

A Simple, Efficient Catalyst System For the Palladium-Catalyzed Amination of Aryl Chlorides, Bromides, and Triflates

SUPPORTING INFORMATION

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N-Methyl-N-phenyl-p-toluidine¹ (Table 1, entry 1) ¹H NMR (250 MHz, CDCl₃) δ 7.35-7.19 (m, 2H), 7.15-7.09 (m, 2H), 7.02-6.82 (m, 5H), 3.28 (s, 3H), 2.32 (s, 3H).

N-(4-Methylphenyl)morpholine^{1,2} (Table 1, entry 2) mp 47-48 °C (lit. mp 48 °C):² ¹H NMR (300 MHz, CDCl₃) δ 7.09 (d, 2H, J=8.5 Hz), 6.84 (d, 2H, J=8.2 Hz), 3.86 (t, 4H, J=4.7 Hz), 3.11 (t, 4H, J=4.6 Hz), 2.28 (s, 3H).

N,N-Dibutyl-p-toluidine^{1,3} (Table 1, entry 3) ¹H NMR (300 MHz, CDCl₃) δ 7.00 (d, 2H, J=8.6 Hz), 6.57 (d, 2H, J=8.6 Hz), 3.22 (t, 4H, J=7.7 Hz), 2.23 (s, 3H), 1.56-1.48 (m, 4H), 1.37-1.29 (m, 4H), 0.94 (t, 6H, J=7.4 Hz).

N-Benzyl-p-toluidine (Table 1, entry 4).⁴ ¹H NMR (250 MHz, CDCl₃) δ 7.25-7.39 (m, 5H), 6.98 (d, 2H, J=8.1 Hz), 6.56 (d, 2H, J=8.5 Hz), 4.31 (s, 2H), 3.90 (br s, 1H), 2.23 (s, 3H).

N-(2,5-Xylyl)pyrrolidine^{5,6} (Table 1, entry 5) ¹H NMR (250 MHz, CDCl₃) δ 6.99 (d, 1H, J=7.5 Hz), 6.69-6.63 (m, 2H), 3.25-3.10 (m, 4H), 2.29 (s, 3H), 2.28 (s, 3H), 1.95-1.85 (m, 4H).

N-(4-Methoxyphenyl)morpholine^{1,2} (Table 1, entry 7) mp 73-74 °C (lit. mp 71 °C):² ¹H NMR (300 MHz, CDCl₃) δ 6.91-6.81 (m, 4H), 3.88-3.85 (m, 4H), 3.78 (s, 3H), 3.08-3.05 (m, 4H).

N-(4-Cyanophenyl)morpholine^{5,7} (Table 1, entry 8) mp 85 °C (lit. mp 75-76.5 °C):⁷ ¹H NMR (300 MHz, CDCl₃) δ 7.52 (d, 2H, J=9.1 Hz), 6.86 (d, 2H, J=9.1 Hz), 3.87-3.84 (m, 4H), 3.29-3.26 (m, 4H).

N-(4-Cyanophenyl)-n-hexylamine (Table 1, entry 9)⁵ mp 33–34 °C (lit. mp 35.1–35.7 °C);⁵ ¹H NMR (CDCl₃, 300 MHz) δ 7.43–7.39 (m, 2H), 6.56–6.51 (m, 2H), 4.16 (s, br, 1H), 3.14 (m, 2H), 1.65–1.29 (m, 8H), 0.90 (t, 3H, J = 6.6 Hz).

N-(4-Cyanophenyl)-p-toluidine (Table 1, entry 10)⁸ mp 105–107 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.45 (d, 2H, J = 9.0 Hz), 7.16 (d, 2H, J = 8.5 Hz), 7.06 (d, 2H, J = 8.3 Hz), 6.89 (d, 2H, J = 9.0 Hz), 5.95 (s, br, 1H), 2.35 (s, 3H).

N-(2-Methoxyphenyl)benzylamine⁹ (Table 1, entry 11) ¹H NMR (300 MHz, CDCl₃) δ 7.40–7.20 (m, 5H), 6.86–6.76 (m, 2H), 6.70–6.57 (m, 2H), 4.66 (s, br, 1H), 4.35 (s, 2H), 3.84 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 146.7, 139.5, 138.0, 128.5, 127.4, 127.0, 121.2, 116.5, 110.0, 109.3, 55.3, 47.9; IR (neat, cm⁻¹) 3425, 2937, 1511, 1027, 735. Anal Calcd for C₁₄H₁₅NO: C, 78.84; H, 7.09. Found: C, 78.54; H, 6.79.

N-Methyl-N-(4-t-butylphenyl)aniline (Table 6, entry 1).¹⁰ ¹H NMR (CDCl₃, 300 MHz) δ 7.20–7.31 (m, 4H), 6.86 (m, 5H), 3.32 (s, 0.45H), 3.30 (s, 3H), 1.32 (s, 9H).

N,N-Dibutyl-4-t-butylaniline (Table 6, entry 3).¹¹ ¹H NMR (300 MHz, CDCl₃) δ 7.21 (d, 2H, J = 9.0 Hz), 6.59 (d, 2H, J = 8.7 Hz), 3.23 (t, 4H, J = 7.8 Hz), 1.62–1.50 (m, 4H), 1.41–1.28 (m, 4H), 1.28 (s, 9H), 0.94 (t, 6H, J = 7.5 Hz).

