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Study of glycosylation with *N*-trichloroacetyl-D-glucosamine derivatives in the syntheses of the spacer-armed pentasaccharides sialyl lacto-*N*-neotetraose and sialyl lacto-*N*-tetraose, their fragments, and analogues

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Abstract

The syntheses of 2-aminoethyl glycosides of the pentasaccharides Neu5Ac-α(2→3)-Gal-β(1→4)-GlcNAc-β(1→3)-Gal-β(1→4)-Glc and Neu5Ac-α(2→3)-Gal-β(1→3)-GlcNAc-β(1→3)-Gal-β(1→4)-Glc, their asialo di-, tri-, and tetrasaccharide fragments, and analogues included a systematic study of glycosylation with variously protected mono- and disaccharide donors derived from *N*-trichloroacetyl-D-glucosamine of galactose, lactose, and lactosamine glycosyl acceptors bearing benzoyl protection around the OH group to be glycosylated. Despite the low reactivity of these acceptors, stereospecificity and good to excellent yields were obtained with NIS–TfOH-activated thioglycoside donors of such type, or with AgOTf-activated glycosyl bromides, while other promotors, as well as a trichloroacetimidate donor, were less effective, and a β-acetate donor was inactive. In NIS–TfOH-promoted glycosylation with the thioglycosides, the use of TfOH in catalytic amount led to rapid formation of the corresponding oxazoline, but the quantity of TfOH necessary for further efficient coupling with an acceptor depended on the reactivity of the donor, varying from 0.07 equiv for a 3,6-di-*O*-benzylated monosaccharide derivative to 2.1 equiv for a peracetylated disaccharide one. In the glycosylation products, the *N*-trichloroacetyl group was easily converted into *N*-acetyl by alkaline hydrolysis followed by *N*-acetylation.

Keywords: Thioglycosides; 2-Deoxy-2-trichloroacetamido-D-glucose; Sialyl-oligosaccharides

1. Introduction

Synthetic oligosaccharides and neoglycoconjugates thereof are indispensable tools for the research into carbohydrate lectin interactions directed towards determining the structural requirements necessary for specific recognition by these proteins, defining the binding mode, and understanding the biological functions of the corresponding natural glycoconjugates.[1] In this paper we describe the syntheses of the pentasaccharides sialyl-*N*-acetyllactosaminyl-lactose **8**, sialyl-*iso*-*N*-

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acetyllactosaminyl-lactose **9**, and their asialo tetra- (**5**, **6**, respectively), tri- (**2**), and disaccharide (**1**) fragments (Fig. 1). For further comparison, tetrasaccharides bis-(*N*-acetylglucosaminyl)-lactose **4** and *N*-acetyllactosaminyl-*N*-acetyllactosamine **7** which are analogues of compounds **2** and **5**, respectively, were also synthesized. All the target compounds were obtained as the spacer-armed β-2-aminoethyl glycosides for further preparation of neoglycoconjugates, but oligosaccharides **3** and **10** were prepared as allyl glycosides as well. The group of oligosaccharides **1**–**10** was synthesized in order to study the carbohydrate specificity of galectins[2–5] and a new colon tumor-associated antigen called Tk.[6]

The syntheses of the glycosyl ceramides of lacto-*N*-neotetraose,[7] sialyl-lacto-*N*-neotetraose,[8] and sialyl-lacto-*N*-tetraose[9,10] have been described earlier. Also, the syntheses have been reported of lacto-*N*-neotetraose,[11] its methyl,[12,13] 2-trimethylsilylethyl,[14] and benzyl glycosides,[15,16] lacto-*N*-tetraose,[11,17] and its *p*-nitrophenyl glycoside.[18] Reducing *N*-acetyllactosamine β(1 → 3′) dimer[19] and GlcNAc-β(1 → 3)-Gal disaccharide[12] have already been prepared, as well as methyl glycoside analogues of tetrasaccharide **4**[20] and trisaccharide **2**.[13]

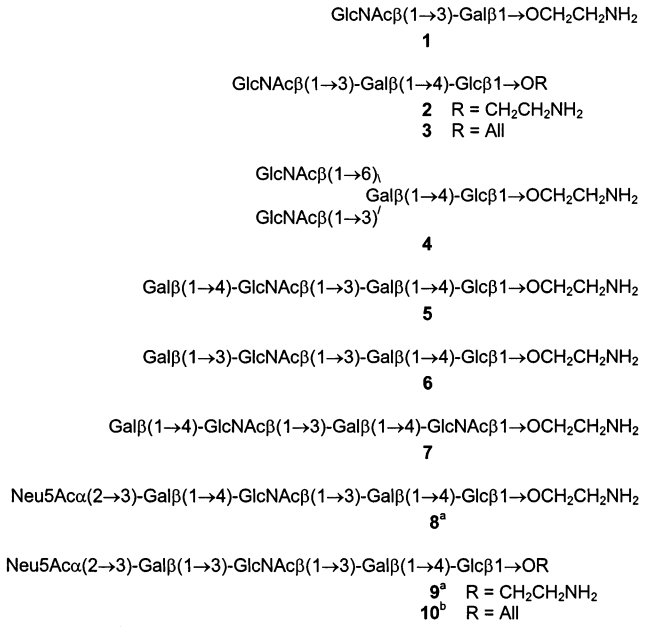


Fig. 1. (a) Inner salt. (b) Potassium salt.

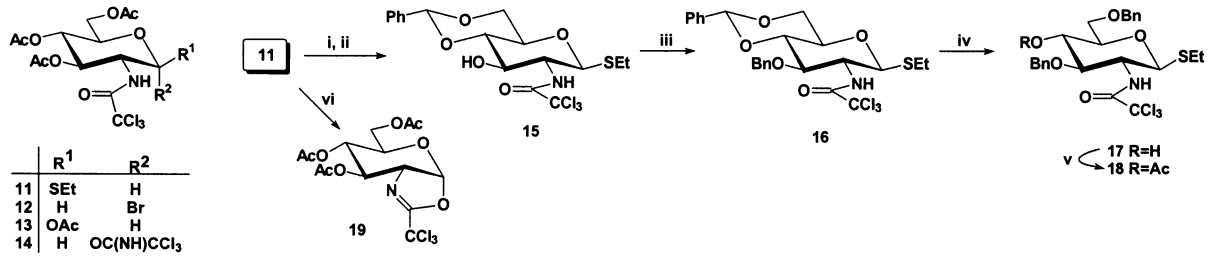
Successful preparation of the group of oligosaccharides **1**–**10** required an efficient method for the stereoselective construction of the β-glycosaminyl linkage. Among the numerous procedures reported, the phthalimido method[21,22] is still the most widely used. However, rather harsh conditions of dephthaloylation have led to the development of other glucosamine derivatives with novel participating groups. Examples of new methods described recently include donors with such moieties as tetrachlorophthaloyl,[23,24] sulfonamido,[25,26] trichloroethoxycarbonyl,[27] *N*,*N*-dithiasuccinylimido,[28,29] dimethylmaleoyl,[11,30] and *N*-acetylacetamido.[31]

Recently, Jacquinet and his coworkers[32] suggested the use of 2-deoxy-2-trichloroacetamido derivatives of glucose and galactose which were then successfully applied for the syntheses of oligosaccharide fragments of hyaluronic acid,[33,34] chondroitin sulfate,[35–37] and dermatan sulfate.[38] Compatibility with such delicate structures, high glycosylation yields, and complete stereoselectivity reported, encouraged us to investigate this new promising type of glucosamine glycosyl donor in the preparation of oligosaccharides **1**–**10**. In the present work, an attempt was made to perform a systematic study of variously protected mono- and disaccharide glycosyl donors **11**–**14**, **18**, **19**, **23**, **24**, **30**, **36** with the 2-deoxy-2-trichloroacetamido moiety. Selectively substituted derivatives of galactose (**45**), lactose (**41**, **43**, **50**), and lactosamine (**55**) with benzoyl protections around the glycosylation position were employed as glycosyl acceptors.

In the present work, oligosaccharides **1** and **4** were synthesized through a scheme[39,40] which involved their preparation as the corresponding allyl glycosides **59** and **61** followed by conversion into 2-azidoethyl glycosides **60**, **62**, and deprotection. Other spacer-armed oligosaccharides **2**, **5**–**9** were obtained by the shorter route, based on the glycosylation of the acceptors with the 2-azidoethyl function already present.

2. Results and discussion

In order to study the various types of *N*-trichloroacetyl-D-glucosaminyl donors, we se-



Scheme 1. Reagents and conditions: (i) MeONa, MeOH; (ii) $PhCH(OMe)_2$, $\pm$CSA, DMF, 70 °C; (iii) NaH (3 equiv), BnBr (1.1 equiv), DMF, −15 °C; (iv) $Me_3N{\cdot}BH_3$ (4 equiv), $AlCl_3$ (6 equiv), H_2O (2 equiv), THF, rt; (v) Ac_2O, Py; (vi) NIS, TfOH (0.1 equiv), CH_2Cl_2, MS-4 Å, −30 °C.

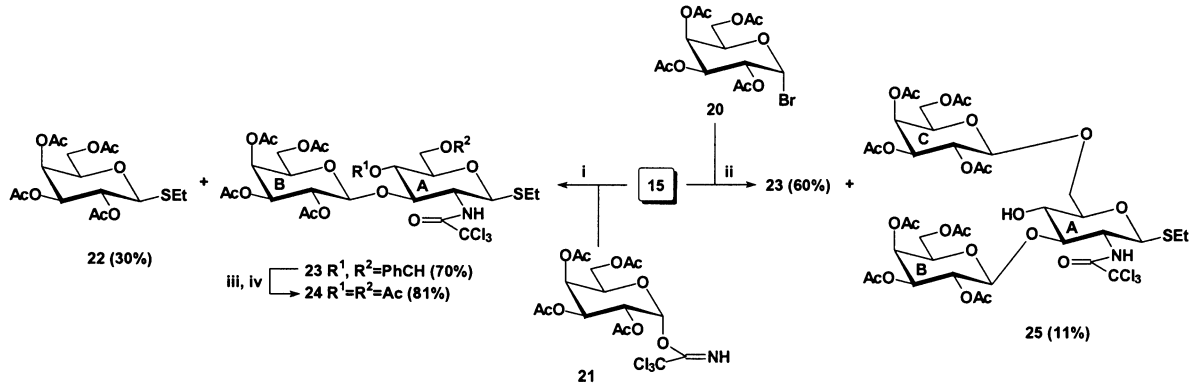
lected the monosaccharide derivatives thioglycosides **11** and **18**, bromide **12**, β-acetate **13**, imidate **14**, oxazoline **19** (Scheme 1), and their disaccharide analogues **23**, **24**, **30**, and **36**. Donors **11**,[33] **13**,[32] and **14**[32] were synthesized as described, while the known oxazoline **19**[32] was prepared by treatment of thioglycoside **11** with NIS in the presence of a catalytic amount (0.1 equiv) of TfOH at −30 °C as described for its galacto analogue.[36] Glycosyl bromide **12**[32] was obtained in 95% yield by treatment of the acetate **13** with HBr–AcOH.[41] It is worth noting that the instability of **12** in aqueous acidic media required the workup to be performed as fast as possible, and therefore lower yields with the need of chromatographic purification were obtained in gram scale reactions. The pure compound **12** was stable and could be stored at −20 °C for at least 1 year.

In order to prepare the 3,6-di-*O*-benzylated thioglycoside **18**, triacetate **11** was subjected to catalytic deacetylation with MeONa followed by treatment with $PhCH(OMe)_2$ and CSA to give the highly crystalline benzylidene acetal **15** in 94% yield.

For the benzylation of **15** into **16**, various conditions were tested. Alkylation of **15**, with BnBr promoted by BaO and $Ba(OH)_2$ in DMF,[42] gave the crystalline **16** in ca. 50% yield, and the major byproduct was *N*,*O*-bis-benzylated derivative, while the minor ones were originated from the loss of the *N*-trichloroacetyl group. The use of BnBr, KI, and Ag_2O in DMF[43] diminished *N*,*O*-bis-benzylation, but gave irreproducible yields of **16** (from 20 to 70%) and recovered the starting compound, **15**.

Treatment of **15** with NaH (3 equiv) and BnBr (1.1 equiv) in DMF at −20 °C gave **16**, isolated by crystallization, in 91% yield. In this reaction, the excess of NaH was used for protection of the base-liable *N*-trichloroacetyl group by metallation.[44] The dianion formed upon treatment of **15** with excess of NaH was regioselectively *O*-alkylated with benzyl bromide and then protonated with acetic acid to give **16** in high yield. The origin of the regioselective *O*-alkylation of *O*,*N*-bis-anion may be attributed to the preferential and faster reaction of the hard electrophile benzyl bromide with the hard nucleophile alcoholate anion, rather than with the much softer nucleophile trichloroacetamide anion. Therefore, conducting the reaction at a low temperature and using only small excess of benzyl bromide was essential for avoiding undesired overalkylation into *O*,*N*-bis-benzylated derivative. Similar conditions have recently been recommended[38] for the benzylation of *p*-methoxyphenyl 4,6-*O*-benzylidene-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside.

Reductive benzylidene acetal ring opening in **16** was performed with $Me_3N{\cdot}BH_3$ and $AlCl_3$ in THF in the presence of water.[44] In complete agreement with our previous report,[44] virtually no reaction took place in the absence of water, indicating that the protic acid formed from $AlCl_3$ and water is a much more powerful reagent rather than the equivalent Lewis acid. Acetylation of the crude 4-OH derivative **17** afforded **18**, isolated by crystallization, in 83% overall yield. Location of the benzyloxy group at C-6 and not at C-4 in **18** was confirmed by the downfield shift of C-6 (69.6 ppm) and upfield shift of C-4 (71.4 ppm), while the value $\delta_{H\text{-}4}$ 5.19 ppm indicated that position 4 was acetylated. The isomeric 4-*O*-benzyl derivative was not detected in the reaction mixture.



Scheme 2. Reagents and conditions: (i) TMSOTf, CH_2Cl_2; (ii) AgOTf, 2,4,6-collidine, MS-4 Å, CH_2Cl_2; (iii) 90% aq CF_3CO_2H, CH_2Cl_2; (iv) Ac_2O, Py.

The key step in the preparation of *N*-trichloroacetyl-*iso*-lactosaminyl donor **23** was 3-*O*-β-galactosylation of 4,6-*O*-benzylidenated thioglycoside **15** (Scheme 2). Recently, glycosylation with methyl glucuronyl trichloroacetimidates of phenyl 2-deoxy-4,6-*O*-isopropylidene-1-thio-2-trichloroacetamido-β-D-gluco- and galactopyranoside have been studied[35] and reported to yield efficiently the disaccharide GlcA–GlcN products; however when the acceptor with galacto configuration was used, the main product was glucuronic acid thioglycoside originated from the aglycon transfer.

TMSOTf promoted glycosylation of **15** (1.6 equiv) with acetylated galactosyl trichloroacetimidate **21** afforded disaccharide **23** and aglycon transfer product **22** in 70 and 30% yields based on the imidate **21**, respectively. On the contrary, in glycosylation of **15** with acetobromogalactose **20** (1.5 equiv) promoted by AgOTf, thiogalactoside **22** formation was not detected, and disaccharide **23** was obtained in 60% yield. The β-galactose linkage in **23** was confirmed by the value of $J^{B}_{1,2}{}^{B}$ 7.5 Hz (superscript capital letter denotes the monosaccharide residue starting from the reducing end of an oligosaccharide as shown in Scheme 2). Despite the use of 2,4,6-trimethylpyridine, a branched trisaccharide **25** was also isolated in 11% yield, apparently because of partial cleavage of the benzylidene acetal, followed by primary hydroxy group glycosylation.[†] The value 8 Hz of both $J^{B}_{1,2}{}^{B}$ and $J^{C}_{1,2}{}^{C}$ showed β configuration of both galactose residues in compound **25**, while (1→6) linkage was deduced from the downfield shift of C-6^{A} 69.4 ppm.

For the preparation of *N*-trichloroacetyl-lactosaminyl donor **30**, 4-*O*-β-galactosylation of thioglycoside acceptor **17** was studied (Scheme 3). The use of temporary 3-*O*-acetyl protected galactosyl bromide **29** as a donor was suggested by a possibility to utilize the resulting disaccharide derivative in the synthesis of longer oligosaccharide chains containing repeated lactosamine units. Galactosyl bromide **29** was obtained from the known diol **26**[45] through the reaction sequence involving preparation of 4-*O*-benzoate **27** via the orthoester procedure (99%), 3-*O*-acetylation followed by acetolysis (→**28**, 97%), and finally bromination (→**29**, 96%).

Stoichiometric condensation of bromide **29** and thioglycoside acceptor **17** promoted by AgOTf in CH_2Cl_2 (−25→0 °C) gave the glycosylation product, lactosamine **30**, and the aglycon transfer product, thiogalactoside **31**, in 45 and 40% yields, respectively. The value of $J^{B}_{1,2}{}^{B}$ 8 Hz confirmed the β-Gal linkage, while the preservation of 1-thioethyl moiety in **30** was evident from the characteristic upfield chemical shift of C-1^{A} (82.5 ppm). A plethora of byproducts originating from the aglycon transfer was obtained, but among them only trisaccharide **37** (3.2% yield) could be isolated and characterized. Such acceptor self-condensation has already been observed during glycosylations of thioglycosides in which aglycon

[†] The alternative mechanism was proposed by a referee: the trisaccharide **25** may be formed by glycosylation of compound **23** on O-6, with subsequent cleavage of the benzylidene acetal.

transfer took place.[46] Neither lowering the temperature to −40 °C nor changing the solvent to toluene improved the yield of lactosamine **30** and suppressed an aglycon transfer byprocess.

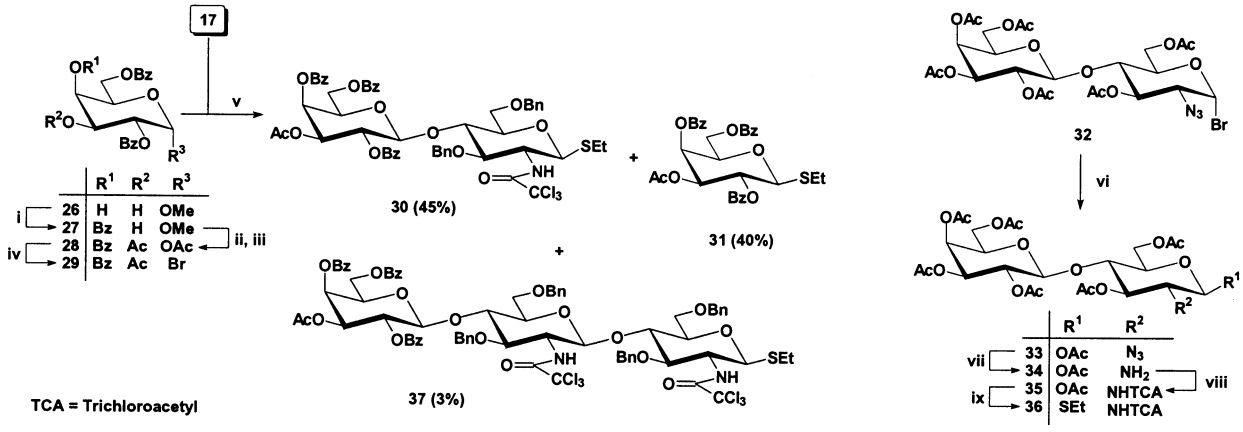
The preparation of the alternative *N*-trichloroacetyl-lactosamine thioglycoside **36** was started from the known 2-azido derivative **32**[47] which, in turn, is available from D-lactal by azidonitration methodology. Treatment of the α-bromide **32** with $Hg(OAc)_2$[48] afforded the β-acetate **33** nearly quantitatively. Hydrogenation of **33** could be best performed over Pd–C in THF in the presence of TsOH to give amine **34**, which was immediately *N*-trichloroacetylated into **35** (76% overall). In contrast, hydrogenation of **33** both in acetic acid and in methanol, both with and without 1 equiv of dilute aq HCl was accompanied by partial loss[49] or O→N migration of acetyl groups. The use of Pt–C as a catalyst gave very similar results as compared to Pd–C in terms of the reaction rate, the yield of **34**, and the formation of byproducts. Finally, the ethylthio function was introduced into **35** by treatment with EtSH and $BF_3{\cdot}Et_2O$ to give **36**, isolated by crystallization, in 80% yield.

Preparation of glycosyl acceptors derived from galactose (**45**), lactose (**41**, **43**, **50**), and lactosamine (**55**) was the next synthetic stage. Tri-*O*-benzoyl galactoside **45** was obtained from the known diol **44**[50] via the orthoester procedure (Scheme 4).

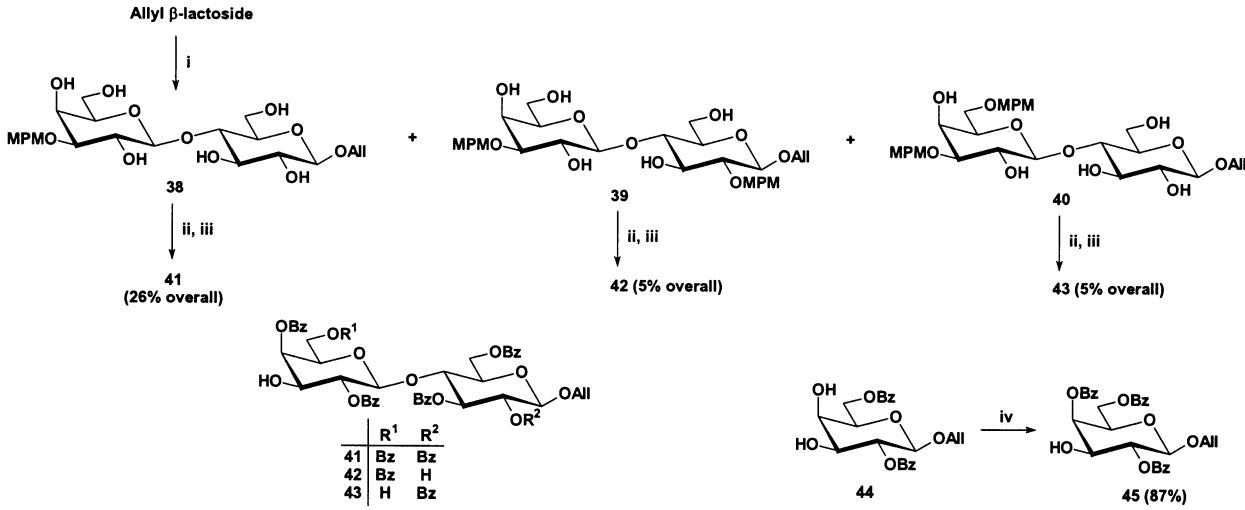
For the preparation of hexabenzoate **41**, allyl β-lactoside[50] was subjected to dibutyltin-mediated 3^B-*O*-(*p*-methoxy)-benzylation[9,50] into **38**. Total benzoylation of the crude **38** followed by removal of the *p*-methoxybenzyl group with trifluoroacetic acid[51] gave **41** (26% overall yield for three steps) in which the presence of free OH group at C-3^B was evident from ^1H NMR spectrum (Table 2, $\delta^B_{H\text{-}3}$ 3.98 ppm).

The above mentioned 3^B-*O*-(*p*-methoxy)-benzylation of allyl β-lactoside afforded a dark-brown reaction mixture, from which water-soluble **38** was isolated sufficiently pure by simple partitioning between water and CH_2Cl_2.[52] The dark-colored organic phase contained, in turn, an inseparable mixture of bis-alkylated derivatives **39** and **40**. Treatment of this crude mixture, as described above for **38**, afforded readily separable 2^A,3^B- and 3^B,6^B-diols **42** and **43** each in 5% overall yield. In compound **42**, unsubstitution of the 2^A and 3^B positions was deduced from the upfield shifts of H-2^A (3.70 ppm) and H-3^B (3.91 ppm), while in **43** the values of $\delta^B_{H\text{-}3}$ (3.92 ppm), $\delta^B_{H\text{-}6a}$ (2.88 ppm), $\delta^B_{H\text{-}6b}$ (2.53 ppm) indicated the 3^B,6^B-diol structure.

Conversion of allyl lactoside **41** into 2-azidoethyl glycoside **50** was performed following the reaction sequence described previously[39,40] which involved acetylation of **41** (Ac_2O–Py, →**46**), ozonolysis followed by reduction with $NaBH_4$ into alcohol **47**, its mesylation (MsCl–

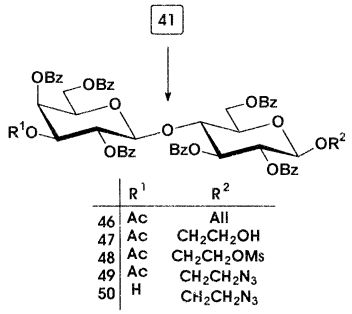


Scheme 3. Reagents and conditions: (i) $PhC(OEt)_3$, ±CSA, C_6H_6, then aq AcOH; (ii) Ac_2O, Py; (iii) AcOH, Ac_2O, H_2SO_4; (iv) HBr, AcOH, CH_2Cl_2; (v) AgOTf, CH_2Cl_2, −25 °C; (vi) $Hg(OAc)_2$, AcOH; (vii) H_2, Pd–C, TsOH, THF; (viii) $Cl_3CC(O)Cl$, Et_3N; (ix) EtSH, $BF_3{\cdot}Et_2O$, CH_2Cl_2.



Scheme 4. Reagents and conditions: (i) Bu_2SnO, MeOH, reflux, then *p*-methoxybenzyl chloride, Bu_4NBr, C_6H_6, 50 °C; (ii) BzCl, Py, CH_2Cl_2; (iii) 90% aq TFA, CH_2Cl_2; (iv) $PhC(OEt)_3$, TsOH, 40 °C, then aq AcOH.

