In situ Activating Glycosylation of 6-Deoxysugars: Synthesis of *O*-α-D-Fucosyl-(1→4)-*O*-α-D-fucosyl-(1→4)-*O*-α-D-quinovosyl-(1→4)-D-quinovose

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The linear tetrasaccharide, α-D-fucopyranosyl-(1→4)-α-D-fucopyranosyl-(1→4)-α-D-quinovopyranosyl-(1→4)-D-quinovopyranose, the sugar cluster of asterosaponin A from the starfish, *Asterias amurensis*, was synthesized in a convergent manner. We employed an in situ activating glycosylation using 1-OH sugar derivatives and a system of *p*-nitrobenzenesulfonyl chloride, silver trifluoromethanesulfonate, and triethylamine as well as a related system. #

In recent time, the development of the methods for glycosylation have brought forth great progress in the technology for the reconstruction of sugar chains having fairly large degrees of polymerization.[1] In view of simplifications of procedure for glycosylation, however, not many protocols in which a 1-OH sugar derivative is directly activated in the presence of an acceptor have been reported.[2] To our knowledge, such a method has not yet been well used for the 1-OH derivatives of 6-deoxysugars, which are found in many kinds of natural products.[3] The cases reported were the use of 2,3,4-tri-*O*-benzyl-L-rhamnopyranose as a glycosyl donor in the synthesis of the trifurcated sugar cluster[4] using the system of *p*-nitrobenzenensulfonyl chloride (NsCl), silver trifluoromethanesulfonate (AgOTf), and triethylamine (TEA) (NST system)[5] and the use of 2,3,4-tri-*O*-benzyl-L-fucopyranose in the stereoselective glycosylation of the protected D-serine in the presence of trimethylsilyl triflate.[6] We now wish to show a new application of in situ activating glycosylation[5,7] for synthesis of 6-deoxysugars. The aim of this paper is the demonstration of a synthesis of the linear tetrasaccharide, α-D-fucopyranosyl-(1→4)-α-D-fucopyranosyl-(1→4)-α-D-quinovopyranosyl-(1→4)-D-quinovopyranose (**1**),[8] the sugar cluster in asterosaponin A from *Asterias amurensis*, by way of an in situ activating glycosylation using 1-OH derivatives of 6-deoxyhexoses and the NST system[5] as well as the related NSDT system.[7] The glycosylation with these reagent systems has been studied using 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (TBG) by us some years ago.

The tetrasaccharide **1** was planned to be synthesized convergently from the four monosaccharide units, **2**, **3**, **4**, and **5**, via the syntheses of the intermediary disaccharide derivatives, **6** and **7**, as shown in Fig. 1. The synthesis was started from the transformation of the acetal **8**[9] into the acceptor **2**, as illustrated in Fig. 2. Compound **8** was benzylated, followed by hydrolysis, to give the diol **9**, of which transformation into the monotosylate **10** was performed by selective tosylation of its primary OH group. This afforded the acceptor **2**, on reduction with lithium tetrahydridoaluminate (LAH). Such a route has been used to prepare a similar benzyl derivative of quinovose.[10] Recently, **2** has been prepared via a different route.[11] The donor **3** was prepared earlier.[12]

The acceptor **4** was prepared from the acetal **11**[13] via selective tosylation of the diol **12**, as illustrated in Fig. 2. The reported procedure[14] for reduction of the tosylate **13** with LAH was slightly modified. The donor **5** was prepared from the galactoside derivative **14**.[15] Direct bromination of **14** with carbon tetrabromide and triphenylphosphine,[16] afforded quantitatively the bromide **15**. This has been prepared via a two-step process.[17] Efficient reduction of **15** with the tributyltin hydride[18] furnished the D-fucoside **16**. Acid hydrolysis of **16** afforded **5**.[19]

The in situ activating glycosylation of the acceptors **17** and **18** was carried out using the quinovosyl donor, **19**,[12] **3**, and the fucosyl donnor **5** (Table 1) in the presence of the NST system[5] as well as of the NSDT system,[7] consisting of NsCl, AgOTf, *N*,*N*-dimethylacetamide (DMA), and TEA (Fig. 3), in order to evaluate the applicability of these systems to the present case. In the case of **19**, the NSDT system was effective to produce the α-linked disaccharides, **20a** (Run 2) and **21a** (Run 4), in comparison with the cases employing the NST system (Runs 1 and 3). The quinovose derivative **3** also selectively afforded the α-linked disaccharides **22a** in the use of the NSDT system (Run 6), whereas the NST system did not show appreciable selectivity (Run 5). These results show that DMA is effective for the selective formation of α-glycoside of the 6-deoxysugar derivatives, **19** and **3**, but its effect was less than that in the previous cases using TBG.[7]

It was found that the glycosylation of the secondary alcohol **17** using the fucosyl donor **5** and the NST system yielded the α-linked disaccharides **23a** selectively (Run 7, α/β = 72/28), differing from the case of the quinovosyl

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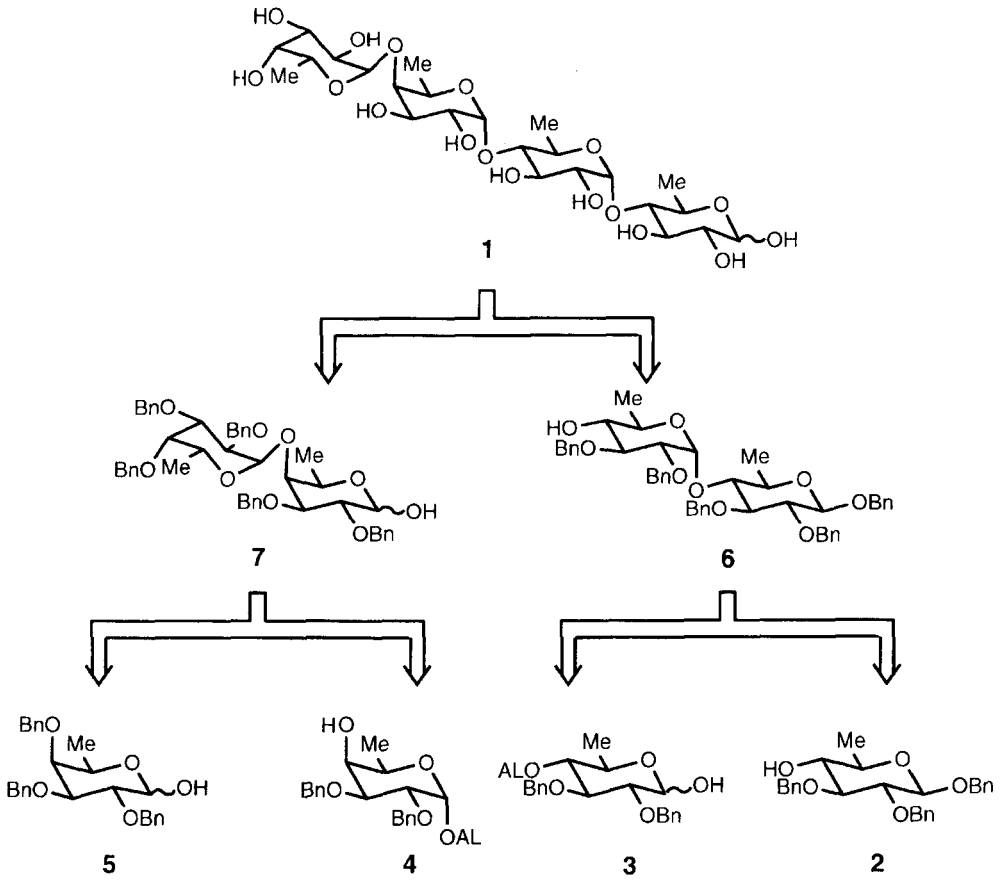

Fig. 1. Retrosynthesis of *O*-α-D-Fuc*p*-(1→4)-*O*-α-D-Fuc*p*-(1→4)-*O*-α-D-Qui*p*-(1→4)-D-Qui*p* (**1**).

Table 1. Results of Glycosylation Using 1-OH Derivatives of 6-Deoxysugars[a,b]

Run	DOH (eq)	AOH (mg, mmol)	N/eq	S/eq	D/eq	T/eq	CH_2Cl_2/ml	DOA (%, α/β)
1	**19** (1.3)	**17** (30.0, 0.065)	2.5	2.5	—	2.5	0.30	**20a+20b** (95, 58/42)
2	**19** (1.3)	**17** (30.0, 0.065)	2.5	2.5	2.5	2.5	0.30	**20a+20b** (97, 83/17)
3	**19** (1.1)	**18** (30.0, 0.065)	1.7	1.7	—	1.7	0.30	**21a+21b** (94, 62/38)
4	**19** (1.3)	**18** (30.0, 0.065)	2.5	2.5	5.0	2.5	0.30	**21a+21b** (89, 66/34)
5	**3** (1.3)	**2** (30.0, 0.069)	2.5	2.5	—	2.5	0.30	**22a+22b** (77, 55/45)
6	**3** (1.3)	**2** (30.0, 0.070)	2.5	2.5	2.5	2.5	0.30	**22a+22b** (92, 78/21)
7	**5** (1.3)	**17** (30.0, 0.065)	2.5	2.5	—	2.5	0.30	**23a+23b** (96, 72/28)
8	**5** (1.1)	**18** (30.0, 0.065)	1.7	1.7	—	1.7	0.30	**24a+24b** (70, 33/67)
9	**5** (1.3)	**4** (31.0, 0.081)	2.5	2.5	—	2.5	0.30	**25a+25b** (71, 65/35)
10	**5** (1.3)	**4** (33.0, 0.086)	2.5	2.5	2.5	2.5	0.30	**25a+25b** (98, 68/32)
11	**7** (1.2)	**6** (34.0, 0.045)	3.0	3.0	—	3.0	0.34	**30a+30b** (87, 94/6)
12	**7** (1.3)	**6** (32.0, 0.042)	3.0	3.0	3.0	3.0	0.32	**30a+30b** (94, 98/2)

a) The reactions started at −60 °C of bath temp which was allowed to rise up to 0 °C at a pace of ca. 0.3 min^{-1}, and then kept at this temp for 24 h. b) DOH = donor, AOH = acceptor, DOA = condensates, N = *p*-$NO_2C_6H_4SO_2Cl$ (NsCl), S = CF_3SO_3Ag (AgOTf), D = $AcNMe_2$ (DMA), T = Et_3N (TEA).

