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Synthesis of a neoglycoprotein containing the Lewis X analogous trisaccharide β-D-Gal*p*NAc-(1→4)[α-L-Fuc*p*-(1→3)]-β-D-Glc*p*NAc

Johannes Bartek, Renate Müller, Paul Kosma*

Institute of Chemistry, University of Agricultural Sciences Vienna, Muthgasse 18, A-1190 Vienna, Austria

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Abstract

The trisaccharide allyl glycoside **36** and related disaccharide part structures have been prepared using the 2-trichloroacetamido-2-deoxy-α-D-galactopyranosyl trichloroacetimidate derivative **9** as glycosyl donor under promotion with TMSOTf or $Sn(OTf)_2$, respectively, to produce the β-(1→4) linkage to suitably protected glucosamine derivatives in fair yields. Fucosylation was effected employing the ethyl 1-thio glycosyl donor **20** in the presence of IDCP. Deprotection of the intermediates afforded the disaccharide allyl glycosides β-D-Gal*p*NAc-(1→4)-β-D-Glc*p*NAc **13**, β-D-Gal*p*NClAc-(1→4)-β-D-Glc*p*NAc **14**, α-L-Fuc*p*-(1→3)-β-D-Glc*p*NAc **24**, α-L-Fuc*p*-(1→4)-β-D-Glc*p*NAc **31** and the branched trisaccharide allyl glycoside β-D-Gal*p*NAc-(1→4)[α-L-Fuc*p*-(1→3)]-β-D-Glc*p*NAc **36**. The trisaccharide which corresponds to a structural motif occurring in N-glycoprotein glycans from human urokinase, human recombinant protein C, phospholipase A_2 as well as O-glycans, was converted into a neoglycoprotein following introduction of a cysteamine-derived spacer group and subsequent activation with thiophosgene.

Keywords: Lewis X; *N*-Acetyl-D-galactosamine; Oligosaccharide synthesis

1. Introduction

The terminal trisaccharide determinant β-D-Gal*p*NAc-(1→4)[α-L-Fuc*p*-(1→3)]-β-D-Glc*p*NAc has been found in N- and O-glycans from various organisms. Thus, it has been isolated from allergenic H-antigens of sea squirt [1] and described as a structural element occurring in phospholipase A_2 and hyaluronidase of the honey bee venom [2,3] and in a serine protease from the snake venom of *Bothrops moojeni* toxins [4]. The presence of this trisaccharide has furthermore been demonstrated for egg jelly coats from *Axolotl maculatum* [5] and N-glycans of *Schistosomas mansoni* [6]. Moreover, it constitutes an important determinant in the N-glycans of bovine pro-opiomelanocortin [7], human urokinase [8] and recombinant human protein C expressed in kidney 293 cells [9]. It has been postulated that the trisaccharide unit effectively inhibits selectin-mediated cell adhesion and thus seems to be a more potent ligand for E-selectin than sialyl Lewis X [10].

* Corresponding author.

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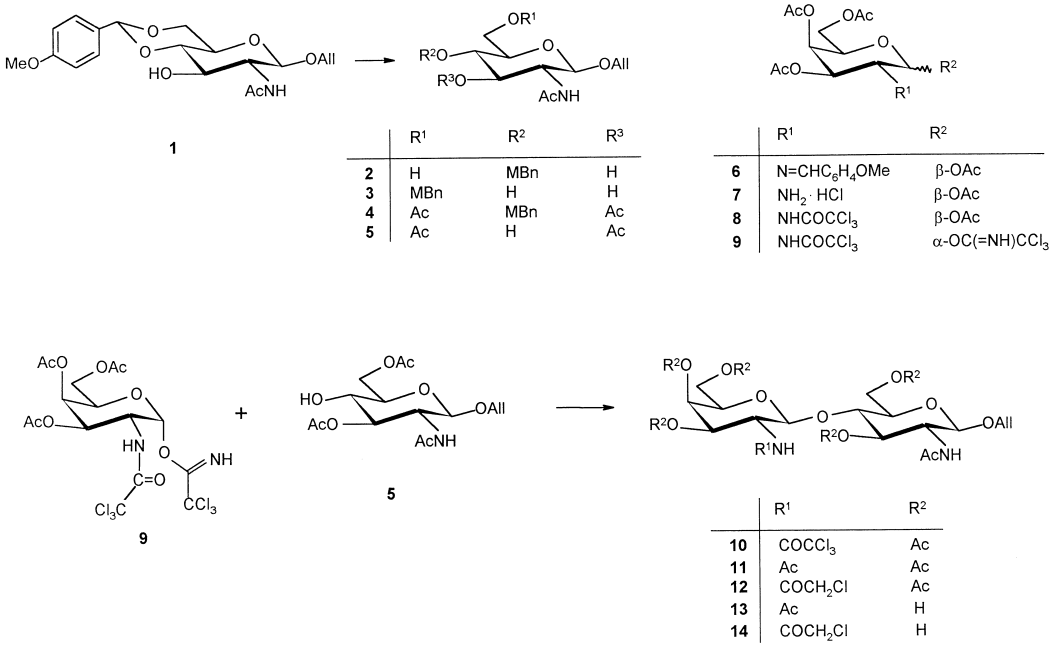
Previously, the trisaccharide has been prepared as the methyl glycoside by a chemo-enzymatic approach employing human milk fucosyltransferase [11]. For further biological studies, we have set out to prepare neoglycoproteins containing this trisaccharide determinant. Here, we report on the synthesis of the corresponding allyl glycoside which may be used for the introduction of a spacer function and the design of glycopolymers. A 2-deoxy-2-trichloro-acetamido-galactopyranosyl donor was elaborated to provide access for additional chemical transformations at the amino group of the terminal galactosamine unit.

2. Results and discussion

For the synthesis of the 2′-amino-2′-deoxy-lactosamine derivatives **13** and **14**, known [12] allyl 2-acetamido-2-deoxy-4,6-*O*-*p*-methoxybenzylidene-β-D-glucopyranoside **1** was subjected to reductive ring-opening [13] in *N,N*-dimethylformamide in the presence of sodium cyanoborohydride–trifluoroacetic acid which proceeded with low selectivity to give the 4-*O*- and 6-*O*-*p*-methoxybenzyl ether derivatives **2** and **3** in a 1:1.1 ratio and 77% yield (Scheme 1). The isomers were separated by chromatography and elaborated into suitable glycosyl acceptors. Thus, compound **2** was converted into the 3,6-di-*O*-acetyl derivative **5** *via* acetylation (→**4**) and subsequent oxidative removal of the 4-*O*-*p*-methoxybenzyl group, which was accomplished in 72% yield by treatment with ceric ammonium nitrate and sonication. As the glycosyl donor for the galactosamine unit, the 2-deoxy-2-trichloroacetamido trichloroacetimidate derivative **9** was elaborated, since related glucosyl donors have been used for efficient synthesis of chitobiosyl units [14]. Starting from previously described [15] *N*-*p*-methoxybenzylidene derivative **6**, amine **7** was obtained by acidic hydrolysis with 1 M HCl in 86% yield, which was then acylated with trichloroacetyl chloride–triethylamine in dichloromethane to give compound **8** in 99% yield. The anomeric acetate was selectively removed with hydrazine acetate [16] and the resulting reducing galactosamine derivative was converted into the α-trichloroacetimidate **9** by reaction with trichloroacetonitrile and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) [17] in dichloromethane in 78% yield. Trimethylsilyl trifluoromethanesulfonate-promoted coupling of the trichloroacetimidate donor **9** with acceptor **5** afforded the β-(1→4)-linked crystalline disaccharide derivative **10** in 37% yield. The structural assignment was evident from the value of the coupling constant $J_{1',2'}$ (8.3 Hz) of the galactosamine unit and the chemical shift of H-4 (δ 3.78) of the glucosamine residue. Promotion of the glycosidation reaction by either stannous trifluoromethanesulfonate or zinc trifluoromethanesulfonate [18] resulted in even



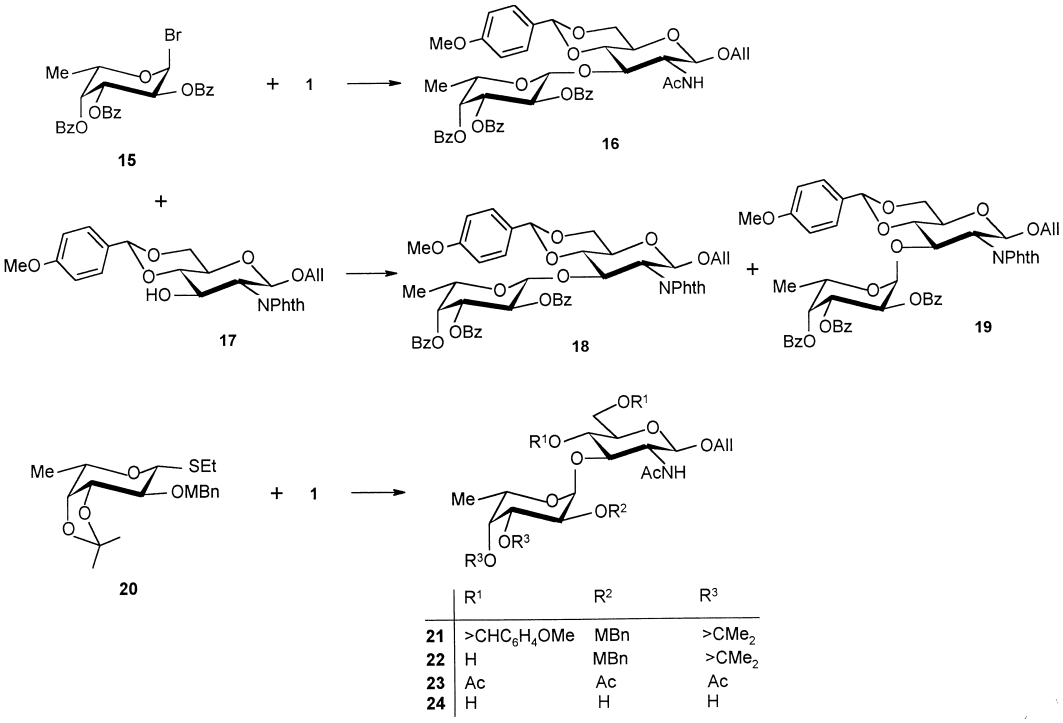
Scheme 1.

lower yields (< 20%) of the disaccharide product. Reduction [19] of the *N*-trichloroacetamido group of **10** could be achieved in the presence of sodium borohydride in ethanol to give after *N*-acetylation the disaccharide derivative **11** in 68% yield. Moreover, partial reduction of the trichloroacetamide was carried out in 78% yield using zinc dust in acetic acid at 110 °C to furnish the *N*-chloroacetamido derivative **12**.

Deprotection of both protected disaccharide derivatives **11** and **12** with sodium methoxide in methanol proceeded in near quantitative yield to give the *N*-acetyl and *N*-chloroacetyl compounds **13** and **14**, respectively. Due to the downfield-shift of the chloromethylene protons, the remaining methyl group of the reducing glucosamine unit and the chloroacetamido group in compound **14** are amenable for selective NOE experiments in conformational studies.