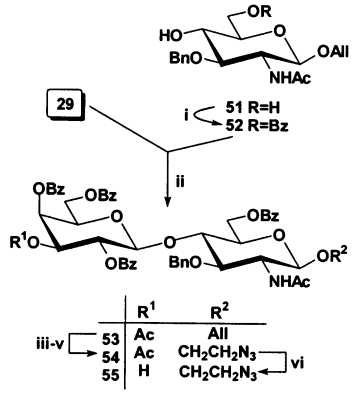
Et_3N–CH_2Cl_2, →**48**, 75% overall), treatment with sodium azide and 18-crown-6 in DMF (→**49**, 72%), and finally 3^B-*O*-deacetylation (→**50**, 86%) with AcCl–MeOH.



In order to obtain lactosaminide acceptor **55**, the known allyl glucosaminide diol **51**[42] was 6-*O*-benzoylated (→**52**) and then glycosylated with selectively protected galactosyl bromide **29** (Scheme 5). This coupling, promoted by AgOTf, gave disaccharide allyl glycoside **53** in 90% yield. Further transformation of **53** into 2-azidoethyl lactosaminide acceptor **55** was performed in the same manner as described above for the transformation of allyl lactoside **41** into **50**.

Glycosylations of the acceptors **41**, **43**, **45**, **50**, **55** with mono- and disaccharide donors **11**–**14**, **18**, **19** and **23**, **24**, **30**, **36** was studied next (Table 1). The results obtained indicate, that bromide- and thioglycoside-type donors gave higher yields, while trichloroacetimidate **14** was less effective. No formation of the trisaccharide **56** took place upon treatment of **41** with β-acetate **13** and TMSOTf in CH_2Cl_2,[53] whereas with $BF_3{\cdot}Et_2O$ only anomerization of the donor into α-acetate was observed. Glycosyl β-acetates have been studied and summarized as glycosyl donors of medium reactivity,[54] which is likely to be insufficient in the case of the low-reactive acceptor **41**.

Condensation of glycosyl bromide **12** with **41**, promoted by AgOTf in CH_2Cl_2, afforded trisaccharide **56** in 88% yield (Scheme 6), whereas only 25% yield of **56** was obtained in glycosylation of **41** with imidate **14** and TMSOTf and MS-4 Å in the same solvent (experimental details are not presented). The latter

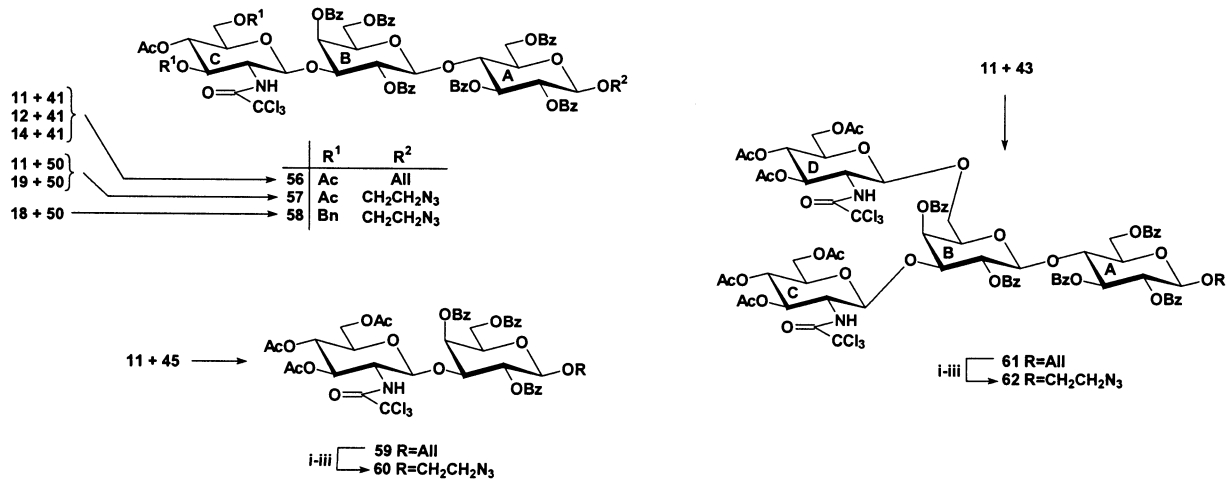


Scheme 5. Reagents and conditions: (i) BzCl, Et_3N, CH_2Cl_2; (ii) AgOTf, MS-4 Å, CH_2Cl_2; (iii) O_3, 2:1 MeOH–CH_2Cl_2, then $NaBH_4$; (iv) MsCl, Et_3N, CH_2Cl_2; (v) NaN_3, 18-crown-6, DMF, rt; (vi) AcCl, MeOH.

Table 1
Glycosylation of acceptors **41**, **43**, **45**, **50**, **55** with donors **11**–**14**, **18**, **19**, **24**, **30**, **36** in CH_2Cl_2

Entry	Donor	Acceptor	Promotor	Equiv of TfOH [a]	Product	Isolated yield (%)
1	**11**	**41**	NIS, TfOH, MS-4 Å	1.1	**56**	68
2	**11**	**43**	NIS, TfOH, MS-4 Å	1	**61**	66
3	**11**	**45**	NIS, TfOH, MS-4 Å	0.5	**59**	86
4	**11**	**50**	NIS, TfOH, MS-4 Å	1.5	**57**	65
5	**12**	**41**	AgOTf		**56**	88
6	**13**	**41**	TMSOTf, MS-4 Å		**56**	0
7	**13**	**41**	$BF_3{\cdot}Et_2O$, MS-4 Å		**56**	0
8	**14**	**41**	TMSOTf, MS-4 Å		**56**	25
9	**18**	**50**	NIS, TfOH, MS-4 Å	0.07	**58**	88
10	**19**	**50**	TfOH, MS-4 Å	1	**57**	66
11	**24**	**41**	NIS, TfOH, MS-4 Å	2.1	**65**	70
12	**24**	**50**	NIS, TfOH, MS-4 Å	2	**66**	50
13	**30**	**55**	NIS, TfOH, MS-4 Å	2	**64**	69
14	**36**	**50**	NIS, TfOH, MS-4 Å	1	**63**	76

[a] The quantity of triflic acid (in equivalents referring to the donor) used in NIS–TfOH promoted glycosylations with thioglycosides **11**, **18**, **24**, **30**, **36**, and in TfOH-promoted glycosylation with oxazoline **19**.



Scheme 6. Reagents and conditions: see Table 1; (i) O_3, 2:1 MeOH–CH_2Cl_2, then $NaBH_4$; (ii) MsCl, Et_3N, CH_2Cl_2; (iii) NaN_3, 18-crown-6, DMF, rt.

reaction gave acceptor trimethylsilyl ether as the main product. The β configuration of the glucosamine residue in **56** was deduced from the value of $J^{C}_{1,2}{}^{C}$ coupling constant 8 Hz, and α anomer was not detected.

Glycosylation with thioglycoside **11** could be best performed using NIS, TfOH, and MS-4 Å in CH_2Cl_2 at $-20\,^{\circ}C$.[55] Under these conditions, condensation of **11** with allyl lactoside **41** or its 2-azidoethyl congener **50** gave trisaccharides **56** and **57** in 68 and 65% yields, respectively. Similar glycosylation with **11** of allyl galactoside **45** and 3^{B},6^{B}-diol **43** afforded di- and tetrasaccharides **59** and **61** in 86 and 66% yields, respectively. In all these glycosylations, pure β-glycosides were obtained solely, as judged by the value of $J_{1,2}$ coupling constant (ca. 8 Hz) of the *N*-trichloroacetyl glucosamine residues (Table 2).

Glycosylation of 2-azidoethyl lactoside acceptor **50** with di-*O*-benzylated donor **18** promoted by NIS and TfOH afforded the β-linked trisaccharide **58** ($J^{C}_{1,2}{}^{C}$ 7.9 Hz) in 88% yield. As expected, benzyl protections increased the reactivity of the donor **18** in comparison with peracetylated **11**. Therefore, a smaller amount of the acid could be used for its activation (0.07 equiv for **18** vs. 1.5 equiv

Table 2
Chemical shifts (δ, ppm) and coupling constants (J, Hz) for carbohydrate ring protons in ^{1}H NMR spectra of compounds **1**, **3**, **5**–**7**, **12**, **15**, **16**, **18**, **19**, **23**–**25**, **27**, **29**–**31**, **33**, **35**, **36**, **41**–**43**, **45**, **49**, **50**, **53**, **55**, **56**, **58**, **59**, **61**, **63**–**65**, **72**, **75**, **82** in the solvent specified (solvent A, $CDCl_3$; B, D_2O; C, 5:1 $CDCl_3$–CD_3OD; D, 10:1 $CDCl_3$–CD_3OD)

Compound (solvent)	Unit	H-1 ($J_{1,2}$)	H-2 ($J_{2,3}$)	H-3 ($J_{3,4}$)	H-4 ($J_{4,5}$)	H-5 ($J_{5,6a}$)	H-6a ($J_{6a,6b}$)	H-6b ($J_{6b,5}$)
1 (B)	Gal^A	4.41 (7.8)	3.56 (10.5)	3.72 (2.9)	4.12 (0)	3.68	3.73	3.72
	GlcN^B	4.67 (8.6)	3.70 (10.7)	3.54	3.43	3.41 (0)	3.88 (11.9)	3.76
3 (B)	Glc^A	4.52 (8)	3.33 (9.3)	3.62	3.62	3.59 (2)	3.97 (12.2)	3.80
	Gal^B	4.43 (7.9)	3.59	3.73 (3.3)	4.14 (0)	3.68	3.75	3.75
	GlcN^C	4.70	3.77	3.57 (9.7)	3.47 (9.8)	3.45 (2)	3.90 (12.1)	3.78
5 (B)	Glc^A	4.54 (8)	3.38 (8.3)	3.67	3.66	3.61 (1)	3.97 (12.5)	3.83
	Gal^B	4.43 (7.8)	3.58 (9.4)	3.73 (2.9)	4.16 (0)	3.68	3.80–3.72	
	GlcN^C	4.70 (8.2)	3.80	3.72	3.72	3.59	3.95	3.86
	Gal^D	4.48 (7.9)	3.53 (9.7)	3.67 (2.7)	3.92 (0)	3.72	3.80–3.72	
6 (B)	Glc^A	4.53 (8)	3.38 (8.4)	3.66	3.65	3.64 (1.7)	3.98 (12.3)	3.80
	Gal^B	4.44 (7.9)	3.60 (10)	3.72 (3.2)	4.17 (0)	3.69	3.79–3.72	
	GlcN^C	4.75 (8.2)	3.88 (10)	3.85 (10)	3.59 (10)	3.49	3.89	3.78
	Gal^D	4.43 (7.7)	3.52 (9.9)	3.64 (3.1)	3.91 (0)	3.71	3.79–3.72	
7 (B)	GlcN^A	4.58 (8.3)	3.78	3.70	3.70	3.61	3.96	3.82
	Gal^B	4.48 (8)	3.59	3.71 (2.9)	4.17 (0)	3.70	3.70–3.80	
	GlcN^C	4.70 (8.1)	3.80	3.73	3.73	3.60	3.93	3.86
	Gal^D	4.49 (8)	3.54 (9.5)	3.68 (3.2)	3.92 (0)	3.73	3.70–3.80	
12 (A)		6.58 (4)	4.25 (10.5)	5.43 (10.5)	5.28 (10.5)	4.28 (4)	4.34 (12.5)	4.13 (2)
15 (C)		4.78 (10.4)	3.61 (10)	3.92 (9.4)	3.49 (9.3)	3.44 (4.7)	4.26 (10.4)	3.59 (10.1)
16 (D)		4.79 (11)	3.81 (10.5)	3.93 (11.2)	3.67 (11.2)	3.45 (5)	4.26 (10.5)	3.70 (10.5)
18 (A)		5.17 (9)	3.75 (7.9)	4.31 (7.9)	5.19 (7.9)	3.79 (5)	3.68 (0)	3.68 (5)
19 (A)		6.34 (7.5)	4.47 (2.3) [a]	5.40 (2.3)	4.93 (8.2)	3.77 (3.2)	4.28 (12.1)	4.18 (5.8)
23 (A)	GlcN^A	5.05 (10)	3.73 (9)	4.47 (9)	3.75	3.55 (4.8)	4.35 (11)	3.77
	Gal^B	4.76 (7.5)	5.18 (10)	4.91 (3.3)	5.33 (0)	3.75	4.07	4.07
24 (A)	GlcN^A	4.69 (10.3)	3.77 (10.5)	4.19 (9.5)	4.87 (9.5)	3.65 (5.2)	4.15 (12.2)	4.10
	Gal^B	4.55 (7.9)	5.01 (10.4)	4.78 (3.6)	5.26 (0)	3.77 (0)	4.10 (10.7)	4.00 (7)
25 (A)	GlcN^A	4.68 (10.4)	3.55	3.93	3.29 (9.6)	3.41 (>1)	4.12 (10.5)	3.55 (9.5)
	Gal^B	4.50 (8)	5.10 (10.5)	4.95 (3.4)	5.27 (0)	3.86 (6.7)	4.06	4.06 (6.7)
	Gal^C	4.51 (8)	5.11 (10.6)	4.80 (3.3)	5.26 (0)	3.93	4.05	4.05
27 (A)		5.21 (3.6)	5.42 (10.5)	4.53 (3.5)	5.83 (0)	4.43	4.55	4.41
29 (A)		6.92 (4)	5.50 (10.4)	5.80 (3.2)	5.98 (0)	4.82 (6.4)	4.58 (11.5)	4.45 (6.4)
30 (A)	GlcN^A	4.79 (8.4)	3.71 (8.9)	4.00 (8.6)	4.21 (8.2)	3.37 (>1)	3.64 (10.5)	3.58 (>1)
	Gal^B	4.83 (8)	5.58 (10.5)	5.21 (2.5)	5.77 (0)	3.98 (6.9)	4.41 (11.2)	4.23 (6.9)
31 (A)		4.87 (9.9)	5.72 (9.9)	5.50 (3.4)	5.98 (0)	4.33 (6.5)	4.70 (11.2)	4.45 (6.5)
33 (A)	GlcN^A	5.51 (8.0)	3.58 (9)	5.09 (9.5)	3.76 (9.5)	3.73	4.42	4.06
	Gal^B	4.46 (7.9)	5.09 (9.5)	4.93 (3.2)	5.36 (0)	3.87	4.15	4.15
35 (A)	GlcN^A	5.80 (8.5)	4.22 (9.5)	5.28 (9.7)	3.88 (9)	3.75 (0)	4.49 (14.7)	4.13 (4.9)
	Gal^B	4.51 (8)	5.12 (8.1)	4.97 (3)	5.36 (0)	3.92 (6.8)	4.12	4.12 (6.8)
36 (A)	GlcN^A	4.58 (10.4)	4.10 (10)	5.26 (10.1)	3.82 (10.1)	3.61	4.52	4.11
	Gal^B	4.49 (7.4)	5.08 (10.4)	4.95 (3.2)	5.36 (0)	3.89 (3.8)	4.09	4.09 (3.8)
41 (A)	Glc^A	4.78 (8)	5.51 (9.2)	5.76 (9.2)	4.23 (9.2)	3.87	4.62	4.58
	Gal^B	4.77 (8)	5.34 (9.8)	3.98 (3)	5.50 (0)	3.77 (5.5)	3.84 (11)	3.50 (6.5)
42 (A)	Glc^A	4.46 (7.7)	3.70 (9.3)	5.41 (9.4)	4.06 (9.3)	3.72 (0)	4.61 (11.9)	4.50 (5.1)
	Gal^B	4.73 (7.8)	5.25 (9.6)	3.91 (3.2)	5.46 (0)	3.75	3.79	3.73
43 (A)	Glc^A	4.75 (7.9)	5.50 (9.8)	5.70 (9.5)	4.19 (9.5)	3.82 (0)	4.66 (11.6)	4.55 (5)
	Gal^B	4.70 (7.8)	5.31 (10)	3.92 (3.3)	5.27 (0)	3.44 (7)	2.88 (11.8)	2.53 (7)
45 (A)		4.80 (7.9)	5.49 (10.6)	4.20 (3.4)	5.81 (0)	4.18 (4.8)	4.41 (13.2)	4.22 (6.3)
49 (A)	Glc^A	4.80 (7.8)	5.48 (9.6)	5.83 (9.6)	4.28 (9.6)	3.85 (1)	4.65 (12.2)	4.49 (4.4)
	Gal^B	4.86 (7.9)	5.57 (10.4)	5.22 (3.4)	5.63 (0)	3.84	3.78	3.78
50 (A)	Glc^A	4.91 (8.1)	5.51 (9.5)	5.79 (9.5)	4.21 (9.5)	3.88 (1.6)	4.66 (12)	4.58 (4.7)
	Gal^B	4.89 (8.3)	5.38 (9.9)	3.99 (2)	5.51 (0)	3.68	3.49	3.49
53 (A)	GlcN^A	4.69 (6.3)	3.80	4.09	4.08	3.76	4.53	4.53
	Gal^B	4.82 (7.9)	5.61 (10.6)	5.33 (3.5)	5.79 (0)	4.02 (6.5)	4.45 (11.5)	4.29 (7)

Table 2 (*Continued*)

Compound (solvent)	Unit	H-1 ($J_{1,2}$)	H-2 ($J_{2,3}$)	H-3 ($J_{3,4}$)	H-4 ($J_{4,5}$)	H-5 ($J_{5,6a}$)	H-6a ($J_{6a,6b}$)	H-6b ($J_{6b,5}$)
55 (A)	$GlcN^A$	4.75 (6.2)	3.63 (7.6)	4.06	4.06	3.73	4.54	4.54
	Gal^B	4.80 (8)	5.47 (9.7)	4.11 (3.5)	5.69 (0)	3.94 (6.6)	4.33	4.33 (6.6)
56 (A)	Glc^A	4.71 (8)	5.45 (9.8)	5.71 (9.5)	4.09 (9.5)	3.73 (3)	4.47 (12)	4.40 (4)
	Gal^B	4.66 (8)	5.51 (10)	4.05 (3.2)	5.57 (0)	3.73 (5)	3.97 (12)	3.23 (7.9)
	$GlcN^C$	4.88 (8)	3.54 (11)	5.23 (10)	4.92 (10)	3.58 (3)	4.11 (11.5)	4.06 (4)
58 (A)	Glc^A	4.78 (7.8)	5.51 (9.4)	5.79 (9.4)	4.21 (9.4)	3.80 (3)	4.46	4.46 (3)
	Gal^B	4.68 (7.8)	5.60 (10)	4.15 (3.2)	5.68 (0)	3.71 (5)	3.91 (11.6)	3.29
	$GlcN^C$	5.17 (7.9)	3.21 (9.5)	4.26 (9.5)	4.95 (9.2)	3.62 (5.6)	3.56 (10.3)	3.52 (3.6)
59 (A)	Gal^A	4.68 (8)	5.62 (10)	4.27 (3.5)	5.84 (0)	4.15	4.51	4.51
	$GlcN^B$	5.02 (8.2)	3.58 (9.5)	5.31 (10)	5.00 (9.5)	3.65	4.24	4.11
61 (A)	Glc^A	4.71 (7.9)	5.38 (9.5)	5.66 (9.5)	4.06 (9)	3.75	4.41	4.41
	Gal^B	4.65 (8)	5.44 (10)	4.02 (4)	5.55 (0)	3.59 (6.5)	3.21 (11)	2.89 (6)
	$GlcN^C$	4.88 (8.3)	3.57	5.21 (10)	5.04 (10)	3.59	4.00	4.00
	$GlcN^D$	4.56 (8)	3.58	5.55 (10)	4.99 (10)	3.60	3.75	3.75
63 (A)	Glc^A	4.72 (7.7)	5.43 (9.5)	5.72 (9.4)	4.15 (9.3)	3.73 (0)	4.45 (12.1)	4.39 (4.3)
	Gal^B	4.66 (8.3)	5.50 (10)	4.03 (3.3)	5.53 (0)	3.73	3.96	3.24
	$GlcN^C$	4.63 (8.5)	3.67 (9)	5.01 (8.75)	3.70 (9)	3.48 (1.7)	4.54 (12.2)	4.00 (8.1)
	Gal^D	4.42 (7.6)	5.04 (10.5)	4.92 (3.4)	5.30 (0)	3.81	4.03	4.03
64 (A)	$GlcN^A$	4.69 (5.6)	3.82	4.02	4.06	3.78	4.51	4.51
	Gal^B	4.70 (7.6)	5.76 (9.6)	4.07	5.78(0)	3.41	3.87	3.20
	$GlcN^C$	5.13 (7.5)	3.31	4.05 (8.5)	4.12 (8.3)	3.41	3.71	3.62
	Gal^D	4.88 (8.4)	5.54 (9.9)	5.22 (3.2)	5.78 (0)	3.90	4.39	4.22
65 (A)	Glc^A	4.72 (8)	5.45 (9.5)	5.70 (10)	4.12 (10)	3.73	4.39	4.39
	Gal^B	4.61 (8)	5.50 (10)	4.04 (3)	5.57 (0)	3.71 (5)	3.92 (12)	3.11 (8)
	$GlcN^C$	5.05 (8)	3.18 (10)	4.37 (10)	4.83 (9.5)	3.55	4.07	4.00
72 (B)	Glc^A	4.43 (8)	3.25 (8.6)	3.55	3.50	3.51	3.88	3.71
	Gal^B	4.33 (7.9)	3.50	3.59 (2.6)	4.03 (0)	3.72	3.89	3.72
	$GlcN^C$	4.60 (8.6)	3.62	3.46	3.34–3.39		3.81	3.65
	$GlcN^D$	4.51 (8.5)	3.58	3.46	3.34–3.39		3.81	3.65
	Gal^D	4.42 (8)	4.97 (10.5)	4.74 (3.5)	5.25 (0)	3.71	3.97	3.92
75 (A)	Glc^A	4.65 (7.9)	5.47 (9.8)	5.72 (9.3)	4.15 (9.5)	3.75 (0)	4.46 (0)	4.46 (0)
	Gal^B	4.72 (7.8)	5.51 (9.7)	4.05 (3)	5.49 (0)	3.71 (5)	3.91 (11.5)	3.22 (3.9)
	$GlcN^C$	4.94 (8)	3.15 (9.4)	3.98 (9.4)	3.33 (9.5)	3.18 (5.2)	3.83 (10.6)	3.50 (10.6)
82 (A)	Glc^A	4.75 (7.7)	5.47 (9)	5.74 (9.4)	4.16 (9.4)	3.77 (4.3)	4.49	4.43 (4.3)
	Gal^B	4.65 (8.1)	5.54 (9.9)	4.09(2.6)	5.56 (0)	3.71	3.96	3.28
	$GlcN^C$	5.04 (7.9)	3.13 (10)	3.90 (10)	3.57 (8.8)	3.44	3.71 (10.9)	3.59 (5)

[a] $J_{2,4}$ 1.2 Hz.

for **11**), and a higher yield of the trisaccharide **58** (88% vs. 65% of **57**) was obtained.

Glycosylations of 2-azidoethyl lactoside **50** and lactosaminide **55** with *N*-trichloroacetyl lactosamine thioglycosides **36** and **30** promoted by NIS and TfOH (afforded tetrasaccharides **63** and **64** in 76 and 69% yields, respectively (Scheme 7). The β configuration of the linkages formed was confirmed by the values of $J^{C,C}_{1,2}$ 8.5 Hz for **63** and 7.5 Hz for **64**, and no α isomer was detected. If a smaller quantity of the acid was used, the reaction stopped at the stage of the transformation of the donor into the corresponding oxazoline, leading to substantial recovery of the unreacted acceptor and a low yield of the tetrasaccharide product.

Attempts to glycosylate lactosides **41** or **50** with benzylidene protected *iso*-lactosamine donor **23** were unsuccessful because of the instability of the acetal protection in **41** and **50** in the medium which is necessary to activate the glycosylation by the corresponding oxazoline intermediate formed from the donor **23**. Therefore, compound **23** was first converted into peracetate **24** by hydrolysis with aq CF_3CO_2H followed by acetylation. Glycosylation of **41** (1.3 equiv) or **50** (1.16 equiv)

with **24** under the above mentioned conditions afforded β-linked tetrasaccharides **65** ($J^{C\ C}_{1,\ 2}$ 8 Hz) and **66** ($J^{C\ C}_{1,\ 2}$ 8 Hz) in 70 and 50% yields, respectively.

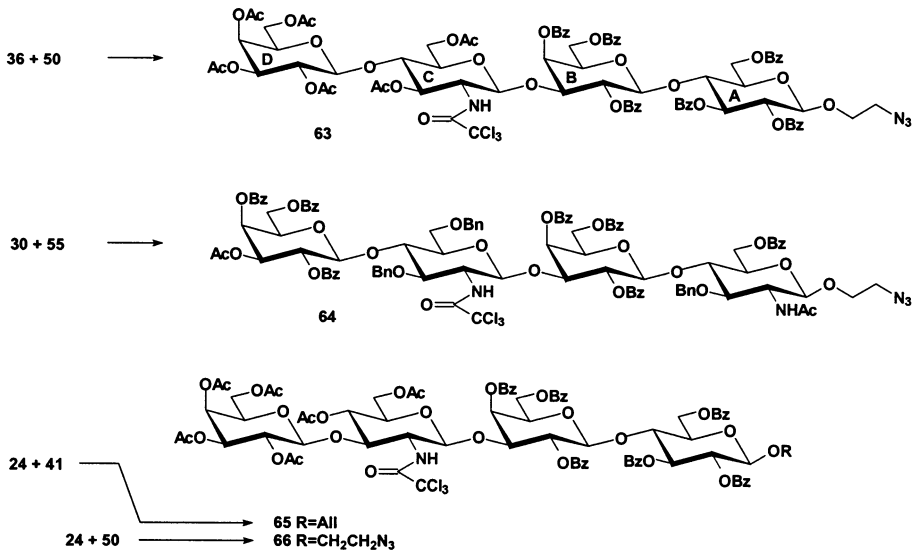
The previous studies by Jacquinet et al. of glycosylation with 2-deoxy-2-trichloroacetamido derivatives of D-glucose have shown the oxazolinium cation to be the major reactive intermediate.[32,36] In complete agreement with such a mechanism, treatment[36] of thioglycoside **11** with NIS and a catalytic amount of TfOH in the presence of MS-4 Å gave oxazoline **19**,[31] isolated nearly quantitatively. Furthermore, no glycosylation of **50** with **19** took place under such conditions, and efficient coupling of the oxazoline **19** and acceptor **50** required the presence of an equivalent amount of TfOH to afford trisaccharide **57** in 66% yield (Scheme 6).

