 4H), 7.63-7.56 (m, 3H), 7.38-7.36 (d, J = 8.0 Hz, 4H), 2.48 (s, 6H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 171.53, 171.43, 142.98, 136.48, 133.66, 132.29, 129.36, 128.94, 128.91, 128.59, 128.56, 21.72. **HRMS (EI)**: calcd for C<sub>23</sub>H<sub>19</sub>N<sub>3</sub>: 335.1579; found: 335.1584

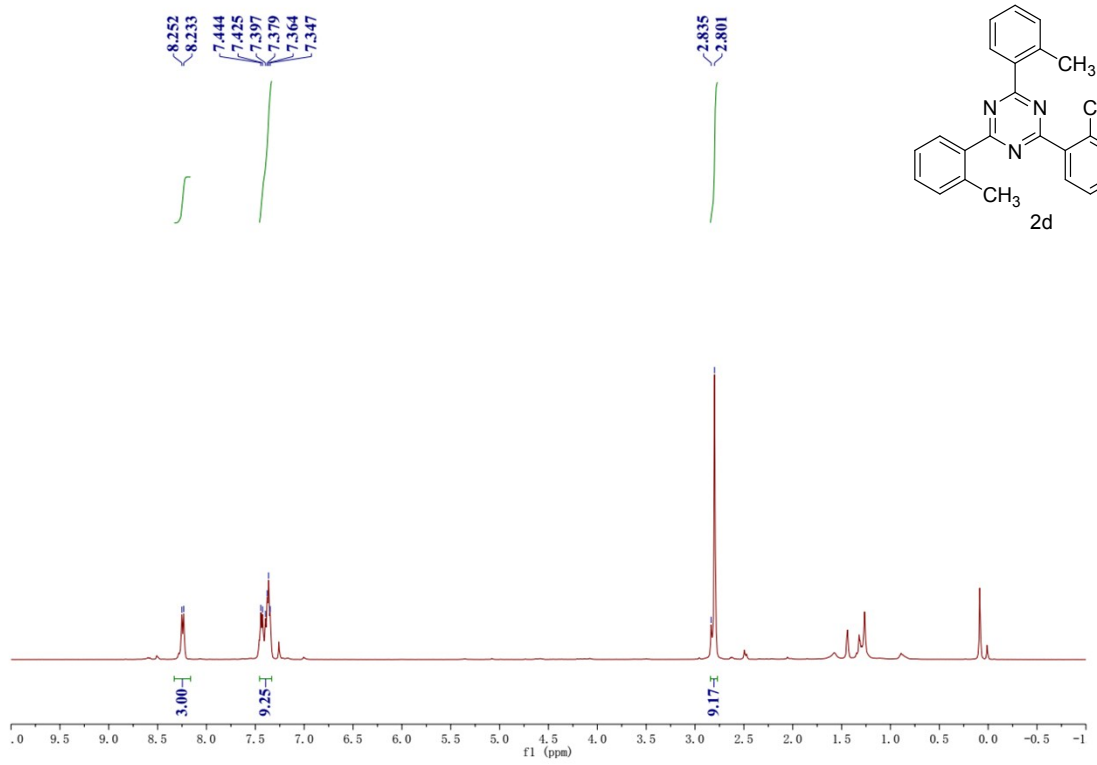
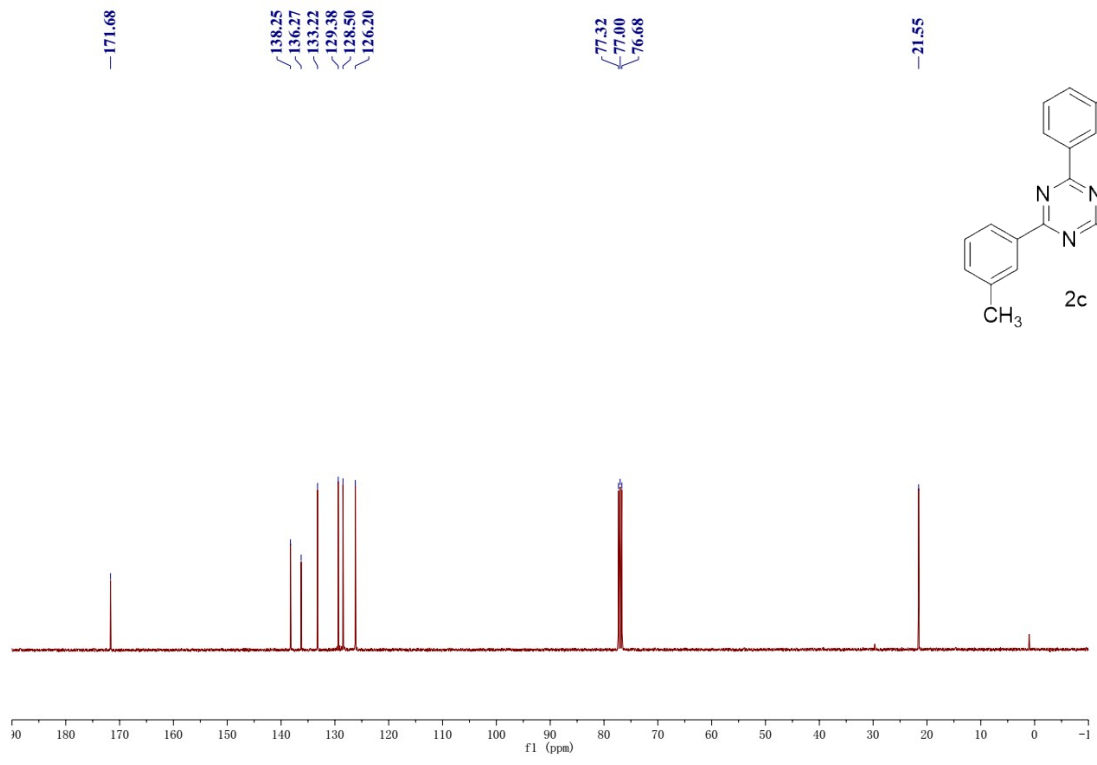
## 5. NMR data of products

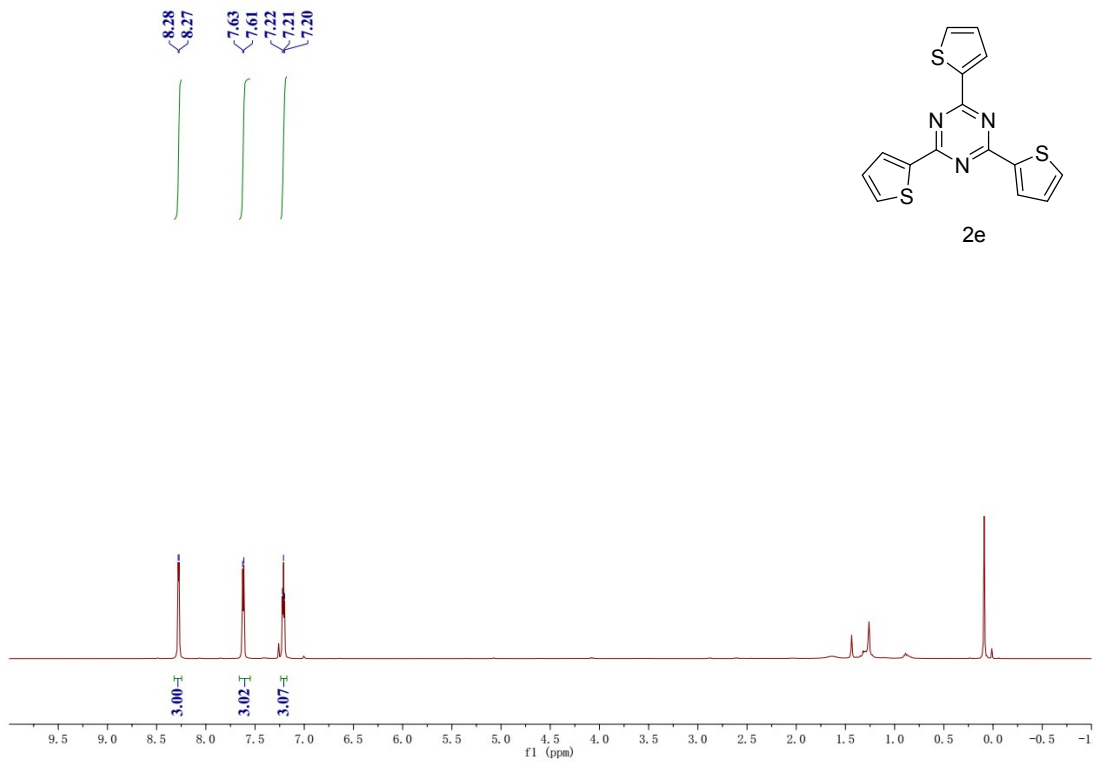
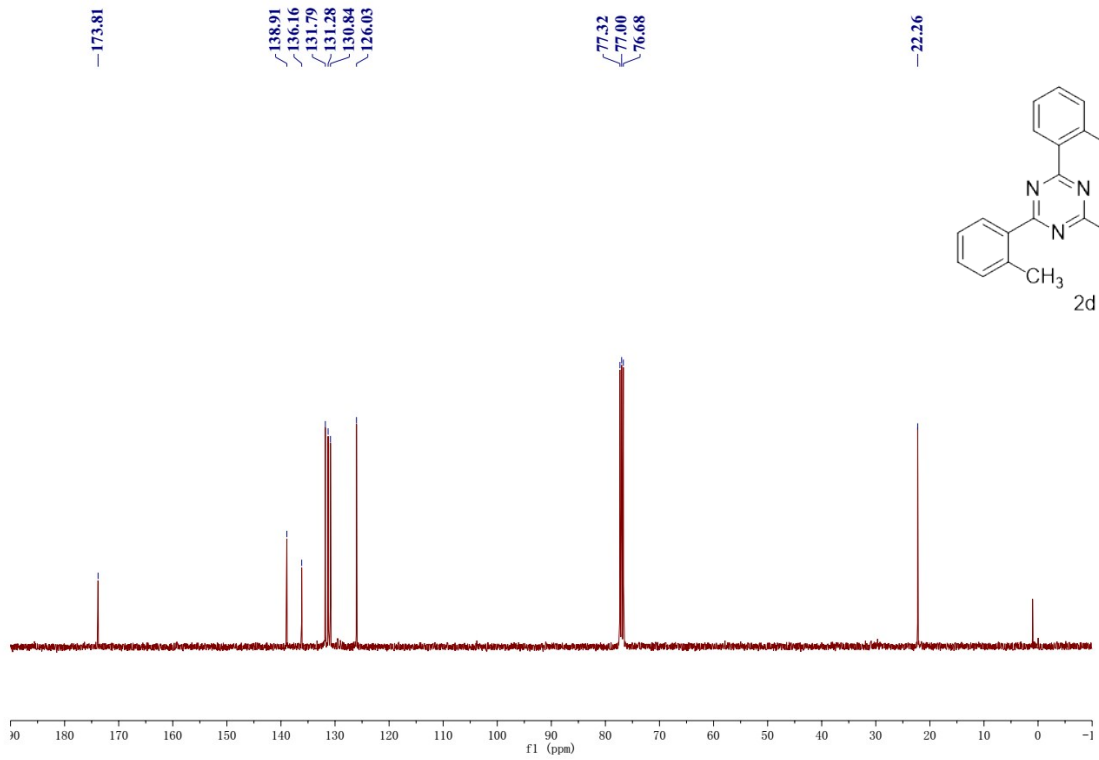


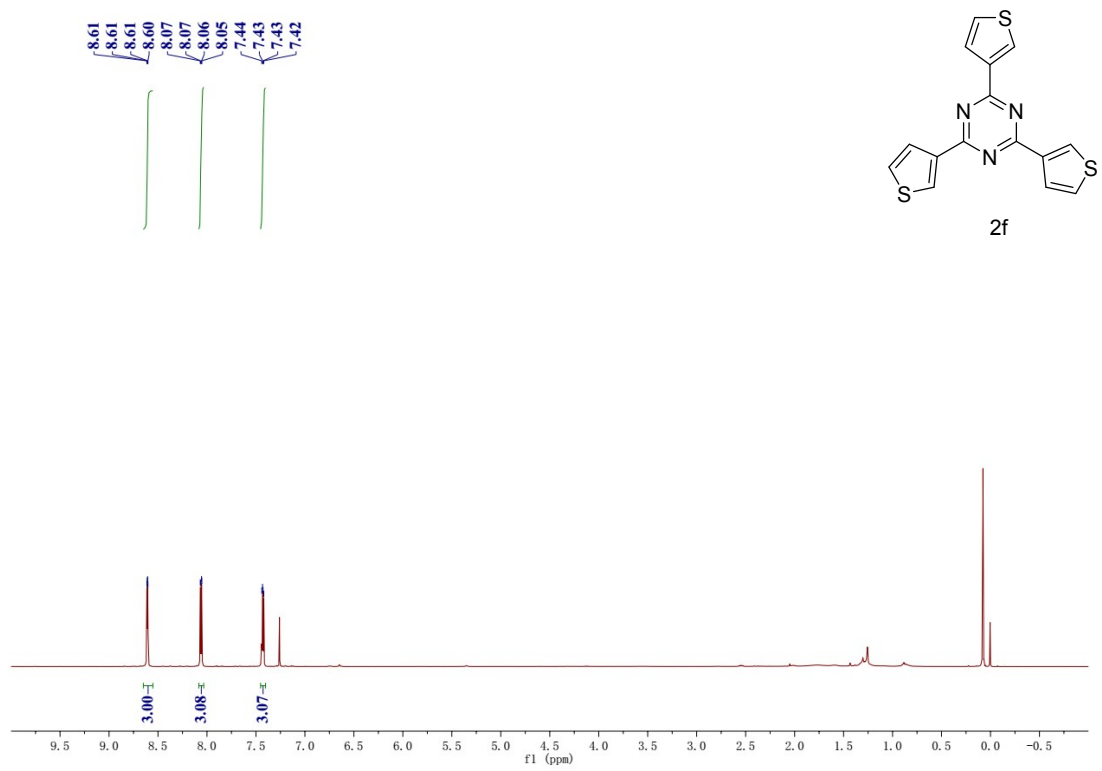
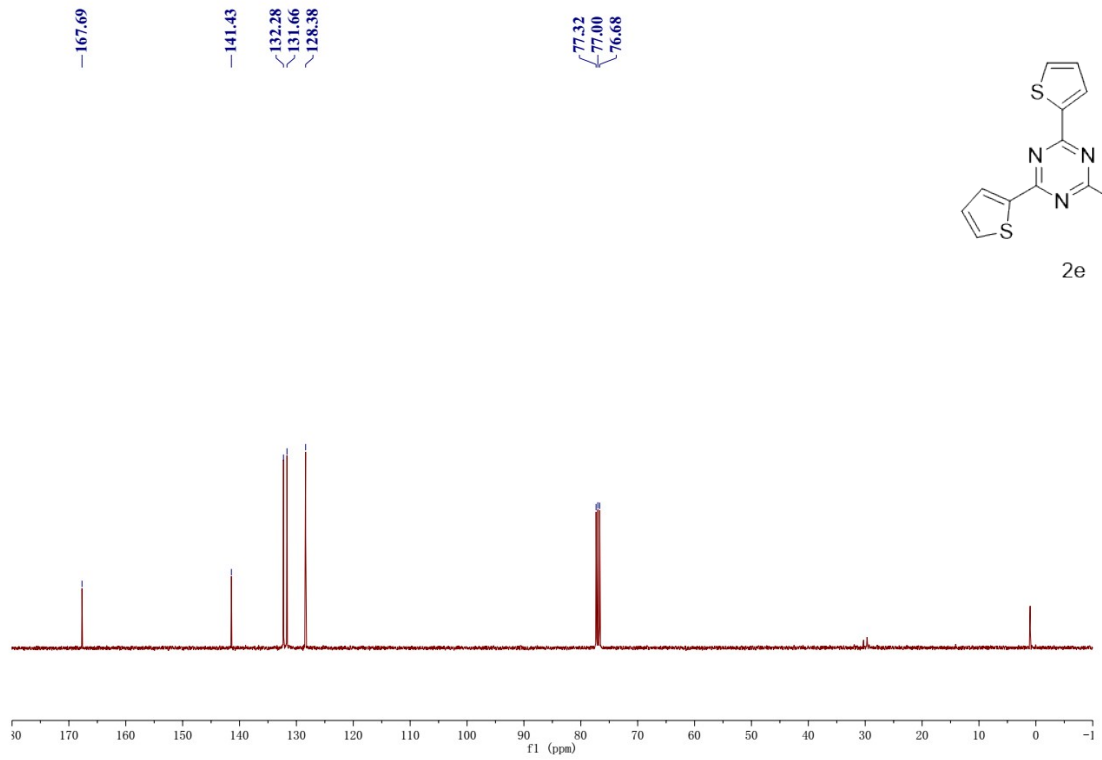


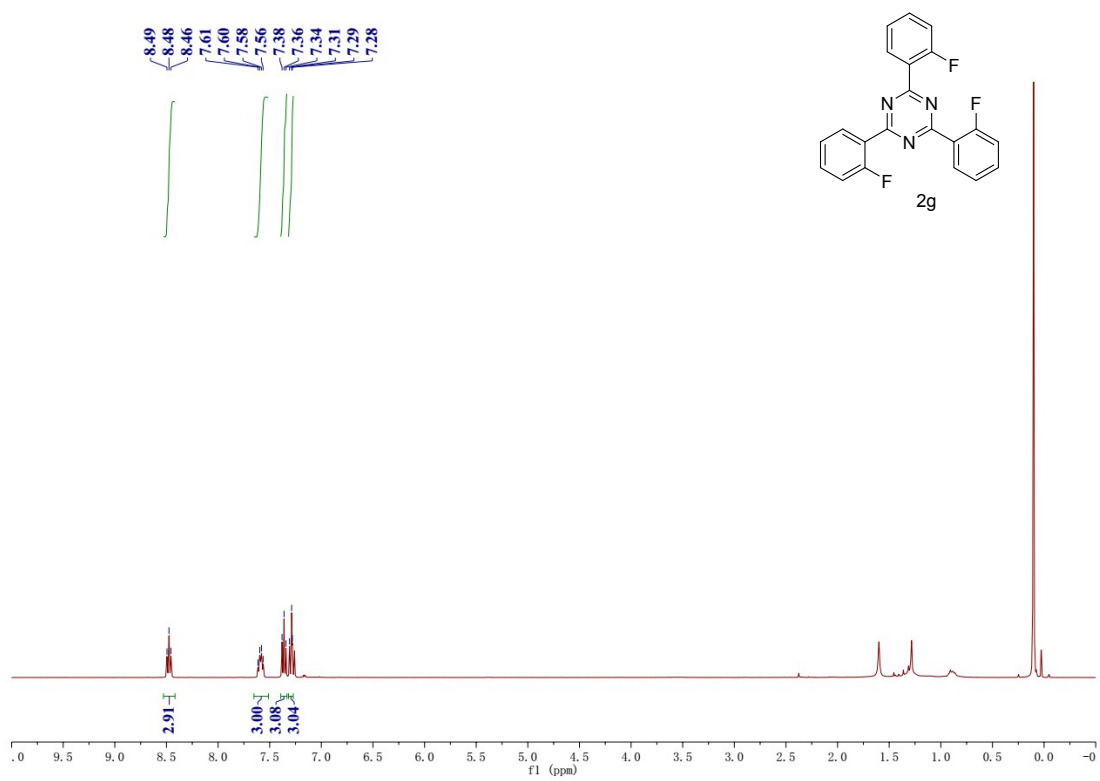
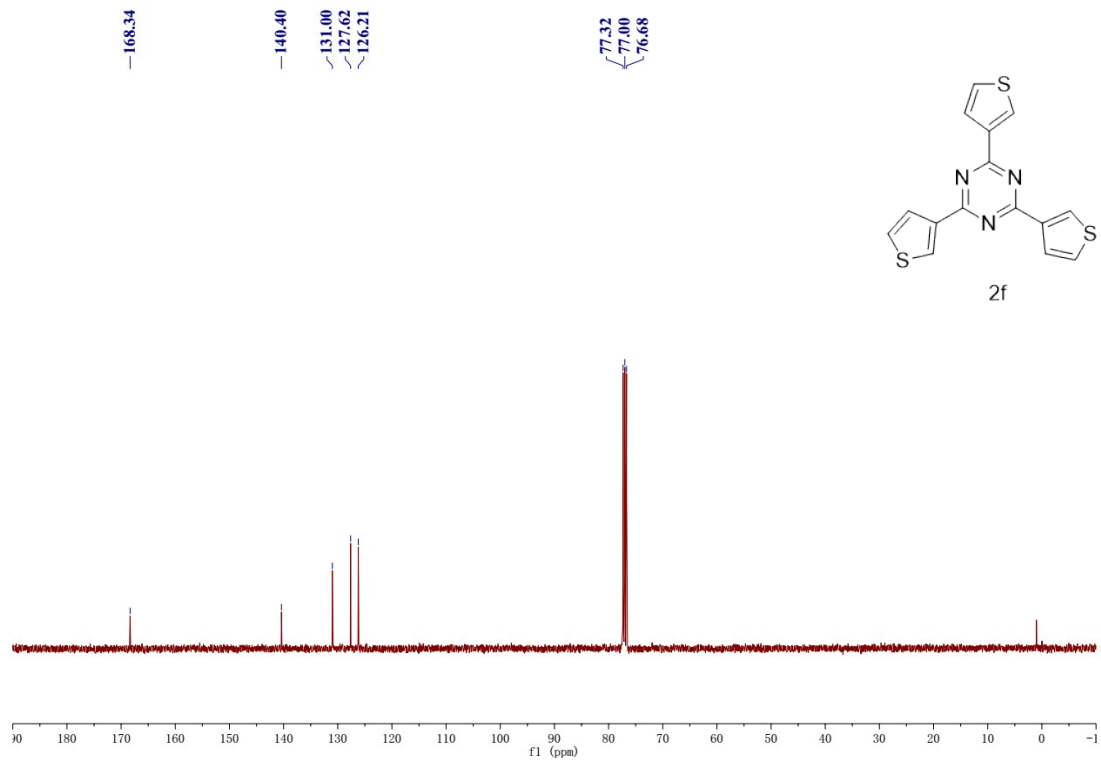


