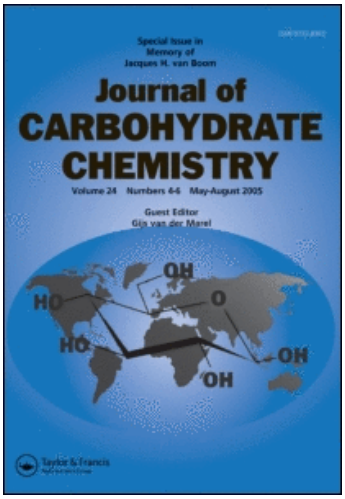

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An Expeditious Route to *Streptococci* and *Enterococci* Glycolipids *Via* Ring-Opening of 1,2-Anhydrosugars with Protic Acids

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AN EXPEDITIOUS ROUTE TO *STREPTOCOCCI* AND *ENTEROCOCCI* GLYCOLIPIDS *VIA* RING-OPENING OF 1,2-ANHYDROSUGARS WITH PROTIC ACIDS

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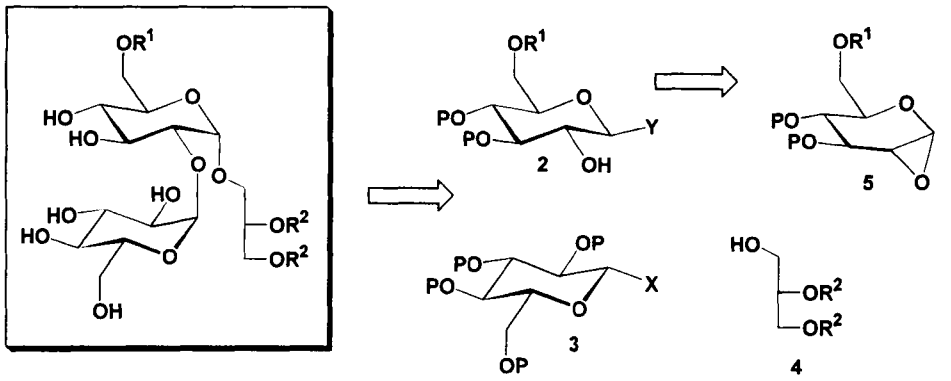
ABSTRACT

1,2-Anhydroglucose **6** reacts smoothly and with a high degree of stereoselectivity with a variety of carboxylic and phosphoric acids resulting in the formation of the predominantly β-oriented 1-*O*-acyl and 1-*O*-phosphorylglucoses **7-17**. This methodology has been successfully applied in the construction of glycolipids **1a,b**. Ring-opening of the 1,2-anhydroglucose derivative **19** with benzoic acid furnished exclusively the β-aligned key intermediate **20**. Subsequent ICDT-assisted chemoselective α-glucosylation of **20** with thioethyl donor **21**, followed by glycosidation of kojibiosyl benzoate **22** with glycerol acceptor **23** gave the fully protected α-diglucosyl glycerol derivative **25**, which upon desilylation (→**28**), acylation (→**29** or **30**) and deprotection afforded the target glycolipids **1a-b** in high overall yield.

INTRODUCTION

It is well documented[1] that glycolipids play a pivotal role as membrane anchors of outer cell-wall components in a variety of organisms. A few years ago, we reported[2] the



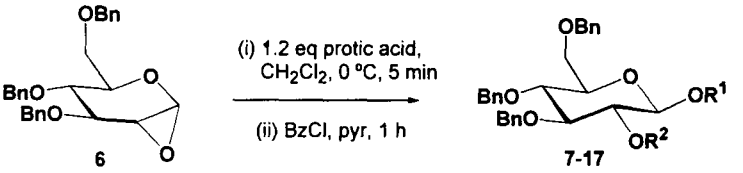
1a $R^1 = R^2$ = palmitoyl
b $R^1 = R^2$ = myristoyl

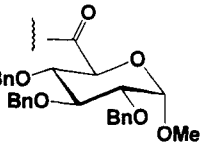
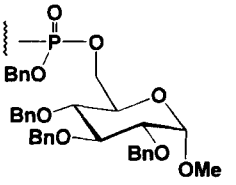
Figure 1

assembly of glycolipid **1** (see Fig. 1, R^1 = stearoyl, R^2 = palmitoyl), which serves as the common metabolic precursor for various *Streptococci*[3] and *Enterococci*[4] glyco(phospho)lipids. Recently, it has been postulated[5] that **1a** ($R^1 = R^2$ = palmitoyl) and **1b** ($R^1 = R^2$ = myristoyl) may enhance HIV replication. The renewed interest in compound **1** was a stimulus to develop a more straightforward and flexible methodology for the introduction of the requisite α-linkages.

Retrosynthetic analysis (see Fig. 1) reveals that **1** is accessible from a glucosyl donor (**2**), bearing an appropriate β-oriented anomeric leaving group (Y), a free hydroxyl at position two and a selectively removable 6-*O*-protecting group (R^1). Chemoselective α-glucosylation of the 2-OH group in **2** with donor **3**, followed by coupling of the resulting dimer *via* activation of Y with the suitably protected glycerol acceptor **4**, would lead to the α-diglucosyl glycerol core unit of **1**.

It was envisaged that the glucosyl donor **2** can be synthesized *via* nucleophilic ring-opening of an appropriately protected α-1,2-anhydroglucose precursor (**5**), which can be prepared[6] from the corresponding glucal by 3,3-dimethyldioxirane (DMD)-mediated epoxidation. In a recent paper, Danishefsky *et al.* showed[7] that 1,2-anhydrosugars can be converted in moderate yields into other glycosyl donors (*i.e.*, **2**, Y = SPh, SePh, 4-pentenyl, F) by nucleophilic displacement at the anomeric center. We here report an alternative approach towards **1** based on the ring-opening of the suitably protected α-1,2-anhydroglucose derivative **19** (see Scheme 2) with benzoic acid.



	α:β	yield (%)
7 R^1 = Ac, R^2 = H	1:5	87
8 R^1 = Bz, R^2 = H (ii)	1:11	91
9 R^1 = Bz, R^2 = Bz	1:11	88
10 R^1 = C(O)H, R^2 = H (ii)		
11 R^1 = C(O)H, R^2 = Bz	1:5	72
12 R^1 =  R^2 = H	3:10	70
13 R^1 = $P(O)(OBn)_2$, R^2 = H (ii)	0:1	82
14 R^1 = $P(O)(OBn)_2$, R^2 = Bz	0:1	72
15 R^1 = $P(O)(OBu)_2$, R^2 = H (ii)	0:1	88
16 R^1 = $P(O)(OBu)_2$, R^2 = Bz	0:1	81
17 R^1 =  R^2 = H	1:4	74

Scheme 1

RESULTS AND DISCUSSION

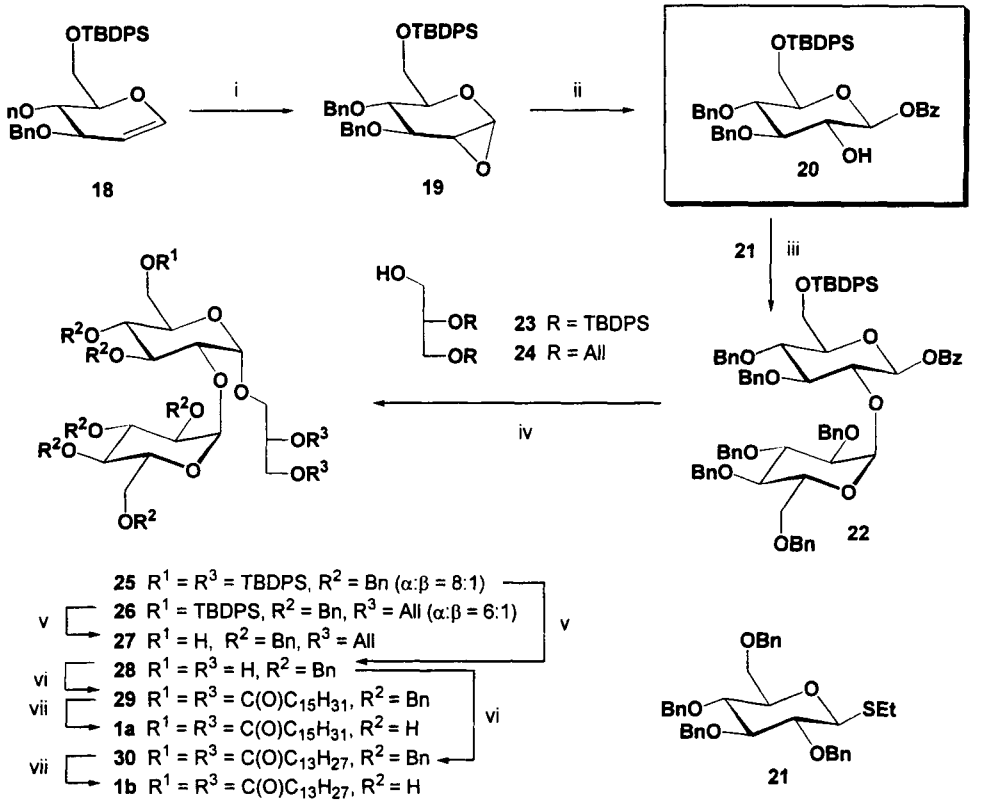
Prior to the assembly of target glycolipid **1**, we investigated the ring-opening of the α-1,2-anhydro function in the known fully benzylated glucopyranose derivative **6**[6] with several carboxylic and phosphoric acids (see Scheme 1). Reaction of **6** with a slight excess of acetic acid in anhydrous dichloromethane at 0 °C, proceeded smoothly to afford anomeric acetate **7** in 87% yield with a high degree of stereoselectivity (α:β = 1:5). In a similar fashion, subjection of oxirane **6** to benzoic acid gave the 1-*O*-benzoyl glucose **8** (91%, α:β = 1:11), one-pot benzoylation of which furnished the dibenzoate **9** (88%). It is

of interest to note that the conversion of 1,2-epoxide **6** with benzoic acid in the more polar solvent THF resulted in a less favorable anomeric mixture of **8** (α:β = 1:3). The latter observation may be attributed to partial dissociation of the acid, inducing ring-opening of 1,2-anhydro derivative **6** into an intermediate oxycarbenium species, which may undergo nucleophilic substitution by benzoate anion from either the α- or the β-side. Treatment of **6** with formic acid in dichloromethane led to the unstable anomeric formate **10** which after benzoylation provided the more stable derivative **11**. Apart from this, the ring-opening of oxirane **6** with a more functionalized carboxylic acid derivative was explored. It was established that reaction of **6** with methyl 2,3,4-tri-*O*-benzyl-α-D-glucuronopyranoside[8] gave the acyl-linked dimer **12** (α:β = 3:10). The latter type of acyl disaccharides has recently been used in a redox glycosidation strategy.[9]

