Benzyl Derivatives of *N*-2,4-Dinitrophenyl- D-glucosamine and Their Use for Oligosaccharide Synthesis

Shinkiti Koto,* Motoko Hirooka,* Kazuo Yago,†,# Mitsuo Komiya, Toshio Shimizu, Kumi Kato, Tsunehiko Takehara, Ayami Ikefuji, Ayako Iwasa, Saho Hagino, Michiyo Sekiya, Yozo Nakase, Shonosuke Zen, Fumiya Tomonaga,† and Shigehiko Shimada†

School of Pharmaceutical Sciences, Kitasato University, Shirokane, Minato-ku, Tokyo 108-8641

†Department of Pharmacy, Kitasato University Hospital, Kitasato, Sagamihara 228-8555

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Four tri-*O*-benzyl derivatives of 2-deoxy-2-(2,4-dinitroanilino)-D-glucopyranose were synthesized. Glycosylation using 3,4,6-tri-*O*-benzyl-2-deoxy-2-(2,4-dinitroanilino)-D-glucopyranose as glycosyl donor and a reagent mixture of *p*-nitrobenzenesulfonyl chloride, silver trifluoromethanesulfonate, and triethylamine produced β-glycosides with complete selectivity. Starting from benzyl 3,6-di-*O*-benzyl-2-deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranoside as acceptor, *O*-α-D-galactopyranosyl-(1→4)-*O*-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-D-glucopyranose, the human blood-group P_1-antigenic determinant, was synthesized.

Among various glycosyl donors for the synthesis of 2-amino-2-deoxy-D-glucosides (D-glucosaminides),[1,2] 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,4-dinitroanilino)-α-D-glucopyranosyl bromide (**1**)[3] (Fig. 1) is known as one of the donors producing α-glycosides selectively.[3,4] However, the glycosylation by way of in situ activation of the known 1-OH sugar derivative **2**[5] with 2,4-dinitroanilino group at the C-2 position has not been studied, although several papers dealing with in situ activating glycosylation using a 1-OH derivative such as 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (**3**) have recently appeared.[6] Such kind of glycosylation is free from the preparation of the activated donor from the corresponding 1-OH sugar derivative. A reagent system of *p*-nitrobenenesulfonyl chloride (NsCl), silver trifluoromethanesulfonate (AgOTf), and triethylamine (Et_3N) (NST-system)[7a] performs direct glycosylation of an acceptor (AOH) with **3** as a donor (DOH) without significant formation of the *p*-nitrobenzenesulfonate of AOH, as expressed by Eq. 1. It was intriguing to us whether in situ activating glycosylation

$$\mathrm{DOH + AOH + NsCl + AgOTf + Et_3N} \longrightarrow \mathrm{DOA + NsOH + AgCl + TfOH \cdot Et_3N} \quad (1)$$

using **2** would proceed in the presence of the NST-system.[7a] The glycosylation was actually found to produce β-glycosides selectively,[7b,7c] in contrast to the known α-selective glycosylation using **1**.[4] Recently, the *N*,*N*-dibenzylamino group has been described as a participation group in the synthesis of β-glycosides.[2] The role of the *N*-dinitrophenyl group for high β-selectivity, however, is unclear now. Although the efficiency of the removal of the dinitrophenyl group is unsatisfactory, **2** might be another potential donor for β-glycosylation. The present paper reports (i) the synthesis of the complete set of the tri-*O*-benzyl derivatives of 2-deoxy-2-(2,4-dinitroanilino)-D-glucopyranose (**4**),[##] (ii) the β-glycosylation using **2** and the NST reagent system,[7a] and (iii) the new synthesis of a trisaccharide constituting of the epitope of P_1-antigen of human erythrocite,[8] starting from the acceptor **5**.

(i) The Synthesis of the Tribenzyl Drivatives of *N*-DNP-D-glucosamine. The first point to be noted is a straightforward synthesis of **2**[5] from 2-amino-2-deoxy-D-glucopyranose hydrochloride (**6**) without exchange of the protecting group of the amino group,[5] as shown in Fig. 1. The convenient bromination[9] of the acetate **7**[10] readily obtainable from **6** and subsequent treatment with allyl alcohol in the presence of mercury(II) salts in acetonitrile[11] was followed by deacetylation to give the β-glycoside **8** mainly. Mild benzylation of **8** with benzyl bromide and sodium hydride in *N*,*N*-dimethylformamide (DMF) furnished the tribenzyl compound **9**. Deallylation via thermal rearrangement over the rhodium complex and subsequent hydrolysis[12] furnished the known **2**.[5] Thus, the 2,4-dinitroanilino group is unchanged during the mild benzylation using sodium hydride and benzyl bromide in DMF. Three monohydroxy compounds, **5**, **10**, and **11** were synthesized next. Similar to the case of **8**, the acetate **7** was transformed into the β-glycoside **12**.[3] From **12**, the 3-OH compound **10** was prepared by way of the benzylidene compound **13**. Mild allylation of **13** with allyl bromide and

Present address: Department of Pharmacy, Kitasato University East Hospital, Asamizodai, Sagamihara 228-5520.

Presented at the 52nd Spring Meeting of Chem. Soc. Jpn., Kyoto, April 3rd, 1986, Abstr. No. 3N26. For convenience, **4** is abbreviated as *N*-DNP-D-glucosamine.

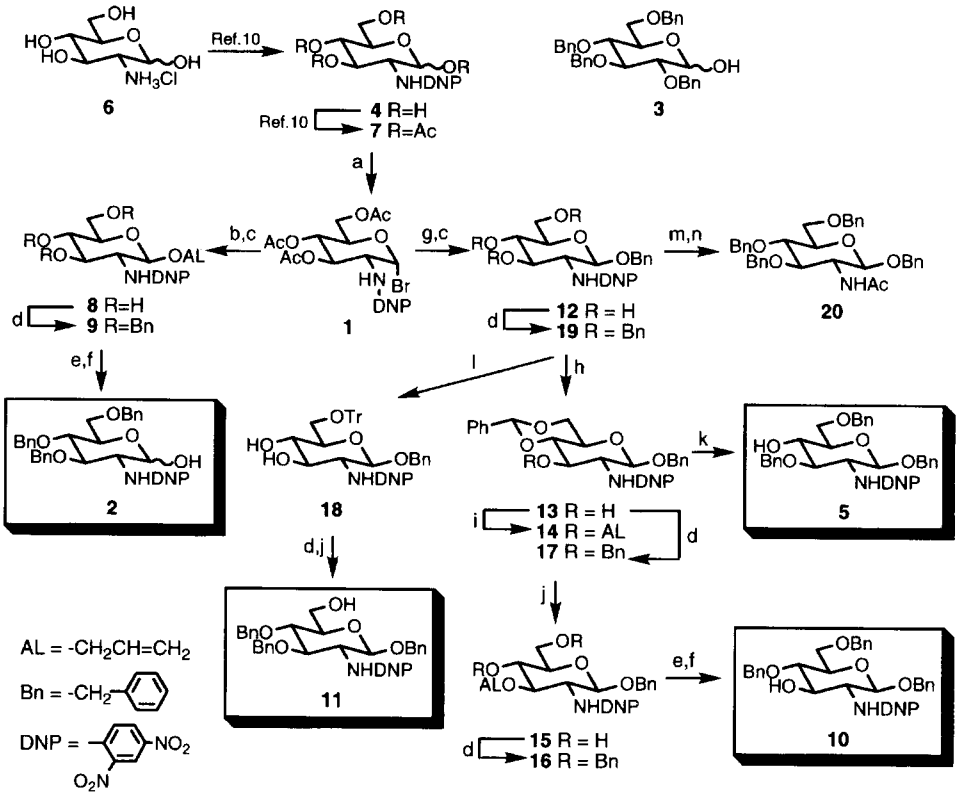

Fig. 1. Derivatives of *N*-DNP-glucosamine. a) AcBr, $H_2O/CHCl_3$, room temp (r.t.); b) ALOH, $Hg(CN)_2$, $HgBr_2$/MeCN, r.t.; c) NaOMe/MeOH, r.t.; d) BnBr, NaH/DMF, 0 °C; e) $RhCl(PPh_3)_3$/EtOH–PhH–H_2O, △; f) dil HCl/Me_2CO, △; g) BnOH, $Hg(CN)_2$, $HgBr_2$/MeCN, r.t.; h) PhCHO, $ZnCl_2$/r.t.; i) ALBr, NaH/DMF, 0 °C; j) aq AcOH (80%)/△; k) Et_3SiH, CF_3CO_2H/CH_2Cl_2, 0 °C; l) TrCl/Pyrd, △; m) Dowex 1×2 (OH)/aq Me_2CO, △; n) Ac_2O/MeOH, r.t.

sodium hydride in DMF afforded the fully protected **14**. Removal of benzylidene group of **14**, followed by benzylation and deallylation, afforded **10**. The 4-OH compound **5** was conveniently prepared via a regioselective reduction of the benzylidene derivative **17** using triethylsilane and trifluoroacetic acid.[13,14] The 6-OH derivative **11** was prepared from the trityl derivative **18** by way of benzylation and detritylation.

Removal of the dinitrophenyl group from the fully benzylated **19** was carried out by heating with a basic resin in boiling aqueous acetone.[15] Successive acetylation in acetic anhydride in methanol afforded the *N*-acetate **20**.[16a,16b]

(ii) β-Glycosylation Using 2 and the NST-System. The next point to be presented is that the condensation of **2** with the acceptors, such as **21**, **22**, **23**, and **24**, (Fig. 2) in the presence of the NST system[7a] was found to produce the corresponding β-glycosides **26**, **27**, **28**, and **29** in moderate or good yields with complete selectivity (Table 1, Runs 1—4). The structures of these four obtained condensates were confirmed by their conversions into the respective *N*-acetates which have been reported in the preceding paper.[17] Compared to the case of the monosaccharide **19**, the de-*N*-dinitrophenylation of the disaccharide derivatives required longer reaction time. The unreacted starting materials were recovered and repeatedly used for de-*N*-dinitrophenylation. The β-glycosylation using **2** and the NST system of the acceptor **25**[18] was used to synthesize *O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-*sn*-glycerol **36**, which has been reported to be formed on *N*-acetylation, followed by alkaline hydrolysis, of the glycosyldiglyceride from *Bacillus megaterium*.[19,20]

(iii) A Synthesis of the Epitope Trisaccharide of P_1-Antigen. Finally, an alternative synthesis of the linear trisaccharide **37**,[8] which constitutes the sugar cluster of the epitope of P_1-antigen of human erythrocite, from the yellow-colored acceptor **5** was performed as shown in Fig. 3. The syntheses of **37** itself[21] and of its derivatives[22] have been carried out by other groups. Glycosylation of **5** with the galactosyl donor **38**[23] and **40**[23] in the presence of the NST system proceeded with α-selectivities (Table 2, Run 6 (83%, 77%α) and Run 7 (86%, 71%α)). The glucosyl donor **42**[23] with acetoxy group at C-4 was then employed, although it has to invert the configuration of the C-4[II] of the disaccharide derivative to be obtained. The glycosylation, however, proceeded α-selectively (Run 9, 93%, 66%α). The 4-*O*-allyl derivative **44**[23] was condensed with **5** in the presence of the NST system to give more of the desired β-linked disaccharide derivative **45b**, but it was still the minor product (Run 10, 96%, 57%α). The addition of lithiumbistrifluoromethanesulfonylamide[24] to the reaction mixture changed the selectivity of the reaction to the β-glycoside (Run 11, 87%, 67%β), whereas lithium perchlorate showed almost no effect (Run 12, 70%, 58%α). This weak but definite β-directing effect of the lithium amide[24] in Run 11 seems to be

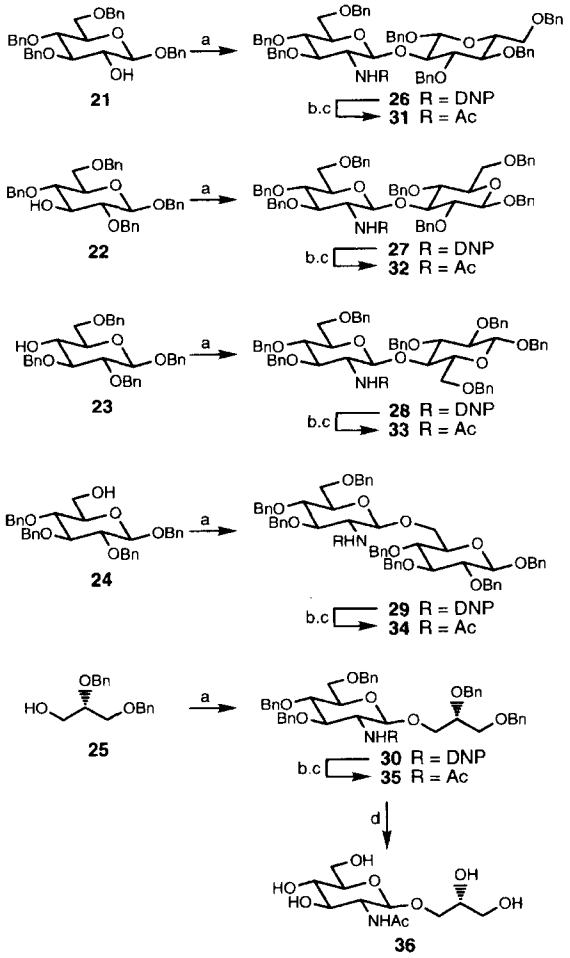

Fig. 2. β-Linked disaccharide derivatives of *N*-DNP-glucosamine. a) **2**, NsCl, AgOTf, Et_3N/CH_2Cl_2, $-60\rightarrow0$ °C; b) Dowex 1×2 (OH)/aq Me_2CO, △; c) Ac_2O/MeOH, r.t.; d) H_2, Pd–C (10%)/AcOH, r.t.

