

Supporting Information
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Supporting Information

Selective Copper-Promoted Cross-Coupling of Aromatic Amines with Alkyl Boronic Acids

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Copper-Promoted Cross-Coupling of Anilines with Alkyl Boronic Acids; General Procedure

Cu(OAc)₂ (1.3–4 mmol) was added to a solution of aniline (1 mmol) and pyridine (3–4 mmol) in dioxane (5 mL), and the mixture was refluxed for 15 min. Boronic acid (1.3–4 mmol) was added, and the reaction mixture was allowed to react at reflux until no unreacted aniline was detected or for a maximum time of 10 h. It was allowed to reach r.t., poured into H₂O (25 mL) and extracted with EtOAc (40 mL). The organic layer was dried over Na₂SO₄ (anhydrous), filtered and concentrated. The crude residue was flash chromatographed on SiO₂ using EtOAc-hexanes as eluent.

N-butyl-*N*-(4-*tert*-butylphenyl)amine (Table 1, entry 2, R = *t*Bu)

Yield: 83%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 7.20 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 3.10 (t, *J* = 6.7 Hz, 2H), 1.55–1.62 (m, 2H), 1.38–1.49 (m, 2H), 1.28 (s, 9H), 0.96 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 146.2, 139.7, 125.9, 112.3, 43.8, 33.8, 33.7, 31.5, 20.3, 13.9.

(ESI+) = 206.7 (M+1).

N-(4-*tert*-butylphenyl)-*N*-isobutylamine (Table 1, entry 3, R = *t*Bu)

Yield: 57%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 7.20 (d, *J* = 8.5 Hz, 2H), 6.57 (d, *J* = 8.5 Hz, 2H), 2.93 (d, *J* = 6.6 Hz, 2H), 1.81–1.94 (m, 1H), 1.29 (s, 9H), 0.99 (d, *J* = 6.6 Hz, 6H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 146.2, 139.6, 125.9, 112.3, 52.0, 33.8, 31.5, 28.0, 24.5.

(ESI+) = 205.9 (M+1).

N-(4-*tert*-butylphenyl)-*N*-(3-methylbutyl)amine (Table 1, entry 4, R = *t*Bu)

Yield: 82%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 7.21 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 3.11 (t, *J* = 7.4 Hz, 2H), 1.65–1.78 (m, 1H), 1.51 (c, *J* = 7.4 Hz, 2H), 1.28 (s, 9H), 0.95 (d, *J* = 6.6 Hz, 6H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 146.2, 139.7, 125.9, 112.4, 42.3, 38.6, 33.7, 31.5, 25.9, 22.6.

(ESI+) = 219.9 (M+1).

N-(4-*tert*-butylphenyl)-*N*-(2-cyclohexylethyl)amine (Table 1, entry 5, R = *t*Bu)

Yield: 72%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 7.20 (d, *J* = 8.5 Hz, 2H), 6.55 (d, *J* = 8.5 Hz, 2H), 3.11 (t, *J* = 7.1 Hz, 2H), 1.71 (m, 6H), 1.49 (m, 3H), 1.35 (m, 2H), 1.28 (s, 11H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 146.2, 139.7, 125.9, 112.3, 41.7, 37.2, 35.4, 33.7, 33.3, 31.5, 26.5, 26.2.

(ESI+) = 260.0 (M+1).

***N*-(4-*tert*-butylphenyl)-*N*-(2-phenylethyl)amine (Table 2, entry 1)**

Yield: 83%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 7.19-7.35 (m, 7H), 6.57 (d, *J* = 8.8 Hz, 2H), 3.39 (t, *J* = 7.1 Hz, 2H), 2.91 (t, *J* = 7.1 Hz, 2H), 1.28 (s, 9H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 145.6, 140.1, 139.3, 128.7, 128.5, 126.3, 125.9, 112.6, 45.2, 35.5, 33.8, 31.5.

(ESI+) = 246.1 (M+1).

