2-Aminopyrimidine-4,6-diol as an Efficient Ligand for Solvent-Free Copper-Catalyzed *N*-Arylations of Imidazoles with Aryl and Heteroaryl Halides

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Supporting Information

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(A) Typical experimental procedure

Typical Experimental Procedure for the Solvent-Free Copper-Catalyzed N-Arylation of Imidazoles. A mixture of imidazole **1** (1.0 mmol), aryl halide **2** (1.2 mmol), CuBr (10 mol %), 2-aminopyrimidine-4,6-diol (**L**₁; 20 mol%) and TBAF (3 equiv) was stirred at 145-150 °C for 24 h until complete consumption of starting material as monitored by TLC. After the reaction was finished, ethyl acetate was poured into the mixture, then washed with water, extracted with diethyl ether, dried by anhydrous Na₂SO₄ and evaporated under vacuum, the residue was purified by flash column chromatography (hexane/ethyl acetate) to afford the desired product.

(B) Analytical data for 3–19

1-(4-Methoxyphenyl)-1*H*-imidazole (**3**)¹

White solid; ¹H NMR (400 MHz, CDCl₃) δ: 7.76 (s, 1H), 7.28 (d, *J* = 9.2 Hz, 2H), 7.19 (d, *J* = 9.6 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 158.5, 135.5, 130.3, 129.7, 122.8, 118.5, 114.6, 55.3; LRMS (EI, 20 eV) *m/z* (%): 174 (M⁺, 100).

1-(4-Nitrophenyl)-1*H*-imidazole (**4**)¹

Slight yellow solid; ¹H NMR (500 MHz, CDCl₃) δ: 8.40 (d, *J* = 9.0 Hz, 2H), 8.01 (s, 1H), 7.60 (d, *J* = 9.0 Hz, 2H), 7.40 (s, 1H), 7.29 (d, *J* = 8.2 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 146.5, 142.0, 135.4, 131.8, 125.7, 121.1, 117.6; LRMS (EI, 20 eV) *m/z* (%): 189 (M⁺, 100).

2-(1H-Imidazol-1-yl)pyridine (5)¹⁻³

Brown oil; ¹H NMR (500 MHz, CDCl₃) δ: 8.51 (d, *J* = 4.5 Hz, 1H), 8.40 (s, 1H), 7.87-7.84 (m, 1H), 7.69 (s, 1H), 7.39 (d, *J* = 3.5 Hz, 1H), 7.29-7.26 (m, 2H); LRMS (EI, 20 eV) *m/z* (%): 145 (M⁺, 100). HRMS (EI) for C₈H₇N₃ (M⁺): calcd. 145.0640, found 145.0640.

2-(1H-imidazol-1-yl)pyrimidine (6)³

White solid; ¹H NMR (500 MHz, CDCl₃) δ: 8.72 (d, *J* = 4.8 Hz, 2H), 8.64 (s, 1H), 7.92 (s, 1H), 7.23 (t, *J* = 4.8 Hz, 1H), 7.19 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 158.7, 156.3, 136.2, 130.7, 118.8, 116.5; LRMS (EI, 20 eV) *m/z* (%): 146 (M⁺, 100).

1-(4-Methoxyphenyl)-1H-benzimidazole (7)²

Slight yellow solid; ¹H NMR (400 MHz, CDCl₃) δ: 8.05 (s, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.46 (d, *J* = 9.2 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.32 (t, *J* = 3.6 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 159.2, 143.7, 142.5, 132.1, 129.0, 125.6, 123.5, 122.5, 120.4, 115.0, 110.3, 55.6; LRMS (EI, 20 eV) *m/z* (%): 224 (M⁺, 100).

1-(4-Nitrophenyl)-1H-benzimidazole (8)³

Yellow solid; ¹H NMR (500 MHz, CDCl₃) δ: 8.51 (d, *J* = 8.7 Hz, 2H), 8.22 (s, 1H), 7.94 (d, *J* = 5.7 Hz, 1H), 7.77 (d, *J* = 9.0 Hz, 2H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.44 (t, *J* = 7.3 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ: 146.7, 144.5, 141.8, 141.5, 132.9, 125.8, 124.6, 123.7 (2C), 121.2, 110.2; LRMS (EI, 20 eV) *m/z* (%): 239 (M⁺, 100).