Table 1. Results of Glycosylation Using 3,4,6-Tri-*O*-benzyl-2-deoxy-2-(2,4-dinitroanilino)-D-glucopyranose **2** Using the NST[a] Reagent System

Run	**2**/mg (mmol)	Acceptor/eq	NST/eq	Condensate/%
1	34.1 (0.055)	**21** 1.0	2.5	**26** 85
2	34.1 (0.055)	**22** 1.0	2.5	**27** 67
3	30.8 (0.050)	**23** 1.0	2.5	**28** 57
4	30.8 (0.050)	**24** 1.0	2.0	**29** 95
5	65.1 (0.106)	**25** 1.0	2.0	**30** 26[b]

a) NST[6] = NsCl+AgOTf+Et_3N. b) 1,2-Di-*O*-benzyl-3-*O*-(*p*-nitrobenzenesulfonyl)-*sn*-glycerol ($[\alpha]_D$ −6 (*c* 1.7, $CHCl_3$). MS (FAB) *m/z* 480.4939 $(M+Na)^+$) was isolated in 47% yield.

unprecedented, although this salt has recently been used for the α-glycosylation with anomerization.[24] In the case of the donor **40**, however, the effect was not enough to invert the selectivity of the reaction (Run 8, 61%, 64%α). Sequential reactions of **45b**, i.e., deallylation, trifluoromethanesulfonylation, and substitution using tetrabutylammonium acetate with configurational inversion,[25] afforded the acetate **39b**, of which deacetylation gave the acceptor **47**. This was condensed with the galactosyl donor **48**[26] in the presence of the NST system[7a] to give the trisaccharide derivative **49a** α-selectively (83%, 63%α). Removal of *N*-dinitrophenyl group by repeated contact of **49a** with a basic resin in refluxing aqueous acetone followed by *N*-acetylation afforded **50**. Final hydrogenolytic total de-*O*-benzylation yielded the target trisaccharide **37**.[8,21]

In summary, (i) the *N*-2,4-dinitroanilino group did not change in the mild benzylation (or allylation) using sodium hydride and benzyl bromide (or allyl bromide) in DMF and even in the reductive ring opening using triethylsilane in the presence of trifluoroacetic acid, (ii) the in situ activating glycosylation using the lactol **2** in the presence of the NST system[7a] afforded β-glycoside with complete selectivity, and (iii) an alternative synthesis of the trisaccharide moiety **37**[8] was performed starting from **5**.

Experimental[27]

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), 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 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 spectrometer, along with the measurements of H,H-COSY, C,H-COSY, and DEPT spectra.

Compound **7** (67%α by ^1H NMR ($CDCl_3$) δ = 5.847 (d, $J_{1,2}$ = 8.5 Hz, H1β), 6.297 (d, $J_{1,2}$ = 3.5 Hz, H1α)) was prepared by the known method[10] from the hydrochloride **6** (Wako Pure Chemicals Industries, Ltd.). The donors **38**,[23] **40**,[23] **42**,[23] **44**,[23] and **48**[26] and the acceptors **21**,[28] **22**,[28] **23**,[13] and **24**[27,29] were the products reported previously. The acceptor **25** was prepared by the known method[18] from 1,2-*O*-isopropylidene-*sn*-glycerol (Tokyo Kasei Kogyo Co., Inc.).

Allyl 2-Deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranoside (8). To a mixture of **7** (11.1 g, 22 mmol), AcBr (10 ml, 0.12 mol) and $CHCl_3$ (25 ml), H_2O (1.9 ml, 0.11 mol)[9] was added under stirring at 0 °C and the mixture was stirred for 15 min. After stirring was carried out at 20 °C for 1.3 h under anhydrous conditions, the mixture was evaporated and co-evaporated with PhMe to give a yellow solid of crude α-bromide **1** (11.0 g), ^1H NMR ($CDCl_3$) δ = 6.552 (d, $J_{1,2}$ = 3.5 Hz, H1); ^{13}C NMR ($CDCl_3$) δ = 88.8 (C1). To a portion (6.55 g, 12 mmol) of this, MeCN (6.1 ml), allyl alcohol (1.5 ml, 22 mmol), $Hg(CN)_2$ (3.57 g, 14 mmol), and $HgBr_2$ (5.08 g, 14 mmol)[11] were added and the resulting mixture was vigorously stirred at room temp overnight under anhydrous conditions. After dilution with $CHCl_3$ (20 ml), insoluble matters were filtered off and the filtrate was washed twice with H_2O (50 ml) and twice with aq KBr (10%, 25 ml). Evaporation and chromatography (TK system, 100 : 1→2 : 1) afforded yellow solid of triacetate of **8** (3.52 g, 57%, 80%β by ^1H NMR ($CDCl_3$) δ = 4.602 (d, $J_{1,2}$ = 8.0 Hz, H1β), 4.938 (d, $J_{1,2}$ = 3.5 Hz, H1α)). A portion (604 mg, 1.2 mmol) of this was treated with dil NaOMe (0.024%, 20 ml) for 3 h. After neutralization with AcOH, evaporation and crystallization with EtOH furnished **8** (0.39 g, 46 % from **7**), mp 182—183 °C, $[\alpha]_D$ +10 (*c* 1.1, Me_2CO), ^1H NMR (CD_3OD) δ = 3.385 (ddd, $J_{4,5}$ = 9.5 Hz, $J_{5,6a}$ = 2.0 Hz, $J_{5,6b}$ = 2.0 Hz, H5), 3.440 (t, $J_{3,4}$ = 9.5

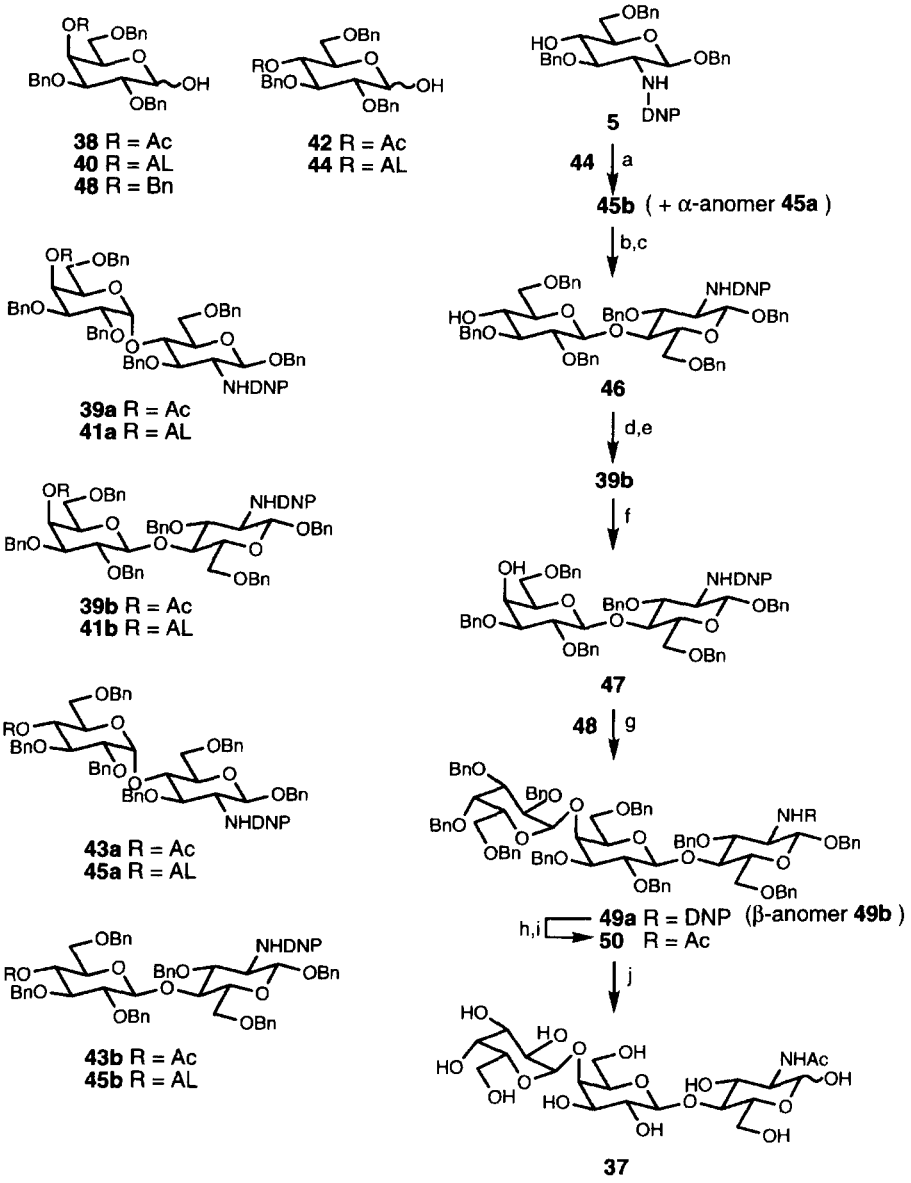

Fig. 3. Synthesis of *O*-α-D-Gal*p*-(1→4)-*O*-β-D-Gal*p*-(1→4)-D-GlcNAc*p* (**37**). a) NsCl, AgOTf, Et_3N/CH_2Cl_2, −60→0 °C; b) RhCl-$(PPh_3)_3$/EtOH–PhH–H_2O, △; c) dil HCl/Me_2CO, △; d) Tf_2O, Pyrd/CH_2Cl_2, −25 °C; e) Bu_4NOAc/DMF, r.t.; f) NaOMe/MeOH; g) NsCl, AgOTf, Et_3N/CH_2Cl_2, −60→0 °C; h) Dowex 1×2 (OH)/aq Me_2CO, △; i) Ac_2O/MeOH, △; j) H_2, Pd–C (10%)/AcOH, r.t.

Table 2. Results of Glycosylation of the 4-OH-derivative **5**

Run	Donor/eq)	**5**/mg	(mmol)	NST/eq	Additive/eq	CH_2Cl_2/ml	Condensates/%	(α/β)
6	**38** 1.3	21.3	(0.035)	2.5	None	0.30	**39a+39b** 83	(77/23)
7	**40** 1.3	29.0	(0.047)	2.5	None	0.30	**41a+41b** 86	(71/29)
8	**40** 1.3	29.0	(0.047)	2.5	$LiNTf_2$ 2.5	0.30	**41a+41b** 61	(64/36)
9	**42** 1.3	29.0	(0.047)	2.5	None	0.30	**43a+43b** 93	(66/34)
10	**44** 1.3	29.0	(0.047)	2.5	None	0.30	**45a+45b** 97	(57/43)
11	**44** 1.3	58.0	(0.094)	2.5	$LiNTf_2$ 2.5	0.60	**45a+45b** 87	(33/67)
12	**44** 1.3	29.0	(0.047)	2.5	$LiClO_4$ 2.5	0.30	**45a+45b** 70	(58/42)

Hz, H4), 3.667 (dd, $J_{2,3}$ = 8.5 Hz, H3), 3.707 (dd, H2), 3.739 (dd, $J_{6a,6b}$ = 12.0 Hz, H6b), 3.913 (dd, H6a), 4.627 (d, $J_{1,2}$ = 7.5 Hz, H1), 7.442 (d, J = 9.5 Hz, DNP), 8.230 (dd, J = 2.5, 9.5 Hz, DNP), 9.013 (d, DNP), 5.755 (m, allyl); ^{13}C NMR (CD_3OD) δ = 61.2 (C2), 62.6 (C6), 72.0 (C4), 76.9 (C3), 78.0 (C5α), 102.9 (C1), 71.2, 117.2, 135.2 (allyl), 118.0, 124.3, 130.3, 132.9, 137.4, 150.9 (DNP).

