

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

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O-β-D-Mannopyranosyl-(1 → 4)-*O*-α-D-mannopyranosyl-(1 → 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 → 4)-*O*-α-D-galactopyranosyl-(1 → 4)-D-galactopyranose, a trisaccharide including a repeating unit of OSP of *Acinetobactor 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 N_3 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 N_3 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 (Et_3N) (the Nst system) as an in-situ-activating

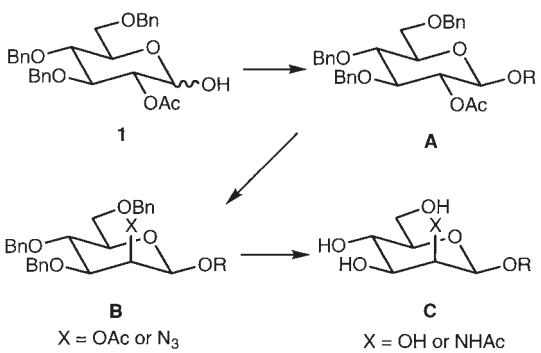

Fig. 1. Synthesis of β-D-mannoside and 2-acetamido-2-deoxy-β-D-mannoside using 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-D-glucopyranose (**1**).

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

$$\mathrm{DOH} + \mathrm{AOH} + \mathit{Reagents} \rightarrow \mathrm{DOA} \quad (1)$$

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→4)-*O*-α-D-mannopyranosyl-(1→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 → 4)-*O*-α-D-galactopyranosyl-(1 → 4)-D-galactopyranose (**3**) (Fig. 3), a trisaccharide including a repeating unit of the OSP of another opportunistic pathogen, *Acinetobactor 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 N_3 group at the $C2^{II}$ position and deallylation.

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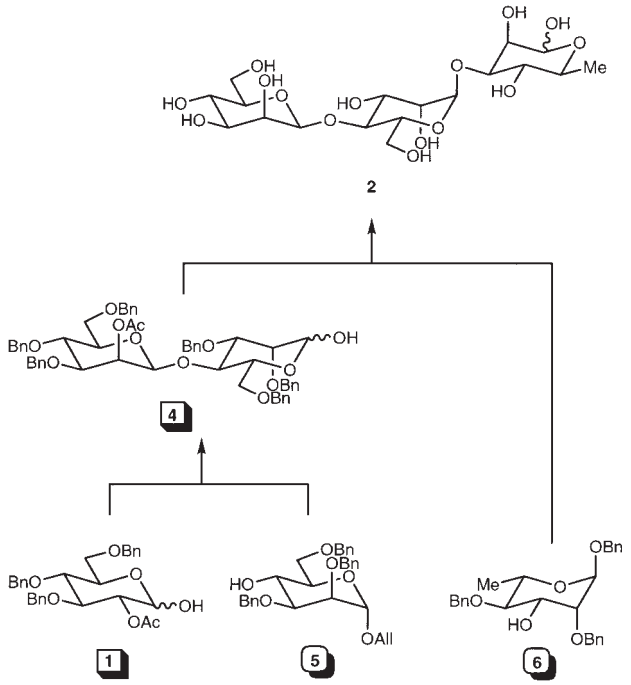

Fig. 2. Synthetic scheme for β-D-Man*p*-(1 → 4)-α-D-Man*p*-(1 → 3)-L-Rha*p*-OH (**2**). A code with square shade is a donor, whereas that with round shade is an acceptor.

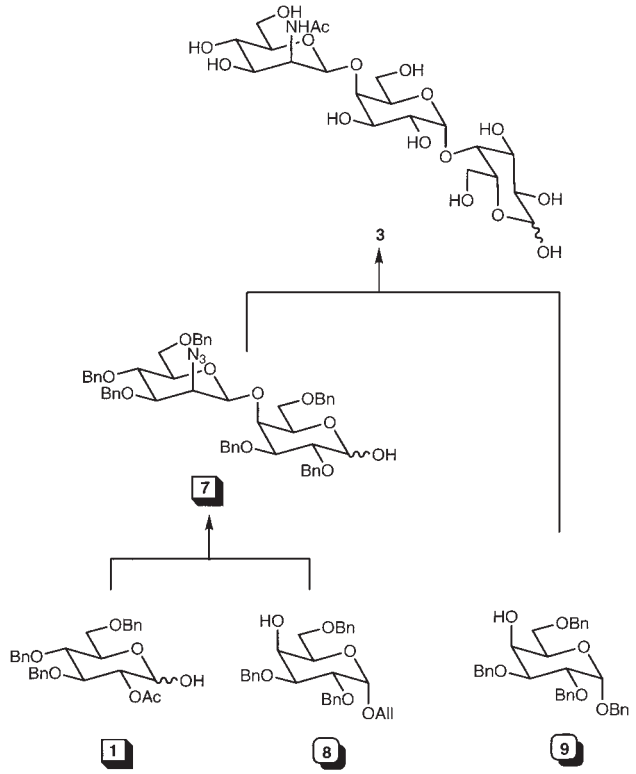

Fig. 3. Synthetic scheme for β-D-Man*N*Ac*p*-(1 → 4)-α-D-Gal*p*-(1 → 4)-D-Gal*p*-OH (**3**). A code with square shade is a donor, whereas that with round shade is an acceptor.

To begin with, the inversive replacements of 2-OH group of **11** as a model compound with OAc group as well as N_3 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 Me_3SiBr, $CoBr_2$, *n*-Bu_4NI,[11a–c] instead of *n*-Bu_4NBr,[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 CD_2Cl_2, 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*-Bu_4NI 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*-Bu_4NOAc in toluene,[2e] to give **12** in 52%. The negative specific rotation (−11° in $CHCl_3$ and −18° in CH_2Cl_2) and the $J_{C1,H1}$ value[12] (155.0 Hz) of **12** indicated its β-mannopyranosyl structure. The reported specific rotation of its α-anomer is +28.2° in CH_2Cl_2.[2p] Similarly, triflation and the reaction with *n*-Bu_4NN_3 in toluene of **11** gave **13** (42%); the negative specific rotation (−54° in $CHCl_3$) 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 Et_3N (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 affored **16**. The triflate of **16** was reacted with *n*-Bu_4NOAc in toluene at 50 °C to give **17** in 71% yield. A ring-contracted furanoide **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 N_3 group of **16** was conducted via triflylation and subsequent treatment with *n*-Bu_4NN_3 in toluene at 50 °C to form **19** in 73% yield. A furanoide **20** was isolated (22%); its GHMBC spectrum showed a coupling between $H5^{II}$ and $C2^{II}$. Although the undesired furanoide 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

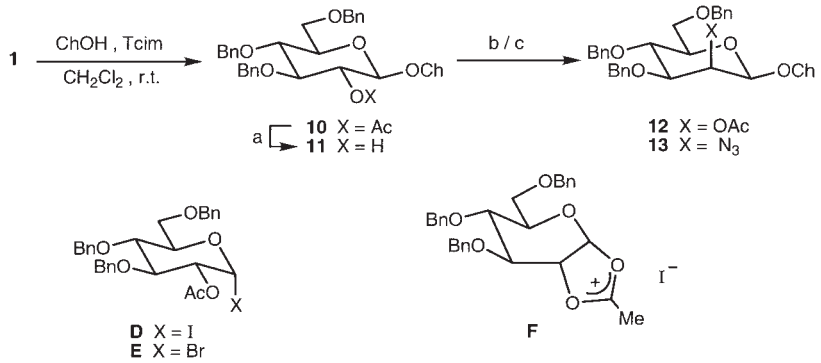

Fig. 4. The inversive displacement of 2-OH group of the glucoside **11** (Tcim = $Me_3SiBr + CoBr_2 + n\text{-}Bu_4NI$ + MS4A, Ch = cyclohexyl): a. NaOMe/MeOH/rt; b. (i) Tf_2O + Py/CH_2Cl_2, −30 °C → 20 °C, (ii) $n\text{-}Bu_4NOAc$/PhMe, 25 °C; c. (i) Tf_2O + Py/CH_2Cl_2, −30 °C → 20 °C, (ii) $n\text{-}Bu_4NN_3$/PhMe, 25 °C.

