

Electronic Supplementary Information

Hydrophobically-enhanced “on water” cycloaddition of CO₂ to long-chain terminal epoxides

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Experimental Section

Materials

1,2-Epoxydodecane (> 95%, TCI), 1,2-epoxydecane (> 97%, TCI), 1,2-epoxyoctane (> 96%, TCI), 1,2-epoxy-9-decene (> 96%, TCI), glycidyl hexadecyl ether (\geq 79.5%, Sigma Aldrich), tetrabutylammonium iodide (TBAI, > 98%, TCI), tetrabutylammonium chloride (TBAC, \geq 97.0%, Merck), tetrabutylammonium bromide (TBAB, > 99%, Acros Organics), triethylamine (Et₃N, 99%, Merck), *N,N*-dimethyldodecylamine (DDA, > 96%, TCI), *n*-hexadecane (HD, 99%, Acros Organics), *n*-octane (> 98.5%, Carlo Erba), dichloromethane (DCM, 99%, Chemex), ethyl alcohol (EtOH, > 99%, Duksan), ethyl acetate (EtOAc, 99%), *n*-hexane (99%, Chemex), *N,N*-dimethylformamide extra dry (DMF, 99.8%, Acros Organics), diethyl ether (Et₂O, 99.5%, Qrec), sodium dodecyl sulfate (SDS, 99%, Acros Organics), chloroform-d₁ (CDCl₃, 99.8%, CIL), hexadecylamine (> 95%, TCI), iodomethane stabilized with silver (99%, Merck), and *N,N*-dimethylacetamide dimethyl acetal stabilized with 5-10% methanol (> 90%, TCI) were used as received. Deionized water was used throughout the research work.

Synthesis of hexadecyltrimethylammonium iodide

Hexadecyltrimethylammonium iodide (CTAI) was synthesized according to a previous report [67]. hexadecylamine (1g, 4.14 mmol) was dissolved in 6.8 mL of DMF and iodomethane (0.77 mL, 12.42 mmol) was added to this solution, followed by stirring at 25 °C for 12 h. Then, the reaction mixture was diluted with Et₂O and stirred for 30 min. The mixture was filtrated, washed with Et₂O and then dried at 45 °C under vacuum for 24 h to yield a white product (405 mg, 24% yield). ¹H NMR spectroscopy (CDCl₃, 600 MHz): δ 3.61 – 3.36 (m, 11H), 1.85 – 1.70 (m, 2H), 1.45 – 1.20 (m, 26H), and 0.88 ppm (t, *J* = 7.0 Hz, 3H).

Synthesis of cyclic carbonates in emulsion

In general, epoxide (1.63 mmol), TBAI (3 mol% relative to the epoxide), and *N,N*-dimethyl dodecylamine (8.9 mM in water) were mixed in a 50 mL sealed centrifugal tube and bubbled with a rubber balloon containing ~ 2 L of CO₂ under ice-cooling for 15 min to ensure that the DDA formed a carbonate. Unless otherwise stated, the ratio between epoxide and water was 0.125 w/w. Then, the mixture was sonicated under ice-cooling in a pulse regime (3 s on, 1 s off) at 50% amplitude for 4 min (Hielscher Ultrasonic Processor UP200St) to form a miniemulsion and transferred to a 50 mL one-neck round bottom flask. The round bottom flask was sealed, and CO₂ was added to the reaction mixture by inserting a long needle connecting with the CO₂ rubber balloon. Part of CO₂ was used to flush the flask to displace air through a second needle before the reaction. The reaction vessel was heated at 60 °C and stirred at 700 rpm for 24 h. Afterwards, the reaction mixture was placed in a separatory funnel and extracted 4 times with 25 mL of dichloromethane. The organic layer was then placed into a 50 mL one-neck round bottom flask and the crude product was obtained by evaporation of solvents with a rotary evaporator. An aliquot of the crude product after evaporation was taken for determining for conversion and selectivity by ¹H NMR spectroscopy. All reactions were conducted at least in duplicate. The products were purified by column chromatography (*n*-hexane:ethyl acetate = 5:1 except for 1,2-epoxydodecane for which we used 9:1 ratio). The cyclic carbonate products (**2a-2d**) were isolated as colorless liquids.

Emulsion preparation for synthesis of 4-((hexadecyloxy)methyl)-1,3-dioxolan-2-one

For the synthesis of 4-((hexadecyloxy)methyl)-1,3-dioxolan-2-one (**2e**), a slightly modified procedure was employed: Glycidyl hexadecyl ether (486 mg, 1.63 mmol), TBAI (18 mg, 3 mol% relative to the epoxide), *N,N*-dimethyl dodecylamine (7.39 mg, 8.9 mM in aqueous solution), and water were mixed in a 50 mL one-neck round bottom flask at 60 °C for 5 min. The reaction was conducted at 60 °C for 18 h. The emulsion was then transferred to a separating funnel, and isolated by adding 2 mL of brine and extracted four times with 20 mL of ethyl acetate. Finally, the crude product was concentrated by evaporation of solvent with a rotary evaporator. A sample of 50 mg of the crude reaction mixture dissolved in 750 μ L CDCl₃ was used to determine the conversion and selectivity of the reaction by ¹H-NMR spectroscopy. The crude product was then mixed with silica gel in acetone/dichloromethane (1:9) at a stirring speed of 400 rpm for 3 h. Afterwards, the product was passed through filter paper by using dichloromethane as the mobile phase and the carbonate was obtained as white solid after removing the solvent by rotary evaporation.

Upscaling of 4-hexyl-1,3-dioxolan-2-one synthesis by CO₂ cycloaddition reaction

The reaction was upscaled 25 times according to the aforementioned procedure. The product was purified via column chromatography (*n*-hexane : ethyl acetate = 20:1 to 5:1) according to a previous report [68]. The carbonated product (**2c**) was isolated as colorless liquid (5.95 g, 85% yield).

Analytical tools

¹H NMR spectra were recorded with a nuclear magnetic resonance spectrometer (600 MHz, Avance III HD, Bruker) at 299 K and the spectra were analyzed with the Bruker Topspin 4.0.7 software. All experiments were repeated two times and averaged. 50 μ L of the emulsions were

diluted in 2 mL water in a quartz cuvette for measuring the hydrodynamic diameter of the droplets by dynamic light scattering (DLS, NanoPlus-3, Micromeritics) with a laser wavelength of 660 nm and a detection angle at 165°. Fourier transform infrared spectra of crude products were recorded on a PerkinElmer Frontier spectrometer with the attenuated total reflection mode at a resolution of 4 cm⁻¹ over wavenumbers from 4000 to 400 cm⁻¹. Interfacial tension was measured with a spinning drop tensiometer (SIT2000B model, LabGeni). 500 µL of a mixture containing 4-hexyl-1,3-dioxolan-2-one, 1,2-epoxyoctane and water (0.125 w/w oil/water) were injected in a glass tube placed in a horizontal position and subsequently rotated at an angular velocity of 5000 rpm at 25 °C. The ratios between 4-hexyl-1,3-dioxolan-2-one and 1,2-epoxyoctane were 0:0.2, 23:177, 4:16, 115:85 and 195:5.0:0.2, 23:177, 4:16, 115:85 and 195:5 w:w. The interfacial tension γ was calculated from the drop radius r perpendicular to the axis of rotation, the angular frequency of the rotation ω , and the density difference between the two phases $\Delta\rho$ following the equation: $\gamma = (r^3 \omega^2 \Delta\rho) / 4$. Experiments were performed in triplicates.

Determination of the conversion

The conversion of long-chain alkyl epoxides **1a-1e** was determined from ¹H NMR spectroscopy measurements from the ratio of the integrals of OCH₂CHR protons in the starting material (*Ha*), the carbonated product (*Hb*) and the diol product (*Hc*) according to **Equation S1** below and to the chemical shifts reported in **Table S1**.

Equation S1. Conversion as calculated from the intensities (I_H) of the corresponding signals of OCH₂CHR protons in the starting material (*Ha*), cyclic carbonate product (*Hb*) and diol by-product (*Hc*).

$$\text{Conversion (\%)} = \frac{I_{Hb} + I_{Hc}}{(I_{Ha} + I_{Hb} + I_{Hc})} \times 100 \quad \text{Eq. (S.1)}$$

Scheme S1. CO₂ conversion with epoxides into cyclic carbonates.