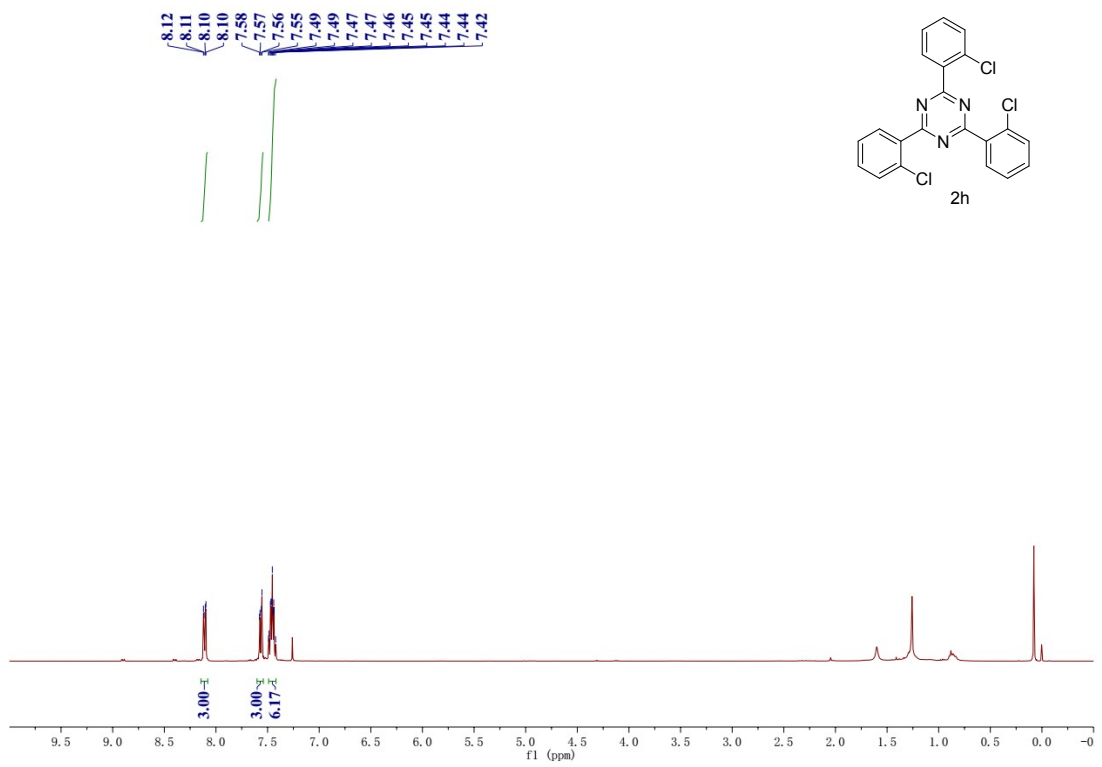
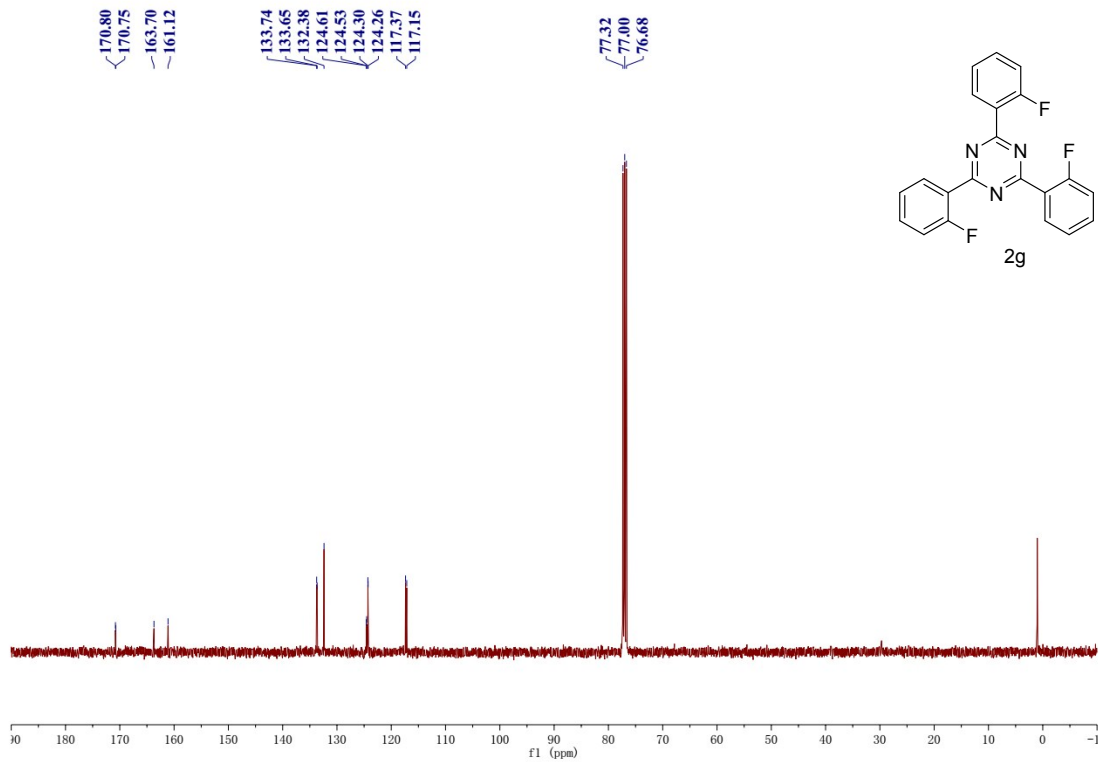


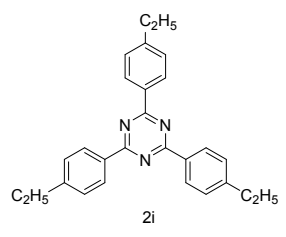
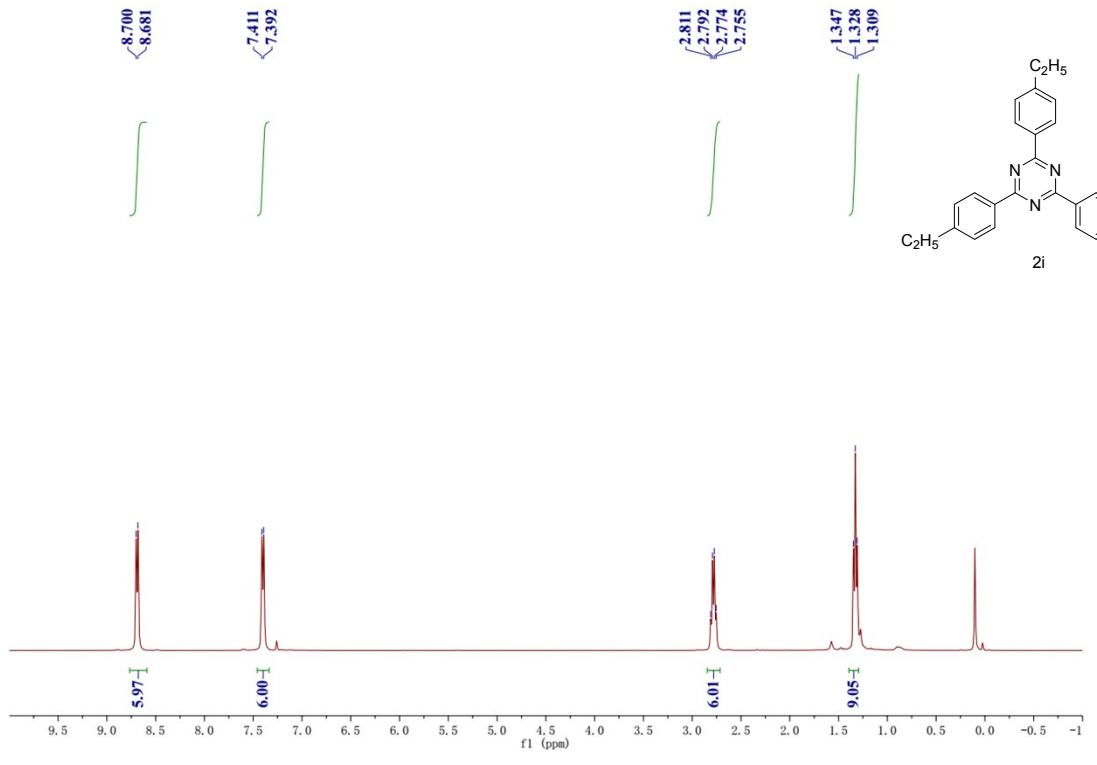
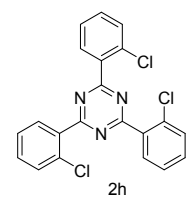
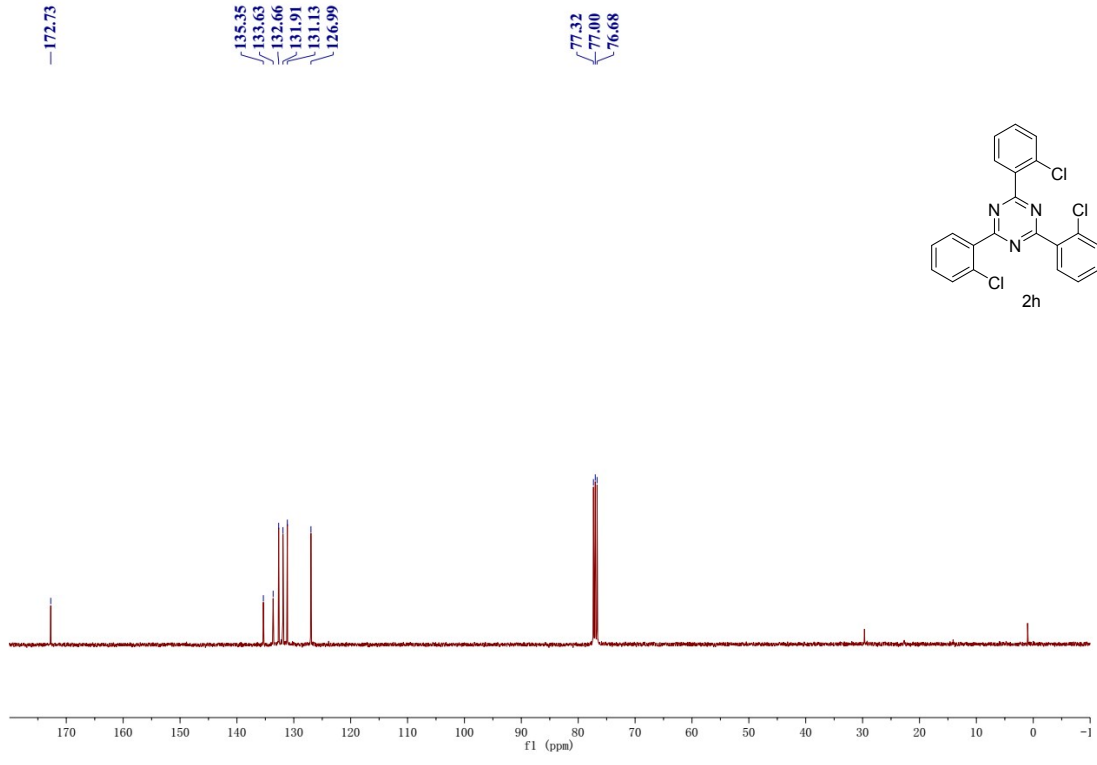












-171.43

-149.09

-134.03

-129.01

-128.11

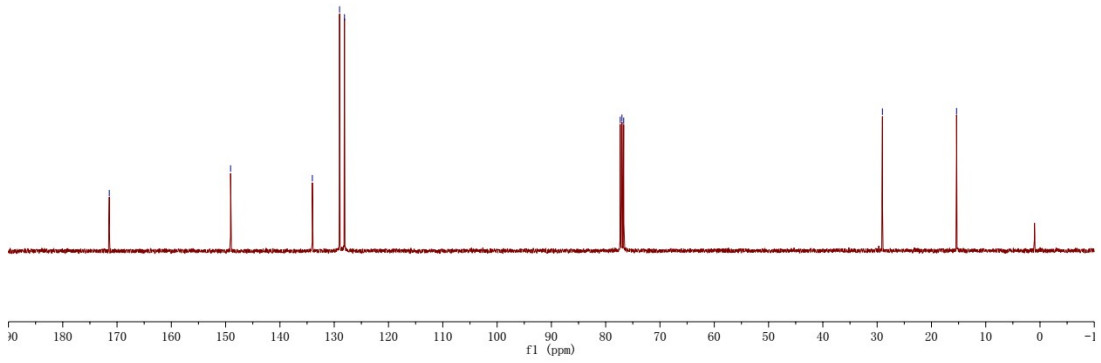
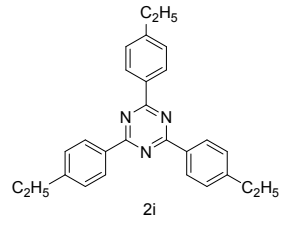
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-76.68

-29.02

-15.37



8.759

8.607

8.587

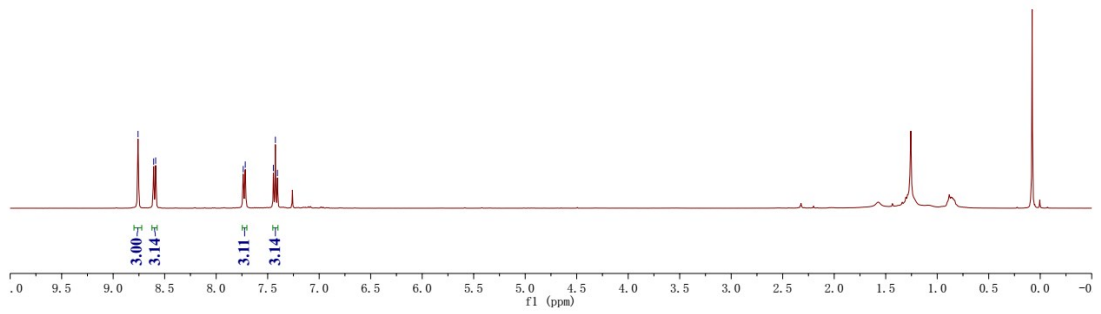
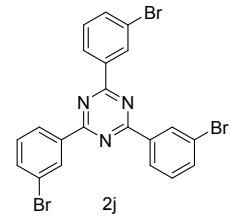
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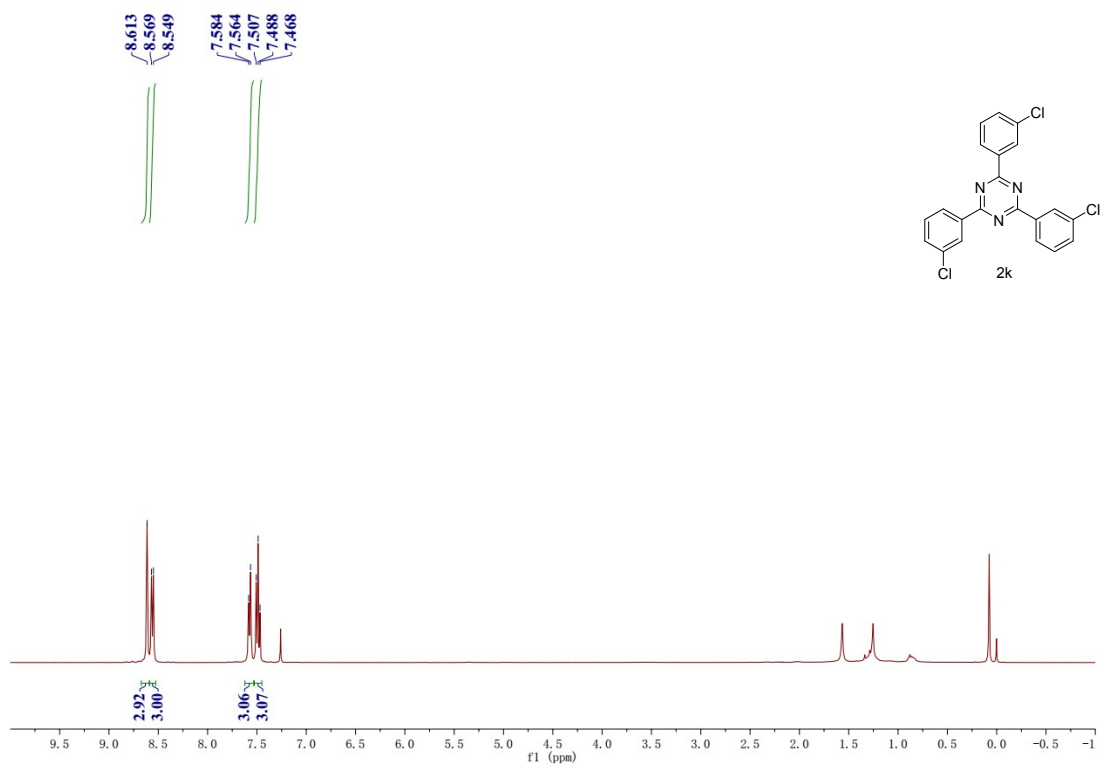
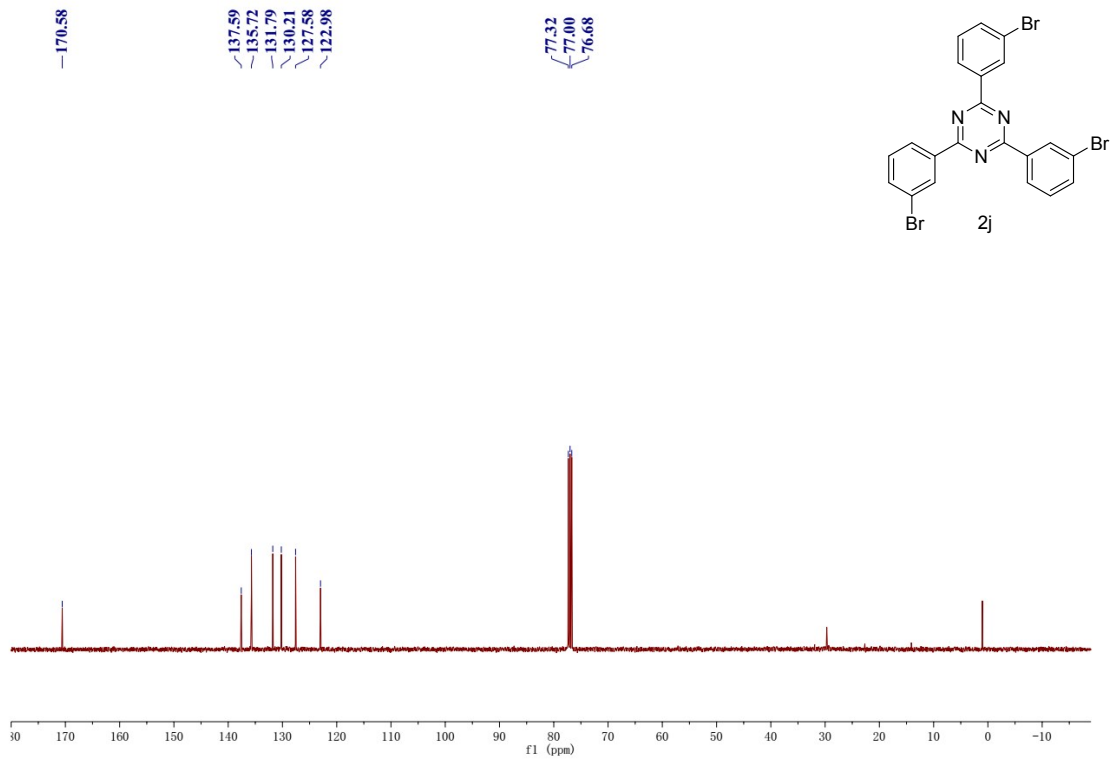
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7.445

