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Synthetic trehalose di- and mono-esters of α-, methoxy- and keto-mycolic acids

Juma'a R. Al Dulayymi, Mark S. Baird *, Maximiliano Maza-Iglesias, Rwoa'a T. Hameed, Klarah S. Baols, Majed Muzael, Ahmed D. Saleh

School of Chemistry, Bangor University, Gwynedd, Wales LL57 2UW, UK

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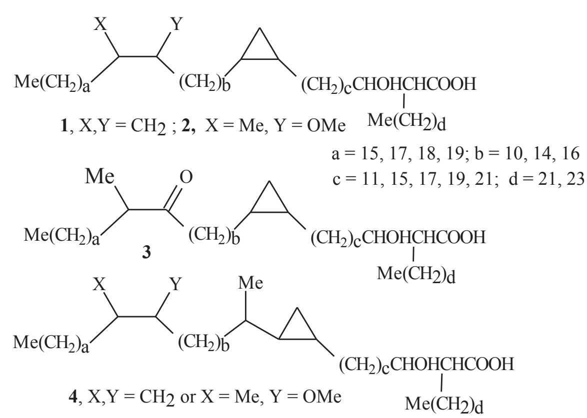
ABSTRACT

Synthetic mycolic acids matching the overall structure of the major mycolic acids of *Mycobacterium tuberculosis* are coupled to trehalose to generate the corresponding synthetic trehalose monomycolate (TMM) and trehalose dimycolate (TDM; cord factor), either with two identical or two different mycolic acids.

1. Introduction

Mycobacteria and some related species contain very long-chain β-hydroxy acids, mycolic acids (MA). These are present in a membrane bound form as penta-arabinose tetra-mycolates, but also as sugar esters including trehalose-6,6′-dimycolates (TDMs, 'cord factors') and trehalose monomycolates (TMMs),[1–3] and as free MAs.[4] Each mycobacterium normally contains several homologues of a number of the classes of MA (Scheme 1), such as α (**1**), methoxy (**2**), and keto-MA containing a *cis*-cyclopropane (**3**) or an α-methyl-*trans*-cyclopropane, eg. **4**.[4–6]

Analysis of TMM by MALDI mass spectrometry has been reported.[7] TMM from *Mycobacterium tuberculosis* showed odd-carbon-numbered monocyclopropanoic (or monoenoic) α-mycolates, dicyclopropanoic mycolates, ranging from C-75 to C-85, odd- and even-carbon methoxymycolates ranging from C-83 to C-94 and even- and odd-carbon keto-mycolates ranging from C-83 to C-90. In contrast, TMM from *Mycobacterium bovis* (wild strain and BCG sub-strains) possessed even-carbon dicyclopropanoic α-mycolates while the BCG Connaught strain lacked methoxymycolates almost completely.[7] The MALDI analysis of TDM, where various combinations of the two MAs bonded to trehalose can lead to a large number of individual structures, is more complicated.[8,9]



Scheme 1. Typical mycolic acids.

MA-containing glycolipids, in particular TDM, stimulate innate, early adaptive and both humoral and cellular adaptive immunity. Most functions can be associated with their ability to induce a range of chemokines (MCP-1, MIP-1α, IL-8) and cytokines (e.g., IL-12, IFN-γ, TNF-α, IL-4, IL-6, IL-10).[10,11] TDM mediates trafficking events during mycobacterial infection of macrophages,[12–15] and induces cytokine message and protein expression during lung granuloma formation.[16–23] It enhances neovascularization through growth factor production by neutrophils and macrophages.[24]

* Corresponding author. Tel.: +44 1248382374; fax: +44 1248370528; e-mail address: chs028@bangor.ac.uk (M.S. Baird).

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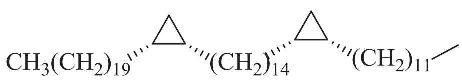
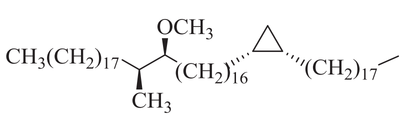
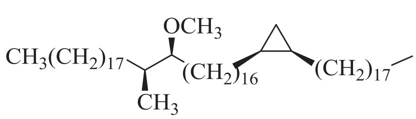
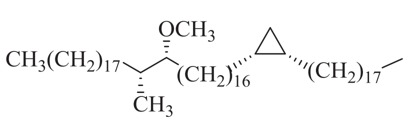
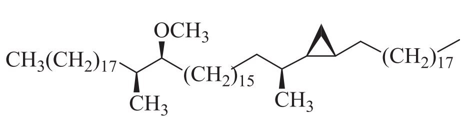
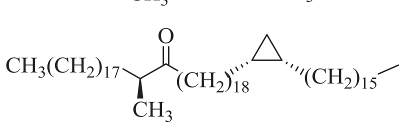
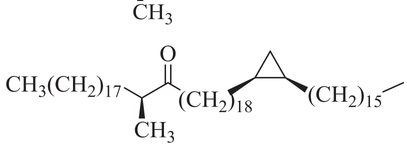
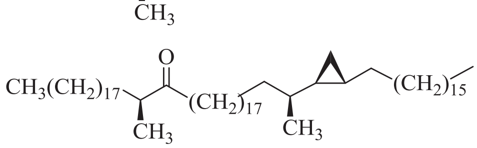
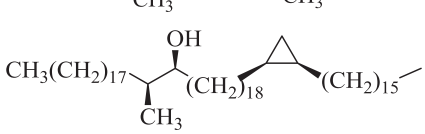
Intraperitoneal TDM treatment of mice inoculated with encephalomyocarditis virus restricts viral growth, pointing to the role of IFN-α/3 production prior to infection in the antiviral activities of TDM and, more generally, in the outcome of viral infection.[25] Besides these innate immune activities, TDM, but not a similar glycolipid without MA, also indirectly promotes adaptive immune responses. A strong release of IFN-γ and expansion of natural killer cells leads to macrophages activated for antigen presentation to T lymphocytes.[13] The role of T lymphocytes in the pathogenesis of TDM induced interstitial pneumonitis has been discussed.[26,27]

The diverse immune activities of TDM and TMM suggest multiple biomedical applications. Thus they are effective against a range of cancers,[28,29] and may be of value for wound-healing and hair growth.[30] A Japanese Patent describes the use of a keratinocyte growth regulating agent, which is a sugar ester of MA extracted from cultured microbial cells.[31] Sugar esters of simpler long chain fatty acids have been claimed to reduce skin changes during ageing.[32] TDM enhances non-specific resistance to influenza virus infection,[33,34] and against infection with *Salmonella typhi* and *Salmonella typhimurium* in mice.[35] TDM induces corneal angiogenesis in rats,[36] enhances resistance to influenza infection in neutropenic animals,[37] and is an adjuvant in mice and rats.[38]

Strong biological effects such as production of NO and stimulation of TNF-α in macrophages are shown by simpler trehalose corynomycolates.[39–41] Even simple C_{22} and C_{26} trehalose monoesters are found to activate macrophages in a Mincle-dependent manner. The activities of the monoesters paralleled those of their diester counterparts, and both mono- and diesters could activate the immune response in the absence of priming.[42] However, cord factors enriched in particular classes of MA show differential antigenic activity towards antibodies of *M. tuberculosis* and *Mycobacterium avium* and have found use in diagnostic assays for the respective diseases.[43–45] Moreover TDM from different mycobacteria is of different activity in granuloma formation,[46] and induces differing anti-infectious activities in combination with muramyl dipeptide.[47] Among TDMs from different mycobacteria, that from *Mycobacterium bovis* showed the greatest activity and toxicity.[48]

Several methods have been reported by which 'semi-synthetic' cord factors may be reconstituted from mixtures of naturally derived MA, re-forming the sugar esters;[49–55] TDM models using simple

Table 1
Yields for synthetic TDMs and TMMs and protected intermediate

R	n		5 %	7 (TDM) %	8 %	9 %	10 (TMM) %	11 %	12 %
	23	a	86	29	53	61	43	40	32
	23	b	68	33	53	54	49	90	22
	23	c	92	70	90	63	30	88	90
	23	d	80	51.3	78	72	41.7	80	78
	23	e	67	22	50	46	78	69	90
	23	f	61	29	61	35	18	47	50
	23	g	82	63	69	60	37	87	54
	21	h	82	22	52	17	82	48	66
	23	i	88	45	75	24	53	44	52
	21	j	81	58	46	56	48		

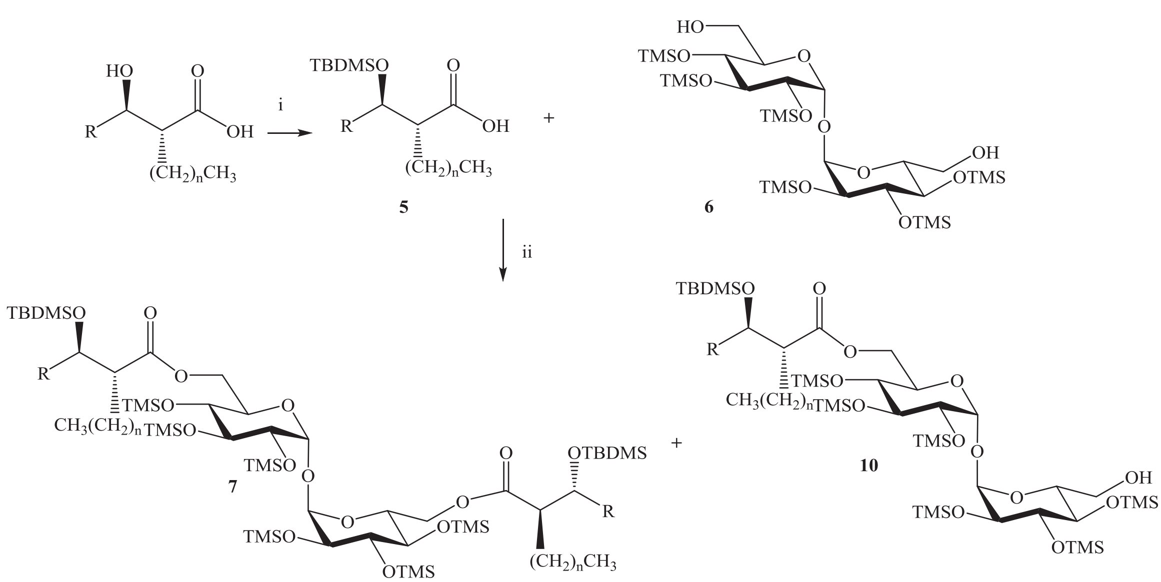
fatty acids have been prepared in the same way. The combination of a cationic surfactant and a model synthetic 'TDM' made from trehalose and behenic acid proved to be an efficient adjuvant for tuberculosis subunit vaccines.[56] Recently the synthesis of a stereodefined trehalose ester of a model corynomycolic acid has been reported and the products found to be active in enhancing IL-6 levels.[41] However, it is known that the detailed structure of the MAs in TDM affects their biological properties; thus, *trans*-cyclopropanated MAs suppress *M. tuberculosis*-induced inflammation and virulence.[57,58] The synthesis of unique molecules of TDM containing complete MAs matching those present in nature therefore offers a unique possibility to identify whether the various biological effects described above are selectively caused by specific TDM molecules.

We have recently reported the synthesis of a number of MAs, which are either identical to the major isomers of α-, methoxy-, keto- and hydroxy-MAs of *M. tuberculosis*, or differ only in their stereochemistry (in some cases this remains to be determined for the natural materials).[59–63] We have reported in brief the first syntheses of TDM and TMM derived from synthetic α- and methoxy-MA;[64] we now report in full the conversions of a range of these synthetic MAs into the corresponding TDM and TMM, and the first synthetic TDMs involving two different MAs.

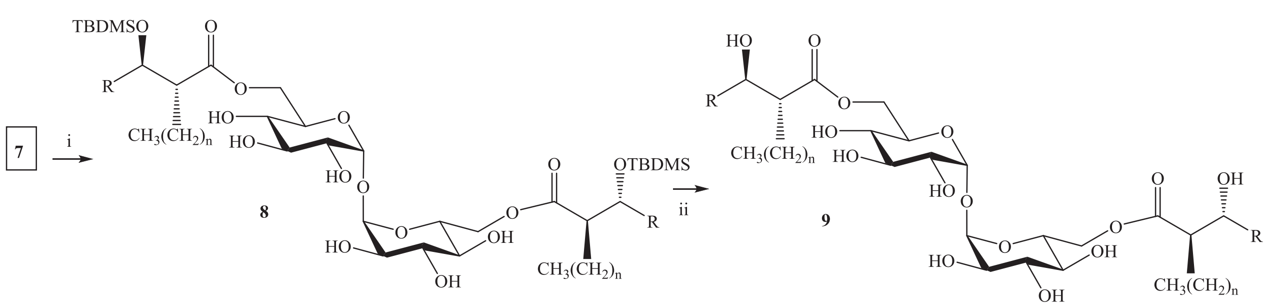
2. Results and discussion

The protected MAs **5** (Table 1 and Scheme 2) were prepared from the corresponding hydroxy acids by reaction with an excess of *tert*-butyldimethylsilyl chloride and imidazole in the presence of 4-dimethylaminopyridine for 24 h at 70 °C, followed by hydrolysis of the TBDMS ester on the acid group using potassium carbonate in THF-water-methanol (10:1:1) then acidification with $KHSO_4$.[50] Coupling of the protected MAs to the protected trehalose (**6**) using 1-(3-dimethylaminopropyl-3-ethylcarbodiimide hydrochloride (EDCI) and 4-dimethylaminopyridine (DMAP) led to the protected TDMs **7** and TMMs **10** (Scheme 2). These were deprotected in two steps, first removing the trimethylsilyl groups, then the *tert*-butyldimethylsilyl groups (Schemes 3 and 4).

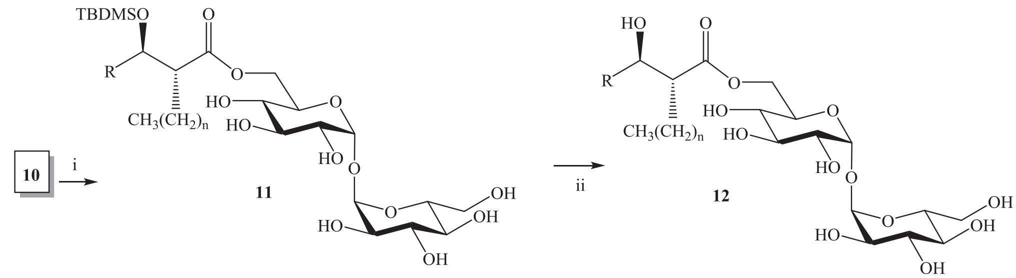
In this way, compound **5d** was coupled to hexatrimethylsilyl-trehalose (**6**) using EDCI, DMAP and 4 Å molecular sieves in dichloromethane for six days at ambient temperature. This gave the protected TDM **7d** (51%) and the protected TMM **10d** (42%). Deprotection of **7d** and **10d**, respectively, using tetrabutylammonium fluoride for 1 h at 5 °C in dry THF removed all the trimethylsilyl groups and led to the TBDMS-protected TDM **8d** and TMM **11d**; these showed one and two acetal carbon signals, respectively, by ^{13}C NMR spectroscopy. Removal of the TBDMS groups released the corresponding unprotected molecules **9d** and **12d**, respectively (Schemes 3 and 4). The ^{1}H NMR spectrum of TMM **12d** showed two signals for the acetal hydrogens (δ 5.07, 5.02). For the TDM **9d**, there was a single acetal signal in the proton NMR spectrum, and a single acetal signal and just eight other signals for carbons adjacent to oxygen in the ^{13}C NMR spectrum. In the same way the TDMs and TMMs molecules shown in Table 1 were prepared from different diasteroisomers of α-mycolic acid (**9a/b** and **12a/b**), of methoxy-mycolic acid (**9c/d/e** and **12c/d/e**) containing a *cis*-cyclopropane, and a *trans*-cyclopropane (**9f** and **12f**), and of the corresponding keto-mycolic acids (**9g/h/i** and **12g/h/i**). In addition, a TDM derived from a less common hydroxy-mycolic acid (**9j**) was obtained.



Scheme 2. (i) Imidazole, TBDMSCl, 4-DMAP; K_2CO_3, THF, H_2O, MeOH (ii) EDCI, 4-DMAP, CH_2Cl_2, 4 Å MS, 6 d, rt (R as per Table 1).



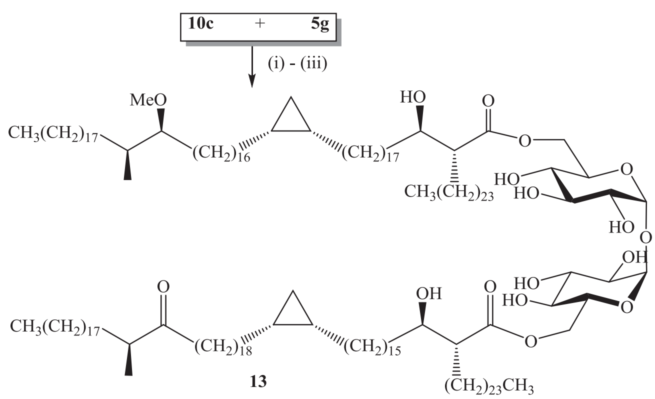
Scheme 3. (i) TBAF, THF, 5 °C., 1 h; (ii) pyridine, THF, HF-pyridine complex, 43 °C, 17 h, then neutralise with aq $NaHCO_3$.



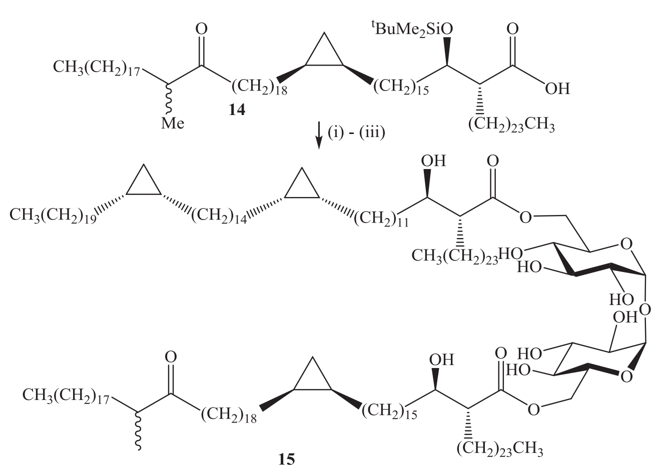
Scheme 4. (i) TBAF, THF, 5 °C., 1 h; (ii) pyridine, THF, HF-pyridine complex, 43 °C, 17 h, then neutralise with aq $NaHCO_3$.

In natural mixtures of TDM, there are many different mycolic acids present, and the chance of two identical molecules being bound to the same trehalose is statistically low, unless there is specific control in the biosynthetic pathway. It is possible that the antigenicity and immune responses caused by different combinations of classes (and indeed homologues) of mycolic acid in the TDM may be different. With this in mind, we now show that the above method may be applied to the synthesis of TDM containing two different mycolic acids, and provide three examples of this approach. In the first, the protected TMM **10c** was coupled with the protected mycolic acid **5g**, to produce a protected mixed cord factor; this was deprotected as above in two steps to provide compound **13** (Scheme 5):

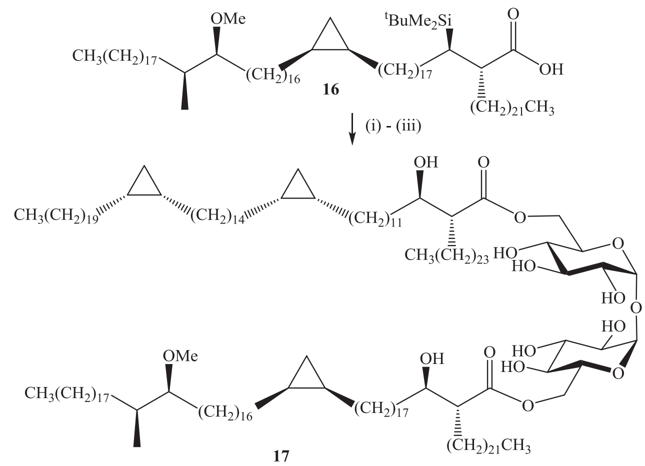
Similarly, the α-mycolic acid containing TMM **10a** could be coupled to protected keto- or methoxy-MAs **14** or **16** to provide the mixed TDMs **15** or **17** (Schemes 6 and 7).



Scheme 5. (i) EDCI, 4-DMAP, CH_2Cl_2, 4 Å MS, 6 d, rt (ii) TBAF, THF, 5 °C, 1 h; (iii) pyridine, THF, HF-pyridine complex, 43 °C, 17 h, then aq $NaHCO_3$.



Scheme 6. (i) **10a**, EDCI, 4-DMAP, CH_2Cl_2, 4 Å MS, 6 d, rt (ii) TBAF, THF, 5 °C, 1 h; (iii) pyridine, THF, HF-pyridine complex, 43 °C, 17 h, then aq $NaHCO_3$.



Scheme 7. (i) **10a**, EDCI, 4-DMAP, CH_2Cl_2, 4 Å MS, 6 d, rt (ii) TBAF, THF, 5 °C, 1 h; (iii) pyridine, THF, HF-pyridine complex, 43 °C, 17 h, then aq $NaHCO_3$.

It is known that natural mixtures of TDM isolated from different mycobacteria show different biological properties. We have reported preliminary results, which show the α-TDM **9a** to be about three times more effective than a commercial sample of TDM in stimulating the production of the pleiotropic inflammatory cytokine TNF-α in human RAW264.7 macrophages.[64] TDM **9a** was also twice as effective in raising the level of the immunoregulatory chemokine MCP-1 as was a commercial TDM sample.[64] The results of a detailed study of the effects of the cord factors described in this work on selected immune signals will be presented elsewhere.[65] In addition, the various trehalose esters described above give differential responses when used as antigens in serodiagnostic assays that measure their binding to antibodies in serum from patients with active tuberculosis; in several cases, they provide a better sensitivity and specificity than natural TDM in distinguishing TB-positive from TB-negative serum from individuals from countries where TB is indigenous; again, this will be reported in detail elsewhere.[66]

3. Conclusion

Trehalose mono- and di-mycolates are important components of mycobacterial cells, and the complex natural mixtures are potent signalling agents in the immune system. In order to explore the biological properties of individual examples, single stereochemically defined synthetic mycolic acids have been converted into trehalose di-mycolates containing two identical mycolic acids, and into the corresponding monomycolates. These cover the major classes of mycolic acid in *M. tuberculosis*, α-, keto- and methoxy, in the latter two cases with either a proximal *cis*-cyclo-propane or an α-methyl-*trans*-cyclopropane. A protected TMM can then be coupled to a second protected mycolic acid leading, after deprotection, to trehalose dimycolates containing combinations of different mycolic acids. This provides a compound library, using which the particular effects of specific MA in the sugar esters on biological properties can be probed.[65,66] The effect of the detailed structure of the TDM and TMM on their physical properties, such as film formation,[67,68] and biological effects will also be reported elsewhere.

4. Experimental section

4.1. General

Chemicals used were obtained from commercial suppliers (Sigma, Aldrich, and Alfa Aeser) or prepared from them by the methods described. Solvents which were required to be dry, e.g. ether, tetrahydrofuran were dried over sodium wire and benzophenone under nitrogen, while dichloromethane was dried over calcium hydride. Petroleum spirit (petrol) was of boiling point 40–60 °C. All reagents and solvents used were of reagent grade unless otherwise stated. Silica gel (Merck 7736) and silica gel plates used for column chromatography and thin layer chromatography were obtained from Aldrich; separated components were detected using variously UV light, I_2 and phosphomolybdic acid solution in IMS followed by charring. Anhydrous magnesium sulfate was used to dry organic solutions. Infra-red (IR) spectroscopy was carried out on a Perkin–Elmer 1600 F.T.I.R. spectrometer as liquid films or KBr disc (solid). Melting points were measured using a Gallenkamp melting point apparatus. NMR spectroscopy was carried out on Bruker Avance 400 or 500 spectrometers. $[\alpha]_D$ values were recorded in $CHCl_3$ on a POLAAR 2001 optical activity polarimeter. Mass spectra were recorded on a Bruker MALDI–TOF MS) to an accuracy of 1 d.p.; accurate mass values obtained in Bangor were run on a Bruker Microtof LC-MS.

In general, the experiments were carried out by a standard set of procedures; these are presented in full for compounds **7a**–**12a**, but only analytical data are presented here for the other series. Full experimental details and NMR spectra are provided in Supplementary data.

