

**Electronic Supplementary Information for New Journal of Chemistry**

**Facile One-Pot Nanocatalysts Encapsulation of Palladium-NHC  
Complexes for Aqueous Suzuki–Miyaura Couplings**

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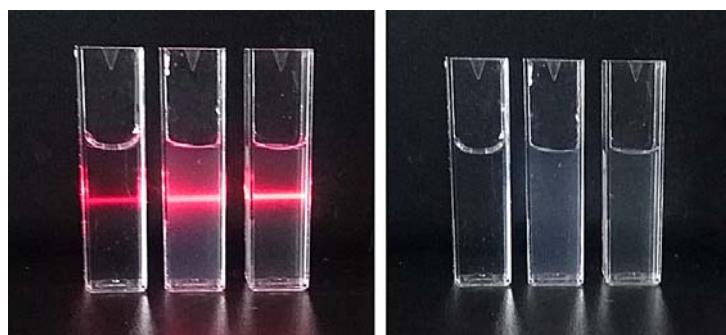
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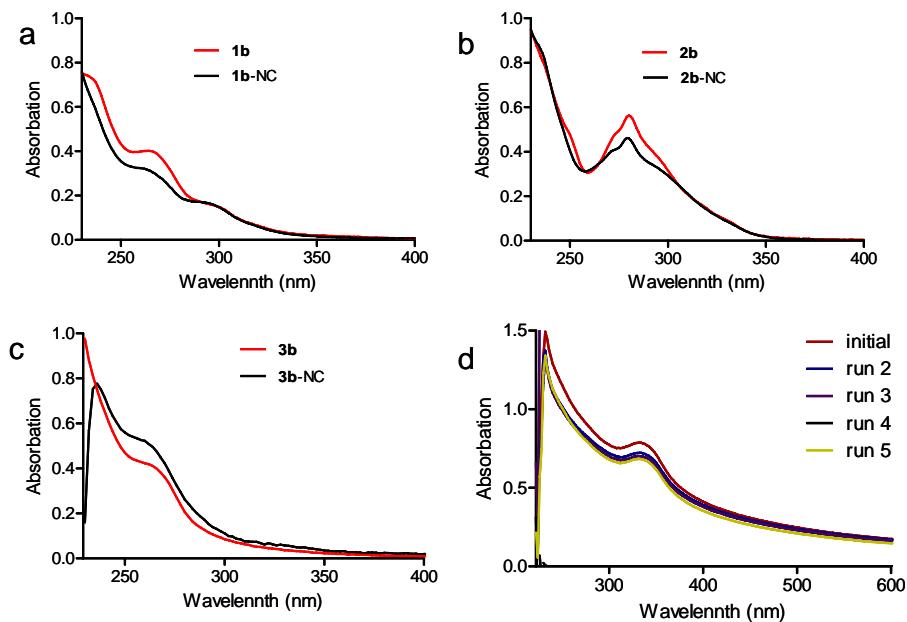
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**Table S1.** X-ray crystallographic data for palladium-NHC complexes **1b**, **2b** and **3b**.

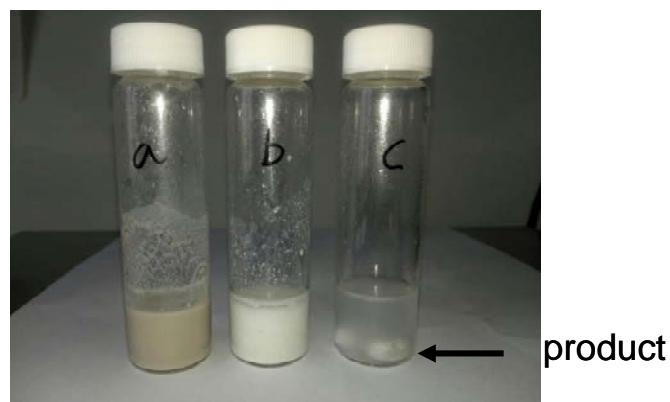
	<b>1b•CH<sub>3</sub>CN</b>	<b>2b</b>	<b>3b</b>
Formula	C <sub>19</sub> H <sub>19</sub> ClF <sub>6</sub> N <sub>5</sub> PPdC <sub>21</sub> H <sub>18</sub> Cl F <sub>6</sub> N <sub>4</sub> PPdC <sub>18</sub> H <sub>19</sub> ClF <sub>6</sub> N <sub>5</sub> PPd		
<i>F</i> <sub>w</sub>	604.21	613.21	592.20
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>n</i>
<i>a</i> , Å	10.8222(10)	9.5629(5)	8.2397(11)
<i>b</i> , Å	13.3189(12)	26.8142(9)	13.5183(13)
<i>c</i> , Å	16.9614(16)	10.2793(4)	21.343(2)
$\alpha$ , deg.	90	90	90
$\beta$ , deg.	97.867(2)	116.742(6)	100.006(2)
$\gamma$ , deg.	90	90	90
<i>V</i> , Å <sup>3</sup>	2421.8(4)	2353.91	2341.1(5)
<i>Z</i>	4	4	4
<i>D</i> <sub>calcd</sub> , Mg/m <sup>3</sup>	1.657	1.730	1.680
Refls collected	12130	14859	11213
Refls independent ( <i>R</i> <sub>int</sub> )	4270 (0.0261)	4141 (0.0451)	4117 (0.0403)
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.084	1.045	1.089
<i>R</i> ( <i>I</i> > 2σ <i>I</i> )	0.0454, 0.1251	0.0435, 0.1034	0.0445, 0.0981
<i>R</i> (all data)	0.0613, 0.1386	0.0533, 0.1105	0.0755, 0.1147



**Fig. S1.** Water solution of **1b**-NC, **2b**-NC, and **3b**-NC.

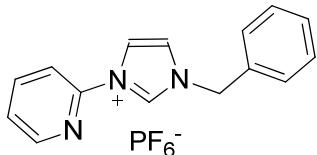


**Fig. S2.** Uv spectral of **1b** and **1b**-NC (a), **2b** and **2b**-NC (b), **3b** and **3b**-NC (c), and **3b**-NC initial and after recycling from the Suzkui-Miyaura reaction mixture (d).



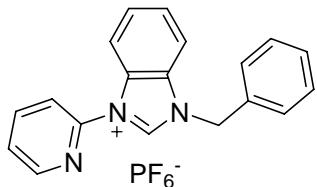
**Fig. S3.** Aqueous Suzuki-Miyaura coupling reaction of 4-bromotoluene and phenylboronic acid catalyzed by 0.1 mol% **3b** (a), **3b**-NC without TBAB (b), and **3b**-NC with TBAB (c) at 60 °C for 3 h in water.

### Synthesis and characterization of **1a** -**1b** and **2a**-**2b**



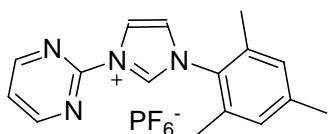
[HL1](PF<sub>6</sub>), **1a**

A solution of *N*-(2-pyridineyl)imidazole (1.45 g, 10 mmol) and benzyl chloride (1.51 g, 12 mmol) in acetonitrile (20 mL) was refluxed overnight. The solvent was removed and the residue was redissolved in water (25mL), and then a saturated NH<sub>4</sub>PF<sub>6</sub> aqueous solution (20 mL) was added dropwise. The resulting precipitate was collected, washed with water and dried. Yield: 3.43 g, 90%. Anal. Calcd for C<sub>15</sub>H<sub>14</sub>F<sub>6</sub>N<sub>3</sub>P: C, 47.25; H, 3.70; N, 11.02. Found: C, 47.15; H, 3.81; N, 11.26. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 10.27 (s, imidazole acidic CH, 1H), 8.66 (dd, *J* = 4.8 and 2.0 Hz, pyridine CH, 1H), 8.55 (t, *J* = 6.0 Hz, imidazole CH, 1H), 8.22 (dt, *J* = 8.0 and 2.0 Hz, pyridine CH, 1H), 8.05-8.02 (m, pyridine and imidazole CH, 2H), 7.65 (dd, *J* = 8.0 and 4.8 Hz, pyridine CH, 1H), 7.54-7.52 (m, phenyl CH, 2H), 7.48-7.41 (m, phenyl CH, 3H), 5.55 (s, CH<sub>2</sub>, 2H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 149.0, 146.4, 140.5, 135.1, 134.4, 129.0, 128.9, 128.4, 125.2, 123.5, 119.8, 114.3, 52.5.



[HL2](PF<sub>6</sub>), **2a**

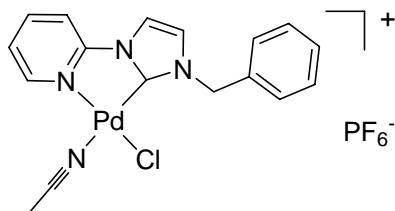
According to the same procedure as for **1a**, **2a** was obtained by the reaction of 1-(2-pyridyl)benzimidazole (1.51 g, 10 mmol) with benzyl chloride (1.51 g, 12 mmol) and a subsequently anion exchange reaction with NH<sub>4</sub>PF<sub>6</sub>. Yield: 3.7 g, 85%. Anal. Calcd for C<sub>19</sub>H<sub>16</sub>F<sub>6</sub>N<sub>3</sub>P: C, 52.91; H, 3.74; N, 9.74. Found: C, 52.43; H, 3.91; N, 9.62. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 10.71 (s, benzimidazole acidic CH, 1H), 8.80 (d, *J* = 4.0 Hz, pyridine CH, 1H), 8.49 (d, *J* = 7.6 Hz, benzimidazole CH, 1H), 8.32 (t, *J* = 6.4 Hz, pyridine CH, 1H), 8.11 (d, *J* = 8.0 Hz, pyridine CH, 1H), 8.01 (d, *J* = 7.6 Hz, benzimidazole CH, 1H), 7.78-7.83 (m, pyridine and imidazole CH, 3H), 7.66-7.64 (m, phenyl CH, 2H), 7.46-7.40 (m, phenyl CH, 3H), 5.90 (s, CH<sub>2</sub>, 2H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 149.9, 147.8, 143.2, 141.0, 134.0, 131.7, 130.3, 129.4, 129.3, 128.9, 128.3, 127.7, 125.6, 117.7, 116.6, 114.7, 51.0.



[HL3](PF<sub>6</sub>), **3a**

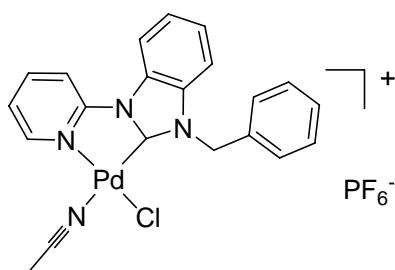
**3a** was prepared similarly as for **1a**, *N*-mesitylimidazole and 2-chloropyrimidine was used as

reaction substrates. Yield: 3.4 g, 84%. Anal. Calcd for  $C_{16}H_{17}F_6N_4P$ : C, 46.84; H, 4.18; N, 13.66; Found: C, 46.34; H, 3.88; N, 13.59.  $^1H$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  10.51 (s, imidazole acid CH, 1H), 9.12 (d,  $J$  = 4.8 Hz, pyrimidine CH, 2H), 8.81, 8.21 (both s, imidazole CH, 2H), 7.84 (t,  $J$  = 4.8 Hz, pyrimidine CH, 1H), 7.21(s, Mes CH, 2H), 2.37(s, Mes CH<sub>3</sub>, 3H), 2.14(s, Mes CH<sub>3</sub>, 6H).  $^{13}C$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  160.5, 152.8, 140.9, 137.6, 134.8, 131.6, 129.7, 125.8, 123.1, 120.5, 21.1, 17.5.



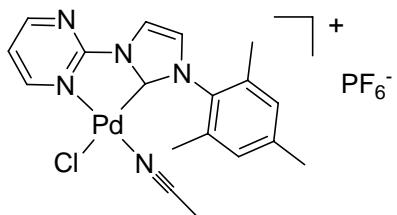
[Pd(L1)(CH<sub>3</sub>CN)Cl](PF<sub>6</sub>) (**1b**)

A mixture of HL1(PF<sub>6</sub>) (381 mg, 1.0 mmol), Ag<sub>2</sub>O (116 mg, 0.5 mmol) in 10 mL of CH<sub>3</sub>CN was stirred at 50 °C for 4 h. After the mixture was cooled to room temperature, [Pd(CH<sub>3</sub>CN)<sub>2</sub>]Cl<sub>2</sub> (260 mg, 1.0 mmol) was added to the solution, and the solution was stirred at room temperature for another 2 h. Then, the mixture was filtered through Celite, and all volatiles were evaporated under reduced pressure. The yellow residue was dissolved in CH<sub>3</sub>CN, and recrystallization by slow addition of Et<sub>2</sub>O into its CH<sub>3</sub>CN solution gave **1b** as a yellow solid, 439 mg, 78%. Anal. Calcd for C<sub>17</sub>H<sub>16</sub>ClF<sub>6</sub>N<sub>4</sub>PPd: C, 36.26; H, 2.86; N, 9.95. Found: C, 36.88; H, 3.06; N, 9.83.  $^1H$  NMR (CD<sub>3</sub>CN): 8.57 (s, pyridine CH, 1H), 8.34 (t,  $J$  = 7.6 Hz, pyridine CH, 1H), 7.90 (s, imidazole CH, 1H), 7.84 (d,  $J$  = 7.6 Hz, pyridine CH, 1H), 7.58 (t,  $J$  = 6.4 Hz, pyridine CH, 1H), 7.42 (m, phenyl, 5H), 7.27 (s, imidazole CH, 1H), 5.97 (s, CH<sub>2</sub>, 2H), 2.19 (s, CH<sub>3</sub>CN, 3H).  $^{13}C$  NMR (dmso- $d_6$ ): 151.3 (Pd-C), 147.7, 146.7, 144.3, 136.5, 129.3, 129.0, 128.7, 128.2, 125.3, 123.9, 119.1, 113.2, 52.9, 1.7.



[Pd(L2)(CH<sub>3</sub>CN)Cl](PF<sub>6</sub>) (**2b**)

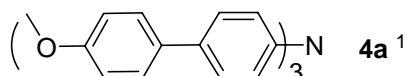
**2b** was prepared by a procedure analogous to what was used for **1b** and was isolated as a yellow solid. Yield: 472 mg, 77%. Anal. Calcd for C<sub>21</sub>H<sub>18</sub>ClF<sub>6</sub>N<sub>4</sub>PPd: C, 41.13; H, 2.96; N, 9.14. Found: C, 41.28; H, 2.65; N, 8.93.  $^1H$  NMR (dmso- $d_6$ ): 8.59-8.55 (m, pyridine CH, 2H), 8.47-8.43 (m, pyridine and benzimidazole CH, 2H), 7.73-7.69 (m, pyridine and benzimidazole CH, 2H), 7.61 (t,  $J$  = 7.6 Hz, pyridine CH, 1H), 7.56-7.48 (m, pyridine and phenyl CH, 3H), 7.38-7.29 (m, phenyl CH, 3H), 6.34 (s, CH<sub>2</sub>, 2H), 2.07 (s, CH<sub>3</sub>CN, 3H).  $^{13}C$  NMR (dmso- $d_6$ ): 151.7 (Pd-C), 146.7, 144.3, 135.1, 133.8, 129.7, 129.0, 128.3, 127.6, 126.9, 126.4, 123.3, 118.5, 114.0, 113.9, 113.6, 50.7, 1.51.



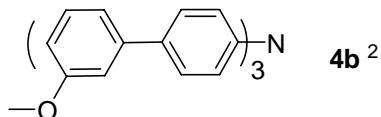
[Pd(L3)(CH<sub>3</sub>CN)Cl](PF<sub>6</sub>) (**3b**)

**3b** was prepared by a procedure analogous to what was used for **1b** and **2b** and was isolated as a yellow solid. Yield: 387 mg, 65%. Anal. Calcd for C<sub>18</sub>H<sub>19</sub>ClF<sub>6</sub>N<sub>5</sub>PPd: C, 36.51; H, 3.23; N, 11.83. Found: C, 36.41; H, 3.10; N, 11.90. <sup>1</sup>H NMR (dmso-d<sub>6</sub>): 9.18 (s, pyrimidine CH, 1H), 8.73 (s, pyrimidine CH, 1H), 8.46 (s, imidazole CH, 1H), 7.79 (t, *J* = 5.2 Hz, pyrimidine CH, 1H), 7.69 (s, imidazole CH, 1H), 7.01 (s, Mes CH, 2H), 2.31 (s, Mes CH<sub>3</sub>, 3H), 2.06 (s, CH<sub>3</sub>CN, 3H), 2.05 (s, Mes CH<sub>3</sub>, 6H), <sup>13</sup>C NMR (dmso-d<sub>6</sub>): 162.3, 156.2, 156.2 (Pd-C), 149.1, 139.3, 134.8, 134.5, 128.9, 126.5, 120.9, 119.1, 118.5, 21.1, 17.8, 1.54.

