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Electronic Supporting Information (ESI):

Fatty acid based biocarbonates: Al-mediated stereoselective preparation of mono-, di- and tricarbonates under mild and solvent-less conditions

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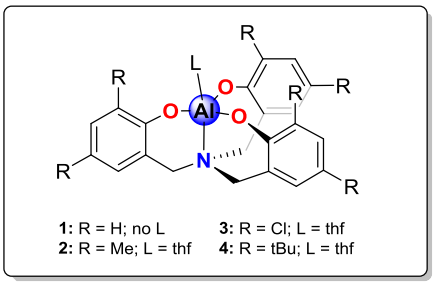
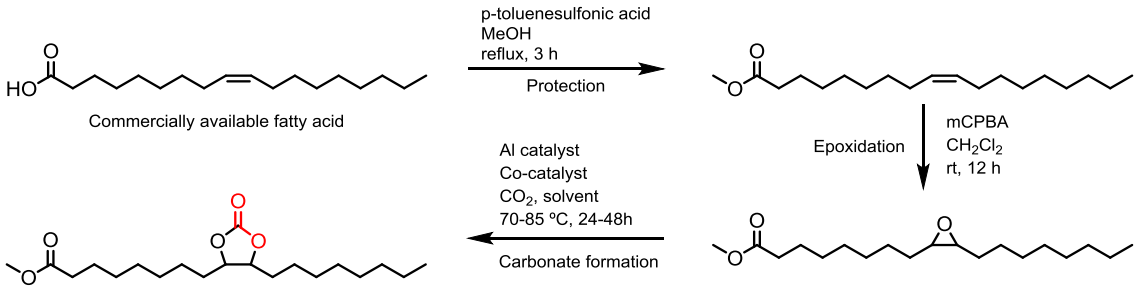
1. General Considerations:



The Al(III) aminotriphenolate complexes and the starting ligands were synthesized according to reported literature procedures.[1,2] Commercially available fatty acids, solvents, co-catalysts, oxidants were purchased from various commercial sources (Acros, Aldrich and TCI) and used without further purification. Carbon dioxide (purchased from PRAXAIR) was used without further purification or drying *prior to* its use.

^{1}H NMR and ^{13}C NMR spectra were recorded at rt on a Bruker AV-300, AV-400 or AV-500 spectrometer and referenced to the residual deuterated solvent signals. Diastereo-isomeric ratios (*dr´*s) were calculated from the corresponding ^{1}H NMR spectra using signal integration where possible; alternatively, integrable ^{13}C NMR spectra were recorded with a 500 MHz AV-500 spectrometer. All reported NMR values are given in parts per million (ppm). FT-IR measurements were carried out on a Bruker Optics FTIR Alpha spectrometer equipped with a DTGS detector, KBr beam splitter at 4 cm^{-1} resolution. Mass spectrometric analyses were performed by the Research Support Group at ICIQ.

2. Experimental Procedures:



<u>Acid protection method (typical procedure):</u>

1 g of fatty acid and 5 mg of *para*-toluenesulfonic acid (mono-hydrate) were dissolved in MeOH (50 mL). The reaction mixture was heated to reflux for 3 h. Hereafter, the solvent was removed *in vacuo* (rotary evaporator) and the fatty ester product was used without further purification in the next step – i.e. epoxidation.

Epoxidation method (typical procedure):

1 g of the methyl ester was dissolved in CH_2Cl_2 (40 mL) and cooled to 0 ºC. Then *meta*-chloroperbenzoic acid (1.2 equiv) was slowly added to this solution. The reaction mixture was left stirring for 12 h at rt. The solution was then washed with an aqueous solution of Na_2SO_3 (3 × 30 mL, 1 M), a saturated aqueous solution of $NaHCO_3$ (3 × 30 mL) and brine. The organic phase was dried over sodium sulfate and the product was obtained after removal of the solvent *in vacuo* using a rotary evaporator.

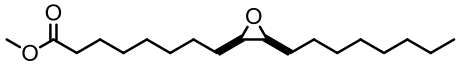
Carbonate formation (Screening experiments):

The screening experiments of all fatty acid carbonate syntheses were done by using a HEL pressure multi-reactor (HEL CAT[24]) with 24 vials of 10 × 75 mm. The epoxide substrate (0.32 mmol) was introduced into a vial of the HEL with a pre-selected loading of catalyst and co-catalyst and solvent volume. The HEL was pressurized to 10 bar with CO_2 and heated to the desired temperature. The reaction mixture was stirring for 24-48 h. After cooling to ambient temperature, the crude product was analyzed by ^{1}H NMR ($CDCl_3$) to determinate the conversion, selectivity and *cis/trans* ratio.

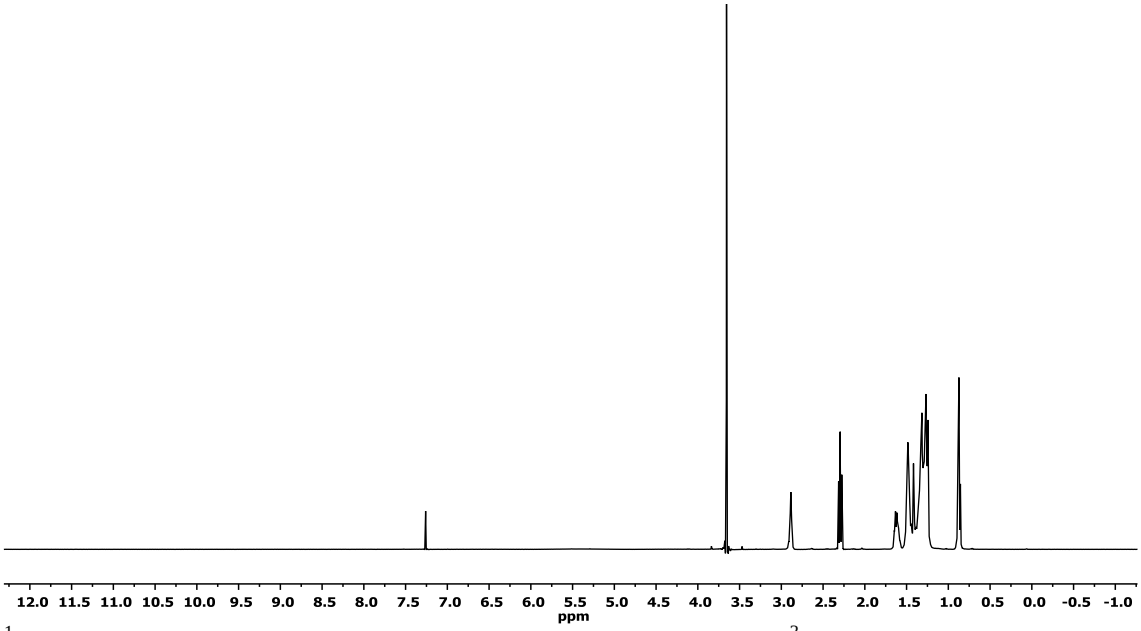
Carbonate formation (scaled-up experiments to isolate):

The epoxide substrate (0.5 g) was introduced into a 30 mL autoclave with a pre-selected loading of catalyst (Al-complex) and co-catalyst (nucleophile) and solvent where required. The autoclave was heated to the desired temperature, pressurized to 10 bar with CO_2 and the reaction mixture left stirring for 24–48 h. Then, after cooling to ambient temperature, the reaction was carefully and slowly vented, and the crude product analyzed by ^{1}H NMR and ^{13}C NMR ($CDCl_3$). The product was purified by flash chromatography (silica gel, EtOAc/hexane) following subsequent removal of the solvent using rotary evaporation.

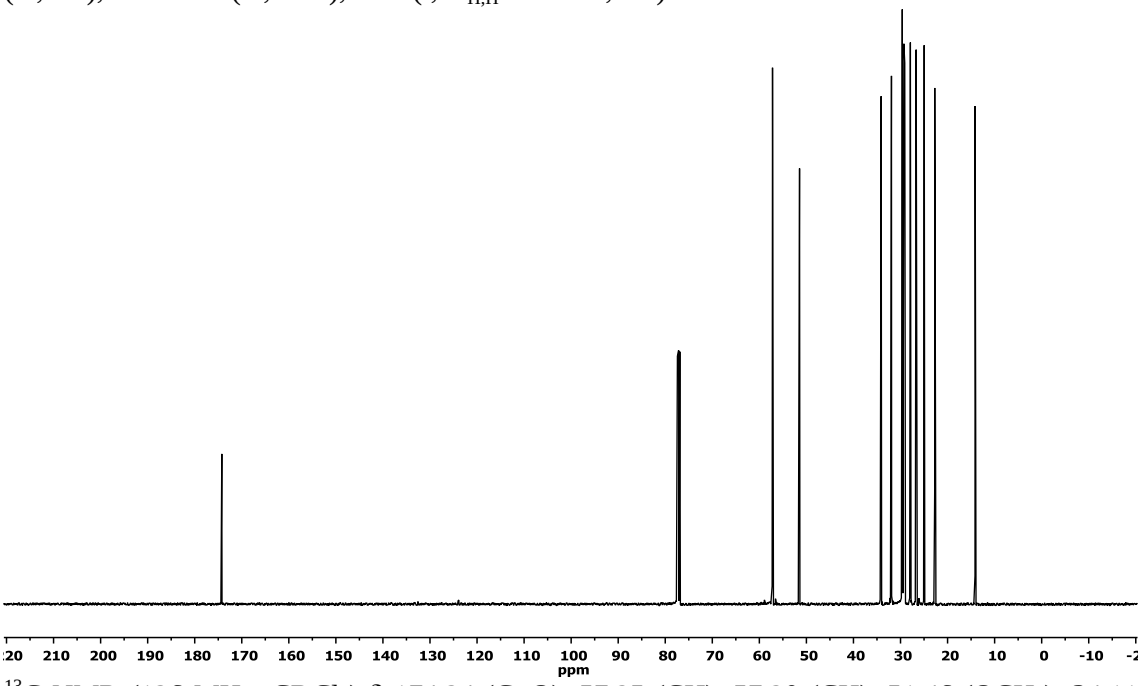
3. ^{1}H-NMR and ^{13}C-NMR Data of Epoxide Products:



cis-Methyl 8-(3-octyloxiran-2-yl)octanoate (**A** in the main text).

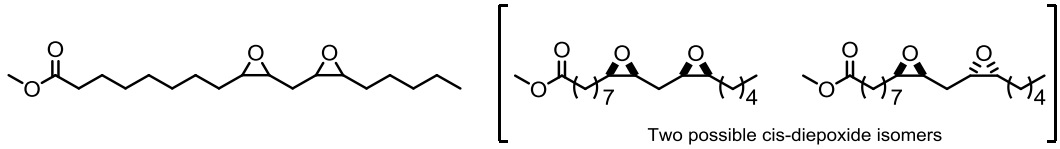


^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.66 (s, 3H), 2.89 (m, 2H), 2.30 (t, $^{3}J_{H,H}$ = 7.5 Hz, 2H), 1.67-1.56 (m, 2H), 1.53-1.20 (m, 24H), 0.87 (t, $^{3}J_{H,H}$ = 6.7 Hz, 3H).

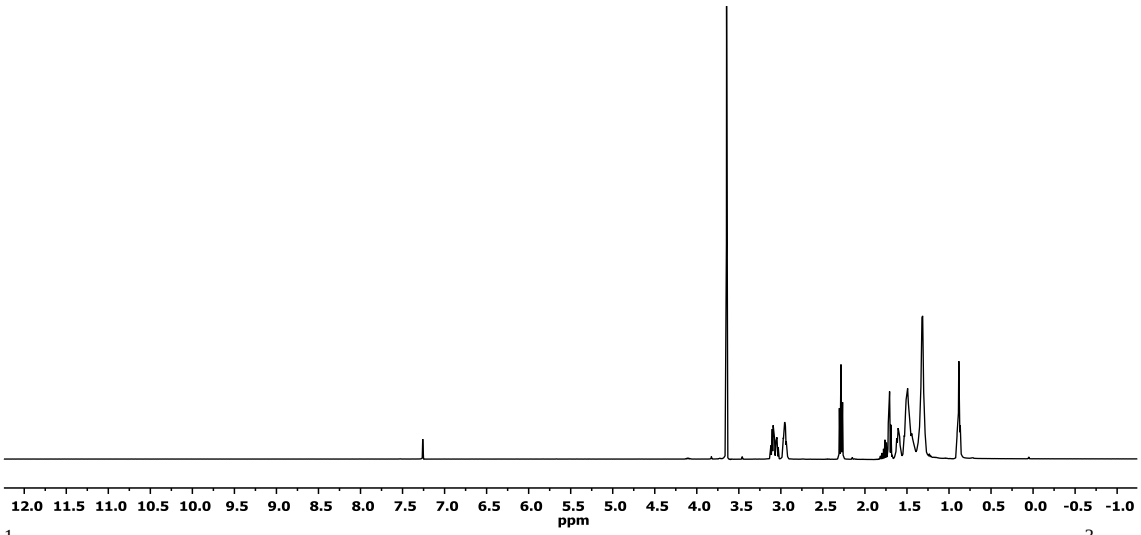


^{13}C NMR (126 MHz, $CDCl_3$) δ 174.24 (C=O), 57.25 (CH), 57.20 (CH), 51.46 (OCH_3), 34.11 (CH_2), 31.92 (CH_2), 29.62 (CH_2), 29.60 (CH_2), 29.40 (CH_2), 29.29 (CH_2), 29.24 (CH_2), 29.10 (CH_2), 27.91 (CH_2), 27.87 (CH_2), 26.68 (CH_2), 26.63 (CH_2), 24.96 (CH_2), 22.73 (CH_2), 14.14 (CH_3).

