

## S1

### Supporting Information

## PTSA-Catalyzed Green Synthesis of 1,3,5-Triarylbenzene under Solvent-Free Conditions

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## S2

### 1. General experimental details

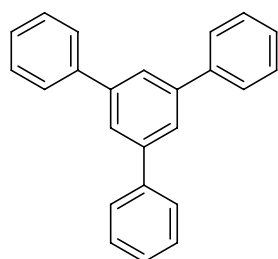
All chemicals were purchased from commercial vendors and used without further purification, unless indicated otherwise. EI-MS were determined with an Agilent 5975N mass spectrometer. Flash column chromatography was performed using silica gel (300–400 mesh). Analytical thinlayer chromatography was performed using glass plates precoated with 200–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Melting points were obtained on a Fisher-Johns apparatus without correction. All NMR spectra ( $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ ) were recorded on a Bruker 500 MHz NMR spectrometer, using  $\text{CDCl}_3$  or  $\text{DMSO-}d_6$  as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts are given in  $\delta$  relative to TMS, the coupling constants  $J$  are given in Hz. All reactions were conducted under air atmosphere.

#### 1.1 General procedure:

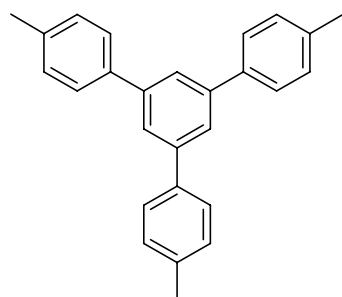
To a 15 mL two necked round bottom bottle, 360.45 mg (3 mmol) of acetophenone **1a** and 57.07 mg (0.30 mmol) of  $\text{TsOH}\cdot\text{H}_2\text{O}$  was added. The reaction mixture was stirred at 130 °C for 10 h, determined by TLC. After completion of the reaction, the reaction mixture was neutralized by saturated  $\text{NaHCO}_3$ , extracted with DCM (3 x 20 mL) or (3 x 50 mL). The combined organic layers were dried by  $\text{MgSO}_4$ , filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (PE/EA = 20:1) and gave 278.82 mg (0.91 mmol, 91 %) of **2a**, as white solid.

### S3

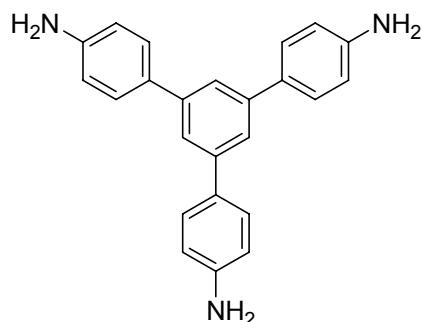
## 2. Experimental characterization data for compounds



Mp: 171-173 °C (Lit <sup>1</sup> 170-172 °C). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz): δ 7.88 (s, 3H), 7.87-7.86 (m, 6H), 7.52-7.49 (t, *J*=7.5 Hz, 6H), 7.43-7.40 (t, *J*=7.5 Hz, 3H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125 MHz): δ 141.6, 140.1, 128.9, 127.7, 127.2, 124.4.

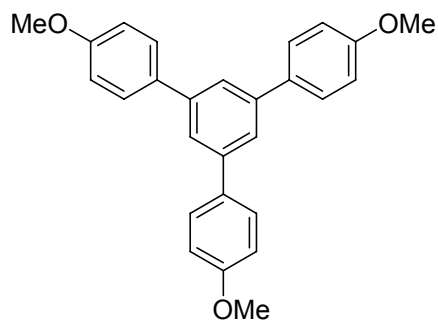


Mp: 176-178 °C (Lit <sup>2</sup> 177-178 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.74 (s, 3H), 7.60 (d, *J*= 8.0 Hz, 6H), 7.29 (d, *J*= 7.5 Hz, 6H), 2.43 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 142.3, 138.5, 137.4, 129.6, 127.3, 124.7, 21.2. MS (EI) *m/z* (M<sup>+</sup>) 348.

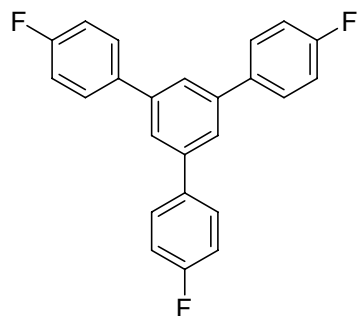


Mp: 164-166 °C (Lit <sup>3</sup> 161-165 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.59 (s, 3H), 7.74 (d, *J*= 8.5 Hz, 6H), 6.78 (d, *J*= 8.0 Hz, 6H), 3.76 (d, *J*= 10.5 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 146.0, 142.1, 132.0, 128.3, 123.0, 115.5. MS (EI) *m/z* (M<sup>+</sup>) 351.

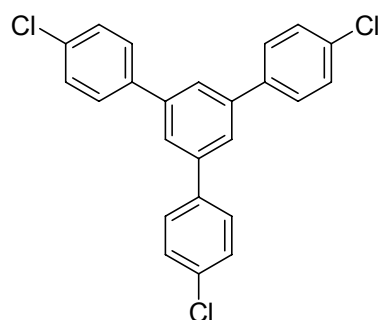
S4



Mp: 141-143 °C (Lit <sup>4</sup> 140-142 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.57 (d, *J* = 9.0 Hz, 6H), 7.32 (s, 3H), 6.99 (d, *J* = 8.5 Hz, 6H), 3.86 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 159.2, 141.4, 134.0, 128.3, 122.7, 114.2, 55.4.

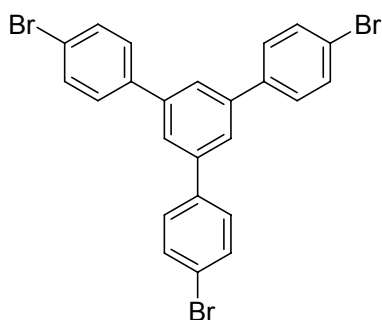


Mp: 238-239 °C (Lit <sup>1</sup> 238-240 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.69 (s, 3H), 7.60 (d, *J* = 8.5 Hz, 6H), 7.53 (d, *J* = 8.5 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 161.8, 137.1, 132.2, 129.0 (d, *J* = 7.5 Hz), 125.0, 115.9 (d, *J* = 22.5 Hz).

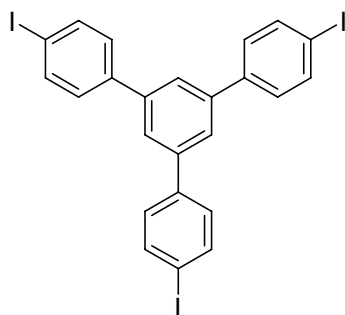


Mp: 245-247 °C (Lit <sup>5</sup> 246 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.69 (s, 3H), 7.60 (d, *J* = 8.5 Hz, 6H), 7.45 (d, *J* = 8.5 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 141.5, 139.3, 134.0, 129.2, 128.7, 125.1. MS (EI) *m/z* (M<sup>+</sup>) 408.

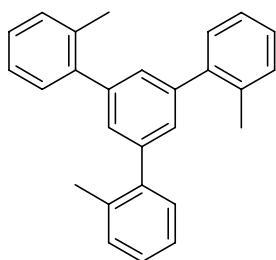
**S5**



Mp: 261-262 °C (Lit 1 260-261 °C).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.68 (s, 3H), 7.60 (d,  $J = 8.5$  Hz, 6H), 7.53 (d,  $J = 8.5$  Hz, 6H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz): 141.6, 139.7, 132.2, 129.0, 125.1, 122.2.

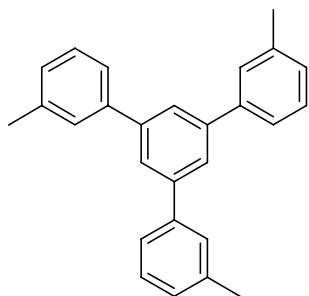


Mp: 264-265 °C (Lit <sup>6</sup> 264.6-265.9 °C).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.80 (d,  $J = 8.5$  Hz, 6H), 7.67 (s, 3H), 7.39 (d,  $J = 8.5$  Hz, 6H).

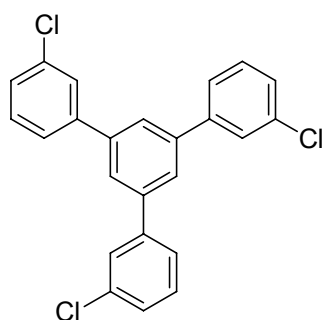


Mp: 135-137 °C (Lit <sup>6</sup> 135.6-135.8 °C).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.43-7.41 (m, 3H), 7.38 (s, 3H), 7.37-7.32 (m, 9H), 2.47 (s, 9H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz): 141.8, 141.5, 135.5, 130.5, 130.0, 128.6, 127.4, 125.9, 20.8.

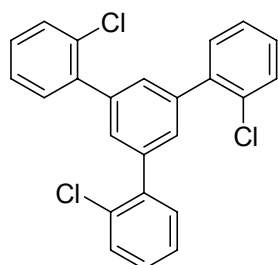
S6



Mp: 117-118 °C (Lit <sup>6</sup> 116.8-118.1 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.77 (s, 3H), 7.52-7.51 (m, 6H), 7.386 (m, 3H), 7.23 (m, 3H), 2.46 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 142.4, 141.3, 138.5, 128.8, 128.3, 128.3, 125.2, 124.6, 21.7.