N-(2,5-Xylyl)-p-anisidine (Table 6, entry 4).⁵ ¹H NMR (CDCl₃, 300 MHz) δ 7.02 (m, 3H), 6.89–6.82 (m, 3H), 6.63 (d, 1H, J = 7.0 Hz), 5.17 (s, br, 1H), 3.80 (s, 3H), 2.23 (s, 3H), 2.20 (s, 3H).

N-Benzyl-3,5-xylidene (Table 6, entry 5).⁵ ¹H NMR (300 MHz, CDCl₃) δ 7.38–7.25 (m, 5H), 6.39 (s, 1H), 6.29 (s, 2H), 4.30 (s, 2H), 3.89 (s, br, 1H), 2.23 (s, 6H).

N-(3,5-Xylyl)morpholine (Table 6, entry 6).¹² ¹H NMR (250 MHz, CDCl₃) δ 6.55 (s, 3H), 3.85 (t, 4H, J = 4.9 Hz), 3.14 (t, 4H, J = 4.8 Hz), 2.29 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 151.4, 138.7, 122.0, 113.7, 67.0, 49.6, 21.6; IR (neat, cm⁻¹) 2961, 1594, 1262, 1119, 826. Anal Calcd for C₁₂H₁₇NO: C, 75.35; H, 8.96. Found: C, 75.14; H, 8.95.

3,5-Dimethyltriphenylamine (Table 6, entry 7).¹³ mp 136–137 °C (lit. mp 130–132 °C);¹³ ¹H NMR (250 MHz, CDCl₃) δ 7.30–7.20 (m, 4H), 7.07 (d, 4H, J = 7.7 Hz), 6.98 (t, 2H, J = 7.2 Hz), 6.71 (s, 2H), 6.67 (s, 1H), 2.22 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 148.0, 147.8,

138.8, 129.1, 124.8, 124.0, 122.3, 21.3; IR (neat, cm^{-1}) 3015, 1583, 1490, 1297, 753. Anal Calcd for $\text{C}_{20}\text{H}_{19}\text{N}$: C, 87.87; H, 7.01. Found: C, 87.93; H, 7.03.

2-Methoxy-2'-methyl diphenylamine (Table 6, entry 9).¹⁴ ^1H NMR (300 MHz, CDCl_3) δ 7.33–7.10 (m, 3H), 7.05–6.80 (m, 5H), 5.86 (s, br, 1H), 3.91 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.0, 140.8, 133.8, 130.8, 129.2, 126.6, 122.1, 120.8, 119.4, 119.3, 114.4, 110.3, 55.6, 17.9; IR (neat, cm^{-1}) 3428, 2937, 1594, 1212, 1027, 737. Anal Calcd for $\text{C}_{14}\text{H}_{15}\text{NO}$: C, 78.84; H, 7.09. Found: C, 78.70; H, 6.99.

N-(4-Methylphenyl)hexylamine (Table 2, entry 1).¹ mp 37 °C (lit. mp 37.1–37.3 °C).¹ This material contained 1% 3 as judged by GC and ^1H NMR analysis: ^1H NMR (CDCl_3 , 300 MHz) δ 6.97 (d, 2H, J = 8.89 Hz), 6.54 (d, 2H, J = 8.7 Hz), 3.45 (s, br, 1H), 3.07 (t, 2H, J = 7.5 Hz), 1.64–1.26 (m, 8H), 0.89 (m, 3H).

Di-p-tolylamine (Table 2, entry 3)^{5,15} mp 78–79 °C (lit. mp 79 °C);¹⁵ ^1H NMR (300 MHz, CDCl_3) δ 7.10 (d, J = 8.2 Hz, 4H), 6.98 (d, J = 8.4 Hz, 4H), 5.53 (s, 1H), 2.33 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 141.3, 130.3, 130.0, 118.1, 20.8; IR (neat, cm^{-1}) 3419, 3026, 2914, 2860, 1609, 1589, 1515, 1320, 1239, 1227, 1177, 1123, 1108, 1381, 1040, 880, 805, 772, 704. Anal. Calcd for $\text{C}_{14}\text{H}_{11}\text{N}$: C, 85.24; H, 7.66. Found: C, 85.29; H, 8.02.

N-(p-Tolyl)diphenylamine (Table 2, entry 4)¹⁶ mp 66–67.5 °C (lit. mp 68–75 °C);¹⁶ ^1H NMR (300 MHz, CDCl_3) δ 7.23 (d, 7.3 Hz, 4H), 7.11–6.96 (m, 10H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.2, 145.4, 132.9, 130.1, 129.3, 125.1, 123.8, 122.4, 21.0; IR (neat, cm^{-1}) 3085, 3058, 3033, 3004, 2975, 2919, 2860, 1594, 1582, 1509, 1490, 1449, 1323, 1293, 1274, 1171, 1150, 1111, 1075, 1028, 917, 899, 888, 814, 749, 712, 695. Anal. Calcd for $\text{C}_{19}\text{H}_{17}\text{N}$: C, 87.99; H, 6.61. Found: C, 88.01; H, 6.84.