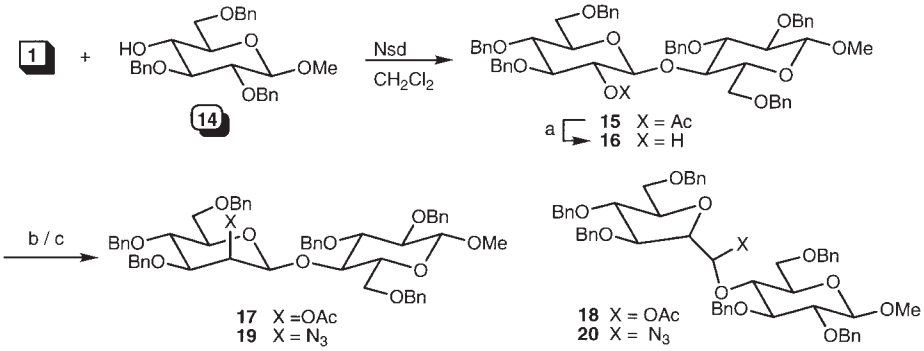

Fig. 5. The inversive displacement of 2^{II}-OH group of the cellobioside **16** (Nsd = NsCl + AgOTf + DBU): a. dil NaOMe/rt; b. (i) Tf_2O + Py/CH_2Cl_2, −30 °C → 20 °C, (ii) $n\text{-}Bu_4NOAc$/PhMe, 50 °C; c. (i) Tf_2O + Py/CH_2Cl_2, −30 °C → 20 °C, (ii) $n\text{-}Bu_4NN_3$/PhMe, 50 °C.

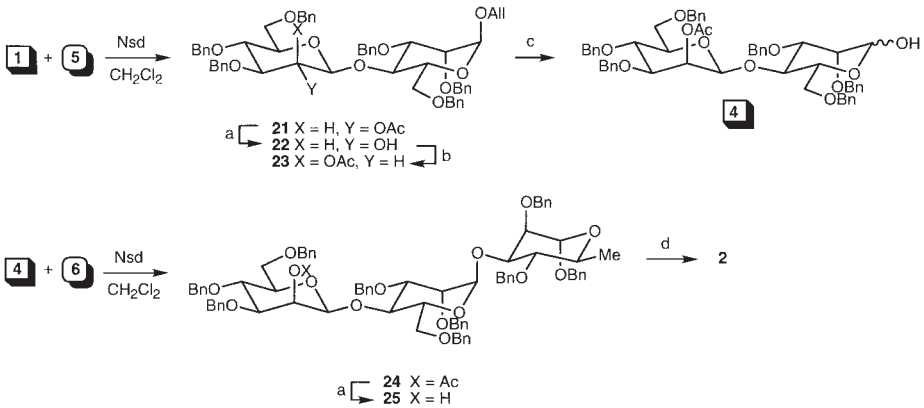

Fig. 6. Synthesis of β-D-Man*p*-(1 → 4)-α-D-Man*p*-(1 → 3)-L-Rha*p*-OH (**2**) (Nsd = NsCl + AgOTf + DBU): a. NaOMe/MeOH/rt; b. (i) Tf_2O + Py/CH_2Cl_2, −30 °C → 20 °C, (ii) $n\text{-}Bu_4NOAc$/PhMe, 50 °C; c. $PdCl_2$ + NaOAc/aq AcOH (95%), rt; d. H_2 + Pd-C (10%)/AcOH, rt.

group with OAc group. Triflation of **22** and the subsequent reaction with $n\text{-}Bu_4NOAc$ in toluene at 50 °C afforded **23** in 72% yield; a furanoid compound was isolated (12%). Mild deallylation[13] of **23** with $(Ph_3P)_3RhCl$ 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 β-$C1^{III}$-to-$C4^{II}$ linkage and the α-$C1^{II}$-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 debenzylation afforded **2**. The NMR spectra of **2** measured in D_2O was consistent with its structure: (1) the $J_{C1,H1}$ value[12] of $C1^{III}$ of 159.0 Hz indicated β-*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

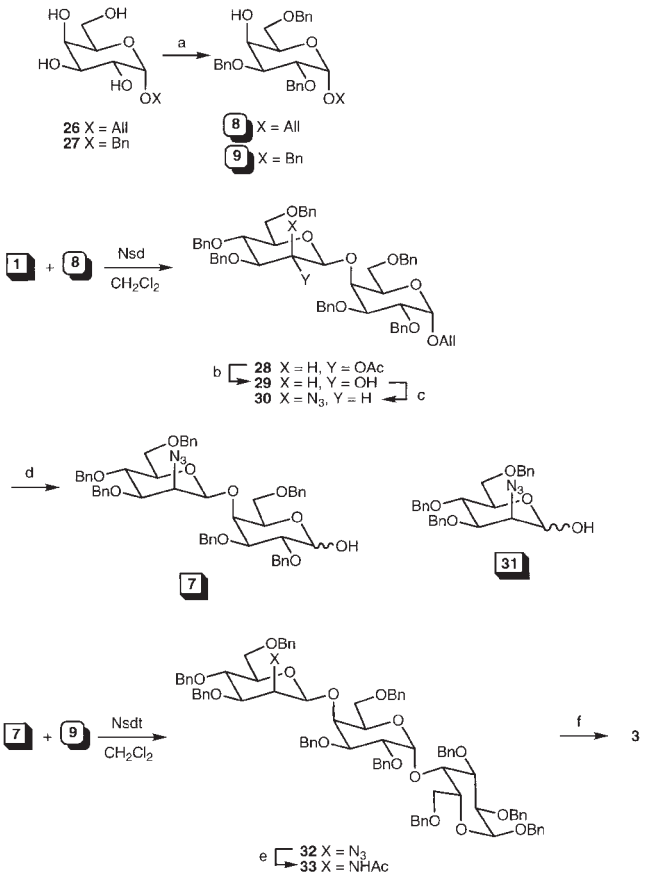

Fig. 7. Synthesis of β-D-Man*N*Ac*p*-(1 → 4)-α-D-Gal*p*-(1 → 4)-D-Gal*p*-OH (**3**) (Nsd = NsCl + AgOTf + DBU, Nsdt = NsCl + AgOTf + DMA + TEA): a. BnCl + LiOH/140 °C; b. NaOMe/MeOH/35 °C; c. (i) Tf_2O + Py/CH_2Cl_2, −30 °C → 20 °C, (ii) CsN_3 + 18-crown-6/PhMe, ultrasonication; d. $PdCl_2$ + NaOAc/aq AcOH (95%), rt; e. (i) $LiAlH_4/Et_2O$, Δ; (ii) Ac_2O/MeOH, rt; f. H_2 + Pd-C (10%)/AcOH, rt.

$H4^{II}$.

Finally, the trisacchride **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*-Bu_4NN_3 in polar solvents (Runs 1–5) were low (<20%). Less polar toluene as solvent gave slightly better results (Run 7, 23%). Ultrasonication[20] improved the yield of **30** (Run 9, 32%). At last, we found that the use of CsN_3 in the presence of 18-crown-6 in toluene under ultrasonication[20] 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 CH_2Cl_2 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 $LiNTf_2$ 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 CH_2Cl_2 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.