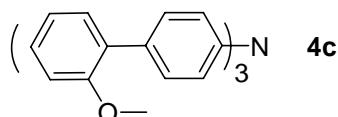
#### <sup>1</sup>H and <sup>13</sup>C NMR data of **4a-4b**



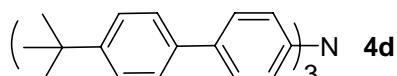
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.52 (d, *J* = 8.8 Hz, phenyl CH, 6H), 7.47 (d, *J* = 8.8 Hz, phenyl CH, 6H), 7.20 (d, *J* = 8.8 Hz, phenyl CH, 6H), 6.97 (d, *J* = 8.8 Hz, phenyl CH, 6H), 3.85 (s, CH<sub>3</sub>, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 158.9, 146.4, 135.2, 133.3, 127.7, 127.4, 124.4, 114.2, 55.4.<sup>1</sup>



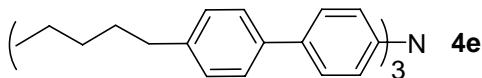
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.52 (d, *J* = 8.8 Hz, phenyl CH, 6H), 7.34 (t, *J* = 8.0 Hz, phenyl CH, 3H), 7.22 (d, *J* = 8.8 Hz, phenyl CH, 6H), 7.18 (d, *J* = 8.0 Hz, phenyl CH, 3H), 7.12 (s, phenyl CH, 3H), 6.87 (d, *J* = 8.0 Hz, phenyl CH, 3H), 3.86 (s, CH<sub>3</sub>, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 160.0, 146.9, 142.1, 135.5, 129.8, 128.0, 124.4, 119.3, 112.5, 112.3, 55.3.<sup>2</sup>



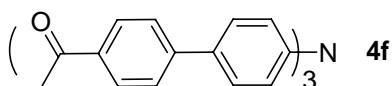
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.47-7.45 (m, phenyl CH, 6H), 7.36 (m, phenyl CH, 3H), 7.27-7.28 (m, phenyl CH, 3H), 7.21-7.23 (m, phenyl CH, 6H), 6.96-7.04 (m, phenyl CH, 6H), 3.83 (s, CH<sub>3</sub>, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 156.5, 146.5, 132.7, 130.7, 130.3, 128.3, 123.7, 120.9, 111.2, 56.5.



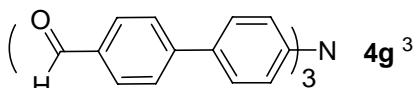
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.52 (t, *J* = 8.8 Hz, phenyl CH, 12H), 7.45 (d, *J* = 8.8 Hz, phenyl CH, 6H), 7.22 (d, *J* = 8.8 Hz, phenyl CH, 6H), 1.36 (s, C(CH<sub>3</sub>)<sub>3</sub>, 27H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 149.8, 146.7, 137.8, 135.4, 127.7, 126.4, 125.7, 124.4, 34.5, 31.4.



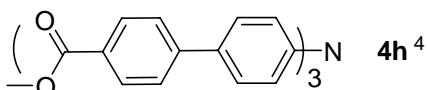
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.49 (d, *J* = 8.4 Hz, phenyl CH, 12H), 7.22 (d, *J* = 8.4 Hz, phenyl CH, 6H), 7.20 (d, *J* = 8.4 Hz, phenyl CH, 6H), 2.63 (t, *J* = 7.6 Hz, CH<sub>2</sub>, 6H), 1.67-1.63 (m, CH<sub>2</sub>, 6H), 1.36-1.33 (m, CH<sub>2</sub>CH<sub>2</sub>, 12H), 0.90 (t, *J* = 6.4 Hz, CH<sub>3</sub>, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 146.7, 141.7, 138.0, 135.6, 128.8, 127.7, 126.6, 124.4, 35.6, 31.6, 31.2, 22.6, 14.1.



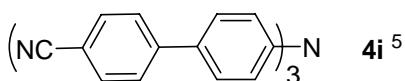
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.03 (d, *J* = 8.4 Hz, phenyl CH, 6H), 7.69 (d, *J* = 8.4 Hz, phenyl CH, 6H), 7.59 (d, *J* = 8.4 Hz, phenyl CH, 6H), 7.27 (d, *J* = 8.4 Hz, phenyl CH, 6H), 2.64 (s, CH<sub>3</sub>, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 197.7, 147.3, 145.0, 135.6, 134.6, 129.0, 128.2, 126.7, 124.6, 26.7.



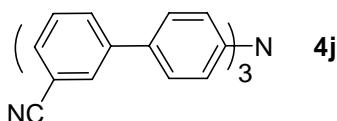
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 10.05 (s, C(O)H, 3H), 7.95 (d, *J* = 8.0 Hz, phenyl CH, 6H), 7.76 (d, *J* = 8.0 Hz, phenyl CH, 6H), 7.61 (d, *J* = 8.4 Hz, phenyl CH, 6H), 7.28 (d, *J* = 8.8 Hz, phenyl CH, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 191.8, 147.5, 146.3, 135.0, 134.5, 130.4, 1287.4, 127.1, 124.7.



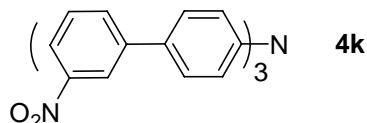
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.10 (d, *J* = 8.4 Hz, phenyl CH, 6H), 7.66 (d, *J* = 8.4 Hz, phenyl CH, 6H), 7.57 (d, *J* = 8.4 Hz, phenyl CH, 6H), 7.25 (d, *J* = 8.4 Hz, phenyl CH, 6H), 3.94 (s, CH<sub>3</sub>, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 167.0, 147.3, 144.8, 134.6, 130.2, 128.6, 128.2, 126.5, 124.6, 52.1.



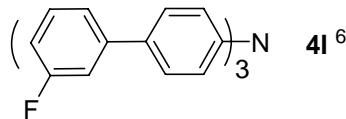
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.70 (q, *J* = 8.8 Hz, phenyl CH, 12H), 7.55 (d, *J* = 8.8 Hz, phenyl CH, 6H), 7.26 (d, *J* = 8.8 Hz, phenyl CH, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 147.5, 144.7, 134.0, 132.7, 128.3, 127.2, 124.7, 119.0, 110.6.



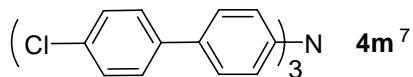
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.87 (s, phenyl CH, 3H), 7.81 (d, *J* = 8.0 Hz, phenyl CH, 3H), 7.61 (d, *J* = 7.6 Hz, phenyl CH, 3H), 7.55 (t, *J* = 7.6 Hz, phenyl CH, 3H), 7.51 (d, *J* = 8.8 Hz, phenyl CH, 6H), 7.26 (d, *J* = 8.8 Hz, phenyl CH, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 147.4, 141.7, 133.7, 131.0, 130.4, 130.3, 1297, 128.1, 124.7, 118.9, 113.1.



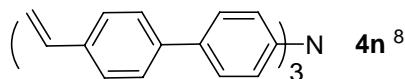
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.46 (s, phenyl CH, 3H), 8.19 (d, *J* = 8.0 Hz, phenyl CH, 3H), 7.92 (d, *J* = 8.0 Hz, phenyl CH, 3H), 7.63-7.58 (m, phenyl CH, 9H), 7.29 (d, *J* = 8.8 Hz, phenyl CH, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 148.8, 147.5, 142.1, 133.6, 132.5, 129.8, 128.3, 124.8, 121.8, 121.5.



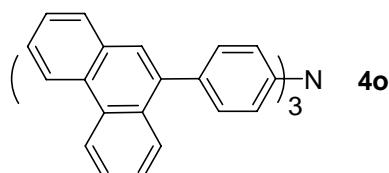
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.51 (d, *J* = 8.8 Hz, phenyl CH, 6H), 7.42-7.35 (m, phenyl CH, 6H), 7.30-7.22 (m, phenyl CH, 9H), 7.04-6.99 (m, phenyl CH, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 163.3(d, *J* = 245.5 Hz), 147.1, 142.8(d, *J* = 6.8 Hz), 134.6, 130.2(d, *J* = 7.9 Hz), 128.0, 124.5, 122.3(d, *J* = 3.4 Hz), 113.7(d, *J* = 20.2 Hz), 113.5(d, *J* = 22.1 Hz).



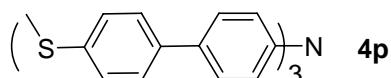
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.51 (d, *J* = 8.4 Hz, phenyl CH, 6H), 7.48 (d, *J* = 8.4 Hz, phenyl CH, 6H), 7.39 (d, *J* = 8.4 Hz, phenyl CH, 6H), 7.22 (d, *J* = 8.4 Hz, phenyl CH, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 146.7, 139.0, 134.6, 133.0, 128.9, 127.9, 127.8, 124.5.



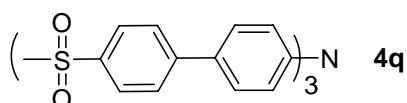
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.57 (d, *J* = 8.4 Hz, phenyl CH, 6H), 7.54 (d, *J* = 8.4 Hz, phenyl CH, 6H), 7.48 (d, *J* = 8.4 Hz, phenyl CH, 6H), 7.24 (d, *J* = 8.4 Hz, phenyl CH, 6H), 6.78-6.71 (m, CH, 3H) 5.80 (d, *J* = 17.6 Hz, CH<sub>2</sub>, 3H), 5.27 (d, *J* = 10.8 Hz, CH<sub>2</sub>, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 146.8, 139.9, 136.5, 136.3, 135.2, 127.7, 126.7, 126.7, 124.5, 113.7.



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.81 (d, *J* = 8.0 Hz, phenanthrenyl CH, 3H), 8.75 (d, *J* = 8.0 Hz, phenanthrenyl CH, 3H), 8.13 (d, *J* = 8.0 Hz, phenanthrenyl CH, 3H), 7.93 (d, *J* = 8.0 Hz, phenanthrenyl CH, 3H), 7.79 (d, *J* = 8.0 Hz, phenanthrenyl CH, 3H), 7.71-7.60 (m, phenanthrenyl CH, 12H), 7.57 (d, *J* = 8.4 Hz, phenyl CH, 6H), 7.48 (d, *J* = 8.4 Hz, phenyl CH, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 147.0, 138.4, 135.4, 131.7, 131.2, 131.1, 130.8, 129.9, 128.6, 127.5, 127.0, 126.9, 126.5, 126.5, 124.1, 123.0, 122.6.



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.50 (t, *J* = 8.4 Hz, phenyl CH, 12H), 7.31 (d, *J* = 8.4 Hz, phenyl CH, 6H), 7.21 (d, *J* = 8.4 Hz, phenyl CH, 6H), 2.52 (s, CH<sub>3</sub>, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 146.7, 137.4, 137.1, 135.0, 127.6, 127.1, 127.0, 124.5, 16.0.

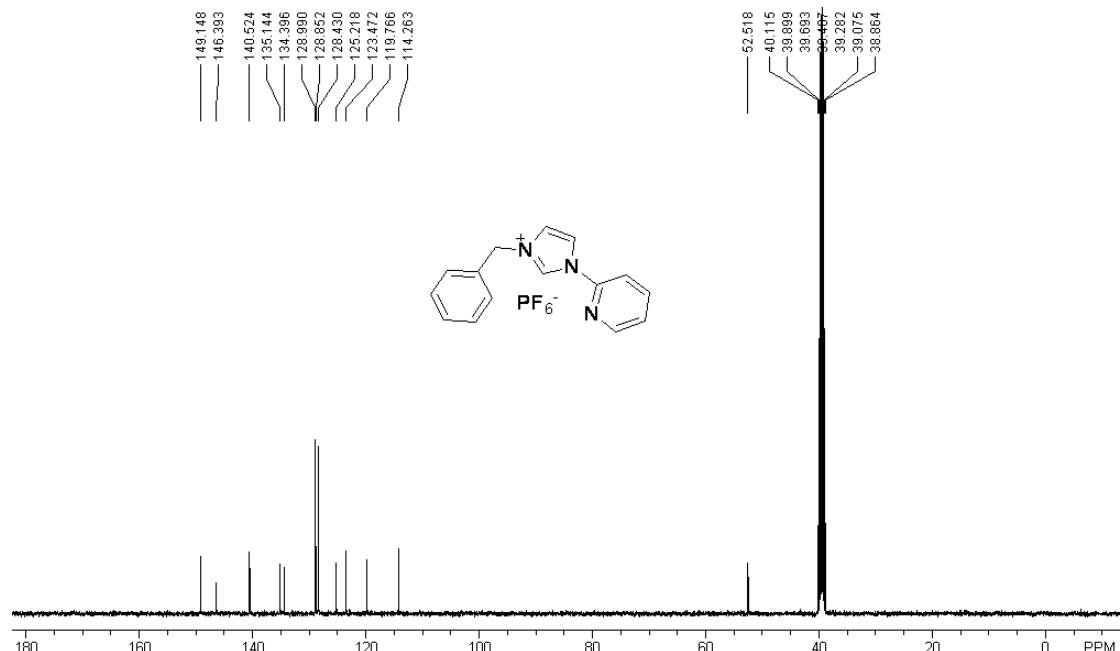
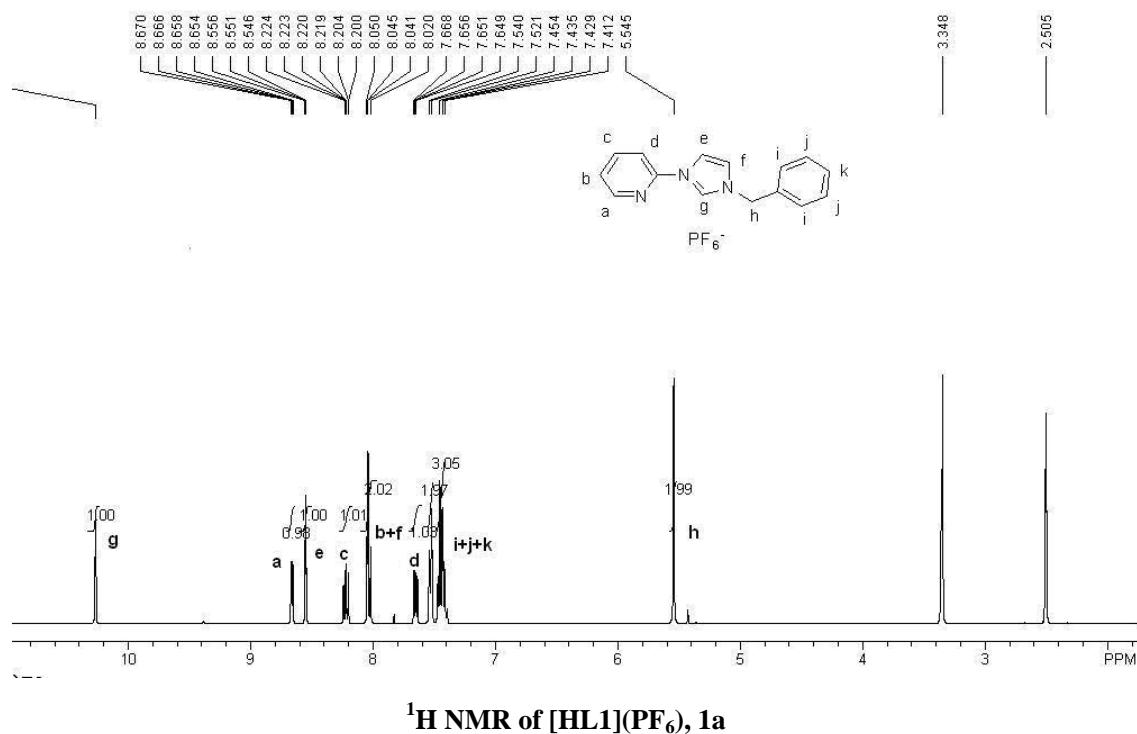


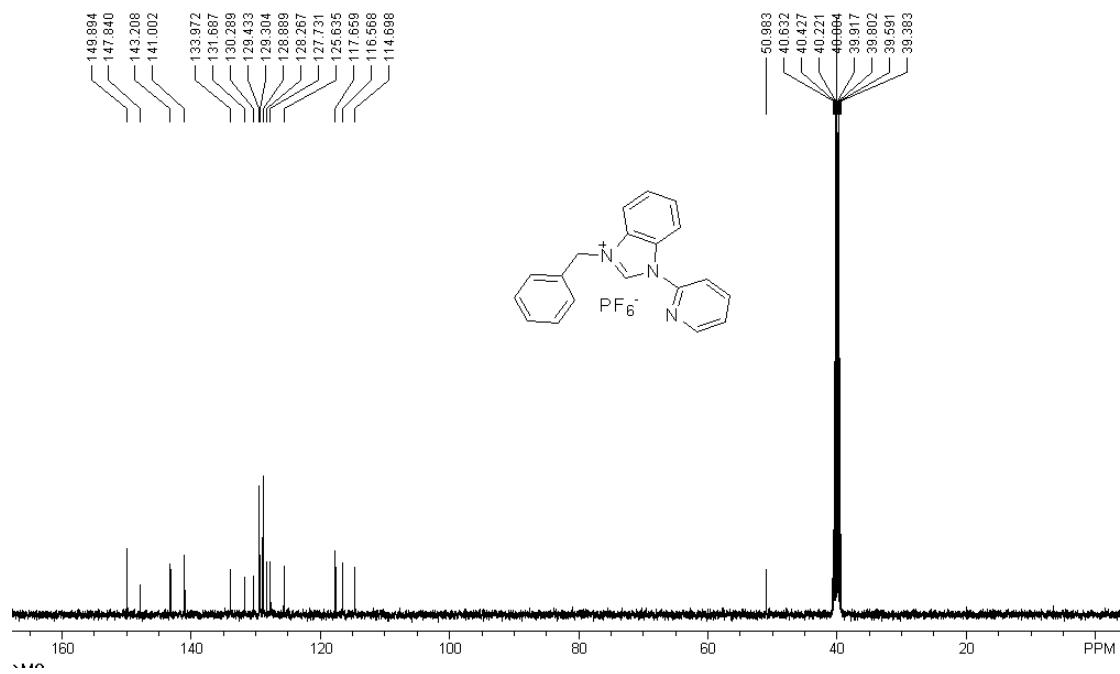
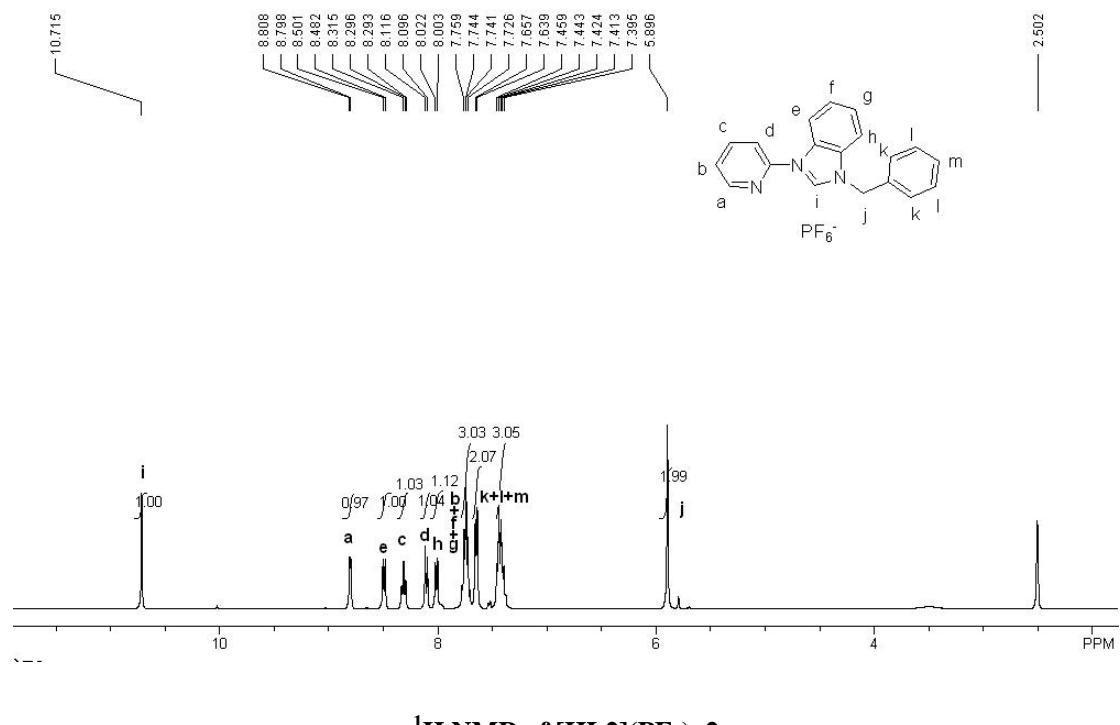
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.01 (d, *J* = 8.4 Hz, phenyl CH, 6H), 7.77 (d, *J* = 8.8 Hz, phenyl CH, 6H), 7.58 (d, *J* = 8.8 Hz, phenyl CH, 6H), 7.29 (d, *J* = 8.4 Hz, phenyl CH, 6H), 3.10 (s, CH<sub>3</sub>, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 147.6, 145.8, 138.8, 134.0, 128.5, 128.0, 127.4, 124.7, 44.6.

