Supporting Information

Synthesis of Cyclic Carbonates from CO₂ and Epoxides Catalyzed by Low Loadings of Benzyl Bromide/DMF at Ambient Pressure

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Table S1. Screening of Solvents.\textsuperscript{a}

\[
\text{Ph} + \text{PhCH}_2\text{Br} + \text{solvent} \xrightarrow{\text{120°C}} \text{Ph}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield (%)\textsuperscript{b}</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>DMF</td>
<td>86</td>
</tr>
<tr>
<td>2</td>
<td>DMAc</td>
<td>83</td>
</tr>
<tr>
<td>3</td>
<td>5-Formylpiperidine</td>
<td>68</td>
</tr>
<tr>
<td>4</td>
<td>N-methylpyrrolidone</td>
<td>51</td>
</tr>
<tr>
<td>5</td>
<td>5-Formylmorpholine</td>
<td>47</td>
</tr>
<tr>
<td>6</td>
<td>5,5,5,5-Tetramethylurea</td>
<td>71</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: catalyst (1 mol%), epoxide (5 mmol), DMF (5 equiv.), CO\textsubscript{2} (99.999%, balloon), temperature 120 °C, total reaction time 24h. \textsuperscript{b} Isolated yield.

Table S2. Screening of Catalysts.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Yield (%)\textsuperscript{b}</th>
</tr>
</thead>
</table>
| 1     | \[
\text{Br}\]
| 2     | \[
\text{Bu} + \text{Bu} + \text{Br} + \text{Br}
\]
| 3     | \[
\text{O}_2\text{N} + \text{Bu} + \text{Br}
\]
| 4     | \[
\text{Br} + \text{Bu} + \text{Br}
\]
| 5     | \[
\text{Bu} + \text{Bu} + \text{Br} + \text{Bu}
\]
| 6     | \[
\text{H}_2\text{O} + \text{Br} + \text{Ph}
\]
| 7     | \[
\text{NC} + \text{Br}
\]
| 8     | \[
\text{CL}
\]
| 9     | \[
\text{SN} + \text{Br} + \text{Ph}
\]
| 10    | \[
\text{SO}_2
\]
| 11    | \[
\text{Ph} + \text{CN}
\]
| 12    | \[
\text{Ph} + \text{CN}
\]
| 13    | \[
\text{Ph} + \text{CN}
\]
| 14    | \[
\text{Ph} + \text{CN}
\]
| 15    | \[
\text{Ph} + \text{CN}
\]

\textsuperscript{a} Reaction conditions: catalyst (1 mol%), epoxide (5 mmol), DMF (5 equiv.), CO\textsubscript{2} (99.999%, balloon), temperature 120 °C, total reaction time 24h. \textsuperscript{b} Isolated yield.
**Experimental Section**

**General information**

All starting materials and solvents commercially available were purchased at the highest quality from Sigma-Aldrich or Wako and used as received unless otherwise indicated. Reactions were monitored by thin layer chromatography using 0.25-mm E. Merck silica gel coated on aluminum plates (60F-254) with UV light to visualize the course of the reaction. Chemical yields refer to the pure isolated substances. $^1$H (500 MHz) and $^{13}$C (125 MHz) NMR spectra were obtained using a Brucker AV-500 (500 MHz) spectrometer. The chemical shifts of the products were reported in ppm with reference to Me$_4$Si as the internal standard in CDCl$_3$ solution. The data were reported in the following order: chemical shift, multiplicity, coupling constants in Hz and integration. On the other hand, the spectra of the reaction system materials were taken using a coaxial dual NMR cell. The inner cell contained DMF, the DMF–BnBr mixture, and the reaction mixture, while the outer cell contained DMSO-d$_6$ as the external standard. Enantiomeric excesses of the carbonates were determined by HPLC analyses with a Daicel Chiralcel OD-3 with detection at 254 nm or 205 nm.
Representative procedure for the Cyclic Carbonate Formation

\[
\begin{array}{c}
\text{R} \\
\text{PhCH}_2\text{Br}
\end{array}
\xrightarrow{\text{CO}_2, \text{DMF} @ 120 \text{°C}}
\begin{array}{c}
\text{R} \\
\text{O}
\end{array}
\]