N-Ethyl-N-phenyl-p-toluidine (Table 2, entry 7).¹³ ^1H NMR (250 MHz, CDCl_3) δ 7.25–7.18 (m, 4H), 7.11 (d, 2H, J = 8.3 Hz), 6.99–6.79 (m, 3H), 3.74 (q, 2H, J = 7.1 Hz), 2.32 (s, 3H), 1.20 (t, 3H, J = 7.0 Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 148.2, 145.0, 132.1, 130.0, 129.0, 123.4, 119.3, 118.2, 46.4, 20.8, 12.6; IR (neat, cm^{-1}) 2974, 1599, 1498, 1259, 810. Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{N}$: C, 85.26; H, 8.11. Found: C, 85.25; H, 8.15.

N-(4-Methylphenyl)piperidine (Table 2, entry 8).¹ ¹H NMR (CDCl₃, 300 MHz) δ 7.05 (d, 2H, J = 8.4 Hz), 6.85 (d, 2H, J = 8.4 Hz), 3.09 (t, 4H, J = 5.4 Hz), 2.26 (s, 3H), 1.73–1.50 (m, 6H).

N-Methyl-N-phenyl-2,5-xylidene (Table 2, entry 9).⁵ ¹H NMR (CDCl₃, 300 MHz) δ 7.19–7.14 (m, 3H), 7.01–6.95 (m, 2H), 6.72–6.67 (m, 1H), 6.54–6.51 (m, 2H), 3.20 (s, 3H), 2.30 (s, 3H), 2.09 (s, 3H).

N-(2,5-Xylyl)morpholine (Table 2, entry 12).⁴ ¹H NMR (300 MHz, CDCl₃) δ 7.05 (d, 1 H, J = 7.6 Hz), 6.81 (s, 1 H), 6.80 (d, 1 H, J = 7.6 Hz), 3.84 (m, 4 H, J = 4.6 Hz), 2.90 (m, 4 H, J = 4.6 Hz), 2.31 (s, 3 H), 2.27 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃) δ 151.1, 136.3, 131.1, 129.4, 124.1, 119.8, 67.6, 52.4, 21.4, 17.7; IR (neat, cm⁻¹) 2962, 2856, 1243, 1117, 996.

N-p-Anisidylpyrrolidine (Table 2, entry 16).¹⁷ mp 40–41 °C (lit. mp 40–41 °C); ¹H NMR (CDCl₃, 300 MHz) δ 6.84 (d, 2H, J = 9.1 Hz), 6.53 (d, 2H, J = 9.0 Hz), 3.76 (s, 3H), 3.28–3.20 (m, 4H), 2.02–1.90 (m, 4H).

1-(4-Methoxyphenyl)-4-methylpiperazine (Table 2, entry 18).¹⁸ mp 67–68 °C (lit. mp 69 °C);¹⁸ ¹H NMR (300 MHz, CDCl₃) δ 6.90 (m, 2 H, J = 9.1 Hz), 6.83 (m, 2 H, J = 9.1 Hz), 3.75 (s, 3 H), 3.10 (m, 4 H, J = 4.9 Hz), 2.56 (m, 4 H, J = 4.9 Hz), 2.34 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃) δ 153.8, 145.7, 118.2, 114.4, 55.6, 55.4, 50.7, 46.3; IR (neat, cm⁻¹) 1509, 1246, 1223, 1036, 832.

4,4'-Dimethoxydiphenylamine (Table 2, entry 19).¹⁴ mp 99.5–101.5 °C (lit. mp 101–103 °C);¹⁴ ¹H NMR (300 MHz, CDCl₃) δ 6.96 (d, J = 8.9 Hz, 4H), 6.84 (d, J = 9.0 Hz, 4H), 5.32 (s, 1H), 3.80 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 154.4, 138.1, 119.7, 114.9, 55.8; IR (neat, cm⁻¹) 3421, 3031, 3014, 2958, 2939, 2916, 2840, 1513, 1466, 1441, 1299, 1248, 1218, 1179, 1115, 1030, 830, 818, 762, 708. Anal. Calcd for C₁₄H₁₅NO₂: C, 73.34; H, 6.59. Found: C, 73.51; H, 6.74.

Benzophenone N-(2-methoxyphenyl)hydrazone (Table 2, entry 20).¹⁹ mp 101.5–102.5 °C (lit. mp 101 °C);¹⁹ ¹H NMR (300 MHz, CDCl₃) δ 8.02 (s, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.66–7.50 (m, 5H), 7.40–7.30 (m, 5H), 7.01 (td, J = 7.7, 1.7 Hz, 1H), 6.85–6.77 (m, 2H), 3.59 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 145.6, 145.0, 138.8, 134.4, 133.2, 129.7, 129.3, 129.2, 128.3, 128.1, 126.7, 121.7, 119.3, 112.5, 110.2, 55.7; IR (neat, cm⁻¹) 3342, 3060, 3010,

2970, 2945, 2840, 1602, 1561, 1511, 1494, 1457, 1441, 1432, 1322, 1256, 1218, 1181, 1127, 1025, 917, 766, 743, 702. Anal. Calcd for $C_{20}H_{18}N_2O$: C, 79.44; H, 6.00. Found: C, 79.48; H, 6.09.