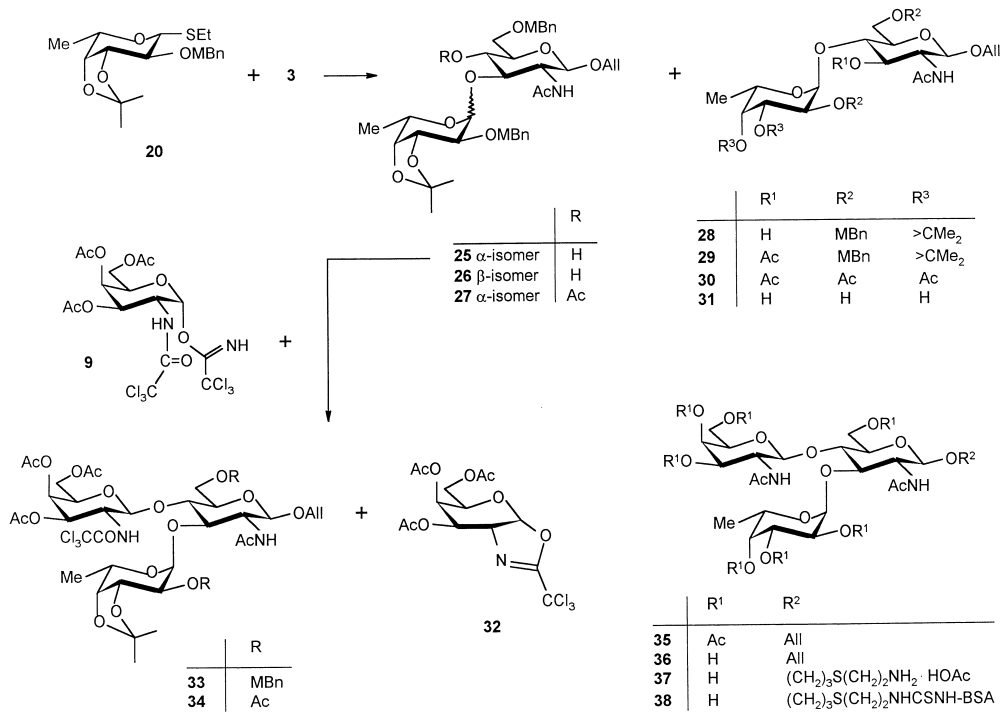
Since the anomeric allyl group was chosen for the introduction of the spacer moiety, the use of benzyl-protected fucopyranosyl donors was not feasible. Instead, the previously described [20] tri-*O*-benzoyl-L-fucopyranosyl bromide **15** was employed (Scheme 2). Glycosylation of either *N*-acetyl or *N*-phthaloyl protected 4,6-*O*-*p*-methoxybenzylidene derivative **1** or **17** [21] was promoted by mercuric cyanide–mercuric bromide to give the β-(1→3)-linked disaccharide **16** in 75% yield and a 1:1 anomeric mixture of the *N*-phthalimido derivatives **18** and **19** in 38% yield, respectively, in accordance with the results of Nifant'ev et al. [20]. By using the ethyl 1-thio glycoside **20** [22] under promotion of iodonium di-*sym*-collidinium perchlorate (IDCP) [23], the α-(1→3)-linked disaccharide derivative **21** was formed with greatly enhanced selectivity (α/β ratio 12:1) and in fair yield (49%). Oxidative removal of the 4,6-*O*-*p*-methoxybenzylidene group with ceric ammonium nitrate furnished the 4,6-diol derivative **22**, whereas treatment of **21** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) lead to simultaneous cleavage of the 2′-*O*-*p*-methoxybenzyl ether and the 3′,4′-*O*-isopropylidene group, respectively, to give, after *O*-acetylation, the acetylated disaccharide derivative **23** in 92% overall yield. Deprotection in the presence of sodium methoxide afforded the disaccharide α-L-Fuc*p*-(1→3)-β-D-Glc*p*NAc allyl glycoside **24**. (Scheme 2).

Since the reductive ring opening of the 4,6-*O*-*p*-methoxybenzylidene group of **21** in the presence of sodium cyanoborohydride–trifluoroacetic acid met with difficulties due to the acid lability of the fucosidic bond, the disaccharide acceptor **25** was prepared *via* regioselective glycosylation of the 3,4-diol compound **3** (Scheme 3). Iodonium



	R1	R2	R3
21	>CHC$_6$H$_4$OMe	MBn	>CMe$_2$
22	H	MBn	>CMe$_2$
23	Ac	Ac	Ac
24	H	H	H

Scheme 2.



Scheme 3.

di-*sym*-collidinium perchlorate-promoted coupling of **3** with 1.1 equivalents of the ethyl 1-thioglycoside donor **20** in 1:5 *N,N*-dimethylformamide–dichloromethane afforded a mixture of three disaccharides which was separated by column chromatography to give 32% of the α-(1→3)-linked disaccharide **25**, a minor portion (4%) of the corresponding β-isomer **26** and the α-(1→4)-linked disaccharide derivative **28** in 11% yield. Whereas the anomeric configurations were deduced from the values of the proton coupling constants $J_{1',2'}$ (3.5 Hz for **25** and **28**, 8.3 Hz for **26**), the attachment site was assigned after subsequent *O*-acetylation to give **27** and **29**, respectively. Upon acetylation, H-4 of compound **27** experienced a downfield shift (to 4.88 ppm), whereas H-3 of **29** was shifted to 5.08 ppm. Compound **28**, corresponding to a synthetic part structure of the Lewis A blood-group antigenic determinant [24] was deprotected *via* hydrolysis of the blocking groups in aqueous 90% trifluoroacetic acid followed by reacetylation to give **30** in 83% yield. Zemplén de-*O*-acetylation of **30** gave the disaccharide α-L-Fuc*p*-(1→4)-β-D-Glc*p*NAc allyl glycoside **31**.

Various attempts to introduce the β-(1→4)-linked galactosamine residues by coupling of the disaccharide acceptor **25** with 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-galactopyranosyl donors (anomeric bromide or trichloroacetimidate) in the presence of silver trifluoromethanesulfonate or borontrifluoride etherate, respectively, under standard and "inverse conditions" [25] did not lead to significant product formation. Employing the *N*-trichloroacetamido donor **9** under promotion of trimethylsilyl trifluoromethanesulfonate, silver trifluoromethanesulfonate, zinc trifluoromethanesulfonate, stannic chloride, or stannous chloride resulted in the formation of by-products or hydrolysis of the protecting groups of the acceptor disaccharide. Finally, stannous trifluoromethanesulfonate-mediated glycosylation [26] under carefully controlled conditions proved to be effective. Thus, using 1.5 equivalents of **9**, 1.3 equivalents of promoter and 1.1 equivalents of *N,N,N′,N′*-tetramethyl urea in dichloromethane–toluene for 1.5 h at room temperature furnished the trichloromethyloxazoline derivative **32** (36%), the β-(1→4)-linked trisaccharide derivative **33** (41%) and unreacted starting material **25** (26%), which were separated by column chromatography. The β-anomeric configuration of **33** was evident from the value $J_{1'',2''}$ (9.0 Hz) indicating a *trans*-diaxial arrangement of the respective protons. Deblocking was achieved by first removing the *p*-methoxybenzyl ether groups of **33** by treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone followed

by *O*-acetylation—to stabilize the fucosidic linkage—which afforded **34** in 96% yield. Hydrolysis of the isopropylidene acetal group was accomplished in the presence of aqueous 90% trifluoroacetic acid at −20 °C, followed by reduction of the trichloroacetamido group with sodium cyanoborohydride at 60 °C. Subsequent *O*-acetylation furnished the per-*O*-acetyl trisaccharide compound **35** in 60% yield (3 steps). Removal of the *O*-acetyl groups by treatment with sodium methoxide afforded the target trisaccharide derivative **36** in near quantitative yield. Due to the branched substitution pattern, the ^{13}C NMR signals of C-4 and C-3 of the glucosamine unit of **36** displayed no significant glycosylation shifts in contrast to the respective signals observed for the disaccharide part structures (Table 1).

Finally, the allyl glycoside was transformed in 96% yield into the 3-(2-aminoethylthio)propyl spacer [27] derivative **37** by radical addition of cysteamine hydrochloride under UV irradiation [28]. The spacer compound **37** was isolated as the acetate, then activated with thiophosgene and coupled to the ε-amino groups of lysine residues of bovine serum albumin (BSA). The ligand/protein ratio of the BSA conjugate **38** based on protein [29] and aminosugar analysis [30] was 6:1 mol/mol.

3. Experimental

General Methods.—Melting points were determined with a Kofler hot stage and are uncorrected. Optical rotations were measured with a Perkin–Elmer 243 B polarimeter; $[\alpha]_D^{20}$ values are given in units of 10^{-1} degcm^2 g^{-1}. ^1H NMR spectra were recorded at 297 K with a Bruker AC 300F instrument operating at 300 MHz for ^1H using $CDCl_3$ as solvent and tetramethylsilane as internal standard, unless stated otherwise. 500 MHz ^1H spectra were recorded on a Bruker AMX instrument. Coupling constants are given in Hz (first order values). ^{13}C NMR spectra were measured at 75.47 MHz and referenced to 1,4-dioxane (δ 67.40). Homo- and heteronuclear 2D NMR spectroscopy was performed with Bruker standard software. TLC was performed on Merck precoated plates (5×10 cm, layer thickness 0.25 mm, Silica Gel $60F_{254}$); spots were detected by spraying with anisaldehyde-H_2SO_4.

Table 1
^{13}C NMR data[a] for disaccharides **13**, **14**, **24**, **31** and trisaccharide **36**

		δ(ppm)				
Residue	Carbon	**13**	**14**	**24**	**31**	**36**
α-L-Fuc*p*	1			100.83	100.44	99.27
	2			68.86	68.88	68.59
	3			70.43	70.22	70.05
	4			72.73	72.71	72.86
	5			67.79	67.82	67.76
	6			16.06	16.02	16.21
β-D-Gal*p*NR	1	102.58	102.01			101.57
	2	53.39	53.98			53.21
	3	71.52	71.26			71.60
	4	68.45	68.51			68.19
	5	76.18	76.22			75.67
	6	61.80	61.82			62.26
β-D-Glc*p*NAc	1	100.82	100.85	100.75	100.78	100.71
	2	55.66	55.74	56.13	56.82	56.39
	3	73.44	73.41	81.31	73.47	75.54
	4	79.77	79.59	69.50	78.25	74.26
	5	75.39	75.38	76.77	76.08	76.31
	6	61.00	61.18	61.67	60.82	60.89
Aglycon	1	71.34	71.34	71.37	71.24	71.40
	2	134.14	134.18	134.23	134.18	134.18
	3	119.04	119.03	119.06	119.00	119.07
NHAc		23.03	23.00	23.07	22.94	23.02
		22.98				23.02
CO		175.63	174.45	175.55	175.20	175.68
		175.45	171.31			175.14
CH_2Cl			43.14			

[a] Spectra (75.47 MHz) were recorded at 297 K and referenced to 1,4-dioxane (δ 67.40).

For column chromatography, silica gel (0.040–0.063 mm) was used. Concentration of solutions was performed at reduced pressure at temperatures <40 °C. Elemental analyses were provided by Dr. J. Theiner, Mikroanalytisches Laboratorium, Institut für Physikalische Chemie, University of Vienna. Electrospray-ionisation mass spectra (ES-MS) were obtained on a Finnigan TSQ7000 instrument in the positive ion mode using 1:1 MeOH–water in 0.1 mM NH_4OAc containing 1% HOAc as the matrix.

*Allyl 2-acetamido-2-deoxy-4-*O*-p-methoxybenzyl-*β-D*-glucopyranoside* (**2**) *and allyl 2-acetamido-2-deoxy-6-*O*-p-methoxybenzyl-*β-D*-glucopyranoside* (**3**).—A suspension of **1** (1.58 g, 4.15 mmol) and 4 Å molecular sieves (0.5 g) in DMF (20 mL) was stirred for 30 min under N_2 at room temperature. $NaCNBH_3$ (5.2 g, 83 mmol) was added followed by dropwise addition of CF_3CO_2H (3.23 mL, 42 mmol) in DMF (5 mL) for 30 min. The suspension was stirred for 24 h, then solid $NaHCO_3$ (8 g) was slowly added. The suspension was diluted with $CHCl_3$ (50 mL), filtered, and the filtrate was washed with ice-cold water. The organic layer was dried (Na_2SO_4), concentrated, and the residue was purified on a column of silica gel (8:1→4:1 EtOAc–MeOH). Pooling of the fractions containing the faster moving component and evaporation afforded **2**. Yield: 568 mg (36%); colourless crystals, mp 227–229 °C (CH_2Cl_2–hexane); $[\alpha]^{20}_D$ −31° (*c* 1.2, MeOH). ^{1}H NMR (CD_3OD): δ 7.30–7.27 (m, 2 H, arom. H), 6.90–6.86 (m, 2 H, arom. H), 5.89 (m, 1 H, CH=), 5.26 (dq, 1 H, $=CH_{2trans}$), 5.13 (dq, 1 H, $=CH_{2cis}$), 4.85 and 4.57 (AB, 2 H, $J_{A,B}$ 10.5 Hz, OCH_2Ar), 4.40 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 4.33 (ddt, 1H, OCH_2), 4.05 (ddt, 1 H, OCH_2), 3.81 (dd, 1 H, $J_{6a,5}$ 2.0, $J_{6a,6b}$ 12.0 Hz, H-6a), 3.78 (s, 3 H, OCH_3), 3.72 (dd, 1 H, $J_{4,3}$ 8.0, $J_{4,5}$ 10.0 Hz, H-4), 3.64 (dd, 1 H, $J_{6b,5}$ 5.0 Hz, H-6b), 3.61 (dd, 1 H, $J_{2,1}$ 8.5, $J_{2,3}$ 10.0 Hz, H-2), 3.38 (dd, 1 H, H-3), 3.26 (ddd, 1 H, H-5), 1.98 (s, 3 H, Ac). Anal. Calcd for $C_{19}H_{27}NO_7$: C, 59.83; H, 7.13; N, 3.67. Found: C, 59.47; H, 7.09; N, 3.60.