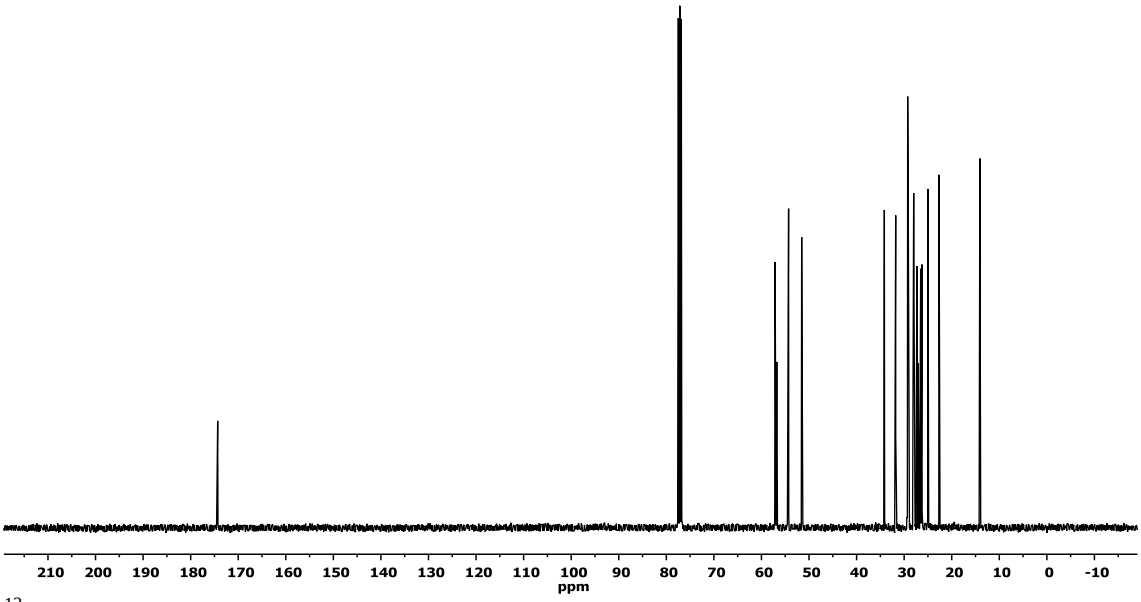
MS (ESI+, CH_3OH): *m/z* calcd. 335.3 $(M+Na)^+$, found: 335.3. [3]



Methyl 8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanoate (**B** in the main text). Note: mixture of two diasteroisomers.

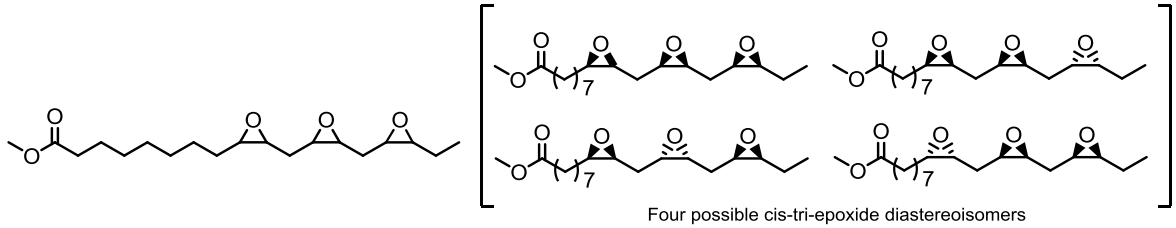


^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65 (s, 3H), 3.12-3.02 (m, 2H), 2.99-2.92 (m, 2H) , 2.28 (t, $^{3}J_{H,H}$ = 7.5 Hz, 2H), 1.82-1.68 (m, 2H), 1.65-1.56 (m, 2H), 1.56-1.41 (m, 8H), 1.38-1.26 (m, 10H), 0.88 (t, $^{3}J_{H,H}$ = 6.9 Hz, 3H)

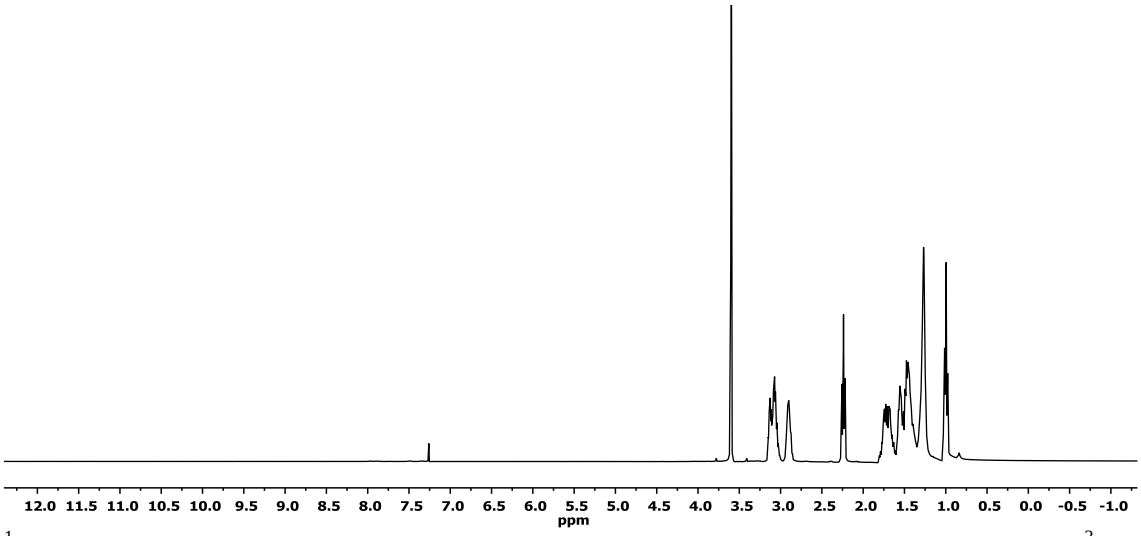


^{13}C NMR (101 MHz, $CDCl_3$) δ 174.32 (C=O), 57.12 (CH), 57.07 (CH), 56.84 (CH), 56.78 (CH), 54.47 (CH), 54.45 (CH), 54.29 (CH), 51.55 (OCH_3), 34.16 (CH_2), 31.78 (CH_2), 29.40 (CH_2), 29.26 (CH_2), 29.13 (CH_2), 28.01 (CH_2), 28.00 (CH_2), 27.93 (CH_2), 27.92 (CH_2), 27.33 (CH_2), 27.05 (CH_2), 26.64 (CH_2), 26.53 (CH_2), 26.36 (CH_2), 26.25 (CH_2), 25.00 (CH_2), 22.67 (CH_2), 14.09 (CH_3).

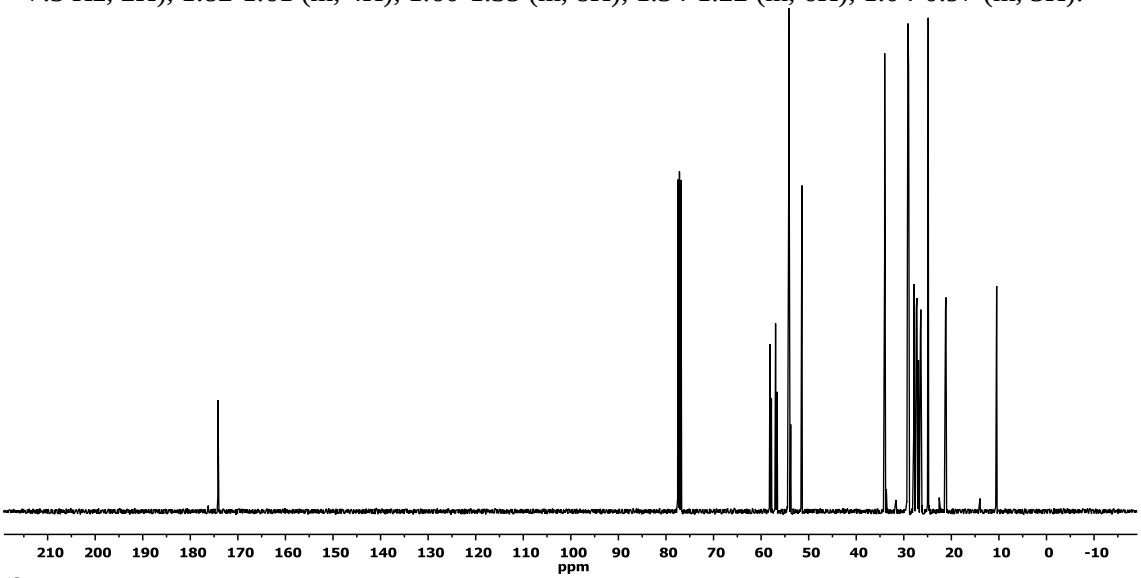
MS (ESI+, CH_3OH): *m/z* calcd. 349.2 $(M+Na)^+$, found: 349.2. [3]



Methyl 8-(3-((3-((3-ethyloxiran-2-yl)methyl)oxiran-2-yl)methyl)oxiran-2-yl)octanoate (**C** in the main text). Note: mixture of four diasteroisomers.

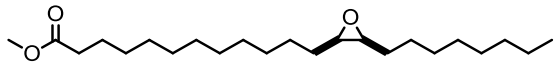


^{1}H NMR (400 MHz, $CDCl_3$) δ 3.60 (s, 3H), 3.16-3.01 (m, 4H), 2.96-2.86 (m, 2H), 2.24 (t, $^{3}J_{H,H}$ = 7.3 Hz, 2H), 1.82-1.61 (m, 4H), 1.60-1.35 (m, 8H), 1.34-1.22 (m, 6H), 1.04-0.97 (m, 3H).

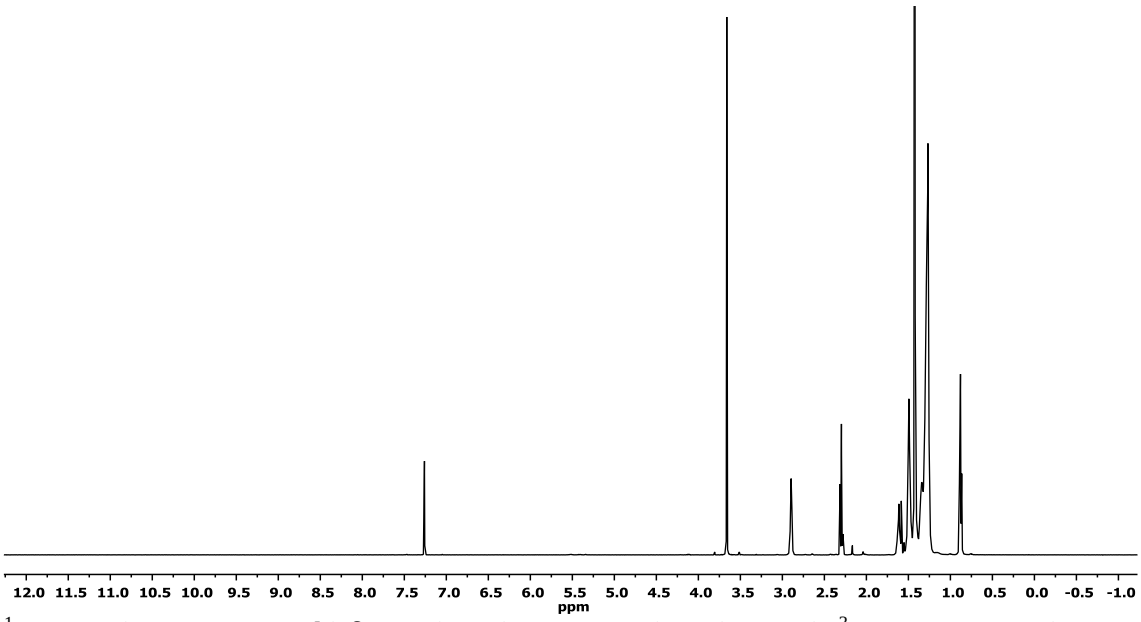


^{13}C NMR (101 MHz, $CDCl_3$) δ 174.19 (C=O), 58.14 (CH), 58.11 (CH), 57.83 (CH), 56.95 (CH), 56.93 (CH), 56.64 (CH), 54.26 (CH), 54.18 (CH), 54.11 (CH), 54.05 (CH), 53.99 (CH), 53.78 (CH), 51.42 (OCH_3), 34.02 (CH_2), 29.26 (CH_2), 29.13 (CH_2), 28.99 (CH_2), 27.88 (CH_2), 27.82 (CH_2), 27.36 (CH_2), 27.29 (CH_2), 27.24 (CH_2), 27.16 (CH_2), 27.03 (CH_2), 26.97 (CH_2), 26.92 (CH_2), 26.85 (CH_2), 26.51 (CH_2), 26.42 (CH_2), 26.40 (CH_2), 24.87 (CH_2), 21.25 (CH_2), 21.22 (CH_2), 21.14 (CH_2), 10.59 (CH_2), 10.48 (CH_3).

