

## Synthesis and Properties of 9,9-Diarylfuorene Based Triaryldiamines

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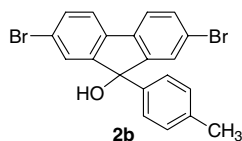
### Supporting Information

**General Experimenters.** All reactions were performed under argon and were magnetically stirred. Solvents were distilled from appropriate drying agent prior to use: THF and Et<sub>2</sub>O from sodium and benzophenone, benzene and toluene from sodium, CH<sub>2</sub>Cl<sub>2</sub> from CaH<sub>2</sub>. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by TLC with Macherey-Nagel pre-coated aluminum foil sheets (0.20 mm with fluorescent indicator UV<sub>254</sub>). Compounds were visualized with UV light at 254 nm and 365 nm. Column chromatography was carried out using flash silica gel from Macherey-Nagel (230~400 mesh). Melting points were measured on a Fargo MP-1D and are uncorrected. Infra-red (IR) spectra were recorded within KBr on a Nicolet FT-IR spectrometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded using a Bruker or Varian spectrometer at 400 MHz and 100 MHz respectively. Low and high resolution mass spectra were recorded using a Jeol SX-102A spectrometer in FAB mode. Microanalyses were carried out on a Perkin-Elmer 240 analyzer. Absorption spectra were recorded on a Shimadzu UV-160 spectrometer. Emission spectra were recorded on a Aminco-Bowman Series 2 Luminescence spectrometer upon excitation at the absorption maxima in the same solvent after saturating with argon. Cyclic voltammetry (CV) was performed on a Princeton Applied Research potentiostat 273A. All CV measurements were carried out in anhydrous CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAPF<sub>6</sub> as a supporting electrolyte, purging with argon prior to conduct the experiment. Carbon electrode was used as working electrode, 0.01 M AgNO<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> as reference electrode, and a platinum wire as counting electrode. Differential scanning calorimetry (DSC) analyses were performed on a TA Instrument DSC-2920 Low-Temperature Difference Scanning Calorimeter, the sample was firstly heated (20 °C/min) to melt, then quenched with liquid nitrogen, *T*<sub>g</sub>s were recorded by heating (10 °C/min) the quenched sample.

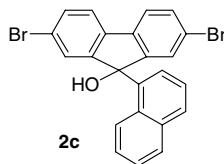
### General procedure for the addition of Grignard reagents to 2,7-dibromofluorene 1:

The Grignard reagents were prepared from magnesium powders (486 mg, 20 mmol) in Et<sub>2</sub>O (5 mL) and the corresponding arylbromide (20 mmol) in Et<sub>2</sub>O (15 mL). The cooled Grignard solution was diluted with dry Et<sub>2</sub>O (20 mL) and 2,7-dibromofluorene **1** (10 mmol) was added into the Grignard solution. The mixture was refluxed for 2~6 h and then stirred for another 2 h at room temperature. The reaction mixture, was hydrolyzed with saturated NH<sub>4</sub>Cl solution, extracted with Et<sub>2</sub>O, washed with brine, dried over MgSO<sub>4</sub>. Evaporation of the solvent under reduced pressure yielded the crude product.

Purification was effected by column chromatography (SiO<sub>2</sub>, EtOAc/Hexane = 1/5) and recrystallization from CH<sub>2</sub>Cl<sub>2</sub> and hexane yielded colorless crystal.



