Synthesis of Structurally Well-Defined Triglyceryl Di-, Tri-, and Tetra-Fatty Acid Esters as New Oil Gelators

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Abstract: We are interested in developing chemically modified linear and cyclic polyglycerols and their esters that have a single polymerization degree and fine structure. Triglyceryl di-, tri-, and tetra-fatty acid esters were synthesized from common substrate as new prominent gelators. The triglyceryl esters were capable of gelling up cooking oils. A comparison of the gelation ability of structurally related compounds clarified that the introduction of alkyl chains of suitable length is required for effective gelation.

Key words: triglycerol, fatty acid esters, gelation, aggregation, mechanistic study

Polyglycerols are oligomers of glycerol (glycerin). Their fatty acid esters are generally dispersible in water and soluble in oil. As these compounds are readily available in bulk quantities by industrial manufacturers, they are widely used as food additives, cosmetic materials and as pharmaceuticals as surfactants.[1] However, commercially available polyglycerols are mixtures of structural isomers with the same hydroxy value.[2] There are a few representative, standard polyglycerols in the literature.[3–8] Rollin and co-workers reported the synthesis of linear, branched, and cyclic polyglycerol standards.[9] We have continuously studied the synthesis of cyclic polyglycerols as authentic standards.[10] However, there are few reports on the synthesis of linear polyglycerol fatty acid esters with highly pure and well-defined structures.

Low-molecular-weight compounds capable of gelling up oils have stimulated considerable interest, in not only academic investigations, but also for technological applications. Various types of small-molecule-based gelators of organic and aqueous solvents have been investigated to determine their essential characteristics for gelation.[11] Although dozens of different categories of gelators have so far been identified, limited compounds have been used to date: 12-hydroxystearic acid,[12] *N*-lauroyl-L-glutamic-α,γ-dibutylamide,[13] 1,3:2,4-dibenzylidene-D-sorbitol,[14] *N*-octyl-D-gluconamide-6-benzoate,[15] and TAISET®.[16] Besides the above gelators, Hanabusa[17] and Shinkai[18] group reported several all-powerful gelators capable of gelling up a wide variety of fluids. We report here the synthesis and measurement of new gelators, triglycerol multi-fatty acid esters.

We synthesized tetra-, tri-, di-stearates with control of both the binding position and number of fatty acids. Readily available bis-acetonide of triglycerol **1**,[18] which was prepared from (±)-solketal and (±)-epichlorohydrin,[10] was used as a common starting material in expectation of macro-scale synthesis (Scheme 1).[19] The hydroxy group of **1** was protected with benzyl bromide to give benzyl ether **2** in 98% yield. The acetonides were deprotected with 80% aqueous acetic acid to afford 1,2,10,11-tetraol **3** quantitatively. The tetraol **3** was reacted with stearoyl chloride in pyridine containing catalytic 4-(dimethylamino)pyridine to give the corresponding tetraester **4** in 35% yield. The deprotection of **4** was carried out by hydrogenolysis with palladium on carbon to give the desired 6-hydroxy-1,2,10,11-tetrastearate **5** in 93% yield.

On the other hand, selective silylation of tetraol **3** with *tert*-butyldiphenylsilyl chloride (TBDPSCl) gave disilyl ether **6** in 81% yield. Debenzylation and esterification of **6** afforded 2,6,10-triester **8**, and then the desilylation by tetrabutylammonium fluoride gave the desired 1,11-dihydroxytristearate **9** in moderate yield. Disilyl ether **6** could also be treated with benzyl bromide, followed by desilylation to give 1,11-diol **11** in good yield. Diol **11** was treated with stearoyl chloride in pyridine with catalytic 4-(dimethylamino)pyridine at 40 °C to give the 1,11-distearate **12a** in 78% yield. Debenzylation of **12a** was carried out with palladium hydroxide on activated carbon in ethanol–tetrahydrofuran under a hydrogen atmosphere to give the desired trihydroxy ester **13a** in moderate yield.

All synthesized esters are white powder having melting points less than 90 °C. These compounds are dissoluble in chloroform and tetrahydrofuran and are insoluble in methanol, ethanol, water, *N*,*N*-dimethylformamide, dimethyl sulfoxide, hexane, benzene, toluene, acetone, and ethyl acetate at room temperature. The etherate solvents and dichloromethane are slightly dissoluble at room temperature. Triglycerol tetra-, tri- and distearates **5**, **9**, and **13a** transform cooking oils into gels. The gelation ability of synthesized esters **5**, **9**, and **13a** was assayed by the values of minimum gel concentration (MGC, mg/mL). The results of gelation tests of are summarized in Table 1. In comparison with those of tetrastearate **5** at 30 mg/mL and