Interestingly, substitution of **6** with dibenzyl or dibutyl phosphoric acid yielded exclusively the respective β-oriented glucosyl phosphates **13** and **15**, benzoylation of which gave the fully protected glucosides **14** and **16**.[10] On the other hand, the phosphotriester-bridged diglucoside **17** was obtained as an anomeric mixture (α:β = 1:4) by treatment of **6** with methyl 2,3,4-tri-*O*-benzyl-6-(benzyl phosphate)-α-D-glucopyranoside.[11]

On the basis of the ring-opening of 1,2-anhydroglucose **6** with benzoic acid, it was anticipated that treatment of 1,2-oxirane **19**, obtained by benzylation of known 6-*O*-*tert*-butyldiphenylsilyl-D-glucal[12] and subsequent DMD-mediated epoxidation of fully protected glucal **18**, with benzoic acid would lead to an anomeric mixture of the corresponding 1-*O*-benzoyl-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-D-glucopyranose (**20**). However, it was very gratifying to establish that the nucleophilic displacement proceeded with complete inversion of configuration at the anomeric center to give exclusively the β-aligned key intermediate **20** in 92% yield. Subsequent glucosylation of the 2-hydroxyl in **20** with the known ethyl thioglucosyl donor **21**[13] under the agency of iodonium di-*sym*-collidine triflate (IDCT)[14] proceeded stereoselectively to give the α-linked disaccharide **22**.

At this stage, the kojibiosyl donor **22** was coupled under the agency of trimethylsilyl triflate (TMSOTf)[15] with 1,2-di-*O*-*tert*-butyldiphenylsilyl-*sn*-glycerol acceptor **23**, readily accessible from commercially available 1,2-*O*-isopropylidene-*sn*-glycerol, to give the diglucosyl glycerol derivative **25** as an inseparable anomeric mixture (α:β = 8:1) in 81% yield. Desilylation of **25** with tetra-*n*-butylammonium fluoride (TBAF) and ensuing separation of the anomeric mixture led to the triol **28**. Finally, acylation of **28** with palmitoyl or myristoyl chloride in pyridine/CH_2Cl_2 gave the fully protected glycolipids **29** and **30**, respectively, in near quantitative yields. The benzyl



Reagents and conditions: (i) 3,3-dimethyldioxirane, CH_2Cl_2/acetone, 5 min, quant.; (ii) BzOH, CH_2Cl_2, 0 °C, 5 min, 92%; (iii) IDCT, Et_2O/$ClCH_2CH_2Cl$ (1:1, v/v), 1 h, 72%; (iv) TMSOTf, $ClCH_2CH_2Cl$, 3 h, **25**: 81%, **26**: 74%; (v) TBAF, THF, 2-4 h, **27**: 83%, **28**: 78%; (vi) palmitoyl or myristoyl chloride, pyridine/CH_2Cl_2 (1:1, v/v), 3 h, **29**: 92%, **30**: 90%; (vii) H_2 (3 atm.), Pd/C, MeOH/CH_2Cl_2 (3:1, v/v), 12 h, **1a**: 96%, **1b**: 94%.

Scheme 2

protective groups in **29** and **30** were removed by hydrogenolysis over Pd/C to afford the respective target molecules **1a** and **1b**, the structure of which was unambiguously ascertained by mass spectrometry and ^1H and ^{13}C NMR analysis. In addition, TMSOTf-mediated glycosylation of the known 1,2-di-*O*-allyl-*sn*-glycerol acceptor **24**[16] with kojibiosyl benzoate **22** led to an inseparable anomeric mixture of the fully protected diglucosyl glycerol derivative **26** (α:β = 6:1). Desilylation of **26** with TBAF followed by separation of the individual anomers provided the partially protected α-diglucosyl

glycerol derivative **27**, which is a useful building block in the construction of various naturally occurring *Streptococci* and *Enterococci* glyco(phospho)lipids.

CONCLUSION

The results presented in this paper show that anomeric acyl or phosphoryl donors are readily accessible by protic acid-mediated ring-opening of 1,2-anhydrosugars. This transformation proceeds predominantly with inversion of configuration at the anomeric center. Furthermore, the high-yielding and efficient synthesis of glycolipids **1a-b** may open the way to the preparation of other biologically interesting glyco(phospho)lipids.

EXPERIMENTAL

Materials and methods. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded with a Jeol JNM-FX-200 (200/50.1/80.7 MHz), a Bruker WM-300 (300/75.1/121.0 MHz) or a Bruker DMX-600 spectrometer (600/150.3/242.1 MHz). ^{1}H and ^{13}C chemical shifts are given in ppm (δ) relative to tetramethylsilane as internal standard and ^{31}P chemical shifts are given in ppm (δ) relative to 85% H_3PO_4 as external standard. Mass spectra were recorded with a Finnigan MAT TSQ70 triple quadropole mass spectrometer. Optical rotations were determined with a Propol automatic polarimeter. Dichloromethane (CH_2Cl_2), diethyl ether, pyridine and toluene were boiled under reflux with CaH_2 for 3 h, distilled and stored over molecular sieves (4 Å). 1,2-Dichloroethane (Biosolvent, HPLC-grade), *N,N*-dimethylformamide (DMF, Baker, p.a.) and tetrahydrofuran (THF, Biosolvent, HPLC-grade) were stored over molecular sieves (4 Å). Methanol (Rathburn, HPLC-grade) was stored over molecular sieves (3 Å). All other chemicals were obtained from commercial sources and were used as received. Column chromatography was performed on Baker silica gel (0.063-0.200 mm). Gel permeation chromatography was accomplished with LH-20 column material (Sephadex). TLC analysis was done on DC-fertigfolien (Schleicher & Schüll F1500, LS254) with detection by UV-absorption (254 nm) where applicable and charring with 20% H_2SO_4 in MeOH or ammonium molybdate (25 g/L) and ceric ammonium sulfate (10 g/L) in 10% aq. H_2SO_4. Reactions were carried out at ambient temperature, unless otherwise stated. Prior to reactions that require anhydrous conditions, traces of water in the glycosides were removed by coevaporation with 1,2-dichloroethane, pyridine or toluene.

General procedure for the protic acid-mediated ring-opening of 1,2-anhydrosugar 6. To a stirred and cooled solution of 1,2-anhydrosugar **6** (0.43 g, 1.0 mmol) in CH_2Cl_2 (5 mL) was added dropwise, over a period of 5 min, a solution of the

carboxylic or phosphoric acid derivative (1.2 mmol) in CH_2Cl_2 (10 mL).* The reaction mixture was subsequently diluted with CH_2Cl_2 (50 mL) and washed with aq. $NaHCO_3$ (2 x 25 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography (10-50% EtOAc/light petroleum) to give an anomeric mixture of the corresponding 1-*O*-acyl or 1-*O*-phosphoryl sugar.

***General procedure for the one-pot 2-OH benzoylation.** After addition of the appropriate acid to the 1,2-anhydrosugar, pyridine (5 mL) and benzoyl chloride (0.17 mL, 1.5 mmol) were sequentially added and the reaction mixture was allowed to stir for 1 h at room temperature. The reaction mixture was subsequently diluted with CH_2Cl_2 (50 mL) and washed with aq. $NaHCO_3$ (2 x 25 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. Traces of pyridine in the residue were removed by coevaporation with toluene (3 x 10 mL). Further purification of the residue was accomplished by silica gel chromatography (10-30% EtOAc/light petroleum) to give an anomeric mixture of the corresponding 2-*O*-benzoyl sugar.

1-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α/β-D-glucopyranose (7). Yield: 0.37 g, 0.87 mmol, 87%, α:β = 1:5. α-anomer: ^{13}C NMR ($CDCl_3$): δ 169.5 (C=O Ac), 138.2, 137.7, 137.6 (C_q Bn), 128.2-127.6 (C_{arom}), 91.9 (C_1, $J_{C,H}$ = 170.0 Hz), 82.0, 79.0, 73.4, 71.2 ($C_2/C_3/C_4/C_5$), 74.8, 74.5, 71.6 (CH_2 Bn), 67.9 (C_6), 20.8 (CH_3 Ac); β-anomer: δ 169.5 (C=O Ac), 138.2, 137.7, 137.6 (C_q Bn), 128.2-127.6 (C_{arom}), 93.8 (C_1, $J_{C,H}$ = 159.4 Hz), 84.4, 76.8, 75.3, 72.8 ($C_2/C_3/C_4/C_5$), 75.0, 74.5, 73.2 (CH_2 Bn), 67.9 (C_6), 20.8 (CH_3 Ac). MS (ESI): *m/z* 493 $(M+H)^+$, 515 $(M+Na)^+$.

