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Supporting information

Homogeneous and Heterogeneous Catalytic (Dehydrogenative) Oxidation of Oleochemical 1,2-Diols to α-Hydroxyketones.

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1. General information

All reagents and solvents used for synthesis were commercial and used without further purification. Methyl oleate (96% purity), technical (90% purity) oleic acid, 1-butanol, 2-ethyl hexanol, hydrogen peroxide (35% in water), nonanal (97%) were purchased from Alfa Aesar. $Pd(OAc)_2$, neocuproin, MeOH, *tert*-butanol and H_3PO_3 were supplied by Sigma-Aldrich and methyl 12-*O*-acyl ricinoleate (80% GC) by TCI. All catalysts such as Ru/C (5%wt), Ru/Al_2O_3 (5%wt), $RuCl_3.xH_20$ were purchased from Strem chemicals. 9,10-dihydroxy octadecanoic acid (75% GC purity), sunflower oil and rapeseed oil were supplied by Oleon. All new compounds were characterized by spectroscopic data. Reactions were monitored by TLC using aluminium silica gel ($60F_{254}$). They were carried out on a plate of 0.20 mm silica gel. For revelations, UV (λ = 254 nm) light was provided (Universal UV lamp CAMAC). A phosphomolybdic acid solution was used to reveal the TLC plate if necessary. Purification by flash chromatography was performed using silica gel 60H (40-63µm). Nuclear magnetic resonance spectra were recorded on a Brüker DRX 300 or Brüker ALS 300 (^{1}H-300 MHz, ^{13}C-75 MHz). Chemical shifts are given in ppm with reference to residual DMSO or $CHCl_3$ central peaks: 2.50 and 7.26 ppm for proton, 39.52 and 77.16 ppm for carbon, respectively. *J* values are given in Hertz (Hz). Abbreviations are defined as follows: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quadruplet, m = multiplet, br = broad. Mass spectra were performed in positive-ion mode on a hybrid quadrupole time-of-flight mass spectrometer (MicroTOFQ-II, Bruker Daltonics, Bremen) with an Electrospray Ionization (ESI) ion source. The flow of spray gas was at 0.6 bar and the capillary voltage was 4.5 kV. The solutions were injected at 180 µL/h in a mixture of solvents (methanol/dichloromethane/water 45/40/15). The mass range of the analysis was 50-1000 m/z and the calibration was done with sodium formate. Infra-red (IR) spectra were recorded in a SMART iTR-Nicolet iS10 spectrometer using Attenuated Total Reflectance (ATR) and the wave numbers are expressed in cm^{-1}. Melting points were measured using a BUCHI Melting point (SMPIO) and noted in ^{0}C. A first estimate of the melting point of some of our solids was performed on a Köfler bench and SMP-10 Stuart machine.

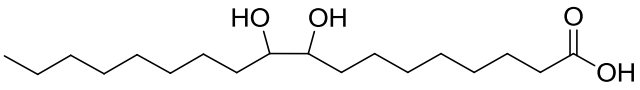
2. GC method

Gas chromatography (GC) analyses for the 1,2-diols starting materials, the corresponding α-hydroxyketones and 1,2-diketone were performed using a Shimadzu GC (GC-2025) apparatus equipped with a ZB-5-MS capillary column (10 m, 0.10 mm i.d., 0.10 µm film thickness). The carrier gas was N_2, at a flow rate of 0.43 mL/min and the injection mode is split (ratio 1:100). The column temperature was initially at 100°C for 1 min, and then was gradually increased to 260°C (25°C/min) and the temperature was kept at 260°C during 2.5 min. Finally, the temperature was increased to 315°C (45°C/min) and kept at 315°C during 2 min. The injector and FID temperature were respectively set at 300°C and 315°C.

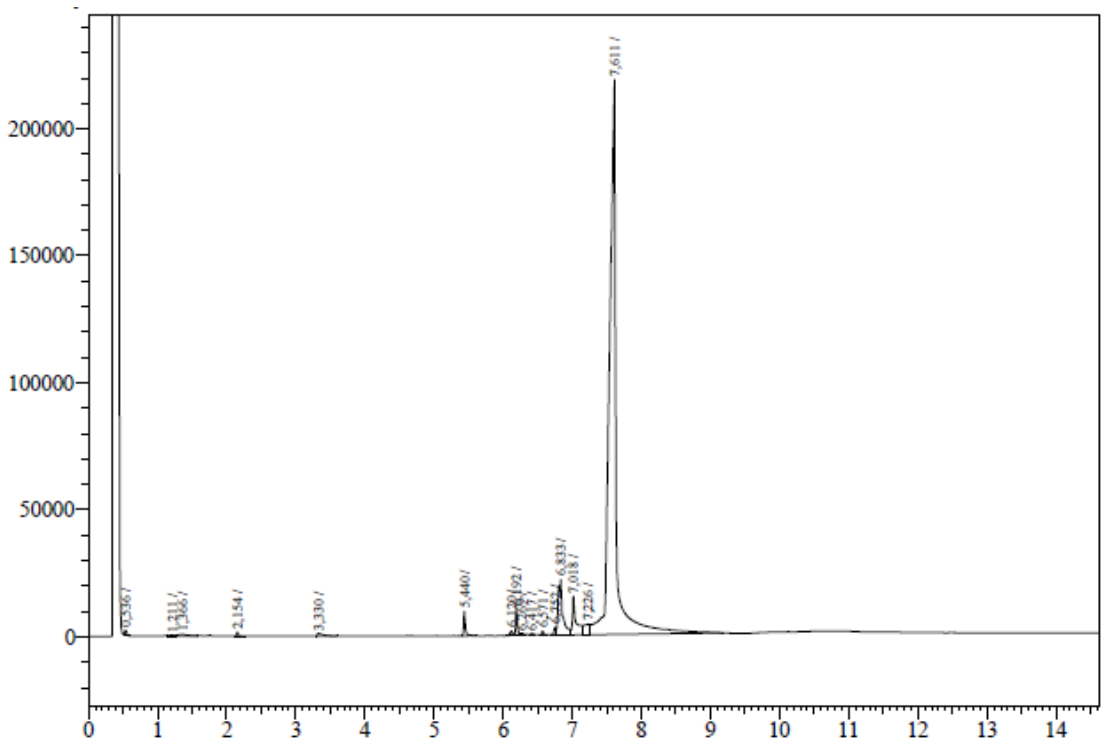
3. Preparation of heterogeneous ruthenium catalyst

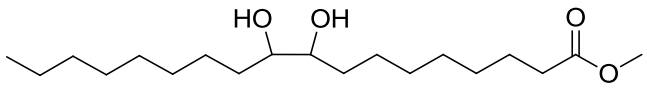
- ✓ The initial procedure to synthesize ruthenium hydroxide supported on Alumina [$Ru(OH)_x/Al_2O_3$] was developed by Yamaguchi and Mizuno.[1] The powder Al_2O_3 (2 g) calcined at 550^0C for 3 hours was vigorously stirred at room temperature with an aqueous solution of $RuCl_3$ (8.3 mM, 60 mL). After 15 minutes, the pH of the solution was adjusted to 13.2 by addition of aqueous solution NaOH (1M) and the resulting slurry was stirred for 24 hours at ambient temperature. Then the solid was filtered off, washed with a large amount of water and dried in *vacuo* to afford $Ru(OH)_x/Al_2O_3$ (2.1 g) as a dark green solid (Ru content 2.1 wt%). The content of Ru could be controlled by changing the concentration of the starting ruthenium solution.
- ✓ 10%w $Ru(OH)_x/Al_2O_3$ catalyst was synthesized from up-scale procedure of Mizuno. A suspension of Al_2O_3 (20 g) previously calcined at 550^0C, was constantly stirred with an aqueous solution of $RuCl_3$ (40 mM, 600 mL). After 15 minutes, the pH of solution was adjusted to 13.2 by addition of a NaOH solution (1M). Then, the resulting slurry was kept stirring for 1 day at room temperature. Subsequently, the solid was filtered off, washed with a large amount of water until the pH of the washing solution was approximately 7 and dried in *vacuo* to afford the desired product (21 g).

4. Preparation of oleochemical 1,2-diols

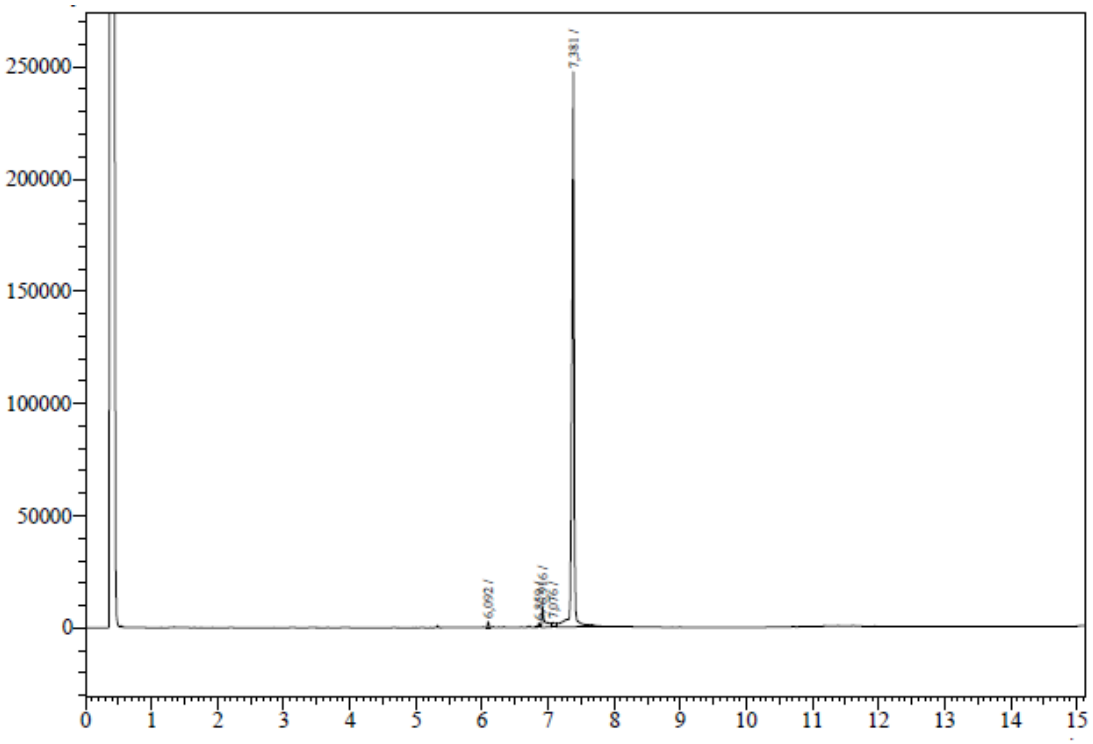


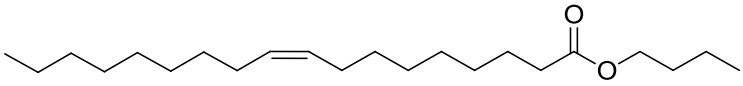
9,10-Dihydroxyoctadecanoic acid [CAS: 120-87-6]:[2] In a 3-litre glass beaker, technical grade (75% purity) 9,10-dihydroxyoctadecanoic acid (800 g) was dissolved in EtOAc (1.6 L) and the suspension was heated at 60^0C until complete dissolution. Next, the solution was slowly cooled down to room temperature over 12 hours. The precipitate formed was filtered and washed several times by cold *n*-pentane (2x500 mL) then the product was dried in vacuum (p= 2.10^{-2} mbar) at 40^0C for 12h to afford the desired product (500 g, 83%) as a white solid (mp = 105^0C). The purity of DHSA was determined by GC analysis (>95% GC ratio) and NMR. **IR** (ν_{max}): 3330 (O-H), 2951, 2913, 2847 (C-H stretching), 1701 (C=O), 1466, 1333, 1296, 891, 862, 791, 657, 549, 534; **HRMS-ESI:** calculated for $C_{18}H_{35}O_4$ $[M-H]^-$ 315.2527, found 315.2541; **^{1}H-NMR** (300 MHz, d_6-DMSO): δ_H = 0.85 (t, *J* = 6.7, 3H, CH_3), 1.24-1.49 (m, 26H, 13-CH_2), 2.17 (t, *J* = 7.3, 2H, $\underline{CH_2}CO$), 3.17-3.21 (m, 2H, 2 $\underline{CH}$-OH), 4.12-4.14 (m, 2H, O-H), 11.95-11.97 (br s, 1H, COOH); **^{13}C-NMR** (75 MHz, d_6-DMSO): δ_c = 14.0 (CH_3), 22.2, 24.6, 25.71, 25.74, 28.7, 28.9, 29.0, 29.2, 29.3, 29.4, 31.4, 32.5, 32.5, 33.7 (14-CH_2), 73.2 (2xCH), 174.5 (C=O); **GC analysis**: Rt=7.6 min.



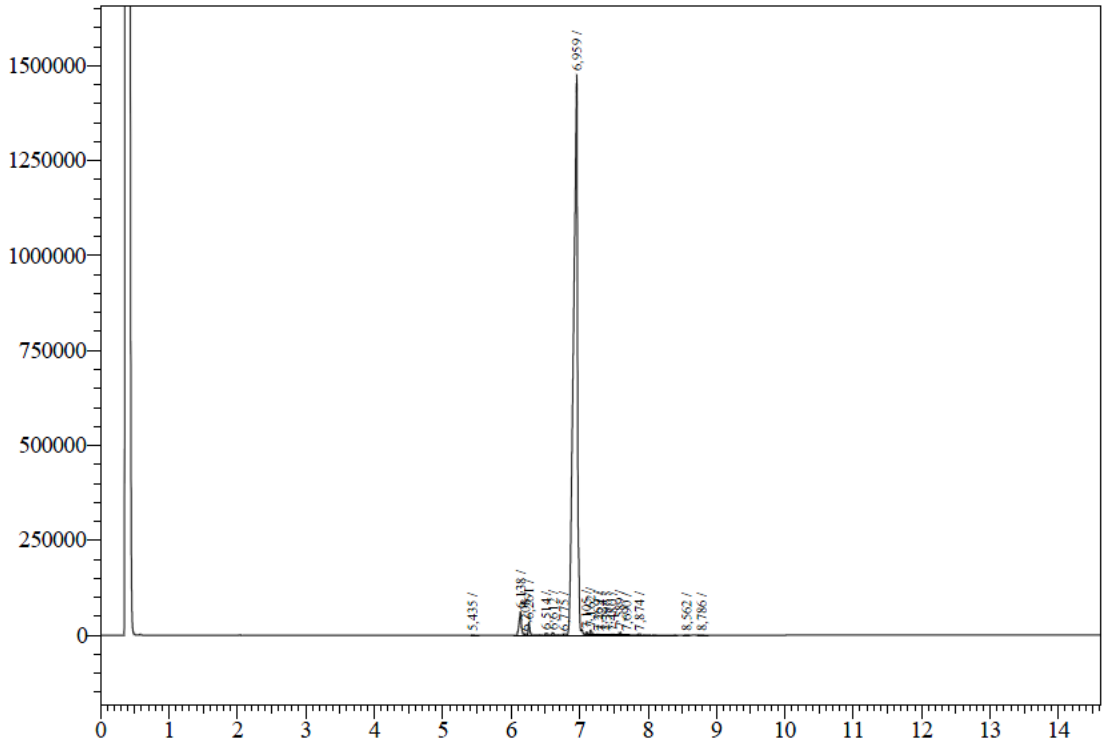


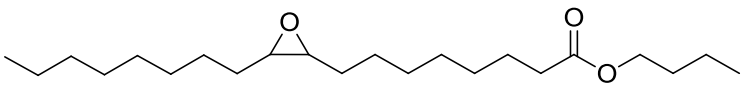
Methyl 9,10-dihydroxyoctadecanoate [CAS: 1115-01-1][3] (1): In a 1-litre round bottom flask equipped with a water condenser and a magnetic stirring bar, 9,10-dihydroxyoctadecanoic acid (110 g, 0.35 mol), Amberlyst-15 (11 g, 10%w) and MeOH (600 mL) were successively introduced under stirring. The reaction mixture was heated at 65^0C for 12 hours. The reaction was monitored by GC analysis. After complete conversion (>99% GC ratio), the solution was filtered to remove Amberlyst-15 and the filtrate was evaporated under reduced pressure. The residue was dried in vacuum (p = 2.10^{-2} mbar) at 80^0C for 12 hours to afford the desired product (114 g, 99%) as a white solid (mp = 90-92^0C). **IR** (ν_{max}): 3339, 3260 (O-H), 2951, 2928, 2913, 2846, 1740 (C=O), 1202, 1189, 1165, 1138, 1112 (C-O); **MS** (ESI^+) m/z = 313.3 ($[MH\text{-}H_2O]^+$, 45), 331.2 ($[MH]^+$, 100), 353.3 ($[MNa]^+$, 57); **HRMS-ESI:** calculated for $C_{19}H_{38}NaO_4$ $[MNa]^+$ 353.2662, found 353.2656; **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.87 (t, *J* = 6.7, 3H, CH_3), 1.26-1.30 (m, 18H, 9-CH_2), 1.40-1.63 (m, 8H, 4-CH_2), 2.29 (t, *J* =7.5, 2H, $\underline{CH_2}$-CO), 3.38-3.40 (m, 2H, 2x$\underline{CH}$-OH), 3.60 (s, 3H, $\underline{CH_3}$O); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_c = 14.2 (CH_3), 22.8, 25.0, 25.7, 25.8, 29.1, 29.3, 29.4, 29.5, 29.7, 29.8, 32.0, 33.6, 33.7, 34.2 (14-CH_2), 51.6 (CH_3O), 74.57, 74.63 (2xCH), 174.5 (C=O); **GC analysis**: Rt= 7.4 min.



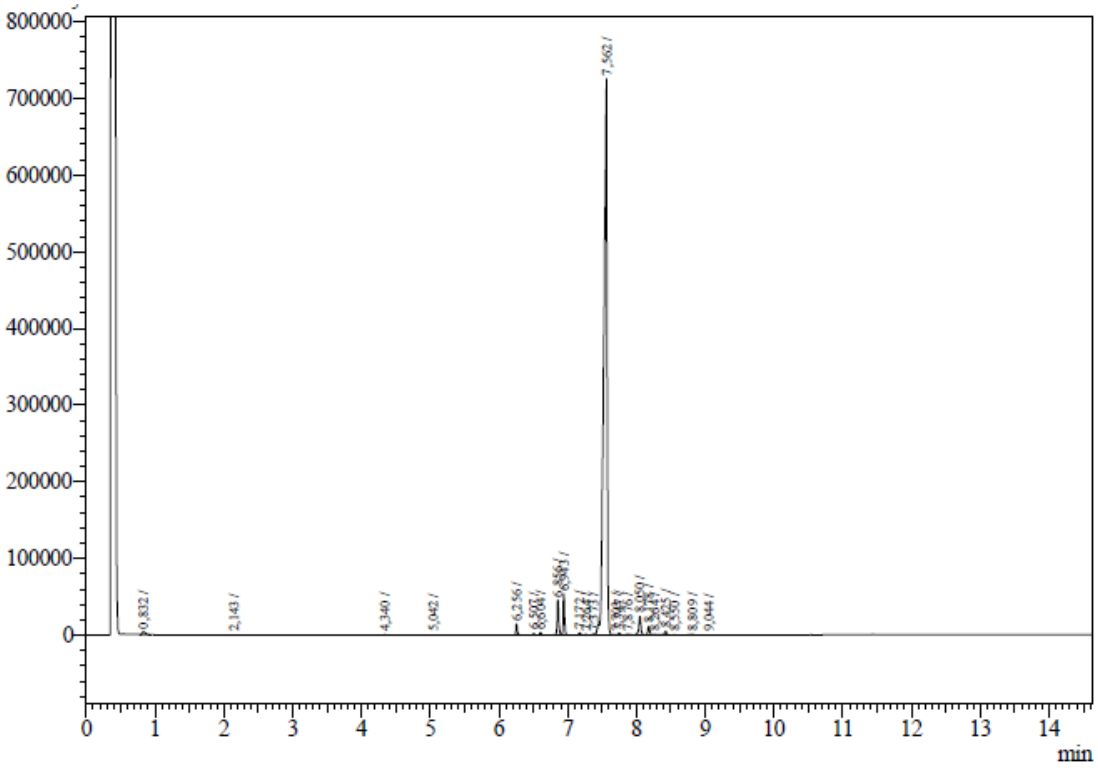


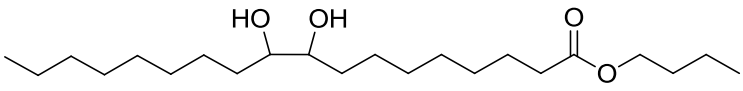
Butyl 9Z-octadecenoate [CAS 142-77-8]:[3] Following a modified procedure,[4] technical grade (90% purity) oleic acid (15 g, 48 mmol), H_2SO_4 (240 mg, 2.4 mmol, 0.05 equiv), Na_2SO_4 (4.5 g, 34 mmol, 0.7 equiv) and *n*-BuOH (22 mL) were introduced in a 250-mL round bottom flask under magnetic stirring. The mixture was heated at 130^{0}C for 75 minutes. The reaction was followed by GC analysis. After reaching complete conversion (>99% GC ratio), the solution was cooled down to room temperature, diluted in heptane (200 mL) and filtered to remove Na_2SO_4. The filtrate was washed with $NaHCO_3$ solution (5wt%, 2 x 100 mL), water (200 mL) and brine (200 mL), then dried ($MgSO_4$) and concentrated under reduced pressure to afford the desired product (12 g, 75%) as a yellowish liquid. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.87 (t, *J* = 6.7, 3H, CH_3), 0.94 (t, *J* = 7.3, 3H, CH_3), 1.26-1.41 (m, 20H, 10-CH_2), 1.56-1.63 (m, 6H, 3-CH_2), 1.97-2.02 (m, 4H, 2-CH_2-C=C), 2.28 (t, *J*= 7.5, 2H,-CH_2-CO), 4.06 (t, *J* = 6.7, 2H,-OCH_2-), 5.32-5.36 (m, 2H, -CH=CH-); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_c = 13.8 (CH_3), 14.2 (CH_3), 19.3, 22.8, 25.1, 27.29, 27.34, 29.23, 29.26, 29.29 (8-CH_2), 29.5 (2xCH), 29.7, 29.8, 29.9, 30.8, 32.0, 34.5 (6-CH_2) 64.2 (OCH_2), 129.9, 130.1 (2 CH), 173.9 (C=O); **GC analysis**: Rt= 7.0 min.



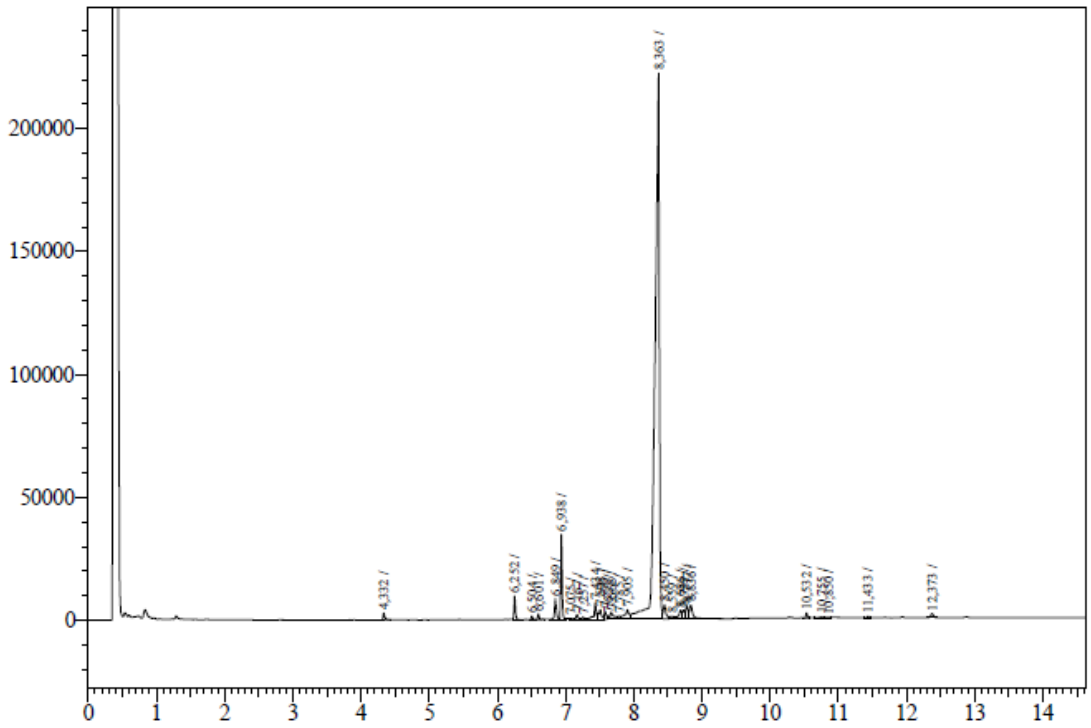


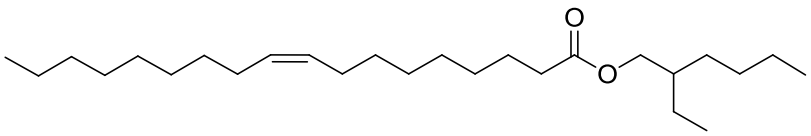
Butyl 8-(3-octyloxiran-2-yl)octanoate [CAS 106-83-2][5]: Following a modified procedure,[6] butyl 9Z-octadecenoate (11 g, 32 mmol) and HCOOH (1.2 g, 26 mmol, 0.8 equiv) were successively introduced in a 200-mL jacketed glass reactor. H_2O_2 (35%w in H_2O, 5.5 mL, 57 mmol, 1.8 equiv) was added dropwise in the reactor over a 30-minute period at room temperature, then the reaction was heated at 50^0C for 6 hours. The reaction was monitored by GC analysis until the conversion was complete. The suspension was partitioned in a mixture of water (50 mL) and heptanes (200 mL) then the water phase was discarded. The organic layer was washed with a 5 wt% $NaHCO_3$ solution (2 x 100 mL), H_2O (200 mL) and brine (200 mL) then dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give the desired product (11.5 g, 98%) as a yellowish liquid. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.84 (t, *J* = 6.8, 3H, CH_3), 0.89 (t, *J* = 7.3, 3H, CH_3), 1.10-1.37 (m, 20H, 10-CH_2), 1.37-1.52 (m, 6H, 3-CH_2), 1.52-1.65 (m, 4H, 2-CH_2), 2.25 (t, *J* = 7.5, 2H, $\underline{CH_2}$-CO), 2.84-2.94 (m, 2H, H-epoxide), 4.02 (t, *J* = 6.7, 2H, -$\underline{CH_2}$O); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_c = 13.8 (CH_3), 14.2 (CH_3), 19.2, 22.7, 25.0, 26.63, 26.67, 27.87, 27.90, 29.1, 29.26, 29.29, 29.4, 29.60, 29.62, 30.8, 31.9, 34.4 (16-CH_2), 57.2, 57.3 (2 x CH-epoxide), 64.2 (OCH_2), 174.0 (C=O); **GC analysis:** Rt = 7.6 min.



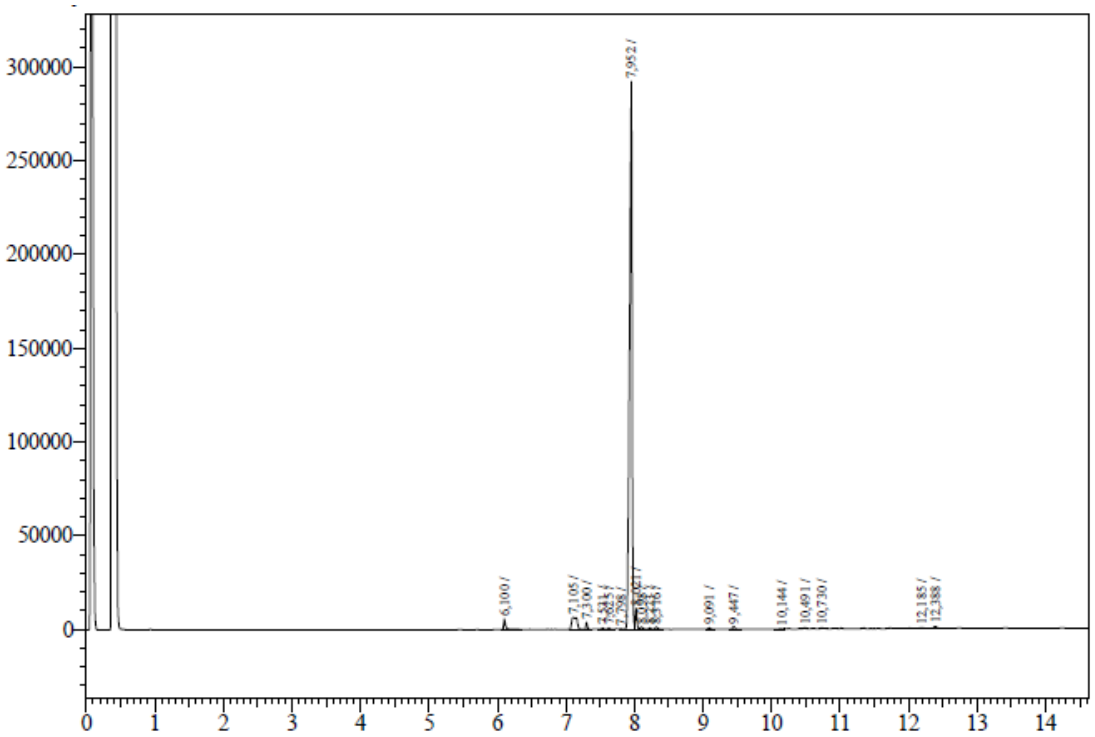


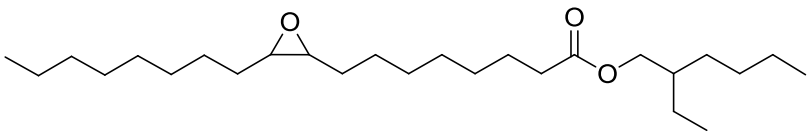
Butyl 9,10-dihydroxyoctadecanoate [CAS 70240-75-4][3] (13): Following a modified procedure patented by Novance®,[7] crude (90% purity) butyl 8-(3-octyloxiran-2-yl)octanoate (11 g, 28 mmol), H_3PO_3 (46 mg, 0.056 mmol, 0.02 equiv) and H_2O (3 mL) were introduced in a 200-mL jacketed glass reactor. The reaction was heated at 90^0C for 3 hours until conversion was complete. The crude was diluted in EtOAc (200 mL) then washed with water (2 x 200 mL), brine (200 mL) and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give an oil (10.6 g, 90% purity in GC). This crude mixture was crystallized in cold heptanes then filtered and dried in *vacuo* to afford the desired product (5.2 g, 56%) as a white solid (mp = 53-55°C). **IR** (ν_{max}): 3339 (br, O-H), 2912, 2847 (C-H stretching), 2530, 2159, 1977, 1736 (C=O ester), 1467, 1415, 1168, 1036, 764, 721, 648; **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.87 (t, *J* = 6.8, 3H, CH_3), 0.93 (t, *J* = 7.3, 3H, CH_3), 1.26-1.36 (m, 20H, 10-CH_2), 1.37-1.60 (m, 10H, 5-CH_2), 1.95 (br s, 2H, 2-OH), 2.28 (t, *J* =7.5, 2H, $\underline{CH_2}$-C=O), 3.39-3.41 (m, 2H, 2-$\underline{CH}$-OH), 4.06 (t, *J* = 6.7, 2H, CH_2O); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_c = 13.8 (CH_3), 14.2 (CH_3), 19.2, 22.8, 25.0, 25.7, 25.8, 29.2, 29.3, 29.4, 29.6, 29.7, 29.8, 30.8, 32.0, 33.6, 33.7, 34.5 (16-CH_2), 64.3 (CH_2), 74.5, 74.6 (2xCH), 174.2 (C=O); **HRMS-ESI:** calculated for $[M+H]^+$, $C_{22}H_{45}O_4$: 373.3300, found 373.3312; **GC analysis:** Rt = 8.4 min.



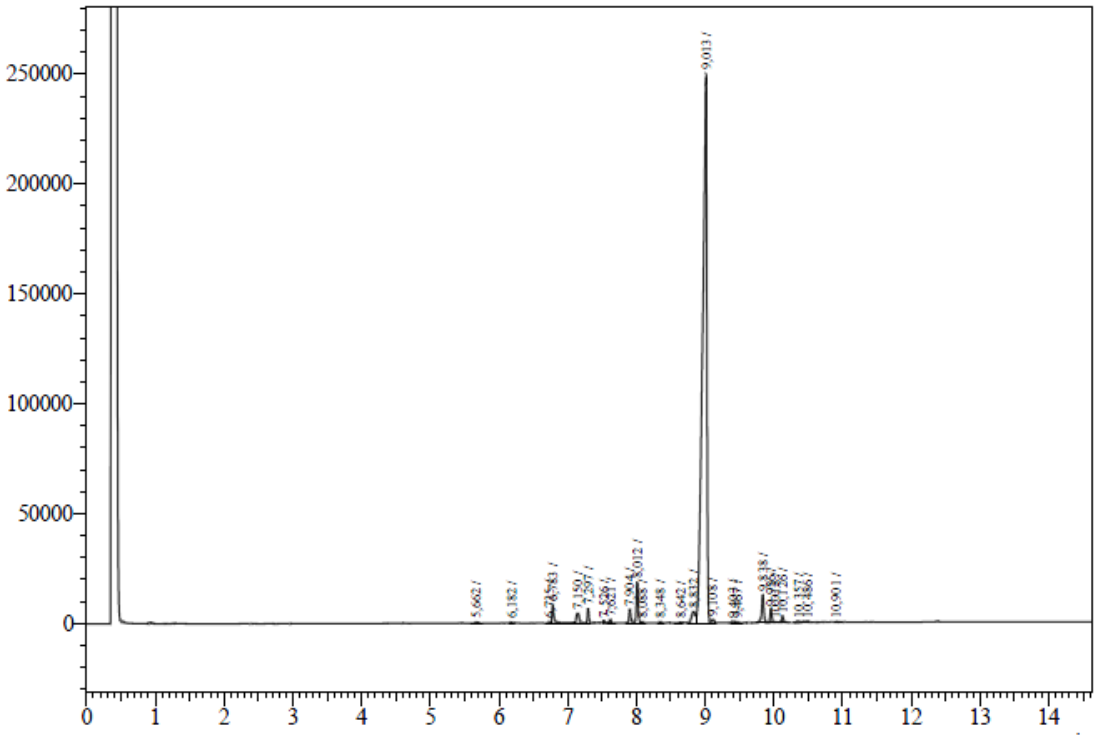


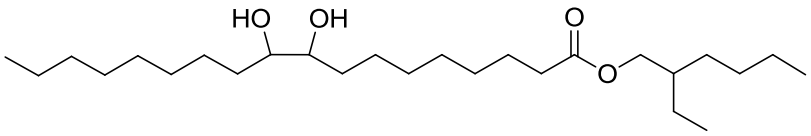
2-Ethylhexyl 9Z-Octadecenoate [CAS 26399-02-0]:[3] Following a reported procedure,[4] technical grade (90% purity) oleic acid (22 g, 70 mmol), H_2SO_4 (350 mg, 3.5 mmol, 0.05 equiv), Na_2SO_4 (6 g, 45 mmol, 0.65 equiv) and 2-ethyl hexanol (30 mL, 190 mmol, 2.7 equiv) were introduced in 250-mL round bottom flask under magnetic stirring. The reaction mixture was heated at 130^{0}C for 75 minutes. The reaction was followed by GC analysis. After reaching complete conversion (>99% GC ratio), the solution was cooled down to room temperature and diluted in heptane (200 mL) then filtered to remove Na_2SO_4. The filtrate was washed with $NaHCO_3$ solution (5%w, 2 x 100 mL), water (200 mL) and brine (200 mL), then dried ($MgSO_4$) and concentrated under reduced pressure to give a crude oil. The excess of 2-ethyl hexanol was eliminated by distillation under reduced pressure (85^{0}C, p=0.4 mbar) and the desired product was obtained in the residue as a colourless oil (29 g, 95%). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.85-0.91 (m, 9H, 3-CH_3), 1.27-1.37 (m, 27H, 13-CH_2 + 1-CH), 1.54-1.64 (m, 4H, 2-CH_2), 1.99-2.03 (m, 4H, 2 $\underline{CH_2}$-C=C), 2.29 (t, *J* = 7.5, 2H, $\underline{CH_2}$-C=O), 3.98 (dd, *J* = 5.8, 0.7, 2H, $\underline{CH_2}$O), 5.32-5.36 (m, 2H, CH=CH); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_c = 11.1 (CH_3), 14.1 (CH_3), 14.2 (CH_3), 22.8, 23.1, 23.9, 25.2, 27.29, 27.34, 29.1, 29.24, 29.27, 29.3 (10-CH_2), 29.5 (2 x CH_2), 29.7, 29.8, 29.9, 30.6, 32.0, 34.6 (6-CH_2), 38.9 (CH), 66.7 (CH_2), 129.9, 130.1 (2=CH-), 174.2 (C=O); **GC analysis**: Rt = 7.9 min.



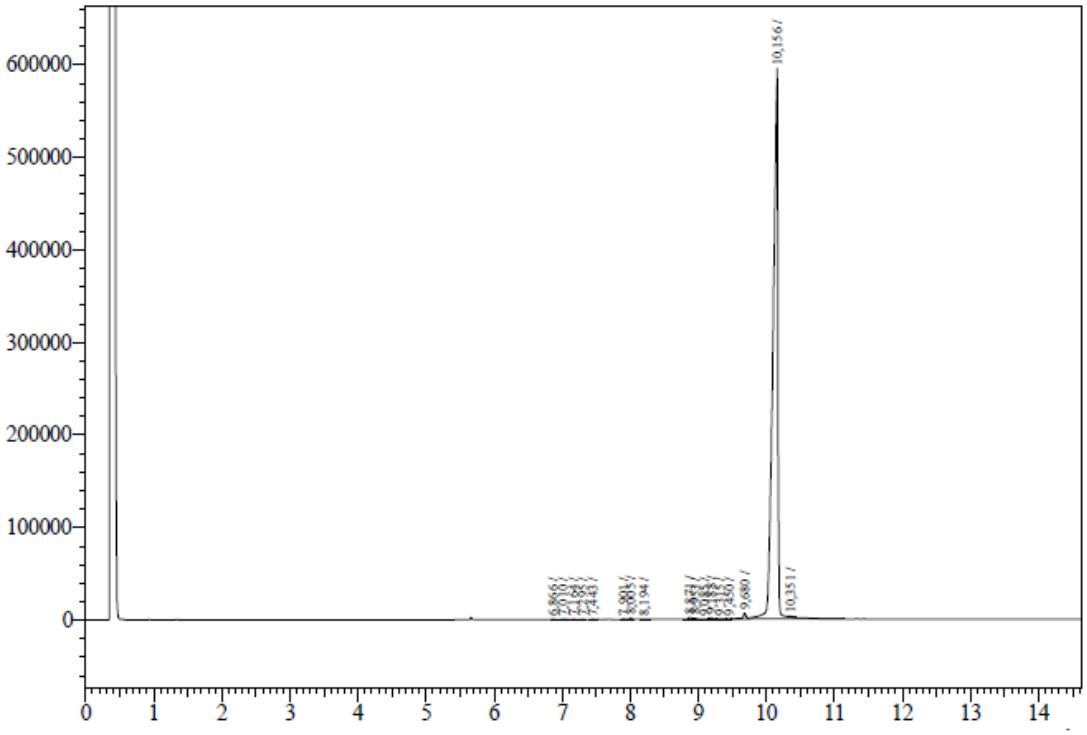


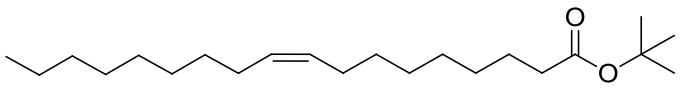
2-Ethylhexyl 8-(3-octyloxiran-2-yl)octanoate [CAS 141-38-8][8]: Following a reported procedure,[6] crude (90% purity) 2-ethylhexyl 9Z-Octadecenoate (29.5 g, 66 mmol) and HCOOH (3 g, 66 mmol, 1 equiv) were introduced in a 200-mL jacketed glass reactor. H_2O_2 (35%w in H_2O, 16 mL, 160 mmol, 2.4 equiv) was added dropwise over a 1-hour period at room temperature then the reaction was heated at 50^{0}C for 6h30. The reaction mixture was cooled down to room temperature and the suspension was partitioned in a mixture of water (50 mL) and heptane (200 mL) then the water layer was discarded. The organic phase was washed with a 5wt% $NaHCO_3$ solution (2 x 100 mL), water (200 mL) and brine (200 mL), dried ($MgSO_4$) and filtered. The filtrate was concentrated under reduced pressure to afford the desired product (29.9 g, 98%) as colourless oil (85% purity in GC). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.83-0.89 (m, 9H, 3-CH_3), 1.23-1.62 (m, 35H, 17-CH_2+ 1-CH), 2.28 (t, *J* = 7.5, 2H, $\underline{CH_2}$-CO), 2.87-2.96 (m, 2H, $\underline{CH}$-epoxide), 3.96 (dd, *J* = 5.8, 0.8, 2H, O$\underline{CH_2}$); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_c = 11.1 (CH_3), 14.15 (CH_3), 14.20 (CH_3), 22.8, 23.1, 23.9, 25.1, 26.67, 26.70, 27.89, 27.93, 29.0, 29.2, 29.31, 29.32, 29.5, 29.64, 29.65, 30.5, 31.9, 34.5, 38.8 (18-CH_2+1-CH), 57.29, 59.34 (2x CH epoxide), 66.6 (O$\underline{CH_2}$), 174.2 (C=O); **GC analysis:** Rt= 9.0 min.



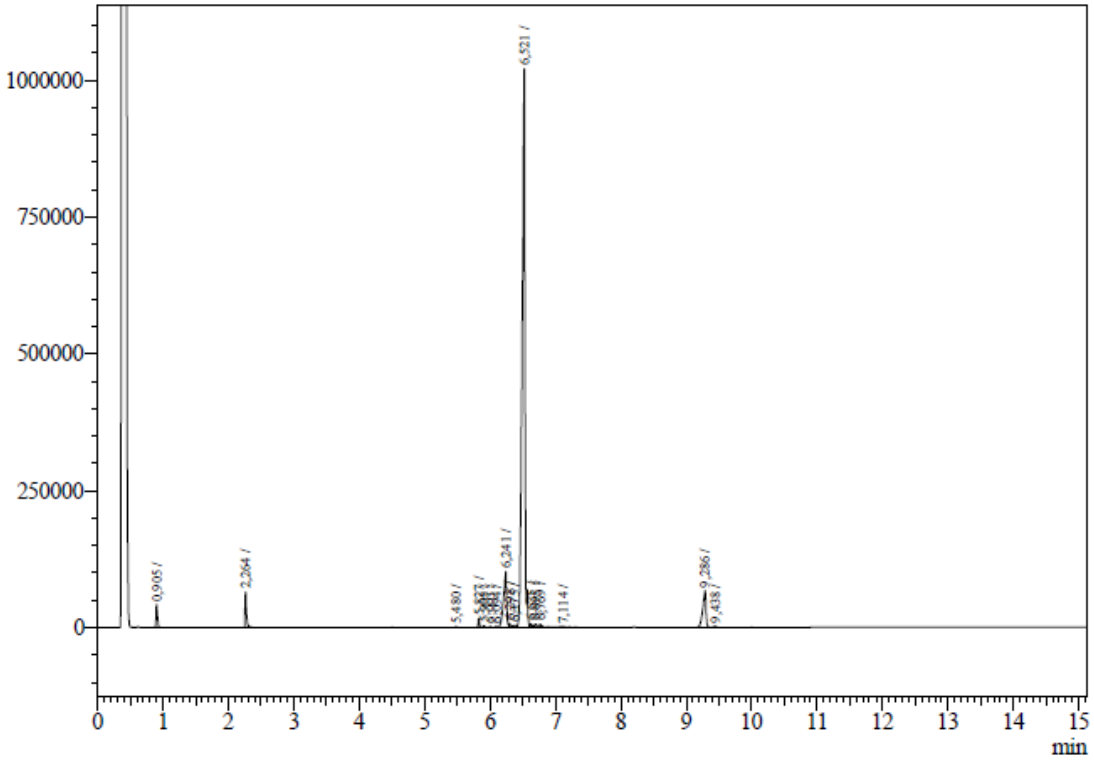


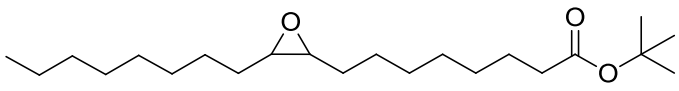
2-Ethylhexyl 9,10-dihydroxyoctadecanoate [CAS 124102-92-7][3] (14): Following a reported procedure,[7] crude (85%) 2-ethylhexyl 8-(3 octyloxiran-2-yl) octanoate (29 g, 60mmol), H_3PO_3 (100 mg, 1.2 mmol, 0.02 equiv) and H_2O (6 mL) were introduced in 200-mL jacketed glass reactor. The reaction was heated at 90^0C in 3 hours. The mixture was diluted in EtOAc (200 mL) then washed with water (2 x 200 mL), brine (200 mL), dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure to give a crude (80% purity) colourless oil (29.5 g, 92%). This crude was crystallized in cold heptane then filtered and dried in *vacuo* to give the desired product (7.9 g, 30%) as white solid (mp = 41-43°C). **IR** (ν_{max}): 3341 (br, O-H), 2913, 2847 (C-H stretching), 2159, 2026, 1737, 1466, 1202, 1167, 722, 650; **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.85-0.91 (m, 9H, 3-CH_3), 1.27-1.39 (m, 26H, 13-CH_2), 1.40-1.64 (m, 9H, 4-CH_2+1-CH), 1.93 (br s, 2H, 2-OH), 2.29 (t, *J* =7.5, 2H, $\underline{CH_2}$-C=O), 3.38-3.41 (m, 2H, 2x $\underline{CH}$-OH), 3.98 (dd, *J* = 5.8, 0.7, 2H, OCH_2); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_c = 11.1 (CH_3), 14.1 (CH_3), 14.2 (CH_3), 22.8, 23.1, 23.9, 25.1, 25.7, 25.8, 29.0, 29.2, 29.3, 29.4, 29.6, 29.7, 29.8, 30.5, 32.0, 33.65, 33.69, 34.5, 38.8 (19-CH_2), 66.8 (CH_2), 74.54, 74.59 (2x$\underline{CH}$-OH), 174.3 (C=O); **HRMS-ESI:** calculated for $[M+H]^+$, $C_{26}H_{53}O_4$: 429.3922, found 429.3938; **GC analysis:** Rt= 10.2 min.



