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Convergent synthesis of 4,5-branched inner-core oligosaccharides of lipopoly- and lipooligosaccharides

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The convergent synthesis of branched inner-core oligosaccharides of lipopoly- and lipooligosaccharide with a 3-deoxy-D-*manno*-oct-2-ulosonic acid (Kdo) disaccharide acceptor was achieved. The L-*glycero*-D-*manno*-heptopyranose (Hep) units for the branched core oligosaccharide Galβ(1-4)Glcβ(1-4)Hep and Hepα(1-3)Hep were prepared from the corresponding Hep building blocks. To obtain 4,5-branched core oligosaccharide structures, the common acceptor Kdoα(2-4)Kdo was glycosylated with the Hep units.

Key words: glycosylation; oligosaccharide; heptose; lipopolysaccharide; lipooligosaccharide

Lipopolysaccharides (LPSs) and lipooligosaccharides (LOSs) are the major glycolipids expressed in the outer membrane of gram-negative bacteria.[1)] LPSs and LOSs are the first line of defense for bacteria against a range of environmental factors, including detergents and antimicrobial agents,[2,3)] and also play an important role in the pathogenesis of bacterial infections. Structurally, an LPS consists of a lipid A, a core oligosaccharide (core OS), and an O-antigen polysaccharide, whereas LOS which is limited to 10 saccharide units lacks an O-antigen polysaccharide.[4)] The core OS can be further subdivided into the inner core and outer core. The inner core consists of mostly the higher carbon sugars 3-deoxy-D-*manno*-oct-2-ulosonic acid (Kdo), and L-*glycero*-D-*manno*-heptopyranose (Hep). In Fig. 1, for example, the inner core of LPSs/LOSs from many gram-negative bacteria contains a 4,5-branched Hepα(1-3)Hepα(1-5)[Kdoα(2-4)]Kdo tetrasaccharide as the common structure.[5)] An R (R = Lac, Glc, P) residue is usually substituted at the 4-O position of Hep I.[6–8)]

To develop vaccines, immunotherapeutics, and diagnostics for pathogenic gram-negative bacteria, a detailed knowledge of branched inner-core OS structures is required. Although many chemical syntheses of linear inner-core OS structures have been described,[9,10)] there are few reports of branched inner-core OS structures.[11)] In a recent paper, we reported the synthesis of 4,5-branched inner-core trisaccharides by coupling monosaccharides (Hep, Man, $GalN_3$) with a common Kdo acceptor **1** (Fig. 1).[12,13)] To extend the utility of this approach, here we prepared more complex 4,5-banched inner-core OS structures by using the same Kdo disaccharide as the acceptor. A lactose donor was initially chosen as a model compound to try to introduce branching structure. Based on the model glycosylation, the corresponding Hep units constructed from the Hep building blocks were coupled with the Kdo moiety to obtain the desired branched inner-core OS.

Results and discussion

Synthesis of Hep units

To install the Kdo moiety, the Hep units, Galβ(1-4)Glcβ(1-4)Hep trisaccharide and Hepα(1-3)Hep disaccharide, were prepared. All the Hep building blocks (**3**, **4**, **7**) required for the Hep units were obtained from known methyl 6,7-di-*O*-acetyl-2-*O*-benzyl-L-*glycero*-D-*manno*-heptopyranoside **2**[14)] (Scheme 1). Treatment of 3,4-diol **2** with *t*-butyldimethylsilyl chloride (TBDMSCl) and 1*H*-imidazole in *N*,*N*-dimethylformamide (DMF) at room temperature gave 3-*O*-TBDMS ether **3**[14)] in 94% yield. The acetylation of **3** in acetic anhydride (Ac_2O)/pyridine and subsequent de-*O*-silylation of TBDMS group in aqueous trifluoroacetic acid gave 3-OH product **4**[14)] in 88% yield. L-*Glycero*-D-*manno*-heptosyl trichloroacetimidate **7** was also prepared from 3,4-diol **2** in a 69% yield over four steps as follows: sequential acetylation of 3,4-diol **2**, acetolysis of **5**, selective anomeric deacetylation, and treatment of hemiacetal **6** with trichloroacetonitrile in the presence of potassium carbonate.

Next, glycosylation of 4-OH Hep building block **3** with hepta-*O*-acetyl-β-lactosyl trichloroacetimidate **8**[15)] using TMSOTf as the catalyst in CH_2Cl_2 proceeded smoothly to afford (1-4)-linked Galβ(1-4)Glcβ(1-4)Hep trisaccharide **9**[16)] as a Hep unit in 79% yield

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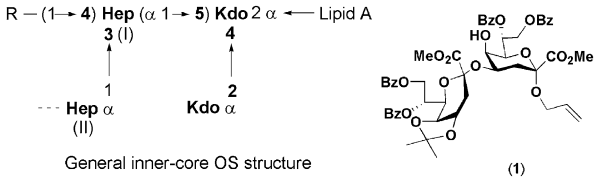
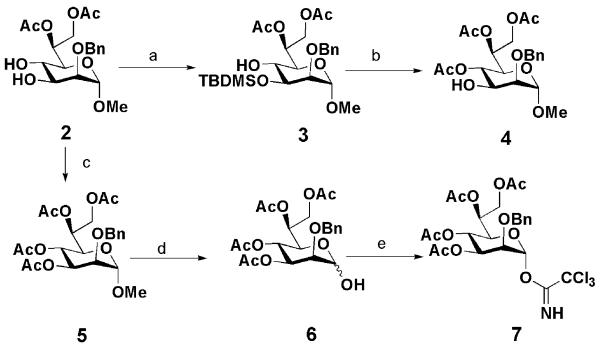


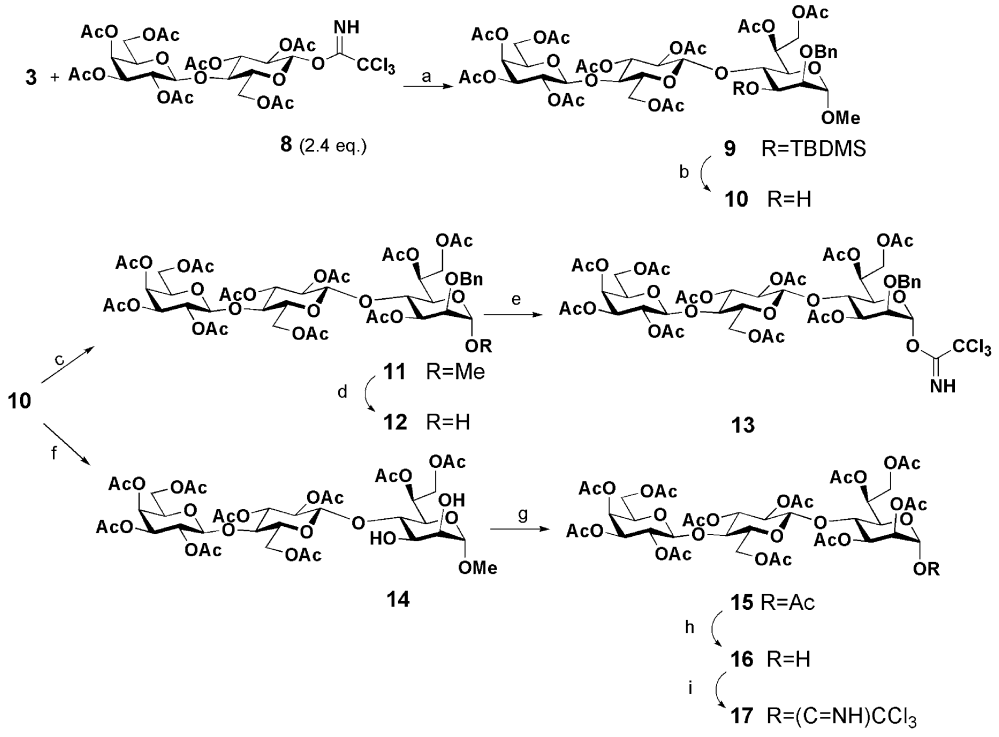
Fig. 1. General inner-core oligosaccharide structure of LPS/LOS and Kdoα(2-4)Kdo dimer **1**.



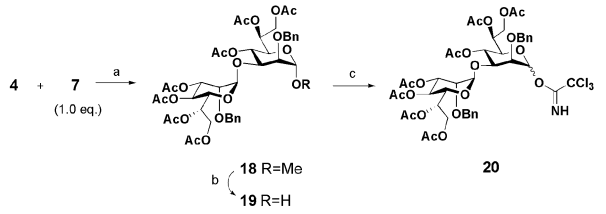
Scheme 1. Conditions: (a) TBDMSCl, 1*H*-imidazole, DMF, rt, 4 h, 94%; (b) (i) Ac_2O, DMAP, pyridine, 0 °C→ rt, 17 h, 95%; (ii) 90% TFA aq., rt, 1 h, 93%; (c) Ac_2O, DMAP, pyridine, 0 °C→ rt, 2 h, 94%; (d) (i) H_2SO_4, Ac_2O, AcOH, rt, 2 h, 95%; (ii) hydrazine acetate, 0 °C→ rt, DMF, 2 h, 80%; (e) Cl_3CCN, K_2CO_3, CH_2Cl_2, rt, 22 h, 96%. TBDMSCl: *t*-butyldimethylsilyl chloride; DMF: *N*,*N*-dimethylformamide; DMAP: *N*,*N*-dimethyl-4-aminopyridine; TFA: trifluoroacetic acid.

(Scheme 2). The glucosyl-(1-4)-heptose linkage in trisaccharide **9** was assigned as β based on the coupling constant between H-1 and H-2 of the glucose residue ($^3J_{H1,H2}$ = 8.0 Hz).[17] Cleavage of the TBDMS group in Galβ(1-4)Glcβ(1-4)Hep trisaccharide **9** with aqueous trifluoroacetic acid produced the free 3-OH **10**[16] in 97% yield. To characterize the effect of the protecting group of donor moiety on the glycosidation, two types of Galβ(1-4)Glcβ(1-4)Hep donors (**13** and **17**) with the different protecting groups at C-2 of the Hep residue were prepared from **10**, respectively, as follows. Immediate acetylation of **10** with acetic anhydride in pyridine gave **11** in 73% yield. Acetolysis of **11** in H_2SO_4/Ac_2O/AcOH and subsequent selective anomeric deacetylation afforded hemiacetal **12**. Galβ(1-4)Glcβ(1-4)Hep hemiacetal **12** was transformed in quantitative yield to the corresponding trichloroacetimidate **13**. In addition, to obtain a per-*O*-acetylated Galβ(1-4)Glcβ(1-4)Hep donor, the benzyl group at C-2 of the Hep residue in **10** was removed by hydrogenolysis (10% Pd/C in EtOAc) to give 2,3-diol **14**[16] in 97% yield. Acetylation of **14** with acetic anhydride in pyridine, followed by acetolysis, produced **15** in 67% yield. Selective anomeric deacetylation of **15** with hydrazine acetate in DMF at 0 °C gave hemiacetal **16** in 90% yield. Treatment of **16** with trichloroacetonitrile in the presence of K_2CO_3 gave per-*O*-acetylated Galβ(1-4)Glcβ(1-4)Hep trichloroacetimidate **17** in 92% yield. Galβ(1-4)Glcβ(1-4)Hep trichloroacetimidates **13** and **17** were expected to undergo [3 + 2] coupling with the Kdo moiety.

The (1-3)-linked heptobiose unit **18** was prepared in 50% yield by glycosidation of imidate **7** with Hep



Scheme 2. Conditions: (a) TMSOTf, CH_2Cl_2, MS-AW 300 molecular sieves, 0 °C, 3 h, 79%; (b) TFA/H_2O, 9:1, rt, 5 min, 97%; (c) Ac_2O, DMAP, pyridine, rt, 2 h, 73%; (d) (i) H_2SO_4, Ac_2O, AcOH, rt, 3 h, 64%; (ii) hydrazine acetate, DMF, 0 °C, 8 h, 77%; (e) Cl_3CCN, K_2CO_3, CH_2Cl_2, rt, 13 h, quant; (f) 10% Pd/C, H_2, ethyl acetate, rt, 3.5 h, 97%; (g) (i) Ac_2O, pyridine, rt, 24 h; (ii) H_2SO_4, Ac_2O, AcOH, rt, 15 h, two steps: 67%; (h) hydrazine acetate, DMF, 0 °C, 8 h, 90%; (i) Cl_3CCN, K_2CO_3, CH_2Cl_2, rt, 24 h, 92%. TMSOTf: trimethylsilyl trifluoromethanesulfonate.



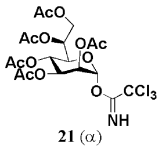
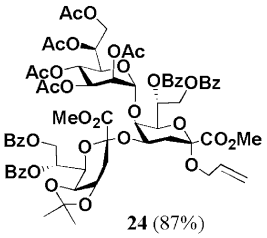
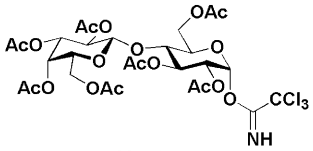
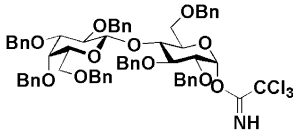
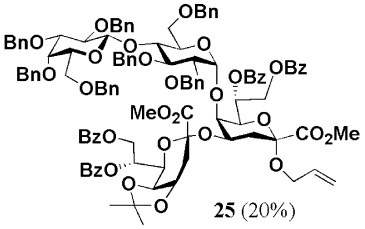
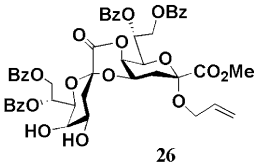
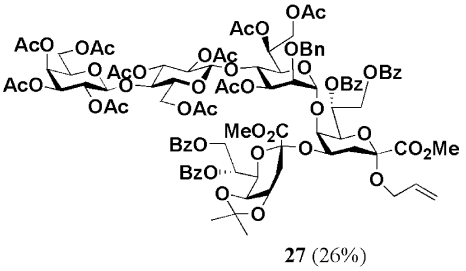
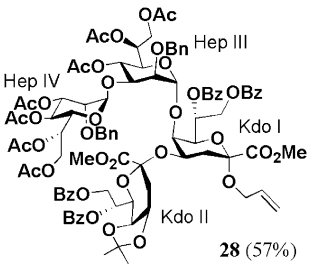
Scheme 3. Conditions: (a) TMSOTf, CH_2Cl_2, 4Å molecular sieves, −78 °C→ rt, 2 h, 50%; (b) (i) H_2SO_4, Ac_2O, AcOH, rt, 2 h, (ii) hydrazine acetate, DMF, 0 °C, 7 h, two steps: 78%; (c) Cl_3CCN, K_2CO_3, CH_2Cl_2, rt, 21 h, 80%, α/β = 6:1.

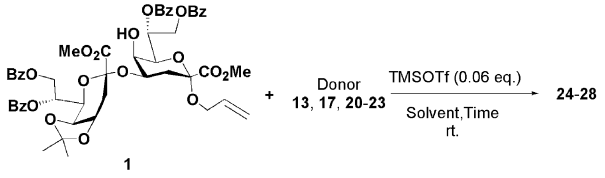
building block **4** using TMSOTf as a promoter in CH_2Cl_2 (Scheme 3). The coupling constant between C-1 and H-1 ($^1J_{C,H}$ = 174 Hz) of reducing heptose residue suggested the (1-3) linkage was an α-linkage.[17] No β-isomer was detected. Acetolysis of the methyl ether in **18**, followed by selective cleavage of the anomeric acetyl group with hydrazine acetate in DMF at 0 °C, produced disaccharide hemiacetal **19** in 78% yield over two steps. Treatment of **19** with trichloroacetonitrile in the presence of K_2CO_3 gave Hep(1-3)Hep trichloroacetimidate **20**, which was expected to undergo [2 + 2] coupling with the Kdo moiety.

Synthesis of 4,5-branched inner-core OS structures

Next, we focused on the glycosylation of the Kdo moiety with the Hep units. A model glycosylation using a lactose derivative as a donor was performed to test this convergent approach. Because the glycosidation of

Table 1. Glycosyl coupling of Kdoa(2-4)Kdo acceptor 1 and glycosyl donors 13,17, and 20–23.

Donor	Solvent	Time/h	Product	**1**/%
 **21** (α)	CH_2Cl_2	2	 **24** (87%)	9
 **22** (α)	CH_2Cl_2	2	–	90
 **23** (α)	CH_2Cl_2/Et_2O(3/1)	2	 **25** (20%)	75
17 (α)	CH_2Cl_2	15	 **26**	–
13 (α)	CH_2Cl_2	2	 **27** (26%)	69
20 (α/β=6/1)	CH_2Cl_2	1	 **28** (57%)	42



Scheme 4. Glycosylation of compound 1 with Donors 13, 17, and 20–23.

Hep imidate **21** containing acetyl groups could provide Hepα(1-5)[Kdoα(2-4)]Kdo trisaccharide **24** in good yield (Table 1), per-*O*-acetylated lactosyl imidate **22** was used for coupling with Kdoα(2-4)Kdo acceptor **1** (Scheme 4 and Table 1). However, no Lac-Kdo tetrasaccharide was formed. The reactivity of the per-*O*-acetylated lactose donor was too low to form the linkage. Therefore, a more reactive donor, hepta-*O*-benzyl-α-lactosyl trichloroacetimidate **23**[18], was examined. To increase the α-selectivity in the lactosylation, the reaction was carried out in CH_2Cl_2/Et_2O[19] and gave branched Galβ(1-4)Glc(1-5)[Kdoα(2-4)]Kdo tetrasaccharide **25** in 20% yield as only a single isomer. The coupling constant between H-1 and H-2 of the glucose residue ($^3J_{H1,H2}$ = 3.4 Hz) indicated that the (1-5) linkage was an α-linkage. The high stereoselectivity was due to the anomeric effect[20] and the solvent effect[21,22]. The introduction of benzyl ethers meant that imidate **23** was more effective in providing desired tetrasaccharide **25**, despite the high steric hindrance.

