

# Supporting Information

## **Cu(I)-catalyzed cross-coupling of primary amine with 2,2'-dibromo-1,1'-biphenyl for the synthesis of polysubstituted carbazole**

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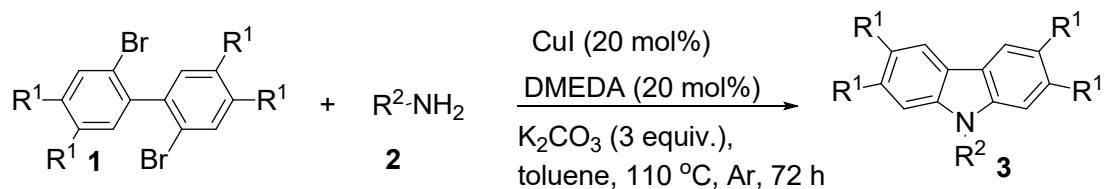
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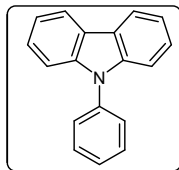
## General Remarks.

Column chromatography was carried out on silica gel (200–300 mesh).  $^1\text{H}$  NMR spectra were recorded on 400 MHz in  $\text{CDCl}_3$ , Chemical Shifts are reported in ppm using TMS as internal standard. Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz).  $^{13}\text{C}$  NMR spectra were recorded on a Varian 100 MHz spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal standard (deuteriochloroform:  $\delta$  77.0 ppm). Melting points were determined on a microscopic apparatus and were uncorrected. All compounds were further characterized by element analysis; High resolution mass analyses were performed on a Bruker ESI-Q-TOF mass spectrometer. Copies of their  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra are provided. Commercially available reagents and solvents were used without further purification.

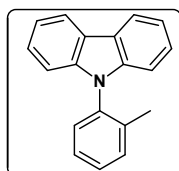
## Experimental Procedure for synthesis of carbazole.



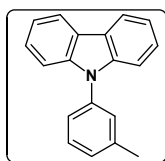
To a stirred solution of **1** (0.2 mmol), **2** (0.6 mmol), CuI (20 mol %),  $\text{K}_2\text{CO}_3$  (0.6 mmol) in toluene (3.0 mL) was added DMEDA (20 mol %) in a test tube. The gas in the tube was changed to argon and the reaction tube was sealed. The reaction mixture was stirred at 110 °C for 72 h. After cooling to room temperature, 10 mL water was added to quench the reaction, the mixtures were extracted with EtOAc (3  $\times$  10 mL). The organic layer was washed with saturated NaCl solution (2  $\times$  10 mL), dried with  $\text{Na}_2\text{SO}_4$  and the solvent was evaporated and the residue was purified by column chromatography, eluting with hexanes/EtOAc (10:1) to give the pure **3**



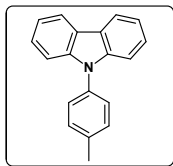
**9-phenyl-9H-carbazole(3a)** White solid; 31 mg, 64% yield; mp 89-90°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.16 (d, *J* = 7.7 Hz, 2H), 7.65 – 7.56 (m, 4H), 7.50 – 7.46 (m, 1H), 7.44 – 7.40 (m, 4H), 7.33 – 7.27 (m, 2H). Anal. Calcd. For C<sub>18</sub>H<sub>13</sub>N: C, 88.86; H, 5.39; N, 5.76 Found: C, 88.69; H, 5.52; N, 5.71. This is a known compound and has been reported in the literature.<sup>1</sup>



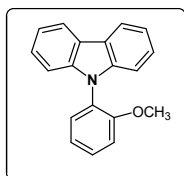
**9-(o-tolyl)-9H-carbazole(3b)**, White solid, 26 mg, 50% yield; mp 64-65°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17 (d, *J* = 7.7 Hz, 2H), 7.46 (dd, *J* = 6.4, 1.7 Hz, 2H), 7.43 – 7.35 (m, 4H), 7.31– 7.27 (m, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 1.98 (s, 3H). Anal. Calcd. For C<sub>19</sub>H<sub>15</sub>N: C, 88.68; H, 5.88; N, 5.44 Found: C, 88.58; H, 5.81; N, 5.51. This is a known compound and has been reported in the literature.<sup>1</sup>



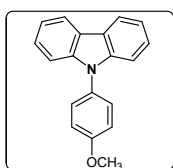
**9-(m-tolyl)-9H-carbazole (3c)**, Yellow viscous oil; 28mg, 55% yield;<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17 (d, *J* = 7.7 Hz, 2H), 7.53 – 7.48 (d, *J* = 7.7 Hz, 1H), 7.46 – 7.36 (m, 6H), 7.34 – 7.28 (m, 3H), 2.49 (s, 3H). Anal. Calcd. For C<sub>19</sub>H<sub>15</sub>N: C, 88.68; H, 5.88; N, 5.44 Found: C, 88.56; H, 5.83; N, 5.49. This is a known compound and has been reported in the literature.<sup>1</sup>



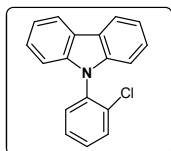
**9-(*p*-tolyl)-9*H*-carbazole(3d)** White solid; 35 mg, 68% yield; mp 103-104°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.15 (d, *J* = 7.7 Hz, 2H), 7.46 – 7.36 (m, 8H), 7.30 – 7.27 (m, 2H), 2.49 (s, 3H). Anal. Calcd. For C<sub>19</sub>H<sub>15</sub>N: C, 88.68; H, 5.88; N, 5.44 Found: C, 88.60; H, 5.79; N, 5.42. This is a known compound and has been reported in the literature.<sup>1</sup>



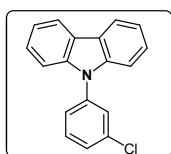
**9-(2-methoxyphenyl)-9*H*-carbazole(3e)** White solid; 28 mg, 51% yield; mp 76-77°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.16 (d, *J* = 7.7 Hz, 2H), 7.49 (dd, *J* = 16.7, 7.9 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.17 (m, 4H), 3.71 (s, 3H). Anal. Calcd. For C<sub>19</sub>H<sub>15</sub>NO: C, 83.49; H, 5.53 N, 5.12 Found: C, 83.47; H, 5.46; N, 5.07. This is a known compound and has been reported in the literature.<sup>2</sup>



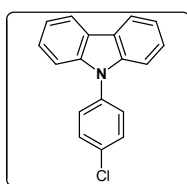
**9-(4-methoxyphenyl)-9*H*-carbazole(3f)** White solid; 38 mg, 70% yield; mp 103-104°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.15 (d, *J* = 7.7 Hz, 2H), 7.46 – 7.36 (m, 8H), 7.30 – 7.27 (m, 2H), 2.49 (s, 3H). Anal. Calcd. For C<sub>19</sub>H<sub>15</sub>NO: C, 83.49; H, 5.53 N, 5.12 Found: C, 83.53; H, 5.48; N, 5.11. This is a known compound and has been reported in the literature.<sup>1</sup>



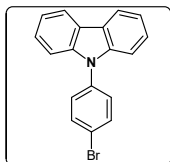
**9-(2-chlorophenyl)-9H-carbazole(3g)** : Pale yellow solid; 27 mg, 48% yield; mp 90-91°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.15 (d,  $J = 7.7$  Hz, 2H), 7.61 (d,  $J = 1.8$  Hz, 1H), 7.55 (t,  $J = 7.9$  Hz, 1H), 7.51 – 7.42 (m, 6H), 7.34 – 7.29 (m,  $J = 7.9, 5.2, 2.9$  Hz, 2H). Anal. Calcd. For  $\text{C}_{18}\text{H}_{12}\text{ClN}$ : C, 77.84; H, 4.35 N, 5.04 Found: C, 77.73; H, 4.41; N, 5.01. This is a known compound and has been reported in the literature.<sup>2</sup>



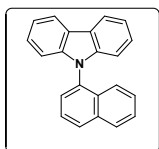
**9-(3-chlorophenyl)-9H-carbazole(3h)** Pale yellow viscous oil; 29 mg, 52% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.17 (d,  $J = 7.7$  Hz, 2H), 7.72 – 7.67 (m, 1H), 7.55 – 7.48 (m, 3H), 7.45 – 7.39 (m, 2H), 7.34 – 7.28 (m, 2H), 7.11 (d,  $J = 8.1$  Hz, 2H). Anal. Calcd. For  $\text{C}_{18}\text{H}_{12}\text{ClN}$ : C, 77.84; H, 4.35 N, 5.04 Found: C, 77.76; H, 4.31; N, 5.07. This is a known compound and has been reported in the literature.<sup>2</sup>



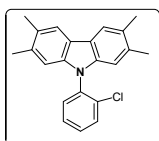
**9-(4-chlorophenyl)-9H-carbazole(3i)** White solid; 28 mg, 50% yield; mp 134-135°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.15 (d,  $J = 7.8$  Hz, 2H), 7.61 – 7.56 (m, 2H), 7.54 – 7.50 (m, 2H), 7.45 – 7.36 (m, 4H), 7.33 – 7.28 (m, 2H). Anal. Calcd. For  $\text{C}_{18}\text{H}_{12}\text{ClN}$ : C, 77.84; H, 4.35 N, 5.04 Found: C, 77.82; H, 4.23; N, 4.99. This is a known compound and has been reported in the literature.<sup>1</sup>



**9-(4-bromophenyl)-9H-carbazole(3j)** Yellow solid; 21 mg, 33% yield; mp 137-138°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14 (d, *J* = 7.7 Hz, 2H), 7.76 – 7.71 (m, 2H), 7.48 – 7.43 (m, 2H), 7.43 – 7.35 (m, 4H), 7.32 – 7.27 (m, 2H). Anal. Calcd. For C<sub>18</sub>H<sub>12</sub>BrN: C, 67.10; H, 3.75 N, 4.35 Found: C, 67.02; H, 3.68; N, 4.29. This is a known compound and has been reported in the literature.<sup>3</sup>

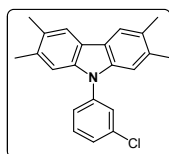


**9-(naphthalen-1-yl)-9H-carbazole(3k)** White solid; 31 mg, 53% yield; mp 124-125°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.24 – 8.20 (m, 2H), 8.07 – 7.99 (m, 2H), 7.70 – 7.63 (m, 2H), 7.57 – 7.52 (m, 1H), 7.37 – 7.27 (m, 6H), 7.03 – 6.99 (m, 2H) Anal. Calcd. For C<sub>22</sub>H<sub>15</sub>N: C, 90.07; H, 5.15 N, 4.77 Found: C, 90.00; H, 5.18; N, 4.68. This is a known compound and has been reported in the literature.<sup>1</sup>

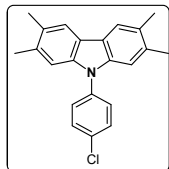


**9-(2-chlorophenyl)-2,3,6,7-tetramethyl-9H-carbazole ( 3l )** Yellow solid; 34 mg, 51% yield mp 162-163°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84 (s, 2H), 7.70 – 7.66 (m, 1H), 7.49 (t, *J* = 4.6 Hz, 3H), 6.82 (s, 2H), 2.44 (s, 6H), 2.36 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 141.29, 137.20, 135.85, 135.33, 132.43, 132.39, 130.90, 129.68, 129.48, 122.90, 121.95, 111.88, 22.23, 21.51. HRMS (ESI<sup>+</sup>) *m/z* calculated for

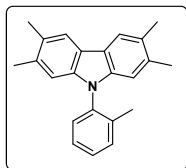
$C_{22}H_{20}ClN$   $[M+H]^+$  334.1357, found 334.1353. Anal. Calcd. For  $C_{22}H_{20}ClN$ : C, 79.15; H, 6.04 N, 4.20 Found: C, 79.03; H, 6.07; N, 4.11.



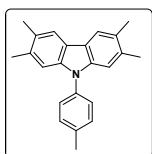
**9-(3-chlorophenyl)-2,3,6,7-tetramethyl-9H-carbazole(3m)** Orange solid; 36 mg, 54% yield; mp 161-162°C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.82 (s, 2H), 7.55 (dt,  $J = 15.8, 4.9$  Hz, 2H), 7.47 – 7.40 (m, 2H), 7.15 (s, 2H), 2.44 (s, 6H), 2.39 (s, 6H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  141.19, 140.86, 136.74, 136.02, 132.20, 130.07, 128.53, 128.52, 126.57, 123.15, 121.92, 111.56, 22.27, 21.47. HRMS (ESI $^+$ )  $m/z$  calculated for  $C_{22}H_{20}ClN$   $[M+H]^+$  334.1357, found 334.1355. Anal. Calcd. For  $C_{22}H_{20}ClN$ : C, 79.15; H, 6.04 N, 4.20 Found: C, 79.11; H, 5.96; N, 4.21.



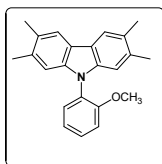
**9-(4-chlorophenyl)-2,3,6,7-tetramethyl-9H-carbazole(3n)** Yellow solid; 36 mg, 54% yield; mp 178-179°C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.83 (s, 2H), 7.57 (d,  $J = 8.7$  Hz, 2H), 7.51 – 7.47 (m, 2H), 7.13 (s, 2H), 2.44 (s, 6H), 2.38 (s, 6H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  140.96, 138.40, 135.93, 133.83, 131.43, 129.88, 129.66, 123.02, 121.88, 111.46, 22.22, 21.43. HRMS (ESI $^+$ )  $m/z$  calculated for  $C_{22}H_{20}ClN$   $[M+H]^+$  334.1357, found 334.1358. Anal. Calcd. For  $C_{22}H_{20}ClN$ : C, 79.15; H, 6.04 N, 4.20 Found: C, 79.06; H, 5.98; N, 4.10.



**2,3,6,7-tetramethyl-9-(o-tolyl)-9H-carbazole(3o)** Yellow solid; 24 mg, 38% yield; mp 132-133°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (s, 2H), 7.49 – 7.37 (m, 3H), 7.36 – 7.32 (m, 1H), 6.78 (s, 2H), 2.44 (s, 6H), 2.35 (s, 6H), 2.00 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.05, 137.46, 136.64, 134.25, 131.34, 129.30, 128.34, 127.61, 127.12, 121.06, 120.38, 110.14, 20.65, 19.96, 17.62. HRMS (ESI $^+$ )  $m/z$  calculated for  $\text{C}_{23}\text{H}_{23}\text{N}$   $[\text{M}+\text{Na}]^+$  336.1723, found 336.1725. Anal. Calcd. For  $\text{C}_{23}\text{H}_{23}\text{N}$ : C, 88.13; H, 7.40 N, 4.47 Found: C, 88.01; H, 7.31; N, 4.34



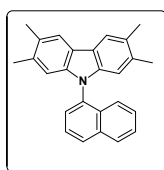
**2,3,6,7-tetramethyl-9-(p-tolyl)-9H-carbazole(3p)** White solid; 28 mg, 45% yield mp 164-165°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (s, 2H), 7.44 – 7.38 (m, 4H), 7.13 (s, 2H), 2.49 (s, 3H), 2.44 (s, 6H), 2.37 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.84, 136.72, 135.62, 134.16, 130.28, 127.84, 126.82, 121.27, 120.23, 110.12, 21.15, 20.67, 19.91. HRMS (ESI $^+$ )  $m/z$  calculated for  $\text{C}_{23}\text{H}_{23}\text{N}$   $[\text{M}+\text{Na}]^+$  336.1723, found 336.1719. Anal. Calcd. For  $\text{C}_{23}\text{H}_{23}\text{N}$ : C, 88.13; H, 7.40 N, 4.47 Found: C, 88.05; H, 7.33; N, 4.44.



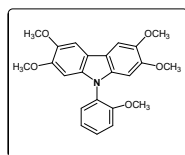
**9-(2-methoxyphenyl)-2,3,6,7-tetramethyl-9H-carbazole(3q)** Yellow solid; 28 mg, 43% yield; mp 169-170°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (s, 2H), 7.51 – 7.45



(m, 1H), 7.41 (dd,  $J = 7.7, 1.7$  Hz, 1H), 7.20 – 7.12 (m, 2H), 6.87 (s, 2H), 3.70 (s, 3H), 2.43 (s, 6H), 2.36 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  157.72, 141.67, 135.47, 131.50, 130.58, 129.06, 128.06, 122.76, 122.64, 121.71, 114.43, 111.99, 57.26, 22.22, 21.49. HRMS (ESI<sup>+</sup>)  $m/z$  calculated for  $\text{C}_{23}\text{H}_{23}\text{NO}$   $[\text{M}+\text{H}]^+$  330.1852, found 330.1851. Anal. Calcd. For  $\text{C}_{23}\text{H}_{23}\text{NO}$ : C, 83.85; H, 7.04 N, 4.25 Found: C, 83.77; H, 6.94; N, 4.14.

