CO$_2$ Promoted Synthesis of Asymmetric Organic Carbonate
by Switchable Agents Based on DBU and Alcohols

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Table S1 The comparison of the catalytic performance of the reported catalytic
systems and that used in this work.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Reaction</th>
<th>T /°C</th>
<th>t /h</th>
<th>Con. %</th>
<th>Sel. %</th>
<th>Recyclable</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBD$^{[5]}$</td>
<td>Transesterification of DMC and alcohols</td>
<td>80</td>
<td>1</td>
<td>96-98</td>
<td>83-93</td>
<td>No</td>
</tr>
<tr>
<td>PS-DBU$^{[23]}$</td>
<td>N-phenoxycarbonylation of N-Heteroaromatics (HetNH) and diphenyl carbonate</td>
<td>120</td>
<td>24</td>
<td>73-90</td>
<td>99</td>
<td>Yes</td>
</tr>
<tr>
<td>MCM-41-TBD$^{[24]}$</td>
<td>Transesterification of EMC and alcohols/amines</td>
<td>125</td>
<td>15</td>
<td>80-96</td>
<td>94-99</td>
<td>Yes</td>
</tr>
<tr>
<td>TiO$_2$ nanofibers$^{[19]}$</td>
<td>Transesterification of DMC and alcohols</td>
<td>100</td>
<td>8</td>
<td>31-70</td>
<td>99</td>
<td>Yes</td>
</tr>
<tr>
<td>DBU+CO$_2$ (this work)</td>
<td>Transesterification of DMC and alcohols/amines</td>
<td>100</td>
<td>8</td>
<td>47-92</td>
<td>92-99</td>
<td>Yes</td>
</tr>
</tbody>
</table>

The numbers in the square brackets refer to the reference number cited in the article.
Tables S2 The $pK_a$ values of different bases used in this work.

<table>
<thead>
<tr>
<th>Bases</th>
<th>$pK_a$ (25 °C, in water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBD</td>
<td>-1.2±1.0</td>
</tr>
<tr>
<td>KOH</td>
<td>-0.70</td>
</tr>
<tr>
<td>DBU</td>
<td>0.5±1.5</td>
</tr>
<tr>
<td>TMG</td>
<td>1.0±1.0</td>
</tr>
<tr>
<td>Et$_3$N</td>
<td>3.25</td>
</tr>
<tr>
<td>K$_2$CO$_3$</td>
<td>3.75</td>
</tr>
</tbody>
</table>
Fig. S2 Visual observations of a reaction mixture containing DBU, ethanol, DMC, toluene, and CO$_2$ under reaction conditions. The working volume of the viewing cell was about 60 mL. DBU 5 mmol, ethanol 5 mmol, DMC 15 mmol and toluene 3.0 ml. CO$_2$ was charged for b−h. (a) DBU, ethanol, DMC, toluene, 25 °C, (b) DBU, ethanol, DMC, toluene, purging three times with 0.1 MPa CO$_2$ and then charged with CO$_2$ up to 0.5 MPa at 25 °C, (c) 0.5 MPa, 50°C, (d) 0.5 MPa, 70°C, (e) 0.5 MPa, 90°C, (f) 1.0 MPa, 90°C, (g) 2.0 MPa, 90 °C, (h) 3.0 MPa, 90 °C, (i) 0.1 MPa, 25 °C, autoclave was cooled and CO$_2$ was released.
Fig. S3 $^1$H NMR spectra of equimolar mixture of DBU/methanol, before and after bubbling CO$_2$. (a) DBU/methanol, (b) bubbling CO$_2$ to DBU/methanol for 10 min.
Fig. S4 $^1$H NMR spectra of equimolar mixture of DBU/ethanol, before and after bubbling CO$_2$. (a) DBU/ethanol, (b) bubbling CO$_2$ to DBU/ethanol for 10 min.
Fig. S5 $^{13}$C NMR (CDCl$_3$ as a solvent) spectra of [DBUH][O(CO)OCH$_2$CH$_3$].
**Reaction Kinetics**

The reaction was periodically monitored by the GC. In a typical kinetics experiment, the concentration of DMC (3.0 M), CO$_2$ pressure (1.0 MPa) and alcohol (1.0 M) was constant. In order to examine the effect of DBU concentration on the rate of transesterification reaction, the concentration of DBU was varied from 0.50 M to 1.25 M. The other reaction conditions have been given in the Figure captions (Fig.S6). Reaction rates ($R_0$) for the kinetic studies were determined from the slopes of reaction profiles ([DBU]$_0$-[DBU]$_t$ vs time) at low conversions (<15%) (Initial rate method).