Further elution furnished **3** (652 mg, 41%) as colourless crystals, mp 130–132 °C (CH_2Cl_2–hexane); $[\alpha]^{20}_D$ +2° (*c* 1.1, MeOH). ^{1}H NMR (CD_3OD): δ 7.31–7.26 (m, 2 H, arom. H), 6.91–6.86 (m, 2 H, arom. H), 5.89 (m, 1 H, CH=), 5.29 (dq, 1 H, $=CH_{2trans}$), 5.13 (dq, 1 H, $=CH_{2cis}$), 4.52 (s, 2 H, OCH_2Ar), 4.38 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 4.30 (ddt, 1 H, OCH_2), 4.05 (ddt, 1 H, OCH_2), 3.82 (dd, 1 H, $J_{6a,5}$ 2.0, $J_{6a,6b}$ 11.0 Hz, H-6a), 3.78 (s, 3 H, OCH_3), 3.67 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 3.64 (dd, 1 H, $J_{6b,5}$ 5.8 Hz, H-6b), 3.43 (dd, 1 H, $J_{3,4}$ 8.5 Hz, H-3), 3.39 (ddd, 1 H, $J_{5,4}$ 9.5 Hz, H-5), 3.34–3.28 (unresolved signal, 1 H, H-4), 1.96 (s, 3 H, Ac). Anal. Calcd for $C_{19}H_{27}NO_7$: C, 59.83; H, 7.13; N, 3.67. Found: C, 59.85; H, 7.27. N, 3.61.

*Allyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-p-methoxybenzyl-*β-D*-glucopyranoside* (**4**).—A solution of **2** (200 mg, 0.52 mmol) and Ac_2O (0.25 mL, 2.65 mmol) in dry pyridine (5 mL) was stirred for 24 h at room temperature. The reaction was quenched by adding MeOH (2.5 mL) at 0 °C. The solution was coevaporated with toluene (10 mL) and taken to dryness. Crystallization of the residue from EtOAc–hexane gave **4** as colourless crystals (230 mg, 95%), mp 151–153 °C (EtOAc–hexane); $[\alpha]^{20}_D$ −21° (*c* 0.6, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.19–7.14 (m, 2 H, arom. H), 6.89–6.84 (m, 2 H, arom. H), 5.84 (m, 1 H, CH=), 5.55 (d, 1 H, $J_{NH,2}$ 9.5 Hz, NH), 5.25 (dq, 1 H, $=CH_{2trans}$), 5.17 (dq, 1 H, $=CH_{2cis}$), 5.09 (dd, 1 H, $J_{3,2}$ 10.5, $J_{3,4}$ 8.5 Hz, H-3), 4.56 and 4.47 (AB, 2 H, $J_{A,B}$ 10.5 Hz, OCH_2Ar), 4.42 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.35 (dd, 1 H, $J_{6a,5}$ 2.5, $J_{6a,6b}$ 12.0 Hz, H-6a), 4.31 (ddt, 1 H, OCH_2), 4.18 (dd, 1 H, $J_{6b,5}$ 4.5 Hz, H-6b), 4.08 (ddd, 1 H, H-2), 4.03 (ddt, 1 H, OCH_2), 3.80 (s, 3 H, OCH_3), 3.65 (t, 1 H, H-4), 3.53 (ddd, 1 H, $J_{5,4}$ 9.5 Hz, H-5), 2.06, 2.05, 1.95 (3 s, each 3 H, 3 Ac). Anal. Calcd for $C_{23}H_{31}NO_9$: C, 59.35; H, 6.71; N, 3.01. Found: C, 59.39; H, 6.86; N, 3.15.

*Allyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-*β-D*-glucopyranoside* (**5**).—A solution of **4** (300 mg, 0.64 mmol) in 18:1 CH_2Cl_2–H_2O (7 mL) was treated with ceric ammonium nitrate (710 mg, 1.3 mmol) at 4 °C with ultrasonication for 70 min. $NaHCO_3$ was added until the solution had pH 5. The solution was dried (Na_2SO_4) and filtered. Solids were washed thoroughly with EtOAc, the organic phases were combined and concentrated. Purification of the residue on silica gel (5:5:1 CH_2Cl_2–hexane–EtOH) furnished **5** (159 mg, 72%) as colourless crystals, mp 146–148 °C (EtOAc–hexane); $[\alpha]^{20}_D$ −69° (*c* 0.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 5.87 (m, 1 H, CH=), 5.70 (d, 1 H, $J_{NH,2}$ 9.0 Hz, NH), 5.27 (dq, 1 H, $=CH_{2trans}$), 5.19 (dq, 1 H, $=CH_{2cis}$), 5.10 (dd, 1 H, $J_{3,2}$ 10.5, $J_{3,4}$ 8.5 Hz, H-3), 4.57 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 4.51 (dd, 1 H, $J_{6a,5}$ 4.0, $J_{6a,6b}$ 12.0 Hz, H-6a), 4.38 (ddt, 1 H, OCH_2), 4.31 (dd, 1 H, $J_{6b,5}$ 2.5 Hz, H-6b), 4.09 (ddt, 1 H, OCH_2), 3.92 (ddd, 1 H, H-2), 3.62–3.54 (m, 1 H, H-4), 3.52 (ddd, 1 H, $J_{5,4}$ 10.0 Hz, H-5), 3.14 (d, 1 H, $J_{OH,4}$ 5.0 Hz, OH), 2.13, 2.11, and 1.96

(3 s, each 3 H, 3 Ac). Anal. Calcd for $C_{15}H_{23}NO_8$: C, 52.17; H, 6.71; N, 4.06. Found: C, 52.15; H, 6.61; N, 3.98.

1,3,4,6-Tetra-O-*acetyl-2-amino-2-deoxy*-β-D-*galactopyranose hydrochloride* (**7**).—A solution of **6** (3.5 g, 7.5 mmol) in acetone (30 mL) was heated to reflux temperature. After addition of 1 M HCl (11.3 mmol), the solution was cooled to 0 °C. The crystalline mass formed was filtered, washed with acetone, and dried to give **7** (2.9 g, 86%) as colourless needles, mp 210 °C (dec.); $[\alpha]^{20}_D$ +30° (*c* 0.3, H_2O). ^{1}H NMR (D_2O): δ 5.97 (d, 1 H, $J_{1,2}$ 9.0 Hz, H-1), 5.54 (dd, 1 H, $J_{4,3}$ 3.5, $J_{4,5}$ 1.0 Hz, H-4), 5.34 (dd, 1 H, $J_{3,2}$ 11.0 Hz, H-3), 4.42 (t, 1 H, $J_{5,6a} = J_{5,6b} = 5.5$ Hz, H-5), 4.26–4.24 (m, 2 H, H-6a,6b), 3.87 (dd, 1 H, H-2), 2.25, 2.22, 2.11, and 2.09 (4 s, each 3 H, 4 Ac). Anal. Calcd for $C_{14}H_{22}C1NO_9$: C, 43.81; H, 5.77; N, 3.65. Found: C, 43.65; H, 5.51; N, 3.51.

1,3,4,6-Tetra-O-*acetyl-2-deoxy-2-trichloroacetamido*-β-D-*galactopyranose* (**8**).—A suspension of **7** (200 mg, 0.52 mmol) in CH_2Cl_2 (5 mL) was cooled to 0 °C. Et_3N (0.2 mL, 1.5 mmol) and trichloroacetyl chloride (0.09 mL, 0.81 mmol) was added. After 50 min the reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed with satd aq $NaHCO_3$. The organic layer was dried (Na_2SO_4), concentrated, and the residue was purified on a column of silica gel (2:1 toluene–EtOAc) to give **8** (255 mg, 99%) as colourless syrup; $[\alpha]^{20}_D$ +4° (*c* 0.8, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 6.84 (d, 1 H, $J_{NH,2}$ 9.5 Hz, NH), 5.84 (d, 1 H, $J_{1,2}$ 9.0 Hz, H-1), 5.42 (dd, 1 H, $J_{4,3}$ 3.3, $J_{4,5}$ 1.1 Hz, H-4), 5.25 (dd, 1 H, $J_{3,2}$ 11.3 Hz, H-3), 4.45 (ddd, 1 H, H-2), 4.20 (dd, 1 H, $J_{6a,5}$ 6.5, $J_{6a,6b}$ 11.5 Hz, H-6a), 4.14 (dd, 1 H, $J_{6b,5}$ 6.5 Hz, H-6b), 4.07 (dt, 1 H, H-5), 2.20, 2.14, 2.07, and 2.03 (4 s, each 3 H, 4 Ac). Anal. Calcd for $C_{16}H_{20}Cl_3NO_{10}$: C, 39.00; H, 4.11; N, 2.85. Found: C, 39.67; H, 3.95; N, 2.72.

3,4,6-Tri-O-*acetyl-2-deoxy-2-trichloroacetamido*-α-D-*galactopyranosyl trichloroacetimidate* (**9**).—A solution of **8** (1.7 g, 3.45 mmol) in DMF (15 mL) was stirred with hydrazine acetate (479 mg, 5.2 mmol) for 1 h at room temperature. The solution was diluted with CH_2Cl_2 (50 mL), washed with aq $NaHCO_3$, dried (Na_2SO_4), and evaporated to dryness. A solution of the residue in CH_2Cl_2 (25 mL) was stirred with DBU (0.13 mL, 34.5 mmol) and trichloroacetonitrile (3.5 mL, 34.5 mmol) for 75 min. After concentration, the residue was purified on silica gel (2:1 hexane–EtOAc containing 0.1% Et_3N). Yield for **9**: 1.6 g (78%), colourless crystals, mp 91–92 °C (hexane–EtOAc); $[\alpha]^{20}_D$ +81° (*c* 0.7, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 8.83 (s, 1 H, =NH), 6.83 (d, 1 H, $J_{NH,2}$ 9.0 Hz, NH), 6.52 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.54 (dd, 1 H, $J_{4,3}$ 3.0, $J_{4,5}$ 1.0 Hz, H-4), 5.42 (dd, 1 H, $J_{3,2}$ 11.0 Hz, H-3), 4.72 (ddd, 1 H, H-2), 4.41 (dt, 1 H, $J_{5,6a} = J_{5,6b} = 6.5$ Hz, H-5), 4.20 (dd, 1 H, $J_{6a,6b}$ 11.5 Hz, H-6a), 4.09 (dd, 1 H, H-6b), 2.22, 2.05, and 2.03 (3 s, each 3 H, 3 Ac). Anal. Calcd for $C_{16}H_{18}Cl_6N_2O_9$: C, 32.30; H, 3.05; N, 4.70. Found: C, 32.60; H, 3.06; N, 4.47.

Allyl (3,4,6-tri-O-*acetyl-2-deoxy-2-trichloroacetamido*-β-D-*galactopyranosyl)-(1→4)-2-acetamido-3,6-di*-O-*acetyl-2-deoxy*-β-D-*glucopyranoside* (**10**).—A solution of TMSOTf (0.311 mmol) in toluene (1 mL) was added at 0 °C to a solution of **5** (72 mg, 0.208 mmol) and **9** (185 mg, 0.311 mmol) in dry CH_2Cl_2 (5 mL) under N_2. The solution was stirred for 30 min at 0 °C, then diluted with CH_2Cl_2 (50 mL) and washed with satd aq $NaHCO_3$. The organic layer was dried (Na_2SO_4), concentrated, and the residue was applied on silica gel. Elution with EtOAc gave **10** (60 mg, 37%) as the major reaction product and **32** (not isolated) as side-product. Colourless crystals, mp 211–213 °C (hexane–EtOAc); $[\alpha]^{20}_D$ −38° (*c* 0.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.20 (d, 1 H, $J_{NH',2'}$ 9.5 Hz, NH′), 5.85 (m, 1 H, CH=), 5.72 (d, 1 H, $J_{NH,2}$ 9.5 Hz, NH), 5.37 (dd, 1 H, $J_{4',3'}$ 3.4, $J_{4',5'}$ 0.9 Hz, H-4′), 5.26 (dq, 1 H, $=CH_{2trans}$), 5.22 (dq, 1 H, $=CH_{2cis}$), 5.20 (dd, 1 H, $J_{3',2'}$ 11.3 Hz, H-3′), 5.12 (dd, 1 H, $J_{3,2}$ 9.5, $J_{3,4}$ 8.0 Hz, H-3), 4.64 (d, 1 H, $J_{1',2'}$ 8.3 Hz, H-1′), 4.51 (d, 1 H, $J_{1,2}$ 7.4 Hz, H-1), 4.45 (dd, 1 H, $J_{6a,5}$ 4.7, $J_{6a,6b}$ 12.1 Hz, H-6a), 4.35–4.28 (m, 2 H, H-6b, OCH_2), 4.18–4.00 (m, 5 H, H-2,2′,6a′,6b′, and OCH_2), 3.91 (dt, 1 H, $J_{5',6a'} = J_{5',6b'} = 6.6$ Hz, H-5′), 3.78 (t, 1 H, $J_{4,5}$ 8.0 Hz, H-4), 3.67–3.61 (m, 1 H, H-5), 2.17, 2.13, 2.08, 2.07, 1.99, and 1.987 (6 s, each 3 H, 6 Ac). Anal. Calcd for $C_{29}H_{39}Cl_3N_2O_{16}$: C, 44.77; H, 5.05; N, 3.60. Found: C, 45.17; H, 4.92; N, 3.33.