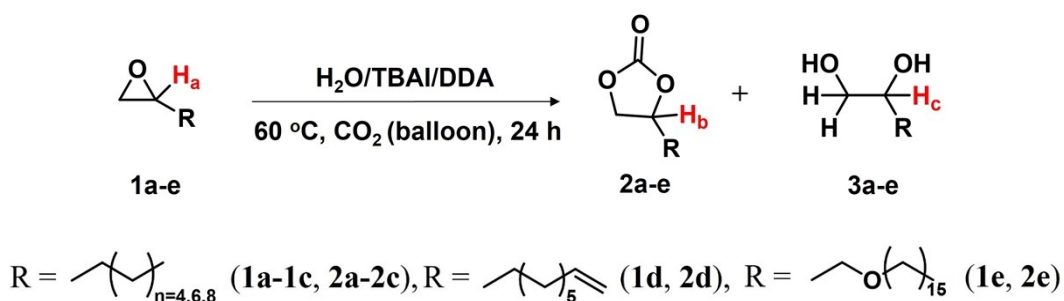


Table S1. Chemical shifts (δ , ppm, CDCl₃) for the corresponding OCH₂CHR protons in the epoxides, cyclic carbonate products and diol by-product. See also the ¹H NMR spectra in the following section.

Entry	d Ha (ppm)	d Hb (ppm)	d Hc (ppm)
1a/2a/3a	2.90	4.70	3.39
1b/2b/3b	2.90	4.69	3.48
1c/2c/3c	2.90	4.69	3.23
1d/2d/3d	2.90	4.97	3.23
1e/2e/3e	3.08	4.76	3.79

Determination of the selectivity

The selectivity for the carbonate product was determined via ¹H NMR from the ratio of the integrals of the protons of carbonated product (*Hb*) and diol by-product (*Hc*) shown in Scheme S1 according to **Equation S2**. The selectivity was calculated from the integral values (I) of the RHCOCOOCH₂ protons in cyclic carbonate product (*Hb*) and RHC(OH)COHH₂ protons in diol by-product (*Hc*).

$$\text{Selectivity of cyclic carbonates (\%)} = \frac{I_{Hb}}{(I_{Hb} + I_{Hc})} \times 100 \quad \text{Eq. (S.2)}$$

¹H NMR of byproduct in crude products

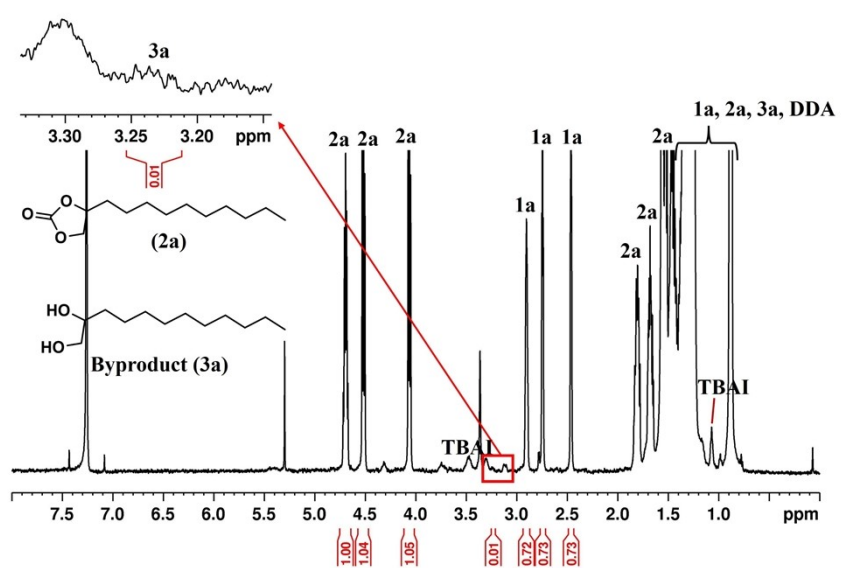


Fig. S1. Crude ¹H-NMR spectrum of **2b** obtained by cycloaddition of 1,2-epoxydodecane with CO₂ in miniemulsion for 15 h (CDCl₃).

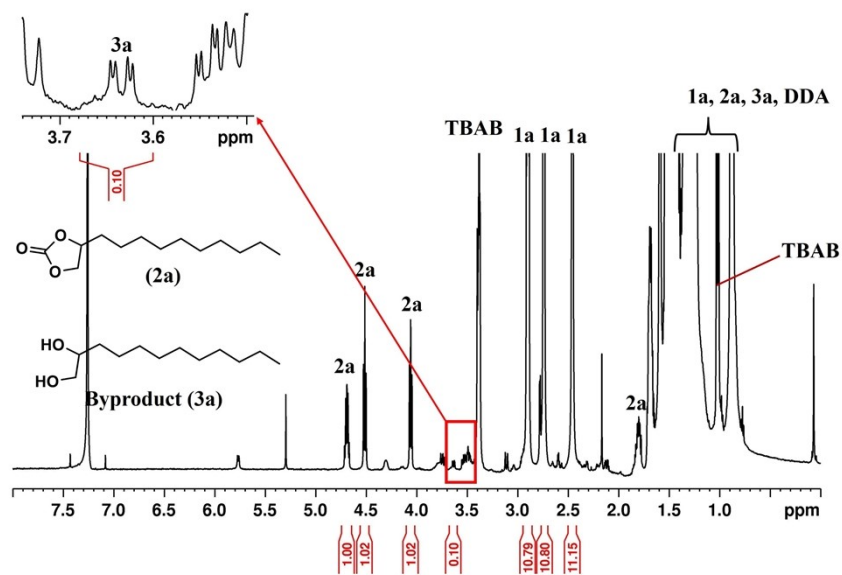


Fig. S2. Crude ¹H-NMR spectrum of **2b** obtained by cycloaddition of 1,2-epoxydodecane with CO₂ in miniemulsion using tetrabutylammonium bromide for 15 h (CDCl₃).

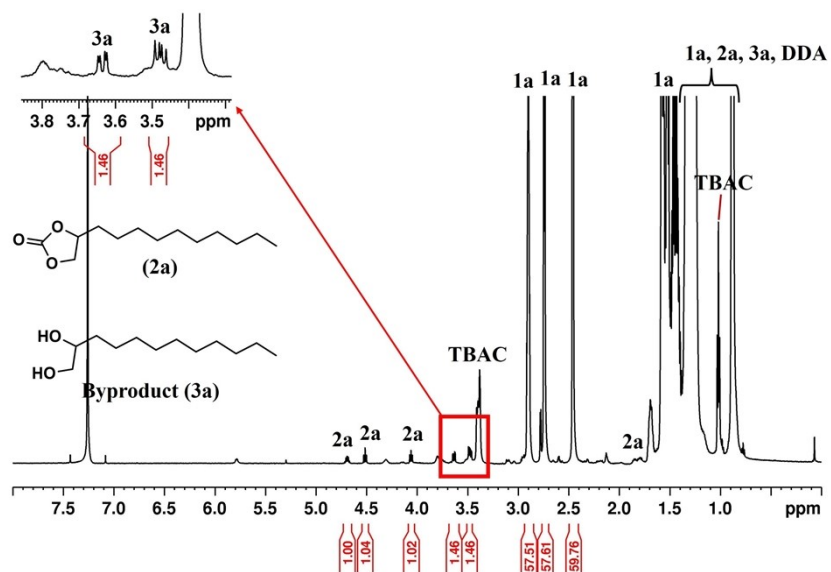


Fig. S3. Crude ¹H-NMR spectrum of **2b** obtained by cycloaddition of 1,2-epoxydodecane with CO₂ in miniemulsion using tetrabutylammonium chloride for 15 h (CDCl₃).

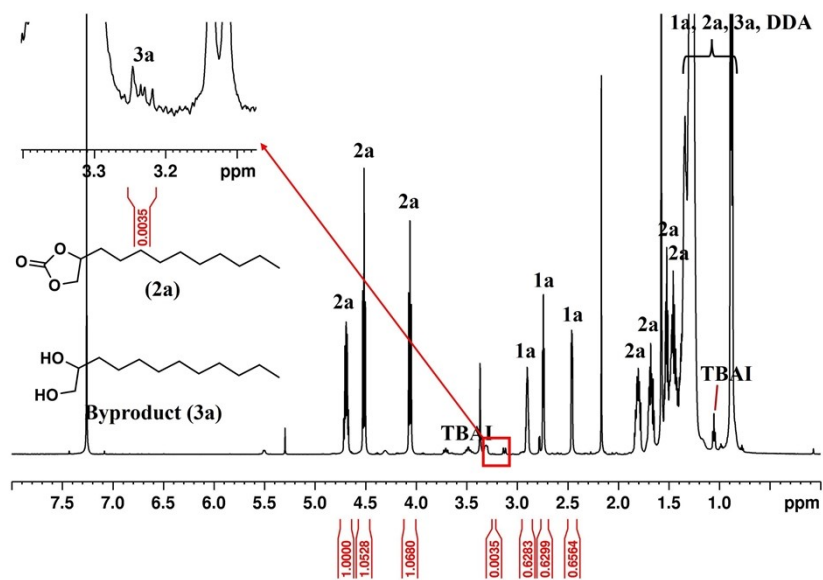


Fig. S4. Crude ¹H-NMR spectrum of **2b** obtained by cycloaddition of 1,2-epoxydodecane with CO₂ in miniemulsion at a stirring rate of 300 rpm for 15 h (CDCl₃).

