Supporting Information

Clean Synthesis of Triarylamines: Buchwald-Hartwig Reaction in Water with Amphiphilic Resin-Supported Palladium Complexes

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General: All manipulations were performed under a nitrogen atmosphere. Nitrogen gas was dried by passage through P_2O_5. Water was deionized with a Millipore system as a Milli-Q grade and was degassed by the freeze-pump-thaw method prior to use. NMR spectra were recorded on a JEOL JNM-A500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C, 202 MHz for ^{31}P) or a JEOL JNM–AL400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, 162 MHz for ^{31}P). Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane standard for ^{1}H NMR. Chemical shifts of ^{13}C NMR are given relative to $CDCl_3$ as an internal standard (δ 77.0). The ^{31}P NMR data are reported relative to external Ph_3P. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ or CD_3OD at 25 °C. ICP-AES analyses were performed on Leeman Labs Inc. Profile Plus using palladium standard solution (KANTO CHEMICAL) and phosphine standard solution (KANTO CHEMICAL) as a standard (detection limit for Pd = 0.044 ppm). The ESI mass spectra were recorded on a JEOL JMS-T100LC spectrometer. The GC-MS was measured by an Agilent 6890 GC/5973N MS detector. The FAB and high-resolution mass spectra were recorded on a JEOL MS700V. The IR spectra were obtained using a JASCO FT/IR-460plus spectrophotometer in ATR mode. PS-PEG bromo-resin was purchased from RAPP POLYMERE™ (TentaGel®S Br, average diameter 0.90 μm, 1% divinylbenzene crosslinked, loading value of bromo residue 0.2-0.3 mmol/g).

Preparation of PS-PEG-P(*tert*-C_4H_9)$_2$ (1): To a mixture of di-*t*-butylphosphine (1.83 g, 1.25 mmol) and THF (10 mL, three freeze pump thaw cycles) was added *n*-butyllithium (2.69 mol/L in hexane, 0.47 mL, 1.25 mmol) over 1 h and the mixture was stirred at -78 °C for 1 h under a nitrogen atmosphere. The reaction mixture was added to the TentaGel S Br (2.01 g, 0.50 mmol of bromine residue) dispersed in THF (20 mL, three freeze pump thaw cycles) at -78 °C under a nitrogen atmosphere and the resulting mixture was stirred for 1 h. The reaction mixture was warmed to room temperature slowly (for 1 h) and stirred for an additional 1 h at ambient temperature. The mixture was filtered and washed with water (20 mL, 3 times), THF (20 mL, 3 times) and CH_2Cl_2 (20 mL, 3 times). The residue was dried in vacuo for 18 h to give the polymer-supported ligand (**1**). ^{31}P NMR (400 MHz, $CDCl_3$, 25 °C): δ +19.7. . The loading amount of phosphine was analyzed by ICP-AES. The ligand (**1**) (19.7 mg) was treated with 20% HNO_3 (3 mL) at 90 °C for 21 h and filtered. The filtrate was filled with pure water up to 50 mL and analyzed by ICP-AES to determine that the loading value of phosphine was 0.21 mmol/g.

Preparation of 1-Pd complex (P/Pd = 2/1): The polymer-supported ligand (**1**) (1.57 g, 0.33 mmol of phosphine residue) was mixed with $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (30.2 mg, 0.17 mmol of Pd) in CH_2Cl_2 (15.7 mL) at ambient temperature and shaken for 1 h under a nitrogen atmosphere. The mixture was filtered and the resulting resin beads were washed with CH_2Cl_2 (15 mL x 3 times), dried in vacuo overnight to provide the **1**-Pd complex (1.60 g). ^{31}P NMR (400 MHz, $CDCl_3$, 25 °C): δ + 54.4. A ratio of P/Pd was determined by ICP-AES analysis to be 1.94/1.

Preparation of PS-PEG-P(*cyclo*-C_6H_{11})$_2$ (2): Prepared by similar procedure for the preparation of the PS-PEG-P(tert-C_4H_9)$_2$ (**1**). ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ -11.4. The loading value of phosphine was 0.21 mmol / g.

