Supporting Information

Gold-Catalyzed Cycloisomerization of *o*-Alkynylbenzaldehydes with a Pendant Unsaturated Bond: [3+2] Cycloaddition of Gold-Bound 1,3-Dipolar Species with Dipolarophiles

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Characterization of new compounds **3a-d**, **2e**, **3e**, **3g**, **7a-b**, **8a-b**, and **9** are therein.

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1. A general experimental procedure for the gold-catalyzed cycloisomerization.

In a 5 mL oven-dried test tube, *o*-alkynylbenzaldehydes **1** (71.0 mg, 0.216 mmol), AuBr₃ (4.7 mg, 0.0108 mmol), and dry dichloroethane (1.0 mL) were added at 0 °C and the reaction mixture was kept under argon atmosphere. The resulting mixture was stirred for 8-12 h at 25-30 °C. The solvent was removed under vacuum. The crude product was subjected for flash column chromatography (SiO₂, *n*-hexane/EtOAc = 10:1) to afford the pure products **3**.

2. Spectroscopic data of compounds 3a-d, 2e, 3e, 3g, 7a-b, and 12

Spectroscopic data of compound 3a: IR (NaCl, cm^{-1}) 2960, 2931, 2873, 2861, 1731, 1583, 1568, 1464, 1367, 1274, 1123, 1073; ^1H NMR (400 MHz, CDCl_3) δ 8.54 (d, $J = 8.0$ Hz, 1H), 7.59-7.69 (m, 3H), 7.24 (s, 1H), 4.23 (q, $J = 7.2$ Hz, 4H), 3.81 (s, 2H), 3.69 (s, 2H), 2.35 (s, 3H), 1.28 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 184.45, 171.39, 146.49, 142.26, 136.85, 136.66, 135.70, 133.72, 133.68, 131.95, 130.17, 129.43, 61.92, 55.50, 45.30, 43.33, 24.82, 13.98; HRMS EI calcd for $\text{C}_{21}\text{H}_{22}\text{O}_5$ 354.1467, obsd 354.1471.

Spectroscopic data of compound 3b: IR (NaCl, cm^{-1}) 2959, 2872, 1732, 1584, 1563, 1447, 1365, 1255, 1157, 1048; ^1H NMR (400 MHz, CDCl_3) δ 8.51-8.53 (d, $J = 8.0$ Hz, 1H), 7.58-7.69 (m, 3H), 7.19 (s, 1H), 4.22 (q, $J = 7.2$ Hz, 4H), 3.80 (s, 2H), 3.72 (s, 2H), 2.58 (t, $J = 7.8$ Hz, 2H), 1.58-1.66 (m, 2H), 1.41-1.50 (m, 2H), 1.27 (t, $J = 7.15$ Hz, 6H), 0.98 (t, $J = 7.32$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 184.96, 171.70, 146.52, 143.20, 138.70, 137.06, 136.77, 136.13, 134.12, 132.24, 130.45, 129.78, 62.23, 56.08, 44.91, 43.52, 38.02, 32.99, 22.88, 14.32, 14.26; HRMS EI calcd for $\text{C}_{24}\text{H}_{28}\text{O}_5$ 396.1937, obsd 396.1936.

Spectroscopic data of compound 3c : IR (NaCl, cm^{-1}) 2962, 2924, 2852, 1730, 1610, 1587, 1564, 1460, 1445, 1256, 1194, 1161, 1074; ^1H NMR (400 MHz, CDCl_3) δ 8.57-8.59 (d, $J = 8.0$ Hz, 1H), 7.64-7.70 (m, 3H), 7.36-7.48 (m, 5H), 7.28 (s, 1H), 4.13-4.21 (m, 4H), 3.84 (d, $J = 0.51$ Hz, 2H), 3.40 (t, $J = 1.41$ Hz, 2H), 1.22 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 184.66, 171.27, 145.19, 143.03, 142.51, 139.33, 138.58, 137.11, 135.35, 134.40, 132.14, 130.35, 130.26, 128.56, 128.38, 127.77, 61.84, 56.04, 46.48, 43.53, 13.95; HRMS EI calcd for $\text{C}_{26}\text{H}_{24}\text{O}_5$ 416.1624, obsd 416.1644.

