Synthesis and Properties of 9,9-Diarylfluorene Based Triaryldiamines

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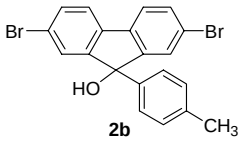
Supporting Information

General Experimernts. All reactions were performed under argon and were magnetically stirred. Solvents were distilled from appropriate dying agent prior to use: THF and Et_2O from sodium and benzophenone, benzene and toluene from sodium, CH_2Cl_2 from CaH_2. 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_{254}). 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. ^1H NMR and ^{13}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 Shimazu UV-160 spectrometer. Emission spectra were recorded on a Aminco-Bowman Series 2 Lumincence 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_2Cl_2 contaning 0.1 M $TBAPF_6$ as a supporting elctrolyte, purging with argon prior to conduct the experiment. Carbon electrode was used as working electrode, 0.01 M $AgNO_3$ in CH_2Cl_2 as reference electrode, and a platinum wire as counting electrode. Differential scanning calorimetry (DSC) analyses were performed on a TA Instrument DSC-2920 Low-Temperture Difference Scanning Calorimeter, the sample was firstly heated (20 ^oC/min) to melt, then quenched with liquid nitrogen, T_gs were recorded by heating (10 ^oC/min) the quenched sample.

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

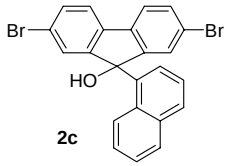
The Grignard reagents were prepared from magnesium powders (486 mg, 20 mmol) in Et_2O (5 mL) and the corresponding arylbromide (20 mmol) in Et_2O (15 ml). The cooled Grignard solution was diluted with dry Et_2O (20 ml) and 2,7-dibromofluorenone **1** (10 mmol) was added into the Grignard solution. The 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_4Cl solution, extracted with Et_2O, washed with brine, dried over $MgSO_4$. Evaporation of the solvent under reduced pressure yielded the crude product.

Purification was effected by column chromatography (SiO_2, EtOAc/Hexane = 1/5) and recrystallization from CH_2Cl_2 and hexane yielded colorless crystal.



2b

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_2O (40 mL) refluxed 6 h to afford **2b** (3.50 g , 82%). mp 150~151 ^oC; IR (KBr) ν 3528 (br), 1511 (m), 1448 (m), 1399 (m), 1254 (m), 1168 (m), 1056 (m), 1037 (m), 817(m) cm^{-1}; ^1H NMR (Acetone-d_6, 400 MHz) δ 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); ^{13}C NMR (Acetone-d_6, 100 MHz) δ 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^+) 428 (80), 413 (100), 307 (40); HRMS Cacld for $C_{20}H_{14}{}^{79}Br^{81}BrO$ 429.9391, found 429.9398. Anal Cacld for $C_{20}H_{14}Br_2O$ C, 55.85; H, 3.28 found C, 56.01; H, 3.24.



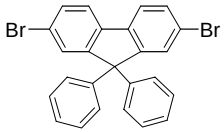
2c

2,7-dibromofluorene **1** (3.4g, 10 mmol), 1-bromonaphthlene (4.59g, 20 mmol), manesium powder (0.48 g, 20 mmol), Et_2O (40 mL) refluxed for 3 h afford **2c** (9.2 g, 97%). mp 226~227 ^OC; IR (KBr) ν 3435 (br), 1563 (m), 1543 (m), 1451 (m), 1392 (s), 1247 (w), 1215 (w), 1162 (m), 1057 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 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); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 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^+) 466 (5), 449 (5), 391 (1), 341 (2), 154 (100); HRMS (FAB) cacld for $C_{23}H_{14}{}^{79}Br_2O$ 463.9411, found 463.9394, Cacld for $C_{23}H_{14}{}^{79}Br^{81}BrO$ 465.9391, found 465.9383, Cacld for $C_{23}H_{14}{}^{81}Br_2O$ 467.9370, found 467.9371. Anal. Cacld for $C_{23}H_{14}Br_2O$ 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_3SO_3H–promoted Friedel-Crafts reaction of alcohol 2:

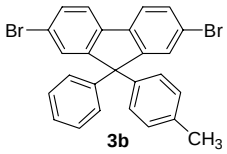
Alcohol **2** (1 equivalent) was dissolved in dried toluene or benzene. To this solution was heated to 50 ^0C. CF_3SO_3H (1 equivalent) was added dropwisely to afford a light brown solution. The mixture was stirred for another 10 min. The mixture was poured into a ice cold sat. $NaHCO_3$ aq. solution. The organic layer was separated, the aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine and dried over $MgSO_4$. Concentration of the organic solution afforded

crude product which was further purified by column chromatography on SiO_2 (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.