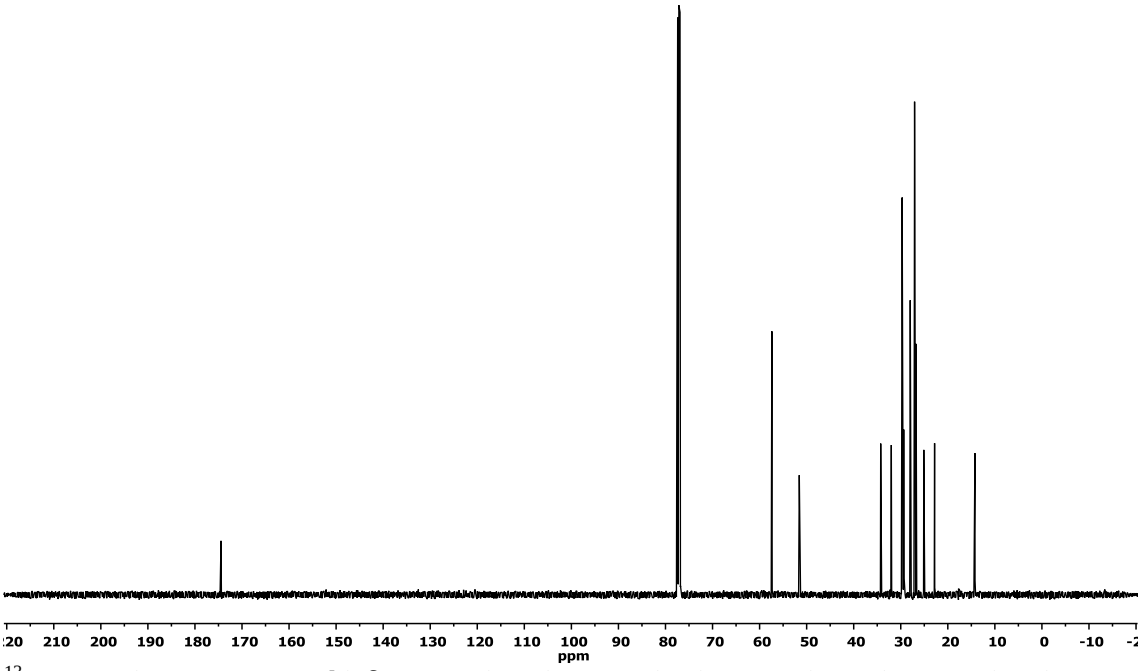
HRMS (ESI+, CH_3OH): *m/z* calcd. 363.2142 $(M+Na)^+$, found: 363.2147.



Methyl 12-3-octyloxiran-2-yl)dodecanoate (**D** in the main text).

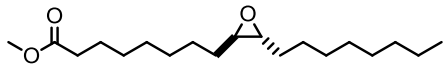


^{1}H NMR (500 MHz, $CDCl_3$) δ 3.66 (s, 3H), 2.92-2.87 (s, 2H), 2.30 (t, $^{3}J_{H,H}$ = 7.5 Hz, 2H), 1.65-1.59 (m, 2H), 1.53-1.45 (m, 6H), 1.39-1.19 (m, 26H), 0.88 (t, $^{3}J_{H,H}$ = 7.1 Hz, 3H).

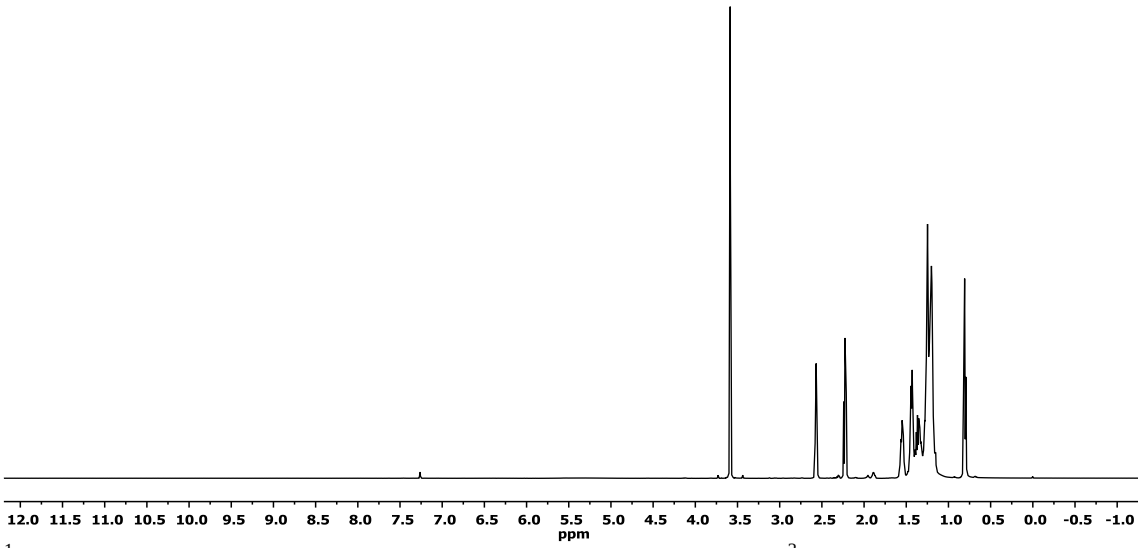


^{13}C NMR (126 MHz, $CDCl_3$) δ 174.46 (C=O), 57.39 (CH), 51.57 (OCH_3), 34.26 (CH_2), 31.01 (CH_2), 29.70 (CH_2), 29.68 (CH_2), 29.67 (CH_2), 29.58 (CH_2), 29.40 (CH_2), 29.37 (CH_2), 29.30 (CH_2), 27.98 (CH_2), 27.06 (CH_2), 26.75 (CH_2), 25.11 (CH_2), 22.81 (CH_2), 14.24 (CH_3).

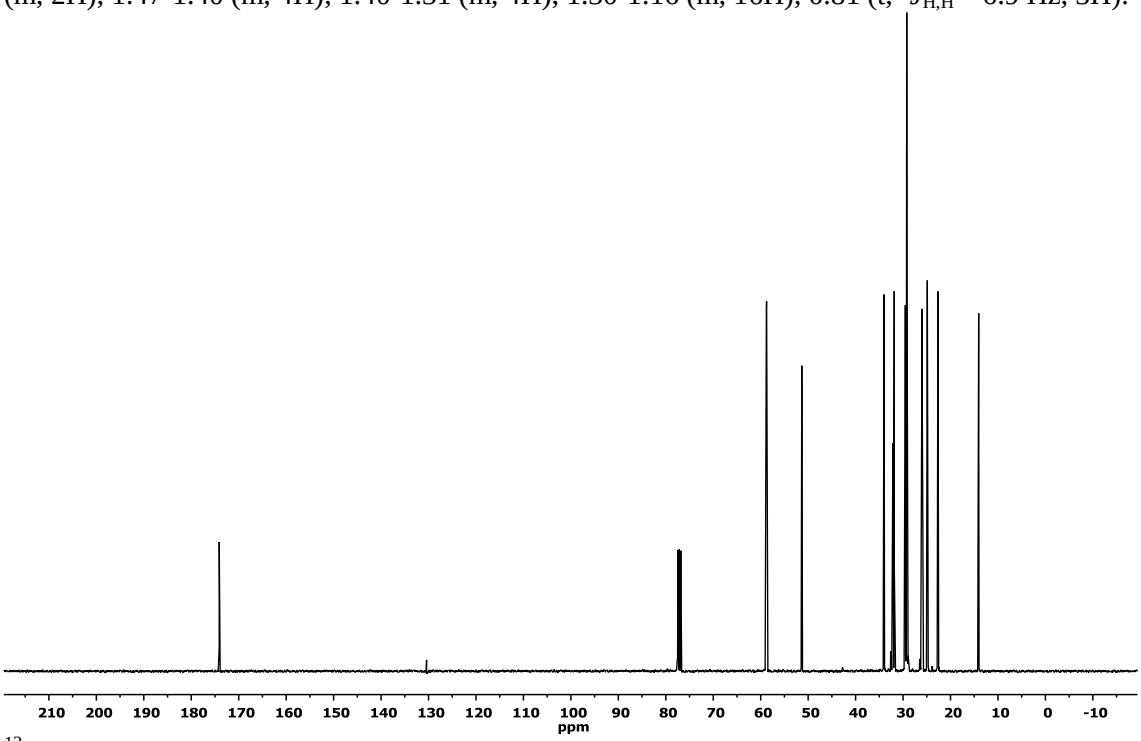
MS (ESI+, CH_3OH): *m/z* calcd. 391.3 $(M+Na)^+$, found: 391.3. [3]



Methyl 8-3-octyloxiran-2-yl)octanoate (**E** in the main text).



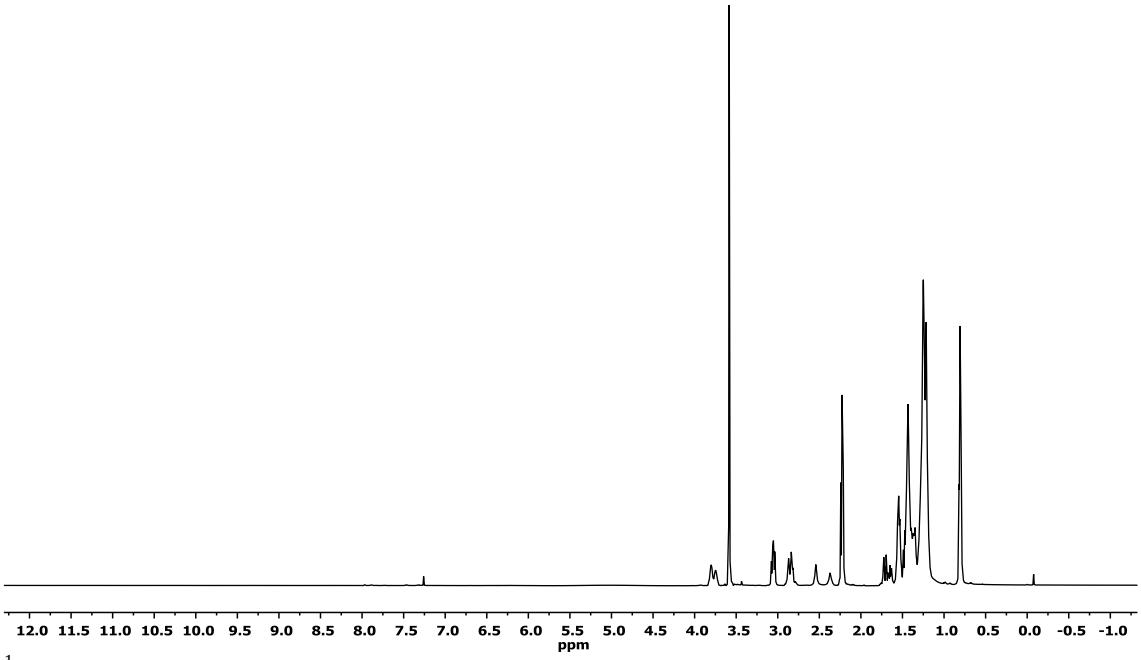
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.59 (s, 3H), 2.57 (m, 2H), 2.23 (t, $^{3}J_{H,H}$ = 7.4 Hz, 2H), 1.58-1.51 (m, 2H), 1.47-1.40 (m, 4H), 1.40-1.31 (m, 4H), 1.30-1.16 (m, 16H), 0.81 (t, $^{3}J_{H,H}$ = 6.9 Hz, 3H).



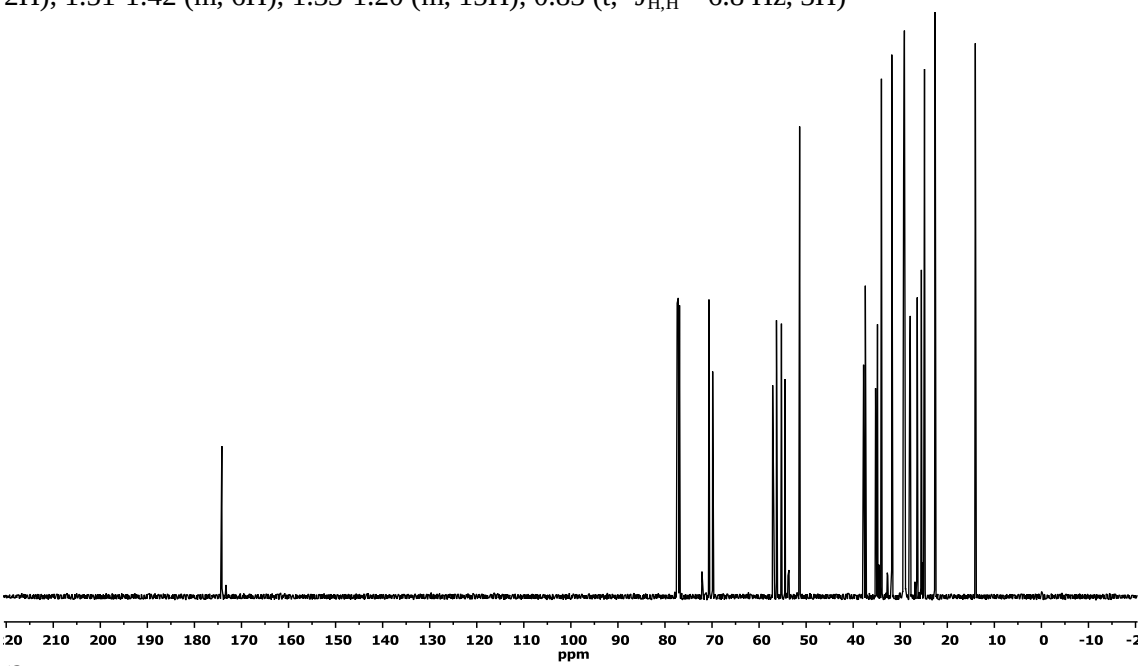
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.10 (C=O), 58.80 (CH), 58.75 (CH), 51.34 (OCH_3), 34.01 (CH_2), 32.13 (CH_2), 32.09 (CH_2), 31.85 (CH_2), 29.52 (CH_2), 29.46 (CH_2), 29.23 (CH_2), 29.16 (CH_2), 29.02 (CH_2), 26.06 (CH_2), 25.99 (CH_2), 24.88 (CH_2), 22.65 (CH_2), 14.07 (CH_3).

HRMS (ESI+, CH_3OH): *m/z* calcd. 251.0526 $(M+Na)^+$, found: 251.0527.

Methyl 8-(3-(2-hydroxyoctyl)oxiran-2-yl)octanoate (**F** in the main text). Note: mixture of two diasteroisomers (*dr* = 56:44).



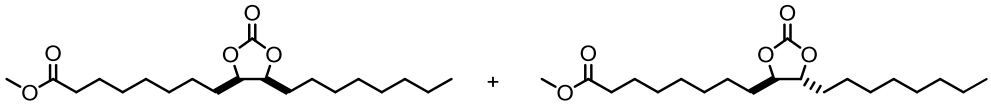
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.86-3.74 (m, 1H), 3.61 (s, 3H), 3.11-3.05 (m, 1H), 2.93-2.82 (m, 1H), 2.60-2.35 (2 × br s, 1H, OH), 2.25 (t, $^{3}J_{H,H}$ = 7.5 Hz, 2H), 1.77-1.64 (m, 1H), 1.61-1.54 (m, 2H), 1.51-1.42 (m, 6H), 1.33-1.20 (m, 15H), 0.83 (t, $^{3}J_{H,H}$ = 6.8 Hz, 3H)



^{13}C NMR (126 MHz, $CDCl_3$) δ 174.19 (C=O), 174.18 (C=O), 70.65 (CH), 69.87 (CH), 57.12 (CH), 56.31 (CH), 55.25 (CH), 54.50 (CH), 51.38 (OCH_3), 37.79 (CH_2), 37.42 (CH_2), 35.25 (CH_2), 34.84 (CH_2), 34.00 (CH_2), 31.80 (CH_2), 29.28 (CH_2), 29.27 (CH_2), 29.25 (CH_2), 29.23 (CH_2), 29.12 (CH_2), 28.97 (CH_2), 28.00 (CH_2), 27.87 (CH_2), 26.41 (CH_2), 26.38 (CH_2), 25.58 (CH_2), 25.51 (CH_2), 24.85 (CH_2), 22.58 (CH_2), 14.04 (CH_3).

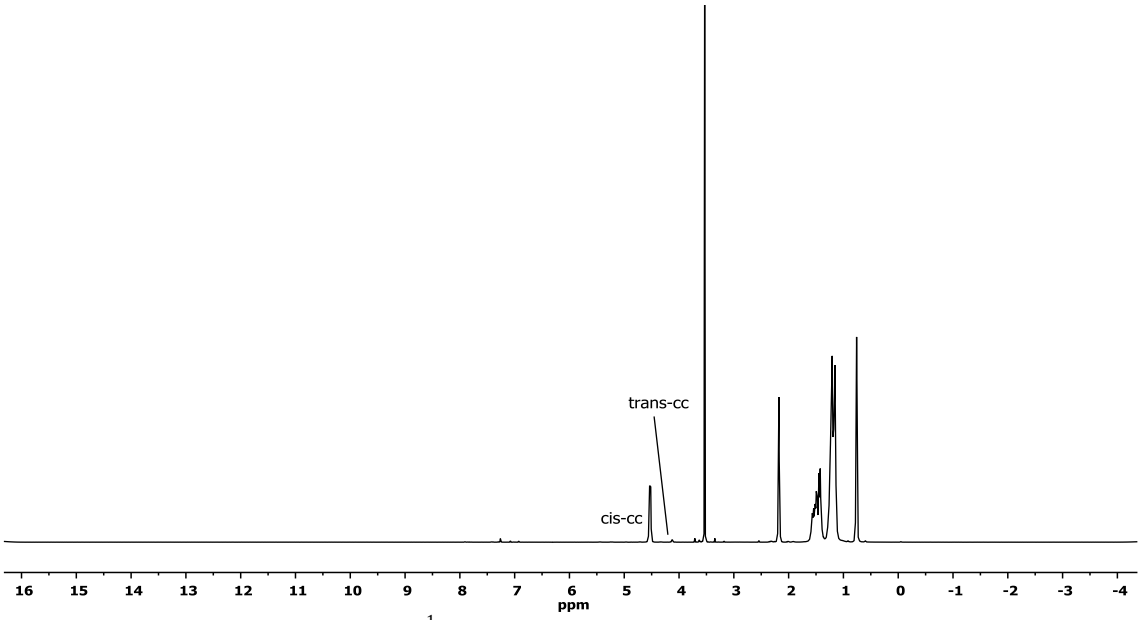
MS (ESI+, CH_3OH): *m/z* calcd. 351.3 $(M+Na)^+$, found: 351.3. [3]

4. ^{1}H-NMR and ^{13}C-NMR Data of Carbonate Products and MS Analysis.

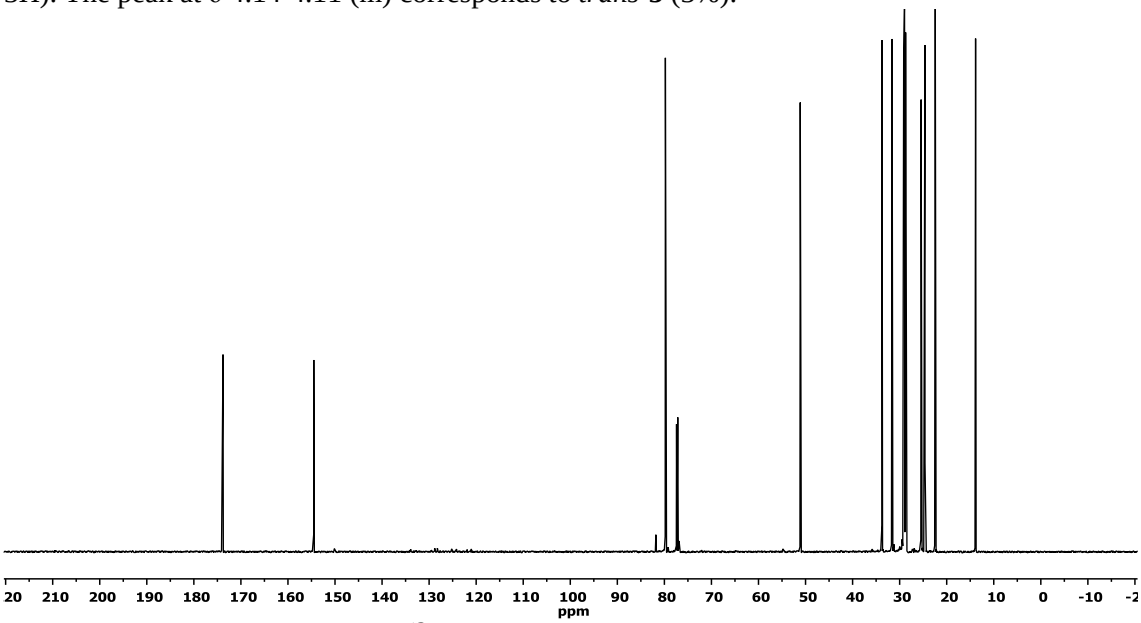


5 *cis* cyclic carbonate (cis-COC) 97% + **5** *trans* cyclic carbonate (*trans*-COC) 3%

Methyl 8-(5-octyl-2-oxo-1,3-dioxolan-4-yl)octanoate (**5** in the main text).

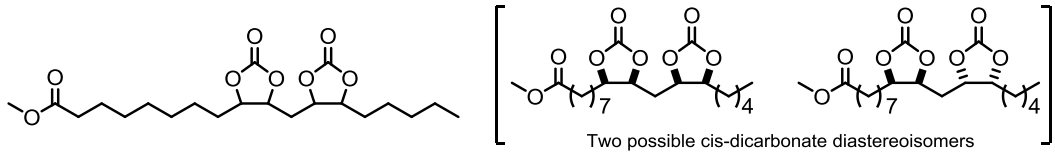


For the major isomer of 5 (*cis*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.55-4.50 (m, 2H), 3.53 (s, 3H), 2.18 (t, $^{3}J_{H,H}$= 7.5 Hz, 2H), 1.60-1.40 (m, 8H), 1.30-1.10 (m, 18H), 0.76 (t, $^{3}J_{H,H}$ = 7.1 Hz, 3H). The peak at δ 4.14-4.11 (m) corresponds to *trans*-**5** (3%).

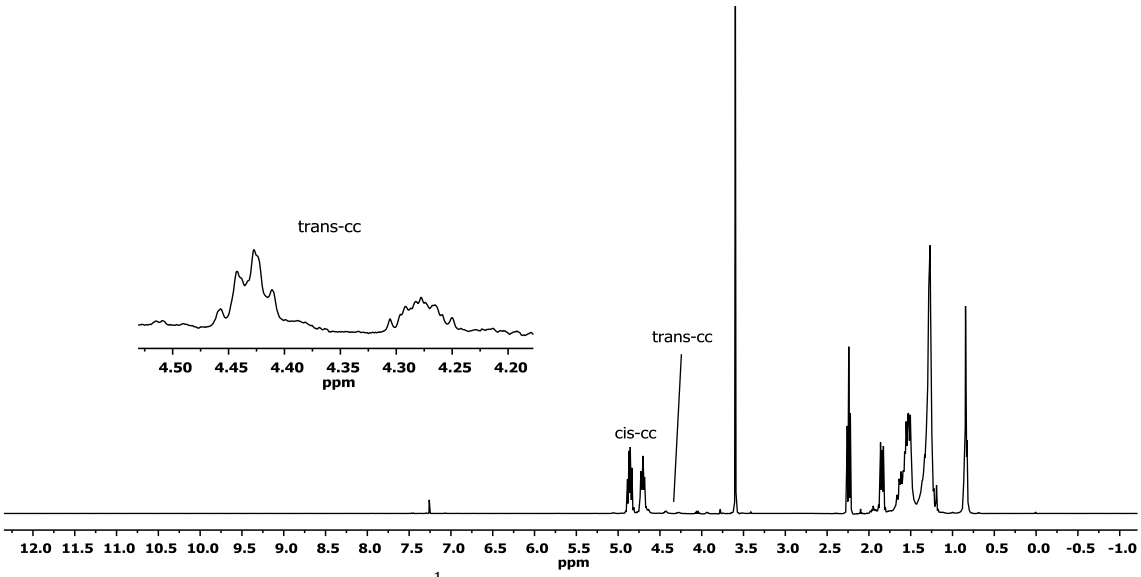


For the major isomer of 5 (*cis*): ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.80 (C=O), 154.51 (C=O), 79.78 (CH), 79.75 (CH), 51.13 (OCH_3), 33.74 (CH_2), 31.61 (CH_2), 29.15 (CH_2), 29.05 (CH_2), 28.96 (CH_2), 28.82 (CH_2), 28.79 (CH_2), 28.73 (CH_2), 28.68 (CH_2), 28.64 (CH_2), 25.44 (CH_2), 25.37 (CH_2), 24.63 (CH_2), 22.43 (CH_2), 13.86 (CH_3).

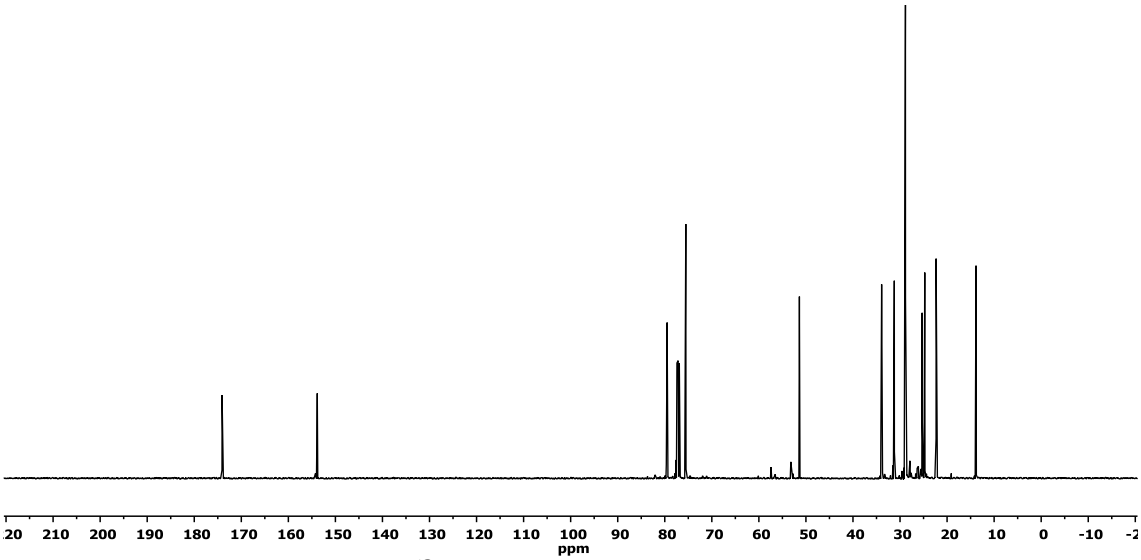
MS (ESI+, CH_3OH): *m/z* calcd. 379.2 $(M+Na)^+$, found: 379.2. [3]



Methyl 8-(2-oxo-5-((2-oxo-5-pentyl-1,3-dioxolan-4-yl)methyl)-1,3-dioxolan-4-yl)octanoate (**6** in the main text). Note: mixture of diasteroisomers, two *cis* diastereoisomers (97%) and two *trans* diastereoisomers (3%).

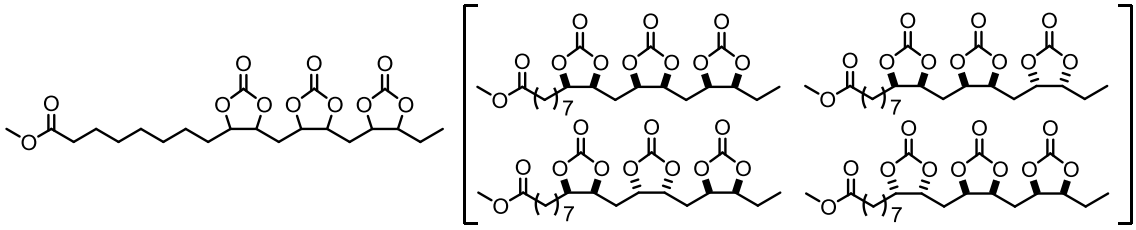


For the major isomers of 6 (*cis*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90-4.65 (m, 4H), 3.60 (s, 3H), 2.24 (t, $^{3}J_{H,H}$= 7.6 Hz, 2H), 1.88-1.81(m, 2H), 1.67-1.48 (m, 8H), 1.37-1.22 (m, 12H), 0.84 (t, $^{3}J_{H,H}$ = 7.2 Hz, 3H). The peaks at δ 4.47-4.25 (m) correspond to *trans*-**6** (3%).



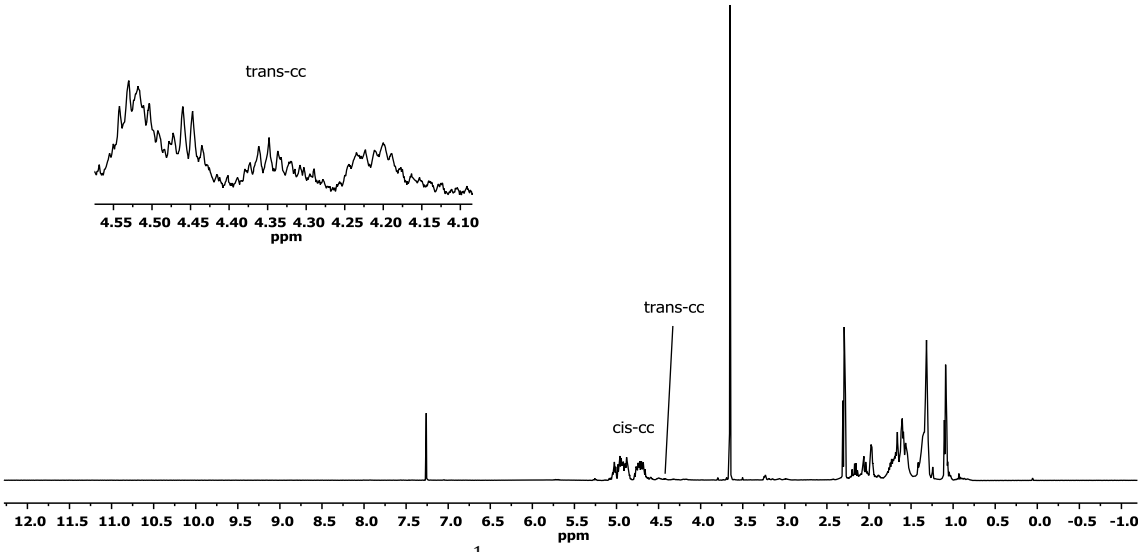
For the major isomers of 6 (*cis*): ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.09 (C=O), 153.87 (C=O), 153.85 (C=O), 79.55 (CH), 79.50 (CH), 75.53 (CH), 51.39 (OCH_3), 33.91 (CH_2), 31.21 (CH_2), 28.89 (CH_2), 28.85 (CH_2), 28.77 (CH_2), 25.56 (CH_2), 25.30 (CH_2), 24.75 (CH_2), 22.33(CH_2), 13.85 (CH_3).

MS (ESI+, CH_3OH): *m/z* calcd. 437.2 $(M+Na)^+$, found: 437.2. [3]

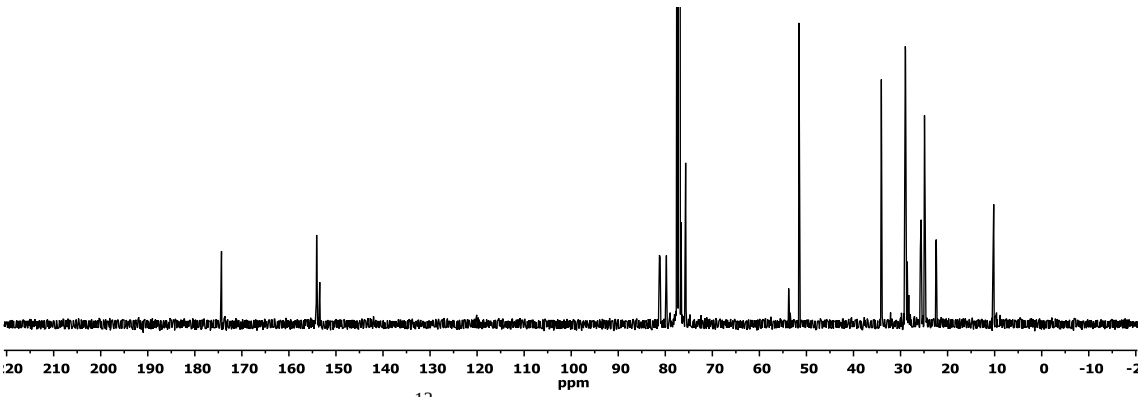


Four possible cis-tri-carbonate diastereoisomers

Methyl 8-(5-((5-((5-ethyl-2-oxo-1,3-dioxolan-4-yl)methyl)-2-oxo-1,3-dioxolan-4-yl)methyl)-2-oxo-1,3-dioxolan-4-yl)octanoate (**7**). Note: mixture of diastereoisomers, four *cis* diastereoisomers (96%) and four *trans* diastereoisomers (4%).

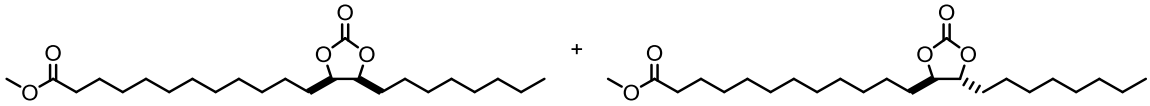


For the major isomers of 7 (*cis*): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.06-4.66 (m, 6H), 3.65 (s, 3H), 2.29 (t, $^{3}J_{H,H}$ = 7.4 Hz, 2H), 2.23-1.93 (m, 4H), 1.80-1.50 (m, 6H), 1.40-1.27 (m, 8H), 1.09 84 (t, $^{3}J_{H,H}$ = 7.2 Hz, 3H). The peaks at δ 4.55-4.15 (m) correspond to *trans*-**7** (4%).



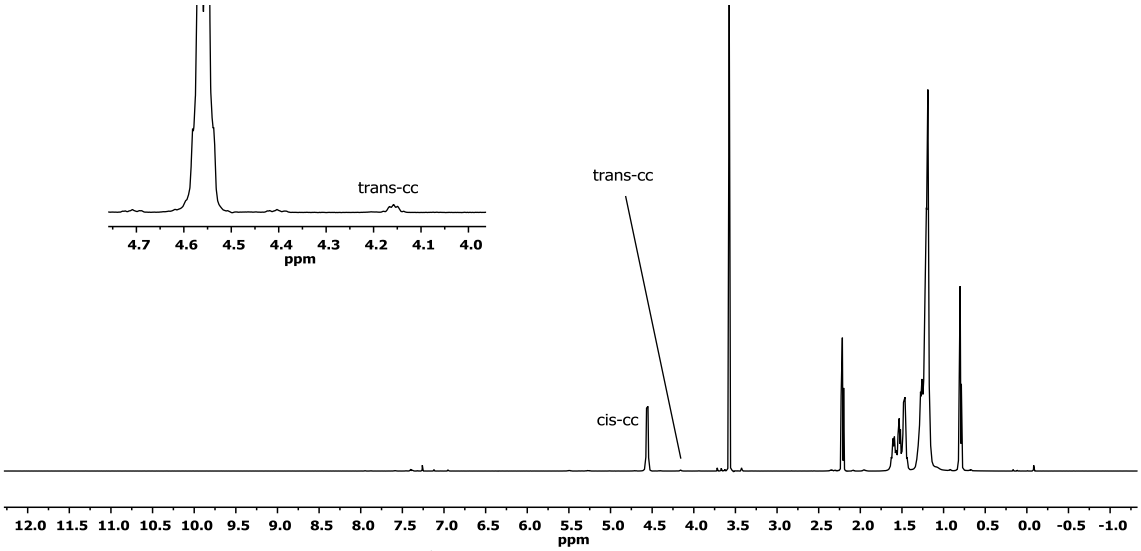
For the major isomers of 7 (*cis*): ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.33 (C=O), 154.19 (C=O), 154.11 (C=O), 153.44 (C=O), 81.24 (CH), 81.10 (CH), 79.90 (CH), 79.77 (CH), 76.63 (CH), 75.68 (CH), 51.59 (OCH_3), 34.08 (CH_2), 29.03 (CH_2), 29.03 (CH_2), 28.95 (CH_2), 28.88 (CH_2), 28.53 (CH_2), 28.25 (CH_2), 25.79 (CH_2), 25.62 (CH_2), 24.89 (CH_2), 24.89 (CH_2), 22.47 (CH_2), 22.40 (CH_2), 10.33 (CH_3).

HRMS (ESI+, CH_3OH): *m/z* calcd. 495.1837 $(M+Na)^+$, found: 495.1848.

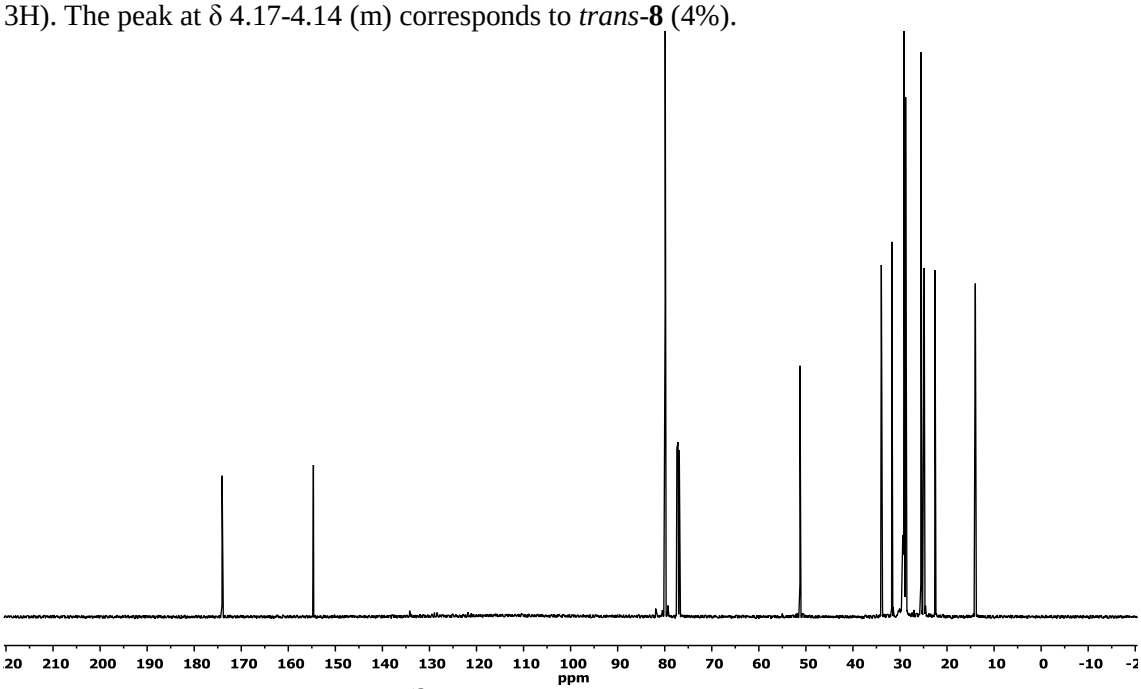


8 cis cyclic carbonate (cis-COC) 96% + **8** trans cyclic carbonate (trans-COC) 4%

Methyl 12-(5-octyl-2-oxo-1,3-dioxolan-4-yl)dodecanoate (**8**).

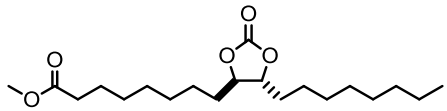


For the major isomer of 8 (*cis*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.59-4.53 (m, 2H), 3.57 (s, 3H), 2.22 (t, $^3J_{H,H}$ = 7.5 Hz, 2H), 1.65-1.40 (m, 8H), 1.33-1.14 (m, 26H), 0.80 (t, $^3J_{H,H}$ = 7.1 Hz, 3H). The peak at δ 4.17-4.14 (m) corresponds to *trans*-**8** (4%).

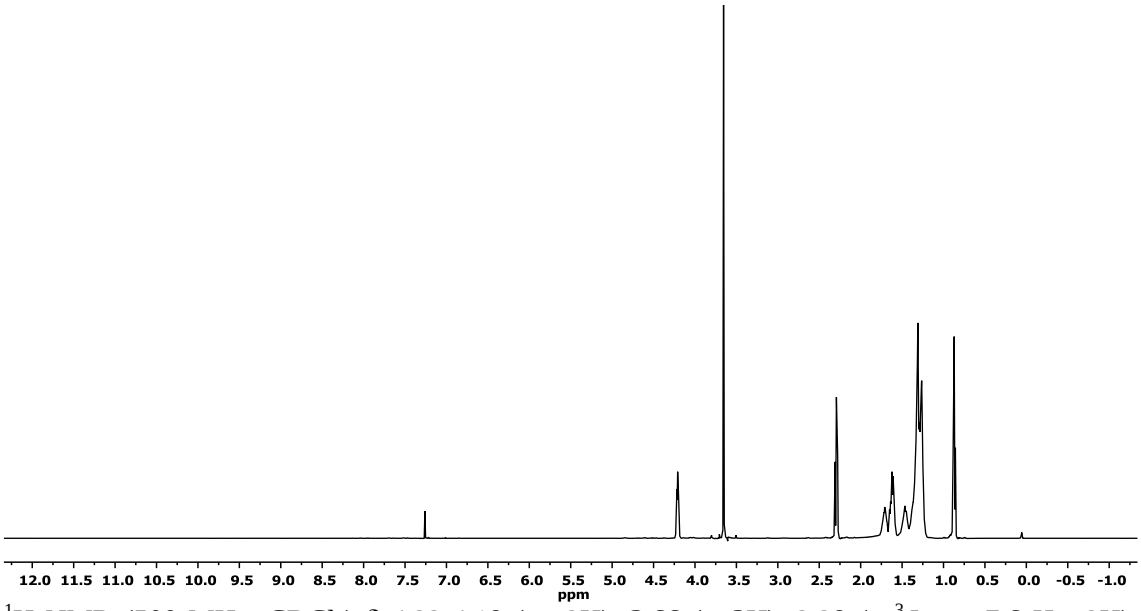


For the major isomer of 8 (*cis*): ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.07 (C=O), 154.66 (C=O), 79.90 (CH), 51.25 (OCH_3), 33.96 (CH_2), 31.72 (CH_2), 29.40 (CH_2), 29.36 (CH_2), 29.31 (CH_2), 29.27 (CH_2), 29.26 (CH_2), 29.17 (CH_2), 29.15 (CH_2), 29.07 (CH_2), 29.03 (CH_2), 28.80 (CH_2), 25.54 (CH_2), 24.85 (CH_2), 22.55 (CH_2), 13.98 (CH_3).

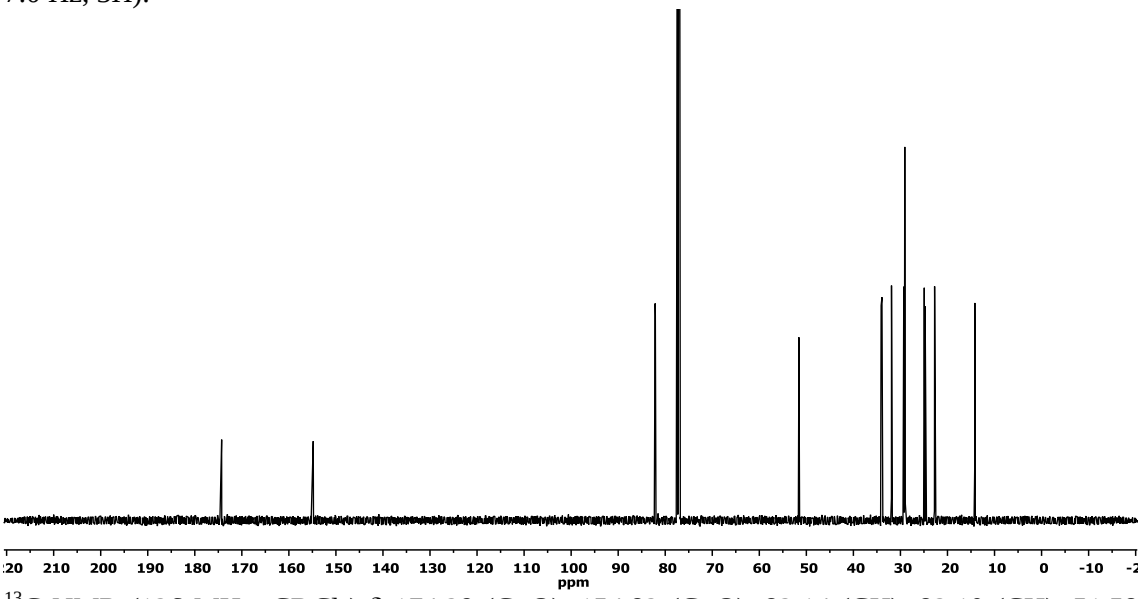
MS (ESI+, CH_3OH): *m/z* calcd. 435.3 $(M+Na)^+$, found: 435.3. [3]



Methyl 8-5-octyl-2-oxo-1,3-dioxolan-4-yl)octanoate (**9**) – *dr* >99:1.

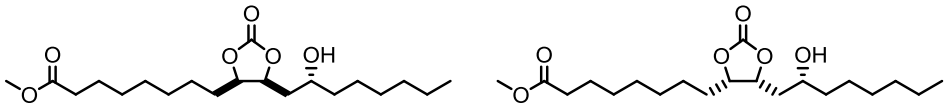


^{1}H NMR (500 MHz, $CDCl_3$) δ 4.22-4.19 (m, 2H), 3.66 (s, 3H), 2.29 (t, $^{3}J_{H,H}$ = 7.6 Hz, 2H), 1.76-1.67 (m, 2H), 1.66-1.56 (m, 4H), 1.52-1.41 (m, 2H), 1.35-1.24 (m, 18H), 0.87 (t, $^{3}J_{H,H}$ = 7.0 Hz, 3H).

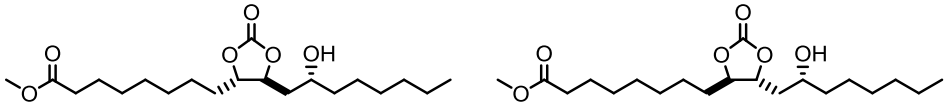


^{13}C NMR (126 MHz, $CDCl_3$) δ 174.29 (C=O), 154.82 (C=O), 82.14 (CH), 82.10 (CH), 51.58 (OCH_3), 34.11 (CH_2), 33.94 (CH_2), 33.93 (CH_2), 31.90 (CH_2), 29.42 (CH_2), 29.29 (CH_2), 29.23 (CH_2), 29.08 (CH_2), 29.03 (CH_2), 24.93 (CH_2), 24.76 (CH_2), 24.72 (CH_2), 22.74 (CH_2), 14.19 (CH_3).

HRMS (ESI+, CH_3OH): *m/z* calcd. 379.2455 $(M+Na)^+$, found: 379.2458.

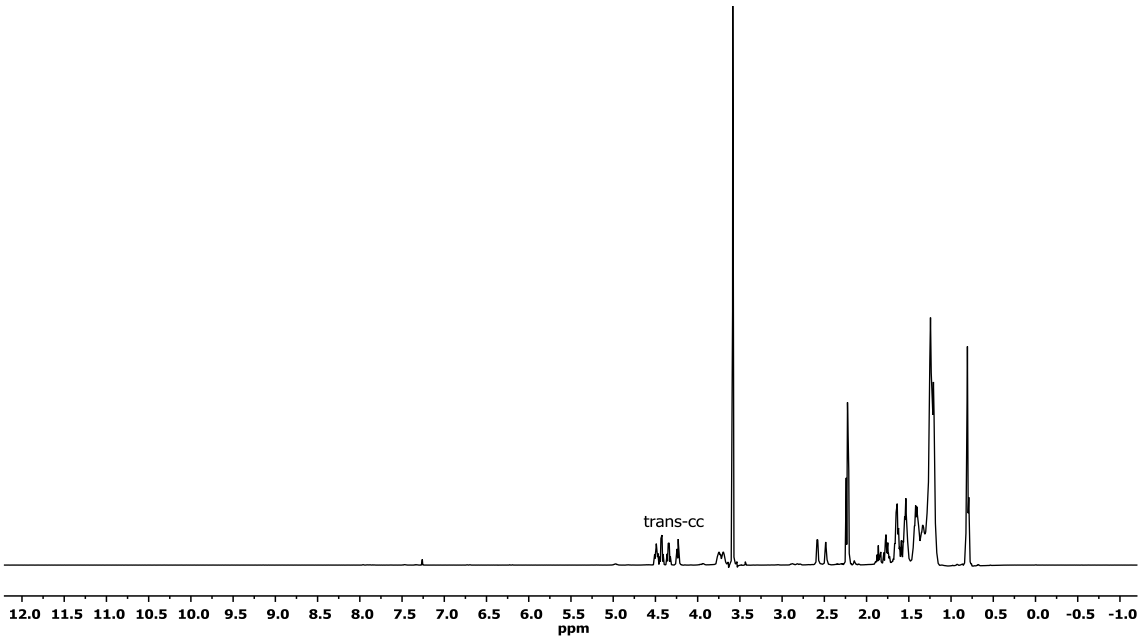


10, cis cyclic carbonates (cis-CC) 4%

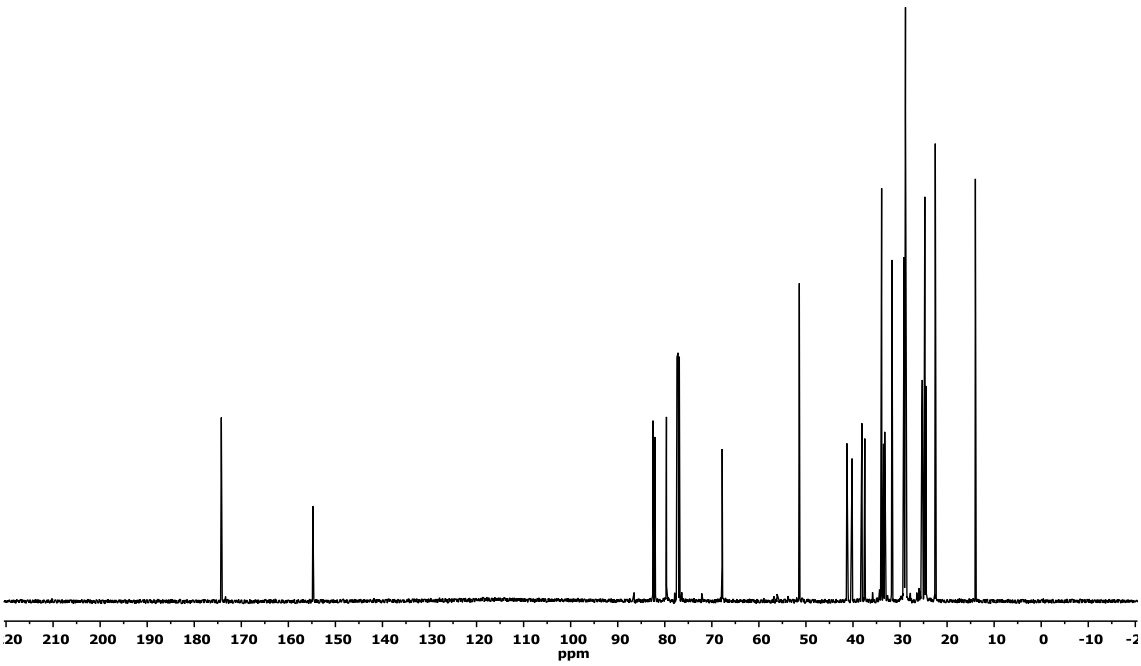


10, trans cyclic carbonates (trans-CC) 96%

Methyl 8-(5-(2-hydroxyoctyl)-2-oxo-1,3-dioxolan-4-yl)octanoate (**10**). Note: mixture of four diastereoisomers.



For the major isomers of 10 (*trans*): ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.55-4.23 (m, 2H), 3.81-3.69 (m, 1H), 3.58 (s, 3H), 2.62-2.49 (2 × br s, 1H, OH), 2.23 (t, $^{3}J_{H,H}$ = 7.4 Hz, 2H), 1.91-1.19 (m, 24H), 0.81 (t, $^{3}J_{H,H}$ = 7.1 Hz, 3H).



For the major isomers of 10 (*trans*): ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.25 (C=O), 154.80 (C=O), 154.77 (C=O), 82.52 (CH), 82.10 (CH), 79.84 (CH), 79.64 (CH), 67.80 (CH), 67.61 (CH), 51.40(OCH_3), 41.29 (CH_2), 40.19 (CH_2), 38.10 (CH_2), 37.49 (CH_2), 33.91 (CH_2), 33.50 (CH_2), 33.25 (CH_2), 31.70 (CH_2), 29.14 (CH_2), 28.84 (CH_2), 28.80 (CH_2), 25.36 (CH_2), 25.27 (CH_2), 24.74 (CH_2), 24.48 (CH_2), 22.51 (CH_2), 13.99 (CH_3).

MS (ESI+, CH_3OH): *m/z* calcd. 395.2 $(M+Na)^+$, found: 395.2. [3]

5. ^{1}H-NMR Analysis of the Crude Reaction Mixture for (5).

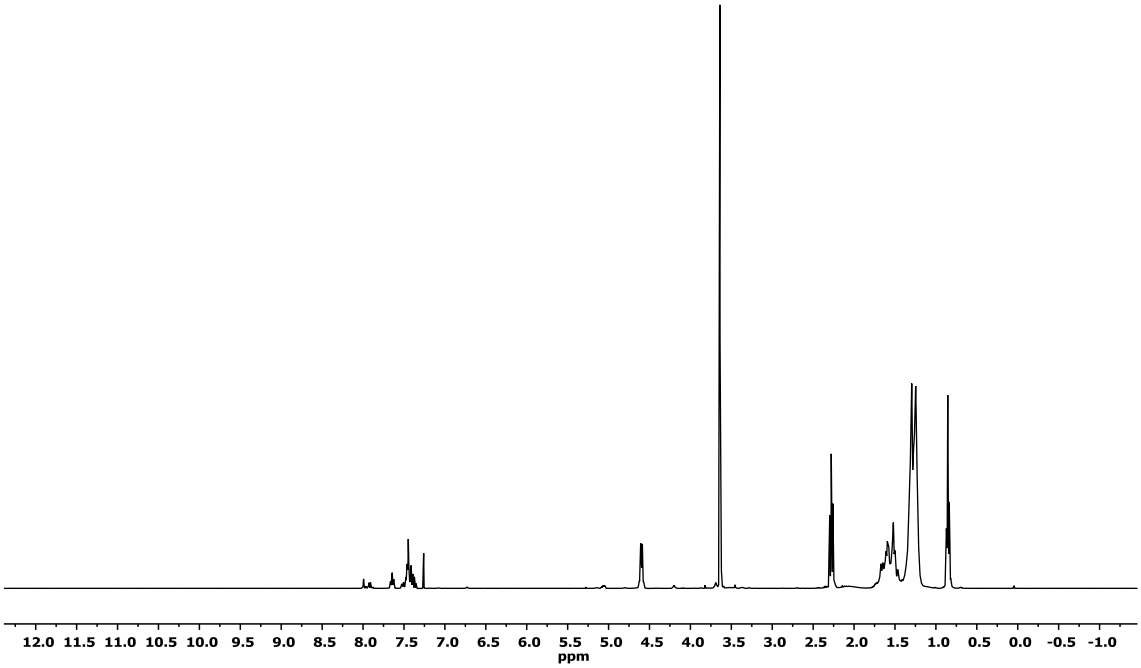
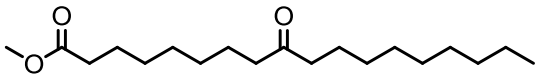
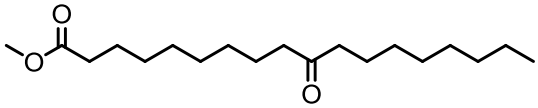


Figure S1. ^{1}H-NMR reaction crude of cyclic carbonate **5** (data for the product obtained using the conditions reported in Table 1, entry 18). The NMR analysis shows the high chemo-selectivity towards cyclic carbonate formation and the virtual absence of methyl 9-oxooctadecanoate (**5b**) and methyl 10-oxooctadecanoate (**5c**), see below for a visual:



methyl 9-oxooctadecanoate (**5b**)

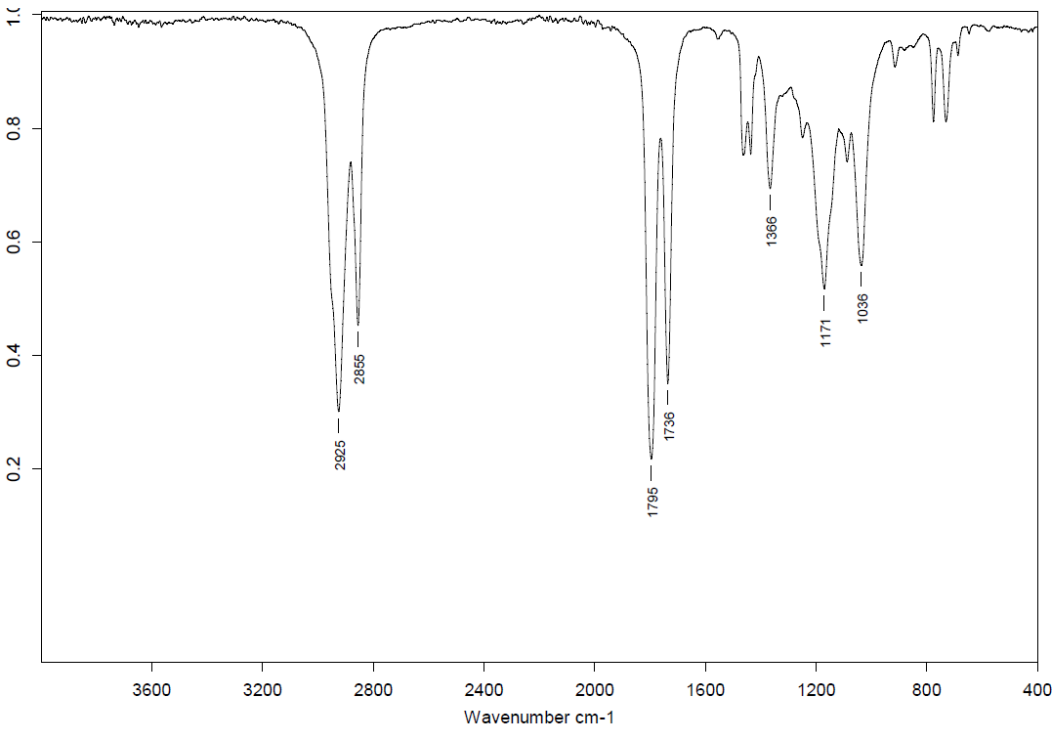


methyl 10-oxooctadecanoate (**5c**)

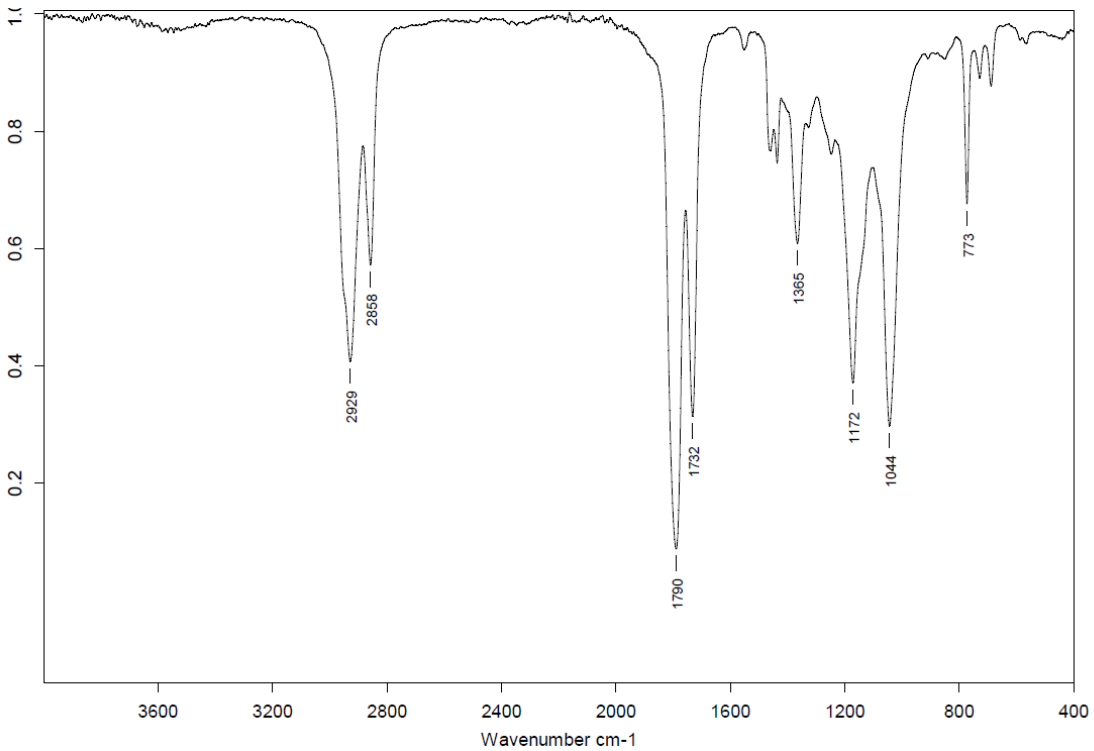
Figure S2. Methyl 9-oxooctadecanoate (**5b**) and Methyl 10-oxooctadecanoate (**5c**). Original data (^{1}H-NMR and ^{13}C-NMR data) for **5b** and **5c** can be found in the Supplementary Information of reference [3].

6. IR Data of All Carbonate Products.

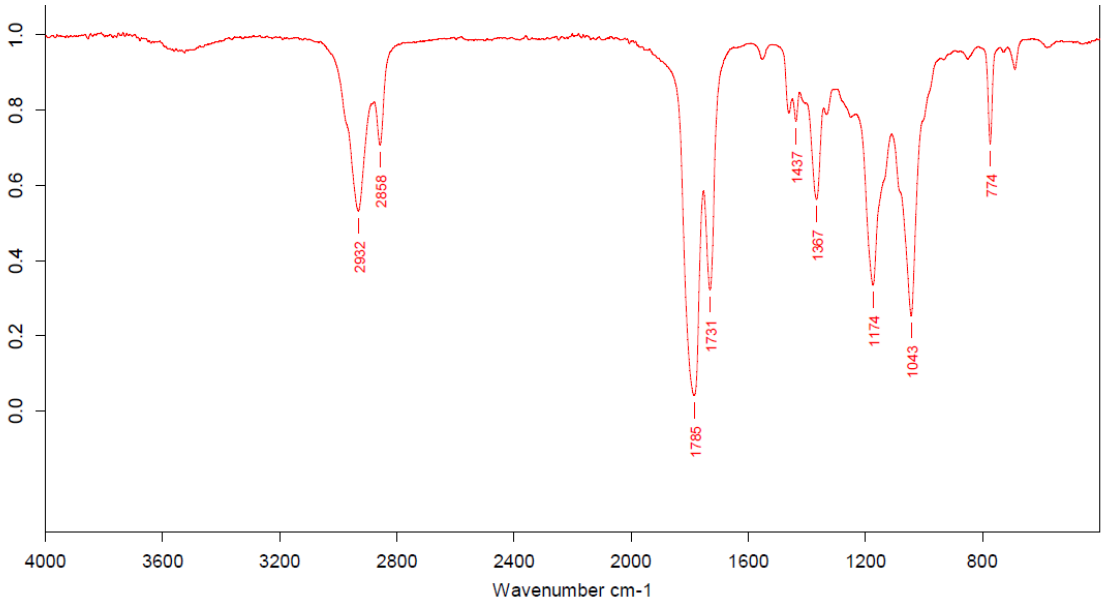
IR spectrum (neat) for **5**.