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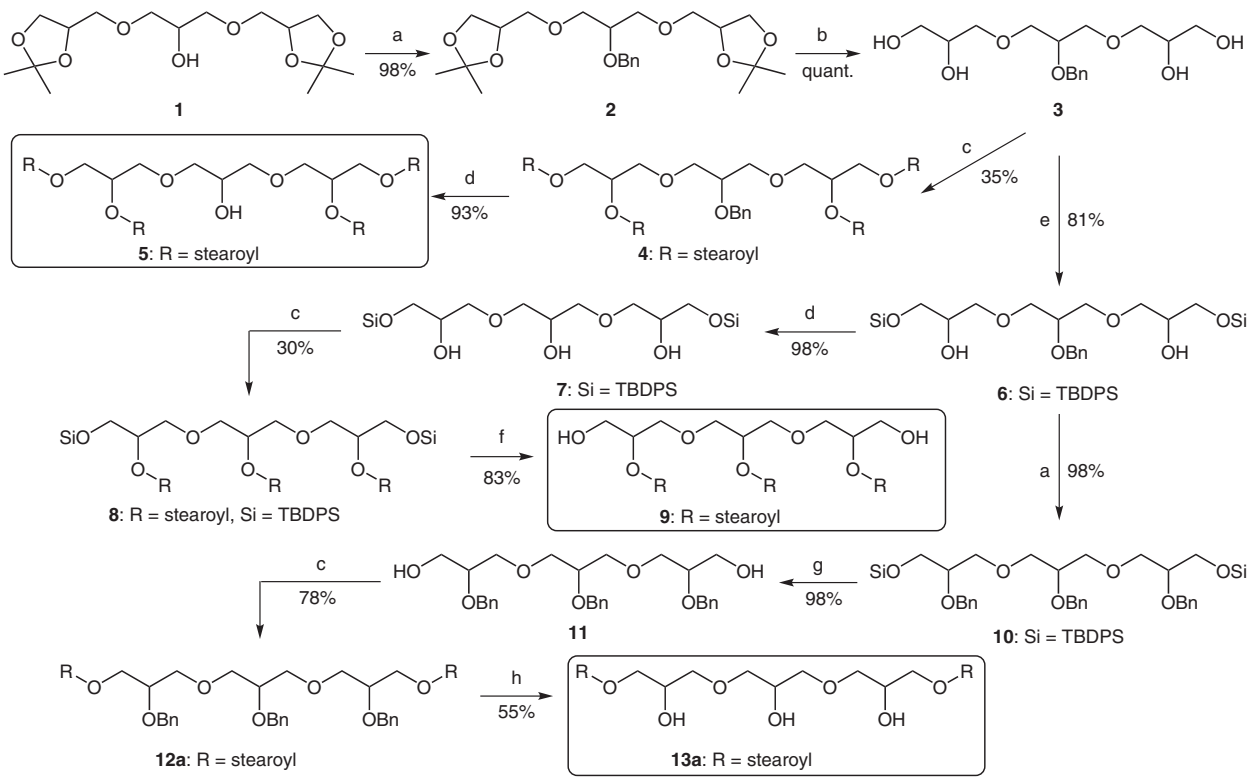
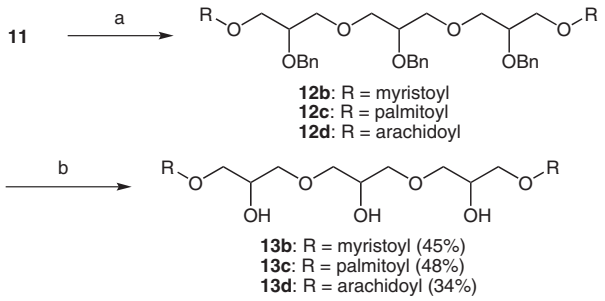


Scheme 1 *Reagents and conditions*: (a) NaH, THF, 0 °C, 20–30 min; BnBr, r.t., 16–20 h; (b) 80% aq AcOH, r.t., 6 h; (c) RC(O)Cl, cat. DMAP, py, r.t.; (d) H_2, Pd/C (10%), EtOH or THF–EtOH (1:1), r.t.; (e) TBDPSCl, Et_3N, DMAP, CH_2Cl_2, r.t.; (f) TBAF, AcOH, THF, r.t.; (g) TBAF, THF, r.t.; (h) H_2, $Pd(OH)_2$/C, THF–EtOH, 40 °C.



Scheme 2 *Reagents and conditions*: (a) RC(O)Cl, cat. DMAP, py, r.t.; (b) H_2, $Pd(OH)_2$/C, THF–EtOH, 40 °C.

Table 1 Gelation Test of the Esters with Rapeseed Oil

Entry	Ester	Minimum gel concentration[a]
1	**5**	30
2	**9**	40
3	**13a** (stearate)	10
4	**13b** (myristate)	40
5	**13c** (palmitate)	30
6	**13d** (arachidate)	>40

[a] The gel formation was judged by test tube titling method after standing at 25 °C for 2 h. Values mean minimum gel concentration, whose unit is mg/mL.

tristearate **9** at 40 mg/mL, distearate **13a** has an effective gelation ability at 10 mg/mL. This ability showed the same range of TAISET®.

Our next attention was focused on the length of the carbon chain of the fatty acid moiety in the esters. The myristoyl diesters **13b**, palmitoyl diesters **13c**, arachidoyl diesters **13d**, which had different length carbon chains in the fatty acid moiety, were prepared from **11** by a two-step sequence to give **13b**, **13c**, and **13d** in 45%, 48%, and 34% yields, respectively (Scheme 2).

The gelation ability of esters **13b–d** was also assayed for their minimum gel concentration values (mg/mL) as shown in Table 1. It has become apparent that the gelation ability requires a suitable length carbon chain on the fatty acid. The gelation ability rises as the carbon chain is lengthened from C14 to C18 (Table 1, entries 3–5). It is interesting to note that **13d** was found to have a slight gelation ability.

The gelation ability of esters **13a–d** was also assayed for their minimum gel concentration values (mg/mL) compared to TAISET® in various oils (Table 2). TAISET® and **13a** have good oil gelation ability. Stearate **13a**, in particular, transforms various oils into gels at concentrations of less than 20 mg/mL. The carbon chain length is very important for oil gelation ability: arachidate (**13d**) did not show oil gelation ability even at 40 mg/mL.

