Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

© Wiley-VCH 2005

69451 Weinheim, Germany

One-pot Sequential N- and C-Arylations: A Novel and Efficient Methodology For The Synthesis of trans-4-N,N-diarylaminostilbenes

Mecheril V. Nandakumar and John G. Verkade*

General Considerations: All reactions were performed under an atmosphere of argon in oven dried glassware. Toluene was collected from a Grubbs type solvent purification system (Innovative Technologies) and stored over 4 Å molecular sieves. ^{1}H and ^{13}C NMR spectra were recorded on Varian VXR 300 MHz NMR spectrometer. NMR spectra were obtained using $CHCl_3$-d as solvent. Chemical shifts are given in the d scale with tetramethylsilane or the $CHCl_3$ proton at 7.23 as the internal standard. Mass spectra were recorded on a Kratos MS-50 mass spectrometer.

General procedure for the one-pot synthesis of trans-4-N,N-diarylaminostilbenes (Tables 1 & 2).

An oven dried Schlenk tube equipped with a magnetic stirring bar was charged with Pd_2dba_3 (2 mol %) and NaO*t*Bu (3.5 mmol). The tube was capped with a rubber septum, evacuated and then flushed with argon three times. Ligand **1** (4 mol %) was then added via syringe. 4-aminostyrene (1 mmol), aryl halide (3.2 mmol) and toluene (10 mL) were then successively added via syringe. The tube was heated at the temperature and for the time specified in Table 1. After the reaction was complete, as judged by TLC, the reaction mixture was cooled to room temperature. The reaction mixture was filtered through a celite pad to remove solid impurities and the filtrate was concentrated in *vacuo*. The crude products were purified by column

chromatography using mixtures of EtOAc/hexane mixtures as eluants to afford the coupled products.

4-ethenyl-N,N-diphenylbenzenamine (4) (Table 1 & Entry 1)

Following the general procedure, Pd_2dba_3 (18.3 mg, 2 mol %), NaO*t*Bu (336 mg, 3.5 mmol), Ligand **1** (13.6 mg, 4 mol %), 4-aminostyrene (119 mg, 1 mmol), bromobenzene (502 mg, 3.2 mmol), and 10 mL of dry toluene at 110 ° C for 16 h afforded N, N-diphenylaminostyrene (24 mg, 9 %) as a colorless solid (24 mg, 9 %) and trans-4-N, N-diphenylaminostilbene (287 mg, 83 %) as a yellow solid after chromatography with hexane. Total yield = 92 %.

^{1}H NMR (300 MHz, $CDCl_3$): d 5.13 (d, J = 10.86 Hz, 1H), 5.61 (d, J = 17.58 Hz, 1H), 6.61 (dd, J_1 = 10.86 Hz, J_2 = 17.58 Hz, 1H), 7.01 – 7.10 (m, Ar, 8H), 7.21 – 7.27 (m, Ar, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): d 112.34, 123.12, 123.81, 124.57, 127.25, 129.45, 132.07, 136.42, 147.68, 147.80. m.p. 90–92 ° C. HRMS: Cald. for $C_{20}H_{17}N$ (M^+) 271.1361, Found: 271.1359.

N,N-diphenyl-4-[2-phenylethenyl]benzenamine (5)

^{1}H NMR (300 MHz, $CDCl_3$): d 7.04 – 7.15 (m, 10H), 7.26 – 7.31 (m, 5H), 7.34 - 7.42 (m, 4H), 7.50 (d, J = 7.32 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): d 123.27, 123.85, 124.72, 126.56, 127.29, 127.53, 127.61, 128.41, 128.91, 129.54, 131.67, 137.86, 147.60, 147.79. m.p. 152–154 °C. HRMS: Cald. for $C_{26}H_{21}N$ (M^+) 347.1674, Found: 347.1681.

4-ethenyl-N,N-bis(4-methylphenyl)benzenamine (Table 2, Entry 1)

Following the general procedure, Pd_2dba_3 (18.3 mg, 2 mol %), NaO*t*Bu (336 mg, 3.5 mmol), ligand **1** (13.6 mg, 4 mol %), 4-aminostyrene (119 mg, 1 mmol), 4-bromotoluene (547 mg, 3.2 mmol), and 10 mL of dry toluene at 110 ° C for 16 h afforded 4-ethenyl-N,N-bis(4-methylphenyl)benzenamine (32 mg, 11 %) as a viscous liquid and N,N-bis(4-methylphenyl)-4-[2-(4-

methylphenyl)ethenyl]benzenamine (325 mg, 84 %) as a yellow solid after chromatography with 1% EtOAc/hexane mixture. Total yield = 95 %.

