

## Electronic Supplementary Information

# Enhanced catalytic performance of Pd–Pt nanodendrites for ligand-free Suzuki cross-coupling reactions

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**General protocol for Suzuki cross-coupling reaction:** Aryl halides (0.5 mmol, 1 equiv), phenylboronic acids (0.6 mmol, 1.2 equiv), Cs<sub>2</sub>CO<sub>3</sub> (0.6 mmol, 1.2 equiv), and Pd-Pt NDs (4 mg) were put into 2 mL ethanol/water (v/v = 1/1). The solution was stirred for desired time at 80 °C under air atmosphere. The reaction was monitored by thin layer chromatography (TLC). Afterward, the reaction mixture was cooled to room temperature and the catalyst was recovered by simple filtration and thoroughly washed with ethyl acetate and water. The combined organic layer was dried by Na<sub>2</sub>SO<sub>4</sub>, and the filtered residue was purified by flash column chromatography on silica gel.

**<sup>1</sup>H NMR, <sup>13</sup>C NMR, and mass spectral data of products from the Suzuki cross-coupling reactions:** 2a-2k are known compounds,<sup>1-7</sup> and analytical data of the isolated product are summarized as follows:

**Biphenyl (2a):** White solid, M. p.: 68-70 °C; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 7.52 (d, 2H, J = 7.6 Hz), 7.36 (t, 4H, J = 7.6Hz), 7.27 (t, 4H, J = 7.4 Hz). <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 141.27, 128.80, 127.30, 127.21. MS(EI): m/z 154.1.

**2-Methoxybiphenyl (2b):** White solid, M. p.: 31-33 °C; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 7.45 (d, 2H, J = 7.2 Hz), 7.33 (t, 2H, J = 7.2 Hz), 7.24 (d, 3H, J = 4.0Hz), 6.90-6.98 (m, 2H), 3.74 (s, 3H); <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 156.47, 138.55, 130.91, 129.56, 128.63, 128.0, 126.93, 120.84, 114.21, 111.23, 55.57. MS(EI): m/z 184.1.

**3-Methoxybiphenyl (2c):** White solid, M. p.: 49-50 °C; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 7.58 (d, 2H, J = 7.6 Hz), 7.43 (t, 2H, J= 7.6 Hz), 7.37-7.7.33 (m, 2H), 7.17 (t, 3H, J = 12.4 Hz), 6.90-6.8 (d-d, 1H, J = 8.0 Hz, 2.4 Hz), 3.84 (s, 3H); <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 159.97, 142.82, 141.14, 129.81, 128.80, 127.47, 127.25, 119.73, 112.94, 112.71., 55.34. MS(EI): m/z 184.1.

**4-Methoxybiphenyl (2d):** White solid, M. p.: 85-86 °C; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 7.46 (t, 4H, J = 9.0 Hz), 7.34 (t, 2H, J = 7.6 Hz), 7.23 (d, 1H, J = 7.2 Hz), 6.90 (d, 2H, J = 8.4 Hz), 3.77 (s, 3H); <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 159.16, 140.85, 133.80, 128.75, 128.18, 126.77, 114.22, 55.37. MS(EI): m/z 184.1.

**4-Nitrobiphenyl 2e:** Yellow solid, M. p.: 111-113 °C; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 8.30 (d, 2H, J = 8.8Hz), 7.75-7.72 (m, 2H), 7.64-7.61 (m, 2H), 7.52-7.43 (m, 3H); <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 147.65, 147.10, 138.79, 129.18, 128.94, 127.82, 127.41, 124.13. MS(EI): m/z 199.1.

**2-Methylbiphenyl (2f):** Colourless liquid; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ (ppm), 7.34 (t, 2H, J = 7.2 Hz), 7.28-7.24 (m, 3H), 7.20-7.17 (m, 4H), 2.20 (S, 3H); <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 141.96, 135.36, 130.32, 129.81, 129.21, 128.08, 127.26, 126.77, 125.77. MS(EI): m/z 168.1.

**4-Formylbiphenyl (2g):** Yellow solid, M. p.: 58-60 °C; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 9.65 (t, 1H, J = 8.6 Hz), 7.60-7.55 (m, 2H), 7.49 (t, 2H, J = 7.4 Hz), 7.40-7.33 (m, 3H), 6.73-6.61 (m, 1H); <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>): 193.48, 151.22, 132.44, 129.83, 129.08, 128.45, 127.76, 127.11, 125.95, 125.74. MS(EI): m/z 182.1.

**4-Methylbiphenyl (2h):** White solid, M. p.: 46–48 °C; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 7.48 (d, 2H, J = 7.6 Hz), 7.40 (d, 2H, J = 8.0 Hz), 7.32 (t, 2H, J = 7.6 Hz), 7.22 (t, 1H, J = 7.4 Hz), 7.15 (d, 2H, J = 8.0 Hz), 2.30 (s, 3H); <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 141.23, 138.42, 137.09, 129.56, 128.80, 127.07, 127.05. MS(EI): m/z 168.1.

**3-Methylbiphenyl (2i):** Colourless liquid; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 7.51 (d, 2H, J = 7.6 Hz), 7.38-7.32 (m, 4H), 7.26 (t, 2H, J = 7.4 Hz), 7.09 (d, 1H, J = 7.6 Hz), 2.35 (s, 3H); <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 140.31, 140.19, 137.30, 127.66, 127.63, 126.96, 126.15, 123.24, 20.53. MS(EI): m/z 168.1.

**4-Fluorobiphenyl (2j):** White solid, M. p.: 73–76 °C; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 7.48-7.45 (m, 4H), 7.36 (t, 2H, J = 7.6 Hz), 7.27 (t, 1H, J = 7.4 Hz), 7.05 (t, 3H, J= 10.0 Hz); <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 160.19, 139.21, 127.78, 127.69, 127.61, 126.22, 125.98, 114.68; <sup>19</sup>F NMR (400MHz, CDCl<sub>3</sub>): 115.83. MS(EI): m/z 172.1.

**4-Chlorobiphenyl (2k):** White solid, M. p.: 78–79 °C; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 7.48-7.42 (m, 4H) 7.38-7.33 (m, 3H), 7.31-7.26 (m, 2H); <sup>13</sup>C NMR (400MHz,

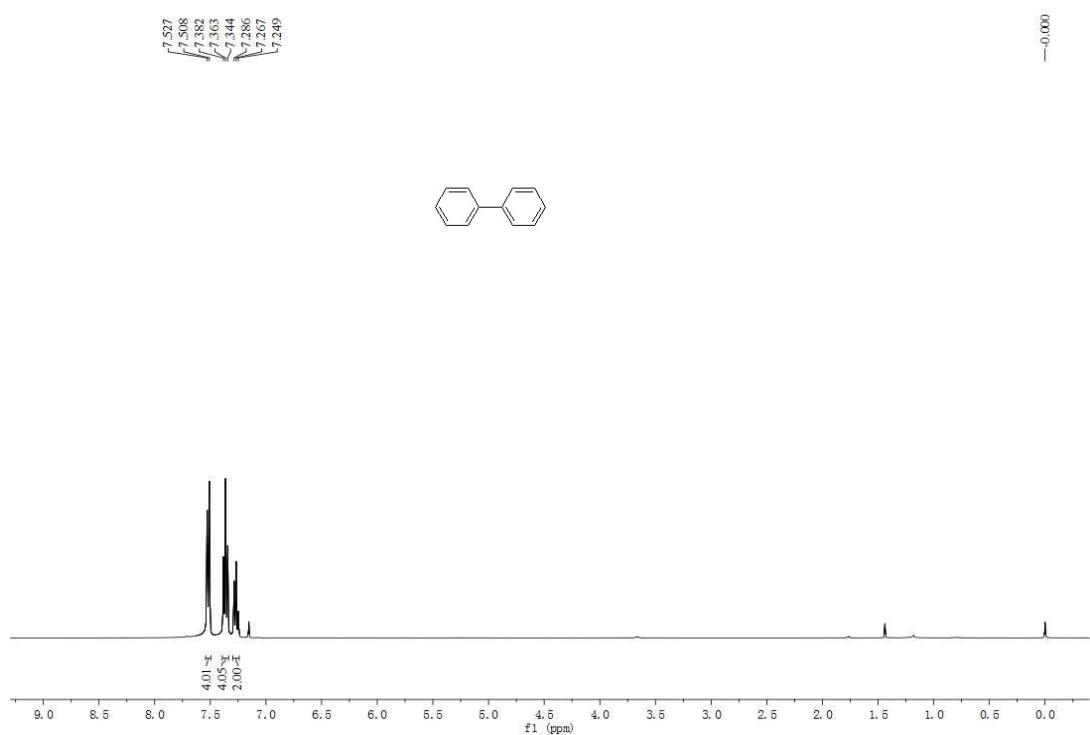
$\text{CDCl}_3$ ):  $\delta$  (ppm) 140.01, 139.68, 133.40, 128.94, 128.92, 128.43, 127.62, 127.02. MS(EI): m/z 188.1.