To quantitatively observe this aggregation, we measured the transmittance at 500 nm from 85 °C to 20 °C containing various concentrations of gelator under variable tem-

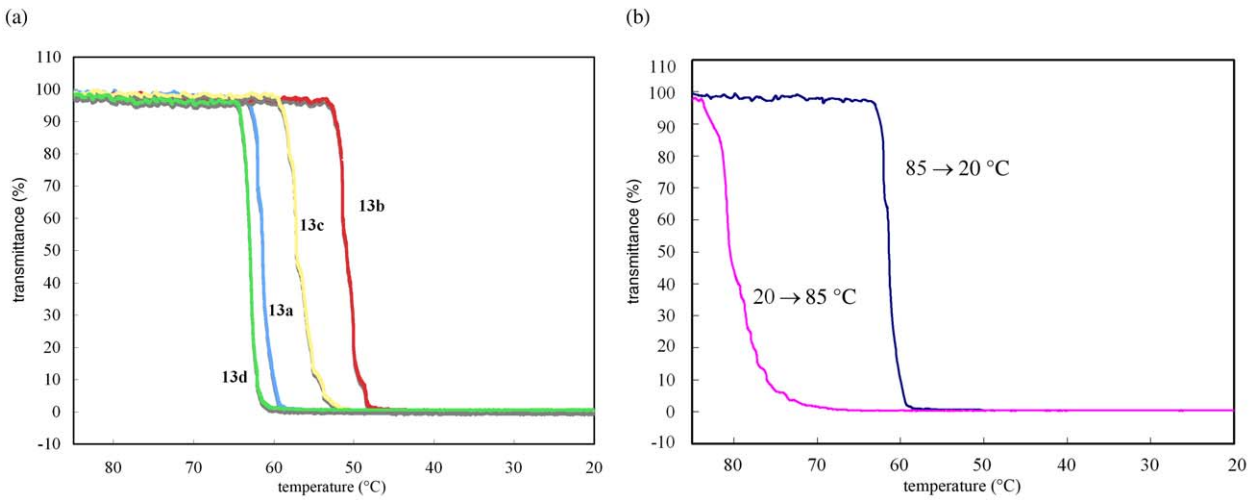


Figure 1 (a) Aggregation curves for esters **13a–d** (10 mg); (b) aggregation curve (blue line) and dissociation curve (purple) for ester **13a** (10 mg).

Table 2 Gelation Test of the Diesters for Oils

	Minimum gel concentration[a]				
Oil	**13a**	**13b**	**13c**	**13d**	TAISET®
rapeseed	10	40	30	>40	10
soybean	10	30	>40	>40	15
sunflower seed	10	30	40	>40	10
sesame	20	30	>40	>40	35

[a] The gel formation was judged by test tube titling method after standing at 25 °C for 2 h. Values mean minimum gel concentration, whose unit is mg/mL.

peratures. The aggregation curves of rapeseed oil with 10 mg of each of esters **13a–d** is showed in Figure 1(a). In all cases, the transmittance value suddenly decreased after a certain temperature. This temperature was read from each spectrum and is regarded an apparent critical aggregation temperature (CAT).

As shown in Table 3, the critical aggregation temperatures increased when the amount of ester increased and also the carbon chain lengthened. On the other hand, dissociation curves were depicted by the measurement of transmittance at 500 nm from 20 °C to 85 °C. In the all samples, a hysteresis curve was observed. The apparent critical dissociation temperatures were higher than the critical aggregation temperatures and dissociation curves were a gentler slope than the aggregation curves [see Figure 1(b)].

In conclusion, we have developed new gelators, triglyceryl di-, tri-, tetra-fatty acid esters, with well-defined structure. The triglyceryl ester gelators exhibit prominent gelation ability and gel up a wide variety of oils. The measurement of transmittance at 500 nm could be the appraisal standard for the aggregation level.

Table 3 The Apparent Critical Aggregation Temperatures (°C)

Amount of ester (mg)	**13a** stearate	**13b** myristate	**13c** palmitate	**13d** arachidate
1	37.6	34.8	36.5	41.7
5	57.1	47.1	54.1	56.9
10	63.0	52.7	59.1	64.2
20	67.3	58.8	64.9	68.2
40	73.9	64.2	77.1	72.9

Melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were measured with a Shimazu OR-800 spectrophotometer. ATR-IR spectra were measured with a Perkin-Elmer Spectrum 100 spectrometer equipped with Universal ATR accessory. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Biospin Avance II 400 spectrometer or a Jeol JNM LA-400 spectrometer using TMS or solvent peak as an internal standard. LR- and HRMS (FAB) spectra were recorded on a Jeol JMS-AX500 spectrometer. LR-ESI or APCI-MS spectra were recorded on an Agilent Technology 1100 LC-MSD spectrometer flowing a mixed soln of MeOH or MeCN and H_2O or diluted AcOH. HRMS (ESI) spectra were recorded on a Bruker Daltonics micrOTOF focus spectrometer. The transmittance in Figure 1 was measured on a Jasco V-550 UV-Vis spectrophotometer with non-adding rapeseed oil as a blank. Analytical TLC was conducted on precoated TLC plate (silica gel $60F_{254}$, Merck). Column chromatography was performed using Kanto Chemical silica gel 60N (70–230 mesh). All reagents were used of commercial quality. THF and CH_2Cl_2 were used of Kanto Chemical dehydrated grade without purification. All air- and moisture-sensitive reactions were carried out under inert gas (N_2 or argon).

Compound **1** was supplied from Riken Vitamin Co., Ltd. TAISET® and rapeseed oil were supplied from Taiyo Chemical Co., Ltd.

6-(Benzyloxy)-1,2;10,11-bis(isopropylidenedioxy)-4,8-dioxaundecane (2)

To a suspension of NaH (60% in oil, 449 mg, 18.7 mmol) in THF (60 mL) was added a soln of 1,2;10,11-bis(isopropylidenedioxy)-

4,8-dioxaundecan-6-ol (**1**, 3.0 g, 9.36 mmol) in THF (30 mL) at 0 °C; the mixture was stirred at this temperature for 20 min. BnBr (2.41 g, 14.1 mmol) was added to the mixture at 0 °C and then the mixture was warmed to r.t. and stirred for 20 h. When the reaction was complete (TLC), the mixture was treated with H_2O and extracted with EtOAc. The organic layer was washed with brine and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residual oil was purified by column chromatography (silica gel, hexane–EtOAc, 4:1) to give **2** (3.74 g, 98%) as a colorless oil; R_f = 0.41 (hexane–EtOAc, 2:1).