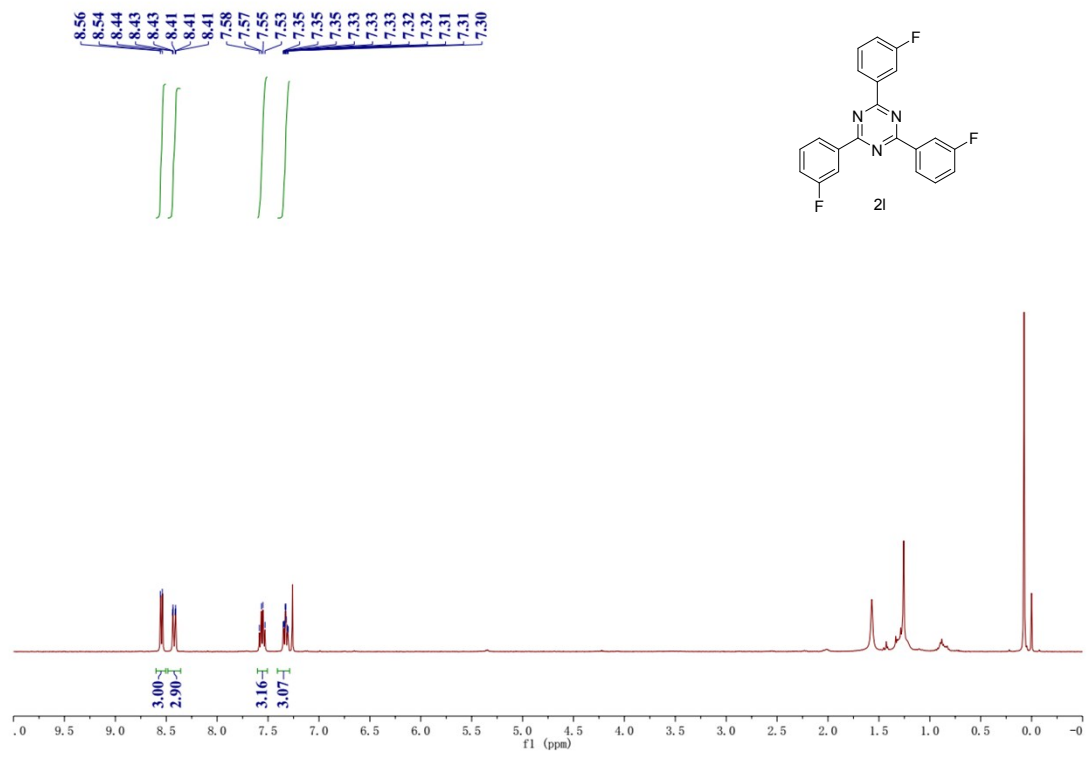
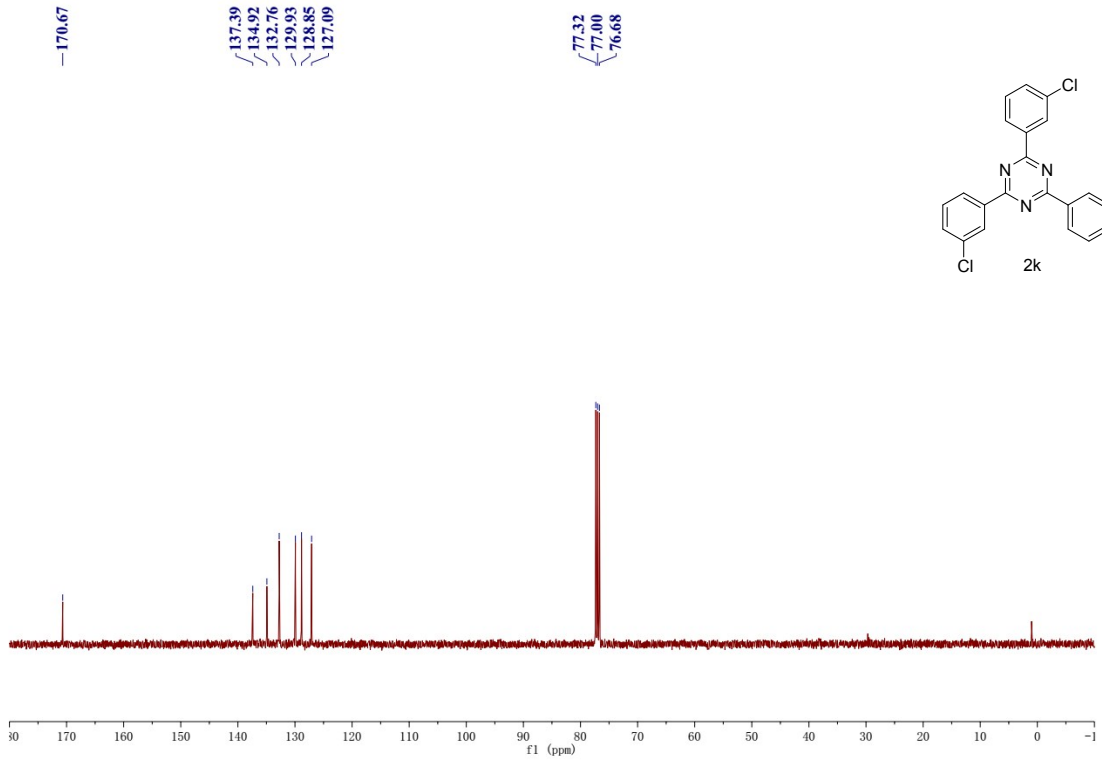
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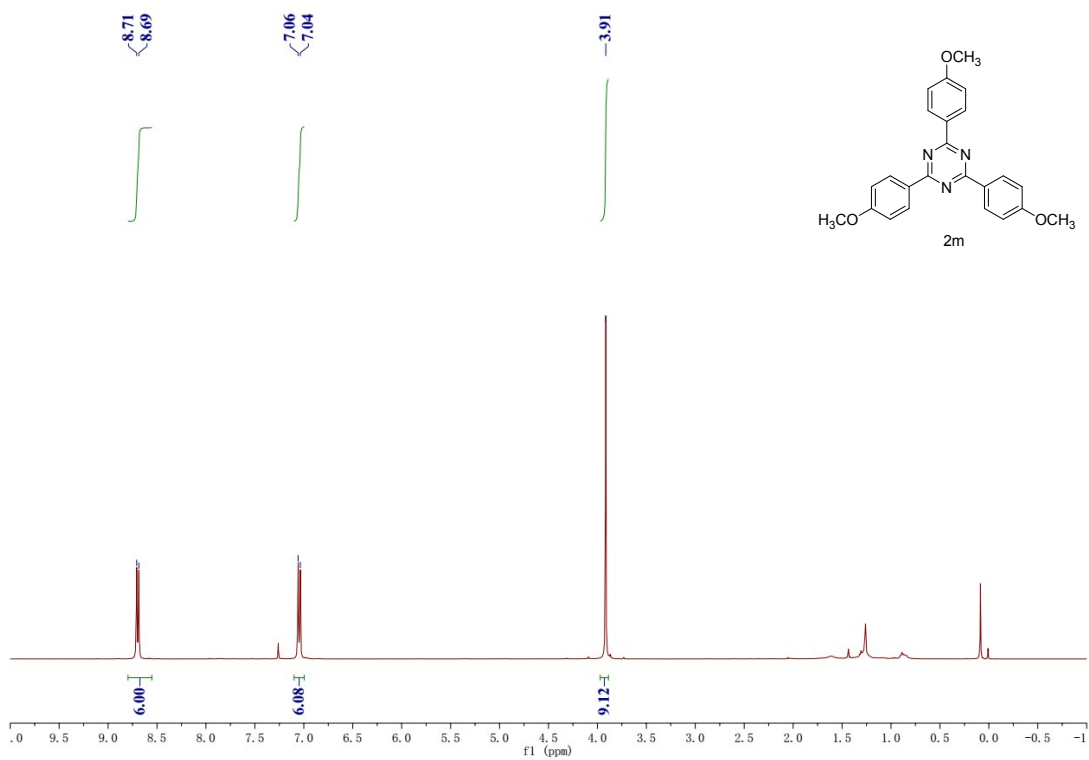
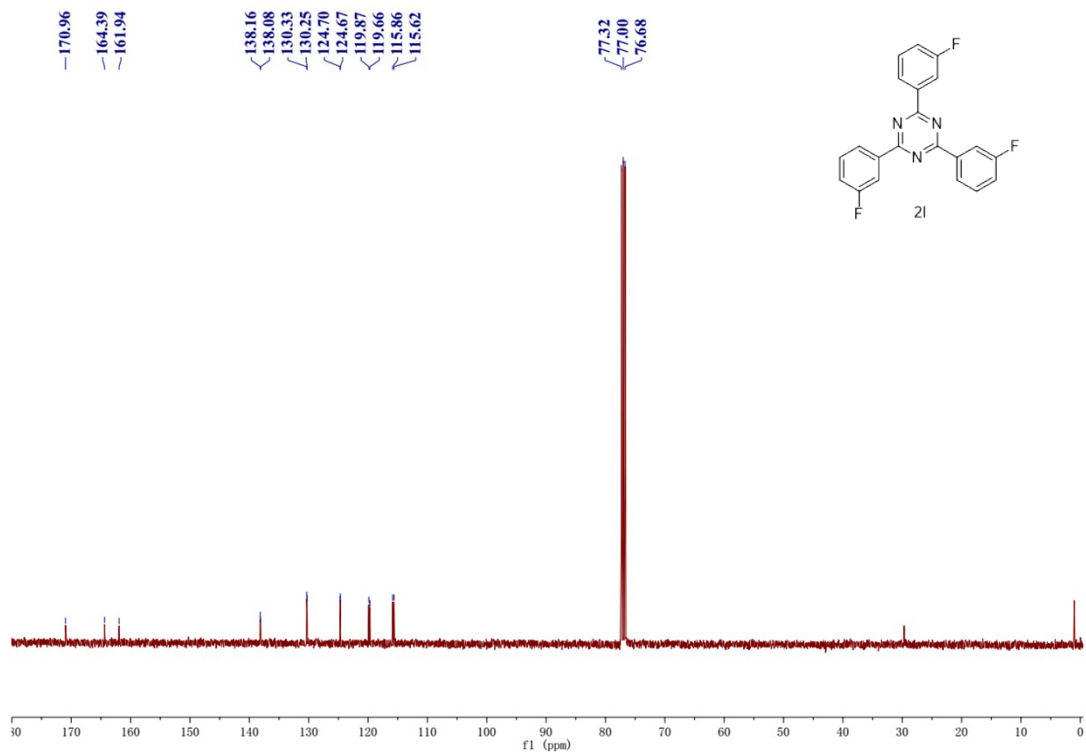
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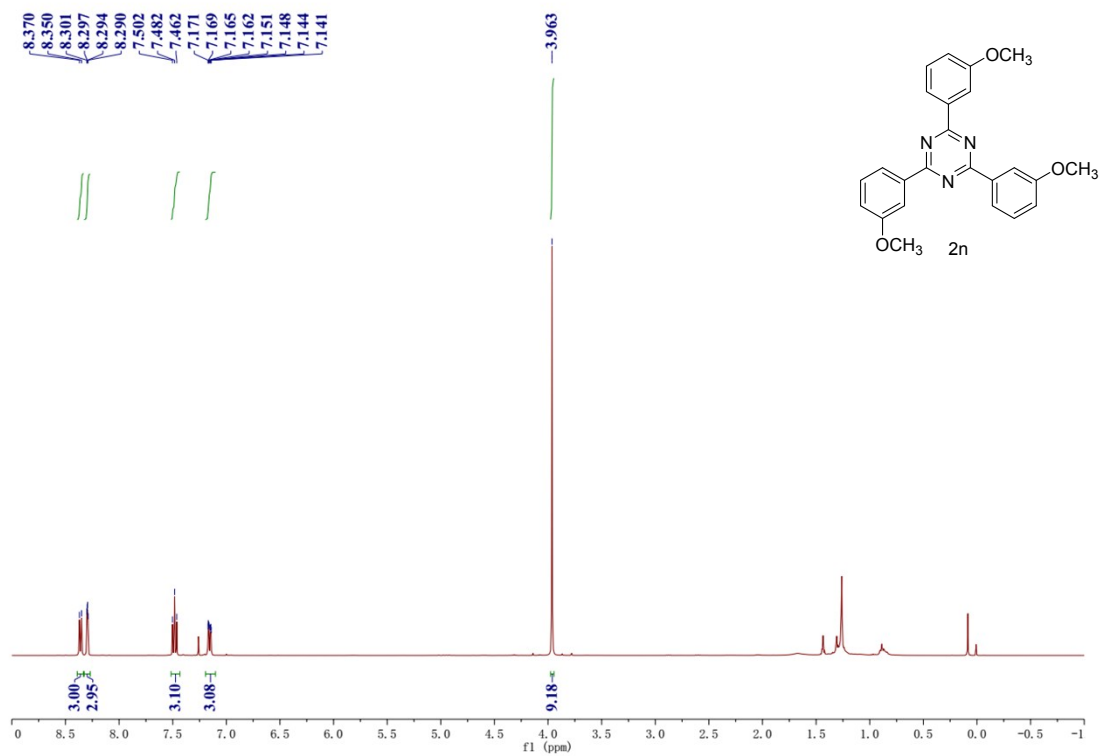
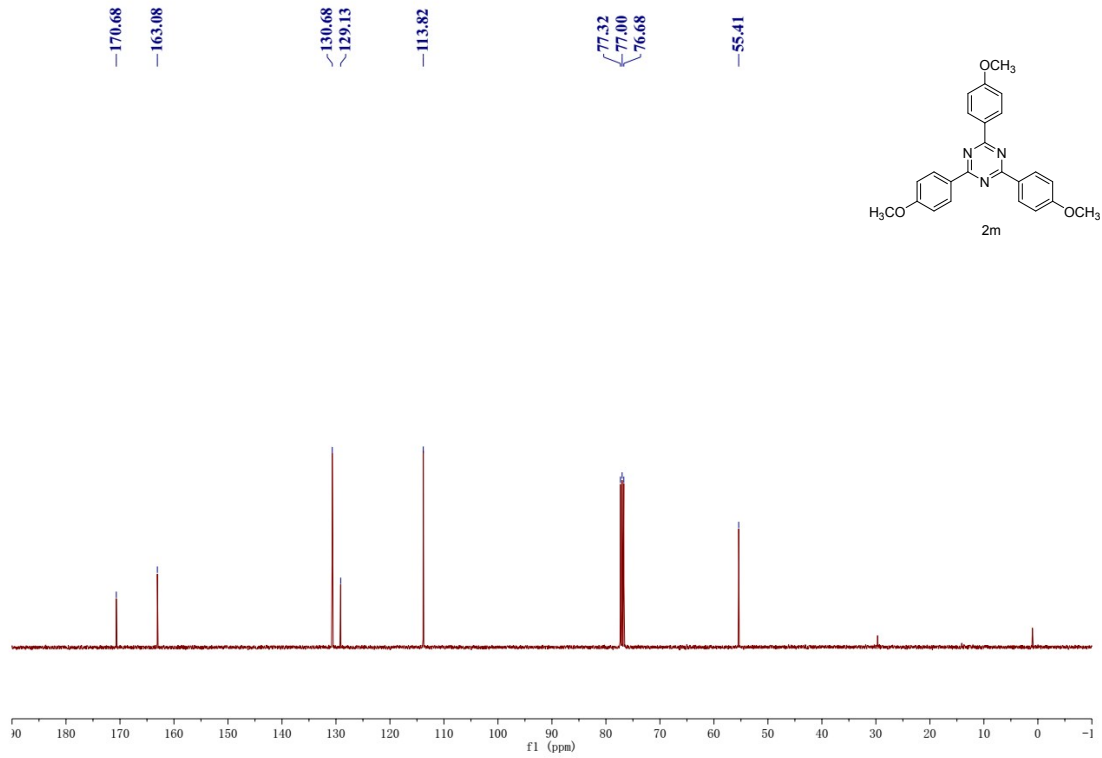