4.2. 6-*O*-[(*R*)-2-((*R*)-1-Hydroxy-12-{(1*S*,2*R*)-2-[14-((1*S*,2*R*)-2-eicosylcyclopropyl)tetradecyl]cyclopropyl}do-decyl)-hexacosanoate]-α-*D*-glucopyranosyl-(1→1)-6′-*O*-[(*R*)-2-((*R*)-1-hydroxy-12-{(1*S*,2*R*)-2-[14-((1*S*,2*R*)-2-eicosylcyclo-propyl)tetradecyl]cyclopropyl}dodecyl)hexa-cosanoate]-α-*D*-glucopyranoside (9a) and 6-*O*-[(*R*)-2-((*R*)-1-hydroxy-12-{(1*S*,2*R*)-2-[14-((1*S*,2*R*)-2-eicosylcyclo-propyl)tetra-decyl]cyclopropyl}-dodecyl)hexacosanoate]-α-*D*-gluco-pyranosyl-(1→1)-α-*D*-gluco-pyranoside (12a)

(i) Imidazole (0.730 g, 10.8 mmol) was added to a stirred solution of (*R*)-2-((*R*)-1-hydroxy-12-{(1*S*,2*R*)-2-[14-((1*S*,2*R*)-2-eicosyl cyclopropyl)tetradecyl]cyclopropyl}dodecyl)-hexacosanoic acid[59] (1.23 g, 1.08 mmol) in dry DMF (6 ml and toluene (10 ml) at room temperature followed by the addition of *tert*-butyldimethylsilylchloride (2.44 g, 16.2 mmol) and 4-dimethylaminopyridine (0.13 g, 10.8 mmol). The mixture was stirred at 70 °C for 24 h. The solvent was removed under high vacuum and the residue was diluted with petrol/ethyl acetate (10:2, 50 ml) and water (20 ml). The aqueous layer was re-extracted with petrol/ethyl acetate (10:2, 2×30 ml). The combined organic layers were washed with water, dried and evaporated. The residue was dissolved in THF (10 ml), water (1.4 ml) and methanol (1.4 ml); to this was added potassium carbonate (0.20 g). The mixture was stirred at 45 °C for 12 h, diluted with petrol/diethyl ether (5:2, 30 ml) and water (2 ml), then acidified with potassium hydrogen sulfate to pH 2. The aqueous layer was re-extracted with petrol/ethyl acetate (2×20 ml). The combined organic layers were washed with water, dried and evaporated to give a residue; column chromatography on silica eluting with petrol/ethyl acetate (20:1) gave acid **5a** as a colourless oil (1.16 g, 86%), $[\alpha]_D^{24}$ +1.64 (c 1.76, $CHCl_3$) {Found $[M+Na]^+$: 1275.3242; $C_{84}H_{166}NaO_3Si$ requires: 1275.3243}. This showed δ_H (500 MHz, $CDCl_3$): 3.83 (1H, ddd, *J* 2.6, 5.1, 7.9 Hz), 2.53 (1H, ddd, *J* 2.9, 6.4, 9.2 Hz), 1.75–1.48 (12H, m), 1.26 (123H, br s), 0.93 (9H, s), 0.89 (6H, t, 6.7 Hz), 0.67–0.64 (4H, m), 0.57 (2H, dt, *J* 4.2, 8.2 Hz), 0.15 (3H, s), 0.14 (3H, s), −0.31 (2H, q, *J* 5.4 Hz); δ_C: 173.4, 73.6, 50.6, 35.9, 31.9, 30.2, 29.7, 29.65, 29.62, 29.6, 29.54, 29.5, 29.4, 29.35, 28.7, 27.4, 25.7, 25.2, 22.7, 17.9, 15.8, 14.1, 10.9, −4.2, −4.9; ν_{max}: 2924, 2853, 1709, 1464, 1255, 1073, 835, 775, 720 cm^{-1}.

(ii) 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (100 mg, 0.510 mmol) and 4-dimethylamino-pyridine (55 mg, 0.45 mmol) were added to a stirred solution of **5a** (0.202 g, 0.160 mmol), protected trehalose **6** (50 mg, 0.064 mmol) and powdered 4 Å molecular sieves in dry dichloromethane (4 ml) at room temperature under nitrogen. After 6 days, it was diluted with dichloromethane (5 ml) and silica (2 g) was added. The solvent was removed under reduced pressure and the residue purified by column chromatography on silica eluting with petrol/ethyl acetate (20:1) to give first glucopyranoside **7a** as a colourless thick oil (0.15 g, 29%), $[\alpha]_D^{24}$ +15.7 (c 0.51, $CHCl_3$) {Found $[M+Na]^+$: 3266.3, $C_{198}H_{398}NaO_{15}Si_8$ requires: 3266.9}, which showed δ_H (500 MHz, $CDCl_3$): 4.86 (2H, d, *J* 2.9 Hz), 4.37 (2H, d, *J* 10.4 Hz), 4.04 (2H, d, *J* 12.6 Hz), 3.95 (4H, br q, *J* 5.1 Hz), 3.90 (2H, t, *J* 8.8 Hz), 3.52 (2H, t, *J* 9.2 Hz), 3.39 (2H, dd, *J* 2.9, 9.5 Hz), 2.55 (2H, dt, *J* 4.8, 9.8 Hz), 1.54–1.13 (268H, m), 0.89 (12H, t, *J* 4.8 Hz), 0.88 (18H, s), 0.60–0.56 (8H, m), 0.57 (4H, dt, *J* 3.8, 8.5 Hz), 0.17 (18H, s), 0.15 (18H, s), 0.14 (18H, s), 0.07 (12H, s), −0.31 (4H, q, *J* 5.4 Hz); δ_C: 173.8, 94.8, 73.6, 73.2, 72.8, 71.8, 70.7, 67.7, 64.7, 62.4, 51.9, 43.0, 33., 31.9, 30.2, 30.0, 29.8, 29.75, 29.72, 29.68, 29.5, 29.4, 28.7, 25.98, 25.93, 25.89, 25.84, 22.7, 18.0, 15.8, 14.1, 10.9, 1.1, 0.95, 0.2, −4.4, −4.5, −4.6; ν_{max}: 2922, 2851, 1741, 1460, 1250, 1164, 1110, 1075, 1006, 897, 872, 841, 747 cm^{-1}. The second fraction was gluco-pyranoside **10a** (0.14 g, 43%), $[\alpha]_D^{24}$ +49 (c 0.58, $CHCl_3$) {Found $[M+Na]^+$: 2032.1, $C_{114}H_{234}NaO_{13}Si_7$ requires: 2032.7}. This showed δ_H (500 MHz, $CDCl_3$): 4.91 (1H, d, *J* 3.2 Hz), 4.85 (1H, d, *J* 3.2 Hz), 4.35 (1H, dd, *J* 2.2, 11.7 Hz), 4.07 (1H, dd, *J* 4.1, 12.0 Hz), 3.99 (1H, dt, *J* 2.2, 6.0 Hz), 3.96–3.94 (1H, m), 3.91 (2H, dt, *J* 2.2, 6.6 Hz), 3.84 (1H, dt, *J* 3.5, 6.6 Hz), 3.72–3.67 (2H, m), 3.49 (2H, dt, *J* 5.7, 9.2 Hz), 3.42 (1H, dd, *J* 3.2, 9.5 Hz), 3.39 (1H, dd, *J* 3.2, 9.5 Hz), 2.55 (1H, ddd, *J* 3.5, 5.6, 9.5 Hz), 1.62–1.60 (4H, m), 1.38–1.14 (131H, v br s), 0.88 (6H, t, *J* 7.0 Hz), 0.88 (9H, s), 0.67–0.64 (4H, m), 0.57 (2H, dt, *J* 4.1, 8.2 Hz), 0.17 (9H, s), 0.16 (9H, s), 0.156 (9H, s), 0.151 (9H, s), 0.15 (9H, s), 0.12 (9H, s), 0.06 (3H, s), 0.05 (3H, s), −0.32 (2H, q, *J* 5 Hz); δ_C: 174.1, 94.5, 94.4, 73.4, 73.35, 72.9, 72.8, 72.75, 72.0, 71.4, 70.7, 62.5, 61.7, 51.8, 33.4, 31.9, 30.2, 29.82, 29.8, 29.7, 29.66, 29.5, 29.4, 28.7, 28.1, 26.4, 25.8, 24.9, 22.7, 18.0, 15.8, 14.1, 10.9, 1.05, 1.0, 0.9, 0.8, 0.2, 0.04, −4.5, −4.7; ν_{max}: 3056, 2922, 2851, 1741, 1459, 1379, 1250, 1164, 1075, 1005, 964, 841, 747, 719 cm^{-1}.

A minor product was provisionally identified as (*R*)-2-((*R*)-1-(*tert*-butyldimethylsilanyloxy)-12-{(1*S*,2*R*)-2-[14-((1*S*, 2*R*)-2-eicosylcyclopropyl)tetradecyl]cyclopropyl}dodecyl)-hexacosanoic anhydride {MALDI Found $[M+Na]^+$: 2509.6, $C_{168}H_{330}NaO_5Si_2$ requires: 2509.6}, which showed δ_H (500 MHz, $CDCl_3$): δ 3.92 (2H, dt, *J* 5.7, 11.4 Hz), 2.60 (2H, dt, *J* 5.1, 11.1 Hz), 1.38–1.33 (30H, br m), 1.17 (238H, v br s), 0.89 (12H, t, *J* 6.8 Hz), 0.87 (18H, s), 0.66–0.64 (8H, m), 0.58 (4H, dt, *J* 4.1, 7.9 Hz), 0.08 (6H, s), 0.07 (3H, s), 0.05 (3H, s), −0.31 (4H, q, *J* 5.4 Hz); ν_{max}: 2963, 2856, 1815, 1745, 1466, 1369, 1254, 1093, 902, 831, 774, 732 cm^{-1}.

(iii) Tetrabutylammonium fluoride (0.2 ml, 0.2 mmol) was added to a stirred solution of **7a** (0.11 g, 0.035 mmol) in dry THF (5 ml) at 5 °C under nitrogen, allowed to reach room temperature and stirred for 1 h, then evaporated and the residue was purified by column chromatography on silica eluting with chloroform: methanol (10:1) to give glucopyranoside **8a** as a colourless thick oil (0.051 g, 53%), $[\alpha]_D^{26}$ +16 (c 3.2 g, $CHCl_3$) {Found $[M+Na]^+$: 2833.8709, $C_{180}H_{350}NaO_{15}Si_2$ requires: 2833.8628}. This showed δ_H (500 MHz, $CDCl_3$+few drops of CD_3OD): 4.99 (2H, d, *J* 3.5 Hz), 4.22 (2H, br dd, *J* 3.5, 13.2 Hz), 4.17 (2H, d, *J* 11 Hz), 3.88 (2H, br d, *J* 9.5 Hz), 3.82 (2H, br q, *J* 5.4 Hz), 3.71 (2H, d, *J* 6.3 Hz), 3.39 (2H, dd, *J* 3.5, 9.5 Hz), 3.25 (2H, d, *J* 9.2 Hz), 2.46 (2H, ddd, *J* 3.5, 6.4, 10.1 Hz), 1.16 (274H, br s), 0.79 (12H, t, *J* 4.1 Hz), 0.77 (18H, s), 0.56–0.55 (8H, m), 0.47 (4H, dt, *J* 4.1, 8.2, Hz), −0.04 (6H, s), −0.06 (6H, s), −0.41 (4H, q, *J* 5.1 Hz); δ_C (126 MHz, $CDCl_3$+few drops of CD_3OD): 175.1, 93.4, 73.1, 70.2, 69.8, 62.8, 51.5, 33.4, 31.7, 30.1, 30.0, 29.5, 29.4, 29.2, 28.5, 27.6, 25.6, 25.5, 22.5, 17.8, 15.6, 13.8, 10.7, 10.66, −4.7, −5.1; ν_{max}: 3381, 2927, 2857, 2366, 1742, 1468, 1257, 1076, 833, 772, 722 cm^{-1}.

(iv) Tetrabutylammonium fluoride (0.5 ml, 0.5 mmol, 1 M) was added to a stirred solution of **10a** (0.126 g, 0.0628 mmol) in dry THF (3 ml) at 5 °C under nitrogen. The mixture was allowed to reach room temperature and stirred for 1 h, then worked up and purified as before to give **11a** as a colourless syrup (0.04 g, 40%), $[\alpha]_D^{26}$ +44 (c 0.57, $CHCl_3$) {[Found $M+Na]^+$: 1599.3, $C_{96}H_{186}NaO_{13}Si$ requires: 1599.6}. This showed δ_H (500 MHz, $CDCl_3$+few drops of CD_3OD)): 4.93 (2H, d, *J* 3.5 Hz), 4.15 (1H, d, *J* 2.8 Hz), 3.81 (1H, br dt, *J* 2.8, 6.0 Hz), 3.77 (1H, q, *J* 6 Hz), 3.68 (1H, d, *J* 2.9 Hz), 3.65–3.61 (3H, m), 3.55–3.50 (1H, m), 3.35 (1H, dt, *J* 3.2, 7 Hz), 3.23–3.17 (2H, m), 2.90–2.86 (2H, m), 2.40 (1H, ddd, *J* 3.8, 6.7, 10.4 Hz), 1.59–1.52 (2H, m), 1.21–0.96 (139H, m), 0.83 (3H, t, *J* 7.6 Hz), 0.72 (3H, t, *J* 3.8 Hz), 0.70 (9H, s), 0.51–0.49 (4H, m), 0.39 (2H, dt, *J* 4.1 8.2 Hz), −0.10 (3H, s), −0.12 (3H, s), −0.48 (2H, q, *J* 5.1 Hz); δ_C (126 MHz, $CDCl_3$+few drops of CD_3OD): 175.0, 93.5, 73.1, 73.0, 72.5, 72.0, 71.5, 70.6, 70.1, 69.8, 62.6, 61.8, 52.15, 51.5, 33.4, 31.7, 30.0, 29.5, 29.1, 28.5, 27.5, 26.8, 25.5, 25.0, 24.0, 22.5, 19.8, 15.5, 13.8, 13.2, 10.6, −4.8, −5.2; ν_{max}: 3423, 2919, 2851, 1729, 1646, 1468, 1253, 1077, 991, 835 cm^{-1}.

(v) A dry polyethylene vial equipped with an acid proof rubber septum was charged with **8a** (0.10 g, 0.27 mmol) and pyridine (0.1 ml) in dry THF (10 ml) and stirred at room temperature under nitrogen. Hydrogen fluoride-pyridine complex (~70% HF) was added. The mixture was stirred at 43 °C for 17 h; then TLC showed no starting material was left. The reaction mixture was neuteralized by pouring slowly into aqueous solution of sodium bicarbonate until no more CO_2 was liberated. The product was extracted with chloroform (3×40 ml), dried and evaporated. The residue was purified by column chromatography on silica eluting with chloroform/methanol (10:1) to give pyranoside **9a** as a syrup (0.04 g, 61%), $[\alpha]_D^{27}$ +33 (c 0.47, $CHCl_3$) {Found $[M+Na]^+$: 2603.4370; $C_{168}H_{322}NaO_{15}$ requires: 2603.4326}. This showed δ_H (500 MHz, $CDCl_3$+few drops of CD_3OD): 4.88 (2H, d, *J* 3.2 Hz), 4.42 (2H, br d, *J* 10.8), 4.01 (2H, t, *J* 8.9 Hz), 3.91 (2H, dd, *J* 6.7, 11.4 Hz), 3.61 (2H, t, *J* 9.2 Hz), 3.51–3.48 (2H, m), 3.33 (2H, dd, *J* 3.2, 9.5 Hz), 3.12 (2H, br t, *J* 9.5 Hz), 2.25 (2H, ddd, *J*,4.8, 7.9, 12 Hz), 1.41–1.09 (276H, m), 0.71 (12H, t, *J* 6.6 Hz), 0.49–0.47 (8H, m), 0.39 (4H, dt, *J* 4.1, 7.9 Hz), −0.49 (4H, br q, *J* 5.1 Hz); δ_C (126 MHz, $CDCl_3$+few drops of CD_3OD): 175.1, 93.4, 72.6, 73.1, 71.6, 70.2, 69.8, 62.8, 51.5, 33.4, 31.7, 30.1, 30.0, 29.5, br 29.4, 29.2, 28.5, 27.6, 25.6, 25.5, 22.5, 17.8, 15.6, 13.8, 10.7, 10.66, −4.7, −5.1; ν_{max}: 3389, 2929, 2858, 2357, 1743, 1468, 1256, 1074, 835, 771, 720 cm^{-1}.

(vi) A dry polyethylene vial equipped with a rubber septum was charged with **11a** (0.040 g, 0.022 mmol) and pyridine (0.05 ml) in dry tetrahydrofuran (4 ml) and stirred at room temperature under nitrogen. Hydrogen fluoride-pyridine complex as above (0.4 ml) was added. The mixture was stirred at 43 °C for 17 h, then worked up and purified as before to give the glucopyranoside **12a** as a syrup (0.014 g, 32%), $[\alpha]_D^{26}$ +59 (c 0.53, $CHCl_3$) {Found $[M+Na]^+$: 1484.2685; $C_{90}H_{172}NaO_{13}$ requires: 1484.2690}. This showed δ_H (500 MHz, $CDCl_3$+few drops of CD_3OD): 4.99 (1H, d, *J* 3.5 Hz), 4.96 (1H, d, *J* 3.5 Hz), 4.52 (1H, br d, *J* 10.8 Hz), 4.07 (1H, t, *J* 7.3 Hz), 3.97 (1H, dd, *J* 7.3, 11.7 Hz), 3.57–3.54 (3H, m), 3.45 (1H, dd, *J* 3.5, 9.8 Hz), 3.39 (1H, dd, *J* 3.8, 9.8 Hz), 3.21 (2H, q, *J* 1.6 Hz), 3.21–3.15 (2H, m), 2.32 (1H, ddd, *J* 4.1, 7.9, 9.5 Hz), 1.15 (138H, v br s), 1.03 (6H, q, *J* 6 Hz), 0.93 (2H, t, *J* 5.7 Hz), 0.77 (3H, t, *J* 6.3 Hz), 0.56–0.52 (4H, m), 0.45 (2H, dt, *J* 3.8, 8.2 Hz), −0.43 (2H, q, *J* 5.1 Hz); δ_C (126 MHz, $CDCl_3$+few drops of CD_3OD): 175.3, 94.3, 72.6, 72.5, 72.4, 72.2, 71.5, 71.3, 70.9, 70.7, 69.8, 63.9, 61.9, 52.4, 34.5, 31.7, 30.0, 29.9, br 29.6, 29.4, 29.3, 29.2, 29.1, 28.5, 27.1, 25.0, 22.4, 15.5, 13.8, 10.6; ν_{max}: 3369, 2920, 2851, 1730, 1466, 1150, 1118,1025, 997, 725 cm^{-1}.

4.3. 6-*O*-[(*R*)-2-((*R*)-1-Hydroxy-12-{(1*R*,2*S*)-2-[14-((1*R*,2*S*)-2-eicosylcyclopropyl)tetradecyl]cyclopropyl}do-decyl)-hexacosanoate]-α-*D*-glucopyranosyl-(1→1)-6′-*O*-[(*R*)-2-((*R*)-1-hydroxy-12-{(1*R*,2*S*)-2-[14-((1*R*,2*S*)-2-eicosylcyclopropyl)tetradecyl]cyclopropyl}dodecyl)hexa-cosanoate]-α-*D*-glucopyranoside (9b) and 6-*O*-[(*R*)-2-((*R*)-1-hydroxy-12-{(1*R*,2*S*)-2-[14-((1*R*,2*S*)-2-eicosylcyclo-propyl)tetradecyl]cyclopropyl}dodecyl) hexacosanoate]-α-*D*-glucopyranosyl-(1→1)-α-*D*-glucopyranoside (12b)

(i) R)-2-((*R*)-1-Hydroxy-12-{(1*R*,2*S*)-2-[14-((1*R*,2*S*)-2-eicosylcyclopropyl)tetradecyl]cyclopropyl}dodecyl)hexa-cosanoic acid,[59] (0.39 g, 0.34 mmol) gave acid **5b** as a colourless oil (0.38 g, 88%), $[\alpha]_D^{24}$ +4.0 (c 1.13, $CHCl_3$), {Found $[M+Na]^+$: 1275.3245; $C_{84}H_{166}NaO_3Si$ requires: 1275.3243}, which showed δ_H (500 MHz, $CDCl_3$): 3.85–3.88 (1H, br q, *J* 5.4 Hz), 2.53 (1H, br p, *J* 4.7 Hz), 1.75–1.10 (135H, m), 0.91 (9H, s), 0.89 (6H, t, *J* 7 Hz), 0.66–0.64 (4H, m), 0.57 (2H, dt, *J* 4.1, 8.2 Hz), 0.12 (3H, s), 0.10 (3H, s), −0.32 (2H, br q, *J* 5.4 Hz); δ_C (126 MHz, $CDCl_3$): 177.3, 73.6, 50.6, 35.1, 31.9, 30.2, 29.7, 29.6, 29.52, 29.5, 29.4, 29.1, 28.7, 27.5, 25.7, 24.6, 22.7, 17.9, 15.8, 14.1, 10.9, −4.3, −4.9; υ_{max}: 3500–2500 (very br, OH for the carboxylic group), 2919, 2850, 1707, 1466, 1361, 1254, 1215, 1075, 939, 836, 761, 669, 420 cm^{-1}.

(ii) Glucopyranoside **7b** as a colourless thick oil (33%), $[\alpha]_D^{23}$ +23.1 (c 1.32 g, $CHCl_3$), {MALDI Found $[M+Na]^+$: 3266.8; $C_{198}H_{398}NaO_{15}Si_8$ requires: 3266.9}, which showed δ_H (500 MHz, $CDCl_3$): 4.86 (2H, d, *J* 2.8 Hz), 4.37 (2H, br d, *J* 10.4 Hz), 4.04–3.99 (2H, m), 3.94 (2H, br q, *J* 5.4 Hz), 3.9 (2H, t, *J* 9.1 Hz), 3.53 (2H, t, *J* 8.9 Hz), 3.38 (2H, dd, *J* 2.8, 9.1 Hz), 3.32 (2H, m), 2.56 (2H, ddd, *J* 3.5, 4.8, 10.1 Hz), 1.55–1.05 (268H, m), 0.89 (12H, t, *J* 7 Hz), 0.88 (18H, s), 0.65 (8H, br m), 0.57 (4H, dt, *J* 4.1, 8.2 Hz), 0.166 (18H, s), 0.15 (18H, s), 0.14 (18H, s), 0.07 (12H, s), −0.32 (4H, br q, *J* 5.4 Hz); δ_C (126 MHz, $CDCl_3$): 173.8, 130.5, 94.8, 73.6, 73.4, 72.8, 71.8, 70.7, 62.4, 51.9, 33.5, 31.9, 30.2, 30.0, 29.8, 29.7, 29.52, 29.5, 29.48, 29.4, 28.7, 28.1, 26.2, 26.0, 25.9, 25.9, 25.2, 22.7, 18.0, 15.8, 14.1, 10.9, 1.1, 0.9, 0.2, −4.5, −4.6; υ_{max}: 2922, 2852, 1743, 1466.7, 1252, 1077, 838 cm^{-1}. The second fraction was glucopyranoside **10b** (0.14 g, 49%), $[\alpha]_D^{23}$ +34 (c 0.96 g, $CHCl_3$) {MALDI Found $[M+Na]^+$: 2032.7; $C_{114}H_{234}NaO_{13}Si_7$ requires: 2032.7}, which showed δ_H (500 MHz, $CDCl_3$): 4.91 (1H, d, *J* 2.9 Hz), 4.84 (1H, d, *J* 3.2 Hz), 4.35 (1H, dd, *J* 2.2, 11.7 Hz), 4.08 (1H, dd, *J* 4.1, 12 Hz), 3.99 (1H, br dq, *J* 2.5, 9.5 Hz), 3.95 (1H, m), 3.91 (2H, dt, *J* 6.7, 9.2 Hz) 3.85 (1H, dt, *J* 3.5, 9.5 Hz), 3.74–3.66 (2H, m), 3.48 (2H, dt, *J* 6, 9.2 Hz), 3.43 (1H, dd, *J* 3.2, 9.2 Hz), 3.39 (1H, dd, *J* 3.2, 9.2 Hz), 2.55 (1H, ddd, *J* 3.5, 5.4, 9.2 Hz), 1.72 (1H, dd, *J* 5.1, 7.6 Hz), 1.64–1.60 (2H, m), 1.44–1.08 (132H, m), 0.89 (6H, t, *J* 7 Hz), 0.88 (9H, s), 0.67–0.64 (4H, m), 0.57 (2H, dt, *J* 4.1, 8.2 Hz), 0.174 (9H, s), 0.164 (9H, s), 0.16 (9H, s), 0.155 (9H, s), 0.15 (9H, s), 0.13 (9H, s), 0.07 (3H, s), 0.06 (3H, s), −0.32 (2H, q, *J* 5 Hz); δ_C (126 MHz, $CDCl_3$): 174.1, 94.5, 94.4, 73.42, 73.4, 73.38, 72.9, 72.82, 72.8, 72.0, 71.4, 70.7, 62.5, 61.7, 51.8, 41.4, 33.4, 31.9, 30.2, 29.8, 29.7, 29.6, 29.4, 28.7, 28.1, 26.4, 25.9, 25.8, 24.9, 22.7, 19.4, 18.4, 18.0, 15.8, 14.1, 10.9, 1.1, 1.0, 0.9, 0.8, 0.2, 0.0, −4.5, −4.7; υ_{max}: 2924, 2853, 1742, 1465, 1251, 1165, 1110, 1076, 1006, 898, 873, 842, 748 cm^{-1}. A minor product was isolated (4.5 mg), (*R*)-2-((*R*)-1-(*tert*-butyldimethylsilanyloxy)-12-{(1*R*,2*S*)-2-[14-((1*R*,2*S*)-2-eicosylcyclopropyl)tetradecyl]cyclopropyl}dodecylhexacosanoic anhydride {MALDI Found $[M+Na]^+$: 2509.6; $C_{168}H_{330}NaO_5Si_2$ requires: 2509.6}, which showed δ_H (500 MHz, $CDCl_3$): 3.85–3.88 (2H, br q, *J* 5.4 Hz), 2.62–2.52 (2H, m), 1.50–1.10 (268H, m), 0.90 (18H, s), 0.91–0.85 (12H, t, *J* 7 Hz), 0.66–0.64 (8H, m), 0.57 (4H, dt, *J* 4.1, 8.6 Hz), 0.07 (12H, s), −0.32 (4H, br q, *J* 5.4 Hz); δ_C (126 MHz, $CDCl_3$): 178.4, 73.6, 50.8, 35.1, 31.9, 30.3, 30.2, 29.72, 29.7, 29.51, 29.5, 29.4, 28.7, 26.0, 25.9, 25.9, 25.8, 22.7, 18.0, 15.8, 14.1, 10.9, 1.0, −4.4, −4.5. ν_{max}: 2964, 2856, 1817, 1745, 1466, 1369, 1254 cm^{-1}.