1-(Pyridin-2-yl)-1*H*-benzimidazole (9)⁴

White solid; ¹H NMR (500 MHz, CDCl₃) δ: 8.54 (s, 1H), 8.51 (d, *J* = 4.8 Hz, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.76 (t, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 3.6 Hz, 2H), 7.18 (d, *J* = 5.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 149.5, 149.0, 144.3, 141.0, 138.6, 131.8, 123.9, 123.0, 121.5, 120.2, 113.9, 112.5; LRMS (EI, 20 eV) *m/z* (%): 195 (M⁺, 100).

1-(Pyrimidin-2-yl)-1*H*-benzimidazole (10)

White solid, m.p. 108.4 °C (uncorrected); ¹H NMR (500 MHz, CDCl₃) δ: 9.11 (s, 1H), 8.79 (d, *J* = 4.8 Hz, 2H), 8.62 (t, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.46-7.38 (m, 2H), 7.23 (t, *J* = 5.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 158.5, 156.4, 145.1, 141.8, 131.9, 124.6, 123.8, 120.4, 118.0, 115.6; LRMS (EI, 20 eV) *m/z* (%): 196 (M⁺, 100); HRMS (EI) for C₁₁H₈N₄ (M⁺): calcd. 196.0749, found 196.0749.

1-(4-(1*H*-Benzo[*d*]imidazol-1-yl)phenyl)ethanone (11)¹

White solid; ¹H NMR (400 MHz, CDCl₃) δ: 8.20-8.18 (m, 3H), 7.92-7.90 (m, 1H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.62-7.60 (m, 1H), 7.40-7.37 (m, 2H), 2.69 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 196.6, 144.3, 141.8, 140.2, 136.1, 130.4, 124.2, 123.3 (2C), 123.3, 120.9, 110.4, 26.7; LRMS (EI, 20 eV) *m/z* (%): 236 (M⁺, 100).

1-Phenyl-1*H*-benzimidazole (12)²

White solid; ¹H NMR (400 MHz, CDCl₃) δ: 8.13 (s, 1H), 7.90-7.88 (m, 1H), 7.60-7.45 (m, 6H), 7.34 (t, *J* = 4.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 144.0, 142.3, 136.3,

133.7, 130.0, 128.0, 124.0, 123.6, 122.7, 120.5, 110.4; LRMS (EI, 20 eV) m/z (%): 194 (M^+ , 100).

3-(1*H*-Benzo[*d*]imidazol-1-yl)quinoline (13)⁵

White solid; ^1H NMR (500 MHz, CDCl_3) δ : 9.16 (s, 1H), 8.32 (s, 1H), 8.27 (t, $J = 7.2$ Hz, 2H), 7.96 (d, $J = 7.9$ Hz, 2H), 7.87 (t, $J = 8.4$ Hz, 1H), 7.72 (t, $J = 7.5$ Hz, 1H), 7.53 (s, 1H), 7.42 (t, $J = 3.5$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 147.5, 146.5, 130.4, 130.0, 129.8, 129.7, 128.2, 127.8, 124.3, 123.3, 121.0, 110.1; LRMS (EI, 20 eV) m/z (%): 245 (M^+ , 100); HRMS (EI) for $\text{C}_{16}\text{H}_{11}\text{N}_3$ (M^+): calcd. 245.0953, found 245.0953.

1-(Thiophen-2-yl)-1*H*-benzimidazole (14)⁶

Slight yellow solid; ^1H NMR (500 MHz, CDCl_3) δ : 9.36 (s, 1H), 9.04 (s, 2H), 8.16 (s, 1H), 7.94 (d, $J = 9.0$ Hz, 1H), 7.54 (d, $J = 9.2$ Hz, 1H), 7.45-7.42 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ : 157.8, 151.9, 144.2, 141.2, 133.1, 132.1, 124.8, 123.8, 121.3, 109.6; LRMS (EI, 20 eV) m/z (%): 200 (M^+ , 100).

1-(Thiazol-2-yl)-1*H*-benzimidazole (15)

Yellow solid, m.p. 100.9 °C (uncorrected); ^1H NMR (500 MHz, CDCl_3) δ : 8.59 (s, 1H), 8.11 (d, $J = 8.1$ Hz, 1H), 7.90 (s, 1H), 7.72 (s, 1H), 7.49-7.41 (m, 2H), 7.26 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ : 157.1, 144.2, 141.2, 140.5, 131.9, 125.0, 124.1, 121.0, 115.1, 112.3; LRMS (EI, 20 eV) m/z (%): 201 (M^+ , 100); HRMS (EI) for $\text{C}_{10}\text{H}_7\text{N}_3\text{S}$ (M^+): calcd. 201.0361, found 201.0360.