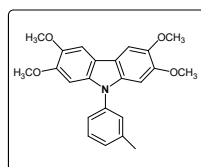


**2,3,6,7-tetramethyl-9-(naphthalen-1-yl)-9H-carbazole(3r)** Orange solid; 28 mg, 40% yield mp 207-208°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (t,  $J = 8.5$  Hz, 2H), 7.89 (s, 2H), 7.70 – 7.64 (m, 1H), 7.59 (dd,  $J = 7.2, 1.1$  Hz, 1H), 7.54 (ddd,  $J = 8.2, 4.9, 3.1$  Hz, 1H), 7.33 – 7.30 (m, 2H), 6.73 (s, 2H), 2.44 (s, 6H), 2.27 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.60, 136.24, 136.18, 135.80, 132.63, 130.06, 129.76, 129.36, 128.26, 128.16, 128.04, 127.38, 125.22, 122.70, 121.81, 111.99, 22.08, 21.46. HRMS (ESI<sup>+</sup>)  $m/z$  calculated for  $\text{C}_{26}\text{H}_{23}\text{N}$   $[\text{M}+\text{H}]^+$  350.1903, found 350.1894. Anal. Calcd. For  $\text{C}_{26}\text{H}_{23}\text{N}$ : C, 89.36; H, 6.63 N, 4.01 Found: C, 89.25; H, 6.51; N, 3.95.

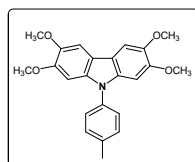


**2,3,6,7-tetramethoxy-9-(2-methoxyphenyl)-9H-carbazole(3s)** White solid; 32 mg, 41% yield; mp 159-160°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 – 7.43 (m, 4H), 7.21 – 7.14 (m, 2H), 6.62 (s, 2H), 4.02 (s, 6H), 3.85 (s, 6H), 3.74 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.78, 148.18, 144.40, 135.62, 129.59, 129.21, 126.17, 121.28,

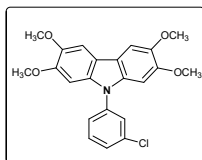
115.39, 112.92, 101.82, 94.11, 56.60, 56.17, 55.60. HRMS (ESI<sup>+</sup>) m/z calculated for C<sub>23</sub>H<sub>23</sub>NO<sub>5</sub> [M+H]<sup>+</sup> 394.1649, found 394.1647. Anal. Calcd. For C<sub>23</sub>H<sub>23</sub>NO<sub>5</sub>: C, 70.21; H, 5.89 N, 3.56 Found: C, 70.15; H, 5.83; N, 3.54.



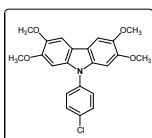
**2,3,6,7-tetramethoxy-9-(m-tolyl)-9H-carbazole(3t)** White solid; 27 mg, 36% yield; mp 177-178°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.53 – 7.45 (m, 3H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 1H), 6.87 (s, 2H), 4.03 (s, 6H), 3.88 (s, 6H), 2.48 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.25, 144.58, 140.00, 138.00, 135.31, 129.71, 128.00, 127.35, 123.80, 115.52, 101.80, 93.79, 56.58, 56.22, 21.41. HRMS (ESI<sup>+</sup>) m/z calculated for C<sub>22</sub>H<sub>23</sub>NO<sub>4</sub> [M+H]<sup>+</sup> 378.1700, found 378.1694. Anal. Calcd. For C<sub>22</sub>H<sub>23</sub>NO<sub>4</sub>: C, 73.19; H, 6.14 N, 3.71 Found: C, 73.08; H, 6.07; N, 3.78.



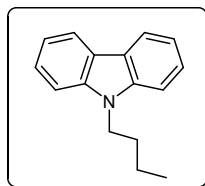
**2,3,6,7-tetramethoxy-9-(p-tolyl)-9H-carbazole(3u)** White solid; 31 mg, 41% yield; mp 160-161°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.46 (s, 2H), 7.42 (s, 3H), 6.84 (s, 2H), 4.03 (s, 6H), 3.87 (s, 6H), 2.50 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.26, 144.52, 137.06, 135.41, 135.37, 130.56, 126.62, 115.40, 101.80, 93.65, 56.59, 56.16, 21.16. HRMS (ESI<sup>+</sup>) m/z calculated for C<sub>22</sub>H<sub>23</sub>NO<sub>4</sub> [M+H]<sup>+</sup> 378.1700, found 378.1700. Anal. Calcd. For C<sub>22</sub>H<sub>23</sub>NO<sub>4</sub>: C, 73.19; H, 6.14 N, 3.71 Found: C, 73.16; H, 6.09; N, 3.61.



**9-(3-chlorophenyl)-2,3,6,7-tetramethoxy-9H-carbazole(3v)** Brown solid; 28 mg, 35% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 – 7.68 (m, 1H), 7.54 – 7.46 (m, 5H), 6.54 (s, 2H), 4.03 (s, 6H), 3.85 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.38, 144.91, 139.39, 135.50, 134.87, 130.95, 127.37, 126.94, 124.88, 115.81, 101.85, 93.62, 56.56, 56.27. HRMS (ESI<sup>+</sup>)  $m/z$  calculated for  $\text{C}_{22}\text{H}_{20}\text{ClNO}_4$   $[\text{M}+\text{H}]^+$  398.1154, found 398.1151. Anal. Calcd. For  $\text{C}_{22}\text{H}_{20}\text{ClNO}_4$ : C, 66.42; H, 5.07 N, 3.52 Found: C, 66.30; H, 5.09; N, 3.41.



**9-(4-chlorophenyl)-2,3,6,7-tetramethoxy-9H-carbazole(3w)** White solid; 33mg, 38% yield; mp 171-172°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d,  $J = 8.5$  Hz, 2H), 7.51 – 7.44 (m, 4H), 6.82 (s, 2H), 4.02 (s, 6H), 3.89 (d,  $J = 7.6$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.37, 144.80, 136.66, 135.02, 132.74, 130.23, 128.08, 115.67, 101.85, 93.45, 56.56, 56.20. HRMS (ESI<sup>+</sup>)  $m/z$  calculated for  $\text{C}_{22}\text{H}_{20}\text{ClNO}_4$   $[\text{M}+\text{H}]^+$  398.1154, found 398.1152. Anal. Calcd. For  $\text{C}_{22}\text{H}_{20}\text{ClNO}_4$ : C, 66.42; H, 5.07 N, 3.52 Found: C, 66.36; H, 5.01; N, 3.59.



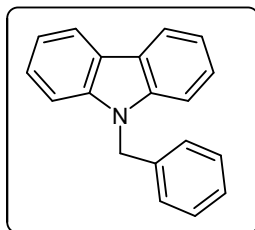
**9-butyl-9H-carbazole (3x)** White solid; 28mg, 63 % yield; mp 57-58°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 (d,  $J = 5.6$  Hz, 2H), 7.45 – 7.39 (m, 4H), 7.22 (s, 2H), 4.29

(t,  $J = 7.2$  Hz, 2H), 1.86-1.83 (m, 2H), 1.50-1.38 (m, 2H), 0.94 (t,  $J = 7.6$ Hz, 3H).

HRMS (ESI<sup>+</sup>)  $m/z$  calculated for C<sub>16</sub>H<sub>17</sub>N [M+H]<sup>+</sup> 224.1439 found 224.1436. Anal.

Calcd. For C<sub>16</sub>H<sub>17</sub>N: C, 86.05; H, 7.67; N, 6.27 Found: C, 86.01; H, 7.60; N, 6.21.

This is a known compound and has been reported in the literature.<sup>4</sup>



**9-benzyl-9H-carbazole (3y)** White solid; 39 mg, 75% yield; mp 122-123°C. <sup>1</sup>H

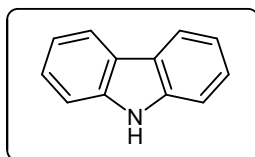
NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.13 (d,  $J = 7.6$  Hz, 2H), 7.44-7.35(m, 4H), 7.27-7.21 (m,

5H), 7.14(d,  $J = 6.4$ Hz, 2H), 5.51 (s, 2H). HRMS (ESI<sup>+</sup>)  $m/z$  calculated for C<sub>19</sub>H<sub>15</sub>N

[M+H]<sup>+</sup> 258.1283, found 258.1281. Anal. Calcd. For C<sub>19</sub>H<sub>15</sub>N: C, 88.68; H, 5.88 N,

5.44 Found: C, 88.60; H, 5.81; N, 5.47. This is a known compound and has been

reported in the literature.<sup>5</sup>



**9H-carbazole (3z)** Add N-benzylcarbazole (514 mg 2 mmol) to the dry flask, and

then add 10 mL DMSO to dissolve. While stirring the solution at room temperature,

KO<sup>t</sup>Bu (10 mmol, in 10 mLTHF) was added. Oxygen was then bubbled into the

solution, via a gas tube for 20 min. 10 mL NH<sub>4</sub>Cl was added to quench the reaction,

the mixtures were extracted with EtOAc (3 × 10 mL). The organic layer was washed

with saturated NaCl solution (2 × 10 mL), dried with Na<sub>2</sub>SO<sub>4</sub> and the solvent was

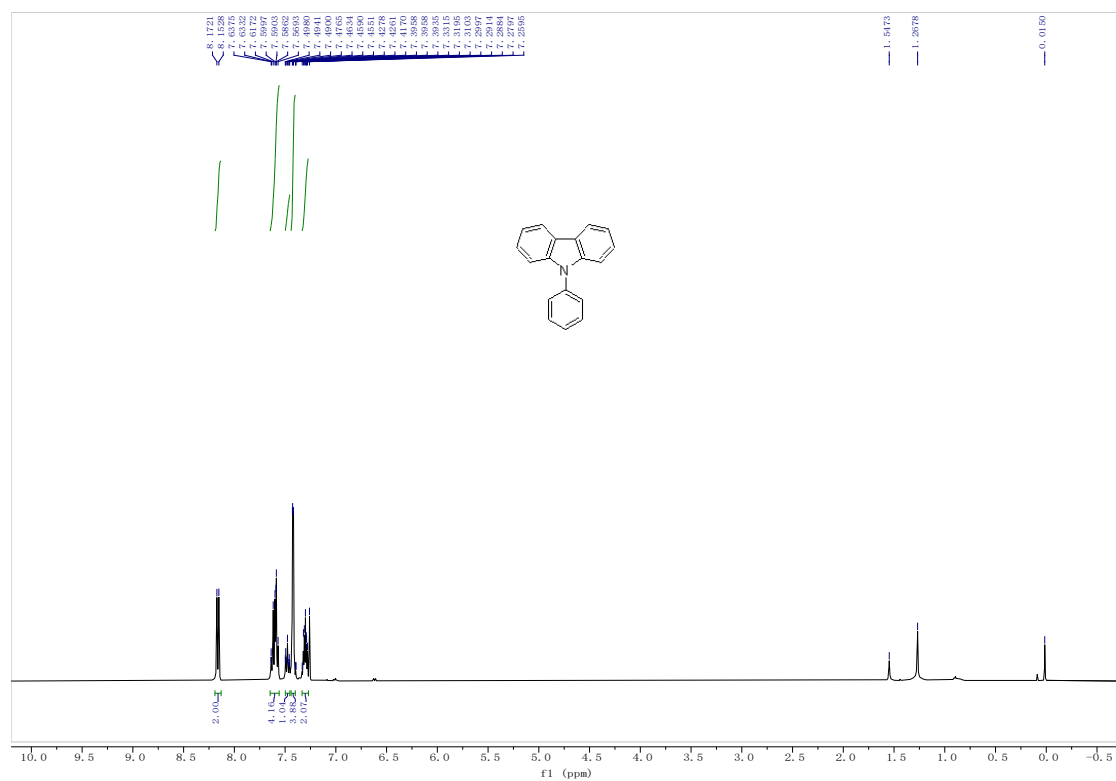
evaporated and the residue was purified by column chromatography, eluting with MeOH/EtOAc (1:10) to give the pure **9H-carbazole (3z)** White solid; 301 mg, 90% yield; mp 243-245°C. <sup>1</sup>H NMR (400 MHz, DMSO-d) δ 11.24 (s, 1H), 8.11 (d, *J* = 7.6 Hz, 2H), 7.50-7.36 (m, 4H), 7.17-7.13 (m, 2H). HRMS (ESI<sup>+</sup>) *m/z* calculated for C<sub>12</sub>H<sub>9</sub>N [M+H]<sup>+</sup> 168.0813, found 168.0810. Anal. Calcd. For C<sub>12</sub>H<sub>9</sub>N: C, 86.20; H, 5.43 N, 8.38 Found: C, 86.16; H, 5.39; N, 8.41. This is a known compound and has been reported in the literature.<sup>6</sup>

## References

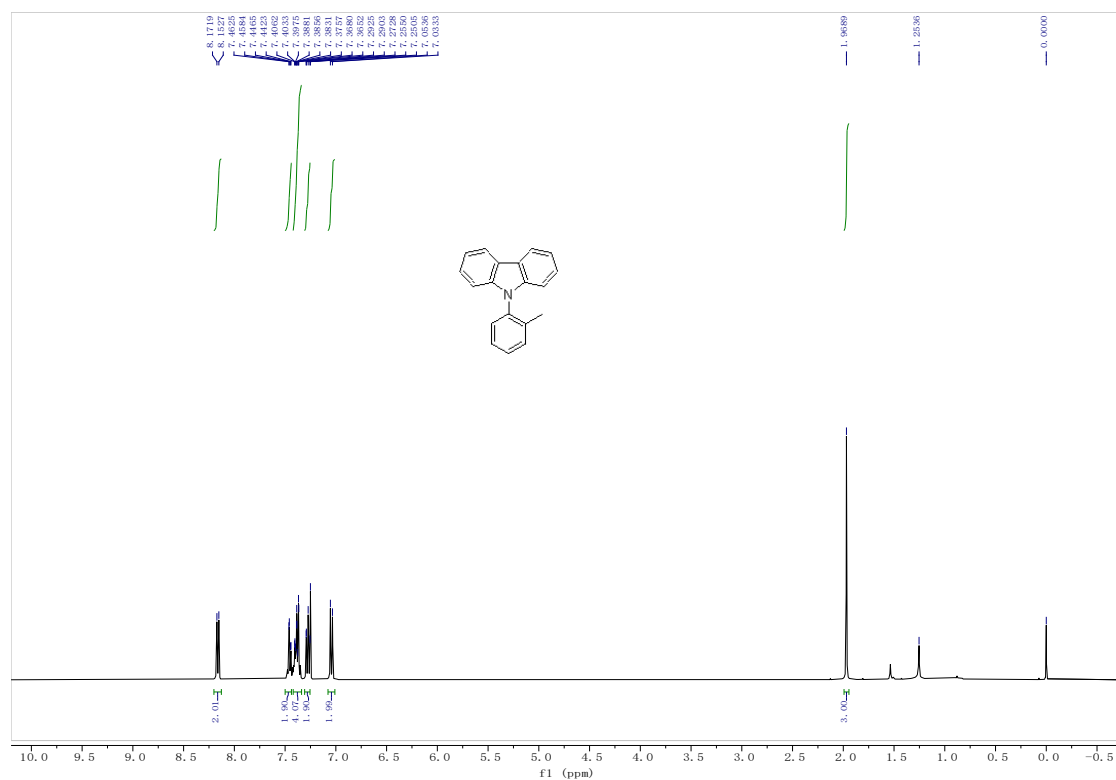
1. W. J. Yoo, T. Tsukamoto, and S. Kobayashi, *Org. Lett.*, 2015, **17**, 3640.
2. Y. Zhou, J. Verkade. *Adv. Synth. Catal.*, 2010, **352**, 616.
3. F. Chen, N. Liu, E. Ji, and B. Dai. *RSC Adv.*, 2015, **5**, 51512.
4. J.-X. Yang, X.-T. Tao, C. X. Yuan, Y. X. Yan, L. Wang, Z. Liu, Y. Ren, and M. H. Jiang, *J. Am. Chem. Soc.*, 2005, **127**, 3278
5. H. N. Do, N. M. Quan, B. V. Phuc, D. V. Tinh, N. Q. Tien, T. T. T. Nga, V. T. Nguyen, T. Q. Huang, T. T. Dang, P. Langer, *Synlett*, 2021, **32**, 611.
6. A. A. Haddach, A. Kelleman, M. V. Deaton-Rewolinski, *Tetrahedron Lett.*, 2002, **43**, 399.