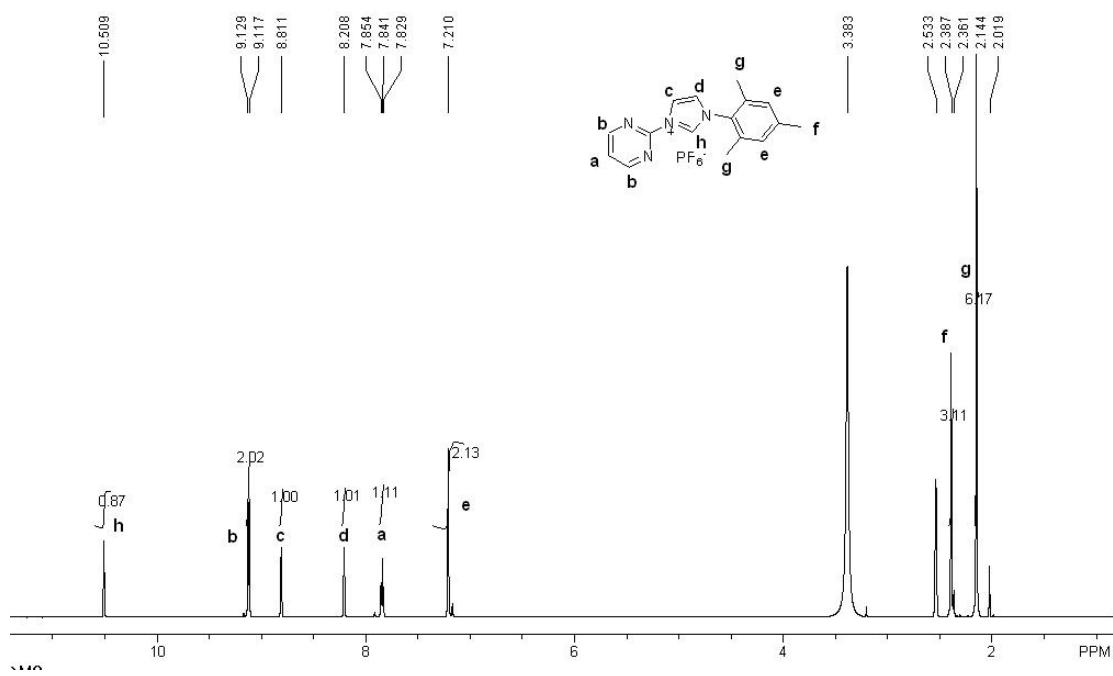


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.53 (d, *J* = 8.4 Hz, phenyl CH, 6H), 7.26-7.25 (m, thiophenyl CH, 6H), 7.15 (d, *J* = 8.0 Hz, phenyl CH, 6H), 7.09-7.07 (m, thiophenyl CH, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 146.5, 144.1, 129.3, 128.1, 126.9, 124.4, 124.3, 122.5.

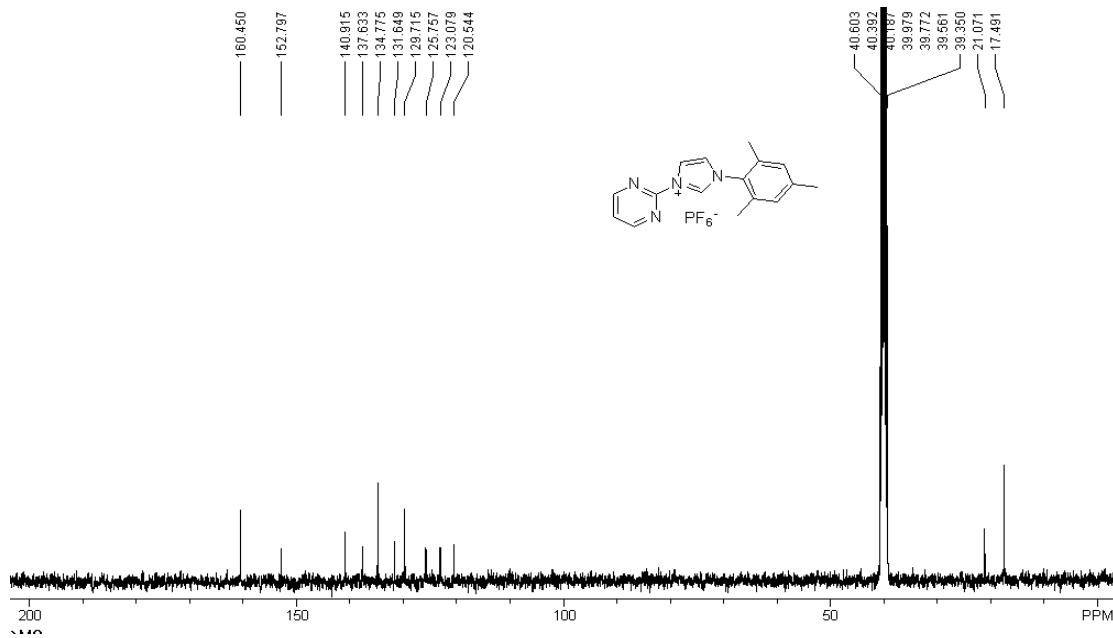
**<sup>1</sup>H and <sup>13</sup>C NMR Spectrum of 1a-4q**



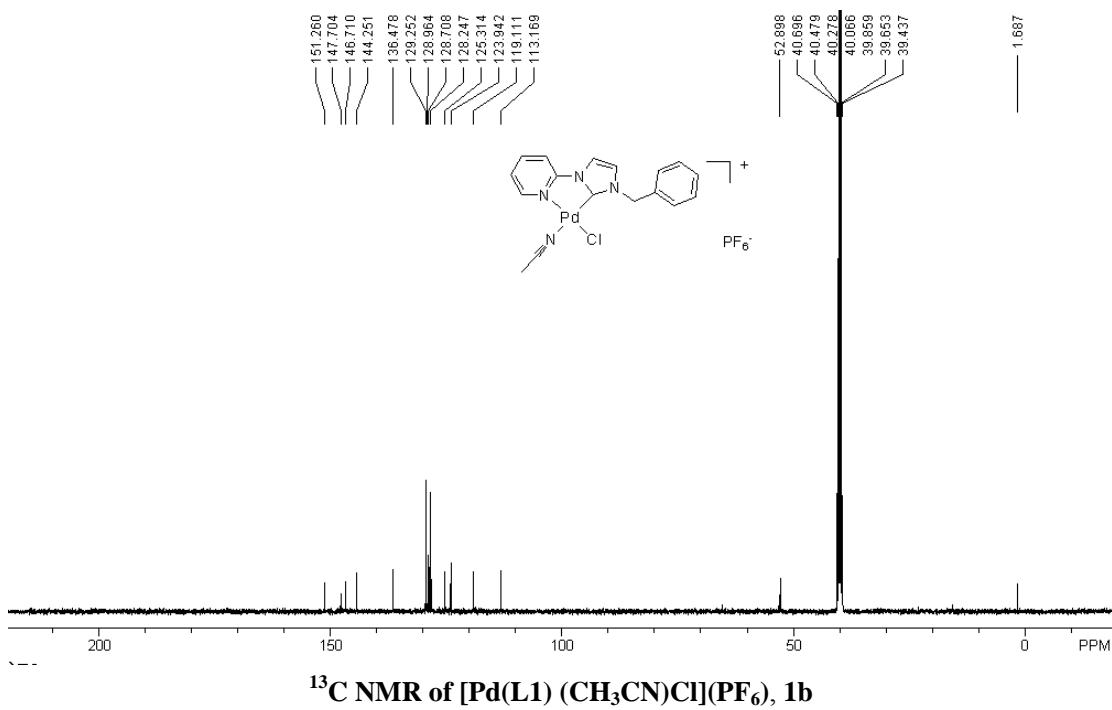
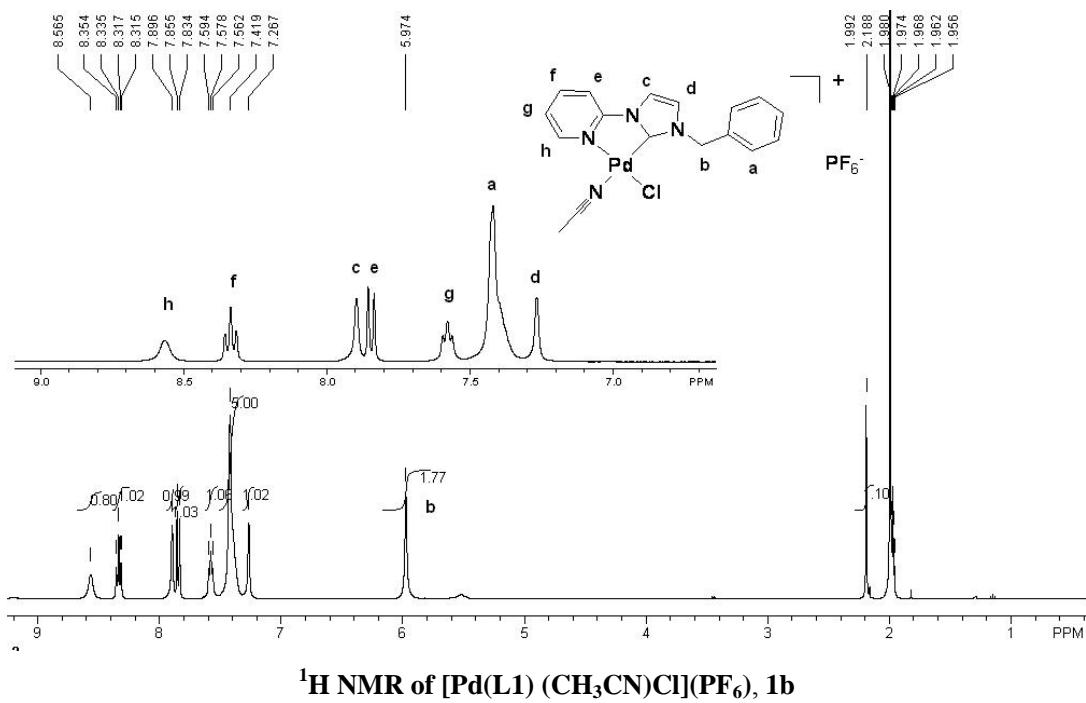


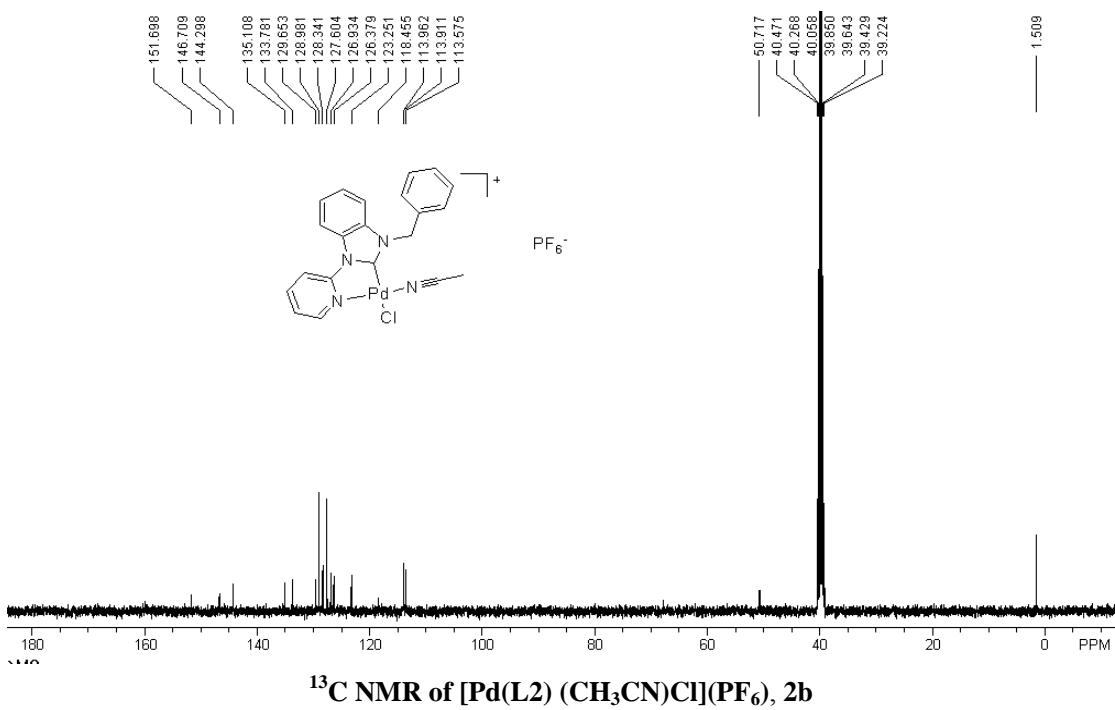
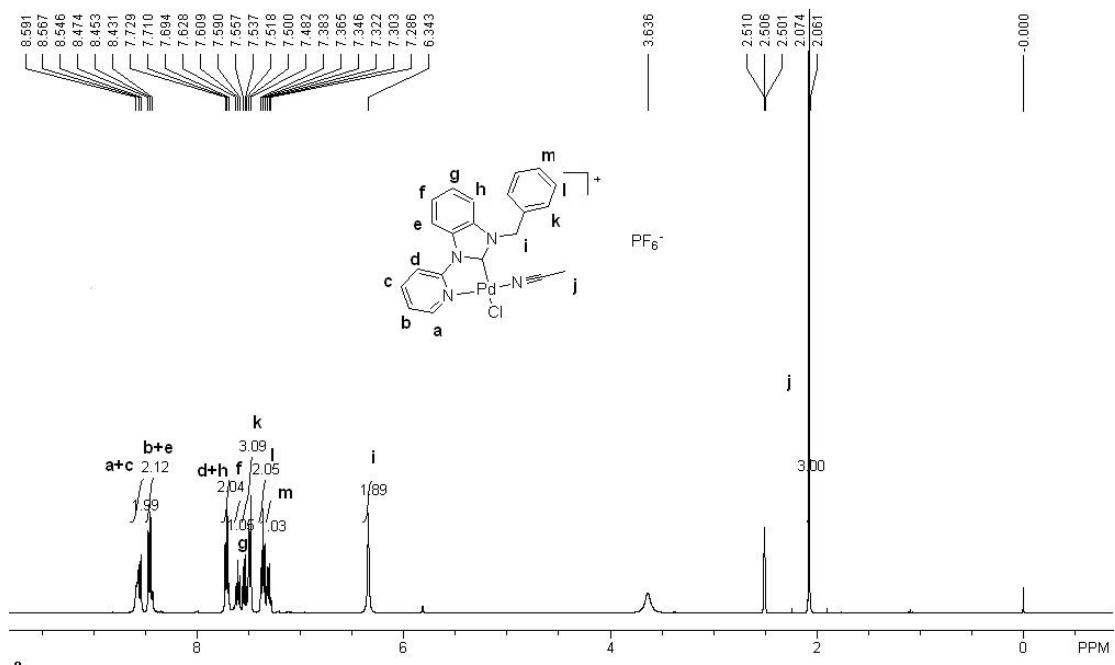