1-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-α/β-D-glucopyranose (8). Yield: 0.50 g, 0.91 mmol, 91%, α:β = 1:11. α-anomer: ^{13}C NMR ($CDCl_3$): δ 164.8 (C=O Bz), 138.1, 137.9, 137.7 (C_q Bn), 133.6-127.8 (C_{arom}), 91.8 (C_1, $J_{C,H}$ = 167.0 Hz), 83.4, 79.2, 77.0, 73.1 ($C_2/C_3/C_4/C_5$), 74.9, 74.5, 71.9 (CH_2 Bn), 68.1 (C_6); β-anomer: δ 165.0 (C=O Bz), 138.1, 138.0, 137.9 (C_q Bn), 133.6-127.8 (C_{arom}), 93.5 (C_1, $J_{C,H}$ = 160.0 Hz), 83.4, 77.0, 76.0, 72.9 ($C_2/C_3/C_4/C_5$), 74.9, 74.5, 71.9 (CH_2 Bn), 68.3 (C_6). MS (ESI): *m/z* 555 $(M+H)^+$, 572 $(M+NH_4)^+$, 577 $(M+Na)^+$.

1,2-Di-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α/β-D-glucopyranose (9). Yield: 0.58 g, 0.88 mmol, 88%, α:β = 1:11. α-anomer: ^{13}C NMR ($CDCl_3$): δ 164.9, 163.8 (C=O Bz), 138.1, 138.0, 137.9 (C_q Bn), 133.6-127.7 (C_{arom}), 91.2 (C_1, $J_{C,H}$ = 168.2 Hz), 82.6, 79.1, 74.8, 72.7 ($C_2/C_3/C_4/C_5$), 75.3, 75.0, 73.5 (CH_2 Bn), 68.1 (C_6); β-anomer: δ 165.3, 165.0 (C=O Bz), 138.1, 138.0, 137.9 (C_q Bn), 133.6-127.7 (C_{arom}), 93.1 (C_1, $J_{C,H}$ = 159.8 Hz), 82.6, 77.6, 76.1, 72.9 ($C_2/C_3/C_4/C_5$), 75.1, 75.0, 73.6 (CH_2 Bn), 68.3 (C_6). MS (ESI): *m/z* 659 $(M+H)^+$, 676 $(M+NH_4)^+$, 681 $(M+Na)^+$.

Anal. Calcd for $C_{41}H_{38}O_8$ (658.1): C, 74.76; H, 5.81. Found: C, 74.58; H, 5.92.

1-*O*-Formyl-2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α/β-D-glucopyranose (11). Yield: 0.42 g, 0.72 mmol, 72%, α:β = 1:5. α-anomer: ^{13}C NMR ($CDCl_3$): δ 165.0 (C=O Bz), 161.3 (HC=O), 137.5, 137.4, 137.2 (C_q Bn), 134.0-127.1 (C_{arom}), 89.6 (C_1, $J_{C,H}$ = 169.2 Hz), 78.0, 76.9, 73.2, 70.9 ($C_2/C_3/C_4/C_5$), 75.5, 74.2, 72.3 (CH_2 Bn), 67.9 (C_6); β-anomer: δ 161.7 (C=O Bz), 160.9 (HC=O), 137.5, 137.4, 137.2 (C_q Bn), 134.0-127.1 (C_{arom}), 91.4 (C_1, $J_{C,H}$ = 158.0 Hz), 81.8, 76.8, 75.5, 71.9 ($C_2/C_3/C_4/C_5$), 74.9, 74.4, 71.7 (CH_2 Bn), 67.6 (C_6). MS (ESI): *m/z* 583 $(M+H)^+$.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(3,4,6-tri-*O*-benzyl-α/β-D-glucopyranosyl)-α-D-glucuronopyranoside (12). Yield: 0.64 g, 0.70 mmol, 70%, α:β = 3:10. α-anomer: ^{13}C NMR ($CDCl_3$): δ 168.0 (C_6), 138.2, 138.0, 137.7, 137.5, 137.4, 137.4 (C_q Bn), 128.9-127.2 (C_{arom}), 98.1 (C_1, $J_{C,H}$ = 169.8 Hz), 93.1 ($C_{1'}$, $J_{C,H}$ = 168.6 Hz), 84.2, 81.7, 80.7, 75.3, 72.5, 71.1, 70.0, 69.8 ($C_2/C_3/C_4/C_5/C_{2'}/C_{3'}/C_{4'}/C_{5'}$), 75.2, 74.6, 74.2, 74.0, 72.8, 72.8 (CH_2 Bn), 67.6 ($C_{6'}$), 55.2 (OMe); β-anomer: δ 168.1 (C_6), 138.2, 138.0, 137.7, 137.5, 137.4, 137.4 (C_q Bn), 128.9-127.2 (C_{arom}), 98.1 (C_1, $J_{C,H}$ = 169.8 Hz), 94.5 ($C_{1'}$, $J_{C,H}$ = 158.9 Hz), 84.0, 80.7, 79.0, 78.8, 77.4, 76.6, 72.5, 69.8 ($C_2/C_3/C_4/C_5/C_{2'}/C_{3'}/C_{4'}/C_{5'}$), 75.2, 74.6, 74.2, 74.0, 72.8, 72.8 (CH_2 Bn), 68.0 ($C_{6'}$), 55.2 (OMe). MS (ESI): *m/z* 912 $(M+H)^+$, 929 $(M+NH_4)^+$, 934 $(M+Na)^+$.

Anal. Calcd for $C_{55}H_{58}O_{12}$ (911.0): C, 72.51; H, 6.42. Found: C, 72.43; H, 6.45.

Dibenzyl-(3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl) phosphate (13). Yield: 0.58 g, 0.82 mmol, 82%. ^{31}P NMR ($CDCl_3$): δ -2.01. ^1H NMR ($CDCl_3$): δ 7.58-7.06 (m, 25H, H_{arom}), 5.02 (t, 1H, H_1, $J_{1,2} = J_{1,P}$ = 7.8 Hz), 4.84-4.41 (m, 10H, CH_2 Bn), 4.03 (dd, 1H, H_2, $J_{2,3}$ = 8.6 Hz), 3.99 (dd, 1H, H_3, $J_{3,4}$ = 7.7 Hz), 3.76 (m, 1H, H_5), 3.68-3.58 (m, 2H, H_4/H_6), 3.54 (dd, 1H, $H_{6'}$, $J_{5,6'}$ = 4.8 Hz, $J_{6,6'}$ = 10.9 Hz), 2.60 (bs, 1H, OH). ^{13}C NMR ($CDCl_3$): δ 138.2, 138.1, 137.8 (C_q Bn sugar), 135.0 (C_q Bn phosph.), 128.6-127.2 (C_{arom}), 98.4 (C_1, $J_{1,P}$ = 4.6 Hz), 83.9, 77.4, 75.0 ($C_3/C_4/C_5$), 75.2, 74.9, 73.9 (CH_2 Bn sugar), 74.8 (C_2, $J_{2,P}$ = 7.2 Hz), 70.2, 69.9 (CH_2 Bn phosph., $J_{C,P}$ = 4.0 Hz), 68.4 (C_6). MS (ESI): *m/z* 711 $(M+H)^+$, 733 $(M+Na)^+$.

***Dibenzyl-(2-O-benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)* phosphate (14).** Yield: 0.59 g, 0.72 mmol, 72%. ^{31}P NMR ($CDCl_3$): δ -2.21. ^1H NMR ($CDCl_3$): δ 8.10-7.10 (m, 30H, H_{arom}), 5.40 (t, 1H, H_1, $J_{1,2} = J_{1,P}$ = 7.6 Hz), 4.89 (dd, 1H, H_2, $J_{2,3}$ = 8.6 Hz), 4.80-4.46 (m, 10H, CH_2 Bn), 4.06 (dd, 1H, H_3, $J_{3,4}$ = 7.2 Hz), 3.90-3.62 (m, 4H, $H_4/H_5/H_6/H_{6'}$). ^{13}C NMR ($CDCl_3$): δ 165.1 (C=O Bz), 138.0, 137.9, 137.8 (C_q Bn sugar), 135.1 (C_q Bn phosph.), 133.2 (C_q Bz), 133.1-128.0 (C_{arom}), 96.2 (C_1, $J_{1,P}$ = 4.8 Hz), 81.0, 76.8, 74.9 ($C_3/C_4/C_5$), 74.9, 74.8, 73.3 (CH_2 Bn sugar), 71.8 (C_2, $J_{2,P}$ = 8.2 Hz), 70.1, 69.9 (CH_2 Bn phosph., $J_{C,P}$ = 4.0 Hz), 68.4 (C_6). MS (ESI): *m/z* 815 $(M+H)^+$, 832 $(M+NH_4)^+$, 837 $(M+Na)^+$.