Spectroscopic data of compound 3d : IR (NaCl, cm^{-1}) 2980, 2960, 2541, 1734, 1608, 1440, 1366, 1255, 1190, 1075; ^1H NMR (400 MHz, CDCl_3) δ 8.48 (d, $J = 7.81$ Hz, 1H), 7.63-7.70 (m, 3H), 7.55 (s, 1H), 4.22 (q, $J = 7.2$ Hz, 4H), 3.76 (s, 4H), 1.27 (t, $J = 7.21$ Hz, 6H), 0.41 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 185.21, 171.31, 148.31, 145.22, 142.41, 138.08, 137.79, 135.85, 134.53, 131.92, 130.35, 130.01, 61.88, 56.78, 46.38, 42.51, 14.01; HRMS EI calcd for $\text{C}_{23}\text{H}_{28}\text{O}_5\text{Si}$ 412.1706, obsd 412.1708.

Spectroscopic data of compound 2e : IR (NaCl, cm^{-1}) 2978, 1728, 1670, 1591, 1427, 1360, 1302, 1250, 1203, 1182, 1072, 1051, 1005; ^1H NMR (400 MHz, CDCl_3) δ 9.43 (d, $J = 8.76$ Hz, 1H), 7.97 (d, $J = 8.4$ Hz, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.61-7.66 (m, 1H), 7.49-7.53 (m, 1H), 7.33 (d, $J = 8.4$ Hz, 1H), 4.15 (q, $J = 6.8$ Hz, 4H), 3.66 (s, 2H), 3.26 (s, 2H),

1.16 (t, $J = 6.8$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.53, 169.75, 141.98, 135.23, 133.10, 131.04, 129.27, 128.34, 126.74, 126.68, 126.26, 126.12, 62.06, 54.89, 45.18, 36.68, 13.91; HRMS EI calcd for $\text{C}_{20}\text{H}_{20}\text{O}_5$ 340.1311, obsd 340.1303.

Spectroscopic data of compound 3e : IR (NaCl, cm^{-1}) 2939, 2853, 1730, 1607, 1576, 1477, 1366, 1256, 1188, 1155, 1074; ^1H NMR (400 MHz, CDCl_3) δ 8.61-8.64 (m, 1H), 7.65-7.69 (m, 3H), 7.29 (d, $J = 11.4$ Hz, 1H), 6.72 (d, $J = 11.50$ Hz, 1H), 4.22 (q, $J = 7.2$ Hz, 4H), 3.79 (s, 2H), 3.71 (s, 2H), 1.27 (t, $J = 7.6$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 184.05, 171.30, 145.64, 142.76, 138.40, 137.96, 135.87, 134.24, 131.99, 130.80, 130.43, 124.86, 61.90, 56.32, 46.23, 43.23, 13.98; HRMS EI calcd for $\text{C}_{20}\text{H}_{20}\text{O}_5$ 340.1311, obsd 340.1318.

Spectroscopic data of compound 3g : IR (NaCl, cm^{-1}) 2939, 2853, 1736, 1720, 1610, 1485, 1370, 1256, 1180, 1165; ^1H NMR (400 MHz, CDCl_3) δ 8.61-8.64 (m, 1H), 7.32-7.71 (m, 3H), 7.30 (d, $J = \text{Hz}$, 1H), 6.71 (d, $J = \text{Hz}$, 1H), 4.22-4.27 (m, 2H), 3.52-3.85 (m, 4H), 2.27 (s, 3H), 1.29 (t, $J = 8.0$, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.93, 184.05, 171.99, 145.94, 142.29, 138.46, 137.94, 135.89, 134.29, 132.06, 130.84, 130.49, 124.93, 62.71, 62.06, 44.50; HRMS EI calcd for $\text{C}_{19}\text{H}_{18}\text{O}_4$ 310.1205, obsd 310.1211.

