Supporting Information for:

Hydroheteroarylation of Alkynes Under Mild Nickel-Catalysis

Yoshiaki Nakao,* Kyalo Stephen Kanyiva, Shinichi Oda, and Tamejiro Hiyama*

Department of Material Chemistry, Graduate School of Engineering,

Kyoto University, Kyoto 615-8510 Japan

General. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon atmosphere or in a dry box under a nitrogen atmosphere. Flush column chromatography was performed using Kanto Chemical silica gel (spherical, 40–50 μm). Analytical thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F₂₅₄ (0.25 mm) plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline KMnO₄ solution followed by heating.

Apparatus. Proton and carbon nuclear magnetic resonance spectra (¹H NMR and ¹³C NMR) were recorded on a Varian Mercury 400 (¹H NMR, 400 MHz; ¹³C NMR, 101 MHz) spectrometer with solvent resonance as the internal standard (¹H NMR, CHCl₃ at 7.26 ppm; ¹³C NMR, CDCl₃ at 77.0 ppm). ¹H 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) or JEOL JMS-HX110A (FAB+) 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. Toluene was distilled from sodium/benzophenone ketyl. 9-Methylpurine (**1m**) was prepared according to the reported procedure.¹

Preparation of 3-cyano-1-methoxycarbonylindole (1a). Following the reported procedure,² 3-cyanoindole (1.00 g, 7.0 mmol) was treated with NaH (0.26 g, 10.9 mmol) in DMF (15 mL) at 0 °C, and then methyl chloroformate (1.35 g, 14.2 mmol) was added to the resulting mixture at rt. After being stirred at rt for 1 h, the reaction was quenched with H₂O and extracted with CH₂Cl₂. Combined organic layers were washed with H₂O and brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give **1a** (1.12 g, 80%) as a colorless solid (mp = 89.2–90.2 °C), *R*_f 0.75 (hexane–ethyl acetate = 1:1). ¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, *J* = 8.4 Hz, 1H), 8.13 (s, 1H), 7.73 (dq, *J* = 7.9, 0.7 Hz, 1H), 7.51–7.37 (m, 2H), 4.11 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 150.2, 134.2, 132.8, 127.9, 126.6, 124.7, 119.9, 115.6, 113.9, 93.3, 54.8; Anal. Calcd for C₁₁H₈N₂O₂; C, 66.00; H, 4.03. Found: C, 66.18; H, 4.20.

Preparation of 3-cyano-1-methylindole (1b).³ 3-Cyanoindole (2.0 g, 14.1 mmol) was treated with NaH (0.40 g, 16.8 mmol) in DMF (30 mL) at 0 °C for 10 min, and then iodomethane (2.4 g, 16.8 mmol) was added to the resulting mixture at rt. After being stirred at rt for 1 h, the reaction was quenched with H₂O and extracted with ethyl acetate. Combined organic layers were washed with H₂O and brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give **1b** (1.38 g, 84%) as a colorless solid, mp = 60.5–61.5 °C, *R*_f 0.50 (hexane–ethyl acetate = 1:1). ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 7.9 Hz, 1H), 7.55 (s, 1H), 7.42–7.27 (m, 3H), 3.85 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 136.0, 135.5, 127.8, 123.8, 122.1, 119.8, 115.9, 110.3, 85.4, 33.6.

Preparation of 3-cyano-2-deuterio-1-methylindole (1b-d₁). To a solution of **1b** (0.50 g, 3.2 mmol) in THF (10 mL) was added a 1.6 M solution of BuLi in hexane (3.5 mL, 5.6 mmol) at –78 °C, and the resulting mixture was stirred at the same temperature for 30 min. The reaction was quenched with D₂O (0.55 g, 27 mmol) at –78 °C, and the mixture was warmed gradually at rt and extracted with diethyl ether. Combined organic layers were dried over anhydrous Na₂SO₄, concentrated in vacuo, and purified by flash chromatography on silica gel to give **1b-d₁** (0.36 g, 71%) as a colorless solid, mp = 58.0–59.0 °C, *R*_f 0.50 (hexane–ethyl acetate = 1:1). ¹H NMR (400 MHz, CDCl₃) δ 7.76 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.42–7.27 (m, 3H), 3.85 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 135.7, 135.2 (t, *J* = 28.8 Hz), 127.4, 123.5, 121.8, 119.3, 115.8, 110.2, 84.7, 33.3; HRMS (EI) Calcd for C₁₀H₇N₂D: M⁺, 157.0750. Found: *m/z* 157.0748.

Preparation of methyl 1-methylindole-3-carboxylate (1c).³ Following the procedure for **1b**, the reaction using methyl indole-3-carboxylate (3.0 g, 17.1 mmol) gave **1c** (2.8 g, 87%) as a colorless solid, mp = 87.6–88.7 °C, R_f 0.60 (hexane–ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 8.22–8.14 (m, 1H), 7.78 (s, 1H), 7.39–7.25 (m, 3H), 3.91 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 137.1, 135.1, 126.6, 122.7, 121.8, 121.6, 109.7, 106.9, 50.9, 33.4.