donor **19** (Run 1, α/β = 58/42). The benzyloxy group at the C-4 position oriented into the β-side of **5** appears to interfere with the incoming bulky **17** to its anomeric center from the β-side to depress the yield of the β-linked **23b**. On the contrary to this, however, the analogous glycosylation of the primary alcohol **18** using **5** and the NST system gave the β-linked disaccharides **24b** selectively (Run 8, α/β = 33/67). These results contrast to those (Run 3, α/β = 62/38) obtained in the case of the quinovosyl donor **19**. We consider that the selective formation of the β-linked **24b** is due to the high ratio (α/β = 71/29) of the α-anomer of **5** comparing to that (α/β = 55/45) of **19**. Reactive primary alcohol **18** will react, even at lower temperature, with the intermediary α-sulfonate[7] formed from the major α-anomer of **5** in S_N2 manner to produce the β-glycoside **24b** significantly. On condensation of **4** and **5**, the NSDT system improved the yield of the condensates, **25a** and **25b** (Run 10), in comparison with the case using the NST system (Run 9), although

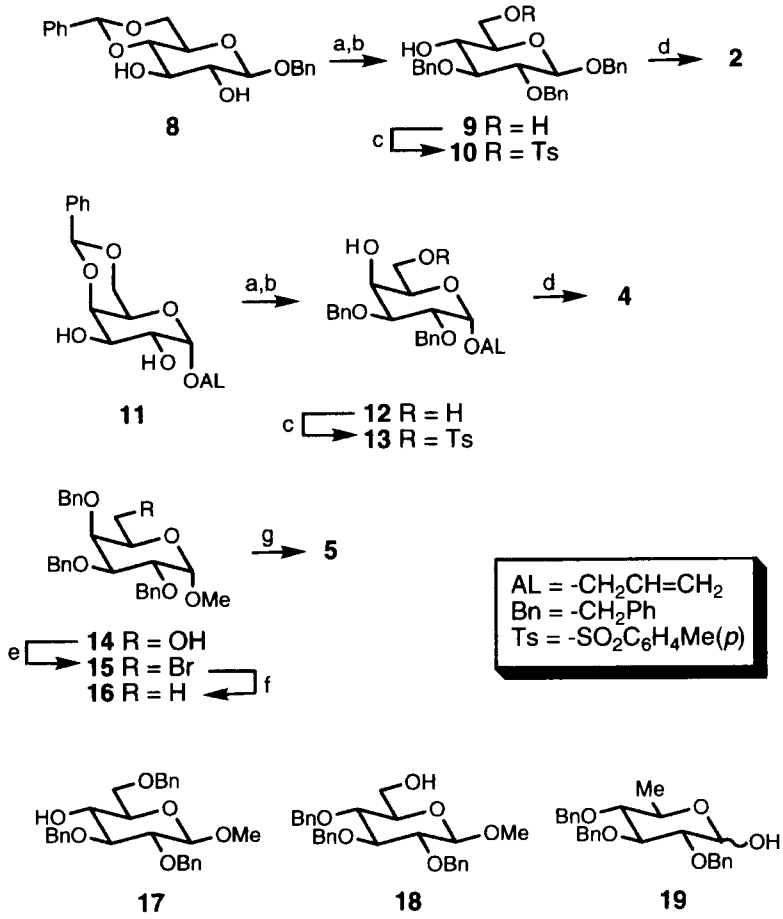

Fig. 2. Syntheses of the monosaccharide units. a) BnBr, NaH/DMF, 0 °C; b) aq AcOH (80%), △; c) TsCl/Pyridine, 0 °C→room temp; d) $LiAlH_4/Et_2O$, △; e) CBr_4, Ph_3P/Pyridine, △; f) Bn_3SnH, AIBN/PhMe, △; g) H_2SO_4/aq AcOH, △.

the α-selectivity was not much improved.

Removal of allyl group from the disaccharide derivative **22a** produced the acceptor **6**. This could also be synthesized alternatively from the maltose derivative **26** (Fig. 4). Tritylation of **26** afforded **27**, of which conversion into the diol **28** was carried out via benzylation and successive hydrolysis. Controlled tosylation of **28** on its primary OH groups afforded the ditosylate **29**, which was then transformed reductively into **6**, using LAH.

Mild deallylation of **25a** was carried out to give the donor **7** (Fig. 3). The condensation of **6** and **7** furnished the totally benzylated tetrasaccharide **30a** with excellent α-selectivity (Fig. 3); the yield was better in the use of the NSDT (Run 12) than that in the use of the NST system (Run 11) as was true in the case of **5** (Run 10). The final total debenzylation of **30a** afforded the desired **1**. The component disaccharides, **31** and **32**, obtained through debenzylation of **6** and **7**, respectively (Fig. 3).

In summary, (1) in situ activating glycosylation using a 1-OH sugar derivative and the NST system[5] or the NSDT system[7] was applicable to the 6-deoxysygars, D-quinovose, and D-fucose, and (2) a synthesis of the tetrasaccharide **1**,[8] starting from the monosaccharide units, **2**, **3**, **4**, and **5**, was demonstrated by the use of the α-glycosylation with the NSDT system.[7]

Experimental[9,21]

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–MeOH (CM), hexane–AcOEt (HE), PhMe–AcOEt (TE), and PhMe–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 melting points were determined by a Micro-melting-point apparatus (Yanagimoto Mfg., Co.). The optical rotations were measured on a JASCO DIP-180 Digital Polarimeter at room temp. The ^1H and ^{13}C NMR spectra were recorded with a Varian VXR300, occasionally with a Varian XL-400, spectrometer, along with the measurements of H,H-COSY, C,H-COSY, and DEPT spectra. The assignments of the spectra of **31a** and of **1** were made by auxiliary measurements of HOHAHA, HMQC, and HMBC spectra. The described data of ^1H NMR for the hydrogens in a sugar framework are based on the signals showing clear splitting patterns. As for ^{13}C NMR, the data described are those for the carbons in a sugar structure together with some charactaristic chemical shifts of substituents. The chemical shifts of the ^{13}C NMR spectra of **31**, **32**, and **1** in D_2O are summarized in Table 2.

Compounds **3**,[12] **8**,[9] **19**[12] ^1H NMR ($CDCl_3$, 300 MHz) δ = 4.43 (0.45H, d, $J_{1,2}$ = 7.5 Hz, H1β (this expression means the H atom at the position 1 of the β-anomer and so on)), 4.99 (0.55H, d,

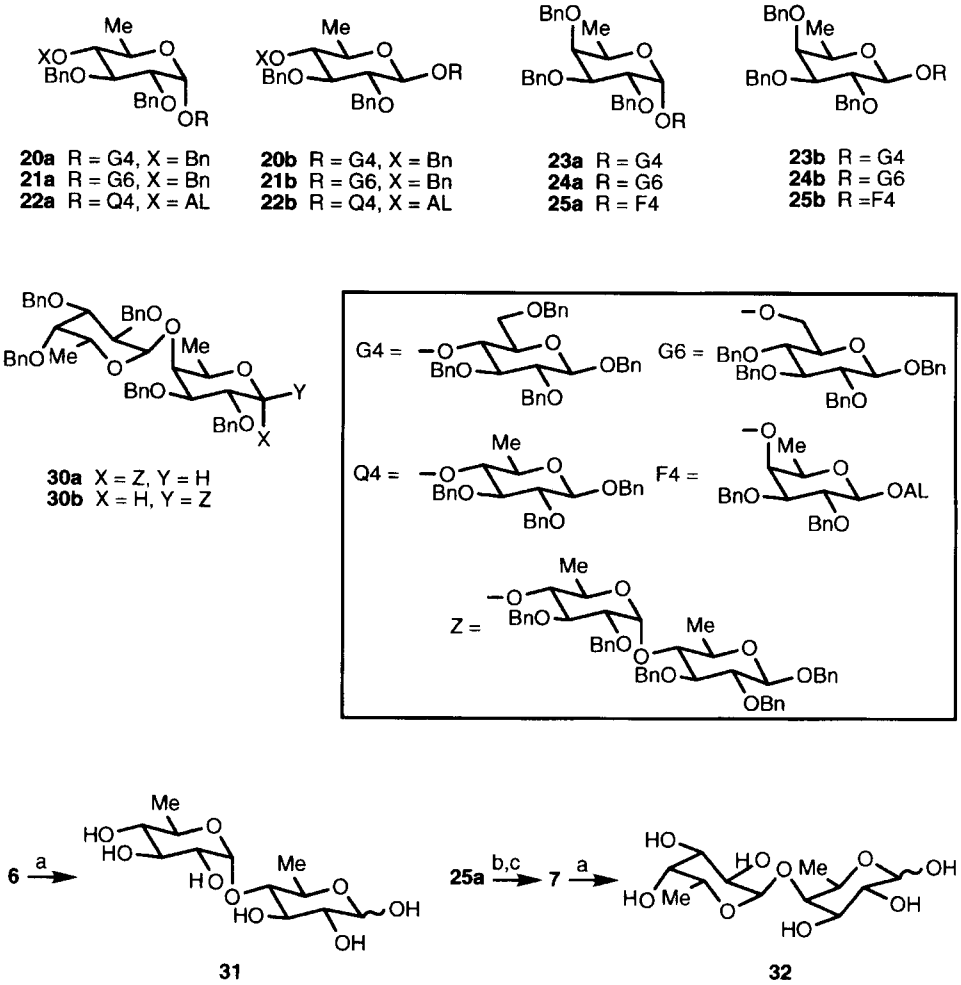

Fig. 3. Glycosylation by in situ activation of 1-OH derivatives and synthesis of disaccharide fragments **31** and **32**. a) H_2, Pd–C (10%)/AcOH; b) $RhCl(Ph_3P)_3$/EtOH–PhH–H_2O, △; c) dil HCl/Me_2CO, △.

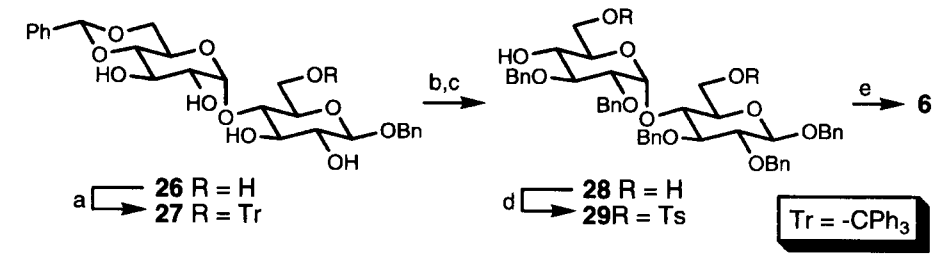

Fig. 4. Alternative synthesis of monohydroxy derivative of α-D-quinovosyl-(1→4)-D-quinovose. a) TrCl/Pyridine, △; b) BnBr, NaH/DMF, 0 °C; c) aq AcOH (80%), △; d) TsCl/Pyridine, 0 °C→room temp; e) $LiAlH_4$/Et_2O, △; f) $RhCl(Ph_3P)_3$/EtOH–PhH–H_2O, △; g) dil HCl/Me_2CO, △.

