

Supporting Information
for
Bromine-Catalyzed Conversion of CO₂ and Epoxides to Cyclic Carbonates
under Continuous Flow Conditions

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General Experimental Information:

All reactions sensitive to air or moisture were carried out in flame-dried glassware under an atmosphere of argon. Volumetric flasks were oven-dried and cooled in a desiccator prior to use. Anhydrous *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMA) were purchased from Sigma-Aldrich and used without any further purification. 1,2-Epoxyoctane (**1a**) was distilled from calcium hydride prior to use. All other commercial reagents or materials were used as received without purification: 1,2-epoxy-3-phenoxypropane (**1b**), (2,3-epoxypropyl)benzene (**1c**), propylene oxide (**1d**), (1,2-epoxyhexane (**1e**), epichlorohydrin (**1f**), styrene oxide (**1g**), 3,4-epoxy-1-butene (**1h**), 1,2-epoxy-5-hexene (**1i**), 1,2-epoxy-9-decene (**1j**), (*R*)-(+)-styrene oxide ((*R*)-**1g**; 97% ee), cyclohexene oxide, 1,2-epoxy-3-methylpropane, and *trans*-stilbene oxide. Ethyl-2,3-epoxypropanoate was synthesized following a literature procedure of a similar compound.¹ (*S*)-1,2-Epoxy-3-phenoxypropane ((*S*)-**1b**) was synthesized using the Jacobsen kinetic resolution (>99.5% ee).² 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 Bruker-AVANCE 600 spectrometer (600 MHz) or Bruker-AVANCE 400 spectrometers (400 MHz) in deuteriochloroform (CDCl₃) unless otherwise noted. Chemical shifts are recorded in parts per million (ppm) and are referenced to the centerline of deuteriochloroform (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, qt = quintet, 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. Gas chromatographic (GC)

¹ Stevenson, C. P.; Nielsen, L. C. P.; Jacobsen, E. N. *Org. Synth.* **2006**, 83, 162-169.

² Schaus, S. E.; Brandes, B. D.; Larrow, J. F.; Tokunaga, M.; Hansen, K. B.; Gould, A. E.; Furrow, M. E.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2002**, 124, 1307-1315.

analysis was performed on an Agilent 7890A GC system on an Agilent HP-5 column (30 m, 0.32 mm i.d., 25 μ m film thickness) with a flow rate of 1 mL/min using the following method: the oven temperature was held at 50 °C for 5 min and then increased linearly to 250 °C over 20 min with a final hold of 5 min.

Design and Construction of the Flow Apparatus:

Figure S1: Schematic of the continuous flow apparatus.

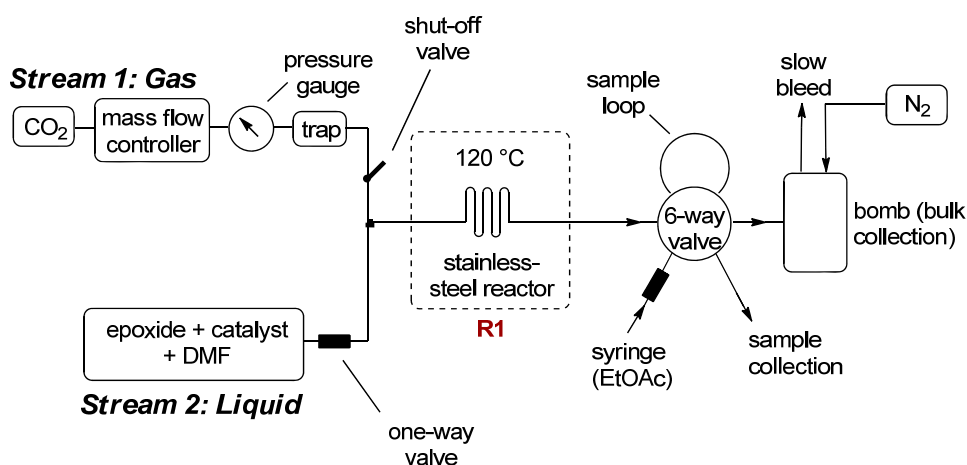


Figure S2: The full continuous flow set-up.

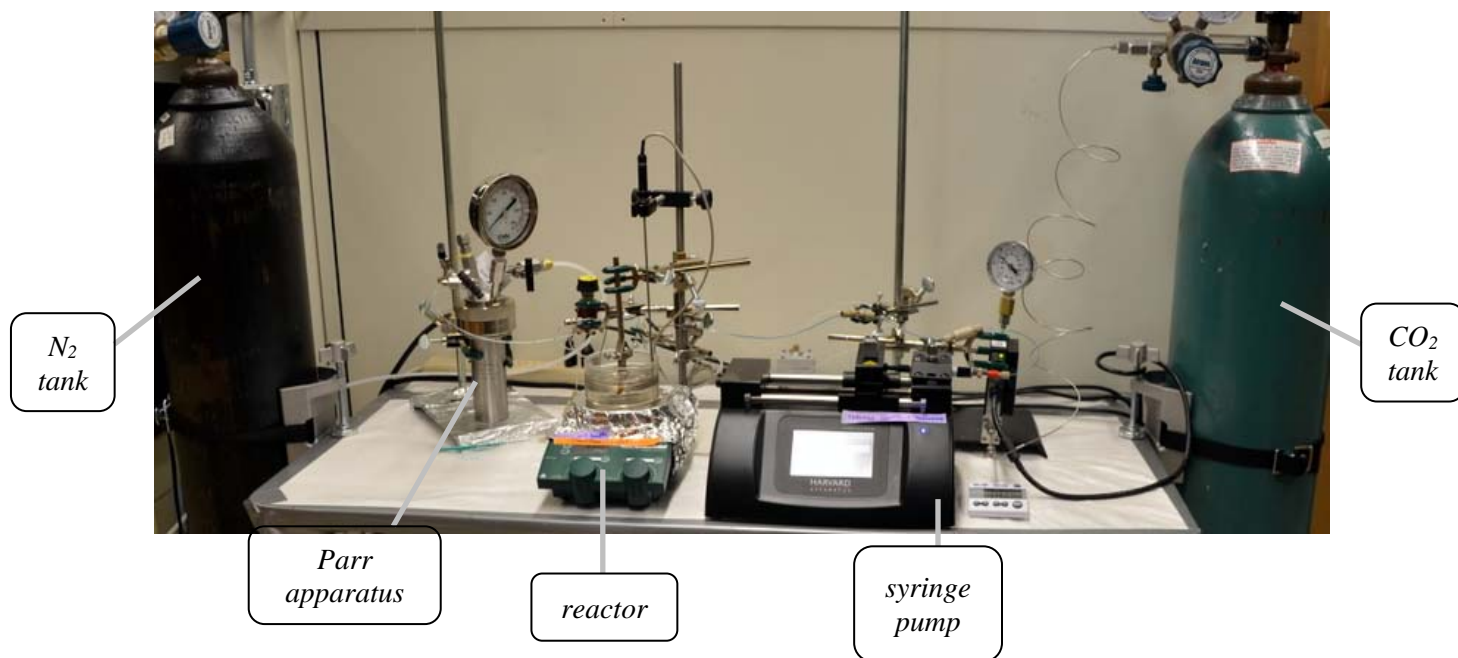


Figure S3: Close-up of the mass flow controller (back), gauge, and aluminum trap.

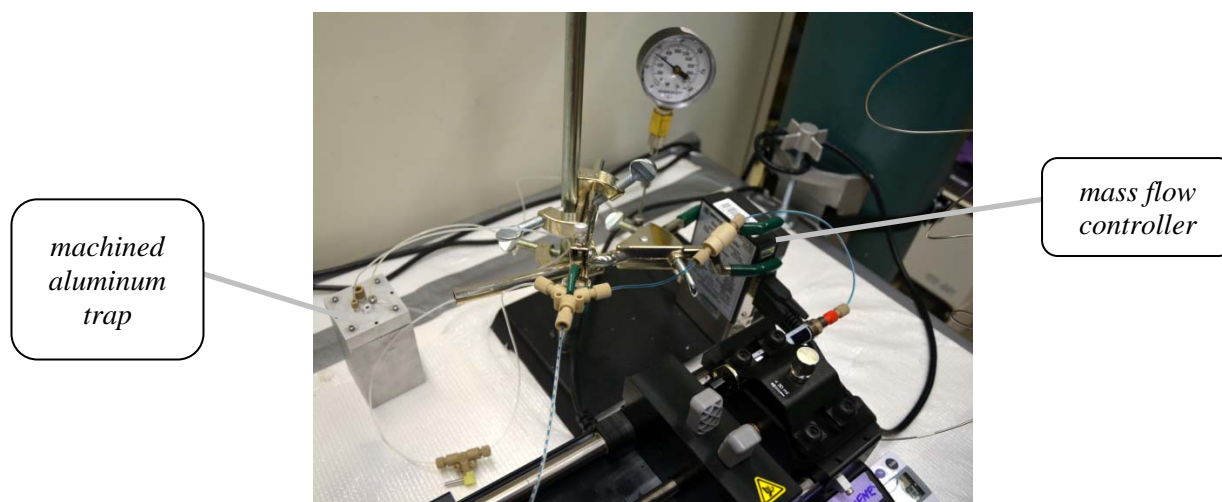


Figure S4: A. Demonstration of slug-flow (blue food coloring was added to the liquid phase).
B. Close-up of the reactor and the 6 way valve.