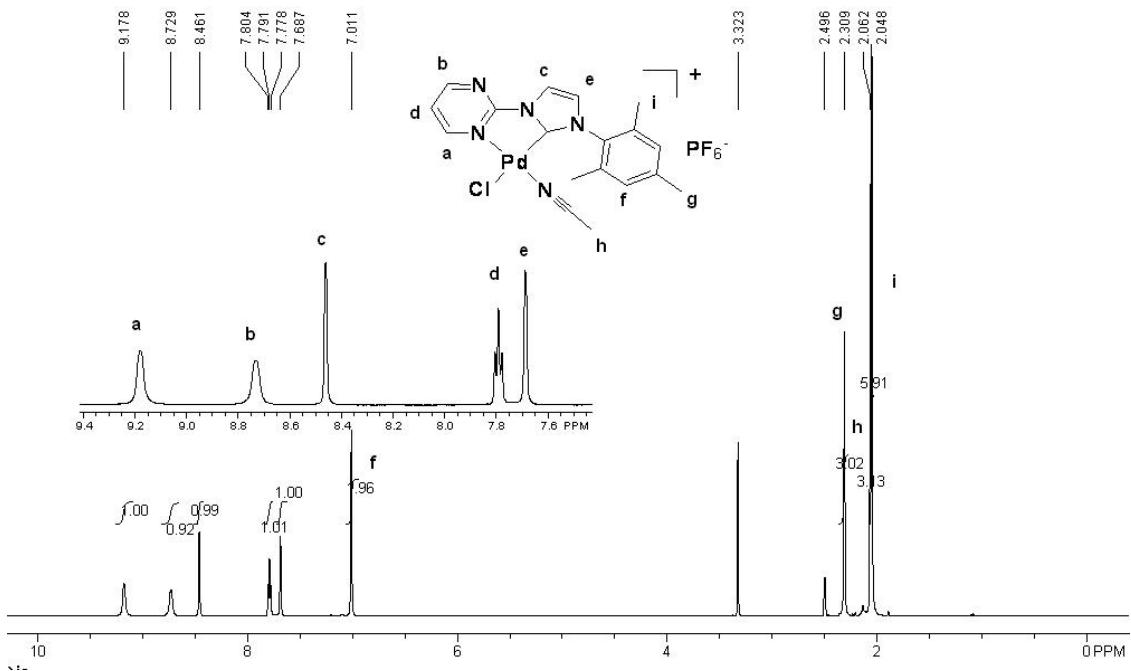
<sup>1</sup>H NMR of [HL3](PF<sub>6</sub>), 3a



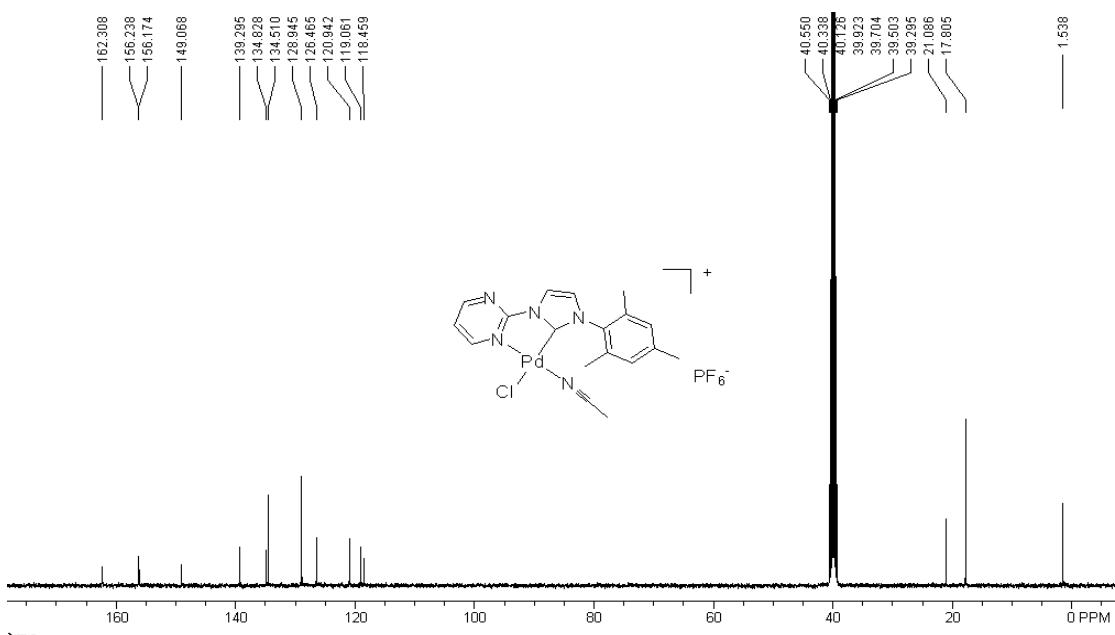
<sup>13</sup>C NMR of [HL3](PF<sub>6</sub>), 3a

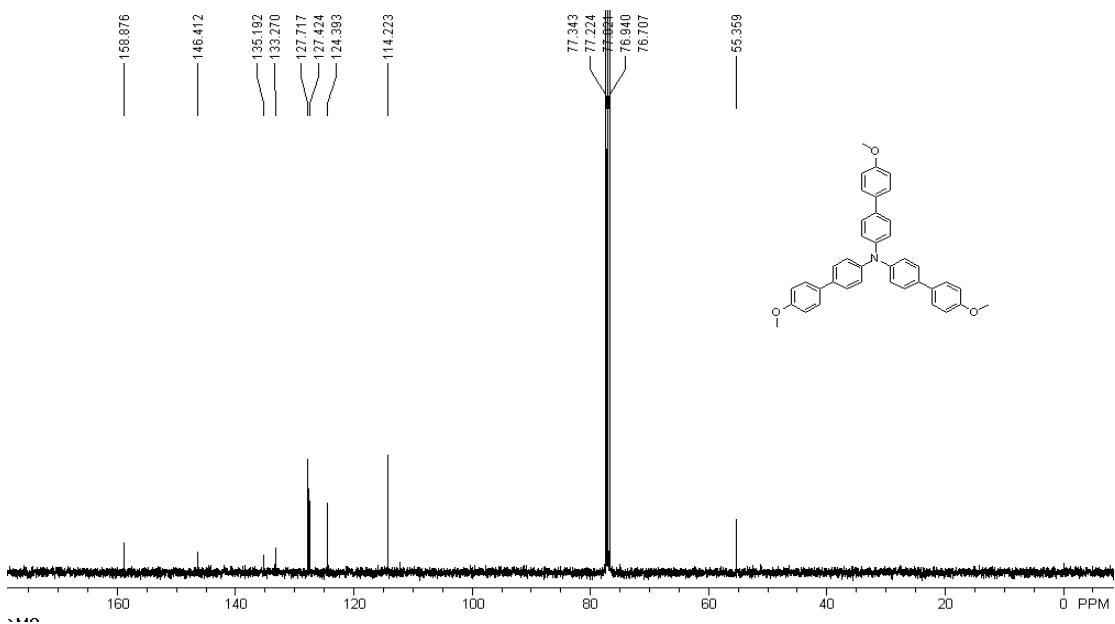
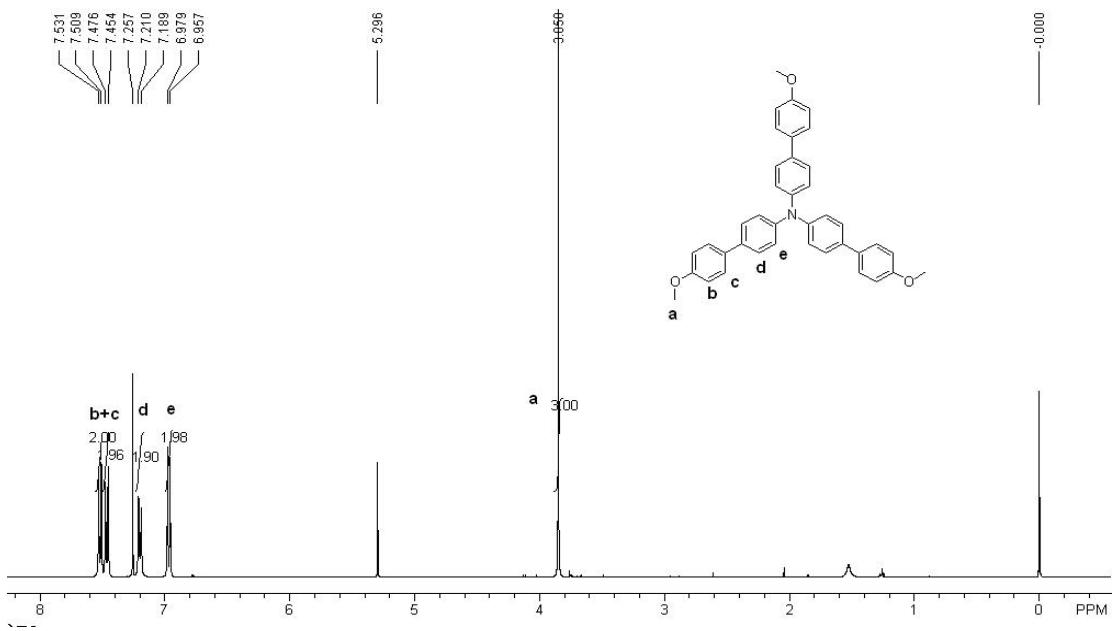


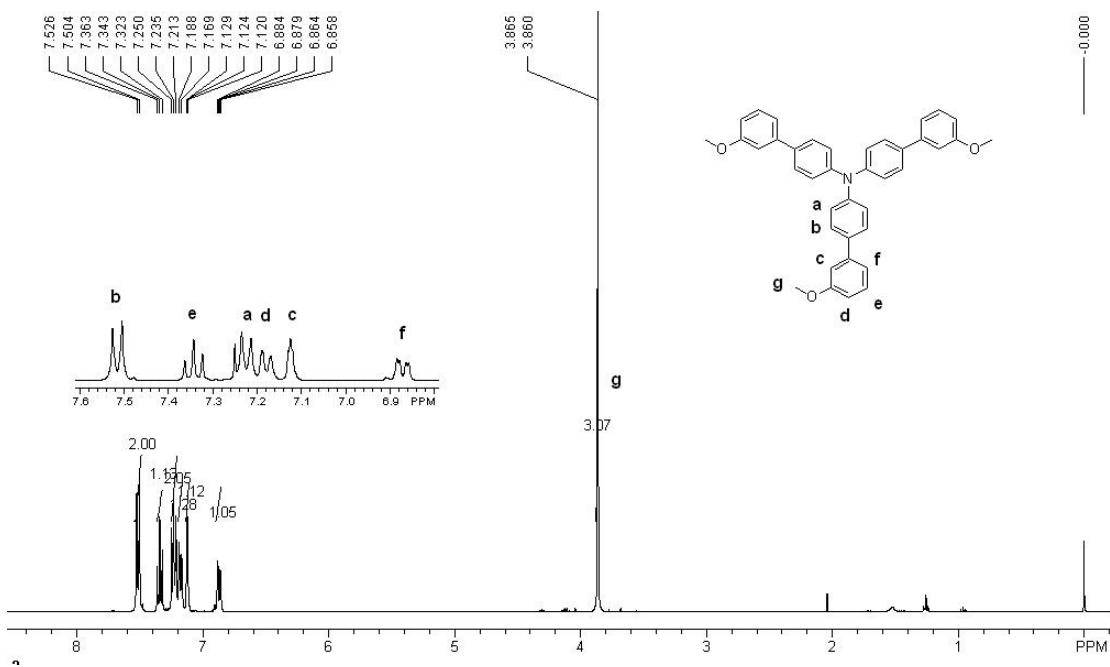




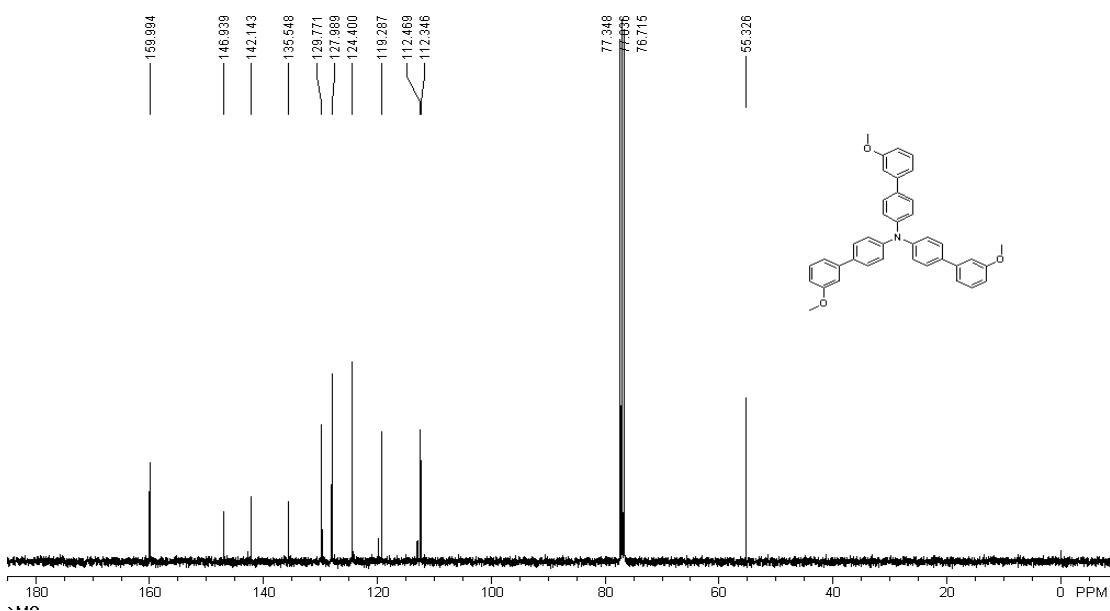
<sup>1</sup>H NMR of  $[\text{Pd}(\text{L3}) (\text{CH}_3\text{CN})\text{Cl}](\text{PF}_6)$ , 3b



