SUPPORTING INFORMATION

A Novel Class of Organo- (Hydro-) Gelators Based on Ascorbic Acid

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Contents

Experimental section:

All chemicals were purchased from the Fluka Company and have been used without any further purification. All solvents used were HPLC grade. Structure determinations were carried out using a Bruker 400 MHz or 600 MHz NMR and Bruker micrOTOF-MS.

Syntheses:

(*S*)-2,5-dioxotetrahydrofuran-3-yl dodecanoate (1a): 30 g of finely powdered *L*-malic acid (0.22 mol) and 106.4 mL of lauroyl chloride (0.44 mol) were heated slowly up to 70 °C for 4 hours and then the reaction mixture was allowed to cool down to room temperature.The product was then precipitated with *n*-hexane in the following manner: a total of 400 mL *n*-hexane was added and the precipitate filtered, washed thoroughly with 200 mL *n*-hexane, and dried under vacuum. 60 g (90%) of **1a** was obtained as white powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.50 (dd, *J* = 9.5, 6.2 Hz, 1H), 3.36 (dd, *J* = 18.9, 9.6 Hz, 1H), 2.97 (dd, *J* = 18.9, 6.2 Hz, 1H), 2.40 (t, *J* = 7.5 Hz, 2H), 1.72 – 1.53 (m, 2H), 1.26 (d, *J* = 14.9 Hz, 16H), 0.86 (t, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.59, 167.97, 166.61, 67.46, 35.05, 33.35, 32.20, 31.81, 29.48, 29.30, 29.22, 29.06, 28.84, 24.50, 22.57, 13.98 ppm.

(*S*)-2,5-dioxotetrahydrofuran-3-yl tetradecanoate (1b): 30 g of *L*-malic acid (0.22 mol) was reacted as described for the synthesis of **1a** with 121.6 mL of tetradecanoyl chloride (0.44 mol)**.** 67 g of **1b** (92%) was obtained as white powder.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 5.54 (dd, *J* = 9.6, 6.3 Hz, 1H), 3.39 (dd, *J* = 18.9, 9.5 Hz, 1H), 3.01 (dd, *J* = 18.9, 6.3 Hz, 1H), 2.50 – 2.38 (m, 2H), 1.72 – 1.55 (m, 2H), 1.50 – 1.07 (m, 20H), 0.89 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ = 172.60, 167.90, 166.51, 67.45, 35.10, 33.39, 31.86, 29.61, 29.58, 29.57, 29.51, 29.33, 29.28, 29.10, 28.87, 24.53, 22.62, 14.03 ppm.

***(S)*-2,5-dioxotetrahydrofuran-3-yl palmitate (1c):** 30 g of *L*-malic acid (0.22 mol) was reacted as described for the synthesis of **1a** with 135.8 mL of palmitoyl chloride (0.44 mol)**.** 73 g of **1c** (92%) was obtained as white powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.51 (dd, *J* = 9.6, 6.2 Hz, 1H), 3.36 (dd, *J* = 18.9, 9.5 Hz, 1H), 2.99 (dd, *J* = 18.8, 6.2 Hz, 1H), 2.41 (t, *J* = 7.5 Hz, 2H), 1.76 – 1.52 (m, 2H), 1.27 (d, *J* = 17.0 Hz, 24H), 0.87 (t, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.57, 167.82, 166.41, 67.43, 35.13, 33.41, 31.88, 29.64, 29.62, 29.61, 29.58, 29.52, 29.34, 29.30, 29.11, 28.89, 24.55, 22.63, 14.04 ppm.

(3*R*,4*R*)-2,5-dioxotetrahydrofuran-3,4-diyl didodecanoate (2a): 142.3 mL of lauroyl chloride (0.6 mol) was added to 30 g of finely powdered *L*-tartaric acid (0.2 mol) in a round bottom flask under stirring and the reaction mixture was heated at 90 ^{o}C for 24 hours and then cooled to room temperature. The product was precipitated with *n*-hexane in the following manner: a total of 400 mL *n*-hexane was added, the precipitate filtered, washed thoroughly with 200 mL *n*-hexane, and dried under vacuum. 89 g of **2a** (90%) was obtained as white powder.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 5.68 (s, 2H), 2.59 – 2.35 (m, 4H), 1.69 (dt, *J* = 15.1, 7.5 Hz, 4H), 1.51 – 1.07 (m, 32H), 0.90 (t, *J* = 7.1 Hz, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ = 172.60, 163.48, 72.05, 33.30, 31.87, 29.55, 29.54, 29.36, 29.29, 29.12, 28.85, 24.51, 22.64, 14.04 ppm.

(3*R*,4*R*)-2,5-dioxotetrahydrofuran-3,4-diyl ditetradecanoate (2b): 30 g of *L*-tartaric acid (0.2 mol) was reacted with 162.1 mL of tetradecanoyl chloride (0.6 mol) as described for **2a**. 99 g of **2b** (90%) was obtained as white powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.67 (s, 2H), 2.48 (t, *J* = 7.5 Hz, 4H), 1.82 – 1.52 (m, 4H), 1.30 (d, *J* = 16.1 Hz, 40H), 0.90 (t, *J* = 6.8 Hz, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.60, 163.50, 72.04, 33.28, 31.89, 29.64, 29.61, 29.54, 29.36, 29.32, 29.12, 28.84, 24.50, 22.65, 14.05 ppm.

(3*R*,4*R*)-2,5-dioxotetrahydrofuran-3,4-diyl dipalmitate (2c): 30 g of *L*-tartaric acid (0.2 mol) was reacted with 177.2 mL of palmitoyl chloride (0.6 mol) as described for **2a**. 111 g of **2c** (91%) was obtained as white powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.68 (s, 2H), 2.48 (t, *J* = 7.5 Hz, 4H), 1.81 – 1.54 (m, 4H), 1.52 – 1.08 (m, 48H), 0.91 (t, *J* = 6.8 Hz, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.62, 163.50, 72.06, 33.31, 31.93, 29.69, 29.67, 29.66, 29.64, 29.57, 29.39, 29.36, 29.15, 28.87, 24.52, 22.68, 14.09 ppm.

(2*R*,3*R*)-4-((*S*)-2-((*R*)-3,4-dihydroxy-5-oxo-2,5-dihydrofuran-2-yl)-2-hydroxyethoxy)-2,3-bis(dodecanoyloxy)-4-oxobutanoic acid (4a) : To a solution of 20 g *L*-ascorbic acid (0.114 mol) in 75 mL anhydrous DMF 11.3 g of **2a** (0.023 mol) was added. The reaction mixture was cooled to 0 °C and 1.83 mL of dry pyridine (0.023 mol) was added. Stirring was continued under argon atmosphere at 0 °C for 30 minutes and then for 3 days at room temperature. After completion of the reaction the mixture was poured into 2 N HCl at 0 °C under vigorous stirring. The reaction mixture was extracted with ethyl acetate and the organic fraction was washed 3 times with brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was precipitated twice with *n*-hexane to obtain 10.2 g of **4a (**67%) as white amorphous solid.

^{1}H NMR (400 MHz, MeOH-d_4) δ = 5.73 (d, *J*=7.1, 2H), 4.66 (s, 1H), 4.30 (d, *J*=5.8, 2H), 4.04 (s, 1H), 2.40 (s, 4H), 1.62 (s, 4H), 1.28 (s, 32H), 0.88 (s, 6H) ppm.

^{13}C NMR (101 MHz, MeOH-d_4) δ = 173.92, 173.86, 172.92, 168.91, 167.44, 153.67, 120.12, 76.88, 72.19, 71.82, 67.90, 67.08, 34.53, 33.05, 30.74, 30.59, 30.54, 30.45, 30.40, 30.35, 30.02, 25.88, 25.81, 23.70, 14.44 ppm.

HRMS (ESI$^-$, m/z, $[M-H]^-$) calculated for $C_{34}H_{55}O_{13}$: 671.3643. Found: 671.3638.

$[\alpha]^{20}_D$ +10.4 (c 0.6, MeOH).

(2*R*,3*R*)-4-((*S*)-2-((*R*)-3,4-dihydroxy-5-oxo-2,5-dihydrofuran-2-yl)-2-hydroxyethoxy)-4-oxo-2,3-bis(tetradecanoyloxy)butanoic acid (4b): To a solution of 20 g *L*-ascorbic acid (0.114 mol) in anhyhrous DMF (75 mL) 12.6 g of **2b** (0.023 mol) was added. The reaction mixture was cooled to 0 °C in an ice-water bath and 1.83 mL of dry pyridine (0.023 mol) was added. Stirring was continued under argon atmosphere at 0 °C for 30 minutes and then 3 days at room temperature. After completion of the reaction the mixture was poured into 2 N HCl at 0 °C under vigorous stirring. The reaction mixture was extracted with ethyl acetate, the organic fraction was washed 3 times with brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was precipitated twice with *n*-hexane to get 8.4 g (51%) of **4b** as a while solid.

^{1}H NMR (600 MHz, Acetone-d_6) δ = 5.79 (dt, *J* = 26.2, 13.1 Hz, 2H), 4.80 (d, *J* = 2.2 Hz, 1H), 4.37 (dd, *J* = 6.4, 3.8 Hz, 2H), 4.18 (td, *J* = 6.5, 2.2 Hz, 1H), 2.48 – 2.25 (m, 4H), 1.71 – 1.50 (m, 4H), 1.51 – 1.05 (m, 40H), 0.90 (t, *J* = 7.0 Hz, 6H) ppm.

^{13}C NMR (151 MHz, Acetone-d_6) δ = 173.40, 170.93, 168.16, 168.03, 167.27, 151.51, 120.78, 76.58, 72.22, 71.87, 68.18, 67.55, 34.80, 33.28, 31.25, 31.07, 31.04, 31.02, 30.89, 26.19, 26.15, 23.96, 23.96, 15.01ppm.

HRMS (ESI$^-$, m/z, $[M-H]^-$) calculated for $C_{38}H_{63}O_{13}$: 727.4274. Found: 727.4271.

$[\alpha]^{20}_D$ +7.2 (c 0.6, MeOH).

(2*R*,3*R*)-4-((*S*)-2-((*R*)-3,4-dihydroxy-5-oxo-2,5-dihydrofuran-2-yl)-2-hydroxyethoxy)-4-oxo-2,3-bis(palmitoyloxy)butanoic acid (4c): To a solution of 20 g *L*-ascorbic acid (0.114 mol) in anhyhrous DMF (75 mL) 13.8 g of **2c** (0.023 mol) was added. The reaction mixture was cooled to 0 °C in an ice-water bath and 1.83 mL of dry pyridine (0.023 mol) was added. Stirring was continued under argon atmosphere at 0 °C for 30 minutes and then 3 days at room temperature. After completion of the reaction the mixture was poured into 2 N HCl at 0 °C under vigorous stirring. The reaction mixture was extracted with ethyl acetate and the organic fraction was washed 3 times with brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was precipitated twice with *n*-hexane to get 11.2 g (63%) of **4c** as a while solid.

^{1}H NMR (400 MHz, Acetone-d_6) δ = 6.21 – 5.30 (m, 2H), 4.79 (d, *J* = 2.2 Hz, 1H), 4.37 (d, *J* = 6.5 Hz, 2H), 4.19 (td, *J* = 6.4, 2.1 Hz, 1H), 2.50 – 2.33 (m, 4H), 1.74 – 1.57 (m, 4H), 1.46 – 1.24 (m, 48H), 0.90 (t, *J* = 6.8 Hz, 6H) ppm.

^{13}C NMR (101 MHz, Acetone-d_6) δ = 173.49, 173.48, 170.85, 168.13, 167.44, 151.48, 121.01, 76.69, 72.40, 72.04, 68.44, 67.68, 34.96, 33.35, 31.25, 31.12, 31.08, 30.95, 30.92, 30.88, 30.76, 29.92, 26.29, 26.26, 24.01, 15.01 ppm.

HRMS (ESI$^-$, m/z, $[M-H]^-$) calculated for $C_{42}H_{71}O_{13}$:783.4895. Found : 783.4886.

$[\alpha]^{20}_D$ +4.4 (c 0.6, MeOH).

(*S*)-4-((*S*)-2-((*R*)-3,4-dihydroxy-5-oxo-2,5-dihydrofuran-2-yl)-2-hydroxyethoxy)-3-(dodecanoyloxy)-4-oxobutanoic acid (3a): To a solution of 20 g *L*-ascorbic acid (0.114 mol) in 75 mL anhydrous DMF 6.8 g of **1a** (0.023 mol) was added. The reaction mixture was cooled to 0 °C and 1.83 mL of dry pyridine (0.023 mol) was added. Stirring was continued under argon atmosphere at 0 °C for 30 minutes and 12 hours at room temperature. After completion of the reaction the mixture was poured into 2 N HCl at 0 °C under vigorous stirring. The reaction mixture was extracted with ethyl acetate and the organic fraction was washed 3 times with brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was washed twice with *n*-hexane to obtain 9.4 g of **3a** (87%) as white solid.

^{1}H NMR (400 MHz, MeOH-d_4) δ = 5.47 (dd, *J*=7.1, 4.9, 1H), 4.76 (d, *J*=2.1, 1H), 4.34 (dd, *J*=6.4, 4.3, 2H), 4.14 (td, *J*=6.4, 2.1, 1H), 2.91 (ddd, *J*=29.4, 15.2, 5.3, 2H), 2.50 – 2.31 (m, 2H), 1.64 (dd, *J*=14.4, 7.1, 2H), 1.46 – 1.14 (m, 16H), 0.92 (t, *J*=6.9, 3H) ppm.

^{13}C NMR (101 MHz, MeOH-d_4) δ = 174.33, 173.04, 172.71, 170.34, 153.85, 120.05, 76.98, 69.72, 67.71, 66.72, 36.67, 34.58, 33.00, 30.67, 30.51, 30.40, 30.33, 30.01, 25.82, 23.67, 14.42 ppm.

HRMS (ESI$^-$, m/z, [M-H]$^-$) calculated for $C_{22}H_{33}O_{11}$: 473.2023. Found: 473.2016.

$[\alpha]^{20}_D$ -4.1 (c 0.6, MeOH).

(*S*)-4-((*S*)-2-((*R*)-3,4-dihydroxy-5-oxo-2,5-dihydrofuran-2-yl)-2-hydroxyethoxy)-4-oxo-3-(tetradecanoyloxy)butanoic acid (3b): To a solution of 20 g *L*-ascorbic acid (0.114 mol) in 75 mL anhydrous DMF 7.4 g of **1b** (0.023 mol) was added. The reaction mixture was cooled to 0 °C and 1.83 mL of dry pyridine (0.023 mol) was added. Stirring was continued under argon atmosphere at 0 °C for 30 minutes and 12 hours at room temperature. After completion of the reaction the mixture was poured into 2 N HCl at 0 °C under vigorous stirring. The reaction mixture was extracted with ethyl acetate, the organic fraction was washed 3 times with brine, dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The residue was washed twice with *n*-hexane to obtain 9 g of **3b** (79%) as white solid.

^{1}H NMR (600 MHz, MeOH-d_4) δ = 5.48 (dd, *J* = 7.5, 4.6 Hz, 1H), 4.76 (d, *J* = 2.1 Hz, 1H), 4.34 (qd, *J* = 11.1, 6.4 Hz, 2H), 4.14 (td, *J* = 6.4, 2.0 Hz, 1H), 3.08 – 2.68 (m, 2H), 2.51 – 2.33 (m, 2H), 1.65 (dd, *J* = 14.9, 7.4 Hz, 2H), 1.53 – 1.09 (m, 20H), 0.92 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, MeOH-d_4) δ = 174.34, 173.04, 172.71, 170.36, 153.86, 120.08, 77.00, 69.74, 67.74, 66.73, 36.70, 34.60, 33.02, 30.75, 30.71, 30.68, 30.53, 30.42, 30.33, 30.03, 25.83, 23.67, 14.41 ppm.

HRMS (ESI$^-$, m/z, [M-H]$^-$) calculated for $C_{24}H_{37}O_{11}$: 501.2341. Found: 501.2340.

$[\alpha]^{20}_D$ -1.4 (c 0.6, MeOH).

(*S*)-4-((*S*)-2-((*R*)-3,4-dihydroxy-5-oxo-2,5-dihydrofuran-2-yl)-2-hydroxyethoxy)-4-oxo-3-(palmitoyloxy)butanoic acid (3c) : To a solution of 20 g *L*-ascorbic acid (0.114 mol) in 75 mL anhydrous DMF 8.1 g of **1c** (0.023 mol) was added. The reaction mixture was cooled to 0 °C and 1.85 mL of dry pyridine (0.023 mol) were added. Stirring was continued under argon atmosphere at 0 °C for 30 minutes and then 12 hours at room temperature. After completion of the reaction the mixture was poured into 2 N HCl at 0 °C with vigorous stirring. The reaction mixture was extracted with ethyl acetate and the organic fraction was washed 3 times with brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was washed twice with *n*-hexane to obtain 10.1 g of **3c** (84%) as white solid.

^{1}H NMR (400 MHz, MeOH-d_4) δ = 5.47 (dd, *J*=7.2, 4.9, 1H), 4.76 (d, *J*=2.1, 1H), 4.33 (dd, *J*=6.4, 4.4, 2H), 4.14 (d, *J*=2.1, 1H), 2.94 (dd, *J*=6.0, 3.3, 2H), 2.41 (t, *J*=7.3, 2H), 1.64 (d, *J*=7.4, 2H), 1.48 – 1.16 (m, 24H), 0.92 (t, *J*=6.8, 3H) ppm.

^{13}C NMR (101 MHz, MeOH-d_4) δ = 174.34, 173.06, 172.71, 170.36, 153.86, 120.08, 77.00, 69.74, 67.73, 66.74, 36.69, 34.61, 33.04, 30.76, 30.73, 30.70, 30.55, 30.44, 30.36, 30.05, 25.85, 23.69, 14.43 ppm.

HRMS (ESI$^-$, m/z, [M-H]$^-$) calculated for $C_{26}H_{41}O_{11}$: 529.2649. Found: 529.2653.

$[\alpha]^{20}_D$ -1.7 (c 0.6, MeOH).

