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Synthesis of 1-deoxyhept-2-ulosyl-glycono-1,5-lactone utilizing α-selective O-glycosidation of 2,6-anhydro-1-deoxy-D-hept-1-enitols

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Abstract—A series of 1-deoxy-heptulo-2-pyranosyl-glycono-1,5-lactones were synthesized utilizing completely α-selective O-glycosidation of heptenitols. Anomeric configuration of the products was confirmed by $^{3}J_{C,H}$ coupling measurement and X-ray crystal structural analysis. The benzyl-protected ketosyl saccharides were partly unstable, and glycosidic linkage was prone to cleave under the usual debenzylation conditions. To prevent this, we surveyed various additives for the Pd-catalyzed hydrogenation reaction and found that basic alumina was the most effective.

1. Introduction

Bioactive sugar chains containing ketoses such as fructose and sialic acids are abundant in nature. The sialic acid family, represented by *N*-acetylneuraminic acid (Neu5Ac), consists of oligosaccharides or glycoconjugates in the form of α-ketosides. To take a notable example, 3-deoxy-D-*manno*-oct-2-ulosonic acid is a constituent of glycolipids of Gram-negative bacteria and is α-linked to lipid A. Since sialic acids are involved in numerous biological processes, they are attractive targets for drug discovery.[1] It is also known that 1-deoxy-α-D-*gluco*-heptulose 2-phosphate, which is a 1-*C*-methyl analogue of D-glucose 1-phosphate, is a potent phosphorylase inhibitor. The interaction of heptulose 2-phosphate with enzymes has been examined thoroughly.[2] It is expected that heptulosyloligosaccharides can be utilized as a new class of bioactive oligosaccharides. In the synthetic field, therefore, stereoselective construction of ketosides[3,4] as well as artificial ones[5–8] has been enthusiastically investigated.

For the synthesis of ketosyl saccharides, several methods have been developed by our group.[6,7] We have used *exo*-glycals in the construction of artificial sugar chains and reported the O-glycosidation of heptenitols,[9–12] which are among the simplest *exo*-glycals formed by Tebbe-type methylenation[13] of glyconolactone. The acid-promoted O-glycosidation of 2,6-anhydro-1-deoxyhept-1-enitols **1a–c** (Fig. 1) with

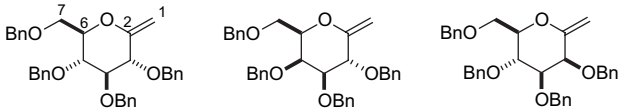
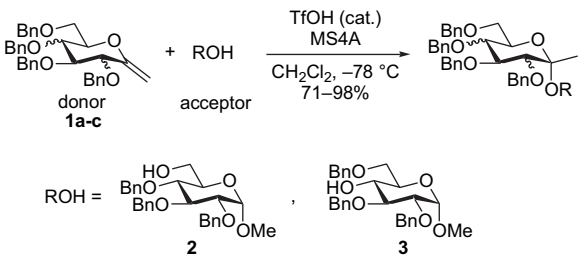


Figure 1. 2,6-Anhydro-1-deoxyhept-1-enitols as glycosyl donors.

methyl α-D-glucopyranosides **2** and **3** afforded 1-deoxyhept-2-ulosylglucosides, i.e., the 1′-*C*-methyl-substituted analogue of naturally occurring aldoside (Scheme 1). This glycosidation was promoted by various acids such as $TiCl_4$, $SnCl_4$, trimethylsilyl trifluoromethanesulfonate (TMSOTf), and trifluoromethanesulfonic acid (TfOH). The best result was achieved using TfOH as a promoter at −78 °C. As far as we have examined, the glycosidation of D-*gluco*-, D-*galacto*-, and D-*manno*-hept-1-enitols **1a–c** gave only α-ketoside, and the formation of β-ketoside was not detected. The glycosidation of peracetylated heptenitols with a 3-*O*-acetyl group also took place in an α-selective manner.



Scheme 1. Glycosidation of hept-1-enitols **1a–c**.

Keywords: Ketoside; *exo*-Glycal; Heptenitol; Heptuloside; O-Glycosidation; Basic alumina.
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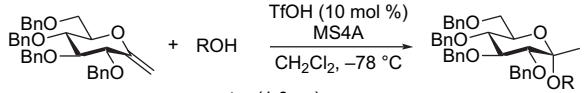
To investigate the generality of this α-selective glycosidation, we planned to examine the O-glycosidation of heptenitols using various glycosyl acceptors. We herein present a new library of hept-2-ulosylsaccharides and their X-ray crystallographic analyses.

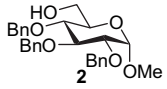
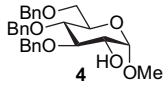
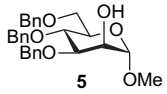
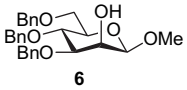
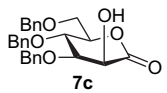
2. Results and discussion

2.1. Glycosidation of heptenitols

As the ketosyl saccharides have quaternary anomeric carbons, we suspected that the unreactive axial hydroxyl group of the pyranose might not be glycosylated efficiently. We first examined the O-glycosidation of heptenitol **1a** with pyranosides **2**, **4**, **5**, and **6** (Table 1). The reaction was performed in CH_2Cl_2 at −78 °C in the presence of 10 mol % of TfOH. After quenching the reaction with triethylamine, the solvent was removed and the residue was subjected to column chromatography to afford the desired disaccharide in pure form. In the case of the primary alcohol **2**, the corresponding disaccharide was obtained in 97% yield with α-stereoselectivity.[6a] The glucopyranoside **4**, which has an equatorial secondary hydroxyl group, showed similar reactivity (Table 1, entry 2). On the other hand, glycosidation with mannopyranosides **5** and **6**, which have axial secondary hydroxyl groups, proceeded very slowly (3 h) to give disaccharides in low yields (Table 1, entries 3 and 4). It is clear that pyranoside with an axially oriented hydroxyl group is reluctantly glycosylated. We next used the mannono-1,5-lactone **7c** as an acceptor because we were interested in its conformational and electronic differentiation from $^4C_1$ pyranoside. Surprisingly, the reaction with **7c** proceeded rapidly (15 min), and the corresponding disaccharide was obtained in 86% yield with complete α-stereoselectivity. It should be noted that the secondary alcohol **7c** reacted more rapidly than the primary alcohol **2**. The rate of this glycosidation with glycosyl acceptors increased roughly in the following order:Axial secondary OH (**5**, **6**)≪equatorial secondary OH (**4**)≈primary OH (**2**)<secondary OH on lactone ring (**7c**).

Table 1. O-Glycosidation of **1a**



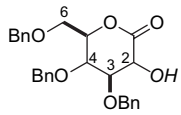
Entry	Acceptor (ROH)	Time (min)	Yield (%)
1	 **2**	60	97
2	 **4**	50	94
3	 **5**	180	34
4	 **6**	180	26
5	 **7c**	15	86

Encouraged by the promising results obtained, we attempted the synthesis of heptulosylsaccharide using glycono-1,5-lactones as the most reactive glycosyl acceptors. The use of lactones provides an additional advantage, enabling the transformation of the resulting disaccharides by methylenation,[6b,13] reduction, or alkylation to afford a wide variety of sugar-related compounds.

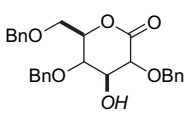
Thus, the glycosidation of a combination of heptenitols **1a–c** as glycosyl donors and sugar lactones **7–10**[14] derived from D-glucose, D-galactose, and D-mannose as acceptors (Fig. 2) was explored (Table 2).

Hydroxyl groups at C-2 in glyconolactones were smoothly glycosylated to afford heptulosyl-(2→2)-glyconolactones **11aa–cc** in high yields (Table 2, entries 1–9). As we expected, C-2-OH in mannono-1,5-lactone reacted easily with the heptenitol **1a**, **1b**, and **1c** giving the corresponding disaccharides in high yield (Table 2, entries 3, 6, 9). Similarly, C-3-OH and C-4-OH were efficiently glycosylated to afford the corresponding heptulosyl-(2→3)-glyconolactones **12** and heptulosyl-(2→4)-glyconolactones **13**, respectively (Table 2, entries 10–27). Glycosidation with C-4-OH in galactono-1,5-lactone **9b** also proceeded well and yielded the corresponding disaccharides (Table 2, entries 20, 23, 26). No remarkable differences in reactivity were observed in the glycosidation of *gluco*-, *galacto*-, and *manno*-heptenitols. In addition, it is noteworthy that all heptulosides were obtained as their respective single isomers.

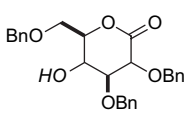
The glycosidation of **1a–c** with primary alcohols **10a–c** was performed in the same manner (Table 2, entries 28–38). In entries 33 and 35 in Table 2, disaccharides were obtained in excellent yields within 15 min. In other cases, a longer reaction time was required for the completion of glycosidation. In addition, a longer reaction time caused the decomposition of heptenitols and heptulosides (Table 2, entries 30, 31, 37).



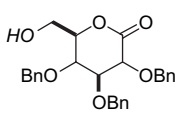
7a (Glc): 2-OH(α), 4-OBn(α)
7b (Gal): 2-OH(α), 4-OBn(β)
7c (Man): 2-OH(β), 4-OBn(α)



8a (Glc): 2-OBn(α), 4-OBn(α)
8b (Gal): 2-OBn(α), 4-OBn(β)
8c (Man): 2-OBn(β), 4-OBn(α)



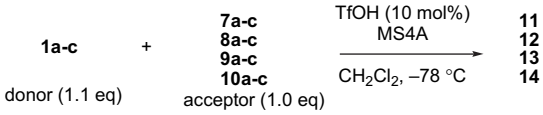
9a (Glc): 2-OBn(α), 4-OH(α)
9b (Gal): 2-OBn(α), 4-OH(β)
9c (Man): 2-OBn(β), 4-OH(α)



10a (Glc): 2-OBn(α), 4-OBn(α)
10b (Gal): 2-OBn(α), 4-OBn(β)
10c (Man): 2-OBn(β), 4-OBn(α)

Figure 2. Glycono-1,5-lactones as glycosyl acceptors.

Table 2. O-Glycosidation of **1a–c** with glycono-1,5-lactones



Entry	Donor	Acceptor	Time (min)	Product	Yield (%)
1	**1a**	**7a**	40	**11aa** Glc-(2→2)-Glc	89
2	**1a**	**7b**	30	**11ab** Glc-(2→2)-Gal	95
3	**1a**	**7c**	15	**11ac** Glc-(2→2)-Man	86
4	**1b**	**7a**	15	**11ba** Gal-(2→2)-Glc	99
5	**1b**	**7b**	17	**11bb** Gal-(2→2)-Gal	83
6	**1b**	**7c**	17	**11bc** Gal-(2→2)-Man	98
7	**1c**	**7a**	17	**11ca** Man-(2→2)-Glc	89
8	**1c**	**7b**	15	**11cb** Man-(2→2)-Gal	95
9	**1c**	**7c**	12	**11cc** Man-(2→2)-Man	89
10	**1a**	**8a**	30	**12aa** Glc-(2→3)-Glc	93
11	**1a**	**8b**	15	**12ab** Glc-(2→3)-Gal	91
12	**1a**	**8c**	20	**12ac** Glc-(2→3)-Man	81
13	**1b**	**8a**	20	**12ba** Gal-(2→3)-Glc	88
14	**1b**	**8b**	15	**12bb** Gal-(2→3)-Gal	89
15	**1b**	**8c**	30	**12bc** Gal-(2→3)-Man	77
16	**1c**	**8a**	15	**12ca** Man-(2→3)-Glc	84
17	**1c**	**8b**	15	**12cb** Man-(2→3)-Gal	88
18	**1c**	**8c**	30	**12cc** Man-(2→3)-Man	84
19	**1a**	**9a**	30	**13aa** Glc-(2→4)-Glc	99
20	**1a**	**9b**	30	**13ab** Glc-(2→4)-Gal	81
21	**1a**	**9c**	20	**13ac** Glc-(2→4)-Man	81
22	**1b**	**9a**	22	**13ba** Gal-(2→4)-Glc	94
23	**1b**	**9b**	20	**13bb** Gal-(2→4)-Gal	82
24	**1b**	**9c**	20	**13bc** Gal-(2→4)-Man	83
25	**1c**	**9a**	16	**13ca** Man-(2→4)-Glc	97
26	**1c**	**9b**	15	**13cb** Man-(2→4)-Gal	97
27	**1c**	**9c**	30	**13cc** Man-(2→4)-Man	73
28	**1a**	**10a**	50	**14aa** Glc-(2→6)-Glc	72
29[a]	**1a**	**10a**	10	**14aa** Glc-(2→6)-Glc	67
30[b]	**1a**	**10b**	210	**14ab** Glc-(2→6)-Gal	77
31	**1a**	**10c**	120	**14ac** Glc-(2→6)-Man	74
32[a]	**1a**	**10c**	15	**14ac** Glc-(2→6)-Man	82
33	**1b**	**10a**	14	**14ba** Gal-(2→6)-Glc	96
34	**1b**	**10b**	60	**14bb** Gal-(2→6)-Gal	75
35	**1b**	**10c**	10	**14bc** Gal-(2→6)-Man	97
36	**1c**	**10a**	90	**14ca** Man-(2→6)-Glc	69
37	**1c**	**10b**	60	**14cb** Man-(2→6)-Gal	70
38	**1c**	**10c**	40	**14cc** Man-(2→6)-Man	79

[a] The amount of TfOH was increased to 15 mol %.
[b] After 200 min, 5 mol % of TfOH was added.

In particular, glycosidation of *gluco*-heptenitol **1a** with galactono-1,5-lactone **10b** was quite slow, and therefore another portion of TfOH was added for the completion of the reaction (Table 2, entry 30). In entries 29 and 32 in Table 2, although the amount of TfOH was increased to 15 mol % to complete the reaction in a shorter time, yields were not increased.

It was surprising that the primary alcohols **10a–c** were unreactive in some cases. The reactivity may depend on the combination of a glycosyl donor and an acceptor. For example, glycosidation of *gluco*-heptenitol **1a** with mannonolactone **10c** required 2 h (Table 2, entry 31), but otherwise the reaction of *galacto*-heptenitol **1b** with **10c** was completed in 10 min (Table 2, entry 35). Although the reactivity varied, heptulosyl-(2→6)-glyconolactones **14aa–cc** were obtained as their respective single isomers.

We therefore achieved the synthesis of 36 examples of 1-deoxy-2-heptulopyranosyl-glycono-1,5-lactone in a combination of heptenitols **1a–c** as glycosyl donors and **7–10** as acceptors. All *gluco*-, *galacto*-, and *manno*-heptuloside products were isolated as their respective single anomeric isomers.

2.2. Determination of the configurations at anomeric position

The configurations at C-2′ anomeric position of hept-2-ulosides were determined by X-ray crystallographic analyses and NMR study.

manno-Hept-2-uloside **14cc** was obtained as colorless crystals. The X-ray crystallographic structure of **14cc** is shown in Figure 3.[15] Based on this X-ray crystallographic analysis, it was elucidated that *manno*-heptuloside possessed a $^5C_2$ chair conformation and α-anomeric configuration. Additionally, the mannonolactone part had a $B_{2,5}$ boat conformation. As only one isomer was formed in every case, it is suggested that other *manno*-heptulosides also possess the α-anomeric configuration.

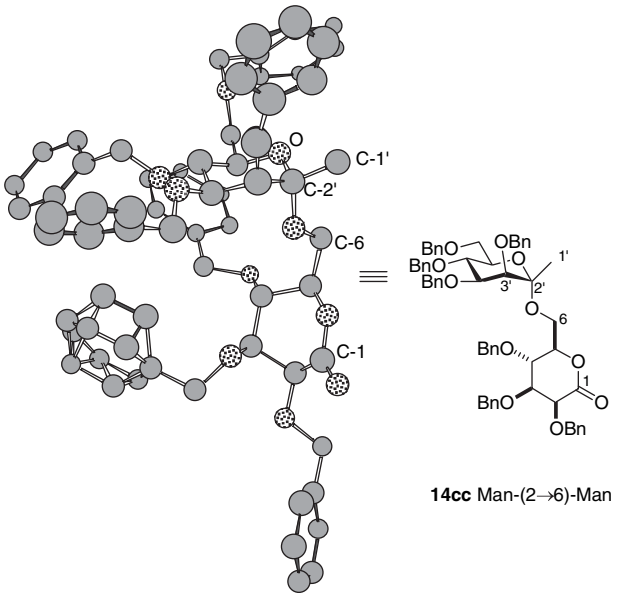
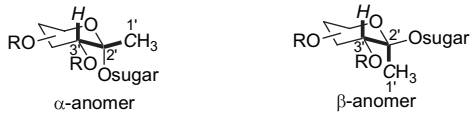


Figure 3. X-ray crystal structure of **14cc**. Hydrogen atoms are omitted for clarity.

The anomeric configuration of *gluco*- and *galacto*- heptulopyranosides was anticipated by analyzing the vicinal C–H coupling constants $^{3}J_{C,H}$ in NMR spectra.[10,16] It is known that the magnitude of $^{3}J_{C,H}$ depends on the dihedral angle between the C-1/C-2 bond and C-3/H-3 bond. As shown in Figure 4, the C-1′ exocyclic carbon and H-3′ axial proton are oriented synclinally in α-ketoside and antiperiplanarly in β-ketoside. By the measurement of the vicinal coupling constant $^{3}J_{C\text{-}1',H\text{-}3'}$ of our products, which were approximately 1.8–2.0 Hz, it is obvious that newly formed glycosidic bonds have the α-configuration. We can be fairly certain that the O-glycosidation of *gluco*-, *galacto*-, and *manno*-heptenitols gave α-glycosides.



11aa Glc-(2→2)-Glc 1.9 Hz
12ba Gal-(2→3)-Glc 2.0 Hz
13ab Glc-(2→4)-Gal 1.8 Hz
14bb Gal-(2→6)-Gal 1.9 Hz

Figure 4. Vicinal coupling constants $^{3}J_{C\text{-}1',H\text{-}3'}$.

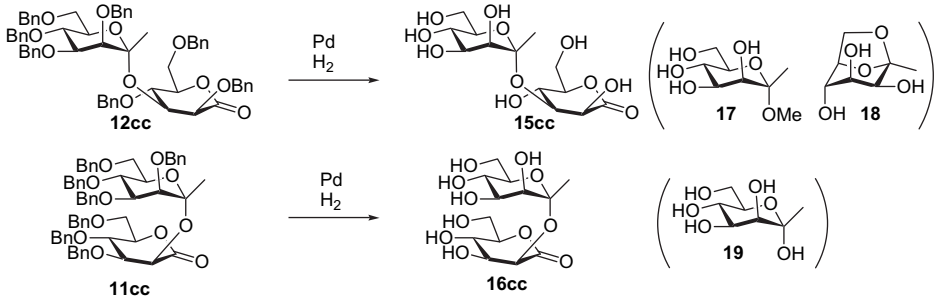
2.3. Deprotection

We then focused on the deprotection of protected hydroxyl groups. In preliminary experiments, it was found that the removal of benzyl groups by hydrogenolysis was accompanied by the cleavage of ketoside bonds. Other reactions such as Birch reduction, catalytic hydrogen transfer,[17] the use of lithium naphthalenide,[18] and oxidation[19–21] gave unsatisfactory results.

We therefore returned to the use of Pd-catalyzed hydrogenolysis. The deprotection of Man-(2→3)-Man **12cc** was examined in various solvents using Pd/C or $Pd(OH)_2/C$ as a catalyst (Table 3). When the reaction proceeded in MeOH, solvolysis occurred to afford **17** (Table 3, entry 1). Using less nucleophilic trifluoroethanol (TFE) as a solvent, intramolecular cyclization followed by cleavage of the ketoside bond gave the cyclized product **18** quantitatively (Table 3, entry 2). It was speculated that the acidity of TFE caused the cleavage of ketoside. Similarly, the use of THF as a solvent resulted in the formation of **18** (Table 3, entry 3). On the hypothesis that the formation of a hydrogen bond would prevent intramolecular nucleophilic attack of the anomeric center, hydrogenolysis was performed in mixed solvents THF/H_2O, and the desired product **15cc** was obtained in 44% yield (Table 3, entry 4).

Although the use of such mixed solvents appeared promising, unexpected solvolysis occurred in the case of Man-(2→2)-Man **11cc** (Table 3, entry 6). It was found that deprotected disaccharides vary in stability. In order to prevent solvolysis, slightly basic conditions were examined. In the presence of

Table 3. Deprotection of **11cc** and **12cc**



Entry	Substrate	Pd	Cat. (wt %)	Solvent	Time (h)	Yield (%)	Other products
1	**12cc**	Pd/C	20	MeOH	4	0	**17**
2		$Pd(OH)_2/C$	25	TFE	48	0	**18**
3		Pd/C	50	THF	9	0	**18**
4		$Pd(OH)_2/C$	20	THF/H_2O	15	44	
5[a]		$Pd(OH)_2/C$	50	THF; MeOH	70	97	
6	**11cc**	$Pd(OH)_2/C$	50	THF/H_2O	2	0	**19**
7[a]		$Pd(OH)_2/C$	50	THF; MeOH	37	65	

[a] Hydrogenation was performed in the presence of basic alumina (50 wt %).

organic or inorganic bases such as pyridine, triethylamine, sodium acetate, and potassium carbonate, hydrogenolysis did not proceed smoothly.[22] We finally found that basic alumina was effective: it prevented undesired side reactions and maintained the catalyst activity. In the presence of basic alumina, the solubility of substrates in solvent markedly affected the reaction rate. In the early stage of hydrogenolysis, the reaction proceeds much faster in THF than in MeOH or *t*-BuOH. Then, as debenzylation progresses, the solubility in THF becomes low, requiring MeOH to be added. Under these conditions, both **12cc** and **11cc** were debenzylated in satisfactory yields (Table 3, entries 5 and 7).

Thus, debenzylation of 36 heptulosides **11**–**14** was explored using catalytic hydrogenation in the presence of $Pd(OH)_2/C$ and basic alumina (Table 4). In many cases, debenzylation afforded the desired deprotected disaccharides. However, some substrates were quite unstable even under basic conditions, and deprotected disaccharides could not be isolated. Particularly, the removal of benzyl groups in heptulosyl-(2→6)-glyconolactone was difficult. It appears that deprotected heptulosides **21** are fairly unstable.[23] Although considerable effort was made, further improvement was not achieved in these cases except for Gal-(2→6)-Gal **14b**. Ultimately, the 25 disaccharides shown in Table 4 were obtained in a deprotected form.

3. Conclusion

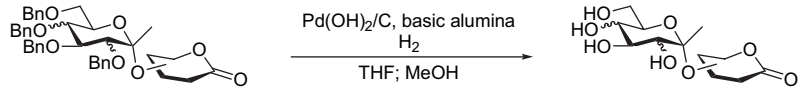
We achieved the synthesis of disaccharides, hept-2-ulosyl-glyconolactones, by acid-promoted O-glycosidation of 2,6-anhydro-1-deoxyhept-1-enitols **1a**–**c**. Under the reaction conditions described here, O-glycosidation of heptenitols **1a**–**c** proceeded with complete stereoselectivity, and each disaccharide was isolated as a single anomeric isomer. Their configurations at anomeric position were identified as α-stereochemistry by X-ray crystallography and NMR vicinal coupling constant $^3J_{C\text{-}1',H\text{-}3'}$. Although the removal of benzyl groups was problematic, we found that Pd-catalyzed hydrogenolysis in the presence of basic alumina was effective in preventing cleavage of the ketoside bonds.

4. Experimental

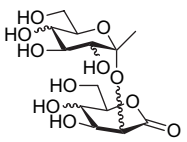
4.1. General methods

Melting points were measured on a YANACO Micro Melting Point Apparatus and were uncorrected. IR spectra were recorded on a Jasco FT-IR-8000 Fourier-transform infrared spectrometer. ^1H and ^{13}C NMR, and three-bond carbon–proton coupling constants $^3J_{C,H}$ were measured on a JEOL ECP 600 (600 MHz) NMR spectrometer in $CDCl_3$, CD_3OD,

Table 4. Deprotection



Entry	*O*-benzylated disaccharide	Product	Yield (%)
1	**11aa** Glc-(2→2)-Glc	**16aa** Glc-(2→2)-Glc	quant.
2	**11ab** Glc-(2→2)-Gal	**16ab** Glc-(2→2)-Gal	89
3	**11ac** Glc-(2→2)-Man	**16ac** Glc-(2→2)-Man	quant.
4	**11ba** Gal-(2→2)-Glc	**16ba** Gal-(2→2)-Glc	78
5	**11bb** Gal-(2→2)-Gal	**16bb** Gal-(2→2)-Gal	quant.
6	**11bc** Gal-(2→2)-Man	**16bc** Gal-(2→2)-Man	quant.
7	**11ca** Man-(2→2)-Glc	**16ca** Man-(2→2)-Glc	89
8	**11cb** Man-(2→2)-Gal	**16cb** Man-(2→2)-Gal	83
9	**11cc** Man-(2→2)-Man	**16cc** Man-(2→2)-Man	65
10	**12aa** Glc-(2→3)-Glc	**15aa** Glc-(2→3)-Glc	quant.
11	**12ab** Glc-(2→3)-Gal	**15ab** Glc-(2→3)-Gal	99
12	**12ba** Gal-(2→3)-Glc	**15ba** Gal-(2→3)-Glc	97
13	**12bb** Gal-(2→3)-Gal	**15bb** Gal-(2→3)-Gal	quant.
14	**12ca** Man-(2→3)-Glc	**15ca** Man-(2→3)-Glc	98
15	**12cb** Man-(2→3)-Gal	**15cb** Man-(2→3)-Gal	83
16	**12cc** Man-(2→3)-Man	**15cc** Man-(2→3)-Man	65
17	**13aa** Glc-(2→4)-Glc	**20aa** Glc-(2→4)-Glc	quant.
18	**13ab** Glc-(2→4)-Gal	**20ab** Glc-(2→4)-Gal	91
19	**13ac** Glc-(2→4)-Man	**20ac** Glc-(2→4)-Man	quant.
20	**13ba** Gal-(2→4)-Glc	**20ba** Gal-(2→4)-Glc	75
21	**13bb** Gal-(2→4)-Gal	**20bb** Gal-(2→4)-Gal	quant.
22	**13bc** Gal-(2→4)-Man	**20bc** Gal-(2→4)-Man	quant.
23	**13cb** Man-(2→4)-Gal	**20cb** Man-(2→4)-Gal	94
24	**13cc** Man-(2→4)-Man	**20cc** Man-(2→4)-Man	quant.
25	**14bb** Gal-(2→6)-Gal	**21bb** Gal-(2→6)-Gal	59



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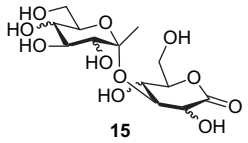
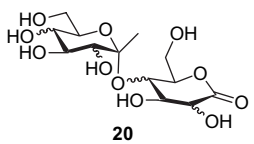
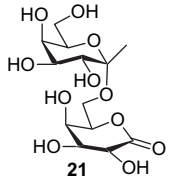


15



20



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or D_2O solutions. Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded with a JEOL JMS-SX102A mass spectrometer with FAB using 3-nitrobenzyl alcohol (NBA) as the matrix. Optical rotations were measured with a Jasco DIP-370 digital polarimeter. X-ray crystallographic measurements were performed with a Rigaku RAXIS-RAPID Imaging Plate Diffractometer with graphite monochromated MoK_α radiation at 123 K. TLC was performed on precoated plates (Merck TLC Aluminum sheets silica 60 F_{254}) with detection by UV light or with phosphomolybdic acid in EtOH/H_2O followed by heating. Column chromatography was performed using SiO_2 (Silica Gel 60 N, spherical, neutral, Kanto).

4.2. General procedure 1: glycosidation of heptenitols with alcohols

To a stirred mixture of hept-1-enitol **1a** (237.0 mg, 0.44 mmol), hydroxylactone **7a** (180.0 mg, 0.40 mmol), and molecular sieves 4 Å (400.0 mg) in CH_2Cl_2 (8.0 mL) was added TfOH (3.5 μL, 0.04 mmol) at −78 °C. The reaction mixture was stirred at −78 °C and then quenched with triethylamine. After the removal of the solvent, the residue was purified by column chromatography (silica gel, neutral, hexane/ethyl acetate 3:1) to give disaccharide **11aa** (350.0 mg).[24]

4.2.1. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*gluco*-hept-2-ulosyl-(2→2)-3,4,6-tri-*O*-benzyl-D-glucono-1,5-lactone (11aa). Colorless syrup; $[\alpha]_D^{26}$ +64.9 (*c* 1.16, $CHCl_3$); IR (neat): 3031, 2913, 2869, 1763, 1105, 1082, 1028, 1029, 739, 700 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4096.

4.2.2. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*gluco*-hept-2-ulosyl-(2→2)-3,4,6-tri-*O*-benzyl-D-galactono-1,5-lactone (11ab). Colorless needle; mp 81–83 °C; $[\alpha]_D^{25}$ +70.6 (*c* 0.5, $CHCl_3$); IR (KBr): 3031, 2913, 2869, 1761, 1497, 1455, 1362, 735, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4096.

4.2.3. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*gluco*-hept-2-ulosyl-(2→2)-3,4,6-tri-*O*-benzyl-D-mannono-1,5-lactone (11ac). Colorless syrup; $[\alpha]_D^{27}$ +47.6 (*c* 1.15, $CHCl_3$); IR (neat): 3031, 2928, 2867, 1775, 1455, 1127, 1082, 1065, 1028, 737, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4076.

4.2.4. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*galacto*-hept-2-ulosyl-(2→2)-3,4,6-tri-*O*-benzyl-D-glucono-1,5-lactone (11ba). Colorless syrup; $[\alpha]_D^{29}$ +59.4 (*c* 1.21, $CHCl_3$); IR (neat): 3031, 2917, 2869, 1763, 1455, 1100, 737, 700 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4096.

4.2.5. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*galacto*-hept-2-ulosyl-(2→2)-3,4,6-tri-*O*-benzyl-D-galactono-1,5-lactone (11bb). Colorless syrup; $[\alpha]_D^{26}$ +52.5 (*c* 1.05, $CHCl_3$); IR (neat): 3031, 2923, 2874, 1763, 1455, 1101, 739, 700 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4084.

4.2.6. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*galacto*-hept-2-ulosyl-(2→2)-3,4,6-tri-*O*-benzyl-D-mannono-1,5-lactone (11bc). Colorless syrup; $[\alpha]_D^{27}$ +48.9 (*c* 1.03, $CHCl_3$); IR (neat): 3031, 2915, 2867, 1775, 1455, 1096, 1059, 737, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4061.

4.2.7. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*manno*-hept-2-ulosyl-(2→2)-3,4,6-tri-*O*-benzyl-D-glucono-1,5-lactone (11ca). Colorless syrup; $[\alpha]_D^{27}$ +49.1 (*c* 1.06, $CHCl_3$); IR (neat): 3031, 2911, 2869, 1763, 1455, 1098, 1078, 737, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4086.

4.2.8. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*manno*-hept-2-ulosyl-(2→2)-3,4,6-tri-*O*-benzyl-D-galactono-1,5-lactone (11cb). Colorless syrup; $[\alpha]_D^{26}$ +57.7 (*c* 1.13, $CHCl_3$); IR (neat): 3031, 2915, 2867, 1758, 1455, 1096, 737, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4105.

4.2.9. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*manno*-hept-2-ulosyl-(2→2)-3,4,6-tri-*O*-benzyl-D-mannono-1,5-lactone (11cc). Colorless syrup; $[\alpha]_D^{25}$ +65.5 (*c* 1.01, $CHCl_3$); IR (neat): 3031, 2923, 2867, 1777, 1455, 1073, 739, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4084.

4.2.10. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*gluco*-hept-2-ulosyl-(2→3)-2,4,6-tri-*O*-benzyl-D-glucono-1,5-lactone (12aa). Colorless syrup; $[\alpha]_D^{26}$ +98.8 (*c* 1.14, $CHCl_3$); IR (neat): 3031, 2927, 2863, 1754, 1455, 1073, 737, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}Na$ 1007.4346, found 1007.4355.

4.2.11. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*gluco*-hept-2-ulosyl-(2→3)-2,4,6-tri-*O*-benzyl-D-galactono-1,5-lactone (12ab). Colorless syrup; $[\alpha]_D^{30}$ +90.9 (*c* 1.04, $CHCl_3$); IR (neat): 3032, 2921, 2867, 1750, 1455, 1096, 737, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4075.

4.2.12. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*gluco*-hept-2-ulosyl-(2→3)-2,4,6-tri-*O*-benzyl-D-mannono-1,5-lactone (12ac). Colorless syrup; $[\alpha]_D^{27}$ +35.3 (*c* 1.08, $CHCl_3$); IR (neat): 3031, 2924, 2869, 1765, 1455, 1125, 1088, 739, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4085.

4.2.13. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*galacto*-hept-2-ulosyl-(2→3)-2,4,6-tri-*O*-benzyl-D-glucono-1,5-lactone (12ba). Colorless syrup; $[\alpha]_D^{26}$ +101.7 (*c* 1.08, $CHCl_3$); IR (neat): 3031, 2924, 2870, 1754, 1455, 1096, 1069, 737, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}Na$ 1007.4346, found 1007.4354.

4.2.14. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*galacto*-hept-2-ulosyl-(2→3)-2,4,6-tri-*O*-benzyl-D-galactono-1,5-lactone (12bb). Colorless needle; mp 127–128 °C; $[\alpha]_D^{24}$ +101.0 (*c* 1.0, $CHCl_3$); IR (KBr): 3031, 2867, 1732, 1497, 1098, 735, 696 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4094.

4.2.15. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*galacto*-hept-2-ulosyl-(2→3)-2,4,6-tri-*O*-benzyl-D-mannono-1,5-lactone (12bc). Colorless syrup; $[\alpha]_D^{28}$ +44.2 (*c* 1.28, $CHCl_3$); IR (neat): 3031, 2915, 2869, 1765, 1455, 1098, 737,

698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4082.

4.2.16. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*manno*-hept-2-ulosyl-(2→3)-2,4,6-tri-*O*-benzyl-D-glucono-1,5-lactone (12ca). Colorless syrup; $[\alpha]_D^{27}$ +68.3 (*c* 1.18, $CHCl_3$); IR (neat): 3031, 2911, 2867, 1757, 1455, 1092, 1073, 745, 702 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4093.

4.2.17. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*manno*-hept-2-ulosyl-(2→3)-2,4,6-tri-*O*-benzyl-D-galactono-1,5-lactone (12cb). Colorless syrup; $[\alpha]_D^{26}$ +77.9 (*c* 1.10, $CHCl_3$); IR (neat): 3031, 2919, 2869, 1750, 1455, 1119, 1071, 752, 735, 696 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4064.

4.2.18. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*manno*-hept-2-ulosyl-(2→3)-2,4,6-tri-*O*-benzyl-D-mannono-1,5-lactone (12cc). Colorless syrup; $[\alpha]_D^{30}$ +39.7 (*c* 1.16, $CHCl_3$); IR (neat): 3031, 2915, 2867, 1773, 1455, 1113, 739, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4083.

4.2.19. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*gluco*-hept-2-ulosyl-(2→4)-2,3,6-tri-*O*-benzyl-D-glucono-1,5-lactone (13aa). Colorless syrup; $[\alpha]_D^{28}$ +47.6 (*c* 1.09, $CHCl_3$); IR (neat): 3031, 2924, 2869, 1792, 1455, 1088, 735, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1007.4346, found 1007.4331.

4.2.20. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*gluco*-hept-2-ulosyl-(2→4)-2,3,6-tri-*O*-benzyl-D-galactono-1,5-lactone (13ab). Colorless syrup; $[\alpha]_D^{27}$ +29.8 (*c* 1.13, $CHCl_3$); IR (neat): 3031, 2924, 2867, 1791, 1455, 1090, 7367, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4074.

4.2.21. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*gluco*-hept-2-ulosyl-(2→4)-2,3,6-tri-*O*-benzyl-D-mannono-1,5-lactone (13ac). Colorless syrup; $[\alpha]_D^{27}$ +26.8 (*c* 1.06, $CHCl_3$); IR (neat): 3031, 2924, 2869, 1769, 750, 739, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4111.

4.2.22. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*galacto*-hept-2-ulosyl-(2→4)-2,3,6-tri-*O*-benzyl-D-glucono-1,5-lactone (13ba). Colorless syrup; $[\alpha]_D^{30}$ +60.6 (*c* 0.83, $CHCl_3$); IR (neat): 3031, 2921, 2870, 1790, 1455, 1098, 737, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4082.

4.2.23. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*galacto*-hept-2-ulosyl-(2→4)-2,3,6-tri-*O*-benzyl-D-galactono-1,5-lactone (13bb). Colorless syrup; $[\alpha]_D^{30}$ +27.4 (*c* 0.85, $CHCl_3$); IR (neat): 3031, 2923, 2870, 1788, 1455, 1100, 737, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4083.

4.2.24. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*galacto*-hept-2-ulosyl-(2→4)-2,3,6-tri-*O*-benzyl-D-mannono-1,5-lactone (13bc). Colorless syrup; $[\alpha]_D^{27}$ +28.6 (*c* 1.02, $CHCl_3$); IR (neat): 3031, 2923, 2872, 1769, 1455, 1101, 1082, 735, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4081.

4.2.25. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*manno*-hept-2-ulosyl-(2→4)-2,3,6-tri-*O*-benzyl-D-glucono-1,5-lactone (13ca). Colorless syrup; $[\alpha]_D^{27}$ +36.9 (*c* 1.06, $CHCl_3$); IR (neat): 3031, 2915, 2867, 1786, 1455, 1100, 1084, 745, 700 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4087.

4.2.26. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*manno*-hept-2-ulosyl-(2→4)-2,3,6-tri-*O*-benzyl-D-galactono-1,5-lactone (13cb). Colorless syrup; $[\alpha]_D^{27}$ −0.43 (*c* 1.07, $CHCl_3$); IR (neat): 3031, 2907, 2869, 1788, 1455, 1111, 739, 700 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4074.

4.2.27. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*manno*-hept-2-ulosyl-(2→4)-2,3,6-tri-*O*-benzyl-D-mannono-1,5-lactone (13cc). Colorless syrup; $[\alpha]_D^{30}$ +9.8 (*c* 1.05, $CHCl_3$); IR (neat): 3031, 2924, 2870, 1767, 1455, 1109, 748, 737, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4080.

4.2.28. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-D-*gluco*-hept-2-ulosyl-(2→6)-2,3,4-tri-*O*-benzyl-D-glucono-1,5-lactone (14aa). Colorless syrup; mp 79–81 °C; $[\alpha]_D^{25}$ +70.3 (*c* 1.00, $CHCl_3$); IR (KBr): 3031, 2867, 1759, 1455, 1123, 1071, 739, 696 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4102.

4.2.29. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-D-*gluco*-hept-2-ulosyl-(2→6)-2,3,4-tri-*O*-benzyl-D-galactono-1,5-lactone (14ab). Colorless syrup; $[\alpha]_D^{25}$ +78.8 (*c* 1.17, $CHCl_3$); IR (neat): 3031, 2921, 2869, 1752, 1455, 1067, 735, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}Na$ 1007.4346, found 1007.4333.

4.2.30. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-D-*gluco*-hept-2-ulosyl-(2→6)-2,3,4-tri-*O*-benzyl-D-mannono-1,5-lactone (14ac). Colorless syrup; $[\alpha]_D^{29}$ +19.8 (*c* 1.07, $CHCl_3$); IR (neat): 3031, 2928, 2870, 1775, 1455, 1096, 739, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4088, found 1023.4066.

4.2.31. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-D-*galacto*-hept-2-ulosyl-(2→6)-2,3,4-tri-*O*-benzyl-D-glucono-1,5-lactone (14ba). Colorless syrup; $[\alpha]_D^{27}$ +66.6 (*c* 1.12, $CHCl_3$); IR (neat): 3031, 2919, 2874, 1757, 1455, 1096, 739, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4086.

4.2.32. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*galacto*-hept-2-ulosyl-(2→6)-2,3,4-tri-*O*-benzyl-D-galactono-1,5-lactone (14bb). Colorless syrup; $[\alpha]_D^{27}$ +75.8 (*c* 1.19, $CHCl_3$); IR (neat): 3031, 2917, 2869, 1750, 1455, 1109, 1057, 745, 737, 745, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}Na$ 1007.4346, found 1007.4362.

4.2.33. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*galacto*-hept-2-ulosyl-(2→6)-2,3,4-tri-*O*-benzyl-D-mannono-1,5-lactone (14bc). Colorless syrup; $[\alpha]_D^{26}$ +23.1 (*c* 1.14, $CHCl_3$); IR (neat): 3031, 2917, 2870, 1775, 1455, 1113, 1098, 735, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4099.

4.2.34. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*manno*-hept-2-ulosyl-(2→6)-2,3,4-tri-*O*-benzyl-D-glucono-1,5-lactone (14ca). Colorless syrup; $[\alpha]_D^{27}$ +57.2 (*c* 1.32, $CHCl_3$); IR

(neat): 3031, 2921, 2867, 1757, 1455, 1094, 1078, 735, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4081.

4.2.35. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*manno*-hept-2-ulosyl-(2→6)-2,3,4-tri-*O*-benzyl-D-galactono-1,5-lactone (14cb). Colorless syrup; $[\alpha]_D^{27}$ +56.8 (*c* 1.28, $CHCl_3$); IR (neat): 3031, 2921, 2869, 1750, 1455, 1104, 737, 698 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4101.

4.2.36. 3,4,5,7-Tetra-*O*-benzyl-1-deoxy-α-D-*manno*-hept-2-ulosyl-(2→6)-2,3,4-tri-*O*-benzyl-D-mannono-1,5-lactone (14cc). Colorless block; mp 111 °C; $[\alpha]_D^{27}$ +22.7 (*c* 0.92, $CHCl_3$); IR (KBr): 3032, 2936, 2346, 1775, 1499, 1456, 1109, 739, 700 cm^{-1}; HRMS (FAB): calcd for $C_{62}H_{64}O_{11}K$ 1023.4086, found 1023.4168.

4.3. General procedure 2: deprotection

To a solution of **11aa** (73.0 mg, 0.07 mmol) in THF (2.5 mL) were added basic alumina (18.0 mg) and 20% $Pd(OH)_2$/C (37.0 mg) under an argon atmosphere, and the mixture was stirred under a hydrogen atmosphere (balloon) at room temperature. After 20 h, to the mixture was added MeOH (0.3 mL) and stirred for 28 h. The reaction mixture was filtered through filter paper, and the filtrate was evaporated and dried to give **16aa** (28.0 mg).

4.3.1. 1-Deoxy-D-*gluco*-hept-2-ulosyl-(2→2)-D-glucono-1,5-lactone (16aa). Colorless amorphous solid; $[\alpha]_D^{23}$ +96.2 (*c* 1.24, CH_3OH); ^1H NMR (600 MHz, CD_3OD): δ 4.61 (m, 1H), 4.52 (m, 1H), 4.48 (m, 1H), 3.99 (m, 1H), 3.86–3.58 (m, 8H), 1.53 (s, 3H, H-1′); ^{13}C NMR (150 MHz, CD_3OD): δ 176.0, 103.5, 81.5, 77.8, 75.2, 75.1, 74.0, 73.8, 71.8, 71.4, 64.4, 62.8, 23.2.

4.3.2. 1-Deoxy-α-D-*gluco*-hept-2-ulosyl-(2→2)-D-galactono-1,5-lactone (16ab). Colorless amorphous solid; $[\alpha]_D^{27}$ +60.8 (*c* 0.23, CH_3OH); ^1H NMR (600 MHz, CD_3OD): δ 4.67 (d, *J*=8.8 Hz, 1H, H-2), 4.36 (dd, *J*=8.3, 8.8 Hz, 1H), 4.15 (dd, *J*=2.2, 8.8 Hz, 1H, H-3), 3.82 (ddd, *J*=2.2, 5.8, 10.2 Hz, 1H), 3.74 (dd, *J*=2.5, 11.6 Hz, 1H), 3.70 (m, 1H), 3.58–3.52 (m, 4H), 3.23 (m, 1H), 3.09 (d, *J*=9.9 Hz, 1H, H-3′), 1.47 (s, 3H, H-1′); ^{13}C NMR (150 MHz, CD_3OD): δ 175.0, 103.3, 81.2, 78.1, 75.7, 75.1, 74.4, 73.4, 71.7, 70.3, 63.5, 62.5, 22.8.

4.3.3. 1-Deoxy-α-D-*gluco*-hept-2-ulosyl-(2→2)-D-mannono-1,5-lactone (16ac). Colorless amorphous solid; $[\alpha]_D^{24}$ +118.6 (*c* 0.5, CH_3OH); ^1H NMR (600 MHz, CD_3OD): δ 4.86 (d, *J*=2.8 Hz, 1H, H-2), 4.12 (ddd, *J*=8.3, 5.8, 2.5 Hz, 1H, H-5), 3.95 (dd, *J*=1.1, 2.8 Hz, 1H, H-3), 3.87 (ddd, *J*=9.9, 2.2, 6.6 Hz, 1H, H-6′), 3.78 (dd, *J*=9.1, 9.6 Hz, 1H, H-4′), 3.75 (dd, *J*=2.5, 12.4 Hz, 1H, H-6), 3.71 (dd, *J*=2.2, 11.8 Hz, 1H, H-7′), 3.7 (dd, *J*=1.1, 8.3 Hz, 1H, H-4), 3.64 (dd, *J*=6.6, 11.8 Hz, 1H, H-7′), 3.49 (dd, *J*=5.8, 12.4 Hz, 1H, H-6), 3.13 (dd, *J*=9.9, 9.1 Hz, 1H, H-5′), 3.11 (d, *J*=9.6 Hz, 1H, H-3′), 1.45 (s, 3H, –CH_3); ^{13}C NMR (150 MHz, CD_3OD): δ 172.5, 103.1, 82.2, 78.3, 77.2, 75.3, 74.9, 72.1, 70.8, 69.9, 63.0, 62.8, 22.7.

4.3.4. 1-Deoxy-α-D-*galacto*-hept-2-ulosyl-(2→2)-D-glucono-1,5-lactone (16ba). Colorless amorphous solid; ^1H NMR (600 MHz, CD_3OD): δ 4.52–4.47 (m, 2H), 4.39 (dd, *J*=4.7, 5.0 Hz, 1H), 3.91 (m, 1H), 3.80 (m, 2H), 3.70–3.66 (m, 2H), 3.63–3.55 (m, 3H), 3.49 (d, *J*=10.2 Hz, 1H, H-3′), 1.46 (s, 3H, H-1′).

4.3.5. 1-Deoxy-α-D-*galacto*-hept-2-ulosyl-(2→2)-D-galactono-1,5-lactone (16bb). Colorless amorphous solid; $[\alpha]_D^{28}$ +60.2 (*c* 1.01, CH_3OH); ^1H NMR (600 MHz, CD_3OD): δ 4.68 (d, *J*=8.8 Hz, 1H, H-2), 4.35 (dd, *J*=8.5, 8.5 Hz, 1H), 4.16 (dd, *J*=2.2, 8.8 Hz, 1H, H-3), 4.04 (m, 1H), 3.81 (m, 1H), 3.71–3.65 (m, 3H), 3.61–3.51 (m, 4H), 1.49 (s, 3H, H-1′); ^{13}C NMR (150 MHz, CD_3OD): δ 175.0, 103.6, 81.2, 75.7, 74.7, 73.4, 73.0, 71.7, 71.2, 70.4, 63.5, 62.9, 22.7.

4.3.6. 1-Deoxy-α-D-*galacto*-hept-2-ulosyl-(2→2)-D-mannono-1,5-lactone (16bc). Colorless amorphous solid; ^1H NMR (600 MHz, CD_3OD): δ 4.91 (d, *J*=2.5 Hz, 1H, H-2), 4.16 (ddd, *J*=8.3, 2.5, 5.8 Hz, 1H, H-5), 4.12 (ddd, *J*=1.4, 4.1, 7.7 Hz, 1H, H-6′), 4.00 (dd, *J*=2.5, 0.8 Hz, 1H, H-3), 3.95 (dd, *J*=9.9, 3.3 Hz, 1H, H-4′), 3.85 (dd, *J*=3.3, 1.4 Hz, 1H, H-5′), 3.79 (dd, *J*=2.5, 12.4 Hz, 1H, H-6), 3.75 (dd, *J*=0.8, 8.3 Hz, 1H, H-4), 3.69 (dd, *J*=5.8, 12.4 Hz, 1H, H-6), 3.67 (dd, *J*=7.7, 11.5 Hz, 1H, H-7′), 3.57 (d, *J*=9.9 Hz, 1H, H-3′), 3.56 (dd, *J*=4.1, 11.5 Hz, 1H, H-7′), 1.45 (s, 3H, H-1′); ^{13}C NMR (150 MHz, CD_3OD): δ 172.8, 103.4, 82.2, 77.3, 74.8, 74.2, 71.6, 71.6, 70.8, 69.8, 63.3, 62.8, 22.6.

4.3.7. 1-Deoxy-α-D-*manno*-hept-2-ulosyl-(2→2)-D-glucono-1,5-lactone (16ca). Colorless amorphous solid; ^1H NMR (600 MHz, CD_3OD): δ 4.46 (m, 1H), 4.38 (m, 1H), 3.90 (m, 1H), 3.77 (dd, *J*=1.7, 11.8 Hz, 1H), 3.72 (dd, *J*=3.3, 9.1 Hz, 1H, H-4′), 3.68 (dd, *J*=3.9, 11.8 Hz, 1H), 3.63–3.59 (m, 3H), 3.55 (d, *J*=3.3 Hz, 1H, H-3′), 3.51 (dd, *J*=1.9, 6.1 Hz, 1H), 3.47 (dd, *J*=9.1, 9.4 Hz, 1H, H-5′), 1.41 (s, 3H, H-1′); ^{13}C NMR (150 MHz, CD_3OD): δ 176.0, 104.6, 81.4, 76.0, 74.4, 73.8, 73.7, 72.5, 71.2, 67.9, 64.3, 63.0, 22.3.

4.3.8. 1-Deoxy-α-D-*manno*-hept-2-ulosyl-(2→2)-D-galactono-1,5-lactone (16cb). Colorless amorphous solid; ^1H NMR (600 MHz, CD_3OD): δ 4.69 (d, *J*=8.8 Hz, 1H, H-2), 4.32 (dd, *J*=8.5, 8.5 Hz, 1H, H-6), 4.14 (dd, *J*=2.5, 8.8 Hz, 1H, H-3), 3.82 (ddd, *J*=2.2, 5.8, 9.9 Hz, 1H, H-6′), 3.78 (dd, *J*=3.3, 9.6 Hz, 1H, H-4′), 3.73 (dd, *J*=2.2, 11.6 Hz, 1H, H-7′), 3.69 (m, 1H, H-5), 3.64 (d, *J*=3.3 Hz, 1H, H-3′), 3.59 (dd, *J*=5.8, 11.6 Hz, 1H, H-7′), 3.56 (m, 1H, H-4), 3.55 (dd, *J*=6.6, 8.5 Hz, 1H, H-6), 3.53 (dd, *J*=9.6, 9.9 Hz, 1H, H-5′) 1.39 (s, 3H, H-1′); ^{13}C NMR (150 MHz, CD_3OD): δ 174.8, 104.4, 81.2, 75.3, 75.1, 74.5, 73.5, 72.6, 70.3, 67.8, 63.6, 62.8, 21.9.

4.3.9. 1-Deoxy-α-D-*manno*-hept-2-ulosyl-(2→2)-D-mannono-1,5-lactone (16cc). Colorless amorphous solid; ^1H NMR (600 MHz, CD_3OD): δ 4.79 (d, *J*=4.4 Hz, 1H, H-2), 4.43 (dd, *J*=4.4, 2.8 Hz, 1H, H-3), 4.24 (dd, *J*=2.8, 9.1 Hz, 1H, H-4), 3.96 (dd, *J*=3.3, 9.6 Hz, 1H, H-4′), 3.89–3.85 (m, 2H, H-5, H-6′), 3.74 (dd, *J*=2.2, 11.6 Hz, 1H, H-7′), 3.71 (d, *J*=3.3 Hz, 1H, H-3′), 3.7 (dd, *J*=2.6, 11.6 Hz, 1H, H-6), 3.57 (dd, *J*=6.6, 11.6 Hz, 1H, H-7′), 3.56 (dd, *J*=5.2, 11.6 Hz, 1H, H-6), 3.47 (dd, *J*=9.6, 9.6 Hz, 1H, H-5′), 1.39 (s, 3H, H-1′); ^{13}C NMR (150 MHz, CD_3OD): δ 176.0,

103.9, 79.7, 75.6, 74.2, 72.5, 71.4, 70.9, 69.5, 68.1, 64.3, 63.1, 21.9.

4.3.10. 1-Deoxy-α-D-*gluco*-hept-2-ulosyl-(2→3)-D-glucono-1,5-lactone (15aa). Colorless amorphous solid; $[\alpha]_D^{28}$ +87.7 (*c* 1.02, CH_3OH); ^1H NMR (600 MHz, CD_3OD): δ 4.57 (dd, *J*=6.9, 6.9 Hz, 1H, H-3), 4.49 (d, *J*=6.9 Hz, 1H, H-2), 4.43 (dd, *J*=6.9, 8.0 Hz, 1H, H-4), 3.89 (m, 1H, H-5), 3.72–3.66 (m, 3H, H-6, H-5′, H-6′), 3.62–3.53 (m, 3H, H-6, H-4′, H-7′), 3.29 (m, 1H, H-7′), 3.14 (d, *J*=9.4 Hz, 1H, H-3′), 1.46 (s, 3H, H-1′); ^{13}C NMR (150 MHz, CD_3OD): δ 176.1, 102.9, 78.8, 77.7, 76.1, 75.3, 74.5, 72.1, 71.4, 71.2, 64.0, 62.2, 21.9.

4.3.11. 1-Deoxy-α-D-*gluco*-hept-2-ulosyl-(2→3)-D-galactono-1,5-lactone (15ab). Colorless amorphous solid; $[\alpha]_D^{25}$ +44.4 (*c* 1.02, CH_3OH); ^1H NMR (600 MHz, CD_3OD): δ 4.52–4.48 (m, 2H), 4.28 (m, 1H), 3.80 (m, 1H), 3.72–3.69 (m, 2H), 3.60–3.50 (m, 4H), 3.17 (dd, *J*=9.4, 9.6 Hz, 1H), 3.10 (dd, *J*=9.6 Hz, 1H, H-2), 1.45 (s, 3H, H-1′); ^{13}C NMR (150 MHz, CD_3OD): δ 175.9, 102.8, 80.1, 78.2, 76.0, 75.1, 75.1, 74.6, 72.1, 70.5, 63.7, 62.7, 22.1.

4.3.12. 1-Deoxy-α-D-*galacto*-hept-2-ulosyl-(2→3)-D-glucono-1,5-lactone (15ba). Colorless amorphous solid; ^1H NMR (600 MHz, CD_3OD): δ 4.58 (dd, *J*=6.9, 7.2 Hz, 1H, H-3), 4.51 (d, *J*=7.2 Hz, 1H, H-2), 4.43 (dd, *J*=6.9, 7.7 Hz, 1H, H-4), 3.95 (m, 1H), 3.87 (m, 1H, H-5), 3.82 (m, 1H), 3.68–3.65 (m, 2H), 3.63–3.52 (m, 4H), 1.46 (s, 3H, H-1′); ^{13}C NMR (150 MHz, CD_3OD): δ 176.1, 103.2, 78.7, 76.0, 74.4, 73.1, 72.1, 71.9, 71.6, 71.0, 64.0, 62.6, 21.9.

4.3.13. 1-Deoxy-D-*galacto*-hept-2-ulosyl-(2→3)-D-galactono-1,5-lactone (15bb). Colorless amorphous solid; ^1H NMR (600 MHz, CD_3OD): δ 4.53 (d, *J*=8.0 Hz, 1H, H-2), 4.48 (dd, *J*=8.0, 8.0 Hz, 1H), 4.27 (dd, *J*=2.5, 8.0 Hz, 1H, H-3), 3.93 (m, 1H), 3.79 (m, 1H, H-4), 3.71–3.69 (m, 2H), 3.66 (dd, *J*=3.0, 10.2 Hz, 1H, H-4′), 3.60–3.54 (m, 3H), 3.50 (dd, *J*=10.2 Hz, 1H, H-3′), 1.48 (s, 3H, H-1′); ^{13}C NMR (150 MHz, CD_3OD): δ 176.0, 103.1, 80.0, 76.0, 74.9, 74.5, 73.7, 71.7, 71.4, 70.6, 63.7, 63.1, 21.9.

4.3.14. 1-Deoxy-α-D-*manno*-hept-2-ulosyl-(2→3)-D-glucono-1,5-lactone (15ca). Colorless amorphous solid; $[\alpha]_D^{26}$ +59.6 (*c* 0.69, CH_3OH); ^1H NMR (600 MHz, CD_3OD): δ 4.63 (d, *J*=7.2 Hz, 1H, H-2), 4.59 (dd, *J*=6.9, 7.2 Hz, 1H, H-3), 4.53 (dd, *J*=4.4, 6.9 Hz, 1H, H-4), 3.87 (m, 1H), 3.78 (dd, *J*=3.3, 9.6 Hz, 1H, H-4′), 3.72–3.69 (m, 2H), 3.64–3.58 (m, 3H), 3.59 (d, *J*=3.3 Hz, 1H, H-3′), 3.52 (dd, *J*=9.6, 9.6 Hz, 1H, H-5′), 1.42 (s, 3H, H-1′); ^{13}C NMR (150 MHz, CD_3OD): δ 176.8, 104.1, 80.1, 76.2, 75.2, 74.7, 73.0, 72.7, 72.3, 67.9, 64.2, 62.6, 20.8.

4.3.15. 1-Deoxy-α-D-*manno*-hept-2-ulosyl-(2→3)-D-galactono-1,5-lactone (15cb). Colorless amorphous solid; $[\alpha]_D^{25}$ +7.39 (*c* 0.57, CH_3OH); ^1H NMR (600 MHz, CD_3OD): δ 4.61 (dd, *J*=7.7, 8.0 Hz, 1H, H-5′), 4.51 (d, *J*=8.0 Hz, 1H, H-2), 4.23 (dd, *J*=1.7, 8.0 Hz, 1H, H-3), 3.80 (dd, *J*=2.2, 11.3 Hz, 1H, H-6), 3.75 (dd, *J*=3.3, 9.6 Hz, 1H, H-7′), 3.67 (dd, *J*=2.2, 7.7 Hz, 1H, H-4′), 3.67 (m, 1H, H-5), 3.57–3.52 (m, 4H, H-4, H-6, H-3′, H-6′), 3.47 (dd, *J*=9.6, 9.9 Hz, 1H, H-7′), 1.44 (s, 3H, H-1′); ^{13}C NMR (150 MHz, CD_3OD): δ 175.9, 104.0, 80.0, 79.6, 75.9, 75.6, 75.0, 74.7, 72.6, 69.7, 68.0, 63.5, 20.8.

4.3.16. 1-Deoxy-α-D-*manno*-hept-2-ulosyl-(2→3)-D-mannono-1,5-lactone (15cc). Colorless amorphous solid; $[\alpha]_D^{28}$ +76.4 (*c* 0.99, CH_3OH); ^1H NMR (600 MHz, CD_3OD): δ 4.61 (dd, *J*=3.3 Hz, 1H, H-2), 4.18 (dd, *J*=3.3, 0.6 Hz, 1H, H-3), 4.15 (ddd, *J*=2.5, 5.0, 9.9 Hz, 1H, H-6′), 4.03 (ddd, *J*=2.5, 5.2, 8.0 Hz, 1H, H-5), 3.82 (m, 1H, H-4), 3.75 (dd, *J*=2.5, 12.7 Hz, 1H, H-6), 3.72 (dd, *J*=3.3, 9.6 Hz, 1H, H-4′), 3.67 (dd, *J*=2.5, 11.8 Hz, 1H, H-7′), 3.62 (dd, *J*=5.0, 12.7 Hz, 1H, H-6), 3.60 (dd, *J*=5.2, 11.8 Hz, 1H, H-7′), 3.48 (d, *J*=3.3 Hz, 1H, H-3′), 3.46 (dd, *J*=9.6, 9.9 Hz, 1H, H-5′), 1.41 (s, 3H, H-1′); ^{13}C NMR (150 MHz, CD_3OD): δ 175.0, 103.3, 82.6, 76.5, 75.2, 74.4, 72.4, 70.2, 68.8, 68.0, 62.9, 62.4, 22.4.

4.3.17. 1-Deoxy-α-D-*gluco*-hept-2-ulosyl-(2→4)-D-glucono-1,5-lactone (20aa). Colorless amorphous solid; $[\alpha]_D^{25}$ +93.0 (*c* 0.96, CH_3OH); ^1H NMR (600 MHz, D_2O): δ 4.65 (m, 1H), 4.41 (m, 1H), 4.15 (m, 1H), 3.74–3.62 (m, 5H), 3.57–3.51 (m, 2H), 3.19 (m, 1H), 3.12 (m, 1H), 1.28 (s, 3H, H-1′); ^{13}C NMR (150 MHz, D_2O): δ 178.0, 102.9, 80.1, 77.0, 74.1, 74.0, 73.8, 73.7, 73.4, 70.7, 62.3, 61.4, 21.4.

4.3.18. 1-Deoxy-α-D-*gluco*-hept-2-ulosyl-(2→4)-D-galactono-1,5-lactone (20ab). Colorless amorphous solid; $[\alpha]_D^{25}$ +135.2 (*c* 0.6, H_2O); ^1H NMR (600 MHz, D_2O): δ 4.46 (m, 2H), 4.40 (m, 1H), 4.04 (m, 1H), 3.84 (m, 1H), 3.70 (m, 1H), 3.66–3.58 (m, 3H), 3.54 (m, 1H), 3.24 (m, 1H), 3.19 (m, 1H), 1.28 (s, 3H, H-1′); ^{13}C NMR (150 MHz, D_2O): δ 177.0, 102.0, 81.0, 77.0, 74.6, 73.6, 73.3, 73.3, 71.4, 70.3, 61.0, 60.5, 21.4.

4.3.19. 1-Deoxy-α-D-*gluco*-hept-2-ulosyl-(2→4)-D-mannono-1,5-lactone (20ac). Colorless amorphous solid; $[\alpha]_D^{25}$ +135.2 (*c* 0.6, H_2O); ^1H NMR (600 MHz, D_2O): δ 4.65 (d, *J*=2.8 Hz, 1H, H-2), 4.29 (m, 1H, H-5), 4.03 (m, 1H, H-3), 3.93 (m, 1H, H-4), 3.71 (dd, *J*=2.2, 12.4 Hz, 1H, H-7′), 3.63–3.59 (m, 2H, H-6, H-6), 3.55 (dd, *J*=5.0, 12.4 Hz, 1H, H-7′), 3.46 (dd, *J*=9.4, 9.6 Hz, 1H), 3.37 (ddd, *J*=2.2, 5.0, 9.9 Hz, 1H, H-6′), 3.21 (dd, *J*=9.6, 9.6 Hz, 1H), 3.10 (d, *J*=9.9 Hz, 1H, H-3′), 1.37 (s, 3H, H-1′); ^{13}C NMR (150 MHz, D_2O): δ 175.2, 102.7, 81.3, 76.4, 73.9, 73.8, 73.4, 70.3, 70.1, 68.9, 61.9, 61.1, 22.1.

4.3.20. 1-Deoxy-α-D-*galacto*-hept-2-ulosyl-(2→4)-D-glucono-1,5-lactone (20ba). Colorless amorphous solid; ^1H NMR (600 MHz, CD_3OD): δ 4.62 (dd, *J*=4.9, 7.1 Hz, 1H, H-4), 4.24 (dd, *J*=3.6, 4.9 Hz, 1H, H-3), 4.21 (d, *J*=3.6 Hz, 1H, H-2), 4.07 (ddd, *J*=1.1, 4.1, 8.2 Hz, 1H, H-6′), 4.05 (ddd, *J*=7.1, 3.3, 3.6 Hz, 1H, H-5), 3.88 (dd, *J*=3.3, 12.7 Hz, 1H, H-6), 3.76 (dd, *J*=3.3, 1.1 Hz, 1H, H-5′), 3.67–3.64 (m, 3H, H-6, H-4′, H-7′), 3.56 (dd, *J*=4.1, 11.3 Hz, 1H, H-7′), 3.48 (d, *J*=9.9 Hz, 1H, H-3′), 1.44 (s, 3H, H-1′).

4.3.21. 1-Deoxy-α-D-*galacto*-hept-2-ulosyl-(2→4)-D-galactono-1,5-lactone (20bb). Colorless amorphous solid; ^1H NMR (600 MHz, CD_3OD): δ 4.99 (dd, *J*=2.2, 5.8 Hz, 1H, H-4), 4.33 (dd, *J*=5.8, 6.3 Hz, 1H, H-3), 4.17 (d, *J*=6.3 Hz, 1H, H-2), 3.96–3.90 (m, 2H), 3.78–3.76 (m, 2H), 3.62–3.55 (m, 4H), 3.46 (d, *J*=9.9 Hz, 1H), 1.46 (s, 3H, H-1′); ^{13}C NMR (150 MHz, CD_3OD): δ 177.1, 102.9, 83.0, 76.3, 75.4, 75.3, 73.4, 73.2, 71.3, 71.1, 62.7, 61.5, 21.6.

4.3.22. 1-Deoxy-α-D-*galacto*-hept-2-ulosyl-(2→4)-D-mannono-1,5-lactone (20bc). Colorless amorphous solid; ^{13}C NMR (150 MHz, CD_3OD): δ 174.8, 103.5, 82.9, 74.7, 74.6, 73.7, 71.6, 71.1, 70.8, 69.6, 63.2, 62.8, 22.9.

4.3.23. 1-Deoxy-α-D-*manno*-hept-2-ulosyl-(2→4)-D-galactono-1,5-lactone (20cb). Colorless amorphous solid; ^{1}H NMR (600 MHz, CD_3OD): δ 4.37 (m, 2H), 4.18 (dd, *J*=8.5, 8.5 Hz, 1H), 4.13 (m, 1H), 4.02 (dd, *J*=5.0, 11.3 Hz, 1H), 3.84–3.80 (m, 2H), 3.71–3.62 (m, 4H), 3.52 (m, 1H), 1.46 (s, 3H, H-1′); ^{13}C NMR (150 MHz, CD_3OD): δ 177.1, 102.9, 83.0, 76.3, 75.4, 75.3, 73.4, 73.2, 71.3, 71.1, 62.7, 61.5, 21.6.

4.3.24. 1-Deoxy-α-D-*manno*-hept-2-ulosyl-(2→4)-D-mannono-1,5-lactone (20cc). Colorless amorphous solid; $[\alpha]_D^{25}$ +76.8 (*c* 0.48, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD): δ 4.47 (d, *J*=3.0 Hz, 1H, H-2), 4.34 (ddd, *J*=5.2, 5.5, 3.3 Hz, 1H, H-5), 4.12 (dd, *J*=2.2, 5.2 Hz, 1H, H-4), 4.01 (ddd, *J*=3.0, 2.2 Hz, 1H, H-3), 3.78 (dd, *J*=3.3, 12.4 Hz, 1H, H-6), 3.74 (dd, *J*=2.2, 11.8 Hz, 1H, H-7′), 3.73–3.69 (m, 2H, H-4′, H-6), 3.59 (dd, *J*=6.1, 11.8 Hz, 1H, H-7′), 3.54 (d, *J*=3.3 Hz, 1H, H-3′), 3.48 (dd, *J*=9.6, 9.9 Hz, 1H, H-5′), 3.39 (ddd, *J*=2.2, 6.1, 9.9 Hz, 1H, H-6′), 1.45 (s, 3H, H-1′); ^{13}C NMR (150 MHz, CD_3OD): δ 174.4, 104.4, 83.7, 76.2, 75.1, 74.8, 72.5, 70.5, 69.5, 67.9, 63.4, 63.0, 21.7.

4.3.25. 1-Deoxy-α-D-*galacto*-hept-2-ulosyl-(2→6)-D-galactono-1,5-lactone (21bb). Colorless amorphous solid; ^{1}H NMR (600 MHz, CD_3OD): δ 4.26 (d, *J*=8.8 Hz, 1H, H-2), 4.17 (dd, *J*=8.3, 8.8 Hz, 1H, H-3), 4.08 (dd, *J*=3.3, 8.3 Hz, 1H, H-4), 3.80–3.78 (m, 2H, H-5, H-5′), 3.70 (dd, *J*=3.3, 9.9 Hz, 1H, H-4′), 3.68 (m, 1H, H-6′), 3.61 (dd, *J*=6.9, 11.3 Hz, 1H), 3.58 (dd, *J*=5.5, 11.3 Hz, 1H), 3.55 (dd, *J*=5.8, 9.6 Hz, 1H), 3.51 (dd, *J*=6.3, 9.6 Hz, 1H), 3.47 (dd, *J*=9.9 Hz, 1H, H-3′), 1.34 (s, 3H, H-1′).

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.07.032.

References and notes

1. Boons, G.-J.; Demchenko, A. V. *Carbohydrate-based Drug Discovery*; Wong, C. H., Ed.; Wiley-VCH: Weinheim, 2003; Vol. 1, pp 55–102.
2. Johnson, L. N.; Hu, S.-H.; Barford, D. *Faraday Discuss.* **1992**, *93*, 131–142.
3. For recent reviews on sialylation: (a) Boons, G.-J.; Demchenko, A. V. *Chem. Rev.* **2000**, *100*, 4539–4565; (b) Hansson, J.; Oscarson, S. *Curr. Org. Chem.* **2000**, *4*, 535–564; (c) Kiefel, M. J.; Itzstein, M. *Chem. Rev.* **2002**, *102*, 471–490.
4. Krog-Jensen, C.; Oscarson, S. *J. Org. Chem.* **1998**, *63*, 1780–1784.
5. Dondoni, A. *Pure Appl. Chem.* **2000**, *72*, 1577–1588 and references cited therein.
6. (a) Li, X. L.; Ohtake, H.; Takahashi, H.; Ikegami, S. *Tetrahedron* **2001**, *57*, 4283–4295; (b) Li, X. L.; Ohtake, H.; Takahashi, H.; Ikegami, S. *Synlett* **2001**, 1885–1888; (c) Namme, R.; Mitsugi, T.; Takahashi, H.; Ikegami, S. *Tetrahedron Lett.* **2005**, *46*, 3033–3036.
7. (a) Li, X. L.; Ohtake, H.; Takahashi, H.; Ikegami, S. *Tetrahedron* **2001**, *57*, 4297–4309; (b) Li, X. L.; Takahashi, H.; Ohtake, H.; Shiro, M.; Ikegami, S. *Tetrahedron* **2001**, *57*, 8053–8066.
8. Yamanoi, T.; Oda, Y.; Yamazaki, I.; Shinbara, M.; Morimoto, K.; Matsuda, S. *Lett. Org. Chem.* **2005**, *2*, 242–246.
9. Other groups also investigated the O-glycosidation of *exo*-glycals: (a) Chang, C.-F.; Yang, W.-B.; Chang, C.-C.; Lin, C.-H. *Tetrahedron Lett.* **2002**, *43*, 6515–6519; (b) Lin, H.-C.; Yang, W.-B.; Gu, Y.-F.; Chen, C.-Y.; Wu, C.-Y.; Lin, C.-H. *Org. Lett.* **2003**, *5*, 1087–1089; (c) Colinas, P. A.; Lieberknecht, A.; Bravo, R. D. *Tetrahedron Lett.* **2002**, *43*, 9065–9068; (d) Colinas, P. A.; Ponzinibbio, A.; Lieberknecht, A.; Bravo, R. D. *Tetrahedron Lett.* **2003**, *44*, 7985–7988.
10. Enzymatic O-glycosidation of heptenitols: Schlesselmann, P.; Fritz, H.; Lehmann, J.; Uchiyama, T.; Brewer, C. F.; Hehre, E. J. *Biochemistry* **1982**, *21*, 6606–6614.
11. O-Glycosidation of heptenitols promoted by iodonium ion, see: Noort, D.; Veeneman, G. H.; Boons, G.-J. P. H.; van der Marel, G. A.; Mulder, G. J.; van Boom, J. H. *Synlett* **1990**, 205–206.
12. For reviews of *exo*-glycal chemistry, see: (a) Taillefumier, C.; Chapleur, Y. *Chem. Rev.* **2004**, *104*, 263–292; (b) Lin, C.-H.; Lin, H.-C.; Yang, W.-B. *Curr. Top. Med. Chem.* **2005**, *5*, 1431–1457.
13. (a) RajanBabu, T. V.; Reddy, G. S. *J. Org. Chem.* **1986**, *51*, 5458–5461; (b) Petasis, N. A.; Lu, S.-P. *Tetrahedron Lett.* **1995**, *36*, 2393–2396.
14. For synthetic procedures of compounds **7**–**10**, see Supplementary data.
15. CCDC 610513 contains the supplementary crystallographic data for compound **14cc**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.
16. Tvaroska, I.; Travel, F. R. Carbon–proton coupling constants in the conformational analysis of sugar molecules. In *Advances in Carbohydrate Chemistry and Biochemistry*; Horton, D., Ed.; Academic: San Diego, CA, 1995; Vol. 51, pp 15–61.
17. Bieg, T.; Szeja, W. *Synthesis* **1985**, 76–77.
18. Liu, H.-J.; Yip, J. *Tetrahedron Lett.* **1997**, *38*, 2253–2256.
19. Schuda, P. F.; Cichowicz, M. B.; Heimann, M. R. *Tetrahedron Lett.* **1983**, *24*, 3829–3830.
20. Binkley, R. W.; Hehmann, D. G. *J. Org. Chem.* **1990**, *55*, 378–380.
21. (a) Hirama, M.; Shimizu, M. *Synth. Commun.* **1983**, *13*, 781–786; (b) Angibeaud, P.; Defaye, J.; Gadelle, A.; Utille, J.-P. *Synthesis* **1985**, 1123–1125.
22. (a) Czech, B. P.; Bartsh, R. A. *J. Org. Chem.* **1984**, *49*, 4076–4078; (b) Sajiki, H.; Hirota, K. *Tetrahedron* **1998**, *54*, 13981–13996.
23. In some cases, decomposition of debenzylated disaccharides **15**, **16**, **20**, and **21** was observed during work-up. Filtration through a celite pad caused decomposition, and therefore filter paper was used for separation of the catalyst.
24. For the peak assignments in ^{1}H and ^{13}C NMR spectra for compounds **11**–**14**, see Supplementary data.