$J_{1,2}$ = 3.0 Hz, H1α); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 100.9 (C1α (this expression means the C atom at the position 1 of the α-anomer and so on)), 105.2 (C1β)), and **26**[9] were those reported previously. The acceptors **17**[21] and **18**[22] were prepared by the known methods.

The results of glycosylation are summarized in Table 1. The ratios of α-linked glycoside to β-linked one, expressed as α/β, are based on the weight of the products obtained through chromatographical separation using the solvent systems specified below.

Benzyl 2,3-Di-*O*-benzyl-6-*O*-tosyl-β-D-glucopyranoside (10). The known procedure was modified as follows: A mixture of **8**[9] (5 g, 0.014 mol), $PhCH_2Cl$ (35 ml, 0.30 mol), and crushed KOH (7.5 g, 0.13 mol) was vigorously stirred at 120 °C for 1.3 h. The cooled mixture was diluted with PhMe (150 ml) and H_2O (100 ml). The aqueous layer was extracted with PhMe (75 ml and 30 ml). The combined organic layer was washed five times with water (50 ml) and concentrated to give a yellow oil. This was treated with aq AcOH (80%, 70 ml) at 95 °C for 40 min. Concentration and chromatography with TK system gave almost pure **Benzyl 2,3-Di-*O*-benzyl-β-D-glucopyranoside** (**9**) (5.1 g, 81%), mp 108—109 °C (lit,[23] mp 112—113 °C). To a solution of **9** (3.5 g, 7.8 mmol)

Table 2. ^{13}C NMR Spectral Data[a] of **1**,[b] **31**,[c] and **32**[c]

	31		32		1	
	α	β	α	β	α	β
C1^{I}	95.1	99.0	95.7	99.8	95.2	99.0
C2^{I}	74.9	77.6	71.5	74.9	74.9	77.6
C3^{I}	76.5	79.5	72.1	75.8	76.5	79.5
C4^{I}	86.5	86.0	83.4	82.6	86.9	86.4
C5^{I}	69.3	73.9	70.4	74.4	69.3	73.9
C6^{I}	20.7	20.8	18.9	19.0	20.68	20.73
C1^{II}	103.2	103.0	103.78	103.82	103.1	103.0
C2^{II}	75.4	75.3	72.1	72.1	75.2	75.1
C3^{II}	76.0	76.0	72.8	72.8	76.7	76.7
C4^{II}	78.2	78.2	75.3	75.3	86.2	86.2
C5^{II}	71.9	71.9	70.3	70.3	70.5	70.5
C6^{II}	19.8	19.8	18.6	18.6	20.2	20.2
C1^{III}					103.7	103.7
C2^{III}					71.8	71.8
C3^{III}					72.4	72.4
C4^{III}					83.3	83.3
C5^{III}					71.3	71.3
C6^{III}					18.3	18.3
C1^{IV}					103.8	103.8
C2^{IV}					72.1	72.1
C3^{IV}					72.8	72.8
C4^{IV}					75.4	75.4
C5^{IV}					70.4	70.4
C6^{IV}					18.6	18.6

a) The spectra were measured at 100.8 MHz, in D_2O. b) The spectra were measured at 75.6 MHz, in D_2O. c) The assignments were made by the measurements of H,H-COSY and C,H-COSY spectra. For the tetrasaccharide **1**, the assignments were assisted by the auxilary measurements of HOHAHA, HMQC, and HMBC spectra.

in pyridine (31 ml), a solution of TsCl (1.9 g, 10 mmol) in pyridine (3.5 ml) was added portionwise under stirring at 0 °C for 30 min. After being kept at room temp for 3 d, the reaction mixture was concentrated and chromatographed with TK system to give **10** (4.3 g, 74% from **8**), $[\alpha]_D$ −36 (*c* 1.2, $CHCl_3$) (lit,[24] $[\alpha]_D$ −36 (*c* 2, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 2.34 (1H, br, OH), 2.43 (3H, s, Ts), 4.24 (1H, dd, $J_{5,6a}$ = 5.0 Hz, $J_{6a,6b}$ = 11.0 Hz, H6a), 4.36 (1H, dd, $J_{5,6b}$ = 1.0 Hz, H6b), 4.48 (1H, d, $J_{1,2}$ = 7.0 Hz, H1); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 21.6 (Ts), 69.0 (C6), 69.5 (C4), 73.1 (C5), 81.6 (C2), 83.6 (C3), 102.2 (C1).

Found: C, 67.35; H, 6.07%. Calcd for $C_{34}H_{36}O_8S$: C, 67.53; H, 6.00%.

Benzyl 2,3-Di-*O*-benzyl-6-deoxy-β-D-glucopyranoside (2). To a solution of **10** (3.9 g, 6.5 mmol) in Et_2O (92 ml), LAH (0.97 g, 25.6 mmol) was carefully added portionwise. After refluxing for 50 min at 50 °C, the resulting mixture was cooled in an ice-bath and diluted with PhMe (50 ml), followed by the addition of AcOEt (9.7 ml) dropwise under stirring. Concentration and chromatography with TE system gave colorless crystalline material (3.0 g). Recrystallization from hexane gave **2** (2.0 g, 71%), mp 125—126 °C, $[\alpha]_D$ −59 (*c* 0.6, $CHCl_3$) (lit,[11] mp 125—127 °C, $[\alpha]_D$ −56 (*c* 0.6, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.34 (3H, d, $J_{5,6}$ = 6.0 Hz, H6), 2.15 (1H, d, $J_{4,OH}$ = 2.3 Hz, OH), 3.25 (1H, dt, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, H4), 3.34 (1H, dq, H5), 3.39 (1H, t, $J_{2,3}$ = 9.0 Hz, H3), 3.51 (1H, dd, $J_{1,2}$ = 7.5 Hz, H2), 4.53 (1H, d, H1); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 17.7 (C6), 71.3 (C5), 74.9 (C4), 82.2 (C2), 84.0 (C3), 102.5 (C1).

Found: C, 74.55; H, 7.04%. Calcd for $C_{27}H_{30}O_5$: C, 74.63; H, 6.96%.

Allyl 2,3-Di-*O*-benzyl-α-D-galactopyranoside (12). This was prepared from D-galactose via a modified process as follows: A mixture of anhydrous D-galactose (Kanto Chemical Co., Inc., 10 g, 0.056 mol), allyl alcohol (81 ml, 1.2 mol), and $MeSO_3H$ (0.81 ml, 13 mmol) was refluxed at 90 °C for 3 h. After the addition of $NaHCO_3$ (1.3 g, 16 mmol), the mixture was stirred overnight at room temp. Concentration and chromatography with CM system afforded colorless solid **allyl D-galactopyranoside** (7.8 g, 64%), ^{1}H NMR (D_2O, 300 MHz) δ = 4.43 (0.33H, d, $J_{1,2}$ = 7.5 Hz, H1β), 4.99 (0.67H, d, $J_{1,2}$ = 3.0 Hz, H1α); ^{13}C NMR (D_2O, 75 MHz) δ = 100.9 (C1α), 105.2 (C1β). This was dissolved in DMF (47 ml, 0.107 mmol) containing benzaldehyde dimethyl acetal (16ml) and $TsOH\cdot H_2O$ (0.54 g, 3 mmol) and the resulting solution was kept standing overnight at room temp. After $NaHCO_3$ (0.48 g) was added, concentration and chromatography with CM system afforded pure colorless solid **11** (7.8 g, 45% from D-galactose), mp 102—103 °C (lit,[13] mp 115—117 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 5.09 (1H, d, $J_{1,2}$ = 1.5 Hz, H1), 5.56 (1H, s, benzylidene), 5.93 (1H, m, allyl); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 98.2 (C1), 101.3 (benzylidene). Further elution furnished the β-anomer (> 2 g); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 4.33 (1H, d, $J_{1,2}$ = 7.5 Hz, H1), 5.55 (1H, s, benzylidene), 5.96 (1H, m, allyl); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 101.4 (benzylidene), 101.6 (C1).

To a mixture of **11** (4.4 g, 14 mmol), DMF (44 ml), and $PhCH_2Br$ (10 ml, 84 mmol) was added NaH (ca. 60% in oil, 2.2 g, 55 mmol) at 0 °C. After this mixture was stirred for 1.7 h at room temp, MeOH (10 ml) was added under stirring in cold bath. The mixture was diluted with PhMe (300 ml) and H_2O (100 ml). The aqueous layer was extracted with PhMe (200 ml and 100 ml) and then the combined organic layer was washed four times with water (100 ml). After concentration, chromatography with TE system afforded colorless syrupy benzyl ether (6.7 g). A portion of this (320 mg, 0.66 mmol) was heated with aq AcOH (80%, 2.3 ml) at 95 °C for 15 min. Concentration and chromatography with TE system gave colorless syrupy **12** (190 mg, 70% from **11**), $[\alpha]_D$ +68 (*c* 1.0, $CHCl_3$) (lit,[14] $[\alpha]_D$ +96.1 (*c* 0.6, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 2.35 (1H, dd, *J* = 4.0, 8.5 Hz, OH6), 2.72 (1H, s, OH4), 3.83 (1H, dd, $J_{4,5}$ = 0 Hz, $J_{5,6}$ = 4.0, 6.0 Hz, H5), 3.86 (1H, dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 10.0 Hz, H2), 3.92 (1H, dd, $J_{3,4}$ = 3.0 Hz, H3), 4.09 (1H, d, $J_{3,4}$ = 3.0 Hz, H4), 4.91 (1H, d, H1), 5.93 (1H, m, allyl); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 63.1 (C6), 69.1 (C5), 69.3 (C4), 75.6 (C2), 77.3 (C3), 96.3 (C1), 118.1, 133.8 (allyl).

Found: C, 68.31; H, 7.12%. Calcd for $C_{23}H_{28}O_5$: C, 68.98; H, 7.05%.