(iii) Glucopyranoside **8b** as a colourless thick oil (53%), $[\alpha]_D^{23}$ +15 (c 3.2, $CHCl_3$) {MALDI Found $[M+Na]^+$: 2833.9; $C_{180}H_{350}NaO_{15}Si_2$ requires: 2833.9}, which showed δ_H (500 MHz, $CDCl_3$+few drops of CD_3OD): 5.05 (2H, d, *J* 3.2 Hz), 4.29 (2H, br dd, *J* 4.4, 12.3 Hz), 4.2 (2H, br d, *J* 10.8 Hz), 3.91 (2H, br d, *J* 9.2 Hz), 3.87 (2H, br q, *J* 5.4 Hz), 3.80 (2H, br t, *J* 9.5 Hz), 3.45 (2H, dd, *J* 3.5, 9.8 Hz), 3.32 (2H, m), 2.93 (2H, br dt, *J* 4.3 Hz), 2.52 (2H, ddd, *J* 3.8, 6.4, 10.4 Hz), 1.6–1.01 (272H, m), 0.83 (12H, t, *J* 7.3 Hz), 0.82 (18H, s), 0.63–0.56 (8H, m), 0.52 (4H, dt, *J* 4.1, 8.2 Hz), 0.02 (6H, s), −0.02 (6H, s), −0.38 (4H, br q, *J* 5.4 Hz); δ_C (126 MHz, $CDCl_3$+few drops of CD_3OD): 175.1, 93.4, 85.4, 73.3, 72.8, 71.7, 70.4, 70.3, 62.8, 57.7, 51.5, 35.2, 33.7, 32.4, 31.9, 30.5, 30.4, 30.3, 30.2, 30.1, 30.0, 29.9, 29.8, 29.73, 29.7, 29.6, 29.52, 29.5, 29.45, 29.4, 29.3, 28.7, 27.8, 27.6, 27.1, 26.2, 25.9, 25.8, 24.3, 22.7, 18.0, 15.8, 14.8, 14.1, 10.9, −4.4, −4.7; υ_{max}: 3384, 2920, 2851, 2360, 1739, 1469, 1253, 1077, 837, 775, 721 cm^{-1}.

(iv) Glucopyranoside **11b** as a colourless syrup (90%), {$[\alpha]_D^{23}$ +11.9 (c 2.95, $CHCl_3$)} {MALDI Found $[M+Na]^+$: 1599.3; $C_{96}H_{186}NaO_{13}Si$ requires: 1599.6}, which showed δ_H (500 MHz, $CDCl_3$+few drops of CD_3OD): 5.03 (2H, d, *J* 2.2 Hz), 4.22 (1H, br s), 4.0 (1H, br dt, *J* 2.9, 9.4 Hz), 3.92 (1H, br d, *J* 9.7 Hz), 3.85 (1H, m), 3.73–3.77 (3H, m), 3.65 (1H, m), 3.41 (4H, m), 2.45 (1H, m), 1.17–1.30 (142H, m), 0.79 (15H, m, including t at 0.80, *J* 7.3 Hz), 0.56 (4H, m), 0.47 (2H, dt, *J* 4.1, 8.5 Hz), −0.04 (3H, s), −0.06 (3H, s), −0.42 (2H, q, *J* 5.3 Hz); δ_C (126 MHz, $CDCl_3$+few drops of CD_3OD): 93.4, 73.0, 72.7, 72.6, 72.3, 72.1, 70.1, 62.8, 52.1, 49.2, 49.0, 31.7, 30.0, 29.6, 29.53, 29.5, 29.2, 28.5, 25.7, 25.0, 23.9, 22.5, 19.6, 15.6, 13.9, 13.5, 10.7, −4.7, −4.9, υ_{max}: 3385, 2924, 2852, 1731, 1467, 1382, 992, 483 cm^{-1}.

(v) Glucopyranoside **9b** as a syrup (54%), $[\alpha]_D^{23}$ +28 (c 2.2, $CHCl_3$) {Found $[M+Na]^+$: 2603.4329; $C_{168}H_{322}NaO_{15}$ requires: 2605.4326}, which showed δ_H (500 MHz, $CDCl_3$+few drops of CD_3OD): 4.98 (2H, br d, *J* 3.8 Hz), 4.6 (2H, br d, *J* 11.4 Hz), 4.16 (2H, br t, *J* 9.5 Hz), 4.0 (2H, br dd, *J* 7.6, 11.7 Hz), 3.73 (2H, br t, *J* 9.5 Hz), 3.64–3.6 (2H, m), 3.46 (2H, br dd, *J* 3.5, 9.8 Hz), 3.21 (2H, br t, *J* 9.8 Hz), 2.39–2.34 (2H, br m), 1.38–1.05 (282H, m), 0.83 (6H, t, *J* 6.7 Hz), 0.62–0.57 (8H, m), 0.52 (4H, dt, *J* 4.1, 8.2 Hz), −0.36 – −0.39 (4H, br q, *J* 5.1 Hz); δ_C (126 MHz, $CDCl_3$+few drops of CD_3OD): 175.4, 94.9, 72.5, 72.5, 71.3, 71.2, 69.8, 64.4, 52.2, 34.7, 31.8, 30.1, 30.1, 29.7, 29.62, 29.6, 29.4, 29.3, 29.2, 28.6, 27.2, 25.1, 22.5, 15.6, 13.9, 10.8, 0.8; υ_{max}: 3391, 2918, 2850, 1730, 1467, 1260, 1020, 800, 464 cm^{-1}.

(vi) Glucopyranoside **12b** (22%), $[\alpha]_D^{23}$ +41.5 (c 1.83, $CHCl_3$) {Found $[M+Na]^+$: 14,854.2746; $C_{90}H_{172}NaO_{13}$ requires: 1484.2690}, which showed δ_H (500 MHz, $CDCl_3$+few drops of CD_3OD): 5.11 (1H, br s), 5.07 (1H, br s), 4.62 (1H, br d, *J* 8.2 Hz), 4.13 (1H, br m), 4.06 (1H, br m), 3.92–3.83 (5H, m), 3.58 (1H, br d, *J* 7.5 Hz), 3.53 (1H, br d, *J* 8.9 Hz), 3.39 (1H, m), 3.36 (1H, t, *J* 6.5 Hz), 2.69 (1H, br s), 2.41–2.39 (1H, br m), 1.72 (1H, m), 1.61 (3H, m), 1.50–1.11 (138H, m), 0.87–0.84 (6H, t, *J* 7 Hz), 0.62 (4H, m), 0.56–0.51 (2H, dt, *J* 4.1, 8.2 Hz), −0.34–−0.37 (2H, q, *J* 5 Hz); δ_C (126 MHz, $CDCl_3$+few drops of CD_3OD): 175.4, 94.1, 72.6, 72.5, 72.3, 71.4, 70.9, 70.1, 64.0, 62.1, 58.8, 52.1, 31.8, 30.2, 30.2, 30.1, 29.8, 29.63, 29.6, 29.5, 29.4, 29.3, 28.7, 28.6, 23.8, 22.6, 19.6, 15.71, 15.7, 14.0, 13.5, 10.9, 10.8; υ_{max}: 3356, 2919, 2850, 1728, 1468, 1148, 1106, 992, 721, 427 cm^{-1}.

4.4. 6-*O*-[(*R*)-2-((*R*)-1-Hydroxy-18-((1*S*,2*R*)-2-((17*S*,18*S*)-17-methoxy-18-methylhexatriacontyl)cyclopropyl)^{oc}ta-decyl) hexacosanoate]-α-*D*-glucopyranosyl-(1→1)-6′-*O*-[(*R*)-2-((*R*)-1-hydroxy-18-((1*S*,2*R*)-2-((17*S*,-18*S*)-17-methoxy-18-methylhexatriacontyl)cyclopropyl)octa-decyl)hexacosanoate]-α-*D*-glucopyranoside (9c) and 6-*O*-[(*R*)-2-((*R*)-1-Hydroxy-18-((1*S*,2*R*)-2-((17*S*,18*S*)-17-methoxy-18-methylhexatriacontyl)cyclopropyl)octa-decyl)hexacosanoate]-α-*D*-glucopyranosyl-(1→1)-α-*D*-glucopyranoside (12c)

(i) Imidazole (0.271 g, 3.98 mmol) was added to a stirred solution of (*R*)-2-((*R*)-1-hydroxy-18-((1*S*,2*R*)-2-((17*S*,18*S*)-17-methoxymethylhexatriacontyl)cyclopropyl)octadecyl)-hexacosanoic acid[60] (0.50 g, 0.39 mmol) gave acid **5c** as a colourless oil (0.50 g, 92%) {MALDI Found $[M+Na]^+$: 1390.2; $C_{91}H_{182}NaO_4Si$ requires: 1390.4}, which showed δ_H (400 MHz, $CDCl_3$): 3.87–3.82 (1H, m), 3.34 (3H, s), 2.96 (1H, br pent, *J* 4.6 Hz), 2.58–2.52 (1H, m), 1.73–1.11 (148H, m), 0.91 (9H, s), 0.89 (6H, t, *J* 6.6 Hz), 0.86 (3H, m), 0.67–0.63 (2H, m), 0.58 (1H, dt, *J* 4.2, 8.2 Hz), 0.16 (3H, s), 0.14 (3H, s), −0.31 (1H, br q, *J* 5.1 Hz); δ_C (101 MHz, $CDCl_3$): 177.2, 85.4, 73.7, 57.7, 50.0, 35.2, 35.1, 32.4, 31.9, 30.5, 30.2, 30.0, 29.9, 29.72, 29.71, 29.56, 29.54, 29.5, 29.45, 29.4, 29.0, 28.7, 27.5, 27.4, 26.1, 25.7, 25.1, 22.6, 17.9, 15.7, 14.8, 14.1, 10.9, −4.2, −4.1; ν_{max}: 3676 (broad, OH for the carboxylic group), 2925, 2853, 1708, 1465, 1361, 1301, 1254, 1098, 1050, 907, 835 cm^{-1}.

(ii) Glucopyranoside **7c** as a colourless thick oil (70%), $[\alpha]_D^{23}$ +18 (c 0.5, $CHCl_3$) {MALDI Found $[M+Na]^+$: 3499.5; $C_{214}H_{430}NaO_{17}Si_8$ requires: 3499.4}, which showed δ_H (400 MHz, $CDCl_3$): 4.85 (2H, d, *J* 3.0 Hz), 4.37 (2H, br d, *J* 10.4 Hz), 4.04–3.97 (4H, m), 3.95–3.88 (4H, m), 3.53 (2H, t, *J* 8.8 Hz), 3.39 (2H, dd, *J* 2.5, 8.9 Hz), 3.34 (6H, s), 2.97 (2H, br. pent, *J* 4.0 Hz) 2.57–2.53 (2H, m), 1.64–1.58 (4H, m), 1.52–1.01 (290H, m), 0.89 (12H, br t, *J* 6.6 Hz), 0.88 (18H, s), 0.85 (6H, d, *J* 6.8 Hz), 0.66–0.64 (4H, br. m), 0.58 (2H, dt, *J* 3.8, 7.7 Hz), 0.16 (18H, s), 0.14 (18H, s), 0.13 (18H, s), 0.06 (12H, s), −0.31 (2H, br. q, *J* 5.1 Hz); δ_C (101 MHz, $CDCl_3$): 173.8, 94.8, 85.4, 73.5, 73.4, 72.8, 71.8, 70.7, 62.3, 57.7, 51.8, 35.3, 33.4, 32.3, 31.9, 30.4, 30.2, 30.0, 29.95, 29.7, 29.5, 29.3, 28.7, 28.1, 27.5, 26.1, 25.9, 25.8, 25.6, 25.1, 22.6, 18.0, 15.7, 14.8, 14.1, 10.9, 1.9, 1.0, 0.9, 0.1, −4.5, −4.6; ν_{max}: 2925, 2854, 1734, 1494, 1251.6, 1077, 1050, 907, 825 cm^{-1}.

The second fraction was glucopyranoside **10c** as a colourless thick oil (30%), $[\alpha]_D^{23}$ +45 (c 0.5, $CHCl_3$) {MALDI Found $[M+Na]^+$: 2147.3; $C_{121}H_{250}NaO_{14}Si_7$ requires: 2147.7}, which showed δ_H (400 MHz, $CDCl_3$): 4.91 (1H, d, *J* 3.0 Hz), 4.84 (1H, d, *J* 3.0 Hz), 4.36

(1H, dd, J 2.0, 11.9 Hz), 4.09 (1H, dd, J 4.1, 11.8 Hz), 4.01–3.97 (1H, m), 3.95–3.87 (4H, m), 3.86 (1H, t, J 3.4 Hz), 3.83 (1H, t, J 3.3 Hz), 3.71–3.67 (1H, m), 3.51–3.45 (2H, m), 3.44–3.37 (2H, m), 3.34 (3H, s), 2.97 (1H, br pent, J 4.1 Hz), 2.58–2.53 (1H, m), 1.73–1.70 (1H, m), 1.64–1.59 (2H, m), 1.39–1.26 (148H, m), 0.90–0.84 (15H, m, including s at 0.88), 0.66–0.64 (2H, m), 0.58 (1H, dt, J 3.8, 7.6 Hz), 0.17 (9H, s), 0.16 (9H, s), 0.15 (9H, s), 0.14 (9H, s), 0.12 (9H, s), 0.09 (9H, s), 0.07 (3H, s), 0.06 (3H, s), −0.31 (1H, br. q, J 5.0 Hz); δ_C (101 MHz, $CDCl_3$): 174.0, 94.5, 94.3, 85.4, 73.4, 73.3, 72.9, 72.8, 72.7, 71.9, 71.4, 70.7, 62.4, 61.6, 57.7, 51.8, 35.3, 33.4, 32.3, 31.9, 30.4, 30.2, 30.0, 29.9, 29.8, 29.7, 29.6, 29.5, 29.3, 28.7, 28., 27.5, 26.3, 26.1, 25.8, 24.8, 22.6, 18.0, 15.7, 14.8, 14.1, 10.9, 1.9, 1.1, 1.0, 0.9, 0.8, 0.1, 0.0, −4.4, −4.6; ν_{max}: 3436, 2926, 2856, 1733, 1494, 1252, 1215, 1076, 907 cm^{-1}.

(iii) Glucopyranoside **8c** as a colourless thick oil (90%), $[\alpha]_D^{20}$ +12 (*c* 0.5, $CHCl_3$) {MALDI Found $[M+Na]^+$: 3065.8; $C_{194}H_{384}NaO_{17}Si_2$ requires: 3065.9}, which showed δ_H (400 MHz, $CDCl_3$+few drops of CD_3OD): 5.26 (2H, d, J 3.2 Hz), 4.32 (2H, br dd, J 3.8, 11.9 Hz), 4.20 (2H, br d, J 11.8 Hz), 3.92–3.86 (4H, m), 3.76 (2H, br t, J 9.6 Hz), 3.46 (2H, dd, J 3.5, 9.6 Hz), 3.35–3.33 (2H, m), 3.29 (6H, s), 2.92–2.90 (2H, m), 2.52–2.48 (2H, m), 1.32–1.09 (298H, m), 0.86–0.84 (12H, m), 0.83 (18H, s), 0.81–0.79 (6H, m), 0.61–0.58 (4H, m), 0.53 (2H, dt, J 3.8, 7.5 Hz), 0.0 (6H, s), −0.02 (6H, s), −0.36 (2H, br q, J 5.2 Hz); δ_C (101 MHz, $CDCl_3$+few drops of CD_3OD): 175.1, 93.5, 85.5, 73.1, 73.0, 72.5, 71.6, 70.2, 69.8, 67.8, 62.8, 57.5, 51.6, 35.2, 33.5, 32.2, 31.8, 30.3, 30.1, 29.8, 29.7, 29.6, 29.5, 29.2, 28.6, 27.6, 27.4, 27.1, 26.9, 25.9, 25.7, 25.6, 25.46, 25.43, 24.1, 22.5, 17.8, 15.6, 14.6, 13.9, 10.7, −4.6, −5.0; ν_{max}: 3436, 2925, 2853, 1734, 1456, 1252, 1100, 1078, 992, 874, 825, 760, 720, 672 cm^{-1}.

(iv) Glucopyranoside **11c** as a colourless syrup (88%), $[\alpha]_D^{23}$ +30 (c 0.5, $CHCl_3$) {MALDI Found $[M+Na]^+$: 1714.6; $C_{103}H_{202}NaO_{14}Si$ requires: 1714.5}, which showed δ_H (400 MHz, $CDCl_3$+few drops of CD_3OD): 5.03 (2H, d, J 3.2 Hz), 4.27–4.21 (2H, m), 3.92 (1H, br d, J 9.7 Hz), 3.85 (3H, br t, J 8.4 Hz), 3.79–3.76 (2H, br m), 3.65 (1H, br q, J 5.5 Hz), 3.46 (2H, br d, J 9.9 Hz), 3.32 (2H, br d, J 9.7 Hz), 3.28 (3H, s), 2.97–2.90 (1H, m), 2.51–2.46 (1H, m), 1.27–1.19 (150H, m), 0.82 (6H, t, J 6.4 Hz), 0.79 (9H, s), 0.77 (3H, d, J 4.9 Hz), 0.59–0.57 (2H, m), 0.51 (1H, dt, J 3.9, 7.8 Hz), −0.01 (3H, s), −0.03 (3H, s), −0.38 (1H, br q, J 4.9 Hz); δ_C (101 MHz, $CDCl_3$+few drops of CD_3OD): 175.1, 93.5, 93.3, 85.3, 72.9, 72.7, 72.3, 71.9, 71.3, 70.4, 69.9, 69.6, 62.4, 61.7, 57.3, 51.7, 51.3, 34.9, 33.2, 31.9, 31.5, 30.1, 29.8, 29.6, 29.5, 29.48, 29.41, 29.4, 29.35, 29.3, 29.2, 29.0, 28.3, 27.4, 27.1, 26.6, 25.7, 25.3, 24.8, 23.8, 22.3, 19.6, 15.4, 14.4, 13.7, 13.1, 10.5, −4.6, −5.0; ν_{max}: 3400, 2926, 2854, 1716, 1464, 1078, 824, 760 cm^{-1}.

(v) The glucopyranoside **9c** as a syrup (63%), $[\alpha]_D^{23}$ +27 (c 0.5, $CHCl_3$)} {Found $[M+Na]^+$: 2835.6647; $C_{182}H_{354}NaO_{17}$ requires: 2835.6728}, which showed δ_H (400 MHz, $CDCl_3$+few drops of CD_3OD): 5.0 (2H, d, J 3.0 Hz), 4.8 (2H, br d, J 11.8 Hz), 4.34 (2H, br t, J 8.3 Hz), 3.89–3.84 (2H, m), 3.79 (2H, t, J 10.0 Hz), 3.71–3.67 (2H, br. m), 3.53 (2H, dd, J 2.4, 11.2 Hz), 3.32 (6H, s), 3.21 (2H, t, J 9.5 Hz), 2.96 (2H, br pent, J 4.2 Hz), 2.43–2.38 (2H, m), 1.39–1.10 (302H, m), 0.88 (12H, t, J 6.6 Hz), 0.83 (6H, d, J 6.8 Hz), 0.65–0.60 (4H, m), 0.55 (2H, dt, J 3.9, 7.6 Hz), −0.33 (2H, br q, J 5.0 Hz); δ_C (101 MHz, $CDCl_3$+few drops of CD_3OD): 175.3, 94.9, 85.5, 72.4, 72.3, 71.2, 71.0, 70.8, 69.76, 69.7, 64.3, 57.4, 52.2, 36.9, 35.1, 34.5, 32.5, 32.2, 31.7, 30.3, 30.0, 29.8, 29.79, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 28.5, 27.3, 27.1, 26.9, 25.9, 25.0, 22.5, 19.5, 15.6, 14.6, 13.8, 10.7; ν_{max}: 3436, 2922, 2852, 1721, 1466, 1098, 734 cm^{-1}.

(vi) The glucopyranoside **12c** as a colourless syrup (90%) $[\alpha]_D^{23}$ +46 (c 0.50, $CHCl_3$)} {Found $[M+Na]^+$: 1600.3882; $C_{97}H_{188}NaO_{14}$ requires: 1600.3897}, δ_H (400 MHz, $CDCl_3$+few drops of CD_3OD): 5.1 (1H, br s), 5.1 (1H, br s), 4.70 (1H, br d, J 10.3 Hz), 4.21–4.20 (1H, m), 3.90–3.84 (4H, br m), 3.66–3.62 (4H, m), 3.54–3.51 (2H, m), 3.33–3.30 (4H, m, including s (OMe) at 3.3), 2.96–2.92 (1H, m), 2.41–2.23 (1H, m), 1.62–1.54 (2H, m), 1.37–1.09 (153H, m), 0.86 (6H, t, J 6.6 Hz), 0.82 (3H, d, J 6.9 Hz), 0.63–0.61 (2H, m), 0.55 (1H, dt, J 3.8, 7.6 Hz), −0.33 (1H, br. q, J 5.1 Hz); δ_C (101 MHz, $CDCl_3$+few drops of CD_3OD): 175.4, 94.5, 85.5, 72.5 (br.), 72.5, 72.3, 71.4, 71.2, 71.0, 70.8, 70.0, 64.2, 62.0, 57.5, 52.3, 35.2, 34.6, 32.2, 31.8, 30.4, 30.1, 29.82, 29.8, 29.7, 29.63, 29.6, 29.5, 29.3, 29.2, 28.6, 27.4, 27.2, 26.0, 25.1, 22.5, 15.6, 14.7, 13.9, 10.7; ν_{max}: 3400, 2924, 2853, 1721, 1466, 993 cm^{-1}.

4.5. 6-*O*-[(*R*)-2-((*R*)-1-Hydroxy-18-((1*R*,2*S*)-2-((17*S*,18*S*)-17-methoxy-18-methylhexatriacontyl)cyclopropyl)octa-decyl) hexacosanoate]-α-*D*-glucopyranosyl-(1→1)-6′-*O*-[(*R*)-2-((*R*)-1-hydroxy-18-((1*R*,2*S*)-2-((17*S*,18*S*)-17-methoxy-18-methylhexatriacontyl)cyclopropyl)octa-decyl)hexacosanoate]-α-*D*-glucopyranoside (9d) and 6-*O*-[(*R*)-2-((*R*)-1-Hydroxy-18-((1*R*,2*S*)-2-((17*S*,18*S*)-17-methoxy-18-methylhexatriacontyl)cyclopropyl)octa-decyl)hexacosanoate]-α-*D*-glucopyranosyl-(1→1)-α-*D*-glucopyranoside (12d)

(i) (*R*)-2-{(*R*)-1-Hydroxy-18-[(1*R*,2*S*)-2-((17*S*,18*S*)-17-methoxy-18-methylhexatriacontyl)cyclopropyl]octadecyl}-hexacosanoic acid,[60] (0.70 g, 0.56 mmol) gave acid **5d** as a colourless oil (80%) {Found $[M+Na]^+$: 1390.3687; $C_{91}H_{182}NaO_4Si$ requires: 1390.3705}, which showed δ_H (500 MHz, $CDCl_3$): 3.85–3.8 (1H, ddd, J 3.2, 5, 7.6 Hz), 3.36 (3H, s), 2.96 (1H, br pent, J 4.1 Hz), 2.53 (1H, ddd, J 3.2, 5.7, 9.2 Hz), 1.75–1.05 (148H, m), 0.93 (9H, s), 0.89 (6H, t, J 6.6 Hz), 0.85 (3H, d, J 6.9 Hz), 0.67–0.63 (2H, m), 0.57 (1H, dt, J 4.1, 7.9 Hz), 0.15 (3H, s), 0.13 (3H, s), −0.33 (1H, br q, J 5.4 Hz); δ_C (500 MHz, $CDCl_3$): 177.3, 85.5, 73.6, 57.7, 50.7, 35.3, 35.0, 32.4, 31.9, 30.5, 30.2, 30.0, 29.9, 29.7 (very br), 29.69, 29.6, 29.52, 29.5, 29.43, 29.4, 29.0, 28.7, 27.6, 27.5, 26.2, 25.7, 24.6, 22.7, 18.0, 15.8, 14.9, 14.1, 10.9, −4.3, −4.9; υ_{max}: 3500–2500 (very br, OH for COOH), 2922, 2852, 1708, 1465, 1361, 1293, 1253, 1099, 1005, 939, 836 cm^{-1}.