Preparation of 2-Pd complex (P/Pd = 2/1): Prepared by similar procedure for the preparation of the **1**-Pd complex (P/Pd = 2/1). ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ +32.0, +27.2, +17.8. The loading value of phosphine and palladium were 0.20 mmol / g and 0.10 mmol / g, respectively.

General procedure for the amination of haloarenes: A mixture of the catalyst (**1**-Pd complex (P/Pd = 2/1), 0.015 mmol of Pd), arylhalides (0.45 mmol) and diphenylamine (0.30mmol) in 20 M KOH aqueous solution (0.6 mL) under a nitrogen atmosphere was shaken for 24 h under reflux conditions. After being cooled, the mixture was filtered, and the recovered resin beads were extracted with EtOAc (2 mL x 4 times). The combined extracts were dried over anhydrous

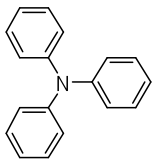
Na_2SO_4. The solvent was evaporated and the residue was purified by flash chromatography to give the corresponding triarylamines. The chemical purity of the isolated triarylamines was determined by GC-MS analysis to be >95%. Pd residue was not detected by ICP-AES analysis (detection limit (Pd) = 0.044 ppm).

General recycling procedure for the amination of haloarenes: After the amination reaction (vide supra), the resin beads were recovered by simple filtration under inert atmosphere and rinsed 4 times with EtOAc. The recovered beads catalyst was dried in vacuo and subjected to the next series of amination without additional charge of palladium. ^{31}P NMR (400 MHz, $CDCl_3$, 25 °C): δ + 53-58 broad resonace. A ratio of P/Pd was determined by ICP-AES analysis to be 1.92/1.

General procedure for the double arylation of anilins: A mixture of catalyst (**1**-Pd complex (P/Pd = 2/1), 0.015 mmol of Pd), bromobenzene (0.90 mmol) and anilines (0.30 mmol) in 20 M KOH aqueous solution (0.6 mL) under a nitrogen atmosphere was shaken for 24 h under reflux conditions. After being cooled, the mixture was filtered, and the recovered resin beads were extracted with EtOAc (2 mL x 4 times). The combined extracts were dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash chromatography to give the corresponding triarylamines and diarylamines.

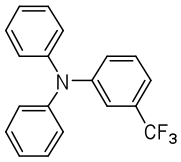
General procedure for the double amination of dihaloarenes: A mixture of catalyst (**1**-Pd complex (P/Pd = 2/1), 0.015 mmol of Pd), dihaloarenes (0.30 mmol) and diarylamines (0.90 mmol) in 20 M KOH aqueous solution (0.6 mL) under a nitrogen atmosphere was shaken for 24 to 48 h under reflux conditions. After being cooled, the mixture was filtered, and the recovered resin beads were extracted with EtOAc or CH_2Cl_2 (2 mL x 4 times). The combined extracts were dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash chromatography or GPC to give the corresponding bis(*N*,*N*-diarylamino)arenes.

Triphenylamine (5A):



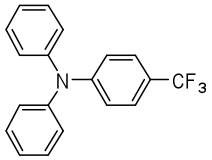
CAS: 603-34-9;
Isolated by silica gel flash column chromatography (eluent: hexane/EtOAc = 10/1). Yield: 92% (Table 1, entry 2).
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.23 (t, *J* = 7.0 Hz, 6H), 7.08 (d, *J* = 8.0 Hz, 6H), 6.99 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR(125 MHz, $CDCl_3$, 25 °C): δ 147.8, 129.2, 124.1 122.6; MS (EI(+)): *m/z* 245 (M^+). EI-HRMS *m/e* 245.1204 (M^+ calcd for 245.1205 $C_{18}H_{15}N$).