**2,6-dimethyl-1,1'-biphenyl (2l):** White solid, M. p.: 119–121 °C;  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 6.86 (d, 4H,  $J$  = 8.8 Hz), 6.77 (d, 4H,  $J$  = 8.8 Hz), 3.70 (s, 6H);  $^{13}\text{C}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 137.30, 132.44, 129.21, 128.08, 125.77, 122.40, 115.12, 113.58, 28.68. MS(EI): m/z 182.2.

## References

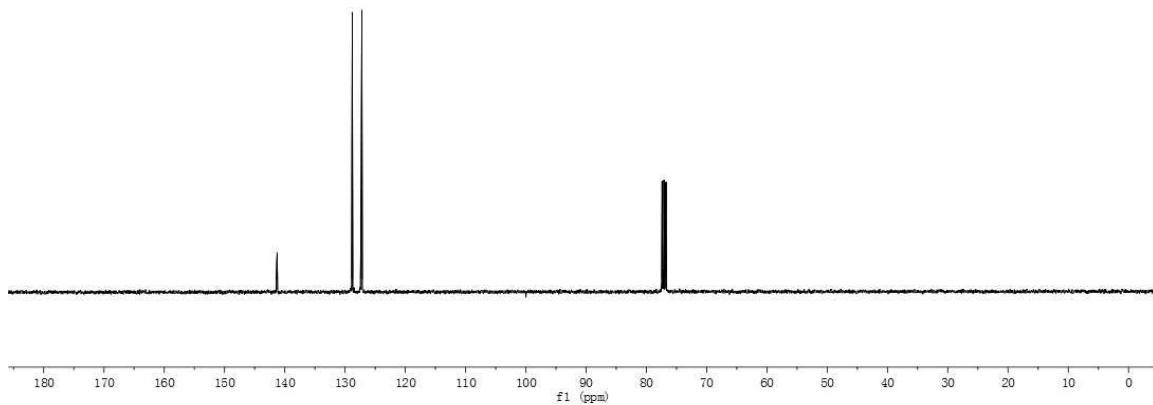
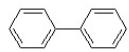
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- (7) Shen, A.; Ni, C.; Cao, Y.-C.; Zhou, H.; Song, G.-H.; Ye, X.-F. *Tetrahedron Lett.*, 2014, **55**, 3278-3282.

**<sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of all compounds**

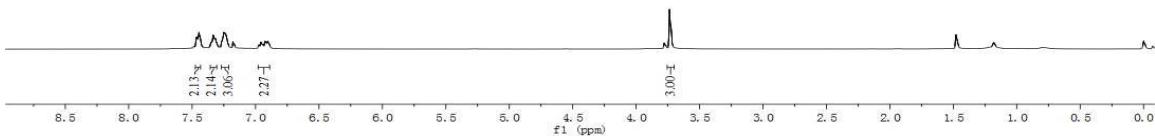
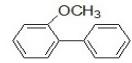


<sup>1</sup>H NMR of 2a in  $\text{CDCl}_3$

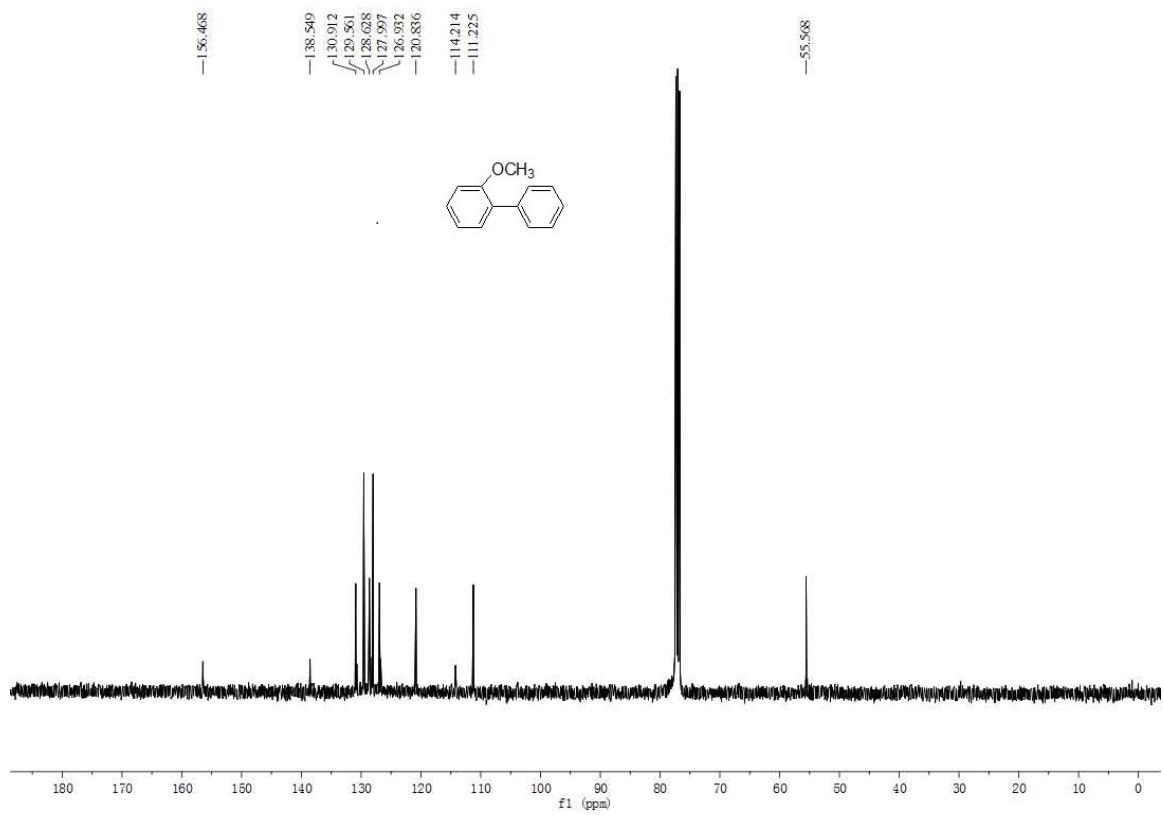
-141.269  
128.799  
127.296  
127.213



$^{13}\text{C}$  NMR of 2a in  $\text{CDCl}_3$



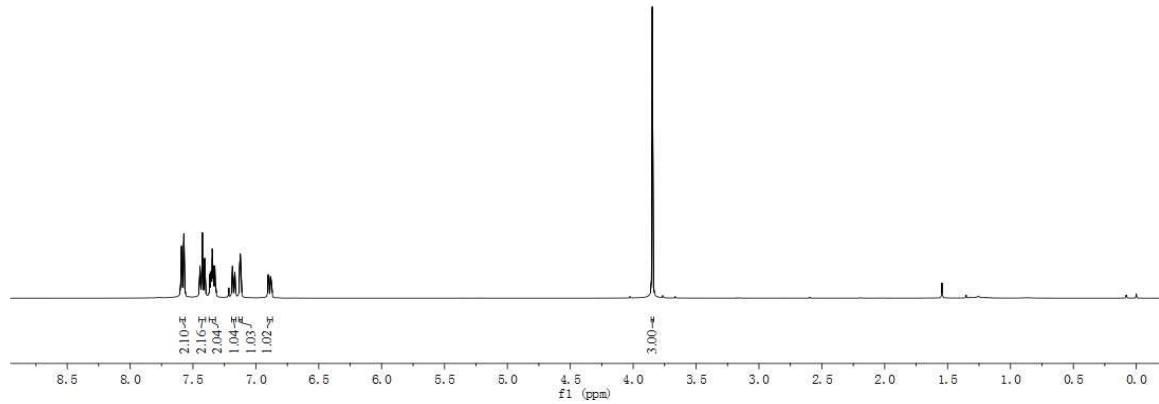
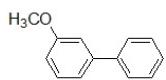
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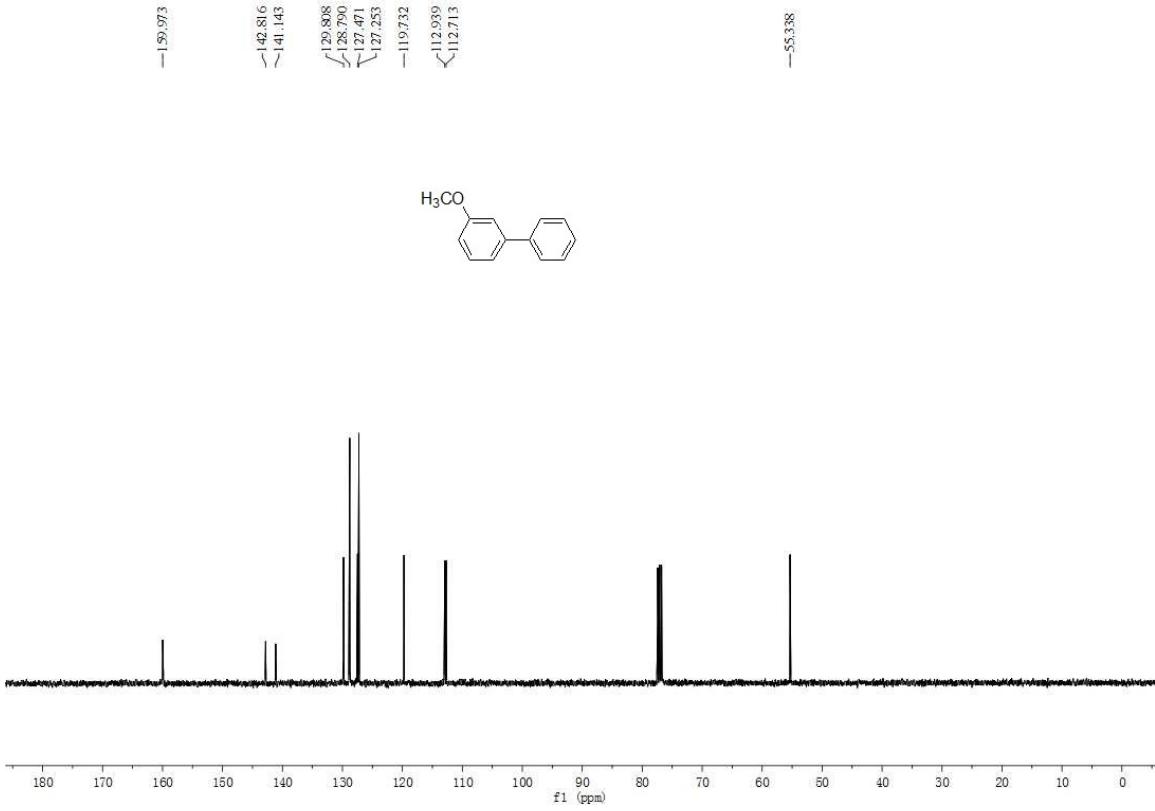
<sup>13</sup>C NMR of 2b in CDCl<sub>3</sub>