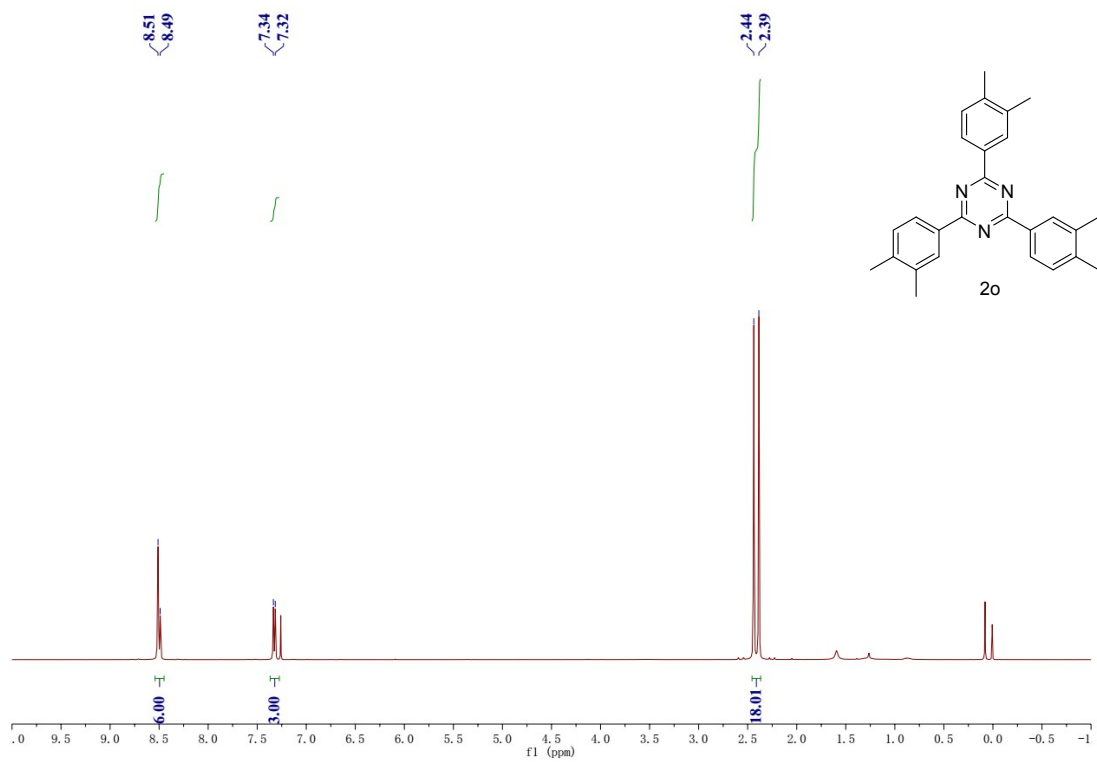
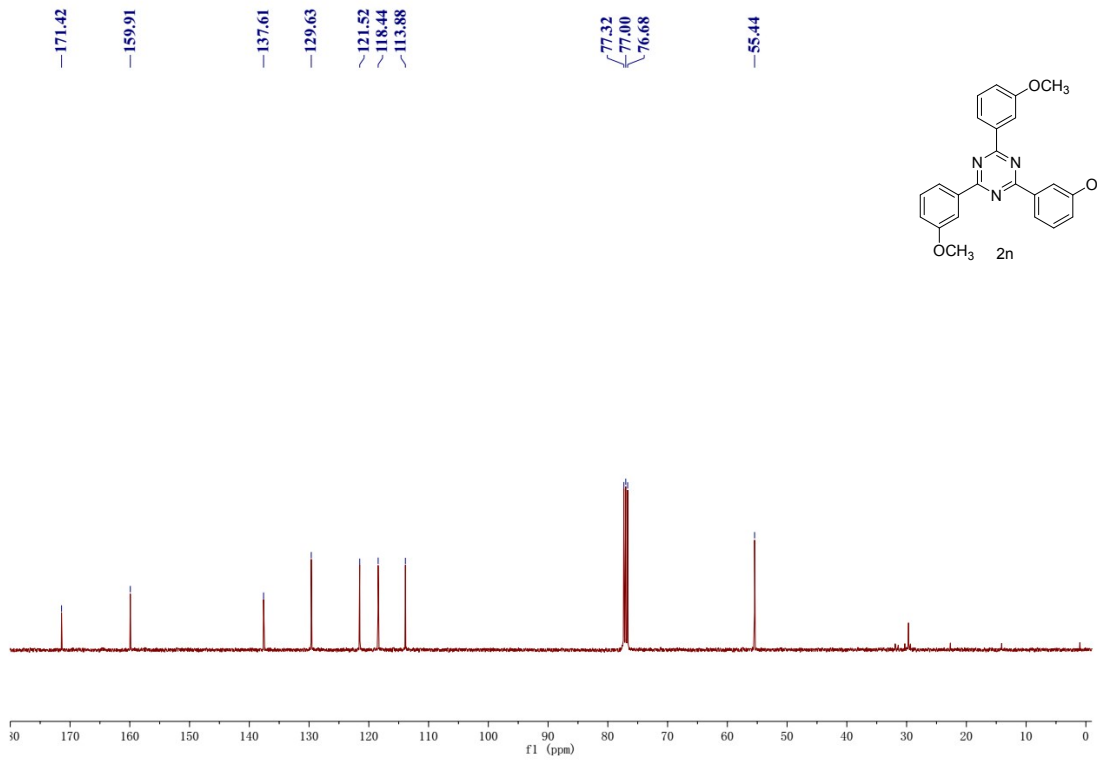


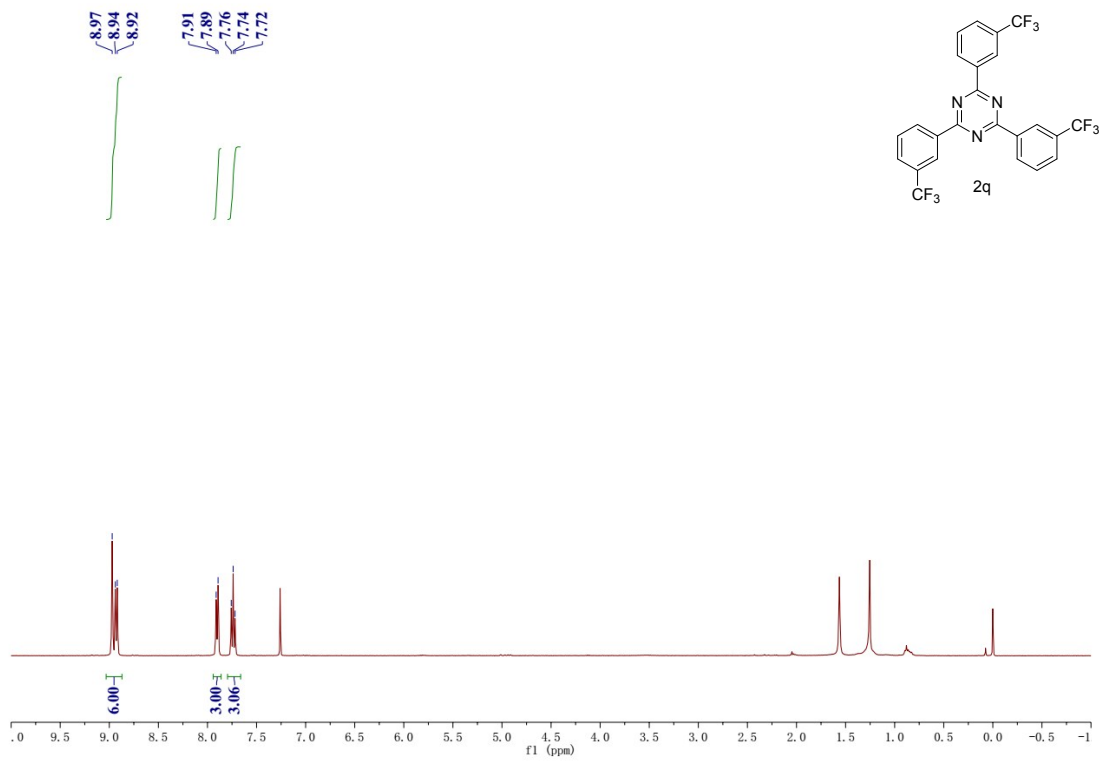
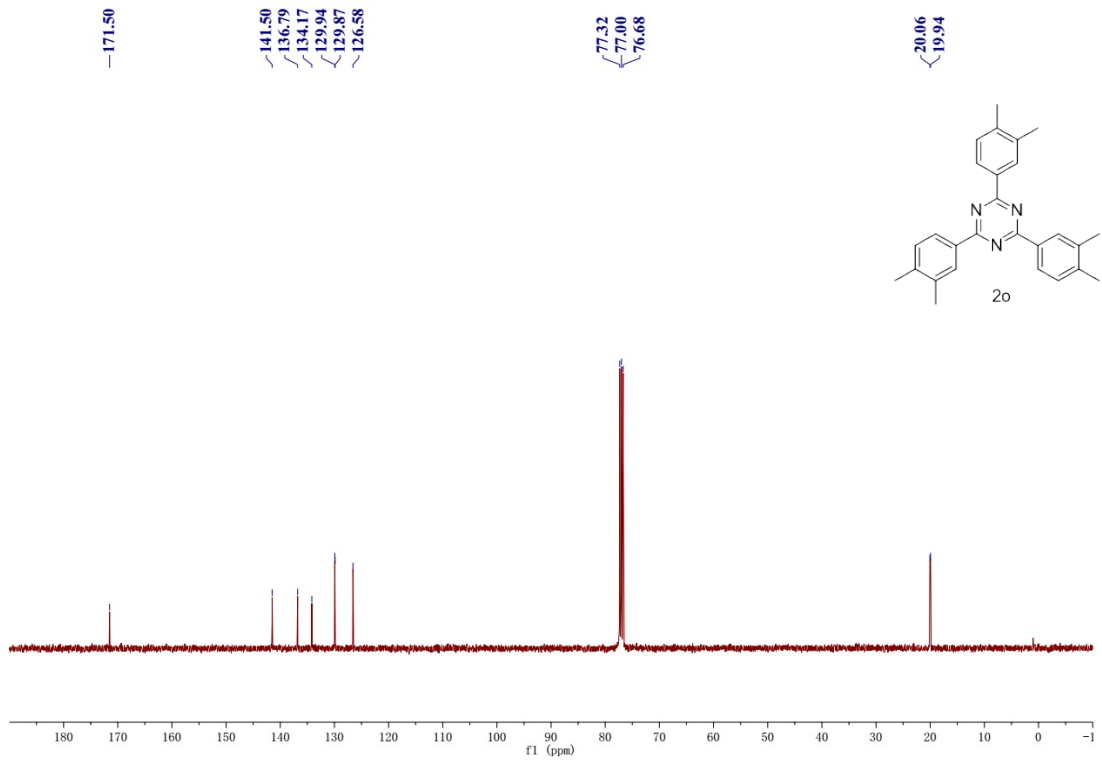


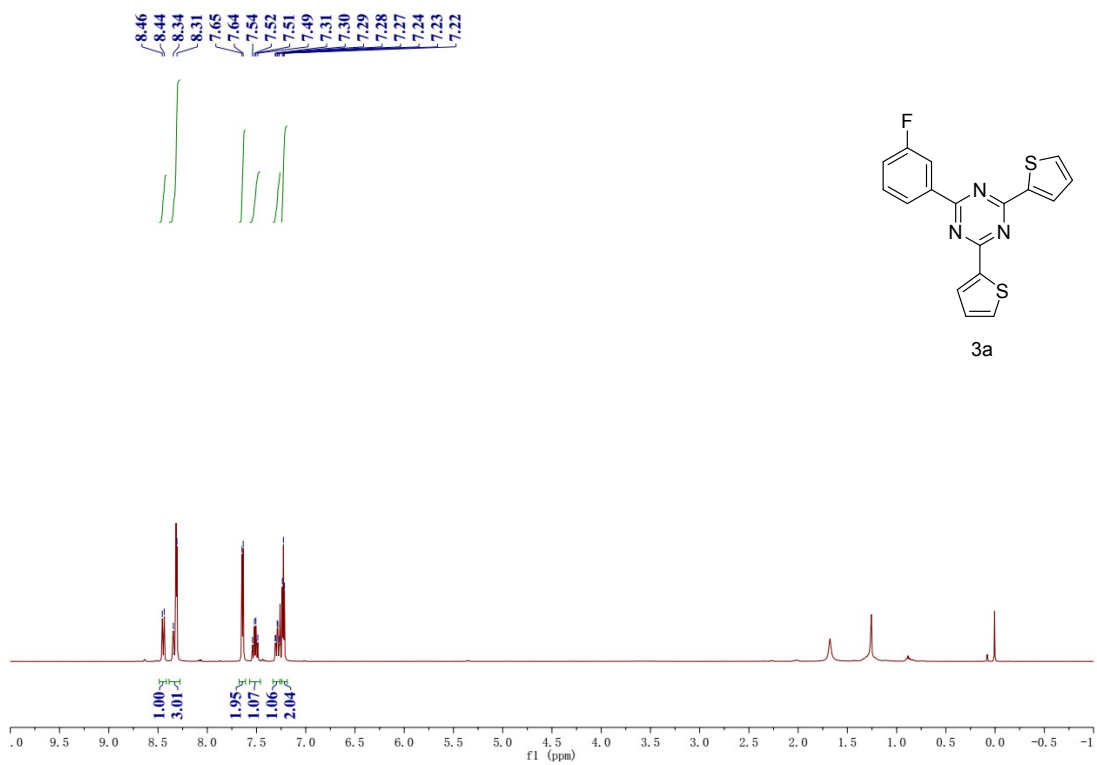
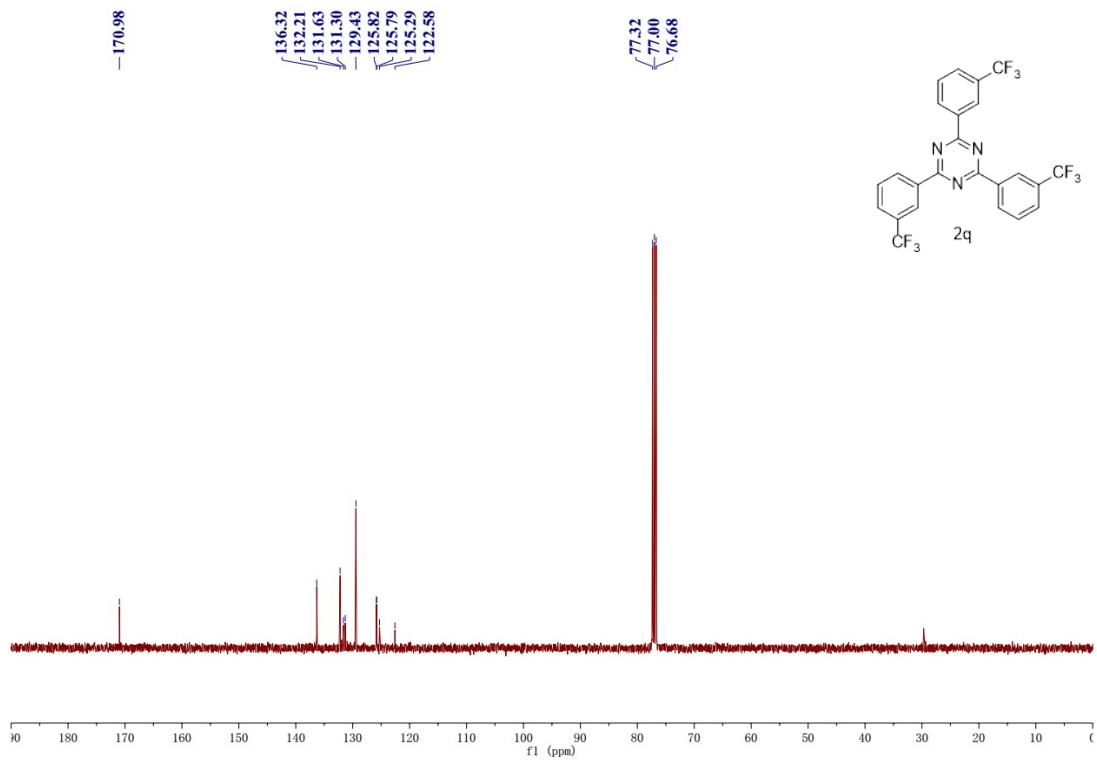


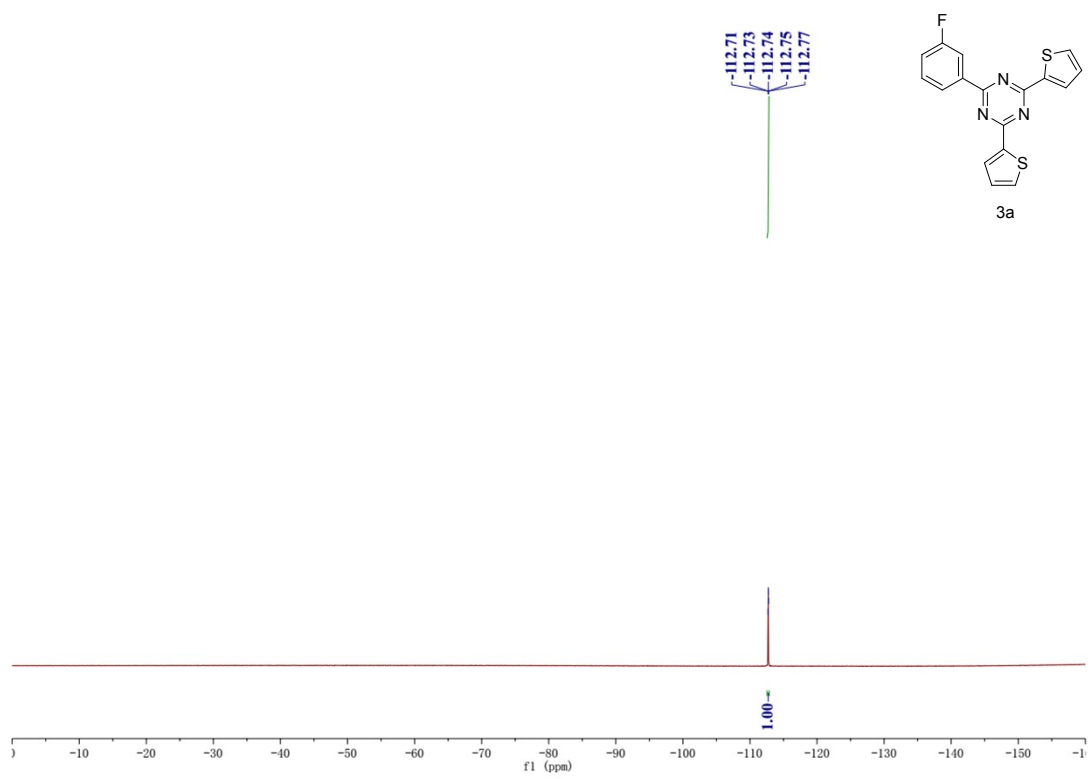
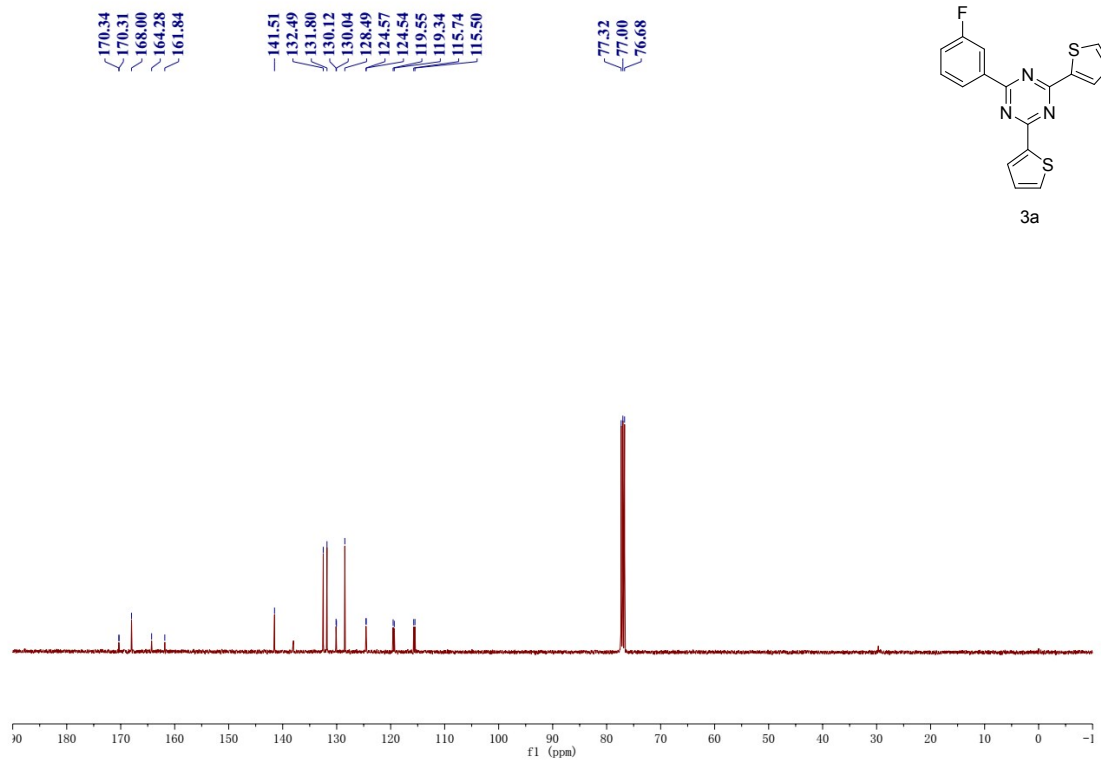