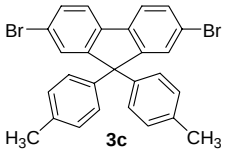
3a

2a (10.45g, 25 mmol), CF_3SO_3H (4.48 ml, 50 mmol), and benzene (136 ml) stirred at 80 ^oC for 6h, recrystallization from THF/Hexane afforded **3a** (10.5 g, 88%). mp 279-280 ^oC; IR (KBr) ν 1494 (w), 1457 (w), 813 (m), 701 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 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). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 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^+) 476 (58), 474 (30), 460 (100), 443 (15), 399 (38). HRMS (FAB) Calcd for $C_{25}H_{16}{}^{79}Br_2$ 473.9619, found 473.9608; Calcd for $C_{25}H_{16}{}^{79}Br^{81}Br$ 475.9598, found 475.9586; Calcd for $C_{25}H_{16}{}^{81}Br_2$ 477.9578, found 477.9587. Anal. Calcd. C, 63.05; H, 3.39. found C, 62.65; H, 3.25.



3b

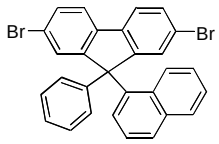
2a (2.08 g, 5.0 mmol), CF_3SO_3H (0.92 mL, 10 mmol), and toluene (20 mL) reacted at 50 ^oC for 10 min. Sublimation at 240 ^oC (0.01 torr) gave **3b** (2.06 g, 84%). mp 228~230 ^oC; IR (KBr) ν 3043 (w), 2916 (w), 1602 (w), 1589 (w), 1510 (m), 1491 (m), 1451 (m), 1398 (m), 1247 (m), 1063 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 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); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 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^+) 490 (6), 460 (4), 409 (2). Anla. Cacld for $C_{26}H_{18}Br_2$ C, 63.70, H, 3.70, found C, 63.69, ; H, 3.85.



3c

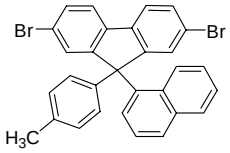
2b (1.29 g, 3.0 mmol), CF_3SO_3H (0.54 mL, 6.0 mmol), toluene (20 mL) reacted at 50 oC for 10 min. Sublimation was conducted at 240 ^oC (0.01 torr), giving **3c** (1.38g, 91%). mp 280~282 ^oC; IR (KBr) ν 3021 (w), 2922 (w), 1595 (m), 1503 (m), 1451 (m), 1398 (s), 1057 (m), 932 (w), 807 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 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}C NMR ($CDCl_3$, 100MHz) δ 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, FAB^+) 504 (2), 502 (1), 460 (5), 443 (1), 413 (1), 391 (1), 154 (100). Anal. Cacld for $C_{27}H_{20}Br_2$ C, 64.30; H, 4.00, found C, 64.19; H, 4.10.



3d

2c (1.86 g, 4.0 mmol), CF_3SO_3H (0.72 mL, 8.0 mmol), benzene (50 mL) reacted at 50 °C for 30 min. Recrystallization from $CHCl_3$ and hexanes gave 3d (1.18 g, 56%). mp 282~284 °C; IR (KBr) ν 3441(s), 1596 (m), 1491 (m), 1449 (s), 1398 (m), 1254 (m), 1065 (m), 809 (m), 777 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 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}C NMR ($CDCl_3$, 100 MHz) δ 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, FAB^+) 526 (1); HRMS Cacld for $C_{29}H_{18}{}^{81}Br_2$ 527.9734, found 527.9717; Cacld for $C_{29}H_{18}{}^{79}Br^{81}Br$ 525.9755, found 525.9753, Cacld for $C_{29}H_{18}{}^{79}Br_2$ 523.9775, found 523.9755. Anal. Cacld for $C_{29}H_{18}Br_2$ C, 66.19; H, 3.45, found C, 66.21; H,3.30.