N-(2-Methoxyphenyl)pyrrolidine (Table 2, entry 22)²⁰ 1H NMR (300 MHz, $CDCl_3$) δ 6.91–6.77 (m, 4H), 3.84 (s, 3H), 3.35–3.25 (m, 4H), 1.95–1.85 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.4, 139.9, 121.0, 119.6, 115.4, 111.6, 55.5, 50.4, 24.6; IR (neat, cm^{-1}) 2960, 1596, 1503, 1229, 735. Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53. Found: C, 74.63; H, 8.46.

N-(2,6-dimethylphenyl)benzylamine (Table 2, entry 26)²¹ 1H NMR (300 MHz, $CDCl_3$) δ 7.39–7.22 (m, 5 H), 7.02 (m, 2 H, J = 7.4 Hz), 6.85 (m, 1 H, J = 7.4 Hz), 4.17 (s, 2 H), 3.20 (br s, 1 H), 2.27 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.0, 140.5, 129.9, 128.9, 128.7, 128.1, 127.4, 122.3, 53.0, 18.7; IR (neat, cm^{-1}) 3361, 3029, 2941, 1218, 1096.

2,6-Diisopropyl-2',6'-dimethylidiphenylamine (Table 2, entry 27).²² mp 40.5–44 °C: 1H NMR (300 MHz, $CDCl_3$) δ 7.16–7.11 (m, 3H), 6.96 (d, J = 7.2 Hz, 2H), 6.74 (t, J = 7.5 Hz, 1H), 4.81 (s, 1H), 3.17 (sept, 6.8 Hz, 1H), 2.00 (s, 6H), 1.15 (s, 6H), 1.12 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.4, 143.3, 139.0, 129.7, 125.8, 125.0, 123.4, 119.8, 28.3, 23.7, 19.6; IR (neat, cm^{-1}) 3421, 3064, 3041, 3027, 2958, 2925, 2867, 1590, 1470, 1447, 1378, 1362, 1333, 1275, 1225, 1098, 1179, 1162, 1057, 1034, 990, 938, 920, 888, 793, 768, 737, 695, 683. Anal. Calcd for $C_{20}H_{27}N$: C, 85.35; H, 9.67. Found: C, 85.11; H, 9.56.

N-Benzyl-2-aminopyridine (Table 4, entry 1).²³ mp 93–94 °C which was determined to be a 19/1 mixture (by 1H NMR) of the title compound and bis(2-pyridyl)benzylamine. Data are given for the title compound: 1H NMR (300 MHz, $CDCl_3$) δ 8.07 (ddd, 1 H, J = 5.0, 1.8, 0.8 Hz), 7.40–7.23 (m, 6 H), 6.56 (ddd, 1 H, J = 7.1, 5.0, 0.9 Hz), 6.35 (ddd, 1 H, J = 8.4, 0.9, 0.8 Hz), 5.07 (s, br, 1 H), 4.48 (d, 2 H, J = 5.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 148.3, 139.3, 137.6, 128.7, 127.5, 127.3, 113.2, 106.9, 46.5; IR (neat, cm^{-1}) 3222, 1598, 1441, 770, 748, 699.

N-(2-Pyridyl)morpholine (Table 4, entry 2).²⁴ 1H NMR (300 MHz, $CDCl_3$) δ 8.20 (ddd, 1 H, J = 5.0, 2.0, 0.9 Hz), 7.49 (ddd, 1 H, J = 8.6, 7.1, 2.0 Hz), 6.66 (ddd, 1 H, J = 5.0, 2.0,

0.9 Hz), 6.63 (ddd, 1 H, $J = 8.6, 0.9, 0.9$ Hz), 3.82 (t, 4 H, $J = 4.9$ Hz), 3.49 (t, 4 H, $J = 4.9$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 158.8, 148.0, 137.6, 113.9, 107.0, 66.9, 45.7; IR (neat, cm^{-1}) 2964, 2858, 1256, 1121, 982, 944.

N-Methyl-N-(3-pyridyl)aniline (Table 4, entry 3)²⁴ ^1H NMR (300 MHz, CDCl_3) δ 8.31 (d, 1 H, $J = 2.8$ Hz), 8.12 (dd, 1 H, $J = 4.6, 1.5$ Hz), 7.33-7.02 (m, 7 H), 3.31 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ 143.2, 140.4, 136.5, 135.9, 125.0, 120.1, 118.8, 118.6, 117.7, 37.5; IR (neat, cm^{-1}) 3035, 1582, 1345, 1256, 1133.

N-Benzyl-3-aminopyridine (Table 4, entry 4)²⁵ mp 87-88 °C (lit. mp 88-89 °C).²⁵ ^1H NMR (300 MHz, CDCl_3) δ 8.07 (dd, 1 H, $J = 3.0, 0.6$ Hz), 7.96 (dd, 1 H, $J = 4.6, 1.5$ Hz), 7.38-7.26 (m, 5 H), 7.06 (ddd, 1 H, $J = 8.4, 4.6, 0.6$ Hz), 6.87 (ddd, 1 H, $J = 8.4, 3.0, 1.5$ Hz), 4.22 (br s, 1 H), 4.33 (s, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ 144.1, 138.9, 138.6, 136.2, 128.8, 127.52, 127.46, 123.8, 118.6, 47.9; IR (neat, cm^{-1}) 3261, 1590, 1578, 1328, 712.