3-Trifluoromethyl-*N*,*N*-diphenylaniline (5B):



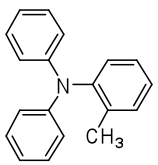
CAS:106336-12-3;
Isolated by silica gel flash column chromatography (eluent: hexane/EtOAc = 10/1). Yield: 85% (Table 1, entry 4).
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.29-7.25 (m, 6H), 7.18 (t, *J* = 7.5 Hz, 2H), 7.10-7.04 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 148.5, 147.1, 131.6 (q, $J_{C\text{-}F}$ = 31.9 Hz), 129.6, 129.5, 125.7, 124.8, 124.0 (q, $J_{C\text{-}F}$ = 271.4 Hz), 123.8, 119.1 (q, $J_{C\text{-}F}$ = 4.1 Hz), 118.3 (q, $J_{C\text{-}F}$ = 4.1 Hz); MS (EI(+)): *m/z* 313 (M^+). EI-HRMS *m/e* 313.1080 (M^+ calcd for 313.1078 $C_{19}H_{14}F_3N$).

4-Trifluoromethyl-*N*,*N*-diphenylaniline (5C):



CAS: 36809-32-2;
Isolated by silica gel flash column chromatography (eluent: hexane/EtOAc = 10/1). Yield: 91% (Table 1, entry 5).
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.41 (d, *J* = 9.2 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 4H), 7.13-7.09 (m, 6H), 7.05 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 150.9, 146.8, 129.6, 126.2 (q, $J_{C\text{-}F}$ = 4.1 Hz), 125.5, 124.2, 124.5 (q, $J_{C\text{-}F}$ = 269.4 Hz), 122.8 (q, $J_{C\text{-}F}$ = 33.0 Hz), 121.0; MS (EI(+)): *m/z* 313 (M^+). EI-HRMS *m/e* 313.1080 (M^+ calcd for 313.1078 $C_{19}H_{14}F_3N$).

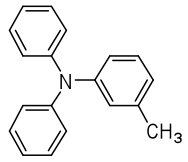
2-(Diphenylamino)toluene (5D (= 7c)):



CAS: 4316-55-6;
Isolated by silica gel flash column chromatography (eluent: hexane/EtOAc = 10/1). Yield: 44% (Table 1, entry 6), 83% (Table 2, entry 3).
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.25-7.11 (m, 8H), 6.97-6.90 (m, 6H), 2.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 147.5, 145.4, 136.5, 131.7, 129.7, 129.0, 127.3, 126.0, 121.5, 121.3, 18.6; MS

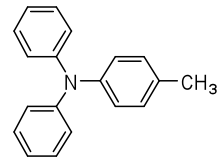
(EI(+)): *m/z* 259 (M^+). EI-HRMS *m/e* 259.1359 (M^+ calcd for 259.1361 $C_{19}H_{17}N$).

3-(Diphenylamino)toluene (5E (= 7d)):



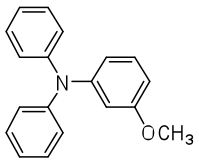
CAS:4316-54-5;
Isolated by silica gel flash column chromatography (eluent: hexane/EtOAc = 10/1). Yield: 88% (Table 1, entry 7), 87% (Table 2, entry 4).
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 7.23 (t, *J* = 7.9 Hz, 4H), 7.13 (t, *J* = 7.9 Hz, 1H), 7.07 (d, *J* = 7.3 Hz, 4H), 6.99 (t, *J* = 7.3 Hz, 2H), 6.91 (s, 1H), 6.88 (d, *J* = 8.5 Hz, 1H), 6.83 (d, *J* = 7.3 Hz, 1H) 2.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 147.9, 147.8, 139.1, 129.1, 129.0, 125.0, 124.1, 123.7, 122.5, 121.5, 21.4; MS (EI(+)): *m/z* 259 (M^+). EI-HRMS *m/e* 259.1362 (M^+ calcd for 259.1361 $C_{19}H_{17}N$).

4-(Diphenylamino)toluene (5F (= 7e)):



CAS: 4316-53-4;
Isolated by silica gel flash column chromatography (eluent: hexane/EtOAc = 10/1). Yield: 95% (Table 1, entry 8), 83% (Table 2, entry 5).
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 7.25-7.20 (m, 4H), 7.08-7.05 (m, 6H), 7.01-6.95 (m, 4H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 148.0, 145.2, 132.7, 129.9, 129.1, 124.9, 123.6, 122.2, 20.8; MS (EI(+)): *m/z* 259 (M^+). EI-HRMS *m/e* 259.1359 (M^+ calcd for 259.1361 $C_{19}H_{17}N$).