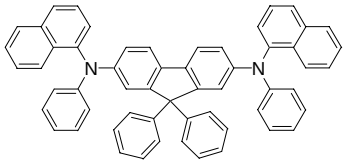
3e

2c (1.86 g, 4.0 mmol), CF_3SO_3H (0.72 mL, 8.0 mmol), toluene (50 mL) reacted at 50 °C for 10 min. Recrystallization from CH_2Cl_2 and hexanes gave **3e** (1.86 g, 86%). mp 264~266 °C; IR (KBr) ν 3021 (w), 1595 (s), 1486 (s), 1466 (s), 1318 (s), 1296 (s), 1272 (s), 761(s), 721(s), 697(m) ; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 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}C NMR (Acetone, 100 MHz) δ 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, FAB^+) 539.9(15), 307.0(30), 289.0(20), 154.0(100), 136.0(60); Anla. Cacld for $C_{30}H_{20}Br_2$ 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:

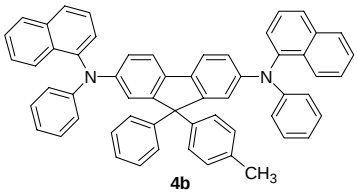
9,9-diaryl-2,7-dibromofluorene **3** (0.5 mmol), diarylamine (1.0 mmol), and sodium *tert*-butoxide (115.7 mg, 1.25 mmol) were mixed in a flask. The flask was evacuated, refilled with argon. $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), P^tBu_3 (2 mL, 0.05 M in toluene, 0.1 mmol) , dry toulene (4 mL) were added 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_2O and extracted with EtOAc, combined organic solution was washed with brine and dried over $MgSO_4$. Evaporation in vacuum vacuo afforded the crude product which was further purified by column chromatography on SiO_2 (EtOAc/hexane = 1/6). Analytical pure product was obtained by sublimation at 300 ^oC (bath temperature) under high vacuum (1.0 x 10^{-6} torr).



4a

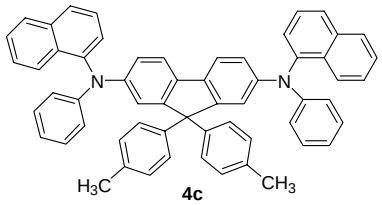
3a (474 mg, 1 mmole), *N*-α-naphthyl-*N*-phenylamine (438 mg, 2 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05mmol), P^tBu_3 (4 mL, 0.055M in toluene, 0.22 mmol), NaO^tBu_3 (230 mg, 2.4mmol), toluene (5 mL), stirred for 4 h stirred to give **4a** (640 mg, 85%). IR (KBr) ν 1595 (m), 1494 (m), 1468 (m), 1304 (w), 1272 (m), 775 (w), 699 (w) cm^{-1}. ^1H NMR (Acetone-d_6, 400 MHz) δ 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). ^{13}C NMR (Acetone-d_6, 100 MHz): δ 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^+) 752 (100), 751 (7), 535 (9). HRMS (FAB) Calcd for $C_{57}H_{40}N_2$: 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.



4b

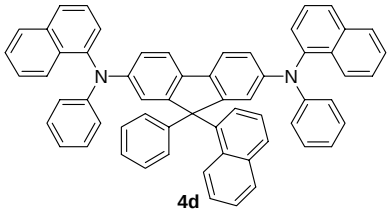
3b (263 mg, 0.5 mmol), *N*-α-naphthyl-*N*-phenylamine (219.1 mg, 1.0 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), P^tBu_3 (2 mL, 0.05 M in toluene, 0.1 mmol), sodium *tert*-butoxide (115.7 mg, 1.2 mmol), toluene (4.0 mL) stirred for 8 h at 100 ^oC to afford **4b** (343 mg, 89%). IR (KBr) ν 3047 (m), 2923 (s), 1602 (s), 1491 (s), 1392 (s), 1267 (m), 1307 (m), 1123 (m), 1070 (s), 774 (m) cm^{-1}; ^1H NMR (Acetone-d_6, 400 MHz) δ 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); ^{13}C NMR (Acetone-d_6, 100MHz) δ 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^+) 766 (100), 307 (20), 154 (50), HRMS (FAB) Cacld for $C_{58}H_{42}N_2$ 766.3348, found 766.3338; Anal. Cacld for $C_{58}H_{42}N_2$ C,

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



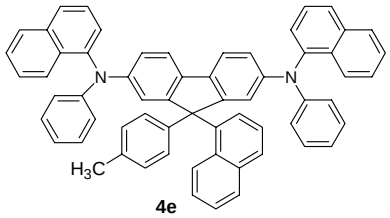
4c

3c (250 mg, 0.5 mmol), *N*-α-naphthyl-*N*-phenylamine (219 mg, 1.0 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), P^tBu_3 (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 ^oC to afford **4c** (374 mg, 96%). IR (KBr) ν 3021 (w), 1595 (m), 1486 (m), 1466 (m), 1318 (m), 1296 (m), 1272 (m) cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 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); ^{13}C NMR (Acetone-d_6, 100 MHz) δ 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^+) 832 (100), 741 (10), 589 (20), 244 (10) HRMS (FAB) Cacld for $C_{63}H_{48}N_2$ 833.3817, found 832.3837 . Anal. Cacld for $C_{63}H_{48}N_2$ C, 90.83; H, 5.81; N, 3.36, found C, 91.08; H, 5.58; N, 3.39.