N-Hexyl-3-aminopyridine (Table 4, entry 5)²⁴ mp 57-58 °C (lit. mp 73-75 °C).²⁴ ^1H NMR (300 MHz, CDCl_3) δ 8.01 (d, 1 H, $J = 2.8$ Hz), 7.93 (dd, 1 H, $J = 4.6, 1.0$ Hz), 7.06 (dd, 1 H, $J = 8.3, 4.6$ Hz), 6.84 (ddd, 1 H, $J = 8.3, 2.8, 1.0$ Hz), 3.80 (br s, 1 H), 3.10 (t, 2 H, $J = 6.9$ Hz), 1.62 (tt, 2 H, 6.9, 6.9 Hz), 1.46-1.26 (m, 6 H), 0.90 (t, 3 H, $J = 6.0$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 144.5, 138.4, 136.0, 123.8, 118.3, 43.7, 31.8, 29.5, 26.9, 22.8, 14.2; IR (neat, cm^{-1}) 3251, 1584, 1418, 789, 704.

N-(3-Pyridyl)morpholine (Table 4, entry 6)²⁴ ^1H NMR (300 MHz, CDCl_3) δ 8.31 (dd, 1 H, $J = 2.1, 1.5$ Hz), 8.13 (dd, 1 H, $J = 3.3, 2.4$ Hz), 7.20-7.17 (m, 2 H), 3.87 (m, 4 H, $J = 4.9$ Hz), 3.18 (m, 4 H, $J = 4.9$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 146.9, 141.1, 138.3, 123.5, 122.1, 66.7, 48.6; IR (neat, cm^{-1}) 2856, 1582, 1246, 1123, 930.

N,N-Dibutyl-3-aminopyridine (Table 4, entry 7)¹¹ ^1H NMR (300 MHz, CDCl_3) δ 8.05 (d, 1 H, $J = 3.0$ Hz), 7.87 (dd, 1 H, $J = 4.6, 1.2$ Hz), 7.08 (dd, 1 H, $J = 8.5, 4.6$ Hz), 6.88 (ddd, 1 H, $J = 8.5, 3.0, 1.2$ Hz), 3.26 (t, 4 H, $J = 7.5$ Hz), 1.56 (m, 4 H), 1.32 (q, 4 H, $J = 7.3, 7.3$ Hz), 0.95 (t, 6 H, $J = 7.3$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 143.9, 136.5, 134.5, 123.6, 117.7, 50.6, 29.3, 20.4, 14.2; IR (neat, cm^{-1}) 2962, 2935, 2873, 1584, 1225, 1181.

N-(4-Pyridyl)morpholine (Table 4, entry 8)²⁴ mp 107-109 °C (lit. mp 112-115 °C).²⁴ ¹H NMR (300 MHz, CDCl₃) δ 8.30 (dd, 2H, J=5.1, 1.5 Hz), 6.66 (dd, 2H, J=5.0, 1.6 Hz), 3.84 (t, 4H, J=4.9 Hz), 3.29 (t, 4H, J=5.0 Hz).

N-Benzyl-4-aminopyridine (Table 4, entry 9)²⁶ mp 108-110 °C (CH₂Cl₂/hexanes) (lit mp 110.5-111 °C)²⁶ which was determined to contain 3.6 % of bis (4-pyridyl)benzylamine by ¹H NMR analysis: ¹H NMR (300 MHz, CDCl₃) δ 8.20-8.18 (m, 2H), 7.39-7.27 (m, 5H), 6.46 (dd, 2H, J=4.7, 1.7 Hz), 4.54 (s, br, 1H), 4.37 (d, 2H, J=5.5 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 153.4, 149.7, 138.0, 128.7, 127.4, 127.2, 107.7, 46.8; IR (neat, cm⁻¹) 3204, 1602, 1505, 1349, 1316, 1216, 988, 810, 741, 699.

N-Methyl-N-(4-pyridyl)aniline (Table 4, entry 10)⁵ ¹H NMR (300 MHz, CDCl₃) δ 8.20-8.18 (m, 2H), 7.45-7.40 (m, 2H), 7.29-7.20 (m, 3H), 6.54 (dd, 2H, J=5.0, 1.7 Hz), 3.32 (s, 3H).

4-Methoxy-4'-(dimethylamino)diphenylamine (Table 7, entry 2)²⁷ mp 77-78 °C (lit. mp 78 °C):²⁷ ¹H NMR (300 MHz, C₆D₆) δ 6.97 (d, J = 8.9 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 6.64 (d, J = 8.9 Hz, 2H), 4.78 (s, 1H), 3.37 (s, 3H), 2.57 (s, 6H); ¹³C NMR (75 MHz, C₆D₆) δ 154.6, 147.2, 140.1, 135.6, 121.8, 118.9, 115.4, 115.1, 55.6, 41.6; IR (neat, cm⁻¹) 3273, 3039, 3013, 2966, 2954, 2879, 2832, 2792, 1507, 1476, 1457, 1437, 1304, 1295, 1252, 1237, 1208, 1169, 1129, 1034, 938, 818, 797, 762, 731. Anal. Calcd for C₁₅H₁₈N₂O: C, 74.35; H, 7.49. Found: C, 74.23; H, 7.47.