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

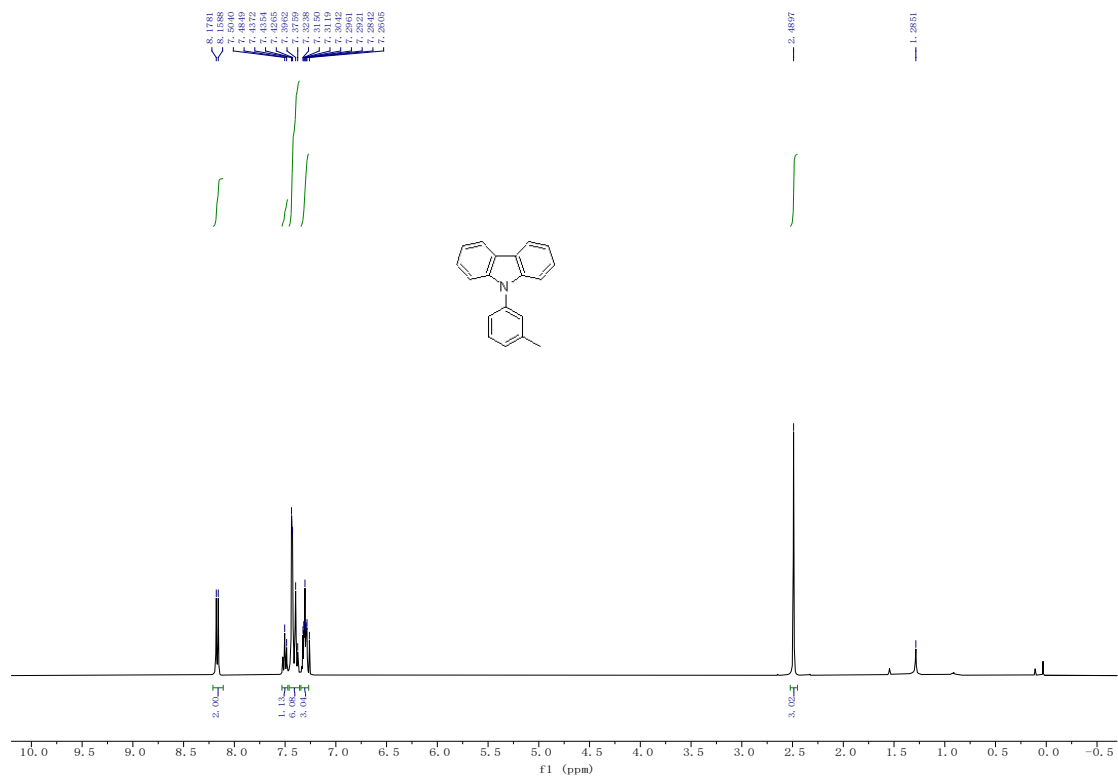
#### 9-phenyl-9*H*-carbazole(3a)



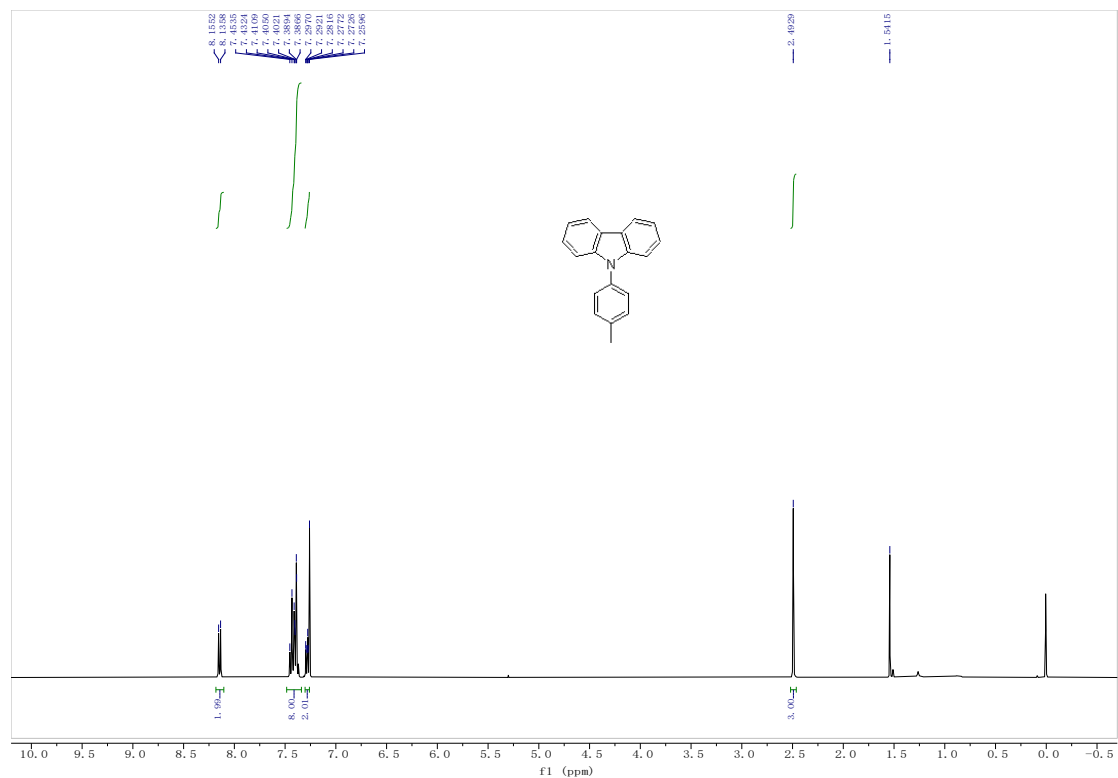
#### 9-(*o*-tolyl)-9*H*-carbazole(3b)



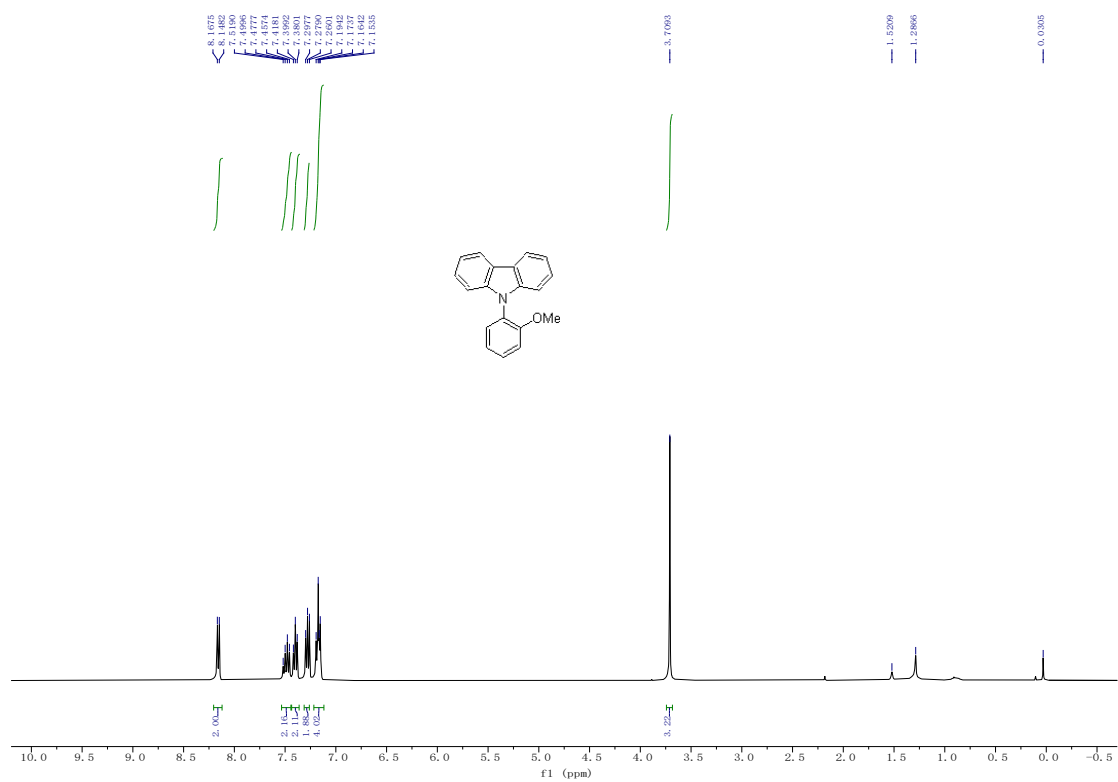
### 9-(*m*-tolyl)-9*H*-carbazole (3c)



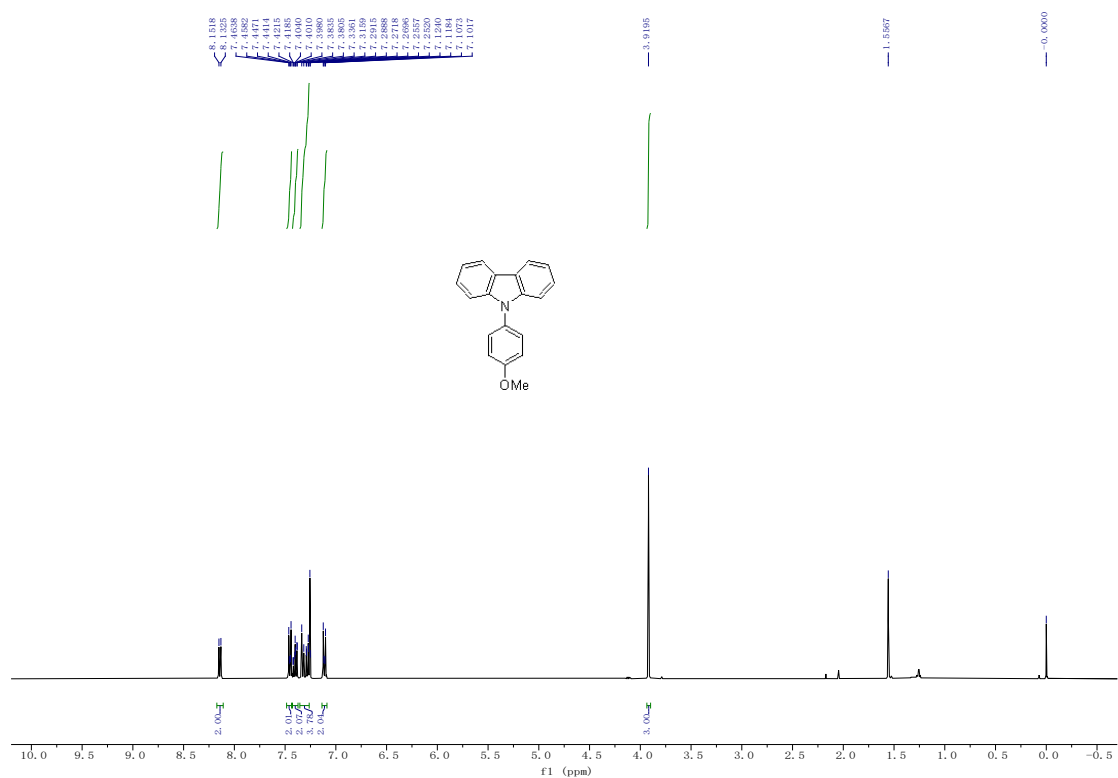
### 9-(*p*-tolyl)-9*H*-carbazole(3d)