IR (neat): 2986, 2936, 2874, 1497, 1456, 1379, 1372, 1256, 1213, 1144, 1055 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.34 (s, 6 H, CH_3 of acetonide), 1.39 (s, 6 H, CH_3 of acetonide), 3.46 (q, *J* = 5.4 Hz, 2 H, H2, H10), 3.51–3.63 (m, 6 H), 3.69–3.75 (m, 3 H), 4.01 (t, *J* = 7.2 Hz, 2 H), 4.24 (q, *J* = 5.8 Hz, 2 H), 4.65 (s, 2 H, benzylic), 7.24–7.34 (m, 5 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.4, 26.7, 66.7(2), 66.7(4), 66.8, 71.6, 72.2(6), 72.3(3), 72.3(9), 72.4, 74.6, 127.6, 127.7, 127.7(1), 127.7(3), 128.3.

MS (FAB): *m*/*z* (%) = 411 (13) $[M + H]^+$, 395 (14), 114 (28), 91 (100).

HRMS (FAB): *m*/*z* $[M + H]^+$ calcd for $C_{22}H_{35}O_7$: 411.2383; found: 411.2390.

6-(Benzyloxy)-4,8-dioxaundecane-1,2,10,11-tetraol (3)

A soln of **2** (2.47 g, 6.0 mmol) in 80% aq AcOH (60 mL) was stirred at r.t. for 6 h, followed by concentration under reduced pressure to give tetraol **3** (1.98 g, quant.) as a colorless oil. This compound was used in the next step without further purification.

IR (neat): 3600–3200, 3090, 3063, 3032, 2876, 2244, 1717, 1500, 1455, 1395, 1352, 1256, 1115, 1049, 926, 866, 739, 700 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.47–3.75 (m, 13 H), 3.82–3.86 (m, 2 H, H2, H10), 4.63 (s, 2 H, benzylic), 7.26–7.37 (m, 5 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 63.7, 70.5(9), 70.6(4), 70.7, 72.0, 72.8, 73.0, 76.4, 127.9, 128.5, 137.8.

MS (FAB): *m*/*z* (%) = 353 (66) $[M + Na]^+$, 331 (61) $[M + H]^+$, 131 (11), 92 (100).

HRMS (FAB): *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{27}O_7$: 331.1757; found: 331.1749.

6-(Benzyloxy)-1,2,10,11-tetrakis(stearoyloxy)-4,8-dioxaundecane (4); Typical Procedure for the Esterification of Triglycerol Derivatives

To a soln of alcohol **3** (2.17 g, 6.56 mmol) and DMAP (1.60 g, 13.1 mmol) in pyridine (40 mL) was added stearoyl chloride (7.54 g, 24.9 mmol) at r.t. and the mixture was stirred at r.t. for 18 h. When the reaction was complete, the mixture was treated with MeOH (10 mL) and concentrated under reduced pressure. The residual mixture was diluted with $CHCl_3$, washed with brine, and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, hexane–EtOAc, 7:1) and by PTLC (silica gel $60F_{254}$, Merck, hexane–EtOAc, 5:1) to give tetraester **4** (3.21 g, 35%) as a white solid; mp 45–47 °C (hexane–EtOAc); R_f = 0.80 (hexane–EtOAc, 3:1).

IR (neat): 2910, 2845, 1743, 1738 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.6 Hz, 12 H, CH_3), 1.25 (s, 112 H, CH_2 of fatty acid), 1.56–1.61 (m, 8 H, CH_2 of fatty acid), 2.27–2.32 (m, 8 H, CH_2 of fatty acid), 3.50–3.69 (m, 8 H), 3.83 (br s, 1 H, OH), 4.11–4.16 (m, 2 H), 4.31–4.33 (m, 2 H), 4.65–4.66 (m, 2 H), 5.05–5.35 (br, 2 H, CH), 7.33–7.52 (m, 5 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 14.2, 20.7, 20.9(8), 21.0, 22.7, 24.7, 24.8(8), 24.9, 29.1(0), 29.1(4), 29.2, 29.3, 29.3(5), 29.4, 29.5, 29.6(5), 29.7, 31.9, 33.7, 34.1, 34.3, 60.4, 62.5, 62.6, 62.9, 69.8, 69.8(5), 69.9, 70.3, 71.6, 72.4, 127.6, 127.7, 128.3, 138.4, 170.6, 171.1, 173.1, 173.4.

MS (ESI): *m*/*z* (%) = 1418 (100) $[M + Na]^+$.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{88}H_{162}NaO_{11}$: 1418.2009; found: 1418.2033.

1,2,10,11-Tetrakis(stearoyloxy)-4,8-dioxaundecan-6-ol (5)

A soln of **4** (1.02 g, 0.73 mmol) and Pd-C (10% containing Pd, 77 mg) in THF (10 mL) and EtOH (10 mL) was stirred at r.t. for 1 d under a H_2 atmosphere. When the reaction was complete, the mixture was filtered and concentrated under reduced pressure. The residual solid was purified by column chromatography (silica gel, $CHCl_3$–MeOH, 100:1) to give **5** (886 mg, 93%) as a white solid; mp 57–58 °C (EtOAc); R_f = 0.40 ($CHCl_3$–MeOH, 100:1).

IR (neat): 2910, 2850, 1730 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.6 Hz, 12 H, CH_3), 1.25 (s, 112 H, CH_2 of fatty acid), 1.60–1.61 (m, 8 H, CH_2 of fatty acid), 2.28–2.34 (m, 8 H, CH_2 of fatty acid), 3.45–3.66 (m, 8 H), 3.90 (br s, 1 H, OH), 4.13–4.18 (m, 2 H), 4.30–4.35 (m, 2 H), 5.18–5.23 (m, 2 H, H2, H10).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 24.8(9), 24.9, 29.1(0), 29.1(4), 29.3, 29.4, 29.5, 29.6(6), 29.7, 31.9, 34.1, 34.3, 62.5, 69.9, 173.4.