Foaming properties: Numerous procedures have been described in the literature[1] for measuring the amount of foam formed by surfactant solutions in water. We decided to measure both foaming ability and stability based on such a literature procedure[1,2,3]. For this 0.1% solutions of the surfactants were prepared in water (double distilled) and 200 mL of such freshly prepared solutions were poured into a graduated cylinder. The solutions were manually beaten with a standardized

perforated disc with a frequency of 60 beats per minutes. The volume of the such produced foam was measured after 30 seconds and after 5 minutes, the values corresponding to foaming ability and stability, respectively.

Determination of HLB values: HLB values were determined using an emulsion comparative method for oil/water emulsions 20:80 (O/W) based on a published procedure[4] as follows: To 2 g of the corresponding oil, 200 mg of a mixture of two emulsifiers were added, one with a known HLB-value and one for which the HLB-value is unknown. The mixture was heated to 70–80 °C until the emulsifiers were fully dispersed. Using this approach, a series of mixtures with different weight proportions were prepared (normally 6–10). To these mixtures 8 mL portions of hot (70–80 °C) water were added and the mixtures were shaken intensively for 10 s or treated with an Ultra Turrax high performance disperser for 10 s. The thus prepared samples were subsequently stored at room temprature and inspected visually after 24h. As oil phases, paraffin oil ($r^{\#}_{HLB}$ = 10), canola oil r_{HLB} = 7) and toluene (r_{HLB} = 15) were employed.

$^{\#}r_{HLB}$ = required HLB value.

Figure S1: A photographic representation of the determination of HLB value.

DSC measurement: Gel to solution phase transition temperature (T_{gel}) was determined using a DSC instrument (Netzsch STA 409). DSC thermograms were recorded for all hydrogels (10%, w/v) in the temperature range of 20 °C to 80 °C with a heating rate of 1 °C/min. DSC thermograms (Figure S2) show an endothermic peak corresponding to the phase transition from gel to solution state.

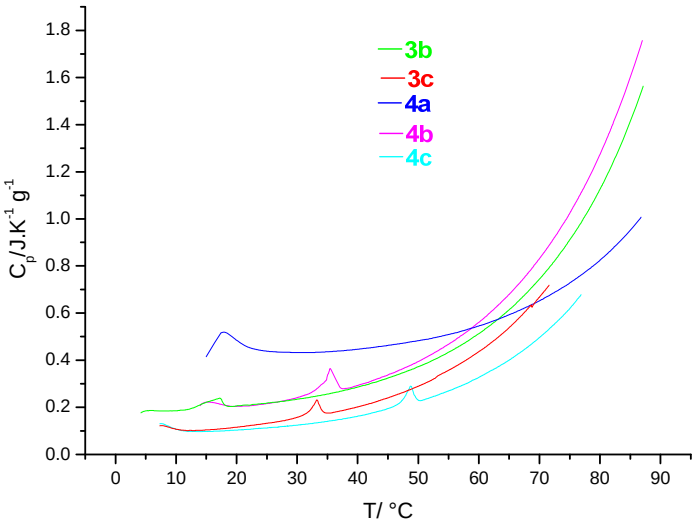


Figure S2: DSC thermographs of ascorbic acid amphiphiles **3b**, **3c**, **4a**, **4b**, **4c** in the temperature range of 20 °C to 80 °C.

Table S1: Minimum gelation concentrations (MGCs) and Tgel values of ascorbic acid amphiphiles in water

Compounds	MGC* (minimum gelation concentration, w/v).	T**gel
3a	10%	5 °C
3b	5.2%	17 °C
3c	0.9%	33 °C
4a	10.4%	18 °C
4b	4.5%	36 °C
4c	1.7%	49 °C

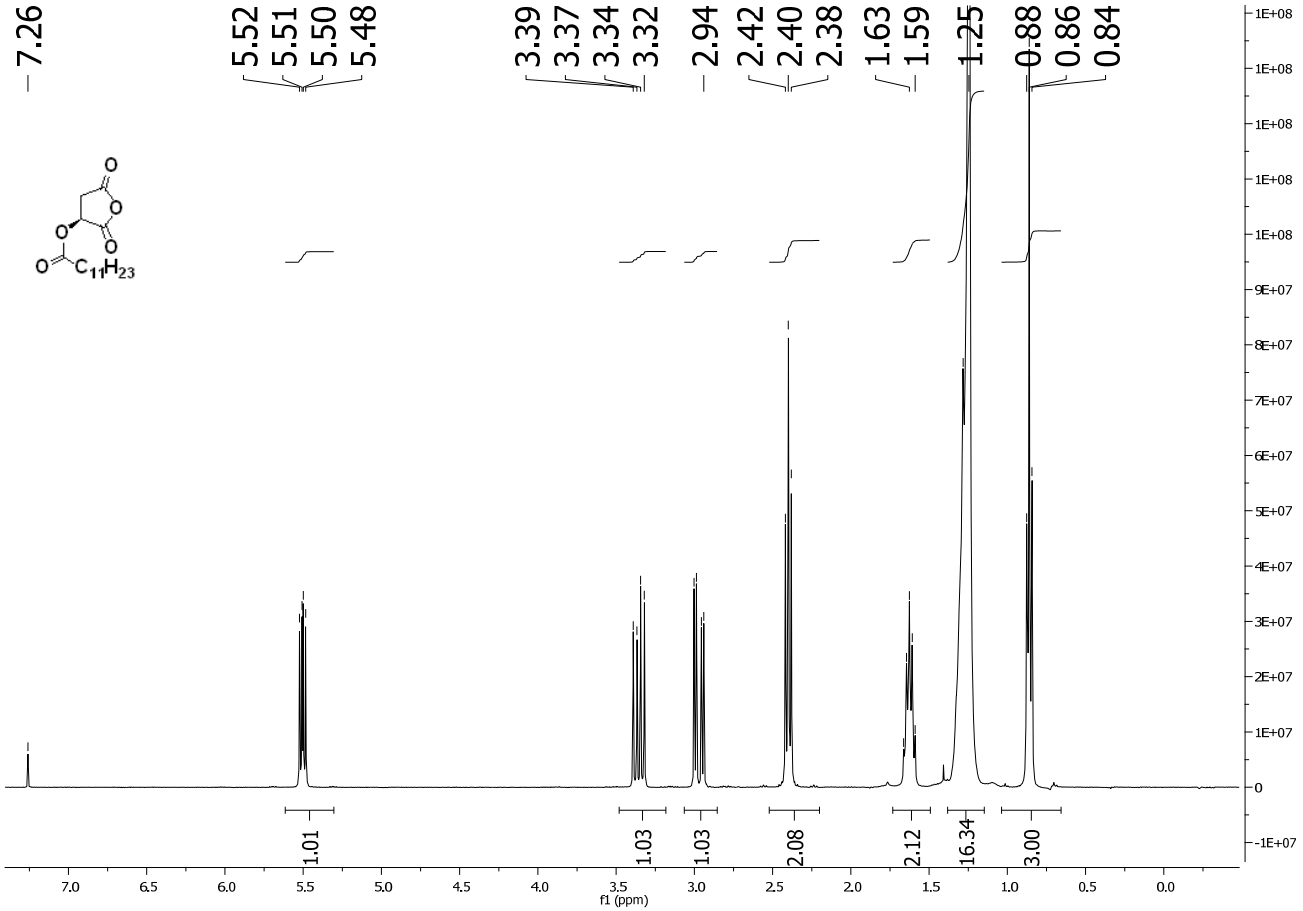
***** For **3a**, **3b** detemined at + 5 °C.
** For **3a** determined by inversion tube method.

Measurement of antioxidant activity: Antioxidant activity of these amphiphiles were determined using the stable free radical DPPH *(α-α*-biphenyl-*β*-picrylhydrazyl-radical) according to a slightly modified method described in the literature[5]. The antioxidant activities of these amphiphiles have been interpreted by comparing their "efficient concentration" or EC_{50} values (concentration of antioxidant which causes 50% loss of the DPPH radical activity). For this 3000 µL portions of the reaction mixture containing 2000 µL DPPH solution (approximately 60-100 µM in methanol) and 1000 µL of the amphiphiles at different concentrations were incubated at room temperature for 30 min and the absorbance of the test sample was determined at 517 nm using a UV-Vis spectrophotometer. Antioxidant activity towards DPPH radical was determined from the difference in absorbance with and without addition of amphiphile.

SEM measurement: SEM pictures of the xerogels were taken on a scanning electron microscopy spectrometer (Philips SFEG 30). The accelerating voltage was 15 kV, with 5 mm working distance .The Xerogel was prepared by freezing the hydrogel in liquid nitrogen and then water was evaporated by a vacuum pump Prior to examination. The xerogel was attached to a copper holder by using a conductive adhesive tape, and then coated with a thin layer of gold by the sputtering technique and was then observed in a SEM apparatus.

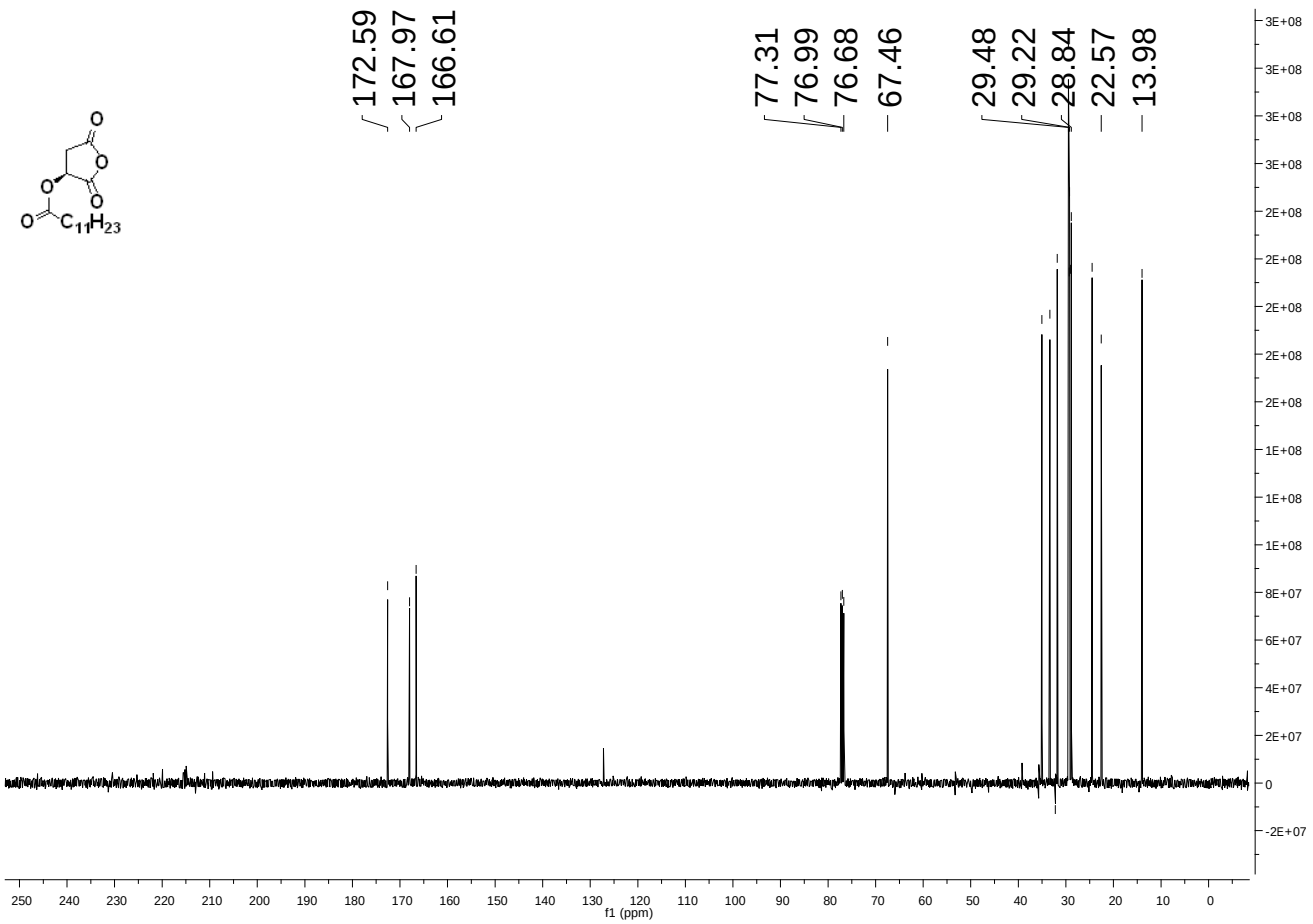
Apparatus for spectroscopy measurements: The FT-IR spectra of the sample **4a** in DMSO solution and xerogel (10%, w/v) in D_2O were recorded in an attenuated total reflectance (ATR) mode using a JASCO FT/IR-4200 infrared spectrometer.

(*S*)-2,5-dioxotetrahydrofuran-3-yl dodecanoate (1a):



^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.50 (dd, *J* = 9.5, 6.2 Hz, 1H), 3.36 (dd, *J* = 18.9, 9.6 Hz, 1H), 2.97 (dd, *J* = 18.9, 6.2 Hz, 1H), 2.40 (t, *J* = 7.5 Hz, 2H), 1.73 – 1.49 (m, 2H), 1.26 (d, *J* = 14.9 Hz, 16H), 0.86 (t, *J* = 6.8 Hz, 3H) ppm.

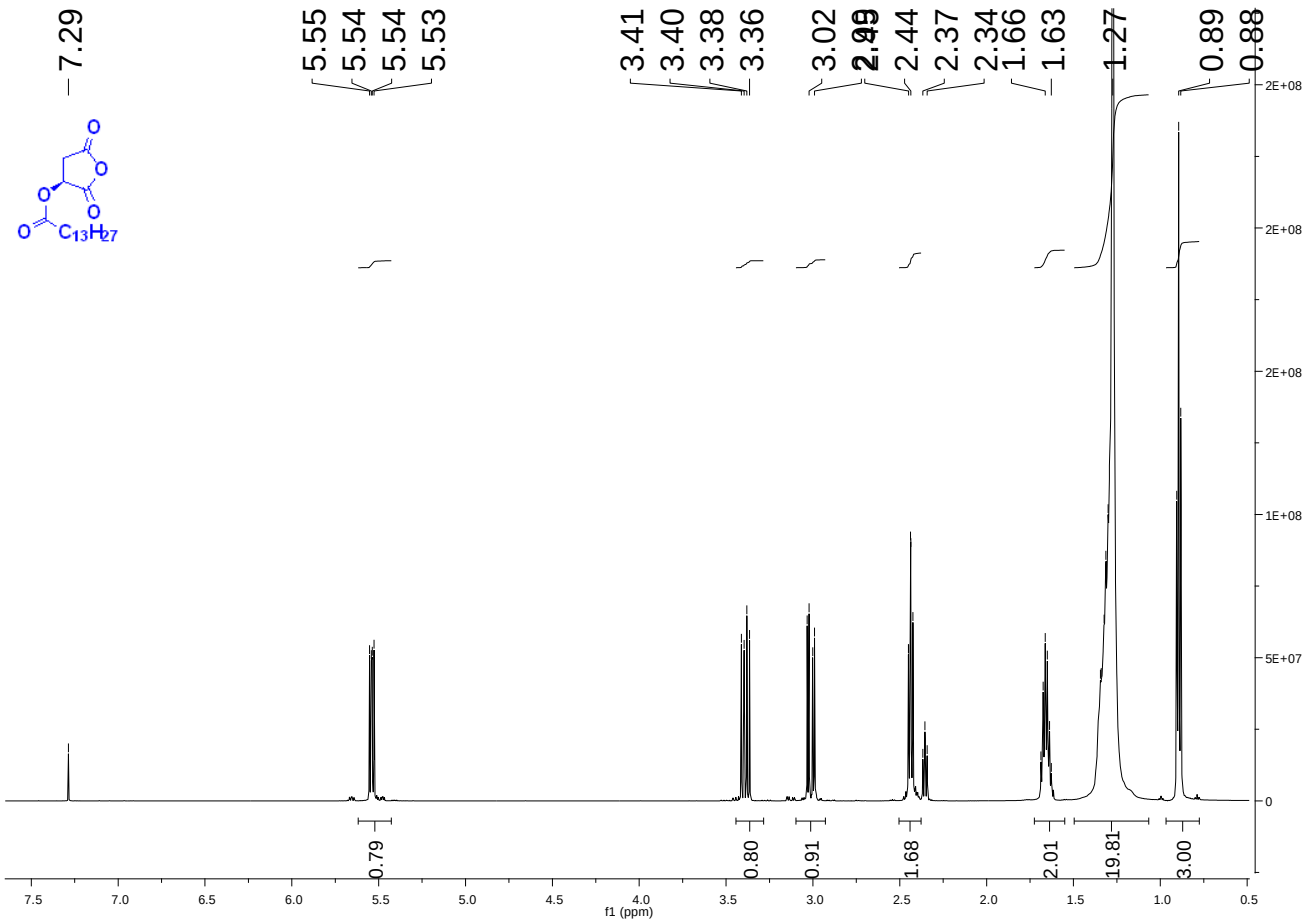
Figure S3: ^{1}H NMR spectrum of **1a** in $CDCl_3$ recorded at 298 ºK in a Bruker Avance spectrometer.



^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.59, 167.97, 166.61, 67.46, 35.05, 33.35, 32.20, 31.81, 29.48, 29.30, 29.22, 29.06, 28.84, 24.50, 22.57, 13.98 ppm.