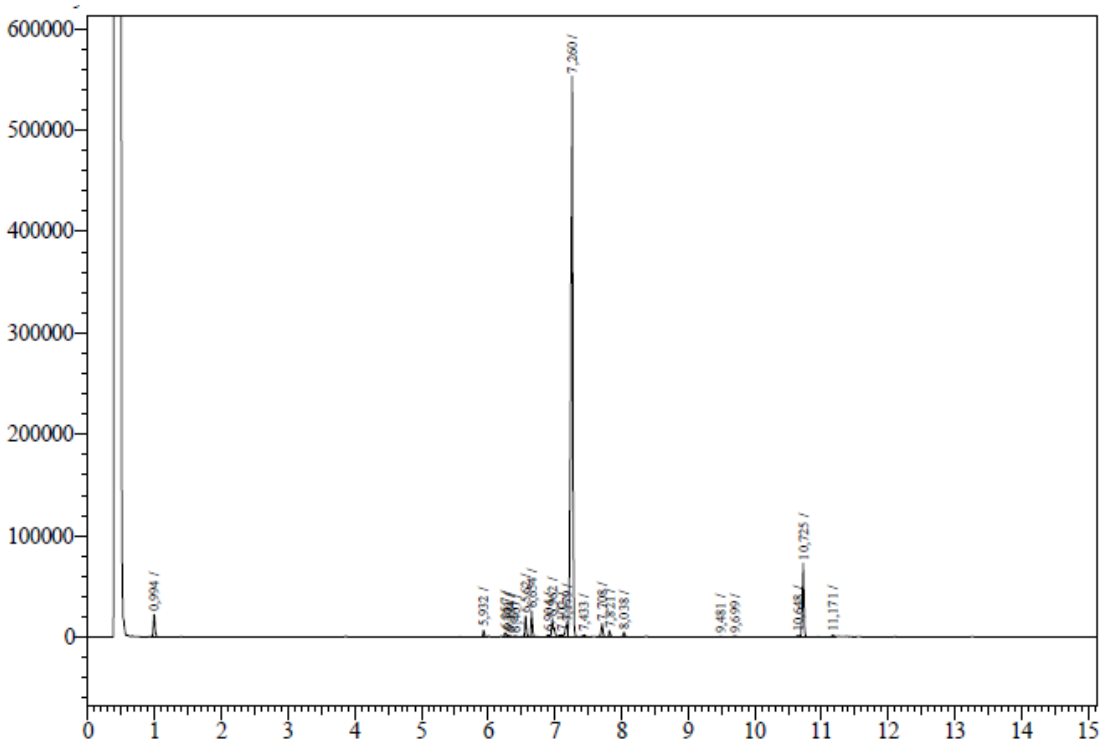


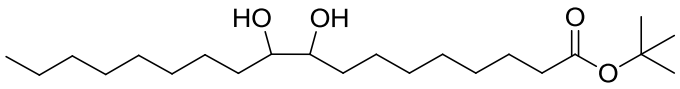
***tert*-Butyl octadecenoate [CAS 16792-04-4]:**[9] Following a modified procedure,[9] technical grade (90% purity) oleic acid (15.7 g, 45 mmol), *tert*-BuOH (10 mL, 90 mmol, 2 equiv), DMAP (0.6 g, 5 mmol, 0.11 equiv) and toluene (5 mL) were introduced in a two-neck round bottom flask and was strirred at room temperature. Then, the flask was cooled by ice bath and a solution of *N,N'*-dicyclohexylcarbodiimide (DCC, 10.3 g, 50 mmol, 1.1 equiv) in toluene (15 mL) was added dropwise over a 30-minute period. Subsequently, the reaction was stirred at room temperature for 6 hours (conversion was followed by GC analysis). The reaction mixture was filtered to remove a white precipitate (dicyclohexylurea) and washed with toluene (20 mL). The resulting filtrate was washed with a 0.5 M HCl solution (2x20 mL), $NaHCO_3$ 5%w (2x 20mL), H_2O (20 mL) and brine (20 mL), dried over $MgSO_4$ and filtered off. The filtrate was concentrated under reduced pressure to give the desired product (15.1 g, 90%) as colourless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.83 (t, *J* = 6.6, 3H, CH_3), 1.22-1.31 (m, 20H, 10-CH_2), 1.39 (s, 9H, 3-CH_3), 1.49-1.54 (m, 2H, CH_2), 1.93-1.97 (m, 4H, 2x$\underline{CH_2}$-C=C-), 2.15 (t, *J* = 7.5, 2H, -$\underline{CH_2}$-C=O), 5.27-5.31 (m, 2H, 2 CH); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_c = 14.2 (CH_3), 22.8, 25.2, 27.29, 27.33 (4-CH_2), 28.2 (3xCH_3), 29.20, 29.24, 29.33 (3-CH_2), 29.4 (2xCH_2), 29.6, 29.8, 29.9, 32.0, 35.7 (5-CH_2), 80.0 ($\underline{C}(CH_3)_3$), 129.9, 130.1 (2 CH), 173.4 (-C=O) ; **GC analysis:** Rt = 6.5 min.



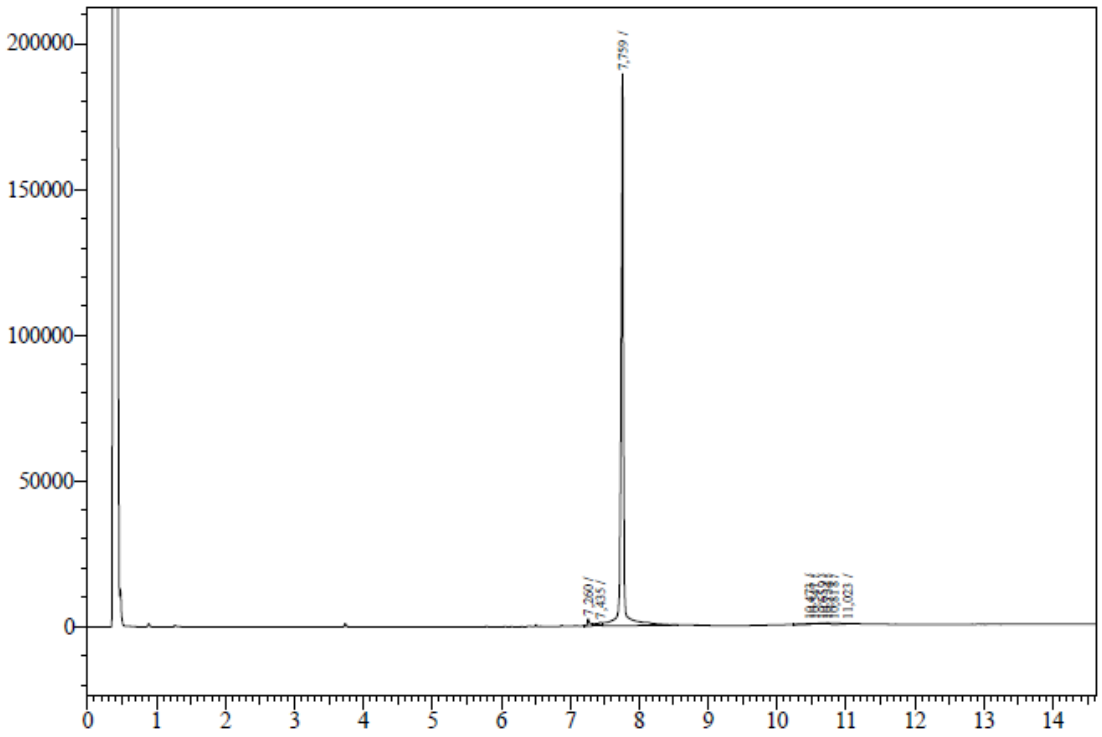


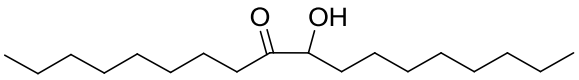
***tert*-Butyl 8-(3-octyloxiran-2-yl)octanoate [No CAS]**: Following a modified procedure,[6] crude (90% purity) *tert*-butyl octadecenoate (15 g, 45 mmol) and HCOOH (2 g, 45 mmol, 1 equiv) were introduced in 200-mL jacketed glass reactor. H_2O_2 (35%w in water, 10 mL, 90 mmol, 2 equiv) was added dropwise over a 1-hour period then the reaction was heated at 50^0C for 6 hours. After cooling to room temperature, the suspension was partitioned in a mixture of H_2O (50 mL) and heptanes (200 mL) then the water phase was discarded. The organic layer was washed with a 5wt% $NaHCO_3$ solution (2 x 100 mL), H_2O (200 mL) and brine (200 mL) then dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give the desired product (15 g, 95%) as a colourless oil. **IR** (ν_{max}): 2920, 2853 (C-H stretching), 1730 (C=O), 1456, 1390, 1366, 1253, 1150, 894, 847, 754, 703; **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.87 (t, *J* = 6.7, 3H, CH_3), 1.22-1.35 (m, 20H, 10-CH_2), 1.43 (s, 9H, 3xCH_3), 1.46-1.60 (m, 6H, 3xCH_2), 2.19 (t, *J* = 7.5, 2H, $\underline{CH_2}$-C=O), 2.82-2.95 (m, 2H, 2H-epoxide); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_c = 14.1 (CH_3), 22.7, 25.1, 26.58, 26.62, 27.80, 27.82 (6-CH_2), 28.1 (3xCH_3), 29.0 (CH_2), 29.2 (2xCH_2), 29.4, 29.55, 29.56, 31.8, 35.6 (5-CH_2), 57.26, 57.30 (2-CH), 79.9 (C_q), 173.3 (C=O); **GC analysis** : Rt = 7.3 min.



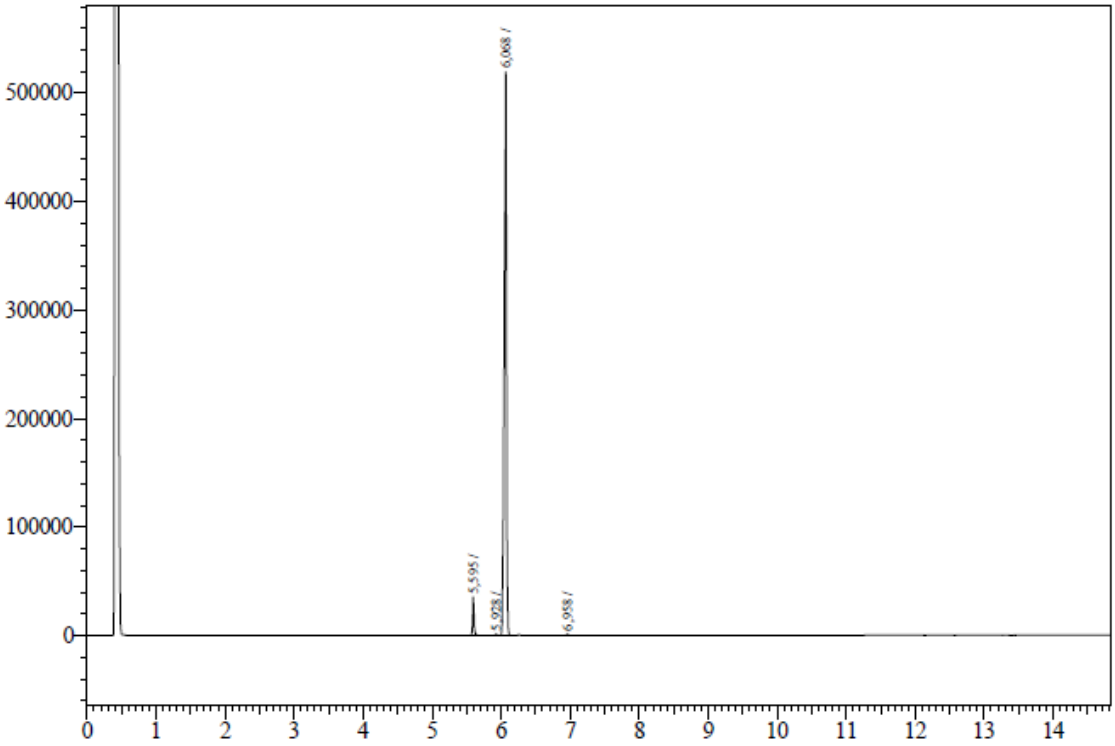


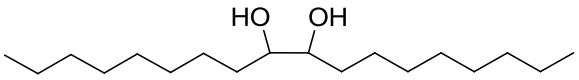
***tert*-Butyl 9,10-dihydroxyoctadecanoate [No CAS] (4)**: Following a reported procedure,[7] crude (90% purity) epoxydized *tert*-butyl oleate (15 g, 42 mmol), H_3PO_3 (70 mg, 0.84 mmol, 0.02 equiv), H_2O (4 mL) were introduced in a 200-mL jacketed glass reactor then the reaction was heated at 90^0C for 5 hours. The conversion was followed by GC analysis. After cooling to room temperature, the crude product was diluted in EtOAc (200 mL) then washed with water (2 x 200 mL), brine (200 mL), dried over $MgSO_4$ and filtered off. The filtrate was concentrated under reduced pressure to give an oil (14.8 g, 80% purity in GC). This crude mixture was crystallized in cold heptane then filtered and dried in *vacuo* to afford the desired product (4.8 g, 32%) as a white solid (mp=63-65°C). **IR** (ν_{max}): 3340 (br, O-H), 2914, 2847 (C-H stretching), 2512, 2160, 1732 (C=O), 1466, 1154, 720, 649**; ^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.88 (t, *J* = 6.7, 3H, CH_3), 1.27-1.37 (m, 20H, 10-CH_2), 1.44 (s, 9H, 3-$\underline{CH_3}$), 1.47-1.59 (m, 6H, 3-CH_2), 1.94 (br s, 2H, 2-OH), 2.20 (t, *J* = 7.5, 2H, $\underline{CH_2}$-C=O), 3.39-3.41 (m, 2H, 2-$\underline{CH}$-OH); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_c = 14.2 (CH_3), 22.8, 25.1, 25.7, 25.8 (4-CH_2), 28.2 (3xCH_3), 29.1, 29.3, 29.4, 29.6, 29.7, 29.8, 32.0, 33.6, 33.7, 35.7 (10-CH_2), 74.7 (2x$\underline{CH}$-OH), 80.2 (C_q), 173.6 (C=O); **HRMS-ESI**: calculated for $[M+H]^+$, $C_{22}H_{45}O_4$: 373.3300, found 373.3301; **GC analysis**: Rt = 7.8 min.



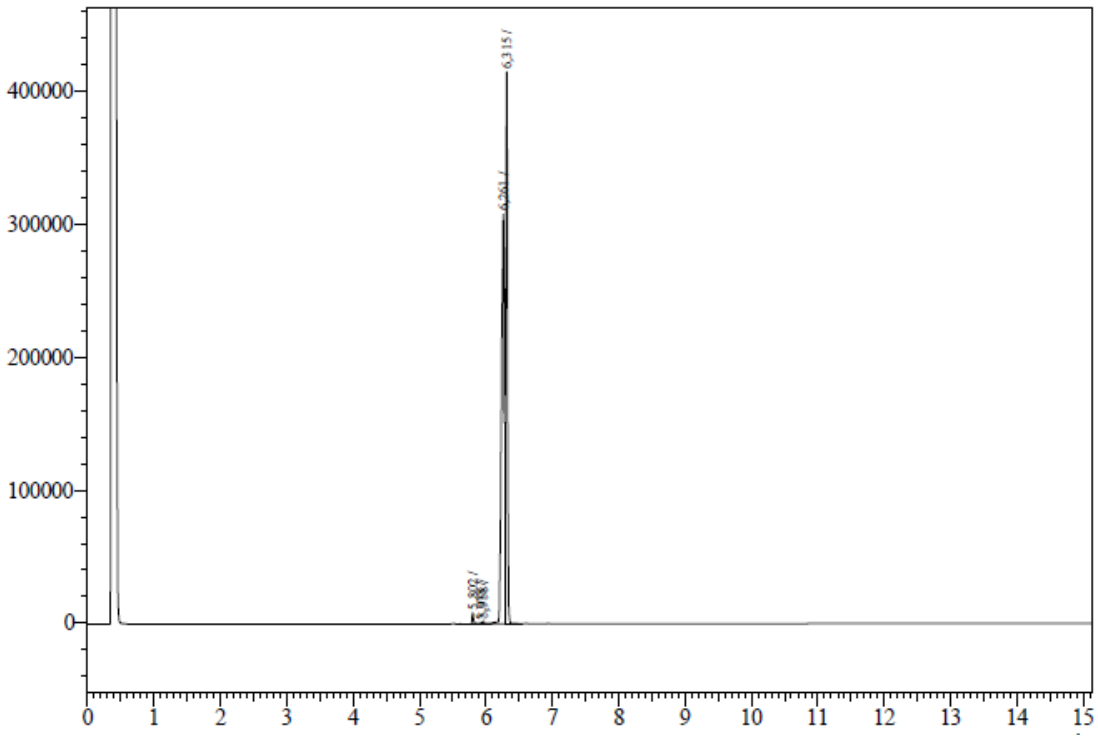


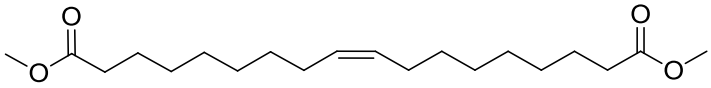
10-Hydroxyoctadecan-9-one [CAS 4444-91-1][10] (9): Following a modified procedure,[11] a hot-dried round-bottom flask was charged with 3-ethyl-5-(2-hydroxyethyl)-4-methylthiazol-3-ium bromide (1.31 g, 5.2 mmol, 0.05 equiv). The catalyst was suspended in anhydrous EtOH (45 mL) then Et_3N (4.5 ml, 32 mmol, 0.3 equiv) was introduced in the flask and nonanal (18 mL, 105 mmol) was added slowly at room temperature. The reaction was heated at 80^0C for 4 hours until the conversion was complete. Subsequently, the mixture was directly poured into ice (135 mL). The suspension was stirred until all ice was molten. Then the white precipitate was filtered off and the crude was recrystallized from EtOH to afford the desired product (10.3 g, 73%) as a white solid (mp = 46-48°C). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.88 (t, *J* = 6.7, 6H, 2-CH_3), 1.20-1.37 (m, 20H, 10-CH_2), 1.42-1.80 (m, 6H, 3-CH_2), 2.36-2.51 (m, 2H, $\underline{CH_2}$-C=O), 3.48 (d, *J* = 4.9, 1H, O-H), 4.16-4.19 (m, 1H, $\underline{CH}$-OH); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_C = 14.16 (CH_3) 14.17 (CH_3), 22.73, 22.75, 23.7, 24.9, 29.2, 29.32, 29.33, 29.4, 29.5, 29.6 31.89, 31.94, 33.9, 37.9 (14-CH_2), 76.5 (CH), 212.6 (C=O); **IR** (ν_{max}): 3319-3231 (O-H), 2953, 2915, 2872, 2848, 1710 (C=O), 1462, 1405, 1374, 1335, 1254, 1127, 1091 (C-O), 1031, 908, 831, 701; **MS (ESI$_+$)** m/z = 307.3 ([M+Na]$^+$, 100); **HRMS (ESI):** calculated for [M+Na]$^+$, $C_{18}H_{36}NaO_2$: 307.2608, found 307.2605 (0.9 ppm); **GC analysis**: Rt = 6.1 min.



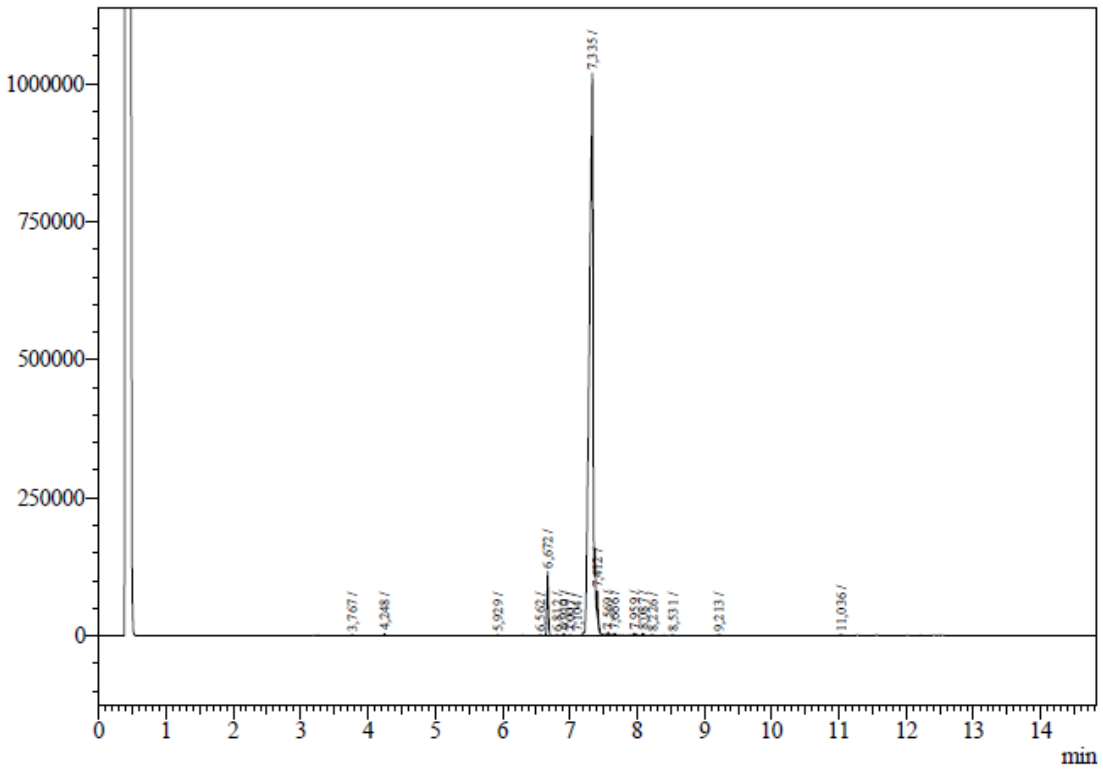


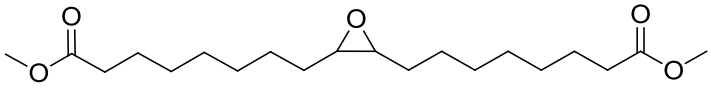
Octadecane-9,10-diol [CAS 15962-87-5][12] **(5)**: 10-hydroxyoctadecan-9-one (6.5 g, 23 mmol) was dissolved in anhydrous MeOH (80 mL) in a 300-mL stainless steel autoclave and $^{5wt\%}$Ru/C (0.9 g, 0.46 mmol, 0.02 equiv) was introduced. The reactor was tightly closed, purged three times with hydrogen then hydrogen pressure was introduced (10 bar). The system was heated at 50°C and mechanically stirred for 5 hours. After cooling to room temperature, hydrogen pressure was released, the solution was filtered through micropaper (pore size 0.1 µm) and the filtrate was concentrated under reduced pressure then dried in *vacuo* to afford the desired product (1:1 mixture of isomers, 6.2 g, 95%) as a white solid (mp = 109-111°C). **IR** (ν_{max}): 3255 (br, O-H), 2954, 2916, 2848, 2520, 2361, 2160, 1976, 1466, 1122, 1048, 908, 871, 720, 668 cm^{-1}; **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.88 (t, *J* = 6.7, 6H, 2xCH_3), 1.27-1.47 (m, 28H, 14-CH_2), 1.75-2.11 (br s, 2H, 2-OH), 3.37-3.43 (m, 1H, CH(OH)), 3.58-3.61 (m, 1H, CH(OH)); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_c = 14.2 (2xCH_3), 22.8 (2xCH_2), 25.8, 26.2 (2-CH_2), 29.4 (2xCH_2), 29.7 (2xCH_2), 29.8 (2xCH_2), 32.0 (2xCH_2), 31.3, 33.8 (2-CH_2), 74.7, 74.9 (2-CH); **HRMS-ESI**: calculated for $[M+Na]^+$, $C_{18}H_{38}NaO_2$: 309.2753, found 309.2764; **GC analysis**: Rt = 6.26 and 6.31 min.



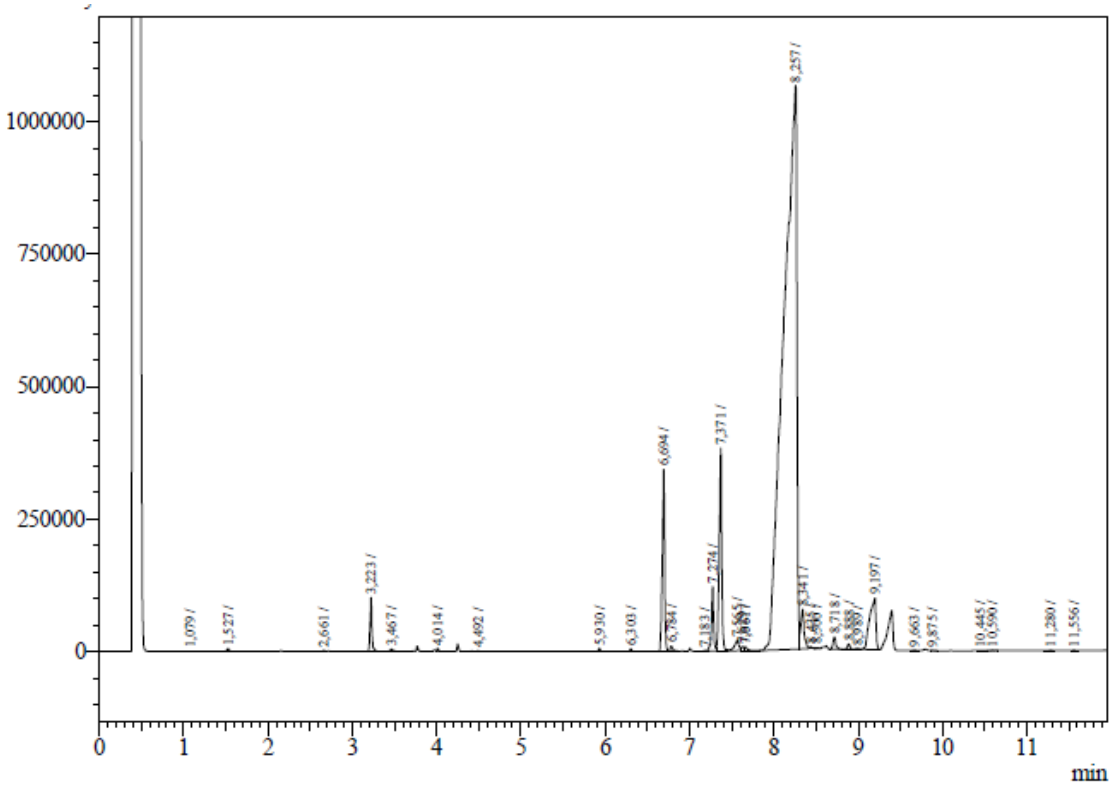


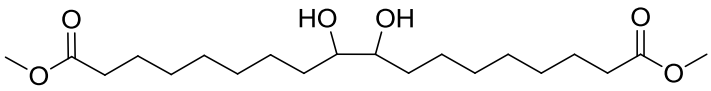
(Z)-Dimethyl octadec-9-enedioate [CAS 40393-46-2][13] : Following a modified procedure,[14] crude (80% purity) (Z)-octadec-9-enedioic acid (51 g, 130 mmol), dry Amberlyst-15 (5 g, 10wt% of diacid) and MeOH (500 mL) were introduced in 1-L round bottom flask. Then the reaction was heated at 70^0C for 18 hours. The conversion was followed by GC analysis. After the conversion was completed, the reaction mixture was concentrated under reduced pressure. The residue was diluted in EtOAc (500 mL) and filtered to remove Amberlyst-15. The filtrate was washed with water (2x 400 mL), brine (400 mL), dried over $MgSO_4$ and filtered off. The filtrate was concentrated under reduced pressure to give the desired product (55.8 g, 93%) as a colourless liquid. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 1.15-1.32 (m, 16H, 8-CH_2), 1.45-1.60 (m, 4H, 2-CH_2), 1.85-1.95 (m, 4H, 2-$\underline{CH_2}$-C=C), 2.19 (t, *J* = 7.3, 4H, 2x$\underline{CH_2}$-C=O), 3.55 (s, 6H, 2xCH_3O), 5.18-5.28 (m, 2H, 2=C$\underline{H}$-); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_c = 24.8 (2xCH_2), 27.1 (2xCH_2), 28.98 (2xCH_2), 29.03 (2xCH_2), 29.07 (2xCH_2), 29.6 (2xCH_2), 33.9 (2xCH_2), 51.2 (2xCH_3O), 129.7 (2-CH), 174.0 (2xC=O); **GC analysis:** Rt = 7.3 min



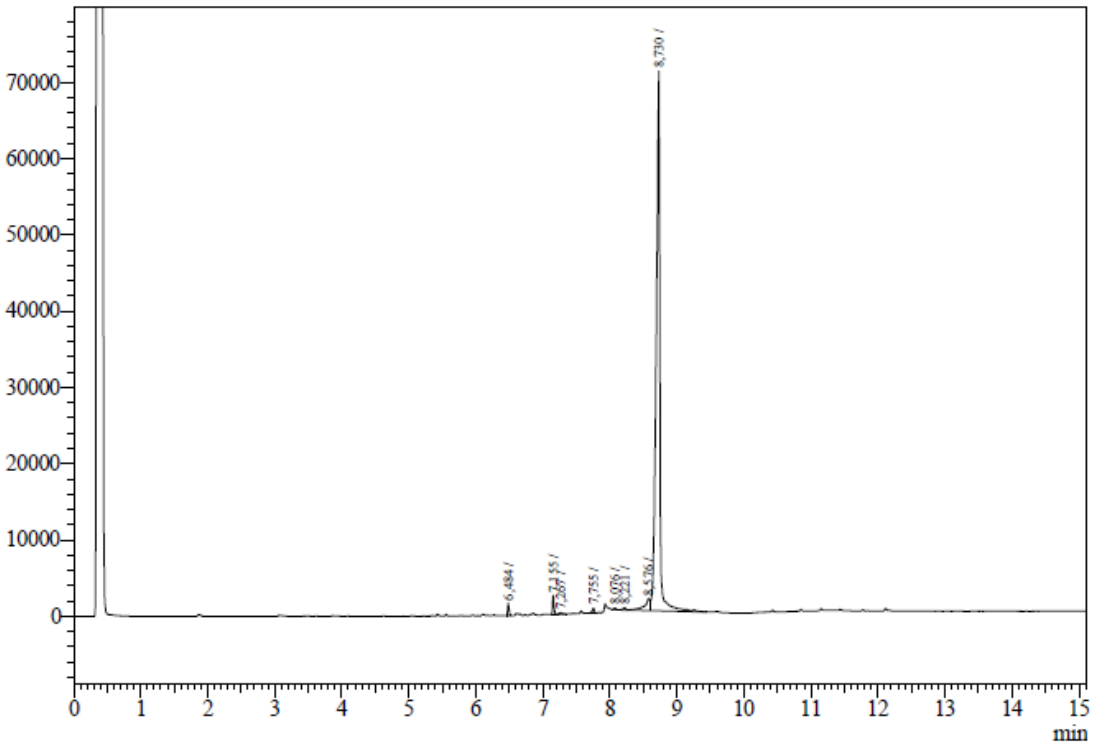


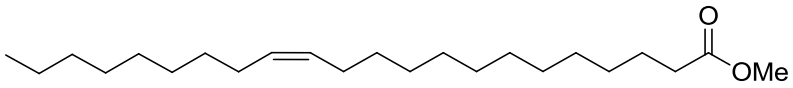
Dimethyl 8,8'-(oxirane-2,3-diyl)dioctanoate [65492-88-8][15] : Following a reported procedure,[6] a crude (88% purity) (Z)-dimethyl octadec-9-enedioate (55 g, 130 mmol) and HCOOH (7.4 g, 160 mmol, 1.2 equiv) were introduced in a 200-mL jacketed glass reactor at room temperature. H_2O_2 (35%w in H_2O, 36 mL, 370 mmol, 2.8 equiv) was added dropwise over a 60-minute period. Then the reaction mixture was heated at 60°C for 6 hours. After conversion was complete, the reaction was cooled down at room temperature and the water phase was discarded and the residue was dissolved in EtOAc (500 mL) then washed with hot water (2x500 mL), $NaHCO_3$ 5% solution (2x300 mL) and brine (500 mL), dried over $MgSO_4$ and filtered off. The filtrate was concentrated under reduced pressure to give the desire product (53.4 g, 94%) as a colourless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 1.10-1.49 (m, 24H, 12-CH_2), 2.12 (t, *J* = 7.3, 4H, 2x$\underline{CH_2}$-C=O), 2.65-2.75 (m, 2H, 2xCH-epoxide), 3.47 (s, 6H, 2xCH_3O); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_c = 24.7 (2xCH_2), 26.4 (2xCH_2), 27.6 (2xCH_2), 28.8 (2xCH_2), 29.0 (2xCH_2), 29.1 (2xCH_2), 33.8 (2xCH_2), 51.1 (2xCH_3O), 56.8 (2x$CH_{epoxide}$), 173.8 (2xC=O); **GC analysis**: Rt= 8.2 min.



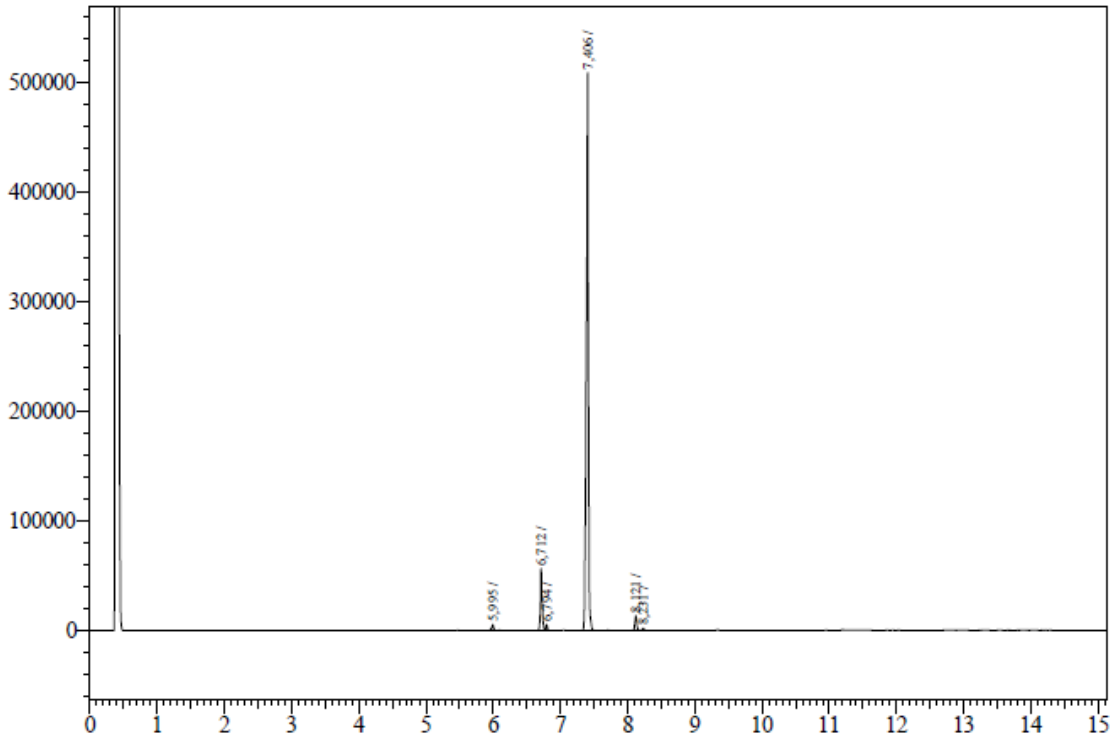


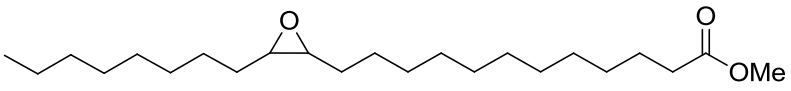
Dimethyl 9,10-dihydroxyoctadecanedioate [CAS 67852-29-3][16] (6): Following a modified procedure,[7] crude (80% purity) dimethyl 8,8'-(oxirane-2,3-diyl)dioctanoate (53 g, 120 mmol), phosphorous acid (20 mg, 2.4 mmol, 0.02 equiv) and water (12 mL) were introduced in a 200-mL jacketed glass reactor then the reaction mixture was heated at 90^{0}C for 3 hours. After conversion was complete, the reaction was cooled down and the water phase was discarded. The organic layer was diluted in EtOAc (500 mL) and washed with water (3x400 mL) and brine (400 mL) until pH was neutral. The obtained solution was dried by $MgSO_4$ and filtered off. The filtrate was concentrated under reduced pressure to give a crude product (51.5 g, 78% purity). This crude was crystallized from a mixture of heptane/EtOAc (5/1) then filtered off and dried in *vacuo* to afford the desired product (33.3 g, 62%) as a white solid (mp= 81-83°C). **IR** (ν_{max}): 3333 (br, O-H), 2912, 2847 (C-H stretching), 2362, 2160, 1976, 1742 (C=O ester), 1319, 1225, 1167, 1078, 882, 870, 750, 719, 653 cm^{-1}; **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 1.25-1.52 (m, 20H, 10-CH_2), 1.59-1.64 (m, 4H, 2-CH_2), 1.99 (br s, 2H, 2xO-H), 2.30 (t, *J* = 7.5, 4H, 2xCH_2-C=O), 3.35-3.45 (m, 2H, 2xCH-OH), 3.66 (s, 6H, 2 xCH_3O); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_c = 24.9 (2xCH_2), 25.6 (2xCH_2), 29.1 (2xCH_2), 29.2 (2xCH_2), 29.5 (2xCH_2), 33.6 (2xCH_2), 34.1 (2xCH_2), 51.5 (2xCH_3O), 74.5 (2xCH-OH), 174.5 (2xC=O); **HRMS-ESI** : calculated for $[M+H]^+$, $C_{20}H_{31}O_6$: 375.2732, found 375.2741; **GC analysis** : Rt = 8.7 min.



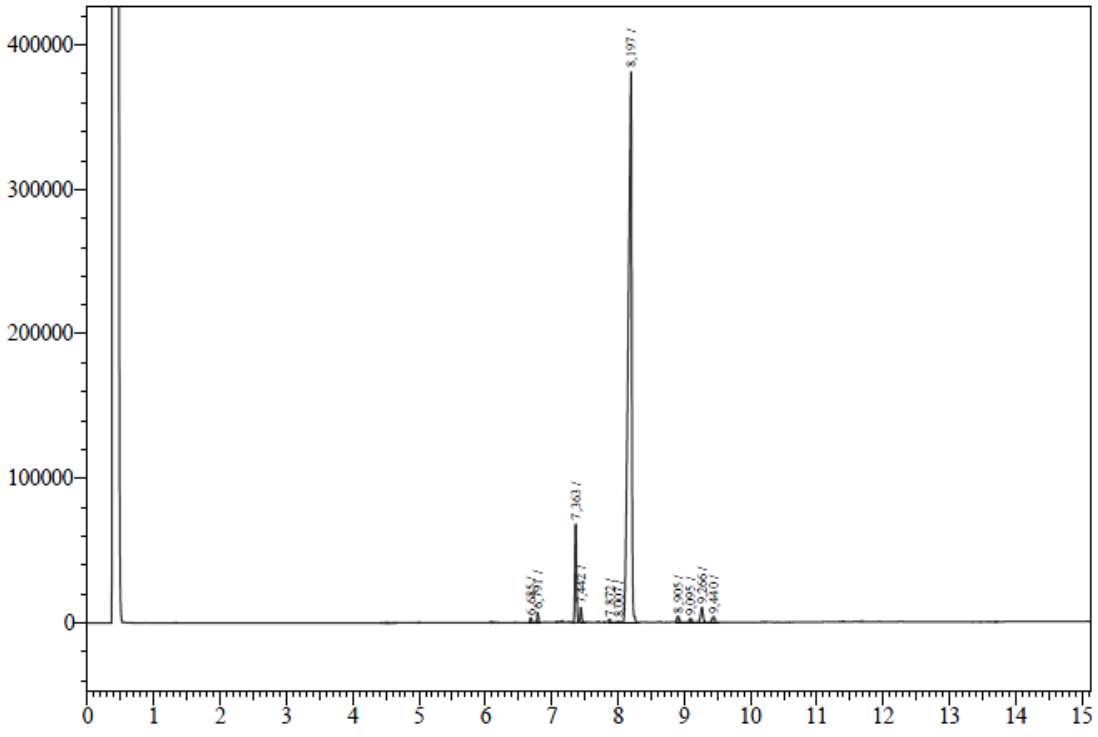


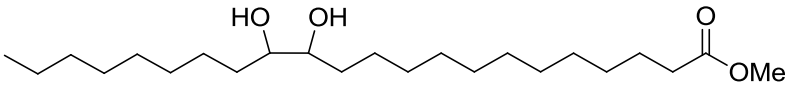
(Z)-methyl docos-13-enoate [CAS 1120-34-9]: Following a reported procedure,[17] rapeseed oil (103 g), K_3PO_4 (4 g, 4% weight of oil) was introduced in 1-L round bottom flask with MeOH (600 mL). The reaction mixture was heated at 70^0C for 2 hours. The conversion was controlled by NMR analysis. Then, the reaction mixture was cooled down to 5°C (cold water bath) to give two distinct phases, containing methyl fatty esters (upper phase, **F1**) and methanol phase (lower phase). The methanol phase was concentrated under reduced pressure to give a crude product containing methyl fatty esters (about 30%), glycerol and K_3PO_4. This residue was diluted in CH_2Cl_2 (300 mL) then filtered off (to remove solid catalyst). The filtrate was evaporated under reduced pressure to give a mixture of red heavily liquid (glycerol) and methyl fatty ester. This residue was introduced in a separatory funnel. The lower phase containing glycerol was discarded and the upper phase containing the fatty products was combined with fraction 1 (**F1**). The combined fractions were dissolved in heptanes (500 mL), washed with water (300 mL), brine (300 mL), dried over $MgSO_4$ and filtered off. The filtrate was evaporated under reduced pressure to give a mixture of fatty methyl esters (100 g, 97%) containing 41% of methyl erucate. The shorter fatty esters (such as methyl oleate, methyl linoleate, methyl palmitate) were eliminated by distillation under reduced pressure ($p_{constant}$ =0.02 mbar, t = 50°C to 140°C) and the desired product was obtained in the residue as a yellowish oil (44 g, 94%). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.88 (t, *J* = 6.6, 3H, CH_3), 1.20-1.41 (m, 28H, 14-CH_2), 1.55-1.70 (m, 2H, CH_2), 1.95-2.05 (m, 4H, 2-CH_2), 2.30 (t, *J* = 7.5 , $\underline{CH_2}$-C=O), 3.66 (s, 3H, $\underline{CH_3}$O), 5.32-5.36 (m, 2H, 2=CH-); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_c = 14.2 (CH_3), 22.8, 25.1 (2xCH_2), 27.3 (2xCH_2), 29.3, 29.37 (2-CH_2), 29.43 (3xCH_2), 29.56, 29.63, 29.65, 29.69, 29.72 (5-CH_2), 29.9 (2xCH_2), 32.0, 34.2 (2-CH_2), 51.5 (CH_3O), 129.95, 129.97 (2-CH), 174.4 (C=O); **GC analysis**: Rt = 7.4 min.



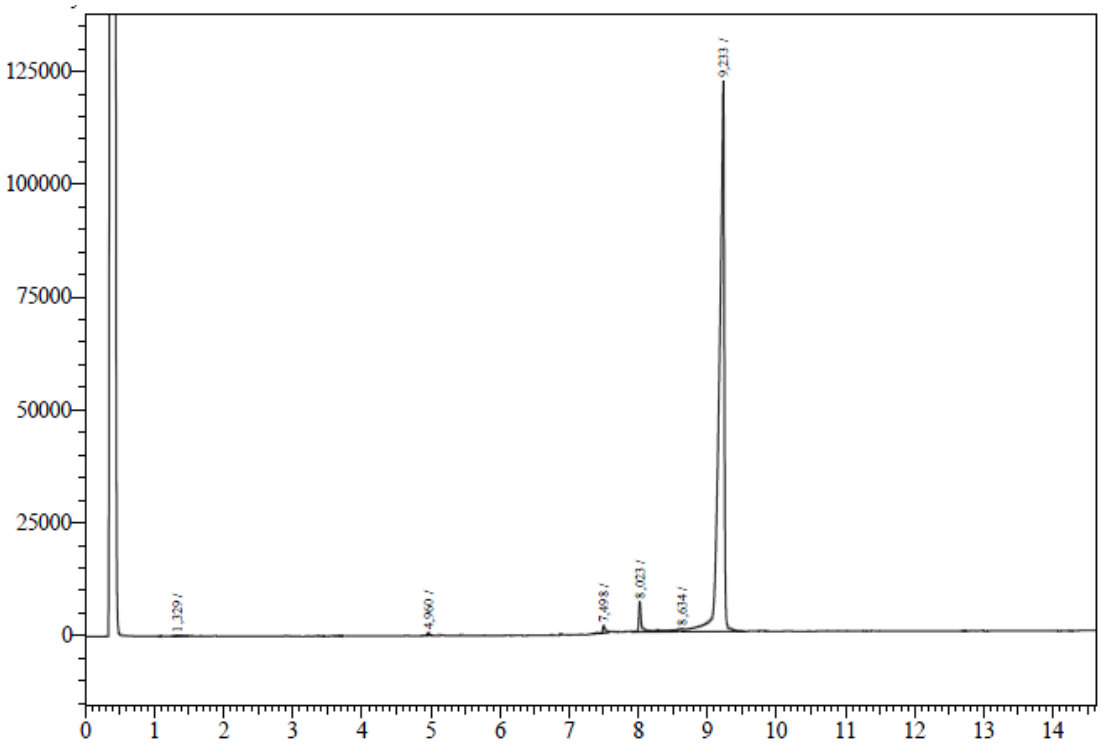


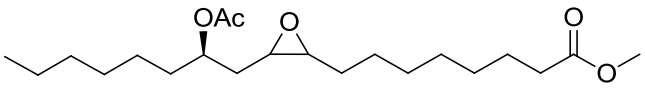
Methyl 12-(3-octyloxiran-2-yl)dodecanoate [CAS 87575-32-4]:[18] Following a modified procedure,[6] crude (88% purity) methyl erucate (44 g, 110 mmol), and HCOOH (5.5 g, 110 mmol, 1 equiv) were introduced in 200-mL jacketed glass reactor at room temperature. H_2O_2 (35%w in H_2O, 25 mL, 220 mmol, 2 equiv) was added dropwise over a 1-hour period then the reaction mixture was heated at 50^0C for 6 hours. The conversion was followed by GC. The reaction was cooled down to ambient temperature and water layer was discarded. The organic layer was dissolved in heptanes (400 mL) and washed with hot water (2x300 mL), $NaHCO_3$ 5% solution (300 mL) and brine (300 mL) until the pH was neutral. The resulting solution was dried over $MgSO_4$, filtered then concentrated under reduced pressure to give the desired product (48.5 g, 95%). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.88 (t, *J* = 6.7 , 3H, CH_3), 1.25-1.67 (m, 34H, 17-CH_2), 2.30 (t, *J* = 7.5, 2H, $\underline{CH_2}$-C=O), 2.88-2.92 (m, 2H, H-epoxide), 3.67 (s, 3H, $\underline{CH_3}$O); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_c = 14.2 (CH_3), 22.7, 25.0 (2-CH_2), 26.7 (2xCH_2), 27.9 (2xCH_2), 29.2 (CH_2), 29.3 (2xCH_2), 29.5 (CH_2), 29.6 (6xCH_2), 31.9, 34.1 (2-CH_2), 51.5 (CH_3O), 57.3 (2xCH epoxide), 174.3 (C=O); **GC analysis**: Rt = 8.2 min.