Found: C, 45.73; H, 5.01; N, 10.76%. Calcd for $C_{15}H_{19}N_3O_9 \cdot 0.5H_2O$: C, 45.69; H, 5.11; N, 10.66%.

Allyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranoside (9). To a cold mixture of **8** (1.05 g, 1.7 mmol),

$PhCH_2Br$ (1.85 ml, 15.5 mmol), and DMF (11 ml), NaH (ca. 60% dispersion in oil, 0.60 g, 15 mmol) was added under stirring at 0 °C. The mixture was stirred at this temperature for 30 min and then at 20 °C for 30 min under anhydrous conditions. The dark-colored mixture was again cooled at 0 °C and the reaction was quenched by adding MeOH (0.6 ml). After stirring at room temp for 30 min at 20 °C, the mixture was diluted with PhMe (200 ml) and H_2O (30 ml). The organic layer was washed with H_2O, evaporated, and chromatographed with TK system (100 : 1→2 : 1) to give **9** (1.63 g, 91%), $[\alpha]_D$ −58 (*c* 1.4, $CHCl_3$), ^1H NMR ($CDCl_3$) δ = 3.534 (dt, $J_{4,5}$ = 9.5 Hz, $J_{5,6a}$ = $J_{5,6b}$ = 3.0 Hz, H5), 3.647 (dt, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 8.5 Hz, H3), 3.808 (br q, $J_{1,2}$ = 8.0 Hz, $J_{2,NH}$ = 9.5 Hz, H2), 3.828 (br t, H4), 4.443 (d, H1), 8.460 (d, NH), 8.135 (dd, *J* = 2.5, 8.5 Hz, DNP), 9.050 (d, *J* = 2.5 Hz, DNP), 5.737 (m, allyl); ^{13}C NMR ($CDCl_3$) δ = 59.2 (C2), 68.3 (C6), 75.1 (C5), 78.3 (C4), 84.0 (C3), 101.0 (C1), 116.3, 123.7, 129.6, 149.0 (DNP), 70.2, 118.0, 133.1 (allyl), 73.6, 75.0, 75.8 (Bn).

Found: C, 65.53; H, 5.72; N, 6.36%. Calcd for $C_{36}H_{37}N_3O_9$: C, 65.94; H, 5.69; N, 6.41%.

3,4,6-Tri-*O*-benzyl-2-deoxy-2-(2,4-dinitroanilino)-α-D-glucopyranose (2). A mixture of **9** (1.02 g, 1.56 mmol), EtOH (77 ml),benzene (31 ml), H_2O (11 ml), and $RhCl(Ph_3P)_3$ (551 mg, 1.2 mmol) was stirred under reflux for 4 d. After evaporation to dryness, the residue was dissolved in Me_2CO (4.0 ml) containing 1 M HCl (0.44 ml, 1 M = 1 mol dm^{-3}). After heating for 1 h at 45 °C, the mixture was evaporated to dryness and chromatographed with TK system (100 : 1→2 : 1) to give **2** (420 mg, 44%), mp 143—144 °C, $[\alpha]_D$ +89 (*c* 1.0, $CHCl_3$) (lit,[5] mp 145—146 °C, $[\alpha]_D$ +36.9 (*c* 1.0, $CHCl_3$), ^1H NMR ($CDCl_3$) (100%α) δ = 3.686 (dd, $J_{5,6b}$ = 4.0 Hz, $J_{6a,6b}$ = 10.5 Hz,H6b), 3.739 (dd, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 10.0 Hz, H4), 3.748 (dd, $J_{5,6a}$ = 2.0 Hz, H6a), 3.897 (br dt, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.0 Hz, $J_{2,NH}$ = 8.5 Hz, H2), 4.008 (dd, H3), 4.142 (m, H5), 5.293 (br t, $J_{1,OH}$ = 3.5 Hz, H1), 3.394 (br d, OH), 8.795 (d, NH), 8.060 (dd, *J* = 2.5, 9.0 Hz, DNP), 9.015 (d, *J* = 2.5 Hz, DNP); ^{13}C NMR ($CDCl_3$) δ = 56.6 (C2), 68.4 (C6), 70.9 (C5), 78.6 (C4), 82.0 (C3), 91.9 (C1), 116.0, 123.9, 148.3 (DNP).

Found: C, 64.49; H, 5.34; N, 6.78%. Calcd for $C_{33}H_{33}N_3O_9$: C, 64.38; H, 5.40; N, 6.83%.

Benzyl 2-Deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranoside (12). To a crude bromide **1** (10.0 g) obtained from **7** (10.0 g, 19.5 mmol) by the bromination described for the case of preparation of **8**, MeCN (10 ml), $PhCH_2OH$ (3.6 ml, 35 mmol), $Hg(CN)_2$ (5.34 g, 21 mmol), and $HgBr_2$ (7.60 g, 21 mmol)[11] were added and the resulting mixture was vigorously stirred at room temp overnight under anhydrous conditions. Work-up as in the manner described for **8**, followed by chromatography (TK system, 100 : 1→2 : 1) gave the triacetate of **12** (7.97 g, 73%, >80%β by ^1H NMR ($CDCl_3$) δ = 4.567 (d, $J_{1,2}$ = 7.5 Hz, H1β), 5.032 (d, $J_{1,2}$ = 3.5 Hz, H1α)). This was treated with dil NaOMe (0.033%, 100 ml) for 2 h at 40 °C. After neutralization with AcOH, evaporation and crystallization with EtOH afforded **12** (2.93 g, 35% from **7**), mp 193—194 °C (lit,[3] mp 198 °C), $[\alpha]_D$ −113 (*c* 0.7, MeOH, C_5H_5N (1 : 1)); ^1H NMR (CD_3OD, $(CD_3)_2SO$ (1 : 1)) δ = 3.441 (ddd, $J_{4,5}$ = 9.5 Hz, $J_{5,6a}$ = 2.0 Hz, $J_{5,6b}$ = 6.0 Hz, H5), 3.481 (dd, $J_{3,4}$ = 8.5 Hz, H4), 3.753 (dd, $J_{6a,6b}$ = 12.0 Hz, H6b), 3.780 (dd, $J_{2,3}$ = 10.0 Hz, H3), 3.839 (dd, $J_{1,2}$ = 7.5 Hz, H2), 3.957 (dd, H6a), 4.757 (d, H1), 7.490 (d, *J* = 9.5 Hz, DNP), 8.213 (dd, *J* = 2.5, 9.5 Hz, DNP), 8.588 (d, DNP); ^{13}C NMR (CD_3OD, $(CD_3)_2SO$ (1 : 1)) δ = 61.2 (C2), 62.7 (C6), 72.1 (C4), 76.6 (C3), 78.1 (C5), 102.7 (C1), 72.1 (Bn); 118.3, 124.3, 150.9 (DNP).

Found: C, 49.93; H, 4.98; N, 9.25%. Calcd for $C_{19}H_{21}N_3O_9 \cdot H_2O$: C, 50.33; H, 5.11; N, 9.27%.

Benzyl 4,6-*O*-Benzylidene-2-deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranoside (13). A mixture of **12** (1.00 g, 2.3 mmol), PhCHO (10 ml, 98 mmol), and $ZnCl_2$ (0.5 g, 3.7 mmol) was kept stirring overnight at room temp under anhydrous conditions. After addition of $CHCl_3$ (30 ml) and H_2O (25 ml), the mixture was well stirred to give a yellow solid. Filtration and washing with $CHCl_3$ afforded pure **13** (0.95 g, 79%), mp 139—140 °C, $[\alpha]_D$ −16 (*c* 1.3, $CHCl_3$); ^1H NMR ($(CD_3)_2SO$) δ = 3.503 (dt, $J_{4,5}$ = 9.5 Hz, $J_{5,6eq}$ = 5.0 Hz, $J_{5,6ax}$ = 9.5 Hz, H5), 3.596 (t, $J_{3,4}$ = 9.0 Hz, H4), 3.772 (t, $J_{6eq,6ax}$ = 10.0 Hz, H6ax), 3.888 (br q, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 9.0 Hz, $J_{2,NH}$ = 9.5 Hz, H2), 4.048 (dt, $J_{3,OH}$ = 5.0 Hz, H3), 4.284 (dd, H6eq), 4.869 (d, H1), 5.256 (s, benzylidene), 5.674 (d, OH), 8.678 (d, NH), 8.174 (dd, *J* = 2.5, 9.5 Hz, DNP), 8.823 (d, *J* = 2.5 Hz, DNP); ^{13}C NMR ($(CD_3)_2SO$) δ = 60.7 (C2), 65.8 (C5), 67.9 (C6), 71.0 (C3), 80.9 (C4), 101.5 (C1), 70.8 (Bn), 100.8 (benzylidene), 117.0, 123.3, 149.3 (DNP).

Found: C, 58.15; H, 4.81; N, 7.89%. Calcd for $C_{26}H_{25}N_3O_9 \cdot 0.5H_2O$: C, 58.64; H, 4.88; N, 7.89%.

Benzyl 3-*O*-Allyl-2,4-*O*-benzylidene-2-deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranoside (14). To a cold mixture of **13** (300 mg, 0.57 mmol), allyl bromide (242 μl, 2.8 mmol), and DMF (3.0 ml), NaH (ca. 60% dispersion, 105 mg, 2.6 mmol) was added under stirring at 0 °C. The mixture was stirred at this temperature for 30 min and then at 20 °C for 30 min under anhydrous conditions. The mixture was again cooled at 0 °C and the reaction was quenched by adding MeOH (0.3 ml). Work-up and chromatography with TK system (100 : 1→2 : 1) gave **14** (247.5 mg, 78%), mp 176—178 °C, $[\alpha]_D$ −82 (*c* 1.0, MeOH, C_5H_5N (1 : 2)); ^1H NMR ($CDCl_3$) δ = 3.510 (d, m, H5), 3.679 (dd, $J_{2,3}$ = 9.0 Hz, $J_{3,4}$ = 10.0 Hz, H3), 3.785 (t, $J_{4,5}$ = 10.0 Hz, H4), 3.835 (br q, $J_{1,2}$ = 8.0 Hz, $J_{2,NH}$ = 8.5 Hz, H2), 3.876 (dd, $J_{5,6ax}$ = 10.0 Hz, $J_{6ax,6eq}$ = 10.5 Hz, H6ax), 4.438 (dd, H6eq), 4.567 (d, H1), 5.607 (s, benzylidene), 5.695 (m, allyl), 8.493 (d, NH), 7.312 (d, *J* = 9.5 Hz, DNP), 8.169 (dd, *J* = 2.5, 9.5 Hz, DNP), 9.112 (d, DNP); ^{13}C NMR ($CDCl_3$) δ = 59.3 (C2), 66.3 (C5), 68.6 (C6), 78.8 (C3), 82.1 (C4), 101.7 (C1), 101.4 (benzylidene), 71.7 (benzyl), 74.0, 116.6, 133.8 (allyl), 118.6, 123.7, 145.2 (DNP).

Found: C, 61.99; H, 5.13; N, 7.43%. Calcd for $C_{29}H_{29}N_3O_9$: C, 61.81; H, 5.19; N, 7.46%.

Benzyl 3-*O*-Allyl-2-deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranoside (15). A mixture of **14** (541.4 mg, 0.96 mmol) and aq AcOH (80%, 40 ml) was heated under stirring at 95 °C. Evaporation and chromatography using TK system (100 : 1→2 : 1), followed by crystallization with diisopropyl ether afforded **15** (340.6 mg, 75%), mp 172—173 °C, $[\alpha]_D$ −25 (*c* 1.0, Me_2CO); ^1H NMR ($(CD_3)_2CO$, CD_3OD (1 : 1)) δ = 3.462 (ddd, $J_{4,5}$ = 9.5 Hz, $J_{5,6a}$ = 2.5 Hz, $J_{5,6b}$ = 6.0 Hz, H5), 3.625 (dd, $J_{3,4}$ = 8.0 Hz, H4), 3.733 (dd, $J_{2,3}$ = 9.5 Hz, H3), 3.783 (dd, $J_{6a,6b}$ = 12.0 Hz, H6b), 3.890 (dd, $J_{1,2}$ = 8.0 Hz, H2), 3.963 (dd, H6a), 4.803 (d, H1), 7.492 (d, *J* = 9.5 Hz, DNP), 8.210 (dd, *J* = 2.5, 9.5 Hz, DNP), 8.893 (d, DNP), 5.763 (m, allyl); ^{13}C NMR ($(CD_3)_2CO$, CD_3OD (1 : 1)) δ = 60.5 (C2), 62.7 (C6), 72.2 (C4), 77.8 (C5), 84.3 (C3), 102.4 (C1), 75.1 (Bn), 72.0, 117.0, 136.4 (allyl), 118.2, 124.3, 138.7, 150.7 (DNP).