Preparation of methyl 1-benzylindole-3-carboxylate (1d).⁴ Methyl indole-3-carboxylate (1.00 g, 5.7 mmol) was treated with NaH (0.164 g, 6.8 mmol) in THF (30 mL) at 0 °C for 10 min, and then benzyl bromide (0.98 g, 5.7 mmol) was added to the resulting mixture at rt. After being stirred at rt for 1 h, the reaction was quenched with H_2O and extracted with CH_2Cl_2 . Combined organic layers were washed with H_2O and brine, dried over anhydrous Na_2SO_4 , and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give **1d** (1.41 g, 93%) as a brownish solid, mp = 70.2–71.2 °C, R_f 0.40 (hexane–ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 8.20 (dd, J = 7.9, 0.7 Hz, 1H), 7.85 (s, 1H), 7.36–7.22 (m, 6H), 7.18–7.13 (m, 2H), 5.34 (s, 2H), 3.91 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 136.7, 135.9, 134.5, 129.0, 128.1, 127.1, 126.8, 122.9, 122.0, 121.8, 110.3, 107.5, 51.0, 50.7.

Preparation of methyl 1-methoxymethylindole-3-carboxylate (1e). Methyl indole-3-carboxylate (1.00 g, 5.7 mmol) was treated with NaH (0.164 g, 6.8 mmol) in DMF (30 mL) at 0 °C for 15 min, and then chloromethyl methyl ether (0.92 g, 11.4 mmol) was added to the resulting mixture at rt. After being stirred at rt for 1 h, the reaction was quenched with H_2O and extracted with ethyl acetate. Combined organic layers were washed with H_2O and brine, dried over anhydrous Na_2SO_4 , and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give **1e** (1.25 g, 100%) as a colorless solid, mp = 64.9–65.7 °C, R_f 0.80 (hexane–ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 8.22–8.16 (m, 1H), 7.89 (s, 1H), 7.55–7.49 (m, 1H), 7.35–7.28 (m, 2H), 5.48 (s, 2H), 3.93 (s, 3H), 3.27 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 165.3, 136.5, 134.3, 126.9, 123.4, 122.5, 121.8, 110.5, 108.4, 78.1, 56.2, 51.1; Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_3$; C, 65.74; H, 5.98. Found: C, 65.78; H, 5.88.

Preparation of 3-acetyl-1-methylindole (1f).⁵ Following the procedure for **1b**, the reaction using 3-acetylindole (2.0 g, 12.6 mmol) gave **1f** (1.70 g, 80%) as a colorless solid, mp = 106.0–107.0 °C, R_f 0.40 (hexane–ethyl acetate = 7:3). ¹H NMR (400 MHz, CDCl₃) δ 8.40–8.34 (m, 1H), 7.69 (s, 1H), 7.35–7.28 (m, 3H), 3.84 (s, 3H), 2.52 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 192.8, 137.4, 135.7, 126.2, 123.3, 122.5, 116.9, 109.7, 109.5, 33.4, 27.6.

Preparation of 1-methylindole-3-carboxaldehyde (1g).³ Following the procedure for **1b**, the reaction using indole-3-carboxaldehyde (2.0 g, 13.8 mmol) gave **1g** (1.67 g, 83%) as a colorless solid, mp = 69.9–70.8 °C, R_f 0.60 (hexane–ethyl acetate = 1:1). ¹H NMR (400 MHz, CDCl₃) δ 9.99 (s, 1H), 8.31 (d, J = 6.4 Hz, 1H), 7.67 (s, 1H), 7.38–7.30 (m, 3H), 3.87 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 184.6, 139.4, 138.1, 125.5, 124.3, 123.2, 122.3, 118.3, 110.1, 33.9.

Preparation of methyl (*E*)-2-(1-methylindol-3-yl)acrylate (1h). Following the procedure for **1b**, the reaction using methyl (*E*)-2-(3-indolyl)acrylate (0.25 g, 1.23 mmol)⁶ gave **1h** (0.26 g, 100%) as a reddish solid, mp = 97.9–98.8 °C, R_f 0.45 (hexane–ethyl acetate = 1:1). ¹H NMR (400 MHz, CDCl₃) δ 7.94–7.87 (m, 2H), 7.37–7.24 (m, 4H), 6.42 (d, J = 15.9 Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 168.7, 138.2, 138.0, 133.1, 126.0, 122.9, 121.3, 120.5, 112.1, 112.0, 109.9, 51.3, 33.1; HRMS (EI) Calcd for C₁₃H₁₃NO₂: M⁺, 215.0946. Found: m/z 215.0939.

Preparation of 1-methyl-3-phenylindole (1i).⁷ Following the procedure for **1b**, the reaction using 3-phenylindole (0.68 g, 3.5 mmol)⁸ gave **1i** (0.71 g, 97%) as a brownish solid, mp = 48.5–49.0 °C, R_f 0.65 (hexane–ethyl acetate = 3:1). ¹H NMR (400 MHz, CDCl₃) δ 7.96 (dd, J = 8.1, 0.7 Hz, 1H), 7.67 (dd, J = 7.3, 0.9 Hz, 2H), 7.44 (t, J = 7.9 Hz, 2H), 7.38 (d, J = 8.2 Hz, 1H), 7.33–7.16 (m, 4H), 3.85 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 137.4, 135.6, 128.7, 127.3, 126.5, 126.1, 125.7, 121.9, 119.91, 119.86, 116.7, 109.5, 32.9.

Preparation of 6-chloro-1-methylbenzimidazole (1k). 5-Chlorobenzimidazole (1.07 g, 7.0 mmol) was treated with NaH (0.26 g, 10.8 mmol) in THF (30 mL) at 0 °C for 15 min, and then iodomethane (2.7 g, 19.2 mmol) was added to the resulting mixture at rt. After being stirred at rt for 30 min, the reaction was quenched with H₂O and extracted with CH₂Cl₂. Combined organic layers were washed with H₂O and brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give a mixture of 5- and 6-chloro-1-methylbenzimidazole (0.73 g, 62%), which after recrystallization from hexane–Et₂O (9:1) for three times gave **1k** as colorless crystals, mp = 119.0–120.0 °C, R_f 0.60 (hexane–ethyl acetate = 1:1). ¹H NMR (400 MHz, CDCl₃) δ 7.83 (s, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.36 (d, *J* = 1.6 Hz, 1H), 7.23 (dd, *J* = 8.5, 1.9 Hz, 1H), 3.79 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.2, 142.4, 128.7, 123.3, 122.7, 122.1, 109.5, 31.1; Anal. Calcd for C₈H₇ClN₂; C, 57.67; H, 4.23. Found: C, 57.41; H, 4.19.

