Synthesis of Lactam and Acetamido Analogues of Sialyl Lewis x Tetrasaccharide and Lewis x Trisaccharide

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Virtually complete regioselective galactosylation of the diol acceptor *p*-methoxyphenyl 6-*O*-benzyl-2-deoxy-2-tetrachlorophthalimido-*β*-D-glucopyranoside (**15**) with the donors ethyl 3,4-di-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-[[(2,2,2-trichloroethoxy)carbonyl]amino]-1-thio-*β*-D-galactopyranoside (**14**), 4-methylphenyl 2,3-di-*O*-acetyl-4-azido-6-*O*-benzyl-4-deoxy-1-thio-*β*-D-galactopyranoside (**30**), and 4-methylphenyl 2-*O*-acetyl-4-azido-6-*O*-benzyl-4-deoxy-3-*O*-(methoxyethanoyl)-1-thio-*β*-D-galactopyranoside (**44**) gave the lactose-diamine derivatives **16**, **33**, and **45**, respectively. Fucosylation of the NHAc derivatives of **16** and **33** (**17** and **34**) with the donor **18** gave, after deprotection and N-acetylation, the 2-NHAc-Le^x and 4-NHAc-Le^x trisaccharides **3** and **5**, respectively. Removal of the Troc group from the tetrasaccharide intermediate **23**, followed by N-acetylation (→ **24**), gave the NHAc-SLe^x tetrasaccharide **2**. Regioselective sialylation of the partially protected trisaccharide diols **21** and **37** with the sialyl donors **22** and **38** gave, after deprotection and lactamization, the SLe^x-1‴→2′-lactam **1** and the SLe^x-1‴→4′-lactam **4**, respectively. The stannylidene acetal of the trisaccharide diol **21** was regioselectively 3-O-alkylated with *tert*-butyl bromoacetate; reductive removal of the Troc protecting group and addition of methanolic MeONa caused formation of a lactam ring. Compound **40** was thus obtained over four steps in an overall yield of 52%. Deprotection of **40** furnished the Le^x-3,2-lactam **6** in 74% yield. Fucosylation of the lactose−diamine derivative **46** with donor **18** gave the N_3-Le^x trisaccharide derivative **47**. The azido function of **47** was reduced with H_2S, which caused spontaneous closure of a lactam ring. Removal of the protecting groups then gave the Le^x-3,4-lactam **7**. The total yields of **1**, **2**, **3**, **4**, **5**, and **7** from the monosaccharide starting materials **14**, **15**, **18**, **22**, **30**, **38**, and **44** were 10%, 10%, 22%, 14%, 62%, and 28%, respectively.

Introduction

The Sialyl Lewis x ganglioside (SLe^x) has been identified as an important compound for intercellular molecular recognition. References to the biological background, as well as the different syntheses of SLe^x glycosides, were summarized in the preceding paper in this issue.[1] Following the initial investigations of the biological effects of SLe^x, the focus has now turned toward the synthesis and biological potential of SLe^x analogues, where an anionic (e.g., carboxylate) center is retained.[2]

Gangliosides are known to lactonize upon treatment with acid in vitro, thus removing the anionic charge present in the parent ganglioside.[3] The question of lactonization in vivo has been debated for decades, and experimental evidence has come from investigations such as reductive radiolabeling with tritium[3b] and immunostaining of cells with antibodies raised against ganglioside lactones.[4] However, the hydrolytic lability of the lactones has made it difficult to draw any safe conclusions about their presence in vivo, especially since some of the anti-ganglioside-lactone antibodies cross-reacted with the nonlactonized form of the ganglioside.[4]

In an alternative approach, we have synthesized ganglioside lactams, which are quite stable against hydrolysis and have conformations very similar to those of the ganglioside lactones.[5] A cyclic ether analogue of G_{M3}-1″→2′-lactone has also been reported.[6] Antibodies raised against the G_{M3}-1″→2′-lactam were found to cross-react with G_{M3}-lactone in vitro, but not with the open form of G_{M3}-ganglioside.[7] Mouse melanoma cells that are known to carry large amounts of surface-bound G_{M3}-ganglioside were stained by the anti-G_{M3}-1″→2′-lactam antibodies, which strongly indicates that G_{M3}-lactone is present on the cell surface.[8]

The question of SLe^x-lactones as naturally occurring entities has not been subject to experimental investigation, except for a molecular mechanics calculation (MM3)

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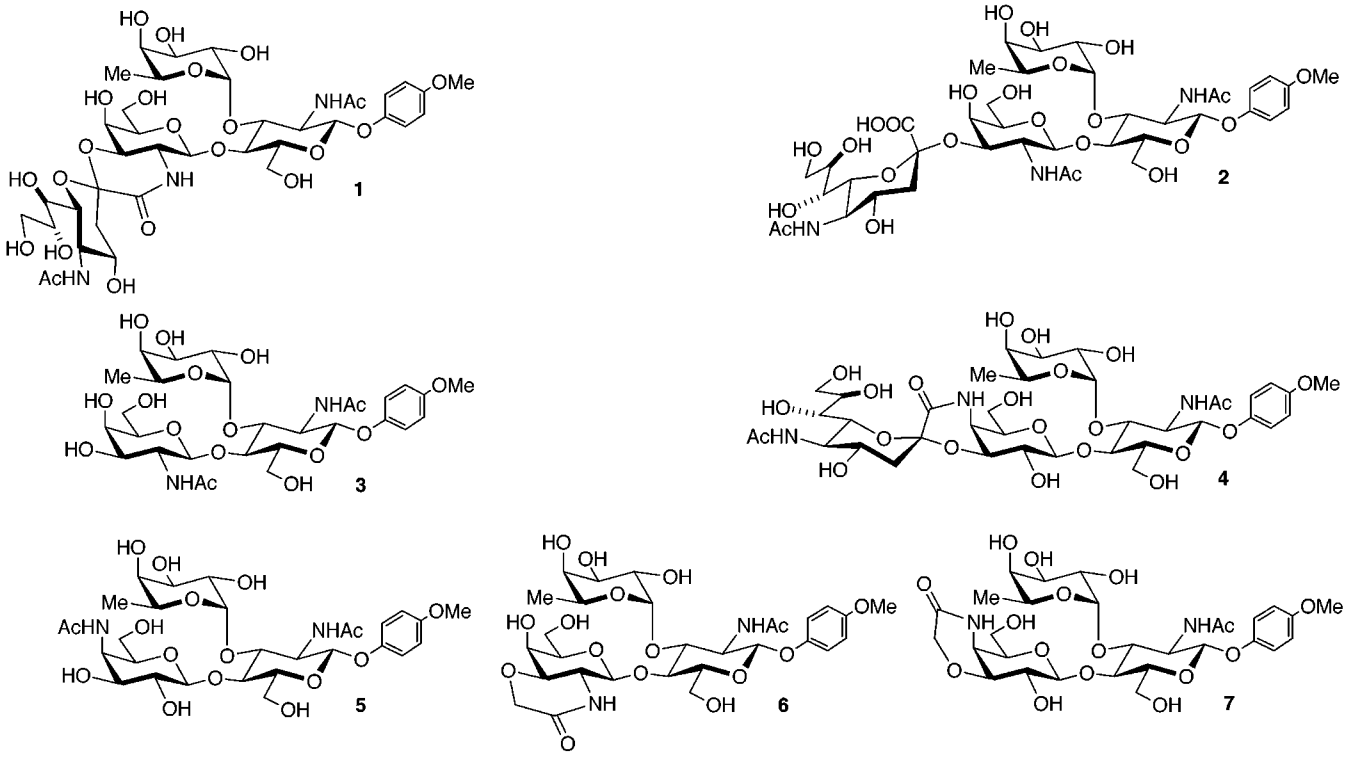

Figure 1. Structures of lactam and acetamido analogues of SLe^x tetrasaccharide and Le^x trisaccharide.

of their conformations.[9] A few reports have appeared where SLe^x-lactones were found to be intermediates formed during synthesis.[10] Similar to the situation with G_{M3}-lactones, SLe^x-lactones are potentially strong tumor antigens in vivo. Consequently, we have developed synthetic routes to the SLe^x-lactams. We now disclose the details of our syntheses of SLe^x-1‴→2′-lactam (**1**) and SLe^x-1‴-4′-lactam (**4**), as well as the acetamido analogues of SLe^x tetrasaccharide (**2**) and Lewis x trisaccharide (**3** and **5**), depicted in Figure 1.

We realized the possibility that the lactam ring per se was mainly responsible for the immunogenicity action, and it was therefore deemed to be of interest to prepare ganglioside lactam analogues, where the sialic acid ring system had been removed. We report therefore the synthesis of the Le^x-3,2- and -3,4-lactam trisaccharides **6** and **7** (Figure 1), which are simplified analogues of the SLe^x-lactams. We plan to use these compounds as potential inhibitors of recognition between SLe^x-lactam and the corresponding antibodies obtainable by immunization of mice with SLe^x-lactam neoglycoproteins, essentially as described for the G_{M3}-lactam system.[5,7,8]

The fully O-acetylated derivatives of **6** and **7** were important for securing the structure of the SLe^x-1‴→4′-lactam (**4**). In addition, the synthetic targets **6** and **7** provided incentive to further investigate the versatility of NTroc-protection[11] en route to lactams (**21** → **40**) and to develop and test a complex galactosyl donor (**44**) for regioselective glycosylation (→ **45**).

Results and Discussion

I. Synthesis of Sialyl Lewis x-1‴→2′-lactam and the Corresponding Acetamido Analogues of Sialyl Lewis x Tetrasaccharide and Lewis x Trisaccharide. The overall synthetic strategy was based on considerations of the various functionalities in the final products and on the need to develop generally useful intermediates that would lead to both the lactam (**1**) and the acetamido (**2**, **3**) analogues. Since both the glucosamine and galactosamine moieties are present as β-glycosides in **1**−**3**, the nitrogens had to carry participating protecting groups that permitted selective manipulations following the glycosylation steps. This was realized by using the tetrachlorophthalimido[12] (NTCP) and [(2,2,2-trichloroethoxy)carbonyl]amino[11,13] (NTroc) protecting groups. We also used regioselective glycosylations of diol acceptors for the introduction of the galactosamine and sialic acid units, in correspondence with earlier successful similar reactions (see below).

Synthesis of the Galactosamine Donor 14. We have developed a route to **14** starting with glucosamine instead of galactosamine. The known route to **8** from glucosamine is straightforward and includes high-yield-

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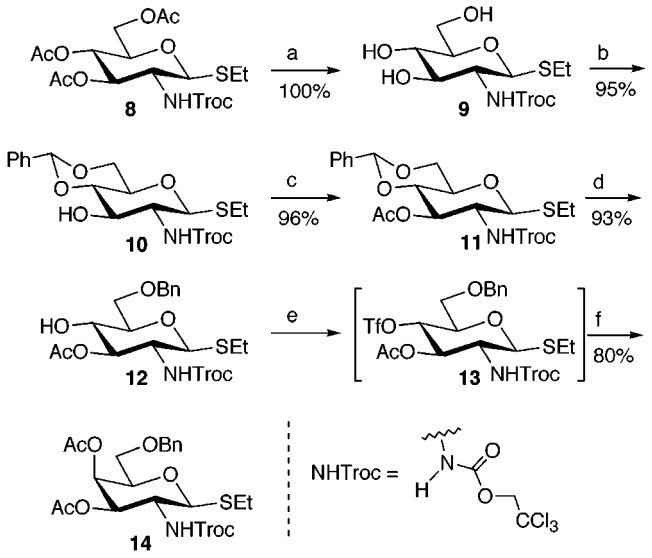
Scheme 1[a]



[a] Key: (a) HCl−MeOH, ∼22 °C, 16 h; (b) $C_6H_5CH(OMe)_2$, TsOH, MeCN, 4 h; (c) Ac_2O, pyridine, DMAP, ∼22 °C, 1 h; (d) $NaBH_3CN$, THF, then HCl−OEt_2 (pH 2−3), 0 °C, 2 h; (e) $(CF_3SO_2)_2O$, pyridine, CH_2Cl_2, −20 °C, 2 h; (f) CsOAc, DMF, ∼22 °C, 2.5 h.

ing steps and a crystalline intermediate,[11] whereas the corresponding reactions starting with galactosamine were much less efficient and gave syrups that were difficult to purify. The reactions leading from **8** to **14** (Scheme 1) are highly efficient and the only (formal) drawback is the glucosamine → galactosamine inversion step (**12** → **14**), which, however, proceeds in high yield.

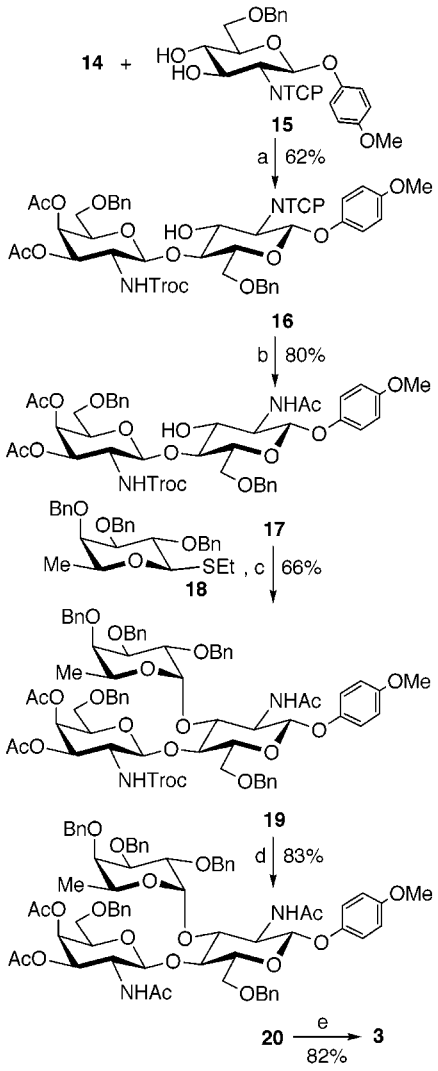
De-O-acetylation of the known[11] NTroc-protected thioglycoside **8** was accomplished by treatment with HCl-saturated methanol overnight to give **9** (100%). Treatment of **9** with α,α-dimethoxytoluene under acidic conditions furnished **10** (95%), and the ensuing O-acetylation gave **11** (96%). Reductive opening of the 4,6-*O*-benzylidene ring[14] in **11** yielded **12** (93%), and trifluoromethanesulfonylation of HO-4 gave crude **13**, which was treated with cesium acetate in freshly distilled DMF to furnish the NTroc-protected galactosamine donor **14** (80%). Treatment of **13** with sodium acetate instead of cesium acetate also provided **14**, albeit in low yield and purity.

Regioselective Glycosylation of Diol Acceptor 15 and Synthesis of Le^x Trisaccharide Analogue 3. Regioselective methylsulfenyl bromide[15] (MSB)- and silver trifluoromethanesulfonate (AgOTf)-mediated glycosylation of the known[1] acceptor **15** with the donor **14** yielded the disaccharide derivative **16** (62%) as depicted in Scheme 2. The structure of **16** was confirmed by ^{1}H NMR analysis of the 3-O-acetylated derivative. The isomeric β-1,3-glycoside could not be detected in the reaction mixture. Such high regioselectivity was also observed in previous glycosylations of **15** and its NPhth analogue.[1,11] Several attempts to improve the synthesis of **16** were unsuccessful; in all cases, the yield was approximately 60%.

As in the SLe^x synthesis described in the previous paper,[1] the large NTCP group (which had served its purpose to guide the regioselective glycosylation with **14**) was replaced by the smaller NHAc group in order to ease the ensuing fucosylation. Thus, treatment of **16** with 1.2 equiv of 1,2-diaminoethane[12] in ethanol at 60 °C overnight, followed by selective N-acetylation with aqueous acetic anhydride furnished the NTroc-protected disaccharide **17** (80%). The efficient regioselective deblocking of the NTCP group in the presence of an NTroc group is a potentially useful reaction for the synthesis of other saccharides containing multiple amino sugar units.

Fucosylation of HO-3 in **17** was performed by first treating the thiofucoside **18**[16] with bromine (Br_2, distilled from P_2O_5) to generate the corresponding fucosyl bromide[17] and then add the mixture to **17** in the presence of Bu_4NBr[18] (kept under vacuum at 80 °C overnight), thus furnishing **19** (66%).

Scheme 2[a]



[a] Key: (a) AgOTf, MeCN, −70 °C, Ar, 5 min, then MeSBr, $ClCH_2CH_2Cl$, −78 °C, 2 h; (b) $H_2NCH_2CH_2NH_2$, EtOH, 60 °C, 16 h, then Ac_2O, MeOH, H_2O, ∼22 °C, 1.5 h; (c) Br_2, CH_2Cl_2, cyclohexene, then MS 4 Å, Bu_4NBr, CH_2Cl_2, DMF, ∼22 °C, 48 h, then pyridine, 3 h; (d) Zn, AcOH, ∼22 °C, 1.5 h, then Ac_2O, pyridine; (e) H_2, Pd−C, AcOH, then MeONa, MeOH.