MS (FAB): *m*/*z* (%) = 1329 (13) $[M + Na]^+$.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{81}H_{156}NaO_{11}$: 1328.1540; found: 1328.1539.

6-(Benzyloxy)-1,11-bis(*tert*-butyldiphenylsiloxy)-4,8-dioxaundecane-2,10-diol (6)

To a soln of **3** (10.4 g, 31.5 mmol), Et_3N (13.15 g, 0.13 mol), and DMAP (1.93 g, 15.8 mmol) in CH_2Cl_2 (300 mL) was added TBDPSCl (18.2 g, 66.2 mmol) at 0 °C. The mixture was stirred at r.t. for 1 d. When the reaction was complete, the mixture was treated with H_2O and extracted with CH_2Cl_2. The organic layer was washed with brine and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residual oil was purified by column chromatography (silica gel, hexane–EtOAc, 3:1) to give disilyl ether **6** (20.5 g, 81%) as a colorless oil; R_f = 0.27 (hexane–EtOAc, 3:2).

IR (neat): 3600–3200, 3071, 3049, 2955, 2930, 2859, 2361, 1590, 1472, 1428, 1391, 1362, 1188, 1113, 1028, 999, 939, 824, 741, 702, 613, 505, 492, 419 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.08 [s, 18 H, $C(CH_3)_3$], 2.66–2.73 (br, 2 H, OH), 3.48–3.61 (m, 7 H), 3.70 (d, *J* = 4.8 Hz, 4 H), 3.89 (br, 2 H, CH), 4.63 (s, 2 H, benzylic), 7.22–7.31 (m, 5 H, Bn), 7.35–7.45 (m, 12 H, Ph-H), 7.66–7.68 (m, 8 H, Ph-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.3, 21.1, 26.9, 60.4, 64.7(9), 64.8(2), 70.7(1), 70.7(4), 71.4(9), 71.5(5), 72.3, 72.5, 127.6, 127.8, 128.3, 129.8, 133.2, 135.5, 138.4.

MS (FAB): *m*/*z* (%) = 830 (100) $[M + Na]^+$.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{48}H_{62}NaO_7Si_2$: 829.3926; found: 829.3914.

1,11-Bis(*tert*-butyldiphenylsiloxy)-4,8-dioxaundecane-2,6,10-triol (7)

A mixture of diol **6** (2.22 g, 3.10 mmol) and Pd-C (10% containing Pd, 328 mg) in EtOH (40 mL) was stirred at r.t. for 1 d under a H_2 atmosphere. When the reaction was complete, the mixture was filtered and concentrated under reduced pressure to give pure **7** (2.17 g, 98%) as a colorless oil; R_f = 0.13 (hexane–EtOAc, 1:1).

IR (ATR, neat): 3370, 3071, 3049, 2930, 2857, 1589, 1472, 1427, 1104, 1006, 998, 823, 739, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.05 [s, 18 H, $C(CH_3)_3$], 3.03 (br, 3 H, OH), 3.43–3.60 (m, 8 H), 3.66 (d, *J* = 5.6 Hz, 4 H, H1, H11), 3.86–3.93 (m, 3 H), 7.35–7.44 (m, 12 H, Ar-H), 7.63–7.65 (m, 8 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2, 26.8, 64.6(6), 64.6(8), 69.5, 70.7(8), 70.8(2), 72.4(8), 72.5(8), 72.6(6), 72.7(0), 77.2, 127.8, 129.8, 133.1, 135.5.

MS (ESI): *m*/*z* (%) = 739 (100) $[M + Na]^+$, 561 (28), 483 (8).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{41}H_{56}NaO_7Si_2$: 739.3457; found: 739.3439.

1,11-Bis(*tert*-butyldiphenylsiloxy)-2,6,10-tris(stearoyloxy)-4,8-dioxaundecane (8)

Following the typical procedure for **4**, **8** (962 mg, 30%) was obtained as an amorphous solid; R_f = 0.39 (hexane–EtOAc, 6:1).

IR (ATR, neat): 2923, 2854, 1739, 1591, 1465, 1429, 1113, 824, 740, 700 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 9 H, CH_3 of fatty acid), 1.03 [s, 18 H, $C(CH_3)_3$], 1.25 (s, 84 H, CH_2 of fatty acid), 1.55–1.60 (m, 6 H, CH_2 of fatty acid), 2.21–2.28 (m, 6 H, CH_2 of fatty acid), 3.52–3.61 (m, 8 H), 3.76 (d, *J* = 4.9 Hz, 4 H, H1, H11), 5.04–5.07 (m, 3 H, CH), 7.37–7.41 (m, 12 H, Ar-H), 7.63–7.65 (m, 8 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 19.2, 22.7, 24.9, 26.7, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6(7), 29.7(2), 31.9, 34.4, 62.5, 69.7, 69.9, 72.5, 127.7, 129.7, 133.2, 133.3, 135.5, 135.6, 173.1.

MS (ESI): *m*/*z* (%) = 1542 (10), 1541 (29), 1540 (69), 1539 (100), 1538 (95) $[M + Na]^+$.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{95}H_{158}NaO_{10}Si_2$: 1538.1286; found: 1538.1279.

2,6,10-Tris(stearoyloxy)-4,8-dioxaundecane-1,11-diol (9)

To a soln of **8** (937 mg, 0.62 mmol) in THF (15 mL) was added AcOH (445 mg, 7.41 mmol) and 1.0 M TBAF in THF (3.71 mL, 3.71 mmol); the mixture was stirred at r.t. for 20 h. When the reaction was complete, the mixture was treated with sat. aq NH_4Cl and extracted with $CHCl_3$. The organic layer was washed with brine and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, $CHCl_3$–MeOH, 10:1) to give **9** (532 mg, 83%) as a white solid; mp 59–61 °C (EtOAc); R_f = 0.29 (hexane–EtOAc, 3:2).

