Supporting Information

for

Microwave Assisted Synthesis of Cyclic Carbonates from Olefins with Sodium Bicarbonates as the C1 Source

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**General Experimental Information:**

All reactions in this project are not sensitive to air or moisture. Volumetric flasks were oven-dried and cooled in a desiccator prior to use. Anhydrous N-Bromosuccinimide (NBS), N,N-dimethylformamide (DMF), acetone and bicarbonates were purchased from Sigma-Aldrich and used without any further purification. All other commercial reagents or materials were used as received without purification: styrene (1a), 1-vinylnaphthalene (1b), 4-vinylanisole (1c), 4-acetoxy styrene (1d), 1-chloro-4-vinylbenzene (1e), 1-(trifluoromethyl)-3-vinylbenzene (1f), 4-fluorostyrene (1g), 3-vinylbenzaldehyde (1h), 1-octene (1j), hex-5-enenitrile (1k), methyl pent-4-enoate (1l), 4penten-1-ol (1m), hex-5-en-1-ol (1n), hex-5-en-2-one (1o), allyl phenyl ether (1p), cyclopentene (1q) and trans-3-hexene (1r). Thin layer chromatography (TLC) was performed on DC-Fertigplatten SIL G-25 UV254 pre-coated TLC plates. The developed chromatogram was visualized by UV lamp or stained using one of the following: aqueous potassium permanganate (KMnO4) or ethanolic para-anisaldehyde. Selected purifications were performed using a Biotage Isolera One flash purification system, as noted in the experimental procedures.

Proton nuclear magnetic resonance (1H NMR) and carbon nuclear magnetic resonance (13C NMR) spectra were recorded on a Varian Inova (500 MHz) spectrometers in deuterochloroform (CDCl3) unless otherwise noted. Chemical shifts are recorded in parts per million (ppm) and are referenced to the centerline of deuterochloroform (δ 7.24 ppm 1H NMR; δ 77.0 ppm 13C NMR). Data was recorded as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). Coupling constants (J values) are given in Hertz (Hz). Infrared (IR) spectra were recorded on an Agilent Cary 630 FTIR. High resolution mass spectra (HRMS) were obtained on a Bruker Daltonics APEXIV 4.7 Tesla Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FT-ICR-MS) by Li Li of the Massachusetts Institute of Technology Department of Chemistry Instrumentation Facility.
Representative Batch Procedure for Cyclic Carbonate Formation:

In a microwave-transparent tube (CEM Discover and Explorer SP 35ml tube) containing a stir bar, NBS (4.8 mmol, 1.2 equiv) was mixed with 4 mL of water and 4 mL of acetone immediately followed by the addition of sodium bicarbonate (4.4 mmol, 1.1 equiv) and styrene (4 mmol, 1 equiv). The tube was sealed and the reaction mixture was stirred and placed in oil bath. The temperature was maintained at 60 °C for 18 hours, and the mixture was cooled down to room temperature and depressurized. Ethyl acetate was used to extract any organic material. Further purification was performed using a Biotage Isolera One flash purification system to afford cyclic carbonate 2a (360.9 mg, 55% yield).

Representative Microwave Assisted Synthesis Procedure for Cyclic Carbonate Formation:

In a microwave-transparent tube (CEM Discover and Explorer SP 35ml tube) containing a stir bar, NBS (4.8 mmol, 1.2 equiv) was mixed with 4 mL of water and 4 mL of acetone followed by the addition of sodium bicarbonate (4.4 mmol, 1.1 equiv) and styrene (4 mmol, 1 equiv). The tube was put into the CEM Discover and Explorer SP reactor. The temperature measured by the fiber optic sensor was set up at rising from 24°C to 60 °C in 10 minutes and maintained at 60 °C in 17 hours and 50 minutes. The reactor was cooled down to room temperature and depressurized. Ethyl acetate was used to extract any organic material. Further purification was performed using a
Biotage Isolera One flash purification system to afford cyclic carbonate 2a (564.3 mg, 86% yield).

4-Phenyl-1, 3-dioxolan-2-one (2a)
Styrene (458 μL, 4 mmol) was added according to the representative microwave procedure. Following the general procedure, compound 2a was isolated and analysis of the final sample indicated 86% yield (564.3 mg). IR (neat): 1784, 1670, 1160, 1050 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 7.44-7.36 (m, 3H), 7.36-7.28 (m, 2H), 5.64 (t, J = 8.0 Hz, 1H), 4.78 (t, J = 8.4 Hz, 1H), 4.30 (dd, J = 8.6, 7.9 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 154.9, 135.8, 129.8, 129.3, 125.9, 78.0, 71.2. HRMS (DART) m/z calcd for C₉H₁₂NO₃ [M+NH₄]⁺: 182.0812. Found: 182.0810.