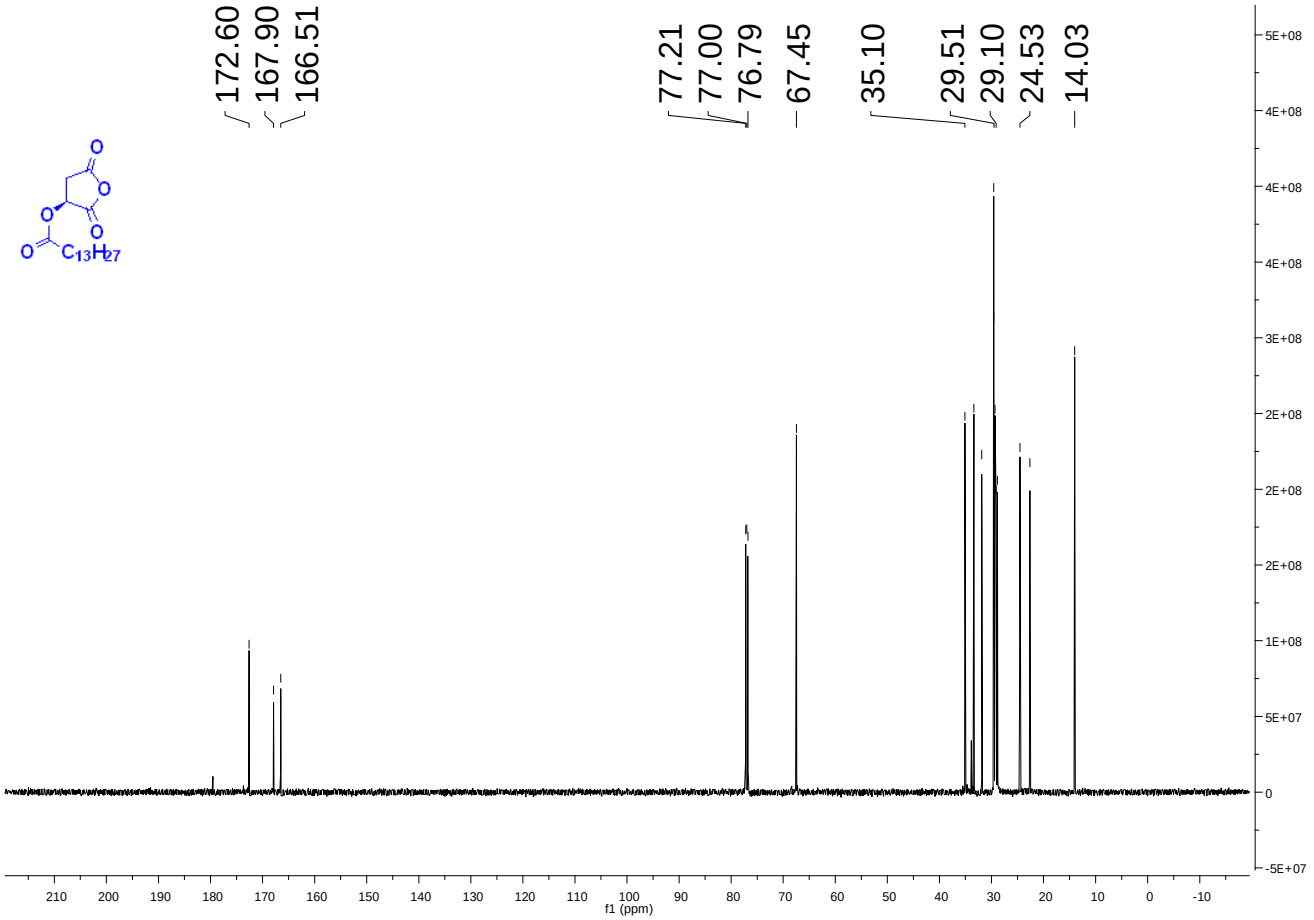
Figure S4: ^{13}C NMR spectrum of **1a** in $CDCl_3$ recorded at 298 ºK in a Bruker Avance spectrometer.

(*S*)-2,5-dioxotetrahydrofuran-3-yl tetradecanoate (1b):



^{1}H NMR (600 MHz, $CDCl_3$) δ = 5.54 (dd, *J* = 9.6, 6.3 Hz, 1H), 3.39 (dd, *J* = 18.9, 9.5 Hz, 1H), 3.01 (dd, *J* = 18.9, 6.3 Hz, 1H), 2.50 – 2.38 (m, 2H), 1.72 – 1.55 (m, 2H), 1.50 – 1.07 (m, 20H), 0.89 (t, *J* = 7.1 Hz, 3H) ppm.

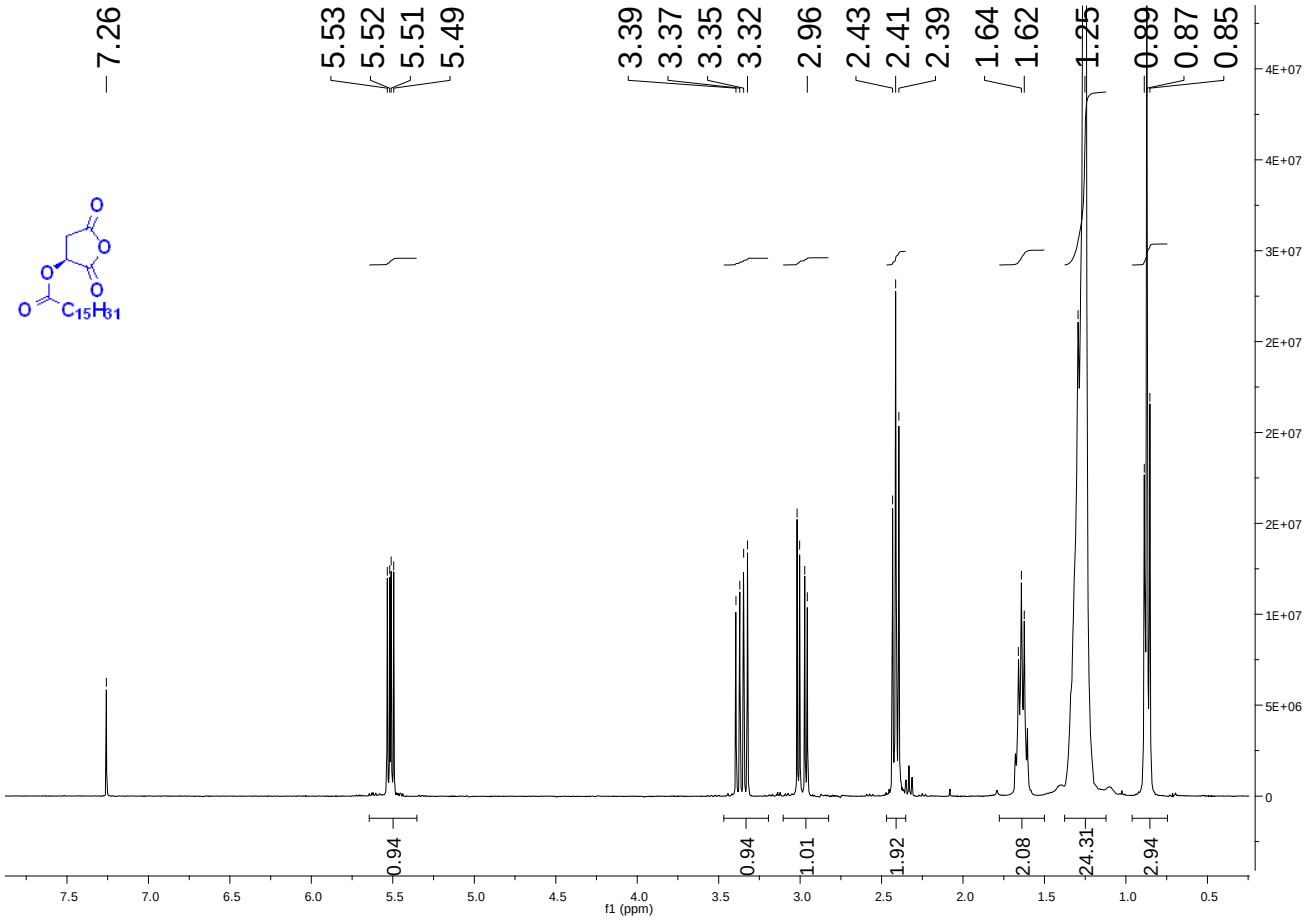
Figure S5: ^{1}H NMR spectrum of **1b** in $CDCl_3$ recorded at 298 ºK in a Bruker Avance spectrometer.



^{13}C NMR (151 MHz, $CDCl_3$) δ = 172.60, 167.90, 166.51, 67.45, 35.10, 33.39, 31.86, 29.61, 29.58, 29.57, 29.51, 29.33, 29.28, 29.10, 28.87, 24.53, 22.62, 14.03 ppm.

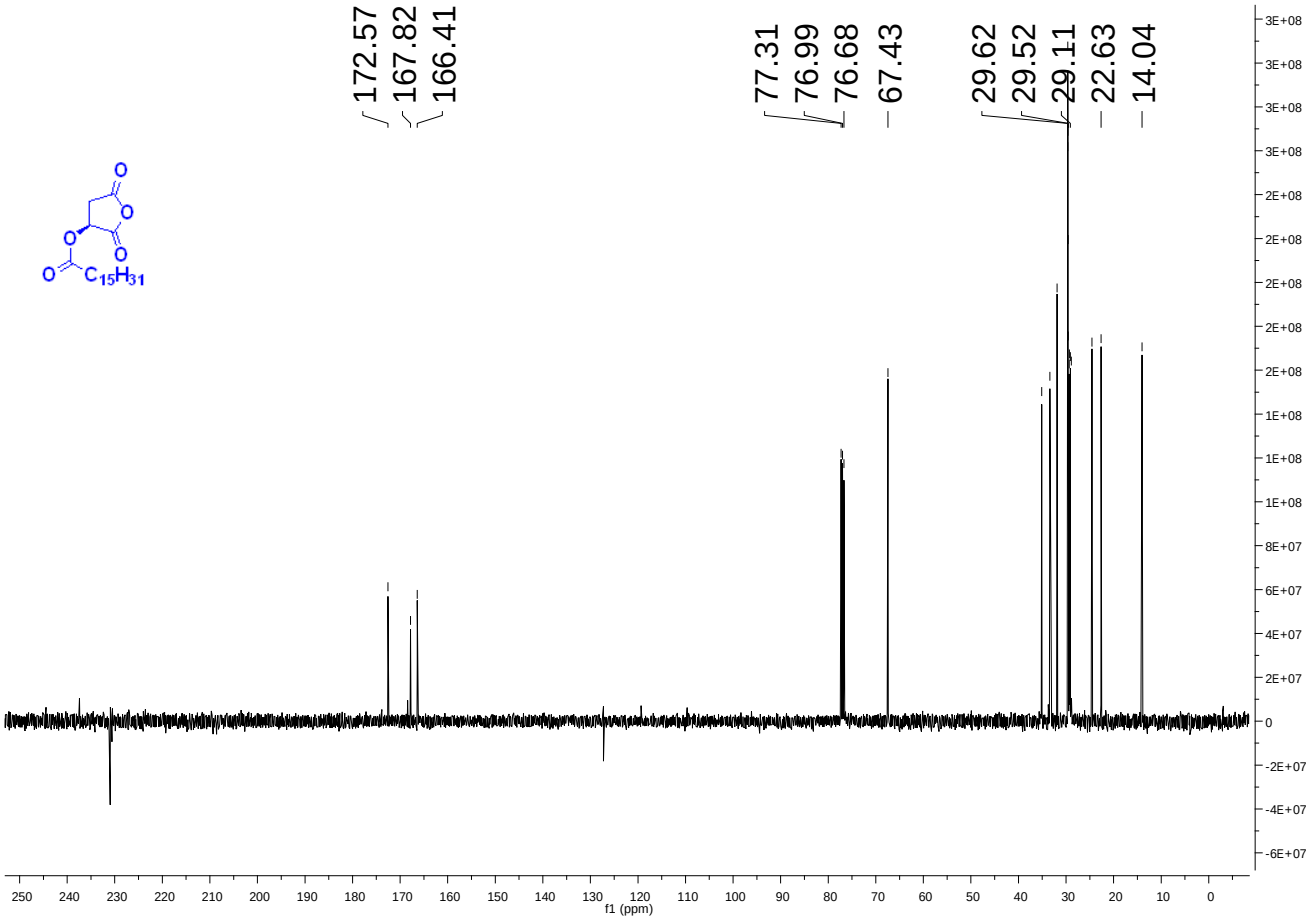
Figure S6: ^{13}C NMR spectrum of **1b** in $CDCl_3$ recorded at 298 ºK in a Bruker Avance spectrometer.

(*S*)-2,5-dioxotetrahydrofuran-3-yl palmitate (1c):



^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.51 (dd, *J* = 9.6, 6.2 Hz, 1H), 3.36 (dd, *J* = 18.9, 9.5 Hz, 1H), 2.99 (dd, *J* = 18.8, 6.2 Hz, 1H), 2.41 (t, *J* = 7.5 Hz, 2H), 1.76 – 1.52 (m, 2H), 1.27 (d, *J* = 17.0 Hz, 24H), 0.87 (t, *J* = 6.8 Hz, 3H) ppm.

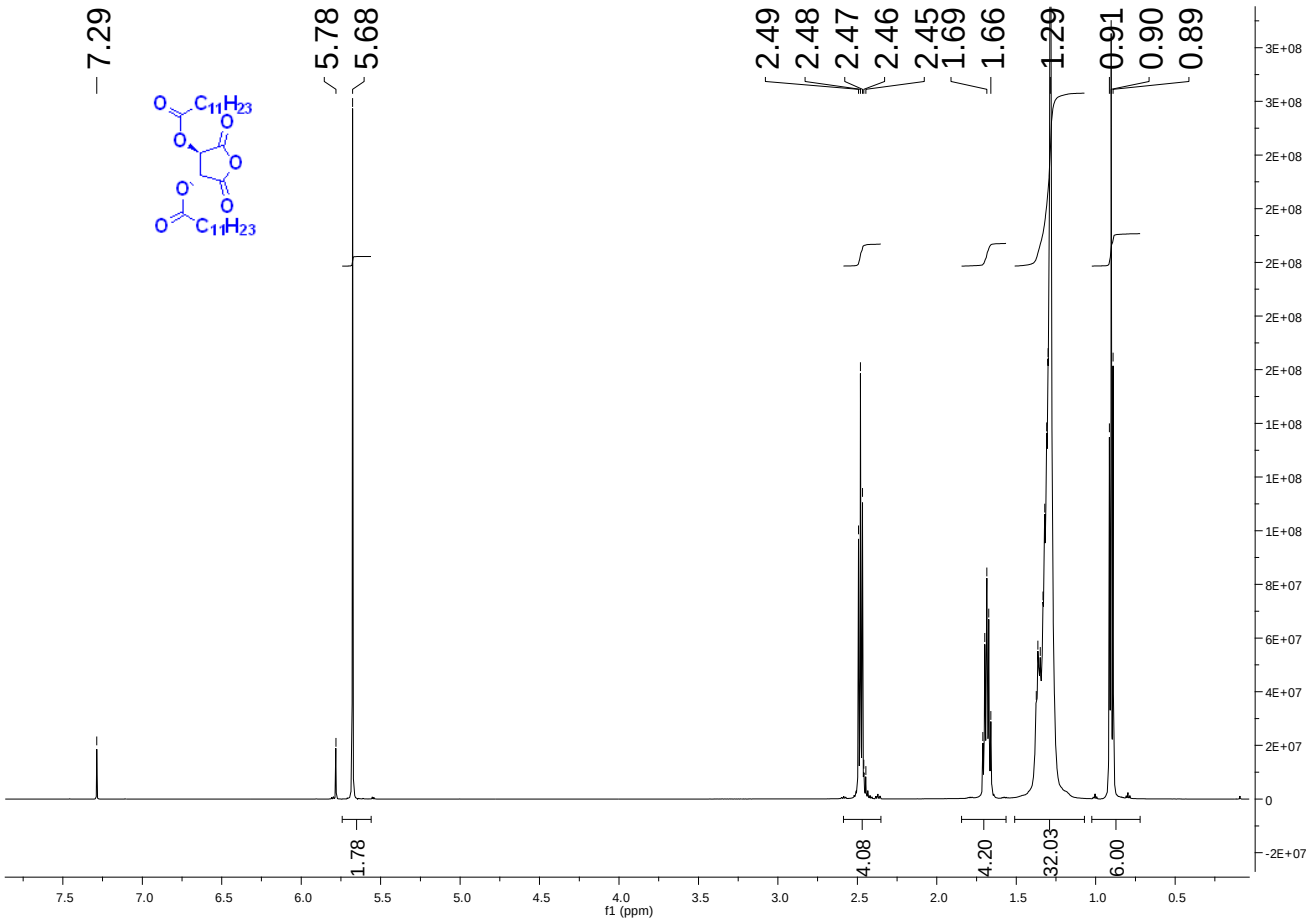
Figure S7: ^{1}H NMR spectrum of **1c** in $CDCl_3$ recorded at 298 ºK in a Bruker Avance spectrometer.



^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.57, 167.82, 166.41, 67.43, 35.13, 33.41, 31.88, 29.64, 29.62, 29.61, 29.58, 29.52, 29.34, 29.30, 29.11, 28.89, 24.55, 22.63, 14.04 ppm.