^{1}H NMR (300 MHz, $CDCl_3$): d 2.29 (s, 6H), 5.09 (d, J = 11.1 Hz, 1H), 5.56 (d, J = 17.58 Hz, 1H), 6.58 (dd, J_1 = 10.86 Hz, J_2 = 17.58 Hz, 1H), 6.94 – 7.06 (m, 10 H), 7.22 – 7.25 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): d 20.80, 111.56, 122.35, 124.61, 126.87, 129.84, 130.91, 132.53, 136.27, 145.13, 147.87. HRMS: Cald. for $C_{22}H_{21}N$ (M^+) 299.1674, found: 299.16800.

N,N-bis(4-methylphenyl)-4-[2-(4-methylphenyl)ethenyl]benzenamine

^{1}H NMR (300 MHz, $CDCl_3$): d 2.31 (s, 6H), 2.34 (s, 3H), 6.96 – 7.15 (m, 14 H), 7.32 – 7.39 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): d 20.81, 21.21, 122.46, 124.63, 126.12, 126.47, 127.06, 127.27, 129.31, 129.85, 130.80, 132.56, 134.90, 136.95, 145.10, 147.54. mp. 133–135 ° C. HRMS: Cald. for $C_{29}H_{27}N$ (M^+) 389.21435, Found: 389.21510.

4-ethenyl-N,N-bis(3,5-dimethylphenyl)benzenamine (Table 2, Entry 2)

Following the general procedure, Pd_2dba_3 (18.3 mg, 2 mol %), NaO*t*Bu (336 mg, 3.5 mmol), ligand **1** (13.6 mg, 4 mol %), 4-aminostyrene (119 mg, 1 mmol), 5-bromo-*m*-xylene (592 mg, 3.2 mmol), and 10 mL of dry toluene at 110° C for 16 h afforded 4-ethenyl-N,N-bis(3,5-dimethylphenyl)benzenamine (124 mg, 37 %) as a colorless solid and N,N-bis(3,5-dimethylphenyl)-4-[2-(3,5dimethylphenyl)ethenyl]benzenamine (262 mg, 61 %) as a yellow solid after chromatography with 1% EtOAc/hexane mixture. Total yield = 98 %.

^{1}H NMR (300 MHz, $CDCl_3$): d 2.23 (s, 12H), 5.12 (d, J = 10.86 Hz, 1H), 5.60 (d, J = 17.56 Hz, 1H), 6.68-6.71 (m, 7H), 6.97 (d, J = 8.55 Hz, 2H), 7.26 (d, J = 8.67 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): d 21.54, 111.96, 122.68, 123.46, 125.04, 127.11, 131.35, 136.55, 139.02, 147.83, 148.17. mp. 155–157 ° C. HRMS: Cald. for $C_{24}H_{25}N$ (M^+) 327.1987, Found: 327.1978.

N,N-bis(3,5-dimethylphenyl)-4-[2-(3,5-dimethylphenyl) ethenyl]benzenamine

^{1}H NMR (300 MHz, $CDCl_3$): d 2.22 (s, 12H), 2.32 (s, 6H), 6.68-6.72 (m, 6H), 6.87 (s, 1H), 6.95 – 7.00 (m, 4H), 7.11 (s, 2H), 7.33 (d, J = 8.55, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): d 21.29, 122.50, 123.22, 124.15, 124.85, 126.83, 127.09, 127.86, 128.98, 130.95, 137.60, 138.03, 138.79, 147.54, 147.65. mp. 150–152 ° C. HRMS: Cald. for $C_{32}H_{33}N$ (M^+) 431.26130, Found: 431.26200.

4-ethenyl-N,N-bis(3-methylphenyl)benzenamine (Table 2, Entry 3)

Following the general procedure, Pd_2dba_3 (18.3 mg, 2 mol %), NaO*t*Bu (336 mg, 3.5 mmol), ligand **1** (13.6 mg, 4 mol %), 4-aminostyrene (119 mg, 1 mmol), 3-bromotoluene (547 mg, 3.2 mmol), and 10 mL of dry toluene at 110 ° C for 16 h afforded 4-ethenyl-N,N-bis(3-methylphenyl)benzenamine (84 mg, 28 %) as a viscous liquid and N,N-bis(3-methylphenyl)-4-[2-(3-dimethylphenyl)ethenyl]benzenamine (232 mg, 60 %) as a yellow solid after chromatography with 1% EtOAc/hexane mixture. Total yield = 88 %.