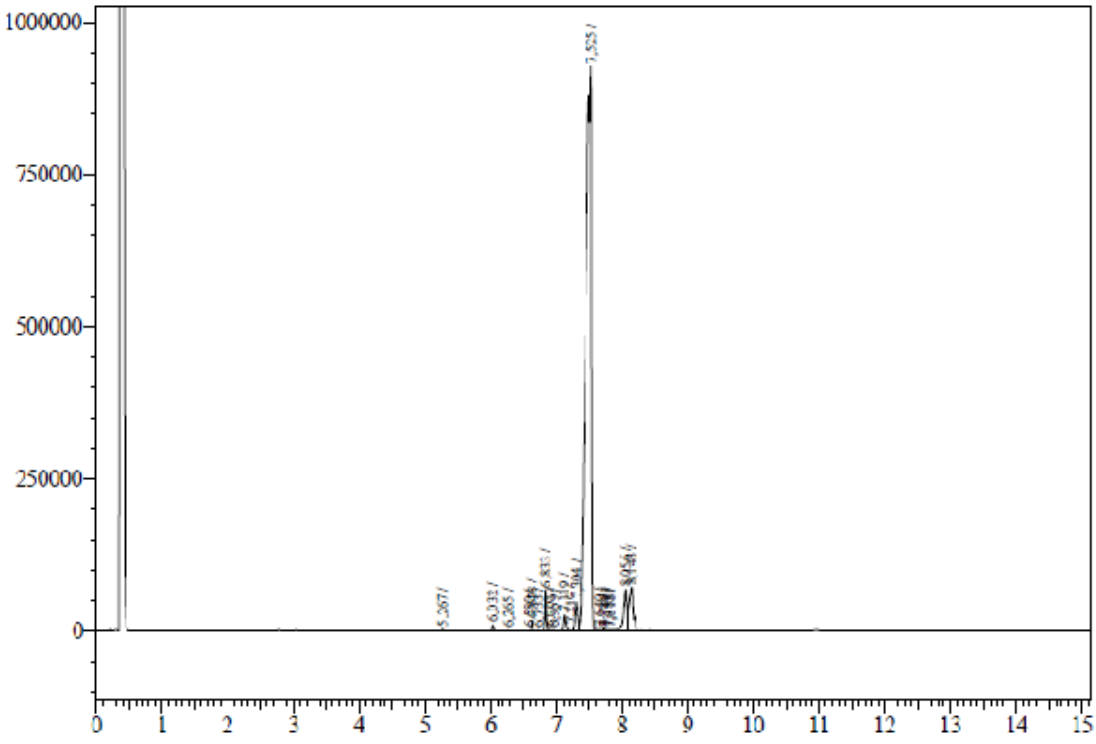


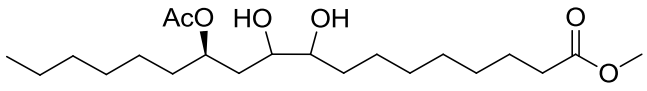
Methyl 13,14-dihydroxydocosanoate [CAS 2189-23-3][19] (7): Following a modified procedure,[7] crude (90% purity) methyl 12-(3-octyloxiran-2-yl)dodecanoate (48.5 g, 110 mmol), H_3PO_3 (182 mg, 2.2 mmol, 0.02 equiv) and H_2O (11 mL) were introduced in a 200-mL jacketed glass reactor then the reaction mixture was heated at 90^0C for 3 hours until conversion was complete. The reaction was cooled down to room temperature and the water phase was discarded. The resulting oil was diluted in EtOAc (400 mL), washed with water (2x 300 mL), brine (300 mL) until pH was neutral, dried over $MgSO_4$ and filtered off. The filtrate was concentrated under reduced pressure to give a crude product (52.3 g). This crude was crystallized in heptanes, filtered off and dried in *vacuo* to afford the desired product (32 g, 75%, 94% purity) as a white solid (mp =78-80°C). **IR** (ν_{max}): 3330 (br, O-H), 2912, 2847 (C-H stretching), 2159, 1742 (C=O ester), 1467, 1142, 904, 750, 720, 653; **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.88 (t, *J* = 6.6, 3H, CH_3), 1.26-1.64 (m, 34H, 17-CH_2), 2.03 (br s, 2H, O-H), 2.31 (t, *J* = 7.5, 2H, $\underline{CH_2}$-C=O), 3.40-3.42 (m, 2H, 2x$\underline{CH}$-OH), 3.66 (s, 3H, $\underline{CH_3}$O); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_c = 14.2 (CH_3), 22.8, 25.0 (2-CH_2), 25.8 (2xCH_2) 29.2, 29.3, 29.4, 29.5, 29.64 (5-CH_2), 29.67 (3xCH_2), 29.78, 29.80, 31.97 (3-CH_2), 33.7 (2xCH_2), 34.2 (CH_2), 51.6 (CH_3O), 74.6 (2xCH-OH), 174.6 (C=O); **HRMS-ESI:** calculated for $[M+H]^+$, $C_{23}H_{47}O_2$: 387.3474, found 387.3464; **GC analysis** Rt = 9.2 min.



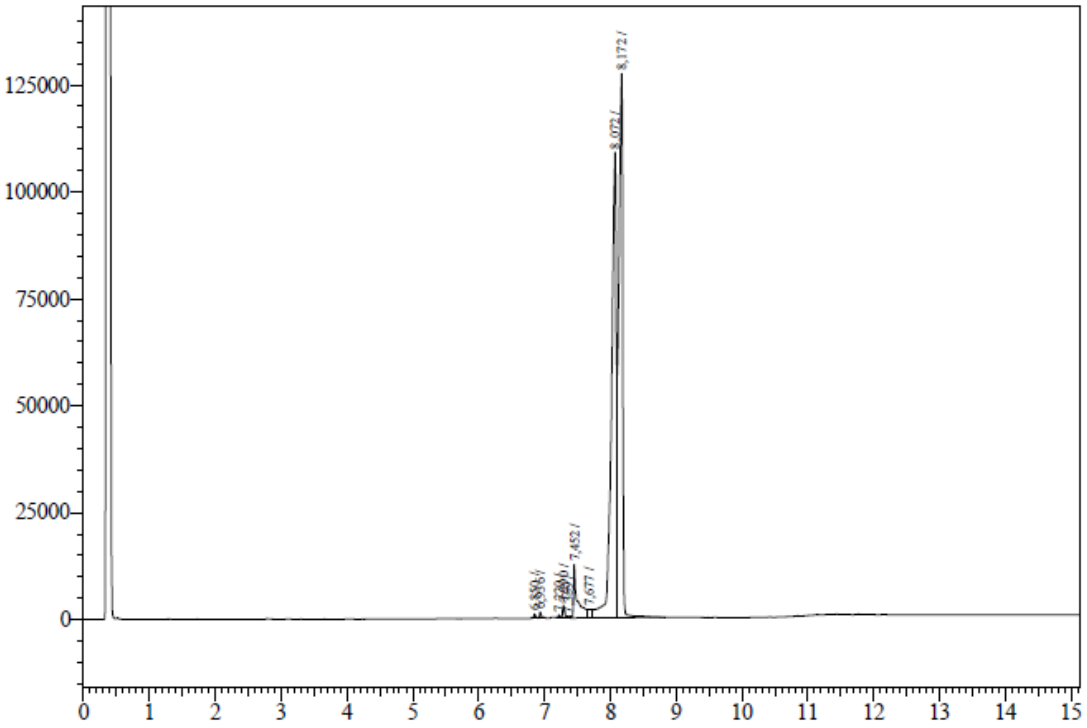


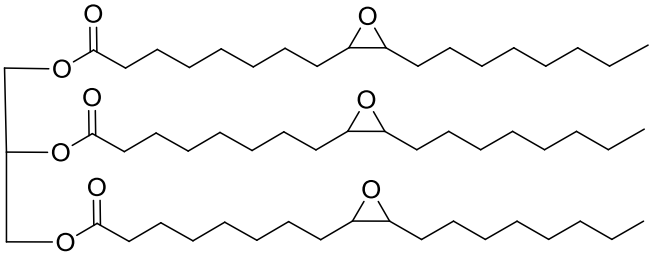
Methyl 8-(3-((R)-2-acetoxyoctyl)oxiran-2-yl)octanoate [CAS 428506-93-8]:[20] Methyl 12-*O*-acetyl ricinoleate (99% purity GC) was obtained through fractioned distillation (t = 190°C, p = 3.10^{-2} mbar) from a technical grade (>80% GC purity) starting material. Following a reported procedure,[6] methyl 12-*O*-acetyl ricinoleate (10.5 g, 30 mmol) and HCOOH (1.4 g, 30 mmol, 1 equiv) were successively introduced in a 200-mL jacketed glass reactor. H_2O_2 (35%w in water, 6 mL, 2 equiv) was added dropwise over a 30-minute period at room temperature, then the reaction mixture was heated at 50^0C for 6 hours. After cooling to room temperature, the suspension was partitioned in a mixture of water (50 mL) and heptane (200 mL) then the water phase was discarded. The organic layer was washed with $NaHCO_3$ solution (5wt%, 2x100 mL), H_2O (200 mL) and brine (200 mL), dried ($MgSO_4$) then filtered. The filtrate was concentrated under reduced pressure to give the desired product (1:1 mixture diastereoisomers, 11.2 g, 87%) as colourless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.87 (t, *J* = 6.7, 3H, CH_3), 1.27-1.68 (m, 22H, 11-CH_2), 1.69-1.85 (m, 2H, CH_2), 2.04 and 2.06 (2s, 3H, $\underline{CH_3}CO$ in isomer 1 and $\underline{CH_3}CO$ in isomer 2), 2.30 (t, *J* = 7.5, 2H, CH_2C=O), 2.85-2.89 and 2.92-2.99 (2m, 2H, CH epoxide in isomer 1 and CH epoxide in isomer 2), 3.66 (s, 3H, $\underline{CH_3}O$), 4.96-5.09 (m, 1H, $\underline{CH}$-OAc); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_C = 14.1 (2xCH_3), 21.23 (CH_3), 21.27 (CH_3), 22.6 (2xCH_2), 24.9 (2xCH_2), 25.2 (CH_2), 25.8 (CH_2), 26.50 (CH_2), 26.54 (CH_2), 27.89 (CH_2), 27.96 (CH_2), 29.03 (2xCH_2), 29.08 (CH_2), 29.10 (CH_2), 29.17 (2xCH_2), 29.31 (2xCH_2), 31.7 (2xCH_2), 32.6 (CH_2), 32.8 (CH_2), 34.0 (2xCH_2), 34.1 (CH_2), 34.4 (CH_2), 51.5 (2xCH_3O), 53.7 (CH), 53.9 (CH), 56.2 (CH), 56.8 (CH), 72.43 (CH), 72.45 (CH), 170.7 (C=O), 170.8 (C=O), 174.2 (2xC=O); **MS (ESI$^+$)**: m/z = 371.0 $[M+H]^+$, 339.3 $[M+H\text{-}OMe]^+$, 310.3 $[M\text{-}AcOH]^+$, 213.1 $[M\text{-}(CH_2)_7CO_2Me]^+$; **GC analysis**: Rt = 7.51, 7.52 min.





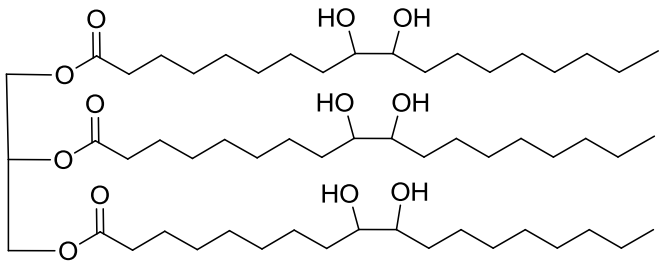
Methyl (12R)-acetoxy-9,10-dihydroxyoctadecanoate [CAS 147593-31-5] (15):[21] Following a modified procedure,[7] crude (86%) methyl 8-(3-((S)-2-acetoxyoctyl)oxiran-2-yl)octanoate (10.6 g, 25 mmol), H_3PO_3 (42 mg, 0.2 mmol, 0.02 equiv) and H_2O (2.5 mL) were introduced in 200-mL jacketed glass reactor. The reaction mixture was heated at 90^0C for 3 hours. The crude product was diluted in EtOAc (200 mL), then washed with water (2x200 mL), brine (200 mL), dried over $MgSO_4$ and filtered off. The filtrate was evaporated under reduced pressure to give a colourless oil (10.8 g, 99%, 90% purity). A crude sample (90% purity, 4.8 g) was purified by column chromatography (eluent CH_2Cl_2: MeOH 100/0 to 98/2) to afford the desired product (mixture of 4 diastereoisomers, 3.4 g, 78%) as a colourless oil. **IR** (ν_{max}): 3440 (br, O-H), 2926, 2855, 2159, 1734 (C=O), 1436, 1371, 1239, 1022, 847, 704; **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.83 (t, *J* = 6.6, 3H, CH_3), 1.23-1.74 (m, 24H, 12-CH_2), 1.99 and 2.04 and 2.05 and 2.07 (4s, 3H, $\underline{CH_3}$-C=O in 4 isomers), 2.26 (t, *J* = 7.5, 2H, CH_2-C=O), 2.92 (br s, 2H, 2xO-H), 3.24-3.46 and 3.77-3.88 (m, 2H, 2x$\underline{CH}$-OH), 4.75-4.82 and 4.92-5.03 (m, 1H, $\underline{CH}$-OAc); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_C = 14.1 (CH_3), 21.07, 21.15, 21.19, 21.4 (4x$\underline{CH_3}$-C=O in 4 isomers), 22.60, 22.64, 24.9, 25.2, 25.3, 25.4, 25.6, 25.7, 25.75, 25.82, 29.1, 29.17, 29.2, 29.3, 29.5, 30.1, 31.7, 31.8, 33.3, 33.5, 34.1, 34.3, 35.0, 37.5, 38.2, 38.4, 38.9 (multi-signal CH_2), 51.5 (CH_3O), 67.7, 70.4, 71.9, 72.0, 72.9, 73.2, 74.2, 74.4 (multi-signal $\underline{CH}$-OH), 171.0, 171.1, 171.2, 171.3 (4-C=O in 4 isomers), 174.39, 174.42 (C=O ester); **HRMS-ESI**: calculated for $[M+Na]^+$, $C_{21}H_{40}NaO_6$: 411.2723, found 411.2698; **GC analysis:** Rt = 8.07, 8.17 min.





Tris(Epoxy) high-oleic sunflower oil: High-oleic sunflower oil (>85% oleic acid content) was supplied by OLEON®. The percentage of oleic acid was confirmed by NMR analysis and GC analysis of methyl oleate obtained after methanolysis of this sunflower oil. Following a modified procedure,[6] high-oleic sunflower oil (50 g, 48 mmol), HCOOH (6.9 g, 144 mmol, 3 equiv) and H_2SO_4 (0.25 mL, 0.05 mmol, 0.01 equiv) were introduced in a 200-mL jacketed glass reactor at 40^0C. Then, H_2O_2 (35wt% in H_2O, 46 mL, 470 mmol, 9 equiv) was added dropwise over a-60 minute period. The reaction mixture was heated at 60^0C for 3 hours. The conversion was controlled by ^{1}H-NMR. The reaction mixture was cooled down to room temperature and the water phase was discarded. The resulting oil was diluted in EtOAc (500 mL) then washed with warm water and brine until pH was neutral. Then, the organic phase was dried over $MgSO_4$ and filtered off. The filtrate was concentrated under reduced pressure to afford the desired product (53.5 g) as a viscous oil containing 2.5% of diol, 75% epoxide oleic and 6% epoxide linoleic (confirmed by ^{1}H-NMR). **IR** (ν_{max}): 2953, 2916, 2850 (C-H stretching), 2361, 2340, 1734 (C=O), 1464, 1336, 1168, 919, 890, 844 (ring deformation band), 752, 721; **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.86 (t, *J* = 6.7, 9H, 3x$\underline{CH_3}$), 1.23-1.39 (m, 54H, 27-CH_2), 1.34-1.73 (m, 24H, 12-CH_2), 2.27-2.33 (t, *J* = 7.5, 6H, 3x$\underline{CH_2}$-C=O), 2.83-2.91 (m, 6H, CH epoxide oleic, 75%), 4.12 (dd, *J* = 11.9, 5.9, 2H, CH_2-glycerol), 4.28 (dd, *J* = 11.9, 4.3, 2H, CH_2-glycerol), 5.21-5.28 (m, 1H, CH-glycerol).

Visible peaks for epoxidized linoleic: 2.92-3.11 (m, 12H, CH epoxide linoleic, 6%). Visible peaks for diol oleic: 3.33-3.40 (m, 6H, $\underline{CH}$-OH, 2.5%).



Tris(diol) high-oleic sunflower oil (16): Following a modified procedure,[7] epoxydized high-oleic sunflower oil (50 g, 50 mmol), H_3PO_3 (248 mmg, 3.0 mmol, 0.02 equiv per epoxy function), H_2O (25 mL) were introduced into 200-mL jacketed glass reactor then the reaction mixture was heated at 90^0C for 3 hours. The conversion was monitored by ^{1}H-NMR analysis. After the conversion was complete, the reaction was cooled down to room temperature and the water phase was discarded. The organic residue was dissolved in CH_2Cl_2 (500 mL) then washed with warm water (3x400 mL), brine (400 mL), dried over $MgSO_4$ and filtered off. The filtrate was concentrated under reduced pressure to afford the desired product (52.8 g) as a white sticky solid containing 71% Tris(diol-oleic), 5% Tris(tetraol-linoleic) and 8% monoketone oleic (confirmed by ^{1}H-NMR and GC). **IR** (ν_{max}): 3359 (br, O-H), 2918, 2850 (C-H stretching), 2361, 2311, 1740 (C=O), 1462, 1415, 1377, 1072, 841, 721, 668; **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.86 (t, *J* = 6.6, 9H, 3-CH_3), 1.25-1.40 (m, 60H, 30-CH_2), 1.40-1.63 (m, 18H, 9-CH_2), 2.31 (t, *J* = 7.5, 6H, 3x$\underline{CH_2}$C=O), 2.54-2.76 (br s, 6H, CH-$\underline{OH}$ oleic, 70%), 3.20-3.36 (m, 6H, $\underline{CH}$-OH oleic, 70%), 4.09-4.16 and 4.26-4.31 (2m, 4H, 2xOCH_2-glycerol), 5.20-5.29 (m, 1H, OCH-glycerol); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_c = 14.2 (3-CH_3), 22.6, 24.8, 25.6, 25.7, 28.9, 29.0, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 31.8, 33.5, 33.6, 33.9, 34.1 (42-CH_2), 62.1 (2-OCH_2 glycerol), 69.0 (1-OCH glycerol), 74.6 (6-CH(OH)) 172.8, 173.2, 173.3 (3-C=O).

Visible peaks for linoleic: 3.45-3.58 (m, 12H, $\underline{CH}$-OH linoleic, about 5-6%). Visible peaks for monoketone: 2.35 (t, *J* = 7.3, 12H, CH_2 in monoketone, about 8%).

5. General procedures

Procedure A: Typical procedure for the preparation of α-hydroxyketones using homogeneous $Pd(OAc)_2$ / neocuproine complex:

In 30-mL steel reactor, methyl 9,10-dihydroxyoctadecanoate **1** (4 g, 12 mmol), $Pd(OAc)_2$ (54 mg, 0.24 mmol, 2 mol% in Pd), neocuproine (50 mg, 0.24 mmol, 2 mol%) were successively introduced in MeOH (8 mL) under stirring. The mixture was stirring at room temperature in a few minutes until the medium became more homogeneous. Next, glacial acetic acid (43 mg, 0.72 mmol, 6 mol%) was added to the solution before closing the apparatus. Oxygen (3 bar) was charged in the reactor, then the reaction was heated at 50^0C (oil bath) for 1.5 hour. The reaction mixture was cooled down to 25^0C by stream of water before adding EtOAc (20 mL). The suspension was filtered and the filtrate was evaporated under reduced pressure to give a green oil (3.97 g). The crude product was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc, 100:0 → 95:5) to give the α-hydroxyketone **2** (3.20 g, 80%) as white solid.

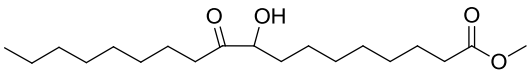
Procedure B: Typical procedure for the preparation of α-hydroxyketones using heterogeneous Ru/C:

In a Schlenk flash, methyl 9,10-dihydroxyoctadecanoate **1** (0.92 g, 2.8 mmol) and activated $^{5wt\%}$Ru/C (0.26 g, 5 mol% of Ru) were introduced. Then, argon was filled inside the equipment. The outline of apparatus was connected with evaporator system to control the vacuum pressure at 100 mbar. The reaction was heated at 175^0C (oil bath) for 3 hours. After cooling to room temperature, EtOAc (2 x 20 mL) was added in the mixture then the resulting slurry was filtered though millipore system (pore size 0.1 μm). The filtrate was evaporated under reduced pressure to give the crude product (0.89 g). The residue was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc, 100:0 → 95:5) to give the α-hydroxyketone **2** (0.61 g, 67%) as white solid.

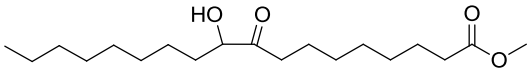
Procedure C: General procedure for the preparation of α-hydroxyketones using heterogeneous Ru/C:

In a Schlenk flash, oleochemical 1,2 diols (3 mmol) and activated $^{5wt\%}$Ru/C (0.3 g, 5 mol% of Ru) were introduced. Then, argon was filled inside the equipment. The outline of apparatus was connected with evaporator system to control the vacuum pressure at 100 mbar. The reaction was heated at 175^0C (oil bath) for 3 hours. After cooling to room temperature, EtOAc (2 x 20 mL) was added in the mixture then the resulting slurry was filtered though millipore system (pore size 0.1 μm). The filtrate was evaporated under reduced pressure to give the crude product. The residue was purified by column chromatography on silica gel (cyclohexane/EtOAc) to give the oleochemical α-hydroxyketones.

6. Characterization data of oleochemical α-hydroxyketones

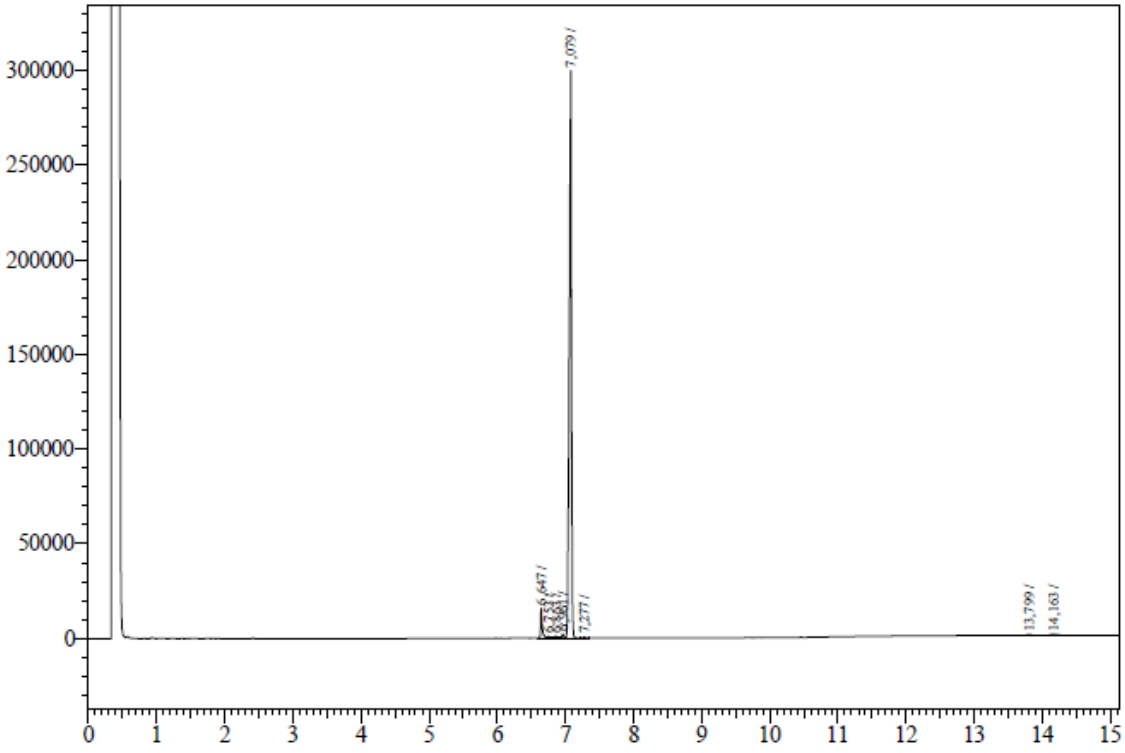


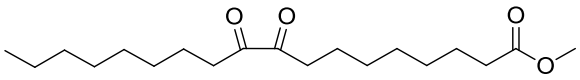
CAS 7297-29-2



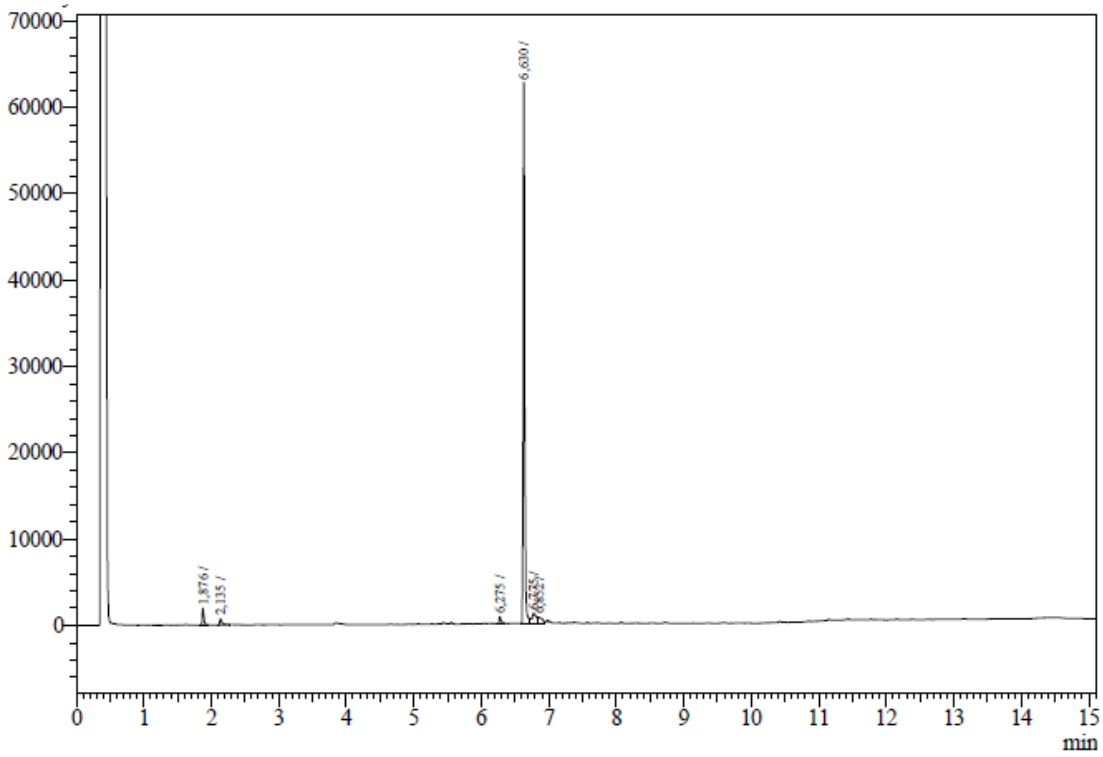
CAS 7108-21-6

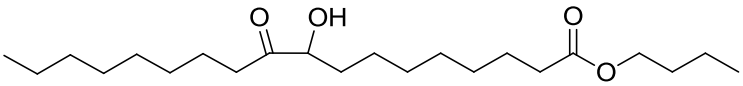
Methyl 9(10)-hydroxy 10(9)-oxo octadecanoate (2):[22] The title compound was obtained from methyl 9,10-dihydroxyoctadecanoate **1** (0.92 g, 2.8 mmol) following procedure B. The residue was purified by column chromatography (CH_2Cl_2/EtOAc, 100:0 → 95:5) to give α-hydroxyketone **2** (1:1 mixture of regioisomers, 0.61 g, 67%) as a white solid (mp = 36-40°C). **IR (ν_{max})**: 3317 (br, O-H), 2931, 2915, 2849, 1735 (C=O ester), 1710 (C=O ketone), 1245, 1215, 1177, 1105, 1087 (C-O); **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.82 (t, *J* = 6.6, 3H, CH_3), 1.14-1.33 (m, 17H), 1.35-1.64 (m, 6H, 3-CH_2), 1.64-1.85 (m, 1H), 2.24 (t, *J* = 7.5, 2H, $\underline{CH_2}$-C=O ester), 2.40 (dd, *J* = 12.5, 7.2, 2H, $\underline{CH_2}$-C=O ketone), 3.52 (br s, 1H, O-H), 3.63 (s, 3H, CH_3O), 4.08-4.12 (m, 1H, $\underline{CH}$-OH); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_C = 14.1 (CH_3), 22.6 (CH_2), 23.5 and 23.6 (CH_2), 24.8 and 24.9 (CH_2), 28.9 and 29.00 (CH_2), 29.02 (CH_2), 29.08 and 29.12 (CH_2), 29.24, 29.25, 29.33 (3-CH_2), 29.44 and 29.48 (CH_2), 31.81 and 31.86 (CH_2), 33.73 and 33.79 (CH_2), 34.00 and 34.04 (CH_2), 37.78 and 37.85 (CH_2), 51.4 (CH_3O), 76.38 and 76.44 ($\underline{CH}$-OH), 174.19 and 179.24 (C=O ester), 212.51 and 212.56 (C=O ketone); **ESI-MS**: m/z = 329.3 ([M+H]$^+$, 100), 351.2 ([M+Na]$^+$, 55), 678.8 ([2M+Na]$^+$, 58); **HRMS-ESI:** calculated for [M+Na]$^+$, $C_{19}H_{36}NaO_4$: 351.2506, found 351.2502; **GC analysis**: Rt = 7.1 min.



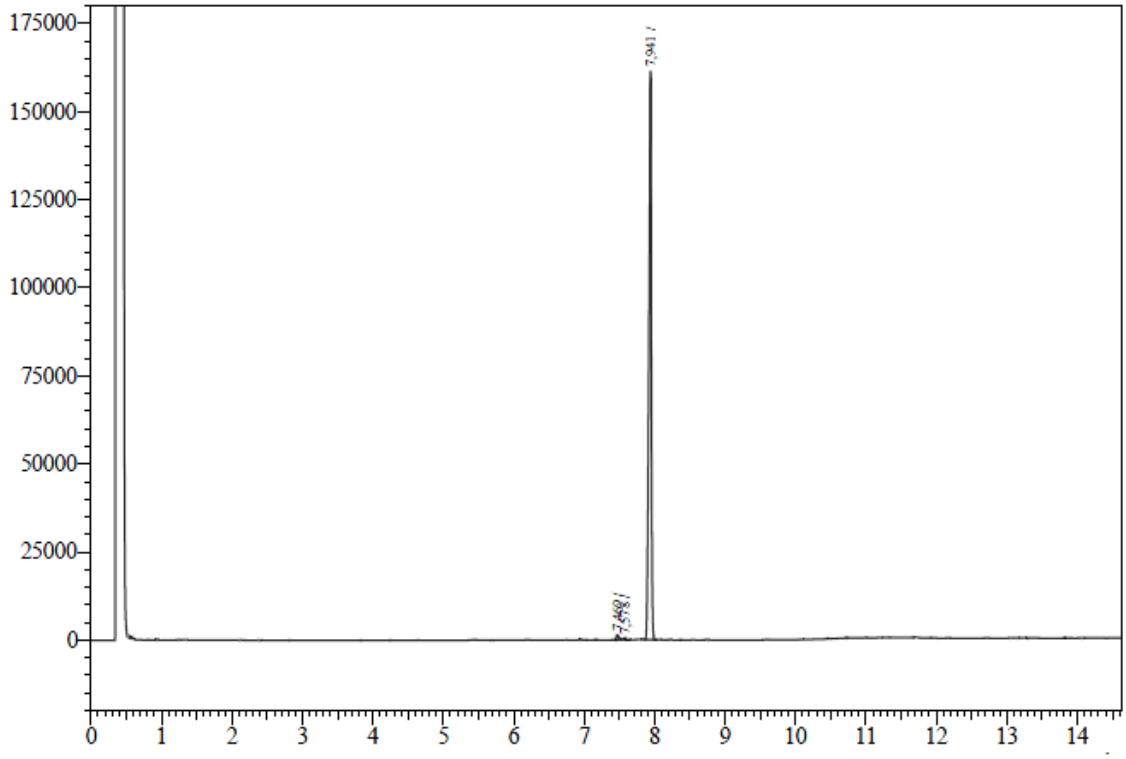


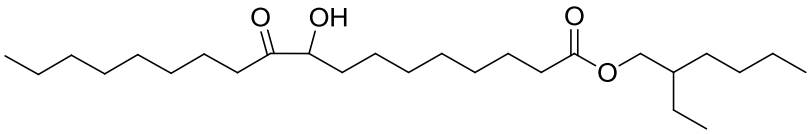
Methyl 9,10-dioxo octadecanoate (3) [CAS 7108-68-1]:[23] The title compound was obtained from methyl 9,10-dihydroxyoctadecanoate **1** following procedure B. This by-product was obtained from the purification of **2** by column chromatography (CH_2Cl_2/EtOAc, 100:0 → 98:2) to give diketone **3** as greenish solid (mp = 57-59°C). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.87 (t, *J* = 6.6, 3H, CH_3), 1.22-1.35 (m, 20H, 10-CH_2), 1.47-1.65 (m, 8H, 4-CH_2), 2.29 (t, *J* =7.5, 2H, $\underline{CH_2}$-C=O ester), 2.72 (t, *J* = 7.3, 4H, 2-$\underline{CH_2}$-C=O ketone), 3.66 (s, 3H, CH_3O); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_C = 14.2 (CH_3), 22.7, 23.1, 23.2, 24.9 (4-CH_2), 29.0 (2xCH_2), 29.1, 29.19, 29.24, 29.4, 31.9, 34.1, 36.1, 36.2 (8-CH_2), 51.6 (CH_3O), 174.3 (C=O ester), 200.1, 200.2 (2-C=O ketone); **HRMS-ESI:** calculated for $[M+Na]^+$, $C_{20}H_{38}NaO_4$: 349.2355, found 349.2348; **GC analysis**: Rt = 6.6 min.



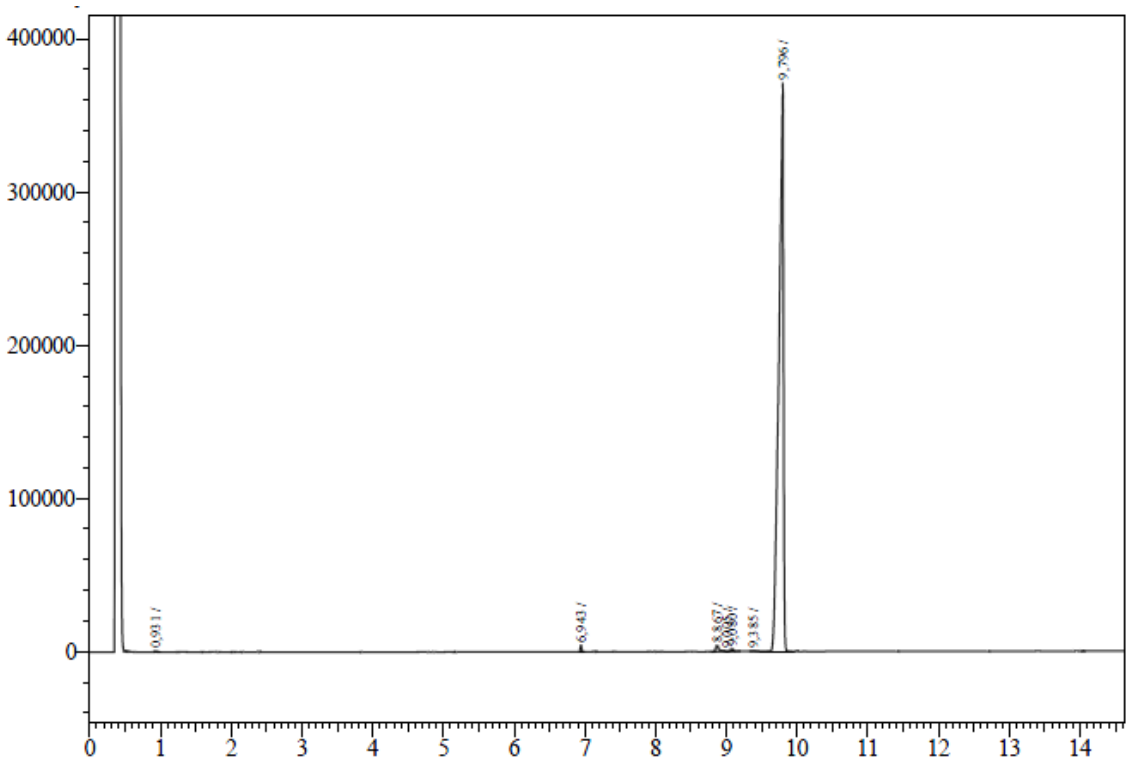


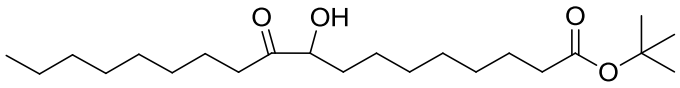
Butyl 9(10)-hydroxy-10(9)-oxooctadecanoate (17) [No CAS]: The title compound was obtained from butyl 9,10-dihydroxyoctadecanoate **13** (1.1 g, 3.0 mmol) following the general procedure C. The residue was purified by column chromatography (cyclohexane/EtOAc, 100:0 → 95:5) to give α-hydroxyketone **17** (1:1 mixture of regioisomers, 0.71 g, 65%) as a white solid (mp= 35-38°C). **IR (ν_{max}):** 3322 (br, O-H), 2955, 2914, 2849 (C-H stretching), 2159, 2029, 1731 (C=O ester), 1710 (C=O ketone), 1462, 1183, 1087, 924, 751, 699, 660; **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.87 (t, *J* = 6.7, 3H, CH_3), 0.94 (t, *J* = 7.3, 3H, CH_3), 1.27-1.50 (m, 22H, 11-CH_2), 1.50-1.83 (m, 8H, 4-CH_2), 2.28 (t, *J* = 7.5, 2H, $\underline{CH_2}$-C=O ester), 2.38-2.51 (m, 2H, $\underline{CH_2}$-C=O ketone), 3.48 (br s, 1H, O-H), 4.06 (t, *J* = 6.7, 2H, $\underline{CH_2}$O), 4.13-4.17 (m, 1H, $\underline{CH}$-OH); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_c = 13.8 (CH_3), 14.2 (CH_3), 19.23 (CH_2), 22.71 and 22.73 (CH_2), 23.6 and 23.7 (CH_2), 24.88 and 24.92 (CH_2), 24.97 and 25.01 (CH_2), 28.99 and 29.07 (CH_2), 29.10 (CH_2), 29.18 (CH_2), 29.2-9 and 29.31 (CH_2), 29.34 and 29.39 (CH_2), 29.50 and 29.54 (CH_2), 30.78 (CH_2), 31.87 and 31.92 (CH_2), 33.80 and 33.86 (CH_2), 34.37 and 37.40 (CH_2), 37.85 and 37.92 (CH_2), 64.19 and 64.21 (CH_2O), 76.43 and 76.49 ($\underline{CH}$-OH), 173.95 and 174.00 (C=O ester), 212.55 and 212.61 (C=O ketone); **HRMS-ESI**: calculated for $[M+Na]^+$, $C_{22}H_{42}NaO_4$:393.2975, found 393.2966; **GC analysis**: Rt = 7.9 min.



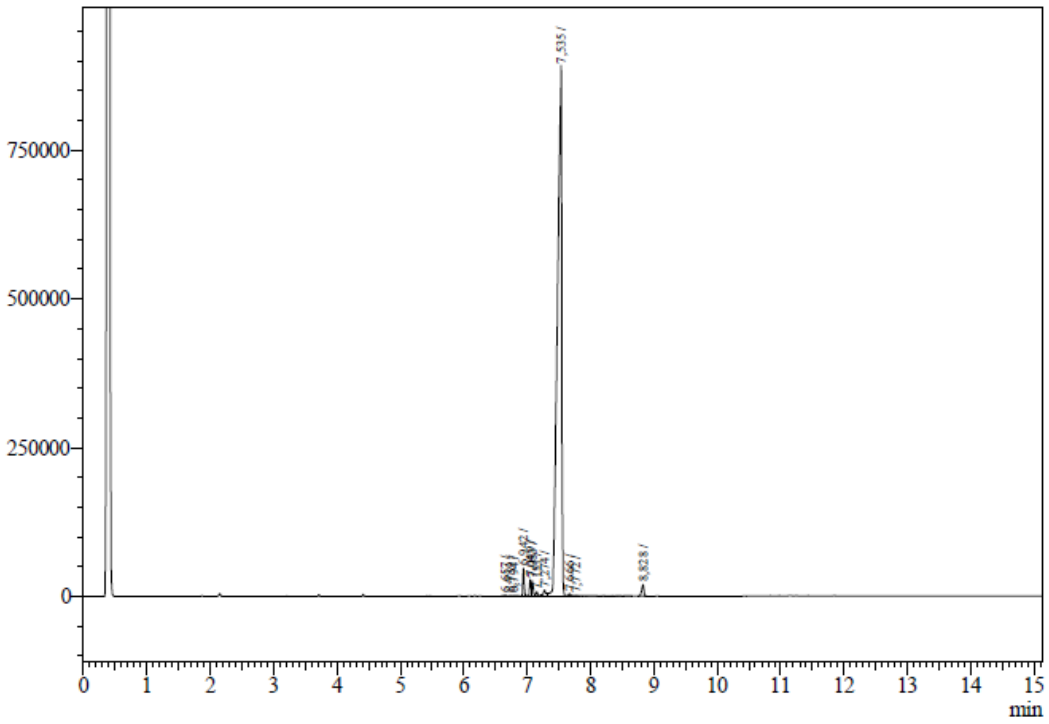


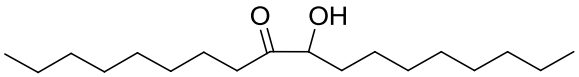
2-Ethylhexyl 9(10)-hydroxy-10(9)-oxooctadecanoate (18) [No CAS]. The title compound was obtained from 2-ethylhexyl 9,10-dihydroxyoctadecanoate **14** (1.30 g, 3 mmol) following the general procedure C. The residue was purified by column chromatography (cyclohexane/EtOAc, 100:0 → 95:5) to give α-hydroxyketone **18** (1:1 mixture of regioisomers, 0.73 g, 56%) as a colourless liquid. **IR (ν_{max})**: 2924, 2855 (C-H stretching), 2159, 2029, 1976, 1734 (C=O ester), 1710 (C=O ketone), 1462, 1171, 724, 647; **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.73-0.82 (m, 9H, 3-CH_3), 1.13-1.29 (m, 26H, 13-CH_2), 1.32-1.74 (m, 8H, 4-CH_2), 2.19 (t, *J* = 7.5, 2H, CH_2-C=O ester), 2.27-2.42 (m, 2H, CH_2-C=O ketone), 3.38 (br s, 1H, O-H), 3.87 (dd, *J* = 5.8, 0.8, 2H, CH_2O), 4.02-4.08 (m, 1H, CH-OH); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_c = 11.1, 14.11, 14.15 (3-CH_3), 22.71 and 22.72 (CH_2), 23.1 (CH_2), 23.6 and 23.7 (CH_2), 23.9 (CH_2), 24.88 and 24.91 (CH_2), 24.99 and 25.03 (CH_2), 28.99 (2xCH_2), 29.08 and 29.11 (CH_2), 29.18 (CH_2), 29.29 and 29.31 (CH_2), 29.35 and 29.38 (CH_2), 29.50 and 29.54 (CH_2), 30.5 (CH_2), 31.87 and 31.91 (CH_2), 33.80 and 33.85 (CH_2), 34.40 and 34.45 (CH_2), 37.84 and 37.91 (CH_2), 38.8 (CH_2), 66.7 (CH_2O), 76.4 and 76.5 (CH-OH), 173.9 (C=O ester), 212.4 (C=O ketone); **HRMS-ESI**: calculated for $[M+H]^+$, $C_{26}H_{51}O_4$: 427.3775, found 427.3782; **GC analysis:** Rt = 9.8 min.