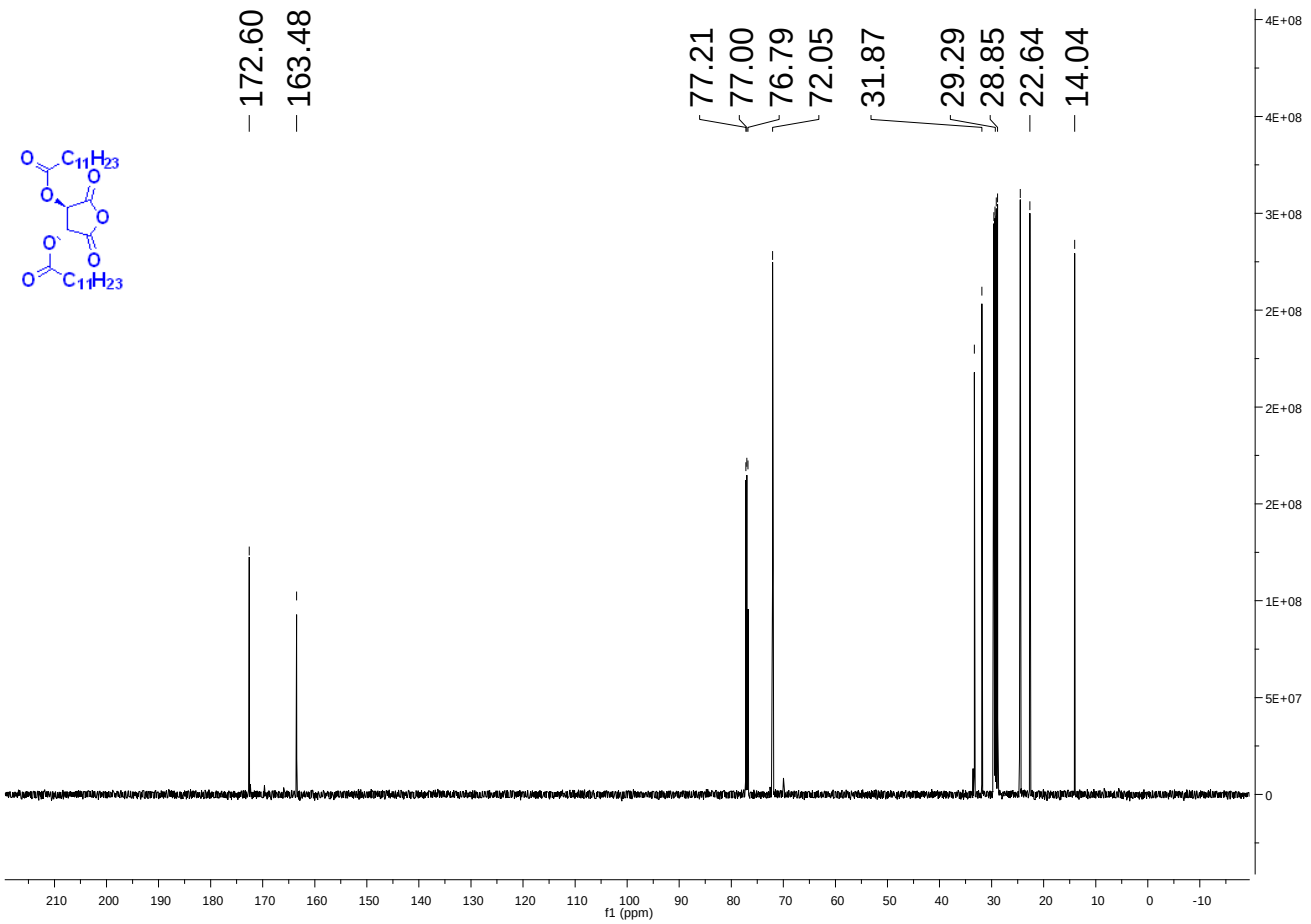
Figure S8: ^{13}C NMR spectrum of **1c** in $CDCl_3$ recorded at 298 ºK in a Bruker Avance spectrometer.

(*3R,4R*)-2,5-dioxotetrahydrofuran-3,4-diyl didodecanoate (2a):



^{1}H NMR (600 MHz, $CDCl_3$) δ = 5.68 (s, 2H), 2.59 – 2.35 (m, 4H), 1.69 (dt, *J* = 15.1, 7.5 Hz, 4H), 1.51 – 1.07 (m, 32H), 0.90 (t, *J* = 7.1 Hz, 6H) ppm.

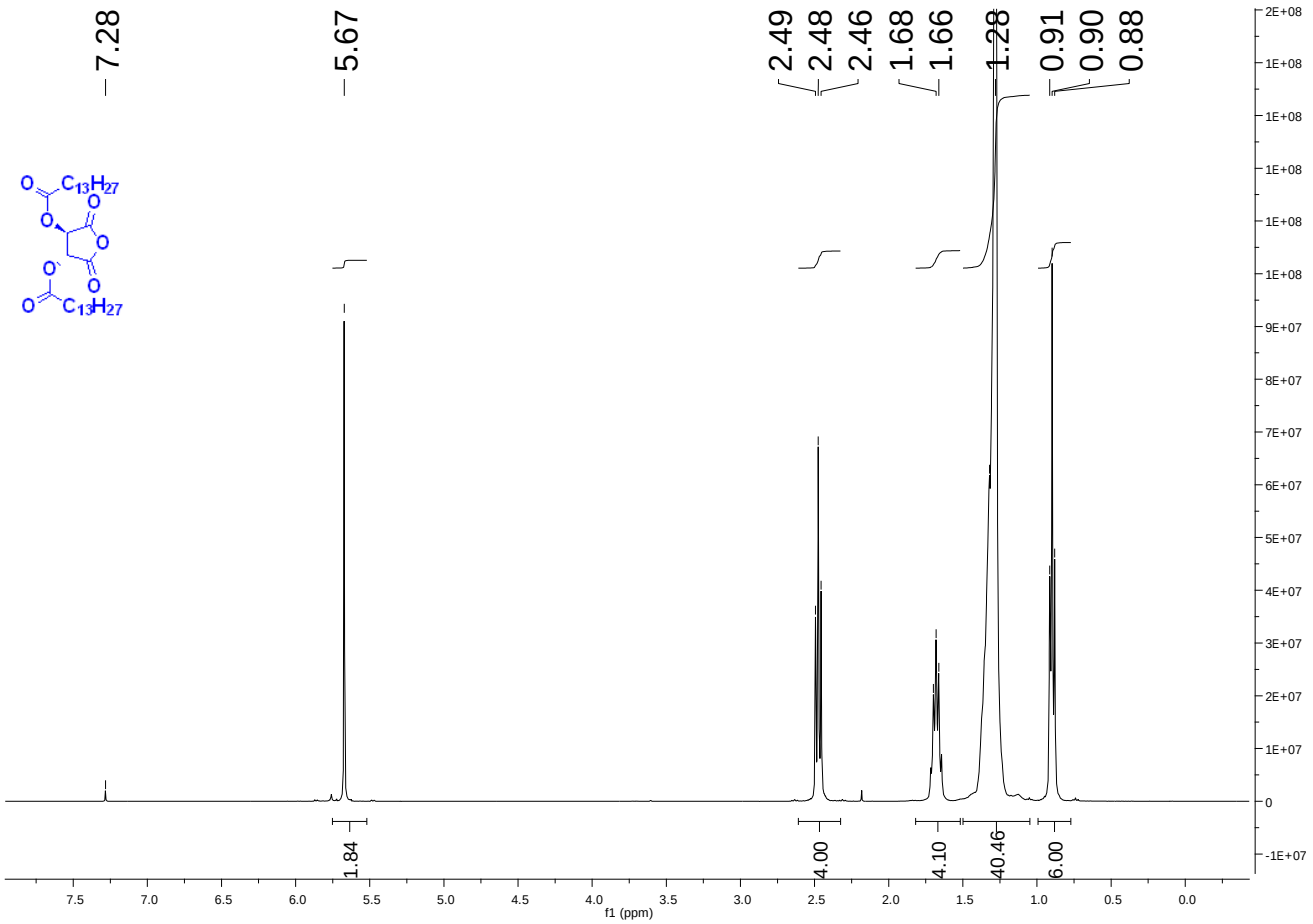
Figure S9: ^{1}H NMR spectrum of **2a** in $CDCl_3$ recorded at 298 ºK in a Bruker Avance spectrometer.



^{13}C NMR (151 MHz, $CDCl_3$) δ = 172.60, 163.48, 72.05, 33.30, 31.87, 29.55, 29.54, 29.36, 29.29, 29.12, 28.85, 24.51, 22.64, 14.04 ppm.

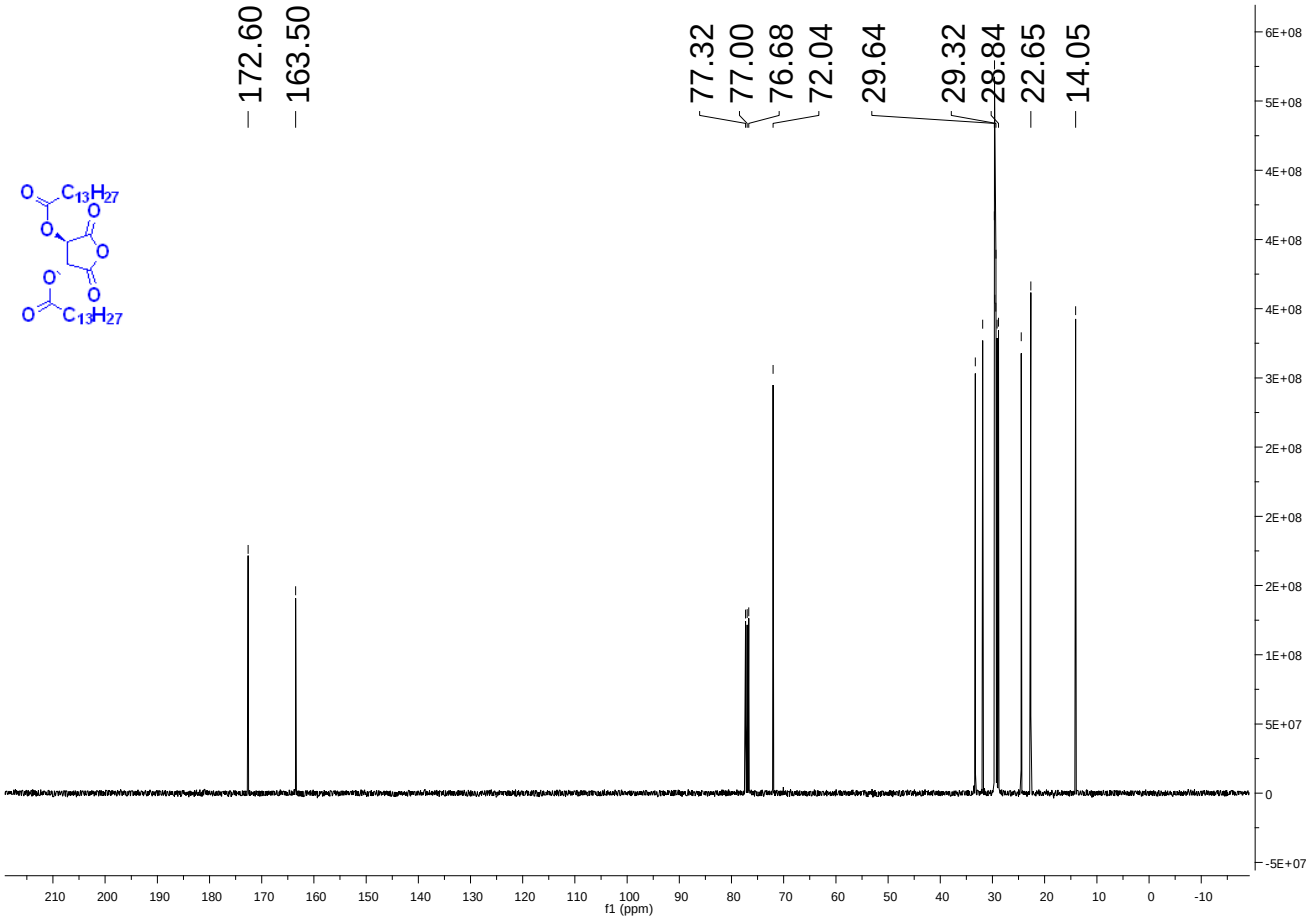
Figure S10: ^{13}C NMR spectrum of **2a** in $CDCl_3$ recorded at 298 ºK in a Bruker Avance spectrometer.

(3*R*,4*R*)-2,5-dioxotetrahydrofuran-3,4-diyl ditetradecanoate (2b):



^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.67 (s, 2H), 2.48 (t, *J* = 7.5 Hz, 4H), 1.82 – 1.52 (m, 4H), 1.30 (d, *J* = 16.1 Hz, 40H), 0.90 (t, *J* = 6.8 Hz, 6H) ppm.

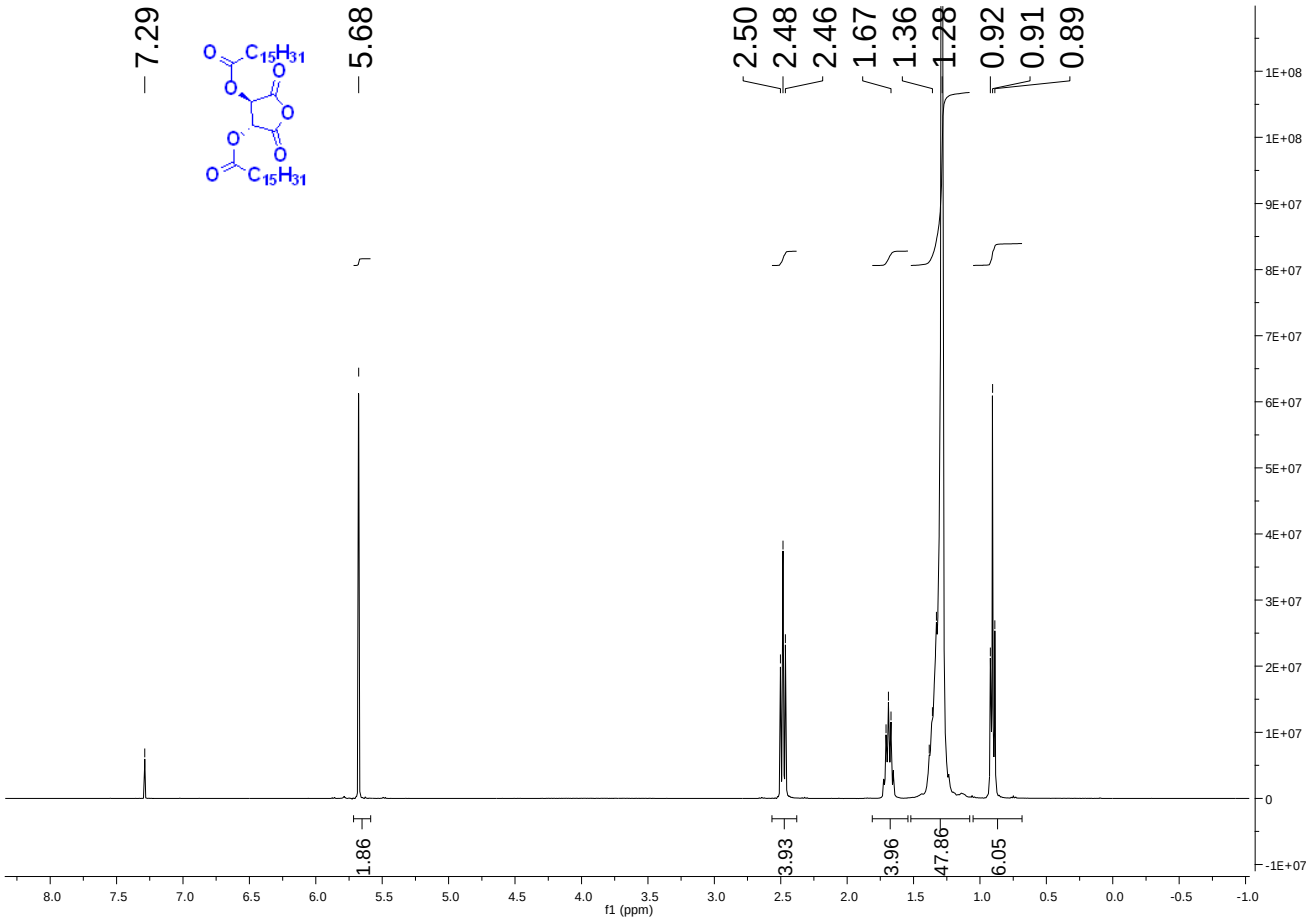
Figure S11: ^{1}H NMR spectrum of **2b** in $CDCl_3$ recorded at 298 ºK in a Bruker Avance spectrometer.



^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.60, 163.50, 72.04, 33.28, 31.89, 29.64, 29.61, 29.54, 29.36, 29.32, 29.12, 28.84, 24.50, 22.65, 14.05 ppm.

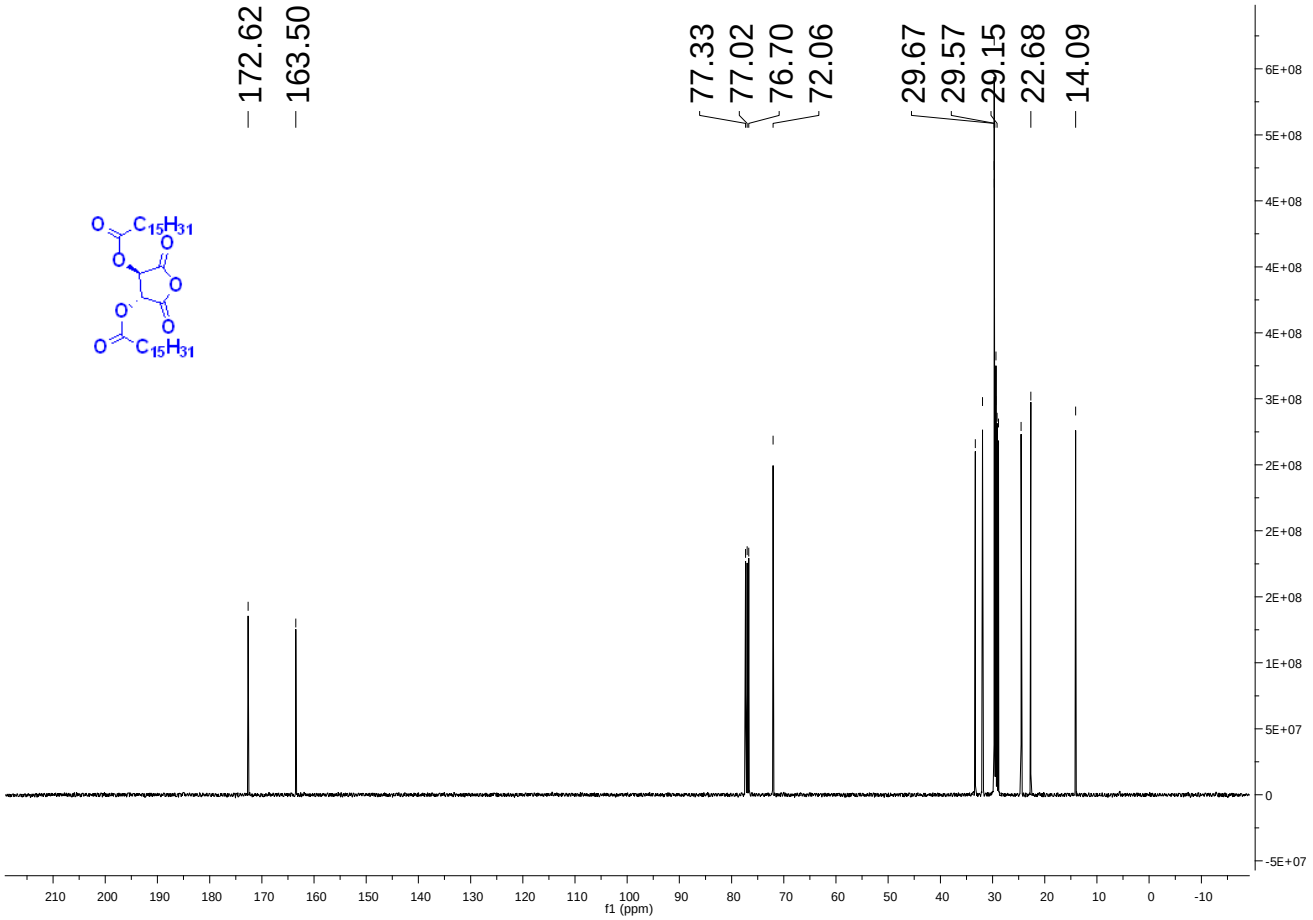
Figure S12: ^{13}C NMR spectrum of **2b** in $CDCl_3$ recorded at 298 ºK in a Bruker Avance spectrometer.