7.91  
7.572  
7.444  
7.426  
7.406  
7.366  
7.356  
7.346  
7.338  
7.326  
7.186  
7.167  
7.124  
6.903  
6.897  
6.883  
6.876

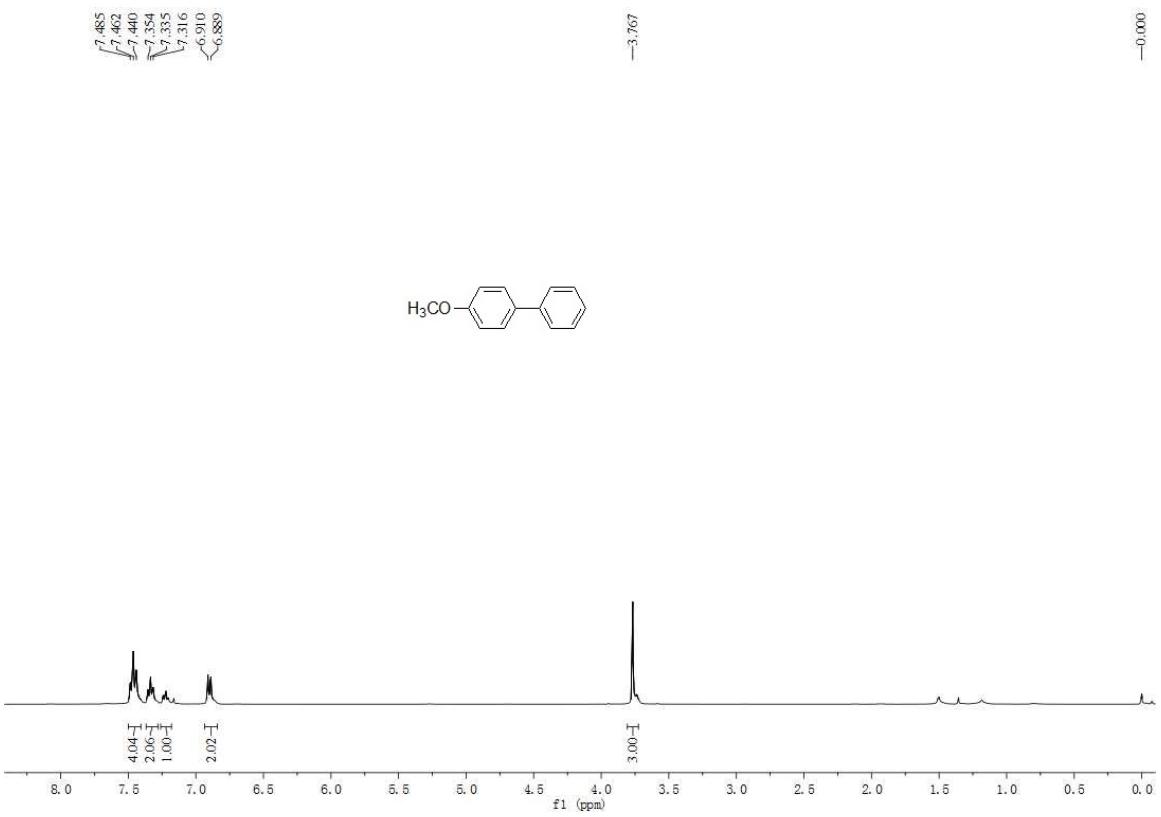
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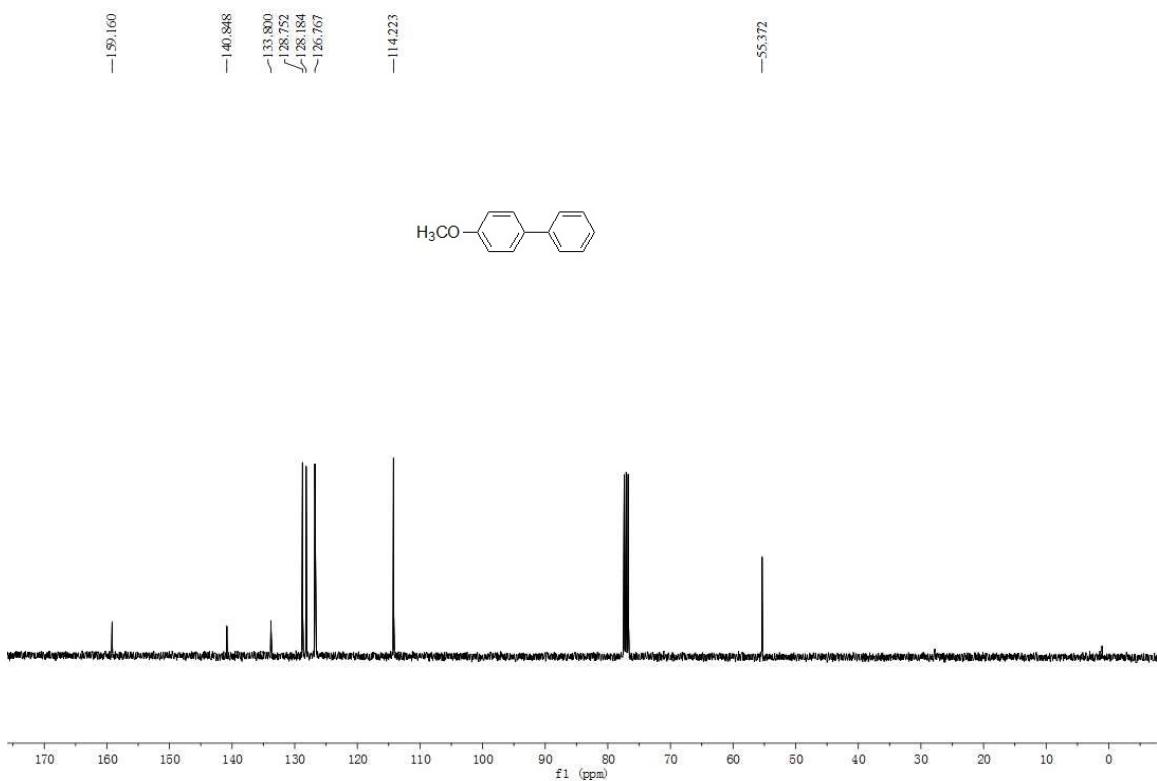
<sup>1</sup>H NMR of 2c in  $\text{CDCl}_3$