Allyl 2,3-Di-*O*-benzyl-6-*O*-*p*-tosyl-α-D-galactopyranoside (13). To a solution of **12** (540 mg, 1.3 mmol) in pyridine (3.3 ml) was added TsCl (510 mg, 2.7 mmol) under stirring at 0 °C. After the mixture was stirred overnight at room temp, MeOH (0.5 ml) was added. Concentration and chromatography with TE system afforded **13** (680 mg, 91%), $[\alpha]_D$ +51 (*c* 0.50, $CHCl_3$) (lit,[14] $[\alpha]_D$ +69.5 (*c* 1.0, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 2.40 (3H, t, *J* = 1.2 Hz, OH4), 2.45 (3H, s, Ts), 3.78 (1H, dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.5 Hz, H2), 3.89 (1H, dd, $J_{3,4}$ = 3.5 Hz, H3), 3.98 (1H, dd, $J_{4,5}$ = 1.2 Hz, H4), 4.02 (1H, ddd, $J_{5,6a}$ = 7.0 Hz, $J_{1,6b}$ = 5.0 Hz, H5), 4.16 (1H, dd, $J_{6a,6b}$ = 10.0 Hz, H6a), 4.23 (1H, dd, H6b), 4.81 (1H, d, H1), 5.92 (1H, m, allyl); ^{13}C NMR ($CDCl_3$, 75 MHz)

δ = 21.6 (Ts), 67.4 (C4), 67.5 (C5), 69.0 (C6), 75.5 (C2), 77.1 (C3), 96.0 (C1), 118.3, 133.5 (allyl).

Found: C, 64.52 ; H, 6.15%. Calcd for $C_{30}H_{34}O_8S$: C, 64.96 ; H, 6.18%.

Allyl 2,3-Di-*O*-benzyl-6-deoxy-α-D-galactopyranoside (4). To a solution of **13** (5.413 g, 9.8 mmol) in Et_2O (130 ml), LAH (1.486 g, 39 mmol) was added portionwise. After refluxing for 20 min, a mixture was cooled in an ice bath. After the dilution with added toluene (65 ml), AcOEt (15 ml) was added dropwise under stirring. Concentration and chromatography with TE system gave **4** (3.48 g, 93%), $[\alpha]_D$ +68 (*c* 1.0, $CHCl_3$) (lit,[14] $[\alpha]_D$ +47.1 (*c* 1.7, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.26 (3H, d, $J_{5,6}$ = 6.5 Hz, H6), 2.45 (1H, br, OH4), 3.83 (1H, dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 10.0 Hz, H2), 3.83 (1H, dd, $J_{3,4}$ = 3.0 Hz, $J_{4,5}$ = 1.0 Hz, H4), 3.91 (1H, dd, H3), 3.94 (1H, dq, H5), 4.82 (1H, d, H1), 5.93 (1H, m, allyl); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 16.1 (C6), 65.2 (C5), 70.3 (C4), 75.5 (C2), 77.9 (C3), 96.1 (C1), 117.8, 134.0 (allyl).

Found: C, 71.56 ; H, 7.27%. Calcd for $C_{23}H_{28}O_5$: C, 71.85 ; H, 7.34%.

Methyl 2,3,4-Tri-*O*-benzyl-6-bromo-6-deoxy-α-D-galactopyranoside (15). To a solution of **14** (2.2 g, 4.7 mmol) in pyridine (20 ml) and Ph_3P (2.4 g, 9.2 mmol) was added CBr_4 (1.6 g, 4.8 mmol) under stirring at 0 °C. After stirring overnight at 65 °C, MeOH (40 ml) was added and the mixture was stirred for a while. Concentration and chromatography with TE system afforded **15** (2.5 g, 100%), $[\alpha]_D$ +21 (*c* 0.57, $CHCl_3$) (lit,[17] $[\alpha]_D$ +27.1 (*c* 1.8, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.30 (1H, dd, $J_{5,6a}$ = 7.0 Hz, $J_{6a,6b}$ = 10.0 Hz, H6a), 3.39 (1H, dd, $J_{5,6b}$ = 7.0 Hz, H6b), 3.40 (3H, s, Me), 3.88 (1H, dt, $J_{4,5}$ = 1.0 Hz, H5), 3.95 (1H, dd, $J_{2,3}$ = 10.0 Hz, $J_{3,4}$ = 2.5 Hz, H3), 4.02 (1H, dd, H4), 4.03 (1H, dd, $J_{1,2}$ = 3.5 Hz, H2), 4.66 (1H, d, H1); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 30.7 (C6), 55.6 (Me), 70.8 (C5), 75.3 (C4), 76.2 (C2), 79.0 (C3), 98.9 (C1).

Found: C, 63.59; H, 5.97%. Calcd for $C_{28}H_{31}BrO_5$: C, 63.76; H, 5.92%.

Methyl 2,3,4-Tri-*O*-benzyl-6-deoxy-α-D-galactopyranoside (16). A solution of **15** (1.456 g, 2.8 mmol) in PhMe (127 ml) containing Bu_3SnH (4.52 ml, 17 mmol) was stirred for 5 min under N_2 at 95 °C. To this, AIBN (164 mg, 1 mmol) was added in one portion and the mixture was stirred for 30 min at 95 °C. The reaction mixture was concentrated and chromatographed with TE system to yield **16** (1.21 g, 98%), $[\alpha]_D$ +21 (*c* 1.0, $CHCl_3$) (lit,[25] for the L-enantiomer, $[\alpha]_D$ −20 (*c* 1.02, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.12 (3H, d, $J_{5,6}$ = 6.5 Hz, H6), 3.36 (3H, s, Me), 3.64 (1H, dd, $J_{5,6}$ = 2.8 Hz, $J_{4,5}$ = 1.0 Hz, H4), 3.83 (1H, dq, H5), 3.93 (1H, dd, $J_{2,3}$ = 10.0 Hz, H3), 4.04 (1H, dd, $J_{1,2}$ = 3.5, H2), 4.65 (1H, d, H1); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 16.6 (C6), 55.3 (Me), 66.1 (C5), 76.4 (C2), 77.9 (C4), 79.4 (C3), 98.8 (C1).

Found: C, 74.65; H, 7.19%. Calcd for $C_{28}H_{32}O_5$: C, 74.98; H, 7.19%.

2,3,4-Tri-*O*-benzyl-6-deoxy-α-D-galactopyranose (5). A mixture of **15** (490 mg, 1.1 mmol), AcOH (6.6 ml), H_2O (0.049 ml), and dil H_2SO_4 (3M, 0.069 ml) was stirred for 30 min at 88 °C. After the slow addition of $NaHCO_3$ (460 mg), the mixture was concentrated and chromatographed with TE system to give **5** (230 mg, 48%), mp 82—84 °C, $[\alpha]_D$ +30 (*c* 0.62, $CHCl_3$) (lit,[19] mp 94.5—95.6 °C, $[\alpha]_D$ +24.0 (*c* 1.0, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) (71%α) δ = 1.15 (d, $J_{5,6}$ = 6.5 Hz, H6α), 1.21 (d, $J_{5,6}$ = 6.2 Hz, H6β), 3.00 (br, OHα), 3.29 (br d, $J_{1,OH}$ = 7.2 Hz, OHβ), 3.54 (dq, $J_{4,5}$ = 1.0 Hz, H5β), 3.55 (qt, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 3.0 Hz, H3β), 3.59 (dd, H4β), 3.68 (dd, $J_{3,4}$ = 3.0 Hz, $J_{4,5}$ = 1.0 Hz, H4α), 3.75 (dd, $J_{1,2}$ = 7.2 Hz, H2β), 3.91 (1H, dd, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 3.0 Hz, H3α), 4.05 (dd, $J_{1,2}$ = 3.5 Hz, H2α), 4.11 (dq, H5α), 4.62 (t, H1β); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 16.7 (C6α), 16.9 (C6β), 66.7 (C5α), 76.4 (C4β), 76.5 (C2α), 77.3 (C4α), 79.1 (C3α), 80.7 (C2β), 82.5 (C3β), 91.8 (C1α), 97.7 (C1β). The ^{1}H and ^{13}C NMR spectra of **5** were identical with those of the L-enantiomer of **5**, prepared via the known method[25] from L-fucose.

Found: C, 73.86; H, 6.89%. Calcd for $C_{27}H_{30}O_5$: C, 74.63 ; H, 6.96%.

Benzyl *O*-(4,6-*O*-Benzylidene-α-D-glucopyranosyl)-(1→4)-6-*O*-trityl-β-D-glucopyranoside (27). A mixture of benzyl *O*-α-D-glucopyranosyl-(1→4)-β-D-glucopyranoside[9] (3.9 g, 9.0 mmol), DMF (35 ml), benzaldehyde dimethyl acetal (3.9 mg, 26 mmol), and TsOH·H_2O (0.39 g, 2.1 mmol) was kept stirring for 4 d at room temp. Work-up and chromatography with CM system as described above afforded the acetal **26**,[9] which was then reacted with TrCl (3.2 g, 11.5 mmol) in pyridine (23 ml) under stirring overnight at 78 °C. After the addition of TEA (23 ml), the mixture was concentrated and chromatographed with CM system to give **27** (5.5 g, 80%), $[\alpha]_D$ +30 (*c* 2.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.77 (1H, t, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, H3^{II}), 4.34 (1H, d, $J_{1,2}$ = 7.5 Hz, H1^{I}), 4.85 (1H, d, $J_{1,2}$ = 3.5 Hz, H1^{II}), 5.66 (1H, s, benzylidene); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 63.1 (C6^{I}), 63.4 (C5^{II}), 68.6 (C6^{II}), 70.3 (benzyl), 70.8 (C3^{II}), 73.5 (C5^{I} and C2^{II}), 74.4 (C4^{I}), 76.3 (C2^{I}), 80.6 (C4^{II}), 81.2 (C3^{I}), 86.7 (Tr), 100.7 (C1^{I}), 101.7 (C1^{II}).

Found: C, 69.97; H, 6.24%. Calcd for $C_{45}H_{46}O_{11}$·0.5H_2O: C, 70.02; H, 6.14%.