2,7-dibromofluorene **1** (3.4g, 10 mmol), 1-bromo-4-methylbenzene (2.55 g, 15 mmol), magnesium powder (0.36 g, 15 mmol), Et<sub>2</sub>O (40 mL) refluxed 6 h to afford **2b** (3.50 g, 82%). mp 150~151 °C; IR (KBr)  $\nu$  3528 (br), 1511 (m), 1448 (m), 1399 (m), 1254 (m), 1168 (m), 1056 (m), 1037 (m), 817 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (Acetone-d<sub>6</sub>, 400 MHz)  $\delta$  7.77 (d,  $J$  = 8.1 Hz, 2H), 7.56 (d,  $J$  = 8.1, 1.9 Hz, 2H), 7.41 (d,  $J$  = 1.9 Hz, 2H), 7.23 (d,  $J$  = 8.3 Hz, 2H), 7.30 (d,  $J$  = 8.3 Hz, 2H), 5.46 (s, 1H), 2.28 (s, 3H); <sup>13</sup>C NMR (Acetone-d<sub>6</sub>, 100 MHz)  $\delta$  153.6, 140.3, 137.8, 136.9, 131.8, 128.9, 127.9, 125.1, 122.1, 121.6, 82.8, 20.1; MS (m/z, FAB<sup>+</sup>) 428 (80), 413 (100), 307 (40); HRMS Calcd for C<sub>20</sub>H<sub>14</sub><sup>79</sup>Br<sup>81</sup>BrO 429.9391, found 429.9398. Anal Calcd for C<sub>20</sub>H<sub>14</sub>Br<sub>2</sub>O C, 55.85; H, 3.28 found C, 56.01; H, 3.24.

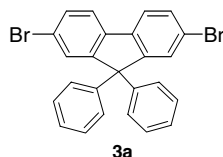


2,7-dibromofluorene **1** (3.4g, 10 mmol), 1-bromonaphthylene (4.59g, 20 mmol), magnesium powder (0.48 g, 20 mmol), Et<sub>2</sub>O (40 mL) refluxed for 3 h afford **2c** (9.2 g, 97%). mp 226~227 °C; IR (KBr)  $\nu$  3435 (br), 1563 (m), 1543 (m), 1451 (m), 1392 (s), 1247 (w), 1215 (w), 1162 (m), 1057 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  8.52 (d,  $J$  = 6.8 Hz, 1H), 7.89 (d,  $J$  = 7.8 Hz, 1H), 7.81 (d,  $J$  = 7.8 Hz, 1H), 7.58~7.72 (m, 3H), 7.53 (dd,  $J$  = 1.6, 6.8 Hz, 2H), 7.14~7.34 (m, 3H), 6.96 (t,  $J$  = 7.2 Hz, 1H), 6.79 (d,  $J$  = 8.4 Hz, 1H), 2.51 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  152.5, 137.5, 135.1, 134.2, 132.6, 129.6, 129.1, 128.9, 127.8, 126.0, 125.1, 124.2, 122.9, 122.2, 82.3; MS (m/z, FAB<sup>+</sup>) 466 (5), 449 (5), 391 (1), 341 (2), 154 (100); HRMS (FAB) calcd for C<sub>23</sub>H<sub>14</sub><sup>79</sup>Br<sup>81</sup>BrO 463.9411, found 463.9394, Calcd for C<sub>23</sub>H<sub>14</sub><sup>79</sup>Br<sup>81</sup>BrO 465.9391, found 465.9383, Calcd for C<sub>23</sub>H<sub>14</sub><sup>81</sup>Br<sub>2</sub>O 467.9370, found 467.9371. Anal. Calcd for C<sub>23</sub>H<sub>14</sub>Br<sub>2</sub>O C, 59.26; H, 3.03, found C, 59.15; H, 3.23.

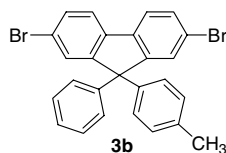
#### General procedure for the synthesis of 9,9-diaryl-2,7-dibromofluorene **3** by CF<sub>3</sub>SO<sub>3</sub>H-promoted Friedel-Crafts reaction of alcohol **2**:

Alcohol **2** (1 equivalent) was dissolved in dried toluene or benzene. To this solution was heated to 50 °C. CF<sub>3</sub>SO<sub>3</sub>H (1 equivalent) was added dropwisely to afford a light brown solution. The mixture was stirred for another 10 min. The mixture was poured into a ice cold sat. NaHCO<sub>3</sub> aq. solution. The organic layer was separated, the aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine and dried over MgSO<sub>4</sub>. Concentration of the organic solution afforded

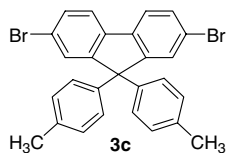
crude product which was further purified by column chromatography on SiO<sub>2</sub> (EtOAc/hexane = 1/5) to give the desired product. Analytical pure product can be obtained as a colorless solid by recrystallization or sublimation under vacuum.