### 9-(2-methoxyphenyl)-9H-carbazole(3e)

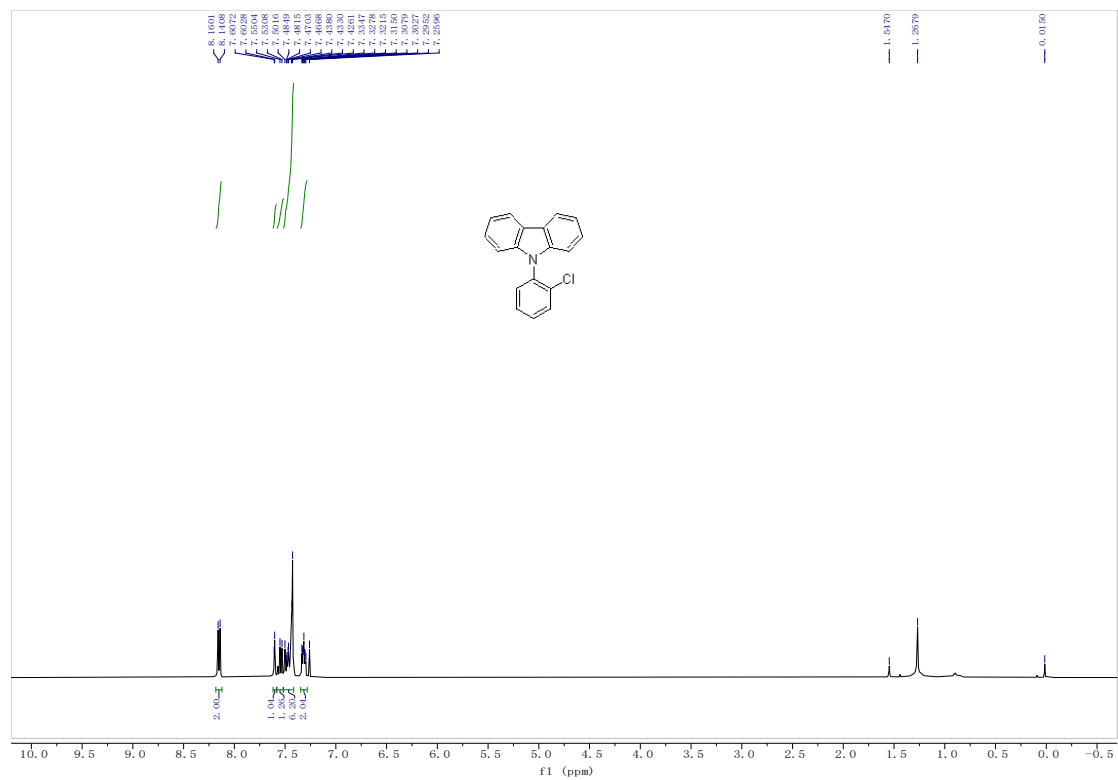


### 9-(4-methoxyphenyl)-9H-carbazole(3f)

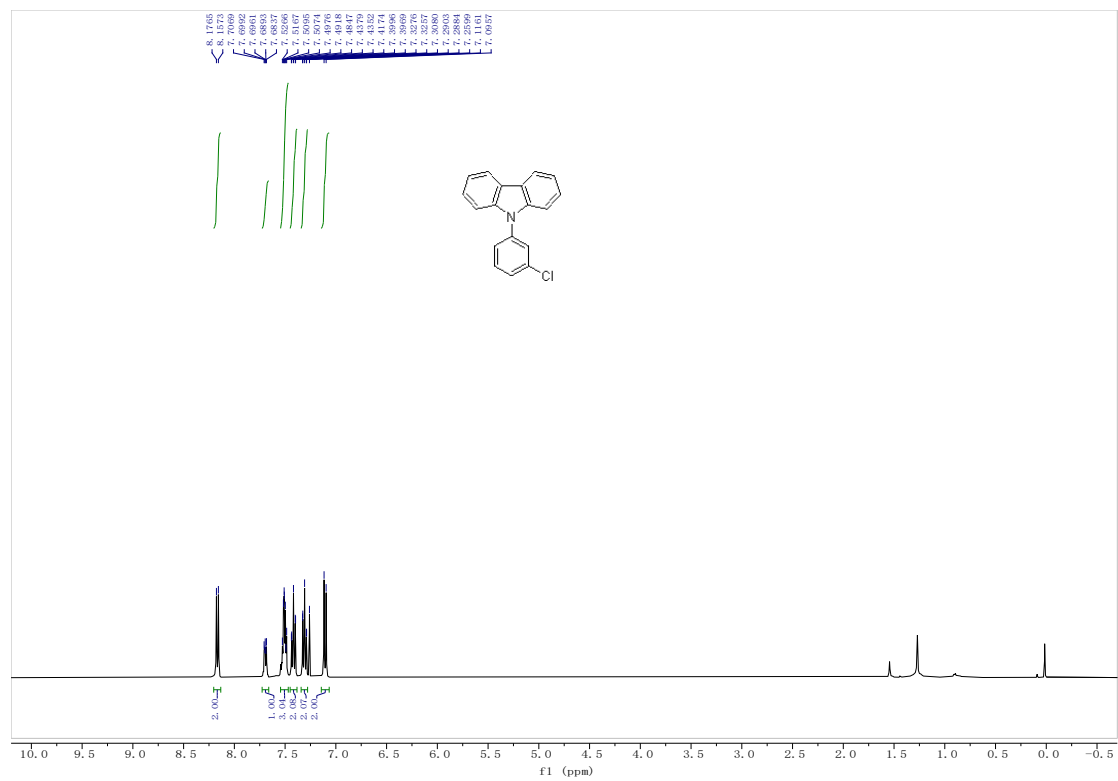




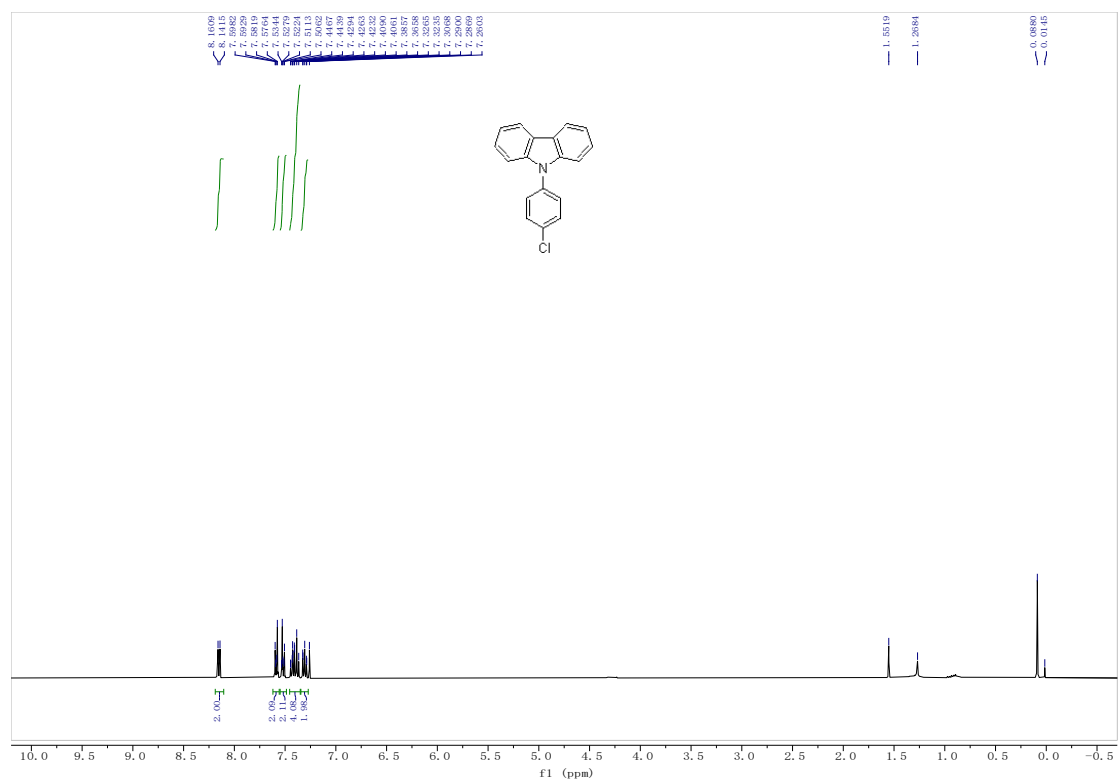
### 9-(2-chlorophenyl)-9H-carbazole(3g)



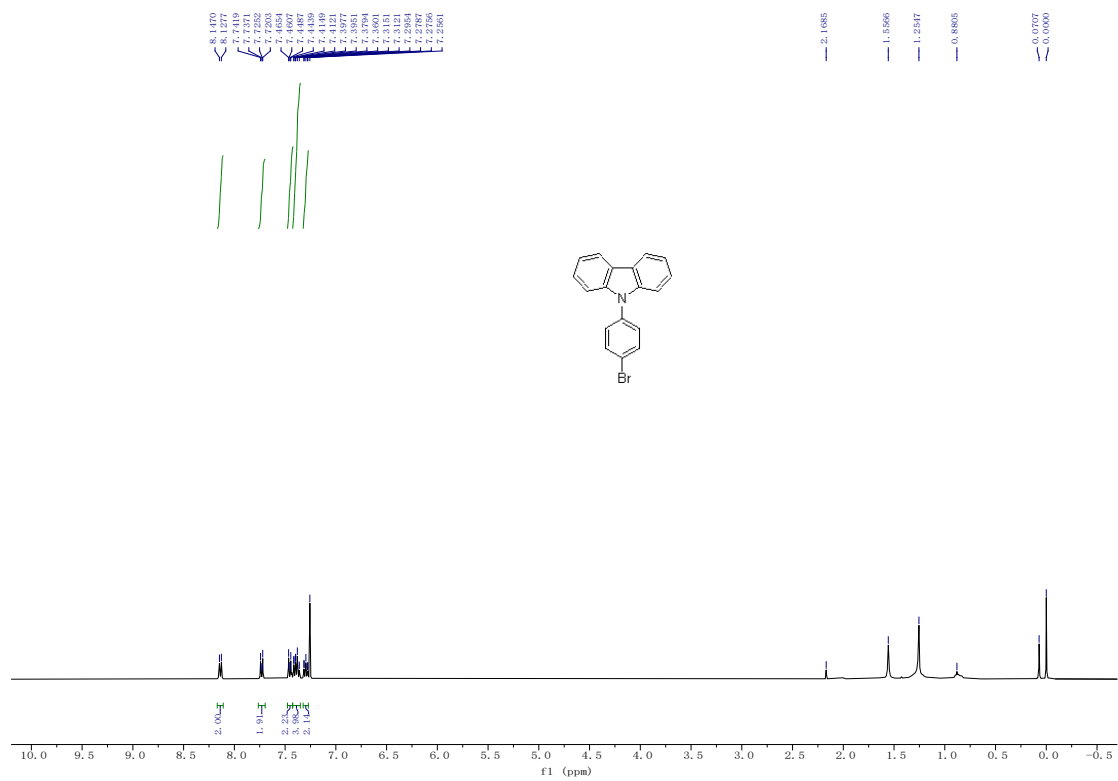
### 9-(3-chlorophenyl)-9H-carbazole(3h)



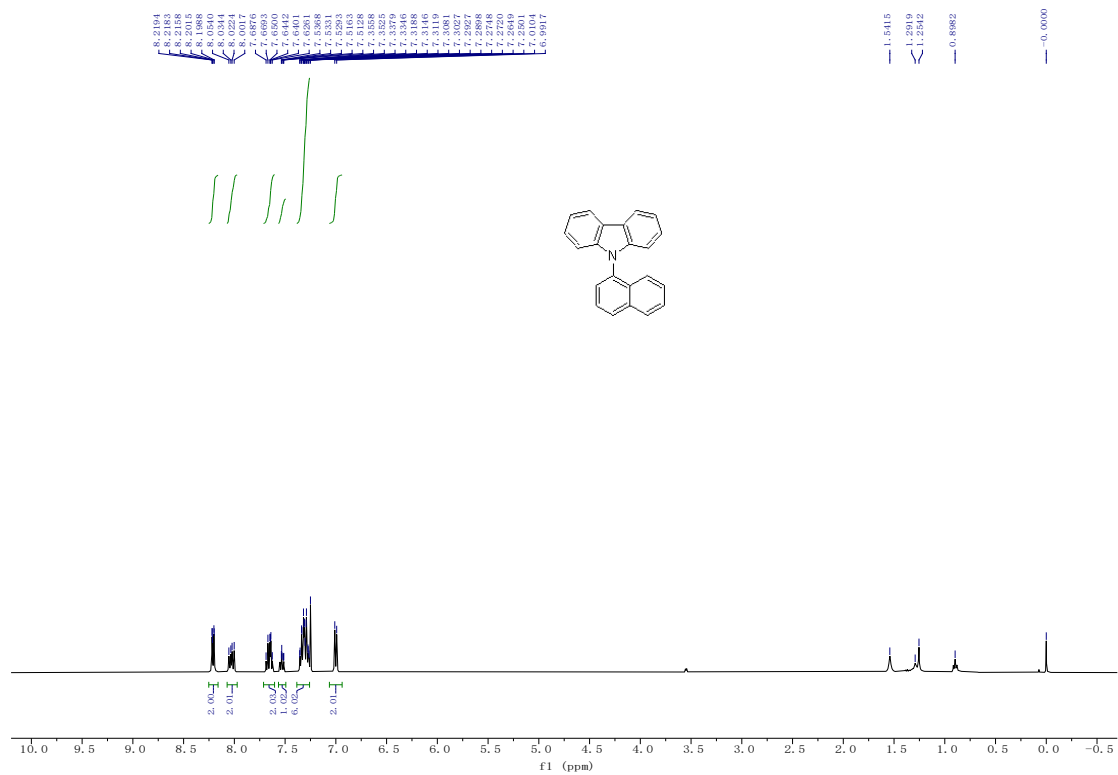
### 9-(4-chlorophenyl)-9H-carbazole(3i)



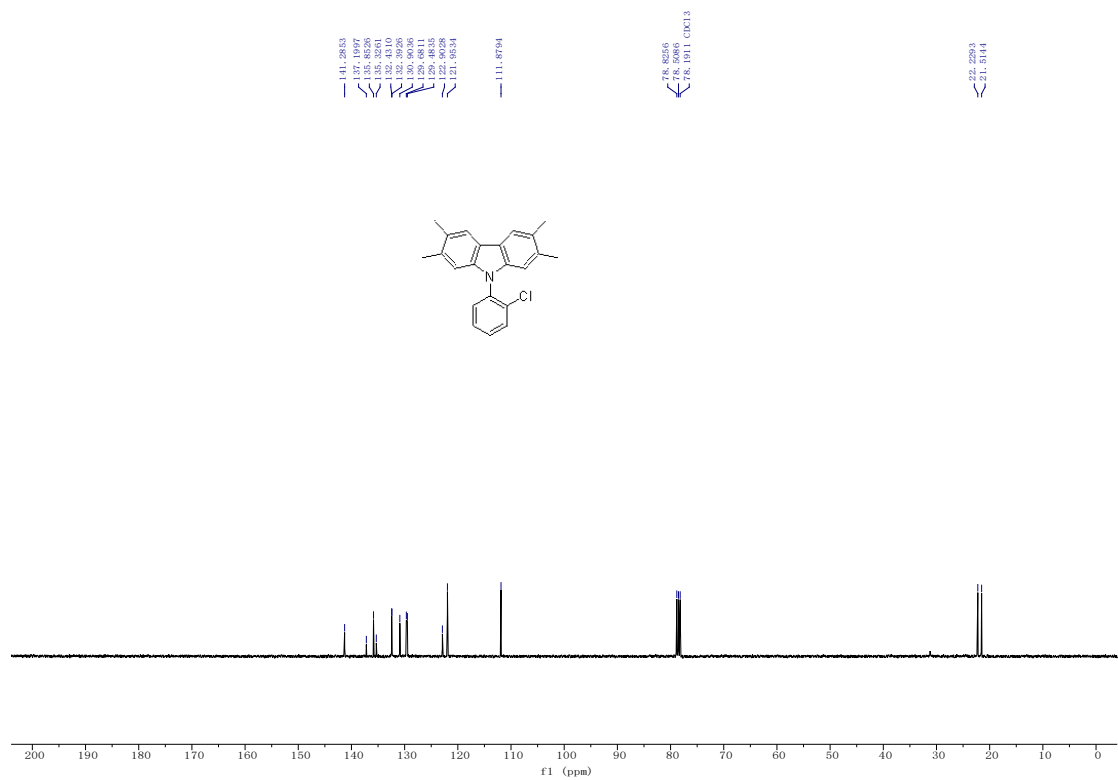
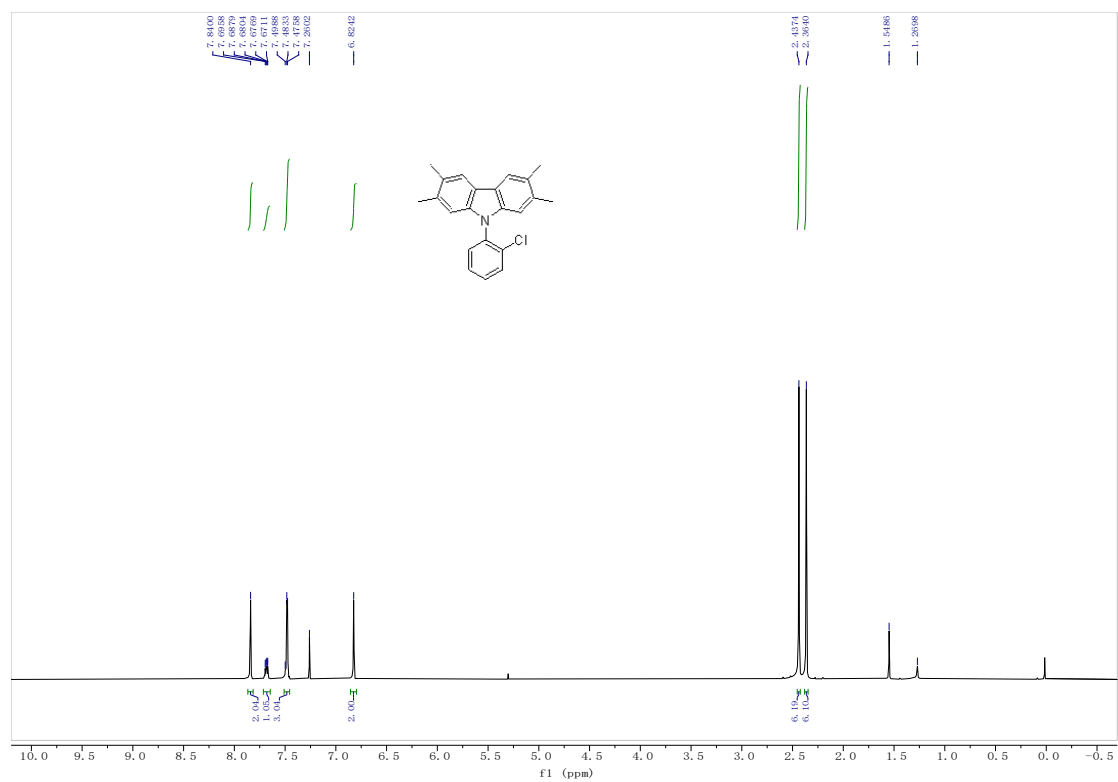
### 9-(4-bromophenyl)-9H-carbazole(3j)



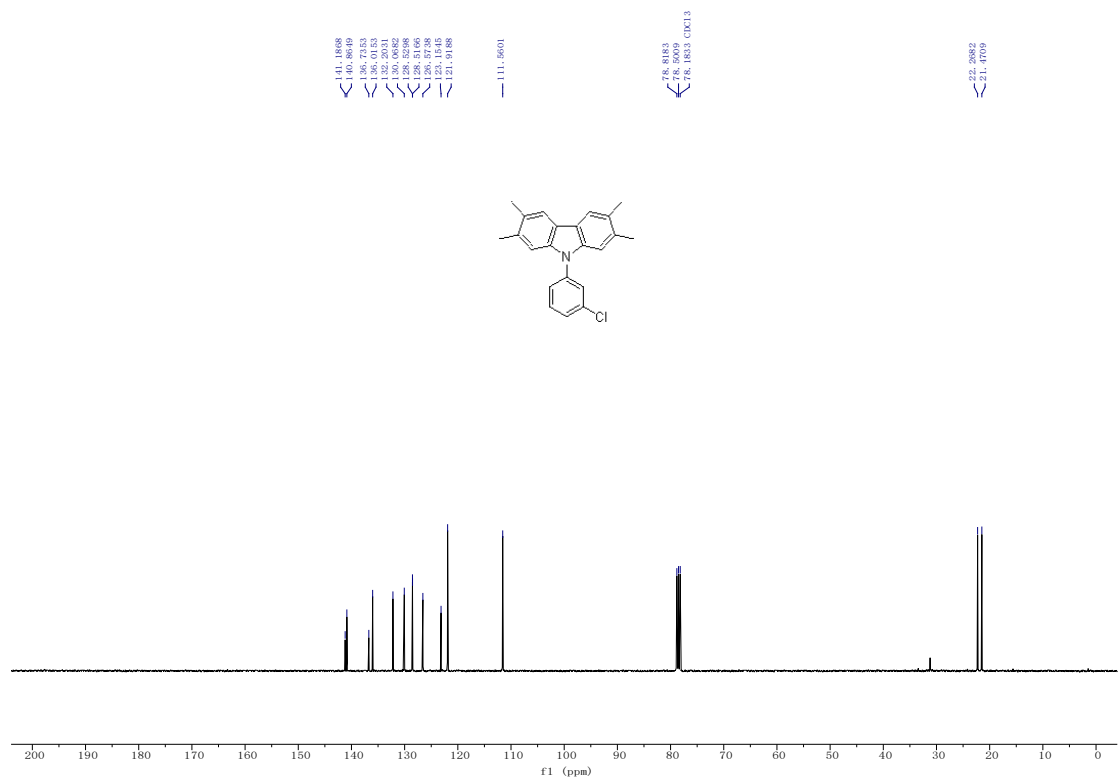
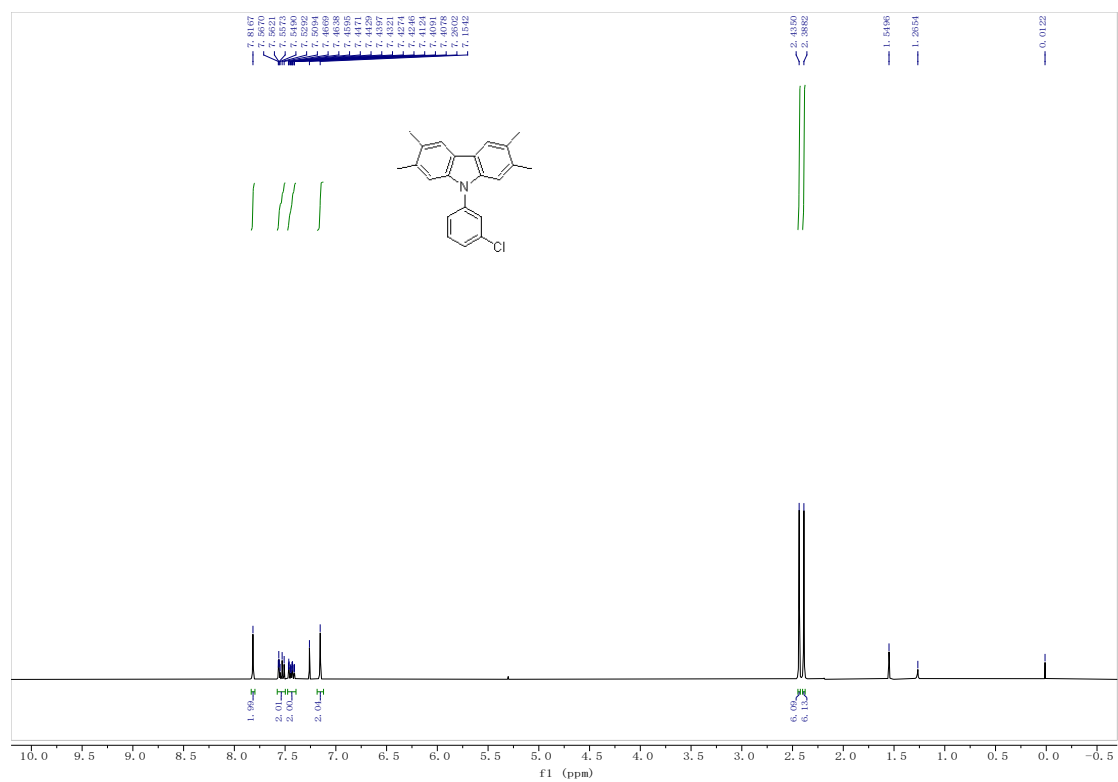
# 9-(naphthalen-1-yl)-9H-carbazole(3k)



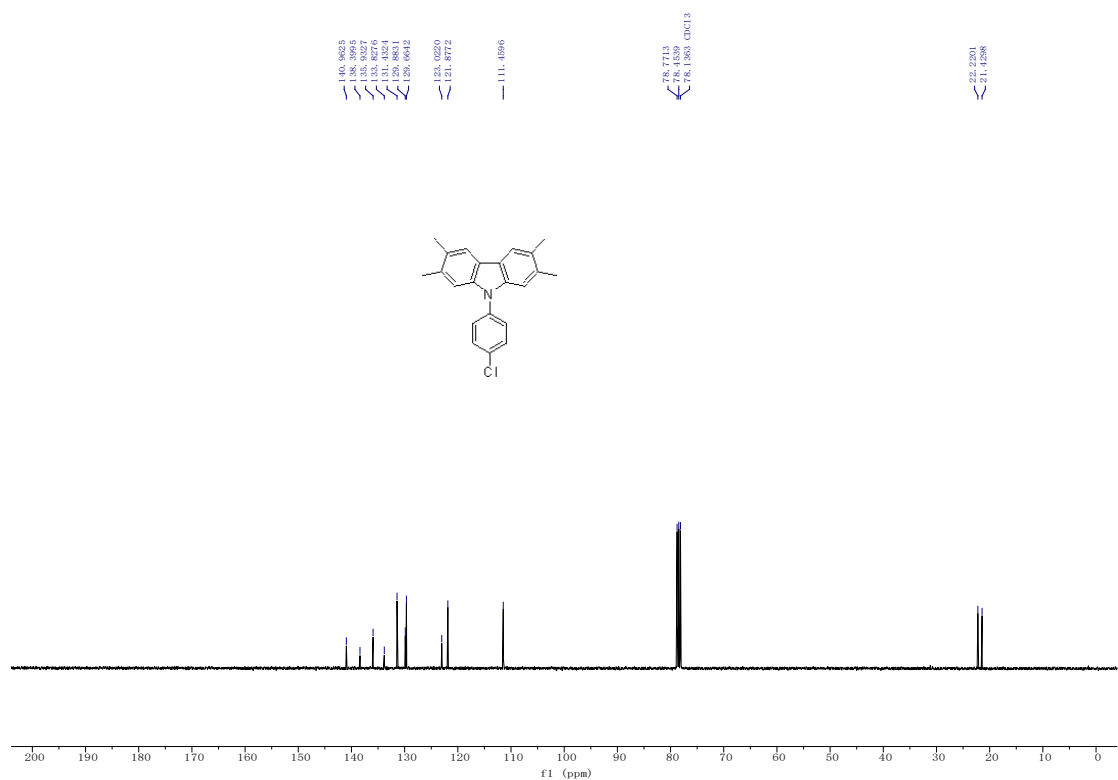
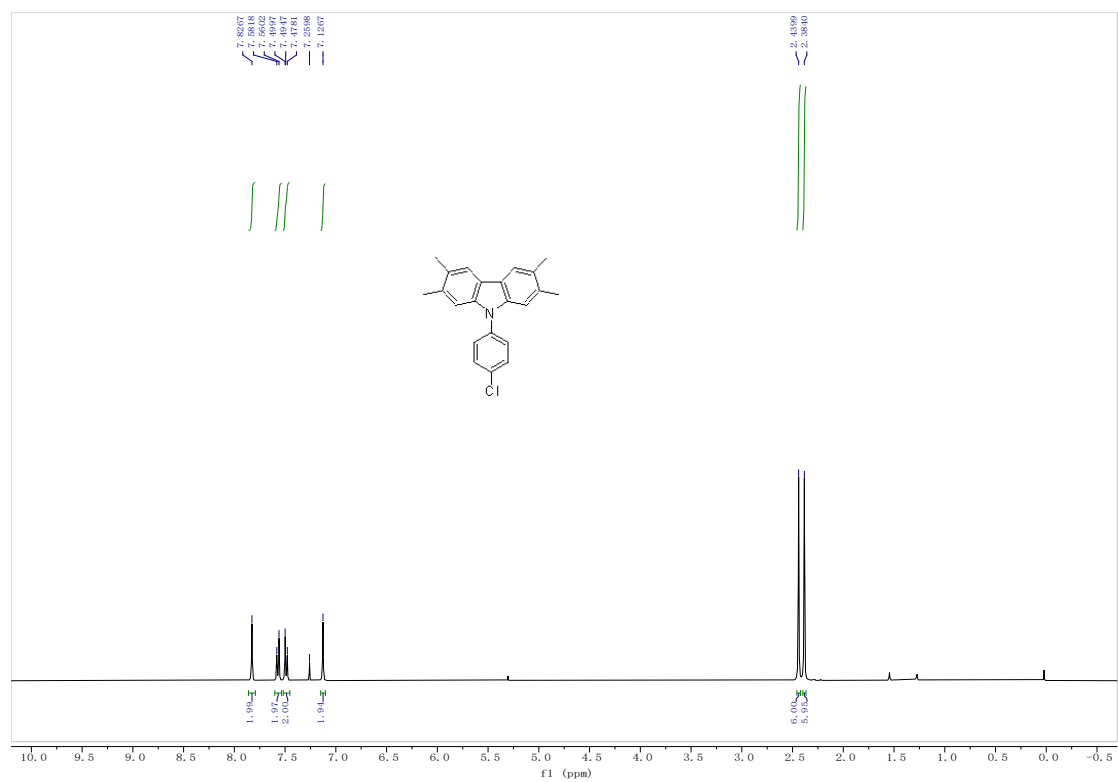
**9-(2-chlorophenyl)-2,3,6,7-tetramethyl-9H-carbazole ( 3l )**



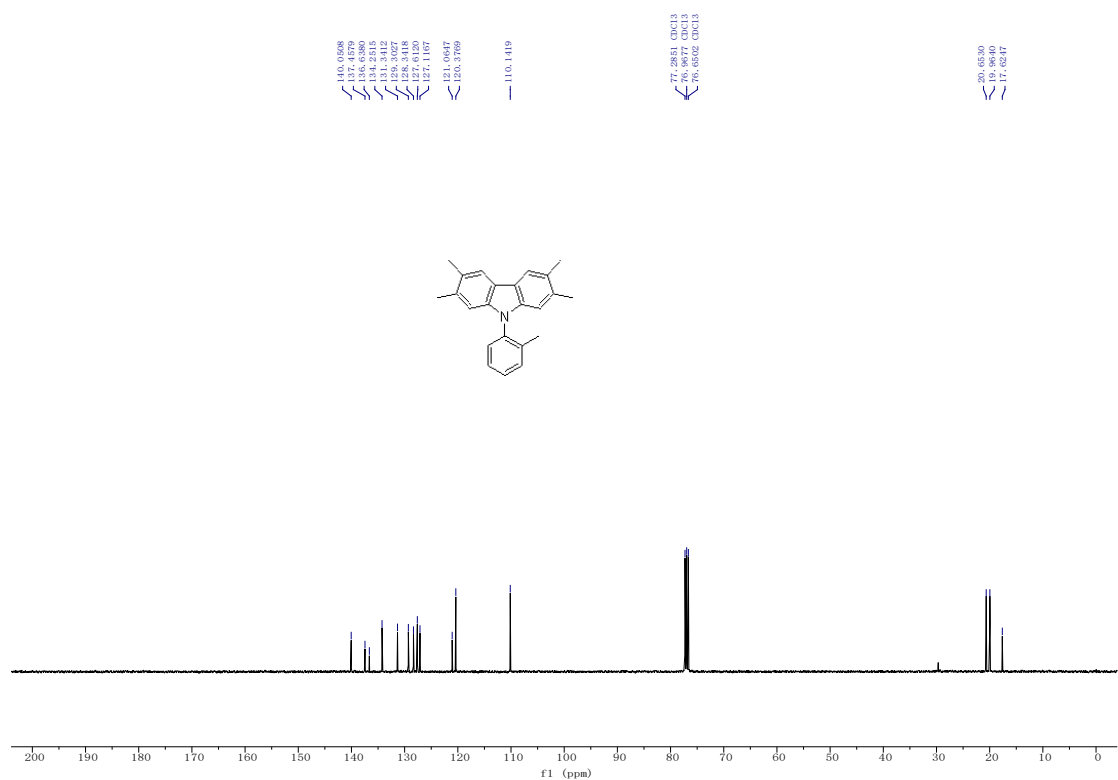
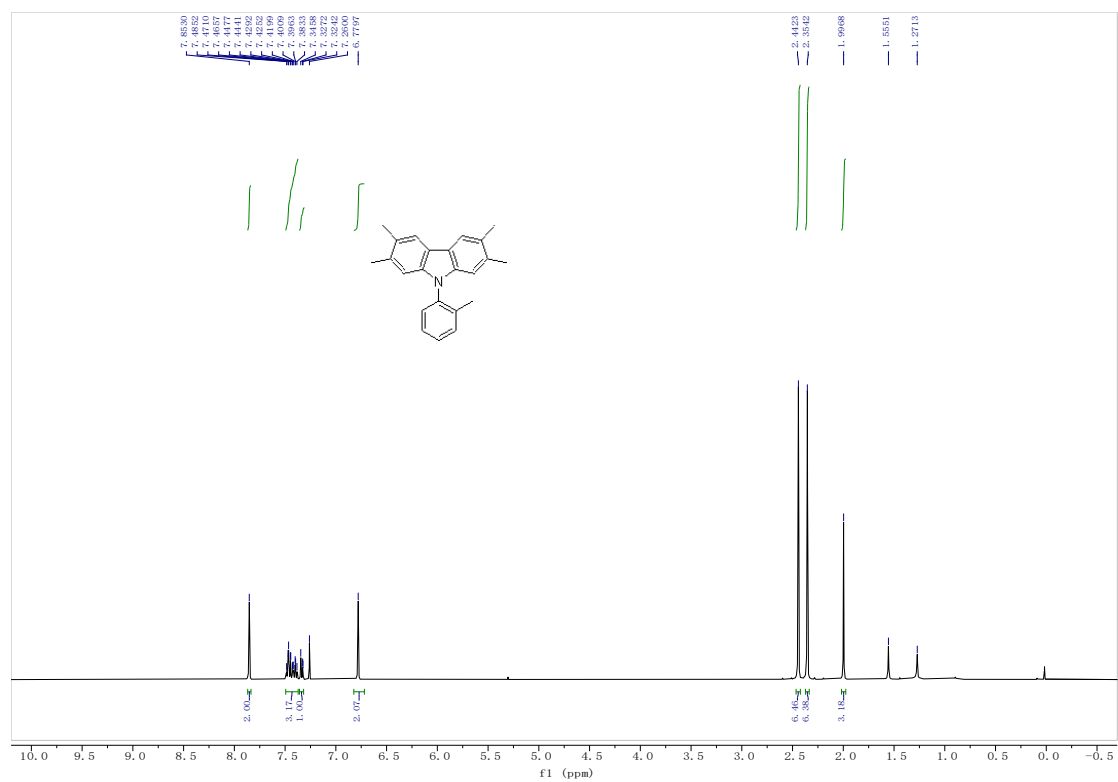
# 9-(3-chlorophenyl)-2,3,6,7-tetramethyl-9H-carbazole(3m)



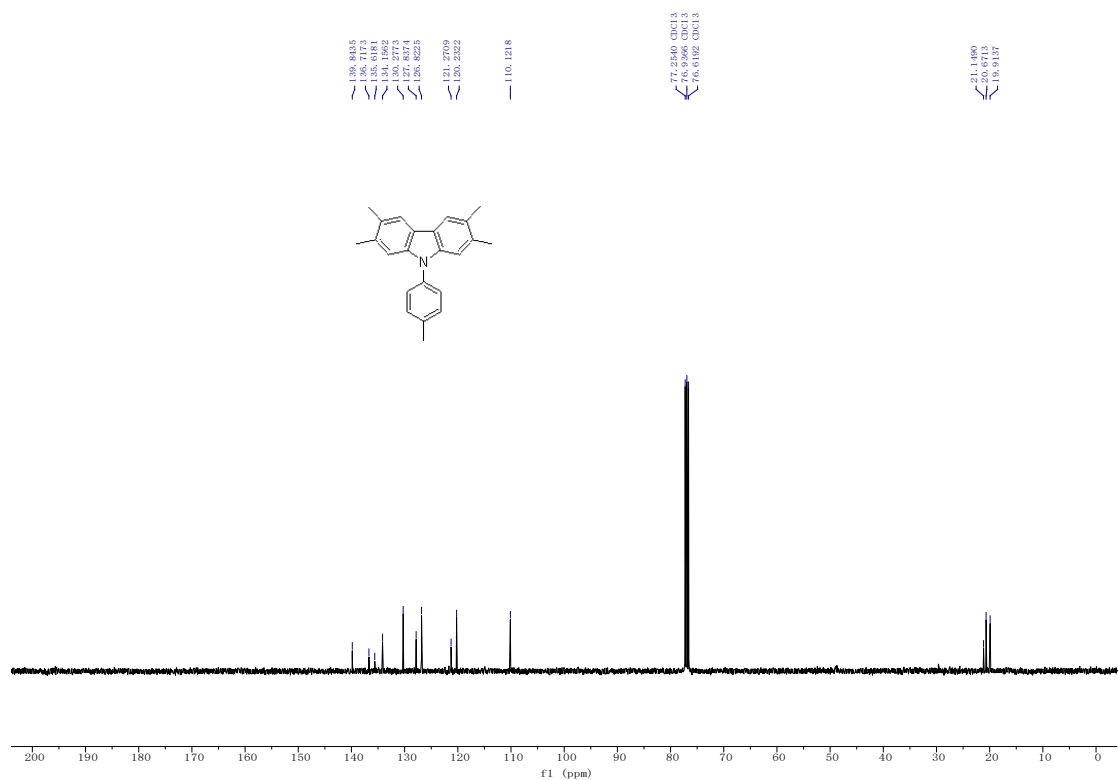
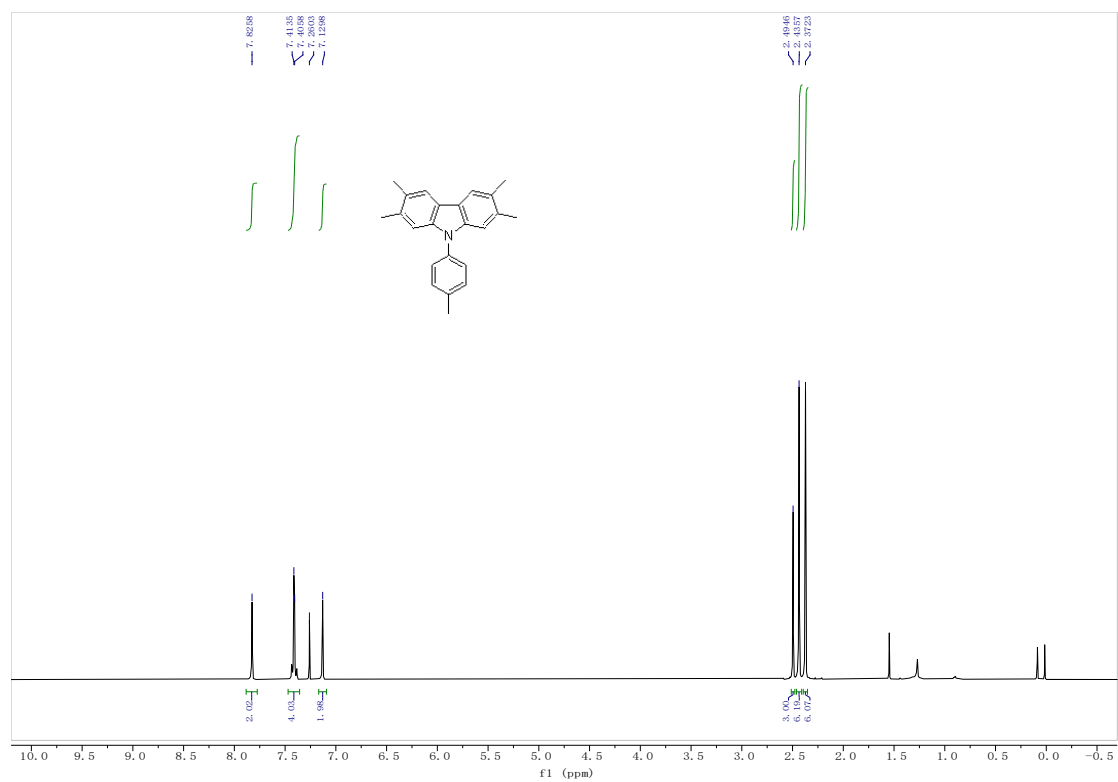
**9-(4-chlorophenyl)-2,3,6,7-tetramethyl-9H-carbazole(3n)**



2,3,6,7-tetramethyl-9-(*o*-tolyl)-9*H*-carbazole(3o)

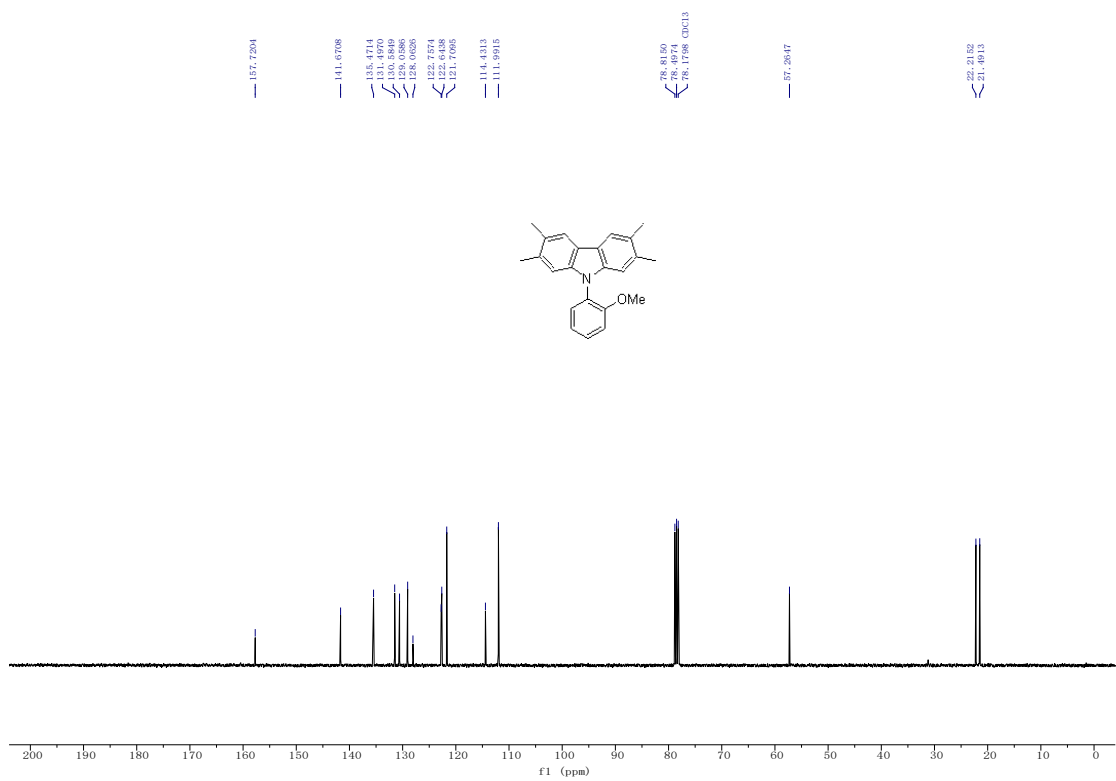
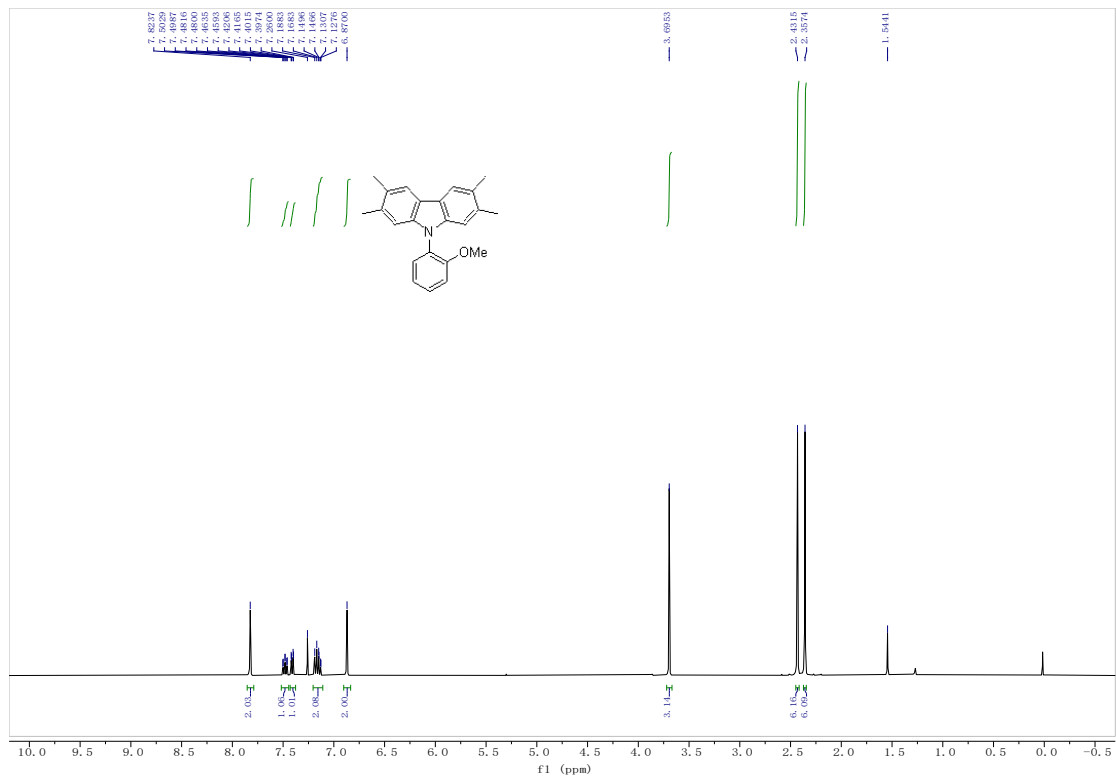


**2,3,6,7-tetramethyl-9-(p-tolyl)-9H-carbazole(3p)**

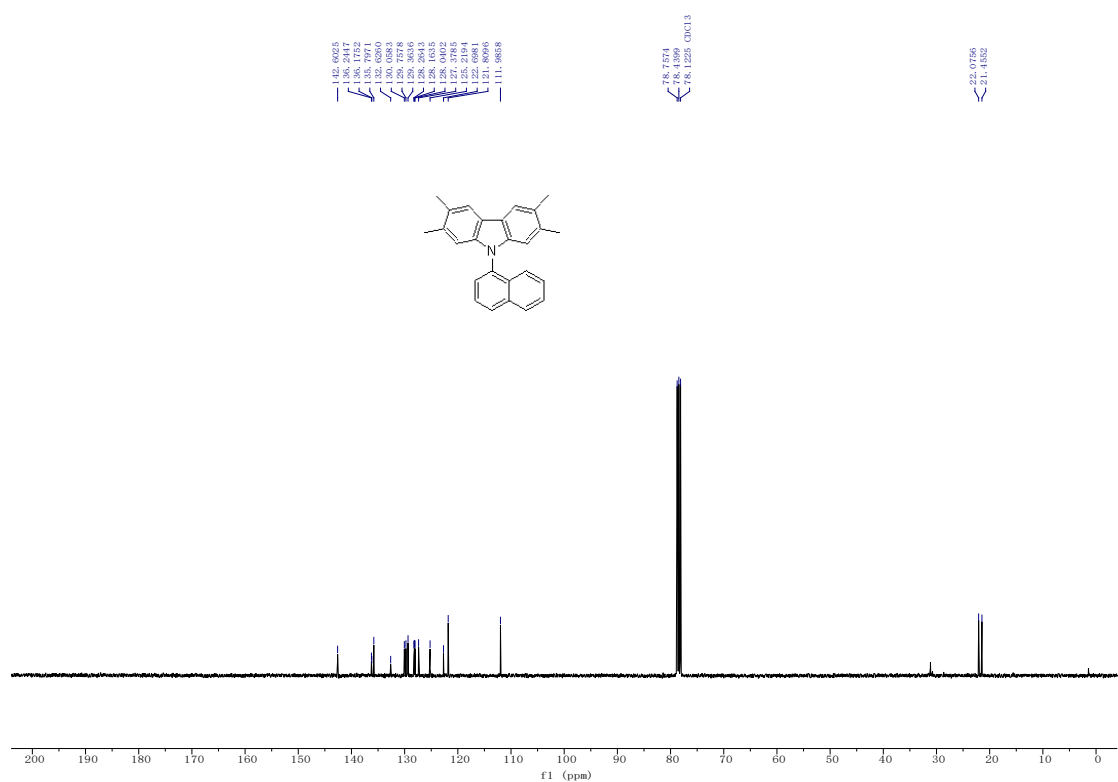
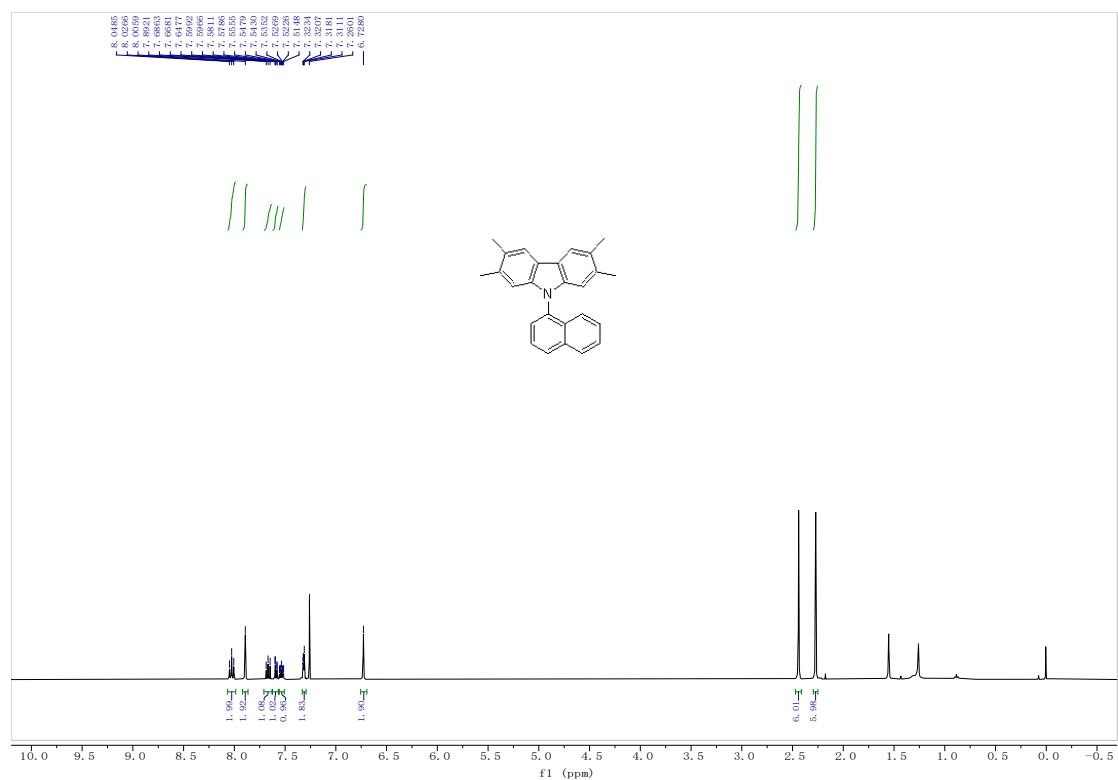




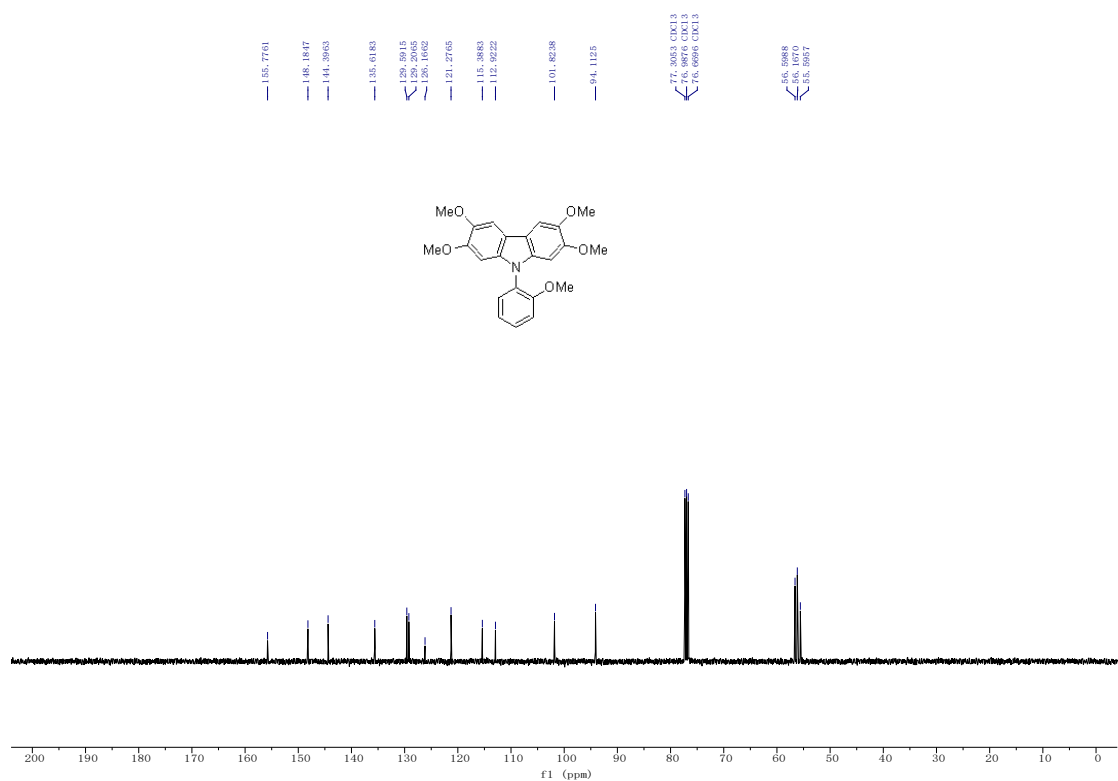
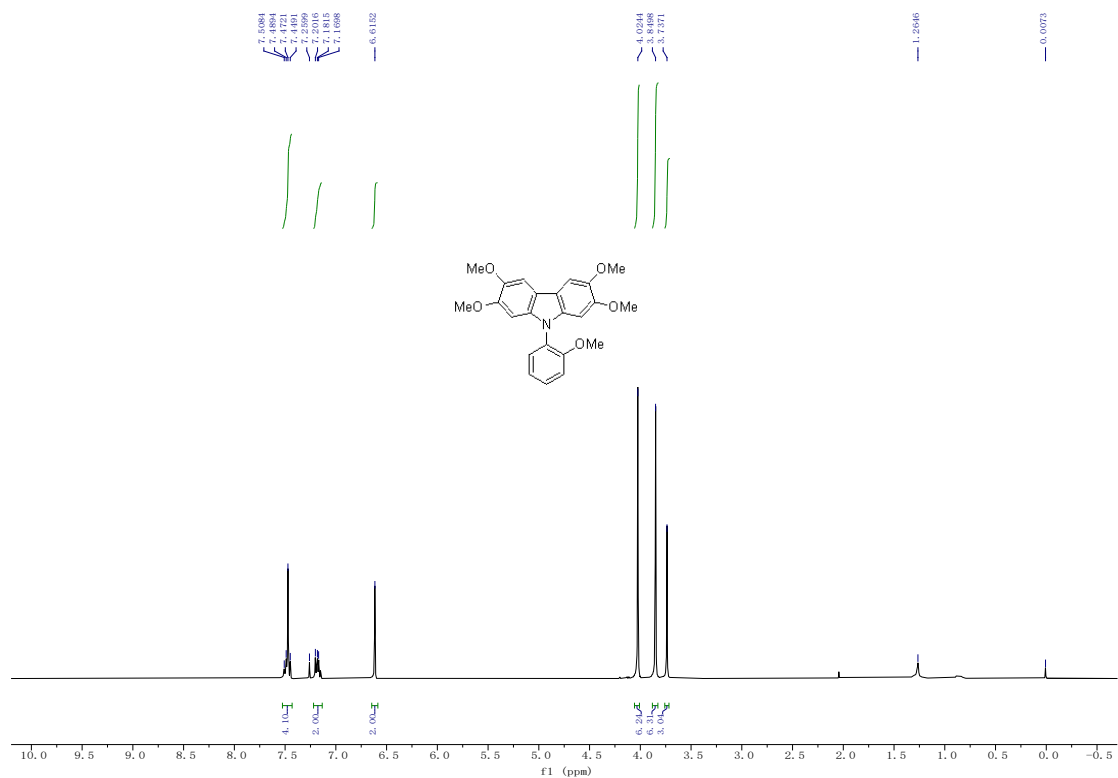
### 9-(2-methoxyphenyl)-2,3,6,7-tetramethyl-9H-carbazole(3q)



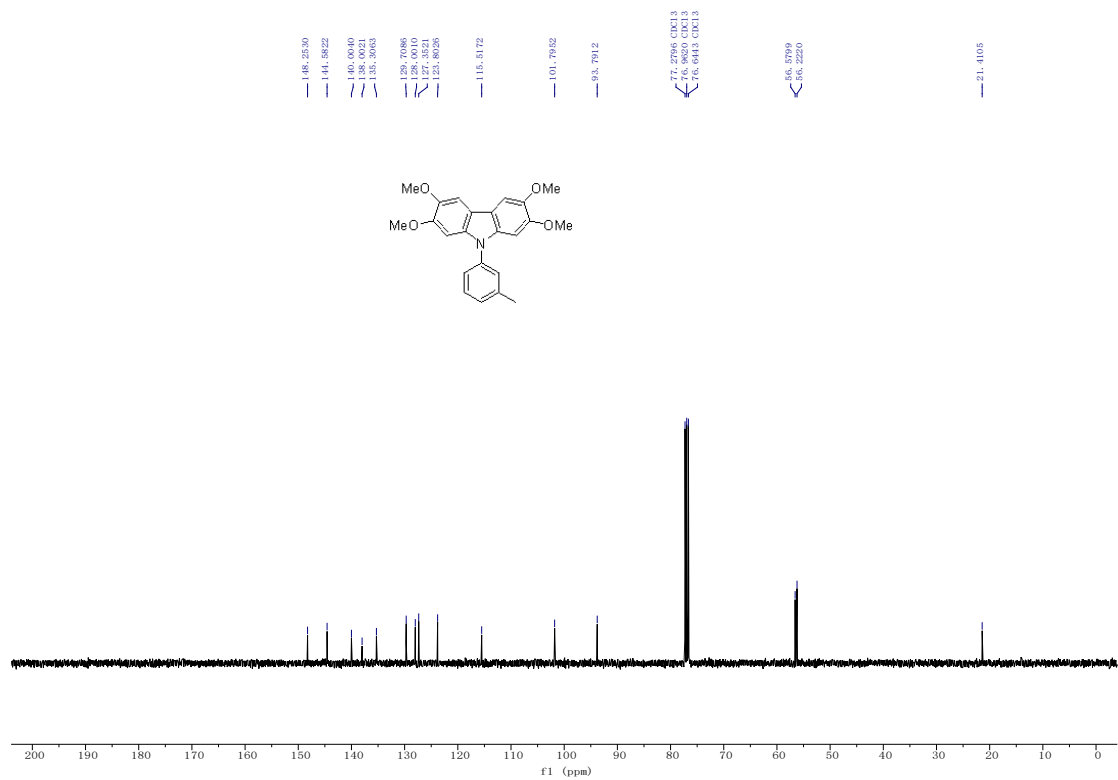
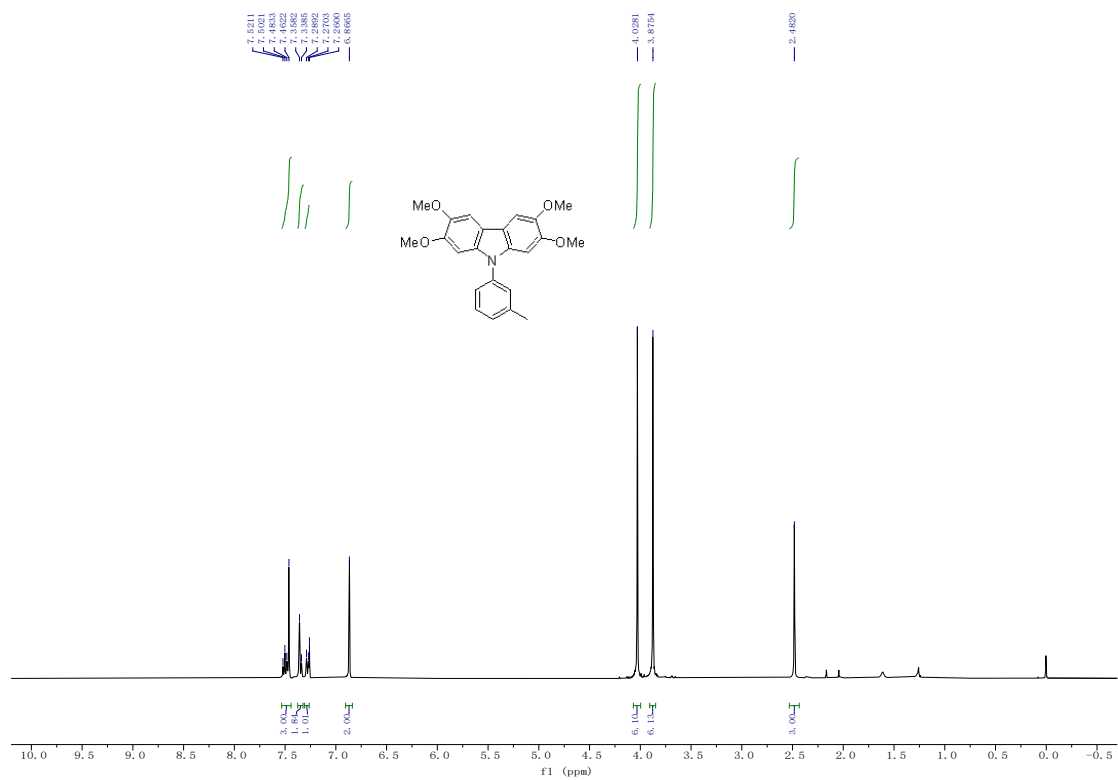
**2,3,6,7-tetramethyl-9-(naphthalen-1-yl)-9H-carbazole(3r)**



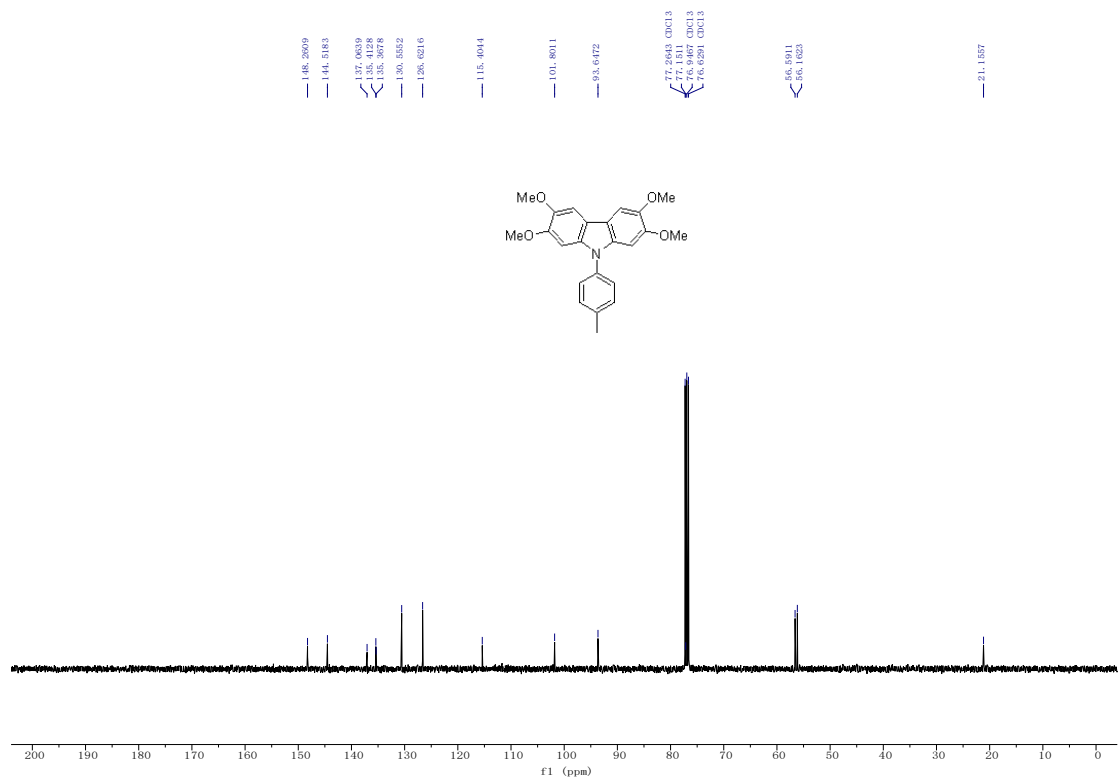
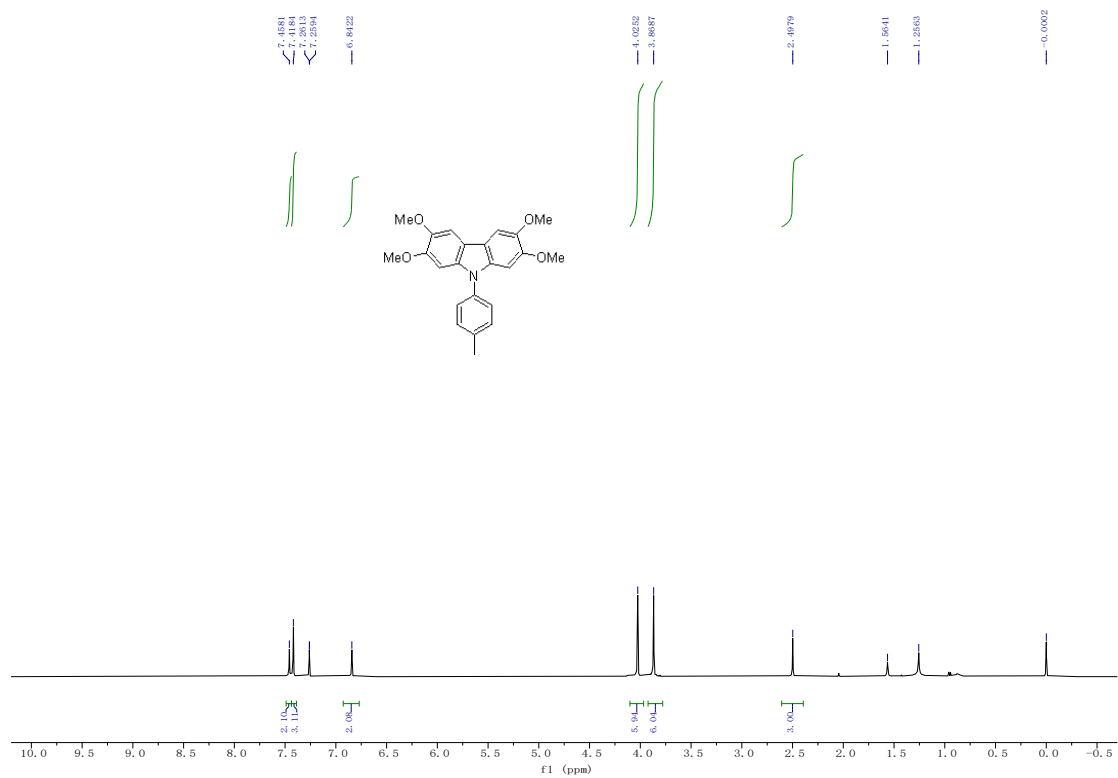
# 2,3,6,7-tetramethoxy-9-(2-methoxyphenyl)-9H-carbazole(3s)



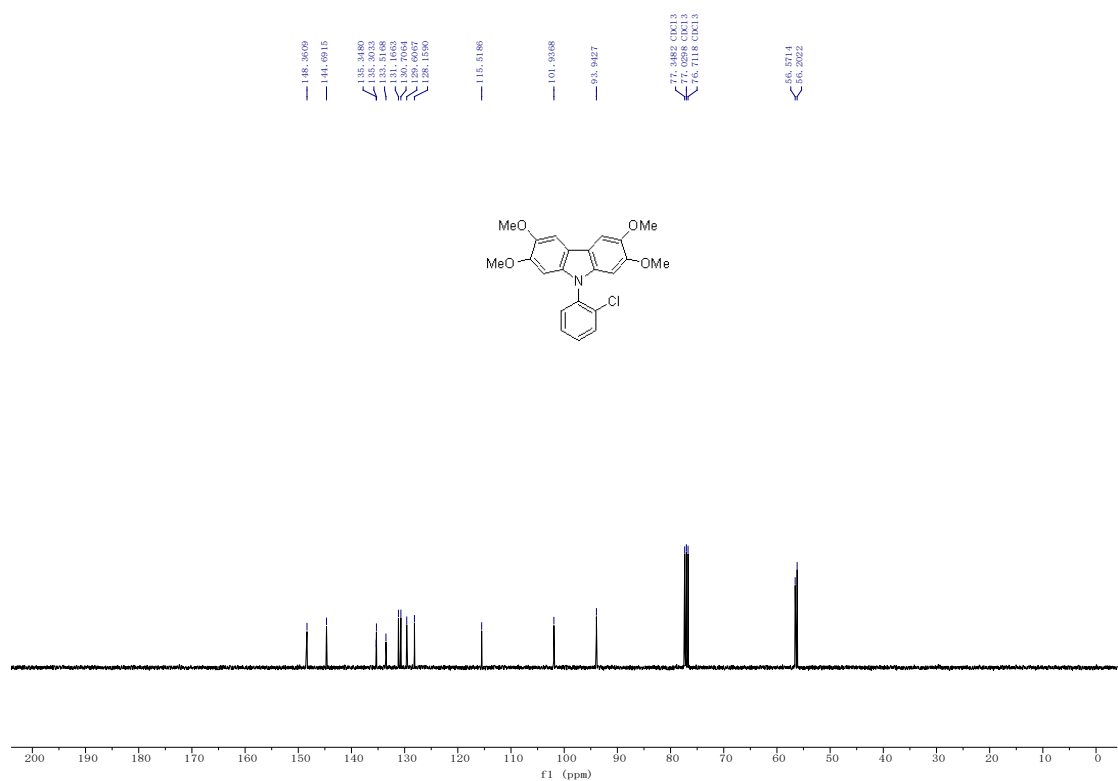
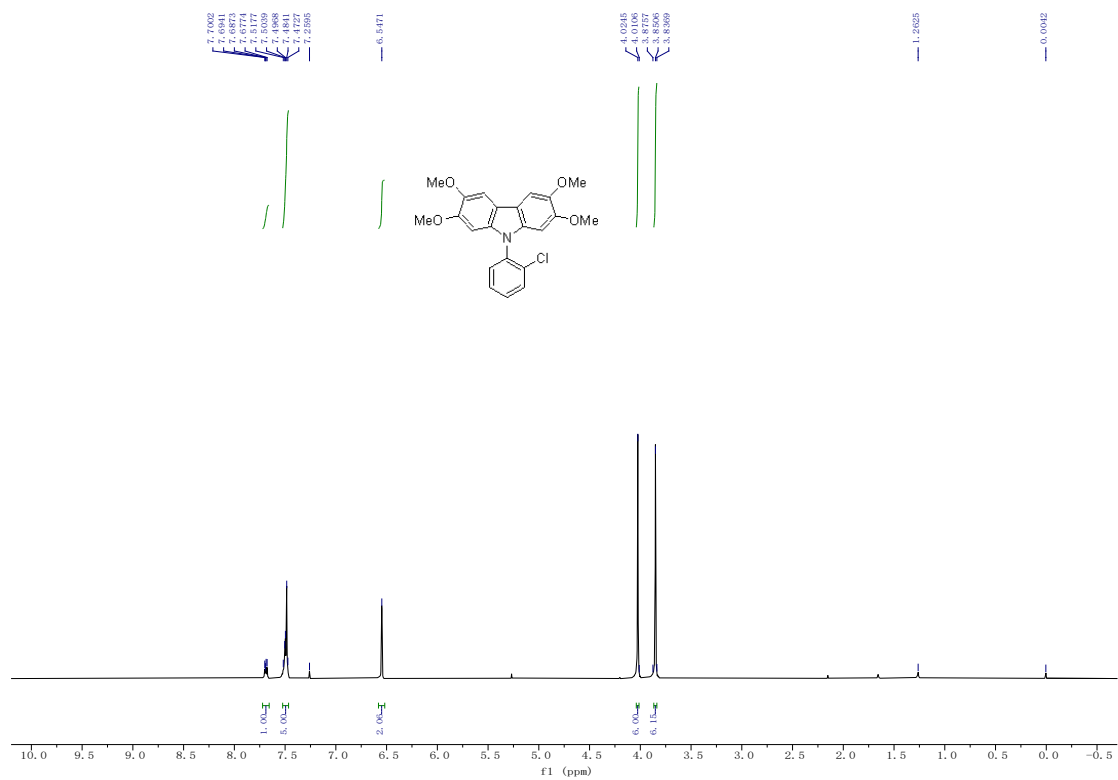
# 2,3,6,7-tetramethoxy-9-(m-tolyl)-9H-carbazole(3t)



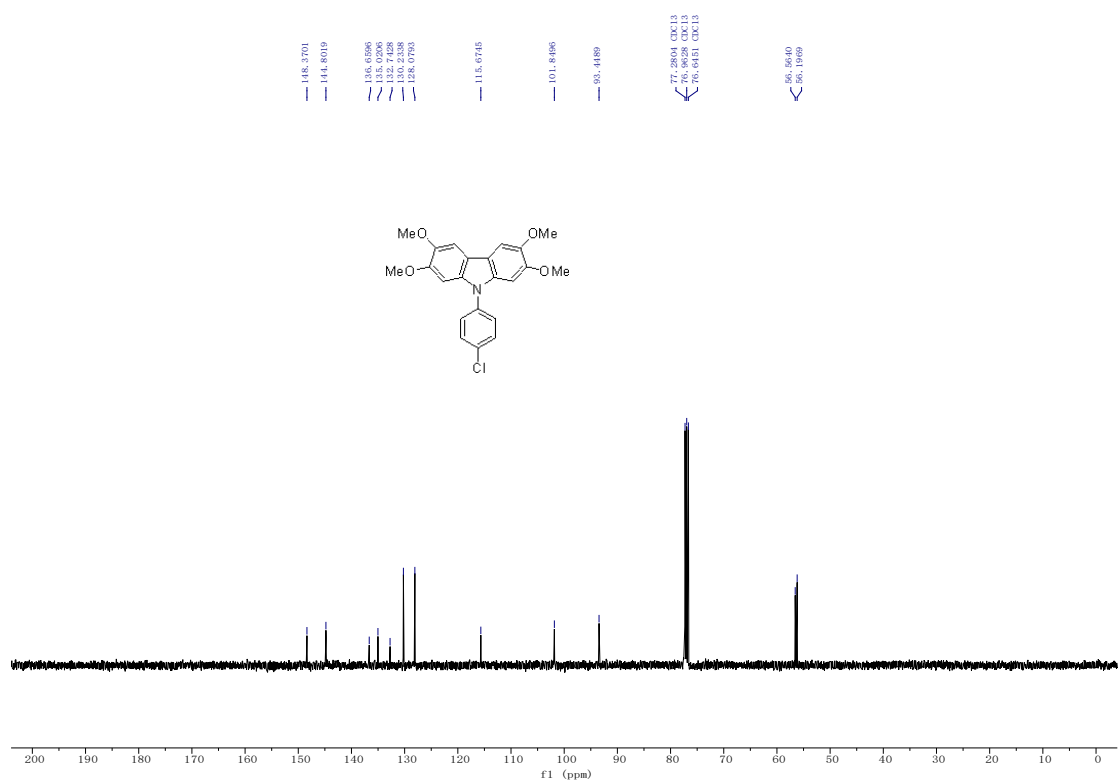
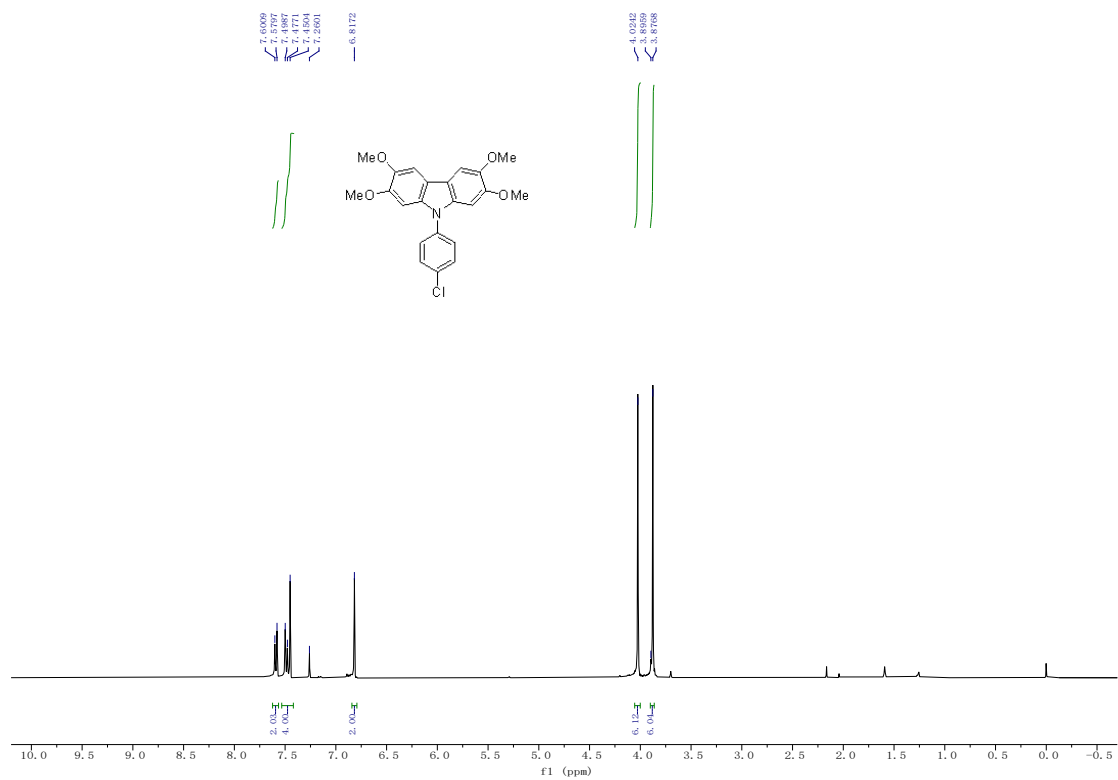
**2,3,6,7-tetramethoxy-9-(p-tolyl)-9H-carbazole(3u)**



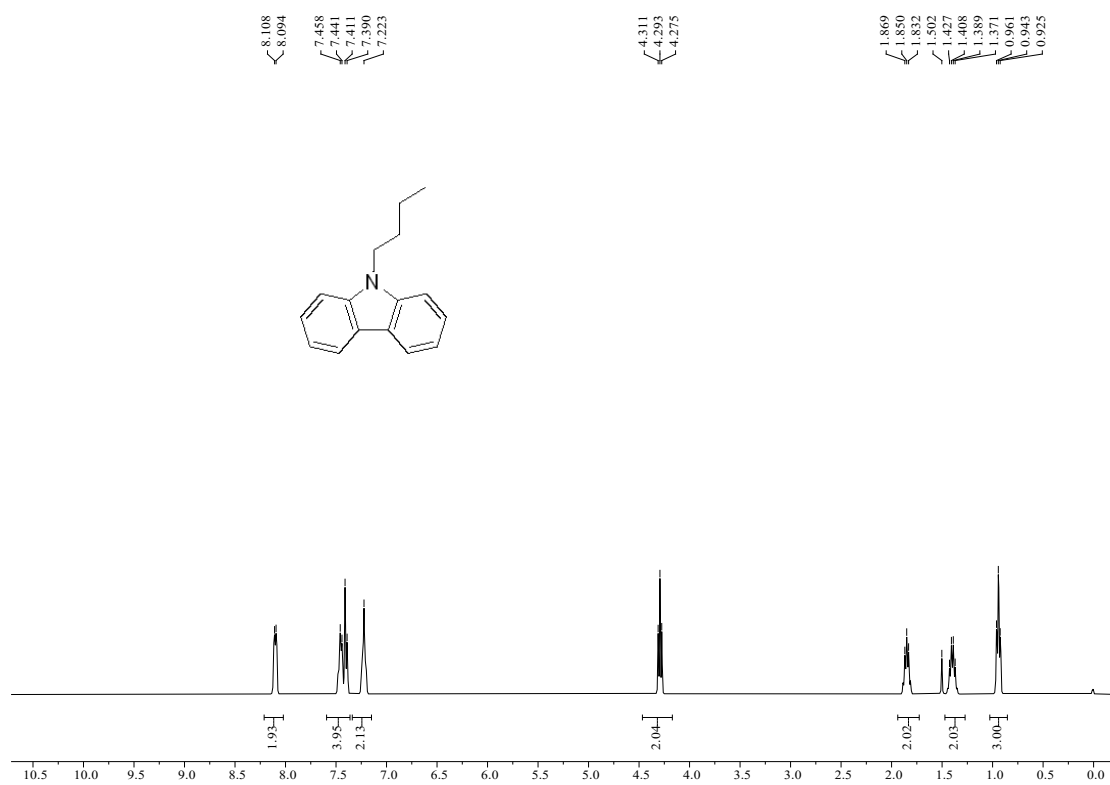
**9-(2-chlorophenyl)-2,3,6,7-tetramethoxy-9H-carbazole(3v)**



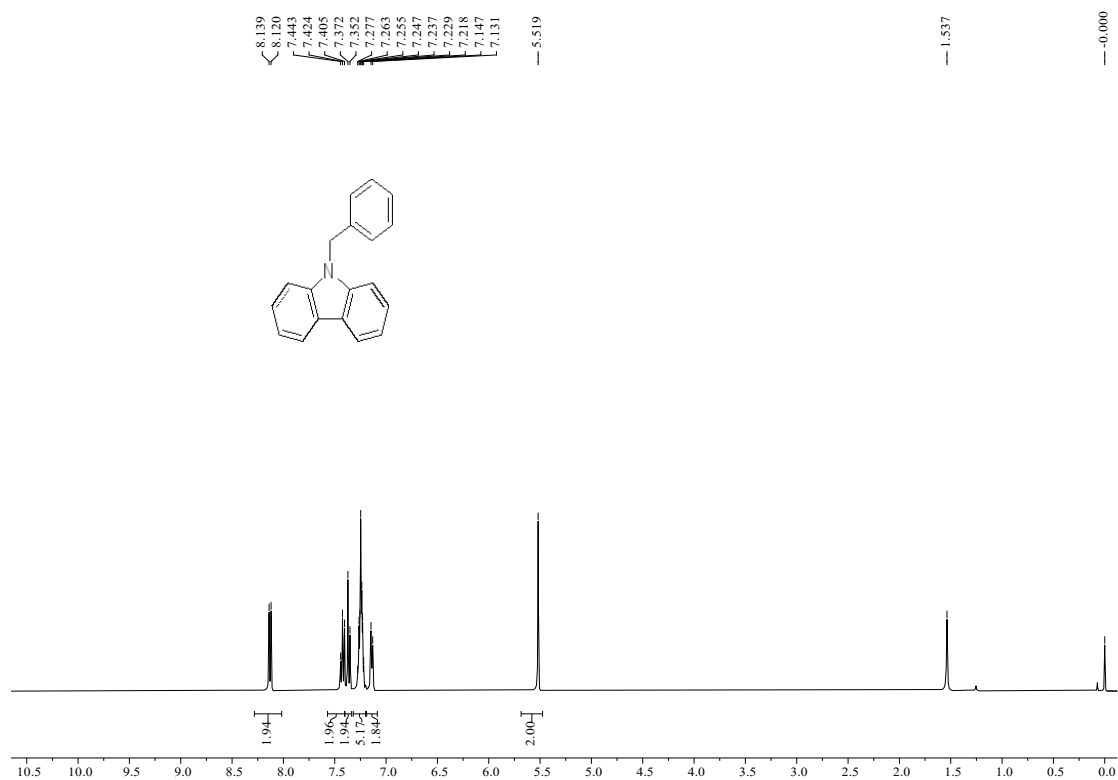
9-(4-chlorophenyl)-2,3,6,7-tetramethoxy-9H-carbazole(3w)



### 9-butyl-9H-carbazole(3x)



### 9-benzyl-9H-carbazole (3y)





9H-carbazole(3z)