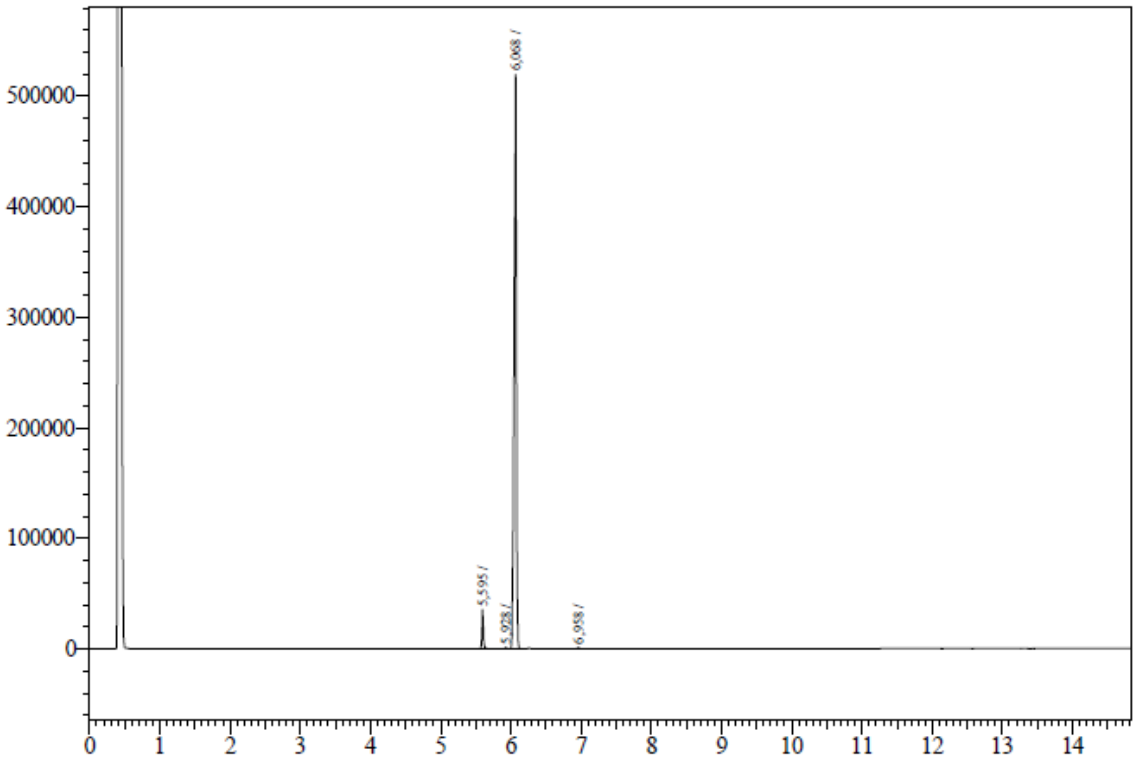


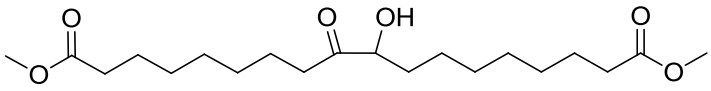
***tert*-Butyl 9(10)-hydroxy-10(9)-oxooctadecanoate (8) [No CAS].** The title compound was obtained from *tert*-butyl 9,10-dihydroxyoctadecanoate **4** (1.10 g, 3 mmol) following the general procedure C. The residue was purified by column chromatography (cyclohexane/EtOAc, 100:0 → 95:5) to give α-hydroxyketone **8** (1:1 mixture of regioisomers, 0.30 g, 28%) as a white solid (mp= 35-38°C). **IR (ν_{max}):** 3333 (br, O-H), 2914, 2848 (C-H stretching), 1732 (C=O ester), 1711 (C=O ketone), 1417, 1104, 752, 726, 701, 658; **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.87 (t, *J* = 6.7, 3H, CH_3), 1.20-1.38 (m, 18H, 9-CH_2), 1.43 (s, 9H, 3xCH_3), 1.50-1.85 (m, 6H, 3-CH_2), 2.19 (t, *J* = 7.5, 2H, $\underline{CH_2}$-C=O ester), 2.37-2.50 (m, 2H, $\underline{CH_2}$-C=O), 3.43 (br s, 1H, O-H), 4.13-4.18 (m, 1H, $\underline{CH}$-OH); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_c = 14.2 (CH_3), 22.71 and 22.72 (CH_2), 23.6 and 23.7 (CH_2), 24.88 and 24.92 (CH_2), 25.06 and 25.09 (CH_2), 28.2 (3xCH_3), 28.93 and 29.05 (CH_2), 29.10 and 29.12 (CH_2), 29.18 and 29.20 (CH_2), 29.29 and 29.31 (CH_2), 29.35 and 29.39 (CH_2), 29.50 and 29.54 (CH_2), 31.87 and 31.91 (CH_2), 33.80 and 33.85 (CH_2), 35.58 and 35.62 (CH_2), 37.86 and 37.92 (CH_2), 76.43 and 76.49 ($\underline{CH}$-OH), 79.98 and 80.02 ($\underline{C}(CH_3)_3$), 173.29 and 173.34 (C=O ester), 212.58 and 212.63 (C=O ketone); **HRMS-ESI**: calculated for $[M+Na]^+$, $C_{22}H_{42}NaO_4$: 393.2975, found 393.2966; **GC analysis:** Rt = 7.5 min.



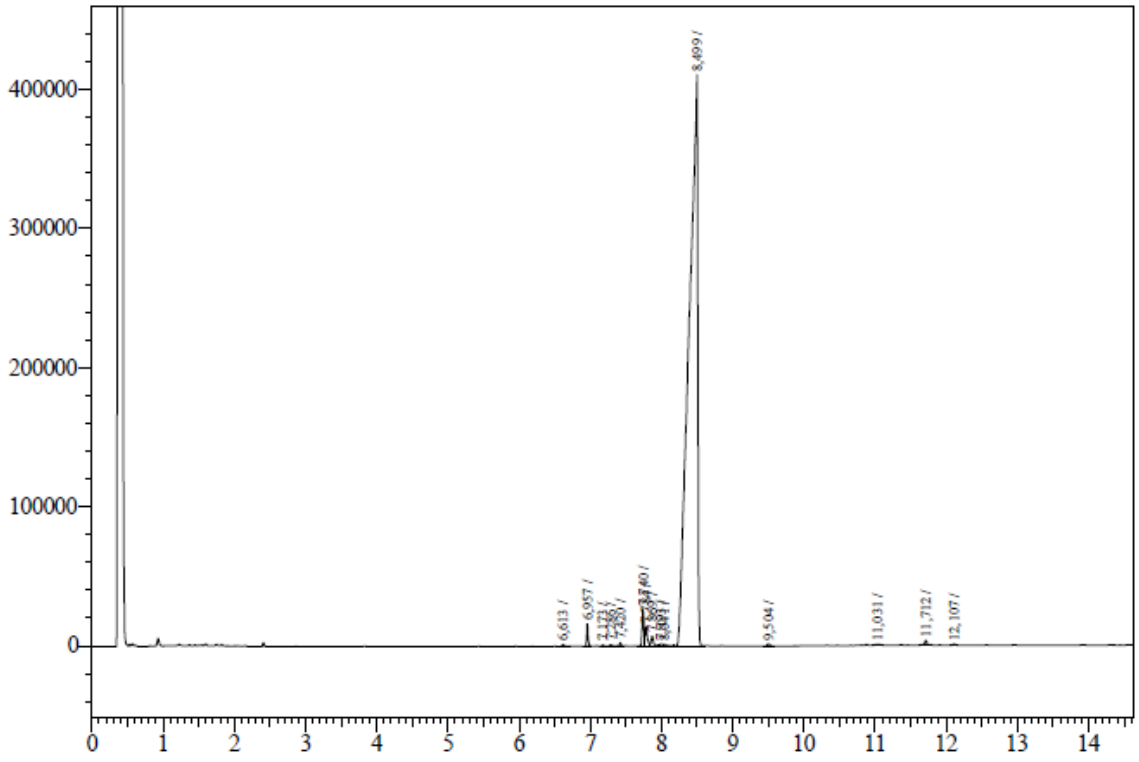


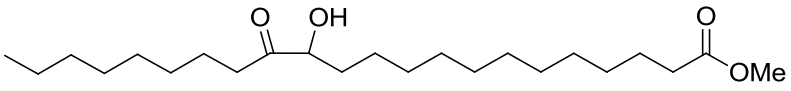
10-Hydroxyoctadecan-9-one [CAS 4444-91-1][10] (9). The title compound was obtained from octadecane-9,10-diol **5** (0.86 g, 3 mmol) following the general procedure C. The residue was purified by column chromatography (cyclohexane/EtOAc, 100:0 → 95:5) to give α-hydroxyketone **9** (0.64 g, 74%) as a white solid (mp= 46-48°C). **IR (ν_{max})**: 3319-3231 (br, O-H), 2953, 2915, 2872, 2848, 1710 (C=O), 1462, 1405, 1374, 1335, 1254, 1127, 1091 (C-O), 1031, 908, 831, 701; **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.88 (t, *J* = 6.7, 6H, 2-CH_3), 1.20-1.37 (m, 20H, 10-CH_2), 1.42-1.80 (m, 6H, 3-CH_2), 2.36-2.51 (m, 2H, CH_2-C=O), 3.48 (d, *J* = 4.9, 1H, O-H), 4.16-4.19 (m, 1H, CH-OH); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_C = 14.16 (CH_3) 14.17 (CH_3), 22.73, 22.75, 23.7, 24.9, 29.2, 29.32, 29.33, 29.4, 29.5, 29.6 31.89, 31.94, 33.9, 37.9 (14-CH_2), 76.5 (CH), 212.6 (C=O); **MS (ESI$^+$)** m/z = 307.3 ([M+Na]$^+$, 100); **HRMS-ESI:** calculated for [M+Na]$^+$, $C_{18}H_{36}NaO_2$: 307.2608, found 307.2605 (0.9 ppm); **GC analysis**: Rt = 6.1 min.



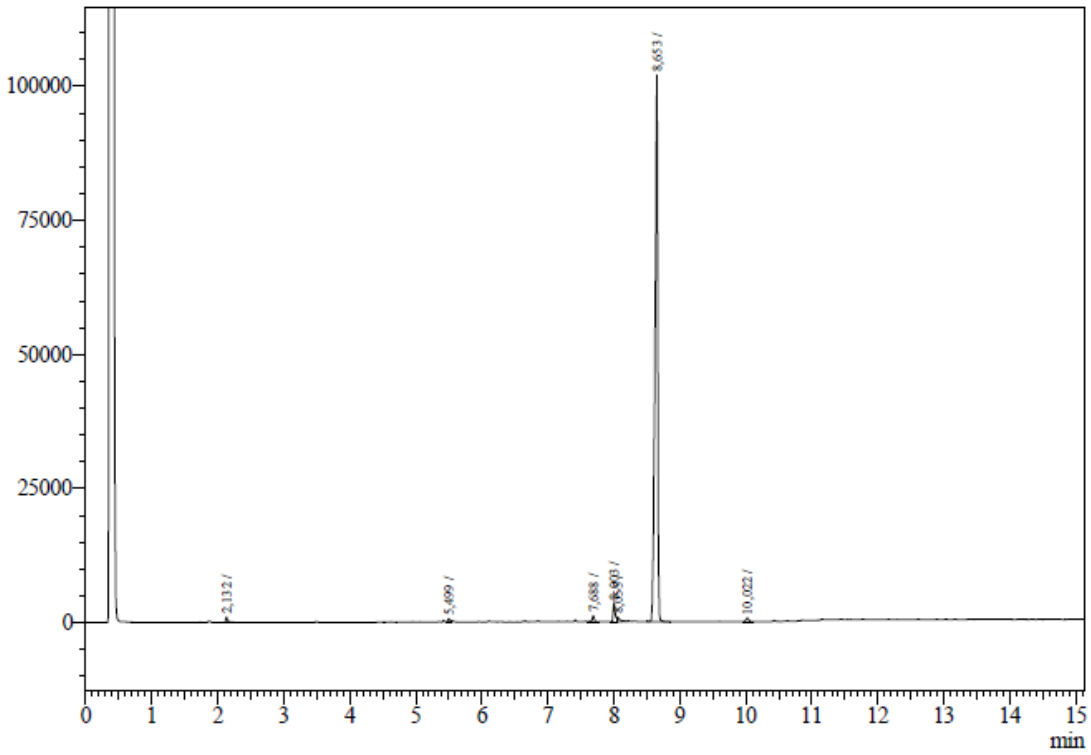


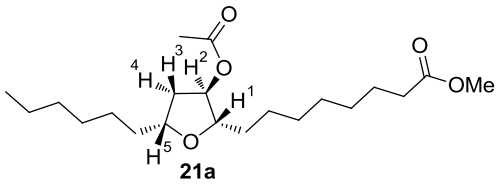
Dimethyl 9-hydroxy-10-oxooctadecanedioate [CAS 67136-05-4][24] (10). The title compound was obtained from dimethyl 9,10-dihydroxyoctadecanedioate **6** (1.20 g, 3 mmol) following the general procedure C. The residue was purified by column chromatography (cyclohexane/EtOAc, 100:0 → 95:5) to give α-hydroxyketone **10** (0.62 g, 57%) as a white solid (mp = 43-46°C). **IR (ν_{max})**: 3490-3349 (br, O-H), 2916, 2846, 1737 (C=O), 1708 (C=O), 1463, 1435, 1383, 1367, 1301, 1262, 1212, 1171, 1099, 1081, 1041, 977, 927, 882, 761, 721, 682; **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 1.20-1.43 (m, 14H), 1.43-1.81 (m, 8H, 4-CH_2), 2.24 (t, *J* = 7.5, 4H, 2x$\underline{CH_2}$-C=O ester), 2.36-2.48 (m, 2H, $\underline{CH_2}$-C=O ketone), 3.35 (br s ,1H, O-H), 3.60 (s, 6H, 2x$\underline{CH_3}$O), 4.07-4.10 (m, 1H, $\underline{CH}$-OH); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_C = 23.5, 24.81, 24.83, 24.87, 28.89, 28.98 (6-CH_2), 29.0 (2xCH_2), 29.1, 29.2, 33.7, 34.00, 34.03, 37.77 (6-CH_2), 51.4 (2xCH_3O), 76.4 (CH-OH), 174.20, 174.24 (2-C=O ester), 212.5 (C=O ketone); **MS (ESI$^+$):** m/z = 373.3 ([M+H]$^+$, 100), 395.3 ([M+Na]$^+$, 71); **HRMS-ESI:** calculated for [M+Na]$^+$, $C_{20}H_{36}NaO_6$: 395.2404, found 395.2394 (2.5 ppm); **GC analysis:** Rt= 8.5 min.

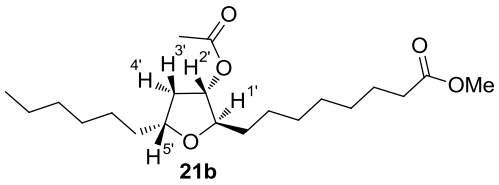




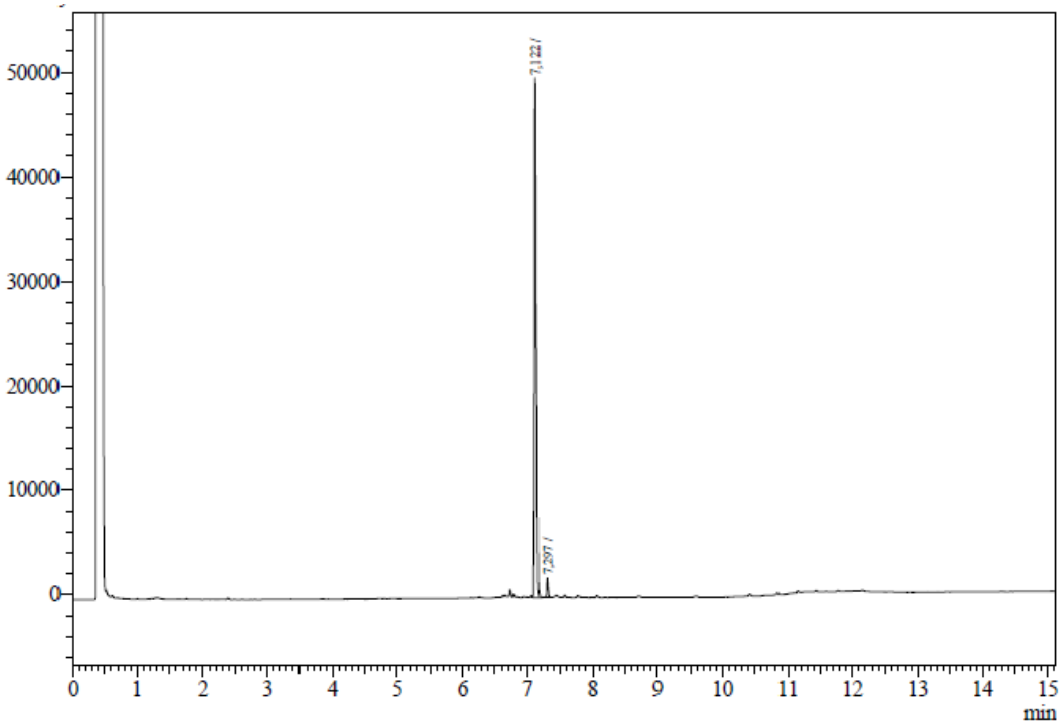
Methyl 13(14)-hydroxy-14(13)-oxodocosanoate [CAS 113057-94-6 and 113058-47-2][25] (11). The title compound was obtained from methyl 13,14-dihydroxydocosanoate **7** (1.20 g, 3 mmol) following the general procedure C. The residue was purified by column chromatography (cyclohexane/EtOAc, 100:0 → 95:5) to give α-hydroxyketone **11** (1:1 mixture of regioisomers, 0.54 g, 46%) as a white solid (mp= 50-52°C); **IR (ν_{max})**: 2914, 2848 (C-H stretching), 2160, 1977, 1735 (C=O ester), 1710 (C=O ketone), 1228, 1091, 1027, 995, 885, 773, 661, 571; **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.83 (t, *J* = 6.7, 3H, CH_3), 1.18-1.31 (m, 26H, 13-CH_2), 1.35-1.80 (m, 6H, 3-CH_2), 2.24 (t, *J* = 7.5, 2H, $\underline{CH_2}$-C=O ester), 2.32-2.49 (m, 2H, $\underline{CH_2}$-C=O ketone), 3.36 (br s, 1H, O-H), 3.61 (s, 3H, CH_3O), 4.10-4.14 (m, 1H, $\underline{CH}$-OH); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_C = 14.1 (CH_3), 22.7, 23.7, 24.9, 24.98, 29.14, 29.17 (6-CH_2), 29.3 (2xCH_2), 29.35, 29.42, 29.45, 29.46, 29.50, 29.54 (6-CH_2), 31.83 and 31.88 (CH_2), 33.8, 34.1, 37.9 (3-CH_2), 51.4 (CH_3O), 76.4 ($\underline{CH}$-OH), 174.3 (C=O ester), 212.6 (C=O ketone); **HRMS-ESI:** calculated for $[M+H]^+$, $C_{23}H_{45}O_4$: 385.3301, found 385.3312; **GC analysis**: Rt= 8.7 min.

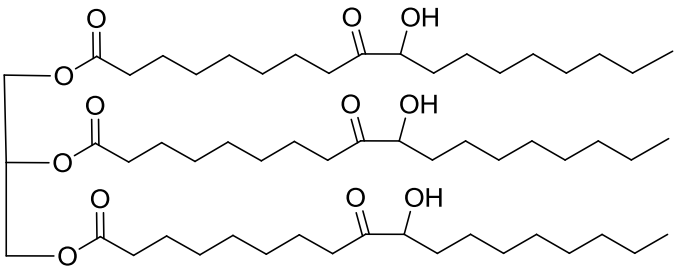






Methyl 8-(3-acetoxy-5-hexyltetrahydrofuran-2-yl)octanoate (21a and 21b). The title compounds were obtained from methyl (12R)-acetoxy-9,10-dihydroxyoctadecanoate **15** (1.25 g, 3 mmol) following the general procedure C. The residue was purified by column chromatography (cyclohexane/EtOAc, 100:0 → 97:3) to give tetrahydrofurans **21a** and **21b** (mixture of two inseparable diastereoisomers, dr=2:1 according to ^{13}C-NMR, 0.68 g, 60%) as a colourless liquid. **IR** (υ_{max}): 2922, 2855 (C-H stretching), 1737 (C=O), 1435, 1365, 1238, 1197, 1171, 1104, 1022, 705; **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.84 (t, *J* = 6.6, 3H, CH_3), 1.24-1.62 (m, 23H, 11-CH_2 + $H^{4'}$), 1.68 (ddd, *J* = 10.9, 8.9, 5.1, 1H, H^4), 1.90 (ddd, *J* = 13.6, 5.2, 1.5, 1H, H^3), 2.011, 2.013 (s, 3H, $\underline{CH_3}$-C=O), 2.26 (t, *J* = 7.5, 2H, $\underline{CH_2}$-C=O), 2.33-2.44 (m, 1H, $H^{3'}$), 3.62 (s, 3H, CH_3O), 3.75 (td, *J* = 6.4, 2.8, 1H, H^5), 3.86-3.99 (m, 2H, $H^{1,1'}$ and $H^{5'}$), 4.84-4.90 (m, 1H, $H^{2,2'}$); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_C for the <u>major</u> isomer = 14.2 (CH_3), 21.3 (CH_3), 22.7 (CH_2), 24.98 (CH_2), 25.6 (CH_2), 26.08 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.37 (CH_2), 29.45 (CH_2), 31.85 (CH_2), 34.4 (CH_2), 34.1 (CH_2), 35.6 (CH_2), 38.4 (CH_2), 51.5 (OCH_3), 78.5 (CH), 79.0 (CH), 83.9 (CH), 170.8 (C=O), 174.4 (C=O), δ_C for the <u>minor</u> isomer = 14.2 (CH_3), 21.3 (CH_3), 22.7 (CH_2), 24.98 (CH_2), 26.7 (CH_2), 26.14 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.38 (CH_2), 29.45 (CH_2), 31.88 (CH_2), 32.7 (CH_2), 34.1 (CH_2), 36.1 (CH_2), 37.6 (CH_2), 51.5 (OCH_3), 77.4 (CH), 78.8 (CH), 82.7 (CH), 170.9 (C=O), 174.4 (C=O) (COSY, HSQC, HMBC were also used for determination the structure of compounds); **MS (ESI$^+$):** 311.3 $[M\text{-}OAc]^+$, 371.3 $[M+H]^+$, 393.3 $[M+Na]^+$, 763.5 $[2M+Na]^+$; **HRMS-ESI:** calculated for $[M+Na]^+$, $C_{21}H_{38}NaO_5$: 393.2611, found 393.2611; **GC analysis:** Rt = 7.12, 7.14 min.

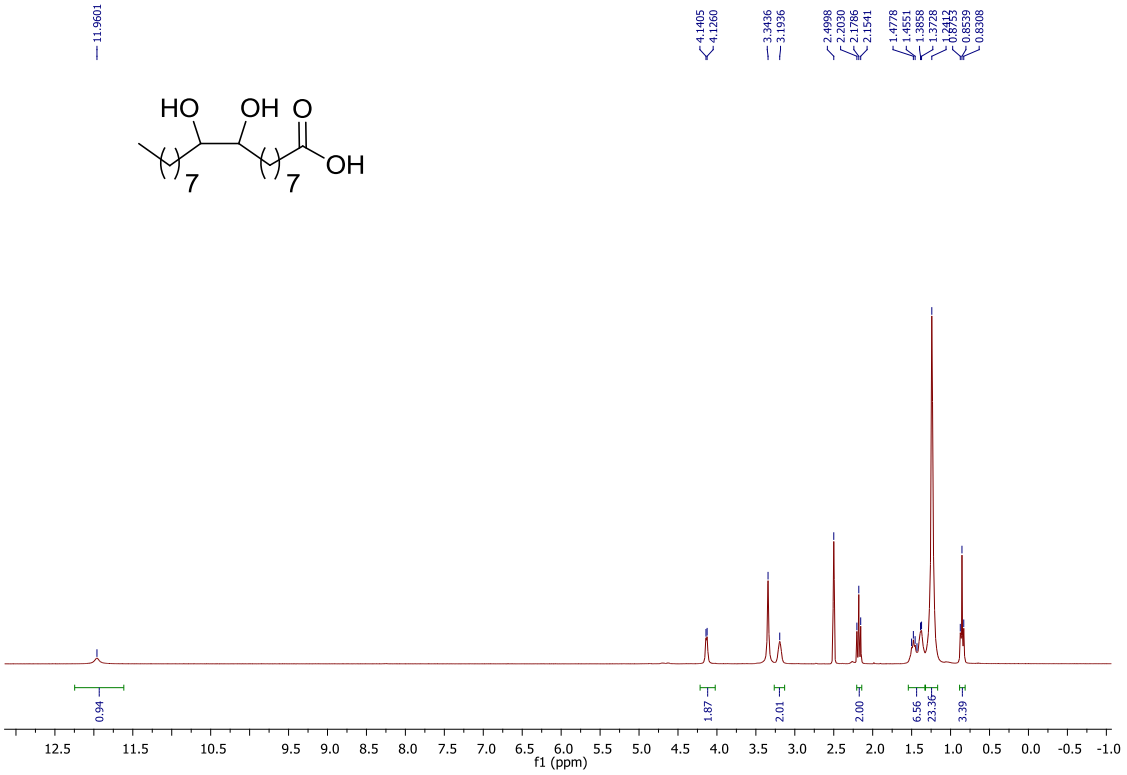




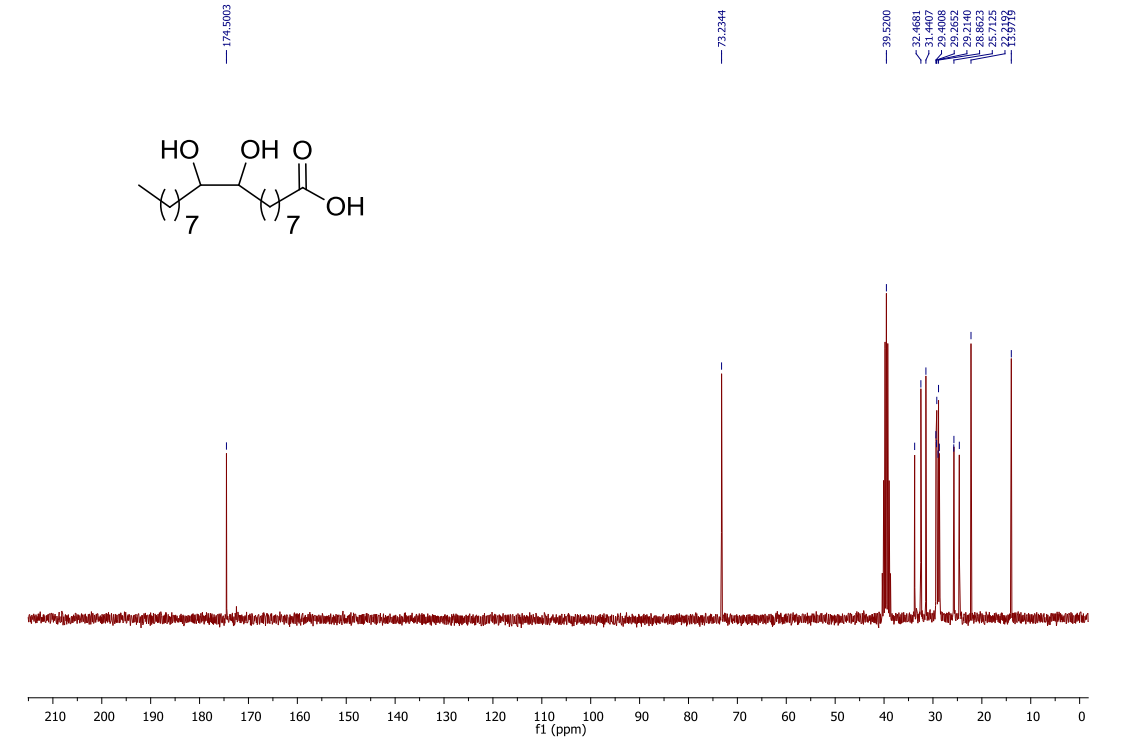
Tris(ketol) + tris(diol) high-oleic sunflower oil (22). The title compound was obtained from tris(diol) high-oleic sunflower oil **16** (1.00 g, 3 mmol of diol function) following the general procedure C (except the reaction time = 6 hours) and the residue was obtained as a viscous liquid. **IR (υ_{max})**: 3460 (br, O-H), 2919, 2851 (C-H stretching), 1740 (C=O), 1465, 1372, 1238, 1164, 1046, 722, 634, 607; **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 0.87 (t, *J* = 6.7, 9H, 3-CH_3), 1.25-1.33 (m, 60H, 30-CH_2), 1.42-1.88 (m, 18H, 9-CH_2), 2.31 (t, *J* = 7.5, 6H, 3x$\underline{CH_2}$-C=O), 2.35-2.53 (m, 6H, 3x$\underline{CH_2}$-C=O), 3.23-3.42 (m, 6H, $\underline{CH}$-OH in tris(diol)), 3.56 (br, O-H), 4.08-4.19 (m, 3H, 3x$\underline{CH}$-OH in hydroxyketone, about 40%), 4.14 (dd, *J* = 11.8, 6.0, 2H, OCH_2-glycerol), 4.29 (dd, *J* = 11.8, 4.0, 2H, OCH_2-glycerol), 5.26-5.28 (m, 1H, OCH-glycerol); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_C = 14.1 (CH_3), 22.6-42.7 (multi-signals CH_2), 62.0 (CH_2O), 68.8 (CH), 74.3, 74.4 (CH-OH in diol), 76.3, 76.4 (CH-OH in hydroxyketone), 172.7, 173.1 (C=O ester), 212.5 (C=O ketone).

7. ^{1}H and ^{13}C-NMR spectra

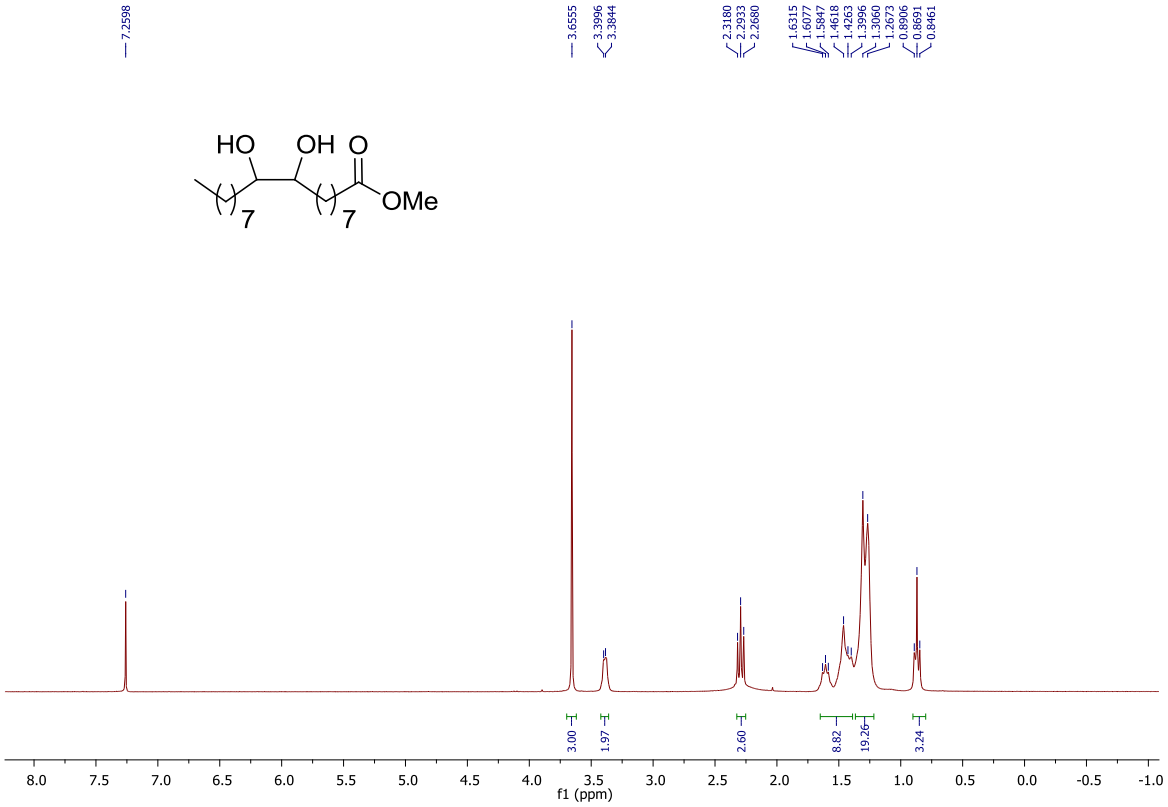
^{1}H-NMR (300 MHz, d_6-DMSO) *9,10-dihydroxyoctadecanoic acid (DHSA)*



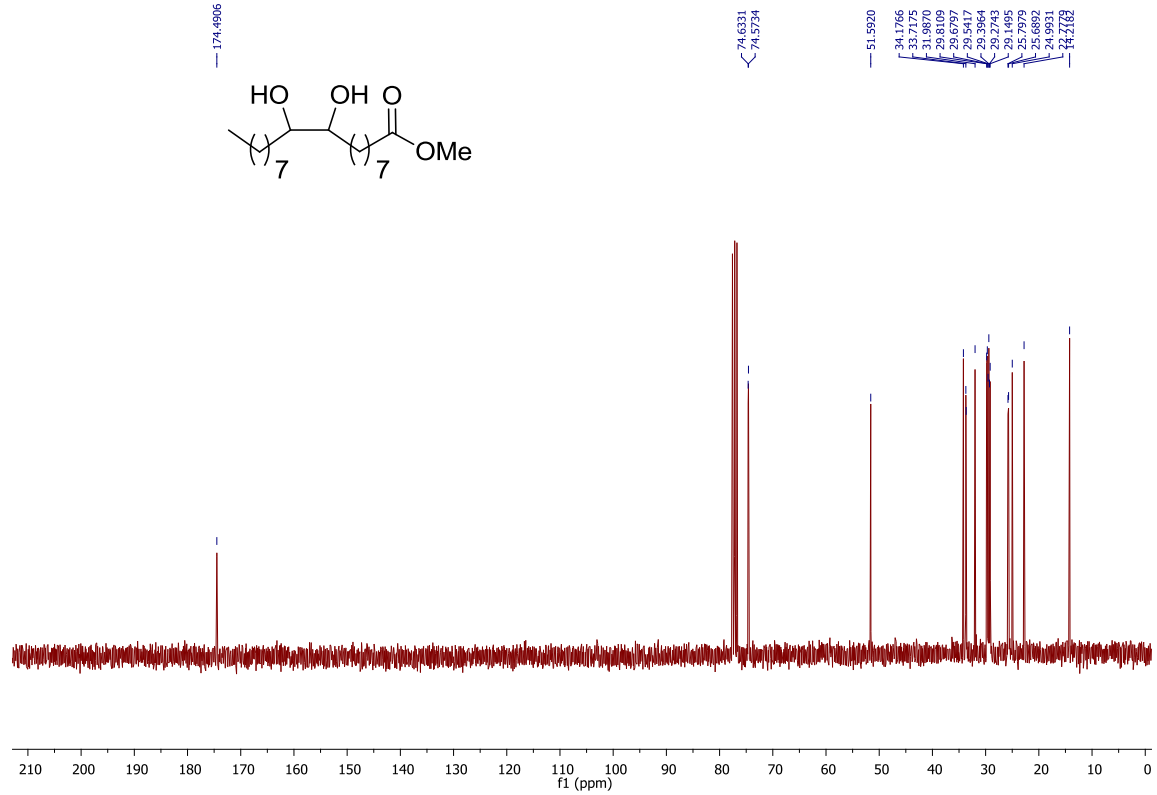
^{13}C-NMR (75 MHz, d_6-DMSO) *9,10-dihydroxyoctadecanoic acid (DHSA)*



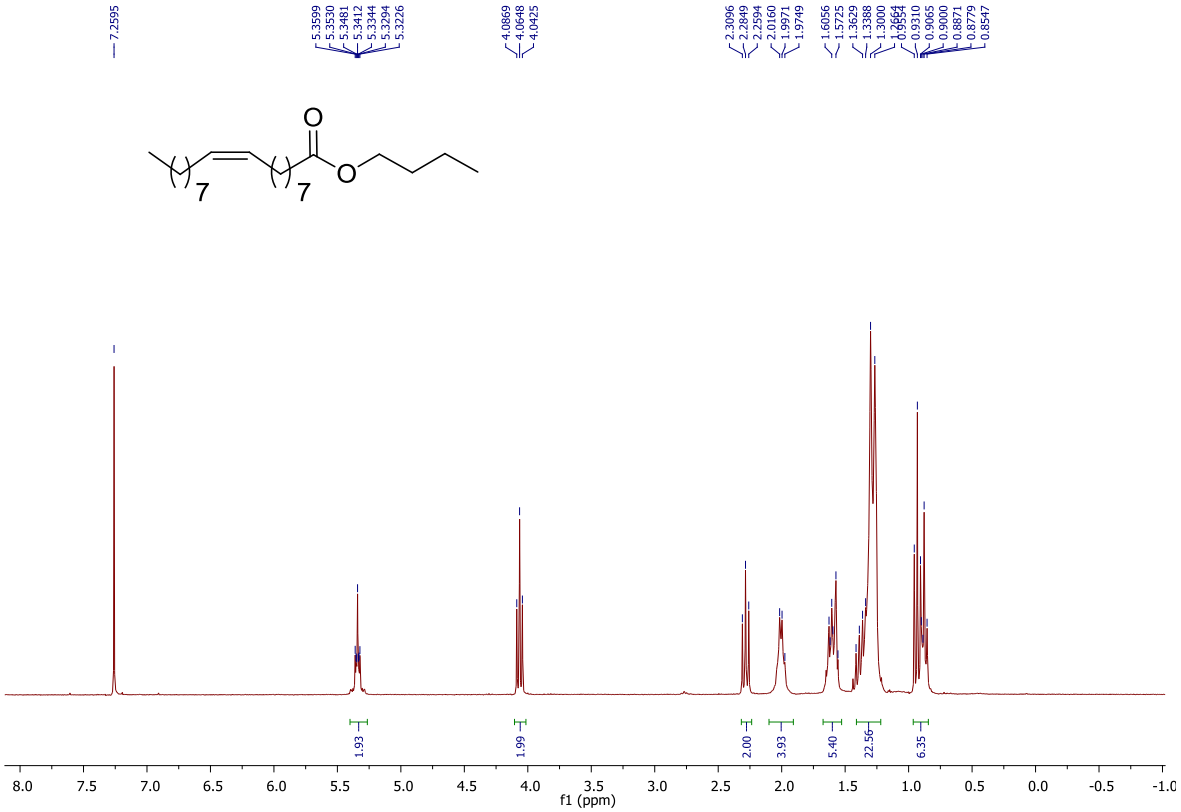
^{1}H-NMR (300 MHz, $CDCl_3$) *Methyl 9,10-dihydroxyoctadecanoate* (**1**)



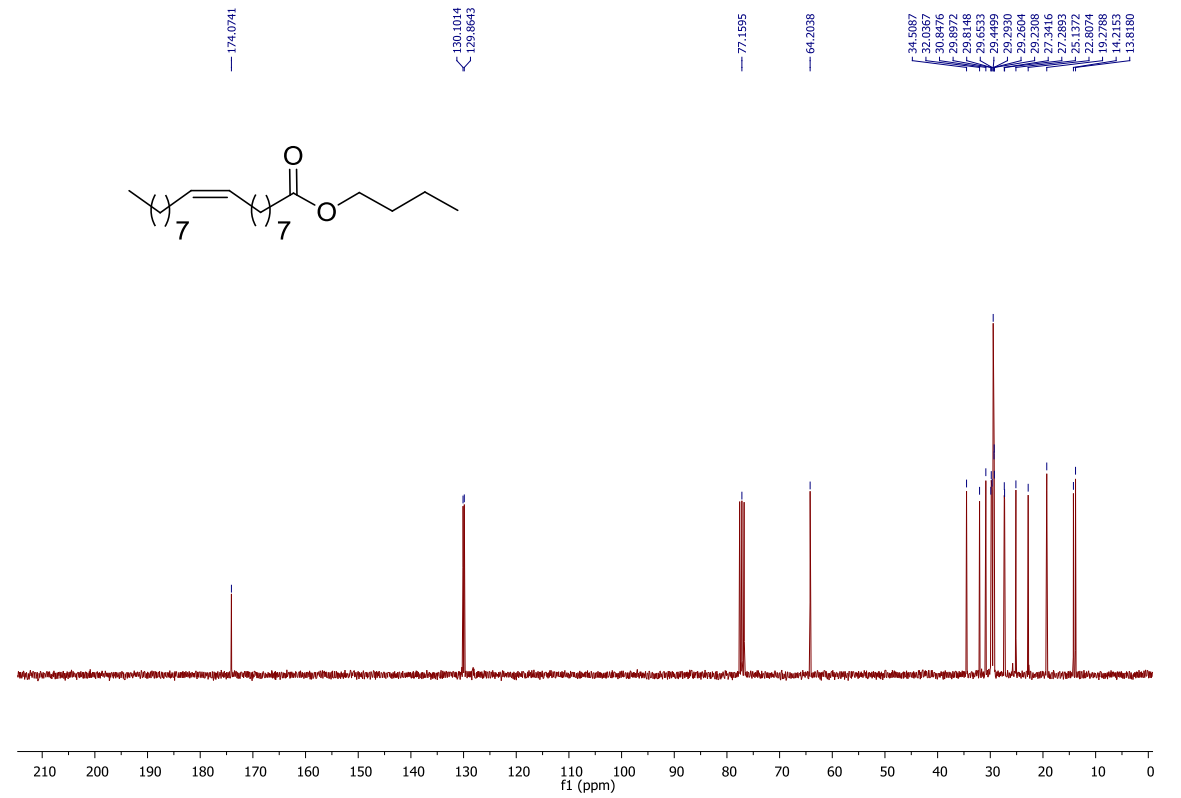
^{13}C-NMR (75 MHz, $CDCl_3$) *Methyl 9,10-dihydroxyoctadecanoate* (**1**)



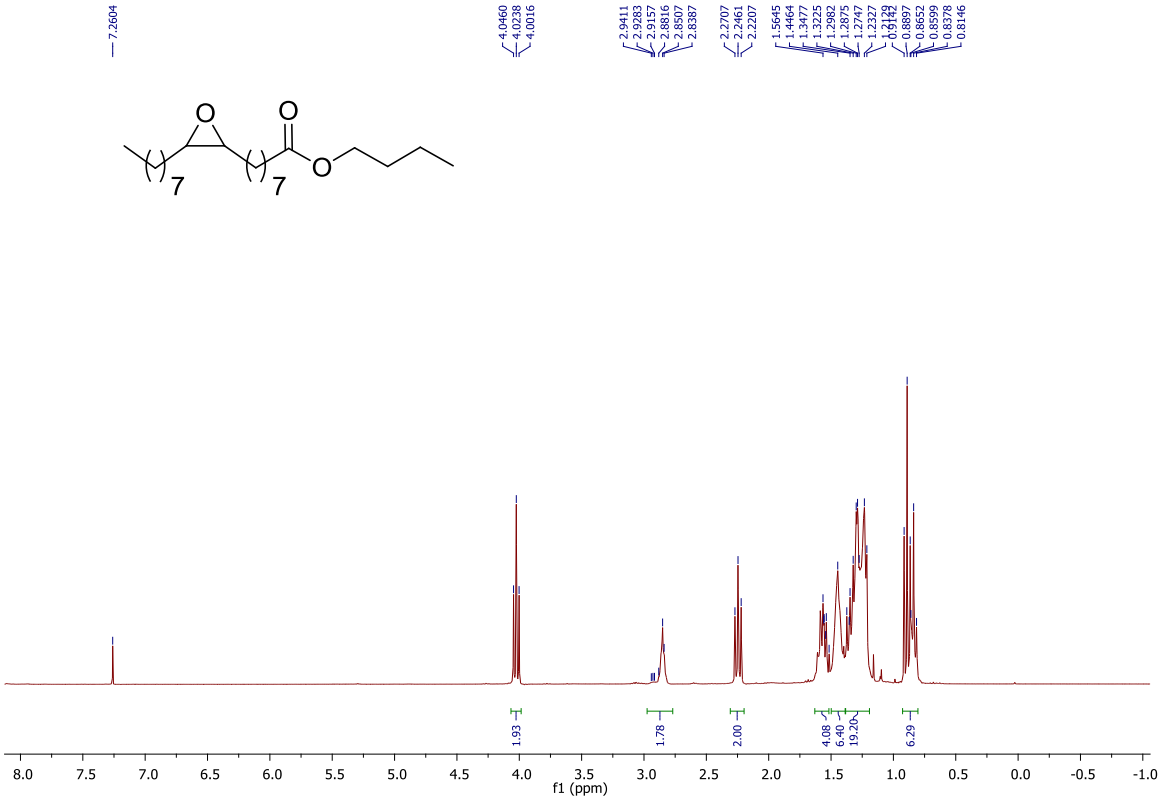
^{1}H-NMR (300 MHz, $CDCl_3$) *Butyl 9Z-octadecenoate*