***N*-(4-*tert*-butylphenyl)-*N*-isopropylamine (Table 1, entry 7, R = *t*Bu)**

Yield: 22%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 7.20 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 8.8 Hz, 2H), 3.60 (c, *J* = 6.3 Hz, 1H), 1.28 (s, 9H), 1.21 (d, *J* = 6.6 Hz, 6H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 145.1, 139.7, 126.0, 112.8, 44.3, 33.8, 31.5, 23.1.

(ESI+) = 192.4 (M+1).

***N*-(4-*tert*-butylphenyl)-*N*-cyclohexylamine (Table 1, entry 8, R = *t*Bu)**

Yield: 62%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 7.20 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 8.8 Hz, 2H), 3.22 (m, 1H), 2.05 (m, 2H), 1.60-1.79 (m, 3H), 1.17-1.40 (m, 14H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 145.0, 139.5, 125.9, 112.7, 51.8, 33.7, 33.6, 31.5, 25.9, 25.0.

(ESI+) = 232.1 (M+1).

***N*-butyl-*N*-(4-methoxyphenyl)amine (Table 1, entry 2, R = OMe)**

Yield: 91%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 6.78 (d, *J* = 9.0 Hz, 2H), 5.59 (d, *J* = 9.0 Hz, 2H), 3.75 (s, 3H), 3.07 (t, *J* = 6.9 Hz, 2H), 1.60 (m, 2H), 1.44 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 151.8, 142.7, 114.8, 113.9, 55.7, 44.6, 31.7, 20.2, 13.8.

(ESI+) = 180.4 (M+1).

***N*-isobutyl-*N*-(4-methoxyphenyl)amine (Table 1, entry 3, R = OMe)**

Yield: 90%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 6.78 (d, *J* = 8.8 Hz, 2H), 5.59 (d, *J* = 8.8 Hz, 2H), 3.74 (s, 3H), 2.88 (d, *J* = 6.9 Hz, 2H), 1.80-1.95 (m, 1H), 0.97 (d, *J* = 6.6 Hz, 6H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 151.7, 124.2, 114.8, 113.8, 55.7, 52.7, 27.9, 20.4.

(ESI+) = 180.3 (M+1).

***N*-(4-methoxyphenyl)-*N*-(3-methylbutyl)amine (Table 1, entry 4, R = OMe)**

Yield: 89%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 6.78 (d, *J* = 9.0 Hz, 2H), 6.58 (d, *J* = 9.0 Hz, 2H), 3.75 (s, 3H), 3.07 (t, *J* = 7.5 Hz, 2H), 1.70 (m, 1H), 1.50 (m, 2H), 0.95 (d, *J* = 6.6 Hz, 6H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 151.8, 142.8, 114.8, 113.9, 55.7, 43.1, 38.6, 25.9, 22.6.

(ESI+) = 194.1 (M+1).

***N*-(2-cyclohexylethyl)-*N*-(4-methoxyphenyl)amine (Table 1, entry 5, R = OMe)**

Yield: 69%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 6.79 (d, *J* = 8.8 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 3.75 (s, 3H), 3.08 (t, *J* = 7.4 Hz, 2H), 1.72 (m, 6H), 1.49 (m, 2H), 1.23 (m, 3H), 0.96 (m, 2H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 151.8, 142.8, 114.8, 113.9, 55.7, 42.5, 37.2, 35.5, 33.3, 26.5, 26.2.

(ESI+) = 243.3 (M+1).

***N*-(2-phenylethyl)-*N*-(4-methoxyphenyl)amine (Table 2, entry 5)**

Yield: 94%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 7.15-7.30 (m, 5H), 6.72 (d, *J* = 9.0 Hz, 2H), 6.53 (d, *J* = 9.0 Hz, 2H), 3.69 (s, 3H), 3.30 (t, *J* = 7.1 Hz, 2H), 2.85 (t, *J* = 7.1 Hz, 2H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 152.0, 142.1, 139.3, 128.7, 128.4, 126.2, 114.8, 114.2, 55.6, 45.9, 35.4.

(ESI+) = 228.0 (M+1).