Benzyl *O*-(2,3-Di-*O*-benzy-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-benzyl-β-D-glucopyranosides (28). To a solution of **27** (5.5 g, 7.2 mmol) in DMF (600 ml) containing $PhCH_2Br$ (16 ml, 135 mmol) was added NaH (ca. 60% in oil, 2.5 g, 63 mmol) portionwise under stirring at 0 °C. After stirring for 2.4 h at room temp, MeOH (18 ml) was added dropwise under stirring at 0 °C. The mixture was diluted with PhMe (300 ml) and H_2O (200 ml). The aqueous layer was extracted with PhMe (200 ml and 100 ml) and the organic layer was washed four times with H_2O (100 ml), concentrated and chromatographed with HE system to give the benzyl derivative of **27**. This was treated with aq AcOH (80%, 110 ml) at 93 °C for 2 h. Concentration and chromatography with TE system gave **28** (> 5.6 g, > 98%), $[\alpha]_D$ +11 (*c* 0.72, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.44 (1H, t, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, H4^{II}), 3.44 (1H, dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.5 Hz, H2^{II}), 3.56 (1H, dd, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 9.0 Hz, H2^{I}), 3.74 (1H, t, H3^{II}), 3.83 (1H, t, $J_{3,4}$ = 9.0 Hz, H3^{I}), 4.13 (1H, t, $J_{4,5}$ = 9.0 Hz, H4^{I}), 4.66 (1H, d, H1^{I}), 5.74 (1H, d, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 61.4 (C6^{I}), 62.5 (C6^{II}), 70.7 (C4^{II}), 71.4 (C4^{I}), 72.6 (C5^{II}), 74.6 (C5^{I}), 78.9 (C2^{II}), 81.3 (C3^{II}), 82.2 (C2^{I}), 84.7 (C3^{I}), 96.6 (C1^{II}), 102.5 (C1^{I}),

Found: C, 70.59 ; H, 6.63%. Calcd for $C_{47}H_{52}O_{11}$·0.5H_2O: C, 70.39 ; H, 6.66%.

Benzyl *O*-(2,3-Di-*O*-benzy-6-*O*-tosyl-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-benzyl-6-*O*-tosyl-β-D-glucopyranosides (29). To a solution of **28** (180 mg, 0.23 mmol) in pyridine (1.3 ml) was added TsCl (150 mg, 0.78 mmol) under stirring at 0 °C. After this mixture was stirred overnight at room temp, MeOH (0.15 ml) was added to the mixture; this was stirred for a while. Concentration and chromatography with TE system afforded **29** (230 mg, 92%), $[\alpha]_D$ +21 (*c* 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 2.38 (3H, s, Ts), 2.42 (3H, s, Ts), 2.41 (1H, d, $J_{4,OH}$ = 4.0 Hz, OH4^{II}), 3.37 (1H, dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.5 Hz, H2^{II}), 3.44 (1H, dd, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 8.5 Hz, H2^{I}), 3.52 (1H, dt, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4^{II}), 3.58 (1H, ddd, $J_{4,5}$ = 9.0 Hz, $J_{5,6a}$ = 2.5 Hz, $J_{5,6b}$ = 4.5 Hz, H5^{I}), 3.70 (1H, t, $J_{3,4}$ = 8.5 Hz, H3^{I}), 3.71 (1H, t, H3^{II}), 3.72 (1H, ddd, $J_{5,6a}$ = 3.0 Hz, $J_{5,6b}$ = 2.5 Hz, H5^{II}), 3.80 (1H, dd, H4^{I}),

4.25 (1H, dd, $J_{6a,6b}$ = 11.0 Hz, H6a^{I}), 4.27 (1H, dd, H6b^{I}), 4.30 (1H, dd, $J_{6a,6b}$ = 11.0 Hz, H6a^{II}), 4.33 (1H, dd, H6b^{II}), 4.45 (1H, d, H1^{I}), 5.49 (1H, d, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 21.6 (Ts), 68.7 (C6^{I}), 69.1 (C6^{II}), 69.3 (C4^{II}), 70.5(C5^{II}), 72.3(C5^{I}), 73.2 (C4^{I}), 78.5 (C2^{II}), 80.7 (C3^{II}), 81.6 (C2^{I}), 84.0 (C3^{I}), 96.8 (C1^{II}), 101.7 (C1^{I}).

Found: C, 66.68 ; H, 5.99%. Calcd for $C_{61}H_{64}O_{15}S_2$: C, 66.53 ; H, 5.86%.

Benzyl *O*-(2,3-Di-*O*-benzy-6-deoxy-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-benzyl-6-deoxy-β-D-glucopyranosides (6). To a solution of **29** (52 mg, 0.047 mmol), LAH (7.3 mg, 0.19 mmol) was added. After reflux for 30 min at 50 °C, the mixture was cooled in ice bath, followed by the addition of PhMe (1.3 ml) and AcOEt (0.2 ml). Concentration and chromatography with TE system gave **6** (25 mg, 70%), $[\alpha]_D$ +8.6 (*c* 1.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.26 (3H, d, $J_{5,6}$ = 6.5 Hz, H6^{II}), 1.43 (3H, d, $J_{5,6}$ = 6.0 Hz, H6^{I}), 2.20 (1H, d, $J_{4,OH}$ = 1.5 Hz, OH4^{II}), 3.17 (1H, dt, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4^{II}), 3.45 (1H, dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.5 Hz, H2^{II}), 3.57 (1H, dd, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 8.5 Hz, H2^{I}), 3.56 (1H, dq, $J_{4,5}$ = 8.5 Hz, H5^{I}), 3.67 (1H, t, $J_{3,4}$ = 8.5 Hz, H4^{I}), 3.70 (1H, t, H3^{II}), 3.78 (1H, t, H3^{I}), 3.80 (1H, dq, H5^{II}), 4.55 (1H, d, H1^{I}), 5.66 (1H, d, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 17.6 (C6^{II}), 19.1 (C6^{I}), 67.8 (C5^{II}), 70.8 (C5^{I}), 75.3 (C4^{II}), 77.4 (C4^{I}), 79.5(C2^{II}), 81.2 (C3^{II}), 82.6 (C2^{I}), 84.7 (C3^{I}), 96.4 (C1^{II}), 102.2 (C1^{I}).

Found: C, 73.38 ; H, 6.89%. Calcd for $C_{47}H_{52}O_9$: C, 74.19 ; H, 6.89%.

This was synthesized alternatively from **22a** as follows: A mixture of **22a** (33 mg, 0.041 mmol), NaOAc (19 mg, 0.23 mmol), and $PdCl_2$ (10 mg, 0.056 mmol) in aq AcOH (95%, 1.3 ml) was stirred overnight at room temp. After the addition of allyl alcohol (0.2 ml), the mixture was concentrated and chromatographed with TK system to afford **6** (26.3 mg, 84%).

General Procedure for Glycosylation. a) Glycosylation in the presence of a ternary mixture of NST[5] (Table 1). To a rubber-stoppered vessel containing a mixture of an acceptor, a donor, NsCl, AgOTf, and CH_2Cl_2, TEA was injected under stirring at −60 °C (bath temp). The bath temp was allowed to rise (ca. 0.3 °C min^{-1}) to 0 °C, at which temperature the mixture was well stirred for 18 h. After the dilution with PhMe (about 6 times vol of the solvent), $NaHCO_3$ (the same wt of AgOTf) was added to the reaction mixture; this was stirred for 15 min and then chromatographed with TK system. Traces of any nitrogenous compounds in the condensates were removed by rechromatography on silica gel with HE system. The anomeric separations of the condensates were preformed using the solvent specified in each case below. b) Glycosylation in the presence of a quaternary mixture of NSDT[8] (Table 1). To a mixture of an acceptor, donor, NsCl, AgOTf, and CH_2Cl_2, DMA and then TEA were successively added at −60 °C (bath temp). After that, the reaction and work-up were conducted in the same manner as described above for the NST system.

Methyl *O*-(2,3,4-Tri-*O*-benzyl-6-deoxy-α- and -β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosides (20a and 20b). 20a: R_f 0.56 (HE 2 : 1), $[\alpha]_D$ +24 (*c* 0.35, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.18 (3H, d, $J_{5,6}$ = 6.0 Hz, H6^{II}), 3.12 (1H, t, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, H4^{II}), 3.46 (1H, dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.5 Hz, H2^{II}), 3.52 (1H, dd, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 8.5 Hz, H2^{I}), 3.598 (3H, s, Me), 3.604 (1H, dt, $J_{4,5}$ = 9.0 Hz, $J_{5,6}$ = 3.5 Hz, H5^{I}), 3.80 (1H, dq, $J_{4,5}$ = 9.0 Hz, $J_{5,6}$ = 6.0 Hz, H5^{II}), 3.81 (1H, t, $J_{3,4}$ = 8.5 Hz, H3^{I}), 3.815 (1H, dd, $J_{61,6b}$ = 10.0 Hz, H6a^{I}), 3.823 (1H, dd, H6b^{I}), 3.90 (1H, dd, H3^{II}), 4.05 (1H, dd, H4^{I}), 4.37 (1H, d, $J_{1,2}$ = 7.5 Hz, H1^{I}), 5.57 (1H, d, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 17.9 (C6^{II}), 56.9 (Me), 67.5 (C5^{II}), 69.1 (C6^{I}), 72.8(C4^{I}), 74.5 (C5^{I}), 79.7 (C2^{II}), 81.7 (C3^{II}), 82.2 (C2^{I}), 83.9 (C4^{II}), 84.7 (C3^{I}), 96.3 (C1^{II}), 104.5 (C1^{I}).

20b: R_f 0.59 (HE 2 : 1), $[\alpha]_D$ +25 (*c* 0.47, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.22 (3H, d, $J_{5,6}$ = 6.0 Hz, H6^{II}), 3.15 (1H, t, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, H4^{II}), 3.25 (1H, dq, H5^{II}), 3.36 (1H, dd, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 9.0 Hz, H2^{I}), 3.37 (1H, ddd, $J_{4,5}$ = 9.0 Hz, $J_{5,6a}$ = 1.5 Hz, $J_{5,6b}$ = 4.0 Hz, H5^{I}), 3.43 (1H, dd, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 9.0 Hz, H2^{II}), 3.51 (1H, t, H3^{II}), 3.565 (3H, s, Me), 3.573 (1H, dd, $J_{3,4}$ = 9.5 Hz, H3^{I}), 3.73 (1H, dd, $J_{6a,6b}$ = 11.0 Hz, H6a^{I}), 3.85 (1H, dd, H6b^{I}), 4.02 (1H, dd, H4^{I}), 4.30 (1H, d, H1^{I}), 4.50 (1H, d, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 17.9 (C6^{II}), 57.0 (Me), 68.1 (C6^{I}), 71.1 (C5^{II}), 75.2 (C5^{I}), 76.5 (C4^{I}), 81.7 (C2^{I}), 82.9 (C3^{I}), 83.1 (C2^{II}), 83.7 (C4^{II}), 84.7 (C3^{II}), 102.2 (C1^{II}), 104.7 (C1^{I}).

Found: **20a**, C, 74.98 ; H, 6.91%. **20b**, C, 74.87 ; H, 6.84%. Calcd for $C_{55}H_{60}O_{10}$: C, 74.98 ; H, 6.86%.