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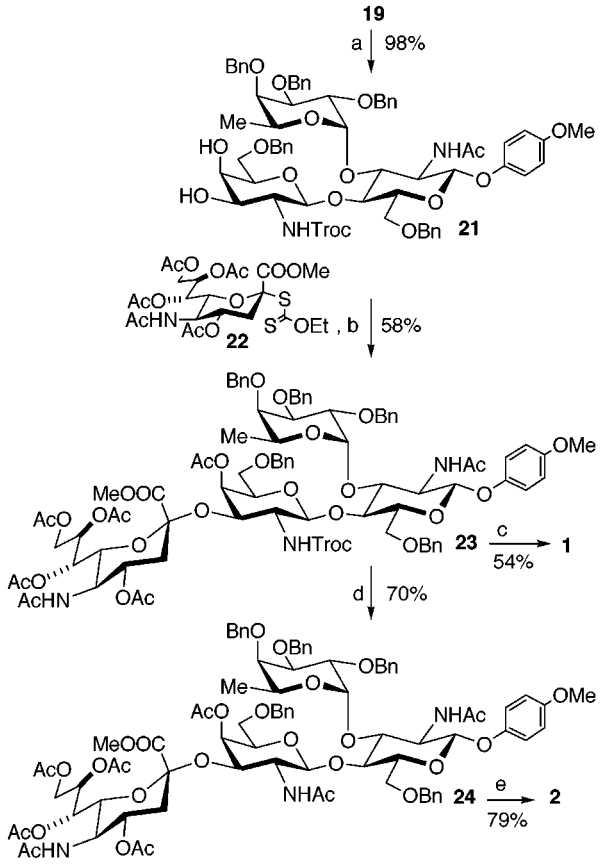
Scheme 3[a]



[a] Key: (a) guanidinium nitrate, MeONa, MeOH, CH_2Cl_2, ~22 °C, 15 min; (b) MS 3 Å, CH_2Cl_2, MeCN, Ar, −60 °C, 5 min, then AgOTf, MeCN, MeSBr, $ClCH_2CH_2Cl$, −60 °C, 3 h, then Ac_2O, pyridine; (c) Zn, AcOH, ~22 °C, 2.5 h, then MeONa, MeOH, ~22 °C, 14 h, then H_2, $Pd(OH)_2$−C, EtOH, ~22 °C, 5 h; (d) Zn, AcOH, ~22 °C, 15 h, then Ac_2O, pyridine, 4.5 h; (e) H_2, Pd−C, AcOH, ~22 °C, 3 h, then MeONa, MeOH, ~22 °C, 1 h, then aqueous NaOH, ~22 °C, 1.5 h.

Removal of the NTroc protecting group in **19** was performed by treatment with zinc in regular (not dried) acetic acid.[13] Activation of the zinc dust prior to use was important for obtaining a good yield. Thus, the zinc was washed with 2 M aqueous HCl, followed by washing with water, ethanol, and ether and drying under vacuum. The resulting crude amine was N-acetylated with acetic anhydride in pyridine to give **20** (83%).

Compound **20** was de-O-benzylated by hydrogenolysis in freshly distilled acetic acid, and the crude product was de-O-acetylated in methanolic MeONa to furnish **3** (82%) as a bis-acetamido analogue of the Le^x trisaccharide.

Synthesis of SLe^x-1‴→2′-lactam 1 and SLe^x Tetrasaccharide Analogue 2. A critical step in the synthesis was the removal of the *O*-acetyl groups of **19** while leaving the NTroc group intact. We have recently reported that dilute guanidine−guanidinium nitrate solution is an effective reagent for such selective de-O-acetylations.[19] In the present case, **19** was transformed within 15 min into **21** (Scheme 3) in 98% isolated yield. Compound **21** crystallized from a mixture of EtOAc and heptane, thus ensuring the purity of this important intermediate, which was used for the preparation of compounds **1**, **2**, and **6**.

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Regioselective α-sialylation of **21** with the donor **22**[20] under promotion of AgOTf and MSB,[15] followed by O-acetylation, furnished **23** in 58% yield; dry AgOTf and freshly distilled acetonitrile were essential for a good result. The primary sialylation product was difficult to purify, but the O-acetylated derivative **23** was easily obtained in pure form by chromatography. The α-sialyl linkage was deduced from the coupling constant between the carbonyl carbon and the axial proton in the 3‴-position[21] ($J_{C-1''':H-3'''ax} = 6.1$ Hz).

The NTroc group of **23** was transformed into an acetamido group by reduction with activated zinc, followed by *N*-acetylation, to give **24** (70%). Hydrogenolytic de-O-benzylation of **24**, followed by de-O-acetylation gave the SLe^x tetrasaccharide analogue **2** (79%).

The final transformations of **23** to obtain the lactam **1** required four different reactions (removal of the Troc group, de-O-acetylation, lactamization, and de-O-benzylation). The product lactamized under the conditions used for de-O-acetylation. The yield and purity of **1** was highly dependent on the reaction sequence and the quality of the reagents, as revealed by several preliminary experiments.

It was eventually found that removal of the Troc group by zinc reduction, followed by de-O-acetylation with concomitant lactamization and a final hydrogenolytic de-O-benzylation with $Pd(OH)_2$−C as catalyst, furnished the SLex-1‴→2′-lactam **1** in an overall yield of 54%.

It is essential to use newly activated zinc (see the Experimental Section) in the removal of the Troc group in order to reduce the reaction time (from 15 h with unactivated Zn to 2.5 h) and thereby obtain a pure product; nonactivated zinc gives several byproducts. In addition, the acetic acid solvent should not be dried, since this seriously decreased the reaction rate. The de-O-acetylation/lactamization step should be performed in regular methanol, since methanol dried over molecular sieves gave mainly undesired products. The de-O-benzylation step was best performed in ethanol with Pd-$(OH)_2$−C as catalyst; Pd−C in AcOH caused substantial cleavage of the Fuc-α glycosidic bond.

II. Synthesis of Sialyl Lewis x-1‴→4′-lactam and the Corresponding Acetamido Analogue of Lewis x Trisaccharide. The synthetic strategy was to develop generally useful intermediates leading to both the lactam **4** and the acetamido analogue **5**. Furthermore, the previous[1] successful regioselective glycosylation of the acceptor **15** was planned to be a key step also in the present synthesis.

Synthesis of the Galactosamine Donors 30 and 32. Treatment of the known[22] thioglucoside **25** with α,α-dimethoxytoluene and *p*-toluenesulfonic acid (Scheme 4) gave the 4,6-*O*-benzylidene derivative **26** (96%), and O-acetylation of **26** gave the di-*O*-acetate **27** (97%). Reductive opening[14] of the benzylidene ring of **27** with $NaBH_3CN$ then furnished the partially protected thioglucoside **28** (92%).

Trifluoromethanesulfonylation of HO-4 in **28** provided the crude triflate **29**, which was treated, without further

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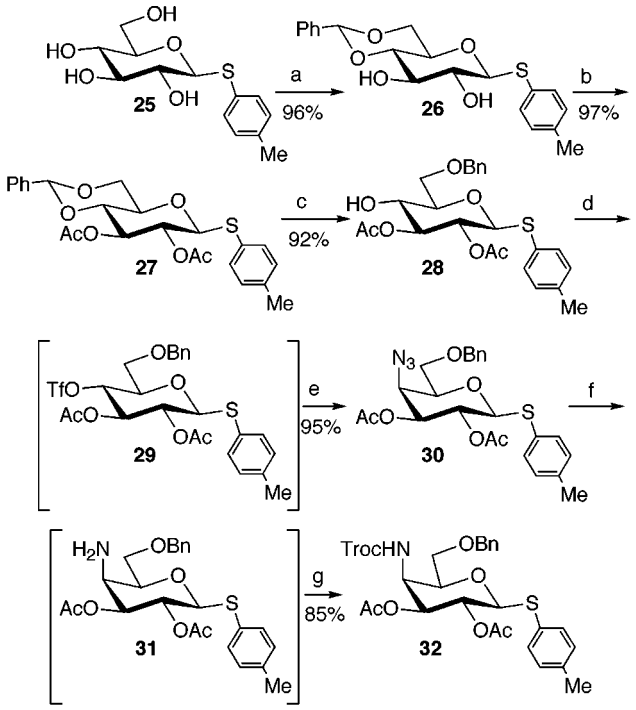
Scheme 4[a]



[a] Key: (a) $C_6H_5CH(OMe)_2$, TsOH, MeCN, 17 h; (b) Ac_2O, pyridine, ~22 °C, 18 h; (c) $NaBH_3CN$, THF, MS 3 Å, HCl−OEt_2 (pH 2), 0 °C, 40 min; (d) $(F_3CSO_2)_2O$, pyridine, CH_2Cl_2, −78 → ~20 °C, 3 h; (e) NaN_3, DMF, ~22 °C, 17 h; (f) H_2S, pyridine, H_2O, 0 → ~22 °C, 42 h; (g) Cl_3CCH_2OCOCl, pyridine, ~22 °C, 1 h.

purification, with NaN_3 in DMF to furnish the 4-azido-4-deoxygalactoside **30** in 95% overall yield. The donor **30** was used for the glycosylation of **15** (see below).

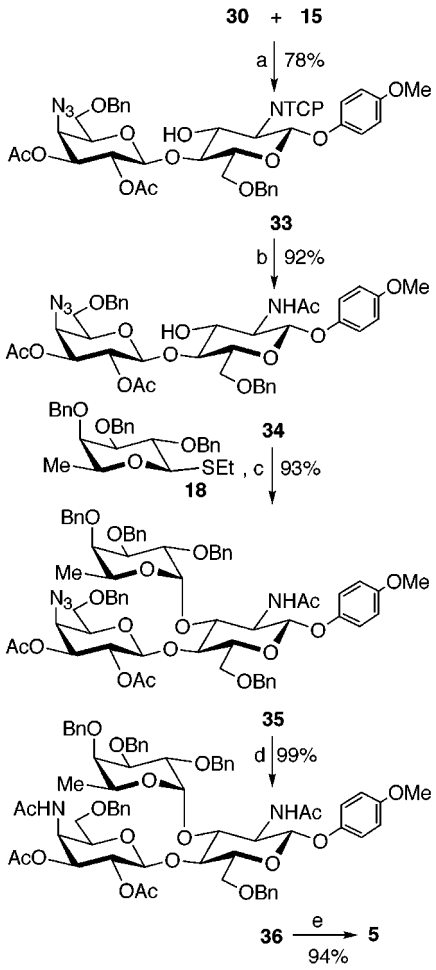
Reduction of the azido group of **30** with H_2S gave the crude amine **31**, which was transformed into the NTroc derivative **32** in 85% overall yield. Compound **32** is a potential glycosyl donor, although in the present case, attempted glycosylation of the acceptor **15** failed. More specifically, compound **32** was not fully stable under the same glycosylation conditions that were used successfully with donor **30**.

Regioselective Glycosylation of Diol Acceptor 15 and Synthesis of Le^x Trisaccharide Analogue 5. Regioselective methylsulfenyl bromide[15] (MSB)- and silver trifluoromethanesulfonate (AgOTf)-mediated glycosylation (Scheme 5) of the known[1] acceptor **15** with the donor **30** furnished the disaccharide **33** (78%); no isomeric glycosides could be isolated from the reaction mixture. Such high regioselectivity was also observed in previous glycosylations of **15**.[1,11] The structure of **33** was confirmed by ^{1}H NMR analysis of the corresponding 3-O-acetylated derivative.

As in the SLe^x and SLe^x-1‴→2′-lactam syntheses described previously, the large NTCP group in **33** (which had served its purpose to guide the regioselective glycosylation with **30**) was replaced by the smaller NHAc group in order to ease the ensuing fucosylation. Thus, treatment of **33** with 1,2-diaminoethane[12] in ethanol at 60 °C, followed by selective N-acetylation with aqueous acetic anhydride, furnished the acetamido compound **34** (92%).

Fucosylation of HO-3 in **34** is a highly efficient process. Thus, treatment of the thiofucoside **18**[16] with bromine (Br_2, distilled from P_2O_5) to generate the corresponding

Scheme 5[a]



[a] Key: (a) AgOTf, CH_2Cl_2, MeCN, −78 °C, Ar, 5 min, then MeSBr, $ClCH_2CH_2Cl$, −78 °C, 2 h; (b) $H_2NCH_2CH_2NH_2$, EtOH, 60 °C, 4 h, then Ac_2O, MeOH, H_2O, ~22 °C, 1 h; (c) Br_2, CH_2Cl_2, cyclohexene, then MS 4 Å, Bu_4NBr, CH_2Cl_2, DMF, ~22 °C, 3 d, then pyridine, 3 h; (d) H_2S, pyridine, H_2O, ~22 °C, 48 h; (e) H_2, Pd−C, AcOH, ~22 °C, 4 h, then MeONa, MeOH.

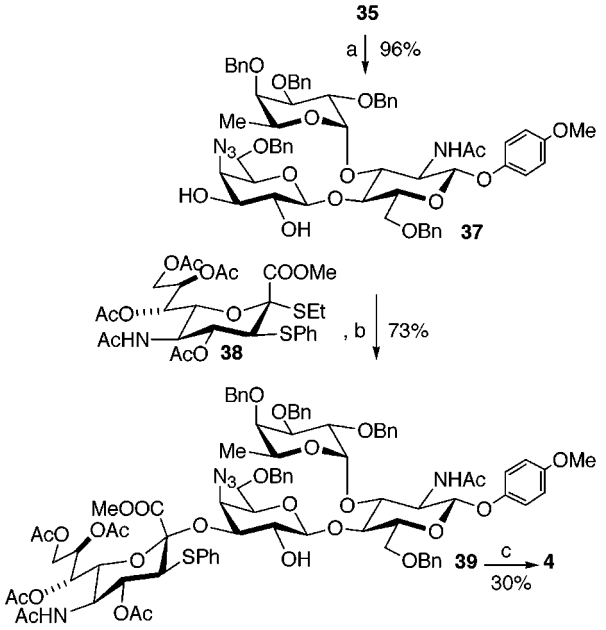
fucosyl bromide[17] and addition of the mixture to **34** in the presence of Bu_4NBr[18] (kept under vacuum at 80 °C overnight) furnished the trisaccharide **35** in a very pleasing 93% yield.

Reduction of the azido group in **35** with H_2S gave a crude amine, which was N-acetylated with acetic anhydride in pyridine to furnish **36** (99%). Compound **36** was de-O-benzylated by hydrogenolysis in freshly distilled acetic acid, and the crude product was de-O-acetylated in methanolic MeONa to furnish **5** (94%), a bis-acetamido analogue of the Le^x trisaccharide.

Synthesis of the SLe^x-1‴→4′-lactam 4. Compound **35** was treated with methanolic MeONa (Scheme 6) to give the diol acceptor **37** (96%). Attempted sialylation of **37** with the xanthate sialyl donor used in the syntheses of SLe^x and SLe^x-1‴→2′-lactam was unsuccessful; the desired tetrasaccharide could not be detected in the reaction mixture, and 82% of the acceptor **37** was recovered unchanged.

We have developed the donor **38** for demanding sialylations where normal donors are ineffective, as exemplified by our syntheses of a bis-sialic acid disaccharide and

Scheme 6[a]



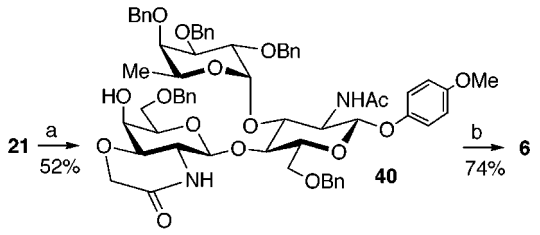
[a] Key: (a) MeONa, MeOH, ~22 °C, 30 min; (b) CH_2Cl_2, MS 3 Å, MeCN, Ar, −45 °C, 5 min, then AgOTf, MeSBr, $ClCH_2CH_2Cl$, −45 °C, 2.5 h; (c) RaNi, EtOH, ~22 °C, 1 H, then MeONa, MeOH, ~22 °C, 1.5 H, then H_2, $Pd(OH)_2$−C, ~22 °C, 14 h.

its lactone and lactam analogues.[23] It was found that these sialylations with **38** proceeded with very high regio- and stereoselectivities, which is difficult to obtain with most other sialyl donors. This trend was followed in the present investigation, where **38** effectively sialylated the acceptor **37** to give the tetrasaccharide **39** (73%), free of isomeric compounds. The 2′-O-acetylated derivative of **39** confirmed the regioselectivity in the sialylation step. A structural variant of **38** was recently reported.[24]

The deprotection−lactamization of compound **39** was much more troublesome than anticipated. Even so, the final product **4** could be obtained in 30% overall yield from **39** in conjunction with substantial amounts (32%) of a byproduct. Compound **39** was treated with Raney nickel (RaNi) in EtOH in order to remove the phenylthio group and reduce the azido group. A crude product was obtained by trituration with MeOH−toluene. Residual aluminum salts (emanating from the RaNi) were removed by filtration on SiO_2. Aluminum salts are detrimental to catalytic hydrogenolysis with Pd catalysts.[25] Treatment with MeONa-MeOH caused de-O-acetylation and lactamization, and the resulting crude product was hydrogenated (H_2, $Pd(OH)_2$−C) to give pure **4** in 30% yield after chromatographic purification, together with 32% of the unidentified byproduct.

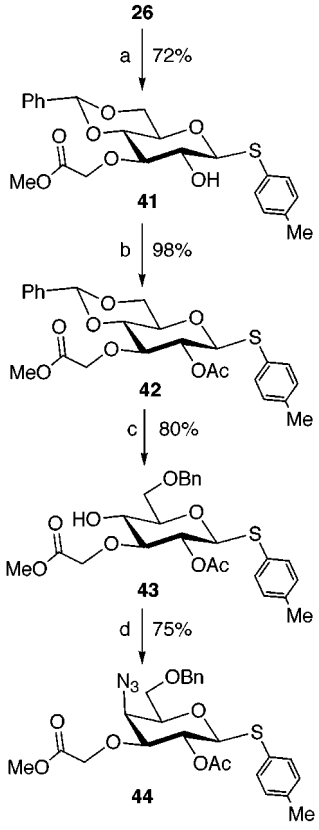
The byproduct was acetylated to furnish a product with the following NMR characteristics: (1) the signals for the "Le^x" trisaccharide moiety were essentially identical with those of acetylated **4**; (2) only 11 *O*-and *N*-acetyl groups were present, as compared to 12 groups in fully acetylated **4**; (3) the carbon chain of the sialic acid residue seemed to be intact, but NMR data differed from those of acetylated **4**. We cannot at present provide a structure for the unknown byproduct.

