Supporting Information

Highly Functionalized and Stereocontrolled Syntheses of 2-(2-Methylenecyclopentyl)-furan derivatives by Pd-catalyzed cycloreduction

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1. General experimental procedure :

In a 5 mL new test tube, diyne **1a-j** (0.3 mmol), Pd(PPh₃)₄ (3 mol%), HCOOH (0.45 mmol) and dried solvent(0.5mL) were charged at 0 °C and the reaction mixture was kept under argon atmosphere. The resulting mixture was stirred for 0.5 to 3 h at pre-heated oil bath (70-80 °C) by monitoring TLC of the reaction periodically. Upon completion, the solvent was removed under vacuum and the crude product was subjected for flash column chromatography to afford the pure products **2a-j**. In case of substrate **8**, diethyl acetylenedicarboxylate (0.5 mmol) in dioxane (0.5 mL) was added upon disappearance of the starting material **8**. The resultant mixture was stirred at 80 °C for additional 1h. Then, the solvent was removed under vacuum and the crude product was subjected for flash column chromatography to afford the pure products **11** in 45% yield.

2. Spectroscopic data of compounds

Spectroscopic data of compound 2a: IR (NaCl, cm⁻¹) 1739, 1673, 1598; ¹H NMR (400 MHz, CDCl₃) δ 6.95 (s, 1H), 5.02 (d, *J* = 2.4 Hz, 1H), 4.81 (d, *J* = 2.4 Hz, 1H), 4.21 (q, *J* = 7.6 Hz, 2H), 4.17 (qd, *J* = 7.6, 6.8 Hz, 2H), 3.84 (t, *J* = 8.8 Hz, 1H), 3.09 (dq, *J* = 17.2, 2.4 Hz, 1H), 3.03 (d, *J* = 17.2, 1H), 2.72 (dd, *J* = 13.6, 8.4 Hz, 1H), 2.58-2.49 (m, 4H), 2.42 (dd, *J* = 13.2 Hz, 10.4 Hz, 1H), 2.34-2.26 (m, 2H), 1.26 (t, *J* = 7.6 Hz, 3H), 1.24 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.82, 171.41, 148.85, 144.62, 133.63, 131.46, 128.57, 108.91, 61.82, 61.75, 58.79, 42.35, 40.36, 38.98, 32.43, 29.92, 23.94, 23.47, 14.25; HRMS calculated for C₁₉H₂₄KO₅ 371.1261; found, 371.1268.

Spectroscopic data of compound 2b: IR (NaCl, cm^{-1}) 1779, 1732, 1561; ^1H NMR (400 MHz, CDCl_3) δ 7.05 (t, $J = 1.2$ Hz, 1H), 4.98 (q, $J = 2.0$ Hz, 1H), 4.63 (q, $J = 2.0$ Hz, 1H), 4.22 (qd, $J = 7.2, 6.8$ Hz, 2H), 4.20 (d, $J = 7.2$ Hz, 2H), 3.85 (t, $J = 8.8$ Hz, 1H), 3.12 (dq, $J = 16.8, 2.4$ Hz, 1H), 3.06 (d, $J = 16.8$, 1H), 2.66 (ddd, $J = 13.2, 8.0, 0.8$ Hz, 1H), 2.51 (m, 2H), 2.46 (m, 2H), 2.44 (dd, $J = 13.2, 11.6$ Hz, 1H), 1.68 (m, 4H), 1.27 (t, $J = 7.2$ Hz, 3H), 1.25 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.02, 171.46, 148.95, 147.99, 135.80, 122.30, 117.58, 108.37, 61.81, 61.77, 58.68, 41.51, 40.21, 38.55, 23.62, 23.49, 20.62, 20.46, 14.26; HRMS calculated for $\text{C}_{20}\text{H}_{26}\text{KO}_5$ 385.1417; found, 385.1415.

Spectroscopic data of compound 2c: IR (NaCl, cm^{-1}) 1766, 1731, 1565; ^1H NMR (400 MHz, CDCl_3) δ 7.03 (s, 1H), 4.96 (d, $J = 2.0$ Hz, 1H), 4.58 (d, $J = 2.0$ Hz, 1H), 4.23 (qd, $J = 7.2, 6.8$ Hz, 2H), 4.20 (d, $J = 7.2$ Hz, 2H), 3.86 (m, 1H), 3.13 (dq, $J = 17.2, 2.4$ Hz, 1H), 3.06 (d, $J = 17.2$, 1H), 2.64 (ddd, $J = 13.2, 7.6, 1.2$ Hz, 1H), 2.51-2.47 (m, 5H), 1.78 (m, 2H), 1.65-1.57 (m, 4H), 1.27 (t, $J = 7.2$ Hz, 3H), 1.25 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.86, 171.21, 149.21, 148.35, 136.01, 127.94, 123.51, 107.94, 61.57, 61.51, 58.42, 40.61, 39.93, 38.43, 32.79, 29.88, 29.76, 25.93, 25.65, 14.04, 13.99; HRMS calculated for $\text{C}_{21}\text{H}_{28}\text{KO}_5$ 399.1574; found, 399.1568.