Methyl *O*-(2,3,4-Tri-*O*-benzyl-6-deoxy-α- and -β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranosides (21a and 21b). 21a: R_f 0.61 (HE 2 : 1), mp 138—140 °C, $[\alpha]_D$ +43 (*c* 0.36, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.24 (3H, d, $J_{5,6}$ = 6.5 Hz, H6^{II}), 3.13 (1H, t, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, H4^{II}), 3.50 (1H, dt, $J_{4,5}$ = 9.0 Hz, $J_{5,6a}$ = $J_{5,6b}$ = 1.5 Hz, H5^{I}), 3.546 (1H, dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.0 Hz, H2^{II}), 3.553 (3H, s, Me), 3.68 (1H, dd, $J_{2,3}$ = 8.5 Hz, $J_{3,4}$ = 9.0 Hz, H3^{I}), 3.70 (1H, t, $J_{4,5}$ = 9.0 Hz, H4^{I}), 3.86 (1H, dq, H5^{II}), 3.97 (1H, t, H3^{II}), 4.32 (1H, d, $J_{1,2}$ = 8.0 Hz, H1^{I}), 4.96 (1H, d, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 18.0 (C6^{II}), 56.9 (Me), 65.8 (C6^{I}), 66.7 (C5^{II}), 74.8 (C5^{I}), 77.8 (C4^{I}), 80.4 (C2^{II}), 81.4 (C3^{II}), 82.4 (C2^{I}), 83.9 (C4^{II}), 84.6 (C3^{I}), 96.9 (C1^{II}), 104.6 (C1^{I}).

21b: R_f 0.68 (HE 2 : 1), mp 126—128 °C, $[\alpha]_D$ +18 (*c* 0.28, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.32 (3H, d, $J_{5,6}$ = 6.0 Hz, H6^{II}), 3.21 (1H, t, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, H4^{II}), 3.39 (1H, dq, H5^{II}), 3.42 (1H, dd, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 9.0 Hz, H2^{I}), 3.46 (3H, s, Me), 3.47 (1H, dd, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 9.0 Hz, H2^{II}), 3.57 (1H, t, H3^{II}), 3.59 (1H, ddd, $J_{4,5}$ = 9.0 Hz, $J_{5,6a}$ = 1.5 Hz, $J_{5,6b}$ = 6.5 Hz, H5^{I}), 3.67 (1H, t, $J_{3,4}$ = 9.0 Hz, H3^{I}), 3.69 (1H, dd, $J_{6a,6b}$ = 11.0 Hz, H6a^{I}), 3.84 (1H, t, H4^{I}), 4.20 (1H, dd, H6b^{I}), 4.27 (1H, d, H1^{I}), 4.47 (1H, d, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 17.9 (C6^{II}), 57.0 (Me), 68.6 (C6^{I}), 71.1 (C5^{II}), 75.0 (C5^{I}), 78.3 (C2^{I}), 82.3 (C2^{II}), 82.4 (C3^{I}), 83.4 (C4^{II}), 84.5 (C4^{I}), 84.6 (C3^{II}), 103.6 (C1^{II}), 104.6 (C1^{I}).

Found: **21a**, C, 74.74 ; H, 6.93%. **21b**, C, 74.98 ; H, 6.86%. Calcd for $C_{55}H_{60}O_{10}$: C, 74.98 ; H, 6.86%.

Benzyl *O*-(4-*O*-Allyl-2,3-di-*O*-benzyl-6-deoxy-α- and -β-D-glucopyranosyl)-(1→4)-2,3-di-*O*-benzyl-6-deoxy-β-D-glucopyranosides (22a and 22b). 22a: R_f 0.59 (TK 10 : 1), $[\alpha]_D$ +32 (*c* 0.33, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.27 (3H, d, $J_{5,6}$ = 6.5 Hz,H6^{II}), 1.43 (3H, d, $J_{5,6}$ = 6.0 Hz, H6^{I}), 2.99 (1H, dd, $J_{3,4}$ = 9.0 Hz, $J_{3,4}$ = 9.5 Hz, H4^{II}), 3.42 (1H, dd, $J_{1,2}$ = 4.0 Hz, $J_{2,3}$ = 10.0 Hz, H2^{II}), 3.551 (1H, dd, $J_{1,2}$ = 4.0 Hz, $J_{2,3}$ = 10.0 Hz, H2^{I}), 3.551 (1H, dq, $J_{4,5}$ = 9.0 Hz, H5^{I}), 3.65 (1H, t, $J_{3,4}$ = 9.0 Hz, H4^{I}), 3.76 (1H, dd, H3^{I}), 3.83 (1H, dd, H3^{II}), 3.84 (1H, dq, H5^{II}), 4.47 (1H, d, H1^{I}), 5.61 (1H, d, H1^{II}), 5.92 (1H, m, allyl); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 17.7 (C6^{II}), 19.1 (C6^{I}), 67.4 (C5^{II}), 70.8 (C5^{I}), 77.8 (C4^{I}), 79.6 (C2^{II}), 81.7 (C3^{II}), 82.7 (C2^{I}), 83.7 (C4^{II}), 84.7 (C3^{I}), 96.6 (C1^{II}), 102.2 (C1^{I}), 117.1, 134.9 (allyl).

22b: R_f 0.53 (TK 10 : 1), $[\alpha]_D$ +2.6 (*c* 0.23, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.22 (3H, d, $J_{5,6}$ = 6.0 Hz, H6^{II}), 1.41 (3H, d, $J_{5,6}$ = 6.0 Hz, H6^{I}), 3.40 (1H, t, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, H4^{II}), 3.29 (1H, dq, H5^{II}), 3.37 (1H, dd, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 9.0 Hz, H2^{II}), 3.38 (1H, dq, $J_{4,5}$ = 8.5 Hz, H5^{I}), 3.51 (1H, dd, $J_{1,2}$ = 7.0 Hz, $J_{2,3}$ = 8.0 Hz, H2^{I}), 3.53 (1H, dd, $J_{3,4}$ = 9.5 Hz, H4^{I}), 3.547 (1H, t, H3^{II}),

3.549 (1H, dd, H3^{I}), 4.50 (1H, d, H1^{I}), 4.57 (1H, d, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 17.9 (C6^{II}), 18.1 (C6^{I}), 71.2 (C5^{II}), 71.6 (C5^{I}), 82.1 (C2^{I}), 82.6 (C4^{I}), 82.9 (C3^{I}), 83.1 (C2^{II}), 83.5 (C4^{II}), 84.7 (C3^{II}), 102.3 (C1^{I}), 102.9 (C1^{II}), 117.0, 134.8 (allyl).

Found: **22a**, C, 74.87 ; H, 7.10%. **22b**, C, 74.71 ; H, 7.02%. Calcd for $C_{50}H_{56}O_9$: C, 74.98 ; H, 7.05%.

Methyl *O*-(2,3,4-Tri-*O*-benzyl-6-deoxy-α- and -β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosides (23a and 23b). 23a: R_f 0.39 (TK 10 : 1), $[\alpha]_D$ +29 (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 0.98 (3H, d, $J_{5,6}$ = 6.5 Hz, H6^{II}), 3.44 (1H, dd, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 9.0 Hz, H2^{I}), 3.52 (1H, dd, $J_{3,4}$ = 2.5 Hz, $J_{4,5}$ = 1.0 Hz, H4^{II}), 3.58 (3H, s, Me), 3.68 (1H, dq, H5^{II}), 3.76 (1H, t, $J_{3,4}$ = 9.0 Hz, H3^{I}), 3.77 (1H, dd, $J_{2,3}$ = 10.5 Hz, H3^{II}), 3.88 (1H, t, $J_{4,5}$ = 9.0 Hz, H4^{I}), 3.97 (1H, dd, $J_{1,2}$ = 4.0 Hz, H2^{II}), 4.33 (1H, d, H1^{I}), 5.66 (1H, d, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 16.7 (C6^{II}), 56.9 (Me), 67.0 (C5^{II}), 69.6 (C6^{I}), 72.8 (C4^{I}), 74.5 (C5^{I}), 75.5 (C2^{II}), 77.1 (C4^{II}), 79.5 (C3^{II}), 82.4 (C2^{I}), 84.7 (C3^{I}), 97.3 (C1^{II}), 104.4 (C1^{I}).

23b: R_f 0.38 (TK 10 : 1), $[\alpha]_D$ +17 (*c* 0.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.10 (3H, d, $J_{5,6}$ = 6.5 Hz, H6^{II}), 3.21 (1H, dq, $J_{4,5}$ = 1.0 Hz, H5^{II}), 3.38 (1H, dd, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 3.0 Hz, H3^{II}), 3.40 (1H, ddd, $J_{4,5}$ = 8.5 Hz, $J_{5,6a}$ = 2.0 Hz, $J_{5,6b}$ = 4.0 Hz, H5^{I}), 3.41 (1H, dd, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 9.0 Hz, H2^{I}), 3.50 (1H, dd, H4^{II}), 3.57 (3H, s, Me), 3.59 (1H, t, $J_{3,4}$ = 9.0 Hz, H3^{I}), 3.73 (1H, dd, $J_{1,2}$ = 8.0 Hz, H2^{II}), 3.77 (1H, dd, $J_{6a,6b}$ = 11.5 Hz, H6a^{I}), 3.81 (1H, dd, H6b^{I}), 3.97 (1H, dd, H4^{I}), 4.29 (1H, d, H1^{I}), 4.43 (1H, d, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 16.9 (C6^{II}), 57.0 (Me), 68.5 (C6^{I}), 70.3 (C5^{II}), 75.2(C5^{I}), 76.5 (C4^{I}), 76.8 (C4^{II}), 79.9 (C2^{II}), 81.9 (C2^{I}), 82.9 (C3^{II}), 83.1 (C3^{I}), 102.6 (C1^{II}), 104.6 (C1^{I}).

Found: **23a**, C, 74.87 ; H, 6.85%. **23b**, C, 74.76 ; H, 6.86%. Calcd for $C_{55}H_{60}O_{10}$: C, 74.98 ; H, 6.86%.

Methyl *O*-(2,3,4-Tri-*O*-benzyl-6-deoxy-α- and -β-D-galactopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranosides (24a and 24b). 24a: R_f 0.54 (HE 2 : 1), mp 126—128 °C, $[\alpha]_D$ +42 (*c* 0.72, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.09 (3H, d, $J_{5,6}$ = 6.5 Hz, H6^{II}), 3.32 (1H, dd, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 8.5 Hz, H2^{I}), 3.49 (3H, s, Me), 3.58 (1H, dd, $J_{3,4}$ = 2.5 Hz, $J_{4,5}$ = 1.0 Hz, H4^{II}), 3.87 (1H, dq, H5^{II}), 3.91 (1H, dd, $J_{2,3}$ = 10.0 Hz, H3^{II}), 4.04 (1H, dd, $J_{1,2}$ = 3.5 Hz, H2^{II}), 4.28 (1H, d, H1^{I}), 5.00 (1H, d, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 16.7 (C6^{II}), 56.7 (Me), 66.3 (C5^{II} and C6^{I}), 74.7 (C5^{I}), 76.6 (C2^{II}), 78.1 (C4^{I} and C4^{II}), 78.6 (C3^{II}), 82.4 (C2^{I}), 84.6 (C3^{I}), 97.9 (C1^{II}), 104.5 (C1^{I}).