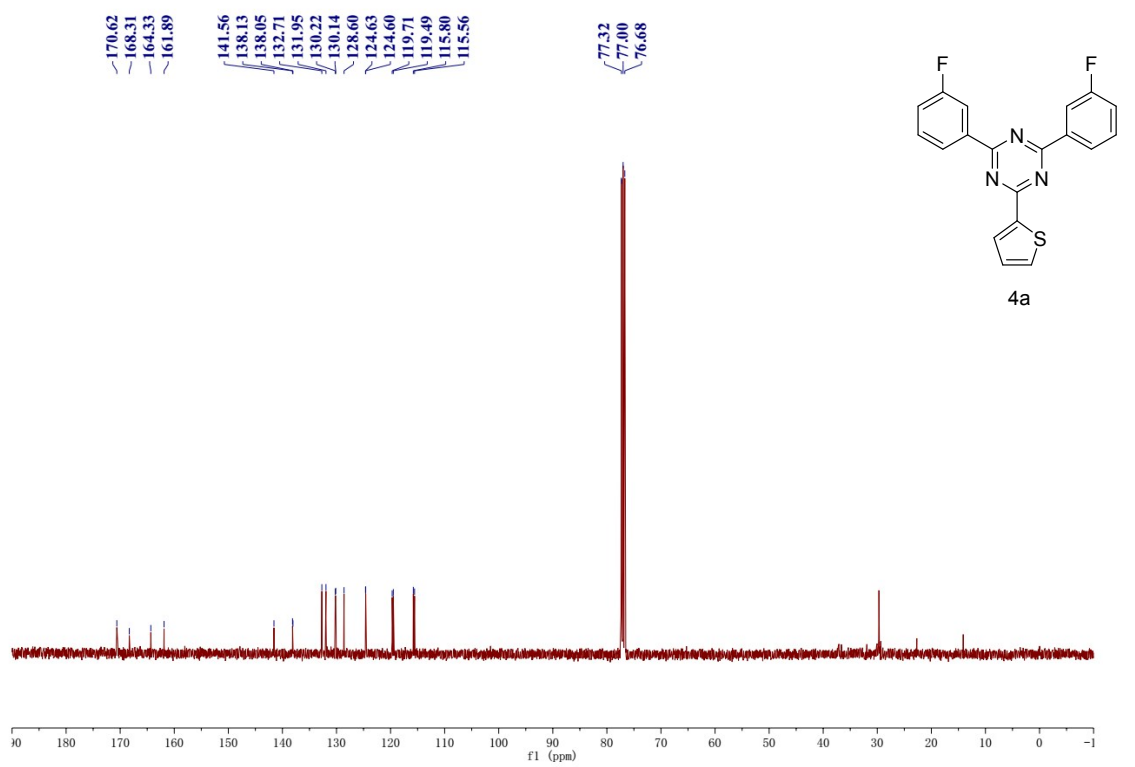
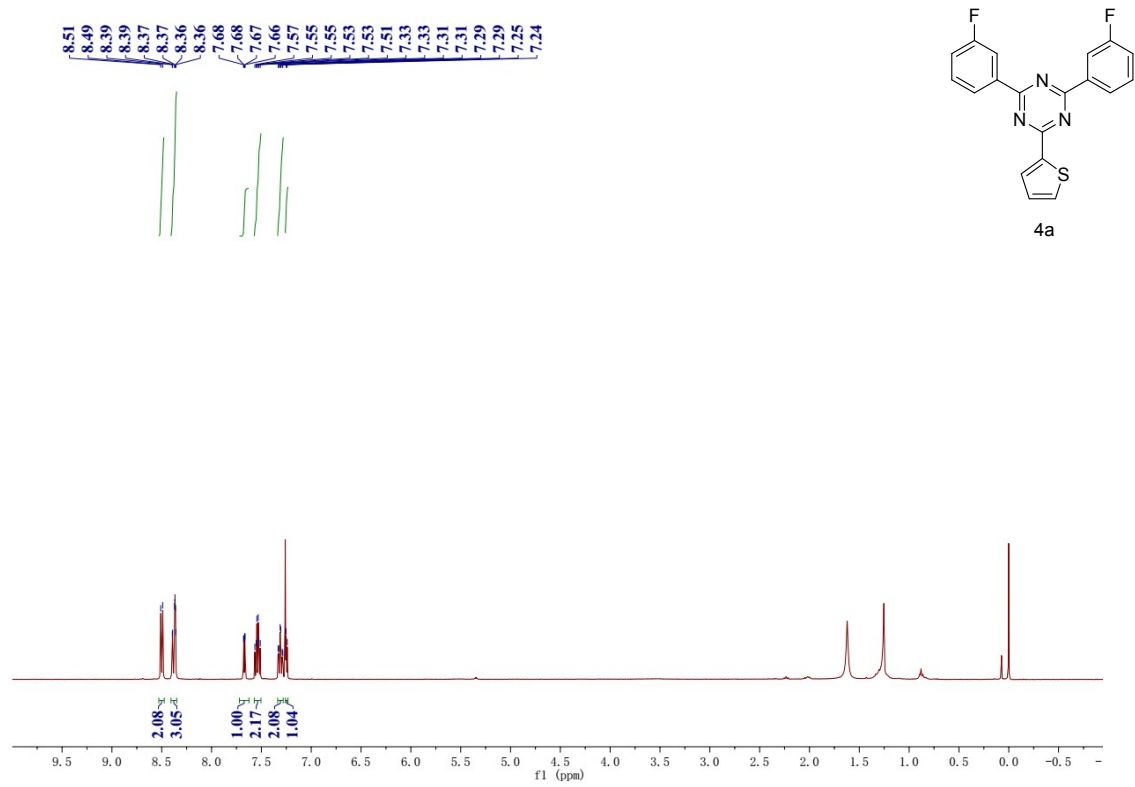




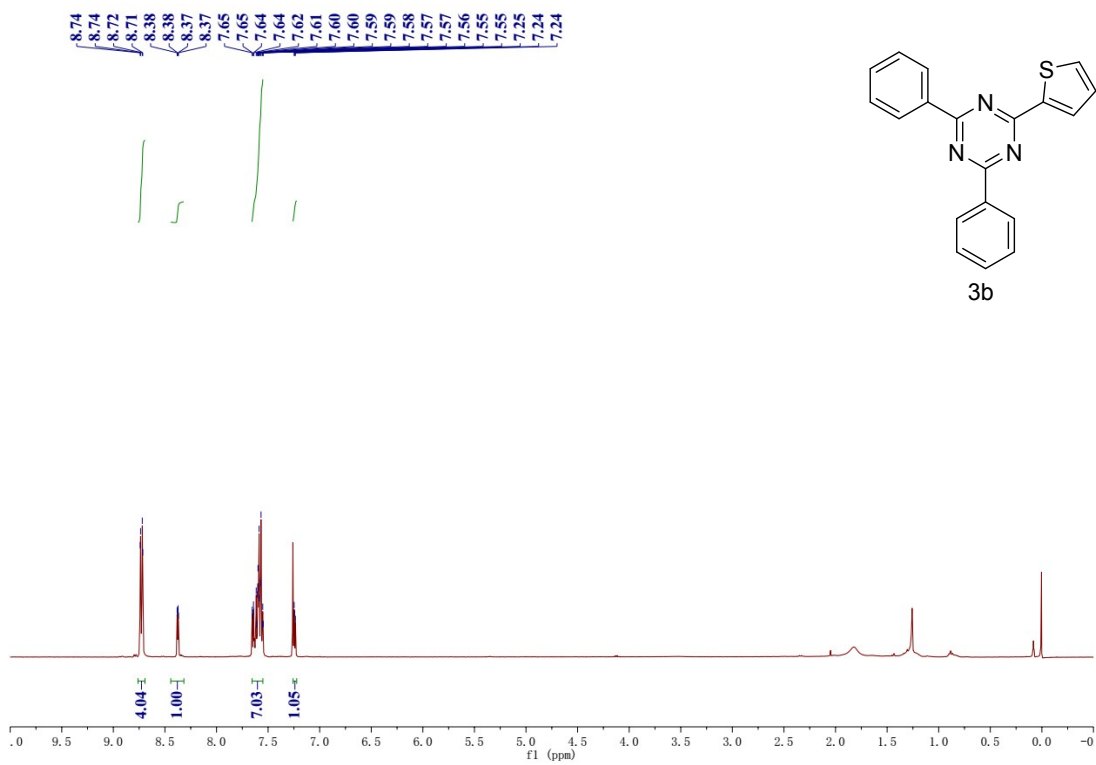
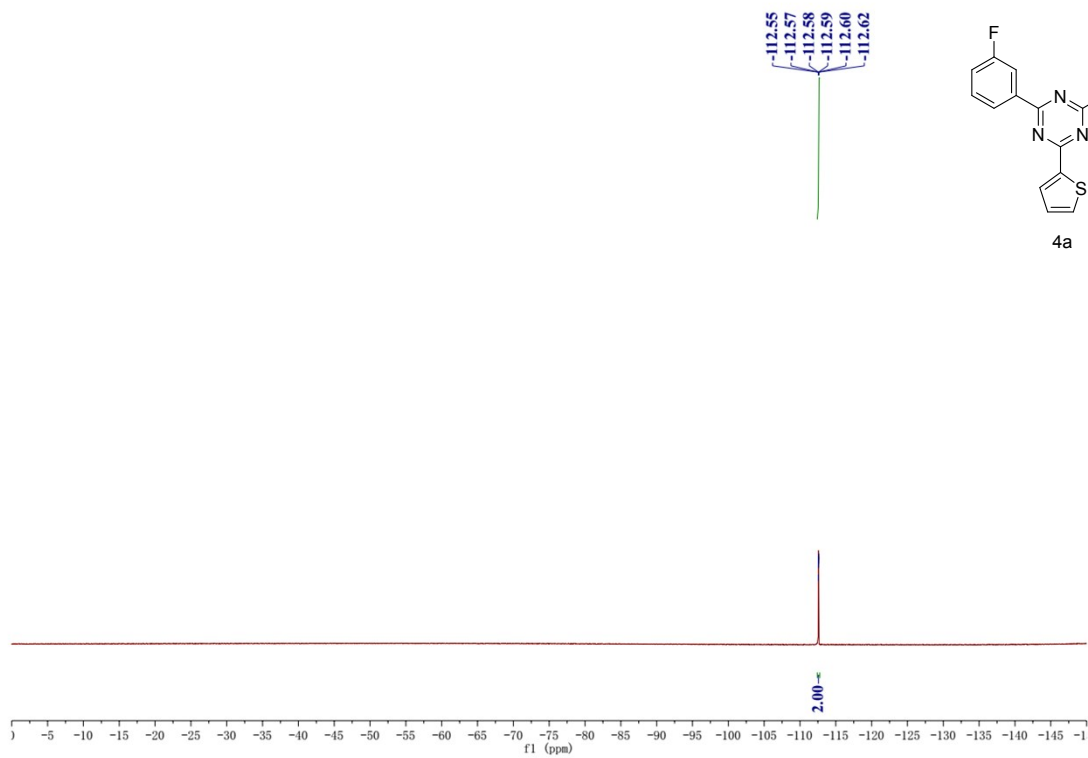


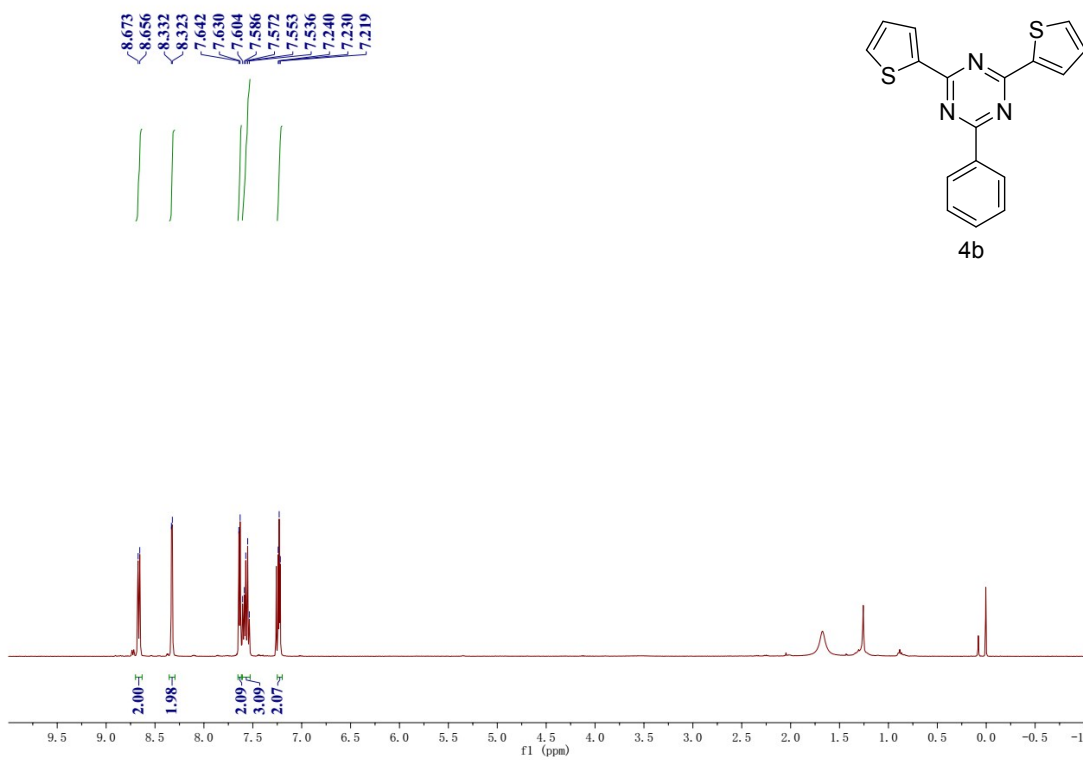
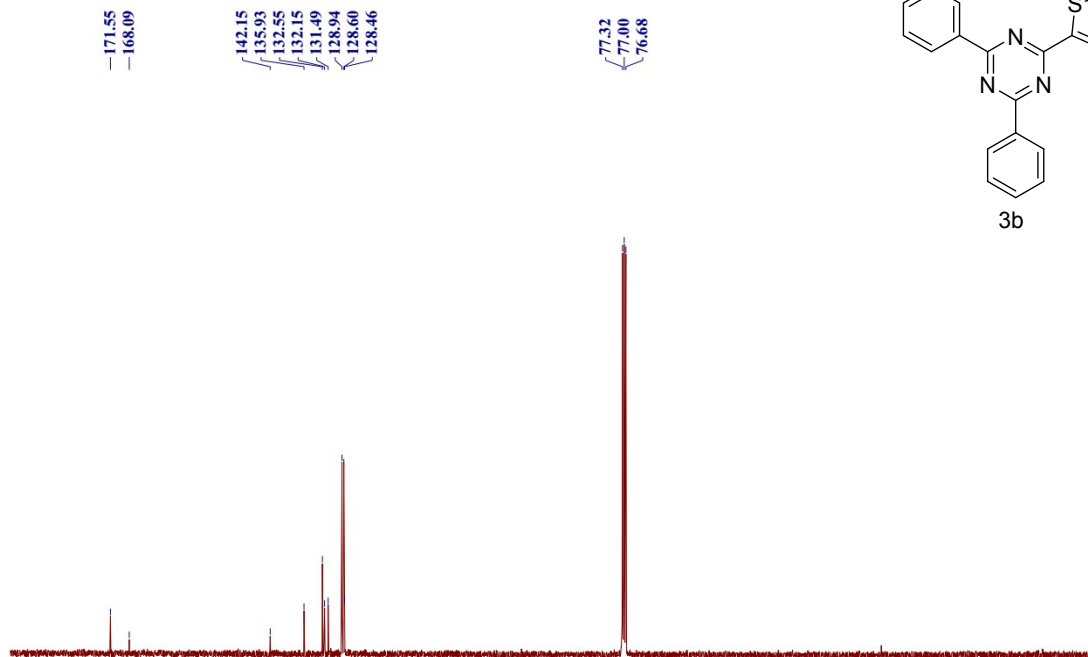


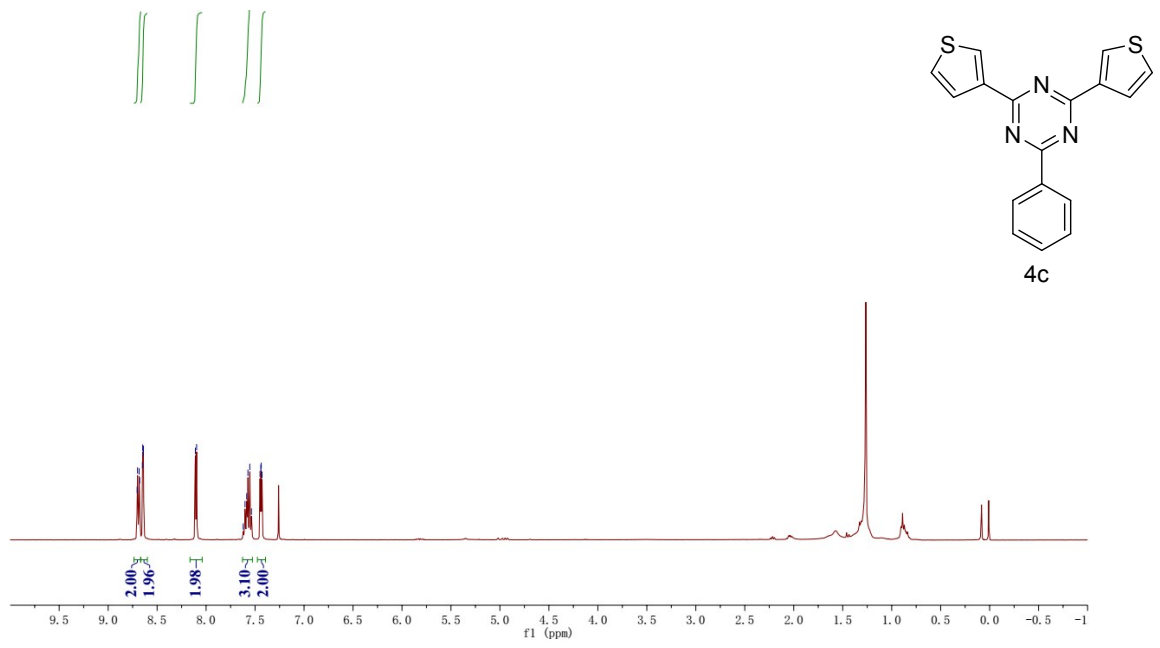
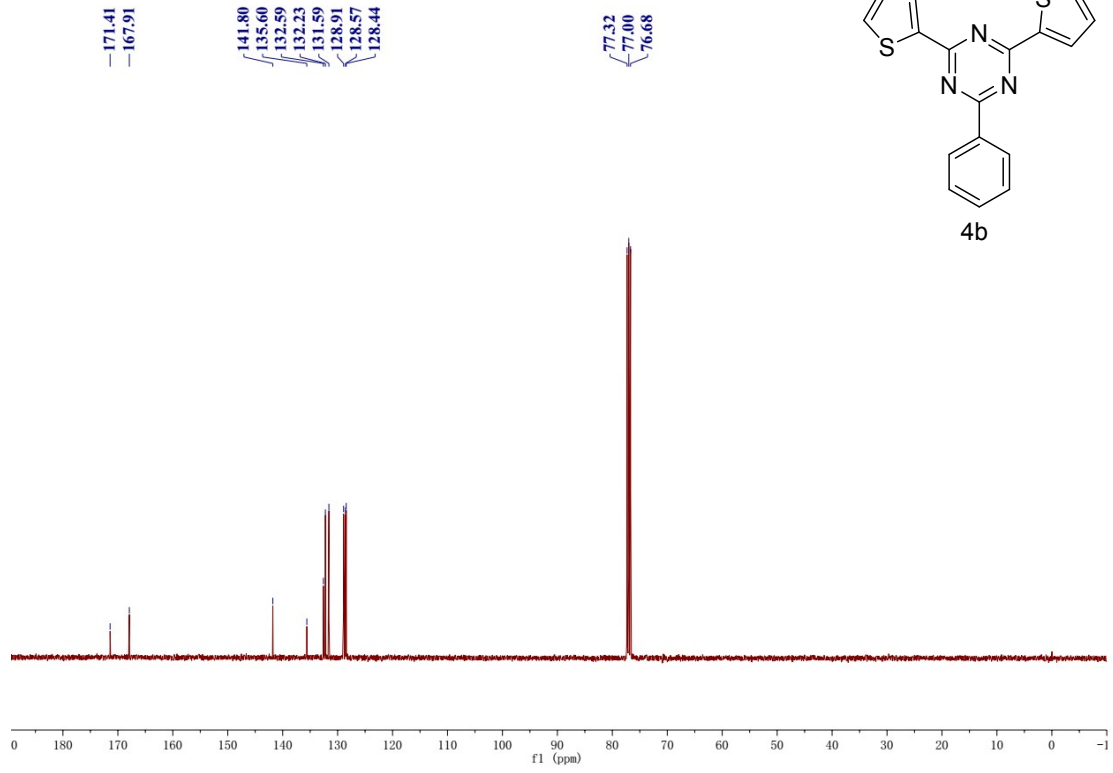


