Glycosylation Using 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucose, -galactose, and -mannose with the Aid of *p*-Nitrobenzenesulfonyl Chloride–Silver Trifluoromethanesulfonate–Triethylamine System

Shinkiti Koto,* Kazuyasu Asami, Motoko Hirooka,* Kazuo Nagura, Mizue Takizawa,
Satoko Yamamoto, Nami Okamoto, Mitsuko Sato, Hiromi Tajima, Toyosaku Yoshida, Nobuo Nonaka,
Tadaaki Sato, Shonosuke Zen, Kazuo Yago,†,# and Fumiya Tomonaga†

School of Pharmaceutical Sciences, Kitasato University, Shirokane, Minato-ku, Tokyo 108
†Department of Pharmacy, Kitasato University Hospital, Kitasato, Sagamihara 228

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This report describes a simple synthesis of 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranose. Glycosylation using this as well as 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactopyranose and -mannopyranose was achieved with the aid of a reagent system consisting of *p*-nitrobenzenesulfonyl chloride, silver trifluoromethanesulfonate, and triethylamine, and its modifications. *O*-(2-Acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-*O*-α-D-mannopyranosyl-(1→4)-α-D-mannopyranose, the repeating unit of the main chain of the O-specific cell wall polysaccharide of *E. coli* 058 was synthesized.

The unceasing progress of methods for glycosylation has marked the developments of glyco-engineering.[1] In the sence of handiness,[2] the glycosylation by way of in situ activation of a 1-OH sugar derivative[3] (Eq. 1; DOH expresses a protected reducing sugar such as

$$\mathrm{DOH} + \mathrm{AOH} \rightarrow \mathrm{DOA} \qquad (1)$$

2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (**1**) (Fig. 1) and AOH means an alcohol to be glycosylated) has an attractive point that it is free from any preparation step of reactive glycosyl donors from the corresponding 1-OH sugar derivatives.[4] The aim of this paper is to present simple synthesis of 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranose (**2**) and its use for the formally dehydrative glycosylation using the NST system[5] consisting of *p*-nitrobenzenesulfonyl chloride (NsCl), silver trifluromethanesulfonate (AgOTf), and triethylamine (Et_3N) as well as the NSDT system[6] composed of NsCl, AgOTf, *N*,*N*-dimethylacetamide (DMA), and Et_3N.## Similar glycosylations employing 2-azido-2-deoxy-D-galactopyranose (**3**) and -D-mannopyranose (**4**) were also carried out. This may provide an alternative route to 2-acetaminodeoxyglycoside starting from benzylated glycal (Scheme 1). Although many syntheses of 2-amino-2-deoxyhexopyranosides have been reported,[7] those employing such kind of glycosylation are very rare.[8]

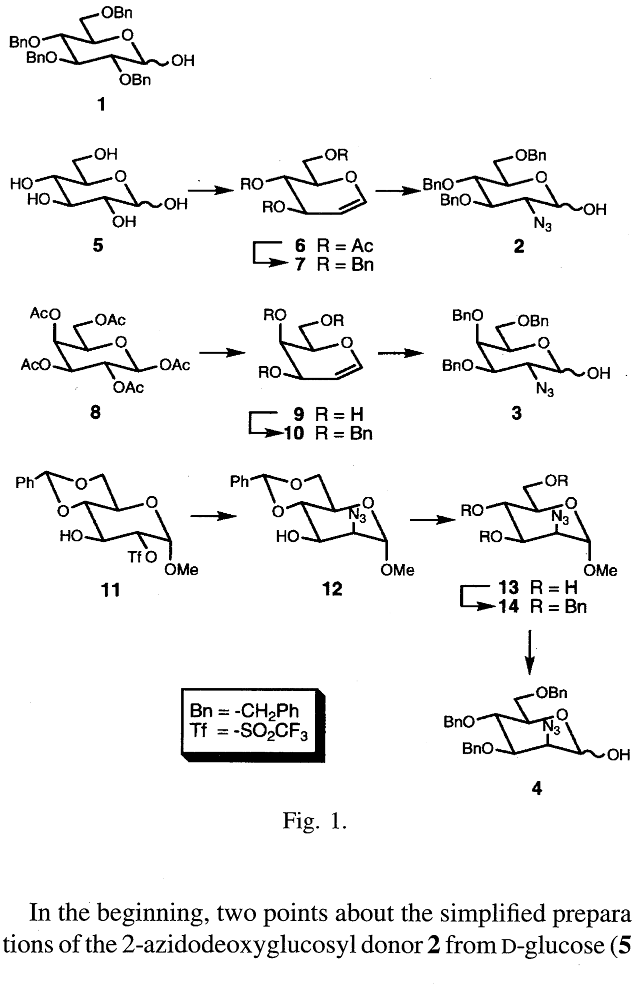

Fig. 1.

In the beginning, two points about the simplified preparations of the 2-azidodeoxyglucosyl donor **2** from D-glucose (**5**)

\# Present address: Department of Pharmacy, Kitasato University East Hospital, Asamizodai, Sagamihara 228.

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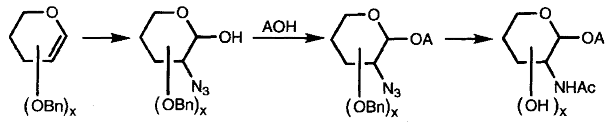

Scheme 1. A route to 2-acetamidodeoxyglycosides from benzyated glycal.

are worth noting. Many methods of transformation of **5** into the versatile acetylglucal **6** have been presented from time to time.[9] One practical drawback of the authentic method[10] is the filtration process to remove insoluble matters from the reaction mixture saturated with hydrogen bromide before treatment of the acetobromoglucose with zinc dust. The first point to be noted here is it that the use of a mixture of acetyl bromide and acetic acid[11,12] for acetobromination of **5**, followed by careful addition of aq sodium acetate, made it possible to omit this filtration process.[10] Thus, **6** was directly prepared from **5**, all in one-pot manner.[13] Convenient direct benzylation of the acetate **6** using neat benzyl chloride and potassium hydroxide[14] gave the benzylglucal **7**. The second point is that the 1-*O*-nitrate obtained by azidonitration[15] of **7** was found to hydrolyze simply on a silica-gel column[16] without use of any additional reagents.[17] Thus, adsorption of the crude nitrate on a column which was then kept standing overnight and subsequent elution afforded the hydrolyzate **2**.[18] After all, **2** was prepared from **5** in 21% of overall yield.

For the 2-azidodeoxygalactosyl donor **3**, the intermediate D-galactal (**9**) was prepared from the acetate **8** by way of a simplified process consisting of a one-pot 1-bromination[19] and reduction with zinc dust. Azidonitration of the benzyl-potected **10**, followed by hydrolysis on a silica gel column as described above, furnished **3**.[20] Overall yield of **3** from **8** was 35%.

Conversion of **5** into the 2-azidodeoxymannosyl donor **4** was carried out by way of controlled azidonitration of **7** in ethyl acetate at −40 °C.[21] Since **4** was syrupy, its complete separation from the main product **2** had to be done by repeating the chromatographies of the mother liquor of **2**. So **4** was prepared from the known triflate **11**[22] via displacement of the 2-OTf group by N_3 group with the inversion of the configuration at the C-2 position.[23] Treatment of **11**[22] with tetrabutylammonium azide (4.4 equiv)[24] in place of sodium azide (10 equiv)[23] for a significantly shorter reaction time (16 h vs. 4 d[23]) improved notably the yield of the 2-azidodeoxymannoside **12** (89% vs. 79%[23]). Removal of benzylidene group of **12**, followed by benzylation and hydrolysis, afforded **4**.[25] The overall yield of **4** from **11** was 36%.

The 2-azidodeoxyhexosyl donors, **2**, **3**, and **4**, thus prepared, were reacted with the acceptors **15**, **16**, **17**, and **18** (Fig. 2), with the aid of the NST system (Fig. 3).[5] As observed in the previously reported glycosylation using **1** and the NST system,[5,26] the present cases using **2** and the NST system showed moderate to marginal *β*-selectivities. The acceptor **18** having a primary OH group was glycosylated with **2** with acceptable *β*-selectivity (Table 1, Run 7). With the other acceptors, **15**, **16**, and **17**, having a secondary OH group, the *β*-selectivities diminished (Runs 1, 3, and 5).

The *β*-selectivities of the galacto-isomer **3** (Runs 9, 11, and 15) were less than those of **2** described above; the condensation with **17** (Run 13) became slightly *α*-selective. Increase of the amount of the *α*-linked glycosides comparing to the cases of the gluco-isomer **2** could be explained if one considered that the benzyloxy group at C4 of the galacto-isomer **3** would stick out and interfere with the nucleophile coming from the *β*-side of the anomeric center as depicted by **a**. The manno-isomer **4** afforded the corresponding *α*-linked glycosides with good selectivities (Runs 17, 18, 19, and 20).

As shown in Table 1, the NSDT system[6] performed *α*-selective glycosylation of the acceptors, except for **18** (Run 8), with **2** (Runs 2, 4, and 6). Similarly, the donor **3** afforded the corresponding *α*-linked products with good selectivities (Runs 10, 12, 14, and 16).

The fully-benzylated 2$^{\text{II}}$-azidodeoxyglucobiosides### were reduced with lithium aluminum hydride in diethyl ether,[27] followed by acetylation; they gave the corresponding fully-benzylated 2$^{\text{II}}$-acetamidodeoxyglucobiosides; e.g., **19** gave **43**. Their catalytic total debenzylation furnished the corresponding 2$^{\text{II}}$-acetamidodeoxyglucobioses; e.g., **43** afforded **51** (Fig. 4).

The above-described *β*-glycosylation using **2** and the NST system was applied to the synthesis of the trisaccharide **59**, the repeating unit of the main chain of O-specific acidic cell wall polysaccharide of *E. coli* 058,[28] following Scheme 2. Starting from D-mannose (**67**), the preparation of the 4-OH compound **60** included four steps (Fig. 5). The selective monoacetalization[29] of **68** and the convenient reductive ring-opening reaction with the aid of triethylsilane and trifluoroacetic acid[30,31] afforded **60**. The mannoside **71** was similarly converted into the 4-OH compound **64**.

Condensation of **2** and **60** gave the desired *β*-linked product **62** (45%) with concomitant formation of the *α*-linked **61** (36%). Deallylation of **62** with palladium(II) chloride[32] gave the biosyl donor **63**. Condensation of **64** with the biosyl donor **63** using the NST was performed to form the desired *α*-linked trisaccharide derivative **65** (52%) with complete

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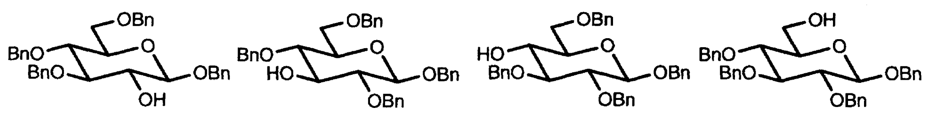
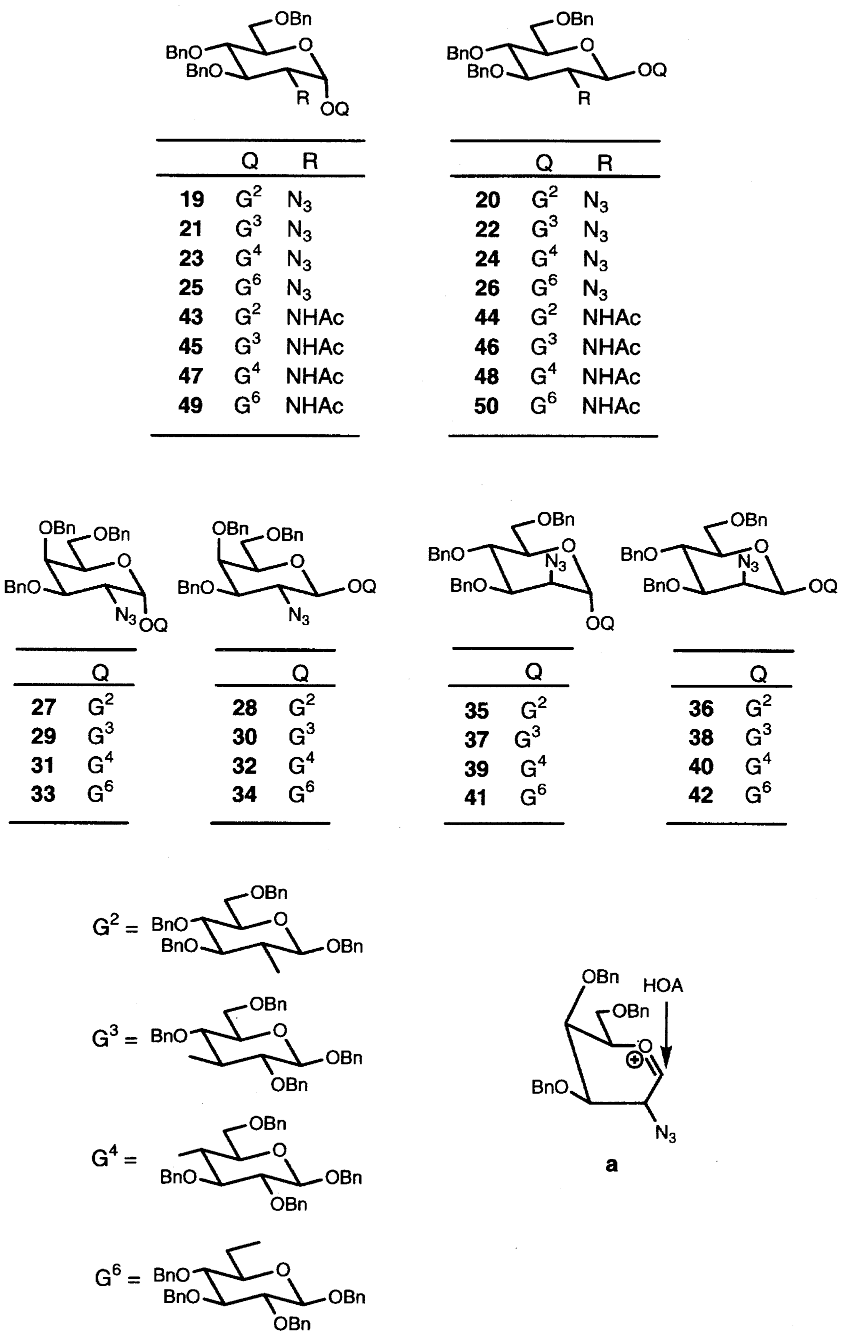
###The codes using Roman numerals follow the systematic nomenclature issued recently: *Adv. Carbohydr. Chem. Biochem.*, **52**, 154 (1997).



15 **16** **17** **18**

Fig. 2.



	Q	R
19	G^2	N_3
21	G^3	N_3
23	G^4	N_3
25	G^6	N_3
43	G^2	NHAc
45	G^3	NHAc
47	G^4	NHAc
49	G^6	NHAc

	Q	R
20	G^2	N_3
22	G^3	N_3
24	G^4	N_3
26	G^6	N_3
44	G^2	NHAc
46	G^3	NHAc
48	G^4	NHAc
50	G^6	NHAc

	Q
27	G^2
29	G^3
31	G^4
33	G^6

	Q
28	G^2
30	G^3
32	G^4
34	G^6

	Q
35	G^2
37	G^3
39	G^4
41	G^6

	Q
36	G^2
38	G^3
40	G^4
42	G^6

Fig. 3.

selectivity. Reduction of **65** with lithium aluminum hydride and acetylation afforded **66**. The final catalytic total debenzylation furnished the desired trisaccharide **59**.