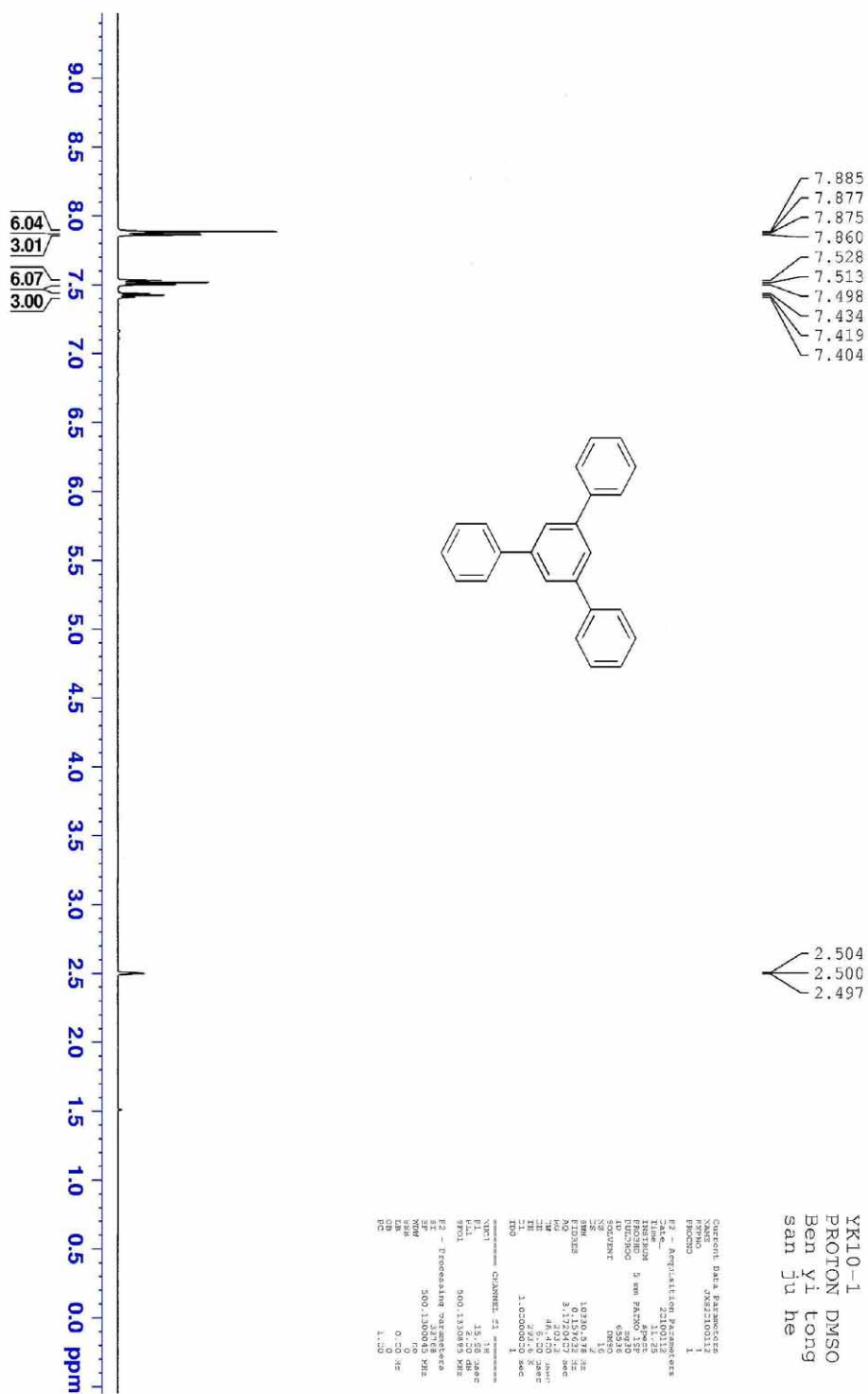
Mp: 169-170 °C (Lit <sup>1</sup> 168-170 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.72 (s, 3H), 7.67-7.66 (m, 3H), 7.57-7.55 (m, 3H), 7.44-7.37 (m, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 142.5, 142.5, 141.4, 134.9, 130.3, 127.9, 127.5, 125.6. MS (EI) *m/z* (M<sup>+</sup>) 408.



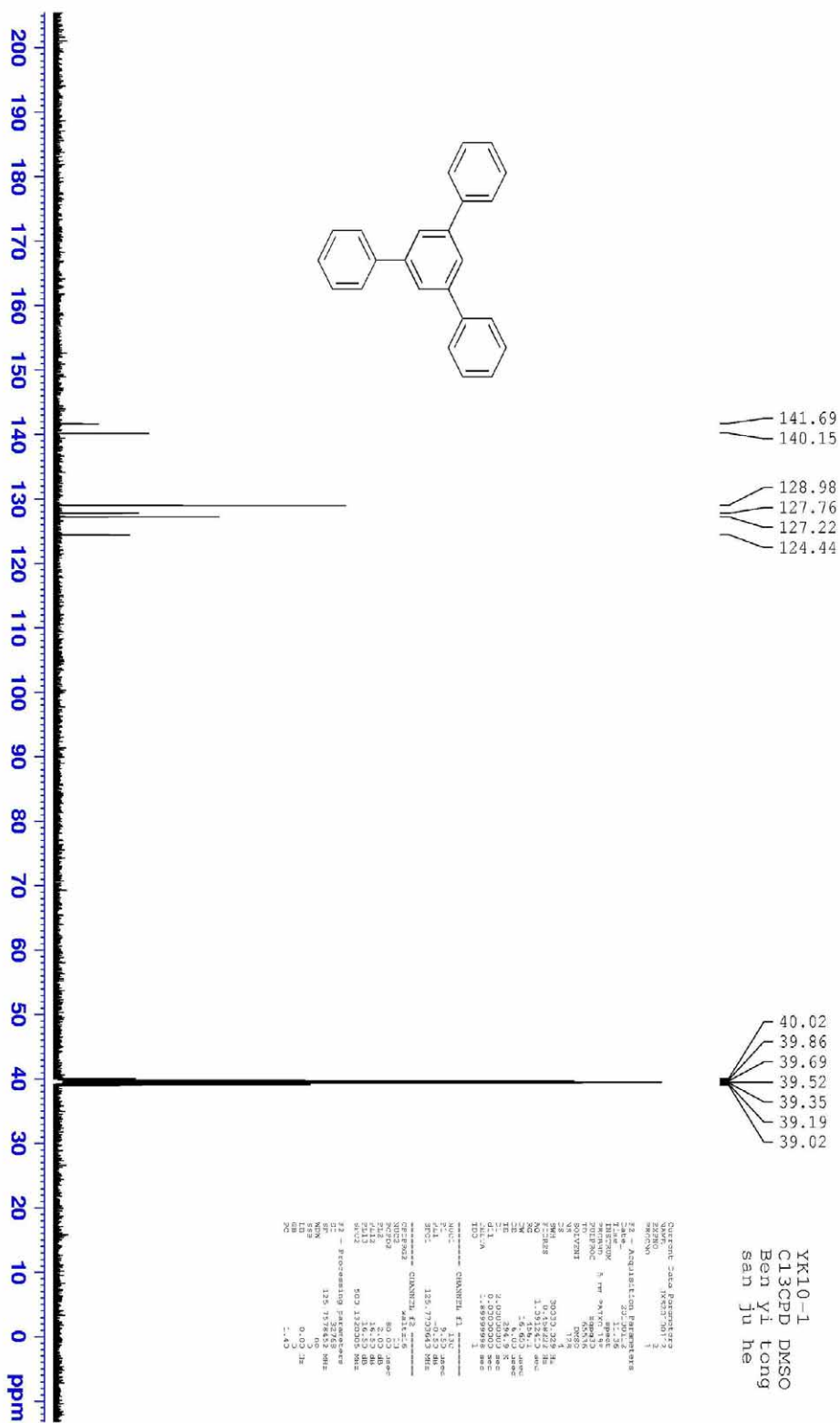
Mp: 164-166 °C (Lit <sup>6</sup> 165.1-165.5 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.58 (s, 3H), 7.50-7.46 (m, 6H), 7.35-7.28 (m, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 140.0, 140.0, 132.7, 131.7, 130.2, 129.9, 128.8, 127.0. MS (EI) *m/z* (M<sup>+</sup>) 408.

**S7**

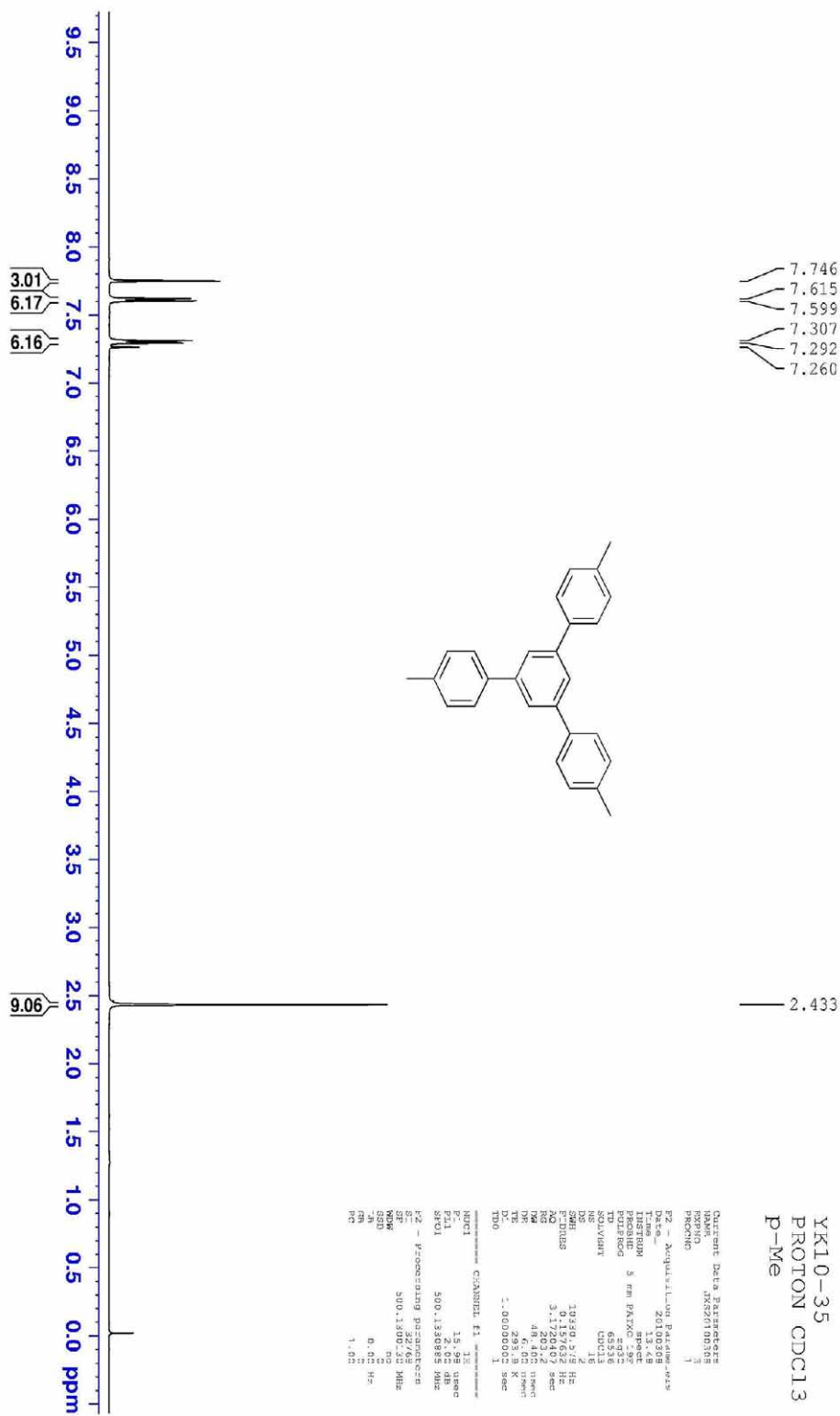
**3. Copies of product  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR**