N-(p-Tolyl)-p-anisidine (Table 7, entry 3)¹⁴ mp 81-83 °C (lit. mp 82-83 °C):¹⁴ ¹H NMR (300 MHz, CDCl₃) δ 7.05 (d, J = 8.5 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H) 5.42 (s, 1H), 3.81 (s, 3H), 2.29 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 155.0, 142.5, 136.8, 130.0, 129.5, 121.3, 116.7, 114.8, 55.8, 20.8; IR (neat, cm⁻¹) 3415, 3026, 3014, 2952, 2911, 2858, 2836, 1613, 1582, 1515, 1466, 1316, 1295, 1241, 1225, 1179, 1125, 1105, 1032, 812, 768, 704. Anal. Calcd for C₁₄H₁₅NO: C, 78.84; H, 7.09. Found: C, 78.78; H, 7.02.

N-Ethyl-N-(3,5-dimethylphenyl)aniline (Table 7, entry 4)¹¹ ¹H NMR (300 MHz, CDCl₃) δ 7.29 (dd, J = 8.8, 8.5 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.92 (t, J = 8.5 Hz, 1H), 6.67 (s,

2H), 6.65 (s, 1H), 3.77 (q, $J = 6.8$ Hz, 2H), 2.28 (s, 6H), 1.23 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.1, 147.8, 139.0, 129.3, 123.6, 120.6, 120.3, 119.6, 46.6, 21.7, 13.0; IR (neat, cm^{-1}) 3035, 2972, 2917, 2869, 1590, 1495, 1470, 1370, 1351, 1289, 1268, 1250, 1191, 1129, 1106, 1071, 1032, 992, 847, 824, 809, 749, 693. Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{N}$: C, 85.28; H, 8.50. Found: C, 84.99; H, 8.69.

N-Mesityl-3,4-(methylenedioxy)aniline (Table 7, entry 6)¹⁴ mp 104.5–106.5 °C (lit. mp 77–79 °C):¹⁴ ^1H NMR (300 MHz, CDCl_3) δ 6.96 (s, 2H), 6.65 (d, $J = 8.3$ Hz, 1H), 6.14 (d, $J = 2.1$ Hz, 1H), 5.97 (dd, $J = 8.3, 2.3$ Hz, 1H), 5.87 (s, 2H), 4.98 (s, 1H), 2.33 (s, 3H), 2.21 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.5, 142.5, 140.1, 136.4, 135.7, 135.3, 129.4, 108.7, 105.4, 100.8, 96.5, 21.1, 18.4; IR (neat, cm^{-1}) 3369, 2953, 2917, 2885, 2856, 1632, 1615, 1497, 1482, 1245, 1227, 1194, 1038, 944, 932, 859, 822, 795. Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_2$: C, 75.27; H, 6.71. Found: C, 75.20; H, 6.76.

N-(4-t-Butylphenyl)piperidine (Table 7, entry 7).¹⁷ mp 36–37 °C (lit. mp 37–38 °C):¹⁷ ^1H NMR (300 MHz, CDCl_3) δ 7.26 (d, 2H, $J = 9.8$ Hz), 6.89 (d, 2H, $J = 9.7$ Hz), 3.11 (t, 4H, $J = 5.5$ Hz), 1.75–1.67 (m, 4H), 1.60–1.50 (m, 2H), 1.29 (s, 9H).

N-Allyl-2,5-xylidene (Table 7, entry 10).²⁸ ^1H NMR (250 MHz, CDCl_3) δ 6.93 (d, 1H, $J = 7.4$ Hz), 6.49 (d, 1H, $J = 7.6$ Hz), 6.44 (s, 1H), 6.06–5.93 (m, 1H), 5.33–5.16 (m, 2H), 3.81 (m, 2H), 3.60 (s, br, 1H), 2.28 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 145.6, 136.5, 135.4, 129.8, 118.9, 117.6, 116.6, 110.8, 46.5, 21.6, 17.1; IR (neat, cm^{-1}) 3435, 2918, 1581, 1521, 1301, 919, 795. Anal. Calcd for $\text{C}_{11}\text{H}_{15}\text{N}$: C, 81.94; H, 9.38. Found: C, 81.67; H, 9.41.

N-(4-t-Butylphenyl)morpholine (Table 9, entry 1).¹⁰ mp 63 °C (lit. mp 59 °C):¹⁰ ^1H NMR (300 MHz, CDCl_3) δ 7.30 (d, 2H, $J = 8.9$ Hz), 6.87 (d, 2H, $J = 8.9$ Hz), 3.86 (t, 4H, $J = 4.7$ Hz), 3.14 (t, 4H, $J = 4.9$ Hz), 1.30 (s, 9H).

N-(4-Nitrophenyl)piperidine (Table 9, entry 10).^{8,29} mp 103–104 °C (lit. mp 104 °C):²⁹ ^1H NMR (300 MHz, CDCl_3) δ 8.09 (d, 2H, $J = 9.3$ Hz), 6.79 (d, 2H, $J = 9.9$ Hz), 3.50 (m, 4H), 1.75–1.65 (m, 6H).