As a general rule, in NIS–TfOH promoted glycosylation with acetylated thioglycosides **11**, **23**, **24**, **36**, the use of triflic acid in catalytic amount (ca. 0.1 equiv) led to quantitative conversion of the donor into the corresponding oxazoline within minutes, but only a small amount ($\sim 20\%$) of the desired glycosylation product was present in the reaction mixture, together with the unconsumed acceptor (TLC data). Much higher concentrations of TfOH were necessary to bring the glycosylations to completion, either by using the appropriate amount of the acid from the very beginning, or by adding more after the formation of the oxazoline.

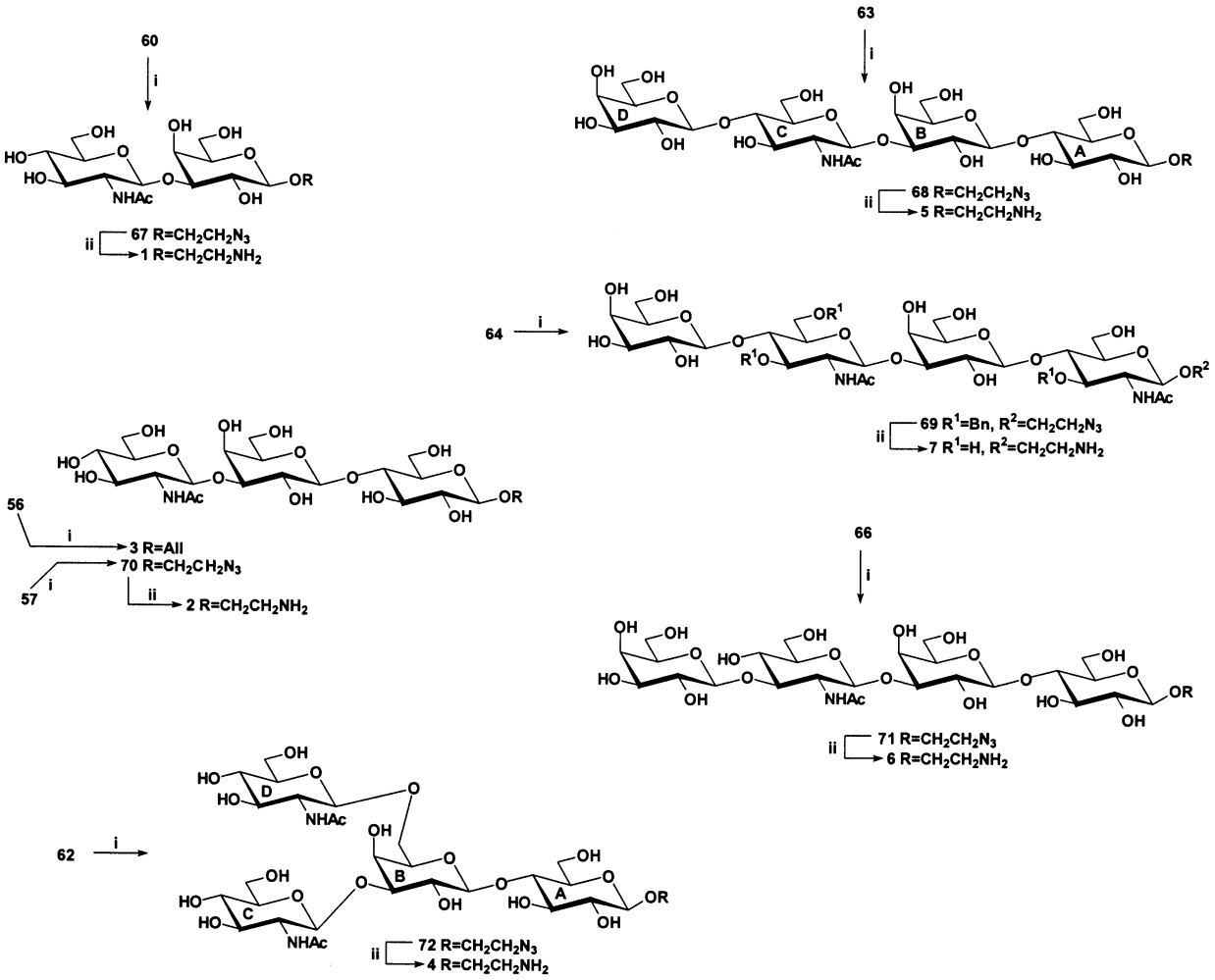
Similar behavior was observed when glycosylation of **41** with **11**, promoted by MeOTf and MS-4 Å in CH_2Cl_2, was attempted (experimental details are not presented). After stirring overnight at rt, oxazoline **19** and unreacted acceptor **41** were the only detectable components in the reaction mixture. However, they could be coupled into the trisaccharide **56** upon cooling to -20 °C and addition of 1 equiv of TfOH. Replacement of TfOH with TMSOTf in this reaction gave the trimethylsilyl ether of the acceptor **41** as the main product. The use of the promoting system $CuBr_2$–Bu_4NBr–AgOTf and MS-4 Å in $MeNO_2$[56] in the glycosylation with **11** led only to complete decomposition of the donor. Thus, NIS–TfOH was found to be the promotor of choice for the glycosylation with thioglycosides with the 2-deoxy-2-trichloroacetamido moiety.

Conversion of the allyl glycosides **59** and **61** into the corresponding 2-azidoethyl glycosides **60** and **62** was performed by the ozonolysis–reduction–mesylation–substitution sequence as described for the transformation of allyl lactoside **41** into **50** (Scheme 6).

Deprotection of di- (**60**), tri- (**56**, **57**), and tetrasaccharides **62**–**64**, **66** was studied next (Scheme 8). Previously, *N*-deacylation with methanolic $Ba(OH)_2$ or ammonia has been



Scheme 7. Reagents and conditions: see Table 1.



Scheme 8. Reagents and conditions: (i) NaOH, MeOH, then addition of Ac_2O; (ii) H_2, Pd–C, H_2O.

employed for *N*-dichloroacetyl,[57] *N*-trichloroacetyl,[58,59] and *N*-trifluoroacetyl[59] derivatives of 2-amino-2-deoxyglucose. Alternatively, reductive free-radical dechlorination with Bu_3SnH has been used[32–34,36–38] for the direct conversion of the *N*-trichloroacetyl moiety into *N*-acetyl. However, the latter is incompatible with the presence of an azido function, which undergoes reduction by this reagent.

Treatment of compounds **56**, **57**, **60**, **62**–**64**, **66** with sodium hydroxide in aqueous methanol gave the expected aminopolyols, which were *N*-acetylated by addition of acetic anhydride to the reaction mixtures and afforded oligosaccharides **3**, **67**–**72** in high yields after gel-permeation chromatography. Subsequent hydrogenation of the azido group, with concomitant debenzylation in the case of **69**, gave the spacer-armed derivatives **1**, **2**, and **4**–**7**.

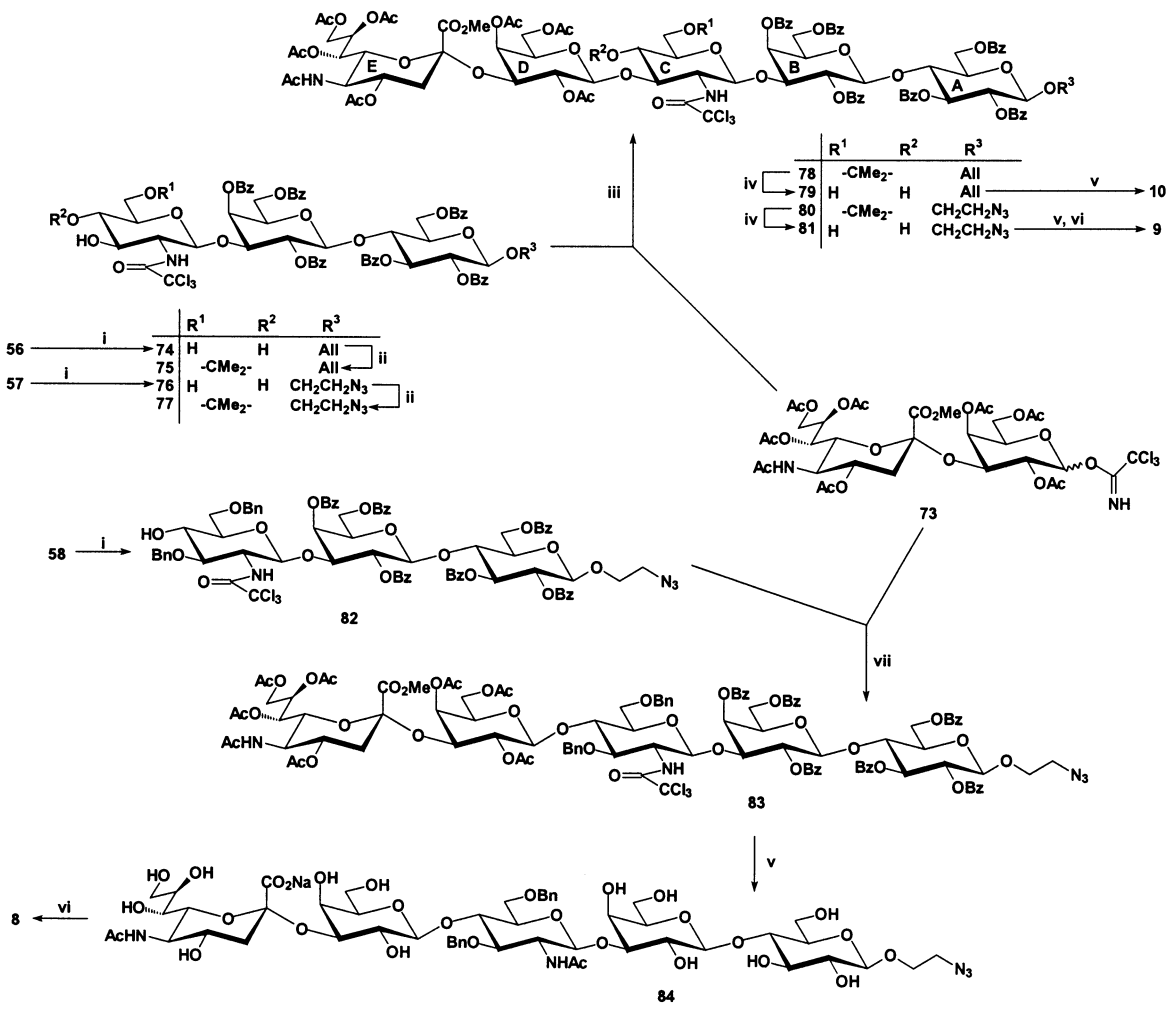
It is worth noting that alkaline hydrolysis of the *N*-trichloroacetyl group in compounds **64** and **66**, in which the neighboring to this function 3^C-hydroxyl is benzylated or glycosylated, proceeded much more slowly and required heating to 50 °C in comparison with 3^C-*O*-acetylated derivatives **56**, **57**, **60**, **62**, **63**. Similar observations were made during hydrolytic removal of trichloroacetyl protection from the pentasaccharides **79**, **81**, **83** (vide infra), and by other authors.[60]

In order to obtain sialyl-oligosaccharides **8**–**10** (Scheme 9), peracetylated sialyl-galactosyl trichloroacetimidate **73** was employed as a common synthetic block. The five-step synthesis of this compound from sialyl-α-(2 → 3′)-lactose trisaccharide, using regioselective removal of the glucose unit by acetolysis, will be published elsewhere. Alternative preparation of such disaccharide sialyl-galactosyl donors

from monosaccharides was elaborated by Hasegawa et al.[10] This approach has been used for the 13-step synthesis of compound **73**[61] from *N*-acetylneuraminic acid and D-galactose, where the key reaction was glycosylation of 2-trimethysilylethyl 4,6-*O*-benzylidene-β-D-galactopyranoside acceptor with the peracetylated 2-phenylthioglycoside of Neu5Ac methyl ester.

For the synthesis of $1^D \rightarrow 3^C$ linked allyl and 2-aminoethyl glycosides **10** and **9**, the trisaccharides **56** and **57** were deacetylated using acid-catalyzed methanolysis[62] to give triols **74** (92%) and **76** (86%), which were then converted into acetonides **75** and **77** in 77 and 90% yields, respectively. Glycosylation of these acceptors (1.2 equiv) with sialyl-galactosyl trichloroacetimidate **73** promoted by TMSOTf afforded, after deacetonation, pentasaccharides **79** and **81** in 75 and 71% yields based on the imidate, respectively. It is worth noting that in these reactions, the use of TMSOTf pre-treated with MS-4 Å[63] improved the coupling yields significantly. We suppose that such pre-treatment with molecular sieves removes traces of the protic acid present in the catalyst.

In the ^{1}H NMR spectra of the initially obtained pentasaccharide acetonides **78** and **80**, a substantial broadening of the signals of Gal^D residue was observed. Therefore, complete characterization and assignment of the ^{1}H NMR spectra was made for the diols **79** and **81** after removal of the acetonide protections. In these compounds, the value of $J^{D\,D}_{1,\,2}$ coupling constant (7.8 Hz in both **79** and **81**)



Scheme 9. Reagents and conditions: (i) AcCl, MeOH; (ii) 2,2-dimethoxypropane, ± CSA; (iii) TMSOTf, CH_2Cl_2, MS-4 Å, rt; (iv) 90% aq CF_3CO_2H, CH_2Cl_2; (v) NaOH, MeOH, then addition of Ac_2O; (vi) H_2, Pd–C, H_2O; (vii) $BF_3{\cdot}Et_2O$, CH_2Cl_2, MS AW-300, −25 °C.

indicated the Gal^D anomeric configuration to be β, and α isomer was not detected.

For the synthesis of $1^D \rightarrow 4^C$ linked pentasaccharide **8**, 4^C-hydroxy acceptor **82** was prepared from the trisaccharide **58**. Acid-catalyzed deacetylation[62] of **58** proceeded slowly, and partial degradation of the target *O*-deacetylated derivative **82** into the products with much lower chromatographic mobility occurred prior to complete consumption of the starting **58**. Therefore it was found beneficial to stop the reaction at the stage of ca. 70% of conversion of the starting **58**, isolate the readily separable **82**, and repeat *O*-deacetylation of the recovered **58**. Such treatment gave the requisite trisaccharide acceptor **82** in 87% yield after two cycles.

Glycosylation of **82** with sialyl-galactosyl trichloroacetimidate **73** (2.1 equiv) could be best performed by promotion with $BF_3 \cdot Et_2O$ (0.1 equiv with respect to the imidate) and acid washed molecular sieves MS AW-300 in CH_2Cl_2 for 6 days at −27 °C to give the β-linked pentasaccharide **83** ($J^{D\ D}_{1,\ 2}$ 8 Hz) in 81% yield. The above mentioned pre-treatment of the catalyst with MS-4 Å gave at least 30% increase of the coupling yield. The quantity of the promotor was also crucial in this reaction, and the use of more $BF_3 \cdot Et_2O$ under the same conditions gave **83** in ca. 50% yield. Therefore, acid-washed molecular sieves were indispensable because the untreated MS-4 Å were found to be basic enough to consume all the catalyst and stop the glycosylation.

Deblocking of the pentasaccharides **79** and **81**, achieved by simultaneous alkaline hydrolysis of methyl ester, *O*-acyl protections, and trichloroacetyl group afforded after *N*-acetylation allyl glycoside **10** (86%) and its 2-azidoethyl congener, respectively. These compounds were stable as salts, but in acidic form the sialic acid moiety was prone to partial $\alpha \rightarrow \beta$ anomerisation. Therefore, allyl glycoside **10** was isolated as potassium salt by Sephadex G-10 gel-permeation chromatography in water, while its 2-azidoethyl analogue, obtained as free acid after TSK HW-40S chromatography in 0.1 M aq acetic acid, was immediately hydrogenated into the inner amino acid salt **9** (93% overall yield from **81**).

In a similar fashion, alkaline deprotection of the pentasaccharide **83** afforded the di-*O*-benzyl ether **84** (91%) after *N*-acetylation, which was then hydrogenated to give the target 2-aminoethyl glycoside **8** nearly quantitatively.

As illustrated by the syntheses of pentasaccharides **8**–**10**, *N*-trichloroacetyl protected sialyl-oligosaccharides could be deblocked directly in a single step by treatment with alkali. This is an obvious advantage over the widely used phthalimido group, which can be removed from sialyl-oligosaccharides only after conversion of the sialic acid methyl ester into a salt. This additional transformation, conventionally performed by refluxing with lithium iodide in pyridine, complicates deprotection, which proved to be troublesome in certain cases.[64,65]

In conclusion, a group of spacer-armed oligosaccharide chains comprising di-, tri-, tetra-, and pentasaccharides was synthesized in order to investigate the carbohydrate specificity of galectin receptors. A systematic study of mono- and disaccharide glycosyl donors derived from *N*-trichloroacetyl glucosamine revealed them to be very efficient for stereospecific incorporating a β-D-GlcNAc residue into an oligosaccharide chain, even for glycosylation of low-reactive glycosyl acceptors with benzoyl-protected neighboring hydroxy groups. Among the various types of such donors tested thioglycosides, activated by NIS–TfOH, and glycosyl bromide, activated with AgOTf, were found to be the most efficient. Removal of the *N*-trichloroacetyl group by alkaline hydrolysis followed by *N*-acetylation proved, for base-stable substrates, a reasonable alternative to free radical dechlorination.

3. Experimental

General methods.—The reagents were purchased from Fluka and E. Merck, all of the highest grade available. Molecular Sieves were activated by heating (180 °C) under vacuum (0.1 mmHg) for 5–8 h. In glycosylation reactions, freshly activated molecular sieve Union Carbide type 4 Å (Fluka), or molecular sieve acid washed MSAW-300 (Fluka) were used. The catalyst used for hydrogenolysis was 10% Pd–C, oxide form, (E. Merck–Schuchardt).

Column chromatography was performed on Silica Gel 60 (Fluka, 70–230 mesh), and TLC was performed on Silica Gel 60 F_{254} (E. Merck, Darmstadt, Germany). For TLC analysis of deblocked oligosaccharides, solvent systems 1:2:1 *n*-butanol–*n*-propanol–0.1 M aq HCl (BPHCl), 1:1:1 MeCN–MeOH–water (AMW), and their combination was used. Optical rotation was measured with JASCO DIP-360 digital polarimeter at 26–30 °C. NMR spectra were recorded at 27 °C with Bruker DRX-500 instrument (500 MHz for ^{1}H and 125 MHz for ^{13}C), assignments were aided by APT, COSY, TOCSY, and ^{1}H–^{13}C correlation spectroscopy. *tert*-Butyl alcohol was used as an internal standard for D_2O solutions (1.24 ppm (^{1}H) and 30.29 ppm (^{13}C)) and Me_4Si for other ones. Superscript capital letters are used to define the monosaccharide residues starting from the reducing end of an oligosaccharide, i.e. from right to left. Mass spectra were recorded using either matrix-assisted laser desorption-ionization (MALDI)-time of flight (TOF) or atmospheric pressure chemical ionization (APCI) on VISION 2000 mass spectrometer. Melting points were determined with a Kofler apparatus and are uncorrected.

3,4,6-Tri-O-*acetyl-2-deoxy-2-trichloroacetamido-α*-D-*glucopyranosyl bromide* (**12**).—To a solution of **13** (663 mg, 1.34 mmol) in abs CH_2Cl_2 (4 mL), a solution of HBr in AcOH (33% of HBr w/v, stabilized with 1% of Ac_2O, 5 mL) was added, and the tightly closed flask was kept for 15 h at −30 °C. The mixture was allowed to attain rt, diluted with CH_2Cl_2 (50 mL), and poured into a separating funnel containing crushed ice. The organic phase was immediately separated and washed with ice-cold satd aq $NaHCO_3$, dried by filtration through cotton wool, and concentrated to give bromide **12** (678 mg, 95%) as a white foam: R_f 0.53 (3:2 petroleum ether–EtOAc); $[\alpha]_D$ 120° (*c* 1, $CHCl_3$), lit.[32] 129°; NMR ($CDCl_3$): ^{1}H, the spectrum was identical to the published one;[32] see Table 2 for carbohydrate ring protons; δ 7.09 (d, 1 H, $J_{N\text{-}H,2}$ 8.5 Hz, N-H), 2.10, 2.07, 2.03 (3 s, 9 H, 3 OAc). Anal. Calcd for $C_{14}H_{17}BrCl_3NO_8$: C, 32.74; H, 3.34; N, 2.73. Found: C, 32.95; H, 3.50; N, 2.99.

Ethyl 4,6-O-*benzylidene-2-deoxy-1-thio-2-trichloroacetamido-β*-D-*glucopyranoside* (**15**).—To a solution of **11** (5.38 g, 10.8 mmol) in abs MeOH (15 mL) solid MeONa (54 mg, 1 mmol) was added, and the mixture was kept for 3 h at rt, then neutralized with KU-2(H^+) cation-exchange resin, filtered, concentrated, and dried in vacuo to give the expected triol, R_f 0.3 (EtOAc), which was used without further purification. A mixture of the triol, Ph-$CH(OMe)_2$ (2.5 mL, 16.7 mmol), and (±)-camphor-10-sulfonic acid (CSA) (30 mg) in abs DMF (15 mL) was stirred for 2 h at 70 °C, neutralized with Et_3N (0.1 mL), and evaporated at 80 °C/0.1 mmHg. The solid residue was refluxed for 1 min in *i*-PrOH (150 mL) until dissolution; the crystals formed upon slow cooling were filtered off, washed with *i*-PrOH (50 mL), and dried to give **15** (4.2 g, 85%). Recrystallization of the mother liquor afforded additional crop of **15** (463 mg, 9%): R_f 0.5 (3:2 petroleum ether–EtOAc); $[\alpha]_D$ −53° (*c* 0.9, 10:1 CH_2Cl_2–MeOH); mp 224–226 °C; NMR (5:1 $CDCl_3$–CD_3OD): ^{1}H, see Table 2 for carbohydrate ring protons; δ 7.40–7.25 (m, 5 H, Ph), 5.49 (s, 1 H, PhCH), 2.65 (m, 2 H, S–CH_2), 1.19 (t, *J* 7.4 Hz, S–CH_2CH_3); ^{13}C, see Table 4 for carbohydrate ring carbons; δ 162.6 (N–*C*(O)CCl_3), 136.8 (ipso Ph), 129.0, 128.0, 126.0 (Ph), 101.6 (PhCH), 93.0 (CCl_3), 24.2 (S-CH_2), 14.6 (S-CH_2CH_3); APCI-MS: Calcd for $[C_{17}H_{20}Cl_3NO_5S + H]^+$: 456.0. Found: 455.6. Anal. Calcd for $C_{17}H_{20}Cl_3NO_5S \cdot 0.5$ *i*-PrOH: C, 45.64; H, 4.97; Cl, 21.85; N, 2.88; S, 6.59. Found: C, 45.51; H, 4.74; Cl, 21.51; N, 3.18; S, 6.48.

Ethyl 3-O-*benzyl-4,6*-O-*benzylidene-2-deoxy-1-thio-2-trichloroacetamido-β*-D-*glucopyranoside* (**16**).—NaH (60% suspension in mineral oil, 3 g, 75 mmol) was added portionwise to abs DMF (150 mL) at −20 °C under Ar (the solvent should be redistilled if any gas evolution is observed at this stage). The mixture was stirred until the homogeneous suspension was formed and solid **15** (12.12 g, 26.5 mmol) was added portionwise during 15 min. The stirring was continued until gas evolution ceased (ca. 1 h at −20 °C), BnBr (3.6 mL, 30 mmol) was added, and the mixture was stirred for 1.5 h at −15 °C, then cooled to −40 °C and glacial AcOH (7.5 mL, 125 mmol) was carefully added dropwise. The reaction mixture was allowed to attain rt slowly,

diluted with EtOAc (500 mL), washed with water, satd aq $NaHCO_3$, dried, and concentrated. Crystallization from *i*-PrOH (100 mL) gave **16** (13.18 g, 91%) as fine powder: R_f 0.75 (3:2 petroleum ether–EtOAc); $[\alpha]_D$ −48° (*c* 1, acetone); mp 245–247 °C; NMR (10:1 $CDCl_3$–CD_3OD): ^1H, see Table 2 for carbohydrate ring protons; δ 7.40–7.12 (m, 10 H, Ph), 5.50 (s, 1 H PhCH), 4.77 (d, 1 H, *J* 11.2 Hz, $PhCH_2$), 4.62 (d, 1 H, $PhCH_2$), 2.61 (m, 2 H, S–CH_2), 1.15 (t, 3 H, *J* 7.5 Hz, S–CH_2CH_3); ^{13}C, see Table 4 for carbohydrate ring carbons; δ 162.3 (N–*C*(O)CCl_3), 137.6, 136.9 (2 ipso Ph), 128.8–125.7 (Ph), 101.0 (PhCH), 74.4 ($PhCH_2$), 24.1 (S-CH_2), 14.6 (SCH_2CH_3); APCI-MS: Calcd for $[C_{24}H_{26}Cl_3NO_5S]^+$: 545.1. Found: 544.8. Anal. Calcd for $C_{24}H_{26}Cl_3NO_5S$·*i*-PrOH: C, 53.43; H, 5.65; N, 2.31; S, 5.28. Found: C, 53.45; H, 5.52; N, 2.15; S, 5.74.