Scheme 7[a]



[a] Key: (a) Bu_2SnO, MS 4 Å, toluene, 80 °C, 8 h, then Bu_4NBr, $BrCH_2COOC(CH_3)_3$, 80 °C, 4 h, then Zn, AcOH, ~22 °C, 4 h, then MeONa, MeOH, ~22 °C, 1 h; (b) H_2, $Pd(OH)_2$−C, EtOH, ~22 °C, 19 h.

Scheme 8[a]



[a] Key: (a) Bu_2SnO, MeOH, reflux, 75 min, then Bu_4NBr, $BrCH_2COOC(CH_3)_3$, MS 3 Å, reflux, 3 h, then MeONa, MeOH, ~22 °C, 1 h; (b) Ac_2O, pyridine, DMAP, ~22 °C, 40 min; (c) $NaBH_3CN$, THF, MS 4 Å, then HCl−OEt_2 (pH 2), 0 °C, 1.5 h; (d) $(F_3CSO_2)_2O$, pyridine, CH_2Cl_2, ~22 °C, 3 h, then NaN_3, DMF, ~22 °C, 15 h.

III. Synthesis of Two Lactam Analogues of the Lewis x Trisaccharide. The synthetic strategy for the preparation of **6** was based on the use of trisaccharide derivative **21** (Scheme 3) as starting material for regioselective alkylation, followed by closure of the lactam ring (Scheme 7). The synthesis of the isomeric lactam **7** was conducted by assembly of the monosaccharide moieties **15**, **44**, and **18** (Scheme 9).

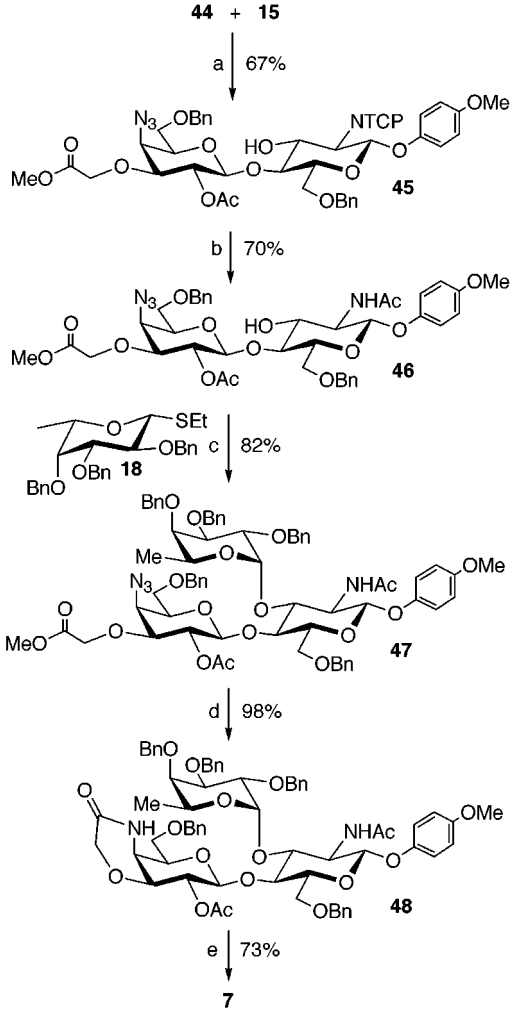
Synthesis of the Le^x 3,2-Lactam Trisaccharide 6. The NTroc-protected trisaccharide **21** was transformed in one sequence into the lactam **40**, without purification of the intermediates (Scheme 7). Thus, compound **21** was

(23) (a) Ercégovic, T.; Magnusson, G. *J. Org. Chem.* **1995**, *60*, 3378−3384. (b) Ercégovic, T.; Magnusson, G. *J. Org. Chem.* **1996**, *61*, 179−184.

(24) Martichonok, V.; Whitesides, G. M. *J. Am. Chem. Soc.* **1996**, *118*, 8187−8191.

(25) Freifelder, M. *Practical Catalytic Hydrogenation*; Wiley-Interscience: New York, 1971; p 24.

Scheme 9[a]



[a] Key: (a) AgOTf, MeCN, CH_2Cl_2, −78 °C, Ar, 5 min, then MeSBr, $ClCH_2CH_2Cl$, −78 °C, 1.5 h; (b) $H_2NCH_2CH_2NH_2$, EtOH, 60 °C, 15 h, then Ac_2O, MeOH, H_2O, ∼22 °C, 1 h; (c) Br_2, CH_2Cl_2, cyclohexene, then MS 4 Å, Bu_4NBr, CH_2Cl_2, DMF, ∼22 °C, 3 d, then pyridine, 3 h; (d) H_2S, pyridine, Et_3N, MeOH, 0 °C, 16 h; (e) H_2, Pd−C, AcOH, ∼22 °C, 1.5 h, then MeONa, MeOH, ∼22 °C, 3 h.

treated with Bu_2SnO to provide the corresponding 3,4-stannylene acetal. Bu_4NBr-mediated regioselective *O*-alkylation of the 3-position of the galactosamine moiety, using *tert*-butyl bromoacetate as alkylating agent, gave an intermediate where the NTroc group was then reduced with activated zinc dust in acetic acid to give the corresponding primary amine. (Attempted alkylation with ethyl bromoacetate, instead of *tert*-butyl bromoacetate, gave mainly the 3,4-di-O-alkylated product). Final treatment of the crude amine with methanolic MeONa closed the lactam ring. Compound **40** was thus obtained over four steps in an overall yield of 52%, which is equivalent to an average yield of 85% per step. Removal of the benzyl protecting groups of **40** by Pd-$(OH)_2$−C-catalyzed hydrogenolysis in EtOH then furnished the Le^x-3,2-lactam **6** in 74% yield.

An attempt to perform the same sequence of reactions with ethylthio 6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-galactopyranoside (prepared by de-O-acetylation of compound **14**) to create the corresponding monosaccharide lactam was unsuccessful, indicating that the NTroc group is sensitive toward the reaction conditions used, unless protected by steric hindrance, as presumed in the trisaccharide **21**.

Synthesis of the 4-Azido-4-deoxygalactose Donor 44. Thioglucoside **26** (Scheme 4) was regioselectively alkylated with *tert*-butyl bromoacetate via the corresponding 2,3-stannylene acetal. The crude alkylated intermediate was treated with methanolic MeONa to give the methyl ester **41** (Scheme 8) in an overall yield over three steps of 72% (average yield per step: 90%). As in the reaction of **21** above, ethyl bromoacetate gave mainly the corresponding di-O-alkylated product. Obviously, introduction of the *tert*-butyl (but not ethyl) ester group at O-3 blocks HO-2 against further alkylation.

Conventional O-acetylation of **41** gave **42** (98%), and reductive $NaBH_3CN-HCl-Et_2O$-mediated opening[14] of the 4,6-*O*-benzylidene ring of **42** yielded **43** (80%). Treatment of **43** with trifluoromethanesulfonic anhydride in pyridine and removal of the reagents and solvent gave the corresponding 4-*O*-triflate, which was dried under vacuum. The crude triflate was then treated with NaN_3 in freshly distilled DMF, thus providing the glycosyl donor **44** (75%). The ester and azido functionalities of **44** were left intact until the trisaccharide stage (**47**), in order not to jeopardize the two ensuing glycosylation steps: the donor properties of lactamized intermediates would probably be hampered due to unwanted strain and/or steric hindrance in the pyranosidic ring.

Regioselective Glycosylation of Diol Acceptor 15 and Synthesis of the Le^x 3,4-Lactam Trisaccharide 7. Regioselective 4-O-glycosylation of the 3,4-diol **15**[1] with donor **44** (Scheme 9) by activation with methylsulfenyl bromide[15] (MSB) and silver triflate (AgOTf) gave the disaccharide **45** (67%). It is important to use freshly distilled solvents in the glycosylation reaction in order to obtain a high yield of **45**. The regioselectivity was virtually complete, which is in accordance with glycosylations of **15** en route to the SLe^x and SLe^x-lactam tetrasaccharides.

As in the previous syntheses, the large NTCP group (which had served its purpose to guide the regioselective glycosylation of **15**) was replaced by the NHAc group. Thus, treatment of **45** with 1.2 equiv of 1,2-diaminoethane[12] in ethanol at 60 °C overnight, followed by selective *N*-acetylation with aqueous acetic anhydride (Ac_2O), furnished the disaccharide **46** (70%). To obtain **46** in high yield and free from contaminants, it was necessary to use freshly distilled 1,2-diaminoethane in only a small excess (to minimize reaction with the ester function) for removal of the TCP group.

Fucosylation of HO-3 in **46** was performed by first treating the thiofucoside **18**[16] with bromine (Br_2, distilled from P_2O_5) to generate the corresponding fucosyl bromide[17] and then add the mixture to **46** in the presence of Bu_4NBr[18] (kept under vacuum at 80 °C overnight) to furnish **47** in 82% yield. As before, a high yield in this and similar glycosylations requires that solvents and volatile reagents are distilled prior to use.

Compound **48** was formed by H_2S reduction of the azido function in **47**, followed by spontaneous closure of the lactam ring.[5] This reaction sequence is very efficient, and **48** was obtained in 98% yield after chromatography. Hydrogenolytic cleavage of the benzyl protecting groups of **48**, using Pd−C as catalyst and freshly distilled acetic acid as solvent, followed by de-O-acetylation with methanolic MeONa gave the Le^x-3,4-lactam **7** in 73% yield. An

attempt to prepare **48** by *tert*-butyl bromoacetate−alkylation of compound **37** (Scheme 6) was totally unsuccessful.

Experimental Section

The general methods were essentially as described in the preceding paper in this issue.[1] In addition zinc dust was washed with aqueous HCl (2 M, three times), H_2O (twice), EtOH (twice), and Et_2O (once) before use; 1,2-diaminoethane was distilled before use; a clear stock solution of guanidinium nitrate reagent was prepared by dissolving guanidinium nitrate (622 mg, 5 mmol) in 9:1 MeOH−CH_2Cl_2 (50 mL) and adding methanolic 1 M MeONa (1 mL); the stock solution was kept at room temperature for several weeks without any observed decrease in activity.[19] Compounds **8**,[11] **15**,[1] **18**,[16] **22**,[20] **25**,[22] and **38**[23] were synthesized as described in the literature.

4-Methoxyphenyl (5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyloyl-1‴→2′-lactam)-(1→3)-(2-deoxy-2-amino-3-*O*-*β*-D-galactopyranosyl)-(1→4)-[α-L-fucopyranosyl]-(1→3)-(2-acetamido-2-deoxy-*β*-D-glucopyranoside) (1). Compound **23** (120 mg, 0.07 mmol) was dissolved in AcOH (10 mL), and freshly activated zinc dust (750 mg) was added. The mixture was stirred for 2.5 h and filtered through a short column (SiO_2, 2:1 CH_2Cl_2−acetone). The crude compound was dissolved in methanolic 0.04 M NaOMe (14 mL), and the solution was stirred for 14 h, neutralized with Amberlite IR 120 H^+, and concentrated. The residue was filtered through a short column (SiO_2, 5:1 CH_2Cl_2−MeOH), and the solvent was removed. The residue was dissolved in EtOH (4 mL), and $Pd(OH)_2$−C (20%, 200 mg) was added. The mixture was hydrogenated (H_2, 1 atm) for 5 h, filtered through Celite, and concentrated. The residue was chromatographed (SiO_2, 65:30:5 CH_2Cl_2−MeOH−H_2O) to give **1** (33 mg, 54%): $[\alpha]^{20}_D$ −53.4 (*c* 1.0, MeOH); ^{1}H NMR (CD_3OD) δ 6.80−6.95 (m, 4 H, OPMP), 5.06 (d, 1 H, J = 3.9 Hz, H-1″), 5.01 (d, 1 H, J = 8.3 Hz, H-1), 4.70 (q, 1 H, J = 6.4 Hz, H-5″), 4.64 (d, 1 H, J = 7.3 Hz, H-1′), 4.36 (m, 1 H, H-4‴), 3.73 (s, 3 H, OMe), 2.51 (d, 1 H, J = 13.4, 5.5 Hz, H-3‴eq), 1.97, 2.00 (s, 3 H each, NHAc), 1.64 (dd, 1 H, J = 13.3, 10.8 Hz, H-3‴ax), 1.20 (d, 3 H, J = 6.6 Hz); ^{13}C NMR (CD_3OD) δ 172.7, 171.5, 167.7, 154.3, 150.5, 116.7, 113.0, 98.9, 98.6, 97.9, 96.8, 75.9, 75.0, 74.2, 74.0, 73.7, 71.7, 71.1, 68.7, 68.5, 67.5, 67.1, 66.4, 65.4, 64.3, 62.1, 59.89, 59.85, 55.2, 53.5, 51.5, 49.5, 39.5, 20.6, 20.1, 14.5; HRMS calcd for $C_{38}H_{57}O_{22}N_3Na$ (M + Na) 930.3331, found 930.3332.

A sample of **1** was conventionally acetylated (Ac_2O−pyridine−DMAP): ^{1}H NMR ($CDCl_3$) δ 7.34 (d, 1 H, J = 11.3, NH), 6.80−7.05 (m, 4 H, OPMP), 5.64 (d, 1 H, J = 9.8 Hz, NH‴), 5.51 (d, 1 H, J = 3.6 Hz, H-1″), 5.46 (dt, 1 H, J = 11.2, 6.2 Hz, H-4‴), 5.41 (bs, 1 H, H-4′), 5.37 (dd, 1 H, J = 9.9, 1.8 Hz, H-7‴), 5.29−5.35 (m, 3 H, H-1,3″,4″), 5.22 (dd, 1 H, J = 10.6, 3.8 Hz, H-2″), 5.12 (dt, 1 H, J = 9.9, 3.9 Hz, H-8‴), 4.54−4.60 (m, 2 H, H-1′,6′), 4.49 (bd, 1 H, J = 9.2 Hz, H-2), 4.35 (bs, 1 H, H-3), 4.15−4.25 (m, 5 H, H-6,6′,5″,5‴,9‴), 4.03 (dd, 1 H, J = 8.9, 4.0 Hz, H-9‴), 3.97 (t, 1 H, J = 8.0 Hz, H-6), 3.91 (bs, 1 H, H-4), 3.43−3.85 (m, 5 H, H-5,2′,3′,5′,6‴), 3.73 (s, 3 H, OMe), 2.42 (dd, 1 H, J = 13.1, 5.4 Hz, H-3eq‴), 2.19, 2.18, 2.16, 2.12, 2.09, 2.05, 2.04, 2.03, 2.02, 2.00, 1.97, 1.90 (s, 3 H each, OAc, NHAc), 1.86 (t, 1 H, J = 13.1 Hz, H-3ax‴), 1.18 (d, 3 H, J = 6.5 Hz, H-6″).

4-Methoxyphenyl (5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid)-(1→3)-(2-acetamido-2-deoxy-*β*-D-galactopyranosyl)-(1→4)-[α-L-fucopyranosyl]-(1→3)-(2-acetamido-2-deoxy-*β*-D-glucopyranoside) (2). Compound **24** (94 mg, 0.06 mmol) was dissolved in AcOH (4 mL), and Pd−C (10%, 100 mg) was added. The mixture was hydrogenated (H_2, 1 atm) for 3 h, filtered through Celite, and concentrated. The residue was chromatographed (SiO_2, 5:1 CH_2Cl_2-MeOH). The product was dissolved in methanolic 0.03 M NaOMe (5 mL), the mixture was stirred for 1 h, 1 M aqueous NaOH (0.3 mL) was added, and the stirring was continued for 1.5 h. AcOH (0.19 mL) was added, the mixture was concentrated, and the residue was chromatographed (SiO_2, 60:35:5 CH_2Cl_2−MeOH−H_2O plus 0.1% AcOH) to give **2** (44 mg, 79%): $[\alpha]^{20}_D$ −62.3 (*c* 1.0 H_2O); ^{1}H NMR (D_2O) δ 6.80−6.91 (m, 4 H, OPMP), 5.00 (d, 1 H, J = 4.0 Hz, H-1″), 4.87 (d, 1 H, J = 8.4 Hz, H-1), 4.60−4.75 (m, H-5″, HDO), 4.45 (d, 1 H, J = 8.6 Hz, H-1′), 3.66 (s, 3 H, OMe), 2.56 (dd, 1 H, J = 12.7, 4.7 Hz, H-3‴eq), 1.88, 1.89, 1.95 (s, 3 H each, NHAc), 1.46 (t, 1 H, J = 12.1 Hz, H-3‴ax), 1.11 (d, 1 H, J = 6.6 Hz, H-6″); ^{13}C NMR (D_2O) δ 181.7, 175.5, 1.75.3, 174.9, 174.7, 155.2, 151.5, 118.6, 115.4, 100.8, 100.6, 99.5, 98.8, 75.9, 75.0, 74.7, 73.3, 73.04, 72.96, 72.3, 71.9, 69.5, 68.7, 68.4, 68.0, 67.3, 66.8, 62.9, 61.9, 60.1, 56.11, 56.05, 52.2, 51.3, 40.3, 23.6, 22.6, 22.5, 22.4, 15.8; HRMS calcd for $C_{40}H_{61}O_{24}N_3Na$ (M + Na) 990.3543, found 990.3541.