In conclusion, the formally dehydrative glycosylation using the NST system performs β-selective 2-azidodeoxyglycosylation for the 1-OH sugar derivatives **2** and **3**, whereas that for **4** proceeds in an α-selective manner. The NSDT system is convenient for α-selective 2-azidodeoxyglycosylation using **2** and **3**.

Experimental[33]

The acetate **8** was purchased from Kyowa Junyaku Kogyo Co., Ltd. Compounds **15**,[14] **16**,[14] **17**,[31] and **18**,[34] were prepared by way of the published methods. 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 chloroform–methanol (CM), hexane–ethyl acetate (HE), and toluene–2-butanone (TK). Hydrogenolytic debenzylation was carried out using a Parr-3911 hydrogenation apparatus under 340 kPa of H_2 at room temp. Evaporation was carried out under reduced pressure. The optical rotations were measured on a JASCO DIP-180 Digital Polarimeter at room temp. The ^{1}H and ^{13}C NMR spectra were recorded with a Varian VXR300 spectrometer, along with the measurements of H,H-COSY, C,H-COSY, and DEPT spectra.

^{13}C NMR results of eight *O*-(2-acetamido-2-deoxy-D-glucopyranosyl)-(1→*x*)-D-glucopyranoses are summarized in Table 2.

Table 1. Results of Glycosylation Using 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-hexoses[a)]

Run	Acceptor/mmol		Donor/equiv		Reagent[b,c)]/equiv		Condensates	% (α/β)
1	**15**	0.081	**2**	1.3	NST	3.0	**19+20**	82 (33/67)
2	**15**	0.081	**2**	1.3	NSDT	3.5	**19+20**	56 (70/30)
3	**16**	0.081	**2**	1.3	NST	3.0	**21+22**	81 (34/66)
4	**16**	0.081	**2**	1.3	NSDT	3.5	**21+22**	54 (79/21)
5	**17**	0.081	**2**	1.3	NST	3.0	**23+24**	82 (47/53)
6	**17**	0.081	**2**	1.3	NSDT	3.5	**23+24**	52 (100/0)
7	**18**	0.096	**2**	1.1	NST	2.0	**25+26**	98 (10/90)
8	**18**	0.096	**2**	1.1	NSDT[d)]	2.5	**25+26**	65 (42/58)
9	**15**	0.100	**3**	1.3	NST	3.0	**27+28**	78 (48/52)
10	**15**	0.072	**3**	1.3	NSDT	3.5	**27+28**	66 (82/18)
11	**16**	0.090	**3**	1.3	NST	3.0	**29+30**	81 (32/68)
12	**16**	0.076	**3**	1.3	NSDT	3.5	**29+30**	73 (73/27)
13	**17**	0.089	**3**	1.3	NST	3.0	**31+32**	81 (58/42)
14	**17**	0.074	**3**	1.3	NSDT	3.5	**31+32**	61 (81/19)
15	**18**	0.061	**3**	1.1	NST	2.0	**33+34**	73 (27/73)
16	**18**	0.083	**3**	1.1	NSDT[d)]	2.5	**33+34**	71 (52/48)
17	**15**	0.155	**4**	1.3	NST	3.0	**35+36**	66 (82/18)
18	**16**	0.141	**4**	1.3	NST	3.0	**37+38**	66 (82/18)
19	**17**	0.083	**4**	1.3	NST	3.0	**39+40**	66 (82/18)
20	**18**	0.083	**4**	1.1	NST	2.0	**41+42**	66 (82/18)

a) Reaction was carried out in CH_2Cl_2 (10 ml mg^{-1} of donor). b) NST[5)] = NsCl+AgOTf+Et_3N. c) NSDT[6)] = NsCl+AgOTf+DMA+Et_3N. d) The amount of DMA was 5.0 equiv and those of NsCl, AgOTf, and Et_3N were 2.5 equiv.[6)]

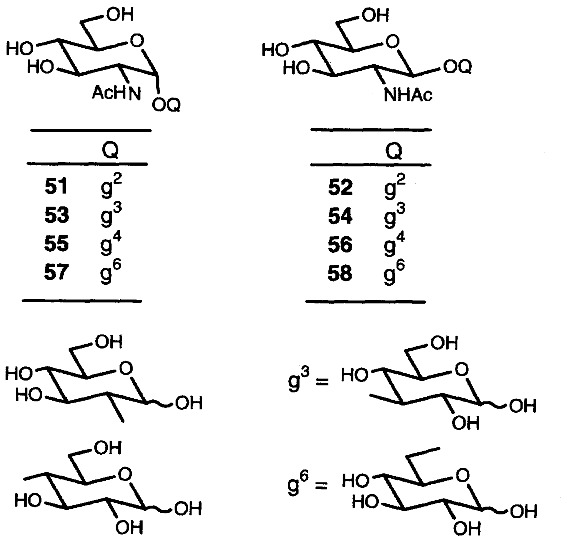
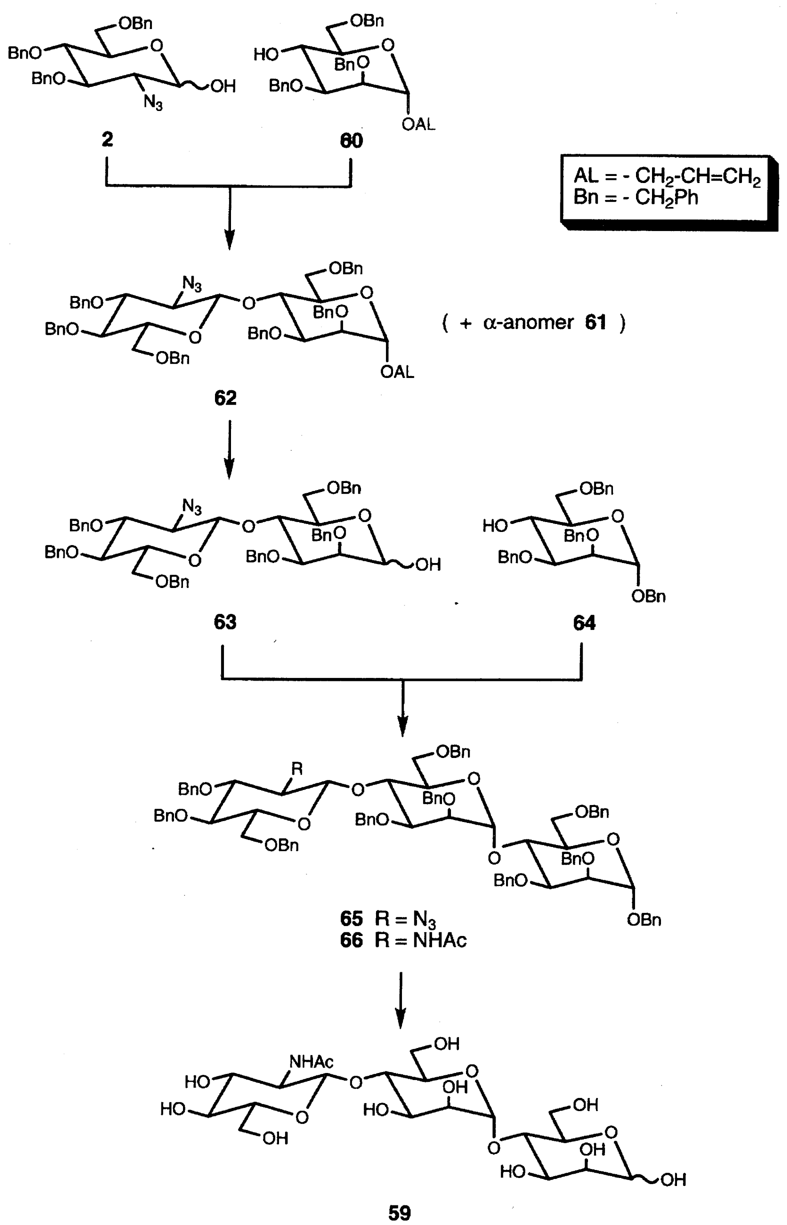


Fig. 4.

2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranose (2). To a cooled mixture of anhydrous **5** (5.0 g, 27.8 mmol) and AcBr (28 ml), AcOH (13 ml) was added under stirring in a hood. The mixture was stirred for 1 h at 20 °C. To the mixture, crushed ice (5 g) and a cold solution composed of NaOAc (43 g), AcOH (107 ml), and H_2O (61 ml) were slowly added under stirring at −5 °C. The temperature of the mixture was kept below 10 °C. To the resulting mixture, Zn dust (10 g) and $CuSO_4{\cdot}5H_2O$ (1.0 g) were added under stirring at 0 °C. After being stirred for 1 h at 0 °C, the mixture was filtered and the combined filtrate was extracted with PhMe (200 ml) three times. The organic layer was washed with aq $NaHCO_3$ (5%, 200 ml) three times and H_2O (200 ml). After concentration, the residue was chromatographed using TK system (100 : 1 → 3 : 1) to give **3,4,6-tri-*O*-acetyl-D-glucal (6)** (3.9 g, 52%), mp 53—55 °C, $[\alpha]_D$ −23 (*c* 1.5, $CHCl_3$) (lit,[8)] mp 54—55 °C, $[\alpha]_D$ −12.4 (*c*, $CHCl_3$)). A mixture of **6** (5.0 g, 18.2 mmol), powdered KOH (25 g), and $PhCH_2Cl$ (70 ml), was vigorously stirred for 2 h at 110 °C. To a cooled mixture, PhMe (200 ml) and H_2O (100 ml) were added under stirring. The organic layer was washed with H_2O (100 ml) three times. After concentration at 95 °C under reduced pressure, chromatography using HE (100 : 1 → 3 : 1) system afforded **3,4,6-tri-*O*-benzyl-D-glucal (7)** (6.45 g, 84%), mp 53—54 °C, $[\alpha]_D$ −2 (*c* 0.8, $CHCl_3$) (lit,[35)] mp 55 °C, $[\alpha]_D$ −2.7 (*c* 16.5, $CHCl_3$)). To a cold mixture of **7** (2.19 g, 5.2 mmol) and MeCN (44 ml), $(NH_4)_2Ce^{IV}(NO_3)_6$ (7.37 g) and NaN_3 (0.675 g) were successively added with stirring at −20 °C under atmosphere of N_2.[18)] After this reaction mixture had been stirred for 1 h, CH_2Cl_2 (100 ml) and H_2O (50 ml) were added under stirring. Organic layer was washed with H_2O (50 ml) twice, concentrated and adsorbed on the top of a silica-gel column. After being kept standing at room temp overnight, the column was eluted with TK (100 : 1 → 3 : 1) system to furnish the title **2** (1.21 g, 21% from **5**), mp 100—102 °C, $[\alpha]_D$ +17 (*c* 0.8, $CHCl_3$) (lit,[18)] mp 96—100 °C, $[\alpha]_{578}$ +18.1 (*c*, $CHCl_3$)); ^{1}H NMR ($CDCl_3$) (72% α) δ = 3.236 (d, *J* = 3.0 Hz, OH α), 3.372 (dd, *J* = 7.5, 9.5 Hz, H2 β), 3.758 (d, *J* = 5.5 Hz, OH β), 4.022 (dd, *J* = 9.0, 10.0 Hz, H3 α), 4.084 (ddd, *J* = 2.5, 9.0, 10.0 Hz, H5 α), 5.325 (qt, *J* = 3.0, 3.5 Hz, H1 α); ^{13}C NMR ($CDCl_3$) δ = 64.0 (C2 α), 67.5 (C2 β), 68.5 (C6 α), 68.6 (C6 β), 70.7 (C5 α), 74.9 (C5 β), 77.7 (C4 β), 78.5 (C4 α), 80.1 (C3 α), 83.1 (C3 β), 92.1 (C1 α), 96.2 (C1 β).

Found: C, 68.11; H, 6.09; N, 8.73%. Calcd for $C_{27}H_{29}N_3O_5$: C, 68.19; H, 6.15; N, 8.84%.

2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactopyranose (3). To a cold solution of **8** (3.0 g, 7.7 mmol) and $CHCl_3$ (9.0 ml), AcBr (3.0 ml) and H_2O (0.5 ml) were successively added under stirring at 0 °C. After being stirred for 1 h at 20 °C, the mixture was evaporated and co-evaporated with PhMe to give a residue which was dissolved in AcOH (24 ml). To this, H_2O (24 ml), Zn dust



Scheme 2. Synthesis of *O*-*β*-D-GlcNAc*p*-(1→4)-*O*-*α*-Man*p*-(1→4)-D-Man*p* (**59**).

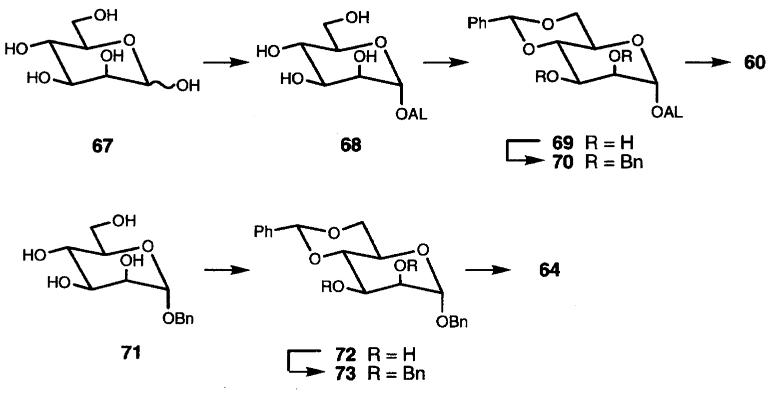


Fig. 5.