N-(3-Cyanophenyl)pyrrolidine (Table 5, entry 2).³⁰ mp 85-86 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.22 (ddd, 1 H, J = 7.5, 7.5, 2.1 Hz), 6.84 (d, 1 H, J = 7.5 Hz), 6.67-6.64 (m, 2 H), 3.29-3.24 (m, 4 H), 2.05-2.01 (m, 4 H); ¹³C NMR (75 MHz, CDCl₃) δ 147.7, 129.8, 120.0, 118.6, 115.8, 114.3, 112.7, 47.7, 25.6; IR (neat, cm⁻¹) 2225, 1596, 1380, 791, 687.

N-(Diphenylmethylene)-4-nitroaniline (Table 5, entry 3).³¹ mp 157-159 °C (lit. mp 156 °C);³¹ ¹H NMR (300 MHz, CDCl₃) δ 8.05 (d, J = 8.8 Hz, 2H), 7.77 (broad s, 2H), 7.44 (broad s, 2H), 7.32 (s, br, 4H), 7.12 (s, br, 2H), 6.81 (d, J = 8.8 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 169.8, 157.7, 143.5, 138.6, 135.4, 131.7, 129.8, 129.4, 128.5, 124.8, 121.1; IR (neat, cm⁻¹) 3064, 2927, 2844, 1586, 1511, 1441, 1339, 1318, 1293, 1231, 1110, 959, 849, 785, 756, 706, 693, 666. Anal. Calcd for C₁₉H₁₄N₂O₂: C, 75.48; H, 4.67. Found: C, 75.33; H, 4.65.

4-Methoxy-4'-nitrodiphenylamine (Table 5, entry 4).³² mp 152-152.5 °C (lit. mp 151 °C);³² ¹H NMR (300 MHz, CDCl₃) δ 8.09 (d, J = 9.2 Hz, 2H), 7.17 (d, J = 8.9 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 6.77 (d, J = 9.2 Hz, 2H), 6.15 (s, 1H), 3.85 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 157.6, 151.9, 139.2, 132.2, 126.5, 125.7, 115.1, 112.8, 55.7; IR (neat, cm⁻¹) 3325, 3191, 3124, 3110, 3082, 3066, 3041, 3022, 2954, 2931, 2906, 2835, 1592, 1544, 1526, 1511, 1480, 1461, 1445, 1320, 1293, 1231, 1181, 1167, 1111, 1028, 1000, 830, 812, 801, 762, 749, 697, 675. Anal. Calcd for C₁₃H₁₂N₂O₃: C, 63.93; H, 4.95. Found: C, 63.73, H, 4.86.

N-(3-Acetylphenyl)aniline (Table 5, entry 6).³³ mp 91.5-92.5 (lit. mp 93 °C);³³ ¹H NMR (300 MHz, CDCl₃) δ 7.62 (dd, 1 H, J = 2.0, 1.4 Hz), 7.46 (ddd, 1 H, J = 7.5, 1.4, 1.4 Hz), 7.34-7.22 (m, 4 H), 7.11-7.05 (m, 2 H), 6.97 (tt, 1 H, J = 7.3, 1.1 Hz), 5.92 (br s, 1 H), 2.56 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃) δ 198.3, 143.9, 142.4, 138.4, 129.6, 121.9, 121.6, 120.8, 118.6, 116.6, 27.0; IR (neat, cm⁻¹) 3355, 1667, 1580, 1324, 687.

N-(4-Acetylphenyl)morpholine (Table 5, entry 7).^{4,34} mp 96-97 °C (lit. mp 97-98 °C);³⁴ ¹H NMR (300 MHz, CDCl₃) δ 7.89 (d, 2H, J=9.1 Hz), 6.87 (d, 2H, J=9.1 Hz), 3.86 (t, 4H, J=4.8 Hz), 3.31 (t, 4H, J=5.1 Hz), 2.54 (s, 3H).

N-(4-Acetylphenyl)-p-toluidine (Table 5, entry 8).^{8,35} mp 114-115 °C (lit. mp 115 °C);³⁵ ¹H NMR (300 MHz, CDCl₃) δ 7.83 (d, 2 H, J = 9.0 Hz), 7.14 (d, 2 H, J = 8.5 Hz), 7.07 (m, 2 H, J = 8.5 Hz), 6.91 (m, 2 H, J = 9.0 Hz), 6.20 (br s, 1 H), 2.51 (s, 3 H), 2.33 (s, 3 H); ¹³C NMR

(75 MHz, CDCl₃) δ 196.5, 149.2, 137.9, 133.4, 130.8, 130.1, 128.5, 121.6, 113.9, 26.4, 21.1; IR (neat, cm⁻¹) 3325, 1648, 1563, 1277, 809.

N-(4-Carbomethoxyphenyl)morpholine (Table 5, entry 9).⁴ mp 162–163 °C: (lit. mp 152–154 °C):⁴ ¹H NMR (300 MHz, CDCl₃) δ 7.94 (d, 2H, J = 9.1 Hz), 6.86 (d, 2H, J = 9.1 Hz), 3.87 (s, 3H), 3.87–3.84 (m, 4H), 3.30–3.25 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 167.0, 154.1, 131.2, 120.2, 113.4, 66.6, 51.7, 47.6; IR (neat, cm⁻¹) 2970, 1700, 1115, 770. Anal. Calcd for C₁₂H₁₅NO₃: C, 65.14; H, 6.83. Found: C, 65.18; H, 6.78.