Spectroscopic data of compound 7a : IR (NaCl, cm^{-1}) 2981, 1730, 1673, 1442, 1367, 1286, 1259, 1193, 1068, 1015; ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 6.8$ Hz, 1H), 7.45 (td, $J = 7.6, 1.2$ Hz, 1H), 7.23 (d, $J = 7.2$ Hz, 1H), 7.16 (d, $J = 7.6$ Hz, 1H), 6.40 (s, 1H), 4.21 (m, $J = 7.2$ Hz, 4H), 3.19-3.30 (m, 2H), 2.97-3.00 (m, 1H), 2.92 (m, 2H), 2.75 (ddd, $J = 12.0, 6.0, 0.8$ Hz, 1H), 2.07 (dd, $J = 12.8, 9.6$ Hz, 1H), 1.26 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.47, 171.04, 149.52, 136.65, 134.91, 132.87, 131.40, 130.32, 126.47, 123.60, 61.78, 61.75, 59.09, 46.62, 41.72, 41.04, 36.83, 14.01, 13.98; HRMS EI calcd for $\text{C}_{20}\text{H}_{22}\text{O}_5$ 342.1467, obsd 342.1468.

Spectroscopic data of compound 7b : IR (NaCl, cm^{-1}) 2940, 1669, 1595, 1509, 1430, 1329, 1196, 1117; ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, $J = 7.6$ Hz, 1H), 7.41 (td, $J = 7.6, 1.2$ Hz, 1H), 7.19-7.24 (m, 2H), 6.31 (s, 1H), 4.12-4.28 (m, 4H), 3.06 (dd, $J = 13.6, 1.6$ Hz, 1H), 2.86-2.98 (m, 2H), 2.67 (d, $J = 14.0$ Hz, 1H), 2.59-2.63 (m, 1H), 2.47 (dd, $J = 13.6, 2.4$ Hz, 1H), 1.97 (dq, $J = 13.6, 4.0$ Hz, 1H), 1.87 (td, $J = 13.2, 4.0$ Hz, 1H), 1.51-1.59 (m, 1H), 1.21-1.27 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.36, 172.40, 171.51, 148.18, 133.70, 128.16, 127.75, 127.55, 123.17, 86.76, 76.05, 61.66, 61.28, 50.87, 39.14, 35.32, 29.11, 25.57, 25.20, 14.01, 13.94; HRMS EI calcd for $\text{C}_{21}\text{H}_{24}\text{O}_5$ 356.1624, obsd 356.1630.

Spectroscopic data of compound 9¹: ¹H NMR (400 MHz, CDCl₃) δ 9.41 (dd, *J* = 8.8, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.81 (dd, *J* = 7.91, 1.3 Hz, 1H), 7.61-7.65 (m, 1H), 7.47-7.51 (m, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 3.13 (t, *J* = 6.2 Hz, 2H), 2.79 (t, *J* = 6.2 Hz, 2H), 2.17-2.23 (m, 2H);

¹³C NMR (100 MHz, CDCl₃) δ 200.45, 146.71, 134.14, 132.69, 131.29, 128.75, 128.21, 127.18, 126.90, 126.59, 125.74, 41.01, 31.51, 22.93.

¹ Asao, N.; Sato, K.; Menggenbateer, Yamamoto, Y. *J. Org. Chem.* **2005**, *70*, 3682.

3. ^1H and ^{13}C NMR Spectra of Compounds 3a-d, 2e, 3e, 3g, 7a-b, and 9

^1H -NMR Spectrum of Compound **3a**

^{13}C -NMR Spectrum of Compound **3a**

¹H-NMR Spectrum of Compound 3c

¹³C-NMR Spectrum of Compound 3c

¹H-NMR Spectrum of Compound **3d**

¹³C-NMR Spectrum of Compound **3d**

^1H -NMR Spectrum of Compound **3e**

^{13}C -NMR Spectrum of Compound **3e**

^1H -NMR Spectrum of Compound **7a**

^{13}C -NMR Spectrum of Compound **7a**

¹H-NMR Spectrum of Compound **7b**

¹³C-NMR Spectrum of Compound **7b**

¹H-NMR Spectrum of Compound **9**

¹³C-NMR Spectrum of Compound **9**