Fig. S6 The relationship between the initial reaction rate ($R_0$) and the initial concentrations of DBU. Reaction conditions: DBU (0.50-1.25 M), DMC (3.0 M), ethanol (1.0 M), CO$_2$ pressure (1.0 MPa), 100 °C.
Table S3 The conductivity of DBU, ethanol and their mixture (30 °C)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity/μs cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBU</td>
<td>2.85</td>
</tr>
<tr>
<td>EtOH</td>
<td>4.14</td>
</tr>
<tr>
<td>DBU/EtOH</td>
<td>77.9</td>
</tr>
</tbody>
</table>

aThe molar ratio of DBU and EtOH was 1:3.
Propyl methyl carbonate: colorless liquid, petroleum ether/ethyl acetate = 12:1. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.97 (t, $J = 7.4$ Hz, 3H, -CH$_3$), 1.69 (m, 2H, -CH$_2$-CH$_3$-), 3.78 (s, 3H, -O-CH$_3$), 4.10 (m, 2H, -CH$_2$-O-). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.90, 69.54, 54.60, 22.02, 10.18. MS (ESI): calculated [M + H]$^+$:119.1, found:119.1. FT-IR ($\nu$, cm$^{-1}$): 2966, 2878, 1753, 1544, 1448, 1274.

![Fig. S7 $^1$H NMR spectra of propyl methyl carbonate.](image)

![Fig. S8 $^{13}$C NMR spectra of propyl methyl carbonate.](image)
**Butyl methyl carbonate** colorless liquid, petroleum ether/ethyl acetate = 12:1. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta \) 0.94 (t, \(J = 7.4\) Hz, 3H, -CH\(_3\)-), 1.41 (m, 2H, -CH\(_2\)-CH\(_2\)-CH\(_3\)-), 1.66 (m, 2H, -CH\(_2\)-CH\(_2\)-CH\(_3\)-), 3.78 (s, 3H, -O-CH\(_3\)-), 4.15 (t, \(J = 6.8\) Hz, 3H, -CH\(_2\)-O-). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta \) 155.90, 67.93, 54.59, 30.65, 18.88, 13.61. MS (ESI): calculated [M]: 132.1, found: 132.1. FT-IR (\(\nu, \text{ cm}^{-1}\)): 2961, 2875, 1750, 1541, 1444, 1274.

![Fig. S9 \(^1\)H NMR spectra of butyl methyl carbonate.](image)

![Fig. S10 \(^{13}\)C NMR spectra of butyl methyl carbonate.](image)
**Hexyl methyl carbonate**:<sup>2</sup> colorless liquid, petroleum ether/ethyl acetate = 12:1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.89 (t, <i>J</i> = 6.8 Hz, 3H, -CH<sub>3</sub>-), 1.33 (m, 6H, aliphatic -CH<sub>2</sub>-), 1.66 (m, 2H, aliphatic -CH<sub>2</sub>-), 3.78 (s, 3H, -O-CH<sub>3</sub>-), 4.14 (t, <i>J</i> = 6.8 Hz, 3H, -CH<sub>2</sub>-O-).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 155.91, 68.28, 54.62, 31.39, 28.62, 25.35, 22.51, 13.98. MS (ESI): calculated [M + H]<sup>+</sup>:161.1, found:161.0. FT-IR (<i>v</i>, cm<sup>-1</sup>): 2963, 2878, 1753, 1547, 1446, 1275.

![Fig. S11](image1.png)  
**Fig. S11** <sup>1</sup>H NMR spectra of hexyl methyl carbonate.

![Fig. S12](image2.png)  
**Fig. S12** <sup>13</sup>C NMR spectra of hexyl methyl carbonate.
Benzyl methyl carbonate: colorless liquid, petroleum ether/ethyl acetate = 10:1. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 3.79 (s, 3H, -CH$_3$-O-), 5.17 (m, 2H, -O-CH$_2$-), 7.36 (m, 10H, -CH$_2$).$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.75, 135.25, 128.61, 128.55, 128.31, 69.66, 54.89. MS (ESI): calculated [M]:166.1, found:166.1. FT-IR ($\nu$, cm$^{-1}$): 3034, 2957, 1749, 1585, 1444, 1269.

Fig. S13 $^1$H NMR spectra of benzyl methyl carbonate.

Fig. S14 $^{13}$C NMR spectra of benzyl methyl carbonate.
1,3-dioxolan-2-one: colorless liquid, petroleum ether/ethyl acetate = 3:1. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.54 (s, 4H, -(CH$_2$)$_2$). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.54, 64.48. MS (ESI): calculated [M]: 88.0, found: 88.1. FT-IR (v, cm$^{-1}$): 2994, 1798, 1161, 1065.

Fig. S15 $^1$H NMR spectra of 1,3-dioxolan-2-one.

Fig. S16 $^{13}$C NMR spectra of 1,3-dioxolan-2-one.
**Furan-2-ylmethyl methyl carbonate**: yellow liquid, petroleum ether/ethyl acetate = 12:1. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 3.79 (s, 3H, -CH$_3$-O-), 5.12 (s, 2H, -C-CH$_2$-O-), 6.36 (dd, $J$ = 2.0, 3.2 Hz, 1H, -CH-CH-C-), 6.46 (d, $J$ = 3.2 Hz, 1H, -CH-CH-CH-), 7.43 (dd, $J$ = 0.8, 2.0 Hz, 1H, -O-CH-CH-). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.54, 148.70, 143.54, 111.28, 110.58, 61.35, 54.93. MS (ESI): calculated [M]: 156.1, found: 156.0. FT-IR ($\nu$, cm$^{-1}$): 2959, 1751, 1502, 1445, 1265.

![1H NMR spectra of furan-2-ylmethyl methyl carbonate.](image1)

**Fig. S17** $^1$H NMR spectra of furan-2-ylmethyl methyl carbonate.

![13C NMR spectra of furan-2-ylmethyl methyl carbonate.](image2)

**Fig. S18** $^{13}$C NMR spectra of furan-2-ylmethyl methyl carbonate.
**Methyl propyl carbamate**: colorless oil, petroleum ether/ethyl acetate = 10:1.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 0.92 (t, $J = 9.5$ Hz, 3H, -CH$_3$-), 1.52 (m, 2H, -CH$_2$-CH$_3$-), 3.14 (dd, $J = 16.5$, 8.0 Hz, 2H, -CH$_2$-NH-), 3.66 (s, 3H, -CH$_3$-O-), 4.77 (s, 1H, -NH-).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 157.15, 51.91, 42.74, 23.17, 11.14. MS (ESI): calculated [M + H]$^+$: 117.1, found: 117.1. FT-IR ($\nu$, cm$^{-1}$): 3336, 2965, 1705, 1543, 1462, 1269.

![Fig. S19 $^1$H NMR spectra of methyl propyl carbamate.](image1)

![Fig. S20 $^{13}$C NMR spectra of methyl propyl carbamate.](image2)
**Methyl isopropyl carbamate**[^6]: colorless oil, petroleum ether/ethyl acetate = 10:1. $^1$H NMR (400 MHz, CDCl$_3$): δ 1.15 (d, $J = 7.4$ Hz, 6H, -($CH_3$)$_2$-CH-), 3.67 (s, 3H, -CH$_3$-O-), 3.81 (m, 1H, -CH-), 4.55(s, 1H, -NH-). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 156.26, 51.76, 43.02, 22.99. MS (ESI): calculated [M + 2H]$^+$:118.1, found:118.1. FT-IR ($\nu$, cm$^{-1}$): 3326, 2974, 1697, 1535, 1460, 1257.

![Fig.S21 $^1$H NMR spectra of methyl isopropyl carbamate.](image1)

![Fig. S22 $^{13}$C NMR spectra of methyl isopropyl carbamate.](image2)
**Methyl butyl carbamate**: colorless oil, petroleum ether/ethyl acetate = 10:1. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 0.92 (t, $J$ = 9 Hz, 3H, -CH$_3$), 1.34 (m, 2H, -CH$_2$-CH$_2$-CH$_3$), 1.48 (m, 2H, -CH$_2$-CH$_2$-CH$_3$), 3.18 (dd, $J$ = 16, 8 Hz, 2H, -CH$_2$-NH-), 3.66 (s, 3H, -CH$_3$-O-), 4.70 (s, 1H, -NH-). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 157.12, 51.91, 40.74, 32.04, 19.84, 13.68. MS (ESI): calculated [M + 2H]$^+$: 132.1, found: 132.1. FT-IR ($v$, cm$^{-1}$): 3336, 2959, 1708, 1538, 1464, 1269.

Fig. S23 $^1$H NMR spectra of methyl butyl carbamate.

Fig. S24 $^{13}$C NMR spectra of methyl butyl carbamate.
References