Following the model glycosylation, the [3 + 2] coupling of the Lacβ(1-4)Hep unit with the Kdo moiety was examined. According to the glycosidation results of both Hep donor **7** and **21** giving products in high α-selectivity in CH_2Cl_2, CH_2Cl_2 was used as a solvent for the following heptosylation. The synthesis of Lacβ(1-4)Hepα(1-5)[Kdoα(2-4)]Kdo pentasaccharide by coupling of per-*O*-acetylated Galβ(1-4)Glcβ(1-4)Hep trichloroacetimidate **17** with Kdo acceptor **1** failed. No branched pentasaccharide was found and mainly imidate **17** was recovered, even though the reaction time was extended to 15 h. In addition, the decomposition of the acceptor **1** to lactone **26** was observed. The donor was changed to Galβ(1-4)Glcβ(1-4)Hep imidate **13**, which contained a benzyl group at C-2 of the Hep residue, and desired Galβ(1-4)Glcβ(1-4)Hep(1-5)[Kdoα(2-4)]Kdo pentasaccharide **27** was obtained in a 26% yield as the α-anomer. No β-isomer was detected. The anomeric configuration of the Hep residue in pentasaccharide **27** was confirmed by the coupling constants between C-1 and H-1 of the heptose residue ($^1J_{C,H}$ = 174 Hz). This was consistent with the results of the model glycosylation, which indicated that the reactivity of the donor is important for this convergent approach. The introduction of a benzyl ether at C-2 of the Hep residue increased the reactivity of the Galβ(1-4)Glcβ(1-4)Hep unit to provide the branched pentasaccharide. Therefore, in our convergent approach, the sterically crowded heptose unit can be added to the Kdo moiety to produce the desired 4,5-branched core OS structures. This approach was also expected to provide the common inner-core OS structure containing the heptobiose unit. For this purpose, dibenzyl Hepα(1-3)Hep trichloroacetimidate **20** was coupled with

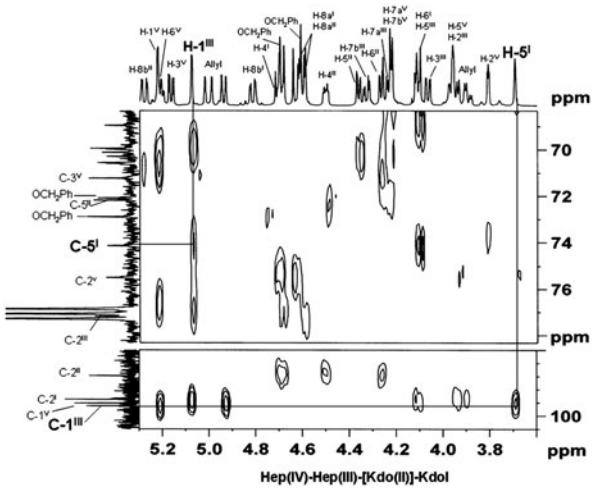


Fig. 2. Partial HMBC spectrum of tetrasaccharide **28** in $CDCl_3$ at 25 °C.

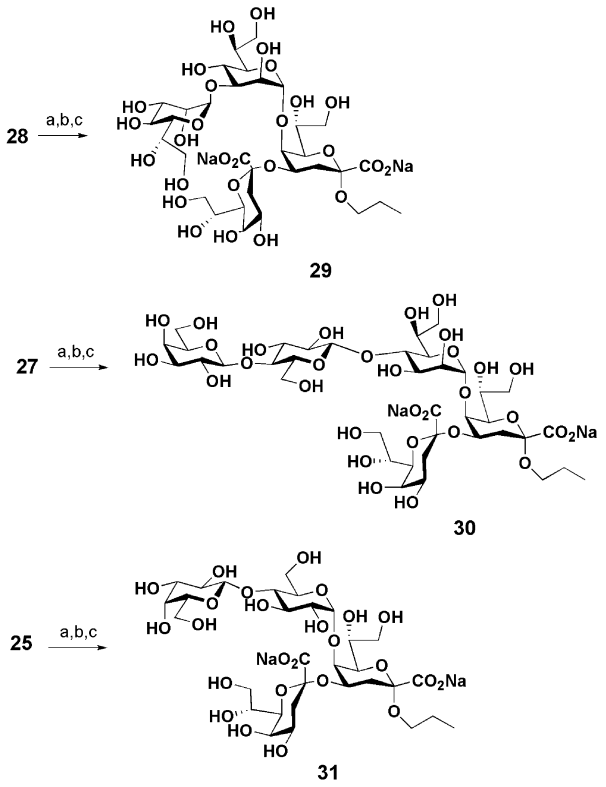
Kdoα(2-4)Kdo acceptor **1** using 0.06 equiv of TMSOTf as the activator. As expected, the introduction of the dibenzyl group substantially increased the reactivity of the Hepα(1-3)Hep unit to provide Hepα(1-3)Hep(1-5)[Kdoα(2-4)]Kdo tetrasaccharide **28** in moderate yield (57%) as only the α-isomer. The configuration of tetrasaccharide **28** was confirmed by the coupling constants between C-1 and H-1 of the corresponding heptoses (Hep III: $^1J_{C,H}$ = 172 Hz, Hep IV: $^1J_{C,H}$ = 174 Hz).

Furthermore, all branched structures we synthesized were characterized by analyzing the corresponding 2D NMR spectra (COSY, HMQC, and HMBC). For example, the existence of the (1-5) linkage in Hepα(1-3)Hepα(1-5)[Kdoα(2-4)]Kdo tetrasaccharide **28** was supported by the HMBC analysis. The cross-relay peaks, Kdo H-5^I/Hep C-1^{III}, Hep H-1^{III}/Kdo C-5^I, in the HMBC spectrum (Fig. 2) confirmed that the Hep unit is linked to the 5-position of the Kdo moiety.

These results suggest that it is possible to obtain 4,5-branched inner-core OSs of LPS/LOS using common Kdo dimer **1** as an acceptor via a convergent approach. The Lac-Hep imidate **13** with a benzyl group at C-2 of the reducing residue, other than the Lac-Hep peracetate **17**, giving the desired product of glycoside indicates that the effective improvement of the reactivity is supported by the benzyl group. Meanwhile, the glycosidation of perbenzylated Lac imidate **23** giving less product might indicate that the perbenzylated donor should be too active to obtain the glycoside in good yield. These results suggest that the introduction of appropriate number of benzyl protecting groups appears to be important for the yield of this convergent glycosylation.

Finally, deprotection of Hepα(1-3)Hepα(1-5)[Kdoα(2-4)]Kdo tetrasaccharide **28** was performed over three steps. $Pd(OH)_2$/C-promoted hydrolysis of the benzyl groups, acid hydrolysis of the isopropylidene group with aqueous trifluoroacetic acid, and hydrolysis of the ester group in 0.1 M NaOH produced the target 4,5-branched tetrasaccharide **29** in 90% yield as the disodium salt.

Galβ(1-4)Glcβ(1-4)Hepα(1-5)[Kdoα(2-4)]Kdo pentasaccharide **27** and Galβ(1-4)Glcα(1-5)[Kdoα(2-4)]Kdo



Scheme 5. Conditions: (a) $Pd(OH)_2/C$, H_2, MeOH, rt; (b) 80% TFA aq., CH_2Cl_2, rt; (c) 0.1 M NaOH, MeOH, three steps: **29** (90%), **30** (53%), **31** (60%).

tetrasaccharide **25** were subjected to similar deprotection to afford the corresponding deprotected compounds, **30** (53%) and **31** (60%) (Scheme 5).

Experimental

General procedures. Optical rotation was measured with a polarimeter (SEPA500, Horiba) in $CHCl_3$. All NMR spectra were recorded at 25 °C in $CDCl_3$ or D_2O on a 600 MHz NMR spectrometer (Avance II, Bruker). Me_4Si was used as an internal standard for $CDCl_3$, and 1% CH_3CN (δ = 2.06 ppm for ^1H; δ = 1.47 and 119.68 ppm for ^{13}C) was used for D_2O. Multiplicities are quoted as singlet (s), broad singlet (brs), doublet (d), doublet of doublet (dd), triplet (t), or multiplet (m). All NMR chemical shifts (δ) are recorded in parts per million (ppm), and coupling constants (*J*) are reported in hertz (Hz). Mass spectrometry (MS) was performed by positive- and negative-mode electrospray ionization (LCT Premier, Waters). For high-precision measurements, the mass spectra were obtained by scanning the voltage over a narrow mass range at a resolution of 10,000. MALDI-TOF spectra (Autoflex-T2, Bruker) were obtained using 3,5-dihydroxybenzoic acid as the matrix. Elemental analysis was performed on two different instruments (Vario ELCUBE and Vario EL III, Elementar). Analytical TLC was performed on Silica Gel 60 F254 glass plates. The TLC plates were visualized with UV light and by staining with Hanessian solution (ceric sulfate and ammonium molybdate in aqueous sulfuric acid) and then heating at 200–160°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).

*Methyl 3,4,6,7-tetra-O-acetyl-2-O-benzyl-l-glycero-α-D-manno-heptopyranoside (**5**).* A catalytic amount of *N*,*N*-dimethyl-4-aminopyridine (DMAP) was added to a solution of methyl 6,7-di-*O*-acetyl-2-*O*-benzyl-L-*glycero*-D-*manno*-heptopyranoside (**2**; 1.9 g, 4.8 mmol) in acetic anhydride (4.5 mL)/pyridine (9.7 mL) at 0 °C. After stirring for 2 h at room temperature, the mixture was concentrated and purified by silica gel chromatography (ethyl acetate/hexane, 4:5) to give **5** (2.2 g, 94%). $[\alpha]^{25}_D = -19.2$ (*c* 3.1, $CHCl_3$), ^1H NMR (600 MHz, $CDCl_3$): δ 1.96, 2.01, 2.05, 2.13 (s, 3H x 4, Ac), 3.35 (s, 3H, OCH_3), 3.82 (dd, 1H, $J_{1,2}$ = 1.4 Hz, $J_{2,3}$ = 3.2 Hz, H-2), 3.99 (dd, 1H, $J_{4,5}$ = 10.2 Hz, $J_{5,6}$ = 2.0 Hz, H-5), 4.25 (dd, 1H, $J_{6,7a}$ = 7.6 Hz, $J_{7a,7b}$ = 11.2 Hz, H-7a), 3.34 (dd, 1H, $J_{6,7b}$ = 5.8 Hz, $J_{7a,7b}$ = 11.2 Hz, H-7b), 4.63 (d, 1H, *J* = 12.4 Hz, OCH_2Ph), 4.69 (d, 1H, *J* = 12.4 Hz, OCH_2Ph), 4.78 (d, 1H, $J_{1,2}$ = 1.4 Hz, H-1), 5.19 (dd, 1H, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 10.2 Hz, H-3), 5.27 (ddd, 1H, $J_{5,6}$ = 2.0 Hz, $J_{6,7a}$ = 7.6 Hz, $J_{6,7b}$ = 5.8 Hz, H-6), 5.44 (dd, 1H, $J_{3,4}$ = 10.2 Hz, $J_{4,5}$ = 10.2 Hz, H-4), 7.29–7.37 (m, 5H, Ph). ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.6, 20.7, 20.8, 20.84 (Ac-CH_3), 55.2 (OCH_3), 62.0 (C-7), 65.2 (C-4), 67.1 (C-6), 68.5 (C-5), 71.5 (C-3), 73.2 (OCH_2Ph), 74.9 (C-2), 99.4 (C-1), 128.0, 128.4, 129.9, 137.6 (Ph), 169.6, 170.2, 170.5, 170.51 (Ac: C=O). ESI-HRMS for $C_{23}H_{30}O_{11}$: 505.1686 $[M + Na]^+$. Found 505.1644.

*3,4,6,7-Tetra-O-acetyl-2-O-benzyl-L-glycero-D-manno-heptopyranose (**6**).* A mixture of H_2SO_4/AcOH/Ac_2O (9.0 mL, 2:50:25) was added to a solution of methyl 3,4,6,7-tetra-*O*-acetyl-2-*O*-benzyl-L-*glycero*-α-D-*manno*-heptopyranoside (**5**; 2.2 g, 4.5 mmol) in acetic acid and acetic anhydride (1:2, 10.0 mL). After stirring for 2 h at room temperature, the reaction mixture was neutralized by the addition of sodium acetate (3.5 g), poured into saturated sodium hydrogen carbonate, and extracted with dichloromethane. The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by silica gel chromatography (ethyl acetate/hexane, 4:5) to give a syrup (2.2 g, 95%). The syrup was treated with hydrazine acetate (0.5 g, 5.6 mmol) in DMF (30.0 mL) for 2 h at room temperature. The reaction mixture was diluted with ethyl acetate, washed with water and brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by silica gel chromatography (ethyl acetate/hexane, 1:1) to give **6** (1.6 g, 80%). ^1H NMR (600 MHz, $CDCl_3$): δ 1.98, 2.02, 2.06, 2.14 (s, 3H x 4, Ac), 3.86 (dd, 1H, $J_{1,2}$ = 1.8 Hz, $J_{2,3}$ = 3.2 Hz, H-2), 4.14 (dd, 1H, $J_{6,7a}$ = 7.0 Hz, $J_{7a,7b}$ = 11.4 Hz, H-7a), 4.18 (dd, 1H, $J_{4,5}$ = 10.0 Hz, $J_{5,6}$ = 2.0 Hz, H-5), 4.40 (dd, 1H, $J_{6,7b}$ = 5.4 Hz, $J_{7a,7b}$ = 11.4 Hz, H-7b), 4.64 (d, 1H, *J* = 12.4 Hz, OCH_2Ph), 4.67 (d, 1H, *J* = 12.4 Hz, OCH_2Ph), 5.23 (ddd, 1H, $J_{5,6}$ = 2.0 Hz, $J_{6,7a}$ = 7.0 Hz, $J_{6,7b}$ = 5.4 Hz, H-6), 5.27 (dd, 1H, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 10.2 Hz, H-3), 5.29 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 5.44 (dd, 1H, $J_{3,4}$ = 10.2 Hz,

$J_{4,5}$ = 10.0 Hz, H-4), 7.30–7.37 (m, 5H, Ph). ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.7, 20.8, 20.85 (Ac-CH_3), 62.8 (C-7), 65.5 (C-4), 67.2 (C-6), 68.7 (C-5), 71.4 (C-3), 73.2 (OCH_2Ph), 75.6 (C-2), 93.0 (C-1), 127.9, 128.0, 128.4, 137.7 (Ph), 169.8, 170.3, 170.6, 171.3 (Ac: C=O). ESI-HRMS for $C_{22}H_{28}O_{11}$: 491.1529 $[M + Na]^+$. Found 491.1514.

3,4,6,7-Tetra-O-acetyl-2-O-benzyl-L-glycero-α-D-manno-heptopyranosyl trichloroacetimidate (7). Compound **6** (1.5 g, 3.2 mmol) was dissolved in dry dichloromethane (3.0 mL). Potassium carbonate (2.2 g, 16.0 mmol) was added followed by trichloroacetonitrile (3.2 mL, 32.0 mmol), and the mixture was stirred for 22 h at room temperature. The reaction mixture was filtered through Celite. The solution was concentrated and purified by silica gel column chromatography (ethyl acetate/hexane, 2:3 + 1% Et_3N) to give **7** (1.9 g, 96%). $[\alpha]^{25}_D$ = −13.4 (*c* 3.7, $CHCl_3$), ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.96, 2.01, 2.02, 2.13 (s, 3H x 4, Ac), 4.06 (dd, 1 H, $J_{1,2}$ = 1.8 Hz, $J_{2,3}$ = 3.4 Hz, H-2), 4.18 (dd, 1H, $J_{6,7a}$ = 7.6 Hz, $J_{7a,7b}$ = 11.4 Hz, H-7a), 4.20 (dd, 1H, $J_{4,5}$ = 9.2 Hz, $J_{5,6}$ = 2.0 Hz, H-5), 4.28 (dd, 1H, $J_{6,7b}$ = 5.6 Hz, $J_{7a,7b}$ = 11.4 Hz, H-7b), 4.65 (d, 1H, *J* = 12.2 Hz, OCH_2Ph), 4.78 (d, 1H, *J* = 12.2 Hz, OCH_2Ph), 5.23 (dd, 1H, $J_{2,3}$ = 3.4 Hz, $J_{3,4}$ = 10.2 Hz, H-3), 5.27 (ddd, 1H, $J_{5,6}$ = 2.0 Hz, $J_{6,7a}$ = 7.6 Hz, $J_{6,7b}$ = 5.6 Hz, H-6), 5.54 (dd, 1H, $J_{3,4}$ = 10.2 Hz, $J_{4,5}$ = 9.2 Hz, H-4), 6.35 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 7.27–7.40 (m, 5H, Ph), 8.68 (s, 1H, OC(NH)CCl_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.7, 20.8, 20.86 (Ac-CH_3), 62.0 (C-7), 64.6 (C-4), 66.8 (C-6), 71.0 (C-5), 71.3 (C-3), 73.1 (OCH_2Ph), 73.3 (C-2), 90.6 ($OCNHCCl_3$), 95.3 (C-1), 128.1, 128.4, 137.2 (Ph), 160.0 ($OCNHCCl_3$), 169.5, 170.4, 170.5 (Ac: C=O). ESI-HRMS for $C_{24}H_{28}Cl_3NO_{11}$: 634.0626 $[M + Na]^+$. Found 634.0639.