24b: R_f 0.50 (HE 2 : 1), mp 139—140 °C, $[\alpha]_D$ +2.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.19 (3H, d, $J_{5,6}$ = 6.5 Hz, H6^{II}), 3.398 (1H, dd, $J_{3,4}$ = 8.5 Hz, $J_{4,5}$ = 10.0 Hz, H4^{I}), 3.399 (1H, dd, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 8.5 Hz, H2^{I}), 3.42 (3H, s, Me), 3.43 (1H, dq, $J_{4,5}$ = 1.0 Hz, H5^{II}), 3.48 (1H, dd, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 3.0 Hz, H3^{II}), 3.56 (1H, dd, H4^{II}), 3.60 (1H, ddd, $J_{5,6a}$ = 7.0 Hz, $J_{5,6b}$ = 1.0 Hz, H5^{I}), 3.66 (1H, t, H3^{I}), 3.67 (1H, dd, $J_{6a,6b}$ = 11.0 Hz, H6a^{I}), 3.84 (1H, dd, $J_{1,2}$ = 7.5 Hz, H2^{II}), 4.23 (1H, dd, H6b^{I}), 4.25 (1H, d, H1^{I}), 4.42 (1H, d, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 16.8 (C6^{II}), 57.1(Me), 68.4 (C6^{I}), 70.3 (C5^{II}), 75.2 (C5^{I}), 76.4 (C4^{II}), 78.6 (C4^{I}), 79.3 (C2^{II}), 82.4 (C2^{I}), 82.5 (C3^{II}), 84.7 (C3^{I}), 104.1 (C1^{II}), 104.5 (C1^{I}).

Found: **24a**, C, 74.64 ; H, 6.97%. **24b**, C, 74.83 ; H, 6.75%. Calcd for $C_{55}H_{60}O_{10}$: C, 74.98 ; H, 6.86%.

Allyl *O*-(2,3,4-Tri-*O*-benzyl-6-deoxy-α- and -β-D-galactopyranosyl)-(1→4)-2,3-di-*O*-benzyl-6-deoxy-α-D-galactopyranosides (25a and 25b). 25a: R_f 0.60 (TK 10 : 1), $[\alpha]_D$ +88 (*c* 1.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 0.91 (3H, d, $J_{5,6}$ = 6.5 Hz, H6^{II}), 1.28 (3H, d, $J_{5,6}$ = 6.5 Hz, H6^{I}), 3.62 (1H, dd, $J_{3,4}$ = 2.5 Hz, $J_{4,5}$ = 1.0 Hz, H4^{II}), 3.80 (1H, d, $J_{3,4}$ = 2.0 Hz, $J_{4,5}$ = 0 Hz, H4^{I}), 3.865 (1H, q, H5^{I}), 3.866 (1H, dd, $J_{2,3}$ = 10.0 Hz, H3^{I}), 3.92 (1H, dd, $J_{1,2}$ = 3.0 Hz, H2^{I}), 3.95 (1H, dd, $J_{2,3}$ = 10.0 Hz, H3^{II}), 4.09 (1H, dd, $J_{1,2}$ = 3.5 Hz, H2^{II}), 4.26 (1H, dq, H5^{II}), 4.93 (1H, d, H1^{II}), 4.94 (1H, d, H1^{I}), 5.94 (1H, m, allyl); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 16.4 (C6^{I}), 16.5 (C6^{II}), 66.9 (C5^{I} and C5^{II}), 68.2 (allyl), 75.3 (C2^{I}), 76.5 (C2^{II}), 77.6 (C3^{I}), 78.0 (C4^{II}), 78.6 (C4^{I}), 79.4 (C3^{II}), 96.1 (C1^{I}), 100.0 (C1^{II}), 117.7, 134.2 (allyl).

25b: R_f 0.56 (TK 10 : 1), $[\alpha]_D$ +41 (*c* 0.90, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.15 (3H, d, $J_{5,6}$ = 6.0 Hz, H6^{II}), 1.26 (3H, d, $J_{5,6}$ = 6.5 Hz, H6^{I}), 3.33 (1H, dq, $J_{4,5}$ = 1.0 Hz, H5^{II}), 3.47 (1H, dd, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 3.0 Hz, H3^{II}), 3.51 (1H, dd, H4^{II}), 3.81 (1H, dd, $J_{1,2}$ = 7.5 Hz, H2^{II}), 3.96 (1H, dq, $J_{4,5}$ = 1.0 Hz, H5^{I}), 4.10 (1H, d, $J_{3,4}$ = 0 Hz, H4^{I}), 4.82 (1H, d, $J_{1,2}$ = 1.5 Hz, H1^{I}), 4.88 (1H, d, H1^{II}), 5.93 (1H, m, allyl); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 16.8 (C6^{II}), 16.9 (C6^{I}), 66.4 (C5^{I}), 68.2 (allyl), 70.1 (C5^{II}), 74.5 (C4^{I}), 76.9 (C2^{I} and C4^{II}), 79.1 (C3^{I}), 79.8 (C2^{II}), 82.3 (C3^{II}), 96.4 (C1^{I}), 102.9 (C1^{II}), 117.7, 134.2 (allyl).

Found: **25a**, C, 74.94 ; H, 7.07%. **25b**, C, 74.81 ; H, 6.98%. Calcd for $C_{50}H_{56}O_9$: C, 74.98; H, 7.05%.

Benzyl *O*-(2,3,4-Tri-*O*-benzyl-6-deoxy-α-D-galactopyranosyl)-(1→4)-*O*-2,3-di-*O*-benzyl-6-deoxy-α- and -β-D-galactopyranosyl-(1→4)-*O*-(2,3-di-*O*-benzyl-6-deoxy-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-benzyl-6-deoxy-β-D-glucopyranosides (30a and 30b). 30a: R_f 0.34 (HE 3 : 1), $[\alpha]_D$ +88 (*c* 1.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 0.82 (3H, d, $J_{5,6}$ = 6.5 Hz, H6^{IV}), 1.23 (3H, d, $J_{5,6}$ = 6.0 Hz, H6^{II}), 1.26 (3H, d, $J_{5,6}$ = 6.5 Hz, H6^{III}), 1.45 (3H, d, $J_{5,6}$ = 5.8 Hz, H6^{I}), 3.47 (1H, dd, $J_{1,2}$ = 3.8 Hz, $J_{2,3}$ = 9.5 Hz, H2^{II}), 3.54 (1H, dd, $J_{3,4}$ = 2.8 Hz, $J_{4,5}$ = 1.0 Hz, H4^{IV}), 3.546 (1H, dq, $J_{4,5}$ = 8.5 Hz, H5^{I}), 3.503 (1H, t, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, H4^{II}), 3.56 (1H, dd, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 9.0 Hz, H2^{I}), 3.63 (1H, t, $J_{3,4}$ = 8.5 Hz, H4^{I}), 3.76 (1H, dd, H3^{I}), 3.795 (1H, d, $J_{2,3}$ = 7.0 Hz, $J_{3,4}$ = 0 Hz, H3^{III}), 3.801 (1H, br s, H4^{III}), 3.81 (1H, dd, $J_{1,2}$ = 2.0 Hz, H2^{III}), 3.85 (1H, dd, $J_{2,3}$ = 10.5 Hz, H3^{IV}), 3.92 (1H, dq, $J_{4,5}$ = 1.0 Hz, H5^{III}), 3.93 (1H, dq, H5^{II}), 3.95 (1H, dd, H3^{II}), 4.05 (1H, dd, $J_{1,2}$ = 3.5 Hz, H2^{IV}), 4.07 (1H, dq, H5^{IV}), 4.55 (1H, d, H1^{I}), 4.88 (1H, d, H1^{IV}), 5.53 (1H, d, H1^{II}), 5.64 (1H, d, H1^{III}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 16.37 (C6^{III}), 16.44 (C6^{IV}), 18.5 (C6^{II}), 19.1 (C6^{I}), 66.9 (C5^{IV}), 67.0 (C5^{II}), 67.5 (C5^{III}), 70.8 (C5^{I}), 74.5 (C2^{III}), 76.4 (C2^{IV}), 77.6 (C4^{III}), 77.9 (C4^{IV}), 78.5 (C3^{III}), 78.6 (C4^{I} and C4^{II}), 79.2 (C3^{IV}), 79.7 (C2^{II}), 81.3 (C3^{II}), 82.6 (C2^{I}), 84.6 (C3^{I}), 96.6 (C1^{II}), 97.8 (C1^{III}), 100.2 (C1^{IV}), 102.2 (C1^{I}).

Found: C, 74.94 ; H, 7.07%. Calcd for $C_{94}H_{102}O_{17}$: C, 74.98 ; H, 7.05%.

30b: R_f 0.31 (HE 3 : 1), $[\alpha]_D$ +44 (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 5.60 (1H, d, $J_{1,2}$ = 4.0 Hz, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 96.5 (C1^{II}), 100.5 (C1^{IV}), 102.3 (C1^{I}), 103.6 (C1^{III}), MS (FAB) *m/z* 1526 $(M+Na)^+$.