2-Methyl-1-(pyridin-2-yl)-1*H*-benzimidazole (16)⁷

Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ: 8.72 (d, *J* = 3.7 Hz, 1H), 7.99 (t, *J* = 8.0 Hz, 1H), 7.80 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 5.0 Hz, 2H), 7.31-7.24 (m, 2H), 2.70 (s, 3H); LRMS (EI, 20 eV) *m/z* (%): 209 (M⁺, 100); HRMS (EI) for C₁₃H₁₁N₃ (M⁺): calcd. 209.0953, found 209.0950.

2-Methyl-1-(pyrimidin-2-yl)-1*H*-benzimidazole (17)

Slight yellow solid, m.p. 77.3 °C (uncorrected); ¹H NMR (500 MHz, CDCl₃) δ: 8.81 (s, 2H), 8.26 (t, *J* = 3.0 Hz, 1H), 7.74-7.72 (m, 1H), 7.33-7.22 (m, 3H), 2.97 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 158.3, 157.2, 152.7, 142.7, 134.0, 123.4, 119.0, 118.0, 114.4, 18.4; LRMS (EI, 20 eV) *m/z* (%): 210 (M⁺, 100); HRMS (EI) for C₁₂H₁₀N₄ (M⁺): calcd. 210.0906, found 210.0905.

2-(2-Methyl-1*H*-imidazol-1-yl)pyrimidine (18)

Slight yellow solid, m.p. 90.3-90.8 °C (uncorrected); ¹H NMR (500 MHz, CDCl₃) δ: 8.75-8.70 (m, 2H), 7.85 (d, *J* = 6.0 Hz, 1H), 7.19 (t, *J* = 9.7 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 2.81 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 158.4, 156.3, 146.7, 127.5, 118.4, 118.2, 18.0; LRMS (EI, 20 eV) *m/z* (%): 160 (M⁺, 100); HRMS (EI) for C₈H₈N₄ (M⁺): calcd. 160.0749, found 160.0747.

1-(4-Nitrophenyl)-2-phenyl-1*H*-imidazole (19)⁸

Yellow solid; ^1H NMR (500 MHz, CDCl_3) δ : 8.28 (d, $J = 9.0$ Hz, 2H), 7.41-7.33 (m, 8H), 7.25 (s, 1H); ^{13}C NMR (1125 MHz, CDCl_3) δ : 147.1, 146.9, 143.7, 130.2, 129.7, 129.1, 128.9, 128.6, 126.2, 125.0, 122.1; LRMS (EI, 20 eV) m/z (%): 265 (M^+ , 100).

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(D) Spectra

1-(4-Methoxyphenyl)-1H-imidazole (3)

1-(4-Methoxyphenyl)-1H-imidazole (3)

2-(1H-Imidazol-1-yl)pyrimidine (6)

2-(1H-Imidazol-1-yl)pyrimidine (6)

1-(4-Methoxyphenyl)-1H-benzimidazole (7)

1-(4-Methoxyphenyl)-1H-benzimidazole (7)

1-(4-Nitrophenyl)-1H-benzimidazole (8)

1-(4-Nitrophenyl)-1H-benzimidazole (8)

1-(Pyridin-2-yl)-1H-benzimidazole (9) c1ccc2c(c1)c(c3ccccc23)n4ccncc4

1-(Pyridin-2-yl)-1H-benzimidazole (9)

c1ccc2c(c1)c(c3c2nnc3)nc4c5cncn45

1-(Pyrimidin-2-yl)-1H-benzimidazole (10)

1-(4-(1H-Benzo[d]imidazol-1-yl)phenyl)ethanone (11)

1-(4-(1H-Benzo[d]imidazol-1-yl)phenyl)ethanone (11)

1-Phenyl-1H-benzimidazole (12)

1-Phenyl-1H-benzimidazole (12)

3-(1*H*-Benzo[d]imidazol-1-yl)quinoline (13)

1-(Thiophen-2-yl)-1*H*-benzimidazole (14)

1-(Thiophen-2-yl)-1H-benzimidazole (14) c1ccc2c(c1)c3ccccc3n2-c4ccsc4

2-Methyl-1-(pyrimidin-2-yl)-1H-benzimidazole (17)

2-Methyl-1-(pyrimidin-2-yl)-1H-benzimidazole (17)

2-(2-Methyl-1H-imidazol-1-yl)pyrimidine (18)

2-(2-Methyl-1H-imidazol-1-yl)pyrimidine (18)

1-(4-Nitrophenyl)-2-phenyl-1H-imidazole (19)

1-(4-Nitrophenyl)-2-phenyl-1H-imidazole (19)