Supporting Information for
An Efficient and Convenient Cu(OAc)$_2$/Air Mediated Oxidative Coupling of Azoles via C-H Activation

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Experimental Section

$^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$ on Bruker AMX-400 MHz instrument with TMS as internal standard. Coupling constants are reported in Hertz (Hz). MS was obtained using EI ionization. Melting points were uncorrected.

In a typical procedure:

*Formation of homo-coupling product:* A dry Schlenk tube was charged with the N-methylbenzimidazole (0.5mmol, 0.066g) and Cu(OAc)$_2$ (0.1mmol, 0.0182g) in 2 mL xylene. Then the Schlenk tube was sealed and the reaction mixture was heated to 140 °C for 12 h. Purification was done by column chromatography on silica gel (200-300 mesh) with dichloromethane and ethyl acetate (5:1) as the eluent to give the pure product.

*Formation of cross-coupling product:* A dry Schlenk tube was charged with N-methylbenzimidazole (0.5mmol, 0.066g), N-benzylbenzimidazole (0.25mmol, 0.052g) and Cu(OAc)$_2$ (0.1mmol, 0.0182g) in 2 mL xylene. Then the Schlenk tube was sealed and the reaction mixture was heated to 140 °C for 12 h. Purification was done by column chromatography on silica gel (200-300 mesh) with dichloromethane and ethyl acetate (10:1) as the eluent to give the pure product 3a.

Characterization of all products

![Chemical structure](image)

1,1'-dimethyl-1H,1'H-2,2'-bienzo[α]imidazole

m.p.: 208-209 °C $^1$H NMR (400 MHz, CDCl$_3$/TMS): $\delta$ 4.33 (s, 6H), 7.36 (t, $J$ = 7.4 Hz, 2H), 7.41 (t, $J$ = 7.4 Hz, 2H), 7.49 (d, $J$ = 7.6 Hz, 2H), 7.88 (d, $J$ = 7.6 Hz, 2H), $^{13}$C NMR (100 MHz, CDCl$_3$/TMS): 32.4, 110.0, 120.3, 122.8, 123.9, 136.2, 142.5, 143.2.
1,1'-diphenyl-1H,1'H-2,2'-bibenzo[d]imidazole²
m.p.: 189-199 °C ¹H NMR (400 MHz, CDCl₃/TMS): δ 6.85 (d, J = 7.6 Hz, 4H), 7.19-7.31 (m, 10H), 7.36 (t, J = 7.4 Hz, 2H), 7.92 (d, J = 8.4 Hz, 2H), ¹³C NMR (100 MHz, CDCl₃/TMS): 110.5, 120.9, 123.2, 124.3, 125.4, 127.7, 129.3, 135.1, 135.2, 142.9, 143.0.

1,1'-dibenzyl-1H,1'H-2,2'-bibenzo[d]imidazole³
m.p.: 215-216 °C ¹H NMR (400 MHz, CDCl₃/TMS): δ 6.22 (s, 4H), 7.00-7.01 (m, 4H), 7.11-7.14 (m, 6H), 7.27-7.32 (m, 4H), 7.36-7.38 (m, 2H), 7.83-7.85 (m, 2H), ¹³C NMR (100 MHz, CDCl₃/TMS): 48.5, 110.8, 120.4, 122.9, 124.1, 126.8, 127.4, 128.6, 135.5, 136.8, 142.6, 142.8.

1,1'-dimethyl-1H,1'H-2,2'-biimidazole⁴
m.p.: 105-106 °C ¹H NMR (400 MHz, CDCl₃/TMS): δ 4.03 (s, 6H), 6.95 (d, J = 0.4 Hz, 2H), 7.10 (d, J = 0.4 Hz, 2H), ¹³C NMR (100 MHz, CDCl₃/TMS): 35.2, 122.5, 127.7, 138.5.
1,1'-dibenzyl-1H,1'H-2,2'-biimidazole

m.p.: 148-149 °C

$^1$H NMR (400 MHz, CDCl$_3$/TMS): $\delta$ 5.69 (s, 4H), 6.92 (d, $J = 1.2$ Hz, 2H), 7.01-7.04 (m, 4H), 7.12 (d, $J = 1.2$ Hz, 2H), 7.22-7.24 (m, 6H), $^{13}$C NMR (100 MHz, CDCl$_3$/TMS): 50.7, 121.4, 127.4, 127.5, 128.3, 128.6, 137.2, 138.2.

1,1'-dimethyl-4,4',5,5'-tetraphenyl-1H,1'H-2,2'-biimidazole

m.p.: 258-259 °C

$^1$H NMR (400 MHz, CDCl$_3$/TMS): $\delta$ 3.94 (s, 6H), 7.13-7.16 (m, 2H), 7.19-7.23 (m, 4H), 7.41-7.43 (m, 4H), 7.47-7.55 (m, 10H), $^{13}$C NMR (100 MHz, CDCl$_3$/TMS): 33.6, 126.3, 126.6, 128.1, 128.7, 129.0, 130.7, 130.9, 134.4, 137.2, 138.2. Anal. Calc. for C$_{32}$H$_{26}$N$_4$: C, 82.38; H, 5.62; N, 12.01. Found: C, 82.41; H, 5.65; N, 11.96%

4,4'-dimethyl-2,2'-bithiazole

m.p.: 136-137 °C

$^1$H NMR (400 MHz, CDCl$_3$/TMS): $\delta$ 2.50 (s, 6H), 6.95 (s, 2H), $^{13}$C NMR (100 MHz, CDCl$_3$/TMS): 17.1, 115.3, 154.0, 160.7.

