Supporting Information for:

PRACTICAL APPROACH FOR HYDROHETEROARYLATION OF ALKYNES USING BENCH-STABLE CATALYST

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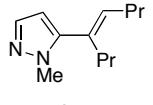
General. Flash column chromatography was performed using Kanto Chemical silica gel (spherical, 40–50 μm). Analytical thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F_{254} (0.25 mm) plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline $KMNO_4$ solution followed by heating.

Apparatus. Proton and carbon nuclear magnetic resonance spectra (^{1}H and ^{13}C NMR) were recorded on a Varian Mercury 400 (^{1}H NMR, 400MHz; ^{13}C NMR 101 MHz) spectrometer with solvent resonance as the internal standard (^{1}H NMR, $CHCl_3$ at 7.26 ppm; ^{13}C NMR, $CDCl_3$ at 77.0 ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, br = broad, m = multiplet), coupling constants (Hz), and integration. Melting points were determined using a YANAKO MP-500D. Mass spectra were obtained with a JEOL JMS-700 (EI) spectrometer. GC analysis was performed on a Shimadzu GC 2010 equipped with a DB-5 column (30 m x 0.53 mm, pressure = 31.7 kPa, detector = FID, 290 °C) with helium gas as a carrier.

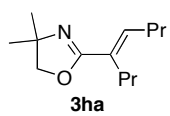
Chemicals. Unless otherwise noted, commercially available reagents were used without purification. All alkynes were distilled before use. Anhydrous toluene purchased from Kanto Chemical was degassed vigorously with argon for 20 min and further purified by passage through activated alumina under positive argon pressure as described by Grubbs et al [1]. Methyl 1-methylindole-3-carboxylate (**1a**), 3-acetyl-1-methylindole (**1b**), 3-cyano-1-methylindole (**1c**) [2], and $[Cyp_3PH]BF_4$ [3] were prepared according to the reported procedure.

Nickel-catalyzed hydroheteroarylation of alkynes. ***A general procedure.*** $Ni(acac)_2$ (26 mg, 0.10 mmol), $[Cyp_3PH]BF_4$ (33 mg, 0.10 mmol) and toluene (2.5 mL) were put in a 20 mL Schlenck tube. To the suspension was added a 1.03 M solution of $AlMe_3$ in hexane (0.39 mL, 0.40 mmol) dropwise, and then the resulting black suspension was stirred for an additional 5 min. Heteroarene (1.0 mmol) and alkyne (1.5 mmol) were added sequentially, and the mixture was stirred at 35 °C. After completion of the reaction (monitored by GC), the mixture was filtered through a silica gel pad. The filtrate was concentrated in vacuo, and the residue was purified on flash column chromatography on silica gel to afford the corresponding hydroheteoarylation products in yields listed in Tables 1 and 2. The spectra of **3aa–3fa** agreed well with those reported by us previously [4].



3ga

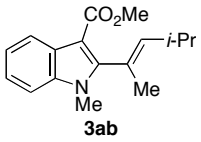
(*E*)-5-(4-Octen-4-yl)-1-methylpyrazole (3ga). A colorless oil, R_f 0.25 (hexane–ethyl acetate = 9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 1.6 Hz, 1H), 6.05 (d, *J* = 1.6 Hz, 1H), 5.51 (t, *J* = 7.2 Hz, 1H), 3.81 (s, 3H), 2.32 (t, *J* = 7.6 Hz, 2H), 2.19 (q, *J* = 7.2 Hz, 2H), 1.48 (sext, *J* = 7.2 Hz, 2H), 1.39–1.27 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 137.8, 133.5, 130.2, 104.5, 37.1, 33.2, 30.2, 22.8, 21.6, 13.92, 13.88; HRMS (EI) Calcd for $C_{12}H_{20}N_2$: M+, 192.1626. Found: *m*/*z* 192.1634.



3ha

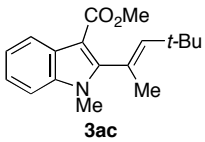
(*E*)-2-(4-Octen-4-yl)-4,4-dimethyloxazoline (3ha). A colorless oil. R_f 0.75 (hexane–ethyl acetate = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.38 (t, *J* = 7.6 Hz, 1H), 3.91 (s, 2H), 2.35 (t, *J* = 7.4 Hz, 2H), 2.15 (q, *J* = 7.6 Hz, 2H), 1.52–1.39 (m, 4H), 1.29 (s, 6H),

0.88–0.98 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 137.7, 129.1, 78.3, 67.2, 30.5, 29.6, 28.4, 22.6, 22.5, 14.1, 14.0; Anal. Calcd for $C_{13}H_{23}NO$; C, 74.59; H, 11.07. Found: C, 74.59; H, 10.82.



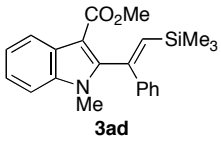
3ab

Methyl (*E*)-1-methyl-2-(4-methyl-2-penten-2-yl)indole-3-carboxylate (3ab). A colorless solid (mp = 96.5–97.5 °C), R_f 0.36 (hexane–ethyl acetate = 9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19–8.13 (m, 1H), 7.33–7.20 (m, 3H), 5.32 (dq, *J* = 9.4, 1.6 Hz, 1H), 3.86 (s, 3H), 3.65 (s, 3H), 2.87–2.74 (m, 1H), 2.00 (d, *J* = 1.6 Hz, 3H), 1.15 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 150.1, 141.5, 136.1, 126.4, 124.1, 122.1, 121.7, 121.5, 109.5, 103.3, 50.6, 30.1, 27.7, 22.5, 17.2; Anal. Calcd for $C_{17}H_{21}NO_2$; C, 75.25; H, 7.80. Found: C, 75.26; H, 7.81.



3ac

Methyl (*E*)-1-methyl-2-(4,4-dimethyl-2-penten-2-yl)indole-3-carboxylate (3ac). A colorless solid (mp = 99.5–100.0°C), R_f 0.33 (hexane–ethyl acetate = 9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19–8.20 (m, 1H), 7.32–7.21 (m, 3H), 5.48 (q, *J* = 1.6 Hz, 1H), 3.86 (s, 3H), 3.65 (s, 3H), 2.09 (d, *J* = 1.6 Hz, 3H), 1.27 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 151.3, 143.8, 135.9, 126.4, 125.7, 122.1, 121.6, 121.4, 109.4, 102.7, 50.5, 33.1, 30.5, 29.9, 18.4; Anal. Calcd for $C_{18}H_{23}NO_2$; C, 75.76; H, 8.12. Found: C, 75.77; H, 8.03.



3ad

Methyl (*E*)-1-methyl-2-(1-trimethylsilyl-2-phenylethen-2-yl)indole-3-carboxylate (3ad). A colorless solid (mp = 126.5–127.5 °C), R_f 0.33 (hexane–ethyl acetate = 9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24–8.17 (m, 1H), 7.32–7.23 (m, 8H), 6.05 (s, 1H), 3.78 (s, 3H), 3.57 (s, 3H), 0.07 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 149.1, 147.6, 140.5, 139.0, 136.2, 128.6, 127.9, 127.7, 126.6, 122.5, 121.8, 121.7, 109.5, 104.1, 50.6, 30.7, 0.32; Anal. Calcd for $C_{22}H_{25}NO_2Si$; C, 72.69; H, 6.93. Found: C, 72.57; H, 6.75.

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4. Y. Nakao, K. S. Kanyiva, S. Oda, and T. Hiyama, *J. Am. Chem. Soc.*, 2006, **128**, 8146.