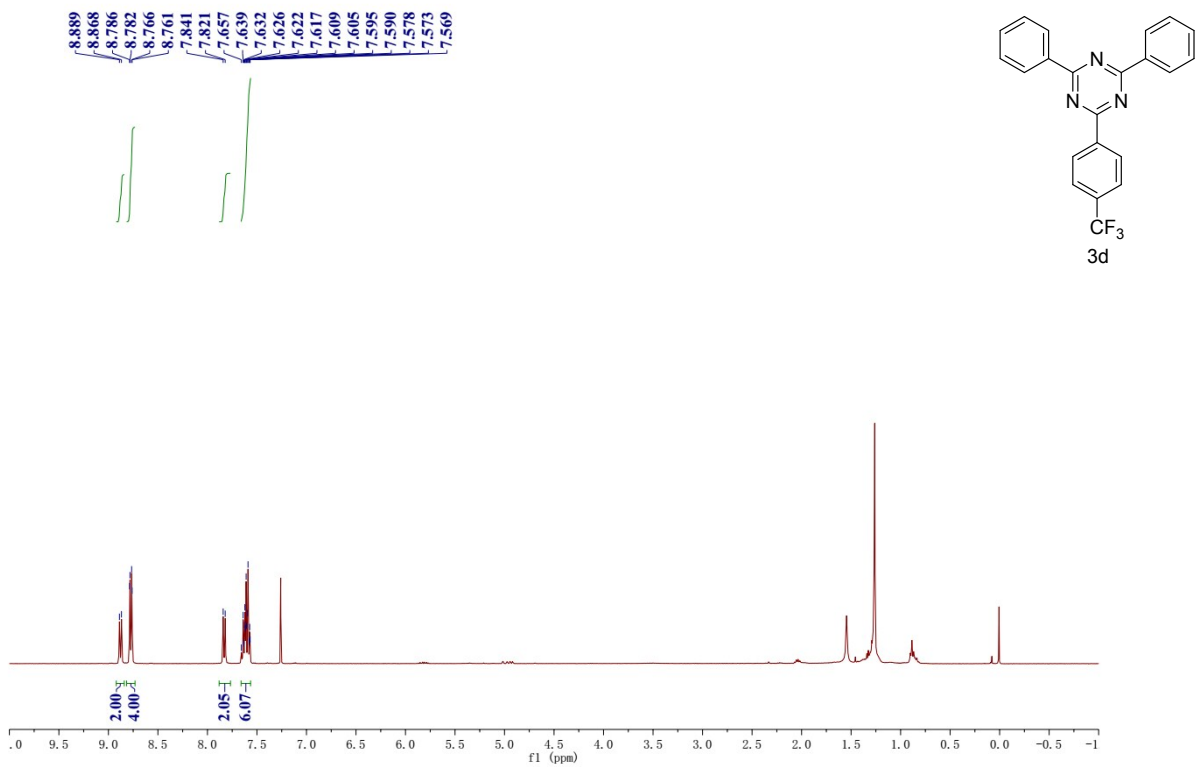
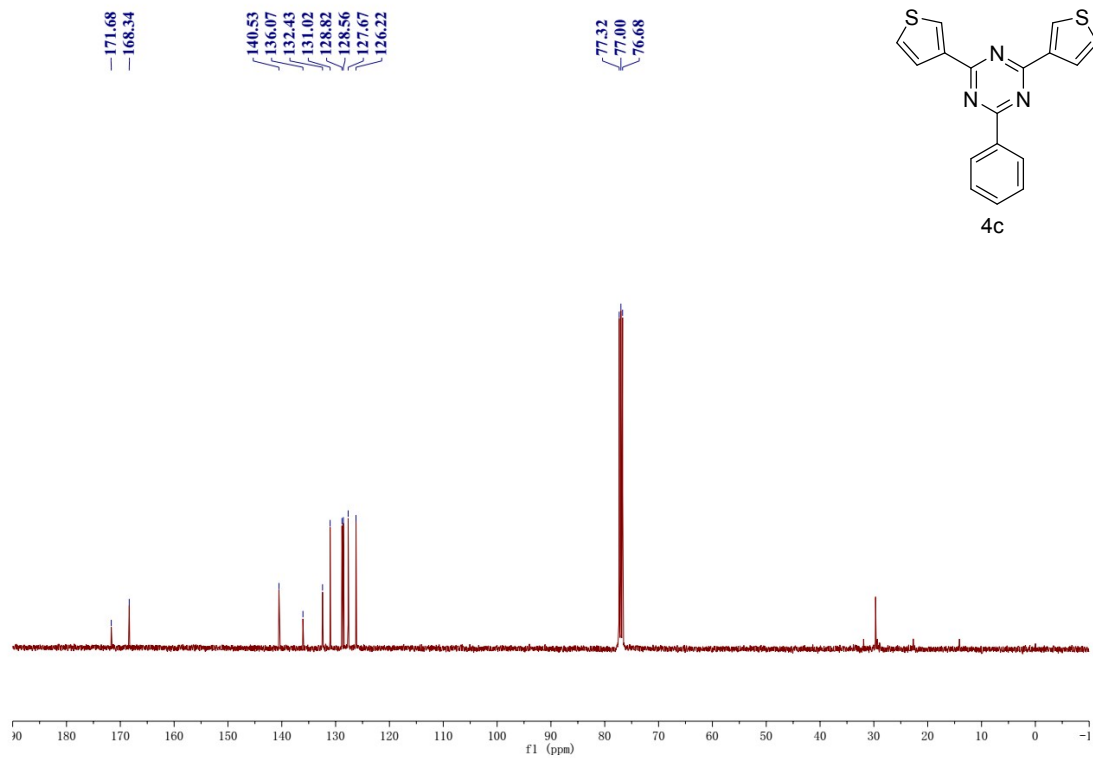


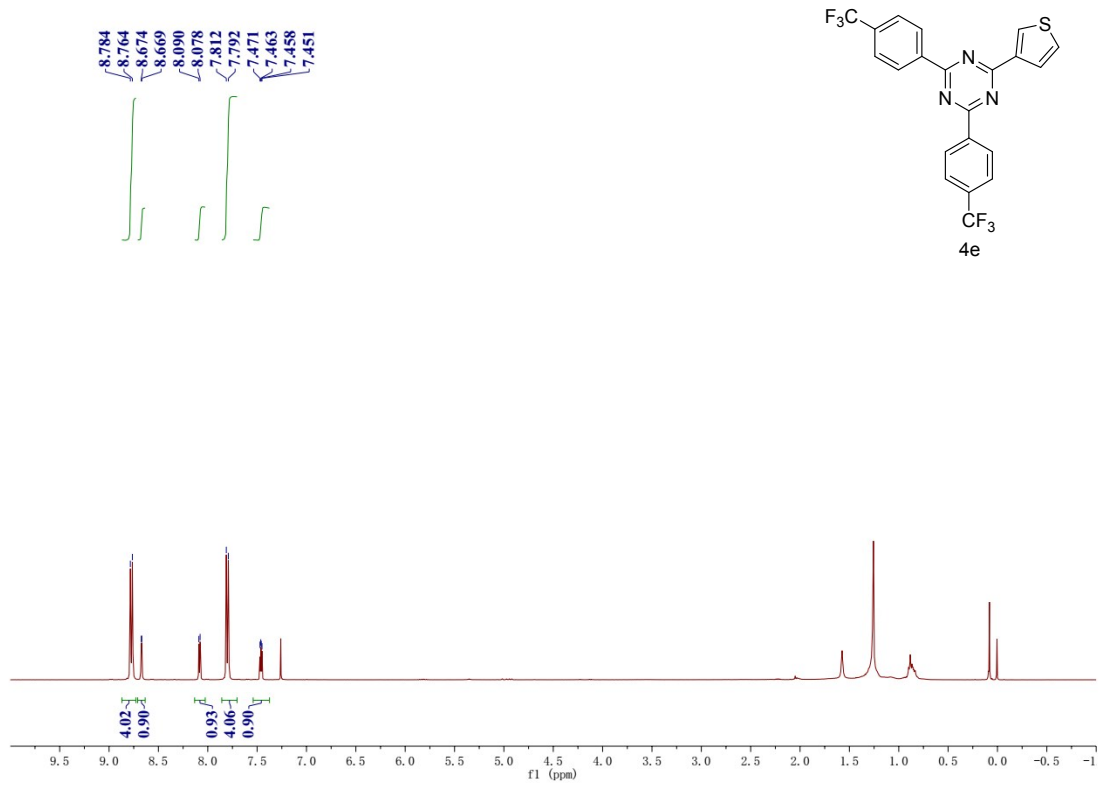
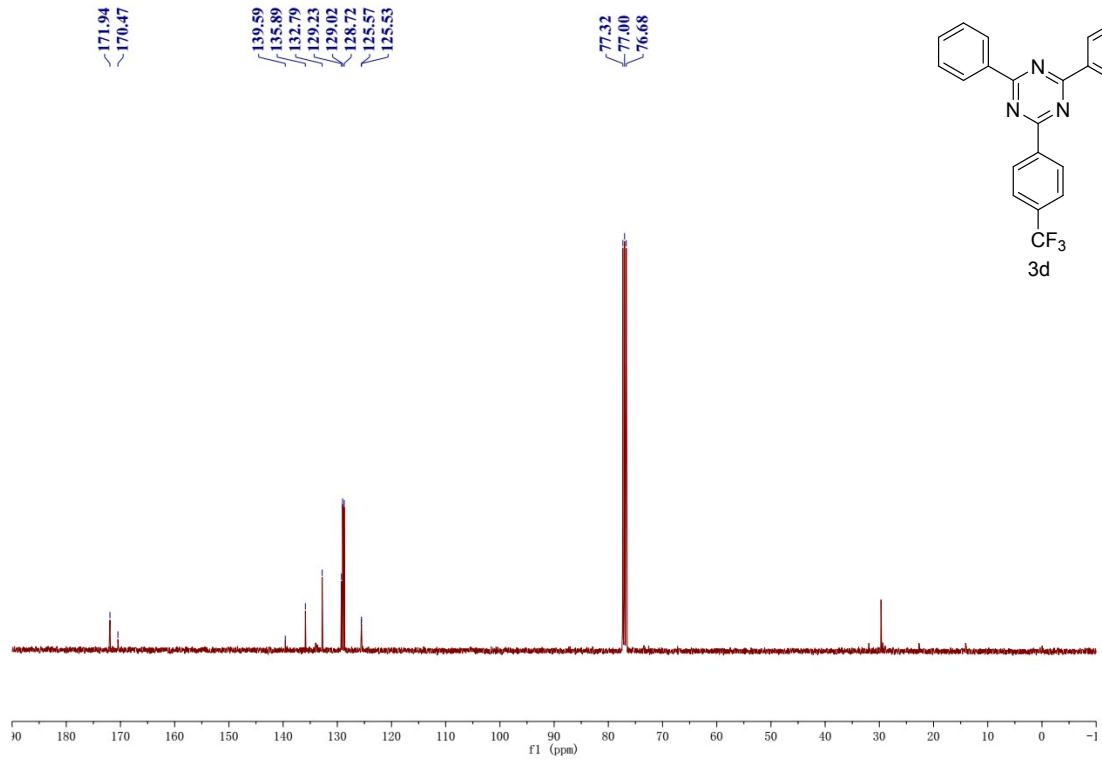


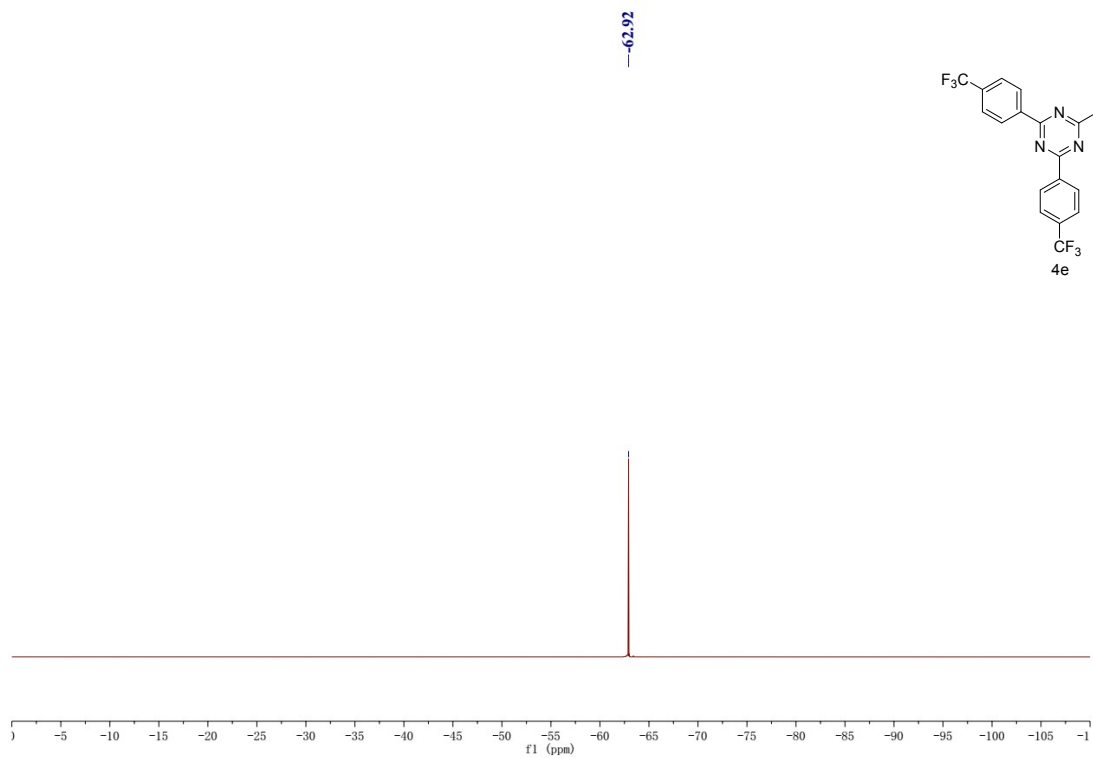
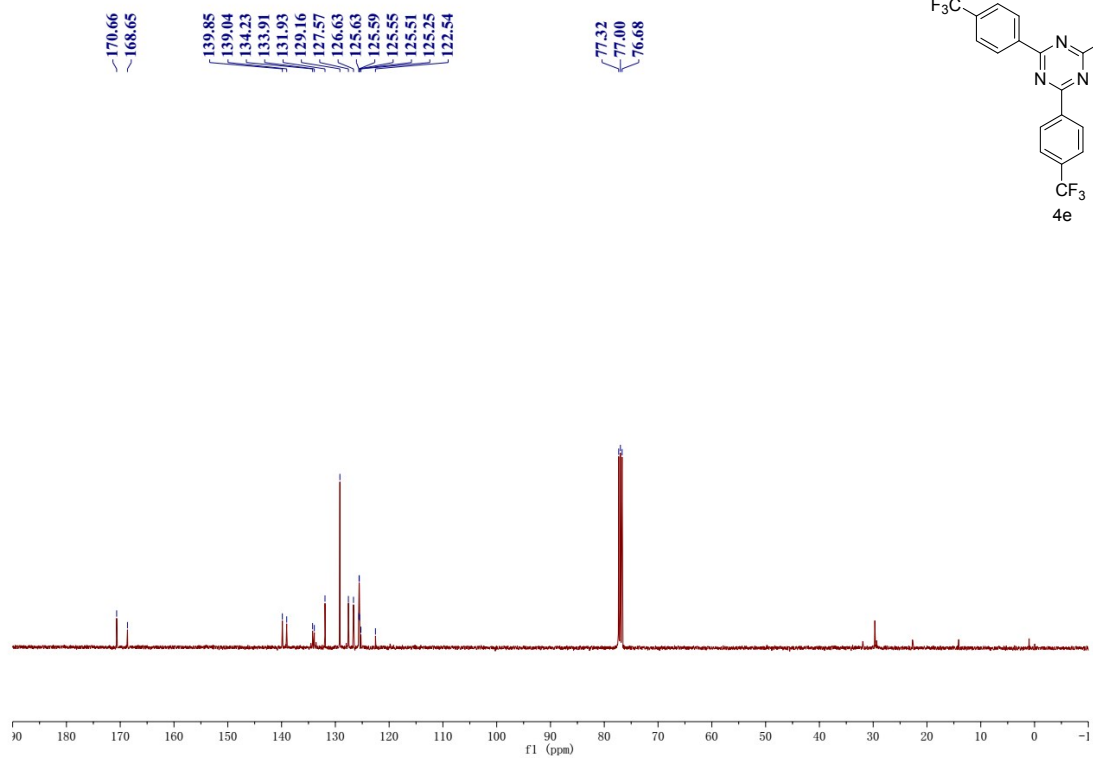


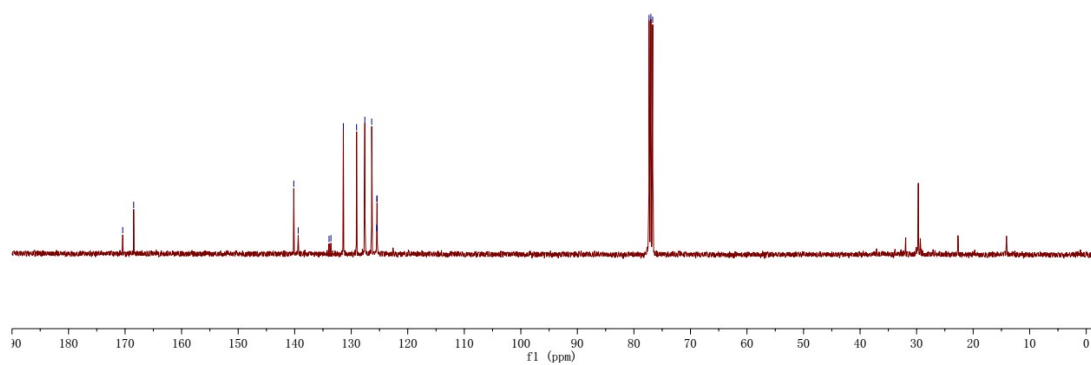
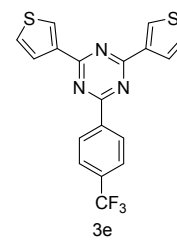
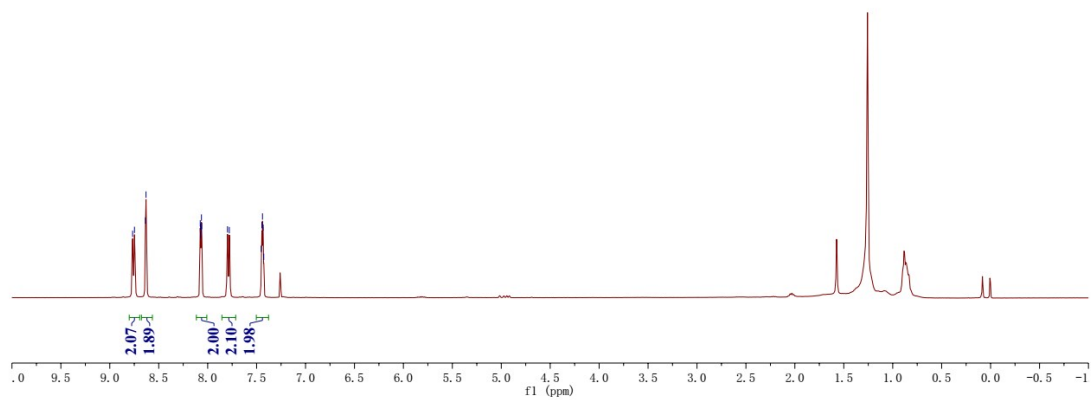
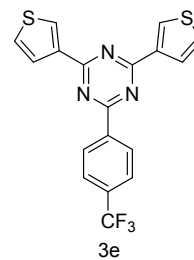
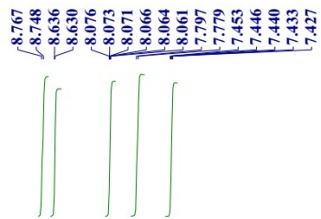


