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Synthesis of 4,5-disubstituted-3-deoxy-D-*manno*-octulosonic acid (Kdo) derivatives

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ABSTRACT

In this study, a new synthetic approach to 4,5-branched Kdo trisaccharides based on the common acceptor Kdo(α2-4)Kdo was developed. The synthesis of three types of 4,5-branched trisaccharides, Hep(α1-5)[Kdo(α2-4)]Kdo, Man(α1-5)[Kdo(α2-4)]Kdo, and GalNAc(α1-5)[Kdo(α2-4)]Kdo, was achieved in good yield and high α-selectivity.

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1. Introduction

Lipopolysaccharide (LPS) and lipooligosaccharide (LOS) are produced by gram-negative bacteria on their outer membrane and play an important role in the mechanism of bacterial infection. LPS is composed of O-specific polysaccharide, a core oligosaccharide (core OS), and lipid A, whereas LOS lacks an O-antigen.[1] The lipid A moiety causes the biological toxicity of LPS/LOS;[2] although the function of the core oligosaccharide of LPS/LOS is still unknown. Recently, it has been reported that human antibodies recognized a core OS of LOS derived from pathogenic strains of bacteria.[3] Thus, the core OS is a target for vaccine development.

The core OS can be further subdivided into a highly conserved inner core and a structurally variable region. The unique component of the inner core is 2-keto-3-deoxy-α-D-*manno*-octulosonic acid (Kdo). The inner core of many LPS/LOSs is composed of a 4,5-branched Kdo structure. For example, the inner core of *Neisserial* LOS contains the branched Kdo trisaccharide, Hep(α1-5)[Kdo(α2-4)]Kdo.[4] Although many chemical syntheses of core LPS/LOS have been reported,[5] only Paulsen et al. have described the synthesis of the 4,5-branched Kdo structure.[6] They installed the L-*glycero*-α-D-*manno*-heptopyranosyl donor (Hep) on the 5-OH of the Kdo acceptor to form a Hep(α1-5)Kdo dimer and then linked a Kdo donor to the 4-OH of the Kdo moiety.

Previously, we have reported the synthesis of the Kdo derivative from D-mannose and the preparation of 2-4 and 2-8 linked Kdo disaccharides.[7] To extend the utility of this synthesis, we prepared the 4,5-branched Kdo trisaccharides by glycosylation of the 5-OH group of the 2-4 linked Kdo disaccharide using an approach different from Paulsen's method. Three types of 4,5-branched Kdo trisaccharide were synthesized through this new route.

2. Results and discussion

2.1. Synthesis of α2-4 linked Kdo disaccharide

For the synthesis of the 4,5-branched trisaccharide, 2-4 linked Kdo acceptor **6**α was prepared from common intermediate **1**.[7] Previously, we reported the regioselective glycosylation of glycosyl fluoride **3**α with 4,5-diol acceptor **2**, although we did not investigate the limitations of this reaction. Therefore, several types of glycosyl donors (**3**β, **4**, **5**) were examined.

Kdo donors **4** and **5** were synthesized as follows. Treatment of compound **1** with 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride in the presence of potassium carbonate gave the *N*-phenyl trifluoroacetimidate **4** in quantitative yield.[8] However, the reaction needed 1 week to reach completion. The reaction for preparing the Kdo trichloroacetimidate donor also demanded a week. This showed that the reactivity of the anomeric hydroxyl group of the Kdo derivatives was lower than that of aldose because of steric

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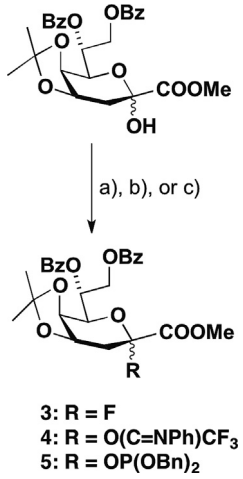
hindrance and low nucleophilicity. Dibenzyl phosphite **5** was prepared in moderate yield (56%) from compound **1** with 1*H*-tetrazole and dibenzyl *N*,*N*-diisopropylphosphoramidite (DDP) (Scheme 1).[9]



Scheme 1. Conditions: (a) DAST, 0 °C, 0.5 h, 81%, α/β=3:1; (b) *N*-phenyl trifluoroacetimidoyl chloride, K_2CO_3, CH_2Cl_2, rt, 7 days, quant, α/β=3:2; (c) 1*H*-tetrazole, DDP, CH_2Cl_2, 0 °C→rt, 3 h, 56%, α/β=23:1. DAST: *N*,*N*-diethylaminosulfur trifluoride; DDP: dibenzyl *N*,*N*-diisopropylphosphoramidite.

Next, glycosylation of 4,5-diol acceptor **2** with these glycosyl donors was examined (Scheme 2). The results are summarized in Table 1. Using β-fluoride **3**β with boron trifluoride as an activator gave a moderate yield (entry 3), whereas using TMSOTf as a promoter gave a poor yield (entry 4). The longer reaction time and higher reaction temperature also suggest that the reactivity of β-fluoride was lower than that of α-fluoride. In contrast, the combined promoter Cp_2HfCl_2–AgOTf[10] readily converted fluoride **3**α to glycal **7** (90%, entry 2). The use of *N*-phenyl trifluoroacetimidate **4**α, **4**β (entries 5 and 6) with TMSOTf as an activator gave a good yield although the stereoselectivity was modest. The use of glycosyl phosphite (entries 7 and 8) with boron trifluoride or TMSOTf gave a poor yield and low selectivity. These donors gave glycal **7** as the major product. Glycosyl fluoride **3**α (entry 1) with boron trifluoride as the activator provided the best yield and α-selectivity. Thus, the reaction of glycosyl fluoride **3**α in the presence of boron trifluoride was the most effective for this reaction.

Table 2. The reaction of heptosyl trichloroacetimidate **8**[12] with acceptor **6**α in the presence of 0.04 equiv of TMSOTf at 0 °C gave the corresponding 4,5-branched trisaccharide, Hep(α1-5)[Kdo(α2-4)]Kdo (**11**), in only 10% yield, and orthoester **12** was the major product (35%). To reduce the formation of **12**, the reaction temperature was raised to room temperature (entry 2). Correspondingly, the yield of orthoester **12** reduced to 28%, and that of the target Hep(α1-5)[Kdo(α2-4)]Kdo (**11**) increased to 28%. To suppress the formation of orthoester **12** further, more TMSOTf should be used, because the orthoester is unstable in acid.[13] Increasing the amount of TMSOTf (entry 3) afforded trisaccharide **11** in good yield (87%) and only a small amount of orthoester **12** was detected (3%).

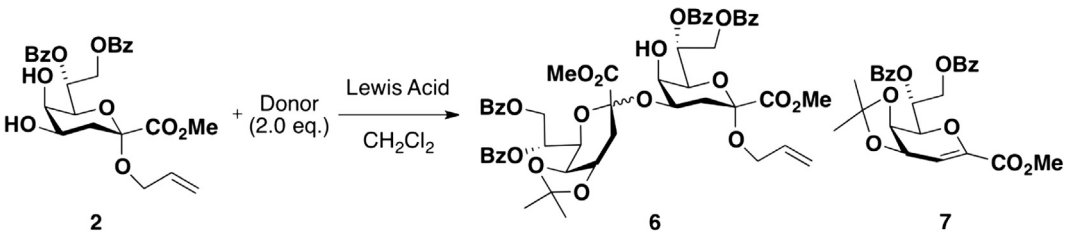
The 4,5-branched structure of **11** was determined by 2D NMR analysis (COSY, HMQC, and HMBC). From the COSY and HMBC spectra, we were able to identify the cyclic proton and carbon atoms of each residue of **11**. The newly formed 1-5 linkage was identified by HMBC analysis. Fig. 1 shows part of the HMBC spectrum. The cross-relay peaks in the HMBC spectrum (Kdo H-5^{I}/Hep C-1^{III}, Hep H-1^{III}/Kdo C-5^{I}) confirmed that heptosyl donor **8** is linked to the 5-position of acceptor **6**α. Moreover, the anomeric configuration was determined from the $^{1}J_{C\text{-}1,H\text{-}1}$ value.[14] The coupling constant between H-1^{III} and C-1^{III} ($^{1}J_{H-1^{III},C-1^{III}}$ = 178 Hz) of the Hep residue suggested that the newly formed glycosidic bond was an α-linkage. Thus, the trisaccharide, Hep(α1-5)[Kdo(α2-4)]Kdo, was successfully synthesized from the Kdo dimer with a heptosyl donor.

Following the synthesis of Hep(α1-5)[Kdo(α2-4)]Kdo (**11**), other 4,5-branched Kdo trisaccharides were also synthesized by the same route with **6**α as an acceptor. By coupling **6**α with mannosyl tri-

Table 1
Glycosylation of Kdo donors **3**–**5** with 4,5-diol acceptor **2**

Entry	Donor	Lewis acid (equiv)	Temp	Time (h)	Yield (%)	α/β	**7** (%)	**2** (%)[a]
1[b]	3α	$BF_3{\cdot}OEt_2$ (6.0)	−20 °C	1.5	72	5:1	—	—
2	3α	$Cp_2Hf(OTf)_2$ (2.2)	−20 °C	1.5	16	3.5:1	90	79
3	3β	$BF_3{\cdot}OEt_2$ (6.0)	−20 °C to rt	10	41	2.5:1	73	44
4	3β	TMSOTf (0.1)	−20 °C to rt	10	—	—	35[c]	75
5	4α	TMSOTf (0.1)	−78 °C	2.0	48	2.4:1	52	42
6	4β	TMSOTf (0.1)	−78 °C	2.0	61	2.6:1	38	27
7	5α	TMSOTf (0.1)	−20 °C	2.5	35	3.8:1	61	50
8	5α	$BF_3{\cdot}OEt_2$ (1.0)	−20 °C	2.0	30	2.1:1	—	—

[a] The yield was based on the donor.
[b] See Ref. 7.
[c] Twenty four percent of the donor was recovered.



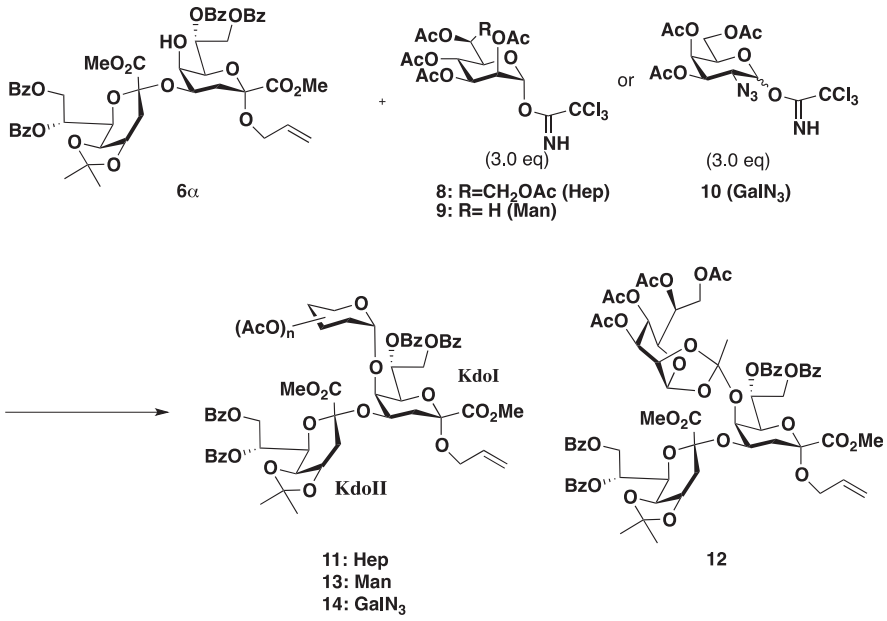
Scheme 2. Glycosylation of the 4,5-diol acceptor.

All donors produced the α-glycoside as the main product, but the stereoselectivity was not influenced by the type of leaving group. Our results are consistent with the results reported by Yoshizaki et al. that glycosylation with a 4,5-*O*-isopropylidinene-protected Kdo fluoride donor has a high α-selectivity.[11]

2.2. Synthesis of 4,5-branched trisaccharides

Glycosylation of Kdo acceptor **6**α with L-*glycero*-D-mannoheptosyl, mannosyl, and 2-azido-2-deoxy-galactosyl imidates **8**–**10** was examined (Scheme 3), and the results are presented in

chloroacetimidate **9**,[15] branched trisaccharide **13** was also obtained in good yield (91%) (entry 4). The effect of the participating group (Ac) at the C-2 position meant that only α-isomer, which was identified by the $^{1}J_{H-1^{III},C-1^{III}}$ value of the Man residue (175 Hz), was isolated. In contrast, for the heptose derivative, mannosylation proceeded smoothly at 0 °C with 0.04 equiv TMSOTf, and no orthoester was detected. These results suggest that mannosyl donor **9** was more active than heptosyl donor **8**. Glycosylation of Kdo dimer **6**α with $GalN_3$ trichloroacetimidate **10**[16] was accomplished to give $GalN_3$ containing branched trisaccharide **14** as a single isomer in moderate yield (56%) (entry 5). The coupling constant



Scheme 3. Syntheses of 4,5-branched trisaccharides **11**–**14**.

Table 2
Glycosylation of Kdo acceptor **6**α with L-*glycero*-D-mannoheptosyl, mannosyl, and 2-azido-2-deoxy-galactosyl imidates **8**–**10**

Entry	Donor	Temp (°C)	TMSOTf (equiv)	Time (h)	Product (%)	**12** (%)	**6**α (%)
1	**8**(α)	0	0.04	4	**11** (10)	35	44
2	**8**(α)	rt	0.04	2	**11** (28)	28	19
3	**8**(α)	rt	0.06	2	**11** (87)	3	9
4	**9**(α)	0	0.04	2	**13** (91)	—	—
5	**10** (α/β=1:3)	0	0.04	2	**14** (56)	—	40

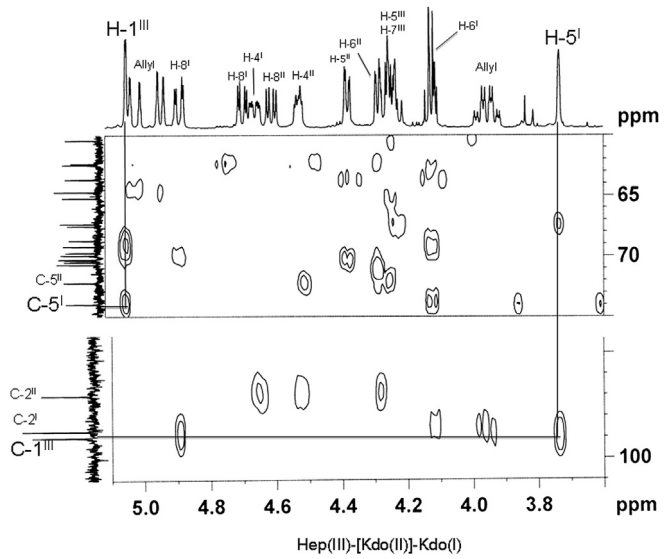


Fig. 1. Partial HMBC spectrum of compound **11** in $CDCl_3$ at 25 °C.

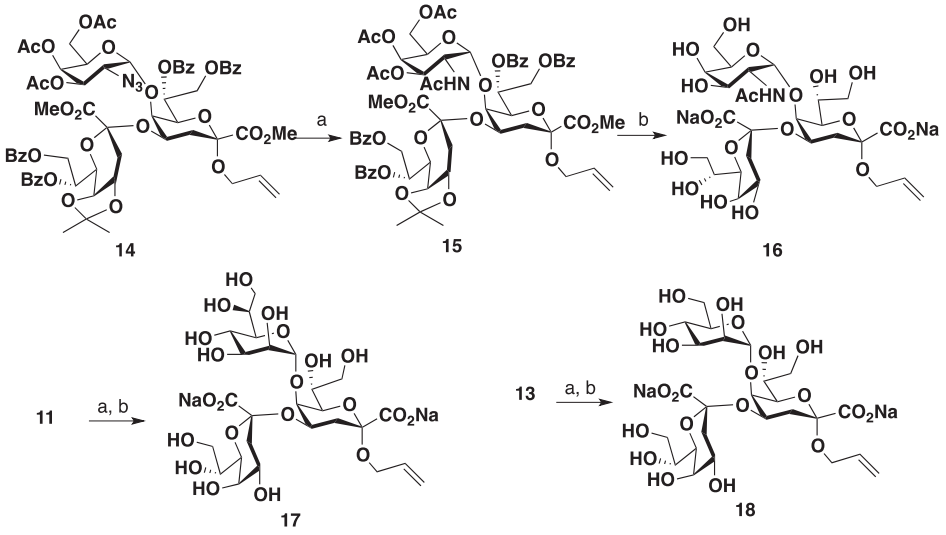
between H-1^{III} and H-2^{III} ($J_{H\text{-}1,H\text{-}2}$=3.4 Hz) of the $GalN_3$ residue indicated that an α-glycosidic linkage was formed.[14] The position of azide group meant this glycosylation exploited the anomeric effect to give the α-isomer. In addition, the presence of acetyl groups at the 3- and 4-position was also favorable for α-isomer formation.[17] Thin layer chromatography (TLC) also suggested that for the $GalN_3$ donor, the β-isomer is more active than the α-isomer (Table 3).

Table 3
^1H and ^{13}C NMR spectrum data for compounds **11**, **13**, and **14**

	11[a]		**13**[a]		**14**[a]	
	δ_H (J in Hz)	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)	δ_C
KdoI						
1		167.4		167.3		167.1
2		98.7		98.7		98.2
3a	2.05 (12.6, 12.0)	34.4	2.23 (12.6, 12.2)	25.1	2.11 (12.6, 12.4)	34.4
3b	2.27 (12.6, 4.4)		2.28 (12.6, 4.8)		2.27 (12.6, 4.6)	
4	4.65 (12.0, 4.4, 2.0)	67.6	4.73 (12.2, 4.8, 2.2)	67.5	4.79 (12.4, 4.6, 2.0)	67.7
5	3.73 (2.0, 1.8)	72.3	3.78 (2.2, 1.6)	72.5	3.83 (2.0, n.d.)	72.02
6	4.12 (1.8, 10.0)	70.5	4.11 (1.6, 9.4)	70.5	4.14 (n.d., 9.6)	70.4
7	5.69 (10.0, 3.6, 2.6)	69.2	5.46 (9.4, 3.8, 2.4)	68.9	5.70 (9.6, 3.0, 2.6)	69.4
8a	4.69 (3.6, 12.6)	62.4	4.63 (3.8, 12.6)	62.3	4.64 (3.0, 12.0)	62.2
8b	4.88 (2.6, 12.6)		4.82 (2.4, 12.6)		5.00 (2.6, 12.0)	
KdoII						
1		169.2		168.7		169.0
2		97.0		96.7		96.6
3a	2.12 (15.4, 2.2)	31.9	1.85 (15.4, 2.2)	24.6	1.92 (15.4, 2.2)	31.9
3b	2.95 (15.4, 3.6)		2.95 (15.4, 3.6)		3.01 (15.6, 3.6)	
4	4.52 (2.2, 3.6, 8.0)	70.0	4.52 (2.2, 3.6, 7.8)	69.6	4.52 (2.2, 3.6, 7.8)	69.9
5	4.37 (8.0, 2.0)	74.0	4.35 (7.8, 1.8)	72.2	4.36 (7.8, 1.6)	72.15
6	4.28 (2.0, 7.4)	70.4	4.18 (1.8, 7.2)	70.6	4.21 (1.6, 7.6)	70.4
7	5.65 (7.4, 5.0, 2.4)	70.7	5.67 (7.2, 5.2, 2.4)	70.8	5.67 (7.6, 4.2, 2.5)	70.7
8a	4.60 (5.0, 12.6)	62.5	4.63 (5.2, 12.6)	62.2	4.62 (4.2, 12.6)	62.0
8b	5.28 (2.4, 12.6)		5.30 (2.4, 12.6)		5.33 (2.5, 12.6)	
	Hep		Man		$GalN_3$	
1	5.04 (2.0)	99.0	4.82 (2.2)	98.5	5.05 (3.4)	97.9
2	5.24 (2.0, 3.2)	70.3	5.42 (3.4, 11.0)	69.2	3.74 (3.4, 11.0)	58.2
3	5.51 (3.2, 10.2)	68.7	5.40 (11.0, 3.4)	69.8	5.32 (11.0, 3.2)	68.8
4	5.32 (10.2, 10.0)	65.2	5.34 (3.4, 10.0)	66.0	5.48 (3.2, 0.8)	67.1
5	4.22 (10.0, 8.0)	69.2	4.32 (10.0, 2.0, 3.2)	68.7	4.54 (0.8, 5.5, 9.0)	66.6
6a	5.37 (8.0, 2.4, 4.0)	67.4	4.09 (2.0, 12.2)	61.8	4.08 (5.5, 10.8)	60.4
6b			4.39 (3.2, 12.2)		4.15 (9.0, 10.8)	
7a	4.23 (2.4, 12.0)	63.7				
7b	4.26 (4.0, 12.0)					

[a] Data were acquired in $CDCl_3$ at 25 °C. Only the data for the skeletal carbon atoms are presented, and those for other carbon atoms are listed in Experimental section.

Next, the transformation of the azide group to the acetamide group in trisaccharide **14** was carried out. The azide group could not be converted directly to the acetamide group by thioacetic acid (data not shown).[18] Hence, a stepwise conversion was used (Scheme 4). First, the azide group of $GalN_3$ **14** was reduced to the amine group under Staudinger conditions,[19] and was then acetylated with anhydrous acetic acid in the presence of *N*,*N*-dimethylaminopyridine (DMAP). Finally, GalNAc trisaccharide **15** was obtained in moderate yield (64%).



Scheme 4. Conditions: (a) (i) Ph_3P, THF/H_2O=19:1, rt, 16 h; (ii) Ac_2O, DMAP, pyridine, rt, 17 h, two steps: 64%; (b) 80% TFA, CH_2Cl_2, rt, then 0.1 M NaOH, MeOH, two steps: GalNAc **16** (quant), Hep **17** (87%), Man **18** (93%). DMAP: *N*,*N*-dimethylaminopyridine; TFA: trifluoroacetic acid.

Finally, acid hydrolysis of the isopropylidene group of the Kdo trisaccharide (**11**, **13**, and **15**) with aqueous trifluoroacetic acid and subsequent hydrolysis in 0.1 M sodium hydroxide to remove the ester groups afforded fully deprotected 4,5-branched Kdo trisaccharides **16**–**18** as disodium salts in good yield (GalNAc **16**: quantitative; Hep **17**: 87%; Man **18**: 93%).

2.3. Conclusion

A new synthetic strategy using Kdo (2-4)Kdo **6**α as an acceptor was developed for the synthesis of 4,5-branched Kdo trisaccharides. Glycosylation at the 4-OH position of the Kdo acceptor followed by a second glycosylation at 5-OH position produced the heptosyl Kdo dimer, Hep(α1-5)[Kdo(α2-4)]Kdo. We also achieved the first synthesis of the 4,5-branched partial inner-core trisaccharides Man(α1-5)[Kdo(α2-4)]Kdo (**13**) from *Francisella tularensis*[20] and $GalN_3$(α1-5)[Kdo(α2-4)]Kdo (**14**) from *Pseudomonas cichorii*[21] in good yield and high α-selectivity. The most suitable reaction conditions for the synthesis of Kdo(2-4)Kdo **6** were an α-fluoride donor with boron trifluoride as the activator. This new route should be more effective for the synthesis of the inner-core oligosaccharide of LPS/LOS than Paulsen's method. Ultimately, the fully deprotected 4,5-branched trisaccharides **16**–**18** will be used for immunological assessments.

3. Experiment section

3.1. General procedures

Optical rotation was measured with a Horiba SEPA500 polarimeter in $CHCl_3$, and melting point (uncorrected) was measured with a Yanagimoto micro melting point apparatus. All NMR spectra were recorded at 25 °C on a Bruker Avance II 600 MHz NMR spectrometer. ^1H NMR spectra were referenced to internal standards of the residual protonated solvent peaks: δ_H 7.24 ppm for solutions in $CDCl_3$, and δ_H 4.75 ppm for solutions in D_2O. The ^{13}C NMR spectra were recorded at 150 MHz and were referenced to the residual $CDCl_3$ peak (77.0 ppm). Multiplicities are reported as singlet (s), broad singlet (br s), doublet (d), double doublets (dd), triplet (t), or multiplet (m). Spectra were assigned using COSY, HMQC, and HMBC experiments. All NMR chemical shifts (δ) were recorded in parts per million (ppm), and coupling constants (J) were reported in hertz (Hz). Mass spectrometry (MS) was performed by positive- and negative-mode electrospray ionization on a Waters LCT Premier spectrometer. For high-precision measurements, the spectra were obtained by scanning the voltage over a narrow mass range at a resolution of 10,000. MALDI-TOF spectra were recorded on a Bruker Daltonics instrument, using 3,5-dihydroxybenzoic acid as the matrix. Elemental analysis was carried out on a Vario ELCUBE and a Vario EL III from Elementar. Infrared spectra were determined on a JASCO FT/IR-4100 spectrometer. Analytical TLC was performed on Merck silica gel 60 F_{254} glass plates. The TLC plates were visualized with UV light and by staining with Hannessian solution (ceric sulfate and ammonium molybdate in aqueous sulfuric acid), and then heating at 200 °C for 3 min. Column chromatography was performed on silica gel 60 (flash column: 0.040–0.063 mm; open column: 0.063–0.200 mm).

3.2. Methyl (7,8-di-*O*-benzoyl-4,5-*O*-isopropylidene-3-deoxy-D-*manno*-2-octulopyranosyl *N*-phenyl trifluoroacetimidate) onate (4)

To a solution of methyl (7,8-di-*O*-benzoyl-4,5-*O*-isopropyli dene-3-deoxy-D-*manno*-2-octulopyranoside)onate **1** (250 mg, 0.5 mmol) in dry dichloromethane (5 mL) under argon was added *N*-phenyl trifluoroacetimidoyl chloride[22] (716 μL, 5.0 mmol). Then potassium carbonate (113 mg, 5.0 mmol) was added into the reaction mixture. After stirring for 1 week, the mixture was filtered through Celite®. The solution was concentrated and purified by silica gel column chromatography (ethyl acetate/toluene=1:5) to give a mixture of anomers in quantitative yield (343 mg, α/β=3:2). α-isomer: $[\alpha]_D^{25}$ +75.6 (*c* 1.0, $CHCl_3$). ^1H NMR (600 MHz,

$CDCl_3$): δ 1.24 (s, 3H, Me), 1.50 (s, 3H, Me), 2.33 (1H, $J_{3a,3e}$=15.6 Hz, $J_{3a,4}$=3.4 Hz, H-3a), 2.78 (dd, 1H, $J_{3a,3e}$=15.6 Hz, $J_{3e,4}$=4.0 Hz, H-3e), 3.78 (s, 3H, OMe), 4.37 (dd, 1H, $J_{5,6}$=2.0 Hz, $J_{6,7}$=8.6 Hz, H-6), 4.41 (dd, 1H, $J_{4,5}$=7.6 Hz, $J_{5,6}$=2.0 Hz, H-5), 4.62 (ddd, 1H, $J_{3a,4}$=3.4 Hz, $J_{3e,4}$=4.0 Hz, $J_{4,5}$=7.6 Hz, H-4), 4.72 (dd, 1H, $J_{7,8a}$=4.0 Hz, $J_{8a,8b}$=12.4 Hz, H-8a), 5.00 (dd, 1H, $J_{7,8b}$=2.4 Hz, $J_{8a,8b}$=12.4 Hz, H-8b), 5.75 (ddd, 1H, $J_{6,7}$=8.6 Hz, $J_{7,8a}$=4.0 Hz, $J_{7,8b}$=2.4 Hz, H-7), 6.74–6.75 (m, 2H, *N*Ph–Ar), 7.05 (m, 1H, *N*Ph–Ar), 7.24–7.25 (m, 2H, *N*Ph–Ar), 7.37–7.44 (m, 4H, Ar), 7.51–7.57 (m, 2H, Ar), 7.98–8.03 (m, 4H, Ar). ^{13}C NMR (150 MHz, $CDCl_3$): δ 24.8, 25.6 (CH_3), 33.0 (C-3), 52.8 (OCH_3), 62.6 (C-8), 69.5 (C-4), 70.1 (C-7), 70.2 (C-6), 70.8 (C-5), 99.0 (C-2), 110.1 (C_{isop}), 116.5 (CF_3), 119.1 (*N*Ph–Ar), 124.3 (*N*Ph–Ar), 128.4, 128.47, 128.7, 129.4, 129.6, 129.7, 129.8, 133.1, 133.3 (14C, *N*Ph–Ar and Ar), 143.15 (C=N), 165.08, 166.15 (C=O), 168.06 (C-1). IR (neat): 1736, 1727, 1229, 1215, 1202 cm^{-1}. ESI-HRMS calcd for $C_{34}H_{32}F_3NO_{10}$: 694.1876 $[M+Na]^+$. Found 694.1873. β-isomer: $[\alpha]_D^{25}$ +6.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.29 (s, 3H, Me), 1.54 (s, 3H, Me), 2.34 (dd, 1H, $J_{3a,3b}$=16.2 Hz, $J_{3a,4}$=3.4 Hz, H-3a), 2.78 (dd, 1H, $J_{3a,3b}$=16.2 Hz, $J_{3e,4}$=3.0 Hz, H-3b), 3.66 (s, 3H, OMe), 4.26 (dd, 1H, $J_{5,6}$=1.8 Hz, $J_{6,7}$=8.0 Hz, H-6), 4.44 (dd, 1H, $J_{4,5}$=8.2 Hz, $J_{5,6}$=1.8 Hz, H-5), 4.68 (ddd, 1H, $J_{3a,4}$=3.4 Hz, $J_{3b,4}$=3.0 Hz, $J_{4,5}$=8.2 Hz, H-4), 4.70 (dd, 1H, $J_{7,8a}$=5.2 Hz, $J_{8a,8b}$=12.4 Hz, H-8a), 4.97 (dd, 1H, $J_{7,8b}$=2.4 Hz, $J_{8a,8b}$=12.4 Hz, H-8b), 5.68–5.71 (ddd, 1H, $J_{6,7}$=8.6 Hz, $J_{7,8a}$=5.2 Hz, $J_{7,8b}$=2.4 Hz, H-7), 6.74–6.75 (m, 2H, *N*Ph–Ar), 7.09 (m, 1H, *N*Ph–Ar), 7.27–7.28 (m, 2H, *N*Ph–Ar), 7.39–7.44 (m, 4H, Ar), 7.51–7.57 (m, 2H, Ar), 7.98–8.03 (m, 4H, Ar). ^{13}C NMR (150 MHz, $CDCl_3$): δ 25.6, 25.8 (CH_3), 29.7 (C-3), 52.8 (OCH_3), 62.9 (C-8), 69.2 (C-4), 70.5 (C-7), 70.9 (C-5), 71.5 (C-6), 99.3 (C-2), 110.0 (C_{isop}), 114.6 (CF_3), 119.3 (*N*Ph–Ar), 124.33 (*N*Ph–Ar), 128.36, 128.45, 128.56, 128.79, 129.64, 129.72, 129.75, 129.83, 129.98, 133.99, 133.24 (14C, *N*Ph–C_{meta} and Ar), 143.21 (C=N), 165.24, 166.09 (C=O), 167.91 (C-1). IR(neat): 1736, 1725, 1230, 1214, 1205 cm^{-1}. ESI-HRMS calcd for $C_{34}H_{32}F_3NO_{10}$: 694.1876 $[M+Na]^+$. Found 694.1855.

3.3. Methyl (dibenzyl-7,8-di-*O*-benzoyl-4,5-*O*-isopropylidene-3-deoxy-D-*manno*-2-octulopyranosyl phosphite)onate (5)

To a solution of methyl (7,8-di-*O*-benzoyl-4,5-*O*-isopropylidene-3-deoxy-D-*manno*-2-octulopyranoside)onate **1** (200 mg, 0.40 mmol) in dry dichloromethane (13.0 mL) under argon was added 1*H*-tetrazole (112 mg, 1.6 mmol). Then the reaction mixture was cooled to 0 °C and treated with dibenzyl *N*,*N*-diisopropylphosphoramidite (DDP, 320 μL/0.96 mmol). After stirring for 3 h, the solution was quenched with triethylamine (Et_3N) and concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/hexane=2:3 containing with 1% Et_3N) to give a mixture of anomers in 56% yield (167 mg, α/β=23:1). α-isomer: $[\alpha]_D^{25}$ +33.8 (*c* 1.1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.20 and 1.43 (s, 2H, CH_3), 2.06 (dd, 1H, $J_{3a,3b}$=15.0 Hz, $J_{3a,4}$=3.4 Hz, H-3a), 2.82 (dd, 1H, $J_{3a,3b}$=15.0 Hz, $J_{3b,4}$=5.2 Hz, H-3e), 3.70 (s, 3H, OMe), 4.25 (dd, 1H, $J_{4,5}$=7.0 Hz, $J_{5,6}$=2.0 Hz, H-5), 4.34 (dd, 1H, $J_{5,6}$=2.0 Hz, $J_{6,7}$=7.4 Hz, H-6), 4.47 (ddd, IH, $J_{3a,4}$=3.4 Hz, $J_{3e,4}$=5.2 Hz, $J_{4,5}$=7.0 Hz, H-4), 4.66 (dd, 1H, $J_{7,8a}$=6.0 Hz, $J_{8a,8b}$=12.4 Hz, H-8a), 4.77 (dd, 1H, *J*=12.4 and 7.8 Hz, OC*H*$_2$Ph), 4.81 (d, 2H, *J*=7.8 Hz, OC*H*$_2$Ph), 4.83 (dd, 1H, *J*=12.2 and 8.4 Hz, OC*H*$_2$Ph), 5.00 (dd, 1H, $J_{7,8b}$=2.4 Hz, $J_{8a,8b}$=12.4 Hz, H-8b), 5.74 (ddd, 1H, $J_{6,7}$=7.4 Hz, $J_{7,8a}$=6.0 Hz, $J_{7,8b}$=2.4 Hz, H-7), 7.18–7.54 (m, 16H, Ar), 7.97–8.03 (m, 4H, Ar). ^{13}C NMR (150 MHz, $CDCl_3$): δ 25.04, 26.01 (CH_3), 33.69 (C-3), 52.74 (OCH_3), 63.28 (C-8), 64.2 (d, $^2J_{C,P}$=6.3 Hz, OCH_2), 64.6 (d, $^2J_{C,P}$=8.8 Hz, OCH_2), 69.82 (C-4), 70.56 (C-7), 70.66 (C-6), 71.38 (C-5), 97.29, 97.33 (C-2), 109.73 (C_{isop}), 127.62, 127.69, 127.72, 128.06, 128.30, 128.37, 128.39, 128.74, 129.75, 129.91, 130.10, 132.87, 133.13, 137.91, 137.95, 137.98 (Ar), 165.30, 166.21 (C=O), 168.66 (C-1). IR(neat): 1749, 1713, 1282, 1252, 1213, 973 cm^{-1}. ESI-HRMS calcd for $C_{40}H_{41}O_{12}P$: 767.2233 $[M+Na]^+$. Found 767.2222. β-isomer: $[\alpha]_D^{25}$ +23.4 (*c* 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.21, 1.42 (s, 2H, CH_3), 2.40 (dd, 1H, $J_{3a,3b}$=15.2 Hz, $J_{3a,4}$=3.0 Hz, H-3a), 2.94 (dd, 1H, $J_{3a,3b}$=15.2 Hz, $J_{3b,4}$=5.6 Hz, H-3e), 3.73 (s, 3H, OMe), 4.35 (dd, 1H, $J_{4,5}$=7.6 Hz, $J_{5,6}$=2.0 Hz, H-5), 4.52 (ddd, IH, $J_{3a,4}$=3.0 Hz, $J_{3b,4}$=5.6 Hz, $J_{4,5}$=7.6 Hz, H-4), 4.65 (dd, 1H, $J_{5,6}$=2.0 Hz, $J_{6,7}$=7.4 Hz, H-6), 4.66 (dd, 1H, $J_{7,8a}$=7.0 Hz, $J_{8a,8b}$=12.4 Hz, H-8a), 4.95–5.02 (m, 4H, OCH_2), 5.02 (dd, 1H, $J_{7,8b}$=2.4 Hz, $J_{8a,8b}$=12.4 Hz, H-8b), 5.78 (ddd, 1H, $J_{6,7}$=7.4 Hz, $J_{7,8a}$=7.0 Hz, $J_{7,8b}$=2.4 Hz, H-7), 7.25–7.53 (m, 16H, Ar), 7.98–8.03 (m, 4H, Ar). ^{13}C NMR (150 MHz, $CDCl_3$): δ 24.6, 25.4 (CH_3), 32.2 (C-3), 53.0 (OCH_3), 63.5 (C-8), 69.5 (C-4), 69.56, 69.6 (2C, OCH_2), 70.3 (C-7), 71.3 (C-5), 72.1 (C-6), 100.0 (C-2), 109.8 (C_{isop}), 128.1, 128.2, 128.3, 128.36, 128.42, 128.46, 128.48, 128.50, 129.7, 129.75, 129.79, 130.1, 132.8, 133.1, 135.6 (Ar), 165.3, 166.2 (C=O), 167.2 (C-1). IR(neat): 1748, 1717, 1253, 1213, 954 cm^{-1}. ESI-HRMS calcd for $C_{40}H_{41}O_{12}P$: 767.2233 $[M+Na]^+$. Found 767.2223.

3.4. 2,3,4,6,7-Penta-*O*-acetyl-L-*glycero*-α-D-*manno*-heptopyranosyl-(1-5)-[methyl *O*-[methyl (7,8-di-*O*-benzoyl-4,5-*O*-isopropylidene-3-deoxy-α-D-*manno*-2-octulopyranosyl)onate]]-(2-4)-(allyl 7,8-di-*O*-benzoyl-3-deoxy-α-D-*manno*-2-octulopyranosyl)onate (11)

A mixture of methyl *O*-[methyl (7,8-di-*O*-benzoyl-4,5-*O*-isopropylidene-3-deoxy-α-D-*manno*-2-octulopyranosyl)onate]-(2-4)-(allyl 7,8-di-*O*-benzoyl-3-deoxy-α-D-*manno*-2-octulopyranosyl) onate **6**α (32.0 mg, 32.6 μmol), 2,3,4,6,7-penta-*O*-acetyl-L-*glycero*-α-D-*manno*-heptopyranosyl trichloroacetimidate **8** (55.0 mg, 98.7 μmol), and MS-AW 300 (40 mg) was suspended in dichloromethane (1.0 mL). The reaction mixture was stirred for 1 h under argon, and then 0.01 M TMSOTf (196.0 μL, 1.96 μmol) in dichloromethane was added dropwise to the reaction mixture. After stirring for 2 h, the reaction mixture was neutralized by the addition of a few drops of triethylamine and aqueous saturated sodium hydrogen carbonate. The reaction mixture was diluted with dichloromethane and was filtered through Celite®. The filtrate was extracted twice with dichloromethane. The combined organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by BioRad S-X3 (toluene/ethyl acetate=1:1) to give compound **11** (39 mg, 87%) as colorless syrup. Mp 88.2 °C, $[\alpha]_D^{25}$ +19.7 (*c* 1.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.20 (s, 3H, Me), 1.38 (s, 3H, Me), 1.93, 2.02, 2.03, 2.14 (s, 3H×5), Ac), 3.43 (s, 3H, OMe^I), 3.47 (s, 3H, OMe^{II}), 3.93 (dd, 1H, *J*=1.6, 1.6, 4.8, 13.0 Hz, OCH_2–), 3.97 (dd, 1H, *J*=1.4, 1.6, 5.4, 13.0 Hz, OCH_2–), 4.93 (dd, 1H, *J*=1.4, 1.6, 3.0, 10.6 Hz, =CH_2), 5.01 (dd, 1H, *J*=1.6, 1.6, 3.2, 17.2 Hz, =CH_2), 5.62–5.68 (m,1H, –CH=), 7.37–7.45 (m, 8H, Ar^I, Ar^{II}), 7.51–7.56 (m, 4H, Ar^I, Ar^{II}), 7.93–8.01 (m, 8H, Ar^I, Ar^{II}). ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.69, 20.74, 20.8 and 21.1 (Ac–CH_3), 24.7 and 25.1 (Isop–Me), 52.25 (OMe^I), 52.28 (OMe^{II}), 64.7 (OCH_2–), 109.7 (C_{isop}), 116.2 (=CH_2), 128.3, 128.4, 128.5, 129.3, 129.6, 129.85, 129.90, 130.2, 132.8, 133.1 (Ar^I and Ar^{II}), 133.4 (–CH=), 165.1, 165.2, 165.8, 167.4 (Bz: C=O), 169.6, 169.7, 169.8, 170.4 and 170.7 (Ac: C=O). IR (neat): 1745, 1725, 1278, 1248, 1218 cm^{-1}. Anal. Calcd for $C_{69}H_{76}O_{30}$: C, 59.82; H, 5.53. Found C, 59.65; H, 5.67. *Orthoester* ***12***: mp 99.0 °C. $[\alpha]_D^{25}$ +7.5 (*c* 1.0, $CHCl_3$), ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.21 (s, 3H, Me), 1.40 (s, 3H, Me), 1.65 (s, 3H, ester-Me), 1.91 (dd, 1H, $J_{3a,3b}$=15.4 Hz, $J_{3a,4}$=2.2 Hz, H-3a^{II}), 1.97, 2.03, 2.04, 2.07 (s, 3H×4, Ac), 2.31 (dd, 1H, $J_{3a,3b}$=12.6 Hz, $J_{3a,4}$=12.4 Hz, H-3a^I), 2.47 (dd, 1H, $J_{3a,3b}$=12.6 Hz, $J_{3b,4}$=4.0 Hz, H-3b^I), 2.86 (dd, 1H, $J_{3a,3b}$=15.4 Hz, $J_{3b,4}$=3.6 Hz, H-3b^{II}), 3.38 (ddd, 1H, $J_{4,5}$=9.6 Hz, $J_{5,6}$=2.0 Hz, H-5^{III}), 3.43 (s, 3H, OMe^I), 3.81 (s, 3H, OMe^{II}), 3.86 (dd, 1H, *J*=1.6, 1.6, 3.4, 13.4 Hz, OCH_2–), 3.97 (dd, 1H, *J*=1.6, 1.6, 3.2, 13.4 Hz, OCH_2–), 4.05 (dd, 1H, $J_{5,6}$=nd, $J_{6,7}$=8.6 Hz, H-6^I), 4.09 (dd, 1H, $J_{6,7a}$=7.8 Hz, $J_{7a,7b}$=11.6 Hz, H-7a^{III}), 4.11 (br s, 1H, $J_{4,5}$=2.4 Hz, $J_{5,6}$=nd, H-5^I),

4.15 (dd, 1H, $J_{6,7b}$=4.8 Hz, $J_{7a,7b}$=11.6 Hz, H-7b^{III}), 4.21 (dd, 1H, $J_{5,6}$=1.8 Hz, $J_{6,7}$=7.0 Hz, H-6^{II}), 4.31 (dd, 1H, $J_{4,5}$=7.6 Hz, $J_{5,6}$=1.8 Hz, H-5^{II}), 4.33 (ddd, 1H, $J_{3a,4}$=12.4 Hz, $J_{3e,4}$=4.0 Hz, $J_{4,5}$=2.4 Hz, H-4^{I}), 4.47 (ddd, 1H, $J_{3a,4}$=2.2 Hz, $J_{3e,4}$=3.6 Hz, $J_{4,5}$=7.6 Hz, H-4^{II}), 4.50 (dd, 1H, $J_{1,2}$=2.2 Hz, $J_{2,3}$=3.8 Hz, H-2^{III}), 4.60 (ddd, 1H, $J_{7,8a}$=4.6 Hz, $J_{8a,8b}$=12.4 Hz, H-8a^{II}), 4.64 (dd, 1H, $J_{7,8a}$=3.4 Hz, $J_{8a,8b}$=12.6 Hz, H-8a^{I}), 4.65 (d, 1H, $J_{1,2}$=2.2 Hz, H-1^{III}), 4.94 (dd, 1H, J=1.4, 1.4, 3.0, 10.6 Hz, =CH$_2$), 5.00 (dd, 1H, $J_{7,8b}$=2.4 Hz, $J_{8a,8b}$=12.6 Hz, H-8b^{I}), 5.02 (dd, 1H, $J_{2,3}$=3.8 Hz, $J_{3,4}$=10.0 Hz, H-3^{III}), 5.05 (dd, 1H, J=1.6, 1.6, 3.4, 17.2 Hz, =CH$_2$), 5.11 (dd, 1H, $J_{3,4}$=10.0 Hz, $J_{4,5}$=9.6 Hz, H-4^{III}), 5.14 (ddd, 1H, $J_{5,6}$=2.0 Hz, $J_{6,7a}$=7.8 Hz, $J_{6,7b}$=4.8 Hz, H-6^{III}), 5.24 (dd, 1H, $J_{7,8b}$=2.4 Hz, $J_{8a,8b}$=12.4 Hz, H-8b^{II}), 5.38 (ddd, 1H, $J_{6,7}$=8.6 Hz, $J_{7,8a}$=3.4 Hz, J$_{7,8b}$=2.4 Hz, H-7^{I}), 5.59–5.64 (m, 1H, −CH=), 5.65 (ddd, 1H, $J_{6,7}$=7.0 Hz, $J_{7,8a}$=4.6 Hz, $J_{7,8b}$=2.4 Hz, H-7^{II}), 7.39–7.47 (m, 8H, Ar^{I}, Ar^{II}), 7.54–7.55 (m, 4H, Ar^{I}, Ar^{II}), 7.95–8.01 (m, 8H, Ar^{I}, Ar^{II}). ^{13}C NMR (150 MHz, CDCl$_3$): δ 20.6, 20.6, 20.7 (Ac−CH$_3$), 24.7 and 25.3 (Isop−Me), 26.3 (ester-Me), 32.6 (C-3^{II}), 34.3 (C-3^{I}), 52.2 (OMe^{I}), 52.5 (OMe^{II}), 62.2 (C-8^{II}), 62.4 (C-8^{I}), 62.5 (C-7^{III}), 64.2 (OCH$_2$−), 64.6 (C-4^{III}), 66.8 (C-6^{III}), 67.5 (C-5^{I}), 69.2 (C-4^{I}), 69.8 (C-4^{II}), 70.2 (C-6^{II}), 70.3 (C-3^{III}), 70.4 (C-7^{I}), 70.96 (C-7^{II}), 70.96 (C-6^{I}), 71.1 (C-5^{III}), 72.1 (C-5^{II}), 76.2 (C-2^{II}), 97.2 (C-1^{III}), 98.5 (C-2^{I}), 98.8 (C-2^{II}), 109.7 (C$_{isop}$), 115.6 (=CH$_2$), 124.8 (ester-C), 128.40, 128.43, 128.5, 129.5, 129.7, 129.8, 129.9, 130.0, 130.4, 133.0, 133.07, 133.14 (Ar^{I} and Ar^{II}), 133.7 (−CH=), 165.1, 165.3, 165.9, 166.2 (Bz: C=O), 167.5 (C-1^{I}), 169.4 (C-1^{II}), 170.1, 170.17, 170.24 and 170.6 (Ac: C=O). IR(neat): 1746, 1724, 1279, 1248, 1219 cm^{-1}. ESI-HRMS calcd for $C_{69}H_{76}O_{30}$: 1407.4319 [M+Na]$^+$. Found 1407.4302.

3.5. 2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl-(1-5)-[methyl *O*-[methyl (7,8-di-*O*-benzoyl-4,5-*O*-isopropylidene-3-deoxy-α-D-*manno*-2-octulopyranosyl)onate]]-(2-4)-(allyl 7,8-di-*O*-benzoyl-3-deoxy-α-D-*manno*-2-octulopyranosyl)onate (13)

A reaction mixture of 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl trichloroacetimidate **9** (75.2 mg, 152.6 μmol), methyl *O*-[methyl (7,8-di-*O*-benzoyl-4,5-*O*-isopropylidene-3-deoxy-α-D-*manno*-2-octulopyranosyl)onate]-(2-4)-(allyl 7,8-di-*O*-benzoyl-3-deoxy-α-D-*manno*-2-octulopyranosyl)onate **6**α (50.0 mg, 51.0 μmol), and MS-AW 300 (57.8 mg) was suspended in dichloromethane (1.4 mL). The reaction mixture was stirred for 1 h under argon, and then cooled to 0 °C. To the reaction mixture, 0.01 M TMSOTf (200.0 μL, 2.00 μmol) in dichloromethane was added dropwise. After stirring for 2 h, the reaction mixture was neutralized by the addition of triethylamine and saturated sodium hydrogen carbonate. The reaction solution was diluted with dichloromethane and then filtered through Celite®. The filtrate was extracted twice with dichloromethane. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by BioRad S-X3 (toluene/ethyl acetate=1:1) to give compound **13** (60.9 mg, 91%) as colorless powder. Mp 85.5 °C, $[\alpha]_D^{25}$ +37.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.21 (s, 3H, Me), 1.38 (s, 3H, Me), 2.00, 2.02, 2.05, 2.16 (s, 3H×4, Ac), 3.42 (s, 3H, OMe^{I}), 3.56 (s, 3H, OMe^{II}), 3.92 (dd, 1H, J=1.6, 1.6, 5.0, 13.0 Hz, OCH$_2$−), 3.97 (dd, 1H, J=1.4, 1.4, 5.4, 13.0 Hz, OCH$_2$−), 4.92 (dd, 1H, J=1.4, 1.6, 2.8, 10.6 Hz, =CH$_2$), 5.01 (dd, 1H, J=1.4, 1.6, 3.2, 17.2 Hz, =CH$_2$), 5.63–570 (m,1H, −CH=), 7.37–7.44 (m, 8H, Ar^{I}, Ar^{II}), 7.52–7.57 (m, 4H, Ar^{I}, Ar^{II}), 7.94–7.99 (m, 8H, Ar^{I}, Ar^{II}). ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.7, 20.76, 20.78 and 20.9 (Ac−CH$_3$), 24.6 and 25.1 (Me), 52.2 (OMe^{I}), 52.4 (OMe^{II}), 64.8 (OCH$_2$−), 109.8 (C$_{isop}$), 116.3 (=CH$_2$), 128.36, 128.41, 128.46, 128.50, 129.0, 129.62, 129.64, 129.7, 129.8, 130.17 and 133.15 (Ar^{I} and Ar^{II}), 133.47 (−CH=), 164.8, 165.3, 165.8, and 166.2 (Bz: C=O), 169.56, 169.61, 169.8 and 170.8 (Ac: C=O). IR (neat): 1746, 1724, 1278, 1249, 1217 cm^{-1}. ESI-HRMS calcd for $C_{66}H_{72}O_{28}$: 1335.4108 [M+Na]$^+$. Found 1335.4097.

3.6. 3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl-(1-5)-[methyl *O*-[methyl (7,8-di-*O*-benzoyl-4,5-*O*-isopropylidene-3-deoxy-α-D-*manno*-2-octulopyranosyl)onate]]-(2-4)-(allyl 7,8-di-*O*-benzoyl-3-deoxy-α-D-*manno*-2-octulopyranosyl)onate (14)

A reaction mixture of methyl *O*-[methyl (7,8-di-*O*-benzoyl-4,5-*O*-isopropylidene-3-deoxy-α-D-*manno*-2-octulopyranosyl)onate]-(2-4)-(allyl 7,8-di-*O*-benzoyl-3-deoxy-α-D-*manno*-2-octulopyranosyl) onate **6**α (50.0 mg, 51.0 μmol), 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-D-galactopyranosyl trichloroacetimidate **10** (72.6 mg, 152.6 μmol), and MS-AW 300 (57.8 mg) in dichloromethane (1.4 mL) was stirred for 1 h under argon and cooled to 0 °C. Then 0.01 M TMSOTf (200 μL, 2.00 μmol) in dichloromethane was added dropwise to the reaction mixture and stirred for 4 h. The solution was neutralized by the addition of triethylamine and saturated $NaHCO_3$ and diluted with dichloromethane. The reaction mixture was filtered through Celite®, and the filtrate was extracted with dichloromethane. The organic phase was dried over Na_2SO_4, filtered, and concentrated. Purification of the residue by BioRad S-X3 (toluene/ethyl acetate=1:1) obtained compound **14** (38 mg, 58%) as colorless powder. Mp 96.0 °C, $[\alpha]_D^{25}$ +51.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.21 (s, 3H, Me), 1.39 (s, 3H, Me), 1.96, 2.06, 2.11 (s, 3H×3, Ac), 3.32 (s, 3H, OMe^{I}), 3.59 (s, 3H, OMe^{II}), 3.95 (dd, 1H, J=5.4 and 13.0 Hz, OCH$_2$−), 3.97 (dd, 1H, J=5.0 and 13.0 Hz, OCH$_2$−), 4.91 (dd, 1H, J=10.0 and 1.4 Hz, =CH$_2$), 4.99 (dd, 1H, J=10.0 and <0.2 Hz, =CH$_2$), 5.63–5.67 (m,1H, −CH=), 7.36–7.39 (m, 2H, Ar^{I}, Ar^{II}), 7.42–7.45 (m, 3H, Ar^{I}, Ar^{II}), 7.51–7.58 (m, 4H, Ar^{I}, Ar^{II}), 7.94–8.03 (m, 8H, Ar^{I}, Ar^{II}). ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.6 and 20.7 (Ac−CH$_3$), 24.6 and 25.1 (Me), 52.1 (OMe^{II}), 52.2 (OMe^{I}), 64.8 (OCH$_2$−), 109.8 (C$_{isop}$), 116.4 (=CH$_2$), 128.4, 128.47, 128.52, 129.5, 129.65, 129.72, 129.8, 130.2, 132.9, 133.1 and 133.5 (Ar^{I} and Ar^{II}), 133.15 (−CH=), 165.2, 165.8, 166.2 (Bz: C=O), 169.7, 170.1 and 170.2 (Ac: C=O). IR (neat): 2112, 1748, 1723, 1278, 1251, 1218 cm^{-1}. ESI-HRMS calcd for $C_{64}H_{69}N_3O_{26}$: 1318.4067 [M+Na]$^+$. Found 1318.4072.

3.7. 3,4,6-Tri-*O*-acetyl-2-acetamido-2-deoxy-α-D-galactopyranosyl-(1-5)-[methyl *O*-[methyl (7,8-di-*O*-benzoyl-4,5-*O*-isopropylidene-3-deoxy-α-D-*manno*-2-octulopyranosyl)onate]]-(2-4)-(allyl 7,8-di-*O*-benzoyl-3-deoxy-α-D-*manno*-2-octulopyranosyl)onate (15)

To a solution of 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl-(1-5)-[methyl *O*-[methyl(7,8-di-*O*-benzoyl-4,5-*O*-isopropylidene-3-deoxy-α-D-*manno*-2-octulopyranosyl)onate]]-(2-4)-(allyl 7,8-di-*O*-benzoyl-3-deoxy-α-D-*manno*-2-octulopyranosyl) onate **14** (23.7 mg, 18.3 μmol) dissolved in a mixed solvent (THF/H_2O=19:1, 0.36 mL) was added triphenylphosphine (6.2 mg, 23.7 μmol). After stirring for 16 h, the reaction mixture was diluted with toluene and concentrated by evaporation. Without purification, the residue was directly acetylated with pyridine/Ac_2O (1:0.04, v/v, 190.0 μL) in the presence of a catalytic amount of DMAP over 18 h. After removing the solvent, the residue was purified by TLC (CH_2Cl_2/EtOAc/hexane=3:3:1) to give compound **15** (15.4 mg, 64%) as colorless powder. Mp 99.0 °C, $[\alpha]_D^{25}$ +62.1 (*c* 1.2, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.20 (s, 3H, Me), 1.37 (s, 3H, Me), 1.88 (dd, 1H, $J_{3a,3b}$=15.6 Hz, $J_{3a,4}$=2.0 Hz, H-3a^{II}), 1.97, 2.00, 2.14 (s, 3H×3, Ac), 2.02 (s, 3H, NHAc), 2.18 (dd, 1H, $J_{3a,4}$=11.8 Hz, $J_{3a,3b}$=13.0, H-3a^{I}), 2.23 (dd, 1H, $J_{3b,4}$=5.6 Hz, $J_{3a,3b}$=13.0, H-3b^{I}), 3.02 (dd, 1H, $J_{3a,3b}$=15.6 Hz, $J_{3b,4}$=3.4 Hz, H-3b^{II}), 3.35 (s, 3H, OMe^{I}), 3.43 (s, 3H, OMe^{II}), 3.74 (brs, 1H, $J_{4,5}$=2.0 Hz, $J_{5,6}$=1.6 Hz, H-5^{I}), 3.83 (dddd, 1H, J=1.4, 1.6, 4.8 and 11.0 Hz, OCH$_2$−), 3.90 (dddd, 1H, J=1.6, 1.6, 6.0 and 12.4 Hz, OCH$_2$−), 4.06 (dd, 1H, $J_{5,6a}$=5.0 Hz, $J_{6a,6b}$=10.8 Hz, H-6a^{III}), 4.11 (dd, 1H, $J_{5,6}$=1.6 Hz, $J_{6,7}$=9.8 Hz, H-6^{I}), 4.14 (dd, 1H, $J_{5,6b}$=9.4 Hz, $J_{6a,6b}$=10.8 Hz, H-6b^{III}), 4.19 (dd, 1H, $J_{5,6}$=1.6 Hz, $J_{6,7}$=8.0 Hz, H-6^{II}), 4.36 (dd, 1H, $J_{4,5}$=7.8 Hz, $J_{5,6}$=1.6 Hz, H-5^{II}), 4.53 (ddd, 1H,

$J_{3a,4}$=2.0 Hz, $J_{3e,4}$=3.4 Hz, $J_{4,5}$=7.8 Hz, H-4^{II}), 4.53 (ddd, 1H, $J_{4,5}$=2.2 Hz, $J_{5,6a}$=5.0 Hz, $J_{5,6b}$=9.4 Hz, H-5^{III}), 4.53 (ddd, 1H, $J_{7,8a}$=4.0 Hz, $J_{8a,8b}$=12.4 Hz, H-8a^{I}), 4.60 (dd, 1H, $J_{7,8a}$=4.0 Hz, $J_{8a,8b}$=12.6 Hz, H-8a^{II}), 4.71 (dd, 1H, $J_{1,2}$=3.4 Hz, $J_{2,3}$=11.4 Hz, $J_{NH,2}$=10.0 Hz, H-2^{III}), 4.75 (ddd, 1H, $J_{3a,4}$=11.4 Hz, $J_{3e,4}$=5.6 Hz, $J_{4,5}$=2.0 Hz, H-4^{I}), 4.85 (dd, 1H, $J_{7,8b}$=2.6 Hz, $J_{8a,8b}$=12.4 Hz, H-8b^{I}), 4.94 (dd, 1H, J=1.2 and 17.6 Hz, =CH$_2$), 4.96 (dd, 1H, J=1.8 and 10.6 Hz, =CH$_2$), 5.03 (d, 1H, $J_{1,2}$=3.4 Hz, H-1^{III}), 5.34 (dd, 1H, $J_{2,3}$=11.4 Hz, $J_{3,4}$=3.2 Hz, H-3^{III}), 5.34 (dd, 1H, $J_{7,8b}$=2.4 Hz, $J_{8a,8b}$=12.6 Hz, H-8b^{II}), 5.40 (dd, 1H, $J_{3,4}$=3.2 Hz, $J_{4,5}$=2.2 Hz, H-4^{III}), 5.53 (ddd, 1H, $J_{6,7}$=9.8 Hz, $J_{7,8a}$=4.0 Hz, $J_{7,8b}$=2.6 Hz, H-7^{I}), 5.66 (ddd, 1H, $J_{6,7}$=8.0 Hz, $J_{7,8a}$=4.0 Hz, $J_{7,8b}$=2.4 Hz, H-7^{II}), 5.70 (m, 1H, −CH=), 6.43 (d, 1H, $J_{NH,2}$=10.0 Hz, NHAc), 7.37–7.38 (m, 2H, Ar^{I}, Ar^{II}), 7.40–7.46 (m, 6H, Ar^{I}, Ar^{II}), 7.51–7.59 (m, 4H, Ar^{I}, Ar^{II}), 7.93–8.07 (m, 8H, Ar^{I}, Ar^{II}). ^{13}C NMR (150 MHz, CDCl$_3$): δ 20.6, 20.75, 20.84 (Ac−CH$_3$), 23.0 (NHAc−CH$_3$), 25.0 and 25.1 (Me), 31.7 (C-3^{II}), 34.9 (C-3^{I}), 47.6 (C-2^{III}), 52.1 (OMe^{II}), 52.4 (OMe^{I}), 60.4 (C-6^{III}), 61.9 (C-8^{II}), 62.4 (C-8^{I}), 65.43 (OCH$_2$−), 66.45 (C-5^{III}), 66.8 (C-4^{III}), 67.4 (C-4^{I}), 68.5 (C-3^{III}), 68.6 (C-7^{I}), 69.9 (C-4^{II}), 70.2 (C-6^{II}), 70.5 (C-7^{II}), 70.6 (C-5^{I}), 70.7 (C-6^{I}), 72.1 (C-5^{II}), 96.2 (C-2^{II}), 97.9 (C-1^{III}), 99.2 (C-2^{I}), 109.9 (C$_{isop}$), 117.0 (=CH$_2$), 128.39, 128.42, 128.5, 128.6, 128.8, 129.3, 129.6, 129.70, 129.73, 129.8, 129.9 and 130.1 (Ar^{I} and Ar^{II}), 133.0 (−CH=), 164.9, 165.1, 165.7, 166.2 (Bz: C=O), 168.3 (C-1^{I}), 168.6 (C-1^{II}), 170.1, 107.3, 170.5 (Ac: C=O). 170.9 (NHAc−C=O). IR(neat): 1746, 1723, 1278, 1249, 1217 cm^{-1}. ESI-HRMS calcd for $C_{66}H_{73}NO_{27}$: 1334.4268 [M+Na]$^+$. Found 1334.4253.

3.8. 2-Acetamido-2-deoxy-α-D-galactopyranosyl-(1-5)-[*O*-(sodium 3-deoxy-α-D-*manno*-2-octulopyranosylonate)]-(2-4)-sodium (allyl 3-deoxy-α-D-*manno*-2-octulopyranoside)onate (16)

The procedure was similar to that described for compound **17**. The reaction was performed with 27.4 mg of 3,4,6-tri-*O*-acetyl-2-acetamido-2-deoxy-α-D-galactopyranosyl- (1-5)-[methyl *O*-[methyl (7,8-di-*O*-benzoyl-4,5-*O*-isopropylidene-3-deoxy-α-D-*manno*-2-octulopyranosyl)onate]]-(2-4)-(allyl 7,8-di-*O*-benzoyl-3-deoxy-α-D-*manno*-2- octulopyranosyl)onate **15**, 80% trifluoroacetic acid (0.9 mL), and 0.1 M sodium hydroxide (2.5 mL) to afford compound **16** (15.6 mg) in quantitative yield. $[\alpha]_D^{25}$ +116.5 (*c* 0.3, H$_2$O). ^{1}H NMR (600 MHz, D$_2$O): δ 1.73 (dd, 1H, $J_{3a,4}$=12.6 Hz, $J_{3a,3e}$=13.0 Hz, H-3a^{II}), 1.94–2.04 (m, 2H, H-3a^{I}, H-3e^{I}), 2.02 (s, 3H, Ac), 2.10 (d, 1H, $J_{3b,4}$=4.4 Hz, $J_{3a,3e}$=13.0 Hz, H-3e^{II}), 3.51–3.53 (m, 1H, H-6^{I}), 3.54 (dd, $J_{7,8a}$=6.0 Hz, $J_{8a,8b}$=11.8 Hz, 1H, H-8a^{II}), 3.66 (dd, 1H, $J_{5,6}$=1.0 Hz, $J_{6,7}$=8.0 Hz, H-6^{II}), 3.66–3.75 (m, 5H, H-8a^{I}, H-7^{I}, OCH$_2$, H-6a^{III}, H-6b^{III}), 3.81–3.86 (m, 3H, H-8b^{II}, H-8b^{I}, OCH$_2$), 3.88–3.91 (m, 1H, H-7^{II}), 3.94–3.99 (m, 4H, H-5^{II}, H-3^{III}, H-4^{II}, H-4^{III}), 4.26 (ddd, 1H, J=2.0, 5.4, 11.2 Hz, H-4^{I}), 4.16 (dd, 1H, $J_{1,2}$=3.4 Hz, H-2^{III}), 4.17 (br s, 1H, H-5^{I}), 4.25–4.27 (m, 1H, H-5^{III}), 5.13–5.15 (m, 1H, =CH$_2$), 5.19 (d, 1H, $J_{1,2}$=3.4 Hz, H-1^{III}), 5.23–5.28 (m, 1H, =CH$_2$), 5.86–5.92 (m, 1H, −CH=). ^{13}C NMR (150 MHz, D$_2$O): δ 22.0 (CH$_3$), 34.5 (C-3^{I}), 34.6 (C-3^{II}), 50.3 (C-2^{III}), 60.4 (C-6^{III}), 62.8 (C-8^{I}), 63.3 (C-8^{II}), 64.1 (OCH$_2$), 66.0 (C-4^{II}), 66.6 (C-5^{II}), 67.6 (C-3^{III}), 68.4 (C-4^{III}), 69.2 (C-7^{II}), 70.3 (C-7^{I}), 70.5 (C-5^{III}), 70.9 (C-4^{I}), 71.9 (C-6^{II}), 72.60 (C-6^{I}), 72.63 (C-5^{I}), 97.7 (C-1^{III}), 100.4 (C-2^{II}), 101.2 (C-2^{I}), 117.0 (=CH$_2$), 134.1 (−CH=), 174.7, 175.0, 175.2 (3C, C-1^{I}, C-1^{II}, C=O). IR(neat): 3295, 1680, 1614 cm^{-1}. ESI-HRMS calcd for $C_{27}H_{42}NO_{20}$: 700.2300 [M−2Na+H]$^-$. Found 700.2294.

3.9. L-*glycero*-α-D-*manno*-Heptopyranosyl-(1-5)-[*O*-(sodium 3-deoxy-α-D-*manno*-2-octulopyranosylonate)]-(2-4)-sodium(allyl 3-deoxy-α-D-*manno*-2-octulopyranoside)onate (17)

To a solution of 2,3,4,6,7-penta-*O*-acetyl-L-*glycero*-α-D-*manno*-heptopyranosyl-(1-5)-[methyl *O*-[methyl(7,8-di-*O*-benzoyl-4,5-*O*-isopropylidene-3-deoxy-α-D-*manno*-2-octulopyranosyl)onate]]-(2-4)-(allyl 7,8-di-*O*-benzoyl-3-deoxy-α-D-*manno*-2-octulopyranosyl)onate **11** (21 mg, 15.2 μmol) in dichloromethane (2.2 mL) was added aqueous 80% trifluoroacetic acid (TFA, 220 μL) at room temperature. After stirring for 1 h, the solvent was removed by evaporation under an argon stream to give a crude compound that was not subjected to further purification. The crude compound was dissolved in methanol (3.0 mL), and then 0.1 M sodium hydroxide (2.4 mL, 0.24 mmol) was added at room temperature. After stirring for 24 h, the mixture was concentrated by evaporation. The residue was purified by gel filtration chromatography (Biogel P-2) to give compound **17** as colorless powder in 87% yield. $[\alpha]_D^{25}$ +30.2 (*c* 0.5, H$_2$O). ^{1}H NMR (600 MHz, D$_2$O): δ 1.62 (dd, 1H, $J_{3a,3e}$=13.0 Hz, $J_{3a,4}$=12.6 Hz, H-3a^{II}), 1.82 (dd, 1H, $J_{3a,4}$=12.4 Hz, $J_{3a,3e}$=12.8 Hz, H-3a^{I}), 1.91 (dd, 1H, $J_{3a,3e}$=12.8 Hz, $J_{3e,4}$=4.2 Hz, H-3e^{I}), 2.06 (dd, 1H, $J_{3a,3e}$=13.0 Hz, $J_{3e,4}$=4.8 Hz, H-3e^{II}), 3.44 (dd, 1H, $J_{5,6}$=2.4 Hz, $J_{6,7}$=8.8 Hz, H-6^{I}), 3.46 (dd, 1H, $J_{7,8a}$=6.2 Hz, $J_{8a,8b}$=11.6 Hz, H-8a^{II}), 3.54 (dd, 1H, $J_{5,6}$=0.6 Hz, $J_{6,7}$=8.0 Hz, H-6^{II}), 3.59–3.83 (m, 12H, H-8a^{I}, H-8b^{I}, H-7^{I}, H-8b^{II}, H-7^{II}, H-7a^{III}, H-7b^{III}, H-5^{III}, H-4^{III}, H-3^{III}, OCH$_2$), 3.87–3.90 (m, 3H, H-6^{III}, H-5^{II}, H-2^{III}), 3.96 (ddd, 1H, $J_{4,5}$=3.0 Hz, $J_{3e,4}$=4.8 Hz, and $J_{3a,4}$=12.6 Hz, H-4^{II}), 4.07 (br s, 1H, H-5^{I}), 4.11 (ddd, 1H, $J_{4,5}$=2.0 Hz, $J_{3e,4}$=4.2, and $J_{3a,4}$=12.6 Hz, H-4^{I}), 5.06–5.08 (m, 1H, =CH$_2$), 5.17 (d, 1H, $J_{1,2}$=1.8 Hz, H-1^{III}), 5.19 (ddd, 1H, J=1.4, 3.2, and 17.2 Hz, =CH$_2$), 5.78–5.85 (m, 1H, −CH=). ^{13}C NMR (150 MHz, D$_2$O): δ 34.3 (C-3^{I}), 34.5 (C-3^{II}), 62.9 (C-8^{I}), 63.2 (C-8^{II}), 63.9 (C-7^{III}), 64.0 (OCH$_2$), 66.1 (C-4^{II}), 66.2 (C-5^{II}), 66.3 (C-4^{III}), 69.0 (C-7^{I}), 69.2 (C-6^{III}), 69.5 (C-4^{I}), 70.0 (C-2^{III}), 70.2 (C-7^{II}), 70.4 (C-3^{III}), 71.9 (C-6^{I}), 72.0 (C-6^{II}), 72.6 (C-5^{III}), 72.8 (C-5^{I}), 100.0 (C-2^{I}, C-2^{II}), 101.1 (C-1^{III}), 117.1 (=CH$_2$), 134.0 (−CH=), 174.87 (C-1^{I}), 174.93 (C-1^{II}). IR (neat): 3346, 3333, 1678, 1623 cm^{-1}. ESI-HRMS calcd for $C_{26}H_{41}O_{21}$: 689.2149 [M−2Na+H]$^-$. Found 689.2140.

3.10. α-D-Mannopyranosyl-(1-5)-[*O*-(sodium 3-deoxy-α-D-*manno*-2-octulo pyranosylonate)]-(2-4)-sodium (allyl 3-deoxy-α-D-*manno*-2-octulopyranoside)onate (18)

The procedure was similar to that described for compound **17**. The reaction was performed with 51.3 mg of 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1-5)-[methyl *O*-[methyl (7,8-di-*O*-benzoyl-4,5-*O*-isopropylidene-3-deoxy-α-D-*manno*-2-octulopy ranosyl)onate]]-(2-4)-(allyl 7,8-di-*O*-benzoyl-3-deoxy-α-D-*manno*-2-octulopyranosyl)onate **13**, 80% trifluoro acetic acid (1.7 mL), and 0.1 M sodium hydroxide (5.0 mL) to afford 26.1 mg (93%) of compound **18**. $[\alpha]_D^{25}$ +80.4 (*c* 0.8, H$_2$O). ^{1}H NMR (600 MHz, D$_2$O): δ 1.70 (dd, 1H, $J_{3a,3e}$=12.8 Hz, $J_{3a,4}$=12.0 Hz, H-3a^{II}), 1.90 (dd, 1H, $J_{3a,3e}$=12.2 Hz, $J_{3a,4}$=12.2 Hz, H-3a^{I}), 2.01 (dd, 1H, $J_{3a,3e}$=12.2 Hz, $J_{3e,4}$=4.4 Hz, H-3e^{I}), 2.05 (dd, 1H, $J_{3a,3e}$=12.8 Hz, $J_{3e,4}$=4.6 Hz, H-3e^{II}), 3.49–3.53 (m, 1H, H-6^{I}), 3.50–3.53 (m, 1H, H-8a^{II}), 3.62–3.72 (m, 5H, H-8a^{I}, H-6^{II}, H-7^{I}, OCH$_2$, and H-6a^{III}), 3.77–3.95 (m, 10H, H-4^{III}, H-5^{II}, OCH$_2$, H-8b^{II}, H-8b^{I}, H-3^{III}, H-7^{II}, H-6b^{III}, H-4^{II}, and H-5^{III}), 4.01–4.03 (m, 2H, H-4^{I} and H-2^{III}), 4.15 (br s, 1H, H-5^{I}), 5.09–5.12 (m, 1H, =CH$_2$), 5.13 (d, 1H, $J_{1,2}$=1.6 Hz, H-1^{III}), 5.21–5.24 (m, 1H, −CH=), 5.82–5.88 (m, 1H, −CH=). ^{13}C NMR (150 MHz, D$_2$O): δ 34.4 (C-3^{I}), 34.6 (C-3^{II}), 60.5 (C-4^{III}), 62.7 (C-8^{I}), 63.3 (C-8^{II}), 64.0 (OCH$_2$), 65.9 (C-6^{III}), 66.1 (C-4^{II}), 66.7 (C-5^{II}), 69.2 (C-7^{I}), 70.1 (C-2^{III}), 70.3 (C-3^{III}), 70.5 (C-7^{II}), 70.7 (C-4^{I}), 71.7 (C-6^{II}), 72.2 (C-6^{I}), 72.7 (C-5^{III}), 73.2 (C-5^{I}), 100.00 (C-2^{I}), 100.6 (C-1^{III}), 101.5 (C-2^{II}), 117.0 (=CH$_2$), 134.0 (−CH=), 175.0 (C-1^{I}), 175.1 (C-1^{II}). IR (neat): 3381, 3274, 1604, 1568 cm^{-1}. ESI-HRMS calcd for $C_{25}H_{39}O_{20}$: 659.2035 [M−2Na+H]$^-$. Found 659.2061.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.04.024.

References and notes

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