(ii) Glucopyranoside **7d** as a colourless thick oil (51%), $[\alpha]_D^{24}$ +19.6 (c 1.08, $CHCl_3$) {MALDI Found $[M+Na]^+$: 3498.7; $C_{212}H_{430}NaO_{17}Si_8$ requires: 3499.4}, which showed δ_H (500 MHz, $CDCl_3$): 4.85 (2H, d, J 2.9 Hz), 4.37 (2H, br d, J 9.8 Hz), 4.04–3.98 (2H, m), 3.96 (2H, br pent, J 4.1 Hz), 3.94 (2H, br q, J 5.2 Hz), 3.9 (2H, t, J 9.0 Hz), 3.52 (2H, t, J 9.0 Hz), 3.38 (2H, dd, J 2.8, 9 Hz), 3.35 (6H, s), 2.55 (2H, ddd, J 3.5, 4.8, 10.1 Hz), 1.67–1.6 (4H, m), 1.56–1.05 (290H, m), 0.89 (12H, t, J 7 Hz), 0.88 (18H, s), 0.85 (6H, d, J 7 Hz), 0.65 (4H, br m), 0.57 (2H, dt, J 3.8, 8 Hz), 0.16 (18H, s), 0.145 (18H, s), 0.138 (18H, s), 0.062 (12H, s), −0.32 (2H, br q, J 5.1 Hz); δ_C (126 MHz, $CDCl_3$): 173.8, 94.9, 85.5, 73.5, 73.4, 72.8, 71.8, 70.7, 62.4, 57.7, 51.9, 35.4, 33.5, 32.4, 31.9, 30.5, 30.2, 30.0, 29.9, 29.8, 29.7 (very br), 29.68, 29.5, 29.4, 28.7, 28.1, 27.6, 26.2, 25.8, 25.2, 22.7, 18.0, 15.8, 14.9, 14.1, 10.9, 1.1, 0.9, 0.2, −4.5, −4.6; υ_{max}: 2924, 2853, 1743, 1464.9, 1251.6, 1163, 1099, 872, 839 cm^{-1}. The second fraction was glucopyranoside **10d** (42%), $[\alpha]_D^{24}$ +42.5 (c 1.13, $CHCl_3$) {Found $[M+Na]^+$: 2146.7125; $C_{121}H_{250}NaO_{14}Si_7$ requires: 2146.7128}, which showed δ_H (500 MHz, $CDCl_3$): 4.91 (1H, d, J 3.2 Hz), 4.84 (1H, d, J 2.9 Hz), 4.35 (1H, dd, J 2.2, 11.7 Hz), 4.08 (1H, dd, J 4.1, 11.7 Hz), 3.99 (1H, br qd, J 2.2, 11.7 Hz), 3.95 (1H, br m), 3.91 (2H, dt, J 6.6, 9.0 Hz) 3.85 (1H, br td, J 3.5, 9.5 Hz), 3.73–3.65 (2H, m), 3.48 (2H, dt, J 6.3, 9.0 Hz), 3.43 (1H, dd, J 3.2, 9.5 Hz), 3.39 (1H, dd, J 2.9, 9.2 Hz), 3.34 (3H, s), 2.96 (1H, br pent, J 4.4 Hz), 2.55 (1H, ddd, J 3.5, 5.7, 10.4 Hz), 1.71 (1H, dd, J 5.1, 7.6 Hz), 1.64–1.58 (2H, m), 1.51–1.06 (148H, m), 0.89 (3H, t, J 7 Hz), 0.88 (9H, s), 0.86

(3H, d, *J* 7 Hz), 0.67–0.64 (2H, m), 0.57 (1H, dt, *J* 4.1, 8.2 Hz), 0.17 (9H, s), 0.16 (9H, s), 0.16 (9H, s), 0.151 (9H, s), 0.15 (9H, s), 0.12 (9H, s), 0.06 (3H, s), 0.057 (3H, s), −0.32 (1H, br q, *J* 5.4 Hz); δ_C (126 MHz, $CDCl_3$): 174.1, 94.5, 94.4, 85.4, 73.4, 73.4, 72.9, 72.8, 72.8, 72.0, 71.4, 70.7, 62.4, 61.7, 57.7, 51.8, 35.4, 33.4, 32.4, 31.9, 30.5, 30.2, 30.0, 29.9, 29.9, 29.8, 29.73, 29.7 (very br), 29.5, 29.4, 28.7, 28.1, 27.6, 26.4, 26.2, 25.8, 24.8, 22.7, 18.0, 15.8, 14.9, 14.1, 10.8, 1.1, 1.03, 1.0, 0.9, 0.8, 0.2, 0.0, −4.4, −4.7; υ_{max}: 2924, 2853, 1742, 1465, 1251, 1215, 1100, 965 cm^{-1}. A minor product (<5%) was (*R*)-2-((*R*)-1-(*tert*-butyldimethylsilyloxy)-18-((1*R*,2*S*)-2-((17*S*,18*S*)-17-methoxy-18-methylhexatriacontyl)cyclo-propyl)octadecyl)hexacosanoic anhydride {MALDI Found $[M+Na]^+$: 2742.1; $C_{182}H_{362}NaO_7Si_2$ requires: 2742.1}, which showed δ_H (500 MHz, $CDCl_3$): 3.98–3.95 (2H, q, *J* 6, 10.4 Hz), 3.35 (6H, s), 3.00–2.95 (2H, pent, *J* 4.1 Hz), 2.58–2.54 (2H, m), 1.75–1.05 (292H, m), 0.90 (18H, **s**), 0.89 (12H, t, *J* 6.6 Hz), 0.85 (6H, d, *J* 6.9 Hz), 0.67–0.63 (4H, m), 0.57 (4H, dt, *J* 4.1, 7.9 Hz), 0.07 (12H, s), −0.33 (2H, br q, *J* 5.4 Hz); δ_C (126 MHz, $CDCl_3$): 169.5, 85.4, 72.7, 57.7, 52.8, 35.3, 33.7, 32.4, 31.9, 30.5, 30.2, 30.0, 29.9, 29.7 (very br), 29.5, 29.42, 29.4, 28.7, 27.9, 27.5, 26.6, 26.2, 25.9, 25.8, 24.7, 22.7, 18.0, 15.8, 14.9, 14.1, 10.9, −4.4, −4.7; υ_{max}: 2962, 2853, 1816, 1748, 1465, 1361, 1255, 1099, 908, 836, 776, 735 cm^{-1}.

(iii) Glucopyranoside **8d** as a colourless thick oil (78%), $[\alpha]_D^{24}$ +11 (c 0.09, $CHCl_3$) {Found $[M+Na]^+$: 3063.8; $C_{194}H_{382}NaO_{17}Si_2$ requires: 3063.8}, which showed δ_H (500 MHz, $CDCl_3$+few drops of CD_3OD): 5.05 (2H, d, *J* 3.5 Hz), 4.32 (2H, br dd, *J* 4.4, 12.3 Hz), 4.2 (2H, br d, *J* 10.8 Hz), 3.91 (2H, br d, *J* 8.2 Hz), 3.87 (2H, br q, *J* 5.7 Hz), 3.76 (2H, br t, *J* 9.5 Hz), 3.45 (2H, dd, *J* 3.8, 9.8 Hz), 3.31–3.28 (8H, including s for the MeO-groups at 3.3), 2.93 (2H, br pent, *J* 4.3 Hz), 2.52 (2H, ddd, *J* 3.8, 6.4, 10.4 Hz), 1.6–1.01 (300H, m), 0.84 (12H, t, *J* 7 Hz), 0.82 (18H, s), 0.81 (6H, d, *J* 7 Hz), 0.63–0.56 (4H, m), 0.52 (2H, dt, *J* 4.1, 7.9 Hz), 0.004 (6H, s), −0.02 (6H, s), −0.38 (2H, br q, *J* 5.4 Hz); δ_C (500 MHz, $CDCl_3$): 175.6, 93.4, 85.4, 73.3, 72.8, 71.8, 70.4, 70.3, 62.8, 57.7, 51.5, 35.2, 33.7, 32.4, 31.9, 30.5, 30.4, 30.3, 30.2, 30.1, 30.0, 29.9, 29.8, 29.73, 29.7, 29.6, 29.51, 29.5, 29.42, 29.4, 29.3, 28.7, 27.8, 27.6, 27.1, 26.2, 25.9, 25.8, 24.3, 22.7, 18.0, 15.8, 14.9, 14.1, 10.9, −4.4, −4.7; υ_{max}: 3406, 2925, 1737, 1465, 1373, 1254, 1100, 1078, 992, 939, 836, 775, 720, 665 cm^{-1}.

(iv) Glucopyranoside **11d** as a colourless syrup (80%), $[\alpha]_D^{24}$ +28 (c 0.97, $CHCl_3$) {MALDI Found $[M+Na]^+$: 1714.5; $C_{103}H_{202}NaO_{14}Si$ requires: 1714.5}, which showed δ_H (500 MHz, $CDCl_3$+few drops of CD_3OD): 5.05 (2H, d, *J* 3.2 Hz), 4.29–4.22 (2H, m), 3.92 (1H, br d, *J* 9.5 Hz), 3.87 (3H, br t, *J* 9.0 Hz), 3.78 (2H, br m), 3.66 (1H, br d, *J* 7 Hz), 3.49 (2H, br d, *J* 9.5 Hz), 3.34 (2H, br d, *J* 8.5 Hz), 3.3 (3H, s), 2.93 (1H, br pent, *J* 4.4 Hz), 2.5 (1H, m), 1.6–1.03 (154, m), 0.83 (6H, t, *J* 6.7 Hz), 0.81 (9H, s), 0.8 (3H, d, *J* 7 Hz), 0.61–0.56 (2H, m), 0.51 (1H, dt, *J* 3.8, 8.2 Hz), −0.003 (3H, s), −0.03 (3H, s), −0.38 (1H, br q, *J* 5.1 Hz); δ_C (126 MHz, $CDCl_3$+few drops of CD_3OD): 175.1, 93.5, 93.4, 85.5, 73.2 (br), 72.9, 72.6, 72.1, 71.6, 70.7, 70.2, 69.9, 62.7, 62.0, 57.5, 51.6, 35.2, 33.5, 29.64, 29.63, 29.6, 29.52, 29.5, 29.2, 28.6, 27.6, 27.4, 26.9, 26.0, 25.6, 24.2, 22.6, 17.8, 15.6, 14.7, 13.9, 10.8, −4.6, −5.0; υ_{max}: 3363, 2923, 2853, 1733, 1464, 1100, 836, 760 cm^{-1}.

(v) Glucopyranoside **9d** as a syrup (72%), $[\alpha]_D^{24}$ +31 (c 0.84, $CHCl_3$) {Found $[M+Na]^+$: 2835.6642; $C_{182}H_{354}O_{17}Na$ requires: 2835.6733}, which showed δ_H (500 MHz, $CDCl_3$+few drops of CD_3OD): 4.93 (2H, d, *J* 3.2 Hz), 4.56 (2H, br d, *J* 11.1 Hz), 4.15 (2H, br t, *J* 9.2 Hz), 3.93 (2H, br q, *J* 7.3 Hz), 3.71 (2H, t, *J* 9.5 Hz), 3.58 (2H, br m), 3.42 (2H, dd, *J* 3.2, 9.8 Hz), 3.25 (6H, s), 3.17 (2H, t, *J* 9.5 Hz), 2.89 (2H, br pent, *J* 4.4 Hz), 2.35 (2H, m), 1.57–0.98 (302H, m), 0.78 (12H, t, *J* 7 Hz), 0.76 (6H, d, *J* 7 Hz), 0.6–0.52 (4H, m), 0.47 (2H, dt, *J* 4.1, 8.2 Hz), −0.43 (2H, br q, *J* 5.1 Hz); δ_C: 175.4, 94.7, 85.5, 72.4, 71.13, 71.1, 69.7, 64.1, 57.4, 52.2, 35.2, 34.6, 32.2, 31.7, 30.3, 30.1, 30.0, 29.7, 29.68, 29.6, 29.5, 29.48, 29.46, 29.4, 29.3, 29.2, 29.1, 28.5, 27.3, 27.1, 25.9, 25.1, 22.5, 15.6, 14.6, 13.8, 10.7; υ_{max}: 3362, 2920, 2851, 1722, 1467, 1100, 720 cm^{-1}.

(vi) Glucopyranoside **12d** as a syrup (78%), $[\alpha]_D^{24}$ +48, (c 0.49, $CHCl_3$) {Found $[M+Na]^+$: 1600.3913; $C_{97}H_{188}NaO_{14}$ requires: 1600.3891}, which showed δ_H (500 MHz, $CDCl_3$+few drops of CD_3OD): 5.07 (1H, br s), 5.02 (1H, br s), 4.62 (1H, br d, *J* 10.7 Hz), 4.17 (1H, br s), 3.99 (1H, br m), 3.87–3.81 (4H, m), 3.64–3.61 (2H, m), 3.54 (1H, br d, *J* 9.5 Hz), 3.48 (1H, br d, *J* 9.8 Hz), 3.32–3.27 (4H, including s (OMe) at 3.30), 3.23 (1H, br t, *J* 9.5 Hz), 2.93 (1H, m), 2.36 (1H, m), 1.65–1.50 (2H, m), 1.45–1.02 (153H, m), 0.83 (6H, t, *J* 7 Hz), 0.8 (3H, d, *J* 7 Hz), 0.63–0.55 (2H, m), 0.51 (1H, dt, *J* 3.8, 7.9 Hz), −0.38 (1H, br q, *J* 5.1 Hz); δ_C (126 MHz, $CDCl_3$+few drops of CD_3OD): 175.5, 94.4, 85.5, 72.5 (br), 72.4, 72.3, 71.4, 71.2, 71.0, 70.9, 70.0, 64.2, 62.1, 57.6, 52.3, 35.3, 34.6, 32.3, 31.8, 30.4, 30.1, 29.82, 29.8, 29.7, 29.63, 29.6, 29.5, 29.3, 29.2, 28.6, 27.4, 27.2, 26.0, 25.1, 22.6, 15.6, 14.7, 13.9, 10.8; υ_{max}: 3349, 2919, 2850, 1719, 1467, 992 cm^{-1}.

4.6. 6-*O*-[(*R*)-2-((*R*)-1-Hydroxy-18-((1*S*,2*R*)-2-((17*R*,18*R*)-17-methoxy-18-methylhexatriacontyl)cyclopropyl)octa-decyl) hexacosanoate]-α-*D*-glucopyranosyl-(1→1)-6′-*O*-[(*R*)-2-((*R*)-1-hydroxy-18-((1*S*,2*R*)-2-((17*R*,18*R*)-17-methoxy-18-methylhexatriacontyl)cyclopropyl)octa-decyl)hexacosanoate]-α-*D*-glucopyranoside (9e) and 6-*O*-[(*R*)-2-((*R*)-1-Hydroxy-18-((1*S*,2*R*)-2-((17*R*,18*R*)-17-methoxy-18-methylhexatriacontyl)cyclopropyl)octa-decyl)hexacosanoate]-α-*D*-glucopyranosyl-(1→1)-α-*D*-glucopyranoside (12e)

(i) (*R*)-2-{(*R*)-1-hydroxy-18-(1*S*,2*R*)-2-[(17*R*,18*R*)-17-methoxy-18-methylhexatricontyl)cyclopropyl]octadecyl}-hexacosanoic acid[60] (0.66 g, 0.53 mmol) gave acid **5e** as a colourless oil (67%), $[\alpha]_D^{23}$ +5.6 (*c* 0.80, $CHCl_3$) {Found $[M+Na]^+$: 1390.3708, $C_{91}H_{182}NaO_4Si$ requires: 1390.3705}, which showed δ_H (500 MHz, $CDCl_3$): 3.87–3.84 (1H, m), 3.34 (3H, s), 2.96 (1H, pent, *J* 5.1 Hz), 2.53 (1H, ddd, *J*, 3.8, 5.8, 9.5 Hz), 1.73–1.10 (148H, m), 0.91 (9H, s), 0.89 (6H, t, *J* 6.9 Hz), 0.86 (3H, d, *J* 6.6 Hz) 0.67–0.63 (2H, m), 0.56 (1H, dt, *J* 4.1, 8.2 Hz), 0.12 (3H, s), 0.11 (3H, s), −0.32 (1H, br.q, *J* 5.1 Hz); δ_C (126 MHz, $CDCl_3$): 176.5, 85.5, 73.4, 57.7, 50.5, 41.4, 36.1, 35.3, 33.7, 32.4, 32.1, 31.9, 31.6, 30.5, 30.4, 30.2, 23.0, 29.9, 29.6, 29.5, 29.45, 29.4, 29.35, 29.1, 28.9, 28.7, 27.7, 27.6, 27.5, 26.2, 25.7, 24.8, 22.7, 22.6, 20.4, 19.4, 18.7, 17.9, 15.8, 14.9, 14.3, 14.1, 10.9, −4.3, −4.9; ν_{max}: 3450, 2921, 2851, 1709, 1465, 1362, 1254, 836 cm^{-1}.

(ii) Glucopyranoside **7e** as a colourless thick oil (22%), $[\alpha]_D^{23}$ +25 (*c* 0.98, $CHCl_3$) {MALDI Found $(M+Na)^+$: 3496.8, $C_{212}H_{430}NaO_{17}Si_8$ requires: 3496.1}, which showed δ_H (500 MHz, $CDCl_3$): 4.86 (2H, d, *J* 2.9 Hz), 4.37 (2H, br d, *J* 10.1 Hz), 4.04–3.99 (4H, m), 3.96–3.88 (4H, m), 3.52 (2H, t, *J* 9.2 Hz), 3.39 (2H, dd, *J* 3.2, 9.5 Hz), 3.34 (6H, s), 2.96 (2H, br pent, *J* 4.1 Hz), 2.55 (2H, ddd, *J* 3.6, 4.7, 10.1 Hz), 1.67–1.61 (4H, m), 1.46–1.10 (290H, m), 0.89 (12H, t, *J* 6.9 Hz), 0.88 (18H, s), 0.85 (6H, d, *J* 6.9 Hz) 0.66–0.63 (4H, m), 0.56 (2H, dt, *J* 4.1, 8.2 Hz), 0.16 (18H, s), 0.148 (18H, s), 0.14 (18H, s), 0.06 (12H, s), −0.31 (2H, br q, *J* 5.1 Hz); δ_C (126 MHz, $CDCl_3$): 173.8, 94.9, 85.5, 73.6, 73.4, 73.2, 72.9, 71.8, 70.8, 62.4, 57.7, 51.9, 35.4, 33.5, 32.4, 31.9, 30.5, 30.2, 30.0, 29.95, 29.9, 29.7, 29.61, 29.6, 29.5, 29.44, 29.4, 28.7, 28.1, 27.8, 27.6, 27.5, 26.24, 26.2, 25.8, 25.2, 22.7, 18.0, 15.8, 14.9, 14.1, 10.9, 1.2, 1.1, 0.2, −4.5, −4.6; ν_{max}: 2924, 2853, 1742, 1465, 1251, 1099, 1077, 872, 841 cm^{-1}. The second fraction was glucopyranoside **10e** (78%), $[\alpha]_D^{23}$ +46 (*c* 0.96, $CHCl_3$) {MALDI Found $(M+Na)^+$: 2146.8, $C_{121}H_{250}NaO_{14}Si_7$ requires:

2146.7}, which showed δ_H (500 MHz, $CDCl_3$): 4.91 (1H, d, *J* 3.2 Hz), 4.84 (1H, d, *J* 2.9 Hz), 4.35 (1H, dd, *J* 4.1, 11.9 Hz), 4.08 (1H, dd, *J* 4.1, 12.0 Hz), 3.98 (1H, br q, *J* 5.3 Hz), 3.94–3.83 (4H, m), 3.72–3.66 (2H, m), 3.48 (2H, dt, *J* 6.6, 8.9 Hz), 3.44 (1H, dd, *J* 3.2, 9.5 Hz), 3.39 (1H, dd, *J* 2.9, 9.2 Hz), 3.34 (3H, s), 2.96–2.94 (1H, m), 2.55 (1H, ddd, *J*, 3.7, 5.8, 10.4 Hz), 1.73–1.70 (1H, m), 1.63–1.59 (2H, m), 1.49–0.96 (148H, m), 0.90–0.81 (15H, m, including s at 0.86), 0.65 (2H, br m), 0.56 (1H, dt, *J* 3.8, 8.2 Hz), 0.17 (9H, s), 0.16 (9H, s), 0.155 (9H, s), 0.150 (9H, s), 0.148 (9H, s), 0.12 (9H, s), 0.06 (3H, s), 0.05 (3H, s), −0.32 (1H, br q, *J*, 4.8 Hz); δ_C (126 MHz, $CDCl_3$): 174.1, 94.5, 94.4, 85.4, 73.4, 73.35, 72.9, 72.83, 72.78, 72.0, 71.4, 70.8, 62.5, 61.7, 57.7, 51.8, 35.4, 33.4, 32.4, 31.9, 30.5, 30.2, 30.0, 29.9, 29.8, 29.7, 29.5, 29.4, 28.7, 28.1, 27.6, 26.4, 26.2, 25.8, 24.9, 22.7, 18.0, 15.8, 14.9, 14.1, 10.9, 1.1, 1.0, 0.9, 0.8, 0.2, 0.1, −4.5, −4.7; ν_{max}: 2924, 2854, 1743, 1464, 1251, 1165, 1077, 843 cm^{-1}.

(iii) Glucopyranoside **8e** as a syrup (50%), $[\alpha]_D^{23}$ +39 (c 0.92, $CHCl_3$) {MALDI Found $[M+Na]^+$: 3063.9, $C_{194}H_{382}NaO_{17}Si_2$ requires: 3063.8}, which showed δ_H (500 MHz, $CDCl_3$+few drops of CD_3OD): 5.03 (2H, d, *J* 3.2 Hz), 4.28 (2H, br d, *J* 8.2 Hz), 4.20 (2H, br d, *J* 10.7 Hz), 3.92 (2H, br d, *J* 9.2 Hz), 3.86 (2H, d *J* 5.1 Hz), 3.79 (2H, t, *J* 9.5 Hz), 3.44 (2H, d, *J* 9.8 Hz), 3.32–3.27 (8H, m, including s at 3.29), 2.93 (2H, d, *J* 3.8 Hz), 2.53 (2H, ddd, *J* 3.6, 7.0, 10.7 Hz), 1.56–1.05 (300H, m), 0.83 (12H, t, *J* 7.3 Hz), 0.82 (18H, s), 0.79 (6H, d, *J* 7.3 Hz), 0.62–0.56 (4H, br m), 0.50 (2H, dt, *J* 4.1, 8.2 Hz), −0.007 (6H, s), −0.02 (6H, s), −0.32 (2H, br q, *J* 5.3 Hz); δ_C (126 MHz, $CDCl_3$): 175.1, 94.2, 93.6, 85.5, 73.2, 73.0, 71.6, 70.2, 69.9, 62.8, 57.5, 51.6, 35.3, 33.5, 32.3, 31.8, 30.4, 30.1, 29.83, 29.8, 29.7, 29.6, 29.55, 29.3, 29.2, 28.6, 27.7, 27.4, 26.9, 26.0, 25.7, 25.6, 24.2, 22.54, 17.8, 15.6, 14.7, 13.9, 10.8, −4.6, −5.0; ν_{max}: 3368, 2920, 2851, 1732, 1466, 1377, 1254, 760, 720 cm^{-1}.

(iv) Glucopyranoside **11e** as a colourless thick oil (69%), $[\alpha]_D^{23}$ +31 (c 0.88, $CHCl_3$) {MALDI Found $(M+K)^+$: 1730.4, $C_{103}H_{202}KO_{14}Si$ requires: 1730.4}, which showed δ_H (500 MHz, $CDCl_3$+few drops of CD_3OD): 5.05 (2H, br s), 4.32–4.24 (2H, m), 3.92–3.89 (3H, m), 3.81 (2H, br d, *J* 9.5 Hz), 3.72–3.68 (2H, m), 3.52 (2H, br m), 3.37–3.34 (2H, m), 3.31 (3H, s), 2.95–2.92 (1H, m), 2.52 (1H, br m), 1.61–1.07 (154H, m), 0.86–0.79 (18H, m, including s at δ 0.83), 0.62–0.61 (2H, br m), 0.53 (1H, dt, *J* 3.8, 7.9 Hz), 0.02 (3H, s), 0.0 (3H, s), −0.35 (1H, br q, *J* 5.4 Hz); δ_C (126 MHz, $CDCl_3$+few drops of CD_3OD): 175.0, 93.5, 93.45, 85.5, 73.1, 73.0, 72.7, 72.1, 71.6, 70.7, 70.2, 69.9, 67.8, 62.7, 61.9, 60.4, 57.4, 51.6, 35.2, 33.5, 32.3, 31.7, 30.3, 30.0, 29.7, 29.65, 29.6, 29.5, 29.48 29.4, 29.2, 29.1, 28.5, 27.6, 27.3, 26.8, 25.9, 25.6, 25.5, 25.3, 24.1, 22.5, 17.8, 15.6, 14.6, 13.83, 13.8, 10.7, −4.7, −5.1; ν_{max}: 3369, 2919, 2851, 1723, 1465, 1100, 1048, 994, 836, 760 cm^{-1}.

