Supporting Information

Cobalt-Catalyzed Thiolative Lactonization of Alkynes with Double CO Incorporation

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General Comments

All reagents were purified by distillation before use, and freshly distilled acetonitrile was used. Catalyst was purchased from commercial source and used without further purification. \(^1\)H NMR spectra were recorded on JEOL JNM-GSX-270 (270 MHz), JEOL JNM-AL 400 (400 MHz), or Varian GEMINI 2000 (300 MHz) spectrometers using CDCl\(_3\) as the solvent with Me\(_4\)Si as the internal standard. \(^{13}\)C NMR spectra were taken on JEOL JNM-GSX-270 (68 MHz), JEOL JNM-GSX-400 (100 MHz), or Varian GEMINI 2000 (75 MHz) spectrometers using CDCl\(_3\) as the solvent. Chemical shifts in \(^1\)H NMR were measured relative to CDCl\(_3\) and converted to \(\delta\) (Me\(_4\)Si) value by using \(\delta\) (CDCl\(_3\)) = 7.26 ppm. Chemical shifts in \(^{13}\)C NMR were measured relative to CDCl\(_3\) and converted to \(\delta\) (Me\(_4\)Si) value by using \(\delta\) (CDCl\(_3\)) = 77.16 ppm. IR spectra were determined on a Perkin Elmer Model 1600 spectrometer or JASCO FT/IR-8900 \(\mu\) Fourier Transform Infrared Microsampling System. Mass spectra were obtained on JEOL JMS-DX303 in the analytical section of Osaka University. Elemental analyses were performed in the analytical section of Osaka University. Purification of the product was carried out (by using a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., Model LC-908) equipped with JAIGEL-1H and -2H columns (GPC) using CHCl\(_3\) as an eluent.)

General Procedure of the Cobalt-Catalyzed Thiolative Lactonization

In a 50 mL stainless steel autoclave with a magnetic stirring bar under N\(_2\) atmosphere, were placed Co\(_2\)(CO)\(_8\) (0.09 mmol), freshly distilled acetonitrile (1-10 mL), alkyne (3.0 mmol), and thiol (1.0 mmol) in this order. Carbon monoxide was purged three times and then charged at 2-5 MPa. The reaction was conducted with magnetic stirring for 17 h upon heating at 120-140 °C. After carbon monoxide was purged, the resulting mixture was filtered through Celite with Et\(_2\)O and concentrated \textit{in vacuo} to give a brown-black oil. Purification was performed by silica gel column chromatography (hexanes/AcOEt = 4/1) followed by a recycling preparative LC equipped with GPC columns (JAIGEL-1H and -2H) with CHCl\(_3\) as eluent.

Additional Information: By the use of 1,2-bis(diphenylphosphino)ethane (dppe, 0.18 mmol), the desired lactone was obtained selectively. Dppe was added before the addition of acetonitrile, and other procedure was not changed.

Preparation of Cobalt Alkyne Complex (A)

In a flask (30 mL) equipped with a magnetic stirring bar, were placed Co\(_2\)(CO)\(_8\) (2.0 mmol), freshly distilled acetonitrile (1 mL), and 1-octyne (2.0 mmol). The mixture was stirred for 24 h at room temperature under N\(_2\) atmosphere. The resulting mixture was concentrated \textit{in vacuo}. The purification was performed by a preparative TLC on Wakogel B-5F silica gel eluted by hexanes.
Co$_2$(CO)$_8$-Catalyzed Carbonylation of 1-Octyne with PhSH under Several Conditions

When the reaction of 1-octyne (1a) with benzenthiol (2d) was conducted under the pressure of CO (2 MPa) in the presence of dicobalt octacarbonyl as a catalyst, a novel thiolative lactonization product 3ad, which incorporated two molecules of CO, was obtained in 7% yield, along with the formation of thiolative monocarbonylation product 4ad (Table A, entry 1). When the pressure of CO was increased (3 MPa), the yields of the carbonylation products (3ad and 4ad) were improved (entry 2).

Table A. Co$_2$(CO)$_8$-Catalyzed Carbonylation of 1-Octyne with PhSH$^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>CO (MPa)</th>
<th>solv. (mL)</th>
<th>yield (%)$^d$</th>
<th>3ad</th>
<th>4ad</th>
<th>total</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>1</td>
<td>7</td>
<td>4</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>2$^b$</td>
<td>3</td>
<td>1</td>
<td>12</td>
<td>31</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>3$^c$</td>
<td>3</td>
<td>1</td>
<td>20</td>
<td>9</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>1.5</td>
<td>34</td>
<td>11</td>
<td>45</td>
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<tr>
<td>5</td>
<td>5</td>
<td>1</td>
<td>7</td>
<td>9</td>
<td>16</td>
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</tr>
<tr>
<td>6</td>
<td>4</td>
<td>3</td>
<td>27</td>
<td>23</td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: 1a (3 mmol), 2d (1 mmol), Co$_2$(CO)$_8$ (9 mol%), CH$_3$CN (1-3 mL). $^b$120 °C. $^c$130 °C. $^d$Determined by $^1$H NMR.