Allyl (2-acetamido-3,4,6-tri-O-*acetyl-2-deoxy*-β-D-*galactopyranosyl)-(1→4)-2-acetamido-3,6-di*-O-*acetyl-2-deoxy*-β-D-*glucopyranoside* (**11**).—A solution of **10** (38 mg, 0.05 mmol) and $NaBH_4$ (67 mg, 1.77 mmol) in EtOH (8 mL) was stirred for 48 h at 60 °C. The solution was diluted with EtOH (5 mL), cooled to 0 °C and neutralized with HOAc (0.1 mL). The solution was coevaporated five times with MeOH (10 mL portions) and taken to dryness. The residue was dissolved in pyridine (8 mL) and stirred with Ac_2O (0.2 mL) for 60 h.

The solution was concentrated and the residue was purified on silica gel (10:1 EtOAc–MeOH). The crude product obtained (28 mg) was further subjected to LC on silica gel (10 μm, 10:1 EtOAc–MeOH) which gave **11** as colourless crystals. Yield: 22.5 mg (68%), mp 223–225 °C (EtOAc); $[\alpha]^{20}_{D}$ −23° (*c* 0.5, MeOH). ^{1}H NMR ($CDCl_3$): δ 5.86 (m, 1 H, CH=), 5.78 (d, 1 H, $J_{NH',2'}$ 8.8 Hz, NH′), 5.77 (d, 1 H, $J_{NH,2}$ 9.8 Hz, NH), 5.32 (dd, 1 H, $J_{4',3'}$ 3.5, $J_{4',5'}$ < 1.0 Hz, H-4′), 5.26 (dq, 1 H, $=CH_{2trans}$), 5.18 (dq, 1 H, $=CH_{2cis}$), 5.15 (dd, 1 H, $J_{3',2'}$ 11.5 Hz, H-3′), 5.12 (t, 1 H, $J_{3,4}=J_{3,2}=8.5$ Hz, H-3), 4.60 (d, 1 H, $J_{1',2'}$ 8.3 Hz, H-1′), 4.51 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1), 4.41 (dd, 1 H, $J_{6a,5}$ 3.0, $J_{6a,6b}$ 12.0 Hz, H-6a), 4.35–4.28 (m, 1 H, OCH_2), 4.31 (dd, 1 H, $J_{6b,5}$ 5.0 Hz, H-6b), 4.14–3.94 (m, 4 H, H-2,2′,6b′, and OCH_2), 4.09 (dd, 1 H, $J_{6a',5'}$ 6.5, $J_{6a',6b'}$ 11.0 Hz, H-6a′), 3.87 (td, 1 H, $J_{5',6b'}$ 6.5 Hz, H-5′), 3.76 (t, 1 H, $J_{4,5}$ 8.5 Hz, H-4), 3.69–3.64 (m, 1 H, H-5), 2.14, 2.13, 2.08, 2.05, 1.99, 1.96, and 1.958 (7 s, each 3 H, 7 Ac). Anal. Calcd for $C_{29}H_{42}N_2O_{16}$: C, 51.62; H, 6.27; N, 4.15. Found: C, 51.51; H, 5.96; N, 4.00.

*Allyl (3,4,6-tri-*O*-acetyl-2-chloroacetamido-2-deoxy-*β*-*D*-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-acetyl-2-deoxy-*β*-*D*-glucopyranoside* (**12**).—A solution of **10** (7 mg, 9 μmol) in HOAc (2 mL) was treated with zinc-dust (35 mg, 0.535 mmol) for 4 h at 110 °C. The solution was diluted with CH_2Cl_2 (50 mL), filtered, and the filtrate was concentrated. Purification of the residue on silica gel (EtOAc) gave **12** as an amorphous solid. Yield: 5 mg (78%). $[\alpha]^{20}_{D}$ −23° (*c* 0.4, MeOH). ^{1}H NMR ($CDCl_3$): δ 6.70 (d, 1 H, $J_{NH',2'}$ 8.5 Hz, NH′), 5.86 (m, 1 H, CH=), 5.72 (d, 1 H, $J_{NH,2}$ 9.0 Hz, NH), 5.35 (dd, 1 H, $J_{4',3'}$ 3.5, $J_{4',5'}$ 1.0 Hz, H-4′), 5.28 (dd, 1 H, $J_{3',2'}$ 11.5 Hz, H-3′), 5.26 (dq, 1 H, $=CH_{2trans}$), 5.19 (dq, 1 H, $=CH_{2cis}$), 5.12 (dd, 1 H, $J_{3,4}$ 8.0, $J_{3,2}$ 9.5 Hz, H-3), 4.75 (d, 1 H, $J_{1',2'}$ 7.2 Hz, H-1′), 4.51 (d, 1 H, $J_{1,2}$ 7.2 Hz, H-1), 4.42 (dd, 1 H, $J_{6a,5}$ 3.0, $J_{6a,6b}$ 12.0 Hz, H-6a), 4.31 (ddt, 1 H, OCH_2), 4.18 (dd, 1 H, $J_{6b,5}$ 5.6 Hz, H-6b), 4.14–4.00 (m, 4 H, H-2,6a′,6b′, and OCH_2), 4.03 (s, 2 H, $ClCH_2$), 3.96 (dd, 1 H, H-2′), 3.90 (dt, 1 H, $J_{5',6a'}=J_{5',6b'}=7.0$ Hz, H-5′), 3.78 (t, 1 H, $J_{4,5}$ 8.0 Hz, H-4), 3.63 (m, 1 H, H-5), 2.14, 2.12, 2.08, 2.06, 1.99, and 1.98 (6 s, each 3 H, 6 Ac). Anal. Calcd for $C_{29}H_{41}ClN_2O_{16}$: C, 49.12; H, 5.83; N, 3.95. Found: C, 48.84; H, 5.77; N, 3.89.

*Allyl (2-acetamido-2-deoxy-*β*-*D*-galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-*β*-*D*-glucopyranoside* (**13**).—A solution of **11** (16 mg, 0.024 mmol) in MeOH (4 mL) was stirred with 0.1 M methanolic NaOMe (1 mL) for 24 h at room temperature. The solution was made neutral by addition of Dowex 50 (H^+) resin and filtered. The filtrate was evaporated and the residue was dissolved in water (2 mL) and lyophilized giving **13** as an amorphous solid. Yield: 11 mg (quant.); $[\alpha]^{20}_{D}$ −3° (*c* 0.6, H_2O). ^{1}H NMR (500 MHz, D_2O): δ 5.84 (m, 1 H, CH=), 5.24 (dq, 1 H, $=CH_{2trans}$), 5.20 (dq, 1 H, $=CH_{2cis}$), 4.50 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1), 4.46 (d, 1 H, $J_{1',2'}$ 8.4 Hz, H-1′), 4.27 (ddt, 1 H, OCH_2), 4.09 (ddt, 1 H, OCH_2), 3.88 (dd, 1 H, $J_{4',3'}$ 3.3, $J_{4',5'}$ < 1.0 Hz, H-4′), 3.87 (dd, 1 H, $J_{2',3'}$ 10.9 Hz, H-2′), 3.79 (dd, 1 H, $J_{6a,5}$ 2.1, $J_{6a,6b}$ 12.1 Hz, H-6a), 3.74 (dd, 1 H, $J_{2,3}$ 11.8 Hz, H-2), 3.72–3.65 (m, 3 H, H-5′,6a′,6b′), 3.70 (dd, 1 H, H-3′), 3.64 (dd, 1 H, $J_{3,4}$ 8.2 Hz, H-3), 3.60 (dd, 1 H, $J_{6b,5}$ 5.6 Hz, H-6b), 3.56 (dd, 1 H, $J_{4,5}$ 9.6 Hz, H-4), 3.45 (ddd, 1 H, H-5), 2.01 and 1.97 (2 s, each 3 H, 2 Ac). ES-MS ($C_{19}H_{32}N_2O_{11}$): *m*/*z* 465.1 $(M+H)^+$.

*Allyl (2-chloroacetamido-2-deoxy-*β*-*D*-galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-*β*-*D*-glucopyranoside* (**14**).—A solution of **12** (3.5 mg, 4.9 μmol) in MeOH (2 mL) was stirred with 0.1 M methanolic NaOMe (0.3 mL) for 24 h at room temperature. Work-up as described for **13** gave **14** as amorphous powder. Yield 2.5 mg (∼ quant.); $[\alpha]^{20}_{D}$ −4° (*c* 0.2, H_2O). ^{1}H NMR (D_2O): δ 5.90 (m, 1 H, CH=), 5.33–5.22 (m, 2 H, $=CH_2$), 4.59 (d, 1 H, $J_{1',2'}$ 8.3 Hz, H-1′), 4.55 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 4.32 (ddt, 1 H, OCH_2), 4.21 and 4.18 (AB, 2 H, J_{AB} 14.3 Hz, $ClCH_2$), 4.14 (ddt, 1 H, OCH_2), 3.98 (dd, 1 H, $J_{2',3'}$ 10.9 Hz, H-2′), 3.95 (dd, 1 H, $J_{4',3'}$ 2.8, $J_{4',5'}$ < 1.0 Hz, H-4′), 3.86 (dd, 1 H, $J_{6a,5}$ 2.6, $J_{6a,6b}$ 11.9 Hz, H-6a), 3.82 (dd, 1 H, H-3′), 3.79 (dd, 1 H, $J_{6a',5'}$ 3.3, $J_{6a',6b'}$ 10.9 Hz, H-6a′), 3.77-3.61 (m, 6 H, H-2,3,4,6b,5′,6b′), 3.50 (ddd, 1 H, H-5), 2.02 (s, 3 H, Ac). ES-MS ($C_{19}H_{31}ClN_2O_{11}$): *m*/*z* 499.1 $(M+H)^+$.

*Allyl (2,3,4-tri-*O*-benzoyl-*β*-*L*-fucopyranosyl)-(1→3)-2-acetamido-2-deoxy-4,6-*O*-p-methoxybenzylidene-*β*-*D*-glucopyranoside* (**16**).—Compound **15** (170 mg, 0.317 mmol) and **1** (105 mg, 0.264 mmol) were dissolved in dry nitromethane (10 mL) under N_2. After addition of 4 Å molecular sieves and stirring for 0.5 h, $Hg(CN)_2$ (72 mg, 0.285 mmol) and $HgBr_2$ (34 mg, 0.095 mmol) were added, and stirring was continued for 14 h at ambient temperature. The mixture was diluted with CH_2Cl_2 (50 mL) and filtered through Celite®. The filtrate was washed with aq 10% KI and satd aq $NaHCO_3$ (2×), dried over $MgSO_4$, and concentrated. Purification of the residue by column

chromatography (2:1 toluene–EtOAc) yielded **16** (175 mg, 75%) as crystals, mp 228–234 °C (EtOAc–MeOH); $[\alpha]^{20}_D$ −110° (*c* 0.8, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.09–6.96 (m, 19 H, arom. H), 5.92 (d, 1 H, $J_{NH,2}$ 7.0 Hz, NH), 5.88 (m, 1 H, CH=), 5.70 (dd, 1 H, $J_{3',4'}$ 3.5, $J_{4',5'}$ 1.0 Hz, H-4′), 5.67 (dd, 1 H, $J_{2',3'}$ 10.5, $J_{2',1'}$ 8.0 Hz, H-2′), 5.47 (dd, 1 H, H-3′), 5.28 (dq, 1 H, $=CH_{2trans}$), 5.21 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 5.19 (dq, 1 H, $=CH_{2cis}$), 5.07 (s, 1 H, OCHO), 5.01 (d, 1 H, H-1′), 4.64 (dd, 1 H, $J_{3,2}$ 10.0, $J_{3,4}$ 9.0 Hz, H-3), 4.32 (ddt, 1 H, OCH_2), 4.24 (dd, 1 H, $J_{6a,6b}$ 10.0, $J_{6b,5}$ 4.5 Hz, H-6b), 4.10 (ddt, 1 H, OCH_2), 4.07 (dq, 1 H, $J_{5',6'}$ 6.5 Hz, H-5′), 3.87 (s, 3 H, OMe), 3.60 (t, 1 H, $J_{6a,5}$ 10.0 Hz, H-6a), 3.49 (ddd, 1 H, $J_{5,4}$ 9.0 Hz, H-5), 3.37 (t, 1 H, H-4), 3.15 (ddd, 1 H, H-2), 1.99 (s, 3 H, Ac), 1.32 (d, 3 H, H-6′). Anal. Calcd for $C_{46}H_{47}NO_{14}$: C, 65.94; H, 5.65; N, 1.67. Found: C, 65.61; H, 5.72; N, 1.67.

Allyl (2,3,4-tri-O-*benzoyl*-β-L-*fucopyranosyl)-(1→3)-2-deoxy-4,6*-O-p-*methoxybenzylidene-2-phthalimido*-β-D-*glucopyranoside* (**18**) and *allyl(2,3,4-tri*-O-*benzoyl*-α-L-*fucopyranosyl)-(1→3)-2-deoxy-4,6*-O-p-*methoxybenzylidene-2-phthalimido*-β-D-*glucopyranoside* (**19**).—Donor **15** (5.06 g, 9.38 mmol) and compound **17** (3.95 g, 8.44 mmol) were dissolved in dry nitromethane (60 mL) under N_2. After addition of 4 Å molecular sieves and stirring for 0.5 h, $Hg(CN)_2$ (2.13 g, 8.44 mmol) and $HgBr_2$ (1.01 g, 2.81 mmol) were added, and stirring at ambient temperature was continued for 24 h. The mixture was diluted with CH_2Cl_2 and filtered through Celite®. The filtrate was washed with aq 10% KI and satd aq $NaHCO_3$ (2×), dried over $MgSO_4$, and concentrated. Purification of the residue by column chromatography (12:1 toluene–EtOAc) yielded **18** (1.46 g, 19%) as crystals, mp 131–135 °C (CH_2Cl_2–MeOH); $[\alpha]^{20}_D$ −38° (*c* 0.57, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.82–6.93 (m, 23 H, arom. H), 5.72 (m, 1 H, CH=), 5.49 (dd, 1 H, $J_{2',3'}$ 10.3, $J_{2',1'}$ 7.8 Hz, H-2′), 5.42 (dd, 1 H, $J_{4',3'}$ 3.5, $J_{4',5'}$ < 1.0 Hz, H-4′), 5.42 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 5.32 (dd, 1 H, H-3′), 5.20 (s, 1 H, OCHO), 5.15 (dq, 1 H, $=CH_{2trans}$), 5.05 (dq, 1 H, $=CH_{2cis}$), 4.89 (d, 1 H, H-1′), 4.71 (dd, 1 H, $J_{3,2}$ 10.0, $J_{3,4}$ 9.0 Hz, H-3), 4.33 (dd, 1 H, H-2), 4.31 (dd, 1 H, $J_{6a,6b}$ 10.0, $J_{6b,5}$ 4.5 Hz, H-6b), 4.28 (ddt, 1 H, OCH_2), 4.04 (ddt, 1 H, OCH_2), 3.88 (s, 3 H, OMe), 3.82 (dq, 1 H, $J_{5',6'}$ 6.5 Hz, H-5′), 3.72 (t, 1 H, $J_{6a,5}$ ~10 Hz, H-6a), 3.65–3.55 (m, 2 H, H-4,5), 0.55 (d, 3 H, H-6′). Anal. Calcd for $C_{52}H_{47}NO_{15}$: C, 67.45; H, 5.12; N, 1.51. Found: C, 67.03; H, 5.28; N, 1.48.

Further elution gave **19** (1.49 g, 19%) as crystals, mp 111–115 °C (CH_2Cl_2–MeOH); $[\alpha]^{20}_D$ −158° (*c* 0.75, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.89–6.88 (m, 23 H, arom. H), 5.85 (dd, 1 H, $J_{3',2'}$ 11.0, $J_{3',4'}$ 3.3 Hz, H-3′), 5.58 (s, 1 H, OCHO), 5.53 (m, 1 H, CH=), 5.49 (dd, 1 H, $J_{4',5'}$ 1.0 Hz, H-4′), 5.38 (dd, 1 H, $J_{2',1'}$ 3.8 Hz, H-2′), 5.16 (d, 1 H, H-1′), 5.09 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 5.01 (dq, 1 H, $=CH_{2trans}$), 4.96 (dd, 1 H, $J_{3,2}$ 10.5, $J_{3,4}$ 9.0 Hz, H-3), 4.92 (dq, 1 H, $=CH_{2cis}$), 4.56 (dq, 1 H, $J_{5',6'}$ 6.5 Hz, H-5′), 4.40 (dd, 1 H, $J_{6a,6b}$ 10.0, $J_{6b,5}$ 4.5 Hz, H-6b), 4.33 (dd, 1 H, H-2), 4.20 (ddt, 1 H, OCH_2), 3.91 (ddt, 1 H, OCH_2), 3.87 (t, 1 H, $J_{6a,5}$ ~10 Hz, H-6a), 3.82 (m, 1 H, H-4), 3.78 (s, 3 H, OMe), 3.71 (dt, 1 H, $J_{5,4}$ ~9.5 Hz, H-5), 0.55 (d, 3 H, H-6′). Anal. Calcd for $C_{52}H_{47}NO_{15}$: C, 67.45; H, 5.12; N, 1.51. Found: C, 67.44; H, 5.33; N, 1.52.

Allyl (3,4-O-*isopropylidene-2*-O-p-*methoxybenzyl*-α-L-*fucopyranosyl)-(1→3)-2-acetamido-2-deoxy-4,6*-O-p-*methoxybenzylidene*-β-D-*glucopyranoside* (**21**).—Compound **1** (1.423 g, 3.75 mmol) and **20** (1.656 g, 4.5 mmol) were dissolved in 5:1 CH_2Cl_2–DMF (96 mL) under N_2. After addition of 4 Å molecular sieves, and stirring for 0.5 h, IDCP (1.757 g) was added in 5 portions over 15 h, and stirring at room temperature was continued for further 25 h. Then the mixture was diluted with CH_2Cl_2, and filtered through Celite®. The filtrate was washed with aq 5% $Na_2S_2O_3$, dried over $MgSO_4$, and concentrated. Purification of the residue by column chromatography (1:1 toluene–EtOAc) and crystallization from EtOAc–hexane yielded **21** (1.262 g, 49%), mp 184–186 °C; $[\alpha]^{20}_D$ −78° (*c* 1.1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.43–7.38 (m, 2 H, arom. H), 7.30–7.25 (m, 2 H, arom. H), 6.91–6.85 (m, 4 H, arom. H), 5.84 (m, 1 H, CH=), 5.75 (d, 1 H, $J_{NH,2}$ 7.0 Hz, NH), 5.46 (s, 1 H, OCHO), 5.25 (dq, 1 H, $=CH_{2trans}$), 5.17 (dq, 1 H, $=CH_{2cis}$), 5.07 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 4.90 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1′), 4.84 (d, 1 H, J_{gem} 11.5 Hz, OCH_2Ar), 4.35 (dq, 1 H, $J_{5',6'}$ 6.5, $J_{5',4'}$ 2.5 Hz, H-5′), 4.35 (d, 1 H, OCH_2Ar), 4.23 (dd, 1 H, $J_{3',2'}$ 8.0, $J_{3',4'}$ 5.5 Hz, H-3′), 4.40–4.22 (m, 3 H, H-3,6a, OCH_2), 4.06 (ddt, 1 H, OCH_2), 3.93 (dd, 1 H, H-4′), 3.80 (2 s, each 3 H, 2 OMe), 3.74 (br t, 1 H, $J_{6a,6b}=J_{6b,5}$ ~10 Hz, H-6b), 3.53 (dd, 1 H, H-2′), 3.45–3.56 (m, 2 H, H-4, 5), 3.23 (ddd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 1.73 (s, 3 H, Ac), 1.43, and 1.31 (2 s, each 3 H, Me_2C), 0.69 (d, 3 H, H-6′). Anal. Calcd for $C_{36}H_{47}NO_{12}$: C, 63.05; H, 6.91; N, 2.04. Found: C, 63.07; H, 6.92; N, 2.02.

*Allyl (3,4-*O*-isopropylidene-2-*O*-*p*-methoxybenzyl-α-*L*-fucopyranosyl)-(1→3)-2-acetamido-2-deoxy-β-*D*-glucopyranoside* (**22**).—To a solution of **21** (590 mg, 0.86 mmol) in 9:1 CH_3CN–water (150 mL) was added ceric ammonium nitrate (456 mg, 0.833 mmol), and the mixture was stirred for 1 h at room temperature. Then, $NaHCO_3$ (0.5 g) was added, and the mixture was concentrated to dryness. The residue was purified by column chromatography (9:1 EtOAc–MeOH) to give **22** (267 mg, 55%), which crystallized from Et_2O–CH_2Cl_2, mp 175–177 °C; $[\alpha]_D^{20}$ −45° (*c* 0.6, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.31–7.25 (m, 2 H, arom. H), 6.92–6.86 (m, 2 H, arom. H), 5.87 (m, 1 H, CH=), 5.56 (d, 1 H, $J_{NH,2}$ 7.5 Hz, NH), 5.27 (dq, 1 H, $=CH_{2trans}$), 5.19 (dq, 1 H, $=CH_{2cis}$), 4.94 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 4.85 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1′), 4.72 (d, 1 H, *J* 11.7 Hz, OCH_2Ar), 4.60 (d, 1 H, OCH_2Ar), 4.35 (dq, 1 H, $J_{5',6'}$ 6.5, $J_{5',4'}$ 2.0 Hz, H-5′), 4.32 (m, 1 H, H-3′), 4.31 (ddt, 1 H, OCH_2), 4.10 (ddt, 1 H, OCH_2), 4.06 (dd, 1 H, $J_{4',3'}$ 6.5 Hz, H-4′), 3.96 (dd, 1 H, $J_{3,2}$ 10.5, $J_{3,4}$ 8.0 Hz, H-3), 3.90 (dd, 1 H, $J_{6a,6b}$ ∼ 12.0 Hz, H-6b), 3.81 (s, 3 H, OMe), 3.80 (dd, 1 H, H-6a), 3.58 (dd, 1 H, $J_{2',3'}$ 3.5 Hz, H-2′), 3.48 (m, 1 H, $J_{4,5}$ 9.0 Hz, H-4), 3.40 (ddd, 1 H, $J_{5,6a}$ 5.0, $J_{5,6b}$ 3.0 Hz, H-5), 3.26 (ddd, 1 H, H-2), 2.20 (br m, 2 H, OH), 1.77 (s, 3 H, Ac), 1.43 and 1.34 (2 s, each 3 H, Me_2C), 1.31 (d, 3 H, H-6′). Anal. Calcd for $C_{28}H_{41}NO_{11}$: C, 59.25; H, 7.28; N, 2.47. Found: C, 59.26; H, 7.12; N, 2.40.

*Allyl (2,3,4-tri-*O*-acetyl-α-*L*-fucopyranosyl)-(1→3)-2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-*D*-glucopyranoside* (**23**).—A solution of **21** (15 mg, 0.021 mmol) in 18:1 CH_2Cl_2–water (9 mL) was vigorously stirred with DDQ (21 mg, 0.093 mmol) at room temperature for 24 h. The solution was taken to dryness, the residue was dissolved in pyridine (6 mL) and stirred with Ac_2O (1.8 mL) for 20 h at room temperature. MeOH (1 mL) was added and the solution was concentrated. Purification of the residue on silica gel (EtOAc) gave **23** as colourless syrup. Yield: 12 mg (92%); $[\alpha]_D^{20}$ −57° (*c* 0.7, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 5.87 (m, 1 H, CH=), 5.70 (d, 1 H, $J_{NH,2}$ 7.1 Hz, NH), 5.31 (dd, 1 H, $J_{3',4'}$ 3.2, $J_{3',2'}$ 11.0 Hz, H-3′), 5.27 (dq, 1 H, $=CH_{2trans}$), 5.26 (d, 1 H, H-1′), 5.24 (dd, 1 H, $J_{5',4'}$ 1.5 Hz, H-4′), 5.21 (dq, 1 H, $=CH_{2cis}$), 5.09 (dd, 1 H, $J_{1',2'}$ 3.4 Hz, H-2′), 5.03 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.96 (t, 1 H, $J_{3,4} \sim J_{4,5}$ = 9.3 Hz, H-4), 4.45 (t, 1 H, $J_{3,2}$ 9.3 Hz, H-3), 4.32 (m, 1 H, OCH_2), 4.19 (dd, 1 H, $J_{6a,6b}$ 12.5, $J_{6a,5}$ 5.5 Hz, H-6a), 4.16 (m, 1 H, H-5′), 4.08 (dd, 1 H, $J_{6b,5}$ 2.9 Hz, H-6b), 4.08 (m, 1 H, OCH_2), 3.61 (ddd, 1 H, H-5), 3.25 (m, 1 H, H-2), 2.15, 2.11, 2.09, 2.00, 1.99, and 1.98 (6 s, each 3 H, 6 Ac), 1.07 (d, 3 H, H-6′). Anal. Calcd for $C_{27}H_{39}NO_{15}$: C, 52.51; H, 6.36; N, 2.27. Found: C, 52.44; H, 6.38; N, 2.10.

*Allyl (α-*L*-fucopyranosyl)-(1→3)-2-acetamido-2-deoxy-β-*D*-glucopyranoside* (**24**).—A solution of **23** (7.2 mg) in dry MeOH (5 mL) was stirred with 0.1 M methanolic NaOMe (0.5 mL) for 2 h at room temperature. The pH of the solution was adjusted to 7.0 by addition of Dowex 50 (H^+) resin, the resin was filtered off and the filtrate was taken to dryness. Purification of the residue on a Bio-Gel P-2 column (1.6×80 cm, aq 5% EtOH) gave **24** as amorphous solid. Yield: 4.1 mg (87%); $[\alpha]^{20}{}_D$ −105° (*c* 0.4, H_2O). ^{1}H NMR (D_2O): δ 5.92 (m, 1 H, CH=), 5.32 (dq, 1 H, $=CH_{2trans}$), 5.28 (dq, 1 H, $=CH_{2cis}$), 5.00 (d, 1 H, $J_{1',2'}$ 4.1 Hz, H-1′), 4.59 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1), 4.37 (m, 1 H, OCH_2), 4.35 (m, 1 H, H-5′), 4.18 (m, 1 H, OCH_2), 3.96 (dd, 1 H, $J_{6a,5}$ 2.2, $J_{6a,6b}$ 12.4 Hz, H-6a), 3.87 (dd, 1 H, H-2), 3.85 (dd, 1 H, $J_{3',2'}$ 10.1, $J_{3',4'}$ 3.2 Hz, H-3′), 3.8 (dd, 1 H, $J_{4',5'}$ 1.0 Hz, H-4′), 3.77 (dd, 1 H, $J_{6b,5}$ 5.4 Hz, H-6b), 3.71 (dd, 1 H, H-2′), 3.66 (dd, 1 H, $J_{3,2}$ 10.1, $J_{3,4}$ 9.8 Hz, H-3), 3.54 (t, 1 H, $J_{4,5}$ 9.8 Hz, H-4), 3.50 (m, 1 H, H-5), 2.04 (s, 3 H, Ac), 1.15 (d, 3 H, $J_{6',5'}$ 6.6 Hz, H-6′).

*Allyl (3,4-*O*-isopropylidene-2-*O*-p-methoxybenzyl-α-*L*-fucopyranosyl)-(1→3)-2-acetamido-2-deoxy-6-*O*-p-methoxybenzyl-β-*D*-glucopyranoside* (**25**), *allyl (3,4-*O*-isopropylidene-2-*O*-p-methoxybenzyl-β-*L*-fucopyranosyl)-(1→3)-2-acetamido-2-deoxy-6-*O*-p-methoxybenzyl-β-*D*-glucopyranoside* (**26**) and *allyl (3,4-*O*-isopropylidene-2-*O*-p-methoxybenzyl-α-*L*-fucopyranosyl)-(1→4)-2-acetamido-2-deoxy-6-*O*-p-methoxybenzyl-β-*D*-glucopyranoside* (**28**).—A suspension of **3** (600 mg, 1.57 mmol), **20** (636 mg, 1.73 mmol) and 4 Å molecular sieves (1 g) in 1:5 dry DMF–CH_2Cl_2 (14 mL) was stirred at room temperature for 75 min under N_2. Iodonium di-*sym*-collidinium perchlorate (IDCP, 785 mg, 1.57 mmol) was added in 7 portions over a period of 7 h. Stirring was continued for one additional hour, the suspension was diluted with CH_2Cl_2 (50 mL) and filtered through Celite®. The filtrate was washed twice with aq 5% $Na_2S_2O_3$, dried (Na_2SO_4), and concentrated. Purification of the residue on silica gel (1:3 toluene–EtOAc) gave **25** as colourless crystals. Yield: 260 mg (32%), mp 162–164 °C (EtOAc–hexane); $[\alpha]^{20}{}_D$ −59° (*c* 0.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.29–7.25 (m, 4 H, arom. H), 6.89–6.85 (m, 4 H, arom. H), 5.88 (m, 1

H, CH=), 5.51 (d, 1 H, $J_{NH,2}$ 7.7 Hz, NH), 5.25 (dq, 1 H, $=CH_{2trans}$), 5.18–5.14 (m, 1 H, $=CH_{2cis}$), 4.89 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1), 4.86 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1′), 4.72 and 4.60 (AB, 2 H, J_{AB} 12.0 Hz, OCH_2Ar), 4.59–4.51 (m, 2 H, OCH_2Ar), 4.36 (dq, 1 H, $J_{5',4'}$ 2.5, $J_{5',6'}$ 6.7 Hz, H-5′), 4.31 (dd, 1 H, $J_{3',2'}$ 6.7, $J_{3',4'}$ 6.0 Hz, H-3′), 4.39–4.29 (m, 1 H, OCH_2), 4.11–4.04 (m, 1 H, OCH_2), 4.05 (dd, 1 H, H-4′), 3.96 (br dd, 1 H, H-3), 3.83–3.80 (m, 8 H, 2 OMe, H-6a,6b), 3.68 (ddd, 1 H $J_{5,6a}$ 5.0, $J_{5,4}$ 10.4 Hz, H-5), 3.75 (dd, 1 H, H-2′), 3.48–3.43 (m, 2 H, H-4, OH), 3.26 (m, 1 H, H-2), 1.76 (s, 3 H, Ac), 1.42 and 1.33 (2 s, each 3 H, Me_2C), 1.31 (d, 3 H, H-6′). Anal. Calcd for $C_{36}H_{49}NO_{12}$: C, 62.87; H, 7.18; N, 2.04. Found: C, 62.94; H, 7.12; N, 1.99.

The column was then eluted with 5:1 EtOAc–MeOH and the eluate was concentrated. The residue was purified on silica gel (10:10:1 CH_2Cl_2–hexane–EtOH), which afforded **26** as colourless crystals. Yield: 33 mg (4%); mp 171–173 °C (CH_2Cl_2–hexane); $[\alpha]^{20}_D$ −8° (*c* 0.6, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.26 (m, 4 H, arom. H), 6.84 (m, 4 H, arom. H), 5.91 (m, 1 H, CH=), 5.78 (d, 1 H, $J_{NH,2}$ 6.8 Hz, NH), 5.27 (dq, 1 H, $=CH_{2trans}$), 5.17 (dq, 1 H, $=CH_{2cis}$), 5.04 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 4.85 and 4.66 (AB, 2 H, J_{AB} 11.5 Hz, OCH_2Ar), 4.52 (s, 2 H, OCH_2Ar), 4.41 (d, 1 H, $J_{1',2'}$ 8.3 Hz, H-1′), 4.34 (ddt, 1 H, OCH_2), 4.23 (br dd, 1 H, H-3), 4.18 (dd, 1 H, $J_{3',2'}$ 7.0, $J_{3',4'}$ 5.5 Hz, H-3′), 4.09 (ddt, 1 H, OCH_2), 3.97 (dd, 1 H, $J_{4',5'}$ 2.1 Hz, H-4′), 3.86–3.78 (m, 1 H, H-6a), 3.82 (dq, 1 H, $J_{5',6'}$ 6.6 Hz, H-5′), 3.79 and 3.76 (2 s, each 3 H, 2 OMe), 3.73 (dd, 1 H, $J_{6b,5}$ 2.0, $J_{6b,6a}$ 11.0 Hz, H-6b), 3.62–3.56 (m, 1 H, H-5), 3.52–3.47 (m, 2 H, H-4, OH), 3.43 (dd, 1 H, H-2′), 3.04 (br td, 1 H, H-2), 1.97 (s, 3 H, Ac), 1.44 and 1.34 (2 s, each 3 H, Me_2C), 1.36 (d, 3 H, H-6′). Anal. Calcd for $C_{36}H_{49}NO_{12}$: C, 62.87; H, 7.18; N, 2.04. Found: C, 62.89; H, 7.19; N, 2.00.

Further elution gave **28** as crystals. Yield: 90 mg (11%); mp 160 °C (EtOAc–hexane); $[\alpha]^{20}_D$ −72° (*c* 0.6, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.22–7.19 (m, 4 H, arom. H), 6.86–6.81 (m, 4 H, arom. H), 5.90 (m, 1 H, CH=), 5.73 (d, 1 H, $J_{NH,2}$ 6.7 Hz, NH), 5.28 (dq, 1 H, $=CH_{2trans}$), 5.19 (dq, 1 H, $=CH_{2cis}$), 4.88 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1′), 4.87 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 4.61 and 4.55 (AB, 2 H, J_{AB} 11.0 Hz, OCH_2Ar), 4.43 and 4.38 (AB, 2 H, J_{AB} 11.0 Hz, OCH_2Ar), 4.39 (dq, 1 H, $J_{5',4'}$ 2.5, $J_{5',6'}$ 6.7 Hz, H-5′), 4.40–4.31 (m, 1 H, OCH_2), 4.26 (t, 1 H, $J_{3',4'} = J_{3',2'} = 5.5$ Hz, H-3′), 4.11–4.01 (m, 2 H, H-3, OCH_2), 4.02 (dd, 1 H, H-4′), 3.79 and 3.77 (2 s, each 3 H, 2 OMe), 3.74 (dd, 1 H, $J_{6a,5}$ 1.9, $J_{6a,6b}$ 10.5 Hz, H-6a), 3.69 (dd, 1 H, $J_{6b,5}$ 3.9 Hz, H-6b), 3.57–3.47 (m, 4 H, H-4,5,2′, and OH), 3.31 (ddd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 2.01 (s, 3 H, Ac), 1.42 and 1.34 (2 s, each 3 H, Me_2C), 1.29 (d, 3 H, H-6′). Anal. Calcd for $C_{36}H_{49}NO_{12}$: C, 62.87; H, 7.18; N, 2.04. Found: C, 63.08; H, 7.34; N, 1.99. Further elution afforded unreacted **3** (150 mg, 25%).

Acetylation of **25**.—A solution of **25** (5 mg) in pyridine (1 mL) was treated with Ac_2O (0.1 mL) for 64 h at room temperature. MeOH (0.2 mL) was added and the solution was taken to dryness. Purification of the residue on silica gel (1:2 toluene–EtOAc) furnished **27** as syrup. Yield: 5 mg (95%). ^{1}H NMR ($CDCl_3$): δ 7.27–7.23 (m, 4 H, arom. H), 6.91–6.85 (m, 4 H, arom. H), 5.90–5.78 (m, 1 H, CH=), 5.81 (d, 1 H, $J_{NH,2}$ 7.5 Hz, NH), 5.24 (dq, 1 H, $=CH_{2trans}$), 5.15 (dq, 1 H, $=CH_{2cis}$), 4.88 (t, 1 H, $J_{4,3} = J_{4,5} = 9.0$ Hz, H-4), 4.78 and 4.58 (AB, 2 H, J_{AB} 11.5 Hz, OCH_2Ar), 4.76 (d, 1 H, $J_{1',2'}$ 3.0 Hz, H-1), 4.64 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1), 4.44 and 4.47 (AB, 2 H, J_{AB} 11.0 Hz, OCH_2Ar), 4.32 (ddt, 1 H, OCH_2), 4.20 (dd, 1 H, $J_{3',2'}$ 8.0, $J_{3',4'}$ 5.5 Hz, H-3′), 4.15 (dq, 1 H, $J_{5',6'}$ 6.7 Hz, H-5′), 4.07 (ddt, 1 H, OCH_2), 3.97 (dd, 1 H, H-4′), 3.81 and 3.80 (2 s, each 3 H, 2 OMe), 3.82–3.76 (m, 1 H, H-3), 3.56–3.51 (m, 4 H, H-2,5,6a,6b), 3.47 (dd, 1 H, H-2′), 1.98 (s, 6 H, 2 Ac), 1.44 and 1.33 (2 s, each 3 H, Me_2C), 1.23 (d, 3 H, H-6′).

Acetylation of **28**.—Compound **28** (5 mg) was treated as described for **27** to give 5 mg (95%) of **29** as a syrup. ^{1}H NMR ($CDCl_3$): δ 7.25–7.18 (m, 4 H, arom. H), 6.87–6.82 (m, 4 H arom. H), 5.86 (m, 1 H, CH=), 5.45 (d, 1 H, $J_{NH,2}$ 9.0 Hz, NH), 5.26 (dq, 1 H, $=CH_{2trans}$), 5.17 (dq, 1 H, $=CH_{2cis}$), 5.03 (dd, 1 H, $J_{3,2}$ 10.5, $J_{3,4}$ 8.5 Hz, H-3), 4.81 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1′), 4.67 and 4.53 (AB, 2 H, J_{AB} 11.5 Hz, OCH_2Ar), 4.47 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.41 and 4.35 (AB, 2 H, J_{AB} 11.7 Hz, OCH_2Ar), 4.32 (ddt, 1 H, OCH_2), 4.15 (dd, 1 H, $J_{3',2'}$ 8.0, $J_{3',4'}$ 5.5 Hz, H-3′), 4.11–4.03 (m, 2 H, H-5′, OCH_2), 4.01–3.90 (m, 3 H, H-2,6a,4′), 3.79 and 3.78 (2 s, each 3 H, 2 OMe), 3.67 (dd, 1 H, $J_{6b,5}$ 5.5, $J_{6b,6a}$ 9.5 Hz, H-6b), 3.63 (dd, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 3.52 (ddd, 1 H, $J_{5,6a}$ 2.0 Hz, H-5), 3.42 (dd, 1 H, H-2′), 2.06 and 1.92 (2 s, each 3 H, 2 Ac), 1.42 and 1.33 (2 s, each 3 H, Me_2C), 1.23 (d, 3 H, H-6′).

*Allyl (2,3,4-tri-*O*-acetyl-*α*-*L*-fucopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-acetyl-2-deoxy-*β*-*D*-glucopyranoside* (**30**).—A solution of **28** (28 mg, 0.041 mmol) in CH_2Cl_2 (7 mL) was cooled to −20 °C and treated with aq 90% CF_3CO_2H

(0.175 mL) for 2.5 h. After concentration, the residue was dissolved in pyridine (6 mL) and treated with Ac_2O (3 mL) for 96 h. MeOH (5 mL) was added at 0 °C and the solution was concentrated. Purification of the residue on silica gel (EtOAc) furnished **30** as a syrup. Yield: 21 mg (83%); $[\alpha]^{20}_D$ −93° (*c* 0.8, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 5.86 (m, 1 H, CH=), 5.46 (d, 1 H, $J_{NH,2}$ 9.0 Hz, NH), 5.31–5.10 (m, 6 H, H-1′,2′,3′,4′, and $=CH_2$), 5.08 (dd, 1 H, $J_{3,2}$ 10.5, $J_{3,4}$ 8.0 Hz, H-3), 4.66 (dd, 1 H, $J_{6a,5}$ 2.0, $J_{6a,6b}$ 11.5 Hz, H-6a), 4.55 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 4.32 (ddt, 1 H, OCH_2), 4.13 (dd, 1 H, $J_{6b,5}$ 5.5 Hz, H-6b), 4.10 (dd, 1 H, $J_{5',4'}$ 1.5, $J_{5',6'}$ 6.5 Hz, H-5′), 4.08 (ddt, 1 H, OCH_2), 3.92 (ddd, 1 H, H-2), 3.71–3.63 (m, 1 H, H-5), 3.60 (dd, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 2.15, 2.11, 2.09, 2.07, 1.98, and 1.94 (6 s, each 3 H, 6 Ac), 1.06 (d, 3 H, H-6′). Anal. Calcd for $C_{27}H_{39}NO_{15}$: C, 52.51; H, 6.36; N, 2.27. Found: C, 52.64; H, 6.28; N, 2.18.

Allyl (α-L-fucopyranosyl)-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (**31**).—A solution of **30** (9.8 mg) in dry MeOH (6 mL) was stirred with 0.1 M methanolic NaOMe (0.8 mL) for 24 h at room temperature. The pH of the solution was adjusted to 7.0 by addition of Dowex 50 (H^+) resin, the resin was filtered off, and the filtrate was taken to dryness to give **31** as an amorphous solid. Yield: 6.5 mg (∼ quant.); $[\alpha]^{20}_D$ −99° (*c* 0.7, H_2O). ^{1}H NMR (D_2O): δ 5.91 (m, 1 H, CH=), 5.34–5.23 (m, 2 H, $=CH_2$), 4.95 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1′), 4.56 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.33 (ddt, 1 H, OCH_2), 4.34 (dq, 1 H, $J_{5',4'}$ 1.5, $J_{5',6'}$ 6.5 Hz, H-5′), 4.15 (ddt, 1 H, OCH_2), 3.98 (dd, 1 H, $J_{6a,5}$ 1.8, $J_{6a,6b}$ 12.5 Hz, H-6a), 3.87–3.80 (m, 2 H, H-6b,2′), 3.80 (dd, 1 H, $J_{4',3'}$ 3.5 Hz, H-4′), 3.72 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 3.77–3.50 (m, 4 H, H-3,4,5,3′), 2.03 (s, 3 H, Ac), 1.15 (d, 3 H, H-6′). ES-MS ($C_{17}H_{29}NO_{10}$): *m*/*z* 407.9 $(M+H)^+$.

Allyl (3,4-O-isopropylidene-2-O-p-methoxybenzyl-α-L-fucopyranosyl)-(1→3)-[(3,4,6-tri-O-acetyl-2-deoxy-2-trichloroacetamido-β-D-galactopyranosyl-(1→4)]-2-acetamido-2-deoxy-6-O-p-methoxybenzyl-β-D-glucopyranoside (**33**).—A suspension of **25** (183 mg, 0.266 mmol), **9** (240 mg, 0.403 mmol), *N,N,N′,N′*-tetramethyl urea (0.035 ml, 0.292 mmol) and 4 Å molecular sieves (500 mg) in CH_2Cl_2 (8 mL) containing toluene (0.4 mL) was stirred for 45 min at room temperature. Then $Sn(OTf)_2$ (146 mg, 0.348 mmol) was added in two portions during 30 min, and the suspension was stirred for one additional hour. Et_3N (0.075 mL) and CH_2Cl_2 (50 mL) were added, solids were removed by filtration, and the filtrate was washed with satd aq $NaHCO_3$, dried (Na_2SO_4), and concentrated. Purification of the residue on silica gel (1:2 toluene–EtOAc) gave 2-trichloromethyl-4,5-dihydro-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-α-D-galactopyranoso)-[2,1-d]-1,3-oxazole (**32**) as a syrup. Yield: 65 mg (36%); $[\alpha]^{20}_D$ +108° (*c* 0.6, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 6.33 (d, 1 H, $J_{1,2}$ 7.0 Hz, H-1), 5.48 (dd, 1 H, $J_{4,3}$ 3.7, $J_{4,5}$ 2.5 Hz, H-4), 4.99 (dd, 1 H, $J_{3,2}$ 7.5 Hz, H-3), 4.31 (td, 1 H, $J_{5,6a}=J_{5,6b}=6.5$ Hz, H-5), 4.29 (dd, 1 H, H-2), 4.22 (dd, 1 H, $J_{6a,6b}$ 11.5 Hz, H-6a), 4.15 (dd, 1 H, H-6b), 2.15, 2.09, and 2.08 (3 s, each 3 H, 3 Ac).

Further elution afforded **33** as a syrup. Yield: 90 mg (41%); $[\alpha]^{20}_D$ −67° (*c* 0.6, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.31–7.25 (m, 4 H, arom. H), 6.94–6.91 (m, 2 H, arom. H), 6.88–6.85 (m, 2 H, arom. H), 6.46 (d, 1 H, $J_{NH'',2''}$ 9.0 Hz, NH″), 6.08 (d, 1 H, $J_{NH,2}$ 8.0 Hz, NH), 5.83 (m, 1 H, CH=), 5.22 (dd, 1 H, $J_{4'',3''}$ 3.5, $J_{4'',5''}$ 1.0 Hz, H-4″), 5.23 (dq, 1 H, $=CH_{2trans}$), 5.13 (dq, 1 H, $=CH_{2cis}$), 5.06 (d, 1 H, $J_{1',2'}$ 3.4 Hz, H-1′), 4.98 (dd, 1 H, $J_{3'',2''}$ 11.3 Hz, H-3″), 4.78–4.73 (m, 2 H, H-1, OCH_2Ar), 4.63 (d, 1 H, J_{AB} 12.0 Hz, OCH_2Ar), 4.63 and 4.36 (AB, 2 H, J_{AB} 12.0 Hz, OCH_2Ar), 4.59 (d, 1 H, $J_{1'',2''}$ 9.0 Hz, H-1″), 4.53 (dq, 1 H, $J_{5',4'}$ 2.5, $J_{5',6'}$ 6.7 Hz, H-5′), 4.25 (dd, 1 H, $J_{3',2'}$ 7.5, $J_{3',4'}$ 6.0 Hz, H-3′), 4.20 (dd, 1 H, $J_{6a'',5''}$ 8.0, $J_{6a'',6b''}$ 11.0 Hz, H-6a″), 4.28–4.17 (m, 1 H, OCH_2), 4.10–3.96 (m, 6 H, H-3,4,4′,2″,6b″, and OCH_2), 3.81 and 3.80 (2 s, each 3 H, 2 OMe), 3.74–3.60 (m, 4 H, H-2,6a,6b,5″), 3.57 (dd, 1 H, H-2′), 3.54–3.49 (m, 1 H, H-5), 2.15, 2.06, 1.99, and 1.90 (4 s, each 3 H, 4 Ac), 1.43 and 1.35 (2 s, each 3 H, Me_2C), 1.35 (d, 3 H, H-6′). Anal. Calcd for $C_{50}H_{65}Cl_3N_2O_{20}$: C, 53.59; H, 5.85; N, 2.50. Found: C, 53.57; H, 6.02; N, 2.33. Further elution of the column gave unreacted starting material **25** (47 mg, 26%).

Allyl (2-O-acetyl-3,4-O-isopropylidene-α-L-fucopyranosyl)-(1→3)-[(3,4,6-tri-O-acetyl-2-deoxy-2-trichloroacetamido-β-D-galactopyranosyl)-(1→4)]-2-acetamido-6-O-acetyl-2-deoxy-β-D-glucopyranoside (**34**).—A solution of **33** (40 mg, 0.036 mmol) and DDQ (41 mg, 0.18 mmol) in 18:1 CH_2Cl_2–H_2O (10 mL) was vigorously stirred for 7 h at room temperature. The reaction was quenched by addition of aq 20% $Na_2S_2O_3$ (2.5 mL), the solution was extracted with EtOAc, the organic layer was dried (Na_2SO_4), and concentrated. The residue was purified by flash-chromatogrphy on silica gel (24:1 EtOAc–MeOH). The product obtained (28.5 mg) was dissolved in pyridine (6 mL) and treated with

Ac_2O (0.7 mL) for 24 h at 0 °C. MeOH (2 mL) was added and the solution was taken to dryness. Chromatography of the residue on silica gel (1:5 toluene–EtOAc) gave **34** as a syrup. Yield: 30 mg (96%); $[\alpha]^{20}_D$ −91° (*c* 0.2, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.08 (d, 1 H, $J_{NH'',2''}$ 9.0 Hz, NH″), 5.90 (d, 1 H, $J_{NH,2}$ 9.0 Hz, NH), 5.83 (m, 1 H, CH=), 5.38 (dd, $J_{4'',3''}$ 3.5, $J_{4'',5''}$ 0.8 Hz, H-4″), 5.29 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1′), 5.29–5.22 (m, 1 H, $=CH_{2trans}$), 5.19–5.12 (m, 1 H, $=CH_{2cis}$), 5.14 (dd, 1 H, $J_{3'',2''}$ 11.5 Hz, H-3″), 4.84 (dd, 1 H, $J_{2',3'}$ 8.0 Hz, H-2′), 4.58–4.56 (m, 1 H, H-5′), 4.56 (d, 1 H, H-1), 4.47 (d, 1 H, $J_{1'',2''}$ 8.0 Hz, H-1″), 4.43 (dd, 1 H, $J_{6a,5}$ 5.5, $J_{6a,6b}$ 12.0 Hz, H-6a), 4.33 (dd, 1 H, $J_{6b,5}$ 4.0 Hz, H-6b), 4.30 (dd, 1 H, $J_{3',4'}$ 5.0 Hz, H-3′), 4.29–4.21 (m, 3 H, H-2″,6a″, and OCH_2), 4.15 (dd, 1 H, $J_{6b'',6a''}$ 11.0 Hz, H-6b″), 4.19–4.14 (m, 1 H, H-4′), 4.04–3.96 (m, 3 H, H-2,3, and OCH_2), 3.90 (td, 1 H, $J_{5'',6a''}$ 6.5 Hz, H-5″), 3.83–3.79 (m, 1 H, H-4), 3.72–3.68 (m, 1 H, H-5), 2.19, 2.13, 2.128, 2.08, 2.02, and 2.01 (6 s, each 3 H, 6 Ac), 1.52 and 1.36 (2 s, each 3 H, Me_2C), 1.42 (d, 3 H, $J_{6',5'}$ 6.7 Hz, H-6′). Anal. Calcd for $C_{38}H_{53}Cl_3N_2O_{20}$: C, 47.33; H, 5.54; N, 2.90. Found: C, 46.86; H, 5.21; N, 2.75.

*Allyl (2,3,4-tri-*O*-acetyl-α-*L*-fucopyranosyl)-(1→3)-[(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-galactopyranosyl)-(1→4)]-2-acetamido-6-*O*-acetyl-2-deoxy-β-*D*-glucopyranoside* (**35**).—A solution of **34** (25 mg, 0.026 mmol) in CH_2Cl_2 (10 mL) was treated with aq 90% CF_3CO_2H (0.2 mL) at −20 °C for 2 h. The solution was evaporated to dryness. The residue was dissolved in EtOH (8 mL) and stirred with $NaBH_4$ (51 mg, 1.35 mmol) for 24 h at 60 °C. After addition of EtOH (10 mL) the solution was cooled to 0 °C and HOAc (0.076 mL) was added. The solution was coevaporated 5 times with MeOH (10 mL). The residue was dissolved in pyridine (8 mL) and stirred with Ac_2O (4 mL) for 96 h at 0 °C. MeOH (5 mL) was added and the solution was concentrated. Purification of the residue on silica gel (24:1 EtOAc–MeOH) furnished 14 mg (60%) of **35** as syrup; $[\alpha]^{20}_D$ −76° (*c* 0.3, MeOH). ^1H NMR ($CDCl_3$): δ 5.95 (d, 1 H, $J_{NH,2}$ 9.0 Hz, NH), 5.88 (d, 1 H, $J_{NH'',2''}$ 9.0 Hz, NH″), 5.85 (m, 1 H, CH=), 5.41 (d, 1 H, $J_{1',2'}$ 4.0 Hz, H-1′), 5.37–5.36 (m, 2 H, H-4′,4″), 5.30–5.22 (m, 1 H, $=CH_{2trans}$), 5.20–5.36 (m, 1 H, $=CH_{2cis}$), 5.20 (dd, 1 H, $J_{3',2'}$ 11.0, $J_{3',4'}$ 3.5 Hz, H-3′), 5.06 (dd, 1 H, H-2′), 4.98 (dd, 1 H, $J_{3'',2''}$ 11.0, $J_{3'',4''}$ 3.5 Hz, H-3″), 4.69 (m, 1 H, H-5′), 4.60 (d, 1 H, $J_{1,2}$ 6.0 Hz, H-1), 4.45 (dd, 1 H, $J_{6a,5}$ 3.5, $J_{6a,6b}$ 11.5 Hz, H-6a), 4.41 (dd, 1 H, $J_{6a'',5''}$ 6.5, $J_{6a'',6b''}$ 11.5 Hz, H-6a″), 4.32 (dd, 1 H, $J_{6b,5}$ 5.5 Hz, H-6b), 4.31 (d, 1 H, $J_{1'',2''}$ 8.5 Hz, H-1″), 4.28 (dd, 1 H, $J_{6b'',5''}$ 6.5 Hz, H-6b″), 4.20 (ddd, 1 H, H-2″), 4.31–4.23 (m, 1 H, OCH_2), 4.06 (t, 1 H, $J_{3,2}=J_{3,4}=7.0$ Hz, H-3), 4.05–3.99 (m, 1 H, OCH_2), 3.91 (m, 1 H, H-2), 3.84 (m, 2 H, $J_{4,5}$ 7.0 Hz, H-4,5), 3.67 (m, 1 H, H-5), 2.19, 2.15, 2.149, 2.094, 2.087, 2.08, 2.014, 2.01, and 1.97 (9 s, each 3 H, 9 Ac), 1.24 (d, 3 H, $J_{6',5'}$ 6.6 Hz, H-6′). Anal. Calcd for $C_{39}H_{56}N_2O_{22}$: C, 51.76; H, 6.24; N, 3.09. Found: C, 52.25; H, 6.08; N, 3.14.

Allyl (α-L-fucopyranosyl)-(1→3)-[(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)]-2-acetamido-2-deoxy-β-D-glucopyranoside (**36**).—A solution of **35** (9.0 mg, 0.010 mmol) in MeOH (2 mL) was stirred with 0.1 M methanolic NaOMe (0.8 mL) for 24 h at ambient temperature. Dowex (H^+) resin was added to adjust the pH of the solution to 7.0. The resin was filtered off, and the filtrate was concentrated to give 6.0 mg (99%) of **36** as amorphous solid; $[\alpha]^{20}_D$ −69° (*c* 0.6, H_2O). ^1H NMR (500 MHz, D_2O): δ 5.84 (m, 1 H, CH=), 5.24 (dq, 1 H, $=CH_{2trans}$), 5.20 (dq, 1 H, $=CH_{2cis}$), 5.05 (d, 1 H, $J_{1',2'}$ 4.0 Hz, H-1′), 4.79 (m, 1 H, H-5′), 4.49 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1), 4.40 (d, 1 H, $J_{1'',2''}$ 8.4 Hz, H-1″), 4.26 (ddt, 1 H, OCH_2), 4.08 (ddt, 1 H, OCH_2), 3.91 (dd, 1 H, $J_{2'',3''}$ 10.8 Hz, H-2″), 3.88 (dd, 1 H, $J_{3',4'}$ 3.3 Hz, H-3′), 3.87 (dd, 1 H, $J_{2,3}$ 12.2 Hz, H-2), 3.88–3.85 (m, 2 H, H-6a,4″), 3.82 (t, 1 H, $J_{4,3}=J_{4,5}=9.0$ Hz, H-4), 3.78 (t, 1 H, H-3), 3.78 (m, 1 H, H-4′), 3.71 (dd, 1 H, $J_{6a'',5''}$ 7.8, $J_{6a'',6b''}$ 11.6 Hz, H-6a″), 3.68 (dd, 1 H, $J_{6b,5}$ 5.2, $J_{6a,6b}$ 12.3 Hz, H-6b), 3.68 (dd, 1 H, $J_{6b'',5''}$ 4.4 Hz, H-6b″), 3.66 (dd, 1 H, $J_{3'',4''}$ 3.3 Hz, H-3″), 3.64 (dd, 1 H, $J_{2',3'}$ 10.1 Hz, H-2′), 3.52 (dd, 1 H, $J_{5'',4''}$ < 1.0 Hz, H-5″), 3.45 (ddd, 1 H, $J_{5,6a}$ 2.3 Hz, H-5), 1.99 and 1.96 (2 s, each 3 H, 2 Ac), 1.20 (d, 3 H, $J_{6',5'}$ 6.6 Hz, H-6′). ES-MS ($C_{25}H_{42}N_2O_{15}$): *m*/*z* 611.3 $(M+H)^+$.

3-(2-Aminoethylthio)propyl (α-L-fucopyranosyl)-(1→3)-[(2-acetamido-2-deoxy-β-D-galactopyanosyl)-(1→4)]-2-acetamido-2-deoxy-β-D-glucopyranoside (**37**).—A solution of **36** (5.0 mg, 8.2 μmol) and cysteamine hydrochloride (7.0 mg, 0.62 mmol) in water (0.2 mL) was irradiated at 254 nm for 6 h at room temperature. The solution was passed through a column of Dowex AGWX8 resin (NH_4^+ form) using 0.1 M aq NH_3 as eluent. Carbohydrate-containing fractions were pooled, lyophilized and further purified on Sephadex G-10 (0.05 M aq NH_4Ac) to give, after lyophilization, **37** as amorphous powder. Yield: 5.9 mg (96%); $[\alpha]^{20}_D$ −46° (*c* 0.5, H_2O). ^1H NMR (D_2O): δ 5.10 (d, 1 H,

$J_{1',2'}$ 3.9 Hz, H-1′), 4.83 (br d, 1 H, H-5′), 4.48 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.45 (d, 1 H, $J_{1'',2''}$ 8.3 Hz, H-1″), 3.99–3.82 (m, 8 H, H-2,6a,3′,4′,2″,3″,4″, and OCH_2), 3.80–3.62 (m, 7 H, H-3,4,6b,2′,6a″,6b″, and OCH_2), 3.56 (dd, 1 H, $J_{5'',6a''}$ 4.5, $J_{5'',6b''}$ 7.6 Hz, H-5″), 3.53–3.48 (m, 1 H, H-5), 3.19 (t, 2 H, CH_2N), 2.82 (t, 2 H, SCH_2), 2.60 (t, 2 H, CH_2S), 2.04 and 2.03 (2 s, each 3 H, 2 Ac), 1.84 (br t, 2 H, CH_2), 1.25 (d, 3 H, $J_{6',5'}$ 6.6 Hz, H-6′). ^{13}C NMR (D_2O): δ 175.73 (C=O), 175.01 (C=O), 101.94 (C-1″), 101.63 (C-1), 99.32 (C-1′), 76.34 (C-5), 75.73 (C-5″), 75.55 (C-3), 74.26 (C-4), 72.89 (C-4′), 71.62 (C-3″), 70.08 (OCH_2), 69.57 (C-3′), 68.61 (C-2′), 68.25 (C-4″), 67.82 (C-5′), 62.34 (C-6″), 60.92 (C-6), 56.55 (C-2), 53.27 (C-2″), 39.55 (CH_2N), 30.40 and 29.41 (2 CH_2S), 27.97 (CH_2), 23.18 and 23.08 (2 CH_3), 16.25 (C-6′). ES-MS ($C_{27}H_{49}N_3O_{15}S$): m/z 688.3 $(M+H)^+$.

Synthesis of BSA-conjugate **38**.—A solution of thiophosgene (1 μL, 13 μmol) in $CHCl_3$ (1 mL) was added to a solution of compound **37** (3.7 mg, 5 μmol) in 0.1 M aq $NaHCO_3$ (1.5 mL) and the mixture was vigorously stirred for 3 h at room temperature. The organic phase was separated and the aqueous phase was washed three times with $CHCl_3$ (2 mL portions) and finally purged with N_2 until a clear solution was obtained. The solution was transferred to a solution of BSA (SIGMA®, 4.0 mg) in 0.1 M aq $NaHCO_3$–0.3 M NaCl (1 mL) and stirred for 48 h at ambient temperature, then passed through a Sephadex G-25 column (1.6×50 cm, 0.01 M aq. $NaHCO_3$). Ninhydrin-positive fractions were combined and dialysed twice against water (2 L) for 24 h. Lyophilization gave the BSA-conjugate **38** as a fluffy white powder. Yield: 4.6 mg.

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