Table 2. ^{13}C NMR Spectral Data of 2-Acetamido-2-deoxy-D-glucopyranosyl-(1→*x*)-D-glucopyranoses (75.5 MHz, in D_2O)

	51		**52**		**53**		**54**		**55**		**56**		**57**		**58**	
	α	β	α	β	α	β	α	β	α	β	α	β	α	β	α	β
1	90.3	98.1	92.5	95.5	93.2	96.9	93.2	97.0	92.9	96.7	92.7	96.6	93.0	97.0	93.0	96.8
2	76.6	80.8	81.5	82.2	71.3	74.0	72.2	74.9	72.8	75.6	72.2	74.7	72.4	75.0	72.2	74.9
3	72.3	75.4	72.5	76.8	81.0	83.4	83.3	85.6	74.4	77.4	72.4	75.4	73.8	76.8	73.6	76.6
4	70.6	70.9	70.6	70.6^6	71.1	71.0	69.2	69.3	77.2	77.1	80.5	80.3	70.2	70.1	70.4	70.4
5	72.2	76.7	72.0	76.6	72.4	76.8	72.1	76.5	71.1	75.8	70.7^4	75.5	71.1	75.2	71.1	75.6
6	61.6	61.9	61.3	61.7	61.2	61.5	61.6	61.8	61.8	61.9	61.1^0	60.9^9	66.4	66.3	69.3	69.5
1′	95.7	97.3	103.6	102.3	98.9	98.8^7	102.9^3	102.8^8	99.1^4	99.0^8	102.3	102.4	97.8	97.7	102.5	102.6
2′	54.6	54.7	56.6	56.7	54.9	54.8	56.8	56.8	54.9^1	54.8^6	56.6^0	56.5^5	54.5	54.4	56.3	56.3
3′	71.7	71.7	74.6	74.6	71.9	71.9	74.7	74.6	71.8	71.8	74.4	74.4	71.9	72.0	74.5	74.5
4′	70.8	70.7	70.7^4	70.7^4	70.9	70.7	70.9	70.9	70.8	70.8	70.6^9	70.6^9	70.7	70.7	70.7	70.7
5′	72.9	72.8	76.5	76.5	72.9^2	72.8^8	76.9	76.9	73.8	73.8	76.8	76.8	72.8	72.8	76.7	76.7
6′	61.3	61.2	61.5	61.5	61.4	61.4	61.7	61.7	61.5	61.5	61.5	61.5	61.3	61.3	61.5	61.5
Me	22.9^1	22.8^6	23.0	23.0	23.0	23.0	23.2	23.2	23.0	23.0	23.0	23.0	25.8	25.8	23.1	23.1
CO	175.4	175.4	175.8	175.7	175.4	175.4	175.9	175.9	175.5	175.5	175.5	175.5	175.2^6	175.3^1	175.5^8	175.6^2

(2.9 g), and $CuSO_4 \cdot 5H_2O$ (0.29 g) were successively added under stirring at 0 °C. After being stirred for 1 h at 0 °C, the mixture was processed as described for **6** and concentrated to give a syrup, which was treated with NaOMe (8%, 0.3 ml) in MeOH (36 ml) for 5 h at room temp. After neutralization with AcOH, concentration and chromatography with CM system (100 : 1 → 4 : 1) afforded **D-galactal (9)** (0.97 g, 86%), mp 87—90 °C (lit,36) mp 104 °C). To a mixture of **9** (1.4 g, 9.5 mmol), DMF (13.8 ml), and $PhCH_2Br$ (6.4 ml), NaH (ca. 60% dispersion in oil. 0.24 g) was added at 0 °C under stirring. After 1 h, PhMe (100 ml) and H_2O (30 ml) were cautiously added to the mixture under stirring. The organic layer was washed with H_2O (30 ml) three times, concentrated at 95 °C under reduced pressure, and chromatographed with HE (100 : 1 → 3 : 1) system to furnish **3,4,6-tri-*O*-benzyl-D-galactal (10)** (3.9 g, 98%), mp 47—48 °C, $[\alpha]_D$ −46 (*c* 0.9, $CHCl_3$) (lit,37) mp 51 °C, $[\alpha]_D$ −45 (*c* 1.0, $CHCl_3$)). As described for **2** from **7**, compound **10** (2.57 g, 6.1 mmol) dissolved in MeCN (35 ml) was treated with $(NH_4)_2Ce^{IV}(NO_3)_6$ (11.22 g) and NaN_3 (0.67 g) at −20 °C for 1 h under atmosphere of N_2, followed by hydrolysis on a silica-gel column. Elution with TK system (100 : 1 → 3 : 1) furnished the title **3** (1.23 g, 35% from **8**), $[\alpha]_D$ +25 (*c* 0.9, $CHCl_3$) (lit,20) $[\alpha]_D$ +98.2 (*c* 1, $CHCl_3$)); ^1H NMR ($CDCl_3$) (67% α) δ = 3.347 (dd, *J* = 2.5, 10.0 Hz, H3 β), 3.787 (dd, *J* = 8.0, 10.0 Hz, H2 β), 3.856 (d, *J* = 0.0, 2.5 Hz, H4 β), 4.162 (t, *J* = 0.0, 6.0, 6.0 Hz, H5 α), 5.311 (d, *J* = 2.5 Hz, H1 α); ^{13}C NMR ($CDCl_3$) δ = 60.3 (C2 α), 64.6 (C2 β), 68.6 (C6 β), 69.2 (C6 α), 69.6 (C5 α), 72.2 (C4 β), 73.1 (C5 β), 73.5 (C4 α), 77.3 (C3 α), 80.8 (C3 β), 92.3 (Cl α), 96.4 (C1 β).

Found: C, 67.96; H, 6.15; N, 8.67%. Calcd for $C_{27}H_{29}N_3O_5$: C, 68.19; H, 6.15; N, 8.84%.

Methyl 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-mannopyranoside (14). A solution of **11**22) (1.606 g, 3.9 mmol) in *N*,*N*-dimethylformamide (DMF, 3.6 ml) was treated with tetrabutylammonium azide (4.92 g) at room temp for 16 h. The mixture was diluted with PhMe (200 ml) and H_2O (100 ml). The organic layer was washed twice with H_2O (50 ml), evaporated and chromatographed to give **methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-mannopyranoside (12)** (1.07 g, 89%), $[\alpha]_D$ +76 (*c* 1.3, $CHCl_3$) (lit,23,38) $[\alpha]_D$ +69.5 (*c* 1.059, $CHCl_3$)). A mixture of **14** (535 mg, 1.74 mmol), $CHCl_3$ (50 ml), MeOH (10 ml), and CF_3CO_2H (1.0 ml) was kept standing for 2 h at room temp. A sample of the mixture was evaporated and chromatographed with CM system (100 : 1 → 3 : 1) to give **methyl 2-azido-2-deoxy-α-D-mannopyranoside (13)**, $[\alpha]_D$ +105 (*c* 0.5, MeOH); ^1H NMR ($CDCl_3$) δ = 3.395 (Me), 3.672 (t, *J* = 9.0 Hz, H4), 3.983 (dd, *J* = 3.5, 9.0 Hz, H3), 4.012 (dd, *J* = 1.0, 3.5 Hz, H2), 4.848 (d, *J* = 1.0 Hz, H1); ^{13}C NMR ($CDCl_3$) δ = 57.5 (Me), 63.3 (C6), 66.3 (C2), 69.5 (C5), 73.1 (C4), 75.2 (C3), 101.6 (C1, $J_{C,H}$ = 173.4 Hz).

Found: C, 38.08; H, 5.81; N, 18.96%. Calcd for $C_7H_{13}N_3O_5$: C, 38.36; H, 5.98; N, 19.17%.

The rest of the mixture was evaporated to dryness to give a residue. This was dissolved in DMF (6.1 ml) and treated with benzyl bromide (1.39 ml) and NaH (60% dispersion, 418 mg) under stirring at 0 °C. After being stirred at room temp for 1 h, the mixture was processed as described for **10** and chromatographed with HE system (100 : 1 → 3 : 1) to yield the titled **14** (535 mg, 56% from **11**), $[\alpha]_D$ +58 (*c* 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$) δ = 3.351 (Me), 3.887 (t, *J* = 9.0 Hz, H4), 3.936 (dd, *J* = 2.0, 4.0 Hz, H2), 4.055 (dd, *J* = 4.0, 9.0 Hz, H3), 4.723 (d, *J* = 2.0 Hz, H1); ^{13}C NMR ($CDCl_3$) δ = 54.9 (Me), 61.2 (C2), 68.8 (C6), 71.5 (C5), 74.5 (C4), 79.8 (C3), 99.1 (C1).

Found: C, 68.55; H, 6.41; N, 8.16%. Calcd for $C_{28}H_{31}N_3O_5$: C, 68.69; H, 6.38; N, 8.58%.

2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-α-D-mannopyranose (4). A mixture of **14** (619 mg, 1.27 mmol), AcOH (12 ml) and dil H_2SO_4 (30%, 12 ml), was stirred at 95 °C for 4 h. After being diluted with PhMe (100 ml) and H_2O (50 ml), the organic layer was washed with dil $NaHCO_3$ (5%, 30 ml) and H_2O (30 ml). Evaporation and chromatography with TK system (100 : 1 → 3 : 1) afforded the starting **14** (191.1 mg, 31%) and the title **4** (279.1 mg, 67% based on the consumed **14**), $[\alpha]_D$ +42 (*c* 0.6, $CHCl_3$) (lit,25) $[\alpha]_D$ +27.2 (*c* 1, $CHCl_3$)); ^1H NMR ($CDCl_3$) (82% α) δ = 3.732 (t, *J* = 10.0 Hz, H4), 3.880 (dd, *J* = 2.0, 4.0 Hz, H2 α), 4.010 (ddd, *J* = 2.0, 6.0, 10.0 Hz, H5 α), 4.012 (dd, *J* = 4.0, 10.0 Hz, H3 α), 4.634 (dd, *J* = 1.5, 4.0 Hz, H1 β), 5.157 (dd, *J* = 2.0, 3.0 Hz, H1 α); ^{13}C NMR ($CDCl_3$) δ = 61.6 (C2), 68.7 (C6 β), 69.3 (C6 α), 71.3 (C5 α), 74.1 (C5 β), 74.8 (C4), 79.3 (C3 α), 81.7 (C3 β), 92.8 (C1 α), 92.9 (C1 β).

Found: C, 68.05; H, 6.26; N, 8.73%. Calcd for $C_{27}H_{29}N_3O_5$: C, 68.19; H, 6.15; N, 8.84%.

Glycosylation. To a mixture of donor, acceptor, NsCl, AgOTf, (DMA), and $\mathrm{CH_2Cl_2}$, $\mathrm{Et_3N}$ was added under stirring at −60 °C (bath temp). The bath temp was allowed to rise to 0 °C. After being stirred overnight, the reaction mixture was processed in the manner described before.[33] Preliminary chromatography was carried out using the TK system as before.[33] The system for chromatography used for anomeric separation in each case is specified below.

Benzyl *O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-*α*- and *β*-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranoside (19 and 20). **19** (HE system (3 : 1), faster-moving), $[\alpha]_{\mathrm{D}}$ +43 (*c* 0.7, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.293$ (dd, $J = 3.5$, 10.0 Hz, H2$^{\mathrm{II}}$), 3.487 (ddd, $J = 2.5$, 3.5, 9.0 Hz, H5$^{\mathrm{I}}$), 3.617 (t, $J = 9.0$ Hz, H3$^{\mathrm{I}}$), 3.693 (t, $J = 9.0$ Hz, H4$^{\mathrm{I}}$), 3.715 (dd, $J = 9.0$, 10.0 Hz, H4$^{\mathrm{II}}$), 3.753 (dd, $J = 7.5$, 9.0 Hz, H2$^{\mathrm{I}}$), 3.928 (t, $J = 9.0$ Hz, H3$^{\mathrm{II}}$), 4.010 (dt, $J = 2.0$, 2.0, 10.0 Hz, H5$^{\mathrm{II}}$), 4.577 (d, $J = 7.5$ Hz, H1$^{\mathrm{I}}$), 5.673 (d, $J = 3.5$ Hz, H1$^{\mathrm{II}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 63.2$ (C2$^{\mathrm{II}}$), 67.7 (C6$^{\mathrm{II}}$), 68.7 (C6$^{\mathrm{I}}$), 70.3 (C5$^{\mathrm{II}}$), 75.0 (C5$^{\mathrm{I}}$), 75.9 (C2$^{\mathrm{I}}$), 78.2 (C4$^{\mathrm{II}}$), 78.7 (C4$^{\mathrm{I}}$), 80.1 (C3$^{\mathrm{II}}$), 83.2 (C3$^{\mathrm{I}}$), 96.6 (C1$^{\mathrm{II}}$), 102.4 (C1$^{\mathrm{I}}$).

20: Mp 125—126 °C, $[\alpha]_{\mathrm{D}}$ −27 (*c* 1.8, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.261$ (ddd, $J = 2.5$, 3.5, 9.5 Hz, H5$^{\mathrm{II}}$), 3.387 (t, $J = 9.0$ Hz, H3$^{\mathrm{II}}$), 3.441 (dd, $J = 7.5$, 9.0 Hz, H2$^{\mathrm{II}}$), 3.505 (ddd, $J = 2.0$, 4.0, 9.5 Hz, H5$^{\mathrm{I}}$), 3.775 (t, $J = 8.5$ Hz, H3$^{\mathrm{I}}$), 3.937 (dd, $J = 7.5$, 8.5 Hz, H2$^{\mathrm{I}}$), 4.543 (d, $J = 7.5$ Hz, H1$^{\mathrm{I}}$), 4.738 (d, $J = 7.5$ Hz, H1$^{\mathrm{II}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 66.9$ (C2$^{\mathrm{II}}$), 67.7 (C6$^{\mathrm{II}}$), 68.3 (C6$^{\mathrm{I}}$), 74.9 (C5$^{\mathrm{I}}$), 75.2 (C5$^{\mathrm{II}}$), 77.9 (C4$^{\mathrm{II}}$), 78.3 (C4$^{\mathrm{I}}$), 78.6 (C2$^{\mathrm{I}}$), 83.3 (C3$^{\mathrm{II}}$), 85.2 (C3$^{\mathrm{I}}$), 100.8 (C1$^{\mathrm{I}}$), 101.0 (C1$^{\mathrm{I}}$).

Found: **19**; C, 73.32; H, 6.35; N, 4.30%. **20**; C, 73.05; H, 6.43; N, 4.12%. Calcd for $\mathrm{C_{61}H_{63}N_3O_{10}}$: C, 73.40; H, 6.36; N, 4.21%.

Benzyl *O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-*α*- and *β*-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-*β*-D-glucopyranoside (21 and 22). **21** (TE system (8 : 1), faster-moving), $[\alpha]_{\mathrm{D}}$ +15 (*c* 1.3, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.328$ (dd, $J = 3.5$, 10.0 Hz, H2$^{\mathrm{II}}$), 3.440 (dd, $J = 7.5$, 9.0 Hz, H2$^{\mathrm{I}}$), 3.698 (dd, $J = 9.0$, 10.0 Hz, H4$^{\mathrm{II}}$), 3.845 (t, $J = 9.0$ Hz, H3$^{\mathrm{I}}$), 3.967 (dd, $J = 9.0$, 10.0 Hz, H3$^{\mathrm{II}}$), 4.119 (dt, $J = 2.0$, 2.0, 10.0 Hz, H5$^{\mathrm{I}}$), 4.514 (d, $J = 7.5$ Hz, H1$^{\mathrm{I}}$), 5.525 (d, $J = 3.5$ Hz, H1$^{\mathrm{II}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 63.4$ (C2$^{\mathrm{II}}$), 67.5 (C6$^{\mathrm{II}}$), 68.5 (C6$^{\mathrm{I}}$), 70.1 (C5$^{\mathrm{II}}$), 74.8 (C5$^{\mathrm{I}}$), 78.3 (C4$^{\mathrm{I,II}}$), 79.3 (C3$^{\mathrm{I}}$), 79.6 (C2$^{\mathrm{I}}$), 80.4 (C3$^{\mathrm{II}}$), 97.6 (C1$^{\mathrm{II}}$), 102.7 (C1$^{\mathrm{I}}$).

22: $[\alpha]_{\mathrm{D}}$ −19 (*c* 2.6, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.293$ (ddd, $J = 2.0$, 4.0, 9.0 Hz, H5$^{\mathrm{II}}$), 3.330 (qt, $J = 9.0$, 9.5 Hz, H3$^{\mathrm{II}}$), 3.446 (dd, $J = 8.0$, 9.5 Hz, H2$^{\mathrm{II}}$), 3.593 (qt, $J = 9.0$, 9.5 Hz, H4$^{\mathrm{I}}$), 3.673 (t, $J = 9.0$ Hz, H4$^{\mathrm{II}}$), 4.067 (qt, $J = 9.0$, 9.5 Hz, H3$^{\mathrm{I}}$), 4.488 (d, $J = 7.5$ Hz, H1$^{\mathrm{I}}$), 4.942 (d, $J = 8.0$ Hz, H1$^{\mathrm{II}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 66.9$ (C2$^{\mathrm{II}}$), 68.7 (C6$^{\mathrm{II}}$), 69.2 (C6$^{\mathrm{I}}$), 74.7 (C5$^{\mathrm{I}}$), 75.0 (C5$^{\mathrm{II}}$), 76.3 (C4$^{\mathrm{I}}$), 78.0 (C4$^{\mathrm{II}}$), 81.0 (C3$^{\mathrm{I}}$), 82.6 (C2$^{\mathrm{I}}$), 83.1 (C3$^{\mathrm{II}}$), 101.6 (C1$^{\mathrm{II}}$), 102.3 (C1$^{\mathrm{II}}$).