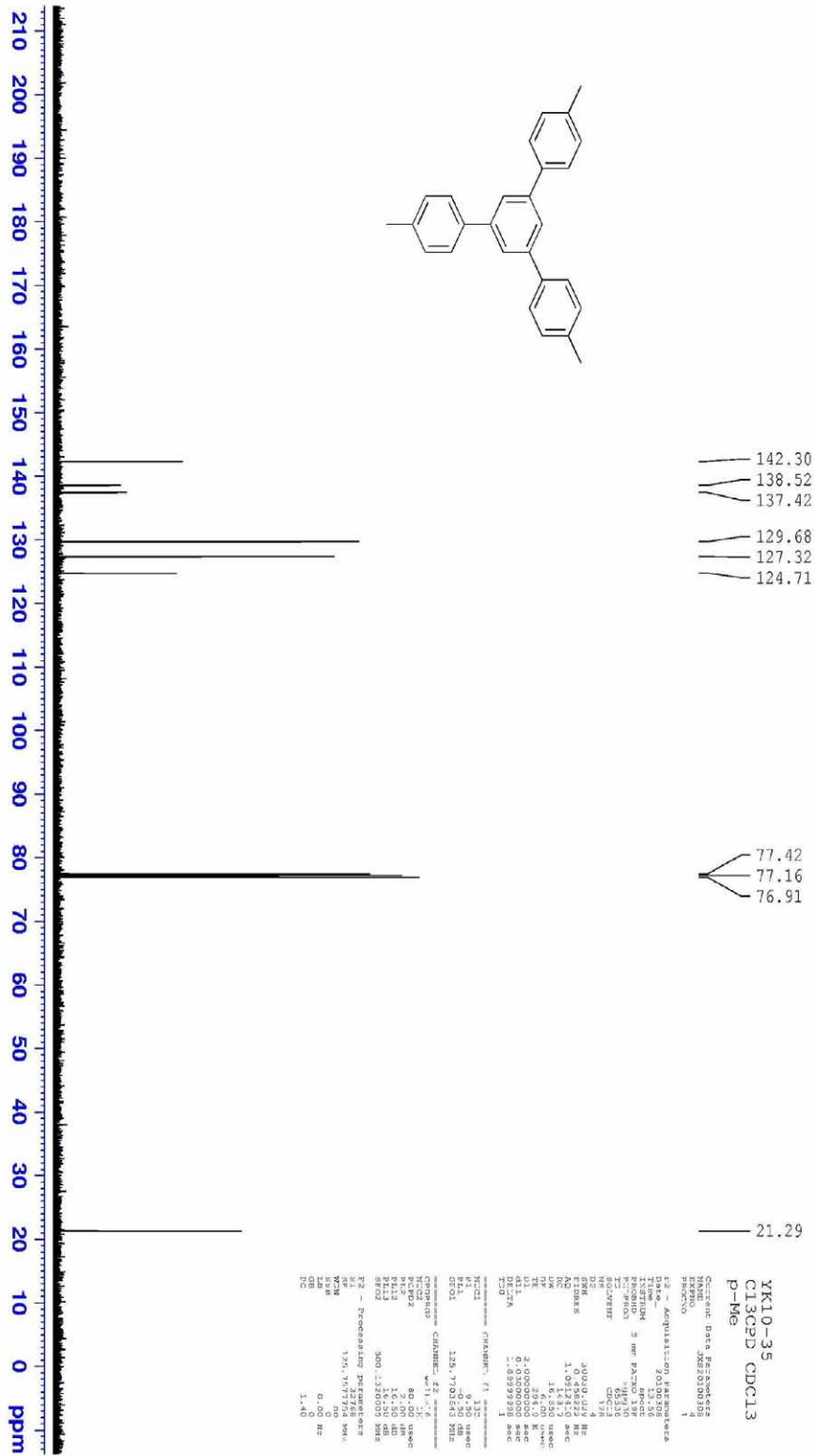




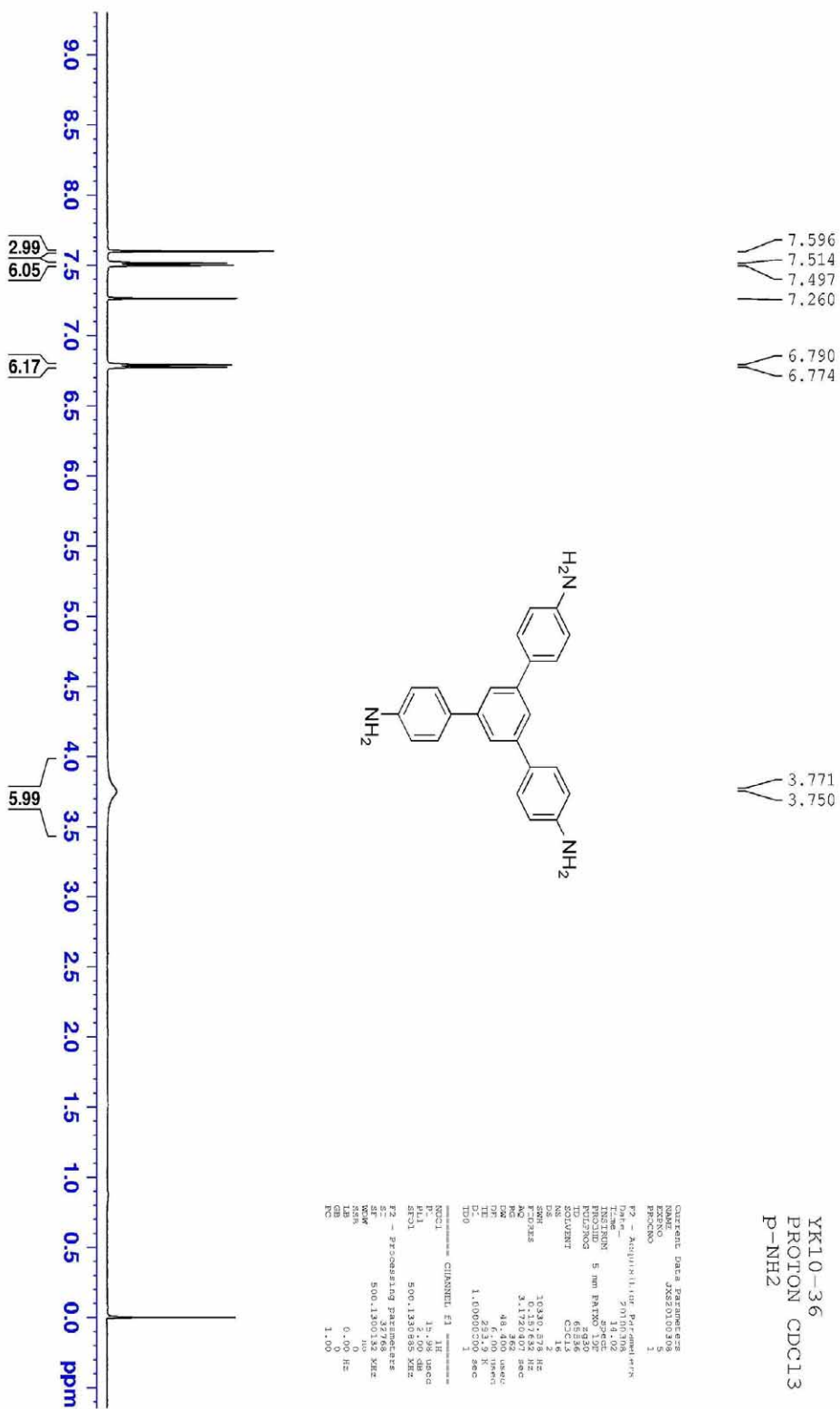










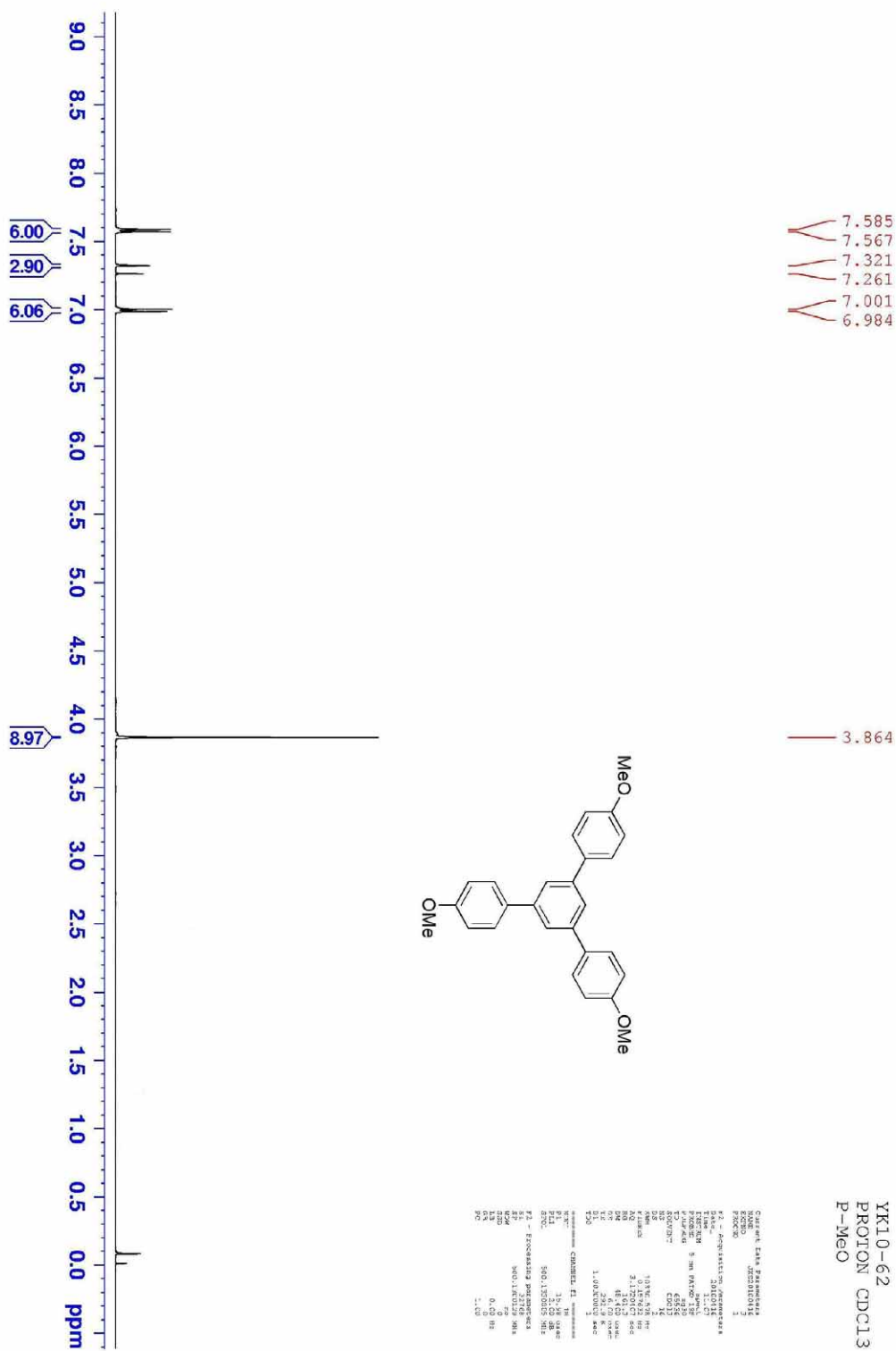