***N*-isopropyl-*N*-(4-methoxyphenyl)amine (Table 1, entry 7, R = OMe)**

Yield: 39%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 6.77 (d, *J* = 9.1 Hz, 2H), 6.58 (d, *J* = 9.1 Hz, 2H), 3.75 (s, 3H), 3.54 (m, 1H), 1.19 (d, *J* = 6.3 Hz, 6H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 151.9, 141.7, 114.9, 114.8, 55.7, 45.2, 23.0.

(ESI+) = 243.3 (M+1).

***N*-cyclohexyl-*N*-(4-methoxyphenyl)amine (Table 1, entry 8, R = OMe)**

Yield: 63%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 6.58 (d, *J* = 9.0 Hz, 2H), 6.41 (d, *J* = 9.0 Hz, 2H), 3.57 (s, 3H), 2.99 (m, 1H), 1.89 (m, 2H), 1.43-1.62 (m, 2H), 0.88-1.25 (m, 6H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 151.7, 141.5, 114.8, 114.7, 55.7, 52.7, 33.5, 25.9, 25.0.

(ESI+) = 206.4 (M+1).

***N*-butyl-*N*-(4-chlorophenyl)amine (Table 1, entry 2, R = Cl)**

Yield: 82%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 7.10 (d, *J* = 8.8 Hz, 2H), 6.51 (d, *J* = 8.8 Hz, 2H), 3.07 (t, *J* = 6.9 Hz, 2H), 1.58 (m, 2H), 1.41 (m, 2H), 0.95 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 147.0, 128.9, 121.4, 113.6, 43.7, 31.5, 20.2, 13.8.

(ESI+) = 180.4 (M+1).

***N*-isobutyl-*N*-(4-chlorophenyl)amine (Table 1, entry 3, R = Cl)**

Yield: 49%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 7.11 (d, *J* = 8.9 Hz, 2H), 6.50 (d, *J* = 8.9 Hz, 2H), 2.88 (d, *J* = 6.6 Hz, 2H), 1.87 (m, 1H), 0.97 (d, *J* = 6.6 Hz, 6H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 147.1, 129.0, 121.4, 113.6, 55.8, 27.9, 20.4.

(ESI+) = 184.2 (M+1).

***N*-(4-chlorophenyl)-*N*-(3-methylbutyl)amine (Table 1, entry 4, R = Cl)**

Yield: 74%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 7.10 (d, *J* = 9.0 Hz, 2H), 6.51 (d, *J* = 9.0 Hz, 2H), 3.08 (t, *J* = 7.7 Hz, 2H), 1.70 (m, 1H), 1.50 (c, *J* = 7.7 Hz, 2H), 0.95 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (CDCl_3 , 62.9 MHz) δ ppm: 147.0, 128.9, 121.4, 113.6, 42.2, 38.3, 25.9, 22.5.
(ESI+) = 198.2 (M+1).

***N*-(4-chlorophenyl)-*N*-(2-cyclohexylethyl)amine (Table 1, entry 5, R = Cl)**

Yield: 68%.

^1H NMR (CDCl_3 , 250 MHz) δ ppm: 7.11 (d, J = 9.0 Hz, 2H), 6.50 (d, J = 9.0 Hz, 2H), 3.08 (t, J = 7.4 Hz, 2H), 1.45-1.73 (m, 8H), 1.24 (m, 3H), 0.94 (m, 2H).

^{13}C NMR (CDCl_3 , 62.9 MHz) δ ppm: 147.0, 128.9, 121.4, 113.6, 41.7, 36.9, 35.4, 33.3, 26.5, 26.2.
(ESI+) = 238.1 (M+1).

***N*-(4-chlorophenyl)-*N*-(2-phenylethyl)amine (Table 2, entry 9)**

Yield: 63%.

^1H NMR (CDCl_3 , 250 MHz) δ ppm: 7.20-7.33 (m, 5H), 7.11 (d, J = 9.0 Hz, 2H), 6.53 (d, J = 9.0 Hz, 2H), 3.37 (t, J = 6.9 Hz, 2H), 2.91 (t, J = 6.9 Hz, 2H).