4-Phenyl-1,3-dioxolan-2-one (8b)

In a 20 mL two-neck flask, styrene oxide 8a (5 mmol, 0.601 g) and DMF (5 equiv., 25 mmol, 1.827 g, flushed with CO\textsubscript{2} for 10 min) were stirred at 120 °C for 4 h under an atmosphere of CO\textsubscript{2} (99.999%, balloon), and then PhCH\textsubscript{2}Br (0.05mmol, 0.0086 g) was added. The reaction mixture was stirred for 20 h at the same temperature and DMF was removed under reduced pressure. The residue was dissolved in ethyl acetate (50 mL) and washed with water (15 ml) and brine (15 mL × 2), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane : ethyl acetate = 3 : 1) to afford the desired cyclic carbonate 0.705 g (yield: 86.0%).

\(^{1}\text{H NMR (500 MHz, CDCl}_3\): 7.42–7.37 (m, 2H), 7.37–7.30 (m, 3H), 5.70–5.60 (m, 1H), 4.81–4.70 (m, 1H), 4.31–4.20 (m, 1H). \(^{13}\text{C NMR (125 MHz, CDCl}_3\): 155.0, 135.9, 129.7, 129.2, 126.0, 78.0, 71.2.}

Propylene carbonate (1b)

Propylene oxide (1a, 10 mmol, 0.581g), DMF (5 equiv., 50 mmol, 3.655 g), benzyl bromide (0.1 mmol, 0.0171 g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 1 : 1) to afford the desired cyclic carbonate 0.766 g (yield: 75.0%).
$^1$H NMR (500 MHz, CDCl$_3$): 4.92–4.80 (m, 1H), 4.62–4.51 (m, 1H), 4.10–3.95 (m, 1H), 1.55–1.40 (m, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): 155.2, 73.7, 70.7, 19.3.

4-Butyl-1,3-dioxolan-2-one (2b)

1,2-Epoxyhexane (2a, 6 mmol, 0.601 g), DMF (5 equiv., 30 mmol, 2.193 g), benzyl bromide (0.06 mmol, 0.0103 g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.618 g (yield: 78.6%).

$^1$H NMR (500 MHz, CDCl$_3$): 4.80–4.65 (m, 1H), 4.60–4.50 (m, 1H), 4.18–4.01 (m, 1H), 1.85–1.62 (m, 2H), 1.55–1.22 (m, 4H), 0.93 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): 155.2, 77.2, 69.4, 33.4, 26.4, 22.2, 13.7.

4-Hexyl-1,3-dioxolan-2-one (3b)

1,2-Epoxyoctane (3a, 5 mmol, 0.641 g), DMF (5 equiv., 25 mmol, 1.827 g), benzyl bromide (0.05 mmol, 0.0086 g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 3 : 1) to afford the desired cyclic carbonate 0.666 g (yield: 81.5%).

$^1$H NMR (500 MHz, CDCl$_3$): 4.79–4.68 (m, 1H), 4.61–4.50 (m, 1H), 4.15–4.02 (m, 1H), 1.85–1.62 (m, 2H), 1.55–1.21 (m, 8H), 0.89 (t, $J = 6.9$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): 155.2, 77.2, 69.4, 33.7, 31.5, 28.7, 24.3, 22.4, 13.9.
4-(Chloromethyl)-1,3-dioxolan-2-one (4b)

Epichlorohydrin (4a, 6 mmol, 0.556 g), DMF (5 equiv., 30 mmol, 2.193 g), benzyl bromide (0.06 mmol, 0.0103 g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 1 : 1) to afford the desired cyclic carbonate 0.602 g (yield: 73.5%).

$^1$H NMR (500 MHz, CDCl$_3$): 5.12–5.01 (m, 1H), 4.69–4.55 (m, 1H), 4.48–4.35 (m, 1H), 3.89 (dd, $J$ = 12.5, 4.0 Hz, 1H), 3.77 (dd, $J$ = 12.5, 3.5 Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): 154.8, 74.7, 67.0, 44.6.