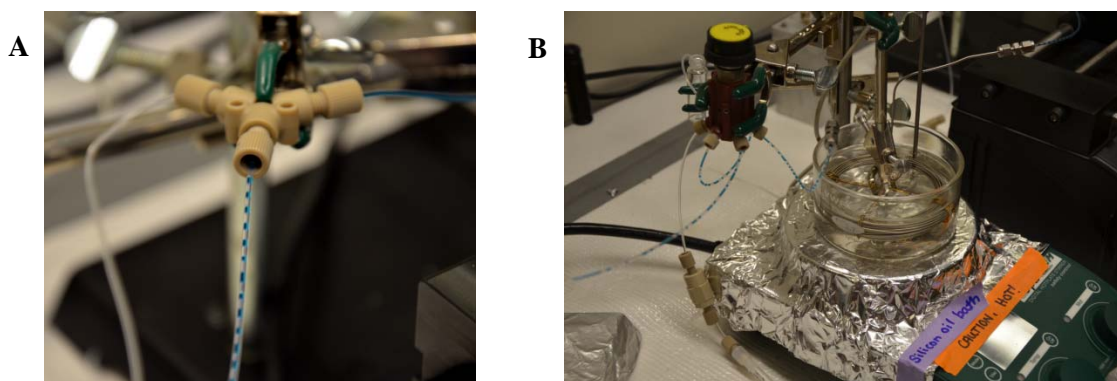
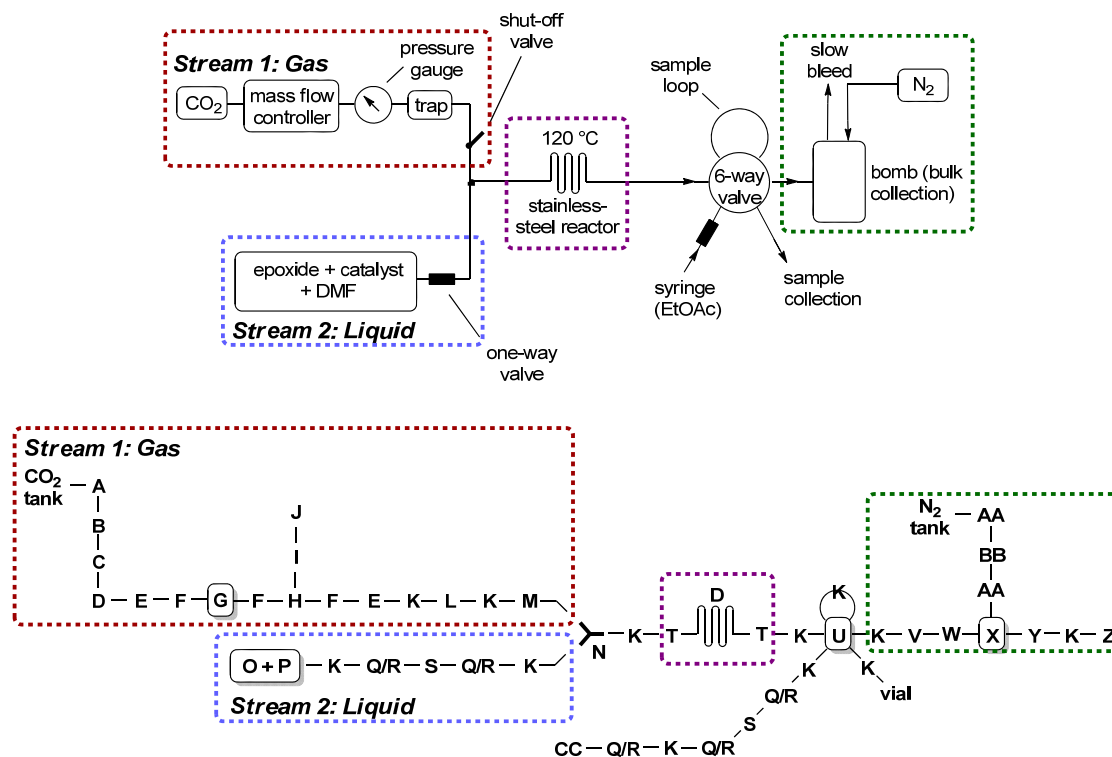


Table S1: Continuous flow apparatus components and order of construction



Item	Vendor	Part #	Part Description
A	Airgas	Y12215F320	two stage brass 0-400 psi general regulator
B	Swagelok	SS-4-HRCG-2	hex reducing coupling 1/4" female NPT x 1/8" female NPT
C	Swagelok	SS-100-1-2	tube fitting; male connector 1/16" tube OD x 1/8" male NPT
D	Upchurch Scientific	U-164	stainless steel tubing 1/16" x 0.030" ID x 25 ft
E	Swagelok	SS-200-6-1	tube fitting; reducing union 1/8" x 1/16" tube OD
F	McMaster-Carr	89895K114	SS Tubing 1/8" OD, .055" ID, .035" wall, 3" length
G	Sierra Instruments	C101-DD-1-OV1-SV1-PV2-V3-S3-C10	mass flow controller
H	Swagelok	SS-200-3	tube fitting; union tee 1/8" tube OD
I	Swagelok	SS-400-R-2	tube fitting; reducer 1/4" x 1/8" tube OD

J	Swagelok	PG1-63C-PG300-LAQX	0-300 psi gauge; ¼" tube ADP lower mount
K	Upchurch Scientific	1912L	Tubing, Teflon® HPFA; .030" x ⅛" x 50 ft
L	First Cut	-	machined aluminum pressure vessel (trap)
M	Upchurch Scientific	P-732	shut off valve
N	Upchurch Scientific	P-514	Y-connector; 0.060" thru hole
O	Harvard Apparatus	703305	PHD Ultra Remote RS485 Infuse only syringe pump
P	Harvard Apparatus	702267	8 mL stainless steel syringe with a ⅛" fitting
Q	Upchurch Scientific	P-255X	super flangeless nut, PEEK, natural
R	Upchurch Scientific	P-259X	super flangeless ferrule, ⅛", ETFE, yellow
S	Upchurch Scientific	CV-3330	check valve
T	Swagelok	SS-100-6	tube fitting, union, ⅛" tube OD
U	Upchurch Scientific	V-541	6-port injection valve
V	Swagelok	SS-102-1	nut for ⅛" Swagelok tube fitting
W	Swagelok	SS-100-7-2	tube fitting, female connector, ⅛" tube OD x ⅛" female NPT
X	Parr Instrument Company	4790 Model No. 4793	general purpose 100 mL pressure vessel (bomb)
Y	Swagelok	SS-200-6-1	tube fitting, reducing union, ⅛" x ⅛" tube OD
Z	Upchurch Scientific	P-445	micro metering valve
AA	Swagelok	SS-400-7-4	tube fitting, female connector ¼" tube OD x ¼" female NPT
BB	McMaster-Carr	5033K31	Teflon® PTFE ⅛" ID, ¼" OD, " ⅛" wall, semi-clear white
CC	Upchurch Scientific	P-628	adapter, female slip luer to female, TEFZEL® (ETFE)

Flow Reactor Preparation and Execution:

First, the CO₂ tank is pressurized to ~20 psi higher than the desired back-pressure of the system (120 psi). The aluminum trap must be pressurized and all the air expelled prior to the start of the reaction. To do this, the shut-off valve is closed and the mass flow controller set to purge. When the pressure gauge reads the same value as the CO₂ tank regulator gauge, it is fully pressurized. At this point the shut-off valve can be opened and closed to expel any air in the system. The back-pressure of the system (the nitrogen tank) is set to the desired pressure (~20 psi *lower* than that of the CO₂ tank, or 100 psi). An SGE syringe (10 mL) is filled with toluene and placed in the syringe pump. Once the back-pressure is set, the syringe pump is started (20 μ L/min) and the mass flow controller is switched from purge to the desired setting (in sccm or mL/min). The system will take approximately 15 minutes to equilibrate. During this time the reactor coil is brought to the desired temperature (120 °C) using a silicon oil bath, and the flow rates adjusted to obtain 1:1 v:v liquid/gas slug flow. The 6-way valve must be in the LOAD position.

Once a steady flow rate is observed, the SGE syringe is removed, and a Harvard Apparatus stainless steel (8 mL) syringe containing the reaction solution is attached. The system then must reach equilibrium. This is approximately four reactor volumes plus the volume of the reagent loop located on the 6-way valve. For example, if a reaction has a t_R of 30 minutes, the equilibration time is approximately 2 h. When the system has reached its equilibrium, a collection vial is placed under the sample collection tube, and the 6-way valve can be switched to the INJECT position. The vial must be in place as the pressurized CO₂ in the reagent loop will expel some of the liquid rapidly. A syringe filled with ethyl acetate then pushes out any remaining product into the vial. After the sample is collected, the 6-way valve can be switched back to LOAD. At this point, the parameters of the system can be changed and the process repeated.

Quantitative conversion and yields were obtained as follows:

Conversion: After collection of a sample from the 6-way valve, the tip of a pipette was used to remove ~2 μ L and transfer the liquid to suitable vial. The vial was filled with ethyl

acetate and GC analysis was performed. GC analysis provided quantitative data based on calibration graphs made using standardized solutions.

Yield: Due to non-linear effects observed for the cyclic carbonate product on the GC instrument, ^1H NMR was used to determine the yields of the products. After collection of a sample from the 6-way valve and removal of an aliquot for GC analysis, a known amount of the solution was accurately measured into a new vial. The solution was then diluted with ethyl acetate and water and brine added. After mixing the biphasic solution, a pipette was used to withdraw the organic layer, and filter it through a pipette containing sodium sulfate, into a 25 mL round-bottomed flask. The aqueous layer was extracted a further three times. The combined organic fractions were concentrated *in vacuo* to afford a brown liquid. A known amount of an external standard (trichloroethylene) was added to the round-bottomed flask, and the mixture was taken into CDCl_3 for ^1H NMR analysis.

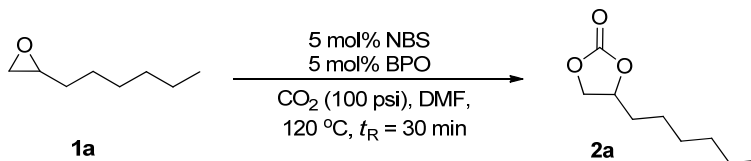
Batch Procedure for Cyclic Carbonate Formation:



4-Hexyl-1,3-dioxolan-2-one (**2a**)

The atmosphere of a large, septa-sealed test-tube reaction flask containing a solution of 0.10 mL of 1,2-epoxyoctane (**1a**, 0.65 mmol), 5.8 mg of NBS (0.033 mmol), 7.9 mg of benzoyl peroxide (0.033 mmol), and 8.3 mg of naphthalene (0.065 mmol) in 1.25 mL of *N,N*-dimethylformamide (0.44 M) was flushed with carbon dioxide (CO_2) gas. A full balloon of CO_2 was then attached. The reaction mixture was heated to $120\text{ }^\circ\text{C}$ and stirred for 6 h. The reaction mixture was cooled to rt and a small sample was removed for GC analysis. The remainder of the reaction mixture was poured into water and extracted three times with ethyl acetate. The combined organic fractions were washed four times with brine, dried over sodium sulfate, filtered, and concentrated by rotary evaporation *in vacuo* to afford a clear oil. The crude oil was purified by a Biotage flash purification system using a 10 g silica gel column (hexanes:ethyl acetate gradient) to afford 0.083 g (75%) of the title compound **2a** as a clear oil.