(3*R*,4*R*)-2,5-dioxotetrahydrofuran-3,4-diyl dipalmitate (2c):



^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.68 (s, 2H), 2.48 (t, *J* = 7.5 Hz, 4H), 1.81 – 1.54 (m, 4H), 1.52 – 1.08 (m, 48H), 0.91 (t, *J* = 6.8 Hz, 6H) ppm.

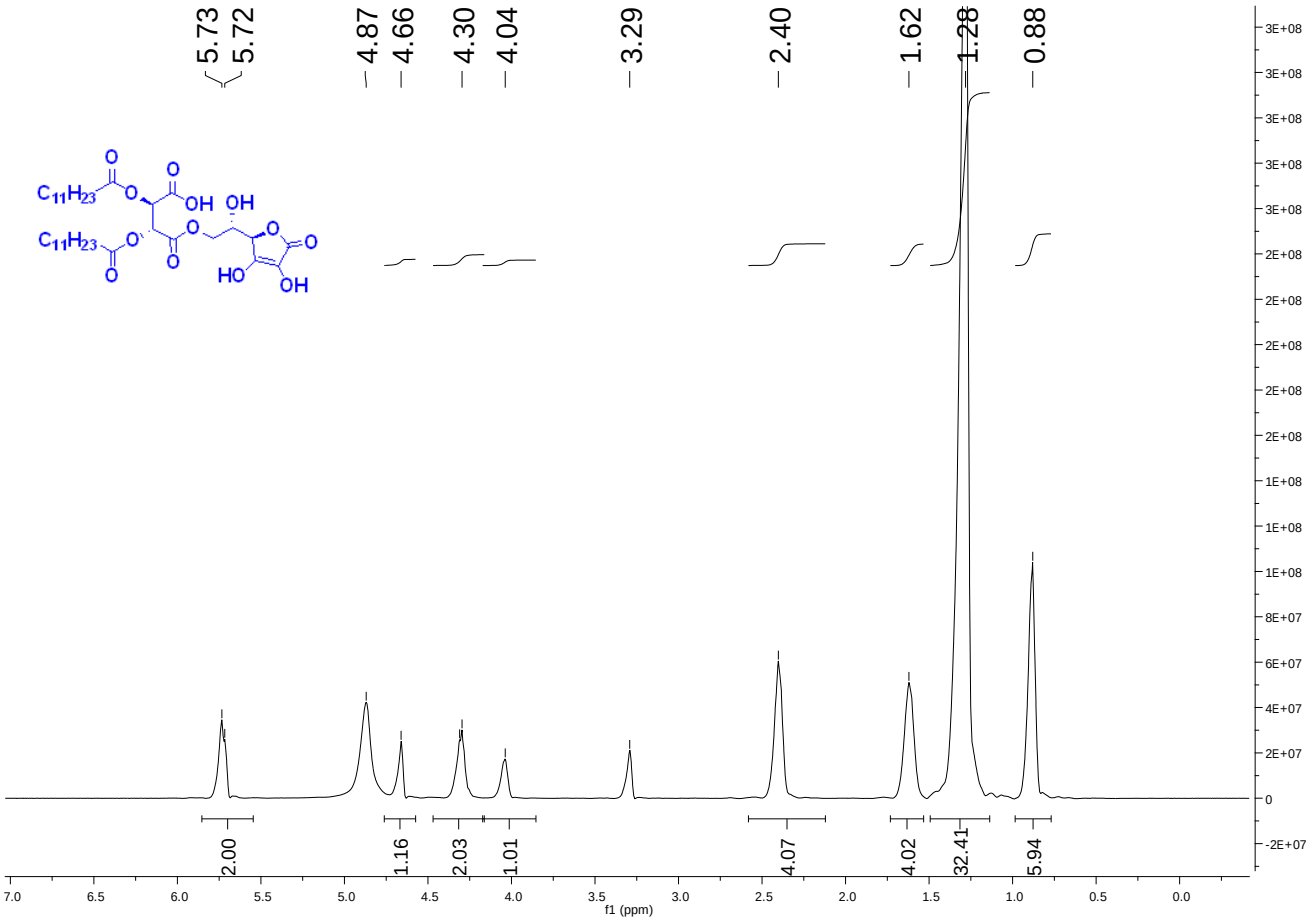
Figure S13: ^{1}H NMR spectrum of **2c** in $CDCl_3$ recorded at 298 ºK in a Bruker Avance spectrometer.



^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.62, 163.50, 72.06, 33.31, 31.93, 29.69, 29.67, 29.66, 29.64, 29.57, 29.39, 29.36, 29.15, 28.87, 24.52, 22.68, 14.09 ppm.

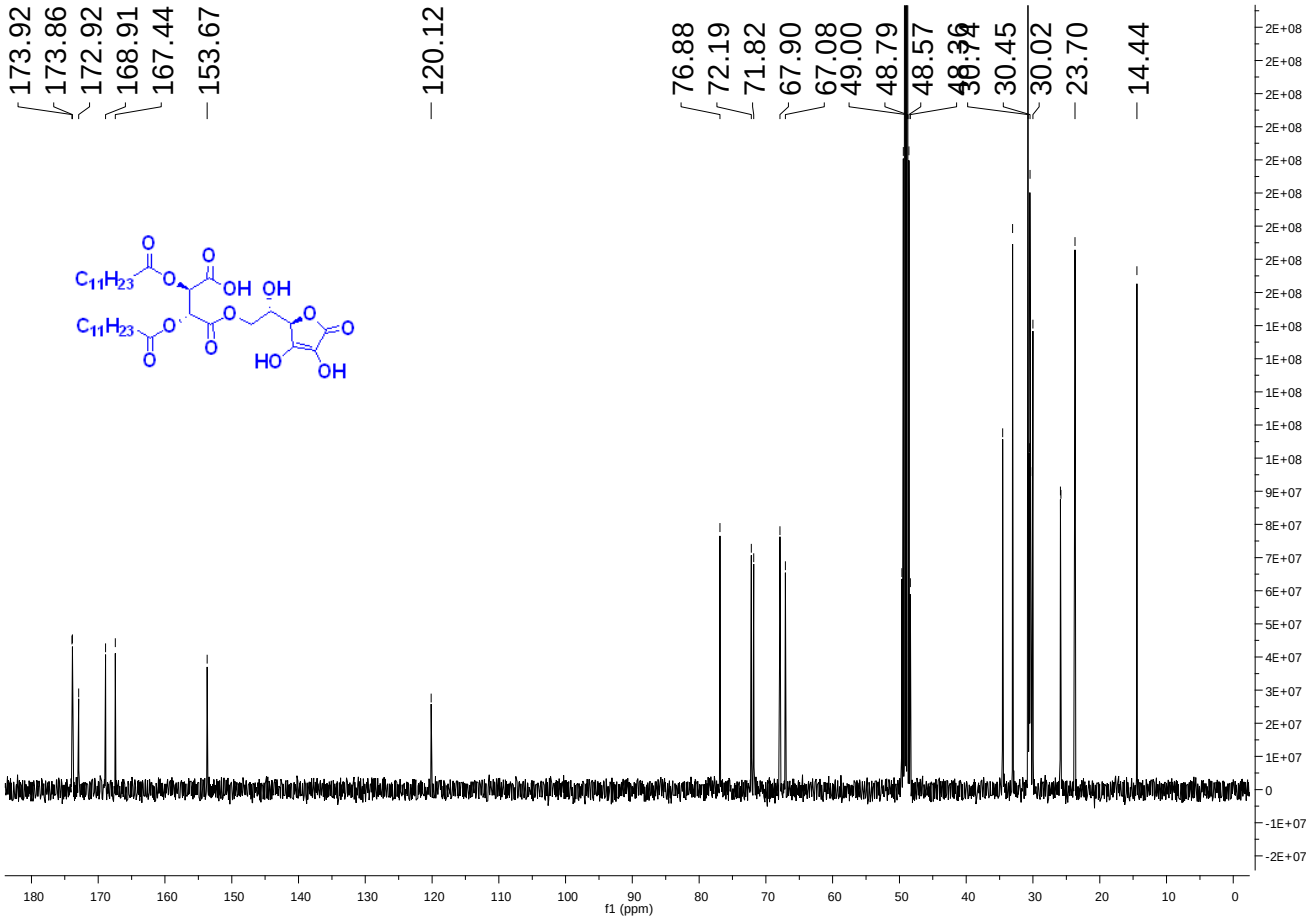
Figure S14: ^{13}C NMR spectrum of **2c** in $CDCl_3$ recorded at 298 ºK in a Bruker Avance spectrometer.

(2*R*,3*R*)-4-((*S*)-2-((*R*)-3,4-dihydroxy-5-oxo-2,5-dihydrofuran-2-yl)-2-hydroxyethoxy)-2,3-bis(dodecanoyloxy)-4-oxobutanoic acid (4a):



^{1}H NMR (400 MHz, MeOH-d$_4$) δ = 5.73 (d, *J*=7.1, 2H), 4.66 (s, 1H), 4.30 (d, *J*=5.8, 2H), 4.04 (s, 1H), 2.40 (s, 4H), 1.62 (s, 4H), 1.28 (s, 32H), 0.88 (s, 6H) ppm.

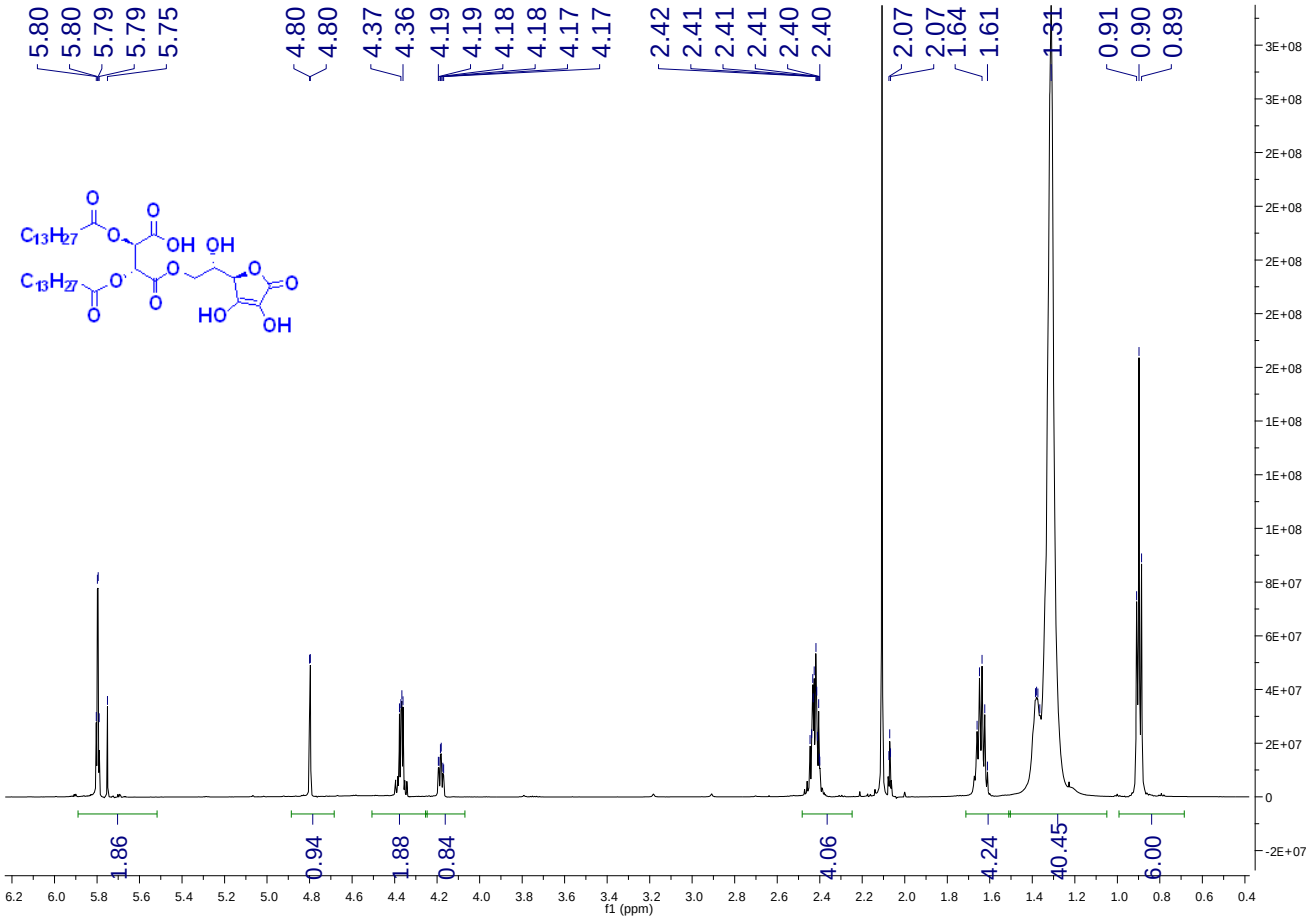
Figure S15: ^{1}H NMR spectrum of **4a** in MeOH-d$_4$ recorded at 300 ºK in a Bruker Avance spectrometer.



^{13}C NMR (101 MHz, MeOH-d_4) δ = 173.92, 173.86, 172.92, 168.91, 167.44, 153.67, 120.12, 76.88, 72.19, 71.82, 67.90, 67.08, 34.53, 33.05, 30.74, 30.59, 30.54, 30.45, 30.40, 30.35, 30.02, 25.88, 25.81, 23.70, 14.44 ppm.

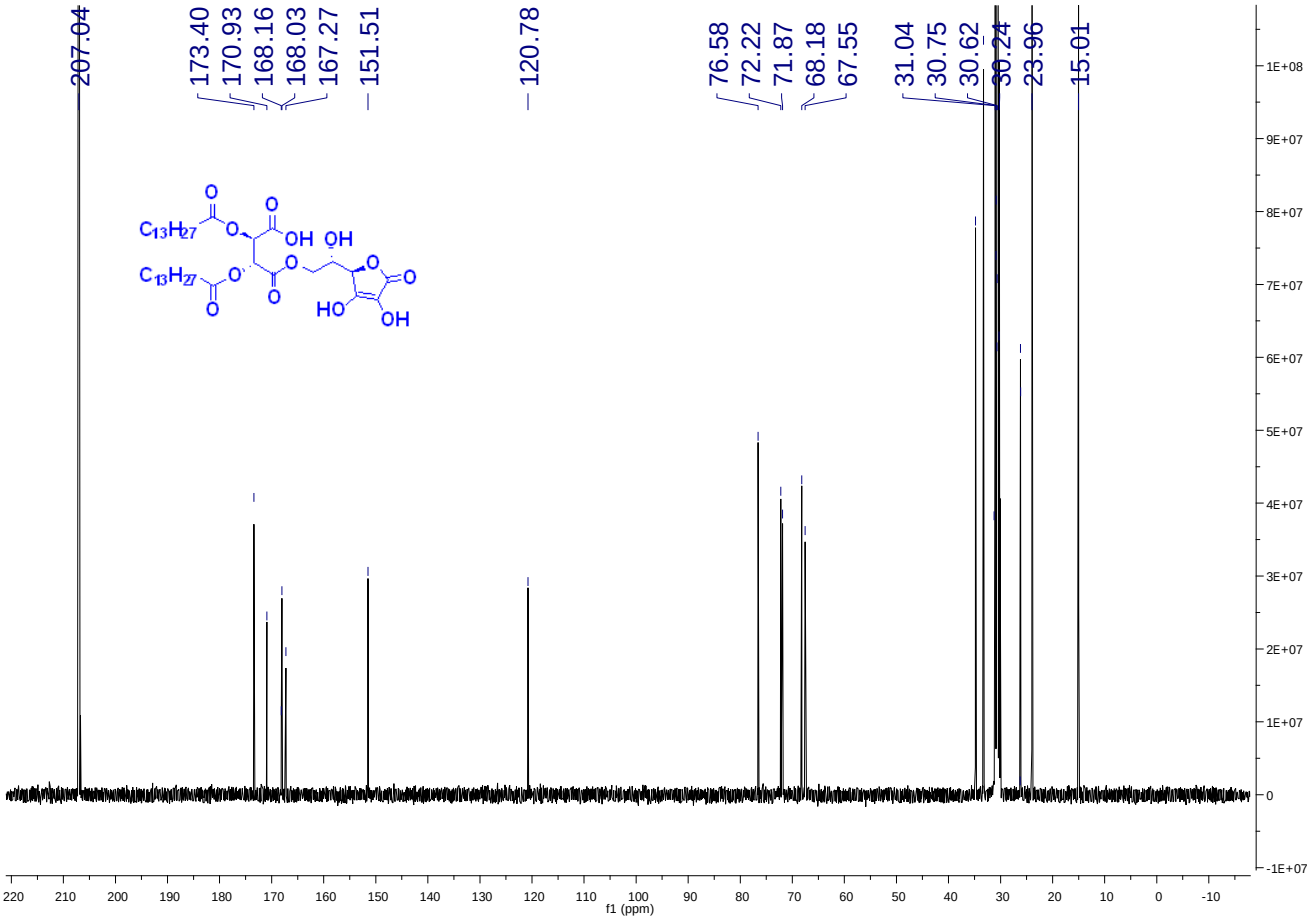
Figure S16: ^{13}C NMR spectrum of **4a** in MeOH-d_4 recorded at 300 ºK in a Bruker Avance spectrometer.