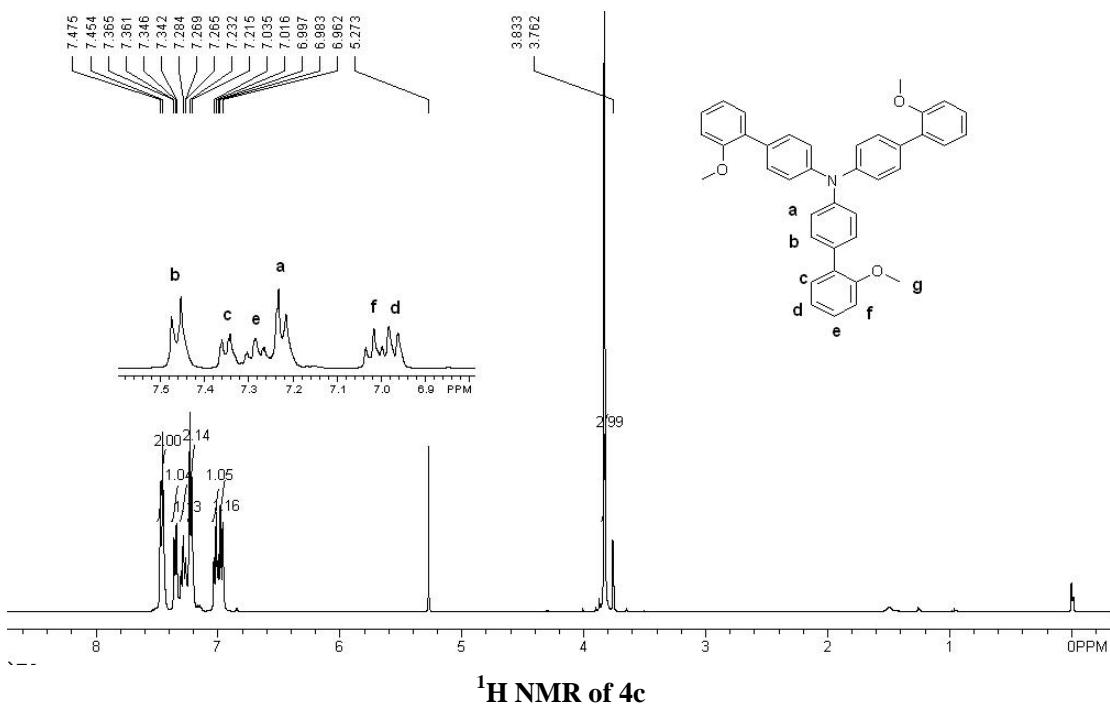




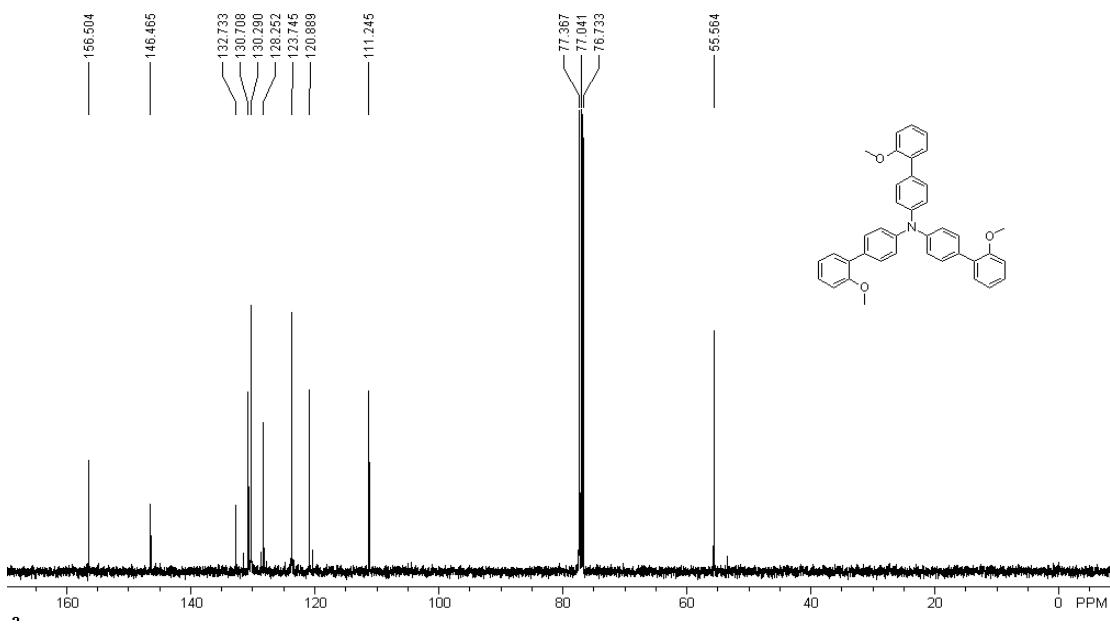
**<sup>1</sup>H NMR of 4b**



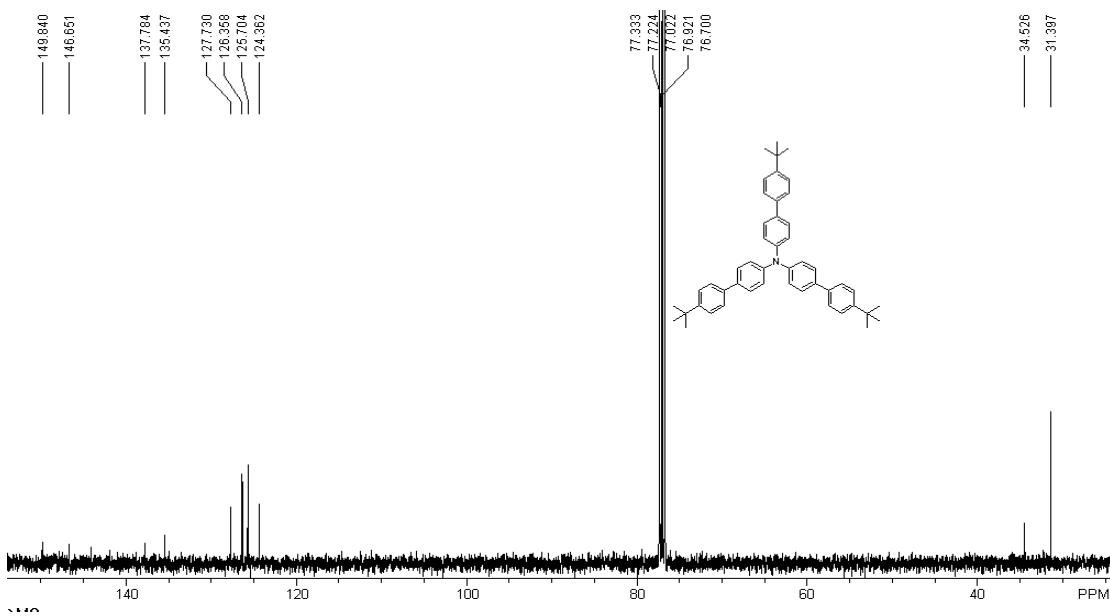
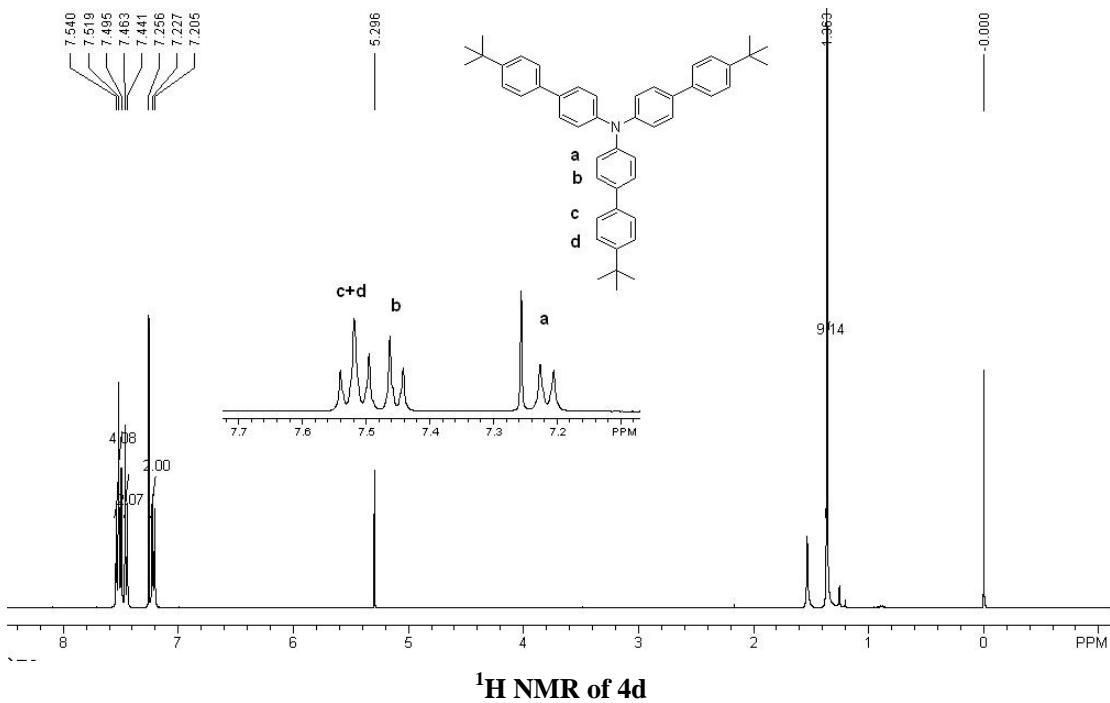
**<sup>13</sup>C NMR of 4b**



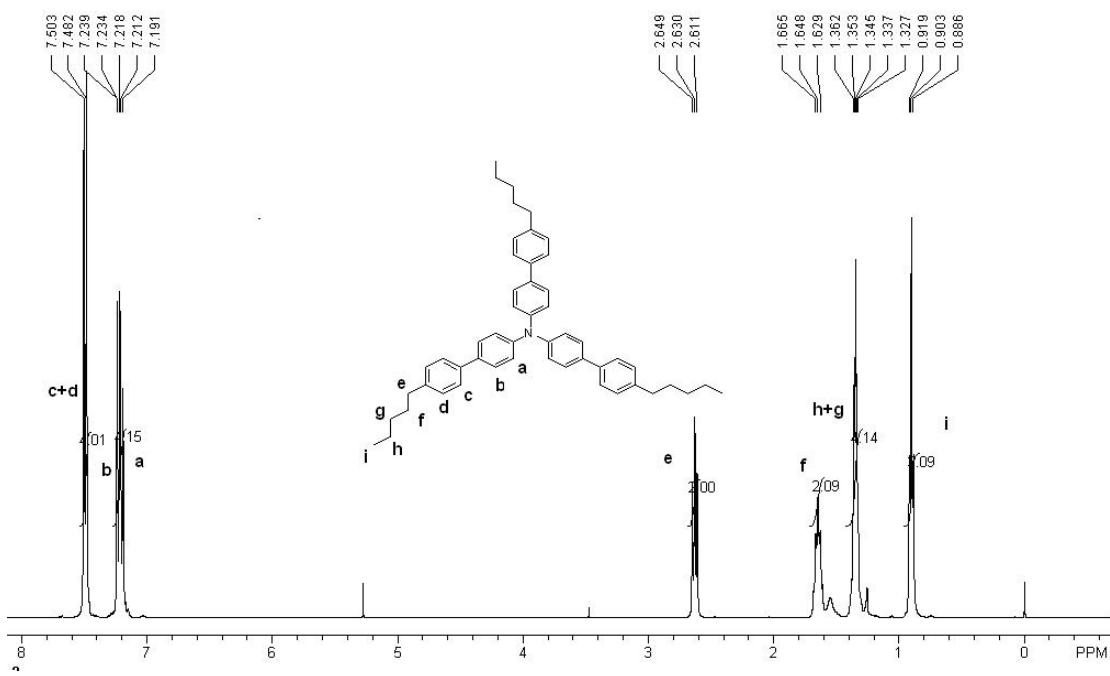
<sup>1</sup>H NMR of 4c



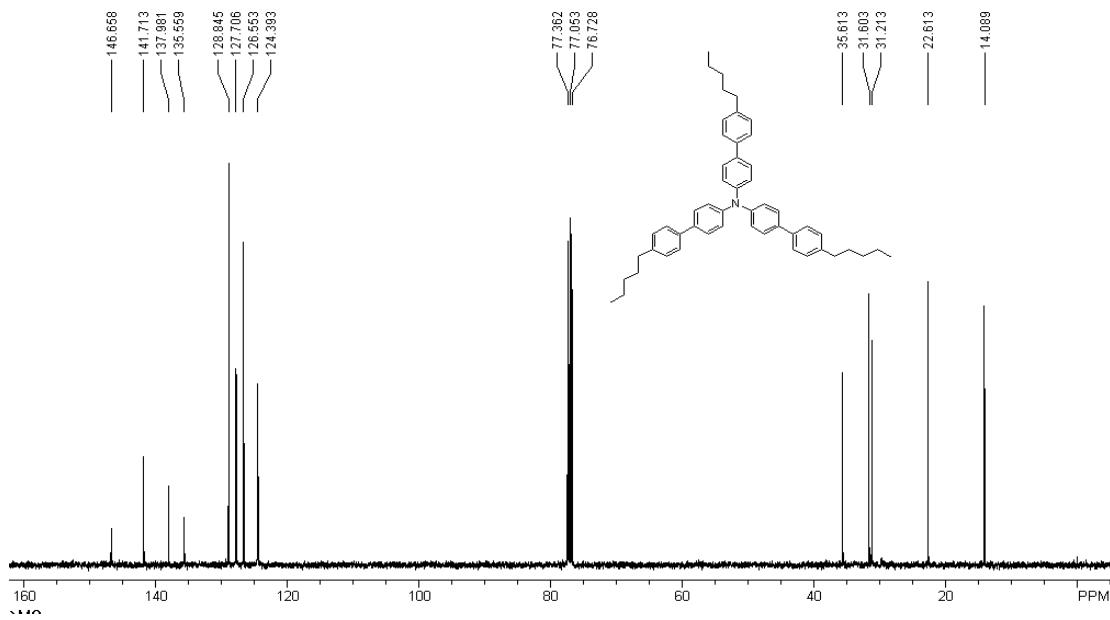
<sup>13</sup>C NMR of 4c



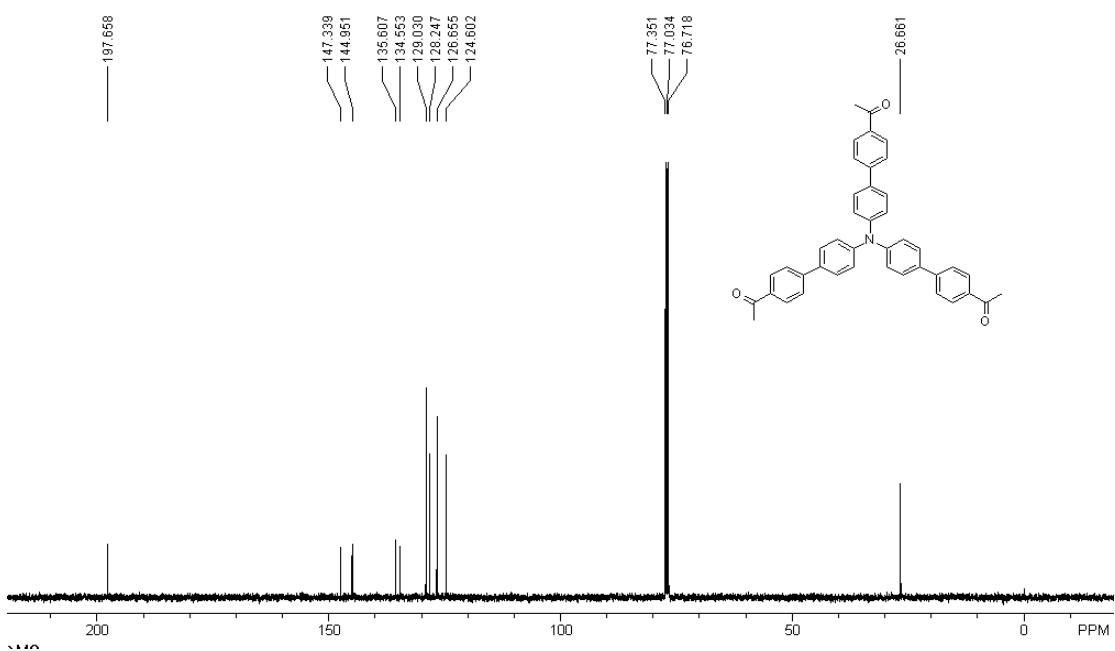
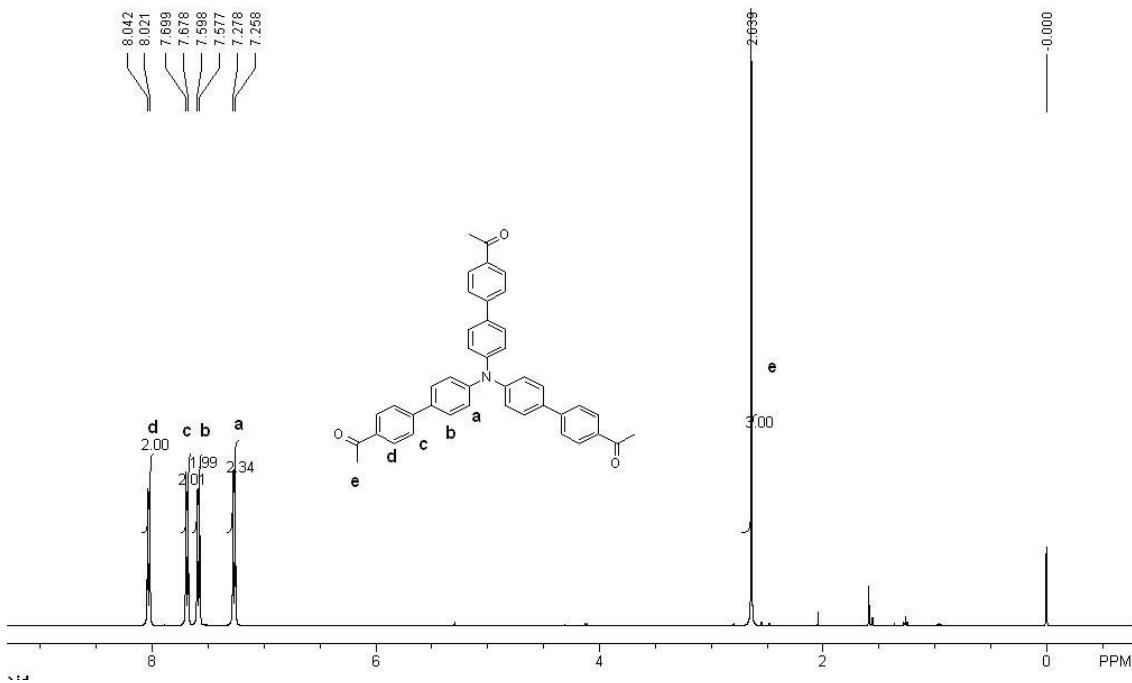
### <sup>13</sup>C NMR of 4d

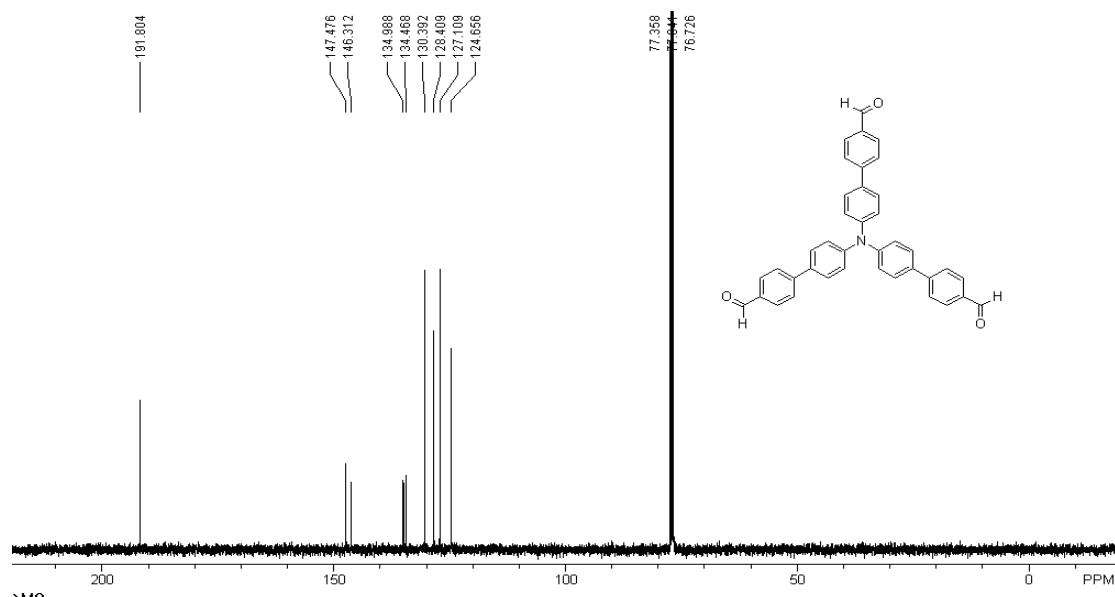
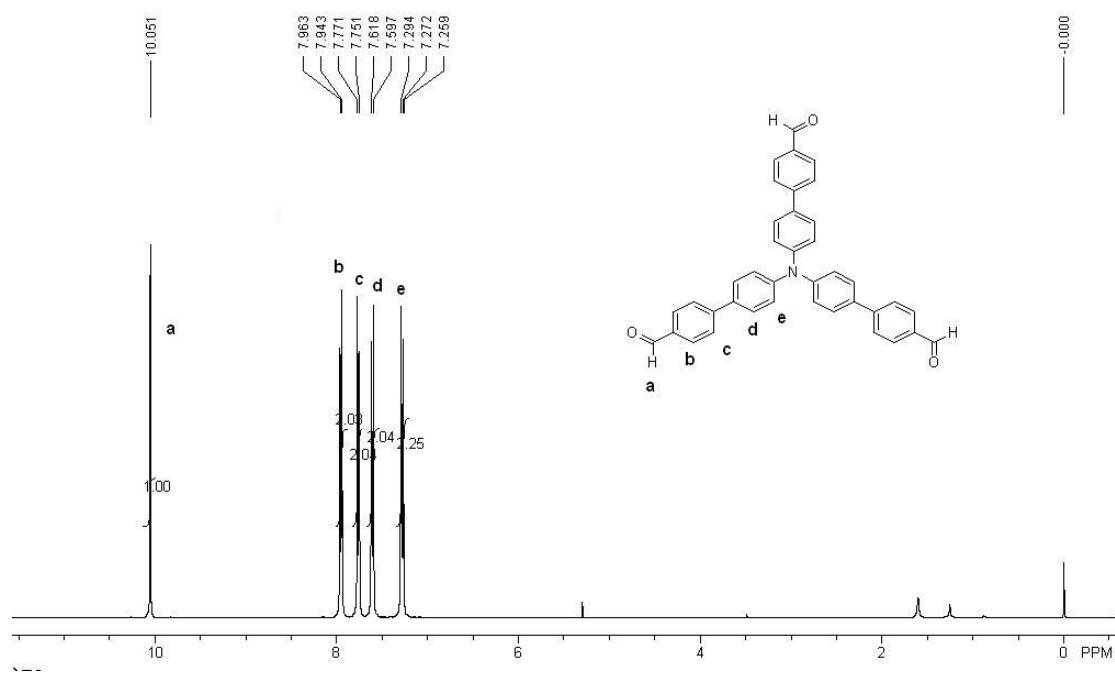


