

Syntheses of *O*- β -D-Mannosyl-(1 $\rightarrow$ 4)-*O*- α -D-mannosyl-(1 $\rightarrow$ 3)-L-rhamnose and *O*-(2-Acetamido-2-deoxy- β -D-mannosyl)-(1 $\rightarrow$ 4)-*O*- α -D-galactosyl-(1 $\rightarrow$ 4)-D-galactose via In-situ-activating Glycosylation Using 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-D-glucose

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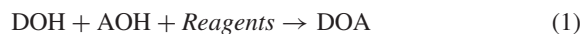
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O- β -D-Mannopyranosyl-(1 $\rightarrow$ 4)-*O*- α -D-mannopyranosyl-(1 $\rightarrow$ 3)-L-rhamnopyranose, a trisaccharide including a repeating unit of the O-specific polysaccharide (OSP) of *Bulkholderia vietnamiensis* strain LMG 6988, and *O*-(2-acetamido-2-deoxy- β -D-mannopyranosyl)-(1 $\rightarrow$ 4)-*O*- α -D-galactopyranosyl-(1 $\rightarrow$ 4)-D-galactopyranose, a trisaccharide including a repeating unit of OSP of *Acinetobacter baumannii* serogroup O18, were synthesized by means of in-situ-activating glycosylation using 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-D-glucopyranose (2ATBG) and a reagent mixture of *p*-nitrobenzenesulfonyl chloride, silver triflate, and 1,8-diazabicyclo[5.4.0]undec-7-ene, and related systems. New syntheses of 2ATBG, allyl 2,3,6-tri-*O*-benzyl- α -D-galactopyranoside, benzyl 2,3,6-tri-*O*-benzyl- α -D-galactopyranoside, and 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-mannopyranose are described.

The synthesis of the β -manno-glycoside has been one of the most difficult problems in synthetic carbohydrate chemistry.^{1a,b} Many approaches have been proposed to overcome the difficulties.^{1c–e} Among the modern methods reported so far, the one involving inversive displacement of 2-triflyloxy group of a compound obtainable from the protected β -glucoside **A** (Fig. 1) with OAc or N₃ group to give the corresponding protected β -manno-glycoside **B** has recently been employed in the synthesis of various β -manno-glycosides.² The OAc or N₃ group in **B** is finally converted into the OH or NHAc group of the β -manno-glycoside **C**. Some years ago, we have reported a simple synthesis of 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-D-glucopyranose^{3a} (**1**) as a donor with the participating group at the C2 position and its use for the β -glucosylation with the aid of a reagent mixture of *p*-nitrobenzenesulfonyl chloride (NsCl), silver triflate (AgOTf), and triethylamine (Et₃N) (the Nst system) as an in-situ-activating

system.^{4a,5} In-situ-activating glycosylation (Eq. 1) using a lactol like **1** as a glycosyl donor (DOH) is convenient because



no pre-activating procedure for DOH is needed in the glycosylation of an acceptor (AOH). Such in-situ-activating glycosylations^{4,6} have not been used so often in syntheses of oligosaccharides.^{5,7} We then thought that **1** has a structure that is suitable for such β -manno-glycoside synthesis, as illustrated in Fig. 1.

β -D-Mannopyranosyl as well as 2-acetamido-2-deoxy- β -D-mannopyranosyl structures are found in various O-specific polysaccharides (OSP) in many kinds of pathogenic microorganisms.⁸ We planned to synthesize *O*- β -D-mannopyranosyl-(1 $\rightarrow$ 4)-*O*- α -D-mannopyranosyl-(1 $\rightarrow$ 3)-L-rhamnopyranose (**2**) (Fig. 2), a trisaccharide including a repeating unit of the OSP in an opportunistic pathogen, *Bulkholderia vietnamiensis* strain LMG 6998,⁹ and *O*-(2-acetamido-2-deoxy- β -D-mannopyranosyl)-(1 $\rightarrow$ 4)-*O*- α -D-galactopyranosyl-(1 $\rightarrow$ 4)-D-galactopyranose (**3**) (Fig. 3), a trisaccharide including a repeating unit of the OSP of another opportunistic pathogen, *Acinetobacter baumannii* serogroup O18.¹⁰ The key step in both syntheses is the in-situ-activating glycosylation using **1**. The route to the trisaccharide **2** was designed to be synthesized via a disaccharide donor **4** (Fig. 2). This might be obtained by the condensation of **1** and acceptor **5**, followed by the inversive displacement with OAc group at the C2^{II} position and deallylation. The trisaccharide **3** was expected to be synthesized via a disaccharide donor **7** (Fig. 3). This could be accessible via condensation of **1** and acceptor **8**, followed by the inversive substitution with an N₃ group at the C2^{II} position and deallylation.

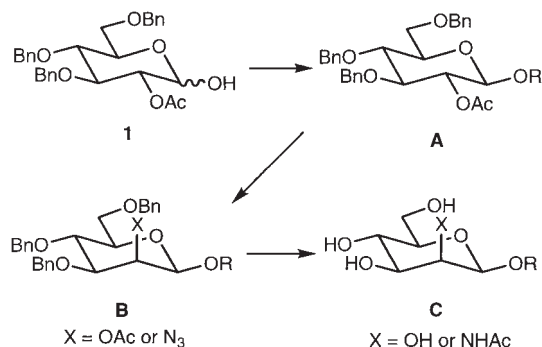


Fig. 1. Synthesis of β -D-mannoside and 2-acetamido-2-deoxy- β -D-mannoside using 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-D-glucopyranose (**1**).

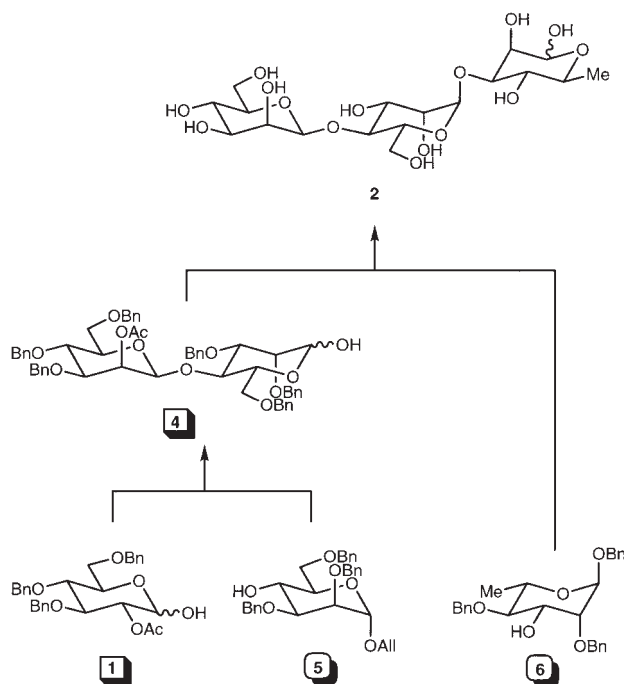


Fig. 2. Synthetic scheme for β -D-Manp-(1 $\rightarrow$ 4)- α -D-Manp-(1 $\rightarrow$ 3)-L-Rhap-OH (2). A code with square shade is a donor, whereas that with round shade is an acceptor.

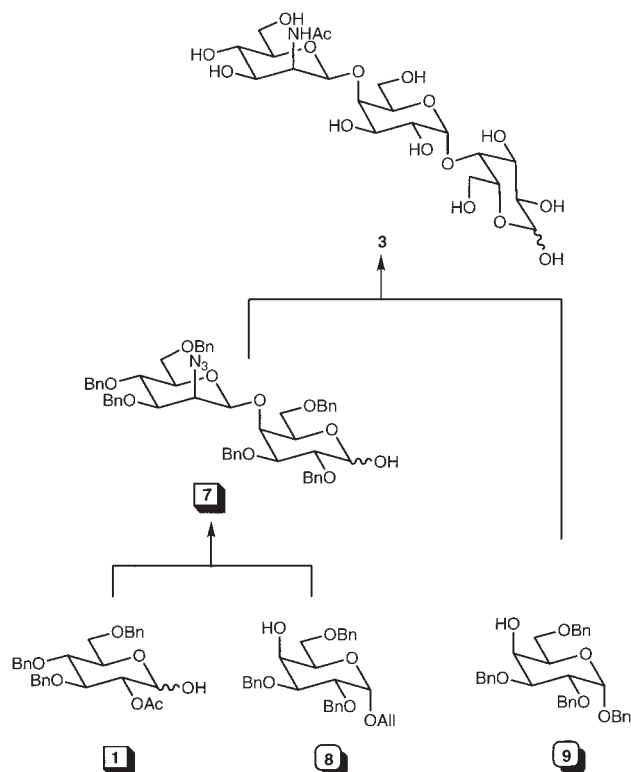


Fig. 3. Synthetic scheme for β -D-ManNAcp-(1 $\rightarrow$ 4)- α -D-Galp-(1 $\rightarrow$ 4)-D-Galp-OH (3). A code with square shade is a donor, whereas that with round shade is an acceptor.

To begin with, the inversive replacements of 2-OH group of **11** as a model compound with OAc group as well as N₃ group were studied (Fig. 4). The β -condensation of cyclohexanol with **1** having a participating OAc group at the C-2 position was performed using a reagent mixture of Me₃SiBr, CoBr₂, *n*-Bu₄NI,^{11a-c} instead of *n*-Bu₄NBr,^{4b} and molecular sieve 4A (MS4A). The desired β -glycoside **10** was obtained in 56% yield with a good β -selectivity (β : α = 95:5). When **1** was reacted with this reagent system in CD₂Cl₂, the ¹H NMR spectrum of the filtrate of the reaction mixture showed two doublets, which indicated the formation of the α -iodide **D** (Fig. 4) (δ 7.04, ^{11d} $J_{1,2}$ = 4.0 Hz) and the α -bromide **E** (δ 6.64, $J_{1,2}$ = 4.0 Hz); the molar ratio of **D**/**E** was ca. 1.5. Thus, *n*-Bu₄NI produces the reactive glycosyl iodide **D**, forming **10**. A possibility that **10** might be formed via an intermediate **F**^{11d,e} from the iodide **D** could not be neglected. Deacetylation of **10** with methanolic NaOMe gave **11**. This was then triflylated, followed by the substitution reaction using *n*-Bu₄NOAc in toluene,^{2e} to give **12** in 52%. The negative specific rotation (-11° in CHCl₃ and -18° in CH₂Cl₂) and the $J_{C1,H1}$ value¹² (155.0 Hz) of **12** indicated its β -mannopyranosyl structure. The reported specific rotation of its α -anomer is $+28.2^\circ$ in CH₂Cl₂.^{2p} Similarly, triflation and the reaction with *n*-Bu₄NN₃ in toluene of **11** gave **13** (42%); the negative specific rotation (-54° in CHCl₃) and the $J_{C1,H1}$ value (156.0 Hz) of **13** were consistent with the β -manno-form.

Next, the cellobiose derivative **16** as a more feasible model was prepared by a condensation of **1** and **14**, followed by deacetylation (Fig. 5). The inversive substitution of its 2^{II}-OH group was then carried out. In the preparation of **15**, we found that a ternary system composed of *p*-nitrobenzenesulfonyl

chloride (NsCl), silver triflate (AgOTf), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (the Nsd system)^{4c,5} was more efficient (69% yield, after 16 h) than the Nst system^{4a} composed of NsCl, AgOTf, and Et₃N (63% yield, after 40 h). We consider that DBU as a strong base enhances the nucleophilicity of the 1-OH with the relatively higher acidity. This will promote the formation of the respective 1-*O-p*-nitrobenzenesulfonate^{4d} that is believed to be the reactive intermediate in this glycosylation reaction. Treatment of **15** with methanolic NaOMe afforded **16**. The triflate of **16** was reacted with *n*-Bu₄NOAc in toluene at 50 $^\circ$ C to give **17** in 71% yield. A ring-contracted furanoid **18** was isolated in 14%. Similar ring-contracting reactions giving furanoides has been reported.^{2m-o} The furanoidal structure of **18** was confirmed by measuring its NMR spectra; a GHMBC spectrum showed a three-bond-coupling between C5^{II} and H2^{II}. Displacement of 2^{II}-OH group with the N₃ group of **16** was conducted via triflylation and subsequent treatment with *n*-Bu₄NN₃ in toluene at 50 $^\circ$ C to form **19** in 73% yield. A furanoid **20** was isolated (22%); its GHMBC spectrum showed a coupling between H5^{II} and C2^{II}. Although the undesired furanoid formations were not avoidable, the crucial inversions at the C2^{II} position were perfect; no trace of *gluco*-compounds was detected in the reaction mixtures of either inversion reaction of **16**.

As shown in Fig. 6, the synthesis of **2** was started from condensation of **1** and **5**^{7a} with the aid of the Nsd system to give the β -glucoside **21** in 80% yield. On reaction with methanolic NaOMe, this was converted into an alcohol **22**, which was then subjected to the subsequent inversive displacement of 2^{II}-OH

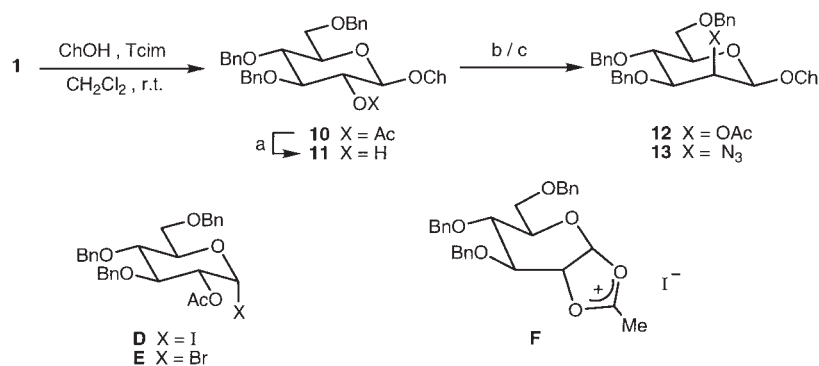


Fig. 4. The inversive displacement of 2-OH group of the glucoside **11** (Tcim = $\text{Me}_3\text{SiBr} + \text{CoBr}_2 + n\text{-Bu}_4\text{NI} + \text{MS4A}$, Ch = cyclohexyl): a. $\text{NaOMe}/\text{MeOH}/\text{rt}$; b. (i) $\text{Tf}_2\text{O} + \text{Py}/\text{CH}_2\text{Cl}_2$, $-30\text{ }^\circ\text{C} \rightarrow 20\text{ }^\circ\text{C}$, (ii) $n\text{-Bu}_4\text{NOAc}/\text{PhMe}$, $25\text{ }^\circ\text{C}$; c. (i) $\text{Tf}_2\text{O} + \text{Py}/\text{CH}_2\text{Cl}_2$, $-30\text{ }^\circ\text{C} \rightarrow 20\text{ }^\circ\text{C}$, (ii) $n\text{-Bu}_4\text{NN}_3/\text{PhMe}$, $25\text{ }^\circ\text{C}$.

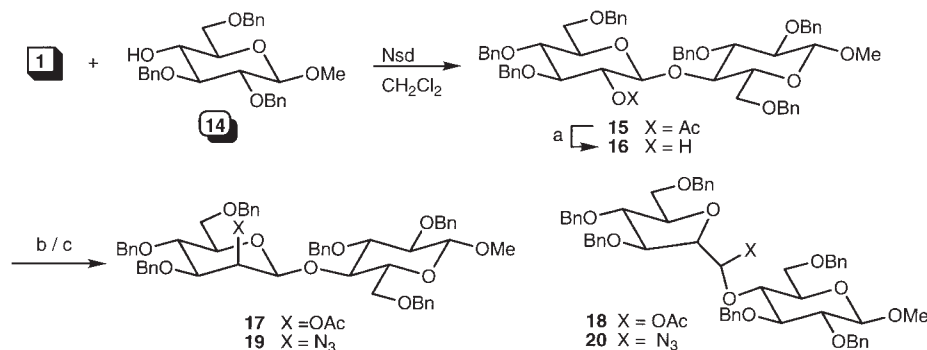


Fig. 5. The inversive displacement of 2^{II}-OH group of the cellobioside **16** (Nsd = $\text{NsCl} + \text{AgOTf} + \text{DBU}$): a. $\text{dil NaOMe}/\text{rt}$; b. (i) $\text{Tf}_2\text{O} + \text{Py}/\text{CH}_2\text{Cl}_2$, $-30\text{ }^\circ\text{C} \rightarrow 20\text{ }^\circ\text{C}$, (ii) $n\text{-Bu}_4\text{NOAc}/\text{PhMe}$, $50\text{ }^\circ\text{C}$; c. (i) $\text{Tf}_2\text{O} + \text{Py}/\text{CH}_2\text{Cl}_2$, $-30\text{ }^\circ\text{C} \rightarrow 20\text{ }^\circ\text{C}$, (ii) $n\text{-Bu}_4\text{NN}_3/\text{PhMe}$, $50\text{ }^\circ\text{C}$.