IR (ATR, neat): 3440, 2916, 2850, 1734, 1468, 1195, 1178, 1105, 721 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 9 H, CH_3 of fatty acid), 1.25 (s, 84 H, CH_2 of fatty acid), 1.59–1.62 (m, 6 H, CH_2 of fatty acid), 2.31–2.36 (m, 6 H, CH_2 of fatty acid), 3.48–3.78 (m, 10 H), 3.99–4.18 (m, 2 H), 4.97–4.99 (m, 2 H, CH), 5.11–5.14 (m, 1 H, CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 24.9, 25.0, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6, 29.6(7), 29.7(1), 31.9, 34.2, 34.3, 65.2, 68.8, 69.9, 72.5, 77.2, 173.6, 174.0.

MS (FAB): *m*/*z* (%) = 1062 (41) $[M + Na]^+$, 681 (22), 341 (98), 176 (49), 97 (34), 91 (40), 84 (49), 82 (48), 72 (54), 70 (64), 58 (100), 56 (88).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{63}H_{122}NaO_{10}$: 1061.8930; found: 1061.8930.

2,6,10-Tris(benzyloxy)-1,11-bis(*tert*-butyldiphenylsiloxy)-4,8-dioxaundecane (10)

To a mixture of NaH (60% in oil, 12.7 g, 0.32 mol) in THF (250 mL) was added a soln of **6** (64.1 g, 79.3 mmol) in THF (250 mL) at 0 °C; the mixture was stirred at this temperature for 30 min. BnBr (40.7 g, 0.24 mol) was added and the mixture was stirred at r.t. for 16 h. When the reaction was complete, the mixture was treated with 50% aq THF at 0 °C and the solvent was removed under reduced pressure. The residual oil was diluted with H_2O and EtOAc. The mixed soln was extracted with EtOAc. The organic layer was washed with H_2O and brine and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residual oil was purified by column chromatography (silica gel, hexane–EtOAc, 9:1) to give **10** (76.4 g, 98%) as a colorless oil; R_f = 0.67 (hexane–EtOAc, 3:2).

IR (neat): 3071, 3033, 3000, 2957, 2930, 2859, 1590, 1497, 1472, 1428, 1391, 1113, 1028, 911, 824, 735, 700, 648, 613, 505 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.04 [s, 18 H, $C(CH_3)_3$], 3.53–3.75 (m, 15 H), 4.62 (s, 6 H, benzylic), 7.23–7.40 (m, 27 H, Ar-H), 7.66 (AB q, *J* = 7.8, 1.5 Hz, 8 H, Ph-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.3, 26.9, 63.9, 71.7, 71.8, 72.1, 72.3, 72.4, 77.2, 78.8(9), 78.9(1), 127.4(7), 127.5(5), 127.5(8), 127.6(9), 127.7(5), 128.1, 128.2(9), 128.3(2), 129.6(1), 129.6(9), 129.7(2), 133.4(9), 133.5(4), 134.9, 135.6(6), 135.6(9), 135.9(8), 135.9(9), 138.8(0), 138.9.

MS (ESI): *m*/*z* (%) = 1009.5 (59) $[M + Na]^+$, 919 (100), 829 (37).

HRMS (FAB): *m*/*z* $[M + Na]^+$ calcd for $C_{62}H_{74}NaO_7Si_2$: 1009.4871; found: 1009.4842.

2,6,10-Tris(benzyloxy)-4,8-dioxaundecane-1,11-diol (11)

To a soln of **10** (12.2 g, 12.3 mmol) in THF (63 mL) was added 1.0 M TBAF in THF (37.0 mL, 37.0 mmol) at 0 °C; the mixture was stirred at r.t. for 6 h. When the reaction was complete, the solvent was removed under reduced pressure and the residual oil was purified by column chromatography (silica gel, hexane–EtOAc, 1:1 to 1:4) to give **11** (6.17 g, 98%) as a colorless oil; R_f = 0.20 ($CHCl_3$–MeOH, 9:1).

IR (neat): 3434, 3088, 3063, 3031, 2872, 1497, 1455, 1208, 911, 737, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.25 (br, 2 H, OH), 3.56–3.72 (m, 15 H), 4.54–4.70 (m, 6 H, benzylic), 7.25–7.38 (m, 15 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 62.4(6), 62.4(9), 62.5(8), 62.6(1), 71.3, 71.3(8), 71.4(0), 71.4(5), 71.5(1), 71.5(4), 71.6, 72.1, 72.2, 72.3, 76.9, 77.9, 127.7, 127.7(8), 127.8(1), 128.3, 128.4, 128.5, 138.3, 138.4.

MS (FAB): *m*/*z* (%) = 511 (100) $[M + H]^+$.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{30}H_{38}NaO_7$: 533.2510; found: 533.2520.

2,6,10-Tris(benzyloxy)-1,11-bis(stearoyloxy)-4,8-dioxaundecane (12a)

Following the typical procedure for **4** using stearoyl chloride gave **12a** (78% yield) as a colorless amorphous; R_f = 0.60 (hexane–EtOAc, 3:1).

IR (neat): 3032, 2924, 2853, 1740, 1497, 1115, 735, 696 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.81 (t, *J* = 6.6 Hz, 6 H, CH_3 of fatty acid), 1.18 (s, 56 H, CH_2 of fatty acid), 1.49–1.57 (m, 4 H, CH_2 of fatty acid), 2.22 (t, *J* = 7.6 Hz, 4 H, CH_2 of fatty acid), 3.57–3.70 (m, 8 H), 3.75–3.80 (m, 3 H), 4.06 (dd, *J* = 11.7, 5.8 Hz, 2 H, H1 or H11), 4.19–4.23 (m, 2 H, H1 or H11), 4.58 (s, 4 H, benzylic), 4.59 (s, 2 H, benzylic), 7.19–7.26 (m, 15 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 25.0, 29.1, 29.2, 29.3, 29.3(6), 29.4(3), 29.5, 29.6, 29.6(6), 29.7(0), 31.9, 34.1(5), 34.2(3),

63.4, 63.6, 71.1(7), 71.2(2), 71.7, 71.8, 72.2, 72.4, 72.7, 75.8, 126.8, 127.0, 127.6, 127.6(7), 127.7(0), 127.7(3), 127.9(8), 128.1, 128.3(2), 128.3(5), 128.3(9), 128.4(2), 129.0, 129.8, 130.1, 133.1, 134.5, 138.2, 138.5, 173.5, 173.7.