4-(Naphthalen-2-yl)-1,3-dioxolan-2-one (2b)
1-Vinylnaphthalene (0.616g, 4 mmol) was added according to the representative microwave procedure. Following the general procedure, compound 2b was isolated and analysis of the final sample indicated 74% yield (633.6mg). IR (neat): 2925, 2855, 1795, 1712, 1165, 1058 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 7.88 (d, J = 8.5Hz, 1H), 7.83 (m, 3H), 7.53 (m, 2H), 7.39(dd, J = 8.4 Hz, 2Hz, 1H), 5.79(t, J =8.0 Hz, 1H), 4.82(t, J = 8.5 Hz, 1H), 4.38(t, J = 8.0 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): 154.9, 133.5, 132.8, 132.8, 129.4, 128.0, 127.7, 127.0, 126.9, 125.7, 122.3, 78.1, 71.0. HRMS (DART) m/z calcd for C₁₃H₁₁O₃ [M+H]⁺: 215.0708. Found: 215.0704.
4-(4-Methoxyphenyl)-1,3-dioxolan-2-one (2c)

4-Vinylanisole (532 μL, 4 mmol) was added according to the representative microwave procedure. Following the general procedure, compound 2c was isolated and analysis of the final sample indicated 68% yield (527.8mg). IR (solid film): 2962, 2925, 1783, 1250, 1161, 1050 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): 7.28 (m, 2H), 6.93 (m, 2H), 5.60 (t, J = 8.0 Hz, 1H), 4.73 (dd, J = 8.5, 8.0 Hz, 1H), 4.32 (t, J = 8.0 Hz, 1H), 3.80 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): 160.7, 154.9, 127.8, 127.3, 114.5, 78.1, 71.1, 55.4. HRMS (DART) m/z calcd for C₁₀H₁₄NO₄ [M+NH₄]⁺: 212.0923. Found: 212.0918.

4-(2-Oxo-1,3-dioxolan-4-yl)phenyl acetate (2d)

4-Acetoxystyrene (612 μL, 4 mmol) was added according to the representative microwave procedure. Following the general procedure, compound 2d was isolated and analysis of the final sample indicated 82% yield (728.3mg). IR (solid film): 1781, 1748, 1510, 1370, 1193, 1157, 1068, 1012 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): 7.28 (d, J = 9 Hz, 2H), 6.93 (d, J = 9 Hz, 2H), 5.60 (t, J = 8.0 Hz, 1H), 4.73 (dd, J = 9.0, 8.5 Hz, 1H), 4.33 (dd, J = 8.5, 8.0 Hz, 1H), 3.81 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): 169.1, 154.6, 151.3, 133.1, 127.1, 121.3, 77.3, 70.9, 20.9. HRMS (DART) m/z calcd for C₁₁H₁₄NO₅ [M+NH₄]⁺: 240.0872. Found: 240.0863.

4-(3-Chlorophenyl)-1,3-dioxolan-2-one (2e)
1-Chloro-4-vinylbenzene (480 µL, 4 mmol) was added according to the representative microwave procedure. Following the general procedure, compound 2e was isolated and analysis of the final sample indicated 78% yield (617.8mg). IR (solid film): 3577, 2966, 2126, 1789, 1489, 1162, 1048, 955 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 7.37 (m, 2H), 7.26 (m, 2H), 5.64 (t, J = 8.0 Hz, 1H), 4.78 (t, J = 8.0 Hz, 1H), 4.27 (t, J = 8.0 Hz, 1H). ¹³C NMR (125MHz, CDCl₃): δ 154.5, 135.5, 134.2, 129.3, 127.2, 77.2, 70.9. HRMS (DART) m/z calcd for C₉H₈ClO₃ [M+H]⁺: 199.0162. Found: 199.0156.