4,4',5,5'-tetramethyl-2,2'-bithiazole

m.p.: 174-175 °C

$^1$H NMR (400 MHz, CDCl$_3$/TMS): $\delta$ 2.36 (s, 6H), 2.38 (s, 6H), $^{13}$C NMR (100 MHz, CDCl$_3$/TMS): 11.5, 14.7, 128.1, 149.5, 157.0.

2,2'-bibenzo[d]oxazole

m.p.: 258-259 °C

$^1$H NMR (400 MHz, CDCl$_3$/TMS): $\delta$ 7.45-7.54 (m, 4H), 7.71 (d, $J =$
8.8 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 2H), $^{13}$C NMR (100 MHz, CDCl$_3$/TMS): 111.4, 121.4, 125.7, 127.4, 141.1, 150.9, 151.8.

5,5'-dimethyl-2,2'-bibenzo[d]oxazole

1 m.p.: 217-218 °C $^1$H NMR (400 MHz, CDCl$_3$/TMS): δ 2.51 (s, 6H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.67 (s, 2H), $^{13}$C NMR (100 MHz, CDCl$_3$/TMS): 21.4, 110.7, 121.0, 128.6, 135.7, 141.3, 149.1, 151.9.

5,5'-diphenyl-2,2'-bi(1,3,4-oxadiazole)

m.p.: 269-270 °C $^1$H NMR (400 MHz, CDCl$_3$/TMS): δ 7.57-7.66 (m, 6H), 8.24 (d, *J* = 7.6 Hz, 4H), $^{13}$C NMR (100 MHz, CDCl$_3$/TMS): 122.5, 127.7, 129.3, 132.9, 153.0, 166.3.

1-benzyl-1'-methyl-1H,1'H-2,2'-bibenzo[d]imidazole

m.p.: 176-177 °C $^1$H NMR (400 MHz, CDCl$_3$/TMS): δ 4.30 (s, 3H), 6.23 (s, 2H), 7.15-7.21 (m, 5H), 7.29-7.34 (m, 3H), 7.36-7.40 (m, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.87-7.89 (m, 1H), $^{13}$C NMR (100 MHz, CDCl$_3$/TMS): 32.4, 48.7, 110.0, 110.9, 120.3, 120.4, 122.8, 122.9, 123.9, 124.1, 127.0, 127.4, 128.6, 135.6, 136.1, 137.0, 142.4, 142.7, 143.0, 143.1. Anal. Calc. for C$_{22}$H$_{18}$N$_4$: C, 78.08; H, 5.36; N, 16.56. Found: C, 78.03; H, 5.38; N, 16.64%.
1-benzyl-1'-phenyl-1H,1'H-2,2'-bibenzo[d]imidazole
m.p.: 186-187°C ¹H NMR (400 MHz, CDCl₃/TMS): δ 6.02 (s, 2H), 7.04-7.06 (m, 2H), 7.16-7.20 (m, 5H), 7.21-7.26 (m, 2H), 7.28-7.36 (m, 3H), 7.38-7.41 (m, 4H), 7.63 (d, J = 7.6 Hz, 1H), 7.92 (d, J = 7.6 Hz, 1H), ¹³C NMR (100 MHz, CDCl₃/TMS): 48.2, 110.5, 111.0, 120.4, 120.8, 122.6, 123.3, 123.9, 124.4, 126.9, 127.2, 127.6, 128.3, 128.6, 129.2, 135.3, 136.4, 136.5, 136.8, 142.5, 142.6, 142.7, 143.0. Anal. Calc. for C₂₇H₂₀N₄: C, 80.98; H, 5.03; N, 13.99. Found: C, 80.90; H, 5.15; N, 14.02%.

2-(1-benzyl-1H-imidazol-2-yl)-1-methyl-1H-benzo[d]imidazole
m.p.: 89-90°C ¹H NMR (400 MHz, CDCl₃/TMS): 4.17 (s, 3H), 5.93 (s, 2H), 7.04 (s, 1H), 7.19-7.35 (m, 8H), 7.40 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 7.2 Hz, 1H), ¹³C NMR (100 MHz, CDCl₃/TMS): 32.1, 51.3, 109.7, 119.9, 122.4, 122.5, 123.2, 127.7, 127.8, 128.7, 128.9, 135.9, 137.2, 137.9, 142.4, 143.6. EI-MS: m/z = 288.

2-(1-methyl-1H-imidazol-2-yl)benzo[d]oxazole
m.p.: 140-141°C ¹H NMR (400 MHz, CDCl₃/TMS): 4.23 (s, 3H), 7.12 (s, 1H), 7.26 (s, 1H), 7.35-7.40 (m, 2H), 7.61-7.63 (m, 1H), 7.75-7.77 (m, 1H), ¹³C NMR (100 MHz, CDCl₃/TMS): 35.6, 111.0, 120.0, 124.7, 125.2, 125.6, 130.1, 135.6, 141.5, 149.8, 154.8. EI-MS: m/z = 199.

2-(1-benzyl-1H-imidazol-2-yl)-4,5-dimethylthiazole
m.p.: 91-92°C ¹H NMR (400 MHz, CDCl₃/TMS): 2.32 (s, 3H), 2.36 (s, 3H), 5.83 (s, 2H), 6.92 (s, 1H), 7.08 (s, 1H), 7.23 (d, J = 7.6 Hz, 2H), 7.26-7.32 (m, 3H), ¹³C NMR (100 MHz, CDCl₃/TMS): 11.1, 14.8, 50.7, 122.3, 127.1, 127.72, 127.73, 128.6, 129.2, 137.1, 140.7, 148.8, 154.8. EI-MS: m/z = 269.
Reference