(v) Glucopyranoside **9e** as a syrup (46%), $[\alpha]_D^{23}$ +21 (c 0.96, $CHCl_3$) {Found $[M+Na]^+$: 2835.6758, $C_{182}H_{354}NaO_{17}$ requires: 2835.6733}, which showed δ_H (500 MHz, $CDCl_3$+few drops of CD_3OD): 4.98)2H, d, *J* 3.2 Hz), 4.74 (2H, br d, *J* 10.4 Hz), 4.29 (2H, br t, *J* 9.2 Hz), 3.89 (2H, br t, *J* 7.9 Hz), 3.75 (2H, t, *J* 9.8 Hz), 3.5 (2H, dd, *J* 2.8, 9.5 Hz), 3.37 (2H, d, *J* 2.0 Hz), 3.31 (6H, s), 3.19 (2H, br t, *J* 9.8 Hz), 2.95 (2H, br q, *J* 5.1 Hz), 2.39–2.28 (2H, m), 1.58–1.07 (302H, m), 0.85 (12H, t, *J* 6.6 Hz), 0.82 (6H, d, *J* 7 Hz), 0.64–0.58 (4H, m), 0.53 (2H, dt, *J* 4.1, 8.2 Hz), −0.35 (2H, br q, *J* 5.1 Hz); δ_C (126 MHz, $CDCl_3$+few drops of CD_3OD): 175.3, 94.5, 85.5, 72.5, 71.2, 71.0, 69.8, 64.0, 57.5, 52.3, 35.2, 34.6, 32.2, 31.7, 30.3, 30.0, 30.03, 29.8, 29.7, 29.5, 29.4, 29.3, 29.2, 28.5, 27.3, 27.1, 25.9, 25.7, 25.1, 22.5, 15.6, 14.6, 13.9, 10.7; ν_{max}: 3389, 2918, 2851, 1731, 1467, 1377, 1149, 720 cm^{-1}.

(vi) Glucopyranoside as a syrup **12e** (90%), $[\alpha]_D^{23}$ +35 (*c* 0.9, $CHCl_3$) {MALDI Found $[M+Na]^+$: 1600.3928, $C_{97}H_{188}NaO_{14}$ requires: 1600.3891}, which showed δ_H (500 MHz, $CDCl_3$+few drops of CD_3OD); 5.07 (1H, d, *J* 4.0 Hz), 5.0 (1H, d, *J* 3.5 Hz), 4.68 (1H, br d, *J* 11.7 Hz), 4.23 (1H, br t, *J* 8.2 Hz), 3.97–3.77 (4H, m), 3.64–3.54 (4H, m), 3.47 (1H, d, *J* 10.4 Hz), 3.31–3.25 (4H, m, including s at 3.30), 3.20 (1H, br t, *J* 9.1 Hz), 2.94–2.93 (1H, m), 2.42–2.36 (1H, m), 1.57–1.55 (2H, m), 1.34–1.04 (153H, m), 0.84 (6H, t, *J* 6.6 Hz), 0.81 (3H, d, *J* 6.6 Hz), 0.62–0.58 (2H, m), 0.52 (1H, dt, *J* 3.8, 8.5 Hz), −0.36 (1H, br q, *J* 5.1); δ_C (126 MHz, $CDCl_3$+few drops of CD_3OD): 175.5, 93.9, 85.5, 72.5, 72.3, 71.4, 70.7, 70.1, 63.9, 62.0, 57.6, 52.4, 35.3, 34.6, 32.3, 31.9, 30.8, 30.4, 30.2, 30.15, 30.1, 30.0, 29.9, 29.85, 29.8, 29.71, 29.7, 29.6, 29.4, 29.3, 28.7, 27.5, 27.2, 26.1, 25.1, 22.6, 15.7, 14.8, 14.0, 13.4, 10.8; ν_{max}: 3429, 2919, 2850, 1643, 1466, 1184, 1106 cm^{-1}.

4.7. 6-*O*-[(*R*)-2-((*R*)-1-Hydroxy-19-((1*S*,2*R*)-2-((2*S*,19*S*, 20*S*)-19-methoxy-20-methyloctatriacontan-2-yl)cyclo-propyl)nonadecyl)hexacosanoate]-α-*D*-glucopyranosyl-(1→1)-6′-*O*-[(*R*)-2-((*R*)-1-hydroxy-19-((1*S*,2*R*)-2-((2*S*,19*S*, 20*S*)-19-methoxy-20-methyloctatriacontan-2-yl)cyclo-propyl)nonadecyl)hexacosanoate]-α-*D*-glucopyranoside (9f) and 6-*O*-[(*R*)-2-((*R*)-1-Hydroxy-19-((1*S*,2*R*)-2-((2*S*, 19*S*,20*S*)-19-methoxy-20-methyloctatriacontan-2-yl)-cyclopropyl)nonadecyl)hexacosanoate]-α-*D*-gluco-pyranosyl-(1→1)-α-*D*-glucopyranoside (12f)

(i) [(*R*)-2-((*R*)-1-Hydroxy-19-((1*S*,2*R*)-2-((2*S*,19*S*,20*S*)-19-methoxy-20-methyloctatriacontan-2-yl)cyclopropyl)nonadecyl)hexacosanoic acid,[69] gave acid **5f** as yellowish oil (61%), $[\alpha]_D^{23}$ +5.65 (c 1.15, $CHCl_3$) {MALDI Found $[M+Na]^+$: 1431.4; $C_{94}H_{188}NaO_4Si$ requires: 1431.0}, which showed δ_H (500 MHz $CDCl_3$): 3.86 (1H, br d, *J* 3.8 Hz), 3.49 (3H, s), 3.34 (1H, br d, *J* 3.8 Hz), 2.53 (1H, dt, *J* 4.5, 8.0 Hz), 1.65–1.62 (2H, m), 1.55–1.50 (2H, m), 1.26 (146H, br s), 0.91 (9H, s), 0.88 (6H, t, *J* 7.2 Hz), 0.86 (6H, d, *J* 5.4 Hz), 0.66–0.63 (1H, m), 0.46–0.43 (1H, m), 0.22–0.02 (9H, including 2×s at 0.12 and 0.1 for the two methyl silyl group); δ_C (126 MHz, $CDCl_3$); 176.9, 85.4, 74.7, 57.6, 50.5, 38.1, 37.4, 35.3, 34.4, 31.9, 29.6, 29.5, 27.5, 27.2, 26.1, 25.7, 24.6, 22.6, 19.6, 18.6, 17.9, 14.1, 10.4, −4.2, −4.9; υ_{max} 2922, 2852, 1708, 1465, 1253, 1099, 836 cm^{-1}.

(ii) Glucopyranoside **7f a**s a viscous colourless oil (29%), $[\alpha]_D^{18}$ +17 (c 1.0, $CHCl_3$) [Found $[M+Na]^+$: 3582.1835; $C_{218}H_{442}NaO_{17}Si_8$ requires: 3582.1836], which showed δ_H (500 MHz $CDCl_3$): 4.86 (2H, d, *J* 2.5 Hz), 4.38 (2H, br d, *J* 11.0 Hz), 4.04 (2H, br t, *J* 4.4 Hz), 4.01 (2H, d, *J* 3.2 Hz), 3.95 (2H, m), 3.92 (3H, t, *J* 7.2 Hz), 3.52 (2H, t, *J* 8.9 Hz), 3.40 (2H, dd, *J* 3.2, 9.4 Hz), 3.34 (6H, s), 2.97 (2H, m), 2.56 (2H, dt, *J* 5.0, 10.7 Hz), 1.66–1.63 (4H, m), 1.59–1.55 (4H, m), 1.26 (279H, br m), 0.93 (12H, t, *J* 6.8 Hz), 0.88 (18H, s), 0.86 (12H, d, *J* 6.8 Hz), 0.68–0.65 (2H, m), 0.45–0.42 (2H, m), 0.22–0.1 (60H, including 3 s at 0.16 (18H), 0.15 (18H), 0.14 (18H), together with six protons of the cyclopropanes), 0.08 (6H, s), 0.06 (6H, s); δ_C (126 MHz, $CDCl_3$); 173.8, 94.8, 85.4, 73.4, 73.0, 72.8, 72.1, 61.2, 57.7, 51.9, 38.5, 36.9, 35.0, 33.3, 30.8, 29.7, 27.5, 26.2, 23.2, 22.9, 19.4, 17.7, 15.8, 14.8, 14.5, 14.2, 11.2, 10.8, 1.8, 0.8, −4.6, −4.7; υ_{max}: 2923, 2852, 1743, 1493, 1251 cm^{-1}. The second fraction was **10f** as a viscous colourless oil (18%), $[\alpha]_D^{18}$ +33.4 (c 1.03, $CHCl_3$) [Found (MALDI) $[M+Na]^+$: 2189.7631; $C_{124}H_{256}NaO_{14}Si_7$ requires: 2189.7639], which showed δ_H (500 MHz, $CDCl_3$): 4.91 (1H, d, *J* 3.0 Hz), 4.85 (1H, d, *J* 2.9 Hz), 4.36 (1H, dd, *J* 1.9, 11.8 Hz), 4.09 (1H, dd, *J* 4.1, 11.8 Hz), 3.98 (1H, br td, *J* 5.7, 10.0 Hz), 3.91 (2H, m), 3.84 (1H, td. *J*, 3.2, 9.4 Hz), 3.70 (2H, br m), 3.47 (2H, td, *J* 9.0, 14.5 Hz), 3.40 (2H, ddd, *J* 2.8, 9.2, 17.6 Hz), 3.34 (3H, s), 2.95 (1H, br pent, *J* 4.1 Hz), 2.54 (1H, dt, *J* 3.8, 8.0 Hz), 1.73–1.69 (2H, m), 1.64–1.60 (2H, br m), 1.26 (147H, br m), 0.93 (6H, t, *J* 7.1 Hz), 0.88 (9H, s), 0.86 (6H, d, *J* 6.8 Hz), 0.68–0.66 (1H, m), 0.45 (1H, dt, *J* 4.0, 8.3 Hz), 0.22–0.1 (57H, including 5 s at 0.17 (9H), 0.16 (9H), 0.155 (9H), 0.15 (18), 0.12 (9H), together with 3 protons of the cyclopropane), 0.06 (3H, s), 0.05 (3H, s); δ_C (126 MHz, $CDCl_3$): 174.0, 94.5, 94.3, 84.4, 73.4, 73.0, 72.9, 72.8, 72.7, 72.3, 72.0, 71.5, 62.4, 61.6, 57.7, 51.8, 38.1, 37.4, 35.3, 34.4, 33.4, 32.3, 31.9, 30.4, 30.0, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 28.1, 27.5, 27.2, 26.3, 26.1, 25.8, 25.7, 24.8, 22.6, 19.6, 18.6, 18.0, 14.8, 14.1, 10.4, 1.1, 1.0, 0.9, 0.8, 0.1, 0.04, −4.4, −4.6; υ_{max}: 3468, 2913, 1742, 1464, 1251 cm^{-1}.

(iii) Glucopyranoside **8f** as a colourless viscous oil (61%), $[\alpha]_D^{18}$ +19 (c 1.0, $CHCl_3$) {Found $[M+Na]^+$: 3149.9469; $C^{13}_{198}C_2H_{394}NaO_{17}Si_2$ requires: 3149.9464}, which showed δ_H (500 MHz $CDCl_3$+few drops of CD_3OD): 4.90 (2H, d, *J* 2.5 Hz), 4.15 (2H, d, *J* 10.1 Hz), 3.78–3.75 (4H, m), 3.57 (2H, t, *J* 7.6 Hz), 3.31 (2H, d, *J* 3.8 Hz), 3.17–3.14 (10H, br m), 2.82–2.80 (2H, m), 2.38–2.35 (2H, m), 1.03 (304H, s), 0.85 (12H, t *J* 7.0 Hz), 0.83 (12H, d, *J* 6.6 Hz), 0.81 (18H, s), 0.63–0.60 (2H, m), 0.45–0.40 (2H, m), 0.2–0.05 (6H, m), 0.02 (6H, s), 0.01 (6H, s); δ_C (126 MHz, $CDCl_3$+few drops of CD_3OD); 175.1, 93.0, 85.4, 73.3, 72.7, 71.8, 71.4, 62.2, 57.4, 51.5, 37.9, 37.1, 35.3, 34.4, 33.5, 31.9, 31.8, 27.6, 27.2, 26.1, 25.9, 24.3, 22.8, 19.4, 18.6, 18.0, 14.6, 14.0, 10.2, 0.9, −4.4, −4.8; υ_{max}: 3436, 2922, 1609, 1493, 1050 cm^{-1}.

(iv) Glucopyranoside **11f** as a viscous colourless thick oil (47%), $[\alpha]_D^{18}$ +40 (c 0.68, $CHCl_3$) {MALDI Found $[M+Na]^+$: 1754.8; $C_{106}H_{208}NaO_{14}Si$ requires: 1755.0}, which showed δ_H (500 MHz $CDCl_3$+few drops of CD_3OD): 5.06 (2H, d, *J* 2.9 Hz), 4.31 (1H, br s), 3.94 (4H, d, *J* 5.0 Hz), 3.60–3.63 (3H, m), 3.41 (2H, d, *J* 8.3 Hz), 3.25 (6H, d, *J* 6.0 Hz), 2.89 (1H, m), 2.42–2.46 (1H, m), 1.45–1.48 (2H, m), 1.21 (154H, s), 0.93 (6H, t, *J* 6.6 Hz), 0.88 (9H, s), 0.85 (6H, d, *J* 6.9 Hz), 0.57–0.54 (1H, m), 0.34–0.31 (1H, m), 0.2–0.05 (3H, m), 0.02 (3H, s), 0.01 (3H, s); δ_C (126 MHz, $CDCl_3$+few drops of CD_3OD): 175.8, 96.0, 93.7, 85.5, 72.6, 72.4, 72.2, 72.1, 71.9, 71.6, 71.1, 70.7, 64.0, 63.4, 57.2, 51.5, 38.3, 37.0, 36.3, 34.0, 31.8, 26.2, 24.6, 19.0, 17.4, 15.8, 13.2, −4.7, −6.3; υ_{max}: 3400, 2923, 1732, 1455, 1246 cm^{-1}.

(v) The glucopyranoside **9f** as a colourless thick oil (35%), $[\alpha]_D^{21}$ +17.0 (c 1.01, $CHCl_3$) {Found $[M+Na]^+$: 2919.7698; $C_{188}H_{366}NaO_{17}$ requires: 2919.7667}, which showed δ_H (400 MHz, $CDCl_3$+few drops of CD_3OD): 5.0 (2H, s), 4.80 (2H, d, *J* 11.2 Hz), 4.36–4.33 (2H, m), 3.87 (2H, m), 3.73 (2H, t, *J* 13.2 Hz), 3.66–3.63 (2H, m), 3.55–3.50 (2H, m), 3.4 (6H, s), 3.20 (2H, br. t, *J* 10.3 Hz), 2.95–2.92 (2H, m), 2.40–2.38 (2H, m), 1.58–1.55 (4H, m), 1.26 (302H, s), 0.88 (12H, t, *J* 7.2 Hz), 0.84 (12H, d, *J* 5.6 Hz), 0.66–0.62 (2H, m), 0.45–0.42 (2H, m), 0.17–0.07 (6H, m); δ_C (101 MHz, $CDCl_3$+few drops of CD_3OD): 175.3, 90.5, 85.4, 72.6, 72.5, 71.5, 70.0, 64.4, 57.5, 52.2, 37.9, 37.3, 35.2, 34.3, 32.2, 31.8, 30.3, 29.9, 29.8, 29.7, 29.5, 29.4, 29.3, 29.2, 27.4, 27.1, 26.0, 25.9, 22.5, 19.5, 18.5, 14.6, 13.9, 10.3; υ_{max}: 3436, 2923, 2852, 1732, 1454, 1050, cm^{-1}.

(vi) The glucopyranoside **12f** as a semi solid (50%), $[\alpha]_D^{18}$ +34 (c 0.20, $CHCl_3$) {Found $[M+NH_4]^+$: 1637.4808; $[C_{100}H_{194}O_{14}+NH_4]^+$ requires: 1637.4807}, which showed δ_H (500 MHz, $CDCl_3$+few drops of CD_3OD): 5.07 (2H, d, *J* 2.9 Hz), 4.48 (1H, d, *J* 7.4 Hz), 4.15 (1H, dd, *J* 5.7, 12.5 Hz), 4.08–4.0 (1H, m), 3.81–3.73 (4H, m), 3.68–3.61 (2H, m), 3.48 (2H, br dt, *J* 3.6, 9.7 Hz), 2.35–2.33 (5H, including s for the methoxy group), 3.01–2.95 (1H, m), 2.45–2.42 (1H, m), 1.7–1.0 (157H, br m), 0.88 (6H, t, *J* 6.8 Hz), 0.84 (6H, d, *J* 5.6 Hz), 0.65–0.61 (1H, m), 0.46–0.42 (1H, m), 0.22–0.05 (3H, m); δ_C (126 MHz, $CDCl_3$): 175.3, 93.2, 93.0, 85.2, 72.6, 72.2, 71.9, 71.8, 71.3, 70.9, 70.5, 70.3, 63.1, 61.2, 57.0, 52.3, 38.1, 37.7, 36.9, 35.7, 34.8, 33.9, 31.8, 31.4, 29.9, 29.8, 29.5, 29.3, 29.1, 28.8, 26.8, 26.7, 25.6, 25.4, 24.8, 23.0, 22.1, 19.0, 18.1, 14.1, 13.3, 9.9; υ_{max}: 3392, 2919, 1654, 1466, 1377, 1101 cm^{-1}.

4.8. 6-*O*-[(*R*)-2-{(*R*)-1-Hydroxy-16-[(1*S*,2*R*)-2-((*S*)-20-methyl-19-oxo-20-octatriacontyl)cyclopropyl]hexadecyl}-hexacosanoate]-α-*D*-glucopyranosyl-(1→1)-6′-*O*-(*R*)-2-{(*R*)-1-hydroxy-16-[(1*S*,2*R*)-2-((*S*)-20-methyl-19-oxo-20-octatriacontyl)cyclopropyl]hexadecyl}hexa-cosanoate]-α-*D*-glucopyranoside (9g) and 6-*O*-[(*R*)-2-{(*R*)-1-Hydroxy-16-[(1*S*,2*R*)-2-((*S*)-20-methyl-19-oxo-20-octatriacontyl)-cyclopropyl]hexadecyl}hexacosanoic]-α-*D*-glucopyrano-syl-(1→1)-α-*D*-glucopyranoside (12g)

(i) (*R*)-2-{(*R*)-1-(*tert*-Butyldimethylsilanyloxy)-16-[(1*S*,2*R*)-2-[(19*S*,20*S*)-19-hydroxy-20-methyloctatriacontyl)cyclo-propyl] hexadecyl}hexacosanoic acid,[70] (0.7 g, 0.513 mmol) gave acid **5g** as a white semi-solid (82%), $[\alpha]_D^{23}$ +7.0 (c 0.71, $CHCl_3$) {Found $[M+Na]^+$: 1374.3350, $C_{90}H_{178}NaO_4Si$ requires: 1374.3367}, which showed δ_H (500 MHz, $CDCl_3$): 3.85–3.82 (1H, m), 2.54–2.48 (2H, m), 2.41 (2H, dt, *J* 2.0, 7.3 Hz), 171–160 (2H, m), 1.58–1.13 (143H, m), 1.05 (3H, d, *J* 6.6 Hz), 0.92 (9H, s), 0.89 (6H, t, *J* 7.0 Hz), 0.67–0.64 (2H, m), 0.56 (1H, br dt, *J* 4.1, 8.2 Hz), 0.14 (3H, s), 0.13 (3H, s), −0.32 (1H, br q, *J* 5.0 Hz); δ_C (126 MHz, $CDCl_3$): 215.2, 175.9, 73.6, 50.4, 46.3, 41.7, 41.4, 41.1, 35.4, 34.1, 33.0, 31.9, 30.2, 29.7, 29.6, 29.55, 29.53, 29.5, 29.45, 29.4, 29.35, 29.34, 29.1, 28.7, 27.7, 27.5, 27.3, 26.1, 25.8, 25.7, 24.9, 23.7, 22.7, 22.6, 20.4, 17.9, 16.35, 15.8, 14.3, 14.1, 10.9, −4.3, −4.9; ν_{max}: 2919, 2851, 1708, 1467, 1361, 1253, 1075, 908, 836, 775, 735 cm^{-1}.

(ii) Glucopyranoside **7g** as a colourless thick oil (63%), $[\alpha]_D^{23}$ +36 (*c* 0.77, $CHCl_3$) {MALDI Found $(M+Na)^+$: 3467.3, $C_{210}H_{422}NaO_{17}Si_8$ requires: 3467.3}, which showed δ_H (400 MHz, $CDCl_3$): 4.85 (2H, d, *J* 2.9 Hz), 4.37 (2H, br d, *J* 10.4 Hz), 4.01 (4H, br t, *J* 11.0 Hz), 3.98–3.88 (4H, m), 3.53 (2H, t, *J* 8.8 Hz), 3.38 (2H, br d, *J* 9.3 Hz), 2.56–2.48 (4H, m), 2.41(4H, t, *J* 7.4 Hz), 1.64–1.15 (288H, m), 1.05 (6H, d, *J* 7.0 Hz), 0.9–0.88 (30H, m, including s at 0.88), 0.65–0.63 (4H, br m), 0.57 (2H, dt, *J* 3.5, 7.5 Hz), 0.16 (18H, s), 0.15 (18H, s), 0.14 (18H, s), 0.06 (12H, s), −0.3 (2H, br q, *J* 4.8 Hz); δ_C (101 MHz, $CDCl_3$): 215.2, 173.8, 94.8, 73.5, 73.4, 72.8, 71.8, 70.7, 62.4, 51.8, 46.3, 41.1, 33.4, 33.0, 31.9, 30.2, 29.84, 29.8, 29.72, 29.7, 29.65, 29.6, 29.51, 29.5, 29.46, 29.4, 29.3, 28.7, 28.1, 27.3, 25.9, 25.8, 25.1, 23.70, 22.68, 18.0, 16.4, 15.8, 14.1, 10.9, 1.1, 0.9, 0.1, −4.5, −4.7; ν_{max}: 2919, 2850, 1743, 1700, 1470, 1251, 1164, 1111, 1077, 872, 820 cm^{-1}. The second fraction was glucopyranoside **10g**, a colourless thick oil (37%), $[\alpha]_D^{23}$ +46 (c 0.80, $CHCl_3$) {MALDI Found $(M+Na)^+$: 2132.0, $C_{120}H_{246}NaO_{14}Si_7$ requires: 2131.7}, which showed δ_H (400 MHz, $CDCl_3$): 4.92 (1H, d, *J* 2.6 Hz), 4.85 (1H, d, *J* 2.4 Hz), 4.35 (1H, br d, *J* 11.4 Hz), 4.07 (1H, dd, *J* 3.8, 11.8 Hz), 3.99 (1H, br d, *J* 9.2 Hz), 3.95–3.88 (3H, m), 3.84 (1H, br d, *J* 9.4 Hz), 3.70–3.65 (2H, m), 3.48 (2H, q, *J* 8.9 Hz), 3.42 (2H, dt, *J* 2.9, 9.5 Hz), 2.57–2.48 (2H, m), 2.41 (2H, t, *J* 7.4 Hz), 1.71 (2H, t, *J* 6.9 Hz), 1.63–1.14 (143H, m), 1.05 (3H, d, *J* 6.8 Hz), 0.88 (6H, t, *J* 8.8 Hz), 0.87 (9H, s), 0.67–0.62 (2H, m), 0.57 (1H, dt, *J* 3.8, 8.4 Hz), 0.17 (9H, s), 0.16 (9H, s), 0.15 (9H, s), 0.147 (9H, s), 0.14 (9H, s), 0.12 (9H, s), 0.06 (3H, s), 0.02 (3H, s), −0.31 (1H, br q, *J* 5.0 Hz); δ_C (101 MHz, $CDCl_3$): 215.2, 174.1, 94.5, 94.4, 73.4, 73.3, 72.9, 72.8, 72.73, 72.0, 71.4, 70.7, 62.4, 61.7, 56.1, 51.8, 46.3, 41.1, 33.4, 33.0, 31.9, 30.2, 29.81, 29.8, 29.71, 29.7, 29.6, 29.53, 29.5, 29.46, 29.4, 29.3, 28.7, 28.1, 27.3, 25.8, 24.8, 23.7, 22.7, 18.0, 16.4, 15.8, 14.1, 10.9, 1.04, 1.0, 0.9, 0.8, 0.2, 0.0, −4.5, −4.7; ν_{max}: 2924, 2853,1742, 1715, 1464, 1251, 1165, 1076, 1007, 898, 843 cm^{-1}.