Found: C, 55.42; H, 5.22; N, 8.78%. Calcd for $C_{22}H_{25}N_3O_9$: C, 55.58; H, 5.30; N, 8.34%.

Benzyl 3-*O*-Allyl-4,6-di-*O*-benzyl-2-deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranoside (16). Compound **15** (137.7 mg, 0.29 mmol) was benzylated with $PhCH_2Br$ (0.33 ml, 2.8 mmol), NaH (60% dispersion, 105 mg, 2.6 mmol), and DMF (3 ml), followed by quenching with MeOH (0.1 ml). Work-up and chromatography using TK system (100 : 1→3 : 1) afforded **16** (175.6 mg, 92%), mp 178—180 °C, $[\alpha]_D$ −9 (*c* 0.8, $CHCl_3$); ^1H NMR

($CDCl_3$) δ = 3.498 (dt, $J_{4,5}$ = 9.5 Hz, $J_{5,6a}$ = $J_{5,6b}$ = 3.0 Hz, H5), 3.513 (dd, $J_{2,3}$ = 9.0 Hz, $J_{3,4}$ = 9.5 Hz, H3), 3.765 (t, H4), 3.826 (br q, $J_{1,2}$ = 8.0 Hz, $J_{2,NH}$ = 8.0 Hz, H2), 4.427 (d, H1), 8.500 (d, NH), 8.125 (dd, J = 2.5, 8.0 Hz, DNP), 9.120 (d, J = 2.5 Hz, DNP), 5.683 (m, allyl); ^{13}C NMR ($CDCl_3$) δ = 59.3 (C2), 68.4 (C6), 75.1 (C5), 78.1 (C4), 83.1 (C3), 100.9 (C1), 74.5, 116.6, 133.9 (allyl), 118.1, 123.8, 149.2 (DNP).

Found: C, 65.78; H, 5.68; N, 6.36%. Calcd for $C_{36}H_{37}N_3O_9$: C, 65.94; H, 5.53; N, 6.41%.

Benzyl 4,6-Di-*O*-benzyl-2-deoxy-2-(2,4-dinitroanilino)-α-D-glucopyranoside (10). A mixture of **16** (24.8 mg, 0.038 mmol), EtOH (2.1 ml), benzene (0.9 ml), H_2O (0.3 ml), and $RhCl(Ph_3P)_3$ (20.0 mg, 0.043 mmol) was stirred under reflux overnight. After evaporation to dryness, the residue was dissolved in Me_2CO (3 ml) containing 1 M HCl (0.25 ml). After heating for 1 h at 45 °C, the mixture was evaporated to dryness and chromatographed with TK system (100 : 1→2 : 1) to give **10** (15.5 mg, 67%), mp 62—64 °C, $[\alpha]_D$ −53 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.516 (dt, $J_{4,5}$ = 9.0 Hz, $J_{5,6a}$ = $J_{5,6b}$ = 3.0 Hz, H5), 3.695 (dd, $J_{3,4}$ = 8.5 Hz, H4), 3.714 (ddd, $J_{2,3}$ = 9.5 Hz, $J_{3,OH}$ = 2.5 Hz, H3), 3.785 (br q, $J_{1,2}$ = 7.5 Hz, $J_{2,NH}$ = 8.0 Hz, H2), 4.443 (d, H1), 2.467 (d, OH), 8.490 (d, NH), 8.135 (dd, J = 2.5, 8.5 Hz, DNP), 9.075 (d, J = 2.5 Hz, DNP); ^{13}C NMR ($CDCl_3$) δ = 59.2 (C2), 68.4 (C6), 75.1 (C5), 75.5 (C3), 78.0 (C4), 101.3 (C1), 116.6, 123.7, 149.2 (DNP).

Found: C, 64.33; H, 5.41; N, 6.63%. Calcd for $C_{33}H_{33}N_3O_9$: C, 64.38; H, 5.40; N, 6.83%.

Benzyl 3-*O*-Benzy-4,6-*O*-benzylidene-2-deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranoside (17). To a cooled solution of **13** (1.00 g, 1.9 mmol), $PhCH_2Br$ (1.1 ml, 9.2 mmol), and DMF (10 ml), NaH (ca. 60% dispersion in oil, 0.35 g, 8.8 mmol) was added under stirring at 0 °C. After the reaction was continued at room temp for 30 min, MeOH (1 ml) was added under cooling. Work-up and chromatography using HE system (100 : 1→2 : 1) afforded **17** (1.0 g, 85%), mp 181—182 °C, $[\alpha]_D$ +0.5 (*c* 1.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.513 (m, H5), 3.703 (t, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, H3), 3.857 (t, $J_{4,5}$ = 9.5 Hz, H4), 4.449 (dd, $J_{5,6eq}$ = 5.0 Hz, $J_{6eq,6ax}$ = 10.0 Hz, H6eq), 4.532 (d, $J_{1,2}$ = 8.0 Hz, H1), 8.295 (d, $J_{2,NH}$ = 9.5 Hz, NH), 8.135 (dd, J = 2.5, 9.5 Hz, DNP), 9.082 (d, J = 2.5 Hz, DNP); ^{13}C NMR ($CDCl_3$) δ = 59.1 (C2), 66.2 (C5), 68.6 (C6), 79.1 (C3), 82.2 (C4), 101.4 (C1), 101.6 (benzylidene), 116.3, 123.6, 149.0 (DNP).

Found: C, 64.61; H, 5.13; N, 6.80%. Calcd for $C_{33}H_{31}N_3O_9$: C, 64.59; H, 5.09; N, 6.85%.

Benzyl 3,6-Di-*O*-benzyl-2-deoxy-2-(2,4-dinitroanilino)-α-D-glucopyranoside (5). To a solution of **17** (570.5 mg, 0.94 mmol) in CH_2Cl_2 (6.0 ml) containing Et_3SiH (1.6 ml, 10.0 mmol), CF_3CO_2H (0.8 ml, 10.8 mmol) was added under stirring at 0 °C. After stirring for 30 min, the solution was evaporated to dryness and chromatographed with TK system (100 : 1→2 : 1) to give **5** (525.8 mg, 90%), mp 127—128 °C, $[\alpha]_D$ +9 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.487 (dd, $J_{2,3}$ = 8.5 Hz, $J_{3,4}$ = 9.5 Hz, H3), 3.512 (dt, $J_{4,5}$ = 9.5 Hz, $J_{5,6a}$ = $J_{5,6b}$ = 4.5, 9.5 Hz, H5), 3.872 (br q $J_{1,2}$ = 8.0 Hz, $J_{2,NH}$ = 8.5 Hz, H2), 3.782 (dt, $J_{4,OH}$ = 2.5 Hz, H4), 4.424 (d, H1), 2.886 (d, OH), 8.360 (d, NH), 7.250 (d, J = 9.5 Hz, DNP), 8.105 (dd, J = 2.5, 9.5 Hz, DNP), 9.060 (d, DNP); ^{13}C NMR ($CDCl_3$) δ = 58.6 (C2), 70.3 (C6), 73.5 (C4), 73.6 (C5), 83.3 (C3), 100.8 (C1), 71,2, 73.6,73.9 (Bn), 116.4, 123.7, 149.0 (DNP).

Found: C, 64.96; H, 5.40; N, 6.67%. Calcd for $C_{33}H_{33}N_3O_9$: C, 64.38; H, 5.40; N, 6.83%.

Benzyl 2-Deoxy-2-(2,4-dinitroanilino)-6-*O*-trityl-β-D-glucopyranoside (18). A mixture of **12** (1.0 g, 2.30 mmol), TrCl (0.77 g, 2.8 mmol), and pyridine (2 ml) was kept stirring at 70 °C overnight. After addition of Et_3N (2 ml) followed by evaporation to dryness, the residue was chromatographed using CM system (100 : 1→10 : 1) to give **18** (1.44 g, 93%), mp 101—102 °C, $[\alpha]_D$ −58 (*c* 1.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.442 (dt, $J_{4,5}$ = 9.0 Hz, $J_{5,6a}$ = $J_{5,6b}$ = 4.5 Hz, H5), 3.505 (dd, $J_{6a,6b}$ = 9.5 Hz, H6b), 3.548 (dd, H6a), 3.644 (t, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, H3), 3.765 (t, H4), 3.775 (br q, $J_{1,2}$ = 8.0 Hz, $J_{2,NH}$ = 8.5 Hz, H2), 4.453 (d, H1), 8.520 (d, NH), 8.073 (dd, J = 2.5, 8.0 Hz, DNP), 9.065 (d, J = 2.5 Hz, DNP); ^{13}C NMR ($CDCl_3$) δ = 58.9 (C2), 64.0 (C6), 72.8 (C4), 73.6 (C5), 75.3 (C3), 101.0 (C1), 71.1 (Bn), 87.4 (Tr), 116.7, 123.6, 149.3 (DNP).

Found: C, 67.12; H, 5.42; N, 6.03%. Calcd for $C_{38}H_{35}N_3O_9$: C, 67.35; H, 5.21; N, 6.20%.

Benzyl 3,4-Di-*O*-benzyl-2-deoxy-2-(2,4-dinitroanilino)-α-D-glucopyranoside (11). Compound **18** (159 mg, 0.23 mmol) was benzylated with $PhCH_2Br$ (107 µl, 0.90 mmol), NaH (60% dispersion, 35 mg, 0.88 mmol), and DMF (0.6 ml), as described for **9**. Work-up and chromatography using TK system (100 : 1→3 : 1), afforded the benzylated product, which was heated in aq AcOH (80%, 20 ml) at 95 °C for 90 min. The mixture was evaporated to dryness and chromatographed with TK system (100 : 1→1 : 1) to yield **11** (73.4 mg, 51%), mp 139—140 °C, $[\alpha]_D$ +34 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.430 (ddd, $J_{4,5}$ = 9.0 Hz, $J_{5,6a}$ = 2.5 Hz, $J_{5,6b}$ = 4.0 Hz, H5), 3.634 (dd, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 8.0 Hz, H3), 3.766 (dd, H4), 3.824 (ddd, $J_{6b,OH}$ = 7.5 Hz, $J_{6a,6b}$ = 12.0 Hz, H6b), 3.879 (br q, $J_{1,2}$ = 8.0 Hz, $J_{2,NH}$ = 8.5 Hz, H2), 3.941 (ddd, $J_{6a,OH}$ = 5.0 Hz, H6a), 4.423 (d, H1), 1.795 (dd, OH), 8.333 (d, NH), 8.125 (dd, J = 2.5, 8.5 Hz, DNP), 9.045 (d, J = 2.5 Hz, DNP); ^{13}C NMR ($CDCl_3$) δ = 59.2 (C2), 61.6 (C6), 75.5 (C5), 77.9 (C4), 83.8 (C3), 100.9 (C1), 116.2, 123.7, 148.9 (DNP).

Found: C, 64.15; H, 5.47; N, 6.68%. Calcd for $C_{33}H_{33}N_3O_9$: C, 64.38; H, 5.40; N, 6.83%.

Benzyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranoside (19). Compound **12** (52.0 mg, 0.12 mmol) was benzylated with $PhCH_2Br$ (84 µl, 0.71 mmol), NaH (60% dispersion, 26 mg, 0.65 mmol), and DMF (0.52 ml). Work-up and chromatography using TK system (100 : 1→3 : 1), afforded **19** (72.7 mg, 86%), mp 155—156 °C, $[\alpha]_D$ +31 (*c* 0.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.554 (dt, $J_{4,5}$ = 9.5 Hz, $J_{5,6a}$ = $J_{5,6b}$ = 3.0 Hz, H5), 3.600 (dd, $J_{2,3}$ = 9.0 Hz, $J_{3,4}$ = 8.5 Hz, H3), 3.865 (dd, H4), 3.873 (br q, $J_{1,2}$ = $J_{2,NH}$ = 8.0 Hz, H2), 4,455 (d, H1), 8.480 (d, NH), 8.125 (dd, J = 2.5, 9.0 Hz, DNP), 9.050 (d, J = 2.5 Hz, DNP); ^{13}C NMR ($CDCl_3$) δ = 59.1 (C2), 68.4 (C6), 75.1 (C5), 75.8 (C4), 78.3 (C3), 100.6 (C1), 116.3, 123.7, 149.0 (DNP).