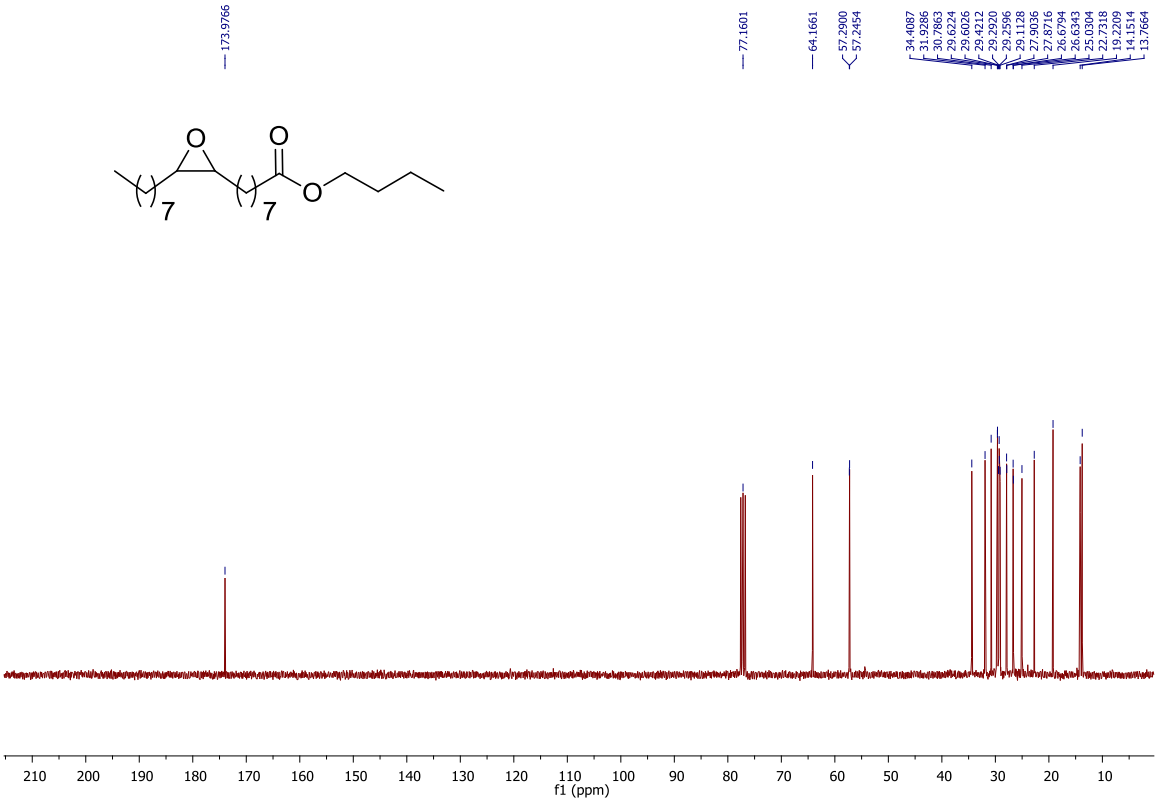
^{13}C-NMR (75 MHz, $CDCl_3$) *Butyl 9Z-octadecenoate*



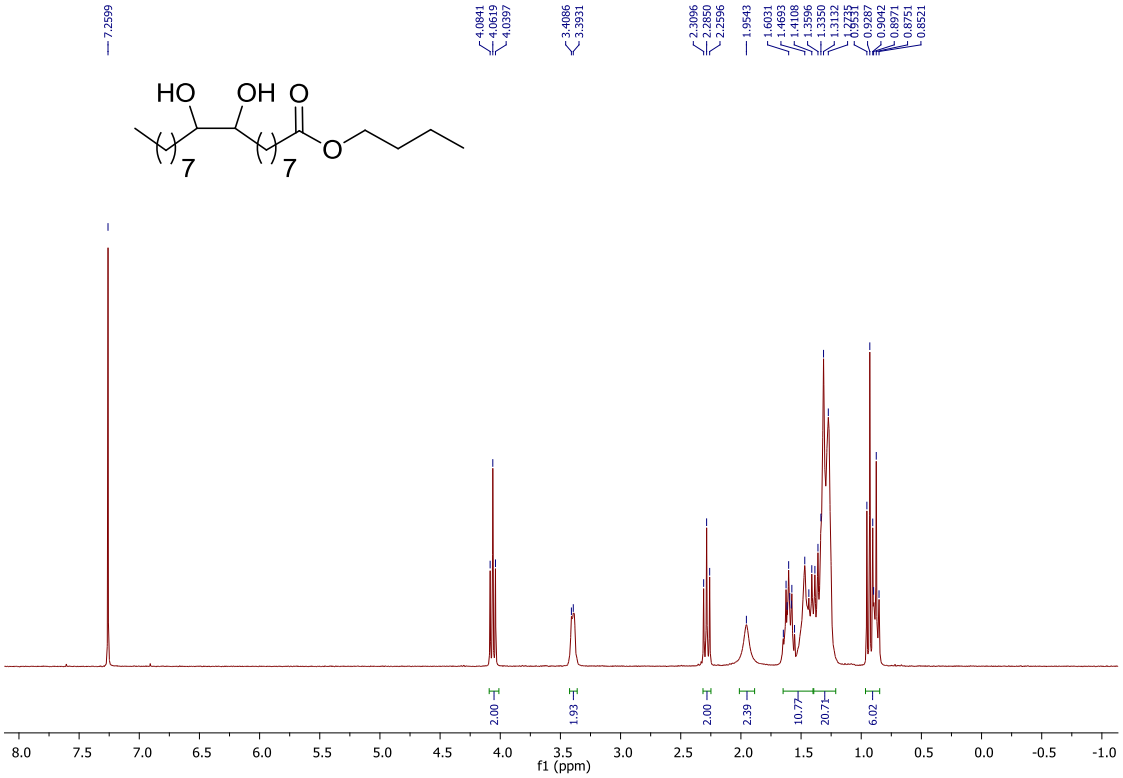
^{1}H-NMR (300 MHz, $CDCl_3$) *Butyl 8-(3-octyloxiran-2-yl)octanoate*



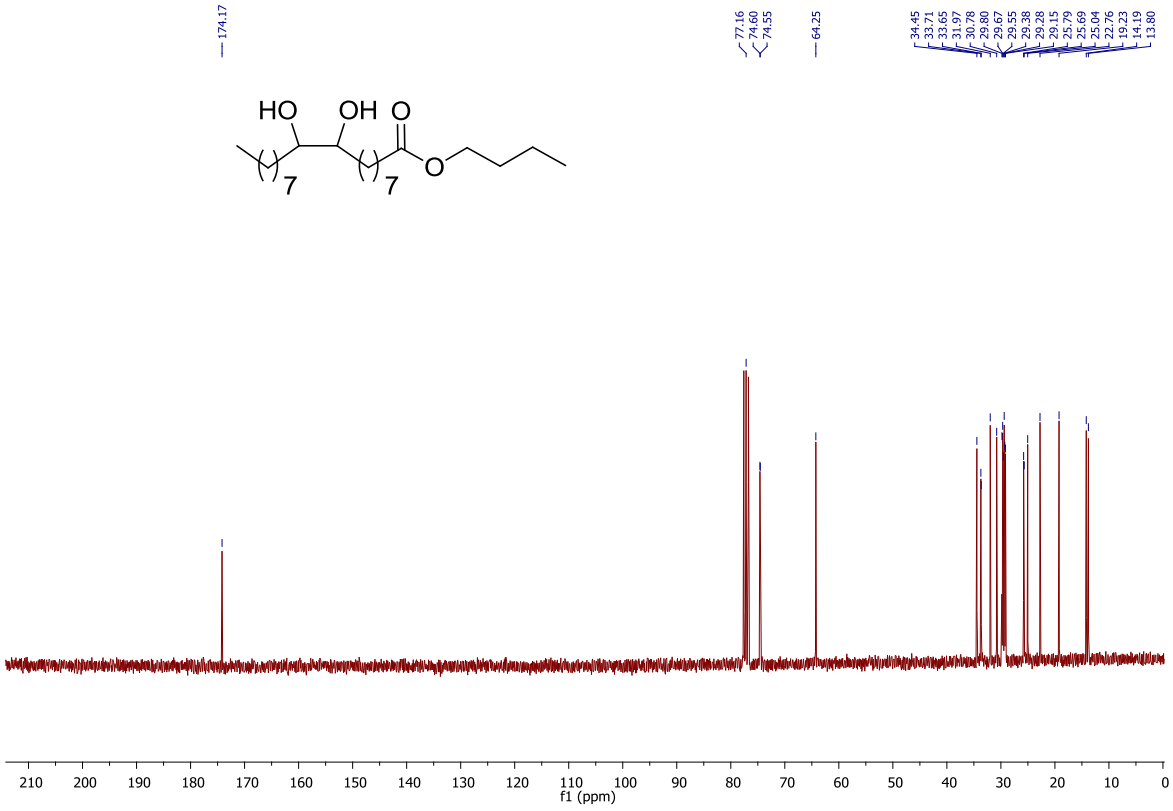
^{13}C-NMR (75 MHz, $CDCl_3$) *Butyl 8-(3-octyloxiran-2-yl)octanoate*



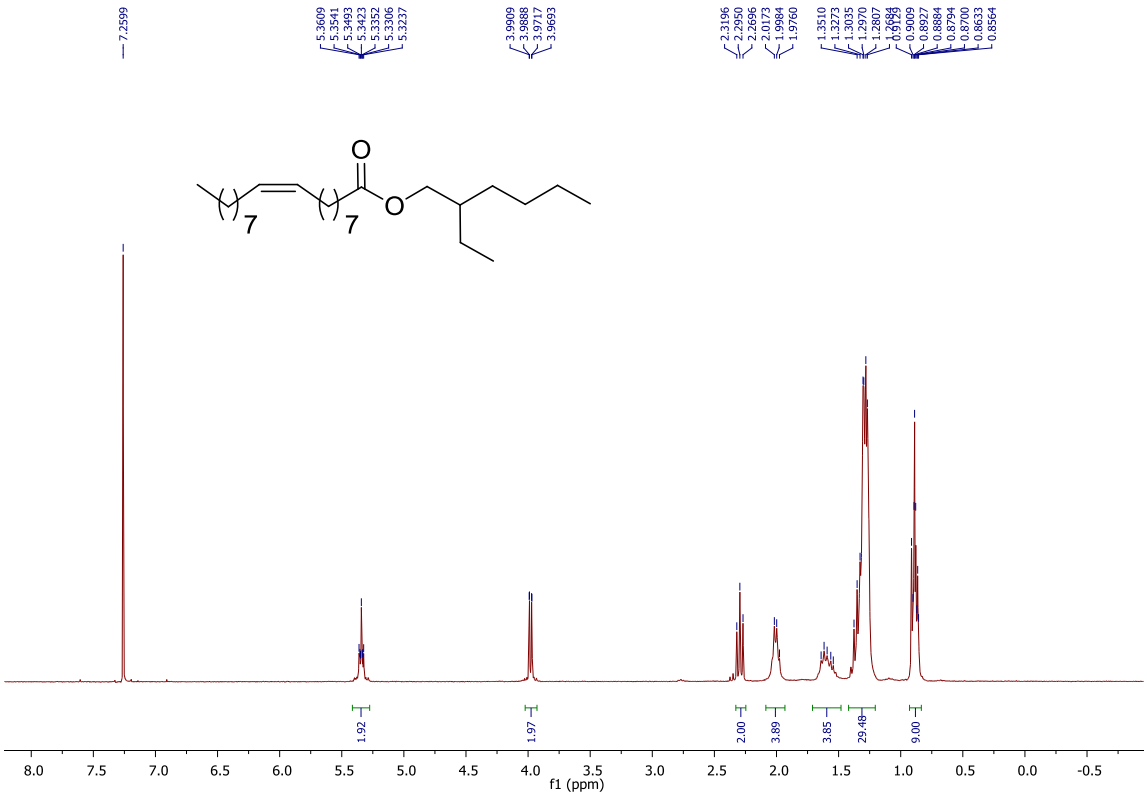
^{1}H-NMR (300 MHz, $CDCl_3$) *Butyl 9,10-dihydroxyoctadecanoate* (**13**)



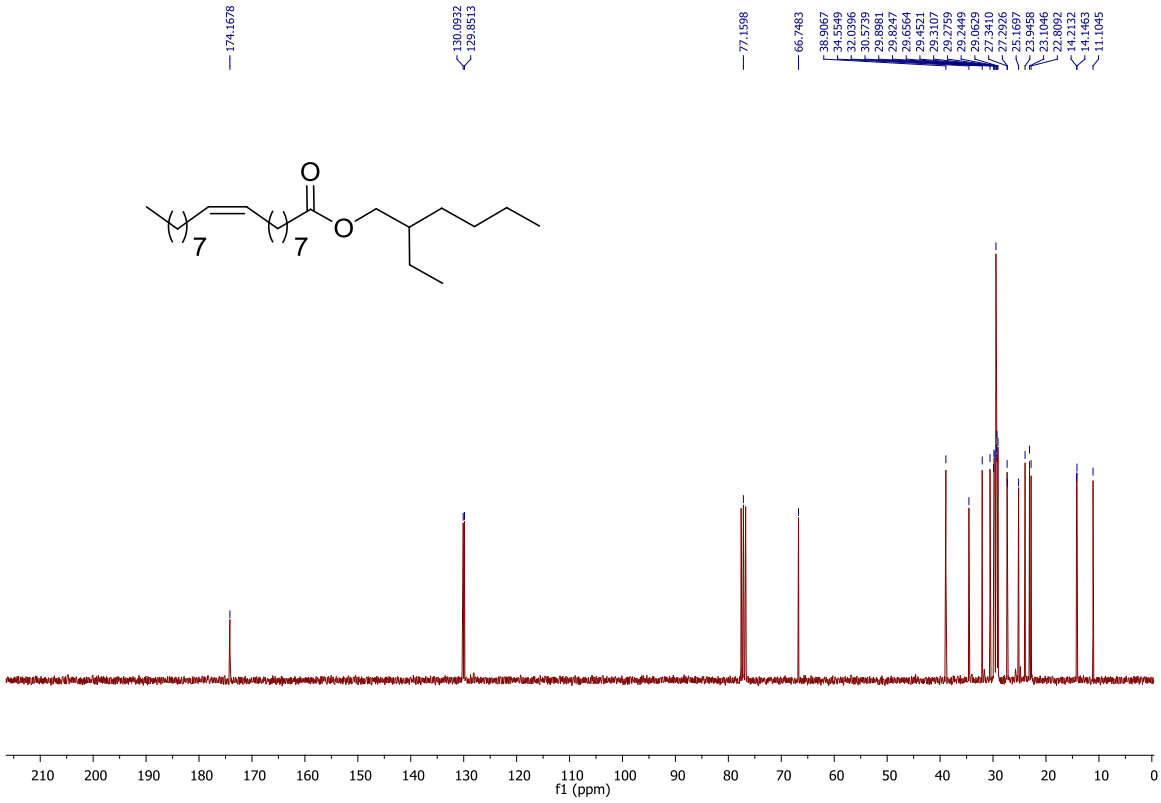
^{13}C-NMR (75 MHz, $CDCl_3$) *Butyl 9,10-dihydroxyoctadecanoate* (**13**)



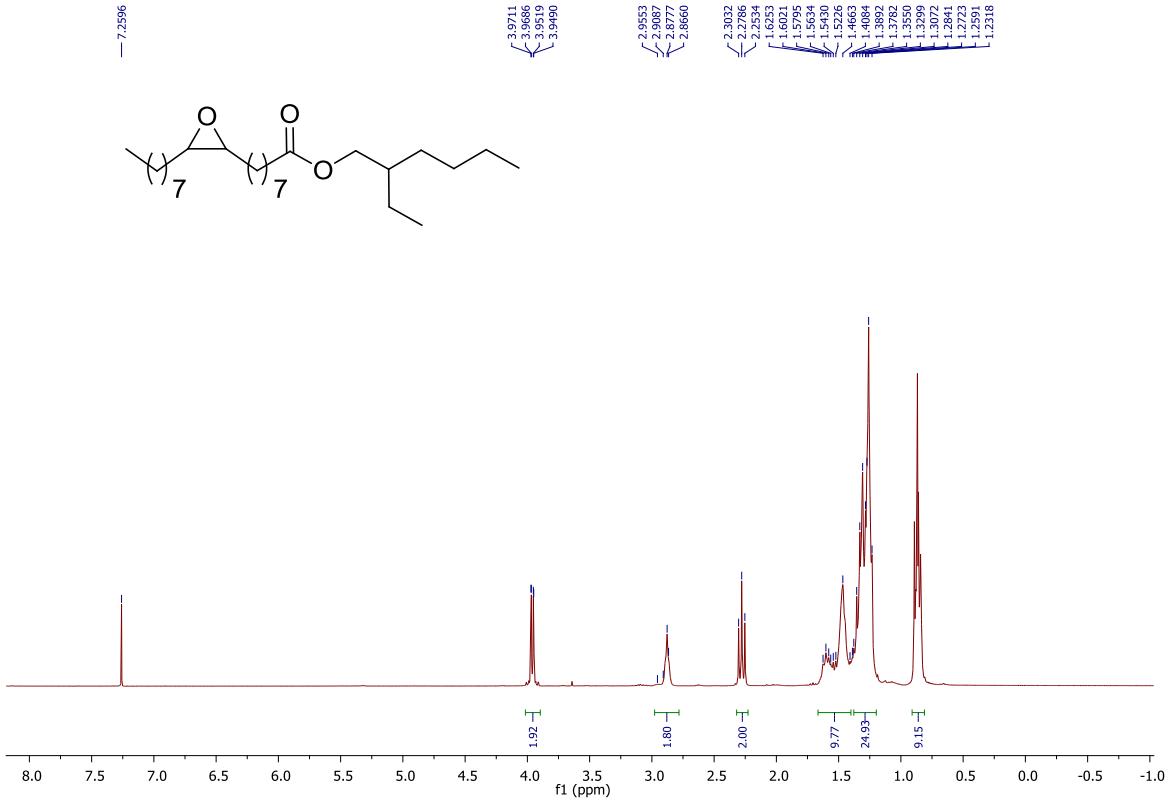
^{1}H-NMR (300 MHz, $CDCl_3$) *2-Ethylhexyl 9Z-Octadecenoate*



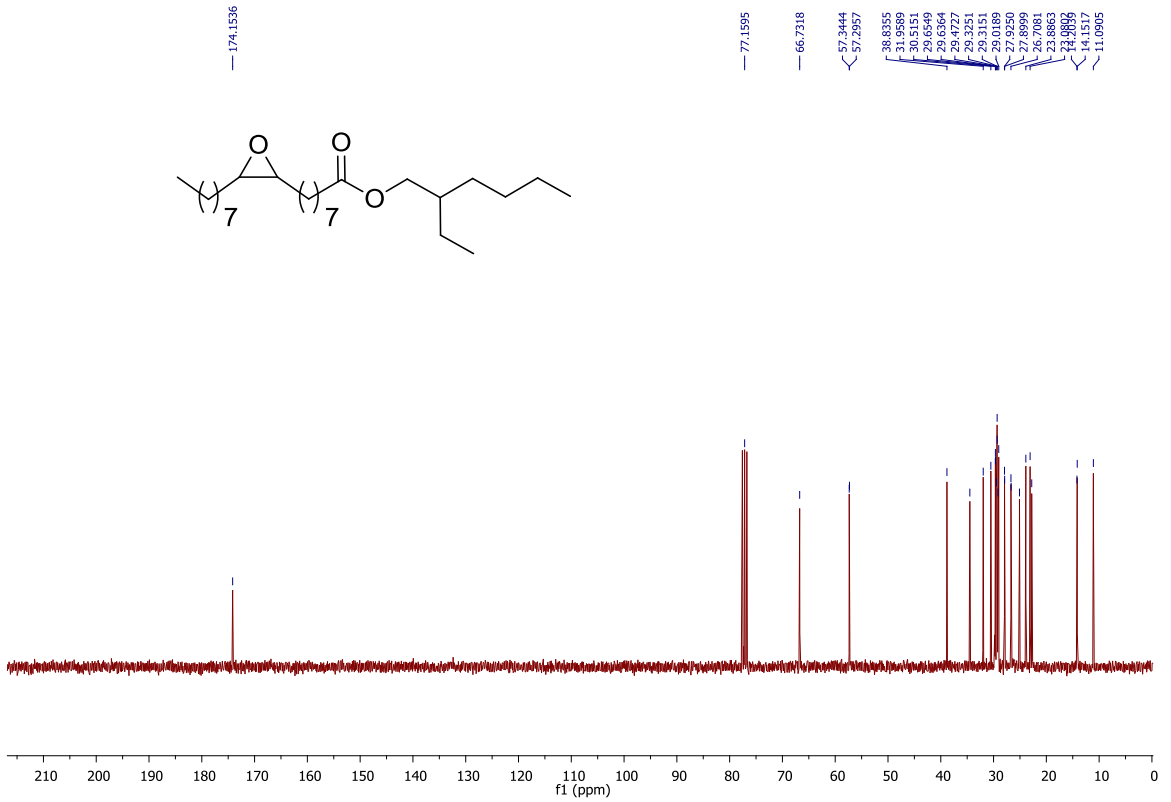
^{13}C-NMR (75 MHz, $CDCl_3$) *2-Ethylhexyl 9Z-Octadecenoate*



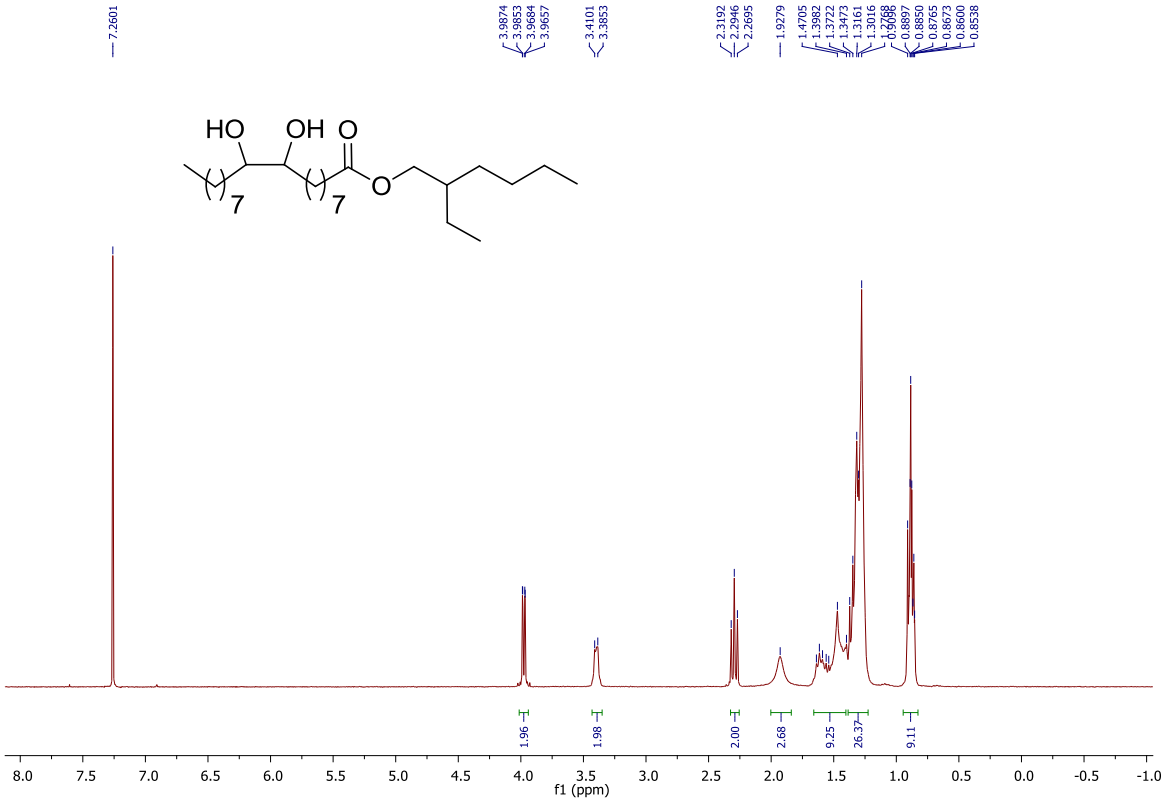
^{1}H-NMR (300 MHz, $CDCl_3$) *2-Ethylhexyl 8-(3-octyloxiran-2-yl)octanoate*



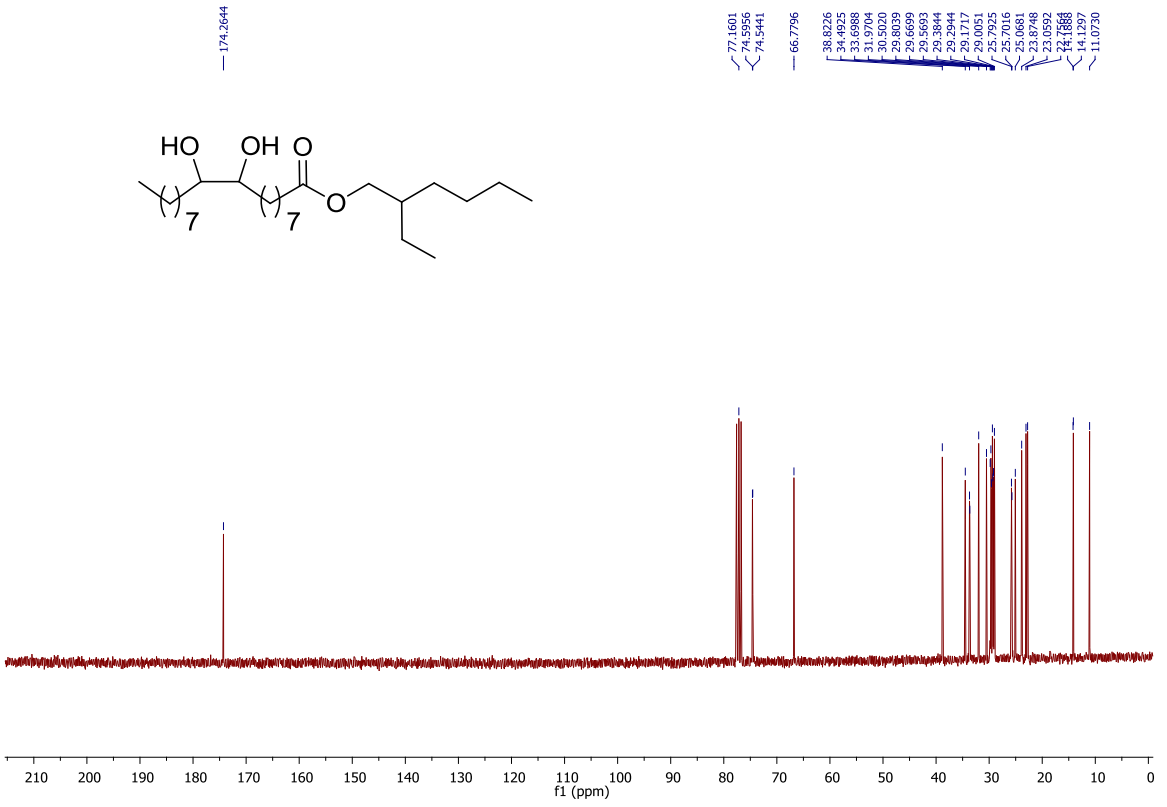
^{13}C-NMR (75 MHz, $CDCl_3$) *2-Ethylhexyl 8-(3-octyloxiran-2-yl)octanoate*



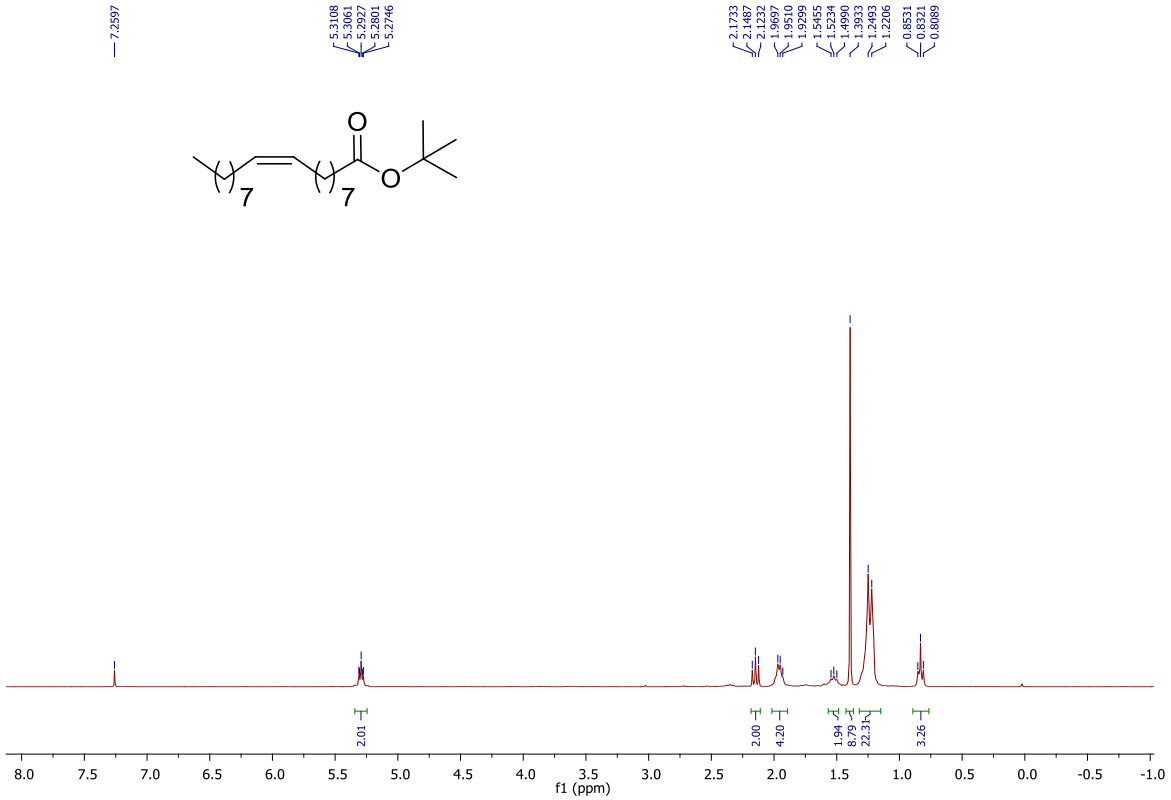
^{1}H-NMR (300 MHz, $CDCl_3$) *2-Ethylhexyl 9,10-dihydroxyoctadecanoate* (**14**)



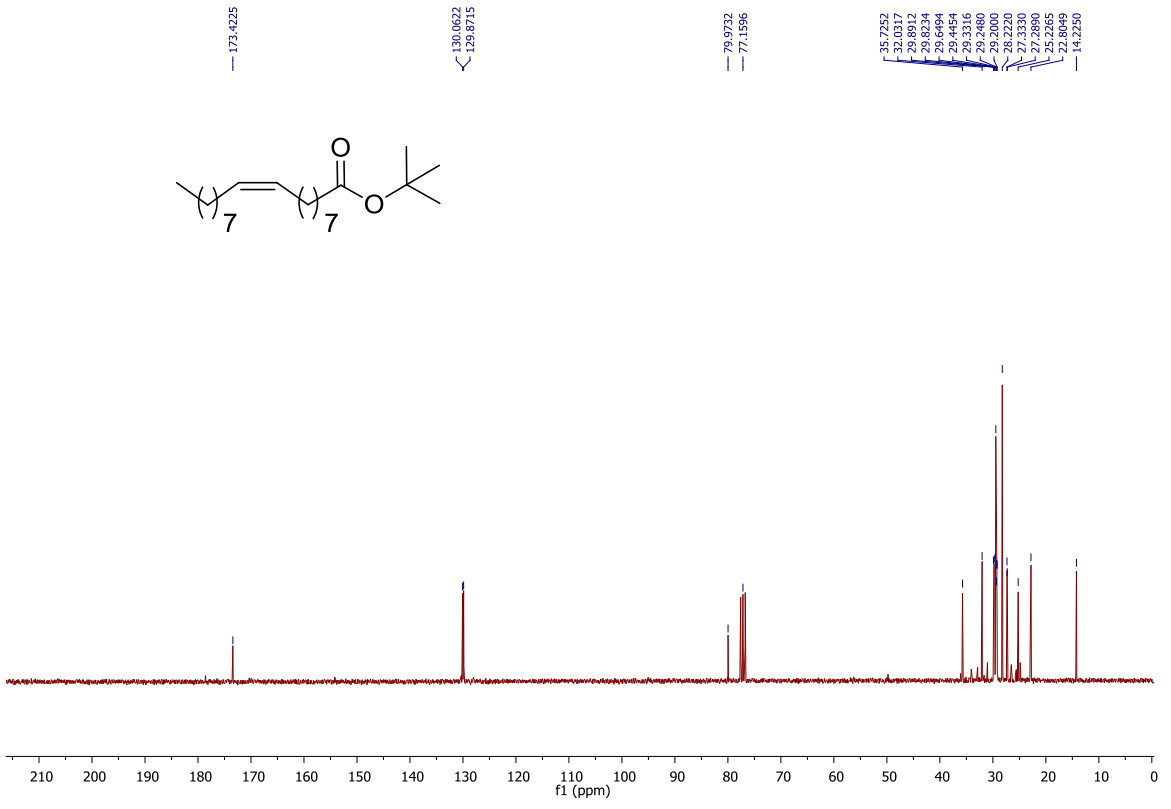
^{13}C-NMR (75 MHz, $CDCl_3$) *2-Ethylhexyl 9,10-dihydroxyoctadecanoate* (**14**)



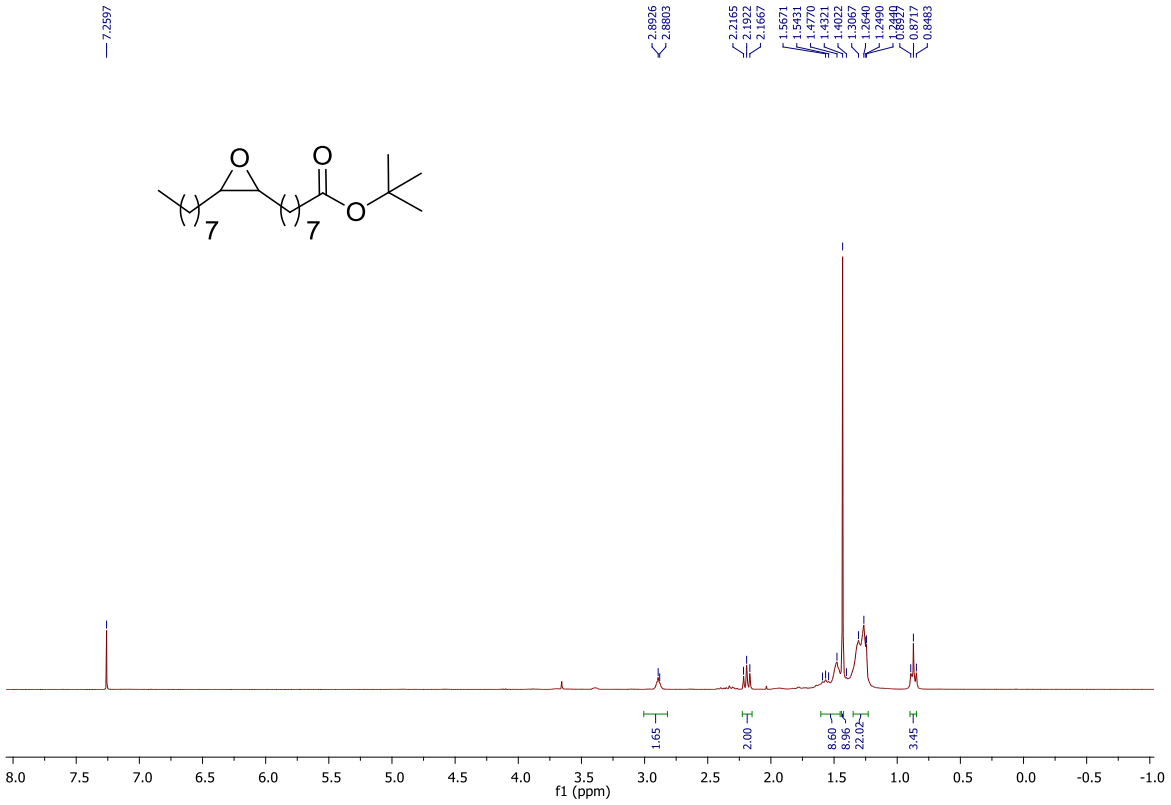
^{1}H-NMR (300 MHz, $CDCl_3$) *tert-Butyl octadecanoate*



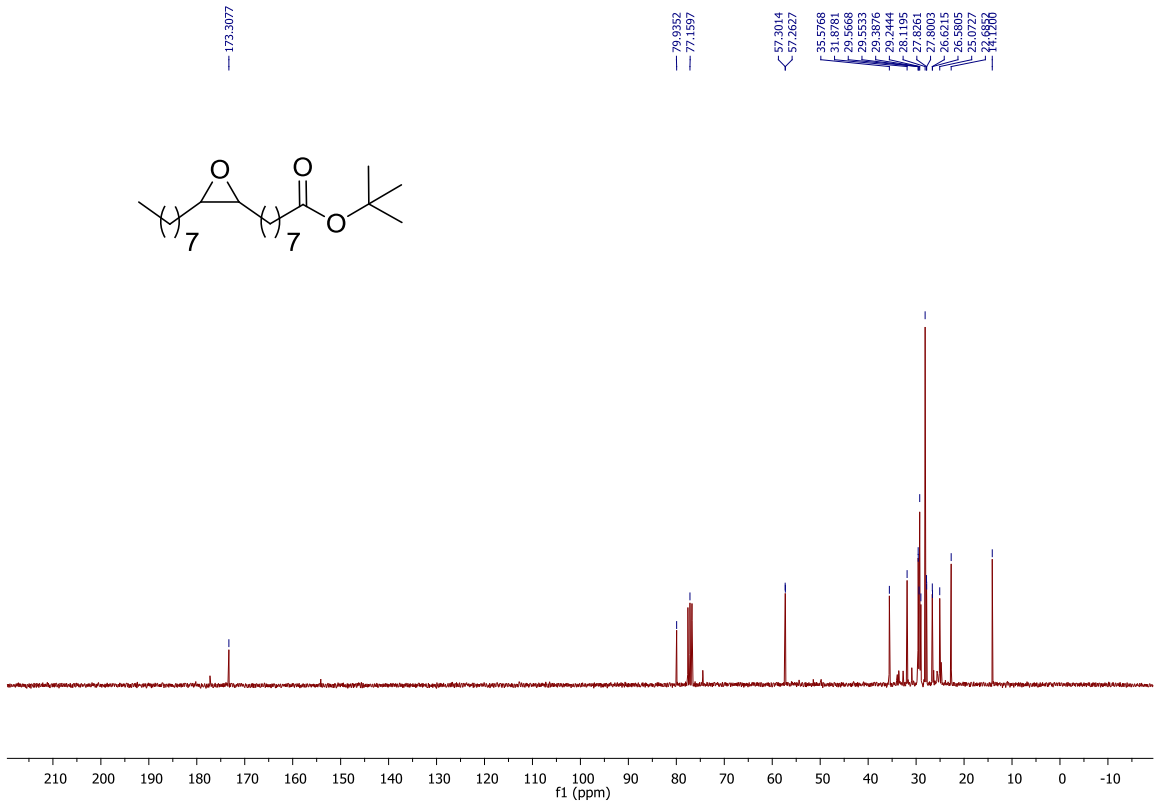
^{13}C-NMR (75 MHz, $CDCl_3$) *tert-Butyl octadecanoate*



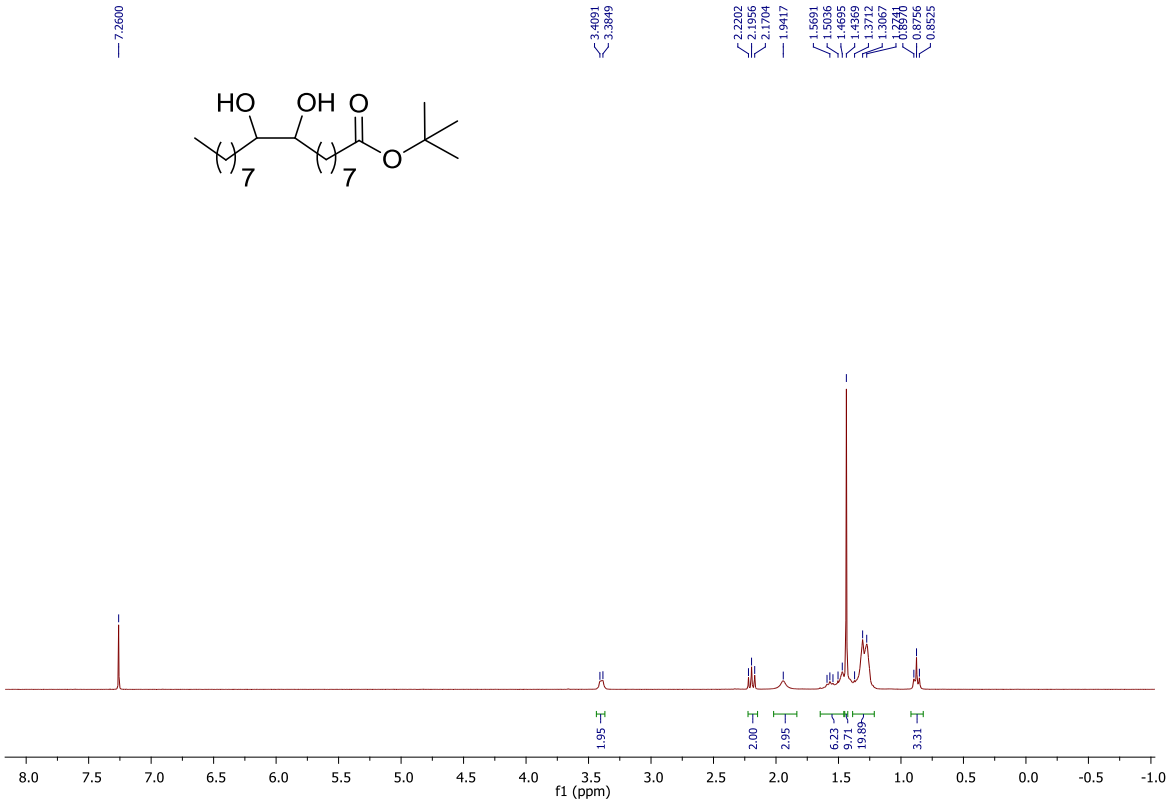
^{1}H-NMR (300 MHz, $CDCl_3$) *tert-Butyl 8-(3-octyloxiran-2-yl)octanoate*



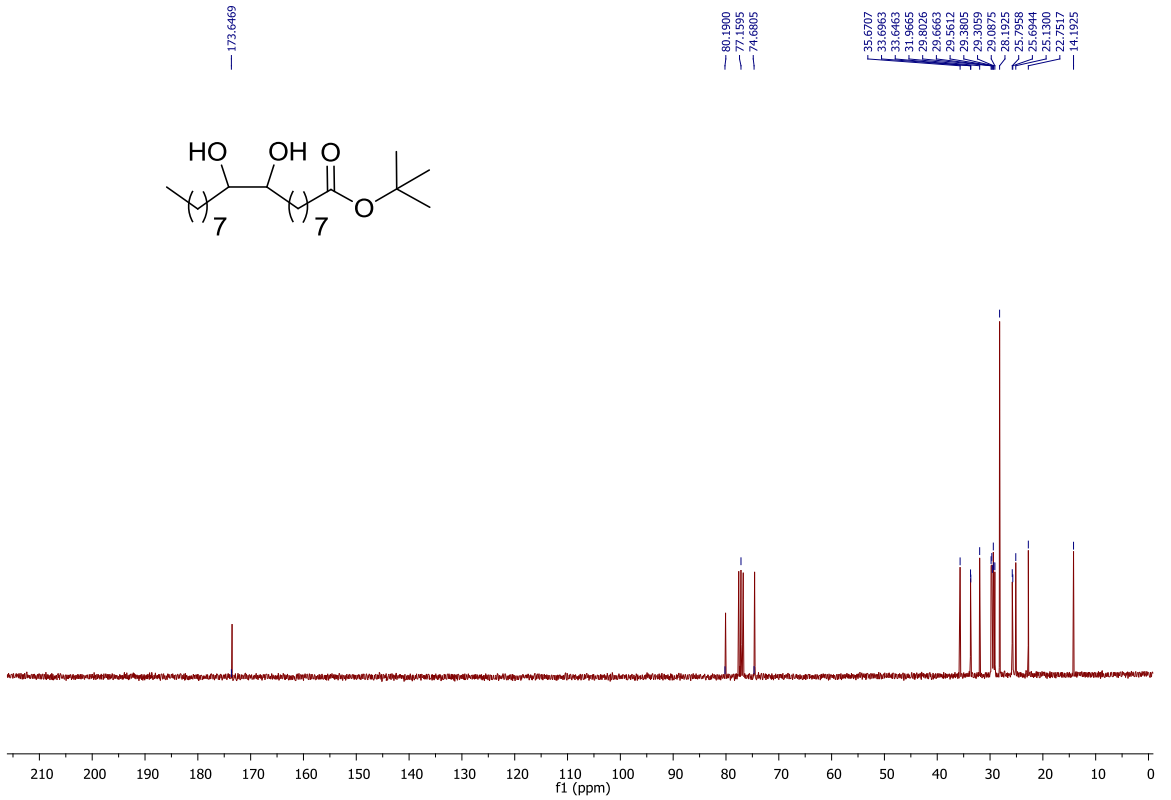
^{13}C-NMR (75 MHz, $CDCl_3$) *tert-Butyl 8-(3-octyloxiran-2-yl)octanoate*