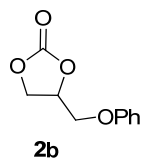
Representative Continuous Flow Procedure for Cyclic Carbonate Formation:



4-Hexyl-1,3-dioxolan-2-one (**2a**)

A 5 mL volumetric flask was charged with 1.5 mL of 1,2-epoxyoctane (**1a**, 10 mmol), 89 mg of NBS (0.5 mmol), 0.12 g of benzoyl peroxide (0.5 mmol), and 0.13 g of naphthalene (1.0 mmol). The volumetric flask was filled to the mark with anhydrous DMF (2 M). An 8 mL, stainless steel Harvard Apparatus syringe was filled with the solution and then attached to the flow apparatus (syringe pump). The flow apparatus itself was set up as described above. After approximately 4 *t_R*'s (~ 2 h), a sample was taken using the 6-way valve. The sample was analyzed by GC and ¹H NMR. GC analysis indicated 96% conversion whereas ¹H NMR analysis indicated a yield of 87% of the title compound **2a**.

IR (neat): 2928, 2859, 1788, 1384, 1165, 1059, 774 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 4.67 (qd, *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, 10H), 0.86 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 155.1, 77.1, 69.4, 33.9, 31.5, 28.8, 24.3, 22.5. HRMS (DART) *m/z* calcd for C₉H₂₀NO₃ [M+NH₄]⁺: 190.1438. Found: 190.1438.

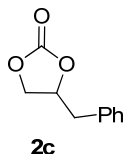


4-(Phenoxymethyl)-1,3-dioxolan-2-one (**2b**)

1,2-Epoxy-3-phenoxy propane (**1b**, 1.4 mL, 10 mmol), NBS (89 mg, 0.50 mmol), benzoyl peroxide (0.12 g, 0.50 mmol), and naphthalene (0.13 g, 1.0 mmol) were combined in a 5 mL volumetric flask according to the representative procedure. GC and ¹H NMR analysis of the final sample indicated 87% conversion and 86% yield to the title compound **2b**.

IR (solid film): 2927, 1783, 1600, 1490, 1396, 1161, 1081, 1009 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 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

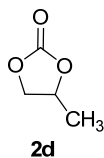
Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 157.8, 154.7, 129.7, 122.0, 114.6, 74.1, 66.9, 66.3. HRMS (DART) m/z calcd for $\text{C}_{10}\text{H}_{14}\text{NO}_4$ $[\text{M}+\text{NH}_4]^+$: 212.0917. Found: 212.0916.



4-Benzyl-1,3-dioxolan-2-one (2c)

(2,3-Epoxypropyl)benzene (**1c**, 1.3 mL, 10 mmol), NBS (89 mg, 0.50 mmol), benzoyl peroxide (0.12 g, 0.50 mmol) and naphthalene (0.13 g, 1.0 mmol) were combined in a 5 mL volumetric flask according to the representative procedure. GC and ^1H NMR analysis of the final sample indicated 93% conversion and 90% yield to the title compound **2c**.

IR (neat): 2920, 1782, 1394, 1159, 1055 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.33-7.23 (m, 3H), 7.21-7.15 (m, 2H), 4.89 (dq, $J = 13.3, 6.6$ Hz, 1H), 4.39 (dd, $J = 8.6, 7.9$ Hz, 1H), 4.12 (dd, $J = 8.6, 6.9$ Hz, 1H), 3.09 (dd, $J = 14.2, 6.3$ Hz, 1H), 2.95 (dd, $J = 14.2, 6.6$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 154.9, 134.0, 129.4, 129.0, 127.6, 76.9, 68.6, 39.5. HRMS (DART) m/z calcd for $\text{C}_{10}\text{H}_{14}\text{NO}_3$ $[\text{M}+\text{NH}_4]^+$: 196.0968. Found: 196.0967.

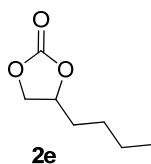


Propylene carbonate (2d)

Propylene oxide (**1d**, 0.70 mL, 10 mmol), NBS (89 mg, 0.50 mmol), benzoyl peroxide (0.12 g, 0.50 mmol), and naphthalene (0.13 g, 1.0 mmol) were combined in a 5 mL volumetric flask according to the representative procedure. ^1H NMR analysis of the final sample indicated 81% yield to the title compound **2d**.³

IR (neat): 2989, 1780, 1388, 1352, 1172, 1117, 1041, 774 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 4.85-4.73 (m, 1H), 4.49 (dt, $J = 8.4, 7.3$ Hz, 1H), 4.01-3.89 (m, 1H), 1.46-1.35 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 155.4, 73.9, 70.9, 19.5. HRMS (DART) m/z calcd for $\text{C}_4\text{H}_{10}\text{NO}_3$ $[\text{M}+\text{NH}_4]^+$: 120.0655. Found: 120.0658.

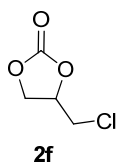
³ GC analysis of the reaction mixture was not taken due to the low boiling point of the starting material.



4-Butyl-1,3-dioxolan-2-one (**2e**)

1,2-epoxyhexane (**1e**, 1.2 mL, 10 mmol), NBS (89 mg, 0.50 mmol), benzoyl peroxide (0.12 g, 0.50 mmol), and naphthalene (0.13 g, 1.0 mmol) were combined in a 5 mL volumetric flask according to the representative procedure. ¹H NMR analysis of the final sample indicated 83% yield to the title compound **2e**.⁴

IR (neat): 2932, 2867, 1785, 1384, 1166, 1058, 774 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 4.68 (qd, *J* = 7.5, 5.6 Hz, 1H), 4.50 (t, *J* = 8.1 Hz, 1H), 4.04 (dd, *J* = 8.3, 7.3 Hz, 1H), 1.86-1.72 (m, 1H), 1.69-1.62 (m, 1H), 1.51-1.27 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 155.1, 69.4, 33.6, 26.5, 22.3, 13.8. HRMS (DART) *m/z* calcd for C₇H₁₆NO₃ [M+NH₄]⁺: 162.1125. Found: 162.1124.

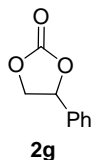


4-(Chloromethyl)-1,3-dioxolan-2-one (**2f**)

Epichlorohydrin (**1f**, 0.78 mL, 10 mmol), NBS (89 mg, 0.50 mmol), benzoyl peroxide (0.12 g, 0.50 mmol), and naphthalene (0.13 g, 1.0 mmol) were combined in a 5 mL volumetric flask according to the representative procedure. ¹H NMR analysis of the final sample indicated 78% yield to the title compound **2f**.³

IR (neat): 2967, 1779, 1395, 1158, 1066 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 5.02-4.90 (m, 1H), 4.55 (t, *J* = 8.6 Hz, 1H), 4.35 (dd, *J* = 8.9, 5.7 Hz, 1H), 3.78 (dd, *J* = 12.3, 4.9 Hz, 1H), 3.68 (dd, *J* = 12.3, 3.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 154.5, 74.5, 67.0, 44.1. HRMS (DART) *m/z* calcd for C₄H₉NO₃Cl [M+NH₄]⁺: 154.0265. Found: 154.0259.

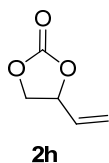
⁴ GC analysis was not performed due to the signal of 1,2-epoxyhexane (**1e**) overlapping with DMF.



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

Styrene oxide (**1g**, 1.1 mL, 10 mmol), NBS (89 mg, 0.50 mmol), benzoyl peroxide (0.12 g, 0.50 mmol), and naphthalene (0.13 g, 1.0 mmol) were combined in a 5 mL volumetric flask according to the representative procedure. ¹H NMR analysis of the final sample indicated 72% yield to the title compound **2g**.⁵

IR (neat): 1784, 1670, 1160, 1050 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.44-7.36 (m, 3H), 7.36-7.28 (m, 2H), 5.64 (t, *J* = 8.0 Hz, 1H), 4.7867 (t, *J* = 8.4 Hz, 1H), 4.30 (dd, *J* = 8.6, 7.9 Hz, 1H). ¹³C NMR (100 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.

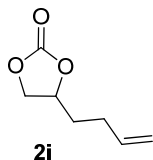


4-Vinyl-1,3-dioxolan-2-one (2h)

3,4-Epoxybutene (**1h**, 0.81 mL, 10 mmol), NBS (90 mg, 0.50 mmol), benzoyl peroxide (0.12 g, 0.50 mmol), and naphthalene (0.13 g, 1.0 mmol) were combined in a 5 mL volumetric flask according to the representative procedure. ¹H NMR analysis of the final sample indicated 52% yield to the title compound **2h**.³

IR (neat): 2992, 1781, 1384, 1325, 1159, 1052, 770 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 5.85 (ddd, *J* = 17.3, 10.4, 6.9 Hz, 1H), 5.45 (dd, *J* = 17.1, 6.8 Hz, 1H), 5.38 (dd, *J* = 10.4, 0.7, 1H), 5.08 (q, *J* = 7.5 Hz, 1H), 4.55 (t, *J* = 8.3 Hz, 1H), 4.10 (t, *J* = 8.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 155.0, 132.4, 121.3, 77.5, 69.2. HRMS (DART) *m/z* calcd for C₅H₁₀NO₃ [M+NH₄]⁺: 132.0655. Found: 132.0653.

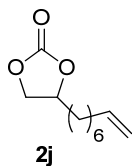
⁵ GC analysis was not taken due to odd behavior of styrene oxide (**1g**) on the instrument.