Di-*n*-butyl-(3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl) phosphate (15). Yield: 0.57 g, 0.88 mmol, 88%. ^{31}P NMR ($CDCl_3$): δ -1.92. ^{1}H NMR ($CDCl_3$): δ 7.34-7.14 (m, 15H, H_{arom}), 5.03 (t, 1H, H_1, $J_{1,2} = J_{1,P} = 7.8$ Hz), 4.89 (AB, 2H, CH_2 Bn), 4.70 (AB, 2H, CH_2 Bn), 4.56 (AB, 2H, CH_2 Bn), 4.18 (dt, 4H, $CH_2\alpha$ Bu, $J_{H,P} = 5.9$ Hz), 4.10-3.99 (m, 2H, H_2/H_3), 3.70 (m, 1H, H_5), 3.62 (dd, 1H, H_4, $J_{3,4} = 8.1$ Hz, $J_{4,5} = 7.7$ Hz), 3.59 (dd, 1H, H_6, $J_{5,6} = 2.9$ Hz, $J_{6,6'} = 10.8$ Hz), 3.52 (dd, 1H, $H_{6'}$, $J_{5,6'} = 4.2$ Hz), 2.95 (bs, 1H, OH), 1.60 (m, 4H, $CH_2\beta$ Bu), 1.36 (m, 4H, $CH_2\gamma$ Bu), 0.90 (t, 6H, CH_3 Bu). ^{13}C NMR ($CDCl_3$): δ 138.4, 137.9, 137.8 (C_q Bn), 127.8-127.3 (C_{arom}), 99.0 (C_1, $J_{1,P} = 4.4$ Hz), 84.2, 76.8, 75.5 ($C_3/C_4/C_5$), 75.2, 74.8, 73.3 (CH_2 Bn), 74.6 (C_2, $J_{2,P} = 7.3$ Hz), 68.4 (C_6), 67.9 ($CH_2\alpha$ Bu, $J_{C,P} = 4.9$ Hz), 32.1 ($CH_2\beta$ Bu, $J_{C,P} = 5.8$ Hz), 18.5 ($CH_2\gamma$ Bu), 13.4 (CH_3 Bu). MS (ESI): *m/z* 643 $(M+H)^+$, 665 $(M+Na)^+$.

Di-*n*-butyl-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl) phosphate (16). Yield: 0.60 g, 0.81 mmol, 81%. ^{31}P NMR ($CDCl_3$): δ -2.10. ^{1}H NMR ($CDCl_3$): δ 8.05-7.11 (m, 20H, H_{arom}), 5.35 (dd, 1H, H_1, $J_{1,2} = 7.9$ Hz, $J_{1,P} = 6.0$ Hz), 4.80 (dd, 1H, H_2, $J_{2,3} = 8.4$ Hz), 4.76 (AB, 2H, CH_2 Bn), 4.68 (AB, 2H, CH_2 Bn), 4.52 (AB, 2H, CH_2 Bn), 4.20 (dt, 4H, $CH_2\alpha$ Bu, $J_{H,P} = 6.2$ Hz), 4.00 (dd, 1H, H_3, $J_{3,4} = 7.9$ Hz), 3.85-3.60 (m, 4H, $H_4/H_5/H_6/H_{6'}$), 1.50 (m, 4H, $CH_2\beta$ Bu), 1.31 (m, 4H, $CH_2\gamma$ Bu), 0.90 (t, 6H, CH_3 Bu). ^{13}C NMR ($CDCl_3$): δ 164.9 (C=O Bz), 137.7, 137.6, 137.4 (C_q Bn), 133.6-127.5 (C_{arom}), 132.9 (C_q Bz), 96.5 (C_1, $J_{1,P} = 4.0$ Hz), 81.9, 77.3, 75.5 ($C_3/C_4/C_5$), 74.9, 74.8, 73.3 (CH_2 Bn), 73.4 (C_2, $J_{2,P} = 7.8$ Hz), 68.1 (C_6), 67.6 ($CH_2\alpha$ Bu, $J_{C,P} = 4.2$ Hz), 31.6 ($CH_2\beta$ Bu, $J_{C,P} = 7.4$ Hz), 18.4 ($CH_2\gamma$ Bu), 13.3 (CH_3 Bu). MS (ESI): *m/z* 747 $(M+H)^+$, 769 $(M+Na)^+$.

Methyl 2,3,4-Tri-*O*-benzyl-6-[benzyl-(3,4,6-tri-*O*-benzyl-α/β-D-glucopyranosyl) phosphate]-α-D-glucopyranoside (17). Yield: 0.79 g, 0.74 mmol, 74%, α:β = 1:4, R_P:S_P = 1:1. ^{13}C NMR ($CDCl_3$): α-anomer: δ 138.4-135.9 (C_q Bn), 128.1-127.7 (C_{arom}), 97.8 ($C_{1'}$, $J_{C,H} = 167.3$ Hz, $J_{C,P} = 4.4$ Hz), 97.7 (C_1, $J_{C,H} = 169.2$ Hz), 84.5-70.1 ($C_2/C_3/C_4/C_5/C_{2'}/C_{3'}/C_{4'}/C_{5'}$), 75.4-73.1 ($CH_2$ Bn sugar), 69.4 ($C_{6'}$), 68.3 (CH_2 Bn phosph., $J_{C,P} = 4.4$ Hz), 65.3 (C_6, $J_{C,P} = 4.9$ Hz), 55.0 (OMe); β-anomer: δ 138.4-137.8 (C_q Bn), 128.1-127.7 (C_{arom}), 98.9 ($C_{1'}$, $J_{C,H} = 160.0$ Hz, $J_{C,P} = 4.5$ Hz), 97.7 (C_1, $J_{C,H} = 169.2$ Hz), 83.9-69.3 ($C_2/C_3/C_4/C_5/C_{2'}/C_{3'}/C_{4'}/C_{5'}$), 75.4-73.1 ($CH_2$ Bn sugar), 69.4 ($C_{6'}$), 68.5 (CH_2 Bn phosph., $J_{C,P} = 4.4$ Hz), 65.7 (C_6, $J_{C,P} = 5.0$ Hz), 55.0 (OMe). MS (ESI): *m/z* 1068 $(M+H)^+$, 1085 $(M+NH_4)^+$, 1090 $(M+Na)^+$.

1,5-Anhydro-2-deoxy-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-D-*arabino*-hex-1-enitol (18). A solution of 6-*O*-*tert*-butyldiphenylsilyl-D-glucal (3.84 g, 10.0 mmol) in THF (30 mL) was heated to 30 °C. To the latter solution, NaH (60% dispersion in mineral oil, 2.4 g, 60 mmol) was added and the mixture was stirred for 10 min. Subsequently methyltriphenylphosphonium iodide (8.1 g, 20 mmol) and benzyl bromide

(7.2 mL, 60 mmol) were added and the reaction mixture was stirred at 30 °C for 3 h. Methanol (3 mL) was added and the heterogeneous mixture was concentrated *in vacuo*. The residue was dissolved in diethyl ether (200 mL), washed with sat. aq. NaCl (3 x 50 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Purification of the residue was effected by silica gel chromatography (0-10% EtOAc/light petroleum) to give fully protected glucal **18** (4.62 g, 8.2 mmol, 82%) as a white solid. ^1H NMR ($CDCl_3$): δ 7.74-7.24 (m, 20H, H_{arom}), 6.40 (dd, 1H, H_1, $J_{1,2}$ = 5.9 Hz, $J_{1,3}$ = 1.3 Hz), 4.84 (dd, 1H, H_2, $J_{2,3}$ = 2.6 Hz), 4.82 (AB, 2H, CH_2 Bn), 4.61 (AB, 2H, CH_2 Bn), 4.21 (ddd, 1H, H_3, $J_{3,4}$ = 7.2 Hz), 4.00 (t, 1H, H_4, $J_{4,5}$ = 7.3 Hz), 3.97-3.91 (m, 3H, $H_5/H_6/H_{6'}$), 1.06 (s, 9H, CH_3 *t*-Bu). ^{13}C NMR ($CDCl_3$): δ 144.9 (C_1), 138.6, 138.5 (C_q Bn), 136.0-127.8 (C_{arom}), 133.7, 133.3 (C_q TBDPS), 99.8 (C_2), 78.1, 76.1, 74.3 ($C_3/C_4/C_5$), 74.0, 70.7 (CH_2 Bn), 62.4 (C_6), 27.0 (CH_3 *t*-Bu), 19.5 (C_q *t*-Bu).

Anal. Calcd for $C_{36}H_{40}O_4Si$ (564.5): C, 76.56; H, 7.14; Si, 4.97. Found: C, 76.50; H, 7.21; Si, 4.98.

1,2-Anhydro-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranose (19). To a stirred and cooled (0 °C) solution of glucal **18** (2.82 g, 5.0 mmol) in CH_2Cl_2 (10 mL) was added a freshly prepared solution of 3,3-dimethyldioxirane (DMD, 67 mL, 0.09 M, 6.0 mmol) in acetone. Immediately after the last addition, the reaction mixture was concentrated under reduced pressure to afford epoxide **19** as a white solid in quantitative yield (2.90 g, 5.0 mmol). ^1H NMR ($CDCl_3$): δ 7.81-7.18 (m, 20H, H_{arom}), 4.96 (d, 1H, H_1, $J_{1,2}$ = 3.4 Hz), 4.76 (AB, 2H, CH_2 Bn), 4.58 (AB, 2H, CH_2 Bn), 3.99 (dd, 1H, H_3, $J_{2,3}$ = 1.4 Hz, $J_{3,4}$ = 7.9 Hz), 3.80 (m, 1H, H_5), 3.60 (dd, 1H, H_6, $J_{5,6}$ = 2.9 Hz, $J_{6,6'}$ = 10.8 Hz), 3.58 (dd, 1H, H_4, $J_{4,5}$ = 7.4 Hz), 3.49 (dd, 1H, $H_{6'}$, $J_{5,6'}$ = 3.6 Hz), 3.12 (dd, 1H, H_2), 1.04 (s, 9H, CH_3 *t*-Bu). ^{13}C NMR ($CDCl_3$): δ 138.8, 137.9 (C_q Bn), 136.1-127.7 (C_{arom}), 133.8, 133.2 (C_q TBDPS), 79.4, 74.4, 70.7 ($C_3/C_4/C_5$), 79.0 (C_1), 74.8, 70.7 (CH_2 Bn), 62.3 (C_6), 52.7 (C_2), 27.1 (CH_3 *t*-Bu), 19.5 (C_q *t*-Bu).

1-*O*-Benzoyl-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-β-D-glucopyranose (20). Anomeric benzoate **20** (3.23 g, 4.6 mmol, 92%) was prepared from 1,2-anhydroglucose derivative **19** (2.90 g, 5.0 mmol) as described in the general procedure for the conversion of epoxide **6**. ^1H NMR ($CDCl_3$): δ 8.12-7.12 (m, 25H, H_{arom}), 5.81 (d, 1H, H_1, $J_{1,2}$ = 7.5 Hz), 4.92 (AB, 2H, CH_2 Bn), 4.80 (AB, 2H, CH_2 Bn), 4.04 (t, 1H, H_2, $J_{2,3}$ = 7.6 Hz), 4.00-3.78 (m, 3H, $H_3/H_4/H_5$), 3.70 (dd, 1H, H_6, $J_{5,6}$ = 2.0 Hz, $J_{6,6'}$ = 10.9 Hz), 3.52 (dd, 1H, $H_{6'}$, $J_{5,6'}$ = 4.1 Hz), 2.60 (bs, 1H, OH), 1.04 (s, 9H, CH_3 *t*-Bu). ^{13}C NMR ($CDCl_3$): δ 164.8 (C=O Bz), 138.2, 138.0 (C_q Bn), 135.5-127.2 (C_{arom}), 133.2, 132.6 (C_q TBDPS), 129.0 (C_q Bz), 94.5 (C_1), 84.2, 76.6, 76.0, 73.1 ($C_2/C_3/C_4/C_5$), 75.0, 74.7 (CH_2 Bn), 62.1 (C_6), 26.5 (CH_3 *t*-Bu), 19.0 (C_q *t*-Bu). MS (ESI): *m/z* 703 $(M+H)^+$, 725 $(M+Na)^+$.

Anal. Calcd for $C_{43}H_{46}O_7Si$ (702.3): C, 73.48; H, 6.60; Si, 4.00. Found: C, 73.40; H, 6.52; Si, 4.12.

1-*O*-Benzoyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-β-D-glucopyranose (22). A mixture of anomeric benzoate **20** (1.40 g, 2.0 mmol), thioethyl donor **21** (1.40 g, 2.4 mmol) and powdered molecular sieves (4 Å, 0.3 g) in 1,2-dichloroethane/diethyl ether (10 mL, 1:1, v/v) was stirred under a continuous stream of dry nitrogen. After 30 min, IDCT (1.55 g, 3.0 mmol) was added in one portion and the resulting mixture was stirred for 1 h, subsequently diluted with diethyl ether (100 mL) and washed with aq. $Na_2S_2O_3$ (1.0 M, 2 x 25 mL) and aq. $NaHCO_3$ (1.0 M, 2 x 25 mL). The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The resulting yellow oil was purified by silica gel chromatography (10-30% EtOAc/light petroleum) and LH-20 gel filtration (eluent: CH_2Cl_2/MeOH, 2:1, v/v) to give dimer **22** as a white solid (1.76 g, 1.44 mmol, 72%). ^1H NMR ($CDCl_3$): δ 8.10-7.00 (m, 45H, H_{arom}), 6.06 (d, 1H, H_1, $J_{1,2}$ = 8.1 Hz), 5.54 (d, 1H, $H_{1'}$, $J_{1',2'}$ = 3.6 Hz), 4.91 (AB, 2H, CH_2 Bn), 4.82 (AB, 2H, CH_2 Bn), 4.80 (AB, 2H, CH_2 Bn), 4.62 (AB, 2H, CH_2 Bn), 4.40 (AB, 2H, CH_2 Bn), 4.31 (AB, 2H, CH_2 Bn), 4.11 (dd, 1H, H_2, $J_{2,3}$ = 9.0 Hz), 4.05-3.93 (m, 3H, $H_4/H_5/H_{3'}$), 3.87 (t, 1H, H_3, $J_{3,4}$ = 9.2 Hz), 3.66 (dd, 1H, $H_{4'}$, $J_{3',4'}$ = 9.8 Hz, $J_{4',5'}$ = 9.4 Hz), 3.57 (dd, 1H, H_{6A}, $J_{5,6A}$ = 2.0 Hz, $J_{6A,6B}$ = 9.5 Hz), 3.51 (dd, 1H, $H_{2'}$, $J_{2',3'}$ = 9.7 Hz), 3.45 (dd, 1H, H_{6B}, $J_{5,6B}$ = 4.2 Hz), 3.37 (dd, 1H, $H_{6'A}$, $J_{5',6'A}$ = 1.8 Hz, $J_{6'A,6'B}$ = 10.9 Hz), 3.25 (dd, 1H, $H_{6'B}$, $J_{5',6'B}$ = 2.3 Hz), 1.04 (s, 9H, CH_3 *t*-Bu). ^{13}C NMR ($CDCl_3$): δ 164.4 (C=O Bz), 138.6, 138.6, 138.0, 137.9, 137.7, 137.6 (C_q Bn), 135.8-127.3 (C_{arom}), 133.4, 132.7 (C_q TBDPS), 129.2 (C_q Bz), 95.8, 95.2 ($C_1/C_{1'}$), 82.9, 81.8, 78.8, 78.1, 77.4, 76.0, 74.0, 69.9 ($C_2/C_3/C_4/C_5/C_{2'}/C_{3'}/C_{4'}/C_{5'}$), 75.5, 75.0, 74.8, 73.3, 73.2, 72.3 (CH_2 Bn), 67.7 ($C_{6'}$), 61.9 (C_6), 26.7 (CH_3 *t*-Bu), 19.3 (C_q *t*-Bu). MS (ESI): *m/z* 1226 $(M+H)^+$.

Anal. Calcd for $C_{77}H_{80}O_{12}Si$ (1225.1): C, 75.46; H, 6.58; Si, 2.29. Found: C 75.38; H, 6.58; Si, 2.27.

1,2-Di-*O*-*tert*-butyldiphenylsilyl-*sn*-glycerol (23). To a stirred solution of commercially available 1,2-*O*-isopropylidene-*sn*-glycerol (2.49 mL, 20 mmol) in DMF (100 mL) were added NaH (60% dispersion in mineral oil, 0.96 g, 24 mmol) and BnBr (2.85 mL, 24 mmol). After 1 h, the reaction mixture was quenched by addition of MeOH (3 mL) and concentrated *in vacuo*. The residue was taken up in diethyl ether (200 mL), washed with aq. NaCl (1.0 M, 2 x 50 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The resulting pale yellow oil was dissolved in AcOH (40 mL) and water (10 mL), heated under reflux for 1 h and subsequently concentrated *in vacuo*. Residual AcOH was removed by coevaporation with dioxane (3 x 50 mL), after which pyridine (100 mL) and TBDPSCl (13.0 mL, 50 mmol) were sequentially added. The

reaction mixture was stirred for 12 h and then quenched by addition of MeOH (3 mL). The resulting solution was concentrated under reduced pressure, dissolved in diethyl ether (200 mL) and washed with aq. $NaHCO_3$ (1.0 M, 3 x 50 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Traces of pyridine in the residue were removed by coevaporation with toluene (3 x 50 mL). The thus obtained yellow oil was dissolved in ethyl acetate (50 mL) and MeOH (10 mL), upon which palladium on charcoal (10% Pd, 500 mg) was added. The latter heterogeneous mixture was hydrogenated at elevated pressure (3 atm.) in a Parr apparatus for 12 h. The metal catalyst was removed by filtration and the filtrate was concentrated under reduced pressure. Purification of the residue was effected by silica gel chromatography (0-15% EtOAc/light petroleum) to give glycerol **23** as a colorless oil (7.72 g, 13.6 mmol, 68%). $[\alpha]_D$ = -24.8 ° (*c* 1.2, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.70-7.24 (m, 20H, H_{arom}), 3.86 (dd, 1H, H_1, $J_{1,1'}$ = 11.4 Hz, $J_{1,2}$ = 4.9 Hz), 3.82 (dd, 1H, $H_{1'}$, $J_{1',2}$ = 3.0 Hz), 3.72-3.65 (m, 2H, H_2/H_3), 3.58 (m, 1H, $H_{3'}$), 1.02, 0.98 (2 x s, 2 x 9H, CH_3 *t*-Bu). ^{13}C NMR ($CDCl_3$): δ 135.5-127.5 (C_{arom}), 133.3, 132.9 (C_q TBDPS), 73.4 (C_2), 64.7 (C_1), 63.9 (C_3), 26.7, 26.6 (CH_3 *t*-Bu), 19.9, 19.0 (C_q *t*-Bu).

1,2-Di-*O*-*tert*-butyldiphenylsilyl-3-*O*-(3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-α/β-D-glucopyranosyl)-*sn*-glycerol (25). A mixture of dimer benzoate **22** (0.61 g, 0.5 mmol), glycerol **23** (0.34 g, 0.6 mmol) and powdered molecular sieves (4 Å, 0.1 g) in 1,2-dichloroethane (3 mL) was stirred under a continuous stream of dry nitrogen for 15 min. To the latter mixture, TMSOTf was added in three portions at 5 min-intervals (3 x 48 μL, 3 x 0.25 mmol). Stirring was continued for 3 h and the reaction mixture was neutralized by addition of triethylamine (1 mL), diluted with diethyl ether (50 mL) and washed with aq. $NaHCO_3$ (3 x 25 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. Purification of the residue was effected with silica gel chromatography (0-15% EtOAc/light petroleum) to furnish **25** as a mixture of anomers (colorless oil, 0.68 g, 0.41 mmol, 81%, α:β = 8:1). ^{13}C NMR ($CDCl_3$): α-anomer: δ 139.8, 139.6, 139.0, 138.7, 138.4, 138.2 (C_q Bn), 137.9-129.0 (C_{arom}), 136.2, 135.8, 135.6, 135.4, 135.3, 135.1 (C_q TBDPS), 96.5 ($C_{1'}$, $J_{C,H}$ = 168.4 Hz), 94.5 ($C_{1''}$, $J_{C,H}$ = 170.0 Hz), 82.1, 81.1, 79.2, 77.8, 77.4, 74.4, 72.4, 71.3, 70.0 ($C_2/C_{2'}/C_{3'}/C_{4'}/C_{5'}/C_{2''}/C_{3''}/C_{4''}/C_{5''}$), 75.5, 75.4, 74.7, 73.3, 73.1, 71.5 (CH_2 Bn), 67.8 ($C_{6''}$), 65.4 (C_3), 62.7, 62.1 ($C_1/C_{6'}$), 25.2, 25.1, 24.9 (CH_3 *t*-Bu), 17.3, 17.2, 17.1 (C_q *t*-Bu); β-anomer: δ 139.7, 139.6, 139.1, 138.7, 138.4, 138.1 (C_q Bn), 137.9-129.0 (C_{arom}), 136.2, 135.8, 135.6, 135.4, 135.3, 135.1 (C_q TBDPS), 99.3 ($C_{1'}$, $J_{C,H}$ = 159.9 Hz), 94.9 ($C_{1''}$, $J_{C,H}$ = 170.6 Hz), 81.9, 80.0, 79.0, 77.8, 77.3, 74.5, 72.4, 71.3, 70.0 ($C_2/C_{2'}/C_{3'}/C_{4'}/C_{5'}/C_{2''}/C_{3''}/C_{4''}/C_{5''}$), 75.5, 75.4, 74.7, 73.3, 73.1, 71.5 (CH_2 Bn), 67.9 ($C_{6''}$), 64.7 (C_3), 63.2, 62.1 ($C_1/C_{6'}$), 25.2, 25.1, 24.9 (CH_3 *t*-Bu), 17.3, 17.2, 17.1 (C_q *t*-Bu). MS (ESI): *m/z* 1673 $(M+H)^+$, 1690 $(M+NH_4)^+$, 1695 $(M+Na)^+$.

Anal. Calcd for $C_{105}H_{118}O_{13}Si_3$ (1672.2): C, 75.41; H, 7.11; Si, 5.04. Found: C, 75.40; H, 7.16; Si, 5.00.

1,2-Di-*O*-allyl-3-*O*-(3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-α/β-D-glucopyranosyl)-*sn*-glycerol (26). A mixture of dimer benzoate **22** (0.61 g, 0.5 mmol), glycerol **24** (0.10 g, 0.6 mmol) and powdered molecular sieves (4 Å, 0.1 g) in 1,2-dichloroethane (3 mL) was stirred under a continuous stream of dry nitrogen for 15 min. To the latter mixture, TMSOTf was added in three portions at 5 min-intervals (3 x 48 μL, 3 x 0.25 mmol). Stirring was continued for 3 h and the reaction mixture was neutralized by addition of triethylamine (1 mL), diluted with EtOAc (50 mL) and washed with aq. $NaHCO_3$ (1.0 M, 3 x 25 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. Purification of the residue was effected with silica gel chromatography (10-25% EtOAc/light petroleum) to furnish anomeric mixture **26** as a white solid (0.47 g, 0.37 mmol, 74%, α:β = 6:1). ^{13}C NMR ($CDCl_3$): α-anomer: δ 138.6, 138.5, 138.3, 138.1, 137.7, 137.6 (C_q Bn), 134.7 (CH All), 133.8-127.5 (C_{arom}), 133.4, 133.0 (C_q TBDPS), 116.7 (CH_2 All), 95.6 ($C_{1'}$, $J_{C,H}$ = 171.2 Hz), 94.5 ($C_{1''}$, $J_{C,H}$ = 169.4 Hz), 81.9, 80.8, 79.0, 78.4, 77.8, 77.4, 76.5, 75.7, 71.5 ($C_2/C_{2'}/C_{3'}/C_{4'}/C_{5'}/C_{2''}/C_{3''}/C_{4''}/C_{5''}$), 76.1, 75.5, 74.8, 73.2, 72.1, 72.0, 71.2, 70.8 (6 x CH_2 Bn, 2 x CH_2 All), 69.9, 67.9, 67.1 ($C_1/C_3/C_{6''}$), 62.5 ($C_{6'}$), 26.7 (CH_3 *t*-Bu), 19.2 (C_q *t*-Bu); β-anomer: δ 138.6, 138.5, 138.3, 138.1, 137.7, 137.6 (C_q Bn), 134.7 (CH All), 133.8-127.5 (C_{arom}), 133.4, 133.0 (C_q TBDPS), 116.8 (CH_2 All), 103.5 ($C_{1'}$, $J_{C,H}$ = 161.8 Hz), 94.7 ($C_{1''}$, $J_{C,H}$ = 169.6 Hz), 82.7, 80.8, 79.0, 78.9, 78.4, 77.8, 76.6, 75.8, 71.6 ($C_2/C_{2'}/C_{3'}/C_{4'}/C_{5'}/C_{2''}/C_{3''}/C_{4''}/C_{5''}$), 76.0, 75.5, 74.8, 73.2, 72.1, 72.0, 70.4, 70.3 (6 x CH_2 Bn, 2 x CH_2 All), 69.9, 67.8, 67.1 ($C_1/C_3/C_{6''}$), 62.2 ($C_{6'}$), 26.7 (CH_3 *t*-Bu), 19.2 (C_q *t*-Bu). MS (ESI): *m/z* 1276 $(M+H)^+$, 1298 $(M+Na)^+$.

1,2-Di-*O*-allyl-3-*O*-(3,4-di-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-α-D-glucopyranosyl)-*sn*-glycerol (27). To a stirred solution of trimer **26** (0.47 g, 0.37 mmol) in THF (3 mL) was added tetra-*n*-butylammonium fluoride (1.0 M solution in THF, 0.5 mL). The reaction mixture was stirred for 2 h, subsequently diluted with EtOAc (50 mL) and washed with sat. aq. NaCl (3 x 25 mL). The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. Purification of the residue was effected with silica gel chromatography (10-50% EtOAc/light petroleum) to furnish primary alcohol **27** as a white solid (0.32 g, 0.31 mmol, 83% based on anomeric mixture **26**). ^1H NMR ($CDCl_3$): δ 7.38-7.03 (m, 30H, H_{arom}), 5.92 (m, 2H, CH All), 5.27, 5.21, 5.16, 5.09 (4 x dd, 4 x 1H, CH_2 All), 5.06 (d, 1H, $H_{1''}$, $J_{1'',2''}$ = 3.5 Hz), 5.03 (d, 1H, $H_{1'}$, $J_{1',2'}$ = 3.4 Hz), 4.91 (AB, 2H, CH_2 Bn), 4.87 (AB, 2H, CH_2 Bn), 4.76 (AB, 2H, CH_2 Bn), 4.60 (AB, 2H, CH_2 Bn), 4.54 (AB, 2H, CH_2 Bn), 4.46 (AB, 2H, CH_2 Bn), 4.07 (m, 2H, CH_2O All), 4.05 (t, 1H, $H_{3''}$, $J_{2'',3''} = J_{3'',4''}$ = 8.4 Hz), 4.02 (m, 1H, H_2), 3.99 (dd, 1H, $H_{3'}$, $J_{2',3'}$ = 9.0 Hz, $J_{3',4'}$ = 8.2

Hz), 3.97-3.90 (m, 6H, $H_{1A}/H_{1B}/H_{3A}/H_{3B}/CH_2O$ All), 3.80 (dt, 1H, $H_{5'}$, $J_{4',5'}$ = 9.7 Hz, $J_{5',6'A} = J_{5',6'B}$ = 4.8 Hz), 3.76 (dd, 1H, $H_{2'}$), 3.74 (m, 1H, $H_{5''}$), 3.66 (dd, 1H, $H_{4''}$, $J_{4'',5''}$ = 9.0 Hz), 3.63 (dd, 1H, $H_{6'A}$, $J_{6'A,6'B}$ = 10.8 Hz), 3.57 (dd, 1H, $H_{2''}$), 3.53 (m, 2H, $H_{6''A}/H_{6''B}$), 3.50 (dd, 1H, $H_{4'}$), 3.46 (dd, 1H, $H_{6'B}$), 1.70 (bs, 1H, OH). ^{13}C NMR ($CDCl_3$): δ 138.6, 138.1, 138.0, 137.9, 137.8, 137.7 (C_q Bn), 135.0, 134.6 (CH All), 128.8-127.8 (C_{arom}), 116.9, 116.8 (CH_2 All), 95.8, 94.5 ($C_{1'}/C_{1''}$), 81.9, 80.5, 79.0, 77.5, 77.4, 76.5, 75.4, 71.0, 70.3 ($C_2/C_{2'}/C_{3'}/C_{4'}/C_{5'}/C_{2''}/C_{3''}/C_{4''}/C_{5''}$), 75.9, 75.5, 75.0, 74.8, 73.6, 72.3 (CH_2 Bn), 72.2, 69.9, 69.5, 68.1, 67.3 (C_1/C_3/2 x CH_2O All/$C_{6''}$), 61.6 ($C_{6'}$).