4-Methoxyphenyl (2-Acetamido-2-deoxy-*β*-D-galactopyranosyl)-(1→4)-[α-L-fucopyranosyl]-(1→3)-(2-acetamido-2-deoxy-*β*-D-glucopyranoside) (3). Compound **20** (120 mg, 0.1 mmol) was dissolved in AcOH (3 mL, distilled from Ac_2O), and Pd−C (10%, 120 mg) was added. The mixture was hydrogenated (H_2, 1 atm) for 5 h, filtered through Celite, and concentrated. The residue was dissolved in methanolic 0.05 M NaOMe (5 mL), and the mixture was stirred for 1 h and then neutralized with Amberlite IR 120 H^+. The mixture was concentrated and chromatographed (SiO_2, 65:30:5 CH_2Cl_2−MeOH−H_2O) to give **3** (55 mg, 82%): $[\alpha]^{23}_D$ −64.9 (*c* 1.0, MeOH); ^{1}H NMR (CD_3OD) δ 6.80−6.97 (m, 4 H, OPMP), 5.08 (d, 1 H, J = 3.9 Hz, H-1″), 4.93 (d, 1 H, J = 8.2 Hz, H-1), 4.75 (q, 1 H, J = 7.0 Hz, H-5″), 4.50 (d, 1 H, J = 8.4 Hz, H-1′), 4.17 (t, 1 H, J = 8.5 Hz, H-2), 3.70−4.00 (m, 10 H, H-3,4,6″,2′,4′,6′,-3″,4″), 3.73 (s, 3 H, OMe), 3.67 (dd, 1 H, J = 10.2, 3.9 Hz, H-2″), 3.59 (dd, 1 H, J = 10.2, 3.2 Hz, H-3′), 3.52 (dt, J = 7.5, 3.9 Hz, H-5), 3.45 (bt, 1 H, J = 6.6 Hz, H-5′), 1.99, 1.96 (s, 3 H each, NHAc), 1.27 (d, 3 H, J = 6.7 Hz, H-6″); ^{13}C NMR (CD_3OD) δ 173.0, 172.8, 155.8, 152.0, 118.1, 114.5, 101.1, 100.5, 99.0, 76.8, 75.7, 74.9, 73.5, 72.8, 71.9, 70.3, 69.0, 68.3, 67.0, 61.8, 60.7, 55.7, 55.0, 53.2, 22.1, 22.0, 15.7; HRMS calcd for $C_{29}H_{44}O_{16}N_2Na$ (M + Na) 699.2589, found 699.2584.

4-Methoxyphenyl (5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyloyl-1‴→4′-lactam)-(1→3)-(4-amino-4-deoxy-*β*-D-galactopyranosyl)-(1→4)-[α-L-fucopyranosyl)-(1→3)-(2-acetamido-2-deoxy-*β*-D-glucopyranoside) (4). To compound **39** (100 mg, 0.059 mmol) was added a slurry of Raney-nickel (approximately 1 g, washed twice with EtOH) in EtOH (6 mL). The mixture was stirred for 1 h, the desired compound was isolated from the Raney-nickel by trituration six times with 1:1 MeOH−toluene (10 mL portions), and the combined solutions were filtered (Celite). The solvent was removed, and the residue was filtered through a short column (SiO_2, 5:1 CH_2Cl_2-EtOH). The solvent was removed, and the residue was dissolved in methanolic 0.03 M MeONa (10 mL). The mixture was stirred for 1.5 h, neutralized with Amberlite IR 120 H^+ resin, and concentrated. The residue was filtered through a short column (SiO_2, 5:1 CH_2Cl_2−EtOH). The solvent was removed, the residue was dissolved in EtOH (5 mL), and $Pd(OH)_2$−C (20%, 300 mg) was added. The mixture was hydrogenated (H_2, 1 atm) for 14 h and then filtered and concentrated. The residue was again dissolved in EtOH (5 mL), and a fresh portion of $Pd(OH)_2$−C (20%, 300 mg) was added. The mixture was hydrogenated (H_2, 1 atm) for 24 h, filtered, and concentrated. The residue was chromatographed (SiO_2, 65:30:5 CH_2Cl_2−MeOH−H_2O) to give **4** (16 mg, 30%) together with an unidentified byproduct (17 mg, 32%). Compound **4**: $[\alpha]^{20}_D$ −33.2 (*c* 0.8, MeOH); ^{1}H NMR (CD_3OD) δ 6.80−6.97 (m, 4 H, OPMP), 5.07 (d, 1 H, J = 4.1 Hz, H-1″), 4.97 (d, 1 H, J = 8.4 Hz, H-1), 4.69 (q, 1 H, J = 6.8 Hz, H-5″), 4.57 (d, 1 H, J = 7.9 Hz, H-1′), 4.46 (dd, 1 H, J = 4.9, 1.5 Hz, H-4′), 4.40 (dt, 1 H, J = 10.9, 5.5 Hz, H-4‴), 3.74 (s, 3 H, OMe), 2.45 (dd, 1 H, J = 12.8, 5.4 Hz, H-3_{eq}‴), 2.02, 1.98 (s, 3 H each, NHAc), 1.68 (dd, 1 H, J = 12.8, 10.9 Hz, H-3_{ax}‴), 1.14 (d, 3 H, J = 6.6 Hz, H-6″); ^{13}C NMR (CD_3OD) δ 174.6, 173.6, 168.7, 155.8, 152.1, 118.2, 114.5, 102.5, 100.6, 99.4, 97.6, 76.3, 75.4, 74.1, 73.2, 72.6, 71.9, 71.3, 70.9, 70.4, 68.9, 68.7, 68.1, 66.7, 64.3, 61.2, 60.0, 56.6, 55.0, 53.2, 50.1, 40.6, 22.1, 21.5, 15.7; HRMS calcd for $C_{38}H_{57}O_{22}N_3Na$ (M + Na) 930.3331, found 930.3314.

A sample of **4** was conventionally acetylated (Ac_2O−pyridine): ^1H NMR ($CHCl_3$) δ 6.77−6.92 (m, 4 H, OPMP), 5.68 (dt, 1 H, J = 11.0, 5.4 Hz, H-4‴), 5.58 (d, 1 H, J = 3.2 Hz, H-1″), 5.57 (d, 1 H, J = 3.1 Hz, H-4″), 5.50 (d, 1 H, J = 8.4 Hz, NH), 5.28−5.36 (m, 2 H, H-8‴, NH‴), 5.22 (dd, 1 H, J = 10.0, 1.8 Hz, H-7‴), 5.19 (dd, 1 H, J = 10.8, 2.8 Hz, H-3″), 5.04 (dd, 1 H, J = 10.9, 3.7 Hz, H-2″), 4.95 (d, 1 H, J = 7.3 Hz, H-1), 4.87 (dd, 1 H, J = 9.0, 8.5 Hz, H-2′), 4.55−4.66 (m, 3 H, H-6,6′,5″), 4.46 (dd, 1 H, J = 12.3, 4.0, H-6′), 4.37 (d, 1 H, J = 8.2 Hz, H-1′), 4.23 (dd, 1 H, J = 12.3, 3.0 Hz, H-9‴), 4.19 (d, 1 H, J = 3.9 Hz, H-4′), 4.05−4.15 (m, 4 H, H-2,6,3′,5‴), 3.98 (dd, 1 H, J = 12.2, 5.8 Hz, H-9‴), 3.66−3.88 (m, 5 H, H-3,4,5,5′,6‴), 3.77 (s, 3 H, OMe), 2.33 (dd, 1 H, J = 13.6, 5.7 Hz, H-3_{eq}‴), 2.23, 2.17, 2.16, 2.15, 2.14, 2.13, 2.11, 2.04, 2.03, 2.00, 1.99, 1.87 (s, 3 H each, OAc, NHAc), 1.71 (dd, 1 H, J = 12.6, 11.9 Hz, H-3_{ax}‴), 1.13 (d, 3 H, J = 6.6 Hz, H-6″); ^{13}C NMR ($CHCl_3$) δ 172.4, 171.8, 171.4, 171.1, 170.93, 170.87, 170.81, 170.75, 170.6, 169.8, 166.3, 156.0, 151.6, 118.6, 115.0, 100.44, 100.42, 97.2, 95.1, 74.7, 74.2, 73.3, 72.5, 71.8, 71.6, 71.5, 70.9, 70.6, 69.9, 68.1, 68.0, 67.2, 65.4, 62.8, 62.5, 62.1, 56.6, 56.1, 49.8, 49.7, 38.3, 23.9, 23.7, 21.5, 21.41, 21.35, 21.24, 21.20, 21.1, 16.3.

4-Methoxyphenyl (4-Acetamido-4-deoxy-β-D-galactopyranosyl)-(1→4)-[α-L-fucopyranosyl]-(1→3)-(2-acetamido-2-deoxy-β-D-glucopyranoside) (5). Compound **36** (145 mg, 0.12 mmol) was dissolved in AcOH (5 mL, distilled from Ac_2O), and Pd−C (10%, 150 mg) was added. The mixture was hydrogenated (H_2, 1 atm) for 4 h, filtered through Celite, and concentrated. The residue was dissolved in methanolic 0.05 M MeONa (6 mL), and the mixture was stirred for 40 min and then neutralized with Amberlite IR 120 H^+. The mixture was concentrated and chromatographed (SiO_2, 65:30:5 CH_2Cl_2−MeOH−H_2O) to give **5** (76 mg, 94%): $[\alpha]^{20}_D$ −53 (*c* 1.0, MeOH); ^1H NMR (D_2O) δ 6.77−6.93 (m, 4 H, OPMP), 5.11 (d, 1 H, J = 3.8 Hz, H-1″), 4.92 (d, 1 H, J = 8.2 Hz, H-1), 4.41 (d, 1 H, J = 8.0 Hz, H-1′), 4.38−4.45 (m, 1 H, H-5″), 4.17 (broad d, 1 H, J = 4.2 Hz, H-4′), 3.45−4.05 (m, 13 H, H-2,3,4,5,6,3′,5′,6′,2″,3″,4″), 3.65 (s, 3 H, OMe), 3.29 (dd, 1 H, J = 10.1, 8.0 Hz, H-3′), 1.95, 1.87 (s, 3 H each, NHAc), 1.10 (d, 3 H, J = 6.6 Hz, H-6″); ^{13}C NMR data ($CDCl_3$) δ 175.5, 174.8, 155.2, 151.4, 118.6, 115.4, 102.7, 100.8, 98.0, 75.9, 75.0, 74.9, 72.5, 71.7, 71.3, 69.5, 68.3, 61.3, 60.2, 56.1, 55.8, 51.3, 22.6, 22.4, 15.9; HRMS calcd for $C_{29}H_{44}O_{16}N_2Na$ (M + Na) 699.2589, found 699.2587.

4-Methoxyphenyl (2-Amino-2-deoxy-2,3-*N*,*O*-(2-oxoethylidene)-β-D-galactopyranosyl)-(1→4)-[α-L-fucopyranosyl]-(1→3)-(2-acetamido-2-deoxy-β-D-glucopyranoside) (6). Compound **40** (76 mg, 0.068 mmol) was dissolved in EtOH (4.0 mL), and $Pd(OH)_2$−C (20%, 150 mg, moist) was added. The mixture was hydrogenolyzed (H_2, 1 atm) for 19 h, filtered through Celite, and concentrated. The residue was chromatographed (SiO_2, 30:10:1 CH_2Cl_2−MeOH−H_2O) to give **6** (33 mg, 74%): $[\alpha]^{20}_D$ −51 (*c* 0.9, MeOH); ^1H NMR (CD_3OD) δ 6.80−6.98 (m, 4 H, OPMP), 5.06 (d, 1 H, J = 4.1 Hz, H-1″), 5.00 (d, 1 H, J = 7.7 Hz, H-1), 4.78 (q, 1 H, J = 6.7 Hz, H-5″), 4.63 (d, 1 H, J = 7.3 Hz, H-1′), 4.28, 4.22 (ABq, 1 H each, J = 16.8 Hz, CH_2), 3.55−4.05 (m, 15 H, H-2,3,4,5,6,2′,3′,4′,5′,6′,2″,3″, 4″), 3.74 (s, 3 H, OMe), 1.98 (s, 3 H, NHAc), 1.18 (d, 3 H, J = 6.6 Hz, H-6″); ^{13}C NMR (CD_3OD) δ 173.0, 170.9, 155.9, 152.1, 118.2, 114.5, 100.6, 100.3, 99.5, 76.9, 76.5, 75.9, 75.3, 73.7, 72.7, 70.2, 69.0, 67.8, 66.7, 65.9, 61.5, 60.5, 56.7, 55.0, 52.3, 27.3, 22.0, 15.6; HRMS calcd for $C_{29}H_{42}O_{16}N_2Na$ (M + Na) 697.2432, found 697.2445.

A sample of **6** was conventionally acetylated (Ac_2O−pyridine): ^1H NMR ($CDCl_3$) δ 6.79−6.95 (m, 4 H, OPMP), 5.94 (d, 1 H, J = 8.7 Hz, NH), 5.52 (d, 1 H, J = 4.1 Hz, H-1″), 5.50 (d, 1 H, J = 2.1 Hz, H-4′), 5.36 (d, 1 H, J = 2.9 Hz, H-4″), 5.25 (dd, 1 H, J = 10.9, 3.2 Hz, H-3″), 5.14 (d, 1 H, J = 7.6 Hz, H-1), 5.07 (dd, 1 H, J = 10.9, 3.8 Hz, H-2″), 4.75 (q, 1 H, J = 6.3 Hz, H-5″), 4.48 (bd, 1 H, J = 12.0 Hz, H-6), 4.44 (dd, 1 H, J = 11.7, 6.8 Hz, H-6′), 4.40 (d, 1 H, J = 8.0 Hz, H-1′), 4.32, 4.19 (ABq, 1 H each, J = 17.1 Hz, OCH_2CO), 4.20−4.31 (m, 3 H, H-3,6,6′), 3.85−4.02 (m, 4 H, H-2,4,5,5′), 3.77 (s, 3 H, OMe), 3.56 (dd, 1 H, J = 9.5, 2.4 Hz, H-3′), 3.48 (dd, 1 H, J = 9.8, 8.0 Hz, H-2′), 2.18, 2.16, 2.14, 2.11, 2.10, 2.00, 1.99 (s, 3 H each, OAc, NHAc), 1.14 (d, 3 H, J = 6.5, Hz, H-6″); ^{13}C NMR ($CDCl_3$) δ 171.6, 171.13, 171.06, 171.0, 170.7, 170.3, 169.4, 155.9, 151.6, 118.6, 115.0, 100.3, 99.7, 95.6, 74.7, 73.9, 73.4, 72.8, 71.5, 68.5, 68.3, 65.6, 64.7, 61.4, 56.1, 53.4, 23.8, 21.8, 21.4, 21.25, 21.19, 21.17 21.1, 21.0, 16.6.

4-Methoxyphenyl (4-Amino-4-deoxy-4,3-*N*,*O*-(2-oxoethylidene)-β-D-galactopyranosyl)-(1→4)-[α-L-fucopyranosyl]-(1→3)-(2-acetamido-2-deoxy-β-D-glucopyranoside) (7). Compound **48** (100 mg, 0.085 mmol) was dissolved in AcOH (3.0 mL, distilled from Ac_2O), and Pd−C (10%, 100 mg) was added. The mixture was hydrogenolyzed (H_2, 1 atm) for 1.5 h, filtered through Celite, and concentrated. The residue was dissolved in MeONa-MeOH (5 mL, 0.05 M), and the mixture was stirred for 3 h, neutralized with Amberlite IR 120 H^+, and concentrated. The residue was chromatographed (SiO_2, 65:30:5 CH_2Cl_2−MeOH−H_2O) to give **7** (44 mg, 73%): $[\alpha]^{20}_D$ −54 (*c* 1.0, MeOH); ^1H NMR (CD_3OD) δ 6.80−6.98 (m, 4 H, OPMP), 5.06 (d, 1 H, J = 3.9 Hz, H-1″), 4.97 (d, 1 H, J = 8.4 Hz, H-1), 4.73 (q, 1 H, J = 6.6 Hz, H-5″), 4.60 (d, 1 H, J = 7.6 Hz, H-1′), 4.22, 4.13 (ABq, 1 H each, J = 17.6 Hz, CH_2), 3.70−4.05 (m, 12 H, H-3,4,6,2′,3′,4′,6′,2″,3″,4″), 3.74 (s, 3 H, OMe), 3.68 (dd, 1 H, J = 10.5, 4.1 Hz, H-2), 3.60 (bt, 1 H, J = 5.4 Hz, H-5′), 3.53 (b dt, 1 H, J = 8.5, 2.4 Hz, H-5), 1.98 (s, 3 H, NHAc), 1.10 (d, 3 H, J = 6.6 Hz, H-6″); ^{13}C NMR (CD_3OD) δ 174.1, 171.4, 157.0, 153.3, 119.4, 115.7, 104.4, 101.8, 100.6, 77.5, 76.3, 75.3, 74.9, 73.7, 71.5, 70.0, 67.8, 66.4, 63.0, 62.8, 61.1, 57.8, 56.2, 53.7, 23.2, 16.6; HRMS calcd for $C_{29}H_{42}O_{16}N_2Na$ (M + Na) 697.2432, found 697.2421.