4-(3-(Trifluoromethyl)phenyl)-1,3-dioxolan-2-one (2f)

1-(Trifluoromethyl)-3-vinylbenzene (592 µL, 4 mmol) was added according to the representative microwave procedure and DMF/H₂O as co-solvent instead of acetone/H₂O to improve the reaction conversion. Following the general procedure, compound 2f was isolated and analysis of the final sample indicated 70% yield (649.7mg). IR (solid film): 2923, 1793, 1326, 1066, 902 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 7.67(d, J = 7.0Hz, 1H), 7.56 (m, 3H), 5.74(t, J = 8.0 Hz, 1H), 4.85(t, J =8.5 Hz, 1H), 4.31 (t, J = 8.0 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 154.4, 136.9, 131.6 (q), 129.9, 129.0, 126.4, 123.5 (q), 122.6, 77.1, 70.9 (q). HRMS (DART) m/z calcd for C₁₀H₇F₃NaO₃ [M+Na]⁺: 255.0245. Found: 255.0255.

4-(4-Fluorophenyl)-1,3-dioxolan-2-one (2g)

4-Fluorostyrene (475 µL, 4 mmol) was added according to the representative microwave procedure. Following the general procedure, compound 2g was isolated and analysis of the final sample indicated 69% yield (502.4mg). IR (solid film): 1780,
1602, 1507, 1329, 1215, 1158, 1052 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.33 (m, 2H), 7.08 (m, 2H), 5.64 (t, $J = 8.5$ Hz, 1H), 4.77 (t, $J = 8.5$ Hz, 1H), 4.28 (t, $J = 8.5$ Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 164.2, 162.2, 154.6, 131.5, 128.0, 116.2, 77.4, 71.0. HRMS (DART) $m/z$ calcld for C$_9$H$_{11}$FNO$_3$ [M+NH$_4$]$^+$: 200.0723. Found: 200.0707.

![2h]

3-(2-Oxo-1,3-dioxolan-4-yl)benzaldehyde (2h)

3-Vinylbenzaldehyde (505 $\mu$L, 4 mmol) was added according to the representative microwave procedure. Following the general procedure, compound 2h was isolated and analysis of the final sample indicated 63% yield (483.9mg). IR (solid film): 1791, 1696, 1607, 1381, 1161, 1068 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 10.03 (s, 1H), 7.92 (m, 2H), 7.87 (s, 2H), 5.76 (t, $J = 8.5$ Hz, 1H), 4.86 (dd, $J = 8.5, 8.0$ Hz, 1H), 4.34 (dd, $J = 9.0, 8.0$ Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 191.4, 154.4, 137.1, 136.8, 131.5, 131.0, 130.0, 126.4, 77.3, 70.9. HRMS (DART) $m/z$ calcld for C$_{10}$H$_9$O$_4$ [M+H]$^+$: 193.0501. Found: 193.0504.

![2i]

4-(Benzo[d][1,3]dioxol-5-yl)-1,3-dioxolan-2-one (2i)

5-Vinylbenzo[d][1,3]dioxole (0.592 g, 4 mmol) was added according to the representative microwave procedure. Following the general procedure, compound 2i was isolated and analysis of the final sample indicated 52% yield (433.5mg). IR (solid film): 2920, 1787, 1447, 1247, 1162, 1033, 923 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 6.8 (m, 3H), 5.96 (s, 2H), 5.55 (t, $J = 8.0$ Hz, 1H), 4.71 (t, $J = 8.5$ Hz, 1H), 4.27 (t, $J = 8.5$ Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 154.7, 148.7, 148.4, 129.1,
120.4, 108.5, 106.1, 101.5, 78.1, 71.0. HRMS (DART) m/z calcd for $\text{C}_{10}\text{H}_{9}\text{O}_5 [\text{M+H}]^+$: 209.0450. Found: 209.0447.

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

1-Octene (1.56 mL, 10 mmol, 1 equiv) was added according to the representative microwave procedure. Following the general procedure, compound 2j was isolated and analysis of the final sample indicated 69% yield (320.3mg). IR (neat): 2928, 2859, 1788, 1384, 1165, 1059, 774 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 4.67 (dd, $J = 7.5$, 5.5 Hz, 1H), 4.50 (t, $J = 8.1$ Hz, 1H), 4.04 (dd, $J = 8.3$, 7.3 Hz, 1H), 1.79-1.73 (m, 1H), 1.68-1.61 (m, 1H), 1.45-1.27 (m, 8H), 0.86 (t, $J = 6.9$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 155.1, 77.1, 69.4, 33.9, 31.5, 28.8, 24.3, 22.5. HRMS (DART) m/z calcd for $\text{C}_9\text{H}_{20}\text{NO}_3 [\text{M+NH}_4]^+$: 190.1438. Found: 190.1438.