(2*R*,3*R*)-4-((*S*)-2-((*R*)-3,4-dihydroxy-5-oxo-2,5-dihydrofuran-2-yl)-2-hydroxyethoxy)-4-oxo-2,3-bis(tetradecanoyloxy)butanoic acid (4b):



^{1}H NMR (600 MHz, Acetone-d_6) δ = 5.79 (dt, *J* = 26.2, 13.1 Hz, 2H), 4.80 (d, *J* = 2.2 Hz, 1H), 4.37 (dd, *J* = 6.4, 3.8 Hz, 2H), 4.18 (td, *J* = 6.5, 2.2 Hz, 1H), 2.48 – 2.25 (m, 4H), 1.71 – 1.50 (m, 4H), 1.51 – 1.05 (m, 40H), 0.90 (t, *J* = 7.0 Hz, 6H) ppm.

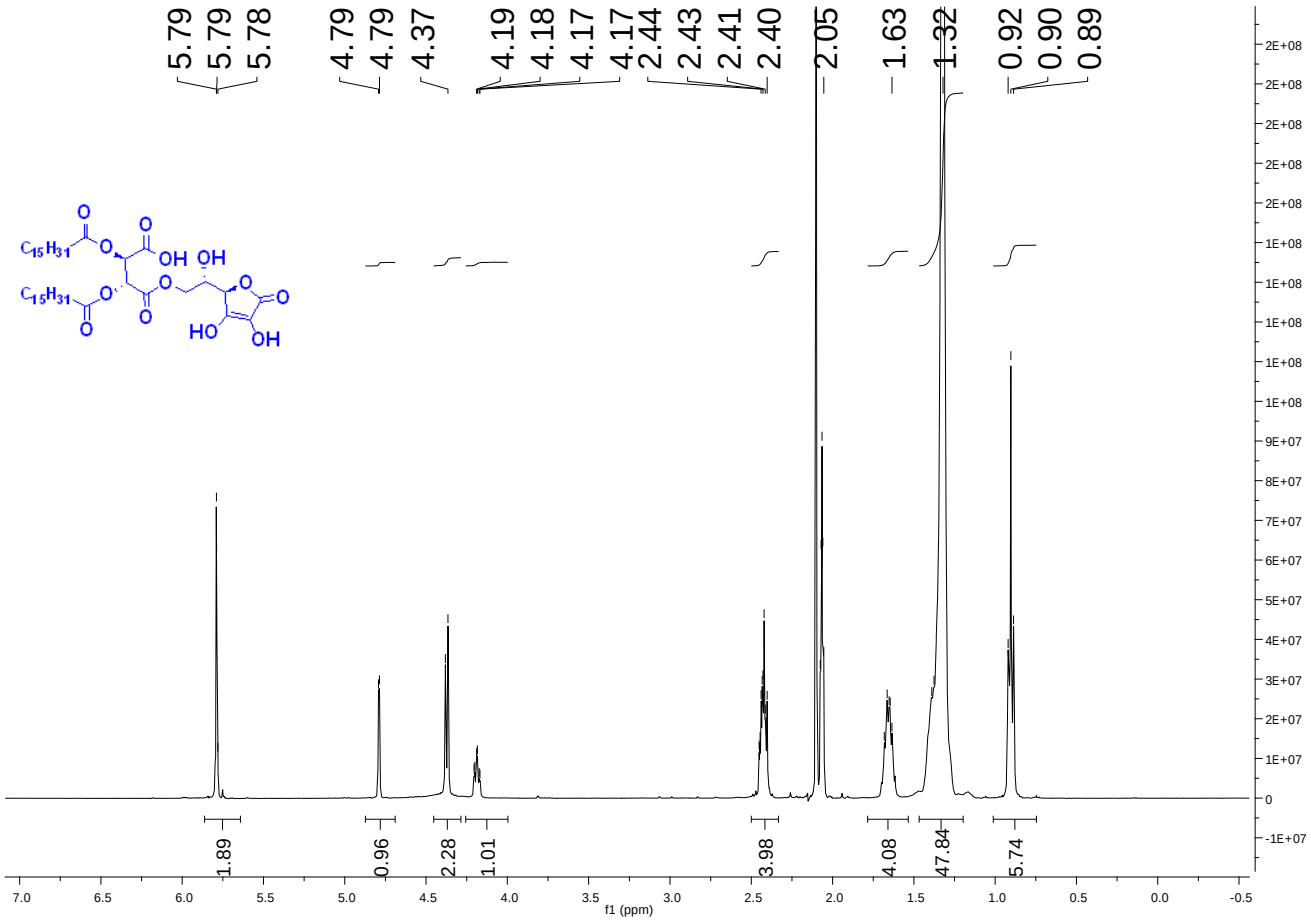
Figure S17: ^{1}H NMR spectrum of **4b** in Acetone-d_6 recorded at 300 ºK in a Bruker Avance spectrometer.



^{13}C NMR (151 MHz, Acetone-d_6) δ = 173.40, 170.93, 168.16, 168.03, 167.27, 151.51, 120.78, 76.58, 72.22, 71.87, 68.18, 67.55, 34.80, 33.28, 31.25, 31.07, 31.04, 31.02, 30.89, 26.19, 26.15, 23.96, 23.96, 15.01ppm.

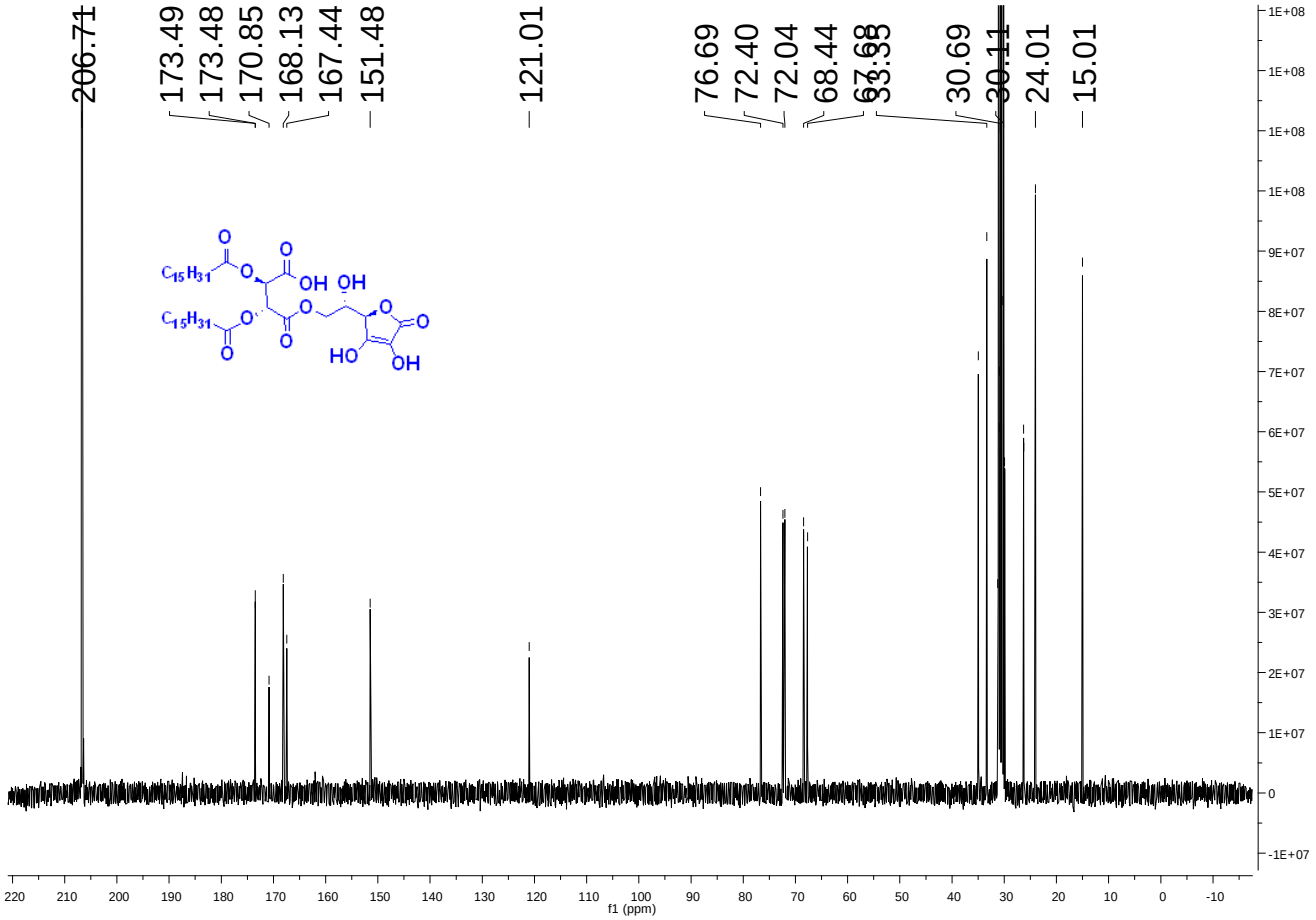
Figure S18: ^{13}C NMR spectrum of **4b** in Acetone-d_6 recorded at 300 ºK in a Bruker Avance spectrometer.

(2*R*, 3*R*)-4-((*S*)-2-((*R*)-3, 4-dihydroxy-5-oxo-2,5-dihydrofuran-2-yl)-2-hydroxyethoxy)-4-oxo-2,3-bis(palmitoyloxy)butanoic acid (4c):



^{1}H NMR (400 MHz, Acetone-d$_6$) δ = 5.82 – 5.76 (m, 2H), 4.79 (d, *J*=2.2, 1H), 4.37 (d, *J*=6.5, 2H), 4.19 (td, *J*=6.4, 2.1, 1H), 2.63 – 2.27 (m, 4H), 1.77 – 1.48 (m, 4H), 1.52 – 1.12 (m, 48H), 0.90 (t, *J*=6.8, 6H) ppm.

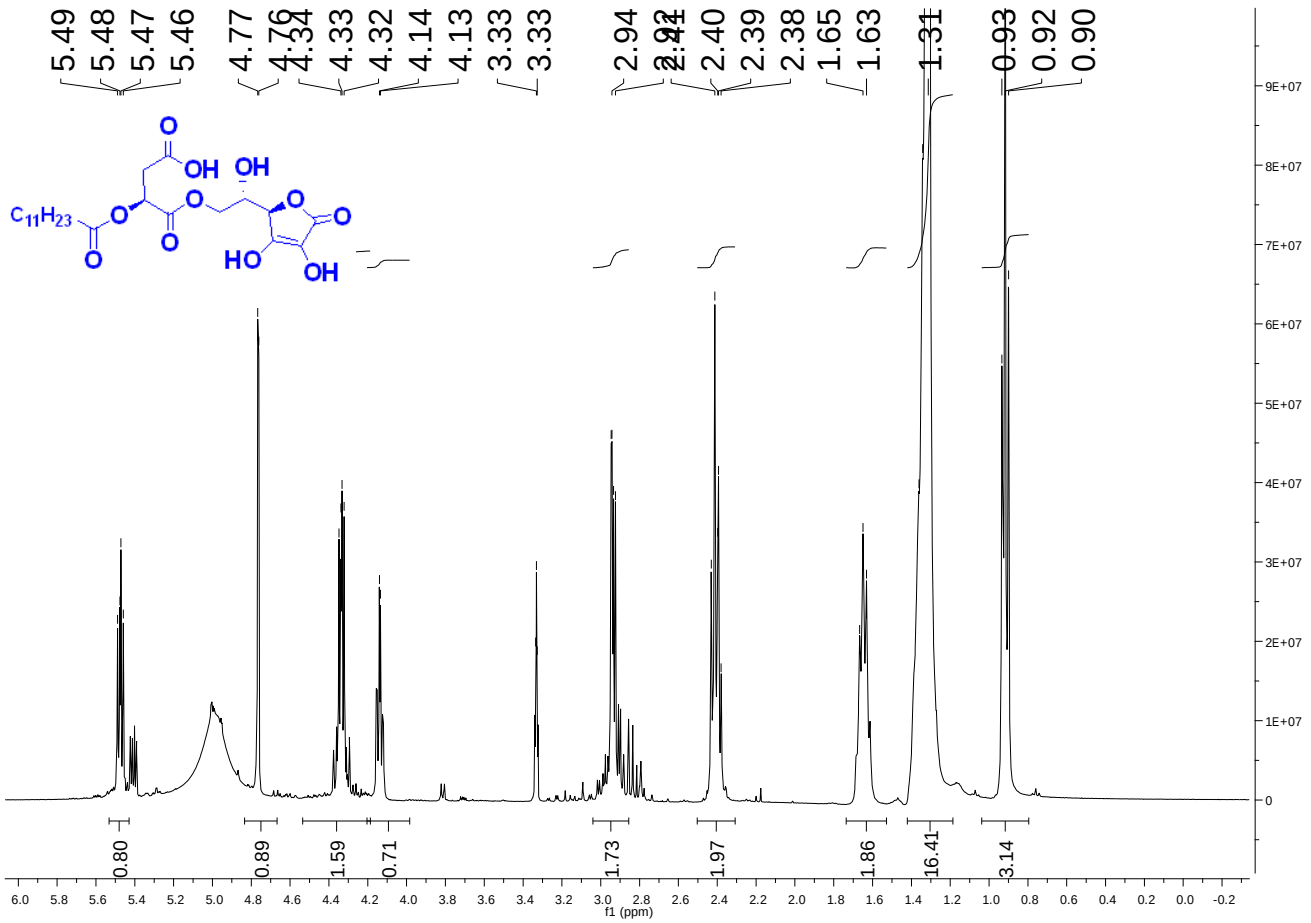
Figure S19: ^{13}C NMR spectrum of **4c** in Acetone-d$_6$ recorded at 318 ºK in a Bruker Avance spectrometer.



^{13}C NMR (101 MHz, Acetone-d_6) δ = 206.71, 206.39, 173.49, 173.48, 170.85, 168.13, 167.44, 151.48, 121.01, 76.69, 72.40, 72.04, 68.44, 67.68, 34.96, 33.35, 31.25, 31.12, 31.08, 30.95, 30.92, 30.88, 30.76, 29.92, 26.29, 26.26, 24.01, 15.01 ppm.

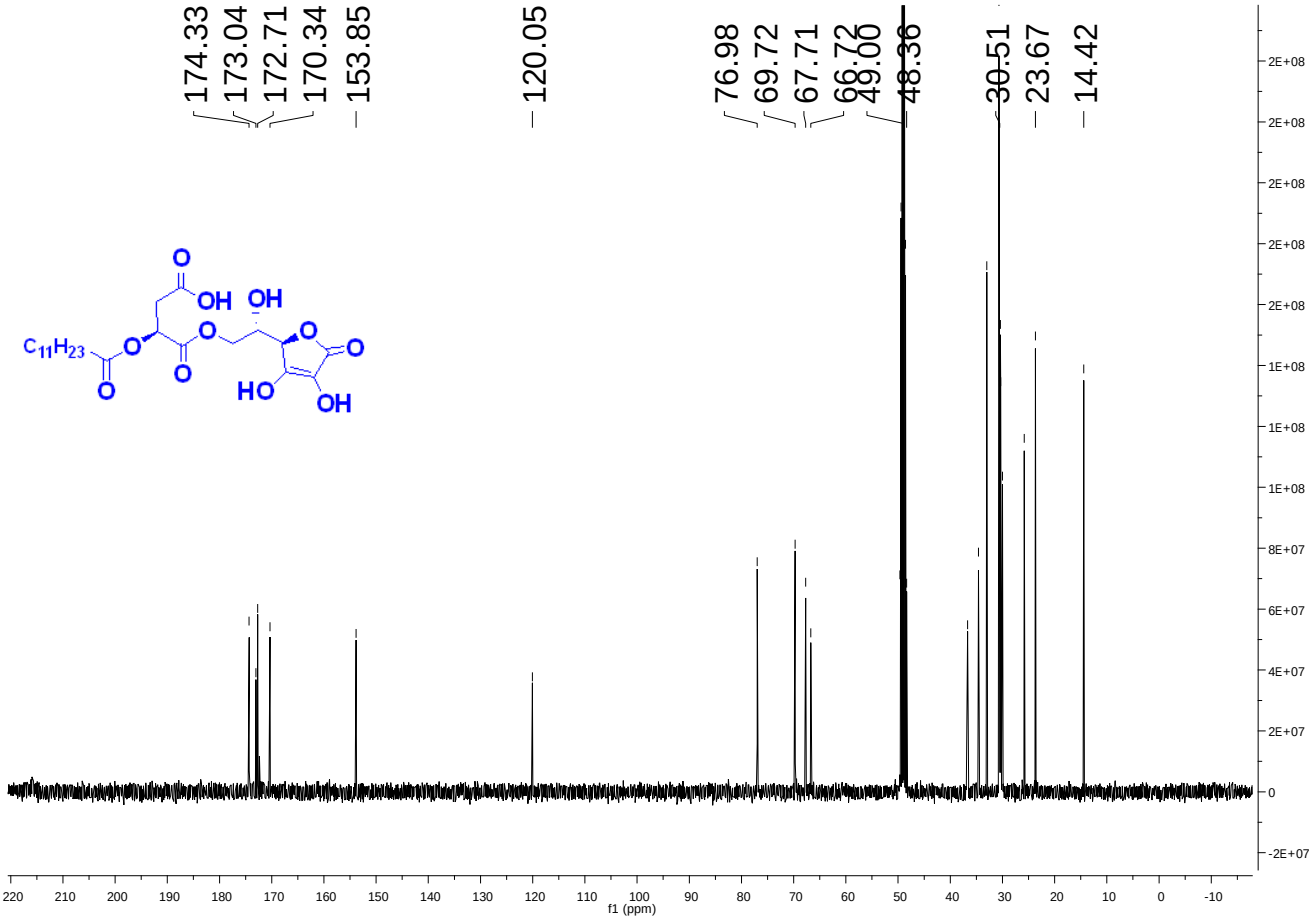
Figure S20: ^{13}C NMR spectrum of **4c** in Acetone-d_6 recorded at 318 ºK in a Bruker Avance spectrometer.