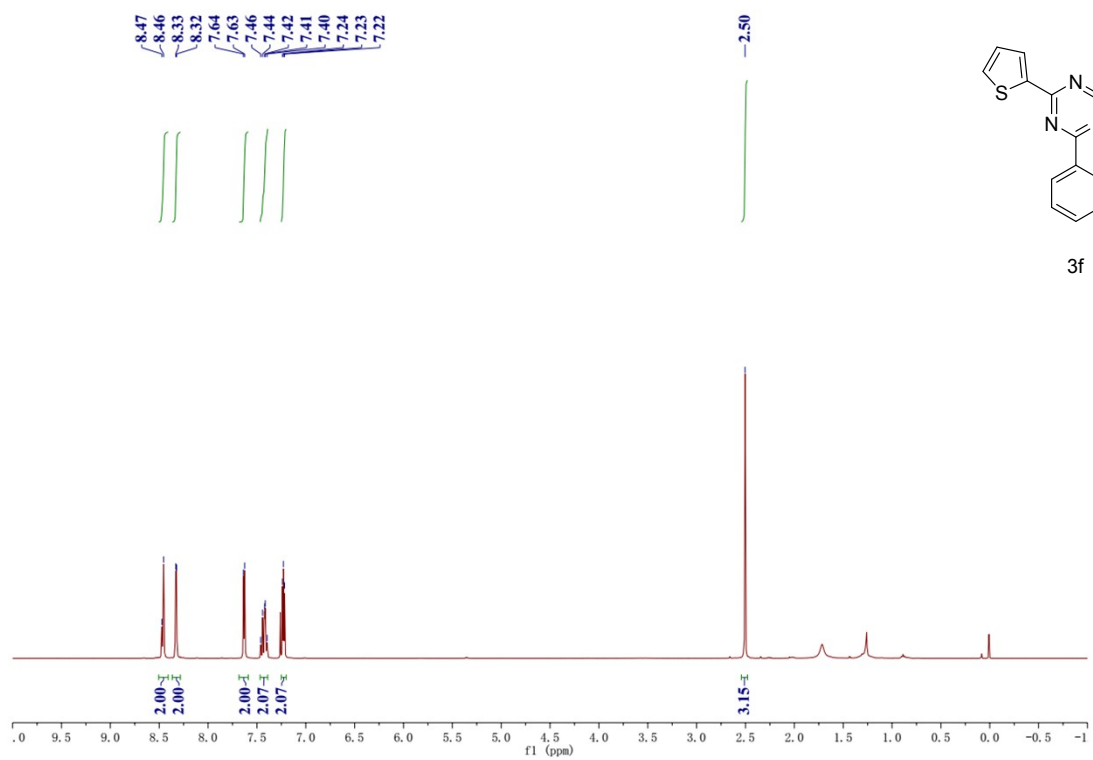
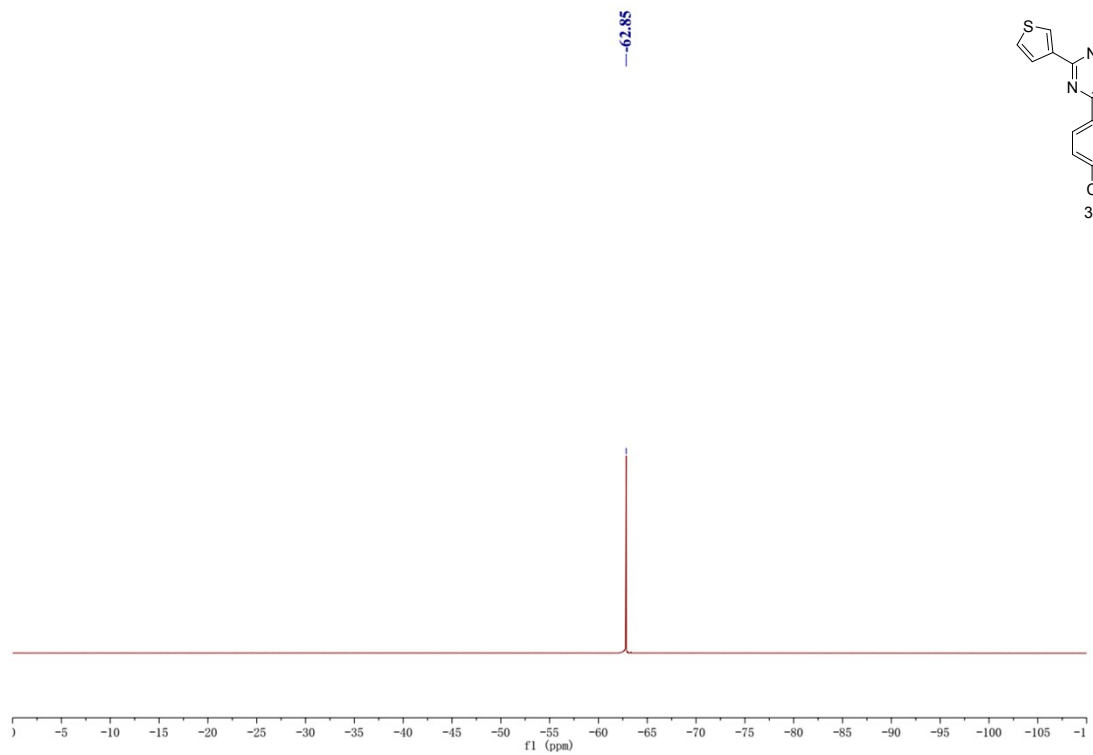




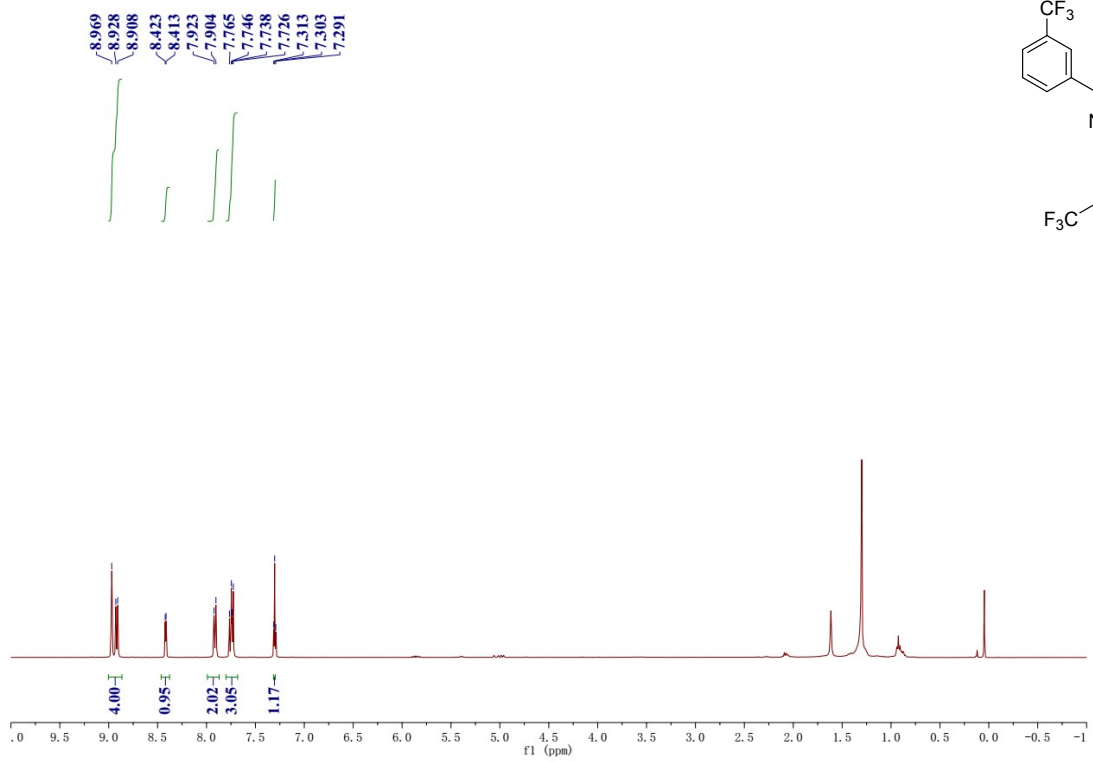
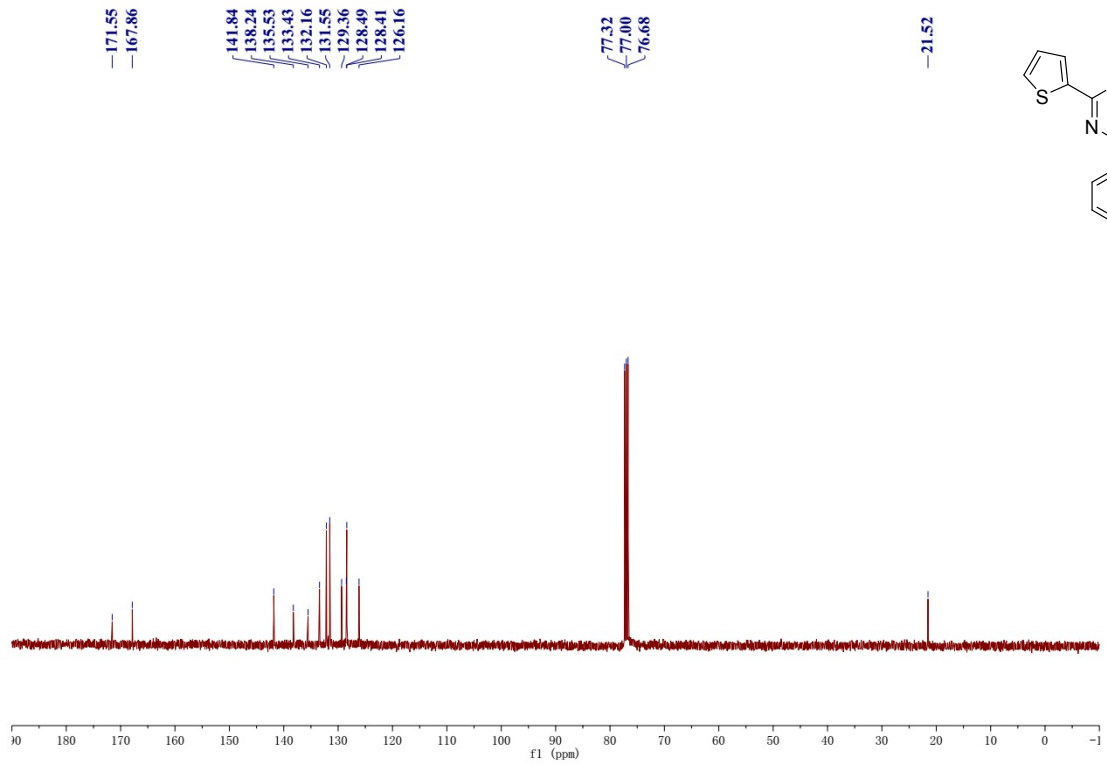


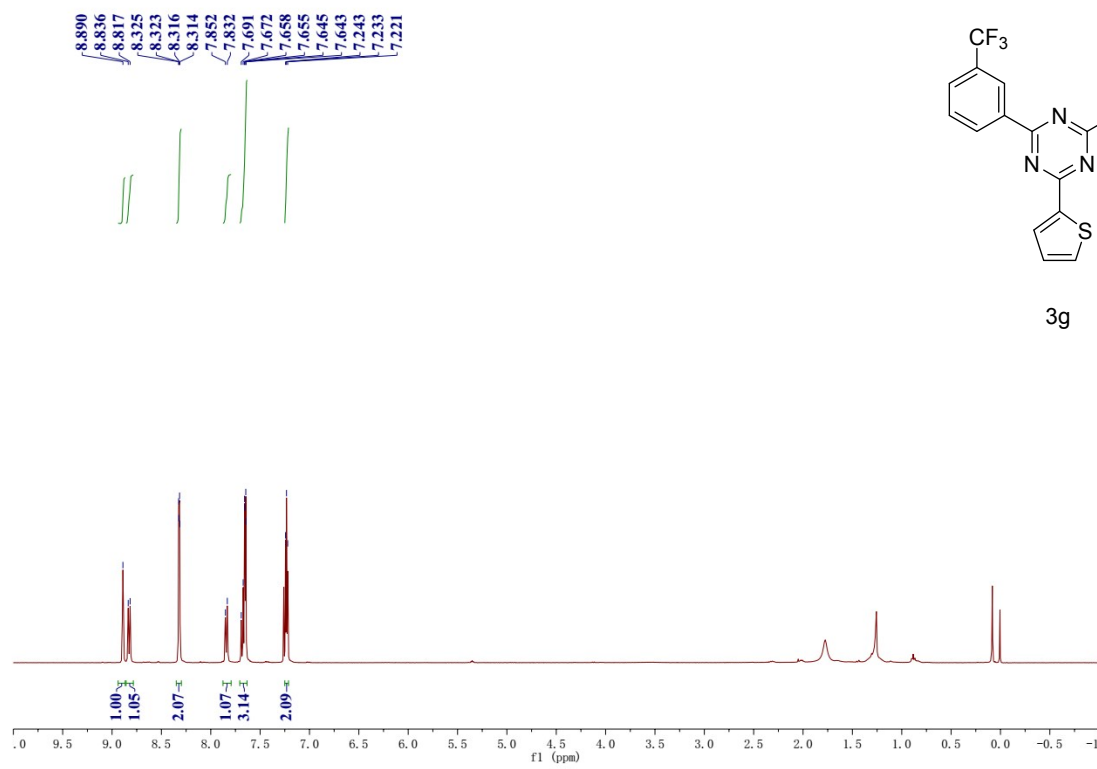
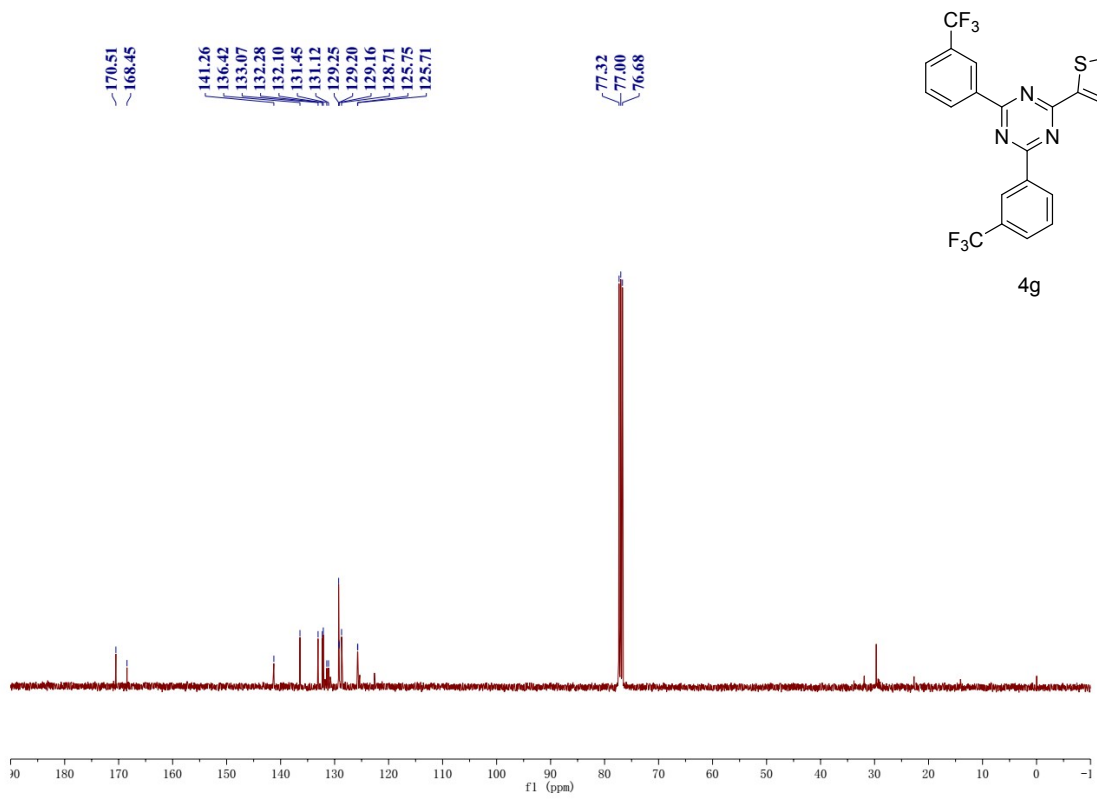


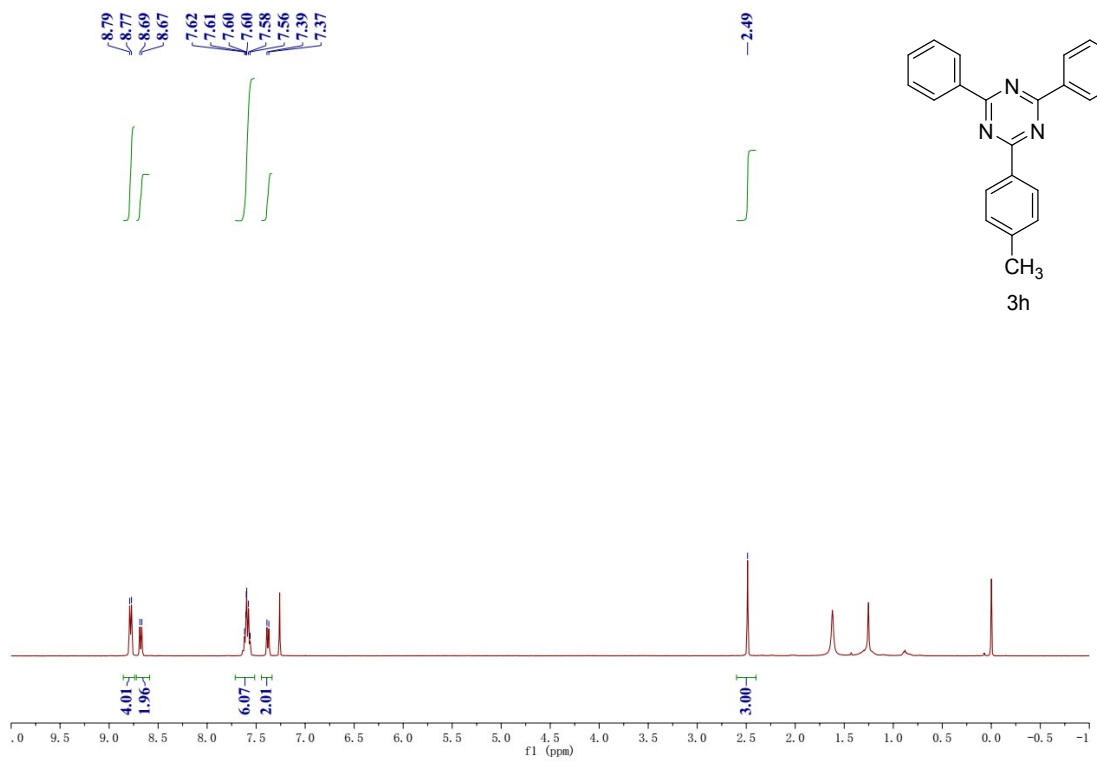
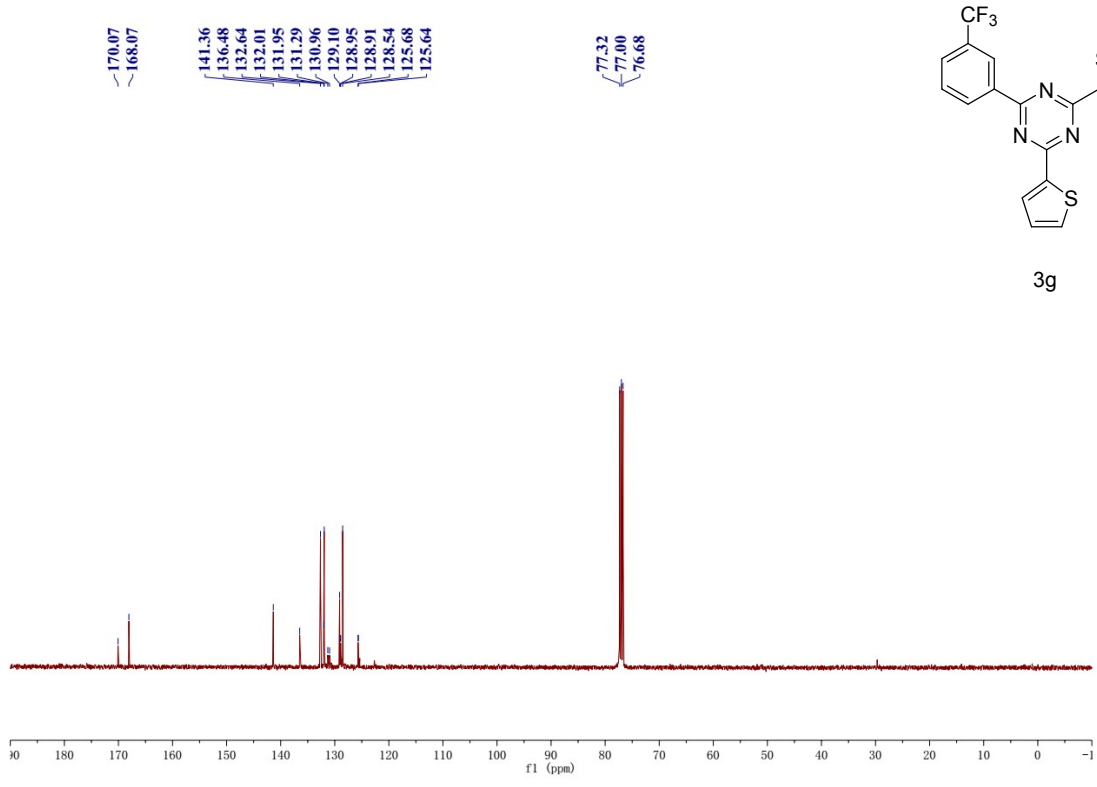