3-*O*-(3,4-Di-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-α-D-glucopyranosyl)-*sn*-glycerol (28). Tetra-*n*-butylammonium fluoride (1.0 M solution in THF, 2.0 mL) was added to a stirred solution of trimer **25** (0.68 g, 0.41 mmol) in THF (5 mL). The reaction mixture was stirred for 4 h, subsequently diluted with EtOAc (50 mL) and washed with sat. aq. NaCl (3 x 25 mL). The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. Purification of the residue was accomplished by silica gel chromatography (10-80% EtOAc/light petroleum) to afford triol **28** as a white solid (0.31 g, 0.32 mmol, 78% based on anomeric mixture **25**). ^1H NMR ($CDCl_3$): δ 7.40-7.05 (m, 30H, H_{arom}), 4.95 (d, 1H, $H_{1'}$, $J_{1',2'}$ = 3.4 Hz), 4.90 (d, 1H, $H_{1''}$, $J_{1'',2''}$ = 3.9 Hz), 4.85 (AB, 2H, CH_2 Bn), 4.70 (AB, 2H, CH_2 Bn), 4.62 (AB, 2H, CH_2 Bn), 4.58 (AB, 2H, CH_2 Bn), 4.50 (AB, 2H, CH_2 Bn), 4.48 (AB, 2H, CH_2 Bn), 4.06 (dd, 1H, $H_{3''}$, $J_{2'',3''}$ = 7.9 Hz, $J_{3'',4''}$ = 8.9 Hz), 4.00 (t, 1H, $H_{3'}$, $J_{2',3'} = J_{3',4'}$ = 9.1 Hz), 3.97 (m, 2H, H_{3A}/H_{3B}), 3.92 (m, 1H, $H_{5''}$), 3.82 (dd, 1H, $H_{6''A}$, $J_{5'',6''A}$ = 4.0 Hz, $J_{6''A,6''B}$ = 10.7 Hz), 3.75 (dd, 1H, $H_{6''B}$, $J_{5'',6''B}$ = 5.3 Hz), 3.71 (dd, 1H, $H_{2'}$), 3.67-3.63 (m, 3H, $H_{5'}/H_{1A}/H_{1B}$), 3.61 (dd, 1H, $H_{4''}$, $J_{4'',5''}$ = 9.2 Hz), 3.57 (dd, 1H, $H_{2''}$), 3.50 (dd, 1H, $H_{4'}$, $J_{4',5'}$ = 8.4 Hz), 3.40 (dd, 1H, $H_{6'A}$, $J_{5',6'A}$ = 3.9 Hz, $J_{6'A,6'B}$ = 10.8 Hz), 3.33 (m, 1H, H_2), 3.30 (dd, 1H, $H_{6'B}$, $J_{5',6'B}$ = 5.6 Hz). ^{13}C NMR ($CDCl_3$): δ 138.4, 138.2, 138.0, 138.0, 137.9, 137.8 (C_q Bn), 128.4-127.6 (C_{arom}), 96.0, 94.9 ($C_{1'}/C_{1''}$), 81.9, 80.5, 79.3, 78.1, 77.8, 77.5, 77.4, 71.3, 70.4 ($C_2/C_{2'}/C_{3'}/C_{4'}/C_{5'}/C_{2''}/C_{3''}/C_{4''}/C_{5''}$), 75.9, 75.5, 75.1, 74.8, 73.3, 72.7 (CH_2 Bn), 71.6, 68.1, 68.0 ($C_1/C_3/C_{6''}$), 61.8 ($C_{6'}$).

1,2-Di-*O*-palmitoyl-3-*O*-(3,4-di-*O*-benzyl-6-*O*-palmitoyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-α-D-glucopyranosyl)-*sn*-glycerol (29). Palmitoyl chloride (0.11 mL, 0.36 mmol) was added dropwise to a stirred solution of triol **28** (95 mg, 0.10 mmol) in pyridine/CH_2Cl_2 (3 mL, 1:1, v/v). After 3 h, the reaction mixture was quenched by addition of H_2O (0.5 mL) and the solvents were removed by evaporation *in vacuo*. The residue was taken up in diethyl ether (25 mL) and washed thoroughly with aq. $NaHCO_3$ (1.0 M, 4 x 10 mL). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Traces of pyridine in the residue were removed by coevaporation with toluene (3 x 10 mL). Further purification was accomplished by LH-20 gel filtration

(eluent: CH_2Cl_2/MeOH, 2:1, v/v) to give fully protected glycolipid **29** as a greasy solid (154 mg, 0.092 mmol, 92%). ^1H NMR ($CDCl_3$): δ 7.36-7.05 (m, 30H, H_{arom}), 5.26 (m, 1H, H_2), 5.16 (d, 1H, $H_{1''}$, $J_{1'',2''}$ = 3.1 Hz), 5.14 (d, 1H, $H_{1'}$, $J_{1',2'}$ = 3.3 Hz), 4.92 (AB, 2H, CH_2 Bn), 4.87 (AB, 2H, CH_2 Bn), 4.82 (AB, 2H, CH_2 Bn), 4.70 (AB, 2H, CH_2 Bn), 4.62 (AB, 2H, CH_2 Bn), 4.49 (AB, 2H, CH_2 Bn), 4.34 (dd, 1H, H_{1A}, $J_{1A,1B}$ = 12.1 Hz, $J_{1A,2}$ = 3.2 Hz), 4.28 (d, 2H, $H_{6'A}/H_{6'B}$, $J_{5',6'}$ = 4.4 Hz), 4.20 (dd, 1H, H_{1B}, $J_{1B,2}$ = 6.3 Hz), 4.04 (t, 1H, $H_{3''}$, $J_{2'',3''} = J_{3'',4''}$ = 9.3 Hz), 3.98 (t, 1H, $H_{3'}$, $J_{2',3'} = J_{3',4'}$ = 8.9 Hz), 3.95 (m, 1H, $H_{5''}$), 3.85 (dt, 1H, $H_{5'}$, $J_{4',5'}$ = 10.0 Hz), 3.75 (dd, 1H, $H_{2'}$), 3.72 (dd, 1H, H_{3A}, $J_{2,3A}$ = 3.9 Hz, $J_{3A,3B}$ = 10.9 Hz), 3.69 (t, 1H, $H_{4''}$, $J_{4'',5''}$ = 9.4 Hz), 3.60 (dd, 1H, H_{3B}, $J_{2,3B}$ = 3.1 Hz), 3.58 (dd, 1H, $H_{2''}$), 3.48 (dd, 1H, $H_{4'}$), 3.46 (dd, 1H, $H_{6''A}$, $J_{5'',6''A}$ = 2.9 Hz, $J_{6''A,6''B}$ = 9.2 Hz), 3.37 (dd, 1H, $H_{6''B}$, $J_{5'',6''B}$ = 3.5 Hz), 2.37-2.22 (m, 6H, 3 x $CH_2\alpha$ palm.), 1.75-0.87 (m, 87H, CH_2/CH_3 palm.). ^{13}C NMR ($CDCl_3$): δ 173.2, 173.1, 172.7 (C=O palm.), 138.6, 138.4, 138.1, 137.9, 137.7, 137.6 (C_q Bn), 128.3-127.3 (C_{arom}), 96.2, 95.3 ($C_{1'}/C_{1''}$), 81.9, 80.4, 79.1, 77.7, 77.5, 75.9, 70.4, 69.7, 69.1 ($C_2/C_{2'}/C_{3'}/C_{4'}/C_{5'}/C_{2''}/C_{3''}/C_{4''}/C_{5''}$), 75.5, 75.0, 74.8, 73.2, 73.1, 72.9 (CH_2 Bn), 67.9 ($C_{6''}$), 66.3 (C_3), 62.5, 62.4 ($C_1/C_{6'}$), 34.0-22.6 (CH_2 palm.), 14.0 (CH_3 palm.).

1,2-Di-*O*-myristoyl-3-*O*-(3,4-di-*O*-benzyl-6-*O*-myristoyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-α-D-glucopyranosyl)-*sn*-glycerol (30). To a stirred solution of triol **28** (95 mg, 0.10 mmol) in pyridine/CH_2Cl_2 (3 mL, 1:1, v/v) was added dropwise myristoyl chloride (0.098 mL, 0.36 mmol). After 3 h, the reaction mixture was quenched by addition of H_2O (0.5 mL) and the solvents were removed by evaporation *in vacuo*. The residue was taken up in diethyl ether (25 mL) and washed thoroughly with aq. $NaHCO_3$ (1.0 M, 4 x 10 mL). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Traces of pyridine in the residue were removed by coevaporation with toluene (3 x 10 mL). Further purification was accomplished by LH-20 gel filtration (eluent: CH_2Cl_2/MeOH, 2:1, v/v) to give fully protected glycolipid **30** as a greasy solid (143 mg, 0.090 mmol, 90%). ^1H NMR ($CDCl_3$): δ 7.45-7.04 (m, 30H, H_{arom}), 5.24 (m, 1H, H_2), 5.16 (d, 1H, $H_{1''}$, $J_{1'',2''}$ = 3.1 Hz), 5.12 (d, 1H, $H_{1'}$, $J_{1',2'}$ = 3.3 Hz), 4.90 (AB, 2H, CH_2 Bn), 4.87 (AB, 2H, CH_2 Bn), 4.81 (AB, 2H, CH_2 Bn), 4.70 (AB, 2H, CH_2 Bn), 4.62 (AB, 2H, CH_2 Bn), 4.43 (AB, 2H, CH_2 Bn), 4.30 (dd, 1H, H_{1A}, $J_{1A,1B}$ = 12.1 Hz, $J_{1A,2}$ = 3.2 Hz), 4.29 (d, 2H, $H_{6'A}/H_{6'B}$, $J_{5',6'}$ = 4.4 Hz), 4.18 (dd, 1H, H_{1B}, $J_{1B,2}$ = 6.3 Hz), 4.02 (t, 1H, $H_{3''}$, $J_{2'',3''} = J_{3'',4''}$ = 9.3 Hz), 3.99 (t, 1H, $H_{3'}$, $J_{2',3'} = J_{3',4'}$ = 8.9 Hz), 3.96 (m, 1H, $H_{5''}$), 3.85 (dt, 1H, $H_{5'}$, $J_{4',5'}$ = 10.0 Hz), 3.74 (dd, 1H, $H_{2'}$), 3.71 (dd, 1H, H_{3A}, $J_{2,3A}$ = 3.9 Hz, $J_{3A,3B}$ = 10.9 Hz), 3.65 (t, 1H, $H_{4''}$, $J_{4'',5''}$ = 9.4 Hz), 3.59 (dd, 1H, H_{3B}, $J_{2,3B}$ = 3.1 Hz), 3.58 (dd, 1H, $H_{2''}$), 3.52 (dd, 1H, $H_{4'}$), 3.46 (dd, 1H, $H_{6''A}$, $J_{5'',6''A}$ = 2.9 Hz, $J_{6''A,6''B}$ = 9.2 Hz), 3.37 (dd, 1H, $H_{6''B}$, $J_{5'',6''B}$ = 3.5 Hz), 2.40-2.27 (m, 6H, 3 x $CH_2\alpha$ myr.), 1.80-0.80 (m, 75H, CH_2/CH_3 myr.). ^{13}C NMR ($CDCl_3$): δ 173.2, 173.0, 172.7 (C=O myr.), 138.6,