(*S*)-4-((*S*)-2-((*R*)-3,4-dihydroxy-5-oxo-2,5-dihydrofuran-2-yl)-2-hydroxyethoxy)-3-(dodecanoyloxy)-4-oxobutanoic acid (3a):



^{1}H NMR (400 MHz, MeOH-d$_4$) δ = 5.47 (dd, *J*=7.1, 4.9, 1H), 4.76 (d, *J*=2.1, 1H), 4.34 (dd, *J*=6.4, 4.3, 2H), 4.14 (td, *J*=6.4, 2.1, 1H), 2.91 (ddd, *J*=29.4, 15.2, 5.3, 2H), 2.50 – 2.31 (m, 2H), 1.64 (dd, *J*=14.4, 7.1, 2H), 1.46 – 1.14 (m, 16H), 0.92 (t, *J*=6.9, 3H) ppm.

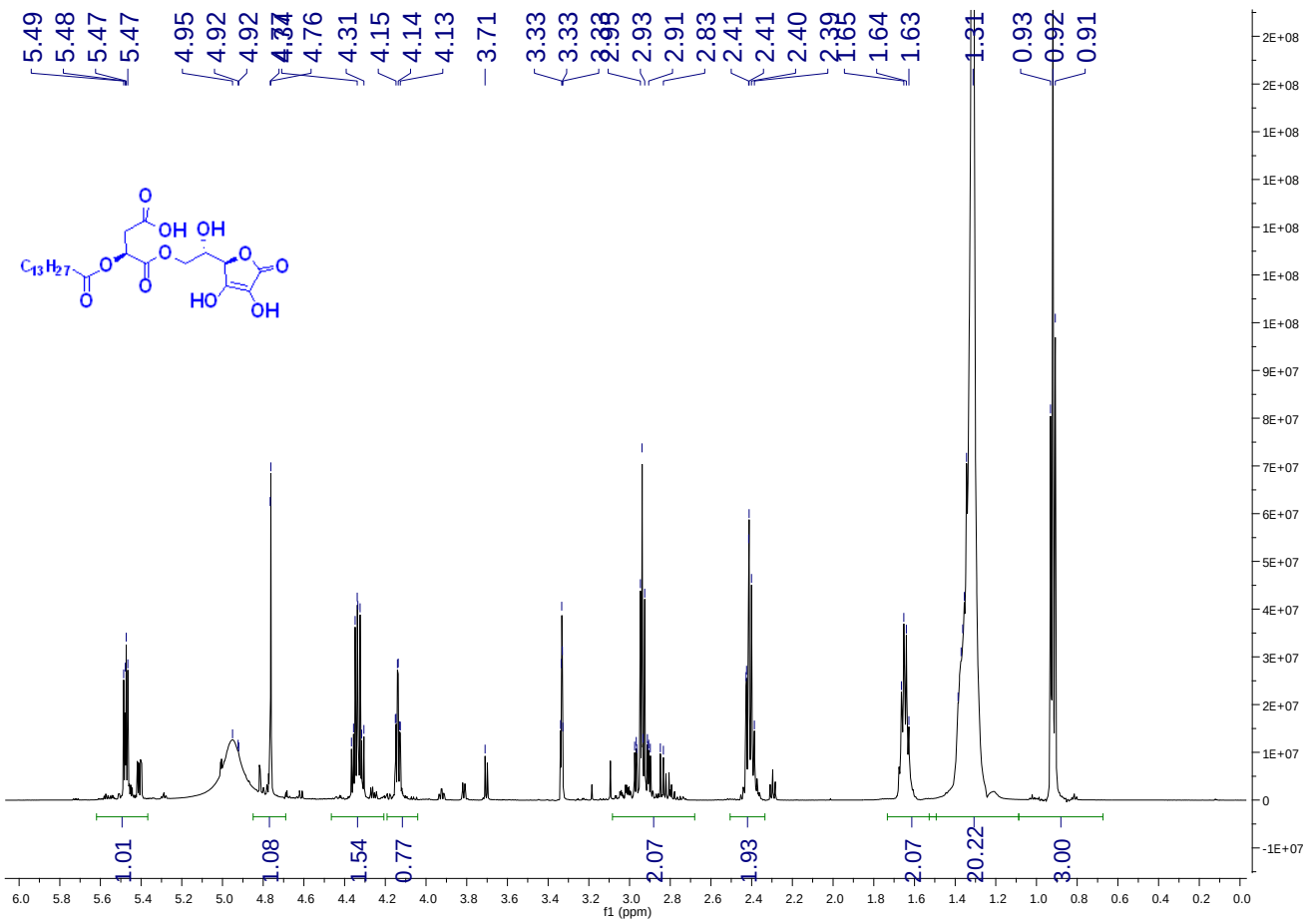
Figure S21: ^{1}H NMR spectrum of **3a** in MeOH-d$_4$ recorded at 298 ºK in a Bruker Avance spectrometer.



^{13}C NMR (101 MHz, MeOH-d_4) δ = 174.33, 173.04, 172.71, 170.34, 153.85, 120.05, 76.98, 69.72, 67.71, 66.72, 36.67, 34.58, 33.00, 30.67, 30.51, 30.40, 30.33, 30.01, 25.82, 23.67, 14.42 ppm.

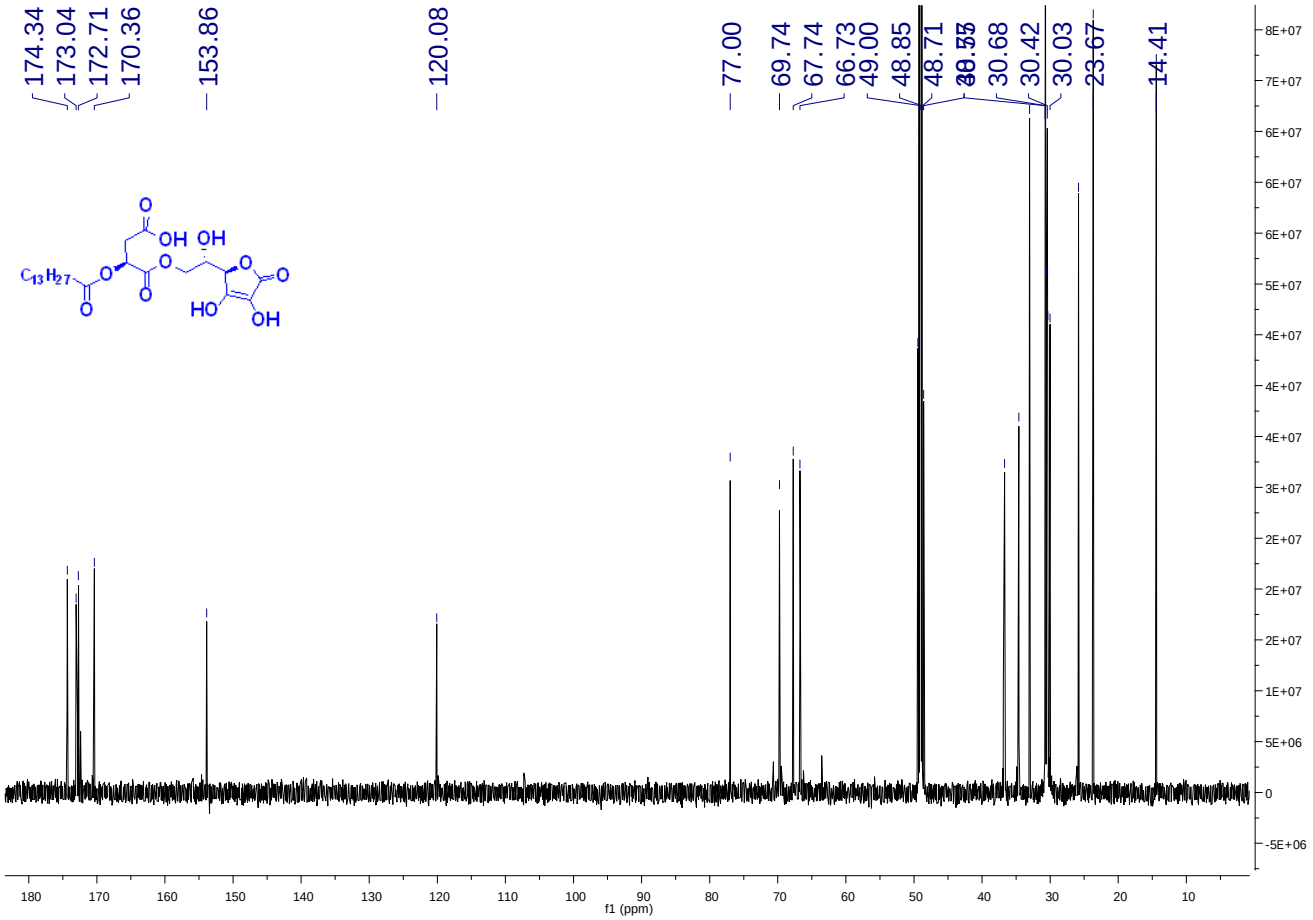
Figure S22: ^{13}C NMR spectrum of **3a** in MeOH-d_4 recorded at 298 ºK in a Bruker Avance spectrometer.

(*S*)-4-((*S*)-2-((*R*)-3, 4-dihydroxy-5-oxo-2,5-dihydrofuran-2-yl)-2-hydroxyethoxy)-4-oxo-3-(tetradecanoyloxy)butanoic acid (3b):



^{1}H NMR (600 MHz, MeOH-d$_4$) δ = 5.48 (dd, *J* = 7.5, 4.6 Hz, 1H), 4.76 (d, *J* = 2.1 Hz, 1H), 4.34 (qd, *J* = 11.1, 6.4 Hz, 2H), 4.14 (td, *J* = 6.4, 2.0 Hz, 1H), 3.08 – 2.68 (m, 2H), 2.51 – 2.33 (m, 2H), 1.65 (dd, *J* = 14.9, 7.4 Hz, 2H), 1.53 – 1.09 (m, 20H), 0.92 (t, *J* = 7.1 Hz, 3H) ppm.

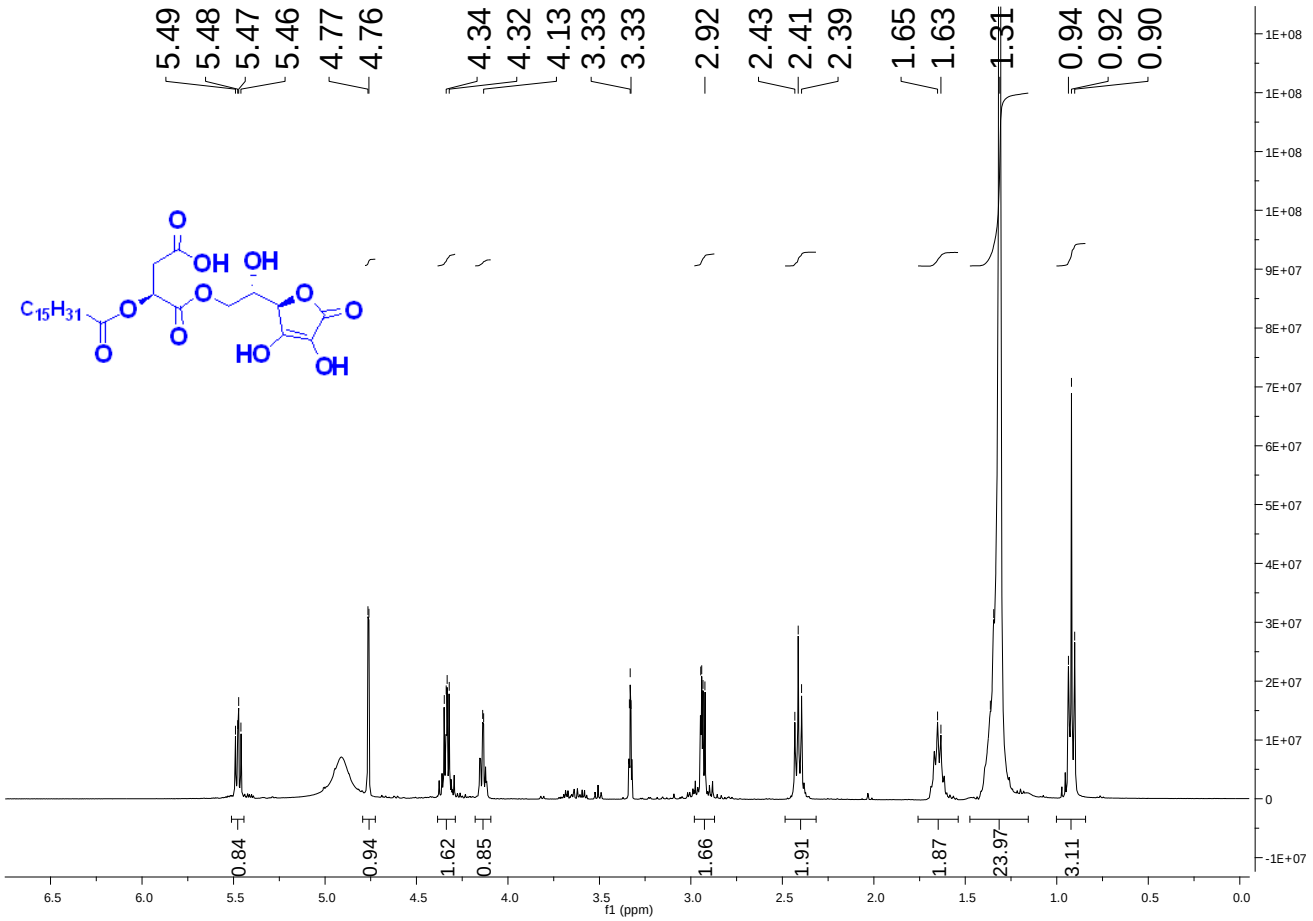
Figure S23: ^{13}C NMR spectrum of **3b** in MeOH-d$_4$ recorded at 300 ºK in a Bruker Avance spectrometer.



^{13}C NMR (151 MHz, MeOH-d_4) δ = 174.34, 173.04, 172.71, 170.36, 153.86, 120.08, 77.00, 69.74, 67.74, 66.73, 49.42, 49.28, 49.14, 49.00, 48.85, 48.71, 48.57, 36.70, 34.60, 33.02, 30.75, 30.71, 30.68, 30.53, 30.42, 30.33, 30.03, 25.83, 23.67, 14.41 ppm.

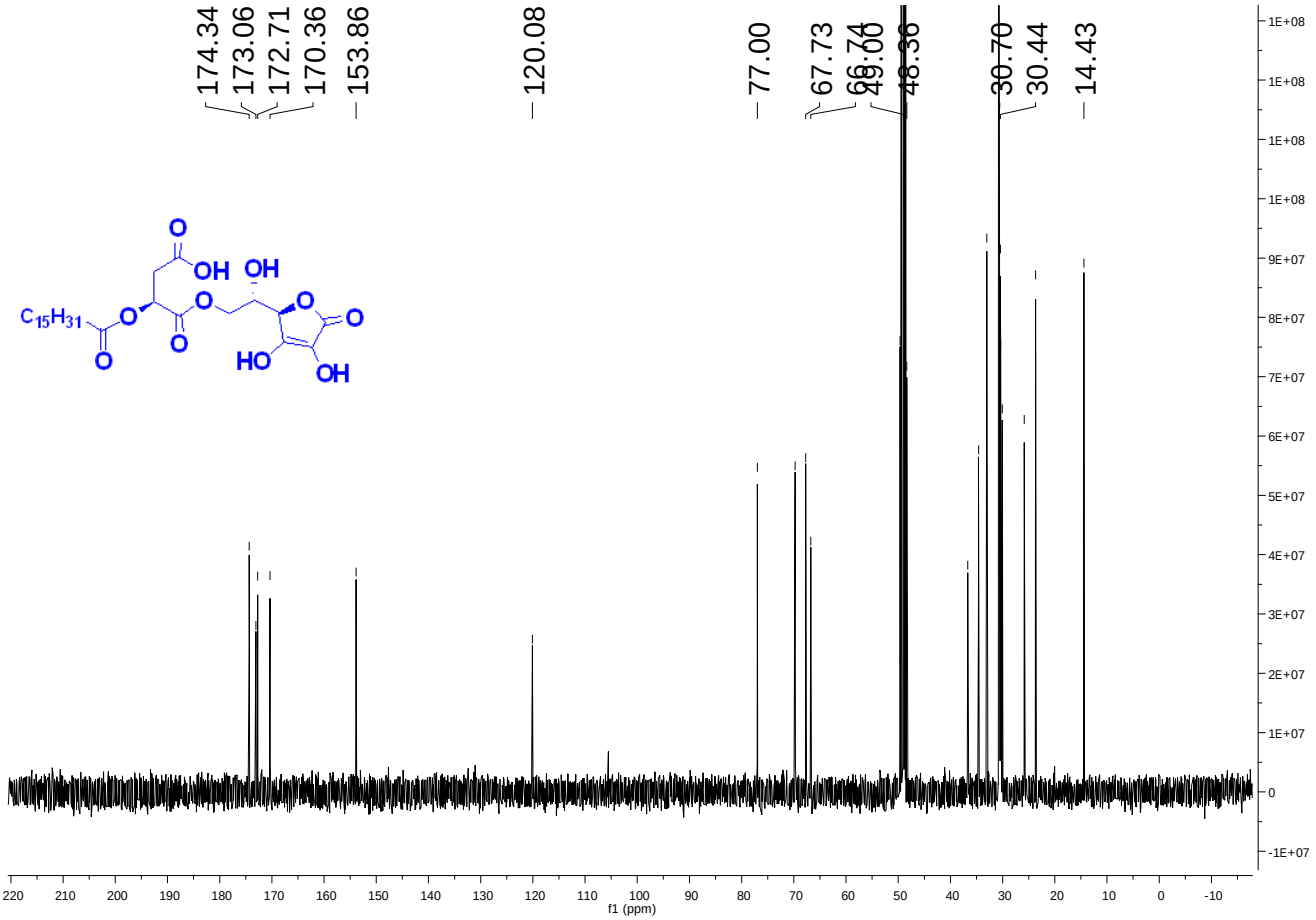
Figure S24: ^{13}C NMR spectrum of **3b** in MeOH-d_4 recorded at 300 ºK in a Bruker Avance spectrometer.

