

Supporting Information

Ruthenium(II)-Catalyzed Cycloaddition of 1,6-Diynes with Isocyanates Leading to Bicyclic Pyridones

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Experimental Section

General. ^1H and ^{13}C NMR spectra were obtained for samples in CDCl_3 solution. Flash chromatography was performed with a silica gel column (Merck Silica gel 60) eluted with mixed solvents [hexane / ethyl acetate]. Elemental analyses were performed by the Microanalytical Center of Kyoto University. Melting points were obtained in sealed capillary tubes and are uncorrected. 1,2-Dichloroethane, benzene, and acetonitrile were dried over CaH_2 and distilled.

Procedure for $\text{Cp}^*\text{Ru}(\text{cod})\text{Cl}$ -Catalyzed Cycloaddition of 1,6-Diynes **1** and Isocyanates **2**.

To a solution of $\text{Cp}^*\text{Ru}(\text{cod})\text{Cl}$ (5.7 mg, 0.015 mmol) and an isocyanate **2** (0.60 mmol) in dry degassed 1,2-dichloroethane (1 mL) was added dropwise a solution of a diyne **1** (62 mg, 0.30 mmol) and the isocyanate **2** (0.6 mmol) in dry degassed 1,2-dichloroethane (4 mL) at 90 °C under Ar atmosphere. The solution was stirred for 1-2 h. The solvent was removed and the residue was purified by silica-gel flash column chromatography with mixed solvents (hexane / ethyl acetate) to give a pyridone **3**. The yields are summarized in Tables 1 and 2.

Analytical data for 3aa: mp. 123.5-124.0 °C (eluent hexane/ethyl acetate = 1:1); IR (CHCl_3) 1735, 1679, 1613, 1269 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 3.37 (2 H, d, $J=1.5$ Hz), 3.47 (2 H, d, $J=1.5$ Hz), 3.78 (6 H, s), 6.49 (1 H, s), 7.17 (1 H, s), 7.32-7.49 (5 H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 36.55, 39.88, 53.27, 60.61, 115.25, 118.94, 126.53, 128.17, 129.13, 131.61, 141.12, 155.47, 162.09, 170.84; MS (FAB) m/z (rel. intensity) 328 (MH^+ , 100), 268 (15); Anal Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_5$: C, 66.05; H, 5.23; N, 4.28. Found: C, 66.18; H, 5.15; N, 4.29.

Analytical data for 3ab: mp. 136.7-137.2 °C (eluent hexane/ethyl acetate = 1:1); IR (CHCl₃) 1735, 1677, 1610, 1260 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.41 (2 H, s), 3.56 (2 H, d, *J*=1.2 Hz), 3.80 (3 H, s), 3.81 (3 H, s), 6.60 (1 H, d, *J*=0.3 Hz), 7.14 (1 H, d, *J*=0.6 Hz), 7.40-7.56 (5 H, m), 7.89-7.94 (2 H, m); ¹³C NMR (75 MHz, CDCl₃) δ 36.42, 39.90, 53.16, 53.18, 60.50, 115.07, 118.85, 122.28, 124.92, 125.24, 126.39, 127.11, 128.16, 129.16, 132.37, 134.09, 137.79, 155.95, 162.34, 170.72, 170.78; MS (FAB) *m/z* (rel. intensity) 378 (MH⁺, 100); Anal Calcd for C₂₂H₁₉NO₅: C, 70.02; H, 5.07; N, 3.71. Found: C, 70.29; H, 5.15; N, 3.73.

Analytical data for 3ac: mp. 108-109 °C (eluent hexane/ethyl acetate = 2:1); IR (CHCl₃) 1736, 1685, 1631, 1263 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.38 (2 H, d, *J*=1.2 Hz), 3.44 (2 H, d, *J*=1.5 Hz), 3.77 (6 H, s), 6.48 (1 H, s), 6.49 (1 H, dd, *J*=3.3, 1.8 Hz), 6.73 (1 H, dd, *J*=3.3, 0.9 Hz), 7.29 (1 H, dd, *J*=1.8, 1.2 Hz), 7.52 (1 H, s); ¹³C NMR (75 MHz, CDCl₃) δ 36.60, 39.86, 53.30, 60.57, 102.12, 111.86, 115.25, 119.57, 127.86, 138.40, 145.17, 155.08, 160.42, 170.70; MS (FAB) *m/z* (rel. intensity) 318 (MH⁺, 100), 258 (20); Anal Calcd for C₁₆H₁₅NO₆: C, 60.57; H, 4.77; N, 4.41. Found: C, 60.65; H, 4.64; N, 4.46.