**2a** (10.45g, 25 mmol), CF<sub>3</sub>SO<sub>3</sub>H (4.48 ml, 50 mmol), and benzene (136 ml) stirred at 80 °C for 6h, recrystallization from THF/Hexane afforded **3a** ( 10.5 g, 88%). mp 279-280 °C; IR (KBr)  $\nu$  1494 (w), 1457 (w), 813 (m), 701 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.60 (d, *J* = 8.0 Hz, 2H), 7.50 (s, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.28~7.25 (m, 6H), 7.17~7.14 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  152.9, 144.4, 138.1, 130.9, 129.4, 128.5, 128.0, 127.2, 121.8, 121.6, 65.6. MS (m/z, FAB<sup>+</sup>) 476 (58), 474 (30), 460 (100), 443 (15), 399 (38). HRMS (FAB) Calcd for C<sub>25</sub>H<sub>16</sub><sup>79</sup>Br<sub>2</sub> 473.9619, found 473.9608; Calcd for C<sub>25</sub>H<sub>16</sub><sup>79</sup>Br<sup>81</sup>Br 475.9598, found 475.9586; Calcd for C<sub>25</sub>H<sub>16</sub><sup>81</sup>Br<sub>2</sub> 477.9578, found 477.9587. Anal. Calcd. C, 63.05; H, 3.39. found C, 62.65; H, 3.25.

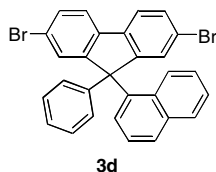


**2a** (2.08 g, 5.0 mmol), CF<sub>3</sub>SO<sub>3</sub>H (0.92 mL, 10 mmol), and toluene (20 mL) reacted at 50 °C for 10 min. Sublimation at 240 °C (0.01 torr) gave **3b** (2.06 g, 84%). mp 228~230 °C; IR (KBr)  $\nu$  3043 (w), 2916 (w), 1602 (w), 1589 (w), 1510 (m), 1491 (m), 1451 (m), 1398 (m), 1247 (m), 1063 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.59 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 0.8 Hz, 2H), 7.48 (dd, *J* = 0.8, 8.0 Hz, 2H), 7.14~7.18 (m, 2H), 7.24~7.28 (m, 3H), 7.01 (dd, *J* = 6.0, 8.4 Hz, 4H), 2.32 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  153.1, 144.5, 141.4, 138.0, 136.8, 130.9, 129.4, 129.2, 128.9, 127.8, 127.1, 121.8, 121.5, 65.3, 21.0; MS (m/z, FAB<sup>+</sup>) 490 (6), 460 (4), 409 (2). Anla. Calcd for C<sub>26</sub>H<sub>18</sub>Br<sub>2</sub> C, 63.70, H, 3.70, found C, 63.69, ; H, 3.85.

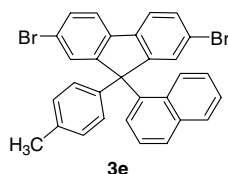


**2b** (1.29 g, 3.0 mmol), CF<sub>3</sub>SO<sub>3</sub>H (0.54 mL, 6.0 mmol), toluene (20 mL) reacted at 50 oC for 10 min. Sublimation was conducted at 240 °C (0.01 torr), giving **3c** (1.38g, 91%). mp 280~282 °C; IR (KBr)  $\nu$  3021 (w), 2922 (w), 1595 (m), 1503 (m), 1451 (m), 1398 (s), 1057 (m), 932 (w), 807 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.57 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 1.4 Hz, 2H), 7.46 (dd, *J* = 1.4, 8.0 Hz,

2H), 7.0~7.14 (m, 8H), 2.32 (s, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100MHz)  $\delta$  153.0, 141.5, 138.0, 136.8, 130.8, 129.3, 129.2, 127.8, 121.8, 121.5, 65.0, 21.0; MS ( $m/z$ ,  $\text{FAB}^+$ ) 504 (2), 502 (1), 460 (5), 443 (1), 413 (1), 391 (1), 154 (100). Anal. Calcd for  $\text{C}_{27}\text{H}_{20}\text{Br}_2$  C, 64.30; H, 4.00, found C, 64.19; H, 4.10.