***O*-(2,3,4-Tri-*O*-benzyl-6-deoxy-α-D-galactopyranosyl)-(1→4)-2,3-di-*O*-benzyl-6-deoxy-β-D-galactopyranose (7).** A mixture of **25a** (33 mg, 0.041 mmol), RhCl $(Ph_3P)_3$ (5.1 mg, 0.006 mmol), EtOH (2.1 ml), PhH (0.9 ml), and H_2O (0.3 ml) was heated at reflux (85 °C) overnight. After evaporation to dryness, the residue was heated in Me_2CO (3.8 ml) containing dil HCl (1 M, 0.11 ml, 1 M = 1 mol dm^{-3}) at 48 °C. After evaporation, chromatography with TK system gave **7** (20 mg, 64%), $[\alpha]_D$ +89 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) (67%α) δ = 0.94 (d, $J_{5,6}$ = 6.5 Hz, H6^{II}), 1.29 (d, $J_{5,6}$ = 6.5 Hz, H6$^{I}\alpha$), 1.34 (d, $J_{5,6}$ = 6.5 Hz, H6$^{I}\beta$), 2.88 (d, $J_{1,OH}$ = 1.5 Hz, OH1$^{I}\alpha$), 3.42 (dd, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 2.5 Hz, H3$^{I}\beta$), 3.54 (dq, $J_{4,5}$ = 1.0 Hz, H5$^{I}\beta$), 3.59 (dd, $J_{1,2}$ = 7.0 Hz, H2$^{I}\beta$), 3.64 (dd, $J_{3,4}$ = 2.5 Hz, $J_{4,5}$ = 1.0 Hz, H4^{II}), 3.68 (d, $J_{1,OH}$ = 8.0 Hz, OH1$^{I}\beta$), 3.79 (dd, H4$^{I}\beta$), 3.80 (dd, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 2.5 Hz, H3$^{I}\alpha$), 3.82 (dd, $J_{4,5}$ = 1.0 Hz, H4$^{I}\alpha$), 3.87 (dd,

$J_{1,2}$ = 3.0 Hz, H2$^{I}\alpha$), 3.96 (dd, $J_{2,3}$ = 10.0 Hz, H3$^{II}\alpha$), 4.01 (dd, $J_{2,3}$ = 10.0 Hz, H3$^{II}\beta$), 4.05 (dq, H5$^{I}\alpha$), 4.09 (dd, $J_{1,2}$ = 3.5 Hz, H2$^{II}\alpha$), 4.10 (dd, $J_{1,2}$ = 10.0 Hz, H2$^{II}\beta$), 4.25 (dq, H5$^{II}\alpha$), 4.28 (dq, H5$^{II}\beta$), 4.63 (dd, H1$^{I}\beta$), 4.94 (d, H1$^{II}\alpha$), 4.97 (d, H1$^{II}\beta$), 5.32 (1H, dd, H1$^{I}\alpha$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 16.6 (C6$^{I}\alpha$ and C6^{II}), 17.2 (C6$^{I}\beta$), 66.96 (C5$^{II}\alpha$), 67.00 (C5$^{II}\beta$), 67.4 (C5$^{I}\alpha$), 71.3 (C5$^{I}\beta$), 75.7 (C2$^{I}\alpha$), 76.35 (C2$^{II}\beta$), 76.40 (C2$^{II}\alpha$ and C4$^{I}\beta$), 77.2 (C4$^{I}\alpha$), 77.77 (C4$^{II}\alpha$), 77.84 (C4$^{II}\beta$), 77.9 (C3$^{I}\alpha$), 79.1 (C3$^{II}\beta$), 79.3 (C3$^{II}\alpha$), 80.4 (C2$^{I}\beta$), 80.5 (C3$^{I}\beta$), 91.6 (C1$^{I}\alpha$), 97.6 (C1$^{I}\beta$), 99.7 (C1$^{II}\beta$), 100.0 (C1$^{II}\alpha$).

Found: C, 74.01 ; H, 6.94%. Calcd for $C_{47}H_{52}O_9$: C, 74.19 ; H, 6.89%.

***O*-(6-Deoxy-α-D-galactopyranosyl)-(1→4)-*O*-(6-deoxy-α-D-galactopyranosyl-(1→4)-*O*-(6-deoxy-α-D-glucopyranosyl)-(1→4)-6-deoxy-D-glucopyranose (1).** Hydrogenation of **30a** (36 mg, 0.024 mmol) was carried out in AcOH (6 ml) containing H_2O (0.03 ml) over Pd on C (10%, 41 mg) in a Parr-3911 hydrogenation apparatus (340 kPa of H_2) at room temp overnight. Chromatography with CM system gave **1** (11 mg, 76%), $[\alpha]_D$ +206 (*c* 0.66, H_2O); ^{1}H NMR (D_2O, 300 MHz) (29%α) δ = 1.12 (d, $J_{5,6}$ = 6.5 Hz, H6^{IV}), 1.29 (d, $J_{5,6}$ = 6.5 Hz, H6$^{I}\alpha$), 1.32 (d, $J_{5,6}$ = 6.0 Hz, H6$^{I}\beta$), 3.27 (dd, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 9.5 Hz, H2$^{I}\beta$), 3.31 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4$^{I}\alpha$), 3.32 (t, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, H4$^{I}\beta$), 3.33 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4^{II}), 3.57 (dd, $J_{1,2}$ = 4.0 Hz, $J_{2,3}$ = 9.5 Hz, H2$^{I}\alpha$), 3.618 (dd, $J_{1,2}$ = 4.0 Hz, $J_{2,3}$ = 9.5 Hz, H2$^{II}\alpha$), 3.622 (dq, H5$^{I}\beta$), 3.63 (dd, $J_{1,2}$ = 4.0 Hz, $J_{2,3}$ = 10.0 Hz, H2$^{II}\beta$), 3.69 (t, H3$^{I}\beta$), 3.79 (dd, $J_{1,2}$ = 4.0 Hz, $J_{2,3}$ = 10.0 Hz, H2^{IV}), 3.83 (t, H3^{II}), 3.85 (t, H3$^{I}\alpha$), 3.92 (dq, $J_{5,6}$ = 6.5 Hz, H5^{II}), 3.97 (dq, H5$^{I}\alpha$), 4.17 (dq, $J_{4,5}$ = 1.0 Hz, $J_{5,6}$ = 6.5 Hz, H5^{III}), 4.47 (dq, $J_{4,5}$ = 1.0 Hz, H5^{IV}), 4.62 (d, H1$^{I}\beta$), 4.95 (d, H1^{IV}), 5.16 (d, H1$^{I}\alpha$), 5.30 (d, H1$^{II}\alpha$), 5.31 (d, H1$^{II}\beta$), 5.35 (1H, d, $J_{1,2}$ = 3.8 Hz, H1^{III}).

Found: C, 44.16 ; H, 7.08%. Calcd for $C_{24}H_{42}O_{17}\cdot 3H_2O$: C, 43.90; H, 7.37%.

***O*-(6-Deoxy-α-D-glucopyranosyl)-(1→4)-6-deoxy-D-glucopyranose (31).** Similar hydrogenation of **6** (50 mg, 0.066 mmol) in AcOH (6 ml) containing H_2O (0.03 ml) over Pd on C (10%, 49 mg), followed by chromatography with CM system, gave **31** (15 mg, 74%), $[\alpha]_D$ +95 (*c* 0.17,H_2O); ^{1}H NMR (D_2O, 300 MHz) (29%α) δ = 1.24 (d, $J_{5,6}$ = 6.2 Hz, H6^{II}), 1.27 (d, $J_{5,6}$ = 6.0 Hz, H6$^{I}\alpha$), 1.30 (d, $J_{5,6}$ = 6.0 Hz, H6$^{I}\beta$), 3.13 (t, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, H4$^{II}\alpha$), 3.14 (t, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, H4$^{II}\beta$), 3.28 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4$^{I}\alpha$), 3.30 (t, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, H4$^{I}\beta$), 3.54 (dd, $J_{1,2}$ = 4.0 Hz, $J_{2,3}$ = 9.5 Hz, H2$^{I}\alpha$), 3.56 (dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.0 Hz, H2$^{II}\alpha$), 3.58 (dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.0 Hz, H2$^{II}\beta$), 3.600 (t, H3^{II}), 3.604 (dq, H5$^{I}\beta$), 3.67 (t, $J_{2,3}$ = 9.0 Hz, H3$^{I}\beta$), 3.82 (dq, H5$^{II}\beta$), 3.83 (dq, H5$^{II}\alpha$), 3.87 (t, H3$^{I}\alpha$), 3.98 (dq, H5$^{I}\alpha$), 4.60 (d, $J_{1,2}$ = 8.0 Hz, H1$^{I}\beta$), 5.30 (d, H1$^{II}\alpha$), 5.31 (d, H1$^{II}\beta$), 5.14 (d, H1$^{I}\alpha$).

Found: C, 41.88 ; H, 6.84%. Calcd for $C_{12}H_{22}O_9\cdot 2H_2O$: C, 41.62; H, 7.57%.

***O*-(6-Deoxy-α-D-galactopyranosyl)-(1→4)-6-deoxy-D-galactopyranose (32).** Similar to **31**, **7** (31 mg, 0.40 mmol) was hydrogenated in moist AcOH (6 ml) over Pd on C (10%, 34 mg). Chromatography with CM system yielded **32** (11.0 mg, 87%), $[\alpha]_D$ +164 (*c* 0.79, H_2O); ^{1}H NMR (D_2O, 300 MHz) (29%α) δ = 1.13 (d, $J_{5,6}$ = 6.5 Hz, H6^{II}), 1.25 (d, $J_{5,6}$ = 6.5 Hz, H6$^{I}\alpha$), 1.29 (d, $J_{5,6}$ = 6.5 Hz, H6$^{I}\beta$), 3.68 (dd, $J_{2,3}$ = 10.0 Hz, $J_{3,4}$ = 3.0 Hz, H3$^{I}\beta$), 3.75 (dd, $J_{1,2}$ = 4.0 Hz, $J_{2,3}$ = 10.0 Hz, H2^{II}), 3.76 (dd, $J_{1,2}$ = 4.0 Hz, $J_{2,3}$ = 10.0 Hz, H2$^{I}\alpha$), 3.78 (d, $J_{3,4}$ = 3.0 Hz, $J_{4,5}$ = 0 Hz, H4$^{I}\alpha$), 3.786 (d, $J_{3,4}$ = 3.0 Hz, $J_{4,5}$ = 0 Hz, H4$^{I}\beta$), 3.789 (d, $J_{3,4}$ = 3.0 Hz, $J_{4,5}$ = 0 Hz, H4$^{II}\beta$), 3.798 (q, H5$^{I}\beta$), 3.803 (d, $J_{3,4}$ = 3.0 Hz, $J_{4,5}$ = 0 Hz, H4$^{II}\alpha$), 3.89 (dd, H3$^{I}\alpha$), 3.904 (dd, H3$^{II}\alpha$), 3.906 (dd, H3$^{II}\beta$), 4.20 (q, H5$^{I}\alpha$), 4.48 (q, $J_{4,5}$ = 0 Hz, H5$^{II}\alpha$), 4.49 (q, $J_{4,5}$ = 0 Hz, H5$^{II}\beta$), 4.57 (d, $J_{1,2}$ = 7.5 Hz, H1$^{I}\beta$), 4.92 (d, $J_{1,2}$ = 4.0 Hz, H1^{II}), 5.20 (d, $J_{1,2}$ = 4.0 Hz, H1$^{I}\alpha$).

Found: C, 43.63 ; H, 7.41%. Calcd for $C_{12}H_{22}O_9\cdot H_2O$: C, 43.90; H,7.37%.

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