Nickel-catalyzed hydroheteroarylation of alkynes. A general procedure. A heteroarene (1.0 mmol) and an alkyne (1.0 mmol) were added to a solution of Ni(cod)₂ (28 mg, 0.10 mmol) and PCyp₃ (24 mg, 0.10 mmol) in toluene (2.0 mL) in a dry box. The vial was taken outside the dry box and heated at 35 °C for the time specified in Tables 1 and 2. The resulting mixture was filtered through a silica gel pad, concentrated in vacuo, and purified by flash silica gel column chromatography to give the corresponding hydroheteroarylation products in yields listed in Tables 1 and 2.

(Z)-3-(1-Methoxycarbonyl-3-indolyl)-2-propyl-2-hexenenitrile (3aa). A colorless oil, R_f 0.65 (hexane–ethyl acetate = 1:1). ¹H NMR (400 MHz, CDCl₃) δ 8.24 (br d, *J* = 8.1 Hz, 1H), 7.70 (s, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.38 (td, *J* = 7.8, 1.1 Hz, 1H), 7.30 (td, *J* = 7.6, 1.1 Hz, 1H), 4.04 (s, 3H), 2.59 (t, *J* = 7.7 Hz, 2H), 2.43 (t, *J* = 7.6 Hz, 2H), 1.73 (sext, *J* = 7.5 Hz, 2H), 1.37 (sext, *J* = 7.5 Hz, 2H), 1.06 (t, *J* = 7.3 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 151.0, 150.4, 135.3, 128.5, 125.0 (CH), 124.2 (CH), 123.1 (CH), 120.8, 119.8 (CH), 119.2, 115.3 (CH), 113.5, 53.8 (CH₃), 35.0 (CH₂), 32.1 (CH₂), 21.7 (CH₂), 21.3 (CH₂), 13.7 (CH₃), 13.4 (CH₃); Anal. Calcd for C₁₉H₂₂N₂O₂; C, 73.52; H, 7.14. Found: C, 73.42; H, 7.19.

(E)-3-Cyano-1-methoxycarbonyl-2-(4-octen-4-yl)indole (4aa, containing 9% of Z-isomer). A colorless oil, R_f 0.60 (hexane–ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 7.70 (dt, J = 8.1, 0.9 Hz, 1H), 7.40–7.22 (m, 3H), 5.79 (t, J = 7.4 Hz, 1H), 3.69 (s, 3H), 2.48 (t, J = 7.8 Hz, 2H), 2.30 (q, J = 7.4 Hz, 2H), 1.54 (sext, J = 7.3 Hz, 2H), 1.37 (sext, J = 7.6 Hz, 2H), 1.01 (t, J = 7.3 Hz, 3H), 0.92 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 151.2, 138.5 (CH), 136.2, 129.4, 127.3, 123.3 (CH), 123.2, 122.0 (CH), 119.3 (CH), 116.7, 110.2 (CH), 110.1, 32.9 (CH_2), 31.1 (CH_3), 30.3 (CH_2), 22.5 (CH_2), 21.7 (CH_2), 13.92 (CH_3), 13.87 (CH_3); HRMS (EI) Calcd for $\text{C}_{17}\text{H}_{19}\text{N}_2$: $[\text{M}-\text{CO}_2\text{Me}]^+$, 251.1548. Found: m/z 251.1545.

(E)-3-Cyano-1-methyl-2-(4-octen-4-yl)indole (4ba). A colorless oil, R_f 0.65 (hexane–ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 7.70 (dt, J = 7.3, 1.0 Hz, 1H), 7.38–7.24 (m, 3H), 5.78 (t, J = 7.4 Hz, 1H), 3.69 (s, 3H), 2.49 (t, J = 7.7 Hz, 2H), 2.30 (q, J = 7.4 Hz, 2H), 1.54 (sext, J = 7.4 Hz, 2H), 1.37 (sext, J = 7.6 Hz, 2H), 1.01 (t, J = 7.4 Hz, 3H), 0.92 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 151.2, 138.5 (CH), 136.2, 129.4, 127.3, 123.3 (CH), 122.0 (CH), 119.3 (CH), 116.7, 110.1 (CH), 84.9, 32.9 (CH_2), 31.1 (CH_3), 30.3 (CH_2), 22.5 (CH_2), 21.7 (CH_2), 13.90 (CH_3), 13.85 (CH_3); Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2$; C, 81.16; H, 8.32. Found: C, 81.37; H, 8.47.

(E)-3-Cyano-2-deuterio-1-methyl-2-(4-octen-4-yl)indole (4ba- d_1). A colorless oil, R_f 0.65 (hexane–ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 7.69 (dt, J = 7.3, 1.0 Hz, 1H), 7.36–7.23 (m, 3H), 3.68 (s, 3H), 2.48 (t, J = 7.7 Hz, 2H), 2.29 (t, J = 7.3 Hz, 2H), 1.54 (sext, J = 7.4 Hz, 2H), 1.37 (sext, J = 7.5 Hz, 2H), 1.01 (t, J = 7.4 Hz, 3H), 0.92 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 151.2, 138.1 (CD, t, J = 23.4 Hz), 136.2, 129.2, 127.3, 123.2 (CH), 121.9 (CH), 119.2 (CH), 116.7, 110.1 (CH), 84.8, 32.8 (CH_2), 31.1 (CH_3), 30.2 (CH_2), 22.4 (CH_2), 21.7 (CH_2), 13.9 (CH_3), 13.8 (CH_3); HRMS (FAB+) Calcd for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{D}$; M^+ , 267.1846. Found: m/z 267.1848.

