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# Structure–activity relationship studies on acremomannolipin A, the potent calcium signal modulator with a novel glycolipid structure 3: Role of the length of alditol side chain

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ABSTRACT

Five homologs of a novel glycolipid acremomannolipin A (**1a**), the potential $Ca^{2+}$ signal modulator isolated from *Acremonium strictum*, bearing alditols of different length (**1g**–**1k**) were synthesized by a stereoselective β-mannosylation of appropriately protected mannosyl sulfoxide (**2**) with five alditols (**1g**: C2, **1h**: C3, **1i**: C4, **1j**: C5 and **1k**: C7 units), and their potential in modulating $Ca^{2+}$ signaling were evaluated. Homologs with alditols of more than 4 carbons (**1i**, **1j** and **1k**) were equally or more potent than the parent compound (**1a**) regardless of the length of the alditol chain. Whereas activities of two homologs with shorter chains (**1g** and **1h**) decreased to a considerable extent. The results indicated that the length of the alditol side chain was a crucial determinant for the potent calcium signal modulating activity.



## 1. Introduction

Calcium signaling pathways are known to be widely proliferated throughout the cell and participate in all basic cellular functions.[1] The ability to manipulate $Ca^{2+}$ signaling pathways would provide a powerful tool for applications in therapeutic and biotechnological settings. Recently, we identified a novel glycolipid acremomannolipin A[2] (**1a**), a constituent isolated from *Acremonium strictum*, as a potential calcium signal modulator using a newly developed chemical-genetic method.[3] The structure of **1a** is quite unique, in which D-mannopyranose is connected to D-mannitol through a β-glycoside linkage. All the hydroxyls in the mannose are highly masked by aliphatic acids to form peresters, and thus the moiety is hydrophobic, whereas the mannitol part exhibits the highly hydrophilic property.[2] The compound (**1a**) was found to show quite characteristic bioactive property, enabling calcineurin deletion cells to grow in the presence of $Cl^-$, which would be caused by calcium signal modulating. The activity was so potent as to exert the effect at a concentration of 200 nM. The first total synthesis of this unique compound was accomplished by us via a stereoselective β-mannosylation as the key reaction.[4a] Concurrently, its α-isomer (*epi*-**1a**) was also synthesized and evaluated. The activity decreased upon inversion of the configuration at the anomeric center, but remained to some extents. Thus, the β-configuration was found not critical for onset of the activity, but preferable for the activity[4b] (Fig. 1).

In our continuing study on the structure–activity relationship (SAR) of **1a**, we next synthesized five side chain diastereomers (**1b**–**1f**) in order to clarify the role of stereochemistry of the alditol side chain. Activities of all candidates were nearly equal or slightly superior to that of **1a** regardless of the stereochemistry of the alditol, revealing that the stereochemistry of the alditol moiety was not critical for the potent calcium signal modulating activity[4c] (Fig. 2). It was speculated that the hexitol chain would function to control the hydrophilic property of the molecule.

In the present study, five homologs with alditols of different carbon chain length having possibly the same stereochemistry as **1a** (**1g**–**1k**) were synthesized and their potential as calcium signal modulators were examined (Fig. 3). Contribution of hydrophilicity caused by the alditol side chain length to the activity is discussed.

## 2. Results and discussion

### 2.1. Preparation of acceptors (3g–3k) for mannosylation

In the synthetic methodology especially for the sugar related molecules, selection of the protecting groups is the most important

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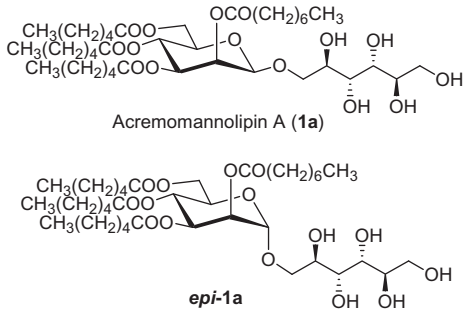



**Figure 1.** Acremomannolipin A (**1a**) and its α-anomer (*epi*-**1a**).

step. In the total synthesis of **1a**, 4,6-benzylidene protected mannosyl sulfoxide (**2**) was proved to be an appropriate donor for the stereoselective β-mannosylation with mannitol as the acceptor.[5] Therefore, the target glycolipids **1g**–**1k** were synthesized by applying the β-selective mannosylation of the donor **2** with protected alditols (**3g**–**3k**) as acceptors (Scheme 1).

Firstly the two-carbon acceptor, 2-(*tert*-butyldimethylsilyloxy)ethanol (**3g**), was prepared by the mono-silylation of ethylene glycol (**4**) according to the literature.[6] The three carbon acceptor, (*R*)-(−)-2,2-dimethyl-1,3-dioxolane-4-methanol (**3h**), was commercially available. Isopropylidene-D-erythritol (**3i**), was prepared as follows. According to the literature[7], D-glucose (**5**) was converted to 2,4-*O*-benzylidene-D-erythritol (**6**). The primary hydroxyl of **6** was selectively protected with an acetyl (Ac) moiety to give 1-*O*-acetyl-2,4-*O*-benzylidene-D-erythritol (**7**) in 89% yield. Subsequent regioselective reductive-cleavage of benzylidene acetal **7** was achieved by treatment with triethylsilane in the presence of $BF_3{\cdot}Et_2O$ to give 1-*O*-acetyl-4-*O*-benzyl-D-erythritol (**8**), which was acetalized with 2,2-dimethoxypropane (DMP) to give 1-*O*-acetyl-4-*O*-benzyl-2,3-*O*-isopropylidene-D-erythritol (**9**). The deacetylation of **9** and subsequent silylation of the resulting monoalcohol, 4-*O*-benzyl-2,3-*O*-isopropylidene-D-erythritol (**10**), gave 4-*O*-benzyl-1-*O*-(*tert*-butyldimethylsilyl)-2,3-*O*-isopropylidene-D-erythritol (**11**). Hydrogenolysis of **11** gave the desired acceptor **3i** in 98% yield.

The five-carbon acceptor, 1,2:3,4-di-*O*-isopropylidene-D-arabinitol (**3j**), was synthesized as follows. The primary hydroxyl in D-arabinose (**12**) was selectively protected with the *tert*-butyldiphenylsilyl (TBDPS) moiety to give a silyl ether, 5-*O*-(*tert*-butyldiphenylsilyl)-D-arabinose[8] (**13**). After the $NaBH_4$ reduction of the hemiacetal moiety in **13**, four hydroxyls in the resulting tetraol, 5-*O*-(*tert*-butyldiphenylsilyl)-D-arabinitol (**14**) were protected with DMP to give 5-*O*-(*tert*-butyldiphenylsilyl)-1,2:3,4-di-*O*-isopropylidene-D-arabinitol (**15**) in overall 40% yield via three steps from **12**. The perprotected arabinitol derivative **15** was then converted to the target acceptor **3j** in 68% yield through de-silylation by using TBAF.

The seven-carbon acceptor, 1,2:3,4:5,6-tri-*O*-isopropylidene-D-*glycero*-D-*galacto*-heptitol (**3k**), was prepared starting from **12** according to the protocol reported by us[9] (Scheme 2).

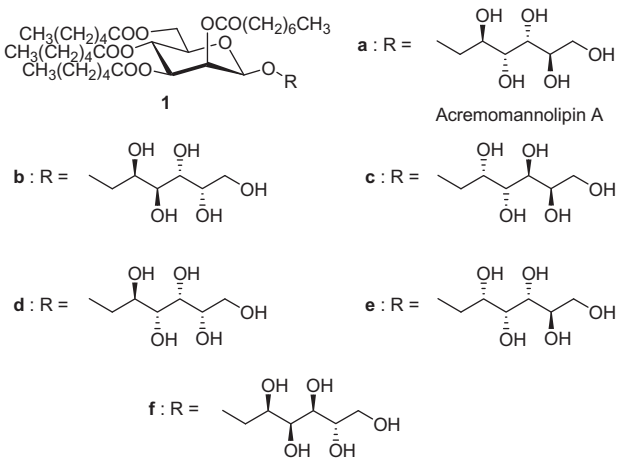



**Figure 2.** Acremomannolipin A (**1a**) and its side chain stereoisomers **1b**–**1f**.

### 2.2. Syntheses of homologs of acremomannolipin A (1g–1k)

With 5 acceptors (**3g**–**3k**) in hand, the coupling reaction of these 5 acceptors with mannosyl sulfoxide **2** in the presence of trifluoromethanesulfonic anhydride ($Tf_2O$) was examined. The coupling reaction of **2** with all the acceptors **3g**, **3h**, **3i**, **3j** and **3k** showed excellent β-selectivity ($\beta/\alpha$ = >ca. 20/1) giving corresponding β-mannosides **16g**, **16h**, **16i**, **16j** and **16k** in 73, 40, 60, 52 and 42% yield, respectively (Scheme 3). The NMR spectral properties of the products were similar with each other. In the $^1H$ NMR spectra of **16g**–**16k**, signals due to anomeric protons were shown at $\delta$ 4.50–4.57. The β-mannoside structure was confirmed by the NOE correlations between the signal due to the anomeric proton at C1′ and signals due to C3′-H and C5′-H as depicted in Scheme 3. The selective removal of the PMB group at C2′ in the coupled products (**16g**–**16k**) were successfully conducted by DDQ oxidation to give corresponding monoalcohols (**17g**–**17k**) in 79–92% yields, which were then treated with octanoyl chloride to give the corresponding octanoyl esters (**18g**–**18k**) in good yields. Simultaneous hydrogenolysis of both the benzyl and benzylidene moieties of **18g**–**18k** over palladium on carbon gave the desired trisalcohols (**19g**–**19k**), which were then derived to the corresponding tetraesters (**20g**–**20k**), by treating with hexanoic anhydride, in 63–86% yields in two steps. Finally, the acetonide moieties and/or the TBDMS group in **20g**–**20k** were selectively removed without affecting ester moieties under acidic conditions to give the target homologs (**1g**–**1k**) of acremomannolipin A (**1a**) in 67–94% yields. The $^{13}C$ NMR spectroscopic properties of mannose moiety in all the final products were similar with those of **1a** as shown in Table 1.

### 2.3. Bioassay of acremomannolipin A homologs (1g–1k)

The potencies of the synthesized homologs **1g**–**1k** as calcium signal modulators were examined.

Disruption of the calcineurin gene (*ppb1*$^+$) in fission yeast resulted in a $Cl^-$-sensitive growth defect, thus calcineurin gene deletion cells (Δ*ppb1*) can grew in yeast extract peptone dextrose (YPD) medium, but fail to grow in YPD medium containing 0.11 M $MgCl_2$ [see filter papers disc containing DMSO (control) in Fig. 4]. When a solution of acremomannolipin A (**1a**) in DMSO was added onto the filter paper disc, Δ*ppb1* cells grew well around

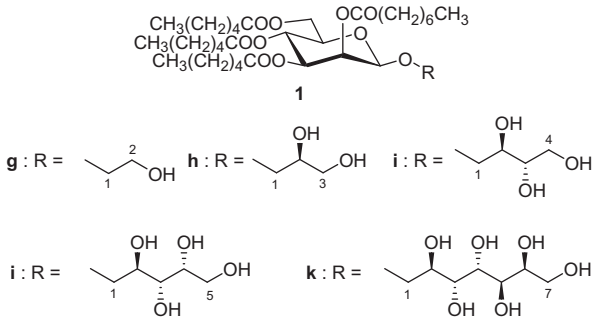
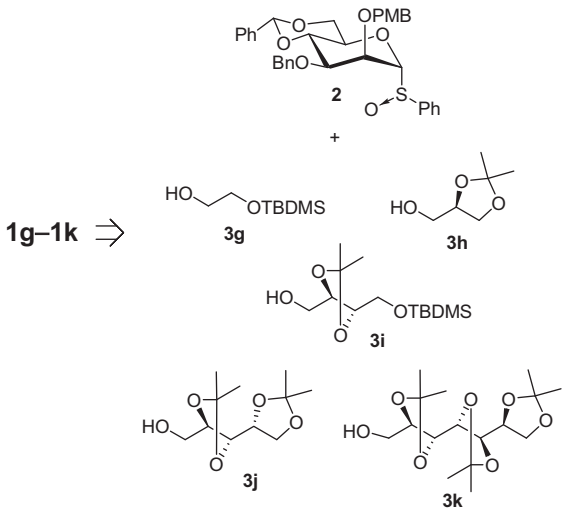



**Figure 3.** Homologs **1g**–**1k** of acremomannolipin A (**1a**) with different alditol chain length.




**Scheme 1.** Retrosynthetic analysis of homologs **1g**–**1k** on acremomannolipin A (**1a**).

the disc 1a. On the basis of the effect of **1a** on the growth of Δ*ppb1* cells in the presence of $MgCl_2$, the activities of homologs **1g**–**1k** were relatively evaluated by comparison of the size of colonies around the discs (Fig. 4).

Upon addition of solutions of **1g** and **1h**, having two- and three-carbon alditol chain, respectively, onto the filter paper disc (**1g** and **1h**), smaller colonies formed around the discs than that around the disc **1a** which contained **1a**, showing that the activities of **1g** and **1h** were significantly inferior to that of **1a**, but remained to some extents. On contrary, addition of a solution of the four-carbon side chain homolog **1i** onto the filter paper (disc 1i), Δ*ppb1* cells more easily grew in the presence of $MgCl_2$, forming the bigger colonies around disc than those around discs 1 g and 1 h. These results suggested that a further increase of hydrophilicity of the alditol chain might lead to increase of the cell proliferation. However, fair-sized colonies were found around discs 1j and 1 k, which contained five- and seven-carbon side chain homologs **1j** and **1k**, respectively. The size of the colonies were nearly equal to that of disc 1a, indicating that **1j** and **1k** were found as potent calcium signal modulators as **1a**. Thus, derivatives bearing alditols of more than five carbons were adequate for the calcium signal modulating. The length of the alditol side chain was found to be a crucial determinant for the activity.

In summary, five homologs (**1g**–**1k**) of acremomannolipin A (**1a**) with alditols of different carbon length from that of **1a** were synthesized by a stereoselective β-mannosylation of mannose **2** with five alditols, and their calcium signal modulating potency were evaluated. Alditols composed of at least four carbons were necessary for the compound to exert the potent activity. Studies on the target of this molecule and further structure–activity relationships of the characteristic activity of **1a** as a potent calcium signal modulator are in progress.

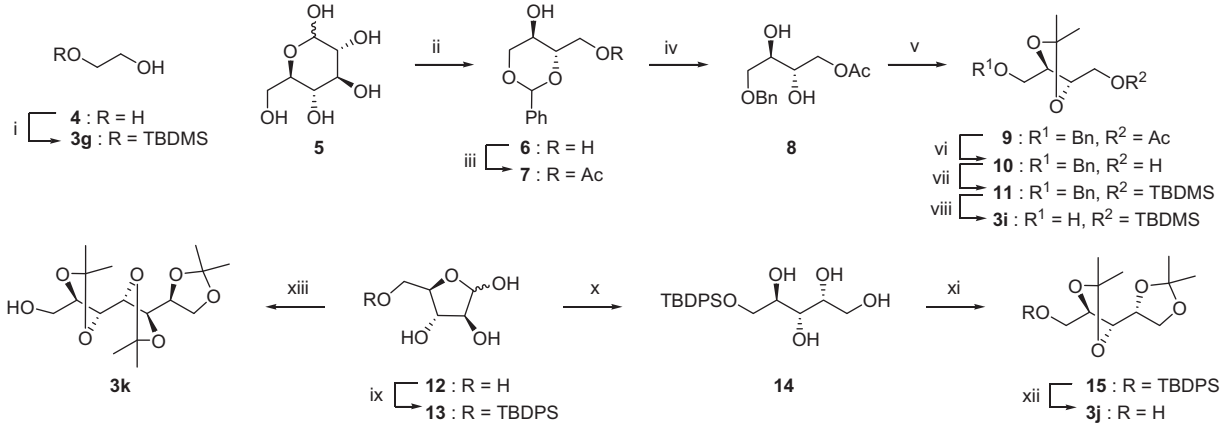
## 3. Experimental

### 3.1. General

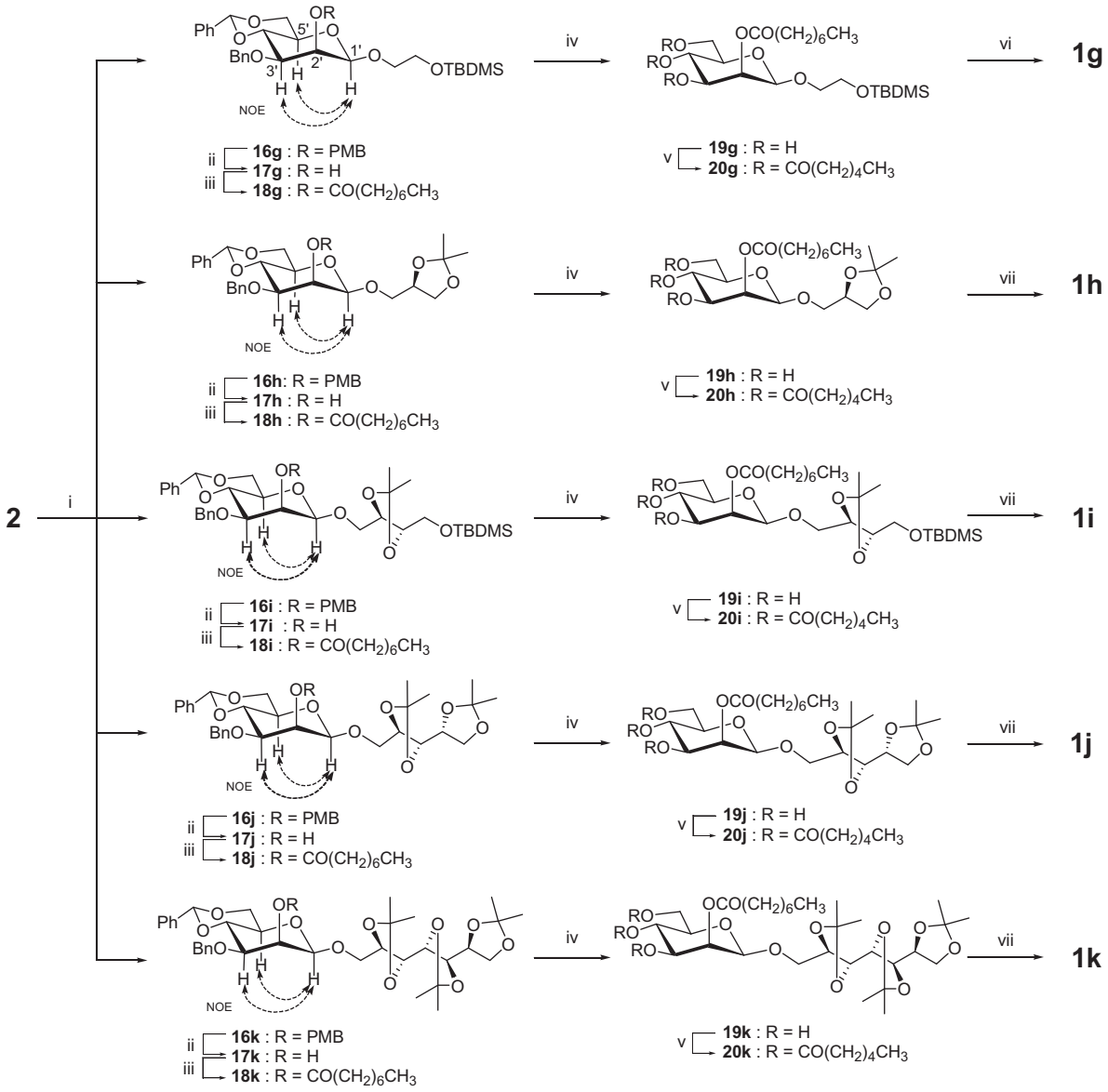
IR spectra were measured on a Shimadzu IRAffinity-1 spectrophotometer. NMR spectra were recorded on a JEOL JNM-ECA 400 (400 MHz $^1$H, 100 MHz $^{13}$C), a JEOL JNM-ECA 500 (500 MHz $^1$H, 125 MHz $^{13}$C), JEOL JNM-ECA 700 (700 MHz $^1$H, 175 MHz $^{13}$C), or a JEOL JNM-ECA 800 (800 MHz $^1$H, 200 MHz $^{13}$C) spectrometer. Chemical shifts ($\delta$) and coupling constants ($J$) are given in ppm and Hz, respectively. Low-resolution and high-resolution mass spectra were recorded on a JEOL JMS-700T spectrometer. Optical rotations were determined with a JASCO P-2200 polarimeter. Column chromatography was performed over Fuji Silysia silica gel BW-200. All the organic extracts were dried over anhydrous sodium sulfate prior to evaporation.

#### 3.1.1. 1-*O*-Acetyl-2,4-*O*-benzylidene-D-erythritol (7)

To a solution of 2,4-*O*-benzylidene-D-erythritol[7] (**6**, 1.00 g, 4.76 mmol) in pyridine (9.5 mL) was added dropwise acetyl chloride (0.4 mL, 5.23 mmol) at 0 °C. After being stirred at 0 °C for 30 min, the reaction mixture was diluted with water. The resulting mixture was extracted with EtOAc. The extract was washed with brine and concentrated in vacuo. The residue was purified by column chromatography (*n*-hexane–EtOAc, 10/1) to give **7** (1.06 g, 89%) as a colorless solid. $[\alpha]_D^{25}$ 29.4 (*c* 1.33, $CHCl_3$). IR (neat) $cm^{-1}$: 3441, 1732, 1454, 1373, 1238, 1080, 1030. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 2.15 (s, 3H, $COCH_3$), 2.76 (d, $J$ = 4.0 Hz, 1H, OH), 3.64 (dd, $J$ = 10.0, 9.6 Hz, 1H, H-1a), 3.68 (dddd, $J$ = 10.0, 9.2, 4.0, 4.0 Hz, 1H, H-2), 3.77 (ddd, $J$ = 9.2, 4.0, 2.4 Hz, 1H, H-3), 4.29 (dd, $J$ = 12.4, 2.4 Hz, 1H, H-4a), 4.33 (dd, $J$ = 9.6, 4.0 Hz, 1H, H-1b), 4.64 (dd, $J$ = 12.4, 4.0 Hz, 1H, H-4b), 5.50 (s, 1H, O*CH*Ph), 7.32–7.40 (m, 3H, Ar), 7.47–7.50 (m, 2H, Ar). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 20.9 ($COCH_3$), 61.8 (C-2), 63.6 (C-4), 70.6 (C-1), 80.5 (C-3), 101.3 (O*C*HPh), 126.1 (2C)/128.3 (2C)/129.1 (d, Ar), 137.3 (s, Ar), 172.4 (*C*OCH$_3$). FABMS *m*/*z* (%): 253 ([M+H]$^+$, 37), 55




**Scheme 2.** Reagents and conditions: (i) Ref. 6; (ii) Ref. 7; (iii) AcCl, Py, 0 °C; (iv) $Et_3SiH$, $BF_3{\cdot}Et_2O$, $CH_3CN$, 0 °C; (v) DMP, PTSA, rt; (vi) NaOMe, MeOH, rt; (vii) TBDMSCl, NaH, DMF, rt; (viii) $H_2$, Pd-C, EtOAc, rt; (ix) TBDPSCl, imidazole, DMF, rt; (x) $NaBH_4$, MeOH, rt; (xi) DMP, PTSA, acetone, rt; (xii) TBAF, THF, rt; (xiii) Ref. 9.




**Scheme 3.** Reagents and conditions: (i) **3g**–**3k**, $Tf_2O$, DTBMP, $CH_2Cl_2$, −78 °C; (ii) DDQ, $CH_2Cl_2$, $H_2O$, rt; (iii) $CH_3(CH_2)_6COCl$, Py, DMAP, $CH_2Cl_2$, rt; (iv) $H_2$, Pd-C, AcOEt, rt; (v) $[CH_3(CH_2)_4CO]_2O$, Py, DMAP, $CH_2Cl_2$, rt; (vi) TBAF, THF, rt; (vii) 90% aq TFA aq, 0 °C.

**Table 1**
$^{13}C$ NMR data for acremomannolipin A (**1a**) and homologs **1g**–**1k** in $CD_3OD$

| | **1a**[a] | **1g**[c] | **1h**[b] | **1i**[a] | **1j**[b] | **1k**[a] |
|---|---|---|---|---|---|---|
| C1 | 73.7 | 73.3 | 72.5 | 73.1 | 73.50 | 72.8 |
| C2 | 71.7 | 61.9 | 72.2 | 72.4 | 71.69 | 69.6 |
| C3 | 71.0 | | 64.3 | 73.6 | 72.1 | 71.1 |
| C4 | 71.2 | | | 64.6 | 71.67 | 70.3 |
| C5 | 73.0 | | | | 64.8 | 71.3 |
| C6 | 65.2 | | | | | 73.3 |
| C7 | | | | | | 65.2 |
| C1′ | 100.5 | 99.4 | 100.3 | 100.3 | 100.3 | 100.0 |
| C2′ | 70.5 | 68.6 | 70.4 | 70.5 | 70.5 | 70.5 |
| C3′ | 72.7 | 70.7 | 72.7 | 72.7 | 72.7 | 72.7 |
| C4′ | 66.8 | 65.7 | 66.9 | 66.8 | 66.8 | 66.8 |
| C5′ | 73.5 | 72.6 | 73.5 | 73.5 | 73.48 | 73.5 |
| C6′ | 63.0 | 62.4 | 63.1 | 63.1 | 63.1 | 63.0 |

[a] Measured at 200 MHz.
[b] Measured at 175 MHz.
[c] Measured at 125 MHz.

(100). FABHRMS calcd for $C_{13}H_{17}O_5$ $[M+H]^+$: 253.1076; found: 253.1081.

### 3.1.2. 1-*O*-Acetyl-4-*O*-benzyl-D-erythritol (8)

To a solution of **7** (784 mg, 3.11 mmol) in acetonitrile (155 mL) was successively added triethylsilane (2.5 mL, 15.5 mmol) and $BF_3{\cdot}Et_2O$ (1.2 mL, 9.33 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min. After the reaction mixture was neutralized with aqueous sodium hydrogen carbonate, the mixture was extracted with EtOAc. The extract was washed with brine and concentrated in vacuo. The residue was purified by column chromatography (*n*-hexane–EtOAc, 5/1) to give **8** (184 mg, 23%) as a colorless oil. $[\alpha]_D^{24}$ −5.7 (*c* 0.62, $CHCl_3$). IR (neat) $cm^{-1}$: 3422, 1718, 1452, 1368, 1246, 1074, 1043, 1028. $^1H$ NMR (400 MHz, $CD_3OD$) $\delta$: 1.96 (s, 3H, $COCH_3$), 3.48 (dd, *J* = 11.2, 5.6 Hz, 1H, H-1a), 3.59 (dd, *J* = 11.2, 3.2 Hz, 1H, H-1b), 3.62 (ddd, *J* = 7.2, 5.6, 3.2 Hz, 1H, H-2), 3.69 (ddd, *J* = 7.2, 6.4, 3.2 Hz, 1H, H-2), 4.02 (dd, *J* = 11.6, 6.4 Hz, 1H, H-4a), 4.19 (dd, *J* = 11.6, 3.2 Hz, 1H, H-4b), 4.47 (s, 2H, $OCH_2Ph$), 7.14–7.28 (m, 5H, Ar). $^{13}C$ NMR (100 MHz,

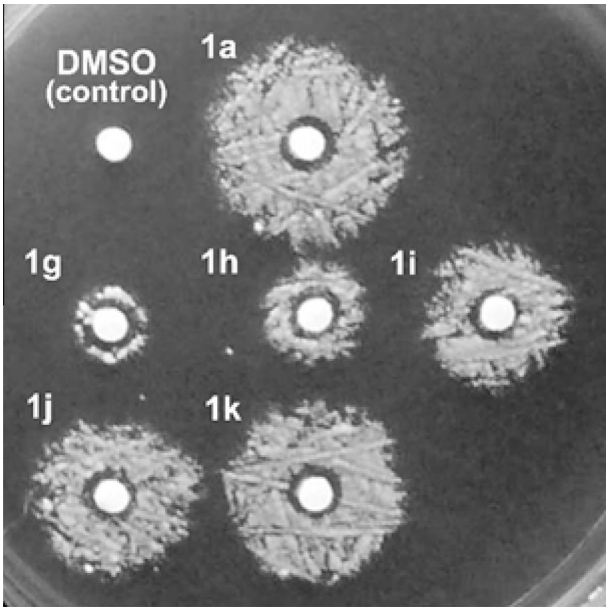



**Figure 4.** Suppression of the $Cl^-$-sensitive growth defect of calcineurin deletion cells by acremomannolipin A (**1a**) and the synthesized homologs **1g–1k**. Calcineurin deletion (Δ*ppb1*) cells were spread onto the YPD medium containing 0.11 M $MgCl_2$. Filter paper containing DMSO (5 μl) is used as a control. Filter papers **1a**, **1g**, **1h**, **1i**, **1j** and **1k** contain 5 μl of 100 μM DMSO solution of **1a**, **1g**, **1h**, **1i**, **1j** and **1k**, respectively. Cells were grown at 27 °C for 3 days.

$CD_3OD$) $\delta$: 20.8 ($COCH_3$), 67.2 (C-4), 71.1/72.1 (C-2 and C-3), 72.7 (C-1), 74.4 ($OCH_2Ph$), 128.6/128.9 (2C)/129.3 (2C) (d, Ar), 139.7 (s, Ar), 173.0 ($COCH_3$). FABMS *m*/*z* (%): 277 ($[M+Na]^+$, 5), 55 (100). FABHRMS calcd for $C_{13}H_{18}O_5Na$ $[M+H]^+$: 277.1052; found: 277.1059.

### 3.1.3. 1-*O*-Acetyl-4-*O*-benzyl-2,3-*O*-isopropylidene-D-erythritol (9)

To a mixture of **8** (183 mg, 0.718 mmol) and 2,2-dimethoxypropane (DMP, 5.0 mL) was added *p*-toluenesulfonic acid (13.7 mg, 0.0718 mmol) at room temperature, and the reaction mixture was stirred at room temperature for 1 h. The reaction was quenched with $Et_3N$, and the resulting mixture was concentrated in vacuo. The residue (245 mg) was purified by column chromatography (*n*-hexane–EtOAc, 15/1) to give **9** (203 mg, 96%) as a colorless oil. $[\alpha]_D^{24}$ −29.4 (*c* 0.73, $CHCl_3$). IR (neat) $cm^{-1}$: 1744, 1454, 1371, 1236, 1219, 1069, 1090, 1043. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 1.38/1.47 [each s, 3H, $C(CH_3)_2$], 2.07 (s, 3H, $COCH_3$), 3.51–3.57 (m, 2H, H-4), 4.05 (dd, *J* = 11.6, 7.2 Hz, 1H, H-1a), 4.31 (dd, *J* = 11.6, 3.6 Hz, 1H, H-1b), 4.37 (ddd, *J* = 7.2, 6.4, 3.6 Hz, 1H, H-2), 4.39 (ddd, *J* = 6.4, 6.4, 6.4 Hz, 1H, H-3), 4.53/4.59 (each d, *J* = 12.0 Hz, 1H, $OCH_2Ph$), 7.28–7.37 (m, 5H, Ar). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 20.7 ($COCH_3$), 25.2/27.6 [$C(CH_3)_2$], 63.0 (C-1), 68.0 (C-4), 73.5 ($OCH_2Ph$), 74.7/75.3 (C-2 and C-3), 109.0 [$C(CH_3)_2$], 127.69/127.74 (2C)/128.3 (2C) (d, Ar), 137.5 (s, Ar), 170.6 ($COCH_3$). FABMS *m*/*z* (%): 295 ($[M+H]^+$, 3), 91 (100). FABHRMS calcd for $C_{16}H_{23}O_5$ $[M+H]^+$: 295.1545; found: 295.1526.

### 3.1.4. 4-*O*-Benzyl-2,3-*O*-isopropylidene-D-erythritol (10)

To a solution of **9** (184 mg, 0.626 mmol) in MeOH (6.3 mL) was added sodium methoxide (33.8 mg, 0.626 mmol) at room temperature. After being stirred at room temperature for 30 min, the reaction mixture was neutralized with Amberlite IR-120. The resin was filtered off and washed with MeOH. The combined filtrate and washings were concentrated in vacuo. The residue was purified by column chromatography (*n*-hexane–EtOAc, 10/1) to give **10** (154 mg, 98%) as a colorless oil. $[\alpha]_D^{25}$ −9.8 (*c* 0.20, $CHCl_3$). IR (neat) $cm^{-1}$: 3456, 1454, 1371, 1248, 1217, 1167, 1076, 1053. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 1.36/1.43 [each s, 3H, $C(CH_3)_2$], 2.59 (dd, *J* = 6.4, 6.4 Hz, 1H, OH), 3.57 (dd, *J* = 9.6, 4.8 Hz, 1H, H-4a), 3.65 (dd, *J* = 9.6, 7.6 Hz, 1H, H-4b), 3.70 (ddd, *J* = 12.0, 6.4, 6.0 Hz, 1H, H-1a), 3.74 (ddd, *J* = 12.0, 6.4, 6.0 Hz, 1H, H-1b), 4.31 (ddd, *J* = 6.0, 6.0, 6.0 Hz, 1H, H-2), 4.39 (ddd, *J* = 7.6, 6.0, 4.8 Hz, 1H, H-3), 4.55/4.59 (each d, *J* = 12.0 Hz, 1H, $OCH_2Ph$), 7.29–7.39 (m, 5H, Ar). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 25.1/27.6 [$C(CH_3)_2$], 60.8 (C-1), 68.2 (C-4), 73.7 ($OCH_2Ph$), 75.3 (C-3), 77.1 (C-2), 108.4 [$C(CH_3)_2$], 127.7 (2C)/127.9/128.5 (2C) (d, Ar), 137.1 (s, Ar). FABMS *m*/*z* (%): 253 ($[M+H]^+$, 4), 91 (100). FABHRMS calcd for $C_{14}H_{21}O_4$ $[M+H]^+$: 253.1440; found: 253.1447.

### 3.1.5. 4-*O*-Benzyl-1-*O*-(*tert*-butyldimethylsilyl)-2,3-*O*-isopropylidene-D-erythritol (11)

To a solution of **7** (150 mg, 0.595 mmol) and imidazole (80.9 mg, 1.19 mmol) in DMF (6.0 mL) was added TBSCl (179 mg, 1.19 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 4 h. After being cooled with ice-water, the reaction mixture was diluted with water. The resulting mixture was extracted with EtOAc. The extract was washed with brine and concentrated in vacuo. The residue was purified by column chromatography (*n*-hexane–EtOAc, 20/1) to give **8** (210 mg, 96%) as a colorless oil. $[\alpha]_D^{24}$ −3.3 (*c* 0.92, $CHCl_3$). IR (neat) $cm^{-1}$: 1454, 1379, 1371, 1252, 1215, 1111, 1094, 1055. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 0.01/0.02 [each s, 3H, $Si(CH_3)_2$], 0.84 [s, 9H, $SiC(CH_3)_3$], 1.36/1.44 [each s, 3H, $C(CH_3)_2$], 3.56 (dd, *J* = 10.4, 7.6 Hz, 1H, H-4a), 3.58 (dd, *J* = 10.4, 4.8 Hz, 1H, H-1a), 3.65 (dd, *J* = 10.4, 7.2 Hz, 1H, H-1b), 3.72 (dd, *J* = 10.4, 3.6 Hz, 1H, H-4b), 4.13 (ddd, *J* = 7.2, 6.4, 4.8 Hz, 1H, H-2), 4.39 (ddd, *J* = 7.6, 6.4, 3.6 Hz, 1H, H-3), 4.52/4.66 (each d, *J* = 12.0 Hz, 1H, $CH_2Ph$), 7.26–7.34 (m, 5H, Ar). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: −5.4/−5.5 [$Si(CH_3)_2$], 18.1 [$SiC(CH_3)_3$], 25.3/27.9 [$C(CH_3)_2$], 25.8 [3C, $SiC(CH_3)_3$], 61.7 (C-1), 68.7 (C-4), 73.5 ($OCH_2Ph$), 76.5 (C-2), 77.0 (C-3), 108.6 [$C(CH_3)_2$], 127.6/127.8 (2C)/128.4 (2C) (d, Ar), 138.0 (s, Ar). FABMS *m*/*z* (%): 367 ($[M+Na]^+$, 14), 91 (100). FABHRMS calcd for $C_{20}H_{35}O_4Si$ $[M+H]^+$: 367.2305; found: 367.2301.

### 3.1.6. 1-*O*-(*tert*-Butyldimethylsilyl)-2,3-*O*-isopropylidene-D-erythritol (3i)

A suspension of **11** (177 mg, 0.482 mmol) and 10% palladium on carbon (30 mg) in EtOAc (4.8 mL) was hydrogenated at room temperature until the uptake of hydrogen ceased. The catalyst was filtered off and washed with EtOAc. The combined filtrate and washings were concentrated in vacuo. The residue was purified by column chromatography (*n*-hexane–EtOAc, 10/1) to give **3i** (123 mg, 92%) as a colorless oil. $[\alpha]_D^{23}$ +7.8 (*c* 1.16, $CHCl_3$). IR (neat) $cm^{-1}$: 3483, 1470, 1373, 1254, 1219, 1169, 1084, 1057. $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$: 0.107/0.111 [each s, 3H, $Si(CH_3)_2$], 0.90 [s, 9H, $SiC(CH_3)_3$], 1.36/1.42 [each s, 3H, $C(CH_3)_2$], 3.01 (dd, *J* = 8.3, 5.4 Hz, 1H, OH), 3.68 (dd, *J* = 10.6, 4.0 Hz, 1H, H-1a), 3.76 (ddd, *J* = 11.8, 8.3, 5.5 Hz, 1H, H-4a), 3.79 (dd, *J* = 10.6, 9.2 Hz, 1H, H-1b), 3.82 (ddd, *J* = 11.8, 7.5, 5.4 Hz, 1H, H-4b), 4.23 (ddd, *J* = 9.2, 6.0, 4.0 Hz, 1H, H-2), 4.35 (ddd, *J* = 7.5, 6.0, 5.5 Hz, 1H, H-3). $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$: −5.6/−5.5 [$Si(CH_3)_2$], 18.2 [$SiC(CH_3)_3$], 25.2/27.8 [$C(CH_3)_2$], 25.8 [3C, $SiC(CH_3)_3$], 60.8 (C-4), 61.5 (C-1), 76.8 (C-2), 77.3 (C-3), 108.4 [$C(CH_3)_2$]. FABMS *m*/*z* (%): 277 ($[M+H]^+$, 26), 73 (100). FABHRMS calcd for $C_{13}H_{29}O_4Si$ $[M+H]^+$: 277.1835; found: 277.1831.

### 3.1.7. 5-*O*-(*tert*-Butyldiphenylsilyl)-1,2:3,4-di-*O*-isopropylidene-D-arabinitol (15)

To a solution of D-arabinose (**12**) (300 mg, 2.00 mmol) and imidazole (272 mg, 4.00 mmol) in DMF (15 mL) was added dropwise a solution of *tert*-butyldiphenylsilyl chloride (TBDPSCl, 0.57 mL,

2.20 mmol) in DMF (5 mL) at 0 °C. The reaction mixture was stirred at room temperature for 23 h. After being cooled with ice-water, the reaction mixture was diluted with water. The resulting mixture was extracted with EtOAc. The extract was washed with brine, and concentrated to give a pale yellow oil (**13**, 828 mg). To a mixture of **13** (828 mg) and MeOH (15 mL) was added $NaBH_4$ (113 mg, 3.00 mmol), and the reaction mixture was stirred at room temperature for 30 min. After the reaction was quenched with acetone, the solvent was evaporated, and the residue **14** was dissolved in DMP (15 mL). To the solution was added *p*-toluenesulfonic acid (500 mg), and the reaction mixture was stirred at room temperature for 2 h. The reaction was quenched with $Et_3N$, and the resulting mixture was concentrated in vacuo. The residue was purified by column chromatography (*n*-hexane–EtOAc, 30/1) to give **15** (379 mg, 40% from **12**) as a colorless oil. $[\alpha]_D^{25}$ +4.80 (*c* 1.27, $CHCl_3$). IR (neat) $cm^{-1}$: 1250, 1215, 1111, 1072. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 1.06 [s, 9H, C(C$H_3$)$_3$], 1.35/1.36.1.42.1.46 [each s, 3H, C(C$H_3$)$_2$], 3.62 (dd, *J* = 10.8, 4.0 Hz, 1H, H-5a), 3.73 (dd, *J* = 8.4, 6.4 Hz, 1H, H-1a), 3.81 (dd, *J* = 10.8, 7.6 Hz, 1H, H-5b), 4.08 (dd, *J* = 8.4, 6.8 Hz, 1H, H-1b), 4.16 (dd, *J* = 6.4, 6.0 Hz, 1H, H-3), 4.19 (ddd, *J* = 7.6, 6.4, 4.0 Hz, 1H, H-4), 4.41 (ddd, *J* = 6.8, 6.4, 6.0 Hz, 1H, H-2), 7.37–7.47 (m, 6H, Ar), 7.63–7.67 (m, 4H, Ar). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 19.2 [Si*C*(CH$_3$)$_3$], 25.2/25.4/26.8/27.6 [C(*C*H$_3$)$_2$], 26.9 [3C, SiC(*C*H$_3$)$_3$], 62.7 (C-5), 66.7 (C-1), 74.3 (C-2), 76.9 (C-4), 78.5 (C-3), 109.0/109.6 [*C*(CH$_3$)$_2$], 127.79 (2C)/129.81 (2C)/129.86/129.90/135.5 (4C) (d, Ar), 132.8/132.9 (s, Ar). FABMS *m*/*z* (%): 493 ([M+Na]$^+$, 13), 135 (100). FABHRMS calcd for $C_{27}H_{38}O_5SiNa$ [M+Na]$^+$: 493.2386; found: 493.2387.

### 3.1.8. 1,2:3,4-Di-*O*-isopropylidene-D-arabinitol (3j)

To a solution of **15** (379 mg, 0.805 mmol) in THF (6.9 mL) was added 1 M solution of tetrabutylammonium fluoride (TBAF) in THF (1.2 mL, 1.21 mmol) at 0 °C. After being stirred at room temperature for 5 h, the reaction mixture was diluted with water. The resulting mixture was extracted with EtOAc. The extract was washed with brine, and concentrated in vacuo. The residue was purified by column chromatography (*n*-hexane–EtOAc, 4/1) to give **3j** (128 mg, 68%) as a colorless amorphous. $[\alpha]_D^{25}$ +7.03 (*c* 0.69, $CHCl_3$). IR (neat) $cm^{-1}$: 3406, 1373, 1250, 1215, 1161, 1049. $^1H$ NMR (700 MHz, $CDCl_3$) $\delta$: 1.388/1.391/1.47/1.52 [each s, 3H, C(C$H_3$)$_2$], 2.33 (dd, *J* = 7.2, 5.2 Hz, 1H, OH), 3.66 (ddd, *J* = 11.8, 5.2, 5.2 Hz, 1H, H-5a), 3.70 (ddd, *J* = 11.8, 7.2, 5.2 Hz, 1H, H-5b), 3.81 (dd, *J* = 8.2, 7.0 Hz, 1H, H-1a), 4.13 (dd, *J* = 8.2, 6.6 Hz, 1H, H-1b), 4.15 (dd, *J* = 6.4, 5.6 Hz, 1H, H-3), 4.20 (ddd, *J* = 6.4, 5.2, 5.2 Hz, 1H, H-4), 4.32 (ddd, *J* = 7.0, 6.6, 5.6 Hz, 1H, H-2). $^{13}C$ NMR (175 MHz, $CDCl_3$) $\delta$: 25.3/25.4/26.3/27.4 [C(*C*H$_3$)$_2$], 61.4 (C-5), 66.4 (C-1), 74.0 (C-2), 77.0 (C-4), 77.5 (C-3), 109.1/110.0 [*C*(CH$_3$)$_2$]. FAB MS *m*/*z* (%): 233 ([M+H]$^+$, 35), 59 (100). FAB HRMS calcd for $C_{11}H_{21}O_5$ [M+H]$^+$: 233.1389; found: 233.1402.

### 3.1.9. Coupling reaction between mannosyl sulfoxide (2) and protected alditols (3g–3k)

Under argon atmosphere, to a solution of **2**[4b] (500 mg, 0.852 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP, 350 mg, 1.70 mmol) in $CH_2Cl_2$ (8.5 mL) was added trifluoromethanesulfonic anhydride ($Tf_2O$, 0.15 mL, 0.938 mmol) at −78 °C, and the mixture was stirred at −78 °C for 10 min. A solution of **3g**[6] (165 mg, 0.938 mmol) in $CH_2Cl_2$ (8.5 mL) was added to the mixture, and the resulting mixture was stirred at −78 °C for another 1 h. After addition of aqueous sodium hydrogen carbonate, the resulting mixture was extracted with $CH_2Cl_2$. The extract was washed with brine, and condensed in vacuo. The residue was purified by column chromatography (*n*-hexane–EtOAc, 12/1) to give 2-(*tert*-butyldimethylsiloxy)ethanol-1-yl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-*p*-methoxybenzyl-β-D-mannopyranoside (**16g**, 397 mg, 73%) as a colorless oil. $[\alpha]_D^{25}$ −47.4 (*c* 1.08, $CHCl_3$). IR (neat) $cm^{-1}$:1512, 1454, 1385, 1250, 1096. $^1H$ NMR (800 MHz, $CDCl_3$) $\delta$: 0.06/0.07 [each s, 3H, Si(C$H_3$)$_2$], 0.89 [s, 9H, SiC(C$H_3$)$_3$], 3.31 (ddd, *J* = 10.3, 9.8, 4.8 Hz, 1H, H-5′), 3.55 (dd, *J* = 9.8, 3.2 Hz, 1H, H-3′), 3.63 (ddd, *J* = 10.5, 7.8, 4.6 Hz, 1H, H-1a), 3.77 (ddd, *J* = 11.0, 4.6, 4.1 Hz, 1H, H-2a), 3.80 (s, 3H, OC$H_3$), 3.82 (ddd, *J* = 11.0, 7.8, 4.4 Hz, 1H, H-2b), 3.926 (dd, *J* = 10.3, 10.3 Hz, 1H, H-6′a), 3.933 (ddd, *J* = 10.5, 4.4, 4.1 Hz, 1H, H-1b), 3.94 (dd, *J* = 3.2, 0.7 Hz, 1H, H-2′), 4.18 (dd, *J* = 9.8, 9.8 Hz, 1H, H-4′), 4.30 (dd, *J* = 10.3, 4.8 Hz, 1H, H-6′b), 4.54/4.64 (each d, *J* = 12.4 Hz, 1H, OC$H_2$Ph), 4.56 (d, *J* = 0.7 Hz, 1H, H-1′), 4.81/4.90 (each d, *J* = 11.6 Hz, 1H, OC$H_2$C$_6$H$_4$OCH$_3$), 5.61 (s, 1H, C*H*Ph), 6.84 (d, *J* = 8.8 Hz, 2H, Ar), 7.25−7.30 (m, 5H, Ar), 7.34−7.38 (m, 3H, Ar), 7.38 (d, *J* = 8.8 Hz, 2H, Ar), 7.49−7.50 (m, 2H, Ar). $^{13}C$ NMR (200 MHz, $CDCl_3$) $\delta$: −5.32/−5.30 [Si(*C*H$_3$)$_2$], 18.3 [Si*C*(CH$_3$)$_3$], 25.9 [3C, SiC(*C*H$_3$)$_3$], 55.2 (OC$H_3$), 62.7 (C-2), 67.6 (C-5′), 68.6 (C-6′), 71.1 (C-1), 72.2 (OC$H_2$Ph), 74.3 (OC$H_2$C$_6$H$_4$OCH$_3$), 75.3 (C-2′), 77.8 (C-3′), 78.6 (C-4′), 101.4 (*C*HPh), 102.7 (C-1′), 113.5 (2C)/126.0 (2C)/127.5 (3C)/128.2 (2C)/128.3 (2C)/128.8/130.3 (2C) (d, Ar), 130.6/137.6/138.3/159.2 (s, Ar). FAB MS *m*/*z* (%): 659 ([M+Na]$^+$, 7), 121 (100). FAB HRMS calcd for $C_{36}H_{48}O_8SiNa$ [M+Na]$^+$: 659.3016; found: 659.3041.

Following the method described above, (*R*)-(−)-2,2-dimethyl-1,3-dioxolane-4-methanol (**3h**, 476 mg, 3.60 mmol), **3i** (116 mg, 0.421 mmol), **3j** (476 mg, 2.05 mmol), and **3k** (300 mg, 0.903 mmol) were converted to the corresponding coupled products, 1, 2-*O*-isopropylidene-D-glycerol-3-yl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-*p*-methoxybenzyl-β-D-mannopyranoside (**16h**, 692 mg, 40%), 2,3:4,5-di-*O*-isopropylidene-D-arabinitol-1-yl 1-*O*-(*tert*-butyldimethylsilyl)-2,3-*O*-isopropylidene-D-erythritol-4-yl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-*p*-methoxybenzyl-β-D-mannopyranoside (**16i**, 161 mg, 62%), 1,2:3,4-di-*O*-isopropylidene-D-arabinitol-5-yl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-*p*-methoxybenzyl-β-D-mannopyranoside (**16j**, 620 mg, 52%), and 2,3:4,5:6,7-tri-*O*-isopropylidene-D-glycero-D-galactoheptitol-1-yl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-*p*-methoxybenzyl-β-D-mannopyranoside (**16k**, 250 mg, 42%), respectively.

***16h***: A colorless oil. $[\alpha]_D^{24}$ −62.3 (*c* 0.79, $CHCl_3$). IR (neat) $cm^{-1}$: 1612, 1512, 1454, 1373, 1250, 1215, 1096, 1053. $^1H$ NMR (700 MHz, $CDCl_3$) $\delta$: 1.38/1.42 [each s, 3H, C(C$H_3$)$_2$], 3.32 (ddd, *J* = 10.2, 9.6, 4.8 Hz, 1H, H-5′), 3.57 (dd, *J* = 9.6, 3.2 Hz, 1H, H-3′), 3.59 (dd, *J* = 10.0, 6.2 Hz, 1H, H-3a), 3.75 (dd, *J* = 8.4, 6.2 Hz, 1H, H-1a), 3.80 (s, 3H, OC$H_3$), 3.88 (dd, *J* = 10.0, 5.8 Hz, 1H, H-3b), 3.93 (dd, *J* = 10.2, 10.2 Hz, 1H, H-6′a), 3.96 (dd, *J* = 3.2, 0.8 Hz, 1H, H-2′), 4.09 (dd, *J* = 8.4, 6.4 Hz, 1H, H-1b), 4.19 (dd, *J* = 9.6, 9.6 Hz, 1H, H-4′), 4.29 (dddd, *J* = 6.4, 6.2, 6.2, 5.8 Hz, 1H, H-2), 4.30 (dd, *J* = 10.2, 4.8 Hz, 1H, H-6′b), 4.52 (d, *J* = 0.8 Hz, 1H, H-1′), 4.58/4.68 (each d, 1H, *J* = 12.4 Hz, OC$H_2$Ph), 4.81/4.88 (each d, 1H, *J* = 11.8 Hz, OC$H_2$C$_6$H$_4$OCH$_3$), 5.61 (s, 1H, C*H*Ph), 6.85 (d, *J* = 8.6 Hz, 2H, Ar), 7.26–7.31 (m, 5H, Ar), 7.34–7.39 (m, 5H, Ar), 7.49–7.50 (m, 2H, Ar). $^{13}C$ NMR (175 MHz, $CDCl_3$) $\delta$: 25.4/26.8 [C(*C*H$_3$)$_2$], 55.3 (OC$H_3$), 67.0 (C-1), 67.7 (C-5′), 68.5 (C-6′), 70.9 (C-3), 72.4 (OC$H_2$Ph), 74.3 (OC$H_2$C$_6$H$_4$OCH$_3$), 74.7 (C-2), 75.1 (C-2′), 77.8 (C-3′), 78.6 (C-4′), 101.4 (*C*HPh), 102.2 (C-1′), 109.6 [*C*(CH$_3$)$_2$], 113.5 (2C)/126.0 (2C)/127.52 (2C)/127.55/128.2 (2C)/128.3 (2C)/128.8/130.2 (2C) (d, Ar), 130.5/137.5/138.3/159.2 (s, Ar). FABMS *m*/*z* (%): 615 ([M+Na]$^+$, 13), 57 (100). FABHRMS calcd for $C_{34}H_{40}O_9Na$ [M+Na]$^+$: 615.2570; found: 615.2593.

***16i***: A colorless oil. $[\alpha]_D^{25}$ −34.1 (*c* 0.73, $CHCl_3$). IR (neat) $cm^{-1}$: 1612, 1512, 1454, 1373, 1304, 1250, 1219, 1173, 1111, 1057. $^1H$ NMR (700 MHz, $CDCl_3$) $\delta$: 0.039/0.042 [each s, 3H, Si(C$H_3$)$_2$], 0.87 [s, 9H, SiC(C$H_3$)$_3$], 1.38/1.45 [each s, 3H, C(C$H_3$)$_2$], 3.31 (ddd, *J* = 10.0, 9.6, 4.8 Hz, 1H, H-5′), 3.565 (dd, *J* = 9.6, 3.2 Hz, 1H, H-3′), 3.573 (dd, *J* = 10.5, 4.8 Hz, 1H, H-1a), 3.60 (dd, 11.0, 8.6 Hz, 1H, H-4a), 3.62 (dd, *J* = 10.5, 7.6 Hz, 1H, H-1b), 3.80 (s, 3H, OC$H_3$), 3.92 (dd, *J* = 10.4, 10.0 Hz, 1H, H-6′a), 4.01 (d, *J* = 3.2 Hz, 1H, H-2′), 4.13 (ddd, *J* = 7.6, 6.2, 4.8 Hz, 1H, H-2), 4.19 (dd, *J* = 9.6, 9.6 Hz, 1H, H-4′), 4.27 (dd, *J* = 10.4, 4.8 Hz, 1H, H-6′b), 4.29 (dd, *J* = 11.0,

2.4 Hz, 1H, H-4b), 4.44 (ddd, *J* = 8.6, 6.2, 2.4 Hz, 1H, H-3), 4.55 (s, 1H, H-1′), 4.58/4.66 (each d, *J* = 12.4 Hz, 1H, OC*H*$_2$Ph), 4.85/4.91 (each d, *J* = 11.8 Hz, 1H, OC*H*$_2$C$_6$H$_4$OCH$_3$), 5.62 (s, 1H, C*H*Ph), 6.85 (d, *J* = 8.6 Hz, 2H, Ar), 7.25–7.33 (m, 5H, Ar), 7.33–7.39 (m, 3H, Ar), 7.41 (d, *J* = 8.6 Hz, 2H, Ar), 7.49–7.50 (m, 2H, Ar). $^{13}$C NMR (175 MHz, $CDCl_3$) $\delta$: −5.6/−5.5 [Si(*C*H$_3$)$_2$], 18.1 [Si*C*(CH$_3$)$_3$], 25.4/28.0 [C(*C*H$_3$)$_2$], 25.8 [3C, SiC(*C*H$_3$)$_3$], 55.2 (O*C*H$_3$), 61.6 (C-1), 67.6 (C-5′), 68.56/68.58 (C-4 and C-6′), 72.2 (O*C*H$_2$Ph), 74.3 (O*C*H$_2$C$_6$H$_4$OCH$_3$), 74.9 (C-2′), 76.7 (C-2), 77.0 (C-3), 77.7 (C-3′) 78.6 (C-4′), 101.4 (*C*HPh), 102.2 (C-1′), 108.6 [*C*(CH$_3$)$_2$], 113.5 (2C)/126.0 (2C)/127.51 (2C)/127.53/128.2 (2C)/128.3 (2C)/128.8/130.3 (2C) (d, Ar), 130.5/137.6/138.3/159.2 (s, Ar). FABMS *m*/*z* (%): 759 ([M+Na]$^+$, 6), 121 (100). FABHRMS calcd for $C_{41}H_{56}O_{10}SiNa$ [M+Na]$^+$: 759.3540; found: 759.3548.

***16j***: A colorless oil. $[\alpha]_D^{23}$ −43.6 (*c* 0.19, $CHCl_3$). IR (neat) cm$^{-1}$: 1377, 1250, 1219, 1092, 1049. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$: 1.34/1.40/1.46/1.49 [each s, 3H, C(*C*H$_3$)$_2$], 3.32 (ddd, *J* = 9.8, 9.8, 4.8 Hz, 1H, H-5′), 3.58 (dd, *J* = 9.8, 3.0 Hz, 1H, H-3′), 3.60 (dd, *J* = 10.0, 6.2 Hz, 1H, H-5a), 3.70 (dd, *J* = 8.4, 7.1 Hz, 1H, H-1a), 3.80 (s, 3H, O*C*H$_3$), 3.89 (dd, *J* = 10.2, 9.8 Hz, 1H, H-6′a), 3.95 (dd, *J* = 3.0, 0.8 Hz, 1H, H-2′), 3.98 (dd, *J* = 10.0, 6.4 Hz, 1H, H-5b), 4.126 (dd, *J* = 6.4, 6.4 Hz, 1H, H-3), 4.132 (dd, *J* = 8.4, 6.6 Hz, 1H, H-1b), 4.18 (dd, *J* = 9.8, 9.8 Hz, 1H, H-4′), 4.22 (ddd, *J* = 7.1, 6.6, 6.4 Hz, 1H, H-2), 4.296 (ddd, *J* = 6.4, 6.4, 6.2 Hz, 1H, H-4), 4.300 (dd, *J* = 10.2, 4.8 Hz, 1H, H-6′b), 4.50 (d, *J* = 0.8 Hz, 1H, H-1′), 4.58/4.70 (each d, *J* = 12.4 Hz, 1H, OC*H*$_2$Ph), 4.82 (s, 2H, OC*H*$_2$C$_6$H$_4$OCH$_3$), 5.62 (s, 1H, C*H*Ph), 6.85 (d, *J* = 8.8 Hz, 2H, Ar), 7.26–7.32 (m, 5H, Ar), 7.34–7.39 (m, 5H, Ar), 7.49–7.50 (m, 2H, Ar). $^{13}$C NMR (175 MHz, $CDCl_3$) $\delta$: 25.3/25.5/26.6/27.6 [C(*C*H$_3$)$_2$], 55.2 (O*C*H$_3$), 66.3 (C-1), 67.6 (C-5′), 68.1 (C-5), 68.6 (C-6′), 72.5 (O*C*H$_2$Ph), 74.2 (C-2), 74.5 (O*C*H$_2$C$_6$H$_4$OCH$_3$), 75.5 (2C, C-4 and C-2′), 77.7 (C-3), 77.9 (C-3′), 78.6 (C-4′), 101.4 (*C*HPh), 101.9 (C-1′), 109.2/109.6 [*C*(CH$_3$)$_2$], 113.5 (2C)/126.0 (2C)/127.5 (2C)/127.6/128.2 (2C)/128.3 (2C)/128.9/130.2 (2C) (d, Ar), 130.4/137.5/138.3/159.2 (s, Ar). FABMS *m*/*z* (%): 715 ([M+Na]$^+$, 7), 121 (100). FABHRMS calcd for $C_{39}H_{48}O_{11}Na$ [M+Na]$^+$: 715.3094; found: 715.3069.

***16k***: A colorless amorphous. $[\alpha]_D^{24}$ −44.3 (*c* 1.06, $CHCl_3$). IR (neat) cm$^{-1}$: 1512, 1454, 1377, 1250, 1215, 1092, 1049. $^1$H NMR (800 MHz, $CDCl_3$) $\delta$: 1.370/1.374/1.39/1.45/1.50/1.55 [each s, 3H, C(*C*H$_3$)$_2$], 3.32 (ddd, *J* = 10.3, 9.6, 4.8 Hz, 1H, H-5′), 3.58 (dd, *J* = 9.6, 3.2 Hz, 1H, H-3′), 3.67 (dd, *J* = 9.8, 6.2 Hz, 1H, H-7a), 3.68 (dd, *J* = 8.0, 7.4 Hz, 1H, H-1a), 3.80 (s, 3H, O*C*H$_3$), 3.89 (dd, *J* = 10.3, 10.3 Hz, 1H, H-6′a), 3.95 (dd, *J* = 3.2, 0.6 Hz, 1H, H-2′), 4.01 (dd, *J* = 8.0, 6.2 Hz, 1H, H-1b), 4.03 (dd, *J* = 9.8, 6.2 Hz, 1H, H-7b), 4.17 (dd, *J* = 9.6, 9.6 Hz, 1H, H-4′), 4.19 (dd, *J* = 6.2, 6.2 Hz, 1H, H-3), 4.26 (ddd, *J* = 7.4, 6.2, 6.2 Hz, 1H, H-2), 4.27 (dd, *J* = 6.2, 6.2 Hz, 1H, H-4), 4.28 (dd, *J* = 10.3, 4.8 Hz, 1H, H-6′b), 4.29 (dd, *J* = 6.2, 6.2 Hz, 1H, H-5), 4.38 (ddd, *J* = 6.2, 6.2, 6.2 Hz, 1H, H-6), 4.51 (d, *J* = 0.6 Hz, 1H, H-1′), 4.58/4.70 (each d, *J* = 12.4 Hz, 1H, OC*H*$_2$Ph), 4.82 (s, 2H, OC*H*$_2$C$_6$H$_4$OCH$_3$), 5.61 (s, 1H, C*H*Ph), 6.85 (d, *J* = 8.7 Hz, 2H, Ar), 7.26–7.31 (m, 5H, Ar), 7.35–7.39 (m, 5H, Ar), 7.49–7.50 (m, 2H, Ar). $^{13}$C NMR (200 MHz, $CDCl_3$) $\delta$: 25.2/25.56/25.59/26.5/26.9/27.4 [C(*C*H$_3$)$_2$], 55.2 (O*C*H$_3$), 66.2 (C-1), 67.6 (C-5′), 68.5 (C-6′), 68.6 (C-7), 72.5 (O*C*H$_2$Ph), 74.3 (O*C*H$_2$C$_6$H$_4$OCH$_3$), 74.7 (C-4), 75.0 (C-5), 75.41/74.44 (C-2 and C-2′), 75.7 (C-6), 77.5 (C-3), 77.9 (C-3′), 78.6 (C-4′), 101.4 (*C*HPh), 101.9 (C-1′), 109.09/109.15/109.4 [*C*(CH$_3$)$_2$], 113.5 (2C)/126.0 (2C)/127.5 (2C)/127.6/128.2 (2C)/128.3 (2C)/128.9/129.9 (2C) (d, Ar), 130.4/137.5/138.3/159.2 (s, Ar). FABMS *m*/*z* (%): 815 ([M+Na]$^+$, 3), 121 (100). FABHRMS calcd for $C_{44}H_{56}O_{13}Na$ [M+Na]$^+$: 815.3619; found: 815.3624.

### 3.1.10. Deprotection of PMB group at C2′position in coupled products (16g–16k)

To a mixture of **16g** (368 mg, 0.577 mmol) $CH_2Cl_2$ (5.0 mL), and $H_2O$ (200 μL) was added 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ, 191 mg, 0.808 mmol), and the mixture was stirred at room temperature for 1 h. After addition of aqueous sodium hydrogen carbonate, the resulting mixture was extracted with $CH_2Cl_2$. The extract was washed with brine, and concentrated in vacuo. The residue was purified by column chromatography (*n*-hexane–EtOAc, 1/1) to give 2-(*tert*-butyldimethylsiloxy)ethanol-1-yl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (**17k**, 214 mmol, 72%) as a colorless oil. $[\alpha]_D^{25}$ −18.0 (*c* 0.99, $CHCl_3$). IR (neat) cm$^{-1}$: 3451, 1385, 1256, 1094. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 0.05/0.06 [each s, 3H, Si(*C*H$_3$)$_2$], 0.88 [s, 9H, SiC(*C*H$_3$)$_3$], 3.34 (ddd, *J* = 9.6, 9.6, 4.8 Hz, 1H, H-5′), 3.63 (dd, *J* = 9.6, 3.2 Hz, 1H, H-3′), 3.71 (ddd, *J* = 10.4, 7.6, 4.0 Hz, 1H, H-1a), 3.76 (ddd, *J* = 11.2, 4.0, 4.0 Hz, 1H, H-2a), 3.83 (ddd, *J* = 11.2, 7.6, 4.4 Hz, 1H, H-2b), 3.89 (dd, *J* = 10.4, 9.6 Hz, 1H, H-6′a), 3.91 (ddd, *J* = 10.4, 4.4, 4.0 Hz, 1H, H-1b), 4.14 (dd, *J* = 3.2, 0.8 Hz, 1H, H-2′), 4.15 (dd, *J* = 9.6, 9.6 Hz, 1H, H-4′), 4.33 (dd, *J* = 10.4, 4.8 Hz, 1H, H-6′b), 4.63 (d, *J* = 0.8 Hz, 1H, H-1′), 4.78/4.86 (each d, *J* = 12.0 Hz, 1H, OC*H*$_2$Ph), 5.61 (s, 1H, C*H*Ph), 7.27−7.41 (m, 8H, Ar), 7.49−7.52 (m, 2H, Ar). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: −5.4/−5.3 [Si(*C*H$_3$)$_2$], 18.2 [Si*C*(CH$_3$)$_3$], 25.8 [3C, SiC(*C*H$_3$)$_3$], 62.6 (C-2), 66.9 (C-5′), 68.6 (C-6′), 70.0 (C-2′), 70.8 (C-1), 72.5 (O*C*H$_2$Ph), 76.7 (C-3′), 78.4 (C-4′), 100.7, (C-1′) 101.5 (*C*HPh), 126.0 (2C)/127.8/127.9 (2C)/128.2 (2C)/128.4 (2C)/128.9 (d, Ar), 137.4/137.9 (s, Ar). FABMS *m*/*z* (%): 539 ([M+Na]$^+$, 50), 91 (100). FABHRMS calcd for $C_{28}H_{40}O_7SiNa$ [M+Na]$^+$: 539.2441; found: 539.2432.

Following the method described above, **16h** (680 mg, 1.15 mmol), **16i** (134 mg, 0.182 mmol), **16j** (596 mg, 0.860 mmol), and **16k** (229 mg, 0.289 mmol) were converted to 1,2-*O*-isopropylidene-D-glycerol-3-yl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (**17h**, 490 mg, 90%), 1-*O*-(*tert*-butyldimethylsilyl)-2,3-*O*-isopropylidene-D-erythritol-4-yl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (**17i**, 91.0 mg, 81%), 1,2:3,4-di-*O*-isopropylidene-D-arabinitol-5-yl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (**17j**, 453 mg, 92%), and 2,3:4,5:6,7-tri-*O*-isopropylidene-D-glycero-D-galactoheptitol-1-yl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (**17k**, 165 mg, 85%), respectively.

***17h***: A colorless oil. $[\alpha]_D^{25}$ −20.7 (*c* 0.51, $CHCl_3$). IR (neat) cm$^{-1}$: 3483, 1454, 1373, 1258, 1211, 1153, 1096, 1049. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 1.36/1.42 [each s, 3H, C(*C*H$_3$)$_2$], 2.04 (br s, 1H, OH), 3.35 (ddd, *J* = 10.0, 9.6, 4.8 Hz, 1H, H-5′), 3.65 (dd, *J* = 9.6, 3.2 Hz, 1H, H-3′), 3.66 (dd, *J* = 10.8, 6.8 Hz, 1H, H-3a), 3.70 (dd, *J* = 8.4, 6.0 Hz, 1H, H-1a), 3.88 (dd, *J* = 10.8, 4.8 Hz, 1H, H-3b), 3.89 (dd, *J* = 10.4, 10.0 Hz, 1H, H-6′a), 4.08 (dd, *J* = 8.4, 6.4 Hz, 1H, H-1b), 4.14 (dd, *J* = 9.6, 9.6 Hz, 1H, H-4′), 4.19 (d, *J* = 3.2 Hz, 1H, H-2′), 4.33 (dd, *J* = 10.4, 4.8 Hz, 1H, H-6′b), 4.34 (dddd, *J* = 6.8, 6.4, 6.0, 4.8 Hz, 1H, H-2), 4.60 (s, 1H, H-1′), 4.78/4.86 (each d, *J* = 12.4 Hz, 1H, OC*H*$_2$Ph), 5.61 (s, 1H, C*H*Ph), 7.27–7.42 (m, 8H, Ar), 7.49–7.51 (m, 2H, Ar). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 25.3/26.8 [C(*C*H$_3$)$_2$], 66.7 (C-1), 67.0 (C-5′), 68.5 (C-6′), 69.7 (C-2′), 70.9 (C-3), 72.5 (O*C*H$_2$Ph), 74.7 (C-2), 76.7 (C-3′), 78.3 (C-4′), 100.4 (C-1′), 101.6 (*C*HPh), 109.8 [*C*(CH$_3$)$_2$], 126.0 (2C)/127.9 (3C)/ 128.2 (2C)/128.5 (2C)/129.0 (d, Ar), 137.4/137.9 (s, Ar). FABMS *m*/*z* (%): 495 ([M+Na]$^+$, 4), 55 (100). FABHRMS calcd for $C_{26}H_{32}O_8Na$ [M+Na]$^+$: 495.1995; found: 495.2010.

***17i***: A colorless oil. $[\alpha]_D^{24}$ −7.6 (*c* 0.99, $CHCl_3$). IR (neat) cm$^{-1}$: 3478, 1454, 1381, 1372, 1254, 1213, 1096, 1047. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 0.05 [s, 6H, Si(*C*H$_3$)$_2$], 0.88 [s, 9H, SiC(*C*H$_3$)$_3$], 1.35/1.44 [each s, 3H, C(*C*H$_3$)$_2$], 2.61 (br s, 1H, OH), 3.34 (ddd, *J* = 10.0, 9.6, 4.8 Hz, 1H, H-5′), 3.58 (dd, *J* = 10.8, 5.2 Hz, 1H, H-1a), 3.61 (dd, *J* = 10.8, 7.6 Hz, 1H, H-1b), 3.656 (dd, *J* = 9.2, 3.2 Hz, 1H, H-3′), 3.67 (dd, *J* = 11.2, 8.8 Hz, 1H, H-4a), 3.89 (dd, *J* = 10.4, 10.0 Hz, 1H, H-6′a), 4.13 (ddd, *J* = 7.6, 6.4, 5.2 Hz, 1H, H-2), 4.15 (dd, *J* = 9.6, 9.2 Hz, 1H, H-4′), 4.23 (dd, *J* = 3.2, 0.8 Hz, 1H, H-2′), 4.27 (dd, *J* = 11.2, 2.4 Hz, 1H, H-4b), 4.29 (dd, *J* = 10.4, 4.8 Hz, 1H, H-6′b), 4.44 (ddd, *J* = 8.8, 6.4, 2.4 Hz, 1H, H-3), 4.61 (d, *J* = 0.8 Hz, 1H, H-1′), 4.78/4.85 (each d, *J* = 12.4 Hz, 1H, OC*H*$_2$Ph), 5.61 (s, 1H,

C*H*Ph), 7.27–7.42 (m, 8H, Ar), 7.49–7.52 (m, 2H, Ar). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: −5.61/−5.58 [Si($CH_3$)$_2$], 18.0 [Si$C$($CH_3$)$_3$], 25.3/27.9 [C($CH_3$)$_2$], 25.7 [3C, SiC($CH_3$)$_3$], 61.5 (C-1), 66.9 (C-5′), 68.5 (2C, C-4 and C-6′), 69.6 (C-2′), 72.3 (O$CH_2$Ph), 76.47/76.49 (C-2 and C-3), 76.7 (C-3′), 78.3 (C-4′), 100.5 (C-1′), 101.5 (*C*HPh), 108.8 [$C$($CH_3$)$_2$], 126.0 (2C)/127.78/127.82 (2C)/128.2 (2C)/128.4 (2C)/129.0 (d, Ar), 137.4/137.9 (s, Ar). FABMS *m*/*z* (%): 639 ([M+Na]$^+$, 56), 91 (100). FABHRMS calcd for $C_{33}H_{48}O_9SiNa$ [M+Na]$^+$: 639.2965; found: 639.2973.

***17j***: A colorless oil. $[\alpha]_D^{23}$ −13.4 (*c* 1.19, $CHCl_3$). IR (neat) cm$^{-1}$: 3483, 1454, 1373, 1250, 1215, 1092, 1045. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 1.37/1.38/1.46/1.48 [each s, 3H, C(C$H_3$)$_2$], 3.35 (ddd, *J* = 10.0, 9.6, 4.8 Hz, 1H, H-5′), 3.62 (dd, *J* = 10.0, 6.4 Hz, 1H, H-5a), 3.65 (dd, *J* = 9.6, 3.2 Hz, 1H, H-3′), 3.70 (dd, *J* = 7.6, 6.0 Hz, 1H, H-1a), 3.87 (dd, *J* = 10.4, 10.0 Hz, 1H, H-6′a), 3.97 (dd, *J* = 10.0, 6.4 Hz, 1H, H-5b), 4.12 (dd, *J* = 9.6, 9.6 Hz, 1H, H-4′), 4.13 (dd, *J* = 6.4, 6.4 Hz, 1H, H-3), 4.14 (d, *J* = 3.2 Hz, 1H, H-2′), 4.19 (dd, *J* = 7.6, 6.8 Hz, 1H, H-1b), 4.23 (ddd, *J* = 6.8, 6.4, 6.0 Hz, 1H, H-2), 4.30 (ddd, *J* = 6.4, 6.4, 6.4 Hz, 1H, H-4), 4.33 (dd, *J* = 10.4, 4.8 Hz, 1H, H-6′b), 4.56 (s, 1H, H-1′), 4.77/4.85 (each d, *J* = 12.0 Hz, 1H, O$CH_2$Ph), 5.61 (s, 1H, C*H*Ph), 7.28–7.42 (m, 8H, Ar), 7.48–7.51 (m, 2H, Ar). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 25.2/25.4/26.6/27.7 [C($CH_3$)$_2$], 66.3 (C-1), 67.0 (C-5′), 68.0 (C-5), 68.6 (C-6′), 69.7 (C-2′), 72.5 (O$CH_2$Ph), 74.1 (C-2), 75.4 (C-4), 76.6 (C-3′), 77.9 (C-3), 78.3 (C-4′), 100.5 (C-1′), 101.6 (*C*HPh), 109.3/109.7 [$C$($CH_3$)$_2$], 126.0 (2C)/127.8 (2C)/127.9/128.2 (2C)/128.5 (2C)/129.0 (d, Ar), 137.3/137.8 (s, Ar). FABMS *m*/*z* (%): 595 ([M+Na]$^+$, 20), 154 (100). FABHRMS calcd for $C_{31}H_{40}O_{10}Na$ [M+Na]$^+$: 595.2519; found: 595.2512.

***17k***: A colorless oil. $[\alpha]_D^{25}$ −7.4 (*c* 0.38, $CHCl_3$). IR (neat) cm$^{-1}$: 3483, 1454, 1377, 1246, 1215, 1092, 1049. $^1$H NMR (800 MHz, $CDCl_3$) $\delta$: 1.375/1.384/1.39/1.45/1.48/1.55 [each s, 3H, C(C$H_3$)$_2$], 3.34 (ddd, *J* = 10.3, 9.6, 4.8 Hz, 1H, H-5′), 3.60 (dd, *J* = 9.8, 5.5 Hz, 1H, H-7a), 3.65 (dd, *J* = 9.6, 3.4 Hz, 1H, H-3′), 3.79 (dd, *J* = 8.0, 7.8 Hz, 1H, H-1a), 3.85 (dd, *J* = 10.3, 10.3 Hz, 1H, H-6′a), 4.01 (dd, *J* = 9.8, 7.6 Hz, 1H, H-7b), 4.04 (dd, *J* = 8.0, 6.6 Hz, 1H, H-1b), 4.09 (dd, *J* = 9.6, 9.6 Hz, 1H, H-4′), 4.11 (dd, *J* = 3.4, 0.9 Hz, 1H, H-2′), 4.23 (ddd, *J* = 7.8, 6.6, 4.1 Hz, 1H, H-2), 4.326 (dd, *J* = 6.9, 6.6 Hz, 1H, H-4), 4.328 (dd, *J* = 10.3, 4.8 Hz, 1H, H-6′b), 4.37 (ddd, *J* = 7.6, 6.0, 5.5 Hz, 1H, H-6), 4.39 (dd, *J* = 6.9, 4.1 Hz, 1H, H-3), 4.41 (dd, *J* = 6.6, 6.0 Hz, 1H, H-5), 4.55 (d, *J* = 0.9 Hz, 1H, H-1′), 4.76/4.86 (each d, *J* = 12.4 Hz, 1H, O$CH_2$Ph), 5.60 (s, 1H, C*H*Ph), 7.29–7.40 (m, 8H, Ar), 7.49 (m, 2H, Ar). $^{13}$C NMR (200 MHz, $CDCl_3$) $\delta$: 25.1/25.6/25.8/26.4/26.8/27.8 [C($CH_3$)$_2$], 66.4 (C-1), 66.9 (C-5′), 68.1 (C-7), 68.6 (C-6′), 69.7 (C-2′), 72.6 (O$CH_2$Ph), 75.20/75. 21 (C-4 and C-5), 75.3 (C-2), 75.7 (C-6), 76.3 (C-3), 76.6 (C-3′), 78.4 (C-4′), 100.4 (C-1′), 101.6 (*C*HPh), 108.8/109.0/109.6 [$C$($CH_3$)$_2$], 126.0 (2C)/127.9 (2C)/128.0/128.3 (2C)/128.5 (2C)/129.0 (d, Ar), 137.3/137.7 (s, Ar). FABMS *m*/*z* (%): 695 ([M+Na]$^+$, 36), 91 (100). FABHRMS calcd for $C_{36}H_{48}O_{12}Na$ [M+Na]$^+$: 695.3043; found: 695.3030.

### 3.1.11. Esterification of monoalcohols (17g–17k)

To a solution of **17g** (216 mg, 0.418 mmol) and *N*,*N*-dimethylaminopyridine (DMAP, 153 mg, 1.25 mmol) in a mixture of $CH_2Cl_2$ (4.2 mL) and pyridine (0.14 mL, 1.67 mmol) was added *n*-octanoyl chloride (0.36 mL, 2.09 mmol), and the mixture was stirred at room temperature for 7 h. After the reaction was quenched with water, the resulting mixture was extracted with $CH_2Cl_2$. The extract was successively washed with aqueous sodium bicarbonate, water and brine, and concentrated in vacuo. The residue was purified by column chromatography (*n*-hexane–EtOAc, 20/1) to give 2-(*tert*-butyldimethylsiloxy)ethanol-1-yl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-octanoyl-β-D-mannopyranoside (**18g**, 207 mg, 77%) as a colorless oil. $[\alpha]_D^{25}$ −50.8 (*c* 1.08, $CHCl_3$). IR (neat) cm$^{-1}$: 1746, 1456, 1373, 1256, 1157, 1096. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 0.05/0.06 [each s, 3H, Si($CH_3$)$_2$], 0.87 [t, *J* = 7.2 Hz, 3H, $CO(CH_2)_6CH_3$], 0.89 [s, 9H, SiC($CH_3$)$_3$], 1.25−1.33 [m, 8H, $CO(CH_2)_2(CH_2)_4CH_3$], 1.66 [tt, *J* = 7.6, 7.6 Hz, 2H, $COCH_2CH_2(CH_2)_4CH_3$], 2.46 [t, *J* = 7.6 Hz, 2H, $COCH_2(CH_2)_5CH_3$], 3.38 (ddd, *J* = 10.0, 10.0, 4.8 Hz, 1H, H-5′), 3.68 (ddd, *J* = 10.0, 7.6, 4.0 Hz, 1H, H-1a), 3.70 (dd, *J* = 10.0, 3.2 Hz, 1H, H-3′), 3.73 (ddd, *J* =11.2, 4.0, 4.0 Hz, 1H, H-2a), 3.79 (ddd, *J* = 11.2, 7.6, 4.0 Hz, 1H, H-2b), 3.86 (ddd, *J* = 10.0, 4.0, 4.0 Hz, 1H, H-1b), 3.90 (dd, *J* = 10.0, 10.0 Hz, 1H, H-6′a), 3.99 (dd, *J* = 10.0, 10.0 Hz, 1H, H-4′), 4.33 (dd, *J* = 10.0, 4.8 Hz, 1H, H-6′b), 4.62/4.74 (each d, *J* = 12.4 Hz, 1H, O$CH_2$Ph), 4.73 (d, *J* = 1.2 Hz, 1H, H-1′), 5.61 (s, 1H, C*H*Ph), 5.69 (dd, *J* = 3.2, 1.2 Hz, 1H, H-2′), 7.24–7.40 (m, 8H, Ar), 7.49–7.52 (m, 2H, Ar). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: −5.4/−5.3 [Si($CH_3$)$_2$], 14.1 [$CO(CH_2)_6CH_3$], 18.3 [Si$C$($CH_3$)$_3$], 22.6 [$CO(CH_2)_5CH_2CH_3$], 25.0 [$COCH_2CH_2(CH_2)_5CH_3$], 25.9 [3C, SiC($CH_3$)$_3$], 28.95/28.99 [$CO(CH_2)_2(CH_2)_2(CH_2)_2CH_3$], 31.7 [$CO(CH_2)_4CH_2CH_2CH_3$], 34.1 [$COCH_2(CH_2)_5CH_3$], 62.7 (C-2), 67.3 (C-5′), 68.47 (C-2′), 68.53 (C-6′), 71.2 (C-1), 71.6 (O$CH_2$Ph), 75.8 (C-3′), 78.0 (C-4′), 100.1 (C-1′), 101.5 (*C*HPh), 126.1 (2C)/127.7/127.8 (2C)/128.2 (2C)/128.3 (2C)/128.9 (d, Ar), 137.4/137.7 (s, Ar), 173.1 (O$COCH_2$). FABMS *m*/*z* (%): 665 ([M+Na]$^+$, 2), 91 (100). FABHRMS calcd for $C_{36}H_{54}O_8SiNa$ [M+Na]$^+$: 665.3486; found: 665.3501.

Following the method described above, **17h** (474 mg, 0.997 mmol), **17i** (91.0 mg, 0.148 mmol), **17j** (417 mg, 0.728 mmol), and **17k** (150 mg, 0.223 mmol) were converted to 1,2-*O*-isopropylidene-D-glycerol-3-yl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-octanoyl-β-D-mannopyranoside (**18h**, 565 mg, 95%), 1-*O*-(*tert*-butyldimethylsilyl)-2,3-*O*-isopropylidene-D-erythritol-4-yl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-octanoyl-β-D-mannopyranoside (**18i**, 97.0 mg, 88%), 1,2:3,4-di-*O*-isopropylidene-D-arabinitol-5-yl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-octanoyl-β-D-mannopyranoside (**18j**, 509 mg, quant.), and 2,3:4,5:6,7-tri-*O*-isopropylidene-D-glycero-D-galactoheptitol-1-yl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-octanoyl-β-D-mannopyranoside (**18k**, 160 mg, 90%), respectively.

***18h***: A colorless oil. $[\alpha]_D^{23}$ −66.3 (*c* 1.31, $CHCl_3$). IR (neat) cm$^{-1}$: 1744, 1454, 1373, 1250, 1215, 1157, 1096, 1053. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 0.87 [t, *J* = 7.2 Hz, 3H, $CO(CH_2)_6CH_3$], 1.25–1.34 [m, 8H, $CO(CH_2)_2(CH_2)_4CH_3$], 1.35/1.40 [each s, 3H, C(C$H_3$)$_2$], 1.66 [tt, *J* = 7.2, 7.2 Hz, 2H, $COCH_2CH_2(CH_2)_4CH_3$], 2.45 [t, *J* = 7.2 Hz, 2H, $COCH_2(CH_2)_5CH_3$], 3.38 (ddd, *J* = 10.0, 9.6, 4.8 Hz, 1H, H-5′), 3.66 (dd, *J* = 10.4, 6.0 Hz, 1H, H-3a), 3.71 (dd, *J* = 8.4, 6.0 Hz, 1H, H-1a), 3.72 (dd, *J* = 9.6, 3.6 Hz, 1H, H-3′), 3.79 (dd, *J* = 10.4, 5.6 Hz, 1H, H-3b), 3.90 (dd, *J* = 10.4, 10.0 Hz, 1H, H-6′a), 3.99 (dd, *J* = 9.6, 9.6 Hz, 1H, H-4′), 4.03 (dd, *J* = 8.4, 6.4 Hz, 1H, H-1b), 4.25 (dddd, *J* = 6.4, 6.0, 6.0, 5.6 Hz, 1H, H-2′), 4.33 (dd, *J* = 10.4, 4.8 Hz, 1H, H-6′b), 4.63/4.74 (each d, *J* = 12.4 Hz, 1H, O$CH_2$Ph), 4.70 (d, *J* = 1.2 Hz, 1H, H-1′), 5.61 (s 1H, C*H*Ph), 5.67 (dd, *J* = 3.6, 1.2 Hz, 1H, H-2′), 7.27–7.41 (m, 8H, Ar), 7.49–7.51 (m, 2H, Ar). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 14.1 [$CO(CH_2)_6CH_3$], 22.6 [$CO(CH_2)_5CH_2CH_3$], 25.0 [$COCH_2CH_2(CH_2)_5CH_3$], 25.4/26.8 [C($CH_3$)$_2$], 28.9/29.0 [$CO(CH_2)_2(CH_2)_2(CH_2)_2CH_3$], 31.7 [$CO(CH_2)_4CH_2CH_2CH_3$], 34.1 [$COCH_2(CH_2)_5CH_3$], 66.8 (C-1), 67.3 (C-5′), 68.3 (C-2′), 68.5 (C-6′), 70.5, (C-3) 71.6 (O$CH_2$Ph), 74.5 (C-2), 75.6 (C-3′), 77.9 (C-4′), 99.6 (C-1′), 101.5 (*C*HPh), 109.6 [$C$($CH_3$)$_2$], 126.0 (2C)/127.7 (3C)/128.2 (2C)/128.3 (2C)/129.0 (d, Ar), 137.3/137.7 (s, Ar), 173.2 (O$COCH_2$). FABMS *m*/*z* (%): 621 ([M+Na]$^+$, 20), 73 (100). HRMSFAB calcd for $C_{34}H_{46}O_9Na$ [M+Na]$^+$: 621.3040; found: 621.3039.

***18i***: A colorless oil. $[\alpha]_D^{24}$ −43.8 (*c* 1.29, $CHCl_3$). IR (neat) cm$^{-1}$: 1744, 1458, 1377, 1254, 1215, 1157, 1096, 1049. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$: 0.047/0.048 [each s, 3H, Si($CH_3$)$_2$], 0.87 [t, *J* = 7.4 Hz, 3H, $CO(CH_2)_6CH_3$], 0.88 [s, 9H, SiC($CH_3$)$_3$], 1.22–1.31 [m, 8H, $CO(CH_2)_2(CH_2)_4CH_3$], 1.35/1.42 [each s, 3H, C(C$H_3$)$_2$], 1.67 [tt, *J* = 7.6, 7.6 Hz, 2H, $COCH_2CH_2(CH_2)_4CH_3$], 2.46 [t, *J* = 7.6 Hz, 2H, $COCH_2(CH_2)_5CH_3$], 3.38 (ddd, *J* = 10.0, 9.6, 4.8 Hz, 1H, H-5′), 3.57 (dd, *J* = 10.8, 4.8 Hz, 1H, H-1a), 3.62 (dd, *J* = 10.8, 7.2 Hz, 1H, H-1b), 3.70 (dd, *J* = 11.4, 8.2 Hz, 1H, H-4a), 3.73 (dd, *J* = 9.6,

3.4 Hz, 1H, H-3′), 3.89 (dd, *J* = 10.4, 10.0 Hz, 1H, H-6′a), 3.98 (dd, *J* = 9.6, 9.6 Hz, 1H, H-4′), 4.11 (ddd, *J* = 7.2, 6.4, 4.8 Hz, 1H, H-2), 4.14 (dd, *J* = 11.4, 3.0 Hz, 1H, H-4b), 4.31 (dd, *J* = 10.4, 4.8 Hz, 1H, H-6′b), 4.34 (ddd, *J* = 8.2, 6.4, 3.0 Hz, 1H, H-3), 4.62/4.745 (each d, *J* = 12.4 Hz, 1H, OC*H*$_2$Ph), 4.744 (d, *J* = 1.2 Hz, 1H, H-1′), 5.61 (s, 1H, C*H*Ph), 5.72 (dd, *J* = 3.4, 1.2 Hz, 1H, H-2′), 7.26–7.32 (m, 3H, Ar), 7.36–7.40 (m, 5H, Ar), 7.49–7.51 (m, 2H, Ar). $^{13}$C NMR (175 MHz, $CDCl_3$) *δ*: −5.52/−5.49 [Si(*C*H$_3$)$_2$], 14.0 [CO(CH$_2$)$_6$*C*H$_3$], 18.1 [Si*C*(CH$_3$)$_3$], 22.6 [CO(CH$_2$)$_5$*C*H$_2$CH$_3$], 25.0 [COCH$_2$*C*H$_2$(CH$_2$)$_5$CH$_3$], 25.3/27.9 [C(*C*H$_3$)$_2$], 25.8 [3C, SiC(*C*H$_3$)$_3$], 28.9/29.0 [CO(CH$_2$)$_2$(*C*H$_2$)$_2$(CH$_2$)$_2$CH$_3$], 31.7 [CO(CH$_2$)$_4$*C*H$_2$CH$_2$CH$_3$], 34.2 [CO*C*H$_2$(CH$_2$)$_5$CH$_3$], 61.6 (C-1), 67.3 (C-5′), 68.4 (C-4), 68.49 (C-2′), 68.52 (C-6′), 71.5 (O*C*H$_2$Ph), 75.7 (C-3′), 76.78 (C-3), 76.82 (C-2), 78.0 (C-4′), 99.7 (C-1′), 101.5 (*C*HPh), 108.7 [*C*(CH$_3$)$_2$], 126.1 (2C)/127.67/127.72 (2C)/128.2 (2C)/128.3 (2C)/128.9 (d, Ar), 137.4/137.7 (s, Ar), 173.2 (OCOCH$_2$). FABMS *m*/*z* (%): 765 ([M+Na]$^+$, 1), 73 (100). FABHRMS calcd for $C_{41}H_{62}O_{10}SiNa$ [M+Na]$^+$: 765.4010; found: 765.3992.

***18j***: A colorless oil. $[\alpha]_D^{24}$ −53.9 (*c* 1.55, $CHCl_3$). IR (neat) cm$^{-1}$: 1744, 1454, 1373, 1250, 1219, 1157, 1092, 1049. $^1$H NMR (400 MHz, $CDCl_3$) *δ*: 0.87 [t, *J* = 6.8 Hz, 3H, CO(CH$_2$)$_6$*CH*$_3$], 1.24–1.38 [m, 8H, CO(CH$_2$)$_2$(*CH*$_2$)$_4$CH$_3$], 1.37 [s, 6H, C(*CH*$_3$)$_2$], 1.456/1.462 [each s, 3H, C(*CH*$_3$)$_2$], 1.67 [tt, *J* = 7.6, 7.6 Hz, 2H, COCH$_2$*CH*$_2$(CH$_2$)$_4$CH$_3$], 2.43/2.48 [each dt, *J* = 16.0, 7.6 Hz, 1H, COC*H*$_2$(CH$_2$)$_5$CH$_3$], 3.37 (ddd, *J* = 10.0, 10.0, 4.8 Hz, 1H, H-5′), 3.56 (dd, *J* = 10.0, 4.8 Hz, 1H, H-5a), 3.61 (dd, *J* = 8.4, 7.2 Hz, 1H, H-1a), 3.71 (dd, *J* = 10.0, 3.2 Hz, 1H, H-3′), 3.87 (dd, *J* = 10.4, 10.0 Hz, 1H, H-6′a), 3.93 (dd, *J* = 10.0, 8.0 Hz, 1H, H-5b), 3.96 (dd, *J* = 10.0, 10.0 Hz, 1H, H-4′), 4.09 (dd, *J* = 6.4, 5.6 Hz, 1H, H-3), 4.12 (dd, *J* = 8.4, 6.8 Hz, 1H, H-1b), 4.19 (ddd, *J* = 8.0, 5.6, 4.8 Hz, 1H, H-4), 4.25 (ddd, *J* = 7.2, 6.8, 6.4 Hz, 1H, H-2), 4.34 (dd, *J* = 10.4, 4.8 Hz, 1H, H-6′b), 4.62/4.73 (each d, *J* = 12.4 Hz, 1H, OC*H*$_2$Ph), 4.64 (d, *J* = 0.8 Hz, 1H, H-1′), 5.61 (s, 1H, C*H*Ph), 5.65 (dd, *J* = 3.2, 0.8 Hz, 1H, H-2′), 7.25–7.42 (m, 8H, Ar), 7.49–7.51 (m, 2H, Ar). $^{13}$C NMR (100 MHz, $CDCl_3$) *δ*: 14.1 [CO(CH$_2$)$_6$*C*H$_3$], 22.6 [CO(CH$_2$)$_5$*C*H$_2$CH$_3$], 24.9 [COCH$_2$*C*H$_2$(CH$_2$)$_5$CH$_3$], 25.2/25.4/26.6/27.8 [C(*C*H$_3$)$_2$], 28.96/29.00 [CO(CH$_2$)$_2$(*C*H$_2$)$_2$(CH$_2$)$_2$CH$_3$], 31.7 [CO(CH$_2$)$_4$*C*H$_2$CH$_2$CH$_3$], 34.2 [CO*C*H$_2$(CH$_2$)$_5$CH$_3$], 66.4 (C-1), 67.4 (C-5′), 67.8 (C-5), 68.4 (C-2′), 68.5 (C-6′), 71.6 (O*C*H$_2$Ph), 74.1 (C-2), 74.9 (C-4), 75.6 (C-3′), 77.9 (C-4′), 78.4 (C-3), 99.6 (C-1′), 101.6 (*C*HPh), 109.2/109.5 [*C*(CH$_3$)$_2$], 126.1 (2C)/127.7 (3C)/128.2 (2C)/128.3 (2C)/129.0 (d, Ar), 137.3/137.6 (s, Ar), 173.1 (OCOCH$_2$). FABMS *m*/*z* (%): 721 ([M+Na]$^+$, 2), 91 (100). FABHRMS calcd for $C_{39}H_{54}O_{11}Na$ [M+Na]$^+$: 721.3564; found: 721.3592.

***18k***: A colorless amorphous. $[\alpha]_D^{25}$ −42.9 (*c* 1.07, $CHCl_3$). IR (neat) cm$^{-1}$: 1744, 1454, 1377, 1246, 1215, 1157, 1092, 1049. $^1$H NMR (800 MHz, $CDCl_3$) *δ*: 0.87 [t, *J* = 7.2 Hz, 3H, CO(CH$_2$)$_6$*CH*$_3$], 1.22–1.39 [m, 8H, CO(CH$_2$)$_2$(*CH*$_2$)$_4$CH$_3$], 1.37 [s, 6H, C(*CH*$_3$)$_2$], 1.38/1.45/1.47/1.55 [each s, 3H, C(*CH*$_3$)$_2$], 1.61–1.69 [m, 2H, COCH$_2$*CH*$_2$(CH$_2$)$_4$CH$_3$], 2.41/ 2.45 [each ddd, *J* = 15.8, 8.2, 6.9 Hz, 1H, COC*H*$_2$(CH$_2$)$_5$CH$_3$], 3.38 (ddd, *J* = 9.8, 9.8, 4.8 Hz, 1H, H-5′), 3.61 (dd, *J* = 10.5, 5.3 Hz, 1H, H-7a), 3.71 (dd, *J* = 9.8, 3.2 Hz, 1H, H-3′), 3.77 (dd, *J* = 8.0, 7.3 Hz, 1H, H-1a), 3.87 (dd, *J* = 10.6, 9.8 Hz, 1H, H-6′a), 3.96 (dd, *J* = 9.8, 9.8 Hz, 1H, H-4′), 3.99 (dd, *J* = 10.5, 8.0 Hz, 1H, H-7b), 4.08 (dd, *J* = 8.0, 6.4 Hz, 1H, H-1b), 4.11 (dd, *J* = 6.7, 4.6 Hz, 1H, H-3), 4.16 (ddd, *J* = 7.3, 6.4, 4.6 Hz, 1H, H-2), 4.3057 (dd, *J* = 6.7, 6.0 Hz, 1H, H-4), 4.3061 (ddd, *J* = 8.0, 6.0, 5.3 Hz, 1H, H-6), 4.32 (dd, *J* = 10.6, 4.8 Hz, 1H, H-6′b), 4.35 (dd, *J* = 6.0, 6.0 Hz, 1H, H-5), 4.62/4.72 (each d, *J* = 12.3 Hz, 1H, OC*H*$_2$Ph), 4.66 (d, *J* = 1.2 Hz, 1H, H-1′), 5.61 (s, 1H, C*H*Ph), 5.63 (dd, *J* = 3.2, 1.2 Hz, 1H, H-2′), 7.26–7.28 (m, 1H, Ar), 7.30–7.32 (m, 2H, Ar), 7.34–7.35 (m, 2H, Ar), 7.36–7.40 (m, 3H, Ar), 7.49–7.50 (m, 2H, Ar). $^{13}$C NMR (100 MHz, $CDCl_3$) *δ*: 14.1 [CO(CH$_2$)$_6$*C*H$_3$], 22.6 [CO(CH$_2$)$_5$*C*H$_2$CH$_3$], 24.9 [COCH$_2$*C*H$_2$(CH$_2$)$_5$CH$_3$], 25.1/25.6/25.7/26.5/26.9/27.6 [C(*C*H$_3$)$_2$], 28.9/29.0 [CO(CH$_2$)$_2$(*C*H$_2$)$_2$(CH$_2$)$_2$CH$_3$], 31.7 [CO(CH$_2$)$_4$*C*H$_2$CH$_2$CH$_3$], 34.1 [CO*C*H$_2$(CH$_2$)$_5$CH$_3$], 66.3 (C-1), 67.5 (C-5′), 68.3/68.4 (C-7 and C-6′), 68.4 (C-2′), 71.7 (OCH$_2$Ph), 74.8/75.1/75.2/75.3 (C-2, C-4, C-5 and C-6), 75.7 (C-3′), 76.8 (C-3), 77.9 (C-4′), 99.8 (C-1′), 101.6 (*C*HPh), 109.0/109.2/109.5 [*C*(CH$_3$)$_2$], 126.0 (2C)/127.69 (2C)/127.72/128.2 (2C)/128.3 (2C)/129.0 (d, Ar), 137.2/137.6 (s, Ar), 173.1 (OCOCH$_2$). FABMS *m*/*z* (%): 821 ([M+Na]$^+$, 4), 91 (100). FABHRMS calcd for $C_{44}H_{62}O_{13}Na$ [M+Na]$^+$: 821.4088; found: 821.4090.

### 3.1.12. Hydrogenolysis of octanoyl esters (18g–18k)

A suspension of **18g** (207 mg, 0.322 mmol) and 10% palladium on carbon (20 mg) in EtOAc (3.2 mL) was hydrogenated at room temperature until the uptake of hydrogen ceased. The catalyst was filtered off and washed with MeOH. The combined filtrate and washings were condensed in vacuo. The residue was purified by column chromatography ($CHCl_3$–MeOH, 50/1) to give 2-(*tert*-butyldimethylsiloxy)ethanol-1-yl 2-*O*-octanoyl-β-D-mannopyranoside (**19g**, 116 mg, 78%) as a colorless oil. $[\alpha]_D^{25}$ −29.0 (*c* 1.02, $CHCl_3$). IR (neat) cm$^{-1}$: 3383, 1748, 1472, 1362, 1256, 1161, 1074. $^1$H NMR (400 MHz, $CD_3OD$) *δ*: 0.067/0.071 [each s, 3H, Si(*CH*$_3$)$_2$], 0.90 [s, 9H, SiC(*CH*$_3$)$_3$], 0.91 [t, *J* = 7.2 Hz, 3H, CO(CH$_2$)$_6$*CH*$_3$], 1.27–1.39 [m, 8H, CO(CH$_2$)$_2$(*CH*$_2$)$_4$CH$_3$], 1.63 [ddt, *J* = 7.6, 7.6, 7.6 Hz, 2H, COCH$_2$*CH*$_2$(CH$_2$)$_4$CH$_3$], 2.35/2.40 [each dt, *J* = 15.6, 7.6 Hz, 1H, COC*H*$_2$(CH$_2$)$_5$CH$_3$], 3.26 (ddd, *J* = 9.6, 6.4, 2.4 Hz, 1H, H-5′), 3.50 (dd, *J* = 9.6, 9.6 Hz, 1H, H-4′), 3.63 (dd, *J* = 9.6, 3.6 Hz, 1H, H-3′), 3.64 (ddd, *J* = 10.8, 6.8, 4.4 Hz, 1H, H-1a), 3.70 (dd, *J* = 11.6, 6.4 Hz, 1H, H-6′a), 3.75−3.80 (m, 2H, H-2a and H-2b), 3.88 (ddd, *J* = 10.8, 4.8, 4.0 Hz, 1H, H-1b), 3.90 (dd, *J* = 11.6, 2.4 Hz, 1H, H-6′b), 4.71 (d, *J* = 0.8 Hz, 1H, H-1′), 5.36 (dd, *J* = 3.6, 0.8 Hz, 1H, H-2′). $^{13}$C NMR (100 MHz, $CD_3OD$) *δ*: −5.2/−5.1 [Si(*C*H$_3$)$_2$], 14.4 [CO(CH$_2$)$_6$*C*H$_3$], 19.2 [Si*C*(CH$_3$)$_3$], 23.7 [CO(CH$_2$)$_5$*C*H$_2$CH$_3$], 26.0 [COCH$_2$*C*H$_2$(CH$_2$)$_5$CH$_3$], 26.4 [3C, SiC(*C*H$_3$)$_3$], 30.1/30.2 [CO(CH$_2$)$_2$(*C*H$_2$)$_2$(CH$_2$)$_2$CH$_3$], 32.9 [CO(CH$_2$)$_4$*C*H$_2$CH$_2$CH$_3$], 35.1 [CO*C*H$_2$(CH$_2$)$_5$CH$_3$], 62.9 (C-6′), 63.9 (C-2), 68.9 (C-4′), 71.9 (C-1), 72.9 (C-2′), 73.7 (C-3′), 78.6 (C-5′), 100.7 (C-1′), 175.0 (OCOCH$_2$). FABMS *m*/*z* (%): 487 ([M+Na]$^+$, 100). FABHRMS calcd for $C_{22}H_{44}O_8SiNa$ [M+Na]$^+$: 487.2703; found: 487.2723.

Following the method described above, **18h** (107 mg, 0.179 mmol), **18i** (84.9 mg, 0.114 mmol), **18j** (454 mg, 0.650 mmol), and **18k** (150 mg, 0.188 mmol) were converted to 1,2-*O*-isopropylidene-D-glycerol-3-yl 2-*O*-octanoyl-β-D-mannopyranoside (**19h**, 55.9 mg, 74%), 1-*O*-(*tert*-butyldimethylsilyl)-2,3-*O*-isopropylidene-D-erythritol-4-yl 2-*O*-octanoyl-β-D-mannopyranoside (**19i**, 47.2 mg, 73%), 1,2:3,4-di-*O*-isopropylidene-D-arabinitol-5-yl 2-*O*-octanoyl-β-D-mannopyranoside (**19j**, 294 mg, 87%), and 2,3:4,5:6,7-tri-*O*-isopropylidene-D-glycero-D-galactoheptitol-1-yl 2-*O*-octanoyl-β-D-mannopyranoside (**19k**, 81.0 mg, 70%), respectively.

***19h***: A colorless oil. $[\alpha]_D^{24}$ −42.0 (*c* 0.79, $CHCl_3$). IR (neat) cm$^{-1}$: 3383, 1732, 1454, 1416, 1373, 1261, 1219, 1165, 1072. $^1$H NMR (400 MHz, $CDCl_3$) *δ*: 0.88 [t, *J* = 7.2 Hz, 3H, CO(CH$_2$)$_6$*CH*$_3$], 1.25–1.35 [m, 8H, CO(CH$_2$)$_2$(*CH*$_2$)$_4$CH$_3$], 1.35/1.40 [each s, 3H, C(*CH*$_3$)$_2$], 1.63 [tt, *J* = 7.6, 7.6 Hz, 2H, COCH$_2$*CH*$_2$(CH$_2$)$_4$CH$_3$], 2.41 [t, *J* = 7.6 Hz, 2H, COC*H*$_2$(CH$_2$)$_5$CH$_3$], 3.34 (ddd, *J* = 8.0, 4.8, 3.2 Hz, 1H, H-5′), 3.64 (dd, *J* = 10.4, 5.6 Hz, 1H, H-3a), 3.72–3.76 (m, 2H, H-3′ and H-4′), 3.73 (dd, *J* = 8.0, 6.0 Hz, 1H, H-1a), 3.81 (dd, *J* = 10.4, 5.6 Hz, 1H, H-3b), 3.86 (dd, *J* = 12.0, 4.8 Hz, 1H, H-6′a), 3.94 (dd, *J* = 12.0, 3.2 Hz, 1H, H-6′b), 4.02 (dd, *J* = 8.0, 6.0 Hz, 1H, H-1b), 4.25 (dddd, *J* = 6.0, 6.0, 5.6, 5.6 Hz, 1H, H-2), 4.71 (s, 1H, H-1′), 5.39 (br s, 1H, H-2′). $^{13}$C NMR (100 MHz, $CDCl_3$) *δ*: 14.0 [CO(CH$_2$)$_6$*C*H$_3$], 22.6 [CO(CH$_2$)$_5$*C*H$_2$CH$_3$], 24.9 [COCH$_2$*C*H$_2$(CH$_2$)$_5$CH$_3$], 25.4/26.7 [C(*C*H$_3$)$_2$], 28.9/29.0 [CO(CH$_2$)$_2$(*C*H$_2$)$_2$(CH$_2$)$_2$CH$_3$], 31.7 [CO(CH$_2$)$_4$*C*H$_2$CH$_2$CH$_3$], 34.2 [CO*C*H$_2$(CH$_2$)$_5$CH$_3$], 62.4 (C-6′), 66.6 (C-1), 68.4 (C-4′), 70.2 (C-3), 70.9 (C-2′), 72.9 (C-3′), 74.5 (C-2), 75.7 (C-5′), 98.9 (C-1′), 109.6 [*C*(CH$_3$)$_2$], 174.2 (OCOCH$_2$). FABMS *m*/*z* (%): 443 ([M+Na]$^+$, 40), 57 (100).

FABHRMS calcd for $C_{20}H_{36}O_9Na$ $[M+Na]^+$: 443.2257; found: 443.2260.

***19i***: A colorless oil. $[\alpha]_D^{23}$ −22.2 (*c* 1.11, $CHCl_3$). IR (neat) $cm^{-1}$: 3399, 1744, 1458, 1377, 1254, 1219, 1165, 1076. $^1H$ NMR (400 MHz, $CD_3OD$) $\delta$: 0.085/0.087 [each s, 3H, $Si(CH_3)_2$], 0.90 [t, *J* = 7.2 Hz, 3H, $CO(CH_2)_6CH_3$], 0.91 [s, 9H, $SiC(CH_3)_3$], 1.27–1.39 [m, 8H, $CO(CH_2)_2(CH_2)_4CH_3$], 1.32/1.40 [each s, 3H, $C(CH_3)_2$], 1.62 [ddt, *J* = 7.6, 7.6, 7.6 Hz, 2H, $COCH_2CH_2(CH_2)_4CH_3$], 2.35/2.39 [each dt, *J* = 16.0, 7.6 Hz, 1H, $COCH_2(CH_2)_5CH_3$], 3.24 (ddd, *J* = 9.6, 6.0, 2.4 Hz, 1H, H-5′), 3.51 (dd, *J* = 9.6, 9.6 Hz, 1H, H-4′), 3.63 (dd, *J* = 9.6, 3.2 Hz, 1H, H-3′), 3.65 (dd, *J* = 11.2, 6.0 Hz, 1H, H-1a), 3.66 (dd, *J* = 11.2, 6.8 Hz, 1H, H-4a), 3.71 (dd, *J* = 12.0, 6.0 Hz, 1H, H-6′a), 3.75 (dd, *J* = 11.2, 5.2 Hz, 1H, H-1b), 3.89 (dd, *J* = 12.0, 2.4 Hz, 1H, H-6′b), 4.01 (dd, *J* = 11.2, 4.8 Hz, 1H, H-4b), 4.16 (ddd, *J* = 6.4, 6.0, 5.2 Hz, 1H, H-2), 4.29 (ddd, *J* = 6.8, 6.4, 4.8 Hz, 1H, H-3), 4.70 (d, *J* = 0.8 Hz, 1H, H-1′), 5.35 (dd, *J* = 3.2, 0.8 Hz, 1H, H-2′). $^{13}C$ NMR (100 MHz, $CD_3OD$) $\delta$: −5.2/−5.1 [$Si(CH_3)_2$], 14.5 [$CO(CH_2)_6CH_3$], 19.1 [$SiC(CH_3)_3$], 23.7 [$CO(CH_2)_5CH_2CH_3$], 25.5/28.1 [$C(CH_3)_2$], 26.0 [$COCH_2CH_2(CH_2)_5CH_3$], 26.4 [3C, $SiC(CH_3)_3$], 30.1/30.2 [$CO(CH_2)_2(CH_2)_2(CH_2)_2CH_3$], 32.9 [$CO(CH_2)_4CH_2CH_2CH_3$], 35.1 [$COCH_2(CH_2)_5CH_3$], 62.9 (C-6′), 63.2 (C-1), 68.9 (C-4′), 69.0 (C-4), 72.9 (C-2′), 73.6 (C-3′), 77.4 (C-3), 78.5 (C-5′), 79.0 (C-2), 100.4 (C-1′), 109.8 [$C(CH_3)_2$], 175.0 ($OCOCH_2$). FABMS *m*/*z* (%): 587 ($[M+Na]^+$, 20), 73 (100). FABHRMS calcd for $C_{27}H_{52}O_{10}SiNa$ $[M+Na]^+$: 587.3227; found: 587.3250.

***19j***: A colorless oil. $[\alpha]_D^{25}$ −32.8 (*c* 0.51, $CHCl_3$). IR (neat) $cm^{-1}$: 3395, 1736, 1458, 1373, 1250, 1215, 1161, 1072. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 0.88 [t, *J* = 7.2 Hz, 3H, $CO(CH_2)_6CH_3$], 1.24–1.38 [m, 8H, $CO(CH_2)_2(CH_2)_4CH_3$], 1.37/1.38/1.45/1.46 [each s, 3H, $C(CH_3)_2$], 1.64 [tt, *J* = 7.2, 7.2 Hz, 2H, $COCH_2CH_2(CH_2)_4CH_3$], 2.39/2.44 [each dt, *J* = 16.0, 7.2 Hz, 1H, $COCH_2(CH_2)_5CH_3$], 3.34 (ddd, *J* = 8.8, 4.4, 3.6 Hz, 1H, H-5′), 3.58 (dd, *J* = 10.0, 4.8 Hz, 1H, H-5a), 3.59 (dd, *J* = 8.0, 7.2 Hz, 1H, H-1a), 3.74 (dd, *J* = 9.6, 2.4 Hz, 1H, H-3′), 3.79 (dd, *J* = 9.2, 8.8 Hz, 1H, H-4′), 3.87 (dd, *J* = 12.0, 4.4 Hz, 1H, H-6′a), 3.92 (dd, *J* = 10.0, 8.0 Hz, 1H, H-5b), 3.94 (dd, *J* = 12.0, 3.6 Hz, 1H, H-6′b), 4.10 (dd, *J* = 6.8, 6.0 Hz, 1H, H-3), 4.18 (dd, *J* = 8.0, 6.0 Hz, 1H, H-1b), 4.16–4.21 (m, 1H, H-4), 4.24 (ddd, *J* = 7.2, 6.8, 6.0 Hz, 1H, H-2), 4.67 (s, 1H, H-1′), 5.38 (d, *J* = 2.4 Hz, 1H, H-2′). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 14.0 [$CO(CH_2)_6CH_3$], 22.6 [$CO(CH_2)_5CH_2CH_3$], 24.9 [$COCH_2CH_2(CH_2)_5CH_3$], 25.4 (2C)/26.6/27.7 [$C(CH_3)_2$], 28.9/29.0 [$CO(CH_2)_2(CH_2)_2(CH_2)_2CH_3$], 31.7 [$CO(CH_2)_4CH_2CH_2CH_3$], 34.2 [$COCH_2(CH_2)_5CH_3$], 62.3 (C-6′), 66.4 (C-1), 67.8 (C-5), 68.2 (C-4′), 70.9 (C-2′), 73.0 (C-3′), 74.3 (C-2), 75.0 (C-4), 75.7 (C-5′), 78.2 (C-3), 98.8 (C-1′), 109.2/109.6 [$C(CH_3)_2$], 174.2 ($OCOCH_2$). FABMS *m*/*z* (%): 543 ($[M+Na]^+$, 100). FABHRMS calcd for $C_{25}H_{44}O_{11}Na$ $[M+Na]^+$: 543.2781; found: 543.2778.

***19k***: A colorless amorphous. $[\alpha]_D^{24}$ −19.1 (*c* 1.01, $CHCl_3$). IR (neat) $cm^{-1}$: 3445, 1740, 1458,1377, 1250, 1215, 1157, 1069. $^1H$ NMR (400 MHz, $CD_3OD$) $\delta$: 0.90 [t, *J* = 6.8 Hz, 3H, $CO(CH_2)_6CH_3$], 1.26–1.38 [m, 8H, $CO(CH_2)_2(CH_2)_4CH_3$], 1.33/1.34/1.35/1.39/1.42/1.48 [each s, 3H, $C(CH_3)_2$], 1.62 [tdd, *J* = 7.6, 7.6, 7.6 Hz, 2H, $COCH_2CH_2(CH_2)_4CH_3$], 2.34/2.40 [each dt, *J* = 16.0, 7.6 Hz, 1H, $COCH_2(CH_2)_5CH_3$], 3.28 (ddd, *J* = 9.6, 6.4, 2.0 Hz, 1H, H-5′), 3.47 (dd, *J* = 9.6, 9.6 Hz, 1H, H-4′), 3.58 (dd, *J* = 10.8, 4.8 Hz, 1H, H-7a), 3.63 (dd, *J* = 9.6, 3.2 Hz, 1H, H-3′), 3.69 (dd, *J* = 12.0, 6.4 Hz, 1H, H-6′a), 3.77 (dd, *J* = 7.6, 7.6 Hz, 1H, H-1a), 3.91 (dd, *J* = 12.0, 2.0 Hz, 1H, H-6′b), 4.00 (dd, *J* = 10.8, 8.4 Hz, 1H, H-7b), 4.06 (dd, *J* = 7.6, 6.4 Hz, 1H, H-1b), 4,13 (dd, *J* = 6.4, 4.0 Hz, 1H, H-3), 4.17 (ddd, *J* = 7.6, 6.4, 4.0 Hz, 1H, H-2), 4.33 (ddd, *J* = 8.4, 5.6, 4.8 Hz, 1H, H-6), 4.37 (dd, *J* = 6.4, 6.4 Hz, 1H, H-4), 4.42 (dd, *J* = 6.4, 5.6 Hz, 1H, H-5), 4.71 (d, *J* = 0.8 Hz, 1H, H-1′), 5.31 (dd, *J* = 3.2, 0.8 Hz, 1H, H-2′). $^{13}C$ NMR (100 MHz, $CD_3OD$) $\delta$: 14.4 [$CO(CH_2)_6CH_3$], 23.7 [$CO(CH_2)_5CH_2CH_3$], 25.6 [$COCH_2CH_2(CH_2)_5CH_3$], 25.8/25.9/26.0/26.8/27.2/27.9 [$C(CH_3)_2$], 30.2 [2C, $CO(CH_2)_2(CH_2)_2(CH_2)_2CH_3$], 32.9 [$CO(CH_2)_4CH_2CH_2CH_3$], 35.1 [$COCH_2(CH_2)_5CH_3$], 63.0 (C-6′), 67.4 (C-1), 69.0 (C-4′), 69.1 (C-7), 72.9 (C-2′), 73.6 (C-3′), 76.3/76.46/76.50/76.8 (C-2, C-4, C-5 and C-6), 77.6 (C-3), 78.8 (C-5′), 100.7 (C-1′), 109.8/110.1/110.6 [$C(CH_3)_2$], 175.0 ($OCOCH_2$). FABMS *m*/*z* (%): 643 ($[M+Na]^+$, 99), 127 (100). FABHRMS calcd for $C_{30}H_{52}O_{13}Na$ $[M+Na]^+$: 643.3306; found: 643.3305.

### 3.1.13. Esterification of trisalcohols (19g–19k)

To a solution of **19g** (103 mg, 0.221 mmol) and DMAP (80.9 mg, 0.662 mmol) in a mixture of $CH_2Cl_2$ (2.2 mL) and pyridine (0.07 mL, 0.883 mmol) was added hexanoic anhydride (0.20 mL, 0.883 mmol) at room temperature, and the reaction mixture was stirred at room temperature for 30 min. After the reaction was quenched with water, the resulting mixture was extracted with $CH_2Cl_2$. The extract was successively washed with aqueous sodium bicarbonate, water and brine, and condensed in vacuo. The residue was purified by column chromatography (*n*-hexane–EtOAc, 30/1) to give 2-(*tert*-butyldimethylsiloxy)ethanol-1-yl 3,4,6-tri-*O*-hexanoyl-2-*O*-octanoyl-β-D-mannopyranoside (**20g**, 134 mg, 80%) as a colorless oil. $[\alpha]_D^{25}$ −25.4 (*c* 1.06, $CHCl_3$). IR (neat) $cm^{-1}$: 1748, 1456, 1248, 1161, 1103, 1070. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 0.045/0.049 [each s, 3H, $Si(CH_3)_2$], 0.86–0.91 (m, 12H, acyl $CH_3$), 0.89 [s, 9H, $SiC(CH_3)_3$], 1.22–1.36 (m, 20H, acyl $CH_2$), 1.50–1.67 (m, 8H, acyl $CH_2$), 2.17/2.22/2.23/2.28/2.40/2.45 (dt, *J* = 16.0, 7.6 Hz, 1H, $COCH_2$), 2.34 (t, *J* = 7.6 Hz, 2H, $COCH_2$), 3.65 (ddd, *J* = 10.0, 5.6, 2.4 Hz, 1H, H-5′), 3.66 (ddd, *J* = 10.0, 7.6, 4.0 Hz, 1H, H-1a), 3.73 (ddd, *J* = 11.2, 4.0, 4.0 Hz, 1H, H-2a), 3.79 (ddd, *J* = 11.2, 7.6, 4.0 Hz, 1H, H-2b), 3.87 (ddd, *J* = 10.0, 4.0, 4.0 Hz, 1H, H-1b), 4.17 (dd, *J* = 12.0, 2.4 Hz, 1H, H-6′a), 4.25 (dd, *J* = 12.0, 5.6 Hz, 1H, H-6′b), 4.77 (s, 1H, H-1′), 5.05 (dd, *J* = 10.0, 3.6 Hz, 1H, H-3′), 5.26 (dd, *J* = 10.0, 10.0 Hz, 1H, H-4′), 5.50 (d, *J* = 3.6 Hz, 1H, H-2′). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: −5.4/−5.3 [$Si(CH_3)_2$], 13.8 (2C)/13.9/14.0 (acyl $CH_3$), 18.3 [$SiC(CH_3)_3$], 22.2 (2C)/22.3/22.6 (acyl $CH_2$), 24.2/24.4/24.5/25.0 ($COCH_2CH_2$), 25.8 [3C, $SiC(CH_3)_3$], 28.95/28.99 [$CO(CH_2)_2(CH_2)_2(CH_2)_2CH_3$], 31.2 (2C)/31.3/31.7 (acyl $CH_2$), 33.9/34.0 (2C)/34.1 ($COCH_2$), 62.45/62.53 (C-2 and C-6′), 65.8 (C-4′), 68.6 (C-2′), 71.0 (C-3′), 71.1 (C-1), 72.5 (C-5′), 99.1 (C-1′), 172.3/172.6/173.0/173.5 ($OCOCH_2$). FABMS *m*/*z* (%): 781 ($[M+Na]^+$, 4), 99 (100). FABHRMS calcd for $C_{40}H_{74}O_{11}SiNa$ $[M+Na]^+$: 781.4898; found: 781.4883.

Following the method described above, **19h** (45.5 mg, 0.108 mmol), **19i** (40.0 mg, 0.069 mmol), **19j** (286 mg, 0.550 mmol), and **19k** (70.0 mg, 0.113 mmol) were converted to 1,2-*O*-isopropylidene-D-glycerol-3-yl 3,4,6-tri-*O*-hexanoyl-2-*O*-octanoyl-β-D-mannopyranoside (**20h**, 77.0 mg, quant.), 1-*O*-(*tert*-butyldimethylsilyl)-2,3-*O*-isopropylidene-D-erythritol-4-yl 3,4,6-tri-*O*-hexanoyl-2-*O*-octanoyl-β-D-mannopyranoside (**20i**, 58.7 mg, 97%), 1,2:3,4-di-*O*-isopropylidene-D-arabinitol-5-yl 3,4,6-tri-*O*-hexanoyl-2-*O*-octanoyl-β-D-mannopyranoside (**20j**, 351 mg, 78%), and 2,3:4,5:6,7-tri-*O*-isopropylidene-D-glycero-D-galactoheptitol-1-yl 3,4,6-tri-*O*-hexanoyl-2-*O*-octanoyl-β-D-mannopyranoside (**20k**, 95.0 mg, 92%), respectively.

***20h***: A colorless oil. $[\alpha]_D^{25}$ −41.6 (*c* 1.05, $CHCl_3$). IR (neat) $cm^{-1}$: 1748, 1458, 1373, 1242, 1165, 1103, 1072. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 0.86–0.92 (m, 12H, acyl $CH_3$), 1.24–1.36 (m, 20H, acyl $CH_2$), 1.35/1.40 [each s, 3H, $C(CH_3)_2$], 1.50–1.68 (m, 8H, acyl $CH_2$), 2.17/2.225/2.234/2.29/2.40/2.44 (each dt, *J* = 16.0, 7.2 Hz, 1H, $COCH_2$), 2.34 (t, *J* = 7.6 Hz, 2H, $COCH_2$), 3.64–3.68 (m, 1H, H-5′a), 3.66 (dd, *J* = 10.4, 6.0 Hz, 1H, H-3a), 3.69 (dd, *J* = 8.4, 6.0 Hz, 1H, H-1a), 3.78 (dd, *J* = 10.4, 5.6 Hz, 1H, H-3b), 4.02 (dd, *J* = 8.4, 6.0 Hz, 1H, H-1b), 4.17 (dd, *J* = 12.0, 2.4 Hz, 1H, H-6′a), 4.244 (dd, *J* = 12.2, 5.6 Hz, 1H, H-6′b), 4.244 (dddd, *J* = 6.0, 6.0, 6.0, 5.6 Hz, 1H, H-2), 4.77 (s, 1H, H-1′), 5.06 (dd, *J* = 10.0, 3.2 Hz, 1H, H-3′), 5.26 (dd, *J* = 10.0, 10.0 Hz, 1H, H-4′), 5.50 (d, *J* = 3.2 Hz, 1H, H-2′). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 13.8 (2C)/13.9/14.0 (acyl $CH_3$), 22.2 (2C)/22.3/22.6 (acyl $CH_2$), 24.3/24.4/24.5/25.0 ($COCH_2CH_2$), 25.3/

26.8 [C($CH_3$)$_2$], 28.9/29.0 [CO($CH_2$)$_2$($CH_2$)$_2$($CH_2$)$_2$$CH_3$], 31.1 (2C)/31.2/31.7 (acyl $CH_2$), 33.9/34.0 (2C)/34.1 (CO$CH_2$), 62.4 (C-6′), 65.8 (C-4′), 66.7 (C-1), 68.4 (C-2′), 70.4 (C-3), 70.9 (C-3′), 72.6 (C-5′), 74.6 (C-2), 98.5 (C-1′), 109.6 [$C$($CH_3$)$_2$], 172.2/172.6/173.0/173.4 (O$CO$$CH_2$). FABMS $m/z$ (%): 737 ([M+Na]$^+$, 8), 99 (100). FABHRMS calcd for $C_{38}H_{66}O_{12}Na$ [M+Na]$^+$: 737.4452; found: 737.4425.

***20i***: A colorless oil. $[\alpha]_D^{23}$ −17.4 ($c$ 1.05, $CHCl_3$). IR (neat) cm$^{-1}$: 1748, 1466, 1377, 1250, 1219, 1165, 1099, 1072. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 0.050/0.052 [each s, 3H, Si($CH_3$)$_2$], 0.86–0.92 (m, 12H, acyl C$H_3$), 0.88 [s, 9H, SiC($CH_3$)$_3$], 1.20–1.36 (m, 20H, acyl C$H_2$), 1.34/1.43 [each s, 3H, C($CH_3$)$_2$], 1.51–1.70 (m, 8H, acyl C$H_2$), 2.17/2.22 (each dt, $J$ = 16.0, 7.6 Hz, 1H, COC$H_2$), 2.23/2.28/2.41/2.45 (each dt, $J$ = 15.6, 7.6 Hz, 1H, COC$H_2$), 2.34 (t, $J$ = 7.6 Hz, 2H, COC$H_2$), 3.57 (dd, $J$ = 10.8, 5.2 Hz, 1H, H-1a), 3.62 (dd, $J$ = 10.8, 7.2 Hz, 1H, H-1b), 3.65 (ddd, $J$ = 10.0, 5.2, 2.4 Hz, 1H, H-5′), 3.72 (dd, $J$ = 11.6, 8.0 Hz, 1H, H-4a), 4.10 (ddd, $J$ = 7.2, 6.0, 5.2 Hz, 1H, H-2), 4.11 (dd, $J$ = 11.6, 2.8 Hz, 1H, H-4b), 4.15 (dd, $J$ = 12.4, 2.4 Hz, 1H, H-6′a), 4.26 (dd, $J$ = 12.4, 5.2 Hz, 1H, H-6′b), 4.32 (ddd, $J$ = 8.0, 6.0, 2.8 Hz, 1H, H-3), 4.83 (d, $J$ = 0.4 Hz, 1H, H-1′), 5.07 (dd, $J$ = 10.0, 3.2 Hz, 1H, H-3′), 5.29 (dd, $J$ = 10.0, 10.0 Hz, 1H, H-4′), 5.53 (dd, $J$ = 3.2, 0.4 Hz, 1H, H-2′). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: −5.48/−5.46 [Si($CH_3$)$_2$], 13.8 (2C)/13.9/14.1 (acyl $CH_3$), 18.2 [Si$C$($CH_3$)$_3$], 22.2 (2C)/22.3/22.6 (acyl $CH_2$), 24.3/24.4/24.5/25.0 (CO$CH_2$$CH_2$), 25.3/27.9 [C($CH_3$)$_2$], 25.8 [3C, SiC($CH_3$)$_3$], 28.96/29.00 [CO($CH_2$)$_2$($CH_2$)$_2$($CH_2$)$_2$$CH_3$], 31.2 (2C)/31.3/31.7 (acyl $CH_2$), 33.95/33.98/34.02/34.2 (CO$CH_2$), 61.6 (C-1), 62.3 (C-6′), 65.7 (C-4′), 68.4 (C-4), 68.7 (C-2′), 71.1 (C-3′), 72.6 (C-5′), 76.8/77.2 (C-2 and C-3), 98.7 (C-1′), 108.7 [$C$($CH_3$)$_2$], 172.2/172.7/173.0/173.5 (O$CO$$CH_2$). FABMS $m/z$ (%): 881 ([M+Na]$^+$, 8), 73 (100). FABHRMS calcd for $C_{45}H_{82}O_{13}SiNa$ [M+Na]$^+$: 881.5422; found: 881.5446.

***20j***: A colorless oil. $[\alpha]_D^{25}$ −29.6 ($c$ 0.80, $CHCl_3$). IR (neat) cm$^{-1}$: 1748, 1458, 1373, 1246, 1219, 1161, 1099, 1069, 1045. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 0.83–0.92 (m, 12H, acyl C$H_3$), 1.20–1.40 (m, 20H, acyl C$H_2$), 1.35/1.37 [each s, 3H, C(C$H_3$)$_2$], 1.46 [s, 6H, C($CH_3$)$_2$], 1.51–1.71 (m, 8H, acyl C$H_2$), 2.17/2.22/2.23/2.29/2.31/2.35/2.40/2.46 (each dt, $J$ = 16.0, 7.2 Hz, 1H, COC$H_2$), 3.56 (dd, $J$ = 10.0, 4.8 Hz, 1H, H-5a), 3.59 (dd, $J$ = 8.0, 6.8 Hz, 1H, H-1a), 3.65 (ddd, $J$ = 10.0, 5.6, 2.4 Hz, 1H, H-5′), 3.92 (dd, $J$ = 10.0, 8.0 Hz, 1H, H-5b), 4.09 (dd, $J$ = 7.2, 5.6 Hz, 1H, H-3), 4.11 (dd, $J$ = 8.0, 7.2 Hz, 1H, H-1b), 4.16 (dd, $J$ = 12.0, 2.4 Hz, 1H, H-6′a), 4.18 (ddd, $J$ = 8.0, 5.6, 4.8 Hz, 1H, H-4), 4.24 (dd, $J$ = 12.0, 5.6 Hz, 1H, H-6′b), 4.24 (ddd, $J$ = 7.2, 7.2, 6.8 Hz, 1H, H-4), 4.70 (s, 1H, H-1′), 5.04 (dd, $J$ = 10.0, 3.2 Hz, 1H, H-3′), 5.26 (dd, $J$ = 10.0, 10.0 Hz, 1H, H-4′), 5.49 (d, $J$ = 3.2 Hz, 1H, H-2′). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 13.8 (2C)/13.9/14.1 (acyl $CH_3$), 22.2 (2C)\22.3\22.6 (acyl $CH_2$), 24.2/24.4/24.5/24.98 (CO$CH_2$$CH_2$), 24.99/25.4/26.6/27.8 [C($CH_3$)$_2$], 28.97/29.02 [CO($CH_2$)$_2$($CH_2$)$_2$($CH_2$)$_2$$CH_3$], 31.2 (2C)/31.3/31.7 (acyl $CH_2$), 33.9/33.95/34.00/34.1 (CO$CH_2$), 62.3 (C-6′), 65.6 (C-4′), 66.4 (C-1), 67.7 (C-5), 68.4 (C-2′), 71.0 (C-3′), 72.7 (C-5′), 74.1 (C-2), 74.9 (C-4), 78.5 (C-3), 98.5 (C-1′), 109.2/109.5 [$C$($CH_3$)$_2$], 172.2/172.6/172.9/173.4 (O$CO$$CH_2$). FABMS $m/z$ (%): 837 ([M+Na]$^+$, 9), 99 (100). FABHRMS calcd for $C_{43}H_{74}O_{14}Na$ [M+Na]$^+$: 837.4976; found: 837.4995.

***20k***: A colorless oil. $[\alpha]_D^{24}$ −20.2 ($c$ 1.01, $CHCl_3$). IR (neat) cm$^{-1}$: 1748, 1458, 1377, 1246, 1219, 1161, 1096, 1069. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 0.86–0.94 (m, 12H, acyl C$H_3$), 1.20–1.41 (m, 20H, acyl C$H_2$), 1.36 [s, 6H, C($CH_3$)$_2$], 1.38/1.44/1.47/1.54 [each s, 3H, C(C$H_3$)$_2$], 1.50–1.67 (m, 8H, acyl C$H_2$), 2.17/2.21/2.23/2.28/2.30/2.34/2.38/2.44 (each dt, $J$ = 15.6, 7.6 Hz, 1H, COC$H_2$), 3.59 (dd, $J$ = 10.4, 5.2 Hz, 1H, H-7a), 3.66 (ddd, $J$ = 10.0, 5.6, 2.4 Hz, 1H, H-5′), 3.74 (dd, $J$ = 7.6, 7.6 Hz, 1H, H-1a), 3.99 (dd, $J$ = 10.4, 7.6 Hz, 1H, H-7b), 4.03 (dd, $J$ = 7.6, 6.0 Hz, 1H, H-1b), 4,09 (dd, $J$ = 6.4, 6.4 Hz, 1H, H-3), 4.11 (ddd, $J$ = 7.6, 6.4, 6.0 Hz, 1H, H-2), 4.16 (dd, $J$ = 12.0, 2.4 Hz, 1H, H-6′a), 4.23 (dd, $J$ = 12.0, 5.6 Hz, 1H, H-6′b), 4.296 (ddd, $J$ = 7.6, 5.6, 5.2 Hz, 1H, H-6), 4.303 (dd, $J$ = 6.4, 6.4 Hz, 1H, H-4), 4.36 (dd, $J$ = 6.4, 5.6 Hz, 1H, H-5), 4.73 (d, $J$ = 0.8 Hz, 1H, H-1′), 5.04 (dd, $J$ = 10.0, 3.2 Hz, 1H, H-3′), 5.25 (dd, $J$ = 10.0, 10.0 Hz, 1H, H-4′), 5.47 (dd, $J$ = 3.2, 0.8 Hz, 1H, H-2′). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 13.8 (2C)/13.9/14.0 (acyl $CH_3$), 22.2 (2C)/22.3/22.6 (acyl $CH_2$), 24.2/24.4/24.5/24.97 (CO$CH_2$$CH_2$), 25.03/25.6/25.7/26.4/26.8/27.7 [C($CH_3$)$_2$], 28.95/29.03 [CO($CH_2$)$_2$($CH_2$)$_2$($CH_2$)$_2$$CH_3$], 31.2 (2C)/31.3/31.7 (acyl $CH_2$), 33.89/33.94/34.0/34.1 (CO$CH_2$), 62.3 (C-6′), 65.5 (C-4′), 66.2 (C-1), 68.2 (C-7), 68.4 (C-2′), 71.0 (C-3′), 72.7 (C-5′), 74.8/75.1 (2C)/75.3 (C-2, C-4, C-5 and C-6), 76.6 (C-3), 98.7 (C-1′), 109.0/109.2/109.6 [$C$($CH_3$)$_2$], 172.2/172.6/172.9/173.4 (O$CO$$CH_2$). FABMS $m/z$ (%): 937 ([M+Na]$^+$, 3), 99 (100). FABHRMS calcd for $C_{48}H_{82}O_{16}Na$ [M+Na]$^+$: 937.5501; found: 937.5511.

### 3.1.14. Preparation of acremomannolipin A homolog (1g)

To a solution of **20g** (114 mg, 0.150 mmol) in THF (1.5 mL) was added 1 M solution of TBAF in THF (0.23 mL, 0.23 mmol) at room temperature, and the reaction mixture was stirred for 2 h. After the reaction mixture was diluted with water, the resulting mixture was extracted with EtOAc. The extract was washed with brine, and concentrated in vacuo. The residue was purified by column chromatography ($n$-hexane–EtOAc, 3/1) to give **1g** (98.1 mg, quant.) as a colorless amorphous. $[\alpha]_D^{25}$ −29.6 ($c$ 1.05, $CHCl_3$). IR (neat) cm$^{-1}$: 3422, 1748, 1458, 1362, 1242, 1165, 1103, 1069. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$: 0.882 (t, $J$ = 7.2 Hz, 3H, acyl C$H_3$), 0.885 (t, $J$ = 7.2 Hz, 6H, acyl C$H_3$), 0.90 (t, $J$ = 7.2 Hz, 3H, acyl C$H_3$), 1.22–1.38 (m, 20H, acyl C$H_2$), 1.51–1.59 (m, 2H, acyl C$H_2$), 1.57/1.63 (each ddt, $J$ = 7.6, 7.6, 7.6 Hz, 2H, acyl C$H_2$), 1.66 (tt, $J$ = 7.6, 7.6, Hz, 2H, acyl C$H_2$), 2.20/2.21(each ddd, $J$ = 15.6, 7.6 Hz, 1H, COC$H_2$), 2.26/2.29/2.34/2.36 (each dt, $J$ = 15.6, 7.6 Hz, 1H, COC$H_2$), 2.44 (t, $J$ = 7.6 Hz, 2H, COC$H_2$), 3.69 (ddd, $J$ = 12.6, 5.8, 2.8 Hz, 1H, H-2a), 3.71 (ddd, $J$ = 10.0, 6.2, 2.8 Hz, 1H, H-5′), 3.72 (ddd, $J$ = 12.6, 5.8, 2.8 Hz, 1H, H-2b), 3.83 (ddd, $J$ = 11.2, 5.8, 2.8 Hz, 1H, H-1a), 3.87 (ddd, $J$ = 11.2, 5.8, 2.8 Hz, 1H, H-1b), 4.19 (dd, $J$ = 12.3, 6.2 Hz, 1H, H-6′a), 4.22 (dd, $J$ = 12.3, 2.8 Hz, 1H, H-6′b), 4.70 (d, $J$ = 1.0 Hz, 1H, H-1′), 5.08 (dd, $J$ = 10.0, 3.2 Hz, 1H, H-3′), 5.26 (dd, $J$ = 10.0, 10.0 Hz, 1H, H-4′), 5.52 (dd, $J$ = 3.2, 1.0 Hz, 1H, H-2′).$^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$:13.8 (2C)/13.9/14.0 (acyl $CH_3$), 22.2 (2C)/22.3/22.6 (acyl $CH_2$), 24.3/24.4/24.5/25.0 (CO$CH_2$$CH_2$), 28.9/29.0 [CO($CH_2$)$_2$($CH_2$)$_2$($CH_2$)$_2$$CH_3$], 31.1 (2C)/31.2/31.7 (acyl $CH_2$), 33.88/33.91/34.0/34.1 (CO$CH_2$), 61.9 (C-2), 62.4 (C-6′), 65.7 (C-4′), 68.6 (C-2′), 70.7 (C-3′), 72.6 (C-5′), 73.3 (C-1), 99.4 (C-1′), 172.3/172.6/173.2/173.4 (O$CO$$CH_2$). FABMS $m/z$ (%): 667 ([M+Na]$^+$, 98), 99 (100). FABHRMS calcd for $C_{34}H_{60}O_{11}Na$ [M+Na]$^+$: 667.4033; found: 667.4022.

### 3.1.15. Preparation of acremomannolipin A homologs (1h–1k)

A solution of **20h** (29.8 mg, 0.0417 mmol) in 90% aqueous trifluoroacetic acid (TFA, 1.0 mL) was stirred at 0 °C for 10 min. After removal of the solvent, the residue was co-evaporated five times with MeOH in vacuo. The residue was purified by column chromatography ($CHCl_3$–MeOH, 100/1) to give D-glycerol-3-yl 3,4,6-tri-*O*-hexanoyl-2-*O*-octanoyl-β-D-mannopyranoside (**1h**, 20.4 mg, 72%) as a colorless amorphous. $[\alpha]_D^{25}$ −29.6 ($c$ 0.67, $CHCl_3$). IR (neat) cm$^{-1}$: 3476, 1748, 1682, 1458, 1362, 1246, 1165, 1103, 1069. $^1$H NMR (700 MHz, $CD_3OD$) $\delta$: 0.901 (t, $J$ = 7.4 Hz, 3H, acyl C$H_3$), 0.902 (t, $J$ = 7.2 Hz, 3H, acyl C$H_3$), 0.91 (t, $J$ = 7.0 Hz, 3H, acyl C$H_3$), 0.93 (t, $J$ = 7.2 Hz, 3H, acyl C$H_3$), 1.24–1.44 (m, 20H, acyl C$H_2$), 1.52–1.60 (m, 4H, acyl C$H_2$), 1.63–1.70 (m, 4H, acyl C$H_2$), 2.19/2.21 (each dt, $J$ = 15.4, 7.4 Hz, 1H, COC$H_2$), 2.27/2.32 (each dt, $J$ = 15.9, 7.4 Hz, 1H, COC$H_2$), 2.34/2.37 (each dt, $J$ = 15.8, 7.4 Hz, 1H, COC$H_2$), 2.40/2.46 (each dt, $J$ = 15.4, 7.2 Hz, 1H, COC$H_2$), 3.48 (dd, $J$ = 11.4, 5.8 Hz, 1H, H-3a), 3.53 (dd, $J$ = 11.4, 5.4 Hz, 1H, H-3b), 3.57 (dd, $J$ = 10.4, 6.6 Hz, 1H, H-1a), 3.75 (dddd, $J$ = 6.6, 5.8, 5.4, 4.4 Hz, 1H, H-2), 3.83 (ddd, $J$ = 10.0, 4.4, 2.2 Hz, 1H, H-5′), 3.88 (dd, $J$ = 10.4, 4.4 Hz, 1H, H-1b), 4.15 (dd, $J$ = 12.2, 2.2 Hz, 1H, H-6′a), 4.27 (dd, $J$ = 12.2, 4.4 Hz, 1H, H-6′b), 4.90 (d, $J$ = 1.0 Hz, 1H, H-1′), 5.16 (dd, $J$ = 10.0, 3.2 Hz, 1H, H-

3′), 5.29 (dd, *J* = 10.0, 10.0 Hz, 1H, H-4′), 5.48 (dd, *J* = 3.2, 1.0 Hz, 1H, H-2′). $^{13}$C NMR (175 MHz, $CD_3OD$) *δ*: 14.2 (2C)/14.3/14.5 (acyl $CH_3$), 23.36/23.38/23.41/23.8 (acyl $CH_2$), 25.5/25.60/25.62/26.4 ($COCH_2CH_2$), 30.2/30.3 [$CO(CH_2)_2(CH_2)_2(CH_2)_2CH_3$], 32.3/32.36/32.44/33.0 (acyl $CH_2$), 34.86/34.92/32.96/35.2 ($COCH_2$), 63.1 (C-6′), 64.3 (C-1), 66.9 (C-4′), 70.4 (C-2′), 72.2 (C-2), 72.5 (C-3), 72.7 (C-3′), 73.5 (C-5′), 100.3 (C-1′), 173.8/173.9/174.7/175.0 ($OCOCH_2$). FABMS *m*/*z* (%): 697 ([M+Na]$^+$, 100). FABHRMS calcd for $C_{35}H_{62}O_{12}Na$ [M+Na]$^+$: 697.4139; found: 697.4169.

Following the method described above, **20i** (48.4 mg, 0.055 mmol), **20j** (331 mg, 0.406 mmol), and **20k** (74.0 mg, 0.808 mmol) were converted to D-erythritol-4-yl 3,4,6-tri-*O*-hexanoyl-2-*O*-octanoyl-β-D-mannopyranoside (**1i**, 29.6 mg, 75%), D-arabinitol-5-yl 3,4,6-tri-*O*-hexanoyl-2-*O*-octanoyl-β-D-mannopyranoside (**1j**, 195 mg, 65%), and D-glycero-D-galactoheptitol-1-yl 3,4,6-tri-*O*-hexanoyl-2-*O*-octanoyl-β-D-mannopyranoside (**1k**, 62.0 mg, 97%), respectively.

***1i***: A colorless oil. $[\alpha]_D^{25}$ −26.4 (*c* 0.49, $CHCl_3$). IR (neat) cm$^{-1}$: 3445, 1748, 1458, 1416, 1362, 1246, 1169, 1107, 1069. $^1$H NMR (700 MHz, $CD_3OD$) *δ*: 0.90 (t, *J* = 7.2 Hz, 6H, acyl $CH_3$), 0.91 (t, *J* = 6.8 Hz, 3H, acyl $CH_3$), 0.92 (t, *J* = 7.0 Hz, 3H, acyl $CH_3$), 1.23–1.43 (m, 20H, acyl $CH_2$), 1.51–1.59 (m, 4H, acyl $CH_2$), 1.62–1.71 (m, 4H, acyl $CH_2$), 2.19/2.21 (each dt, *J* = 15.4, 7.4 Hz, 1H, $COCH_2$), 2.27/2.31 (each dt, *J* = 15.8, 7.2 Hz, 1H, $COCH_2$), 2.34/2.37 (each dt, *J* = 15.8, 7.6 Hz, 1H, $COCH_2$), 2.40/2.46 (each dt, *J* = 15.2, 7.2 Hz, 1H, $COCH_2$), 3.52 (ddd, *J* = 6.8, 6.2, 3.6 Hz, 1H, H-2), 3.57 (dd, *J* = 11.4, 6.2 Hz, 1H, H-1a), 3.64 (dd, *J* = 10.0, 6.8 Hz, 1H, H-4a), 3.67 (ddd, *J* = 6.8, 6.8, 2.2 Hz, 1H, H-3), 3.70 (dd, *J* = 11.4, 3.6 Hz, 1H, H-1b), 3.82 (ddd, *J* = 10.1, 4.4, 2.2 Hz, 1H, H-5′), 4.05 (dd, *J* = 10.0, 2.2 Hz, 1H, H-4b), 4.14 (dd, *J* = 12.4, 2.2 Hz, 1H, H-6′a), 4.27 (dd, *J* = 12.4, 4.4 Hz, 1H, H-6′b), 4.90 (d, *J* = 0.8 Hz, 1H, H-1′), 5.16 (dd, *J* = 10.1, 3.4 Hz, 1H, H-3′), 5.29 (dd, *J* = 10.1, 10.1 Hz, 1H, H-4′), 5.50 (dd, *J* = 3.4, 0.8 Hz, 1H, H-2′). $^{13}$C NMR (175 MHz, $CD_3OD$) *δ*: 14.2 (2C)/14.3/14.5 (acyl $CH_3$), 23.36/23.38/23.41/23.8 (acyl $CH_2$), 25.5/25.60/25.62/26.4 ($COCH_2CH_2$), 30.2/30.3 [$CO(CH_2)_2(CH_2)_2(CH_2)_2CH_3$], 32.34/32.36/32.5/33.0 (acyl $CH_2$), 34.8/34.9/35.0/35.2 ($COCH_2$), 63.1 (C-6′), 64.6 (C-1), 66.8 (C-4′), 70.5 (C-2′), 72.4 (C-3), 72.7 (C-3′), 73.1 (C-4), 73.5 (C-5′), 73.6 (C-2), 100.5 (C-1′), 173.78/173.84/174.7/175.0 ($OCOCH_2$). FABMS *m*/*z* (%): 727 ([M+Na]$^+$, 30), 73 (100). FABHRMS calcd for $C_{36}H_{64}O_{13}Na$ [M+Na]$^+$: 727.4245; found: 727.4277.

***1j***: A colorless amorphous. $[\alpha]_D^{24}$ −26.6 (*c* 1.11, $CHCl_3$). IR (neat) cm$^{-1}$: 3395, 1748, 1458, 1366, 1242, 1165, 1099, 1069. $^1$H NMR (700 MHz, $CD_3OD$) *δ*: 0.901 (t, *J* = 7.4 Hz, 3H, acyl $CH_3$), 0.902 (t, *J* = 7.4 Hz, 3H, acyl $CH_3$), 0.91 (t, *J* = 7.0 Hz, 3H, acyl $CH_3$), 0.93 (t, *J* = 7.2 Hz, 3H, acyl $CH_3$), 1.24–1.42 (m, 20H, acyl $CH_2$), 1.52–1.60 (m, 4H, acyl $CH_2$), 1.63–1.70 (m, 4H, acyl $CH_2$), 2.19/2.21/2.27/2.32/2.34/2.37 (each dt, *J* = 15.8, 7.4 Hz, 1H, $COCH_2$), 2.40/2.47 (each dt, *J* = 15.5, 7.2 Hz, 1H, $COCH_2$), 3.48 (dd, *J* = 8.4, 2.0 Hz, 1H, H-3), 3.61 (d, *J* = 6.2 Hz, 2H, H-1), 3.69 (dd, *J* = 10.8, 6.4 Hz, 1H, H-5a), 3.78 (ddd, *J* = 8.4, 6.4, 2.8 Hz, 1H, H-4), 3.83 (ddd, *J* = 10.0, 4.4, 2.2 Hz, 1H, H-5′), 3.86 (td, *J* = 6.2, 2.0 Hz, 1H, H-2), 4.11 (dd, *J* = 10.8, 2.8 Hz, 1H, H-5b), 4.15 (dd, *J* = 12.4, 2.2 Hz, 1H, H-6′a), 4.28 (dd, *J* = 12.4, 4.4 Hz, 1H, H-6′b), 4.92 (d, *J* = 1.0 Hz, 1H, H-1′), 5.16 (dd, *J* = 10.0, 3.2 Hz, 1H, H-3′), 5.30 (dd, *J* = 10.0, 10.0 Hz, 1H, H-4′), 5.51 (dd, *J* = 3.2, 1.0 Hz, 1H, H-2′). $^{13}$C NMR (175 MHz, $CD_3OD$) *δ*: 14.2 (2C)/14.3/14.5 (acyl $CH_3$), 23.38 (2C)/23.42/23.8 (acyl $CH_2$), 25.5/25.60/25.62/26.3 ($COCH_2CH_2$), 30.2/30.3 [$CO(CH_2)_2(CH_2)_2(CH_2)_2CH_3$], 32.3/32.4/32.5/33.0 (acyl $CH_2$), 34.8/34.9/35.0/35.2 ($COCH_2$), 63.1 (C-6′), 64.8 (C-1), 66.8 (C-4′), 70.5 (C-2′), 71.67 (C-2), 71.69 (C-4), 72.1 (C-3), 72.7 (C-3′), 73.48 (C-5′), 73.50 (C-5), 100.6 (C-1′), 173.77/173.84/174.8/175.0 ($OCOCH_2$). FABMS *m*/*z* (%): 757 ([M+Na]$^+$, 100). FAB HRMS calcd for $C_{37}H_{66}O_{14}Na$ [M+Na]$^+$: 757.4350; found: 757.4342.

***1k***: A colorless amorphous. $[\alpha]_D^{24}$ −27.7 (*c* 1.07, $CHCl_3$). IR (neat) cm$^{-1}$: 3383, 1748, 1246, 1169, 1103, 1069. $^1$H NMR (800 MHz, $CD_3OD$) *δ*: 0.90 (t, *J* = 7.3 Hz, 9H, acyl $CH_3$), 0.92 (t, *J* = 7.3 Hz, 3H, acyl $CH_3$), 1.24–1.42 (m, 20H, acyl $CH_2$), 1.52–1.59 (m, 4H, acyl $CH_2$), 1.63–1.70 (m, 4H, acyl $CH_2$), 2.19/2.21/2.27/2.31/2.34/2.37 (each dt, *J* = 15.8, 7.3 Hz, 1H, $COCH_2$), 2.40/2.47 (each dt, *J* = 15.3, 7.3 Hz, 1H, $COCH_2$), 3.63 (dd, *J* = 9.2, 1.8 Hz, 1H, H-3), 3.64 (d, *J* = 6.2 Hz, 2H, H-1), 3.69 (dd, *J* = 10.5, 6.4 Hz, 1H, H-7a), 3.75 (dd, *J* = 8.5, 0.9 Hz, 1H, H-5), 3.80 (ddd, *J* = 8.5, 6.4, 2.3 Hz, 1H, H-6), 3.83 (ddd, *J* = 10.1, 4.3, 2.3 Hz, 1H, H-5′), 3.89 (dd, *J* = 9.2, 0.9 Hz, 1H, H-4), 3.92 (td, *J* = 6.2, 1.8 Hz, 1H, H-2), 4.141 (dd, *J* = 10.5, 2.3 Hz, 1H, H-7b), 4.143 (dd, *J* = 12.4, 2.3 Hz, 1H, H-6′a), 4.28 (dd, *J* = 12.4, 4.3 Hz, 1H, H-6′b), 4.93 (d, *J* = 0.9 Hz, 1H, H-1′), 5.16 (dd, *J* = 10.1, 3.2 Hz, 1H, H-3′), 5.30 (dd, *J* = 10.1, 10.1 Hz, 1H, H-4′), 5.51 (dd, *J* = 3.2, 0.9 Hz, 1H, H-2′). $^{13}$C NMR (200 MHz, $CD_3OD$) *δ*: 14.2 (2C)/14.3/14.5 (acyl $CH_3$), 23.37/23.39/23.42/23.8 (acyl $CH_2$), 25.5/25.59/25.63/26.4 ($COCH_2CH_2$), 30.2/30.3 [$CO(CH_2)_2(CH_2)_2(CH_2)_2CH_3$], 32.3/32.4/32.5/33.0 (acyl $CH_2$), 34.8/34.9/35.0/35.2 ($COCH_2$), 63.0 (C-6′), 65.0 (C-1), 66.8 (C-4′), 70.2 (C-4), 70.5 (C-2′), 71.0 (C-5), 71.4 (C-3), 71.9 (C-6), 72.0 (C-2), 72.7 (C-3′), 73.5 (C-5′), 73.8 (C-7), 100.6 (C-1′), 173.75/173.85/174.8/175.0 ($OCOCH_2$). FABMS *m*/*z* (%): 817 ([M+Na]$^+$, 54), 99 (100). FABHRMS calcd for $C_{39}H_{70}O_{16}Na$ [M+Na]$^+$: 817.4562; found: 817.4579.

### 3.2. Bioassay of acremomannolipin A homologs[3]

The *Schizosaccharomyces pombe* strains used in this study are calcineurin deletion cells (*h*$^+$ *leu1 ura4-D18 ppb1::ura4*$^+$), the preparation of which is described in a Supplementary data. In the present study the cells were provided by Dr. M. Yanagida. The cells were grown at 27 °C in the YPD (the complete medium yeast extract-peptone-dextrose) and harvested in the early logarithmic growth phase. The cells were resuspended in fresh YPD, and the optical density was adjusted to 0.5 at 660 nm. The cells were spread onto the YPD agar medium containing 0.1 M $MgCl_2$ and then put a filter paper disk (3 mm in diameter) in each section. Next, 5 μL of DMSO or the compound which was dissolved in DMSO at a concentration of 100 μM was spotted onto each paper and the cells were incubated at 27 °C for 3 days.

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## Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.bmc.2015.03.079.

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