*Ethyl 4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-1-thio-2-trichloroacetamido-β-*D*-glucopyranoside* (**18**).—$Me_3N{\cdot}BH_3$ (3.79 g, 52 mmol) was added with stirring under Ar to a solution of **16** (7.11 g, 13 mmol) in abs THF (195 mL, freshly distilled from Na–Ph_2CO), followed by anhyd $AlCl_3$ (10.4 g, 78 mmol). After the reagents had dissolved, water (0.47 mL, 26 mmol) was added dropwise and stirring was continued for 6 h at rt until the complete conversion of the starting **16** into the product **17** (R_f 0.33 in 4:1 toluene–EtOAc). The reaction was terminated by addition of water (100 mL) followed by 1 M aq HCl (100 mL) and extracted with EtOAc (3 × 200 mL), the extracts were washed with brine, dried, concentrated, and dried in vacuo. The crude **17** obtained was acetylated with Ac_2O (10 mL) in Py (20 mL) overnight at rt, then coevaporated with toluene (4 × 50 mL). Crystallization from *i*-PrOH (70 mL) gave **18** (6.38 g, 83%) as needles: R_f 0.5 (4:1 toluene–EtOAc); $[\alpha]_D$ −15° (*c* 1, $CHCl_3$); mp 156–158 °C; NMR ($CDCl_3$): ^1H, see Table 2 for carbohydrate ring protons; δ 7.45–7.31 (m, 10 H, Ph), 7.12 (d, 1 H, $J_{N\text{-}H,2}$ 10 Hz, N-H), 4.79 (d, 1 H, *J* 12 Hz, $PhCH_2$), 4.68 (d, 1 H, $PhCH_2$), 4.62 (s, 2 H, $PhCH_2$), 2.82 (m, 2 H, S–CH_2), 1.98 (s, 3 H, Ac), 1.40 (t, 3 H, *J* 6 Hz, S–CH_2CH_3); ^{13}C, see Table 4 for carbohydrate ring carbons; δ 169.7 (O–*C*(O)CH_3), 161.7 (N–*C*(O)CCl_3), 137.7, 137.4 (2 ipso Ph), 128.3–127.6 (Ph), 92.2 (CCl_3), 74.3 ($PhCH_2$), 73.4 ($PhCH_2$), 24.6 (S–CH_2), 20.7 (O–C(O)CH_3), 15.1 (S–CH_2-CH_3). Anal. Calcd for $C_{26}H_{30}Cl_3NO_6S$: C, 52.85; H, 5.12; Cl, 18.00; N, 2.37; S, 5.43. Found: C, 53.04; H, 5.21; Cl, 17.79; N, 2.30; S, 5.36.

*(3,4,6-Tri-*O*-acetyl-1,2-dideoxy-α-*D*-glucopyranoso)4,5-dihydro-2-trichloromethyl-[2,1-d]2-oxazole* (**19**).—A mixture of thioglycoside **11** (238 mg, 0.48 mmol) and MS-4 Å (300 mg) in abs CH_2Cl_2 (5 mL) was stirred under Ar for 1 h, NIS (126 mg, 0.56 mmol) was added, and the reaction mixture was cooled to −30 °C. TfOH (0.003 mL, 0.034 mmol) was added, and after stirring for 30 min at this temperature, the reaction was terminated with Et_3N (0.1 mL); the mixture was filtered through a pad of Celite, diluted with CH_2Cl_2, washed with satd aq $NaHCO_3$, 3 M aq $Na_2S_2O_3$, dried, and concentrated. Chromatography (petroleum ether–EtOAc) of the residue on a column of silica gel (20 g) gave **19** (202 mg, 97%) as a syrup: R_f 0.4 (3:1 toluene–EtOAc); $[\alpha]_D$ 20° (*c* 1, $CHCl_3$), lit.[32] $[\alpha]_D$ 22.5°; NMR ($CDCl_3$): ^1H, the spectrum was identical to the published one;[32] see Table 2 for carbohydrate ring protons; δ 2.12 (s, 3 H, Ac), 2.09 (s, 3 H, Ac), 2.07 (s, 3 H, Ac); ^{13}C, δ 170.4, 169.4, 168.9 (3 O*C*(O)CH_3), 163.1 (*C*-CCl_3), 103.1 (C-1), 68.8, 68.5, 67.5, 64.5, 63.4 (C-2–C-6), 20.8 (OC(O)CH_3). Anal. Calcd for $C_{14}H_{16}Cl_3NO_8$: C, 38.87; H, 3.73; Cl, 24.58; N, 3.24. Found: C, 38.94; H, 3.65; Cl, 24.79; N, 3.12.

Ethyl O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-(1→3)-4,6-*O*-benzylidene-2-deoxy-1-thio-2-trichloroacetamido-β-*D*-glucopyranoside* (**23**) *and ethyl* O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-(1→3)-*O*-[2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl-(1→6)]-2-deoxy-1-thio-2-trichloroacetamido-β-*D*-glucopyranoside* (**25**).—(a) A mixture of acetobromogalactose **20** (671 mg, 1.63 mmol), acceptor **15** (513 mg, 1.12 mmol), 2,4,6-collidine (0.1 mL, 0.8 mmol), and MS-4 Å (1.5 g) in abs CH_2Cl_2 (25 mL) was stirred for 2 h under Ar, then cooled to −30 °C and powdered AgOTf (550 mg, 2.14 mmol) was added. During 6 h of stirring, the mixture was allowed to attain 0 °C, then terminated with Et_3N (0.5 mL), diluted with CH_2Cl_2, filtered

through a pad of Celite, washed with satd aq $NaHCO_3$, 3 M aq $Na_2S_2O_3$, dried, and concentrated. Chromatography (2:3 → 3:2 EtOAc–petroleum ether) of the residue on a column of silica gel (60 g) afforded (in order of elution) disaccharide **23** (529 mg, 60%) and trisaccharide **25** (124 mg, 11%).

Data for disaccharide **23**: white foam, R_f 0.21 (2:3 EtOAc–petroleum ether); $[\alpha]_D$ −28° (*c* 2, CH_2Cl_2); NMR ($CDCl_3$): ^{1}H, see Table 2 for carbohydrate ring protons; δ 7.31–7.50 (m, 5 H, Ph), 7.15 (d, 1 H, $J_{N\text{-}H,2}$ 9 Hz, N-H), 5.54 (PhCH), 2.71 (m, 2 H, S-CH_2), 2.11, 2.03, 1.95, 1.89 (4 s, 12 H, 4 OAc), 1.25 (t, 3 H, *J* 6 Hz, S–CH_2CH_3); ^{13}C, δ 170.3 (4 O*C*(O)CH_3), 161.5 (N–*C*(O)CCl_3), 136.9 (ipso Ph), 129.2, 128.2, 126.0 (Ph), 101.1 (PhCH), 99.4 (C-1^B), 83.1 (C-1^A), 78.6, 77.1 (C-3^A, C-4^A), 61.1 (C-6^B), 57.1 (C-2^A), 24.7 (S–CH_2), 20.6 (OC(O)*C*H_3), 14.9 (S–CH_2CH_3); APCI-MS: Calcd for $[C_{31}H_{38}Cl_3NO_{14}S + H_2O]^+$ 803.1. Found 802.7. Calcd for $[C_{31}H_{38}Cl_3NO_{14}S–C_2H_5SH]^+$ 724.1. Found 723.8. Anal. Calcd for $C_{31}H_{38}Cl_3NO_{14}S$: C, 47.31; H, 4.87; Cl, 13.51; N, 1.78; S, 4.07. Found: C, 47.26; H, 4.79; Cl, 13.20; N, 1.93; S, 3.99.

Data for trisaccharide **25**: white foam, R_f 0.2 (3:2 EtOAc–petroleum ether); $[\alpha]_D$ −9° (*c* 2, CH_2Cl_2); NMR ($CDCl_3$): ^{1}H, see Table 2 for carbohydrate ring protons; δ 7.18 (d, 1 H, $J_{N\text{-}H,2}$ 8.4 Hz, N-H), 2.54 (m, 2 H, S–CH_2), 2.07, 1.95, 1.86 (8 s, 24 H, 8 Ac), 1.15 (t, 3 H, *J* 7.5 Hz, S–CH_2CH_3); ^{13}C, δ 170.4–169.5 (O*C*(O)CH_3), 161.7 (N–*C*(O)CCl_3), 101.6, 100.8 (C-1^B, C-1^C), 92.5 (CCl_3), 83.1 (C-1^A), 82.2 (C-3^A), 79.2 (C-5^A), 69.4 (C-6^A), 61.2, 61.1 (C-6^B, C-6^C), 56.0 (C-2^A), 24.1 (S–CH_2), 20.7-20.4 (OC(O)*C*H_3), 14.9 (S–CH_2CH_3). Anal. Calcd for $C_{38}H_{52}Cl_3NO_{23}S$: C, 44.35; H, 5.09; N, 1.36. Found: C, 44.51; H, 4.97; N, 1.19.

(b) A mixture of trichloroacetimidate **21** (52 mg, 0.11 mmol), acceptor **15** (83 mg, 0.18 mmol), and MS-4 Å (300 mg) in abs CH_2Cl_2 (3 mL) was stirred for 1 h under Ar, then cooled to −10 °C and neat TMSOTf (0.006 mL, 0.033 mmol) was added. After stirring for 0.5 h at −10 °C, the reaction was terminated by addition of solid $NaHCO_3$ (100 mg), the mixture was filtered through a pad of Celite, diluted with CH_2Cl_2, washed with satd aq $NaHCO_3$, dried, and concentrated. Chromatography (2:3 EtOAc–petroleum ether) of the residue on a column of silica gel (20 g) afforded thiogalactoside **22** (13 mg, 30%), which was found to be identical in all respect to the authentic sample obtained upon treatment of 1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranose with EtSH and $ZnCl_2$ as described.[66] Next eluted was disaccharide **23** (61 mg, 70%).

Ethyl O-*(2,3,4,6-tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1 → 3)-4,6-di*-O-*acetyl-2-deoxy-1-thio-2-trichloroacetamido-β*-D-*glucopyranoside* (**24**).—To a solution of **23** (225 mg, 0.29 mmol) in CH_2Cl_2 (5 mL), 90% aq CF_3CO_2H (0.4 mL) was added. After stirring for 1 h at rt, the mixture was poured into satd aq $NaHCO_3$ and extracted with CH_2Cl_2. The extracts were concentrated, the residue was dissolved in pyridine (2 mL) and treated with Ac_2O (1.5 mL) overnight at rt. Coevaporation with toluene followed by chromatography (benzene → 2:1 benzene–EtOAc) on a column of silica gel (30 g) afforded **24** (182 mg, 81%) as a white foam: R_f 0.25 (1:2 EtOAc–benzene); $[\alpha]_D$ −18° (*c* 2, CH_2Cl_2); NMR ($CDCl_3$): ^{1}H, see Table 2 for carbohydrate ring protons; δ 7.01 (d, $J_{N\text{-}H,2}$ 8.7 Hz, N–H), 2.62 (m, 2 H, S–CH_2), 2.09 (s, 3 H, Ac), 2.01 (4 s, 12 H, 4 Ac), 1.84 (s, 3 H, Ac), 1.19 (t, 3 H, *J* 7.5 Hz, S–CH_2CH_3); ^{13}C, δ 170.7–169.2 (O*C*(O)CH_3), 161.5 (N–*C*(O)CCl_3), 100.3 (C-1^B), 92.5 (CCl_3), 82.8 (C-1^A), 62.5, 60.9 (C-6^A, C-6^B), 56.6 (C-2^A), 24.2 (S–CH_2), 20.7–20.4 (OC(O)*C*H_3), 14.9 (S–CH_2CH_3). Anal. Calcd for $C_{28}H_{38}Cl_3NO_{16}S$: C, 42.95; H, 4.89; Cl, 13.58; N, 1.79; S, 4.09. Found: C, 43.16; H, 4.83; Cl, 13.26; N, 2.08; S, 4.0.

Methyl 2,4,6-tri-O-*benzoyl*-α-D-*galactopyranoside* (**27**).—A mixture of diol **26**[45] (4.48 g, 11.1 mmol), $PhC(OEt)_3$ (7.3 mL, 32.3 mmol) and ± CSA (50 mg) in abs benzene (15 mL) was stirred overnight at rt. Acetic acid (80% aq, 100 mL) was added, and the biphasic mixture was stirred vigorously for 1 h, then diluted with CH_2Cl_2, washed with water, satd aq $NaHCO_3$, dried, concentrated, and coevaporated with toluene. Chromatography (toluene → 1:1 toluene–EtOAc) of the residue on a column of silica gel (150 g) gave **27** (5.6 g, 99%) as a white foam: R_f 0.45 (4:1 toluene–

EtOAc); $[\alpha]_D$ 120° (*c* 1, $CHCl_3$); NMR ($CDCl_3$): ^1H, see Table 2 for carbohydrate ring protons; δ 8.12–8.01 (3 d, 6 H, *J* 7.5 Hz, ortho-protons of 3 Bz), 7.65–7.49 (m, 9 H, Ph), 3.42 (s, 3 H, OMe), 2.85 (broaden s, 1 H, OH). Anal. Calcd for $C_{28}H_{26}O_9$: C, 66.40; H, 5.17. Found: C, 66.44; H, 5.28.

*1,3-Di-*O*-acetyl-2,4,6-tri-*O*-benzoyl-α-*D*-galactopyranose* (**28**).—Compound **27** (5.5 g, 10.9 mmol) was acetylated with Ac_2O (2 mL) in Py (10 mL) for 2 days at rt. MeOH (5 mL) was added, and the reaction mixture was kept overnight at 0 °C, then coevaporated with toluene and dried in vacuo to give the expected 3-*O*-acetyl derivative (5.9 g, quant.) as a white foam: R_f 0.3 (13:1 toluene–EtOAc); $[\alpha]_D$ 113° (*c* 1, $CHCl_3$). Anal. Calcd for $C_{30}H_{28}O_{10}$: C, 65.69; H, 5.17. Found: C, 65.38; H, 5.26.

To a cold (0 °C) solution of this compound (1.5 g, 2.76 mmol) in 1:1 AcOH–Ac_2O (35 mL) was added a cold solution of concd H_2SO_4 (3.67 mL) in 1:1 AcOH–Ac_2O (35 mL). The reaction mixture was allowed to attain rt slowly, and kept overnight. The mixture was poured into crushed ice (500 g), stirred for 2 h, and extracted with CH_2Cl_2 (3 × 50 mL). The extracts were washed with water, satd aq $NaHCO_3$, and water, coevaporated with toluene, and dried in vacuo. Chromatography (10:1 toluene–EtOAc) of the residue on a short column of silica gel gave **28** (1.5 g, 96%) as a white foam: R_f 0.27 (13:1 toluene–EtOAc); $[\alpha]_D$ 98° (*c* 1, $CHCl_3$); NMR ($CDCl_3$): ^1H, δ 8.15 (d, 2 H, *J* 7.9 Hz, ortho protons of 1 Bz), 8.00 (t, 4 H, *J* 7.7 Hz, ortho protons of 2 Bz), 7.68–7.39 (m, 9 H, Ph), 6.70 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 5.99 (d, 1 H, $J_{4,3}$ 3.3 Hz, H-4), 5.74 (t, 2 H, H-2, H-3), 4.62 (m, 2 H, H-5, H-6a), 4.36 (dd, 1 H, $J_{6a,6b}$ 11, $J_{6b,5}$ 6.5 Hz, H-6b), 2. 18 (s, 3 H, Ac), 1.96 (s, 3 H, Ac). Anal. Calcd for $C_{31}H_{28}O_{11}$: C, 64.58; H, 4.89. Found: C, 64.67; H, 5.00.

*3-*O*-acetyl-2,4,6-tri-*O*-benzoyl-α-*D*-galacto-pyranosyl bromide* (**29**).—Treatment of diacetate **28** (1 g, 1.82 mmol) in abs CH_2Cl_2 (2.5 mL) with HBr–AcOH (5 mL) for 3 h at rt and subsequent aqueous workup as described for the preparation of **12** gave **29** (1.012 g, 97%) as a white foam: R_f 0.32 (13:1 toluene–EtOAc); NMR ($CDCl_3$): ^1H, see Table 2 for carbohydrate ring protons; δ 8.11, 8.04, 8.01 (3 d, 2 H each, *J* 7.6 Hz, ortho protons of 3 Bz), 7.70–7.40 (m, 9 H, Ph), 1.87 (s, 3 H, Ac). Anal. Calcd for $C_{29}H_{25}BrO_9$: C, 58.30; H, 4.22; Br, 13.37. Found: C, 58.44; H, 4.34; Br 13.39.

Ethyl O-*(3-*O*-acetyl-2,4,6-tri-*O*-benzoyl-β-*D*-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-1-thio-2-trichloroacetamido-β-*D*-glucopy-ranoside* (**30**), *ethyl 3-*O*-acetyl-2,4,6-tri-*O*-benzoyl-1-thio-β-*D*-galactopyranoside* (**31**), *and ethyl* O-*(3-*O*-acetyl-2,4,6-tri-*O*-benzoyl-β-*D*-galactopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-β-*D*-glucopyrano-syl)-(1→4)-*O*-3,6-di-*O*-benzyl-2-deoxy-1-thio-2-trichloroacetamido-β-*D*-gluco-pyranoside* (**37**).—A mixture of bromide **29** (570 mg, 0.95 mmol), acceptor **17** (525 mg, 0.95 mmol), and MS-4 Å (1 g) in abs CH_2Cl_2 (10 mL) was stirred under Ar for 1 h, then cooled to −25 °C and powdered AgOTf (470 mg, 1.83 mmol) was added. Under stirring, the reaction mixture was allowed to attain 0 °C during 1.5 h, then quenched with Et_3N (5 mL), filtered through a pad of Celite, diluted with CH_2Cl_2 (150 mL), washed with satd aq $NaHCO_3$, 3 M aq $Na_2S_2O_3$, dried, and concentrated. Chromatography (toluene → 3:1 toluene–EtOAc) of the residue on a column of silica gel (50 g) afforded, in order of elution, thiogalactoside **31** (220 mg, 40%) and a mixed fraction. It was subjected to gel-permeation chromatography on a 3 × 70 cm column of Bio-Beads SX3 in toluene to give lactosamine **30** (461 mg, 45%) and trisaccharide **37** (48 mg, 3.2%).

Data for lactosamine **30**: R_f 0.43 (5:1 toluene–EtOAc); $[\alpha]_D$ −16° (*c* 1, $CHCl_3$); NMR ($CDCl_3$): ^1H, see Table 2 for carbohydrate ring protons; δ 8.09–7.96 (2 d, 6 H, ortho protons of 3 Bz), 7.68-7.15 (m, 19 H, Ph), 6.96 (d, 1 H, $J_{N\text{-}H,2}$ 9 Hz, N-H), 5.11, 4.79, 4.77, 4.40 (4 d, 1 H each, *J* 11 Hz, 4 $PhCH_2$), 2.60 (m, 2 H, S–CH_2), 1.89 (s, 3 H, Ac), 1.20 (t, 3 H, *J* 7.2 Hz, S–CH_2CH_3); ^{13}C, see Table 4 for carbohydrate ring carbons; δ 170.3 ($OC(O)CH_3$), 165.9–165.1 (3 $PhC(O)O$), 161.7 ($N–C(O)CCl_3$), 138.2, 137.9 (2 ipso Bn), 133.7–127.8 (Ph), 74.5, 73.7 (2 $PhCH_2$), 24.6 (S–CH_2), 20.7 ($OC(O)CH_3$), 15.1 (S–CH_2CH_3). Anal. Calcd for $C_{53}H_{52}Cl_3NO_{14}S$: C, 59.75; H, 4.92; N, 1.31; S, 3.01. Found: C, 59.76; H, 5.15; N, 2.0; S, 2.66.

Data for thiogalactoside **31**: R_f 0.47 (5:1 toluene–EtOAc); $[\alpha]_D$ 47° (*c* 1, CH_2Cl_2); mp 124–126 °C (from EtOH); NMR ($CDCl_3$): ^1H, see Table 2 for carbohydrate ring protons; δ 8.22 (d, 2 H, *J* 7.5 Hz, ortho protons of 1 Bz), 8.07 (2 d, 4 H, ortho protons of 2 Bz); 7.70–7.35 (m, 9 H, Ph), 2.85 (m, 2 H, S–CH_2), 1.90 (s, 3 H, Ac), 1.35 (t, 3 H, *J* 7 Hz S–CH_2CH_3); ^{13}C, see Table 4 for carbohydrate ring carbons; δ 170.1 (O*C*(O)CH_3), 165.9–165.2 (3 PhC(O)O), 133.6–128.1 (Ph), 24.4 (S–CH_2), 20.4 (OC(O)*C*H_3), 14.9 (S–CH_2CH_3). Anal. Calcd for $C_{31}H_{30}O_9S$: C, 64.35; H, 5.23; S, 5.54. Found: C, 64.65; H, 5.27; S, 5.13.

Data for trisaccharide **37**: R_f 0.42 (5:1 toluene–EtOAc); $[\alpha]_D$ −27° (*c* 1, CH_2Cl_2); NMR ($CDCl_3$): ^1H, δ 8.10–7.90 (m, 6 H, ortho protons of 3 Bz), 7.69–7.05 (m, 29 H, Ph), 6.81 (d, 1 H, $J^{B}_{N-H,\ 2^B}$ 7.8 Hz, N–H^B), 6.45 (d, 1 H, $J_{N-H^{A},2^{A}}$ 8.2 Hz, N–H^A), 5.74 (d, 1 H, $J^{C\ C}_{4,\ 3}$ 3.3 Hz, H-4^C), 5.59 (dd, 1 H, $J^{C\ C}_{2,\ 1}$ 8, $J^{C\ C}_{2,\ 3}$ 10.2 Hz, H-2^C), 5.18 (dd, 1 H, H-3^C), 5.17 (d, 1 H, *J* 10.5 Hz, PhCH_2), 4.97 (d, 1 H, *J* 11.6 Hz, PhCH_2), 4.81 (d, 1 H, H-1^C), 4.74 (d, $J^{B\ B}_{1,\ 2}$ 6.7 Hz, H-1^B), 4.70 (d, $J^{A\ A}_{1,\ 2}$ 7.5 Hz, H-1^A), 2.70 (m, 2 H, S–CH_2), 1.88 (s, 3 H, Ac), 1.33 (t, 3 H, *J* 7.3 Hz S–CH_2CH_3); ^{13}C, δ 170.2 (N–*C*(O)CH_3), 165.9–164.9 (3 PhC-(O)O), 161.7 (2 N–C(O)CCl_3), 138.3–137.7 (4 ipso Bn), 133.8–127.5 (Ph), 100.0, 98.9 (C-1^C, C-1^B), 82.9 (C-1^A), 61.4 (C-6^C), 57.8 (C-2^B), 56.2 (C-2^A), 24.5 (S–CH_2), 20.7 (OC(O)*C*H_3), 15.1 (S–CH_2CH_3). Anal. Calcd for $C_{75}H_{74}Cl_6N_2O_{19}S$: C, 58.04; H, 4.81; N, 1.80; S, 2.07. Found: C, 58.09; H, 4.88; N, 1.66; S, 1.92.

*1,3,6-Tri-*O*-acetyl-2-azido-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-β-*D*-glucopyranose* (**33**).—A mixture of **32**[47] (682 mg, 1 mmol) and $Hg(OAc)_2$ (637 mg, 2 mmol) in glacial AcOH (10 mL) was stirred for 17 h at rt, then diluted with CH_2Cl_2 (100 mL), washed with satd aq KBr and water, dried, and concentrated. Chromatography (benzene → 2:1 benzene–EtOAc) of the residue on a short column of silica gel afforded **33** (635 mg, 96%) as a white foam: R_f 0.45 (1:1 EtOAc–toluene); $[\alpha]_D$ +4° (*c* 1, CH_2Cl_2); NMR ($CDCl_3$): ^1H, see Table 2 for carbohydrate ring protons; δ 2.18, 2.16, 2.13, 2.11, 2.08, 2.02, 1.96 (7 s, 21 H, 7 Ac). Anal. Calcd for $C_{26}H_{35}N_3O_{17}$: C, 47.20; H, 5.33; N, 6.35. Found: C, 47.15; H, 5.39; N, 6.31.

Ethyl O-*(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-(1→4)-3,6-di-*O*-acetyl-2-deoxy-1-thio-2-trichloroacetamido-β-*D*-glucopyranoside* (**36**).—To a solution of azide **33** (420 mg, 0.64 mmol) and *p*-TsOH·H_2O (121 mg, 0.64 mmol) in THF (12 mL) Pd–C (40 mg) was added, the mixture was degassed under vacuum with stirring, refilled with hydrogen, and stirred at rt. After 6 h, TLC indicated complete conversion into amine **34** (R_f 0.37 in 50:3:2 CH_2Cl_2–MeOH–AcOH), and the reaction mixture was cooled to 0 °C. Trichloroacetyl chloride (0.31 mL, 2.8 mmol) was added, followed by Et_3N (0.58 mL, 4.2 mmol) and after stirring for 1 h at 0 °C, the mixture was filtered through a pad of Celite, diluted with CH_2Cl_2 (50 mL), washed with satd aq $NaHCO_3$, dried, and concentrated. The residue was filtered through a short column of silica gel in 1:1 EtOAc–toluene to give **35** (375 mg, 76%) as a white foam: R_f 0.44 (1:1 EtOAc–toluene); ^1H NMR ($CDCl_3$): see Table 2 for carbohydrate ring protons; δ 7.30 (d, 1 H, $J_{N\text{-}H,2}$ 9 Hz, N-H), 2.16, 2.15, 2.10, 2.09, 2.07, 2.06, 1.98 (7 s, 21 H, 7 Ac); ^{13}C NMR ($CDCl_3$): δ 170.7–169.1 (O–*C*(O)CH_3), 162.4 (N–*C*(O)CCl_3), 101.3 (C-1^B), 91.9 (C-1^A), 75.7, 73.9, 71.7, 70.9, 70.8, 69.0, 66.6 (carbohydrate ring carbons), 61.8, 60.8 (C-6^A,C-6^B), 54.5 (C-2^A), 20.7–20.4 (O–C(O)-*C*H_3).

To a solution of **35** (277 mg, 0.35 mmol) and EtSH (0.044 mL, 0.6 mmol) in abs CH_2Cl_2 (5 mL) $BF_3{\cdot}Et_2O$ (0.067 mL, 0.53 mmol) was added. After stirring for 2 h at rt the reaction mixture was poured into satd aq $NaHCO_3$ (30 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The extracts were dried and concentrated, the residue was dissolved in EtOAc (0.3 mL), *i*-PrOH (3 mL) was added, followed by petroleum ether (3 mL), and the mixture was kept for 3 days at +5 °C. The crystals formed were filtered off and washed with cold *i*-PrOH to give **36** (225 mg, 80%): R_f 0.28 (2:3 EtOAc–toluene); mp 196–198 °C; $[\alpha]_D$ −93° (*c* 1, CH_2Cl_2); NMR ($CDCl_3$): ^1H, see Table 2 for carbohydrate ring protons; δ 7.19 (d, $J_{N\text{-}H,2}$ 9.4 Hz, N–H), 2.71 (m, 2 H, S–CH_2), 2.13 (s, 3 H, Ac), 2.10 (s, 3 H, Ac), 2.08 (s, 6 H, 2 Ac), 2.06 (s, 3 H, Ac), 1.95 (s 3 H, Ac), 1.27 (t, 3 H, *J* 7.5 Hz, S–CH_2CH_3); ^{13}C, δ

170.9–169.1 ($OC(O)CH_3$), 162.0 ($N–C(O)CCl_3$), 101.4 (C-1^B), 92.2 (CCl_3), 83.8 (C-1^A), 62.1, 60.7 (C-6^A, C-6^B), 54.4 (C-2^A), 24.1 ($S–CH_2$), 20.8–20.5 ($OC(O)CH_3$), 14.9 ($S–CH_2CH_3$). Anal. Calcd for $C_{28}H_{38}Cl_3NO_{16}S$: C, 42.95; H, 4.89; Cl, 13.58; N, 1.79; S, 4.09. Found: C, 43.19; H, 4.94; Cl, 13.00; N, 1.96; S, 3.92.

Allyl 2,3,6-tri-O-*benzoyl-4*-O-*(2,4,6-tri*-O-*benzoyl-β*-D-*galactopyranosyl)-β*-D-*galactopyranoside* (**41**), *allyl 3,6-di*-O-*benzoyl-4*-O-*(2,4,6-tri*-O-*benzoyl-β*-D-*galactopyranosyl)-β*-D-*galactopyranoside* (**42**), *and allyl 2,3,6-tri*-O-*benzoyl-4*-O-*(2,4-di*-O-*benzoyl-β*-D-*galactopyranosyl)-β*-D-*galactopyranoside* (**43**). —A suspension of allyl β-lactoside[50] (4.68 g, 12.25 mmol) and Bu_2SnO (4.52 g, 18.15 mmol) in abs MeOH (60 mL) was refluxed under Ar for 3 h until a homogeneous solution was formed. Under stirring, the pressure was diminished to 10 mmHg, the solvent was distilled off, and the solid residue was dried for 1 h at 60 °C/0.1 mmHg. Absolute benzene (150 mL) was added under Ar, followed by 4-methoxybenzyl chloride (2.5 mL, 18.31 mmol) and *n*-Bu_4NBr (5.93 g, 18.41 mmol), and the mixture was stirred for 20 h at 50 °C. The dark-brown mixture was poured into water (300 mL) and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts, containing bis-alkylated derivatives **39** and **40** were concentrated and treated as described below. The aqueous phase, containing monoalkylated product **38** was concentrated, dried in vacuo, the residue was dissolved in Py (15 mL), and treated with a solution of BzCl (10 mL, 86 mmol) in CH_2Cl_2 (20 mL) dropwise at 0 °C. After stirring for 18 h at rt, the excess of BzCl was decomposed with water (5 mL), the mixture was diluted with CH_2Cl_2 (300 mL), washed with 1 M aq H_2SO_4 (185 mL), water, satd aq $NaHCO_3$, dried, and concentrated. In order to remove 4-methoxybenzyl group, the residue was dissolved in CH_2Cl_2 (30 mL) and treated with 90% aq CF_3CO_2H (17 mL) for 30 min at rt. Coevaporation with toluene followed by chromatography (toluene → 3:1 toluene–EtOAc) on a column of silica gel (200 g) afforded **41** (3.19 g, 26% overall) as a white foam. The above mentioned organic extracts were treated in the same way to give (in order of elution) 2^A,3^B-diol **42** (549 mg, 5%) and 3^B,6^B-diol **43** (552 mg, 5%).

Data for monohydroxy derivative **41**: R_f 0.18 (1:8 EtOAc–toluene); $[\alpha]_D$ 4° (*c* 3, CH_2Cl_2); NMR ($CDCl_3$): ^1H, see Table 2 for carbohydrate ring protons; δ 8.15–7.85 (6 d, 12 H, *J* 7.5 Hz, 12 ortho protons of 6 Bz), 7.68–7.11 (m, 16 H, Ph), 7.02 (t, 2 H, *J* 8 Hz, Ph), 5.77 (m, 2 H, H-3^A, $CH_2CH{=}CH_2$), 5.17 (dd, 1 H, J_{trans} 17.5, J_{gem} 1.5 Hz, $CH_2CH{=}CH_2$), 5.09 (dd, 1 H, J_{cis} 10 Hz, $CH_2CH{=}CH_2$), 4.22 (m, 2 H, H-4^A, $OCH_2CH{=}CH_2$), 4.10 (dd, J_{gem} 14, J_{vic} 6.5 Hz, $OCH_2CH{=}CH_2$), 2.80 (broad s, 1 H, OH); ^{13}C, δ 166.4–165.2 (6 PhC(O)O), 133.5–128.0 (Ph, $CH_2CH{=}CH_2$), 117.7 ($CH{=}CH_2$), 100.6, 99.7 (C-1^A, C-1^B), 75.9, 73.6, 73.0, 72.8, 71.8, 71.7, 71.6, 70.1 (carbohydrate ring carbons), 70.1 ($OCH_2CH{=}CH_2$), 62.7, 61.6 (C-6^A, C-6^B). Anal. Calcd for $C_{57}H_{50}O_{17}$: C, 67.99; H, 5.00. Found: C, 67.82; H, 4.91.

Data for 2^A, 3^B-diol **42**: R_f 0.7 (1:3 EtOAc–toluene); $[\alpha]_D$ −18° (*c* 2, EtOAc); NMR ($CDCl_3$): ^1H, see Table 2 for carbohydrate ring protons; δ 8.05–7.89 (4 d, 8 H, *J* 7.6 Hz, 8 ortho protons of 4 Bz), 7.86 (d, 2 H, *J* 7.6 Hz, 2 ortho protons of 1 Bz), 7.66–7.26 (m, 13 H, Ph), 7.09 (t, 2 H, *J* 8 Hz, Ph), 5.84 (m, 1 H, $CH_2CH{=}CH_2$), 5.25 (d, 1 H, J_{trans} 17.3 Hz, $CH_2CH{=}CH_2$), 5.12 (d, 1 H, J_{cis} 10.5 Hz, $CH_2CH{=}CH_2$), 4.27 (dd, 1 H, J_{gem} 12.6, J_{vic} 5.1 Hz, $OCH_2CH{=}CH_2$), 4.06 (dd, $OCH_2CH{=}CH_2$), 2.80 (d, 1 H, *J* 5.1 Hz, 3^B-OH), 2.48 (broad s, 1 H, 2^A-OH); ^{13}C, δ 166.3–165.9 (5 PhC(O)O), 133.4–128.1 (Ph, $CH_2CH{=}CH_2$), 118.3 ($CH{=}CH_2$), 101.6, 100.3 (C-1^A, C-1^B), 70.5 ($OCH_2CH{=}CH_2$), 62.8, 61.8 (C-6^A, C-6^B). Anal. Calcd for $C_{50}H_{46}O_{16}$: C, 66.51; H, 5.14. Found: C, 66.38; H, 5.02.

Data for 3^B, 6^B-diol **43**: R_f 0.25 (1:3 EtOAc–toluene); $[\alpha]_D$ 29° (*c* 2, CH_2Cl_2); NMR ($CDCl_3$): ^1H, see Table 2 for carbohydrate ring protons; δ 8.15–7.85 (5 d, 10 H, *J* 7.6 Hz, 10 ortho protons of 5 Bz), 7.66–7.12 (m, 13 H, Ph), 7.00 (t, 2 H, *J* 8 Hz, Ph), 5.75 (m, 1 H, $CH_2CH{=}CH_2$), 5.19 (dd, 1 H, J_{trans} 17.3, J_{gem} 1.5 Hz, $CH_2CH{=}CH_2$), 5.07 (dd, 1 H, J_{cis} 10.5 Hz, $CH_2CH{=}CH_2$), 4.27 (dd, 1 H, J_{gem} 13.3, J_{vic} 4.8 Hz, $OCH_2CH{=}CH_2$), 4.07 (dd, J_{vic} 6.3 Hz, $OCH_2CH{=}CH_2$), 2.77 (broaden s, 1 H, OH), 2.48 (broad s, 1 H, OH); ^{13}C, δ 166.9–165.2 (5 PhC(O)O), 133.8–128.1 (Ph, $CH_2CH{=}CH_2$), 117.7 ($CH{=}CH_2$),

100.6, 99.5 (C-1^A, C-1^B), 69.9 (O*C*H$_2$CH=CH$_2$), 62.7 (C-6^A), 59.4 (C-6^B). Anal. Calcd for $C_{50}H_{46}O_{16}$: C, 66.51; H, 5.14. Found: C, 66.64; H, 5.07.

Allyl 2,4,6-tri-O-*benzoyl-β*-D-*galactopyranoside* (**45**).—Ortho-esterification of diol **44**[50] (1.7 g, 4 mmol) followed by hydrolysis with AcOH as described for the preparation of **27** and subsequent chromatography (1:5→2:1 EtOAc–petroleum ether) of the residue on a column of silica gel (50 g) gave **45** (1.84 g, 87%) as a white foam: R_f 0.75 (1:1 EtOAc–petroleum ether); $[\alpha]_D$ 1° (*c* 1, EtOAc); NMR ($CDCl_3$): ^{1}H, see Table 2 for carbohydrate ring protons; δ 8.19 (d 2 H, *J* 7.5 Hz, ortho protons of 1 Bz), 8.09 (d, 4 H, *J* 7.8 Hz, ortho protons of 2 Bz), 7.67–7.45 (m, 9 H, Ph), 5.89 (m, 1 H, OCH$_2$C*H*=CH$_2$), 5.29 (d, 1 H, J_{trans} 17.1 Hz, OCH$_2$CH=C*H*$_2$), 5.18 (d, 1 H, J_{cis} 10.5 Hz, OCH$_2$CH=C*H*$_2$), 4.63 (dd, 1 H, J_{vic} 7, J_{gem} 11 Hz, OC*H*$_2$CH=CH$_2$), 4.46 (dd, 1 H, J_{vic} 5.9 Hz, OC*H*$_2$CH=CH$_2$), 3.15 (broaden s, 1 H, OH). Anal. Calcd for $C_{30}H_{28}O_9$: C, 67.66; H, 5.30. Found: C, 67.50; H, 5.41.

2-Azidoethyl 2,3,6-tri-O-*benzoyl-4*-O-*(3*-O-*acetyl-2,4,6-tri*-O-*benzoyl-β*-D-*galactopyranosyl)-β*-D-*galactopyranoside* (**49**).—Conventional acetylation of allyl lactoside **41** with Ac_2O in Py afforded **46** quantitatively. Ozone was bubbled through a solution of **46** (1.29 g, 1.23 mmol) in 2:1 anhyd MeOH–CH_2Cl_2 (75 mL) at −78 °C until a blue color persisted; the excess of ozone was removed by a stream of Ar; $NaBH_4$ (467 mg, 12.35 mmol) was added with vigorous stirring, and the mixture was allowed to attain −5 °C over a period of 1.5 h. The next portion of $NaBH_4$ (480 mg, 12.7 mmol) was added and the mixture was stirred for 0.5 h at 0 °C. The reaction mixture was neutralized with AcOH, diluted with CH_2Cl_2, washed with water, satd aq $NaHCO_3$, concentrated, and dried in vacuo. To a solution of the crude alcohol **47** in abs CH_2Cl_2 (15 mL), Et_3N (0.36 mL, 2.6 mmol) was added at 0 °C, followed by methanesulfonyl chloride (0.21 mL, 2.6 mmol). After stirring for 1 h at 0 °C, the reaction was diluted with CH_2Cl_2, washed with satd aq $NaHCO_3$, dried, concentrated, and filtered through a short column of silica gel in 4:1 EtOAc–toluene to give mesylate **48** (1.05 g, 75%) and recovered alcohol **47** (193 mg, 15%) which was recycled. A mixture of mesylate **48** (1.05 g, 0.93 mmol), NaN_3 (0.65 g, 10 mmol) and 18-crown-6 (60 mg, 0.23 mmol) in abs DMF (8 mL) was stirred for 96 h at rt, then diluted with EtOAc, washed with water, dried, and concentrated. Chromatography (3:1 EtOAc–toluene) of the residue on a column of silica gel (50 g) gave azide **49** (723 mg, 72%): as a white foam: R_f 0.52 in 9:1 toluene–acetone; $[\alpha]_D$ 23° (*c* 1, $CHCl_3$); NMR ($CDCl_3$): ^{1}H, see Table 2 for carbohydrate ring protons; δ 1.8 (s, 3 H, OAc), 3.23 (dd, 1 H, CH_2N_3), 3.34 (dd, 1 H, CH_2N_3), 3.75 (m, OC*H*$_2$CH$_2$N$_3$), 4.02 (m, 1 H, OC*H*$_2$CH$_2$N$_3$), 7.09–7.69 (m, 18 H, Ph), 7.91–8.12 (m, 12 H, Ph); ^{13}C, see Table 4 for carbohydrate ring carbons; δ 20.3 (CH_3CO), 50.4 (CH_2N_3), 69.8 (O*C*H$_2$CH$_2$N$_3$), 164.6–165.7 (6 PhC(O)O), 169.9 (CH_3*C*(O)O). Anal. Calcd for $C_{58}H_{51}O_{18}N_3$: C, 64.62; H, 4.77; N, 3.89. Found C, 64.68; H, 4.81; N, 3.97.

2-Azidoethyl 2,4,6-tri-O-*benzoyl-β*-D-*galactopyranosyl-(1→4)-2,3,6-tetra*-O-*benzoyl-β*-D-*glycopyranoside* (**50**).—The reagent was prepared by dropwise addition, at 0 °C, of acetyl chloride (2 mL, 28 mmol) to abs MeOH (20 mL). After 10 min, the reagent was added to a solution of compound **49** (2.29 g, 2.14 mmol) in abs CH_2Cl_2 (10 mL). After 5 h at rt, the mixture was poured into ice-cold water and extracted with CH_2Cl_2 (200 mL). The organic phase was then washed with satd aq $NaHCO_3$ and water, dried, and concentrated. Chromatography (toluene→6:1 toluene–acetone) of the residue on a column of silica gel (200 g) afforded **50** (1.88 g, 86%) as a white foam: R_f 0.33 in 9:1 toluene–acetone; $[\alpha]_D$ 5° (*c* 1, $CHCl_3$); NMR ($CDCl_3$): ^{1}H, see Table 2 for carbohydrate ring protons; δ 2.9 (broad s, 1 H, OH), 3.28 (m, 1 H, CH_2N_3), 3.38 (m, 1 H, CH_2N_3), 3.67 (m, 1 H, OC*H*$_2$CH$_2$N$_3$), 3.99 (m, OC*H*$_2$CH$_2$N$_3$), 7.12–7.73 (m, 18 H, Ph), 7.88–8.09 (m, 12 H, Ph); ^{13}C, δ 50.5 (CH_2N_3), 61.6, 62.5 (C-6^A, C-6^B), 100.6, 101.1 (C-1^A, C-1^B). Anal. Calcd for $C_{56}H_{49}O_{17}N_3$: C, 64.92; H, 4.77; N, 4.06. Found C, 65.13; H, 4.73; N, 4.02.

Allyl 2-acetamido-6-O-*benzoyl-3*-O-*benzyl-2-deoxy-β*-D-*glucopyranoside* (**52**).—To a cold (−5 °C) solution of diol **51**[42] (1.24 g, 3.53 mmol) in CH_2Cl_2 (20 mL) and Et_3N (10

mL), BzCl (0.83 mL, 7.1 mmol) was added dropwise, and the reaction mixture was kept overnight at 0 °C. The mixture was diluted with CH_2Cl_2, washed with satd aq $NaHCO_3$, dried, and concentrated Crystallization from EtOAc–petroleum ether afforded **52** (1.13 g, 70%): R_f 0.55 (EtOAc); mp 209–211°C; $[\alpha]_D$ 5° (*c* 1, MeOH); NMR (10:1 $CDCl_3$–CD_3OD): ^1H, δ 8.01 (d, 2 H, *J* 7.6 Hz, ortho protons of Bz), 7.59–7.18 (m, 8 H, Ph), 5.70 (m, 1 H, $OCH_2CH{=}CH_2$), 5.19 (d, 1 H, J_{trans} 17.9 Hz, $OCH_2CH{=}CH_2$), 5.05 (d, 1 H, J_{cis} 10.8 Hz, $OCH_2CH{=}CH_2$), 4.83–4.55 (m, 5 H, H-1, H-6a, H-6b, $PhCH_2$), 4.23 (dd, 1 H, J_{gem} 12.8, J_{vic} 4.9 Hz, $OCH_2CH{=}CH_2$), 4.04 (dd, 1 H, J_{vic} 6.8 Hz, $OCH_2CH{=}CH_2$), 3.89 (t, 1 H, $J_{3,2} = J_{3,4}$ 9.6 Hz, H-3), 3.64–3.41 (m, 3 H, H-4, H-2, H-5), 1.83 (s, 3 H, Ac); ^{13}C, see Table 4 for carbohydrate ring carbons; δ 171.1 ($N{-}C(O)CH_3$), 166.9 (PhC(O)O), 138.3 (ipso Bn), 133.1 ($OCH_2CH{=}CH_2$), 133.8–127.7 (Ph), 117.4 ($OCH_2CH{=}CH_2$), 74.3 ($PhCH_2$), 69.8 ($OCH_2CH{=}CH_2$), 23.1 ($N{-}C(O)CH_3$). Anal. Calcd for $C_{25}H_{29}NO_7$: C, 65.92; H, 6.42; N, 3.07. Found: C, 65.69; H, 6.25; N, 2.96.

Allyl O-*(3*-O-*acetyl-2,4,6-tri*-O-*benzoyl-β*-D-*galactopyranosyl)-(1→4)-2-acetamido-6*-O-*benzoyl-3*-O-*benzyl-2-deoxy-β*-D-*glucopyranoside* (**53**).—A mixture of bromide **29** (1 g, 1.75 mmol), acceptor **52** (0.72 g, 1.58 mmol), and MS-4 Å (0.7 g) in abs CH_2Cl_2 (40 mL) was stirred under Ar at rt for 1 h, then cooled to −15 °C and powdered AgOTf (0.64 g, 2.4 mmol) was added. After stirring for 4 h at −5 °C, the reaction was terminated with Et_3N (1 mL), diluted with CH_2Cl_2 (100 mL), filtered through a pad of Celite, washed with satd aq $NaHCO_3$, 3 M aq $Na_2S_2O_3$, dried, and concentrated. Chromatography (toluene→1:2 toluene–EtOAc) of the residue on a column of silica gel (50 g) gave **53** (1.43 g, 93%) as a white foam: R_f 0.41 (3:2 toluene–EtOAc); $[\alpha]_D$ −4° (*c* 1, CH_2Cl_2); NMR ($CDCl_3$): ^1H, see Table 2 for carbohydrate ring protons; δ 8.10–7.93 (m, 8 H, ortho protons of 4 Bz), 7.65–7.15 (m, 17 H, Ph), 6.02 (d, 1 H, $J_{N-H,2}$ 8.8 Hz, N–H), 5.77 (m, 1 H, $OCH_2CH{=}CH_2$), 5.14 (dd, 1 H, J_{trans} 18, J_{gem} 1.6 Hz, $OCH_2CH{=}CH_2$), 5.07 (dd, 1 H, J_{cis} 10.5 Hz, $OCH_2CH{=}CH_2$), 4.91 (d, 1 H, *J* 12 Hz, $PhCH_2$), 4.81 (d, 1 H, $PhCH_2$), 4.17 (dd, 1 H, J_{gem} 13.5, J_{vic} 5.5 Hz, $OCH_2CH{=}CH_2$), 3.84 (dd, 1 H, J_{vic} 6.5 Hz, $OCH_2CH{=}CH_2$), 2.02 (s, 3 H, Ac), 1.89 (s, 3 H, Ac); ^{13}C, see Table 4 for carbohydrate ring carbons; 170.2 ($2\ C(O)CH_3$), 165.9–164.9 (PhC(O)O), 138.2 (ipso Bn), 133.6–127.6 (Ph), 117.2 ($OCH_2CH{=}CH_2$), 73.3 ($PhCH_2$), 69.7 ($OCH_2CH{=}CH_2$), 23.4 ($N{-}C(O)CH_3$), 20.5 ($OC(O)CH_3$). Anal. Calcd for $C_{54}H_{53}NO_{16}$: C, 66.73; H, 5.50; N, 1.44. Found: C, 66.38; H, 5.56; N, 1.43.

2-Acetamido-2-azidoethyl O-*(2,4,6-tri*-O-*benzoyl-β*-D-*galactopyranosyl)-(1→4)-6*-O-*benzoyl-3*-O-*benzyl-2-deoxy-β*-D-*glucopyranoside* (**55**).—Ozonolysis of **53** (1 g, 1.03 mmol) in MeOH (120 mL) and CH_2Cl_2 (60 mL), followed by reduction with $NaBH_4$ (1.56 g, 41 mmol), mesylation with MsCl (0.5 mL) and Et_3N (2 mL) in abs CH_2Cl_2 (120 mL) (→0.89 g, 82% overall yield) and mesylate→azide substitution as described above for the preparation of **49** gave 2-azidoethyl glycoside **54** (0.79 g, 93% yield). Subsequent HCl-catalyzed methanolysis of the acetate ester in **54** (0.79 g, 0.79 mmol) as described for the preparation of **50** afforded **55** (0.66 g, 87%) as a white foam: R_f 0.6 (3:2 toluene–acetone); $[\alpha]_D$ −6° (*c* 1, $CHCl_3$); NMR ($CDCl_3$): ^1H, see Table 2 for carbohydrate ring protons; δ 8.15–7.91 (4 d, 8 H, ortho protons of 4 Bz), 7.59–7.11 (m, 17 H, Ph), 5.97 (d, 1 H, $J_{N-H,2}$ 7.8 Hz, N–H), 4.95 (d, 1 H, *J* 11.6 Hz, $PhCH_2$), 4.73 (2 d, 2 H, $H\text{-}1^A$, $PhCH_2$), 3.84 (m, 1 H, $OCH_2CH_2N_3$), 3.44 (m, 1 H, $OCH_2CH_2N_3$), 3.35 (m, 1 H, CH_2N_3), 3.15 (m, 1 H, CH_2N_3), 1.91 (s, 3 H, Ac); ^{13}C, δ 170.6 ($N{-}C(O)CH_3$), 166.3–165.9 (4 PhC(O)O), 138.5 (ipso Bn), 133.6–127.6 (Ph), 100.4, 100.0 ($C\text{-}1^A$, $C\text{-}1^B$), 63.6, 62.0 ($C\text{-}6^A$, $C\text{-}6^B$), 54.7 ($C\text{-}2^A$), 50.5 (CH_2N_3), 23.4 ($N{-}C(O)CH_3$). Anal. Calcd for $C_{51}H_{50}N_4O_{15}$: C, 63.88; H, 5.26; N, 5.84. Found: C, 63.79; H, 5.32; N, 5.56.

Allyl O-*(3,4,6-tri*-O-*acetyl-2-deoxy-2-trichloroacetamido-β*-D-*glucopyranosyl)-(1→3)*-O-*(2,4,6-tri*-O-*benzoyl-β*-D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*benzoyl-β*-D-*glucopyranoside* (**56**).—(a) To a stirred solution of bromide **12** (223 mg, 0.42 mmol) and acceptor **41** (235 mg, 0.23 mmol) in abs CH_2Cl_2 (6 mL), powdered AgOTf (117 mg, 0.46 mmol) was added under Ar at −45 °C. After stirring for

3 h at −20 °C, the reaction was terminated by addition of satd aq $NaHCO_3$ (20 mL) and 3 M aq $Na_2S_2O_3$ (20 mL), and extracted with CH_2Cl_2 (50 mL); the extracts were dried and concentrated. Chromatography (petroleum ether → 6:4 EtOAc–petroleum ether) of the residue on a column of silica gel (30 g) afforded **56** (296 mg, 88%) as transparent glass: R_f 0.24 (2:3 EtOAc–petroleum ether); $[\alpha]_D$ 22° (*c* 2, CH_2Cl_2); NMR ($CDCl_3$): ^{1}H, see Table 2 for carbohydrate ring protons; δ 8.15–7.80 (6 d, 12 H, *J* 7.9 Hz, ortho-protons of 6 Bz), 7.65–7.18 (m, 16 H, Ph), 6.91 (t, 2 H, *J* 8 Hz, Ph), 6.45 (d, 1 H, $J_{N-H,2}$ 8 Hz, N–H), 5.74 (m, 2 H, H-3^A, CH_2CH=CH_2), 5.15 (dd, 1 H, J_{trans} 17, J_{gem} 1.5 Hz, CH_2CH=CH_2), 5.06 (dd, 1 H, J_{cis} 10 Hz, CH_2CH=CH_2), 4.22 (m, 1 H, OCH_2CH=CH_2), 4.05 (m, OCH_2CH=CH_2), 1.95, 1.93, 1.87 (3 s, 9 H, OAc); ^{13}C, δ 170.5, 170.1, 169.2 (3 OC(O)CH_3), 165.7–164.5 (6 PhC(O)O), 160.8 (N–C(O)CCl_3), 133.5–127.8 (Ph, CH_2CH=CH_2), 117.6 (CH=CH_2), 100.6, 99.7, 99.2 (3 C-1), 62.5, 61.9, 61.3 (3 C-6), 56.5 (C-2^C), 20.5 (3 OC(O)CH_3); APCI-MS: Calcd for $[C_{71}H_{66}Cl_3NO_{25}]^-$ 1437.3. Found 1437.8. Calcd for $[C_{71}H_{66}Cl_3NO_{25} + H_2O + H]^+$ 1456.3. Found 1456.3. Anal. Calcd for $C_{71}H_{66}Cl_3NO_{25}$: C, 59.24; H, 4.62; Cl, 7.39; N, 0.97. Found: C, 59.31; H, 4.59; Cl, 7.48; N, 1.03.

(b) A mixture of thioglycoside **11** (33 mg, 0.067 mmol), acceptor **41** (51 mg, 0.05 mmol), and MS-4 Å (300 mg) was stirred in abs CH_2Cl_2 (2 mL) under Ar for 1 h; NIS (15 mg, 0.067 mmol) was added, and the mixture was cooled to −15 °C. TfOH (0.006 mL, 0.072 mmol) was added, and after stirring for 1 h at −15 °C the reaction mixture was quenched with Et_3N, diluted with CH_2Cl_2 (30 mL), filtered through a pad of Celite, washed with satd aq $NaHCO_3$, 3 M aq $Na_2S_2O_3$, dried, and concentrated. Chromatography of the residue as in (a) gave **56** (50 mg, 68%): identical in all respect to the material described above.

2-Azidoethyl O-*(3,4,6-Tri*-O-*acetyl-2-deoxy-2-trichloroacetamido-β-*D-*glucopyranosyl)-(1→3)-*O-*(2,4,6-tri*-O-*benzoyl-β-*D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*benzoyl-β-*D-*glucopyranoside* (**57**).—(a) A mixture of thioglycoside **11** (78 mg, 0.154 mmol), acceptor **50** (121 mg, 0.117 mmol), and MS-4 Å (400 mg) in abs CH_2Cl_2 (2.5 mL) was stirred under Ar for 1 h; NIS (40 mg, 0.178 mmol) was added, and the mixture was cooled to −35 °C. TfOH was added in three equal 0.007 mL portions with 40 min intervals (in total 0.021 mL, 0.237 mmol). The reaction was terminated with Et_3N (0.1 mL), diluted with CH_2Cl_2 (30 mL), filtered through a pad of Celite, washed with satd aq $NaHCO_3$, 3 M aq $Na_2S_2O_3$, dried, and concentrated. Chromatography (toluene → 1:1 toluene–EtOAc) of the residue on a column of silica gel (20 g) gave **57** (111 mg, 65%): R_f 0.45 (2:1 toluene–EtOAc); $[\alpha]_D$ 17° (*c* 1, CH_2Cl_2); NMR ($CDCl_3$): ^{1}H, the spectrum was identical to that of **56** excepting the absence of the signals of allyl moiety at δ 5.74 (CH_2CH=CH_2), 5.15 (CH_2CH=CH_2), 5.06 (CH_2CH=CH_2), 4.22 (OCH_2CH=CH_2), 4.05 (OCH_2CH=CH_2), and the presence of two one-proton multiplets at δ 3.92, 3.64 (OC$H_2$$CH_2N_3$) and two one proton multiplets at δ 3.36 and 3.24 ($OCH_2CH_2N_3$); ^{13}C, the spectrum was identical to that of **56** excepting the absence of the signal of allyl moiety at δ 117.6 (CH=CH_2), and the presence of the signals at δ 69.4 (O$CH_2CH_2N_3$) and 50.4 (CH_2N_3); Anal. Calcd for $C_{70}H_{65}Cl_3N_4O_{25}$: C, 57.25; H, 4.46; N, 3.81. Found: C, 56.96; H, 4.60; N, 3.49.

(b) A mixture of oxazoline **19** (109 mg, 0.252 mmol), acceptor **50** (168 mg, 0.162 mmol), and MS-4 Å (300 mg) in abs CH_2Cl_2 (3 mL) was stirred under Ar for 1 h, then cooled to −35 °C, and TfOH (0.022 mL, 0.252 mmol) was added. After stirring for 0.5 h at −20 °C, the reaction was terminated with Et_3N (0.1 mL), diluted with CH_2Cl_2 (30 mL), filtered through a pad of Celite, washed with satd aq $NaHCO_3$, dried, and concentrated. Chromatography of the residue as in (a) gave **57** (157 mg, 66%): identical in all respect to the material described in (a).

2-Azidoethyl O-*(4*-O-*acetyl-3,6-di*-O-*benzyl-2-deoxy-2-trichloroacetamido-β-*D-*glucopyranosyl)-(1→3)-*O-*(2,4,6-tri*-O-*benzoyl-β-*D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*benzoyl-β-*D-*glucopyranoside* (**58**).—A mixture of thioglycoside **18** (281 mg, 0.47 mmol), acceptor **50** (467 mg, 0.45 mmol), and MS-4 Å (500 mg) in abs CH_2Cl_2 (5 mL) was stirred

under Ar for 1 h; NIS (120 mg, 0.53 mmol) was added, and the mixture was cooled to −20 °C. TfOH (0.003 mL, 0.034 mmol) was added, and stirring was continued for 1 h. The reaction was terminated with Et_3N (0.1 mL), diluted with CH_2Cl_2 (30 mL), filtered through a pad of Celite, washed with satd aq $NaHCO_3$, 3 M aq $Na_2S_2O_3$, dried, and concentrated. Chromatography (toluene → 7:1 toluene–acetone) of the residue on a column of silica gel (50 g) gave **58** (623 mg, 88%): R_f 0.39 (10:1 toluene–acetone); $[\alpha]_D$ 19° (*c* 1, EtOAc); NMR ($CDCl_3$): ^{1}H, see Table 2 for carbohydrate ring protons; δ 8.16, 8.12, 8.08 (3 d, 2 H each, *J* 7.6 Hz, 6 ortho protons of 3 Bz), 7.99 (d, 4 H, *J* 7.7 Hz, 4 ortho protons of 2 Bz), 7.82 (d, 2 H, *J* 7.8 Hz, ortho protons of 1 Bz), 7.70–7.12 (m, 26 H, Ph), 6.95 (t, 2 H, *J* 7.8 Hz, Ph), 6.81 (d, 1 H, $J_{N-H,2}$ 7 Hz, N–H^C), 4.52 (t, 2 H, *J* 10.5 Hz, $PhCH_2$), 4.43 (broad s, 2 H, $PhCH_2$), 3.97 (m, 1 H, $OCH_2CH_2N_3$), 3.68 (m, 1 H, $OCH_2CH_2N_3$), 3.40 (m, 1 H, CH_2N_3), 3.29 (m, 1 H, CH_2N_3), 1.81 (s, 3 H, Ac); ^{13}C, δ 169.5 ($OC(O)CH_3$), 165.8–164.6 (6 PhC(O)O), 161.6 ($N–C(O)CCl_3$), 138.9, 138.1 (2 ipso Bn), 137.8–127.4 (Ph), 101.0 (C-1^A), 100.8 (C-1^B), 98.3 (C-1^C), 62.3 (C-6^A), 61.9 (C-6^B), 59.0 (C-2^C), 50.5 (CH_2N_3), 20.6 ($OC(O)CH_3$). Anal. Calcd for $C_{80}H_{73}Cl_3N_4O_{23}$: C, 61.40; H, 4.70; N, 3.58. Found: C, 61.24; H, 4.93; N, 3.25.

Allyl O-*(3,4,6-tri*-O-*acetyl-2-deoxy-2-trichloroacetamido-β*-D-*glucopyranosyl)-(1→3)-2,4,6-tri*-O-*benzoyl-β*-D-*galactopyranoside* (**59**).—Glycosylation of galactoside **45** (1.25 g, 2.37 mmol) with thioglycoside **11** (1.6 g, 3.22 mmol) in abs CH_2Cl_2 (30 mL) promoted by NIS (730 mg, 3.24 mmol), TfOH (0.142 mL, 1.61 mmol), and MS-4 Å (1.5 g) at −20 °C for 40 min as described above for the preparation of **56** and subsequent chromatography (3:1 → 1:1 petroleum ether–EtOAc) afforded **59** (1.95 g, 86%) as a white foam: R_f 0.41 (1:1 petroleum ether–EtOAc); $[\alpha]_D$ 23° (*c* 1, EtOAc); NMR ($CDCl_3$): ^{1}H, see Table 2 for carbohydrate ring protons; δ 8.17–8.01 (m, 6 H, ortho-protons of 3 Bz), 7.69–7.45 (m, 9 H, Ph), 6.55 (d, 1 H, $J_{N-H,2}$ 9 Hz, N–H^B), 5.73 (m, 1 H, $OCH_2CH{=}CH_2$), 5.14 (d, 1 H, J_{trans} 18, $J_{gem} > 1$ Hz, $CH_2CH{=}CH_2$), 5.05 (m, 3 H, $CH_2CH{=}CH_2$, H-1^B, H-4^B), 4.32 (m, $OCH_2CH{=}CH_2$), 4.05 (m, $OCH_2CH{=}CH_2$), 2.01, 1.99, 1.92 (3 s, 9 H, OAc); APCI-MS: Calcd for $[C_{44}H_{44}Cl_3NO_{17} - H^+]^-$: 962.2. Found: 962.3. Anal. Calcd for $C_{44}H_{44}Cl_3NO_{17}$: C, 54.75; H, 4.59; Cl, 11.02; N, 1.45. Found: C, 54.50; H, 4.86; Cl, 11.32; N, 1.56.

2-Azidoethyl O-*(3,4,6-tri*-O-*acetyl-2-deoxy-2-trichloroacetamido-β*-D-*glucopyranosyl)-(1→3)-2,4,6-tri*-O-*benzoyl-β*-D-*galactopyranoside* (**60**).—Ozonolysis of **59** (442 mg, 0.46 mmol) followed by reduction with $NaBH_4$, mesylation, and mesylate → azide substitution as described above for the preparation of **49** and **54** gave 2-azidoethyl glycoside **60** (361 mg, 79% overall) as a white foam: R_f 0.5 (2:3 EtOAc–toluene); $[\alpha]_D$ 26° (*c* 1, EtOAc); NMR ($CDCl_3$): ^{1}H, the spectrum was identical to that of **59**, excepting the absence of the signals of allyl moiety at δ 5.73 ($OCH_2CH{=}CH_2$), 5.14 ($CH_2CH{=}CH_2$), 5.05 ($CH_2CH{=}CH_2$), 4.32 ($OCH_2CH{=}CH_2$), 4.05 ($OCH_2CH{=}CH_2$), and the presence of four one-proton multiplets at δ 4.00, 3.69 ($OCH_2CH_2N_3$), 3.39, 3.27 (CH_2N_3); ^{13}C, δ 170.8, 170.3, 169.6 (3 $OC(O)CH_3$), 166.2, 165.6, 165.1 (3 PhC(O)O), 161.6 ($N–C(O)CCl_3$), 133.5–128.4 (Ph), 101.4, 99.3 (2 C-1), 62.9, 61.3 (2 C-6), 56.5 (C-2^B), 50.6 (CH_2N_3), 20.7, 20.6, 20.4 (3 $OC(O)CH_3$). APCI-MS: Calcd for $[C_{44}H_{44}Cl_3NO_{17} - H^+]^-$: 991.2. Found: 991.1. Anal. Calcd for $C_{43}H_{43}Cl_3N_4O_{17}$: C, 51.95; H, 4.36; Cl, 10.70; N, 5.64. Found: C, 52.09; H, 4.72; Cl, 10.45; N, 5.46.

Allyl O-*(3,4,6-tri*-O-*acetyl-2-deoxy-2-trichloroacetamido-β*-D-*glucopyranosyl)-(1→3)*-O-*[3,4,6-tri*-O-*acetyl-2-deoxy-2-trichloroacetamido-β*-D-*glucopyranosyl-(1→6)]*-O-*(2,4-di*-O-*benzoyl-β*-D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*benzoyl-β*-D-*glucopyranoside* (**61**).—Bis-glycosylation of diol **43** (149 mg, 0.165 mmol) with thioglycoside **11** (248 mg, 0.5 mmol) in abs CH_2Cl_2 (8 mL) promoted by NIS (112 mg, 0.5 mmol), TfOH (0.044 mL, 0.5 mmol), and MS-4 Å (2 g) at −15 °C for 2 h as described above for the preparation of **56** and subsequent chromatography (benzene → 2:3 benzene–EtOAc) afforded **61** (194 mg, 66%) as a white foam: R_f 0.24 (2:3 EtOAc–toluene); $[\alpha]_D$ 18° (*c* 1, CH_2Cl_2); NMR ($CDCl_3$): ^{1}H, see Table 2 for carbohydrate ring protons; δ 8.10–7.88 (m, 8 H, ortho-pro-

tons of 4 Bz), 7.82 (d, 2 H, *J* 7.9 Hz, ortho-protons of 1 Bz), 7.65–7.18 (m, 13 H, Ph), 7.11 (m, 3 H, Ph, N–H^{D}), 6.51 (d, 1 H, $J_{N-H,2}$ 9 Hz, N–H^{C}), 5.66 (m, 2 H, H-3^{A}, $CH_2CH{=}CH_2$), 5.15 (dd, 1 H, J_{trans} 16.9, J_{gem} 1.8 Hz, $CH_2CH{=}CH_2$), 5.06 (dd, 1 H, J_{cis} 10 Hz, $CH_2CH{=}CH_2$), 4.22 (m, 1 H, $OCH_2CH{=}CH_2$), 4.05 (m, $OCH_2CH{=}CH_2$), 2.11–1.84 (6 s, 18 H, Ac); ^{13}C, δ 171.1–169.2 ($OC(O)CH_3$), 165.9–164.6 (PhC(O)O), 162.0, 161.4 (2 N–$C(O)CCl_3$), 133.6–128.1 (Ph, $CH_2CH{=}CH_2$), 117.7 ($CH{=}CH_2$), 100.9, 99.4 (2 C-1), 98.9 (2 C-1), 66.5 (C-6^{B}), 62.6, 61.8, 60.8 (C-6^{A}, C-6^{C}, C-6^{D}), 57.0 56.3 (C-2^{C}, C-2^{D}), 20.8–20.4 (3 $OCOCH_3$). Anal. Calcd for $C_{78}H_{78}Cl_6N_2O_{32}$: C, 52.98; H, 4.45; Cl, 12.03; N, 1.58. Found: C, 52.86; H, 4.31; Cl, 11.71; N, 1.33.

2-Azidoethyl O-*(3,4,6-tri*-O-*acetyl-2-deoxy-2-trichloroacetamido-β-*D-*glucopyranosyl)-(1→3)*-O-*[3,4,6-tri*-O-*acetyl-2-deoxy-2-trichloroacetamido-β-*D-*glucopyranosyl)-(1→6]*-O-*(2,4-di*-O-*benzoyl-β-*D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*benzoyl-β-*D-*glucopyranoside* (**62**).—Ozonolysis of **61** (177 mg, 0.1 mmol) followed by reduction with $NaBH_4$, mesylation, and mesylate→azide substitution as described above for the preparation of **49** and **54** gave 2-azidoethyl glycoside **62** (134 mg, 75% overall) as a white foam: R_f 0.24 (4:1 toluene–acetone); $[\alpha]_D$ 16° (*c* 1, acetone); NMR ($CDCl_3$): ^{1}H, the spectrum was identical to that of **61** excepting the disappearance of the signals of the allyl moiety at δ 5.66 ($CH_2CH{=}CH_2$), 5.15 ($CH_2CH{=}CH_2$), 5.06 ($CH_2CH{=}CH_2$), 4.22 ($OCH_2CH{=}CH_2$), 4.05 ($OCH_2CH{=}CH_2$) and the presence of four one-proton multiplets at δ 3.90, 3.45 ($OCH_2CH_2N_3$), 3.35, 3.20 (CH_2N_3). ^{13}C, the spectrum was identical to that of **61** excepting the disappearance of the signal of the allyl moiety at δ 117.7 ($CH{=}CH_2$) and the presence of the signal at δ 50.5 (CH_2N_3). Anal. Calcd for $C_{77}H_{77}Cl_6N_5O_{32}$: C, 51.46; H, 4.32; N, 3.90. Found: C, 51.40; H, 4.44; N, 3.70.

2-Azidoethyl O-*(2,3,4,6-tetra*-O-*acetyl-β-*D-*galactopyranosyl)-(1→4)*-O-*(3,6-di*-O-*acetyl-2-deoxy-2-trichloroacetamido-β-*D-*glucopyranosyl)-(1→3)*-O-*(2,4,6-tri*-O-*benzoyl-β-*D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*benzoyl-β-*D-*glucopyranoside* (**63**).—Glycosylation of acceptor **50** (200 mg, 0.193 mmol) with thioglycoside **36** (206 mg, 0.263 mmol) in abs CH_2Cl_2 (7 mL) promoted by NIS (65 mg, 0.29 mmol), TfOH (0.023 mL, 0.263 mmol), and MS-4 Å (900 mg) for 1 h at −20 °C as described for the preparation of **56** and subsequent chromatography (petroleum ether→1:1 petroleum ether–EtOAc) of the residue on a column of silica gel (20 g) followed by rechromatography (toluene→5:1 toluene–acetone) gave **63** (259 mg, 76%): R_f 0.17 (1:1 petroleum ether–EtOAc); $[\alpha]_D$ 10° (*c* 2, CH_2Cl_2); NMR ($CDCl_3$): ^{1}H, δ see Table 2 for carbohydrate ring protons; δ 8.25–7.85 (5 d, 10 H, *J* 8 Hz, 10 ortho-protons of 5 Bz), 7.75 (d, 2 H, *J* 8 Hz, 2 ortho protons of 1 Bz), 7.65–7.18 (m, 16 H, Ph), 6.81 (t, 2 H, *J* 8 Hz, Ph), 6.40 (d, 1 H, $J_{N-H,2}$ 8.8 Hz, N–H), 3.94 (m, 1 H, $OCH_2CH_2N_3$), 3.62 (m, 1 H, $OCH_2CH_2N_3$), 3.34 (m, 1 H, CH_2N_3), 3.24 (m, 1 H, CH_2N_3), 2.19 (s, 3 H, Ac), 2.01 (3 s, 9 H, 3 Ac), 1.80 (s, 3 H, Ac), 1.75 (s, 3 H, Ac); ^{13}C, δ 170.3–169.4 ($CH_3C(O)O$), 165.9–164.4 (PhC(O)O), 161.4 (N–$C(O)CCl_3$), 133.6–125.3 (Ph), 101.2, 101.0, 100.7, 99.9 (4 C-1), 91.7 (CCl_3), 62.4, 61.9, 61.1, 60.8 (4 C-6), 55.7 (C-2^{C}), 50.5 (CH_2N_3), 21.4–20.6 ($OC(O)CH_3$). Anal. Calcd for $C_{82}H_{81}Cl_3N_4O_{33}$: C, 56.06; H, 4.65; Cl, 6.05; N, 3.19. Found: C, 56.19; H, 4.81; Cl, 5.73; N, 3.30.

2-Azidoethyl O-*(3*-O-*acetyl-2,4,6-tri*-O-*benzoyl-β-*D-*galactopyranosyl)-(1→4)*-O-*(3,6-di*-O-*benzyl-2-deoxy-2-trichloroacetamido-β-*D-*glucopyranosyl)-(1→3)*-O-*(2,4,6-tri*-O-*benzoyl-β-*D-*galactopyranosyl)-(1→4)-2-acetamido-6*-O-*benzoyl-3*-O-*benzyl-2-deoxy-β-*D-*glucopyranoside* (**64**).—Glycosylation of lactosamine acceptor **55** (150 mg, 0.16 mmol) with lactosamine thioglycoside **30** (220 mg, 0.23 mmol) in abs CH_2Cl_2 (5 mL) promoted by NIS (70 mg, 0.31 mmol), TfOH (0.028 mL, 0.31 mmol), and MS-4 Å (500 mg) for 3 h at −20 °C as described for the preparation of **56** and subsequent chromatography (toluene→6:1 toluene–acetone) of the residue on a column of silica gel (30 g) followed by gel-permeation chromatography on a 3×70 cm column of Bio-Beads SX3 in toluene gave **64** (212 mg, 69%): R_f 0.36 (3:1 toluene–acetone); $[\alpha]_D$ 11° (*c* 1, EtOAc); NMR ($CDCl_3$): ^{1}H, see Table 2 for carbohydrate ring protons; δ 8.15–7.93 (m, 14 H, ortho protons of 7 Bz),

7.70–7.12 (m, 36 H, Ph), 6.70 (d, 1 H, $J_{N-H^C,2^C}$ 7.7 Hz, N–H^C), 6.06 (d, 1 H, $J_{N-H^A,2^A}$ 8.3 Hz, N–H^A), 5.09, 4.58 (2 d, 1 H each, *J* 11 Hz, $PhCH_2$), 4.86, 4.78 (2 d, 1 H each, *J* 11.9 Hz, $PhCH_2$), 4.62, 4.30 (2 d, 1 H each, *J* 11.9 Hz, $PhCH_2$), 3.71, 3.63 (2 m, $OCH_2CH_2N_3$), 3.50, 3.32 (2 m, CH_2N_3), 2.05 (s, 3 H, Ac), 1.92 (s, 3 H, Ac); ^{13}C, δ 170.6, 170.4 ($C(O)CH_3$), 166.2–165.1 (7 PhC(O)O), 161.8 (N–$C(O)CCl_3$), 138.5, 138.4, 138.2 (3 ipso Bn), 133.8–127.5 (Ph), 100.5, 100.4, 100.2, 99.1 (4 C-1), 58.2 (C-2^C), 53.5 (C-2^A), 50.6 (CH_2N_3), 23.5 (N–C(O)CH_3), 20.7 (OC(O)CH_3). Anal. Calcd for $C_{102}H_{96}Cl_3N_5O_{29}$: C, 62.43; H, 4.93; Cl, 5.43; N, 3.57. Found: C, 62.56; H, 5.40; Cl, 5.41; N, 3.45.

Allyl O-*(2,3,4,6-tetra*-O-*acetyl-β*-D-*galacto-pyranosyl)-(1→3)*-O-*(4,6-di*-O-*acetyl-2-de-oxy-2-trichloroacetamido-β*-D-*glucopyranosyl)-(1→3)*-O-*(2,4,6-tri*-O-*benzoyl-β*-D-*galacto-pyranosyl)-(1→4)-2,3,6-tri*-O-*benzoyl-β*-D-*glucopyranoside* (**65**).—Glycosylation of acceptor **41** (182 mg, 0.18 mmol) with donor **24** (104 mg, 0.133 mmol) in abs CH_2Cl_2 (5 mL) promoted by NIS (36 mg, 0.16 mmol), TfOH (0.024 mL, 0.28 mmol), and MS-4 Å (500 mg) for 1 h at −20 °C as described for the preparation of **56** and subsequent chromatography (toluene→5:1 toluene–acetone) of the residue on a column of silica gel (30 g) gave recovered acceptor **41** (73 mg, 40%) and tetrasaccharide **65** (156 mg, 70% based on the donor): R_f 0.14 (8:1 toluene–acetone); $[\alpha]_D$ 13° (*c* 2, CH_2Cl_2); NMR ($CDCl_3$): ^{1}H, see Table 2 for carbohydrate ring protons; δ 8.15–7.95 (3 d, 6 H, *J* 8 Hz, 6 ortho protons of 3 Bz), 7.90 (t, 4 H, *J* 8 Hz, 4 ortho protons of 2 Bz), 7.75 (d, 2 H, *J* 8 Hz, 2 ortho protons of 1 Bz), 7.65–7.18 (m, 16 H, Ph), 6.90 (m, 3 H, Ph, N–H), 5.71 (m, 2 H, H-3^A, $CH_2CH{=}CH_2$), 5.15 (dd, 1 H, J_{trans} 17, J_{gem} 1.8 Hz, $CH_2CH{=}CH_2$), 5.06 (dd, 1 H, J_{cis} 10.5 Hz, $CH_2CH{=}CH_2$), 4.24 (m, 1 H, $OCH_2CH{=}CH_2$), 4.05 (m, $OCH_2CH{=}CH_2$), 2.08 (s, 3 H, Ac), 1.95 (2 s, 6 H, 2 Ac), 1.89 (3 s, 9 H, 3 Ac); ^{13}C, δ 171.1–168.9 (6 OC(O)CH_3), 165.9–164.7 (5 PhC(O)O), 161.7 (N–$C(O)CCl_3$), 133.6–127.8 (Ph, $CH_2CH{=}CH_2$), 117.7 ($CH{=}CH_2$), 100.8, 99.7, 99.6, 98.0 (4 C-1), 62.5, 61.9, 61.6, 60.8, (4 C-6), 59.1 (C-2^C), 20.6 (OCOCH_3). Anal. Calcd for $C_{83}H_{82}Cl_3NO_{33}$: C, 57.69; H, 4.78; Cl, 6.16; N, 0.81. Found: C, 57.57; H, 5.00; Cl, 6.12; N, 1.09.