However, the monocarbonylation product 4ad was obtained in preference to the thiolative lactonization product 3ad. Elevating the temperature and the pressure of CO led to the preferential formation of the desired thiolative lactonization product 3ad: the ratio of 3ad/4ad = 69/31 for 3 MPa, 130 °C; 76/24 for 4 MPa, 140 °C) (entries 3 and 4). Further higher CO pressure (5 MPa) retarded the carbonylation (entry 5), and dilution resulted in the decrease in the 3ad/4ad ratio (entry 6).
Characterization Data for the Lactones

5-Cyclohexylthio-4-hexyl-5H-furan-2-one (3aa).

Pale yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.90 (t, $J = 6.8$ Hz, 3H), 1.25–1.50 (m, 12H), 1.56–1.64 (m, 2H), 1.76–1.80 (m, 2H), 2.00–2.06 (m, 2H), 2.34–2.36 (m, 1H), 2.48–2.50 (m, 1H), 2.93–2.98 (m, 1H), 5.89 (s, 1H), 5.99 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.1, 22.6, 25.6, 26.0, 26.1, 27.0, 28.9, 29.0, 31.5, 34.2, 44.3, 86.5, 117.0, 170.8, 172.0; IR (NaCl) 2927, 2855, 2353, 1790, 1759, 1636, 1448, 968 cm$^{-1}$; MS (EI), $m/z$ = 282 (M$^+$); HRMS (EI) calcd for C$_{16}$H$_{26}$O$_2$S: 282.1653, found: 282.1652. Anal. Calcd for C$_{16}$H$_{26}$O$_2$S: C, 68.04; H, 9.28. Found: C, 68.22; H, 9.40.

5-(1-Dodecylthio)-4-hexyl-5H-furan-2-one (3ab)

Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.88 (t, $J = 6.9$ Hz, 3H), 0.90 (t, $J = 6.9$ Hz, 3H), 1.22–1.41 (m, 24H), 1.52–1.66 (m, 4H), 2.28–2.39 (m, 1H), 2.45–2.69 (m, 3H), 5.88 (s, 1H), 5.90 (dd, $J = 3.2$, 1.8 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 13.9, 14.1, 22.4, 22.6, 26.9, 28.6, 28.77, 28.82, 29.1, 29.3, 29.4, 29.51, 29.58 (overlap), 31.4, 31.9, 86.9, 116.8, 170.4, 171.6; IR (NaCl) 2923, 2855, 2927, 2855, 1790, 1763, 1636, 1466, 1377, 1288, 1165, 972 cm$^{-1}$; HRMS (EI) calcd for C$_{22}$H$_{40}$O$_2$S: 368.2749, found: 368.2762.

5-Ethylthio-4-hexyl-5H-furan-2-one (3ac)

Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.90 (t, $J = 6.9$ Hz, 3H), 1.29–1.40 (m, 9H), 1.53–1.69 (m, 2H), 2.28–2.40 (m, 1H), 2.45–2.55 (m, 1H), 2.56–2.66 (m, 2H), 5.91 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 13.9, 14.7, 22.4, 23.8, 26.8, 28.5, 28.8, 31.3, 86.7, 116.8, 170.4, 171.6; IR (NaCl) 2958, 2932, 2868, 2970, 1759, 1636, 1454, 1377, 1288, 1265, 1165, 972 cm$^{-1}$; HRMS (EI) calcd for C$_{12}$H$_{20}$O$_2$S: 228.1184, found: 228.1163.
5-Phenylthio-4-hexyl-5H-furan-2-one (3ad)

Pail brown oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.90 (t, $J = 6.8$ Hz, 3H), 1.23-1.40 (m, 6H), 1.44-1.64 (m, 2H), 2.34-2.43 (m, 1H), 2.48-2.57 (m, 1H), 5.73 (d, $J = 2.0$ Hz, 1H), 6.01 (s, 1H), 7.29-7.35 (m, 3H), 7.50-7.52 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.0, 22.5, 26.8, 28.6, 28.9, 31.4, 88.5, 117.4, 129.17, 129.18, 129.21, 134.1, 169.4, 171.4; IR (NaCl) 2924, 2862, 1790, 1759, 1636, 1535, 1466, 1165, 972 cm$^{-1}$; MS (EI) m/z = 276 (M$^+$); HRMS (EI) calcd for C$_{16}$H$_{20}$O$_2$S: 276.1184, found: 276.1184.

5-(4-Tolylthio)-4-hexyl-5H-furan-2-one (3ae)

Pail yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.91 (t, $J = 6.8$ Hz, 3H), 1.24–1.40 (m, 6H), 1.42–1.64 (m, 2H), 2.33 (s, 3H), 2.34–2.41 (m, 1H), 2.45–2.57 (m, 1H), 5.71 (s, 1H), 5.97 (s, 1H), 7.12 (d, $J = 7.2$ Hz, 2H), 7.38 (d, $J = 7.2$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.0, 21.2, 22.5, 26.8, 28.6, 28.9, 31.4, 88.6, 117.2, 125.2, 129.9, 134.5, 139.6, 169.5, 171.5; IR (NaCl) 2958, 2928, 2858, 1786, 1755, 1636, 1436, 1458, 1289, 1165, 976 cm$^{-1}$; HRMS (EI) calcd for C$_{17}$H$_{22}$O$_2$S: 290.1340, found: 290.1318.