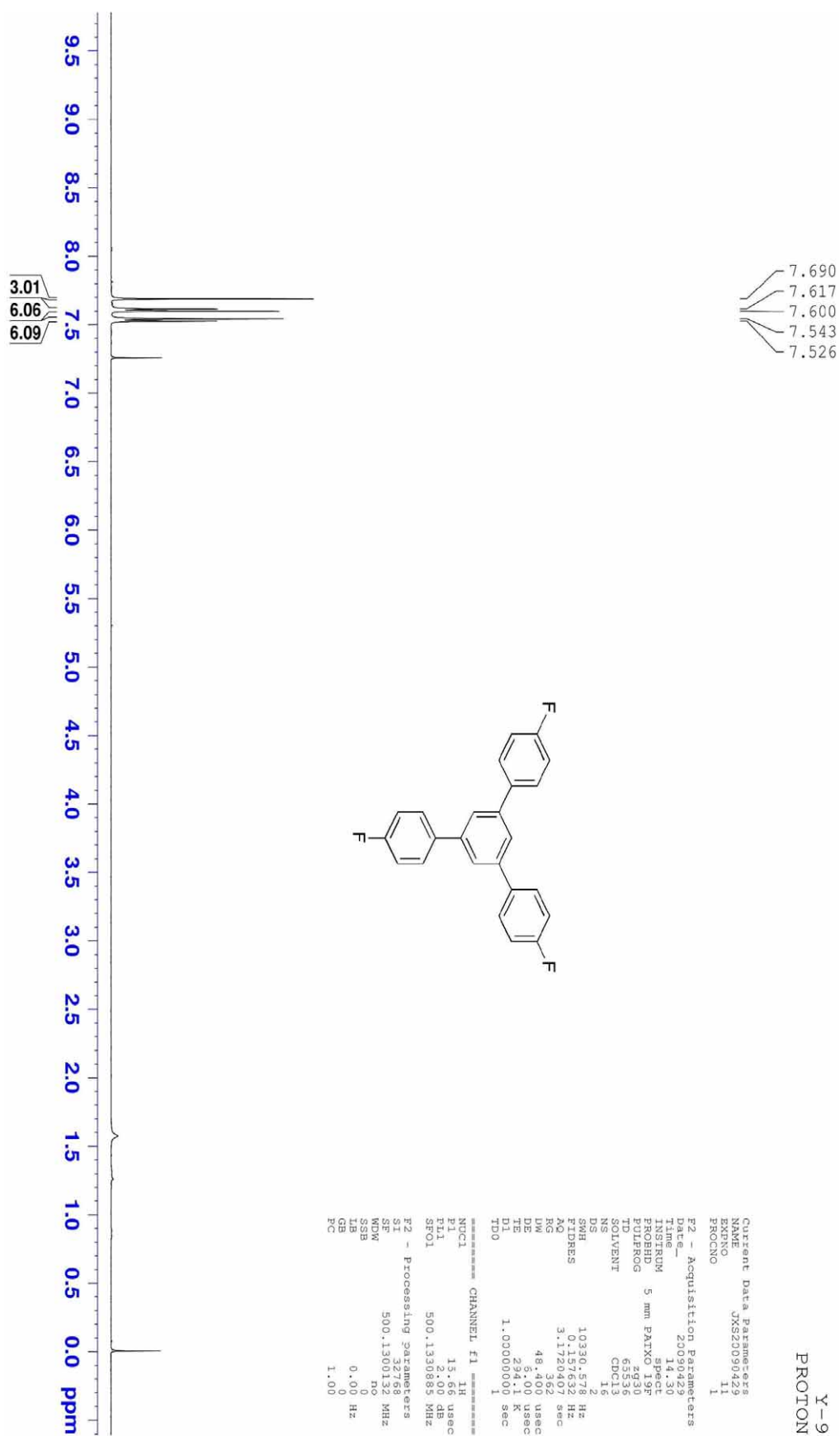




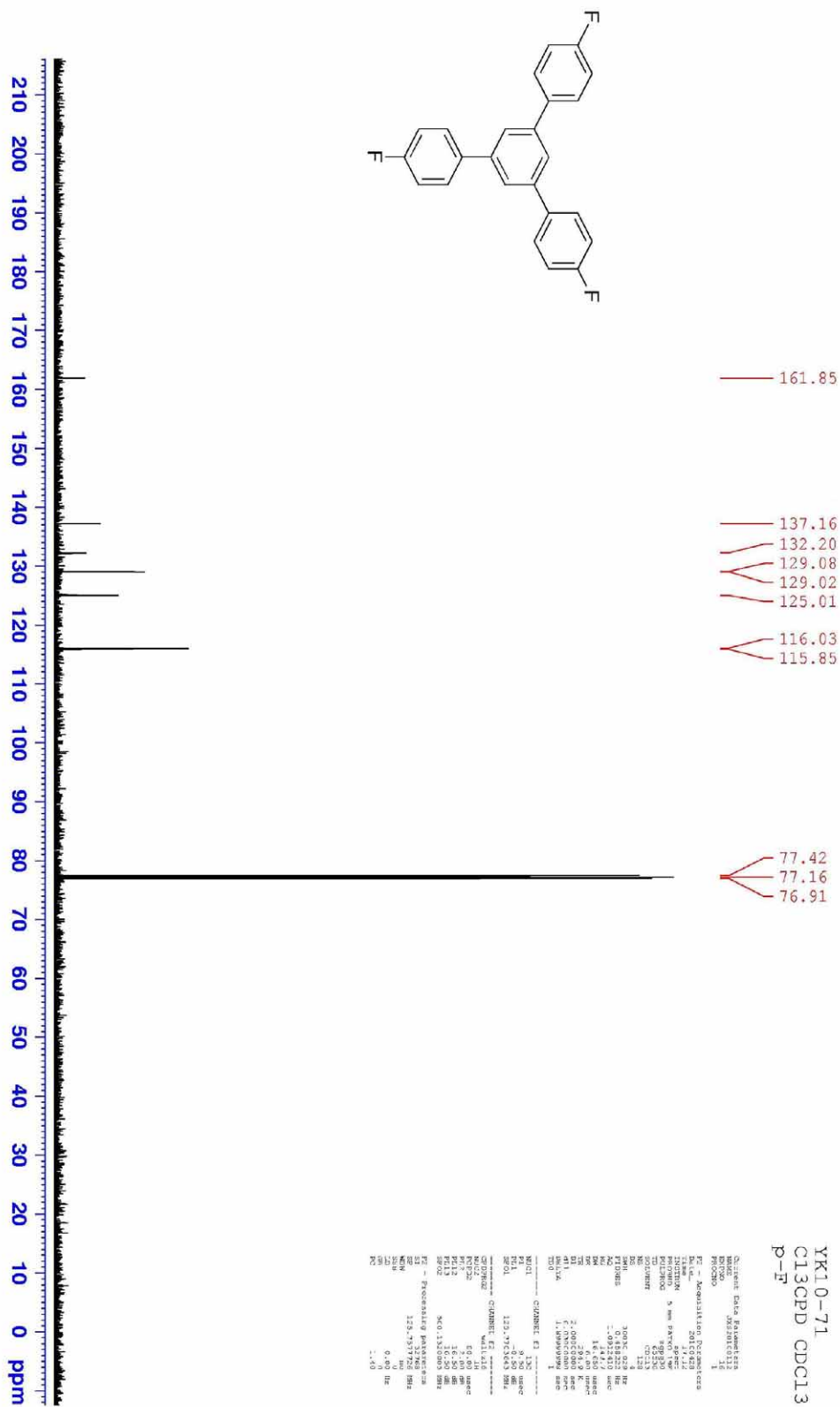
S13



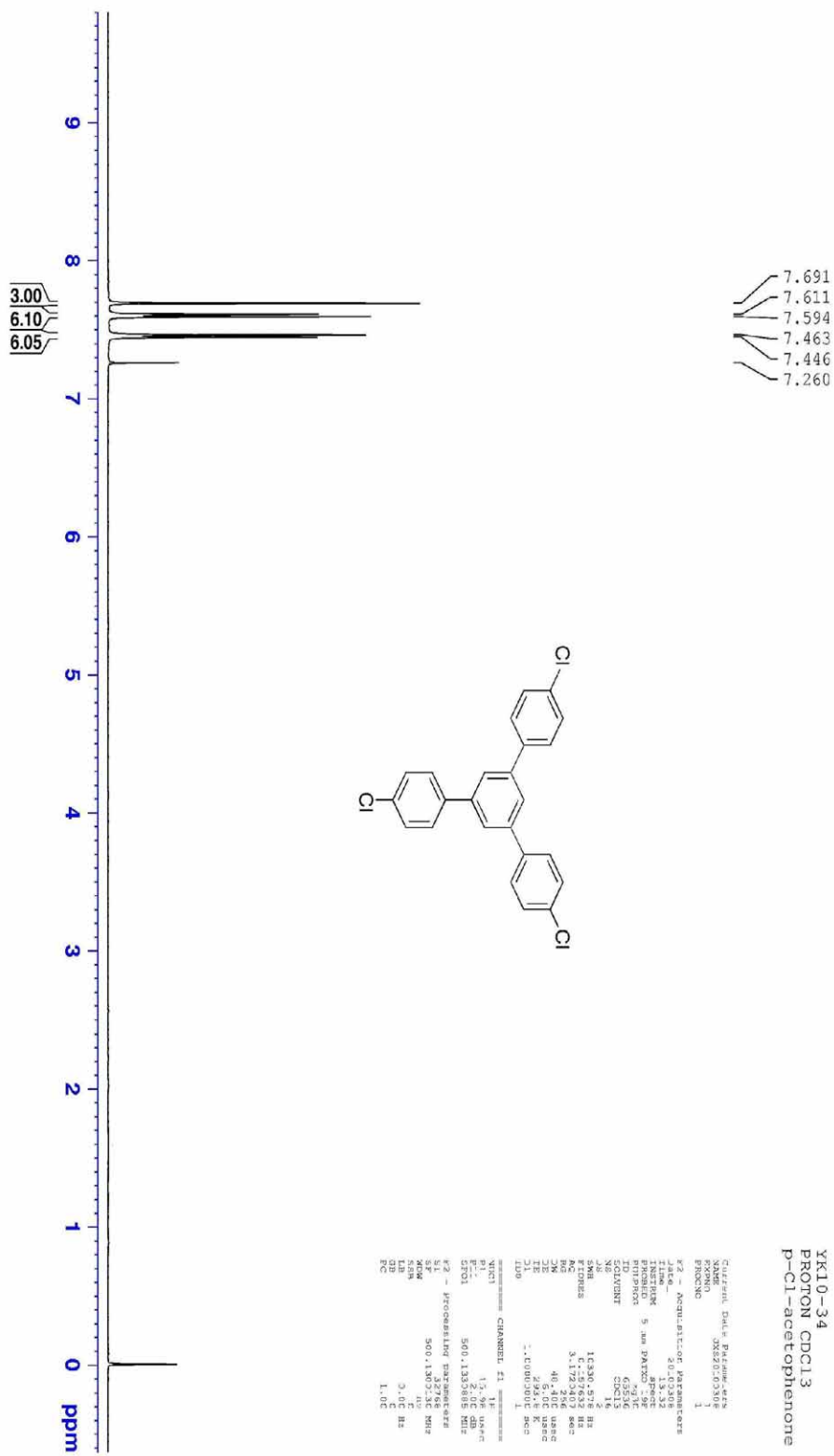






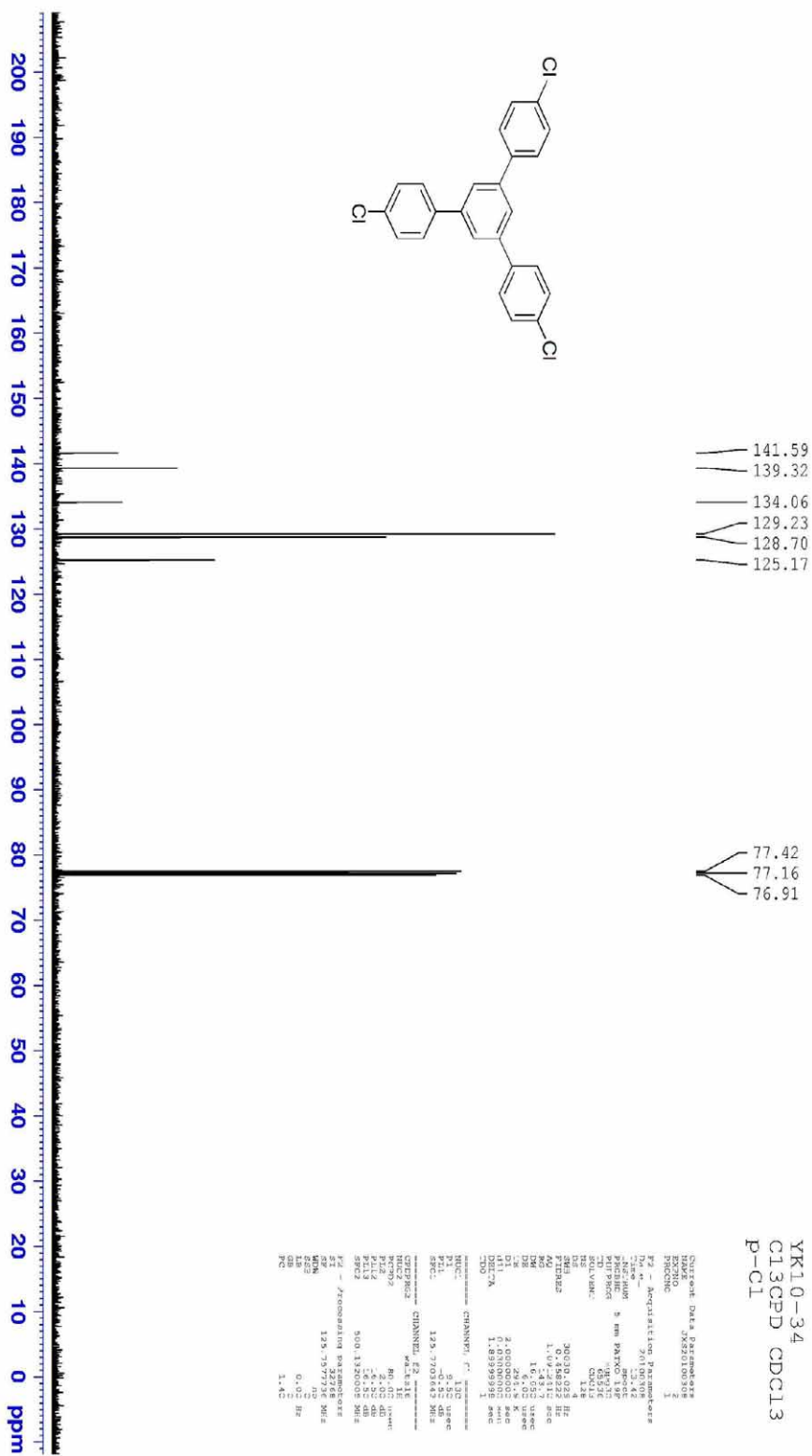