Spectroscopic data of compound 2d: IR (NaCl, cm^{-1}) 1737, 1670, 1597; ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 6.98 (s, 1H), 4.98 (q, $J = 2.4$ Hz, 1H), 4.69 (q, $J = 2.4$ Hz, 1H), 4.11 (d, $J = 14.4$ Hz, 1H), 3.89 (t, $J = 8.4$ Hz, 1H), 3.77 (ddd, $J = 14.0, 4.0, 2.0$ Hz, 1H), 3.73 (dd, $J = 14.0, 8.0$ Hz, 1H), 3.21 (t, $J = 9.6$ Hz, 1H), 2.48 (m, 2H), 2.45 (s, 3H), 2.36 (m, 2H), 1.66 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.73, 144.27, 143.73, 136.13, 132.56, 129.70, 127.81, 122.16, 118.81, 108.42, 51.77, 51.59, 41.58, 23.17, 23.05, 21.51, 20.16, 20.05; HRMS calculated for $\text{C}_{20}\text{H}_{23}\text{KNO}_3\text{S}$ 396.1036; found, 396.1038

Spectroscopic data of compound 2e: (NaCl, cm^{-1}) 1772, 1683, 1655; ^1H NMR (400 MHz, CDCl_3) δ 7.04 (t, $J = 1.2$ Hz, 1H), 4.92 (bs, 1H), 4.61 (bs, 1H), 3.61 (t, $J = 2.8$ Hz, 1H), 2.52 (m, 2H), 2.49-2.42 (m, 3H), 2.05-1.98 (m, 1H), 1.97-1.84 (m, 2H), 1.72-1.62 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.10, 149.95, 135.06, 121.96, 116.29, 106.37, 42.80, 32.68, 32.13, 24.91, 23.50, 23.32, 20.52, 20.29; HRMS calculated for $\text{C}_{14}\text{H}_{18}\text{KO}$ 241.0995; found, 241.0989.

Spectroscopic data of compound 2f: IR (NaCl, cm^{-1}) 1677, 1646, 1557; ^1H NMR (400 MHz, CDCl_3) δ 7.07 (t, $J = 1.2$ Hz, 1H), 4.68 (bs, 1H), 4.23 (bs, 1H), 3.32 (t, $J = 2.8$ Hz, 1H), 2.53 (m, 2H), 2.42 (m, 2H), 2.37 (m, 1H), 2.21 (m, 1H), 1.88 (m, 3H), 1.78-1.60 (m, 5H), 1.54-1.43 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.88, 149.67, 134.88, 121.94, 116.36, 107.39, 42.55, 35.42, 31.72, 28.10, 25.82, 23.46, 23.31, 20.56, 20.33; HRMS calculated for $\text{C}_{15}\text{H}_{20}\text{KO}$ 255.1151; found, 255.1156.

Spectroscopic data of compound 2f-d₂: ¹H NMR (400 MHz, CDCl₃) δ 7.07 (t, J = 1.2 Hz, 1H), 4.68 (bs, 0.5H), 4.23 (bs, 0.5H), 3.32 (0H), 2.53 (m, 2H), 2.42 (m, 2H), 2.37 (m, 1H), 2.21 (m, 1H), 1.88 (m, 3H), 1.78-1.60 (m, 5H), 1.54-1.43 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 149.88, 149.67, 134.88, 121.94, 116.36, 107.39, 42.55, 35.42, 31.72, 28.10, 25.82, 23.46, 23.31, 20.56, 20.33;.

Spectroscopic data of compound 2g-1: IR (NaCl, cm⁻¹) 1767, 1668; ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.27 (m, 5H), 7.05 (s, 1H), 4.97 (q, J = 2.4 Hz, 1H), 4.66 (q, J = 2.4 Hz, 1H), 4.53 (s, 2H), 4.18 (m, 1H), 3.95 (m, 1H), 2.72 (dq, J = 17.2, 2.4 Hz, 1H), 2.64 (d, J = 17.2 Hz, 1H), 2.52 (m, 2H), 2.48 (m, 2H), 2.23 (ddt, J = 13.2, 8.0, 2.0 Hz, 1H), 2.10 (ddd, J = 13.2, 10.8, 4.8 Hz, 1H), 1.72-1.64 (m, 4H); HRMS calculated for C₂₁H₂₄KO₂ 347.1413; found, 347.1410.

Spectroscopic data of compound 2g-2 (major): IR (NaCl, cm⁻¹) 1768, 1670; ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.25 (m, 5H), 7.06 (s, 1H), 4.94 (q, J = 2.4 Hz, 1H), 4.62 (q, J = 2.4 Hz, 1H), 4.55 (s, 2H), 4.05 (m, 1H), 3.62 (m, 1H), 2.80 (m, 1H), 2.51 (m, 3H), 2.45 (m, 2H), 2.32 (m, 1H), 2.08 (m, 1H), 1.72-1.64 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 136.61, 135.52, 128.62, 127.85, 127.73, 125.72, 125.55, 122.30, 117.16, 108.10, 78.52, 70.72, 40.12, 39.39, 37.53, 23.72, 23.56, 20.67, 20.51; HRMS calculated for C₂₁H₂₄KO₂ 347.1413; found, 347.1418.