Deallylation[13] of **30** with $(Ph_3P)_3RhCl$ afforded the disaccharide donor **7**, which was finally condensed with **9** by a system composed of NsCl, AgOTf, *N*,*N*-dimethylacetamide (DMA), and Et_3N (Nsdt 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	*n*-Bu_4NN_3	3	DMF	−	−	40	16	14
2	*n*-Bu_4NN_3	6	DMF	−	−	40	16	18
3	*n*-Bu_4NN_3	9	DMF	−	−	40	16	8
4	*n*-Bu_4NN_3	6	DMA	−	−	40	16	16
5	*n*-Bu_4NN_3	6	DMSO	−	−	40	16	<10
6	*n*-Bu_4NN_3	6	PhMe	−	−	60	16	18
7	*n*-Bu_4NN_3	9	PhMe	−	−	60	16	23
8	*n*-Bu_4NN_3	12	PhMe	−	−	60	16	<10
9	*n*-Bu_4NN_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^{II} linkage and the α-C1^{II}-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 $LiAlH_4$ in diethyl ether, followed by acetylation, afforded **33** in 59% yield. The last catalytic debenzylation of **33** gave **3**. The NMR spectra of **3** measured in D_2O was consistent with its structure: (1) the $J_{C1,H1}$ value[12] 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) CsN_3 in toluene with ultrasonical treatment was useful in the azide-substitution of the 2-*O*-triflate of **29**.

Experimental[5]

The solvent systems for column chromatography on silica gel (Kanto Chemical, No. 37047; gradient elusion) and thin-layer chromatography (TLC) (Merck, DC-Plastikfolien Kieselgel 60 F 254, Art. 5735) were $CHCl_3$–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 ^{13}C 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 $J_{C1,H1}$ values[12] 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, GHMQC, 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), Et_3N (Tokyo Kasei), DBU (diazabicyclo[5.4.0]undec-7-ene, Tokyo Kasei), Me_3SiBr (Tokyo Kasei), $CoBr_2$ (Wako), molecular sieve 4A (MS4A, Hydrous), Tf_2O (Tokyo Kasei), anhydrous pyridine (Tokyo Kasei), *n*-Bu_4NOAc (Fluka), *n*-Bu_4NI (Tokyo Kasei), *n*-Bu_4NN_3 (Tokyo Kasei), CsN_3 (Aldrich), 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane, Aldrich), and anhydrous solvents (DMF (*N*,*N*-dimethylformamide), DMA (*N*,*N*-dimethylacetamide), 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 $MeNO_2$ (22 mL) at room temperature overnight. The mixture was diluted with PhMe, washed with dil $NaHCO_3$ (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 H_2O (70 mL) were added. This organic layer was washed well with H_2O, 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 H_2O (1.0 mL, 56 mmol) in $CHCl_3$ (15 mL)[3a] was treated with 2,6-dimethylpyridine (4.7 mL, 41 mmol), MeOH (4.0 mL, 100 mmol) in $MeNO_2$ (13 mL), followed by work-up, to give an 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), $TsOH \cdot H_2O$ (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 CH_2Cl_2 (16 mL) containing Et_3SiH (2.7 mL, 17 mmol) and CF_3CO_2H (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 μL, 0.11 mmol), $CoBr_2$ (22 mg, 0.10 mmol), *n*-Bu_4NI (37 mg, 0.10 mmol), powdered MS4A (49 mg), and CH_2Cl_2 (0.25 mL), Me_3SiBr (13 μL, 0.10 mmol) was added at 20 °C; the resulting mixture was stirred for 1.0 h. After the addition of powdered $NaHCO_3$ (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: $[\alpha]_D^{23}$ −12° (*c* 0.4, $CHCl_3$); ^{1}H 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 $C_{35}H_{42}NaO_7$ $[M + Na]^+$: 597.2828.

The α-anomer: $[\alpha]_D^{24}$ +76° (*c* 0.5, $CHCl_3$); ^{1}H 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 $C_{35}H_{42}NaO_7$ $[M + Na]^+$: 597.2828.

When *n*-Bu_4NBr[4b] (32 mL, 0.10 mmol) was used instead of *n*-Bu_4NI 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*-Bu_4NI (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 ^{1}H 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*-Bu_4NBr (16.4 mg, 0.051 mmol), and MS4A (49 mg) in CD_2Cl_2 containing TMS (1%) (Aldrich, 1.0 mL). The ^{1}H 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 → 20:1) afforded **11**[22] (188 mg, 93%); $[\alpha]_D^{25}$ −11° (*c* 1.1, $CHCl_3$); ^{1}H 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 $C_{33}H_{40}O_6$: 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), Tf_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 → 20:1) to yield a homogeneous syrup. To this, *n*-Bu_4NOAc (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 → 20:1) to give **12** (14 mg, 52%); $[\alpha]_D^{25}$ −11° (*c* 1.1, $CHCl_3$), $[\alpha]_D^{24}$ −11° (*c* 0.9, CH_2Cl_2) (Ref. 2p, α-anomer, $[\alpha]_D^{20}$ +28.2° (*c* 1.77, CH_2Cl_2)); ^{1}H 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, $J_{C1,H1}$ = 155.0 Hz), 170.8 (Ac). HRMS (FAB) Found: *m*/*z* 597.2864. Calcd for $C_{35}H_{42}NaO_7$ $[M + Na]^+$: 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 Tf_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*-Bu_4NN_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%); $[\alpha]_D^{24}$ −54° (*c* 1.3, $CHCl_3$); ^{1}H 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, $J_{C1,H1}$ = 156.0 Hz). Found: C, 70.91; H, 7.09; N, 7.35%. Calcd for $C_{33}H_{39}N_3O_5$: C, 71.07; H, 7.05; N, 7.53%.

Methyl *O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-(1 → 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), NsCl (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 °C/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 → 10:1) to afford **15** (42 mg, 69%); $[\alpha]_D^{24}$ +18° (*c* 0.2, $CHCl_3$) (Ref. 3a, $[\alpha]_D^{20}$ +21° (*c*

1.8, $CHCl_3$)); ^1H NMR ($CDCl_3$, 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, $J_{1,2} = 8.0$ H, $J_{2,3} = 9.0$ 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, $J_{4,5} = 10.0$, $H4^{I}$), 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, $H2^{II}$); ^{13}C NMR ($CDCl_3$, 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 ($C1^{II}$), 169.3 (Ac); HRMS (FAB) Found: m/z 961.4146. Calcd for $C_{57}H_{62}NaO_{12}$ $[M + Na]^+$: 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%); $[\alpha]_D^{24}$ +20° (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$, 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, $J_{4,5} = 10.0$, $H4^{II}$), 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, $H1^{II}$); ^{13}C NMR ($CDCl_3$, 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 ($C1^{II}$). Found: C, 73.55; H, 6.87%. Calcd for $C_{55}H_{60}O_{11}$: 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 Tf_2O (82 μL, 0.50 mmol) and pyridine (55 μL, 0.68 mmol) in CH_2Cl_2 (0.46 mL) in a manner similar to the transformation of **11** into **12** gave a syrup (24 mg). To this, *n*-Bu_4NOAc (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%); $[\alpha]_D^{25}$ −5° (*c* 0.6, $CHCl_3$); ^1H NMR ($CDCl_3$, 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, $H2^{II}$); ^{13}C NMR ($CDCl_3$, 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 $C_{57}H_{62}O_{12}$: 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-mannityl]]-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**18**) (3.3 mg, 14%); $[\alpha]_D^{24}$ +22° (*c* 0.4, $CHCl_3$); ^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 $C_{57}H_{62}NaO_{12}$ $[M + Na]^+$: 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 Tf_2O (77 μL, 0.47 mmol) and pyridine (49 μL, 0.60 mmol) in CH_2Cl_2 (0.41 mL) as described for **12** gave a syrup (21.7 mg). To this, *n*-Bu_4NN_3 (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%); $[\alpha]_D^{24}$ −1° (*c* 0.3, $CHCl_3$); ^1H NMR ($CDCl_3$, 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, $H1^{I}$); ^{13}C NMR ($CDCl_3$, 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 $C_{55}H_{59}N_3NaO_{10}$ $[M + Na]^+$: 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%); $[\alpha]_D^{25}$ +19° (*c* 0.3, $CHCl_3$); ^1H NMR ($CDCl_3$, 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, $H1^{II}$); ^{13}C NMR ($CDCl_3$, 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 $C_{55}H_{59}N_3NaO_{10}$ $[M + Na]^+$: 944.4098.