Analytical data for 3ad: mp. 157.8-158.5 °C (eluent hexane/ethyl acetate = 1:1); IR (CHCl₃) 1736, 1676, 1598, 1264 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.29 (2 H, d, *J*=1.2 Hz), 3.41 (2 H, d, *J*=1.5 Hz), 3.75 (6 H, s), 5.08 (2 H, s), 6.47 (1 H, s), 7.09 (1 H, s), 7.26-7.34 (5 H, m); ¹³C NMR (75 MHz, CDCl₃) δ 36.51, 39.67, 51.77, 53.08, 60.41, 114.49, 119.12, 127.66, 127.89, 128.57, 130.74, 136.36, 154.85, 162.14, 170.70; MS (FAB) *m/z* (rel. intensity) 342 (MH⁺, 100), 252 (15); Anal Calcd for C₁₉H₁₉NO₅: C, 66.85; H, 5.61; N, 4.10. Found: C, 66.71; H, 5.67; N, 4.06.

Analytical data for 3ae: mp. 139.1-139.5 °C (eluent hexane/ethyl acetate = 2:1); IR (CHCl₃) 1740, 1677, 1585, 1269 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.15-1.91 (10 H, m), 3.35 (2 H, d, *J*=1.5 Hz), 3.41 (2 H, d, *J*=1.2 Hz), 3.75 (6 H, s), 4.84 (1 H, tt, *J*=12, 3.6, Hz), 6.41 (1 H, s), 7.16 (1 H, s); ¹³C NMR (75 MHz, CDCl₃) δ 25.53, 25.84, 32.79, 36.93, 39.80, 53.19, 53.75, 60.59, 114.11, 118.78, 127.19, 153.61, 161.87, 170.97; MS (FAB) *m/z* (rel. intensity) 334 (MH⁺, 100), 252 (50), 192 (20); Anal Calcd for C₁₈H₂₃NO₅: C, 64.85; H, 6.95; N, 4.20. Found: C, 65.00; H, 7.00; N, 4.18.

Analytical data for 3ba: mp. 116.0-116.5 °C (eluent hexane/ethyl acetate = 2:1); IR (CHCl₃) 1674, 1611 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.07 (2 H, q, *J*=7.2 Hz), 2.72 (2 H, dt, *J*=7.2, 1.2 Hz), 2.82 (2 H, dt, *J*=7.2, 1.5 Hz), 6.52 (1 H, s), 7.16 (1 H, s), 7.34-7.41 (3 H, m), 7.43-7.50 (2 H, m); ¹³C NMR (75 MHz, CDCl₃) δ 26.03, 28.70, 32.61, 114.60, 122.94, 126.49, 127.81, 128.94, 130.78, 141.40, 160.03, 162.21; MS (FAB) *m/z* (rel. intensity) 212 (MH⁺, 100); Anal Calcd for C₁₄H₁₃NO: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.57; H, 6.23; N, 6.64.

Analytical data for 3ca: mp. 165.8-166.2 °C (eluent hexane/ethyl acetate = 2:1); IR (CHCl₃) 1682, 1619 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 4.89-4.90 (2 H, m), 4.92-4.93 (2 H, m), 6.52 (1 H, s), 7.25 (1 H, d, *J*=0.9 Hz), 7.35-7.53 (5 H, m); ¹³C NMR (75 MHz, CDCl₃) δ 69.77, 71.54, 111.89, 118.66, 126.47, 128.32, 129.19, 129.39, 141.04, 154.86, 161.95; MS (FAB) *m/z* (rel. intensity) 214 (MH⁺, 100), 154 (29); Anal Calcd for C₁₃H₁₁NO₂: C, 73.23; H, 5.20; N, 6.57. Found: C, 73.09; H, 5.42; N, 6.53.

Analytical data for 3da: mp. 220.8-221.0 °C (eluent hexane/ethyl acetate = 1:1); IR (KBr) 1685, 1620, 1340, 1154 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.44 (3 H, s), 4.40 (2 H, s), 4.44 (2 H, s), 6.45 (1 H, s), 7.20 (1 H, s), 7.27-7.30 (2 H, m), 7.36 (2 H, d, *J*= 8.5 Hz), 7.42-7.50 (3 H, m), 7.76 (2 H, d, *J*=8.5 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 21.64, 50.01, 52.23, 113.90, 115.60, 126.36, 127.56, 128.54, 129.29, 129.86, 131.28, 132.78, 140.66, 144.09, 151.34, 161.55; MS (FAB) *m/z* (rel. intensity) 367 (MH⁺, 100), 211 (99); Anal Calcd for C₂₀H₁₈N₂O₃S: C, 65.55; H, 4.95; N, 7.64. Found: C, 65.74; H, 4.97; N, 7.43.