*Methyl (2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-(1-4)-(2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-(1-4)-6,7-di-O-acetyl-2-O-benzyl-3-O-tert-butyldimethylsilyl-L-glycero-α-D-manno-heptopyranoside (**9**).* A mixture of methyl 6,7-di-*O*-acetyl-2-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-L-*glycero*-α-D-*manno*-heptopyranoside (**3**; 1.5 g, 2.9 mmol), (2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1-4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl trichloroacetimidate (**8**; 5.6 g, 7.2 mmol), and MS-AW 300 molecular sieves (7.0 g) in dry dichloromethane (50.0 mL) was stirred for 1 h under argon and then cooled to 0 °C. TMSOTf (106.0 μL, 0.6 mmol) in dry dichloromethane (0.5 mL) was added dropwise to the reaction mixture, and the mixture was stirred for 3 h. The solution was neutralized by the addition of triethylamine and saturated sodium hydrogen carbonate and diluted with dichloromethane. The mixture was filtered through Celite, and the filtrate was extracted with dichloromethane. The organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated. Purification of the residue by BioRad S-X1 size exclusion beads (toluene/ethyl acetate, 1:1) and flash column chromatography (toluene/acetone, 5:1) afforded **9** (2.6 g, 79%). $[\alpha]^{25}_D$ = +1.0 (*c* 1.0, $CHCl_3$), ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.08, 0.09 [s, 3H x 2, $Si(CH_3)_2C(CH_3)_3$], 0.90 [s, 9H, $Si(CH_3)_2C(CH_3)_3$], 1.96, 1.98, 2.04, 2.05, 2.05, 2.06, 2.09, 2.13, 2.15 (s, 3H x 8, Ac), 3.33 (s, 3H, OCH_3), 3.55 (ddd, 1H, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 5.2 Hz, $J_{5,6b}$ = 2.0 Hz, H-5^{II}), 3.56 (brs, 1H, $J_{1,2}$ = 3.4 Hz, H-2^{I}), 3.64 (dd, 1H, $J_{4,5}$ = 8.8 Hz, H-5^{I}), 3.76 (dd, 1H, $J_{3,4}$ = 9.2 Hz, $J_{4,5}$ = 10.0 Hz, H-4^{II}), 3.80 (m, 1H, $J_{4,5}$ = 8.8 Hz, H-4^{I}), 3.86 (ddd, 1H, $J_{4,5}$ = 0.8 Hz, $J_{5,6a}$ = 7.4 Hz, $J_{5,6b}$ = 6.2 Hz, H-5^{III}), 4.06 (m, 1H, H-3^{I}), 4.07 (dd, 1H, $J_{5,6a}$ = 7.4 Hz, $J_{6a,6b}$ = 11.2 Hz, H-6a^{III}), 4.09 (dd, 1H, $J_{5,6a}$ = 5.2 Hz, $J_{6a,6b}$ = 10.2 Hz, H-6a^{II}), 4.15 (dd, 1H, $J_{5,6b}$ = 6.2 Hz, $J_{6a,6b}$ = 11.2 Hz, H-6b^{III}), 4.21 (dd, 1H, $J_{6,7a}$ = 7.4 Hz, $J_{7a,7b}$ = 11.2 Hz, H-7a^{I}), 4.33 (dd, 1H, $J_{6,7b}$ = 5.6 Hz, $J_{7a,7b}$ = 11.2 Hz, H-7b^{I}), 4.38 (dd, 1H, $J_{5,6b}$ = 2.0 Hz, $J_{6a,6b}$ = 10.2 Hz, H-6b^{II}), 4.48 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^{III}), 4.55 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^{II}), 4.63 (d, 1H, *J* = 11.8 Hz, OCH_2Ph), 4.72 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1^{I}), 4.77 (d, 1H, *J* = 11.8 Hz, OCH_2Ph), 4.87 (dd, 1H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 9.4 Hz, H-2^{II}), 4.93 (dd, 1H, $J_{2,3}$ = 10.4 Hz, $J_{3,4}$ = 3.4 Hz, H-3^{III}), 5.10 (dd, 1H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 10.4 Hz, H-2^{III}), 5.18 (dd, 1H, $J_{2,3}$ = 9.4 Hz, $J_{3,4}$ = 9.2 Hz, H-3^{II}), 5.34 (dd, 1H, $J_{3,4}$ = 3.4 Hz, $J_{4,5}$ = 0.8 Hz, H-4^{III}), 5.35 (m, 1H, $J_{6,7a}$ = 7.4 Hz, $J_{6,7b}$ = 5.6 Hz, H-6^{I}), 7.24–7.36 (m, 5H, Ph). ^{13}C NMR (150 MHz, $CDCl_3$): δ −4.8, −4.6 (Si$(CH_3)_2C(CH_3)_3$), 18.1 ($Si(CH_3)_2C(CH_3)_3$), 20.5, 20.6, 20.67, 20.7, 20.85, 20.9, 25.9, 29.7 (Ac-CH_3), 25.8 (Si$(CH_3)_2C(CH_3)_3$), 55.2 (OCH_3), 60.6 (C-6^{III}), 62.3 (C-6^{II}), 62.5 (C-7^{I}), 66.5 (C-4^{III}), 68.7 (C-6^{I}), 69.1 (C-2^{III}), 70.2 (C-5^{I}), 70.6 (C-5^{III}), 70.9 (C-3^{III}), 71.0 (C-3^{I}), 71.9 (C-2^{II}), 72.4 (C-5^{II}), 72.9 (C-3^{II}, CH_2Ph), 76.5 (C-4^{II}), 77.4 (C-4^{I}), 78.3 (C-2^{I}), 100.3 (C-1^{I}, C-1^{II}), 100.9 (C-1^{III}), 127.3, 127.37, 128.1, 138.5 (Ph), 169.0, 169.5, 169.7, 170.0, 170.1, 170.2, 170.23, 170.3, 170.36 (Ac: C=O). Anal. Calcd for $C_{51}H_{74}O_{26}Si$: C, 54.15; H, 6.59. Found: C, 53.94; H, 6.48.

*Methyl (2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-(1-4)-(2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-(1-4)-6,7-di-O-acetyl-2-O-benzyl-L-glycero-α-D-manno-heptopyranoside (**10**).* Compound **9** (486.0 mg, 429.7 μmol) was dissolved in a mixture of trifluoroacetic acid and water (9:1, v/v, 10.0 mL) at room temperature. After stirring for 5 min, the mixture was diluted with toluene and concentrated. The residue was purified by flash column chromatography (dichloromethane/acetone, 9:1) to give **10** (424.0 mg, 97%). $[\alpha]^{25}_D$= +8.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.97, 2.04, 2.04, 2.05, 2.06, 2.09, 2.12, 2.13, 2.16 (s, 3H x 9, Ac), 3.30 (s, 3H, OCH_3), 3.64 (m, 1H, $J_{4,5}$ = 9.5 Hz, H-5^{I}), 3.66 (dd, 1H, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 9.5 Hz, H-4^{I}), 3.73 (ddd, 1H, $J_{5,6a}$ = 6.5 Hz, $J_{5,6b}$ = 2.0 Hz, H-5^{II}), 3.76 (dd, 1H, $J_{3,4}$ = 9.5 Hz, H-4^{II}), 3.77 (dd, 1H, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.3 Hz, H-2^{I}), 3.88 (ddd, 1H, $J_{4,5}$ = 1.5 Hz, $J_{5,6a}$ = 7.5 Hz, $J_{5,6b}$ = 6.5 Hz, H-5^{III}), 3.92 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.5 Hz, H-3^{I}), 3.98 (d, 1H, $J_{3\text{-OH},3}$ = 2.5 Hz, 3-OH), 4.04 (dd, 1H, $J_{5,6a}$ = 6.5 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6a^{II}), 4.08 (dd, 1H, $J_{5,6a}$ = 7.5 Hz, $J_{6a,6b}$ = 11.0 Hz, H-6a^{III}), 4.13 (dd, 1H, $J_{5,6b}$ = 6.5 Hz, $J_{6a,6b}$ = 11.0 Hz, H-6b^{III}), 4.27 (dd, 1H, $J_{6,7a}$ = 6.5 Hz, $J_{7a,7b}$ = 11.0 Hz, H-7a^{I}), 4.30 (dd, 1H, $J_{6,7b}$ = 7.0 Hz,

$J_{7a,7b}$ = 11.0 Hz, H-7b^{I}), 4.49 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^{III}), 4.54 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^{II}), 4.59 (dd, 1H, $J_{5,6b}$ = 2.0 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6b^{II}), 4.70 (d, 1H, J = 12.0 Hz, OCH_2Ph), 4.75 (d, 1H, $J_{1,2}$ = 2.0 Hz, H-1^{I}), 4.84 (d, 1H, J = 12.0 Hz, OCH_2Ph), 4.94 (dd, 1H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2^{II}), 4.97 (dd, 1H, $J_{2,3}$ = 10.8 Hz, $J_{3,4}$ = 3.5 Hz, H-3^{III}), 5.19 (dd, 1H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 10.8 Hz, H-2^{III}), 5.22 (dd, 1H, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 9.5 Hz, H-3^{II}), 5.25 (ddd, 1H, $J_{6,7a}$ = 6.5 Hz, $J_{6,7b}$ = 7.0 Hz, H-6^{I}), 5.35 (dd, 1H, $J_{3,4}$ = 3.5 Hz, $J_{4,5}$ = 1.5 Hz, H-4^{III}), 7.38–7.25 (m, 5H, Ph). ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.3, 20.34, 20.4, 20.5, 20.6, 20.7 (Ac-CH_3), 55.0 (OCH_3), 60.7 (C-6^{III}), 61.8 (C-6^{II}), 62.0 (C-7^{I}), 66.5 (C-4^{III}), 68.0 (C-6^{I}), 68.4 (C-5^{I}), 69.0 (C-2^{III}), 69.8 (C-3^{I}), 70.6 (C-5^{III}), 70.8 (C-3^{III}), 71.3 (C-2^{II}), 72.55 (C-5^{II}), 72.6 (C-3^{II}), 73.0 (OCH_2Ph), 76.0 (C-2^{I}), 76.2 (C-4^{II}), 79.6 (C-4^{I}), 99.0 (C-1^{I}), 100.4 (C-1^{II}), 100.9 (C-1^{III}), 127.3, 127.34, 128.1, 138.4 (Ph), 168.9, 169.3, 169.87, 169.9, 170.0, 170.1, 170.2, 170.23 (Ac: C=O). ESI-HRMS for $C_{45}H_{60}O_{26}$: 1039.3271 $[M + Na]^+$. Found: 1039.3303.

*Methyl (2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-(1-4)-(2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-(1-4)-3,6,7-tri-O-acetyl-2-O-benzyl-L-glycero-α-D-manno-heptopyranoside (**11**).* Compound **10** (280.3 mg, 275.8 μmol) was acetylated with pyridine/Ac_2O (1:1, v/v, 1.6 mL) in the presence of a catalytic amount of *N*,*N*-dimethyl-4-aminopyridine (DMAP) over 2 h. After removing the solvent, the residue was purified by flash column chromatography (dichloromethane/ethyl acetate, 5:2) to give **11** (180.9 mg, 73%). $[\alpha]^{25}_D$ = +6.1 (*c* 0.8, $CHCl_3$), ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.96, 1.97, 2.04, 2.05, 2.06, 2.08, 2.09, 2.15, 2.16 (s, 3H x 10, Ac), 3.34 (s, 3H, OCH_3), 3.61 (ddd, 1H, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 1.8 Hz, H-5^{II}), 3.76 (dd, 1H, $J_{1,2}$ = 2.4 Hz, $J_{2,3}$ = 3.4 Hz, H-2^{I}), 3.80 (dd, 1H, $J_{4,5}$ = 9.6 Hz, $J_{5,6}$ = 1.0 Hz, H-5^{I}), 3.84 (dd, 1H, $J_{3,4}$ = 8.6 Hz, $J_{4,5}$ = 10.0 Hz, H-4^{II}), 3.86 (ddd, 1H, $J_{4,5}$ = 0.8 Hz, $J_{5,6a}$ = 7.6 Hz, $J_{5,6b}$ = 6.6 Hz, H-5^{III}), 3.88 (dd, 1H, $J_{3,4}$ = 8.4 Hz, $J_{4,5}$ = 9.6 Hz, H-4^{I}), 4.07 (dd, 1H, $J_{5,6a}$ = 7.6 Hz, $J_{6a,6b}$ = 11.4 Hz, H-6a^{III}), 4.10 (dd, 1H, $J_{5,6a}$ = 5.4 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6a^{II}), 4.12 (dd, 1H, $J_{5,6b}$ = 6.6 Hz, $J_{6a,6b}$ = 11.4 Hz, H-6b^{III}), 4.25 (dd, 1H, $J_{6,7a}$ = 7.4 Hz, $J_{7a,7b}$ = 11.2 Hz, H-7a^{I}), 4.32 (dd, 1H, $J_{6,7b}$ = 6.0 Hz, $J_{7a,7b}$ = 11.2 Hz, H-7b^{I}), 4.38 (dd, 1H, $J_{5,6b}$ = 1.8 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6b^{II}), 4.47 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^{III}), 4.55 (d, 1H, J = 12.2 Hz, OCH_2Ph), 4.57 (d, 1H, $J_{1,2}$ = 7.2 Hz, H-1^{II}), 4.64 (d, 1H, J = 12.2 Hz, OCH_2Ph), 4.77 (d, 1H, $J_{1,2}$ = 2.4 Hz, H-1^{I}), 4.82 (dd, 1H, $J_{1,2}$ = 7.2 Hz, $J_{2,3}$ = 8.2 Hz, H-2^{II}), 4.93 (dd, 1H, $J_{2,3}$ = 10.4 Hz, $J_{3,4}$ = 3.4 Hz, H-3^{III}), 5.10 (dd, 1H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 10.4 Hz, H-2^{III}), 5.15 (dd, 1H, $J_{2,3}$ = 8.2 Hz, $J_{3,4}$ = 8.6 Hz, H-3^{II}), 5.27 (dd, 1H, $J_{2,3}$ = 3.4 Hz, $J_{3,4}$ = 8.4 Hz, H-3^{I}), 5.34 (dd, 1H, $J_{3,4}$ = 3.4 Hz, $J_{4,5}$ = 0.8 Hz, H-4^{III}), 5.39 (ddd, 1H, $J_{5,6}$ = 1.0 Hz, $J_{6,7a}$ = 7.2 Hz, $J_{6,7b}$ = 6.0 Hz, H-6^{I}), 7.26–7.33 (m, 5H, Ph). ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.5, 20.6, 20.68, 20.7, 20.74, 20.8, 20.9 (Ac-CH_3), 55.3 (OCH_3), 60.7 (C-6^{III}), 62.2 (C-6^{II}), 62.4 (C-7^{I}), 66.6 (C-4^{III}), 68.1 (C-6^{I}), 69.0 (C-2^{III}), 69.3 (C-3^{I}), 70.6 (C-5^{III}), 70.7 (C-5^{I}), 71.0 (C-3^{III}), 71.9 (C-2^{II}), 72.1 (C-5^{II}), 72.7 (OCH_2Ph), 73.3 (C-3^{II}), 73.9 (C-4^{I}), 75.2 (C-2^{I}), 76.2 (C-4^{II}), 99.1 (C-1^{I}), 99.9 (C-1^{II}), 101.1 (C-1^{III}), 127.8, 127.9, 128.4, 137.7 (Ph), 169.1, 169.7, 169.9, 170.2, 170.3, 170.4, (Ac: C=O). ESI-HRMS for $C_{47}H_{62}O_{27}$: 1067.3376 $[M + Na]^+$. Found 1081.3368.

*(2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl)-(1-4)-(2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-(1-4)-3,6,7-tri-O-acetyl-2-O-benzyl-L-glycero-D-manno-heptopyranose (**12**).* A solution of **11** (195.0 mg, 184.1 μmol) in a mixture of H_2SO_4/AcOH/Ac_2O (4.0 mL, 0.1:6:14) was stirred for 3 h at room temperature. The reaction mixture was neutralized by the addition of sodium acetate, poured into saturated sodium hydrogen carbonate, and extracted with dichloromethane. The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by flash column chromatography (ethyl acetate/hexane, 2:1) to give a syrup (124.5 mg, 64%). The syrup was treated with hydrazine acetate (13.0 mg, 120.4 μmol) in DMF (1.0 mL) for 8 h at 0 °C. The reaction mixture was diluted with ethyl acetate, washed with water and brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/hexane, 2:1) to give **12** (89.1 mg, 77%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.96, 1.98, 2.04, 2.06, 2.06, 2.07, 2.15, 2.15 (s, 3H x 10, Ac), 3.37 (brs, 1H, OH), 3.61 (ddd, 1H, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 4.6 Hz, $J_{5,6b}$ = 2.0 Hz, H-5^{II}), 3.79 (dd, 1H, $J_{1,2}$ = 2.8 Hz, $J_{2,3}$ = 3.2 Hz, H-2^{I}), 3.85 (dd, 1H, $J_{3,4}$ = 9.0 Hz, $J_{4,5}$ = 10.0 Hz, H-4^{II}), 3.86 (ddd, 1H, $J_{4,5}$ = 1.2 Hz, $J_{5,6a}$ = 7.6 Hz, $J_{5,6b}$ = 6.2 Hz, H-5^{III}), 3.89 (dd, 1H, $J_{3,4}$ = 8.6 Hz, $J_{4,5}$ = 9.8 Hz, H-4^{I}), 3.98 (dd, 1H, $J_{4,5}$ = 9.8 Hz, H-5^{I}), 4.07 (dd, 1H, $J_{5,6a}$ = 7.6 Hz, $J_{6a,6b}$ = 11.0 Hz, H-6a^{III}), 4.09 (dd, 1H, $J_{5,6a}$ = 4.6 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6a^{II}), 4.15 (dd, 1H, $J_{5,6b}$ = 6.2 Hz, $J_{6a,6b}$ = 11.0 Hz, H-6b^{III}), 4.15 (dd, 1H, $J_{6,7a}$ = 7.0 Hz, $J_{7a,7b}$ = 11.0 Hz, H-7a^{I}), 4.38 (dd, 1H, $J_{6,7b}$ = 6.2 Hz, $J_{7a,7b}$ = 11.0 Hz, H-7b^{I}), 4.39 (dd, 1H, $J_{5,6b}$ = 2.0 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6b^{II}), 4.48 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^{III}), 4.56 (d, 1H, J = 12.2 Hz, OCH_2Ph), 4.57 (d, 1H, $J_{1,2}$ = 7.2 Hz, H-1^{II}), 4.63 (d, 1H, J = 12.2 Hz, OCH_2Ph), 4.82 (dd, 1H, $J_{1,2}$ = 7.2 Hz, $J_{2,3}$ = 8.4 Hz, H-2^{II}), 4.93 (dd, 1H, $J_{2,3}$ = 10.4 Hz, $J_{3,4}$ = 3.4 Hz, H-3^{III}), 5.10 (dd, 1H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 10.4 Hz, H-2^{III}), 5.15 (dd, 1H, $J_{2,3}$ = 8.4 Hz, $J_{3,4}$ = 9.0 Hz, H-3^{II}), 5.27 (d, 1H, $J_{1,2}$ = 2.8 Hz, H-1^{I}), 5.33 (dd, 1H, $J_{3,4}$ = 3.4 Hz, $J_{4,5}$ = 1.2 Hz, H-4^{III}), 5.33 (dd, 1H, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 8.6 Hz, H-3^{I}), 5.37 (ddd, 1H, $J_{6,7a}$ = 7.0 Hz, $J_{6,7b}$ = 6.2 Hz, H-6^{I}), 7.27–7.33 (m, 5H, Ph). ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.5, 20.6, 20.65, 20.66, 20.7, 20.79, 20.8, 20.9 (Ac-CH_3), 60.7 (C-6^{III}), 62.4 (C-6^{II}), 62.6 (C-7^{I}), 66.6 (C-4^{III}), 68.1 (C-6^{I}), 69.0 (C-2^{III}), 69.3 (C-3^{I}), 70.5 (C-5^{III}), 70.6 (C-5^{I}), 71.0 (C-3^{III}), 71.9 (C-2^{II}), 72.0 (C-5^{II}), 72.7 (OCH_2Ph), 73.2 (C-3^{II}), 74.0 (C-4^{I}), 75.7 (C-2^{I}), 76.2 (C-4^{II}), 92.4 (C-1^{I}), 99.8 (C-1^{II}), 101.1 (C-1^{III}), 127.7, 127.8, 128.4, 137.7 (Ph), 169.2, 169.66, 169.7, 170.0, 170.15, 170.2, 170.24, 170.4, 170.9 (Ac: C=O). ESI-HRMS for $C_{46}H_{60}O_{27}$: 1067.3220 $[M + Na]^+$. Found 1067.3226.