4-(2-Oxo-1,3-dioxolan-4-yl)butanenitrile (2k)

Hex-5-enenitrile (454 µL, 4 mmol) was added according to the representative microwave procedure. Following the general procedure, compound 2k was isolated and analysis of the final sample indicated 83% yield (514.8mg). IR (solid film): 2927, 2247, 1781, 1390, 1164, 1057 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 4.71 (m, 1H), 4.55(t, $J = 8.5$ Hz, 1H), 4.06 (t, $J = 7.0$ Hz, 1H), 2.42 (m, 2H), 1.85(m, 3H), 1.74 (m, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 154.6, 118.9, 75.9, 69.0, 32.5, 20.8, 16.6. HRMS (DART) m/z calcd for $\text{C}_7\text{H}_{10}\text{NO}_3 [\text{M+H}]^+$: 156.0661. Found: 156.0661.
Methyl 3-(2-oxo-1,3-dioxolan-4-yl)propanoate (2l)

Methyl pent-4-enoate (0.456 g, 4 mmol) was added according to the representative microwave procedure. Following the general procedure, compound 2l was isolated and analysis of the final sample indicated 85% yield (591.8mg). IR (solid film): 1786, 1729, 1360, 1158, 1059, 980 cm\(^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 4.77 (m, 1H), 4.54 (t, \(J = 8.1\) Hz, 1H), 4.07 (dd, \(J = 6.9, 15.6\) Hz, 1H), 3.67 (s, 3H), 2.51 (m, 2H), 2.03 (m, 2H). \(^13\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 172.4, 154.6, 75.8, 69.2, 51.8, 28.9. HRMS (DART) \(m/z\) calcd for C\(_7\)H\(_{14}\)NO\(_5\) [M+NH\(_4\)]\(^+\): 192.0872. Found: 192.0855.

4-(3-Hydroxypropyl)-1,3-dioxolan-2-one (2m)

4-Penten-1-ol (395 \(\mu\)L, 4 mmol) was added according to the representative microwave procedure. Following the general procedure, compound 2m was isolated and analysis of the final sample indicated 65% yield (379.8mg). IR (solid film): 2922, 1780, 1707, 1388, 1171, 1053 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)): 4.77 (m, 1H), 4.55 (t, \(J = 8.0\) Hz, 1H), 4.09 (t, \(J = 7.0\) Hz, 1H), 3.71 (m, 2H), 1.87 (m, 2H), 1.68 (m, 2H). \(^13\)C NMR (125 MHz, CDCl\(_3\)): 155.0, 76.9, 69.4, 61.7, 30.6, 27.4. HRMS (DART) \(m/z\) calcd for C\(_6\)H\(_{14}\)NO\(_4\) [M+NH\(_4\)]\(^+\): 164.0923. Found: 164.0926.

4-(4-Hydroxybutyl)-1,3-dioxolan-2-one (2n)
Hex-5-en-1-ol (480 µL, 4 mmol) was added according to the representative microwave procedure. Following the general procedure, compound 2n was isolated and analysis of the final sample indicated 84% yield (537.8mg). IR (solid film): 3414, 2932, 2868, 1775, 1165, 1055 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): 4.70 (m, 1H), 4.51(t, J = 8.0 Hz, 1H), 4.06 (t, J = 7.0 Hz, 1H), 3.64 (t, J = 5.5 Hz, 2H), 1.81 (m, 1H), 1.73 (m, 1H), 1.64 (br, 1H), 1.56(m, 3H), 1.46(m, 1H). ¹³C NMR (125 MHz, CDCl₃): 155.2, 77.0, 69.3, 61.9, 33.4, 31.8, 20.7. HRMS (DART) m/z calcd for C₇H₁₆NO₄ [M+NH₄]⁺: 178.1079. Found: 178.1070.

4-(3-Oxobutyl)-1,3-dioxolan-2-one (2o)

Hex-5-en-2-one (480 mL, 4 mmol) was added according to the representative microwave procedure. Following the general procedure, compound 2o was isolated and analysis of the final sample indicated 83% yield (524.8mg). IR (solid film): 2920, 1782, 1394, 1159, 1055 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): 4.72 (m, 1H), 4.52 (dd, J = 8.5, 8.0 Hz, 1H), 4.04 (dd, J = 9.0, 7.0 Hz, 1H), 2.64 (t, J = 7.0Hz, 2H), 2.14 (s, 3H), 2.01 (m, 1H), 1.87 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 206.8, 154.7, 76.0, 69.4, 38.0, 29.9, 27.6. HRMS (DART) m/z calcd for C₇H₁₄NO₄ [M+NH₄]⁺: 176.0923. Found: 176.0914.

