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Total Synthesis of Myrmekioside A, a Mono-*O*-alkyl-diglycosylglycerol from Marine Sponge *Myrmekioderma* sp.

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Myrmekioside A, which was isolated from the marine sponge *Myrmekioderma* sp. as a member of the family of natural mono-*O*-alkyl-diglycosylglycerols, and which has a strong reversion effect on the tumor cell morphology of ras-transformed cells at 5 μg/mL, was synthesized for the first time in 17 steps and 14 % overall yield. The β-glycosidic linkages in myrmekioside A were successfully constructed by the neighbouring-group-participation approach using trichloroacetimidates and thioglycosides as glycosyl donors. The 2*R* absolute configuration at C-2 of the glycerol backbone was derived from (*S*)-1,2-isopropylideneglycerol (**8**). This synthetic approach may be applicable to the preparation of other myrmekioside analogues featuring different sugars and alkyl chains for further structure–activity relationship studies.

Introduction

A new family of glycolipids with a unique mono-*O*-alkyl-diglycosylglycerol structure were isolated from the marine sponges *Myrmekioderma* sp. and *Trikentrion loeve*, and were reported to have potent antitumor activities.[1] These compounds all consisted of a glycerol backbone bearing an alkyl chain and a xylose at the terminal hydroxyl positions, and a mono- or diglucosyl unit or a monoglucosamine residue attached to C-2 of the glycerol (Figure 1). Among these compounds, myrmekiosides A–C, which all contain the same sugar moieties but have different *O*-alkyl chains, showed antitumor effects against melanoma H-ras-transformed NIH3T3 and THP1 cells.[1b,2] Myrmekioside E-2, a peracetylated derivative of myrmekioside E, which contains xylose and *N*-acetylglucosamine and a long alkyl chain with a terminal alcohol group, was reported to inhibit the proliferation of two human non-small-cell lung cancer cell lines (NSCLC-N6 and A549).[3]

As a part of our continuing studies on the synthesis of therapeutically potent glycolipids from marine organisms,[4] we describe in this paper the first total synthesis of the mono-*O*-alkyl-diglycosyl glycerol myrmekioside A, which was isolated from the marine sponge *Myrmekioderma* sp.

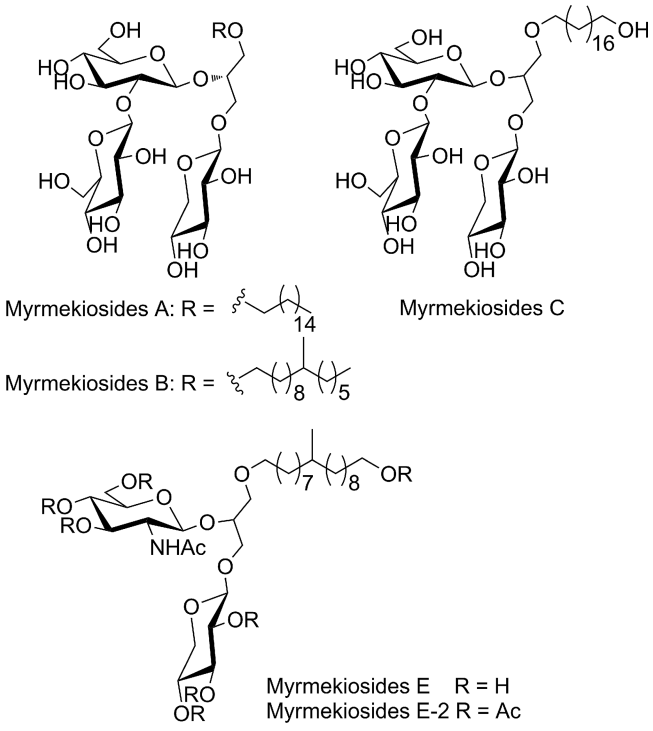

Figure 1. Mono-*O*-alkyl-diglycosylglycerols from natural products.

Results and Discussion

The retrosynthetic analysis of myrmekioside A is shown in Scheme 1. After careful consideration of possible protecting groups, we envisaged that myrmekioside A could be synthesized by an etherification reaction between diglycosylglycerol **2** and an alkyl unit **1** with an activating group. Diglycosylglycerol **2** was disconnected into thioglycoside **4** and another diglycosylglycerol **3** at the β(1→2) linkage of

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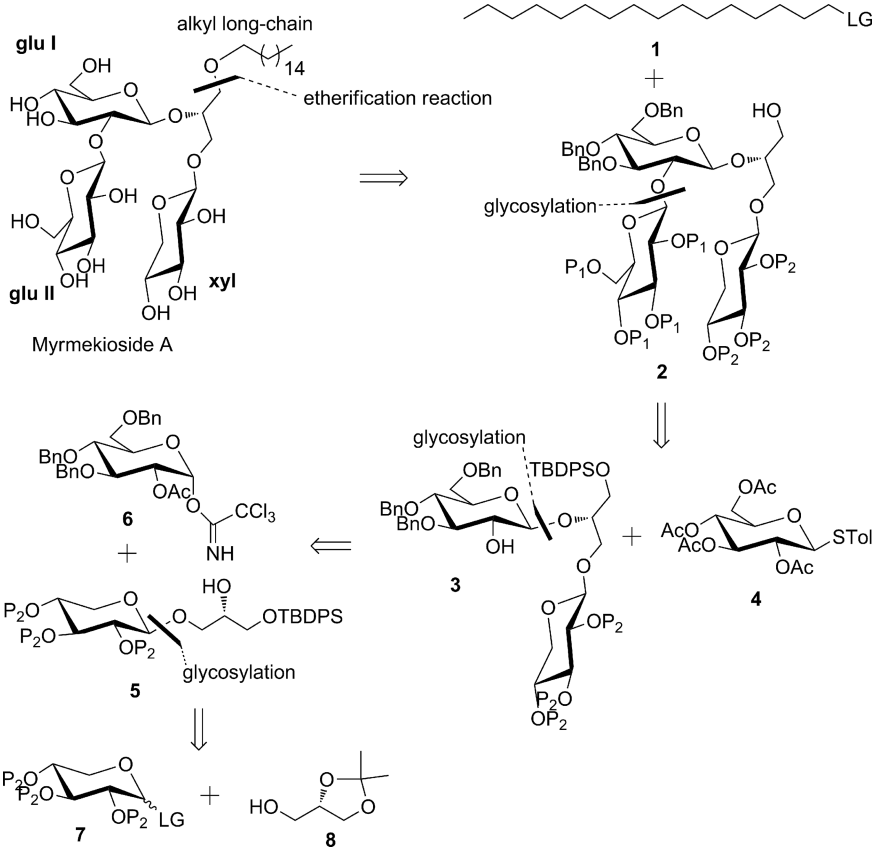
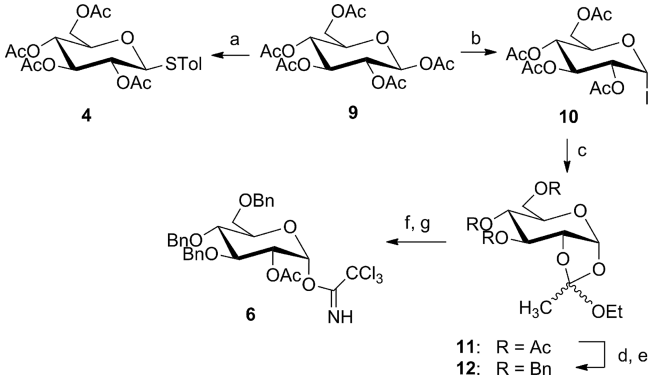


Scheme 1. Retrosynthetic approach to myrmekioside A (P = protecting group; LG = leaving group).

the two glucose residues. To construct **3**, we would require imidate donor **6** with an acetyl protecting group at C-2 – different from the protection of the other hydroxy groups – which could be prepared from the peracetylated sugar via the in situ generation of a glycosyl iodide.[5] (*S*)-1,2-Isopropylideneglycerol **8** could be coupled to xylose unit **7** to form chiral xylosylglycerol **5**, consistent with natural absolute 2*R* configuration at C-2 of the glycerol residue.

Our initial efforts were aimed at the preparation of the two glucose units **4** and **6** as shown in Scheme 2. Thioglycoside donor **4**[6] was synthesized from peracetylated glucose **9** using thiocresol and $BF_3{\cdot}OEt_2$ in dichloromethane.[7] Imidate **6**[5a] was prepared in 70% overall yield, also from starting material **9**. Peracetylated glucose **9** was converted into orthoester **11** via glycosyl iodide **10**, which was cyclized immediately in the presence of base and ethanol. The remaining three acetate groups of **11** were then replaced with benzyl groups to give orthoester **12**[5b] in 88% yield. Acidic hydrolysis of **12** gave the corresponding hemiacetal, which was then treated with trichloroacetonitrile (CCl_3CN) and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) as a base[8] to give glucosyl trichloroacetimidate **6** in 87% yield.

To construct chiral xylosylglycerol **5a** with a β-glycosidic linkage, perbenzoylated xylosyl donors **7a**[9] and **7b**[10] were prepared to glycosylate with (*S*)-1,2-*O*-isopropylidene-*sn*-glycerol **8** using the neighbouring-group participation effect (Scheme 3).[11] Thioglycoside **7a** was synthesized from per-

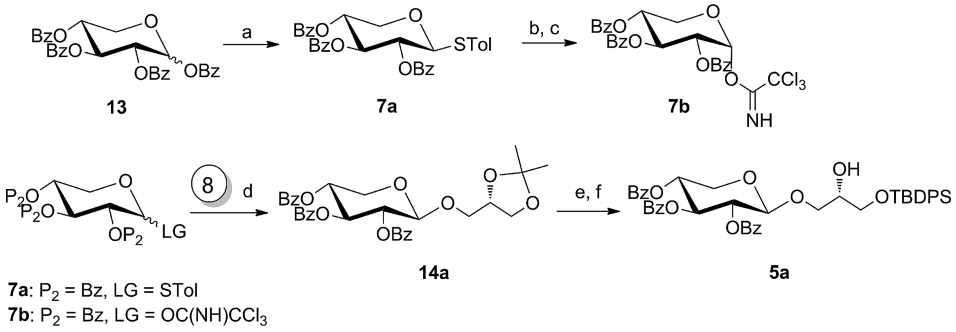


Scheme 2. Preparation of the building blocks **4** and **6**. Reagents and conditions: (a) *p*-thiocresol, $BF_3{\cdot}OEt_2$, CH_2Cl_2, 83%; (b) I_2, Et_3SiH, CH_2Cl_2; (c) 2,6-lutidine, TBAI (tetrabutylammonium iodide), EtOH; (d) CH_3ONa, CH_3OH; (e) BnBr, NaH, DMF, 81% over four steps; (f) *p*TsOH, dimethoxyethane/H_2O; (g) $CNCCl_3$, DBU, CH_2Cl_2, 87% over two steps.

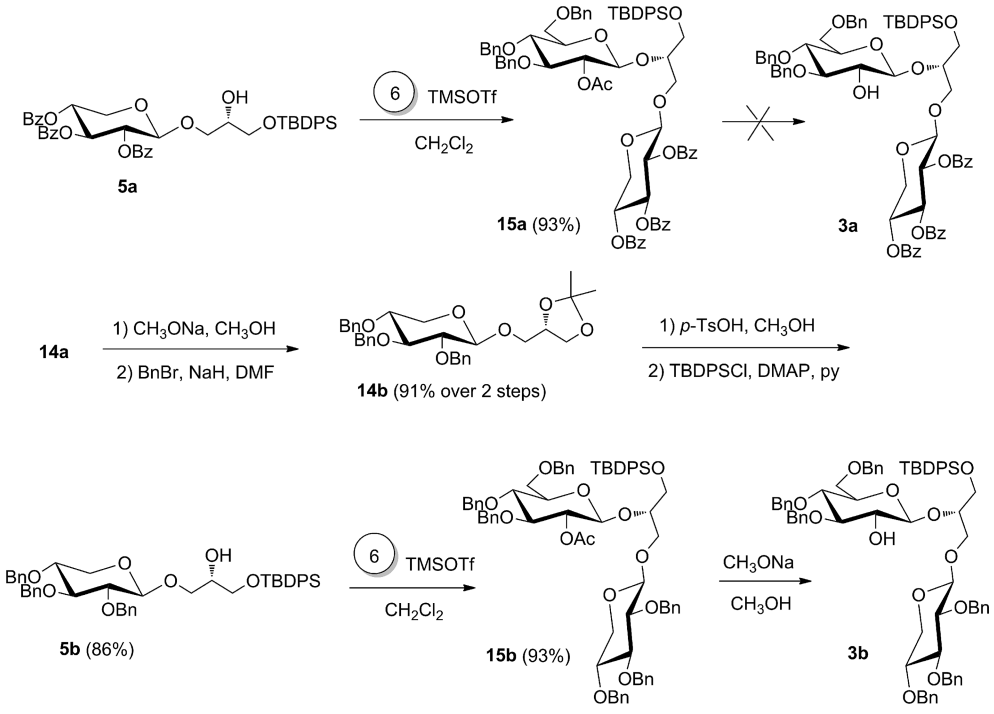
benzoylated xylose **13**[12] in 88% yield by reaction with thiocresol and $BF_3{\cdot}OEt_2$. With **7a** in hand, we attempted its coupling with **8** under the conditions of *N*-iodosuccinimide (NIS) and trifluoromethanesulfonic acid (TfOH).[13] Unfortunately, the yield was rather disappointing because of the low reactivity of the donor, and a glycoside with undesired C-2 racemization of isopropylidene group was observed as a by-product, even when excess DTBMP (2,6-di-*tert*-butyl-4-methylpyridine) was added to prevent this racemiza-

tion.[14] Therefore, we turned our attention to the trichloroacetimidate glycosylation methodology developed by Schmidt, which would allow reaction with the chiral 1,2-*O*-isopropylidene-*sn*-glycerol without racemization.[15] Removal of the *p*-toluenethio group using *N*-bromosuccinimide (NBS) in acetone/water was followed by treatment with $CNCCl_3$ and DBU to give imidate donor **7b**.[10] Coupling of **7b** with **8** using a catalytic amount of trimethylsilyl trifluoromethanesulfonate (TMSOTf)[16] in dichloromethane gave the desired glycoside (i.e., **14a**) as a single β isomer in 97% yield. Hydrolysis of **14a** with *p*TsOH·H_2O in methanol, and selective protection of the resulting xylosyl glycerol with *tert*-butyldiphenylsilane (TBDPS)[17] gave building block **5a** in 74% yield over two steps.

With the building blocks in hand, we next attempted to prepare diglycosylglycerol **3a** (Scheme 4). Under the Schmidt glycosylation conditions of TMSOTf in dry CH_2Cl_2,[16] xylosylglycerol derivative **5a** was glycosylated with D-glucosyl donor **6** to deliver β-D-glucopyranoside **15a** in 93% yield. At this point, we encountered difficulties in selectively cleaving the C-2 acetyl group in the presence of the benzoyl groups under various hydrolysis conditions. Initial attempts with DBU/CH_2Cl_2[18] or CSA (camphorsulfonic acid) in a CH_3OH/CH_2Cl_2 (1:9) solvent mixture[19] were unsuccessful, and none of the product (i.e., **3a**) was detected. This was probably due to steric hindrance around the secondary 2-OH position as a result of the bulkiness of the anomeric substituent and the Bn group at C-3. Treatment of **15a** with DBU in CH_3OH/CH_2Cl_2 (1:1)[20] or HCl/CH_3OH[21] gave large amounts of undesired debenzoylated or desilylated (TBDPS) by-products, respectively, which indicated that the TBDPS group was more stable to a basic environment than to acid-catalysed hydrolysis.[22] Therefore, we had to change the protecting groups on the xylose moiety to avoid the side-reactions during deacetylation of C-2 of the glucose residue. We first attempted the direct glycos-



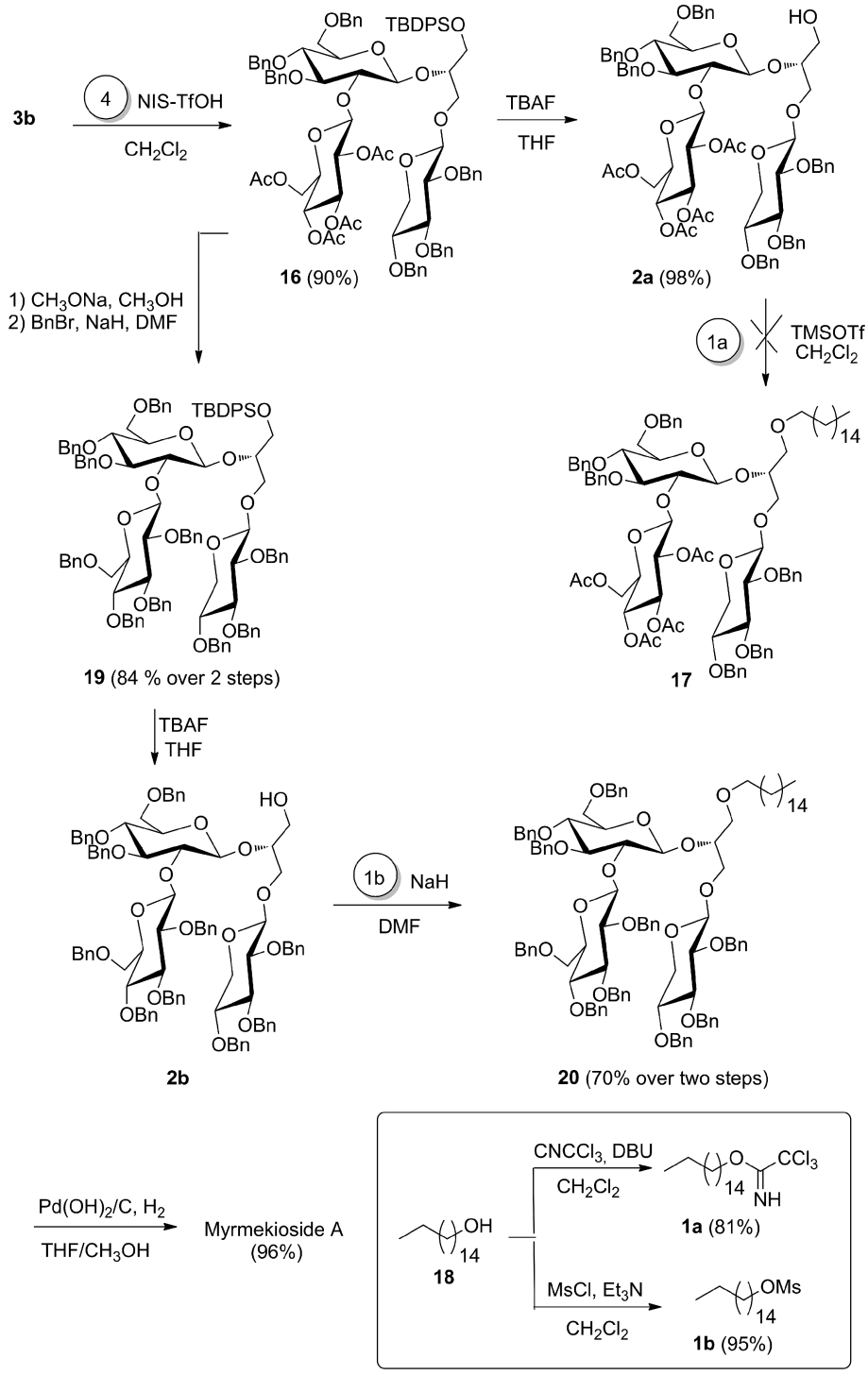
Scheme 3. Preparation of building block **5**. Reagents and conditions: (a) *p*-thiocresol, BF_3·OEt_2, CH_2Cl_2, 88%; (b) NBS, acetone/water (9:1); (c) DBU, $CNCCl_3$, CH_2Cl_2, 82% over two steps; (d) from **7a**: NIS, TfOH, CH_2Cl_2, 75% (isomeric mixture); from **7b**: TMSOTf, CH_2Cl_2, 97%; (e) *p*TsOH, CH_3OH; (f) TBDPSCl, DMAP [4-(dimethylamino)pyridine], pyridine, 74% over two steps.



Scheme 4. Synthesis of diglycosylglycerol acceptor **3b**.

ylation of perbenzylated xylose imidate and **8**, aiming to prepare perbenzylated glycerol derivative **14b**, but the product proved to be an inseparable anomeric mixture (α/β = 1:1). Thus **14b** was prepared from its benzoyl derivative **14a** in 91% yield, and this was followed by a hydrolysis and protection process to give xylosyl acceptor **5b** in 86% yield. Glycosylation of **5b** and **6** under Schmidt conditions produced diglycosylglycerol **15b**, which was quantitatively hydrolysed using CH_3ONa/CH_3OH[23] for at least 8 h to give product **3b** with a free hydroxyl group at C-2 for the next glycosylation step.

With diglycosylglycerol acceptor **3b** available, we carried out glycosylation with building block **4** using NIS/TfOH as shown in Scheme 5 to obtain diglycosylglycerol **16**. Removal of the TBDPS protecting group of **16** by treatment with tetrabutylammonium fluoride (TBAF) in THF yielded



Scheme 5. Synthesis of myrmekioside A.

2a (98%). Generally, alkyl sulfonates or halides are used in etherification reactions with free hydroxyl groups under basic conditions. But under such conditions, acetyl groups could potentially be hydrolysed, and indeed we observed large amounts of hydrolysis by-products in the reaction of hexadecyl methanesulfonate (**1b**) [1-hexadecanol (**18**; 1.0 equiv.), MsCl (1.5 equiv.), Et_3N (0.8 equiv.), DMAP (0.1 equiv.), CH_2Cl_2, 95%] with compound **2a** in the presence of sodium hydride (NaH). In order to limit this deacetylation, a coupling reaction between hexadecyl trichloroacetimidate (**1a**) [1-hexadecanol (**18**; 1.0 equiv.), $CNCCl_3$ (3.0 equiv.), DBU (0.6 equiv.), CH_2Cl_2, 81%] and **2a** was then attempted under acidic conditions (TfOH).[24] However, none of the desired product (i.e., **17**) was detected. Thus, we had to convert **16** into its benzylated derivative **19** in 84% yield over two steps. Afterwards, the TBDPS group was quantitatively removed to give **2b** with a free hydroxyl group at the glycerol residue. Etherification of **2b** with **1b** using NaH in dimethyl formamide (DMF)[25] at 50 °C overnight successfully produced **20** in 70% yield. Final catalytic hydrogenation using $H_2/Pd(OH)_2$ generated the target compound myrmekioside A. The structure of the synthetic compound was identified by ^1H and ^{13}C NMR spectroscopy and HR-ESI-MS, all of which were consistent with natural myrmekioside A.[2]

Conclusions

The total synthesis of myrmekioside A, containing a chiral glycerol backbone linked to xylose, a diglucose moiety, and an long alkyl chain with a terminal alcohol group, was completed in 17 steps in 14% overall yield. To the best of our knowledge, this is the first synthesis of this natural mono-*O*-alkyl-diglycosylglycerol. Strategies for protecting groups and glycosylation conditions were studied and optimized to ensure high stereo- and regioselectivity. The absolute 2*R* configuration at C-2 of the glycerol residue in myrmekioside A was achieved by using commercially available (*S*)-1,2-isopropylideneglycerol **8**. The synthetic approach presented here is of a modular character, and should thus be applicable to other natural mono-*O*-alkyl-diglycosylglycerols and structural variants.

Experimental Section

General Remarks: Solvents were purified in a conventional manner. Thin-layer chromatography (TLC) was carried out on pre-coated HSGF254 plates (Yantai, China). Flash column chromatography was carried out on silica gel (200–300 mesh, Qingdao, China). Optical rotations were determined with a Perkin–Elmer Model 241 MC polarimeter. ^1H and ^{13}C NMR spectra were recorded with JEOL JNM-ECP 600 MHz and Agilent 500 MHz DD2 spectrometers, using tetramethylsilane (Me_4Si) as an internal standard, and chemical shifts are reported as δ values. Mass spectra were recorded with Global Q-TOF and IonSpec 4.7 Tesla FTMS (MALDI/DHB) mass spectrometers.

***p*-Methylphenyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (4):**[6] Compound **4** (4.8 g, 83%) was obtained as a white solid from peracetylated glucose **9** (5.0 g, 12.8 mmol). ^1H NMR (600 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 8.1 Hz, 2 H, Ar*H*), 7.12 (d, *J* = 8.0 Hz, 2 H, Ar*H*), 5.20 (t, *J* = 9.4 Hz, 1 H, 3-H), 5.02 (t, *J* = 9.8 Hz, 1 H, 2-H), 4.92 (t, *J* = 9.8 Hz, 1 H, 4-H), 4.63 (d, *J* = 10.0 Hz, 1 H, 1-H), 4.21 (dd, *J* = 12.2, 5.0 Hz, 1 H, 6-Ha), 4.16 (dd, *J* = 12.2, 2.5 Hz, 1 H, 6-Hb), 3.69 (ddd, *J* = 10.1, 5.0, 2.5 Hz, 1 H, 5-H), 2.35 (s, 3 H, PhCH_3), 2.09, 2.08, 2.01, 1.98 (4 s, 12 H, 4 CH_3) ppm. MS (ESI): *m*/*z* = 477.1 $[M + Na]^+$.

3,4,6-Tri-*O*-benzyl-1,2-*O*-ethoxyethylidene-α-D-glucopyranose (12):[5b] Compound **12** (81% over four steps; *exo*/*endo* = 9:1) was obtained from peracetylated glucose **9** (3.9 g, 10.0 mmol). R_f = 0.7 (petroleum ether/EtOAc, 2:1, *exo*). ^1H NMR (500 MHz, $CDCl_3$, *exo*): δ = 7.35–7.17 (m, 15 H, ArH), 5.77 (d, *J* = 5.2 Hz, 1 H, 1-H), 4.71 (d, *J* = 11.8 Hz, 1 H, PhC*H*), 4.61–4.57 (m, 3 H, 3 PhC*H*), 4.50 (d, *J* = 12.1 Hz, 1 H, PhC*H*), 4.42 (dd, *J* = 5.2, 4.1 Hz, 1 H, 2-H), 4.39 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 3.88 (t, *J* = 4.0 Hz, 1 H, 3-H), 3.80–3.77 (m, 1 H, 5-H), 3.71 (dd, *J* = 9.5, 4.4 Hz, 1 H, 4-H), 3.66–3.64 (m, 2 H, 2 6-H), 3.60–3.50 (m, 2 H, OCH_2), 1.67 (s, 3 H, CH_3), 1.20 (t, *J* = 7.0 Hz, 3 H, OCH_2CH_3) ppm. MS (ESI): *m*/*z* = 515.2 $[M - C_2H_4 + Na]^+$.

3,4,6-Tri-*O*-benzyl-2-*O*-acetyl-α-D-glucopyranosyl Trichloroacetimidate (6):[5a] Compound **12** (0.52 g, 1.0 mmol) was dissolved in dimethoxyethane/H_2O (10:1; 6.6 mL), and *p*TsOH (96 mg, 0.5 mmol) was added at room temperature. After 2 h, the reaction mixture was extracted with CH_2Cl_2 (2 × 20 mL), and the organic phase was washed with saturated $NaHCO_3$ and brine, and dried (Na_2SO_4), and the solvents were evaporated in vacuo.

The residue was dissolved in CH_2Cl_2 (10 mL), and the solution was cooled to 0 °C. CCl_3CN (0.6 mL, 6.0 mmol) and DBU (44 μL, 0.3 mmol) were added. The mixture was stirred for 2 h, after which time TLC indicated that the reaction was complete. The solution was concentrated, and the residue was purified by column chromatography (petroleum ether/EtOAc, 6:1) to give **6** (0.55 g, 87% over two steps) as an oil. R_f = 0.7 (petroleum ether/EtOAc, 3:1). ^1H NMR (600 MHz, $CDCl_3$): δ = 8.56 (s, 1 H, N*H*), 7.33–7.16 (m, 15 H, Ar*H*), 6.52 (d, *J* = 3.5 Hz, 1 H, 1-H), 5.07 (dd, *J* = 10.0, 3.5 Hz, 1 H, 2-H), 4.85 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.83 (d, *J* = 10.6 Hz, 1 H, PhC*H*), 4.76 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.63 (d, *J* = 11.9 Hz, 1 H, PhC*H*), 4.77 (d, *J* = 10.6 Hz, 1 H, PhC*H*), 4.50 (d, *J* = 11.9 Hz, 1 H, PhC*H*), 4.09 (t, *J* = 9.5 Hz, 1 H, 3-H), 4.02–3.98 (m, 1 H, 5-H), 3.88 (d, *J* = 9.6 Hz, 1 H, 4-H), 3.81 (dd, *J* = 11.1, 3.3 Hz, 1 H, 6-Ha), 3.69 (dd, *J* = 11.1, 1.6 Hz, 1 H, 6-Hb), 1.92 (s, 3 H, CH_3) ppm. MS (ESI): *m*/*z* = 658.2 $[M + Na]^+$.

***p*-Methylphenyl 2,3,4-Tri-*O*-benzoyl-1-thio-β-D-xylopyranoside (7a):**[9] Compound **7a** (3.1 g, 88%) was obtained from perbenzoylated xylose **13** (3.5 g, 6.2 mmol). R_f = 0.8 (petroleum ether/EtOAc, 2:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.04–7.98 (m, 6 H, Ar*H*), 7.55–7.33 (m, 11 H, Ar*H*), 7.14 (d, *J* = 8.3 Hz, 2 H, Ar*H*), 5.76 (t, *J* = 6.8 Hz, 1 H, 3-H), 5.43 (t, *J* = 6.6 Hz, 1 H, 2-H), 5.30–5.26 (m, 1 H, 4-H), 5.19 (d, *J* = 6.6 Hz, 1 H, 1-H), 4.68 (dd, *J* = 12.2, 4.2 Hz, 1 H, 5-Ha), 3.79 (dd, *J* = 12.2, 6.7 Hz, 1 H, 5-Hb), 2.35 (s, 3 H, CH_3) ppm. MS (ESI): *m*/*z* = 591.3 $[M + Na]^+$ 591.1.

2,3,4-Tri-*O*-benzoyl-α-D-xylopyranosyl Trichloroacetimidate (7b):[10b] Compound **7b** (82% over two steps) was obtained as a colourless oil from **7a**. R_f = 0.7 (petroleum ether/EtOAc, 3:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.04–7.98 (m, 4 H, Ar*H*, N*H*), 7.58–7.30 (m, 12 H, Ar*H*), 6.36 (d, *J* = 4.7 Hz, 1 H, 1-H), 5.82 (t, *J* = 5.8 Hz, 1 H, 3-H), 5.62 (dd, *J* = 5.5, 4.8 Hz, 1 H, 2-H), 5.41–5.37 (m, 1 H, 4-H), 4.57 (dd, *J* = 12.6, 3.5 Hz, 1 H, 5-Ha), 4.01 (dd, *J* = 12.6, 5.5 Hz, 1 H, 5-Hb) ppm. MS (ESI): *m*/*z* = 628.1 $[M + Na]^+$.

3-*O*-(2′,3′,4′-Tri-*O*-benzoyl-β-D-xylopyranosyl)-1,2-isopropylidene-*sn*-glycerol (14a): (*S*)-1,2-Isopropylideneglycerol **8** (38 μL, 0.31 mmol) and imidate **7b** (0.16 g, 0.26 mmol) were dissolved in dry CH_2Cl_2 (15 mL). Molecular sieves (4 Å; 0.50 g) were added, and the mixture was cooled to –15 °C under nitrogen. A solution of TMSOTf (5 μL, 0.03 mmol) in CH_2Cl_2 (1.0 mL) was added dropwise over a period of 30 min. The mixture was stirred for 30 min at –15 °C, and then it was neutralized with Et_3N, and filtered. The filtrate was concentrated. The residue was purified by column chromatography (petroleum ether/EtOAc, 6:1) to give compound **14a** (0.15 g, 97%) as a colourless solid. R_f = 0.5 (petroleum ether/EtOAc, 3:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.01–7.96 (m, 6 H, Ar*H*), 7.56–7.32 (m, 9 H, Ar*H*), 5.75 (t, *J* = 7.0 Hz, 1 H, 3-H), 5.37 (dd, *J* = 7.0, 5.3 Hz, 1 H, 2-H), 5.29 (td, *J* = 6.7, 4.2 Hz, 1 H, 4-H), 4.88 (d, *J* = 5.4 Hz, 1 H, 1-H), 4.46 (dd, *J* = 12.2, 4.2 Hz, 1 H, 5-Ha), 4.31–4.26 (m, 1 H, 2_{sn}-H), 3.97 (dd, *J* = 8.6, 6.5 Hz, 1 H, 1_{sn}-Ha), 3.94 (dd, *J* = 10.1, 5.1 Hz, 1 H, 3_{sn}-Ha), 3.75–3.70 (m, 2 H, 5-Hb, 1_{sn}-Hb), 3.58 (dd, *J* = 10.0, 5.9 Hz, 1 H, 3_{sn}-Hb), 1.34 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3) ppm. MS (ESI): *m*/*z* = 599.3 [M + Na]$^+$.

1-*O*-*tert*-Butyldiphenylsilyl-3-*O*-(2′,3′,4′-tri-*O*-benzoyl-β-D-xylopyranosyl)-*sn*-glycerol (5a): *p*TsOH (0.13 g, 0.69 mmol) was added to a solution of **14a** (0.80 g, 1.39 mmol) in CH_3OH (16 mL) at room temperature. The mixture was stirred for 2 h, then it was concentrated, and the residue was purified by column chromatography (petroleum ether/EtOAc, 1:1).

The product was dissolved in dry pyridine (15 mL) at room temparature, and DMAP (32 mg, 0.26 mmol) and TBDPSCl (0.37 mL, 1.40 mmol) were added. The reaction mixture was stirred overnight. After this time, TLC analysis showed complete consumption of the starting material, and the mixture was evaporated in vacuo. The residue was dissolved in CH_2Cl_2 (30 mL), and the solution was washed with aq. HCl (1 M) and brine, dried with Na_2SO_4, and concentrated. The residue was purified by column chromatography (petroleum ether/EtOAc, 4:1) to give compound **5a** (1.28 g, 74% over two steps) as an oil. R_f = 0.5 (petroleum ether/EtOAc, 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00–7.93 (m, 6 H, Ar*H*), 7.61–7.25 (m, 19 H, Ar*H*), 5.75 (t, *J* = 7.2 Hz, 1 H, 3-H), 5.35 (dd, *J* = 7.3, 5.4 Hz, 1 H, 2-H), 5.29 (td, *J* = 6.9, 4.4 Hz, 1 H, 4-H), 4.83 (d, *J* = 5.4 Hz, 1 H, 1-H), 4.41 (dd, *J* = 12.2, 4.4 Hz, 1 H, 5-Ha), 3.89–3.85 (m, 2 H, 2 3_{sn}-H), 3.77–3.72 (m, 1 H, 2_{sn}-H), 3.68 (dd, *J* = 12.2, 7.1 Hz, 1 H, 5-Hb), 3.66 (d, *J* = 4.9 Hz, 2 H, 2 1_{sn}-H), 2.57 (d, *J* = 4.9 Hz, 1 H, O*H*), 1.03 (s, 9 H, 3 CH_3) ppm. MS (ESI): *m*/*z* = 797.3 [M + Na]$^+$.

1-*O*-*tert*-Butyldiphenylsilyl-2-*O*-(2′-*O*-acetyl-3′,4′,6′-tri-*O*-benzoyl-β-D-glucopyranosyl)-3-*O*-(2″,3″,4″-tri-*O*-benzyl-β-D-xylopyranosyl)-*sn*-glycerol (15a): Compound **5a** (0.21 g, 0.27 mmol) and compound **6** (0.20 g, 0.31 mmol) were dissolved in dry CH_2Cl_2 (8 mL), and molecular sieves (4 Å; 0.30 g) were added. The mixture was cooled to 0 °C under nitrogen, and TMSOTf (7 μL, 0.03 mmol) was added. The mixture was stirred for 30 min at 0 °C, and then it was neutralized with Et_3N, and filtered. The filtrate was concentrated. The residue was purified by column chromatography (petroleum ether/EtOAc, 6:1) to give compound **15a** (0.32 g, 93%) as a white solid. R_f = 0.5 (petroleum ether/EtOAc, 3:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98–7.86 (m, 6 H, Ar*H*), 7.54–7.17 (m, 34 H, Ar*H*), 5.75 (t, *J* = 7.8 Hz, 1 H, 3″-H), 5.30 (dd, *J* = 8.0, 6.2 Hz, 1 H, 2″-H), 5.24 (td, *J* = 7.6, 4.6 Hz, 1 H, 4″-H), 4.97 (dd, *J* = 9.4, 8.2 Hz, 1 H, 2′-H), 4.92 (d, *J* = 6.1 Hz, 1 H, 1″-H), 4.79–4.76 (m, 2 H, 2 PhC*H*), 4.66 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.61 (d, *J* = 12.2 Hz, 1 H, PhC*H*), 4.58 (d, *J* = 8.1 Hz, 1 H, 1′-H), 4.56–4.53 (m, 2 H, 2 PhC*H*), 4.28 (dd, *J* = 11.9, 4.5 Hz, 1 H, 5″-Ha), 3.96–3.89 (m, 2 H, 3_{sn}-Ha, 2_{sn}-H), 3.84 (dd, *J* = 10.5, 5.1 Hz, 1 H, 3_{sn}-Hb), 3.74 (dd, *J* = 10.9, 4.0 Hz, 1 H, 1_{sn}-Ha), 3.71–3.66 (m, 3 H, 4′-H, 2 6′-H), 3.62–3.54 (m, 3 H, 3′-H, 5″-Hb, 1_{sn}-Hb), 3.39 (dt, *J* = 9.7, 3.0 Hz, 1 H, 5′-H), 1.82 (s, 3 H, CH_3), 1.57 (s), 0.97 (s, 9 H, 3 CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 169.50, 165.54, 165.44, 165.02, 138.17, 138.04, 137.88, 135.44, 135.42, 133.29–133.03, 129.87–127.67, 100.39, 100.26, 82.87, 78.31, 77.93, 74.99, 74.97, 74.94, 73.47, 73.23, 70.91, 70.79, 69.56, 68.63, 68.08, 63.28, 61.48, 26.78, 20.89, 19.16 ppm. MS (ESI): *m*/*z* = 1271.6 [M + Na]$^+$.

3-*O*-(2′,3′,4′-Tri-*O*-benzyl-β-D-xylopyranosyl)-1,2-isopropylidene-*sn*-glycerol (14b): Compound **14a** (0.40 g, 0.69 mmol) was dissolved in CH_3OH (8 mL), and a catalytic amount of NaOMe was added until pH 9.0. The reaction mixture was stirred for 30 min, after which time it was neutralized with Amberlite IR120 resin (H^+). The mixture was then filtered, and the filtrate was concentrated in vacuo.

The residue was dissolved in DMF (10 mL), and then NaH (0.11 g, 2.65 mmol) and BnBr (0.32 mL, 2.65 mmol) were added at 0 °C. The mixture was stirred for 1.5 h, then it was quenched with CH_3OH (5 mL) and concentrated. The residue was dissolved in CH_2Cl_2 (30 mL), and the solution was washed with brine, dried with Na_2SO_4, and concentrated. The residue was purified by column chromatography (petroleum ether/EtOAc, 8:1) to give **14b** (0.34 g, 91% over two steps) as a syrup. R_f = 0.8 (petroleum ether/EtOAc, 3:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36–7.27 (m, 15 H, Ar*H*), 4.88 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.85 (d, *J* = 2.2 Hz, 2 H, 2 PhC*H*), 4.72 (d, *J* = 11.6 Hz, 1 H, PhC*H*), 4.70 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.62 (d, *J* = 11.6 Hz, 1 H, PhC*H*), 4.36 (d, *J* = 7.6 Hz, 1 H, 1-H), 4.32–4.27 (m, 1 H, 2_{sn}-H), 4.05 (dd, *J* = 8.1, 6.4 Hz, 1 H, 1_{sn}-Ha), 3.94 (dd, *J* = 11.8, 5.1 Hz, 1 H, 5-Ha), 3.91 (dd, *J* = 10.3, 5.1 Hz, 1 H, 3_{sn}-Ha), 3.80 (dd, *J* = 8.3, 6.1 Hz, 1 H, 1_{sn}-Hb), 3.63–3.54 (m, 3 H, 3-H, 4-H, 3_{sn}-Hb), 3.38 (dd, *J* = 8.8, 7.6 Hz, 1 H, 2-H), 3.20 (dd, *J* = 11.5, 9.8 Hz, 1 H, 5-Hb), 1.41 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3) ppm. MS (ESI): *m*/*z* = 557.3 [M + Na]$^+$.

1-*O*-*tert*-Butyldiphenylsilyl-3-*O*-(2′,3′,4′-tri-*O*-benzyl-β-D-xylopyranosyl)-*sn*-glycerol (5b): *p*TsOH (80 mg, 0.42 mmol) was added to a solution of **14b** (0.45 g, 0.85 mmol) in CH_3OH (10 mL) at room temperature. The mixture was stirred for 3 h, then it was concentrated, and the residue was purified by column chromatography (petroleum ether/EtOAc, 1:1).

The product was dissolved in dry pyridine (12 mL), and DMAP (20 mg, 0.17 mmol) and TBDPSCl (0.34 mL, 1.26 mmol) were added at room temparature. The reaction mixture was stirred overnight, after which time TLC analysis revealed that the starting material had been completely consumed. The mixture was then concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (30 mL), and the solution was washed with aq. HCl (1 M) and brine, dried with Na_2SO_4, and concentrated. The residue was purified by chromatography (petroleum ether/EtOAc, 6:1) to give compound **5b** (0.55 g, 90% over two steps) as an oil. R_f = 0.7 (petroleum ether/EtOAc, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65–7.29 (m, 25 H, Ar*H*), 4.85 (s, 2 H, 2 PhC*H*), 4.78 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.72 (d, *J* = 11.6 Hz, 1 H, PhC*H*), 4.68 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.62 (d, *J* = 11.6 Hz, 1 H, PhC*H*), 4.33 (d, *J* = 7.6 Hz, 1 H, 1-H), 3.91 (dd, *J* = 11.7, 4.8 Hz, 1 H, 5-Ha), 3.92–3.87 (m, 1 H, 2_{sn}-H), 3.85–3.78 (m, 2 H, 2 3_{sn}-H), 3.69 (dd, *J* = 10.3, 5.4 Hz, 1 H, 1_{sn}-Ha), 3.65 (dd, *J* = 10.3, 5.6 Hz, 1 H, 1_{sn}-Hb), 3.61 (td, *J* = 9.2, 4.9 Hz, 1 H, 4-H), 3.56 (t, *J* = 8.7 Hz, 1 H, 3-H), 3.56 (t, *J* = 8.7 Hz, 1 H, 3-H), 3.35 (t, *J* = 8.2 Hz, 1 H, 2-H), 3.20 (dd, *J* =

11.6, 9.8 Hz, 1 H, 5-Hb), 1.05 (s, 9 H, 3 CH_3) ppm. MS (ESI): *m*/*z* = 755.5 [M + Na]$^+$.

1-*O*-*tert*-Butyldiphenylsilyl-2-*O*-(2′-*O*-acetyl-3′,4′,6′-tri-*O*-benzyl-β-D-glucopyranosyl)-3-*O*-(2′′,3′′,4′′-tri-*O*-benzyl-β-D-xylopyranosyl)-*sn*-glycerol (15b): Compound **5b** (0.51 g, 0.70 mmol) and compound **6** (0.48 g, 0.77 mmol) were dissolved in dry CH_2Cl_2 (20 mL). Molecular sieves (4 Å; 0.50 g) were added, and the mixture was cooled to 0 °C under nitrogen. TMSOTf (19 μL, 0.11 mmol) was added. The mixture was stirred for 30 min at 0 °C, and then it was neutralized with Et_3N, and filtered. The filtrate was concentrated. The residue was purified by column chromatography (petroleum ether/EtOAc, 6:1) to give compound **15b** as a colourless oil (0.78 g, 93%). R_f = 0.75 (petroleum ether/EtOAc, 3:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62–7.18 (m, 40 H, Ar*H*), 4.98 (dd, *J* = 9.3, 8.1 Hz, 1 H, 2′-H), 4.83–4.76 (m, 4 H, 4 PhC*H*), 4.69–4.63 (m, 4 H, 3 PhC*H*, 1′-H), 4.59–4.48 (m, 5 H, 5 PhC*H*), 4.34 (d, *J* = 7.6 Hz, 1 H, 1′′-H), 4.01–3.98 (m, 2 H, 2_{sn}-H, 3_{sn}-Ha), 3.87 (dd, *J* = 10.7, 3.5 Hz, 1 H, 1_{sn}-Ha), 3.81 (dd, *J* = 11.4, 4.6 Hz, 1 H, 5′′-Ha), 3.75–3.64 (m, 5 H, 4′-H, 2 6′-H, 1_{sn}-Hb, 3_{sn}-Hb), 3.61 (t, *J* = 9.2 Hz, 1 H, 3′-H), 3.53–3.48 (m, 2 H, 3′′-H, 4′′-H), 3.40 (dt, *J* = 6.2, 2.7 Hz, 1 H, 5′-H), 3.24 (t, *J* = 8.1 Hz, 1 H, 2′′-H), 3.20 (dd, *J* = 11.3, 9.5 Hz, 1 H, 5′′-Hb), 1.77 (s, 3 H, CH_3), 1.03 (s, 9 H, 3 CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 169.49, 138.72, 138.53, 138.23, 138.18, 137.91, 135.54, 135.49, 133.33, 133.13, 129.71, 129.69, 128.42–127.35, 104.17, 100.76, 83.60, 82.98, 81.68, 78.38, 77.96, 77.87, 75.55, 75.08–74.51, 73.51, 73.22, 73.14, 68.76, 68.70, 64.06, 63.71, 26.80, 20.85, 19.18 ppm. MS (ESI): *m*/*z* = 1229.7 [M + Na]$^+$.

1-*O*-*tert*-Butyldiphenylsilyl-2-*O*-[2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl-(1′→2′′)-3′′,4′′,6′′-tri-*O*-benzyl-β-D-glucopyranosyl]-3-*O*-(2′′′,3′′′,4′′′-tri-*O*-acetyl-β-D-xylopyranosyl)-*sn*-glycerol (16): NaOMe was added to a solution of **15b** (0.50 g, 0.41 mmol) in CH_2Cl_2/CH_3OH (1:5; 6 mL) until pH 9.0. The reaction mixture was stirred for 8 h, after which time it was neutralized with Amberlite IR120 resin (H^+). The mixture was then filtered, and the filtrate was concentrated in vacuo.

The residue (i.e., **3b**) and compound **4** (0.27 g, 0.62 mmol) were dissolved in dry CH_2Cl_2 (30 mL) with molecular sieves (4 Å; 0.30 g). The mixture was cooled to 0 °C under nitrogen, then NIS (0.14 g, 0.62 mmol) and TfOH (10 μL, 0.10 mmol) were added. The mixture was stirred for 1 h, and then it was neutralized with Et_3N, and filtered. The filtrate was concentrated. The residue was purified by column chromatography (petroleum ether/EtOAc, 8:1) to give compound **16** (0.56 g, 90% over two steps) as a white solid. R_f = 0.4 (petroleum ether/EtOAc, 3:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.69–7.66 (m, 4 H, Ar*H*), 7.41–7.22 (m, 34 H, Ar*H*), 7.10–7.08 (m, 2 H, Ar*H*), 5.02 (d, *J* = 9.7 Hz, 1 H, 3′-H), 4.97 (t, *J* = 9.7 Hz, 1 H, 4′-H), 4.92–4.85 (m, 2 H, 2′-H, PhC*H*), 4.84 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.82 (d, *J* = 7.1 Hz, 1 H, 1′-H), 4.81 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.76 (d, *J* = 11.2 Hz, 1 H, PhC*H*), 4.75–4.69 (m, 3 H, 3 PhC*H*), 4.62–4.59 (m, 2 H, 2 PhC*H*), 4.55 (d, *J* = 7.4 Hz, 1 H, 1′′-H), 4.53 (d, *J* = 12.4 Hz, 1 H, PhC*H*), 4.51 (d, *J* = 11.7 Hz, 1 H, PhC*H*), 4.47 (d, *J* = 12.3 Hz, 1 H, PhC*H*), 4.40 (d, *J* = 7.6 Hz, 1 H, 1′′′-H), 4.09 (dd, *J* = 10.4, 4.7 Hz, 1 H, 3_{sn}-Ha), 4.04–4.00 (m, 2 H, 2_{sn}-H, 6′-Ha), 3.90–3.78 (m, 4 H, 5′′′-Ha, 2 1_{sn}-H, 3_{sn}-Hb), 3.76 (dd, *J* = 12.5, 1.8 Hz, 1 H, 6′-Hb), 3.62–3.56 (m, 4 H, 2′′-H, 4′′-H, 6′′-Ha, 4′′′-H), 3.55–3.51 (m, 3 H, 3′′-H, 6′′-Hb, 3′′′-H), 3.38–3.34 (m, 1 H, 5′-H), 3.34 (t, *J* = 7.8 Hz, 1 H, 2′′′-H), 3.31–3.29 (m, 1 H, 5′′-H), 3.15 (dd, *J* = 11.4, 9.8 Hz, 1 H, 5′′′-Hb), 1.98, 1.95, 1.88, 1.77 (4 s, 12 H, 4 CH_3), 1.05 (s, 9 H, 3 CH_3) ppm. MS (ESI): *m*/*z* = 1517.6 [M + Na]$^+$.

1-*O*-*tert*-Butyldiphenylsilyl-2-*O*-[2′,3′,4′,6′-tetra-*O*-benzyl-β-D-glucopyranosyl-(1′→2′′)-3′′,4′′,6′′-tri-*O*-benzyl-β-D-glucopyranosyl]-3-*O*-(2′′′,3′′′,4′′′-tri-*O*-benzyl-β-D-xylopyranosyl)-*sn*-glycerol (19): Compound **16** (0.20 g, 0.13 mmol) was dissolved in CH_3OH (5 mL), and a catalytic amount of NaOMe was added until pH 9.0. The reaction mixture was stirred for 1 h, and then it was neutralized with Amberlite IR120 resin (H^+). The mixture was filtered, and the filtrate was concentrated in vacuo.

The residue was dissolved in DMF (5 mL), and then NaH (32 mg, 0.80 mmol) and BnBr (96 μL, 0.80 mmol) were added at 0 °C. The mixture was stirred for 2 h at room temperature, then it was quenched with CH_3OH (5 mL), and concentrated. The residue was dissolved in CH_2Cl_2 (20 mL), and the solution was washed with brine (2× 20mL), dried with Na_2SO_4, and concentrated. The residue was purified by chromatography (petroleum ether/EtOAc, 8:1) to give **19** (0.19 g, 84% over two steps) as a syrup. R_f = 0.7 (petroleum ether/EtOAc, 3:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.69–7.64 (m, 4 H, Ar*H*), 7.35–7.12 (m, 56 H, Ar*H*), 4.84–4.72 (m, 9 H, 9 PhC*H*), 4.81 (d, *J* = 7.6 Hz, 1 H, 1′-H), 4.68–4.65 (m, 2 H, 2 PhC*H*), 4.58 (d, *J* = 7.4 Hz, 1 H, 1′′-H), 4.56 (d, *J* = 11.7 Hz, 1 H, PhC*H*), 4.56–4.46 (m, 7 H, PhC*H*), 4.42 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.29 (d, *J* = 7.6 Hz, 1 H, 1′′′-H), 4.08–4.03 (m, 1 H, 2_{sn}-H), 4.01 (dd, *J* = 10.2, 5.2 Hz, 1 H, 3_{sn}-Ha), 3.86 (dd, *J* = 10.5, 5.3 Hz, 1 H, 1_{sn}-Ha), 3.85–3.80 (m, 2 H, 2′′-H, 1_{sn}-Hb), 3.80 (dd, *J* = 11.5, 4.9 Hz, 1 H, 5′′′-Ha), 3.68 (dd, *J* = 10.2, 5.2 Hz, 1 H, 3_{sn}-Hb), 3.67–3.63 (m, 2 H, 2 6′-H), 3.61–3.56 (m, 4 H, 3′-H, 4′-H, 2 6′′-H), 3.54–3.45 (m, 4 H, 3′′-H, 4′′-H, 3′′′-H, 4′′′-H), 3.38 (ddd, *J* = 9.0, 5.3, 3.0 Hz, 1 H, 5′-H), 3.29–3.26 (m, 2 H, 2′-H, 2′′′-H), 3.23 (dt, *J* = 9.5, 2.6 Hz, 1 H, 5′′-H), 3.08 (dd, *J* = 11.6, 9.7 Hz, 1 H, 5′′′-Hb), 1.04 (s, 9 H, 3 CH_3) ppm. MS (MALDI): *m*/*z* = 1709.8 [M + Na]$^+$.

1-*O*-Hexadecyl-2-*O*-[2′,3′,4′,6′-tetra-*O*-benzyl-β-D-glucopyranosyl-(1′→2′′)-3′′,4′′,6′′-tri-*O*-benzyl-β-D-glucopyranosyl]-3-*O*-(2′′′,3′′′,4′′′-tri-*O*-benzyl-β-D-xylopyranosyl)-*sn*-glycerol (20): TBAF (1 M in THF; 120 μL, 0.12 mmol) was added to a solution of **19** (0.14 g, 0.08 mmol) in THF (6 mL) at room temperature. The mixture was stirred overnight, then it was concentrated. The residue was purified by column chromatography (petroleum ether/EtOAc, 4:1) to give compound **2b** (0.12 g, 100%) as a syrup.

The product (0.10 g, 0.07 mmol) was dissolved in dry DMF (3 mL), and NaH (14 mg, 0.35 mmol) and **1b** (112 mg, 0.35 mmol) were added at at room temperature. The mixture was stirred at 40 °C overnight, then it was quenched with CH_3OH, and concentrated. The residue was purified by column chromatography (petroleum ether/EtOAc, 10:1) to give **20** (80 mg, 70%) as a white solid. R_f = 0.8 (petroleum ether/EtOAc, 3:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35–7.14 (m, 50 H, Ar*H*), 4.98 (d, *J* = 11.2 Hz, 1 H, PhC*H*), 4.93 (d, *J* = 8.0 Hz, 1 H, 1′-H), 4.92 (d, *J* = 11.2 Hz, 1 H, PhC*H*), 4.89 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.86–4.71 (m, 6 H, 6 PhC*H*), 4.69 (d, *J* = 7.5 Hz, 1 H, 1′′-H), 4.68–4.50 (m, 11 H, 11 PhC*H*), 4.29 (d, *J* = 7.6 Hz, 1 H, 1′′′-H), 4.08–4.03 (m, 1 H, 2_{sn}-H), 4.00 (dd, *J* = 10.0, 4.6 Hz, 1 H, 3_{sn}-Ha), 3.85 (dd, *J* = 8.5, 7.5 Hz, 1 H, 2′′-H), 3.82 (dd, *J* = 11.5, 4.9 Hz, 1 H, 5′′′-Ha), 3.70–3.65 (m, 5 H, 3′-H, 3′′-H, 6′′-Ha, 1_{sn}-Ha, 3_{sn}-Hb), 3.65–3.58 (m, 4 H, 5′-H, 6′-Ha, 6′′-Hb, 1_{sn}-Hb), 3.57–3.49 (m, 4 H, 4′-H, 4′′-H, 3′′′-H, 4′′′-H), 3.46 (dt, *J* = 9.7, 3.2 Hz, 1 H, 5′′-H), 3.38 (dd, *J* = 8.8, 8.0 Hz, 1 H, 2′-H), 3.37–3.29 (m, 4 H, 6′-Hb, 2′′′-H, OCH_2), 3.10 (dd, *J* = 11.4, 9.7 Hz, 1 H, 5′′′-Hb), 1.51–1.46 (m, 2 H, OCH$_2$CH_2), 1.29–1.22 [m, 26 H, (CH_2)$_{13}$], 0.89 (t, *J* = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 138.89–138.19, 128.55–128.66, 104.48, 101.99, 101.52, 85.98, 84.97, 83.85, 83.26, 81.95, 78.33, 78.22, 78.06, 77.85, 75.77, 75.68, 75.35, 75.13, 75.04, 74.79, 73.81,

73.59, 73.40, 71.95, 71.17, 69.54, 69.06, 68.93, 63.86, 32.08, 30.12, 30.12–29.82, 29.52, 26.42, 22.84, 14.28 ppm. HRMS (MALDI): calcd. for $C_{106}H_{128}O_{17}Na$ 1695.9044 $[M + Na]^+$; found 1695.8974.

1-*O*-Hexadecyl-2-*O*-[β-D-glucopyranosyl-(1′→2′′)-β-D-glucopyranosyl]-3-*O*-β-D-xylopyranosyl-*sn*-glycerol (Myrmekioside A):[2] A solution of **20** (50 mg, 0.03 mmol) in THF/CH_3OH (9:1; 3 mL) was treated with palladium hydroxide (10%; 50 mg), and the mixture was stirred at room temperature under a hydrogen atmosphere for 1 h. The mixture was then filtered, and the solvent was evaporated in vacuo to give myrmekioside A (22 mg, 96%) as a white solid. R_f = 0.3 (CH_2Cl_2/CH_3OH, 5:1). ^1H NMR (500 MHz, C_5D_5N): δ = 5.27 (d, J = 7.8 Hz, 1 H, 1′-H), 5.22 (d, J = 7.8 Hz, 1 H, 1′′-H), 4.82 (d, J = 7.3 Hz, 1 H, 1′′′-H), 4.57 (dd, J = 11.0, 2.5 Hz, 1 H, 6′-Ha), 4.54–4.51 (m, 1 H, 2_{sn}-H), 4.49–4.45 (m, 2 H, 6′′-Ha, 3_{sn}-Ha), 4.38 (dd, J = 11.0, 5.2 Hz, 1 H, 6′-Hb), 4.33–4.28 (m, 3 H, 5′′′-Ha, 6′′-Hb, 3′′-H), 4.23–4.17 (m, 4 H, 3′-H, 4′′-H, 4′′′-H, 3_{sn}-Hb), 4.15–4.10 (m, 6 H, 4′-H, 2′-H, 2′′-H, 3′′′-H, 2 1_{sn}-H), 4.04–4.00 (m, 2 H, 2′′′-H, 5′-H), 3.87 (ddd, J = 7.4, 4.7, 1.7 Hz, 1 H, 5′′-H), 3.65 (dd, J = 11.0, 9.7 Hz, 1 H, 5′′′-Hb), 3.54 (t, J = 6.6 Hz, 2 H, OCH_2), 1.62–1.58 (m, 2 H, OCH_2CH_2), 1.34–1.24 [m, 26 H, $(CH_2)_{13}$], 0.87 (t, J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, C_5D_5N): δ = 106.47 (C-1′), 105.49 (C-1′′′), 102.84 (C-1′′), 84.14 (C-2′), 79.17 (C-5′′), 78.74 (C-5′), 78.49 (C-3′′), 78.32 (C-3′, C-3′′′), 78.11 (C-2_{sn}), 76.79 (C-2′′), 75.16 (C-2′′′), 72.21 (O-CH_2), 72.17 (C-4′′), 71.64 (C-4′), 71.45 (C-4′′′), 71.25 (C-1_{sn}), 70.27 (C-3_{sn}), 67.43 (C-5′′′), 63.35 (C-6′′), 62.87 (C-6′), 32.61, 30.65, 30.51–30.48, 30.42, 30.35, 30.11, 27.03, 23.43 (14 CH_2), 14.78 (CH_3) ppm. HRMS (ESI): calcd. for $C_{36}H_{68}O_{17}Na$ $[M + Na]^+$ 795.4349; found 795.4355.

Supporting Information (see footnote on the first page of this article): ^1H and ^{13}C NMR spectra for key intermediates and final products.

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