Methyl (E)-1-methyl-2-(4-octen-4-yl)indole-3-carboxylate (4ca). A colorless oil, R_f 0.65 (hexane–ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 8.20–8.14 (m, 1H), 7.35–7.23 (m, 3H), 5.51 (t, J = 7.3 Hz, 1H), 3.87 (s, 3H), 3.68 (s, 3H), 2.50 (t, J = 8.1 Hz, 2H), 2.30 (q, J = 7.3 Hz, 2H), 1.53 (sext, J = 7.4 Hz, 2H), 1.29 (sext, J = 7.9 Hz, 2H), 1.01 (t, J = 7.3 Hz, 3H), 0.88 (t, J = 7.3 Hz,

3H); ^{13}C NMR (101 MHz, CDCl_3) δ 165.6, 150.0, 134.7 (CH), 131.9, 126.6, 122.3 (CH), 121.8 (CH), 121.7 (CH), 109.6 (CH), 108.17, 108.15, 50.6 (CH_3), 34.1 (CH_2), 30.4 (CH_3), 30.2 (CH_2), 22.7 (CH_2), 21.8 (CH_2), 14.4 (CH_3), 13.9 (CH_3); Anal. Calcd for $\text{C}_{19}\text{H}_{25}\text{NO}_2$; C, 76.22; H, 8.42. Found: C, 76.25; H, 8.41.

Methyl (*E*)-1-benzyl-2-(4-octen-4-yl)indole-3-carboxylate (4da). A colorless oil, R_f 0.55 (hexane–ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 8.21 (dt, J = 7.9, 1.0 Hz, 1H), 7.30–7.07 (m, 6H), 6.96 (d, J = 7.9 Hz, 2H), 5.48 (t, J = 7.3 Hz, 1H), 5.35 (s, 2H), 3.89 (s, 3H), 2.44 (br, 2H), 2.19 (br q, J = 7.3 Hz, 2H), 1.40–1.19 (m, 4H), 0.93–0.78 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 165.6, 150.0, 137.2, 136.0, 135.0 (CH), 131.4, 128.6 (CH), 127.3 (CH), 126.8, 125.8 (CH), 122.5 (CH), 122.0 (CH), 121.7 (CH), 110.8 (CH), 104.3, 50.7 (CH_3), 47.5 (CH_2), 34.1 (CH_2), 30.1 (CH_2), 22.4 (CH_2), 21.7 (CH_2), 14.4 (CH_3), 13.7 (CH_3); Anal. Calcd for $\text{C}_{25}\text{H}_{29}\text{NO}_2$; C, 79.96; H, 7.78. Found: C, 80.20; H, 7.79.

Methyl (*E*)-1-methoxymethyl-2-(4-octen-4-yl)indole-3-carboxylate (4ea). A colorless oil, R_f 0.60 (hexane–ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 8.23–8.13 (m, 1H), 7.56–7.44 (m, 1H), 7.34–7.21 (m, 2H), 5.64 (t, J = 7.4 Hz, 1H), 5.40 (br, 2H), 3.88 (s, 3H), 3.31 (s, 3H), 2.47 (br t, J = 8.1 Hz, 2H), 2.30 (q, J = 7.4 Hz, 2H), 1.53 (sext, J = 7.3 Hz, 2H), 1.30 (sext, J = 7.9 Hz, 2H), 1.02 (t, J = 7.3 Hz, 3H), 0.88 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 165.5, 149.6, 136.0, 135.7 (CH), 130.9, 126.7, 122.8 (CH), 122.3 (CH), 121.7 (CH), 110.5 (CH), 105.2, 74.8 (CH_2), 55.9 (CH_3), 50.7 (CH_3), 34.2 (CH_2), 30.3 (CH_2), 22.6 (CH_2), 21.5 (CH_2), 14.4 (CH_3), 13.9 (CH_3); Anal. Calcd for $\text{C}_{20}\text{H}_{27}\text{NO}_3$; C, 72.92; H, 8.26. Found: C, 72.84; H, 8.08.

(*E*)-3-Acetyl-1-methyl-2-(4-octen-4-yl)indole (4fa). A colorless oil, R_f 0.70 (hexane–ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 8.42–8.35 (m, 1H), 7.35–7.25 (m, 3H), 5.66 (t, J = 7.3 Hz, 1H), 3.66 (s, 3H), 2.52 (s, 3H), 2.48 (br, 2H), 2.32 (q, J = 7.4 Hz, 2H), 1.54 (sext, J = 7.3 Hz, 2H), 1.34 (sext, J = 8.0 Hz, 2H), 1.02 (t, J = 7.3 Hz, 3H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 194.2, 149.4, 136.4 (CH), 132.0, 126.7, 122.8 (CH), 122.5 (CH), 122.4 (CH), 114.6, 109.5 (CH), 108.2, 35.1 (CH_2), 30.6 (CH_3), 30.4 (CH_2), 30.0 (CH_3), 22.4 (CH_2), 21.7 (CH_2), 14.5 (CH_3), 14.1 (CH_3); Anal. Calcd for $\text{C}_{19}\text{H}_{25}\text{NO}$; C, 80.52; H, 8.89. Found: C, 80.37; H, 8.83.