**2c** (1.86 g, 4.0 mmol),  $\text{CF}_3\text{SO}_3\text{H}$  (0.72 mL, 8.0 mmol), benzene (50 mL) reacted at 50 °C for 30 min. Recrystallization from  $\text{CHCl}_3$  and hexanes gave **3d** (1.18 g, 56%). mp 282~284 °C; IR (KBr)  $\nu$  3441(s), 1596 (m), 1491 (m), 1449 (s), 1398 (m), 1254 (m), 1065 (m), 809 (m), 777 (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.81~7.84 (d,  $J$  = 8.0 Hz, 1H), 7.74~7.81 (d,  $J$  = 8.0 Hz, 1H), 7.54~7.70 (m, 4H), 7.44~7.52 (dd,  $J$  = 8.0 Hz, 1.6 Hz, 2H), 7.39 (t,  $J$  = 7.6 Hz, 1H), 7.18~7.28 (m, 5H), 7.06~7.18 (br, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  153.3, 144.7, 137.8, 135.4, 131.5, 131.0, 129.4, 129.3, 129.2, 128.9, 127.0, 125.3, 125.2, 125.0, 121.8, 121.7, 66.4; MS ( $m/z$ ,  $\text{FAB}^+$ ) 526 (1); HRMS Calcd for  $\text{C}_{29}\text{H}_{18}^{81}\text{Br}_2$  527.9734, found 527.9717; Calcd for  $\text{C}_{29}\text{H}_{18}^{79}\text{Br}^{81}\text{Br}$  525.9755, found 525.9753, Calcd for  $\text{C}_{29}\text{H}_{18}^{79}\text{Br}_2$  523.9775, found 523.9755. Anal. Calcd for  $\text{C}_{29}\text{H}_{18}\text{Br}_2$  C, 66.19; H, 3.45, found C, 66.21; H, 3.30.

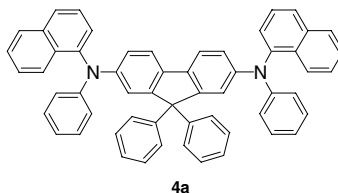


**2c** (1.86 g, 4.0 mmol),  $\text{CF}_3\text{SO}_3\text{H}$  (0.72 mL, 8.0 mmol), toluene (50 mL) reacted at 50 °C for 10 min. Recrystallization from  $\text{CH}_2\text{Cl}_2$  and hexanes gave **3e** (1.86 g, 86%). mp 264~266 °C; IR (KBr)  $\nu$  3021 (w), 1595 (s), 1486 (s), 1466 (s), 1318 (s), 1296 (s), 1272 (s), 761 (s), 721 (s), 697 (m);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.84 (d,  $J$  = 8.6 Hz, 1H), 7.77 (d,  $J$  = 8.6 Hz, 1H), 7.48 (d,  $J$  = 8.3 Hz, 4H), 7.46 (dd,  $J$  = 8.3, 1.8 Hz, 2H), 7.38 (t,  $J$  = 7.2 Hz, 1H), 7.24~7.07 (br, 3H), 7.01 (s, 5H), 2.29 (s, 3H);  $^{13}\text{C}$  NMR (Acetone, 100 MHz)  $\delta$  153.6, 141.6, 139.4, 137.8, 136.6, 135.3, 131.5, 130.9, 129.6, 129.4, 129.3, 129.1, 126.4, 125.9, 125.3, 125.2, 124.9, 121.8, 121.6, 66.1, 20.8; MS ( $m/z$ ,  $\text{FAB}^+$ ) 539.9(15), 307.0(30), 289.0(20), 154.0(100), 136.0(60); Anla. Calcd for  $\text{C}_{30}\text{H}_{20}\text{Br}_2$  C, 66.69, H, 3.73, found C, 66.36, ; H, 3.65.