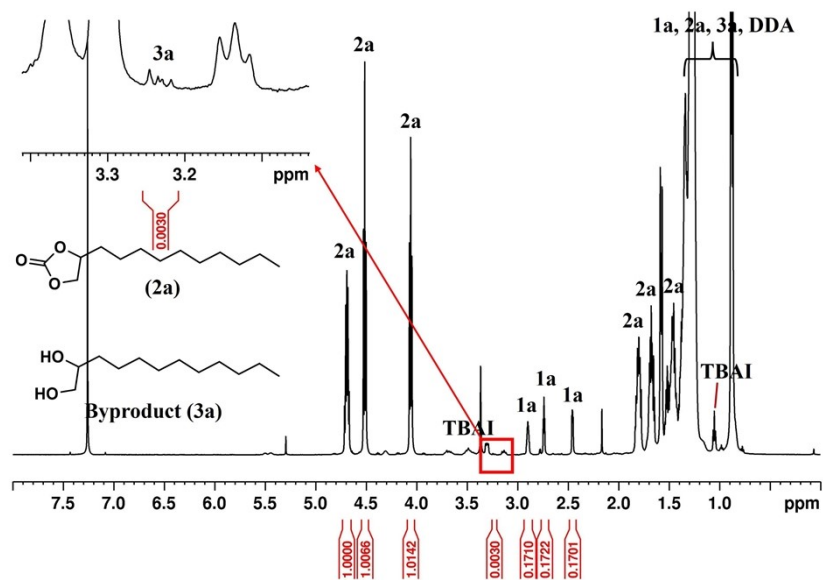


Fig. S5. Crude ¹H-NMR spectrum of **2b** obtained by cycloaddition of 1,2-epoxydodecane with CO₂ in miniemulsion at a stirring rate of 1000 rpm for 15 h (CDCl₃).

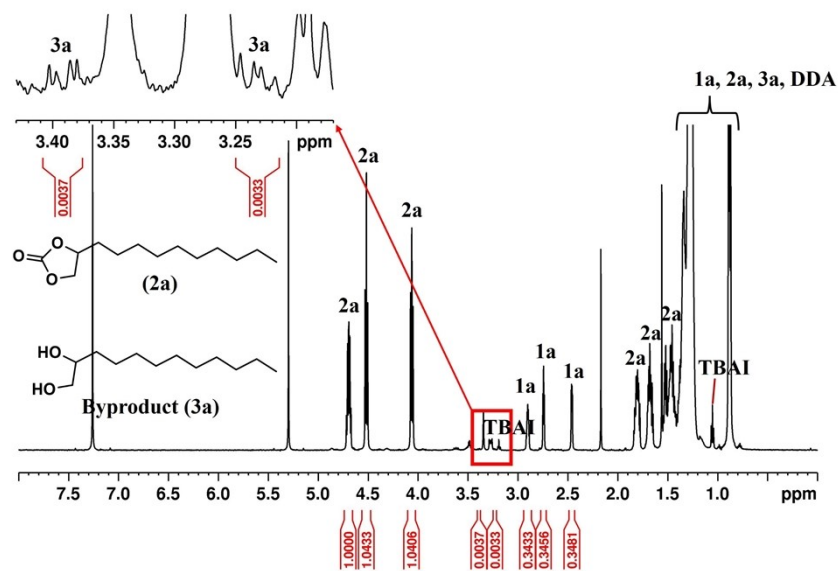


Fig. S6. Crude $^1\text{H-NMR}$ spectrum of **2b** obtained by cycloaddition of 1,2-epoxydodecane with CO_2 in miniemulsion using water/epoxide ratio to 4:1 (w/w) (CDCl_3).

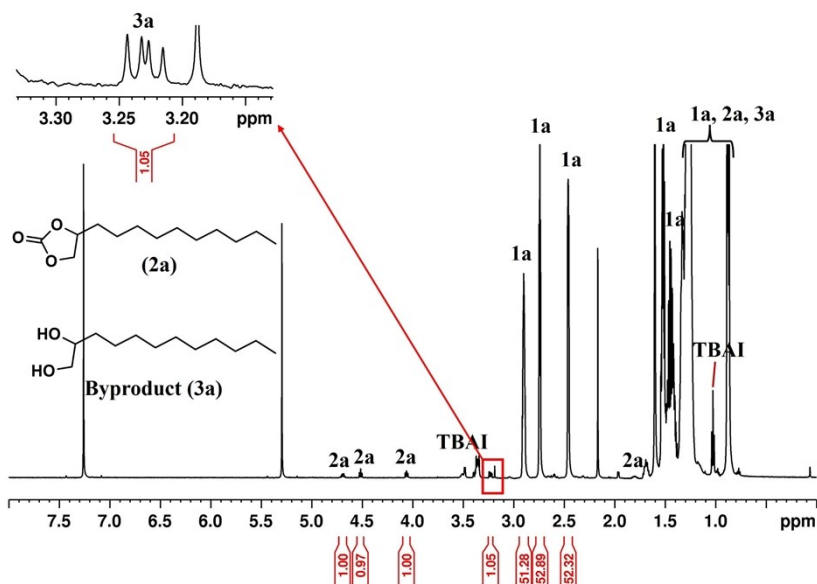


Fig. S7. Crude $^1\text{H-NMR}$ spectrum of **2a** obtained by cycloaddition of 1,2-epoxydodecane with CO_2 in non-emulsion (CDCl_3).

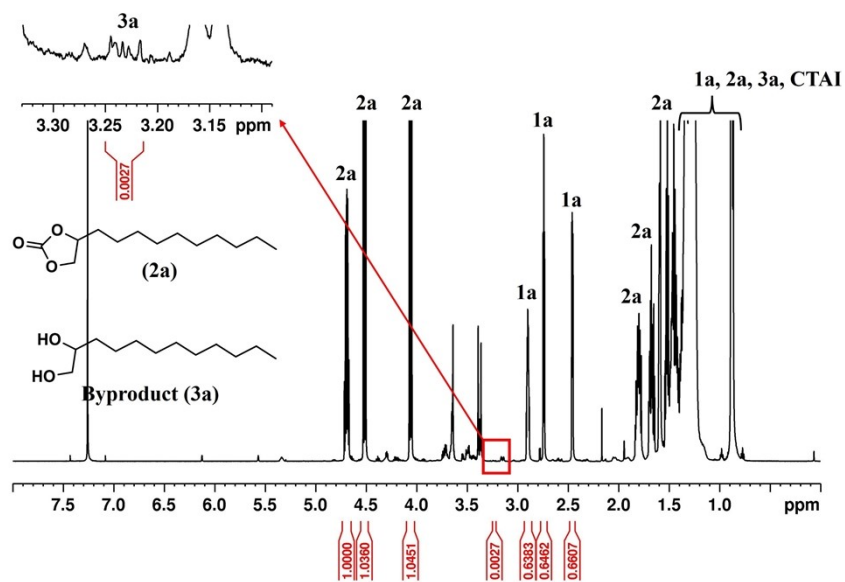


Fig. S8. Crude $^1\text{H-NMR}$ spectrum of **2a** obtained by cycloaddition of 1,2-epoxydodecane with CO_2 in miniemulsion using cetyltrimethylammonium iodide (CDCl_3).