3-Methoxy-*N*,*N*-diphenylaniline (5G):

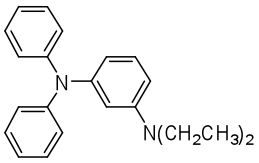


CAS:20588-62-9;
Isolated by silica gel flash column chromatography (eluent: hexane/EtOAc = 10/1). Yield: 96% (Table 1, entry 6).
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 7.24 (t, *J* = 7.9 Hz, 4H), 7.14 (t, *J* = 8.5 Hz, 1H), 7.09 (d, *J* = 7.9 Hz, 4H), 7.01 (d, *J* = 7.3 Hz, 2H) , 6.65 (d, *J* = 8.5 Hz, 1H) , 6.62 (s, 1H) , 6.56 (d, *J* = 8.5 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 160.4, 149.1, 147.7, 129.8, 129.2, 124.4, 122.8, 116.4, 109.7, 107.9, 55.2; MS (EI(+)): *m/z* 275 (M^+). EI-HRMS *m/e* 275.1311 (M^+ calcd for 275.1310 $C_{19}H_{17}NO$).

4-Methoxy-*N*,*N*-diphenylaniline (5H (= 7f)):

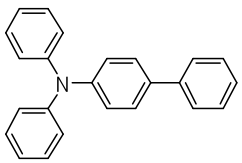
CAS: 4316-51-2;
Isolated by silica gel flash column chromatography (eluent: hexane/EtOAc = 10/1). Yield: 65% (Table 1, entry 10), 85% (Table 2, entry 6).
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 7.21 (t, *J* = 7.3 Hz, 4H), 7.09-7.03 (m, 6H), 6.94 (t, *J* = 7.3 Hz, 2H), 6.84 (dt, *J* = 9.2, 2.4 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 156.1, 148.2, 140.8, 129.0, 127.3, 122.9, 121.8, 114.7, 55.5; MS (EI(+)): *m/z* 275 (M^+). EI-HRMS *m/e* 275.1308 (M^+ calcd for 275.1310 $C_{19}H_{17}NO$).

3-(*N*,*N*-Diethylamino)-*N*,*N*-diphenylaniline (5I):



CAS: 775347-48-3;
Isolated by silica gel flash column chromatography (eluent: hexane/EtOAc = 10/1). Yield: 84% (Table 1, entry 11).
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 7.21 (t, *J* = 7.5 Hz, 4H), 7.10 (d, *J* = 7.5 Hz, 4H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 2H), 6.39 (s, 1H), 6.38 (d, *J* = 8.5 Hz, 1H), 6.35 (d, *J* = 7.5 Hz, 1H), 3.20 (q, *J* = 7.5 Hz, 4H), 1.07 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 148.8, 148.7, 148.0, 129.8, 128.9, 123.9, 122.1, 112.3, 108.6, 107.1, 44.4, 12.6; MS (EI(+)): *m/z* 316 (M^+). EI-HRMS *m/e* 316.1939 (M^+ calcd for 316.1940 $C_{22}H_{24}N_2$).

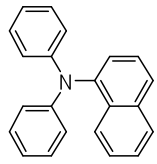
4-Phenyl-*N*,*N*-diphenylaniline (5J);



CAS: 4432-94-4;
Isolated by silica gel flash column chromatography (eluent: hexane/EtOAc = 20/1). Yield: 91% (Table 1, entry 12).
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 7.57 (d, *J* = 7.3 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.31-7.25 (m, 5H), 7.13 (d, *J* = 8.5 Hz, 6H) , 7.03 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 25

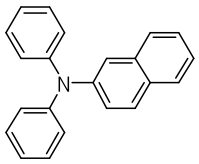
ºC): δ 147.7, 147.2, 140.6, 135.1, 129.3, 128.7, 127.8, 126.8, 126.6, 124.4, 123.9, 122.9; MS (EI(+)): *m/z* 321 (M^+). EI-HRMS *m/e* 321.1518 (M^+ calcd for 321.1517 $C_{24}H_{19}N$).