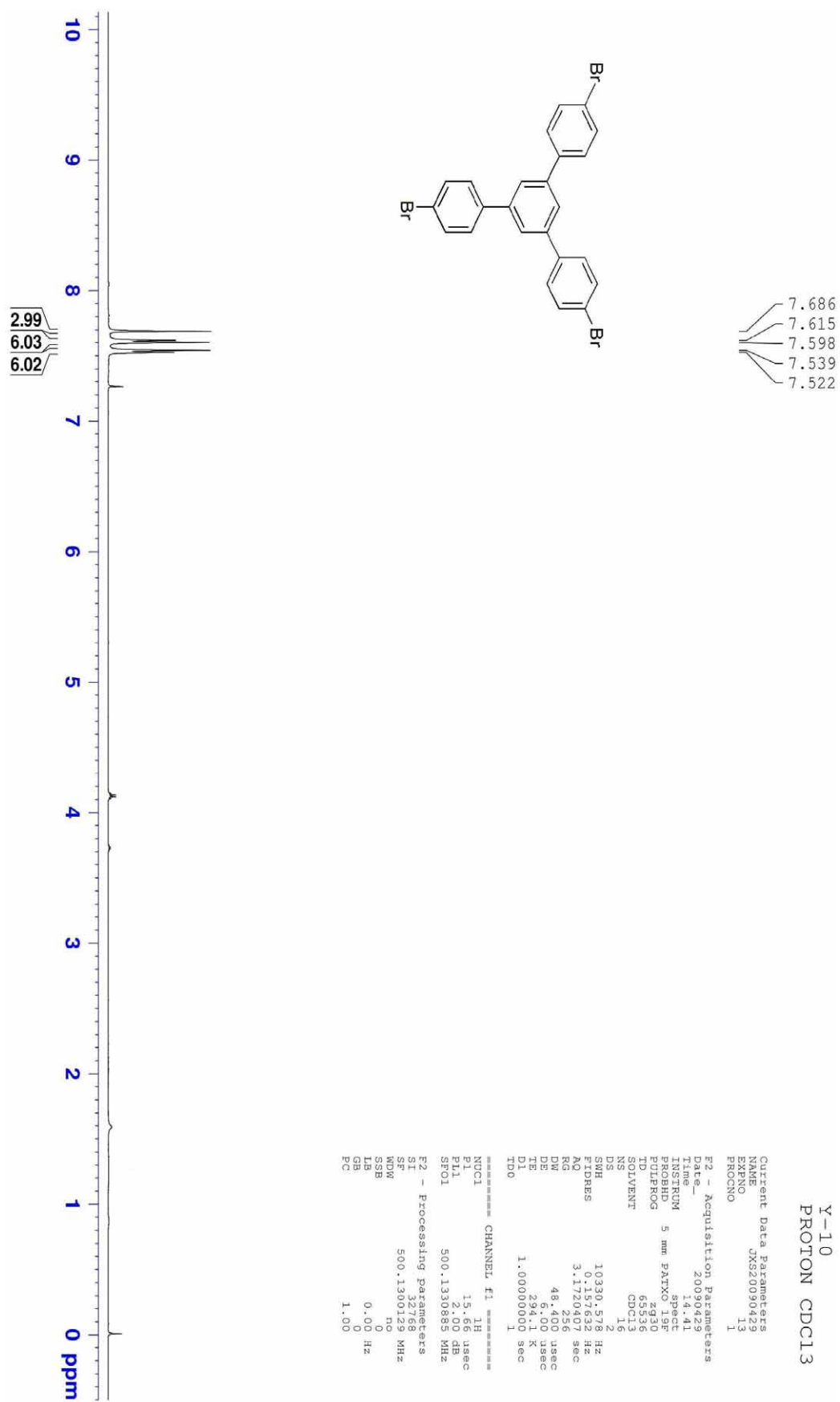




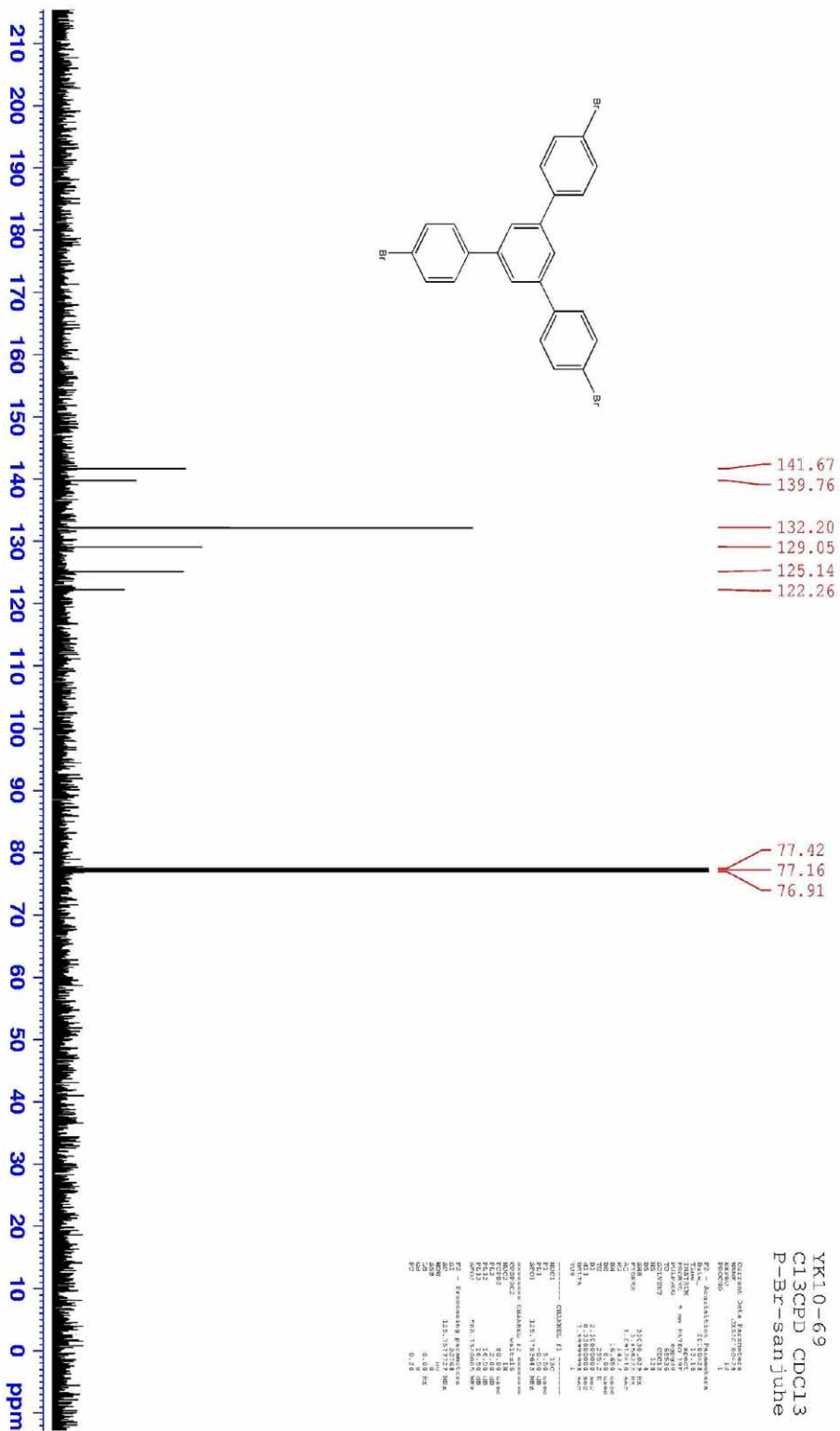
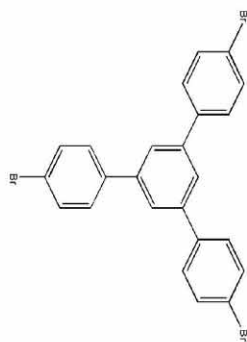