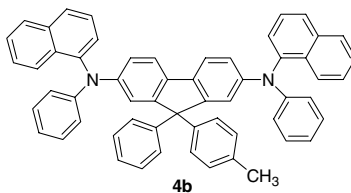
#### General procedure for the Pd-catalyzed amination of 9,9-diaryl-2,7-dibromofluorene **3** with diarylamines:

9,9-diaryl-2,7-dibromofluorene **3** (0.5 mmol), diarylamine (1.0 mmol), and sodium *tert*-butoxide (115.7 mg, 1.25 mmol) were mixed in a flask. The flask was evacuated, refilled with argon.  $\text{Pd}(\text{OAc})_2$  (5.6 mg, 0.025 mmol),  $\text{P}^t\text{Bu}_3$  (2 mL, 0.05 M in toluene, 0.1 mmol), dry toluene (4 mL) were added into the flask. The flask was heated to 100 °C with stirring until the dibromo compound **3** has been consumed

(4~8 h). The reaction mixture was then cooled to room temperature, diluted with H<sub>2</sub>O and extracted with EtOAc, combined organic solution was washed with brine and dried over MgSO<sub>4</sub>. Evaporation in vacuum vacuo afforded the crude product which was further purified by column chromatography on SiO<sub>2</sub> (EtOAc/hexane = 1/6). Analytical pure product was obtained by sublimation at 300 °C (bath temperature) under high vacuum (1.0 x 10<sup>-6</sup> torr).

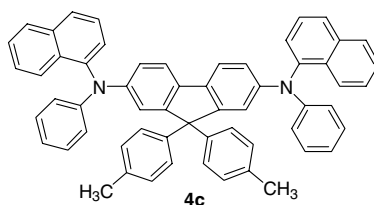


**3a** (474 mg, 1 mmole), *N*- $\alpha$ -naphthyl-*N*-phenylamine (438 mg, 2 mmol), Pd(OAc)<sub>2</sub> (11.2 mg, 0.05mmol), P<sup>t</sup>Bu<sub>3</sub> (4 mL, 0.055M in toluene, 0.22 mmol), NaO<sup>t</sup>Bu<sub>3</sub> (230 mg, 2.4mmol), toluene (5 mL), stirred for 4 h stirred to give **4a** (640 mg, 85%). IR (KBr)  $\nu$  1595 (m), 1494 (m), 1468 (m), 1304 (w), 1272 (m), 775 (w), 699 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (Acetone-d<sub>6</sub>, 400 MHz)  $\delta$  7.95 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.52~7.473 (m, 4H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 2H), 7.19~7.07 (m, 10H), 7.05 (d, *J* = 2.4 Hz, 2H), 6.95~6.90 (m, 12H). <sup>13</sup>C NMR (Acetone-d<sub>6</sub>, 100 MHz):  $\delta$  152.8, 149.2, 148.4, 146.5, 144.3, 136.4, 134.8, 131.7, 130.0, 129.4, 128.9, 128.7, 127.7, 127.4, 127.3, 127.2, 127.1, 127.0, 124.9, 122.7, 122.6, 122.1, 121.1, 120.5, 65.9. MS (*m/z*, FAB<sup>+</sup>) 752 (100), 751 (7), 535 (9). HRMS (FAB) Calcd for C<sub>57</sub>H<sub>40</sub>N<sub>2</sub>: 752.3191, found 752.3179. Anal. Calcd. For C, 90.92; H, 5.35; N, 3.72, found C, 91.06; H, 5.33; N, 3.71.