A sample of **7** was conventionally acetylated (Ac_2O−pyridine): ^1H NMR ($CDCl_3$) δ 7.06, (s, 1 H, NH′), 6.77−6.93 (m, 4 H, OPMP), 5.53−5.57 (m, 3 H, NH, H-1″,4″), 5.21 (dd, 1 H, J = 9.4, 8.0 Hz, H-2′), 5.15 (dd, 1 H, J = 10.9, 3.0 Hz, H-3″), 5.04 (dd, 1 H, J = 11.2, 3.5 Hz, H-2″), 5.03 (d, 1 H, J = 7.2 Hz, H-1), 4.65 (dd, 1 H, J = 12.0, 7.1 Hz, H-6′), 4.55−4.60 (m, 2 H, H-6,5″), 4.49 (d, 1 H, J = 7.7 Hz, H-1′), 4.35, 4.20 (ABq, 1 H each, J = 17.7 Hz, OCH_2CO), 4.34 (dd, 1 H, J = 11.9, 7.4 H, H-6′), 3.95−4.19 (m, 5 H, H-2,3,6,3′,4′), 3.90 (t, 1 H, J = 9.0 Hz, H-4), 3.70−3.81 (m, 2 H, H-5,5′), 3.77 (s, 3 H, OMe), 2.16, 2.15, 2.14, 2.12, 2.11, 2.06, 2.00 (s, 1 H each, OAc, NHAc), 1.15 (d, 3 H, J = 6.6 Hz, H-6″); ^{13}C NMR ($CDCl_3$) δ 172.0, 171.8, 171.0, 170.8, 170.5, 170.0, 168.5, 155.9, 151.7, 118.6, 115.0, 101.0, 100.2, 95.3, 74.3, 73.3, 72.8, 72.4, 71.5, 70.9, 69.5, 68.3, 66.5, 65.5, 63.0, 62.6, 60.9, 56.1, 51.1, 23.9, 21.6, 21.5, 21.25, 21.19, 21.1, 16.2.

Ethyl 2-Deoxy-2-[[(2,2,2-trichloroethoxy)carbonyl]amino]-1-thio-β-D-glucopyranoside (9). Compound **8**[11] (12.65 g, 24.1 mmol) was dissolved in MeOH (300 mL), and the mixture was saturated with HCl at 0 °C and then stirred for 16 h at room temperature. The solvent was removed, and the resulting syrup was chromatographed (SiO_2, 9:1 CH_2Cl_2−MeOH) to give **9** (9.80 g, 100%): $[\alpha]^{20}_D$ −7.5 (*c* 0.8, D_2O); ^1H NMR (CD_3OD) δ 4.89, 4.75 (ABq, 1 H each, J = 12.1 Hz, Cl_3CCH_2), 4.55 (m, virtual coupling similar to entry 19 in ref 26, H-1), 3.91, 3.70 (dABq, 1 H each, J = 12.1, 5.5, 2.2 Hz, H-6), 3.30−3.50 (m, 4 H, H-2,3,4,5), 2.81, 2.76 (ddABq, 1 H each, J = 12.5, 7.5, 5.0 Hz, SCH_2CH_3), 1.28 (t, 3 H, J = 7.4 Hz, SCH_2CH_3); ^{13}C NMR (CD_3OD): δ 155.9, 96.2, 84.7, 81.1, 76.3, 74.6, 71.0, 62.0, 57.3, 23.9, 14.2; HRMS calcd for $C_{11}H_{18}O_6NCl_3SNa$ (M + Na) 419.9818, found 419.9839.

Ethyl 4,6-*O*-Benzylidene-2-deoxy-2-[[(2,2,2-trichloroethoxy)carbonyl]amino]-1-thio-β-D-glucopyranoside (10). Compound **9** (9.74 g, 24 mmol) was dissolved in MeCN (110 mL), α,α-dimethoxytoluene (6.5 mL) and *p*-toluenesulfonic acid (50 mg) were added and the mixture was stirred for 4 h. Et_3N (5 mL) was added and the mixture was co-concentrated with toluene. The residue was chromatographed (SiO_2, 1:1 heptane−EtOAc) to give **10** (11.1 g, 95%): $[\alpha]^{20}_D$ −38.5 (*c* 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.35−7.50 (m, 5 H, ArH), 5.57 (s, 1 H, ArCH), 5.22 (bd, 1 H, J = 8.7 Hz, NH), 4.81, 4.73 (ABq, 1 H each, J = 12.2 Hz, Cl_3CCH_2), 4.68 (d, 1 H, J = 8.7 Hz, H-1), 4.35 (dd, 1 H, J = 10.5, 4.9 Hz, H-5), 3.96 (bt, 1 H, J = 9.0 Hz, H-3), 3.78 (t, 1 H, J = 10.2 Hz, H-6), 3.50−3.65 (m, 3

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H, H-2,4,6), 3.05 (bs, 1 H, OH), 2.76, 2.72 (ddABq, 1 H each, J = 12.4, 7.7, 5.0 Hz, SCH_2CH$_3$), 1.30 (t, 3 H, J = 7.6 Hz, SCH$_2$CH_3); ^{13}C NMR ($CDCl_3$): δ 155.0, 137.4, 129.9, 128.9, 126.8, 102.3, 95.8, 84.9, 81.7, 75.1, 72.8, 70.8, 69.0, 57.7, 24.8, 15.3; HRMS calcd for $C_{18}H_{22}O_6NCl_3SNa$ (M + Na) 508.0131, found 508.0133.

Ethyl 3-*O*-Acetyl-4,6 -*O*-benzylidene-2-deoxy-2-[[(2,2,2-trichloroethoxy)carbonyl]amino]-1-thio-β-D-glucopyranoside (11). Compound **10** (10.24 g, 21 mmol) was dissolved in pyridine (100 mL) at 0 °C, and Ac_2O (80 mL) and *N*,*N*-(dimethylamino)pyridine (20 mg) was added. The mixture was stirred at 0 °C for 45 min and at room temperature for another 45 min. The mixture was co-concentrated with toluene, and the residue was chromatographed (SiO_2, 1:1 heptane−EtOAc) to give **11** (10.61 g, 96%): $[\alpha]^{20}_D$ −59.5 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.30−7.50 (m, 5 H, ArH), 5.52 (s, 1 H, ArCH), 5.46 (d, 1 H, J = 9.8 Hz, NH), 5.32 (t, 1 H, J = 9.8 Hz, H-3), 4.84, 4,68 (ABq, 1 H each, J = 12.1 Hz, Cl_3CCH_2), 4.55 (d, 1 H, J = 10.4 Hz, H-1), 4.36 (dd, 1 H, J = 10.5, 4.9 Hz, H-5), 3.87 (q, 1 H, J = 10.2 Hz, H-2), 3.77 (t, 1 H, J = 10.2 Hz, H-6), 3.72 (t, 1 H, J = 9.5 Hz, H-6), 3.56 (dt, 1 H, J = 9.8, 4.9 Hz, H-4), 2.72, 2.67 (ABq, 1 H each, J = 7.5 Hz, SCH_2CH$_3$), 2.08 (s, 3 H, OAc), 1.26 (t, 3 H, J = 7.4 Hz, SCH$_2$CH_3). ^{13}C NMR ($CDCl_3$) δ 171.5, 164.9, 137.3, 129.6, 128.7, 126.5, 101.7, 95.9, 86.0, 79.1, 75.0, 73.0, 71.0, 68.9, 55.9, 24.8, 21.3, 15.2; HRMS calcd for $C_{20}H_{24}O_7NCl_3SNa$ (M + Na) 550.0237, found 550.0215.

Ethyl 3-*O*-Acetyl-6-*O*-benzyl-2-deoxy-2-[[(2,2,2-trichloroethoxy)carbonyl]amino]-1-thio-β-D-glucopyranoside (12). Compound **11** (10.45 g, 19.8 mmol) was dissolved in dry THF (150 mL), and the mixture was cooled to 0 °C. $NaBH_3$CN (7.5 g) and 3A molecular sieves (10 g) were added. An ice-cold, saturated solution of HCl in Et_2O was added until the pH (checked with a moist pH paper) reached 2−3. The mixture was stirred for 2 h, diluted with CH_2Cl_2, and filtered through Celite. The solution was washed with saturated aqueous $NaHCO_3$ and brine, dried (Na_2SO_4), concentrated, and chromatographed (SiO_2, 3:1 → 1:1 heptane−EtOAc) to give **12** (9.80 g, 93%): $[\alpha]^{20}_D$ −33.6 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.30−7.40 (m, 5 H, ArH), 5.52 (d, 1 H, J = 9.8 Hz, NH), 5.07 (t, 1 H, J = 9.9 Hz, H-3), 4.80, 4.69 (ABq, 1 H each, J = 12.2 Hz, Cl_3CCH_2), 4.62, 4.57 (ABq, 1 H each, J = 11.7 Hz, OBn), 4.56, (d, 1 H, J = 10.3 Hz, H-1), 3.55−3.90 (m, 5 H, H-2,4,5,6), 3.30 (bs, 1 H, OH), 2.76, 2.71 bddABq, 1 H each, J = 12.3, 7.3, 5.0 Hz, SCH_2CH$_3$), 2.10 (s, 3 H, OAc), 1.26 (t, 3 H, J = 7.4 Hz, SCH$_2$CH_3); ^{13}C NMR ($CDCl_3$) δ 172.1, 154.7, 137.8, 129.0, 128.5, 128.2, 95.9, 85.1, 78.2, 76.4, 74.9, 74.3, 71.2, 71.0, 55.3, 24.7, 21.3, 15.3; HRMS calcd for $C_{20}H_{26}O_7NCl_3SNa$ (M + Na) 552.0393, found 552.0367.

Ethyl 3-*O*-Acetyl-6-*O*-benzyl-2-deoxy-2-[[(2,2,2-trichloroethoxy)carbonyl]amino]-4-*O*-(trifluoromethansulfonyl)-1-thio-β-D-glucopyranoside (13). Compound **12** (1.00 g, 1.9 mmol) was dissolved in CH_2Cl_2 (7 mL), the mixture was cooled to −50 °C, and pyridine (0.62 mL) was added. Trifluoromethansulfonic anhydride (0.62 mL, 3.8 mmol) was added during 10 min. The temperature was gradually raised to −20 °C during 2 h. The mixture was diluted with CH_2Cl_2, washed with 1 M aqueous HCl and saturated aqueous $NaHCO_3$, dried, and concentrated. The residue was dried under vacuum and used in the next step without further purification.

Ethyl 3,4-Di-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-[[(2,2,2-trichloroethoxy)carbonyl]amino]-1-thio-β-D-galactopyranoside (14). Crude **13** was dissolved in DMF (35 mL), CsOAc (3.6 g, 18.8 mmol) was added, and the mixture was stirred for 2.5 h at room temperature, diluted with Et_2O, and washed with H_2O. The aqueous phase was extracted with four portions of Et_2O. The organic phase was dried (Na_2SO_4) and concentrated, and the residue was chromathographed (SiO_2, 3:1 heptane−EtOAc) to give **14** (864 mg, 80% overall yield from **12**): $[\alpha]^{20}_D$ −36.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.20−7.35 (m, 5 H, ArH), 5.49 (d, 1 H, J = 2.9 Hz, H-4), 5.11 (dd, 1 H, J = 10.8, 2.9 Hz, H-3), 5.03 (d, 1 H, J = 9.6 Hz, NH), 4.81, 4.70 (ABq, 1 H each, J = 11.2 Hz, Cl_3CCH_2), 4.63 (d, 1 H, J = 10.3, H-1), 4.55, 4.42 (ABq, 1 H each, J = 12.1 Hz, OBn), 3.98 (q, 1 H, J = 10.3 Hz, H-2), 3.87 (dt, 1 H, J = 6.8, 6.0 Hz, H-5), 3.58, 3.48 (dABq, 1 H each, J = 9.5, 6.9, 5.9, H-6), 2.79, 2.73 (ddABq, 1 H each, J = 12.4, 7.4, 5.0 Hz, SCH_2CH$_3$), 2.08, 2.00 (s, 3 H each, OAc), 1.20−1.30 (m, 3 H, SCH$_2$CH_3); ^{13}C NMR ($CDCl_3$) δ 170.89, 170.59, 154.59, 137.92, 128.90, 128.89, 128.38, 128.32, 95.90, 85.43, 77.65, 76.39, 74.91, 74.00, 71.78, 68.05, 67.76, 52.12, 25.01, 21.16, 21.09, 15.27; HRMS calcd for $C_{22}H_{28}O_8NCl_3SNa$ (M + Na) 594.0499, found 594.0492.

4-Methoxyphenyl [3,4-Di-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-[[(2,2,2-trichloroethoxy)carbonyl]amino]-β-D-galactopyranosyl]-(1→4)-(6-*O*-benzyl-2-deoxy-2-(tetrachlorophthalimido)-β-D-glucopyranoside) (16). To a solution of **14** (310 mg, 0.54 mmol) and **15**[1] (250 mg, 0.39 mmol) in CH_2Cl_2 (3.5 mL) at −78 °C under Ar was added a solution of AgOTf (300 mg, 1.16 mmol) in MeCN (1.75 mL). After 5 min, a 4 M solution of methylsulfenyl bromide[15] in 1,2-dichloroethane (0.245 mL) was added during 10 min, and the mixture was stirred for 2 h at −78 °C. Isopropylamine (0.5 mL) was added, and the mixture was stirred at −78 °C for 1.5 h and then filtered through a short column (SiO_2, 1:1 heptane−EtOAc). The solvent was removed, and the residue was chromatographed (SiO_2, 3:1 → 2:1 heptane−EtOAc) to give **16** (278 mg, 62%): $[\alpha]^{20}_D$ −9.4 (*c* 0.9 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.20−7.50 (m, 10 H, Ar), 6.70−6.90 (m, 4 H, OPMP), 5.67 (m, 1 H, virtual coupling similar to entry 23 in ref 26, H-1), 5.32 (d, 1 H, J = 3.0 Hz, H-4′), 4.87, 4.32 (ABq, 1 H each, J = 12.1 Hz, OBn), 4.76, 4.67 (ABq, 1 H each, J = 12.0 Hz, Cl_3CCH_2), 4.57−4.71 (m, 1 H, H-3), 4.51, 4.36 (ABq, 1 H each, J = 11.7 Hz, OBn), 4.43−4.49 (m, 2 H, H-2, NH), 4.27 (s, 1 H, OH), 4.12 (d, 1 H, J = 8.4 Hz, H-1′), 3.65−3.95, m, 7 H, H-3,4,5,6,2′,-5′), 3.75 (s, 3 H, OMe), 3.54, 3.44 (dABq, 1 H each, J = 9.5, 7.1, 5.6 Hz, H-6′), 2.05, 1.98 (s, 3 H each, OAc); ^{13}C NMR ($CDCl_3$) δ 170.4, 155.9, 154.6, 150.9, 140.6, 138.6, 137.5, 129.6, 129.3, 129.1, 128.9, 128.31, 128.27, 119.0, 114.9, 102.2, 97.5, 95.9, 81.7, 75.1, 74.4, 74.1, 73.7, 72.8, 70.5, 69.6, 68.1, 67.4, 67.0, 57.0, 56.0, 52.5, 20.99, 20.97. HRMS calcd for $C_{48}H_{45}O_{16}N_2Cl_7Na$ (M + Na) 1173.0486, found 1173.0484.

A sample of **16** was conventionally O-acetylated (Ac_2O−pyridine), which gave a signal at δ 5.64 (t, 1 H, J = 9.3 Hz, H-3).

4-Methoxyphenyl (3,4-Di-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-[[(2,2,2-trichloroethoxy)carbonyl]amino]-β-D-galactopyranosyl)-(1→4)-(2-acetamido-6-*O*-benzyl-2-deoxy-β-D-glucopyranoside) (17). Compound **16** (408 mg, 0.35 mmol) was dissolved in dry EtOH (10 mL), and diaminoethane[12] (0.029 mL, 0.42 mmol) was added. The mixture was kept at 60 °C for 16 h and then co-concentrated with toluene. The residue was dissolved in MeOH−H_2O−Ac_2O (5.0, 1.0, 1.5 mL) and stirred for 1.5 h, co-concentrated with toluene, and chromatographed (SiO_2, 5:1 CH_2Cl_2−acetone) to give **17** (263 mg, 80%): $[\alpha]^{20}_D$ −30.4 (*c* 1.1 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.30−7.50 (m, 10 H, Ar), 6.78 (m, 4 H, OPMP), 5.75 (d, 1 H, J = 7.6 Hz, NH), 5.37 (d, 1 H, J = 8.4 Hz, H-1), 3.53 (d, 1 H, J = 2.6 Hz, H-4′), 4.83, 4.32 (ABq, 1 H each, J = 12.3 Hz, OBn), 4.72, 4.65 (ABq, 1 H each, J = 12.2 Hz, Cl_3CCH_2), 4.63−4.68 (m, 1 H, H-3), 4.55, 4.42 (ABq, 1 H each, J = 11.8 Hz, OBn), 4.25 (s, 1 H, OH), 4.17 (q, 1 H, J = 9.5 Hz, H-3), 4.15 (d, 1 H, J = 8.4 Hz, H-1′), 4.10 (d, 1 H, J = 6.9 Hz, NH), 3.50−3.85 (m, 7 H, H-2,5,6,2′,5′,6′), 3.77 (s, 3 H, OMe), 3.42 (dd, 1 H, J = 9.1, 6.4 Hz, H-6′), 2.04, 2.02, 1.98 (s, 3 H each, OAc, NHAc); ^{13}C NMR ($CDCl_3$) δ 171.0, 170.5, 155.8, 154.6, 151.8, 138.6, 137.6, 129.5, 129.3, 129.0, 128.5, 119.1, 114.9, 102.1, 99.9, 95.9, 81.5, 75.0, 74.1, 73.7, 72.6, 71.4, 70.6, 67.7, 67.0, 58.1, 56.1, 52.6, 24.1, 21.00, 20.97; HRMS calcd for $C_{42}H_{49}O_{15}N_2Cl_3Na$ (M + Na) 949.2096, found 949.2111.