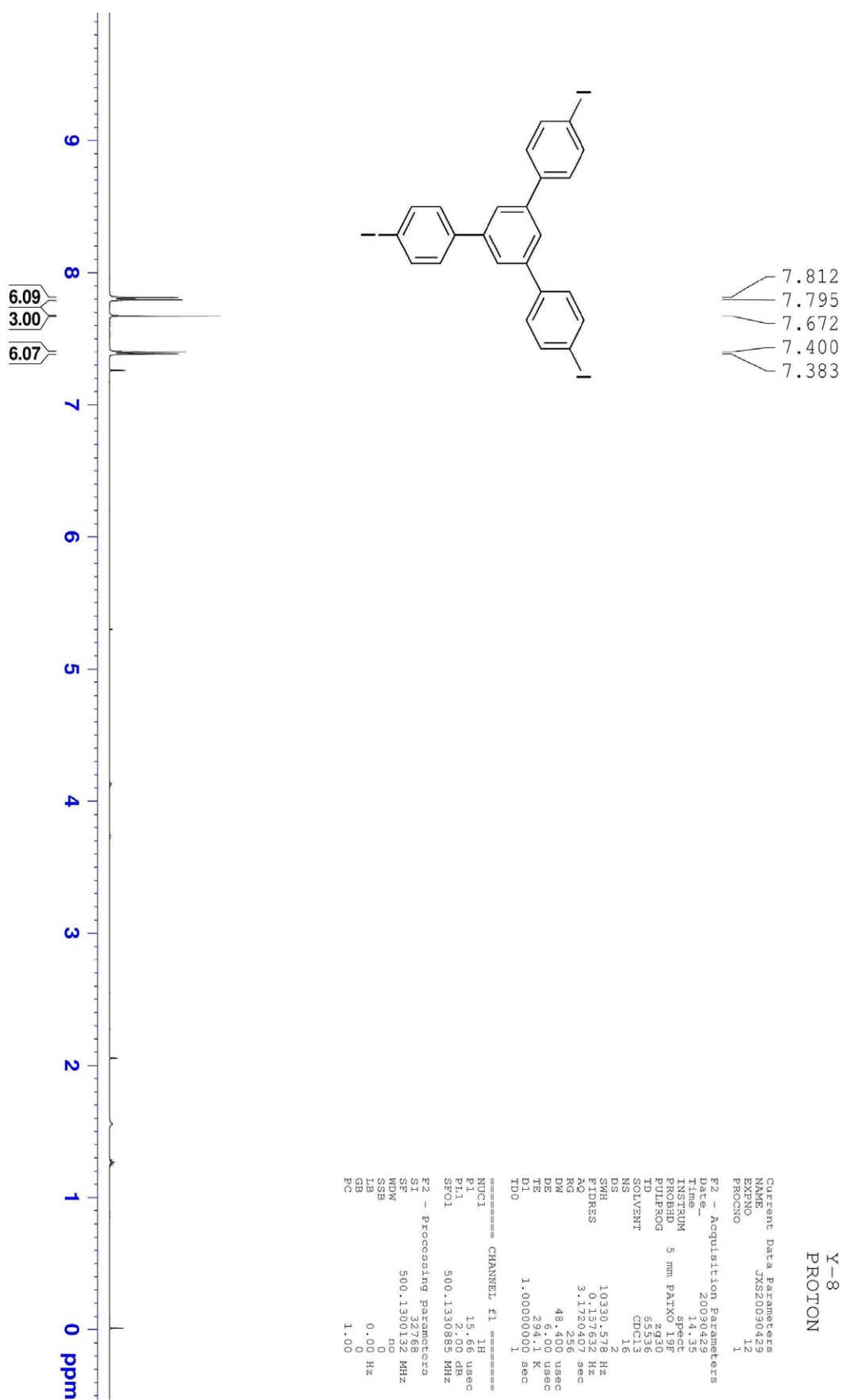






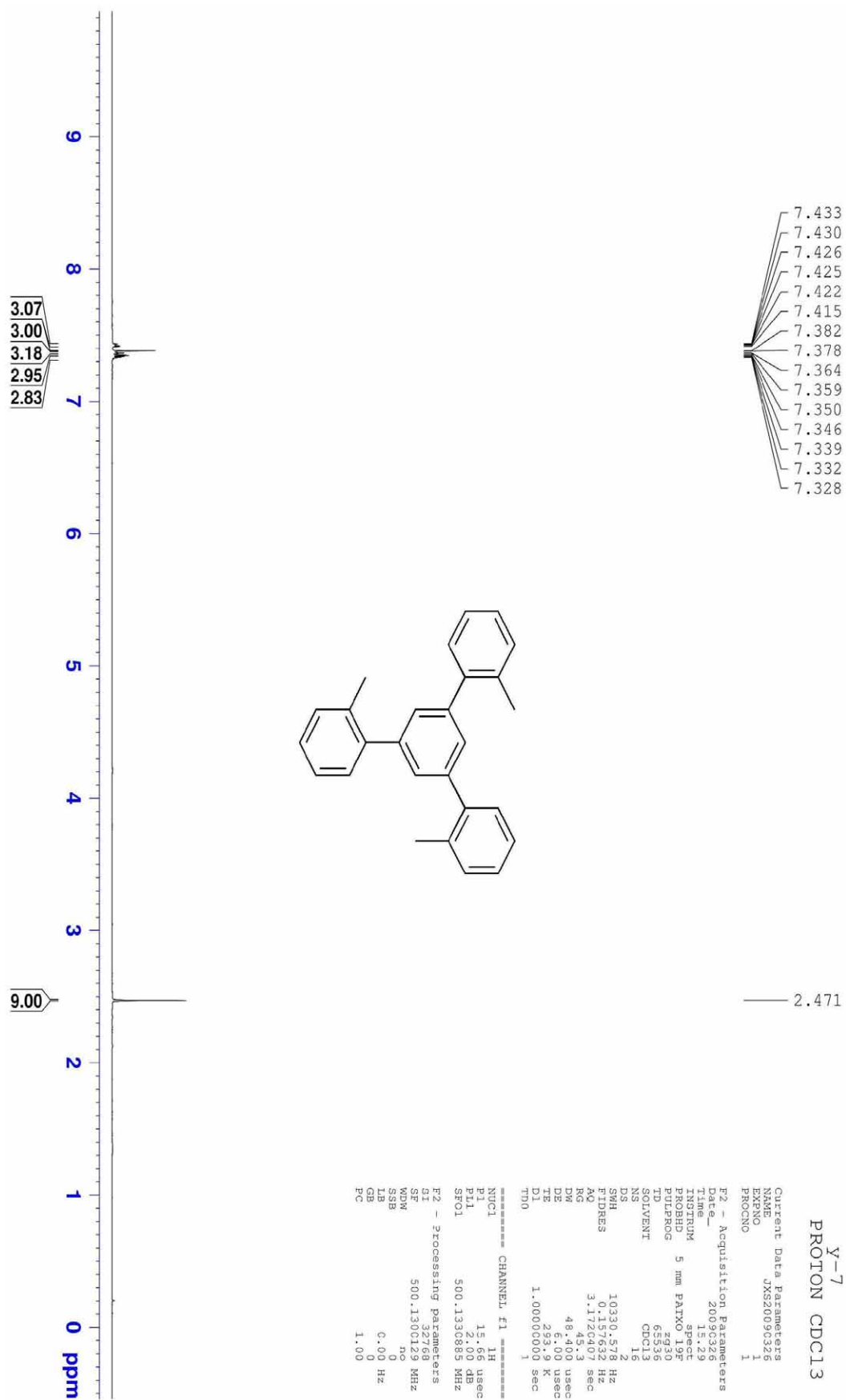








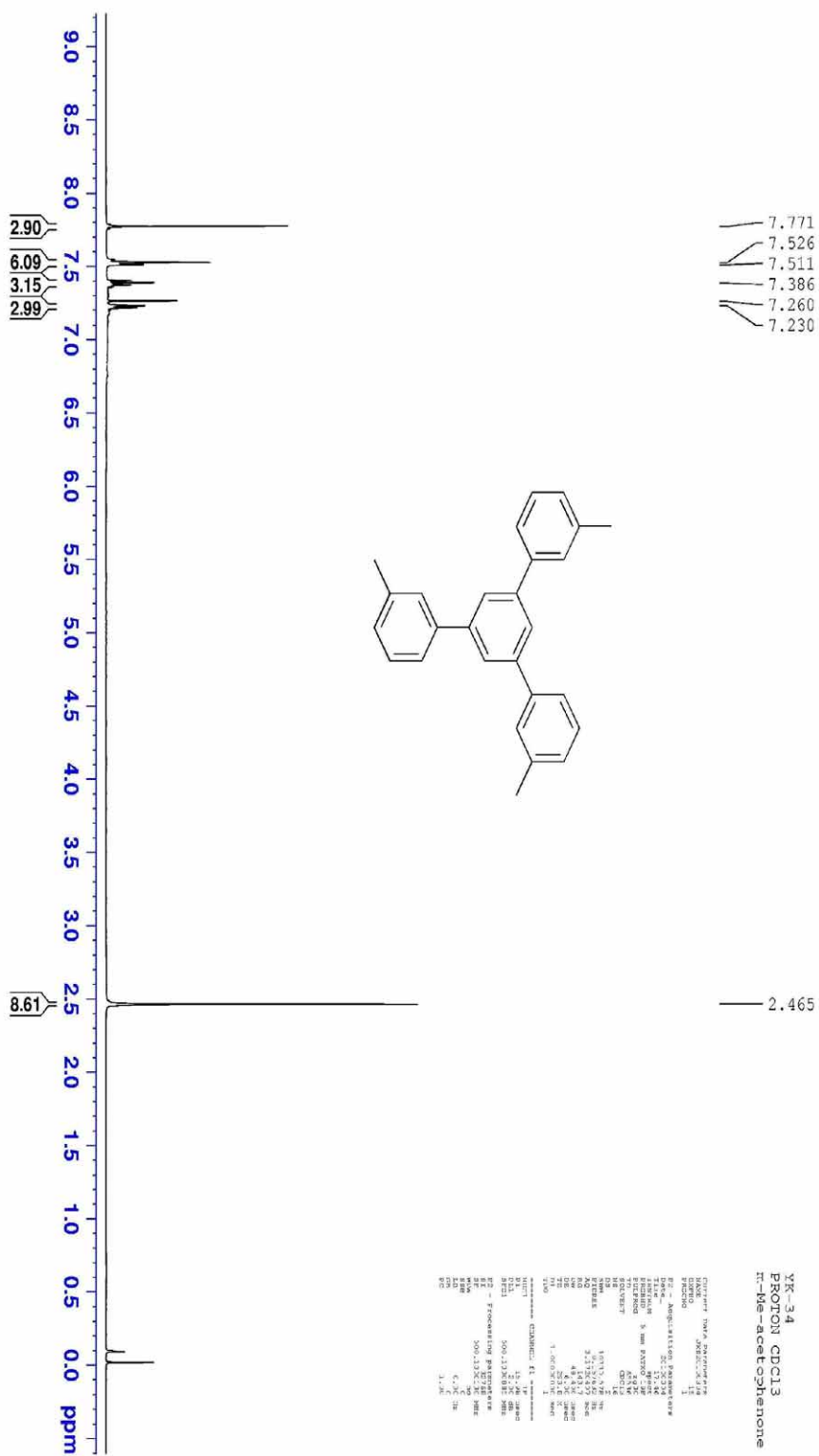