(iii) Glucopyranoside **8g** as a thick oil (69%), $[\alpha]_D^{22}$ +29 (*c* 0.74, $CHCl_3$) {MALDI Found $(M+Na)^+$: 3033.9, $C_{192}H_{374}NaO_{17}Si_2$ requires: 3033.8}, which showed δ_H (400 MHz, $CDCl_3$+few drops of CD_3OD): 5.04 (2H, d, *J* 3.5 Hz), 4.32 (2H, br d, *J* 11.9 Hz), 4.19 (2H, br d, *J* 11.3 Hz), 3.87 (4H, br t, *J* 11.4 Hz), 3.72 (2H, t, *J* 9.3 Hz), 3.44 (2H, dd, *J* 4.2, 9.6 Hz), 3.29 (2H, t, *J* 9.8 Hz), 2.52–2.44 (4H, m), 2.37 (4H, t, *J* 7.5 Hz), 1.56–1.07 (294H, m), 1.0 (6H, d, *J* 6.9 Hz), 0.83 (12H, t, *J* 6.3 Hz), 0.81 (18H, s), 0.67–0.63 (4H, m), 0.52 (2H, dt, J 3.6, 7.6 Hz), 0.002 (6H, s), −0.02 (6H, s), −0.37 (2H, br q, J 5.2 Hz); δ_C (101 MHz, $CDCl_3$+few drops of CD_3OD): 216.0, 175.2, 93.4, 73.2, 73.0, 71.7, 70.2, 70.0, 62.9, 51.6, 46.3, 41.1, 33.6, 33.0, 31.9, 30.8, 30.2, 30.15, 29.8, 29.7, 29.62, 29.6, 29.5, 29.43, 29.4, 29.3, 29.2, 28., 27.72, 27.2, 25.8, 25.7, 23.6, 22.6, 17.9, 16.3, 15.7, 14.0, 10.8, −4.6, −5.0; ν_{max}: 3411, 2919, 2850, 1734, 1714, 1467, 1254, 1076, 1050, 991, 939, 835, 720 cm^{-1}.

(iv) Glucopyranoside **11g** as a thick oil (87%), $[\alpha]_D^{23}$ +31 (c 0.67, $CHCl_3$) {MALDI Found $(M+Na)^+$: 1698.9, $C_{102}H_{198}NaO_{14}Si$ requires: 1698.4}, which showed δ_H (400 MHz, $CDCl_3$+few drops of CD_3OD): 5.00 (2H, d, J 2.2 Hz), 4.26−4.18 (2H, m), 3.89−3.87 (1H, m), 3.86 (2H, br d, J 4.3 Hz), 3.83 (2H, br d, J 4.6 Hz), 3.61 (1H, dd, J 4.9, 11.0 Hz), 3.44−3.39 (3H, m), 3.37−3.25 (2H, m), 2.47−2.41 (2H, m), 2.34 (2H, t, J 7.2 Hz), 1.47−1.05 (151H, m), 0.95 (3H, d, J 6.9 Hz), 0.78 (6H, t, J 6.6 Hz), 0.76 (9H, s), 0.56−0.57 (2H, m), 0.48 (1H, dt, J 3.5, 8.2 Hz), −0.04 (3H, s), −0.06 (3H, s), −0.41 (1H, br q, J 4.9 Hz); δ_C (101 MHz, $CDCl_3$+few drops of CD_3OD): 216.3, 175.1, 93.5, 93.45, 73.1, 72.1, 71.5, 70.6, 70.2, 69.8, 61.8, 51.5, 46.2, 41.0, 33.4, 32.85, 31.7, 29.6, 29.5, 29.3, 29.2, 29.1, 28.5, 26.8, 25.5, 23.5, 22.5, 17.75, 15.6, 13.9, 10.7, −4.8, −5.2; ν_{max}: 3436, 2920, 2851, 1735, 1714, 1493, 1452, 1050, 990, 824 cm^{-1}.

(v) The glucopyranoside **9g** as a syrup (60%) $[\alpha]_D^{23}$ +35 (c 0.76, $CHCl_3$) {MALDI Found $[M+Na]^+$: 2803.6068, $C_{180}H_{346}O_{17}Na$ requires: 2803.6102}, which showed δ_H (400 MHz, $CDCl_3$+few drops of CD_3OD): 4.98 (2H, d, J 3.0 Hz), 4.67 (2H, br d, J 11.1 Hz), 4.23 (2H, br d, J 8.3 Hz), 3.93 (2H, br t, J 11.4 Hz), 3.72 (2H, br t, J 9.3 Hz), 3.63 (2H, m), 3.48 (2H, dd, J 3.3, 9.8 Hz), 3.19 (2H, br t, J 9.4 Hz), 2.47 (4H, q, J 6.6 Hz), 2.38 (4H, t, J 7.4 Hz), 1.63−1.50 (4H, m), 1.40−1.08 (292H, m), 1.0 (6H, d, J 7.0 Hz), 0.83 (12H, t, J 6.5 Hz), 0.60 (4H, m), 0.53 (2H, dt, J 3.8, 8.4 Hz), −0.37 (2H, br q, J 5.2 Hz); δ_C (101 MHz, $CDCl_3$+few drops of CD_3OD): 215.9, 175.5, 95.1, 72.6, 72.4, 71.5, 71.1, 69.9, 64.6, 52.2, 46.3, 41.1, 34.6, 33.0, 31.8, 30.1, 29.5, 29.42, 29.36, 28.6, 27.2, 25.7, 25.1, 23.6, 22.6, 16.2, 15.7, 14.0, 10.8; ν_{max}: 3436, 2920, 2850, 1733, 1714, 1494, 1467, 1147, 1107, 1050, 907, 824, 734 cm^{-1}.

(vi) The glucopyranoside **12g** as a syrup (40 mg, 54%) $[\alpha]_D^{23}$ +43 (c 0.73, $CHCl_3$) {MALDI Found $[M+Na]^+$: 1584.3574, $C_{96}H_{184}NaO_{14}$ requires: 1584.3578}, which showed δ_H (400 MHz, $CDCl_3$+few drops of CD_3OD): 5.08 (1H, d, J 2.9 Hz), 5.01 (1H, d, J 3.3 Hz), 4.67 (1H, br t, J 10.6 Hz), 4.23 (1H, br t, J 8.9 Hz), 3.96 (1H, br d, J 10.9 Hz), 3.91 (1H, br d, J 10.0 Hz), 3.87 (1H, d, J 4.9 Hz), 3.83−3.76 (2H, m), 3.63−3.58 (2H, m), 3.55 (1H, dd, J 3.6, 9.8 Hz), 3.47 (1H, dd, J 3.6, 10.3 Hz), 3.26 (1H, br t, J 9.4 Hz), 3.20 (1H, br t, J 9.5 Hz), 2.47 (2H, q, J 6.6 Hz), 2.38 (2H, t, J 7.4 Hz), 1.57−1.51 (4H, m), 1.33−1.08 (148H, m), 1.01 (3H, d, J 7.0 Hz), 0.84 (6H, t, J 6.6 Hz), 0.61−0.60 (2H, m), 0.52 (1H, dt, J 3.6, 7.8 Hz), −0.36 (1H, br q, J 4.8 Hz); δ_C (101 MHz, $CDCl_3$+few drops of CD_3OD): 216.3, 175.5, 94.4, 72.6, 72.4, 71.4, 71.1, 71.0, 70.9, 70.0, 64.2, 62.2, 52.3, 41.1, 34.6, 32.9, 31.8, 30.2, 29.7, 29.63, 29.62, 29.6, 29.55, 29.5, 29.4, 29.35, 29.3, 28.6, 27.2, 25.1, 23.6, 22.6, 16.2, 15.7, 14.0, 10.8; ν_{max}: 3435, 2918, 2850, 1735,1714, 1494, 1452, 1105, 1049, 992, 824 cm^{-1}.

4.9. 6-*O*-[(*R*)-2-((*R*)-1-Hydroxy-16-((1*R*,2*S*)-2-((*S*)-20-methyl-19-oxooctatriacontyl)cyclopropyl)hexadecyl)-tetracosanoate]-α-*D*-glucopyranosyl-(1→1)-6′-*O*-[(*R*)-2-((*R*)-1-hydroxy-16-((1*R*,2*S*)-2-((*S*)-20-methyl-19-oxo-octatriacontyl)cyclopropyl)hexadecyl)tetracosanoyl]-α-*D*-glucopyranoside (9h) and 6-*O*-[(*R*)-2-((*R*)-1-hydroxy)-16-((1*R*,2*S*)-2-((*S*)-20-methyl-19-oxo-octatriacontyl)cyclo-propyl)hexadecyl)tetracosanoic acid]-α-*D*-glucopyranosyl-(1→1)-α-*D*-glucopyranoside (12h)

(i) (*R*)-2-((*R*)-1-((*tert*-butyldimethylsilyl)oxy)-16-((1*R*,2*S*)-2-((19*S*,20*S*)-19-hydroxy-20-methyloctatriacontyl)cyclo-propyl)hexadecyl)tetracosanoic acid,[70] gave **5h** as a colourless oil (82%), $[\alpha]_D^{23}$ +14.5 (c 1.15, $CHCl_3$) {MALDI Found $[M+Na]^+$: 1347.4; $C_{88}H_{174}NaO_4Si$ requires: 1347.4}, which showed δ_H (400 MHz $CDCl_3$): 3.85 (1H, dt, J 6.6, 13.1 Hz), 2.52 (2H, m), 2.42 (2H, dt, J 7.2, 15.0 Hz), 1.74−1.70 (1H, m), 1.60−1.56 (2H, m), 1.25 (138H, br s), 1.05 (3H, d, J 6.9 Hz), 0.93 (9H, s), 0.89 (6H, t, J 6.8 Hz), 0.68−0.65 (2H, m), 0.61−0.51 (1H, dt, J 3.5, 8.1 Hz), 0.15 (3H, s), 0.14 (3H, s), −0.32 (1H, q, J 5.0 Hz); δ_C (101 MHz, $CDCl_3$): 215.2, 175.0, 73.7, 50.0, 35.7, 33.0, 31.9, 30.2, 30.0, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.7, 27.4, 27.3, 25.7, 25.1, 23.7, 22.6, 16.3, 15.7, 14.1, 10.9, −4.2, −4.8; υ_{max}: 3467, 2918, 2850, 1708, 1452, 1050 cm^{-1}.

(ii) Glucopyranoside **7h** as a viscous colourless oil (22%), $[\alpha]_D^{21}$ +20 (c 1.0, $CHCl_3$) {MALDI Found $[M+Na]^+$: 3411.8; $C_{206}H_{414}NaO_{17}Si_8$ requires: 3411.2}, which showed δ_H (400 MHz, $CDCl_3$): 4.85 (2H, d, J 3.0 Hz), 4.38 (2H, d, J 10.1 Hz), 4.04 (4H, dd, J 6.7, 17.6 Hz), 3.96 (4H, br m), 3.52 (2H, t, J 8.9 Hz), 3.39 (2H, dd, J 3.0, 9.3 Hz), 2.53 (2H, dt, J 6.8, 10.9 Hz), 2.41 (6H, t, J 7.1 Hz), 1.59−1.50 (2H, m), 1.26 (278H, br s), 0.90 (18H, s), 0.88 (6H, d, J 6.7 Hz), 0.80 (12H, t, J 6.9 Hz), 0.64−0.60 (4H, br m), 0.58 (2H, dt, J 3.4, 7.7 Hz), 0.16 (18H, s), 0.15 (18H, s), 0.14 (18H, s), 0.07 (6H, s), 0.06 (6H, s), −0.32 (2H, q, J 5.0 Hz); δ_C (101 MHz, $CDCl_3$): 215.1, 173.8, 94.8, 73.5, 72.8, 71.8, 71.3, 70.7, 62.3, 51.8, 50.2, 41.1, 37.1, 33.0, 31.9, 30.2, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 28.7, 28.1, 27.3, 25.9, 25.8, 25.1, 23.7, 22.6, 18.2, 18.0, 16.3, 15.7, 14.1, 10.9, 1.0, 0.9, 0.1, −4.5, −4.6; υ_{max}: 3468, 2924, 2853, 1744, 1716, 1455, 1251 cm^{-1}. The second fraction was glucopyranoside **10h** (82%), $[\alpha]_D^{21}$ +17 (c 1.0, $CHCl_3$) {MALDI Found $[M+Na]^+$: 2103.5; $C_{118}H_{242}NaO_{14}Si_7$ requires: 2103.8], which showed δ_H (400 MHz, $CDCl_3$): 4.92 (1H, d, J 2.9 Hz), 4.85 (1H, d, J 2.8 Hz), 4.36 (1H, d, J 9.9 Hz), 4.13 (1H, dt, J 7.1, 14.2 Hz), 4.0 (1H, br d, J 9.9 Hz), 3.92 (2H, m), 3.87 (2H, m), 3.70 (1H, m), 3.50 (2H, dd, J 4.0, 9.0 Hz), 3.45 (1H, dd, J 3.5, 8.5 Hz), 3.41 (1H, t, J 4.0 Hz), 3.38 (1H, d, J 3.0 Hz), 2.53 (2H, dd, J 7.0, 13.7, Hz), 2.42 (2H, dd, J 8.0, 6.9 Hz), 1.56 (1H, t, J 7.5 Hz), 1.26 (140H, s), 0.90 (9H, s), 0.89 (3H, d, J 6.7 Hz), 0.80 (6H, t, J 6.7 Hz), 0.64−0.61 (2H, br m), 0.56 (1H, dt, J 3.8, 7.7 Hz), 0.17 (9H, s), 0.16 (9H, s), 0.15 (9H, s), 0.14 (9H, s), 0.13 (9H, s), 0.12 (9H, s), 0.06 (3H, s), 0.05 (3H, s), −0.32 (1H, br q, J 5.0 Hz); δ_C (101 MHz, $CDCl_3$): 215.0, 174.0, 94.5, 94.3, 73.4, 73.3, 72.8, 72.7, 72.6, 72.1, 71.6, 71.4, 70.7, 62.4, 61.6, 51.8, 50.4, 33.4, 33.0, 31.9, 30.2, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.7, 28.1, 27.3, 26.4, 25.9, 25.8, 24.8, 23.7, 22.1, 18.0, 16.3, 15.7, 14.1, 10.9, 1.05, 1.0, 0.9, 0.8, 0.2, 0.1, −4.5, −4.7; $\upsilon_{max:}$ 3479, 2924, 2854, 1742, 1715, 1464, 1251 cm^{-1}.

(iii) Glucopyranoside **8h** as a viscous colourless oil (52%), $[\alpha]_D^{21}$ +19 (c 1.0, $CHCl_3$) {MALDI Found $[M+Na]^+$: 2978.5; $C_{188}H_{366}NaO_{17}Si_2$ requires: 2978.1}, which showed δ_H (400 MHz, $CDCl_3$+few drops of CD_3OD): 5.13 (2H, d, J 4.0 Hz), 4.50 (2H, m), 4.22 (2H, d, J 12.0 Hz), 3.98 (4H, d, J 4.0 Hz), 3.56 (4H, m), 3.32 (2H, t, J 8.0 Hz), 2.53 (2H, pent, J 12.0 Hz), 2.41 (2H, t, J 8.0 Hz), 1.57 (2H, m), 1.26 (288H, s), 1.06 (6H, d, J 8.0 Hz), 0.89 (12H, t, J 6.9 Hz), 0.86 (18H, s), 0.65−0.62 (4H, br m), 0.56 (2H, dt, J 3.9, 7.7 Hz), 0.05 (6H, s), 0.04 (6H, s), −0.32 (2H, q, J 5.0 Hz); δ_C (101 MHz, $CDCl_3$+few drops of CD_3OD): 216.0, 175.4, 94.8, 72.5, 71.4, 71.1, 70.5, 70.1, 62.9, 52.2, 50.1, 32.9, 31.7, 30.7, 30.1, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.6, 27.1, 23.5, 22.5, 16.1, 15.6, 13.9, 10.7; υ_{max}: 3467, 2923, 2853, 1734, 1716, 1452, 1050 cm^{-1}.

(iv) Glucopyranoside **11h** as a viscous colourless oil (48%), $[\alpha]_D^{21}$ +21 (c 1.0, $CHCl_3$) [Found (MALDI) $[M+Na]^+$: 1671.4; $C_{100}H_{194}NaO_{14}Si$ requires: 1671.7], which showed δ_H (400 MHz $CDCl_3$+few drops of CD_3OD): 5.08 (2H, d, J 3.7 Hz), 4.35 (1H, d, J 10.3 Hz), 4.26 (1H, d, J 11.7 Hz), 3.94 (2H, br m), 3.86 (4H, m), 3.70 (1H, m), 3.52 (2H, m), 3.37 (2H, t, J 8.6 Hz), 2.51 (2H, dd, J

6.9, 12.7 Hz), 2.40 (2H, t, *J* 7.6 Hz), 1.53 (1H, t, *J* 9.6 Hz), 1.23 (146H, s), 0.88 (9H, s), 0.83 (3H, d, *J* 6.7 Hz), 0.80 (6H, t, *J* 6.6 Hz), 0.62–0.60 (2H, br m), 0.53–0.50 (1H, dt, *J* 3.8, 7.7 Hz), 0.02 (3H, s), 0.01 (3H, s), −0.34 (1H, q, *J* 5.0 Hz); δ_C (101 MHz, $CDCl_3$+few drops of CD_3OD): 215.7, 175.1, 93.4, 93.3, 73.2, 72.9, 72.5, 72.1, 71.5, 70.6, 70.2, 70.0, 69.8, 62.7, 62.0, 51.6, 50.2, 32.9, 31.8, 30.1, 29.7, 29.6, 29.5, 29.4, 29.2, 28.6, 27.4, 25.6, 23.6, 22.6, 18.1, 17.8, 16.2, 15.6, 14.0, 10.8; υ_{max}: 3436, 2922, 2851, 1738, 1714, 1452, 1050 cm^{-1}.

(v) Glucopyranoside as a colourless thick oil **9h** (0.004 g, 17%), $[\alpha]_D^{21}$ +17 (c 1.0, $CHCl_3$) {MALDI Found $[M+Na]^+$: 2747.5380; $C_{176}H_{338}NaO_{17}$ requires: 2747.5481}, which showed δ_H (400 MHz $CDCl_3$+few drops of CD_3OD): 4.97 (2H, d, *J* 3.2 Hz), 4.63 (2H, s), 4.19 (2H, t, *J* 9.2 Hz), 3.94 (2H, t, *J* 12.4 Hz), 3.71 (2H, t, *J* 9.4 Hz), 3.61 (2H, d, *J* 6.1 Hz), 3.47 (2H, dd, *J* 2.7, 9.6 Hz), 3.19 (2H, t, *J* 9.4 Hz), 2.47 (1H, q, *J* 6.7 Hz), 2.37 (3H, t, *J* 7.3 Hz), 1.48 (2H, m), 1.18 (290, s), 1.0 (6H, d, *J* 6.9 Hz), 0.83 (12H, t, *J* 6.4 Hz), 0.64–0.61 (4H, br m), 0.48 (2H, dt, *J* 3.4, 8.0 Hz), −0.40 (2H, q, *J* 4.9 Hz), δ_C (101 MHz, $CDCl_3$+few drops of CD_3OD): 216.0, 175.4, 94.8, 72.5, 71.4, 71.1, 70.5, 70.1, 62.9, 52.2, 50.2, 32.9, 31.7, 30.7, 30.1, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 28.6, 27.1, 23.5, 22.5, 16.1, 15.6, 13.9, 10.7; υ_{max}: 3436, 2920, 2851, 1726, 1716, 1452, 1050, cm^{-1}.

(vi) Glucopyranoside **12h** as a colourless thick oil (66%), $[\alpha]_D^{21}$ +24 (c 1.0, $CHCl_3$) [Found $[M+Na]^+$: 1557.3286; $C_{94}H_{180}NaO_{14}$ requires: 1537.3299], which showed δ_H (400 MHz, $CDCl_3$+few drops of CD_3OD): 5.06 (1H, d, *J* 3.0 Hz), 5.0 (1H, d, *J* 3.4 Hz), 4.68 (1H, d, *J* 11.5 Hz), 4.22 (1H, t, *J* 9.0 Hz), 3.92 (1H, m), 3.87 (1H, m), 3.78 (3H, dt, *J* 4.5, 9.7 Hz), 3.59 (2H, m), 3.52 (1H, dd, *J* 3.4, 18.6 Hz), 3.47 (1H, dd, *J* 3.4, 11.4 Hz), 3.25 (1H, t, *J* 9.3 Hz), 3.19 (1H, t, *J* 9.8 Hz), 2.47 (2H, dd, *J* 13.8, 7.0 Hz), 2.37 (2H, t, *J* 7.6 Hz), 1.51 (1H, m), 1.27 (147H, s), 0.83 (3H, d, *J* 7.0 Hz), 0.80 (6H, t, *J* 6.5 Hz), 0.61–0.58 (2H, br m), 0.52 (1H, dt, *J* 3.7, 8 Hz), −0.37 (1H, q, *J* 5.0 Hz), δ_C (101 MHz, $CDCl_3$+few drops of CD_3OD): 215.9, 175.4, 94.2, 94.2, 72.5, 72.4, 72.3, 71.7, 71.5, 71.4, 71.3, 70.4, 70.2, 62.4, 61.9, 52.3, 50.1, 32.9, 31.8, 30.7, 30.1, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.6, 27.1, 25.0, 23.5, 22.5, 16.1, 15.6, 13.9, 10.7; υ_{max}: 3436, 2919, 2851, 1726, 1716, 1558, 1493, 1050, cm^{-1}.

4.10. 6-*O*-[(*R*)-2-((*R*)-1-Hydroxy-17-((1*S*,2*R*)-2-((2*S*,22*S*)-22-methyl-21-oxotetracontan-2-yl)cyclopropyl)hepta-decyl)hexacosanoic acid]-α-*D*-gluco-pyranosyl-(1→1)-6′-*O*-[(*R*)-2-{(*R*)-17-[(1*S*,2*R*)-2-((1*S*,21*S*)-1,21-dimethyl-20-oxononatriacontyl) cyclopropyl]-1-hydroxyheptadecyl}-hexacosanoicacid]-α-*D*-glucopyranoside (9i) and 6-*O*-[(*R*)-2-{(*R*)-17-[(1*S*,2*R*)-2-((1*S*,21*S*)-1,21-dimethyl-20-oxononatriacontyl)cyclopropyl]-1-hydroxyheptadecyl}-hexacosanoic acid]-α-*D*-glucopyranosyl-(1→1)-α-*D*-glucopyranoside (12i)

(i) (*R*)-2-{(*R*)-1-(*tert*-Butyldimethylsilanyloxy)-17-[(1*S*,2*R*)-2-((1*S*,20*S*,21*S*)-20-hydroxy-1,21-dimethylnonatriacontyl)-cyclopropyl]heptadecyl}hexacosanoic acid,[69] gave **5i** as a white semi-solid (88%) {Found $[M+Na]^+$: 1416.6, $C_{93}H_{184}NaO_4Si$ requires: 1416.4}, $[\alpha]_D^{21}$ +6.3 (c 0.71, $CHCl_3$). This showed δ_H (500 MHz, $CDCl_3$): 3.82 (1H, ddd, *J* 2.6, 5.4, 7.9 Hz), 2.55–2.49 (1H, m), 2.41(1H, td, *J* 2.2, 7.3 Hz), 1.55–1.49 (28H, v br m), 1.26 (153H, br s), 1.06 (3H, d, *J* 6.9 Hz), 0.94 (9H, s), 0.90 (3H, d, *J* 6.2 Hz), 0.89 (6H, t, *J* 6.9 Hz), 0.48–0.42 (1H, m), 0.21–0.09 (9H, including 2×s for the dimethyl of the silyl group at 0.16 and 0.13, 3H of the cyclopropane); δ_C (126 MHz, $CDCl_3$): 215.4, 175.9, 73.6, 50.4, 46.3, 38.1, 31.92, 29.73, 29.7, 29.66, 29.54, 29.5, 29.4, 29.36, 25.7, 22.6, 19.7, 18.6, 16.3, 14.1, 10.5, −4.2, −4.9; ν_{max}: 2943, 2857, 1689, 1468, 1372, 1209 cm^{-1}.