(E)-1-Methyl-2-(4-octen-4-yl)indole-3-carboxaldehyde (4ga). A colorless oil, R_f 0.40 (hexane–ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 9.87 (s, 1H), 8.39–8.34 (m, 1H), 7.35–7.28 (m, 3H), 5.75 (t, $J = 7.4$ Hz, 1H), 3.67 (s, 3H), 2.43 (br, 2H), 2.31 (q, $J = 7.4$ Hz, 2H), 1.53 (sext, $J = 7.3$ Hz, 2H), 1.35 (sext, $J = 7.6$ Hz, 2H), 1.01 (t, $J = 7.3$ Hz, 3H), 0.90 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 186.4 (CH), 154.9, 139.3 (CH), 137.0, 128.8, 125.1, 123.6 (CH), 122.9 (CH), 122.0 (CH), 115.5, 109.4 (CH), 33.7 (CH_2), 30.7 (CH_3), 30.4 (CH_2), 22.6 (CH_2), 21.5 (CH_2), 14.1 (CH_3), 13.9 (CH_3); HRMS (EI) Calcd for $\text{C}_{18}\text{H}_{23}\text{NO}$: M^+ , 269.1780. Found: m/z 269.1790.

Methyl (E)-3-[(E)-1-methyl-2-(4-octen-4-yl)indol-3-yl]acrylate (4ha). A colorless oil, R_f 0.40 (hexane–ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 7.92 (dd, $J = 6.9, 1.3$ Hz, 1H), 7.88 (dd, $J = 15.9, 1.1$ Hz, 1H), 7.34–7.20 (m, 3H), 6.44 (d, $J = 15.9$ Hz, 1H), 5.60 (t, $J = 7.3$ Hz, 1H), 3.78 (s, 3H), 3.62 (s, 3H), 2.37 (br, 2H), 2.31 (q, $J = 7.3$ Hz, 2H), 1.55 (sext, $J = 7.3$ Hz, 2H), 1.30 (sext, $J = 7.7$ Hz, 2H), 1.03 (t, $J = 7.4$ Hz, 3H), 0.88 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.0, 148.6, 139.4 (CH), 138.2 (CH), 137.4, 129.8, 125.5, 122.5 (CH), 121.3 (CH), 120.4 (CH), 111.0 (CH), 109.7 (CH), 109.6, 51.1 (CH_3), 33.8 (CH_2), 30.6 (CH_3), 30.3 (CH_2), 22.6 (CH_2), 21.4 (CH_2), 14.1 (CH_3), 13.8 (CH_3); Anal. Calcd for $\text{C}_{21}\text{H}_{27}\text{NO}_2$: C, 77.50; H, 8.36. Found: C, 77.23; H, 8.33.

(E)-1-Methyl-2-(4-octen-4-yl)-3-phenylindole (4ia). A colorless oil, R_f 0.40 (hexane–ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, $J = 8.1$ Hz, 1H), 7.55 (d, $J = 7.9$ Hz, 2H), 7.36 (q, $J = 7.6$ Hz, 3H), 7.25 (t, $J = 7.5$ Hz, 2H), 7.13 (t, $J = 7.4$ Hz, 1H), 5.68 (t, $J = 7.3$ Hz, 1H), 3.70 (s, 3H), 2.25 (q, $J = 7.3$ Hz, 2H), 2.12 (t, $J = 7.8$ Hz, 2H), 1.51 (sext, $J = 7.3$ Hz, 2H), 1.15 (sext, $J = 7.6$ Hz, 2H), 0.98 (t, $J = 7.4$ Hz, 3H), 0.70 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 140.1, 136.7, 136.6 (CH), 135.9, 131.8, 129.4 (CH), 128.1 (CH), 127.0, 125.5 (CH), 121.4 (CH), 119.8 (CH), 119.2 (CH), 113.4, 109.4 (CH), 33.6 (CH_2), 30.4 (CH_3), 30.3 (CH_2), 22.8 (CH_2), 21.5 (CH_2), 14.1 (CH_3), 14.0 (CH_3); Anal. Calcd for $\text{C}_{23}\text{H}_{27}\text{N}$: C, 87.02; H, 8.57. Found: C, 87.25; H, 8.66.

(E)-1-Methyl-2-(4-octen-4-yl)benzimidazole (4ja). A colorless oil, R_f 0.55 (hexane–ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 7.79–7.73 (m, 1H), 7.33–7.21 (m, 3H), 5.77 (t, $J = 7.3$ Hz, 1H), 3.74 (s, 3H), 2.64 (t, $J = 7.7$ Hz, 2H), 2.30 (q, $J = 7.4$ Hz, 2H), 1.52 (sext, $J = 7.4$ Hz, 2H), 1.39 (sext,

$J = 7.5$ Hz, 2H), 1.00 (t, $J = 7.3$ Hz, 3H), 0.89 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 155.9, 142.5, 136.6 (CH), 135.9, 130.9, 122.2 (CH), 121.9 (CH), 119.4 (CH), 109.3 (CH), 32.3 (CH_2), 31.2 (CH_3), 30.4 (CH_2), 22.6 (CH_2), 21.7 (CH_2), 13.9 (CH_3), 13.8 (CH_3); Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{N}_2$; C, 79.29; H, 9.15. Found: C, 78.99; H, 9.06.