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

syl)-(1 → 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 μL, 0.91 mmol) in CH_2Cl_2 (1.8 mL), followed by chromatography with the TK system (100:1 → 20:1), yielded **21** (279.7 mg, 80%); $[\alpha]_D^{22}$ +16° (*c* 0.7, $CHCl_3$); ^{1}H 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, H5^{II}), 3.50 (t, $J_{2,3} = J_{3,4} = 9.5$ Hz, H3^{II}), 3.54 (dd, $J_{5,6a} = 4.0$ Hz, $J_{6a,6b} = 11.5$ Hz, H6a^{II}), 3.57 (dd, $J_{5,6b} = 2.5$ Hz, $J_{6a,6b} = 11.5$ Hz, H6b^{II}), 3.66 (dd, $J_{5,6a} = 1.5$ Hz, $J_{6a,6b} = 10.0$ Hz, H6a^{I}), 3.68 (~t, $J_{3,4} = 9.5$ Hz, $J_{4,5} = 10.0$ Hz, H4^{II}), 3.69 (ddd, $J_{4,5} = 9.0$ Hz, $J_{5,6a} = 1.5$ Hz, $J_{5,6b} = 4.5$ Hz, H5^{I}), 3.73 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, H2^{I}), 3.80 (dd, $J_{5,6b} = 4.5$ Hz, $J_{6a,6b} = 10.0$ Hz, H6b^{I}), 3.90 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.0$ Hz, H3^{I}), 4.22 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, H4^{I}), 4.53 (d, $J_{1,2} = 8.0$ Hz, H1^{II}), 4.86 (d, $J_{1,2} = 2.0$ Hz, H1^{I}), 4.94 (dd, $J_{1,2} = 8.0$ Hz, $J_{2,3} = 9.5$ Hz, H2^{II}), 5.87 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.9 (Ac), 67.9 (All), 68.4 (C6^{II}), 68.7 (C6^{I}), 71.6 (C5^{I}), 73.8 (C2^{II}), 75.1 (2C, C4^{I} and C5^{II}), 75.4 (C2^{I}), 78.0 (C4^{II}), 78.5 (C3^{I}), 97.3 (C1^{I}, $J_{C1,H1} = 167.0$ Hz), 100.7 (C1^{II}, $J_{C1,H1} = 158.2$ Hz), 117.3, 133.8 (All), 169.5 (Ac). HRMS (FAB) Found: *m/z* 987.4336. Calcd for $C_{59}H_{64}NaO_{12}$ $[M + Na]^+$: 987.4295.

Allyl *O*-(3,4,6-Tri-*O*-benzyl-β-D-glucopyranosyl)-(1→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 → 20:1), and crystallization from *n*-hexane gave **22** (149.0 mg, 88%); mp 87–88 °C, $[\alpha]_D^{25}$ +34° (*c* 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.27 (m, H5^{II}), 3.41 (dd, $J_{5,6a} = 2.0$ Hz, $J_{6a,6b} = 10.5$ Hz, H6a^{I}), 3.75 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, H2^{I}), 3.78 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, H4^{II}), 3.84 (ddd, $J_{4,5} = 9.0$ Hz, $J_{5,6a} = 2.0$ Hz, $J_{5,6b} = 4.0$ Hz, H5^{I}), 3.97 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.0$ Hz, H3^{I}), 4.36 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, H4^{I}), 4.61 (d, $J_{1,2} = 7.5$ Hz, H1^{II}), 4.87 (d, $J_{1,2} = 2.0$ Hz, H1^{I}), 5.85 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 67.8 (All), 68.7 (C6^{I}), 69.7 (C6^{II}), 71.0 (C5^{I}), 74.7 (C4^{I}), 74.9 (C2^{I}), 75.1 (C5^{II}), 75.5 (C2^{II}), 77.2 (C4^{II}), 79.3 (C3^{I}), 84.4 (C3^{II}), 97.3 (C1^{I}, $J_{C1,H1} = 169.0$ Hz), 103.4 (C1^{II}, $J_{C1,H1} = 158.0$ Hz), 117.2, 133.7 (All). Found: C, 73.89; H, 6.65%. Calcd for $C_{57}H_{62}O_{11}$: C, 74.16; H, 6.77%.

Allyl *O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-α-D-mannopyranoside (23). Triflylation of **22** (77.9 mg, 0.084 mmol) with Tf_2O (277 μL, 1.7 mmol) and pyridine (181 μL, 2.2 mmol) in CH_2Cl_2 (1.6 mL), quenching with H_2O (46 μL, 2.6 mmol) and subsequent chromatography with the TK system (100:1 → 10:1) were carried out as described for **12** to give a syrup (79.2 mg). This was reacted with *n*-Bu_4NOAc (272 mg, 0.90 mmol) in anhydrous PhMe (0.72 mL) with stirring at 50 °C overnight, followed by chromatography with the TK system (100:1 → 10:1), to give **23** (59.0 mg, 72%); $[\alpha]_D^{24}$ +10° (*c* 0.8, $CHCl_3$); ^{1}H 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, H6^{II}), 3.44 (dd, $J_{2,3} = 3.5$ Hz, $J_{3,4} = 9.5$ Hz, H3^{II}), 3.48 (dd, $J_{5,6a} = 1.5$ Hz, $J_{6a,6b} = 11.0$ Hz, H6a^{II}), 3.57 (dd, $J_{5,6b} = 5.0$ Hz, $J_{6a,6b} = 11.0$ Hz, H6b^{II}), 3.69 (dd, $J_{5,6a} = 3.5$ Hz, $J_{6a,6b} = 10.0$ Hz, H6a^{I}), 3.71 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4^{II}), 3.71 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, H2^{I}), 3.79 (ddd, $J_{4,5} = 9.0$ Hz, $J_{5,6a} = 3.5$ Hz, $J_{5,6b} = 2.0$ Hz, H5^{I}), 3.93 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.0$ Hz, H3^{I}), 4.29 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, H4^{I}), 4.69 (d, $J_{1,2} = 1.0$ Hz, H1^{II}), 4.87 (d, $J_{1,2} = 2.0$ Hz, H1^{I}), 5.45 (dd, $J_{1,2} = 1.0$ Hz, $J_{2,3} = 3.5$ Hz, H2^{II}), 5.85 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.1 (Ac), 67.9 (All), 68.6 (C2^{II}), 69.0 (C6^{II}), 69.3 (C6^{I}), 71.0 (C5^{I}), 74.2 (C2^{I}), 75.4 (C4^{II}), 75.5 (C4^{I}), 75.7 (C5^{II}), 79.1 (C3^{I}), 80.5 (C3^{II}), 97.3 (C1^{I}, $J_{C1,H1} = 171.6$ Hz), 99.6 (C1^{II}, $J_{C1,H1} = 152.0$ Hz), 117.2, 133.8 (All), 170.5 (Ac). HRMS (FAB) Found: *m/z* 987.4274. Calcd for $C_{59}H_{64}NaO_{12}$ $[M + Na]^+$: 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%); $[\alpha]_D^{22}$ +20° (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.56 (dd, $J_{5,6a} = 5.5$ Hz, $J_{6a,6b} = 10.0$ Hz, H6a^{II}), 3.60 (dd, $J_{5,6b} = 5.5$ Hz, $J_{6a,6b} = 10.0$ Hz, H6b^{II}), 3.79 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, H2^{I}), 4.08 (dd, $J_{1,2} = 4.5$ Hz, $J_{2,3} = 3.5$ Hz, H2^{II}), 4.30 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4^{I}), 4.35 (t, $J_{2,3} = J_{3,4} = 3.5$ Hz, H3^{II}), 4.87 (d, $J_{1,2} = 2.0$ Hz, H1^{I}), 6.19 (d, $J_{1,2} = 4.5$ Hz, H1^{II}); 1.78 (s, Ac), 5.88 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 69.1 (C6^{I}), 69.8 (C6^{II}), 72.2 (C5^{I}), 75.7 (C2^{I}), 75.8 (C4^{I}), 78.2 (C3^{I}), 81.7 (C5^{II}), 83.1 (C2^{II}), 84.3 (C3^{II}), 84.7 (C4^{II}), 95.5 (C1^{II}), 97.4 (C1^{I}); 21.1, 170.3 (Ac); 67.9, 117.2, 133.8 (All). HRMS (FAB) Found: *m/z* 987.4337. Calcd for $C_{59}H_{64}NaO_{12}$ $[M + Na]^+$: 987.4295.