Found: **21**; C, 73.13; H, 6.42; N, 4.17%. **22**; C, 73.21; H, 6.43; N, 4.15%. Calcd for $\mathrm{C_{61}H_{63}N_3O_{10}}$: C, 73.40; H, 6.36; N, 4.21%.

Benzyl *O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-*α*- and *β*-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-*β*-D-glucopyranoside (23 and 24). **23** (HE system (3 : 1), faster-moving), $[\alpha]_{\mathrm{D}}$ +27 (*c* 0.8, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.260$ (dd, $J = 4.0$, 10.0 Hz, H2$^{\mathrm{II}}$), 3.578 (dd, $J = 7.5$, 9.0 Hz, H2$^{\mathrm{I}}$), 3.690 (dd, $J = 8.0$, 9.5 Hz, H4$^{\mathrm{II}}$), 3.787 (t, $J = 9.0$ Hz, H3$^{\mathrm{I}}$), 3.871 (dd, $J = 8.0$, 10.0 Hz, H3$^{\mathrm{II}}$), 4.557 (d, $J = 7.5$, Hz, H1$^{\mathrm{I}}$), 5.737 (d, $J = 4.0$ Hz, H1$^{\mathrm{II}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 63.2$ (C2$^{\mathrm{II}}$), 67.9 (C6$^{\mathrm{II}}$), 69.4 (C6$^{\mathrm{I}}$), 71.4 (C5$^{\mathrm{II}}$), 73.2 (C4$^{\mathrm{I}}$), 74.4 (C5$^{\mathrm{I}}$), 78.1 (C4$^{\mathrm{II}}$), 80.0 (C3$^{\mathrm{II}}$), 82.6 (C2$^{\mathrm{I}}$), 97.6 (C1$^{\mathrm{II}}$), 102.4 (C1$^{\mathrm{I}}$).

24: $[\alpha]_{\mathrm{D}}$ −19 (*c* 2.1, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.219$ (ddd, $J = 2.0$, 4.0, 9.5 Hz, H5$^{\mathrm{II}}$), 3.308 (t, $J = 9.0$ Hz, H4$^{\mathrm{II}}$), 3.356 (dd, $J = 7.5$, 9.0 Hz, H2$^{\mathrm{II}}$), 3.517 (dd, $J = 7.5$, 9.0 Hz, H2$^{\mathrm{I}}$), 3.640 (t, $J = 9.0$ Hz, H3$^{\mathrm{I}}$), 3.656 (qt, $J = 9.0$, 9.5 Hz, H4$^{\mathrm{II}}$), 4.078 (qt, $J = 9.0$, 9.5 Hz, H4$^{\mathrm{I}}$), 4.420 (d, $J = 7.5$ Hz, H1$^{\mathrm{II}}$), 4.533 (d, $J = 7.5$ Hz, H1$^{\mathrm{I}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 67.0$ (C2$^{\mathrm{II}}$), 68.4 (C6$^{\mathrm{I}}$), 68.5 (C6$^{\mathrm{II}}$), 74.7 (C5$^{\mathrm{I}}$), 75.1 (C5$^{\mathrm{II}}$), 76.7 (C4$^{\mathrm{I}}$), 77.8 (C4$^{\mathrm{II}}$), 81.8 (C2$^{\mathrm{I}}$), 82.9 (C3$^{\mathrm{I}}$), 83.3 (C3$^{\mathrm{II}}$), 100.9 (C1$^{\mathrm{II}}$), 102.5 (C1$^{\mathrm{I}}$).

Found: **23**; C, 73.35; H, 6.44; N, 4.31%. **24**; C, 73.24; H, 6.42; N, 4.15%. Calcd for $\mathrm{C_{61}H_{63}N_3O_{10}}$: C, 73.40; H, 6.36; N, 4.21%.

Benzyl *O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-*α*- and *β*-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-*β*-D-glucopyranoside (25 and 26). **25** (TE system (8 : 1), faster-moving), mp 92—93 °C, $[\alpha]_{\mathrm{D}}$ +47 (*c* 1.5, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.376$ (dd, $J = 4.0$, 10.0 Hz, H2$^{\mathrm{II}}$), 4.000 (dd, $J = 9.0$, 10.0 Hz, H3$^{\mathrm{II}}$), 4.515 (d, $J = 7.5$ Hz, H1$^{\mathrm{I}}$), 5.631 (d, $J = 4.0$ Hz, H1$^{\mathrm{II}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 63.4$ (C2$^{\mathrm{II}}$), 66.4 (C6$^{\mathrm{I}}$), 68.2 (C6$^{\mathrm{II}}$), 70.6 (C5$^{\mathrm{II}}$), 74.3 (C5$^{\mathrm{I}}$), 78.0 (C4$^{\mathrm{I}}$), 78.2 (C4$^{\mathrm{II}}$), 80.1 (C3$^{\mathrm{II}}$), 82.3 (C2$^{\mathrm{I}}$), 84.7 (C3$^{\mathrm{I}}$), 97.9 (C1$^{\mathrm{II}}$), 102.3 (C1$^{\mathrm{I}}$).

26: Mp 152—153 °C, $[\alpha]_{\mathrm{D}}$ −8 (*c* 1.1, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.363$ (qt, $J = 9.0$, 9.5 Hz, H3$^{\mathrm{II}}$), 3.447 (t, $J = 9.0$ Hz, H4$^{\mathrm{II}}$), 3.486 (dd, $J = 8.0$, 9.5 Hz, H2$^{\mathrm{II}}$), 3.525 (dd, $J = 8.0$, 9.0 Hz, H2$^{\mathrm{I}}$), 4.403 (d, $J = 8.0$ Hz, H1$^{\mathrm{II}}$), 4.584 (d, $J = 8.0$ Hz, H1$^{\mathrm{I}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 66.3$ (C2$^{\mathrm{II}}$), 68.6 (C6$^{\mathrm{II}}$), 69.0 (C6$^{\mathrm{I}}$), 75.0 (C5$^{\mathrm{I,II}}$), 77.7 (C4$^{\mathrm{I}}$), 78.2 (C4$^{\mathrm{II}}$), 82.3 (C2$^{\mathrm{I}}$), 83.1 (C3$^{\mathrm{II}}$), 84.7 (C3$^{\mathrm{I}}$), 102.5^{5} (C1$^{\mathrm{II}}$), 102.5^{9} (C1$^{\mathrm{I}}$).

Found: **25**; C, 73.20; H, 6.38; N, 4.29%. **26**; C, 73.62; H, 6.30; N, 4.30%. Calcd for $\mathrm{C_{61}H_{63}N_3O_{10}}$: C, 73.40; H, 6.36; N, 4.21%.

Benzyl *O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-*α*- and *β*-D-galactopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranoside (27 and 28). **27** (DE system (20 : 1), faster-moving), $[\alpha]_{\mathrm{D}}$ +60 (*c* 1.5, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.634$ (t, $J = 9.0$, Hz, H3$^{\mathrm{I}}$), 3.677 (dd, $J = 4.5$, 9.0 Hz, H3$^{\mathrm{II}}$), 4.127 (t, $J = 0.0$, 6.5, 6.5 Hz, H5$^{\mathrm{II}}$), 4.575 (d, $J = 8.0$ Hz, H1$^{\mathrm{I}}$) 5.678 (d, $J = 1.5$ Hz, H1$^{\mathrm{I}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 59.7$ (C2$^{\mathrm{II}}$), 68.5 (C6$^{\mathrm{II}}$), 68.7 (C6$^{\mathrm{I}}$), 69.1 (C5$^{\mathrm{II}}$), 73.5 (C4$^{\mathrm{II}}$), 74.8 (C2$^{\mathrm{I}}$), 75.0 (C5$^{\mathrm{I}}$), 76.7 (C4$^{\mathrm{I}}$), 78.5 (C3$^{\mathrm{II}}$), 83.6 (C3$^{\mathrm{I}}$), 96.4 (C1$^{\mathrm{II}}$), 102.4 (C1$^{\mathrm{I}}$).

28: $[\alpha]_{\mathrm{D}}$ −12 (*c* 0.7, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.330$ (dd, $J = 2.5$, 10.0 Hz, H3$^{\mathrm{II}}$), 3.512 (ddd, $J = 2.0$, 4.5, 9.0 Hz, H5$^{\mathrm{I}}$), 3.658 (qt, $J = 8.5$, 9.0 Hz, H4$^{\mathrm{I}}$), 3.778 (t, $J = 8.5$ Hz, H3$^{\mathrm{I}}$), 3.867 (dd, $J = 8.0$, 10.0 Hz, H2$^{\mathrm{II}}$), 3.882 (dd, $J = 7.5$, 8.5 Hz, H2$^{\mathrm{I}}$), 4.549 (d, $J = 7.5$ Hz, H1$^{\mathrm{I}}$), 4.658 (d, $J = 8.0$ Hz, H1$^{\mathrm{II}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 63.7$ (C2$^{\mathrm{II}}$), 68.1 (C6$^{\mathrm{II}}$), 68.9 (C6$^{\mathrm{I}}$), 72.1 (C4$^{\mathrm{II}}$), 73.2 (C5$^{\mathrm{II}}$), 74.7 (C5$^{\mathrm{I}}$), 78.1 (C4$^{\mathrm{I}}$), 79.7 (C2$^{\mathrm{I}}$), 81.2 (C3$^{\mathrm{II}}$), 84.9 (C3$^{\mathrm{I}}$), 101.3^{8} (C1$^{\mathrm{I}}$), 101.4^{1} (C1$^{\mathrm{II}}$).

Found: **27**; C, 73.06; H, 6.41; N, 4.32%. **28**; C, 73.27; H, 6.43; N, 4.30%. Calcd for $\mathrm{C_{61}H_{63}N_3O_{10}}$: C, 73.40; H, 6.36; N, 4.21%.

Benzyl *O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-*α*- and *β*-D-galactopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-*β*-D-glucopyranoside (29 and 30). **29** (TE system (8 : 1), faster-moving), $[\alpha]_{\mathrm{D}}$ +43 (*c* 0.6, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.500$ (dd, $J = 7.5$, 9.0 Hz, H2$^{\mathrm{I}}$), 3.864 (t, $J = 9.0$ Hz, H3$^{\mathrm{I}}$), 4.317 (t, $J = 0.0$, 6.5, 6.5 Hz, H5$^{\mathrm{II}}$), 4.484 (d, $J = 7.5$ Hz, H1$^{\mathrm{I}}$), 5.507 (d, $J = 2.0$ Hz, H1$^{\mathrm{II}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 59.9$ (C2$^{\mathrm{II}}$), 68.4^{1} (C6$^{\mathrm{II}}$), 68.4^{4} (C6$^{\mathrm{I}}$), 68.9 (C5$^{\mathrm{II}}$), 73.4 (C4$^{\mathrm{II}}$), 74.8 (C5$^{\mathrm{I}}$), 77.1 (C4$^{\mathrm{I}}$), 77.3 (C3$^{\mathrm{I}}$), 79.3 (C3$^{\mathrm{II}}$), 80.0 (C2$^{\mathrm{I}}$), 97.5 (C1$^{\mathrm{II}}$), 102.8 (C1$^{\mathrm{I}}$).

30: $[\alpha]_{\mathrm{D}}$ −23 (*c* 2.9, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.259$ (dd, $J = 2.0$, 10.0 Hz, H3$^{\mathrm{II}}$), 3.394 (t, $J = 0.0$, 5.5, 5.5 Hz, H5$^{\mathrm{II}}$), 3.456 (ddd, $J = 2.0$, 4.0, 9.0 Hz, H5$^{\mathrm{I}}$), 3.593 (t, $J = 9.0$ Hz, H4$^{\mathrm{I}}$), 3.903 (dd, $J = 7.5$, 10.0 Hz, H2$^{\mathrm{II}}$), 3.648 (dd, $J = 7.5$, 9.0 Hz, H2$^{\mathrm{I}}$), 3.929 (d, $J = 0.0$, 2.5 Hz, H4$^{\mathrm{II}}$), 4.021 (t, $J = 9.0$ Hz, H3$^{\mathrm{I}}$), 4.470 (d, $J = 7.5$ Hz, H1$^{\mathrm{I}}$), 4.852 (d, $J = 7.5$ Hz, H1$^{\mathrm{II}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 63.8$ (C2$^{\mathrm{II}}$), 67.9 (C6$^{\mathrm{II}}$), 69.0 (C6$^{\mathrm{I}}$), 72.6 (C4$^{\mathrm{II}}$), 73.1 (C5$^{\mathrm{II}}$), 74.7 (C5$^{\mathrm{I}}$), 76.0 (C4$^{\mathrm{I}}$), 80.4 (C3$^{\mathrm{II}}$), 80.8 (C3$^{\mathrm{I}}$), 82.6 (C2$^{\mathrm{I}}$), 101.8 (C1$^{\mathrm{II}}$), 102.3 (C1$^{\mathrm{I}}$).

Found: **29**; C, 73.61; H, 6.36; N, 4.42%. **30**; C, 73.10; H, 6.41;

N, 4.06%. Calcd for $\mathrm{C_{61}H_{63}N_3O_{10}}$: C, 73.40; H, 6.36; N, 4.21%.

Benzyl *O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-α- and β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (31 and 32). **31** (HE system (3 : 1), faster-moving), $[\alpha]_\mathrm{D}$ +37 (*c* 1.4, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.700$ (dd, $J = 7.5$, 9.0 Hz, $\mathrm{H2^{I}}$), 3.915 (t, $J = 0.0$, 7.0, 7.0 Hz, $\mathrm{H5^{II}}$), 3.990 (s, $J = 0.0$, 0.0 Hz, $\mathrm{H4^{II}}$), 4.568 (d, $J = 7.5$ Hz, $\mathrm{H1^{I}}$), 5.714 (d, $J = 3.0$ Hz, $\mathrm{H1^{II}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 59.4$ ($\mathrm{C2^{II}}$), 68.6 ($\mathrm{C6^{II}}$), 69.9 ($\mathrm{C6^{I}}$), 70.1 ($\mathrm{C5^{II}}$), 72.9 ($\mathrm{C4^{II}}$), 73.7 ($\mathrm{C4^{I}}$), 74.4 ($\mathrm{C5^{I}}$), 77.1 ($\mathrm{C3^{II}}$), 82.6 ($\mathrm{C2^{I}}$), 84.9 ($\mathrm{C3^{I}}$), 97.9 ($\mathrm{C1^{II}}$), 102.3 ($\mathrm{C1^{I}}$).

32: $[\alpha]_\mathrm{D}$ −9 (*c* 1.2, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.263$ (dd, $J = 2.5$, 10.0 Hz, $\mathrm{H3^{II}}$), 3.589 (t, $J = 9.0$ Hz, $\mathrm{H3^{I}}$), 3.775 (ddd, $J = 8.0$, 10.0 Hz, $\mathrm{H2^{II}}$), 3.890 (d, $J = 0.0$, 2.5 Hz, $\mathrm{H4^{II}}$), 4.317 (d, $J = 8.0$ Hz, $\mathrm{H1^{II}}$), 4.517 (d, $J = 7.5$ Hz, $\mathrm{H1^{I}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 63.9$ ($\mathrm{C2^{II}}$), 67.8 ($\mathrm{C6^{II}}$), 68.4 ($\mathrm{C6^{I}}$), 72.2 ($\mathrm{C4^{II}}$), 73.1 ($\mathrm{C5^{II}}$), 74.8 ($\mathrm{C5^{I}}$), 76.6 ($\mathrm{C4^{I}}$), 80.9 ($\mathrm{C3^{II}}$), 81.8 ($\mathrm{C2^{I}}$), 82.9 ($\mathrm{C3^{I}}$), 101.2 ($\mathrm{C1^{II}}$), 102.6 ($\mathrm{C1^{I}}$).

Found: **31**; C, 73.53; H, 6.34; N, 4.18%. **32**; C, 73.30; H, 6.37; N, 4.16%. Calcd for $\mathrm{C_{61}H_{63}N_3O_{10}}$: C, 73.40; H, 6.36; N, 4.21%.

Benzyl *O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-α- and β-D-galactopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (33 and 34). **33** (HI system (3 : 2), faster-moving), mp 83—85 °C, $[\alpha]_\mathrm{D}$ +62 (*c* 0.7, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.850$ (d, $J = 3.5$, 10.5 Hz, $\mathrm{H2^{II}}$), 3.936 (dd, $J = 2.5$, 10.5 Hz, $\mathrm{H3^{II}}$), 4.003 (d, $J = 0.0$, 2.5 Hz, $\mathrm{H4^{II}}$), 4.030 (t, $J = 0.0$, 6.5, 6.5 Hz, $\mathrm{H5^{II}}$), 4.503 (d, $J = 8.0$ Hz, $\mathrm{H1^{I}}$), 5.645 (d, $J = 3.5$ Hz, $\mathrm{H1^{II}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 59.8$ ($\mathrm{C2^{II}}$), 66.7 ($\mathrm{C6^{II}}$), 68.6 ($\mathrm{C6^{I}}$), 69.7 ($\mathrm{C5^{II}}$), 73.5 ($\mathrm{C4^{II}}$), 74.4 ($\mathrm{C5^{I}}$), 76.9 ($\mathrm{C3^{II}}$), 78.2 ($\mathrm{C4^{I}}$), 82.3 ($\mathrm{C2^{I}}$), 84.7 ($\mathrm{C3^{I}}$), 98.6 ($\mathrm{C1^{II}}$), 102.4 ($\mathrm{C1^{I}}$).

34: Mp 124—126 °C, $[\alpha]_\mathrm{D}$ −13 (*c* 2.3, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.270$ (dd, $J = 2.5$, 10.0 Hz, $\mathrm{H3^{II}}$), 3.424 (qt, $J = 8.5$, 9.0 Hz, $\mathrm{H4^{I}}$), 3.492 (qt, $J = 0.0$, 6.0, 7.0 Hz, $\mathrm{H5^{II}}$), 3.538 (dd, $J = 7.5$, 8.5 Hz, $\mathrm{H2^{I}}$), 3.698 (d, $J = 8.5$ Hz, $\mathrm{H3^{I}}$), 3.913 (dd, $J = 8.0$, 10.0 Hz, $\mathrm{H3^{II}}$), 4.382 (d, $J = 8.0$ Hz, $\mathrm{H1^{II}}$), 4.593 (d, $J = 7.5$ Hz, $\mathrm{H1^{I}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 63.2$ ($\mathrm{C2^{II}}$), 68.3 ($\mathrm{C6^{II}}$), 68.7 ($\mathrm{C6^{I}}$), 72.1 ($\mathrm{C4^{II}}$), 73.4 ($\mathrm{C5^{II}}$), 75.0 ($\mathrm{C5^{I}}$), 78.2 ($\mathrm{C4^{I}}$), 80.5 ($\mathrm{C3^{II}}$), 82.3 ($\mathrm{C2^{I}}$), 84.5 ($\mathrm{C3^{I}}$), 101.4 ($\mathrm{C1^{I}}$), 102.8 ($\mathrm{C1^{II}}$).

Found: **33**; C, 73.16; H, 6.39; N, 4.23%. **34**; C, 73.15; H, 6.35; N, 4.16%. Calcd for $\mathrm{C_{61}H_{63}N_3O_{10}}$: C, 73.40; H, 6.36; N, 4.21%.

Benzyl *O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-α- and β-D-mannopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (35 and 36). **35** (TK system (10 : 1), faster-moving), $[\alpha]_\mathrm{D}$ +24 (*c* 3.9, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.490$ (t, $J = 9.5$ Hz, $\mathrm{H3^{I}}$), 3.655 (t, $J = 9.5$ Hz, $\mathrm{H4^{I}}$), 3.705 (d, $J = 8.0$, 9.5 Hz, $\mathrm{H2^{I}}$), 4.405 (d, $J = 8.0$ Hz, $\mathrm{H1^{I}}$), 5.417 (d, $J = 2.0$ Hz, $\mathrm{H1^{II}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 61.2$ ($\mathrm{C2^{II}}$), 68.1 ($\mathrm{C6^{I}}$), 68.7 ($\mathrm{C6^{II}}$), 71.6 ($\mathrm{C5^{II}}$), 74.4 ($\mathrm{C4^{II}}$), 75.2 ($\mathrm{C5^{I}}$), 78.4 ($\mathrm{C4^{I}}$), 76.8 ($\mathrm{C2^{I}}$), 79.3 ($\mathrm{C3^{II}}$), 83.3 ($\mathrm{C3^{I}}$), 97.8 ($\mathrm{C1^{II}}$, $J_{\mathrm{C,H}} = 173.4$ Hz), 102.4 ($\mathrm{C1^{I}}$, $J_{\mathrm{C,H}} = 160.7$ Hz).

36: $[\alpha]_\mathrm{D}$ −32 (*c* 1.2, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.442$ (dd, $J = 4.0$, 9.0 Hz, $\mathrm{H3^{II}}$), 3.813 (qt, $J = 9.0$, 9.5 Hz, $\mathrm{H4^{II}}$), 4.582 (d, $J = 8.0$ Hz, $\mathrm{H^{I}}$), 4.743 (s, $\mathrm{H1^{II}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 61.8$ ($\mathrm{C2^{II}}$), 68.8 ($\mathrm{C6^{I}}$), 68.9 ($\mathrm{C6^{II}}$), 74.3 ($\mathrm{C4^{II}}$), 74.8 ($\mathrm{C5^{I}}$), 75.9 ($\mathrm{C5^{I}}$), 78.2 ($\mathrm{C3^{I}}$), 80.9 ($\mathrm{C2^{I}}$), 81.5 ($\mathrm{C3^{II}}$), 85.0 ($\mathrm{C3^{I}}$), 100.2 ($\mathrm{C1^{II}}$, $J_{\mathrm{C,H}} = 161.6$ Hz), 100.9 ($\mathrm{C1^{I}}$, $J_{\mathrm{C,H}} = 157.9$ Hz).

Found: **35**; C, 73.38; H, 6.41; N, 4.14%. **36**; C, 72.91; H, 6.33; N, 4.41%. Calcd for $\mathrm{C_{61}H_{63}N_3O_{10}}$: C, 73.40; H, 6.36; N, 4.21%.

Benzyl *O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-α- and β-D-mannopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-β-D-glucopyranoside (37 and 38). **37** (TK system (10 : 1), faster-moving), $[\alpha]_\mathrm{D}$ +4 (*c* 2.0, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.396$ (dd, $J = 8.0$, 9.0 Hz, $\mathrm{H2^{I}}$), 3.417 (dt, $J = 3.0$, 3.0, 9.0 Hz, $\mathrm{H5^{I}}$), 3.604 (dd, $J = 2.0$, 2.5 Hz, $\mathrm{H2^{II}}$), 3.700 (t, $J = 9.0$ Hz, $\mathrm{H3^{I}}$), 3.772 (t, $J = 9.0$ Hz, $\mathrm{H4^{I}}$), 4.512 (d, $J = 8.0$ Hz, $\mathrm{H1^{I}}$), 5.524 (d, $J = 2.0$ Hz, $\mathrm{H1^{I}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 61.4$ ($\mathrm{C2^{II}}$), 68.0 ($\mathrm{C6^{I}}$), 68.5 ($\mathrm{C6^{II}}$), 71.3 ($\mathrm{C5^{II}}$), 74.4 ($\mathrm{C4^{II}}$), 74.6 ($\mathrm{C5^{I}}$), 78.8 ($\mathrm{C4^{I}}$), 79.0 ($\mathrm{C3^{I}}$), 79.8 ($\mathrm{C2^{I}}$, $\mathrm{C3^{II}}$), 98.4 ($\mathrm{C1^{II}}$, $J_{\mathrm{C,H}} = 174.0$ Hz), 102.7 ($\mathrm{C1^{I}}$, $J_{\mathrm{C,H}} = 160.6$ Hz).

38: $[\alpha]_\mathrm{D}$ −20 (*c* 0.5, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.268$ (ddd, $J = 2.0$, 5.0, 9.5 Hz, $\mathrm{H5^{I}}$), 3.350 (t, $J = 9.0$ Hz, $\mathrm{H3^{II}}$), 3.432 (ddd, $J = 2.0$, 5.0, 9.0 Hz, $\mathrm{H5^{II}}$), 3.530 (dd, $J = 8.0$, 9.0 Hz, $\mathrm{H2^{I}}$), 3.573 (qt, $J = 9.0$, 9.5 Hz, $\mathrm{H4^{I}}$), 3.734 (qt, $J = 9.0$, 9.5 Hz, $\mathrm{H4^{II}}$), 3.905 (t, $J = 9.0$ Hz, $\mathrm{H3^{I}}$), 4.455 (d, $J = 8.0$ Hz, $\mathrm{H1^{I}}$), 4.840 (d, $J = 1.0$ Hz, $\mathrm{H1^{II}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 62.0$ ($\mathrm{C2^{II}}$), 69.1 ($\mathrm{C6^{I,II}}$), 74.5 ($\mathrm{C4^{II}}$), 75.3 ($\mathrm{C5^{II}}$), 75.8 ($\mathrm{C5^{I}}$), 76.2 ($\mathrm{C4^{I}}$), 81.5 ($\mathrm{C3^{II}}$), 82.5 ($\mathrm{C2^{I}}$), 82.8 ($\mathrm{C3^{I}}$), 100.5 ($\mathrm{C1^{II}}$, $J_{\mathrm{C,H}} = 161.0$ Hz), 102.1 ($\mathrm{C1^{I}}$, $J_{\mathrm{C,H}} = 158.8$ Hz).

Found: **37**; C, 73.16; H, 6.40; N, 4.20%. **38**; C, 73.34; H, 6.47; N, 4.00%. Calcd for $\mathrm{C_{61}H_{63}N_3O_{10}}$: C, 73.40; H, 6.36; N, 4.21%.

Benzyl *O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-α- and β-D-mannopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (39 and 40). **39** (TK system (10 : 1), faster-moving), mp 114.5—115.5 °C, $[\alpha]_\mathrm{D}$ −8 (*c* 0.6, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.470$ (ddd, $J = 2.0$, 6.0, 9.5 Hz, $\mathrm{H5^{I}}$), 3.664 (dd, $J = 2.0$, 2.5 Hz, $\mathrm{H2^{II}}$), 3.760 (m, $\mathrm{H5^{II}}$), 4.553 (d, $J = 8.0$ Hz, $\mathrm{H1^{I}}$), 5.206 (d, $J = 2.0$ Hz, $\mathrm{H1^{II}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 61.3$ ($\mathrm{C2^{II}}$), 68.7 ($\mathrm{C6^{I}}$), 69.6 ($\mathrm{C6^{II}}$), 72.6 ($\mathrm{C5^{II}}$), 74.3 ($\mathrm{C4^{II}}$), 74.5 ($\mathrm{C5^{I}}$), 77.3 ($\mathrm{C4^{I}}$), 79.5 ($\mathrm{C3^{II}}$), 82.2 ($\mathrm{C2^{I}}$), 84.2 ($\mathrm{C3^{I}}$), 100.2 ($\mathrm{C1^{II}}$, $J_{\mathrm{C,H}} = 172.8$ Hz), 102.1 ($\mathrm{C1^{I}}$, $J_{\mathrm{C,H}} = 158.5$ Hz).

40: $[\alpha]_\mathrm{D}$ −49 (*c* 0.2, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.179$ (ddd, $J = 3.0$, 4.0, 9.0 Hz, $\mathrm{H5^{I}}$), 3.413 (dd, $J = 3.5$, 9.0 Hz, $\mathrm{H3^{II}}$), 3.487 (dd, $J = 7.5$, 9.0 Hz, $\mathrm{H2^{I}}$), 3.687 (t, $J = 9.0$ Hz, $\mathrm{H3^{I}}$), 3.748 (t, $J = 9.0$ Hz, $\mathrm{H4^{II}}$), 3.867 (dd, $J = 1.0$, 3.5 Hz, $\mathrm{H2^{II}}$), 3.954 (t, $J = 9.0$ Hz, $\mathrm{H4^{I}}$), 4.505 (d, $J = 7.5$ Hz, $\mathrm{H1^{I}}$), 4.707 (d, $J = 1.0$ Hz, $\mathrm{H1^{II}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 61.8$ ($\mathrm{C2^{II}}$), 68.8 ($\mathrm{C6^{I}}$), 68.9 ($\mathrm{C6^{II}}$), 74.1^{6} ($\mathrm{C4^{II}}$), 74.2^{4} ($\mathrm{C5^{II}}$), 75.9 ($\mathrm{C5^{I}}$), 76.8 ($\mathrm{C4^{I}}$), 81.3 ($\mathrm{C3^{II}}$), 82.1 ($\mathrm{C2^{I}}$), 83.0 ($\mathrm{C3^{I}}$), 99.6 ($\mathrm{C1^{II}}$, $J_{\mathrm{C,H}} = 165.6$ Hz), 102.7 ($\mathrm{C1^{I}}$, $J_{\mathrm{C,H}} = 157.8$ Hz).

Found: **39**; C, 73.11; H, 6.39; N, 4.39%. **40**; C, 73.17; H, 6.43; N, 4.22%. Calcd for $\mathrm{C_{61}H_{63}N_3O_{10}}$: C, 73.40; H, 6.36; N, 4.21%.

Benzyl *O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-α- and β-D-mannopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (41 and 42). **41** (TK system (10 : 1), faster-moving), $[\alpha]_\mathrm{D}$ +22 (*c* 0.9, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.407$ (m, $\mathrm{H5^{I}}$), 3.408 (t, $J = 9.0$ Hz, $\mathrm{H4^{I}}$), 3.485 (dd, $J = 8.0$, 9.5 Hz, $\mathrm{H2^{I}}$), 3.657 (qt, $J = 9.0$, 9.5 Hz, $\mathrm{H3^{I}}$), 3.770 (m, $\mathrm{H5^{II}}$), 3.906 (t, $J = 9.0$ Hz, $\mathrm{H5^{II}}$), 3.950 (dd, $J = 2.0$, 4.0 Hz, $\mathrm{H2^{II}}$), 4.041 (dd, $J = 4.0$, 9.0 Hz, $\mathrm{H3^{II}}$), 4.505 (d, $J = 8.0$ Hz, $\mathrm{H1^{I}}$), 4.913 (d, $J = 2.0$ Hz, $\mathrm{H1^{II}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 61.1$ ($\mathrm{C2^{II}}$), 66.1 ($\mathrm{C6^{I}}$), 68.6 ($\mathrm{C6^{II}}$), 71.6 ($\mathrm{C5^{II}}$), 73.3 ($\mathrm{C5^{I}}$), 74.4 ($\mathrm{C4^{II}}$), 77.7 ($\mathrm{C4^{I}}$), 79.3 ($\mathrm{C3^{II}}$), 82.3 ($\mathrm{C2^{I}}$), 84.7 ($\mathrm{C3^{I}}$), 98.5 ($\mathrm{C1^{II}}$, $J_{\mathrm{C,H}} = 170.1$ Hz), 102.4 ($\mathrm{C1^{I}}$, $J_{\mathrm{C,H}} = 158.7$ Hz).

42: Mp 118—120 °C, $[\alpha]_\mathrm{D}$ −24 (*c* 0.8, $\mathrm{CHCl_3}$) (lit,[39)] $[\alpha]_\mathrm{D}$ −23° (*c* 0.9, $\mathrm{CHCl_3}$)); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 3.343$ (ddd, $J = 3.0$, 5.0, 9.0 Hz, $\mathrm{H5^{I}}$), 3.357 (t, $J = 9.0$ Hz, $\mathrm{H4^{I}}$), 3.487 (dd, $J = 7.5$, 9.0 Hz, $\mathrm{H2^{I}}$), 3.561 (dd, $J = 4.0$, 9.0 Hz, $\mathrm{H3^{II}}$), 3.660 (t, $J = 9.0$ Hz, $\mathrm{H3^{I}}$), 3.767 (t, $J = 9.0$ Hz, $\mathrm{H4^{II}}$), 3.866 (dd, $J = 1.0$, 4.0 Hz, $\mathrm{H2^{II}}$), 4.437 (d, $J = 1.0$ Hz, $\mathrm{H1^{II}}$), 4.514 (d, $J = 7.5$ Hz, $\mathrm{H1^{I}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta = 62.0$ ($\mathrm{C2^{II}}$), 69.0 ($\mathrm{C6^{I}}$), 69.2 ($\mathrm{C6^{II}}$), 74.4 ($\mathrm{C4^{II}}$), 74.5 ($\mathrm{C5^{II}}$), 75.7 ($\mathrm{C5^{I}}$), 78.4 ($\mathrm{C4^{I}}$), 80.8 ($\mathrm{C3^{II}}$), 82.3 ($\mathrm{C2^{I}}$), 84.7 ($\mathrm{C3^{I}}$), 100.1 ($\mathrm{C1^{II}}$, $J_{\mathrm{C,H}} = 158.5$ Hz), 102.3 ($\mathrm{C1^{I}}$, $J_{\mathrm{C,H}} = 160.9$ Hz).

Found: **41**; C, 73.01; H, 6.40; N, 4.34%. **42**; C, 73.24; H, 6.62; N, 4.28%. Calcd for $\mathrm{C_{61}H_{63}N_3O_{10}}$: C, 73.40; H, 6.36; N, 4.21%.

Benzyl *O*-(2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (43). A mixture of **19** (50.0 mg, 0.050 mml), $\mathrm{Et_2O}$ (3.0 ml), and $\mathrm{LiAlH_4}$ (17.8 mg) was refluxed for 30 min. After AcOEt (20 ml) was added, the mixture was evaporated to give a residue. This was treated with $\mathrm{Ac_2O}$ (0.15 ml) in MeOH (0.4 ml) for 2 h. Filtration, evaporation, and chromatography with TE system (100 : 1 → 5 : 2) furnished **43** (39.3 mg, 78%), mp 92—94 °C, $[\alpha]_{\mathrm{D}}$ +36 (c 0.8, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) δ = 1.595 (s, Ac), 3.473 (ddd, J = 2.0, 4.0, 9.0 Hz, H5$^{\mathrm{I}}$), 3.545 (t, J = 9.0 Hz, H3$^{\mathrm{I}}$), 3.620 (t, J = 9.0 Hz, H4$^{\mathrm{I}}$), 3.682 (t, J = 9.5 Hz, H3$^{\mathrm{II}}$), 3.780 (t, J = 9.5 Hz, H4$^{\mathrm{II}}$), 4.348 (dd, J = 3.5, 9.5 Hz, H2$^{\mathrm{II}}$), 4.420 (d, J = 7.5 Hz, H1$^{\mathrm{I}}$), 4.500 (ddd, J = 1.5, 3.0, 9.5 Hz, H5$^{\mathrm{II}}$), 5.328 (d, J = 3.5 Hz, H1$^{\mathrm{II}}$), 5.951 (d, J = 9.5 Hz, NH); ^{13}C NMR ($\mathrm{CDCl_3}$) δ = 23.0 (Ac), 52.8 (C2$^{\mathrm{II}}$), 68.5^{5} (C6$^{\mathrm{II}}$), 68.5^{8} (C6$^{\mathrm{I}}$), 71.7 (C5$^{\mathrm{II}}$), 75.1 (C5$^{\mathrm{I}}$), 78.0 (C4$^{\mathrm{II}}$), 78.4 (C4$^{\mathrm{I}}$), 78.5 (C2$^{\mathrm{I}}$), 80.8 (C3$^{\mathrm{II}}$), 84.3 (C3$^{\mathrm{I}}$), 98.8 (C1$^{\mathrm{II}}$), 101.3 (C1$^{\mathrm{I}}$), 169.8 (Ac).

Found: C, 74.56; H, 6.75; N, 1.34%. Calcd for $\mathrm{C_{63}H_{67}NO_{11}}$: C, 74.60; H, 6.66; N, 1.38%.

Similarly, **20**, **21**, **22**, **23**, **24**, **25**, and **26** were converted into **44**, **45**, **46**, **47**, **48**, **49**, and **50**, respectively.

Benzyl *O*-(2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (44). 90%, mp 176—178 °C, $[\alpha]_{\mathrm{D}}$ −5.3 (c 0.4, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) δ = 1.465 (s, Ac), 3.197 (dd, J = 8.0, 9.0 Hz, H2$^{\mathrm{II}}$), 3.366 (ddd, J = 2.0, 4.0, 9.5 Hz, H5$^{\mathrm{II}}$), 3.613 (t, J = 9.5 Hz, H4$^{\mathrm{I}}$), 4.114 (qt, J = 9.0, 9.5 Hz, H3$^{\mathrm{II}}$), 4.516 (d, J = 8.0 Hz, H1$^{\mathrm{I}}$), 5.015 (J = 7.5 Hz, NH), 5.120 (d, J = 8.0 Hz, H1$^{\mathrm{II}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) δ = 23.2 (Ac), 58.7 (C2$^{\mathrm{II}}$), 68.7 (C6$^{\mathrm{I,II}}$), 74.7^{7} (C5$^{\mathrm{II}}$), 74.8^{3} (C5$^{\mathrm{I}}$), 78.2 (C4$^{\mathrm{II}}$), 78.5 (C4$^{\mathrm{I}}$), 80.5 (C2$^{\mathrm{I}}$), 80.6 (C3$^{\mathrm{II}}$), 84.8 (C3$^{\mathrm{I}}$), 99.5 (C1$^{\mathrm{II}}$), 101.8 (C1$^{\mathrm{I}}$), 169.8 (Ac).

Found: C, 74.83; H, 6.85; N, 1.43%. Calcd for $\mathrm{C_{63}H_{67}NO_{11}}$: C, 74.60; H, 6.66; N, 1.38%.

Benzyl *O*-(2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-β-D-glucopyranoside (45). 73%, $[\alpha]_{\mathrm{D}}$ +24 (c 1.2, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) δ = 1.590 (s, Ac), 3.417 (dd, J = 8.0, 9.0 Hz, H2$^{\mathrm{I}}$), 3.687 (t, J = 9.0 Hz, H4$^{\mathrm{I}}$), 3.723 (dd, J = 9.0, 10.0 Hz, H3$^{\mathrm{II}}$), 4.375 (dd, J = 3.5, 10.0 Hz, H2$^{\mathrm{II}}$), 4.500 (d, J = 8.0 Hz, H1$^{\mathrm{I}}$), 5.338 (J = 3.5 Hz, H1$^{\mathrm{II}}$), 5.768 (d, J = 9.5 Hz, NH); ^{13}C NMR ($\mathrm{CDCl_3}$) δ = 23.0 (Ac), 52.3 (C2$^{\mathrm{II}}$), 68.3 (C6$^{\mathrm{II}}$), 68.5 (C6$^{\mathrm{I}}$), 71.4 (C5$^{\mathrm{II}}$), 74.5 (C5$^{\mathrm{I}}$), 78.1 (C4$^{\mathrm{II}}$), 78.4 (C4$^{\mathrm{I}}$), 80.1 (C2$^{\mathrm{I}}$), 80.2 (C3$^{\mathrm{I}}$), 80.8 (C3$^{\mathrm{I}}$), 98.6 (C1$^{\mathrm{II}}$), 102.7 (C1$^{\mathrm{I}}$), 169.6 (Ac).

Found: C, 74.32; H, 6.76; N, 1.23%. Calcd for $\mathrm{C_{63}H_{67}NO_{11}}$: C, 74.60; H, 6.66; N, 1.38%.

Benzyl *O*-(2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-β-D-glucopyranoside (46). 70%, mp 91—92 °C, $[\alpha]_{\mathrm{D}}$ −0.4 (c 0.7, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) δ = 1.635 (s, Ac), 3.410 (t, J = 9.0 Hz, H3$^{\mathrm{II}}$), 3.470 (dd, J = 7.5, 9.0 Hz, H2$^{\mathrm{I}}$), 3.551 (t, J = 9.0 Hz, H4$^{\mathrm{I}}$), 3.817 (dd, J = 8.0, 9.0 Hz, H2$^{\mathrm{II}}$), 3.964 (t, J = 9.0 Hz, H3$^{\mathrm{I}}$), 4.466 (d, J = 7.5 Hz, H1$^{\mathrm{I}}$), 4.551 (d, J = 9.0 Hz, NH), 4.900 (d, J = 8.0 Hz, H1$^{\mathrm{II}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) δ = 23.3 (Ac), 55.9 (C2$^{\mathrm{II}}$), 69.0 (C6$^{\mathrm{I,II}}$), 74.8 (C5$^{\mathrm{II}}$), 75.2 (C5$^{\mathrm{I}}$), 76.3 (C4$^{\mathrm{I}}$), 78.5 (C4$^{\mathrm{II}}$), 81.1 (C3$^{\mathrm{I}}$), 82.4 (C2$^{\mathrm{I}}$), 82.5 (C3$^{\mathrm{I}}$), 100.9 (C1$^{\mathrm{II}}$), 102.0 (C1$^{\mathrm{I}}$), 170.0 (Ac).

Found: C, 74.71; H, 6.65; N, 1.27%. Calcd for $\mathrm{C_{63}H_{67}NO_{11}}$: C, 74.60; H, 6.66; N, 1.38%.

Benzyl *O*-(2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (47). 79%, mp 102—104 °C, $[\alpha]_{\mathrm{D}}$ +24 (c 0.7, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) δ = 1.421 (s, Ac), 3.380 (ddd, J = 2.0, 4.0, 9.0 Hz, H5$^{\mathrm{I}}$), 4.378 (dd, J = 3.5, 9.5 Hz, H2$^{\mathrm{II}}$), 4.537 (d, J = 7.5 Hz, H1$^{\mathrm{I}}$), 5.073 (d, J = 3.5 Hz, H1$^{\mathrm{II}}$), 6.900 (d, J = 9.5 Hz, NH); ^{13}C NMR ($\mathrm{CDCl_3}$) δ = 22.6 (Ac), 53.1 (C2$^{\mathrm{II}}$), 68.5 (C6$^{\mathrm{I}}$), 68.9 (C6$^{\mathrm{II}}$), 72.2 (C5$^{\mathrm{II}}$), 73.0 (C4$^{\mathrm{I}}$), 75.3 (C5$^{\mathrm{I}}$), 77.9 (C4$^{\mathrm{II}}$), 81.3 (C3$^{\mathrm{II}}$), 82.3 (C3$^{\mathrm{I}}$), 83.2 (C2$^{\mathrm{I}}$), 99.8 (C1$^{\mathrm{II}}$), 102.3 (C1$^{\mathrm{I}}$), 170.1 (Ac).

Found: C, 74.85; H, 6.69; N, 1.21%. Calcd for $\mathrm{C_{63}H_{67}NO_{11}}$: C, 74.60; H, 6.66; N, 1.38%.

Benzyl *O*-(2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (48). 80%, mp 186—187 °C, $[\alpha]_{\mathrm{D}}$ +3.8 (c 0.9, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) δ = 1.715 (s, Ac), 3.343 (ddd, J = 2.0, 4.0, 9.0 Hz, H5$^{\mathrm{II}}$), 3.742 (dd, J = 8.5, 9.5 Hz, H3$^{\mathrm{I}}$), 3.977 (t, J = 9.0 Hz, H4$^{\mathrm{I}}$), 4.497 (d, J = 7.5 Hz, H1$^{\mathrm{I}}$), 4.797 (d, J = 8.0 Hz, H1$^{\mathrm{II}}$), 5.037 (d, J = 8.5 Hz, NH); ^{13}C NMR ($\mathrm{CDCl_3}$) δ = 23.4 (Ac), 57.1 (C2$^{\mathrm{II}}$), 68.7 (C6$^{\mathrm{I,II}}$), 74.5 (C5$^{\mathrm{I}}$), 74.9 (C5$^{\mathrm{II}}$), 76.7 (C4$^{\mathrm{I}}$), 78.6 (C4$^{\mathrm{II}}$), 81.5 (C3$^{\mathrm{II}}$), 81.9 (C2$^{\mathrm{I}}$), 82.9 (C3$^{\mathrm{I}}$), 99.8 (C1$^{\mathrm{II}}$), 102.5 (C1$^{\mathrm{I}}$), 170.1 (Ac).

Found: C, 74.35; H, 6.56; N, 1.33%. Calcd for $\mathrm{C_{63}H_{67}NO_{11}}$: C, 74.60; H, 6.66; N, 1.38%.

Benzyl *O*-(2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (49). 96%, mp 179—181 °C, $[\alpha]_{\mathrm{D}}$ +46 (c 1.1, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) δ = 1.840 (s, Ac), 3.793 (t, J = 9.5 Hz, H4$^{\mathrm{II}}$), 3.860 (m, H5$^{\mathrm{II}}$), 4.293 (dd, J = 3.5, 9.5 Hz, H2$^{\mathrm{II}}$), 4.540 (d, J = 8.0 Hz, H1$^{\mathrm{I}}$), 4.843 (d, J = 3.5 Hz, H1$^{\mathrm{II}}$), 5.450 (d, J = 9.5 Hz, NH); ^{13}C NMR ($\mathrm{CDCl_3}$) δ = 23.5 (Ac), 52.6 (C2$^{\mathrm{II}}$), 67.0 (C6$^{\mathrm{I}}$), 68.3 (C6$^{\mathrm{II}}$), 71.3 (C5$^{\mathrm{II}}$), 73.9 (C5$^{\mathrm{I}}$), 77.6 (C4$^{\mathrm{I}}$), 78.2 (C4$^{\mathrm{II}}$), 80.0 (C3$^{\mathrm{II}}$), 82.3 (C2$^{\mathrm{I}}$), 84.6 (C3$^{\mathrm{I}}$), 99.0 (C1$^{\mathrm{II}}$), 102.4 (C1$^{\mathrm{I}}$), 169.8 (Ac).

Found: C, 74.32; H, 6.66; N, 1.33%. Calcd for $\mathrm{C_{63}H_{67}NO_{11}}$: C, 74.60; H, 6.66; N, 1.38%.

Benzyl *O*-(2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (50). 89%, mp 185—186 °C, $[\alpha]_{\mathrm{D}}$ −1 (c 0.6, $\mathrm{CHCl_3}$); ^{1}H NMR ($\mathrm{CDCl_3}$) δ = 1.761 (s, Ac), 4.112 (dd, J = 8.0, 9.0 Hz, H3$^{\mathrm{II}}$), 4.520 (d, J = 8.0 Hz, H1$^{\mathrm{I}}$), 4.893 (d, J = 7.5 Hz, H1$^{\mathrm{II}}$), 5.451 (d, J = 9.5 Hz, NH); ^{13}C NMR ($\mathrm{CDCl_3}$) δ = 23.6 (Ac), 56.2 (C2$^{\mathrm{II}}$), 67.3 (C6$^{\mathrm{I}}$), 69.1 (C6$^{\mathrm{II}}$), 74.4 (C5$^{\mathrm{I}}$), 74.8 (C5$^{\mathrm{II}}$), 78.0 (C4$^{\mathrm{I}}$), 78.4 (C4$^{\mathrm{II}}$), 80.1 (C3$^{\mathrm{II}}$), 82.2 (C2$^{\mathrm{I}}$), 84.6 (C3$^{\mathrm{I}}$), 99.7 (C1$^{\mathrm{II}}$), 102.5 (C1$^{\mathrm{I}}$), 170.1 (Ac).

Found: C, 74.75; H, 6.69; N, 1.25%. Calcd for $\mathrm{C_{63}H_{67}NO_{11}}$: C, 74.60; H, 6.66; N, 1.38%.

***O*-(2-Acetamido-2-deoxy-α-D-glucopyranosyl)-(1→2)-D-glucopyranose (51).** Compound **43** (31.3 mg, 0.031 mmol) was hydrogenated over Pd on C (37 mg) in AcOH (6 ml) containing $\mathrm{H_2O}$ (0.05 ml) overnight. Filtration, evaporation, and chromatography using CM system (100 : 1 → 3 : 2) afforded **53** (9.1 mg, 77%), $[\alpha]_{\mathrm{D}}$ +133 (c 0.4, $\mathrm{H_2O}$); ^{1}H NMR ($\mathrm{D_2O}$) (43% α) δ = 1.962 (s, Ac β), 1.978 (s, Ac α), 3.220 (dd, J = 8.0, 9.0 Hz, H2$^{\mathrm{I}}$ β), 3.317 (qt, J = 9.0, 9.5 Hz, H4$^{\mathrm{I}}$ β), 3.373 (t, J = 9.5 Hz, H4$^{\mathrm{I}}$ α), 3.460 (t, J = 9.0 Hz, H3$^{\mathrm{I}}$ β), 3.470 (t, J = 9.5 Hz, H4$^{\mathrm{II}}$ α), 3.541 (dd, J = 3.5, 9.5 Hz, H2$^{\mathrm{I}}$ α), 3.713 (t, J = 9.5 Hz, H3$^{\mathrm{I}}$ α), 3.825 (dd, J = 3.5, 10.0 Hz, H2$^{\mathrm{II}}$ α), 3.851 (dd, J = 3.5, 10.0 Hz, H3$^{\mathrm{II}}$ β), 3.882 (ddd, J = 2.5, 4.5, 9.5 Hz, H5$^{\mathrm{II}}$ α), 3.968 (dt, J = 2.5, 2.5, 9.5 Hz, H5$^{\mathrm{II}}$ β), 4.670 (d, J = 8.0 Hz, H1$^{\mathrm{I}}$ β), 4.996 (d, J = 3.5 Hz, H1$^{\mathrm{II}}$ α), 5.158 (d, J = 3.5 Hz, H1$^{\mathrm{II}}$ β), 5.287 (d, J = 3.5 Hz, H1$^{\mathrm{I}}$ α).

Found: C, 39.16; H, 6.86; N, 3.04%. Calcd for $\mathrm{C_{14}H_{25}NO_{11}\cdot 2.5H_2O}$: C, 39.25; H, 7.06; N, 3.27%.

Similarly, **44**, **45**, **46**, **47**, **48**, **49**, and **50** were converted into **52**, **53**, **54**, **55**, **56**, **57**, and **58** respectively.

***O*-(2-Acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-β-D-glucopyranose (52).** 96%, $[\alpha]_{\mathrm{D}}$ +12 (c 0.5, $\mathrm{H_2O}$); ^{1}H NMR ($\mathrm{D_2O}$) (60% α) δ = 1.965 (s, Ac α), 1.975 (s, Ac β), 3.494 (dd, J = 3.5, 9.0 Hz, H2$^{\mathrm{I}}$ α), 4.583 (d, J = 8.0 Hz, H1$^{\mathrm{II}}$ α), 4.610 (d, J = 8.0 Hz, H1$^{\mathrm{I}}$ β), 4.742 (d, J = 8.0 Hz, H$^{\mathrm{II}}$ β), 5.328 (d, J = 3.5 Hz, H1$^{\mathrm{I}}$ α).

Found: C, 40.38; H, 6.41; N, 3.18%. Calcd for $\mathrm{C_{14}H_{25}NO_{11}\cdot 2H_2O}$: C, 40.09; H, 6.97; N, 3.34%.

***O*-(2-acetamido-2-deoxy-α-D-glucopyranosyl)-(1→3)-D-glucopyranose (53).** 95%, $[\alpha]_{\mathrm{D}}$ +136 (c 0.5, $\mathrm{H_2O}$) (lit,[40] $[\alpha]_{\mathrm{D}}$ +157.8 (c 0.9, $\mathrm{H_2O}$)); ^{1}H NMR ($\mathrm{D_2O}$) (35% α) δ = 1.965 (s, Ac), 3.232 (t, $J = 8.0$ Hz, $\mathrm{H2^{I}}\ \beta$), 3.362 (ddd, $J = 2.0$, 5.5, 9.0 Hz, $\mathrm{H5^{I}}\ \beta$), 3.850 (dd, $J = 3.5$, 10.5 Hz, $\mathrm{H2^{II}}\ \beta$), 3.857 (dd, $J = 3.5$, 10.5 Hz, $\mathrm{H2^{II}}\ \alpha$), 4.570 (d, $J = 8.0$ Hz, $\mathrm{H1^{I}}\ \beta$), 5.147 (d, $J = 7.5$ Hz, $\mathrm{H1^{I}}\ \alpha$), 5.167 (d, $J = 3.5$ Hz, $\mathrm{H1^{II}}\ \beta$), 5.182 (d, $J = 3.5$ Hz, $\mathrm{H1^{II}}\ \alpha$).

Found: C, 40.55; H, 7.49; N, 3.09%. Calcd for $C_{14}H_{25}NO_{11}\cdot 2H_2O$: C, 40.09; H, 6.97; N, 3.34%.

***O*-(2-Acetamido-2-deoxy-*β*-D-glucopyranosyl)-(1→3)-*β*-D-glucopyranose (54).** 94%, $[\alpha]_D$ +25 (*c* 0.7, H_2O) (lit,[41] $[\alpha]_D$ +59 (*c* 2.8, H_2O)); ^{1}H NMR (D_2O) (40% α) $\delta = 1.963$ (s, Ac), 3.211 (dd, $J = 8.0$, 9.0 Hz, $\mathrm{H2^{I}}\ \beta$), 4.527 (d, $J = 8.0$ Hz, $\mathrm{H1^{I}}\ \beta$), 4.658 (d, $J = 8.0$ Hz, $\mathrm{H1^{II}}\ \alpha$), 4.667 (d, $J = 8.0$ Hz, $\mathrm{H1^{II}}\ \beta$), 5.091 (d, $J = 3.5$ Hz, $\mathrm{H1^{I}}\ \alpha$).

Found: C, 39.19; H, 7.22; N, 3.12%. Calcd for $C_{14}H_{25}NO_{11}\cdot 2.5H_2O$: C, 39.25; H, 7.06; N, 3.27%.

***O*-(2-Acetamido-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-D-glucopyranose (55).** 95%, $[\alpha]_D$ +123 (*c* 0.7, H_2O); ^{1}H NMR (D_2O) (40% α) $\delta = 1.973$ (s, Ac β), 1.980 (s, Ac α), 3.157 (dd, $J = 8.0$, 9.0 Hz, $\mathrm{H2^{I}}\ \beta$), 3.445 (d, $J = 3.5$, 10.0 Hz, $\mathrm{H2^{I}}\ \alpha$), 4.550 (d, $J = 8.0$ Hz, $\mathrm{H1^{I}}\ \beta$), 5.137 (d, $J = 3.5$ Hz, $\mathrm{H1^{I}}\ \alpha$), 5.280 (d, $J = 3.5$ Hz, $\mathrm{H1^{II}}$).

Found: C, 41.41; H, 6.48; N, 3.07%. Calcd for $C_{14}H_{25}NO_{11}\cdot 1.5H_2O$: C, 40.97; H, 6.88; N, 3.41%.

***O*-(2-Acetamido-2-deoxy-*β*-D-glucopyranosyl)-(1→4)-*β*-D-glucopyranose (56).** 92%, $[\alpha]_D$ +34 (*c* 0.6, H_2O) (lit,[42] $[\alpha]_D$ +30 (*c* 0.7, H_2O)); ^{1}H NMR (D_2O) (33% α) $\delta = 1.987$ (s, Ac), 3.178 (dd, $J = 8.0$, 9.0 Hz, $\mathrm{H2^{I}}\ \beta$), 4.485 (d, $J = 8.0$ Hz, $\mathrm{H1^{II}}\ \beta$), 4.495 (d, $J = 8.0$ Hz, $\mathrm{H1^{II}}\ \alpha$), 4.567 (d, $J = 8.0$ Hz, $\mathrm{H1^{I}}\ \beta$), 5.217 (d, $J = 3.5$ Hz, $\mathrm{H1^{I}}\ \alpha$).

Found: C, 42.99; H, 6.84; N, 3.40%. Calcd for $C_{14}H_{25}NO_{11}\cdot 0.5H_2O$: C, 42.86; H, 6.68; N, 3.57%.

***O*-(2-Acetamido-2-deoxy-*α*-D-glucopyranosyl)-(1→6)-D-glucopyranose (57).** 95%, $[\alpha]_D$ +116 (*c* 0.8, H_2O); ^{1}H NMR (D_2O) (40% α) $\delta = 1.970$ (s, Ac α), 1.977 (s, Ac β), 3.168 (dd, $J = 8.0$, 9.0 Hz, $\mathrm{H2^{II}}\ \beta$), 3.409 (t, $J = 9.0$ Hz, $\mathrm{H3^{I}}\ \beta$), 4.591 (d, $J = 8.0$ Hz, $\mathrm{H1^{I}}\ \beta$), 4.838 (d, $J = 3.5$ Hz, $\mathrm{H1^{II}}$), 5.163 (d, $J = 3.5$ Hz, $\mathrm{H1^{I}}\ \alpha$).

Found: C, 41.28; H, 6.97; N, 2.87%. Calcd for $C_{14}H_{25}NO_{11}\cdot 1.5H_2O$: C, 40.99; H, 6.88; N, 3.41%.

***O*-(2-Acetamido-2-deoxy-*β*-D-glucopyranosyl)-(1→6)-D-glucopyranose (58).** 66%, $[\alpha]_D$ +3 (*c* 0.4, H_2O) (lit,[43] $[\alpha]_D^{20}$+3.7 (*c* 0.49, H_2O)); ^{1}H NMR (D_2O) (40% α) $\delta = 1.973$ (s, Ac), 3.133 (dd, $J = 8.0$, 9.0 Hz, $\mathrm{H2^{II}}\ \beta$), 4.447 (d, $J = 8.0$ Hz, $\mathrm{H1^{II}}\ \alpha$), 4.461 (d, $J = 8.0$ Hz, $\mathrm{H1^{II}}\ \beta$), 4.527 (d, $J = 8.0$ Hz, $\mathrm{H1^{II}}\ \beta$), 5.111 (d, $J = 3.5$ Hz, $\mathrm{H1^{I}}\ \alpha$).

Found: C, 40.87; H, 6.51; N, 3.26%. Calcd for $C_{14}H_{25}NO_{11}\cdot 1.5H_2O$: C, 40.99; H, 6.88; N, 3.41%.

Allyl 2,3,6-Tri-*O*-benzyl-*α*-D-mannopyranoside (60). To a cooled suspension of **67** (Nacalai Tesque, Inc., 10 g, 55.6 mmol) in allyl alcohol (50 ml), $TsOH\cdot H_2O$ (0.5 g) was added under stirring and the mixture was stirred at 85 °C for 1.5 h. After neutralization with powdery $NaHCO_3$ (0.88 g), the mixture was evaporated and chromatographed with CM system (100 : 1 → 3 : 1) to give **allyl *α*-D-mannopyranoside (68)** (8.4 g, 69%), mp 134—136 °C (lit,[44] mp 138—139 °C). A mixture of **68** (8.3 g, 37.3 mmol), DMF (83 ml), *α*,*α*-dimethoxytoluene (8.3 ml), and pyridinium *p*-toluenesulfonate (149 mg) was stirred at 80 °C for 3 h. After being neutralized with powdered $NaHCO_3$ (0.30 g), the mixture was evaporated and chromatographed with CM system to afford **allyl 4,6-*O*-benzylidene-*α*-D-mannopyranoside (69)** (8.284 g, 71%), mp 134—136°C (lit, mp 148—149 °C,[44] mp 119—122 °C[45]). To a mixture of **69** (2.33 g, 7.6 mmol), DMF (20 ml), and $PhCH_2Br$ (3.39 ml), NaH (60% dispersion, 1.41 g) was added under stirring at 0 °C. After being stirred at 20 °C for 1 h, MeOH (3 ml) was added at 0 °C. Processing and chromatography using HE system (3 : 1) afforded **allyl 2,3-*O*-benzyl-4,6-*O*-benzylidene-*α*-D-mannopyranoside (70)** (2.922 g, 50%), $[\alpha]_D$ +50 (*c* 1.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta = 4.864$ (d, $J = 1.5$ Hz, H1), 5.672 (s, benzylidene), 5.882 (m, allyl); ^{13}C NMR ($CDCl_3$) $\delta = 64.3$ (C5), 68.8 (C6), 76.5 (C2, C3), 79.2 (C4), 98.6 (C1), 101.4 (benzylidene), 117.5, 133.5 (allyl).

Found: C, 73.59; H, 6.64%. Calcd for $C_{30}H_{32}NO_6$: C, 73.75; H, 6.60%.

To a solution of **70** (3.303 g, 7.8 mmol) in CH_2Cl_2 (40 ml) containing Et_3SiH (7.0 ml), CF_3CO_2H (3.5 ml) was added at 0 °C under stirring. After being stirred for 30 min at 0 °C, the mixture was evaporated and chromatographed with TK system (100 : 1 → 10 : 1) to furnish the title **60** (2.593 g, 30% from **67**), $[\alpha]_D$ +12 (*c* 0.4, $CHCl_3$) (lit,[46] $[\alpha]_D$ +3 (*c* 1.6, $CHCl_3$)); ^{1}H NMR ($CDCl_3$) $\delta = 3.820$ (dd, $J = 2.0$, 2.5 Hz, H2), 4.093 (t, $J = 9.0$ Hz, H4), 4.945 (d, $J = 2.0$ Hz, H1), 5.880 (m, All); ^{13}C NMR ($CDCl_3$) $\delta = 67.9$ (All, C4), 70.4 (C6), 71.6 (C5), 74.0 (C2), 79.7 (C3), 97.2 (C1), 117.3, 133.8 (allyl).

Found: C, 73.05; H, 6.94%. Calcd for $C_{30}H_{34}O_6$: C, 73.45; H, 6.99%.

Benzyl 2,3,6-Tri-*O*-benzyl-*α*-D-mannopyranoside (64). A mixture of **67** (10 g, 55.5 mmol), $TsOH\cdot H_2O$ (3.0 g), and $PhCH_2OH$ (10 ml) was stirred at 90 °C for 1.5 h.[47] After addition of $NaHCO_3$ (5.3 g), the mixture was stirred at 50 °C for 1 h and chromatographed to give **71** (5.225 g, 34%), mp 131—132 °C (lit,[48] mp 131—132 °C). A solution of **71** (8.2 g, 30 mmol), DMF (67 ml), *α*,*α*-dimethoxytoluene (6.7 ml), and pyridinium *p*-toluenesulfonate (120 mg) was kept standing at 90 °C for 1 h. Processing as described for **69** and chromatography with CM system (100 : 1 → 3 : 1) afforded **benzyl 4,6-*O*-benzylidene-*α*-D-mannopyranoside (72)** (7.643 g, 70%), mp 149—153 °C, (lit,[44] mp 155—156 °C). To a solution of **72** (1.378 g, 3.8 mmol) in DMF (10 ml) containing $PhCH_2Br$ (1.37 ml), NaH (60% dispersion, 0.46 g) was added under stirring at 0 °C. After the mixture had been stirred at room temp for 1 h, MeOH (1 ml) was added at 0 °C under stirring. Processing and chromatography using HE system gave **benzyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-*α*-D-mannopyranoside (73)**, (1.577 g, 77%), $[\alpha]_D$ +60 (*c* 3.1, $CHCl_3$) (lit,[49]) $[\alpha]_D$ +69 (*c* 0.77, C_5H_5N)). To a solution of **73** (1.467 g, 2.7 mmol) in CH_2Cl_2 (17 ml) containing Et_3SiH (3.0 ml), CF_3CO_2H (1.5 ml) was added at 0 °C under stirring. After being stirred for 30 min at 0 °C, the mixture was evaporated and chromatographed with TK system (100 : 1 → 5 : 1) to furnish the title **64** (0.957 g, 19% from **71**), $[\alpha]_D$ +5 (*c* 3.2, $CHCl_3$) (lit,[46] $[\alpha]_D$ +30 (*c* 0.3, $CHCl_3$)); ^{1}H NMR ($CDCl_3$) $\delta = 3.850$ (dd, $J = 2.0$, 3.5 Hz, H2), 3.958 (dd, $J = 3.5$, 9.5 Hz, H3), 4.119 (t, $J = 9.5$ Hz, H4), 5.103 (d, $J = 2.0$ Hz, H1); ^{13}C NMR ($CDCl_3$) $\delta = 67.8$ (C4), 70.4 (C6), 71.7^6 (C5), 73.9 (C2), 79.6 (C3), 97.2 (C1).

Found: C, 75.15; H, 6.68%. Calcd for $C_{34}H_{36}O_6$: C, 75.53; H, 6.71%.

Allyl *O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-*α*- and *β*-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-*α*-D-mannopyranoside (61 and 62). Condensation of **2** (57.8 mg, 0.12 mmol) and **60** (45.9 mg, 0.094 mmol) in CH_2Cl_2 (0.9) ml containing NsCl (51.9 mg), AgOTf (60.2 mg), and Et_3N (32.7 μl) and chromatography with TK system (10 : 1) gave **61** (37.3 mg, 41%), $[\alpha]_D$ +48 (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta = 3.287$ (dd, $J = 4.0$, 10.0 Hz, $\mathrm{H2^{II}}$), 4.078 (dd, $J = 3.0$, 9.0 Hz, $\mathrm{H3^{1}}$), 3.860 (dd, $J = 2.0$, 3.0 Hz, $\mathrm{H2^{I}}$), 4.303 (t, $J = 9.0$ Hz, $\mathrm{H4^{I}}$), 4.957 (d, $J = 2.0$ Hz, $\mathrm{H1^{I}}$), 5.750 (d, $J = 4.0$ Hz, $\mathrm{H1^{II}}$), 5.906 (m, All); ^{13}C NMR ($CDCl_3$) $\delta = 63.5$ ($\mathrm{C2^{II}}$), 67.9 ($\mathrm{C6^{II}}$), 69.6 ($\mathrm{C6^{I}}$), 71.3 ($\mathrm{C4^{I}}$, $\mathrm{C5^{I,II}}$), 74.2 ($\mathrm{C2^{I}}$), 78.1

(C4$^{\mathrm{II}}$), 80.2 (C3$^{\mathrm{II}}$), 80.9 (C3$^{\mathrm{I}}$), 97.1 (C1$^{\mathrm{I}}$), 97.9 (C1$^{\mathrm{II}}$), 117.3, 133.8 (All), and **62** (40.4 mg, 45%), [α]$_{\mathrm{D}}$ +13 (*c* 0.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta = 3.203$ (dt, $J = 3.0$, 3.0, 9.0 Hz, H5$^{\mathrm{II}}$), 3.630 (t, $J = 9.5$ Hz, H4$^{\mathrm{II}}$), 3.783 (dd, $J = 2.0$, 2.5 Hz, H2$^{\mathrm{I}}$), 3.927 (dd, $J = 2.0$, 9.0 Hz, H3$^{\mathrm{I}}$), 4.341 (t, $J = 9.0$ Hz, H4$^{\mathrm{I}}$), 4.356 (d, $J = 8.0$ Hz, H1$^{\mathrm{II}}$), 4.930 (d, $J = 2.0$ Hz, H1$^{\mathrm{I}}$), 5.882 (m, All); ^{13}C NMR ($CDCl_3$) $\delta = 67.2$ (C2$^{\mathrm{II}}$), 68.4 (C6$^{\mathrm{II}}$), 69.1 (C6$^{\mathrm{I}}$), 71.5 (C5$^{\mathrm{I}}$), 75.2 (C5$^{\mathrm{II}}$), 75.3 (C4$^{\mathrm{I}}$), 75.6 (C2$^{\mathrm{I}}$), 77.9 (C4$^{\mathrm{II}}$), 78.4 (C3$^{\mathrm{I}}$), 83.3 (C3$^{\mathrm{II}}$), 97.5 (C1$^{\mathrm{I}}$), 101.4 (C1$^{\mathrm{II}}$), 117.2, 133.8 (All).

Found: **61**; C, 72.58; H, 6.54; N 4.31%. **62**; C, 72.06; H, 6.58; N, 4.39%. Calcd for $C_{57}H_{61}N_3O_{10}$: C, 72.21; H, 6.49; N, 4.43%.

***O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-D-mannopyranose (63).** A mixture of **62** (90.0 mg, 0.095 mmol), NaOAc (43.7 mg), $PdCl_2$ (23.7 mg), and aq AcOH (95%, 3.55 ml) was stirred at room temp overnight. Allyl alcohol (0.72 ml) was added to the mixture at 0 °C, which was further stirred for 2 h at room temp. Evaporation to dryness and chromatography using TK system (100 : 1 → 10 : 1) gave **63** (82.9 mg, 96%), [α]$_{\mathrm{D}}$ −7 (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$) (73% α) $\delta = 2.841$ (br, OH), 3.197 (dt, $J = 3.0$, 3.0, 10.0 Hz, H5$^{\mathrm{II}}$ α), 3.645 (dd, $J = 3.0$, 9.5 Hz, H3$^{\mathrm{I}}$ β), 3.751 (dd, $J = 2.0$, 2.5 Hz, H2$^{\mathrm{I}}$ α), 4.087 (ddd, $J = 2.5$, 4.5, 9.0 Hz, H5$^{\mathrm{I}}$ α), 4.227 (t, $J = 9.0$ Hz, H4$^{\mathrm{I}}$ α), 4.340 (d, $J = 7.5$ Hz, H1$^{\mathrm{II}}$ β), 5.240 (br, H1$^{\mathrm{I}}$ α); ^{13}C NMR ($CDCl_3$) $\delta = 67.1$ (C2$^{\mathrm{II}}$ β), 67.2 (C6$^{\mathrm{II}}$ α), 68.3 (C6$^{\mathrm{II}}$ α), 68.5 (C6$^{\mathrm{II}}$ β), 68.9 (C6$^{\mathrm{I}}$ β), 69.4 (C6$^{\mathrm{I}}$ α), 71.5 (C5$^{\mathrm{I}}$ α), 74.3 (C4$^{\mathrm{I}}$ β), 75.0 (C5$^{\mathrm{I}}$ β), 75.1^6 (C5$^{\mathrm{II}}$ α), 75.2^2 (C5$^{\mathrm{II}}$ β), 75.7 (C2$^{\mathrm{I}}$ α, C4$^{\mathrm{I}}$ α), 76.4 (C2$^{\mathrm{I}}$ β), 77.7 (C3$^{\mathrm{I}}$ α), 77.8 (C4$^{\mathrm{II}}$ α), 77.9 (C4$^{\mathrm{II}}$ β), 80.0 (C2$^{\mathrm{I}}$ β), 83.2 (C3$^{\mathrm{II}}$ β), 83.3 (C3$^{\mathrm{II}}$ α), 93.0 (C1$^{\mathrm{I}}$ α, $J = 169.0$ Hz), 93.5 (C1$^{\mathrm{I}}$ β, $J = 161.1$ Hz), 101.0 (C1$^{\mathrm{II}}$ β, $J = 162.1$ Hz), 101.5 (C1$^{\mathrm{II}}$ α, $J = 161.0$ Hz).

Found: C, 70.99; H, 6.39; N, 4.65%. Calcd for $C_{54}H_{57}N_3O_{10}$: C, 71.43; H, 6.33; N, 4.63%.

Benzyl *O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-mannopyranoside (65). Condensation of **63** (35.8 mg, 0.039 mmol) and **64** (31.3 mg, 0.058 mmol) was performed in CH_2Cl_2 (0.4 ml) in the presence of NsCl (21.9 mg), AgOTf (25.4 mg), and Et_3N (13.8 µl) and chromatography with TK system (100 : 1 → 10 : 1) gave **61** (29.2 mg, 52%), [α]$_{\mathrm{D}}$ +4.5 (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta = 4.293$ (d, $J = 7.5$ Hz, H1$^{\mathrm{III}}$), 4.993 (d, $J = 2.0$ Hz, H1$^{\mathrm{I}}$), 5.377 (d, $J = 2.5$ Hz, H1$^{\mathrm{II}}$); ^{13}C NMR ($CDCl_3$) $\delta = 67.1$ (C2$^{\mathrm{III}}$), 68.4 (C6$^{\mathrm{III}}$), 68.9 (C6$^{\mathrm{II}}$), 70.2 (C6$^{\mathrm{I}}$), 71.7 (C5$^{\mathrm{II}}$), 72.1 (C4$^{\mathrm{II}}$), 72.5 (C5$^{\mathrm{I}}$), 73.8^5 (C2$^{\mathrm{I}}$), 73.9^2 (C4$^{\mathrm{I}}$), 75.1 (C5$^{\mathrm{III}}$), 76.7 (C3$^{\mathrm{II}}$), 77.8 (C4$^{\mathrm{III}}$), 78.1 (C3$^{\mathrm{II}}$), 80.2 (C3$^{\mathrm{I}}$), 83.3 (C3$^{\mathrm{III}}$), 96.9 (C1$^{\mathrm{I}}$), 99.9 (C$^{\mathrm{II}}$), 101.4 (C1$^{\mathrm{III}}$).

Found: C, 73.49; H, 6.48; N, 3.18%. Calcd for $C_{88}H_{91}N_3O_{15}$: C, 73.88; H, 6.41; N, 2.94%.

Benzyl *O*-(2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-mannopyranoside (66). A mixture of **65** (48.2 mg, 0.034 mmol), $LiAlH_4$ (15.5 mg), and Et_2O (6.6 ml) was refluxed for 30 min. After AcOEt (2.0 ml) was added, the mixture was evaporated to dryness. To the resulting solid, MeOH (6.6 ml), AcOH (0.06 ml) and Ac_2O (0.60 ml) were added. After 15 min, the mixture was evaporated to dryness and chromatographed using TK system (100 : 1 → 2 : 1) to furnish **66** (42.2 mg, 86%), [α]$_{\mathrm{D}}$ +63 (*c* 0.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta = 1.608$ (s, Ac), 4.635 (d, $J = 7.5$ Hz, H1$^{\mathrm{III}}$), 4.963 (d, $J = 8.0$, NH), 4.992 (d, $J = 2.0$ Hz, H1$^{\mathrm{I}}$), 5.351 (d, $J = 2.5$ Hz, H1$^{\mathrm{II}}$); ^{13}C NMR ($CDCl_3$) $\delta = 23.4$ (Ac), 56.8 (C2$^{\mathrm{III}}$), 68.7 (C6$^{\mathrm{III}}$), 69.4 (C6$^{\mathrm{II}}$), 70.1 (C6$^{\mathrm{I}}$), 71.8 (C5$^{\mathrm{I,II}}$), 72.1 (C4$^{\mathrm{II}}$), 73.8 (C4$^{\mathrm{I}}$), 73.9 (C2$^{\mathrm{I}}$), 75.1 (C5$^{\mathrm{III}}$), 76.4 (C2$^{\mathrm{II}}$), 78.3 (C4$^{\mathrm{III}}$), 78.4 (C3$^{\mathrm{II}}$), 80.2 (C3$^{\mathrm{I}}$), 81.9 (C3$^{\mathrm{III}}$), 96.9 (C1$^{\mathrm{I}}$), 99.9 (C$^{\mathrm{II}}$), 100.8 (C1$^{\mathrm{III}}$), 170.1 (Ac).

Found: C, 74.08; H, 6.65; N, 0.85%. Calcd for $C_{90}H_{95}N_3O_{16}$: C, 74.22; H, 6.62; N, 0.97%.

***O*-(2-Acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-*O*-α-D-mannopyranosyl)-(1→4)-D-mannopyranose (59).** Hydrogenation of **66** (35.0 mg, 0.024 mmol) over Pd on C (10%, 29 mg) in AcOH (6.0 ml) containing H_2O (0.05 ml) at room temp for 18 h, followed by chromatography with CM system (100 : 1 → 1 : 1) afforded **59** (8.9 mg, 69%), [α]$_{\mathrm{D}}$ +47 (*c* 0.4, H_2O); ^{1}H NMR (D_2O) (80% α) $\delta = 2.050$ (s, Ac), 4.083 (dd, $J = 2.0$, 3.0 Hz, H2$^{\mathrm{II}}$), 4.540 (d, $J = 8.0$ Hz, H1$^{\mathrm{III}}$), 4.857 (d, $J = 1.0$ Hz, H1$^{\mathrm{II}}$), 5.140 (d, $J = 2.0$ Hz, H1$^{\mathrm{I}}$ α), 5.210 (d, $J = 2.0$ Hz, H1$^{\mathrm{I}}$ β); ^{13}C NMR (D_2O) $\delta = 24.8$ (Ac), 58.2 (C2$^{\mathrm{III}}$), 63.0 (C6$^{\mathrm{III}}$), 63.3 (C6$^{\mathrm{II}}$), 63.6 (C6$^{\mathrm{I}}$), 71.8 (C2$^{\mathrm{I}}$ α), 72.4 (C2$^{\mathrm{I}}$ β, C2$^{\mathrm{II}}$, C4$^{\mathrm{III}}$), 73.3 (C3$^{\mathrm{I}}$ α), 73.6 (C3$^{\mathrm{II}}$), 73.8 (C5$^{\mathrm{I}}$ α), 74.4 (C3$^{\mathrm{I}}$ β), 74.6 (C5$^{\mathrm{II}}$), 76.1 (C5$^{\mathrm{III}}$), 76.7 (C4$^{\mathrm{I}}$ β), 77.0 (C4$^{\mathrm{I}}$ α), 77.3 (C5$^{\mathrm{I}}$ β), 78.5 (C4$^{\mathrm{II}}$), 80.6 (C3$^{\mathrm{III}}$), 96.2 (C1$^{\mathrm{I}}$ β, $J = 159.3$ Hz), 96.5 (C1$^{\mathrm{I}}$ α, $J = 170.3$ Hz), 103.6^8 (C1$^{\mathrm{II}}$ β, $J = 171.8$ Hz), 103.7^3 (C1$^{\mathrm{II}}$ α, $J = 171.8$ Hz), 104.2 (C1$^{\mathrm{III}}$, $J = 162.7$ Hz).

Found: C, 39.66; H, 6.87; N, 1.96%. Calcd for $C_{20}H_{35}NO_{16}\cdot 3.5H_2O$: C, 39.47; H, 6.96; N, 2.30%.

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