(E)-6-Chloro-1-methyl-2-(4-octen-4-yl)benzimidazole (4ka). A colorless oil,

R_f 0.70 (hexane–ethyl acetate = 9:1). ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, $J = 8.6$ Hz, 1H), 7.31 (d, $J = 2.0$ Hz, 1H), 7.21 (dd, $J = 8.6, 2.0$ Hz, 1H), 5.78 (t, $J = 7.4$ Hz, 1H), 3.73 (s, 3H), 2.62 (t, $J = 7.7$ Hz, 2H), 2.30 (q, $J = 7.3$ Hz, 2H),

1.53 (sext, $J = 7.4$ Hz, 2H), 1.38 (sext, $J = 7.5$ Hz, 2H), 1.00 (t, $J = 7.3$ Hz, 3H), 0.90 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 156.7, 141.2, 137.0 (CH), 136.6, 130.6, 127.9, 122.6 (CH), 120.2 (CH), 109.5 (CH), 32.3 (CH_2), 31.3 (CH_3), 30.4 (CH_2), 22.6 (CH_2), 21.8 (CH_2), 13.9 (CH_3), 13.8 (CH_3); HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{21}\text{ClN}_2$: M^+ , 276.1393. Found: m/z 276.1393.

(E)-1,3,7-Trimethyl-8-(4-octen-4-yl)-3,7-dihydropurine-2,6-dione (4la). A

colorless solid (mp = 92.7–93.6 °C), R_f 0.60 (hexane–ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 5.73 (t, $J = 7.4$ Hz, 1H), 3.89 (s, 3H), 3.53 (s, 3H), 3.36 (s, 3H), 2.48 (t, $J = 7.6$ Hz, 2H), 2.23 (q, $J = 7.4$ Hz, 2H), 1.47 (sext, $J =$

7.3 Hz, 2H), 1.32 (sext, $J = 7.5$ Hz, 2H), 0.95 (t, $J = 7.4$ Hz, 3H), 0.86 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 155.3, 154.4, 151.7, 147.8, 137.6 (CH), 129.4, 107.5, 33.4 (CH_3), 32.0 (CH_2), 30.3 (CH_2), 29.6 (CH_3), 27.8 (CH_3), 22.4 (CH_2), 21.7 (CH_2), 13.9 (CH_3), 13.8 (CH_3); Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{N}_4\text{O}_2$; C, 63.13; H, 7.95. Found: C, 62.91; H, 8.04.

(E)-9-Methyl-8-(4-octen-4-yl)purine (4ma). A colorless oil, R_f 0.70

(hexane–ethyl acetate = 9:1). ^1H NMR (400 MHz, CDCl_3) δ 8.97 (s, 1H), 8.87 (s, 1H), 5.91 (t, $J = 7.4$ Hz, 1H), 3.80 (s, 3H), 2.59 (t, $J = 7.7$ Hz, 2H), 2.28 (q, $J =$

7.4 Hz, 2H), 1.49 (sext, $J = 7.4$ Hz, 2H), 1.36 (sext, $J = 7.5$ Hz, 2H), 0.95 (t, $J = 7.3$ Hz, 3H), 0.85 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.1, 153.1, 152.0 (CH), 147.0 (CH), 138.8 (CH), 133.6, 130.4, 31.8 (CH_2), 30.5 (CH_2), 30.3 (CH_3), 22.5 (CH_2), 21.8 (CH_2), 13.9 (CH_3), 13.8 (CH_3); HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{20}\text{N}_4$: M^+ , 244.1688. Found: m/z 244.1688.

(E)-2-(4-Octen-4-yl)benzofuran (4na). A colorless oil, R_f 0.50 (hexane–ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 7.49 (dd, $J = 7.7$, 1.4 Hz, 1H), 7.41 (dd, $J = 7.5$, 1.2 Hz, 1H), 7.21 (td, $J = 7.7$, 1.2 Hz, 1H), 7.16 (td, $J = 7.4$, 1.4 Hz, 1H), 6.54 (s, 1H), 6.38 (t, $J = 7.5$ Hz, 1H), 2.43 (t, $J = 7.8$ Hz, 2H), 2.23 (q, $J = 7.4$ Hz, 2H), 1.62–1.47 (m, 4H), 1.03–0.95 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 157.8, 154.5, 129.8 (CH), 129.5, 129.3, 123.7 (CH), 122.5 (CH), 120.4 (CH), 110.7 (CH), 100.8 (CH), 30.2 (CH_2), 30.0 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 14.2 (CH_3), 14.0 (CH_3); HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{20}\text{O}$: M^+ , 228.1514. Found: m/z 228.1513.

(E)-2-(4-Octen-4-yl)benzothiophene (4oa). A colorless oil, R_f 0.60 (hexane–ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 7.72 (dd, $J = 7.7$, 0.9 Hz, 1H), 7.66 (dd, $J = 7.0$, 1.3 Hz, 1H), 7.31–7.22 (m, 2H), 7.13 (s, 1H), 6.01 (t, $J = 7.3$ Hz, 1H), 2.51 (t, $J = 7.8$ Hz, 2H), 2.21 (q, $J = 7.4$ Hz, 2H), 1.62–1.45 (m, 4H), 1.02–0.94 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 147.3, 140.6, 138.4, 134.0, 130.9 (CH), 124.1 (CH), 123.9 (CH), 123.0 (CH), 121.9 (CH), 118.6 (CH), 31.7 (CH_2), 30.6 (CH_2), 22.8 (CH_2), 22.4 (CH_2), 14.1 (CH_3), 14.0 (CH_3); Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{S}$: C, 78.63; H, 8.25. Found: C, 78.83; H, 8.35.