Spectroscopic data of compound 2h: IR (NaCl, cm⁻¹) 1772, 1668; ¹H NMR (400 MHz, CDCl₃) δ 7.05 (s, 1H), 4.92 (d, J = 2.0 Hz, 1H), 4.61 (bs, 1H), 4.24 (m, 1H), 3.61 (m, 1H), 2.72 (dd, J = 15.6, 7.2 Hz, 1H), 2.52 (m, 3H), 2.48-2.38 (m, 2H), 2.21 (ddd, J = 12.8, 6.6, 6.0 Hz, 1H), 2.00 (td, J = 12.0, 9.6 Hz, 1H), 1.72-1.64 (m, 4H), 0.90 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 149.48, 148.95, 135.19, 122.02, 116.48, 107.70, 71.77, 42.21, 40.53, 40.30, 25.86, 23.47, 23.31, 20.55, 20.29, 18.14, -4.70, -4.74; HRMS calculated for C₂₀H₃₂KO₂Si 371.1089; found, 371.1080.

Spectroscopic data of compound 2i: IR (NaCl, cm⁻¹) 1731, 1713, 1660cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.05 (s, 1H), 5.41 (q, J = 2.4 Hz, 1H), 4.27-4.18 (m, 4H), 4.14 (dd, J = 7.2, 6.8 Hz, 2H), 3.85 (m, 1H), 3.72 (d, J = 20.4 Hz, 1H), 3.45 (dt, J = 20.4, 2.0 Hz, 1H), 2.64 (ddd, J = 13.2, 8.0, 2.0 Hz, 1H), 2.54-2.42 (m, 5H), 1.70 (m, 4H), 1.27 (t, J = 7.2 Hz, 3H), 1.26 (t, J = 7.2 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.85, 171.09, 166.66, 163.22, 146.01, 136.53, 122.35, 118.89, 114.49, 61.99, 61.94, 60.12, 58.78, 43.45, 40.01, 37.52, 23.50, 23.39, 20.49, 20.37, 14.53, 14.27, 14.23; HRMS calculated for C₂₃H₃₀KO₇ 457.1629; found, 457.1621.

Spectroscopic data of compound 2j: IR (NaCl, cm⁻¹) 1731, 1713, 1660; ¹H NMR (400 MHz, CDCl₃) δ 7.03 (s, 1H), 5.36 (q, J = 2.4 Hz, 1H), 4.27-4.18 (m, 4H), 4.15 (dd, J = 7.2, 6.8 Hz, 2H), 3.99 (m, 1H), 3.71 (d, J = 20.0 Hz, 1H), 3.46 (dt, J = 20.0, 2.8 Hz, 1H), 2.63 (ddd, J = 12.8, 7.2, 2.0 Hz, 1H), 2.54-2.42 (m, 5H), 1.78 (m, 2H), 1.61 (m, 4H), 1.27 (t, J = 7.2 Hz, 3H), 1.26 (t, J = 7.2 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.94, 171.07, 166.65, 163.51,

146.69, 136.98, 128.19, 124.95, 114.50, 61.98, 61.91, 60.09, 58.77, 42.87, 40.06, 37.80, 32.96, 30.02, 29.86, 26.12, 25.92, 14.54, 14.27, 14.22; HRMS calculated for $C_{24}H_{32}KO_7$ 471.1785; found, 471.1785.

Spectroscopic data of compound 7: IR (NaCl, cm^{-1}) 2984, 1732, 1634, 1448, 1369, 1262, 1237; 1H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, $J = 6.8, 0.4$ Hz, 1H), 7.09 (td, $J = 7.2$ Hz, 1.2 Hz, 1H), 7.04 (td, $J = 6.8, 1.2$ Hz, 1H), 5.94 (s, 1H), 5.13 (s, 1H), 4.93 (s, 1H), 4.29-4.00 (m, 9H), 3.12 (bd, $J = 12.0$ Hz, 1H), 2.89 (d, $J = 12.0$ Hz, 1H), 2.84 (dd, $J = 13.2, 8.4$ Hz, 1H), 2.10 (dd, $J = 13.2, 9.2$ Hz, 1H), 1.31 (t, $J = 6.8$ Hz, 3H), 1.27 (t, $J = 7.2$ Hz, 3H), 1.26 (t, $J = 7.2$ Hz, 3H), 1.18 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.45, 170.72, 163.82, 162.05, 153.26, 151.36, 148.37, 146.57, 146.05, 125.91, 125.75, 122.02, 121.14, 111.24, 98.39, 82.26, 61.57 (3C), 61.44, 58.59, 42.44, 39.87, 36.09, 14.02 (4C); HRMS calculated for $C_{23}H_{32}KO_9$ 551.1683; found, 551.1689.

3. ^1H and ^{13}C Spectra of Compounds