4-Methoxyphenyl (3,4-di-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-[[(2,2,2-trichloroethoxy)carbonyl]amino]-β-D-galactopyranosyl)-(1→4)-[2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl](1→3)-(2-acetamido-6-*O*-benzyl-2-deoxy-β-D-glucopyranoside) (19). Ethyl 2,3,4-tri-*O*-benzyl-1-thio-α-L-fucopyranoside[16] (**18**, 114 mg, 0.24 mmol) was dissolved in dry CH_2Cl_2 (0.9 mL), and freshly distilled Br_2 (0.011 mL in 0.140 mL CH_2Cl_2) was added. The mixture was stirred for 15 min, and cyclohexene was added until the color of Br_2 disappeared. The solvent was removed, and the residue was dissolved in dry CH_2Cl_2 (0.9 mL). The solution was added to a mixture of **17** (112 mg, 0.12 mmol), 4 A molecular sieves (450 mg), Bu_4-

NBr (70 mg), and 5:3 CH_2Cl_2−DMF (0.96 mL). The mixture was stirred for 48 h, pyridine (0.35 mL) was added, and the stirring was continued for another 3 h. The mixture was filtered through Celite and co-concentrated with toluene. The residue was chromatographed (SiO_2, 1:1 heptane−EtOAc) to give **19** (107 mg, 66%): $[\alpha]^{20}_D$ −62.2 (*c* 1.1 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.20−7.45 (m, 25 H, Ar), 6.74−6.90 (m, 4 H, OPMP), 6.38 (d, 1 H, J = 7.9 Hz, NH), 5.44 (d, 1 H, J = 3.1 Hz, H-4′), 5.24 (d, 1 H, J = 4.6 Hz, H-1), 5.17 (d, 1 H, J = 3.6 Hz, H-1″), 4.97, 4.66 (ABq, 1 H each, J = 11.8 Hz, OBn), 4.75−4.85 (m, 4 H, OBn, H-3′), 4.71, 4.45 (ABq, 1 H each, J = 12.1 Hz, OBn), 4.67 (AB, 1 H, J = 11.8 Hz, OBn), 4.50 (AB, 1 H, J = 12.0 Hz, OBn), 4.30−4.42 (m, 4 H, OBn, Cl_3CCH_2, H-1′), 4.00−4.20 (m, 3 H, H-2,2″,5″), 3.97 (t, 1 H, J = 4.7 Hz, H-3″), 3.76 (s, 3 H, OMe), 3.50−3.85 (m, 8 H, H-3,5,6,2′,5′,6′,4″), 3.43 (t, 1 H, J = 8.4 Hz, H-6′), 2.00, 1.97, 1.90 (s, 3 H each, OAc, NHAc), 1.07 (d, 3 H, J = 6.4 Hz, H-6″); ^{13}C NMR ($CDCl_3$) δ 170.8, 170.6, 170.4, 155.4, 155.2, 151.7, 139.2, 139.1, 139.0, 138.2, 137.7, 129.1, 129.0, 128.9, 128.7, 128.6, 128.38, 128.35, 128.28, 128.1, 128.02, 127.97, 127.8, 118.4, 114.8, 100.9, 99.0, 97.5, 95.7, 79.6, 74.9, 74.7, 74.0, 73.8, 73.6, 73.32, 72.29, 70.4, 69.9, 67.3, 67.2, 67.0, 56.1, 53.1, 52.9, 23.5, 21.1, 21.0, 17.2; HRMS calcd for $C_{69}H_{77}O_{19}N_2Cl_3Na$ (M + Na) 1365.4084, found 1365.4075.

A sample of **19** was conventionally de-O-benzylated (H_2, Pd−C, AcOH) and O-acetylated (Ac_2O−pyridine): ^{1}H NMR ($CDCl_3$) δ 6.80−6.95 (m, 4 H, OPMP), 6.04 (d, 1 H, J = 6.2 Hz, NH), 5.50 (d, 1 H, J = 3.9 Hz, H-1″), 5.42 (d, 1 H, J = 3.1 Hz, H-4′), 5.39 (d, 1 H, J = 2.6 Hz, H-4″), 5.34 (d, 1 H, J = 9.4 Hz, H-1′), 5.25 (dd, 1 H, J = 10.9, 3.3 Hz, H-3″), 5.11 (dd, 1 H, J = 10.8, 3.9 Hz, H-2″), 5.09 (d, 1 H, J = 4.0 Hz, H-1), 5.04 (dd, 1 H, J = 11.7, 2.3 Hz, H-3′), 4.60−4.70 (m, 3 H, Cl_3CCH_2, H-5″), 4.35−4.50 (m, 3 H, H-6, 6′), 4.29 (dd, 1 H, J = 12.8, 5.4 Hz, H-6), 3.80−4.20 (m, 5 H, H-2,3,4,5,2′), 3.77 (s, 3 H, OMe), 2.22, 2.17, 2.10, 2.08, 2.07, 2.04, 2.03, 1.99 (s, 3 H each, OAc, NHAc), 1.23 (d, 3 H, J = 6.5 Hz, H-6″).

4-Methoxyphenyl (2-Acetamido-3,4-di-*O*-acetyl-6-*O*-benzyl-2-deoxy-*β*-D-galactopyranosyl)-(1→4)-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-2-acetamido-6-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside (20). Compound **19** (50 mg, 0.04 mmol) was dissolved in AcOH (1.5 mL), and freshly activated zinc dust (200 mg) was added. After 1.5 h, the reaction mixture was filtered through a short column (SiO_2, 1:1 toluene−acetone plus 0.1% Et_3N). The crude product was dissolved in pyridine (3 mL), and Ac_2O (2.5 mL) was added. The mixture was stirred for 2.5 h, co-concentrated with toluene, and chromatographed (SiO_2, 1:1 toluene−acetone) to give **20** (37 mg, 83%): $[\alpha]^{20}_D$ −102.2 (*c* 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.10−7.45 (m, 25 H, Ar), 6.85 (bd, 1 H, J = 9.2 Hz, NH), 6.70−6.90 (m, 4 H, OPMP), 5.44 (d, 1 H, J = 3.0 Hz, H-4′), 5.39 (d, 1 H, J = 8.9 Hz, NH), 5.25 (d, 1 H, J = 3.5 Hz, H-1″), 5.15 (d, 1 H, J = 3.7 Hz, H-1), 4.97, 4.66 (ABq, 1 H each, J = 11.8 Hz, OBn), 4.94 (dd, 1 H, J = 11.4, 3.4 Hz, H-3′), 4.85, 4.66 (ABq, 1 H each, J = 11.6 Hz, OBn), 4.81, 4.68 (ABq, 1 H each, J = 12.2 Hz, OBn), 4.51, 4.37 (ABq, 1 H each, J = 11.8 Hz, OBn), 4.35−4.42 (m, 1 H, H-2), 4.31 (d, 1 H, J = 8.4 Hz, H-1′), 4.29, 4.26 (ABq, 1 H each, J = 13.0 Hz, OBn), 4.16−4.22 (m, 1 H, H-2′), 4.11 (dd, 1 H, J = 10.0, 3.6 Hz, H-2″), 4.07 (bt, 1 H, J = 3.5 Hz, H-3), 3.98 (bs, 1 H, H-4), 3.70−3.92 (m, 5 H, H-5,6,5′,3″,5″), 3.76 (s, 3 H, OMe), 3.63 (dd, 1 H, J = 8.9, 4.0 Hz, H-6), 3.43−3.54 (m, 3 H, H-4,6′), 2.05, 2.04, 2.01, 1.86 (s, 3 H each, OAc, NHAc), 1.01 (d, 3 H, J = 6.5 Hz, H-6″); ^{13}C NMR ($CDCl_3$) δ 171.6, 171.5, 170.7, 170.5, 155.2, 151.7, 139.4, 139.1, 139.0, 138.5, 137.7, 128.93, 128.89, 128.81, 128.7, 128.6, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 118.3, 114.8, 100.7, 99.2, 97.1, 79.2, 76.7, 75.0, 74.7, 74.1, 73.9, 73.8, 73.4, 73.1, 72.9, 72.6, 70.6, 70.5, 67.5, 67.4, 67.1, 56.1, 51.3, 23.9, 23.5, 21.2, 21.1, 17.1. HRMS calcd for $C_{68}H_{78}O_{18}N_2Na$ (M+Na) 1233.5147, found 1233.5173.

4-Methoxyphenyl (6-*O*-Benzyl-2-deoxy-2-[[(2,2,2-trichloroethoxy)carbonyl]amino]-*β*-D-galactopyranosyl)-(1→4)-[2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl]-(1→3)-(2-acetamido-6-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside) (21). Compound **19** (81 mg, 0.15 mmol) was dissolved in the guanidinium nitrate stock solution[19] (5 mL), the mixture was stirred for 15 min, neutralized with Amberlite IR-120 H^+, filtered, and concentrated. The residue was chromatographed (SiO_2, 20:1 toluene−EtOH) to give **21** (75 mg, 98%): $[\alpha]^{20}_D$ −42.1 (*c* 0.9 $CHCl_3$). A sample of **21** was crystallized from EtOAc-heptane: mp 167−168 °C; ^{1}H NMR ($CDCl_3$) δ 7.20−7.40 (m, 25 H, Ar), 6.73−6.83 (m, 4 H, OPMP), 6.32 (d, 1 H, J = 7.5 Hz, NH), 5.45 (d, 1 H, J = 6.4 Hz, NH), 5.20 (d, 1 H, J = 3.6 Hz, H-1″), 5.17 (d, 1 H, J = 5.8 Hz, H-1), 4.95, 4.62 (ABq, 1 H each, J = 11.5 Hz, OBn), 4.86, 4.73 (ABq, 1 H each, J = 11.5 Hz, OBn), 4.71−4.74 (m, 2 H, OBn), 4.71, 4.57 (ABq, 1 H each, J = 12.0 Hz, OBn), 4.47, 4.43 (s, 2 H each, OBn, Cl_3CCH_2), 4.34 (d, 1 H, J = 8.2 Hz, H-1′), 4.05−4.20 (m, 3 H, H-4′,2″,5″), 3.92−4.00 (m, 2 H, H-2,3″), 3.89 (dd, 1 H, J = 10.1, 2.5 Hz, H-3′), 3.45−3.80 (m, 11 H, H-3,4,5,6,2′,5′,6′,4″, OH), 3.76 (s, 3 H, OMe), 2.85 (s, 1 H, OH), 1.83 (s, 3 H, NHAc), 1.08 (d, 3 H, J = 6.5 Hz, H-6″); ^{13}C NMR ($CDCl_3$): δ 170.7, 155.5, 151.7, 139.2, 139.1, 138.1, 137.9, 128.99, 128.95, 128.92, 128.8, 128.7, 128.6, 128.42, 128.36, 128.2, 128.1, 128.0, 127.9, 127.7, 118.7, 114.8, 100.0, 99.6, 97.9, 95.7, 79.7, 78.1, 75.4, 75.2, 74.7, 74.5, 74.1, 74.0, 73.9, 73.4, 73.0, 72.7, 70.6, 69.2, 68.4, 67.5, 56.1, 23.6, 17.2; HRMS calcd for $C_{65}H_{73}O_{17}N_2Cl_3Na$ (M + Na) 1281.3873, found 1281.3866.

4-Methoxyphenyl [Methyl(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyl)onate]-(1→3)-[4-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-[[(2,2,2-trichloroethoxy)carbonyl]amino]-*β*-D-galactopyranosyl)-(1→4)-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-(2-acetamido-6-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside) (23). To a mixture of **21** (180 mg, 0.143 mmol), **22**[20] (255 mg, 0.428 mmol), and 3A molecular sieves (200 mg) were added CH_2Cl_2 (1.25 mL) and MeCN (1.50 mL). The mixture was stirred for 10 min at room temperature and for 5 min at −60 °C under Ar. A solution of dry AgOTf (130 mg) in freshly distilled MeCN (0.93 mL) was added. After 5 min, a 4 M solution of methylsulfenyl bromide[15] in 1,2-dichloroethane (0.116 mL) was added during 30 min. The mixture was stirred for 3 h at −60 °C, diisopropylamine (0.475 mL) was added, and the mixture was stirred for 2 h at −60 °C. The reaction mixture was filtered through a short column (SiO_2, 2:1 toluene−acetone). The crude product was conventionally acetylated (Ac_2O−pyridine), the mixture was co-concentrated with three portions of toluene, and the residue was chromatographed (SiO_2, 1:3 CH_2Cl_2−EtOAc) to give **23** (148 mg, 58%) and **19** (26 mg, 13%). Compound **23**: $[\alpha]^{20}_D$ −52.8 (*c* 1.1 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.05−7.45 (m, 26 H, Ar, NH), 6.70−6.90 (m, 4 H, OPMP), 5.72 (d, 1 H, J = 7.6 Hz, NH), 5.44 (dt, 1 H, J = 6.3, 2.5 Hz, H-8‴), 5.36 (dd, 1 H, J = 9.3, 2.2 Hz, H-7‴), 5.25 (d, 1 H, J = 3.4 Hz, H-1″), 5.17 (bs, 1 H, H-1), 5.11 (d, 1 H, J = 2.6 Hz, H-4′), 5.09 (d, 1 H, J = 7.6 Hz, NH), 4.97 (m, 1 H, H-4‴), 4.95, 4.63 (ABq, 1 H each, J = 11.7, OBn), 4.87, 4.74 (ABq, 1 H each, J = 11.7, OBn), 4.82, 4.66 (ABq, 1 H each, J = 12.3 Hz, OBn), 4.78 (d, 1 H, J = 11.7 Hz, OBn), 4.50−4.60 (m, 3 H, H-1′,2, OBn), 4.47, 4.37 (ABq, 1 H each, J = 11.7 Hz, Cl_3CCH_2), 4.42 (bd, 1 H, J = 12.0 Hz, H-3′), 4.32 (dd, 1 H, J = 12.3, 2.3 Hz, H-9‴), 4.27 (AB, 1 H, J = 12.4 Hz, OBn), 4.05−4.20 (m, 4 H, H-5′,2″,5‴, OBn), 4.00 (dd, 1 H, J = 12.1, 6.0 Hz, H-9‴), 3.94 (dt, 1 H, J = 9.5, 8.6 Hz, H-6′), 3.87 (s, 3 H, OMe), 3.65−3.85 (m, 7 H, H-3,4,2′,6′,3″,-4″,5″), 3.75 (s, 3 H, OMe), 3.47 (dd, 1 H, J = 9.7, 5.4 Hz, H-6), 3.35−3.43 (m, 2 H, H-5,6), 2.63 (dd, 1 H, J = 12.8, 4.8 Hz, H-3‴eq), 2.20, 2.13, 2.09, 2.07, 2.04, 1.94, 1.87 (s, 3 H each, OAc, NHAc), 1.83 (dd, 1 H, J = 11.9, 2.9 Hz, H-3‴ax), 0.95 (d, 3 H, J = 6.3 Hz, H-6″); ^{13}C NMR ($CDCl_3$): δ 171.4, 171.3, 171.2, 170.8, 170.6, 170.5, 168.0 (C-1‴, $J_{C-1''':H-3'''ax}$ 6.1 Hz),[21] 156.4, 154.9, 151.7, 139.5, 139.1, 139.1, 138.7, 138.3, 138.1, 128.91, 128.86, 128.80, 128.79, 128.7, 128.6, 128.4, 128.19, 128.16, 128.0, 127.9, 127.8, 127.6, 127.5, 117.9, 114.8, 100.9, 98.6, 97.8, 96.8, 95.9, 79.0, 77.8, 76.7, 75.1, 74.7, 74.3, 73.8, 73.5, 73.4, 73.2, 72.9, 72.1, 72.0, 71.1, 70.7, 69.4, 68.1, 67.9, 67.5, 67.4, 67.2, 63.1, 56.1, 53.8, 49.7, 48.9, 38.0, 30.1, 23.6, 23.4, 21.9, 21.5, 21.3, 21.2, 21.0, 18.7, 17.0; HRMS calcd for $C_{87}H_{102}O_{30}N_3Cl_3Na$ (M + Na) 1796.5511, found 1796.5559.

4-Methoxyphenyl [Methyl(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyl)onate]-(1→3)-(2-acetamido-4-*O*-acetyl-6-*O*-benzyl-2-deoxy-*β*-D-galactopyranosyl)-(1→4)-(2,3,4-tri-*O*-benzyl-

α-L-fucopyranosyl)-(1→3)-(2-acetamido-6-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside) (24). Compound **23** (146 mg, 0.08 mmol) was dissolved in AcOH (5 mL), and freshly activated zinc dust (1.0 g) was added. The mixture was stirred overnight, filtered through Celite, and co-concentrated with toluene. The crude product was dissolved in pyridine (4 mL), and Ac_2O (3 mL) was added. The mixture was stirred for 4.5 h, co-concentrated with toluene, and chromatographed (SiO_2, 4:1 → 1:1 toluene−acetone) to give **24** (95 mg, 70%): $[\alpha]^{20}_D$ −65.8 (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.10−7.45 (m, 26 H, ArH, NH), 6.70−6.95 (m, 4 H, OPMP), 5.99 (d, 1 H, J = 8.3 Hz, NH′), 5.58 (dt, 1 H, J = 9.1, 2.6 Hz, H-8‴), 5.35 (d, 1 H, J = 3.5 Hz, H-1″), 5.27 (dd, 1 H, J = 9.9, 2.4 Hz, H-7‴), 5.14 (d, 1 H, J = 4.3 Hz, H-1), 5.13 (d, 1 H, J = 5.1 Hz, NH‴), 5.01 (d, 1 H, J = 2.9 Hz, H-4′), 4.95, 4.62 (ABq, 1 H each, J = 11.7 Hz, OBn), 4.93, 4.72 (ABq, 1 H each, J = 11.5 Hz, OBn), 4.89 (dd, 1 H, J = 11.9, 4.6 Hz, H-4‴), 4.82, 4.66 (ABq, 1 H each, J = 12.4 Hz, OBn), 4.58 (dd, 1 H, J = 10.0, 3.5 Hz, H-2), 4.49 (d, 1 H, J = 7.8 Hz, H-1′), 4.46, 4.36 (ABq, 1 H each, J = 11.4 Hz, OBn), 4.38 (dd, 1 H, J = 12.1, 2.6 Hz, H-9‴), 4.25−4.31 (m, 2 H, H-3′,3″), 4.00−4.15 (m, 6 H, H-3,4,2′,2″,4″,5‴), 3.60−3.90 (m, 7 H, H-5,6,5′,6′,5″,6‴,9‴), 3.88 (s, 3 H, OMe), 3.75 (s, 3 H, OMe), 3.33−3.45 (m, 2 H, H-6,6′), 2.61 (dd, 1 H, J = 12.8, 4.6, H-3eq‴), 2.16, 2.14, 2.13, 2.08, 2.03, 2.00, 1.92, 1.87 (s, 3 H each, OAc, NHAc), 1.79 (t, 1 H, J = 12.6 Hz, H-3ax‴), 0.91 (d, 3 H, J = 6.5 Hz, H-6″); ^{13}C NMR ($CDCl_3$) δ 172.2, 171.6, 171.4, 171.3, 170.8, 170.64, 170.57, 168.0, 154.9, 152.0, 139.6, 139.2, 139.1, 138.8, 138.1, 128.89, 128.86, 128.75, 128.59, 128.57, 128.50, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 127.4, 117.9, 114.7, 100.0, 99.0, 97.7, 96.6, 78.8, 78.1, 76.5, 75.0, 74.3, 73.9, 73.5, 73.2, 72.7, 72.5, 72.3, 71.6, 71.4, 70.7, 69.3, 68.1, 67.6, 67.43, 67.36, 67.0, 64.2, 56.1, 53.8, 51.2, 49.9, 49.5, 38.0, 23.8, 23.6, 23.5, 21.9, 21.3, 21.2, 20.8, 16.9; HRMS calcd for $C_{86}H_{103}O_{29}N_3Na$ (M + Na) 1664.6575, found 1664.6559.

4-Methylphenyl 4,6-*O*-Benzylidene-1-thio-*β*-D-glucopyranoside (26). 4-Methylphenyl 1-thio-*β*-D-glucopyranoside[22] (**25**, 2.86 g, 10 mmol) was dissolved in MeCN (35 mL). α,α-Dimethoxytoluene (2.80 mL) and *p*-toluenesulfonic acid (35 mg) were added, and the mixture was stirred for 17 h. Et_3N (5 mL) was added, and the mixture was co-concentrated with toluene three times. The residue was chromatographed (SiO_2, 1:1 heptane−EtOAc) to give **26** (3.61 g, 96%). A sample was crystallized from EtOAc−heptane: $[\alpha]^{20}_D$ −40 (*c* 1.0, $CHCl_3$); mp 171−172 °C; ^{1}H NMR ($CDCl_3$) δ 7.14−7.50 (m, 9 H, Ar), 5.51 (s, 1 H, ArCH), 4.54 (broad d, 1 H, J = 9.7 Hz, H-1), 4.36 (broad d, 1 H, J = 10.1 Hz, H-6), 3.72−3.83 (m, 2 H, H-3,6), 3.47 (m, 2 H, H-4,5), 3.41 (t, 1 H, J = 8.9 Hz, H-2), 2.92, 3.15 (broad s, 1 H each, OH), 2.37 (s, 3 H, Me); ^{13}C NMR ($CDCl_3$) δ 137.3, 134.1, 130.3, 129.8, 128.8, 126.8, 102.3, 89.1, 80.6, 74.9, 72.9, 70.9, 69.0, 21.6; HRMS calcd for $C_{20}H_{22}O_5SNa$ (M + Na) 397.1086, found 397.1085.

4-Methylphenyl 2,3-Di-*O*-acetyl-4,6-*O*-benzylidene-1-thio-*β*-D-glucopyranoside (27). Compound **26** (0.97 g, 2.59 mmol) was dissolved in pyridine (25 mL), and Ac_2O (20 mL) was added. The mixture was stirred for 18 h and then co-concentrated with toluene. The residue was chromatographed (SiO_2, 1:1 heptane−EtOAc) to give **27** (1.15 g, 97%). A sample was crystallized from EtOAc−heptane: $[\alpha]^{20}_D$ −59 (*c* 1.2, $CHCl_3$): mp 181−185 °C; ^{1}H NMR ($CDCl_3$) δ 7.15−7.45 (m, 9 H, Ar), 5.50 (s, 1 H, ArCH), 5.35 (t, 1 H, J = 9.0 Hz, H-3), 4.95 (dd, 1 H, J = 10.0, 9.0 Hz, H-2), 4.75 (d, 1 H, J = 10.0 Hz, H-1), 4.40 (dd, 1 H, J = 10.6, 4.9 Hz, H-6), 3.80 (t, 1 H, J = 10.0 Hz, H-6), 3.65 (t, 1 H, J = 9.5 Hz, H-4), 3.57 (dt, 1 H, J = 9.6, 4.8 Hz, H-5), 2.37 (s, 3 H, ArMe), 2.12, 2.04 (s, 3 H, OAc); ^{13}C NMR ($CDCl_3$) δ 170.6, 170.0, 139.3, 137.2, 134.1, 126.6, 101.9, 87.2, 78.5, 73.4, 71.2, 71.1, 68.9, 21.7, 21.3, 21.2; HRMS calcd for $C_{24}H_{26}O_7S$ (M + Na) 481.1297, found 481.1296.

4-Methylphenyl 2,3-Di-*O*-acetyl-6 *O*-benzyl-1-thio-*β*-D-glucopyranoside (28). Compound **27** (500 mg, 1.09 mmol) was dissolved in THF (10 mL), and the mixture was cooled to 0 °C. $NaBH_3CN$ (750 mg) and molecular sieves (1.5 g, 3 Å) were added. Et_2O (nondried) was saturated with HCl and added until pH was ∼2 (moist litmus paper). The mixture was stirred for 40 min, diluted with Et_2O, and filtered through Celite. The mixture was washed with saturated aqueous $NaHCO_3$ solution and water, dried (Na_2SO_4), and concentrated. The residue was chromatographed (SiO_2, 3:1 heptane−EtOAc) to give **28** (464 mg, 92%): $[\alpha]^{20}_D$ −38 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.05−7.45 (m, 9 H, Ar), 5.06 (t, 1 H, J = 9.3 Hz, H-3), 4.92 (dd, 1 H, J = 9.9, 9.3 Hz, H-2), 4.65 (d, 1 H, J = 10.0 Hz, H-1), 4.61, 4.56 (ABq, 1 H each, J = 11.7 Hz, OBn), 3.83, 3.79 (dABq, 1 H each, J = 10.4, 4.9 Hz, H-6), 3.73 (dt, 1 H, J = 9.5, 3.3 Hz, H-4), 3.57 (dt, 1 H, J = 9.5, 4.8 Hz, H-5), 2.99 (d, 1 H, J = 3.4 Hz, OH), 2.34 (s, 3 H, ArMe), 2.10, 2.08 (s, 3 H each, OAc); ^{13}C NMR ($CDCl_3$): δ 171.9, 170.0, 139.0, 137.9, 133.9, 130.2, 128.5, 128.4, 128.2, 86.4, 78.5, 77.4, 74.3, 71.1, 70.6, 70.3, 21.6, 21.30, 21.27; HRMS calcd for $C_{24}H_{28}O_7SNa$ (M + Na) 483.1453, found 483.1450.

4-Methylphenyl 2,3-Di-*O*-acetyl-6-*O*-benzyl-4-*O*-(Trifluoromethansulfonyl)-1-thio-*β*-D-glucopyranoside (29). Compound **28** (345 mg, 0.75 mmol) was dissolved in CH_2Cl_2 (3.5 mL), and the mixture was cooled to −78 °C. Pyridine (0.25 mL) was added, and then trifluoromethansulfonic anhydride (0.236 mL, 1.5 mmol) was added during 10 min. The temperature was gradually raised to 20 °C during 3 h, the mixture was diluted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ solution, dried, and concentrated. The residue was dried under vacuum and used, without further purification, in the next step.

4-Methylphenyl 2,3-Di-*O*-acetyl-4-azido-6-*O*-benzyl-4-deoxy-1-thio-*β*-D-galactopyranoside (30). The crude compound **29** was dissolved in DMF (5 mL), NaN_3 (1.0 g, 14.6 mmol) was added, and the mixture was stirred for 17 h at ∼22 °C. The mixture was diluted with CH_2Cl_2, filtered through a short column (SiO_2, 1:1 heptane−EtOAc), and concentrated. The residue was chromathographed (SiO_2, 3:1 heptane−EtOAc), to give **30** (344 mg, 95%): $[\alpha]^{20}_D$ −34 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.10−7.40 (m, 9 H, Ar), 5.23 (t, 1 H, J = 9.9 Hz, H-2), 5.11 (dd, 1 H, J = 9.7, 3.7 Hz, H-3), 4.59 (d, 1 H, J = 9.9 Hz, H-1), 4.56, 4.53 (ABq, 1 H each, J = 11.6 Hz, OBn), 4.15 (dd, 1 H, J = 3.7, 1.2 Hz, H-4), 3.79 (ddd, 1 H, J = 7.0, 5.6, 1.3 Hz, H-5), 3.70 (dABq, 1 H, J = 9.3, 5.6 Hz, H-6), 3.65 (dABq, 1 H, J = 9.3, 7.6 Hz, H-6), 2.34 (s, 3 H, ArMe), 2.11, 2.10 (s, 3 H each, OAc); ^{13}C NMR ($CDCl_3$) δ 170.5, 169.8, 138.8, 137.9, 133.5, 130.1, 128.93, 128.90, 128.4, 128.3, 87.3, 76.1, 74.4, 74.1, 68.6, 68.1, 60.8, 21.6, 21.3, 21.0; HRMS calcd for $C_{24}H_{27}O_6N_3SNa$ (M + Na) 508.1518, found 508.1518.

4-Methylphenyl 2,3-Di-*O*-acetyl-4-amino-6 *O*-benzyl-4-deoxy-1-thio-*β*-D-galactopyranoside (31). Compound **30** (252 mg, 0.52 mmol) was dissolved in 6:1 pyridine−H_2O (84 mL), and the solution was saturated with H_2S at 0 °C for 1 h and left for 42 h at ∼22 °C. Residual H_2S was removed by bubbling N_2 through the mixture for 1 h, which was then co-concentrated with toluene. The residue was dried under vacuum and used, without further purification, in the next step.

4-Methylphenyl 2,3-Di-*O*-acetyl-6-*O*-benzyl-4-deoxy-4-[[(2,2,2-trichloroethoxy)carbonyl]amino]-1-thio-*β*-D-galactopyranoside (32). The crude compound **31** was dissolved in pyridine (10 mL), and the solution was cooled to 0 °C. (2,2,2-Trichloroethoxy)carbonyl chloride (0.210 mL, 1.56 mmol) was added, and the mixture was stirred at room temperature for 1 h. MeOH (1 mL) was added, and the mixture was co-concentrated with toluene. The residue was chromatographed (SiO_2, 1:1 heptane−EtOAc) to give **32** (280 mg, 85%): $[\alpha]^{20}_D$ +6 (*c* 1.1, $CHCl_3$); ^{1}H NMR (C_6D_6) δ 6.90−7.70 (m, 9 H, Ar), 5.54 (t, 1 H, J = 10.0 Hz, H-2), 5.27 (d, 1 H, J = 9.7 Hz, NH), 5.13 (dd, 1 H, J = 9.6, 4.1 Hz; H-4), 5.00 (dd, 1 H, J = 10.0, 4.1 Hz, H-3), 4.83, 4.49 (ABq, 1 H each, J = 12.0 Hz, OBn), 4.53 (d, 1 H, J = 10.0 Hz, H-1), 4.32, 4.27 (ABq, 1 H each, J = 12.1 Hz, Cl_3CCH_2), 3.40−3.47 (m, 2 H, H-5,6), 3.27 (dd, 1 H, J = 8.3, 3.2 Hz, H-6), 2.07, 1.85 (s, 3 H each, OAc), 1.28 (s, 3 H, ArMe); ^{13}C NMR ($CDCl_3$) δ 170.7, 169.7, 153.4, 139.2, 138.0, 134.0, 130.2, 128.9, 128.4, 128.29, 128.25, 94.7, 86.9, 78.2, 77.6, 77.2, 74.0, 69.1, 67.8, 48.3, 23.6, 21.6, 21.2; HRMS calcd for $C_{27}H_{30}O_8NCl_3SNa$ (M + Na) 656.0655, found 656.0646.

4-Methoxyphenyl (2,3-Di-*O*-acetyl-4-azido-6-*O*-benzyl-4-deoxy-*β*-D-galactopyranosyl)-(1→4)-6-*O*-benzyl-2-deoxy-2-tetrachlorophthalimido-*β*-D-glucopyranoside (33). To a solution of **30** (314 mg, 0.65 mmol) and **15**[1] (295 mg, 0.46

mmol) in CH_2Cl_2 (3.7 mL) at −78 °C under Ar was added a solution of silver trifluoromethanesulfonate (355 mg, 1.37 mmol) in CH_3CN (1.9 mL). After 5 min, a 4 M solution of methylsulfenyl bromide[15] in 1,2-dichloroethane (0.295 mL) was added during 10 min. The mixture was stirred for 2 h, isopropylamine (0.5 mL) was added, and the stirring was continued for 1.5 h at −78 °C. The mixture was filtered through a short column (SiO_2, 2:1 toluene−acetone) and concentrated. The residue was chromatographed (SiO_2, 2:1 heptane−EtOAc) to give **33** (366 mg, 78%) and **15** (63 mg, 21%). Compound **33**: $[\alpha]^{20}_D$ −12 (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.20−7.40 (m, 10 H, Ar), 6.70−6.90 (m, 4 H, OPMP), 5.64 (d, 1 H, J = 8.3 Hz, H-1), 5.24 (dd, 1 H, J = 10.3, 8.0 Hz, H-2′), 5.03 (dd, 1 H, J = 10.0, 3.8 Hz, H-3′), 4.70 (AB, 1 H, J = 12.1 Hz, OBn), 4.49 (d, 1 H, J = 8.0 Hz, H-1′), 4.45−4.55 (m, 4 H, H-3, and OBn), 4.41 (dd, 1 H, J = 10.9, 8.3 Hz, H-2), 4.10 (d, 1 H, J = 1.9 Hz, OH), 4.06 (dd, 1 H, J = 3.6, 1.0 Hz, H-4′), 3.55−3.80 (m, 7 H, H-4,5,6,5,6′), 3.74 (s, 3 H, OMe), 2.12, 2.02, (s, 3 H each, OAc); ^{13}C NMR ($CDCl_3$) δ 170.4, 169.5, 155.9, 150.9, 140.6, 138.4, 137.5, 129.0, 128.9, 128.8, 128.43, 128.39, 128.34, 128.24, 128.22, 127.9, 119.0, 114.9, 101.7, 97.4, 81.8, 74.8, 74.1, 74.0, 73.3, 72.4, 69.8, 69.5, 68.8, 68.3, 60.2, 56.8, 56.0, 21.1, 20.8; HRMS calcd for $C_{45}H_{42}O_{14}N_4Cl_4Na$ (M + Na) 1025.1349, found 1025.1335.

A sample of **33** was conventionally acetylated, which gave a ^{1}H NMR signal at δ 5.63 (dd, 1 H, J = 10.6, 8.9 Hz, H-3).