(*S*)-4-((*S*)-2-((*R*)-3, 4-dihydroxy-5-oxo-2,5-dihydrofuran-2-yl)-2-hydroxyethoxy)-4-oxo-3-(palmitoyloxy)butanoic acid (3c) :



^{1}H NMR (400 MHz, MeOH-d$_4$) δ = 5.47 (dd, *J*=7.2, 4.9, 1H), 4.76 (d, *J*=2.1, 1H), 4.33 (dd, *J*=6.4, 4.4, 2H), 4.14 (d, *J*=2.1, 1H), 2.94 (dd, *J*=6.0, 3.3, 2H), 2.41 (t, *J*=7.3, 2H), 1.64 (d, *J*=7.4, 2H), 1.48 – 1.16 (m, 24H), 0.92 (t, *J*=6.8, 3H) ppm.

Figure S25: ^{1}H NMR spectrum of **3c** in MeOH-d$_4$ recorded at 298 ºK in a Bruker Avance spectrometer.



^{13}C NMR (101 MHz, MeOH-d_4) δ = 174.34, 173.06, 172.71, 170.36, 153.86, 120.08, 77.00, 69.74, 67.73, 66.74, 36.69, 34.61, 33.04, 30.76, 30.73, 30.70, 30.55, 30.44, 30.36, 30.05, 25.85, 23.69, 14.43 ppm.

Figure S26: ^{13}C NMR spectrum of **3c** in MeOH-d_4 recorded at 298 ºK in a Bruker Avance spectrometer.

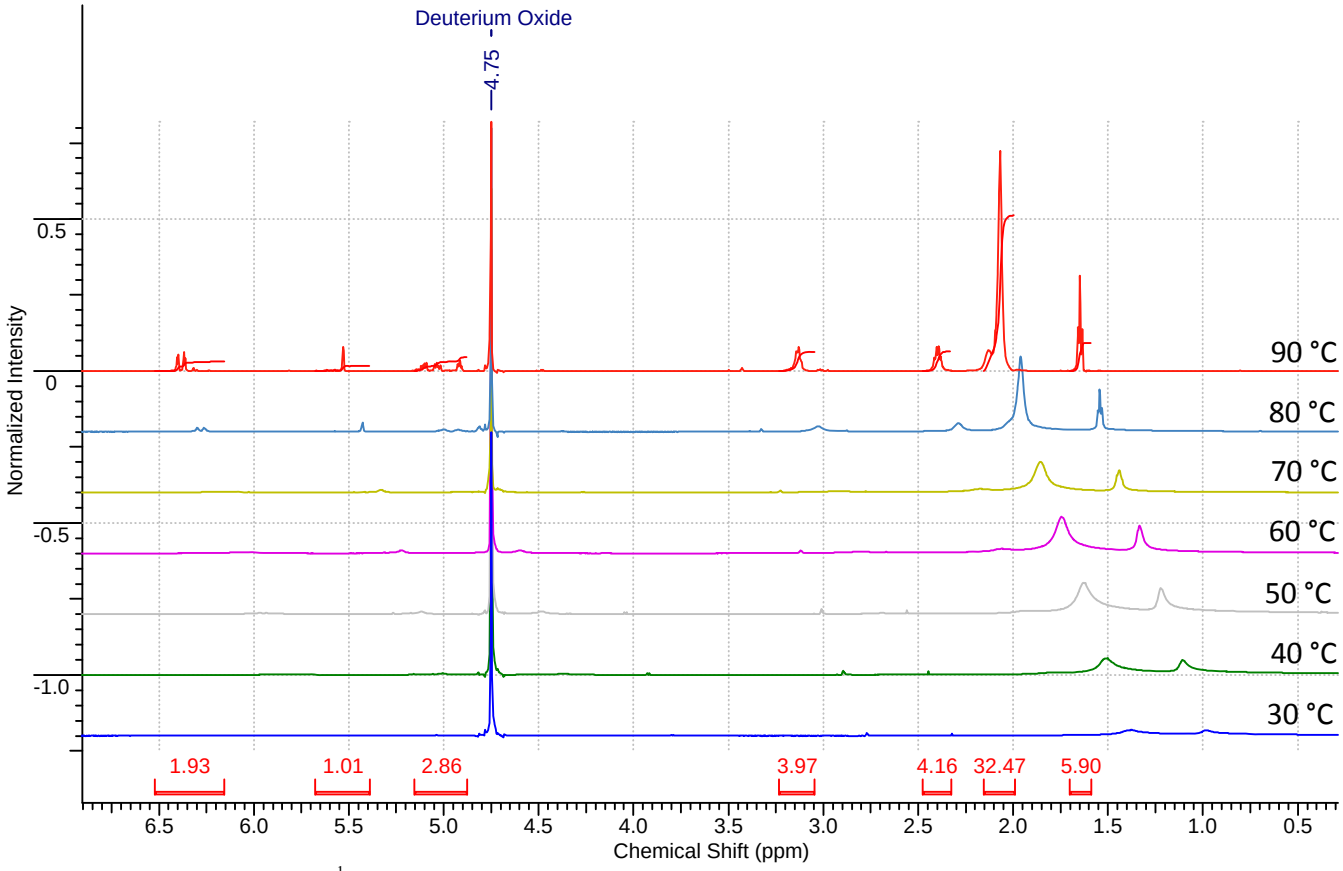


Figure S27: Variable temperature ^{1}H NMR spectra of **4a** in a Bruker Avance spectrometer.

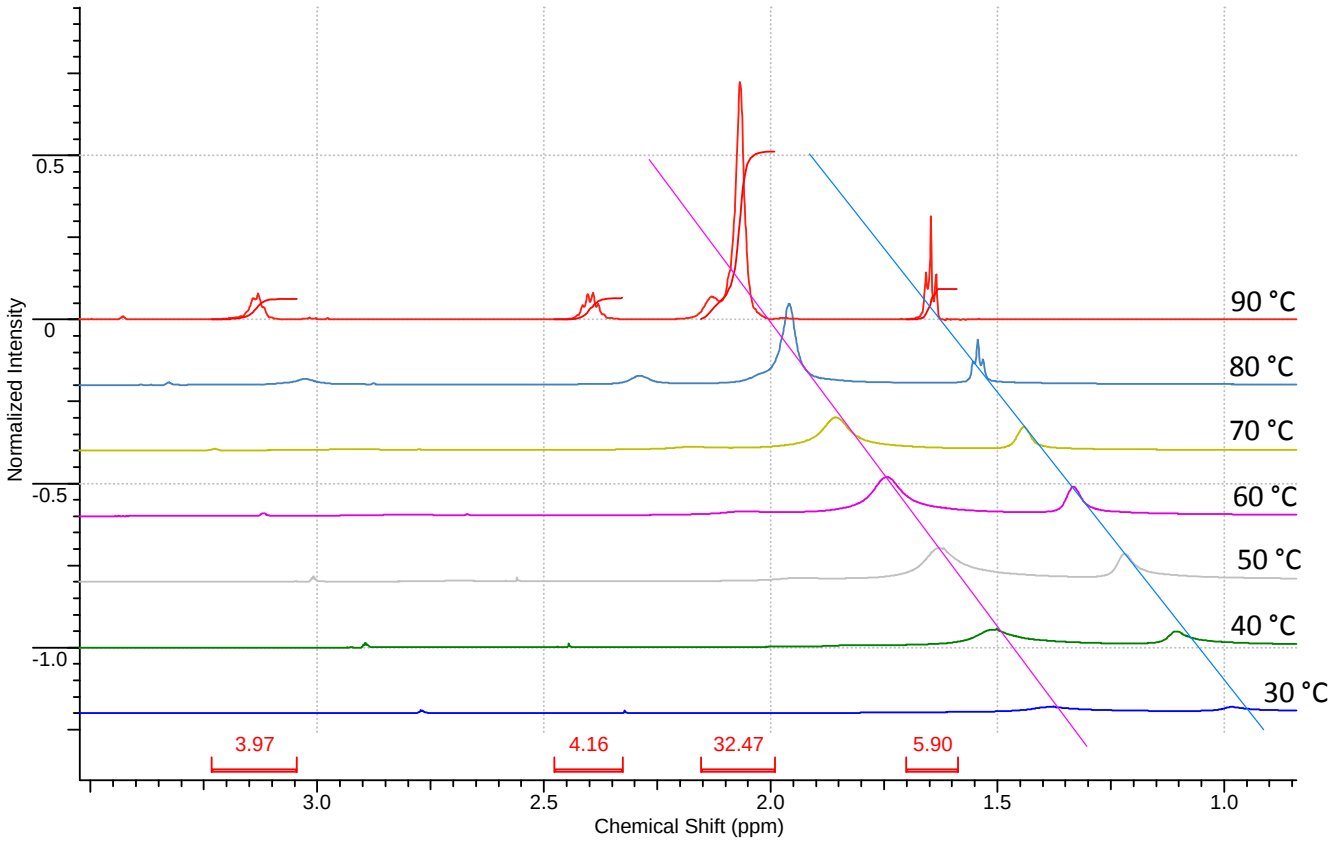


Figure S28: Expanded region of several Variable temperature ^{1}H NMR spectra of **4a** in a Bruker Avance spectrometer.

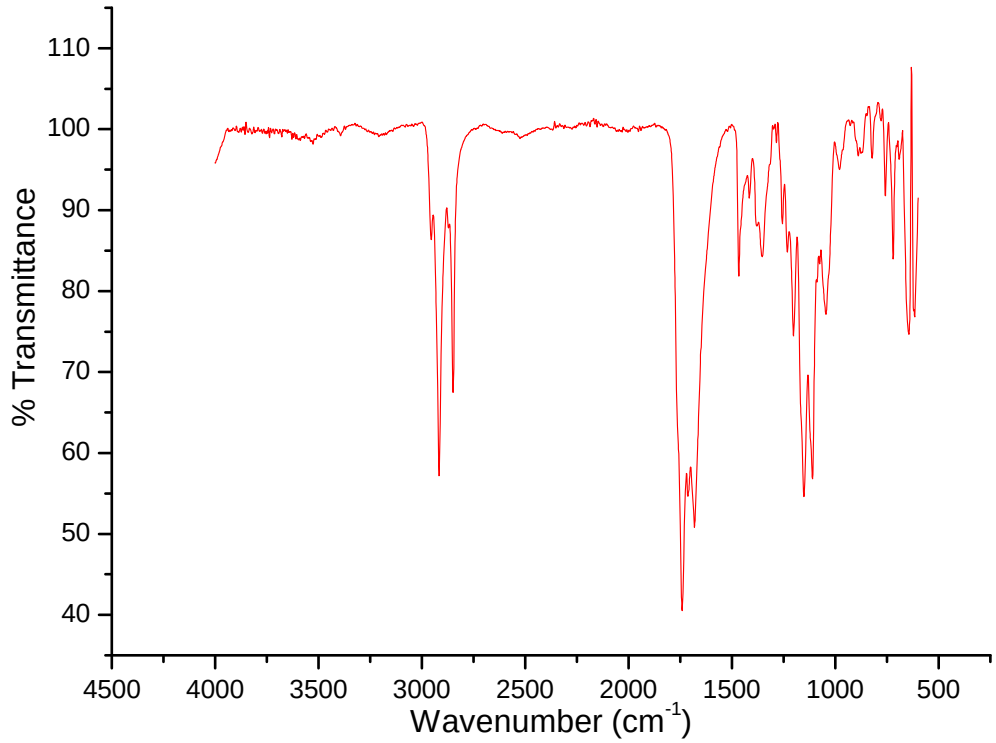


Figure S29: FT-IR spectrum of the xerogel of **4a** in D_2O.

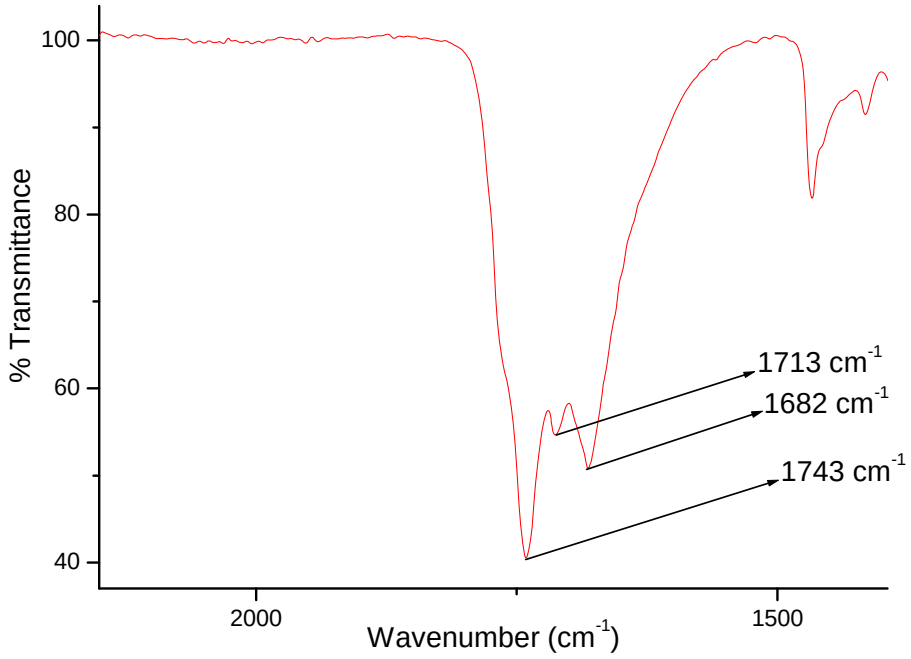


Figure 30: Expanded region of the FT-IR spectrum of the xerogel of **4a** in D_2O.

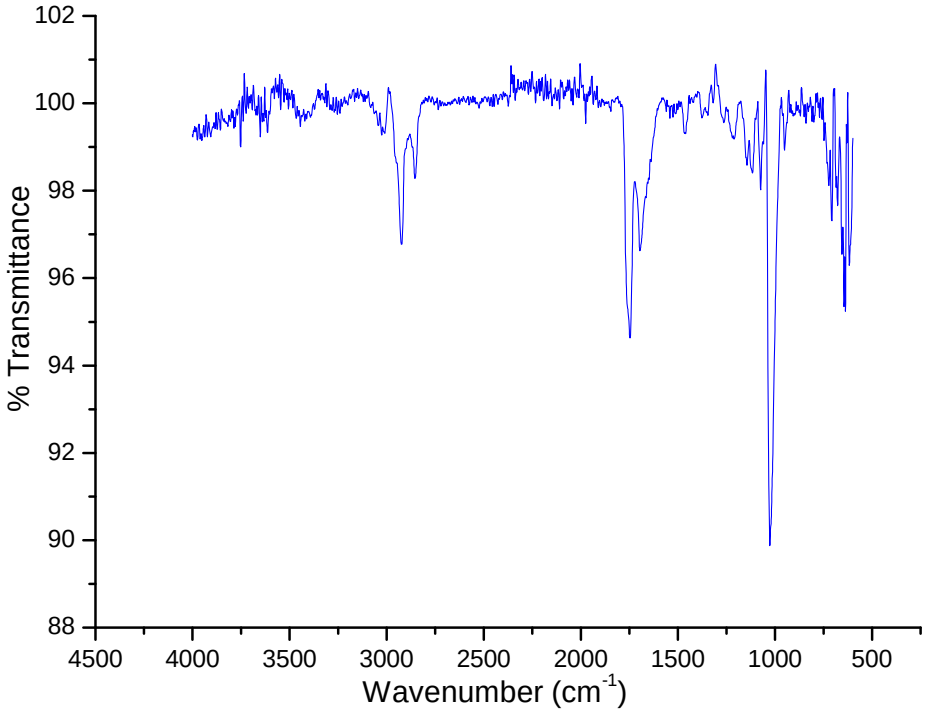


Figure 31: FT-IR spectrum of **4a** in DMSO.

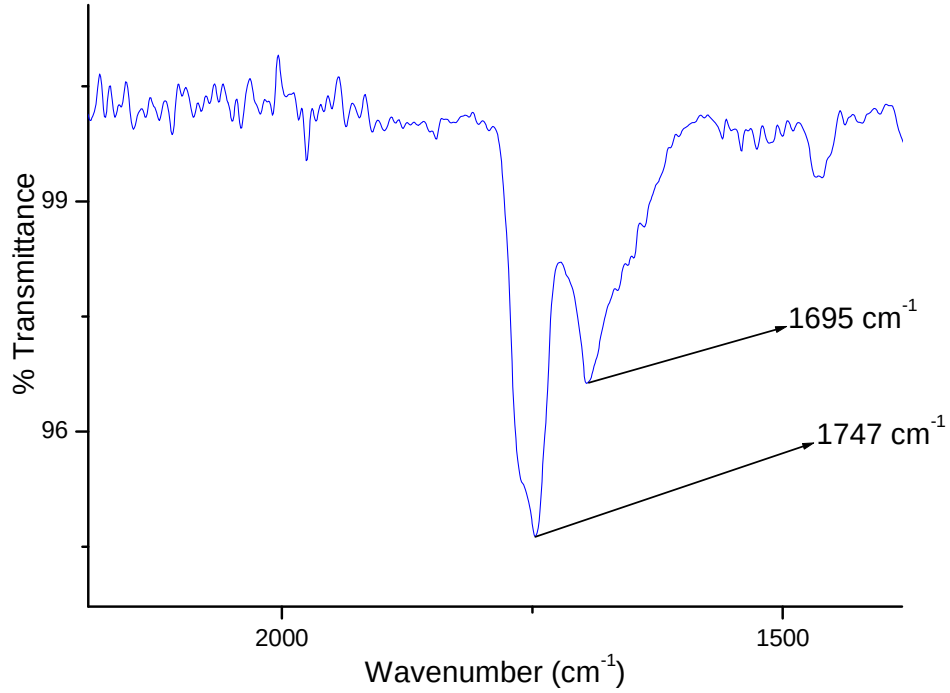


Figure 32:Expanded region of the FT-IR spectrum of **4a** in DMSO.

References

1 Abe, A.; Asakura, K.;Osanai, S. *J. Surfact. Deterg*., **2004**, *7(3),* 297-303.

2 ASTM D1173(US).

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