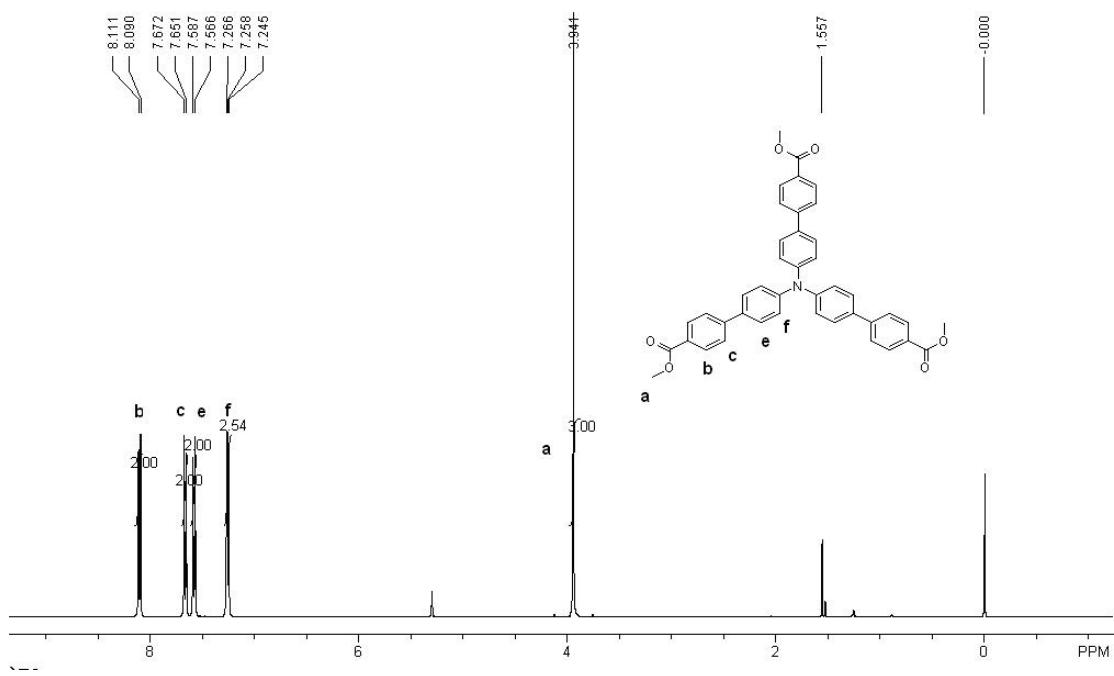
**<sup>1</sup>H NMR of 4e**



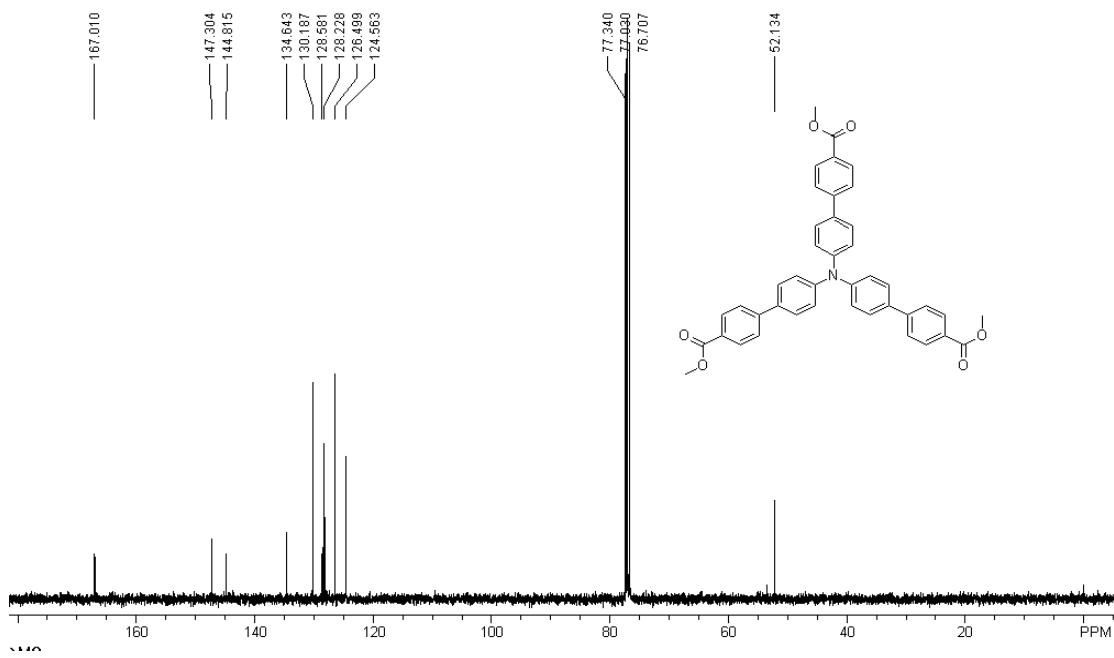
**<sup>13</sup>C NMR of 4e**



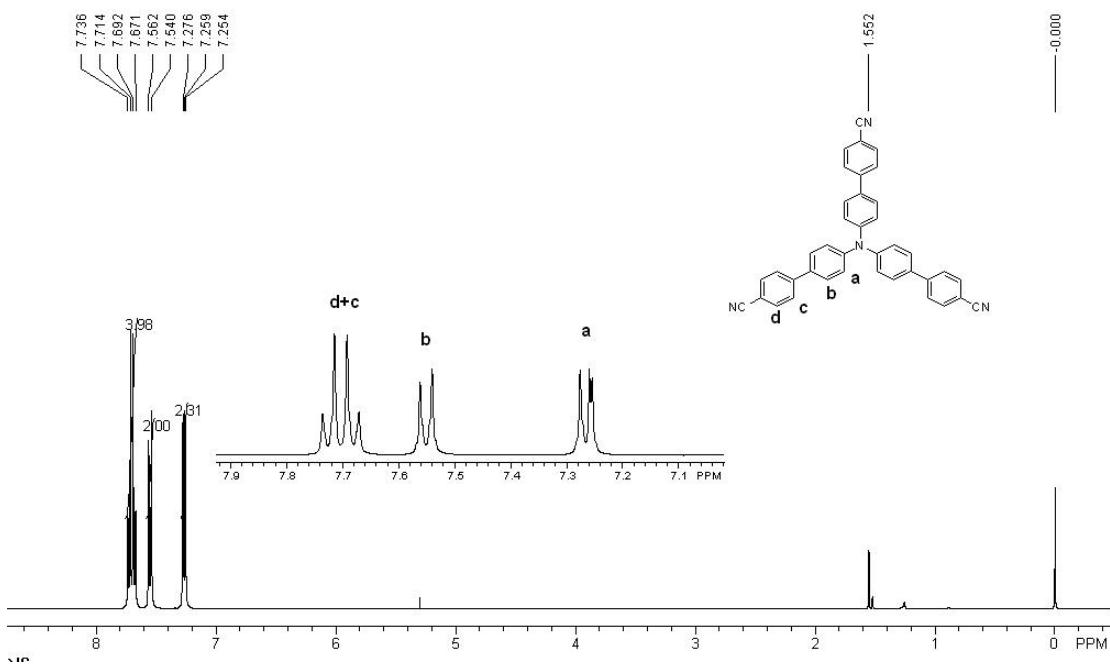




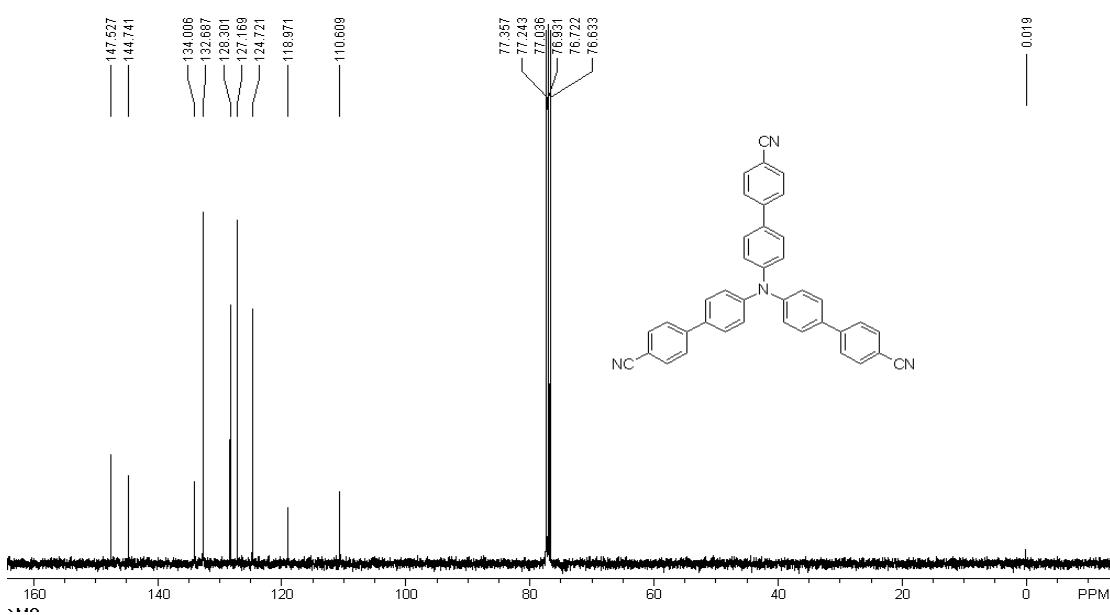
<sup>1</sup>H NMR of 4h



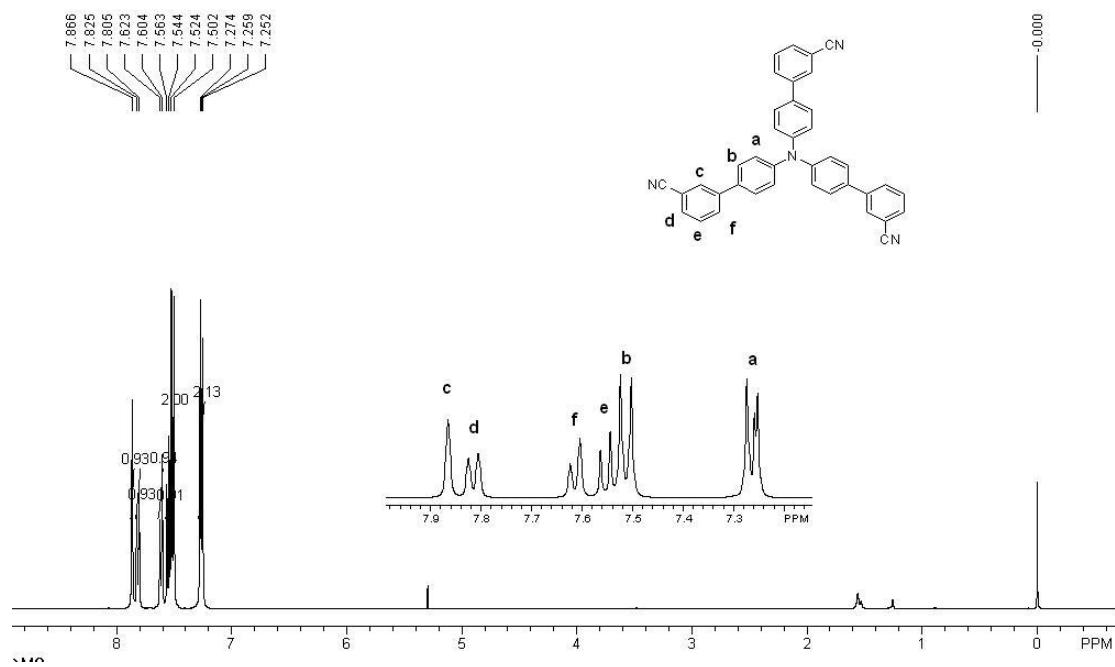
<sup>13</sup>C NMR of 4h



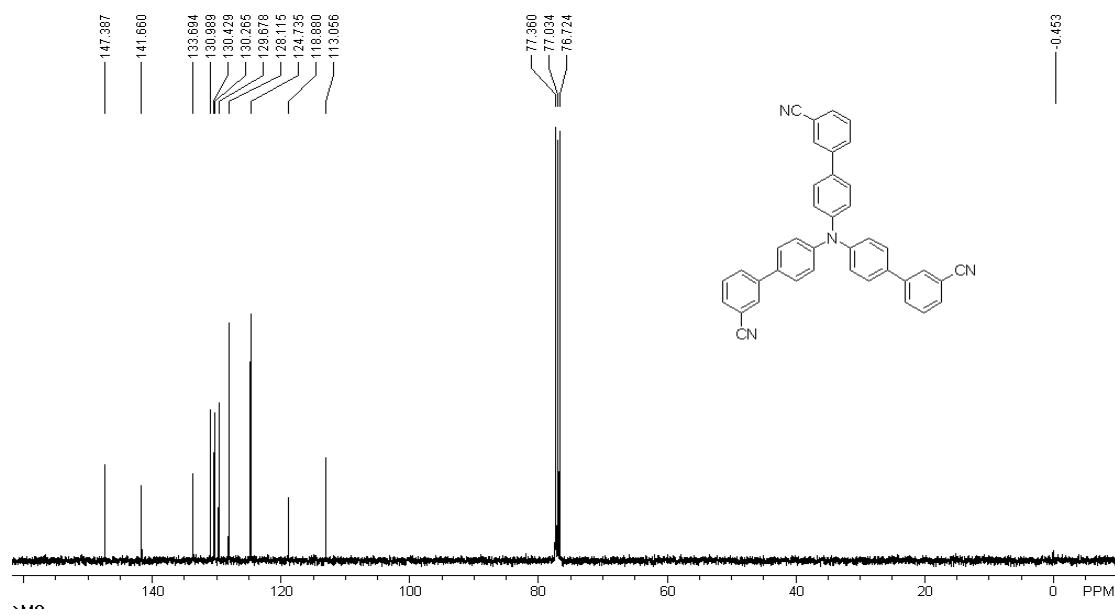