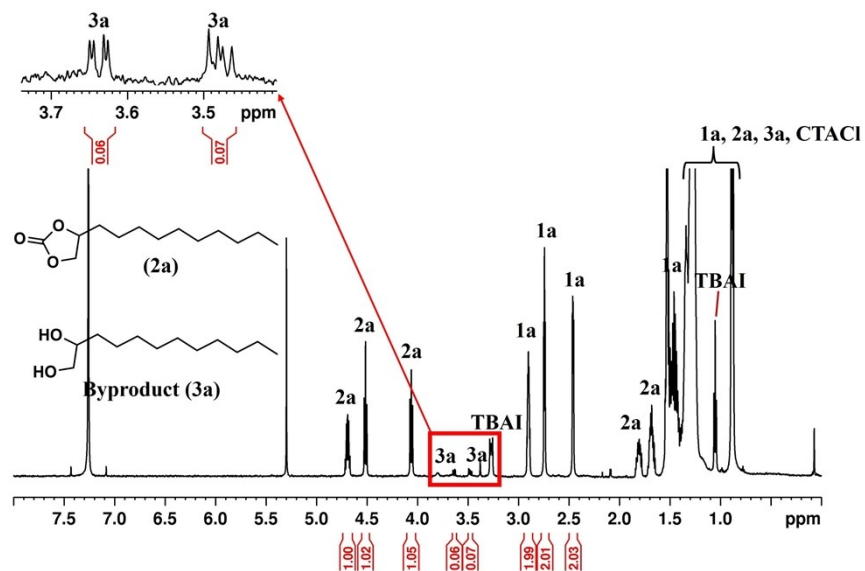


Fig. S9. Crude $^1\text{H-NMR}$ spectrum of **2a** obtained by cycloaddition of 1,2-epoxydodecane with CO_2 in miniemulsion using cetyltrimethylammonium chloride (CDCl_3).

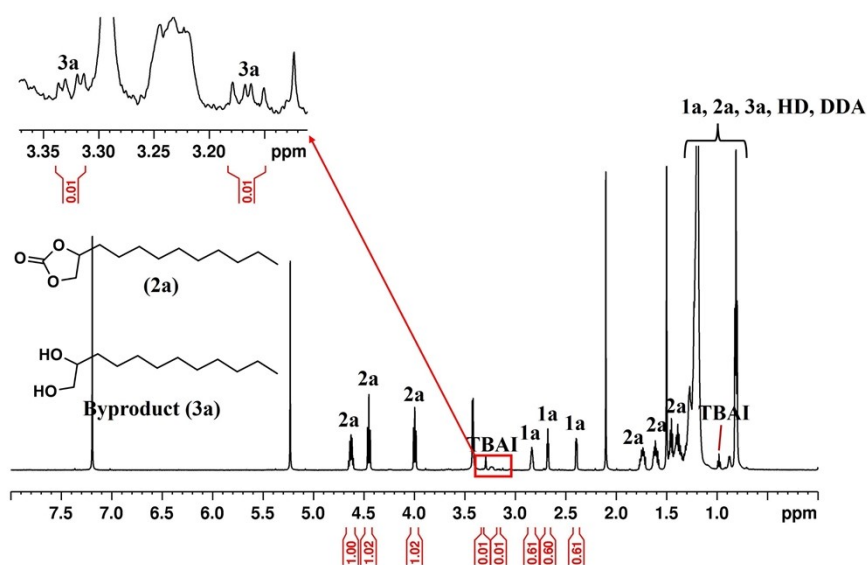


Fig. S12. Crude $^1\text{H-NMR}$ spectrum of **2b** obtained by cycloaddition of 1,2-epoxydodecane with CO_2 in miniemulsion using *n*-hexane (CDCl_3).

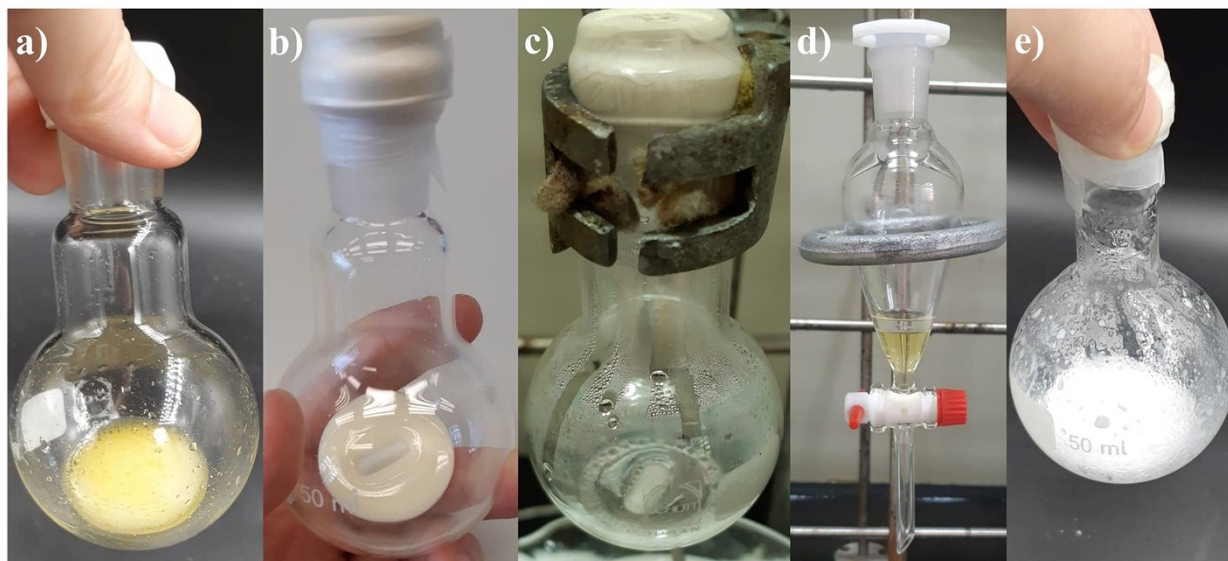


Fig. S13. Photographs of mixtures of the emulsion containing 1,2-epoxydodecane, TBAI, DDA, water and CO_2 before ultrasonication (coarse emulsion) (a) and after ultrasonication before the reaction (b), and separated phases after the reaction was performed for 24 h (c). The crude product was extracted by adding dichloromethane (d). Photograph of the emulsion containing glycidyl hexadecyl ether TBAI, DDA and water after the reaction (e).

¹H NMR and IR spectra of crude products

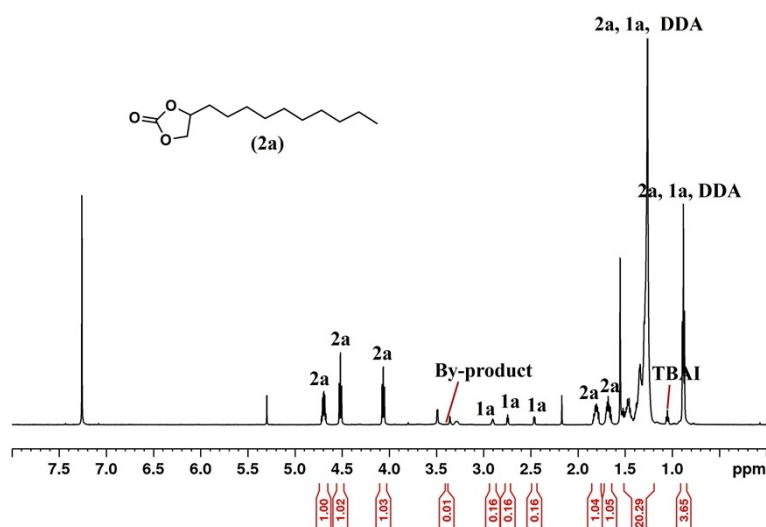


Fig. S14. Crude ¹H NMR spectrum of the reaction mixture containing 4-decyl-1,3-dioxolan-2-one (**2a**) obtained by cycloaddition of 1,2-epoxydodecane (**1a**) with CO₂ in miniemulsion [the signals of 1,2-dodecanediol are observed as impurity (by-product) and there is partial overlap

between the aliphatic **2a** side-chain protons, **1a** side-chain protons and the NCH_2R protons of DDA at 1.0-1.7 ppm] in CDCl_3 .

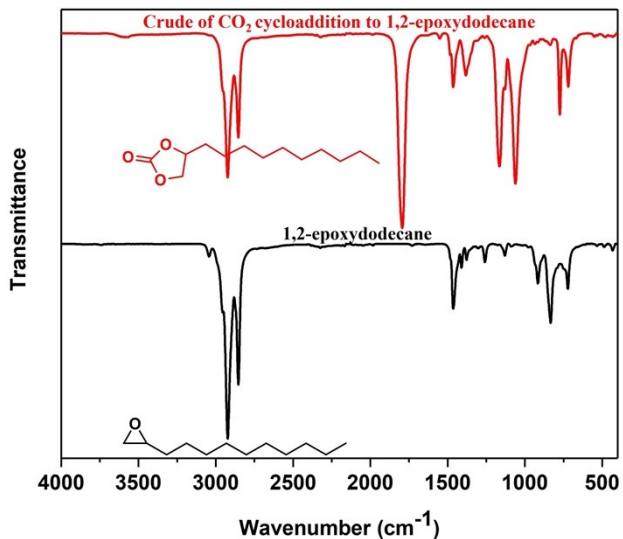


Fig. S15. FTIR spectra of crude product from CO₂ cycloaddition reaction to 1,2-epoxydodecane (**1a**) via miniemulsion.