4-(Phenoxy)methyl-1,3-dioxolan-2-one (2p)

Allyl phenyl ether (545 µL, 4 mmol) was added according to the representative microwave procedure and DMF/H₂O as co-solvent instead of acetone/H₂O to improve the reaction conversion. Following the general procedure, compound 2p was
isolated and analysis of the final sample indicated 55% yield (426.9mg). IR (solid film): 2927, 1783, 1600, 1490, 1396, 1161, 1081, 1009 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.34-7.20 (m, 2H), 7.03-6.94 (m, 1H), 6.93-6.82 (m, 2H), 5.04-4.98 (m, 1H), 4.60 (t, $J = 8.4$ Hz, 1H), 4.51 (dd, $J = 8.5$, 5.9, 1H), 4.21 (dd, $J = 10.6$, 4.2 Hz, 1H), 4.12 (dd, $J = 10.6$, 3.6 Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 157.8, 154.7, 129.7, 122.0, 114.6, 74.1, 66.9, 66.3. HRMS (DART) m/z calcd for C$_{10}$H$_{14}$NO$_4$ [M+NH$_4$]$^+$: 212.0917. Found: 212.0916.

![Cis-hexahydrobenzo[d][1,3]dioxol-2-one (2q)](image)

**Cis-hexahydrobenzo[d][1,3]dioxol-2-one (2q)**

Cyclopentene (404 uL, 4 mmol) was added according to the representative microwave procedure. Following the general procedure, compound 2q was isolated and analysis of the final sample indicated 49% yield (251.0mg). IR (solid film): 2970, 1784, 1717, 1373, 1165, 1043, 929 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): 5.08 (dd, $J = 4.0$, 2.0 Hz, 1H), 2.14 (m, 2H), 1.78 (m, 2H), 1.64 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): 155.4, 81.8, 33.2, 21.5. HRMS (DART) m/z calcd for C$_6$H$_{12}$NO$_3$ [M+NH$_4$]$^+$: 146.0817. Found: 146.0817.

![trans-4,5-Diethyl-1,3-dioxolan-2-one (2r)](image)

**trans-4,5-Diethyl-1,3-dioxolan-2-one (2r)**

trans-3-Hexene (480 mL, 4 mmol) was added according to the representative microwave procedure. Following the general procedure, compound 2r was isolated and analysis of the final sample indicated 86% yield (495.6mg). IR (solid film): 2936, 2864, 1786, 1200, 1052, 965 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 4.10 (s, 2H), 1.88 (m, 2H), 1.75 (m, 2H), 1.63 (m, 2H), 1.5 (m, 3H), 1.38 (m, 1H). $^{13}$C NMR (125 MHz,

Experiments of Reaction Mechanism Analysis

In order to understand the reaction process, we investigated the product distribution at different time and temperature scales. The experiment results were summarized in Table S1 and Table S2.

Table S1 The influence of reaction time (in Acetone/H₂O, 60 °C)

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<th>Condition</th>
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<td><strong>B</strong></td>
<td>Microwave</td>
<td>60 °C</td>
<td>20%</td>
<td>29%</td>
<td>45%</td>
<td></td>
</tr>
<tr>
<td><strong>C</strong></td>
<td>Microwave</td>
<td>60 °C</td>
<td>20%</td>
<td>29%</td>
<td>45%</td>
<td></td>
</tr>
<tr>
<td><strong>D</strong></td>
<td>Microwave</td>
<td>80 °C</td>
<td>10%</td>
<td>10%</td>
<td>65%</td>
<td></td>
</tr>
<tr>
<td><strong>E</strong></td>
<td>Microwave</td>
<td>100 °C</td>
<td>20%</td>
<td>0%</td>
<td>70%</td>
<td></td>
</tr>
<tr>
<td><strong>F</strong></td>
<td>No heating</td>
<td>24 °C</td>
<td>0%</td>
<td>60%</td>
<td>0%</td>
<td></td>
</tr>
</tbody>
</table>

Table S2 The influence of reaction temperature (in DMF/H₂O, 60 min)
$^1$H and $^{13}$C NMR Spectra: