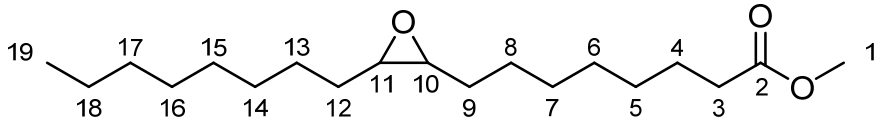
Electronic Supporting Information

Substrate dependent synergetic and antagonistic interaction of ammonium halide and polyoxometalate catalysts in the synthesis of cyclic carbonates from oleo epoxides and CO_2

Jens Langanke, Lasse Greiner and Walter Leitner

Analytic data:

Methyl 8-(3-octyloxiran-2-yl)octanoate **2**:

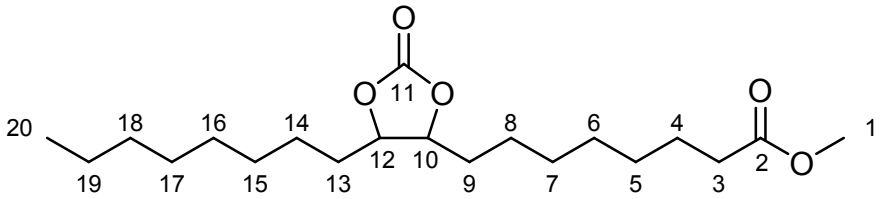


^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.81 (t, *J*=6.4 Hz, 3H, H19), 1.12-1.48 (m, 24H, H5-H9; H12-H18), 1.49-1.62 (m, 2H, H4), 2.23 (t, *J*=7.5 Hz, 2H, H3), 2.83 (brs, 2H, H10-H11), 3.59 (s, 3H, H1) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 14.1 (C19, CH_3), 22.7 (C18, CH_2), 24.9 (C4, CH_2), 26.6 (CH_2), 26.6 (CH_2), 27.8 (CH_2), 27.8 (CH_2), 29.0 (CH_2), 29.2 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 31.9 (C17, CH_2), 34.0 (C3, CH_2), 51.4 (C1, CH_3), 57.2 (C10, CH), 57.2 (C11, CH), 174.2 (C2, C) ppm.

GC (150 °C, 6 °C/min, 280 °C): rt = 13.5 min.

Methyl 8-(5-octyl-2-oxo-1,3-dioxolan-4-yl)octanoate **3**:



^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J*=7.1 Hz, 3H, H20), 1.17-1.42 (m, 18H, H8-H9; H13-H19), 1.49-1.75 (m, 8H, H4-H7), 2.31 (t, *J*=7.5 Hz, 2H, H3), 3.67 (s, 3H, H1), 4.20-4.25 (m, 2H, *trans* H10, *trans* H12), 4.59-4.65 (m, 2H, *cis* H10, *cis* H12) ppm.

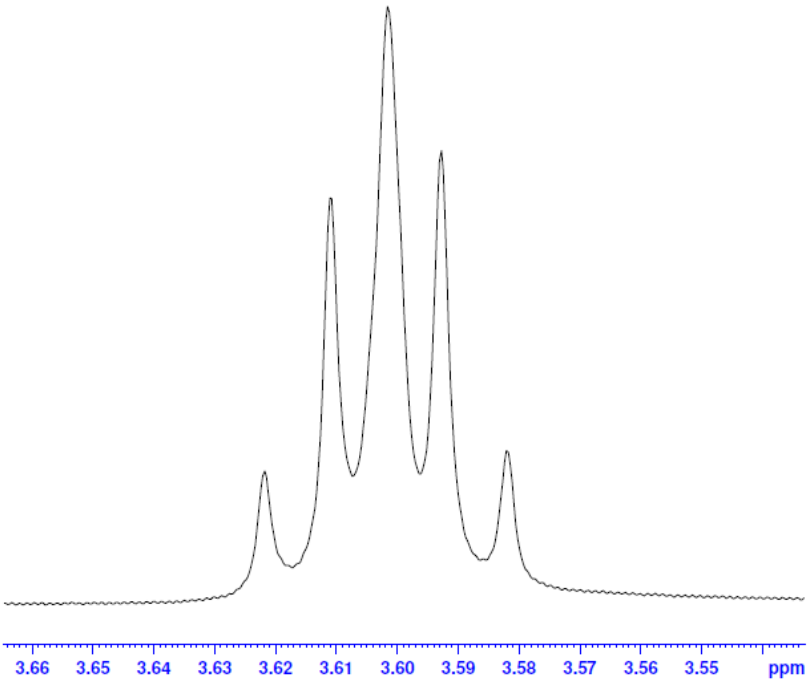
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 14.0 (C20, CH_3), 22.6 (C19, CH_2), 24.8 (C4, CH_2), 25.5 (C8, CH_2), 25.6 (C14, CH_2), 28.9 (CH_2), 28.9 (CH_2), 28.9 (CH_2), 29.0 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 31.8 (CH_2), 34.0 (CH_2), 51.4 (C1, CH_3), 79.9 (C10, CH), 80.0 (C12, CH), 154.7 (C11, C), 174.2 (C2, C) ppm.

MS (EI): 356 (M+), 325, 239, 167, 153, 96, 84, 81, 57 m/z.

GC (150 °C, 6 °C/min, 280 °C): rt = 19.6 (*trans*-**3**), 20.2 (*cis*-**3**) min.

Identifying *cis*/*trans*-isomers of compound **3**:

The coupling partners of the protons H10 and H12 were identified using DGF-COSY spectra in C_6D_6 of both isolated cis- and trans-isomers of compound **3**. Selective decoupling of the these protons in combination with molecular modelling of the two isomers using the software programs Spartan04 and Gaussian03 lead to the assignment of the signal at 3.60 ppm (J = 5.4 Hz) to *trans*-**3** and at 3.79 ppm (J = 8.3 Hz) to *cis*-**3** (spectra see below). The NMR-spectra were recorded in benzene-d6 as solvent resulting in a shift of these signals in comparison to the spectra for compound **3** in $CDCl_3$.



NAME	JLA-CMO-A1B
EXPNO	6
PROCNO	1
Date_	20101118
Time	15.20
INSTRUM	spect
PROBHD	5 mm PABBI 1H/
PULPROG	zg0hd
TD	32768
SOLVENT	C6D6
NS	4
DS	0
SWH	12019.230 Hz
FIDRES	0.366798 Hz
AQ	1.3632404 sec
RG	40.3
DW	41.600 usec
DE	6.50 usec
TE	299.2 K
D1	3.00000000 sec
D12	0.00002000 sec
HDDUTY	20.8 %
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P0	12.20 usec
PL1	-1.00 dB
PL24	40.00 dB
PL1W	14.54647732 W
PL24W	0.00115547 W
SFO1	600.0674003 MHz
SI	65536
SF	600.0650000 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

Figure ESI.3: Decoupled ^{1}H-NMR spectrum of *trans*-**3** (section)

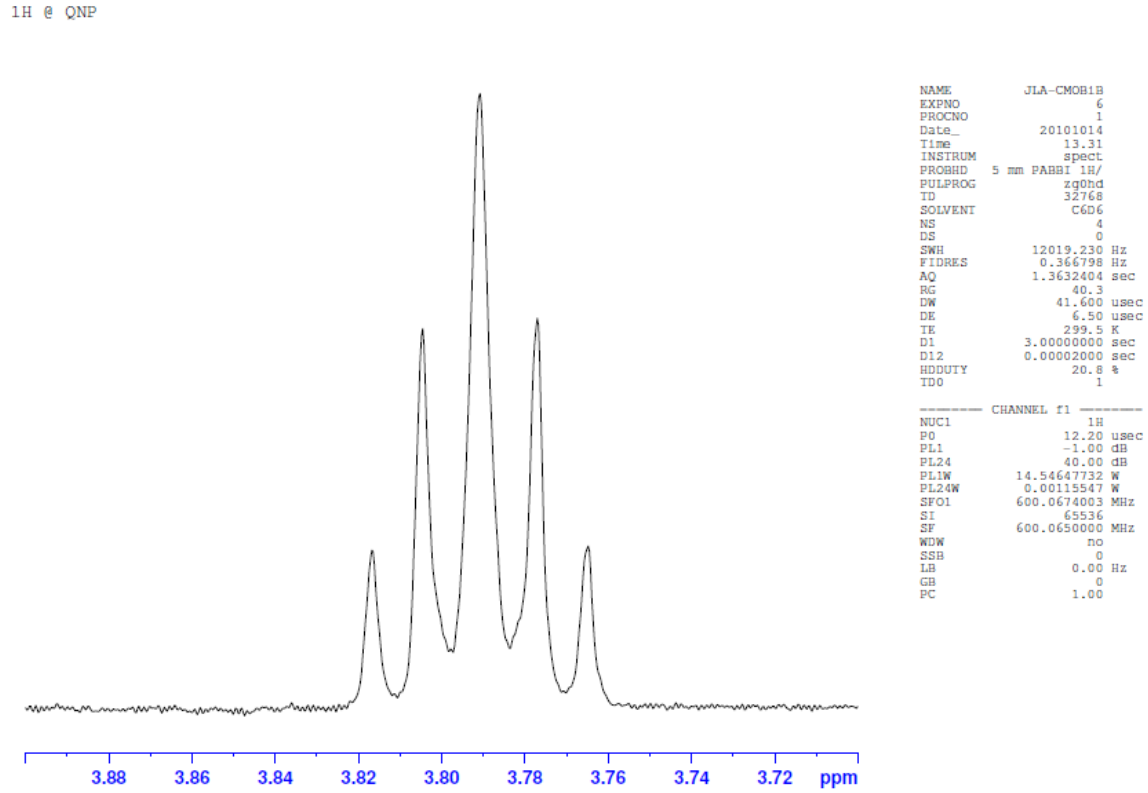


Figure ESI.4: Decoupled ^{1}H-NMR spectrum of *cis*-**3** (section)

$((n\text{-}C_7H_{15})_4N)_5[CrSiW_{11}O_{39}]$ **THA-Cr-Si-POM**:

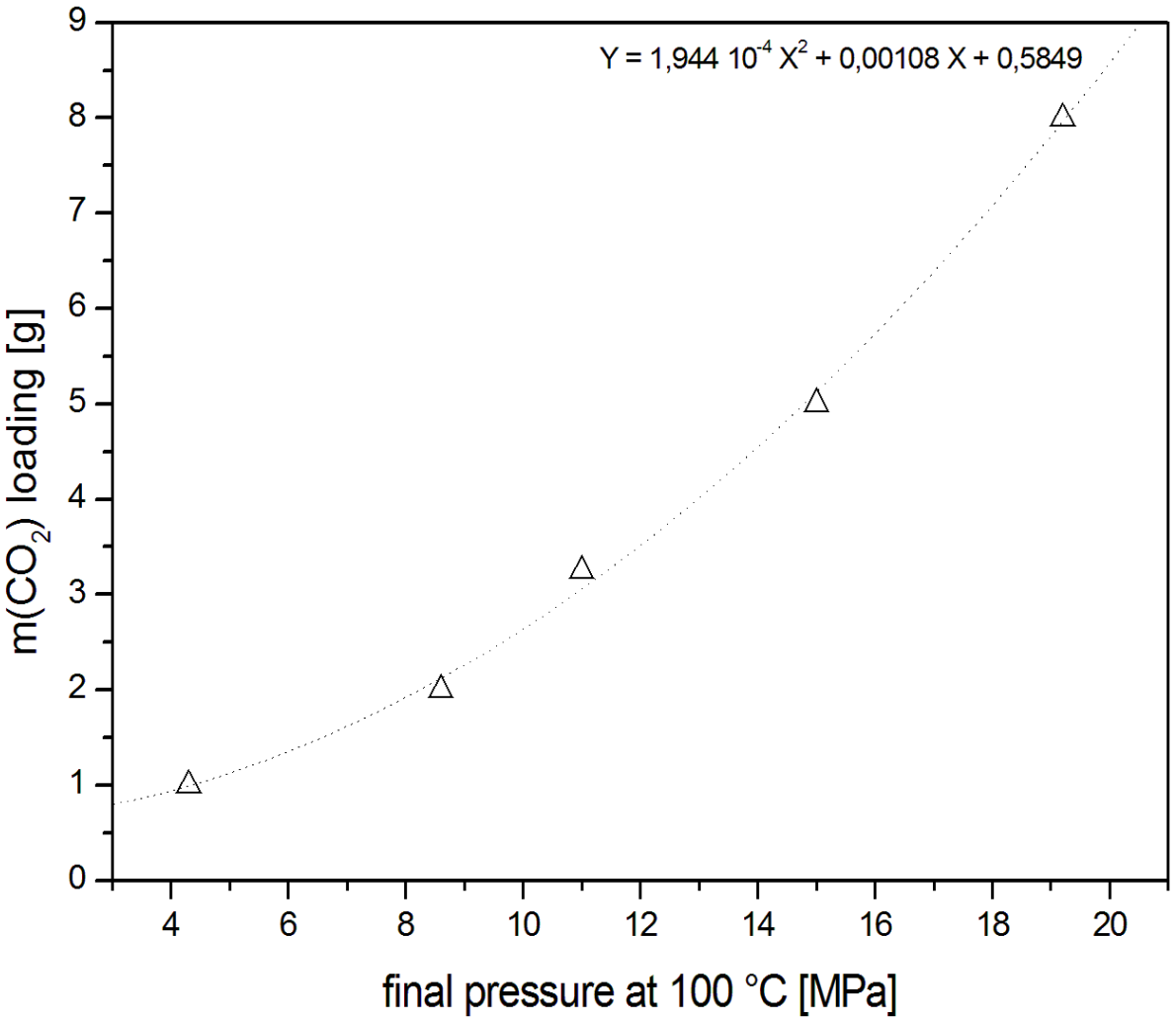
MS (FAB-SIMS (+c/-c), Cs^+, DTE/DTT matrix):
2727 (M−), 2695, 2463, 2216, 1984, 1752, 1518, 696, 481, 462;

411 (M+), 407. 311, 226, 142 m/z.

^{29}Si-NMR (120 MHz, Toluene-d_8): δ= -21.1 ppm.

IR: ν_{max} = 2923 (m), 2855 (w), 146 (w), 1378 (w), 952 (m), 907 (s), 780 (s), 523 (m) cm^{-1}.

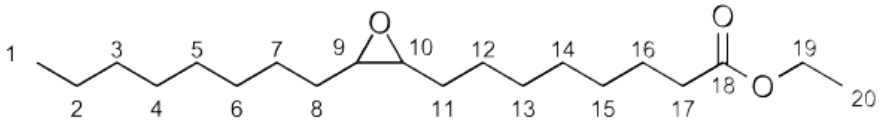
Calibration curve for charging the window-equipped stainless steel high-pressure reactor (V = 11 ml) at room temperature with CO_2:



Synthesis procedures and analytic data:

1) Preparation of ethyl 8-(3-octyloxiran-2-yl)octanoate (**4**)

A 35 mL microwave vial was charged with 1 eq. ethyl (Z)-octadec-9-enoate (2.63 g, 8.47 mmol), and 1.2 eq. meta-chloroperoxybenzoic acid[1] (2.27 g, 77 %, 10.14 mmol) dissolved in 25 mL dichloromethan (DCM) was added slowly under ice cooling. The sealed vial was vigorously stirred and kept at 50 °C for 5 min by radiation with up to 10W power. The resulting reaction mixture was poured into 100 mL aq. $NaHSO_3$ solution (40 %) and stirred for 1 h. Afterwards, 115 mL aq. Na_2CO_3 solution (1 M) was added and it was again stirred for 1 h. A sample was withdrawn and tested for the absence of peroxides. The organic layer was collected, washed several times with water, pre-dried over anhydrous Na_2SO_4, and evaporated. The residue obtained was dissolved in 60 mL chloroform and again washed with water for several times. The organic layer was decanted and dried over anhydrous Na_2SO_4. After removing chloroform under reduced pressure, the pure product ethyl 8-(3-octyloxiran-2-yl)octanoate **4** was obtained as colourless oil (1.62 g, 4.97 mmol, 59 %).



Ethyl 8-(3-octyloxiran-2-yl)octanoate (**4**)

^{1}H-NMR (400 MHz, $CDCl_3$): δ =0.88 (t, J=7.0 Hz, 3H, H1), 1.2-1.7 (m, 29 H, H2-H8, H11-H16, H20), 2.29 (t, J=7.5 Hz, 2 H, H17), 2.84-3.00 (m, 2 H, H9-H10), 4.12 (q, J=7.1 Hz, 2 H, H19) ppm.[2]

^{13}C-NMR (100 MHz, $CDCl_3$): δ =14.1 (C1, CH_3), 14.2 (C20, CH_3), 22.6 (C2, CH_2), 24.9 (C3, CH_2), 26.5-26.6 (C7, C12, 2 CH_2), 27.8 (C8, C11, 2 CH_2), 28.9-29.8 (C4-C6, C13-C15, 6 CH_2), 31.8 (C16, CH_2), 34.3 (C17, CH_3), 57.1-57.2 (C9, C10, 2 CH), 60.1 (C19, CH_2), 173.7 (C18, C) ppm.

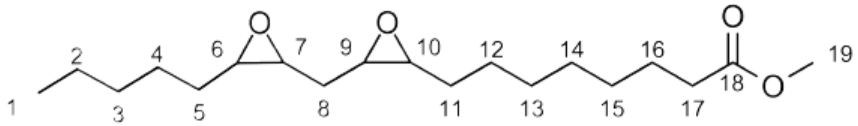
IR: ν_{max} =2925 (m, C-$H_{stretch}$), 2855 (m), 1736 (s, C=O), 1465 (w), 1179 (m), 756 (s) cm^{-1}.

MS (EI, 70 eV): 326 (M+), 213, 157, 155, 153, 109, 101, 97, 95 m/z.

[1] mCPBA
[2] Y. Itoi, M. Inoue, S. Enomoto, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 3941-3943.

2) Preparation of methyl 8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanoate (**6**)

A 35mL microwave vial was charged with 1 eq. (9Z,12Z)-methyl octadeca-9,12-dienoate (2.56 g, 8.68mmol), and 2.3 eq. mCPBA (4.54 g, 77 %, 20.24 mmol) dissolved in 30mL DCM was added slowly under ice cooling. The sealed vial was vigorously stirred and kept at 50 °C for 5 min by radiation with up to 10W power. The resulting reaction mixture was poured into 50mL aq. $NaHSO_3$ solution (40 %) and stirred overnight. The peroxide free DCM layer was decanted and stirred with 75 mL aq. Na_2CO_3 solution (1 M) for 0.5 h. After separating both phases, the aqueous one was extracted with DCM. The collected DCM phase was evaporated. The resulting residue was dissolved in 30mL chloroform and again treated with aq. Na_2CO_3 solution (50 mL, 1 M). After phase separation and extraction with either chloroform or aq. Na_2CO_3 solution, the chloroform phases were collected and dried over anhydrous Na_2SO_4. Finally, the chloroform was evaporated under reduced pressure and the pure product methyl 8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanoate (**6**) was obtained as colourless oil (2.09 g, 6.39 mmol,74 %).



Methyl 8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanoate (**6**)

^{1}H-NMR (400 MHz, $CDCl_3$): δ =0.90 (t, J=6.9 Hz, 3 H, H1), 1.20-1.84 (m, 22 H, H2-H5, H8, H11-H16), 2.30 (t, J=7.5Hz, 2 -H, H17), 2.92-3.15 (m, 4 H, H6, H7, H9, H10), 3.66 (s, 3 H, H19) ppm.[3]

^{13}C-NMR (100 MHz, $CDCl_3$): δ =14.0 (C1, CH_3), 22.6 (C2 , CH_2), 24.9-27.9 (C3, C4, C5, C8, C11, C12, 6 CH_2), 29.0-29.3 (C13-C15, 3 CH_2), 31.7 (C16, CH_2), 34.0 (C17, CH_2), 51.4 (C19, CH_3), 54.2-54.3 (C7, C9, 2 CH), 56.7-57.0 (C6, C10,2 CH), 174.2 (C18, C) ppm.[3]

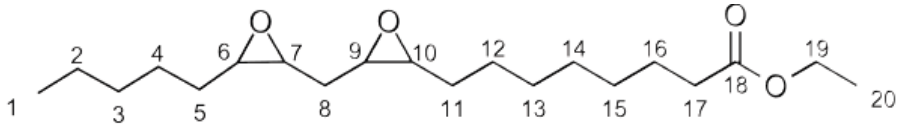
IR: ν_{max} =2930 (m, C-$H_{stretch}$), 1737 (s, C=O), 1436 (w), 1170 (m), 753 (s) cm^{-1}.

MS (EI, 70 eV): 326 (M+), 155, 123, 109, 98, 97, 96, 95, 93 m/z.

[3] K. M. Doll, S. Z. Erhan, *J. Agric. Food Chem.*, 2005, **53**, 9608-9614.

3) Preparation of ethyl 8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanoate (**8**)

A 35 mL microwave vial was charged with 1 eq. of (9Z,12Z)-ethyl octadeca-9,12-dienoate (1.42 g, 4.60 mmol), and 3.3 eq. mCPBA (3.36 g, 77 %, 15.00 mmol) dissolved in 25 mL chloroform was added slowly under ice cooling. The sealed vial was vigorously stirred and kept at 50 °C for 5 min by radiation with up to 10W power. The same procedure was repeated with a second identical batch. Both batches were combined and stirred for 1 h with 100 mL aq. $NaHSO_3$ solution (40 %). The peroxide-free chloroform layer was decanted and stirred for 1 h with 100mL aq. Na_2CO_3 solution (1 M). After separating both phases, the aqueous one was extracted with 100 mL chloroform and the collected chloroform phase was extracted once with 50 mL aq. Na_2CO_3 solution (1 M) and twice with each 100 mL water. The combined chloroform phase was pre-dried over anhydrous Na_2SO_4 and evaporated. The resulting residue was dissolved in 70 mL chloroform, washed six times with each 50 mL water, separated, and dried over anhydrous Na_2SO_4. Finally, the chloroform was evaporated under reduced pressure and the pure product ethyl 8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanoate was obtained as turbid oil (2.06 g, 6.06 mmol, 66 %).



Ethyl 8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanoate (**8**)

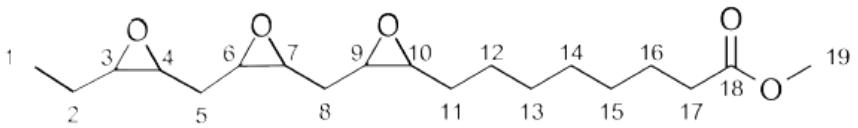
^{1}H-NMR (400 MHz, $CDCl_3$): δ =0.83 (t, J=6.6 Hz, 3 H, H1), 1.15_1.80 (m, 25 H, H2-H5, H8, H11-H16, H20), 2.22 (t, J=7.6 Hz, 2 H, H17), 2.86-3.08 (m, 4 H, H6, H7, H9, H10), 4.05 (q, J=7.1 Hz, 2 H, H19) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$): δ =14.0 (C1, CH_3), 14.2 (C20, CH_3), 22.6 (C2, CH_2), 24.9 (C3, CH_2), 26.1 (C8, CH_2), 26.5 (C4, CH_2), 27.1 (C12, CH_2), 27.8-27.9 (C5, C11, 2 CH_2), 29.0-29.3 (C13-C15, 3 CH_2), 31.7 (C16, CH_2), 34.3 (C17, CH_2), 54.2-54.3 (C7, C9, 2 CH), 56.7-57.0 (C6, C10, 2 CH), 60.2 (C19, CH_2), 173.8 (C18, C) ppm.

MS (EI, 70 eV): 341 (M+), 217, 155, 109, 98, 97, 96, 95 m/z.

4) Preparation of methyl 8-(3-((3-((3-ethyloxiran-2-yl)methyl)oxiran-2-yl)methyl)oxiran-2-yl)octanoate (**10**)

A 35mL microwave vial was charged with 1 eq. of (9Z,12Z,15Z)-methyl octadeca-9,12,15-trienoate 24 (1.14 g, 3.91 mmol), and 3.6 eq. mCPBA (3.13 g, 77 %, 13.98 mmol) dissolved in 25 mL chloroform was added slowly under ice cooling. The sealed vial was vigorously stirred and kept at 50 °C for 5 min by radiation with up to 10W power. The same procedure was repeated with a second identical batch. Both batches were combined and stirred for 1 h with 100 mL aq. $NaHSO_3$ solution (40 %). The peroxide-free chloroform layer was decanted and stirred with 100mL aq. Na_2CO_3 solution (1 M) for 1 h. After separating both phases, the aqueous one was extracted with 100mL chloroform and the collected chloroform phase was extracted twice with each 100 mL water. The combined chloroform phase was dried over anhydrous Na_2SO_4. Finally, the chloroform was evaporated under reduced pressure and the pure product methyl 8-(3-((3-((3-ethyloxiran-2-yl)methyl)oxiran-2-yl)methyl)oxiran-2-yl)octanoate (**10**) was obtained as yellowish oil (2.38 g, 6.98 mmol, 89 %).



Methyl 8-(3-((3-((3-ethyloxiran-2-yl)methyl)oxiran-2-yl)methyl)oxiran-2-yl)octanoate (**10**)

^{1}H-NMR (400 MHz, $CDCl_3$): δ =0.99 (t, J=7.4 Hz, 3 H, H1), 1.2-1.8 (m, 18 H, H2, H5, H8, H11-H16), 2.24 (t, J=7.5 Hz, 2 H, H17), 2.85-3.16 (m, 6 H, H3, H4, H6, H7, H9, H10), 3.60 (s, 3 H, H19) ppm.

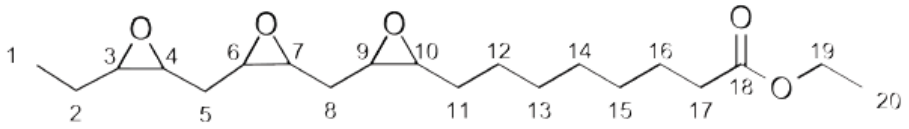
^{13}C-NMR (100 MHz, $CDCl_3$): δ =10.5 (C1, CH_3), 21.2 (C2, CH_2), 24.9 (C12, CH_2), 26.1_27.9 (C3, C5, C8, 3 CH_2), 27.8 (C11, CH_2), 29.0-29.3 (C13-C15, 3 CH_2), 34.0 (C17, CH_2), 51.5 (C19, CH_3), 53.8-58.3 (C4, C6, C7, C9, C10, C16, 6 CH), 174.2 (C18, C) ppm.

IR: ν_{max} =2928 (m, C-$H_{stretch}$), 1736 (s, C=O), 1436 (w), 1169 (m), 821 (m) cm^{-1}.

MS (EI, 70 eV): 340 (M+), 215, 157, 155, 109, 97, 93, 91 m/z.

5) Preparation of ethyl 8-(3-((3-((3-ethyloxiran-2-yl)methyl)oxiran-2-yl)methyl)oxiran-2-yl)octanoate (**12**)

A 35mL microwave vial was charged with 1 eq. (9Z,12Z,15Z)-ethyl octadeca-9,12,15-trienoate 26 (1.25 g, 4.07 mmol), and 4.5 eq. mCPBA (4.07 g, 77 %, 18.17mmol) dissolved in 25 mL chloroform was added slowly under ice cooling. The sealed vial was vigorously stirred and kept at 50 °C for 5 min by radiation with up to 10W power. The same procedure was repeated with a second identical batch. Both batches were combined and stirred for 2 h with 150 mL aq. $NaHSO_3$ solution (40 %). The peroxide-free chloroform layer was decanted and stirred for 1 h with 100mL aq. Na2CO3 solution (1 M). After separating both phases, the aqueous one was extracted with 100 mL chloroform and the collected chloroform phase was extracted with 75mL aq. Na_2CO_3 solution (1 M) and six times with each 100mL water. The combined chloroform phase was dried over anhydrous Na_2SO_4. Finally, the chloroform was evaporated under reduced pressure and the pure product ethyl 8-(3-((3-((3-ethyloxiran-2-yl)methyl)oxiran-2-yl)methyl)oxiran-2-yl)octanoate (**12**) was obtained as turbid oil (1.27 g, 3.58 mmol, 44 %).



Ethyl 8-(3-((3-((3-ethyloxiran-2-yl)methyl)oxiran-2-yl)methyl)oxiran-2-yl)octanoate (**12**)

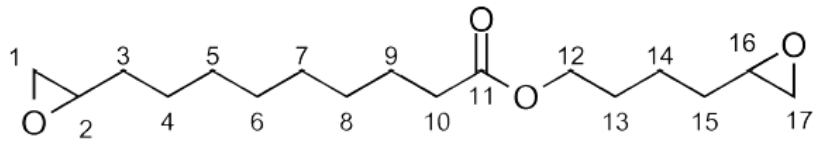
^{1}H-NMR (400 MHz, $CDCl_3$): δ =0.99 (t, J=7.5 Hz, 3 H, H1), 1.13-1.81 (m, 21 H, H2, H5, H8, H11-H16, H20), 2.22 (t, J=7.5 Hz, 2 H, H17), 2.81-3.15 (m, 6 H, H3, H4, H6, H7, H9, H10), 4.06 (q, J = 3.6 Hz, 2 H, H19) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$): δ =10.5 (C1, CH_3), 14.3 (C20, CH_3), 21.3 (C2, CH_2), 24.9 (C3, CH_2), 26.1-28.0 (C5, C8, C12, 3 CH_2), 28.9-29.3 (C13-C15, 3 CH_2), 34.3 (C17, CH_2), 54.2 (C16, CH), 56.6-57.0 (C4, C6, C7, C9, 4 CH), 58.2 (C10, CH), 60.2 (C19, CH_2), 173.8 (C18, C) ppm.

MS (EI, 70 eV): 354 (M+), 213, 157, 110, 108, 107, 98, 96, 95 m/z.

6) Preparation of 4-(oxiran-2-yl)butyl 9-(oxiran-2-yl)nonanoate (**14**)

A 35mL microwave vial was charged with 1 eq. hex-5-enyl undec-10-enoate (1.33 g, 4.97 mmol), and 2.8 eq. mCPBA (3.11 g, 77 %, 13.88 mmol) dissolved in 25 mL chloroform was added slowly under ice cooling. The sealed vial was vigorously stirred and kept at 50 °C for 5 min by radiation with up to 10W power. The same procedure was repeated with a second identical batch. Both batches were combined and stirred for 1 h with 100mL aq. $NaHSO_3$ solution (40 %). The peroxide-free chloroform layer was decanted and stirred for 40 min with 100 mL aq. Na_2CO_3 solution (1 M). After separating both phases, the aqueous one was extracted with 100 mL chloroform and the collected chloroform phase was extracted with 50 mL aq. Na_2CO_3 solution (1 M) and twice with each 100 mL water. The combined chloroform phase was dried over anhydrous Na_2SO_4. Finally, the chloroform was evaporated under reduced pressure and the pure product 4-(oxiran-2-yl)butyl 9-(oxiran-2-yl)nonanoate (**14**) was obtained as viscous colourless liquid (2.44 g, 8.18 mmol, 82 %).



4-(oxiran-2-yl)butyl 9-(oxiran-2-yl)nonanoate (**14**)

^{1}H-NMR (400 MHz, $CDCl_3$): δ =1.16-1.73 (m, 20 H, H3-H9, H13-H15), 2.22 (t, J=7.5 Hz, 2 H, H10), 2.37-2.42 (m, 2 H, H1, H17), 2.65-2.71 (m, 2 H, H2, H16), 2.80-2.88 (m, 2 H, H1, H17), 4.00 (t, J = 6.5 Hz, 2 H, H12) ppm.

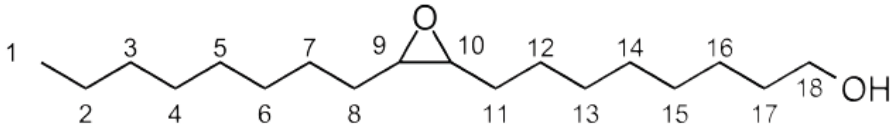
^{13}C-NMR (100 MHz, $CDCl_3$): δ =22.5 (C14, CH_2), 24.9 (C9, CH_2), 25.9 (C4, CH_2), 28.4 (C13, CH_2), 29.1-29.3 (C5-C8, CH_2) 32.1 (C15, CH_2), 32.5 (C3, CH_2), 34.3 (C10, CH_2), 47.0-47.1 (C1, C17, CH_2), 52.1-52.4 (C2, C16, CH), 64.0 (C12, CH_2), 173.9 (C11, C) ppm.

IR: ν_{max} =2926 (m, C-$H_{stretch}$), 2855 (m), 1732 (s, C=O), 1459 (w), 1170 (m), 914 (w), 835 (m) cm^{-1}.

MS (EI, 70 eV): 298 (M+), 139, 123, 121, 99, 98, 97, 95 m/z.

7) Preparation of 8-(3-octyloxiran-2-yl)octane-1-ol (**18**)

A 35 mL microwave vial was charged with 1 eq. (Z)-octadec-9-en-1-ol (2.65 g, 9.96 mmol), and 1.6 eq. mCPBA (3.63 g, 77 %, 16.23 mmol) dissolved in 25 mL chloroform was added slowly under ice cooling. The sealed vial was vigorously stirred and kept at 50 °C for 5 min by radiation with up to 10W power. The reaction mixture was poured into 50mL aq. NaHSO3 solution (40 %) and stirred for 20 min. Afterwards, 50mL aq. Na_2CO_3 solution (1 M) was added and stirred for another 40 min. The peroxide-free chloroform layer was decanted and washed five times with each 200 mL water. The whole procedure was repeated with a second identical batch. The resulting chloroform phases were combined and dried over anhydrous Na_2SO_4. Finally, the chloroform was evaporated under reduced pressure and the pure product 8-(3-octyloxiran-2-yl)octane-1-ol (**18**) was obtained as beige waxy solid (2.89 g, 10.16 mmol, 51 %).



8-(3-octyloxiran-2-yl)octane-1-ol (**18**)

^{1}H-NMR (400 MHz, $CDCl_3$): δ =0.88 (t, J=6.5 Hz, 3 H, H1), 1.2-1.66 (m, 28 H, H2-H8, H11-H17), 2.85-2.94 (m, 2 H, H9, H10), 3.63 (t, J=6.5 Hz, 2 H, H18) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$): δ =14.1 (C1, CH_3), 22.7 (C2, CH_2), 25.7 (C3, CH_2), 26.6-29.7 (C4-C8, C11-C15, 8 CH_2), 31.9 (C16, CH_2), 32.8 (C17, CH_2), 57.3 (C9, C10, 2 CH), 63.0 (C18, CH_2) ppm.

IR: ν_{max} =3359 (br, O-$H_{stretch}$), 2917 (s, C-$H_{stretch}$), 1460 (m, O-$H_{deformation}$), 1074 (s, C-OH), 979 (s), 845 (s), 632 (m) cm^{-1}.

MS (EI, 70 eV): 284 (M+), 171, 155, 125, 124, 123, 112, 111, 98, 97, 96, 95 m/z.