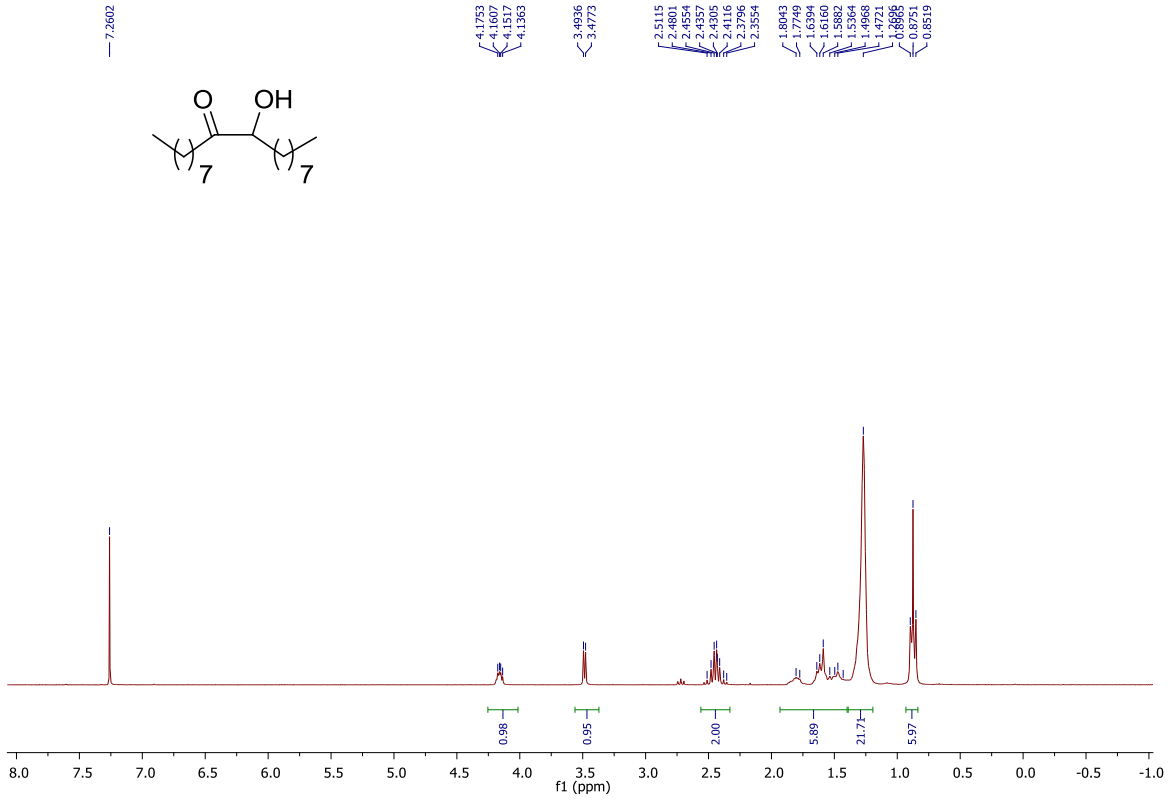
^{1}H-NMR (300 MHz, $CDCl_3$) *tert-Butyl 9,10-dihydroxyoctadecanoate* (**4**)



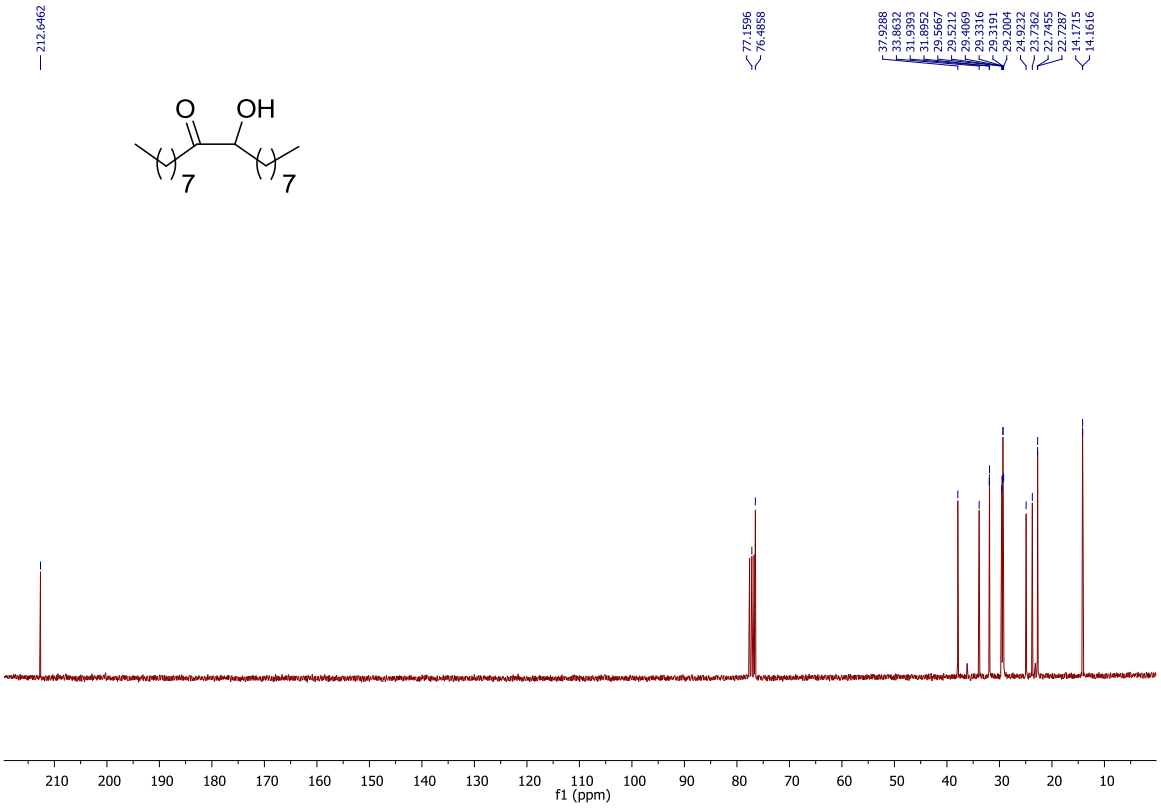
^{13}C-NMR (75 MHz, $CDCl_3$) *tert-Butyl 9,10-dihydroxyoctadecanoate* (**4**)



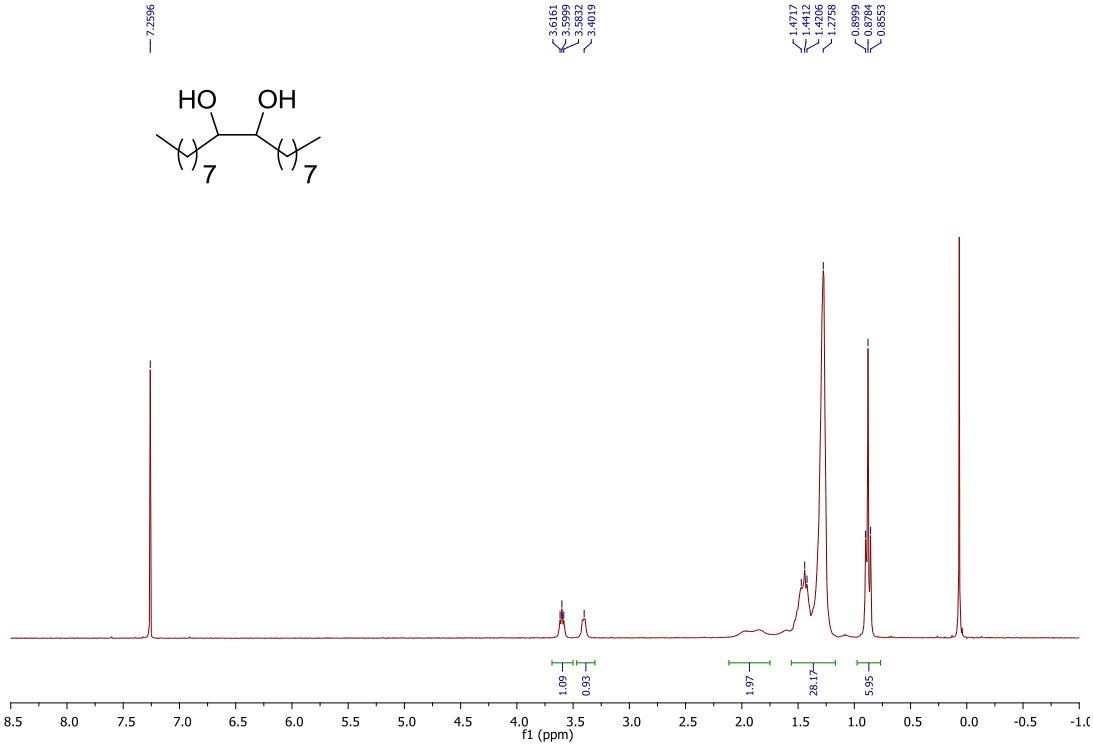
^{1}H-NMR (300 MHz, $CDCl_3$) *10-hydroxyoctadecan-9-one* (**9**)



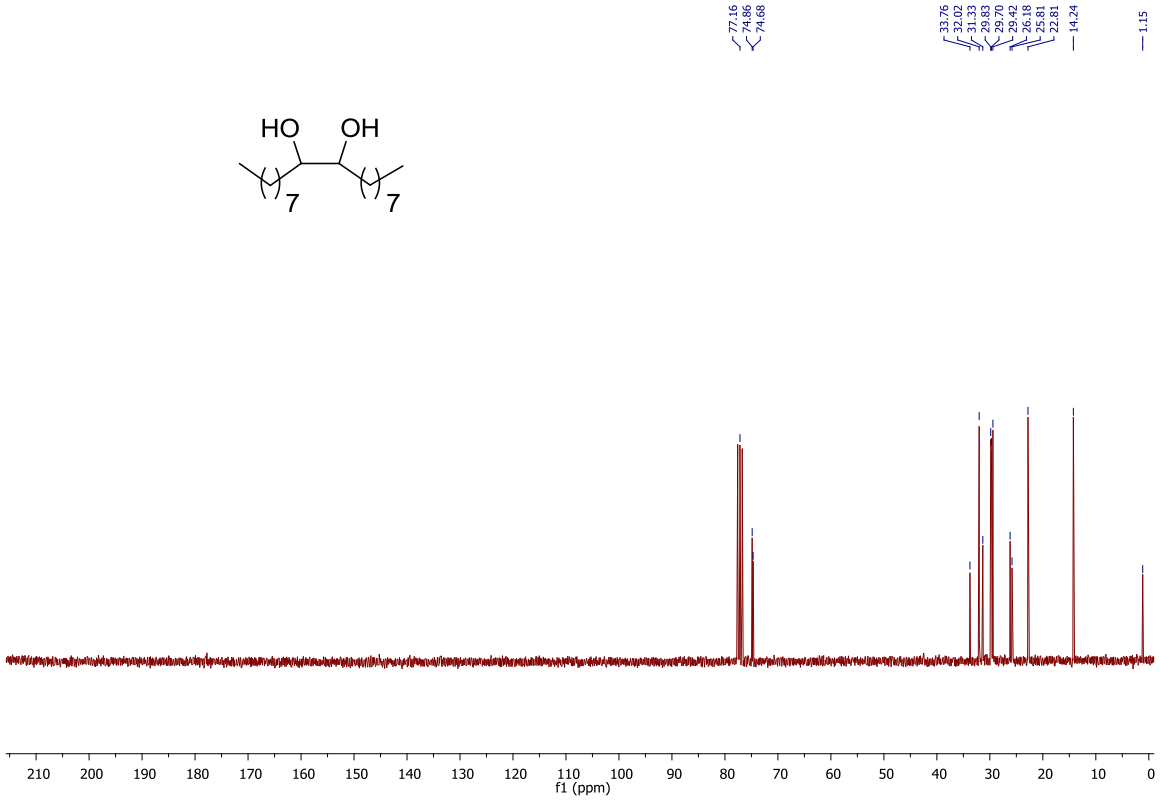
^{13}C-NMR (75 MHz, $CDCl_3$) *10-hydroxyoctadecan-9-one* (**9**)



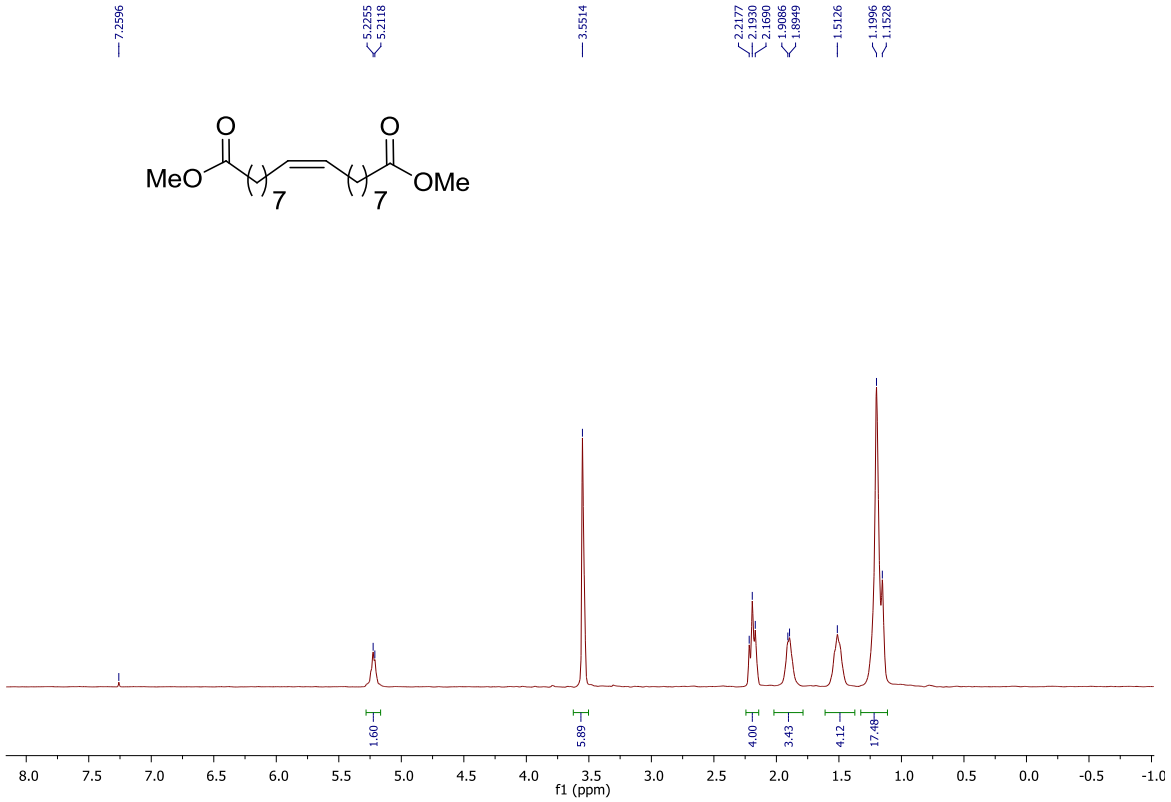
^{1}H-NMR (300 MHz, $CDCl_3$) *octadecane-9,10-diol* (**5**)



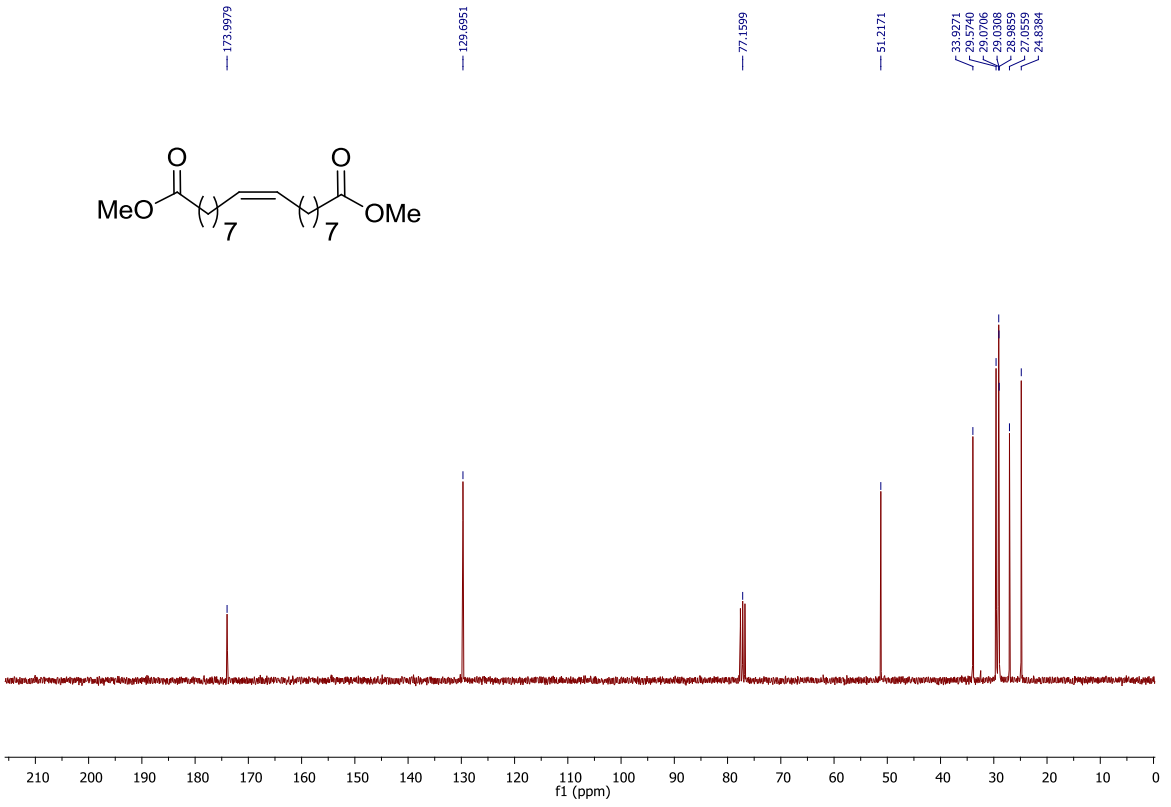
^{13}C-NMR (75 MHz, $CDCl_3$) *octadecane-9,10-diol* (**5**)



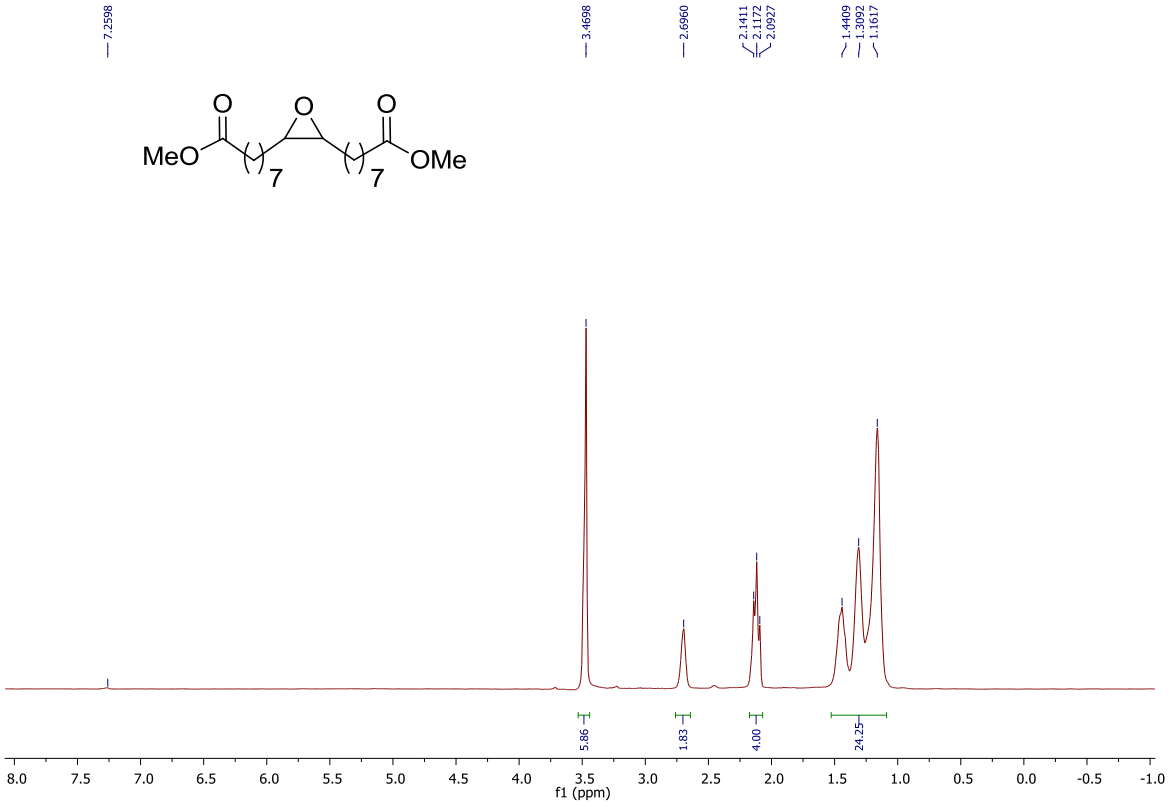
^{1}H-NMR (300 MHz, $CDCl_3$) *(Z)-Dimethyl octadec-9-enedioate*



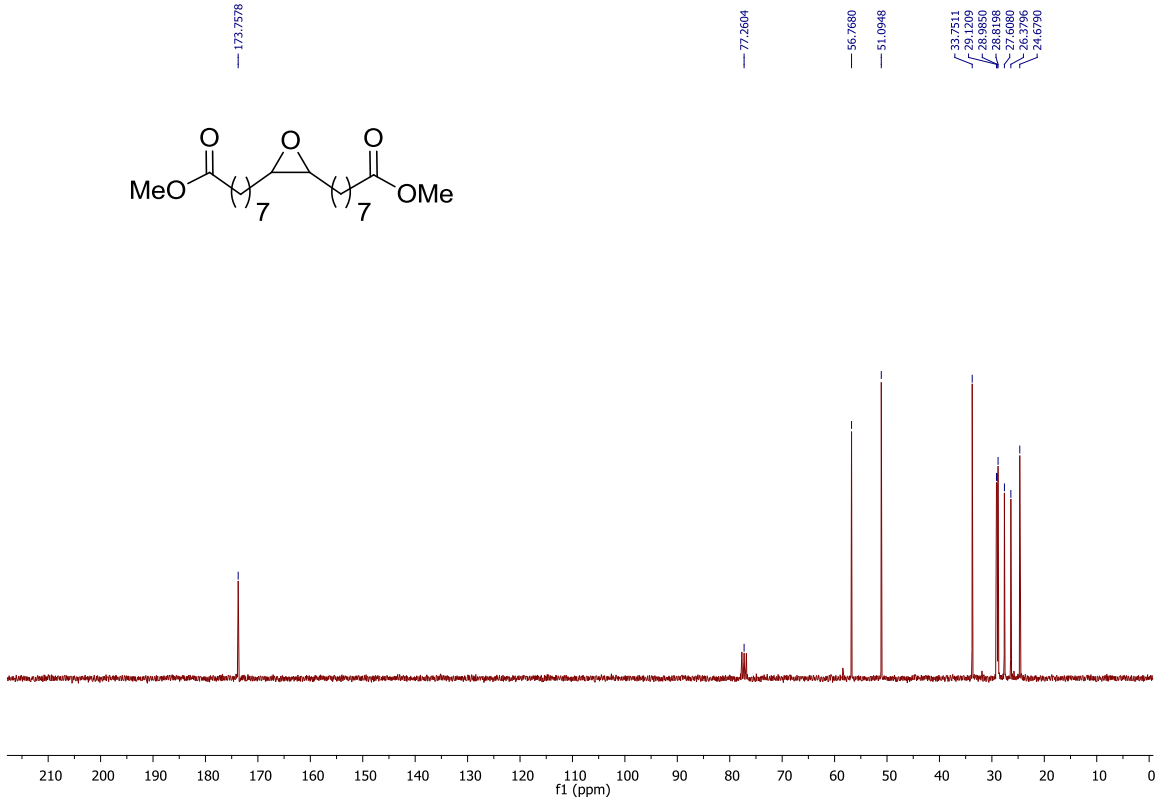
^{13}C-NMR (75 MHz, $CDCl_3$) *(Z)-Dimethyl octadec-9-enedioate*



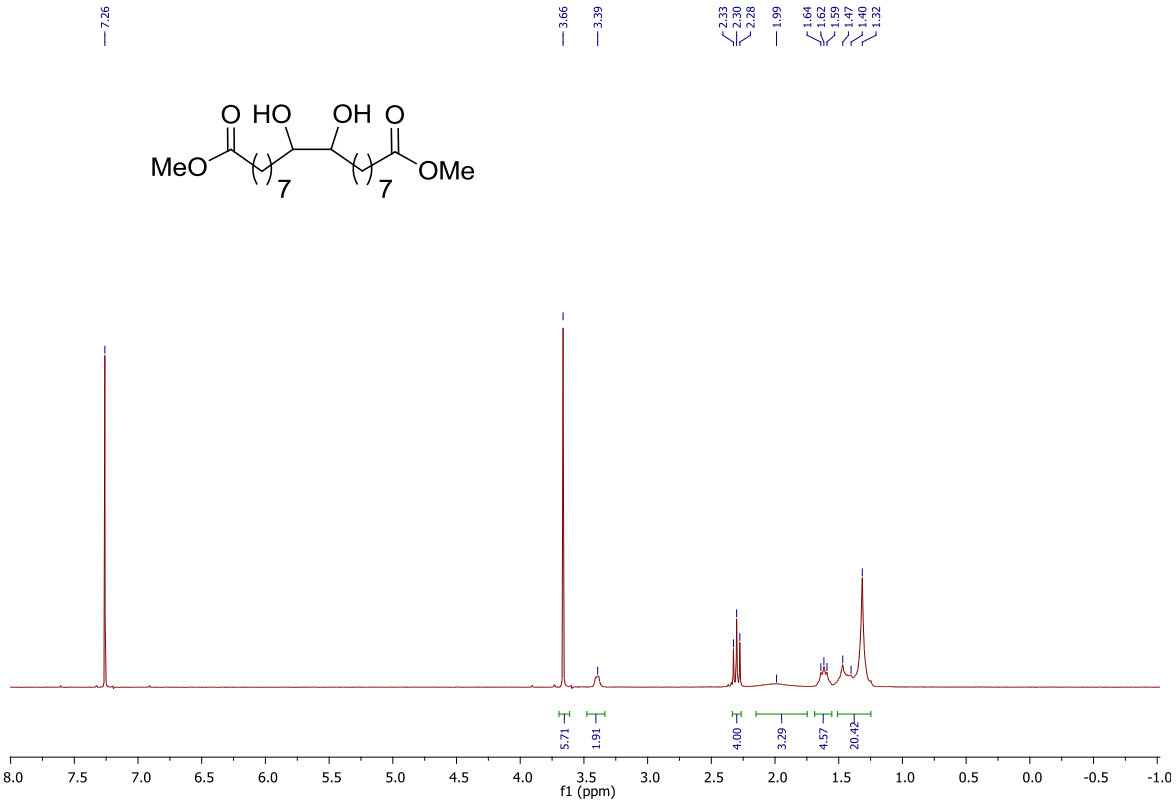
^{1}H-NMR (300 MHz, $CDCl_3$) *Dimethyl 8,8'-(oxirane-2,3-diyl)dioctanoate*



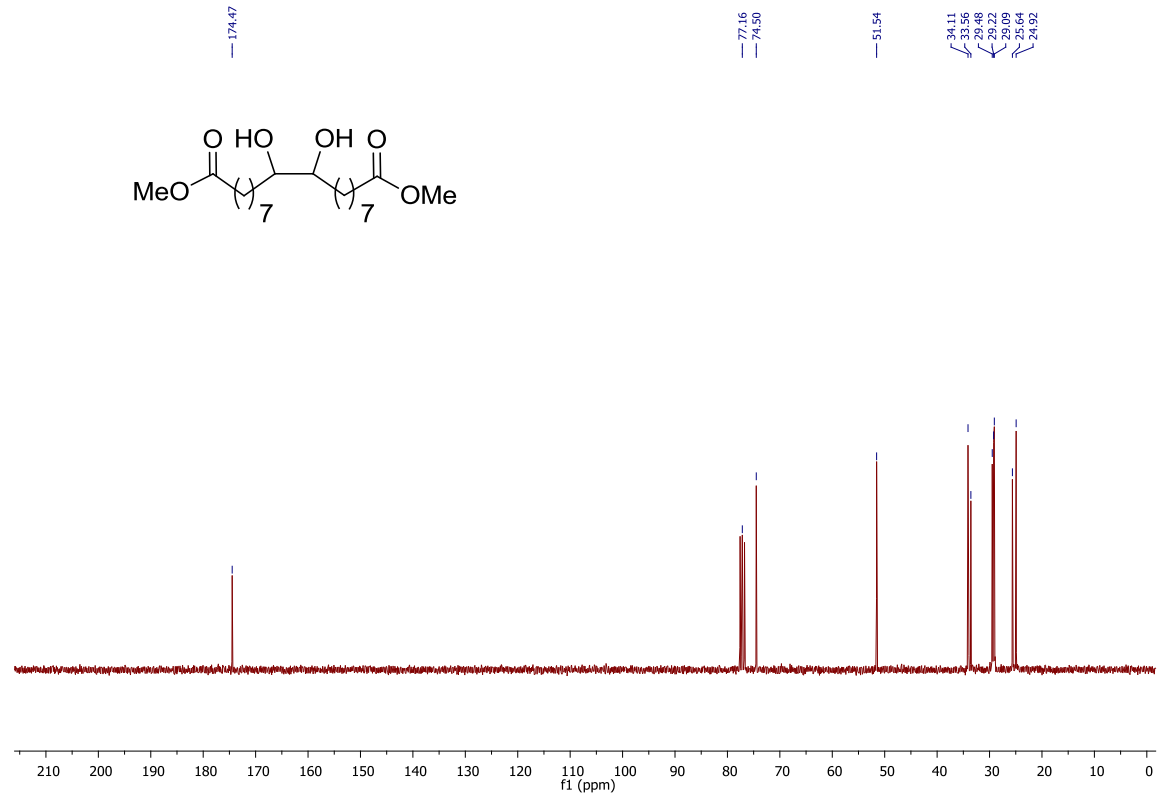
^{13}C-NMR (75 MHz, $CDCl_3$) *Dimethyl 8,8'-(oxirane-2,3-diyl)dioctanoate*



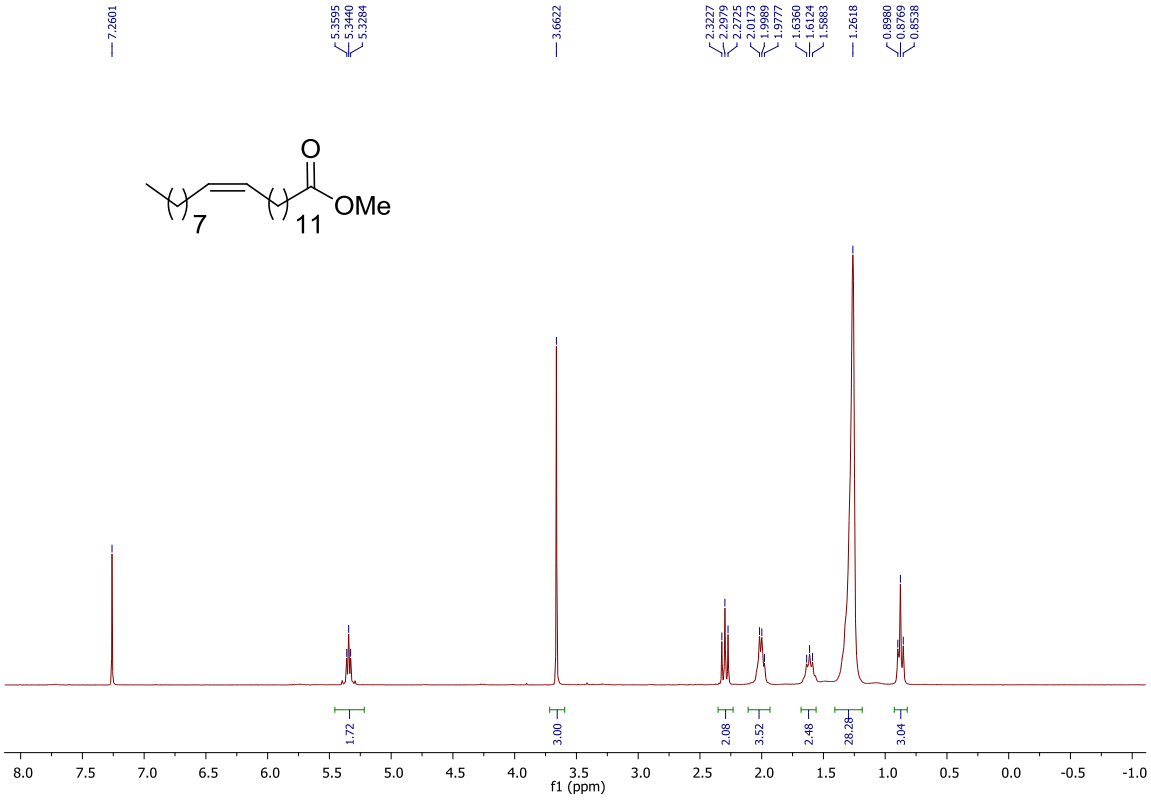
^{1}H-NMR (300 MHz, $CDCl_3$) *Dimethyl 9,10-dihydroxyoctadecanedioate* (**6**)



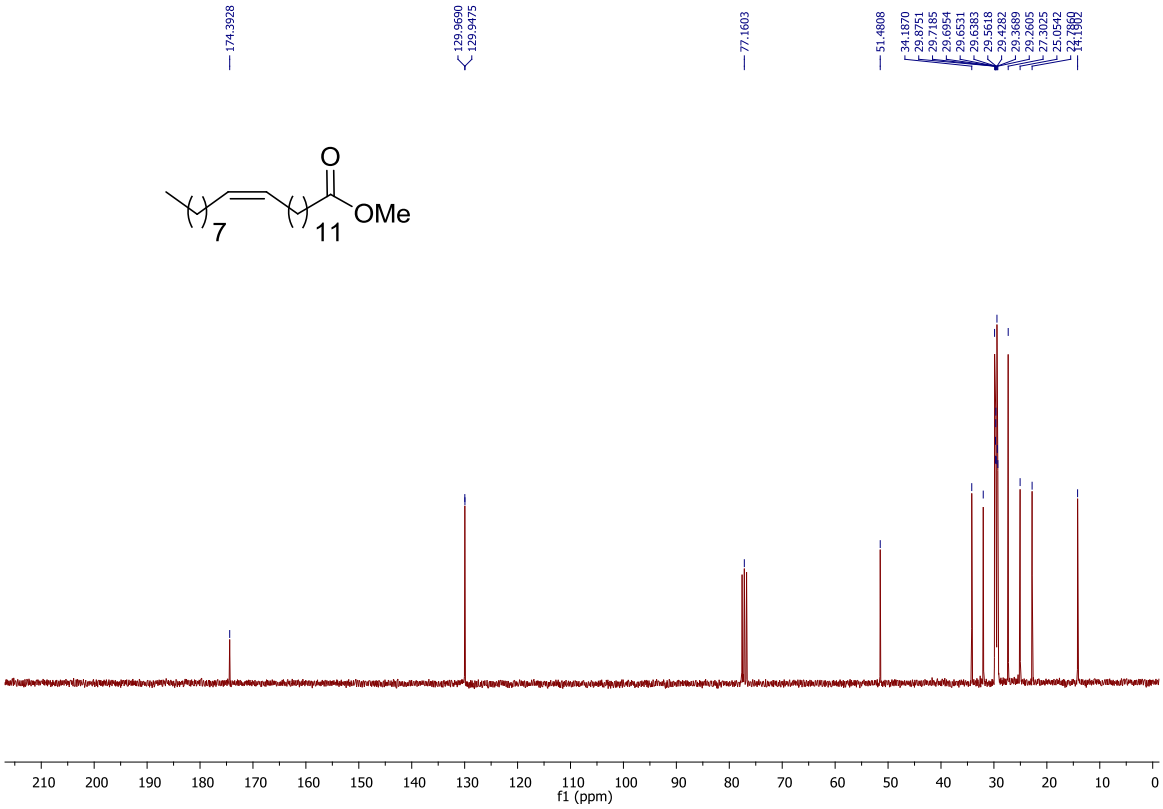
^{13}C-NMR (75 MHz, $CDCl_3$) *Dimethyl 9,10-dihydroxyoctadecanedioate* (**6**)



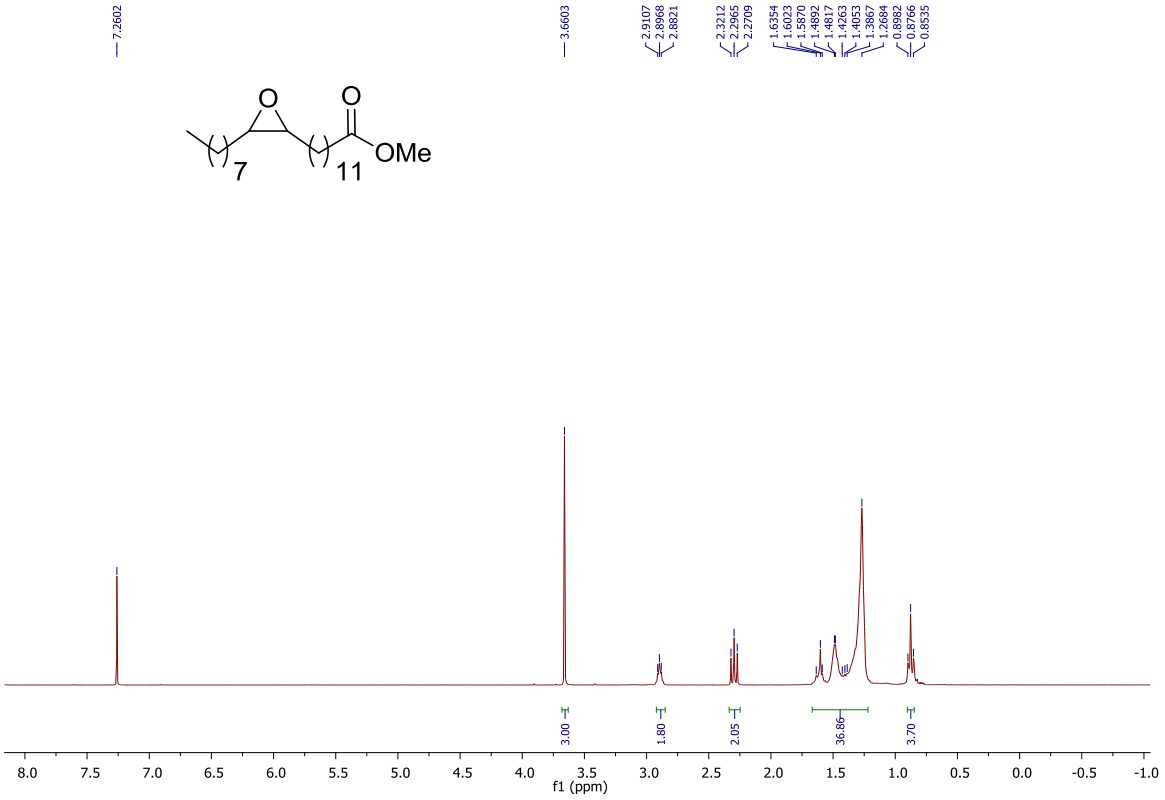
^{1}H-NMR (300 MHz, $CDCl_3$) *Methyl (13Z)-docosenoate*



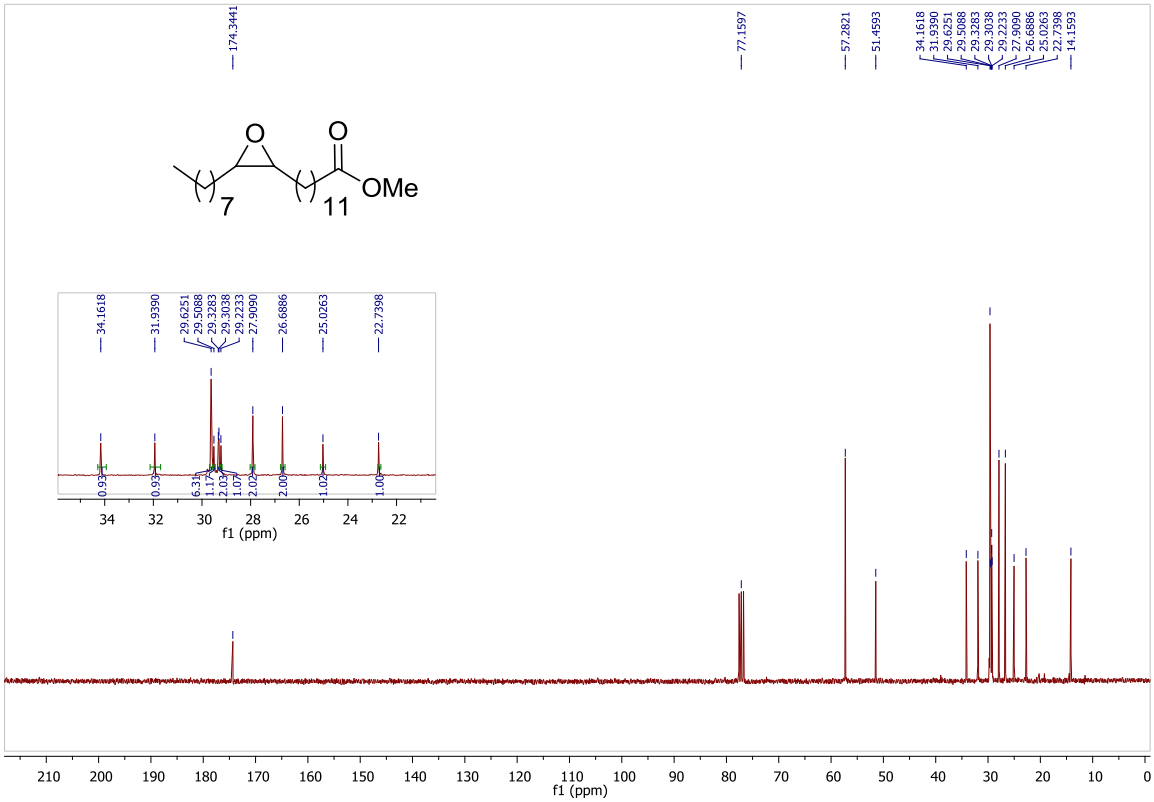
^{13}C-NMR (75 MHz, $CDCl_3$) *Methyl (13Z)-docosenoate*



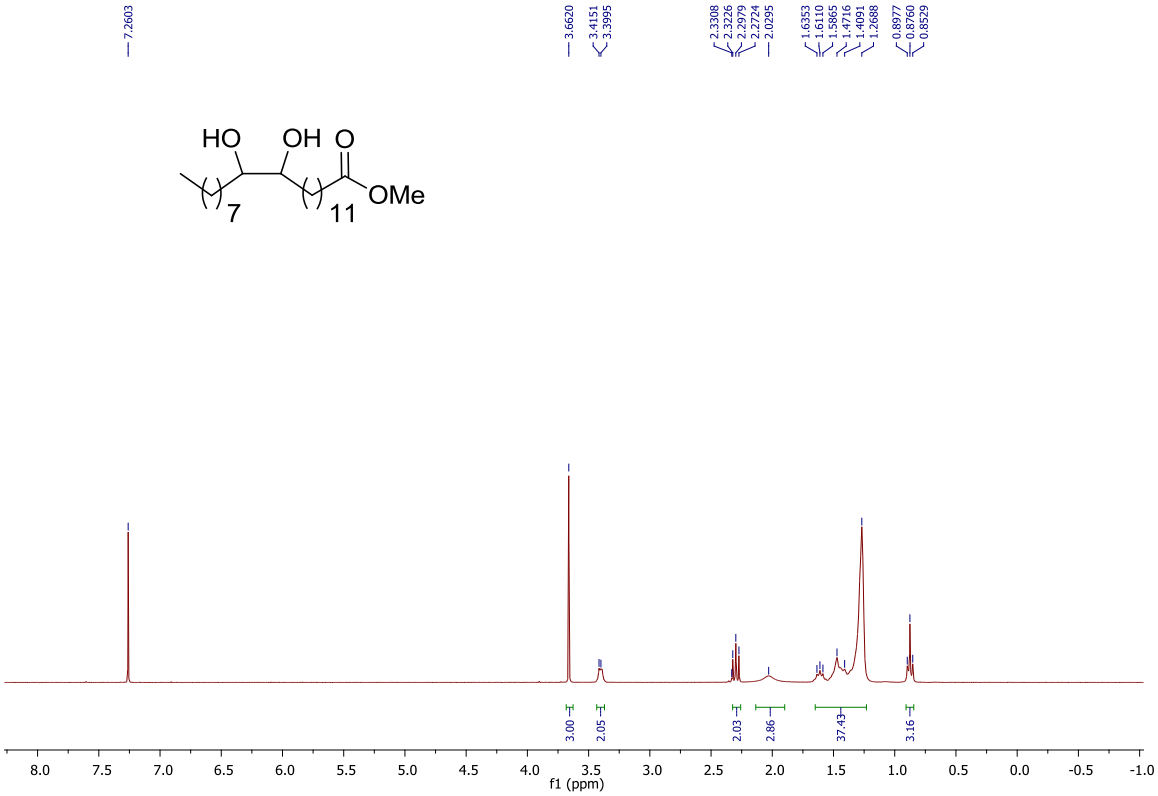
^{1}H-NMR (300 MHz, $CDCl_3$) *Methyl 12-(3-octyloxiran-2-yl)dodecanoate*



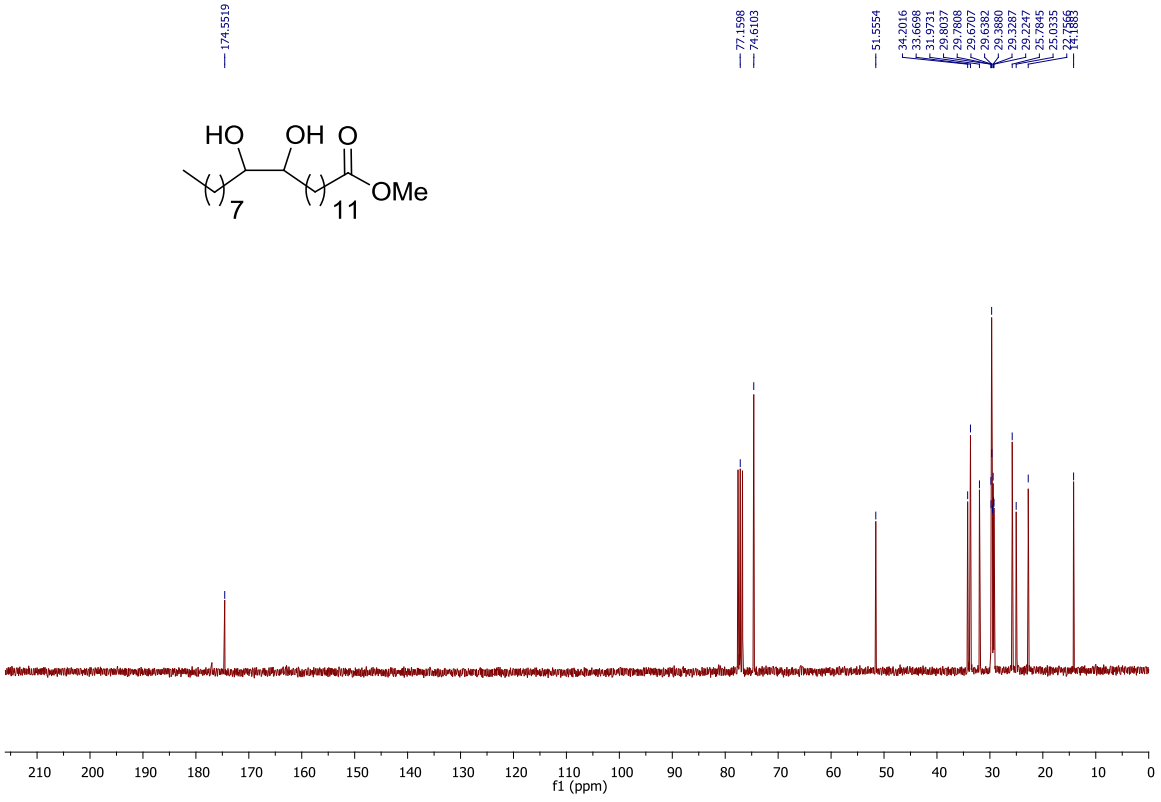
^{13}C-NMR (75 MHz, $CDCl_3$) *Methyl 12-(3-octyloxiran-2-yl)dodecanoate*