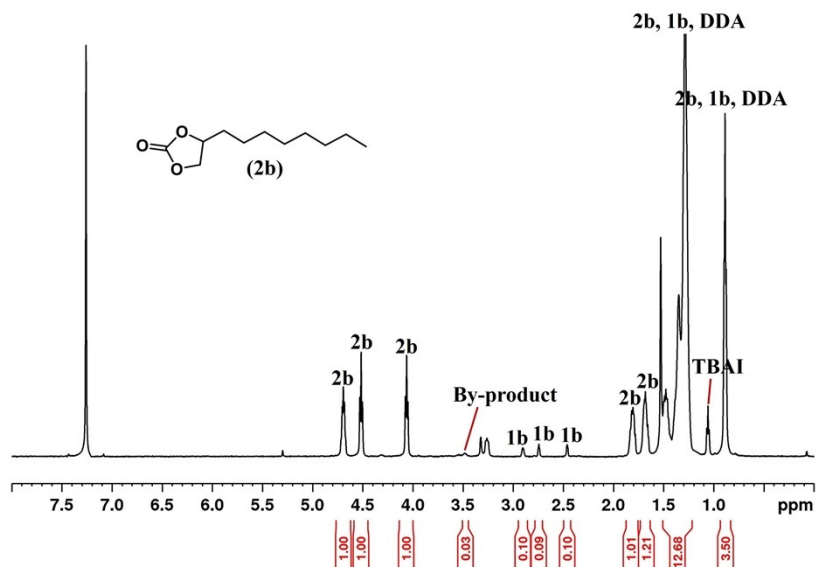


Fig. S16. Crude ¹H-NMR spectrum of **2b** obtained by cycloaddition of 1,2-epoxydodecane with CO₂ in miniemulsion (CDCl_3).

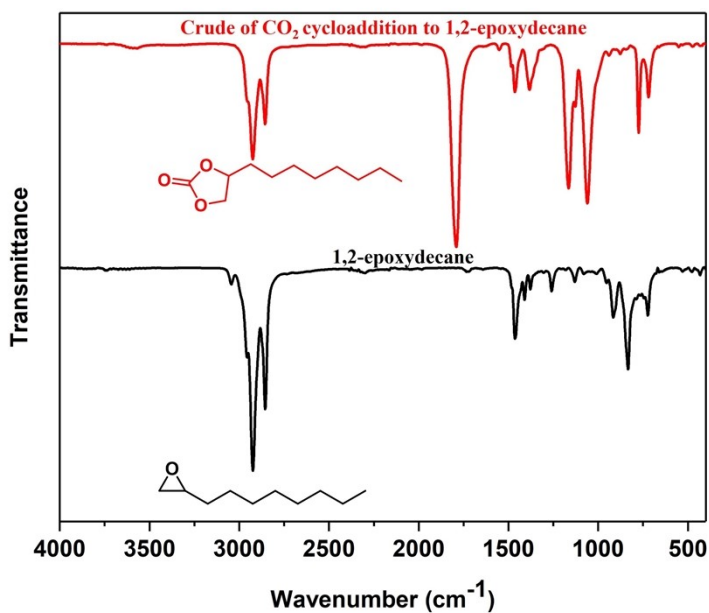


Fig. S17. FTIR spectra of crude product from CO₂ cycloaddition reaction to 1,2-epoxydecane (**1b**) via emulsion.

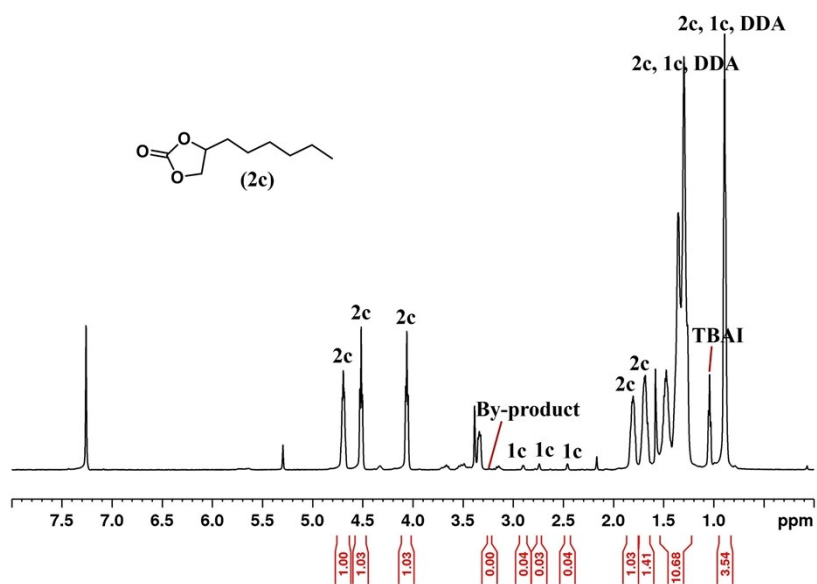


Fig. S18. Crude ¹H-NMR spectrum of **2c** obtained by cycloaddition of 1,2-epoxyoctane with CO₂ via miniemulsion (CDCl₃).

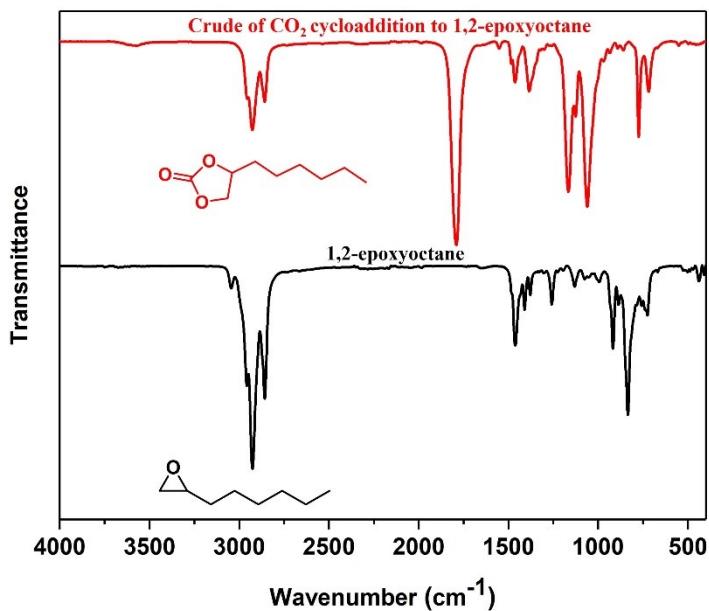


Fig. S19. FTIR spectra of crude product from CO₂ cycloaddition reaction to 1,2-epoxyoctane (**1c**) via emulsion.

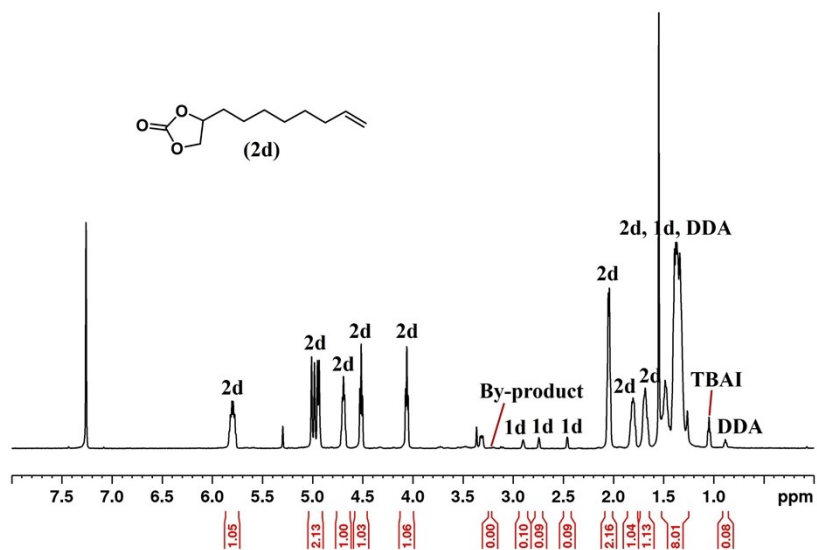


Fig. S20. Crude ¹H-NMR spectrum of **2d** obtained by cycloaddition of 1,2-epoxy-9-decene with CO₂ in miniemulsion (CDCl₃).

