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Synthesis of the Pentasaccharide Moiety of Thornasterside A

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The synthesis of the pentasaccharide moiety of thornasteroside A, the first asterosaponin isolated from starfish in 1978 has been achieved for the first time. Initially, a [3+2] convergent strategy was attempted, but the β(1→4) glycosidic linkage between galactopyranose (sugar IV) and xylopyranose (sugar II) was formed with a low stereoselectivity and in low yield. Subsequently, a [3+1+1] strategy was adopted. A galactopyranosyl donor (**18**) equipped with a neighboring participating Lev (levulinoyl) group at the 2-position was first coupled with a trisaccharide acceptor to construct the β(1→4) glycosidic bond. Then the Lev group was selectively removed, and subsequent glycosylation with a perbenzoylated D-fucopyranosyl Schmidt donor efficiently gave the desired pentasaccharide.

Introduction

Over the last few decades, many secondary metabolites with unusual chemical structures and interesting pharmacological properties have been isolated from marine plants and animals. Steroidal glycosides, the predominant secondary metabolites in starfish, are considered to be responsible for the general toxicity of starfish,[1] and these steroidal glycosides show a broad spectrum of pharmacological activities.[2–4] The structures of steroidal glycosides seem to be quite peculiar in terms of both their carbohydrate and aglycon moieties. They are usually divided into three substructural types: asterosaponin (sulfated steroidal glycosides), steroidal cyclic glycosides, and polyhydroxysteroidal glycosides.[5] Thornasteroside A (Figure 1), the first asterosaponin isolated from *Acanthaster planci* L. in 1978,[6,7] has the typical structural features of asterosaponin: an aglycon with a $\Delta^{9(11)}$-3β,6α-diol structure with a sulfated 3-OH, and an oligosaccharide residue attached to the 6-OH of the aglycon.

The total synthesis of thornasteroside A is a challenge. One of the obstacles to its synthesis is the presence of the 20-OH group β to a carbonyl group in the aglycon. The great instability of this 20-OH group means that a straightforward synthesis in which the sugar residues are attached one by one to the aglycon cannot be achieved efficiently, because the repeated glycosylations and protection/deprotection steps will frequently involve acidic or basic conditions.[8,9] A convergent strategy, in which a preconstructed oligosaccharide donor is coupled with the aglycon under neutral conditions, could address the issue. The carbohydrate portion of thornasteroside A is a pentasaccharide with the sequence: [β-D-Qui*p*-(1→2)]-[β-D-Fuc*p*-(1→2)-β-D-Gal*p*-(1→4)]-β-D-Xyl*p*-(1→3)-β-D-Qui*p*, which is the typical oligosaccharide sequence of asterosaponins. Of the five monosaccharide components, three are 6-deoxypyranoses and one is a five-carbon pyranose (xylose). These monosaccharides are unusual as components of natural glycosides, and as a result, the selective protection of a given hydroxy group is more complicated in these monosaccharides.[10] Therefore, the efficient synthesis of the oligosaccharide chain is not a trivial task. As part of our work towards the total synthesis of thornasteroside A, in this paper, we report the efficient synthesis of the pentasaccharide residue.

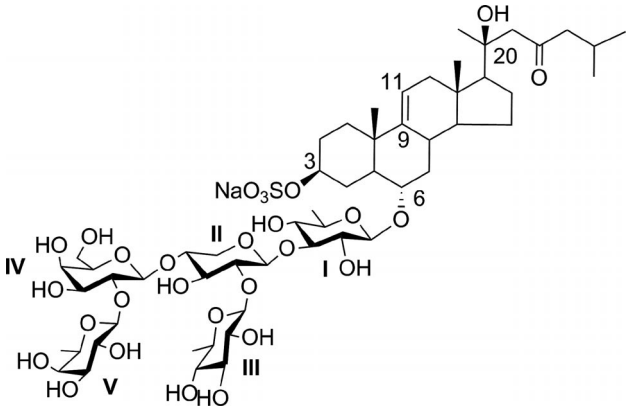

Figure 1. The structure of thornasterside A.

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Results and Discussion

[3+2] Coupling Strategy

Pentasaccharide **1**, with an OMP (4-methoxyphenol) group at the reducing end of the sugar chain, was selected as the target. The OMP glycoside could easily be transformed into an *ortho*-alkynylbenzoate donor, which could be coupled with the aglycon under neutral conditions, catalyzed by a gold(I) complex (e.g., $Ph_3PAuOTf$ or $Ph_3PAuNTf_2$).[11]

Initially, we designed a [3+2] convergent strategy to efficiently construct the pentasaccharide (Figure 2). The key points in this approach were to achieve the stereoselectivity (β-linkage) and regioselectivity (glycosylation of the 4-OH of sugar II) during the glycosylation reaction between acceptor **3** and donor **2**. By using the new method of palladium-mediated β-selective glycosylation,[12,13] a β(1→4) glycosidic bond would be formed with a nonparticipating group at the 2-OH of donor **2** (i.e., in sugar V). The regioselectivity of the glycosylation at the 4-OH of xylopyranose (sugar II) in the presence of the 3-OH would be achieved because of the reactivity difference between the 4-OH and the 3-OH groups (4-OH > 3-OH).[14]

Trisaccharide acceptor **3** and disaccharide donor **2** could be constructed using monosaccharide building blocks **4**–**6** and **7**–**8**, respectively. As all the glycosidic bonds in pentasaccharide **1** have the β configuration, the required monosaccharide building blocks **4**–**8** were all equipped with participating benzoyl or levulinoyl (Lev) groups at the 2-OH.

Synthesis of Trisaccharide Acceptor 3

The synthesis of trisaccharide acceptor **3** is shown in Scheme 1. The glycosylation between building blocks **4** and **5** promoted by TMSOTf gave disaccharide **10** in a low yield of 47%. We rationalized that the low reactivity of the 3-OH group of **4**, resulting from the presence of two neighboring electron-withdrawing benzoyl groups, should be responsible for the low coupling yield. Therefore, the more reactive benzylated acceptor **9** was selected. To our delight, the glycosylation between **5** and **9** promoted by TMSOTf gave disaccharide **11** in a satisfactory 82% yield. Removal of the Lev group from **11** gave **12**. As expected, coupling of monosaccharide donor **6** with acceptor **12** occurred smoothly to give trisaccharide **13** in 78% yield.

We tried to remove the two acetyl groups from **13** to obtain diol **3**, which would serve as the acceptor in the regioselective coupling with disaccharide donor **2**. The reaction was attempted under mildly acidic condition [$CH_3COCl/CH_3OH/CH_2Cl_2$ (1:25:25)] so that the benzoyl groups in **13** would not be affected during the deacetylation. When **13** was treated under these conditions at room temperature for 8 h, only 40% of the intended di-deacetylated product (i.e., **3**) was formed, along with more than 50% of the mono-deacetylated product (i.e., **14**). Obviously, unexpected product **14** would be a more suitable acceptor than **3** in the next glycosylation reaction. To our delight, under milder conditions [$CH_3COCl/CH_3OH/CH_2Cl_2$ (1:50:50)], **14** could be obtained cleanly in an excellent yield of 82%. The structure of **14** was confirmed by careful interpretation of ^1H, ^1H–^1H COSY, HMQC, and HMBC spectra.

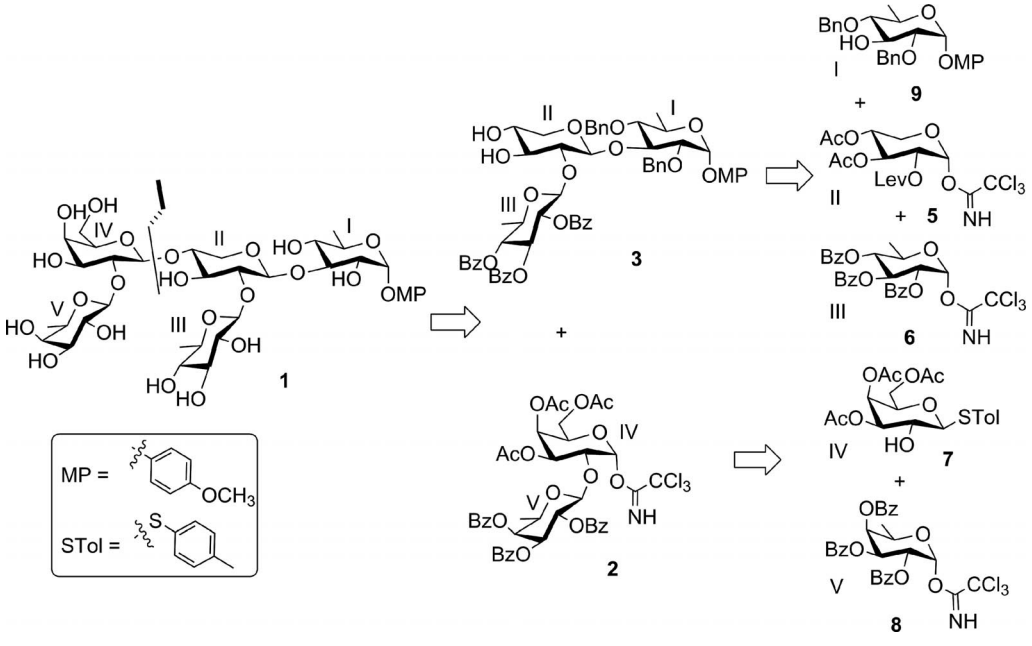
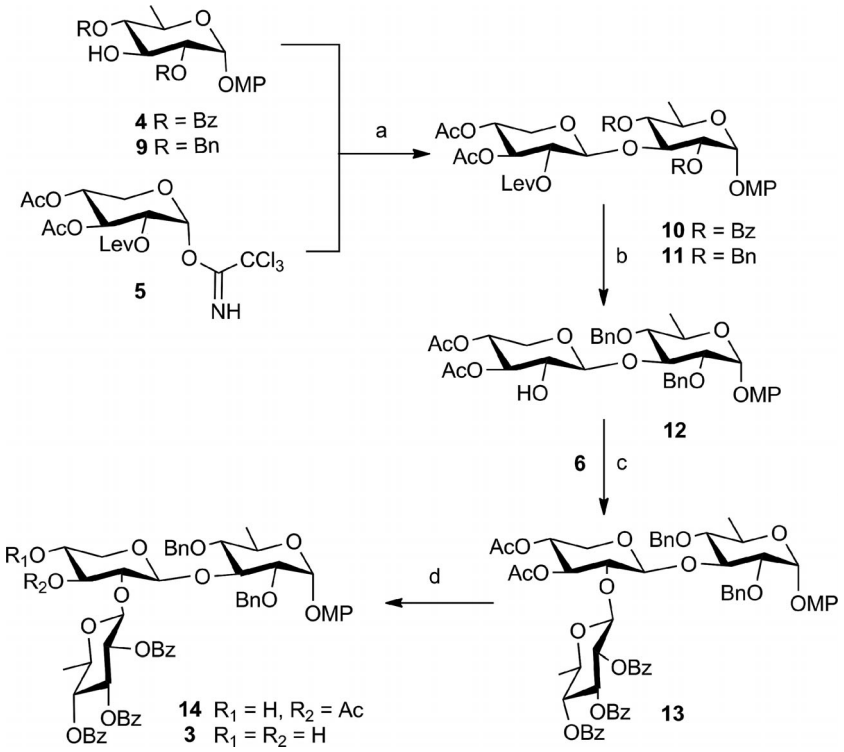


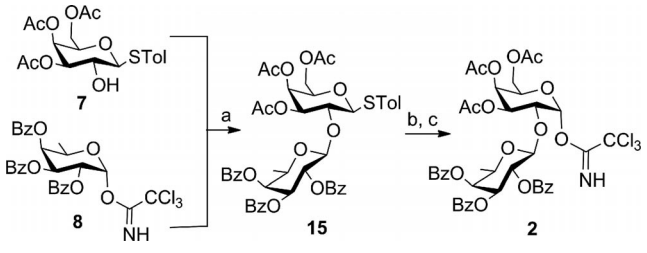
Figure 2. [3+2] coupling strategy.



Scheme 1. Synthesis of trisaccharide acceptors **3** and **14**. Reagents and conditions: a) molecular sieves (4 Å), TMSOTf (TMS = trimethylsilyl; 0.2 equiv.), CH_2Cl_2, –78 °C, 47% for **10**, 82% for **11**; b) $AcOH{\cdot}NH_2NH_2$, CH_3OH/CH_2Cl_2 (1:4), 92%; c) molecular sieves (4 Å), TMSOTf (0.2 equiv.), CH_2Cl_2, –78 °C, 78%; d) $CH_3COCl/CH_3OH/CH_2Cl_2$ (1:50:50), 82% for **14**, 10% for **3**.

Synthesis of Disaccharide Donor 2

The synthetic route to **2** is shown in Scheme 2. Building block **7** was coupled with trichloroacetimidate **8**[15] in the presence of TMSOTf to smoothly give disaccharide **15**. Disaccharide **15** was converted into trichloroacetimidate donor **2** in a two-step procedure in 78% yield. The synthesis of building blocks **4** (**9**), **5**, **6**, and **7** is described in detail in the Supporting Information.



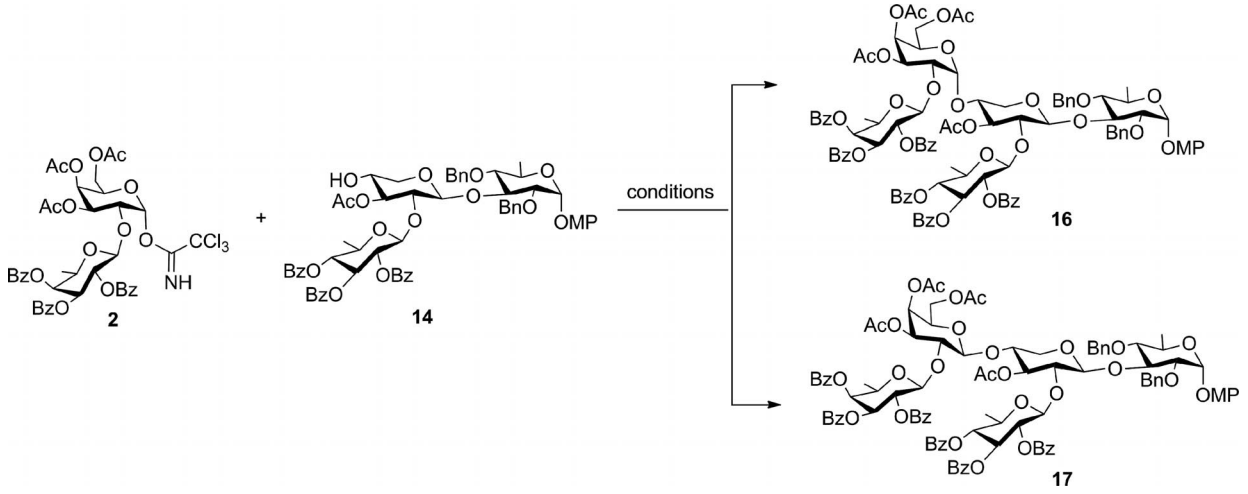
Scheme 2. Synthesis of donor **2**. Reagents and conditions: a) molecular sieves (4 Å), TMSOTf (0.2 equiv.), CH_2Cl_2, –78 °C, 83%; b) NBS (*N*-bromosuccinimide), acetone/H_2O (9:1), 0 °C; c) CCl_3CN, DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), CH_2Cl_2, 78% (2 steps).

Coupling of Disaccharide Donor with Trisaccharide Acceptor

Having synthesized disaccharide donor **2** and trisaccharide acceptor **14**, conditions for the glycosylation between **2** and **14** were investigated. The results are shown in Table 1. Based on Nguyen's method for palladium-mediated β-selective glycosylation in the absence of a traditional C-2-ester neighboring group,[12,13] we used $Pd(CH_3CN)_4(BF_4)_2$ to catalyze the glycosylation between disaccharide donor **2** and trisaccharide acceptor **14**. The reactions were performed with 2 mol-% or 5 mol-% $Pd(CH_3CN)_4(BF_4)_2$ at different temperatures (Table 1, entries 1–8). Unfortunately, in all cases, donor-derived decomposition products were isolated as the major products, and trisaccharide acceptor **14** remained almost unreacted. These results show that this method is not suitable for directing β glycosidic bond formation between **2** and **14**.

When the reaction was conducted under normal conditions [TMSOTf (0.2 equiv.), anhydrous CH_2Cl_2, –78 °C], only the undesired α-linked ($J_{1(IV)\text{-}H,2(IV)\text{-}H}$ = 3.2 Hz) pentasaccharide (i.e., **16**) was obtained in a high 85% yield. Next, we used acetonitrile as the solvent for the glycosylation, expecting a β glycosidic bond between the xylopyranose (sugar II) and galactopyranose (sugar IV) to be formed due to the solvent effect of acetonitrile.[16–18] The expected β-linked pentasaccharide (i.e., **17**) was detected this time, but the yield was quite low (15%), and it was formed along with 10% of the α-linked pentasaccharide (i.e., **16**). Further attempts to vary the solvents and temperatures in the TMSOTf-catalyzed glycosylation did not result in improved selectivity and yield (See Table S1 in the Supporting Information).

Table 1. Glycosylation of **14** and **2**[a] promoted by $Pd(CH_3CN)_4(BF_4)_2$.



Entry	CH_2Cl_2/CH_3CN (v/v)	Amount [mol-%] of $Pd(CH_3CN)_4(BF_4)_2$	*T* [°C]	Yield of **16**	Yield of **17**
1	1:0	2	–78	_[b]	_[b]
2	1:0	2	0	_[b]	_[b]
3	1:0	2	25	_[b]	_[b]
4	1:0	5	–78	_[b]	_[b]
5	1:0	5	0	_[b]	_[b]
6	0:1	5	–40	_[b]	_[b]
7	0:1	5	0	_[b]	_[b]
8	1:1	5	0	_[b]	_[b]

[a] In all the entries, 1.2 equiv. donor **2** and 1.0 equiv. acceptor **14** were used. [b] Undefined products with unreacted **14**, as judged by TLC.

[3+1+1] Coupling Strategy

After the construction of the pentasaccharide by the [3+2] approach with satisfactory stereoselectivity and yield had failed, we then turned our attention to a [3+1+1] strategy (Figure 3). Building block **18**, equipped with a participating Lev group at the 2-position ensured a β configuration for the glycosidic bond formed in the glycosylation between **14** and **18**. The Lev group could be selectively removed to give a tetrasaccharide acceptor, which would be coupled with building block **8** to give the desired pentasaccharide (i.e., **17**).

We conducted glycosylation trials between trichloroacetimidate donor **18** and acceptor **14** to give tetrasaccharide **17**. The proportions of donor/acceptor were varied, as was the amount of TMSOTf, as shown in Table 2. The desired tetrasaccharide (i.e., **19**) was not detected when the reaction was conducted with 1.2 equiv. of donor **18** and catalyzed by 0.2 equiv. of TMSOTf (Table 2, entry 1). When the amount of donor **18** was increased to 4.0 equiv., the desired tetrasaccharide **19** was formed in an isolated yield of 27%. To enhance the yield, a "reverse addition" approach was tried, but no improvement was observed over the normal addition method (Table 2, entry 3). Further increasing the amount of donor **18** to 6.0 equiv. led to a slight improvement in the yield (to 30%, Table 2, entry 4). Further study showed that the amount of TMSOTf had a great impact on the glycosylation. When the amount of TMSOTf was increased to more

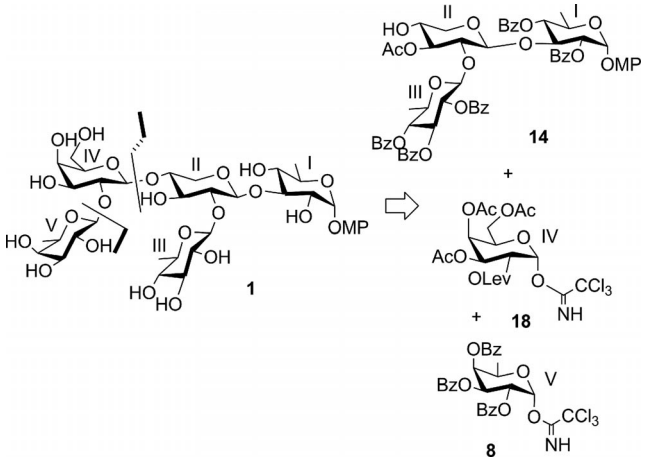
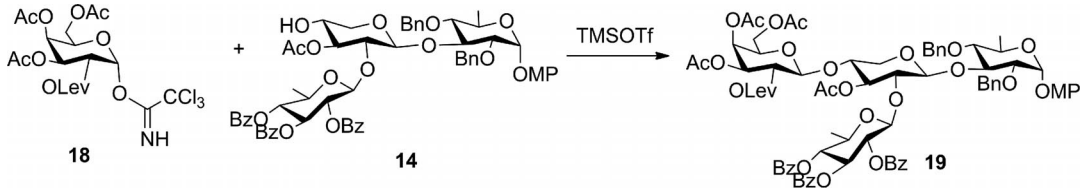


Figure 3. [3+1+1] coupling strategy.

than 1.0 equiv. (with respect to the amount of acceptor **14**), the glycosylation proceeded smoothly to give the desired product. For instance, the glycosylation between **18** (1.2 equiv.) and **14** (1.0 equiv.) activated by 1.0 equiv. of TMSOTf gave tetrasaccharide **19** in a good 68% yield (Table 2, entry 5).

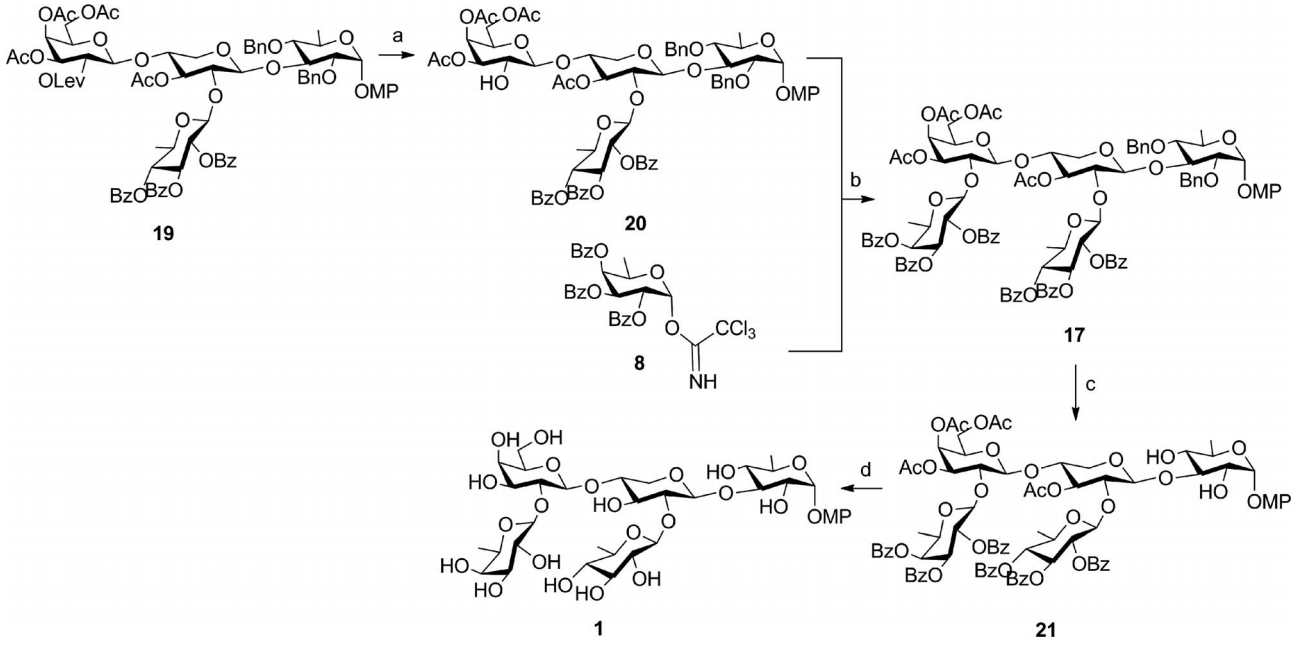
Having synthesized **19**, the Lev group was removed to smoothly give tetrasaccharide acceptor **20** (Scheme 3). TMSOTf-mediated coupling of **20** with monosaccharide **8** gave pentasaccharide **17** in a satisfactory 83% yield. Global

Table 2. Glycosylation of **14** with monosaccharide donor **19**.[a,b]



Entry	Donor **18** (equiv.)	TMSOTf (equiv.)	Yield of **19** [%]
1	1.2	0.2	0
2	4.0	0.2	27
3	4.0[c]	0.2	25
4	6.0	0.2	30
5	1.2	1.0	68
6	4.0	1.0	72
7	4.0	2.0	71

[a] Molar equivalents of the donor and promoters are based on the amount of acceptor (1.0 equiv.). [b] All the reactions were conducted in dry CH_2Cl_2 in the presence of molecular sieves (4 Å) at –78 °C. [c] Reverse addition approach.



Scheme 3. Synthesis of the pentasaccharide by a [3+1+1] strategy. Reagents and conditions: a) $AcOH{\cdot}N_2H_4$, CH_3OH/CH_2Cl_2 (1:4), 93%; b) molecular sieves (4 Å), TMSOTf, CH_2Cl_2, –78 °C, 83%. c) $Pd(OH)_2/C$, H_2, CH_3OH/EtOAc (1:1), 98%; d) CH_3ONa, CH_3OH, 88%.

deprotection of pentasaccharide **17** was achieved by hydrogenolysis of the benzyl ethers over $Pd(OH)_2/C$, followed by deacylation to remove the benzoyl and acetyl groups and give target pentasaccharide **1**. The structure of **1** was confirmed by NMR spectroscopy. The five anomeric proton signals in the ^1H NMR spectrum appear at δ = 5.53 (d, J = 3.75 Hz, H-1^I), 4.75 (d, J = 7.33 Hz), 4.74 (d, J = 7.94 Hz), 4.63 (d, J = 7.33 Hz), and 4.61 (d, J = 7.33 Hz) ppm, and the five anomeric carbon signals appear at δ = 104.03, 103.81, 102.77, 100.71, 97.36 (C-1^I) ppm.

Conclusion

In summary, we have accomplished the first synthesis of the pentasaccharide of thornasteroside A, which is the first asterosaponin isolated from *Acanthaster planci* L. in 1978. Initially, a [3+2] convergent strategy was attempted, but the β-glycosidic bond between the xylopyranose (sugar II) and galactopyranose (sugar IV) could only be constructed with a low stereoselectivity and in a low 15% yield. Subsequently, a [3+1+1] strategy was adopted. Galactopyranosyl donor **18**, equipped with a neighboring participating Lev group at the 2-position, was first coupled with a trisaccharide acceptor to construct the β-glycosidic bond smoothly. Then the Lev group was selectively removed, and subsequent glycosylation with a perbenzoylated D-fucopyranosyl Schmidt donor gave the desired pentasaccharide efficiently. The work reported here significantly facilitates the total synthesis of the whole thornasteroside A molecule and also of other structurally related oligosaccharides isolated from starfish and other marine organisms.

Experimental Section

General Methods: All chemicals used were reagent grade. Chemicals were used as supplied except where noted. Dichloromethane and methanol were heated at reflux over calcium hydride and distilled prior to use. Acetonitrile was heated at reflux over phosphorus pentoxide and distilled prior to use. Analytical thin-layer chromatography was performed on silica gel HF_{254}, and plates were visualized by charring with H_2SO_4 (5% v/v in CH_3OH) or by UV detection. Column chromatography was conducted by elution of a column of silica gel (200–300 mesh) with EtOAc/petroleum ether (b.p. 60–90 °C) as the eluent. ^1H NMR spectra were obtained with a Bruker 400 (400 MHz) instrument, and chemical shifts are reported on the δ scale. $CHCl_3$ (δ = 7.26 ppm) or TMS (δ = 0.00 ppm) were used as internal references. ^{13}C NMR spectra were obtained with a Bruker 400 (100 MHz) instrument, and chemical shifts are reported on the δ scale. $CDCl_3$ (δ = 77.0 ppm) or TMS (δ = 0.00 ppm) were used as internal references. COSY, HMQC, and HMBC experiments were routinely used to definitively assign the signals of ^1H NMR and ^{13}C NMR spectra. Optical rotations were recorded with a Perkin–Elmer 343 polarimeter.

2,3,4-Tri-*O*-benzoyl-6-deoxy-β-D-galactopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-galactopyranosyl Trichloroacetimidate (2): NBS (0.99 g, 5.58 mmol) was added to a stirred solution of compound **15** (1.62 g, 1.86 mmol) in acetone/H_2O (9:1, 40 mL), and the mixture was stirred at 0 °C for 1 h. After this time, TLC (petroleum ether/EtOAc, 3:1) showed complete conversion of the starting material into a more slowly moving component. The mixture was dissolved in EtOAc (200 mL) and washed with $NaHCO_3$ (10% aq.; 20 mL). The organic phase was dried with Na_2SO_4 and then concentrated to a syrup. The crude product was dissolved in dry CH_2Cl_2 (40 mL), and CCl_3CN (0.93 mL, 9.30 mmol) and then DBU (0.13 mL, 0.93 mmol) were added at 0 °C. The solution was stirred at room temperature for 6 h. The solution was concentrated in vacuo, and the crude product was purified by flash chromatography (petroleum ether/EtOAc, 5:1) to give pure compound **2** (1.31 g, 78%) as a white foam. Since glycosyl trichloroacetimidates are not stable, this compound was used for further reaction without detailed characterization.

***p*-Methoxyphenyl 2,3,4-Tri-*O*-benzoyl-6-deoxy-β-D-glucopyranosyl-(1→2)-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-deoxy-α-D-glucopyranoside (3) and *p*-Methoxyphenyl 2,3,4-Tri-*O*-benzoyl-6-deoxy-β-D-glucopyranosyl-(1→2)-3-*O*-acetyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-deoxy-α-D-glucopyranoside (14):** CH_3COCl (0.5 mL) was added to a solution of **13** (1.20 g, 1.07 mmol) in dry CH_3OH/CH_2Cl_2 (25 mL/25 mL). The mixture was stirred at room temperature for 12 h, after which time TLC (petroleum ether/EtOAc, 2:1) indicated that the reaction was complete. The reaction mixture was then neutralized with Et_3N. The mixture was concentrated, passed through a silica gel column (petroleum ether/EtOAc, 3:1) to give **14** (0.95 g, 82%) and **3** (0.11 g, 10%).

Data for **3**: ^1H NMR (400 MHz, $CDCl_3$): δ = 7.95 (t, J = 7.2 Hz, 4 H, ArH), 7.81 (d, J = 7.3 Hz, 2 H, ArH), 7.53 (d, J = 7.3 Hz, 2 H, ArH), 7.47–7.26 (m, 17 H, ArH), 6.92 (d, J = 9.1 Hz, 2 H, ArH), 6.79 (d, J = 9.1 Hz, 2 H, ArH), 5.76 (t, J = 10.0 Hz, 1 H, 3^I-H), 5.51 (dd, J = 9.6, 3.4 Hz, 1 H, 2^I-H), 5.30 (t, J = 9.6 Hz, 1 H, 4^I-H), 5.24 (d, J = 3.5 Hz, 1 H, 1^I-H), 5.21 (d, J = 5.6 Hz, 1 H, 1^{II}-H), 4.90 (d, J = 8.1 Hz, 1 H, 1^{III}-H), 4.87 (d, J = 10.6 Hz, 1 H, CH_2Ph), 4.81 (d, J = 11.2 Hz, 1 H, CH_2Ph), 4.68 (d, J = 11.4 Hz, 1 H, CH_2Ph), 4.58 (d, J = 10.5 Hz, 1 H, CH_2Ph), 4.37 (t, J = 9.2 Hz, 1 H, 3^{III}-H), 4.08 (dd, J = 12.0, 3.8 Hz, 1 H, 5^{II}-H), 3.86 (dd, J = 9.7, 6.3 Hz, 1 H, 2^{II}-H), 3.76 (s, 3 H, OCH_3Ph), 3.67 (t, J = 6.4 Hz, 1 H, 2^{II}-H), 3.59–3.52 (m, 4 H, 5-H, 3^{II}-H, 4^{II}-H, 5^{III}-H), 3.30 (dd, J = 12.0, 7.1 Hz, 1 H, 5^{II}-H), 3.21 (d, J = 4.6 Hz, 1 H, OH), 2.90 (t, J = 9.2 Hz, 1 H, 4^{III}-H), 2.49 (d, J = 5.5 Hz, 1 H, OH), 1.33 (d, J = 6.1 Hz, 3 H, CH_3), 1.17 (d, J = 6.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.87, 165.38, 165.36, 154.91, 150.71, 138.05, 138.00, 133.44, 133.22, 129.77, 129.74, 129.68, 129.22, 129.01, 128.79, 128.66, 128.54, 128.45, 128.37, 128.32, 128.28, 128.16, 127.80, 117.92, 114.48, 100.89, 95.41, 81.74, 80.46, 79.57, 77.79, 74.63, 73.50, 72.83, 72.77, 72.21, 70.72, 69.54, 67.01, 63.65, 55.60, 17.98, 17.70 ppm. HRMS (ESI): calcd. for $C_{59}H_{60}O_{17}Na$ [M + Na]$^+$ 1063.3720; found 1063.3722.

Data for **14**: $[\alpha]_D^{20}$ = +25.1 (c = 0.5, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.95–7.79 (m, 6 H, ArH), 7.52–7.50 (m, 2 H, ArH), 7.47–7.23 (m, 17 H, ArH), 6.92 (d, J = 9.1 Hz, 2 H, ArH), 6.80 (d, J = 9.1 Hz, 2 H, ArH), 5.76 (t, J = 9.6 Hz, 1 H, 3^I-H), 5.46 (dd, J = 9.6, 3.3 Hz, 1 H, 2^I-H), 5.32 (d, J = 3.3 Hz, 1 H, 1^I-H), 5.29 (t, J = 9.6 Hz, 1 H, 3^{II}-H), 5.22 (d, J = 7.2 Hz, 1 H, 1^{II}-H), 5.15–5.04 (m, 2 H, 1^{III}-H, 3^{II}-H), 4.96 (dd, J = 16.1, 9.5 Hz, 2 H, CH_2Ph), 4.82–4.80 (m, 1 H, 4^{II}-H), 4.75 (d, J = 11.4 Hz, 1 H, CH_2Ph), 4.63 (d, J = 10.9 Hz, 1 H, CH_2Ph), 4.45 (t, J = 9.3 Hz, 1 H, 3^{III}-H), 4.05 (dd, J = 11.6, 3.6 Hz, 1 H, 5^{II}-H), 4.00–3.88 (m, 2 H, 2^{II}-H, 5^{III}-H), 3.74 (s, 3 H, OCH_3Ph), 3.73–3.65 (m, 2 H, 5^I-H, 4^{II}-H), 3.35 (dd, J = 11.6, 6.4 Hz, 1 H, 5^{II}-H), 3.10 (t, J = 9.4 Hz, 1 H), 2.72 (1 H, OH), 2.06 (s, 3 H, OAc), 1.31 (d, J = 4.8 Hz, 3 H, CH_3), 1.21 (d, J = 5.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.26, 165.93, 165.40, 165.30, 154.95, 150.89, 138.14, 137.98, 133.39, 133.18, 129.76, 129.71, 129.44, 129.11, 128.89, 128.64, 128.57, 128.45, 128.37, 128.33, 128.28, 128.15, 127.82, 117.97, 114.53, 100.70, 100.21, 95.69, 82.27, 81.02, 75.38, 74.78, 73.90, 73.74, 73.18, 72.91, 72.56, 70.59, 68.16, 67.11, 63.11, 55.63, 21.14, 17.98, 17.65 ppm. HRMS (ESI): calcd. for $C_{61}H_{62}O_{18}Na$ [M + Na]$^+$ 1105.3833; found 1105.3804.

***p*-Methoxyphenyl 3,4-Di-*O*-acetyl-2-*O*-levulinoyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-deoxy-α-D-glucopyranoside (11):** A mixture of compound **9** (1.17 g, 2.59 mmol), compound **5** (1.36 g, 3.11 mmol), and molecular sieves (4 Å; 400 mg) in dry CH_2Cl_2 (50 mL) was stirred under nitrogen for 30 min. The mixture was cooled to –78 °C, and TMSOTf (94 μL, 0.52 mmol) was added. The mixture was stirred for 45 min, after which time TLC showed complete consumption of acceptor **9**. The mixture was filtered through a pad of Celite, and the filtrate was washed successively with $NaHCO_3$ (10 mL) and brine (20 mL). The organic phase was separated and dried (Na_2SO_4), and the solvents were evaporated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 3:1) to give pure disaccharide **11** (1.62 g, 82%) as a white foam. $[\alpha]_D^{20}$ = –67.8 (c = 0.80, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.26 (m, 10 H, ArH), 6.88 (d, J = 7.8 Hz, 2 H, ArH), 6.79 (d, J = 7.8 Hz, 2 H, ArH), 5.23 (d, J = 9.2 Hz, 1 H, 3^{II}-H), 5.18 (d, J = 3.5 Hz, 1 H, 1^I-H), 5.15 (d, J = 7.6 Hz, 1 H, 1^{II}-H), 5.12–5.06 (m, 1 H, 5^I-H), 5.03–5.00 (m, 1 H, 4^I-H), 4.98 (d, J = 10.8, Hz, 1 H, CH_2Ph), 4.79 (d, J = 11.5 Hz, 1 H, CH_2Ph), 4.59 (d, J = 10.8, Hz, 1 H, CH_2Ph), 4.57 (d, J = 11.6 Hz, 1 H, CH_2Ph), 4.41 (t, J = 9.2 Hz, 1 H, 2^{II}-H), 4.09 (t, J = 9.2 Hz, 1 H, 4^I-H), 3.85 (dd, J = 9.6, 6.2 Hz, 1 H, 5^{II}-H), 3.76 (s, 3 H, OCH_3Ph), 3.67 (dd, J = 9.6, 3.5 Hz, 1 H, 2^I-H), 3.31 (t, J = 10.0 Hz, 1 H, 5^{II}-H), 3.14 (t, J = 9.2 Hz, 1 H, 3^I-H), 2.74–2.70 (m, 2 H, $COCH_2CH_2$), 2.59–2.55 (m, 2 H, $COCH_2CH_2$), 2.18 (s, 3 H, OAc), 2.10 (s, 3 H, OAc), 2.05 (s, 3 H, OAc), 1.16 (d, J = 6.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.90, 171.40, 170.34, 169.92, 154.88, 150.52, 138.08, 137.75, 128.61, 128.51, 128.30, 128.10, 127.73, 117.93, 114.41, 100.75 (C-1^{II}), 95.45 (C-1^I), 81.48, 80.72, 78.16, 75.23, 73.32, 72.06, 69.23, 67.12, 62.35, 55.55, 37.53, 29.73, 27.84, 20.75, 20.73, 17.83 ppm. HRMS (ESI): calcd. for $C_{41}H_{48}O_{14}Na$ [M + Na]$^+$ 787.2942; found 787.2936.

***p*-Methoxyphenyl 3,4-Di-*O*-acetyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-deoxy-α-D-glucopyranoside (12):** Compound **11** (1.62 g, 2.12 mmol) was dissolved in dry CH_3OH/CH_2Cl_2 (10 mL/40 mL), and $AcOH{\cdot}NH_2NH_2$ (1.95 g, 21.2 mmol) was added. The reaction mixture was stirred overnight at room temperature, then the mixture was concentrated in vacuo. The residue was purified by chromatography (petroleum ether/EtOAc, 5:1) to give pure compound **12** (1.15 g, 92%) as a white foam. $[\alpha]_D^{20}$ = –36.8 (*c* = 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.26 (m, 10 H, ArH), 6.92 (d, *J* = 8.8 Hz, 2 H, ArH), 6.80 (d, *J* = 8.8 Hz, 2 H, ArH), 5.23 (d, *J* = 3.3 Hz, 1 H, 1^{I}-H), 5.11 (t, *J* = 9.5 Hz, 1 H, 3^{II}-H), 5.03–4.91 (m, 2 H, 4^{II}-H, $PhCH_2$), 4.72 (d, *J* = 7.2 Hz, 1 H, 1^{II}-H), 4.69–4.58 (m, 3 H, $PhCH_2$), 4.37 (t, *J* = 9.4 Hz, 1 H, 3^{I}-H), 3.97 (dd, *J* = 11.5, 5.6 Hz, 1 H, 5^{II}-H), 3.91–3.83 (m, 1 H, 5^{I}-H), 3.80 (s, 1 H, OH), 3.77 (s, 3 H, $PhOCH_3$), 3.66 (dd, *J* = 9.8, 3.4 Hz, 1 H, 2^{I}-H), 3.55 (t, *J* = 8.3 Hz, 1 H, 2^{II}-H), 3.17 (m, 2 H, 4^{I}-H, 5^{II}-H), 2.10 (s, 3 H, $COCH_3$), 2.06 (s, 3 H, $COCH_3$), 1.21 (d, *J* = 6.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.54, 170.10, 155.04, 150.68, 138.21, 136.74, 128.69, 128.41, 128.35, 127.90, 127.72, 117.82, 114.55, 105.42 (C-1^{II}), 95.15 (C-1^{I}), 83.02, 80.95, 79.02, 75.18, 73.85, 73.61, 72.79, 69.03, 67.37, 63.01, 55.63, 20.91, 20.76, 17.82 ppm. HRMS (ESI): calcd. for $C_{36}H_{42}O_{12}Na$ [M + Na]$^+$ 689.2574; found 689.2572.

***p*-Methoxyphenyl 2,3,4-Tri-*O*-benzoyl-6-deoxy-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-acetyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-deoxy-α-D-glucopyranoside (13):** A mixture of compound **12** (1.02 g, 1.53 mmol), compound **6** (1.14 g, 1.84 mmol), and molecular sieves (4 Å; 200 mg) in dry CH_2Cl_2 (30 mL) was stirred under nitrogen for 30 min. The mixture was cooled to 0 °C, and TMSOTf (56 μL, 0.31 mmol) was added. The mixture was stirred for 30 min, after which time TLC showed complete consumption of acceptor **12**. Then, the mixture was filtered through a pad of Celite, and the filtrate was washed successively with $NaHCO_3$ (5 mL) and brine (10 mL). The organic phase was separated and dried with Na_2SO_4, and the solvents were evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether/EtOAc, 3:1) to give pure compound **13** (1.29 g, 78%) as a white foam. $[\alpha]_D^{20}$ = +8.2 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96–7.94 (m, 2 H, ArH), 7.85–7.83 (m, 2 H, ArH), 7.79–7.77 (m, 2 H, ArH), 7.55–7.22 (m, 19 H, ArH), 6.93 (d, *J* = 8.0 Hz, 2 H, ArH), 6.81 (d, *J* = 8.0 Hz, 2 H, ArH), 5.78 (t, *J* = 9.7 Hz, 1 H, 3^{I}-H), 5.49 (dd, *J* = 9.6, 3.4 Hz, 1 H, 2^{II}-H), 5.34 (t, *J* = 9.6 Hz, 1 H, 4^{I}-H), 5.28 (d, *J* = 3.2 Hz, 1 H, 1^{I}-H), 5.25 (d, *J* = 6.4 Hz, 1 H, 1^{II}-H), 5.10–4.99 (m, 2 H, 1^{III}-H, 3^{II}-H), 4.93 (dd, *J* = 16.1, 9.5 Hz, 2 H, CH_2Ph), 4.84–4.82 (m, 1 H, 4^{II}-H), 4.70 (d, *J* = 11.1 Hz, 1 H, CH_2Ph), 4.61 (d, *J* = 10.6 Hz, 1 H, CH_2Ph), 4.42 (t, *J* = 9.1 Hz, 1 H, 3^{III}-H), 4.03 (dd, *J* = 11.8, 5.0 Hz, 1 H, 5^{II}-H), 3.96–3.83 (m, 2 H, 2^{II}-H, 5^{III}-H), 3.77 (s, 3 H, OCH_3Ph), 3.76–3.69 (m, 2 H, 5^{I}-H, 2^{III}-H), 3.32 (dd, *J* = 11.8, 8.8 Hz, 1 H, 5^{II}-H), 3.11 (t, *J* = 9.3 Hz, 1 H, 4^{III}-H), 1.92 (s, 3 H, OAc), 1.91 (s, 3 H, OAc), 1.38 (d, *J* = 4.8 Hz, 3 H, CH_3), 1.21 (d, *J* = 5.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.23, 169.37, 165.91, 165.42, 165.00, 154.85, 150.70, 138.15, 137.95, 133.38, 133.13, 129.73, 129.64, 129.40, 129.02, 128.86, 128.78, 128.62, 128.48, 128.41, 128.34, 128.22, 128.11, 127.81, 117.74, 114.43, 101.29, 100.84, 95.63, 81.92, 80.97, 77.95, 77.70, 75.01, 73.73, 73.60, 73.04, 72.92, 72.52, 70.49, 69.22, 66.90, 61.67, 55.57, 20.83, 20.65, 17.92, 17.75 ppm. HRMS (ESI): calcd. for $C_{63}H_{64}O_{19}Na$ [M + Na]$^+$ 1147.3939; found 1147.3936.

***p*-Tolyl 2,3,4-Tri-*O*-benzoyl-6-deoxy-β-D-galactopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-1-thio-β-D-galactopyranoside (15):** A mixture of compound **7** (1.21 g, 2.93 mmol), compound **8** (2.18 g, 3.52 mmol), and molecular sieves (4 Å; 400 mg) in dry CH_2Cl_2 (60 mL) was stirred under nitrogen for 30 min. The mixture was cooled to 0 °C, and TMSOTf (104 μL, 0.58 mmol) was added. The mixture was stirred for 30 min, after which time TLC showed complete consumption of acceptor **7**. The mixture was filtered through a pad of Celite, and the filtrate was washed successively with $NaHCO_3$ (10 mL) and brine (20 mL). The organic phase was separated and dried with Na_2SO_4, and the solvents were evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether/EtOAc, 3:1) to give pure compound **15** (2.16 g, 83%) as a white foam. $[\alpha]_D^{20}$ = +102 (*c* = 1.20, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 7.3 Hz, 2 H, ArH), 7.84 (d, *J* = 7.3 Hz, 2 H, ArH), 7.79 (d, *J* = 7.3 Hz, 2 H, ArH), 7.61 (t, *J* = 7.4 Hz, 1 H, ArH), 7.53–7.34 (m, 8 H, ArH), 7.30–7.21 (m, 3 H, ArH), 7.16 (d, *J* = 8.0 Hz, 2 H, ArH), 5.77–5.65 (m, 2 H, 2^{II}-H, 4^{II}-H), 5.50 (dd, *J* = 10.4, 3.3 Hz, 1 H, 3^{II}-H), 5.31 (d, *J* = 3.0 Hz, 1 H, 4^{I}-H), 5.14 (d, *J* = 7.8 Hz, 1 H, 1^{II}-H), 4.93 (dd, *J* = 9.8, 3.2 Hz, 1 H, 5^{I}-H), 4.70 (d, *J* = 9.6 Hz, 1 H, 1^{I}-H), 4.17–4.08 (m, 3 H, 2^{I}-H, 6^{I}-H, 5^{II}-H), 4.04 (dd, *J* = 11.3, 6.3 Hz, 1 H, 6^{I}-H), 3.82 (t, *J* = 6.6 Hz, 1 H, 3^{I}-H), 2.37 (s, 3 H, -CH_3Ph), 1.99 (s, 3 H, OAc), 1.96 (s, 3 H, OAc), 1.86 (s, 3 H, OAc), 1.38 (d, *J* = 6.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.33, 170.02, 169.57, 165.90, 165.73, 165.10, 138.04, 133.40, 133.21, 130.01, 129.70, 129.56, 129.50, 129.41, 129.28, 129.21, 128.77, 128.53, 128.31, 128.25, 100.22, 87.14, 74.00, 72.48, 72.31, 70.86, 70.61, 69.88, 67.35, 61.51, 29.65, 21.14, 20.60, 20.51, 20.47, 16.30 ppm. HRMS (ESI): calcd. for $C_{46}H_{46}O_{15}SNa$ [M + Na]$^+$ 893.2455; found 893.2457.

***p*-Methoxyphenyl 2,3,4-Tri-*O*-benzoyl-6-deoxy-β-D-galactopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-galactopyranosyl-(1→4)-[2,3,4-tri-*O*-benzoyl-6-deoxy-β-D-glucopyranosyl-(1→2)]-3-*O*-acetyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-deoxy-α-D-glucopyranoside (16):** A mixture of compound **14** (0.23 g, 0.21 mmol), compound **2** (0.22 g, 0.25 mmol), and molecular sieves (4 Å; 200 mg) in dry CH_2Cl_2 (20 mL) was stirred under nitrogen for 30 min. The mixture was cooled to –78 °C, and TMSOTf (7.6 μL, 0.042 mmol) was added. The mixture was stirred for 30 min, after which time TLC showed complete consumption of acceptor **14**. The mixture was filtered through a pad of Celite, and the filtrate was washed successively with $NaHCO_3$ (5 mL) and brine (10 mL). The organic phase was separated and dried with Na_2SO_4, and the solvents were evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether/EtOAc, 4:1) to give pure compound **16** (0.33 g, 85%) as a white foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 7.2 Hz, 2 H, ArH), 8.00–7.95 (m, 2 H, ArH), 7.94–7.84 (m, 5 H, ArH), 7.84–7.79 (m, 4 H, ArH), 7.78–7.73 (m, 2 H, ArH), 7.68 (t, *J* = 7.8 Hz, 1 H, ArH), 7.60–7.46 (m, 4 H, ArH), 7.42–7.40 (m, 4 H, ArH), 7.38–7.35 (m, 7 H, ArH), 7.34–7.18 (m, 9 H, ArH), 6.92 (d, *J* = 9.2 Hz, 2 H, ArH), 6.80 (d, *J* = 9.2 Hz, 2 H, ArH), 5.89 (t, *J* = 9.7 Hz, 1 H), 5.77–5.65 (m, 2 H), 5.60–5.46 (m, 2 H), 5.37 (t, *J* = 9.6 Hz, 1 H), 5.28 (d, *J* = 3.6 Hz, 1^{I}-H), 5.24 (d, *J* = 3.2 Hz, 1^{IV}-H), 5.23–5.20 (m, 2 H), 5.19 (d, *J* = 7.5 Hz, 1 H, 1^{II}-H), 5.04 (d, *J* = 8.0 Hz, 1^{V}-H), 5.00–4.95 (m, 2 H), 4.93 (d, *J* = 10.8 Hz, 1 H, CH_2Ph), 4.84 (d, *J* = 7.9 Hz, 1 H, 1^{III}-H), 4.72 (d, *J* = 11.0 Hz, 1 H, CH_2Ph), 4.53–4.37 (m, 2 H), 4.21–4.04 (m, 3 H), 4.03–3.91 (m, 2 H), 3.91–3.78 (m, 3 H), 3.77 (s, 3 H, CH_3Ph), 3.69 (dd, *J* = 9.6, 7.6 Hz, 1 H), 3.57 (dd, *J* = 9.6, 6.2 Hz, 1 H), 3.28 (t, *J* = 9.2 Hz, 1 H), 3.01 (t, *J* = 9.2 Hz, 1 H), 2.07 (s, 3 H, OAc), 2.06 (s, 3 H, OAc), 2.01 (s, 3 H, OAc), 1.34 (d, *J* = 6.1 Hz, 3 H, CH_3), 1.26 (d, *J* = 6.2 Hz, 3 H, CH_3), 1.21 (s, 3 H, OAc), 1.15 (d, *J* = 6.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.46, 169.83, 169.70, 169.25, 166.11, 165.73, 165.63, 165.49, 165.13, 164.73, 154.92, 150.87, 138.48, 138.07, 133.87, 133.43, 133.32, 133.18, 130.05, 129.76, 129.72, 129.47, 129.29, 129.20, 128.89, 128.85, 128.72, 128.69, 128.49, 128.42, 128.32, 128.28,

128.21, 128.13, 128.04, 127.56, 118.10, 102.76 (C-1^{III}), 101.02 (C-1^{II}, C-1^{V}), 98.82 (C-1^{IV}), 95.79 (C-1^{I}), 81.85, 81.07, 78.89, 78.14, 74.72, 73.98, 73.87, 73.75, 73.07, 72.55, 72.11, 70.97, 70.40, 69.69, 69.34, 68.31, 67.85, 66.93, 66.77, 63.95, 61.55, 55.63, 20.82, 20.73, 20.62, 19.52, 18.01, 17.91, 16.45 ppm. HRMS (MALDI-DHB): calcd. for $C_{100}H_{100}O_{33}Na$ $[M + Na]^+$ 1851.6044; found 1851.6039.

***p*-Methoxyphenyl 2,3,4-Tri-*O*-benzoyl-6-deoxy-β-D-galactopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-β-D-galactopyranosyl-(1→4)-[2,3,4-tri-*O*-benzoyl-6-deoxy-β-D-glucopyranosyl-(1→2)]-3-*O*-acetyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-deoxy-α-D-glucopyranoside (17):** A mixture of compound **20** (102 mg, 0.074 mmol), compound **8** (60 mg, 0.097 mmol), and molecular sieves (4 Å; 30 mg) in dry CH_2Cl_2 (15 mL) was stirred under nitrogen for 30 min. The mixture was cooled to –78 °C, and TMSOTf (17.6 μL, 0.097 mmol) was added. The mixture was stirred for 30 min, after which time TLC showed complete consumption of acceptor **20**. The mixture was filtered through a pad of Celite, and the filtrate was washed successively with $NaHCO_3$ (5 mL) and brine (10 mL). The organic phase was separated and dried with Na_2SO_4, and the solvents were evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether/EtOAc, 3:1) to give pure compound **17** (113 mg, 83%) as a white foam. $[\alpha]_D^{20}$ = –12.3 (*c* = 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 7.2 Hz, 2 H, ArH), 7.98–7.91 (m, 6 H, ArH), 7.79 (t, *J* = 7.4 Hz, 4 H, ArH), 7.54 (t, *J* = 6.6 Hz, 4 H, ArH), 7.49–7.46 (m, 5 H, ArH), 7.43–7.40 (m, 6 H, ArH), 7.39–7.34 (m, 10 H, ArH), 7.23–7.20 (m, 3 H), 6.91 (d, *J* = 9.1 Hz, 2 H, ArH), 6.80 (d, *J* = 9.1 Hz, 2 H, ArH), 5.86 (t, *J* = 9.7 Hz, 1 H), 5.63–5.54 (m, 3 H), 5.45 (d, *J* = 9.6 Hz, 1 H), 5.38 (dd, *J* = 10.4, 3.4 Hz, 1 H), 5.34 (d, *J* = 3.9 Hz, 1 H, 1^{I}-H), 5.32–5.30 (m, 1 H), 5.28 (d, *J* = 7.6 Hz, 1 H, 1^{IV}-H), 5.20 (d, *J* = 3.3 Hz, 1 H), 5.10–5.05 (m, 2 H), 5.03 (d, *J* = 7.9 Hz, 1 H, 1^{II}-H), 4.98 (d, *J* = 7.9 Hz, 1 H, 1^{V}-H), 4.88 (d, *J* = 10.4 Hz, 1 H, CH_2Ph), 4.81 (dd, *J* = 10.4, 3.4 Hz, 1 H), 4.66 (apparent d, *J* = 11.1 Hz, 2 H, CH_2Ph), 4.45 (t, *J* = 9.0 Hz, 1 H), 4.37 (d, *J* = 7.6 Hz, 1 H, 1^{III}-H), 4.21–4.14 (m, 1 H), 4.02 (dd, *J* = 11.0, 6.2 Hz, 1 H), 3.98–3.87 (m, 3 H), 3.85–3.79 (m, 4 H), 3.77 (s, 3 H, CH_3Ph), 3.73 (d, *J* = 7.2 Hz, 2 H), 3.33 (t, *J* = 9.2 Hz, 1 H), 3.17 (t, *J* = 9.2 Hz, 1 H), 1.99 (s, 3 H, OAc), 1.98 (s, 3 H, OAc), 1.71 (s, 3 H, OAc), 1.65 (s, 3 H, OAc), 1.42 (d, *J* = 6.1 Hz, 3 H, CH_3), 1.22 (d, *J* = 6.2 Hz, 3 H, CH_3), 1.15 (d, *J* = 6.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.30, 170.04, 169.80, 169.39, 165.97, 165.88, 165.46, 165.41, 165.04, 165.01, 154.89, 150.90, 138.51, 137.98, 133.42, 133.38, 133.19, 133.15, 133.08, 130.11, 129.88, 129.82, 129.76, 129.71, 129.59, 129.53, 129.18, 129.12, 128.98, 128.83, 128.65, 128.62, 128.44, 128.38, 128.32, 128.23, 128.20, 127.73, 117.99, 114.49, 101.73, 101.41, 101.05, 100.76, 95.61, 81.80, 81.26, 78.11, 77.61, 75.49, 74.90, 74.11, 73.86, 73.39, 73.12, 72.72, 72.29, 71.48, 71.18, 70.78, 70.65, 70.26, 69.92, 66.87, 66.69, 62.78, 60.80, 55.60, 21.05, 20.62, 20.13, 20.05, 18.04, 17.90, 16.32 ppm. HRMS (MALDI-DHB): calcd. for $C_{100}H_{100}O_{33}Na$ $[M + Na]^+$ 1851.6044; found 1851.6037.

***p*-Methoxyphenyl 3,4,6-Tri-*O*-acetyl-2-*O*-levulinoyl-β-D-galactopyranosyl-(1→4)-[2,3,4-tri-*O*-benzoyl-6-deoxy-β-D-glucopyranosyl-(1→2)]-3-*O*-acetyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-deoxy-α-D-glucopyranoside (19):** A mixture of compound **14** (0.28 g, 0.26 mmol), compound **18** (0.29 g, 0.52 mmol), and molecular sieves (4 Å; 100 mg) in dry CH_2Cl_2 (20 mL) was stirred under nitrogen for 30 min. The mixture was cooled to –78 °C, and TMSOTf (47 μL, 0.26 mmol) was added. The mixture was stirred for 30 min, then it was filtered through a pad of Celite. The filtrate was washed successively with $NaHCO_3$ (5 mL) and brine (10 mL). The organic phase was separated and dried with Na_2SO_4, and the solvents were evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether/EtOAc, 3:1) to give pure compound **19** (0.26 g, 68%) as a white foam. $[\alpha]_D^{20}$ = –29.8 (*c* = 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.3 Hz, 2 H, ArH), 7.84 (d, *J* = 7.4 Hz, 2 H, ArH), 7.78 (d, *J* = 7.4 Hz, 2 H, ArH), 7.54–7.24 (m, 19 H, ArH), 6.94 (d, *J* = 9.0 Hz, 2 H, ArH), 6.81 (d, *J* = 9.1 Hz, 2 H, ArH), 5.84 (t, *J* = 9.7 Hz, 1 H), 5.56–5.45 (m, 1 H), 5.38 (t, *J* = 9.6 Hz, 1 H), 5.33 (s, 1 H), 5.25 (d, *J* = 3.5 Hz, 1 H, 1^{I}-H), 5.16 (d, *J* = 7.4 Hz, 1 H, 1^{IV}-H), 5.09–5.03 (m, 2 H), 5.01 (d, *J* = 7.0 Hz, 1 H, 1^{II}-H), 4.95 (apparent t, *J* = 9.9 Hz, 3 H), 4.68 (d, *J* = 10.9 Hz, 1 H, CH_2Ph), 4.63 (d, *J* = 11.0 Hz, 1 H, CH_2Ph), 4.43 (t, *J* = 9.1 Hz, 1 H), 4.34 (d, *J* = 7.1 Hz, 1 H, 1^{III}-H), 4.10–3.99 (m, 2 H), 3.93–3.78 (m, 5 H), 3.78 (s, 3 H, OCH_3Ph), 3.73–3.64 (m, 1 H), 3.20 (t, *J* = 11.0 Hz, 1 H), 3.12 (t, *J* = 9.2 Hz, 1 H), 2.83–2.75 (m, 1 H), 2.64–2.50 (m, 2 H), 2.36–2.29 (m, 1 H), 2.14 (s, 3 H, CH_3Ph), 2.11 (s, 3 H, CH_3CO), 2.04 (s, 3 H, OAc), 2.00 (s, 3 H, OAc), 1.89 (s, 3 H, OAc), 1.40 (d, *J* = 6.1 Hz, 3 H, CH_3), 1.17 (d, *J* = 6.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.84, 170.75, 170.36, 170.34, 170.18, 169.12, 166.01, 165.52, 165.07, 155.02, 150.89, 138.63, 138.03, 133.41, 133.16, 133.04, 129.82, 129.80, 129.70, 129.65, 129.16, 128.96, 128.92, 128.65, 128.46, 128.42, 128.31, 128.26, 128.16, 128.07, 127.75, 118.23, 114.55, 101.11, 101.02, 100.92, 95.92, 81.88, 81.17, 78.42, 77.54, 74.87, 73.95, 73.81, 73.27, 72.77, 70.80, 70.65, 68.88, 66.93, 66.87, 63.08, 61.07, 55.65, 37.68, 29.69, 27.69, 20.84, 20.67, 20.63, 20.51, 18.02, 17.92 ppm. HRMS (MALDI-TOF): calcd. for $C_{78}H_{84}O_{28}Na$ $[M + Na]^+$ 1491.5046; found 1491.5042.

***p*-Methoxyphenyl 3,4,6-Tri-*O*-acetyl-β-D-galactopyranosyl-(1→4)-[2,3,4-tri-*O*-benzoyl-6-deoxy-β-D-glucopyranosyl-(1→2)]-3-*O*-acetyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-deoxy-α-D-glucopyranoside (20):** Compound **19** (182 mg, 0.124 mmol) was dissolved in dry CH_3OH/CH_2Cl_2 (5 mL/20 mL), and $AcOH{\cdot}N_2H_4$ (114 mg, 1.24 mmol) was added. The reaction mixture was stirred overnight at room temperature, then the mixture was concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/EtOAc, 3:1) to give pure compound **20** (158 mg, 93%) as a white foam. $[\alpha]_D^{20}$ = –18.2 (*c* = 0.20, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 7.3 Hz, 2 H, ArH), 7.82 (d, *J* = 7.4 Hz, 2 H, ArH), 7.76 (d, *J* = 7.4 Hz, 2 H, ArH), 7.54–7.24 (m, 19 H, ArH), 6.94 (d, *J* = 9.0 Hz, 2 H, ArH), 6.81 (d, *J* = 9.1 Hz, 2 H, ArH), 5.84 (t, *J* = 9.7 Hz, 1 H), 5.47 (t, *J* = 8.8 Hz, 1 H), 5.38–5.32 (m, 2 H, 1^{IV}-H), 5.30–5.22 (m, 2 H, 1^{I}-H), 5.02–4.96 (m, 3 H, 1^{II}-H), 4.89–4.83 (m, 2 H), 4.65 (d, *J* = 10.9 Hz, 1 H, $PhCH_2$), 4.63 (d, *J* = 11.0 Hz, 1 H, $PhCH_2$), 4.43 (t, *J* = 9.1 Hz, 1 H), 4.34 (d, *J* = 7.1 Hz, 1 H, 1^{III}-H), 4.10–3.95 (m, 3 H), 3.93–3.78 (m, 1 H), 3.78–3.70 (m, 8 H), 3.58 (t, *J* = 7.8 Hz, 1 H), 3.40–3.30 (m, 1 H), 3.12 (t, *J* = 9.2 Hz, 1 H), 2.64 (s, 1 H, OH), 2.33 (s, 3 H, OAc), 2.18 (s, 3 H, OAc), 2.04 (s, 3 H, OAc), 2.00 (s, 3 H, OAc), 1.89 (s, 3 H, CH_3), 1.40 (d, *J* = 6.1 Hz, 3 H, CH_3), 1.17 (d, *J* = 6.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.36, 170.30, 170.08, 169.80, 165.93, 165.43, 165.14, 154.90, 150.79, 138.40, 137.93, 133.40, 133.17, 133.10, 133.40, 133.17, 133.10, 129.75, 129.66, 129.48, 129.06, 128.85, 128.62, 128.44, 128.31, 128.26, 128.20, 128.10, 127.76, 118.03, 114.48, 101.21, 101.06, 100.83, 95.64, 81.91, 77.71, 77.60, 74.70, 74.42, 73.76, 73.48, 73.19, 73.02, 72.67, 72.17, 70.63, 70.53, 68.65, 66.92, 66.87, 61.02, 55.61, 29.68, 20.96, 20.74, 20.67, 20.59, 17.99, 17.79 ppm. HRMS (MALDI-TOF): calcd. for $C_{73}H_{78}O_{26}Na$ $[M + Na]^+$ 1393.4679; found 1393.4673.

***p*-Methoxyphenyl 2,3,4-Tri-*O*-benzoyl-6-deoxy-β-D-galactopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-β-D-galactopyranosyl-(1→4)-[2,3,4-tri-*O*-benzoyl-6-deoxy-β-D-glucopyranosyl-(1→2)]-3-*O*-acetyl-β-D-xylopyranosyl-(1→3)-6-deoxy-α-D-glucopyranoside (21):** Pd-$(OH)_2$/C (20 wt.-%; 19 mg) was added to a solution of compound

17 (95 mg, 0.052 mmol) in EtOAc (20 mL) and methanol (20 mL). The resulting suspension was vigourously stirred under H_2 (g) at room temperature and atmospheric pressure for 24 h. The reaction mixture was filtered through Celite. The filtrate was concentrated to dryness to give, without further purification, compound **21** (79 mg, 98%) as a pale yellow foam. $[a]_D^{20} = -5.7$ ($c = 0.20$, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, J = 7.5 Hz, 2 H, ArH), 7.95–7.89 (m, 5 H, ArH), 7.78 (d, J = 7.7 Hz, 4 H, ArH), 7.58–7.51 (m, 7 H, ArH), 7.45–7.39 (m, 7 H, ArH), 7.28–7.22 (m, 5 H, ArH), 7.11 (d, J = 7.7 Hz, 2 H, ArH), 6.88 (d, J = 7.8 Hz, 2 H, ArH), 5.90 (t, J = 9.7 Hz, 1 H), 5.69 (s, 1 H), 5.59–5.48 (m, 4 H, 1^{I}-H), 5.39 (t, J = 9.5 Hz, 1 H), 5.21 (s, 1 H), 5.13 (t, J = 9.6 Hz, 1 H), 5.00 (d, J = 8.0 Hz, 1 H, 1^{IV}-H), 4.92 (d, J = 8.0 Hz, 1 H, 1^{II}-H), 4.79 (d, J = 10.5 Hz, 1 H), 4.69 (d, J = 7.5 Hz, 1 H, 1^{V}-H), 4.40 (d, J = 7.1 Hz, 1 H, 1^{III}-H), 4.29–4.20 (m, 2 H), 4.12–4.01 (m, 2 H), 3.98–3.89 (m, 3 H), 3.87–3.78 (m, 7 H), 3.70 (t, J = 8.8 Hz, 1 H), 3.50 (t, J = 10.9 Hz, 1 H), 3.27 (t, J = 8.9 Hz, 1 H), 2.02 (s, 3 H, OAc), 1.81 (s, 3 H, OAc), 1.78 (s, 3 H, OAc), 1.71 (s, 3 H, OAc), 1.48 (d, J = 5.6 Hz, 3 H, CH_3), 1.37 (d, J = 6.1 Hz, 3 H, CH_3), 1.32 (d, J = 5.7 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.24, 169.78, 169.72, 168.92, 165.88, 165.76, 165.46, 165.04, 165.00, 164.97, 154.89, 150.62, 133.36, 133.22, 133.15, 129.76, 129.69, 129.63, 129.59, 129.42, 129.34, 129.08, 128.84, 128.77, 128.66, 128.50, 128.36, 128.24, 128.19, 128.12, 127.26, 118.06, 114.43, 103.20, 102.05, 101.59, 100.96, 97.23, 87.36, 79.65, 75.39, 75.17, 74.05, 73.85, 73.30, 72.60, 72.36, 72.03, 71.83, 71.06, 70.84, 70.68, 70.34, 69.83, 68.22, 66.54, 63.20, 60.83, 55.55, 29.62, 20.66, 20.57, 20.14, 17.68, 17.10, 16.54 ppm. HRMS (MALDI-DHB): calcd. for $C_{86}H_{88}O_{33}Na$ $[M + Na]^+$ 1671.5105; found 1671.5107.

***p*-Methoxyphenyl 6-Deoxy-β-D-galactopyranosyl-(1→2)-β-D-galactopyranosyl-(1→4)-[6-deoxy-β-D-glucopyranosyl-(1→2)]-β-D-xylopyranosyl-(1→3)-6-deoxy-α-D-glucopyranoside (1):** Compound **21** (62 mg, 0.0376 mmol) was dissolved in dry MeOH (10 mL), and NaOMe was added until a pH of 11 was reached. The reaction mixture was stirred for 6 h at 60 °C. The solution was neutralized with DOWEX 50W H^+ resin, and then it was filtered. The filtrate was concentrated, and the residue was purified on a Sephadex LH-20 column ($MeOH/H_2O$, 10:1) to give compound **1** (28 mg, 88%) as a white solid. ^{1}H NMR (400 MHz, D_2O): δ = 7.11 (d, J = 8.86 Hz, 2 H, ArH), 6.97 (d, J = 8.17 Hz, 2 H, ArH), 5.52 (d, J = 3.75 Hz, 1 H, 1^{I}-H), 4.76 (d, J = 7.33 Hz, 1 H, 1-H), 4.74 (d, J = 7.94 Hz, 1 H, 1-H), 4.63 (d, J = 7.33 Hz, 1 H, 1-H), 4.60 (d, J = 7.33 Hz, 1 H, 1-H), 4.18 (dd, J = 11.9, 4.9 Hz, 1 H), 3.94–3.89 (m, 5 H), 3.86–3.82 (m, 5 H), 3.82–3.79 (m, 4 H), 3.78–3.75 (m, 3 H), 3.73–3.51 (m, 5 H), 3.40–3.29 (m, 2 H), 3.24 (t, J = 9.3 Hz, 1 H), 1.34 (d, J = 6.1 Hz, 3 H, CH_3), 1.28 (d, J = 6.4 Hz, 3 H, CH_3), 1.24 (d, J = 6.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.90, 149.99, 119.07, 115.25, 104.03 (C-1), 103.81 (C-1), 102.77 (C-1), 100.71 (C-1), 97.36 (C-1^{I}), 83.95, 81.85, 80.08, 76.90, 75.31, 75.17, 74.84, 74.25, 74.11, 73.53, 72.69, 72.46, 71.99, 71.40, 71.34, 70.65, 68.77, 68.63, 63.13, 61.15, 55.90, 16.73, 16.67, 15.83 ppm. HRMS (MALDI-DHB): calcd. for $C_{36}H_{56}O_{23}Na$ $[M + Na]^+$ 879.3096; found 879.3104.

Supporting Information (see footnote on the first page of this article): Experimental details, ^{1}H and ^{13}C NMR spectra for all new compounds.

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