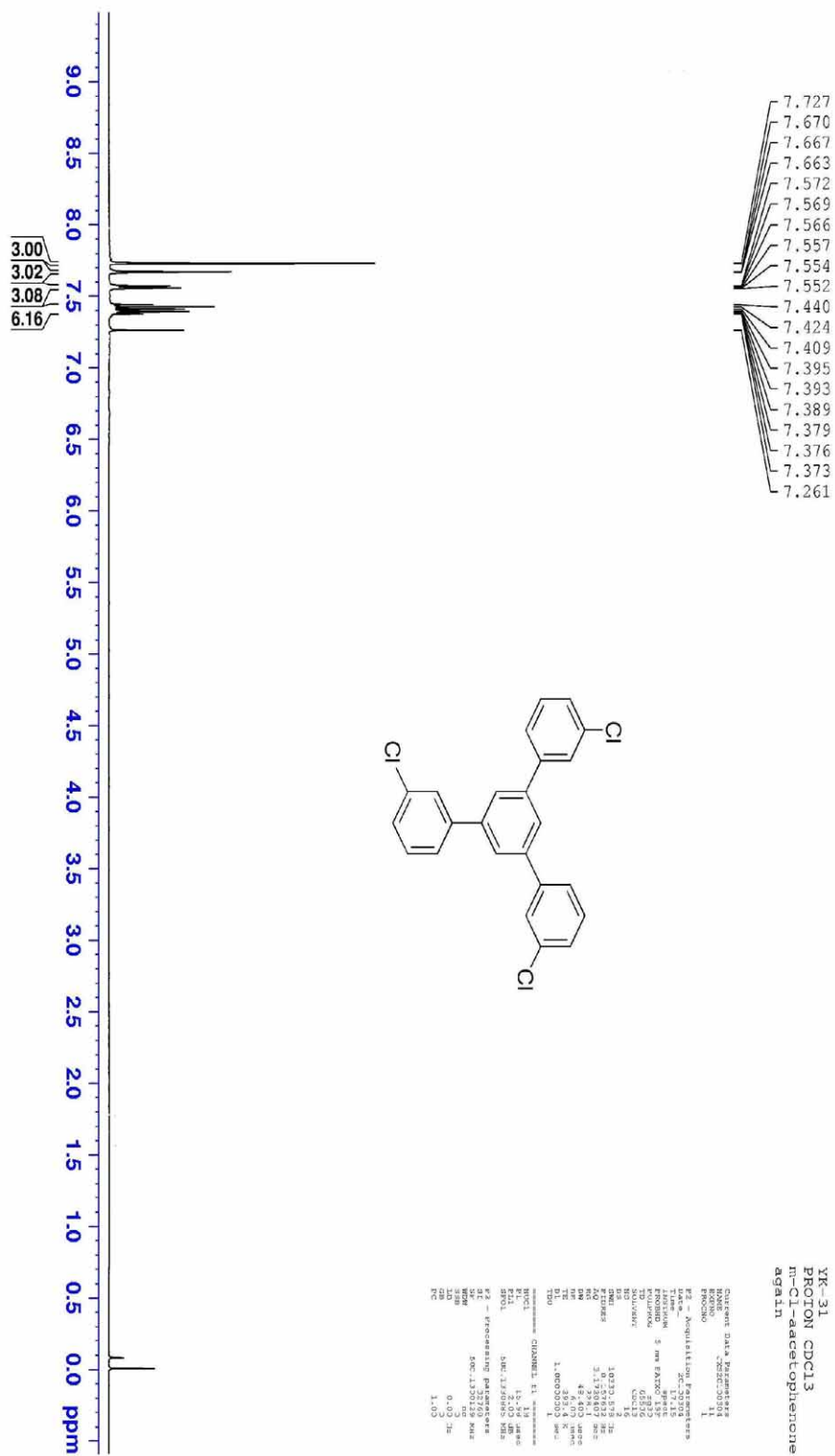




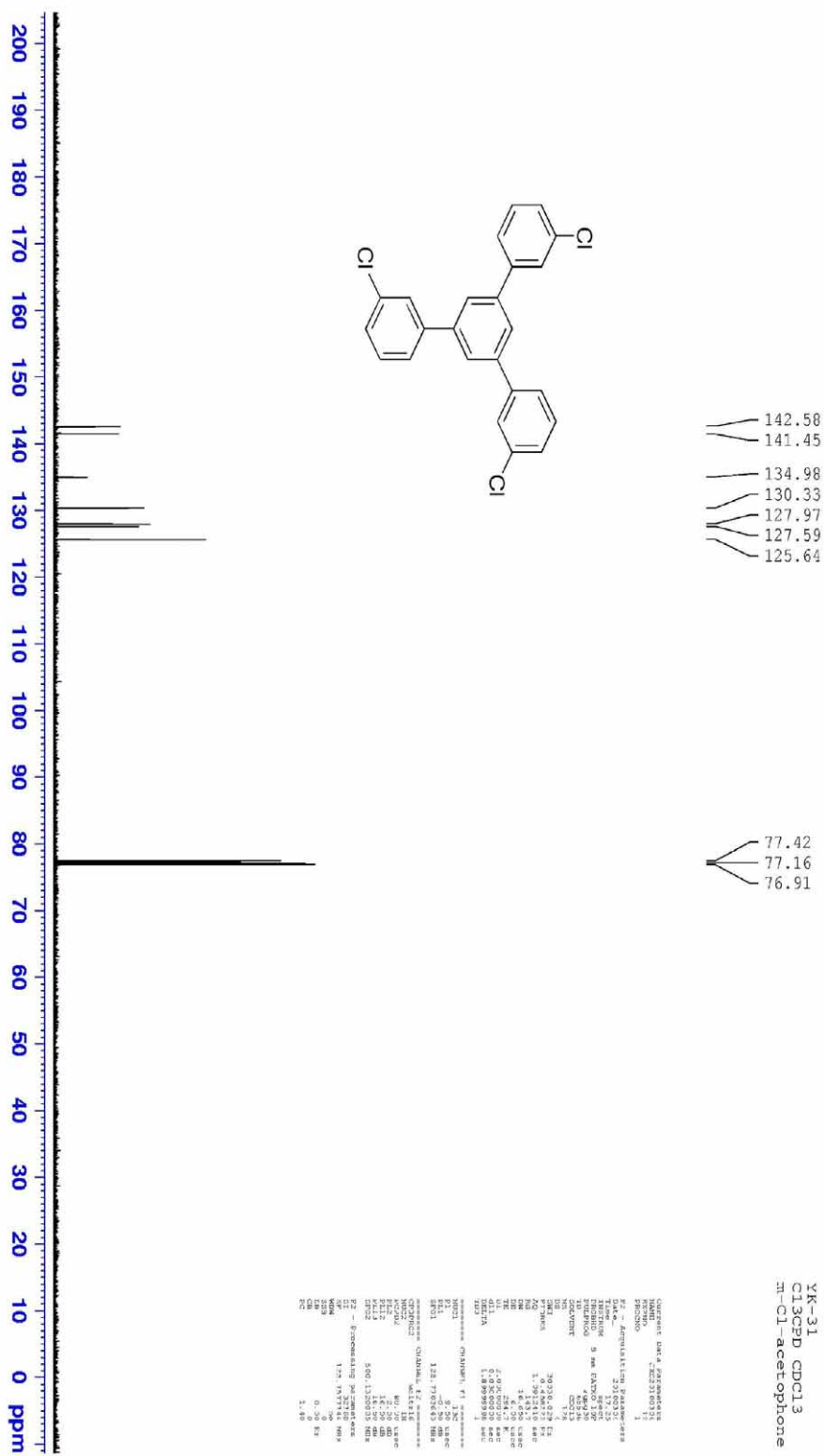




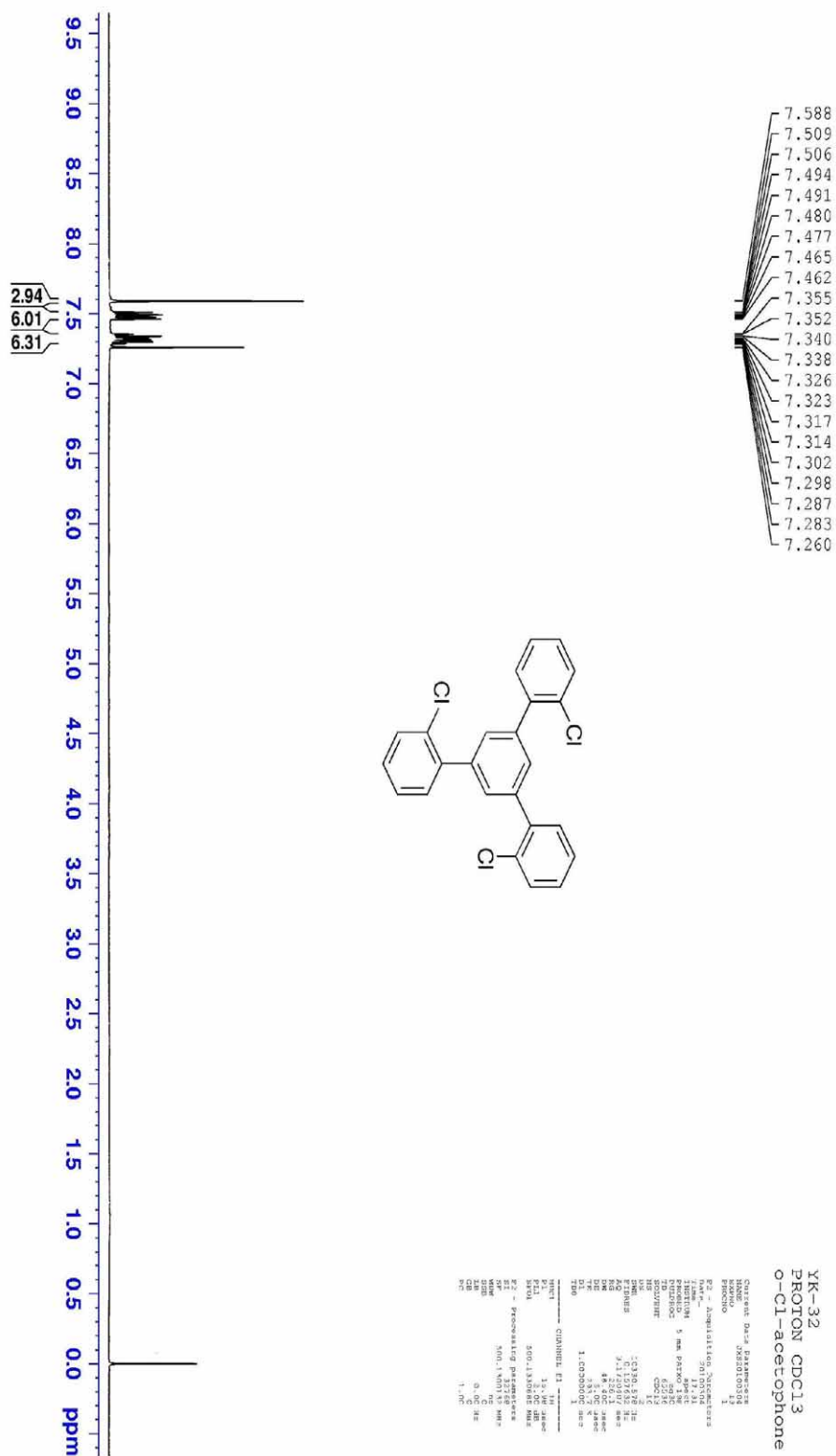