N-(4-Cyanophenyl)hexylamine (Table 5, entry 11).³⁶ mp 36–37 °C (lit. mp 35.1–35.7 °C):³⁶ ¹H NMR (300 MHz, CDCl₃) δ 7.38 (m, 2H, J = 8.3 Hz), 6.54 (m, 2H, J = 8.3 Hz), 4.29 (br s, 1H), 3.12 (t, 2H, J = 7.2 Hz), 1.62 (tt, 2H, J = 7.2, 7.2 Hz), 1.44–1.28 (m, 6H), 0.90 (t, 3H, J = 6.7 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 151.6, 133.7, 120.8, 112.1, 98.1, 43.4, 31.7, 29.3, 26.9, 22.8, 14.2; IR (neat, cm⁻¹) 3352, 2929, 2213, 1607, 1532, 1171.

4-Cyano-2'-carboethoxydiphenylamine (Table 5, entry 12).^{8,37} mp 108–109 °C: ¹H NMR (300 MHz, CDCl₃) δ 9.75 (s, br, 1H), 8.01 (d, 1H, J = 8.8 Hz), 7.54 (d, 2H, J = 8.6 Hz), 7.43–7.40 (m, 2H), 7.23 (d, 2H, J = 8.6 Hz), 6.91 (t, 1H, J = 8.3 Hz), 4.35 (q, 2H, J = 7.0 Hz), 1.40 (t, 3H, J = 7.2 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 168.1, 145.6, 144.4, 133.9, 133.5, 131.8, 119.8, 119.3, 118.7, 116.0, 115.0, 103.9, 61.0, 14.2; IR (neat, cm⁻¹) 3277, 2980, 2219, 1671, 1586, 1258, 1081, 749. Anal. Calcd for C₁₆H₁₄N₂O₂: C, 72.16; H, 5.30. Found: C, 72.03; H, 5.33.

N-(3-Carbomethoxyphenyl)morpholine (Table 5, entry 13).^{8,37} ¹H NMR (300 MHz, CDCl₃) δ 7.58 (dd, 1H, J = 2.6, 1.5 Hz), 7.54 (ddd, 1H, 7.9, 1.5, 0.9 Hz), 7.33 (dd, 1H, J = 7.9, 7.9 Hz), 7.10 (ddd, 1H, J = 7.9, 2.6, 0.9 Hz), 3.90 (s, 3H), 3.87 (t, 4H, J = 4.5 Hz), 3.20 (m, 4H, J = 4.5 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 167.5, 151.4, 131.2, 129.3, 121.2, 120.2, 116.5, 67.0, 52.3, 49.3; IR (neat, cm⁻¹) 1717, 1262, 1117, 998, 756.

2-Nitro-4'-methoxydiphenylamine (Table 5, entry 15).³⁸ mp 88–89 °C (lit. mp 88–90 °C):³⁸ ¹H NMR (250 MHz, CDCl₃) δ 9.41 (s, br, 1H), 8.19 (d, 1H, J = 8.5 Hz), 7.29 (t, 1H, J = 8.2 Hz), 7.19 (d, 2H, J = 8.8 Hz), 7.02–6.93 (m, 3H), 6.71 (t, 1H, J = 8.1 Hz), 3.84 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 157.9, 144.5, 135.7, 132.4, 131.2, 127.1, 126.6, 116.7, 115.7, 114.9, 55.5; IR (neat, cm⁻¹) 3331, 2961, 1617, 1505, 1247, 1224, 1034, 745. Anal. Calcd for C₁₃H₁₂N₂O₃: C, 63.93; H, 4.95. Found: C, 63.74; H, 5.05.

2-Carbomethoxy-3'-methyl diphenylamine (Table 5, entry 16).³⁹ ¹H NMR (250 MHz, CDCl₃) δ 9.42 (s, br, 1H), 7.95 (dd, 1H, J=1.5, 8.1 Hz), 7.31-7.19 (m, 3H), 7.12-7.00 (m, 2H), 6.90 (d, 1H, J=7.4 Hz), 6.74-6.68 (m, 1H), 3.90 (s, 3H), 2.34 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 168.9, 148.0, 140.6, 139.2, 134.0, 131.6, 129.1, 124.4, 123.2, 119.5, 116.9, 114.1, 111.7, 51.7, 21.4; IR (neat, cm⁻¹) 3323, 2953, 1687, 1579, 1517, 1227, 1085, 745. Anal Calcd for C₁₅H₁₅NO₂: C, 74.67; H, 6.27. Found: C, 74.87; H, 6.21.

N-(4-Cyanophenyl)benzylamine (Table 7, entry 13).⁴⁰ mp 78-79 °C (ether/hexanes) (lit. mp 79.5-80 °C).⁴⁰ This material was determined to contain 2.5% 4,4'-dicyanobiphenyl by GC and ¹H NMR analysis: ¹H NMR (300 MHz, CDCl₃) δ 7.39-7.25 (m, 7H), 6.56 (dt, 2H, J=9.3, 2.2 Hz), 4.72 (s, br, 1H), 4.36 (d, 2H, J=5.5 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 151.2, 137.9, 133.7, 128.9, 127.7, 127.3, 120.6, 112.5, 98.9, 47.6; IR (neat, cm⁻¹) 3358, 1610, 1536, 1347, 1173, 818, 733, 691.

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