4-(But-3-en-1-yl)-1,3-dioxolan-2-one (**2i**)

1,2-Epoxy-5-hexene (**1i**, 1.1 mL, 10 mmol), NBS (89 mg, 0.50 mmol), benzoyl peroxide (0.12 g, 0.50 mmol), and naphthalene (0.13 g, 1.0 mmol) were combined in a 5 mL volumetric flask according to the representative procedure. ^1H NMR analysis of the final sample indicated 58% yield to the title compound **2i**.³

IR (neat): 1783, 1384, 1165, 1056, 914, 773 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 5.72 (ddt, J = 17.0, 10.2, 6.7 Hz, 1H), 5.07-4.91 (m, 2H), 4.67 (qd, J = 7.7, 5.2 Hz, 1H), 4.47 (t, J = 8.2 Hz, 1H), 4.02 (dd, J = 8.5, 7.2 Hz, 1H), 2.29-1.99 (m, 2H), 1.85 (dtd, J = 14.1, 8.1, 5.9 Hz, 1H), 1.78-1.61 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 155.2, 136.3, 116.5, 76.6, 69.5, 33.2, 28.8. HRMS (DART) m/z calcd for $\text{C}_7\text{H}_{14}\text{NO}_3$ $[\text{M}+\text{NH}_4]^+$: 160.0968. Found: 160.0968.

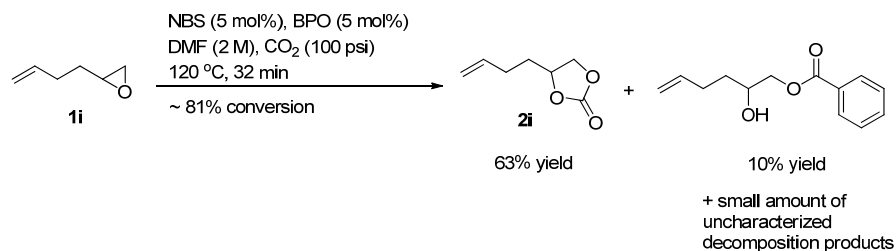


4-(oct-7-en-1-yl)-1,3-dioxolan-2-one (**2j**)

1,2-Epoxy-9-decene (**1j**, 1.8 mL, 10 mmol), NBS (89 mg, 0.50 mmol), benzoyl peroxide (0.12 g, 0.50 mmol), and naphthalene (0.13 g, 1.0 mmol) were combined in a 5 mL volumetric flask according to the representative procedure. ^1H NMR analysis of the final sample indicated 51% yield to the title compound **2j**.³

IR (neat): 2927, 2857, 1790, 1385, 1163, 1059, 909 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 5.73 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 4.93 (ddd, J = 17.1, 3.6, 1.6, 1H), 4.87 (ddt, J = 10.2, 2.2, 1.2 Hz, 1H), 4.64 (qd, J = 7.5, 5.4 Hz, 1H), 4.47 (d, J = 8.0 Hz, 1H), 4.00 (dd, J = 8.4, 7.2 Hz, 1H), 2.04-1.94 (m, 2H), 1.79-1.68 (m, 1H), 1.68-1.56 (m, 1H), 1.51-1.14 (m, 8H). ^{13}C NMR (100 MHz, CDCl_3): δ 155.3, 139.0, 114.5, 77.3, 69.6, 34.0, 33.8, 29.1, 28.9, 28.8. HRMS (DART) m/z calcd for $\text{C}_{11}\text{H}_{22}\text{NO}_3$ $[\text{M}+\text{NH}_4]^+$: 216.1594. Found: 216.1589.

Continuous Reaction with Alkene-Containing Epoxide **1i**:



Yield and conversion based on crude ¹H NMR using naphthalene as the internal standard.

We did not observe any products in which the alkene has been reacted (e.g., bromination). The lower yield was mainly caused by the lower conversion compared with epoxyoctane (**1a**).

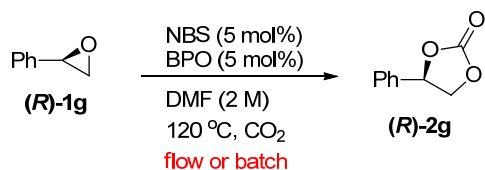
Solvent Studies:

Table S2: Solvent screen

entry	solvent	conversion (%) ^a	yield (%) ^a	notes
1	THF	-	-	
2	acetonitrile	-	-	
3	toluene	-	-	NBS not soluble
4	DMF	100	99	
5	DMA	100	96	
6	NMP	43	53	
7	DMSO	21	16	
8	hexanes	-	-	NBS not soluble
9	MeOH	-	-	
10	EtOH	-	-	
11	acetone	-	-	
12	EtOAc	-	-	
13	propylene carbonate	-	-	

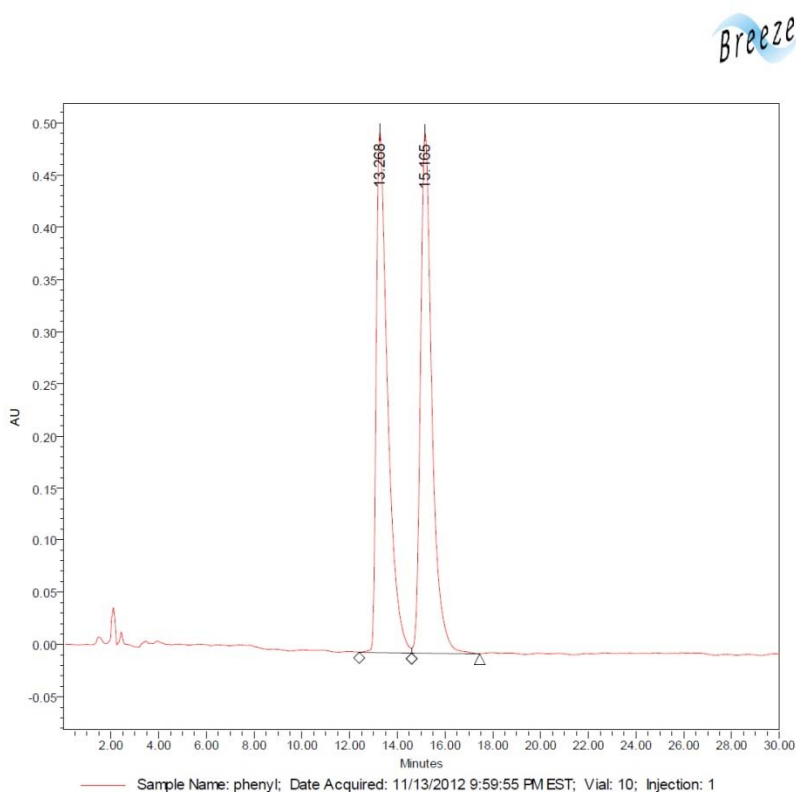
^a Determined by GC analysis.

Analysis of Enantiopure Epoxides:



Reactions were conducted in both flow and batch conditions, and the *ee* of the product in each case was determined by chiral HPLC measurement using ChiralCel OD, 10% IPA/hexanes, 1 mL/min, t_R =13.2 min, t_S =15.2 min. Partial racemization of the products relative to the starting materials was observed under both flow and batch conditions (flow 76% *ee*; batch 50% *ee*).

Chiral HPLC analysis of racemic **2g**:



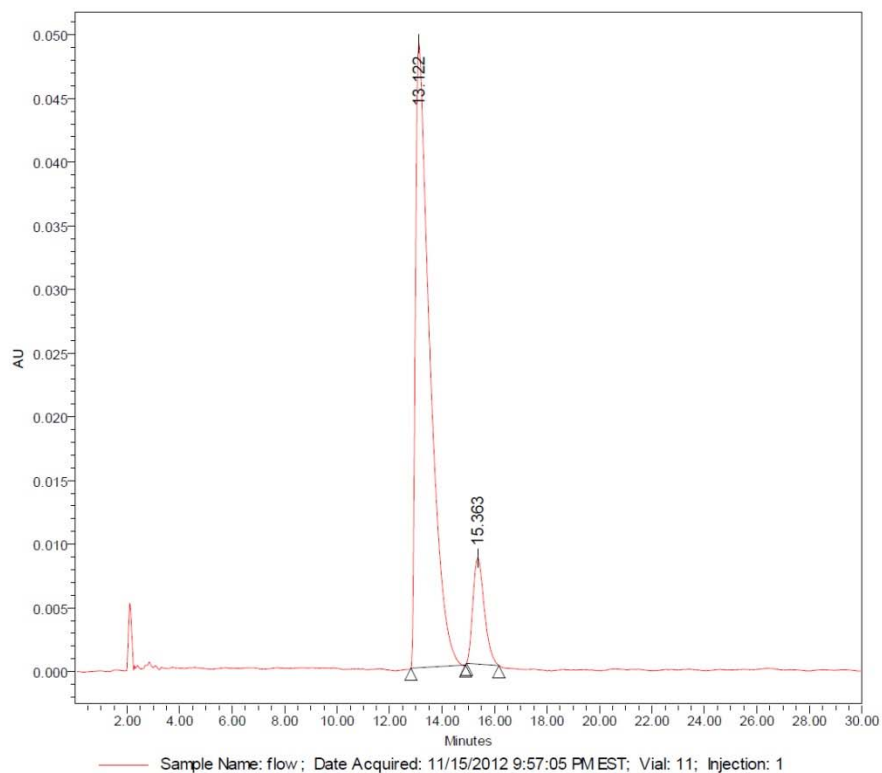
Peak Summary with Statistics

Peak Name:

	Sample Name	Vial	Inj.	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	phenyl	10	1	13.268	16574615	49.95	498995
2	phenyl	10	1	15.165	16607730	50.05	498640
Mean				14.216	16591172.514		498817.583
Std. Dev.				1.342	23415.452		251.57
% RSD				9.44	0.14		0.050

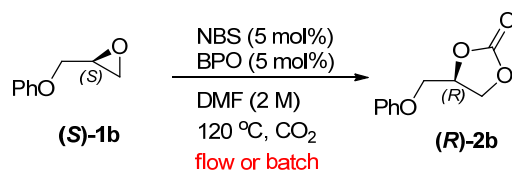
Chiral HPLC measurement of (*R*)-2g obtained from flow condition:

Breeze



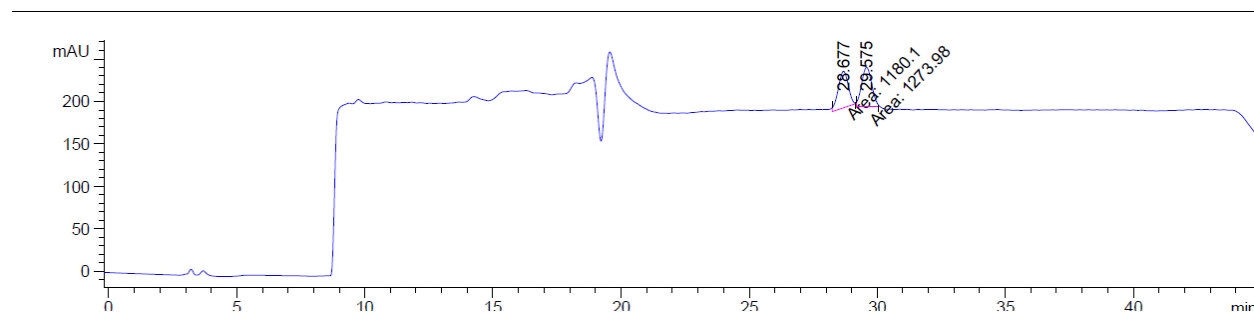
Peak Summary with Statistics
Peak Name:

	Sample Name	Vial	Inj.	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	flow	11	1	13.122	1876630	88.18	49041
2	flow	11	1	15.363	251650	11.82	8342
Mean				14.243	1064140.103		28691.128
Std. Dev.				1.585	1149034.219		28778.47
% RSD				11.13	107.98		100.304

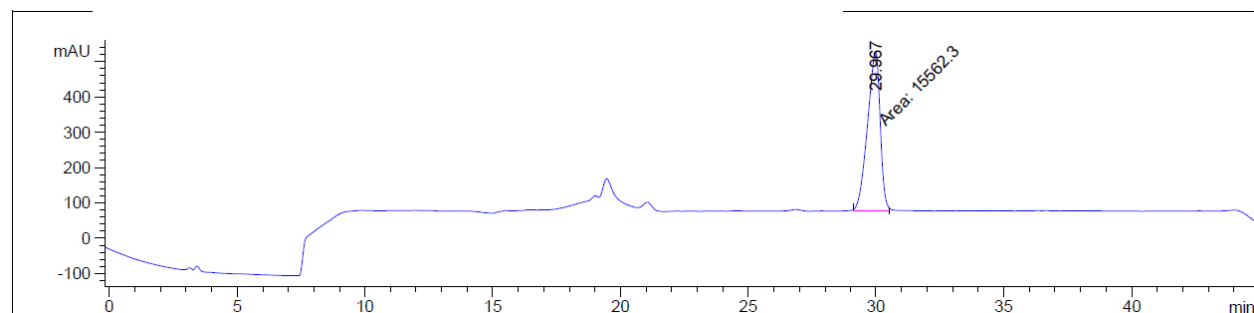


Reactions were conducted in both flow and batch conditions, and *ee* of the product in each case was determined by chiral HPLC measurement using ChiralCel AD, 6% IPA/hexanes, 1 mL/min, $t_R=29.6$ min, $t_S=28.7$ min. The enantioenrichment of the starting epoxide was full transferred into the carbonate product under both flow and batch conditions (flow >99% *ee*; batch >99% *ee*).

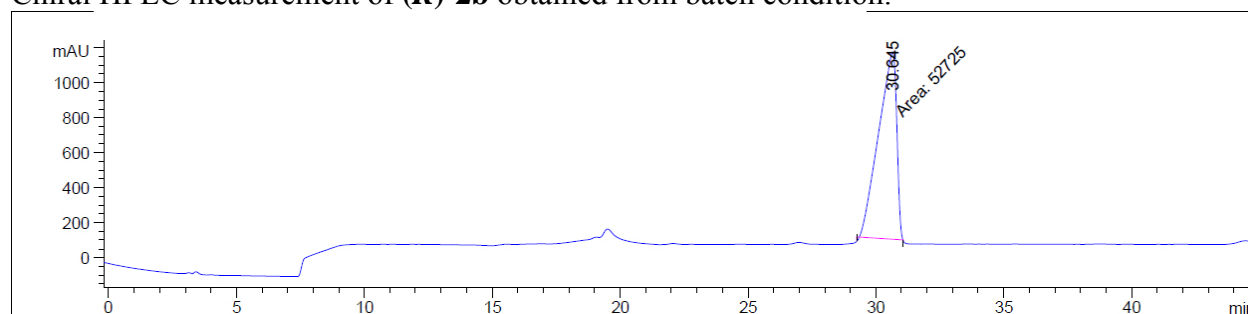
Chiral HPLC analysis of racemic **2b**:



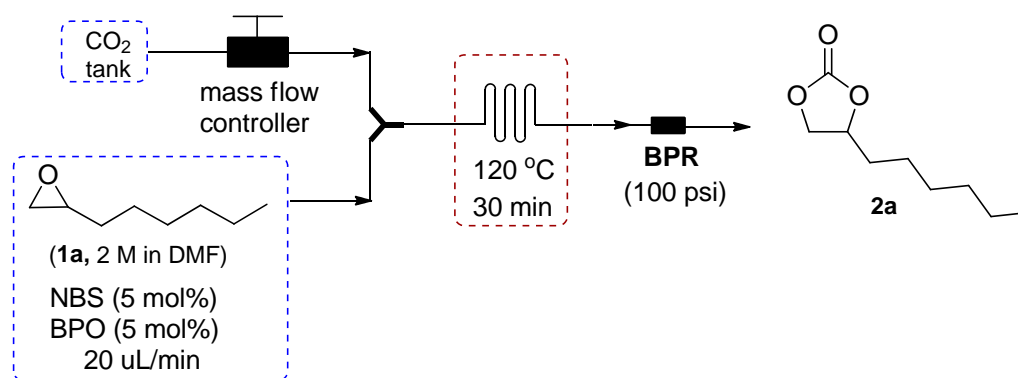
Chiral HPLC measurement of (**R**)-**2b** from flow experiment:



Chiral HPLC measurement of (*R*)-**2b** obtained from batch condition:

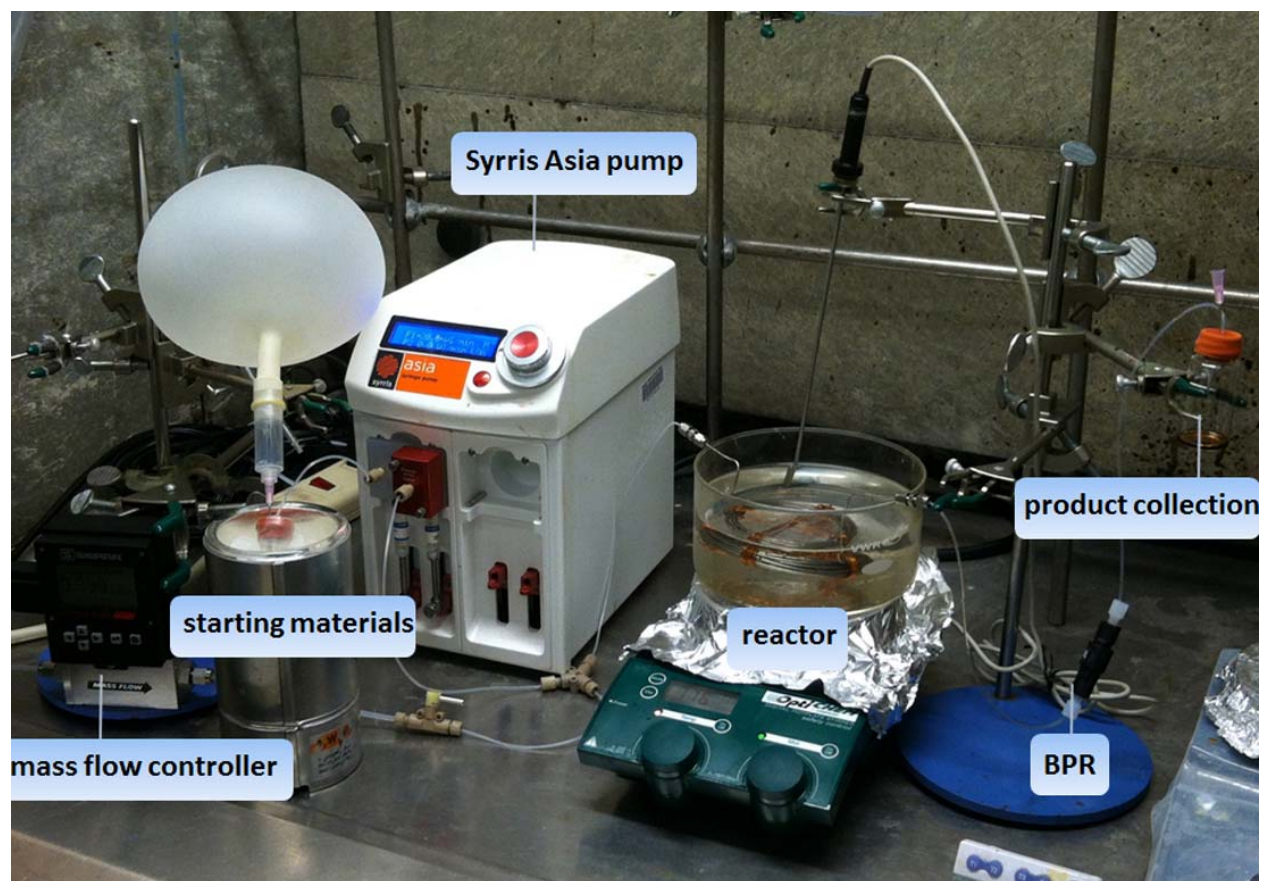


Representative Continuous Flow Procedure for the Long Term Product Collection:



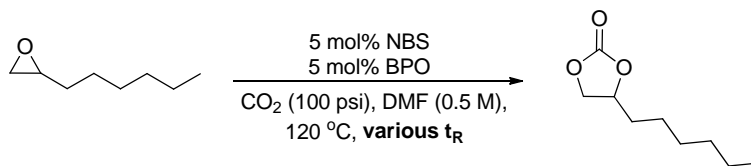
A 50 mL volumetric flask was charged with 890 mg of NBS (5 mmol, 5 mol%), 1.21 g of benzoyl peroxide (5 mmol, 5 mol%) and 20 mL DMF. 15.25 mL of 1,2-epoxyoctane (**1a**, 100 mmol, 1 equiv) was slowly added into the mixture at 0 °C. The volumetric flask was filled to the mark with anhydrous DMF (2 M) and then the solvent was transferred to a 100 mL round bottom flask and kept at 0 °C under N₂ balloon. The flow apparatus itself was set up as shown in the Figure S5. A Syrris Asia pump was pumped with the solution at 20 uL/min flow rate, and the CO₂ gas rate was adjusted to achieve a 30 min residence time. After approximately 4 *t_R*'s (~ 2 h), the product was collected for 14 hours. Then water and Et₂O was added and the organic layer was collected. The water layer was extracted with Et₂O twice. The organic phase was combined and dried over Na₂SO₄. The solution was then filtered and concentrated. Further purification was performed using a Biotage Isolera One flash purification system to afford the desired cyclic carbonate product **2a** 5.77 g (82% yield).