^{1}H NMR (300 MHz, $CDCl_3$): d 2.25 (s, 6H), 5.12 (d, J = 10.86 Hz, 1H), 5.59 (d, J = 17.58 Hz, 1H) 6.60 (dd, J_1 = 10.98 Hz, J_2 = 17.58 Hz, 1H), 6.82 – 6.90 (m, 6H), 6.98 – 7.01 (m, 2H), 7.10 – 7.05 (m, 2H), 7.25 – 7.28 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): d 21.63, 112.13, 121.88, 123.62, 123.99, 125.32, 127.17, 129.21, 131.69, 136.48, 139.27, 147.81, 147.91. HRMS: Cald. for $C_{22}H_{21}N$ (M^+) 299.16740, Found: 299.16704.

N,N-bis(3-methylphenyl)-4-[2-(3-dimethylphenyl) ethenyl]benzenamine

^{1}H NMR (300 MHz, $CDCl_3$): d 2.24 (s, 6H), 2.34 (s, 3H), 6.81-6.83 (m, 2H), 6.87-6.92 (m, 4H), 6.96 – 7.03 (m, 4H), 7.09-7.20 (m, 4H), 7.25-7.28 (m, 2H), 7.35-7.36 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): d 21.61, 121.96, 123.60, 123.66, 124.06, 125.38, 127.17, 127.43, 128.19, 128.25, 128.72,

129.23, 131.44, 137.79, 138.30, 139.26, 147.69, 147.75. mp. 82–84 ° C. HRMS: Cald. for $C_{29}H_{27}N$ (M^+) 389.21435, Found: 389.21493.

4-ethenyl-N,N-bis(3-methyl-4-methoxyphenyl)benzenamine (Table 2, Entry 4)

Following the general procedure, Pd_2dba_3 (18.3 mg, 2 mol %), NaO*t*Bu (336 mg, 3.5 mmol), ligand **1** (13.6 mg, 4 mol %), 4-aminostyrene (119 mg, 1 mmol), 3-methyl-4-bromoanisole (643 mg, 3.2 mmol), and 10 mL of dry toluene at 110 ° C for 16 h afforded 4-ethenyl-N,N-bis(3-methyl-4-methoxyphenyl)benzenamine (95 mg, 27 %) as a viscous liquid and N,N-bis(3-methyl-4-methoxyphenyl)-4-[2-(3-methyl-4-methoxyphenyl) ethenyl]benzenamine (284 mg, 59 %) as a viscous yellow liquid after chromatography with 1 - 5 % EtOAc/hexane mixture. Total yield = 86 %.

^{1}H NMR (300 MHz, $CDCl_3$): d 2.05 (s, 6H), 3.79 (s, 6H), 5.03 (d, J = 11.01 Hz, 1H), 5.51 (d, J = 17.61 Hz, 1H), 6.50 – 6.76 (m, 7H), 6.92 (d, J = 8.67 Hz, 2H), 7.17 – 7.25 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): d 55.56, 110.54, 112.39, 116.78, 118.13, 127.09, 128.81, 128.86, 136.48, 136.69, 139.04, 149.07, 156.96. HRMS: Cald. For $C_{24}H_{25}NO_2$ (M^+) 359.18853, Found: 359.18904.

N,N-bis(3-methyl-4-methoxyphenyl)-4-[2-(3-methyl-4-methoxyphenyl) ethenyl]benzenamine

^{1}H NMR (300 MHz, $CDCl_3$): d 2.08 (s, 6H), 2.39 (s, 3H), 3.80 (s, 9H), 6.55 (d, J = 8.67 Hz, 2H), 6.68-6.78 (m, 7H), 6.84 (s, 1H), 6.94-6.97 (d, J = 8.67 Hz, 2H), 7.26-7.30 (m, 2H), 7.48 (d, J = 8.43 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): d 19.31, 20.40, 55.53, 111.88, 112.38, 115.78, 116.79, 118.37, 123.03, 126.42, 127.23, 128.18, 128.82, 129.97, 136.43, 137.06, 139.03, 148.68, 156.95, 158.81. HRMS: Cald. for $C_{32}H_{33}NO_3$ (M^+) 479.24604, Found: 479.24690.