*(2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl)-(1-4)-(2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-(1-4)-3,6,7-tri-O-acetyl-2-O-benzyl-L-glycero-α-D-manno-heptopyranosyl trichloroacetimidate (**13**).* Trichloroacetonitrile (85.0 μL, 842.1 μmol) was added to a solution of **12** (88.0 mg, 84.2 μmol) in dry dichloromethane (0.8 mL) under argon. Potassium carbonate (58.0 mg, 421.0 μmol) was added to the reaction mixture. After stirring for 13 h at room temperature, the mixture was filtered through Celite. The solution was concentrated and purified by silica gel column chromatography (ethyl acetate/hexane, 2:1) to give **13** (96.0 mg, 100%). $[\alpha]^{25}_{D} = -5.7$ (*c* 1.3, $CHCl_3$), ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.96, 1.99, 2.00, 2.06, 2.04, 2.04, 2.04, 2.05, 2.06, 2.07, 2.15, 2.15 (s, 3H x 10, Ac), 3.65 (ddd, 1H, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 1.6 Hz, H-5^{II}), 3.84 (dd, 1H, $J_{3,4}$ = 9.2 Hz, $J_{4,5}$ = 10.0 Hz, H-4^{II}), 3.87 (ddd, 1H, $J_{5,6a}$ = 7.6 Hz, $J_{5,6b}$ = 6.2 Hz, H-5^{III}), 3.88 (dd, 1H, $J_{3,4}$ = 5.6 Hz, $J_{4,5}$ = 9.4 Hz, H-4^{I}), 3.94 (dd, 1H, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 0.8 Hz, H-5^{I}), 4.04 (dd, 1H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 2.8 Hz, H-2^{I}), 4.07 (dd, 1H, $J_{5,6a}$ = 7.6 Hz, $J_{6a,6b}$ = 11.2 Hz, H-6a^{III}), 4.09 (dd, 1H, $J_{5,6a}$ = 4.8 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6a^{II}), 4.14 (dd, 1H, $J_{5,6b}$ = 6.2 Hz, $J_{6a,6b}$ = 11.2 Hz, H-6b^{III}), 4.16 (dd, 1H, $J_{6,7a}$ = 7.2 Hz, $J_{7a,7b}$ = 11.4 Hz, H-7a^{I}), 4.22 (dd, 1H, $J_{6,7b}$ = 5.8 Hz, $J_{7a,7b}$ = 11.4 Hz, H-7b^{I}), 4.47 (dd, 1H, $J_{5,6b}$ = 1.6 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6b^{II}), 4.49 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^{III}), 4.61 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1^{II}), 4.63 (d, 1H, J = 12.0 Hz, OCH_2Ph), 4.68 (d, 1H, J = 12.0 Hz, OCH_2Ph), 4.85 (dd, 1H, $J_{1,2}$ = 7.6 Hz, $J_{2,3}$ = 8.6 Hz, H-2^{II}), 4.94 (dd, 1H, $J_{2,3}$ = 10.4 Hz, $J_{3,4}$ = 3.6 Hz, H-3^{III}), 5.10 (dd, 1H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 10.4 Hz, H-2^{III}), 5.16 (dd, 1H, $J_{2,3}$ = 8.6 Hz, $J_{3,4}$ = 9.2 Hz, H-3^{II}), 5.29 (ddd, 1H, $J_{5,6}$ = 0.8 Hz, $J_{6,7a}$ = 7.2 Hz, $J_{6,7b}$ = 6.2 Hz, H-6^{I}), 5.33 (dd, 1H, $J_{3,4}$ = 3.6 Hz, H-4^{III}), 5.48 (dd, 1H, $J_{2,3}$ = 2.8 Hz, $J_{3,4}$ = 5.6 Hz, H-3^{I}), 6.31 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1^{I}), 7.26–7.34 (m, 5H, Ph), 8.68 (NH). ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.5, 20.54, 20.7, 20.74, 20.76, 20.79, 20.8, 20.9, 21.0 (Ac-CH_3), 60.7 (C-6^{III}), 62.1 (C-7^{I} and C-6^{II}), 66.6 (C-4^{III}), 67.9 (C-6^{I}), 69.3 (C-2^{III}), 69.9 (C-3^{I}), 70.6 (C-5^{III}), 71.0 (C-3^{III}), 71.5 (C-2^{II}), 71.6 (C-5^{II}), 72.4 (-OCH_2Ph and C-5^{I}), 73.0 (C-3^{II}), 74.0 (C-4^{I}), 74.9 (C-2^{I}), 76.0 (C-4^{II}), 90.8 ($OCNHCCl_3$), 96.0 (C-1^{I}), 99.2 (C-1^{II}), 101.1 (C-1^{III}), 127.9, 128.0, 128.4, 137.2 (Ph), 160.5 ($OCNHCCl_3$), 169.0, 169.6, 169.8, 169.9, 170.1, 170.13, 170.16, 170.2, 170.24, 170.4 (Ac: C=O). ESI-HRMS for $C_{48}H_{60}Cl_3NO_{27}$: 1210.2316 $[M + Na]^+$. Found 1210.2294.

*Methyl (2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-(1-4)-(2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-(1-4)-6,7-di-O-acetyl-L-glycero-α-D-manno-heptopyranoside (**14**).* Compound **10** (227.0 mg, 0.2 mmol) was hydrogenated in the presence of 10% Pd/C (100.0 mg) in ethyl acetate (15.0 mL) under atmospheric pressure of hydrogen. After stirring for 3.5 h at room temperature, the reaction mixture was filtered through Celite and concentrated. The residue was purified by flash column chromatography (dichloromethane/acetone, 3:1) to give **14** (198.0 mg, 97%). $[\alpha]^{25}_{D} = +26.0$ (*c* 1.0, $CHCl_3$), ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.97, 2.04, 2.04, 2.05, 2.07, 2.12, 2.14, 2.16, 2.17 (s, 3H x 9, Ac), 2.55 (d, 1H, $J_{2\text{-OH},H\text{-}2}$ = 1.5 Hz, 2-OH), 3.35 (s, 3H, OCH_3), 3.55 (dd, 1H, $J_{3,4}$ = 8.0 Hz, $J_{4,5}$ = 9.8 Hz, H-4^{I}), 3.71 (dd, 1H, $J_{4,5}$ = 9.8 Hz, $J_{5,6}$ = 1.0 Hz, H-5^{I}), 3.72 (ddd, 1H, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 5.5 Hz, $J_{5,6b}$ = 2.0 Hz, H-5^{II}), 3.78 (dd, 1H, $J_{3,4}$ = 9.0 Hz, $J_{4,5}$ = 10.0 Hz, H-4^{II}), 3.81 (dd, 1H, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 8.0 Hz, H-3^{I}), 3.96 (dd, 1H, $J_{1,2}$ = 1.0 Hz, $J_{2,3}$ = 3.5 Hz, H-2^{I}), 3.88 (ddd, 1H, $J_{4,5}$ = 1.0 Hz, $J_{5,6a}$ = 7.5 Hz, $J_{5,6b}$ = 6.5 Hz, H-5^{III}), 4.03 (dd, 1H, $J_{5,6a}$ = 5.5 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6a^{II}), 4.08 (dd, 1H, $J_{5,6a}$ = 7.5 Hz, $J_{6a,6b}$ = 11.3 Hz, H-6a^{III}), 4.14 (dd, 1H, $J_{5,6b}$ = 6.5 Hz, $J_{6a,6b}$ = 11.3 Hz, H-6b^{III}), 4.22 (m, 1H, $J_{5,6}$ = 1.0 Hz, H-6^{I}), 4.29 (m, 2H, H-7a^{I}, H-7b^{I}), 4.30 (d, 1H, $J_{3\text{-OH},H\text{-}3}$ = 1.0 Hz, 3-OH), 4.46 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^{II}), 4.51 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1^{III}), 4.65 (dd, 1H, $J_{5,6b}$ = 2.0 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6b^{II}), 4.80 (d, 1H, $J_{1,2}$ = 1.0 Hz, H-1^{I}), 4.93 (dd, 1H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H-2^{II}), 4.97 (dd, 1H, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 3.5 Hz, H-3^{III}), 5.11 (dd, 1H, $J_{1,2}$ = 8.5 Hz, $J_{2,3}$ = 10.5 Hz, H-2^{III}), 5.22 (dd, 1H, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 9.0 Hz, H-3^{II}), 5.35 (dd, 1H, $J_{3,4}$ = 3.5 Hz, $J_{4,5}$ = 1.0 Hz, H-4^{III}). ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.4, 20.42, 20.5, 20.54, 20.6, 20.64, 20.9 (Ac-CH_3), 55.2 (OCH_3), 60.7 (C-6^{III}), 61.6 (C-6^{II}), 62.0 (C-7^{I}), 66.5 (C-4^{III}), 67.7 (C-5^{I}), 67.9 (C-6^{I}), 69.0 (C-2^{III}), 69.5 (C-3^{I}), 69.5 (C-2^{I}), 70.8 (C-3^{III}), 71.0 (C-5^{III}), 71.2 (C-2^{II}), 72.5 (C-3^{II}), 72.8 (C-5^{II}), 76.0 (C-4^{II}), 79.0 (C-4^{I}), 100.1 (C-1^{I}), 100.6 (C-1^{II}), 100.9 (C-1^{III}), 169.0, 169.3, 170.0, 170.04, 170.16, 170.2, 170.26, 170.3 (Ac: C=O). ESI-HRMS for $C_{38}H_{54}O_{26}$: 949.2801 $[M + Na]^+$. Found 949.2766.

*(2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl)-(1-4)-(2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-(1-4)-1,2,3,6,7-penta-O-acetyl-L-glycero-α-D-manno-heptopyranose (**15**).* Compound **14** (342.0 mg, 0.4 mmol) was treated with acetic anhydride (1.0 mL) and pyridine (2.0 mL) at room temperature. The reaction mixture was stirred overnight and concentrated. The residue was purified by silica gel column chromatography (dichloromethane/acetone, 4:1) to give a syrup. The syrup was dissolved in a mixture of H_2SO_4/AcOH/Ac_2O (8.0 mL, 0.1:6:14) at room temperature. After stirring for 15 h, the reaction mixture was neutralized by the addition of sodium acetate (0.2 g), poured into saturated sodium hydrogen carbonate, and extracted with chloroform. Combined organic phase was washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by silica gel column chromatography (dichloromethane/acetone, 4:1) to give **15** (257.0 mg, 67%). $[\alpha]^{25}_{D} = +29.0$ (*c* 1.0, $CHCl_3$), ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.97, 1.99, 2.03, 2.05, 2.06, 2.07, 2.08, 2.13, 2.14, 2.15, 2.16, 2.18 (s, 3H x 12, Ac), 3.61 (ddd, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6a}$ = 7.0 Hz, $J_{5,6b}$ = 5.5 Hz, H-5^{II}), 3.82 (dd, 1H, $J_{3,4}$ = 8.5 Hz, $J_{4,5}$ = 9.5 Hz, H-4^{II}), 3.85–3.88 (m, 2H, H-5^{III}, H-4^{I}), 3.91 (dd, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 1.2 Hz, H-5^{I}), 4.05–4.09 (m, 2H, H-6a^{III}, H-7a^{I}), 4.13 (dd, 1H, $J_{5,6b}$ = 6.2 Hz, $J_{6a,6b}$ = 11.0 Hz, H-6b^{III}), 4.19 (dd, 1H, $J_{5,6a}$ = 7.0 Hz, $J_{6a,6b}$ = 11.5 Hz, H-6a^{II}), 4.24 (dd, 1H, $J_{5,6b}$ = 5.5 Hz, $J_{6a,,6b}$ = 11.5 Hz, H-6b^{II}), 4.40 (dd, 1H, $J_{6,7b}$ = 2.0 Hz, $J_{7a,7b}$ = 12.0 Hz, H-7b^{I}), 4.49 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^{III}), 4.61 (d, 1H, $J_{1,2}$ = 7.5 Hz, H-1^{II}), 4.82 (dd, 1H, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 8.0 Hz, H-2^{II}), 4.95

(dd, 1H, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 3.4 Hz, H-3^{III}), 5.11 (dd, 1H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 10.5 Hz, H-2^{III}), 5.16 (dd, 1H, $J_{2,3}$ = 8.0 Hz, $J_{3,4}$ = 8.5 Hz, H-3^{II}), 5.22 (dd, 1H, $J_{1,2}$ = 2.5 Hz, $J_{2,3}$ = 9.0 Hz, H-2^{I}), 5.32–5.36 (m, 3H, H-6^{I}, H-4^{III}, H-3^{I}), 6.06 (d, 1H, $J_{1,2}$ = 2.5 Hz, H-1^{I}). ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.5, 20.51, 20.6, 20.65, 20.7, 20.8, 20.81, 20.9, 21.1 (Ac-CH_3), 60.7 (C-6^{III}), 62.2 (C-6^{II}), 62.3 (C-7^{I}), 66.6 (C-4^{III}), 67.9 (C-3^{I}), 68.4 (C-6^{I}), 68.9 (C-2^{III}), 69.1 (C-2^{I}), 70.6 (C-5^{III}), 71.0 (C-3^{III}), 71.4 (C-5^{I}), 71.9 (C-2^{II}), 72.2 (C-5^{II}), 73.1 (C-3^{II}), 73.2 (C-4^{I}), 76.0 (C-4^{II}), 90.4 (C-1^{I}), 99.8 (C-1^{II}), 101.2 (C-1^{III}), 168.3, 169.1, 169.5, 169.53, 169.6, 169.8, 170.1, 170.14, 170.2, 170.3, 170.4 (Ac: C=O). ESI-HRMS for $C_{43}H_{58}O_{29}$: 1061.2961 $[M + Na]^+$. Found 1061.2981.

*(2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl)-(1-4)-(2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-(1-4)-2,3,6,7-tetra-O-acetyl-L-glycero-D-manno-heptopyranose (**16**).* Compound **15** (256.6 mg, 247.0 μmol) was treated with hydrazine acetate (45.5 mg, 494.0 μmol) in DMF (3.0 mL) for 8 h at 0 °C. The reaction mixture was diluted with ethyl acetate, washed with water and brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by silica gel column chromatography (acetone/dichloromethane, 1:4) to give **16** (223.4 mg, 90%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.96, 1.98, 2.04, 2.06, 2.07, 2.08, 2.13, 2.16, 2.19 (s, 3H x 11, Ac), 3.27 (brs, 1H, OH), 3.62 (ddd, 1H, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 4.6 Hz, $J_{5,6b}$ = 1.6 Hz, H-5^{II}), 3.81 (dd, 1H, $J_{3,4}$ = 9.4 Hz, $J_{4,5}$ = 10.0 Hz, H-4^{II}), 3.87 (ddd, 1H, $J_{5,6a}$ = 7.8 Hz, $J_{5,6b}$ = 6.2 Hz, H-5^{III}), 3.88 (dd, 1H, $J_{4,5}$ = 9.8 Hz, H-4^{I}), 4.06 (dd, 1H, $J_{5,6a}$ = 4.6 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6a^{II}), 4.07 (dd, 1H, $J_{5,6a}$ = 7.8 Hz, $J_{6a,6b}$ = 11.2 Hz, H-6a^{III}), 4.09 (dd, 1H, $J_{4,5}$ = 9.8 Hz, H-5^{I}), 4.12 (dd, 1H, $J_{5,6b}$ = 6.2 Hz, $J_{6a,6b}$ = 11.2 Hz, H-6b^{III}), 4.16 (dd, 1H, $J_{6,7a}$ = 6.8 Hz, $J_{7a,7b}$ = 11.4 Hz, H-7a^{I}), 4.38 (dd, 1H, $J_{5,6b}$ = 1.6 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6b^{II}), 4.39 (dd, 1H, $J_{6,7b}$ = 5.8 Hz, $J_{7a,7b}$ = 11.4 Hz, H-7b^{I}), 4.49 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^{III}), 4.60 (d, 1H, $J_{1,2}$ = 6.8 Hz, H-1^{II}), 4.80 (dd, 1H, $J_{1,2}$ = 6.8 Hz, $J_{2,3}$ = 8.2 Hz, H-2^{II}), 4.94 (dd, 1H, $J_{2,3}$ = 10.4 Hz, $J_{3,4}$ = 3.4 Hz, H-3^{III}), 5.11 (dd, 1H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 10.4 Hz, H-2^{III}), 5.15 (dd, 1H, $J_{2,3}$ = 8.2 Hz, $J_{3,4}$ = 9.4 Hz, H-3^{II}), 5.22–5.23 (m, 2H, H-6^{I}, H-4^{III}), 5.34 (d, 1H, $J_{1,2}$ = 3.2 Hz, H-1^{I}), 5.40 (dd, 1H, H-3^{I}), 5.41 (dd, 1H, $J_{1,2}$ = 3.2 Hz, H-2^{I}). ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.5, 20.6, 20.8, 20.9, 20.92 (Ac-CH_3), 60.7 (C-6^{III}), 62.5 (C-6^{II}), 62.8 (C-7^{I}), 66.6 (C-4^{III}), 68.3 (C-6^{I}), 68.96 (C-3^{I}), 69.0 (C-2^{III}), 69.1 (C-2^{I}), 70.4 (C-5^{I}), 70.6 (C-5^{III}), 71.0 (C-3^{III}), 71.9 (C-2^{II}), 71.92 (C-5^{II}), 73.1 (C-3^{II}), 73.3 (C-4^{I}), 76.0 (C-4^{II}), 92.0 (C-1^{I}), 99.1 (C-1^{II}), 101.1 (C-1^{III}), 169.2, 169.7, 169.8, 170.0, 170.1, 170.2, 170.4, 170.5 (Ac: C=O). ESI-HRMS for $C_{41}H_{56}O_{28}$: 1019.2856 $[M + Na]^+$. Found 1019.2848.

*(2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl)-(1-4)-(2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-(1-4)-2,3,6,7-tetra-O-acetyl-L-glycero-α-D-manno-heptopyranosyl trichloroacetimidate (**17**).* Trichloroacetonitrile (57.0 μL, 565.6 μmol) was added to a solution of **16** (57.1 mg, 57.3 μmol) in dry dichloromethane (1.0 mL) under argon. Potassium carbonate (39.3 mg, 284.4 μmol) was added to the reaction mixture. After stirring for 24 h at room temperature, the mixture was filtered through Celite. The solution was concentrated and purified by silica gel column chromatography (ethyl acetate/hexane, 2:1) to give **17** (60.2 mg, 92%). $[\alpha]^{25}_D$ = +2.4 (*c* 1.0, $CHCl_3$), ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.97, 2.00, 2.00, 2.04, 2.07, 2.12, 2.15, 2.19 (s, 3H x 11, Ac), 3.63 (ddd, 1H, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 4.0 Hz, $J_{5,6b}$ = 2.0 Hz, H-5^{II}), 3.84–3.89 (m, 3H, H-4^{II}, H-5^{III}, H-4^{I}), 4.01 (dd, 1H, $J_{4,5}$ = 9.8 Hz, $J_{5,6}$ = 1.4 Hz, H-5^{I}), 4.06 (dd, 1H, $J_{5,6a}$ = 7.2 Hz, $J_{6a,6b}$ = 11.2 Hz, H-6a^{III}), 4.09 (dd, 1H, $J_{5,6a}$ = 4.0 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6a^{II}), 4.14 (dd, 1H, $J_{5,6b}$ = 6.2 Hz, $J_{6a,6b}$ = 11.2 Hz, H-6b^{III}), 4.17 (dd, 1H, $J_{6,7a}$ = 7.2 Hz, $J_{7a,7b}$ = 11.4 Hz, H-7a^{I}), 4.21 (dd, 1H, $J_{6,7b}$ = 6.0 Hz, $J_{7a,7b}$ = 11.4 Hz, H-7b^{I}), 4.47 (dd, 1H, $J_{5,6b}$ = 2.0 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6b^{II}), 4.53 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^{III}), 4.61 (d, 1H, $J_{1,2}$ = 7.0 Hz, H-1^{II}), 4.83 (dd, 1H, $J_{1,2}$ = 7.0 Hz, $J_{2,3}$ = 7.8 Hz, H-2^{II}), 4.95 (dd, 1H, $J_{2,3}$ = 10.6 Hz, $J_{3,4}$ = 3.4 Hz, H-3^{III}), 5.10 (dd, 1H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 10.6 Hz, H-2^{III}), 5.16 (dd, 1H, $J_{2,3}$ = 7.8 Hz, $J_{3,4}$ = 10.4 Hz, H-3^{II}), 5.34 (dd, 1H, $J_{4,5}$ = 0.8 Hz, $J_{3,4}$ = 3.4 Hz, H-4^{III}), 5.37 (ddd, 1H, $J_{5,6}$ = 1.4 Hz, $J_{6,7a}$ = 7.2 Hz, $J_{6,7b}$ = 6.0 Hz, H-6^{I}), 5.43 (dd, 1H, $J_{1,2}$ = 2.2 Hz, $J_{2,3}$ = 3.4 Hz, H-2^{I}), 5.44 (dd, 1H, $J_{2,3}$ = 3.4 Hz, H-3^{I}), 6.23 (d, 1H, $J_{1,2}$ = 2.2 Hz, H-1^{I}), 8.74 (NH). ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.5, 20.57, 20.6, 20.7, 20.74, 20.8 (Ac-CH_3), 60.7 (C-6^{III}), 62.0 (C-6^{II}), 62.1 (C-7^{I}), 66.6 (C-4^{III}), 67.8 (C-2^{I}), 67.9 (C-6^{I}), 69.0 (C-3^{I} and C-2^{III}), 70.6 (C-5^{III}), 71.0 (C-3^{III}), 71.6 (C-2^{II}), 71.7 (C-5^{II}), 72.1 (C-5^{I}), 73.1 (C-3^{II}), 73.3 (C-4^{I}), 75.8 (C-4^{II}), 90.5 (OCNHCCl_3), 94.6 (C-1^{I}), 99.9 (C-1^{II}), 101.1 (C-1^{III}), 160.0 (OCNHCCl_3), 169.1, 169.4, 169.42, 169.67, 169.7, 170.0, 170.1, 170.2, 170.3, 170.4 (Ac: C=O). ESI-HRMS for $C_{43}H_{56}Cl_3NO_{28}$: 1162.1952 $[M + Na]^+$. Found 1162.1940.

*Methyl (3,4,6,7-tetra-O-acetyl-2-O-benzyl-L-glycero-α-D-manno-heptopyranosyl)-(1-3)-4,6,7-tri-O-acetyl-2-O-benzyl-L-glycero-α-D-manno-heptopyranoside (**18**).* A mixture of **7** (188.0 mg, 308.0 μmol), methyl 4,6,7-tri-*O*-acetyl-2-*O*-benzyl-L-*glycero*-α-D-*manno*-heptopyranoside (**4**; 135.0 mg, 308.0 μmol), and 4 Å molecular sieves (135.0 mg) was suspended in dry dichloromethane (0.9 mL). The reaction mixture was stirred for 1 h under argon and then cooled to -78 °C. TMSOTf (2.2 μL, 12.3 μmol) in dichloromethane was added dropwise to the reaction mixture. The reaction was warmed to room temperature and stirred for 2 h. The reaction 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 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 size exclusion beads (toluene/ethyl acetate, 1:1) to give **18** (136.6 mg, 50%). $[\alpha]^{25}_D$ = +41.2 (*c* 1.0, $CHCl_3$), ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.77, 1.94, 1.96, 2.04, 2.05, 2.09, 2.13 (s, 3H x 7, Ac), 3.31 (s, 3H, OCH_3), 3.66 (dd, 1H,

$J_{1,2}$ = 1.6 Hz, $J_{2,3}$ = 3.0 Hz, H-2^{I}), 3.76 (dd, 1H, $J_{4,5}$ = 10.0 Hz, $J_{5,6}$ = 1.8 Hz, H-5^{II}), 3.81 (dd, 1H, $J_{1,2}$ = 1.6 Hz, $J_{2,3}$ = 3.0 Hz, H-2^{II}), 3.87 (dd, 1H, $J_{4,5}$ = 10.0 Hz, $J_{5,6}$ = 2.0 Hz, H-5^{I}), 4.02 (dd, 1H, $J_{6,7a}$ = 6.4 Hz, $J_{7a,7b}$ = 11.2 Hz, H-7a^{II}), 4.07 (dd, 1H, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.8 Hz, H-3^{I}), 4.11 (dd, 1H, $J_{6,7b}$ = 6.8 Hz, $J_{7a,7b}$ = 11.2 Hz, H-7b^{II}), 4.23 (dd, 1H, $J_{6,7a}$ = 7.6 Hz, $J_{7a,7b}$ = 11.2 Hz, H-7a^{I}), 4.32 (dd, 1H, $J_{6,7b}$ = 5.6 Hz, $J_{7a,7b}$ = 11.2 Hz, H-7b^{I}), 4.59, 4.64 (d, 2H, J = 12.2 Hz, OCH_2Ph), 4.76 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1^{I}), 4.82, 4.84 (d, 2H, J = 12.8 Hz, OCH_2Ph), 5.03 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1^{II}), 5.05 (ddd, 1H, $J_{5,6}$ = 1.8 Hz, $J_{6,7a}$ = 6.4 Hz, $J_{6,7b}$ = 6.8 Hz, H-6^{II}), 5.21 (ddd, 1H, $J_{5,6}$ = 2.0 Hz, $J_{6,7a}$ = 7.6 Hz, $J_{6,7b}$ = 5.6 Hz, H-6^{I}), 5.31 (dd, 1H, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 10.0 Hz, H-3^{II}), 5.40 (dd, 1H, $J_{3,4}$ = 9.8 Hz, $J_{4,5}$ = 10.0 Hz, H-4^{II}), 5.47 (dd, 1H, $J_{3,4}$ = 9.8 Hz, $J_{4,5}$ = 10.0 Hz, H-4^{I}), 7.28–7.45 (m, 10H, Ph). ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.4, 20.66, 20.69, 20.7, 20.8, 20.83 (Ac-CH_3), 55.1 (OCH_3), 61.5 (C-7^{II}), 62.0 (C-7^{I}), 65.5 (C-4^{II}), 66.9 (C-6^{I}), 67.1 (C-6^{II}), 67.8 (C-4^{I}), 68.8 (C-5^{I}), 69.2 (C-5^{II}), 70.8 (C-3^{II}), 72.6 (OCH_2Ph), 73.4 (OCH_2Ph), 74.4 (C-3^{I}), 75.1 (C-2^{I}), 75.5 (C-2^{II}), 99.2 (C-1^{II}), 99.4 (C-1^{I}), 128.0, 128.1, 128.2, 128.4, 128.7, 129.0, 137.4, 137.6 (Ph), 169.3, 169.4, 169.7, 170.1, 170.3, 170.5, 170.6 (Ac: O=C). ESI-HRMS for $C_{43}H_{54}O_{20}$: 913.3106 $[M + Na]^+$. Found 913.3093.

*(3,4,6,7-Tetra-O-acetyl-2-O-benzyl-L-glycero-α-D-manno-heptopyranosyl)-(1-3)-4,6,7-tri-O-acetyl-2-O-benzyl-L-glycero-D-manno-heptopyranose (**19**).* Compound **18** (158.5 mg, 178.0 μmol) was dissolved in a mixture of H_2SO_4/AcOH/Ac_2O (4.0 mL, 0.1:6:14) and stirred for 2 h at room temperature. The reaction mixture was neutralized by the addition of sodium acetate (1.2 g), poured into saturated sodium hydrogen carbonate, and extracted with dichloromethane. The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated to a syrup (156.5 mg). The crude syrup was treated with hydrazine acetate (20.4 mg, 221.0 μmol) in DMF (1.2 mL) for 7 h at 0 °C. The reaction mixture was diluted with ethyl acetate, washed with water and brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/hexane, 1:1) to give **19** (122.4 mg, 78%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.82, 1.95, 1.96, 2.05, 2.06, 2.10, 2.15 (s, 3H x 7, Ac), 3.03 (s, 1H, OH), 3.70 (dd, 1H, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 2.6 Hz, H-2^{I}), 3.72 (dd, 1H, $J_{4,5}$ = 10.0 Hz, $J_{5,6}$ = 1.8 Hz, H-5^{II}), 3.81 (dd, 1H, $J_{1,2}$ = 1.6 Hz, $J_{2,3}$ = 3.0 Hz, H-2^{II}), 4.07 (dd, 1H, $J_{4,5}$ = 10.2 Hz, $J_{5,6}$ = 2.0 Hz, H-5^{I}), 4.10 (dd, 1H, $J_{6,7a}$ = 5.2 Hz, $J_{7a,7b}$ = 11.4 Hz, H-7a^{II}), 4.14 (dd, 1H, $J_{7a,7b}$ = 11.4 Hz, H-7b^{II}), 4.14 (dd, 1H, $J_{7a,7b}$ = 11.4 Hz, H-7a^{I}), 4.16 (dd, 1H, $J_{2,3}$ = 2.6 Hz, $J_{3,4}$ = 7.0 Hz, H-3^{I}), 4.38 (dd, 1H, $J_{6,7b}$ = 5.4 Hz, $J_{7a,7b}$ = 11.4 Hz, H-7b^{I}), 4.59, 4.64 (d, 2H, J = 12.2 Hz, OCH_2Ph), 4.82, 4.85 (d, 2H, J = 12.8 Hz, OCH_2Ph), 5.04 (ddd, 1H, $J_{5,6}$ = 1.8 Hz, $J_{6,7a}$ = 5.2 Hz, H-6^{II}), 5.06 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1^{II}), 5.18 (ddd, 1H, $J_{5,6}$ = 2.0 Hz, $J_{6,7b}$ = 5.4 Hz, H-6^{I}), 5.30 (d, 1H, $J_{1,2}$ = 2.0 Hz, H-1^{I}), 5.31 (dd, 1H, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 10.2 Hz, H-3^{II}), 5.40 (dd, 1H, $J_{3,4}$ = 10.2 Hz, $J_{4,5}$ = 10.0 Hz, H-4^{II}), 5.47 (dd, 1H, $J_{3,4}$ = 7.0 Hz, $J_{4,5}$ = 10.2 Hz, H-4^{I}), 7.30–7.46 (m, 10H, Ph). ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.6, 20.7, 20.75, 20.9, 21.5 (Ac-CH_3), 61.7 (C-7^{II}), 62.6 (C-7^{I}), 65.5 (C-4^{II}), 67.1 (C-6^{I}), 67.16 (C-6^{II}), 68.0 (C-4^{I}), 68.9 (C-5^{I}), 69.3 (C-5^{II}), 70.7 (C-3^{II}), 72.6 (OCH_2Ph), 73.4 (OCH_2Ph), 74.2 (C-3^{I}), 75.4 (C-2^{I}), 75.5 (C-2^{II}), 92.9 (C-1^{I}), 99.4 (C-1^{II}), 128.0, 128.2, 128.25, 128.5, 128.7, 129.1, 137.4, 137.6 (Ph), 169.4, 169.5, 169.8, 170.4, 170.7, 171.1 (Ac: O=C). ESI-HRMS for $C_{42}H_{52}O_{20}$: 899.2950 $[M + Na]^+$. Found 899.2930.

*(3,4,6,7-Tetra-O-acetyl-2-O-benzyl-L-glycero-α-D-manno-heptopyranosyl)-(1-3)-4,6,7-tri-O-acetyl-2-O-benzyl-L-glycero-D-manno-heptopyranosyl trichloroacetimidate (**20**).* Trichloroacetonitrile (192.0 μL, 1.9 mmol) was added to a solution of **19** (139.9 mg, 160.0 μmol) in dry dichloromethane (1.6 mL) under argon. Potassium carbonate (113.0 mg, 0.8 mmol) was added to the reaction. After stirring for 21 h at room temperature, the mixture was filtered through Celite. The solution was concentrated and purified by flash column chromatography (ethyl acetate/hexane, 1:1) to give **20**α (111.0 mg, 66%) and **20**β (18.5 mg, 14%). α-isomer: $[\alpha]^{25}_D$ = +18.6 (*c* 1.5, $CHCl_3$), ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.90, 1.94, 1.97, 2.01, 2.05, 2.06, 2.13 (s, 3H x 7, Ac), 3.40 (dd, 1H, $J_{4,5}$ = 10.0 Hz, $J_{5,6}$ = 2.0 Hz, H-5^{II}), 3.75 (dd, 1H, $J_{1,2}$ = 1.4 Hz, $J_{2,3}$ = 3.0 Hz, H-2^{II}), 3.89 (dd, 1H, $J_{6,7a}$ = 4.0 Hz, $J_{7a,7b}$ = 11.6 Hz, H-7a^{II}), 3.94 (dd, 1H, $J_{1,2}$ = 1.6 Hz, $J_{2,3}$ = 3.2 Hz, H-2^{I}), 4.05 (dd, 1H, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 6.6 Hz, H-3^{I}), 4.08 (dd, 1H, $J_{4,5}$ = 10.0 Hz, $J_{5,6}$ = 2.0 Hz, H-5^{I}), 4.11 (dd, 1H, $J_{6,7b}$ = 7.2 Hz, $J_{7a,7b}$ = 11.6 Hz, H-7b^{II}), 4.16 (dd, 1H, $J_{6,7a}$ = 7.6 Hz, $J_{7a,7b}$ = 11.4 Hz, H-7a^{I}), 4.27 (dd, 1H, $J_{6,7b}$ = 5.4 Hz, $J_{7a,7b}$ = 11.4 Hz, H-7b^{I}), 4.60, 4.62 (d, 2H, J = 12.2 Hz, OCH_2Ph), 4.73, 4.91 (d, 2H, J = 12.4 Hz, OCH_2Ph), 4.98 (ddd, 1H, $J_{5,6}$ = 2.0 Hz, $J_{6,7a}$ = 4.0 Hz, $J_{6,7b}$ = 8.6 Hz, H-6^{II}), 5.02 (d, 1H, $J_{1,2}$ = 1.4 Hz, H-1^{II}), 5.20 (dd, 1H, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 10.2 Hz, H-3^{II}), 5.21 (ddd, 1H, $J_{5,6}$ = 2.0 Hz, $J_{6,7a}$ = 7.6 Hz, $J_{6,7b}$ = 5.4 Hz, H-6^{I}), 5.31 (dd, $J_{3,4}$ = 10.2 Hz, $J_{4,5}$ = 10.0 Hz, H-4^{II}), 5.52 (dd, $J_{3,4}$ = 6.6 Hz, $J_{4,5}$ = 10.0 Hz, H-4^{I}), 6.40 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1^{I}), 7.27–7.50 (m, 10H, Ph), 8.80 (s, 1H, NH). ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.6, 20.7, 20.76, 20.8 (Ac-CH_3), 62.1 (C-7^{I}), 62.6 (C-7^{II}), 65.3 (C-4^{II}), 66.7 (C-6^{I}), 66.9 (C-4^{I}), 67.2 (C-6^{II}), 69.8 (C-5^{II}), 70.8 (C-3^{II}), 71.5 (C-5^{I}), 72.2 (OCH_2Ph), 73.5 (OCH_2Ph), 73.7 (C-2^{I}), 75.3 (C-3^{I}), 75.8 (C-2^{II}), 90.6 ($OCNHCCl_3$), 95.0 (C-1^{I}), 100.2 (C-1^{II}), 127.8, 128.0, 128.2, 128.5, 128.6, 128.9, 136.9, 137.4 (Ph), 159.5 ($OCNHCCl_3$), 169.4, 169.7, 170.2, 170.5 (Ac: O=C). ESI-HRMS for $C_{44}H_{52}Cl_3NO_{20}$: 1042.2046 $[M + Na]^+$. Found 1042.2051. β-isomer: $[\alpha]^{25}_D$ = −12.6 (*c* 0.3, $CHCl_3$), ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.75, 1.88, 1.90, 1.97, 1.98, 2.02, 2.05 (s, 3H x 7, Ac), 3.52 (dd, 1H, $J_{4,5}$ = 9.8 Hz, $J_{5,6}$ = 2.0 Hz, H-5^{II}), 3.64 (dd, 1H, $J_{4,5}$ = 10.0 Hz, $J_{5,6}$ = 2.6 Hz, H-5^{I}), 3.74 (dd, 1H, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.0 Hz, H-2^{II}), 3.78 (dd, 1H, $J_{2,3}$ = 2.8 Hz, $J_{3,4}$ = 9.6 Hz, H-3^{I}), 3.89 (dd, 1H, $J_{1,2}$ = 0.6 Hz, $J_{2,3}$ = 2.8 Hz, H-2^{I}), 4.00 (dd, 1H, $J_{6,7a}$ = 7.8 Hz, $J_{7a,7b}$ = 11.6 Hz, H-7a^{I}), 4.03 (dd, 1H, $J_{6,7a}$ = 6.6 Hz, $J_{7a,7b}$ = 11.2 Hz, H-7a^{II}), 4.11 (dd, 1H,

$J_{6,7b}$ = 6.4 Hz, $J_{7a,7b}$ = 11.2 Hz, H-7b^{II}), 4.38 (dd, 1H, $J_{6,7b}$ = 5.0 Hz, $J_{7a,7b}$ = 11.6 Hz, H-7b^{I}), 4.53, 4.55 (d, 2H, J = 12.8 Hz, OCH_2Ph), 4.98 (ddd, 1H, $J_{5,6}$ = 2.0 Hz, $J_{6,7a}$ = 6.6 Hz, $J_{6,7b}$ = 6.4 Hz, H-6^{II}), 4.93, 4.98 (d, 2H, J = 12.6 Hz, OCH_2Ph), 4.97 (d, 1H, $J_{1,2}$ = 2.0 Hz, H-1^{II}), 5.20 (ddd, 1H, $J_{5,6}$ = 2.0 Hz, $J_{6,7a}$ = 7.8 Hz, $J_{6,7b}$ = 5.0 Hz, H-6^{I}), 5.25 (dd, 1H, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 10.2 Hz, H-3^{II}), 5.32 (dd, 1H, $J_{3,4}$ = 10.2 Hz, $J_{4,5}$ = 9.8 Hz, H-4^{II}), 5.46 (dd, 1H, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 10.0 Hz, H-4^{I}), 5.72 (d, 1H, $J_{1,2}$ = 0.6 Hz, H-1^{I}), 7.19–7.48 (m, 10H, Ph), 8.69 (s, 1H, NH). ^{13}C NMR (150 MHz, $CDCl_3$): δ 19.5, 19.7, 19.71, 19.8, 19.83, 19.9 (Ac-CH_3), 60.0 (C-7^{I}), 61.3 (C-7^{II}), 64.4 (C-4^{II}), 65.6 (C-6^{I}), 66.0 (C-4^{I}), 66.5 (C-6^{II}), 68.1 (C-5^{II}), 69.5 (C-3^{II}), 72.4 (C-5^{I}), 72.5 (OCH_2Ph), 72.53 (OCH_2Ph), 73.1 (C-2^{I}), 74.5 (C-3^{I}), 75.9 (C-2^{II}), 89.4 ($OCNHCCl_3$), 96.0 (C-1^{I}), 98.4 (C-1^{II}), 126.8, 127.0, 127.0, 127.4, 127.6, 136.3, 136.4 (Ph), 159.7 ($OCNHCCl_3$), 168.2, 168.4, 168.7, 169.1, 169.2, 169.6, 169.8 (Ac: O=C). ESI-HRMS for $C_{44}H_{52}Cl_3NO_{20}$: 1042.2046 $[M + Na]^+$. Found 1042.2012.

*(2,3,4,6-Tetra-O-benzyl-β-D-galactopyranosyl)-(1-4)-(2,3,6-tri-O-benzyl-α-D-glucopyranosyl)-(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-octulopyranosid)onate (**25**).* 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-octulopyranosid)onate (**1**; 10.0 mg, 10.2 μmol), (2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-(1-4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl trichloroacetimidate (**23**; 34.1 mg, 30.5 μmol), and MS-AW 300 molecular sieves (10.0 mg) was suspended in diethyl ether and dichloromethane (3:1, 0.4 mL). The reaction mixture was stirred for 1 h under argon and cooled to 0 °C. Then, 0.01 M TMSOTf (60.0 μL, 0.6 μmol) in dichloromethane was added dropwise to the reaction mixture. After stirring for 1 h, the reaction was warmed to room temperature and stirred for 1 h. The reaction solution 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-X1 size exclusion beads (toluene/ethyl acetate, 1:1) and TLC chromatography (ethyl acetate/hexane, 1:3) to give **25** (4.0 mg, 20%). $[\alpha]^{25}_D$ = +41.0 (*c* 0.5, $CHCl_3$), ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.98 (dd, 1H, $J_{3a,3b}$ = 15.4 Hz, $J_{3a,4}$ = 2.4 Hz, H-3a^{II}), 1.18 (s, 3H, Me), 1.34 (s, 3H, Me), 2.23 (dd, 1H, $J_{3a,3b}$ = 12.4 Hz, $J_{3a,4}$ = 5.0 Hz, H-3a^{I}), 2.26 (dd, 1H, $J_{3a,3b}$ = 12.4 Hz, $J_{3b,4}$ = 11.8 Hz, H-3b^{I}), 2.59 (dd, 1H, $J_{3a,3b}$ = 15.4 Hz, $J_{3b,4}$ = 3.4 Hz, H-3b^{II}), 3.31 (ddd, 1H, $J_{5,6a}$ = 5.0 Hz, H-5^{IV}), 3.32 (dd, 1H, $J_{2,3}$ = 9.8 Hz, $J_{3,4}$ = 2.8 Hz, H-3^{IV}), 3.38 (dd, 1H, $J_{5,6a}$ = 5.0 Hz, $J_{6a,6b}$ = 8.8 Hz, H-6a^{IV}), 3.38 (s, 3H, OMe^{I}), 3.48 (s, 3H, OMe^{II}), 3.51 (dd, 1H, $J_{1,2}$ = 3.4 Hz, $J_{2,3}$ = 9.8 Hz, H-2^{III}), 3.56 (dd, 1H, $J_{6a,6b}$ = 8.8 Hz, H-6b^{IV}), 3.64 (dd, 1H, $J_{5,6a}$ = 1.6 Hz, $J_{6a,6b}$ = 9.2 Hz, H-6a^{III}), 3.69 (dd, 1H, $J_{4,5}$ = 3.0 Hz, $J_{5,6}$ = 1.2 Hz, H-5^{I}), 3.74 (dd, 1H, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 9.8 Hz, H-2^{IV}), 3.86 (dd, 1H, $J_{5,6}$ = 1.6 Hz, $J_{6,7}$ = 7.6 Hz, H-6^{II}), 3.86 (dddd, 1H, J = 1.4, 3.2, 4.8, 13.0 Hz, OCH_2-), 3.90 (dd, 1H, $J_{3,4}$ = 2.8 Hz, H-4^{IV}), 3.90 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-3^{III}), 3.94 (dd, 1H, $J_{6a,6b}$ = 9.2 Hz, H-6b^{III}), 3.94 (ddd, 1H, $J_{3a,4}$ = 2.4 Hz, $J_{3b,4}$ = 3.4 Hz, H-4^{II}), 3.95 (dddd, 1H, OCH_2-), 4.03 (dd, 1H, $J_{5,6}$ = 1.2 Hz, $J_{6,7}$ = 9.4 Hz, H-6^{I}), 4.04 (dd, 1H, $J_{5,6}$ = 1.6 Hz, H-5^{II}), 4.05 (dd, 1H, $J_{4,5}$ = 10.0 Hz, H-4^{III}), 4.11 (ddd, 1H, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 1.6 Hz, H-5^{III}), 4.25, 4.37 (d, 2H, J = 11.8 Hz, CH_2Ph), 4.28 (dd, 1H, $J_{7,8a}$ = 3.4 Hz, $J_{8a,8b}$ = 12.6 Hz, H-8a^{I}), 4.35 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1^{IV}), 4.36, 4.60 (d, 2H, J = 12.0 Hz, CH_2Ph), 4.46 (dd, 1H, $J_{7,8b}$ = 2.6 Hz, $J_{8a,8b}$ = 12.6 Hz, H-8b^{I}), 4.55, 4.97 (d, 2H, J = 11.2 Hz, CH_2Ph), 4.58 (dd, 1H, $J_{7,8a}$ = 4.6 Hz, $J_{8a,8b}$ = 12.8 Hz, H-8a^{II}), 4.62, 4.66 (d, 2H, J = 12.0 Hz, CH_2Ph), 4.70 (ddd, 1H, $J_{3a,4}$ = 5.0 Hz, $J_{3b,4}$ = 11.8 Hz, $J_{4,5}$ = 3.0 Hz, H-4^{I}), 4.70, 5.01 (d, 2H, J = 10.4 Hz, CH_2Ph), 4.77, 5.00 (d, 2H, J = 12.4 Hz, CH_2Ph), 4.86, 4.87 (d, 2H, CH_2Ph), 4.86 (dddd, 1H, $=CH_2$), 4.88 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1^{III}), 4.93 (dddd, 1H, J = 1.6, 1.6, 3.2, 17.2 Hz,$=CH_2$), 5.30 (dd, 1H, $J_{7,8b}$ = 2.6 Hz, $J_{8a,8b}$ = 12.8 Hz, H-8b^{II}), 5.58–5.64 (m, 1H, -CH=), 5.59 (ddd, 1H, $J_{6,7}$ = 7.6 Hz, $J_{7,8a}$ = 4.6 Hz, $J_{7,8b}$ = 2.6 Hz, H-7^{II}), 5.75 (ddd, 1H, $J_{6,7}$ = 9.4 Hz, $J_{7,8a}$ = 3.4 Hz, $J_{7,8b}$ = 2.6 Hz, H-7^{I}), 7.03–7.56 (m, 47H, Ar), 7.84–8.00 (m, 8H, Ar). ^{13}C NMR (150 MHz, $CDCl_3$): δ 24.6 and 25.1 (Isop-Me), 31.4 (C-3^{II}), 34.4 (C-3^{I}), 52.0 (OMe^{I}), 52.1 (OMe^{II}), 62.1 (C-8^{I}), 62.1 (C-8^{II}), 64.7 (OCH_2-), 67.7 (C-4^{I}), 67.9 (C-6^{III}), 68.1 (C-6^{IV}), 69.3 (C-7^{I}), 69.8 (C-4^{II}), 69.9 (C-6^{II}), 70.66 (C-7^{II}), 70.7 (C-6^{I}), 71.0 (C-5^{III}), 72.03 (C-5^{I}), 72.06 (C-5^{II}), 72.3, 72.6, 73.0, 73.4, 74.4, 74.7, 75.3 (OCH_2Ph), 72.9 (C-5^{IV}), 73.7 (C-4^{IV}), 76.2 (C-4^{III}), 78.9 (C-2^{III}), 80.2 (C-2^{IV}), 80.3 (C-3^{III}), 82.3 (C-3^{IV}), 96.2 (C-2^{II}), 98.3 (C-1^{III}), 98.8 (C-2^{I}), 102.7 (C-1^{IV}), 109.6 (C_{isop}), 116.2 ($=CH_2$), 126.3, 126.7, 126.9, 127.3, 127.4, 127.5, 127.7, 127.8, 127.9, 128.0, 128.1, 128.14, 128.2, 128.3, 128.31, 128.4, 128.40, 128.45, 128.6, 129.6, 129.65, 129.7, 129.75, 129.8, 130.0, 130.3, 132.9, 133.0, 133.1, 133.4 (Ar), 133.6 (-CH=), 138.14, 138.2, 138.5, 139.0, 139.1, 139.3, 139.9 (Ar), 164.8, 165.1, 165.8, 166.1 (Bz: C=O), 167.7 (C-1^{I}), 168.7 (C-1^{II}). MALDI-TOF MS for $C_{113}H_{116}O_{29}$: 1959.750 $[M + Na]^+$. Found 1959.300.

(2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl)-(1-4)-(2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-(1-4)-(3,6,7-tri-O-acetyl-2-O-benzyl-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-octulopyranosid)onate (27). A mixture of **1** (42.0 mg, 42.7 μmol), **13** (96.0 mg, 84.1 μmol), and MS-AW 300 molecular sieves (43.0 mg) was suspended in dry dichloromethane (1.6 mL). The reaction mixture was stirred for 1 h under argon, and then 0.01 M TMSOTf (260.0 μL, 2.5 μmol) in dichloromethane was added dropwise to the reaction mixture. After stirring for 2 h, the reaction 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 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-X1 size exclusion beads (toluene/ethyl acetate, 1:1) and TLC chromatography (ethyl acetate/hexane, 2:1) to give **27** (22.8 mg, 26%). $[\alpha]^{25}_{D}$ = +2.9 (*c* 1.9, $CHCl_3$), ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.22 (s, 3H, Me), 1.41 (s, 3H, Me), 1.90, 1.91, 1.95, 1.99, 2.01, 2.02, 2.03, 2.03, 2.05, 2.14 (s, 3H x 10, Ac), 2.02 (dd, 1H, $J_{3a,3b}$ = 15.6 Hz, $J_{3a,4}$ = 2.2 Hz, H-3a^{II}), 2.18 (dd, 1H, $J_{3a,3b}$ = 12.6 Hz, $J_{3a,4}$ = 12.4 Hz, H-3a^{I}), 2.38 (dd, 1H, $J_{3a,3b}$ = 12.6 Hz, $J_{3b,4}$ = 4.4 Hz, H-3b^{I}), 2.91 (dd, 1H, $J_{3a,3b}$ = 15.6 Hz, $J_{3b,4}$ = 3.4 Hz, H-3b^{II}), 3.49 (s, 3H, OMe^{I}), 3.55 (s, 3H, OMe^{II}), 3.54 (ddd, 1H, $J_{4,5}$ = 9.6 Hz, $J_{5,6a}$ = 5.0 Hz, $J_{5,6b}$ = 1.6 Hz, H-5^{IV}), 3.79 (dd, 1H, H-5^{I}), 3.79 (dd, 1H, $J_{3,4}$ = 9.0 Hz, $J_{4,5}$ = 9.6 Hz, H-4^{IV}), 3.82 (ddd, 1H, $J_{4,5}$ = 0.6 Hz, $J_{5,6a}$ = 7.2 Hz, $J_{5,6b}$ = 6.2 Hz, H-5 ^{V}), 3.82 (dd, 1H, $J_{1,2}$ = 1.6 Hz, $J_{2,3}$ = 2.8 Hz, H-2^{III}), 3.85 (dd, 1H, $J_{3,4}$ = 9.4 Hz, $J_{4,5}$ = 10.2 Hz, H-4^{III}), 3.91 (dddd, 1H, OCH_2-), 3.92 (dd, 1H, $J_{6,7a}$ = 7.8 Hz, $J_{7a,7b}$ = 11.4 Hz, H-7a^{III}), 3.95 (dd, 1H, $J_{4,5}$ = 10.2 Hz, H-5^{III}), 3.97 (dddd, 1H, OCH_2-), 4.07 (dd, 1H, $J_{5,6a}$ = 7.2 Hz, $J_{6a,6b}$ = 11.2 Hz, H-6a^{V}), 4.08 (dd, 1H, $J_{6,7}$ = 9.4 Hz, H-6^{I}), 4.08 (dd, 1H, $J_{5,6a}$ = 5.0 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6a^{IV}), 4.11 (dd, 1H, $J_{5,6b}$ = 6.2 Hz, $J_{6a,6b}$ = 11.2 Hz, H-6b^{V}), 4.22 (dd, 1H, $J_{6,7b}$ = 5.2 Hz, $J_{7a,7b}$ = 11.4 Hz, H-7b^{III}), 4.30 (dd, 1H, $J_{5,6}$ = 1.6 Hz, $J_{6,7}$ = 6.0 Hz, H-6^{II}), 4.38 (dd, 1H, $J_{4,5}$ = 7.8 Hz, $J_{5,6}$ = 1.6 Hz, H-5^{II}), 4.47 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1^{IV}), 4.35 (dd, 1H, $J_{5,6b}$ = 1.6 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6b^{IV}), 4.43 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1 ^{V}), 4.45, 4.54 (d, 2H, *J* = 12.0 Hz, CH_2Ph), 4.46 (ddd, 1H, $J_{3a,4}$ = 12.4 Hz, $J_{3b,4}$ = 4.4 Hz, H-4^{I}), 4.55 (ddd, 1H, $J_{3a,4}$ = 2.2 Hz, $J_{3b,4}$ = 3.4 Hz, $J_{4,5}$ = 7.8 Hz, H-4^{II}), 4.62 (dd, 1H, $J_{7,8a}$ = 6.2 Hz, $J_{8a,8b}$ = 12.4 Hz, H-8a^{II}), 4.63 (dd, 1H, $J_{7,8a}$ = 3.8 Hz, $J_{8a,8b}$ = 12.4 Hz, H-8a^{I}), 4.79 (dd, 1H, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 8.8 Hz, H-2^{IV}), 4.88 (dd, 1H, $J_{7,8b}$ = 2.4 Hz, $J_{8a,8b}$ = 12.4 Hz, H-8b^{I}), 4.91 (dd, 1H, $J_{2,3}$ = 10.4 Hz, $J_{3,4}$ = 3.4 Hz, H-3 ^{V}), 4.93 (dddd, 1H, *J* = 1.4 Hz, =CH_2), 5.01 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1^{III}), 5.05 (dddd, 1H, *J* = 1.6, 1.6, 3.2, 17.2 Hz,=CH_2), 5.08 (dd, 1H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 10.4 Hz, H-2 ^{V}), 5.12 (dd, 1H, $J_{2,3}$ = 8.8 Hz, $J_{3,4}$ = 9.0 Hz, H-3^{IV}), 5.18 (dd, 1H, $J_{7,8b}$ = 2.2 Hz, $J_{8a,8b}$ = 12.4 Hz, H-8b^{II}), 5.30 (ddd, 1H, $J_{6,7a}$ = 7.8 Hz, $J_{6,7b}$ = 5.2 Hz, H-6^{III}), 5.33 (dd, 1H, $J_{3,4}$ = 3.4 Hz, $J_{4,5}$ = 0.6 Hz, H-4 ^{V}), 5.34 (dd, 1H, $J_{2,3}$ = 2.8 Hz, $J_{3,4}$ = 9.4 Hz, H-3^{III}), 5.58 (ddd, 1H, $J_{6,7}$ = 9.4 Hz, $J_{7,8a}$ = 3.8 Hz, $J_{7,8b}$ = 2.4 Hz, H-7^{I}), 5.63–5.69 (m, 1H, -CH=), 5.75 (ddd, 1H, $J_{6,7}$ = 6.0 Hz, $J_{7,8a}$ = 6.2 Hz, $J_{7,8b}$ = 2.2 Hz, H-7^{II}), 7.27–7.57 (m, 17H, Ar), 7.94–8.00 (m, 8H, Ar). ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.5, 20.54, 20.7, 20.8, 20.84, 20.9, 23.0, 23.8 (Ac-CH_3), 24.6 and 25.1 (Isop-Me), 32.0 (C-3^{II}), 34.7 (C-3^{I}), 52.2 (OMe^{II}), 52.3 (OMe^{I}), 64.5 (OCH_2-), 60.7 (C-6 ^{V}), 62.3 (C-6^{IV}), 62.4 (C-8^{I}), 63.2 (C-8^{II}), 63.5 (C-7^{III}), 66.6 (C-4 ^{V}), 68.2 (C-6^{III}), 68.22 (C-4^{I}), 69.0 (C-2 ^{V}), 69.67 (C-7^{I}), 69.7 (C-3^{III}), 70.0 (C-4^{II}), 70.5 (C-6^{I}), 70.6 (C-5 ^{V}), 70.91 (C-7^{II}), 70.9 (C-5^{III}), 71.0 (C-3 ^{V}), 71.0 (C-6^{II}), 71.4 (C-5^{I}), 71.8 (C-2^{IV}), 72.1 (C-5^{IV}), 72.3 (OCH_2Ph), 72.5 (C-5^{II}), 73.3 (C-3^{IV}), 73.9 (C-4^{III}), 76.9 (C-2^{III}), 76.3 (C-4^{IV}), 97.88 (C-2^{II}), 97.9 (C-1^{III}), 98.7 (C-2^{I}), 100.2 (C-1^{IV}), 101.1 (C-1 ^{V}), 109.5 (C_{isop}), 116.0 (=CH_2), 127.4, 127.6, 128.2, 128.3, 128.4, 128.5, 128.6, 128.8, 129.4, 129.7, 129.8, 130.1, 130.2, 130.9, 132.8, 133.0, 133.2, 133.5 (Ar), 133.53 (-CH=), 138.4 (Ar), 165.2, 165.3, 166.0, 166.2 (Bz: C=O), 167.6 (C-1^{I}), 169.1 (C-1^{II}), 169.6, 169.6, 169.7, 170.1, 170.2, 170.3, 170.4, 170.4 (Ac: C=O). MALDI-TOF MS for $C_{98}H_{112}O_{45}$: 2031.638 $[M + Na]^+$. Found 2030.629.

*(3,4,6,7-Tetra-O-acetyl-2-O-benzyl-L-glycero-α-D-manno-heptopyranosyl)-(1-3)-(2-O-benzyl-4,6,7-tri-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-octulopyranosid) onate (**28**).* A mixture of **1** (62.3 mg, 63.4 μmol), **20** (129.5 mg, 126.8 μmol, α/β = 6:1), and MS-AW 300 molecular sieves (62.0 mg) was suspended in dichloromethane (2.7 mL). The reaction mixture was stirred for 1 h under argon, and then 0.01 M TMSOTf (380.0 μL, 3.8 μmol) in dichloromethane was added dropwise to the reaction mixture. After stirring for 1 h, the reaction 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 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-X1 size exclusion beads (toluene/ethyl acetate, 1:1) and TLC chromatography (ethyl acetate/hexane, 3:2) to give **28** (66.9 mg, 57%). $[\alpha]^{25}_{D}$ = −7.0 (*c* 1.0, $CHCl_3$), ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.19 (s, 3H, Me), 1.36 (s, 3H, Me), 1.88, 1.93, 1.94, 1.97, 1.99, 2.01, 2.11 (s, 3H x 7, Ac), 2.02 (dd, 1H, $J_{3a,3b}$ = 15.6 Hz, $J_{3a,4}$ = 2.6 Hz, H-3a^{II}), 2.08 (dd, 1H, $J_{3a,3b}$ = 12.4 Hz, $J_{3a,4}$ = 12.2 Hz, H-3a^{I}), 2.25 (dd, 1H, $J_{3a,3b}$ = 12.4 Hz, $J_{3b,4}$ = 4.0 Hz, H-3b^{I}), 2.96 (dd, 1H, $J_{3a,3b}$ = 15.6 Hz, $J_{3b,4}$ = 3.6 Hz, H-3b^{II}), 3.38 (s, 3H, OMe^{I}), 3.43 (s, 3H, OMe^{II}), 3.69 (dd, 1H, $J_{4,5}$ = 2.2 Hz, H-5^{I}), 3.80 (dd, 1H, $J_{1,2}$ = 1.8 Hz, $J_{2,3}$ = 3.0 Hz, H-2^{IV}), 3.89 (dddd, 1H, *J* = 1.6, 3.0, 4.8, 13.0 Hz, OCH_2-), 3.94 (dddd, 1H, *J* = 1.4, 2.8, 5.6 Hz, OCH_2-), 3.95 (dd, 1H, $J_{4,5}$ = 9.8 Hz, $J_{5,6}$ = 8.2 Hz, H-5^{IV}), 3.95 (dd, 1H, $J_{1,2}$ = 1.6 Hz, $J_{2,3}$ = 2.4 Hz, H-2^{III}), 4.06 (dd, 1H, $J_{2,3}$ = 2.4 Hz, $J_{3,4}$ = 10.0 Hz, H-3^{III}), 4.09 (dd, 1H, $J_{6,7}$ = 9.6 Hz, H-6^{I}), 4.10 (dd, 1H, $J_{4,5}$ = 9.8 Hz, $J_{5,6}$ = 8.6 Hz, H-5^{III}), 4.21 (dd, 1H, $J_{6,7a}$ = 6.0 Hz, H-7a^{IV}), 4.21 (dd, 1H, $J_{6,7b}$ = 2.0 Hz, H-7b^{IV}), 4.24 (dd, 1H, $J_{6,7a}$ = 5.8 Hz, $J_{7a,7b}$ = 11.8 Hz, H-7a^{III}), 4.26 (dd, 1H, $J_{5,6}$ = 1.8 Hz, $J_{6,7}$ = 7.2 Hz, H-6^{II}), 4.32 (dd, 1H, $J_{6,7b}$ = 3.4 Hz, $J_{7a,7b}$ = 11.8 Hz, H-7b^{III}), 4.35 (dd, 1H, $J_{4,5}$ = 7.8 Hz, $J_{5,6}$ = 1.8 Hz, H-5^{II}), 4.49 (ddd, 1H, $J_{3a,4}$ = 2.6 Hz, $J_{3b,4}$ = 3.6 Hz, $J_{4,5}$ = 7.8 Hz, H-4^{II}), 4.59 (dd, 1H, $J_{7,8a}$ = 3.8 Hz, $J_{8a,8b}$ = 12.4 Hz, H-8a^{I}), 4.61 (dd, 1H, $J_{7,8a}$ = 4.2 Hz, $J_{8a,8b}$ = 12.4 Hz, H-8a^{II}), 4.61, 4.68 (d, 2H, CH_2Ph), 4.62, 4.70 (d, 2H, CH_2Ph), 4.67 (ddd, 1H, $J_{3a,4}$ = 12.2 Hz, $J_{3b,4}$ = 4.0 Hz, $J_{4,5}$ = 2.2 Hz, H-4^{I}), 4.80 (dd, 1H, $J_{7,8b}$ = 2.6 Hz, $J_{8a,8b}$ = 12.4 Hz, H-8b^{I}), 4.93 (dddd, 1H, *J* = 1.2, 1.6,

2.8, 10.6 Hz,=CH_2), 4.98 (dddd, 1H, J = 1.6, 1.6, 3.2, 17.2 Hz,=CH_2), 5.07 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1^{III}), 5.15 (dd, 1H, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 10.0 Hz, H-3^{IV}), 5.20 (ddd, 1H, $J_{5,6}$ = 8.2 Hz, $J_{6,7a}$ = 6.0 Hz, $J_{6,7b}$ = 2.0 Hz, H-6^{IV}), 5.21 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1^{IV}), 5.27 (dd, 1H, $J_{7,8b}$ = 2.4 Hz, $J_{8a,8b}$ = 12.4 Hz, H-$8b^{II}$), 5.31 (ddd, 1H, $J_{5,6}$ = 8.6 Hz, $J_{6,7a}$ = 5.8 Hz, $J_{6,7b}$ = 3.4 Hz, H-6^{III}), 5.41 (dd, $J_{3,4}$ = 10.0 Hz, $J_{4,5}$ = 9.8 Hz, H-4^{IV}), 5.52 (dd, $J_{3,4}$ = 10.0 Hz, $J_{4,5}$ = 9.8 Hz, H-4^{III}), 5.57 (ddd, 1H, $J_{6,7}$ = 9.6 Hz, $J_{7,8a}$ = 3.8 Hz, $J_{7,8b}$ = 2.6 Hz, H-7^{I}), 5.63–5.69 (m,1H, -CH=), 5.68 (ddd, 1H, $J_{6,7}$ = 7.2 Hz, $J_{7,8a}$ = 4.2 Hz, $J_{7,8b}$ = 2.4 Hz, H-7^{II}), 7.21–7.60 (m, 22H, Ar), 7.94–8.04 (m, 8H, Ar). ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.6, 20.8, 20.83, 20.87, 20.9 (Ac-CH_3), 24.6 and 25.1 (Isop-Me), 32.0 (C-3^{II}), 34.5 (C-3^{I}), 52.1 (OMe^{II}), 52.2 (OMe^{I}), 62.4 (C-8^{II}), 62.6 (C-8^{I}), 63.5 (C-7^{IV}), 64.1 (C-7^{III}), 64.8 (OCH_2-), 65.3 (C-4^{IV}), 66.9 (C-4^{III}), 67.6 (C-4^{I}), 67.7 (C-6^{III}), 68.0 (C-6^{IV}), 69.0 (C-7^{I}), 69.9 (C-4^{II}), 70.0 (C-5^{IV}), 70.1 (C-3^{III}), 70.3 (C-6^{I}, C-5^{III}, C-6^{II}), 70.6 (C-7^{II}), 71.2 (C-3^{IV}), 72.1 (OCH_2Ph), 72.2 (C-5^{II}), 72.9 (OCH_2Ph), 74.1 (C-5^{I}), 75.5 (C-2^{IV}), 77.2 (C-2^{III}), 97.0 (C-2^{II}), 98.8 (C-2^{I}), 99.0 (C-1^{IV}), 99.2 (C-1^{III}), 109.6 (C_{isop}), 116.4 (=CH_2), 127.3, 127.4, 127.7, 127.8, 128.3, 128.32, 128.4, 128.6, 128.8, 128.9, 129.5, 129.6, 129.7, 129.75, 129.9, 130.1, 132.9, 133.0, 133.3 (Ar), 133.4 (-CH=), 133.8, 137.8, 138.3 (Ar), 165.2, 165.4, 165.8, 166.2 (Bz: C=O), 167.4 (C-1^{I}), 169.4 (C-1^{II}), 169.6, 169.7, 169.8, 170.4, 170.5, 170.7, 170.8 (Ac: C=O). MALDI-TOF MS for $C_{94}H_{104}O_{38}$: 1863.611 $[M + Na]^+$. Found 1862.589.

*(L-Glycero-α-D-manno-heptopyranosyl)-(1-3)-(L-glycero-α-D-manno-heptopyranosyl)-(1-5)-[O-(sodium 3-deoxy-α-D-manno-2-octulopyranosylonate)]-(2-4)-sodium (propyl 3-deoxy-α-D-manno-2-octulopyranoside)onate (**29**).* Compound **28** (10.0 mg, 5.4 μmol) in dry methanol (0.3 mL) was added to a suspension of $Pd(OH)_2$-C (20%, 0.3 mg) in dry methanol (0.2 mL), under a H_2 atmosphere with stirring at room temperature. After stirring for 3 days, insoluble materials were removed by filtration through Celite and the filtrate was evaporated. The residue was dissolved in dichloromethane (0.7 mL) and aqueous 80% trifluoroacetic acid (80.0 μL) was added 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 (1.0 mL), and then 0.1 M sodium hydroxide (1.3 mL, 0.13 mmol) was added at room temperature. After stirring for 24 h, the mixture was concentrated by evaporation. The residue was passed through a Bio-Gel P-2 column (2.5 × 100 cm, H_2O) and a Sep-Pak C18 column (H_2O) to give **29** (4.5 mg, 90%) as a colorless powder. $[\alpha]^{25}_D$ = +127.6 (*c* 0.5, H_2O), ^{1}H NMR (600 MHz, D_2O): δ 0.92 (t, 3H, J = 7.4 Hz, CH_3), 1.54–1.61 (m, 2H, CH_2), 1.76 (dd, 1H, $J_{3a,3b}$ = 13.2 Hz, $J_{3a,4}$ = 12.6 Hz, H-$3a^{II}$), 1.93 (dd, 1H, $J_{3a,3b}$ = 12.6 Hz, $J_{3a,4}$ = 12.4 Hz, H-$3a^{I}$), 2.06 (dd, 1H, $J_{3a,3b}$ = 12.6 Hz, $J_{3b,4}$ = 4.2 Hz, H-$3b^{I}$), 2.20 (dd, 1H, $J_{3a,3b}$ = 13.2 Hz, $J_{3b,4}$ = 4.8 Hz, H-$3b^{II}$), 3.21–3.24 (m, 1H, OCH_2), 3.28–3.32 (m, 1H, OCH_2), 3.57 (dd, 1H, $J_{6,7}$ = 9.4 Hz, H-6^{I}), 3.61 (dd, 1H, $J_{7,8a}$ = 6.2 Hz, $J_{8a,8b}$ = 11.8 Hz, H-$8a^{II}$), 3.66 (dd, 1H, $J_{6,7}$ = 8.2 Hz, H-6^{II}), 3.68 (dd, 1H, $J_{6,7a}$ = 5.7 Hz, $J_{7a,7b}$ = 10.8 Hz, H-$7a^{III}$), 3.73–3.77 (m, 4H, H-$7b^{III}$, H-$7a^{IV}$, H-$7b^{IV}$, H-5^{III}), 3.81 (dd, 1H, $J_{7,8a}$ = 6.4 Hz, $J_{8a,8b}$ = 11.6 Hz, H-$8a^{I}$), 3.84–3.98 (m, 8H, H-7^{I}, H-3^{III}, H-4^{III}, H-7^{II}, H-$8b^{II}$, H-4^{IV}, H-5^{IV}, H-$8b^{I}$), 4.01–4.06 (m, 4H, H-5^{II}, H-3^{IV}, H-6^{III}, H-6^{IV}), 4.07 (dd, 1H, $J_{1,2}$ = 1.2 Hz, $J_{2,3}$ = 3.2 Hz, H-2^{III}), 4.09 (ddd, 1H, $J_{3a,4}$ = 12.6 Hz, $J_{3b,4}$ = 4.8 Hz, $J_{4,5}$ = 3.0 Hz, H-4^{II}), 4.13 (dd, 1H, $J_{1,2}$ = 1.6 Hz, $J_{2,3}$ = 3.0 Hz, H-2^{IV}), 4.22 (brs, 1H, $J_{4,5}$ = 2.2 Hz, H-5^{I}), 4.26 (ddd, 1H, $J_{3a,4}$ = 12.4 Hz, $J_{3b,4}$ = 4.2 Hz, $J_{4,5}$ = 2.2 Hz, H-4^{I}), 5.17 (d, 1H, $J_{1,2}$ = 1.2 Hz, H-1^{III}), 5.29 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1^{IV}). ^{13}C NMR (150 MHz, D_2O): δ 10.9 (CH_3), 23.9 (CH_2), 35.2 (C-3^{I}, C-3^{II}), 63.5 (C-7^{IV}, C-8^{I}), 64.0 (C-8^{II}), 64.6 (C-7^{III}), 65.4 (OCH_2), 66.4 (C-4^{III}), 66.8 (C-4^{II}), 66.81 (C-5^{II}), 67.0 (C-4^{IV}), 69.4 (C-6^{III}), 69.7 (C-7^{I}), 70.0 (C-6^{IV}), 70.1 (C-4^{I}), 70.6 (C-2^{III}), 70.8 (C-2^{IV}), 70.83 (C-7^{II}), 71.1 (C-3^{IV}), 72.4 (C-5^{III}), 72.6 (C-6^{I}), 72.62 (C-6^{II}), 73.3 (C-5^{IV} and C-5^{I}), 79.2 (C-3^{III}), 100.5, 100.7 (C-2^{I}, C-2^{II}), 101.3 (C-1^{III}), 103.0 (C-1^{IV}), 175.6, 175.9 (C-1^{I}, C-1^{II}). ESI-HRMS for $C_{33}H_{55}O_{27}$: 883.2931 $[M-2Na + H]^-$. Found 883.2929.