^{13}C NMR (CDCl_3 , 62.9 MHz) δ ppm: 146.5, 139.0, 129.0, 128.7, 128.6, 126.5, 121.9, 114.0, 45.0, 35.2.
(ESI+) = 232.2 (M+1).

***N*-(4-chlorophenyl)-*N*-isopropylamine (Table 1, entry 7, R = Cl)**

Yield: 22%.

^1H NMR (CDCl_3 , 250 MHz) δ ppm: 7.10 (d, J = 8.8 Hz, 2H), 6.49 (d, J = 8.8 Hz, 2H), 3.57 (m, 1H), 1.19 (d, J = 6.6 Hz, 6H).

^{13}C NMR (CDCl_3 , 62.9 MHz) δ ppm: 146.0, 129.0, 121.3, 114.2, 44.3, 22.8.
(ESI+) = 205.0 (M+1).

***N*-(4-chlorophenyl)-*N*-cyclohexylamine (Table 1, entry 8, R = Cl)**

Yield: 27%.

^1H NMR (CDCl_3 , 250 MHz) δ ppm: 7.09 (d, J = 8.8 Hz, 2H), 6.49 (d, J = 8.8 Hz, 2H), 3.18 (m, 1H), 2.04 (m, 2H), 1.11-1.80 (m, 8H).

^{13}C NMR (CDCl_3 , 62.9 MHz) δ ppm: 145.9, 129.0, 121.1, 114.1, 51.8, 33.3, 25.8, 24.9.
(ESI+) = 210.2 (M+1).

***N*-(3-methylphenyl)-*N*-(2-phenylethyl)amine (Table 2, entry 3)**

Yield: 65%.

^1H NMR (CDCl_3 , 250 MHz) δ ppm: 7.11-7.35 (m, 6H), 7.01 (m, 1H), 6.66 (m, 2H), 3.43 (t, J = 6.9 Hz, 2H), 2.96 (t, J = 6.9 Hz, 2H), 2.02 (s, 3H).

^{13}C NMR (CDCl_3 , 62.9 MHz) δ ppm: 145.8, 139.3, 130.0, 128.7, 128.6, 127.1, 126.4, 122.0, 116.9, 109.7, 44.9, 35.3, 17.2.
(ESI+) = 212.2 (M+1).

***N*-(2-methylphenyl)-*N*-(2-phenylethyl)amine (Table 2, entry 4)**

Yield: 63%.

^1H NMR (CDCl_3 , 250 MHz) δ ppm: 7.21-7.35 (m, 5H), 7.00 (d, J = 8.5 Hz, 2H), 6.66 (d, J = 8.5 Hz, 2H), 3.38 (t, J = 6.9 Hz, 2H), 2.91 (t, J = 6.9 Hz, 2H), 2.24 (s, 3H).

^{13}C NMR (CDCl_3 , 62.9 MHz) δ ppm: 145.6, 139.4, 139.0, 129.7, 128.7, 128.6, 126.6, 126.4, 126.3, 113.1, 45.3, 35.4, 20.3.
(ESI+) = 212.2 (M+1).

***N*-(3-methoxyphenyl)-*N*-(2-phenylethyl)amine (Table 2, entry 6)**

Yield: 83%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 7.20-7.36 (m, 5H), 7.08 (t, *J* = 8.0 Hz, 1H), 6.16-6.29 (m, 3H), 3.77 (s, 3H), 3.39 ppm (t, *J* = 6.9 Hz, 2H), 2.91 (t, *J* = 6.9 Hz, 2H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 160.8, 149.3, 139.2, 129.9, 128.7, 128.5, 126.3, 106.4, 101.5, 98.8, 55.0, 44.9, 35.4.

(ESI+) = 228.1 (M+1).

***N*-(2-methoxyphenyl)-*N*-(2-phenylethyl)amine (Table 2, entry 7)**

Yield: 69%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 7.22-7.35 (m, 5H), 6.88 (m, 1H), 6.64-6.78 (m, 3H), 3.81 (s, 3H), 3.41 (t, *J* = 7.4 Hz, 2H), 2.95 (t, *J* = 7.4 Hz, 2H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 146.8, 139.4, 137.9, 128.7, 128.4, 126.2, 121.2, 116.4, 109.8, 109.4, 55.3, 45.0, 35.6.