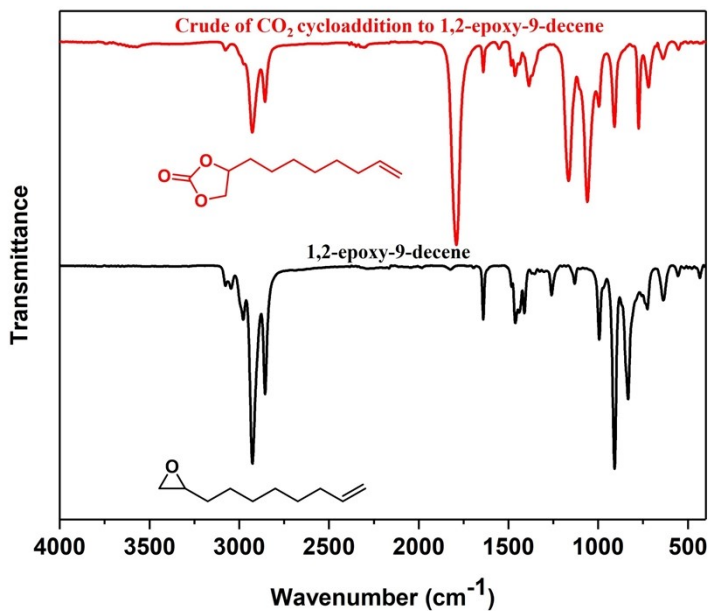


Fig. S21. FTIR spectra of crude product from CO₂ cycloaddition reaction to 1,2-epoxy-9-decene (**1d**) in miniemulsion.

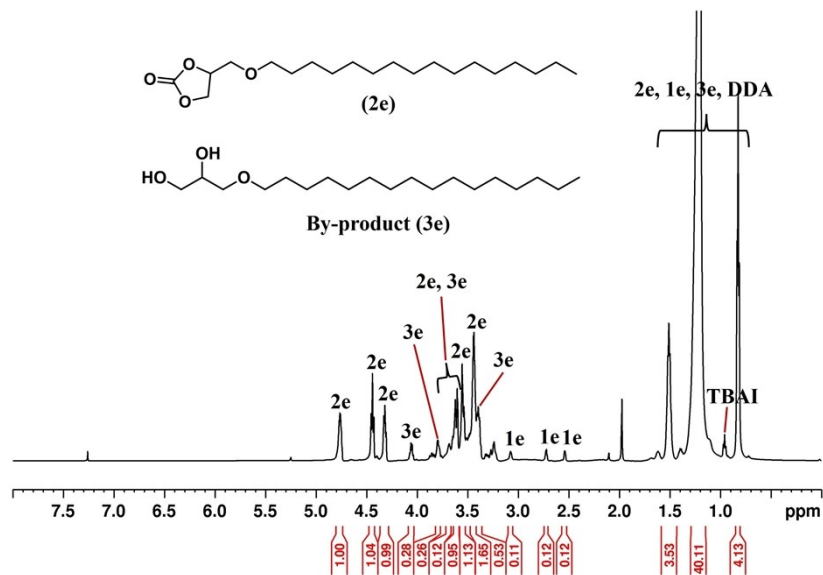


Fig. S22. ¹H-NMR spectrum of **2e** obtained by cycloaddition of glycidyl hexadecyl ether with CO₂ in miniemulsion (CDCl₃).

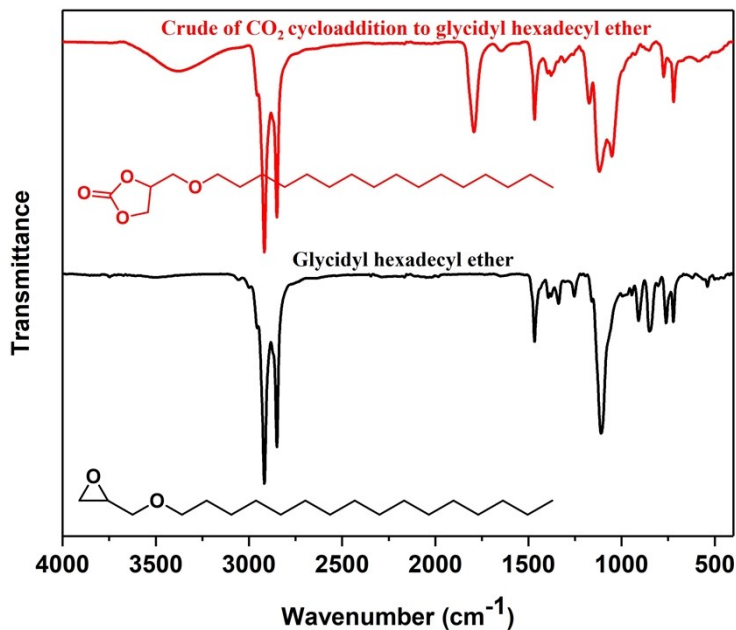


Fig. S23. FTIR spectra of crude product from CO₂ cycloaddition reaction to glycidyl hexadecyl ether (**1e**) in minemulsion.

¹H NMR and ¹³C NMR spectra of products

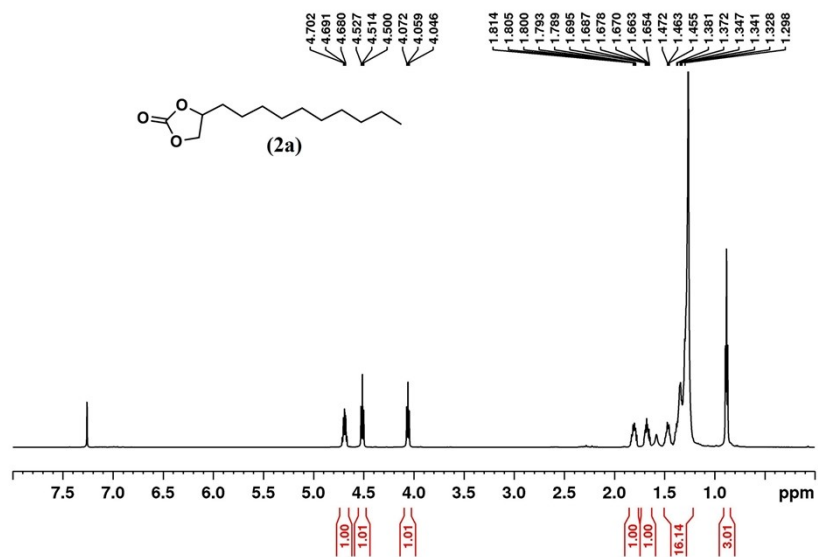


Fig. S24. (4-decyl-1,3-dioxolan-2-one) (1): ^1H NMR (CDCl_3 , 600 MHz): δ 4.74 – 4.65 (m, 1H), 4.51 (t, $J = 8.1$ Hz, 1H), 4.06 (t, $J = 7.8$ Hz, 1H), 1.81 (ddd, $J = 14.0, 11.7, 6.3$ Hz, 1H), 1.73 – 1.63 (m, 1H), 1.52 – 1.20 (m, 16H), and 0.88 ppm (t, 3H).

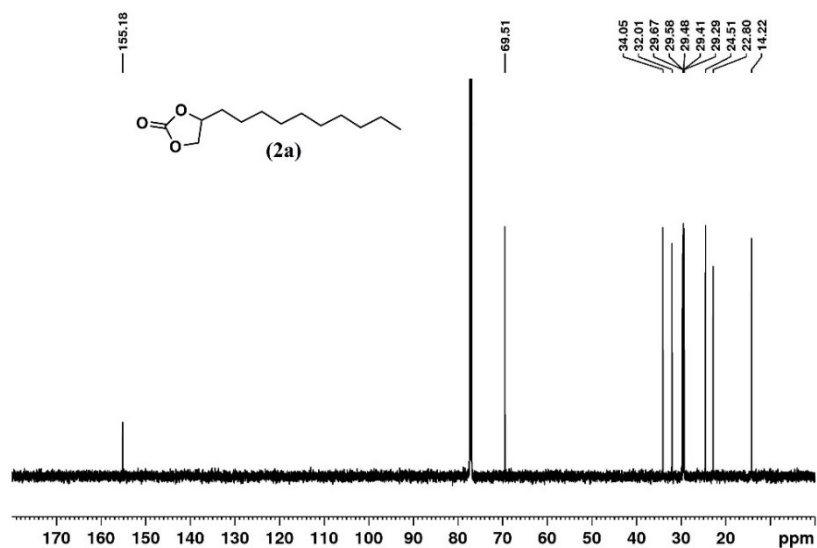


Fig. S25. ^{13}C -NMR spectrum of 4-decyl-1,3-dioxolan-2-one (2a) after purification in CDCl_3 .