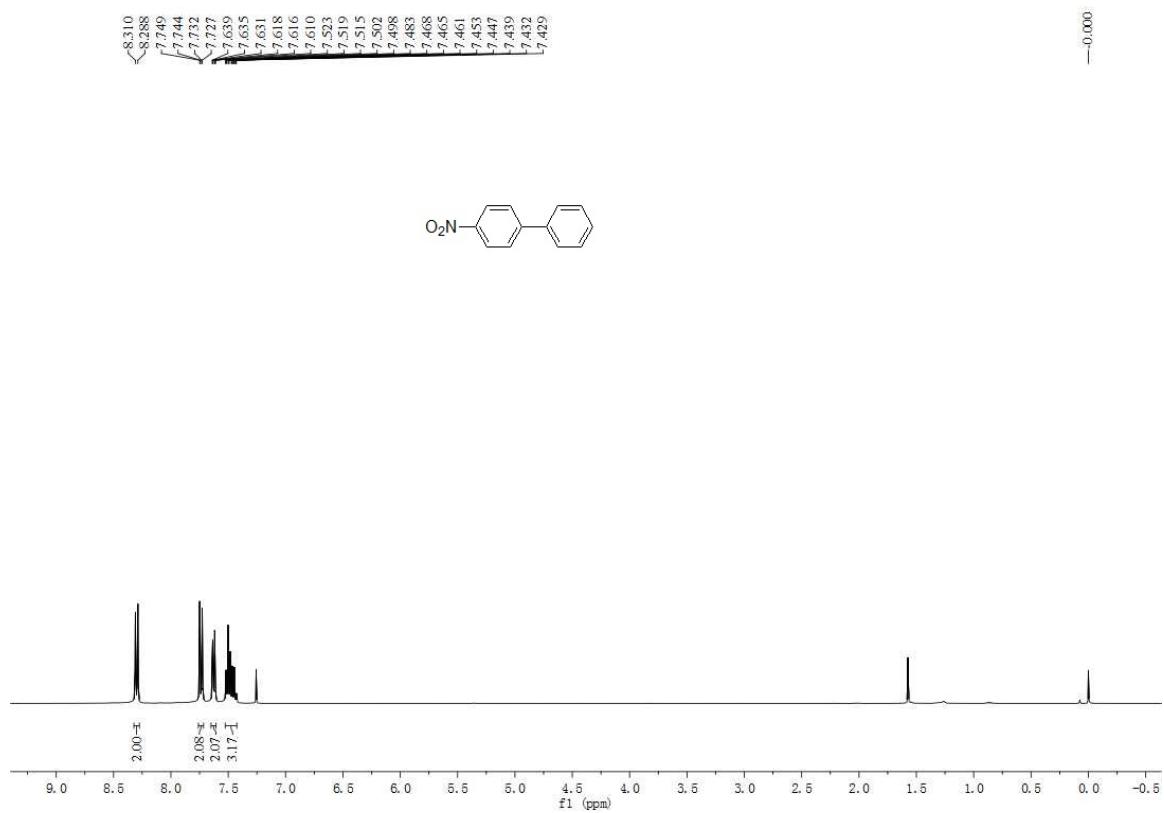
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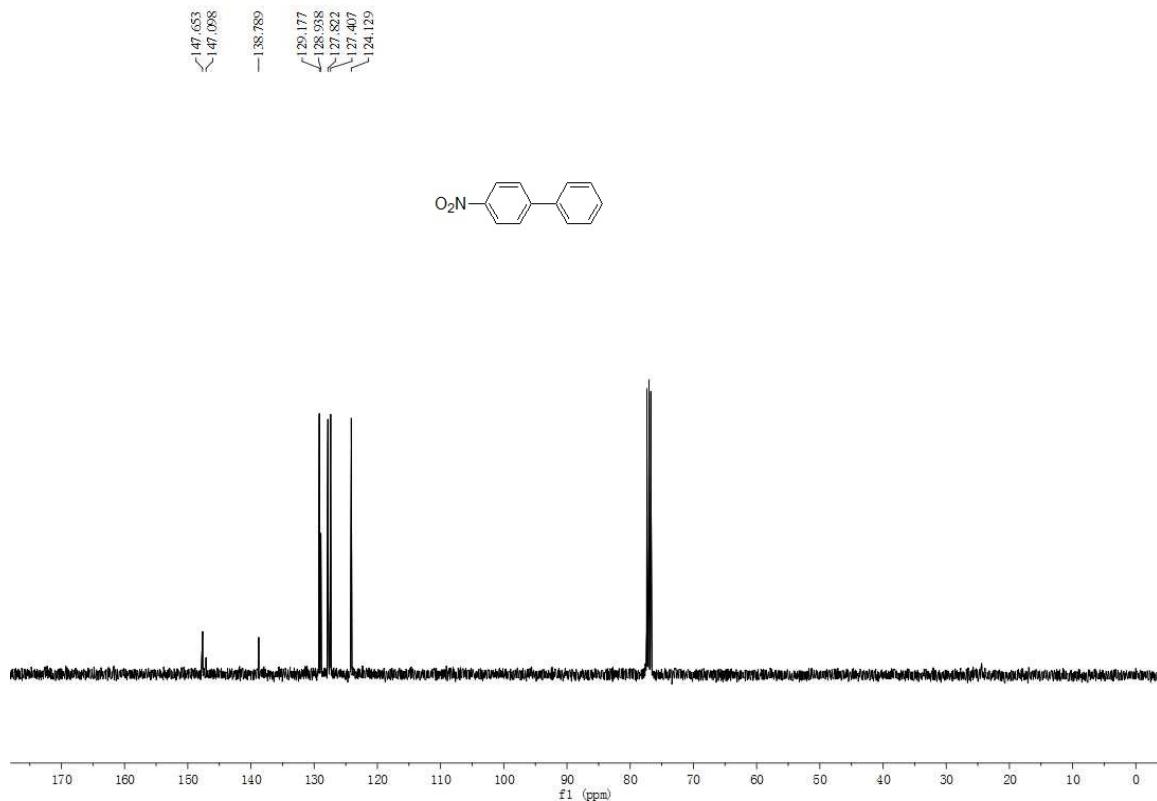
<sup>1</sup>H NMR of 2d in CDCl<sub>3</sub>



<sup>13</sup>C NMR of 2d in CDCl<sub>3</sub>

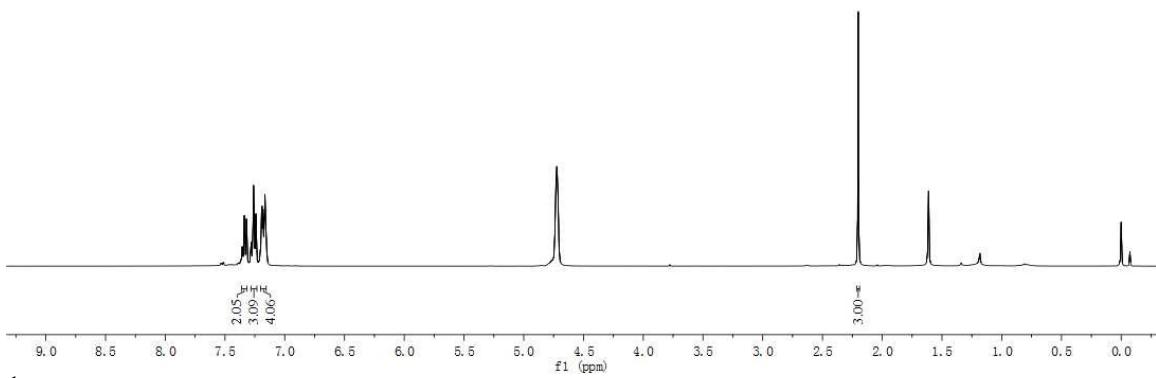
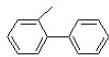