(E)-2-(4-Octen-4-yl)benzoxazole (4pa). A colorless oil, R_f 0.50 (hexane–ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 7.72–7.68 (m, 1H), 7.49–7.45 (m, 1H), 7.31–7.25 (m, 2H), 6.88 (t, $J = 7.6$ Hz, 1H), 2.63 (t, $J = 7.8$ Hz, 2H), 2.31 (q, $J = 7.4$ Hz, 2H), 1.68–1.50 (m, 4H), 1.04–0.96 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 164.7, 150.4, 142.1, 138.8 (CH), 128.5, 124.6 (CH), 124.0 (CH), 119.7 (CH), 110.1 (CH), 30.6 (CH_2), 29.4 (CH_2), 22.43 (CH_2), 22.39 (CH_2), 14.0 (CH_3), 13.8 (CH_3); Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}$: C, 78.56; H, 8.35. Found: C, 78.55; H, 8.24.

(E)-4,5-Dimethyl-2-(4-octen-4-yl)thiazole (4qa). A purple oil, R_f 0.60 (hexane–ethyl acetate = 2:1). ^1H NMR (400 MHz, CDCl_3) δ 6.27 (t, $J = 7.5$ Hz, 1H), 2.51 (t, $J = 7.7$ Hz, 2H), 2.31 (s, 3H), 2.30 (s, 3H), 2.18 (q, $J = 7.4$ Hz, 2H), 1.58–1.43 (m, 4H), 0.98–0.89 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 166.4, 148.1, 134.5, 131.9 (CH), 124.5, 31.3 (CH_2), 30.5 (CH_2), 22.6 (CH_2), 22.3 (CH_2), 14.8 (CH_3), 14.01 (CH_3), 13.97 (CH_3), 11.3 (CH_3); HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{21}\text{NS}$: M^+ , 223.1395. Found: m/z 223.1394.

(E)-3-Cyano-1-methyl-2-(4-methyl-2-penten-2-yl)indole (4bb). A pale yellow solid (mp = 98.5–99.0 °C), R_f 0.50 (hexane–ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 7.70 (ddd, J = 7.9, 1.4, 0.6 Hz, 1H), 7.36–7.24 (m, 3H), 5.68 (dq, J = 9.5, 1.5 Hz, 1H), 3.70 (s, 3H), 2.84–2.74 (m, 1H), 2.09 (d, J = 1.5 Hz, 3H), 1.12 (d, J = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 151.8, 145.7 (CH), 136.2, 127.3, 123.3 (CH), 122.0 (CH), 121.6, 119.2 (CH), 116.6, 110.1 (CH), 83.9, 31.2 (CH_3), 27.9 (CH), 22.3 (CH_3), 16.6 (CH_3); Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{N}_2$; C, 80.63; H, 7.61. Found: C, 80.44; H, 7.64.

(E)-3-Cyano-1-methyl-2-(1-trimethylsilylpropen-2-yl)indole (4bc). A colorless oil, R_f 0.70 (hexane–ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, J = 7.5 Hz, 1H), 7.37–7.24 (m, 3H), 5.91 (q, J = 1.0 Hz, 1H), 3.72 (s, 3H), 2.27 (d, J = 1.1 Hz, 3H), 0.27 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 152.6, 140.6, 139.2 (CH), 136.3, 127.3, 123.6 (CH), 122.2 (CH), 119.5 (CH), 116.5, 110.3 (CH), 83.3, 31.4 (CH_3), 22.0 (CH_3), –0.3 (CH_3); Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{N}_2\text{Si}$; C, 71.59; H, 7.51. Found: C, 71.59; H, 7.55.

(E)-3-Cyano-1-methyl-2-(1-trimethylsilyl-2-phenylethen-2-yl)indole (4bd). A colorless solid (mp = 79.6–80.6 °C), R_f 0.40 (hexane–ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 7.76 (dd, J = 8.3, 1.5 Hz, 1H), 7.39–7.22 (m, 8H), 6.49 (s, 1H), 3.36 (s, 3H), 0.07 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 150.8, 144.9, 142.4 (CH), 139.9, 136.5, 128.9 (CH), 128.6 (CH), 128.4 (CH), 127.3, 123.8 (CH), 122.1 (CH), 119.6 (CH), 116.5, 110.1 (CH), 86.5, 31.6 (CH_3), –0.1 (CH_3); Anal. Calcd for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{Si}$; C, 76.32; H, 6.71. Found: C, 76.16; H, 6.73.

Deuterium crossover experiment. To a solution of $\text{Ni}(\text{cod})_2$ (28 mg, 0.10 mmol) and PCyp_3 (24 mg, 0.10 mmol) in toluene (2.0 mL), **1b-d₁** (134 mg, 0.50 mmol), **1c** (150 mg, 0.50 mmol), and 4-octyne (**2a**: 110 mg, 1.00 mmol) were added in a dry box. The vial was taken outside the dry box and heated at 35 °C for 20 h. The resulting mixture was filtered through a silica gel pad, concentrated in vacuo, and purified by flash silica gel column chromatography to give a mixture of **4ba-d₁** and **4ca** (220 mg, 50% of **4ba-d₁** and 33% of **4ca** based on **2a** as estimated by ^1H NMR analysis).