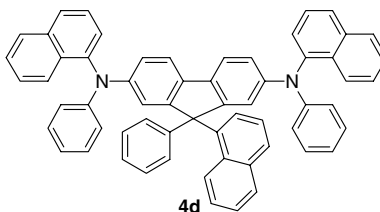


**3b** (263 mg, 0.5 mmol), *N*- $\alpha$ -naphthyl-*N*-phenylamine (219.1 mg, 1.0 mmol), Pd(OAc)<sub>2</sub> (5.6 mg, 0.025 mmol), P<sup>t</sup>Bu<sub>3</sub> (2 mL, 0.05 M in toluene, 0.1 mmol), sodium *tert*-butoxide (115.7 mg, 1.2 mmol), toluene (4.0 mL) stirred for 8 h at 100 °C to afford **4b** (343 mg, 89% ). IR (KBr)  $\nu$  3047 (m), 2923 (s), 1602 (s), 1491 (s), 1392 (s), 1267 (m), 1307 (m), 1123 (m), 1070 (s), 774 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (Acetone-d<sub>6</sub>, 400 MHz)  $\delta$  7.95 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.45~7.52 (m, 4H), 7.35 (td, *J* = 1.6, 2.8 Hz, 2H), 7.28 (dd, *J* = 1.0, 8.0 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 4H), 7.03~7.11 (m, 4H), 7.03 (d, *J* = 1.0 Hz, 2H), 6.88~6.95 (m, 10H), 6.75~6.80 (m, 3H), 2.22 (s, 3H); <sup>13</sup>C NMR (Acetone-d<sub>6</sub>, 100MHz)  $\delta$  153.1, 149.2, 148.3, 146.6, 144.4, 143.5, 136.8, 136.4, 134.8, 131.7, 130.0, 129.5, 129.4, 128.9, 128.7, 128.6, 127.7, 127.4, 127.3, 127.2, 127.1, 127.0, 124.9, 122.7, 122.6, 122.1, 121.1, 120.5, 65.5, 20.9; MS (*m/z*, FAB<sup>+</sup>) 766 (100), 307 (20), 154 (50), HRMS (FAB) Calcd for C<sub>58</sub>H<sub>42</sub>N<sub>2</sub> 766.3348, found 766.3338; Anal. Calcd for C<sub>58</sub>H<sub>42</sub>N<sub>2</sub> C, 90.92; H, 5.35; N, 3.72, found C, 91.06; H, 5.33; N, 3.71.

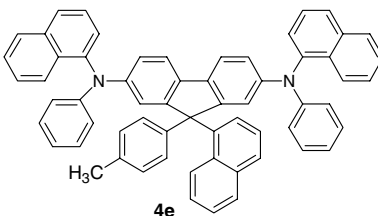
90.83; H, 5.52; N, 3.65, found C, 90.87; H, 5.36; N, 3.91.



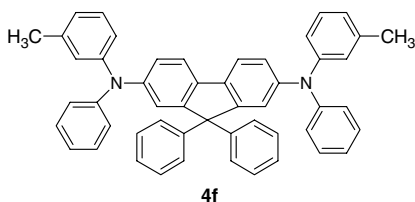
**3c** (250 mg, 0.5 mmol), *N*- $\alpha$ -naphthyl-*N*-phenylamine (219 mg, 1.0 mmol), Pd(OAc)<sub>2</sub> (5.6 mg, 0.025 mmol), P<sup>t</sup>Bu<sub>3</sub> (2 mL, 0.05 M in toluene, 0.1 mmol), sodium *tert*-butoxide (115.7 mg, 1.2 mmol), toluene (4.0 mL) stirred for 8 h at 100 °C to afford **4c** (374 mg, 96%). IR (KBr)  $\nu$  3021 (w), 1595 (m), 1486 (m), 1466 (m), 1318 (m), 1296 (m), 1272 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz)  $\delta$  7.72 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 4H), 7.56 (d, *J* = 8.6 Hz, 4H), 7.43 (t, *J* = 7.5 Hz, 4H), 7.30 (q, *J* = 8.4 Hz, 4H), 7.07–7.00 (m, 16H), 6.98 (d, *J* = 2.0 Hz, 2H), 6.84 (d, *J* = 8.1 Hz, 2H), 2.21 (s, 6H); <sup>13</sup>C NMR (Acetone-d<sub>6</sub>, 100 MHz)  $\delta$  153.1, 147.7, 147.3, 146.9, 142.9, 140.5, 136.3, 135.3, 135.2, 129.6, 129.0, 128.1, 127.8, 127.1, 126.6, 124.5, 124.0, 123.8, 123.4, 122.2, 120.8, 64.8, 20.3; MS (*m/z*, FAB<sup>+</sup>) 832 (100), 741 (10), 589 (20), 244 (10) HRMS (FAB) Calcd for C<sub>63</sub>H<sub>48</sub>N<sub>2</sub> 833.3817, found 832.3837. Anal. Calcd for C<sub>63</sub>H<sub>48</sub>N<sub>2</sub> C, 90.83; H, 5.81; N, 3.36, found C, 91.08; H, 5.58; N, 3.39.