2-Azidoethyl O-*(2,3,4,6-tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→3)*-O-*(4,6-di*-O-*acetyl-2-deoxy-2-trichloroacetamido-β*-D-*glucopyran-osyl)-(1→3)*-O-*(2,4,6-tri*-O-*benzoyl-β*-D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*benzoyl-β*-D-*glucopyranoside* (**66**).—Glycosylation of acceptor **50** (252 mg, 0.243 mmol) with thioglycoside **24** (164 mg, 0.209 mmol) in abs CH_2Cl_2 (7.5 mL) promoted by NIS (65 mg, 0.29 mmol), TfOH (0.035 mL, 0.4 mmol), and MS-4 Å (900 mg) for 1 h at −20 °C as described for the preparation of **56** and subsequent chromatography (20:1 toluene–MeOH) of the residue on a column of silica gel (30 g) followed by rechromatography (toluene→13:1 toluene–isopropanol) gave recovered acceptor **50** (143 mg, 57%) and tetrasaccharide **66** (184 mg, 50% based on the donor): R_f 0.25 (20:1 toluene–MeOH); $[\alpha]_D$ 15° (*c* 1, CH_2Cl_2); NMR ($CDCl_3$): ^{1}H, the spectrum was identical to that of **65**, excepting the absence of the signal of the allyl moiety at δ 5.71 ($CH_2CH{=}CH_2$), 5.15 ($CH_2CH{=}CH_2$), 5.06 ($CH_2CH{=}CH_2$), 4.24 ($OCH_2CH{=}CH_2$), 4.05 ($OCH_2CH{=}CH_2$), and the presence of the multiplets at δ 3.95, 3.59 ($OCH_2CH_2N_3$), 3.35, 3.22 (CH_2N_3). Anal. Calcd for $C_{82}H_{81}Cl_3N_4O_{33}$: C, 56.06; H, 4.65; Cl, 6.05; N, 3.19. Found: C, 55.86; H, 4.91; Cl, 6.45; N, 2.96.

Allyl O-*(2-deoxy-4,6*-O-*isopropylidene-2-trichloroacetamido-β*-D-*glucopyranosyl)-(1→3)*-O-*(2,4,6-tri*-O-*benzoyl-β*-D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*benzoyl-β*-D-*glucopyranoside* (**75**).—The reagent was prepared by dropwise addition, at 0 °C, of acetyl chloride (0.4 mL, 5.6 mmol) to abs MeOH (10 mL). After 10 min, the reagent was added to solid **56** (260 mg, 0.18 mmol) and the mixture was kept for 26 h at rt. Solid $NaHCO_3$ was added in small portions until gas evolution ceased, the mixture was poured into aq $NaHCO_3$ and extracted with CH_2Cl_2 (200 mL). The extracts were dried and concentrated to give triol **74** (219 mg, 92%) as transparent glass: R_f 0.57 (EtOAc). A solution of triol **74** (203 mg, 0.154 mmol) and ±CSA (5 mg) in 2,2-dimethoxypropane (2.5 mL) was stirred for 4 h at rt and then for 1 h at 50 °C, Et_3N (0.05 mL) was added, and the mixture

was coevaporated with toluene (3 × 5 mL). Crystallization from 3:1 acetone–petroleum ether (8 mL) gave **75** (162 mg, 77%): R_f 0.44 (1:1 EtOAc–petroleum ether); $[\alpha]_D$ 7° (*c* 2, CH_2Cl_2); mp 157–159 °C; NMR ($CDCl_3$): ^{1}H, see Table 2 for carbohydrate ring protons; δ 8.20–7.75 (6 d, 12 H, *J* 8 Hz, 12 ortho protons of 6 Bz), 7.65–7.30 (m, 16 H, Ph), 6.93 (t, 2 H, *J* 8 Hz, Ph), 6.82 (d, 1 H, $J_{N-H,2}$ 8 Hz, N–H), 5.72 (m, 2 H, H-3^A, $OCH_2CH{=}CH_2$), 5.14 (dd, 1 H, J_{trans} 18.2, J_{gem} 1.4 Hz, $CH_2CH{=}CH_2$), 5.05 (dd, 1 H, J_{cis} 10.4 Hz, $CH_2CH{=}CH_2$), 4.25 (dd, 1 H, J_{gem} 13.2, J_{vic} 5 Hz, $OCH_2CH{=}CH_2$), 4.05 (m, 2 H, H-3^B, $OCH_2CH{=}CH_2$), 2.89 (broaden s, 1 H, OH), 1.39, 1.31 (2 s, 6 H, 2 CH_3); ^{13}C, δ 165.4–162.4 (6 PhC(O)O), 160.9 (N–*C*(O)CCl_3), 133.6–127.8 (Ph), 117.7 ($CH{=}CH_2$), 100.6, 99.7, 98.7 (3 C-1), 99.7 $(CH_3)_2C$), 70.0 ($OCH_2CH{=}CH_2$), 62.6, 61.8, 61.5 (3 C-6), 59.9 (C-2^C), 28.8, 18.9 (2 CH_3). Anal. Calcd for $C_{68}H_{64}Cl_3NO_{22}$: C, 60.34; H, 4.77; Cl, 7.86; N, 1.03. Found: C, 60.27; H, 4.79; Cl, 8.01; N, 0.96.

2-Azidoethyl O-*(2-deoxy-4,6-*O*-isopropylidene-2-trichloroacetamido-β-*D*-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzoyl-β-*D*-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzoyl-β-*D*-glucopyranoside* (**77**).—Deacetylation of **57** (251 mg, 0.17 mmol) with AcCl (0.2 mL, 2.8 mmol) in MeOH (5 mL) for 18 h at rt as described for the preparation of **75** and subsequent chromatography (toluene→8:1 toluene–MeOH) on a column of silica gel (20 g) afforded triol **76** (197 mg, 86%) as a white foam: R_f 0.34 (7:1 toluene–MeOH). Acetonation of **76** (176 mg, 0.131 mmol) with 2,2-dimethoxypropane (5 mL) and TsOH (10 mg) for 3 h at rt as described for the preparation of **75** followed by chromatography (toluene→1:1 toluene–EtOAc) on a column of silica gel (20 g) afforded **77** (162 mg, 90%) as a white foam: R_f 0.27 (5:2 toluene–EtOAc); $[\alpha]_D$ 11° (*c* 1, EtOAc); NMR ($CDCl_3$): ^{1}H, the spectrum was identical to that of **75** excepting the absence of the signals of the allyl moiety at δ 5.72 ($OCH_2CH{=}CH_2$), 5.14, 5.05 ($CH_2CH{=}CH_2$), 4.25, 4.05 ($OCH_2CH{=}CH_2$) and the presence of the signals at δ 3.89, 3.63 ($OCH_2CH_2N_3$), 3.38, 3.24 (CH_2N_3); ^{13}C, the spectrum was identical to that of **75**, excepting the absence of the signals of allyl moiety at δ 117.7 ($CH{=}CH_2$), 70.0 ($OCH_2CH{=}CH_2$), and the presence of the signals at 68.5 ($OCH_2CH_2N_3$), 50.5 (CH_2N_3). Anal. Calcd for $C_{67}H_{63}Cl_3N_4O_{22}$: C, 58.20; H, 4.59; Cl, 7.69; N, 4.05. Found C, 58.37; H, 4.72; N, 3.84.

Allyl O-*[methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-*D*-glycero-α-*D*-galacto-non-2-ulopyranosyl)onate]-(2→3)-*O*-(2,4,6-tri-*O*-acetyl-β-*D*-galactopyranosyl)-(1→3)-*O*-(2-deoxy-2-trichloroacetamido-β-*D*-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzoyl-β-*D*-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzoyl-β-*D*-glucopyranoside* (**79**).—A 0.1 M solution of TMSOTf in CH_2Cl_2 was prepared as follows. Abs CH_2Cl_2 (5 mL) was stirred under Ar with MS-4 Å (2.5 g) for 1 h, then TMSOTf (0.09 mL, 0.5 mmol) was added, and the mixture was stirred for 1 h. Sieves were allowed to sediment, and 0.03 mL of this solution were added with a syringe to a mixture of imidate **73** (21 mg, 0.023 mmol), acceptor **75** (41 mg, 0.03 mmol), and MS-4 Å in abs CH_2Cl_2 (2 mL) under Ar at −20 °C. After stirring overnight at 0 °C, the reaction was terminated by addition of solid $NaHCO_3$ (100 mg), the mixture was filtered through a pad of Celite, diluted with CH_2Cl_2 (30 mL), washed with satd aq $NaHCO_3$, dried, and concentrated. For deacetonation, a solution of the residue in CH_2Cl_2 (5 mL) was treated with 90% aq CF_3CO_2H (0.5 mL) for 0.5 h at rt, then coevaporated with toluene (4 × 10 mL) with the bath temperature 25 °C. Chromatography (EtOAc) of the residue on a column of silica gel (12 g) gave (in order of elution) triol **74** (17 mg, 41%) and pentasaccharide **79** (36 mg, 75% based on imidate): R_f 0.29 (EtOAc); $[\alpha]_D$ 12° (*c* 1, CH_2Cl_2); NMR ($CDCl_3$): ^{1}H, see Table 3 for carbohydrate ring protons; δ 8.12–8.03 (3 d, 6 H, *J* 7.9 Hz, ortho protons of 3 Bz), 7.95 (2 d, 4 H, *J* 8 Hz, ortho protons of 2 Bz), 7.75 (d, 2 H, *J* 8 Hz, ortho protons of 1 Bz), 7.70–7.13 (m, 16 H, Ph), 6.89 (t, 2 H, *J* 8 Hz, Ph), 6.80 (d, 1 H, *J* 6.9 Hz, N–H^C), 5.71 (m, 3 H, H-4^B, H-3^A, $OCH_2CH{=}CH_2$), 5.16 (dd, 1 H, J_{trans} 17.3 Hz, $CH{=}CH_2$), 5.06 (d, 2 H, *J* 10.4 Hz, $CH{=}CH_2$, N–H^E), 4.23 (dd, 1 H, J_{vic} 4.8, J_{gem} 13 Hz, $OCH_2CH{=}CH_2$), 4.02 (m, $OCH_2CH{=}CH_2$), 3.79 (s, 3 H, OMe), 2.18, 2.13, 2.09 (3 s, 9 H,

Table 3
Chemical shifts (δ, ppm) and coupling constants (J, Hz) for carbohydrate ring protons in ^{1}H NMR spectra of compounds **8**, **9**, **79**, **83** in the solvent specified

Compound (solvent)	Unit	H-1 ($J_{1,2}$)	H-2 ($J_{2,3}$)	H-3eq ($J_{3eq,4}$)	H-3ax ($J_{3ax,4}$)	H-4 ($J_{4,5}$)	H-5 ($J_{5,6a}$)	H-6a ($J_{6a,6b}$)	H-6b ($J_{6b,5}$)	H-7 ($J_{7,8}$)	H-8 ($J_{8,9a}$)	H-9a ($J_{9a,9b}$)	H-9b ($J_{9b,8}$)
8	Glc^A	4.54 (7.8)	3.38 (8)		3.66	3.65	3.63 (1.9)	3.99	3.81				
(D_2O)	Gal^B	4.44 (7.9)	3.58		3.74 (3.3)	4.16 (0)	3.71	3.71–3.78					
	GlcN^C	4.7 (8.3)	3.80		3.73	3.74	3.58	3.96	3.87				
	Gal^D	4.56 (7)	3.57		4.11 (3)	3.94 (0)	3.71	3.71–3.78					
	Neu^E			2.76 (4.4) [a]	1.80 (12.1)	3.69	3.81	3.64		3.58	3.88	3.87	3.65
9	Glc^A	4.51 (7.9)	3.35 (8.3)		3.64	3.62	3.59 (>1)	3.94 (10.9)	3.77				
(D_2O)	Gal^B	4.41 (7.9)	3.58		3.69 (3)	4.11 (0)	3.67	3.75–3.69					
	GlcN^C	4.72 (8.3)	3.83		3.77	3.56	3.44	3.87	3.75				
	Gal^D	4.47 (7.8)	3.52 (9.7)		4.05 (2.9)	3.91 (0)	3.65	3.75–3.69					
	Neu^E			2.73 (4.4) [b]	1.75 (12.1)	3.56	3.81	3.62		3.67	3.84	3.82	3.61
79	Glc^A	4.70 (7.9)	5.46 (9.3)		5.70 (9.6)	4.14 (9.5)	3.69 (2)	4.40 (0)	4.40 (2)				
($CDCl_3$)	Gal^B	4.63 (7.8)	5.52 (8.1)		3.95	5.75 (0)	3.69 (5.6)	3.73 (10.9)	3.30				
	GlcN^C	5.21 (8.2)	2.99		4.11	3.30 (7.1)	3.53	3.80	3.80				
	Gal^D	4.56 (7.8)	4.92 (7.0)		4.50 (3.2)	4.81 (0)	3.89	4.04	4.04				
	Neu^E			2.53 (4.4) [c]	1.60 (12.6)	4.88	3.96 (10.2)	3.57 [d]		5.31 (9.5)	5.26	4.10	3.96
83	Glc^A	4.63 (7.8)	5.36 (9.4)		5.65 (9.4)	4.04 (9.4)	3.68 (>1)	4.40 (11)	4.32				
($CDCl_3$)	Gal^B	4.53 (7.8)	5.48 (10.3)		3.97 (3.8)	5.50 (0)	3.57	3.85 (11.5)	3.05 (8)				
	GlcN^C	4.92 (6.9)	3.21		3.84	3.86	3.50	3.63–3.72					
	Gal^D	4.67 (8)	4.82 (10)		4.45 (3.3)	4.74 (0)	3.60 (6.2)	3.82	3.54 (6.2)				
	Neu^E			2.47 (4.3) [e]	1.61 (12.4)	4.80	3.95	3.55 [f]		5.28 (9.1)	5.49 (2.2)	4.24 (12.4)	3.89 (6.1)

[a] $J_{3eq,3ax}$ 12.1 Hz.
[b] $J_{3eq,3ax}$ 12.1 Hz.
[c] $J_{3eq,3ax}$ 12.6 Hz.
[d] $J_{6,7}$ 2 Hz.
[e] $J_{3eq,3ax}$ 12.4 Hz.
[f] $J_{6,7}$ 2 Hz.

3 Ac), 2.04, 2.02 (2 s, 12 H, 4 Ac), 1.98 (s, 3 H, Ac). Anal. Calcd for $C_{97}H_{103}Cl_3N_2O_{42}$: C, 56.14; H, 5.00; Cl, 5.13; N, 1.35. Found C, 56.13; H, 4.92; Cl, 5.29; N, 1.17.

2-Azidoethyl O-*[methyl (5-acetamido-4,7,8,9-tetra*-O-*acetyl-3,5-dideoxy*-D-glycero-α-D-galacto-*non-2-ulopyranosyl)onate]-(2→3)*-O-*(2,4,6-tri*-O-*acetyl-β*-D-*galactopyranosyl)-(1→3)*-O-*(2-deoxy-2-trichloroacetamido-β*-D-*glucopyranosyl)-(1→3)*-O-*(2,4,6-tri*-O-*benzoyl-β*-D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*benzoyl-β*-D-*glucopyranoside* (**81**).—Glycosylation of acceptor **77** (108 mg, 0.078 mmol) with imidate **73** (60 mg, 0.065 mmol) in CH_2Cl_2 (5 mL) promoted by TMSOTf (0.264 mL of 0.1 M solution in CH_2Cl_2) and MS-4 Å followed by deacetonation with CF_3CO_2H was performed as described for the preparation of **79**. Chromatography (toluene→1:2 toluene–acetone) of the residue on a column of silica gel followed by gel-permeation chromatography in toluene on a 1 × 50 cm column of Bio-Beads SX3 gel gave **81** (91 mg, 71% based on imidate): R_f 0.45 (1:1 toluene–acetone); $[\alpha]_D$ 13° (*c* 1, EtOAc); NMR ($CDCl_3$): ^{1}H, the spectrum was identical to that of **79**, excepting disappearance of the signals of allyl moiety at δ 5.71 (OCH_2CH=CH_2), 5.16, 5.06 (CH=CH_2), 4.23, 4.02 (OCH_2CH=CH_2) and the presence of four one-proton multiplets at δ 3.80, 3.55 ($OCH_2CH_2N_3$), 3.25, 3.15 (CH_2N_3); ^{13}C, δ 170.8–169.4 ($OC(O)CH_3$), 167.8 (C-1^E), 165.8–164.8 (6 PhC(O)O), 161.6 (N–$C(O)CCl_3$), 133.8–127.9 (Ph), 101.0, 100.6, 99.8, 98.9 (4 C-1), 96.6 (C-1^E), 58.7 (C-2^C), 53.2 (OMe), 50.5 (CH_2N_3), 49.1 (C-5^E), 37.7 (C-3^E), 23.1 (N–C(O)CH_3), 21.4–20.5 (OC(O)CH_3). Anal. Calcd for $C_{96}H_{102}Cl_3N_5O_{42}$: C, 54.80; H, 4.89; N, 3.33. Found C, 54.75; H, 4.93; N, 2.98.

2-Azidoethyl O-*(3,6-di*-O-*benzyl-2-deoxy-2-trichloroacetamido-β*-D-*glucopyranosyl)-(1→3)*-O-*(2,4,6-tri*-O-*benzoyl-β*-D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*benzoyl-β*-D-*glucopyranoside* (**82**).—Deacetylation of **58** (520 mg, 0.33 mmol) in MeOH (10 mL) with AcCl (0.4 mL) for 18 h at rt as described for the preparation of **77** and subsequent chromatography (toluene→1:1 toluene–EtOAc) on a column of silica gel (20 g) gave (in order of elution) recovered starting material **58** (156 mg, 30%) and 4-OH derivative **82** (337 mg, 66%) as a white foam. Recycling of recovered **58** (156 mg, 0.1 mmol) gave an additional amount of **82** (101 mg, 65%). Total yield 438 mg, 87%: R_f 0.59 (3:1 toluene–EtOAc); $[\alpha]_D$ 33° (*c* 1, EtOAc); NMR ($CDCl_3$): ^{1}H, see Table 2 for carbohydrate ring protons; δ 8.11, 8.08, 8.01 (3 d, 2 H each, *J* 7.5 Hz, 6 ortho protons of 3 Bz), 7.92 (d, 4 H, *J* 7.5 Hz, 4 ortho protons of 2 Bz), 7.78 (d, 2 H, *J* 7.6 Hz, ortho protons of 1 Bz), 7.65–7.12 (m, 26 H, Ph), 6.90 (t, 2 H, *J* 7.5 Hz, Ph), 6.68 (d, 1 H, $J_{N-H,2}$ 7 Hz, N–H^C), 4.68, 4.58 (2 d, 1 H each, *J* 11.2 Hz, 2 $PhCH_2$), 4.46–4.41 (m, 4 H, 2 $PhCH_2$, H-6a^A, H-6b^A), 3.90 (m, 3 H, H-6a^B, H-3^C, $OCH_2CH_2N_3$), 3.63 (m, 1 H, $OCH_2CH_2N_3$), 3.37 (m, 1 H, CH_2N_3), 3.26 (m, 2 H, H-6b^B, CH_2N_3); ^{13}C, see Table 4 for carbohydrate ring carbons; δ 165.8–164.6 (6 PhC(O)O), 161.6 (N–$C(O)CCl_3$), 139.1, 138.5 (2 ipso Bn), 133.4–127.6 (Ph), 74.6, 73.7 ($PhCH_2$), 68.4 ($OCH_2CH_2N_3$), 50.5 (CH_2N_3). Anal. Calcd for $C_{78}H_{71}Cl_3N_4O_{22}$: C, 61.52; H, 4.70; N, 3.68. Found C, 61.94; H, 5.01; N, 3.56.

2-Azidoethyl O-*[methyl (5-acetamido-4,7,8,9-tetra*-O-*acetyl-3,5-dideoxy*-D-glycero-α-D-galacto-*non-2-ulopyranosyl)onate]-(2→3)*-O-*(2,4,6-tri*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)*-O-*(3,6-di*-O-*benzyl-2-deoxy-2-trichloroacetamido-β*-D-*glucopyranosyl)-(1→3)*-O-*(2,4,6-tri*-O-*benzoyl-β*-D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*benzoyl-β*-D-*glucopyranoside* (**83**).—Abs CH_2Cl_2 (5 mL) was stirred under Ar with MS-4 Å (2.5 g) for 1 h, then $BF_3{\cdot}Et_2O$ (0.063 mL, 0.5 mmol) was added, and the mixture was stirred for 1 h. Sieves were allowed to sediment, and 0.1 M solution of $BF_3{\cdot}Et_2O$ in CH_2Cl_2 thus obtained was used in this reaction. This solution was always freshly prepared, because it lost catalytic activity within 1–2 days.

To a stirred mixture of acceptor **82** (102 mg, 0.067 mmol) and MS AW-300 in abs CH_2Cl_2 (5 mL), three equal portions of imidate **73** (in total 132 mg, 0.143 mmol) and $BF_3{\cdot}Et_2O$ (in total 0.141 mL of the above described 0.1 M solution in CH_2Cl_2) were added under Ar at −27 °C with 48 h intervals. The reaction mixture was diluted with CH_2Cl_2 (30 mL), filtered through a pad of Celite, washed with satd aq $NaHCO_3$, dried, and concentrated. Chro-

Table 4
Chemical shifts (δ, ppm) for carbohydrate ring carbons in ^{13}C NMR spectra of compounds **1**, **3**, **5**–**9**, **15**, **16**, **18**, **30**, **31**, **49**, **52**, **53**, **72**, **82**, **83** in the solvent specified

Compound (solvent)	Unit	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9
1 (D_2O)	Gal^A	103.7	70.7	83.0	69.3	75.8	62.0			
	$GlcN^B$	103.7	56.7	74.6	70.8	76.7	61.5			
3 (D_2O)	Glc^A	102.2	73.9	74.7	79.6	75.9	61.3			
	Gal^B	104.1	71.1	83.1	69.5	76.0	62.1			
	$GlcN^C$	103.9	56.8	75.5	70.9	76.8	61.7			
5 (D_2O)	Glc^A	103.1	73.8	75.3	79.4	75.9	61.0			
	Gal^B	104.1	71.1	83.2	69.4	76.0	62.1			
	$GlcN^C$	103.9	56.3	73.3	79.3	75.7	61.1			
	Gal^D	104.0	72.1	73.6	69.7	76.5	62.2			
6 (D_2O)	Glc^A	103.0	73.8	75.3	79.5	75.9	61.1			
	Gal^B	104.0	71.1	83.1	69.3	76.0	62.0			
	$GlcN^C$	103.5	55.8	83.3	69.6	76.3	61.7			
	Gal^D	104.5	71.8	73.6	69.6	76.3	62.1			
7 (D_2O)	$GlcN^A$	102.1	56.0	73.4	79.5	75.8	61.0			
	Gal^B	104.0	71.1	83.2	69.1	76.0	62.1			
	$GlcN^C$	103.9	56.3	73.3	79.4	75.7	61.0			
	Gal^D	104.0	72.1	73.7	69.7	76.5	62.1			
8 (D_2O)	Glc^A	103.1	73.8	75.4	79.5	75.9	61.1			
	Gal^B	104.1	71.1	83.2	69.4	76.1	62.2			
	$GlcN^C$	103.9	56.4	73.3	79.3	75.7	61.0			
	Gal^D	103.7	70.5	76.7	68.6	76.3	62.2			
	Neu^E	174.9	101.0	40.8	69.4	52.9	74.1	69.3	72.9	63.8
9 (D_2O)	Glc^A	103.0	73.8	75.4	79.5	75.9	61.1			
	Gal^B	104.0	71.1	83.0	69.4	76.0	62.1			
	$GlcN^C$	103.5	55.7	83.3	69.6	76.4	61.7			
	Gal^D	104.5	70.2	76.8	68.4	76.2	62.1			
	Neu^E	175.0	100.8	41.3	69.2	52.8	73.9	69.4	72.9	63.7
15 (5:1 $CDCl_3$–CD_3OD)		83.8	57.2	71.2	81.4	70.4	68.3			
16 (10:1 $CDCl_3$–CD_3OD)		83.6	56.2	81.9	78.1	70.1	68.3			
18 ($CDCl_3$)		82.3	57.5	79.0	71.4	77.5	69.6			
30 ($CDCl_3$)	$GlcN^A$	82.5	56.7	79.2	75.9	78.9	67.8			
	Gal^B	100.1	70.2	70.9	68.0	71.2	61.6			
31 ($CDCl_3$)		84.3	68.2	72.1	68.1	74.9	62.2			
49 ($CDCl_3$)	Glc^A	101.2	71.6	72.8	75.9	73.1	62.2			
	Gal^B	100.9	69.7	71.0	67.4	71.3	61.0			
52 (10:1 $CDCl_3$–CD_3OD)		99.2	56.3	80.6	70.9	73.8	63.9			
53 ($CDCl_3$)	$GlcN^A$	98.9	53.4	77.1	75.8	71.4	63.7			
	Gal^B	100.3	69.9	70.6	67.6	72.7	61.5			
72 (D_2O)	Glc^A	103.2	74.0	75.5	80.1	75.8	61.2			
	Gal^B	104.1	70.9	82.8	69.5	74.6	69.7			
	$GlcN^C$	103.7	56.8	75.0	71.0	77.0	61.9			
	$GlcN^D$	102.1	56.6	74.7	71.1	76.8	61.7			
82 ($CDCl_3$)	Glc^A	101.0	71.5	72.6	75.4	73.1	62.3			
	Gal^B	100.8	71.7	76.1	69.6	71.9	61.9			
	$GlcN^C$	98.4	58.6	78.8	73.4	73.4	70.6			
83 ($CDCl_3$)	Glc^A	100.9	71.3	72.5	75.3	73.0	62.3			
	Gal^B	100.7	71.5	76.3	69.4	71.9	62.0			
	$GlcN^C$	98.7	53.0	76.2	75.3	75.0	68.7			
	Gal^D	99.7	70.4	71.1	67.3	70.4	61.3			
	Neu^E	167.7	96.7	37.4	69.2	48.8	71.9	67.0	67.6	62.3

matography (toluene → 1:2 toluene–acetone) of the residue on a column of silica gel (20 g) gave pentasaccharide **83** (124 mg, 81% based on acceptor): R_f 0.46 (1:1 toluene–acetone);

$[\alpha]_D$ 14° (*c* 1, EtOAc); NMR ($CDCl_3$): ^1H, see Table 3 for carbohydrate ring protons; δ 7.99, 7.96, 7.91 (3 d, 2 H each, *J* 7.7 Hz, 6 ortho protons of 3 Bz), 7.83 (d, 4 H, *J* 7.7 Hz, 4 ortho protons of 2 Bz), 7.66 (d, 2 H, *J* 7.7 Hz, 2 ortho protons of 1 Bz), 7.57–7.05 (m, 26 H, Ph), 6.79 (t, 2 H, *J* 7.6 Hz, Ph), 6.70 (d, 1 H, $J^{C}_{N-H,\,2^{C}}$ 7.4 Hz, N–H^C), 5.08 (d, 1 H, $J_{N-H^E,\,5^E}$ 10.2 Hz, N–H^E), 4.70 (d, 1 H, *J* 11 Hz, $PhCH_2$), 4.32 (s, 2 H, $PhCH_2$), 4.27 (d, 1 H, $PhCH_2$), 3.82 (m, 6 H, H-9b^E, H-4^C, H-6a^B, H-3^C, $OCH_2CH_2N_3$, H-6a^D), 3.72 (s, 3 H, OMe), 3.52 (m, 4 H, H-5^B, H-6^E, H-6b^D, $OCH_2CH_2N_3$), 3.28 (m 1 H, CH_2N_3), 3.14 (m, CH_2N_3), 2.11, 2.05, 2.01, 1.91, 1.88, 1.85, 1.79, 1.77 (8 s, 3 H each, 8 Ac); ^{13}C, see Table 4 for carbohydrate ring carbons; δ 170.7–169.5 ($OC(O)CH_3$), 165.7–164.5 (PhC(O)O), 161.3 ($N–C(O)CCl_3$), 138.4, 137.9 (2 ipso Bn), 133.2–126.8 (Ph), 68.3 ($OCH_2CH_2N_3$), 52.9 (OMe), 50.3 (CH_2N_3), 23.0 ($N–C(O)CH_3$), 21.2–20.4 ($OC(O)CH_3$). Anal. Calcd for $C_{110}H_{114}Cl_3N_5O_{42}$: C, 57.83; H, 5.03; N, 3.07. Found C, 58.09; H, 5.23; N, 2.76.