Figure S5: The modified continuous flow system for long-term product collection



Kinetics Experiments:

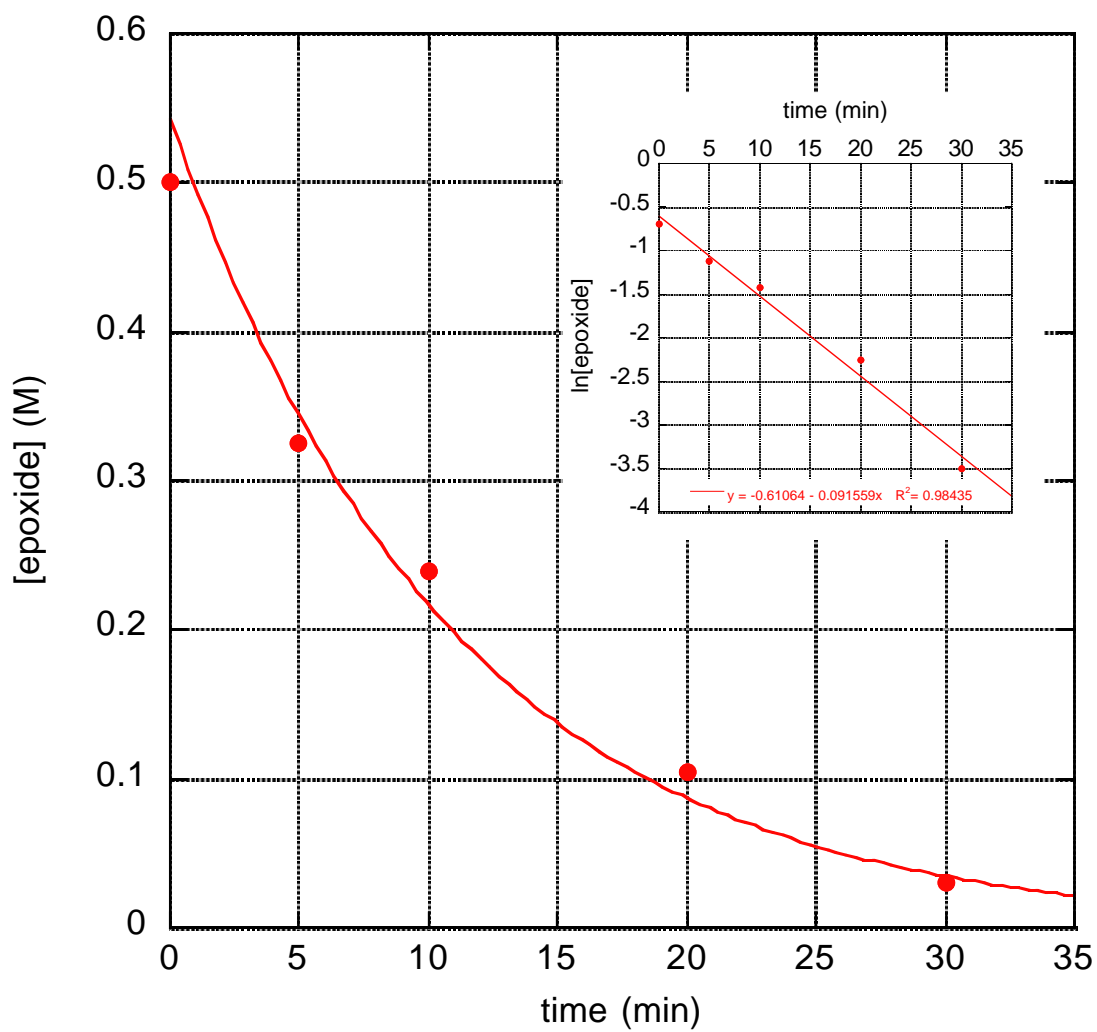
Chart S1: Kinetic order with respect to the concentration of epoxide.



Entry	Reaction time	Conversion	Yield of product
1	5 min	35 %	34 %
2	10 min	52 %	50 %
3	20 min	79 %	75 %
4	30 min	94 %	90 %
5	40 min	99 %	93 %

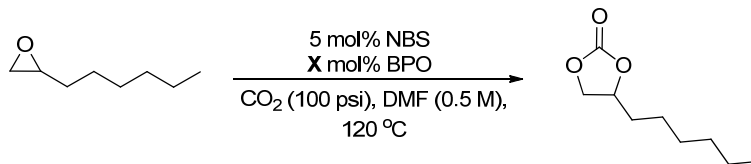
$$\text{rate} = -\frac{d[\text{epoxide}]}{dt} = k_{\text{obs}}[\text{epoxide}]$$

$$\ln[\text{epoxide}]_t = \ln[\text{epoxide}]_o - k_{\text{obs}}t$$



Based on our kinetic study, we propose that the reaction is first order with respect to the concentration of epoxide.

Chart S2: Kinetic order with respect to benzoyl peroxide (BPO; initiator):



$$\text{rate} = -\frac{d[\text{epoxide}]}{dt} = k_{\text{obs}}[\text{epoxide}]$$

$$\ln[\text{epoxide}]_t = \ln[\text{epoxide}]_0 - k_{\text{obs}}t$$

0.1 mol% BPO (0.0005 M)		0.25 mol% BPO (0.00125 M)		1 mol% BPO (0.005 M)	
t_R (min)	epoxide concentration (M)	t_R (min)	epoxide concentration (M)	t_R (min)	epoxide concentration (M)
0	0.5	0	0.5	0	0.5
2.6	0.47	2.75	0.46	3.42	0.43
3.5	0.45	3.4	0.44	4.3	0.4
5.87	0.405	5.84	0.39	8.12	0.275
8.5	0.355	9.67	0.32	11.75	0.24

2.5 mol% BPO (0.0125 M)		0 mol% BPO (0 M)	
t_R (min)	epoxide concentration (M)	t_R (min)	epoxide concentration (M)
0	0.5	0	0.5
2.67	0.415	2.33	0.48
3.38	0.375	3.47	0.46
5.77	0.28	5.63	0.425
9.33	0.20	8.83	0.345

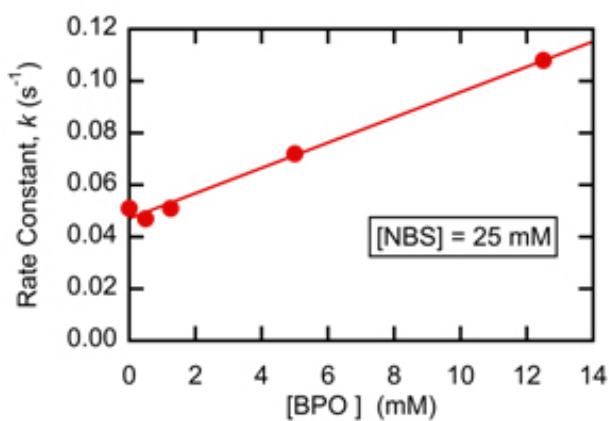
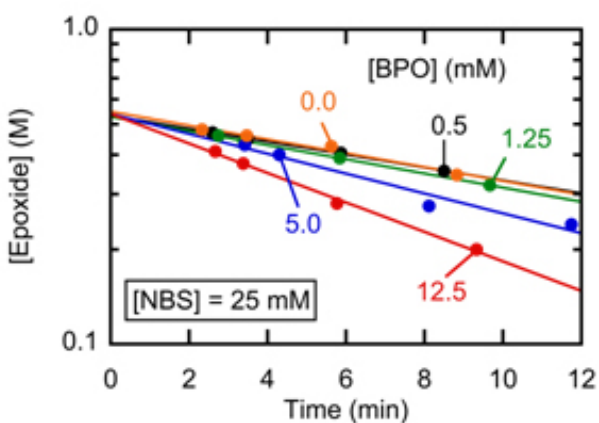
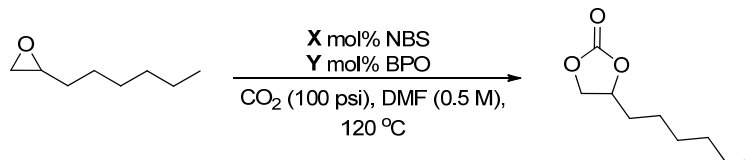


Chart S3: Kinetic order with respect to *N*-bromosuccinimide (NBS; catalyst):



$$\text{rate} = -\frac{d[\text{epoxide}]}{dt} = k_{\text{obs}}[\text{epoxide}]$$

$$\ln[\text{epoxide}]_t = \ln[\text{epoxide}]_o - k_{\text{obs}}t$$

First order reaction with respect to NBS : $k_{\text{obs}} \propto [\text{NBS}]$

2.5% BPO, 1% NBS (0.0125 M BPO, 0.005 M NBS)		2.5% BPO, 2.5% NBS (0.0125 M BPO, 0.0125 M NBS)		2.5% BPO, 5% NBS (0.0125 M BPO, 0.025 M NBS)	
t_R (min)	epoxide concentration (M)	t_R (min)	epoxide concentration (M)	t_R (min)	epoxide concentration (M)
0	0.5	0	0.5	0	0.5
2.58	0.475	2.63	0.47	2.67	0.415
3.33	0.465	3.2	0.455	3.38	0.375
5	0.44	5.17	0.4	5.77	0.28
7.5	0.41	7.67	0.355	9.33	0.2