4-ethenyl-N,N-bis(4-methoxyphenyl)benzenamine (Table 2, Entry 5)

Following the general procedure, Pd_2dba_3 (18.3 mg, 2 mol %), NaO*t*Bu (336 mg, 3.5 mmol), ligand **1** (13.6 mg, 4 mol %), 4-aminostyrene (119 mg, 1 mmol), 4-bromoanisole (598 mg, 3.2 mmol), and 10 mL of dry toluene at 110 ° C for 16 h afforded 4-ethenyl-N,N-bis(4-methoxyphenyl)benzenamine (157 mg, 47 %) as a viscous liquid and N,N-bis(4-methoxyphenyl)-4-[2-(4-methoxyphenyl)ethenyl]benzenamine (148 mg, 34 %) as a yellow solid after chromatography with 1 - 5 % EtOAc/hexane mixture. Total yield = 81 %.

^{1}H NMR (300 MHz, $CDCl_3$): d 3.76 (s, 6H), 5.05 – 5.09 (dd, J_1 = 0.72 Hz, J_2 = 10.86 Hz, 1H), 5.53 – 5.59 (dd, J_1 = 0.84 Hz, J_2 = 17.58 Hz, 1H) 6.56 – 6.65 (dd, J_1 = 10.86 Hz, J_2 = 17.58 Hz, 1H), 6.77 – 6.89 (m, 6H), 7.00 – 7.05 (m, 4H), 7.19 – 7.22 (d, J = 8.67 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): d 55.62, 111.25, 114.83, 120.62, 126.69, 127.04, 130.10, 136.49, 140.99, 148.58, 156.00. HRMS Cald. for $C_{22}H_{21}NO_2$ (M^+) 331.15723, Found: 331.15772.

N,N-bis(4-methoxyphenyl)-4-[2-(4-methoxyphenyl)ethenyl]benzenamine

^{1}H NMR (300 MHz, $CDCl_3$): d 3.77 (s, 6H), 3.79 (s, 3H), 6.80-6.91 (m, 10H), 7.03-7.06 (m, 4H), 7.27 (d, J = 8.76 Hz, 2H), 7.38 (d, J = 8.76 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): d 55.47, 55.64, 114.25, 114.84, 120.88, 125.84, 126.49, 126.66, 127.09, 127.52, 130.18, 130.80, 141.02, 148.11, 155.99, 159.07. mp. 118–120 ° C. HRMS: Cald. for $C_{29}H_{27}NO_3$ (M^+) 437.19909, Found: 437.19988.

4-ethenyl-N,N-bis(3-methoxyphenyl)benzenamine (Table 2, Entry 6)

Following the general procedure, Pd_2dba_3 (18.3 mg, 2 mol %), NaO*t*Bu (336 mg, 3.5 mmol), ligand **1** (13.6 mg, 4 mol %), 4-aminostyrene (119 mg, 1 mmol), 3-bromoanisole (598 mg,3.2 mmol), and 10 mL of dry toluene at 110 ° C for 16 h afforded 4-ethenyl-N,N-bis(3-methoxyphenyl)benzenamine (199 mg, 60 %) and N,N-bis(3-methoxyphenyl)-4-[2-(3-methoxyphenyl) ethenyl]benzenamine (147 mg, 34 %) after chromatography with 1 - 5 % EtOAc/hexane mixture. Total yield = 94 %.

^{1}H NMR (300 MHz, $CDCl_3$): d 3.63 (s, 6H), 5.06 (d, J = 10.86 Hz, 1H), 5.53 (d, J = 17.61 Hz, 1H), 6.48-6.57 (m, 7H), 6.94 (d, J = 8.55 Hz, 2H), 7.04 (t, J = 8.04 Hz, 2H), 7.17 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): d 55.22, 108.42, 110.14, 112.24, 116.86, 124.04, 126.99, 129.77, 132.09, 136.19, 147.16, 148.67, 160.40. HRMS: Cald. for $C_{22}H_{21}NO_2$ (M^+) 331.15723, Found: 331.15790.

N,N-bis(3-methoxyphenyl)-4-[2-(3-methoxyphenyl)ethenyl]benzenamine

^{1}H NMR (300 MHz, $CDCl_3$): d 3.70 (s, 6H), 3.82 (s, 3H), 6.56 – 6.59 (m, 2H), 6.65 – 6.70 (m, 4H), 6.77 – 6.80 (m, 1H), 6.98 – 7.17 (m, 8H), 7.22 – 7.24 (t, J = 7.95 Hz, 1H), 7.36 – 7.38 (d, J = 8.55 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): d 55.22, 108.54, 110.24, 111.49, 112.93, 116.95, 119.01, 123.96, 126.99, 127.32, 128.42, 129.55, 129.80, 131.58, 139.01, 147.08, 148.59, 159.83, 160.41. HRMS: Cald. for $C_{29}H_{27}NO_3$ (M^+) 437.19909, Found: 437.19988.