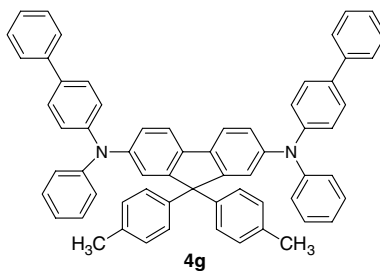
**3d** (263 mg, 0.5 mmol), *N*- $\alpha$ -naphthyl-*N*-phenylamine (219.1 mg, 1.0 mmol), Pd(OAc)<sub>2</sub> (5.6 mg, 0.025 mmol), P<sup>t</sup>Bu<sub>3</sub> (2 mL, 0.05 M in toluene, 0.1 mmol), sodium *tert*-butoxide (115.7 mg, 1.2 mmol), toluene (4.0 mL) stirred for 6 h at 100 °C to afford **4d** (350 mg, 87%). IR (KBr)  $\nu$  3060 (m), 2929 (m), 1595 (s), 1562 (s), 1391 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (Acetone-d<sub>6</sub>, 400 MHz)  $\delta$  7.92 (d, *J* = 8.0 Hz, 2H), 7.75–7.92 (m, 6H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.39–7.48 (m, 4H), 7.31 (t, *J* = 8.4 Hz, 3H), 7.18 (d, *J* = 7.2 Hz, 3H), 7.02–7.18 (m, 9H), 6.92 (dd, *J* = 2.0, 8.4 Hz, 4H), 6.82–6.90 (m, 7H); <sup>13</sup>C NMR (Acetone-d<sub>6</sub>, 100 MHz)  $\delta$  149.1, 148.2, 144.2, 141.2, 136.3, 134.5, 132.3, 131.7, 129.9, 129.7, 129.4, 129.1, 127.6, 127.3, 127.2, 127.1, 127.0, 125.8, 125.5, 125.4, 124.8, 122.7, 122.6, 121.8, 121.3, 120.5, 66.6; MS (*m/z*, FAB<sup>+</sup>) 802 (35), 675 (3), 585 (2), 460 (5), 307 (30), HRMS (FAB) Calcd for C<sub>61</sub>H<sub>42</sub>N<sub>2</sub> 802.3348, found 802.3341. Anal. Calcd for C<sub>61</sub>H<sub>42</sub>N<sub>2</sub> C, 91.24; H, 5.27, N, 3.49 found, C, 91.41, H, 5.20, N, 3.40.



**3e** (270 mg, 0.5 mmol), *N*- $\alpha$ -naphthyl-*N*-phenylamine (219.1 mg, 1.0 mmol), Pd(OAc)<sub>2</sub> (5.6 mg, 0.025 mmol), P<sup>t</sup>Bu<sub>3</sub> (2 mL, 0.05 M in toluene, 0.1 mmol), sodium *tert*-butoxide (115.7 mg, 1.2 mmol), toluene (4.0 mL) stirred for 6 h at 100 °C to afford **4e** (375 mg, 92%). IR (KBr)  $\nu$  2929 (w), 1563 (m), 1503 (m), 1458 (m), 1274 (m), 1116 (w), 1077 (w), 774 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (Acetone-d<sub>6</sub>, 400 MHz)  $\delta$  7.93 (d, *J* = 8.4 Hz, 2H), 7.79 (t, *J* = 8.0 Hz, 6H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.42~7.48 (m, 4H), 7.29 (t, *J* = 8.0 Hz, 3H), 7.20 (d, *J* = 7.2 Hz, 3H), 7.00~7.17 (m, 8H), 6.80~7.00 (m, 12H), 2.24 (s, 3H); <sup>13</sup>C NMR (Acetone-d<sub>6</sub>, 100 MHz)  $\delta$  153.0, 148.5, 147.6, 143.6, 140.7, 136.0, 135.7, 133.8, 131.7, 131.0, 129.3, 129.1, 129.0, 128.8, 128.7, 127.4, 127.0, 126.7, 126.5, 126.4, 126.3, 125.1, 124.9, 124.8, 124.2, 122.2, 122.1, 122.0, 121.2, 120.1, 119.9, 65.6, 20.3; MS (*m/z*, FAB<sup>+</sup>) 816 (100); HRMS (FAB) Calcd for C<sub>62</sub>H<sub>44</sub>N<sub>2</sub> 816.3504, found 816.3519; Anal. Calcd for C<sub>62</sub>H<sub>44</sub>N<sub>2</sub> C, 91.14; H, 5.43; N, 3.43, found C, 91.11; H, 5.21; N, 3.42.