(ii) Glucopyranoside **7i** as a viscous colourless oil (45%), $[\alpha]_D^{21}$ +30 (c 1.0, $CHCl_3$) {Found $[M+NH_4]^+$: 3548.1194; $[C_{216}H_{434}O_{17}Si_8NH_4]^+$ requires: 3548.1142}, which showed δ_H (500 MHz $CDCl_3$): 4.85 (2H, d, *J* 2.9 Hz), 4.38 (2H, d, *J* 10.4 Hz), 4.04 (2H, d, *J* 3.2, Hz), 4.01 (2H, m), 3.92 (2H, m), 3.90 (2H, t, *J* 7.1 Hz), 3.54 (2H, t, *J* 8.9 Hz), 3.38 (2H, dd, *J* 2.8, 9.1 Hz), 2.51 (2H, q, *J* 6.8 Hz), 2.41 (6H, td, *J* 2.2, 7.3 Hz), 1.64 (4H, s), 1.57 (2H, t, *J* 7.0 Hz), 1.26 (286H, s), 1.06 (6H, d, *J* 7.0 Hz), 0.9 (6H, d, *J* 6.7 Hz), 0.89 (12H, t, *J* 7 Hz), 0.88 (18H, s), 0.46 (4H, td, *J* 6.9, 13.9 Hz), 0.48–0.43 (2H, m), 0.17–0.13 (60H, including 3×s at 0.16, 0.15 and 0.14 for trimethyl silyl groups), 0.06 (6H, s), 0.05 (6H, s); δ_C (126 MHz, $CDCl_3$): 215.1, 173.8, 94.8, 73.5, 73.4, 72.8, 71.8, 70.7, 62.5, 51.8, 51.2, 38.0, 37.4, 34.5, 33.0, 31.9, 30.0, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.1, 27.3, 27.8, 26.3, 25.4, 25.3, 25.7, 23.2, 22.9, 19.6, 18.1, 18.2, 16.7, 14.1, 10.4, 1.0, 0.9, 0.1, −4.5, −4.6; υ_{max}: 2923, 1716, 1464, 1251 cm^{-1}. The second fraction was glucopyranoside **10i** as a viscous colourless oil (53%) $[\alpha]_D^{21}$ +44 (c 0.9, $CHCl_3$) {MALDI Found $[M+Na]^+$: 2173.6; $C_{123}H_{252}NaO_{14}Si_7$ requires: 2173.7}, which showed δ_H (500 MHz, $CDCl_3$): 4.91 (1H, d, *J* 3.2 Hz), 4.84 (1H, d, *J* 2.9 Hz), 4.36 (1H, dd, *J* 2.2, 11.9 Hz), 4.08 (1H, dd, *J* 4.1, 11.9 Hz), 4.00 (1H, dt, *J* 2.3, 9.5 Hz), 3.95 (1H, m), 3.91 (2H, td, *J* 6.7, 8.9 Hz), 3.84 (1H, dt, *J* 3.2, 9.3 Hz), 3.73–3.70 (2H, m), 3.48 (2H, td, *J* 4.8, 13.9 Hz), 3.41 (2H, ddd, *J* 3.5, 9.3, 11.7 Hz), 2.55 (1H, q, *J* 4.7 Hz), 2.41 (3H, td, *J* 2.2, 7.3 Hz), 1.63 (2H, s), 1.57–1.54 (1H, m), 1.26 (144H, s), 1.06 (3H, d, *J* 7.0 Hz), 0.90 (6H, t, *J* 6.6 Hz), 0.88 (9H, s), 0.87 (3H, d, *J* 6.8 Hz), 0.68 (1H, dt, *J* 6.8, 13.8 Hz), 0.45–0.43 (1H, m), 0.21–0.19 (3H, m) 0.17 (9H, s), 0.16 (9H, s), 0.15 (9H, s), 0.14 (9H, s), 0.13 (9H, s), 0.12 (9H, s), 0.05 (3H, s), 0.04 (3H, s); δ_C (126 MHz, $CDCl_3$): 215.1, 174.0, 94.5, 94.3, 73.4, 73.3, 73.1, 72.9, 72.8, 72.7, 71.9, 71.4, 70.7, 62.4, 61.6, 51.8, 51.2, 38.1, 37.4, 34.4, 33.0, 31.9, 30.0, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.4, 28.3, 28.2, 27.3, 27.2, 26.1, 25.8, 23.7, 22.6, 19.6, 18.6, 18.0, 16.3, 14.1, 10.4, 1.1, 1.0, 0.9, 0.8, 0.1, 0.04, −4.4, −4.6; υ_{max}: 3448, 2924, 2853, 1715, 1464, 1251 cm^{-1}.

(iii) Glucopyranoside **8i** as a viscous colourless oil, (75%), $[\alpha]_D^{21}$ +15 (c 1.1, $CHCl_3$) {MALDI Found $[M+NH_4]^+$: 3116.9; $[C_{198}H_{386}O_{17}Si_2NH_4]^+$ requires: 3116.9}, which showed δ_H (500 MHz $CDCl_3$+few drops of CD_3OD): 5.04 (2H, d, *J* 2.9 Hz), 4.31 (2H, d, *J* 4.5 Hz), 4.21 (2H, d, *J* 11.1 Hz), 3.94 (3H, d, *J* 8.5 Hz), 3.87 (3H, dd, *J* 4.8, 10.1 Hz), 3.50 (2H, d, *J* 8.5 Hz), 3.30 (2H, t, *J* 9.1 Hz), 2.52–0.50 (2H, m), 2.37 (6H, t, *J* 6.6 Hz), 1.50 (2H, br s), 1.4–1.15 (296H, br s), 1.03 (6H, d, *J* 6.6 Hz), 0.88 (12H, t, *J* 6.7 Hz), 0.87 (6H, d *J* 6.5 Hz), 0.85 (18H, s), 0.63–0.60 (2H, m), 0.42–0.40 (2H, m), 0.09–0.07 (6H, m), 0.06 (6H, s), 0.05 (6H, s); δ_C (125 MHz, $CDCl_3$): 215.8, 175.4, 93.3, 73.0, 72.5, 71.8, 70.8, 70.5, 70.1, 51.2, 50.2, 38.8, 37.9, 37.6, 37.3, 34.4, 32.9, 31.8, 30.7, 299, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.9, 28.8, 27.7, 27.2, 27.1, 26.0, 25.7, 25.6, 24.2, 23.6, 22.5, 19.5, 18.5, 17.8, 16.2, 13.9, 10.3, −4.5, −4.9; υ_{max}: 3401, 2922, 1715, 1464, 1254 cm^{-1}.

(iv) Glucopyranoside **11i** as a viscous colourless oil (44%), $[\alpha]_D^{21}$ +13 (c 1.0, $CHCl_3$) [MALDI Found $[M+Na]^+$: 1740.4929; $C_{105}H_{204}NaO_{14}Si$ requires: 1740.4913], which showed δ_H (500 MHz, $CDCl_3$+few drops of CD_3OD): 5.09 (2H, s), 4.34–4.32 (1H, m), 4.26 (1H, d, *J* 9.2 Hz), 3.92–3.85 (4H, br m), 3.79 (2H, br, d, *J* 10.4 Hz), 3.69 (1H, br s), 3.51 (2H, br s), 3.36 (3H, br m), 2.51 (1H, m), 2.48 (1H, q, *J* 6.5 Hz), 2.39 (2H, t, *J* 6.8 Hz), 1.52 (1H, br s), 1.26 (151H, s), 1.03 (6H, d, *J* 7.0 Hz), 0.87 (6H, t, *J* 7.1 Hz), 0.85 (9H, s), 0.63–0.60 (1H, m), 0.41–0.39 (1H, m), 0.09–0.07 (3H, m), 0.03 (3H, s), 0.02 (3H, s); δ_C (125 MHz, $CDCl_3$+few drops of CD_3OD): 215.9, 175.0, 93.7, 93.3, 73.1, 72.9, 72.4, 72.2, 71.5, 70.9, 70.6, 70.5, 70.3, 62.8, 62.1, 51.9, 51.2, 37.9, 37.3, 34.3, 32.9, 31.8, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 27.6, 27.2, 27.1, 26.0, 25.5, 24.0, 23.1, 22.6, 19.1, 18.9, 17.5, 16.9, 13.5, 10.4, −4.6, −5.0; υ_{max}: 3401, 2924, 2853, 1713, 1464, 1251 cm^{-1}.

(v) The glucopyranoside **9i** as a viscous colourless oil (24%), $[\alpha]_D^{21}$ +24 (c 0.4, $CHCl_3$) [Found $[M+Na]^+$: 2887.6994; $C_{186}H_{358}NaO_{17}$ requires: 2887.7041], which showed δ_H (500 MHz, $CDCl_3$+few drops of CD_3OD): 4.99 (1H, s), 4.10 (1H, d, *J* 6.2 Hz), 3.63−3.60 (1H, m), 3.36−3.33 (4H, m), 3.22 (1H, s), 2.41−2.39 (2H, m), 2.05−2.01 (6H, m), 1.58 (2H, br s), 1.23 (306H, s), 1.03−1.01 (6H, d, *J* 6.8 Hz), 0.88 (12H, t, *J* 7.2 Hz), 0.87 (6H, d *J* 6.7 Hz), 0.66−0.64 (2H, m), 0.42−0.40 (2H, m), 0.05−0.03 (6H, m); δ_C (126 MHz, $CDCl_3$): 216.8, 175.7, 93.7, 72.7, 71.7, 71.3, 70.7, 70.5, 60.6, 51.2, 50.2, 38.2, 37.5, 37.3, 36.2, 34.6, 33.7, 33.0, 32.5, 31.0, 29.6, 28.5, 26.4, 25.4, 23.9, 23.1, 21.3, 18.9, 16.3, 14.5, 12.6, 10.4; υ_{max}: 3429, 2920, 2851, 1720, 1476, 1226 cm^{-1}.

(vi) The glucopyranoside **12i** as a viscous colourless oil (52%), $[\alpha]_D^{21}$ +20 (c 1.0, $CHCl_3$) {Found (MALDI) $[M+NH_4]^+$: 1621.4537; $[C_{99}H_{190}O_{14}NH_4]^+$ requires: 1621.4494}, which showed δ_H (500 MHz $CDCl_3$+few drops of CD_3OD): 5.03 (1H, d, *J* 3.5 Hz), 4.98 (1H, d, *J* 3.5 Hz), 4.60 (1H, d, *J* 10.8 Hz), 4.15 (1H, t, *J* 7.9 Hz), 3.97 (1H, dd, *J* 7.6, 12 Hz), 3.83−3.80 (1H, m), 3.78−3.75 (1H, m), 3.72−3.70 (2H, m), 3.58 (2H, m), 3.49 (1H, dd, *J* 3.5, 9.8 Hz), 3.24 (2H, t, *J* 9.4 Hz), 3.18 (1H, t, *J* 9.6 Hz), 2.46 (1H, q, *J* 7.0 Hz), 2.36 (3H, including, t, *J* 7.1 Hz), 1.46−1.44 (1H, m), 1.26 (153H, s), 0.98 (6H, d, *J* 6.6 Hz), 0.83 (3H, t, *J* 7.2 Hz), 0.81 (3H, t, *J* 6.7 Hz), 0.59−0.57 (1H, m), 0.38−0.36 (1H, m), 0.06−0.04 (3H, m); δ_C (126 MHz, $CDCl_3$): 215.5, 175.4, 94.9, 94.6, 73.0, 72.7, 72.4, 72.2, 72.1, 71.7, 71.4, 70.9, 70.4, 62.0, 61.8, 52.4, 52.0, 38.0, 37.2, 34.6, 25.9, 25.1, 23.5, 22.5, 19.5, 18.4, 16.1, 10.3; υ_{max}: 3392, 2918, 2850, 1715, 1467, 1251 cm^{-1}.

4.11. 6-*O*-[(*R*)-2-((*R*)-1-Hydroxy-16-((1*S*,2*R*)-2-((19*S*,20*S*)-19-hydroxy-20-methyloctatriacontyl)cyclopropyl)hexa-decyl)tetracosanoy]-α-*D*-glucopyranosyl-(1→1)-6′-*O*-[(*R*)-2-((*R*)-1-hydroxy-16-((1*S*,2*R*)-2-((19*S*,20*S*)-19-hydroxy-20-methyloctatriacontyl)cyclopropyl)hexa-decyl)tetracosa-noate]-α-*D*-glucopyranoside (9j) and 6-*O*-[(*R*)-2-((*R*)-1-hydroxy-16-((1*S*,2*R*)-2-((19*S*,20*S*)-19-hydroxy-20-methyloctatriacontyl)cyclopropyl)hexa-decyl)tetracosanoyl]-α-*D*-glucopyranosyl-(1→1-α-*D*-glucopyranoside (12j)

(i) (*R*)-2-((*R*)-1-((*tert*-Butyldimethylsilyl)oxy)-16-((1*R*,2*S*)-2-((19*S*,20*S*)-19-hydroxy-20-methyloctatriacontyl)cyclo-propyl) hexadecyl)tetracosanoic acid[69] (0.21 g, 0.16 mmol) gave acid **5j** as a colourless oil (0.18 g, 81%), $[\alpha]_D^{23}$ +18.5 (c 1.07, $CHCl_3$) [MALDI Found $[M+Na]^+$: 1463.9; $C_{94}H_{190}NaO_4Si_2$ requires: 1463.6], which showed δ_H (400 MHz $CDCl_3$): 3.82 (1H, m), 3.50 (1H, br m), 2.56−2.50 (1H, m), 1.72−168 (1H, m), 1.66−1.51 (2H, m), 1.45−1.26 (141H, br m, including br s, at 1.26), 0.93 (18H, s), 0.89 (6H, t, *J* 6.9 Hz), 0.84 (3H, d, *J* 5.9 Hz), 0.65−0.63 (2H, br m), 0.57 (1H, dt, *J* 4.1, 8.2 Hz), 0.15 (3H, s), 0.14 (3H, s), 0.03 (3H, s), 0.02 (3H, s), −0.30 (1H, q, *J* 5.0 Hz); δ_C (101 MHz, $CDCl_3$): 178.2, 75.8, 73.5, 68.1, 60.3, 50.8, 38.8, 37.7, 34.7, 33.5, 32.5, 31.9, 30.3, 30.2, 30.0, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 28.9, 28.7, 27.7, 27.5, 25.9, 25.8, 25.7, 25.6, 24.4, 23.7, 22.9, 22.7, 21.0, 18.1, 17.9, 15.7, 14.4, 14.3, 14.1, 10.9, −4.2, −4.3, −4.4, −4.9; υ_{max}: 3649, 2924, 2854, 1709, 1455, 1050 cm^{-1}.

(ii) Glucopyranoside **7j** as a viscous colourless oil (58%), $[\alpha]_D^{21}$ +20.1 (c 1.03, $CHCl_3$) [MALDI Found $[M+Na]^+$: 3643.4; $C_{218}H_{446}NaO_{17}Si_{10}$ requires: 3643.7], which showed δ_H (400 MHz $CDCl_3$): 4.86 (2H, d, *J* 3.1 Hz), 4.38 (2H, br d, *J* 10.2 Hz), 4.03 (2H, dd, *J* 2.8, 10.8 Hz), 3.99−3.93 (4H, m), 3.90 (2H, d, *J* 8.9 Hz), 3.52 (4H, br dd, *J* 5.7, 12.4 Hz), 3.39 (2H, dd, *J* 2.8, 9.3 Hz), 2.60−2.51 (2H, m), 1.48−1.44 (2H, m), 1.35−1.27 (4H, m), 1.52−1.27 (284H, br m, including br s, at 1.27), 0.90 (18H, s), 0.89 (18H, s), 0.86 (12H, t, *J* 6.5 Hz), 0.81 (6H, d, *J* 6.7 Hz), 0.70−0.62 (4H, m), 0.57 (2H, dt, *J* 4.2, 8 Hz), 0.16 (18H, s), 0.15 (18H, s), 0.14 (18H, s), 0.06 (6H, s), 0.04 (6H, s), 0.03 (6H, s), 0.01 (6H, s), −0.32 (2H, q, *J* 5.0 Hz); δ_C (101 MHz, $CDCl_3$): 173.8, 94.8, 75.8, 73.5, 73.4, 72.8, 71.8, 70.7, 62.3, 51.8, 37.7, 33.5, 32.5, 31.9, 30.2, 30.0, 29.9, 29.8, 29.7, 29.6, 29.5, 29.3, 28.7, 27.7, 25.9, 25.8, 22.7, 15.7, 14.4, 14.1, 10.9, 1.1, 0.9, 0.1, −4.1, −4.4, −4.5; υ_{max}: 3468, 2925, 2854, 1746, 1452, 1251 cm^{-1}. The second fraction was glucopyranoside **10j** (48%), $[\alpha]_D^{21}$ +20 (c 1.0, $CHCl_3$) [MALDI Found $[M+Na]^+$: 2221.5; $C_{124}H_{258}NaO_{14}Si_8$ requires: 2221.1], which showed δ_H (400 MHz, $CDCl_3$): 4.92 (1H, d, *J* 3.0 Hz), 4.85 (1H, d, *J* 2.8 Hz), 4.38−4.33 (1H, m), 4.09 (1H, dd, *J* 4.0, 8.9 Hz), 4.01 (2H, d, *J* 7.9 Hz), 3.95 (1H, d, *J* 6.1 Hz), 3.94−3.88 (2H, m), 3.85 (1H, d, *J* 6.5 Hz), 3.75−3.65 (2H, m), 3.56−3.44 (4H, m), 3.43−3.36 (1H, m), 2.55−2.50 (1H, m), 1.50 (1H, q, *J* 6.0 Hz), 1.44−1.38 (2H, m), 1.36−1.20 (131H, br m, including br s, at 1.27), 0.97 (9H, s), 0.95 (9H, s), 0.88 (6H, t, *J* 6.5 Hz), 0.81 (3H, d, *J* 6.7 Hz), 0.65−0.62 (2H, br m), 0.57 (1H, dt, *J* 3.9, 7.7 Hz), 0.18 (9H, s), 0.17 (9H, s), 0.16 (9H, s), 0.15 (9H, s), 0.14 (9H, s), 0.12 (9H, s), 0.07 (6H, s), 0.04 (6H, s), −0.32 (1H, q, *J* 5.0 Hz); δ_C (101 MHz, $CDCl_3$): 174.0, 94.5, 94.3, 73.4, 73.3, 72.9, 72.8, 72.7, 71.9, 71.6, 71.4, 70.7, 70.0, 62.4, 61.7, 51.3, 37.2, 33.3, 33.4, 32.4, 31.9, 30.2, 30.0, 29.8, 29.7, 29.5, 29.3, 28.7, 28.1, 27.7, 26.3, 25.9, 25.8, 25.7, 24.8, 22.6, 18.0, 15.7, 14.4, 14.1, 10.9, 1.1, 1.0, 0.9, 0.8, 0.1, 0.04, −4.1, −4.44, −4.49, −4.6; υ_{max}: 3479, 2925, 2855, 1743, 1455, 1251 cm^{-1}.

(ii) Glucopyranoside **8j** as a viscous colourless oil (46%), $[\alpha]_D^{21}$ +17 (c 1.0, $CHCl_3$) [MALDI Found $[M+Na]^+$: 3210.9; $C_{200}H_{398}NaO_{17}Si_4$ requires: 3210.6], which showed δ_H (400 MHz, $CDCl_3$+few drops of CD_3OD): 5.05 (2H, d, *J* 3.0 Hz), 4.26 (2H, t, *J* 12.1 Hz), 3.89 (4H, br d, *J* 4.8 Hz), 3.48−3.45 (4H, m), 3.43 (4H, s), 3.27 (2H, t, *J* 4.3 Hz), 2.25 (2H, dt, *J* 5.5, 10.7 Hz), 1.57−1.53 (2H, m), 1.43−1.40 (4H, m), 1.35−1.29 (286H, br m, including br s, at 1.23), 0.83 (18H, s), 0.81 (18H, s), 0.76 (12H, t, *J* 6.9 Hz), 0.76 (6H, d, *J* 6.6 Hz), 0.65 (4H, br m), 0.52 (2H, dt, *J* 3.9, 7.7 Hz), 0.04 (6H, s), 0.03 (6H, s), 0.02 (6H, s), 0.01 (6H, s), −0.34 (2H, q, *J* 4.9 Hz); δ_C (101 MHz, $CDCl_3$): 175.0, 93.0, 73.0, 72.8, 71.8, 71.6, 70.2, 69.9, 63.0, 51.5, 37.5, 33.3, 33.0, 32.2, 31.7, 30.9, 30.0, 29.8, 29.7, 29.6, 29.5, 29.1, 28.5, 27.5, 26.8, 25.7, 25.6, 25.5, 25.4, 24.1, 23.1, 22.5, 17.7, 15.5, 14.2, 13.8, 10.7, −4.4, −4.6, −4.7, −5.1; υ_{max}: 3436, 2924, 2853, 1734, 1452, 1250 cm^{-1}.

(iii) Glucopyranoside **9j** as a colourless thick oil (0.017 g, 56%), $[\alpha]_D^{21}$ +28 (c 1.0, $CHCl_3$) [MALDI Found $[M+Na]^+$: 2751.5912; $C_{176}H_{342}NaO_{17}$ requires: 2751.5789], which showed δ_H (400 MHz $CDCl_3$+few drops of CD_3OD): 4.98 (2H, d, *J* 3.2 Hz), 4.60 (2H, d, *J* 10.8 Hz), 4.16 (2H, t, *J* 8.9 Hz), 3.97 (2H, t, *J* 11.6 Hz), 3.70 (2H, t, *J* 9.5 Hz), 3.66−3.61 (2H, m), 3.50−3.36 (4H, m), 3.20 (2H, t, *J* 9.5 Hz), 2.41−2.30 (2H, m), 1.52 (2H, m), 1.38−1.35 (4H, m), 1.20 (290H, br s), 1.10 (6H, d, *J* 6.4 Hz), 0.86 (12H, t, *J* 6.4 Hz), 0.59−0.56 (4H, m), 0.51 (2H, dt, *J* 3.9, 8.0 Hz), −0.39 (2H, q, *J* 4.8 Hz); δ_C (101 MHz, $CDCl_3$): 175.4, 95.0, 72.5, 72.3, 71.3, 71.2, 71.0, 70.7, 64.4, 52.1, 37.9, 34.6, 34.1, 33.1, 31.7, 30.0, 29.8, 29.5, 29.3, 29.2, 28.5, 27.2, 27.1, 26.0, 25.0, 22.5; υ_{max}: 3467, 2920, 2850, 1733, 1451, 1210 cm^{-1}.

4.12. 6-*O*-[(*R*)-2-((*R*)-1-Hydroxy-18-((1*S*,2*R*)-2-((17*S*,18*S*)-17-methoxy-18-methylhexatriacontyl)cyclopropyl)octa-decyl) hexacosanoate]-α-*D*-glucopyranosyl-(1→1)-6′-*O*-[(*R*)-2-{(*R*)-1-hydroxy-16-[(1*S*,2R)-2-((*S*)-20-methyl-19-oxo-20-octatriacontyl)cyclopropyl]hexadecyl}hexa-cosanoate]-α-*D*-glucopyranoside (13)

(i) 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI) (0.05 g, 0.26 mmol) and 4-dimethylamino-pyridine (0.02 g, 0.16 mmol) were added to a stirred solution of **5g** (0.1 g, 0.07 mmol), **10c** (0.15 g, 0.07 mmol) and powdered molecular sieves 4 Å in dry dichloromethane (3 ml) at room temperature under nitrogen. The mixture was stirred for 6 days at rt, then diluted with dichloromethane (5 ml) and mixed with silica (1 g), then the solvent was evaporated under reduced pressure; chromatography on silica eluting with petrol/ethyl acetate (20:1 then 10:1) gave 2,3,4-*O*-trimethylsilyl-6-*O*-[(*R*)-2-((*R*)-1-((*tert*-butyldimethylsilyl)-oxy)-18-((1*S*,2*R*)-2-((17*S*,18*S*)-17-methoxy-18-methylhexa-triacontyl)cyclopropyl)octadecyl)hexacosanoate]-*α*-*D*-gluco-pyranosyl-(1→1)-2,3,4-*O*-trimethylsilyl-6′-*O*-[(*R*)-2-{(*R*)-1-((*tert*-butyldimethylsilyl)oxy)-16-[(1*S*,2*R*)-2-((*S*)-20-methyl-19-oxo-20-octatriacontyl)cyclopropyl]hexadecyl}hexacosan-oate]-*α*-*D*-glucopyranoside (0.07 g, 40%) as a colourless thick oil, $[\alpha]_D^{21}$ +19 (c 0.5, $CHCl_3$) {MALDI Found $[M+Na]^+$: 3480.9; $C_{211}H_{426}NaO_{17}Si_8$ requires: 3480.1}, which showed δ_H (400 MHz, $CDCl_3$): 4.81 (2H, d, *J* 3 Hz), 4.33 (2H, br d, *J* 10.0 Hz), 4.00–3.94 (4H, m), 3.92–3.89 (2H, m), 3.87 (2H, t, *J* 8.8 Hz), 3.49 (2H, t, *J* 9 Hz), 3.35 (2H, dd, *J* 3.0, 9.3 Hz), 3.3 (3H, m), 2.93 (1H, br pent, *J* 4.2 Hz), 2.53–2.49 (2H, m), 2.46 (1H, t, *J* 6.8 Hz), 2.39 (2H, dt, *J* 1.2, 7.2 Hz), 1.34–1.13 (288H, m), 1.01 (3H, d, *J* 6.9 Hz), 0.86 (12H, t, *J* 7.0 Hz), 0.84 (18H, s), 0.8 (6H, d, *J* 7.0 Hz), 0.62–0.6 (4H, br m), 0.54 (2H, dt, *J* 3.8, 7.5 Hz), 0.12 (18H, s), 0.10 (18H, s), 0.09 (18H, s), −0.02 (12H, s), −0.35 (2H, br q, *J* 5.1 Hz); δ_C (101 MHz, $CDCl_3$): 215.1, 173.8, 94.8, 85.4, 73.5, 73.4, 72.8, 71.8, 70.7, 62.3, 57.7, 51.8, 46.3, 41.1, 35.3, 33.4, 33.0, 32.3, 31.9, 30.4, 30.2, 30.0, 29.9, 29.8, 29.77, 29.7, 29.66, 29.6, 29.5, 29.4, 29.34, 29.3, 28.7, 28.1, 27.5, 27.3, 26.2, 26.1, 25.9, 25.8, 25.1, 23.7, 22.6, 18.0, 16.3, 15.7, 14.8, 14.1, 10.9, 1.0, 0.9, 0.1, −4.5, −4.6; ν_{max}: 2924, 2853, 1744, 1464, 1251, 1099, 1047, 872, 842 cm^{-1}.