4-ethenyl-N,N-bis(3-methoxyphenyl)benzenamine & N,N-bis(3-methoxyphenyl)-4-[2-(3-methoxyphenyl) ethenyl]benzenamine (Table 2, Entry 7)

Following the general procedure, Pd_2dba_3 (18.3 mg, 2 mol %), NaO*t*Bu (336 mg, 3.5 mmol), ligand **1** (13.6 mg, 4 mol %), 4-aminostyrene (119 mg, 1

mmol), 3-iodoanisole (749 mg,3.2 mmol), and 10 mL of dry toluene at 110 ° C for 16 h afforded 4-ethenyl-N,N-bis(3-methoxyphenyl)benzenamine (106 mg, 32 %) and N,N-bis(3-methoxyphenyl)-4-[2-(3-methoxyphenyl) ethenyl]benzenamine (277 mg, 63 %) after chromatography with 1 - 5 % EtOAc/hexane mixture. Total yield = 95 %.

Same data as in Entry 6 of Table 2.

N,N-bis(4-methoxyphenyl)-4-[2-(4-methoxyphenyl) ethenyl]benzenamine (Table 2, Entry 8)

Following the general procedure, Pd_2dba_3 (18.3 mg, 2 mol %), NaO*t*Bu (336 mg, 3.5 mmol), ligand **1** (13.6 mg, 4 mol %), 4-aminostyrene (119 mg, 1 mmol), 4-iodoanisole (749 mg,3.2 mmol), and 10 mL of dry toluene at 110 ° C for 16 h afforded the N,N-bis(4-methoxyphenyl)-4-[2-(4-methoxyphenyl) ethenyl]benzenamine (180 mg, 41 %) as the sole product after chromatography with 1 - 5 % EtOAc/hexane mixture.

Same data as in Entry 5 of Table 2.

N,N-bis(4-methylphenyl)-4-[2-(4-methylphenyl) ethenyl]benzenamine (Table 2, Entry 9)

Following the general procedure, Pd_2dba_3 (18.3 mg, 2 mol %), NaO*t*Bu (336 mg, 3.5 mmol), ligand **1** (13.6 mg, 4 mol %), 4-aminostyrene (119 mg, 1 mmol), 4-Iodotoluene (698 mg,3.2 mmol), and 10 mL of dry toluene at 110 ° C for 16 h. afforded N,N-bis(4-methylphenyl)-4-[2-(4-methylphenyl) ethenyl]benzenamine (338 mg, 87 %) as the sole product after chromatography with 1 % EtOAc/hexane mixture.

Same data as in Entry 1 of Table 2.

General procedure for the synthesis of unsymmetrically substituted diarylaminostilbene derivatives.

N,N-diphenyl-4-[2-(4-methylphenyl) ethenyl]benzenamine (6a)

An oven dried Schlenk tube equipped with a magnetic stirring bar was charged with Pd_2dba_3 (2 mol %) and NaO*t*Bu (3.5 mmol). The tube was capped with a rubber septum, evacuated and then flushed with argon three times. ligand **1** (4 mol %), 4-aminostyrene (1 mmol), bromobenzene (314 mg, 2 mmol) and toluene (10 mL) were successively added via syringe. After the tube was heated at 60 ° C for 3 h, all the starting material was converted in to the N, N-diphenylaminostyrene as judged by TLC. To this reaction mixture, 4-bromotoluene (205 mg, 1.2 mmol) was added and the temperature was raised to 110 ° C. After heating for another 16 h, the reaction mixture was cooled to room temperature. The reaction mixture was filtered through a celite pad to remove the solid impurities and the filtrate was concentrated *in vacuo*. The crude product was purified by column chromatography using 1 % EtOAc/hexane as eluants to afford the coupled product **6a** (312 mg, 86 %) as a yellow solid

^{1}H NMR (300 MHz, $CDCl_3$): d 3.34 (s, 3H), 7.97 – 8.15 (m, 12H), 8.21 – 8.26 (m, 4H), 8.34 – 8.39 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): d 21.22, 122.90, 123.69, 124.36, 126.19, 126.99, 127.13, 127.19, 129.23, 129.34, 131.74, 134.78, 137.11, 147.10, 147.54. mp. 162–164 ° C. HRMS: Cald. for $C_{27}H_{23}N$ (M^+) 361.18305, Found: 361.18340.