1% BPO, 1% NBS (0.005 M BPO, 0.005 M NBS)		1% BPO, 2.5% NBS (0.005 M BPO, 0.0125 M NBS)		1% BPO, 5% NBS (0.005 M BPO, 0.025 M NBS)	
t_R (min)	epoxide concentration (M)	t_R (min)	epoxide concentration (M)	t_R (min)	epoxide concentration (M)
0	0.5	0	0.5	0	0.5
2.76	0.49	2.83	0.485	3.42	0.43
3.42	0.485	3.42	0.475	4.3	0.4
5.91	0.475	5.1	0.43	8.12	0.275
9.15	0.46	7.83	0.4	11.75	0.24

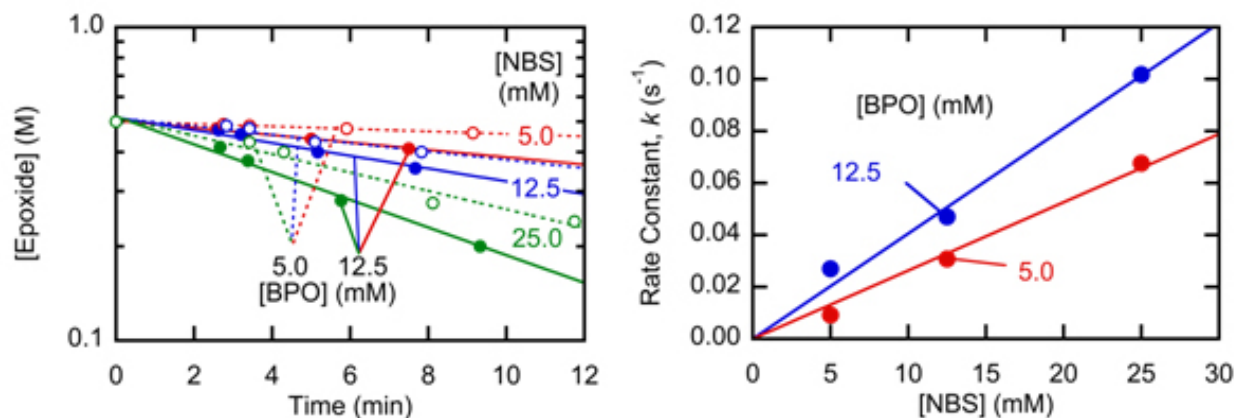
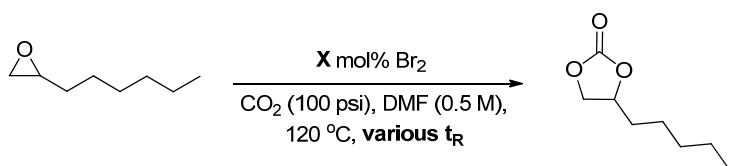


Chart S4: Kinetic order with respect to Br₂:



5 mol% Br ₂ (0.025 M)		2.5 mol% Br ₂ (0.0125 M)		1 mol% Br ₂ (0.005 M)		10 mol% Br ₂ (0.05 M)	
t_R (min)	epoxide concentration (M)	t_R (min)	epoxide concentration (M)	t_R (min)	epoxide concentration (M)	t_R (min)	epoxide concentration (M)
0	0.5	0	0.5	0	0.5	0	0.5
2.67	0.37	2.67	0.44	2.68	0.475	3	0.22
3.58	0.345	3.28	0.425	3.20	0.47	3.42	0.19
5.67	0.295	5.00	0.39	5.02	0.46	5.87	0.11
7.77	0.25	8.1	0.35	7.83	0.45	9	0.07

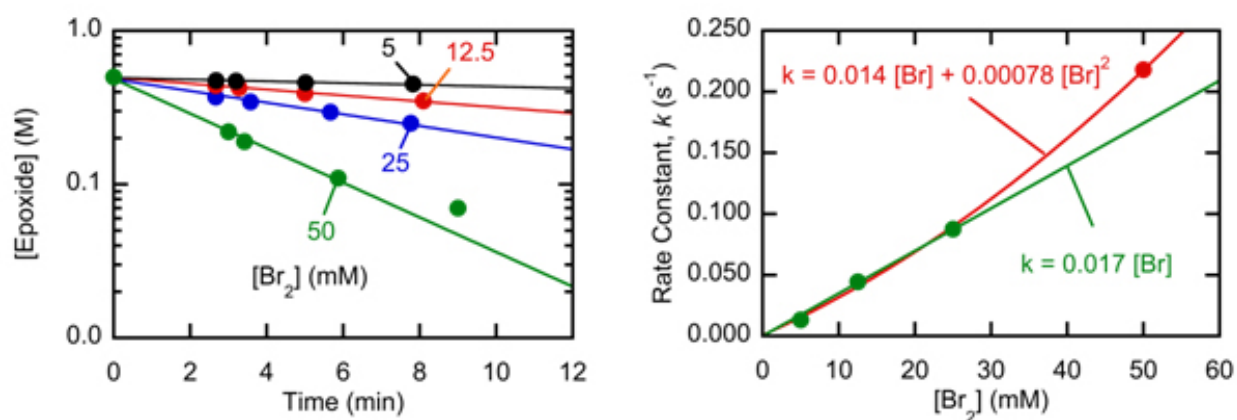
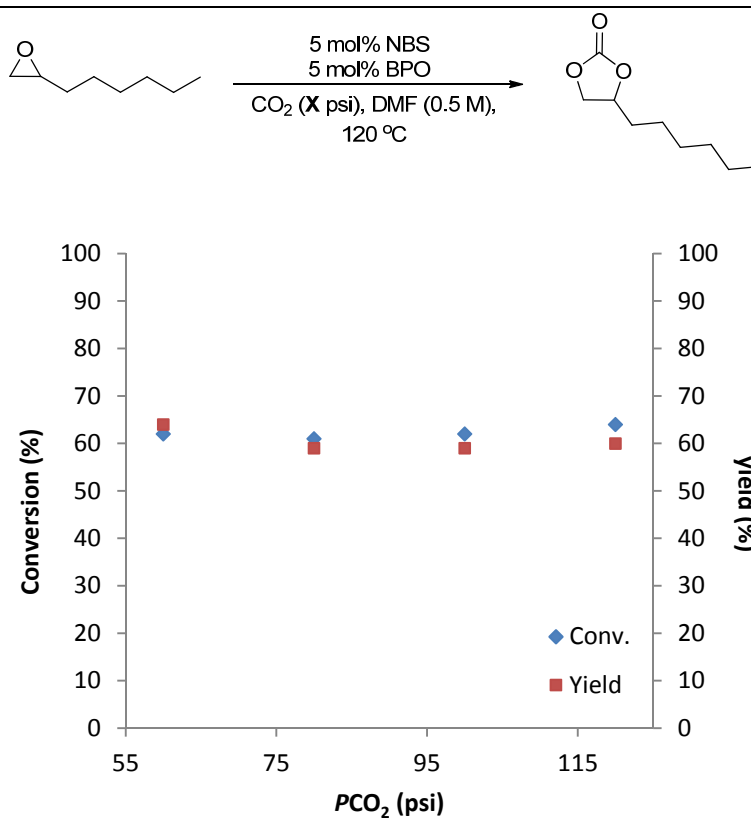


Chart S5: Effect of CO₂ pressure on the yield of the reaction.



[CO ₂] (psi)	Conversion (%)	Yield (%)
60	62	64
80	61	59
100	62	59
120	64	60

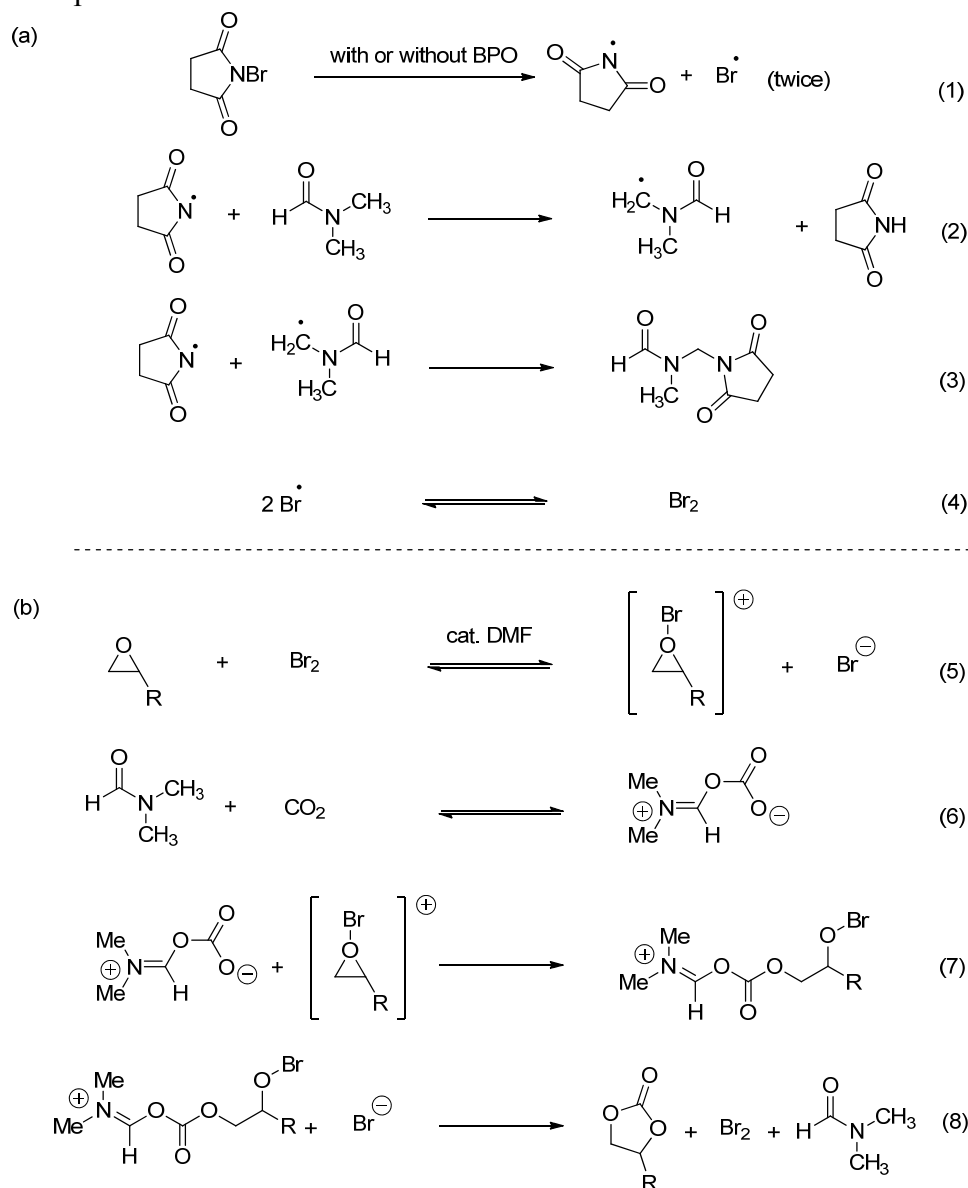
The pressure of the CO₂ (between pressures of 60 and 120 psi) did not significantly affect the final concentration of the epoxide (or the overall yield of the reaction).⁶

⁶ Ji, C.; Gong, L.; Zhang, J.; Shi, K. *J. Nat. Gas. Chem.* **2003**, *12*, 201-204.