***O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)-(1 → 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 → 10:1) gave **5** (35.9 mg, 58%); $[\alpha]_D^{24}$ −6° (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) (75%α) δ 2.10 (s, Acα), 2.11 (s, Acβ), 2.70 (d, $J_{1,OH} = 3.5$ Hz, OHα), 3.26 (ddd, $J_{4,5} = 9.5$ Hz, $J_{5,6a} = 2.0$ Hz, $J_{5,6b} = 4.5$ Hz, H5^{II}α), 3.30 (m, H5^{II}β), 3.44 (dd, $J_{5,6b} = 4.5$ Hz, $J_{5,6b} = 4.5$ Hz, H5^{II}α), 3.46 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.0$ Hz, H3^{II}β), 3.50 (dd, $J_{5,6a} = 2.0$ Hz, $J_{6a,6b} = 11.0$ Hz, H6b^{II}α), 3.58 (dd, $J_{5,6b} = 4.5$ Hz, $J_{6a,6b} = 11.0$ Hz, H6b^{II}β), 3.63 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.0$ Hz, H3^{I}β), 3.68 (dd, $J_{5,6a} = 2.0$ Hz, $J_{6a,6b} = 10.0$ Hz, H6a^{I}α), 3.70 (~t, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, H2^{I}α), 3.72 (~t, $J_{3,4} = 9.0$ Hz, $J_{4,5} = 9.5$ Hz, H4^{II}α), 3.76 (dd, $J_{5,6b} = 5.0$ Hz, $J_{6a,6b} = 10.0$ Hz, H6b^{I}α), 3.97 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.0$ Hz, H3^{I}α), 4.03 (ddd, $J_{4,5} = 9.0$ Hz, $J_{5,6a} = 2.0$ Hz, $J_{5,6b} = 5.0$ Hz, H5^{I}α), 4.20 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, H4^{I}α), 4.65 (s, $J_{1,2} = J_{1,OH} = 0$ Hz, H1^{I}β), 4.68 (s, $J_{1,2} = 0$ Hz, H1^{II}β), 4.72 (s, $J_{1,2} = 0$ Hz, H1^{II}α), 5.22 (dd, $J_{1,2} = 2.0$ Hz, $J_{1,OH} = 3.5$ Hz, H1^{I}α), 5.45 (d, $J_{1,2} = 0$ Hz, $J_{2,3} = 3.0$ Hz, H2^{II}β), 5.46 (d, $J_{1,2} = 0$ Hz, $J_{2,3} = 3.0$ Hz, H2^{II}*lpha*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.1 (Ac), 68.4 (C2^{II}α), 68.5 (C2^{II}β), 69.0 (C6^{II}α), 69.1 (C6^{II}β), 69.6 (C6^{I}α and C6^{I}β), 70.9 (C5^{II}α), 74.1 (C4^{II}α), 74.2 (C4^{II}β), 74.5 (C2^{I}β), 74.8 (C4^{I}β), 75.4 (C2^{I}α and C4^{I}α), 75.6 (C5^{II}α), 75.7 (C5^{II}β), 76.6 (C5^{I}β), 78.3 (C3^{I}α), 80.4 (C3^{II}α and C3^{II}β), 81.5 (C3^{I}β), 92.9 (C1^{I}α, $J_{C1,H1} = 170.0$ Hz), 93.5 (C1^{I}β, $J_{C1,H1} = 159.1$ Hz), 99.1 (C1^{II}β, $J_{C1,H1} = 158.0$ Hz), 99.4 (C1^{II}α, $J_{C1,H1} = 156.0$ Hz), 170.5 (Ac). HRMS (FAB) Found: *m/z* 947.4012. Calcd for $C_{56}H_{60}NaO_{12}$ $[M + Na]^+$: 947.3982.

Benzyl *O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1 → 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 μL, 0.077 mmol) in CH_2Cl_2 (0.25 mL), followed by quenching as above and chromatography with the TK system (100:1 → 10:1), afforded **24** (13.1 mg, 35%) and

the β-linked isomer (5.2 mg, 14%).

24: $[\alpha]_D^{22}$ −13° (*c* 0.7, $CHCl_3$); ^{1}H 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 (~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 (~t, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.0 Hz, H2^{II}), 3.72 (~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 (~t, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 10.0 Hz, H4^{III}), 3.91 (~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 (~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}, $J_{C1,H1}$ = 168.7 Hz), 96.8 (C1^{I}, $J_{C1,H1}$ = 167.4 Hz), 99.5 (C1^{III}, $J_{C1,H1}$ = 158.2 Hz), 170.4 (Ac). HRMS (FAB) Found: *m*/*z* 1363.5999. Calcd for $C_{83}H_{88}NaO_{16}$ $[M + Na]^+$: 1363.5970.

The β-linked isomer: $[\alpha]_D^{22}$ −58° (*c* 0.5, $CHCl_3$); ^{1}H 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^{II}), 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^{III}), 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 (~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}, $J_{C1,H1}$ = 169.5 Hz), 99.7 (C1^{III}, $J_{C1,H1}$ = 157.8 Hz), 103.6 (C1^{II}, $J_{C1,H1}$ = 155.8 Hz), 170.5 (Ac). HRMS (FAB) Found: *m*/*z* 1363.6017. Calcd for $C_{83}H_{88}NaO_{16}$ $[M + Na]^+$: 1363.5970.

Benzyl *O*-(3,4,6-Tri-*O*-benzyl-β-D-mannopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1 → 3)-2,4-di-*O*-benzyl-α-D-rhamnopyranoside (25). A mixture of **24** (25.2 mg, 0.019mmol), 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 → 20:1) produced **25** (22.4 mg, 92%); $[\alpha]_D^{23}$ +13° (*c* 0.8, $CHCl_3$); ^{1}H 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^{II}), 69.0 (C6^{III}), 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}, $J_{C1,H1}$ = 166.7 Hz), 96.7 (C1^{II}, $J_{C1,H1}$ = 167.0 Hz), 100.1 (C1^{III}, $J_{C1,H1}$ = 157.8 Hz). HRMS (FAB) Found: *m*/*z* 1321.5830. Calcd for $C_{81}H_{86}NaO_{15}$ $[M + Na]^+$: 1321.5868.

***O*-β-D-Mannopyranosyl-(1 → 4)-*O*-α-D-mannopyranosyl-(1 → 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 → 1:1) afforded **2** (6.3 mg, 77%); $[\alpha]_D^{26}$ +42° (*c* 0.3, H_2O); ^{1}H NMR (D_2O, 400 MHz) (60%α) δ 1.24 (d, $J_{5,6}$ = 6.5 Hz, H1$^{II}\alpha$), 1.26 (d, $J_{5,6}$ = 6.0 Hz, H1$^{II}\beta$), 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, H5$^{I}\beta$), 3.40 (dd, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 8.5 Hz, H4$^{I}\beta$), 3.45 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4$^{I}\alpha$), 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, H3$^{I}\beta$), 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, H6a$^{II}\beta$), 3.74 (dd, $J_{5,6a}$ = 4.0 Hz, $J_{6a,6b}$ = 12.0 Hz, H6a$^{II}\alpha$), 3.80 (dd, $J_{5,6b}$ = 2.0 Hz, $J_{6a,6b}$ = 12.0 Hz, H6b$^{II}\beta$), 3.81 (dd, $J_{5,6b}$ = 2.0 Hz, $J_{6a,6b}$ = 12.0 Hz, H6b$^{II}\alpha$), 3.84 (dd, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.5 Hz, H3$^{I}\alpha$), 3.84 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.5 Hz, H5$^{I}\alpha$), 3.88 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.0 Hz, H3$^{II}\beta$), 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, H4$^{II}\beta$), 3.92 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4$^{II}\alpha$), 3.94 (m, H5$^{II}\alpha$), 3.95 (m, H5$^{II}\beta$), 4.00 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.5 Hz, H3$^{II}\alpha$), 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, H2$^{II}\alpha$), 4.03 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3.5 Hz, H2$^{II}\beta$), 4.10 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.0 Hz, H2$^{I}\alpha$), 4.12 (d, $J_{1,2}$ = 0 Hz, $J_{2,3}$ = 3.5 Hz, H2$^{I}\beta$), 4.71 (s, H1^{III}), 4.81 (s, H1$^{I}\beta$), 4.99 (d, $J_{1,2}$ = 1.5 Hz, H1$^{II}\alpha$), 5.01 (d, $J_{1,2}$ = 1.5 Hz, H1$^{II}\beta$), 5.10 (d, $J_{1,2}$ = 2.0 Hz, H1$^{I}\alpha$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.7 (C6$^{I}\beta$), 18.8 (C6$^{I}\alpha$), 62.1 (C6^{II}), 62.9 (C6^{III}), 68.6 (C2$^{I}\alpha$ and C4^{III}), 69.1 (C2$^{I}\beta$), 70.1 (C5$^{I}\alpha$), 71.0 (C3^{II}), 71.6 (C2$^{II}\beta$), 71.7 (C2$^{II}\alpha$), 72.0 (C4$^{I}\beta$), 72.3 (C4$^{I}\alpha$), 72.4 (C2^{III}), 73.0 (C5^{II}), 73.8 (C5$^{I}\beta$), 74.7 (C3^{III}), 75.4 (C3^{II}), 76.1 (C3$^{I}\alpha$), 78.3 (C5^{III}), 78.4 (C3$^{I}\beta$ and C4^{II}), 95.3 (C1$^{I}\beta$, $J_{C1,H1}$ = 160.0 Hz), 95.7 (C1$^{I}\alpha$, $J_{C1,H1}$ = 170.0 Hz), 97.9 (C1$^{II}\beta$, $J_{C1,H1}$ = 170.0 Hz), 98.0 (C1$^{II}\alpha$, $J_{C1,H1}$ = 169.5 Hz), 102.0 (C1^{III}, $J_{C1,H1}$ = 159.0 Hz). HRMS (FAB) Found: *m*/*z* 511.1662. Calcd for $C_{18}H_{32}NaO_{15}$ $[M + Na]^+$: 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 °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 → 2:1), followed by crystallization with a seed and diisopropyl ether containing MeOH (5%), gave **26** (2.1 g, 34%); mp 140–142 °C, $[\alpha]_D^{25}$ +173° (*c* 0.8, H_2O) (Ref. 15a, mp 138–142 °C, $[\alpha]_D^{20}$ +171.7° (H_2O); Ref. 15b, mp 145–146 °C, $[\alpha]_D^{25}$ +185.0° (*c* 5.8, H_2O); Ref. 15c, mp 143–145 °C, $[\alpha]_D^{20}$ +181.3° (*c* 1.57, H_2O), Ref. 15e, mp 143–143.5 °C, $[\alpha]_D^{20}$ +181.4° (*c* 5.8, H_2O)). HRMS (FAB) Found: *m*/*z* 243.0853. Calcd for $C_9H_{16}NaO_6$ $[M + Na]^+$: 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 °C for 25 min. After the addi-

tion of Et_3N (1.6 mL, 11 mmol), the mixture was diluted with $CHCl_3$ (5 mL) and chromatographed with the CM system (100:1 → 2:1) to give **27** (0.99 g, 66%); $[\alpha]_D^{25}$ +158° (*c* 0.7, MeOH); ^{1}H NMR (D_2O, 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); ^{13}C NMR (D_2O, 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 $C_{13}H_{18}NaO_6$ [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 → 20:1) to give **8** (0.83 g, 39%); $[\alpha]_D^{21}$ +54° (*c* 0.8, $CHCl_3$) (Ref. 14a, $[\alpha]_D^{25}$ +52.8° (*c* 1, $CHCl_3$), Ref. 14b, $[\alpha]_D^{25}$ +42° (*c* 2.4, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 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, $J_{4,5} \sim 1.0$ Hz, $J_{5,6a} = J_{5,6b} = 6.0$ Hz, H5), 4.09 (∼d, $J_{3,4} = 3.0$ Hz, $J_{4,5} \sim 1.0$ Hz, H4), 4.88 (d, $J_{1,2} = 3.0$ Hz, H1); 5.95 (m, All); ^{13}C NMR ($CDCl_3$, 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 $C_{30}H_{34}NaO_6$ [M + Na]$^+$: 513.2253.

NMR data of the acetate: ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 → 20:1) gave **9** (0.612 g, 40%); $[\alpha]_D^{22}$ +72° (*c* 1.0, $CHCl_3$); (Ref. 18, $[\alpha]_D + 69.0°$ (*c* 0.6, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 $C_{34}H_{36}NaO_6$ [M + Na]$^+$: 563.2410.

NMR data of the acetate: ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 → 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 μL, 0.81 mmol) in CH_2Cl_2 (1.6 mL), followed by quenching and chromatography with the TK system (100:1 → 20:1) as described above, yielded **28** (300.9 mg, 96%); $[\alpha]_D^{23}$ +40° (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 $C_{59}H_{64}O_{12}$: C, 73.42; H, 6.68%.

Allyl *O*-(3,4,6-Tri-*O*-benzyl-β-D-glucopyranosyl)-(1 → 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 → 10:1) gave **29** (258.3 mg, 93%); $[\alpha]_D^{24}$ +29° (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 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, $J_{4,5} \sim 1.0$ 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); ^{13}C NMR ($CDCl_3$, 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 $C_{57}H_{62}O_{11} \cdot H_2O$: C, 72.74; H, 6.85%.

Allyl *O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-mannopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-α-D-galactopyranoside (30). Triflylation of **29** (86.0 mg, 0.093 mmol) with Tf_2O (284.6 μL, 1.74 mmol) and pyridine (186.8 μL, 2.3 mmol) in CH_2Cl_2 (1.6 mL), followed by quenching with H_2O (47 μL, 2.6 mmol), dilution with hexane (5 mL), and chromatography with the TK system (100:1 → 10:1), afforded a syrup (88.2 mg). This was dissolved in anhydrous PhMe (2.1 mL). To the obtained solution, CsN_3 (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 → 10:1) to give **30** (40.0 mg, 45%); $[\alpha]_D^{23}$ +15° (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.27 (ddd, $J_{4,5} = 9.0$ Hz, $J_{5,6a} = 2.0$ Hz, $J_{5,6} = 4.5$ 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 ($C2^{II}$), 68.3 (All), 69.2 ($C5^{I}$), 69.3 ($C6^{II}$), 69.5 ($C6^{I}$), 74.2 ($C4^{II}$), 75.8 ($C5^{II}$), 76.3 ($C4^{I}$), 76.6 ($C2^{I}$), 78.1 ($C3^{I}$), 81.3 ($C3^{II}$), 96.0 ($C1^{I}$, $J_{C1,H1}$ = 170.0 Hz), 101.0 ($C1^{II}$, $J_{C1,H1}$ = 158.0 Hz), 118.0, 134.0 (All). Found: C, 72.10; H, 6.60; N, 4.40%. Calcd for $C_{57}H_{61}N_3O_{10}$: 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 → 10:1), afforded the α-linked isomer, allyl *O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-mannopyranosyl)-(1 → 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: $[\alpha]_D^{23}$ +53° (*c* 0.6, H_2O); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.05 (dd, $J_{5,6a}$ = 1.5 Hz, $J_{6a,6b}$ = 10.5 Hz, $H6a^{I}$), 3.46 (dd, $J_{5,6b}$ = 5.5 Hz, $J_{5,6}$ = 9.0 Hz, $H6b^{II}$), 3.81 (dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.0 Hz, $H2^{I}$), 3.82 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3.0 Hz, $H2^{II}$), 3.92 (dd, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 10.0 Hz, $H3^{II}$), 4.02 (~t, $J_{3,4}$ = 10.0 Hz, $J_{4,5}$ = 9.5 Hz, $H4^{II}$), 4.18 (d, $J_{3,4}$ = 2.5 Hz, $J_{4,5}$ = 0 Hz, $H4^{I}$), 4.82 (d, $J_{1,2}$ = 3.5 Hz, $H1^{I}$), 4.90 (d, $J_{1,2}$ = 1.5 Hz, $H1^{II}$); 5.92 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 61.7 ($C2^{II}$), 67.7 ($C6^{I}$), 67.9 ($C6^{II}$), 68.6 ($C5^{II}$), 71.8 ($C5^{I}$), 74.2 ($C4^{II}$), 74.9 ($C2^{I}$), 75.6 ($C4^{I}$), 77.0 ($C3^{I}$), 79.9 ($C3^{II}$), 99.5 ($C1^{I}$, $J_{C1,H1}$ = 170.0 Hz), 96.3 ($C1^{II}$, $J_{C1,H1}$ = 169.0 Hz); 68.4, 118.1, 133.8 (All). HRMS (FAB) Found: *m*/*z* 970.4275. Calcd for $C_{57}H_{61}N_3NaO_{10}$ $[M + Na]^+$: 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 → 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 → 10:1) to give **7** (26.5 mg, 63%), $[\alpha]_D^{23}$ +2° (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) (67%α) δ 2.86 (d, $J_{1,OH}$ = 2.0 Hz, $OH^{I}\alpha$), 3.18 (d, $J_{1,OH}$ = 6.5 Hz, $OH^{I}\beta$), 3.28 (ddd, $J_{4,5}$ = 9.5 Hz, $J_{5,6a}$ = 3.0 Hz, $J_{5,6b}$ = 4.5 Hz, $H5^{II}\alpha$), 3.29 (br m, $H5^{II}\beta$), 3.41 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.0 Hz, $H3^{II}\alpha$), 3.44 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.5 Hz, $H3^{II}\beta$), 3.51 (dd, $J_{2,3}$ = 9.0 Hz, $J_{3,4}$ = 3.0 Hz, $H3^{I}\beta$), 3.69 (~t, $J_{3,4}$ = 9.0 Hz, $J_{4,5}$ = 9.5 Hz, $H4^{II}\alpha$), 3.79 (dd, $J_{5,6b}$ = 5.5 Hz, $J_{6a,6b}$ = 10.0 Hz, $H6b^{I}\alpha$), 3.90 (dd, $J_{2,3}$ = 9.0 Hz, $J_{3,4}$ = 2.5 Hz, $H3^{I}\alpha$), 3.95 (dd, $J_{1,2}$ = 3.0 Hz, $J_{2,3}$ = 9.0 Hz, $H2^{I}\alpha$), 4.02 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3.5 Hz, $H2^{II}\alpha$), 4.04 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3.5 Hz, $H2^{II}\beta$), 4.15 (dd, $J_{3,4}$ = 3.0 Hz, $J_{4,5}$ = 1.0 Hz, $H4^{I}\beta$), 4.19 (dd, $J_{3,4}$ = 2.5 Hz, $J_{4,5}$ = 1.5 Hz, $H4^{I}\alpha$), 4.20 (~t, $J_{4,5}$ = 1.5 Hz, $J_{5,6a}$ = $J_{5,6b}$ = 1.5 Hz, $H5^{I}\alpha$), 4.66 (dd, $J_{1,2}$ = 7.5 Hz, $J_{1,OH}$ = 6.5 Hz, $H1^{I}\beta$), 4.70 (d, $J_{1,2}$ = 1.5 Hz, $H1^{II}\beta$), 4.71 (d, $J_{1,2}$ = 1.5 Hz, $H1^{II}\alpha$), 5.30 (~t, $J_{1,2}$ = 3.0 Hz, $J_{1,OH}$ = 2.0 Hz, $H1^{I}\alpha$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 61.6 ($C2^{II}\beta$), 61.7 ($C2^{II}\alpha$), 69.15 ($C5^{I}\alpha$), 69.24 ($C6^{II}$), 69.46 ($C6^{I}\beta$), 69.50 ($C6^{I}\alpha$), 74.1 ($C4^{II}\alpha$), 75.7 ($C5^{II}\alpha$), 75.9 ($C4^{I}\alpha$), 76.6 ($C2^{I}\alpha$), 77.7 ($C3^{I}\alpha$), 81.2 ($C3^{II}\alpha$), 81.4 ($C3^{I}\beta$), 91.6 ($C1^{I}\alpha$, $J_{C1,H1}$ = 168.0 Hz), 97.8 ($C1^{I}\beta$, $J_{C1,H1}$ = 156.7 Hz), 100.4 ($C1^{II}\beta$, $J_{C1,H1}$ = 159.0 Hz), 100.9 ($C1^{II}\alpha$, $J_{C1,H1}$ = 157.5 Hz). HRMS (FAB) Found: *m*/*z* 930.3928. Calcd for $C_{54}H_{57}N_3NaO_{10}$ $[M + Na]^+$: 930.3942.

Benzyl O-(2-Azido-3,4,6-tri-O-benzyl-2-deoxy-β-D-mannopyranosyl)-(1 → 4)-2,3,6-tri-O-benzyl-α-D-galactopyranosyl-(1 → 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 → 10:1), afforded **32** (36.0 mg, 56%); $[\alpha]_D^{24}$ +44° (*c* 0.8, $CHCl_3$); ^{1}H 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, $H5^{III}$), 3.32 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.5 Hz, $H3^{III}$), 3.55 (dd, $J_{5,6a}$ = 1.5 Hz, $J_{6a,6b}$ = 11.0 Hz, $H6a^{III}$), 3.64 (dd, $J_{5,6b}$ = 4.5 Hz, $J_{5,6a}$ = 11.0 Hz, $H6b^{III}$), 3.70 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, $H2^{I}$), 3.88 (dd, $J_{1,2}$ = 3.0 Hz, $J_{2,3}$ = 10.0 Hz, $H2^{I}$), 3.88 (dd, $J_{2,3}$ = 10.0 Hz, $J_{3,4}$ = 2.5 Hz, $H3^{II}$), 3.92 (dd, $J_{2,3}$ = 10.0 Hz, $J_{3,4}$ = 2.5 Hz, $H3^{I}$), 3.99 (d, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3.5 Hz, $H2^{III}$), 4.00 (dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 10.0 Hz, $H2^{II}$), 4.09 (dd, $J_{3,4}$ = 2.5 Hz, $J_{3,4}$ = 1.0 Hz, $H4^{I}$), 4.28 (dd, $J_{3,4}$ = 2.5 Hz, $J_{4,5}$ = 1.0 Hz, $H4^{II}$), 4.62 (d, $J_{1,2}$ = 1.5 Hz, $H1^{III}$), 4.91 (d, $J_{1,2}$ = 3.0 Hz, $H1^{I}$), 5.04 (d, $J_{1,2}$ = 3.5 Hz, $H1^{II}$), ^{13}C NMR ($CDCl_3$, 100 MHz) δ 61.9 ($C2^{III}$), 68.0 ($C6^{II}$), 68.2 ($C6^{I}$), 68.9 ($C5^{I}$), 69.0 ($C6^{III}$), 69.7 ($C5^{II}$), 74.0 ($C4^{III}$), 75.3 ($C2^{I}$), 75.8 ($C5^{III}$), 75.7 ($C2^{II}$), 76.0 ($C4^{I}$), 76.8 ($C4^{II}$), 77.7 ($C3^{I}$), 78.4 ($C3^{II}$), 81.2 ($C3^{III}$), 96.2 ($C1^{I}$, $J_{C1,H1}$ = 168.5 Hz), 99.6 ($C1^{II}$, $J_{C1,H1}$ = 166.5 Hz), 101.7 ($C1^{III}$, $J_{C1,H1}$ = 155.0 Hz). HRMS (FAB) Found: *m*/*z* 1452.6338. Calcd for $C_{88}H_{91}N_3NaO_{15}$ $[M + Na]^+$: 1452.6348.

Benzyl O-(2-Acetamido-3,4,6-tri-O-benzyl-2-deoxy-β-D-mannopyranosyl)-(1 → 4)-2,3,6-tri-O-benzyl-α-D-galactopyranosyl-(1 → 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 → 1:1) to give **33** (17.3 mg, 59%); $[\alpha]_D^{22}$ +43° (*c* 0.7, $CHCl_3$). ^{1}H 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, $H6a^{II}$), 3.24 (br d, $H5^{III}$), 3.40 (dd, $J_{5,6a}$ = 4.5 Hz, $J_{6a,6b}$ = 8.5 Hz, $H6a^{I}$), 3.40 (dd, $J_{2,3}$ = 4.0 Hz, $J_{3,4}$ = 8.0 Hz, $H3^{III}$), 3.55 (dd, $J_{5,6a}$ = 1.0 Hz, $J_{6a,6b}$ = 10.5 Hz, $H6a^{III}$), 3.60 (dd, $J_{5,6b}$ = 8.5 Hz, $J_{6a,6b}$ = 8.5 Hz, $H6b^{II}$), 3.62 (~t, $J_{3,4}$ = 8.0 Hz, $J_{4,5}$ = 9.0 Hz, $H4^{III}$), 3.66 (dd, $J_{5,6b}$ = 3.0 Hz, $J_{6a,6b}$ = 10.5 Hz, $H6b^{III}$), 3.84 (~t, $J_{5,6b}$ = 8.0 Hz, $J_{6a,6b}$ = 8.5 Hz, $H6b^{I}$), 3.87 (dd, $J_{2,3}$ = 10.0 Hz, $J_{3,4}$ = 3.0 Hz, $H3^{II}$), 3.88 (br m, $H5^{I}$), 3.88 (br d, $H2^{I}$), 3.92 (dd, $J_{2,3}$ = 10.0 Hz, $J_{3,4}$ = 2.0 Hz, $H3^{I}$), 3.98 (dd, $J_{1,2}$ = 3.0 Hz, $J_{2,3}$ = 10.0 Hz, $H2^{II}$), 4.08 (br s, $H4^{I}$), 4.32 (br s, $H4^{II}$), 4.40 (br dd, $H5^{II}$), 4.82 (s, $H1^{III}$), 4.83 (br d, $J_{2,NH}$ = 10.0 Hz, NH), 4.87 (br d, $H2^{III}$), 4.92 (d, $J_{1,2}$ = 3.0 Hz, $H1^{I}$), 4.98 (d, $J_{1,2}$ = 3.0 Hz, $H1^{II}$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 23.4 (Ac), 50.1 (br, $C2^{III}$), 67.9 ($C6^{II}$), 68.2 ($C6^{I}$), 68.7 ($C6^{III}$), 69.0 ($C5^{II}$), 69.8 ($C5^{I}$), 74.0 ($C4^{III}$), 74.1 ($C4^{II}$), 75.2 ($C5^{III}$), 75.5 ($C2^{I}$), 75.9 ($C4^{I}$), 77.0 ($C2^{II}$), 77.9 ($C3^{I}$), 78.9 ($C3^{II}$), 81.2 ($C3^{III}$), 96.0 ($C1^{I}$, $J_{C1,H1}$ = 168.0 Hz), 99.9 ($C1^{II}$, $J_{C1,H1}$ = 167.0 Hz), 100.0 ($C1^{III}$,

$J_{C1,H1} = 158.0$ 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 → 4)-*O*-α-D-galactopyranosyl-(1 → 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 → 2:1) afforded **3** (8.2 mg, 78%); $[\alpha]_D^{26}$ +67° (*c* 0.3, H_2O); ^{1}H NMR (D_2O, 400 MHz) (~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 (~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$^{II}\alpha$), 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 (~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 (~t, $J_{4,5} = 1.5$ Hz, $J_{5,6a} = 6.0$ Hz, $J_{5,6b} = 6.5$ Hz, H5$^{I}\beta$), 4.35 (~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, H1β^{I}), 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, H1α^{I}); ^{13}C NMR (D_2O, 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 (C1β^{I}, $J_{C1,H1} = 160.0$ 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 $MeSO_3H$ (Wako, 0.10 mL, 1.5 mmol) was refluxed at 105 °C for 10 h. After addition of $NaHCO_3$ (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 $MeSO_3H$ (0.05 mL, 0.77 mmol) in DMF (15 mL) at room temperature overnight. After the addition of $NaHCO_3$ (142 mg, 1.7 mmol), evaporation, and chromatography with the TK system (100:1 → 1:1), crystallization from diisopropyl ether containing 2-butanone (5%), gave allyl 4,6-*O*-benzylidene-α-D-glucopyranoside[23] (0.85 g, 24%), mp 127–128 °C, $[\alpha]_D^{24}$ +108° (*c* 1.0, $CHCl_3$) (Ref. 23a, mp 130–131 °C, Ref. 23b, $[\alpha]_D^{25}$ +112.3° ($CHCl_3$)).

To a stirred solution of this acetal (1.503 g, 4.9 mmol), pyridine (1.8 mL, 22 mmol), and CH_2Cl_2 (40 mL), Tf_2O (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 H_2O (50 mL). The organic layer was washed with H_2O (50 mL × 3), dried over Na_2SO_4 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*-$BuNN_3$ (5.0 g, 18 mmol) at room temperature overnight and then at 40 °C for 4 h. Work-up and chromatography with the TK system (100:1 → 3:1) yielded allyl 2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-mannopyranoside (0.620 g, 38%); mp 141–142 °C, $[\alpha]_D^{22}$ +79° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 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 ($CDCl_3$, 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 $C_{16}H_{19}N_3O_5$: 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 °C for 15 min with stirring. Evaporation and chromatography with the CM system (100:1 → 2:1) afforded allyl 2-azido-2-deoxy-α-D-mannopyranoside (0.9513 g); $[\alpha]_D^{22}$ +127° (*c* 1.1, MeOH) (Ref. 13, $[\alpha]_D^{20}$ +108.7° (*c* 0.8, MeOH)). HRMS (FAB) Found: m/z 268.0913. Calcd for $C_9H_{15}N_3NaO_5$ $[M + Na]^+$: 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 °C for 15 min then 20 °C for 60 min. After quenching with MeOH (10 mL), evaporation at 90 °C and chromatography with the TK system (100:1 → 20:1) yielded a syrup (681.2 mg). This (244.4 mg, 0.47 mmol) was stirred in aq AcOH (95%, 18 mL) containing $PdCl_2$ (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 °C for 20 min, evaporation and chromatography with the TK system (100:1 → 20:1) gave **31** (149.0 mg, 43%), which was identified with the sample prepared before.[7a]

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