Found: C, 67.86; H, 5.58; N, 5.88%. Calcd for $C_{40}H_{39}N_3O_9$: C, 68.07; H, 5.57; N, 5.95%.

Benzyl 2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranoside (20). A mixture of **19** (21.7 mg, 0.031 mmol), Dowex 1×2 (HO^- form, 100—200 mesh, 0.5 ml), Me_2CO (2 ml), and H_2O (1 ml) was stirred under reflux overnight. After removal of the dark-colored resin by filtration and washing with acetone, the filtrate was evaporated to dryness and again heated in Me_2CO (2 ml) containing the resin (0.5 ml) and water (1 ml) overnight. After removal of the resin, the almost colorless filtrate was evaporated to dryness and treated with Ac_2O (0.3 ml) in MeOH (3 ml) overnight. Evaporation and chromatography with TK system (100 : 1→1 : 1) afforded unreacted **19** (16.0 mg, 74%) and **20** (4.3 mg, 24% (92% based on the consumed **19**)), mp 161—162 °C, $[\alpha]_D$ −8 (*c* 0.8, $CHCl_3$) (lit, mp 160—161 °C,[16a] 164—165 °C,[16b] $[\alpha]_D$ −12 (*c* 1.3, $CHCl_3$),[16a] −12.6 (*c* 1.1, $CHCl_3$)[16b]); ^{1}H NMR ($CDCl_3$) δ = 3.562 (br q, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, $J_{2,NH}$ = 8.0 Hz, H2), 3.662 (ddd, $J_{4,5}$ = 9.0 Hz, $J_{5,6a}$ = 3.0 Hz, $J_{5,6b}$ = 4.0 Hz, H5), 3.675 (dd, $J_{3,4}$ = 8.0

Hz, H4), 3.740 (dd, $J_{6a,6b}$ = 10.5 Hz, H6b), 3.792 (dd, H6a), 4.046 (dd, H3), 4.840 (d, H1), 5.461 (d, NH), 1.810 (s, Ac); ^{13}C NMR ($CDCl_3$) δ = 56.5 (C2), 69.1 (C6), 74.8 (C5), 78.5 (C4), 80.3 (C3), 99.2 (C1), 23.5, 170.1 (Ac).

Found: C, 74.10; H, 6.70; N, 2.47%. Calcd for $C_{36}H_{39}N_3O_6$: C, 74.33; H, 6.76; N, 2.41%.

Benzyl *O*-[3,4,6-Tri-*O*-benzyl-2-deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranosyl]-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (26). To a rubber-stoppered vessel containing a mixture of **2** (34.1 mg, 0.055 mmol), **21** (29.9 mg, 0.55 mmol), NsCl (30.7 mg, 0.14 mmol), AgOTf (35.6 mg, 0.14 mmol), and CH_2Cl_2 (0.3 ml), Et_3N (19.3 ml, 0.14 mmol) was added under stirring at −60 °C (bath temp). The reaction mixture was kept stirring while the bath temp allowed to rise to 0 °C and then overnight at this temp. Powdery $NaHCO_3$ (ca. 100 mg) and PhMe (2 ml) were added and the mixture was further stirred for 15 min at room temp. The mixture was transferred onto a silica-gel column which was developed with TK system (100 : 1→2 : 1) to give **26** (53.9 mg, 85%), $[\alpha]_D$ +11 (*c* 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.290 (ddd, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 2.0, 3.0 Hz, H5^I), 3.408 (ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6}$ = 2.0, 4.5 Hz, H5^{II}), 3.475 (dd, $J_{2,3}$ = 9.0 Hz, $J_{3,4}$ = 9.5 Hz, H3^{II}), 3.485 (dd, $J_{2,3}$ = 8.5 Hz, $J_{3,4}$ = 9.0 Hz, H3^I), 3.627 (dd, H4^{II}), 3.805 (br q, $J_{1,2}$ = 7.5 Hz, $J_{2,NH}$ = 8.0 Hz, H2^I), 3.825 (dd, H4^I), 4.500 (d, H1^I), 4.816 (d, H1^{II}), 8.425 (d, NH), 7.815 (d, *J* = 2.5, 8.0 Hz, DNP), 8.615 (d, *J* = 2.5 Hz, DNP); ^{13}C NMR ($CDCl_3$) δ = 59.7 (C2^{II}), 68.1 (C6^I), 68.7 (C6^{II}), 74.8 (C5^{II}), 75.1 (C5^I), 77.8 (C4^{II}), 78.1 (C4^I), 80.8 (C2^I), 84.2 (C3^{II}), 84.6 (C3^I), 101.0 (C1^I), 101.4 (C1^{II}), 115.6, 123.7, 148.6 (DNP).

Found: C, 70.69; H, 6.03; N, 3.65%. Calcd for $C_{67}H_{67}N_3O_{14}$: C, 70.70; H, 5.93; N, 3.69%.

Compound **22**, **23**, **24**, and **25** were condensed with **2** to give **27** (67%), **28** (57%), **29** (95%), and **30** (26%), respectively (Table 1).

Benzyl *O*-[3,4,6-Tri-*O*-benzyl-2-deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranosyl]-(1→3)-2,4,6-tri-*O*-benzyl-β-D-glucopyranoside (27). $[\alpha]_D$ +27 (*c* 2.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.280 (dd, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 8.5 Hz, H2^I), 3.383 (dt, $J_{4,5}$ = 9.0 Hz, $J_{5,6a}$ = $J_{5,6b}$ = 3.0 Hz, H5^{II}), 3.422 (dd, $J_{2,3}$ = 8.5 Hz, $J_{3,4}$ = 9.0 Hz, H3^{II}), 3.494 (dd,$J_{3,4}$ = 8.5 Hz, $J_{4,5}$ = 10.0 Hz, H4^I), 3.620 (br q, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = $J_{2,NH}$ = 8.5 Hz, H2^{II}), 3,848 (t, H4^{II}), 4.093 (t, H3^I), 4.445 (d, H1^I), 5.030 (d, H1^{II}), 8.430 (d, NH), 7.045 (d, *J* = 9.0 Hz, DNP), 8.070 (dd, *J* = 2.5, 9.0 Hz, DNP), 9.020 (d, DNP); ^{13}C NMR ($CDCl_3$) δ = 59.7 (C2^{II}), 68.5 (C6^{II}), 68.8 (C6^I), 74.6 (C5^I), 75.1 (C5^{II}), 76.2 (C4^{II}), 78.4 (C4^I), 80.1 (C3^{II}), 82.7 (C2^I), 84.0 (C3^I), 101.3 (C1^{II}), 101.8 (C1^I), 116.3, 123.7, 149.0 (DNP).

Found: C, 70.10; H, 5.82; N, 3.74%. Calcd for $C_{67}H_{67}N_3O_{14}$: C, 70.70; H, 5.93; N, 3.69%.

Benzyl *O*-[3,4,6-Tri-*O*-benzyl-2-deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranosyl]-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (28). $[\alpha]_D$ −27 (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.023 (dt, $J_{4,5}$ = 9.5 Hz, $J_{5,6a}$ = $J_{5,6b}$ = 2.5 Hz, H5^I), 3.253 (ddd, $J_{4,5}$ = 9.5 Hz, $J_{5,6a}$ = 2.0 Hz, $J_{5,6b}$ = 3.5 Hz, H5^{II}), 3.279 (dd, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 8.5 Hz, H3^{II}), 3.436 (dd, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 8.5 Hz, H3^I), 3.456 (dd, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 9.5 Hz, H2^I), 3.535 (br q, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, $J_{2,NH}$ = 8.5 Hz, H2^{II}), 3.545 (dd, $J_{6a,6b}$ = 11.0 Hz, H6a^I), 3.645 (dd, $J_{6a,6b}$ = 11.0 Hz, H6b^{II}), 3.712 (dd, H6a^{II}), 3.781 (dd, H4^{II}), 3.984 (dd, H4^I), 4.366 (d, H1^{II}), 4.383 (d, H1^I), 7.975 (dd, *J* = 2.5, 8.0 Hz, DNP), 8.975 (d, *J* = 2.5 Hz, DNP); ^{13}C NMR ($CDCl_3$) δ = 59.4 (C2^{II}), 68.0 (C6^I), 68.2 (C6^{II}), 74.5 (C5^I), 75.0 (C5^{II}), 75.5 (C4^I), 78.3 (C4^{II}), 81.9 (C3^I), 82.0 (C2^I), 83.5 (C3^{II}), 100.8 (C1^{II}), 102.3 (C1^I), 116.1, 123.7, 148.8 (DNP).

Found: C, 70.07; H, 5.95; N, 3.55%. Calcd for $C_{67}H_{67}N_3O_{14}$: C, 70.70; H, 5.93; N, 3.69%.

Benzyl *O*-[3,4,6-Tri-*O*-benzyl-2-deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranosyl]-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (29). Mp 175—176 °C, $[\alpha]_D$ +15 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.133 (dd, $J_{3,4}$ = 8.5 Hz, $J_{4,5}$ = 9.5 Hz, H4^I), 3.257 (dd, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 9.0 Hz, H2^I), 3.393 (ddd, $J_{5,6a}$ = 2.0 Hz, $J_{5,6b}$ = 5.5 Hz, H5^I), 3.477 (ddd, $J_{4,5}$ = 9.5 Hz, $J_{5,6a}$ = 2.0 Hz, $J_{5,6b}$ = 3.0 Hz, H5^{II}), 3.538 (dd, $J_{3,4}$ = 8.5 Hz, H3^I), 3.567 (dd, $J_{2,3}$ = 8.0 Hz, $J_{3,4}$ = 9.0 Hz, H3^{II}), 3.621 (dd, $J_{6a,6b}$ = 11.5 Hz, H6b^I), 3.787 (br q, $J_{1,2}$ = 8.0 Hz, $J_{2,NH}$ = 8.5 Hz, H2^{II}), 3.823 (dd, H4^{II}), 4.130 (dd, H6a^I), 4.377 (d, H1^{II}), 4.437 (d, H1^I), 8.445 (d, NH), 8.140 (dd, *J* = 2.5, 9.0 Hz, DNP), 8.883 (d, *J* = 2.5 Hz, DNP); ^{13}C NMR ($CDCl_3$) δ = 59.1 (C2^{II}), 68.3 (C6^{II}), 68.5 (C6^I), 74.3 (C5^I), 75.1 (C5^{II}), 77.6 (C4^I), 78.2 (C4^{II}), 82.2 (C2^I), 83.7 (C3^{II}), 84.3 (C3^I), 83.5 (C3^{II}), 102.5 (C1^{II}), 102.6 (C1^I), 116.5, 123.9, 148.9 (DNP).

Found: C, 70.45; H, 6.02; N, 3.74%. Calcd for $C_{67}H_{67}N_3O_{14}$: C, 70.70; H, 5.93; N, 3.69%.

***O*-[3,4,6-Tri-*O*-benzyl-2-deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranosyl]-(1→3)-1,2-di-*O*-benzyl-*sn*-glycerol (30).** $[\alpha]_D$ +25 (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.353 (dd, $J_{1b,2}$ = 3.5 Hz, $J_{1a,1b}$ = 10.0 Hz, H1b^I), 3.393 (dd, $J_{1a,2}$ = 5.0 Hz, H1a^I), 3.483 (ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 2.5 Hz, $J_{5,6b}$ = 4.0 Hz, H5^{II}), 3.587 (dd, $J_{2,3}$ = 10.0 Hz, $J_{3,4}$ = 9.0 Hz, H3^{II}), 3.725 (br q, $J_{1,2}$ = 8.5 Hz, $J_{2,NH}$ = 8.0 Hz, H2^{II}), 3.813 (dd, H4^{II}), 3.958 (dd, $J_{6a,6b}$ = 11.0 Hz, H6a^{II}), 4.423 (d, H1^{II}), 8.425 (d, NH), 7.599 (dd, *J* = 2.5, 8.5 Hz, DNP), 8.915 (d, *J* = 2.5 Hz, DNP); ^{13}C NMR ($CDCl_3$) δ = 59.2 (C2^{II}), 68.4 (C1^I), 69.1 (C6^{II}), 69.4 (C3^I), 75.0 (C5^{II}), 77.0 (C2^I), 78.3 (C4^{II}), 83.9 (C3^{II}), 102.7 (C1^{II}), 116.2, 123.7, 148.9 (DNP).

Found: C, 68.49; H, 6.07; N, 4.65%. Calcd for $C_{49}H_{51}N_3O_{11}$: C, 68.60; H, 5.99; N, 4.90%.

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 (31). A mixture of **26** (17.0 mg, 0.015 mmol), Dowex 1×2 (HO^- form, 100—200 mesh, 0.5 ml), Me_2CO (4 ml), and H_2O (1 ml) was stirred under reflux overnight. After removal of the resin by filtration and washing with Me_2CO, the filtrate was evaporated to dryness and again heated with the resin (0.5 ml) in Me_2CO (3 ml) containing H_2O (1 ml). This operation was repeated one more time. The filtrate was evaporated to dryness and treated with Ac_2O (0.3 ml) in MeOH (2 ml) overnight. Evaporation and chromatography with TK system (100 : 1→1 : 1) afforded unreacted **26** (12.4 mg, 73%) and **31** (3.7 mg, 24% (90% based on the reacted starting material)), which was identified with the compound reported in the previous paper.[17]

Similarly, **27**, **28**, **29**, and **30** were converted into the corresponding *N*-acetate **32** (44% (>90%)), **33** (33% (>90%)), **34** (14% (>90%)), and **35** (68% (>81%)). Compounds **32**, **33**, and **34** were identified with the corresponding material reported previously.[17]

***O*-(2-Acetamido-3,4,6-Tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-1,2-di-*O*-benzyl-*sn*-glycerol (35).** Mp 127—129 °C, $[\alpha]_D$ +5 (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.563 (br q, $J_{1,2}$ = $J_{2,NH}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H2^{II}), 3.648 (dd, $J_{3,4}$ = 8.0 Hz, $J_{4,5}$ = 9.5 Hz, H4^{II}), 3.863 (dd, H3^{II}), 3.968 (dd, $J_{5,6a}$ = 4.5 Hz, $J_{6a,6b}$ = 10.5 Hz, H6a^{II}), 5.325 (d, NH), 1.717 (s, Ac); ^{13}C NMR ($CDCl_3$) δ = 56.2 (C2^{II}), 68.8 (C1^I), 69.0 (C6^{II}), 70.1 (C3^I), 74.9 (C5^{II}), 77.2 (C2^I), 78.4 (C4^{II}), 80.9 (C3^{II}), 100.9 (C1^{II}), 72.1, 73.4, 73.5, 74.4, 74.6 (Bn), 23.4, 170.1 (Ac).

Found: C, 73.78; H, 6.78; N, 1.95%. Calcd for $C_{46}H_{51}N_3O_8$: C, 74.03; H, 6.89; N, 1.88%.

***O*-(2-Acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-*sn*-glycerol (36).** Hydrogenation of **35** (32.8 mg, 0.044 mmol) over Pd on C (33 mg, 10%) in AcOH (6 ml) at room temp overnight.

Chromatography with CM system (100 : 1→1 : 1) afforded **36** (10.6 mg, 82%), mp 177—178 °C, $[\alpha]_D$ −26 (*c* 0.8, H_2O); ^{1}H NMR (D_2O) δ = 3.676 (dd, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 10.0 Hz, H2^{II}), 3.713 (dd, $J_{3b,2}$ = 5.5 Hz, $J_{3a,3b}$ = 12.0 Hz, H3b^{I}), 3.823 (m, H2^{I}), 3.897 (dd, $J_{3a,2}$ = 2.0 Hz, H3a^{I}), 4.500 (d, H1^{II}), 1.910 (Ac); ^{13}C NMR ($CDCl_3$) δ = 58.9 (C2^{II}), 64.1 (C1^{I}), 65.7 (C6^{II}), 73.7 (C2^{I}), 73.3 (C4^{II}), 74.0 (C3^{I}), 77.1 (C5^{II}), 79.2 (C3^{II}), 104.8 (C1^{II}), 25.5, 178.1 (Ac).

Found: C, 41.77; H, 6.90; N, 4.48%. Calcd for $C_{11}H_{21}NO_8 \cdot H_2O$: C, 42.17; H, 7.40; N, 4.47%.

Benzyl *O*-(4-*O*-Acetyl-2,3,6-tri-*O*-benzyl-2-deoxy-2-α- and -β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranoside (39a and 39b). Condensation of **38** (22.1 mg, 0.045 mmol) and **5** (21.3 mg, 0.035 mmol) in the presence of NsCl (19.1 mg, 0.086 mmol), AgOTf (22.2 mg, 0.086 mmol), and Et_3N (12.1 μl, 0.086 mmol) in CH_2Cl_2 (0.3 ml), followed by work-up and chromatography with TK system (100 : 1→2 : 1) gave **39a** (faster-moving, 24.1 mg, 64%), $[\alpha]_D$ +51 (*c* 2.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.399 (dd, $J_{5,6b}$ = 6.5 Hz, $J_{6a,6b}$ = 9.0 Hz, H6b^{II}), 3.455 (dd, $J_{5,6a}$ = 6.5 Hz, H6a^{II}), 3.644 (ddd, $J_{4,5}$ = 8.0 Hz, $J_{5,6a}$ = 3.5 Hz, $J_{5,6b}$ = 3.0 Hz, H5^{I}), 3.673 (dd, $J_{2,3}$ = 9.0 Hz, $J_{3,4}$ = 8.0 Hz, H3^{I}), 3.794 (dd, $J_{6a,6b}$ = 11.0 Hz, H6b^{I}), 3.822 (br q, $J_{1,2}$ = 7.5 Hz, $J_{2,NH}$ = 8.0 Hz, H2^{I}), 3.878 (dd, $J_{3,4}$ = 3.0 Hz, H3^{II}), 3.897 (dd, H6a^{I}), 4.114 (br t, H5^{II}), 4.137 (t, H4^{I}), 4.418 (d, H1^{I}), 5.484 (d, H1^{II}), 5.603 (br d, H4^{II}), 8.320 (d, NH), 7.975 (dd, *J* = 2.5, 8.0 Hz, DNP), 8.910 (d, *J* = 2.5 Hz, DNP), 2.061 (s, Ac); ^{13}C NMR ($CDCl_3$) δ = 58.4 (C2^{II}), 67.8 (C4^{II}), 68.5 (C6^{II}), 68.7 (C5^{II}), 69.2 (C6^{I}), 74.3 (C4^{I}), 75.0 (C5^{I}), 75.2 (C2^{II}), 76.0 (C3^{II}), 83.9 (C3^{I}), 98.2 (C1^{II}), 100.4 (C1^{I}), 115.9, 123.6, 148.6 (DNP), 20.9, 170.2 (Ac).

39b (7.3 mg, 19%): $[\alpha]_D$ +15 (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.422 (dd, $J_{2,3}$ = 9.0 Hz, $J_{3,4}$ = 4.0 Hz, H3^{II}), 3.518 (dd, $J_{1,2}$ = 7.5 Hz, H2^{II}), 3.548 (dd, $J_{2,3}$ = 8.0 Hz, $J_{3,4}$ = 9.0 Hz, H3^{I}), 3.708 (dd, $J_{5,6b}$ = 2.0 Hz, $J_{6a,6b}$ = 11.0 Hz, H6b^{I}), 3.780 (br q, $J_{1,2}$ = $J_{2,NH}$ = 8.0 Hz, H2^{I}), 3.903 (dd, $J_{5,6a}$ = 2.0 Hz, H6a^{I}), 4.163 (dd, $J_{4,5}$ = 8.5 Hz, H4^{I}), 4.402 (d, H1^{I}), 4.458 (d, H1^{II}), 5.557 (dd, $J_{4,5}$ = 1.0 Hz, H4^{II}), 8.410 (d, NH), 8.025 (dd, *J* = 2.5, 8.0 Hz, DNP), 9.015 (d, *J* = 2.5 Hz, DNP), 2.021 (s, Ac); ^{13}C NMR ($CDCl_3$) δ = 58.6 (C2^{I}), 66.5 (C4^{II}), 67.7 (2C, C6^{I} and C6^{II}), 72.1 (C5^{II}), 75.3 (C5^{I}), 76.1 (C4^{I}), 79.3 (C2^{II}), 79.6 (C3^{II}), 81.5 (C3^{I}), 100.8 (C1^{I}), 102.5 (C1^{II}), 116.6, 123.7, 149.0 (DNP), 20.8, 170.1 (Ac).

Found: **39a**; C, 67.87; H, 5.88; N, 3.78%. **39b**; C, 68.29; H, 5.98; N, 3.78%. Calcd for $C_{62}H_{63}N_3O_{15}$: C, 68.31; H, 5.83; N, 3.85%.

Similarly, the acceptor **5** was condensed with **40** to give **41a** (61%) and **41b** (25%). The donor **42** afforded **43a** (61%) and **43b** (32%).

Benzyl *O*-(4-*O*-Allyl-2,3,6-tri-*O*-benzyl-α- and -β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranoside (41a and 41b). **41a** (faster-moving), $[\alpha]_D$ +76 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.555 (dd, $J_{5,6b}$ = 5.5 Hz, $J_{6a,6b}$ = 8.5 Hz, H6b^{II}), 3.636 (dd, $J_{5,6a}$ = 7.0 Hz, H6a^{II}), 3.647 (ddd, $J_{4,5}$ = 8.0 Hz, $J_{5,6a}$ = 2.0 Hz, $J_{5,6b}$ = 4.0 Hz, H5^{I}), 3.677 (dd, $J_{2,3}$ = 9.0 Hz, $J_{3,4}$ = 8.0 Hz, H3^{I}), 3.813 (dd, $J_{2,3}$ = 10.0 Hz, $J_{3,4}$ = 3.0 Hz, H3^{II}), 3.815 (dd, $J_{6a,6b}$ = 11.0 Hz, H6b^{I}), 3.820 (br q, $J_{1,2}$ = 7.5 Hz, $J_{2,NH}$ = 8.5 Hz, H2^{I}), 3.887 (dd, H6a^{I}), 3.902 (d, $J_{4,5}$ = 0.0 Hz, H4^{II}), 3.981 (dd, H5^{II}), 4.013 (dd, $J_{1,2}$ = 3.5 Hz, H2^{II}), 4.128 (t, H4^{I}), 4.413 (d, H1^{I}), 5.479 (d, H1^{II}), 8.375 (d, NH), 7.935 (dd, *J* = 2.5, 8.5 Hz, DNP), 8.935 (d, *J* = 2.5 Hz, DNP), 5.896 (m, allyl); ^{13}C NMR ($CDCl_3$) δ = 58.4 (C2^{I}), 68.9 (C6^{II}), 69.3 (C6^{I}), 70.2 (C5^{II}), 74.1 (C4^{I}), 74.4 (C4^{II}), 75.1 (C5^{I}), 76.1 (C2^{II}), 78.6 (C3^{II}), 83.9 (C3^{I}), 98.2 (C1^{II}), 100.4 (C1^{I}), 116.0, 123.6, 148.6 (DNP), 117.1, 135.3 (allyl).

41b: $[\alpha]_D$ +21 (*c* 0.8, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ = 4.362 (d, $J_{1,2}$ = 7.5 Hz, H1^{I}), 4.438 (dd, $J_{1,2}$ = 7.5 Hz, H1^{II}), 8.393 (d, $J_{2,NH}$ = 9.0 Hz, NH), 8.021 (dd, *J* = 2.5, 8.5 Hz, DNP), 9.057 (d, *J* = 2.5 Hz, DNP), 5.875 (m, allyl); ^{13}C NMR ($CDCl_3$) δ = 58.8 (C2^{I}), 67.8 (C6^{II}), 68.1 (C6^{I}), 73.1 (C5^{II}), 75.1 (C4^{I}), 75.4 (C5^{I}), 76.3 (C4^{I}), 79.9 (C2^{II}), 81.6 (C3^{II}), 82.1 (C3^{I}), 100.7 (C1^{I}), 102.8 (C1^{II}), 116.4, 123.6, 149.1 (DNP), 116.7, 135.4 (allyl).

Found: **41a**; C, 69.26; H, 5.97; N, 3.85%. **41b**; C, 69.20; H, 5.95; N, 3.87%. Calcd for $C_{63}H_{63}N_3O_{14}$: C, 69.66; H, 5.85; N, 3.87%.

Benzyl *O*-(4-*O*-Acetyl-2,3,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranoside (43a and 43b). **43a** (slower-moving), $[\alpha]_D$ +44 (*c* 2.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.580 (dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.5 Hz, H2^{II}), 3.667 (ddd, $J_{4,5}$ = 8.0 Hz, $J_{5,6a}$ = 2.5 Hz, $J_{5,6b}$ = 4.0 Hz, H5^{I}), 3.720 (dd, $J_{2,3}$ = 9.0 Hz, $J_{3,4}$ = 8.0 Hz, H3^{I}), 3.837 (dd, $J_{6a,6b}$ = 11.0 Hz, H6a^{I}), 3.851 (br q, $J_{1,2}$ = 7.0 Hz, $J_{2,3}$ = 9.0 Hz, $J_{2,NH}$ = 8.5 Hz, H2^{I}), 3.901 (dd, $J_{3,4}$ = 9.0 Hz, H3^{II}), 3.943 (ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 4.5 Hz, $J_{5,6b}$ = 3.0 Hz, H5^{II}), 4.021 (dd, $J_{6a,6b}$ = 11.0 Hz, H6a^{II}), 4.178 (t, H4^{I}), 4.385 (d, H1^{I}), 5.046 (dd, H4^{II}), 5.361 (d, H1^{I}), 8.368 (d, NH), 8.104 (dd, *J* = 2.5, 10.0 Hz, DNP), 8.943 (d, *J* = 2.5 Hz, DNP), 1.874 (s, Ac); ^{13}C NMR ($CDCl_3$) δ = 58.2 (C2^{I}), 69.1 (C6^{II}), 69.2 (C6^{I}), 69.8 (C5^{II}), 70.6 (C4^{II}), 75.1 (C4^{I}), 75.2 (C5^{I}), 78.8 (C3^{II}), 79.6 (C2^{II}), 83.3 (C3^{I}), 97.6 (C1^{II}), 100.4 (C1^{I}), 116.9, 123.6, 148.6 (DNP), 20.8, 169.6 (Ac).

43b: $[\alpha]_D$ +19 (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.555 (dd, $J_{5,6b}$ = 5.5 Hz, $J_{6a,6b}$ = 8.5 Hz, H6b^{II}), 3.636 (dd, $J_{5,6a}$ = 7.0 Hz, H6a^{II}), 3.647 (ddd, $J_{4,5}$ = 8.0 Hz, $J_{5,6a}$ = 2.0 Hz, $J_{5,6b}$ = 4.0 Hz, H5^{I}), 3.677 (dd, $J_{2,3}$ = 9.0 Hz, $J_{3,4}$ = 8.0 Hz, H3^{I}), 3.813 (dd, $J_{2,3}$ = 10.0 Hz, $J_{3,4}$ = 3.0 Hz, H3^{II}), 3.815 (dd, $J_{6a,6b}$ = 11.0 Hz, H6b^{I}), 3.820 (br q, $J_{1,2}$ = 7.5 Hz, $J_{2,NH}$ = 8.5 Hz, H2^{I}), 3.887 (dd, H6a^{I}), 3.902 (d, $J_{4,5}$ = 0.0 Hz, H4^{II}), 3.981 (dd, H5^{II}), 4.013 (dd, $J_{1,2}$ = 3.5 Hz, H2^{II}), 4.128 (t, H4^{I}), 4.413 (d, H1^{I}), 5.479 (d, H1^{II}), 8.375 (d, NH), 7.935 (dd, *J* = 2.5, 8.5 Hz, DNP), 8.935 (d, *J* = 2.5 Hz, DNP), 5.896 (m, allyl); ^{13}C NMR ($CDCl_3$) δ = 58.4 (C2^{I}), 68.9 (C6^{II}), 69.3 (C6^{I}), 70.2 (C5^{II}), 74.1 (C4^{I}), 74.4 (C4^{II}), 75.1 (C5^{I}), 76.1 (C2^{II}), 78.6 (C3^{II}), 83.9 (C3^{I}), 98.2 (C1^{II}), 100.4 (C1^{I}), 116.0, 123.6, 148.6 (DNP), 117.1, 135.3 (allyl).

Found: **43a**; C, 67.86; H, 5.83; N, 3.50%. **43b**; C, 69.02; H, 5.92; N, 3.86%. Calcd for $C_{62}H_{63}N_3O_{15}$: C, 68.31; H, 5.83; N, 3.86%.

Benzyl *O*-(4-*O*-Allyl-2,3,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranoside (45a and 45b). To a vessel containing **44** (30.0 mg, 0.061 mmol), **5** (29.0 mg, 0.047 mmol), NsCl (26.1 mg, 0.118 mmol), AgOTf (30.3 mg, 0.118 mmol), $LiNTf_2$ (33.8 mg, 0.118 mmol), and CH_2Cl_2 (0.3 ml), Et_3N (16.4 μl, 0.118 mmol) was injected under stirring at −60 °C and the reaction and work-up were conducted in the manner described above. Chromatography with TK system afforded **45a** (faster-moving, 20.8 mg, 41%), $[\alpha]_D$ +81 (*c* 1.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.515 (dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 10.0 Hz, H2^{II}), 3.515 (dd, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 8.5 Hz, H4^{II}), 3.536 (dd, $J_{5,6b}$ = 2.5 Hz, $J_{6a,6b}$ = 10.5 Hz, H6b^{II}), 3.615 (dd, $J_{5,6a}$ = 3.5 Hz, H6a^{II}), 3.634 (ddd, $J_{4,5}$ = 9.0 Hz, $J_{5,6a}$ = 4.0 Hz, $J_{5,6b}$ = 2.5 Hz, H5^{I}), 3.713 (dd, $J_{2,3}$ = 9.0 Hz, $J_{3,4}$ = 8.0 Hz, H3^{I}), 3.806 (ddd, H5^{II}), 3.850 (br q, $J_{1,2}$ = 7.5 Hz, $J_{5,6a}$ = 4.0 Hz, $J_{2,NH}$ = 9.0 Hz, H2^{I}), 3.883 (t, H3^{II}), 3.980 (dd, $J_{6a,6b}$ = 11.0 Hz, H6a^{I}), 4.180 (dd, H4^{II}), 4.439 (d, H1^{I}), 5.395 (dd, H1^{II}), 8.356 (d, NH), 8.002 (dd, *J* = 2.5, 9.5 Hz, DNP), 8.932 (d, *J* = 2.5 Hz, DNP), 5.838 (m, allyl); ^{13}C NMR ($CDCl_3$) δ = 58.3 (C2^{I}), 68.5 (C6^{II}), 69.0 (C6^{I}), 71.4 (C5^{II}), 74.2 (C4^{I}), 75.2 (C5^{I}), 77.7 (C4^{II}), 79.7 (C2^{II}), 81.7 (C3^{II}), 83.7 (C3^{I}), 97.6 (C1^{II}), 100.5 (C1^{I}), 116.0, 123.6, 148.6

(DNP), 116.3, 134.8 (allyl).

45b (23.5 mg, 46%): $[\alpha]_D$ +15 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.350 (ddd, $J_{4,5}$ = 9.5 Hz, $J_{5,6a}$ = 2.0 Hz, $J_{5,6b}$ = 4.5 Hz, H5^{II}), 3.382 (dd, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, H2^{II}), 3.423 (ddd, $J_{4,5}$ = 8.5 Hz, $J_{5,6a}$ = 4.0 Hz, $J_{5,6b}$ = 2.0 Hz, H5^{I}), 3.497 (2H, t, $J_{3,4}$ = 9.5 Hz, H3^{II}, H4^{I}), 3.542 (dd, $J_{2,3}$ = 9.0 Hz, $J_{3,4}$ = 8.5 Hz, H3^{I}), 3.600 (dd, $J_{6a,6b}$ = 11.0 Hz, H6a^{II}), 3.707 (dd, $J_{6a,6b}$ = 11.0 Hz, H6b^{I}), 3.760 (dd, H6a^{II}), 3.777 (br q, $J_{1,2}$ = 8.0 Hz, $J_{2,NH}$ = 9.0 Hz, H2^{I}), 3.923 (dd, H6a^{I}), 4.177 (t, H4^{II}), 4.396 (d, H1^{I}), 4.509 (d, H1^{II}), 8.275 (d, NH), 8.000 (dd, *J* = 2.5, 9.5 Hz, DNP), 9.005 (d, *J* = 2.5 Hz, DNP), 5.840 (m, allyl); ^{13}C NMR ($CDCl_3$) δ = 58.4 (C2^{I}), 67.7 (C6^{I}), 69.0 (C6^{II}), 75.1 (C5^{I}), 75.3 (C5^{II}), 76.5 (C4^{I}), 77.4 (C4^{II}), 81.6 (C3^{I}), 82.6 (C2^{II}), 86.7 (C3^{II}), 100.5 (C1^{I}), 102.7 (C1^{I}), 116.3, 123.6, 149.0 (DNP), 116.8, 134.7 (allyl).

Found: **45a**; C, 68.98; H, 6.18; N, 3.79%. **45b**; C, 69.71; H, 6.17; N, 3.53%. Calcd for $C_{63}H_{63}N_3O_{14}$: C, 69.66; H, 5.85; N, 3.87%.

In the absence of $LiNTf_2$, **45a** (55%) and **45b** (41%) were obtained.

Benzyl *O*-(2,3,6-Tri-*O*-benzyl-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranoside (46). A mixture of **45b** (203.6 mg, 0.19 mmol), $RhCl(Ph_3P)_3$ (17 mg, 0.037 mmol), EtOH (9 ml), PhH (4 ml), and H_2O (1.3 ml) was refluxed overnight. After concentration to dryness, the residue obtained was warmed in Me_2CO (12 ml) containing dil HCl (1 M, 0.40 ml) at 45 °C for 1 h. Evaporation and chromatography with TK system (100 : 1→1 : 1) yielded **46** (173.6 mg, 89%), $[\alpha]_D$ +18 (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.326 (dt, $J_{4,5}$ = 9.5 Hz, $J_{5,6a}$ = $J_{5,6b}$ = 6.0 Hz, H5^{II}), 3.386 (t, $J_{2,3}$ = $J_{3,4}$ = 8.5 Hz, H3^{II}), 3.386 (dd, $J_{1,2}$ = 7.5 Hz, H2^{II}), 3.400 (ddd, $J_{4,5}$ = 8.5 Hz, $J_{5,6a}$ = 4.0 Hz, $J_{5,6b}$ = 2.0 Hz, H5^{I}), 3.515 (t, $J_{2,3}$ = 8.5 Hz, H3^{I}), 3.545 (dd, H4^{II}), 3.707 (dd, $J_{6a,6b}$ = 11.0 Hz, H6b^{I}), 3.779 (br q, $J_{1,2}$ = 8.0 Hz, $J_{2,N}$ = 8.5 Hz, H2^{I}), 3.923 (dd, H6a^{I}), 3.924 (dd, H6a^{II}), 4.158 (d, H4^{I}), 4.383 (d, H1^{I}), 4.499 (d, H1^{II}), 8.315 (d, NH), 8.027 (dd, *J* = 2.5, 8.5 Hz, DNP), 9.025 (d, *J* = 2.5 Hz, DNP), 2.693 (br, OH); ^{13}C NMR ($CDCl_3$) δ = 58.5 (C2^{I}), 67.7 (C6^{I}), 70.7 (C6^{II}), 72.6 (C4^{II}), 73.4 (C5^{II}), 75.0 (C5^{I}), 76.5 (C4^{I}), 81.3 (C3^{I}), 82.1 (C2^{II}), 84.3 (C3^{II}), 100.6 (C1^{I}), 102.7 (C1^{II}), 116.4, 123.7, 149.0 (DNP).

Found: C, 68.06; H, 5.80; N, 3.53%. Calcd for $C_{60}H_{61}N_3O_{14}$: C, 68.75; H, 5.87; N, 4.01%.

Benzyl *O*-(4-*O*-Acetyl-2,3,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranoside (39b). To a solution of **46** (113.3 mg, 0.11 mmol) in CH_2Cl_2 (40 ml) containing pyridine (100 µl, 1.23 mmol), Tf_2O (160 µl, 0.98 mmol) was added under stirring at −25 °C. After being stirred at this temp for 45 min, the mixture was diluted with CH_2Cl_2 (40 ml) and washed with H_2O (40 ml) three times. After the mixture was dried over Na_2SO_4 (15 g) for 30 min, the solution was evaporated to dryness to give a residue (121.5 mg). To this, Bu_4NOAc (170 mg, 0.56 mmol) and DMF (1.0 ml) were added and the resulting mixture was stirred at room temp overnight. After dilution with PhMe (20 ml), the solution was washed with H_2O (10 ml), evaporated and chromatographed with TK system to give **39b** (110.8 mg, 94%), which was identified with the compound described above.