<sup>1</sup>H NMR of 4i



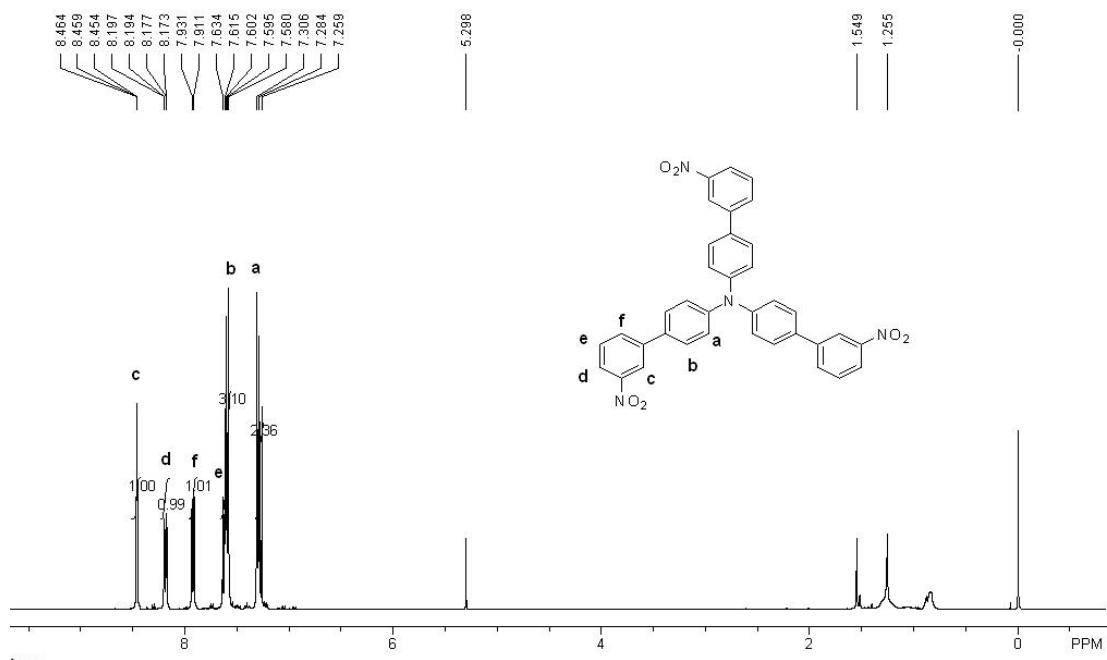
<sup>13</sup>C NMR of 4i



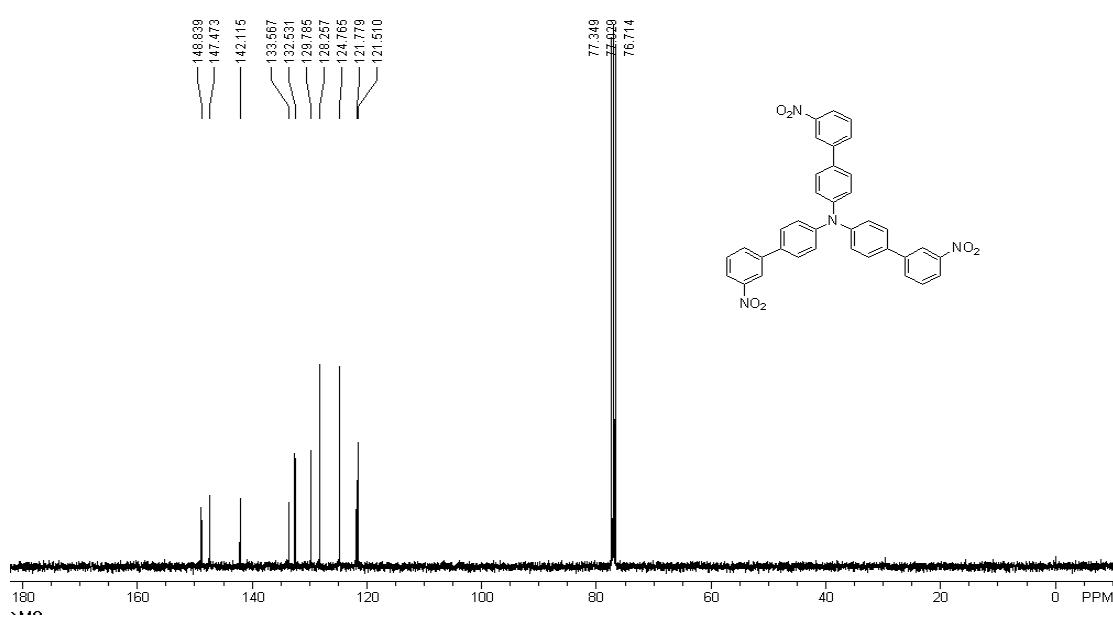
**<sup>1</sup>H NMR of 4j**



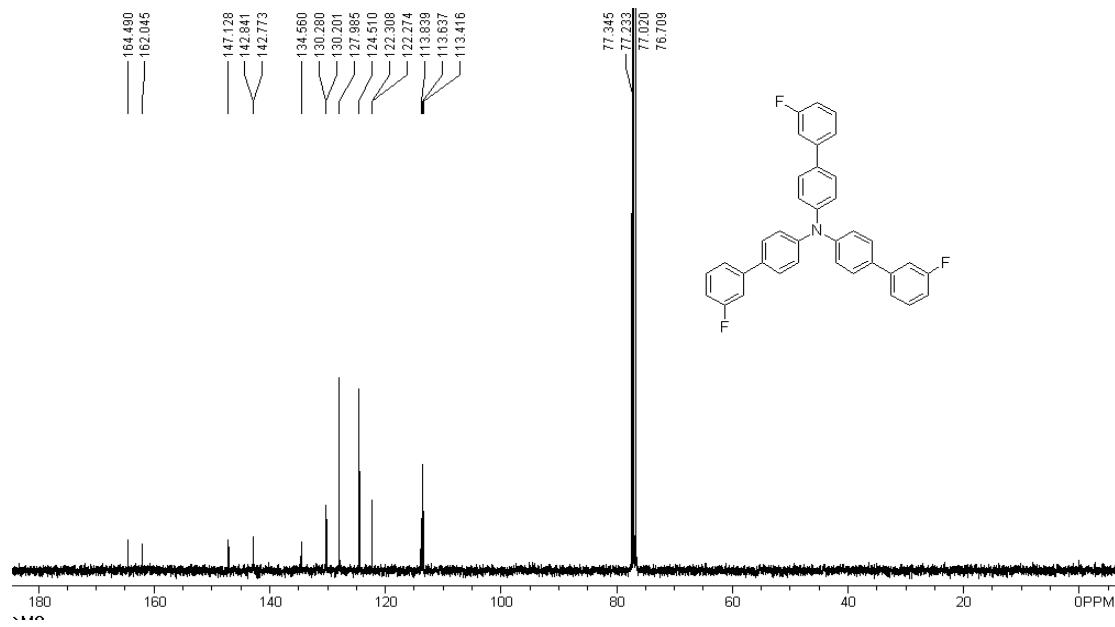
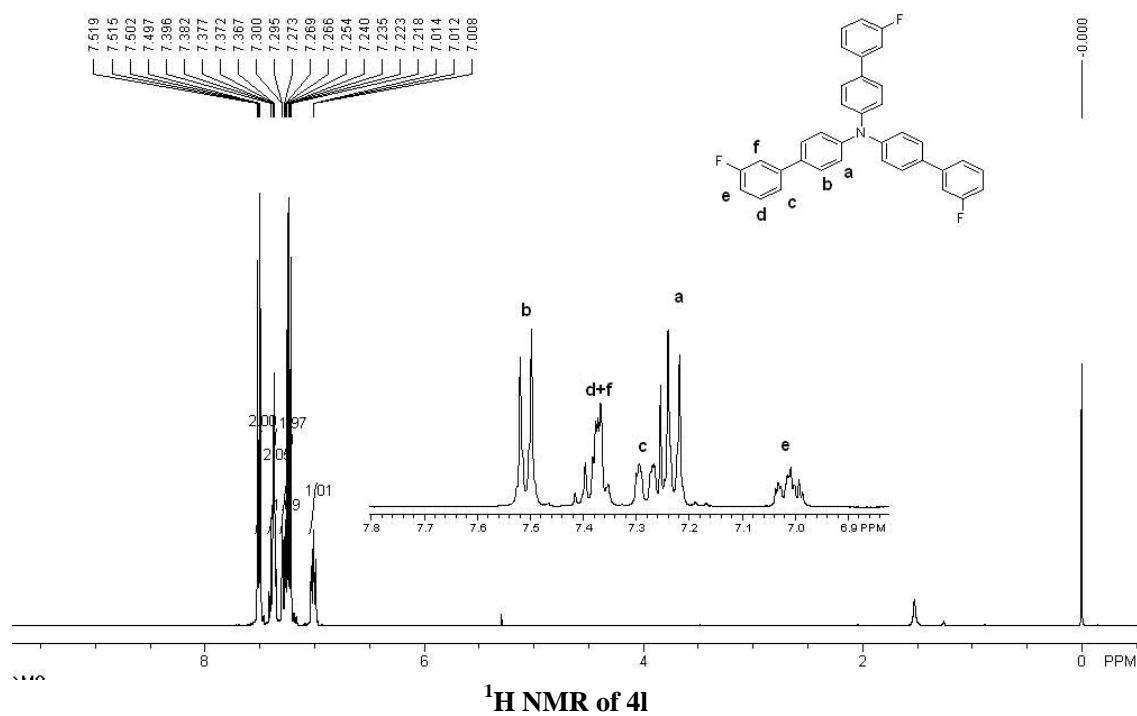
**<sup>13</sup>C NMR of 4j**



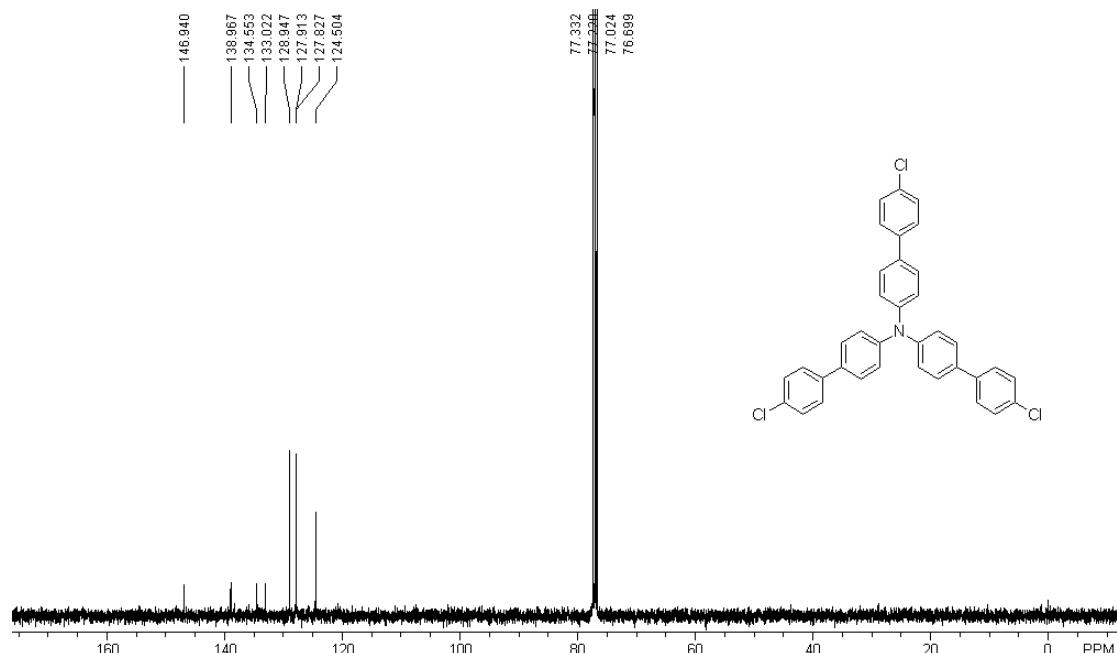
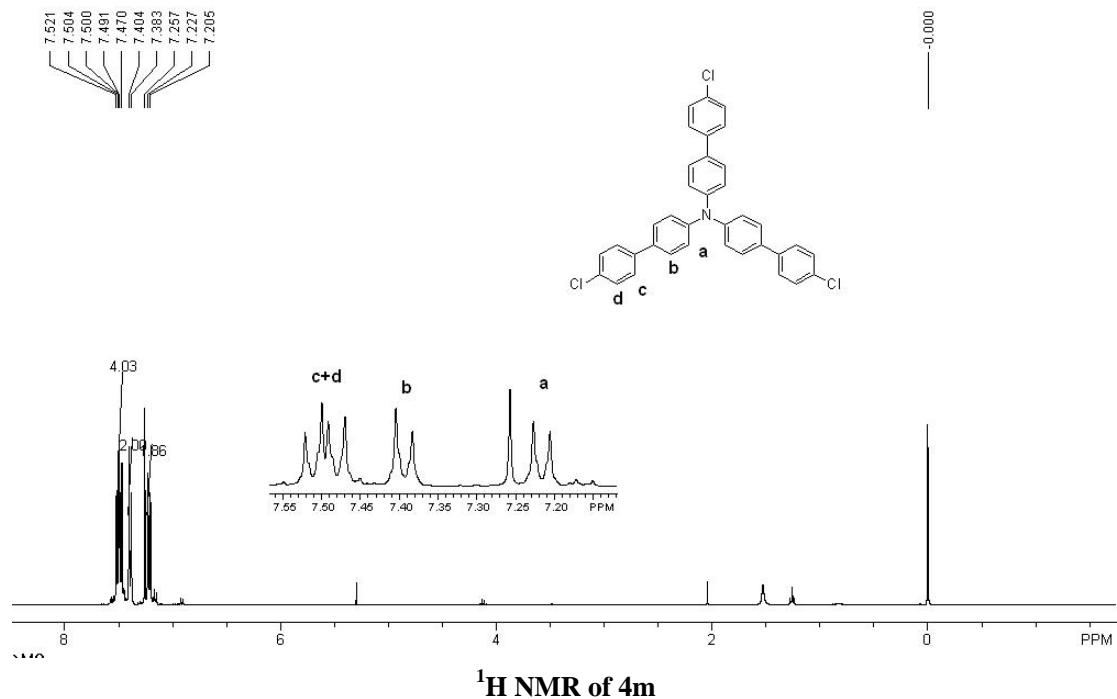
### <sup>1</sup>H NMR of 4k



