Supporting Information

**Pd/C-mediated synthesis of α-pyrone fused with a five-membered nitrogen heteroaryl ring: A new route to pyrano[4,3-*c*]pyrazol-4(1*H*)-ones**

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**General procedure for the preparation of** **3**

A mixture of 5-iodo-1-methyl-1*H*-pyrazole-4-carboxylic acid **1** (1.0 mmol), 10% Pd/C (0.035 mmol), PPh3 (0.3 mmol), CuI (0.06 mmol), and triethylamine (5.0 mmol) in EtOH (10 mL) was stirred at 25–30 °C for 30 min under nitrogen and the terminal alkyne **2** (2.0 mmol) was added. The mixture was then stirred at room temperature for 1.0 h and then at 75–80 °C for the time indicated in Table 2. After completion of the reaction the mixture was cooled to room temperature, diluted with EtOAc (50 mL), and filtered through celite. The filtrate was washed with saturated aqueous sodium hydrogen carbonate (2 × 25 mL) followed by water (2 × 25 mL), dried over anhydrous Na2SO4, and concentrated. The residue was purified by column chromatography on silica gel, using light petroleum (distillation range 60–80 °C)–ethylacetate as eluent.

**Spectral data for selected compounds**

6-Butyl-1-methylpyrano[4,3-c]pyrazol-4(1*H*)-one (**3a**)



Light brown solid; mp 102–104 °C; 1H NMR (CDCl3, 400 MHz) δ8.04 (s, 1H), 6.21 (s, 1H), 3.91 (s, 3H), 2.58 (t, *J* = 7.5 Hz, 2H), 1.73–1.68 (m, 2H), 1.44–1.39 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H); IR cm−1 (KBr) 1730; *m/z* (CI Mass) 207 (M++1, 100%); HPLC 98.5%, Inertsil ODS 3V (250 × 4.6) mm, mobile phase A: 0.01M KH2PO4 (pH 6.5), mobile phase B: CH3CN, gradient (*T*/% B): 0/30, 3/30, 14/80, 20/80, 21/30, 22/30, flow rate: 1.0 mL/min, UV 215 nm, retention time 8.3 min; Elemental Analysis found: C, 64.0; H, 6.80; N, 13.70 C11H14N2O2 Requires C, 64.06, H, 6.84, N, 13.58.

6-(2-Hydroxypropan-2-yl)-1-methylpyrano[4,3-c]pyrazol-4(1*H*)-one (**3e**)



Light brown solid; mp 140–142 °C; 1H NMR (CDCl3, 400 MHz) δ8.09 (s, 1H), 6.67 (s, 1H), 3.95 (s, 3H), 1.59 (s, 6H); IR cm−1 (KBr) 3381, 1720; *m/z* (CI Mass) 209 (M+1, 100%); 13C (CDCl3, 50 MHz): δ 167.1, 157.9, 144.6, 138.1, 132.1, 105.7, 71.6, 36.1, 28.6 (2C); HPLC 98.3%, Inertsil ODS 3V (250 × 4.6) mm, mobile phase A: 0.01M KH2PO4, mobile phase B: CH3CN, gradient (*T*/% B): 0/20, 10/20, 15/70, 24/70, 26/20, 28/20, flow rate: 1.0 mL/min, UV 220 nm, retention time 8.1 min; Elemental Analysis found: C, 57.51; H, 5.69; N, 13.57 C10H12N2O3 Requires C, 57.68, H, 5.81, N, 13.45.

6-(3-Hydroxypropyl)-1-methylpyrano[4,3-c]pyrazol-4(1*H*)-one (**3f**)



Light brown solid; mp 124–126 °C; 1H NMR (CDCl3, 400 MHz) δ8.05 (s, 1H), 6.28 (s, 1H), 3.92 (s, 3H), 3.73 (t, *J* = 6.2, 2H), 2.72–2.68 (m, 2H), 2.01–1.94 (m, 2H), 1.58 (bs, -OH); IR cm−1 (KBr) 3380, 1728; *m/z* (CI Mass) 209 (M+1, 100%); 13C (CDCl3, 50 MHz): δ 162.2, 158.1, 144.3, 137.2, 105.2, 91.2, 60.1, 38.7, 29.9, 29.5; HPLC 97.5%, Inertsil ODS 3V (250 × 4.6) mm, mobile phase A: 0.01 M KH2PO4, mobile phase B: CH3CN, gradient (*T*/% B): 0/15, 5/15, 15/70, 24/70, 26/15, 28/15, flow rate: 1.0 mL/min, UV 215 nm, retention time 10.4 min; Elemental Analysis found: C, 57.79; H, 5.80; N, 13.21 C10H12N2O3 Requires C, 57.68, H, 5.81, N, 13.45.

1-Methyl-6-phenylpyrano[4,3-c]pyrazol-4(1*H*)-one (**3g**)



White solid; mp 226–228 °C; 1H NMR (CDCl3, 400 MHz) δ8.11 (s, 1H), 7.90–7.87 (m, 2H), 7.48–7.46 (m, 3H), 6.86 (s, 1H), 4.00 (s, 3H); IR cm−1 (KBr) 1725; *m/z* (CI Mass) 227 (M+1, 100%); 13C (CDCl3, 50 MHz): δ 157.9, 144.8, 138.2, 131.7, 130.9 (2C), 128.9 (2C), 125.7 (2C), 106.4, 89.4, 36.3; HPLC 98.1%, Inertsil ODS 3V (250 × 4.6) mm, mobile phase A: 0.01M KH2PO4 (pH: 6.5), mobile phase B: CH3CN, gradient (*T*/% B): 0/50, 5/50, 15/80, 24/80, 26/50, 28/50, flow rate: 1.0 mL/min, UV 210 nm, retention time 8.2 min; Elemental Analysis found: C, 68.81; H, 4.45; N, 12.51 C13H10N2O2 Requires C, 69.02, H, 4.46, N, 12.38.