Kinetics Analysis:

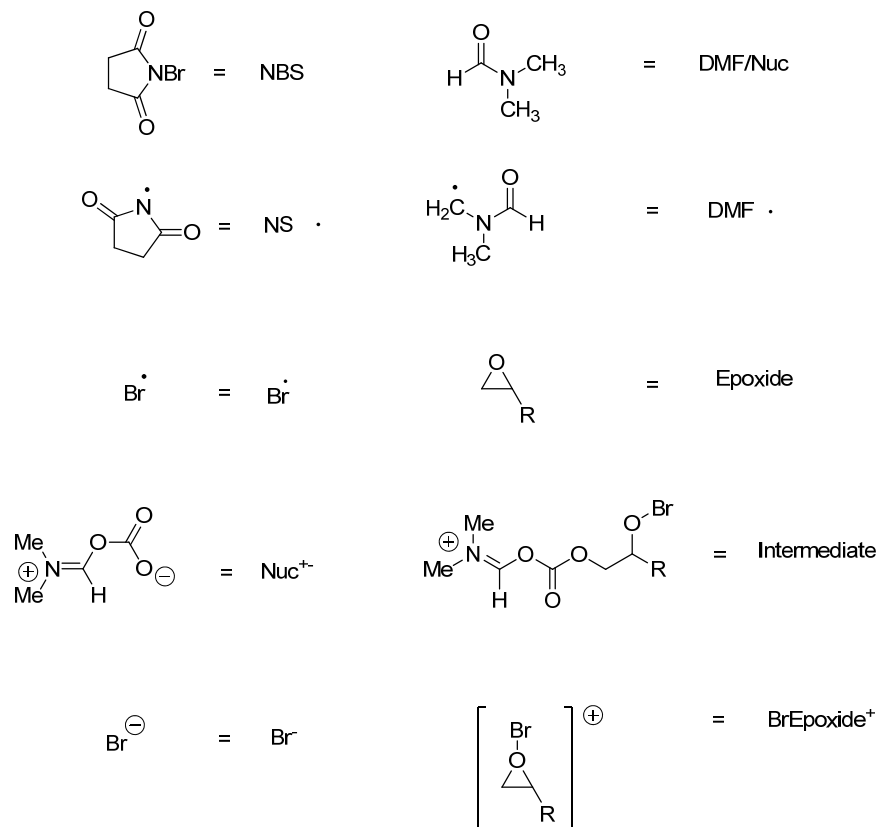
The reaction scheme proposed below (Scheme S1, Reactions 1-8) uses the equation labeling which will be used throughout the supporting info which different from the main text, to make the derived equations more clear. Part (a) of the scheme describes the NBS activation and the suggested route for generation of Br₂, whereas Part (b) describes the epoxide transformation to carbonate.

Scheme S1. Proposed reaction mechanism



The following symbol scheme is used to simplify the mathematical derivation:

Scheme S2. Symbol notation



The kinetic model was solved by performing the mass balance on each of the intermediates of the reaction that were assumed to be at pseudo-steady state. The rate equations (Equations 1-8) for each of the elementary steps were simplified as follows:

$$r_1 = (k_{o1} + k_1[BPO])[NBS] \quad (1)$$

$$r_2 = k_2[NS \cdot] \quad (2)$$

$$r_3 = k_3[NS \cdot][DMF \cdot] \quad (3)$$

$$r_4 = k_4[Br \cdot]^2 - k_{r3}[Br_2] \quad (4)$$

$$r_5 = k_5[Br_2][Epoxide] \quad (5)$$

$$r_6 = k_6[Nuc][CO_2] \quad (6)$$

$$r_7 = k_7[Nuc^{\pm}][BrEpoxide^+] \quad (7)$$

$$r_8 = k_8[Br^-][Intermediate] \quad (8)$$

The quasi-steady state approximation is applied to reactive intermediates which are transient, and these include the radicals and high energy intermediates $NS\cdot$, $DMF\cdot$, $Br\cdot$, Nuc^\pm , $BrEpoxide^+$, Br^- , *Intermediate*):

$$\frac{d[NS\cdot]}{dt} = r_1 - r_2 - r_3 = 0 \quad (9)$$

$$\frac{d[Br\cdot]}{dt} = r_1 - 2r_4 = 0 \quad (10)$$

$$\frac{d[DMF\cdot]}{dt} = r_2 - r_3 = 0 \quad (11)$$

$$\frac{d[BrEpoxide^+]}{dt} = r_5 - r_7 = 0 \quad (12)$$

$$\frac{d[Nuc^\pm]}{dt} = r_6 - r_7 = 0 \quad (13)$$

$$\frac{d[Intermediate]}{dt} = r_7 - r_8 = 0 \quad (14)$$

$$\frac{d[Br^-]}{dt} = r_5 - r_8 = 0 \quad (15)$$

We solve the system of algebraic equations (Equations 9-15) for the unknown intermediate concentrations, which includes $[Br\cdot]$. Reaction 4 is assumed to be at quasi-equilibrium, which we use to calculate effective concentrations for bromine $[Br_2]$ from equation (16). We assume the reaction of the epoxide with the bromine is the rate determining step (reaction 5):

$$[Br_2] = \frac{k_4}{k_{r4}} [Br\cdot]^2 \quad (16)$$

After substituting for $[Br\cdot]$ from the intermediate solution, and solving the equilibrium equation (16), we obtain:

$$[Br_2] = \frac{k_{r4}(k_1[BPO] + k_{10})}{2(k_4^2 - k_{r4}^2)} [NBS] \quad (17)$$

By assuming that the overall rate law is reaction 5, and substituting the solution from equation (17) into (18) we obtain:

$$r_{overall} = k_4[epoxide][Br_2] \quad (18)$$

$$r_{overall} = \frac{k_4 k_{r4} [NBS] [Epoxide] [k_1[BPO] + k_{10}]}{2(k_4^2 - k_{r4}^2)} \quad (19)$$

In the above derived theoretical expression for the overall rate law (Equation 19), the $[BPO]$ concentration was constant due its catalytic role. The NBS concentration was assumed to be approximately constant due to the slow rate of Br_2 production relative to the kinetics of carbonate formation. This may be potentially due to a faster rate of reaction 5 relative to reaction 4. In addition, the succinimide radical was reported to be unlikely a highly reactive radical,⁷ causing its attack on the solvent to be a very slow termination reaction, which would hold back our Br_2 production rate (k_2 and $k_3 \ll k_4$).

⁷ Walling, C.; El-Taliawi, G. M.; Zhao, C. *J. Am. Chem. Soc.* **1983**, *105*, 5119-5124.

Supporting Thermodynamic Calculation for Estimating Effective Br₂ Concentration in the Liquid Phase:

From Henry's law for dilute concentrations, we can relate the liquid concentration of bromine c_{Br_2} to the equilibrium partial pressure of bromine P_{Br_2} by the Henry constant H_{Br_2} :

$$c_{Br_2} = H_{Br_2} P_{Br_2} \quad (20)$$

Since we had a two phase system (liquid solvent and gas slug), and since bromine was initially presented only in the liquid phase, we can perform a total bromine mass balance relative to the initial liquid concentration of Br₂ injected (which we denote by $c_{o,liq}$):

$$V_{liq} c_{o,liq} = V_{liq} c_{eq,liq} + V_{gas} c_{eq,gas} \quad (21)$$

In which V_{liq} and V_{gas} were the liquid and gas volumes respectively, and $c_{eq,liq}$ and $c_{eq,gas}$ were the equilibrium Br₂ concentrations in each of the phases. This can also be written in terms of the void fraction $\phi = V_{liq}/V_{gas}$:

$$c_{o,liq} = c_{eq,liq} + \phi c_{eq,gas} \quad (22)$$

By assuming the ideal-gas law for the bromine in the gas bubble, we had that:

$$c_{o,liq} = c_{eq,liq} + \frac{\phi P_{eq}}{RT} \quad (23)$$

If we substituted Henry's law and re-write in terms of the equilibrium liquid concentration, we had:

$$c_{eq,liq} = \frac{c_{o,liq}}{\left(1 + \frac{\phi}{RT H_{Br_2}}\right)} \quad (24)$$

For an aqueous system, $H_{Br_2} \approx 0.04 \text{ M/atm} \approx 4 \cdot 10^{-6} \text{ M/Pa}$ (from data for 25°C).⁸ Due to the lack experimental data for Br₂ solubility in DMF, we used the Henry's constant from Br₂ in water as a starting point due to its polar nature. Br₂ was known to be more soluble in organic solvents, and from a partition coefficient of 27 between CCl₄ and water (*Perry's Chemical Engineering Handbook, 6th edition*), we estimated its Henry's constant in CCl₄ to be around 0.000108 M/Pa. A 10 mol% of Br₂ corresponds to $c_{o,liq} = 0.05 \text{ M}$, which from equation (24) gave us an effective bromine concentration in water of $c_{eq,water} = 0.000971 \text{ M}$ and $c_{eq,CCl_4} = 0.01745 \text{ M}$, by assuming $\phi = 0.5$ and the temperature being 25 °C.

⁸ Bartlett, W.P.; Margerum, D. W. *Env. Sci. Tech.* **1999**, 33, 3410.

^1H and ^{13}C NMR Spectra:

