Supporting information

Synthesis of Non-symmetrical Alkyl Carbonates from Alcohols and DMC over Nanocrystalline ZSM-5 Zeolite

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1. **Table S1.** Effect of amount of 2a, amount of NZSM-5, and temperature on synthesis of non-symmetrical organic carbonates

\[
1a \xrightarrow{\text{MeO} - \text{MeO}_2} 2a \xrightarrow{\text{NZSM-5}} 24 \text{h} \xrightarrow{\text{NZSM-5}} 2a \xrightarrow{\text{MeO}} 3a
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>2a (mL)</th>
<th>NZSM-5 (mg)</th>
<th>Temperature (°C)</th>
<th>Yieldb (%)</th>
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\(1a\) (1 mmol). \(b\) Isolated yields. \(c\) Reaction conducted in 15 mL RB with condenser.
2. **Fig. S1** Nitrogen adsorption/desorption isotherms of NZSM-5
3. Fig. S2 Pyridine-IR spectra of (a) ZSM-5, (b) Synthesized NZSM-5
4. **Fig. S3** FT-IR spectra of pure DMC, DMC adsorbed NZSM-5 and Pure NZSM-5
5. Table S2. Recyclability of the dried catalyst without calcination

<table>
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<th>S. No.</th>
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<th>Yieldb (%)</th>
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<td>5</td>
<td>5th</td>
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Reaction conditions: 1-Octanol (1a, 1 mmol), DMC (2 mL), NZSM-5 (150 mg), 110 °C. Isolated yields based on 1a.

To regenerate, the NZSM-5 was filtered to separate from the reaction mixture and washed with ethyl acetate, dried at 100 °C for 8 h, without calcination. Recyclability of the NZSM-5 catalyst was tested by performing the reaction of 1a with 2a in optimized reaction parameters (Table S2). The activity of the NZSM-5 was decreased with increase in number of cycles, this may be due to the blocking of active sites inside the micropores of zeolite by water
and DMC. In case of recycled NZSM-5 catalyst with calcination showed consistent activity up to five cycles (Table 3).

6. Spectroscopic Data

**Methyl 1-octyl carbonate (3a)**

\[
\text{\textsuperscript{1}H NMR (CDCl}_3, 400 MHz, ppm): \delta = 4.13 (t, J = 6.72 Hz, 2H), 3.78 (s, 3H), 1.71-1.60 (m, 2H), 1.42-1.21 (m, 10H), 0.88 (t, J = 6.72 Hz, 3H); \text{\textsuperscript{13}C NMR (CDCl}_3, 100 MHz, ppm): \delta = 155.87, 68.25, 54.60, 31.73, 29.12, 28.65, 25.66, 22.60, 14.05; HRMS: m/z calculated for C\textsubscript{10}H\textsubscript{20}O\textsubscript{3} [M+H]\textsuperscript{+} 188.14, found: 188.1440.}

**1-Dodecyl methyl carbonate (3b)**

\[
\text{\textsuperscript{1}H NMR (CDCl}_3, 500 MHz, ppm): \delta = 4.13 (t, J = 6.71 Hz, 2H), 3.78 (s, 3H), 1.71-1.61 (m, 2H), 1.41-1.23 (m, 18H), 0.88 (t, J = 6.86 Hz, 3H); \text{\textsuperscript{13}C NMR (CDCl}_3, 100 MHz, ppm): \delta = 155.87, 68.25, 54.59, 31.89, 29.59, 29.52, 29.46, 29.31, 29.18, 28.65, 25.65, 22.64, 14.09; HRMS: m/z calculated for C\textsubscript{14}H\textsubscript{28}O\textsubscript{3} [M+H]\textsuperscript{+} 245.20, found: 245.0792.}

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Methyl 1-undecyl carbonate (3c)

\[
\begin{align*}
\text{H NMR (CDCl}_3, 500 \text{ MHz, ppm): } & \delta = 4.13 (t, J = 6.72 \text{ Hz, 2H}), 3.78 (s, 3H), 1.71-1.61 (m, 2H), 1.40-1.23 (m, 16H), 0.88 (t, J = 6.86 \text{ Hz, 3H}); \\
\text{C NMR (CDCl}_3, 100 \text{ MHz, ppm): } & \delta = 155.88, 68.25, 54.59, 31.88, 29.56, 29.53, 29.46, 29.30, 29.19, 28.65, 25.66, 22.65, 14.08; \\
\text{HRMS: m/z calculated for C}_{13}\text{H}_{26}\text{O}_3\text{[M+H]}^+ & 231.18, \text{ found: 231.1966.}
\end{align*}
\]

1-Decyl methyl carbonate (3d)

\[
\begin{align*}
\text{H NMR (CDCl}_3, 400 \text{ MHz, ppm): } & \delta = 4.13 (t, J = 6.72 \text{ Hz, 2H}), 3.78 (s, 3H), 1.71-1.60 (m, 2H), 1.41-1.22 (m, 14H), 0.88 (t, J = 6.72 \text{ Hz, 3H}); \\
\text{C NMR (CDCl}_3, 100 \text{ MHz, ppm): } & \delta = 155.86, 68.26, 54.60, 31.85, 29.46, 29.26, 29.19, 28.65, 25.66, 22.64, 14.08; \\
\text{HRMS: m/z calculated for C}_{12}\text{H}_{24}\text{O}_3 \text{[M]}^+ & 216.17, \text{ found: 216.1745.}
\end{align*}
\]

Methyl 1-nonyl carbonate (3e)

\[
\begin{align*}
\text{H NMR (CDCl}_3, 500 \text{ MHz, ppm): } & \delta = 4.13 (t, J = 6.71 \text{ Hz, 2H}), 3.78 (s, 3H), 1.71-1.61 (m, 2H), 1.40-1.23 (m, 12H), 0.88 (t, J = 6.86 \text{ Hz, 3H}); \\
\text{C NMR (CDCl}_3, 100 \text{ MHz, ppm): } & \delta = 155.87, 68.25, 54.60, 31.82, 29.42, 29.19, 28.65, 25.66, 22.64, 14.08; \\
\text{HRMS: m/z calculated for C}_{11}\text{H}_{22}\text{O}_3 \text{[M+H]}^+ & 203.16, \text{ found: 203.1061.}
\end{align*}
\]

1-Heptyl methyl carbonate (3f)

\[
\begin{align*}
\text{H NMR (CDCl}_3, 500 \text{ MHz, ppm): } & \delta = 4.13 (t, J = 6.72 \text{ Hz, 2H}), 3.78 (s, 3H), 1.71-1.61 (m, 2H), 1.41-1.22 (m, 8H), 0.88 (t, J = 6.86 \text{ Hz, 3H}); \\
\text{C NMR (CDCl}_3, 100 \text{ MHz, ppm): } & \delta = 155.86, 68.23, 54.59, 31.65, 28.84, 28.64, 25.60, 22.53, 14.01; \\
\text{HRMS: m/z calculated for C}_{9}\text{H}_{18}\text{O}_3 \text{[M]}^+ & 174.13, \text{ found: 174.1298.}
\end{align*}
\]

1-Hexyl methyl carbonate (3g)

\[
\begin{align*}
\text{H NMR (CDCl}_3, 500 \text{ MHz, ppm): } & \delta = 4.13 (t, J = 6.72 \text{ Hz, 2H}), 3.78 (s, 3H), 1.71-1.61 (m, 2H), 1.41-1.22 (m, 8H), 0.88 (t, J = 6.86 \text{ Hz, 3H}); \\
\text{C NMR (CDCl}_3, 100 \text{ MHz, ppm): } & \delta = 155.86, 68.23, 54.59, 31.65, 28.84, 28.64, 25.60, 22.53, 14.01; \\
\text{HRMS: m/z calculated for C}_{8}\text{H}_{18}\text{O}_3 \text{[M]}^+ & 174.13, \text{ found: 174.1298.}
\end{align*}
\]
$^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta = 4.13$ (t, $J = 6.71$ Hz, 2H), 3.78 (s, 3H), 1.71-1.61 (m, 2H), 1.41-1.22 (m, 6H), 0.89 (t, $J = 6.86$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta =$ 155.87, 68.25, 54.60, 31.36, 28.61, 25.33, 22.48, 13.95; HRMS: m/z calculated for C$_8$H$_{16}$O$_3$ [M+H]$^+$ 161.11, found: 161.0427.

6-Chloro-1-hexyl methyl carbonate (3h)

$^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta = 4.14$ (t, $J = 6.56$ Hz, 2H), 3.78 (s, 3H), 3.53 (t, $J = 6.56$ Hz, 2H), 1.83-1.73 (m, 2H), 1.72-1.64 (m, 2H), 1.52-1.36 (m, 4H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta =$ 155.80, 67.89, 54.63, 44.84, 32.37, 28.49, 26.43, 25.01; HRMS: m/z calculated for C$_8$H$_{15}$O$_3$Cl [M+H]$^+$ 197.07, found: 197.1039.

Methyl 1-pentyl carbonate (3i)

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta = 4.13$ (t, $J = 6.72$ Hz, 2H), 3.78 (s, 3H), 1.72-1.61 (m, 2H), 1.39-1.24 (m, 4H), 0.90 (t, $J = 6.96$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta =$ 155.87, 68.22, 54.60, 28.33, 27.78, 22.26, 13.89; HRMS: m/z calculated for C$_7$H$_{14}$O$_3$, 147.09 [M+H]$^+$ found: 147.0514.

Isopentyl methyl carbonate (3j)

$^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta = 4.17$ (t, $J = 6.86$ Hz, 2H), 3.78 (s, 3H), 1.76-1.68 (m, 1H), 1.59-1.53 (m, 2H), 0.93 (d, $J = 6.56$ Hz, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta =$ 155.85, 66.71, 54.60, 37.28, 24.76, 22.37; HRMS: m/z calculated for C$_7$H$_{14}$O$_3$ [M+H]$^+$ 147.09, found: 147.1158.

1-Butyl methyl carbonate (3k)

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\( ^1H \) NMR (CDCl\(_3\), 400 MHz, ppm): \( \delta = 4.14 \) (t, \( J = 6.60 \) Hz, 2H), 3.78 (s, 3H), 1.71-1.60 (m, 2H), 1.47-1.33 (m, 2H), 0.94 (t, \( J = 7.33 \) Hz, 3H); \( ^13C \) NMR (CDCl\(_3\), 100 MHz, ppm): \( \delta = 155.85, 67.89, 54.55, 30.63, 18.85, 13.58 \); HRMS: m/z calculated for C\(_6\)H\(_{12}\)O\(_3\) [M]\(^+\) 132.08, found: 132.0468.

**Isobutyl methyl carbonate (3l)**

\( ^1H \) NMR (CDCl\(_3\), 500 MHz, ppm): \( \delta = 3.92 \) (d, \( J = 6.71 \) Hz, 2H), 3.78 (s, 3H), 2.02-1.91 (m, 1H), 0.95 (d, \( J = 6.71 \) Hz, 6H); \( ^13C \) NMR (CDCl\(_3\), 100 MHz, ppm): \( \delta = 155.90, 74.12, 54.61, 27.75, 18.84 \); HRMS: m/z calculated for C\(_6\)H\(_{12}\)O\(_3\) [M+H]\(^+\) 133.08, found: 133.0468.

**Dec-9-en-1-yl methyl carbonate (3m)**

\( ^1H \) NMR (CDCl\(_3\), 400 MHz, ppm): \( \delta = 5.87-5.72 \) (m, 1H), 5.04-4.90 (m, 2H), 4.13 (t, \( J = 6.72 \) Hz, 2H), 3.78 (s, 3H), 2.08-2.00 (m, 2H), 1.71-1.60 (m, 2H), 1.45-1.24 (m, 10H); \( ^13C \) NMR (CDCl\(_3\), 100 MHz, ppm): \( \delta = 155.87, 139.13, 114.14, 68.23, 54.61, 33.75, 29.29, 29.12, 28.98, 28.85, 28.64, 25.64 \); HRMS: m/z calculated for C\(_{12}\)H\(_{22}\)O\(_3\) [M+H]\(^+\) 125.18, found: 215.1306.

**Methyl pent-4-en-1-yl carbonate (3n)**

\( ^1H \) NMR (CDCl\(_3\), 500 MHz, ppm): \( \delta = 5.86-5.73 \) (m, 1H), 5.08-4.96 (m, 2H), 4.15 (t, \( J = 6.56 \) Hz, 2H), 3.78 (s, 3H), 2.19-2.10 (m, 2H), 1.82-1.72 (m, 2H); \( ^13C \) NMR (CDCl\(_3\), 100 MHz, ppm): \( \delta = 155.77, 137.17, 115.41, 67.40, 54.64, 29.72, 27.77 \); HRMS: m/z calculated for C\(_7\)H\(_{12}\)O\(_3\) [M]\(^+\) 144.08, found: 144.0798.

**(E)-Hex-3-en-1-yl methyl carbonate (3o)**

\( ^1H \) NMR (CDCl\(_3\), 500 MHz, ppm): \( \delta = 5.62-5.53 \) (m, 1H), 5.42-5.31 (m, 1H), 4.14 (t, \( J = 7.02 \) Hz, 2H), 3.78 (s, 3H), 2.39-2.31 (m, 2H), 2.06-1.96 (m, 2H), 0.97 (t, \( J = 7.48 \) Hz, 3H); \( ^13C \)
NMR (CDCl₃, 100 MHz, ppm): δ = 155.75, 135.43, 123.42, 67.67, 54.63, 31.93, 25.56, 13.62; HRMS: m/z calculated for C₈H₁₄O₃ [M]⁺ 158.09, found: 158.1204.

(Z)-Hex-3-en-1-yl methyl carbonate (3p)

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O}
\end{align*}
\]

¹H NMR (CDCl₃, 400 MHz, ppm): δ = 5.57-5.47 (m, 1H), 5.37-5.26 (m, 1H), 4.13 (t, J = 6.96 Hz, 2H), 3.78 (s, 3H), 2.47-2.37 (m, 2H), 2.11-2.00 (m, 2H), 0.97 (t, J = 7.46 Hz, 3H); 
¹³C NMR (CDCl₃, 100 MHz, ppm): δ = 155.79, 134.95, 123.00, 67.44, 54.64, 26.73, 20.58, 14.13; HRMS: m/z calculated for C₈H₁₄O₃ [M]⁺ 158.09, found: 158.1204.

Methyl 2-octyl carbonate (3q)

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O}
\end{align*}
\]

¹H NMR (CDCl₃, 500 MHz, ppm): δ = 4.80-4.71 (m, 1H), 3.76 (s, 3H), 1.68-1.60 (m, 1H), 1.54-1.45 (m, 1H), 1.38-1.24 (m, 1H), 0.88 (t, J = 6.72 Hz, 3H); 
¹³C NMR (CDCl₃, 100 MHz, ppm): δ = 155.47, 75.52, 54.41, 35.86, 31.66, 29.06, 25.21, 22.54, 19.87, 14.03; HRMS: m/z calculated for C₁₀H₂₀O₃ [M]⁺ 188.14, found: 188.1443.

2-Heptyl methyl carbonate (3r)

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O}
\end{align*}
\]

¹H NMR (CDCl₃, 400 MHz, ppm): δ = 4.81-4.71 (m, 1H), 3.76 (s, 3H), 1.69-1.59 (m, 1H), 1.55-1.44 (m, 1H), 1.38-1.24 (m, 9H), 0.88 (t, J = 6.72 Hz, 3H); 

2-Hexyl methyl carbonate (3s)
\[ \text{\textsuperscript{1}H NMR (CDCl}_3, 400 \text{ MHz, ppm): } \delta = 4.81-4.71 \text{ (m, 1H)}, 3.77 \text{ (s, 3H)}, 1.70-1.60 \text{ (m, 1H)}, 1.56-1.46 \text{ (m, 1H)}, 1.37-1.24 \text{ (m, 7H)}, 0.90 \text{ (t, } J = 6.82 \text{ Hz, 3H); } \text{\textsuperscript{13}C NMR (CDCl}_3, 100 \text{ MHz, ppm): } \delta = 155.46, 75.49, 54.40, 35.54, 27.39, 22.47, 19.86, 13.91; \text{ HRMS: m/z calculated for C}_8\text{H}_{16}\text{O}_3 \ [M+H]^+ 161.11, \text{ found: 161.0968.} \]

\textbf{Methyl 2-pentyl carbonate (3t)}

\[ \text{\textsuperscript{1}H NMR (CDCl}_3, 500 \text{ MHz, ppm): } \delta = 4.81-4.73 \text{ (m, 1H)}, 3.76 \text{ (s, 3H)}, 1.68-1.59 \text{ (m, 1H)}, 1.53-1.44 \text{ (m, 1H)}, 1.43-1.32 \text{ (m, 2H)}, 1.27 \text{ (d, } J = 6.26 \text{ Hz, 3H)}, 0.92 \text{ (t, } J = 7.32 \text{ Hz, 3H); } \text{\textsuperscript{13}C NMR (CDCl}_3, 100 \text{ MHz, ppm): } \delta = 155.47, 75.25, 54.42, 37.95, 29.67, 19.87, 16.50, 13.83; \text{ HRMS: m/z calculated for C}_7\text{H}_{14}\text{O}_3 \ [M]^+ 146.09, \text{ found: 146.1158.} \]

\textbf{Cyclohexyl methyl carbonate (3u)}

\[ \text{\textsuperscript{1}H NMR (CDCl}_3, 500 \text{ MHz, ppm): } \delta = 4.66-4.57 \text{ (m, 1H)}, 3.77 \text{ (s, 3H)}, 1.95-1.89 \text{ (m, 2H)}, 1.79-1.71 \text{ (m, 2H)}, 1.58-1.43 \text{ (m, 3H)}, 1.41-1.24 \text{ (m, 3H); } \text{\textsuperscript{13}C NMR (CDCl}_3, 100 \text{ MHz, ppm): } \delta = 155.23, 76.67, 54.39, 31.51, 25.19, 23.60; \text{ HRMS: m/z calculated for C}_8\text{H}_{14}\text{O}_3 \ [M+H]^+ 159.09, \text{ found: 159.0426.} \]

\textbf{Methyl (2-phenyl)ethyl carbonate (3x)}

\[ \text{\textsuperscript{1}H NMR (400 \text{ MHz, CDCl}_3): } \delta \text{ (ppm) } = 7.28-7.34 \text{ (m, 2H)}, 7.21-7.26 \text{ (m, 3H)}, 4.34 \text{ (t, 2H, } J = 7.21 \text{ Hz)}, 3.76 \text{ (s, 3H)}, 2.98 \text{ (t, 2H, } J = 7.21 \text{ Hz). } \text{\textsuperscript{13}C NMR (75 \text{ MHz, CDCl}_3): } \delta \text{ (ppm) } = 155.93, 137.44, 129.13, 128.77, 126.90, 68.61, 54.94, 35.36. \]
7. Copies of $^1$H and $^{13}$C NMR Spectra

3a
3b

3c
$3k$

$3l$
7. References