$^1\text{H}$  NMR of 2e in  $\text{CDCl}_3$

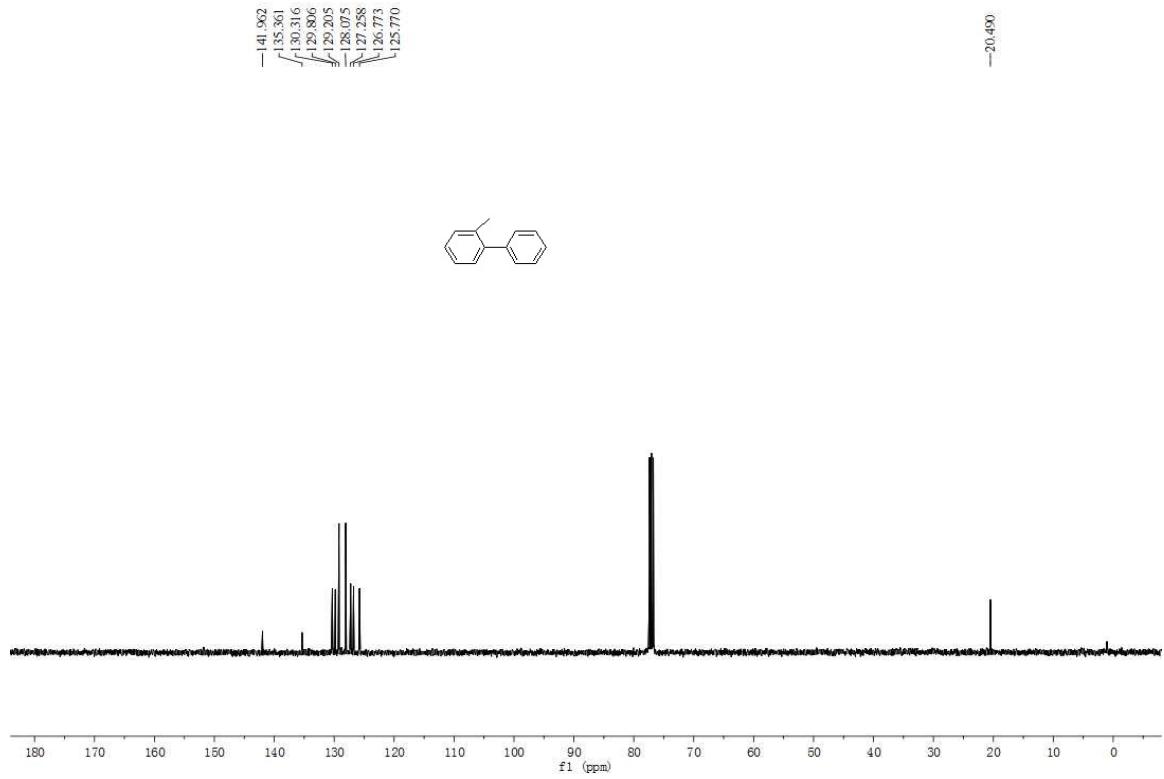


<sup>13</sup>C NMR of 2e in CDCl<sub>3</sub>

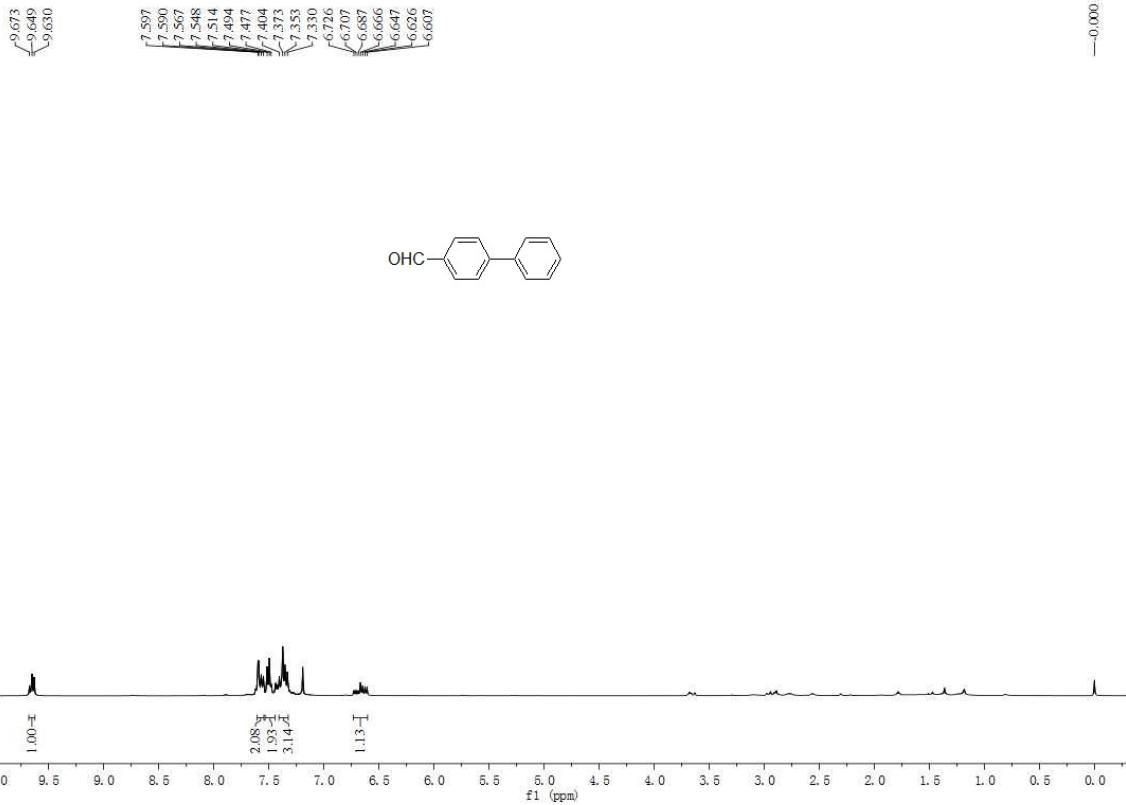
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7.338  
7.320  
7.281  
7.262  
7.258  
7.241  
7.203  
7.190  
7.183  
7.171  
7.166  
—2.201  
—0.000



$^1\text{H}$  NMR of 2f in  $\text{CDCl}_3$



$^{13}\text{C}$  NMR of 2f in  $\text{CDCl}_3$

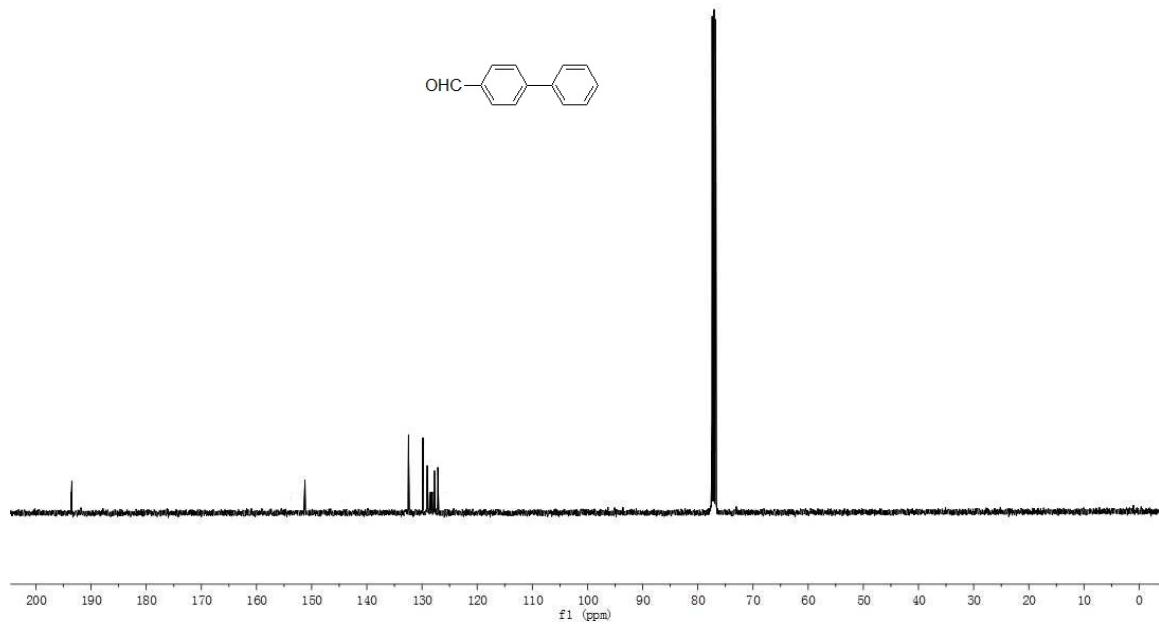
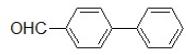


$^1\text{H}$  NMR of 2g in  $\text{CDCl}_3$

-193.481

-151.215

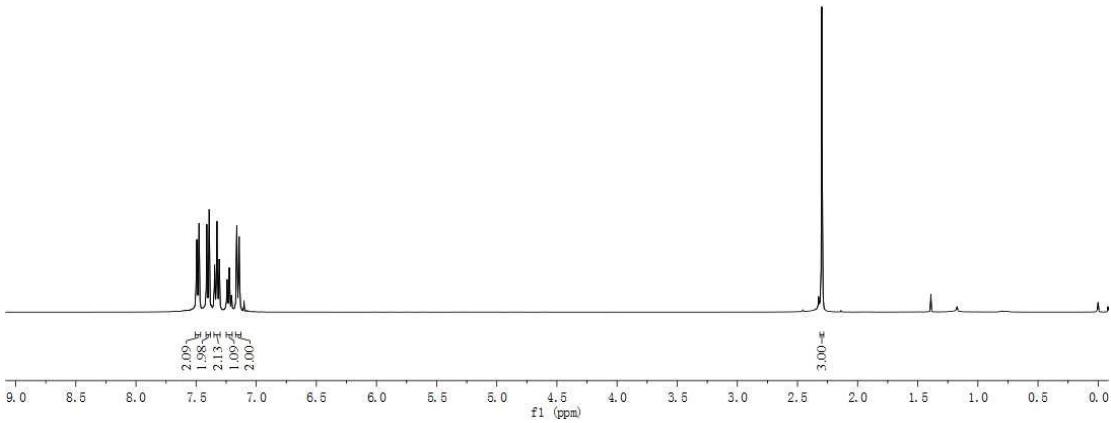
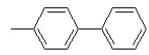
132.444  
129.833  
129.075  
128.449  
127.760  
127.111  
125.951  
125.743