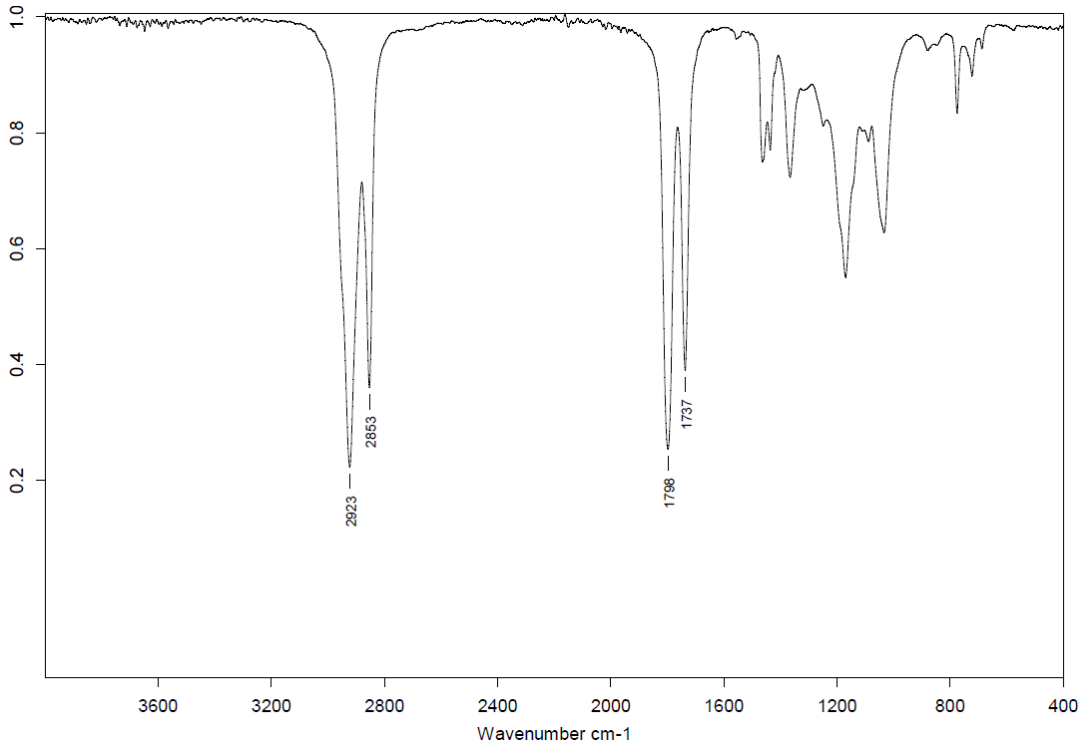
IR spectrum (neat) for **6**.



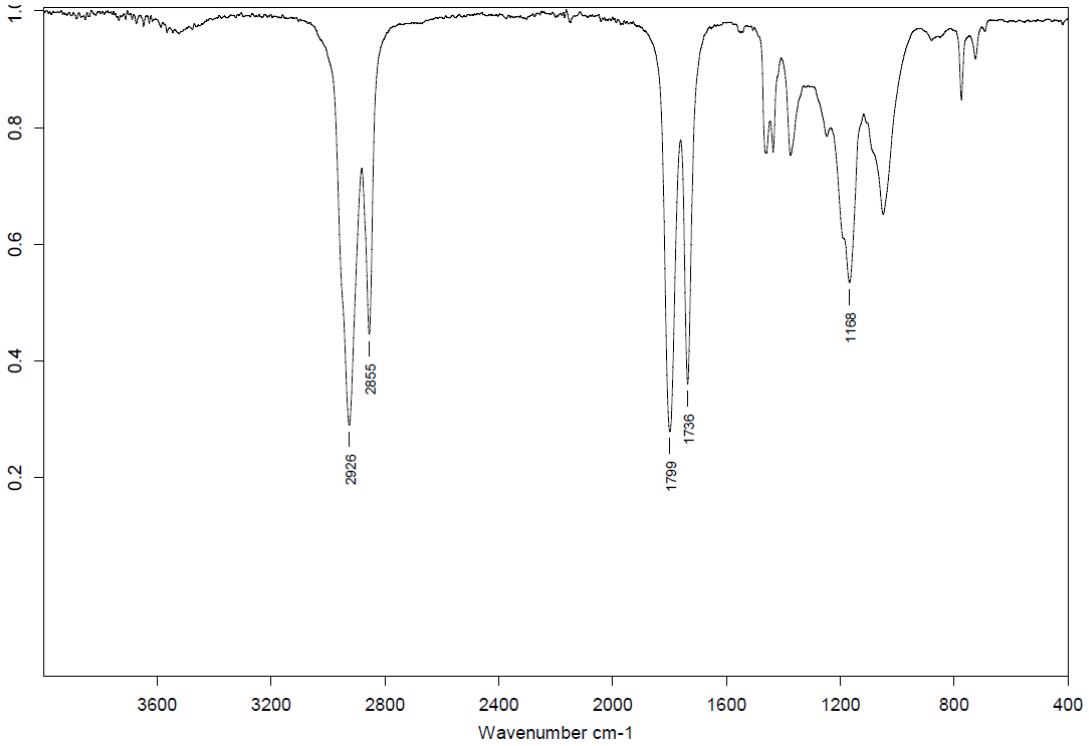
IR spectrum (neat) for **7**.



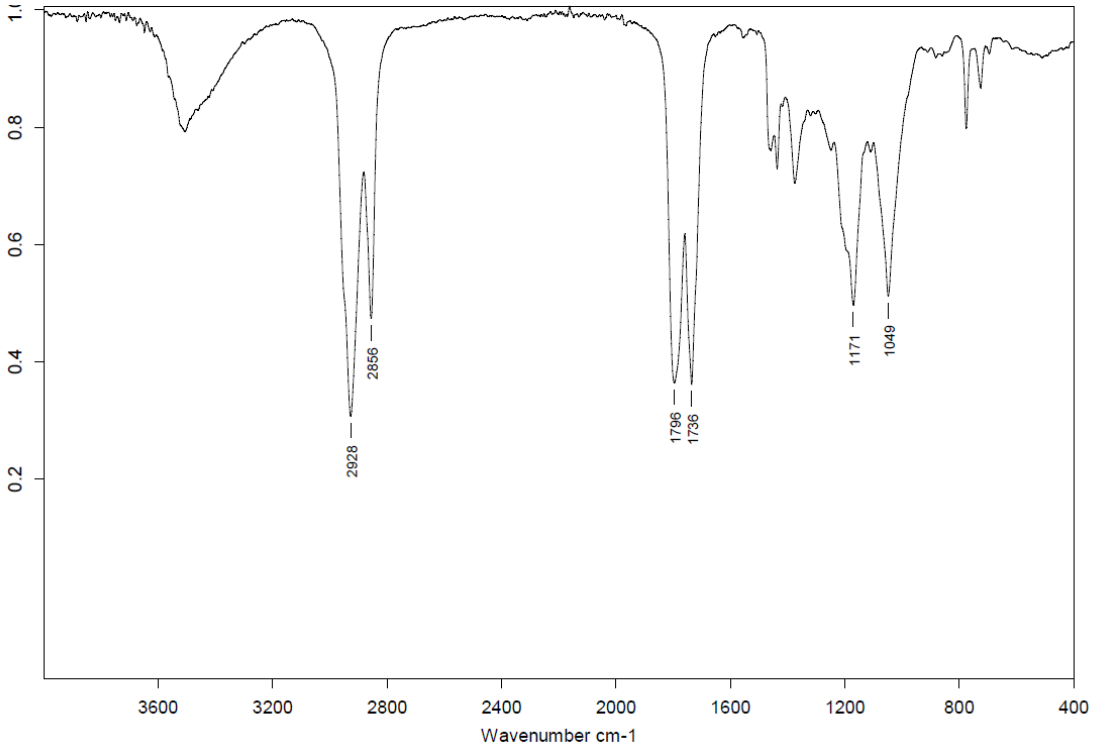
IR spectrum (neat) for **8**.



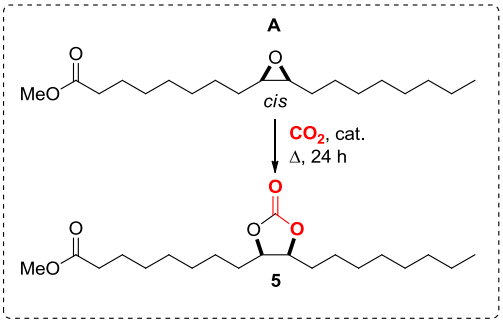
IR spectrum (neat) for **9**.



IR spectrum (neat) for **10**.



7. Kinetic Studies with and without Al Catalyst (3) for the Conversion of Oleate (A).



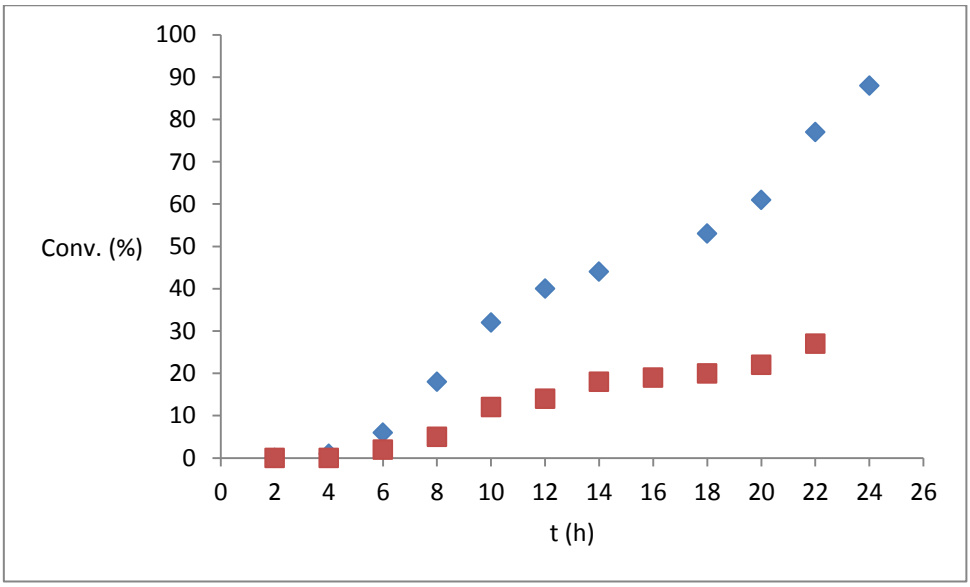


Figure S3:*

In blue: conversion of **A** into **5** in time using 3.2 mmol of **A** 0.5 mol% Al-complex **3**, 3 mol% PPNCl, under neat conditions at 70ºC and 10 bar initial CO_2 pressure.

In red: conversion of **A** into **5** in time under the same conditions in the *absence* of Al-complex **3**.

**Please note that the different kinetic regimes are ascribed to a continuously changing reaction mixture (cf., polarity and viscosity) that may affect the CO_2 dissolution in the liquid phase and the kinetic behavior. Both profiles show the same tendency, but essentially one can notice a clear positive effect of the presence of the Al-complex throughout the reaction.*

8. References:

[1] a) C. J. Whiteoak, E. Martin, M. M. Belmonte, J. Benet-Buchholz and A. W. Kleij, *Adv. Synth. Catal.*, 2012, **354**, 469–476; b) C. J. Whiteoak, N. Kielland, V. Laserna, F. Castro-Gómez, E. Martin, E. C. Escudero-Adán, C. Bo and A. W. Kleij, *Chem. Eur. J.*, 2014, **20**, 2264-2275.

[2] C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin and A. W. Kleij, *J. Am. Chem. Soc.*, 2013, **135**, 1228–1231.

[3] N. Tenhumberg, H. Büttner, B. Schäffner, D. Kruse, M. Blumenstein and T. Werner, *Green Chem.*, 2016, **18**, 3775–3788.