138.4, 138.0, 137.9, 137.7, 137.5 (C_q Bn), 128.3-127.3 (C_{arom}), 96.1, 95.3 ($C_{1'}/C_{1''}$), 82.1, 80.6, 79.2, 77.7, 77.5, 75.9, 70.6, 69.9, 69.4 ($C_2/C_{2'}/C_{3'}/C_4/C_{5'}/C_{2''}/C_{3''}/C_{4''}/C_{5''}$), 75.6, 75.0, 74.2, 73.2, 73.1, 72.7 (CH_2 Bn), 68.1 ($C_{6''}$), 66.4 (C_3), 62.6, 62.4 ($C_1/C_{6'}$), 35.1-22.6 (CH_2 myr.), 14.0 (CH_3 myr.).

1,2-Di-*O*-palmitoyl-3-*O*-[2-*O*-(α-D-glucopyranosyl)-6-*O*-palmitoyl-α-D-glucopyranosyl]-*sn*-glycerol (1a). Fully protected glycolipid **29** (154 mg, 0.092 mmol) was dissolved in CH_2Cl_2/MeOH (10 mL, 1:4, v/v). Palladium on charcoal (10% Pd, 100 mg) was added and the heterogeneous mixture was hydrogenated at elevated pressure (3 atm.) in a Parr apparatus for 12 h. The catalyst was filtered off and the resulting filtrate was concentrated *in vacuo* and subjected to silica gel column chromatography (0-10% MeOH/$CHCl_3$) to afford glycolipid **1a** as a white solid (100 mg, 0.088 mmol, 96%). $[\alpha]_D$ = +64.0 ° (*c* 0.2, MeOH). ^{1}H NMR (MeOD): δ 5.24 (m, 1H, H_2), 4.97 (d, 1H, $H_{1'}$, $J_{1',2'}$ = 3.3 Hz), 4.94 (d, 1H, $H_{1''}$, $J_{1'',2''}$ = 3.7 Hz), 4.41 (dd, 1H, H_{1A}, $J_{1A,1B}$ = 12.1 Hz, $J_{1A,2}$ = 3.3 Hz), 4.35 (dd, 1H, $H_{6'A}$, $J_{5',6'A}$ = 2.4 Hz, $J_{6'A,6'B}$ = 12.5 Hz), 4.26 (dd, 1H, $H_{6'B}$, $J_{5',6'B}$ = 5.4 Hz), 4.19 (dd, 1H, H_{1B}, $J_{1B,2}$ = 6.4 Hz), 3.90 (dd, 1H, H_{3A}, $J_{2,3A}$ = 4.0 Hz, $J_{3A,3B}$ = 10.8 Hz), 3.87 (m, 1H, $H_{5''}$), 3.78 (dd, 1H, $H_{3'}$, $J_{2',3'}$ = 8.9 Hz, $J_{3',4'}$ = 9.4 Hz), 3.72 (t, 1H, $H_{3''}$, $J_{2'',3''} = J_{3'',4''}$ = 9.1 Hz), 3.71-3.68 (m, 3H, $H_{5'}/H_{6''A}/H_{6''B}$), 3.62 (dd, 1H, $H_{2'}$), 3.60 (dd, 1H, H_{3B}, $J_{2,3B}$ = 3.0 Hz), 3.46 (dd, 1H, $H_{4'}$, $J_{4',5'}$ = 9.2 Hz), 3.42 (dd, 1H, $H_{2''}$), 3.34 (dd, 1H, $H_{4''}$, $J_{4'',5''}$ = 8.6 Hz), 2.40-2.28 (m, 6H, 3 x $CH_2\alpha$ palm.), 1.35-0.83 (m, 87H, CH_2/CH_3 palm.). ^{13}C NMR (MeOD): δ 174.0, 173.9, 173.3 (C=O palm.), 96.3, 96.1 ($C_{1'}/C_{1''}$), 75.9, 73.4, 72.0, 71.7, 71.6, 70.1, 69.8, 69.6, 69.5 ($C_2/C_{2'}/C_{3'}/C_4/C_{5'}/C_{2''}/C_{3''}/C_{4''}/C_{5''}$), 65.6 ($C_3$), 63.2, 62.4, 61.5 ($C_1/C_{6'}/C_{6''}$), 34.0-22.4 ($CH_2$ palm.), 13.8 (CH_3 palm.). MS (ESI): *m/z* 1132 $(M+H)^+$.

Anal. Calcd for $C_{63}H_{118}O_{16}$ (1131.3): C, 66.87; H, 10.51. Found: C, 66.76; H, 10.60.

1,2-Di-*O*-myristoyl-3-*O*-[2-*O*-(α-D-glucopyranosyl)-6-*O*-myristoyl-α-D-glucopyranosyl]-*sn*-glycerol (1b). Fully protected glycolipid **30** (143 mg, 0.090 mmol) hydrogenated and purified as described for compound **1a** to give glycolipid **1b** as a white solid (88 mg, 0.085 mmol, 94%). $[\alpha]_D$ = +60.9 ° (*c* 0.2, MeOH). ^{1}H NMR (MeOD): δ 5.28 (m, 1H, H_2), 4.99 (d, 1H, $H_{1'}$, $J_{1',2'}$ = 3.3 Hz), 4.94 (d, 1H, $H_{1''}$, $J_{1'',2''}$ = 3.7 Hz), 4.40 (dd, 1H, H_{1A}, $J_{1A,1B}$ = 12.1 Hz, $J_{1A,2}$ = 3.5 Hz), 4.35 (dd, 1H, $H_{6'A}$, $J_{5',6'A}$ = 2.6 Hz, $J_{6'A,6'B}$ = 12.5 Hz), 4.29 (dd, 1H, $H_{6'B}$, $J_{5',6'B}$ = 5.4 Hz), 4.19 (dd, 1H, H_{1B}, $J_{1B,2}$ = 6.4 Hz), 3.91 (dd, 1H, H_{3A}, $J_{2,3A}$ = 4.0 Hz, $J_{3A,3B}$ = 11.0 Hz), 3.82 (m, 1H, $H_{5''}$), 3.76 (dd, 1H, $H_{3'}$, $J_{2',3'}$ = 8.9 Hz, $J_{3',4'}$ = 9.4 Hz), 3.72 (t, 1H, $H_{3''}$, $J_{2'',3''} = J_{3'',4''}$ = 9.1 Hz), 3.71-3.66 (m, 3H, $H_{5'}/H_{6''A}/H_{6''B}$), 3.62 (dd, 1H, $H_{2'}$), 3.60 (dd, 1H, H_{3B}, $J_{2,3B}$ = 3.3 Hz), 3.40 (dd, 1H, $H_{4'}$, $J_{4',5'}$ = 9.2 Hz), 3.41 (dd, 1H, $H_{2''}$), 3.30 (dd, 1H, $H_{4''}$, $J_{4'',5''}$ = 8.6 Hz), 2.43-2.19 (m, 6H, 3 x $CH_2\alpha$ myr.), 1.39-0.81 (m, 75H, CH_2/CH_3 myr.). ^{13}C NMR (MeOD): δ 174.2, 173.9,

173.1 (C=O myr.), 96.4, 96.2 ($C_{1'}/C_{1''}$), 76.1, 73.4, 72.0, 71.7, 71.6, 70.3, 69.8, 69.7, 69.5 ($C_2/C_{2'}/C_{3'}/C_{4'}/C_{5'}/C_{2''}/C_{3''}/C_{4''}/C_{5''}$), 66.8 ($C_3$), 63.3, 62.4, 61.5 ($C_1/C_{6'}/C_{6''}$), 35.1-22.9 ($CH_2$ myr.), 13.9 (CH_3 myr.). MS (ESI): *m/z* 1048 $(M+H)^+$.

Anal. Calcd for $C_{57}H_{106}O_{16}$ (1047.1): C, 65.36; H, 10.20. Found: C, 65.30; H, 10.25.

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