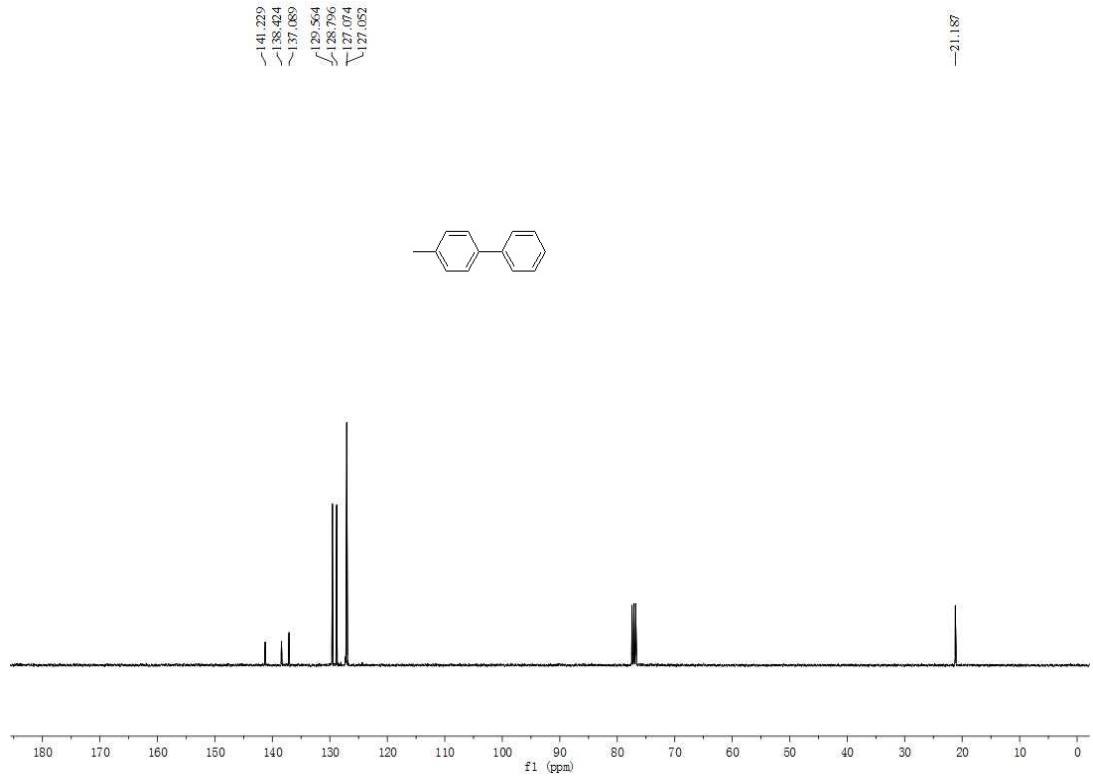
$^{13}\text{C}$  NMR of 2g in  $\text{CDCl}_3$

7.494  
7.475  
7.411  
7.391  
7.345  
7.327  
7.307  
7.242  
7.224  
7.205  
7.162  
7.142

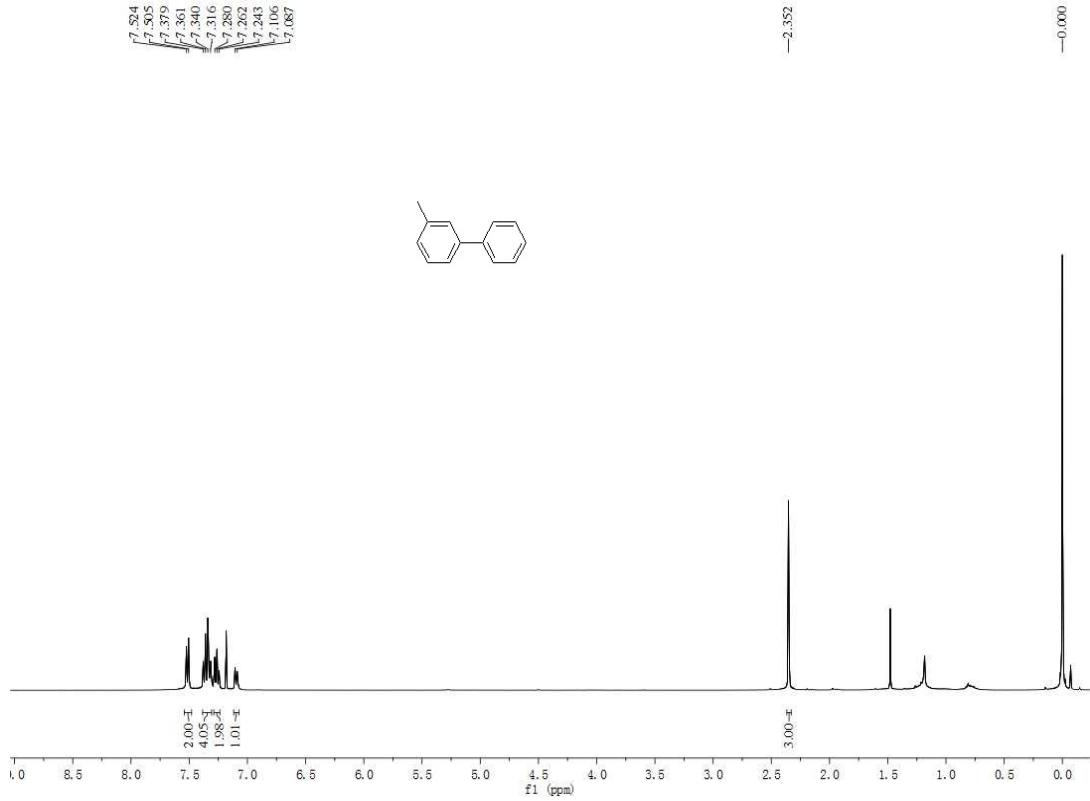
—2.298  
—0.000



<sup>1</sup>H NMR of 2h in CDCl<sub>3</sub>



<sup>13</sup>C NMR of 2h in CDCl<sub>3</sub>

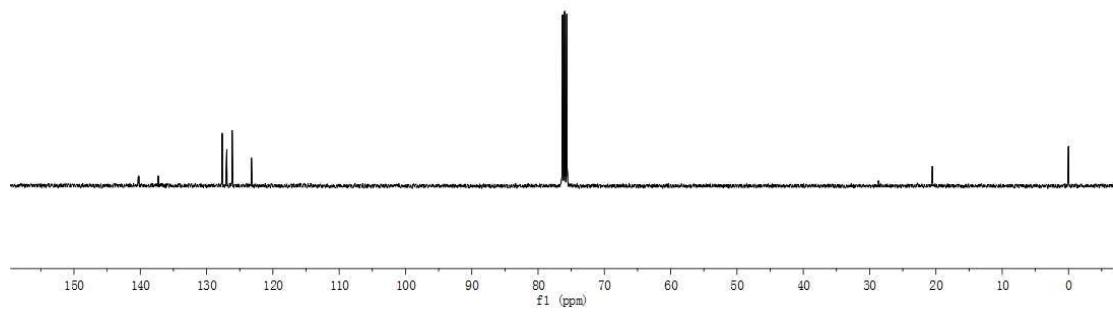
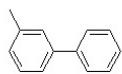


<sup>1</sup>H NMR of 2i in CDCl<sub>3</sub>

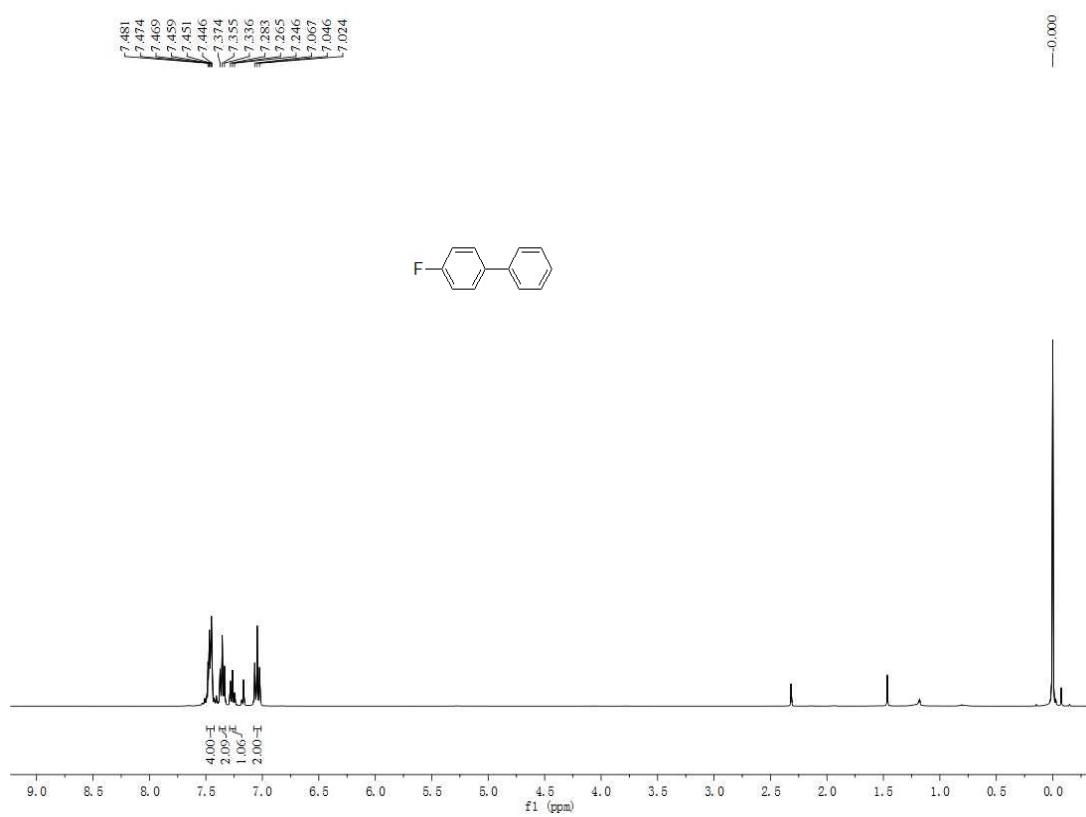
<sup>140</sup>.314  
<sup>140</sup>.194  
~<sup>137</sup>.296

<sup>127</sup>.658  
<sup>127</sup>.628  
~<sup>126</sup>.960  
<sup>126</sup>.146  
~<sup>123</sup>.237

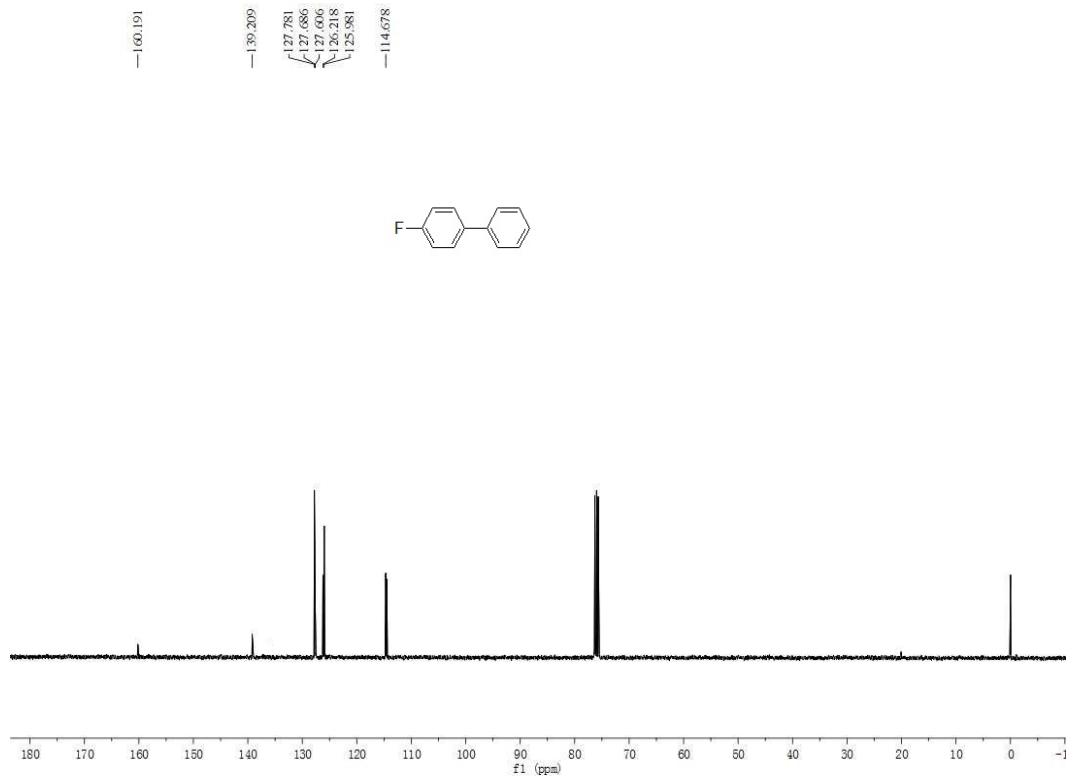
—<sup>20</sup>.525



<sup>13</sup>C NMR of 2i in CDCl<sub>3</sub>

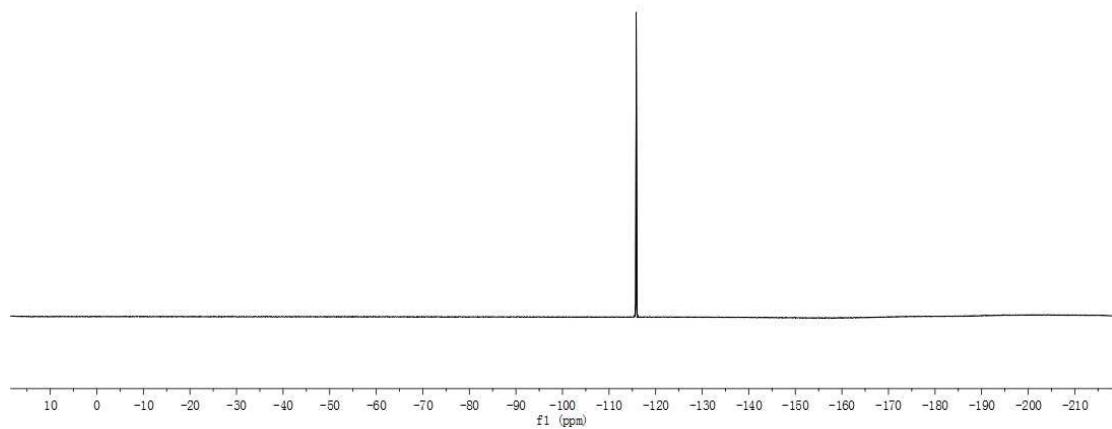
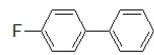


<sup>1</sup>H NMR of 2j in CDCl<sub>3</sub>

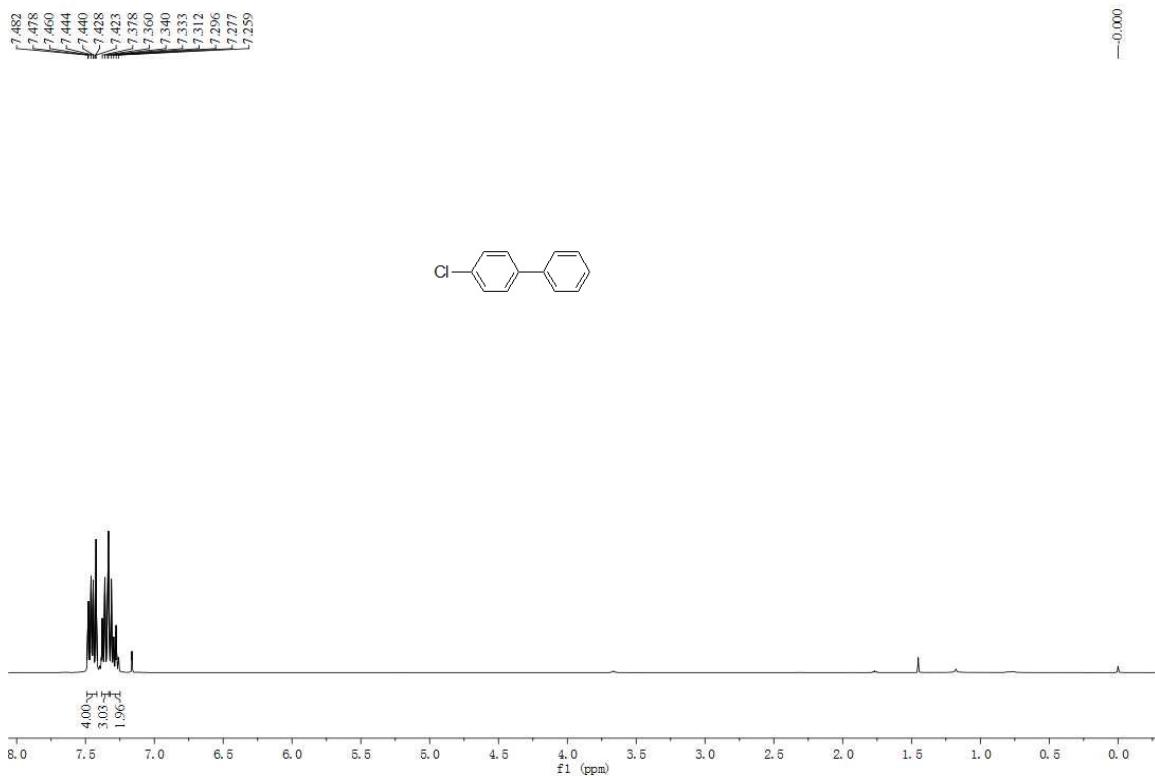


<sup>13</sup>C NMR of 2j in CDCl<sub>3</sub>

—115.83

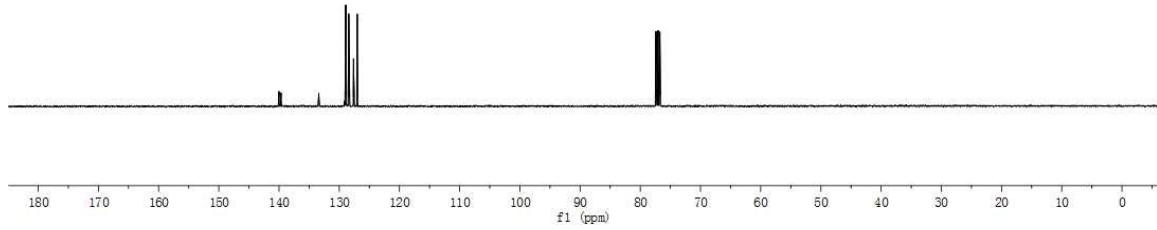
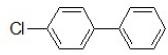


<sup>19</sup>F NMR of 2j in CDCl<sub>3</sub>

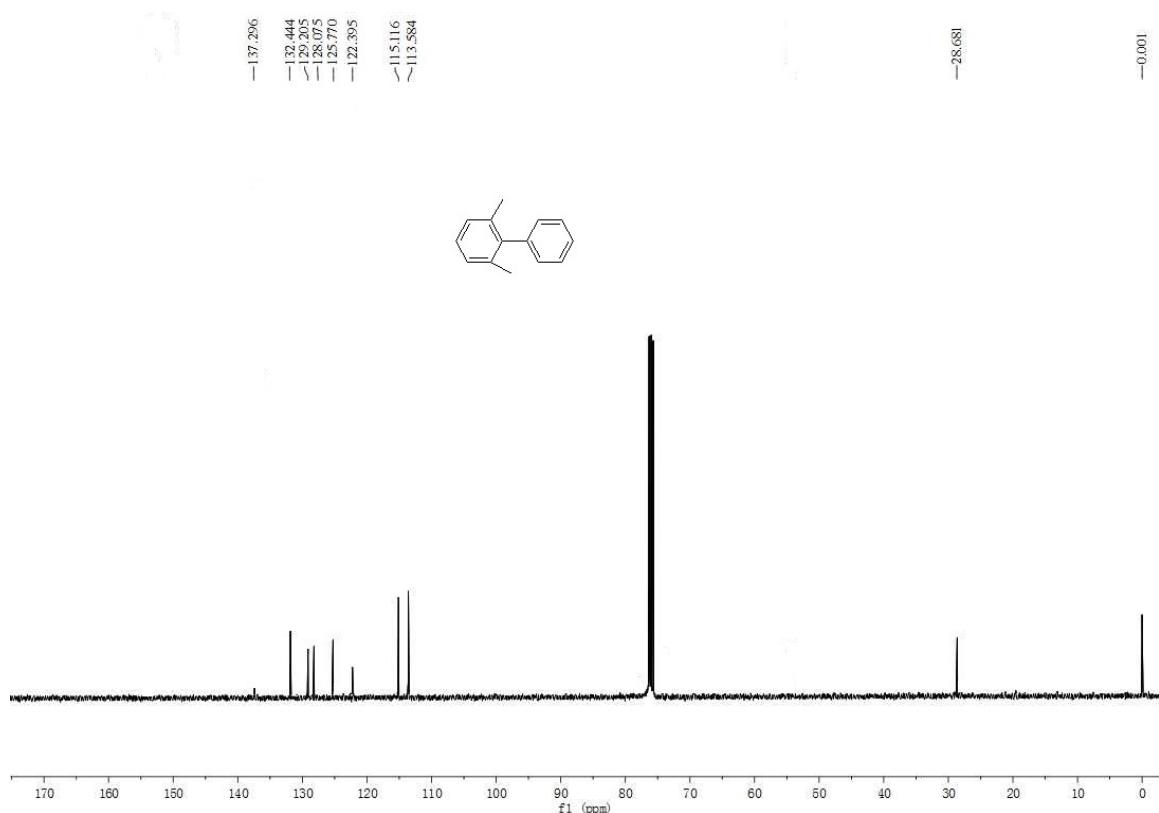
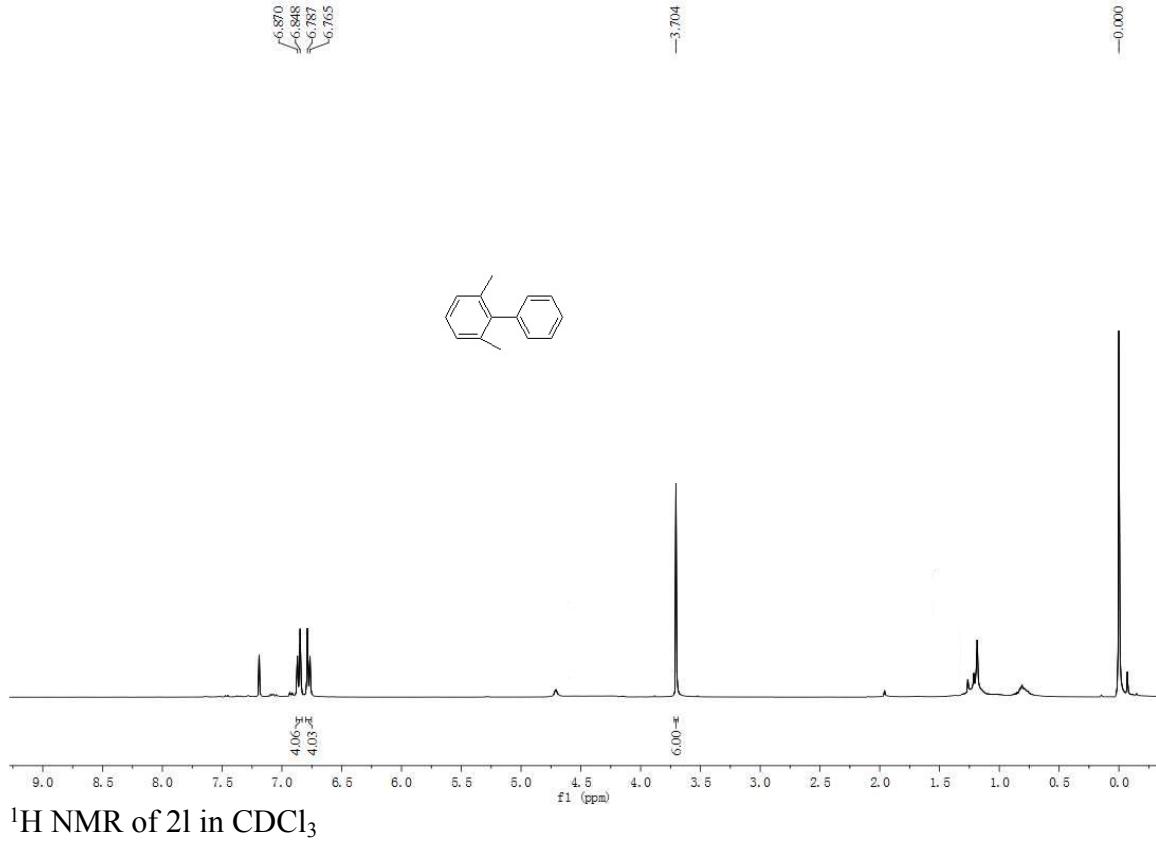


$^1\text{H}$  NMR of 2k in  $\text{CDCl}_3$

140.012  
139.682  
133.597  
128.599  
128.918  
128.426  
127.624  
127.020



<sup>13</sup>C NMR of 2k in  $\text{CDCl}_3$



<sup>13</sup>C NMR of 2l in CDCl<sub>3</sub>