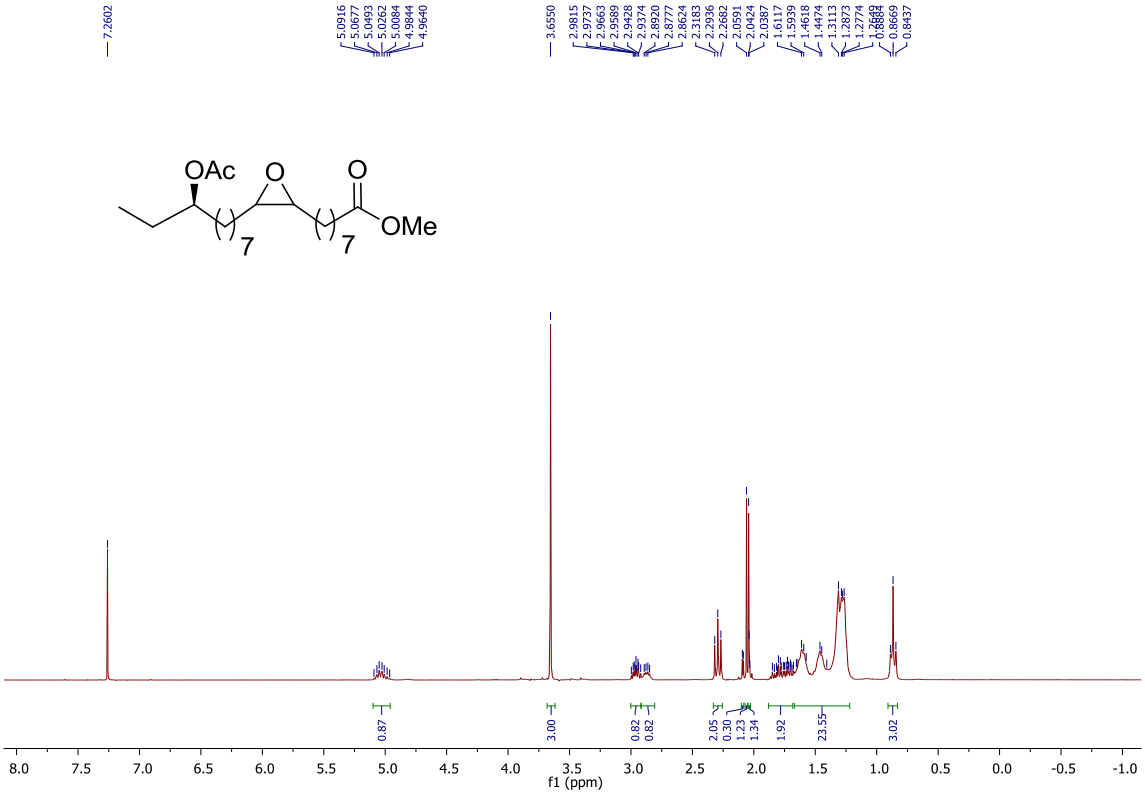
^{1}H-NMR (300 MHz, $CDCl_3$) *Methyl 13,14-dihydroxydocosanoate* (**7**)



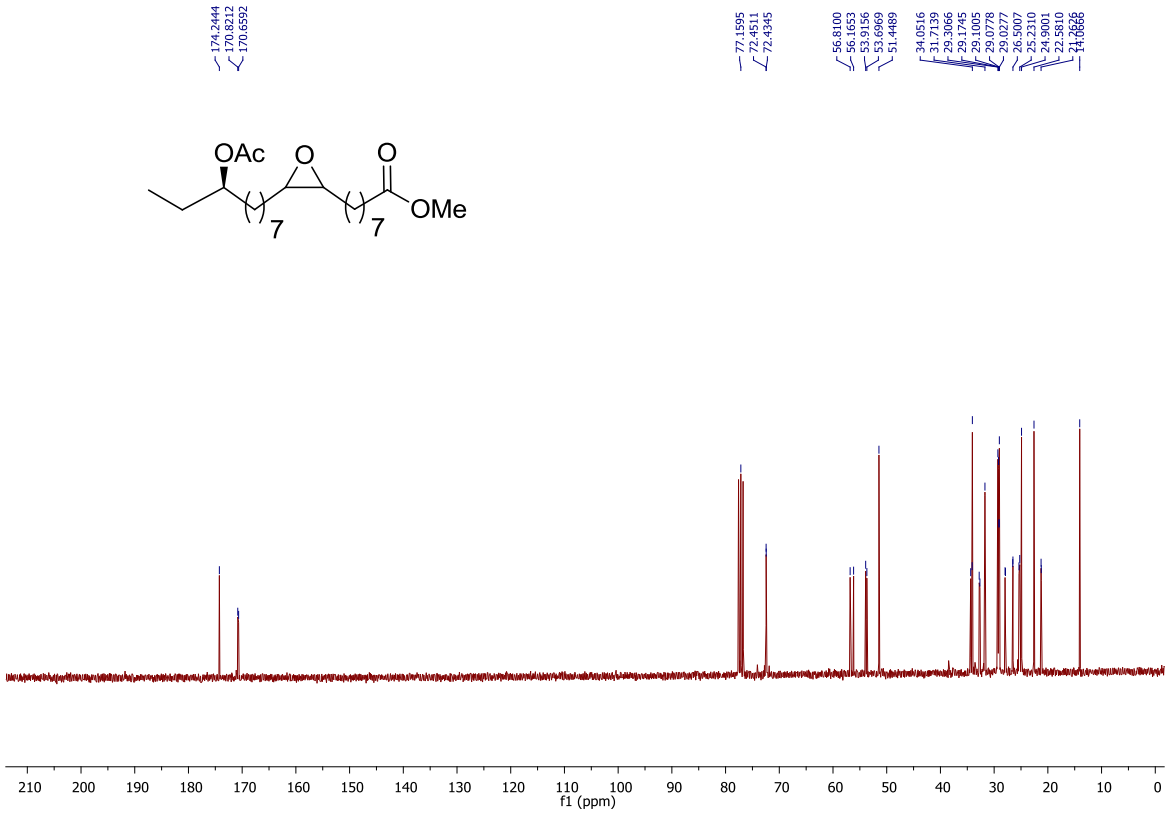
^{13}C-NMR (75 MHz, $CDCl_3$) *Methyl 13,14-dihydroxydocosanoate* (**7**)



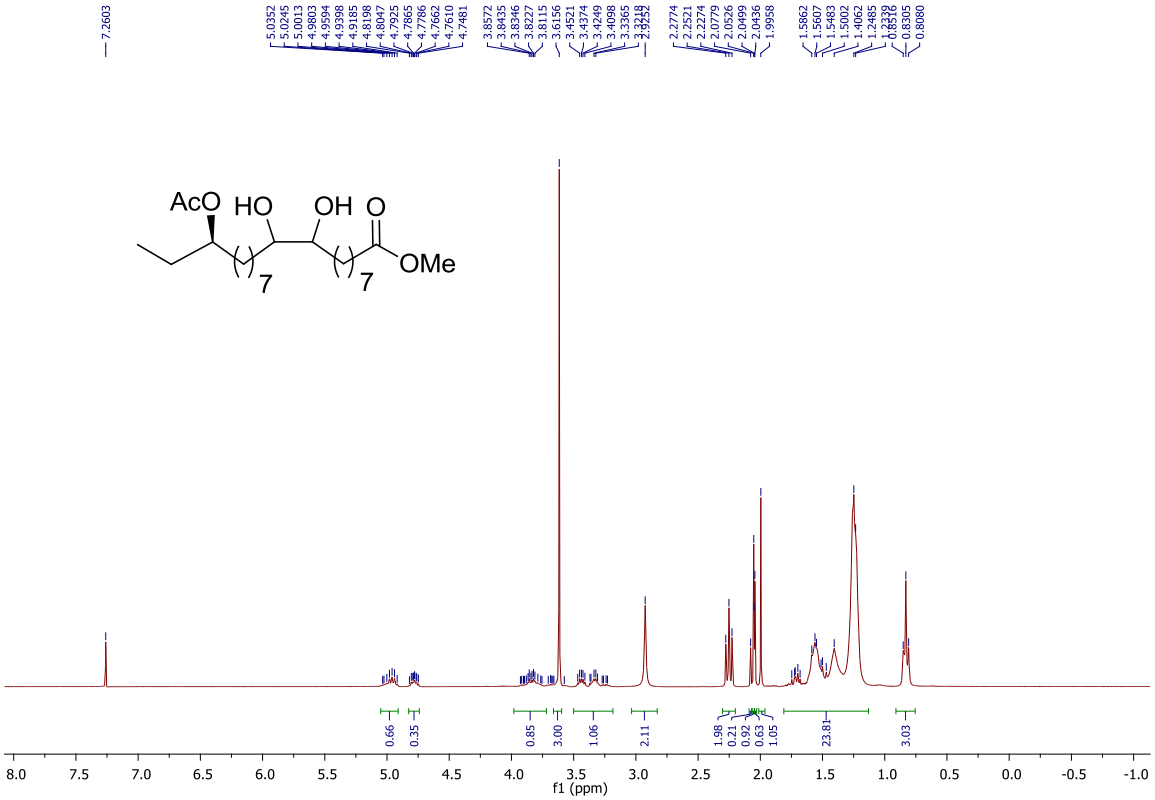
^{1}H-NMR (300 MHz, $CDCl_3$) *Methyl 8-(3-((R)-2-acetoxyoctyl)oxiran-2-yl)octanoate*



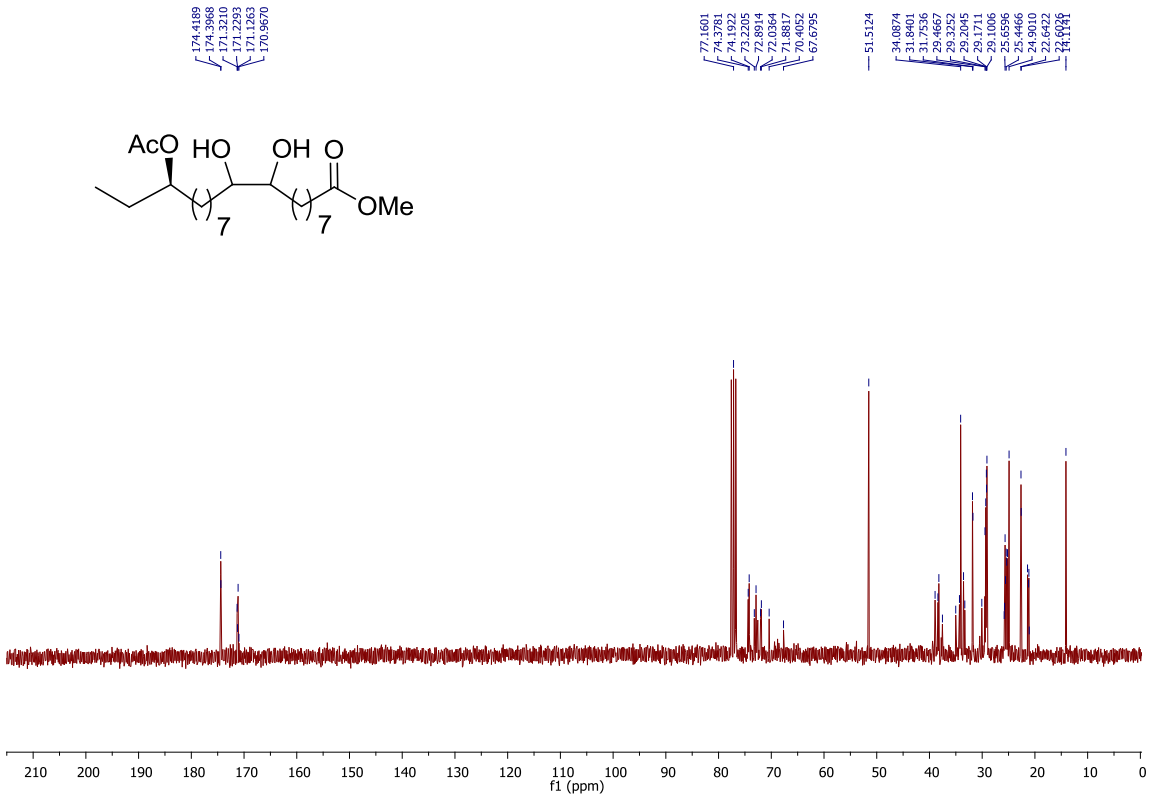
^{13}C-NMR (75 MHz, $CDCl_3$) *Methyl 8-(3-((R)-2-acetoxyoctyl)oxiran-2-yl)octanoate*



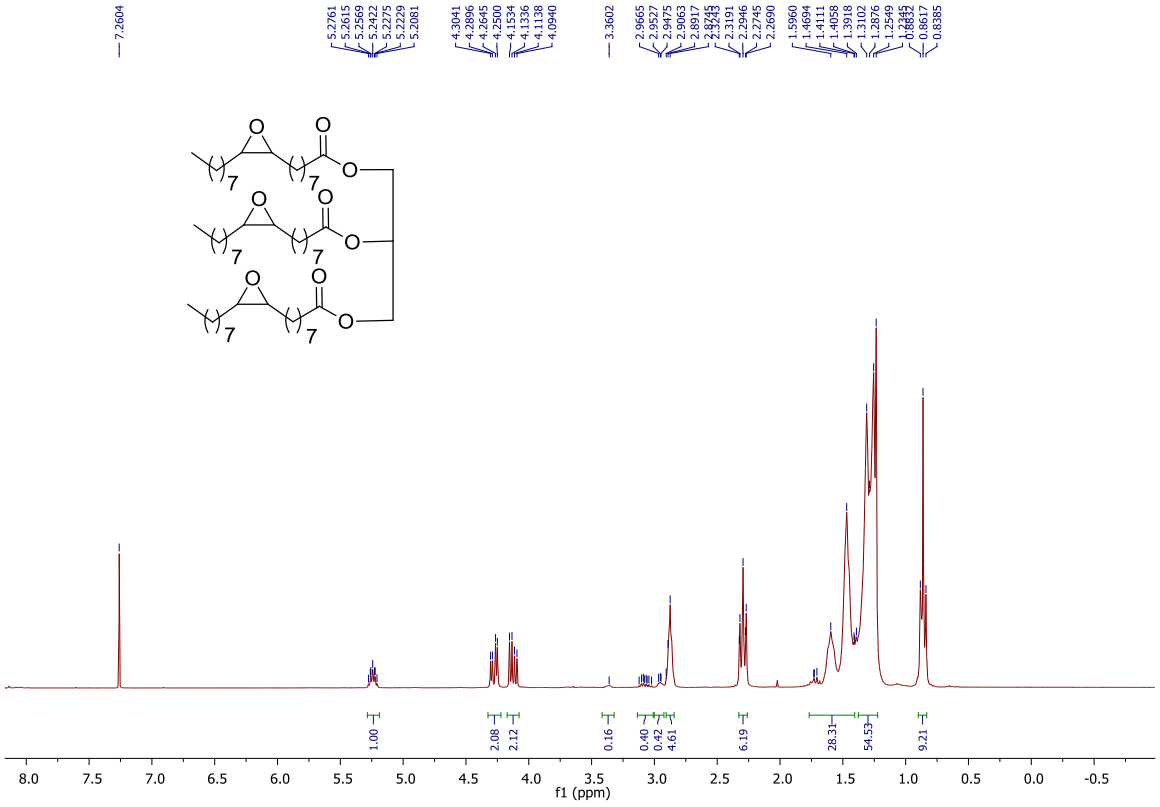
^{1}H-NMR (300 MHz, $CDCl_3$) *Methyl (12R)-acetoxy-9,10-dihydroxyoctadecanoate* (**15**)



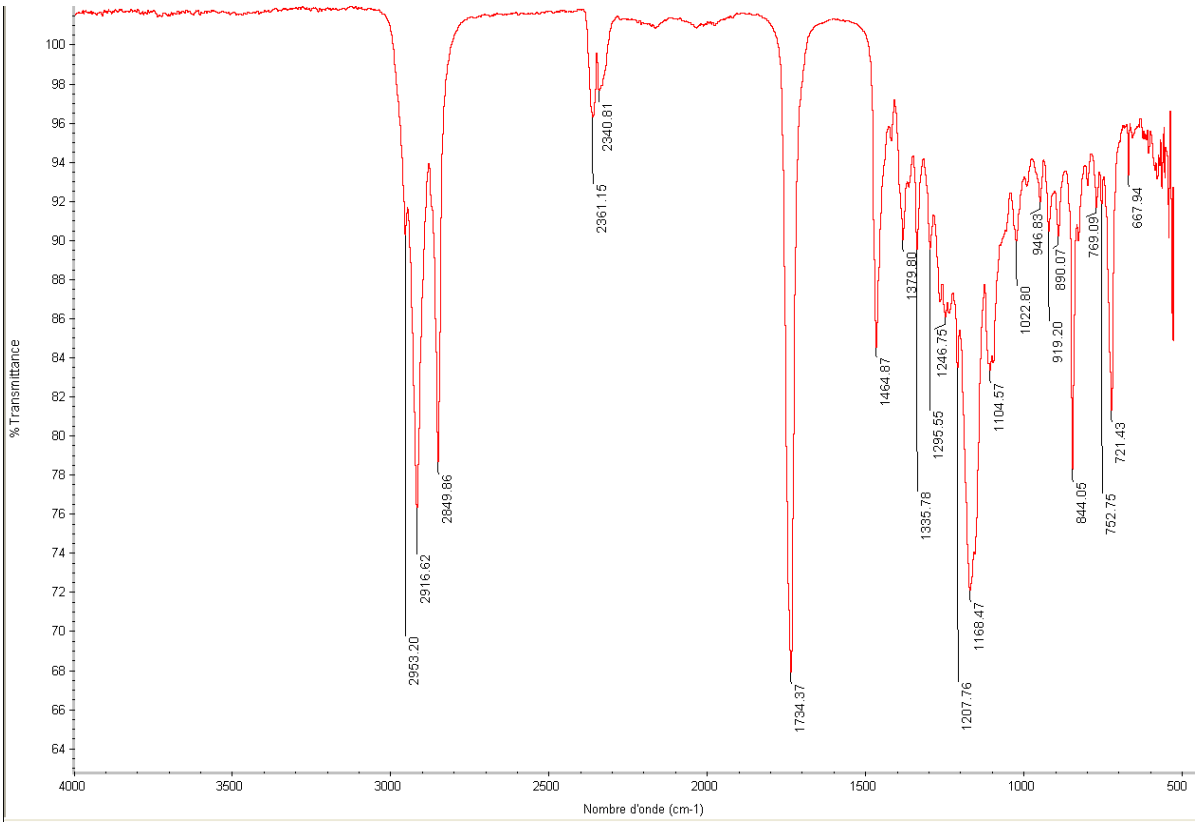
^{13}C-NMR (75 MHz, $CDCl_3$) *Methyl (12R)-acetoxy-9,10-dihydroxyoctadecanoate* (**15**)



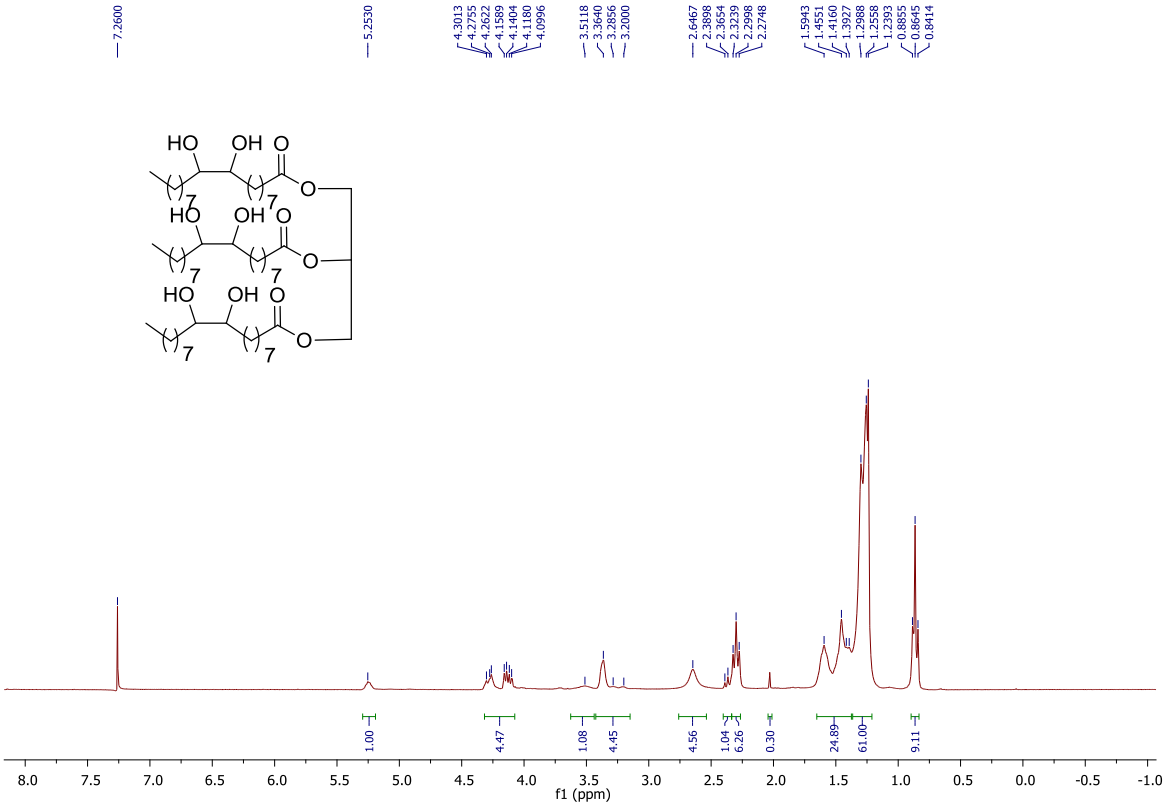
^{1}H-NMR (300 MHz, $CDCl_3$) Tris(*epoxy) high-oleic sunflower oil*



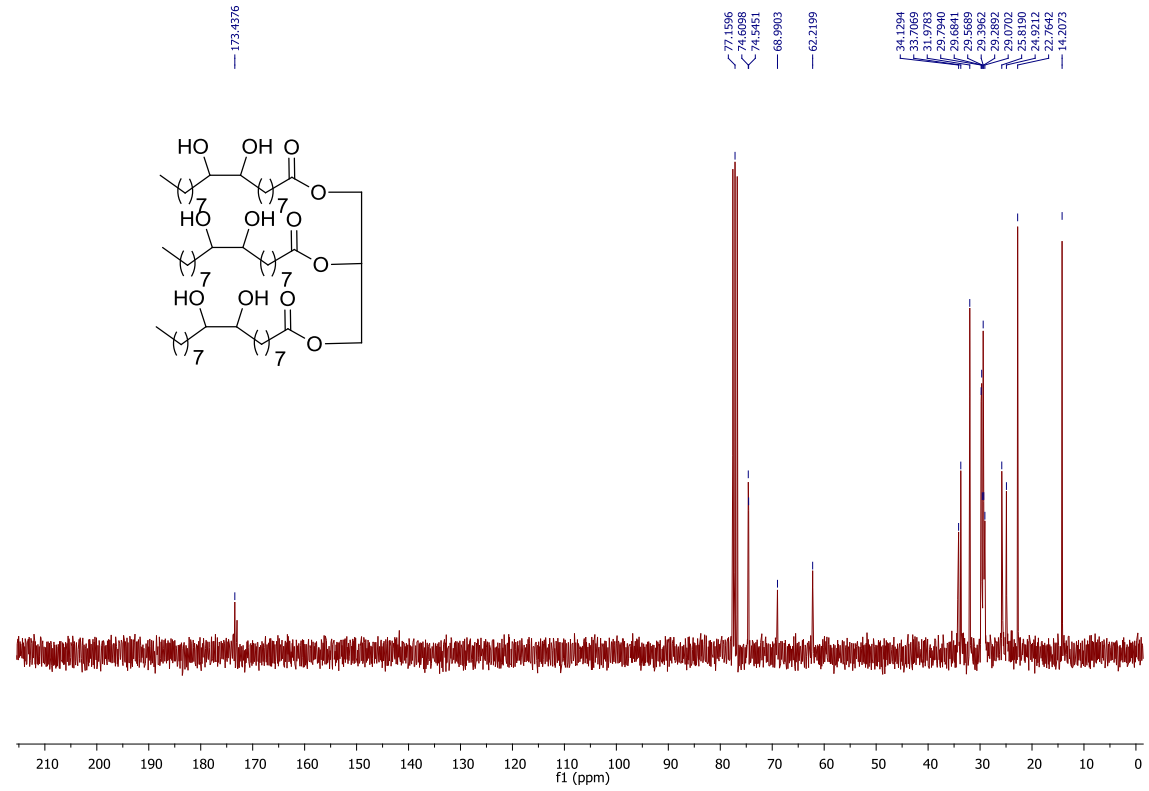
IR *Tris(epoxy) high-oleic sunflower oil*



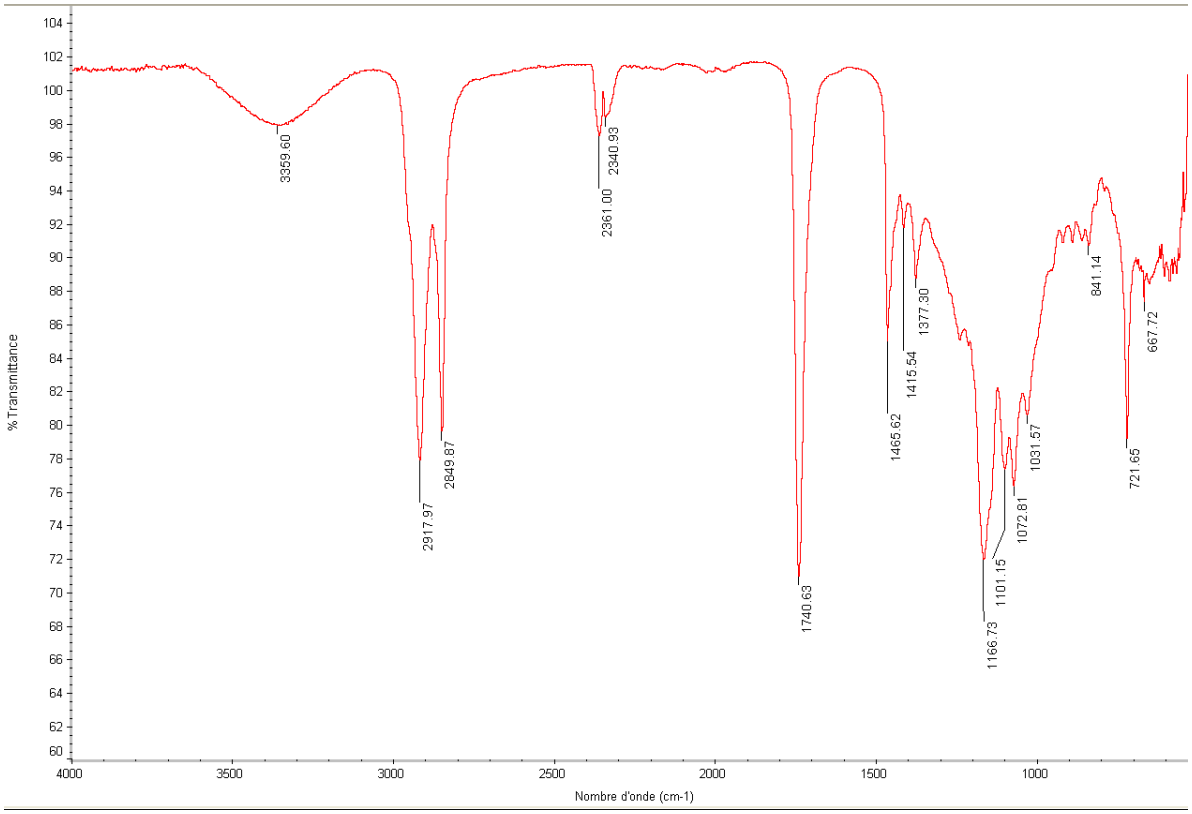
^{1}H-NMR (300 MHz, $CDCl_3$) *Tris(diol) high-oleic sunflower oil (**16**)*



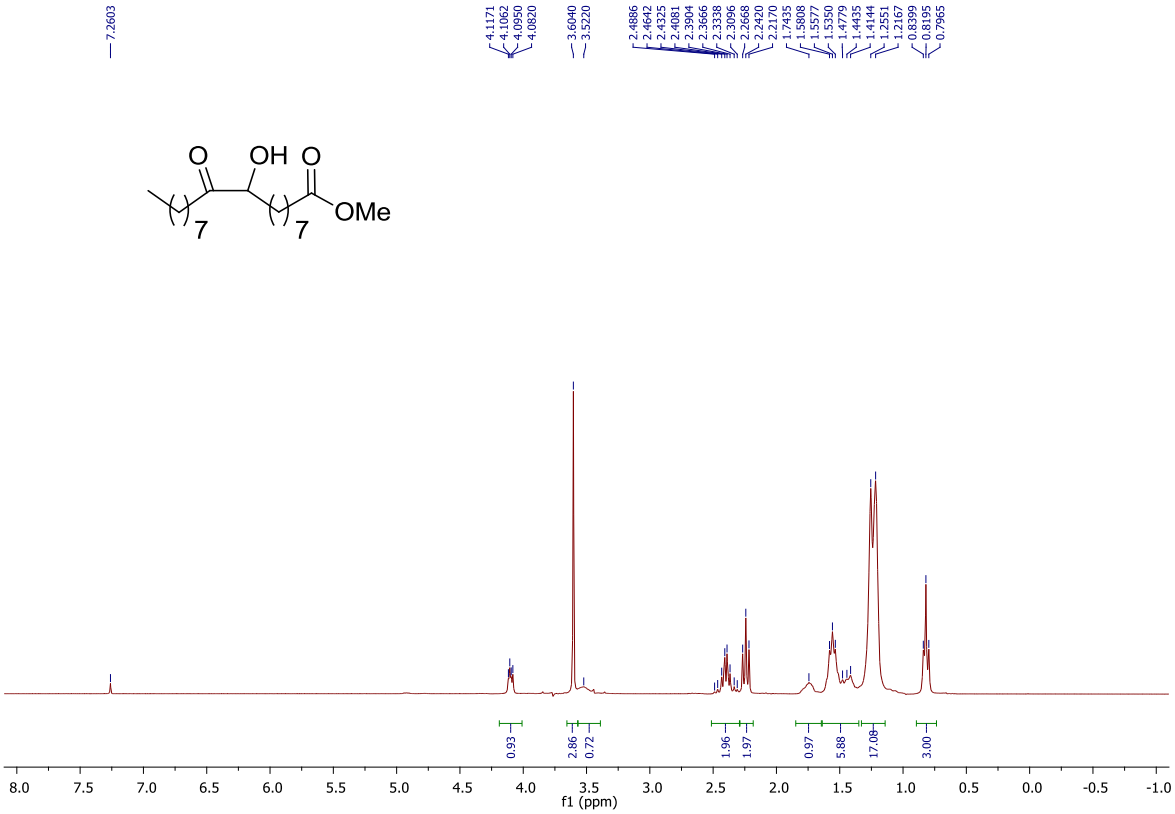
^{13}C-NMR (75 MHz, $CDCl_3$) *Tris(diol) high-oleic sunflower oil (**16**)*



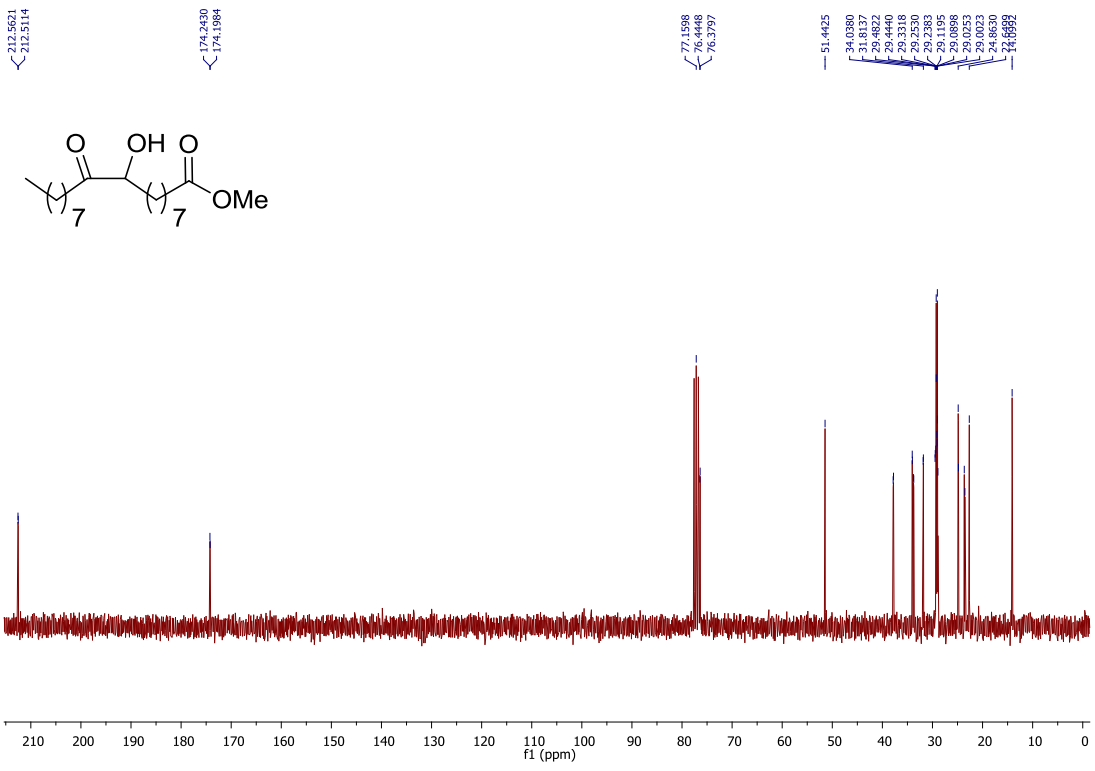
IR *Tris(diol) sunflower oil* (**16**)



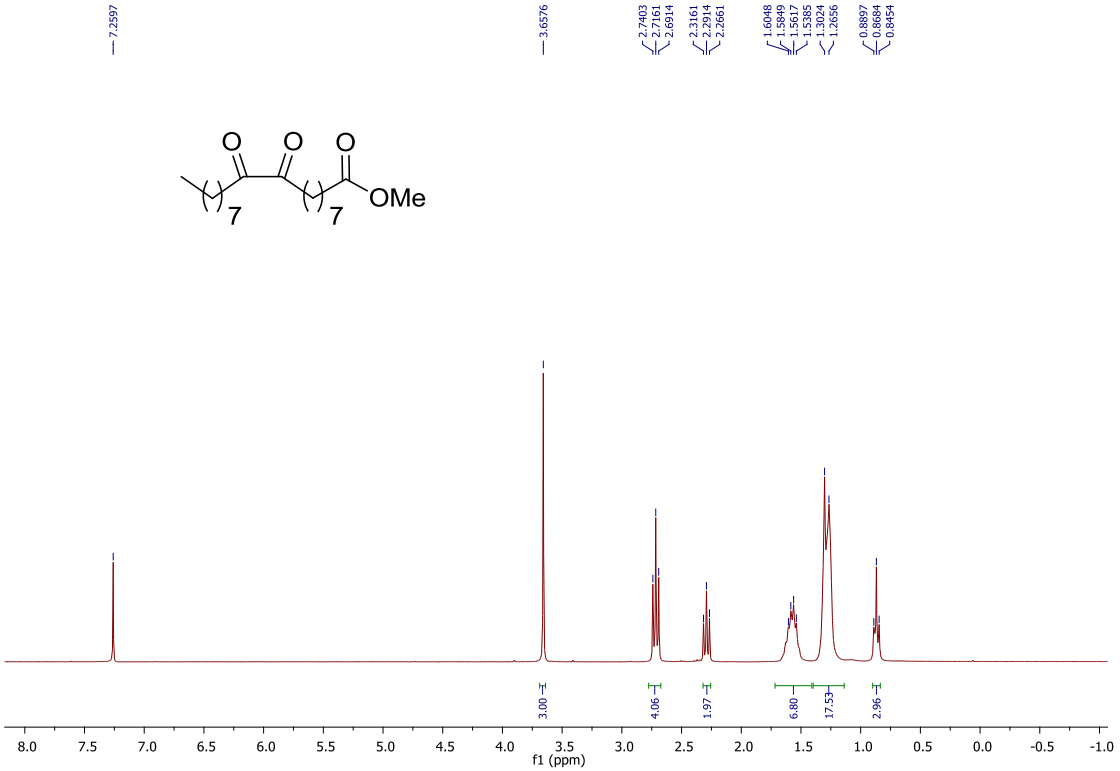
^{1}H-NMR (300 MHz, $CDCl_3$) *Methyl 9(10)-hydroxy 10(9)-oxooctadecanoate* (**2**)



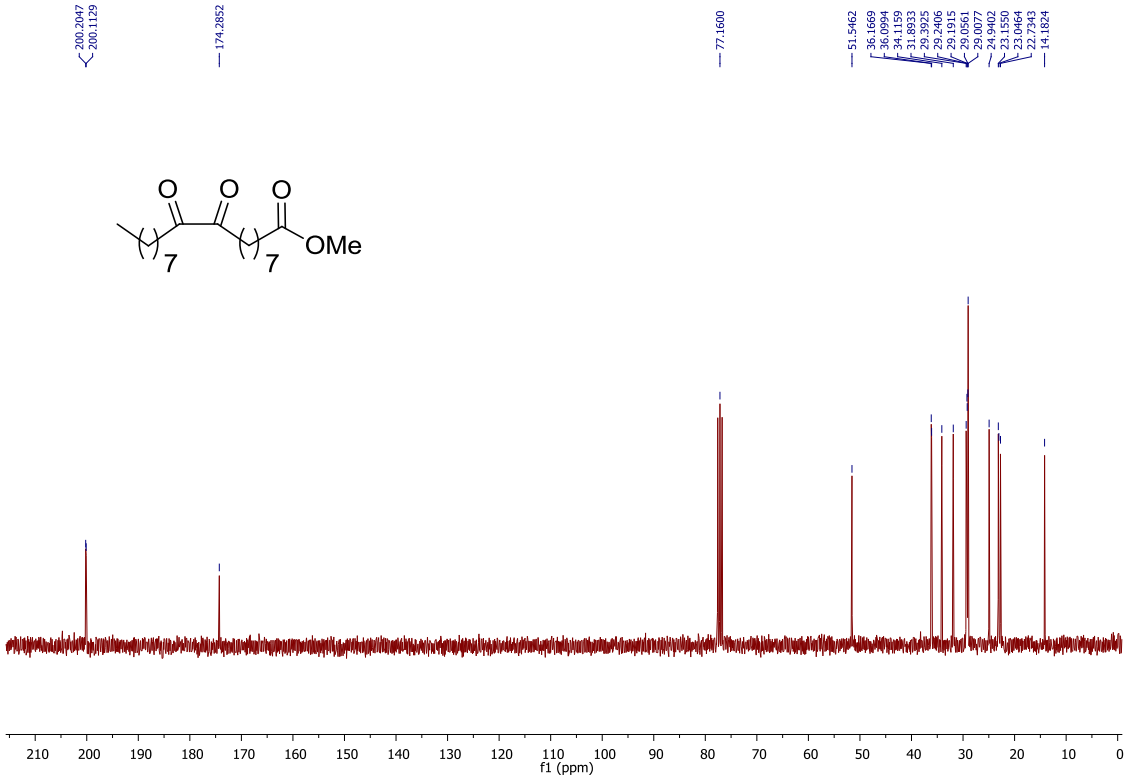
^{13}C-NMR (75 MHz, $CDCl_3$) *Methyl 9(10)-hydroxy 10(9)-oxooctadecanoate* (**2**)



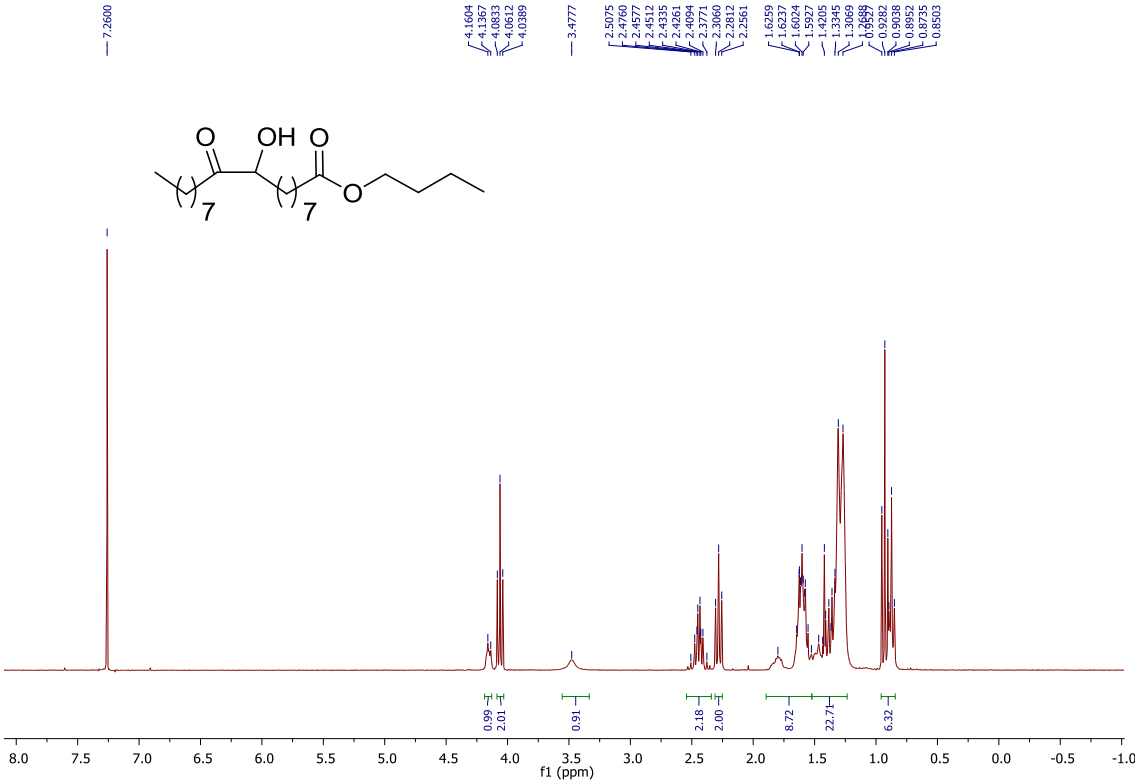
^{1}H-NMR (300 MHz, $CDCl_3$) *Methyl 9,10-dioxooctadecanoate* (**3**)



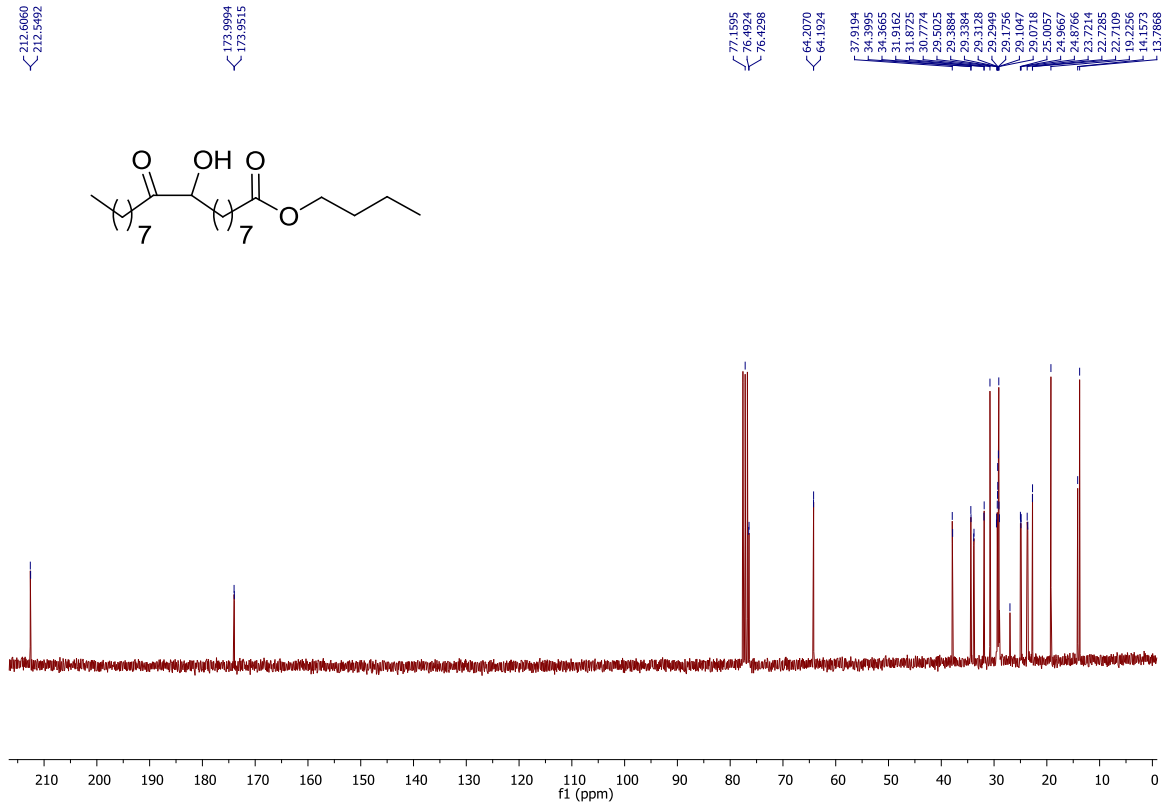
^{13}C-NMR (75 MHz, $CDCl_3$) *Methyl 9,10-dioxooctadecanoate* (**3**)