4-(But-3-en-1-yl)-1,3-dioxolan-2-one (5b)

1,2-Epoxy-5-hexene (5a, 6 mmol, 0.589 g), DMF (5 equiv., 30 mmol, 2.193 g), benzyl bromide (0.06 mmol, 0.0103 g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.490 g (yield: 57.4%).

$^1$H NMR (500 MHz, CDCl$_3$): 5.89–5.63 (m, 1H), 5.18–4.90 (m, 2H), 4.79–4.60 (m, 1H), 4.59–4.42 (m, 1H), 4.15–3.95 (m, 1H), 2.30–2.01 (m, 2H), 1.95–1.65 (m, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$): 155.1, 136.3, 116.0, 76.5, 69.4, 32.8, 28.6.

4-Allyloxymethyl-1,3-dioxolan-2-one (6b)

Allyl glycidyl ether (6a, 5 mmol, 0.571 g), DMF (5 equiv., 25 mmol, 1.827 g), benzyl
bromide (0.05 mmol, 0.0086 g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 1 : 1) to afford the desired cyclic carbonate 0.648 g (yield: 81.9%).

\[
\begin{align*}
\text{H NMR (CDCl}_3, 500 \text{ MHz)}: & \quad 5.95-5.80 (m, 1H), 5.35-5.12 (m, 2H), 4.93-4.80 (m, 1H), 4.60-4.45 (m, 1H), 4.44-4.30 (m, 1H), 4.11-3.99 (m, 2H), 3.75-3.65 (m, 1H), 3.64-3.52 (m, 1H). \\
\text{C NMR (125 MHz, CDCl}_3): & \quad 155.2, 133.9, 117.3, 75.4, 72.3, 68.9, 66.2.
\end{align*}
\]

4-(Phenoxymethyl)-1,3-dioxolan-2-one (7b)

1,2-Epoxy-3-phenoxy propane (7a, 5 mmol, 0.750 g), DMF (5 equiv., 25 mmol, 1.827 g), benzyl bromide (0.05 mmol, 0.0086 g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.870 g (yield: 89.6%).

\[
\begin{align*}
\text{H NMR (500 MHz, CDCl}_3): & \quad 7.36-7.22 (m, 2H), 7.06-6.92 (m, 1H), 6.91-6.85 (m, 2H), 5.06-4.95 (m, 1H), 4.65-4.56 (m, 1H), 4.55-4.46 (m, 1H), 4.22 (dd, J = 10.5, 4.0 Hz, 1H), 4.12 (dd, J = 10.5, 3.5 Hz, 1H). \\
\text{C NMR (125 MHz, CDCl}_3): & \quad 157.8, 154.8, 129.7, 122.0, 114.7, 74.2, 66.9, 66.2.
\end{align*}
\]
Reaction of chiral epoxide

(R)-4-Phenyl-1,3-dioxolan-2-one ((R)-8b)

![](image)

Reaction of (R)-styrene oxide was conducted according to the representative procedure, and the ee of the product was determined by chiral HPLC measurement using Chiralcel OD-3, 10% IPA/hexanes, 1 mL/min, \( t_R=25.83 \text{ min} \), \( t_S=34.15 \text{ min} \), 254 nm. Partial racemization of the product relative to the starting material was observed (68.6% ee). The DMF solution of the isolated product was kept for 24 h at 120 °C and negligible change of optical purity was observed (66.6 %ee).

<table>
<thead>
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<th>No.</th>
<th>Rt</th>
<th>Area</th>
<th>Area (%)</th>
<th>Height</th>
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$^1$H and $^{13}$C NMR Spectra:
$^{13}$C with $^1$H decoupling

$1b$
$^{13}$C with $^1$H decoupling

$2b$
$^{13}$C with $^1$H decoupling
$^{13}$C with $^1$H decoupling

![Chemical Structure](image)

$6b$