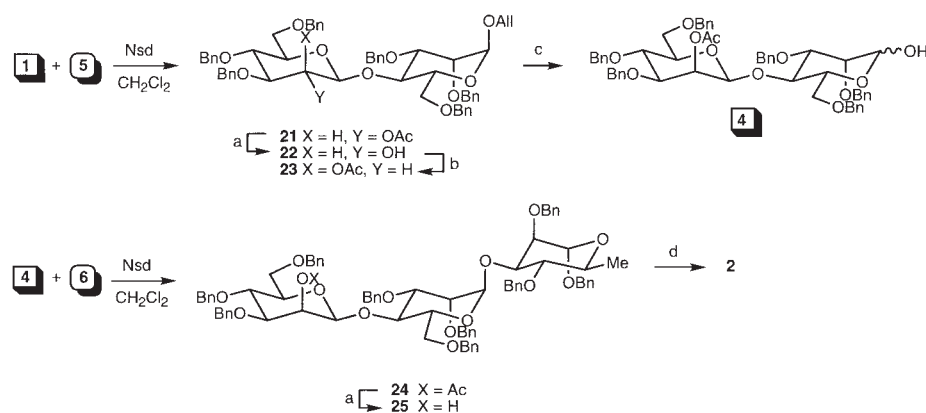


Fig. 6. Synthesis of $\beta\text{-D-Manp}-(1 \rightarrow 4)\text{-}\alpha\text{-D-Manp}-(1 \rightarrow 3)\text{-L-Rhap-OH}$ (**2**) (Nsd = $\text{NsCl} + \text{AgOTf} + \text{DBU}$): a. $\text{NaOMe}/\text{MeOH}/\text{rt}$; b. (i) $\text{Tf}_2\text{O} + \text{Py}/\text{CH}_2\text{Cl}_2$, $-30\text{ }^\circ\text{C} \rightarrow 20\text{ }^\circ\text{C}$, (ii) $n\text{-Bu}_4\text{NOAc}/\text{PhMe}$, $50\text{ }^\circ\text{C}$; c. $\text{PdCl}_2 + \text{NaOAc}/\text{aq AcOH}$ (95%), rt ; d. $\text{H}_2 + \text{Pd-C}$ (10%)/ AcOH , rt .

group with OAc group. Triflation of **22** and the subsequent reaction with $n\text{-Bu}_4\text{NOAc}$ in toluene at $50\text{ }^\circ\text{C}$ afforded **23** in 72% yield; a furanoid compound was isolated (12%). Mild deallylation¹³ of **23** with $(\text{Ph}_3\text{P})_3\text{RhCl}$ gave disaccharide donor **4**, which was condensed with **6**⁵ with the aid of the Nsd system to afford the desired trisaccharide derivative **24** in 35% yield; the β -linked isomer (14% yield) was isolated. The structure of **24** was confirmed by observing its NMR spectra; the $\beta\text{-C1}^{\text{II}}$ -to- C4^{II} linkage and the $\alpha\text{-C1}^{\text{II}}$ -to- C3^{I} linkage were assigned by the GHMBC experiments and by the NOE spectra that

show the proximity between H1^{II} and H3^{I} as well as that between H1^{III} and H4^{II} . Deacetylation of **24** with methanolic NaOMe gave **25**; its catalytic debenzoylation afforded **2**. The NMR spectra of **2** measured in D_2O was consistent with its structure: (1) the $J_{\text{C1,H1}}$ value¹² of C1^{III} of 159.0 Hz indicated $\beta\text{-manno-pyranosyl}$ linkage, (2) the GHMBC experiments showed the coupling between H1^{II} and C3^{I} for the C1^{II} -to- C3^{I} linkage and the coupling between C1^{III} and H4^{II} for the C1^{III} -to- C4^{II} linkage, and (3) the NOE spectra showed the proximity between H1^{II} and H3^{I} as well as that between H1^{III} and

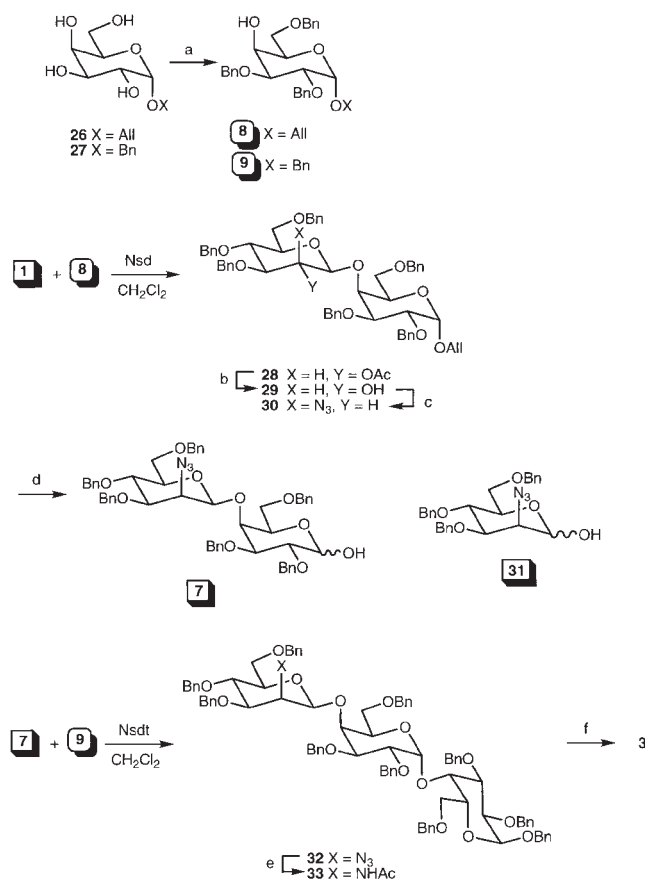


Fig. 7. Synthesis of β -D-ManNAc-(1 $\rightarrow$ 4)- α -D-Galp-(1 $\rightarrow$ 4)-D-Galp-OH (**3**) (Nsd = NsCl + AgOTf + DBU, Nsd = NsCl + AgOTf + DMA + TEA): a. BnCl + LiOH/140 °C; b. NaOMe/MeOH/35 °C; c. (i) Tf₂O + Py/CH₂Cl₂, -30 °C $\rightarrow$ 20 °C, (ii) CsN₃ + 18-crown-6/PhMe, ultrasonication; d. PdCl₂ + NaOAc/aq AcOH (95%), rt; e. (i) LiAlH₄/Et₂O, Δ ; (ii) Ac₂O/MeOH, rt; f. H₂ + Pd-C (10%)/AcOH, rt.

H4^{II}.

Finally, the trisaccharide **3** was synthesized starting from the new synthesis of **8**^{14a,b} from **26**¹⁵ by means of the controlled benzylation.¹⁶ Similar to the case of methyl α -D-galactopyranoside,¹⁷ **26** was simply reacted with benzyl chloride (40 mol. amt.) in the presence of LiOH (8 mol. amt.) at 140 °C to afford **8** in 39% (Fig. 7). This procedure was also applied to the preparation of **9**¹⁸ from **27**;¹⁹ its synthesis from D-galactose was improved. Thus, both versatile 4-OH derivatives of D-galactose, **8** and **9**, were prepared from D-galactose in only two steps from D-galactose. Then, condensation of **1** and **8** was conducted in the presence of the Nsd system to give a β -glucoside **28** in 96% yield. Deacetylation of **28** with methanolic NaOMe at 35 °C gave **29** in 93% yield; this was next subjected to triflylation and the substitution reaction.^{2d-k} As shown in Table 1, the yields of **30** in the reactions using *n*-Bu₄NN₃ in polar solvents (Runs 1–5) were low (<20%). Less polar toluene as solvent gave slightly better results (Run 7, 23%). Ultrasonication²⁰ improved the yield of **30** (Run 9, 32%). At last, we found that the use of CsN₃ in the presence of 18-crown-6 in toluene under ultrasonication²⁰ afforded **30** in 45% yield (Run 11). Thus, the over-all yield of **30** from **8** was 40%. The difficulty in the displacement reaction might occur due to steric hindrance to the azide anion incoming upon the 2^{II}-OTf group of the triflate derived from **29**. So, we alternatively tried the direct β -glycosylation of the donor **31**^{7a} of which the preparation had been improved. However, condensation of **31** and **8** with the Nst system in CH₂Cl₂ afforded **30** (26%), together with the α -linked isomer (53%) (β : α = 33:67). Expecting its known β -directing effect,^{1f-h} we used EtCN as solvent; disappointingly, it made the glycosylation more α -selective^{1i,j} (β : α = 27:73). The amide LiNTf₂ as additive converted the α -selectivity of the glycosylation using 4-*O*-allyl-2,3,6-tri-*O*-benzyl-D-glucopyranose and the Nst in CH₂Cl₂ into the β -one.^{7b} However, its use in the present instance favored the β -anomer a little; the value of α : β remained at 40:60.

Deallylation¹³ of **30** with (Ph₃P)₃RhCl afforded the disaccharide donor **7**, which was finally condensed with **9** by a system composed of NsCl, AgOTf, *N,N*-dimethylacetamide (DMA), and Et₃N (Nsd system)^{4d} to yield the desired trisac-

Table 1. Reaction of the 2-*O*-Triflate of **29** with Azides^{a)}

Run	Azides	mol. amt.	Solvent ^{b)}	18-Crown-6	us ^{c)}	Temperature	Time	Yield of 30
						°C	h	%
1	<i>n</i> -Bu ₄ NN ₃	3	DMF	—	—	40	16	14
2	<i>n</i> -Bu ₄ NN ₃	6	DMF	—	—	40	16	18
3	<i>n</i> -Bu ₄ NN ₃	9	DMF	—	—	40	16	8
4	<i>n</i> -Bu ₄ NN ₃	6	DMA	—	—	40	16	16
5	<i>n</i> -Bu ₄ NN ₃	6	DMSO	—	—	40	16	<10
6	<i>n</i> -Bu ₄ NN ₃	6	PhMe	—	—	60	16	18
7	<i>n</i> -Bu ₄ NN ₃	9	PhMe	—	—	60	16	23
8	<i>n</i> -Bu ₄ NN ₃	12	PhMe	—	—	60	16	<10
9	<i>n</i> -Bu ₄ NN ₃	9	PhMe	—	+	60	11	32
10	CsN ₃	6	PhMe	+	+	60	11	38
11	CsN ₃	7	PhMe	+	+	60	11	45
12	CsN ₃	8	PhMe	+	+	60	11	43

a) Reactions were conducted in 0.03–0.09 mmol scales. b) DMA = *N,N*-dimethylacetamide, DMF = *N,N*-dimethylformamide, DMSO = dimethyl sulfoxide. c) us = ultrasonication.

charide derivative **32** in 56% yield. The structure of **32** was confirmed by observing its NMR spectra; the β -C1^{III}-to-C4^I linkage and the α -C1^I-to-C4^I linkage were assigned by GHMBC experiments and by NOE spectra that show the proximity between H1^{II} and H4^I as well as that between H1^{III} and H4^{II}. Reduction of **32** with LiAlH₄ in diethyl ether, followed by acetylation, afforded **33** in 59% yield. The last catalytic debenzoylation of **33** gave **3**. The NMR spectra of **3** measured in D₂O was consistent with its structure: (1) the $J_{C1,H1}$ value¹² of C1^{III} of 158.0 Hz indicated β -manno-pyranosyl linkage, (2) the GHMBC experiments showed the coupling between H1^{II} and C4^I for the C1^{II}-to-C4^I linkage and the coupling between C1^{III}-and-H4^{II} for the C1^{III} to C4^{II} linkage, and (3) the NOE spectra showed the proximity between H1^{II} and H4^I as well as that between H1^{III} and H4^{II}.

In conclusion, (1) **1**, easily prepared from D-glucose or 1,2,3,4,6-penta-*O*-acetyl- β -D-glucopyranose by a simple process, is useful in the synthesis of the β -D-manno-glycosides, **2** and **3**; (2) the utilities of the Nsd system as well as the Tcim system are shown in the β -glucosylation using **1**; and (3) CsN₃ in toluene with ultrasonical treatment was useful in the azide-substitution of the 2-*O*-triflate of **29**.

Experimental⁵

The solvent systems for column chromatography on silica gel (Kanto Chemical, No. 37047; gradient elution) and thin-layer chromatography (TLC) (Merck, DC-Plastikfolien Kieselgel 60 F 254, Art. 5735) were CHCl₃-MeOH (CM), 1,2-dichloroethane-AcOEt (DE), AcOEt-MeOH (EM), hexane-AcOEt (HE), and PhMe-2-butanone (TK). Ultrasonication was carried out with a Velvo-Clear Ultrason 95-2403 apparatus. The melting points were determined on a Yanaco Micro Melting Point Apparatus (Yanagimoto). The optical rotations were measured on a JASCO DIP-180 Digital Polarimeter at room temperature. The ¹H and ¹³C NMR spectra were recorded with a Varian VXR300 spectrometer or a Varian XL-400 spectrometer, along with the measurements of H,H-COSY, C,H-COSY, and DEPT spectra. The $J_{C1,H1}$ values¹² were determined by gated decoupling with the NOE experiment. The assignments of the spectra of **2**, **3**, **24**, **25**, **32**, and **33** were made by auxiliary measurements of HOHAHA, HMQC, HMBC, GHMBC, and differential NOE spectra. The elemental analyses were carried out with a Yanaco CHN Corder MT-5. The HRMS were recorded with a JEOL JMS-AX505HA spectrometer and a JEOL JMS-700 spectrometer. For other items, see the previous report.⁵

The special abbreviations used here for the assigned substituents are All (allyl), Bn (benzyl), and Ch (cyclohexyl), Ns (*p*-nitrobenzenesulfonyl), and Tf (trifluoromethanesulfonyl).

Commercial NsCl (Wako) was passed through a silica-gel column eluted with benzene, evaporated to dryness, and stored in a dry box in a refrigerator.⁵ Syrupy donors and acceptors were purified by chromatography using the HE system and then stored in a refrigerator. Commercially available AgOTf (Aldrich), Et₃N (Tokyo Kasei), DBU (diazabicyclo[5.4.0]undec-7-ene, Tokyo Kasei), Me₃SiBr (Tokyo Kasei), CoBr₂ (Wako), molecular sieve 4A (MS4A, Hydrous), Tf₂O (Tokyo Kasei), anhydrous pyridine (Tokyo Kasei), *n*-Bu₄NOAc (Fluka), *n*-Bu₄NI (Tokyo Kasei), *n*-Bu₄NN₃ (Tokyo Kasei), CsN₃ (Aldrich), 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane, Aldrich), and anhydrous solvents (DMF (*N,N*-dimethylformamide), DMA (*N,N*-dimethyl-

acetamide), and PhMe, Kanto Kagaku) were used.

Chromatographically pure samples of the acetates of **8** and **9** for the determination of the NMR spectra were prepared as described in the previous report.^{7c}

The donor **1** was prepared from D-glucose instead of 1,2,3,4,6-penta-*O*-acetyl- β -D-glucopyranose (PAG).^{3a} To a stirred mixture of D-glucose (Wako, 2.0 g, 11.1 mmol) and AcBr (11 mL, 136 mmol), AcOH (5.6 mL) was added; the resulting mixture was stirred at 0 °C for 20 min and then at room temperature for 90 min to give a solution. This was evaporated and co-evaporated with PhMe (5 mL, three times) to give a crude solid of 2,3,4,6-tetra-*O*-acetyl- α -D-glucopyranosyl bromide. The solid was further dried in vacuo over NaOH pellets overnight. The residue (4.68 g) was treated with 2,6-dimethylpyridine (8.2 mL, 70 mmol) and MeOH (6.8 mL, 170 mmol) in MeNO₂ (22 mL) at room temperature overnight. The mixture was diluted with PhMe, washed with dil NaHCO₃ (5%), and evaporated to dryness to give a syrup. To this, BnCl (60.7 mL, 0.53 mmol) and crushed KOH (30 g, 0.54 mmol) were added and the mixture was strongly stirred at 120 °C for 1 h. To a cooled mixture, PhMe (150 mL) and H₂O (70 mL) were added. This organic layer was washed well with H₂O, evaporated, and then treated with aq AcOH (80%, 40 mL) for 2 h. Work-up, chromatography using the TK system (100:1 → 10:1), and crystallization with hexane afforded the previously reported **1**^{3a} (1.10 g, 20%).

The original procedure^{3a} for obtaining **1** from PAG was also improved by substituting EtOH with MeOH and extraction after orthoesterification with evaporation. A crude bromide obtained by a reaction of PAG (5.0 g, 13 mmol), AcBr (5.0 mL, 61 mmol), and H₂O (1.0 mL, 56 mmol) in CHCl₃ (15 mL)^{3a} was treated with 2,6-dimethylpyridine (4.7 mL, 41 mmol), MeOH (4.0 mL, 100 mmol) in MeNO₂ (13 mL), followed by work-up, to give a yellow syrup. This was then treated with BnCl (70 mL, 0.61 mol) and crushed KOH (35 g, 0.63 mol), followed by hydrolysis with aq AcOH (80%, 40 mL). Work-up and chromatography afforded **1** (5.3 g, 84%).

The acceptor **14**²¹ was rapidly prepared from commercial methyl β -D-glucopyranoside monohydrate (Tokyo Kasei). A mixture of the starting material (1.0 g, 4.7 mmol), TsOH·H₂O (78.6 mg, 0.41 mmol), PhCH(OMe)₂ (Wako, 2.0 mL, 13.3 mmol), and DMF (6 mL) was stirred at room temperature for 16 h. To the mixture, BnBr (3.7 mL, 31 mmol) and NaH (Wako, ca. 60% in oil, 1.24 g, 31 mmol) were added at 0 °C; this mixture was stirred for 15 min and then at 20 °C for 2 h. After addition of MeOH (3.7 mL, 93 mmol), work-up and chromatography using the TK system (100:1 → 20:1) afforded methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- β -D-glucopyranoside (1.42 g). Reduction of this was performed in CH₂Cl₂ (16 mL) containing Et₃SiH (2.7 mL, 17 mmol) and CF₃CO₂H (1.4 mL, 19 mmol).^{21a} The solution was stirred at 0 °C for 5 min and then at 20 °C for 30 min. Evaporation and chromatography with the TK system (100:1 → 10:1) yielded the previously reported **14**^{4d,21c} (1.23 g, 56%).

Cyclohexyl 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl- β -D-glucopyranosides (10**).** To a stirred mixture of **1** (49 mg, 0.10 mmol), cyclohexanol (12 μ L, 0.11 mmol), CoBr₂ (22 mg, 0.10 mmol), *n*-Bu₄NI (37 mg, 0.10 mmol), powdered MS4A (49 mg), and CH₂Cl₂ (0.25 mL), Me₃SiBr (13 μ L, 0.10 mmol) was added at 20 °C; the resulting mixture was stirred for 1.0 h. After the addition of powdered NaHCO₃ (17 mg, 0.20 mmol), the mixture was stirred for 15 min and transferred onto the top of silica-gel column, which was developed with the TK system (100:1 → 20:1) to give the faster-moving α -anomer of **10** (2 mg, 3%) and **10** (32 mg, 56%) (β : α

= 95:5).

10: $[\alpha]_{\text{D}}^{23} -12^\circ$ (c 0.4, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 1.98 (s, Ac), 3.50 (ddd, $J_{4,5} = 9.5$ Hz, $J_{5,6a} = 5.0$ Hz, $J_{5,6b} = 2.0$ Hz, H5), 3.63 (m, Ch), 3.66 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4), 3.68 (dd, $J_{2,3} = J_{3,4} = 9.5$ Hz, H3), 3.69 (dd, $J_{5,6a} = 5.0$ Hz, $J_{6a,6b} = 10.5$ Hz, H6a), 3.77 (dd, $J_{5,6b} = 2.0$ Hz, $J_{6a,6b} = 10.5$ Hz, H6b), 4.45 (d, $J_{1,2} = 8.0$ Hz, H1), 4.99 (dd, $J_{1,2} = 8.0$ Hz, $J_{2,3} = 9.5$ Hz, H2); ^{13}C NMR (CDCl_3 , 75 MHz) δ 20.9 (Ac), 23.6, 23.7, 25.6, 31.7, 33.4 (Ch), 69.0 (C6), 73.5 (C2), 75.2 (C4), 77.4 (Ch), 78.2 (C4), 83.1 (C3), 99.7 (C1), 169.3 (Ac). HRMS (FAB) Found: m/z 597.2846. Calcd for $\text{C}_{35}\text{H}_{42}\text{NaO}_7$ $[\text{M} + \text{Na}]^+$: 597.2828.

The α -anomer: $[\alpha]_{\text{D}}^{24} +76^\circ$ (c 0.5, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 2.04 (s, Ac), 3.57 (m, Ch), 3.68 (dd, $J_{5,6a} = 2.0$ Hz, $J_{6a,6b} = 10.5$ Hz, H6a), 3.72 (dd, $J_{3,4} = 9.0$ Hz, $J_{4,5} = 10.0$ Hz, H4), 3.79 (dd, $J_{5,6b} = 3.5$ Hz, $J_{6a,6b} = 10.5$ Hz, H6b), 3.95 (ddd, $J_{4,5} = 10.0$ Hz, $J_{5,6a} = 2.0$ Hz, $J_{5,6b} = 3.5$ Hz, H5), 4.05 (dd, $J_{2,3} = 10.0$ Hz, $J_{3,4} = 9.0$ Hz, H3), 4.82 (dd, $J_{1,2} = 4.0$ Hz, $J_{2,3} = 10.0$ Hz, H2), 5.21 (d, $J_{1,2} = 4.0$ Hz, H1); ^{13}C NMR (CDCl_3 , 75 MHz) δ 20.1 (Ac), 23.6, 24.0, 25.6, 31.4, 33.2 (Ch), 68.5 (C6), 70.3 (C5), 74.0 (C2), 75.7 (Ch), 77.9 (C4), 80.4 (C3), 94.2 (C1), 170.3 (Ac); HRMS (FAB) Found: m/z 597.2870. Calcd for $\text{C}_{35}\text{H}_{42}\text{NaO}_7$ $[\text{M} + \text{Na}]^+$: 597.2828.

When $n\text{-Bu}_4\text{NBr}^{4b}$ (32 mL, 0.10 mmol) was used instead of $n\text{-Bu}_4\text{NI}$ and the reaction was conducted for 3 h at room temperature, the α -anomer (9 mg, 16%) and **10** (28 mg, 49%) were obtained (β : α = 75:25).

A glycosylation using Me_3SiBr (13 μL , 0.10 mmol), CoI_2 (31 mg, 0.10 mmol), and MS4A (49 mg) in CH_2Cl_2 (0.25 mL) gave the α -anomer (4 mg, 7%) and **10** (36 mg, 63%) (β : α = 90:10) after 1 h.

A condensation in the presence of Me_3SiI (14.2 μL , 0.10 mmol), CoBr_2 (22 mg, 0.10 mmol), and MS4A (49 mg) in CH_2Cl_2 (0.25 mL) gave the α -anomer (7 mg, 12%) and **10** (32 mg, 56%) (β : α = 82:18) after 1 h, whereas that using Me_3SiBr (13 μL , 0.10 mmol), CoBr_2 (22 mg, 0.10 mmol), and MS4A (49 mg) in CH_2Cl_2 (0.25 mL) gave the α -anomer (4.5 mg, 8%) and **10** (18 mg, 31%) (β : α = 79:21), after 2 h.

NMR Study Detecting 2-O-Acetyl-3,4,6-tri-O-benzyl- α -D-glucopyranosyl Iodide D and Bromide E. To a stirred mixture of **1** (25.0 mg, 0.051 mmol), CoBr_2 (11.1 mg, 0.051 mmol), $n\text{-Bu}_4\text{NI}$ (18.8 mg, 0.051 mmol), MS4A (49 mg), and CD_2Cl_2 containing TMS (1%) (Aldrich, 1.0 mL), Me_3SiBr (6.6 μL , 0.051 mmol) was added at room temperature. After 1 h, the mixture was filtered through a pad of cotton. The ^1H NMR spectrum of the filtrate determined at 300 MHz clearly showed two doublets at δ 6.64 ($J_{1,2} = 4.0$ Hz, H1 of **E**) and at δ 7.04 ($J_{1,2} = 4.0$ Hz, H1 of **D**) in the region of δ 5.4–7.2.

Separately, **1** (25.0 mg, 0.051 mmol) was reacted with Me_3SiBr (6.6 μL , 0.051 mmol), CoBr_2 (11.1 mg, 0.051 mmol), $n\text{-Bu}_4\text{NBr}$ (16.4 mg, 0.051 mmol), and MS4A (49 mg) in CD_2Cl_2 containing TMS (1%) (Aldrich, 1.0 mL). The ^1H NMR spectrum of the filtrate showed one doublet of **E** at δ 6.64 ($J_{1,2} = 4.0$ Hz, H1 of **E**) in the above-described region.

Cyclohexyl 3,4,6-Tri-O-benzyl- β -D-glucopyranoside (11). A mixture of **10** (218 mg, 0.38 mmol), MeOH (17 mL) and methanolic NaOMe (7%, 0.3 mL) was kept standing overnight. Neutralization with AcOH, evaporation and chromatography with the TK system (100:1 $\rightarrow$ 20:1) afforded **11**²² (188 mg, 93%); $[\alpha]_{\text{D}}^{25} -11^\circ$ (c 1.1, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 2.40 (s, OH), 3.51 (ddd, $J_{4,5} = 9.0$ Hz, $J_{5,6a} = 4.5$ Hz, $J_{5,6b} = 2.0$ Hz, H5), 3.60 (dd, $J_{1,2} = 7.5$ Hz, $J_{2,3} = 9.0$ Hz, H2), 3.61 (t, $J_{2,3} = J_{3,4} = 9.0$ Hz, H3), 3.69 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, H4), 3.69 (dd, $J_{5,6a} = 4.5$

Hz, $J_{6a,6b} = 10.0$ Hz, H6a), 3.78 (dd, $J_{5,6b} = 2.0$ Hz, $J_{6a,6b} = 10.0$ Hz, H6b), 4.38 (d, $J_{1,2} = 7.5$ Hz, H1); ^{13}C NMR (CDCl_3 , 75 MHz) δ 24.0, 24.1, 25.5, 32.0, 33.6 (Ch), 69.2 (C6), 74.8 (C2), 75.2 (C5), 77.6 (Ch), 77.7 (C4), 84.6 (C3), 101.1 (C1). Found: C, 74.35; H, 7.67%. Calcd for $\text{C}_{33}\text{H}_{40}\text{O}_6$: C, 74.41; H, 7.57%.

Cyclohexyl 2-O-Acetyl-3,4,6-tri-O-benzyl- β -D-mannopyranoside (12). To a stirred mixture of **11** (25 mg, 0.047 mmol), pyridine (51 μL , 0.63 mmol), and CH_2Cl_2 (0.51 mL), Ti_2O (80 μL , 0.49 mmol) was added at below -30°C bath temperature. The resulting heterogeneous mixture was stirred at below -25°C for 5 min and then at 0°C for 5 min. The mixture was further stirred at 10°C for 5 min and then at 20°C for 20 min. After H_2O (15 μL , 0.83 mmol) was added to the mixture at 0°C with stirring, the mixture was diluted with hexane and chromatographed with the TK system (100:1 $\rightarrow$ 20:1) to yield a homogeneous syrup. To this, $n\text{-Bu}_4\text{NOAc}$ (129 mg, 0.43 mmol) and anhydrous PhMe (0.22 mL) were added. After stirring at 25°C for 16 h, the mixture was diluted with hexane, and chromatographed with the TK system (100:1 $\rightarrow$ 20:1) to give **12** (14 mg, 52%); $[\alpha]_{\text{D}}^{25} -11^\circ$ (c 1.1, CHCl_3), $[\alpha]_{\text{D}}^{24} -11^\circ$ (c 0.9, CH_2Cl_2) (Ref. 2p, α -anomer, $[\alpha]_{\text{D}}^{20} +28.2^\circ$ (c 1.77, CH_2Cl_2)); ^1H NMR (CDCl_3 , 300 MHz) δ 2.20 (s, Ac), 3.48 (ddd, $J_{4,5} = 9.0$ Hz, $J_{5,6a} = 6.0$ Hz, $J_{5,6b} = 2.0$ Hz, H5), 3.64 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.0$ Hz, H3), 3.68 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, H4), 3.72 (dd, $J_{5,6a} = 6.0$ Hz, $J_{6a,6b} = 10.5$ Hz, H6a), 3.80 (dd, $J_{5,6b} = 2.0$ Hz, $J_{6a,6b} = 10.5$ Hz, H6b), 4.63 (d, $J_{1,2} = 1.0$ Hz, H1), 5.58 (dd, $J_{1,2} = 1.0$ Hz, $J_{2,3} = 3.0$ Hz, H2); ^{13}C NMR (CDCl_3 , 75 MHz) δ 21.2 (Ac), 23.8, 23.9, 25.6, 31.6, 33.2 (Ch), 68.8 (C2), 69.5 (C6), 74.5 (C4), 75.5 (C5), 76.9 (Ch), 80.6 (C3), 96.7 (C1, $J_{\text{C1,H1}} = 155.0$ Hz), 170.8 (Ac). HRMS (FAB) Found: m/z 597.2864. Calcd for $\text{C}_{35}\text{H}_{42}\text{NaO}_7$ $[\text{M} + \text{Na}]^+$: 597.2828.

Cyclohexyl 2-Azido-3,4,6-tri-O-benzyl-2-deoxy- β -D-mannopyranoside (13). Triflylation of **11** (27.6 mg, 0.052 mmol) with Ti_2O (87.2 μL , 0.53 mmol), pyridine (55.5 μL , 0.69 mmol), and CH_2Cl_2 (0.55 mL) and following chromatography as described for **12** yielded a homogeneous syrup. Subsequent reaction with $n\text{-Bu}_4\text{NN}_3$ (33.8 mg, 0.12 mmol) in anhydrous PhMe (0.18 mL) for 16 h at 25°C , followed by chromatography as described for **12**, gave **13** (12 mg, 42%); $[\alpha]_{\text{D}}^{24} -54^\circ$ (c 1.3, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 3.40 (ddd, $J_{4,5} = 9.0$ Hz, $J_{5,6a} = 5.5$ Hz, $J_{5,6b} = 2.0$ Hz, H5), 3.63 (dd, $J_{2,3} = 3.5$ Hz, $J_{3,4} = 9.0$ Hz, H3), 3.69 (dd, $J_{5,6a} = 5.5$ Hz, $J_{6a,6b} = 11.0$ Hz, H6a), 3.72 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, H4), 3.76 (dd, $J_{5,6b} = 2.0$ Hz, $J_{6a,6b} = 11.0$ Hz, H6b), 3.92 (dd, $J_{1,2} = 1.0$ Hz, $J_{2,3} = 3.5$ Hz, H2), 4.60 (d, $J_{1,2} = 1.0$ Hz, H1); ^{13}C NMR (CDCl_3 , 75 MHz) δ 23.76, 23.84, 25.6, 31.6, 33.4 (Ch), 62.5 (C2), 69.4 (C6), 74.7 (C4), 75.8 (C5), 76.9 (Ch), 81.2 (C3), 97.7 (C1, $J_{\text{C1,H1}} = 156.0$ Hz). Found: C, 70.91; H, 7.09; N, 7.35%. Calcd for $\text{C}_{33}\text{H}_{39}\text{N}_3\text{O}_5$: C, 71.07; H, 7.05; N, 7.53%.

Methyl O-(2-O-Acetyl-3,4,6-tri-O-benzyl- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-O-benzyl- β -D-glucopyranoside (15). To a stirred mixture of **1** (41 mg, 0.083 mmol), **14** (30 mg, 0.065 mmol), NaCl (36 mg, 0.16 mmol), AgOTf (42 mg, 0.016 mmol), and CH_2Cl_2 (0.30 mL), DBU (24 μL , 0.16 mmol) was added at -60°C (bath temperature); this mixture was stirred under unhydrous conditions, while the reaction temperature was gradually raised to 0°C (ca. $0.3^\circ\text{C}/\text{min}$). The mixture was then stirred at this temperature for 16 h. After the addition of NaHCO_3 (45 mg, 0.53 mmol) and PhMe (2 mL), the mixture was chromatographed with the TK system (100:1 $\rightarrow$ 10:1) to afford **15** (42 mg, 69%); $[\alpha]_{\text{D}}^{24} +18^\circ$ (c 0.2, CHCl_3) (Ref. 3a, $[\alpha]_{\text{D}}^{20} +21^\circ$ (c

1.8, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 1.88 (s, Ac), 3.29 (ddd, *J*_{4,5} = 9.5 Hz, *J*_{5,6a} = 2.0 Hz, *J*_{5,6b} = 4.0 Hz, H5^{II}), 3.37 (m, H5^I), 3.37 (dd, *J*_{1,2} = 8.0 Hz, *J*_{2,3} = 9.0 Hz, H2^I), 3.50 (t, *J*_{2,3} = *J*_{3,4} = 9.0 Hz, H3^{II}), 3.51 (dd, *J*_{5,6a} = 4.0 Hz, *J*_{6a,6b} = 11.0 Hz, H6a^{II}), 3.55 (s, Me), 3.60 (t, *J*_{2,3} = *J*_{3,4} = 9.0 Hz, H3^I), 3.62 (dd, *J*_{5,6b} = 2.0 Hz, *J*_{6a,6b} = 11.0 Hz, H6b^{II}), 3.69 (dd, *J*_{3,4} = 9.0 Hz, *J*_{4,5} = 9.5 Hz, H4^{II}), 3.90 (dd, *J*_{3,4} = 9.0 Hz, *J*_{4,5} = 10.0 Hz, H4^I), 4.26 (d, *J*_{1,2} = 8.0 Hz, H1^I), 4.59 (d, *J*_{1,2} = 8.0 Hz, H1^{II}), 4.96 (dd, *J*_{1,2} = 8.0 Hz, *J*_{2,3} = 9.0 Hz, H2^{II}); ¹³C NMR (CDCl₃, 75 MHz) δ 20.9 (Ac), 56.9 (Me), 68.2 (C6^I), 68.7 (C6^{II}), 73.8 (C2^{II}), 74.9 (C5^I), 75.2 (C5^{II}), 76.9 (C4^I), 78.1 (C4^{II}), 81.9 (C2^I), 82.7 (C3^I), 83.1 (C3^{II}), 100.3 (C1^{II}), 104.6 (C1^I), 169.3 (Ac); HRMS (FAB) Found: *m/z* 961.4146. Calcd for C₅₇H₆₂NaO₁₂ [M + Na]⁺: 961.4139.

Methyl *O*-(3,4,6-Tri-*O*-benzyl-β-D-glucopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (16). A mixture of **15** (174 mg, 0.19 mmol), MeOH (13 mL), and methanolic NaOMe (7%, 0.3 mL) was kept stirring at room temperature overnight. After the neutralization with AcOH, evaporation, and chromatography with the TK system (100:1 → 10:1) afforded **16** (161 mg, 97%); [α]_D²⁴ +20° (c 1.2, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 1.60 (s, OH), 3.21 (ddd, *J*_{4,5} = 10.0 Hz, *J*_{5,6a} = 3.5 Hz, *J*_{5,6b} = 2.0 Hz, H5^{II}), 3.42 (dd, *J*_{1,2} = 8.0 Hz, *J*_{2,3} = 9.0 Hz, H2^I), 3.43 (dd, *J*_{5,6a} = 2.0 Hz, *J*_{6a,6b} = 11.0 Hz, H6a^{II}), 3.48 (dd, *J*_{1,2} = 8.0 Hz, *J*_{2,3} = 9.0 Hz, H2^{II}), 3.48 (t, *J*_{2,3} = *J*_{3,4} = 9.0 Hz, H3^{II}), 3.49 (dd, *J*_{5,6a} = 3.5 Hz, *J*_{6a,6b} = 11.0 Hz, H6b^{II}), 3.49 (ddd, *J*_{4,5} = 9.0 Hz, *J*_{5,6a} = 2.0 Hz, *J*_{5,6b} = 3.5 Hz, H5^I), 3.54 (~t, *J*_{3,4} = 9.0 Hz, *J*_{4,5} = 10.0 Hz, H4^{II}), 3.55 (dd, *J*_{5,6b} = 2.0 Hz, *J*_{6b,6b} = 10.0 Hz, H6b^{II}), 3.57 (s, Me), 3.68 (t, *J*_{2,3} = *J*_{3,4} = 9.0 Hz, H3^I), 3.80 (dd, *J*_{5,6a} = 2.0 Hz, *J*_{6a,6b} = 11.0 Hz, H6a^I), 3.98 (dd, *J*_{5,6b} = 3.5 Hz, *J*_{5a,6b} = 11.0 Hz, H6b^I), 4.03 (t, *J*_{3,4} = *J*_{4,5} = 9.0 Hz, H4^I), 4.31 (d, *J*_{1,2} = 8.0 Hz, H1^I), 4.61 (d, *J*_{1,2} = 8.0 Hz, H1^{II}); ¹³C NMR (CDCl₃, 75 MHz) δ 57.8 (Me), 68.6 (C6^{II}), 68.9 (C6^I), 74.4 (C2^{II}), 75.2 (C5^{II}), 75.8 (C5^I), 77.0 (C4^I), 77.4 (C4^{II}), 82.3 (C2^I), 83.5 (C3^I), 84.5 (C3^{II}), 103.3 (C1^{II}), 104.8 (C1^I). Found: C, 73.55; H, 6.87%. Calcd for C₅₅H₆₀O₁₁: C, 73.64; H, 6.74%.

Methyl *O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (17). Triflylation of **16** (23 mg, 0.026 mmol) with Tf₂O (82 μL, 0.50 mmol) and pyridine (55 μL, 0.68 mmol) in CH₂Cl₂ (0.46 mL) in a manner similar to the transformation of **11** into **12** gave a syrup (24 mg). To this, *n*-Bu₄NOAc (62 mg, 0.21 mmol) and anhydrous PhMe (0.17 mL) were added; the resulting mixture was stirred at 50 °C for 16 h, followed by chromatography using the TK system (100:1 → 10:1), to give **17** (17 mg, 71%); [α]_D²⁵ -5° (c 0.6, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 2.10 (s, Ac), 3.23 (ddd, *J*_{4,5} = 9.5 Hz, *J*_{5,6a} = 2.0 Hz, *J*_{5,6b} = 4.0 Hz, H5^{II}), 3.39 (dd, *J*_{2,3} = 3.0 Hz, *J*_{3,4} = 9.0 Hz, H3^{II}), 3.39 (dd, *J*_{1,2} = 8.0 Hz, *J*_{2,3} = 9.0 Hz, H2^I), 3.45 (ddd, *J*_{4,5} = 10.0 Hz, *J*_{5,6a} = 3.0 Hz, *J*_{5,6b} = 6.0 Hz, H5^I), 3.56 (s, Me), 3.62 (t, *J*_{2,3} = *J*_{3,4} = 9.0 Hz, H3^I), 3.75 (dd, *J*_{3,4} = 9.0 Hz, *J*_{4,5} = 9.5 Hz, H4^{II}), 3.99 (dd, *J*_{3,4} = 9.0 Hz, *J*_{4,5} = 10.0 Hz, H4^I), 4.29 (d, *J*_{1,2} = 8.0 Hz, H1^I), 4.69 (s, H1^{II}), 5.45 (d, *J*_{1,2} = 0 Hz, *J*_{2,3} = 3.0 Hz, H2^{II}); ¹³C NMR (CDCl₃, 75 MHz) δ 21.1 (Ac), 57.1 (Me), 68.5 (C2^{II}), 68.8 (C6^I), 68.9 (C6^{II}), 74.1 (2C, C5^I and C4^{II}), 75.6 (C5^{II}), 77.3 (C4^I), 80.5 (C3^{II}), 82.0 (C2^I), 83.1 (C3^I), 99.2 (C1^{II}), *J*_{C1,H1} = 158.7 Hz, 104.7 (C1^I), *J*_{C1,H1} = 154.5 Hz, 170.6 (Ac). Found: C, 72.59; H, 6.62%. Calcd for C₅₇H₆₂O₁₂: C, 72.90; H, 6.65%.

Before elution of **17**, there appeared a single isomer of methyl 4-*O*-[(1*R*/*S*)-[1-acetoxy-2,5-anhydro-3,4,6-tri-*O*-benzyl-D-manni-

tyl]]-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**18**) (3.3 mg, 14%); [α]_D²⁴ +22° (c 0.4, CHCl₃); ¹H NMR (CDCl₃, 400 MHz) δ 1.65 (s, Ac), 3.33 (ddd, *J*_{4,5} = 10.0 Hz, *J*_{5,6a} = 5.0 Hz, *J*_{5,6b} = 2.0 Hz, H5^I), 3.37 (dd, *J*_{1,2} = 8.0 Hz, *J*_{2,3} = 9.0 Hz, H2^I), 3.47 (t, *J*_{2,3} = *J*_{3,4} = 9.0 Hz, H3^I), 3.53 (s, Me), 3.56 (dd, *J*_{4,5a} = 5.0 Hz, *J*_{5a,5b} = 10.5 Hz, H5a^{II}), 3.59 (dd, *J*_{4,5b} = 9.0 Hz, *J*_{5a,5b} = 10.5 Hz, H5b^{II}), 3.73 (dd, *J*_{5,6a} = 5.0 Hz, *J*_{6a,6b} = 11.0 Hz, H6a^I), 3.78 (dd, *J*_{5,6b} = 2.0 Hz, *J*_{6a,6b} = 11.0 Hz, H6b^I), 3.89 (dd, *J*_{3,4} = 9.0 Hz, *J*_{4,5} = 10.0 Hz, H4^I), 4.05 (dd, *J*_{1,2} = 4.5 Hz, *J*_{2,3} = 3.5 Hz, H2^{II}), 4.08 (dd, *J*_{3,4} = 3.5 Hz, *J*_{4,5} = 5.5 Hz, H4^{II}), 4.20 (~t, *J*_{4,5} = 5.5 Hz, *J*_{5,6a} = *J*_{5,6b} = 5.0 Hz, H5^{II}), 4.22 (d, *J*_{1,2} = 8.0 Hz, H1^I), 4.32 (t, *J*_{2,3} = *J*_{3,4} = 3.5 Hz, H3^{II}), 6.16 (d, *J*_{1,2} = 4.5 Hz, H1^{II}); 3.53 (s, Me); ¹³C NMR (CDCl₃, 100 MHz) δ 20.9 (Ac), 56.9 (Me), 68.5 (C6^I), 69.9 (C6^{II}), 74.9 (C5^I), 77.6 (C4^I), 81.9 (C5^{II}), 82.0 (C2^I), 82.6 (C3^I), 83.2 (C2^{II}), 84.3 (C3^{II}), 84.8 (C4^{II}), 95.3 (C1^{II}), 104.5 (C1^I), 170.5 (Ac). HRMS (FAB) Found: *m/z* 961.4186. Calcd for C₅₇H₆₂NaO₁₂ [M + Na]⁺: 961.4139.

Methyl *O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-mannopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (19). Triflylation of **16** (20 mg, 0.022 mmol) with Tf₂O (77 μL, 0.47 mmol) and pyridine (49 μL, 0.60 mmol) in CH₂Cl₂ (0.41 mL) as described for **12** gave a syrup (21.7 mg). To this, *n*-Bu₄NN₃ (63 mg, 0.22 mmol) and anhydrous PhMe (0.15 mL) were added; the resulting mixture was stirred at 50 °C for 16 h, followed by chromatography using the TK system (100:1 → 10:1) as described for **12**, to give **19** (15 mg, 73%); [α]_D²⁴ -1° (c 0.3, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 3.18 (ddd, *J*_{4,5} = 10.0 Hz, *J*_{5,6a} = 4.0 Hz, *J*_{5,6b} = 2.5 Hz, H5^{II}), 3.41 (dd, *J*_{1,2} = 7.5 Hz, *J*_{2,3} = 9.0 Hz, H2^I), 3.42 (dd, *J*_{2,3} = 3.0 Hz, *J*_{3,4} = 9.0 Hz, H3^{II}), 3.50 (ddd, *J*_{4,5} = 9.0 Hz, *J*_{5,6a} = 2.5 Hz, *J*_{5,6b} = 4.0 Hz, H5^I), 3.52 (dd, *J*_{5,6a} = 4.0 Hz, *J*_{6a,6b} = 11.0 Hz, H6a^{II}), 3.57 (s, OMe), 3.61 (dd, *J*_{5,6b} = 2.0 Hz, *J*_{6a,6b} = 11.0 Hz, H6b^{II}), 3.70 (t, *J*_{2,3} = *J*_{3,4} = 9.0 Hz, H3^I), 3.76 (dd, *J*_{3,4} = 9.0 Hz, *J*_{4,5} = 10.0 Hz, H4^{II}), 3.76 (dd, *J*_{5,6a} = 2.5 Hz, *J*_{6a,6b} = 11.0 Hz, H6a^I), 3.85 (dd, *J*_{5,6b} = 4.0 Hz, *J*_{6a,6b} = 11.0 Hz, H6b^I), 3.87 (dd, *J*_{1,2} = 1.0 Hz, *J*_{2,3} = 3.0 Hz, H2^{II}), 3.95 (t, *J*_{3,4} = *J*_{4,5} = 9.0 Hz, H4^I), 4.31 (d, *J*_{1,2} = 7.5 Hz, H1^I), 4.66 (d, *J*_{1,2} = 1.0 Hz, H1^{II}); ¹³C NMR (CDCl₃, 75 MHz) δ 57.1 (Me), 61.8 (C2^{II}), 68.78 (C6^I), 68.83 (C6^{II}), 74.1 (2C, C4^I and C5^I), 75.8 (C5^{II}), 76.8 (C4^I), 81.2 (C3^{II}), 82.0 (C2^I), 83.0 (C3^I), 99.7 (C1^{II}), *J*_{C1,H1} = 158.0 Hz, 104.7 (C1^{II}), *J*_{C1,H1} = 158.9 Hz. HRMS (FAB) Found: *m/z* 944.4098. Calcd for C₅₅H₅₉N₃NaO₁₀ [M + Na]⁺: 944.4098.

Before the elution of **19**, there appeared a single isomer of methyl 4-*O*-[(1*R*/*S*)-[2,5-anhydro-1-azido-3,4,6-tri-*O*-benzyl-D-mannityl]]-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**20**) (4.6 mg, 22%); [α]_D²⁵ +19° (c 0.3, CHCl₃); ¹H NMR (CDCl₃, 400 MHz) δ 3.24 (ddd, *J*_{4,5} = 9.5 Hz, *J*_{5,6a} = 2.0 Hz, *J*_{5,6b} = 3.5 Hz, H5^I), 3.43 (dd, *J*_{1,2} = 8.0 Hz, *J*_{2,3} = 9.0 Hz, H2^I), 3.54 (s, Me), 3.54 (t, *J*_{2,3} = *J*_{3,4} = 9.0 Hz, H3^I), 3.59 (dd, *J*_{5,6a} = 5.5 Hz, *J*_{6a,6b} = 11.5 Hz, H6a^{II}), 3.60 (dd, *J*_{5,6b} = 5.5 Hz, *J*_{6a,6b} = 11.5 Hz, H6b^{II}), 3.64 (dd, *J*_{5,6a} = 2.0 Hz, *J*_{6a,6b} = 11.0 Hz, H6a^I), 3.71 (dd, *J*_{5,6b} = 3.5 Hz, *J*_{6a,6b} = 11.0 Hz, H6b^I), 3.79 (dd, *J*_{3,4} = 9.0 Hz, *J*_{4,5} = 9.5 Hz, H4^I), 4.07 (dd, *J*_{1,2} = 5.5 Hz, *J*_{2,3} = 3.0 Hz, H2^{II}), 4.09 (dd, *J*_{3,4} = 3.0 Hz, *J*_{4,5} = 4.5 Hz, H4^{II}), 4.15 (t, *J*_{2,3} = *J*_{3,4} = 3.0 Hz, H3^{II}), 4.22 (dt, *J*_{4,5} = 4.5 Hz, *J*_{5,6a} = *J*_{5,6b} = 5.5 Hz, H5^{II}), 4.24 (d, *J*_{1,2} = 8.0 Hz, H1^I), 4.93 (d, *J*_{1,2} = 5.5 Hz, H1^{II}); ¹³C NMR (CDCl₃, 100 MHz) δ 56.9 (Me), 68.1 (C6^I), 69.9 (C6^{II}), 74.7 (C5^I), 76.0 (C4^I), 82.1 (C2^I), 82.4 (2C, C3^I and C5^{II}), 84.3 (C3^{II}), 84.6 (C4^{II}), 84.8 (C2^{II}), 91.0 (C1^{II}), 104.6 (C1^I); HRMS (FAB) Found: *m/z* 944.4096. Calcd for C₅₅H₅₉N₃NaO₁₀ [M + Na]⁺: 944.4098.

Allyl *O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyrano-

synl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-mannopyranoside (21).

Condensation of **1** (231.7 mg, 0.47 mmol) and **5** (177.5 mg, 0.36 mmol) in the presence of NsCl (200.6 mg, 0.91 mmol), AgOTf (232.7 mg, 0.91 mmol), and DBU (134.9 μ L, 0.91 mmol) in CH_2Cl_2 (1.8 mL), followed by chromatography with the TK system (100:1 $\rightarrow$ 20:1), yielded **21** (279.7 mg, 80%); $[\alpha]_{\text{D}}^{22} +16^\circ$ (*c* 0.7, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 1.85 (s, Ac), 3.26 (ddd, $J_{4,5} = 10.0$ Hz, $J_{5,6a} = 4.0$ Hz, $J_{5,6b} = 2.5$ Hz, $\text{H}5^{\text{II}}$), 3.50 (t, $J_{2,3} = J_{3,4} = 9.5$ Hz, $\text{H}3^{\text{II}}$), 3.54 (dd, $J_{5,6a} = 4.0$ Hz, $J_{6a,6b} = 11.5$ Hz, $\text{H}6a^{\text{II}}$), 3.57 (dd, $J_{5,6b} = 2.5$ Hz, $J_{6a,6b} = 11.5$ Hz, $\text{H}6b^{\text{II}}$), 3.66 (dd, $J_{5,6a} = 1.5$ Hz, $J_{6a,6b} = 10.0$ Hz, $\text{H}6a^{\text{I}}$), 3.68 ($\sim$ t, $J_{3,4} = 9.5$ Hz, $J_{4,5} = 10.0$ Hz, $\text{H}4^{\text{II}}$), 3.69 (ddd, $J_{4,5} = 9.0$ Hz, $J_{5,6a} = 1.5$ Hz, $J_{5,6b} = 4.5$ Hz, $\text{H}5^{\text{I}}$), 3.73 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, $\text{H}2^{\text{I}}$), 3.80 (dd, $J_{5,6b} = 4.5$ Hz, $J_{6a,6b} = 10.0$ Hz, $\text{H}6b^{\text{I}}$), 3.90 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.0$ Hz, $\text{H}3^{\text{I}}$), 4.22 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, $\text{H}4^{\text{I}}$), 4.53 (d, $J_{1,2} = 8.0$ Hz, $\text{H}1^{\text{II}}$), 4.86 (d, $J_{1,2} = 2.0$ Hz, $\text{H}1^{\text{I}}$), 4.94 (dd, $J_{1,2} = 8.0$ Hz, $J_{2,3} = 9.5$ Hz, $\text{H}2^{\text{II}}$), 5.87 (m, All); ^{13}C NMR (CDCl_3 , 75 MHz) δ 20.9 (Ac), 67.9 (All), 68.4 ($\text{C}6^{\text{II}}$), 68.7 ($\text{C}6^{\text{I}}$), 71.6 ($\text{C}5^{\text{I}}$), 73.8 ($\text{C}2^{\text{II}}$), 75.1 ($\text{C}2$, $\text{C}4^{\text{I}}$ and $\text{C}5^{\text{II}}$), 75.4 ($\text{C}2^{\text{I}}$), 78.0 ($\text{C}4^{\text{II}}$), 78.5 ($\text{C}3^{\text{I}}$), 97.3 ($\text{C}1^{\text{I}}$, $J_{\text{C}1,\text{H}1} = 167.0$ Hz), 100.7 ($\text{C}1^{\text{II}}$, $J_{\text{C}1,\text{H}1} = 158.2$ Hz), 117.3, 133.8 (All), 169.5 (Ac). HRMS (FAB) Found: m/z 987.4336. Calcd for $\text{C}_{59}\text{H}_{64}\text{NaO}_{12}$ [$\text{M} + \text{Na}$] $^+$: 987.4295.

Allyl *O*-(3,4,6-Tri-*O*-benzyl- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-mannopyranoside (22). A mixture of **21** (177.1 mg, 0.18 mmol), MeOH (10 mL), 1,4-dioxane (1 mL), and methanolic NaOMe (7%, 0.4 mL) was stirred at room temperature overnight. Neutralization with AcOH, evaporation, chromatography with the TK system (100:1 $\rightarrow$ 20:1), and crystallization from *n*-hexane gave **22** (149.0 mg, 88%); mp 87–88 $^\circ\text{C}$, $[\alpha]_{\text{D}}^{25} +34^\circ$ (*c* 0.7, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 3.27 (m, $\text{H}5^{\text{II}}$), 3.41 (dd, $J_{5,6a} = 2.0$ Hz, $J_{6a,6b} = 10.5$ Hz, $\text{H}6a^{\text{I}}$), 3.75 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, $\text{H}2^{\text{I}}$), 3.78 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, $\text{H}4^{\text{II}}$), 3.84 (ddd, $J_{4,5} = 9.0$ Hz, $J_{5,6a} = 2.0$ Hz, $J_{5,6b} = 4.0$ Hz, $\text{H}5^{\text{I}}$), 3.97 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.0$ Hz, $\text{H}3^{\text{I}}$), 4.36 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, $\text{H}4^{\text{I}}$), 4.61 (d, $J_{1,2} = 7.5$ Hz, $\text{H}1^{\text{II}}$), 4.87 (d, $J_{1,2} = 2.0$ Hz, $\text{H}1^{\text{I}}$), 5.85 (m, All); ^{13}C NMR (CDCl_3 , 75 MHz) δ 67.8 (All), 68.7 ($\text{C}6^{\text{I}}$), 69.7 ($\text{C}6^{\text{II}}$), 71.0 ($\text{C}5^{\text{I}}$), 74.7 ($\text{C}4^{\text{I}}$), 74.9 ($\text{C}2^{\text{I}}$), 75.1 ($\text{C}5^{\text{II}}$), 75.5 ($\text{C}2^{\text{II}}$), 77.2 ($\text{C}4^{\text{II}}$), 79.3 ($\text{C}3^{\text{I}}$), 84.4 ($\text{C}3^{\text{II}}$), 97.3 ($\text{C}1^{\text{I}}$, $J_{\text{C}1,\text{H}1} = 169.0$ Hz), 103.4 ($\text{C}1^{\text{II}}$, $J_{\text{C}1,\text{H}1} = 158.0$ Hz), 117.2, 133.7 (All). Found: C, 73.89; H, 6.65%. Calcd for $\text{C}_{57}\text{H}_{62}\text{O}_{11}$: C, 74.16; H, 6.77%.

Allyl *O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-mannopyranoside (23).

Triflylation of **22** (77.9 mg, 0.084 mmol) with $\text{ Tf}_2\text{O}$ (277 μ L, 1.7 mmol) and pyridine (181 μ L, 2.2 mmol) in CH_2Cl_2 (1.6 mL), quenching with H_2O (46 μ L, 2.6 mmol) and subsequent chromatography with the TK system (100:1 $\rightarrow$ 10:1) were carried out as described for **12** to give a syrup (79.2 mg). This was reacted with *n*-Bu₄NOAc (272 mg, 0.90 mmol) in anhydrous PhMe (0.72 mL) with stirring at 50 $^\circ\text{C}$ overnight, followed by chromatography with the TK system (100:1 $\rightarrow$ 10:1), to give **23** (59.0 mg, 72%); $[\alpha]_{\text{D}}^{24} +10^\circ$ (*c* 0.8, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 2.11 (s, Ac), 3.25 (ddd, $J_{4,5} = 9.5$ Hz, $J_{5,6a} = 1.5$ Hz, $J_{5,6b} = 5.0$ Hz, $\text{H}6^{\text{II}}$), 3.44 (dd, $J_{2,3} = 3.5$ Hz, $J_{3,4} = 9.5$ Hz, $\text{H}3^{\text{II}}$), 3.48 (dd, $J_{5,6a} = 1.5$ Hz, $J_{6a,6b} = 11.0$ Hz, $\text{H}6a^{\text{II}}$), 3.57 (dd, $J_{5,6b} = 5.0$ Hz, $J_{6a,6b} = 11.0$ Hz, $\text{H}6b^{\text{II}}$), 3.69 (dd, $J_{5,6a} = 3.5$ Hz, $J_{6a,6b} = 10.0$ Hz, $\text{H}6a^{\text{I}}$), 3.71 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, $\text{H}4^{\text{II}}$), 3.71 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, $\text{H}2^{\text{I}}$), 3.79 (ddd, $J_{4,5} = 9.0$ Hz, $J_{5,6a} = 3.5$ Hz, $J_{5,6b} = 2.0$ Hz, $\text{H}5^{\text{I}}$), 3.93 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.0$ Hz, $\text{H}3^{\text{I}}$), 4.29 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, $\text{H}4^{\text{I}}$), 4.69 (d, $J_{1,2} = 1.0$ Hz, $\text{H}1^{\text{II}}$), 4.87 (d, $J_{1,2} = 2.0$ Hz,

$\text{H}1^{\text{I}}$), 5.45 (dd, $J_{1,2} = 1.0$ Hz, $J_{2,3} = 3.5$ Hz, $\text{H}2^{\text{II}}$), 5.85 (m, All); ^{13}C NMR (CDCl_3 , 75 MHz) δ 21.1 (Ac), 67.9 (All), 68.6 ($\text{C}2^{\text{II}}$), 69.0 ($\text{C}6^{\text{II}}$), 69.3 ($\text{C}6^{\text{I}}$), 71.0 ($\text{C}5^{\text{I}}$), 74.2 ($\text{C}2^{\text{I}}$), 75.4 ($\text{C}4^{\text{II}}$), 75.5 ($\text{C}4^{\text{I}}$), 75.7 ($\text{C}5^{\text{II}}$), 79.1 ($\text{C}3^{\text{I}}$), 80.5 ($\text{C}3^{\text{II}}$), 97.3 ($\text{C}1^{\text{I}}$, $J_{\text{C}1,\text{H}1} = 171.6$ Hz), 99.6 ($\text{C}1^{\text{II}}$, $J_{\text{C}1,\text{H}1} = 152.0$ Hz), 117.2, 133.8 (All), 170.5 (Ac). HRMS (FAB) Found: m/z 987.4274. Calcd for $\text{C}_{59}\text{H}_{64}\text{NaO}_{12}$ [$\text{M} + \text{Na}$] $^+$: 987.4295.

Before the elution of **23**, there appeared the furanoid compound, allyl 4-*O*-[(1*R*/*S*)-[1-acetoxy-2,5-anhydro-3,4,6-tri-*O*-benzyl-D-mannityl]]-2,3,6-tri-*O*-benzyl- α -D-mannopyranoside (9.8 mg, 12%); $[\alpha]_{\text{D}}^{22} +20^\circ$ (*c* 0.4, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 3.56 (dd, $J_{5,6a} = 5.5$ Hz, $J_{6a,6b} = 10.0$ Hz, $\text{H}6a^{\text{II}}$), 3.60 (dd, $J_{5,6b} = 5.5$ Hz, $J_{6a,6b} = 10.0$ Hz, $\text{H}6b^{\text{II}}$), 3.79 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, $\text{H}2^{\text{I}}$), 4.08 (dd, $J_{1,2} = 4.5$ Hz, $J_{2,3} = 3.5$ Hz, $\text{H}2^{\text{II}}$), 4.30 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, $\text{H}4^{\text{I}}$), 4.35 (t, $J_{2,3} = J_{3,4} = 3.5$ Hz, $\text{H}3^{\text{II}}$), 4.87 (d, $J_{1,2} = 2.0$ Hz, $\text{H}1^{\text{I}}$), 6.19 (d, $J_{1,2} = 4.5$ Hz, $\text{H}1^{\text{II}}$); 1.78 (s, Ac), 5.88 (m, All); ^{13}C NMR (CDCl_3 , 75 MHz) δ 69.1 ($\text{C}6^{\text{I}}$), 69.8 ($\text{C}6^{\text{II}}$), 72.2 ($\text{C}5^{\text{I}}$), 75.7 ($\text{C}2^{\text{I}}$), 75.8 ($\text{C}4^{\text{I}}$), 78.2 ($\text{C}3^{\text{I}}$), 81.7 ($\text{C}5^{\text{II}}$), 83.1 ($\text{C}2^{\text{II}}$), 84.3 ($\text{C}3^{\text{II}}$), 84.7 ($\text{C}4^{\text{II}}$), 95.5 ($\text{C}1^{\text{II}}$), 97.4 ($\text{C}1^{\text{I}}$); 21.1, 170.3 (Ac); 67.9, 117.2, 133.8 (All). HRMS (FAB) Found: m/z 987.4337. Calcd for $\text{C}_{59}\text{H}_{64}\text{NaO}_{12}$ [$\text{M} + \text{Na}$] $^+$: 987.4295.

***O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl-D-mannopyranose (4).**

A mixture of **23** (64.7 mg, 0.067 mmol), PdCl_2 (34.5 mg, 0.19 mmol), NaOAc (62.2 mg, 0.76 mmol), and aq AcOH (95%, 2.7 mL) was stirred at room temperature for 16 h. Evaporation and chromatography with the TK system (100:1 $\rightarrow$ 10:1) gave **5** (35.9 mg, 58%); $[\alpha]_{\text{D}}^{24} -6^\circ$ (*c* 0.4, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) (75% α) δ 2.10 (s, $\text{Ac}\alpha$), 2.11 (s, $\text{Ac}\beta$), 2.70 (d, $J_{1,\text{OH}} = 3.5$ Hz, $\text{OH}\alpha$), 3.26 (ddd, $J_{4,5} = 9.5$ Hz, $J_{5,6a} = 2.0$ Hz, $J_{5,6b} = 4.5$ Hz, $\text{H}5^{\text{II}}\alpha$), 3.30 (m, $\text{H}5^{\text{II}}\beta$), 3.44 (dd, $J_{5,6b} = 4.5$ Hz, $J_{5,6b} = 4.5$ Hz, $\text{H}5^{\text{II}}\alpha$), 3.46 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.0$ Hz, $\text{H}3^{\text{II}}\beta$), 3.50 (dd, $J_{5,6a} = 2.0$ Hz, $J_{6a,6b} = 11.0$ Hz, $\text{H}6b^{\text{II}}\alpha$), 3.58 (dd, $J_{5,6b} = 4.5$ Hz, $J_{6a,6b} = 11.0$ Hz, $\text{H}6b^{\text{II}}\beta$), 3.63 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.0$ Hz, $\text{H}3^{\text{I}}\beta$), 3.68 (dd, $J_{5,6a} = 2.0$ Hz, $J_{6a,6b} = 10.0$ Hz, $\text{H}6a^{\text{I}}\alpha$), 3.70 ($\sim$ t, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, $\text{H}2^{\text{I}}\alpha$), 3.72 ($\sim$ t, $J_{3,4} = 9.0$ Hz, $J_{4,5} = 9.5$ Hz, $\text{H}4^{\text{II}}\alpha$), 3.76 (dd, $J_{5,6b} = 5.0$ Hz, $J_{6a,6b} = 10.0$ Hz, $\text{H}6b^{\text{I}}\alpha$), 3.97 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.0$ Hz, $\text{H}3^{\text{I}}\alpha$), 4.03 (ddd, $J_{4,5} = 9.0$ Hz, $J_{5,6a} = 2.0$ Hz, $J_{5,6b} = 5.0$ Hz, $\text{H}5^{\text{I}}\alpha$), 4.20 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, $\text{H}4^{\text{I}}\alpha$), 4.65 (s, $J_{1,2} = J_{1,\text{OH}} = 0$ Hz, $\text{H}1^{\text{I}}\beta$), 4.68 (s, $J_{1,2} = 0$ Hz, $\text{H}1^{\text{II}}\beta$), 4.72 (s, $J_{1,2} = 0$ Hz, $\text{H}1^{\text{II}}\alpha$), 5.22 (dd, $J_{1,2} = 2.0$ Hz, $J_{1,\text{OH}} = 3.5$ Hz, $\text{H}1^{\text{I}}\alpha$), 5.45 (d, $J_{1,2} = 0$ Hz, $J_{2,3} = 3.0$ Hz, $\text{H}2^{\text{II}}\beta$), 5.46 (d, $J_{1,2} = 0$ Hz, $J_{2,3} = 3.0$ Hz, $\text{H}2^{\text{II}}\text{Ipha}$); ^{13}C NMR (CDCl_3 , 75 MHz) δ 21.1 (Ac), 68.4 ($\text{C}2^{\text{II}}\alpha$), 68.5 ($\text{C}2^{\text{II}}\beta$), 69.0 ($\text{C}6^{\text{II}}\alpha$), 69.1 ($\text{C}6^{\text{II}}\beta$), 69.6 ($\text{C}6^{\text{I}}\alpha$ and $\text{C}6^{\text{I}}\beta$), 70.9 ($\text{C}5^{\text{II}}\alpha$), 74.1 ($\text{C}4^{\text{II}}\alpha$), 74.2 ($\text{C}4^{\text{II}}\beta$), 74.5 ($\text{C}2^{\text{I}}\beta$), 74.8 ($\text{C}4^{\text{I}}\beta$), 75.4 ($\text{C}2^{\text{I}}\alpha$ and $\text{C}4^{\text{I}}\alpha$), 75.6 ($\text{C}5^{\text{II}}\alpha$), 75.7 ($\text{C}5^{\text{II}}\beta$), 76.6 ($\text{C}5^{\text{I}}\beta$), 78.3 ($\text{C}3^{\text{I}}\alpha$), 80.4 ($\text{C}3^{\text{II}}\alpha$ and $\text{C}3^{\text{II}}\beta$), 81.5 ($\text{C}3^{\text{I}}\beta$), 92.9 ($\text{C}1^{\text{I}}\alpha$, $J_{\text{C}1,\text{H}1} = 170.0$ Hz), 93.5 ($\text{C}1^{\text{I}}\beta$, $J_{\text{C}1,\text{H}1} = 159.1$ Hz), 99.1 ($\text{C}1^{\text{II}}\beta$, $J_{\text{C}1,\text{H}1} = 158.0$ Hz), 99.4 ($\text{C}1^{\text{II}}\alpha$, $J_{\text{C}1,\text{H}1} = 156.0$ Hz), 170.5 (Ac). HRMS (FAB) Found: m/z 947.4012. Calcd for $\text{C}_{56}\text{H}_{60}\text{NaO}_{12}$ [$\text{M} + \text{Na}$] $^+$: 947.3982.

Benzyl *O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-mannopyranosyl-(1 $\rightarrow$ 3)-2,4-di-*O*-benzyl- α -D-rhamnopyranoside (24).

Condensation of **4** (25.5 mg, 0.028 mmol) and **6** (13.1 mg, 0.030 mmol) in the presence of NsCl (17.1 mg, 0.077 mmol), AgOTf (19.9 mg, 0.077 mmol), and DBU (11.5 μ L, 0.077 mmol) in CH_2Cl_2 (0.25 mL), followed by quenching as above and chromatography with the TK system (100:1 $\rightarrow$ 10:1), afforded **24** (13.1 mg, 35%) and

the β -linked isomer (5.2 mg, 14%).

24: $[\alpha]_{\text{D}}^{22} -13^\circ$ (*c* 0.7, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 1.28 (q, $J_{5,6} = 6.0$ Hz, H6^{I}), 2.00 (s, Ac), 3.27 (ddd, $J_{4,5} = 10.0$ Hz, $J_{5,6a} = 2.0$ Hz, $J_{5,6b} = 4.5$ Hz, H5^{III}), 3.40 (dd, $J_{2,3} = 3.5$ Hz, $J_{3,4} = 9.5$ Hz, H3^{III}), 3.50 ($\sim$ t, $J_{3,4} = 9.0$ Hz, $J_{4,5} = 9.5$ Hz, H4^{I}), 3.53 (dd, $J_{5,6a} = 2.0$ Hz, $J_{6a,6b} = 11.5$ Hz, H6a^{III}), 3.54 (dd, $J_{5,6a} = 2.0$ Hz, $J_{6a,6b} = 11.0$ Hz, H6a^{II}), 3.60 (dd, $J_{5,6b} = 3.0$ Hz, $J_{6a,6b} = 11.0$ Hz, H6b^{II}), 3.61 (dd, $J_{5,6b} = 4.5$ Hz, $J_{6a,6b} = 11.5$ Hz, H6b^{III}), 3.69 ($\sim$ t, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, H2^{II}), 3.72 ($\sim$ t, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, H2^{I}), 3.72 (ddd, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6.0$ Hz, H5^{I}), 3.75 ($\sim$ t, $J_{3,4} = 9.5$ Hz, $J_{4,5} = 10.0$ Hz, H4^{III}), 3.91 ($\sim$ dt, $J_{4,5} = 9.5$ Hz, $J_{5,6a} = 2.0$ Hz, $J_{5,6b} = 3.0$ Hz, H5^{II}), 3.98 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.0$ Hz, H3^{II}), 4.12 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.0$ Hz, H3^{I}), 4.40 ($\sim$ t, $J_{3,4} = 9.0$ Hz, $J_{4,5} = 9.5$ Hz, H4^{II}), 4.65 (s, H1^{III}), 4.82 (d, $J_{1,2} = 2.0$ Hz, H1^{I}), 4.98 (d, $J_{1,2} = 2.0$ Hz, H1^{II}), 5.42 (d, $J_{1,2} = 0$ Hz, $J_{2,3} = 3.5$ Hz, H2^{III}); ^{13}C NMR (CDCl_3 , 75 MHz) δ 18.0 (C6^{I}), 21.1 (Ac), 68.1 (C5^{I}), 68.5 (C2^{III}), 68.8 (C6^{III}), 68.9 (C6^{II}), 71.1 (C5^{II}), 74.2 (C4^{III}), 74.5 (C2^{I}), 74.6 (C3^{I}), 75.0 (C4^{II}), 75.8 (C5^{III}), 78.8 (C3^{II}), 79.7 (C4^{I}), 80.6 (C3^{III}), 94.9 (C1^{II} , $J_{\text{C1,H1}} = 168.7$ Hz), 96.8 (C1^{I} , $J_{\text{C1,H1}} = 167.4$ Hz), 99.5 (C1^{III} , $J_{\text{C1,H1}} = 158.2$ Hz), 170.4 (Ac). HRMS (FAB) Found: m/z 1363.5999. Calcd for $\text{C}_{83}\text{H}_{88}\text{NaO}_{16}$ [$\text{M} + \text{Na}$] $^+$: 1363.5970.

The β -linked isomer: $[\alpha]_{\text{D}}^{22} -58^\circ$ (*c* 0.5, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz): δ 1.33 (q, $J_{5,6} = 6.0$ Hz, H6^{I}), 2.13 (s, Ac), 3.23 (ddd, $J_{4,5} = 9.5$ Hz, $J_{5,6a} = 2.0$ Hz, $J_{5,6b} = 4.5$ Hz, H5^{III}), 3.37 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.5$ Hz, H3^{III}), 3.42 (dd, $J_{5,6a} = 2.0$ Hz, $J_{6a,6b} = 11.0$ Hz, H6a^{III}), 3.43 (ddd, $J_{4,5} = 9.5$ Hz, $J_{5,6a} = 6.0$ Hz, $J_{5,6b} = 5.0$ Hz, H5^{II}), 3.46 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, H4^{I}), 3.48 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.5$ Hz, H3^{II}), 3.55 (dd, $J_{5,6b} = 4.5$ Hz, $J_{6a,6b} = 11.0$ Hz, H6b^{III}), 3.60 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4^{II}), 3.73 (dd, $J_{5,6a} = 6.0$ Hz, $J_{6a,6b} = 11.0$ Hz, H6a^{II}), 3.74 (m, H5^{I}), 3.75 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4^{III}), 3.79 (dd, $J_{5,6b} = 5.0$ Hz, $J_{6a,6b} = 11.0$ Hz, H6b^{II}), 3.99 (t, $J_{1,2} = J_{2,3} = 3.0$ Hz, H2^{II}), 4.10 ($\sim$ t, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, H2^{I}), 4.56 (d, $J_{1,2} = 3.0$ Hz, H1^{II}), 4.74 (d, $J_{1,2} = 2.0$ Hz, H1^{I}), 4.77 (s, $J_{1,2} = 0$ Hz, H1^{III}), 5.50 (d, $J_{1,2} = 0$ Hz, $J_{2,3} = 3.0$ Hz, H2^{III}); ^{13}C NMR (CDCl_3 , 75 MHz) δ 18.0 (C6^{I}), 21.2 (Ac), 68.1 (C5^{I}), 68.5 (C2^{III}), 68.8 (C6^{III}), 69.5 (C6^{II}), 74.0 (C4^{III}), 74.9 (C4^{I}), 75.0 (C4^{II}), 75.2 (C5^{II}), 75.6 (C5^{III}), 78.3 (C2^{II}), 80.5 (C3^{III}), 81.1 (C3^{I}), 81.4 (C3^{II}), 81.6 (C2^{I}), 98.3 (C1^{I} , $J_{\text{C1,H1}} = 169.5$ Hz), 99.7 (C1^{III} , $J_{\text{C1,H1}} = 157.8$ Hz), 103.6 (C1^{II} , $J_{\text{C1,H1}} = 155.8$ Hz), 170.5 (Ac). HRMS (FAB) Found: m/z 1363.6017. Calcd for $\text{C}_{83}\text{H}_{88}\text{NaO}_{16}$ [$\text{M} + \text{Na}$] $^+$: 1363.5970.

Benzyl O-(3,4,6-Tri-O-benzyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-O-benzyl- α -D-mannopyranosyl-(1 $\rightarrow$ 3)-2,4-di-O-benzyl- α -D-rhamnopyranoside (25). A mixture of **24** (25.2 mg, 0.019 mmol), MeOH (4.0 mL), 1,4-dioxane (0.40 mL), and dil NaOMe (7%, 0.3 mL) was stirred at room temperature overnight. After neutralization with AcOH, evaporation and chromatography with the TK system (100:1 $\rightarrow$ 20:1) produced **25** (22.4 mg, 92%); $[\alpha]_{\text{D}}^{23} +13^\circ$ (*c* 0.8, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 1.33 (d, $J_{5,6} = 6.0$ Hz, H6^{I}), 2.32 (s, OH), 3.25 (dt, $J_{4,5} = 9.5$ Hz, $J_{5,6a} = J_{5,6b} = 3.0$ Hz, H5^{III}), 3.32 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.5$ Hz, H3^{III}), 3.50 (dd, $J_{3,4} = 3.0$ Hz, $J_{4,5} = 9.5$ Hz, H4^{I}), 3.53 (d, $J_{5,6a} = J_{5,6b} = 3.0$ Hz, H6^{II}), 3.65 (d, $J_{5,6a} = J_{5,6b} = 3.0$ Hz, H6^{III}), 3.72 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, H2^{I}), 3.74 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, H2^{II}), 3.75 (dq, $J_{3,4} = 9.5$ Hz, $J_{4,5} = 6.0$ Hz, H5^{I}), 3.83 (d, $J_{1,2} = 0$ Hz, $J_{2,3} = 3.0$ Hz, H2^{III}), 3.89 (dt, $J_{4,5} = 9.5$ Hz, $J_{5,6a} = J_{5,6b} = 3.0$ Hz, H5^{II}), 3.90 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4^{III}), 3.96 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.5$ Hz, H3^{II}), 4.12 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.5$ Hz, H3^{I}), 4.36 (t, $J_{3,4} = 9.0$ Hz,

$J_{4,5} = 9.5$ Hz, H4^{II}), 4.53 (s, $J_{1,2} = 0$ Hz, H1^{III}), 4.84 (d, $J_{1,2} = 2.0$ Hz, H1^{I}), 4.97 (d, $J_{1,2} = 2.0$ Hz, H1^{II}); ^{13}C NMR (CDCl_3 , 75 MHz) δ 18.0 (C6^{I}), 67.8 (C2^{III}), 68.2 (C5^{I}), 68.9 (C6^{III}), 69.0 (C6^{II}), 70.1 (C5^{II}), 73.6 (C4^{II}), 74.1 (2C, C3^{I} and C4^{III}), 74.3 (C2^{II}), 75.1 (C2^{I}), 75.7 (C5^{III}), 78.5 (C3^{II}), 79.6 (C4^{I}), 81.5 (C3^{III}), 94.4 (C1^{I} , $J_{\text{C1,H1}} = 166.7$ Hz), 96.7 (C1^{II} , $J_{\text{C1,H1}} = 167.0$ Hz), 100.1 (C1^{III} , $J_{\text{C1,H1}} = 157.8$ Hz). HRMS (FAB) Found: m/z 1321.5830. Calcd for $\text{C}_{81}\text{H}_{86}\text{NaO}_{15}$ [$\text{M} + \text{Na}$] $^+$: 1321.5868.

O- β -D-Mannopyranosyl-(1 $\rightarrow$ 4)-O- α -D-mannopyranosyl-(1 $\rightarrow$ 3)- α -L-rhamnopyranose (2). Hydrogenation of **25** (21.8 mg, 0.017 mmol) over Pd on C (10%, 34 mg) in AcOH (6 mL) at room temperature, filtration of the catalyst, concentration, and chromatography with the EM system (100:1 $\rightarrow$ 1:1) afforded **2** (6.3 mg, 77%); $[\alpha]_{\text{D}}^{26} +42^\circ$ (*c* 0.3, H_2O); ^1H NMR (D_2O , 400 MHz) (60% α) δ 1.24 (d, $J_{5,6} = 6.5$ Hz, $\text{H1}^{\text{II}}\alpha$), 1.26 (d, $J_{5,6} = 6.0$ Hz, $\text{H1}^{\text{II}}\beta$), 3.40 (ddd, $J_{4,5} = 9.5$ Hz, $J_{5,6a} = 6.5$ Hz, $J_{5,6b} = 2.0$ Hz, H5^{III}), 3.40 (dd, $J_{4,5} = 8.5$ Hz, $J_{5,6} = 6.0$ Hz, $\text{H5}^{\text{I}}\beta$), 3.40 (dd, $J_{3,4} = 9.5$ Hz, $J_{4,5} = 8.5$ Hz, $\text{H4}^{\text{I}}\beta$), 3.45 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, $\text{H4}^{\text{I}}\alpha$), 3.52 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4^{III}), 3.62 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.5$ Hz, H3^{III}), 3.67 (dd, $J_{2,3} = 3.5$ Hz, $J_{3,4} = 9.5$ Hz, $\text{H3}^{\text{I}}\beta$), 3.69 (dd, $J_{5,6a} = 6.5$ Hz, $J_{6a,6b} = 12.0$ Hz, H6a^{III}), 3.73 (dd, $J_{5,6a} = 3.0$ Hz, $J_{6a,6b} = 12.0$ Hz, $\text{H6a}^{\text{II}}\beta$), 3.74 (dd, $J_{5,6a} = 4.0$ Hz, $J_{6a,6b} = 12.0$ Hz, $\text{H6a}^{\text{II}}\alpha$), 3.80 (dd, $J_{5,6b} = 2.0$ Hz, $J_{6a,6b} = 12.0$ Hz, $\text{H6b}^{\text{II}}\beta$), 3.81 (dd, $J_{5,6b} = 2.0$ Hz, $J_{6a,6b} = 12.0$ Hz, $\text{H6b}^{\text{I}}\alpha$), 3.84 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.5$ Hz, $\text{H3}^{\text{I}}\alpha$), 3.84 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6.5$ Hz, $\text{H5}^{\text{I}}\alpha$), 3.88 (dd, $J_{2,3} = 3.5$ Hz, $J_{3,4} = 9.0$ Hz, $\text{H3}^{\text{II}}\beta$), 3.91 (dd, $J_{5,6b} = 2.0$ Hz, $J_{6a,6b} = 12.0$ Hz, H6b^{III}), 3.91 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, $\text{H4}^{\text{II}}\beta$), 3.92 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, $\text{H4}^{\text{II}}\alpha$), 3.94 (m, $\text{H5}^{\text{II}}\alpha$), 3.95 (m, $\text{H5}^{\text{II}}\beta$), 4.00 (dd, $J_{2,3} = 3.5$ Hz, $J_{3,4} = 9.5$ Hz, $\text{H3}^{\text{II}}\alpha$), 4.02 (d, $J_{1,2} = 0$ Hz, $J_{2,3} = 3.0$ Hz, H2^{III}), 4.02 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 3.5$ Hz, $\text{H2}^{\text{II}}\alpha$), 4.03 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 3.5$ Hz, $\text{H2}^{\text{II}}\beta$), 4.10 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, $\text{H2}^{\text{I}}\alpha$), 4.12 (d, $J_{1,2} = 0$ Hz, $J_{2,3} = 3.5$ Hz, $\text{H2}^{\text{I}}\beta$), 4.71 (s, H1^{III}), 4.81 (s, $\text{H1}^{\text{I}}\beta$), 4.99 (d, $J_{1,2} = 1.5$ Hz, $\text{H1}^{\text{II}}\alpha$), 5.01 (d, $J_{1,2} = 1.5$ Hz, $\text{H1}^{\text{II}}\beta$), 5.10 (d, $J_{1,2} = 2.0$ Hz, $\text{H1}^{\text{I}}\alpha$); ^{13}C NMR (CDCl_3 , 100 MHz) δ 18.7 ($\text{C6}^{\text{I}}\beta$), 18.8 ($\text{C6}^{\text{I}}\alpha$), 62.1 (C6^{II}), 62.9 (C6^{III}), 68.6 ($\text{C2}^{\text{I}}\alpha$ and C4^{III}), 69.1 ($\text{C2}^{\text{I}}\beta$), 70.1 ($\text{C5}^{\text{I}}\alpha$), 71.0 (C3^{III}), 71.6 ($\text{C2}^{\text{II}}\beta$), 71.7 ($\text{C2}^{\text{II}}\alpha$), 72.0 ($\text{C4}^{\text{I}}\beta$), 72.3 ($\text{C4}^{\text{I}}\alpha$), 72.4 (C2^{III}), 73.0 (C5^{II}), 73.8 ($\text{C5}^{\text{I}}\beta$), 74.7 (C3^{III}), 75.4 (C3^{II}), 76.1 ($\text{C3}^{\text{I}}\alpha$), 78.3 (C5^{III}), 78.4 ($\text{C3}^{\text{I}}\beta$ and C4^{II}), 95.3 ($\text{C1}^{\text{I}}\beta$, $J_{\text{C1,H1}} = 160.0$ Hz), 95.7 ($\text{C1}^{\text{I}}\alpha$, $J_{\text{C1,H1}} = 170.0$ Hz), 97.9 ($\text{C1}^{\text{II}}\beta$, $J_{\text{C1,H1}} = 170.0$ Hz), 98.0 ($\text{C1}^{\text{II}}\alpha$, $J_{\text{C1,H1}} = 169.5$ Hz), 102.0 (C1^{III} , $J_{\text{C1,H1}} = 159.0$ Hz). HRMS (FAB) Found: m/z 511.1662. Calcd for $\text{C}_{18}\text{H}_{32}\text{NaO}_{15}$ [$\text{M} + \text{Na}$] $^+$: 511.1639.

Allyl α -D-Galactopyranoside (26). A mixture of D-galactose (5 g, 0.028 mmol), allyl alcohol (80 mL, 1.2 mmol), and MeSO_3H (0.20 mL, 3.1 mmol) was stirred at 100 $^\circ\text{C}$ for 2 h under reflux. After the addition of NaHCO_3 (0.30 g, 3.6 mmol), the mixture was evaporated. Chromatography with the EM system (100:1 $\rightarrow$ 2:1), followed by crystallization with a seed and diisopropyl ether containing MeOH (5%), gave **26** (2.1 g, 34%); mp 140–142 $^\circ\text{C}$, $[\alpha]_{\text{D}}^{25} +173^\circ$ (*c* 0.8, H_2O) (Ref. 15a, mp 138–142 $^\circ\text{C}$, $[\alpha]_{\text{D}}^{20} +171.7^\circ$ (H_2O); Ref. 15b, mp 145–146 $^\circ\text{C}$, $[\alpha]_{\text{D}}^{25} +185.0^\circ$ (*c* 5.8, H_2O); Ref. 15c, mp 143–145 $^\circ\text{C}$, $[\alpha]_{\text{D}}^{20} +181.3^\circ$ (*c* 1.57, H_2O), Ref. 15e, mp 143–143.5 $^\circ\text{C}$, $[\alpha]_{\text{D}}^{20} +181.4^\circ$ (*c* 5.8, H_2O)). HRMS (FAB) Found: m/z 243.0853. Calcd for $\text{C}_9\text{H}_{16}\text{NaO}_6$ [$\text{M} + \text{Na}$] $^+$: 243.0845.

Benzyl α -D-Galactopyranoside (27). A mixture of D-galactose (1.0 g, 5.6 mmol), BnOH (2.0 mL, 19 mmol), and MeSO_3H (0.20 mL, 3.1 mmol), instead of *p*-toluenesulfonic acid monohydrate,¹⁹ was strongly stirred at 90 $^\circ\text{C}$ for 25 min. After the addi-

tion of Et₃N (1.6 mL, 11 mmol), the mixture was diluted with CHCl₃ (5 mL) and chromatographed with the CM system (100:1 $\rightarrow$ 2:1) to give **27** (0.99 g, 66%); [α]_D²⁵ +158° (*c* 0.7, MeOH); ¹H NMR (D₂O, 300 MHz) δ 3.64 (dd, *J*_{5,6a} = 5.0 Hz, *J*_{6a,6b} = 11.5 Hz, H6a), 3.68 (dd, *J*_{5,6b} = 5.0 Hz, *J*_{6a,6b} = 11.5 Hz, H6b), 3.75 (dd, *J*_{1,2} = 3.0 Hz, *J*_{2,3} = 10.0 Hz, H2), 3.82 (dd, *J*_{2,3} = 10.0 Hz, *J*_{3,4} = 3.0 Hz, H3), 3.90 (dt, *J*_{4,5} = 1.0 Hz, *J*_{5,6a} = *J*_{5,6b} = 5.0 Hz, H5), 3.93 (dd, *J*_{3,4} = 3.0 Hz, *J*_{4,5} = 1.0 Hz, H4), 4.57 (d, *J* = 12.0 Hz, Bn), 4.72 (d, *J* = 12.0 Hz, Bn), 5.01 (d, *J*_{1,2} = 3.0 Hz, H1); ¹³C NMR (D₂O, 75 MHz) δ 63.8 (C6), 70.9 (C2), 71.9 (C4), 72.1 (C3), 72.3 (Bn), 73.7 (C5), 100.5 (C1), 130.9, 131.1 (2C), 131.4 (2C), 139.7 (Bn). HRMS (FAB) Found: *m/z* 293.1001. Calcd for C₁₃H₁₈NaO₆ [M + Na]⁺: 293.1001.

Allyl 2,3,6-Tri-*O*-benzyl- α -D-galactopyranoside (8). A mixture of **26** (0.950 g, 4.3 mmol), BnCl (19 mL, 0.17 mol), and LiOH (0.829 g, 35 mmol) was stirred strongly at 140 °C for 4 h. The mixture was evaporated at 90 °C and chromatographed with the TK system (100:1 $\rightarrow$ 20:1) to give **8** (0.83 g, 39%); [α]_D²¹ +54° (*c* 0.8, CHCl₃) (Ref. 14a, [α]_D²⁵ +52.8° (*c* 1, CHCl₃), Ref. 14b, [α]_D²⁵ +42° (*c* 2.4, CHCl₃)); ¹H NMR (CDCl₃, 300 MHz) δ 2.00 (s, OH), 3.67 (dd, *J*_{5,6a} = 6.0 Hz, *J*_{6a,6b} = 10.0 Hz, H6a), 3.74 (dd, *J*_{5,6b} = 6.0 Hz, *J*_{6a,6b} = 10.0 Hz, H6b), 3.88 (dd, *J*_{1,2} = 3.0 Hz, *J*_{2,3} = 10.0 Hz, H2), 3.91 (dd, *J*_{2,3} = 10.0 Hz, *J*_{3,4} = 3.0 Hz, H3), 3.95 (~dt, *J*_{4,5} ~ 1.0 Hz, *J*_{5,6a} = *J*_{5,6b} = 6.0 Hz, H5), 4.09 (~d, *J*_{3,4} = 3.0 Hz, *J*_{4,5} ~ 1.0 Hz, H4), 4.88 (d, *J*_{1,2} = 3.0 Hz, H1); 5.95 (m, All); ¹³C NMR (CDCl₃, 75 MHz) δ 68.1 (C4), 68.3 (All), 68.5 (C5), 69.5 (C6), 75.7 (C2), 77.6 (C3), 96.1 (C1), 118.0, 133.8 (All). HRMS (FAB) Found: *m/z* 513.2275. Calcd for C₃₀H₃₄NaO₆ [M + Na]⁺: 513.2253.

NMR data of the acetate: ¹H NMR (CDCl₃, 300 MHz) δ 2.06 (s, Ac), 3.47 (dd, *J*_{5,6a} = 6.0 Hz, *J*_{6a,6b} = 10.0 Hz, H6a), 3.52 (dd, *J*_{5,6b} = 6.0 Hz, *J*_{6a,6b} = 10.0 Hz, H6b), 3.79 (dd, *J*_{1,2} = 4.0 Hz, *J*_{2,3} = 10.0 Hz, H2), 3.99 (dd, *J*_{3,4} = 10.0 Hz, *J*_{3,4} = 3.5 Hz, H3), 4.13 (dt, *J*_{4,5} = 1.0 Hz, *J*_{5,6a} = *J*_{5,6b} = 6.0 Hz, H5), 4.90 (d, *J*_{1,2} = 4.0 Hz, H1), 5.63 (dd, *J*_{3,4} = 3.5 Hz, *J*_{4,5} = 1.0 Hz, H4), 5.94 (m, All); ¹³C NMR (CDCl₃, 75 MHz) δ 20.9 (Ac), 67.8 (C5), 68.3 (C4), 68.5 (2C, C6 and All), 75.5 (C2), 76.3 (C3), 96.4 (C1), 118.1, 133.7 (All), 170.3 (Ac).

Benzyl 2,3,6-Tri-*O*-benzyl- α -D-galactopyranoside (9). A mixture of **27** (0.756 g, 2.8 mol), BnCl (15 mL, 0.13 mol), and LiOH (0.538 g, 22 mmol) was stirred strongly at 140 °C for 4 h. Evaporation at 90 °C and chromatography with the TK system (100:1 $\rightarrow$ 20:1) gave **9** (0.612 g, 40%); [α]_D²² +72° (*c* 1.0, CHCl₃); (Ref. 18, [α]_D +69.0° (*c* 0.6, CHCl₃)); ¹H NMR (CDCl₃, 300 MHz) δ 2.60 (s, OH), 3.64 (dd, *J*_{5,6a} = 6.0 Hz, *J*_{6a,6b} = 10.0 Hz, H6a), 3.73 (dd, *J*_{5,6b} = 6.0 Hz, *J*_{6a,6b} = 10.0 Hz, H6b), 3.87 (dd, *J*_{1,2} = 3.5 Hz, *J*_{2,3} = 10.0 Hz, H2), 3.94 (dd, *J*_{2,3} = 10.0 Hz, *J*_{3,4} = 3.0 Hz, H3), 3.99 (~t, *J*_{4,5} = 1.5 Hz, *J*_{5,6a} = *J*_{5,6b} = 6.0 Hz, H5), 4.10 (dd, *J*_{3,4} = 3.0 Hz, *J*_{4,5} = 1.5 Hz, *J*_{4,OH} = 0 Hz, H4), 4.90 (d, *J*_{1,2} = 3.5 Hz, H1); ¹³C NMR (CDCl₃, 75 MHz) δ 68.1 (C4), 68.7 (C5), 69.6 (C6), 75.8 (C2), 77.8 (C3), 96.0 (C1). HRMS (FAB) Found: *m/z* 563.2380. Calcd for C₃₄H₃₆NaO₆ [M + Na]⁺: 563.2410.

NMR data of the acetate: ¹H NMR (CDCl₃, 300 MHz) δ 2.05 (s, Ac), 3.46 (2H, d, *J*_{5,6} = 6.0 Hz, H6), 3.78 (d, *J*_{1,2} = 4.0 Hz, *J*_{2,3} = 10.0 Hz, H2), 4.03 (dd, *J*_{2,3} = 10.0 Hz, *J*_{3,4} = 3.5 Hz, H3), 4.15 (dt, *J*_{4,5} = 1.0 Hz, *J*_{5,6} = 6.0 Hz, H5), 4.91 (d, *J*_{1,2} = 4.0 Hz, H1), 5.64 (dd, *J*_{3,4} = 3.5 Hz, *J*_{4,5} = 1.0 Hz, H4); ¹³C NMR (CDCl₃, 75 MHz) δ 20.9 (Ac), 67.9 (C5), 68.2 (C4), 68.5 (C6), 75.6 (C2), 76.4 (C3), 96.1 (C1), 170.3 (Ac).

Allyl *O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-galactopyranoside (28). Condensation of **1** (207.7 mg, 0.42 mmol) and **8** (159.1 mg, 0.32 mmol) in the presence of NsCl (179.8 mg, 0.81 mmol), AgOTf (208.6 mg, 0.81 mmol), and DBU (120.9 μ L, 0.81 mmol) in CH₂Cl₂ (1.6 mL), followed by quenching and chromatography with the TK system (100:1 $\rightarrow$ 20:1) as described above, yielded **28** (300.9 mg, 96%); [α]_D²³ +40° (*c* 0.8, CHCl₃); ¹H NMR (CDCl₃, 300 MHz): δ 1.75 (s, Ac), 3.39 (ddd, *J*_{4,5} = 9.5 Hz, *J*_{5,6a} = 4.0 Hz, *J*_{5,6b} = 2.0 Hz, H5^{II}), 3.65 (dd, *J*_{5,6a} = 4.0 Hz, *J*_{6a,6b} = 10.5 Hz, H6a^{II}), 3.65 (t, *J*_{2,3} = *J*_{3,4} = 9.0 Hz, H3^{II}), 3.68 (~t, *J*_{3,4} = 9.0 Hz, *J*_{4,5} = 9.5 Hz, H4^{II}), 3.72 (dd, *J*_{5,6b} = 2.0 Hz, *J*_{6a,6b} = 10.5 Hz, H6b^{II}), 3.81 (dd, *J*_{1,2} = 3.0 Hz, *J*_{2,3} = 10.0 Hz, H2^I), 3.82 (dd, *J*_{5,6b} = 6.0 Hz, *J*_{6a,6b} = 10.0 Hz, H6b^I), 3.90 (dd, *J*_{2,3} = 10.0 Hz, *J*_{3,4} = 2.5 Hz, H3^I), 3.96 (~t, *J*_{4,5} = 1.0 Hz, *J*_{5,6a} = *J*_{5,6b} = 6.0 Hz, H5^I), 4.08 (dd, *J*_{3,4} = 2.5 Hz, *J*_{4,5} = 1.0 Hz, H4^I), 4.70 (d, *J*_{1,2} = 7.5 Hz, H1^{II}), 4.86 (d, *J*_{1,2} = 3.0 Hz, H1^I), 5.01 (dd, *J*_{1,2} = 7.5 Hz, *J*_{2,3} = 9.0 Hz, H2^{II}), 5.93 (m, All); ¹³C NMR (CDCl₃, 75 MHz) δ 20.9 (Ac), 68.2 (All), 69.0 (C6^{II}), 69.6 (C5^I), 70.2 (C6^I), 73.2 (C2^{II}), 74.8 (C5^{II}), 75.7 (C4^I), 77.0 (C2^I), 77.8 (C4^{II}), 78.2 (C3^I), 83.1 (C3^{II}), 95.9 (C1^I), 101.0 (C1^{II}), 117.9, 134.0 (All), 169.6 (Ac). Found: C, 73.08; H, 6.75%. Calcd for C₅₉H₆₄O₁₂: C, 73.42; H, 6.68%.

Allyl *O*-(3,4,6-Tri-*O*-benzyl- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-galactopyranoside (29). A mixture of **28** (290 mg, 0.30 mmol), MeOH (10 mL), and methanolic NaOMe (7%, 0.4 mL) was stirred at 35 °C overnight. After neutralization with AcOH, evaporation and chromatography with the TK system (100:1 $\rightarrow$ 10:1) gave **29** (258.3 mg, 93%); [α]_D²⁴ +29° (*c* 0.4, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 3.40 (ddd, *J*_{4,5} = 9.0 Hz, *J*_{5,6a} = 2.5 Hz, *J*_{5,6b} = 4.0 Hz, H5^{II}), 3.50 (t, *J*_{3,4} = *J*_{4,5} = 9.0 Hz, H4^{II}), 3.54 (t, *J*_{2,3} = *J*_{3,4} = 9.0 Hz, H3^{II}), 3.60 (dd, *J*_{1,2} = 7.5 Hz, *J*_{2,3} = 9.0 Hz, *J*_{2,OH} = 0 Hz, H2^{II}), 4.05 (br d, *J*_{3,4} = 3.0 Hz, *J*_{4,5} ~ 1.0 Hz, H4^I), 4.32 (d, *J*_{1,2} = 7.5 Hz, H1^{II}), 4.87 (d, *J*_{1,2} = 3.5 Hz, H1^I), 5.92 (m, All); ¹³C NMR (CDCl₃, 75 MHz) δ 68.7 (C5^I), 68.4 (All), 68.8 (C6^I), 69.4 (C6^{II}), 75.4 (C5^{II}), 76.1 (C2^{II}), 76.8 (C2^I), 77.1 (C4^{II}), 77.8 (C3^I), 79.7 (C4^I), 84.8 (C3^{II}), 96.0 (C1^I), 106.0 (C1^{II}), 118.0, 133.8 (All). Found: C, 72.78; H, 6.72%. Calcd for C₅₇H₆₂O₁₁·H₂O: C, 72.74; H, 6.85%.

Allyl *O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy- β -D-mannopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-galactopyranoside (30). Triflylation of **29** (86.0 mg, 0.093 mmol) with Tf₂O (284.6 μ L, 1.74 mmol) and pyridine (186.8 μ L, 2.3 mmol) in CH₂Cl₂ (1.6 mL), followed by quenching with H₂O (47 μ L, 2.6 mmol), dilution with hexane (5 mL), and chromatography with the TK system (100:1 $\rightarrow$ 10:1), afforded a syrup (88.2 mg). This was dissolved in anhydrous PhMe (2.1 mL). To the obtained solution, CsN₃ (109.8 mg, 0.63 mmol) and 18-crown-6 (165.9 mg, 0.63 mmol) were added; the resulting mixture was ultrasonicated for 11 h at ca. 60 °C. The mixture was diluted with hexane and chromatographed with the TK system (100:1 $\rightarrow$ 10:1) to give **30** (40.0 mg, 45%); [α]_D²³ +15° (*c* 0.8, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 3.27 (ddd, *J*_{4,5} = 9.0 Hz, *J*_{5,6a} = 2.0 Hz, *J*_{5,6b} = 4.5 Hz, H6a^{II}), 3.39 (dd, *J*_{2,3} = 3.0 Hz, *J*_{3,4} = 9.0 Hz, H3^{II}), 3.62 (dd, *J*_{5,6a} = 2.0 Hz, *J*_{6a,6b} = 11.0 Hz, H6a^{II}), 3.69 (t, *J*_{3,4} = *J*_{4,5} = 9.0 Hz, H4^{II}), 3.70 (dd, *J*_{5,6a} = 9.0 Hz, *J*_{6a,6b} = 10.0 Hz, H6a^I), 3.82 (dd, *J*_{5,6b} = 6.0 Hz, *J*_{6a,6b} = 11.0 Hz, H6b^I), 4.00 (~t, *J*_{4,5} = 1.0 Hz, *J*_{5,6a} = *J*_{5,6b} = 6.0 Hz, H5^I), 4.03 (dd, *J*_{1,2} = 1.0 Hz, *J*_{2,3} = 3.0 Hz, H2^{II}), 4.20 (dd, *J*_{3,4} = 3.0 Hz, *J*_{4,5} = 1.0 Hz, H4^I), 4.73 (d, *J*_{1,2} = 1.0 Hz, H1^{II}), 4.85 (d, *J*_{1,2} = 3.0 Hz, H1^I),

5.93 (m, All); ^{13}C NMR (CDCl_3 , 75 MHz) δ 61.7 ($\text{C}2^\text{II}$), 68.3 (All), 69.2 ($\text{C}5^\text{I}$), 69.3 ($\text{C}6^\text{II}$), 69.5 ($\text{C}6^\text{I}$), 74.2 ($\text{C}4^\text{II}$), 75.8 ($\text{C}5^\text{II}$), 76.3 ($\text{C}4^\text{I}$), 76.6 ($\text{C}2^\text{I}$), 78.1 ($\text{C}3^\text{I}$), 81.3 ($\text{C}3^\text{II}$), 96.0 ($\text{C}1^\text{I}$, $J_{\text{C}1,\text{H}1} = 170.0$ Hz), 101.0 ($\text{C}1^\text{II}$, $J_{\text{C}1,\text{H}1} = 158.0$ Hz), 118.0, 134.0 (All). Found: C, 72.10; H, 6.60; N, 4.40%. Calcd for $\text{C}_{57}\text{H}_{61}\text{N}_3\text{O}_{10}$: C, 72.21; H, 6.49; N, 4.43%.

Condensation of **31** (48 mg, 0.10 mmol), of which a new preparation method is described below, and **8** (38 mg, 0.78 mmol) in the presence of NsCl (43 mg, 0.19 mmol), AgOTf (50 mg, 0.19 mmol), and Et_3N (27 μL , 19 mmol) in CH_2Cl_2 (0.38 mL), followed by quenching with NaHCO_3 and PhMe as above and chromatography with the TK system (100:1 $\rightarrow$ 10:1), afforded the α -linked isomer, allyl *O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy- α -D-mannopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-galactopyranoside, (39 mg, 53%) and then **30** (19 mg, 26%) (β : α = 33:67).

The α -linked isomer: $[\alpha]_\text{D}^{23} +53^\circ$ (c 0.6, H_2O); ^1H NMR (CDCl_3 , 300 MHz) δ 3.05 (dd, $J_{5,6a} = 1.5$ Hz, $J_{6a,6b} = 10.5$ Hz, $\text{H}6a^\text{I}$), 3.46 (dd, $J_{5,6b} = 5.5$ Hz, $J_{5,6} = 9.0$ Hz, $\text{H}6b^\text{II}$), 3.81 (dd, $J_{1,2} = 3.5$ Hz, $J_{2,3} = 9.0$ Hz, $\text{H}2^\text{I}$), 3.82 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 3.0$ Hz, $\text{H}2^\text{II}$), 3.92 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 10.0$ Hz, $\text{H}3^\text{II}$), 4.02 ($\sim$ t, $J_{3,4} = 10.0$ Hz, $J_{4,5} = 9.5$ Hz, $\text{H}4^\text{II}$), 4.18 (d, $J_{3,4} = 2.5$ Hz, $J_{4,5} = 0$ Hz, $\text{H}4^\text{I}$), 4.82 (d, $J_{1,2} = 3.5$ Hz, $\text{H}1^\text{I}$), 4.90 (d, $J_{1,2} = 1.5$ Hz, $\text{H}1^\text{II}$); 5.92 (m, All); ^{13}C NMR (CDCl_3 , 75 MHz) δ 61.7 ($\text{C}2^\text{II}$), 67.7 ($\text{C}6^\text{I}$), 67.9 ($\text{C}6^\text{II}$), 68.6 ($\text{C}5^\text{II}$), 71.8 ($\text{C}5^\text{I}$), 74.2 ($\text{C}4^\text{II}$), 74.9 ($\text{C}2^\text{I}$), 75.6 ($\text{C}4^\text{I}$), 77.0 ($\text{C}3^\text{I}$), 79.9 ($\text{C}3^\text{II}$), 99.5 ($\text{C}1^\text{I}$, $J_{\text{C}1,\text{H}1} = 170.0$ Hz), 96.3 ($\text{C}1^\text{II}$, $J_{\text{C}1,\text{H}1} = 169.0$ Hz); 68.4, 118.1, 133.8 (All). HRMS (FAB) Found: m/z 970.4275. Calcd for $\text{C}_{57}\text{H}_{61}\text{N}_3\text{NaO}_{10}$ [$\text{M} + \text{Na}$] $^+$: 970.4255.

Condensation of **31** (40.7 mg, 0.086 mmol) and **8** (32.3 mg, 0.066 mmol) in the presence of NsCl (43.1 mg, 0.19 mmol), AgOTf (50.0 mg, 0.19 mmol), and Et_3N (27.1 μL , 0.19 mmol) in EtCN (0.38 mL) afforded the α -linked anomer (41.4 mg, 66%) and **30** (15.3 mg, 25%) (β : α = 27:73).

Condensation of **31** (44.9 mg, 0.095 mmol) and **8** (35.6 mg, 0.073 mmol) in the presence of NsCl (46.6 mg, 0.21 mmol), AgOTf (54.0 mg, 0.21 mmol), LiNTf_2 (60.3 mg, 0.21 mmol), and Et_3N (29.3 μL , 0.21 mmol) in CH_2Cl_2 (0.41 mL) yielded the α -linked anomer (21.8 mg, 31%) and **30** (14.6 mg, 21%) (β : α = 40:60).

***O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy- β -D-mannopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl-D-galactopyranose (**7**).** A mixture of **30** (44.1 mg, 0.047 mmol), PdCl_2 (22.7 mg, 0.13 mmol), NaOAc (41.1 mg, 0.50 mmol), and aq AcOH (95%, 1.76 mL) was stirred overnight at room temperature. After addition of allyl alcohol (17.3 μL , 0.25 mmol) at 10°C , the mixture was stirred for 30 min, evaporated and chromatographed with the TK system (100:1 $\rightarrow$ 10:1) to give **7** (26.5 mg, 63%), $[\alpha]_\text{D}^{23} +2^\circ$ (c 0.6, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) ($67\%\alpha$) δ 2.86 (dd, $J_{1,\text{OH}} = 2.0$ Hz, $\text{OH}^\text{I}\beta$), 3.18 (d, $J_{1,\text{OH}} = 6.5$ Hz, $\text{OH}^\text{I}\beta$), 3.28 (ddd, $J_{4,5} = 9.5$ Hz, $J_{5,6a} = 3.0$ Hz, $J_{5,6b} = 4.5$ Hz, $\text{H}5^\text{II}\alpha$), 3.29 (br m, $\text{H}5^\text{II}\beta$), 3.41 (dd, $J_{2,3} = 3.5$ Hz, $J_{3,4} = 9.0$ Hz, $\text{H}3^\text{II}\alpha$), 3.44 (dd, $J_{2,3} = 3.5$ Hz, $J_{3,4} = 9.5$ Hz, $\text{H}3^\text{II}\beta$), 3.51 (dd, $J_{2,3} = 9.0$ Hz, $J_{3,4} = 3.0$ Hz, $\text{H}3^\text{I}\beta$), 3.69 ($\sim$ t, $J_{3,4} = 9.0$ Hz, $J_{4,5} = 9.5$ Hz, $\text{H}4^\text{II}\alpha$), 3.79 (dd, $J_{5,6b} = 5.5$ Hz, $J_{6a,6b} = 10.0$ Hz, $\text{H}6b^\text{I}\alpha$), 3.90 (dd, $J_{2,3} = 9.0$ Hz, $J_{3,4} = 2.5$ Hz, $\text{H}3^\text{I}\alpha$), 3.95 (dd, $J_{1,2} = 3.0$ Hz, $J_{2,3} = 9.0$ Hz, $\text{H}2^\text{I}\alpha$), 4.02 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 3.5$ Hz, $\text{H}2^\text{II}\alpha$), 4.04 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 3.5$ Hz, $\text{H}2^\text{II}\beta$), 4.15 (dd, $J_{3,4} = 3.0$ Hz, $J_{4,5} = 1.0$ Hz, $\text{H}4^\text{I}\beta$), 4.19 (dd, $J_{3,4} = 2.5$ Hz, $J_{4,5} = 1.5$ Hz, $\text{H}4^\text{I}\alpha$), 4.20 ($\sim$ t, $J_{4,5} = 1.5$ Hz, $J_{5,6a} = J_{5,6b} = 1.5$ Hz, $\text{H}5^\text{I}\alpha$), 4.66 (dd, $J_{1,2} = 7.5$ Hz, $J_{1,\text{OH}} = 6.5$ Hz, $\text{H}1^\text{I}\beta$), 4.70 (d, $J_{1,2} = 1.5$ Hz, $\text{H}1^\text{II}\beta$), 4.71 (d, $J_{1,2} = 1.5$ Hz, $\text{H}1^\text{II}\alpha$), 5.30 ($\sim$ t, $J_{1,2} = 3.0$ Hz, $J_{1,\text{OH}} = 2.0$ Hz, $\text{H}1^\text{I}\alpha$); ^{13}C NMR (CDCl_3 , 75

MHz) δ 61.6 ($\text{C}2^\text{II}\beta$), 61.7 ($\text{C}2^\text{II}\alpha$), 69.15 ($\text{C}5^\text{I}\alpha$), 69.24 ($\text{C}6^\text{II}$), 69.46 ($\text{C}6^\text{I}\beta$), 69.50 ($\text{C}6^\text{I}\alpha$), 74.1 ($\text{C}4^\text{II}\alpha$), 75.7 ($\text{C}5^\text{II}\alpha$), 75.9 ($\text{C}4^\text{I}\alpha$), 76.6 ($\text{C}2^\text{I}\alpha$), 77.7 ($\text{C}3^\text{I}\alpha$), 81.2 ($\text{C}3^\text{II}\alpha$), 81.4 ($\text{C}3^\text{I}\beta$), 91.6 ($\text{C}1^\text{I}\alpha$, $J_{\text{C}1,\text{H}1} = 168.0$ Hz), 97.8 ($\text{C}1^\text{I}\beta$, $J_{\text{C}1,\text{H}1} = 156.7$ Hz), 100.4 ($\text{C}1^\text{II}\beta$, $J_{\text{C}1,\text{H}1} = 159.0$ Hz), 100.9 ($\text{C}1^\text{II}\alpha$, $J_{\text{C}1,\text{H}1} = 157.5$ Hz). HRMS (FAB) Found: m/z 930.3928. Calcd for $\text{C}_{54}\text{H}_{57}\text{N}_3\text{NaO}_{10}$ [$\text{M} + \text{Na}$] $^+$: 930.3942.

Benzyl *O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy- β -D-mannopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-galactopyranosyl-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-galactopyranoside (32**).** Condensation of **7** (41.1 mg, 0.045 mmol) and **9** (31.9 mg, 0.059 mmol) in the presence of NsCl (30.1 mg, 0.14 mmol), AgOTf (34.9 mg, 0.14 mmol), DMA (12.6 μL , 0.14 mmol), and Et_3N (19.0 μL , 0.14 mmol) in CH_2Cl_2 (0.40 mL), followed by quenching as above and chromatography with the TK system (100:1 $\rightarrow$ 10:1), afforded **32** (36.0 mg, 56%); $[\alpha]_\text{D}^{24} +44^\circ$ (c 0.8, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz) δ 3.23 (ddd, $J_{4,5} = 9.5$ Hz, $J_{5,6a} = 1.5$ Hz, $J_{5,6b} = 4.5$ Hz, $\text{H}5^\text{III}$), 3.32 (dd, $J_{2,3} = 3.5$ Hz, $J_{3,4} = 9.5$ Hz, $\text{H}3^\text{III}$), 3.55 (dd, $J_{5,6a} = 1.5$ Hz, $J_{6a,6b} = 11.0$ Hz, $\text{H}6a^\text{III}$), 3.64 (dd, $J_{5,6b} = 4.5$ Hz, $J_{5,6a} = 11.0$ Hz, $\text{H}6b^\text{III}$), 3.70 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, $\text{H}2^\text{I}$), 3.88 (dd, $J_{1,2} = 3.0$ Hz, $J_{2,3} = 10.0$ Hz, $\text{H}2^\text{I}$), 3.88 (dd, $J_{2,3} = 10.0$ Hz, $J_{3,4} = 2.5$ Hz, $\text{H}3^\text{II}$), 3.92 (dd, $J_{2,3} = 10.0$ Hz, $J_{3,4} = 2.5$ Hz, $\text{H}3^\text{I}$), 3.99 (d, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 3.5$ Hz, $\text{H}2^\text{III}$), 4.00 (dd, $J_{1,2} = 3.5$ Hz, $J_{2,3} = 10.0$ Hz, $\text{H}2^\text{II}$), 4.09 (dd, $J_{3,4} = 2.5$ Hz, $J_{4,5} = 1.0$ Hz, $\text{H}4^\text{I}$), 4.28 (dd, $J_{3,4} = 2.5$ Hz, $J_{4,5} = 1.0$ Hz, $\text{H}4^\text{II}$), 4.62 (d, $J_{1,2} = 1.5$ Hz, $\text{H}1^\text{III}$), 4.91 (d, $J_{1,2} = 3.0$ Hz, $\text{H}1^\text{I}$), 5.04 (d, $J_{1,2} = 3.5$ Hz, $\text{H}1^\text{II}$), ^{13}C NMR (CDCl_3 , 100 MHz) δ 61.9 ($\text{C}2^\text{III}$), 68.0 ($\text{C}6^\text{II}$), 68.2 ($\text{C}6^\text{I}$), 68.9 ($\text{C}5^\text{I}$), 69.0 ($\text{C}6^\text{III}$), 69.7 ($\text{C}5^\text{II}$), 74.0 ($\text{C}4^\text{III}$), 75.3 ($\text{C}2^\text{I}$), 75.8 ($\text{C}5^\text{III}$), 75.7 ($\text{C}2^\text{II}$), 76.0 ($\text{C}4^\text{I}$), 76.8 ($\text{C}4^\text{II}$), 77.7 ($\text{C}3^\text{I}$), 78.4 ($\text{C}3^\text{II}$), 81.2 ($\text{C}3^\text{III}$), 96.2 ($\text{C}1^\text{I}$, $J_{\text{C}1,\text{H}1} = 168.5$ Hz), 99.6 ($\text{C}1^\text{II}$, $J_{\text{C}1,\text{H}1} = 166.5$ Hz), 101.7 ($\text{C}1^\text{III}$, $J_{\text{C}1,\text{H}1} = 155.0$ Hz). HRMS (FAB) Found: m/z 1452.6338. Calcd for $\text{C}_{88}\text{H}_{91}\text{N}_3\text{NaO}_{15}$ [$\text{M} + \text{Na}$] $^+$: 1452.6348.

Benzyl *O*-(2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy- β -D-mannopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-galactopyranosyl-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-galactopyranoside (33**).** A mixture of **32** (29.1 mg, 0.020 mmol), LiAlH_4 (14.0 mg, 0.37 mmol), and anhydrous Et_2O (4.0 mL) was stirred at 40°C under reflux for 0.5 h. After quenching with MeOH (4 mL) and AcOH (0.10 mL, 1.8 mmol), Ac_2O (0.10 mL, 1.1 mmol) was added at 0°C to the mixture. After stirring at room temperature overnight, the mixture was evaporated and chromatographed using the TK system (100:1 $\rightarrow$ 1:1) to give **33** (17.3 mg, 59%); $[\alpha]_\text{D}^{22} +43^\circ$ (c 0.7, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz) δ 1.95 (3H, s, Ac), 3.20 (dd, $J_{5,6a} = 4.5$ Hz, $J_{6a,6b} = 8.5$ Hz, $\text{H}6a^\text{II}$), 3.24 (br d, $\text{H}5^\text{III}$), 3.40 (dd, $J_{5,6a} = 4.5$ Hz, $J_{6a,6b} = 8.5$ Hz, $\text{H}6a^\text{I}$), 3.40 (dd, $J_{2,3} = 4.0$ Hz, $J_{3,4} = 8.0$ Hz, $\text{H}3^\text{III}$), 3.55 (dd, $J_{5,6a} = 1.0$ Hz, $J_{6a,6b} = 10.5$ Hz, $\text{H}6a^\text{III}$), 3.60 (dd, $J_{5,6b} = 8.5$ Hz, $J_{6a,6b} = 8.5$ Hz, $\text{H}6b^\text{II}$), 3.62 ($\sim$ t, $J_{3,4} = 8.0$ Hz, $J_{4,5} = 9.0$ Hz, $\text{H}4^\text{III}$), 3.66 (dd, $J_{5,6b} = 3.0$ Hz, $J_{6a,6b} = 10.5$ Hz, $\text{H}6b^\text{III}$), 3.84 ($\sim$ t, $J_{5,6b} = 8.0$ Hz, $J_{6a,6b} = 8.5$ Hz, $\text{H}6b^\text{I}$), 3.87 (dd, $J_{2,3} = 10.0$ Hz, $J_{3,4} = 3.0$ Hz, $\text{H}3^\text{II}$), 3.88 (br m, $\text{H}5^\text{I}$), 3.88 (br d, $\text{H}2^\text{I}$), 3.92 (dd, $J_{2,3} = 10.0$ Hz, $J_{3,4} = 2.0$ Hz, $\text{H}3^\text{I}$), 3.98 (dd, $J_{1,2} = 3.0$ Hz, $J_{2,3} = 10.0$ Hz, $\text{H}2^\text{II}$), 4.08 (br s, $\text{H}4^\text{I}$), 4.32 (br s, $\text{H}4^\text{II}$), 4.40 (br dd, $\text{H}5^\text{II}$), 4.82 (s, $\text{H}1^\text{III}$), 4.83 (br d, $J_{2,\text{NH}} = 10.0$ Hz, NH), 4.87 (br d, $\text{H}2^\text{III}$), 4.92 (d, $J_{1,2} = 3.0$ Hz, $\text{H}1^\text{I}$), 4.98 (d, $J_{1,2} = 3.0$ Hz, $\text{H}1^\text{II}$); ^{13}C NMR (CDCl_3 , 100 MHz) δ 23.4 (Ac), 50.1 (br, $\text{C}2^\text{III}$), 67.9 ($\text{C}6^\text{II}$), 68.2 ($\text{C}6^\text{I}$), 68.7 ($\text{C}6^\text{III}$), 69.0 ($\text{C}5^\text{II}$), 69.8 ($\text{C}5^\text{I}$), 74.0 ($\text{C}4^\text{III}$), 74.1 ($\text{C}4^\text{II}$), 75.2 ($\text{C}5^\text{III}$), 75.5 ($\text{C}2^\text{I}$), 75.9 ($\text{C}4^\text{I}$), 77.0 ($\text{C}2^\text{II}$), 77.9 ($\text{C}3^\text{I}$), 78.9 ($\text{C}3^\text{II}$), 81.2 ($\text{C}3^\text{III}$), 96.0 ($\text{C}1^\text{I}$, $J_{\text{C}1,\text{H}1} = 168.0$ Hz), 99.9 ($\text{C}1^\text{II}$, $J_{\text{C}1,\text{H}1} = 167.0$ Hz), 100.0 ($\text{C}1^\text{III}$,

$J_{C1,H1} = 158.0$ Hz), 171.1 (br) (Ac); HRMS (FAB) Found: m/z 1468.6554. Calcd for $C_{90}H_{95}NNaO_{16}$ [$M + Na$] $^{+}$: 1468.6549.

O-(2-Acetamido-2-deoxy- β -D-mannopyranosyl)-(1 $\rightarrow$ 4)-O- α -D-galactopyranosyl-(1 $\rightarrow$ 4)-D-galactopyranose (3). Hydrogenation of **33** (27.9 mg, 0.019 mmol) over Pd on C (10%, 36 mg) in AcOH (6 mL) at room temperature overnight, filtration of the catalyst, concentration, and chromatography with the EM system (100:1 $\rightarrow$ 2:1) afforded **3** (8.2 mg, 78%); $[\alpha]_D^{26} +67^\circ$ (c 0.3, H₂O); 1H NMR (D₂O, 400 MHz) ($\sim 40\%$ α) δ 2.03 (3H, s, Ac), 3.36 (ddd, $J_{4,5} = 10.0$ Hz, $J_{5,6a} = 5.5$ Hz, $J_{5,6b} = 2.0$ Hz, H5 III), 3.47 ($\sim t$, $J_{3,4} = 9.5$ Hz, $J_{4,5} = 10.0$ Hz, H4 III), 3.48 (dd, $J_{1,2} = 8.0$ Hz, $J_{2,3} = 10.0$ Hz, H2 $^I\beta$), 3.59 (dd, $J_{5,6a} = 6.0$ Hz, $J_{6a,6b} = 11.5$ Hz, H6a II), 3.60 (dd, $J_{5,6a} = 6.0$ Hz, $J_{6a,6b} = 11.5$ Hz, H6a $^I\beta$), 3.68 (dd, $J_{2,3} = 10.0$ Hz, $J_{3,4} = 3.0$ Hz, H3 $^I\beta$), 3.73 (dd, $J_{1,2} = 3.5$ Hz, $J_{2,3} = 10.0$ Hz, H2 $^{II}\beta$), 3.74 (dd, $J_{1,2} = 3.5$ Hz, $J_{2,3} = 10.0$ Hz, H2 $^{II}\beta$), 3.75 (dd, $J_{5,6b} = 6.5$ Hz, $J_{6a,6b} = 11.5$ Hz, H6b $^I\beta$ and H6b II), 3.77 (dd, $J_{5,6a} = 5.5$ Hz, $J_{6a,6b} = 12.0$ Hz, H6a III), 3.78 (dd, $J_{2,3} = 4.5$ Hz, $J_{3,4} = 9.5$ Hz, H3 III), 3.81 (dd, $J_{1,2} = 3.5$ Hz, $J_{2,3} = 10.5$ Hz, H2 $^I\alpha$), 3.88 (dd, $J_{5,6b} = 2.0$ Hz, $J_{6a,6b} = 12.0$ Hz, H6b III), 3.89 (dd, $J_{2,3} = 10.5$ Hz, $J_{3,4} = 3.0$ Hz, H3 $^I\alpha$), 3.94 (dd, $J_{2,3} = 10.0$ Hz, $J_{3,4} = 3.0$ Hz, H3 $^{II}\alpha$), 3.95 (dd, $J_{3,4} = 3.0$ Hz, $J_{4,5} = 1.5$ Hz, H4 $^I\beta$), 3.96 (dd, $J_{2,3} = 10.0$ Hz, $J_{3,4} = 3.0$ Hz, H3 $^{II}\beta$), 4.01 (dd, $J_{3,4} = 3.0$ Hz, $J_{4,5} = 1.0$ Hz, H4 $^I\alpha$), 4.10 ($\sim t$, $J_{4,5} = 1.0$ Hz, $J_{5,6a} = J_{5,6b} = 6.0$ Hz, H5 $^I\alpha$), 4.18 (dd, $J_{3,4} = 3.0$ Hz, $J_{4,5} = 1.0$ Hz, H4 $^{II}\alpha$), 4.19 (dd, $J_{3,4} = 3.0$ Hz, $J_{4,5} = 1.0$ Hz, H4 $^{II}\beta$), 4.33 ($\sim t$, $J_{4,5} = 1.5$ Hz, $J_{5,6a} = 6.0$ Hz, $J_{5,6b} = 6.5$ Hz, H5 $^I\beta$), 4.35 ($\sim t$, $J_{4,5} = 1.0$ Hz, $J_{5,6a} = J_{5,6b} = 6.0$ Hz, H5 II), 4.58 (dd, $J_{1,2} = 1.0$ Hz, $J_{2,3} = 3.0$ Hz, H2 III), 4.60 (d, $J_{1,2} = 8.0$ Hz, H1 $^I\beta$), 4.86 (d, $J_{1,2} = 3.5$ Hz, H1 $^{II}\beta$), 4.88 (d, $J_{1,2} = 3.0$ Hz, H1 $^{II}\alpha$), 4.89 (d, $J_{1,2} = 1.0$ Hz, H1 III), 5.26 (d, $J_{1,2} = 3.5$ Hz, H1 $^I\alpha$); ^{13}C NMR (D₂O, 100 MHz) δ 24.6 (Ac), 55.9 (C2 III), 62.8 (C6 $^I\beta$ and C6 II), 63.0 (C6 $^I\alpha$), 63.1 (C6 III), 69.6 (C4 III), 71.1 (C2 $^I\alpha$), 71.4 (C3 $^I\alpha$), 71.8 (C3 II), 72.8 (C5 II), 72.9 (C5 $^I\beta$), 73.5 (C5 $^I\alpha$), 74.5 (C2 $^I\beta$ and C3 III), 75.0 (C3 $^I\beta$), 77.7 (C2 II), 78.7 (C5 III), 79.0 (C4 II), 79.9 (C4 $^I\beta$), 81.2 (C4 $^I\alpha$), 95.0 (C1 $^I\alpha$, $J_{C1,H1} = 168.0$ Hz), 99.3 (C1 $^I\beta$, $J_{C1,H1} = 160.0$ Hz), 102.7 (C1 III , $J_{C1,H1} = 158.0$ Hz), 102.8 (C1 $^{II}\beta$, $J_{C1,H1} = 170.0$ Hz), 103.0 (C1 $^{II}\alpha$, $J_{C1,H1} = 168.0$ Hz), 178.3 (Ac). HRMS (FAB) Found: m/z 568.1868. Calcd for $C_{20}H_{35}NNaO_{16}$ [$M + Na$] $^{+}$: 568.1854.

2-Azido-3,4,6-tri-O-benzyl-D-mannopyranose (31). The donor **31** was newly prepared via allyl α -D-glucopyranoside^{23a,e-h} in order to avoid the tedious hydrolytic demethylation using methyl α -D-glucopyranoside.^{4a} A mixture of D-glucose (Wako, 2.0 g, 11.1 mmol), allyl alcohol (20 mL, 0.29 mol), and MeSO₃H (Wako, 0.10 mL, 1.5 mmol) was refluxed at 105 $^\circ$ C for 10 h. After addition of NaHCO₃ (142 mg, 1.7 mmol), the mixture was evaporated, co-evaporated with PhMe, and treated with PhCH(OMe)₂ (Wako, 4.0 mL, 27 mmol) and MeSO₃H (0.05 mL, 0.77 mmol) in DMF (15 mL) at room temperature overnight. After the addition of NaHCO₃ (142 mg, 1.7 mmol), evaporation, and chromatography with the TK system (100:1 $\rightarrow$ 1:1), crystallization from diisopropyl ether containing 2-butanone (5%), gave allyl 4,6-O-benzylidene- α -D-glucopyranoside²³ (0.85 g, 24%), mp 127–128 $^\circ$ C, $[\alpha]_D^{24} +108^\circ$ (c 1.0, CHCl₃) (Ref. 23a, mp 130–131 $^\circ$ C, Ref. 23b, $[\alpha]_D^{25} +112.3^\circ$ (CHCl₃)).

To a stirred solution of this acetal (1.503 g, 4.9 mmol), pyridine (1.8 mL, 22 mmol), and CH₂Cl₂ (40 mL), Tf₂O (1.8 mL, 11 mmol) was added at -25° C (bath temperature). The resulting mixture was stirred for 30 min at this temperature. The mixture was then diluted with PhMe (100 mL) and H₂O (50 mL). The organic layer was washed with H₂O (50 mL $\times$ 3), dried over

Na₂SO₄ for 30 min, filtered, and evaporated, to give a monotriflate as a syrup (1.324 g). This was dissolved in DMF (3.75 mL) and treated with *n*-BuNN₃ (5.0 g, 18 mmol) at room temperature overnight and then at 40 $^\circ$ C for 4 h. Work-up and chromatography with the TK system (100:1 $\rightarrow$ 3:1) yielded allyl 2-azido-4,6-O-benzylidene-2-deoxy- α -D-mannopyranoside (0.620 g, 38%); mp 141–142 $^\circ$ C, $[\alpha]_D^{22} +79^\circ$ (c 1.0, CHCl₃); 1H NMR (CDCl₃, 300 MHz) δ 2.66 (d, $J_{3,OH} = 3.5$ Hz, OH), 3.91 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4), 4.00 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 3.5$ Hz, H2), 4.30 (dt, $J_{2,3} = J_{3,OH} = 3.5$ Hz, $J_{3,4} = 9.5$ Hz, H3), 4.84 (d, $J_{1,2} = 1.5$ Hz, H1), 5.58 (s, benzylidene), 5.90 (m, All); ^{13}C NMR (CDCl₃, 75 MHz) δ 63.5 (C5), 63.7 (C2), 68.4 (All), 68.6 (C6), 68.9 (C3), 80.0 (C4), 98.1 (C1, $J_{C1,H1} = 170.6$ Hz), 102.2 (benzylidene, $J_{C,H} = 162.0$ Hz), 118.1, 133.1 (All). Found: C, 57.87; H, 5.76; N, 12.38%. Calcd for C₁₆H₁₉N₃O₅: C, 57.65; H, 5.75; N, 12.61%. A mixture of this azido acetal (1.6246 g, 4.9 mmol) and aq AcOH (80%, 16 mL) was heated at 95 $^\circ$ C for 15 min with stirring. Evaporation and chromatography with the CM system (100:1 $\rightarrow$ 2:1) afforded allyl 2-azido-2-deoxy- α -D-mannopyranoside (0.9513 g); $[\alpha]_D^{22} +127^\circ$ (c 1.1, MeOH) (Ref. 13, $[\alpha]_D^{20} +108.7^\circ$ (c 0.8, MeOH)). HRMS (FAB) Found: m/z 268.0913. Calcd for C₉H₁₅N₃NaO₅ [$M + Na$] $^{+}$: 268.0909. This (398.6 mg, 1.6 mmol) was reacted with BnBr (1.2 mL, 10 mmol) and NaH (ca. 60% in oil, 393.6 mg, 9.8 mmol) in DMF (4.0 mL) at 0 $^\circ$ C for 15 min then 20 $^\circ$ C for 60 min. After quenching with MeOH (10 mL), evaporation at 90 $^\circ$ C and chromatography with the TK system (100:1 $\rightarrow$ 20:1) yielded a syrup (681.2 mg). This (244.4 mg, 0.47 mmol) was stirred in aq AcOH (95%, 18 mL) containing PdCl₂ (117.4 mg, 0.66 mmol) and NaOAc (216.1 mg, 2.6 mmol) at room temperature overnight.¹³ After quenching with allyl alcohol (0.5 mL, 7.4 mmol) at 10 $^\circ$ C for 20 min, evaporation and chromatography with the TK system (100:1 $\rightarrow$ 20:1) gave **31** (149.0 mg, 43%), which was identified with the sample prepared before.^{7a}

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