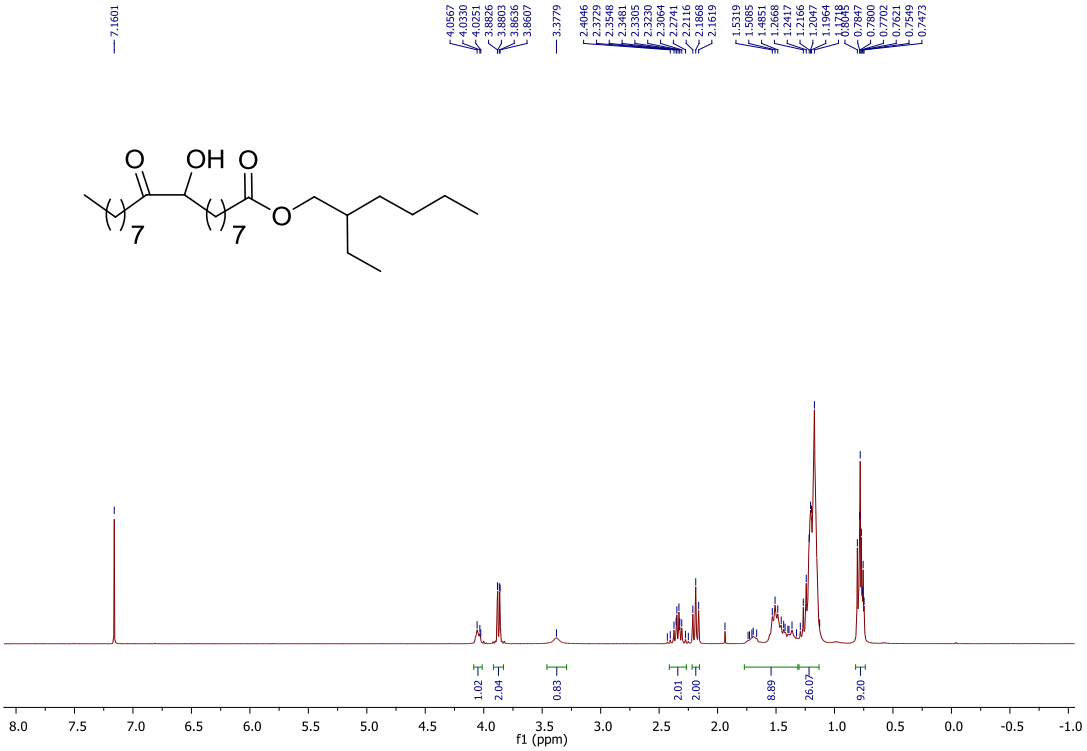
^{1}H-NMR (300 MHz, $CDCl_3$) *Butyl 9(10)-hydroxy-10(9)-oxooctadecanoate* (**17**)



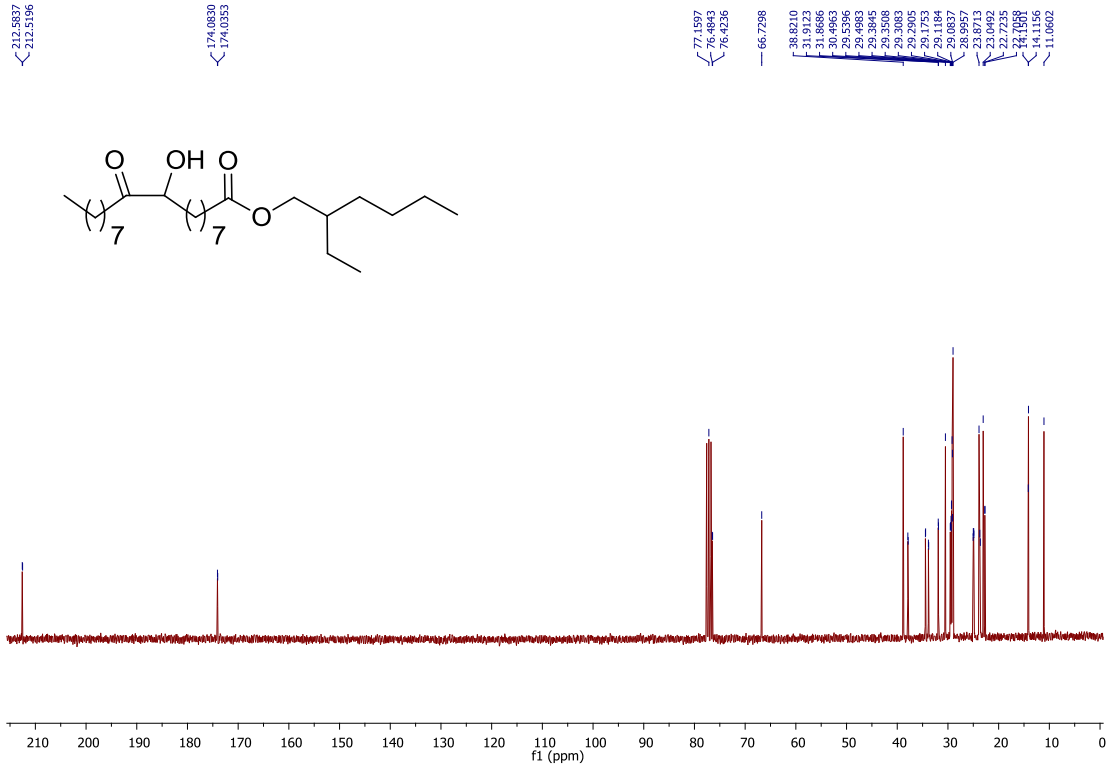
^{13}C-NMR (75 MHz, $CDCl_3$) *Butyl 9(10)-hydroxy-10(9)-oxooctadecanoate* (**17**)



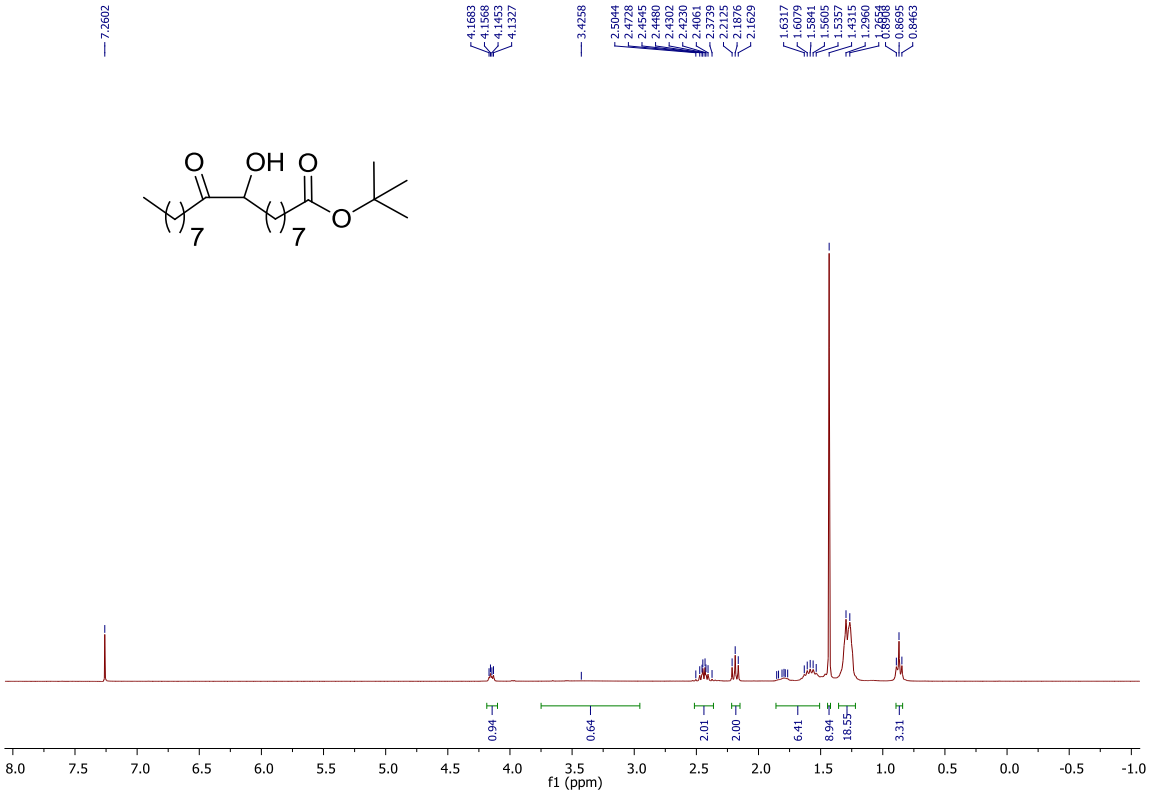
^{1}H-NMR (300 MHz, $CDCl_3$) *2-Ethylhexyl 9(10)-hydroxy-10(9)-oxooctadecanoate* (**18**)



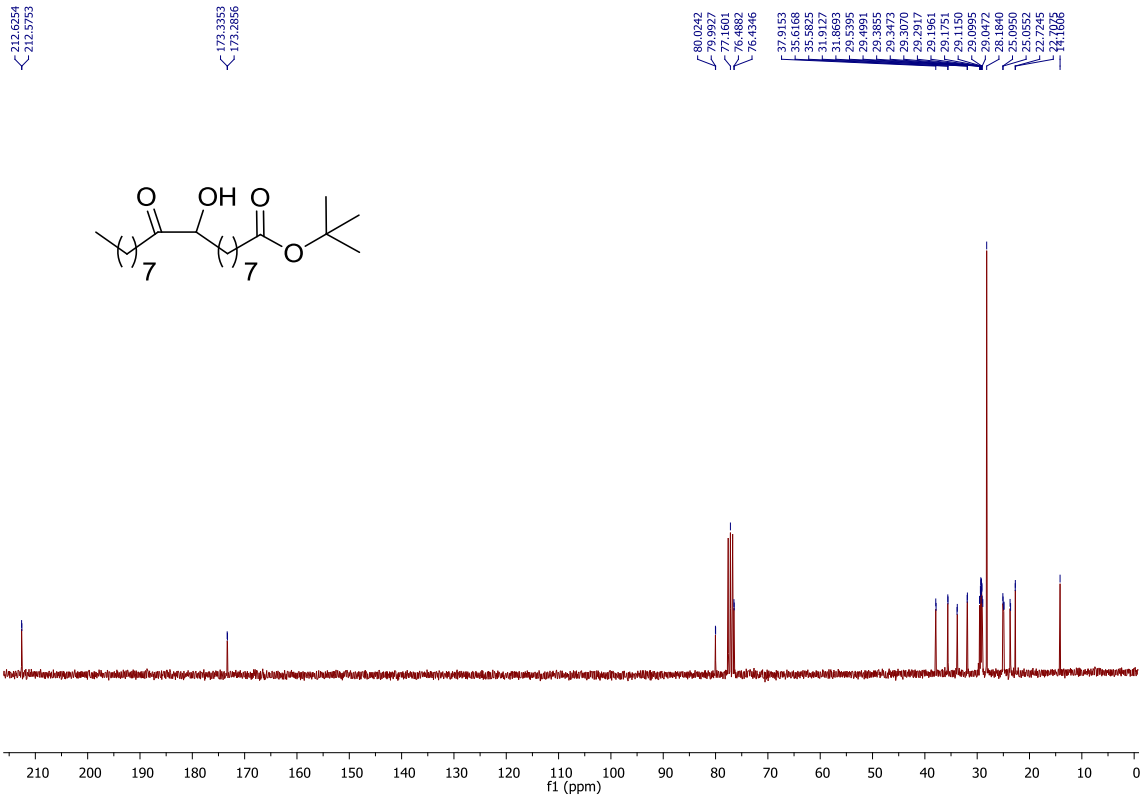
^{13}C-NMR (75 MHz, $CDCl_3$) *2-Ethylhexyl 9(10)-hydroxy-10(9)-oxooctadecanoate* (**18**)



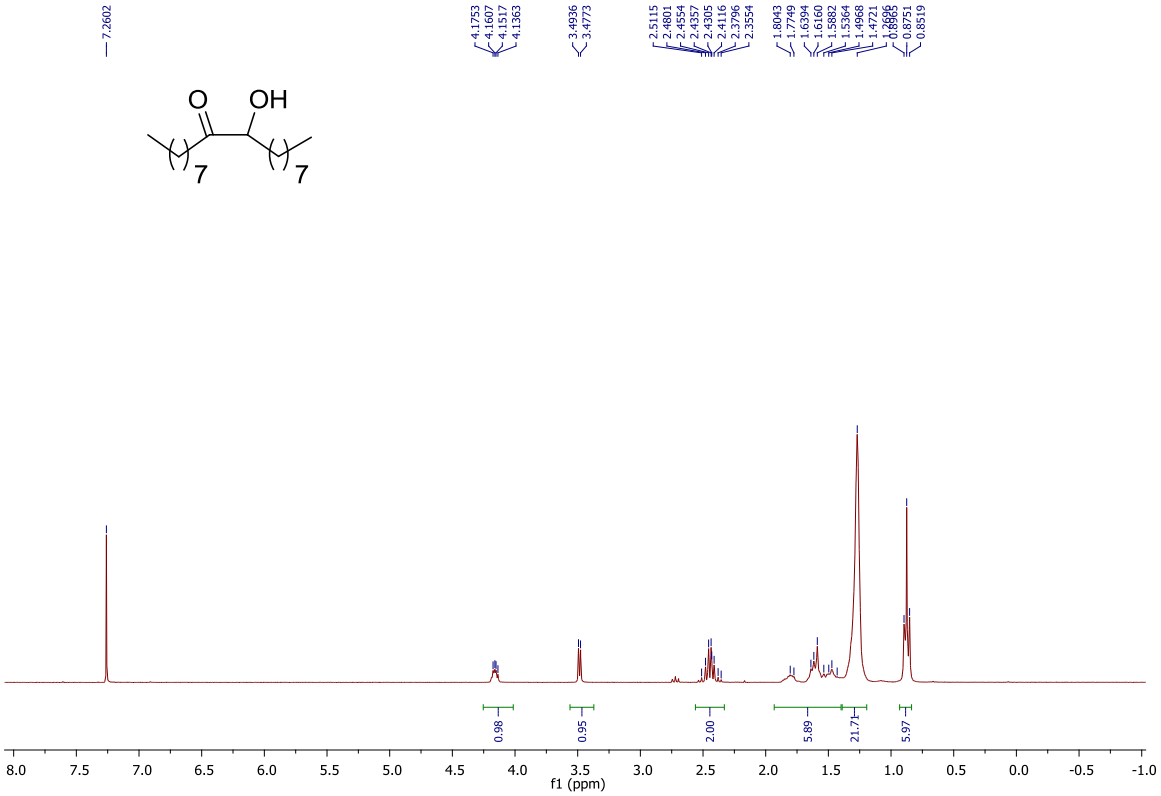
^{1}H-NMR (300 MHz, $CDCl_3$) *tert-Butyl 9(10)-hydroxy-10(9)-oxooctadecanoate* (**8**)



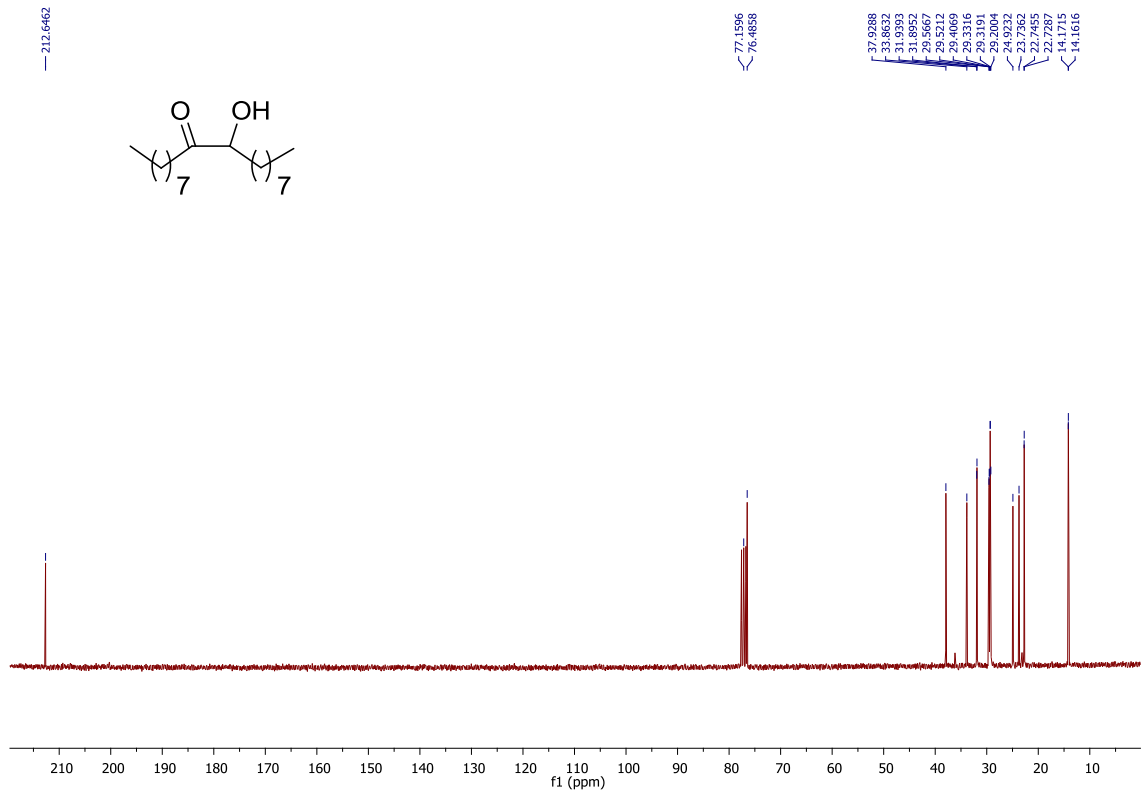
^{13}C-NMR (75 MHz, $CDCl_3$) *tert-Butyl 9(10)-hydroxy-10(9)-oxooctadecanoate* (**8**)



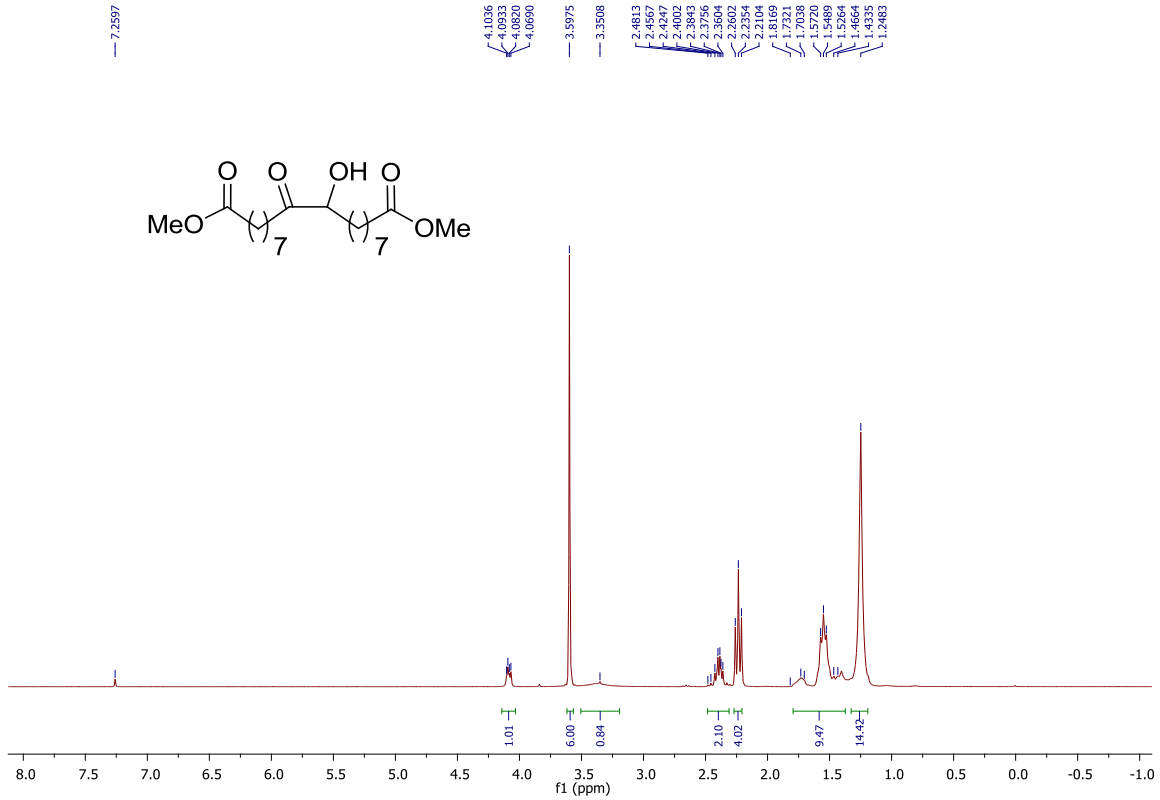
^{1}H-NMR (300 MHz, $CDCl_3$) *10-hydroxyoctadecan-9-one* (**9**)



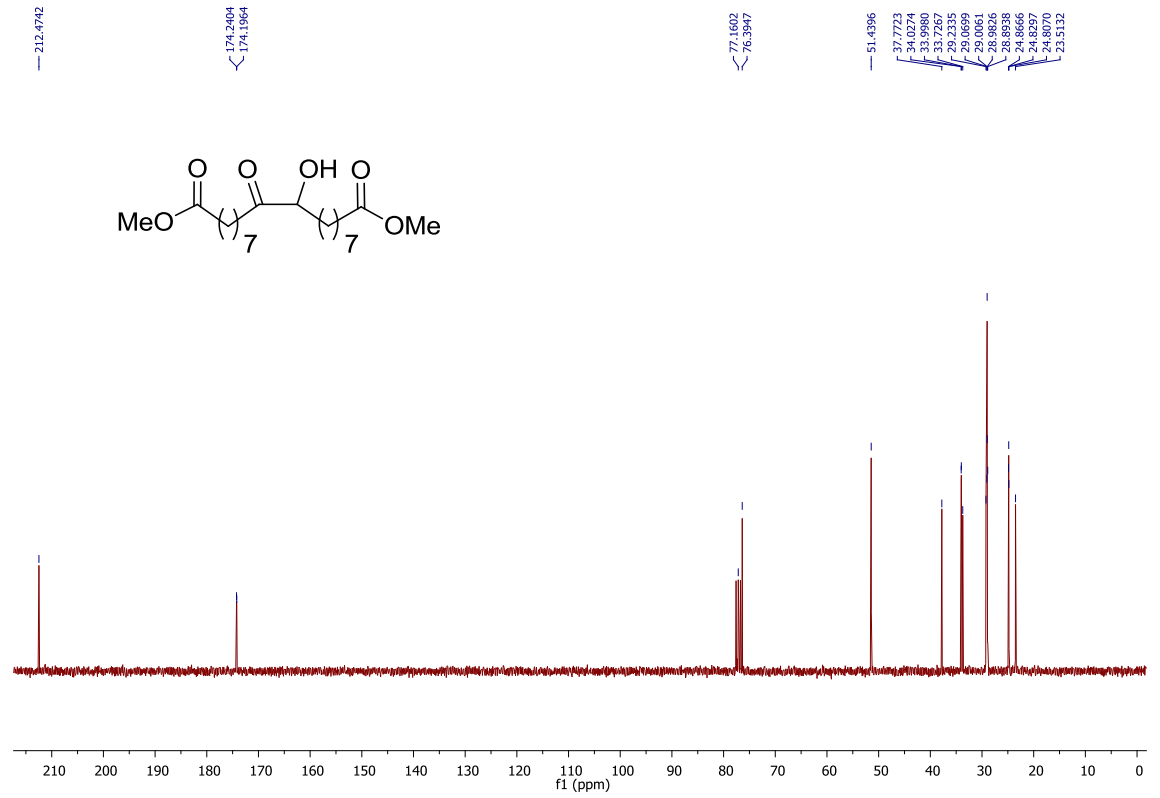
^{13}C-NMR (75 MHz, $CDCl_3$) *10-hydroxyoctadecan-9-one* (**9**)



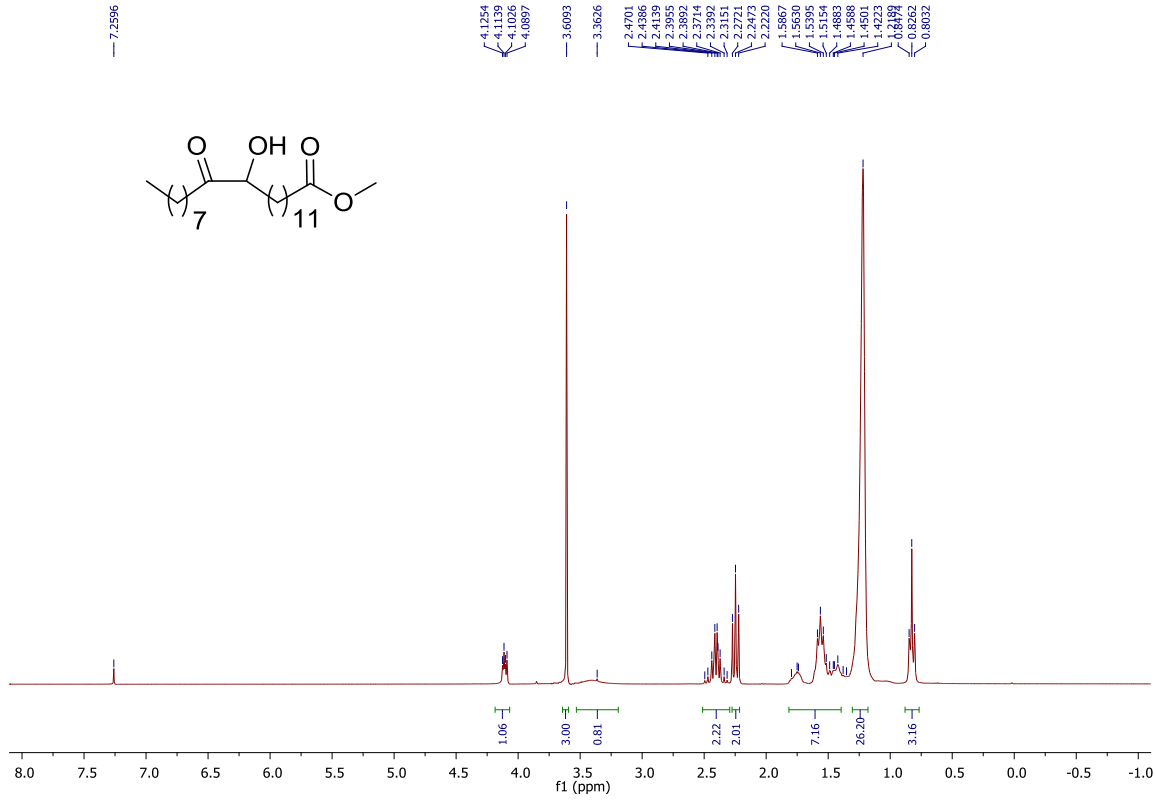
^{1}H-NMR (300 MHz, $CDCl_3$) *Dimethyl 9-hydroxy-10-oxooctadecanedioate* (**10**)



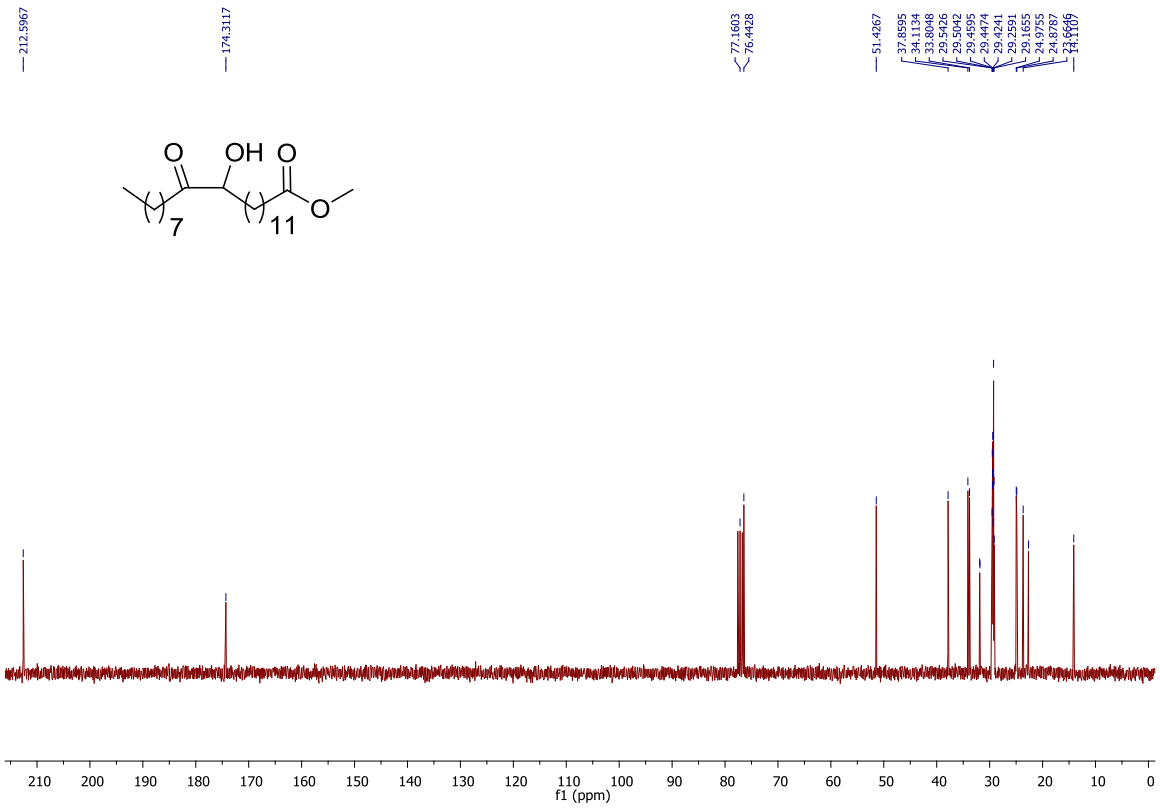
^{13}C-NMR (75 MHz, $CDCl_3$) *Dimethyl 9-hydroxy-10-oxooctadecanedioate* (**10**)



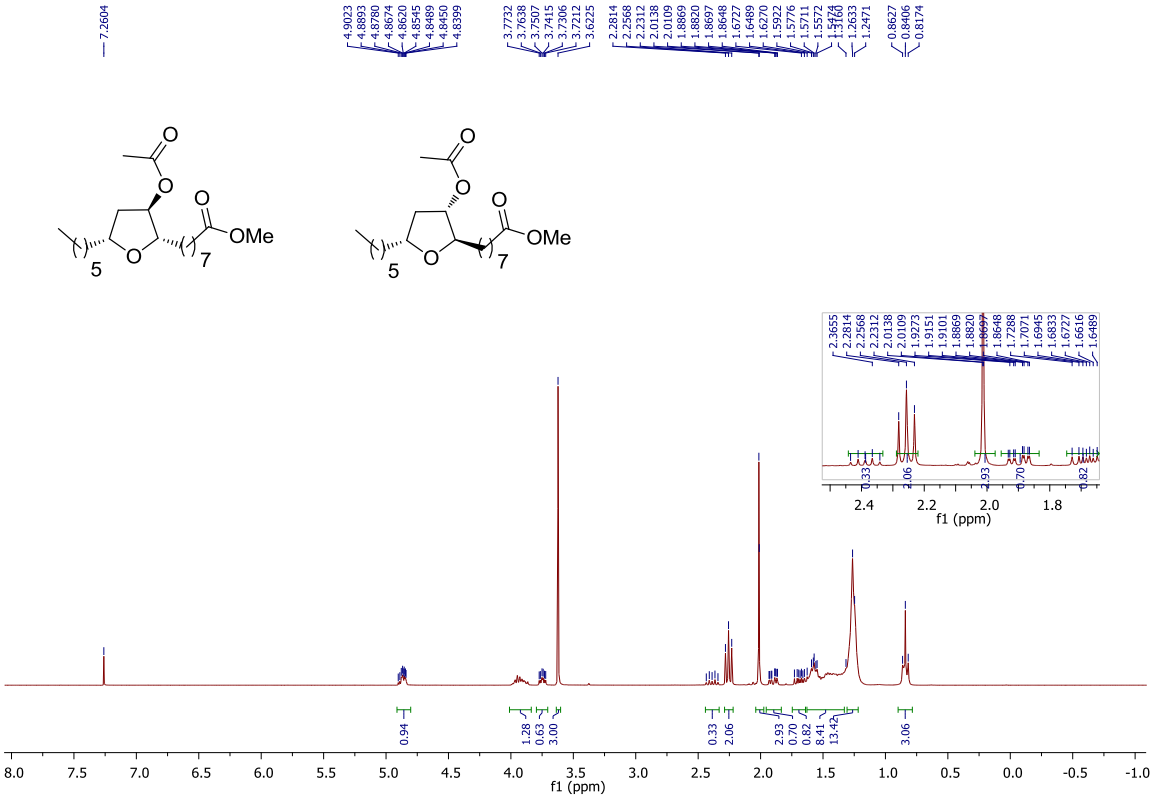
^{1}H-NMR (300 MHz, $CDCl_3$) *13(14)-hydroxy-14(13)-oxodocosanoate* (**11**)



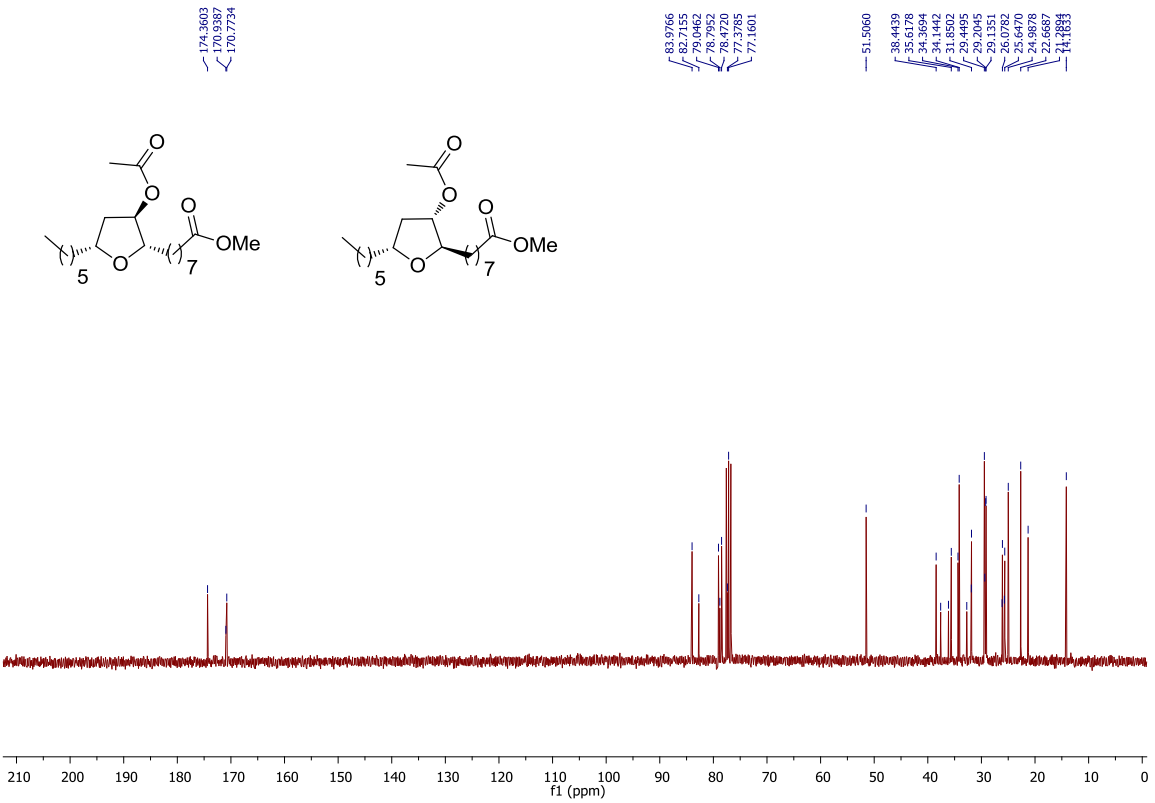
^{13}C-NMR (75 MHz, $CDCl_3$) *Methyl 13(14)-hydroxy-14(13)-oxodocosanoate* (**11**)



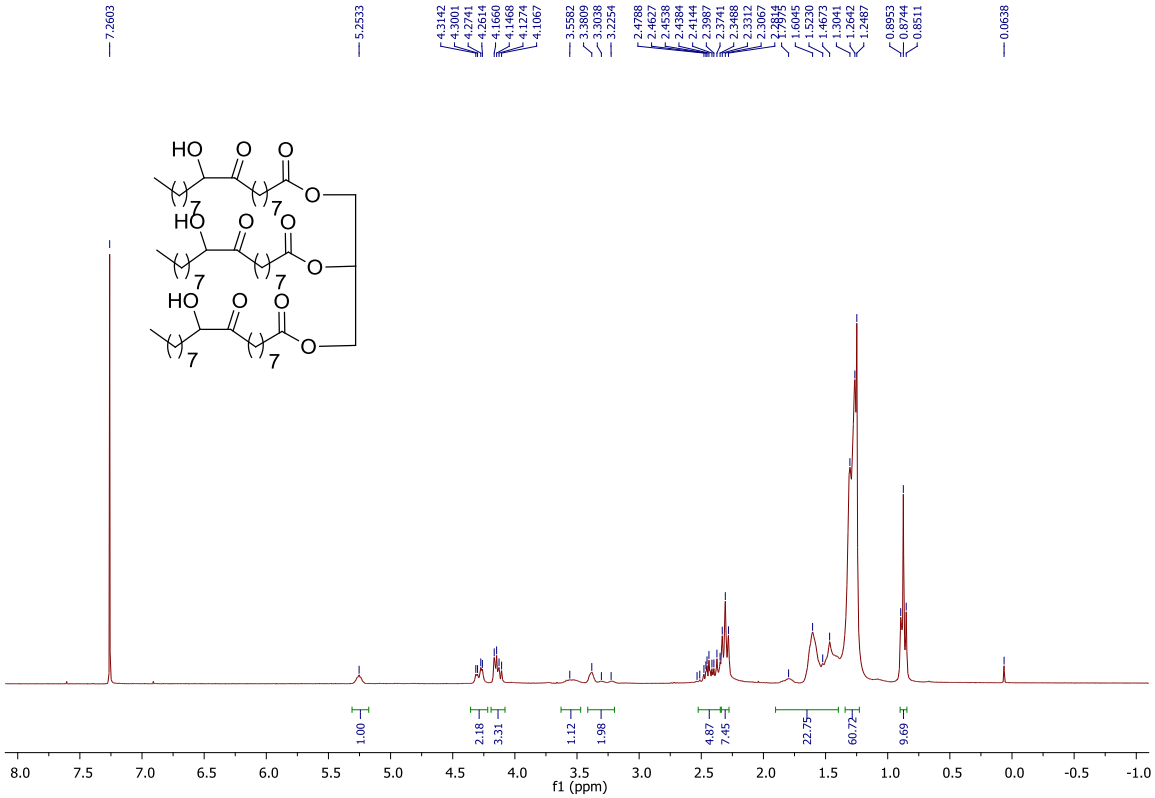
^{1}H-NMR (300 MHz, $CDCl_3$) *Tetrahydrofuran derivatives* **21a** and **21b**



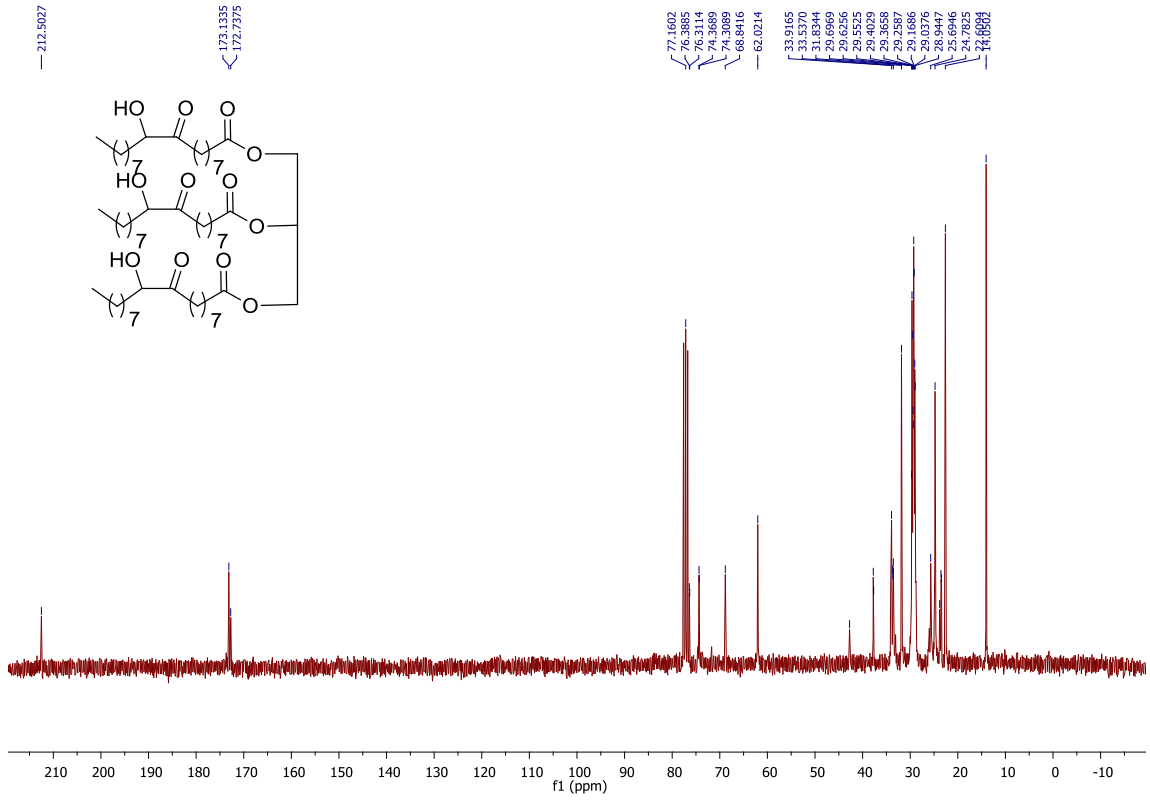
^{13}C-NMR (75 MHz, $CDCl_3$) *Tetrahydrofuran derivatives* **21a** and **21b**



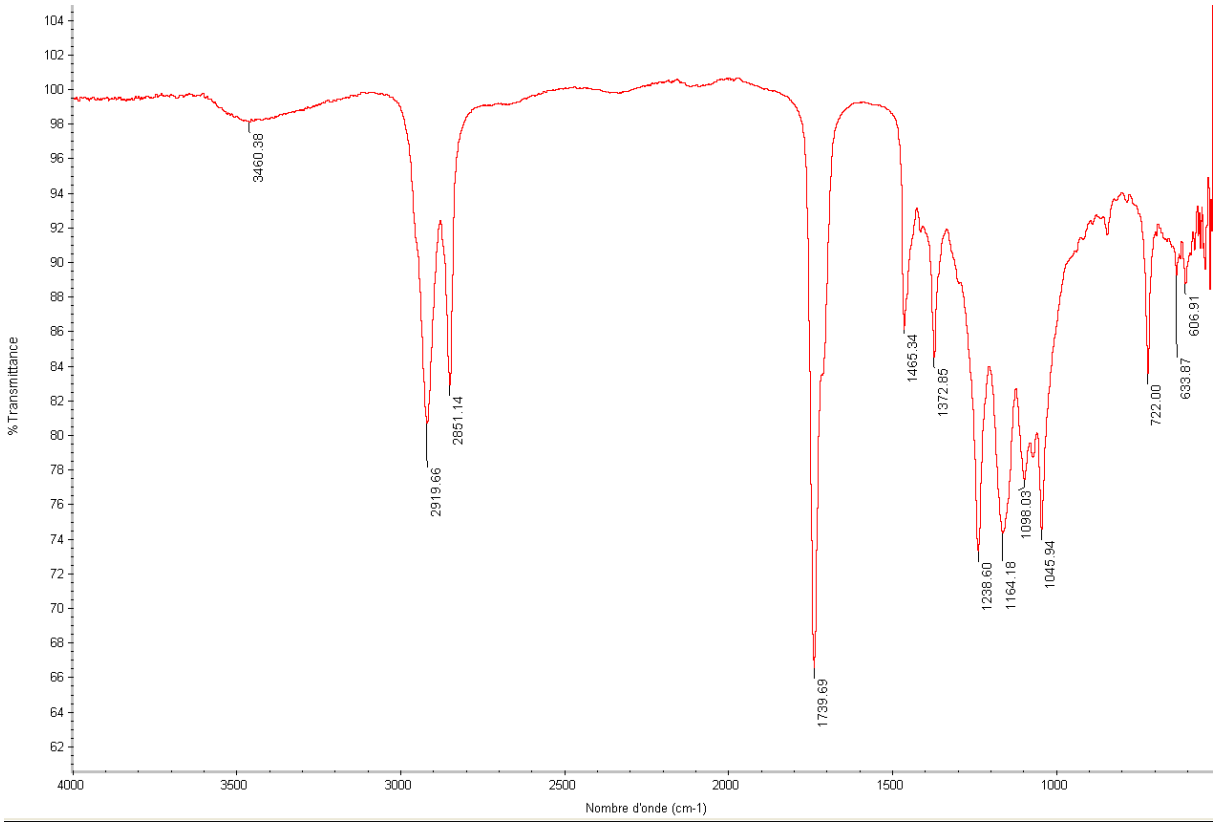
^{1}H-NMR (300 MHz, $CDCl_3$) *Tris(ketol) and tris(diol) high-oleic sunflower oil (**22**)*



^{13}C-NMR (75 MHz, $CDCl_3$) *Tris(ketol) and tris(diol) high-oleic sunflower oil (**22**)*



IR *Tris(ketol) and tris(diol) high-oleic sunflower oil (**22**)*



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