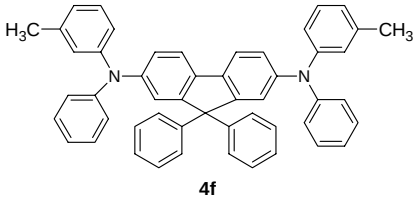
4d

3d (263 mg, 0.5 mmol), *N*-α-naphthyl-*N*-phenylamine (219.1 mg, 1.0 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), P^tBu_3 (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 ^oC to afford **4d** (350 mg, 87%). IR (KBr) ν 3060 (m), 2929 (m), 1595 (s), 1562 (s), 1391 (s) cm^{-1} ; ^1H NMR (Acetone-d_6, 400 MHz) δ 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); ^{13}C NMR (Acetone-d_6, 100 MHz) δ 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^+) 802 (35), 675 (3), 585 (2), 460 (5), 307 (30), HRMS (FAB) Cacld for $C_{61}H_{42}N_2$ 802.3348, found 802.3341. Anal Cacld for $C_{61}H_{42}N_2$ C, 91.24; H, 5.27, N, 3.49 found, C, 91.41, H, 5.20, N, 3.40.



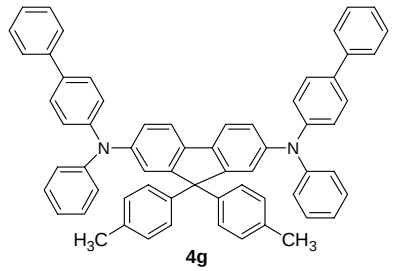
4e

3e (270 mg, 0.5 mmol), *N*-α-naphthyl-*N*-phenylamine (219.1 mg, 1.0 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), P^tBu_3 (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) ν 2929 (w), 1563 (m), 1503 (m), 1458 (m), 1274 (m), 1116 (w), 1077 (w), 774 (m) cm^{-1}; ^1H NMR (Acetone-d_6, 400 MHz) δ 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, 8.H), 6.80~7.00 (m, 12H), 2.24 (s, 3H); ^{13}C NMR (Acetone-d_6, 100 MHz) δ 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^+) 816 (100); HRMS (FAB) Cacld for $C_{62}H_{44}N_2$ 816.3504, found 816.3519; Anal. Cacld for $C_{62}H_{44}N_2$ C, 91.14; H, 5.43; N, 3.43, found C, 91.11; H, 5.21; N, 3.42.



4f

3a (474 mg, 1.0 mmol), *N*-phenyl-*N*-3-methylphenylamine (438 mg, 2.0 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), P^tBu_3 (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) ν 3040 (m), 1586 (m), 1493 (m), 1468 (m), 1428 (m), 1332 (m), 1274 (m), 697(m) cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 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); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 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^+) 680 (100), 603 (10), 499 (15), 420 (7), HRMS (FAB) Cacld for $C_{51}H_{40}N_2$ 680.3191, found 608.3181. Anal. Cacld for $C_{51}H_{40}N_2$ C, 89.96; H, 5.92; N, 4.11, found C, 89.94; H, 5.90; N, 4.12.



4g

3b (250 mg, 0.5 mmol), *N*-phenyl-*N*-4,4'-biphenylamine (245 mg, 1.0 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), P^tBu_3 (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 ^oC to afford **4g** (400 mg, 96%). IR (KBr) ν 3048 (w), 1595 (s), 1569 (s), 1492 (s), 1467 (s), 1394 (s), 1306 (s), 1269 (s), 771(s), 695(m)cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 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); ^{13}C NMR (Acetone-d_6, 100 MHz) δ 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^+) 780 (25), 613 (5), 554 (10), 460 (20), 391 (10), 370 (100), 289 (50), 219 (20) HRMS (FAB) Cacld for $C_{59}H_{44}N_2$ 780.3504, found 780.3496 . Anal. Cacld for $C_{59}H_{44}N_2$ C, 90.73; H, 5.68; N, 3.59, found C, 91.03; H, 5.41; N, 3.60.