2-Aminoethyl O-*(2-deoxy-2-acetamido-β-*D-*glucopyranosyl)-(1→3)-β-*D-*galactopyranoside* (**1**).—To a solution of **60** (245 mg, 0.247 mmol) in abs MeOH (14 mL), solid MeONa (187 mg, 3.46 mmol) was added, and the mixture was stirred for 18 h at rt. At this point, TLC indicated total *O*-deacylation and some *N*-detrichloroacetylation. In order to complete the latter, water (1 mL) was added, and stirring was continued for another 18 h. Ac_2O (0.5 mL) was added dropwise at 0 °C, and after 18 h at rt, the mixture was concentrated. A solution of the residue in water was treated with KU-2 (H^+) cation-exchange resin, the resin was filtered off, and the filtrate was concentrated. The solid residue was extracted with EtOAc (3 × 2 mL) and then subjected to gel-permeation chromatography on a 2.5 × 100 cm column of Sephadex G-10 gel by elution with water, followed by rechromatography by elution with 0.5% aq NH_3 to give after freeze-drying **67** (104 mg, 94%) as transparent glass: R_f 0.32 (BPHCl); $[\alpha]_D$ −5° (*c* 1, water).

To a solution of **67** (70 mg, 0.16 mmol) in water (3 mL), Pd–C (5 mg) was added, the mixture was degassed under vacuum with stirring, refilled with H_2, and stirred for 0.5 h at rt. The mixture was filtered through a pad of Celite, the pad was washed thoroughly with water, and the combined filtrate and washings were concentrated. The residue was subjected to gel-permeation chromatography on a 2.5 × 100 cm column of Sephadex G-10 gel by elution with water to give after freeze-drying **1** (63 mg, 95%) as amorphous powder: R_f 0.12 (BPHCl); $[\alpha]_D$ −124° (*c* 1, water); NMR (D_2O): ^1H, see Table 2 for carbohydrate ring protons; δ 4.09 (m, 1 H, $OCH_2CH_2NH_2$), 3.93 (m, 1 H, $OCH_2CH_2NH_2$), 3.24 (t, 2 H, *J* 5 Hz, $OCH_2CH_2NH_2$), 2.00 (s, 3 H, Ac); ^{13}C, see Table 4 for carbohydrate ring carbons; δ 176.0 ($N–C(O)CH_3$), 66.8 ($OCH_2CH_2NH_2$), 40.5 (CH_2NH_2), 23.2 ($N–C(O)CH_3$). MALDI-TOF-MS: Calcd for $[C_{16}H_{30}N_2O_{11}+H]^+$: 427.2. Found: 427.5.

2-Aminoethyl O-*(2-acetamido-2-deoxy-β-*D-*glucopyranosyl)-(1→3)-*O-*(β-*D-*galactopyranosyl)-(1→4)-β-*D-*glucopyranoside* (**2**).—Deacylation of **57** (44 mg, 0.03 mmol) followed by *N*-acetylation as described for the preparation of **1** and subsequent gel-permeation chromatography on a 2 × 20 cm column of Sephadex G-10 gel by elution with water gave **70** (16.7 mg, 93%) after freeze-drying: R_f 0.26 (BPHCl); $[\alpha]_D$ 3° (*c* 1, water).

Hydrogenation of **70** (16 mg, 0.026 mmol) as described for the preparation of **1** and subsequent gel-permeation chromatography on a 1.5 × 100 cm column of TSK HW-40S gel by elution with 0.1 M aq AcOH gave **2** (14.4 mg, 94%) after freeze-drying: $[\alpha]_D$ 3° (*c* 1, water); NMR (D_2O): ^1H, the spectrum was identical to that of **3** (see below), excepting the disappearance of the signals of the allyl moiety at δ 5.99 ($OCH_2CH{=}CH_2$), 5.37 ($OCH_2CH{=}CH_2$), 5.28 ($OCH_2CH{=}CH_2$), 4.39 ($OCH_2CH{=}CH_2$), 4.23 ($OCH_2CH{=}CH_2$), and the presence of two one-proton multiplets at δ 4.12, 3.96 ($OCH_2CH_2NH_2$) and two-proton triplet at δ 3.27 (CH_2NH_2); ^{13}C, the spectrum was identical to that of **3** (see below), excepting the disappearance of the signals of allyl moiety at δ 134.5 ($OCH_2CH{=}CH_2$), 119.8 ($OCH_2CH{=}CH_2$), 71.8 ($OCH_2CH{=}CH_2$), and the presence of the signals at δ 67.0 ($OCH_2CH_2NH_2$) and 40.5 (CH_2NH_2). MALDI-TOF-

MS: Calcd for $[C_{22}H_{40}N_2O_{16}]^+$: 588.2. Found: 588.3. Calcd for $[C_{22}H_{40}N_2O_{16}+Na]^+$: 611.2. Found: 611.7.

Allyl O-*(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)-(1→3)-*O*-(β-*D*-galactopyranosyl)-(1→4)-β-*D*-glucopyranoside* (**3**).—Deacylation of trisaccharide **56** (71 mg, 0.049 mmol) followed by *N*-acetylation as described for the preparation of **1** and subsequent gel-permeation chromatography on a 1.5 × 100 cm column of TSK HW-40S gel by elution with 0.1 M aq AcOH gave after freeze-drying **3** (12.5 mg, 43%) as transparent glass: R_f 0.37 (BPHCl); $[\alpha]_D$ 3° (*c* 1, water); NMR (D_2O): ^{1}H, see Table 2 for carbohydrate ring protons; δ 5.99 (m, 1 H, $OCH_2CH{=}CH_2$), 5.37 (m, 1 H, J_{trans} 18 Hz, $OCH_2CH{=}CH_2$), 5.28 (m, 1 H, J_{cis} 12 Hz, $OCH_2CH{=}CH_2$), 4.39 (dd, 1 H, J_{gem} 12.7, J_{vic} 4.6 Hz, $OCH_2CH{=}CH_2$), 4.23 (dd, 1 H, J_{vic} 6.4 Hz, $OCH_2CH{=}CH_2$), 2.02 (s, 3 H, Ac); ^{13}C, see Table 4 for carbohydrate ring carbons; δ 176.1 ($N{-}C(O)CH_3$), 134.5 ($OCH_2CH{=}CH_2$), 119.8 ($OCH_2CH{=}CH_2$), 71.8 ($OCH_2CH{=}CH_2$), 23.3 ($N{-}C(O)CH_3$). MALDI-TOF-MS: Calcd for $[C_{23}H_{39}NO_{16}]^+$: 585.2. Found: 585.5. Calcd for $[C_{23}H_{39}NO_{16}+Na]^+$: 608.2. Found: 608.7.

2-Aminoethyl O-*(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)-(1→3)-*O*-[2-acetamido-2-deoxy-β-*D*-glucopyranosyl-(1→6)]-*O*-(β-*D*-galactopyranosyl)-(1→4)-β-*D*-glucopyranoside* (**4**).—Deacylation of **62** (36 mg, 0.02 mmol) followed by *N*-acetylation as described for the preparation of **1** and subsequent gel-permeation chromatography on a 1 × 60 cm column of Sephadex G-10 gel by elution with water gave **72** (13.5 mg, 81%) after freeze-drying: R_f 0.26 (BPHCl); $[\alpha]_D$ −6° (*c* 0.5, water); NMR (D_2O): ^{1}H, see Table 2 for carbohydrate ring protons; δ 3.95 (m, 1 H, $OCH_2CH_2N_3$), 3.76 (m, $OCH_2CH_2N_3$), 3.46 (CH_2N_3), 1.93, 1.96 (2 s, 6 H, 2 N–Ac); ^{13}C, see Table 4 for carbohydrate ring carbons; δ 176.0, 175.6 (2 $N{-}C(O)CH_3$), 69.5 ($OCH_2CH_2N_3$), 51.6 (CH_2N_3), 23.5, 23.3 (2 $N{-}C(O)CH_3$).

Hydrogenation of **72** (13 mg, 0.016 mmol) as described for **1** and subsequent gel-permeation chromatography on a 1.5 × 100 cm column of TSK HW-40S gel by elution with 0.1 M aq AcOH gave **4** (11 mg, 87%) after freeze-drying: R_f 0.35 (3:1 BPHCl–AMW); $[\alpha]_D$ −3° (*c* 0.5, water); NMR (D_2O): ^{1}H, the spectrum was identical to that of **72**, excepting disappearance of the signal at δ 3.46 (CH_2N_3) and the presence of two-proton triplet at δ 3.25 (*J* 5.1 Hz, CH_2NH_2); ^{13}C, the spectrum was identical to that of **72**, excepting disappearance of the signal at δ 51.6 (CH_2N_3) and the presence of the signal at δ 40.3 (CH_2NH_2). MALDI-TOF-MS: Calcd for $[C_{30}H_{53}N_3O_{21}]^+$: 791.3. Found: 791.3. Calcd for $[C_{23}H_{39}NO_{16}+Na]^+$: 814.3. Found: 814.6.

2-Aminoethyl O-*(β-*D*-galactopyranosyl)-(1→4)-*O*-(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)-(1→3)-*O*-(β-*D*-galactopyranosyl)-(1→4)-β-*D*-glucopyranoside* (**5**).—Deacylation of **63** (188 mg, 0.107 mmol), followed by *N*-acetylation as described for the preparation of **1** and subsequent gel-permeation chromatography on a 1.5 × 100 cm column of TSK HW-40S gel by elution with 0.1 M aq AcOH gave **68** (64 mg, 77%) after freeze-drying. Hydrogenation of all obtained **68** as described for the preparation of **1** and subsequent gel-chromatography on a 1.5 × 100 cm column of TSK HW-40S gel by elution with 0.1 M aq AcOH gave **5** (59 mg, 92%) after freeze-drying: R_f 0.26 (BPHCl); $[\alpha]_D$ 5° (*c* 1, water); NMR (D_2O): ^{1}H, see Table 2 for carbohydrate ring protons; δ 4.13 (m, 2 H, H-4^B, $OCH_2CH_2NH_2$), 3.95 (m, 4 H, H-6a^A, H-6a^C, $OCH_2CH_2NH_2$, H-4^D), 3.27 (t, 2 H, *J* 5 Hz, CH_2NH_2), 2.02 (s, 3 H, N–Ac); ^{13}C, see Table 4 for carbohydrate ring carbons; δ 176.0 ($N{-}C(O)CH_3$), 67.0 ($OCH_2CH_2NH_2$), 40.5 (CH_2NH_2), 23.3 ($N{-}C(O)CH_3$). MALDI-TOF-MS: Calcd for $[C_{28}H_{50}N_2O_{21}+Na]^+$: 773.3. Found: 772.9. Calcd for $[C_{28}H_{50}N_2O_{21}]^+$: 750.3. Found: 750.6.

2-Aminoethyl O-*(β-*D*-galactopyranosyl)-(1→3)-*O*-(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)-(1→3)-*O*-(β-*D*-galactopyranosyl)-(1→4)-β-*D*-glucopyranoside* (**6**).—To a solution of **66** (100 mg, 0.057 mmol) in abs MeOH (5 mL), solid MeONa (75 mg, 1.39 mmol) was added, and the reaction mixture was stirred for 15 h at rt. Water (1 mL) was added, and stirring was continued for 24 h at 50 °C. Ac_2O (0.3 mL) was added dropwise at 0 °C, and after 18 h at rt the reaction mixture concentrated. A solution of the residue in water was

treated with KU-2 (H^+) cation-exchange resin, the resin was filtered off, and the filtrate was concentrated. The solid residue was washed with EtOAc (3 × 2 mL) and then subjected to gel-permeation chromatography on a 1 × 60 cm column of Sephadex G-10 gel by elution with water to give **71** (42 mg, 95%) after freeze-drying: R_f 0.27 (BPHCl).

A solution of all obtained **71** in water (2 mL) was stirred overnight with Pd–C (5 mg) under H_2, then filtered through a pad of Celite, the pad was washed thoroughly with water, and the combined filtrate and washings were concentrated. Gel-chromatography of the residue on a 1.5 × 100 cm column of TSK HW-40S gel by elution with 0.1 M aq AcOH gave **6** (27 mg, 66%) after freeze-drying: R_f 0.25 (1:1 BPHCl–AMW); $[\alpha]_D$ 6° (*c* 1, water); NMR (D_2O): ^1H, see Table 2 for carbohydrate ring protons; δ 4.13 (m, 2 H, H-4^B, $OCH_2CH_2NH_2$), 3.96 (m, $OCH_2CH_2NH_2$), 3.25 (t, 2 H, *J* 5.1 Hz, CH_2NH_2), 2.01 (s, 3 H, N–Ac); ^{13}C, see Table 4 for carbohydrate ring carbons; δ 175.9 (N–*C*(O)CH_3), 66.9 ($OCH_2CH_2NH_2$), 40.5 (CH_2NH_2), 23.3 (N–C(O)*C*H_3). MALDI-TOF-MS: Calcd for $[C_{28}H_{50}N_2O_{21} + Na]^+$: 773.3. Found: 773.5. Calcd for $[C_{28}H_{50}N_2O_{21} + H]^+$: 751.3. Found: 751.4.

2-Aminoethyl O-*(β-*D*-galactopyranosyl)-(1→4)*-O-*(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)-(1→3)*-O-*(β-*D*-galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-β-*D*-glucopyranoside* (**7**).—Deacylation of **64** (83 mg, 0.042 mmol) followed by *N*-acetylation as described for the preparation of **6** and subsequent gel-permeation chromatography of the residue on a 2 × 70 column of Sephadex LH-20 gel by elution with MeOH gave **69** (39.4 mg, 86%) after freeze-drying: R_f 0.55 (2:3:1 *i*-PrOH–EtOAc–water); $[\alpha]_D$ −7° (*c* 1, MeOH); Anal. Calcd for $C_{51}H_{69}N_5O_{21}$: C, 56.29; H, 6.39; N, 6.44. Found: C, 56.33; H, 6.50; N, 6.27.

Hydrogenation of **69** (33.9 mg, 0.031 mmol) as described for the preparation of **6** and subsequent gel-permeation chromatography of the residue on a 1.5 × 100 cm column of TSK HW-40S gel by elution with 0.1 M aq AcOH gave **7** (22.8 mg, 93%) after freeze-drying: R_f 0.36 (17:13 BPHCl–AMW); $[\alpha]_D$ −14° (*c* 0.1, water); NMR (D_2O): ^1H, see Table 2 for carbohydrate ring protons; δ 4.05 (m, 1 H, $OCH_2CH_2NH_2$), 3.90 (m, $OCH_2CH_2NH_2$), 3.22 (m, 2 H, CH_2NH_2), 2.04, 2.02 (2 s, 3 H each, 2 N–Ac); ^{13}C, see Table 4 for carbohydrate ring carbons; δ 176.0 (2 N–*C*(O)CH_3), 66.8 ($OCH_2CH_2NH_2$), 40.5 (CH_2NH_2), 23.3 (2 N–C(O)*C*H_3). MALDI-TOF-MS: Calcd for $[C_{30}H_{53}N_3O_{21} + Na]^+$: 814.3. Found: 816.9.

2-Aminoethyl O-*(5-acetamido-3,5-dideoxy-*D*-glycero-α-*D*-galacto-non-2-ulopyranosylonic acid)-(2→3)*-O-*(β-*D*-galactopyranosyl)-(1→4)*-O-*(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)-(1→3)*-O-*(β-*D*-galactopyranosyl)-(1→4)-β-*D*-glucopyranoside* (**8**).—To a solution of **83** (115 mg, 0.05 mmol) in MeOH (5 mL), NaOH (1 M aq, 2.5 mL, 2.5 mmol) was added, and the mixture was stirred for 60 h at rt and then for 24 h at 50 °C. Ac_2O (0.3 mL) was added dropwise at 0 °C, and after stirring overnight at rt, the reaction mixture was coevaporated with water (2 × 3 mL). Gel-permeation chromatography of the residue on a 2 × 70 cm column of Sephadex LH-20 gel by elution with 1:1 MeCN–water gave **84** (57.9 mg, 91%): R_f 0.38 (BPHCl); $[\alpha]_D$ 4° (*c* 1, water); NMR (D_2O): ^1H, δ 7.43–7.60 (m, 10 H, Ph), 5.05, 4.80, 4.73, 4.64 (4 d, 1 H each, *J* 11.5 Hz, $PhCH_2$), 4.75 (d, 1 H, $J^{C\ C}_{1,\ 2}$ 8 Hz, H-1^C), 4.61 (d, 1 H, $J^{A\ A}_{1,\ 2}$ 8 Hz, H-1^A), 4.50 (d, 1 H, $J^{B\ B}_{1,\ 2}$ 7.8 Hz, H-1^B), 4.44 (d, 1 H, $J^{D\ D}_{1,\ 2}$ 7.9 Hz, H-1^D), 4.17 (m, 2 H, H-4^B, $OCH_2CH_2N_3$), 3.42 (t, 1 H, H-2^A), 3.39 (m, 1 H, H-5^C), 2.88 (dd, 1 H, $J^{E\ E}_{3eq,\ 3ax}$ 12.4, $J^{E\ E}_{3eq,\ 4}$ 4.4 Hz, H-3$^E_{eq}$), 2.14, 1.97 (2 s, 3 H each, 2 N–Ac), 1.90 (t, 1 H, H-3$^E_{ax}$); ^{13}C, δ 175.3, 174.6 (2 N–*C*(O)CH_3), 174.0 (C-1^E), 137.8, 137.5 (2 ipso Bn), 129.1–128.5 (Ph), 103.1 (C-1^B), 102.9 (C-1^C), 102.5 (C-1^D), 102.4 (C-1^A), 100.1 (C-2^E), 55.8 (C-2^C), 52.9 (C-5^E), 51.7 (CH_2N_3), 41.0 (C-3^E), 23.3, 23.2 (2 N–C(O)*C*H_3).

A mixture of **84** (15.5 mg, 0.012 mmol) and Pd–C (10 mg) in water (3 mL) was degassed under vacuum with stirring, refilled with H_2, and stirred for 4 h at rt. The reaction mixture was filtered through a pad of Celite, the pad was washed thoroughly with water, and the combined filtrate and washings were concentrated. Gel-permeation chromatography of the residue on a 1.5 × 100 cm column of TSK HW-40S gel by elution with 0.1 M aq AcOH gave **8** (12.9 mg, 99%) after freeze-drying: R_f

0.42 (1:1 BPHCl–AMW); $[\alpha]_D$ 1° (*c* 1, water); NMR (D_2O): ^1H, see Table 3 for carbohydrate ring protons; δ 4.13 (m, 3 H, H-4^B, $OCH_2CH_2NH_2$, H-3^D), 3.95 (m, 4 H, H-6^A, H-6^C, $OCH_2CH_2NH_2$, H-4^D), 3.27 (t, 2 H, *J* 5 Hz, CH_2NH_2), 2.03 (s, 6 H, 2 N–C(O)CH_3); ^{13}C, see Table 4 for carbohydrate ring carbons; δ 176.2, 176.0 (2 O*C*(O)CH_3), 66.9 ($OCH_2CH_2NH_2$), 40.6 (CH_2NH_2), 23.3, 23.2 (2 OC(O)*C*H_3).MALDI-TOF-MS: Calcd for $[C_{39}H_{67}N_3O_{29}+H]^+$: 1042.4. Found: 1044.9.

2-Aminoethyl O-*(5-acetamido-3,5-dideoxy-*D-glycero-α-D-galacto-*non-2-ulopyranosylonic acid)-(2→3)*-O-*(β-*D-*galactopyranosyl)-(1→3)*-O-*(2-acetamido-2-deoxy-β-*D-*glucopyranosyl)-(1→3)*-O-*(β-*D-*galactopyranosyl)-(1→4)-β-*D-*glucopyranoside* (**9**).—To a solution of **81** (14.5 mg, 0.0069 mmol) in MeOH (2 mL), NaOH (1 M aq, 1 mL, 1 mmol) was added, and the mixture was stirred for 18 h at rt and then for 5 h at 50 °C. Ac_2O (0.075 mL) was added dropwise, and after stirring overnight at rt the reaction mixture was coevaporated with water (2 × 3 mL). Gel-permeation chromatography of the residue on a 1.5 × 100 cm column of TSK HW-40S gel by elution with 0.1 M aq AcOH gave a fraction ($V=7$ mL) with pure 2-azidoethyl glycoside of the pentasaccharide free acid. In acidic form, this compound was prone to α→β anomerization of the sialic acid moiety, therefore the fraction without concentration was immediately treated with Pd–C (5 mg) and stirred under H_2 overnight at rt. Filtration through a pad of Celite, concentration, and subsequent gel-permeation chromatography of the residue on a 1.5 × 100 cm column of TSK HW-40S gel by elution with 0.1 M aq AcOH gave **9** (6.7 mg, 93%) after freeze-drying: R_f 0.38 (1:1 BPHCl–AMW); $[\alpha]_D$ −4° (*c* 0.2, water); NMR (D_2O): ^1H, see Table 3 for carbohydrate ring protons; δ 4.08 (m, 3 H, H-4^B, $OCH_2CH_2NH_2$, H-3^D), 3.93 (m, 3 H, H-6^A, $OCH_2CH_2NH_2$, H-4^D), 3.25 (t, 2 H, *J* 5 Hz, CH_2NH_2), 2.00 (s, 6 H, 2 N–Ac); ^{13}C, see Table 4 for carbohydrate ring carbons; δ 176.4 (2 N–*C*(O)CH_3), 66.9 ($OCH_2CH_2NH_2$), 40.5 (CH_2NH_2), 23.3 (2 N–C(O)CH_3). MALDI-TOF-MS: Calcd for $[C_{39}H_{67}N_3O_{29}+H]^+$: 1042.4. Found: 1045.5.

Allyl O-*[potassium (5-acetamido-3,5-dideoxy-*D-glycero-α-D-galacto-*non-2-ulopyranosyl)onate]-(2→3)*-O-*(β-*D-*galactopyranosyl)-(1→3)*-O-*(2-acetamido-2-deoxy-β-*D-*glucopyranosyl)-(1→3)*-O-*(β-*D-*galactopyranosyl)-(1→4)-β-*D-*glucopyranoside* (**10**).—To a solution of **79** (30 mg, 0.0145 mmol) in MeOH (2 mL), KOH (2 M aq, 0.3 mL, 0.6 mmol) was added, and the mixture was stirred for 24 h at rt and then for 36 h at 50 °C. Ac_2O (0.15 mL) was added dropwise at 0 °C, and after stirring overnight at rt, the reaction mixture was coevaporated with water (2 × 3 mL). Gel-permeation chromatography of the residue on a 2 × 20 cm column of Sephadex G-10 gel by elution with water gave **10** (14.2 mg, 86%) after freeze-drying: R_f 0.57 (1:1 BPHCl–MeOH); $[\alpha]_D$ −7° (*c* 1, water); NMR (D_2O): ^1H, the spectrum was identical to that of **9** excepting the absence of the signals at δ 4.08 ($OCH_2CH_2NH_2$), 3.93 ($OCH_2CH_2NH_2$), and 3.25 (CH_2NH_2), and the presence of the signals at δ 5.98 (m, 1 H, $OCH_2CH{=}CH_2$), 5.35 (d, 1 H, J_{trans} 17.2 Hz, $OCH_2CH{=}CH_2$), 5.26 (d, 1 H, J_{cis} 10.2 Hz, $OCH_2CH{=}CH_2$), 4.38 (m, 1 H, $OCH_2CH{=}CH_2$), 4.23 (m, 1 H, $OCH_2CH{=}CH_2$); ^{13}C, the spectrum was identical to that of **9** excepting the absence of the signals at δ 66.9 ($OCH_2CH_2NH_2$), 40.5 (CH_2NH_2), and the presence of the signals at δ 134.8 ($OCH_2CH{=}CH_2$), 120.3 ($OCH_2CH{=}CH_2$), 72.2 ($OCH_2CH{=}CH_2$). MALDI-TOF-MS: Calcd for $[C_{40}H_{65}KN_2O_{29}]^+$: 1076.3. Found: 1076.5.

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