MS (APCI): *m/z* (%) = 1066 (5) $[M + Na]^+$, 1026 (13), 950 (24), 936 (66), 846 (41), 738 (89), 431 (100), 341 (69).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{66}H_{106}NaO_9$: 1065.7729; found: 1065.7757.

2,6,10-Tris(benzyloxy)-1,11-bis(myristoyloxy)-4,8-dioxaundecane (12b)

Following the typical procedure for **4** using myristoyl chloride gave **12b** (100% yield) as a colorless amorphous; R_f = 0.80 (hexane–EtOAc, 2:1).

IR (neat): 2924, 2855, 1740, 1497, 1466, 1455, 1113, 911, 735, 696 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.8 Hz, 6 H, CH_3 of fatty acid), 1.23 (s, 40 H, CH_2 of fatty acid), 1.56–1.61 (m, 4 H, CH_2 of fatty acid), 2.22–2.36 (m, 4 H, CH_2 of fatty acid), 3.52–3.57 (m, 8 H), 3.70–3.75 (m, 3 H, CH), 4.10 (dd, *J* = 6.8, 5.4 Hz, 2 H, H1 or H11), 4.25 (dt, *J* = 11.7, 3.9 Hz, 2 H, H1 or H11), 4.59–4.68 (m, 6 H, benzylic), 7.24–7.34 (m, 15 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 25.0, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6, 29.6(7), 29.7(0), 31.9, 34.2, 63.6, 71.2, 71.3, 71.7, 71.8, 72.1(9), 72.2(0), 72.4, 75.8, 75.9, 127.6, 127.6(7), 127.7(1), 127.7(4), 128.2, 128.3, 128.4, 138.3, 138.6, 173.6.

MS (FAB): *m/z* (%) = 954 (1), $[M + Na]^+$, 375 (5), 285 (9), 181 (18), 91 (100).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{58}H_{90}NaO_9$: 953.6477; found: 953.6459.

2,6,10-Tris(benzyloxy)-1,11-bis(palmitoyloxy)-4,8-dioxaundecane (12c)

Following the typical procedure for **4** using palmitoyl chloride gave **12c** (88% yield) as a colorless amorphous solid; R_f = 0.50 (hexane–EtOAc, 3:1).

IR (neat): 2923, 2853, 1740, 1497, 1466, 1455, 1113, 911, 735, 696 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.8 Hz, 6 H, CH_3 of fatty acid), 1.23 (s, 48 H, CH_2 of fatty acid), 1.55 (s, 4 H, CH_2 of fatty acid), 2.30 (dt, *J* = 22.9, 7.8 Hz, 4 H, CH_2 of fatty acid), 3.52–3.57 (m, 8 H), 3.70–3.75 (m, 3 H, CH), 4.15 (dd, *J* = 6.5, 5.6 Hz, 2 H, H1 or H11), 4.30 (dt, *J* = 11.5, 3.6 Hz, 2 H, H1 or H11), 4.66 (s, 4 H, benzylic), 4.68 (s, 2 H, benzylic), 7.24–7.31 (m, 15 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 24.7, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6, 29.6(6), 29.7(0), 31.9, 34.2, 63.6, 71.1(8), 71.2(4), 71.7, 71.8, 72.2, 72.4, 75.8(2), 75.8(4), 127.6, 127.6(7), 127.6(9), 127.7, 128.3, 128.4, 138.2, 138.6, 173.7.

MS (APCI): *m/z* (%) = 1010 (10) $[M + Na]^+$, 970 (37), 880 (100), 790 (67).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{62}H_{98}NaO_9$: 1009.7103; found: 1009.7118.

1,11-Bis(arachidoyloxy)-2,6,10-tris(benzyloxy)-4,8-dioxaundecane (12d)

Following the typical procedure for **4** using arachidoyl chloride (prepared from arachidic acid and $SOCl_2$) gave **12d** (100% yield) as a colorless amorphous solid; R_f = 0.80 (hexane–EtOAc, 2:1).

IR (neat): 2919, 2851, 1736, 1497, 1464, 1456, 1115, 909, 733, 698, 648 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.6 Hz, 6 H, CH_3 of fatty acid), 1.23 (s, 64 H, CH_2 of fatty acid), 1.56–1.59 (m, 4 H, CH_2 of fatty acid), 2.27 (t, *J* = 7.3 Hz, 4 H, CH_2 of fatty acid), 3.50–3.58 (m, 8 H), 3.69–3.77 (m, 3 H, CH), 4.10 (dd, *J* = 7.1, 5.1 Hz, 2 H, H1 or H11), 4.25 (dt, *J* = 11.7, 3.9 Hz, 2 H, H1 or H11), 4.63 (s, 4 H, benzylic), 4.64 (s, 2 H, benzylic), 7.22–7.31 (m, 15 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 14.2, 22.7, 24.9, 29.1, 29.2(7), 29.3(3), 29.5, 29.6(0), 29.6(3), 29.7, 31.9, 34.2, 63.6, 71.1, 71.7, 71.8, 72.2, 72.3, 75.7(8), 75.8(0), 127.5, 127.6, 127.6(5), 127.6(8), 128.2(9), 128.3(1), 138.2, 138.5, 173.6.