1-(*N,N*-Diphenylamino)naphthalene (5K):



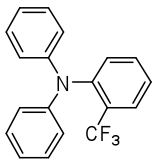
CAS: 61231-45-6;
Isolated by silica gel flash column chromatography (eluent: hexane/EtOAc = 20/1-10/1). Yield: 20% (Table 1, entry 13).
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 7.93 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 8.5 Hz, 4H), 7.02 (d, *J* = 8.5 Hz, 4H), 6.92 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR(125 MHz, $CDCl_3$, 25 ºC): δ 148.5, 143.6, 135.3, 131.3, 129.1, 128.4, 127.2, 126.4, 126.35, 126.32, 126.1, 124.3, 121.8, 121.6; MS (EI(+)): *m/z* 295 (M^+). EI-HRMS *m/e* 295.1364 (M^+ calcd for 295.1361 $C_{22}H_{17}N$).

2-(*N,N*-Diphenylamino)naphthalene (5L):



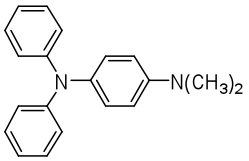
CAS: 6940-30-3;
Isolated by silica gel flash column chromatography (eluent: hexane/EtOAc = 20/1-10/1). Yield: 87% (Table 1, entry 14).
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.42 (d, *J* = 1.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.29-7.25 (m, 5H), 7.13 (d, *J* = 7.5 Hz, 4H), 7.04 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR(125 MHz, $CDCl_3$, 25 ºC): δ 147.8, 145.5, 134.4, 130.0, 129.3, 128.8, 127.5, 126.9, 126.2, 124.45, 124.41, 124.37, 122.9, 120.2; MS (EI(+)): *m/z* 295 (M^+). EI-HRMS *m/e* 295.1363 (M^+ calcd for 295.1361 $C_{22}H_{17}N$).

2-Trifluoromethyl-N,N-diphenylaniline (7b):



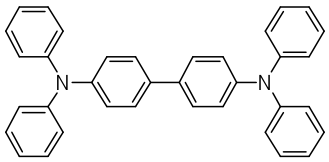
CAS: No Registry;
Isolated by silica gel flash column chromatography (eluent: hexane/EtOAc = 20/1). Yield: 85% (Table 2, entry 2).
colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 7.29-7.25 (m, 6H), 7.18 (t, *J* = 7.5 Hz, 2H), 7.10-7.05 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 148.5, 147.1, 131.6 (q, $J_{C\text{-}F}$ = 31.9 Hz), 129.6, 129.5, 125.7, 124.8, 124.0 (q, $J_{C\text{-}F}$ = 270.5 Hz), 123.8, 119.1 (q, $J_{C\text{-}F}$ = 4.1 Hz), 118.3 (q, $J_{C\text{-}F}$ = 4.1 Hz); MS (FAB(+)): *m/z* 313 (M^+). HRMS (FAB(+)) 313.1075 (calc for 313.1078 $C_{19}H_{14}F_3N$), , IR (ATR): (cm^{-1}) ν 3064, 3037, 2359, 2342, 1587, 1492, 1337, 1323, 1262, 1164, 1120, 1070, 954, 790, 752, 692.

4-(*N,N*-Dimethylamino)-*N,N*-bis(diphenyl)aniline (7g):



CAS: 4316-50-1;
Isolated by silica gel flash column chromatography (eluent: hexane/EtOAc = 10/1). Yield: 92% (Table 1, entry 7).
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 7.20 (t, *J* = 7.9 Hz, 4H), 7.05 (d, *J* = 8.5 Hz, 6H), 6.91 (t, *J* = 7.3 Hz, 2H), 6.70 (d, *J* = 9.2 Hz, 2H), 2.95 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 148.3, 147.7, 137.1, 128.9, 127.7, 122.4, 121.3, 113.5, 40.9; MS (EI(+)): *m/z* 288 (M^+). EI-HRMS *m/e* 288.1625 (M^+ calcd for 288.1626 $C_{20}H_{20}N_2$).

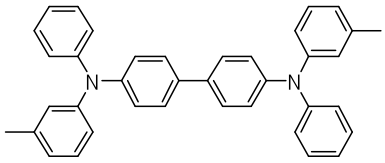
***N,N,N',N'*-Tetraphenyl-1,1'-biphenyl-4,4'-diamine (9):**



A mixture of the catalyst (**1**-Pd complex (P/Pd = 2/1, Pd-loading = 0.11 mmol/g), 1.16 g, 0.128 mmol of Pd), 4,4'-dibromobiphenyl (800 mg, 2.56 mmol) and diphenylamine (1.30 g, 7.69 mmol) in 20 M KOH aqueous solution (5.0 mL) under a nitrogen atmosphere was shaken for 24 h under reflux conditions. After being cooled, the mixture was filtered, and the recovered resin beads were extracted with EtOAc (15 mL x 4 times). The combined extracts were dried over anhydrous Na_2SO_4. The solvent was evaporated to give crude crystals of *N,N,N',N'*-tetraphenyl-1,1'-biphenyl-4,4'-diamine (**9**) (869 mg, 69%), which were evaluated for chemical

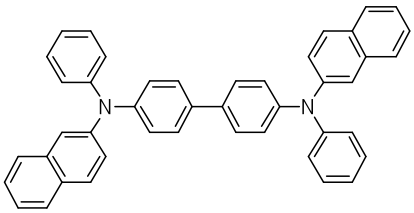
purity and yield by NMR, GC, and ICP-AES analysis. The crude product was chromatographed on silica gel (eluent: CH_2Cl_2/hexane = 1/9) to give 842 mg (67%) of analytically pure **9**. CAS: 15546-43-7; white crystals; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.44 (d, *J* = 8.5 Hz, 4H), 7.26 (t, *J* = 7.5 Hz, 8H), 7.13-7.11 (m, 12H), 7.02 (5, *J* = 7.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 147.7, 146.7, 134.7, 129.2, 127.3, 124.3, 124.1, 122.8; MS (ESI(+)): *m*/*z* 489 (MH^+). Anal calcd for $C_{36}H_{28}N_2$: C 88.49, H 5.78, N 5.73. Found: C 88.22, H 5.80, N 5.58.

***N,N'*-Diphenyl-*N,N'*-di(*metha*-tolyl)-1,1'-biphenyl-4,4'-diamine (11):**



CAS: 65181-78-4;
Isolated by silica gel chromatography (eluent: CH_2Cl_2/hexane = 1/9). Yield: 33%.
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.43 (dt, *J* = 8.5, 2.0 Hz, 4H), 7.24 (dd, *J* = 8.5, 7.5 Hz, 4H), 7.16-7.09 (m, 10H), 7.00 (t, *J* = 7.5 Hz, 2H), 6.95 (s, 2H), 6.92 (d, *J* = 7.5 Hz, 2H), 6.84 (d, *J* = 7.0 Hz, 2H), 2.26 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 147.8, 147.6, 146.8, 139.1, 134.6, 129.2, 129.0, 127.2, 125.1, 124.2, 124.0, 123.8, 122.6, 121.6, 21.4; MS (ESI(+)): *m*/*z* 517 (MH^+). Anal calcd for $C_{36}H_{28}N_2$: C 88.34, H 6.24, N 5.42. Found: C 88.12, H 6.60, N 5.48.

***N,N'*-Dinaphthyl-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (13):**



CAS: 139255-17-7;
Isolated by silica gel chromatography (eluent: hexane/EtOAc = 20/1). Yield: 59% (Scheme 2).
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 9.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 6H), 7.36-7.22 (m, 10H), 7.15-7.13 (m, 8H), 7.02 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 147.6, 146.7, 145.3, 134.9, 134.4, 130.1, 129.3, 128.9, 127.5, 127.3, 126.9, 126.3, 124.50, 124.46, 124.44, 124.30, 123.0, 120.4; MS (FAB(+)): *m*/*z* 588 (M^+). Anal calcd for $C_{44}H_{32}N_2$: C 89.76, H 5.48, N 4.76. Found: C 89.50, H 5.78, N 4.55.