Benzyl *O*-(2,3,6-Tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranoside (47). A mixture of **39b** (120.0 mg, 0.11 mmol), dil NaOMe (0.15%, 22.4 ml), and 1,4-dioxane (2 ml) was kept standing at room temp overnight. Neutralization with AcOH and chromatography with TK system afforded **47** (97.8 mg, 85%), $[\alpha]_D$ +28 (*c* 0.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.381 (dd, $J_{2,3}$ = 9.0 Hz, $J_{3,4}$ = 3.5 Hz, H3^{II}), 3.423 (m, H5^{I}), 3.545 (dd, $J_{1,2}$ = 8.5 Hz, $J_{3,4}$ = 9.0 Hz, H3^{I}), 3.597 (dd, $J_{5,6b}$ = 5.0 Hz, $J_{6a,6b}$ = 11.0 Hz, H6b^{I}), 3.621 (dd, $J_{1,2}$ = 8.0 Hz, H2^{II}), 3.767 (br q, $J_{1,2}$ = 7.5 Hz, $J_{2,NH}$ = 8.5 Hz, H2^{I}), 3.905 (dd, $J_{5,6a}$ = 4.0 Hz, H6a^{I}), 4.015 (br q, H4^{II}), 4.152 (dd, $J_{4,5}$ = 8.5 Hz, H4^{I}), 4.398 (d, H1^{I}), 4.435 (d, H4^{II}), 8.345 (d, NH), 8.015 (dd, *J* = 2.5, 8.5 Hz, DNP), 9.040 (d, *J* = 2.5 Hz, DNP), 2.450 (br, OH); ^{13}C NMR ($CDCl_3$) δ = 58.6 (C2^{I}), 66.4 (C4^{II}), 67.8 (C6^{II}), 68.9 (C6^{I}), 73.2 (C5^{II}), 75.4 (C5^{I}), 76.4 (C4^{I}), 79.3 (C2^{II}), 81.0 (C3^{II}), 81.6 (C3^{I}), 100.6 (C1^{I}), 102.8 (C1^{II}), 116.4, 123.7, 149.0 (DNP).

Found: C, 68.65; H, 5.81; N, 3.86%. Calcd for $C_{60}H_{61}N_3O_{14}$: C, 68.75; H, 5.87; N, 4.01%.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α- and -β-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranoside (49a and 49b). Condensation of **48** (57.2 mg, 0.106 mmol) and **47** (85.2 mg, 0.081 mmol) in the presence of NsCl (45.0 mg, 0.20 mmol), AgOTf (52.2 mg, 0.20 mmol), and Et_3N (28.4 µl, 0.20 mmol) in CH_2Cl_2 (1.0 ml), followed by work-up and chromatography with TK system (100 : 1→1 : 1) afforded **49a** (faster-moving, 65.8 mg, 52%), $[\alpha]_D$ +44 (*c* 0.6, $CHCl_3$); ^{1}H NMR δ = 3.192 (dd, $J_{5,6b}$ = 4.0 Hz, $J_{6,6b}$ = 8.5 Hz, H6b^{III}), 3.320 (dd, $J_{5,6b}$ = 2.0 Hz, $J_{6a,6b}$ = 10.0 Hz, H6b^{II}), 3.430 (dd, $J_{2,3}$ = 9.0 Hz, $J_{3,4}$ = 8.5 Hz, H3^{I}), 3.523 (t, $J_{5,6ba}$ = 8.5 Hz, H6a^{III}), 3.662 (dd, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 10.0 Hz, H2^{II}), 3.721 (br q, $J_{1,2}$ = 8.0 Hz, $J_{2,NH}$ = 9.0 Hz, H2^{I}), 3.841 (dd, $J_{2,3}$ = 10.0 Hz, $J_{3,4}$ = 2.5 Hz, H3^{III}), 4.035 (dd, $J_{1,2}$ = 3.5 Hz, H2^{III}), 4.045 (d, $J_{4,5}$ = 0 Hz, H4^{III}), 4.145 (dd, $J_{4,5}$ = 9.0 Hz, H4^{I}), 4.320 (d, H1^{I}), 4.453 (d, H1^{II}), 5.034 (d, H1^{III}), 8.121 (d, NH), 8.023 (dd, *J* = 2.5, 9.0 Hz, DNP), 9.040 (d, *J* = 2.5 Hz, DNP); ^{13}C NMR ($CDCl_3$) δ = 59.2 (C2^{I}), 68.4 (2C, C6^{I} and C6^{II}), 68.6 (C6^{III}), 70.1 (C5^{III}), 74.1 (C5^{II}), 75.2 (C4^{III}), 75.5 (C2^{III}), 75.9 (C5^{II}), 76.9 (C4^{I}), 74.4 (C4^{II}), 80.0 (C2^{II}), 80.3 (C3^{III}), 81.3 (C3^{II}), 81.9 (C3^{II}), 101.0 (C1^{I}), 101.2 (C1^{III}), 103.1 (C1^{II}), 117.0, 124.3, 149.7 (DNP).

49b (39.4 mg, 31%): Mp 44—47 °C, $[\alpha]_D$ +36 (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.368 (br m, H5^{I}), 3.448 (dd, $J_{2,3}$ = 8.5 Hz, $J_{3,4}$ = 9.0 Hz, H3^{I}), 3.648 (br q, $J_{1,2}$ = 7.5 Hz, $J_{2,NH}$ = 8.5 Hz, H2^{I}), 3.753 (t, $J_{1,2}$ = $J_{2,3}$ = 7.5 Hz, H2^{III}), 3.853 (dd, $J_{5,6a}$ = 4.0 Hz, $J_{6a,6b}$ = 10.5 Hz, H6a^{I}), 3.853 (d, $J_{3,4}$ = 3.0 Hz, $J_{4,5}$ = 0 Hz, H4^{III}), 4.107 (t, $J_{4,5}$ = 9.0 Hz, H4^{III}), 4.249 (d, *J* = 2.5 Hz, $J_{4,5}$ = 0 Hz, H4^{II}), 4.344 (d, H1^{I}), 4.415 (d, $J_{1,2}$ = 7.5 Hz, H1^{II}), 4.865 (d, H1^{III}), 8.380 (d, NH), 7.935 (dd, *J* = 2.5, 9.0 Hz, DNP), 9.050 (d, *J* = 2.5 Hz, DNP); ^{13}C NMR ($CDCl_3$) δ = 58.8 (C2^{I}), 67.6 (C6^{I}), 68.7 (C6^{II}), 69.4 (C6^{III}), 70.5 (C4^{II}), 73.2 (C5^{II}), 74.3 (C5^{III}), 74.4 (C4^{III}), 75.4 (C5^{I}), 76.5 (C4^{I}), 79.5 (C2^{III}), 80.4 (C2^{II}), 81.8 (C3^{II}), 81.9 (C3^{III}), 82.1 (C3^{I}), 100.6 (C1^{I}), 102.8 (C1^{III}), 103.0 (C1^{II}), 116.8, 123.6, 149.2 (DNP).

Found: **49a**; C, 72.03; H, 6.18; N, 2.59%. **49b**; C, 71.77; H, 6.03; N, 2.58%. Calcd for $C_{94}H_{95}N_3O_{19}$: C, 71.88; H, 6.12; N, 2.68%.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (50). A mixture of **49a** (37.5 mg, 0.024 mmol), Dowex 1×2 (HO^- form, 200—400 mesh, 2 ml), Me_2CO (12 ml), and H_2O (4 ml) was stirred under reflux overnight. After removal of the resin by filtration and washing with Me_2CO, the filtrate was evaporated to dryness and again heated with the resin (2 ml) in Me_2CO (12 ml) containing H_2O (4 ml). This operation was repeated two more times. The filtrate was evaporated to dryness and treated with Ac_2O (0.3 ml) in MeOH (3 ml) overnight. Evaporation and chromatography with TK system (100 : 1→1 : 1) afforded unreacted **49a** (30.6 mg, 82%) and

50 (16.1 mg, 18% (96% based on the reacted **49a**)), $[\alpha]_D$ +23 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.188 (dd, $J_{5,6b}$ = 4.5 Hz, $J_{6a,6b}$ = 8.0 Hz, H6b^{III}), 3.315 (dd, $J_{2,3}$ = 10.0 Hz, $J_{3,4}$ = 2.5 Hz, H3^{II}), 3.350 (dd, $J_{4,5}$ = 0 Hz, $J_{5,6a}$ = 5.5 Hz, $J_{5,6b}$ = 7.5 Hz, H5^{II}), 3.505 (dd, $J_{5,6ba}$ = 4.5 Hz, H6a^{III}), 3.540 (br q, $J_{1,2}$ = $J_{2,NH}$ = 8.0 Hz, $J_{2,3}$ = 8.5 Hz, H2^I), 3.634 (ddd, $J_{4,5}$ = 8.5 Hz, $J_{5,6a}$ = 3.0 Hz, $J_{5,6b}$ = 4.0 Hz, H5^I), 3.646 (dd, $J_{1,2}$ = 3.5 Hz, H2^{II}), 3.770 (dd, $J_{6a,6b}$ = 11.0 Hz, H6b^I), 3.845 (dd, H6a^I), 3.915 (dd, $J_{3,4}$ = 8.5 Hz, H4^I), 3.938 (dd, $J_{2,3}$ = 8.5 Hz, $J_{3,4}$ = 2.0 Hz, H3^{III}), 3.980 (t, H3^I), 4.023 (d, H4^{III}), 4.395 (d, H1^{II}), 4.873 (d, H1^I), 5.030 (d, H1^{III}), 5.550 (d, NH), 1.728 (s, Ac); ^{13}C NMR ($CDCl_3$) δ = 54.9 (C2^I), 67.6 (C6^{III}), 67.9 (C6^{II}), 68.7 (C6^I), 69.4 (C5^{III}), 73.3(C5^{II}), 74.6 (C4^{III}), 74.8 (C2^{III}), 75.1 (C5^I), 76.6 (C4^{II}), 76.9 (C4^I), 77.3 (C3^I), 79.3 (C2^{II}), 79.6 (C3^{III}), 81.3 (C3^{II}), 99.2 (C1^I), 100.6 (C1^{III}), 103.1 (C1^{II}), 23.5, 169.9 (Ac).

Found: C, 74.33; H, 6.52; N, 1.01%. Calcd for $C_{90}H_{95}N_3O_{10}$: C, 74.72; H, 6.62; N, 0.97%.

***O*-α-D-Galactopyranosyl-(1→4)-*O*-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranose (37).** Hydrogenation of **50** (28.4 mg, 0.020 mmol) over Pd on C (10%) in AcOH (6 ml) containing H_2O (0.03 ml) at room temp overnight. Chromatography with CM system afforded **37** (7.5 mg, 70%), $[\alpha]_D$ +76 (*c* 0.5, H_2O) (lit,[21] $[\alpha]_D$ +68 (*c* 0.36, MeOH, H_2O (9 : 1))); ^{1}H NMR (D_2O) (67%α) δ = 3.543 (dd, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 10.0 Hz, H2^{II}β), 3.558 (dd, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 10.0 Hz, H2^{II}α), 3.567 (dd, $J_{2,3}$ = 8.0 Hz, $J_{3,4}$ = 4.0 Hz, H3^{I}β), 4.327 (t, $J_{4,5}$ = 0.0 Hz, $J_{5,6}$ = 6.0 Hz, H5^{II}), 4.502 (d, H1^{II}β), 4.506 (d, H1^{II}α), 4.700 (d, $J_{1,2}$ = 8.0 Hz, H1^{I}β), 4.917 (d, $J_{1,2}$ = 4.0 Hz, H1^{III}β), 5.175 (d, $J_{1,2}$ = 2.5 Hz, H1^{I}α), 2.013 (Ac); ^{13}C NMR (D_2O) δ = 57.2 (C2^{I}α), 59.8 (C2^{I}β), 63.3 (C6^{I}α), 63.5 (C6^{I}β), 63.7 (C6^{II}), 63.9 (C6^{III}), 71.9 (C4^{III}), 72.3 (C5^{III}), 72.5 (C2^{III}), 72.7 (C5^{I}α), 73.7 (C3^{I}α), 74.2 (C5^{II}), 74.3 (C2^{II}), 75.6 (C3^{III}), 75.9 (C5^{I}β), 78.3 (C3^{I}β), 78.8 (C3^{II}), 80.7 (C4^{II}), 82.1 (C4^{I}β), 82.5 (C4^{I}α), 93.9 (C1^{I}α), 98.2 (C1^{I}β), 103.7 (C1^{III}), 106.6 (C1^{II}), 25.3, 177.8 (Ac α), 25.6, 178.1 (Ac β).

Found: C, 41.80; H, 6.45; N, 2.72%. Calcd for $C_{20}H_{35}NO_{10}\cdot H_2O$: C, 41.96; H, 6.45; N, 2.45%.

References

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