(ii) Tetrabutylammonium fluoride (0.10 ml, 0.38 mmol, 1 M) was added to a stirred solution of the above ester (0.065 g, 0.018 mmol) in dry THF (3 ml) at 5 °C under nitrogen. The mixture was allowed to reach rt and then it was stirred for 15 min, then worked up and purified as before to give 6-*O*-[(*R*)-2-((*R*)-1-((*tert*-butyldimethylsilyl)oxy)-18-((1*S*,2*R*)-2-((17*S*,18*S*)-17-methoxy-18-methylhexatriacontyl)cyclopropyl)octa-decyl)hexacosanoate]-*α*-*D*-glucopyranosyl-(1 → 1)-6′-*O*-[(*R*)-2-{(*R*)-1-((*tert*-butyldimethylsilyl)oxy)-16-[(1*S*,2*R*)-2-((*S*)-20-methyl-19-oxo-20-octatriacontyl)cyclopropyl]hexa-decyl}hexacosanoate]-*α*-*D*-glucopyranoside (0.04 g, 72%) as a colourless thick oil, $[\alpha]_D^{21}$ +11 (c 0.5, $CHCl_3$) {MALDI Found $[M+Na]^+$: 3053.7; $C_{193}H_{384}NaO_{17}Si_2$ requires: 3053.9}, which showed δ_H (400 MHz, $CDCl_3$+few drops of CD_3OD): 5.04 (2H, d, *J* 3.6 Hz), 4.34 (2H, br dd, *J* 4.4, 12.2 Hz), 4.21 (2H, br dd, *J* 4.6, 12.2 Hz), 3.91–3.84 (4H, m), 3.75 (2H, br t, *J* 9.3 Hz), 3.46 (2H, dd, *J* 3.6, 9.7 Hz), 3.35–3.27 (5H, m, including s for the methoxy groups at δ 3.3), 2.94 (1H, br pent, *J* 4.4 Hz), 2.54–2.49 (2H, m), 2.47 (1H, br t, *J* 6.8 Hz), 2.38 (2H, br t, *J* 7.2 Hz), 1.56–1.05 (300H, m), 1.00 (3H, d, *J* 6.9 Hz), 0.85 (12H, t, *J* 6.9 Hz), 0.81 (18H, s), 0.79 (3H, d, *J* 6.9 Hz), 0.76 (3H, d, *J* 6.5 Hz), 0.61–0.59 (4H, m), 0.53 (2H, dt, *J* 3.7, 7.5 Hz), 0.01 (6H, s), 0.0 (6H, s), −0.36 (2H, br q, *J* 5.0 Hz); δ_C (101 MHz, $CDCl_3$+few drops of CD_3OD): 216.0, 175.2, 93.4, 85.5, 73.1, 73.0, 71.6, 70.1, 69.8, 62.8, 57.5, 51.5, 46.2, 41.0, 35.2, 33.5, 32.9, 32.2, 31.8, 30.3, 30.1, 29.8, 29.6, 29.5, 29.4, 29.34, 29.3, 29.1, 28.6, 27.6, 27.4, 27.2, 26.9, 25.9, 25.7, 25.6, 24.1, 23.5, 22.5, 17.8, 16.2, 15.6, 14.6, 13.9, 10.7, −4.6, −5.0; ν_{max}: 3523, 2918, 2850, 1701, 1467, 1215, 1093, 1050, 908, 874, 824, 759, 736, 669 cm^{-1}.

(iii) A dry polyethylene vial equipped with a rubber septum charged with the above ester (0.04 g, 0.01 mmol) and pyridine (0.1 ml) in dry THF (3 ml) was stirred at rt under argon. Hydrogen fluoride-pyridine complex (0.3 ml) was added; the mixture was stirred at 43 °C for 17 h, then worked up and purified as before to give the title compound **13** (0.012 g, 40%) as a syrup, $[\alpha]_D^{21}$ +30 (c 0.5, $CHCl_3$) {Found $[M+Na]^+$: 2821.6676; $C_{181}H_{353}NaO_{17}$ requires: 2821.6572}, which showed δ_H (400 MHz, $CDCl_3$+few drops of CD_3OD): 5.02 (2H, d, *J* 3.7 Hz), 4.71 (2H, br d, *J* 10.9 Hz), 4.27 (2H, br t, *J* 12.1 Hz), 3.76 (2H, br q, *J* 8.3 Hz), 3.64 (2H, t, *J* 8.0 Hz), 3.49–3.47 (2H, br m), 3.39 (2H, dd, *J* 2.1, 13.6 Hz), 3.35 (3H, s), 3.18 (2H, m), 2.94 (1H, br pent, *J* 3.4 Hz), 2.54–2.49 (2H, m), 2.47–2.40 (1H, m), 2.38 (2H, br t, *J* 7.2 Hz), 1.54–1.06 (299H, m), 1.0 (3H, d, *J* 6.9 Hz), 0.85–0.80 (18H, m), 0.61–0.59 (4H, m), 0.53 (2H, dt, *J* 3.9, 8.4 Hz), −0.36 (2H, br q, *J* 5.0 Hz); δ_C (101 MHz, $CDCl_3$+few drops of CD_3OD): 216.3, 175.2, 94.5, 85.5, 73.0, 72.5, 72.4, 71.1, 70.9, 69.7, 63.9, 57.4, 52.3, 51.5, 46.1, 40.9, 35.1, 34.5, 32.8, 32.1, 31.7, 30.2, 30.0, 29.7, 29.6, 29.5, 29.4, 29.3, 29.27, 29.24, 29.2, 29.1, 29.0, 28.5, 27.2, 27.1, 27.0, 25.8, 25.5, 25.0, 23.4, 22.4, 16.0, 15.5, 14.5, 13.7, 10.6; ν_{max}: 3369, 2920, 2851, 1727, 1467, 1101, 720 cm^{-1}.

4.13. 6-*O*-[(*R*)-2-((*R*)-1-Hydroxy-12-{(1*S*,2*R*)-2-[14-((1*S*, 2*R*)-2-eicosylcyclopropyl)tetradecyl] cyclopropyl}-dodecyl)-hexacosanoate]-α-*D*-glucopyranosyl-(1→1)-6′-*O*-[(*R*)-2-{(*R*)-1-hydroxy-16-[(1*S*,2*R*)-2-(20-methyl-19-oxo-20-octatriacontyl) cyclopropyl] hexadecyl}hexa-cosanoate]-α-*D*-glucopyranoside (15)

(i) 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (0.03 g, 0.15 mmol) and 4-dimethylaminopyridine (0.02 g, 0.16 mmol) were added to a stirred solution of **10a** (0.1 g, 0.05 mmol), **14**[69] (0.20 g, 0.14 mmol) and powdered molecular sieves 4 Å in dry dichloromethane (4 ml) at room temperature under nitrogen. The mixture was stirred for 5 days at room temperature then worked up and purified as before to give 2,3,4-*O*-trimethylsilyl-6-*O*-[(*R*)-2-((*R*)-1-((*tert*-butyldimethylsilyl)oxy)-12-{(1*S*,2*R*)-2-[14-((1*S*,2*R*)-2-eicosylcyclopropyl)tetradecyl]cyclopropyl}dodecyl)hexa-cosanoate]-*α*-*D*-glucopyranosyl-(1→1)-2,3,4-*O*-trimethyl-silyl-6′-*O*-[(*R*)-2-{(*R*)-1-((*tert*-butyldimethylsilyl)oxy)-16-[(1*S*,2*R*)-2-(20-methyl-19-oxo-20-octatriacontyl)cyclo-propyl]hexadecyl} hexacosanoate]-*α*-*D*-glucopyranoside (0.11 g, 68%) as a colourless oil, $[\alpha]_D^{21}$ +18 (c 0.5, $CHCl_3$) {MALDI Found $[M+Na]^+$: 3363.8; $C_{204}H_{410}NaO_{16}Si_8$ requires: 3363.9}, which showed δ_H (400 MHz, $CDCl_3$): 4.85 (2H, d, *J* 3.0 Hz), 4.37 (2H, br d, *J* 10.1 Hz), 4.04–3.99 (4H, m), 3.96–3.93 (2H, m), 3.91(2H, t, *J* 8.9 Hz), 3.53 (2H, t, *J* 8.9 Hz), 3.39 (2H, dd, *J* 3.0, 9.3 Hz), 2.57–2.53 (2H, m), 2.50 (1H, pent, *J* 6.8 Hz), 2.39 (2H, dt, *J* 1.2, 7.2 Hz), 1.38–1.14 (278H, m), 1.05 (3H, d, *J* 6.9 Hz), 0.90–0.86 (30H, including 2 × *tert*-butyl groups and 4 × terminal CH_3 groups), 0.66–0.64 (6H, br. m), 0.58 (3H, dt, *J* 3.8, 7.6 Hz), 0.16 (18H, s), 0.14 (18H, s), 0.13 (18H, s), 0.06 (12H, s), −0.31 (3H, br q, *J* 5.0 Hz); δ_C (101 MHz, $CDCl_3$): 215.1, 173.8, 94.8, 73.5, 73.4, 72.8, 71.8, 70.7, 62.3, 51.8, 46.3, 41.1, 33.4, 33.0, 31.9, 30.2, 29.9, 29.8, 29.74, 29.71, 29.66, 29.6, 29.5, 29.4, 29.37, 29.34, 28.7, 28.1, 27.3, 26.2, 25.9, 25.8, 25.7, 25.1, 23.7, 22.6, 18.0, 16.3, 15.7, 14.1, 10.9, 1.0, 0.9, 0.1, −4.5, −4.6; ν_{max}: 2923, 2853, 1744, 1465, 1251, 1099, 1010, 899, 839 cm^{-1}.

(ii) Tetrabutylammonium fluoride (0.2 ml, 0.2 mmol, 1 M) was added to a stirred solution of the above ester (0.1 g, 0.03 mmol) in dry THF (10 ml) at 5 °C under nitrogen. The mixture was allowed to reach rt and then it was stirred for 20 min. The reaction mixture was worked up and purified as before to give 6-*O*-[(*R*)-2-((*R*)-1-((*tert*-butyldimethylsilyl)-oxy)-12-{(1*S*,2*R*)-2-[14-((1*S*,2*R*)-2-eicosylcyclopropyl)-tetradecyl]cyclopropyl} dodecyl)hexacosanoate]-*α*-*D*-gluco-pyranosyl-(1→1)-6′-*O*-[(*R*)-2-{(*R*)-1-((*tert*-butyldimethyl-silyl)oxy)-16-[(1*S*,2*R*)-2-(20-methyl-19-oxo-20-octatria-contyl)cyclopropyl]hexadecyl}hexacosanoate]-*α*-*D*-gluco-pyranoside (0.06 g, 84%) as a colourless thick oil, $[\alpha]_D^{21}$ +12 (c 0.5, $CHCl_3$), {MALDI Found $[M+Na]^+$: 2931.3; $C_{186}H_{362}NaO_{16}Si_2$ requires: 2931.7}, which showed δ_H (400 MHz, $CDCl_3$+few drops of CD_3OD): 5.05 (2H, d, *J* 3.6 Hz), 4.33 (2H, br dd, *J* 4.3, 12.3 Hz), 4.2 (2H, br dd, *J* 4.0, 10.6 Hz), 3.93–3.85 (4H, m), 3.76 (2H, br t, *J* 9.2 Hz), 3.47 (2H, dd, *J* 3.5, 9.7 Hz), 3.31 (2H, t, *J* 9.5 Hz), 2.55–2.50 (2H, m), 2.48 (1H, pent, *J* 6.8 Hz), 2.39 (2H, t, *J* 7.0 Hz), 1.42–1.07 (286H, m), 1.01 (3H, d, *J* 6.9 Hz), 0.86 (12H, t, *J* 6.8 Hz), 0.82 (18H, s), 0.62–0.59 (6H, m), 0.54 (3H, dt, *J* 3.8, 7.8 Hz), 0.01 (6H, s), −0.01 (6H, s), −0.35 (3H, br q, *J* 5.0 Hz); δ_C (101 MHz, $CDCl_3$+few drops of CD_3OD): 216.0, 175.1, 93.4, 73.1, 72.9, 71.6, 70.1, 69.9, 62.8, 51.5, 46.2, 41.0, 33.5, 32.9, 31.8, 30.12, 29.67, 29.60, 29.5, 29.41, 29.4, 29.34, 29.3, 29.1, 28.6, 27.6, 27.2, 26.9, 25.6, 25.4, 24.14, 23.6, 22.58, 17.8, 16.2, 15.6, 13.9, 10.7, −4.6, −5.0; ν_{max}: 3401, 2926, 2854, 1724, 1466, 1215, 1093, 1078, 991, 929, 836, 757, 736, 669 cm^{-1}.

(iii) A dry polyethylene vial equipped with a rubber septum was charged with the above ester (0.06 g, 0.02 mmol) and pyridine (0.05 ml) in dry THF (182 ml) and stirred at rt under nitrogen. Hydrogen fluoride-pyridine complex as above (0.3 ml) was added, stirred at 43 °C for 15 h, then worked up and purified as before gave the *title* compound **15** (0.04 g, 70%), $[\alpha]_D^{21}$ +31 (c 0.5, $CHCl_3$) {Found $[M+Na]^+$: 2704.5255; $C_{174}H_{334}NaO_{16}$ requires: 2704.5292}, which showed δ_H (400 MHz, $CDCl_3$+few drops of CD_3OD): 4.97 (2H, d, *J* 3.0 Hz), 4.72 (2H, br d, *J* 12.2 Hz), 4.29 (2H, br t, *J* 9.8 Hz), 3.9 (2H, br t, *J* 11.5 Hz), 3.74 (2H, t, *J* 9.4 Hz), 3.66–3.63 (2H, m), 3.49 (2H, dd, *J* 2.8, 8.9 Hz), 3.19 (2H, t, *J* 9.4 Hz), 2.49 (1H, br q, *J* 6.8 Hz), 2.40–2.36 (4H, m), 1.64–1.00 (286H, m), 1.00 (3H, d, *J* 6.9 Hz), 0.84 (12H, m), 0.61–0.59 (6H, m), 0.53 (3H, dt, *J* 3.9, 7.6 Hz), −0.36 (3H, br q, *J* 4.9 Hz); δ_C (101 MHz, $CDCl_3$+few drops of CD_3OD): 216.3, 175.3, 94.7, 72.4 (br), 71.0 (br), 69.6 (br), 64.0, 52.2, 46.1, 41.0, 34.5, 32.8, 31.9, 31.7, 29.9, 29.4, 29.37, 29.34, 29.28, 29.26, 29.23, 29.1, 29.0, 28.5, 27.0, 26.1, 25.0, 23.4, 23.1, 22.4, 16.0, 15.5, 13.8, 10.7, 10.6; ν_{max}: 3368, 2920, 2851, 1727, 1467, 1101, 720 cm^{-1}.

4.14. 6-*O*-[(*R*)-2-((*R*)-1-Hydroxy-12-{(1*S*,2*R*)-2-[14-((1*S*,2*R*)-2-eicosylcyclopropyl)tetradecyl]cyclopropyl}do-decyl)-hexacosanoate]-α-*D*-glucopyranosyl-(1→1)-6′-*O*-[(*R*)-2-((*R*)-1-hydroxy-18-((1*R*,2*S*)-2-((17*S*,18*S*)-17-methoxy-18-methylhexatriacontyl)cyclopropyl)octadecyl)tetracosanoate]-α-*D*-glucopyranoside (17)

(i) 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI) (0.03 g, 0.15 mmol) and 4-dimethylaminopyridine (0.02 g, 0.16 mmol) were added to a stirred solution of **10a** (0.1 g, 0.05 mmol), **16**[60] (0.06 g, 0.04 mmol) and powdered molecular sieves 4 Å in dry dichloromethane (2 ml) at room temperature under nitrogen then worked up and purified as before to give 2,3,4-*O*-trimethylsilyl-6-*O*-[(*R*)-2-((*R*)-1-((*tert*-butyldimethylsilyl)oxy)-12-{(1*S*,2*R*)-2-[14-((1*S*,2*R*)-2-eicosylcyclopropyl)tetradecyl]cyclopropyl}dodecyl)-hexacosanoate]-α-*D*-glucopyranosyl-(1→1)-2,3,4-*O*-tri-methylsilyl-6′-*O*-[(*R*)-2-((*R*)-1-((*tert*-butyldimethylsilyl)-oxy)-18-((1*R*,2*S*)-2-((17*S*,18*S*)-17-methoxy-18-methylhexa-triacontyl)cyclopropyl)octadecyl)tetracosanoate]-α-*D*-gluco-pyranoside (0.1 g, 62%) as a colourless oil, $[\alpha]_D^{21}$ +19 (c 0.5, $CHCl_3$) {MALDI Found $[M+Na]^+$: 3359.4; $C_{203}H_{418}NaO_{16}Si_8$ requires: 3360.0}, which showed δ_H (400 MHz, $CDCl_3$): 4.85 (2H, d, *J* 3.0 Hz), 4.36 (2H, br d, *J* 10.0 Hz), 4.04–3.97 (4H, m), 3.96–3.93 (2H, m), 3.91 (2H, br t, *J* 8.8 Hz), 3.53 (2H, t, *J* 9 Hz), 3.39 (2H, dd, *J* 2.9, 9.3 Hz), 3.3 (3H, s), 2.97 (1H, br p, *J* 4.2), 2.57 (2H, br pent, *J* 3.5 Hz), 1.64–1.13 (285H, m), 0.91–0.84 (33H, including s at 0.9 for 2×*tert*-butyl groups, d at 0.88, *J* 6.9 Hz for the methyl group and t at 0.86 for 4×CH_3 terminal), 0.67–0.64 (6H, br m), 0.58 (3H, dt, *J* 3.8, 7.6 Hz), 0.16 (18H, s), 0.14 (18H, s), 0.13 (18H, s), 0.06 (12H, s), −0.31 (3H, br q, *J* 5.1 Hz); δ_C (101 MHz, $CDCl_3$): 173.8, 94.8, 85.4, 73.5, 73.4, 72.8, 71.8, 70.7, 62.3, 57.7, 51.8, 35.3, 33.4, 32.3, 31.9, 30.5, 30.2, 30.0, 29.95, 29.8, 29.74, 29.7, 29.6, 29.5, 29.3, 29.0, 28.7, 28.1, 27.5, 26.2, 26.1, 25.9, 25.8, 25.1, 22.7, 18.0, 15.7, 14.8, 14.1, 10.9, 1.0, 0.9, 0.1, −4.5, −4.6. υ_{max}: 2923, 2853, 1744, 1465, 1251, 839 cm^{-1};

(ii) Tetrabutylammonium fluoride (0.2 ml, 0.2 mmol, 1 M) was added to a stirred solution of the above ester (0.1 g, 0.03 mmol) in dry THF (10 ml) at 5 °C under nitrogen, allowed to reach rt and stirred for 20 min, then worked up and purified as before to give 6-*O*-[(*R*)-2-((*R*)-1-((*tert*-butyldimethylsilyl) oxy)-12-{(1*S*,2*R*)-2-[14-((1*S*,2*R*)-2-eicosylcyclopropyl)-tetradecyl] cyclopropyl}dodecyl)hexacosanoate]-α-*D*-gluco-pyranosyl-(1→1)-6′-*O*-[(*R*)-2-((*R*)-1-((*tert*-butyldimethyl-silyl)oxy)-18-((1*R*,2*S*)-2-((17*S*,18*S*)-17-methoxy-18-methyl-hexatriacontyl) cyclopropyl)octadecyl)tetracosanoate]-α-*D*-glucopyranoside (0.08 g, 91%) as a colourless thick oil, $[\alpha]_D^{21}$ +12 (c 0.5, $CHCl_3$) {MALDI Found $[M+Na]^+$: 2923.2; $C_{185}H_{366}NaO_{16}Si_2$ requires: 2923.7}, which showed δ_H (400 MHz, $CDCl_3$+few drops of CD_3OD): 5.02 (2H, d, *J* 3.2 Hz), 4.29 (2H, br d, *J* 11 Hz), 4.2 (2H, d, *J* 11 Hz), 3.91 (2H, br d, *J* 9.6 Hz), 3.87 (2H, br q, *J* 4.7 Hz), 3.8 (2H, br t *J* 9.3 Hz), 3.45 (2H, dd, *J* 2.9, 9.6 Hz), 3.32–3.25 (5H, including s for the MeO-groups at 3.2), 2.93–2.90 (1H, m), 2.52–2.47 (2H, m), 1.57–0.91 (287H, m), 0.84–0.77 (33H, including s at 0.84 for 2×*tert*-butyl groups, d at 0.81, *J* 6.9 Hz for the methyl group and t at 0.79 for 4×terminal CH_3), 0.60–0.58 (6H, m), 0.52 (3H, dt, *J* 3.9, 7.8 Hz), 0.00 (6H, s), −0.02 (6H, s), −0.37 (3H, br q, *J* 4.8 Hz); δ_C (400 MHz, $CDCl_3$): 175.0, 93.4, 85.5, 73.1, 72.9, 71.6, 70.2, 69.8, 62.8, 57.5, 51.6, 35.2, 33.5, 32.2, 31.8, 30.3, 30.0, 29.8, 29.7, 29.4, 27.6, 27.3, 26.8, 25.9, 25.7, 25.6, 24.1, 22.5, 17.8, 15.6, 14.6, 13.9, 10.7, −4.6, −5.0; υ_{max}: 3401, 2926, 2854, 1724, 1466, 1215, 1093, 1078, 991, 929, 836, 757, 736, 669 cm^{-1}.

(iii) A dry polyethylene vial equipped with a rubber septum was charged with the above ester (0.08 g, 0.02 mmol) and pyridine (0.1 ml) in dry THF (12 ml) and stirred at rt under nitrogen. Hydrogen fluoride-pyridine complex (0.8 ml) was then added and stirred at 43 °C for 15 h, then worked up and purified as before to give the *title* compound **17** (0.04 g, 50%), $[\alpha]_D^{21}$ +32 (c 0.5, $CHCl_3$) {Found $[M+Na]^+$: 2693.5387; $C_{173}H_{336}NaO_{16}$ requires: 2693.5371}, which showed δ_H (400 MHz, $CDCl_3$+few drops of CD_3OD): 5.0 (2H, br d, *J* 3.0 Hz), 4.73 (2H, br d, *J* 10.8 Hz), 4.28 (2H, br t, *J* 8.9 Hz), 3.91 (2H, br q, *J* 11.8 Hz), 3.49 (2H, t, *J* 11.3 Hz), 3.37–3.36 (2H, br m), 3.53 (2H, dd, *J* 3.9, 11.8 Hz), 3.31 (3H, s), 3.21 (2H, t, *J* 9.3 Hz), 2.95 (2H, br p, *J* 4.3 Hz), 2.41–2.36 (2H, m), 1.31–1.22 (286H, m), 0.86–0.81 (15H, including d at 0.85 for the methyl group, and t at 0.83 for the terminal methyl groups), 0.62–0.60 (6H, m), 0.54 (3H, dt, *J* 3.9, 7.8 Hz), −0.35 (3H, br q, *J* 4.9 Hz); δ_C (101 MHz, $CDCl_3$+few drops of CD_3OD): 175.4, 95.0, 85.5, 72.5, 72.3, 71.1, 69.8, 64.6, 57.5, 52.0, 35.2, 34.6, 32.2, 31.8, 30.7, 30.3, 30.1, 29.86, 29.8, 29.4, 29.3, 29.2, 28.6, 27.4, 27.1, 26.0, 25.7, 25.6, 25.0, 22.5, 15.6, 14.7, 13.9, 10.8; υ_{max}: 3368, 2920, 2851, 1727, 1467, 1101, 720 cm^{-1}.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.10.072.

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