**3a** (474 mg, 1.0 mmol), *N*-phenyl-*N*-3-methylphenylamine (438 mg, 2.0 mmol), Pd(OAc)<sub>2</sub> (11.2 mg, 0.05 mmol), P<sup>t</sup>Bu<sub>3</sub> (0.2 mmol), sodium *tert*-butoxide (230.4mg, 2.4 mmol), toluene (4.0 mL) stirred for 6 h at 100 °C to afford **4f** (467 mg, 69%). IR (KBr)  $\nu$  3040 (m), 1586 (m), 1493 (m), 1468 (m), 1428 (m), 1332 (m), 1274 (m), 697 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz)  $\delta$  7.68 (d, *J* = 8.4 Hz, 2H), 7.27~7.18 (m, 10H), 7.13 (t, *J* = 7.7 Hz, 2H), 7.02~6.90 (m, 14H), 6.82~6.79 (m, 4H), 6.74 (d, *J* = 8.4 Hz, 2H), 2.16 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  152.1, 147.7, 147.6, 146.8, 145.7, 138.9, 134.6, 129.1, 128.9, 128.2, 128.0, 126.4, 124.5, 124.2, 123.5, 123.3, 122.6, 121.9, 121.1, 65.3, 21.4; MS (*m/z*, FAB<sup>+</sup>) 680 (100), 603 (10), 499 (15), 420 (7), HRMS (FAB) Calcd for C<sub>51</sub>H<sub>40</sub>N<sub>2</sub> 680.3191, found 608.3181. Anal. Calcd for C<sub>51</sub>H<sub>40</sub>N<sub>2</sub> C, 89.96; H, 5.92; N, 4.11, found C, 89.94; H, 5.90; N, 4.12.



**3b** (250 mg, 0.5 mmol), *N*-phenyl-*N*-4,4'-biphenylamine (245 mg, 1.0 mmol), Pd(OAc)<sub>2</sub> (5.6 mg, 0.025 mmol), P<sup>t</sup>Bu<sub>3</sub> (2 mL, 0.05 M in toluene, 0.1 mmol), sodium *tert*-butoxide (115.7mg, 1.2 mmol), and toluene (4.0 mL) stirred for 4 h at 100 °C to afford **4g** (400 mg, 96%). IR (KBr)  $\nu$  3048 (w), 1595 (s), 1569 (s), 1492 (s), 1467 (s), 1394 (s), 1306 (s), 1269 (s), 771 (s), 695 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz)  $\delta$  7.97 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.53~7.48 (m, 4H), 7.36 (dt, *J* = 6.9, 1.3 Hz, 2H), 7.28 (d, *J* = 7.4 Hz, 2H), 7.17 (t, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.89~6.81 (m, 10H), 6.80 (d, *J* = 2.1, 2H), 6.61 (d, *J* = 8.2, 2H), 2.08 (s, 6H); <sup>13</sup>C NMR (Acetone-d<sub>6</sub>, 100 MHz)  $\delta$  152.6, 148.6, 147.6, 143.8, 142.9, 136.1, 135.7, 134.1, 131.1, 129.3, 128.8, 128.7, 127.9, 127.0, 126.7, 126.6, 126.5, 126.4, 124.3, 122.1, 121.9, 121.3, 120.4, 119.8, 114.6, 74.6, 20.2; MS (*m/z*, FAB<sup>+</sup>) 780 (25), 613 (5), 554 (10), 460 (20), 391 (10), 370 (100), 289 (50), 219 (20) HRMS (FAB) Calcd for C<sub>59</sub>H<sub>44</sub>N<sub>2</sub> 780.3504, found 780.3496. Anal. Calcd for C<sub>59</sub>H<sub>44</sub>N<sub>2</sub> C, 90.73; H, 5.68; N, 3.59, found C, 91.03; H, 5.41; N, 3.60.