*(β-D-Galactopyranosyl-(1-4)-β-D-glucopyranosyl)-(1-4)-(L-glycero-α-D-manno-heptopyranosyl)-(1-5)-[O-(-sodium 3-deoxy-α-D-manno-2-octulopyranosylonate)]-(2-4)-sodium (propyl 3-deoxy-α-D-manno-2-octulopyranoside)onate (**30**).* Compound **27** (9.0 mg, 4.5 μmol) was hydrogenated in the presence of $Pd(OH)_2$-C (20%, 0.2 mg) in dry methanol (0.5 mL) under atmospheric pressure of hydrogen for 2 days at room temperature. The reaction mixture was filtered through Celite and concentrated. The residue was dissolved in dichloromethane (0.6 mL) and aqueous 80% trifluoroacetic acid (70.0 μL) was added 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 (1.0 mL), and then 0.1 M sodium hydroxide (1.4 mL, 0.14 mmol) was added at room temperature. After stirring for 24 h, the mixture was concentrated by evaporation. The residue was passed through a Bio-Gel P-2 column (2.5 × 100 cm, H_2O) and a Sep-Pak C18 column (H_2O) to give **30** (2.5 mg, 53%) as a colorless powder. $[\alpha]^{25}_D$ = +17.4 (*c* 0.3, H_2O), ^{1}H NMR (600 MHz, D_2O): δ 0.91 (t, 3H, J = 7.4 Hz, CH_3), 1.55–1.62 (m, 2H, CH_2), 1.77 (dd, 1H, $J_{3a,3b}$ = 12.8 Hz, $J_{3a,4}$ = 12.6 Hz, H-$3a^{II}$), 1.92 (dd, 1H, $J_{3a,3b}$ = 12.8 Hz, $J_{3a,4}$ = 12.0 Hz, H-$3a^{I}$), 2.07 (dd, 1H, $J_{3a,3b}$ = 12.8 Hz, $J_{3b,4}$ = 4.4 Hz, H-$3b^{I}$), 2.18 (dd, 1H, $J_{3a,3b}$ = 12.8 Hz, $J_{3b,4}$ = 4.6 Hz, H-$3b^{II}$), 3.19–3.24 (m, 1H, OCH_2), 3.26–3.30 (m, 1H, OCH_2), 3.39 (dd, 1H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 8.8 Hz, H-2^{IV}), 3.54 (dd, 1H, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 10.0 Hz, H-2^{V}), 3.58 (dd, 1H, $J_{6,7}$ = 8.4 Hz, H-6^{I}), 3.59 (dd, 1H, $J_{7,8a}$ = 6.2 Hz, $J_{8a,8b}$ = 11.6 Hz, H-$8a^{II}$), 3.64–3.84 (m, 14H, H-3^{V}, H-6^{II}, H-3^{IV}, H-$6a^{IV}$, H-$6b^{IV}$, H-5^{V}, H-4^{IV}, H-$6a^{V}$, H-$6b^{V}$, H-$7a^{III}$, H-5^{III}, H-$7b^{III}$, H-$8a^{I}$, H-7^{I}), 3.89 (dd, 1H, $J_{7,8b}$ = 2.6 Hz, $J_{8a,8b}$ = 11.6 Hz, H-$8b^{II}$), 3.91–3.99 (m, 4H, H-4^{V}, H-7^{II}, H-5^{IV}, H-$8b^{I}$), 4.00–4.07 (m, 3H, H-4^{III}, H-3^{III}, H-5^{II}), 4.09 (brs, 1H, $J_{1,2}$ = 1.6 Hz, H-2^{III}), 4.10 (ddd,

1H, $J_{3a,4}$ = 12.6 Hz, $J_{3b,4}$ = 4.6 Hz, $J_{4,5}$ = 3.0 Hz, H-4^{II}), 4.14 (ddd, 1H, $J_{6,7a}$ = 7.8 Hz, $J_{6,7b}$ = 4.8 Hz, H-6^{III}), 4.21 (brs, 1H, $J_{4,5}$ = 2.2 Hz, H-5^{I}), 4.24 (ddd, 1H, $J_{3a,4}$ = 12.0 Hz, $J_{3b,4}$ = 4.4 Hz, $J_{4,5}$ = 2.2 Hz, H-4^{I}), 4.44 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1^{V}), 4.58 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^{IV}), 5.32 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1^{III}). ^{13}C NMR (150 MHz, D_2O): δ 10.8 (CH_3), 23.8 (CH_2), 35.0, 35.3 (C-3^{I}, C-3^{II}), 60.6 (C-6^{IV}), 61.6 (C-6^{V}), 63.5 (C-8^{I}), 64.0 (C-8^{II}), 64.6 (C-7^{III}), 65.4 (OCH_2), 66.9 (C-4^{II}), 67.0 (C-5^{II}), 69.2 (C-6^{III}), 69.7 (C-7^{I}), 69.9 (C-4^{V}), 70.2 (C-4^{I}), 70.3 (C3^{III}), 70.5 (C-2^{III}), 70.7 (C-7^{II}), 71.6 (C-5^{III}), 72.0 (C-2^{V}), 72.3 (C-5^{IV}), 72.6 (C-6^{I}), 72.7 (C-6^{II}), 73.1 (C-4^{III}), 73.4 (C-5^{I}), 74.6 (C-3^{IV}), 75.5 (C-2^{IV}), 76.0 (C-3^{V}), 76.5 (C-5^{V}), 78.8 (C-4^{IV}), 100.5, 100.8 (C-2^{I}, C-2^{II}), 101.0 (C-1^{III}), 103.0 (C-1^{IV}), 103.6 (C-1^{V}), 175.5, 175.9 (C-1^{I}, C-1^{II}). ESI-HRMS for $C_{38}H_{63}O_{31}$: 1015.3353 $[M-2Na + H]^-$. Found 1015.3370.

*(β-D-Galactopyranosyl)-(1-4)-(α-D-glucopyranosyl)-(1-5)-[O-(sodium 3-deoxy-α-D-manno-2-octulopyranosylonate)]-(2-4)-sodium (propyl 3-deoxy-α-D-manno-2-octulopyranoside)onate (**31**).* Compound **25** (5.3 mg, 2.7 μmol) was hydrogenated in the presence of Pd$(OH)_2$-C (20%, 1.5 mg) in dry methanol (0.4 mL) under atmospheric pressure of hydrogen for 1 day at room temperature. The reaction mixture was filtered through Celite and concentrated. The residue was treated with aqueous 80% trifluoroacetic acid (40.0 μL) at room temperature. After stirring for 5 min, 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 (0.8 mL), and then 0.1 M sodium hydroxide (0.5 mL, 0.05 mmol) was added at room temperature. After stirring for 24 h, the mixture was concentrated by evaporation. The residue was purified by a Bio-Gel P-2 column (2.5 × 100 cm, H_2O) and a Sep-Pak C18 column (H_2O) to give **31** (1.4 mg, 60%) as a colorless powder. $[\alpha]^{25}_D$ = +20.1 (*c* 0.1, H_2O), ^{1}H NMR (600 MHz, D_2O): δ 0.90 (t, 3H, *J* = 7.4 Hz, CH_3), 1.53–1.60 (m, 2H, CH_2), 1.80 (dd, 1H, $J_{3a,3b}$ = 12.8 Hz, $J_{3a,4}$ = 12.6 Hz, H-3a^{II}), 2.02 (dd, 1H, $J_{3a,3b}$ = 12.6 Hz, H-3a^{I}), 2.06–2.08 (m, 2H, H-3b^{I}, H-3b^{II}), 3.21–3.30 (m, 2H, OCH_2), 3.55 (dd, 1H, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 10.2 Hz, H-2^{IV}), 3.56–3.60 (m, 3H, H-2^{III}, H-6^{I}, H-8a^{II}), 3.66 (dd, 1H, $J_{2,3}$ = 10.2 Hz, $J_{3,4}$ = 3.4 Hz, H-3^{IV}), 3.72–3.82 (m, 6H, H-6^{II}, H-4^{III}, H-6a^{IV}, H-6b^{IV}, H-5^{IV}, H-8a^{I}), 3.89–4.01 (m, 9H, H-8b^{I}, H-7^{II}, H-4^{IV}, H-6a^{III}, H-6b^{III}, H-3^{III}, H-8b^{II}, H-5^{II}, H-4^{I}), 4.06 (ddd, 1H, $J_{6,7}$ = 9.0 Hz, $J_{7,8a}$ = 3.0 Hz, $J_{7,8b}$ = 2.4 Hz, H-7^{I}), 4.09–4.12 (m, 1H, $J_{3a,4}$ = 12.6 Hz, $J_{3b,4}$ = 4.8 Hz, $J_{4,5}$ = 2.2 Hz, H-4^{II}), 4.23 (brs, 1H, H-5^{I}), 4.23–4.26 (m, 1H, H-5^{III}), 4.47 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1^{IV}), 5.28 (dd, 1H, $J_{1,2}$ = 3.6 Hz, H-1^{III}). ^{13}C NMR (150 MHz, D_2O): δ 10.8 (CH_3), 22.8 (CH_2), 35.2 (C-3^{I}, C-3^{II}), 60.2 (C-6^{III}), 61.7 (C-6^{IV}), 63.3 (C-8^{I}), 64.0 (C-8^{II}), 65.3 (OCH_2), 66.7 (C-4^{II}), 67.5 (C-5^{II}), 69.2 (C-7^{I}), 69.3 (C-4^{IV}), 70.1, 71.3, 71.6, 71.8, 72.0, 72.3, 72.4, 73.0, 73.2 (C-4^{I}, C-7^{II}, C-2^{IV}, C-5^{III}, C-6^{II}, C-6^{I}, C-2^{III}, C-3^{III}, C-5^{I}), 74.0 (C-3^{IV}), 75.9 (C-5^{IV}), 78.5 (C-4^{III}), 99.6, 100.5 (C-2^{I}, C-2^{II}), 102.3 (C-1^{III}), 103.5 (C-1^{IV}), 175.9 and 176.1 (C-1^{I}, C-1^{II}). ESI-HRMS for $C_{31}H_{51}O_{25}$: 823.2719 $[M-2Na + H]^-$. Found 823.2732.

Conclusion

The convergent synthetic strategy using Kdoα(2-4)Kdo as a common acceptor was used to prepare more complex 4,5-branched inner-core OS structures. Model glycosylation using a lactose derivative as a test compound suggested that the reactivity of the donor was important for this convergent synthesis, and this was supported by the subsequent glycosylation. Based on the convergent approach, the first synthesis of 4,5-branched inner-core OSs, namely Galβ(1-4)Glcβ(1-4)Hepα(1-5)[Kdoα(2-4)]Kdo pentasaccharide and a common inner-core Hepα(1-3)Hepα(1-5)[Kdoα(2-4)]Kdo tetrasaccharide, was accomplished by coupling the corresponding Hep units with Kdoα(2-4)Kdo. These results suggested that Kdoα(2-4)Kdo **1** is a useful intermediate for the synthesis of 4,5-branched core OS structures.

Author contribution

Ruiqin Yi and Tsuyoshi Ichiyanagi planned the experiments. Ruiqin Yi, Hirofumi Narimoto, and Miku Nozoe performed the experiments. Ruiqin Yi and Tsuyoshi Ichiyanagi analyzed the data. Ruiqin Yi, Hirofumi Narimoto, and Miku Nozoe contributed reagents or other essential material. Ruiqin Yi and Tsuyoshi Ichiyanagi wrote the paper.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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Supplemental material

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References

[1] Holst O, Müller-Loennies S. Microbial polysaccharide structures. Compr. Glycosci. 2007;1:123–179.
[2] Holst O, Ulmer A, Brade H, et al. Biochemistry and cell biology of bacterial endotoxins. FEMS Immunol. Med. Microbiol. 1996;16:83–104.
[3] Caroff M, Karibian D. Structure of bacterial lipopolysaccharides. Carbohydr. Res. 2003;338:2431–2447.

[4] Lüderitz O, Westphal O, Staub, AM, et al. Isolation and chemical and immunological characterization of bacterial lipopolysaccharides. Microbial Toxins. IV. Bacterial Endotoxins. 1971:145–233.

[5] Holst O. Structure of the lipopolysaccharide core region. Knirel Y., Valvano M. Eds. New York, NY: Springer Wien; 2011. p. 21–40.

[6] Tsai C-M, Jankowska-Stephens E, Mizanur R, et al. The fine structure of *neisseria meningitidis* lipooligosaccharide from the M986 strain and three of its variants. J. Biol. Chem. 2009;284: 4616–4625.

[7] Knirel Y, Lindner B, Vinogradov E, et al. Temperature-Dependent Variations and Intraspecies Diversity of the Structure of the Lipopolysaccharide of *Yersinia pestis*. Biochemistry. 2005;44: 1731–1743.

[8] Bystrova O, Knirel Y, Lindner B, et al. Structures of the core oligosaccharide and O-units in the R- and SR-type lipopolysaccharides of reference strains of *Pseudomonas aeruginosa* O-serogroups. FEMS Immunol. Med. Microbiol. 2006;46:85–99.

[9] Bernlind C, Oscarson S. Synthesis of a Branched Heptose- and Kdo-Containing Common Tetrasaccharide Core Structure of Haemophilus influenzae Lipopolysaccharides via a 1,6-Anhydro-l-glycero-β-D-*manno*-heptopyranose Intermediate. J. Org. Chem. 1998;63:7780–7788.

[10] Yang Y, Oishi S, Martin C, et al. Diversity-oriented synthesis of inner core oligosaccharides of the lipopolysaccharide of pathogenic gram-negative bacteria. J. Am. Chem. Soc. 2013;135: 6262–6271.

[11] Paulsen H, Wulff A, Brenken M. Bausteine von Oligosacchariden, IC. Darstellung von synthetischen Antigenen der inneren Core-Region von Lipopolysacchariden durch Copolymerisation mit Acrylamid. Liebigs Ann. Chem. 1991;11:1127–1145.

[12] Ichiyanagi T, Fukunaga M, Tagashira R, et al. A new Kdo derivative for the synthesis of an inner-core disaccharide of lipopolysaccharides and lopooligosaccharides. Tetrahedron. 2011;67:5964–5971.

[13] Yi R, Ogaki A, Fukunaga M, et al. Synthesis of 4,5-disubstituted-3-deoxy-D-*manno*-octulosonic acid (Kdo) derivatives. Tetrahedron. 2014;70:3675–3682.

[14] Ishii K, Esumi Y, Iwasaki Y, et al. Synthesis of a 2,3-Di-O-substituted heptose structure by regioselective 3-O-silylation of a 2-O-substituted heptose derivative. Eur. J. Org. Chem. 2004;6: 1214–1227.

[15] Dean B, Oguchi H, Cai S, et al. Synthesis of multivalent β-lactosyl clusters as potential tumor metastasis inhibitors. Carbohydr. Res. 1993;245:175–192.

[16] Ishii K. Synthesis of oligosaccharides expressed in lipooligosaccharides produced by pathogenic Gram-negative bacteria: construction of the branched core oligosaccharides by using 3-*O*-silyl-heptose. Tottori University; 2005.

[17] Tvaroska I, Taravel FR. Carbon-proton coupling constants in the conformational analysis of sugar molecules. Adv. Carbohydr. Chem. Biochem. 1995;51:15–61.

[18] Ishii K, Kubo H, Yamasaki R. Synthesis of α-lactosyl-(1→3)-L-glycero-α-D-manno-heptopyranoside, a partial oligosaccharide structure expressed within the lipooligosaccharide produced by *Neisseria gonorrhoeae* strain 15253. Carbohydr. Res. 2002;337: 11–20.

[19] Greenberg W, Priestley E, Sears P, et al. Design and synthesis of new aminoglycoside antibiotics containing neamine as an optimal core structure: correlation of antibiotic activity with *in vitro* inhibition of translation. J. Am. Chem. Soc. 1999;121: 6527–6541.

[20] Tvaroška I, Bleha T. Anomeric and exo-anomeric effects in carbohydrate chemistry. Adv. Carbohydr. Chem. Biochem. 1989;47:45–123.

[21] Lönn H. Glycosylation using a thioglycoside and methyl trifluoro-methanesulfonate. a new and efficient method for CIS and trans glycoside formation. J. Carbohydr. Chem. 1987;6:301–306.

[22] Lahmann M, Oscarson S. One-pot oligosaccharide synthesis exploiting solvent reactivity effects. Org. Lett. 2000;2: 3881–3882.