(ESI+) = 228.1 (M+1).

***N*-(3-chlorophenyl)-*N*-(2-phenylethyl)amine (Table 2, entry 8)**

Yield: 95%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 7.20-7.33 (m, 5H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.66 (m, 1H), 6.58 (m, 1H), 6.46 (m, 1H), 3.38 (t, *J* = 6.9 Hz, 2H); 2.91 ppm (t, *J* = 6.9 Hz, 2H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 149.0, 138.9, 134.9, 130.1, 128.7, 128.6, 126.5, 117.1, 112.4, 111.1, 44.6, 35.2.

(ESI+) = 232.3 (M+1).

***N*-(3-bromophenyl)-*N*-(2-phenylethyl)amine (Table 2, entry 10)**

Yield: 68%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 7.20-7.36 (m, 5H), 6.98-7.06 (m, 1H), 6.79 (m, 1H), 6.80 (m, 1H), 6.50 (m, 1H), 3.37 (t, *J* = 6.9 Hz, 2H), 2.91 (t, *J* = 6.9 Hz, 2H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 149.2, 138.8, 130.4, 128.7, 128.6, 126.5, 123.2, 120.0, 115.3, 115.6, 44.6, 35.2.

(ESI+) = 278.2 (M+1).

***N*-[4-(methylthio)phenyl]-*N*-(2-phenylethyl)amine (Table 2, entry 11)**

Yield: 85%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 7.20-7.36 (m, 7H), 6.55 (d, *J* = 8.5 Hz, 2H), 3.39 (t, *J* = 6.9 Hz, 2H), 2.90 (t, *J* = 6.9 Hz, 2H), 2.41 (s, 3H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 146.7, 139.0, 131.4, 128.7, 128.5, 126.4, 121.1, 113.5, 44.9, 35.3, 19.0.

(ESI+) = 244.3 (M+1).

4-[(2-phenylethyl)amino]benzonitrile (Table 2, entry 12)

Yield: 61%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 7.42 (d, *J* = 8.9 Hz, 2H), 7.19-7.33 (m, 5H), 6.54 (d, *J* = 8.9 Hz, 2H), 3.44 (c, *J* = 6.6 Hz, 2H), 2.93 (t, *J* = 6.8 Hz, 2H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 151.0, 138.4, 133.6, 128.7, 128.6, 126.6, 120.4, 112.2, 98.5, 44.1, 35.0.

(ESI+) = 223.3 (M+1).

Methyl 2-[(2-phenylethyl)amino]benzoate (Table 2, entry 13)

Yield: 64%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 7.90 (t, *J* = 8.0 Hz, 1H), 7.24-7.40 (m, 7H), 6.9 (t, *J* = 8.0 Hz, 1H), 3.84 (s, 3H), 3.47 (c, *J* = 6.6 Hz, 2H), 2.98 (t, *J* = 6.6 Hz, 2H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 166.8, 150.8, 139.2, 134.5, 131.6, 128.7, 128.5, 126.4, 114.5, 111.0, 109.9, 51.3, 44.4, 35.5.

(ESI+) = 256.3 (M+1).

***N*-(2-phenylethyl)pyridin-2-amine (Table 2, entry 14)**

Yield: 26%.

¹H NMR (CDCl₃, 250 MHz) δ ppm: 8.09 (m, 1H), 7.22-7.44 (m, 6H), 6.57 (t, *J* = 6.6 Hz, 1H), 6.36 (d, *J* = 8.5 Hz, 1H), 3.55 (c, *J* = 6.9 Hz, 2H), 2.92 (t, *J* = 6.9 Hz, 2H).

¹³C NMR (CDCl₃, 62.9 MHz) δ ppm: 157.6, 145.3, 138.8, 128.7, 128.5, 127.9, 126.4, 112.2, 106.8, 43.6, 35.4.

(ESI+) = 199.2 (M+1).