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Unexpected Anomeric Selectivity of a 1-C-Arylglycal Donor in Kdo Glycoside Synthesis

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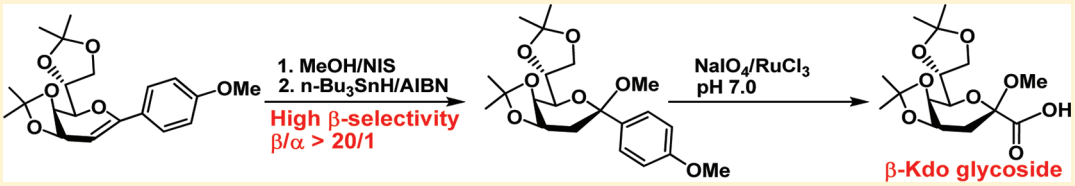
Supporting Information



ABSTRACT: A novel class of 1-*C*-arylglycals was developed and subjected to *N*-iodosuccinimide-mediated glycosylations with alcohols. Unexpectedly, all reactions provided 2-iodo-β-D-ketopyranosides in high yields and excellent stereoselectivity. After removal of the 2-iodide by radical conditions, the aryl group was smoothly oxidized to provide the corresponding β-Kdo glycosides. A mechanism for the stereoselective formation of β-D-ketopyranosides was proposed, which was supported by evidence from X-ray crystallography.

INTRODUCTION

Kdo, or 3-deoxy-D-*manno*-oct-2-ulosonic acid, is an 8-carbon monosaccharide invariably expressed by Gram-negative bacteria which produce characteristic lipopolysaccharides (LPS).[1−4] The negatively charged polysaccharides play a vital role in protecting the structural integrity of the cell membranes against external chemical attack. Kdo is an essential component found at the inner core part of the LPS. Although Kdo glycosides exist as the α-anomer in the majority of the LPS structures (**1**, Figure 1), β-anomeric form has been discovered in *Alteromonas macleodii* ATCC 27126, which is a Gram-negative bacterium.[5] In Gram-positive bacteria, both α- and β-Kdo glycosides[6−8] are found in their capsular polysaccharides. The cytidine 5′-phosphate Kdo (CMP-Kdo, **2**)[9−11] is the key intermediate used by different Kdo transferases to synthesize natural Kdo glycosides.

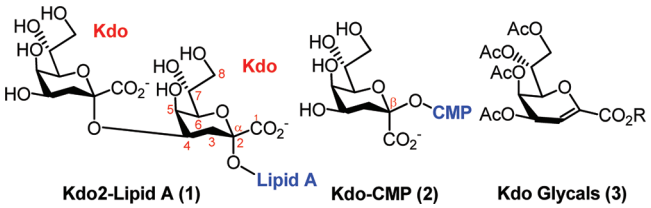


Figure 1. Structures of naturally occurring Kdo glycosides and Kdo-glycals (**3**).

Because of the 3-deoxy functionality as well as the presence of an electron-withdrawing carboxylate at C-1, the chemical synthesis of Kdo glycosides is often hampered by the poor stereocontrol of the anomeric configuration,[6,12,13] and the glycosylation efficiency is commonly hindered by the formation of the α,β-unsaturated ester−Kdo glycals such as **3** (Figure 1), which are formed via a concomitant elimination. Previous work has shown that the use of either glycosyl halides[13−17] or thioglycoside[18] suffered similar problems. This side reaction is extremely wasteful as Kdo monosaccharide is not commercially available, and it is usually chemically synthesized in low yield from the condensation of D-arabinose and oxalacetic acid followed by a nickel-catalyzed decarboxylation.[19,20] The conversion of it to useful donors still requires multistep transformations. Kosma et al. probed the reactivity of peracetylated Kdo glycals. For example, they reacted the peracetylated glycal **3** (R = Me, Figure 1) with acetic acid using *N*-iodosuccinimide (NIS) as an activator[21] and found that compound **3** was relatively unreactive, as the reaction needs to be carried out at 60 °C for 15 h to afford the corresponding α-anomer in 71% yield. The NIS-mediated glycosylation preferred a trans-diaxial addition. In their later work, the same group reported another example of iodoacetoxylation using a peracetylated α(2,8)-linked Kdo disaccharide glycal as a substrate,[22] and they showed that the more complex glycal could also react with acetic acid in a similar manner, but at milder conditions (ambient temperature) to furnish the corresponding trans-diaxial adduct in 77% yield. More recent work from Oscarson's group[18] showed that glycal **3** could react with 2-(4-trifluoroacetamidophenyl)ethanol in a similar addition pattern under the activation of NIS/triflic acid (TfOH) to afford the corresponding α-Kdo glycoside in 53% yield; however, the glycosylation required the use of 4 equiv of TfOH as an activator. Tanaka et al. prepared a more activated glycal which had all the acetyl groups in **3** replaced with benzyl

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groups;[23] this resulted in a more reactive glycal donor because of the electron-donating effect of benzyl groups. Their results showed that the NIS-mediated glycosylations still required a stoichiometric amount of triflic acid to afford the corresponding α-Kdo glycosides in excellent yields and high stereoselectivity. In this work, we report the development of a novel class of 3,4;6,7-di-*O*-isopropylidenated glycals containing a 1-*C*-aryl substituent which showed unexpected β-anomeric selectivity when subjected to NIS-mediated glycosylations, and the oxidation of the 1-*C*-aryl group led to the formation of β-Kdo glycosides.

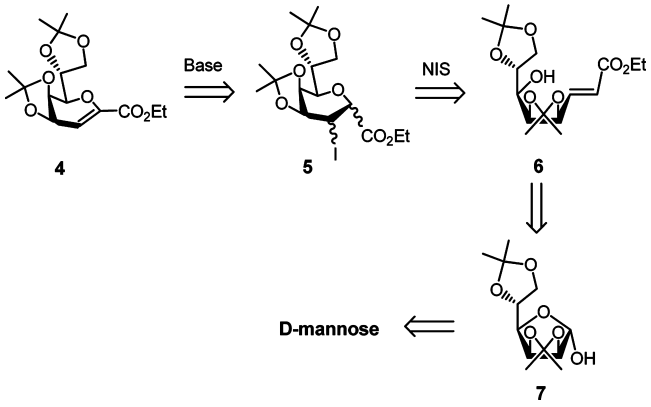
RESULTS AND DISCUSSION

Glycal **4** (Scheme 1) was initially designed to be a donor, and we speculated that it might show different reactivity in NIS-mediated glycosylation compared to **3**, as the glycal **4** contains two isopropylidene protecting groups, which are less electron-withdrawing compared to acetate. Compound **4** could be obtained from a base-catalyzed elimination of the iodide **5**, which in turn could be prepared from an NIS-mediated ring closure of the alkene **6** (Scheme 2).[24,25] The advantage of the route is that the alkene **6** could be synthesized in large amount from the commercially available D-mannose via the 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose **7** as an intermediate.

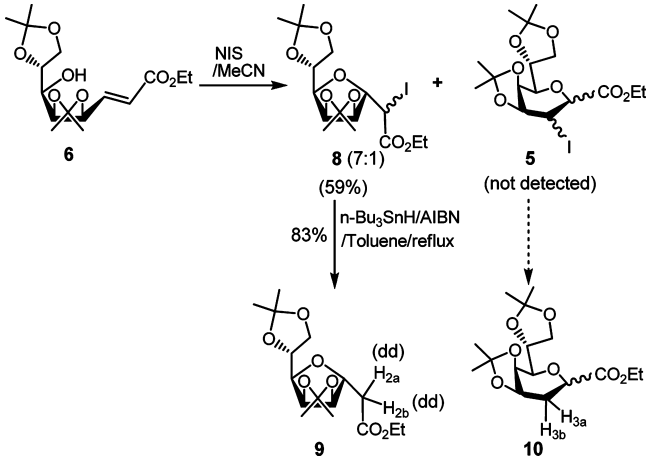
However, previous work from two other groups[26] showed that the NIS-mediated cyclization provided furanosides **8** as a mixture. We also carried out our independent studies by reacting **6** with 1.5 equiv of NIS in acetonitrile; the reaction afforded a major compound which was isolated in 59% by column chromatography. After a tri-*n*-butyltin hydride-mediated radical deiodination, the deoxy compound was obtained and characterized as the furanoside **9**[27] in 83%. The coupling patterns (doublet of doublets) of the two protons attached to the deoxygenated carbon were consistent with the proposed structure. This established that the NIS-mediated ring closure favored the formation of a five-membered ring (compounds **8**), rather than the most desired six-membered ring found in **5**. We attempted to vary reaction conditions by carrying out ring closure at either low or high temperatures or by changing the reaction media to less polar solvents such as dichloromethane; however, all attempts were unsuccessful.

To understand the reason for the preferred furanoside formation in the NIS-mediated ring-closure step on alkene **6**, we hypothesized that the substituent attached to the double bond played a crucial role in controlling the regioselectivity of the ring closure. As illustrated in Scheme 3, the attack of the π-electrons of the alkene on NIS can generate an iodonium which can be considered as a hybrid of two carbocations **A** and **B**. When the substituent R is an electron-withdrawing group such as the carboxyl group found in compound **6**, the carbocation **B** should be less stable than **A** because in **B** the positive charge is closer to the electron-deficient center; consequently, the attack of OH-5 group on the more stable carbocation **A** should be preferred. This led to the preferred formation of furanosides. If our hypothesis holds true, we could substitute the R group with another one that has the ability to stabilize the positive charge developed at C-1—this could force the attack of the OH-5 on

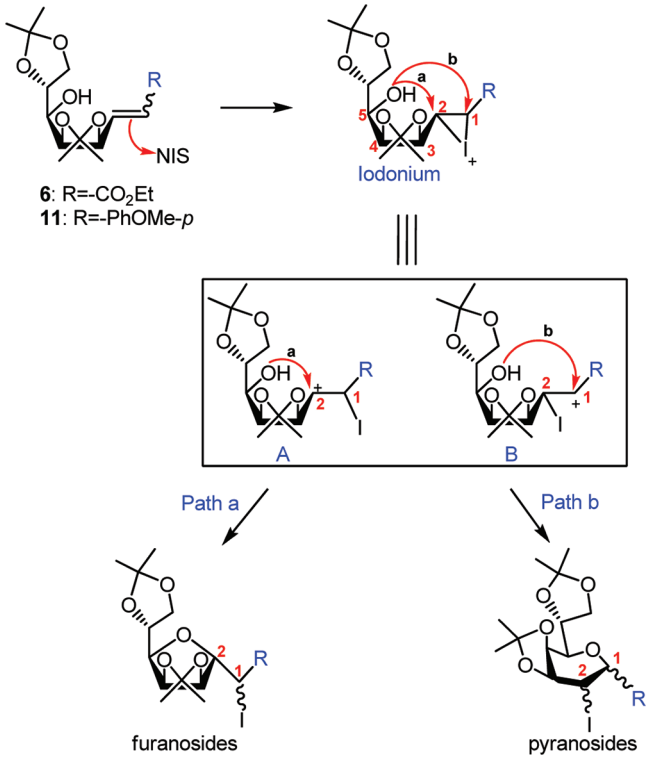
Scheme 1. Initial Plan To Synthesize Kdo Glycal 4



Scheme 2. NIS-Mediated Ring Closure of Alkene 6[26]



Scheme 3. Possible Explanation for the *C*-Furanoside Formation and a Proposed Strategy To Guide the Ring Closure To Form *C*-Pyranosides



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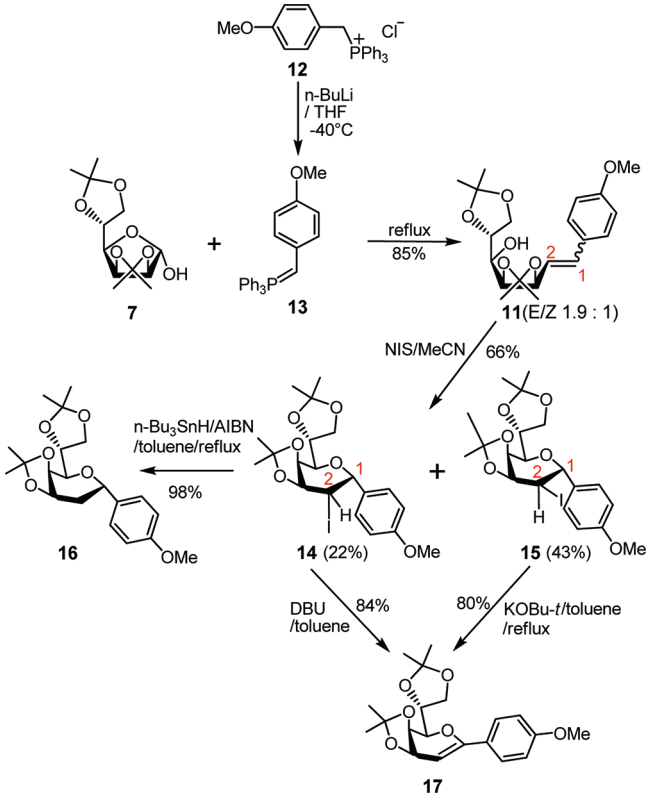
C-1 during the ring-closure step to produce the desired pyranosides. One such substituent is an aryl group because the placement of such a group beside C-1 should make C-1 a benzylic position, thus the positive charge developed at C-1 could be greatly stabilized by the aromatic ring.[28] Previously, thiophenyl group has been used to direct the NIS-mediated cyclizations to pyranosides.[29]

In consideration of our ultimate goal which is to develop an efficient synthesis for Kdo glycosides, this strategy could in fact be advantageous because the aryl group could be considered as a masked carboxyl group, which could be revealed after an oxidation using strong oxidants such ruthenium(III) chloride[30−33] or ozone.[34] To test this idea, we designed the alkene **11** (Scheme 3), which had a *p*-methoxyphenyl group directly attached to the double bond, as our novel synthetic target.

As shown in Scheme 4, starting from the known *p*-methoxybenzyltriphenylphosphonium chloride (**12**),[35] we

Scheme 4. Novel Strategy To Synthesize *C*-Aryl Pyranosides and Form Glycal 17



generated the intermediate ylide **13** by treating with *n*-butyllithium at −40 °C, and after a condensation with the hemiacetal **7**, the alkene **11** was obtained in 85% yield (*E*/*Z* 1.9: 1). Small amounts of pure *E*- and *Z*-isomers were obtained by chromatography on silica gel using 2% dichloromethane−acetone as the eluent.

With the alkene **11** in hand, we investigated the NIS-mediated ring closure reaction. Theoretically, we could obtain eight cyclized products, four furanosides and four pyranosides. However, the NIS-mediated cyclization afforded only two compounds **14** and **15**, which were isolated in 22% (less polar) and 43% (more polar) yields (Scheme 4), respectively. Fortunately, we were able to obtain crystal structures[36] of both cyclized products. As shown from the solved structures (Figure 2), both compounds are *C*-pyranosides which had their *p*-methoxyphenyl group projecting to the bottom face of the

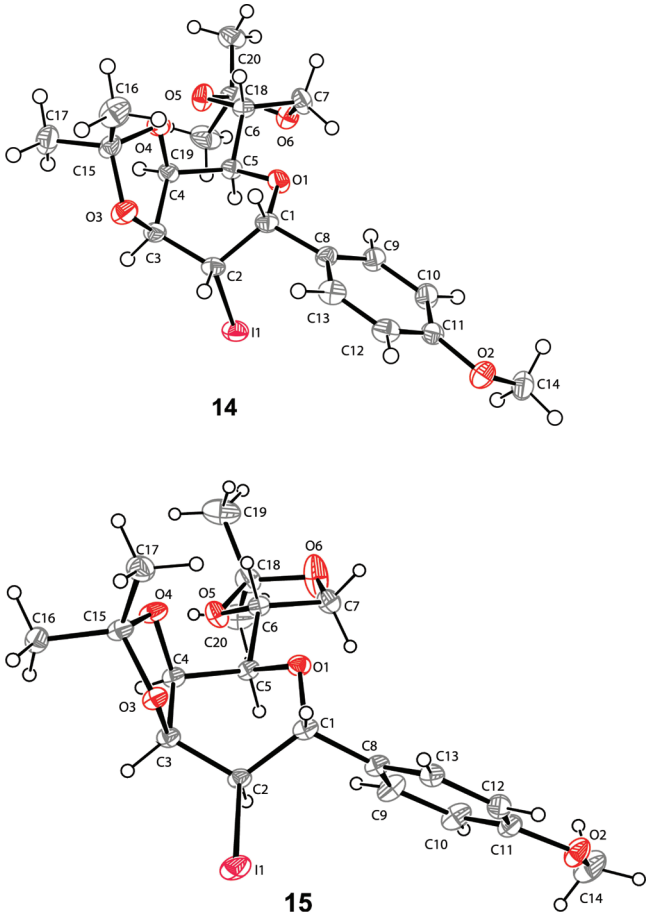


Figure 2. Thermal ellipsoid plot (ORTEP) of compounds **14** and **15**.

pyranose ring. ^{1}H NMR experiment revealed that compound **14** had a small $J_{1,2}$ coupling constant (1.6 Hz), while compound **15** had a larger $J_{1,2}$ (11.2 Hz). A subsequent radical deiodination on either compound resulted in the formation of the same compound **16**

We subsequently studied the base-catalyzed elimination of 2-iodides **14** and **15**. When **14** was subjected to a treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), the glycal **17** was obtained in high yield (84%) after 1 h at room temperature. However, when compound **15** was treated with DBU under the same conditions, no elimination product was formed, even after we extended the reaction time or subjected the reaction at elevated temperatures. Clearly, there are considerable differences in their reactivities when subjected to the base-catalyzed elimination. In the case of **14**, the 2-iodide is in an *anti*-relationship with the proton on C-1; thus, the E_2-elimination is favored. However, for **15**, its 2-iodide is in a *syn*-relationship with the proton on C-1; thus, the E_2-elimination is difficult to proceed. After trying several other conditions, we finally found that the 2-iodide of **15** could be eliminated under much more forcing conditions using the stronger potassium *tert*-butoxide as a base and in refluxing toluene; after 18 h, the same glycal **17** was obtained in 80% yield.

With the glycal **17** in hand, we proceeded to investigate its glycosylation properties with alcohols. As shown in Scheme 5, we first reacted **17** with the methanol as a model reaction; it

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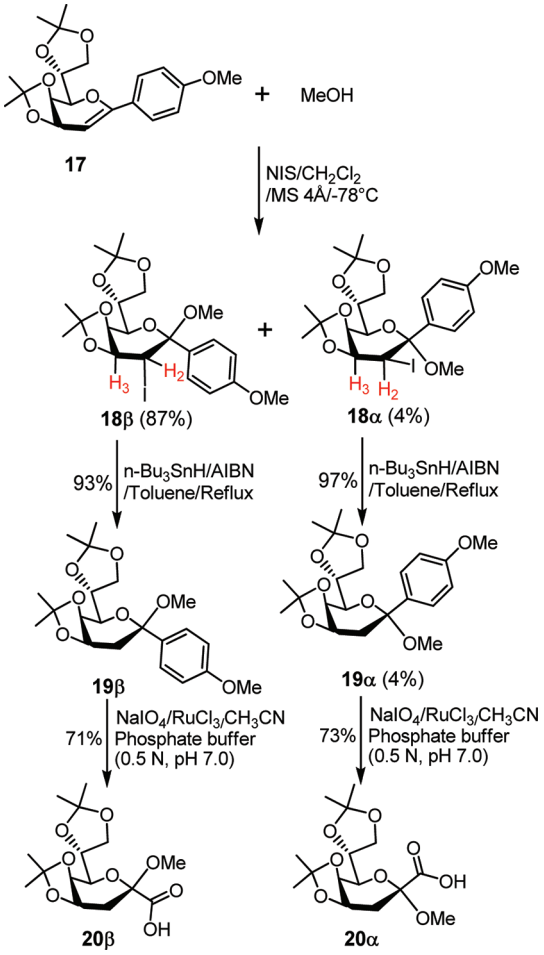
Scheme 5. Synthesis of Methyl Kdo Glycosides from Glycal (17)



was found that under the activation with NIS, the glycal was consumed within 10 min at −78 °C. This illustrates a significant enhancement of reactivity compared to glycal **3**. According to the TLC analysis, a very major compound was formed along with a minor one. The two isomers were isolated in 87% (**18*β***) and 4% (**18*α***) yields, respectively.

To determine the anomeric configuration of formed products, the major isomer was subjected to a radical deiodination as before to afford the 2-deoxy glycoside intermediate in 93% yield. Using the conventional $RhCl_3$−$NaIO_4$ as a reagent,[30] the major product was oxidized to the corresponding Kdo glycoside in 71% yield. Compared with the ^{1}H NMR data of known literature compounds,[37] we concluded that the obtained compound was the *β*-Kdo glycoside **20*β*** (Scheme 5). Thus, logically, compound **19*β*** must be the corresponding deiodinated precursor and the 2-iodo glycoside **18*β*** must have the same anomeric configuration as **19*β***. In a similar manner, we think that the deiodinated **19*α*** must be the precursor of the *α*-Kdo glycoside **20*α***, and the 2-iodo glycoside **18*α*** should have the same anomeric configuration as **19*α***. To assign the configurations of C-2 centers of both **18*β*** and **18*α***, we compared their ^{1}H NMR spectra. The H-2's of both compounds were observed as a doublet; however, compound **18*β*** had a much smaller coupling constant for H-2/H-3 ($J_{2,3}$ = 2.6 Hz) compared to **18*α*** ($J_{2,3}$ = 9.1 Hz). Therefore, we think that the 2-iodo group in **18*β*** must occupy a pseudoaxial position, as this would generate the corresponding *D-glycero-D-galacto*-heptose; according to the molecular model, in the skewed conformation as shown in Scheme 5, the H-2 and H-3 have a dihedral angle of ∼60° which corresponds to a small coupling constant; the 2-iodo group in **18*α*** must occupy a pseudo equatorial position to generate with a *D-glycero-D-talo*-heptose. As shown in Scheme 5, in the skewed conformation, the dihedral angle of H-2 and H-3 in **18*α*** is ∼0°, which corresponds to a larger coupling constant.

The $RhCl_3$−$NaIO_4$-mediated oxidation proceeded smoothly, as the starting material was consumed rapidly according to TLC analysis. However, if no base was present in the reaction mixture, we found that oxidation gave a complex mixture. This could be due to the presence of formic acid which was formed from the oxidation of the aromatic ring; the acid could hydrolyze either the Kdo glycoside or the isopropylidene acetal or both. If we added $NaHCO_3$ into the reaction media, the oxidation was found to be too sluggish. The optimal condition was to perform the oxidation at pH 7 in a 0.5 N phosphate buffer.

Thus, it appeared that the NIS-mediated glycosylations on glycal **17** preferred *β*-anomeric selectivity, which is surprising, as it is opposite to what was previously observed on using glycals such as **3** as a donor. To test the general applicability of our methodology, we reacted glycal **17** with a series of alcohols (Table 1) under the activation with NIS; to simplify the process, the crude 2-iodides were not separated but directly subjected to a radical deiodination to obtain 2-deoxy glycosides which were then purified. As can be seen from Table 1, the glycal **17** is capable of glycosylating both primary and secondary alcohols to afford *β*-glycosides in high yields and with excellent anomeric selectivity. The glycosylations were especially selective for sterically nonhindered primary alcohols (items a−e), which provided the *β*-ketopyranosides in high yields (77−93%) and excellent anomeric selectivity (β/α > 15:1). If the steric bulkiness of the alcohol increased, the anomeric selectivity slightly decreased, but the high *β*-selectivity was maintained (β/α > 8:1, items f−h) and the yields of the glycosides were still high (78−91%). We have also carried out a preliminary study on testing the glycosylation properties of **17** with a glycosyl acceptor **28** (entry i), which has a primary hydroxyl group, and the result showed that the reaction proceeded in an analogous fashion as other primary alcohols to furnish the glycoside **29** in 76% yield (β/α 8:1).

The much improved reactivity of donor **17** compared to **3** could be explained by the presence of the 1-C-aryl group as opposed to the deactivating carboxylic group, which removes electron density from the double bond. However, such difference does not explain the opposite anomeric selectivities between the two donors. Fortunately, we succeeded to obtain a single crystal of glycal **17**.[36] From the solved crystal structure (Figure 3), we clearly observe that one of the methyl groups of the endocyclic isopropylidene is very close to the top face of the glycal double bond. The shortest distance between one of the hydrogen atoms of the methyl to C-2 is 3.14 Å.

Thus, we think that observed anomeric selectivity during NIS-mediated glycosylation could be rationalized by the steric shielding effect of this methyl group. As shown in Scheme 6, the fusing of the endocyclic isopropylidene protecting group forces the pyranose ring of **17** to adopt a skewed conformation; this brings the shaded methyl group closer to the top region of the double bond, which sterically shields the top face. Thus, the nucleophilic attack on NIS prefers to take place from the bottom face of the ring which results in the formation of an

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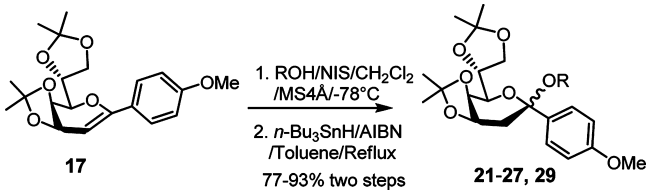
Table 1. Probing the Glycosylation Properties of Glycal 17



17 21-27, 29

Entry	Glycosyl Acceptor	2-Deoxy Glycosides	Yield %[a]	α/β Ratio[b]
a	HOCH$_3$	**19**α/β (R=methyl)	85	<1:20
b	HO	**21**α/β (R=ethyl)	90	<1:20
c	HO	**22**α/β (R=n-butyl)	93	<1:20
d	HO$_{9}$	**23**α/β (R=n-dodecyl)	77	<1:20
e	HO	**24**α/β (R=benzyl)	82	1:15
f	HO	**25**α/β (R=isopropyl)	91	1:10
g	HO	**26**α/β (R=cyclohexyl)	78	1:8
h	HO	**27**α/β (R=cyclopentyl)	91	1:10
i	BnO, BnO, BnO, OH, OMe (**28**)	**29**α/β (R= BnO, BnO, BnO, OMe)	76	1:8

[a]Yields are combined including glycosylation and radical deiodination. [b]Ratios were determined using crude mixtures of 2-iodides by 1D ^{1}H NMR experiment.

intermediate cyclic iodonium (**C**) rather than the unfavorable **D**; a subsequent attack by an alcohol from the top face at the anomeric center produces the observed β-glycosides (**E**) as a major product. In addition, when closely examining the crystal structure of compound **14**, we observed that in the skewed conformation, the 2-iodide and anomeric β-hydrogen in fact have a pseudo trans-diaxial relationship, we conjecture that for

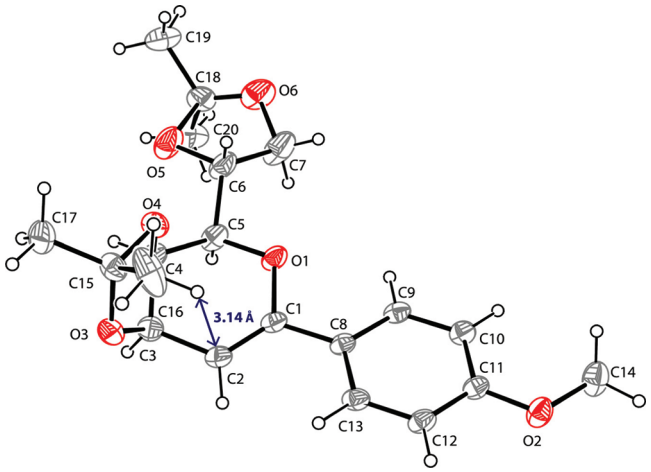


Figure 3. Thermal ellipsoid plot (ORTEP) of glycal **17**.

β-glycosides **E**, the pyranose ring should adopt similar skewed conformation as **14**, this would set the 2-iodide in pseudo trans-diaxial position relative to the anomeric OR group; thus, it appears that although our glycal **17** provides the unexpected β-glycosides compared to glycal **3**, the NIS-mediated glycosylations still follow similar electronic regime.[38] Therefore, we think that it is reasonable to conclude that the origin of the high β-anomeric selectivity for glycal **17** is governed by both steric and stereoelectronic controls. Although the strong stabilization effect of the aromatic ring could also favor the formation of a 2-iodo benzylic carbocation intermediate, this does not appear to be the main glycosylation pathway, as the alcohol could attack the benzylic cation from either the top (β-face) or bottom (α-face). The attack from the bottom face appears to be less sterically hindered; this would lead to the formation of significant amounts of α-glycosides, which we did not observe.

CONCLUSIONS

In conclusion, we have developed a novel glycal donor **17** that contains a 1-*C*-aryl group. Compared to previously known glycal donors, the new glycal **17** exhibits much enhanced reactivity under NIS-mediated glycosylations to furnish β-glycosides in high anomeric selectivity and good to excellent yields. Using the methyl glycoside as an example, we have shown that the aryl group can be oxidized to provide the corresponding β-Kdo glycosides in high yields. We are currently studying other activation conditions or exploring the use of other protecting groups to promote the synthesis of α-Kdo glycosides.

EXPERIMENTAL SECTION

General Methods. Optical rotations were determined in a 5 cm cell at 25 ± 2 °C. $[\alpha]^{25}_{D}$ values are given in units of 10^{-1} deg cm^2 g^{-1}. Analytical TLC was performed on silica gel 60-F_{254} with detection by quenching of fluorescence and/or by charring with 5% sulfuric acid in water or with a ceric ammonium molybdate dip. All commercial reagents were used as supplied unless otherwise stated. Column chromatography was performed on silica gel 60. Organic solutions from extractions were dried with anhydrous Na_2SO_4 prior to concentration under vacuum at <45 °C (bath). NMR spectra were recorded at 300 or 400 MHz (^{1}H) or at 50, 75, or 100 MHz (^{13}C). The first-order proton chemical shifts δ_H and δ_C are reported in δ (ppm) and referenced to either residual $CHCl_3$ (δ_H 7.24, δ_C 77.0, $CDCl_3$), residual CD_3COCD_2H (δ_H 2.06, δ_C 29.92, CD_3COCD_3), or residual CD_2HOD (δ_H 3.30, δ_C 49.5, CD_3OD). ^{1}H and ^{13}C NMR

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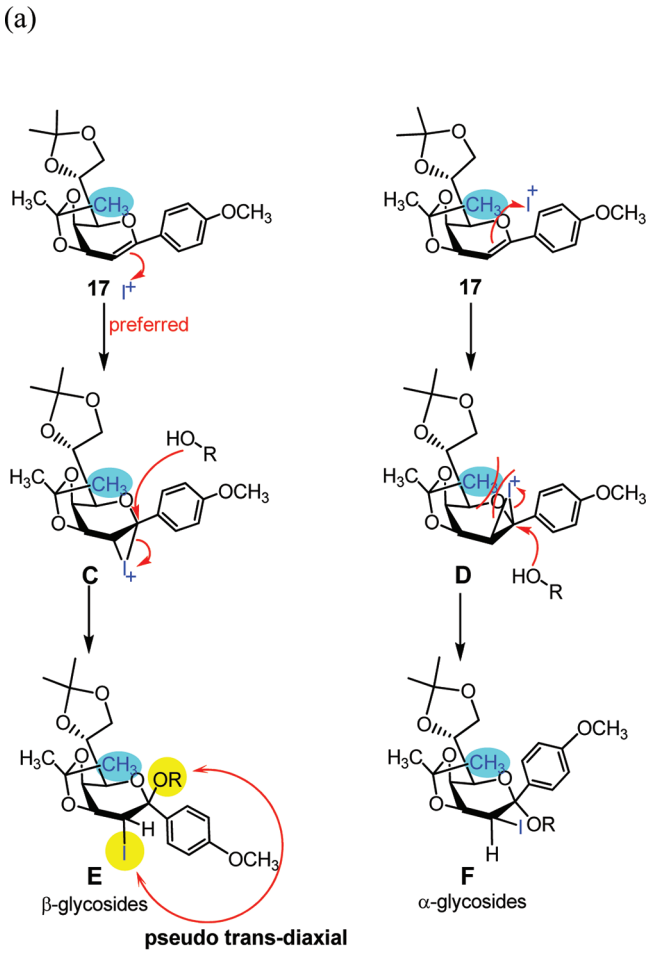
Scheme 6. (a) Proposed Mechanism for the NIS-Mediated Addition of Glycal 17; (b) Molecular Model of β-Glycoside E To Illustrate the Pseudo-Trans-Diaxial Relationship between 2-Iodide and O1



spectra were assigned with the assistance of GCOSY, GHSQC spectra. Mass spectra were obtained by standard EI, CI, or ESI techniques as indicated.

Ethyl 3,6-Anhydro-2-deoxy-2-iodo-4,5:7,8-di-*O*-isopropylidene-D-*glycero*-D-*talo/galacto*-octanoate (8). To a solution of (*E*)-ethyl 2,3-dideoxy-4,5:7,8-di-*O*-isopropylidene-D-*manno*-2-octenoate (7,[24] 500.0 mg, 1.51 mmol) in anhydrous MeCN (3.0 mL) was added NIS (510.8 mg, 2.270 mmol), and the mixture was stirred for 3 h at room temperature. The mixture was diluted with EtOAc, washed with a 10% aqueous solution of $Na_2S_2O_3$, and the organic layer was separated, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel using a mixture of EtOAc–hexane (10:90) as eluent to give compound **8** as a 7:1 mixture (410 mg, 0.899 mmol, 59.4%): R_f 0.44 (EtOAc/hexane 20:80); for the major product, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.86 (dd, 1H, J = 3.4, 6.0 Hz, H-4), 4.74 (dd, 1H, J = 3.6, 6.0 Hz, H-5), 4.38 (d, 1H, J = 10.5 Hz, H-2), 4.34 (ddd, 1H, J = 4.4, 6.1, 7.8 Hz, H-7), 4.27–4.18 (m, 2H, OCH_2), 4.07 (dd, 1H, J = 3.5, 10.5 Hz, H-3), 4.03 (dd, 1H, J = 6.1, 8.8 Hz, H-8b), 3.99 (dd, 1H, J = 4.4, 8.8 Hz, H-8a), 3.59 (dd, 1H, J = 3.6, 7.8 Hz, H-6), 1.49 (s, 3H, $C(CH_3)_2$), 1.41 (s, 3H, $C(CH_3)_2$), 1.36 (s, 6H, 2 × $C(CH_3)_2$), 1.28 (t, 3H, J = 7.2 Hz, OCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8 (CO), 112.8 ($C(CH_3)_2$), 109.3 ($C(CH_3)_2$), 82.9 (C-6), 82.7 (C-3), 81.0 (C-4), 80.3 (C-5), 72.9 (C-7), 66.8 (C-8), 61.9 (OCH_2), 26.9 ($C(CH_3)_2$), 25.8 ($C(CH_3)_2$), 25.3 ($C(CH_3)_2$), 24.6 ($C(CH_3)_2$), 14.8 (C-2), 13.8 (OCH_2CH_3).

Ethyl 3,6-Anhydro-2-deoxy-4,5:7,8-di-*O*-isopropylidene-D-*manno*-octanoate (9). A solution of the above mixture of **8** (200.0 mg, 0.438 mmol), n-Bu_3SnH (153.1 mg, 0.526 mmol), and a catalytic amount AIBN in toluene (4.0 mL) was heated to reflux. After 3 h, the mixture was diluted with CH_2Cl_2, washed with 1% aqueous solution of $NH_3{\cdot}H_2O$, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel using a mixture of EtOAc–hexane (15:85) as eluent to provide compound **9**[27] as a pure compound (120.1 mg, 0.363 mmol, 83.0%): R_f 0.33 (EtOAc/hexane 80:20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.79–4.73 (m, 2H, H-4 + H-5), 4.38 (ddd, 1H, J = 4.8, 6.1, 7.7 Hz, H-7), 4.20–4.12 (m, 2H, $OCH_aH_bCH_3$ + $OCH_aH_bCH_3$) 4.08 (dd, 1H, J = 6.1, 8.6 Hz, H-8a), 4.03 (dd, 1H, J = 4.5, 8.6 Hz, H-8b), 3.94 (m, 1H, H-3), 3.51 (dd, 1H, J = 3.1, 7.7 Hz, H-6), 2.79 (dd, 1H, J = 7.3, 16.8 Hz, H-2a), 2.71 (dd, 1H, J = 6.4, 16.8 Hz, H-2b), 1.47 (s, 3H, $C(CH_3)_2$), 1.44 (s, 3H, $C(CH_3)_2$), 1.37 (s, 3H, $C(CH_3)_2$), 1.33 (s, 3H, $C(CH_3)_2$), 1.27 (t, 3H, J = 7.1 Hz, $OCH_aH_bCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0 (CO), 112.5 ($C(CH_3)_2$), 109.1 ($C(CH_3)_2$), 81.6 (C-6), 81.1 (C-5), 80.7 (C-4), 77.8 (C-3), 73.1 (C-7), 66.9 (C-8), 60.6 (OCH_2CH_3), 33.6 (C-2), 26.9 ($C(CH_3)_2$), 25.7 ($C(CH_3)_2$), 25.3 ($C(CH_3)_2$), 24.7 ($C(CH_3)_2$), 14.2 (OCH_2CH_3); HRMS (ESI) calcd m/z for $C_{16}H_{27}O_7$ ($M + H^+$) 331.17513, found 331.17538. Anal. Calcd for $C_{16}H_{26}O_7$: C, 58.17; H, 7.93. Found: C, 58.30; H, 8.01.

(*E*)-1,2-Dideoxy-3,4:6,7-di-*O*-isopropylidene-1-*C*-(4-methoxyphenyl)-D-*manno*-hept-1-enitol (11E) and (*Z*)-1,2-Dideoxy-3,4:6,7-di-*O*-isopropylidene-1-*C*-(4-methoxyphenyl)-D-*manno*-hept-1-enitol (11Z). A solution of *p*-methoxybenzyltriphenylphosphonium chloride[35] (8.0 g, 19.1 mmol) in anhydrous THF (40 mL) was cooled to −40 °C under Ar, and a solution of *n*-BuLi in hexane (1.6 M, 12.0 mL, 19.2 mmol) was added dropwise. The mixture turned yellow, and the stirring was continued at −40 °C for 1 h to generate the ylide solution. In another flask, the hemiacetal 7 (4.14 g, 15.9 mmol) was dissolved in anhydrous THF (10 mL) under Ar, and a solution of *n*-BuLi in hexane (1.6 M, 10.0 mL, 16.0 mmol) was added dropwise. After being stirred for 10 min, the solution was transferred to the above prepared ylide solution, and the combined mixture was stirred at −40 °C for 1 h, warmed to room temperature within 1 h, and subsequently heated to reflux for 20 h. The reaction mixture was poured into cold water (80 mL) and the mixture was extracted with CH_2Cl_2 (3 × 120 mL); the combined organic solution was washed with saturated brine, dried with anhydrous Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel using a mixture of EtOAc–hexane (10: 90) as eluent to give compound **11** (4.93 g, 13.5 mmol, yield 85%) as a mixture of isomers (*E*/*Z* 1.9: 1 according to NMR): R_f 0.17 (CH_2Cl_2/acetone 95:5). Pure **11*Z*** and **11*E*** could be obtained in small amounts by column chromatography on silica gel using a mixture of CH_2Cl_2/acetone (98:2) as eluent. **Data for 11*Z*:** $[\alpha]^{25}_D$ −168.2 (c 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.12 (m, 2H, H-2_MBn + H-6_MBn), 6.94–6.86 (m, 2H, H-3_MBn + H-5_MBn), 6.75 (d, 1H, J = 11.6 Hz, H-1), 5.97 (dd, 1H, J = 8.8, 11.6 Hz, H-2), 5.20 (ddd, 1H, J = 1.0, 7.7, 8.8 Hz, H-3), 4.55 (dd, 1H, J = 1.0, 8.3 Hz, H-4), 4.15–4.00 (m, 3H, H-7b + H-7a + H-6), 3.78 (s, 3H, OCH_3), 3.59 (ddd, 1H, J = 1.0, 8.3, 9.1 Hz, H-5), 2.35 (d, 1H, J = 9.1 Hz, OH_C-5), 1.56 (s, 3H, $C(CH_3)_2$), 1.40 (s, 3H, $C(CH_3)_2$), 1.36 (s, 6H, 2 × $C(CH_3)_2$); ^{13}C

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NMR (100 MHz, $CDCl_3$) δ 159.1 (C-4_MBn), 133.5 (C-1), 129.7 (2C, C-2 + C-6_ MBn), 128.6 (C-1_MBn), 126.0 (C-2), 113.8 (2C, C-3 + C-5_ MBn), 109.4 ($C(CH_3)_2$), 108.6 ($C(CH_3)_2$), 76.9 (C-4), 76.1 (C-6), 74.0 (C-3), 70.8 (C-5), 67.1 (C-7), 55.3 (OCH_3), 26.9 ($C(CH_3)_2$), 26.6 ($C(CH_3)_2$), 25.3 ($C(CH_3)_2$), 24.2 ($C(CH_3)_2$); HRMS (FAB) calcd m/z for $C_{20}H_{28}O_6$ Na (M + Na^+) 387.1778, found 387.1778. Anal. Calcd for $C_{20}H_{28}O_6$: C, 65.91; H, 7.74. Found: C, 65.56; H, 7.61. **Data for 11*E***: $[\alpha]^{25}_D$ +25.1 (*c* 0.6, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.41−7.34 (m, 2H, H-2_MBn + H-6_MBn), 6.91−6.84 (m, 2H, H-3_MBn + H-5_MBn), 6.70 (d, 1H, *J* = 16.0 Hz, H-1), 6.37 (dd, 1H, *J* = 8.4, 16.0 Hz, H-2), 4.83 (ddd, 1H, *J* = ∼1, 7.5, 8.3 Hz, H-3), 4.39 (dd, 1H, *J* = 1.1, 7.3 Hz, H-4), 4.14−3.96 (m, 3H, H-7b + H-6 + H-7a), 3.82 (s, 3H, OCH_3), 3.51 (ddd, 1H, *J* = 1.1, 8.1, 8.1 Hz, H-5), 2.28 (d, *J* = 8.4 Hz, 1H, OH_C-5), 1.57 (s, 3H, $C(CH_3)_2$), 1.47 (s, 3H, $C(CH_3)_2$), 1.40 (s, 3H, $C(CH_3)_2$), 1.35 (s, 3H, $C(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6 (C-4_MBn), 134.9 (C-1), 128.9 (C-1_MBn), 128.1 (2C, C-2_MBn + C-6_ MBn), 122.5 (C-2), 114.0 (2C, C-3 + C-5_ MBn), 109.3 ($C(CH_3)_2$), 108.5 ($C(CH_3)_2$), 79.3 (C-3), 76.9 (C-4), 76.2 (C-6), 70.8 (C-5), 67.1 (C-7), 55.3 (OCH_3), 26.8 ($C(CH_3)_2$), 26.7 ($C(CH_3)_2$), 25.3 ($C(CH_3)_2$), 24.5 ($C(CH_3)_2$); HRMS (FAB) calcd m/z for $C_{20}H_{28}O_6$ Na (M + Na^+) 387.1778, found 387.1778. Anal. Calcd for $C_{20}H_{28}O_6$: C, 65.91; H, 7.74. Found: C, 65.66; H, 7.91.

1-(2-Deoxy-2-iodo-3,4:6,7-di-*O*-isopropylidene-D-*glycero*-α-D-*galacto*-heptopyranosyl)-4-methoxybenzene (14) and 1-(2-Deoxy-2-iodo-3,4:6,7-di-*O*-isopropylidene-D-*glycero*-α-D-*talo*-heptopyranosyl)-4-methoxybenzene (15). Compound **11** (*E*/*Z* 1.9: 1, 500.0 mg, 1.37 mmol) was treated with NIS (370.0 mg, 1.64 mmol) in MeCN (10.0 mL) for 1 h at room temperature. The mixture was diluted with EtOAc and washed with 10% aqueous solution of $Na_2S_2O_3$. The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel using a mixture of EtOAc−hexane (10: 90) as eluent to yield compounds **14** (150.2 mg, 22.3% yield) and **15** (286.4 mg, 43.2% yield). **Data for 14**: R_f 0.44 (EtOAc/hexane 2:8); $[\alpha]^{25}_D$ +51.5 (*c* 0.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.26−7.19 (m, 2H, H-2_MBn + H-6_MBn), 6.93−6.84 (m, 2H, H-3_MBn + H-5_MBn), 5.00 (dd, 1H, *J* = 1.5, 7.7 Hz, H-3), 4.83 (d, 1H, *J* = 1.6 Hz, H-1), 4.65 (dd, 1H, *J* = 1.7, 7.5 Hz, H-4), 4.45 (dd, 1H, *J* = 1.4, 8.4 Hz, H-5), 4.39 (ddd, 1H, *J* = 4.3, 6.0, 8.4 Hz, H-6), 4.21 (dd, 1H, *J* = 4.3, 8.7 Hz, H-7b), 4.18 (dd, 1H, *J* = 1.6, 1.6 Hz, H-2), 4.17 (dd, 1H, *J* = 6.0, 8.8 Hz, H-7a), 3.81 (s, 3H, OCH_3), 1.59 (s, 3H, $C(CH_3)_2$), 1.49 (s, 3H, $C(CH_3)_2$), 1.43 (s, 3H, $C(CH_3)_2$), 1.41 (s, 3H, $C(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0 (C-4_MBn), 133.5 (C-1_MBn), 126.8 (C-2_MBn + C-6_MBn), 113.3 (C-3_MBn + C-5_MBn), 109.2 (2C, 2 × $C(CH_3)_2$), 77.1 (C-3), 74.6 (C-6), 71.5 (C-4), 70.4 (C-5), 70.0 (C-1), 67.0 (C-7), 55.1 (OCH_3), 36.7 (C-2), 26.9 ($C(CH_3)_2$), 26.6 ($C(CH_3)_2$), 25.4 ($C(CH_3)_2$), 24.0 ($C(CH_3)_2$); HRMS (FAB) calcd m/z for $C_{20}H_{27}IO_6Na$ (M + Na^+) 513.0745, found 513.0740. Anal. Calcd for $C_{20}H_{27}IO_6$: C, 48.99; H, 5.55. Found: C,49.27; H, 5.51. **Data for 15**: R_f 0.27 (EtOAc/hexane 2:8); $[\alpha]^{25}_D$ +58.3 (*c* 0.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.31−7.24 (m, 2H, H-2_MBn + H-6_MBn), 6.92−6.85 (m, 2H, H-3_MBn + H-5_MBn), 5.06 (d, 1H, *J* = 11.2 Hz, H-1), 4.84 (dd, 1H, *J* = 2.5, 8.1 Hz, H-3), 4.53 (dd, 1H, *J* = 1.6, 8.1 Hz, H-4), 4.46 (dd, 1H, *J* = 2.5, 11.3 Hz, H-2), 4.25 (ddd, 1H, *J* = 3.9, 6.2, 8.4 Hz, H-6), 4.03 (dd, 1H, *J* = 6.1, 8.9 Hz, H-7b), 3.92 (dd, 1H, *J* = 3.9, 8.9 Hz, H-7a), 3.83 (s, 3H, OCH_3), 3.80 (dd, 1H, *J* = 1.5, 8.4 Hz, H-5), 1.63 (s, 3H, $C(CH_3)_2$), 1.49 (s, 3H, $C(CH_3)_2$), 1.44 (s, 3H, $C(CH_3)_2$), 1.37 (s, 3H, $C(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6 (C-4_MBn), 133.2 (C-1_MBn), 128.4 (C-2_MBn + C-6_MBn), 113.7 (C-3_MBn + C-5_MBn), 109.4 ($C(CH_3)_2$), 109.3 ($C(CH_3)_2$), 76.3 (C-1), 75.7 (C-3), 73.8 (C-6), 73.6 (C-4), 71.7 (C-5), 67.0 (C-7), 55.2 (OCH_3), 28.8 (C-2), 27.0 ($C(CH_3)_2$), 26.1 ($C(CH_3)_2$), 25.0 ($C(CH_3)_2$), 24.6 ($C(CH_3)_2$); HRMS (FAB) calcd m/z for $C_{20}H_{27}IO_6$ Na (M + Na^+) 513.0745, found 513.0748. Anal. Calcd for $C_{20}H_{27}IO_6$: C, 48.99; H, 5.55. Found: C, 49.25; H, 5.42.

2-Deoxy-3,4:6,7-di-*O*-isopropylidene-α,β-D-*manno*-heptopyranoside-4-methoxybenzene (16). A mixture of compounds **14**/**15** (140.0 mg, 0.286 mmol), obtained as above, was dissolved in toluene (4.0 mL), *n*-Bu_3SnH (124.7 mg, 0.428 mmol) and a catalytic amount of AIBN were added, and the solution was heated to reflux. After 5 h, the mixture was diluted with CH_2Cl_2 and washed with 1% aqueous solution of ammonium hydroxide. The organic layer was separated, dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel using a mixture of EtOAc/hexane (20:80) as eluent to provide pure compound **16** (102 mg, 0.280 mmol, 98.0%): R_f 0.24 (EtOAc/hexane 2:8); $[\alpha]^{25}_D$ +16.8 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.27−7.22 (m, 2H, H-2_MBn + H-6_MBn), 6.91−6.86 (m, 2H, H-3_MBn + H-5_MBn), 5.04 (dd, 1H, *J* = 3.9, 11.8 Hz, H-1), 4.61 (ddd, 1H, *J* = 2.7, 2.8, 8.2 Hz, H-3), 4.45 (dd, 1H, *J* = 1.6, 8.1 Hz, H-4), 4.29 (ddd, 1H, *J* = 5.3, 5.3, 8.2 Hz, H-6), 4.19−4.07 (m, 2H, H-7a + H-7b), 3.81 (s, 3H, OCH_3), 3.69 (dd, 1H, *J* = 1.6, 8.1 Hz, H-5), 2.11 (ddd, 1H, *J* = 2.8, 4.0, 15.2 Hz, H-2eq), 1.92 (ddd, 1H, *J* = 2.8, 11.9, 15.0 Hz, H-2ax), 1.59 (s, 3H, $C(CH_3)_2$), 1.45 (s, 3H, $C(CH_3)_2$) 1.43 (s, 3H, $C(CH_3)_2$), 1.40 (s, 3H, $C(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9 (C-4_MBn), 135.8 (C-1_MBn), 126.7 (C-2_MBn + C-6_MBn), 113.8 (C-3_MBn + C-5_MBn), 109.2 ($C(CH_3)_2$), 108.8 ($C(CH_3)_2$), 74.6 (C-6), 72.2 (C-4), 72.1 (C-5), 70.4 (C-3), 69.8 (C-1), 67.2 (C-7), 55.3 (OCH_3), 33.7 (C-2), 27.0 ($C(CH_3)_2$), 26.3 ($C(CH_3)_2$), 25.3 ($C(CH_3)_2$), 24.5 ($C(CH_3)_2$); HRMS (FAB) calcd m/z for $C_{20}H_{28}O_6Na$ (M + Na^+) 387.1778, found 387.1780. Anal. Calcd for $C_{20}H_{28}O_6$: C, 65.91; H, 7.74. Found: C, 65.52; H, 7.75.

1,5-Anhydro-2-deoxy-3,4:6,7-di-*O*-isopropylidene-1-*C*-(4-methoxyphenyl)-D-*manno*-hept-1-enitol (17). Method 1: Compound **14** (450 mg, 0.918 mmol) was treated with DBU (168 mg, 1.101 mmol) in MeCN (5.0 mL) for 1 h. The pale-pink solution was concentrated under vacuum. The resulted oil was purified by column chromatography on silica gel using a mixture of EtOAc−hexane (85:15) as eluent to provide the desired glycal **17** (280 mg, 0.28 mmol, 84.0%). **Method 2**: To a solution of compound **15** (1.83 g, 3.73 mmol) in toluene (15.0 mL), was added *t*-BuOK (2.09 g, 18.64 mmol), and the mixture was refluxed for 15 h. The dark-red solution was concentrated under the vacuum. The oily residue was purified by column chromatography on silica gel using a mixture of EtOAc−hexane (90:10) as eluent to afford glycal **17** (1.08 g, 2.98 mmol, 80.0% yield): R_f 0.44 (EtOAc/hexane 2:8); $[\alpha]^{25}_D$ +163.9 (*c* 0.9, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.53−7.45 (m, 2H, H-2_MBn + H-6_MBn), 6.91−6.83 (m, 2H, H-3_MBn + H-5_MBn), 5.29 (dd, 1H, *J* = 1.1, 3.5 Hz, H-2), 4.88 (dd, 1H, *J* = 3.5, 6.4 Hz, H-3), 4.56−4.48 (m, 2H, H-4 + H-6), 4.28−4.22 (m, 2H, H-7a + H-7b), 3.92 (dd, 1H, *J* = 1.1, 8.1 Hz, H-5), 3.81 (s, 3H, OCH_3), 1.48 (s, 3H, $C(CH_3)_2$), 1.45−1.38 (m, 9H, $C(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2 (C-4_MBn), 152.6 (C-1), 127.0 (C-1_MBn), 126.4 (2C, C-2_MBn + C-6_MBn), 113.6 (2C, C-3_MBn + C-5_MBn), 110.4 ($C(CH_3)_2$), 109.4 ($C(CH_3)_2$), 96.9 (C-2), 76.2 (C-5), 74.2 (C-6), 71.9 (C-4), 69.8 (C-3), 66.8 (C-7), 55.2 (OCH_3), 28.1 ($C(CH_3)_2$), 27.0 ($C(CH_3)_2$), 26.9 ($C(CH_3)_2$), 25.3 ($C(CH_3)_2$); HRMS (ESI) calcd m/z for $C_{20}H_{27}O_6$ (M + H^+) 363.1808, found 363.1813. Anal. Calcd for $C_{20}H_{26}O_6$: C, 66.28; H, 7.23. Found: C 65.98; H, 7.35.

1-(Methyl 2-deoxy-2-iodo-3,4:6,7-di-*O*-isopropylidene-D-*talo*-α-D-*galacto*-heptopyranoside)-4-methoxybenzene (18α) and 1-(Methyl 2-deoxy-2-iodo-3,4:6,7-di-*O*-isopropylidene-D-*glycero*-β-D-*galacto*-heptopyranoside)-4-methoxybenzene (18β). To a solution of glycal **17** (100 mg, 0.28 mmol) and anhydrous methanol (60 μL, 1.46 mmol) in anhydrous CH_2Cl_2 (1.5 mL) was added molecular sieves 3 Å (200 mg) under argon. The mixture was stirred at −78 °C for 30 min, and NIS (93.2 mg, 0.414 mmol) was added. After the mixture was stirred for 10 min, the insoluble material was filtered off, and the filtrate was concentrated under reduced pressure. The ^1H NMR of the crude mixture showed the β-isomer was predominantly formed (**18β**/**18α** > 20:1). The residue was purified by column chromatography on silica gel using a mixture of hexane−EtOAc (90:10) as eluent to afford the glycoside **18β** (124.5 mg, 86.7% yield) and glycoside **18α** (6.0 mg, 4.2% yield). **Data for 18β isomer:** R_f 0.14 (EtOAc/hexane 1:9); $[\alpha]^{25}_D$ +40.3 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.48−7.34 (m, 2H, H-2_MBn + H-6_MBn), 6.93−6.81 (m, 2H, H-3_MBn + H-5_MBn), 5.12 (dd, 1H, *J* = 2.5, 7.8 Hz, H-3), 4.55 (d, 1H, *J* = 2.6 Hz, H-2), 4.53 (dd, 1H, *J* = 2.6, 7.9 Hz, H-4), 4.44 (ddd, 1H, *J* = 5.1, 6.3, 7.4 Hz, H-6), 4.34 (m, 1H, H-5),

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4.28 (dd, 1H, J = 5.0, 8.6 Hz, H-7b), 4.20 (dd, 1H, J = 6.2, 8.8 Hz, H-7a), 3.82 (s, 3H, OCH_3_MBn), 3.06 (s, 3H, OCH_3), 1.57 (s, 3H, $C(CH_3)_2$), 1.47 (s, 3H, $C(CH_3)_2$), 1.42 (s, 3H, $C(CH_3)_2$), 1.38 (s, 3H, $C(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7 (C-4_MBn), 134.5 (C-1_MBn), 128.3 (C-2_MBn + C-6_MBn), 113.2 (C-3_MBn + C-5_MBn), 109.8 ($C(CH_3)_2$), 109.3 ($C(CH_3)_2$), 100.7 (C-1), 77.8 (C-4),75.0 (C-6), 71.6 (C-5), 71.0 (C-3), 66.8 (C-7), 55.2 (OCH_3_MBn), 50.5 (OCH_3), 33.0 ($C(CH_3)_2$), 26.9 ($C(CH_3)_2$), 25.6 ($C(CH_3)_2$), 25.5 ($C(CH_3)_2$), 24.7 ($C(CH_3)_2$). **Data for the 18α isomer:** R_f 0.17 (EtOAc/hexane 1: 9); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.45 (m, 2H, H-3_MBn + H-5_MBn), 6.93−6.86 (m, 2H, H-2_MBn + H-6_MBn), 4.74 (dd, 1H, J = 5.0, 9.2 Hz, H-3), 4.50 (ddd, 1H, J = 5.6, 5.6, 6.8 Hz, H-6), 4.22 (dd, 1H, J = 2.4, 5.0 Hz, H-4), 4.17−4.12 (m, 2H, H-7b + H-7a), 4.07 (dd, 1H, J = 2.5, 6.9 Hz, H-5), 3.83 (s, 3H, OCH_3_MBn), 3.82 (d, 1H, J = 9.1 Hz, H-2), 3.21 (s, 3H, OCH_3), 1.52 (s, 3H, $C(CH_3)_2$), 1.43 (s, 6H, 2 × $C(CH_3)_2$), 1.41 (s, 3H, $C(CH_3)_2$); ^{13}C NMR (100 MHz, CDCl3) δ 159.7 (C-1_MBn), 130.0 (C-4_MBn), 129.4 (C-3_MBn + C-5_MBn), 112.9 (C-2_MBn + C-6_MBn), 109.3 (2C, 2 × $C(CH_3)_2$), 101.5 (C-1), 80.0 (C-3), 74.8 (C-6), 72.8 (C-4), 69.0 (C-5), 66.4 (C-7), 55.2 (OCH_3_MBn), 50.4 (OCH_3), 41.2 (C-2), 28.4 ($C(CH_3)_2$), 26.9 ($C(CH_3)_2$), 26.3 ($C(CH_3)_2$), 25.6 ($C(CH_3)_2$). Anal. Calcd for $C_{21}H_{29}IO_7$: C, 48.47; H, 5.62. Found: C 48.83; H, 5.83.

1-(Methyl 2-deoxy-3,4:6,7-di-*O*-isopropylidene-α-D-*manno*-heptopyranoside)-4-methoxybenzene (19α) and 1-(Methyl 2-deoxy-3,4:6,7-di-*O*-isopropylidene-β-D-*manno*-heptopyranoside)-4-methoxybenzene (19β). Compound **18β** (100.0 mg, 0.192 mmol) was deiodinated with n-Bu_3SnH (78 μL, 0.288 mol) and a catalytic amount of AIBN in toluene (2.0 mL) as before. Glycoside **19β** (70.6 mg, 93.2% yield) was obtained as a colorless foam by column chromatography on silica gel using a mixture of hexane/EtOAc/TEA (95:5:2) as eluent. The corresponding **18α** anomer could be deiodinated in the same manner. **Data for 19β isomer:** R_f 0.31 (EtOAc/hexane 20:80); $[\alpha]^{25}_D$ +1.0 (c 4.46, CH_2Cl_2); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.49−7.34 (m, 2H, H-2_MBn + H-6_MBn), 7.02−6.87 (m, 2H, H-3_MBn + H-5_MBn), 4.42 (ddd, 1H, J = 4.5, 4.5, 7.6 Hz, H-3), 4.38−4.29 (m, 2H, H-6 + H-4), 4.24 (dd, 1H, J = 6.2, 8.4 Hz, H-7b), 4.14 (dd, 1H, J = 6.4, 8.6 Hz, H-7a), 3.83−3.77 (m, 4H, OCH_3_MBn + H-5), 2.99 (s, 3H, OCH_3), 2.23 (dd, 1H, J = 4.1, 14.9 Hz, H-2b), 2.01 (dd, 1H, J = 4.8, 15.0 Hz, H-2a), 1.48 (s, 3H, $C(CH_3)_2$), 1.40 (s, 3H, $C(CH_3)_2$), 1.35 (s, 3H, $C(CH_3)_2$), 1.29 (s, 3H, $C(CH_3)_2$); ^{13}C NMR (100 MHz, acetone-d_6) δ 160.5 (C-4_MBn), 135.0 (C-1_MBn), 128.7 (C-2_MBn + C-6_MBn), 114.4 (C-3_MBn + C-5_MBn), 109.5 ($C(CH_3)_2$), 109.3 ($C(CH_3)_2$), 101.1 (C-1), 76.6 (C-6), 73.3 (C-5), 72.5 (C-4), 71.5 (C-3), 67.0 (C-7), 55.6 (OCH_3_MBn), 49.2 (OCH_3), 38.3 (C-2), 27.0 ($C(CH_3)_2$), 26.8 ($C(CH_3)_2$), 26.1 ($C(CH_3)_2$), 25.5 ($C(CH_3)_2$); HRMS (EI) calcd m/z for $C_{20}H_{27}O_6$ (M^+ − OCH_3) 363.1808, found 363.1800. Anal. Calcd for $C_{21}H_{30}O_7$: C, 63.94; H, 7.67. Found: C, 63.98; H, 7.78. **Data for 19α isomer:** R_f 0.39 for (EtOAc/hexane 20:80); $[\alpha]^{25}_D$ +89.8 (c 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.45−7.37 (m, 2H, H-2_MBn + H-6_MBn), 6.95−6.88 (m, 2H, H-3_MBn + H-5_MBn), 4.48 (ddd, 1H, J = 5.9, 5.9, 7.3 Hz, H-3), 4.44 (ddd, 1H, J = 6.1, 6.2, 6.2 Hz, H-6), 4.27 (dd, 1H, J = 2.3, 6.1 Hz, H-4), 4.19−4.11 (m, 2H, H-7b + H-7a), 3.94 (dd, 1H, J = 2.3, 6.3 Hz, H-5), 3.81 (s, 3H, OCH_3), 2.25 (dd, 1H, J = 5.6, 14.2 Hz, H-2b), 1.86 (dd, 1H, J = 7.3, 14.1 Hz, H-2a), 1.40 (s, 3H, $C(CH_3)_2$), 1.35 (s, 3H, $C(CH_3)_2$), 1.34 (s, 3H, $C(CH_3)_2$), 1.27 (s, 3H, $C(CH_3)_2$); ^{13}C NMR (100 MHz, acetone-d_6) δ 160.3 (C-4_MBn), 135.1 (C-1_MBn), 128.4 (C-2_MBn + C-6_MBn), 114.2 (C-3_MBn + C-5_MBn), 109.4 ($C(CH_3)_2$), 109.2 ($C(CH_3)_2$), 101.3 (C-1), 76.0 (C-6), 72.1 (C-4), 71.8 (C-3), 70.7 (C-5), 67.3 (C-7), 55.6 (OCH_3_MBn), 49.2 (OCH_3), 40.7 (C-2), 27.9 ($C(CH_3)_2$), 27.2 ($C(CH_3)_2$), 26.1 ($C(CH_3)_2$), 25.9 ($C(CH_3)_2$); HRMS (EI) calcd m/z for $C_{20}H_{27}O_6$ (M^+ − OCH_3) 363.1808, found 363.1808.

General Procedure for Sequential NIS-Mediated Glycosylation with Glycal 17 with Alcohols and Radical Deiodination. A mixture containing compound **17** (0.40 mmol), alcohol (0.48−1.2 mmol), and molecular sieves 4 Å (200.0 mg) in anhydrous CH_2Cl_2 (2.0 mL) was stirred under argon for 30 min and cooled to −50 °C, NIS (0.8 mmol) was added, and the reaction was continued for 15 min at the same temperature. After filtration, the organic solution was concentrated. The residue was dissolved in EtOAc (20 mL), and the organic solution was washed with an aqueous solution of NaS_2O_3 (10%) and dried over anhydrous Na_2SO_4. The ^{1}H NMR of the crude mixture was recorded to determine anomeric ratios of formed glycosides, and the mixture was purified by column chromatography on silica gel using a mixture of hexane/EtOAc (90:10) as eluent to afford the desired 2-iodoglycosides as an anomeric mixture. The above-obtained 2-iodoglycoside (0.19 mmol) was deiodinated with n-Bu_3SnH (0.376 mmol) and a catalytic amount of AIBN in toluene (3.0 mL) as before. The desired 2-iodoglycoside was obtained by column chromatography on silica gel using a mixture of hexane/triethylamine (98: 2) as eluent.

1-(Ethyl 2-deoxy-3,4:6,7-di-*O*-isopropylidene-β-D-*manno*-heptopyranoside)-4-methoxybenzene (21β) and 1-(Ethyl 2-deoxy-3,4:6,7-di-*O*-isopropylidene-α-D-*manno*-heptopyranoside)-4-methoxybenzene (21α). Compound **17** (150 mg, 0.414 mmol), ethanol (200 μL, 3.43 mmol), and NIS (195 mg, 0.867 mmol) were reacted in a manner similar to that used above. The ^{1}H NMR of the crude mixture was recorded to determine anomeric ratios of formed glycosides, and the mixture was passed through a thin layer of silica gel using hexane/EtOAc (90:10) as eluent to afford the desired 2-iodoglycosides as an anomeric mixture. Part of the 2-iodoglycosides (0.19 mmol) was deiodinated with n-Bu_3SnH (100 μL, 0.376 mmol) and a catalytic amount of AIBN as before, and the desired 2-deoxyglycosides **21β** and **21α** were obtained by column chromatography on silica gel using a mixture of hexane/triethylamine (98: 2) as eluent (142.3 mg, **21β**/**21α**: > 20/1, yield 91%). A small amount of pure **21β** and **21α** was obtained by repeated column chromatography. **Data for 21β**: R_f 0.35 (EtOAc/hexane 20:80); $[\alpha]^{25}_D$ +3.6 (c 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.48−7.40 (m, 2H, H-2_MBn + H-6_MBn), 6.98−6.90 (m, 2H, H-3_MBn + H-5_MBn), 4.41 (ddd, 1H, J = 4.5, 4.5, 7.4 Hz, H-3), 4.34 (ddd, 1H, J = 5.6, 6.4, 6.4 Hz, H-6), 4.27 (dd, 1H, J = 2.0, 7.5 Hz, H-4), 4.23 (dd, 1H, J = 6.4, 8.4 Hz, H-7b), 4.09 (dd, 1H, J = 6.4, 8.4 Hz, H-7a), 3.80 (s, 3H, OCH_3), 3.77 (dd, 1H, J = 1.9, 5.4 Hz, H-5), 3.54 (dq, 1H, J = 7.1, 9.5 Hz, $OCH_aH_bCH_3$), 3.04 (dq, 1H, J = 7.1, 9.5 Hz, $OCH_aH_bCH_3$), 2.27 (dd, 1H, J = 4.4, 15.0 Hz, H-2b), 2.03 (dd, 1H, J = 4.7, 14.8 Hz, H-2a), 1.47 (s, 3H, $C(CH_3)_2$), 1.37 (s, 3H, $C(CH_3)_2$), 1.34 (s, 3H, $C(CH_3)_2$), 1.29 (s, 3H, $C(CH_3)_2$), 1.01 (t, 3H, J = 7.1 Hz, OCH_2CH_3); ^{13}C NMR (100 MHz, acetone-d_6) δ 159.4 (C-4_MBn), 134.6 (C-1_MBn), 127.5 (C-2_MBn + C-6_MBn), 113.4 (C-3_MBn + C-5_MBn), 108.4 ($C(CH_3)_2$), 108.2 ($C(CH_3)_2$), 100.2 (C-1), 75.7 (C-6), 72.2 (C-5), 71.6 (C-4), 70.7 (C-3), 65.8 (C-7), 56.9 (OCH_2), 54.6 (OCH_3), 37.2 (C-2), 26.0 (2C, $C(CH_3)_2$), 25.2 ($C(CH_3)_2$), 24.5 ($C(CH_3)_2$), 15.0 (OCH_2CH_3); HRMS (EI) calcd m/z for $C_{22}H_{32}O_7$ (M^+) 408.2148, found 408.2140. **Data for 21α:** R_f 0.42 (EtOAc/hexane 20:80); $[\alpha]^{25}_D$ +68.1 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.46−7.39 (m, 2H, H-2_MBn + H-6_MBn), 6.94−6.88 (m, 2H, H-3_MBn + H-5_MBn), 4.50 (ddd, 1H, J = 5.9, 5.9, 7.3 Hz, H-3), 4.44 (ddd, 1H, J = 6.1, 6.2, 6.2 Hz, H-6), 4.28 (dd, 1H, J = 2.4, 6.0 Hz, H-4), 4.15 (dd, 1H, J = 6.2, 12.1 Hz, H-7a), 4.13 (dd, 1H, J = 5.9, 12.0 Hz, H-7b), 4.13 (dd, 1H, J = 5.9, 8.6 Hz, H-7a), 3.94 (dd, 1H, J = 2.4, 6.4 Hz, H-5), 3.80 (s, 3H, OCH_3), 3.29 (dq, 1H, J = 7.1, 9.5 Hz, $OCH_aH_bCH_3$), 3.02 (dq, 1H, J = 7.1, 9.7 Hz, $OCH_aH_bCH_3$), 2.26 (dd, 1H, J = 5.7, 14.1 Hz, H-2b), 1.89 (dd, 1H, J = 7.5, 14.1 Hz, H-2a), 1.38 (s, 3H, $C(CH_3)_2$), 1.34 (s, 3H, $C(CH_3)_2$), 1.33 (s, 3H, $C(CH_3)_2$), 1.26 (s, 3H, $C(CH_3)_2$), 1.08 (t, 3H, J = 7.0 Hz, CH_3); ^{13}C NMR (100 MHz, acetone-d_6) δ 160.3 (C-4_MBn), 135.8 (C-1_MBn), 128.2 (C-2_MBn + C-6_MBn), 114.2 (C-3_MBn + C-5_MBn), 109.4 ($C(CH_3)_2$), 109.2 ($C(CH_3)_2$), 101.1 (C-1), 76.1 (C-6), 72.1 (C-4), 71.8 (C-3), 70.7 (C-5), 67.2 (C-7), 57.5 (OCH_2), 55.6 (OCH_3), 40.9 (C-2), 27.9 ($C(CH_3)_2$), 27.2 ($C(CH_3)_2$), 26.1 ($C(CH_3)_2$), 25.9 ($C(CH_3)_2$), 15.5 (OCH_2CH_3); HRMS (EI) calcd m/z for $C_{22}H_{32}O_7$ (M^+) 408.2148, found 408.2144.

1-(Butyl 2-deoxy-3,4:6,7-di-*O*-isopropylidene-β-D-*manno*-heptopyranoside)-4-methoxybenzene (22β) and 1-(Butyl 2-deoxy-3,4:6,7-di-*O*-isopropylidene-α-D-*manno*-heptopyranoside)-4-methoxybenzene (22α). Compound **17** (150 mg, 0.414

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mmol), *n*-butanol (200 μL, 2.19 mmol), and NIS (195 mg, 0.867 mmol) were reacted in a manner similar to that used above. The obtained mixture was deiodinated with *n*-Bu_3SnH (100 μL, 0.376 mmol) in a similar manner to afford a mixture of compounds **22*β*** and **22*α*** in 93% yield (**22*β*/22*α***: > 20/1) using a mixture of hexane/triethylamine (98: 2) as eluent. **Data for 22*β*:** $[\alpha]^{25}_D$ +6.1 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, acetone-d_6) δ 7.49−7.42 (m, 2H, H-2_MBn + H-6_MBn), 6.97−6.90 (m, 2H, H-3_MBn + H-5_MBn), 4.41 (ddd, 1H, *J* = 4.8, 4.8, 7.3 Hz, H-3), 4.35 (ddd, 1H, *J* = 5.2, 6.5, 6.5 Hz, H-6), 4.27−4.20 (m, 2H, H-4 + H-7b), 4.12 (dd, 1H, *J* = 6.4, 8.6 Hz, H-7a), 3.80 (s, 3H, OCH_3), 3.76 (dd, 1H, *J* = 2.0, 5.1 Hz, H-5), 3.51 (dt 1H, *J* = 6.3, 9.2 Hz, $OCH_aH_bCH_2$), 3.00 (dt, 1H, *J* = 6.6, 9.2 Hz, $OCH_aH_bCH_2$), 2.30 (dd, 1H, *J* = 4.9, 15.0 Hz, H-2b), 2.09 (dd, 1H, *J* = 4.7, 15.0 Hz, H-2a), 1.49 (s, 3H, $C(CH_3)_2$), 1.45−1.20 (m, 13H, $OCH_aH_bCH_2CH_2CH_3$ + 3 × $C(CH_3)_2$), 0.80 (t, 3H, *J* = 7.3 Hz, CH_3_butyl); ^{13}C NMR (100 MHz, Acetone-d_6) δ 159.4 (C-4_MBn), 134.2 (C-1_MBn), 127.6 (C-2_MBn + C-6_MBn), 113.4 (C-3_MBn + C-5_MBn), 108.4 ($C(CH_3)_2$), 108.1 ($C(CH_3)_2$), 100.1 (C-1), 75.8 (C-6), 72.1 (C-5), 71.6 (C-4), 70.9 (C-3), 65.7 (C-7), 61.1 (OCH_2), 54.6 (OCH_3), 36.9 (C-2), 32.0 (OCH_2CH_2), 26.2 ($C(CH_3)_2$), 26.0 ($C(CH_3)_2$), 25.2 ($C(CH_3)_2$), 24.5 ($C(CH_3)_2$), 19.1 (CH_2CH_3), 13.3 (CH_3); HRMS (EI) calcd *m*/*z* for $C_{24}H_{36}O_7$ (M^+) 436.2461, found 436.2460. Anal. Calcd for $C_{24}H_{36}O_7$: C, 66.03; H, 8.31. Found: C 65.68; H, 8.34. **Data for 22*α*:** R_f 0.42 (EtOAc/hexane 2:8); $[\alpha]^{25}_D$ +76.6 (*c* 1.4, CH_2Cl_2); ^1H NMR (400 MHz, acetone-d_6) δ 7.48−7.37 (m, 2H, H-2_MBn + H-6_MBn), 6.97−6.86 (m, 2H, H-3_MBn + H-5_MBn), 4.50 (ddd, 1H, *J* = 5.9, 5.9, 7.5 Hz, H-3), 4.44 (ddd, 1H, *J* = 6.0, 6.0, 6.0 Hz, H-6), 4.28 (dd, 1H, *J* = 2.4, 6.0 Hz, H-4), 4.17 (high order dd, 1H, *J* = 6.0, 14.8 Hz, H-7a), 4.17 (high order dd, 1H, *J* = 6.0, 14.8 Hz, H-7b), 3.96 (dd, 1H, *J* = 2.4, 6.4 Hz, H-5), 3.79 (s, 3H, OCH_3), 3.24 (dt, 1H, *J* = 6.5, 9.5 Hz, $OCH_aH_bCH_2$), 2.85 (dt, 1H, *J* = 6.4, 9.5 Hz, $OCH_aH_bCH_2$), 2.22 (dd, 1H, *J* = 5.7, 13.9 Hz, H-2b), 1.84 (dd, 1H, *J* = 7.5, 14.1 Hz, H-2a), 1.51−1.23 (m, 16H, $OCH_aH_bCH_2CH_2CH_3$ + + 4 × $C(CH_3)_2$), 0.85 (t, 3H, *J* = 7.3 Hz, CH_3_butyl); ^{13}C NMR (100 MHz, acetone-d_6) δ 160.2 (C-4_MBn), 135.7 (C-1_MBn), 128.2 (C-3_MBn + C-5_MBn), 114.1 (C-2_MBn + C-6_MBn), 109.4 ($C(CH_3)_2$), 109.1 ($C(CH_3)_2$), 100.9 (C-1), 76.0 (C-6), 72.1 (C-4), 71.8 (C-3), 70.6 (C-5), 67.2 (C-7), 61.6 (OCH_2), 55.6 (OCH_3), 40.9 (C-2), 32.6 (OCH_2CH_2), 27.9 ($C(CH_3)_2$), 27.2 ($C(CH_3)_2$), 26.1 ($C(CH_3)_2$), 25.9 ($C(CH_3)_2$), 20.3 (CH_2CH_3), 14.3 (CH_3); HRMS (EI) calcd *m*/*z* for $C_{24}H_{36}O_7$ (M^+) 436.2461, found 436.2446.

1-(Dodecyl 2-deoxy-3,4:6,7-di-*O*-isopropylidene-*β*-D-*manno*-heptopyranoside)-4-methoxybenzene (23*β*) and 1-(Dodecyl 2-deoxy-3,4:6,7-di-*O*-isopropylidene-*α*-D-*manno*-heptopyranoside)-4-methoxybenzene (23*α*). Compound **17** (150 mg, 0.414 mmol), *n*-dodecanol (115.7 mg, 0.621 mmol), and NIS (139.7 mg, 0.621 mmol) were reacted a manner similar to that used above. The obtained mixture was deiodinated with *n*-Bu_3SnH in a similar manner to afford a mixture of compounds **23*β*** and **23*α*** in 77% yield (**23*β*/23*α***: > 20/1) using a mixture of hexane/triethylamine (98: 2) as eluent. **Data for 23*β*:** $[\alpha]^{25}_D$ +16.3 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, acetone-d_6) δ 7.49−7.42 (m, 2H, H-2_MBn + H-6_MBn), 6.98−6.90 (m, 2H, H-3_MBn + H-5_MBn), 4.38 (ddd, 1H, *J* = 4.8, 4.8, 7.4 Hz, H-3), 4.33 (ddd, 1H, *J* = 5.3, 6.5, 6.5 Hz, H-6), 4.26−4.20 (m, 2H, H-4 + H-7b), 4.11 (dd, 1H, *J* = 6.5, 8.5 Hz, H-7a), 3.80 (s, 3H, OCH_3), 3.75 (dd, 1H, *J* = 2.0, 5.2 Hz, H-5), 3.49 (dt, 1H, *J* = 6.4, 9.2 Hz, $OCH_aH_bCH_2$), 3.00 (dt, 1H, *J* = 6.7, 9.2 Hz, $OCH_aH_bCH_2$), 2.29 (dd, 1H, *J* = 5.0, 14.9 Hz, H-2b), 2.06 (overlapped, 1H, H-2b), 1.54−1.08 (m, 32H, 20H_chain +4 × $C(CH_3)_2$), 0.86 (t, 3H, *J* = 6.9 Hz, CH_3); ^{13}C NMR (100 MHz, acetone-d_6) δ 160.4 (C-4_MBn), 135.2 (C-1_MBn), 128.6 (C-2_MBn + C-6_MBn), 114.3 (C-3_MBn + C-5_MBn), 109.4 ($C(CH_3)_2$), 109.1 ($C(CH_3)_2$), 101.1 (C-1), 76.8 (C-6), 73.1(C-5), 72.6 (C-4), 71.8 (C-3), 66.7 (C-7), 62.4 (OCH_2), 55.6 (OCH_3), 37.9 (C-2), 32.7 ($OCH_2CH_2CH_2$), 30.8 (OCH_2CH_2), 30.5, 30.43, 30.42, 30.40, 30.2 (6CH_2_chain,), 27.2 ($C(CH_3)_2$), 27.0 ($CH_2CH_2CH_3$_chain), 26.9 ($C(CH_3)_2$), 26.2 ($C(CH_3)_2$), 25.4 ($C(CH_3)_2$), 23.4 (CH_2CH_3_chain), 14.4 (CH_3_chain); HRMS (FAB) calcd *m*/*z* for $C_{32}H_{52}O_7$ Na (M + Na^+) 571.3605, found 571.3586. Anal. Calcd for $C_{32}H_{52}O_7$: C, 70.04; H, 9.55. Found: C 70.46; H, 9.80. **Data for 23*α*:** $[\alpha]^{25}_D$ +19.4 (*c* 1.5, CH_2Cl_2); ^1H NMR (400 MHz, acetone-d_6) δ 7.45−7.37 (m, 2H, H-2_MBn + H-6_MBn), 6.95−6.86 (m, 2H, H-3_MBn + H-5_MBn), 4.50 (ddd, 1H, *J* = 5.9, 5.8, 7.4 Hz, H-3), 4.44 (ddd, 1H, *J* = 6.0, 6.0, 6.0 Hz, H-6), 4.28 (dd, 1H, *J* = 2.3, 6.0 Hz, H-4), 4.20−4.10 (m, 2H, H-7b + H-7a), 3.96 (dd, 1H, *J* = 2.3, 6.5 Hz, H-5), 3.79 (s, 3H, OCH_3), 3.23 (dt, 1H, *J* = 6.6, 9.4 Hz, $OCH_aH_bCH_2$), 2.89 (dt, 1H, *J* = 6.5, 9.5 Hz, $OCH_aH_bCH_2$), 2.22 (dd, 1H, *J* = 5.7, 14.0 Hz, H-2b), 1.84 (dd, 1H, *J* = 7.6, 14.1 Hz, H-2a), 1.52−1.20 (m, 32H, 20H_chain +4 × $C(CH_3)_2$), 0.88 (t, 3H, *J* = 7.0 Hz, CH_3_Chain); ^{13}C NMR (100 MHz, acetone-d_6) δ 160.3 (C-4_MBn), 135.7 (C-1_MBn), 128.2 (C-2_MBn + C-6_MBn), 114.2 (C-3_MBn + C-5_MBn), 109.4 ($C(CH_3)_2$), 109.2 ($C(CH_3)_2$), 100.9 (C-1), 76.1 (C-6), 72.1 (C-4), 71.8 (C-3), 70.7 (C-5), 67.2 (C-7), 61.9 (OCH_2), 55.6 (OCH_3), 40.9 (C-2), 32.7 ($OCH_2CH_2CH_2$), 30.5 (OCH_2CH_2), 30.45−30.10 (6 × CH_2_chain), 28.0 ($C(CH_3)_2$), 27.3 ($C(CH_3)_2$), 27.2 ($CH_2CH_2CH_3$_chain), 26.1 ($C(CH_3)_2$), 25.9 ($C(CH_3)_2$), 23.4 (CH_2CH_3_chain), 14.4 (CH_3_chain). Anal. Calcd for $C_{32}H_{52}O_7$: C, 70.04; H, 9.55. Found: C 69.68; H, 9.66.

1-(Benzyl 2-deoxy-3,4:6,7-di-*O*-isopropylidene-*β*-D-*manno*-heptopyranoside)-4-methoxybenzene (24*β*) and 1-(Benzyl 2-deoxy-3,4:6,7-di-*O*-isopropylidene-*α*-D-*manno*-heptopyranoside)-4-methoxybenzene (24*α*). Compound **17** (80 mg, 0.22 mmol), benzyl alcohol (75 μL, 0.66 mmol), and NIS (99.6 mg, 0.44 mmol) were reacted in a manner similar to that used above. The obtained mixture was deiodinated with *n*-Bu_3SnH in a similar manner to afford a mixture of compounds **24*β*** and **24*α*** in 82% yield (**24*β*/24*α***: 15/1) using a mixture of hexane/EtOAc/triethylamine (95: 5: 2) as eluent. **Data for 24*β*:** R_f 0.38 (EtOAc/hexane 20:80); $[\alpha]^{25}_D$ +10.6 (*c* 1.1, $CHCl_3$); ^1H NMR (400 MHz, acetone-d_6) δ 7.57−7.49 (m, 2H, H-2_MBn + H-6_MBn), 7.32−7.15 (m, 5H, Ar−H_Bn), 6.98−6.91 (m, 2H, H-3_MBn + H-5_MBn), 4.59 (d, 1H, *J* = 11.9 Hz, CHb_Bn), 4.47 (ddd, 1H, *J* = 4.4, 4.4, 7.7 Hz, H-3), 4.37 (ddd, 1H, *J* = 5.4, 6.5, 6.5 Hz, H-6), 4.30 (dd, 1H, *J* = 2.0, 7.5 Hz, H-4), 4.27 (dd, 1H, *J* = 6.5, 8.5 Hz, H-7b), 4.14 (dd, 1H, *J* = 6.5, 8.5 Hz, H-7a), 4.09 (d, 1H, *J* = 11.9 Hz, CHa_Bn), 3.84 (dd, 1H, *J* = 2.0, 5.3 Hz, H-5), 3.80 (s, 3H, OCH_3), 2.43 (dd, 1H, *J* = 4.2, 15.2 Hz, H-2b), 2.11 (dd, 1H, *J* = 4.6, 15.2 Hz, H-2a), 1.41 (s, 3H, $C(CH_3)_2$), 1.39 (s, 3H, $C(CH_3)_2$), 1.35 (s, 3H, $C(CH_3)_2$), 1.27 (s, 3H, $C(CH_3)_2$); ^{13}C NMR (100 MHz, acetone-d_6) δ 160.6 (C-4_MBn), 140.3 (C-1_Bn), 135.3 (C-1_MBn), 128.9 (Ar−C_Bn), 128.6 (C-3_MBn + C-5_MBn), 128.4 (Ar−C_Bn), 127.8 (Ar−C_Bn), 114.5 (C-2_MBn + C-6_MBn), 109.4 ($C(CH_3)_2$), 109.2 ($C(CH_3)_2$), 101.5 (C-1), 76.7 (C-6), 73.4 (C-5), 72.6 (C-4), 71.7 (C-3), 66.8 (C-7), 64.6 (CH_2_Bn), 55.6 (OCH_3), 38.0 (C-2), 27.0 ($C(CH_3)_2$), 27.0 ($C(CH_3)_2$), 26.1 ($C(CH_3)_2$), 25.3 ($C(CH_3)_2$); HRMS (FAB) calcd *m*/*z* for $C_{27}H_{34}O_7$ Na (M + Na^+) 493.2197, found 493.2189. **Data for 24*α*:** R_f 0.43 (EtOAc/hexane 20:80); $[\alpha]^{25}_D$ +50.4 (*c* 1.6, $CHCl_3$); ^1H NMR (400 MHz, acetone-d_6) δ 7.59−7.50 (m, 2H, H-2_MBn + H-6_MBn), 7.35−7.21 (m, 5H, Ar−H_Bn), 6.99−6.90 (m, 2H, H-3_MBn + H-5_MBn), 4.59−4.51 (m, 1H, H-3), 4.48 (ddd, 1H, *J* = 6.1, 6.1, 6.1 Hz, H-6), 4.35 (d, 1H, *J* = 11.5, Hz, CHb_Bn), 4.31 (dd, 1H, *J* = 2.4, 6.2 Hz, H-4), 4.24−4.14 (m, 2H, H-7b + H-7a), 4.08 (dd, 1H, *J* = 2.2, 6.0 Hz, H-5), 3.97 (d, 1H, *J* = 11.5 Hz, CHa_Bn), 3.81 (s, 3H, OCH_3), 2.33 (dd, 1H, *J* = 5.5, 14.3 Hz, H-2b), 2.00 (dd, 1H, *J* = 7.1, 14.3 Hz, H-2a), 1.37 (s, 3H, $C(CH_3)_2$), 1.36 (s, 3H, $C(CH_3)_2$), 1.34 (s, 3H, $C(CH_3)_2$), 1.27 (s, 3H, $C(CH_3)_2$); ^{13}C NMR (100 MHz, acetone-d_6) δ 160.4 (C-4_MBn), 139.6 (C-1_Bn), 135.5 (C-1_MBn), 129.1 (Ar−C_Bn), 128.5 (Ar−C_Bn), 128.4 (C-2_MBn + C-6_MBn), 128.1 (Ar−C_Bn), 114.3 (C-3_MBn + C-5_MBn), 109.4 ($C(CH_3)_2$), 109.2 ($C(CH_3)_2$), 101.4 (C-1), 76.1 (C-6), 72.2 (C-4), 71.8 (C-3), 70.9 (C-5), 67.1 (C-7), 64.2 (CH_2_Bn), 55.6 (OCH_3), 40.6 (C-2), 27.8 ($C(CH_3)_2$), 27.2 ($C(CH_3)_2$), 26.0 ($C(CH_3)_2$), 25.9 ($C(CH_3)_2$); HRMS (FAB) calcd *m*/*z* for $C_{27}H_{34}O_7$ Na (M + Na^+) 493.2197, found 493.2194.

1-(Isopropyl 2-deoxy-3,4:6,7-di-*O*-isopropylidene-*β*-D-*manno*-heptopyranoside)-4-methoxybenzene (25*β*) and 1-(Isopropyl 2-deoxy-3,4:6,7-di-*O*-isopropylidene-*α*-D-*manno*-heptopyranoside)-4-methoxybenzene (25*α*). Compound **17** (200 mg, 0.552 mmol), benzyl alcohol (99.5 mg, 1.66 mmol), and NIS (186.2 mg, 0.828 mmol) were reacted in a manner similar to that

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used above. The obtained mixture was deiodinated with *n*-Bu_3SnH in a similar manner to afford a mixture of compounds **25*β*** and **25*α*** in 91% yield (**25*β*/25*α***: 10/1) using a mixture of hexane/triethylamine (98:2) as eluent. **Data for 25*β***: R_f 0.36 (EtOAc/hexane 20:80); $[\alpha]^{25}_D$ +11.0 (*c* 1.7, CH_2Cl_2); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.54−7.45 (m, 2H, H-2_MBn + H-6_MBn), 6.99−6.88 (m, 2H, H-3_MBn + H-5_MBn), 4.38 (ddd, 1H, *J* = 5.1, 5.1, 7.1 Hz, H-3), 4.33 (ddd, 1H, *J* = 4.7, 6.6, 6.6 Hz, H-6), 4.24 (dd, 1H, *J* = 6.8, 8.4 Hz, H-7b), 4.16 (dd, 1H, *J* = 2.0, 7.1 Hz, H-4), 4.12 (dd, 1H, *J* = 6.4, 8.4 Hz, H-7a), 3.80 (s, 3H, OMe), 3.79 (septet, 1H, *J* = 6.2 Hz, OC*H*$(CH_3)_2$), 3.75 (dd, 1H, *J* = 2.1, 4.7 Hz, H-5), 2.32 (dd, 1H, *J* = 5.4, 14.9 Hz, H-2b), 2.15 (dd, 1H, *J* = 4.8, 14.8 Hz, H-2a), 1.48 (s, 3H, C$(CH_3)_2$), 1.44 (s, 3H, C$(CH_3)_2$), 1.38 (s, 3H, C$(CH_3)_2$), 1.31 (s, 3H, C$(CH_3)_2$), 1.20 (d, 3H, *J* = 6.2 Hz, OCH$(CH_3)_2$), 0.84 (d, 3H, *J* = 6.2 Hz, OCH$(CH_3)_2$); ^{13}C NMR (100 MHz, acetone-d_6) δ 160.4 (C-4_MBn), 138.3 (C-1_MBn), 128.8 (C-3_MBn + C-5_MBn), 114.3 (C-2_MBn + C-6_MBn), 109.3 (*C*$(CH_3)_2$), 109.0 (*C*$(CH_3)_2$), 101.9 (C-1), 76.8 (C-6), 73.1 (C-5), 72.5 (C-4), 72.0 (C-3), 66.6 (C-7), 65.9 (O*C*H$(CH_3)_2$), 55.6 (OCH_3), 37.9 (C-2), 27.2 (C*C*$H_3)_2$), 26.9 (C*C*$H_3)_2$), 26.1 (C*C*$H_3)_2$), 25.4 (C*C*$H_3)_2$), 25.3 (OCH*C*$H_3)_2$), 24.3 (OCH*C*$H_3)_2$); HRMS (EI) calcd *m*/*z* for $C_{22}H_{31}O_7$ ($M^+ - CH_3$) 407.2070, found 407.2077. **Data for 25*α***: R_f 0.52 (EtOAc/hexane 20:80); $[\alpha]^{25}_D$ +69.4 (*c* 0.9, CH_2Cl_2); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.57−7.45 (m, 2H, H-2_MBn + H-6_MBn), 6.96−6.87 (m, 2H, H-3_MBn + H-5_MBn), 4.50 (ddd, 1H, *J* = 5.1, 6.5, 6.5 Hz, H-3), 4.44 (ddd, 1H, *J* = 5.5, 6.1, 6.1 Hz, H-6), 4.31−4.23 (m, 2H, H-4 + H-7b), 4.20−4.12 (m, 2H, H-5 + H-7a), 3.81 (s, 3H, OCH_3), 3.79 (septet, 1H, *J* = 6.2 Hz, OC*H*$(CH_3)_2$), 2.31 (dd, 1H, *J* = 5.0, 14.3 Hz, H-2b), 2.04 (dd, 1H, *J* = 6.7, 14.3 Hz, H-2a), 1.40 (s, 3H, C$(CH_3)_2$), 1.36 (s, 3H, C$(CH_3)_2$), 1.28 (s, 3H, C$(CH_3)_2$), 1.25 (s, 3H, C$(CH_3)_2$), 1.17 (d, 3H, *J* = 6.2 Hz, OCH$(CH_3)_2$), 0.75 (d, 3H, *J* = 6.2 Hz, OCH$(CH_3)_2$); ^{13}C NMR (100 MHz, acetone-d_6) δ 160.2 (C-4_MBn), 136.5 (C-1_MBn), 128.7 (C-2_MBn + C-6_MBn), 113.8 (C-3_MBn + C-5_MBn), 109.1 (*C*$(CH_3)_2$), 109.0 (*C*$(CH_3)_2$), 100.9 (C-1), 76.6 (C-6), 72.5 (C-4), 71.6 (C-3), 70.2 (C-5), 66.7 (C-7), 65.2 (OCH$(CH_3)_2$), 55.5 (OCH_3), 40.4 (C-2), 27.4 (C*C*$H_3)_2$), 27.1 (C*C*$H_3)_2$), 25.9 (C*C*$H_3)_2$), 25.7 (C*C*$H_3)_2$), 24.8 (OCH*C*$H_3)_2$), 24.1 (OCH*C*$H_3)_2$); HRMS (EI) calcd *m*/*z* for $C_{20}H_{27}O_6$ ($M^+ - OC_3H_7$) 363.1808, found 363.1790. Anal. Calcd for $C_{23}H_{34}O_7$: C, 65.38; H, 8.11. Found: C 65.69; H, 8.13.

1-(Cyclohexyl 2-deoxy-3,4:6,7-di-*O*-isopropylidene-*β*-D-*manno*-heptopyranoside)-4-methoxybenzene (26*β*) and 1-(Cyclohexyl 2-deoxy-3,4:6,7-di-*O*-isopropylidene-*α*-D-*manno*-heptopyranoside)-4-methoxybenzene (26*α*). Compound **17** (150 mg, 0.414 mmol), cyclohexanol (100 μL, 1.23 mmol), and NIS (139.7 mg, 0.621 mmol) were reacted in a manner similar to that used above. The obtained mixture was deiodinated with *n*-Bu_3SnH in a similar manner to afford a mixture of compounds **26*β*** and **26*α*** in 78% yield (**26*β*/26*α***: 8/1) using a mixture of hexane/triethylamine (98:2) as eluent. **Data for 26*β***: R_f 0.38 (EtOAc/hexane 20:80); $[\alpha]^{25}_D$ +12.4 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.55−7.47 (m, 2H, H-2_MBn + H-6_MBn), 6.98−6.87 (m, 2H, H-3_MBn + H-5_MBn), 4.42 (ddd, 1H, *J* = 5.3, 5.3, 7.0 Hz, H-3), 4.32 (ddd, 1H, *J* = 4.3, 6.8, 6.8 Hz, H-6), 4.26 (dd, 1H, *J* = 7.0, 8.4 Hz, H-7b), 4.16−4.07 (m, 2H, H-4+ H-7a), 3.86 (s, 3H, OCH_3), 3.77 (dd, 1H, *J* = 2.1, 4.3 Hz, H-5), 3.58−3.46 (m, 1H, H-1_cyclohexane), 2.29 (dd, 1H, *J* = 5.6, 14. Eight Hz, H-2b), 2.11 (dd, 1H, *J* = 4.8, 14.8 Hz, H-2a), 1.98−1.87 (m, 1H, 1H_cyclohexane), 1.76−0.92 (m, 21H, 9H_cyclohexane +4 × C$(CH_3)_2$); ^{13}C NMR (100 MHz, acetone-d_6) δ 160.4 (C-4_MBn), 135.2 (C-1_MBn), 128.9 (C-2_MBn + C-6_MBn), 114.3 (C-3_MBn + C-5_MBn), 109.3 (*C*$(CH_3)_2$), 108.9 (*C*$(CH_3)_2$), 101.8 (C-1), 77.0 (C-6), 73.0 (C-5), 72.6 (C-4), 72.2 (C-3), 71.7 (OCH), 66.5 (C-7), 55.6 (OCH_3), 37.8 (C-2), 36.0 (C-2 or C-6_cyclohexane), 34.7 (C-6 or C-2_cyclohexane), 27.4 (C*C*$H_3)_2$), 26.8 (C*C*$H_3)_2$), 26.5 (C-4_cyclohexane), 26.3 (C*C*$H_3)_2$), 25.4 (C*C*$H_3)_2$), 25.2 (C-3 or C-5_cyclohexane), 25.1 (C-5 or C-3_cyclohexane); HRMS (EI) calcd *m*/*z* for $C_{20}H_{27}O_6$ ($M^+ - C_6H_{11}O$) 363.1808, found 363.1820. **Data for 26*α***: R_f 0.47 (EtOAc/hexane 20:80); $[\alpha]^{25}_D$ +68.4 (*c* 0.7, CH_2Cl_2); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.52−7.45 (m, 2H, H-2_MBn + H-6_MBn), 6.92−6.84 (m, 2H, H-3_MBn + H-5_MBn), 4.49 (ddd, 1H, *J* = 5.2, 6.5, 6.5 Hz, H-3), 4.42 (ddd, 1H, *J* = 5.3, 6.1, 6.1 Hz, H-6), 4.28−4.20 (m, 2H, H-4 + H-7b), 4.17−4.10 (m, 2H, H-7a + H-5), 3.80 (s, 3H, OCH_3), 3.40−3.32 (m, 1H, H-1_cyclohexane), 2.26 (dd, 1H, *J* = 5.0, 14.3 Hz, H-2b), 2.08 (dd, 1H, *J* = 6.5, 14.4 Hz, H-2a), 1.95 (m, 1H, 1H_cyclohexane), 1.71−1.44 (m, 2H, 2H_cyclohexane), 1.42−0.82 (m, 19H, 4 × C$(CH_3)_2$ + 7H_cyclohexane); ^{13}C NMR (100 MHz, acetone-d_6) δ 160.1 (C-1_MBn), 136.9 (C-4_MBn), 128.7 (C-3_MBn + C-5_MBn), 113.7 (C-2_MBn + C-6_MBn), 109.0 (*C*$(CH_3)_2$), 109.0 (*C*$(CH_3)_2$), 100.9 (C-1), 76.6 (C-6), 72.6 (C-4), 71.7 (C-3), 70.9 (C-1_cyclohexane), 70.2 (C-5), 66.6 (C-7), 55.5 (OCH_3), 40.3 (C-2), 35.0 (C-2 or C-6_cyclohexane), 34.3 (C-6 or C-2_cyclohexane), 27.3 (C*C*$H_3)_2$), 27.1 (C*C*$H_3)_2$), 26.4 (C-4_cyclohexane), 25.9 (C*C*$H_3)_2$), 25.6 (C*C*$H_3)_2$), 25.2 (C-3 or C-5_cyclohexane), 25.0 (C-5 or C-3_cyclohexane); HRMS (EI) calcd *m*/*z* for $C_{20}H_{26}O_6$ ($M^+ - C_6H_{12}O$) 362.1729, found 362.1729.

1-(Cyclopentyl 2-deoxy-3,4:6,7-di-*O*-isopropylidene-*β*-D-*manno*-heptopyranoside)-4-methoxybenzene (27*β*) and 1-(Cyclopentyl 2-deoxy-3,4:6,7-di-*O*-isopropylidene-*α*-D-*manno*-heptopyranoside)-4-methoxybenzene (27*α*). Compound **17** (200 mg, 0.552 mmol), cyclopentanol (95.1 mg, 1.11 mmol), and NIS (186.2 mg, 0.828 mmol) were reacted in a manner similar to that used above. The obtained mixture was deiodinated with *n*-Bu_3SnH in a similar manner to afford a mixture of compounds **27*β*** and **27*α*** in 91% yield (**27*β*/27*α***: 10/1) using a mixture of hexane/triethylamine (98:2) as eluent. **Data for 27*β***: R_f 0.36 (EtOAc/hexane 20:80); $[\alpha]^{25}_D$ +22.4 (*c* 0.6, CH_2Cl_2); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.49−7.43 (m, 2H, H-2_MBn + H-6_MBn), 6.96−6.90 (m, 2H, H-3_MBn + H-5_MBn), 4.40 (ddd, 1H, *J* = 4.8, 4.8, 7.3 Hz, H-3), 4.34 (ddd, 1H, *J* = 5.1, 6.5, 6.5 Hz, H-6), 4.24 (dd, 1H, *J* = 6.7, 8.4 Hz, H-7b), 4.20 (dd, 1H, *J* = 2.0, 7.3 Hz, H-4), 4.12 (dd, 1H, *J* = 6.4, 8.4 Hz, H-7a), 4.01−3.94 (m, 1H, OCH_cyclopentyl), 3.80 (s, 3H, OCH_3), 3.75 (dd, 1H, *J* = 2.0, 5.0 Hz, H-5), 2.31 (dd, 1H, *J* = 4.9, 15.0 Hz, H-2b), 2.07 (dd, 1H, *J* = 4.7, 14.9 Hz, H-2a), 1.86−1.76 (m, 1H, 1H_cyclopentyl), 1.75−1.22 (m, 19H, 7H_cyclopentyl +4 × C$(CH_3)_2$); ^{13}C NMR (100 MHz, Acetone-d_6) δ 160.3 (C-4_MBn), 136.0 (C-1_MBn), 128.7 (C-2_MBn + C-6_MBn), 114.4 (C-3_MBn + C-5_MBn), 109.2 (*C*$(CH_3)_2$), 109.1 (*C*$(CH_3)_2$), 101.8 (C-1), 76.7 (C-6), 75.6 (C-1_cyclopentyl), 73.2 (C-5), 72.5 (C-4), 71.8 (C-3), 66.8 (C-7), 55.6 (OCH_3), 38.1 (C-2), 35.0 (C-2 or C-5_cyclopentyl), 34.5 (C-5 or C-2_cyclopentyl), 27.1 (C*C*$H_3)_2$), 27.0 (C*C*$H_3)_2$), 26.2 (C*C*$H_3)_2$), 25.2 (C*C*$H_3)_2$), 24.5 (C-3 or C-4_cyclopentyl), 24.1 (C-4 or C-5_cyclopentyl); HRMS (FAB) calcd *m*/*z* for $C_{20}H_{27}O_6$ ($M^+ - C_5H_9O_1$) 363.1808, found 363.1800. **Data for 27*α***: R_f 0.45 (EtOAc/hexane 20:80); $[\alpha]^{25}_D$ +84.2 (*c* 0.4, CH_2Cl_2); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.49−7.42 (m, 2H, H-2_MBn + H-6_MBn), 6.93−6.85 (m, 2H, H-3_MBn + H-5_MBn), 4.50−4.41 (m, 2H, H-3 + H-6), 4.26 (dd, 1H, *J* = 2.4, 6.2 Hz, H-4), 4.20 (dd, 1H, *J* = 5.5, 8.6 Hz, H-7b), 4.18 (dd, 1H, *J* = 6.4, 8.6 Hz, H-7a), 4.08 (dd, 1H, *J* = 2.4, 6.2 Hz, H-5), 3.93−3.85 (m, 1H, OCH_cyclopentyl), 3.81 (s, 3H, OCH_3), 2.30 (dd, 1H, *J* = 5.5, 14.1 Hz, H-2b), 1.93 (dd, 1H, *J* = 7.3, 14.1 Hz, H-2a), 1.85−1.76 (m, 1H, 1H_cyclopentyl), 1.64−1.03 (m, 19H, 7H_cyclopentyl +4 × C$(CH_3)_2$); ^{13}C NMR (100 MHz, acetone-d_6) δ 160.2 (C-4_MBn), 136.5 (C-1_MBn), 128.6 (C-3_MBn + C-5_MBn), 113.9 (C-2_MBn + C-6_MBn), 109.3 (*C*$(CH_3)_2$), 109.1 (*C*$(CH_3)_2$), 101.0 (C-1), 76.2 (C-6), 74.6 (C-1_cyclopentyl), 72.2 (C-4), 71.7 (C-3), 70.4 (C-5), 67.0 (C-7), 55.6 (OCH_3), 40.4 (C-2), 34.5 (C-2 or C-5_cyclopentyl), 34.1 (C-5 or C-2_cyclopentyl), 27.8 (C*C*$H_3)_2$), 27.2 (C*C*$H_3)_2$), 26.0 (C*C*$H_3)_2$), 25.9 (C*C*$H_3)_2$), 23.9 (C-3 or C-4_cyclopentyl), 23.9 (C-4 or C-3_cyclopentyl); HRMS (FAB) calcd *m*/*z* for $C_{20}H_{27}O_6$ ($M^+ - C_5H_9O_1$) 363.1808, found 363.1809.

Methyl *O*-(2-Deoxy-3,4:6,7-di-*O*-isopropylidene-1-*C*-*p*-methoxyphenyl-*β*-D-*manno*-heptopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (29*β*) and Methyl *O*-(2-Deoxy-3,4:6,7-di-*O*-isopropylidene-1-*C*-*p*-methoxyphenyl-*α*-D-*manno*-heptopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (29*α*). A mixture containing compound **17** (30 mg, 0.083 mmol), methyl 2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (46.2 mg, 0.099 mmol), and molecular sieves 4 Å (80.0 mg) in anhydrous CH_2Cl_2 (0.8 mL) was purged with argon and stirred for 30 min. The mixture was then cooled to −50 °C, and NIS (26.8 mg, 0.119 mmol) was added. The reaction was stirred for another 20 min and slowly

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warmed to rt. The reacted was worked up as before, and the crude mixture was passed through a thin layer of silica gel using hexane/EtOAc (90: 10) as eluent to give the 2-iodoglycosides as an anomeric mixture (65.5 mg). Part of the 2-iodides (30.0 mg, 0.032 mmol) was deiodinated with n-Bu_3SnH (6.0 μL, 0.022 mmol) in the presence of a catalytic amount of AIBN in toluene (1.0 mL) to provide the desired disaccharide **29*β*** and **29*α*** in 76% yield (**29*β*/29*α***: 8/1) using a mixture of hexane/EtOAc/triethylamine (85:15:5) as eluent. A small amount of pure **29*β*** and **29*α*** was obtained in pure form by column chromatography. **Data for 29*β***: R_f 0.22 (EtOAc/hexane 3:7); $[\alpha]^{25}_D$ +4.3 (c 0.3, CH_2Cl_2); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.50−7.45 (m, 2H, H-2_MBn + H-6_MBn), 7.42−7.16 (m, 15H, Ar−H_OBn), 6.91−6.85 (m, 2H, H-3_MBn + H-5_MBn), 4.93 (d, 1H, J = 11.2 Hz, CH_2_Bn), 4.78−4.72 (m, 3H, CH_2_OBn + H-1_Glc), 4.72−4.70 (m, 2H, CH_2_OBn), 4.46 (d, 1H, J = 11.0 Hz, CH_2_OBn), 4.41−4.29 (m, 2H, H-3 + H-6_Man), 4.24−4.15 (m, 2H, H-7b + H-4_Man), 4.04 (dd, 1H, J = 6.3, 8.5 Hz, H-7a_Man), 3.90 (dd, 1H, J = 1.8, 10.2 Hz, H-6b_Glc), 3.82 (m, 1H, H-3_Glc), 3.77 (s, OCH_3_Man), 3.73−3.65 (m, 2H, H-5_Man + H-5_Glc), 3.46 (dd, 1H, J = 3.6, 9.7 Hz, H-2_Glc), 3.40−3.34 (m, 4H, OCH_3_Glc + H-4_Man), 3.26 (dd, 1H, J = 5.5, 10.2 Hz, H-6a_Glc), 2.28 (m, 2H, H-2b + H-2a), 1.49 (s, 3H, $C(CH_3)_2$), 1.36 (s, 3H, $C(CH_3)_2$), 1.31 (s, 3H, $C(CH_3)_2$), 1.28 (s, 3H, $C(CH_3)_2$); ^{13}C NMR (100 MHz, Acetone-d_6) δ 160.5 (C-4_MBn_Man), 147.4, 140.4, 140.0, 139.95, 133.6, 129.2 (C-2_MBn + C-6_MBn_Man), 129.1, 129.0, 128.63, 128.61, 128.6, 128.4, 128.1, 114.5 (C-3_MBn + C-5_MBn_Man), 109.4 ($C(CH_3)_2$_Man), 109.2 ($C(CH_3)_2$_Man), 101.3 (C-1_Man), 98.3 (C-1_Glc), 83.0 (C-3_Glc), 81.3 (C-2_Glc), 79.1 (C-4_Glc), 76.5 (C-6_Man), 75.9 (CH_2_Bn), 75.2 (CH_2_Bn), 73.3 (C-5_Man), 72.9 (CH_2_Bn), 72.4 (C-4_Man), 71.9 (C-3_Man), 70.9 (C-5_Glc), 67.0 (C-7b_Man), 62.1 (C-6_Glc), 55.6 (OCH_3_Man), 55.1 (OCH_3_Glc), 37.7 (C-2_Man), 27.6 ($C(CH_3)_2$_Man), 27.0 ($C(CH_3)_2$_Man), 26.1 ($C(CH_3)_2$_Man), 25.7 ($C(CH_3)_2$_Man); HRMS (FAB) calcd m/z for $C_{48}H_{58}O_{12}Na$ (M + Na^+) 849.3821, found 849.3810. Anal. Calcd for $C_{48}H_{58}O_{12}$: C, 69.71; H, 7.70. Found: C 69.63; H, 7.54. **Data for 29*α***: R_f 0.35 (EtOAc/hexane 3:7); $[\alpha]^{25}_D$ +11.7 (c 0.6, CH_2Cl_2); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.46−7.42 (m, 2H, H-2_MBn + H-6_MBn), 7.42−7.00 (m, 15H, Ar−H_OBn), 6.96−6.88 (m, 2H, H-3_MBn + H-5_MBn), 4.95 (d, 1H, J = 11.2 Hz, CH_2_Bn), 4.87−4.67 (m, 5H, 2 × CH_2_OBn + H-1_Glc), 4.49 (ddd, 1H, J = 5.8, 5.9, 7.0 Hz, H-3_Man), 4.44−4.36 (m, 2H, H-6_Man +1H_OBn), 4.24 (dd, 1H, J = 2.4, 5.9 Hz, H-4_Man), 4.18 (dd, 1H, J = 2.5, 7.0 Hz, H-5_Man), 4.16−4.11 (m, 2H, H-7b + H-7a_Man), 3.90−3.79 (m, 4H, H-3_Glc + OCH_3_Man), 3.69 (ddd, 1H, J = 2.0, 7.4, 9.7 Hz, H-5_Glc), 3.52 (dd, 1H, J = 3.6, 9.6 Hz, H-2_Glc), 3.38 (s, 3H, OCH_3_Glc), 3.36−3.19 (m, 3H, H-6b + H-6a + H-4_Glc), 2.26 (dd, 1H, J = 5.9, 13.9 Hz, H-2b_Man), 1.80 (dd, 1H, J = 8.1, 13.9 Hz, H-2a_Man), 1.35 (s, 3H, $C(CH_3)_2$), 1.32 (s, 6H, $C(CH_3)_2$), 1.26 (s, 3H, $C(CH_3)_2$); HRMS (FAB) calcd m/z for $C_{48}H_{58}O_{12}Na$ (M + Na^+) 849.3821, found 849.3811.

(Methyl 3-deoxy-4,5:7,8-di-*O*-isopropylidene-*α*-D-*manno*-2-octulopyranosid)onic Acid (20*α*). To a solution of compound **19*α*** (60 mg, 0.152 mmol) in MeCN (3.0 mL) was added a solution of 0.5 M phosphate buffer (pH 7.0, NaH_2PO_4/Na_2HPO_4, 6.0 mL), and $NaIO_4$ (651 mg, 3.04 mmol) was added. After addition of a catalytic amount of $RuCl_3{\cdot}H_2O$ the solution turned dark, and after another 5 min, the solution turned yellow. The suspension was stirred for 3 h. The insoluble salt was filtered off and washed with $MeCN/H_2O$ (3.0 mL, 3:1), and the combined solution was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of CH_2Cl_2/MeOH/$NH_3{\cdot}H_2O$ (95:5:2) as eluent to afford the glycoside **20*α*** (37 mg, 73% yield): R_f 0.33 (CH_2Cl_2/MeOH 8:2); ^{1}H NMR (600 MHz, CD_3OD) δ 4.42 (ddd, 1H, J = 5.5, 5.5, 6.5 Hz, H-4), 4.34−4.21 (m, 3H, H-7 + H-8b + H-5), 4.16 (high order, 1H, H-8a), 3.88 (dd, 1H, J = 1.7, 7.6 Hz, H-6), 3.27 (s, 3H, OCH_3), 2.12 (dd, 1H, J = 5.0, 14.5 Hz, H-3b), 1.95 (dd, 1H, J = 5.7, 14.5 Hz, H-3a), 1.44 (s, 3H, $C(CH_3)_2$), 1.37 (s, 3H, $C(CH_3)_2$), 1.34 (s, 3H, $C(CH_3)_2$), 1.33 (s, 3H, $C(CH_3)_2$); ^{13}C NMR (150 MHz, CD_3OD) δ 173.1 (COOH), 109.0 ($C(CH_3)_2$), 108.7 ($C(CH_3)_2$), 99.6 (C-2), 74.1 (C-7), 73.0 (C-6), 71.3 (C-5), 70.9 (C-4), 66.9 (C-8), 50.2 (OCH_3), 33.6 (C-3), 25.9 ($C(CH_3)_2$), 25.7 ($C(CH_3)_2$), 24.2 ($C(CH_3)_2$), 24.2 ($C(CH_3)_2$); HRMS (FAB) calcd m/z for $C_{15}H_{24}O_8Na$ (M + Na^+) 355.1363, found 355.1365.

(Methyl 3-deoxy-4,5:7,8-di-*O*-isopropylidene-*β*-D-*manno*-2-octulopyranosid)onic Acid (20*β*). Compound **19*β*** isomer (57 mg, 0.15 mmol) was oxidized in a manner similar to that for **19*α*** with $NaIO_4$ (619 mg, 2.89 mmol) and a catalytic amount of $RuCl_3{\cdot}H_2O$. The desired carboxylate was obtained by column chromatography on silica gel using a mixture of CH_2Cl_2/MeOH/$NH_3{\cdot}H_2O$ (95:5:2) as eluent to provide compound **20*β*** (34 mg, 71% yield): R_f 0.30 (CH_2Cl_2/MeOH 8:2); ^{1}H NMR (400 MHz, acetone-d_6) δ 4.53 (ddd, 1H, J = 3.3, 3.8, 7.4 Hz, H-4), 4.37−4.29 (m, 2H, H-7 + H-5), 4.09 (dd, 1H, J = 6.2, 8.6 Hz, H-8b), 3.98 (dd, 1H, J = 5.5, 8.6 Hz, H-8a), 3.98 (dd, 1H, J = 5.5, 8.6 Hz, H-6), 3.27 (s, 3H, OCH_3), 2.62 (dd, 1H, J = 3.9, 15.4 Hz, H-3b), 1.94 (dd, 1H, J = 3.2, 15.4 Hz, H-3a), 1.39 (s, 3H, $C(CH_3)_2$), 1.38 (s, 3H, $C(CH_3)_2$), 1.32 (s, 3H, $C(CH_3)_2$), 1.29 (s, 3H, $C(CH_3)_2$); ^{13}C NMR (100 MHz, acetone-d_6) δ 169.8 (COOH), 109.6 ($C(CH_3)_2$), 109.5 ($C(CH_3)_2$), 98.8 (C-2), 74.9 (C-7), 72.9 (C-5), 72.7 (C-6), 71.2 (C-4), 67.6 (C-8), 50.8 (OCH_3), 33.5 (C-3), 27.2 ($C(CH_3)_2$), 26.2 ($C(CH_3)_2$), 25.9 ($C(CH_3)_2$), 25.1 ($C(CH_3)_2$); HRMS (FAB) calcd m/z for $C_{15}H_{24}O_8Na$ (M + Na^+) 355.1363, found 355.1368.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra for all synthesized compounds and X-ray crystallographic data for compounds **14**, **15**, and **17** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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