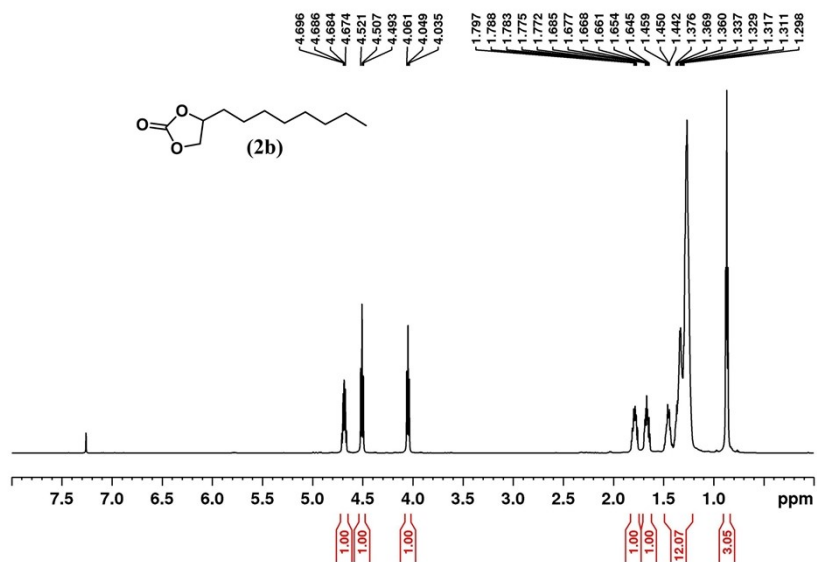


Fig. S26. (4-octyl-1,3-dioxolan-2-one) (**2**): ^1H NMR (CDCl_3 , 600 MHz): δ 4.72 – 4.65 (m, 1H), 4.51 (t, $J = 8.1$ Hz, 1H), 4.05 (t, $J = 7.8$ Hz, 1H), 1.83 – 1.75 (m, 1H), 1.71 – 1.62 (m, 1H), 1.51 – 1.20 (m, 12H), and 0.87 ppm (t, $J = 6.9$ Hz, 3H).

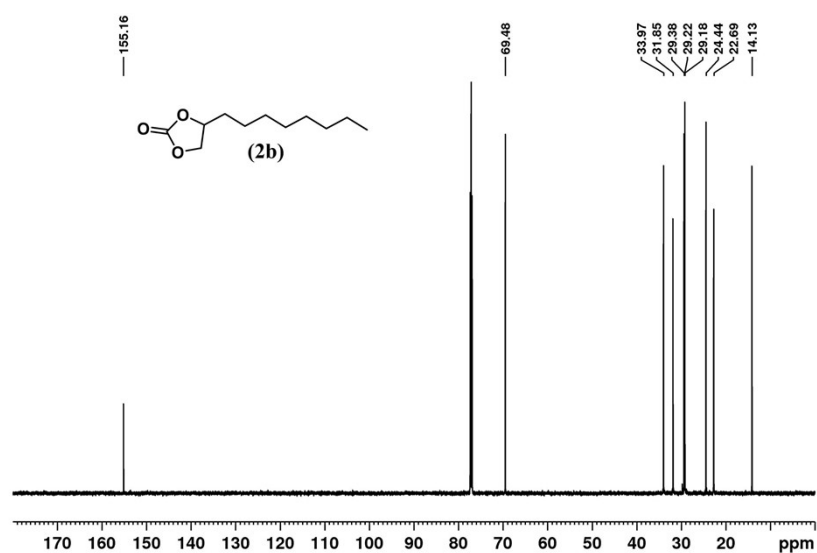


Fig. S27. ^{13}C -NMR spectrum of 4-octyl-1,3-dioxolan-2-one (**2b**) after purification in CDCl_3 .

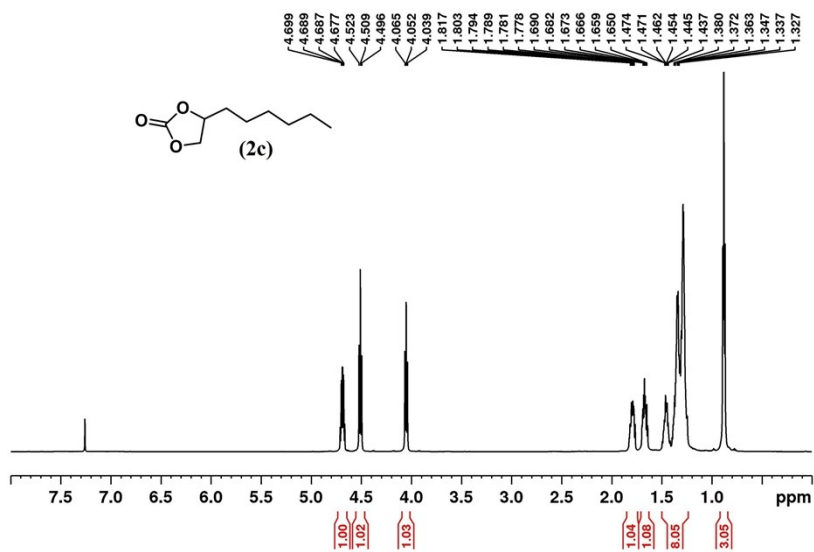


Fig. S28. (4-hexyl-1,3-dioxolan-2-one) (**3**): ^1H NMR (CDCl_3 , 600 MHz): δ 4.73 – 4.65 (m, 1H), 4.51 (t, $J = 8.1$ Hz, 1H), 4.05 (t, $J = 7.8$ Hz, 1H), 1.84 – 1.75 (m, 1H), 1.72 – 1.63 (m, 1H), 1.51 – 1.23 (m, 8H), and 0.88 ppm (t, $J = 6.8$ Hz, 3H).

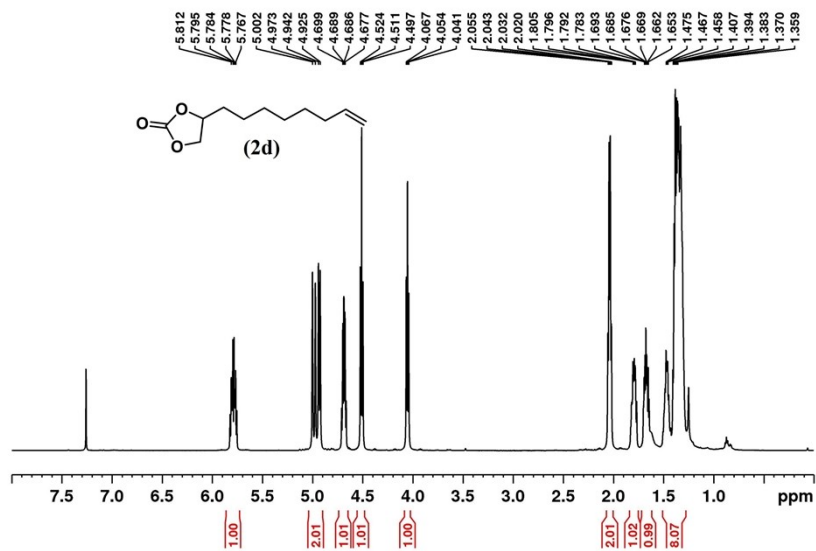
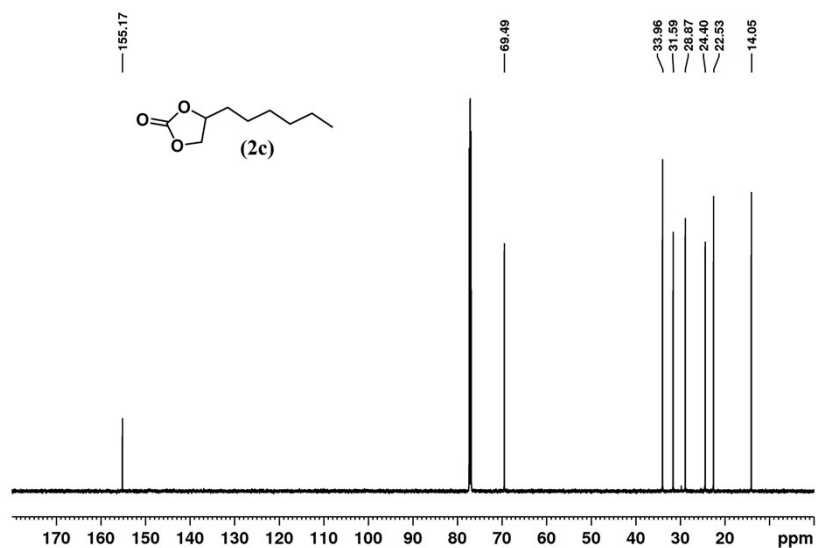


Fig. S30. (4-(oct-7-en-1-yl)-1,3-dioxolan-2-one) (**4**): ^1H NMR (CDCl_3 , 600 MHz): δ 5.79 (ddt, $J = 16.9, 10.1, 6.7$ Hz, 1H), 4.96 (dd, $J = 32.6, 13.6$ Hz, 2H), 4.74 – 4.64 (m, 1H), 4.51 (t, $J = 8.1$ Hz, 1H), 4.05 (t, $J = 7.8$ Hz, 1H), 2.04 (q, $J = 6.9$ Hz, 2H), 1.85 – 1.75 (m, 1H), 1.67 (ddd, $J = 19.5, 10.2, 5.0$ Hz, 1H), and 1.53 – 1.27 ppm (m, 8H).

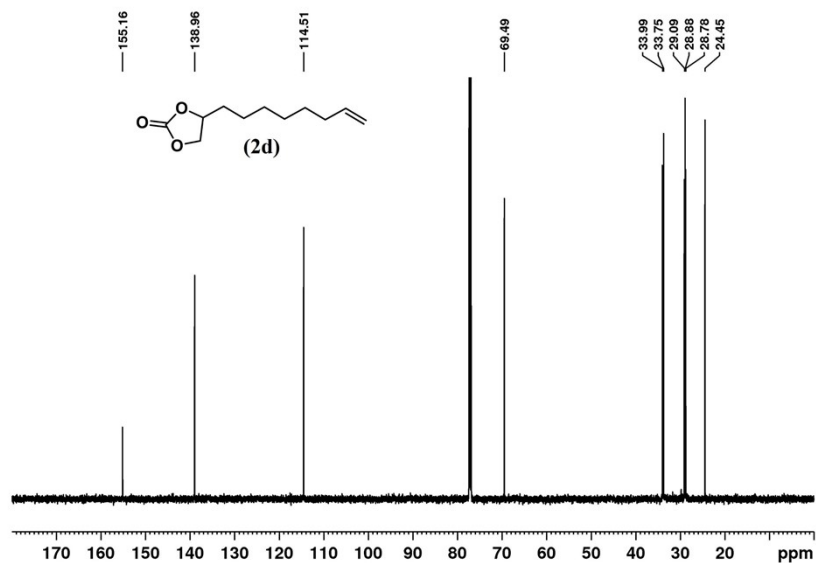


Fig. S31. ^{13}C -NMR spectrum of 4-(oct-7-en-1-yl)-1,3-dioxolan-2-one (**2d**) after purification in CDCl_3 .

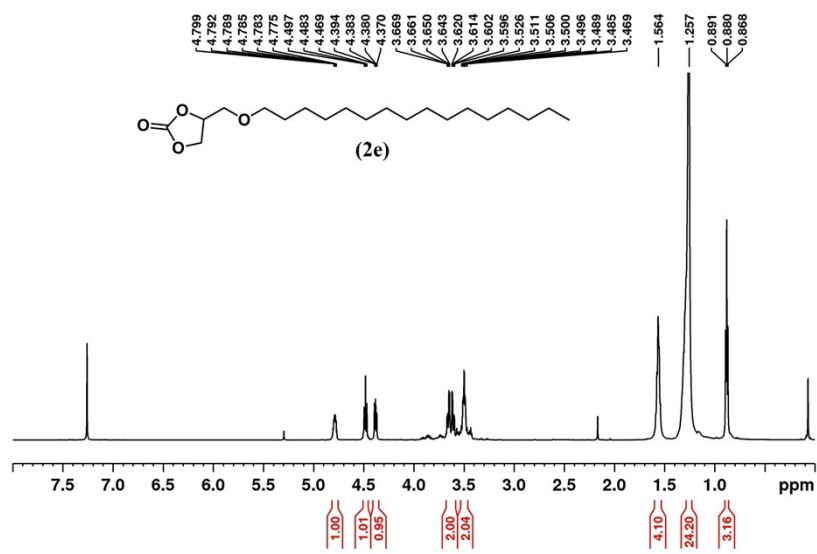


Fig. S32. 4-((hexadecyloxy)methyl)-1,3-dioxolan-2-one (**2e**): ^1H NMR (CDCl_3 , 600 MHz): δ 4.79 (ddd, $J = 10.0, 8.3, 4.1$ Hz, 1H), 4.52 – 4.45 (m, 1H), 4.38 (dd, $J = 8.2, 6.2$ Hz, 1H), 3.69 – 3.58 (m, 2H), 3.55 – 3.45 (m, 2H), 1.60 – 1.53 (m, 4H), 1.28 – 1.23 (m, 24H), and 0.88 ppm (t, $J = 6.9$ Hz, 3H).

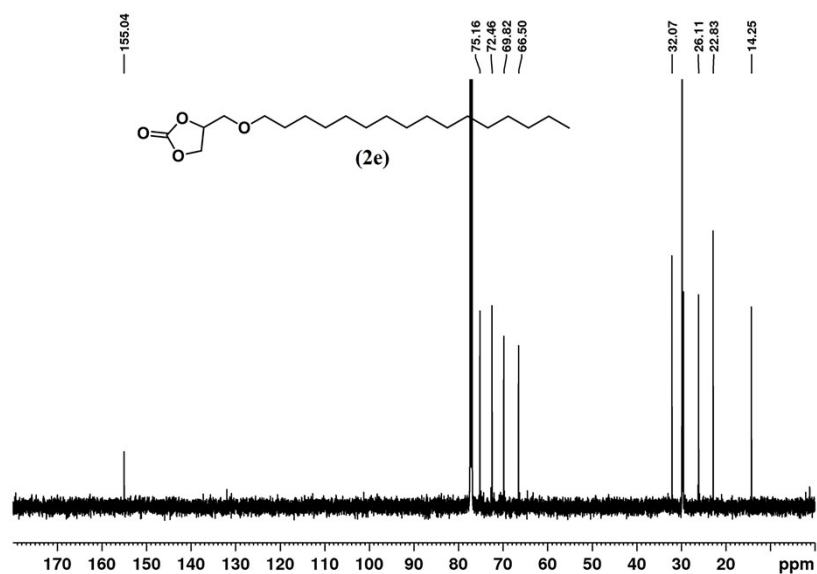
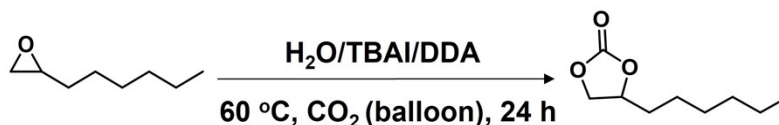


Fig. S33. ^{13}C -NMR spectrum of 4-((hexadecyloxy)methyl)-1,3-dioxolan-2-one (**2e**) after purification in CDCl_3 .

Table S2. Number of phase and hydrodynamic diameters of droplets of the mixtures before and after the reaction. The entries below correspond to the entries shown in Table 1.

Entry	Before reaction			After reaction		
	Number of phases	D_h		Number of phases	D_h	
		nm	PDI		nm	PDI
1	1	566	0.162	2	-	-
2	1	566	0.162	2	-	-
2a (TBAB)	1	454	0.137	1	772	0.382
2a (TBAC)	1	483	0.124	1	532	0.309
2b-300 rpm	1	566	0.162	2	-	-
2b-1000 rpm	1	566	0.162	1	982	0.375
3	1	730	0.164	2	-	-
4	-	-	-	-	-	-
5	-	-	-	-	-	-
6	2	-	-	2	-	-
7	1	592	0.144	1	756	0.266
8	1	-	-	1	-	-
9	1	286	0.091	1	513	0.246
10	1	330	0.13	1	516	0.214
11	1	653	0.151	2	-	-
12	2	-	-	2	-	-
13	1	>1000	-	2	-	-
14	1	295	0.241	1	430	0.227

Table S3. Interfacial tension between water and mixture of 1,2-epoxyoctane and 4-hexyl-1,3-dioxolan-2-one corresponding to the compositions of epoxide and cyclic carbonate at different reaction times.



Time (h)	Conversion (%)	Number of phases	Interfacial tension (mN/m)
0	0	1	12.3
5	12	1	10.4
6	20	2	8.5
10	58	2	4.1
24	98	2	0.8