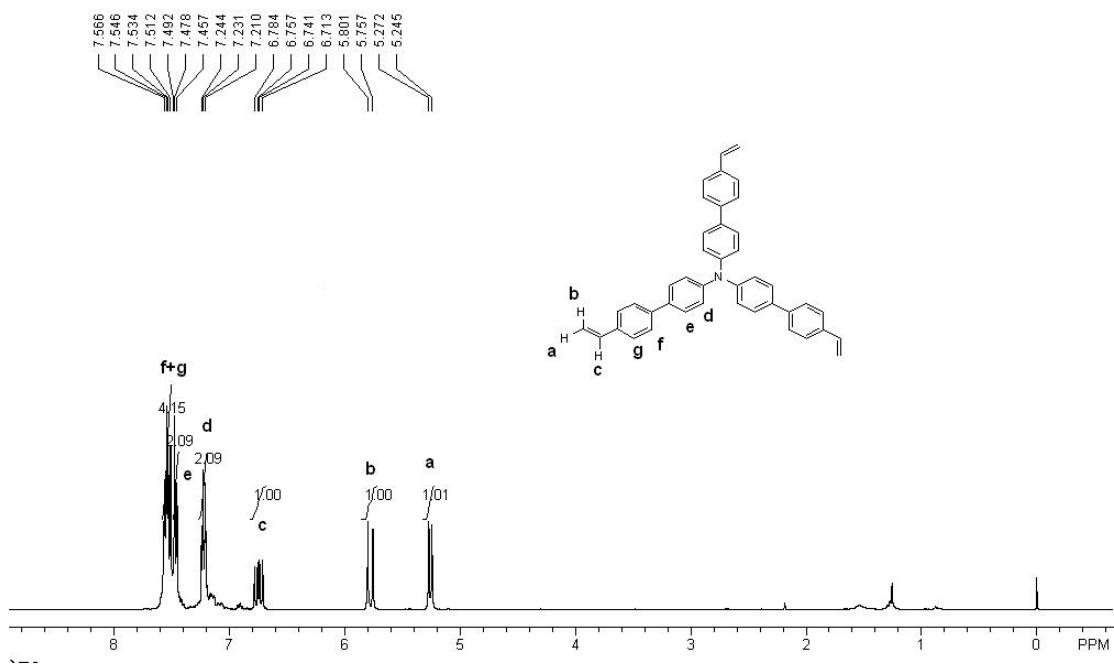
<sup>13</sup>C NMR of 4k



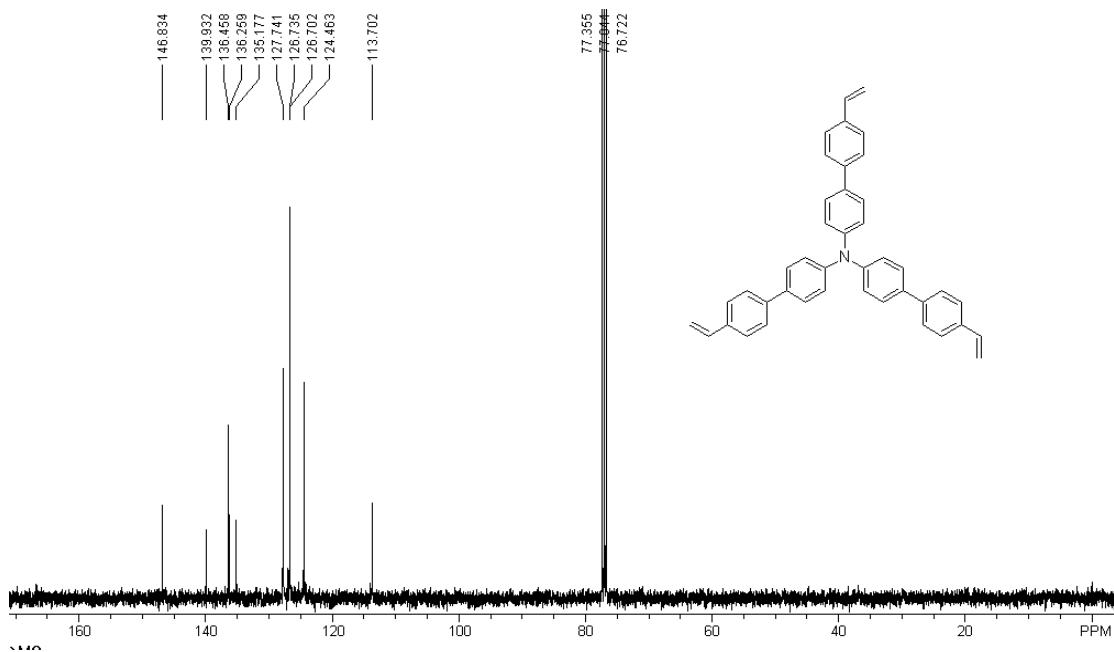
**<sup>13</sup>C NMR of 4l**



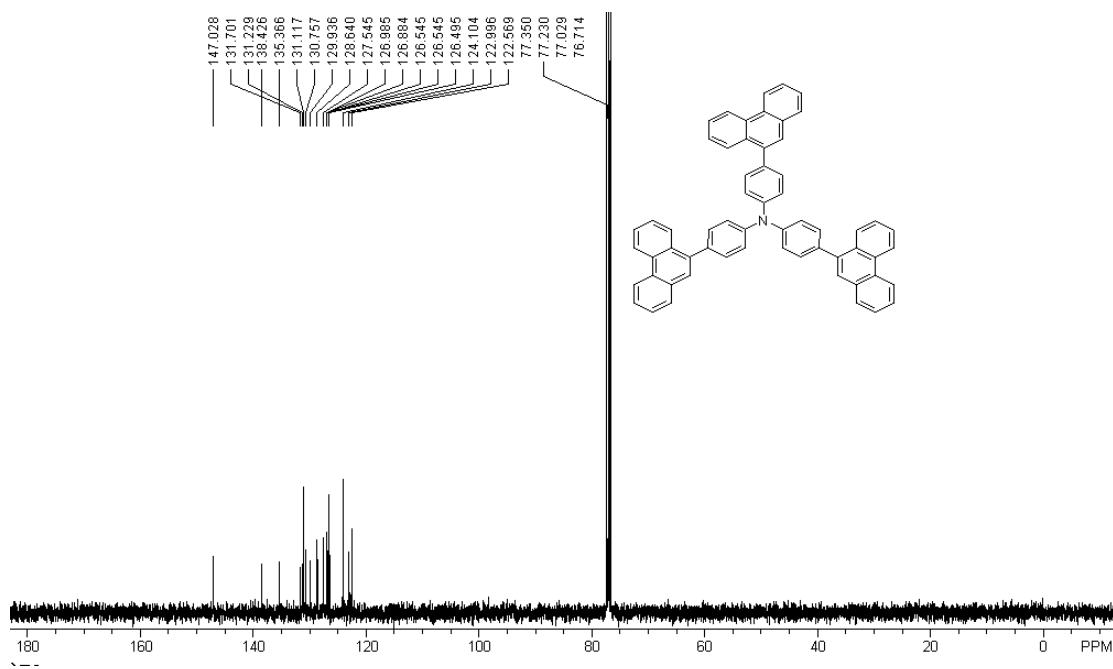
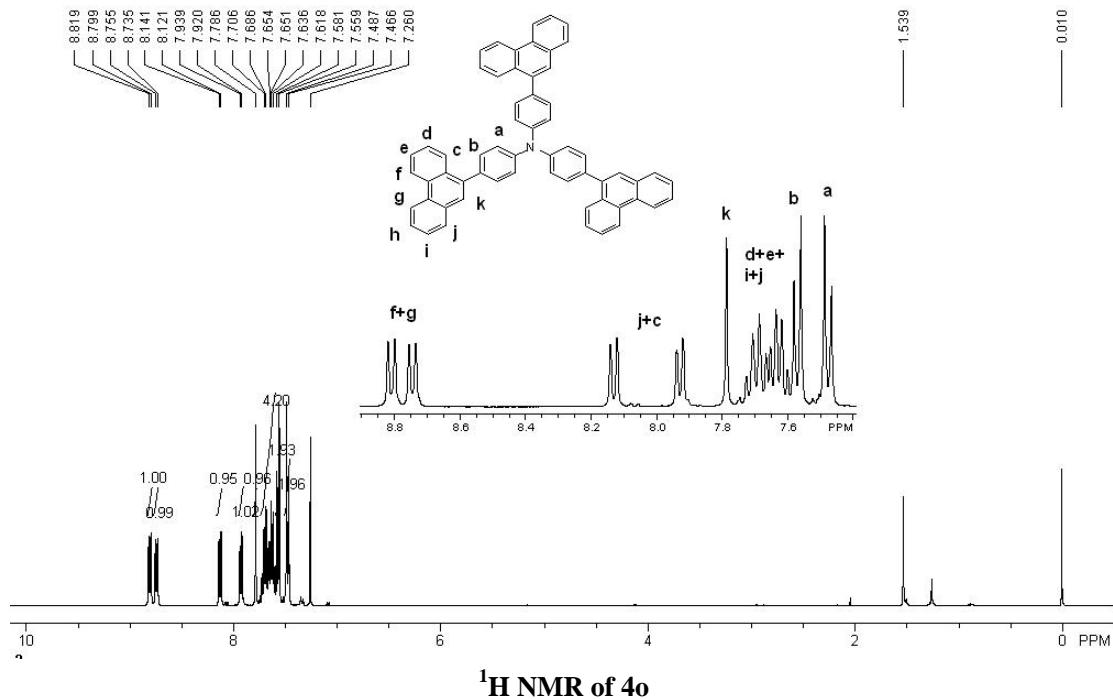
<sup>13</sup>C NMR of 4m



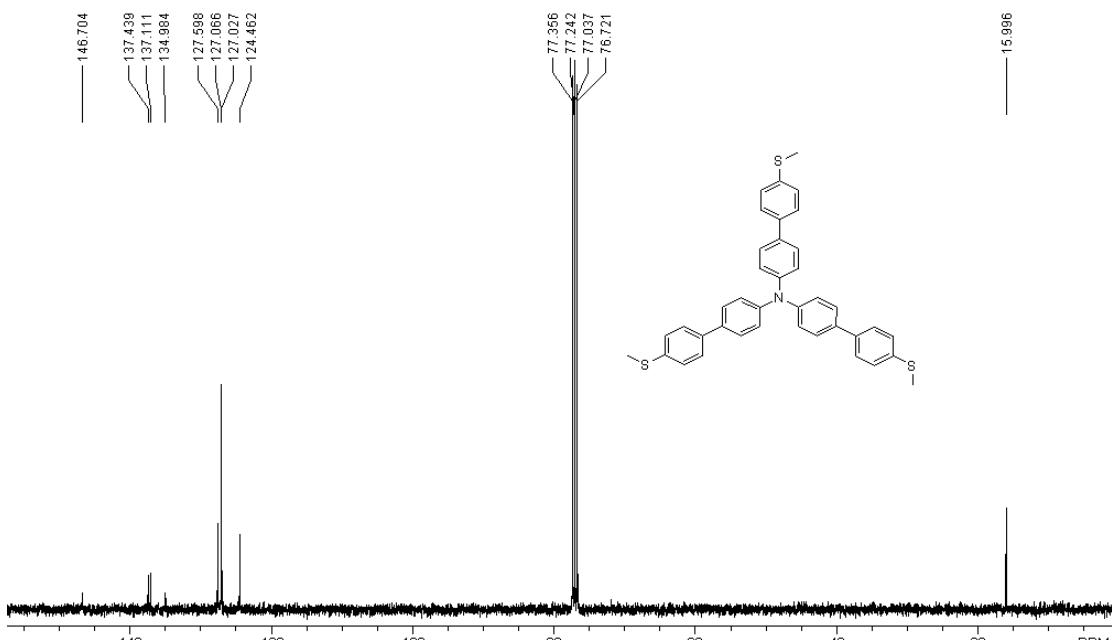
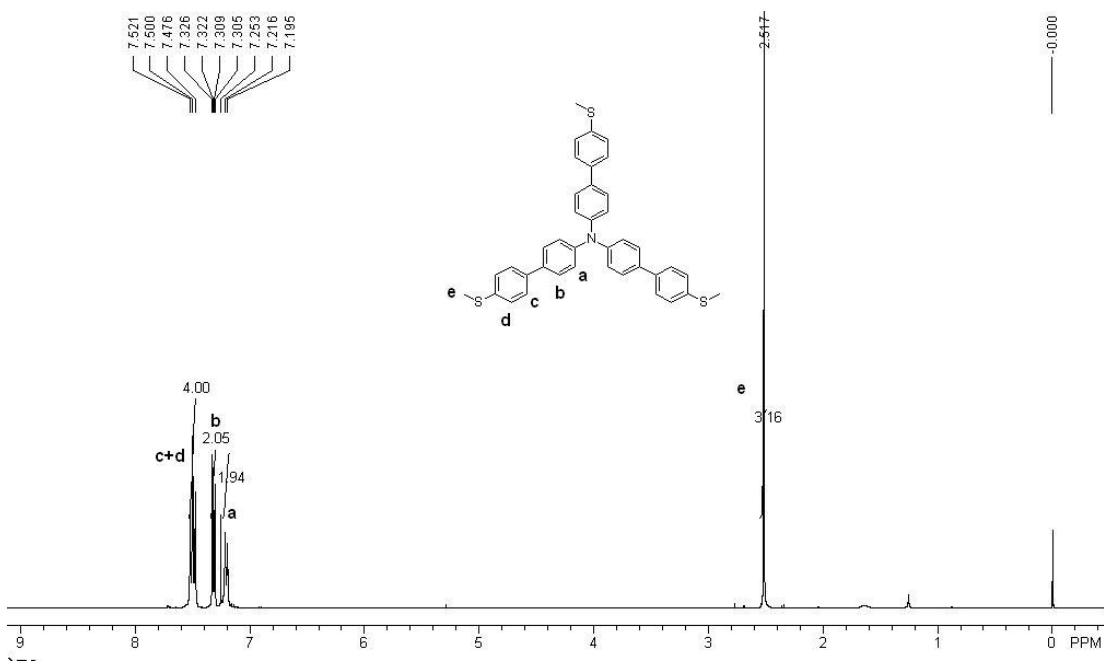
<sup>1</sup>H NMR of 4n

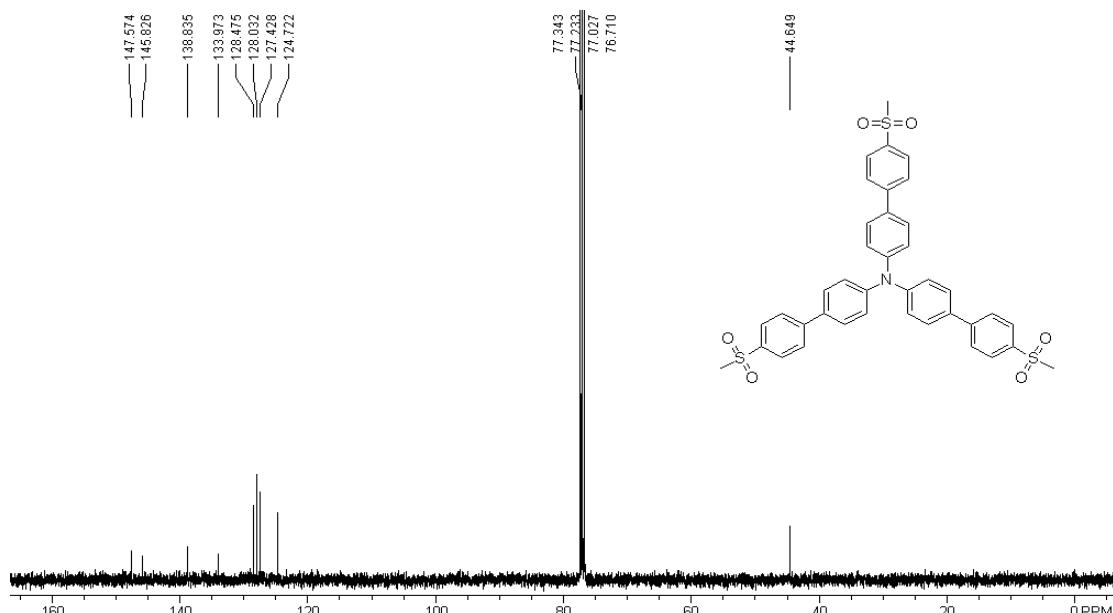
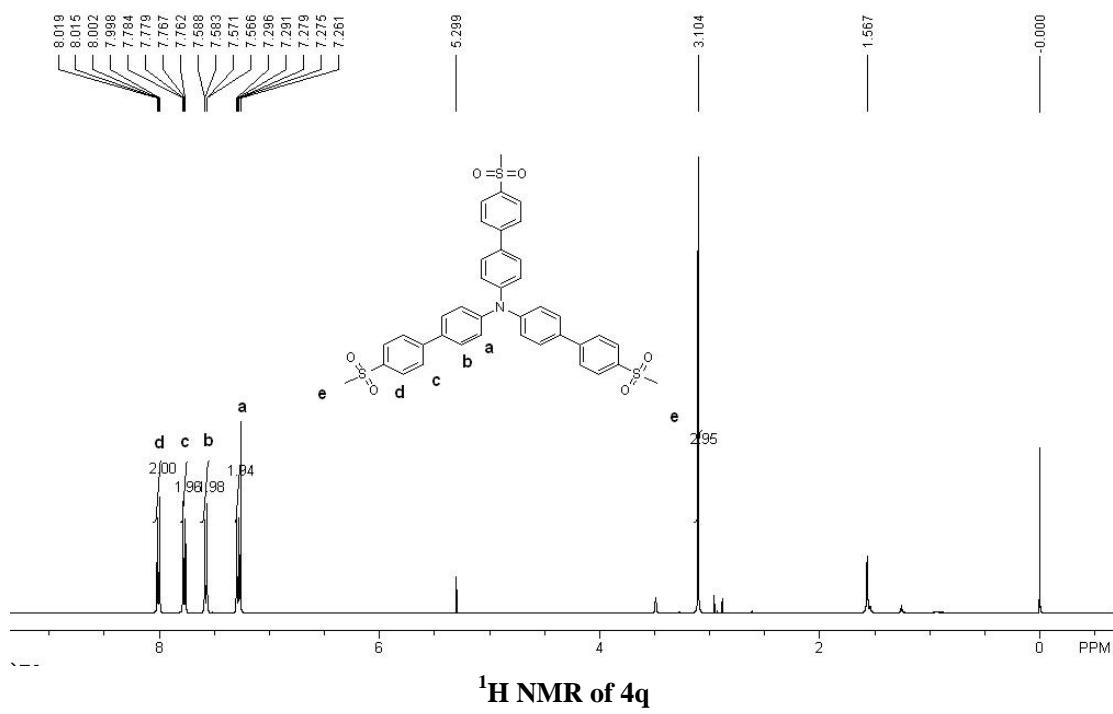


<sup>13</sup>C NMR of 4n

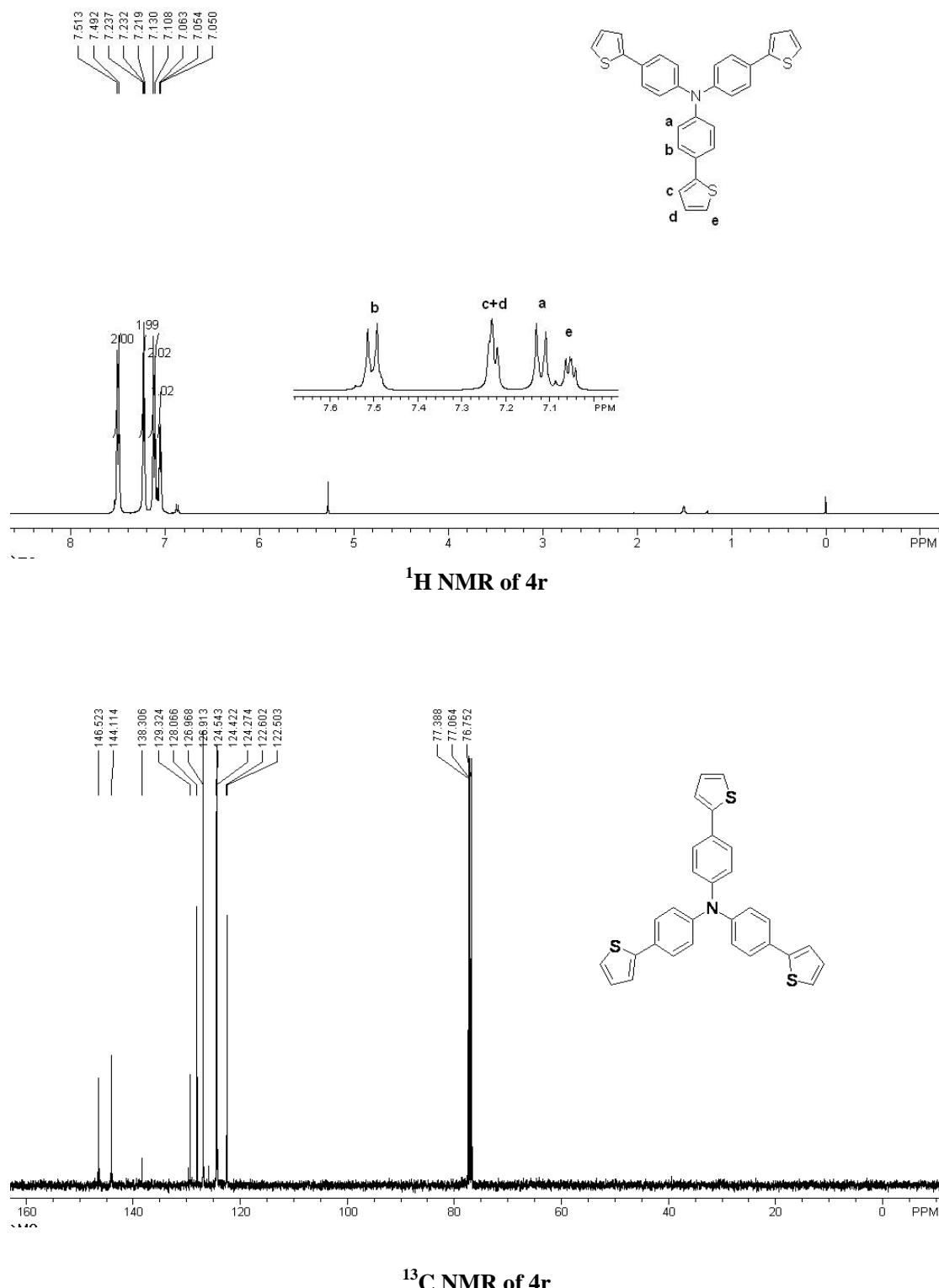


### <sup>13</sup>C NMR of 4o





### <sup>13</sup>C NMR of 4q



## **References of the reported triphenylamine derivatives**

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