MS (ESI): *m/z* (%) = 1122 (100) $[M + Na]^+$.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{70}H_{114}NaO_9$: 1121.8361; found: 1121.8377.

Debenzylation of Triglyceryl Di-Fatty Acid Esters; General Procedure

A mixture of diester **12a–d** (2.00 mmol) and $Pd(OH)_2$-C (20% containing Pd, 400 mg) in THF (30 mL) and EtOH (15 mL) was stirred at 40 °C under a H_2 atmosphere. After stirring overnight, the mixture was filtered and concentrated under reduced pressure. The residue was purified by recrystallization (EtOAc) to give the desired ester as a white solid.

1,11-Bis(stearoyloxy)-4,8-dioxaundecane-2,6,10-triol (13a)

Yield: 55%; mp 82–83 °C (EtOAc); R_f = 0.10 ($CHCl_3$–EtOAc, 1:1).

IR (ATR, neat): 3367, 2956, 2917, 2850, 1732, 1471, 1122, 1033, 1011, 887, 719 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.6 Hz, 6 H, CH_3 of fatty acid), 1.23 (s, 56 H, CH_2 of fatty acid), 1.55–1.65 (m, 4 H, CH_2 of fatty acid), 2.31 (t, *J* = 7.6 Hz, 4 H, CH_2 of fatty acid), 3.47–3.58 (m, 8 H), 3.96–4.01 (m, 3 H, CH), 4.13 (qd, *J* = 10.5, 5.8 Hz, 4 H, H1, H11).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 24.9, 29.1, 29.3, 29.4, 29.5, 29.6, 29.6(5), 29.6(8), 31.9, 34.2, 65.2, 69.0, 72.5, 72.7, 174.0.

MS (FAB): *m/z* (%) = 796 (100) $[M + Na]^+$, 341 (15), 176 (15).

HRMS (FAB): *m/z* $[M + Na]^+$ calcd for $C_{45}H_{88}NaO_9$: 795.6308; found: 795.6308.

1,11-Bis(myristoyloxy)-4,8-dioxaundecane-2,6,10-triol (13b)

Yield: 45%; mp 94–96 °C (EtOAc); R_f = 0.10 ($CHCl_3$–EtOAc, 1:1).

IR (ATR, neat): 3528, 3431, 2917, 2850, 1727, 1472, 1118, 1033, 1012, 888, 716 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.6 Hz, 6 H, CH_3 of fatty acid), 1.23 (s, 40 H, CH_2 of fatty acid), 1.53–1.60 (m, 4 H, CH_2 of fatty acid), 2.32 (t, *J* = 7.6 Hz, 4 H, CH_2 of fatty acid), 3.51–3.59 (m, 8 H), 3.93–4.02 (m, 3 H, CH), 4.29 (qd, *J* = 7.1, 5.8 Hz, 4 H, H1, H11).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 24.9, 29.1, 29.3, 29.4, 29.5, 29.6(0), 29.6(3), 29.7, 31.9, 34.2, 65.2, 69.0, 72.5, 72.7, 174.0.

MS (ESI): *m/z* (%) = 684 (100) $[M + Na]^+$.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{37}H_{72}NaO_9$: 683.5074; found: 683.5068.

1,11-Bis(palmitoyloxy)-4,8-dioxaundecane-2,6,10-triol (13c)

Yield: 55%; mp 79–80 °C (EtOAc); R_f = 0.10 ($CHCl_3$–EtOAc, 1:1).

IR (ATR, neat): 3369, 2917, 2850, 1735, 1467, 1124, 1029, 886, 720 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 6.3 Hz, 6 H, CH_3 of fatty acid), 1.23 (s, 48 H, CH_2 of fatty acid), 1.55 (s, 4 H, CH_2 of fatty acid), 2.32 (t, *J* = 7.3 Hz, 4 H, CH_2 of fatty acid), 3.52–3.59 (m, 8 H), 3.91–4.02 (m, 3 H, CH), 4.08 (qd, *J* = 13.9, 4.6 Hz, 4 H, H1, H11).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 24.9, 29.1, 29.3, 29.4, 29.5, 29.6(0), 29.6(5), 29.6(8), 31.9, 34.2, 65.2, 69.0, 72.5, 72.7, 174.0.

MS (FAB): *m*/*z* (%) = 740 (8) $[M + Na]^+$, 575 (12), 483 (25), 391 (56), 369 (60).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{41}H_{80}NaO_9$: 739.5695; found: 739.5712.

1,11-Bis(arachidoyloxy)-4,8-dioxaundecane-2,6,10-triol (13d)
Yield: 34%; mp 86–87 °C (EtOAc); R_f = 0.10 ($CHCl_3$–EtOAc, 1:1).

IR (ATR, neat): 3363, 2917, 2850, 1735, 1468, 1177, 1108, 885, 720 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.6 Hz, 6 H, CH_3 of fatty acid), 1.23 (s, 64 H, CH_2 of fatty acid), 1.60 (t, *J* = 7.1 Hz, 4 H, CH_2 of fatty acid), 2.32 (t, *J* = 7.3 Hz, 4 H, CH_2 of fatty acid), 3.42–3.59 (m, 8 H), 3.95–4.00 (m, 3 H, CH), 4.13 (qd, *J* = 13.9, 4.4 Hz, 4 H, H1, H11).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 24.9, 29.1, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9, 34.2, 65.2, 72.3, 172.5.

MS (APCI): *m*/*z* (%) = 852 (13) $[M + Na]^+$, 794 (100), 639 (27), 549 (36), 517 (77).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{49}H_{96}NaO_9$: 851.6947; found: 851.6946.

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(19) All synthesized compounds were mixture of diastereomers. However, their spectral data appeared as the single structure. For example, the benzylic protons of compound **12a** were observed at δ = 4.58 (4 H) and 4.59 (2 H), both as singlets (see the experimental section).