N,N-bis(4-methoxyphenyl)-4-[2-phenylethenyl]benzenamine 6b

Following the above procedure, Pd_2dba_3 (18.3 mg, 2 mol %), NaO*t*Bu (336 mg, 3.5 mmol), ligand **1** (13.6 mg, 4 mol %), 4-aminostyrene (119 mg, 1 mmol), 4-bromoanisole (374 mg, 2 mmol), and 10 mL of dry toluene was heated at 60 ° C for 3 h and to the same reaction mixture bromobenzene

(188 mg, 1.2 mmol) was added and heated at 110 ° C for 16 h afforded the coupled product **6b** (245 mg, 60 %) as a yellow solid after chromatography with 5 % EtOAc/hexane mixture.

^{1}H NMR (300 MHz, $CDCl_3$): d 3.77 (s, 6H), 6.80 – 6.83 (m, 4H), 6.88 – 6.95 (m, 3H), 7.00 – 7.06 (m, 5H), 7.21 (d, J = 6Hz, 1H), 7.29 – 7.32 (m, 4H), 7.44 – 7.47 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): d 55.42, 114.63, 120.40, 125.95, 126.13, 126.56, 126.99, 127.16, 128.29, 128.57, 129.47, 137.75, 140.67, 148.24, 155.85. mp. 120–122 ° C. HRMS: Cald. for $C_{28}H_{25}NO_2$ (M^+) 407.18853, Found: 407.18925.

N-(4-methylphenyl)-N-(Phenyl)-4-[2-phenylethenyl]benzenamine (7a)

Following the above procedure, Pd_2dba_3 (18.3 mg, 2 mol %), NaO*t*Bu (336 mg, 3.5 mmol), ligand **1** (13.6 mg, 4 mol %), 4-aminostyrene (119 mg, 1 mmol), 4-iodotoluene (218 mg, 1 mmol), and 10 mL of dry toluene was heated at 60 ° C for 3 h and to the same reaction mixture iodobenzene (449 mg, 2.2 mmol) was added and heated at 110 ° C for 16 h afforded the coupled product **7a** (282 mg, 78 %) as a yellow solid after chromatography with 1 % EtOAc/hexane mixture.

^{1}H NMR (300 MHz, $CDCl_3$): d 2.31 (s, 3H), 6.99 – 7.09 (m, 11H), 7.20 – 7.22 (m, 3H), 7.29 – 7.36 (m, 4H), 7.46 (d, J = 7.32 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): d 21.07, 122.82, 123.21, 124.20, 125.34, 126.47, 126.98, 127.40, 127.49, 128.42, 128.82, 129.38, 130.19, 131.26, 133.24, 137.86, 145.13, 147.73, 147.88. mp. 134–136 ° C. HRMS: Cald. for $C_{27}H_{23}N$ (M^+) 361.18305, Found: 361.18537.

N-(4-methoxyphenyl)-N-(Phenyl)-4-[2-phenylethenyl]benzenamine (7b)

Following the above procedure, Pd_2dba_3 (18.3 mg, 2 mol %), NaO*t*Bu (336 mg, 3.5 mmol), ligand **1** (13.6 mg, 4 mol %), 4-aminostyrene (119 mg, 1 mmol), 4-iodoanisole (234 mg, 1 mmol), and 10 mL of dry toluene was

heated at 60 ° C for 3 h and to the same reaction mixture iodobenzene (449 mg, 2.2 mmol) was added and heated at 110 ° C for 16 h afforded the coupled product **7b** (299 mg, 79%) as a viscous yellow liquid after chromatography with 1 - 2 % EtOAc/hexane mixture.

^{1}H NMR (300 MHz, $CDCl_3$): d 3.80 (s, 3H), 6.83 – 6.86 (m, 2H), 6.97 – 7.10 (m, 9H), 7.20 – 7.25 (m, 3H), 7.31 – 7.37 (m, 4H), 7.46 – 7.49 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): d 55.70, 114.97, 122.47, 123.54, 126.44, 126.77, 127.37, 127.44, 127.61, 128.41, 128.83, 129.34, 130.84, 137.87, 140.59, 147.86, 147.95, 156.48. HRMS: Cald. for $C_{27}H_{23}NO$ (M^+) 377.17796, Found: 377.17850.