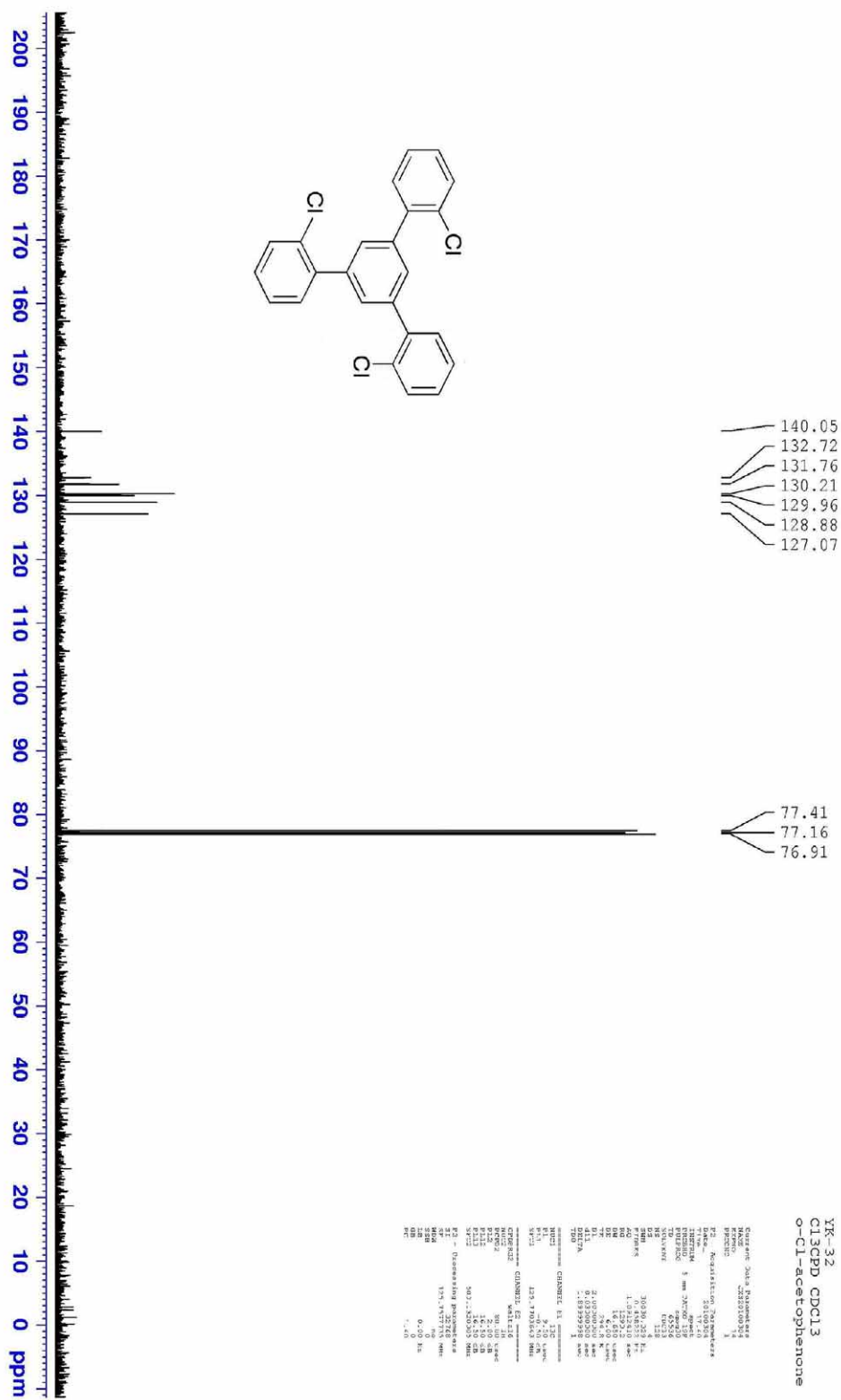














**Reference:**

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