5-(4-Chlorophenylthio)-4-hexyl-5H-furan-2-one (3af)

Pail brown oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (t, $J = 6.8$ Hz, 3H), 1.31–1.37 (m, 6H), 1.45–1.64 (m, 2H), 2.33–2.41 (m, 1H), 2.46–2.55 (m, 1H), 5.75 (s, 1H), 5.98 (s, 1H), 7.30 (d, $J = 7.8$ Hz, 2H), 7.38 (d, $J = 7.8$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.1, 22.6, 26.9, 28.7, 29.0, 31.5, 88.3, 117.7, 127.6, 129.5, 135.6, 135.9, 169.3, 171.2; IR (NaCl) 2928, 2858, 1790, 1759, 1636, 1477, 1389, 1288, 1096, 976 cm$^{-1}$; HRMS (EI) calcd for C$_{16}$H$_{19}$ClO$_2$S: 310.0794, found: 310.0781.
5-Cyclohexylthio-4-(3-methylbutyl)-5H-furan-2-one (3ba).

Pale yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.94 (d, $J = 5.4$ Hz, 6H), 1.24–1.51 (m, 7H), 1.59–1.64 (m, 2H), 1.76–1.80 (m, 2H), 2.03–2.09 (m, 2H), 2.31–2.36 (m, 1H), 2.42–2.54 (m, 1H), 2.92–2.99 (m, 1H), 5.88 (s, 1H), 6.01 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 22.5, 25.6, 26.0, 26.9, 27.9, 34.2, 36.0, 44.3, 86.5, 116.9, 171.0, 172.1; IR (NaCl) 2930, 2855, 2352, 1759, 1636, 1448 cm$^{-1}$; MS (EI), $m/z = 268$ (M$^+$); HRMS (EI) calcd for C$_{15}$H$_{24}$O$_2$S: 268.1497, found: 268.1497.

5-Cyclohexylthio-4-(3-hydroxypropyl)-5H-furan-2-one (3ca).

Pale yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.22–1.57 (m, 6H), 1.59–1.64 (m, 2H), 1.74–1.95 (m, 4H), 2.00–2.10 (m, 2H), 2.44–2.55 (m, 1H), 2.59–2.70 (m, 1H) 2.93–3.02 (m, 1H) 3.73 (t, $J = 6.0$ Hz, 1H), 5.93 (s, 1H), 6.03 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 25.4, 25.6, 26.0, 29.9, 34.2, 44.4, 61.8, 86.6, 117.2, 170.1, 171.9; IR (NaCl) 3400, 2934, 2853, 2065, 1635, 1541, 1448, 1263 cm$^{-1}$; MS (EI), $m/z = 256$ (M$^+$); HRMS (EI) calcd for C$_{13}$H$_{20}$O$_3$S: 256.1133, found: 256.1132.

5-Cyclohexylthio-4-(3-cyanopropyl)-5H-furan-2-one (3da).

Pale brown oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.22–1.67 (m, 4H), 1.75–1.82 (m, 2H), 1.91–2.05 (m, 4H), 2.31–2.77 (m, 6H), 2.96–3.02 (m, 1H) 5.95 (s, 1H), 6.02 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 17.1, 23.0, 25.6, 26.0, 27.7, 34.1, 44.8, 86.4, 118.0, 118.6, 167.6, 171.2; IR (NaCl) 2923, 2844, 2245, 1789, 1755, 1637, 1452, 1168, 966, 895 cm$^{-1}$; HRMS (EI) calcd for C$_{14}$H$_{19}$NO$_2$S: 265.1136, found: 265.1135.
5-Cyclohexylthio-4-phenylmethyl-5H-furan-2-one (3ea).

Pale brown solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.20-1.68 (m, 6H), 1.73–1.79 (m, 2H), 2.00 (m, 2H), 2.93–3.00 (m, 1H), 3.63 (d, $J=16.6$ Hz, 1H), 3.87 (d, $J=16.6$ Hz, 1H), 5.79 (s, 1H), 5.92 (s, 1H), 7.18-7.39 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 25.6, 26.0, 34.1, 35.4, 44.4, 86.2, 118.4, 127.6, 129.1, 129.2, 135.8, 169.3, 171.6; IR (KBr) 2928, 2850, 2345, 1744, 1633, 1450, 1163, 976, 847, 702 cm$^{-1}$; HRMS (EI) calcd for C$_{17}$H$_{20}$O$_2$S: 288.1184, found 288.1184.
$^1$H NMR and $^{13}$C NMR Spectral Data for the Lactones

3aa
Acetamide produced from hydrolysis of acetonitrile was detected in this spectrum.