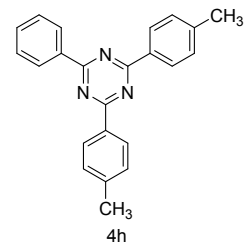
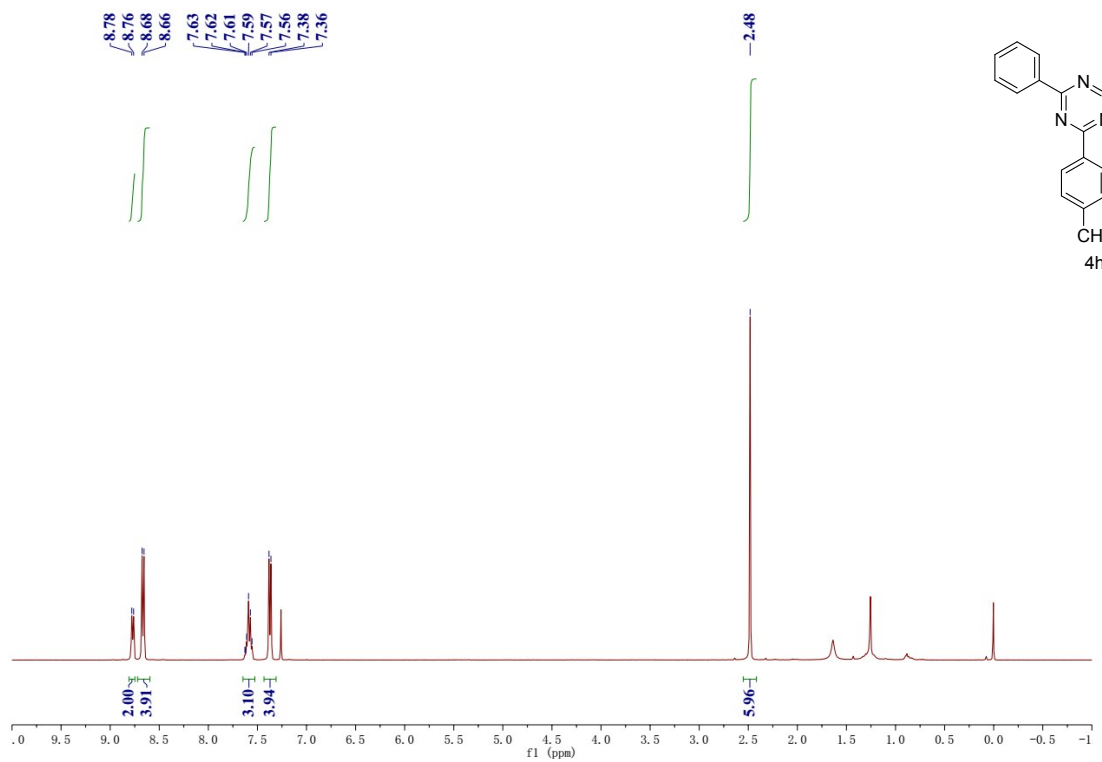
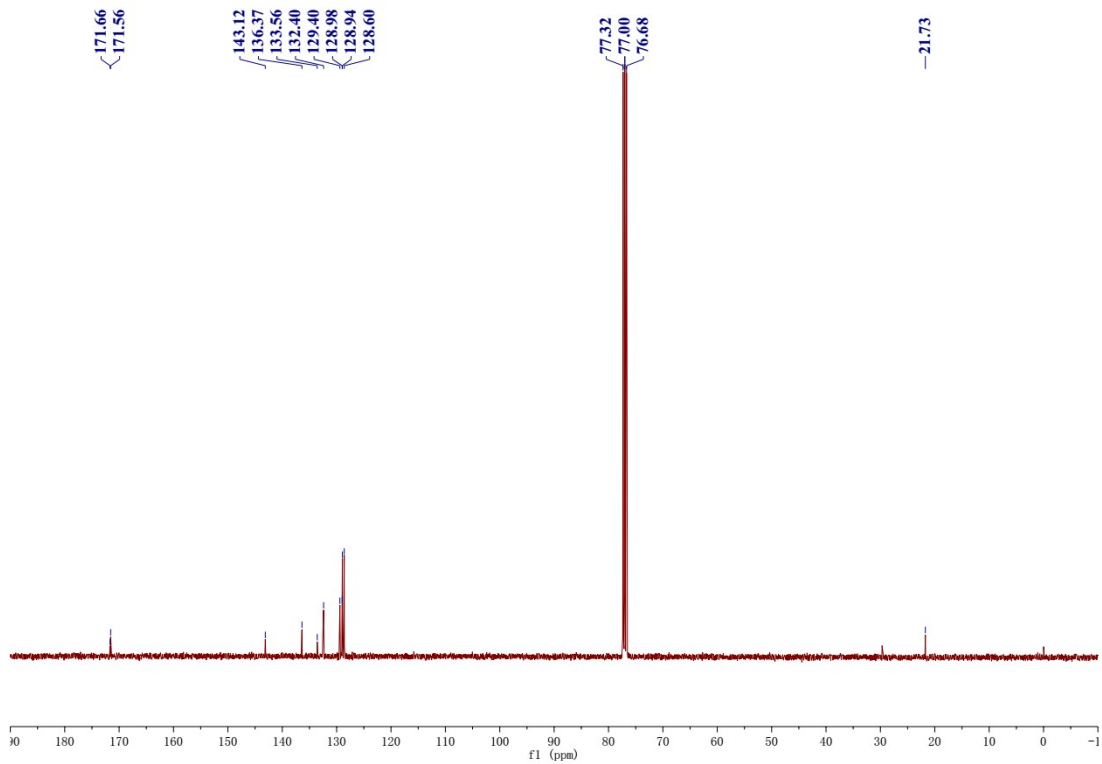


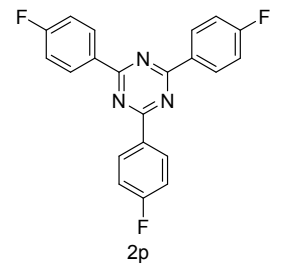
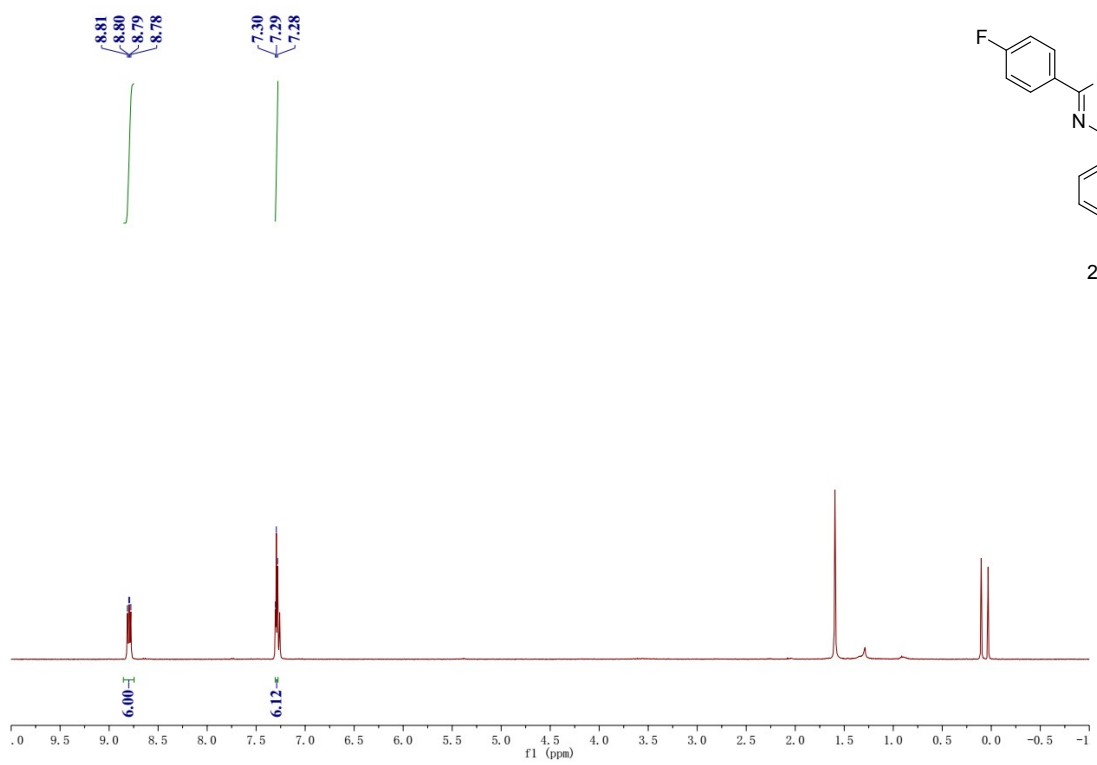
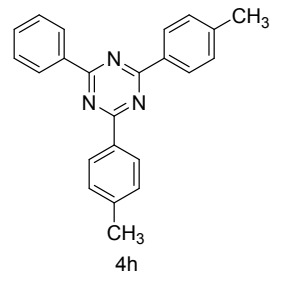
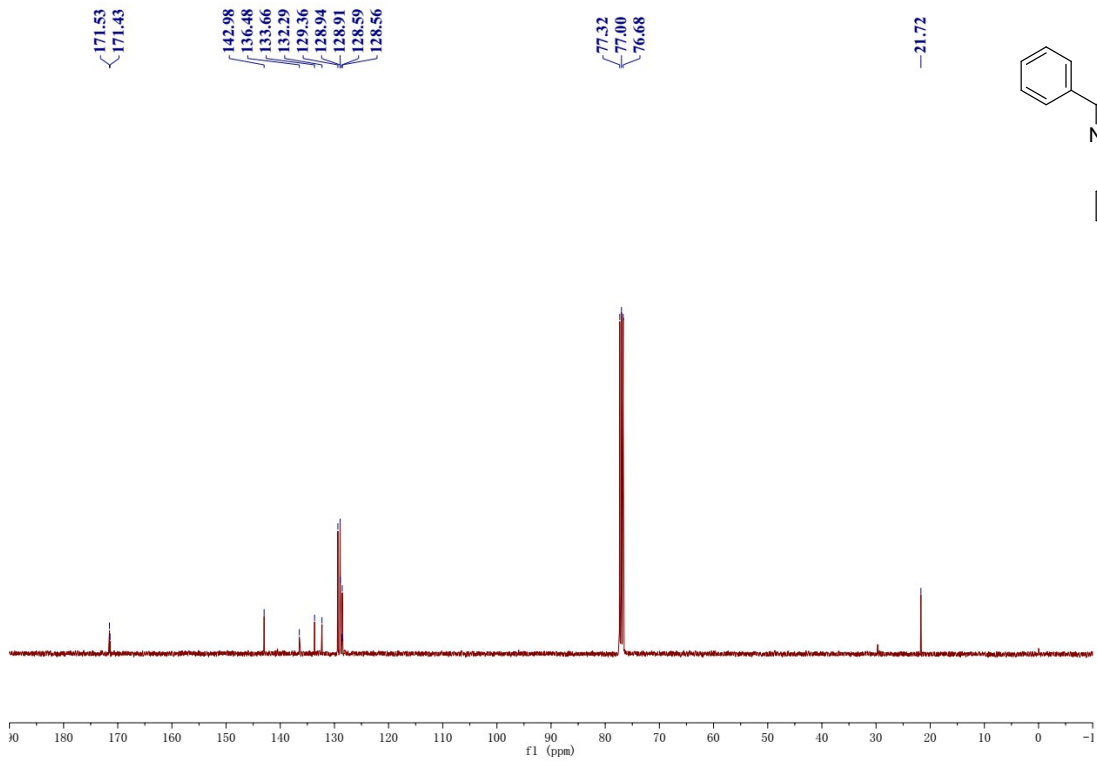


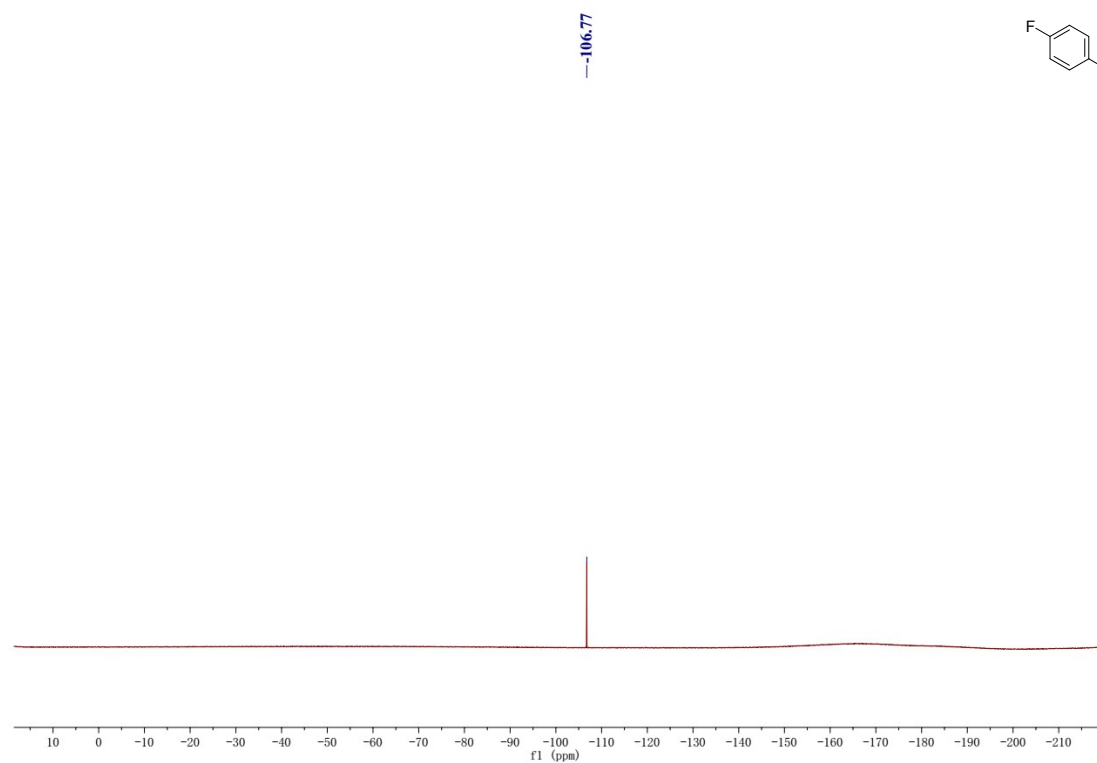
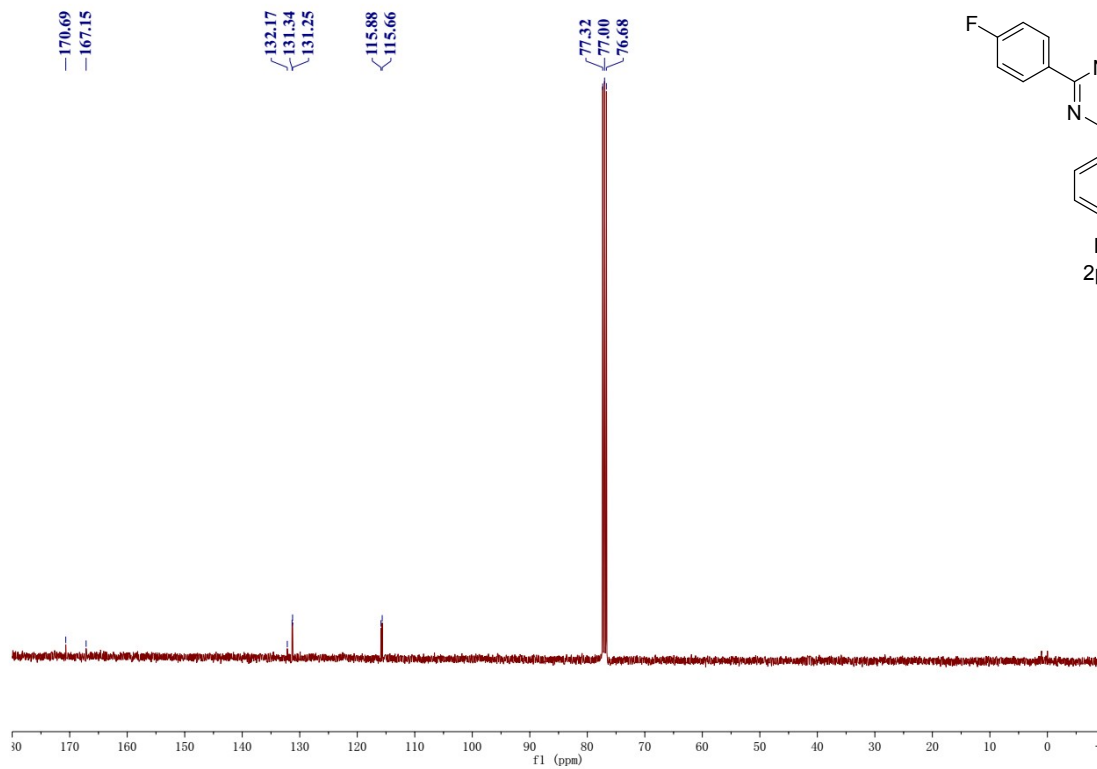












## Notes and references

[1] Q. You, F. Wang, C. Wu, T. Shi, D. Min, H. Chen, W. Zhang, *Org. Biomol. Chem.*, 2015, **13**, 6723–6727.

[2] Y. Li, Z. Sun, *Heterocycles*, 2005, **65**, 1425-1430.

[3] A. Naka, R. Fukuda, R. Kishimoto, Y. Yamashita, Y. Ooyama, J. Ohshita, M. Ishikawa, *Journal*

*of Organometallic Chemistry*, 2012, **702**, 67-72.

[4] A. Isfahani, I. Mohammadpoor-Baltork, V. Mirkhani, A. R. Khosropour, M. Moghadam, S. Tangestaninejad, R. Kia, *Adv. Synth. Catal.*, 2013, **355**, 957-972.

[5] Y. Zu, G. Li, L. Zong, L. Qing, J. Wang, X. Jian, *Polym Int*, 2018, **67**, 189-196.

[6] W. Guo, *Org. Biomol. Chem.*, 2015, **13**, 10285-10289.

[7] S. D. Pardeshi, P. A. Sathe, B. V. Pawar, K. S. Vadagaonkar, A. C. Chaska, *Eur. J. Org. Chem.* 2018, **18**, 2098-2102.

[8] A. R. Tiwari, S. R. Nath, K. A. Joshi, B. M. Bhanage, *J. Org. Chem.* 2017, **82**, 13239-13249.

[9] A. Herrera, A. Riano, R. Martínez-Alvarez, *J. Org. Chem.*, 2014, **79**, 7012-7024.

[10] H. Yoshida, Y. Mimura, J. Ohshita, *Chemistry letters*, 2009, **38**, 1132-1133