Pergamon

Tetrahedron 56 (2000) 8451–8459

TETRAHEDRON

Concise Synthesis of 3-*O*-(2-*O*-α-D-Glucopyranosyl-6-*O*-acyl-α-D-glucopyranosyl)-1,2-di-*O*-acyl-*sn*-glycerols

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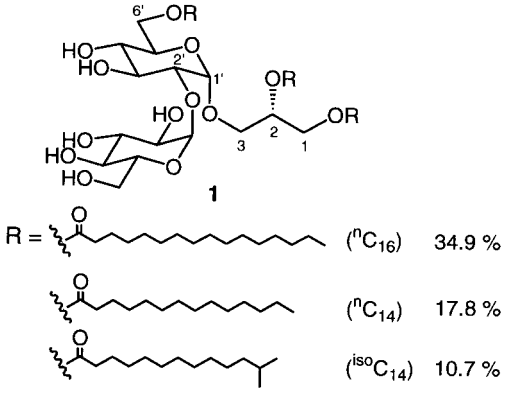
Received 12 July 2000; accepted 4 September 2000

Abstract—A versatile synthetic route to 3-*O*-(2-*O*-α-D-glucopyranosyl-6-*O*-acyl-α-D-glucopyranosyl)-1,2-di-*O*-acyl-*sn*-glycerols, which should provide various acyl derivatives, has been developed.

Introduction

Mycoplasmas, single-celled organisms resembling bacteria but lacking a cell wall, have been frequently isolated from tissue and urine of patients infected with human immunodeficiency virus type 1 (HIV-1).[1] Therefore, mycoplasma infection is suspected as one of the cofactors associated with the progression of acquired immunodeficiency syndrome (AIDS).[2] Arai et al. found that cell membranes from a strain of mycoplasma *Acholeplasma laidlawii* enhanced replication of HIV-1 in vitro experiments.[3] Recently, they isolated an active compound, 3-*O*-(2-*O*-α-D-glucopyranosyl-6-*O*-acyl-α-D-glucopyranosyl)-1,2-di-*O*-acyl-*sn*-glycerol (**1**), as a mixture of various acyl derivatives, while hexadecanoyl (palmitoyl, $^{n}C_{16}$), tetradecanoyl (myristoyl, $^{n}C_{14}$), and 12-methyltridecanoyl (isomyristoyl, $^{iso}C_{14}$) components predominate.[4] Synthesis of **1** [R(C6′)=$^{n}C_{18}$, R(C2,C3)=$^{n}C_{16}$] was reported by van Boom et al.[5] However, a shorter and more versatile synthetic route to **1** with various acyl groups is required for the structure–activity relationship studies. Therefore, we planned to introduce acyl groups at latest step. We describe herein a concise synthesis of **1**.



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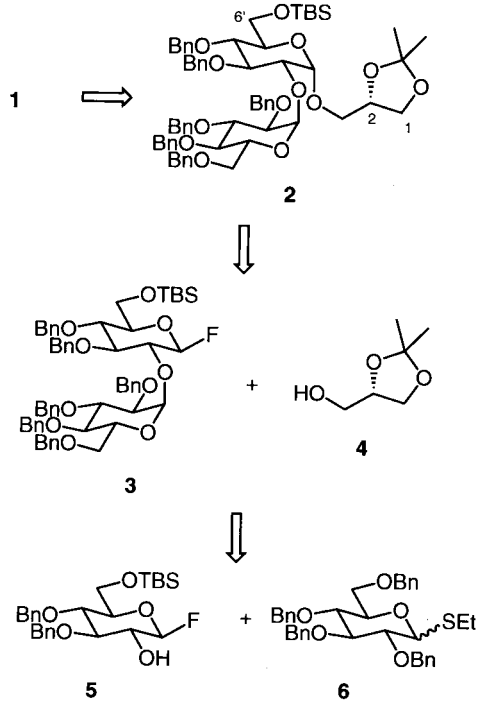
Result and Discussion

Our synthesis plan is outlined in Scheme 1. A properly protected diglycosyl glycerol derivative (**2**) was envisaged



Scheme 1. Synthesis plan.

Keywords: glycolipids; HIV-1 replication; glycosylation; stereocontrolled synthesis.

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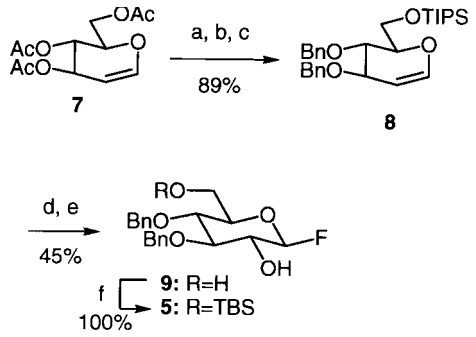
0040–4020/00/$ - see front matter
PII: S0040-4020(00)00793-6



Scheme 2. *Regents and conditions:* (a) NaOMe, MeOH; (b) TIPSCl, DMF, imidazole; (c) BnBr, NaH, DMF; (d) dimethyldioxirane, CH_2Cl_2, 0°C; (e) TBAF, THF; (f) TBSCl, Et_3N, DMAP, CH_2Cl_2.

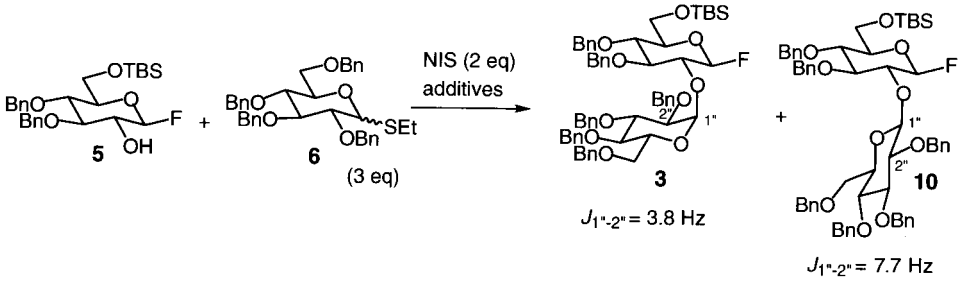
as a key intermediate, in which C6′- and C1, C2-alcohols are protected as TBS ether and acetonide, respectively, while others are all protected as benzyl ethers. Thus, selective deprotection would enable us to acylate only the C6′- and C1, C2-alcohols, and furthermore to differentiate between them. The compound (**2**) can be synthesized starting with glycosyl fluoride (**5**) and thioglycoside (**6**) as well as **4** via disaccharide (**3**) through successive α-selective glycosylations.

Synthesis of glycosyl fluoride **5** is shown in Scheme 2. Commercially available tri-*O*-acetyl-D-glucal (**7**) was converted to **8** via methanolysis of the acetate and protection of the resulting triol as triisopropylsilyl (TIPS) and benzyl ethers. Epoxidation of **8** with 2,2-dimethyldioxirane[6,7] followed by treatment with tetrabutylammonium fluoride (TBAF)[8] resulted in the formation of glycosyl fluoride **9** as a single isomer.[9] Selective protection of the primary alcohol as *tert*-butyldimethylsilyl (TBS) ether gave **5**.

Glycosylation of **5** with thioglycoside (**6**) as a 1:1 anomeric mixture[10] using *N*-iodosuccinimide (NIS) was carefully examined. The results are summarized in Table 1. Use of trifluoromethanesulfonic acid (TfOH)[11,12] as an activator in ether gave a 1.5:1 mixture of α-(**3**) and β-glycoside **10** (entry 1), whereas that in a mixed solvent of toluene and 1,4-dioxane[13] afforded a better ratio (α:β=2.2:1) (entry 2). More substantial α-selectivities were obtained by adding lithium salts as an activator in ether (α:β=4–5:1),[14] while $LiClO_4$ (10 mol%) was more effective (entry 3) than $LiNO_3$ (120 mol%) (entry 4). Higher α-selectivity (α:β=7.3:1) was obtained by using $LiClO_4$ in the mixed solvent (entry 5).[13] Presence of silica gel in the reaction mixture dramatically improved the α-selectivity (α:β=12:1) (entry 6),[14] and the use of large excess of **6** increased the yield up to 73% (α:β=13:1, entry 7). Since **3** and **10** were inseparable, pure **3** was isolated by conversion to the corresponding 6′-free alcohol (see Experimental Section), which was then protected as TBS ether **3** and was used for examination of the subsequent coupling with **4** (Table 2). However, the 13:1 mixture of **3** and **10** could be used for the practical synthesis, because the minor isomer derived from **10** was easily removed from **2** by silica gel column chromatography.

Having completed the synthesis of the glycosyl fluoride (**3**), glycosylation of (*S*)-isopropylideneglycerol (**4**) with **3** was then examined (Table 2). It was found that a racemization of **4** via migration of the isopropylidene group readily occurred under the glycosylation conditions using Lewis acids. However, Danishefsky reported that Mukaiyama method[15] in the presence of 2,6-di-*tert*-butylpyridine (DTBP) can prevent **4** from racemization.[9] Therefore, the glycosylation between **3** and **4** was attempted according to the Danishefsky's protocol ($SnCl_2$, $AgClO_4$, DTBP, and MS4A in ether at room temperature): The α-glycoside (**2**) was obtained as a single product, though the yield was low (entry 1), while the use of larger excess of both promoters and **4** gave 55% yield of **2** (entry 2). Glycosyl fluoride (**3**) was completely consumed, when the reaction was carried out in a sealed tube at 50°C, to give **2** in 68% yield, whereas the C2-epimer (**11**) (~10 %) was formed due to the partial

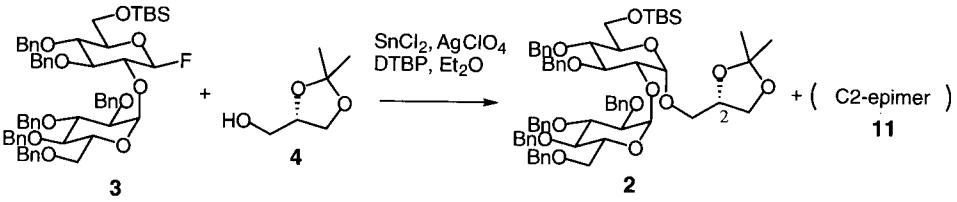
Table 1. Glycosylation of **5** with **6** using NIS and activators



Entry	Additives	Solvent	Time	Yield (%)[a]	Ratio (**3**:**10**)[b]
1	TfOH (3 mol%)	Et_2O	5 min	57 (31)	1.5:1
2	TfOH (5 mol%)	Toluene/dioxane=3/1	5 min	48 (50)	2.2:1
3	$LiClO_4$ (10 mol%)	Et_2O	12 h	59 (41)	3.9:1
4	$LiNO_3$ (120 mol%)	Et_2O	12 h	52[c] (48)	5.0:1
5	$LiClO_4$ (5 mol%)	Toluene/dioxane=3/1	4.5 days	24 (69)	7.3:1
6	$LiClO_4$ (7 mol%), SiO_2	Toluene/dioxane=3/1	3.7 days	50 (23)	12:1
7	$LiClO_4$ (7 mol%), SiO_2	Toluene/dioxane=3/1	3.5 days	73 (0)[d]	13:1

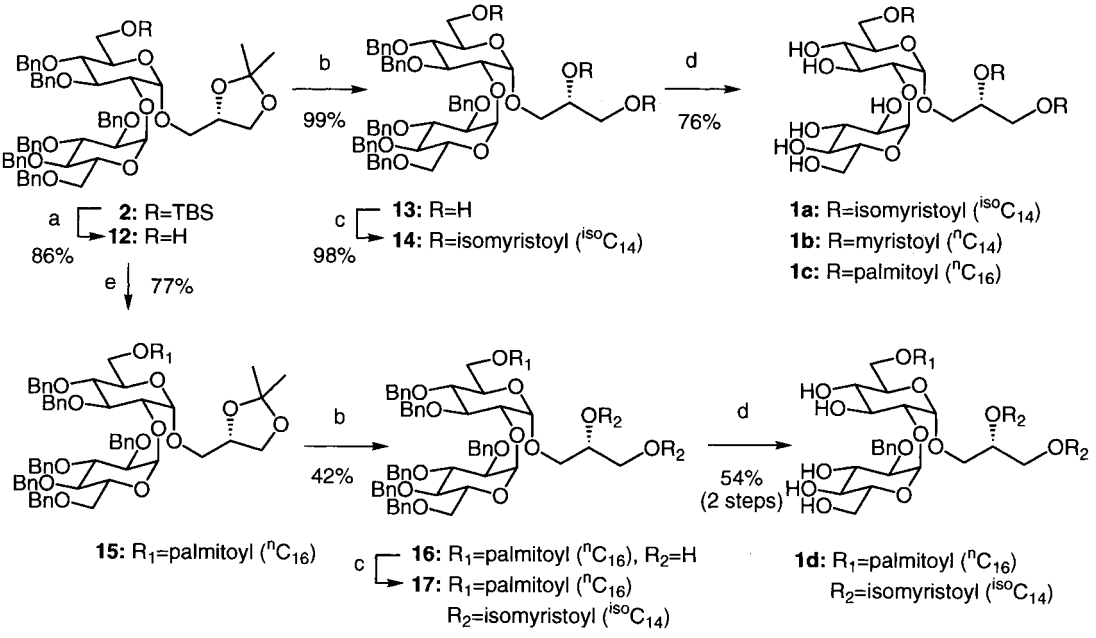
[a] Shown in parentheses is the recovered yield of **5**.
[b] Determined by 200 MHz ^{1}H NMR.
[c] Contaminated with unknown by-products.
[d] Six equivalents of **6** used.

Table 2. Glycosylation of **4** with **3**



Entry	$SnCl_2$/eq	$AgClO_4$ (equiv.)	DTBP (equiv.)	**4** (equiv.)	Temp	Time (h)	Yield (%)[a]
1	2	2	3	10	rt	60	17 (78)
2	4	4	6	25	rt	112	55 (17)
3	4	4	6	25	50°C[b]	40	68[c] (0)
4	4	4	6	20	rt[b]	312	81 (0)

[a] Shown in parentheses is the recovered yield of **3**.
[b] Reaction was performed in a sealed tube.
[c] A mixture of **2** and the C2-epimer (**11**) in 10:1 ratio.



Scheme 3. *Regents and conditions:* (a) TBAF, THF; (b) HCl, MeOH–toluene (9:2); (c) EDC, DMAP, isomyristic acid, CH_2Cl_2; (d) H_2, Pd/C, AcOEt–EtOH (5:1); (e) EDC, DMAP, palmitic acid, CH_2Cl_2.

racemization of **4** (entry 3). The best result was achieved by lengthening the reaction time at room temperature in a sealed tube: **2** was isolated in 81 % yield without contamination of **11** (entry 4).

Removal of the TBS group of **2** with TBAF gave alcohol (**12**). Hydrolysis of the acetonide with 1N HCl in methanol–toluene (9:2) yielded triol (**13**). Condensation of **13** with isomyristic acid using 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC) gave a triacyl derivative (**14**). Hydrogenolysis of the benzyl ethers of **14** gave **1a** as colorless amorphous solid. The 500 MHz ^1H and ^{13}C NMR spectra of the synthetic **1a** are identical with those of the corresponding component of the natural product. Trimyristoyl (**1b**) and tri-palmitoyl derivative (**1c**) were also synthesized from **13** by the analogous sequences. Furthermore, **12** was converted to 6′-*O*-palmitoyl-1,2-*O*-isomyristoyl derivative (**1d**). Acylation of **12** with palmitic acid resulted in the formation of **15**. Hydrolysis of the acetonide followed by acylation of **16** with isomyristic acid and removal of the benzyl groups afforded **1d**. Synthetic **1a**, **1b** and **1c** showed the biological activities similar to the natural product (Scheme 3).[4]

In conclusion, we established a versatile synthetic route to **1** which can have the discrete acyl groups. The present synthesis will provide various acyl derivatives required for the studies on the structure–activity relationship and on the mode of action.

Experimental

General methods

Analytical thin-layer chromatography was performed on Merck silica gel 60 F_{254} plates (0.25 mm). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL α-500,

a Varian Inova 500, a Varian Gemini 200, or a Varian Mercury 2000 instrument. Chemical shifts are reported in δ (ppm) with reference to solvent signals as internal standards [^{1}H NMR: $CHCl_3$ (7.26 ppm), CHD_2OD (3.30 ppm); ^{13}C NMR: $CDCl_3$ (77.0 ppm)]. Signal patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad peak. Coupling constants (J) are given in hertz. Infrared (IR) spectra were recorded on a JASCO FT-IR 7000. Specific rotations were measured on a JASCO DIP-370 polarimator. MALDI TOF-MS spectra were recorded on a PerSeptive Biosystems Voyager™ DE STR SI-3. Elemental analyses were conducted with a Yanaco CHN recorder MT-5. Column chromatography and flash column chromatography were performed using Merck 70–230 mesh silica gel 60 and Merck 230–400 mesh silica gel 60, respectively. Melting points were measured on a Yanaco MP-S3 micro melting point apparatus. Commercial methanol was used without further purification. The following solvents were distilled under positive pressure of dry nitrogen immediately before use: THF from sodium benzophenone ketyl, ether from $LiAlH_4$, toluene, 1,4-dioxane and CH_2Cl_2 from CaH_2. DMF was distilled from CaH_2 under reduced pressure.

3,4-Di-*O*-benzyl-6-*O*-triisopropylsilyl-α-D-glucal (8). To a stirred solution of 3,4,6-tri-*O*-acetyl-D-glucal (**7**) (20.2 g, 74.1 mmol) in methanol (80 mL) was added a solution of sodium methoxide (60.8 mg, 1.17 mmol) in methanol (10 mL). After stirring for 40 min at ambient temperature, the solvent was removed in vacuo, and the residue was dissolved in DMF (98 mL). Imidazole (15.3 g, 225 mmol) and chlorotriisopropylsilane (16 mL, 75.6 mmol) were added to the mixture and stirred at ambient temperature for 2 h. The reaction mixture was diluted with H_2O and extracted with ether. The combined organic layers were washed with H_2O and brine, dried over $MgSO_4$. Concentration followed by silica gel column chromatography gave 6-*O*-triisopropylsilyl-α-D-glucal as colorless oil: $[\alpha]_D^{24}=-1.73°$ (c 0.98, $CHCl_3$); IR (film) ν 3362, 2952, 2870, 1649, 1464, 1386, 1238, 1108, 1054, 998, 949, 882, 779, 743, 681, 663, 644 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.99–1.12 (21H, m, TIPS), 2.59 (1H, brs, 4-OH), 3.47 (1H, brs, 3-OH), 3.78–3.86 (2H, m, H6×2), 3.92–4.13 (2H, m, H4, H5), 4.31–4.24 (1H, m, H3), 4.72 (1H, dd, J=5.7, 2.1 Hz, H2), 6.29 (1H, dd, J=5.7, 1.6 Hz, H1); ^{13}C NMR (50 MHz, $CDCl_3$) δ 11.7, 17.8, 64.6, 69.3, 72.9, 76.1, 102.4, 144.0; MALDI TOF-MS Calcd for M+Na$^+$ ($C_{15}H_{30}O_4SiNa$): 325.181. Found: 325.181. Anal. Calcd for $C_{15}H_{30}O_4Si$:C, 59.56; H, 10.00. Found: C, 59.27; H, 9.97.

To a stirred solution of the glucal in DMF (96 mL) was added sodium hydride (60% dispersion in mineral oil, 6.1 g, 152 mmol) at 0°C and stirred for 5 min. After stirring the reaction mixture was added benzyl bromide (16.8 mL, 141 mmol) and allowed to warm to ambient temperature with stirring for 10 h. The reaction was quenched with H_2O, and extracted with ether. The organic layer was washed with H_2O and brine, dried over $MgSO_4$. Concentration followed by flash column chromatography gave **8** (31.9 g, 66.0 mmol, 89%) as pale yellow oil: $[\alpha]_D^{25}=-2.61°$ (c 1.14, $CHCl_3$); IR (film) ν 3068, 3032, 2946, 2866, 1651, 1497, 1458, 1390, 1359, 1330, 1286, 1241, 1212, 1149, 1106, 1029, 884, 783, 733 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.07–1.12 (21H, m, TIPS), 3.93–4.12 (4H, m, H4, H5 and H6×2), 4.20–4.27 (1H, m, H3), 4.59 (1H, d, J=11.2 Hz, Bn), 4.66 (1H, d, J=11.2 Hz, Bn), 4.78 (1H, d, J=10.7 Hz, Bn), 4.86 (1H, dd, J=5.8, 2.7 Hz, H2), 4.88 (1H, d, J=10.7 Hz, Bn), 6.42 (1H, dd, J=5.8, 1.3 Hz, H1), 7.27–7.42 (10H, m, Bn); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.0, 18.0, 62.0, 70.7, 73.9, 74.1, 75.7, 78.2, 99.6, 127.6–128.4, 138.5, 138.5, 144.8; MALDI TOF-MS Calcd for M+Na$^+$ ($C_{29}H_{42}O_4SiNa$): 505.275. Found: 505.275. Anal. Calcd for $C_{29}H_{42}O_4Si$: C, 72.16; H, 8.77. Found: C, 72.13; H, 8.77.

3,4-Di-*O*-benzyl-β-D-glucopyranosyl fluoride (9). To a stirred solution of **8** (4.02 g, 8.32 mmol) in CH_2Cl_2 (100 mL) was added a solution of dimethyldioxirane (60 mM) in acetone (158 mL, 9.48 mmol) in one portion at 0°C. After the mixture was stirred for 1 h at 0°C, the solvent was removed in vacuo. The residue was dissolved in THF (42 mL), and a solution of tetra-*n*-butylammonium fluoride (58 mL, 1 M in THF, stored over molecular sieves) was added. After being stirred at ambient temperature overnight, the reaction mixture was diluted with $CHCl_3$. The organic layer was washed successively with H_2O (3 times) and brine (2 times), dried over $MgSO_4$, and concentrated in vacuo. The residue was filtered through a plug of silica gel eluted with a mixture of *n*-hexane and AcOEt (1/1), and purified by recrystallization from ether to give **9** (1.36 g, 3.75 mmol, 45%) as a white solid: mp 117°C; $[\alpha]_D^{26}=+23.6°$ (c 0.99, $CHCl_3$); IR (KBr) ν 3392, 3268, 2924, 1456, 1363, 1158, 1114, 1067, 1048, 1017, 978, 735, 694, 634 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.90 (1H, t, J=6.4 Hz, 6-OH), 2.46 (1H, brs, 2-OH), 3.51–3.76 (4H, m, H2, H3, H4, H5), 3.76–3.95 (2H, m, H6×2), 4.68 (1H, d, J=10.4 Hz, Bn), 4.83 (1H, d, J=11.5 Hz, Bn), 4.84 (1H, d, J=10.4 Hz, Bn), 4.88 (1H, d, J=11.5 Hz, Bn), 5.17 (1H, dd, J=51.2, 5.8 Hz, H1), 7.26–7.40 (10H, m, Bn); ^{13}C NMR (50 MHz, $CDCl_3$) δ 61.6, 73.4 (d, J=23.2 Hz), 74.9, 75.1, 75.7 (d, J=3.8 Hz), 76.2, 82.6 (d, J=9.9 Hz), 109.1 (d, J=213.6 Hz), 127.9–128.7, 137.5, 138.1; MALDI TOF-MS Calcd for M+Na$^+$ ($C_{20}H_{23}O_5FNa$): 385.143. Found: 385.143. Anal. Calcd for $C_{20}H_{23}O_5F$: C, 66.29; H, 6.40. Found: C, 66.37; H, 6.39.

3,4-Di-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl fluoride (5). To a stirred solution of **9** (194 mg, 535 μmol), triethylamine (225 μL, 1.61 mmol), and 4-*N*,*N*-dimethylaminopyridine (8.3 mg, 68 μmol, DMAP) in CH_2Cl_2 (2.7 mL) was added TBSCl (117 mg, 778 μmol), and the solution was stirred at ambient temperature for 15 h. The reaction mixture was quenched with aqueous saturated sodium bicarbonate and extracted with ether. The organic layer was washed with brine, and dried over $MgSO_4$. Concentration followed by column chromatography gave **5** (255 mg, 535 μmol, 100%) as pale yellow oil: $[\alpha]_D^{26}=+19.7°$ (c 1.05, $CHCl_3$); IR (film) ν 3426, 3092, 3068, 3034, 2928, 2886, 2860, 1497, 1458, 1390, 1363, 1311, 1255, 1216, 1081, 1007, 990, 940, 919, 837, 814, 777, 752, 698 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.10 (6H, s, TBS), 0.94 (9H, s, TBS), 2.72 (1H, brs, 2-OH), 3.48–4.02 (6H, m, H2, H3, H4, H5, H6×2), 4.74 (1H, d, J=10.6 Hz, Bn), 4.84 (1H, d, J=10.7 Hz, Bn), 4.84 (1H, d, J=10.6 Hz, Bn), 4.87 (1H, d, J=10.7 Hz, Bn), 5.18 (1H, dd,

J=50.8, 6.1 Hz, H1), 7.31–7.43 (10H, m, Bn); ^{13}C NMR (50 MHz, $CDCl_3$) δ −5.4, −5.2, 18.2, 25.8, 61.8, 72.8 (d, J=23.8 Hz), 74.4, 74.8, 75.9, 75.9 (d, J=4.5 Hz), 81.8 (d, J=9.1 Hz), 108.9 (d, J=213.2 Hz), 127.9–128.5, 137.8, 138.1; MALDI TOF-MS Calcd for M+Na$^+$ ($C_{26}H_{37}O_5FNa$): 499.229. Found: 499.229. Anal. Calcd for $C_{26}H_{37}O_5FSi$: C, 65.52; H, 7.82. Found: C, 65.27; H, 7.87.

2-*O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl fluoride (3). To a mixture of **5** (315 mg, 660 μmol) and ethyl-2,3,4,6-tetra-*O*-benzyl-1-thio-D-glucopyranose (**6**) (1.99 g, 3.55 mmol), molecular sieves 4 Å (3.0 g) and silica gel (3.0 g) in a mixed solvent of toluene (1.5 mL) and dioxane (4.5 mL) was added *N*-iodosuccinimide (905 mg, 3.97 mmol, NIS) and lithium perchlorate (4.5 mg, 42 μmol) at ambient temperature, and the mixture was stirred at ambient temperature for 89 h under Ar atmosphere. The reaction was quenched with saturated aqueous sodium bicarbonate and aqueous sodium thiosulfate, the mixture was diluted with ether. The resulting precipitates were removed by filtration. The organic layer was washed with brine and dried over $MgSO_4$. Concentration followed by flash column chromatography gave a mixture of **3** and **10** (483 mg, 483 μmol, 73%, α:β=13:1) as colorless oil. To isolate **3**, a solution of **3** and **10** (18.4 mg, 18.4 μmol) in THF (1.0 mL) was treated with TBAF (50 μL, 1 M in THF), and the mixture was stirred at ambient temperature for 23 h. The solvent was evaporated and the residue was purified by flash column chromatography. 2-*O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-3,4-di-*O*-benzyl-β-D-glucopyranosyl fluoride (6′-OH free **3**) (9.6 mg, 10.8 mmol, 59%) was separated from 2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-3,4-di-*O*-benzyl-β-D-glucopyranosyl fluoride (6′-OH free **10**) (4.8 mg, 5.4 μmol, 30%) as colorless oil. To a stirred solution of 6′-OH free **3** (54.0 mg, 62.7 μmol) and imidazole (18.8 mg, 277 μmol) in DMF (2.8 mL) was added TBSCl (28.1 mg, 186 μmol), and the solution was stirred at ambient temperature for 5 h. The reaction mixture was diluted with H_2O and extracted with ether. The combined organic layers were washed with brine and dried over $MgSO_4$. Concentration followed by silica gel column chromatography gave pure **3** (53.3 mg, 54.1 mmol, 86%) as colorless oil.

2-*O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-3,4-di-*O*-benzyl-β-D-glucopyranosyl fluoride (6′-OH free 3). $[\alpha]_D^{25}$=+52.0° (*c* 0.92, $CHCl_3$); IR (film) ν 3470, 3090, 3066, 3034, 2924, 2872, 1497, 1456, 1363, 1311, 1261, 1212, 1102, 915, 804, 737, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.85 (1H, dd, J=8.3, 5.7 Hz, 6′-OH), 3.28 (1H, dd, J=11.2, 3.9 Hz, H6″), 3.30 (1H, dd, J=11.2, 2.1 Hz, H6″), 3.51–3.55 (1H, m, H5′), 3.60 (1H, dd, J=9.7, 3.8 Hz, H2″), 3.67 (1H, dd, J=10.1, 9.1 Hz, H4″), 3.71–3.76 (2H, m, H3′, H4′), 3.76 (1H, ddd, J=12.4, 8.3, 4.0 Hz, H6′), 3.82 (1H, ddd, J=11.4, 8.9, 6.9 Hz, H2′), 3.90 (1H, ddd, J=12.4, 5.7, 2.6 Hz, H6′), 3.96 (1H, dd, J=9.7, 9.1 Hz, H3″), 3.98 (1H, ddd, J=10.1, 3.9, 2.1 Hz, H5″), 4.27 (1H, d, J=11.9 Hz, Bn), 4.40 (1H, d, J=11.0 Hz, Bn), 4.51 (1H, d, J=11.9 Hz, Bn), 4.68 (1H, d, J=11.0 Hz, Bn), 4.72 (2H, s, Bn), 4.77 (1H, d, J=10.9 Hz, Bn), 4.80(1H, d, J=11.0 Hz, Bn), 4.83 (1H, d, J=10.9 Hz, Bn), 4.87 (1H, d, J=11.0 Hz, Bn), 4.89 (1H, d, J=10.9 Hz, Bn), 4.98 (1H, d, J=10.9 Hz, Bn), 5.32 (1H, d, J=3.8 Hz, H1″), 5.40 (1H, dd, J=53.1, 6.9 Hz, H1′), 7.05–7.37 (30H, m, Bn); ^{13}C NMR (125 MHz, $CDCl_3$) δ 61.3, 67.8, 70.2, 73.1, 73.3, 74.9, 75.1, 57.5 (d, J=4.6 Hz), 75.6, 75.8, 76.1 (d, J=20.5 Hz), 77.2, 77.5, 79.4, 81.8, 81.8 (d, J=11.4 Hz), 96.0 (d, J=6.3 Hz), 110.2 (d, J=214.1 Hz), 127.4–128.5, 137.4, 137.4, 137.7, 137.9, 138.6, 138.8; MALDI TOF-MS Calcd for M+Na$^+$ ($C_{54}H_{57}O_{10}FNa$):907.383. Found: 907.389. Anal. Calcd for $C_{54}H_{57}FO_{10}$:C, 73.28; H, 6.49. Found: C, 73.39; H, 6.41.

2-*O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-3,4-di-*O*-benzyl-β-D-glucopyranosyl fluoride (6′-OH free 10). $[\alpha]_D^{25}$=+18.8° (*c* 1.03, $CHCl_3$); IR (film) ν 3482, 3066, 3034, 2920, 2874, 1497, 1456, 1361, 1309, 1212, 1069, 1029, 737, 698, 621, 607 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.93 (1H, dd, J=8.3, 5.2 Hz, 6′-OH), 3.39–3.44 (1H, m, H5″), 3.50 (1H, dd, J=8.7, 8.2 Hz, H2″), 3.59–3.64 (2H, m, H3″, H4″), 3.65–3.71 (3H, m, H5′, H6″×2), 3.72–3.78 (1H, m, H6′), 3.77 (1H, dd, J=8.0, 6.0 Hz, H3′), 3.85–3.92 (2H, m, H6′, H4′), 4.00 (1H, ddd, J=8.8, 5.7, 4.4 Hz, H2′), 4.54–4.94 (12H, m, Bn), 4.63 (1H, d, J=7.7 Hz, H1″), 5.56 (1H, dd, J=53.6, 4.4 Hz, H1′), 7.17–7.37 (30H, m, Bn); ^{13}C NMR (125 MHz, $CDCl_3$) δ 61.7, 68.6, 73.4, 74.0, 74.8, 75.0, 75.0, 75.1, 75.4, 75.6, 76.0, 77.7, 78.6 (d, J=30.1 Hz), 82.2, 83.8 (d, J=4.6 Hz), 84.7, 102.8, 107.8 (d, J=216.5 Hz), 127.5–128.4, 137.8, 137.8, 138.0, 138.2, 138.4; MALDI TOF-MS Calcd for M+Na$^+$ ($C_{54}H_{57}O_{10}FNa$): 907.383. Found 907.383; Anal. Calcd for $C_{54}H_{57}FO_{10}$: C, 73.28; H, 6.49. Found: C, 73.13; H, 6.55.

2-*O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl fluoride (3). $[\alpha]_D^{29}$=+49.6° (*c* 0.94, $CHCl_3$); IR (film) ν 3068, 3036, 2930, 1497, 1456, 1390, 1365, 1255, 1212, 1100, 835, 779, 735, 696 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.14 (3H, s, TBS), 0.16 (3H, s, TBS), 0.98 (9H, s, TBS), 3.32 (1H, dd, J=11.0, 2.6 Hz, H6″), 3.34 (1H, dd, J=11.0, 2.1 Hz, H6″), 3.48 (1H, dt, J=9.5, 2.6 Hz, H5′), 3.64 (1H, dd, J=9.9, 3.7 Hz, H2″), 3.73 (1H, dd, J=9.9, 9.3 Hz, H4″), 3.74 (1H, dd, J=9.5, 9.2 Hz, H4′), 3.83 (1H, ddd, J=11.7, 9.2, 7.0 Hz, H2′), 3.84 (1H, t, J=9.2 Hz, H3′), 3.96 (2H, brs, H6′×2), 4.02 (1H, dd, J=9.9, 9.3 Hz, H3″), 4.05 (1H, ddd, J=9.9, 2.6, 2.1 Hz, H5″), 4.29 (1H, d, J=11.9 Hz, Bn), 4.44 (1H, d, J=10.9 Hz, Bn), 4.56 (1H, d, J=11.9 Hz, Bn), 4.74 (1H, d, J=11.7 Hz, Bn), 4.78 (1H, d, J=10.1 Hz, Bn), 4.79 (1H, d, J=11.7 Hz, Bn), 4.80 (1H, d, J=10.7 Hz, Bn), 4.84 (1H, d, J=10.9 Hz, Bn), 4.88 (1H, d, J=10.9 Hz, Bn), 4.90 (1H, d, J=10.1 Hz, Bn), 4.95 (1H, d, J=10.7 Hz, Bn), 5.04 (1H, d, J=10.9 Hz, Bn), 5.40 (1H, d, J=3.8 Hz, H1″), 5.41 (1H, dd, J=53.0, 7.0 Hz, H1′), 7.08–7.42 (30H, m, Bn); ^{13}C NMR (125 MHz, $CDCl_3$) δ −5.4, −5.1, 18.3, 25.9, 61.6, 67.8, 70.1, 73.0, 73.3, 74.9, 74.9, 75.6, 75.9 (d, J=5.1 Hz), 75.9, 76.3 (d, J=20.4 Hz), 77.5 (2×C), 79.4, 81.8 (d, J=12.0 Hz), 81.8, 95.9 (d, J=6.3 Hz), 110.3 (d, J=212.5 Hz), 127.3–128.5, 137.6, 137.8, 137.9, 138.0, 138.7, 138.8; MALDI TOF-MASS Calcd. for M+Na$^+$ ($C_{60}H_{71}FO_{10}SiNa$):1021.47. Found: 1021.47. Anal. Calcd for $C_{60}H_{71}FO_{10}Si$:C, 72.12; H, 7.16. Found: C, 72.15; H, 7.33.

3-*O*-[2-*O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-α-D-glucopyranosyl]-1,2-*O*-isopropylidene-*sn*-glycerol (2). In a sealed tube were placed molecular sieves 4 Å (4.6 g), and these were flame-dried under vacuum and cooled to ambient temperature. Anhydrous silver perchlorate (1.07 g, 5.16 mmol), stannous chloride (960 mg, 5.06 mmol) and 2,6-di-*tert*-butylpyridine (1.7 mL, 7.57 mmol) were added to the molecular sieves in a gloved box, and the system was flushed with Ar. A solution of disaccharide **3** (1.27 g, 1.27 mmol) and glycerol **4** (3.2 mL. 26 mmol) in ether (5 mL) was introduced to the salt mixture via a double-tipped needle, and the reaction vessel was wrapped with aluminum foil. After stirring at ambient temperature for 13 days, the mixture was diluted with ether, and added aqueous sodium bicarbonate. The resulting precipitates were removed by filtration through a plug of Celite®. The organic layer was washed with brine and dried over $MgSO_4$. Concentration followed by flash column chromatography gave **2** (1.15 g, 1.03 mmol, 81%) as colorless viscous oil: $[\alpha]_D^{28}=+74.0°$ (*c* 0.89, $CHCl_3$); IR (film) ν 3066, 3036, 2932, 1497, 1458, 1363, 1255, 1212, 1071, 837, 812, 777, 745, 700, 667, 632, 607 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.05 (3H, s, TBS), 0.05 (3H, s, TBS), 0.90 (9H, s, TBS), 1.28 (3H, s, acetonide), 1.38 (3H, s, acetonide), 3.49 (1H, dd, *J*=10.8, 2.1 Hz, H6′), 3.52 (1H, dd, *J*=9.7, 8.9 Hz, H4″), 3.54 (1H, dd, *J*=10.3, 5.9 Hz, H3), 3.60 (1H, dd, *J*=10.8, 2.9 Hz, H6′), 3.63 (1H, dd, *J*=9.6, 3.5 Hz, H2′), 3.63 (1H, dd, *J*=10.3, 6.2 Hz, H3), 3.62–3.67 (1H, m, H5″), 3.68 (1H, dd, *J*=8.3, 6.1 Hz, H1), 3.71 (1H, dd, *J*=10.0, 9.2 Hz, H4′), 3.76 (1H, dd, *J*=9.9, 3.6 Hz, H2″), 3.78–3.80 (2H, m, H6″×2), 3.97 (1H, dd, *J*=8.3, 6.4 Hz, H1), 4.00 (1H, ddd, *J*=10.0, 2.9, 2.1 Hz, H5′), 4.03 (1H, dd, *J*=9.9, 8. 9 Hz, H3″), 4.08 (1H, dd, *J*=9.6, 9.2 Hz, H3′), 4.26 (1H, quintet, *J*=6.0 Hz, H2), 4.35 (1H, d, *J*=12.0 Hz, Bn), 4.40 (1H, d, *J*=11.1 Hz, Bn), 4.58 (1H, d, *J*=12.0 Hz, Bn), 4.63 (1H, d, *J*=11.0 Hz, Bn), 4.71 (1H, d, *J*=12.0 Hz, Bn), 4.77 (1H, d, *J*=10.3 Hz, Bn), 4.80 (1H, d, *J*=12.1 Hz, Bn), 4.80 (1H, d, *J*=10.7 Hz, Bn), 4.82 (1H, d, *J*=11.1 Hz, Bn), 4.87 (1H, d, *J*=11.1 Hz, Bn), 4.94 (1H, d, *J*=10.3 Hz, Bn), 4.96 (1H, d, *J*=10.7 Hz, Bn), 5.11 (1H, d, *J*=3.6 Hz, H1″), 5.14 (1H, d, *J*=3.5 Hz, H1′), 7.01–7.39 (30H, m, Bn); ^{13}C NMR (125 MHz, $CDCl_3$) δ −5.4, −5.2, 18.3, 25.4, 25.9, 26.8, 62.2, 67.1, 68.1, 68.7, 70.3, 71.9, 72.3, 73.3, 74.5, 74.8, 75.0, 75.1, 75.5, 76.2, 77.5, 77.9, 79.1, 80.7, 82.0, 93.9, 95.6, 109.4, 127.4–128.5, 137.9, 138.2, 138.3, 138.5, 138.7, 138.8; MALDI TOF-MS Calcd for $M+Na^+$ ($C_{66}H_{82}O_{13}SiNa$):1133.54. Found: 1133.54. Anal. Calcd for $C_{66}H_{82}O_{13}Si$:C, 71.32; H, 7.44. Found: C, 71.30; H, 7.44.

3-*O*-[2-*O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-3,4-di-*O*-benzyl-α-D-glucopyranosyl]-1,2-*O*-isopropylidene-*sn*-glycerol (12). A solution of **2** (164 mg, 147 μmol) in THF (1.2 mL) was treated with TBAF (0.53 mL, 1 M in THF), and the mixture was stirred at ambient temperature for 5 h. The solvent was evaporated and the residue was purified by column chromatography to afford **12** (126 mg, 126 μmol, 86%) as colorless viscous oil: $[\alpha]_D^{25}=+81.5°$ (*c* 0.63, $CHCl_3$); IR (film) ν 3496, 3068, 3032, 2988, 2928, 1497, 1456, 1363, 1330, 1259, 1214, 1160, 1069, 917, 839 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.29 (3H, s, acetonide), 1.40 (3H, s, acetonide), 1.70–1.74 (1H, br, OH), 3.50 (1H, dd, *J*=10.4, 1.9 Hz, H6″), 3.53 (1H, dd, *J*=9.9, 8.8 Hz, H4′), 3.54 (1H, dd, *J*=10.7, 6.1 Hz, H1), 3.59 (1H, dd, *J*=10.4, 3.2 Hz, H6″), 3.61 (1H, dd, *J*=10.7, 5.1 Hz, H1), 3.63 (1H, dd, *J*=9.7, 3.6 Hz, H2″), 3.69 (1H, dd, *J*=8.2, 5.8 Hz, H3), 3.67–3.73 (3H, m, H6′, H4″, H5″), 3.78 (1H, dd, *J*=9.9, 3.5 Hz, H2′), 3.77–3.82 (1H, m, H6′), 3.96 (1H, dd, *J*=8.2, 6.6 Hz, H3), 4.01 (1H, ddd, *J*=10.0, 3.2, 1.9 Hz, H5′), 4.06 (1H, t, *J*=9.9 Hz, H3′), 4.07 (1H, t, *J*=9.7 Hz, H3″), 4.27 (1H, quintet, *J*=5.9 Hz, H2), 4.35 (1H, d, *J*=12.0 Hz, Bn), 4.44 (1H, d, *J*=11.0 Hz, Bn), 4.57 (1H, d, *J*=12.0 Hz, Bn), 4.62 (1H, d, *J*=11.2 Hz, Bn), 4.72 (1H, d, *J*=12.0 Hz, Bn), 4.77–4.82 (3H, m, Bn×3), 4.83 (1H, d, *J*=11.0 Hz, Bn), 4.88 (1H, d, *J*=11.2 Hz, Bn), 4.95 (1H, d, *J*=10.8 Hz, Bn), 4.96 (1H, d, *J*=10.2 Hz, Bn), 4.12 (1H, d, *J*=3.5 Hz, H1′), 3.13 (1H, d, *J*=3.6 Hz, H1″), 7.04–7.39 (30H, m, Bn); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.3, 26.8, 61.7, 66.8, 68.1, 69.0, 70.3, 71.1, 72.5, 73.3, 74.5, 74.8, 75.0, 75.1, 75.5, 76.0, 77.5 (2×C), 79.2, 80.5, 82.0, 94.1, 95.8, 109.5, 127.4–128.4, 137.9, 138.1, 138.2, 138.2, 138.6, 138.7; MALDI TOF-MASS Calcd for $M+Na^+$ ($C_{60}H_{68}O_{13}Na$):1019.46. Found: 1019.46. Anal. Calcd for $C_{60}H_{68}O_{13}$:C, 72.27; H, 6.87. Found: C, 72.24; H, 7.04.

3-*O*-[2-*O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-3,4-di-*O*-benzyl-α-D-glucopyranosyl]-*sn*-glycerol (13). Hydrochloric acid (0.4 mL, 1N) was added to a stirred solution of **2** (231 mg, 208 μmol) in methanol (3.6 mL) and toluene (0.8 mL). After stirring for 23 h at ambient temperature, the reaction was quenched with aqueous saturated sodium bicarbonate. The mixture was extracted with $CHCl_3$ (2 times) and the combined organic layers were washed with brine and dried over $MgSO_4$. Concentration followed by column chromatography gave **13** (200 mg, 205 μmol, 99%) as colorless viscous oil: $[\alpha]_D^{25}=+65.7°$ (*c* 0.97, $CHCl_3$); IR (film) ν 3418, 3032, 2930, 1497, 1456, 1402, 1363, 1330, 1261, 1216, 1071, 920, 750, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.78–1.96 (2H, br, OH), 2.29 (1H, br, OH), 3.29 (1H, dd, *J*=11.2, 2.1 Hz, H6″), 3.38 (1H, dd, *J*=11.2, 2.8 Hz, H6″), 3.39 (1H, dd, *J*=10.1, 7.4 Hz, H1), 3.51 (1H, dd, *J*=11.3, 4.6 Hz, H3), 3.55 (1H, dd, *J*=9.3, 9.2 Hz, H4′), 3.58 (1H, dd, *J*=10.0, 3.3 Hz, H2″), 3.65 (1H, dd, *J*=11.3, 3.5 Hz, H3), 3.68 (1H, dd, *J*=10.0, 9.1 Hz, H4″), 3.72 (1H, dd, *J*=9.7, 3.4 Hz, H2′), 3.70–3.76 (2H, m, H2, H5′), 3.79 (1H, d, *J*=10.1, 3.0 Hz, H1), 3.81–3.86 (2H, m, H6′×2), 3.98 (1H, ddd, *J*=10.0, 2.8, 2.1 Hz, H5″), 4.02 (1H, dd, *J*=9.7, 9.2 Hz, H3′), 4.07 (1H, dd, *J*=10.0, 9.1 Hz, H3″), 4.27 (1H, d, *J*=12.0 Hz, Bn), 4.41 (1H, d, *J*=11.1 Hz, Bn), 4.52 (1H, d, *J*=12.0 Hz, Bn), 4.64 (1H, d, *J*=10.9 Hz, Bn), 4.72 (1H, d, *J*=11.9 Hz, Bn), 4.79 (1H, d, *J*=11.1 Hz, Bn),4.84 (1H, d, *J*=10.6 Hz, Bn), 4.86 (1H, d, *J*=11.9 Hz, Bn), 4.87 (1H, d, *J*=3.3 Hz, H1″), 4.88 (1H, d, *J*=10.9 Hz, Bn), 4.89 (1H, d, *J*=10.6 Hz, Bn), 4.99 (1H, d, *J*=10.8 Hz, Bn), 4.95 (1H, d, *J*=3.4 Hz, H1′), 4.97 (1H, d, *J*=10.8 Hz, Bn), 7.07–7.37 (30H, m, Bn); ^{13}C NMR (125 MHz, $CDCl_3$) δ 61.6, 63.4, 67.8, 70.3, 70.4, 70.4, 71.3, 73.3, 73.7, 74.8, 75.1, 75.5, 75.8, 76.3, 77.8, 77.9, 78.6, 80.3, 82.1, 96.2, 96.8, 127.4–128.5, 137.8, 137.9, 137.9, 138.1, 138.5, 138.6; MALDI TOF-MS Calcd for $M+Na^+$ ($C_{57}H_{64}O_{13}Na$):979.425. Found: 979.425. Anal. Calcd for $C_{57}H_{64}O_{13}$:C, 71.53; H, 6.74. Found: C, 71.23; H, 6.88.

3-*O*-[2-*O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-3,4-di-*O*-benzyl-6-*O*-12-methyltridecanoyl-α-D-gluco-

pyranosyl]-1,2-di-*O*-12-methyltridecanoyl-*sn*-glycerol (14). To a solution of **13** (40.8 mg, 43.3 μmol), DMAP (5.0 mg, 41 μmol), and 12-methyltridecanoic acid (90.2 mg, 395 μmol) in CH_2Cl_2 was added 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (68.8 mg, 359 μmol), and the solution was stirred for 13 h. The reaction mixture was diluted with ethyl acetate. The mixture was washed with H_2O and brine. The combined organic layers were dried over $MgSO_4$. Concentration followed by flash column chromatography gave **14** (59 mg, 37 μmol, 98%) as colorless viscous oil: $[\alpha]_D^{25.5}=+58.1°$ (*c* 1.04, $CHCl_3$); IR (film) ν 3066, 3032, 2928, 2858, 1742, 1497, 1456, 1383, 1365, 1259, 1210, 1160, 1073, 737, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.86 (18H, d, *J*=6.4 Hz, $CH(CH_3)_2$), 1.11–1.17 (6H, m), 1.21–1.31 (42H, m), 1.51 (3H, septet, *J*=6.4 Hz, $CH(CH_3)_2$), 1.53–1.64 (6H, m), 2.21–2.32 (6H, m), 3.40 (1H, dd, *J*=10.8, 1.9 Hz, H6″), 3.48 (1H, dd, *J*=9.9, 8.8 Hz, H4′), 3.50 (1H, dd, *J*=10.8, 3.0 Hz, H6″), 3.53 (1H, dd, *J*=10.6, 5.0 Hz, H3), 3.59 (1H, dd, *J*=10.3, 3.3 Hz, H2″), 3.68 (1H, dd, *J*=10.2, 9.1 Hz, H4″), 3.73 (1H, dd, *J*=10.6, 5.5 Hz, H3), 3.74 (1H, dd, *J*=9.9, 3.2 Hz, H2′), 3.84 (1H, dt, *J*=9.9, 3.4 Hz, H5′), 3.96 (1H, ddd, *J*=10.2, 3.0, 1.9 Hz, H5″), 3.99 (1H, dd, *J*=9.9, 8.8 Hz, H3′), 4.04 (1H, dd, *J*=10.1, 9.1 Hz, H3″), 4.18 (1H, dd, *J*=11.8, 6.1 Hz, H1), 4.27 (2H, brs, H6′×2), 4.31 (1H, d, *J*=12.5 Hz, Bn), 4.33 (1H, dd, *J*=12.0, 3.4 Hz, H1), 4.43 (1H, d, *J*=10.9 Hz, Bn), 4.53 (1H, d, *J*=10.7 Hz, Bn), 4.53 (1H, d, *J*=12.5 Hz, Bn), 4.72 (1H, d, *J*=11.9 Hz, Bn), 4.75 (1H, d, *J*=11.9 Hz, Bn), 4.80 (1H, d, *J*=11.0 Hz, Bn), 4.81 (1H, d, *J*=10.9 Hz, Bn), 4.82 (1H, d, *J*=11.0 Hz, Bn), 4.86 (1H, d, *J*=10.7 Hz, Bn), 4.94 (1H, d, *J*=10.8 Hz, Bn), 4.95 (1H, d, *J*=3.2 Hz, H1′), 4.95 (1H, d, *J*=10.8 Hz, Bn), 5.00 (1H, d, *J*=3.3 Hz, H1″), 5.12–5.17 (1H, m, H2), 7.06–7.35 (30H, m, Bn); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.6, 24.9, 24.9, 24.9, 27.4, 28.0, 29.1–29.9, 34.1, 34.1, 34.2, 39.0, 62.6, 62.6, 66.4, 68.0, 69.2, 69.8, 70.5, 72.9, 73.3, 74.8, 75.1, 75.6, 75.9, 76.0, 77.6, 77.8, 79.1, 80.5, 82.1, 95.4, 96.3, 127.4–128.4, 137.8, 137.9, 138.1, 138.2, 138.6, 138.7, 172.9, 173.2, 173.4; MALDI TOF-MS Calcd for $M+Na^+$ ($C_{99}H_{142}O_{16}Na$):1610.02. Found: 1610.02. Anal. Calcd for $C_{99}H_{142}O_{16}$:C,74.87; H, 9.01. Found: C, 75.03; H, 9.08.

3-*O*-(2-*O*-α-D-Glucopyranosyl-6-*O*-12-methyltridecanoyl-α-D-glucopyranosyl)-1,2-di-*O*-12-methyltridecanoyl-*sn*-glycerol (1a). A solution of **14** (498 mg, 314 μmol) in ethyl acetate (6 mL) and ethanol (1.2 mL) was treated with 5% palladium on charcoal (360 mg) and stirred at ambient temperature under hydrogen atmosphere for 8 h. The catalyst was filtered off through a plug of Celite®, and the solvent was removed in vacuo. The residue was purified by flash column chromatography to afford **1a** (250 mg, 238 μmol, 76%) as a colorless waxy solid: $[\alpha]_D^{26}=+66.3°$ (*c* 0.11, $CHCl_3$); IR (film) ν 3386, 2924, 2856, 1742, 1466, 1367, 1162, 1058, 919, 762, 725 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3/CD_3OD$=1/1) δ 0.84 (18H, d, *J*=6.6 Hz, $CH(CH_3)_2$), 1.10–1.16 (6H, m, $CH_2CH(CH_3)_2$), 1.22–1.33 (42H, m), 1.49 (3H, septet, *J*=6.6 Hz, $CH(CH_3)_2$), 1.55–1.63 (6H, m, $COCH_2CH_2$), 2.27–2.34 (6H, m, $COCH_2$), 3.27–3.33 (2H, m, H4′, H4″), 3.39 (1H, dd, *J*=9.3, 3.9 Hz, H2″), 3.57 (1H, dd, *J*=9.9, 3.7 Hz, H2′), 3.63 (1H, dd, *J*=10.7, 5.0 Hz, H3), 3.66 (1H, dd, *J*=11.3, 5.5 Hz, H6″), 3.67 (1H, dd, *J*=9.4, 9.3 Hz, H3″), 3.74 (1H, dd, *J*=9.9, 8.6 Hz, H3′), 3.76 (1H, ddd, *J*=9.4, 4.9, 2.0 Hz, H5′), 3.81 (1H, dd, *J*=11.3, 2.3 Hz, H6″), 3.82 (1H, dd, *J*=10.7, 5.4 Hz, H3), 3.84 (1H, ddd, *J*=10.1, 5.5, 2.3 Hz, H5″), 4.20 (1H, dd, *J*=11.8, 4.9 Hz, H1), 4.22 (1H, dd, *J*=11.7, 4.9 Hz, H6′), 4.35 (1H, dd, *J*=11.7, 2.0 Hz, H6′), 4.44 (1H, dd, *J*=11.8, 3.3 Hz, H1), 4.93 (1H, d, *J*=3.7 Hz, H1″), 4.97 (1H, d, *J*=3.9 Hz, H1′), 5.17–5.23 (1H, m, H2); ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$=1/1) δ 22.9, 25.5, 28.0, 28.5, 29.7- 30.5, 34.6, 34.7, 34.8, 39.6, 62.2, 63.3, 64.2, 66.5, 70.5, 70.6, 70.9, 71.0, 72.5, 72.7, 73.0, 74.3, 77.2, 97.0, 97.5, 174.2, 174.7, 174.9; MALDI TOF-MS Calcd for $M+Na^+$ ($C_{57}H_{106}O_{16}Na$):1069.74. Found: 1069.74. Anal. Calcd for $C_{57}H_{108}O_{17}$ ($M+H_2O$):C, 64.26; H, 10.22. Found: C, 64.49; H, 10.36.

3-*O*-(2-*O*-α-D-Glucopyranosyl-6-*O*-tetradecanoyl-α-D-glucopyranosyl)-1,2-di-*O*-tetradecanoyl-*sn*-glycerol (1b). A colorless waxy solid: $[\alpha]_D^{29}=+52.7°$ (*c* 0.12, $CHCl_3$); IR (film) ν 3391, 2918, 2850, 1738, 1468, 1377, 1257, 1164, 1054, 721 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3/CD_3OD$=1/1) δ 0.85 (9H, t, *J*=7.0 Hz, CH_2CH_3), 1.21–1.32 (60H, m), 1.55–1.62 (6H, m, $COCH_2CH_2$), 2,28–2.33 (6H, m, $COCH_2$), 3,29 (1H, dd, *J*=9.9, 9.1 Hz, H4″), 3.30 (1H, dd, *J*=9.9, 9.1 Hz, H4′), 3.39 (1H, dd, *J*=9.7, 3.9 Hz, H2″), 3.56 (1H, dd, *J*=9.8, 3.6 Hz, H2′), 3.62 (1H, dd, *J*=10.8, 5.0 Hz, H3), 3.66 (1H, dd, *J*=11.9, 5.5 Hz, H6″), 3.66 (1H, dd, *J*=9.7, 9.1 Hz, H3″), 3.73 (1H, dd, *J*=9.8, 9.1 Hz, H3′), 3.74 (1H, ddd, *J*=9.9, 6.3, 2.1 Hz, H5′), 3.81 (1H, dd, *J*=10.8, 5.5 Hz, H3), 3.81 (1H, dd, *J*=11.9, 2.5 Hz, H6″), 3.84 (1H, ddd, *J*=9.9, 5.5, 2.5 Hz, H5″), 4.20 (1H, dd, *J*=12.1, 6.2 Hz, H1), 4.21 (1H, dd, *J*=11.8, 6.3 Hz, H6′), 4.34 (1H, dd, *J*=11.8, 2.1 Hz, H6′), 4.43 (1H, dd, *J*=12.1, 3.2 Hz, H1), 4.92 (1H, d, *J*=3.9 Hz, H1″), 4.95 (1H, d, *J*=3.6 Hz, H1′), 5.18–5.22 (1H, m, H2); ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$=1/1) δ 14.3, 23.1, 25.4, 25.4, 25.4, 25.6, 25.6, 29.6, 29.6, 29.8, 29.8, 30.0, 30.1, 30.1, 32.4, 34.6, 34.6, 34.7, 62.1, 63.2, 64.0, 66.4, 70.4, 70.5, 70.7, 70.9, 72.4, 72.6, 72.9, 74.2, 77.2, 97.0, 97.4, 174.1, 174.6, 174.9; MALDI TOF-MS Calcd for $M+Na^+$ ($C_{57}H_{106}O_{16}Na$):1069.74. Found: 1069.74.

3-*O*-(2-*O*-α-D-Glucopyranosyl-6-*O*-hexadecanoyl-α-D-glucopyranosyl)-1,2-di-*O*-hexadecanoyl-*sn*-glycerol (1c). A colorless waxy solid: $[\alpha]_D^{28}=+46.6°$ (*c* 0.12, $CHCl_3$); IR (film) ν 3388, 2918, 2850, 1739, 1467, 1163, 1055, 759, 721 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3/CD_3OD$=1/1) δ 0.84 (9H, t, *J*=6.8 Hz, CH_2CH_3), 1.18–1.31 (72H, m), 1.54–1.63 (6H, m, $COCH_2CH_2$), 2.28–2.33 (6H, m, $COCH_2$), 3.28–3.33 (2H, m, H4′, H4″), 3.37 (1H, dd, *J*=9.6, 3.8 Hz, H2″), 3.56 (1H, dd, *J*=9.7, 3.5 Hz, H2′), 3.59 (1H, dd, *J*=10.5, 5.2 Hz, H3), 3.65 (1H, dd, *J*=9.6, 9.1 Hz, H3″), 3.66 (1H, dd, *J*=12.3, 5.2 Hz, H6″), 3.73 (1H, t, *J*=9.4 Hz, H3′), 3.72–3.77 (1H, m, H5′), 3.80 (1H, dd, *J*=10.5, 5.2 Hz, H3), 3.81 (1H, dd, *J*=12.3, 2.5 Hz, H6″), 3.81–3.85 (1H, m, H5″), 4.19 (1H, dd, *J*=12.2, 6.1 Hz, H1), 4.21 (1H, dd, *J*=12.2. 6.1 Hz, H6′), 4.33 (1H, dd, *J*=12.2, 2.0 Hz, H6′), 4.42 (1H, dd, *J*=12.3, 3.3 Hz, H1), 4.91 (1H, d, *J*=3.8 Hz, H1″), 4.95 (1H, d, *J*=3.5 Hz, H1′), 5.17–5.22 (1H, m, H2); ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$=1/1) δ 14.3, 23.2, 25.5, 25.5, 25.6, 29.7, 29.8, 29.9, 30.0, 30.1, 30.3, 30.3, 32.5, 34.7, 34.7, 34.8, 62.2, 63.4, 64.3, 66.5, 70.6, 70.7, 71.0 (2×C), 72.6, 72.8, 73.0, 74.4, 77.2, 97.1, 97.5, 174.2, 174.7, 175.0; MALDI TOF-MS Calcd for $M+Na^+$ ($C_{63}H_{118}O_{16}Na$): 1153.83. Found: 1153.84.

3-*O*-[2-*O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-3,4-di-*O*-benzyl-6-*O*-hexadecanoyl-α-D-glucopyranosyl]-1,2-*O*-isopropylidene-*sn*-glycerol (15). Colorless oil: $[\alpha]_D^{29}=+57.8°$ (*c* 1.23, $CHCl_3$); IR (film) ν 3064, 3031, 2924, 2854, 1738, 1605, 1497, 1455, 1360, 1211, 1071, 915, 842, 736, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.89 (3H, t, *J*=6.5 Hz, CH_2CH_3), 1.24–1.35 (24H, m), 1.30 (3H, s, acetonide), 1.40 (3H, s, acetonide), 1.58–1.66 (2H, m, $COCH_2CH_2$), 2.26–2.37 (2H, m, $COCH_2$), 3.49 (1H, dd, *J*=9.9, 9.1 Hz, H4′), 3.50 (1H, dd, *J*=10.5, 1.9 Hz, H6″), 3.54 (1H, dd, *J*=9.9, 5.4 Hz, H3), 3.60 (1H, dd, *J*=10.5, 2.9 Hz, H6″), 3.64 (1H, dd, *J*=9.9, 5.0 Hz, H3), 3.65 (1H, dd, *J*=9.2, 3.5 Hz, H2″), 3.71 (1H, dd, *J*=8.0, 5.9 Hz, H1), 3.72 (1H, dd, *J*=9.6, 9.1 Hz, H4″), 3.81 (1H, dd, *J*=9.5, 3.4 Hz, H2′), 3.89 (1H, ddd, *J*=9.9, 4.1, 1.9 Hz, H5′), 3.97 (1H, dd, *J*=8.0, 6.1 Hz, H1), 4.00 (1H, ddd, *J*=9.6, 2.9, 1.9 Hz, H5″), 4.07 (1H, dd, *J*=9.5, 9.1 Hz, H3′), 4.08 (1H, t, *J*=9.2 Hz, H3″), 4.20–4.31 (1H, m, H2), 4.27 (1H, dd, *J*=11.5, 4.1 Hz, H6′), 4.31 (1H, dd, *J*=11.5, 1.9 Hz, H6′), 4.36 (1H, d, *J*=11.8 Hz, Bn), 4.46 (1H, d, *J*=10.8 Hz, Bn), 4.54 (1H, d, *J*=10.4 Hz, Bn), 4.58 (1H, d, *J*=11.8 Hz, Bn), 4.73 (1H, d, *J*=11.8 Hz, Bn), 4.79 (1H, d, *J*=11.8 Hz, Bn), 4.80 (1H, d, *J*=10.1 Hz, Bn), 4.82 (1H, d, *J*=11.3 Hz, Bn), 4.83 (1H, d, *J*=10.8 Hz, Bn), 4.89 (1H, d, *J*=10.4 Hz, Bn), 4.97 (1H, d, *J*=11.3 Hz, Bn), 4.98 (1H, d, *J*=10.1 Hz, Bn), 5.12 (1H, d, *J*=3.4 Hz, H1′), 5.13 (1H, d, *J*=3.5 Hz, H1″), 7.04–7.39 (30H, m, Bn); ^{13}C NMR (50 MHz, $CDCl_3$); δ 14.1, 22.7, 24.9, 25.4, 26.8, 29.2, 29.3, 29.3, 29.5, 29.7, 31.9, 34.1, 62.8, 66.8, 68.1, 69.0, 69.0, 70.4, 72.5, 73.3, 74.4, 74.9, 75.0, 75.1, 75.6, 76.2, 77.5, 77.8, 79.1, 80.6, 82.0, 127.4–128.4, 137.8, 137.8, 138.0, 138.2, 138.6, 138.7, 173.5; MALDI TOF-MS Calcd for $M+Na^+$ ($C_{76}H_{98}O_{14}Na$): 1257.69. Found: 1257.69.

3-*O*-[2-*O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-3,4-di-*O*-benzyl-6-*O*-hexadecanoyl-α-D-glucopyranosyl]-*sn*-glycerol (16). Colorless oil: $[\alpha]_D^{27}=+51.8°$ (*c* 1.11, $CHCl_3$); IR (film) ν 3483, 3031, 2924, 2854, 1736, 1497, 1454, 1360, 1071, 736, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.81 (3H, t, *J*=6.6 Hz, CH_2CH_3), 1.15–1.25 (24H, m), 1.51–1.58 (2H, m, $COCH_2CH_2$), 2.19–2.29 (2H, m, $COCH_2$), 3.17 (1H, dd, *J*=10.6, 2.0 Hz, H6″), 3.26 (1H, dd, *J*=10.6, 2.6 Hz, H6″), 3.30 (1H, dd, *J*=9.7, 6.9 Hz, H3), 3.42 (1H, dd, *J*=11.1, 4.2 Hz, H1), 3.44 (1H, dd, *J*=9.8, 8.9 Hz, H4″), 3.48 (1H, dd, *J*=9.6, 3.2 Hz, H2″), 3.57 (1H, dd, *J*=11.1, 3.8 Hz, H1), 3.60 (1H, dd, *J*=9.7, 8.6 Hz, H4′), 3.65 (1H, dd, *J*=9.3, 3.5 Hz, H2′), 3.71 (1H, dd, *J*=9.7, 2.6 Hz, H3), 3.72–3.76 (1H, m, H2), 3.81 (1H, ddd, *J*=9.7, 4.1, 2.2 Hz, H5′), 3.87 (1H, dt, *J*=9.8, 2.0 Hz, H5″), 3.93 (1H, dd, *J*=9.3, 8.6 Hz, H3′), 3.98 (1H, dd, *J*=9.6, 8.9 Hz, H3″), 4.18 (1H, d, *J*=11.8 Hz, Bn), 4.20 (1H, dd, *J*=11.1, 4.1 Hz, H6′), 4.23 (1H, dd, *J*=11.1, 2.2 Hz, H6′), 4.32 (1H, d, *J*=10.7 Hz, Bn), 4.42 (1H, d, *J*=11.8 Hz, Bn), 4.48 (1H, d, *J*=10.3 Hz, Bn), 4.63 (1H, d, *J*=11.7 Hz, Bn), 4.71 (1H, d, *J*=10.7 Hz, Bn), 4.77 (1H, d, *J*=3.2 Hz, H1″), 4.73–4.81 (4H, m, Bn×4), 4.82 (1H, d, *J*=10.8 Hz, Bn), 4.87 (1H, d, *J*=3.5 Hz, H1′), 4.88 (1H, d, *J*=10.8 Hz, Bn), 6.98–7.29 (30H, m, Bn); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.1, 22.7, 23.8, 24.9, 28.9, 29.2, 29.3, 29.3, 29.5, 29.7, 31.9, 34.2, 62.7, 63.5, 67.9, 69.3, 70.4, 70.6, 70.7, 73.4, 73.9, 74.8, 75.2, 75.5, 75.9, 76.6, 77.9, 78.2, 78.7, 80.4, 82.2, 96.6, 97.0, 127.5–128.8, 137.7, 137.9, 137.9, 138.0, 138.5, 138.6, 173.5; MALDI TOF-MS Calcd for $M+Na^+$ ($C_{73}H_{94}O_{14}Na$): 1217.65. Found: 1217.65.

3-*O*-(2-*O*-α-D-Glucopyranosyl-6-*O*-hexadecanoyl-α-D-glucopyranosyl)-1,2-di-*O*-12-methyltridecanoyl-*sn*-glycerol (1d). A waxy solid: $[\alpha]_D^{27}=+51.6°$ (*c* 0.17, $CHCl_3$); IR (film) ν 3391, 2921, 2851, 1738, 1467, 1366, 1153, 1055, 917, 760, 721 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$/CD_3OD=1/1) δ 0.82 (12H, d, *J*=6.8 Hz, $CH(CH_3)_2$), 0.84 (3H, t, *J*=6.2 Hz, CH_2CH_3), 1.09–1.15 (4H, m, $CH_2CH(CH_3)_2$), 1.19–1.31 (52H, m), 1.48 (2H, septet, *J*=6.8 Hz, $CH(CH_3)_2$), 1.54–1.62 (6H, m, $COCH_2CH_2$), 2.27–2.33 (6H, m, $COCH_2$), 3.29 (1H, dd, *J*=10.0, 9.6 Hz, H4″), 3.30 (1H, dd, *J*=10.1, 9.0 Hz, H4′), 3.39 (1H, dd, *J*=9.7, 4.0 Hz, H2″), 3.56 (1H, dd, *J*=9.6, 3.7 Hz, H2′), 3.61 (1H, dd, *J*=10.5, 4.9 Hz, H3), 3.65 (1H, dd, *J*=9.7, 9.6 Hz, H3″), 3.66 (1H, dd, *J*=11.7, 5.5 Hz, H6″), 3.73 (1H, dd, *J*=9.6, 9.0 Hz, H3′), 3.74 (1H, ddd, *J*=10.1, 6.5, 2.5 Hz, H5′), 3.80 (1H, dd, *J*=10.5, 5.5 Hz, H3), 3.81 (1H, dd, *J*=11.7, 2.7 Hz, H6″), 3.83 (1H, ddd, *J*=10.0, 5.5, 2.7 Hz, H5″), 4.19 (1H, dd, *J*=12.0, 6.5 Hz, H1), 4.21 (1H, dd, *J*=11.8, 6.5 Hz, H6′), 4.33 (1H, dd, *J*=11.8, 2.5 Hz, H6′), 4.42 (1H, dd, *J*=12.0, 3.2 Hz, H1), 4.91 (1H, d, *J*=4.0 Hz, H1″), 4.95 (1H, d, *J*=3.7 Hz, H1′), 5.17–5.22 (1H, m, H2); ^{13}C NMR (125 MHz, $CDCl_3$/CD_3OD=1/1) δ 14.3, 22.9, 23.1, 25.4, 25.4, 25.4, 27.9, 28.4, 29.6, 29.8, 29.8, 30.0, 30.2, 30.4, 32.4, 34.6, 34.7, 39.5, 62.1, 63.2, 64.1, 66.4, 70.4, 70.5, 70.8, 70.9, 72.4, 72.6, 72.9, 74.2, 77.2, 97.0, 97.4, 174.1, 174.6, 174.9; MALDI TOF-MS Calcd for $M+Na^+$ ($C_{59}H_{110}O_{16}Na$): 1097.77. Found: 1097.78.

Acknowledgements

We are grateful to Professor S. Arai for the biological studies (Kurume University, School of Medicine) and to Professor K. Fukase (Osaka University) for his helpful discussion.

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