References

1. Stanovnik, B.; Tisler, M.; Hribar, A.; Barlim, G. B.; Brown, D. J. *Aust. J. Chem.* **1981**, *34*, 1729–1738.
2. Jacquemard, H.; Bénétteau, V.; Lefoix, M.; Routier, S.; Mérour, J.-Y.; Coudert, G. *Tetrahedron* **2004**, *60*, 10039–10047.
3. Jiang, X.; Tiwari, A.; Thompson, M.; Chen, Z.; Cleary, T. P.; Lee, T. B. K. *Org. Process Res. Dev.* **2001**, *5*, 604–608.
4. Hwu, J. R.; Patel, H. V.; Lin, R. J.; Gray, M. O. *J. Org. Chem.* **1994**, *59*, 1577–1582.
5. Ottoni, O.; Cruz, R.; Alves, R. *Tetrahedron* **1998**, *54*, 13915–13928.
6. Grimster, N. P.; Gauntlett, C.; Godfrey, C. R. A.; Gaunt, M. J. *Angew. Chem. Int. Ed.* **2005**, *44*, 3125–3129.
7. Cao, C.; Shi, Y.; Odom, A. L. *Org. Lett.* **2002**, *4*, 2853–2856.
8. Rodríguez, J. C.; Lafuente, A.; García-Almaraz, P. *J. Heterocycl. Chem.* **2000**, *37*, 1281–1287.

6403-74-2-C-D-sm

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

OBSERVE H1, 399.9480279 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 2 min, 4 sec

1b-d₁

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "m400"

Relax. delay 0.801 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

1024 repetitions

OBSERVE C13, 100.5670389 MHz

DECOUPLE H1, 399.9500406 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 1 hr, 39 min, 10 sec

1b-d₁

6221-74-2-CHCH2CO2Me-H

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 6221-74-2-NMe-CHCH2CO2Me-smdata

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

OBSERVE F1, 399.9480266 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 1 min, 42 sec

1h

6221-74-2-CHCH2CO2Me-H

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 6221-74-2-NMe-CHCH2CO2Me-smdata-C

Mercury-400BB "m400"

Relax. delay 0.801 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

266 repetitions

OBSERVE C13, 100.5670136 MHz

DECOUPLE H1, 399.9500406 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 1 hr, 6 min, 54 sec

6315-74-2-CN-NO2Me-PrCCPr-H-data

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

OBSERVE H1, 399.9480270 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 62536

Total time 2 min, 4 sec

¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

Mercury-400EB "m400"

Relax. delay 0.801 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

996 repetitions

OBSERVE C13, 100.5670136 MHz

DECOUPLE H1, 399.9500406 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 1 hr, 6 min, 54 sec

Total time 2 min, 4 sec

¹³C OBSERVE

6403-74-2-CD-PrCPr-C

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

Mercury-400BB "m400"

Relax. delay 0.801 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

14000 repetitions

OBSERVE C13, 100.5670182 MHz

DECOUPLE H1, 399.9500406 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 12 hr, 47 min, 53 sec

¹³C - data

4ba-d₁

138.324
138.095
137.859

77.313
77.000
76.680

151.194

138.324
138.095

137.859
136.189

129.220
127.268

123.235
121.939

119.232
116.724

110.128

84.807

138.2 ppm

32.778
31.101
30.193
22.439
21.669
13.869
13.831

160

140

120

100

80

60

40

20

0 ppm

5707-74-1-CHO-PrCCPr-H

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: 5707-74-1-CHO-PrCCPr-H

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

OBSERVE H1, 399.9480268 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 1 min, 31 sec

4ga

5707-74-01-CHO-PrCCPr-C

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: 5707-74-01-CHO-PrCCPr-C

Mercury-400BB "m400"

Relax. delay 0.801 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

194 repetitions

OBSERVE C13, 100.5670136 MHz

DECOUPLE H1, 399.9500406 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 69 hr, 32 min, 14 sec

4ga

6320-74-2-5Cl-NMe-benzimidz-PrCCPr-H-tms

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

OBSERVE H1, 399.9480259 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 2 min, 4 sec

4ka

13C OBSERVE

Pulse Sequence: s2pul1

Solvent: CDCl3

Ambient temperature

File: 6204-74-2-5ClMe-benzimid-PrCCPr-C

Mercury-400BB "m400"

Relax. delay 0.801 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

1024 repetitions

OBSERVE C13, 100.5670151 MHz

DECOUPLE H1, 399.9500406 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 56 min, 12 sec

4ka

9Mepur-PrCCPr-H

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

OBSERVE H1, 399.9480259 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 2 min, 4 sec

4ma

que-pure.

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

Mercury-400BB "m400"

Relax. delay 0.801 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

14000 repetitions

OBSERVE C13, 100.5670136 MHz

DECOUPLE H1, 399.9500406 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 22 hr, 35 min, 51 sec

4ma

77.313
77.000
76.680

31.825
30.529
30.308
22.462
21.844
13.915
13.831

158.064
153.093
151.956
147.001
138.766
133.566
130.440

220 200 180 160 140 120 100 80 60 40 20 0 ppm

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

OBSERVE H1, 399.9480267 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 2 min, 4 sec

5726-74-01-O-PrCCPr-C

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

Mercury-400BB "m400"

Relax. delay 0.801 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

144 repetitions

OBSERVE C13, 100.5670190 MHz

DECOUPLE H1, 399.9500406 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 42 min, 43 sec

5X28-74-1-3, 4-dimethylthiazole-H

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 5X28-74-1-3

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

OBSERVE H1, 399.9480279 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 6536

Total time 1 min, 36 sec

5X28-74-1-3,4-dimethylthiazole-PrCCPr-C

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: 5X28-74-1-34-dimethylthiazole-PrCCPr-C

Mercury-400BB "m400"

Relax. delay 0.801 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

102 repetitions

OBSERVE C13, 100.5670144 MHz

DECOUPLE H1, 399.9500406 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 56 min, 12 sec

6515-74-2-ArD+Ar*CO2Me+PrCCPr-fr8-21

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 6515-74-2-ArD-ArCO2Me-PrCCPr-H

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

OBSERVE H1, 399.9480365 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 1 min, 36 sec