4-Methoxyphenyl (2,3-Di-*O*-acetyl-4-azido-6-*O*-benzyl-4-deoxy-*β*-D-galactopyranosyl)-(1→4)-2-acetamido-6-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside (34). Compound **33** (758 mg, 0.75 mmol) was dissolved in dry EtOH (34 mL), and 1,2-diaminoethane (0.099 mL, 1.43 mmol) was added.[12] The mixture was heated at 60 °C for 4 h and then co-concentrated with toluene. The residue was dissolved in MeOH−H_2O−Ac_2O (17.0, 3.4, 5.1 mL), and the mixture was stirred for 1 h and co-concentrated with toluene. The residue was chromatographed (SiO_2, 2:1 toluene−acetone) to give **34** (540 mg, 92%): $[\alpha]^{20}_D$ −30 (*c* 0.9 $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.25−7.40 (m, 10 H, Ar), 6.76−6.99 (m, 4 H, OPMP), 5.86 (d, 1 H, J = 8.1 Hz, NH), 5.32 (d, 1 H, J = 8.5 Hz, H-1), 5.20 (dd, 1 H, J = 10.3, 7.9 Hz, H-2′), 5.03 (dd, 1 H, J = 10.2, 3.9 Hz, H-3′), 4.63, 4.48 (ABq, 1 H each, J = 12.1 Hz, OBn), 4.57, 4.49 (ABq, 1 H, each, J = 11.9 Hz, OBn), 4.51 (d, 1 H, J = 7.8 Hz, H-1′), 4.16 (bt, 1 H, J = 8.0 Hz, H-3), 4.09 (broad s, 1 H, OH), 3.84 (broad s, 1 H, H-4′), 3.77 (s, 3 H, OMe), 3.50−3.80 m, 8 H, H-2,4,5,6,5′,6′), 2.13, 2.02, 2.01, (s, 3 H each, OAc, NHAc); ^{13}C NMR ($CDCl_3$): δ 170.9, 170.5, 169.6, 155.8, 151.8, 138.5, 137.7, 129.0, 128.8, 128.54, 128.46, 128.2, 119.0, 114.9, 101.6, 99.8, 81.6, 74.5, 74.2, 73.9, 73.2, 72.3, 71.7, 69.8, 68.6, 60.3, 57.5, 56.1, 24.1, 21.1, 20.9; HRMS calcd for $C_{39}H_{46}O_{13}N_4Na$ (M + Na) 801.2959, found 801.2960.

4-Methoxyphenyl (2,3-Di-*O*-acetyl-4-azido-6-*O*-benzyl-4-deoxy-*β*-D-galactopyranosyl)-(1→4)-[2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl]-(1→3)-(2-acetamido-6-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside) (35). Ethylthio 2,3,4-tri-*O*-benzyl-α-L-fucopyranoside[16] (**18**, 172 mg, 0.36 mmol) was dissolved in dry CH_2Cl_2 (1.44 mL), and a solution of distilled Br_2 (0.020 mL) in CH_2Cl_2 (0.20 mL) was added. The mixture was stirred for 15 min, and cyclohexene was added until the color of Br_2 disappeared. The solvents were evaporated, and the residue was dissolved in dry CH_2Cl_2 (1.44 mL). The fucosyl bromide solution was added to a mixture of **34** (143 mg, 0.18 mmol), molecular sieves (580 mg, 4 Å), Bu_4NBr (110 mg), and 5:3 CH_2Cl_2−DMF (1.64 mL). The mixture was stirred for 3 d, pyridine (1.64 mL) was added, and the stirring was continued for 3 h. The mixture was filtered through Celite and co-concentrated with toluene. The residue was chromatographed (SiO_2, 1:1 heptane−EtOAc) to give **35** (200 mg, 93%): $[\alpha]^{20}_D$ −71 (*c* 1.2 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.17−7.40 (m, 25 h, Ar), 6.72−6.91 (m, 4 H, OPMP), 6.05 (d, 1 H, J = 8.1 Hz, NH), 5.37 (d, 1 H, J = 5.2 Hz, H-1), 5.13 (dd, 1 H, J = 10.3, 8.1 Hz, H-2′), 5.11 (d, 1 H, J = 3.9 Hz, H-1″), 4.99 (dd, 1 H, J = 10.3, 3.8 Hz, H-3′), 4.97, 4.67 (ABq, 1 H each, J = 11.5 Hz, OBn), 4.85, 4.75 (ABq, 1 H each, J = 11.6 Hz, OBn), 4.80, 4.71 (ABq, 1 H each, J = 11 0.7 Hz, OBn), 4.42−4.47 (m, 4 H, H-1′, OBn), 4.32 (ABq, 1 H, J = 11.9 Hz, OBn), 4.10−4.20 (m, 4 H, H-5,4′,2″,5″), 3.96 (t, 1 H, J = 5.8 Hz, H-4), 3.84−3.93 (m, 2 H, H-2,3″), 3.76 (s, 3 H, OMe), 3.54−3.70 (m, 7 H, H-3,6,5′,6′,4″), 2.13, 2.02, 1.85 (s, 3 H each, OAc, NHAc), 1.09 (d, 3 H, J = 6.5 Hz, H-6″); ^{13}C NMR ($CDCl_3$): δ 170.7, 170.5, 170.1, 155.5, 151.7, 139.29, 139.27, 139.1, 138.4, 137.8, 129.0, 128.92, 128.89, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7, 118.8, 114.8, 99.8, 99.0, 97.6, 79.9, 76.9, 75.3, 74.7, 74.0, 73.8, 73.71, 73.68, 73.2, 73.0, 72.9, 71.8, 69.7, 69.3, 67.9, 67.2, 60.5, 56.1, 23.6, 21.2, 21.0, 17.0; HRMS calcd for $C_{66}H_{74}O_{17}N_4Na$ (M + Na) 1217.4947, found 1217.4948.

4-Methoxyphenyl (4-Acetamido-2,3-di-*O*-acetyl-6-*O*-benzyl-4-deoxy-*β*-D-galactopyranosyl)-(1→4)-[2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl]-(1→3)-(2-acetamido-6-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside) (36). H_2S was bubbled through a mixture of **35** (145 mg, 0.12 mmol) and 6:1 pyridine−H_2O (42 mL) at 0 °C for 1 h. The mixture was kept under H_2S at ∼22 °C for 48 h. Residual H_2S was removed by bubbling N_2 through the mixture for 1 h. The mixture was co-concentrated with toluene, and the residue was dissolved in pyridine (3 mL), Ac_2O (2 mL) was added, and the mixture was stirred for 30 min and co-concentrated with toluene. The residue was chromatographed (SiO_2, 2:1 toluene−acetone) to give **36** (145 mg, 99%): $[\alpha]^{20}_D$ −83 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.15−7.40 (m, 25 H, Ar), 6.74−6.87 (m, 4 H, OPMP), 6.36 (d, 1 H, J = 8.8 Hz, NH), 5.89 (d, 1 H, J = 9.5 Hz, NH), 4.90−5.00 (m, 3 H, H-2′,3′, and OBn), 4.85, 4.78 (ABq, 1 H each, J = 11.2 Hz, OBn), 4.80 (d, 1 H, J = 4.4 Hz, H-1), 4.75 (s, 2 H, OBn), 4.71 (dd, 1 H, J = 9.3, 2.3 Hz, H-4′), 4.59 (AB, 1 H, J = 11.4 Hz, OBn), 4.54, 4.41 (ABq, 1 H each, J = 12.2 Hz, OBn), 4.49 (d, 1 H, J = 7.1 Hz, H-1′), 4.39, 4.34 (ABq, 1 H each, J = 12.2 Hz, OBn), 4.32 (dd, 1 H, J = 8.5, 5.5 Hz, H-2), 4.13 (dd, 1 H, J = 10.0, 3.5 Hz, H-2″), 4.07, t, 1 H, J = 5.1 Hz, H-3), 3.42−3.95 (m, 10 H, H-4,5,6,5′,6′,3″,4″,5″), 3.77 (s, 3 H, OMe), 2.07, 2.01, 1.95, 1.92 (s, 3 H each, OAc, NHAc), 0.97 (d, J = 6.5 Hz, H-6″); ^{13}C NMR ($CDCl_3$) δ 170.9, 170.8, 170.7, 170.4, 155.4, 151.8, 139.0, 138.9, 138.7, 138.3, 137.9, 129.1, 128.94, 128.90, 128.87, 128.71, 128.67, 128.65, 128.28, 128.25, 128.20, 128.13, 128.05, 128.0, 127.7, 118.5, 114.8, 100.4, 99.6, 97.7, 79.6, 75.3, 75.1, 74.6, 74.0, 73.8, 73.8, 73.4, 73.1, 73.0, 71.8, 70.3, 69.7, 68.1, 67.9, 56.1, 50.9, 48.4, 32.3, 23.8, 23.6, 23.1, 21.3, 21.2, 17.2, 14.6; HRMS calcd for $C_{68}H_{78}O_{18}N_2Na$ (M + Na) 1233.5148, found 1233.5138.

4-Methoxyphenyl (4-Azido-6-*O*-benzyl-4-deoxy-*β*-D-galactopyranosyl)-(1→4)-[2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl]-(1→3)-(2-acetamido-6-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside) (37). Compound **35** (50 mg, 0.04 mmol) was dissolved in MeONa−MeOH (3 mL, 0.05 M), and the mixture was stirred for 30 min and then neutralized with Amberlite IR 120 H^+ resin. The mixture was filtered and concentrated, and the residue was chromatographed (SiO_2, 2:1 toluene−acetone) to give **37** (44 mg, 96%): $[\alpha]^{20}_D$ −67 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CHCl_3$) δ 7.25−7.45 (m, 25 H, Ar), 6.75−6.95 (m, 4 H, OPMP), 6.05 (d, 1 H, J = 7.2 Hz, NH), 5.29 (d, 1 H, J = 7.6 Hz, H-1), 5.13 (d, 1 H, J = 3.6 Hz, H-1″), 4.97, 4.64 (ABq, 1 H each, J = 11.6 Hz, OBn), 4.93, 4.64 (ABq, 1 H each, J = 11.7 Hz, OBn), 4.77, 4.73 (ABq, 1 H each, J = 11.6 Hz, OBn), 4.61, 4.49 (ABq, 1 H each, J = 12.0 Hz, OBn), 4.48, 4.44 (ABq, 1 H each, J = 11.9 Hz, OBn), 4.47 (d, 1 H, J = 7.5 Hz, H-1′), 4.29−4.35 (m, 2 H, H-3,5″), 4.26 (broad s, 1 H, OH), 4.12 (dd, 1 H, J = 10.3, 3.7 Hz, H-2″), 4.02 (t, 1 H, J = 8.7 Hz, H-4), 3.96 (d, 1 H, J = 3.4 Hz, H-4′), 3.95 (dd, 1 H, J = 10.2, 3.4 Hz, H-3″), 3.87 (dd, 1 H, J = 11.4, 3.9 Hz, H-6′), 3.82 (dd, 1 H, J = 11.1, 2.4 Hz, H-6′), 3.75 (s, 3 H, OMe), 3.72 (broad s, 1 H, H-4), 3.55−3.67 (m, 6 H, H-5, 3′,5′,2,6), 3.50 (bt, 1 H, J = 4.5 Hz, H-2′), 2.97 (d, 1 H, J = 2.1 Hz, OH), 1.14 (d, 3 H, J = 6.5 Hz, H-6″); ^{13}C NMR ($CDCl_3$) δ 171.2, 155.8, 151.8, 138.9, 138.8, 138.4, 138.0, 129.1, 128.9, 128.8, 128.7, 128.5, 128.4, 128.3, 128.13, 128.09, 128.08, 127.7, 119.4, 114.8, 101.4, 99.9, 98.2, 80.1, 76.1, 75.4, 75.1, 75.0, 74.7, 74.1, 73.9, 73.8, 72.8, 72.6, 72.2, 69.2, 68.5, 67.5, 61.5, 57.8, 56.1, 23.7, 17.3; HRMS calcd for $C_{62}H_{70}O_{15}N_4Na$ (M + Na) 1133.4736, found 1133.4745.

4-Methoxyphenyl [Methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-3-(phenylthio)-D-glycero-α-D-galacto-2-nonulopyranosyl)onate]-(1→3)-(4-azido-6-*O*-benzyl-4-deoxy-*β*-D-galactopyranosyl)-(1→4)-[2,3,4-tri-*O*-benzyl-α-

L-fucopyranosyl]-(1→3)-(2-acetamido-6-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside) (39). To a mixture of **37** (400 mg, 0.360 mmol), **38**[23] (459 mg, 0.713 mmol), and molecular sieves (1.6 g, 3 Å) were added dry CH_2Cl_2 (0.92 mL) and freshly distilled MeCN (8.0 mL). The mixture was stirred under Ar for 5 min at ∼22 °C and for 5 min at −45 °C. A solution of silver trifluoromethanesulfonate (200 mg, 0.78 mmol) in MeCN (2.0 mL) was added, and after 5 min, a 4 M solution of methylsulfenyl bromide[15] in 1,2-dichloroethane (0.182 mL) was added during 20 min. The mixture was stirred for 1.5 h at −45 °C, and then diisopropylamine (2.10 mL) was added. The mixture was stirred for 1 h at −45 °C and filtered through a short column (SiO_2, 1:1 toluene−acetone). The crude product was chromatographed (SiO_2, 4:1 → 2:1 toluene−acetone) to give **39** (446 mg, 73%): $[\alpha]^{20}_D$ −34 (*c* 0.9 $CHCl_3$); ^{1}H NMR ($CDCl_3$) *δ* 7.20−7.50 (m, 30 H, Ar), 6.73−6.95 (m, 4 H, OPMP), 5.94 (d, 1 H, *J* = 7.8 Hz, NH), 5.46−5.53 (m, 2 H, H-4‴, NH‴), 5.39 (d, 1 H, *J* = 6.9 Hz, H-1), 5.36 (ddd, 1 H, *J* = 8.8, 5.9, 2.8 Hz, H-8‴), 5.26 (dd, 1 H, *J* = 8.8, 1.5 Hz, H-7‴), 5.15 (d, 1 H, *J* = 3.7 Hz, H-1″), 4.97, 4.65 (ABq, 1 H each, *J* = 11.6 Hz, OBn), 4.90, 4.72 (ABq, 1 H each, *J* = 11.9 Hz, OBn), 4.76, 4.73 (ABq, 1 H each, *J* = 11.5 Hz, OBn), 4.57 (d, 1 H, *J* = 7.6 Hz, H-1′), 4.42−4.53 (m, 4 H, OBn), 4.38 (dd, 1 H, *J* = 9.4, 3.8 Hz, H-3′), 4.28−4.35 (m, 3 H, H-3,4′,6‴), 3.90−4.22 (m, 8 H, H-4,6,2″,3″,5‴,9‴), 3.87 (s, 3 H, OMe‴), 3.75 (s, 3 H, OMe), 3.60−3.72 (m, H-2,5,5′,6′,4″), 3.52 (t, 1 H, *J* = 8.5 Hz, H-2′), 3.47 (d, 1 H, *J* = 11.0 Hz, H-3‴), 3.07 (broad s, 1 H, OH), 2.08, 1.94 (s, 6 H each, OAc), 1.90, 1.72 (s, 3 H each, NHAc), 1.14 (d, 3 H, *J* = 6.4 Hz, H-6″); ^{13}C NMR ($CDCl_3$) *δ* 171.4, 170.8, 170.7, 170.4, 169.9, 167.8 ($J_{C-1''':H-3'''ax}$ 6.1 Hz, C-1‴),[21] 155.6, 151.9, 139.3, 139.2, 139.1, 138.9, 138.1, 135.5, 132.0, 129.4, 129.0, 128.91, 128.85, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.73, 127.65, 119.2, 114.8, 102.2, 100.8, 99.5, 98.0, 80.3, 75.3, 74.6, 74.4, 74.3, 73.8, 73.5, 73.3, 73.1, 72.9, 71.6, 71.0, 69.1, 68.6, 67.14, 67.08, 62.54, 62.46, 57.7, 56.0, 53.4, 50.3, 30.1, 23.8, 23.6, 21.3, 21.1, 21.0, 17.1; HRMS calcd for $C_{88}H_{101}O_{27}N_5SNa$ (M + Na) 1714.6302, found 1714.6273.

A sample of **39** was conventionally acetylated: $[\alpha]^{20}_D$ −18 (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$) *δ* 7.15−7.55 (m, 30 H, Ar), 6.70−6.92 (m, 4 H, OPMP), 6.17 (d, 1 H, *J* = 8.1 Hz, NH), 5.47 (dt, 1 H, *J* = 6.2, 3.1 Hz, H-8‴), 5.39 (dd, 1 H, *J* = 8.9, 2.6 Hz, H-7‴), 5.37 (d, 1 H, *J* = 5.5 Hz, H-1), 5.31 (dd, 1 H, *J* = 11.4, 10.1 Hz, H-4‴), 5.24 (d, 1 H, *J* = 10.4 Hz, NH‴), 5.14 (d, 1 H, *J* = 3.9 Hz, H-1″), 5.12 (dd, 1 H, *J* = 9.9, 8.0 Hz, H-2′), 4.85 (dd, 1 H, *J* = 10.1, 3.9 Hz, H-3′), 4.93, 4.63 (ABq, 1 H each, *J* = 11.8 Hz, OBn), 4.83, 4.78 (ABq, 1 H each, *J* = 11.9 Hz, OBn), 4.77, 4.69 (ABq, 1 H each, *J* = 12.0 Hz, OBn), 4.66 (d, 1 H, *J* = 7.8 Hz, H-1′), 4.40, 4.29 (ABq, 1 H each, *J* = 12.0 Hz, OBn), 4.35 (dd, 1 H, *J* = 8.0, 2.6 Hz, H-9‴), 4.19 (t, 1 H, *J* = 6.1 Hz, H-3), 3.60−4.15 (m, 15 H, H-2,4,5,6,4′,5′,6′,2″,3″,-4″,5″,6‴, 3.83 (s, 3 H, OMe), 3.75 (s, 3 H, OMe), 3.15 (d, 1 H, *J* = 11.3 Hz, H-3‴), 2.17, 2.07, 2.06, 2.00, 1.95, 1.90, 1.86 (s, 3 H each, OAc, NHAc), 1.09 (d, 3 H, *J* = 6.5 Hz, H-6″); ^{13}C NMR ($CDCl_3$) *δ* 171.5, 171.0, 170.8, 170.7, 170.4, 170.3, 170.1, 168.2, 155.3, 151.7, 139.34, 139.28, 139.0, 138.7, 138.2, 137.0, 132.1, 129.5, 128.9, 128.83, 128.81, 128.61, 128.59, 128.4, 128.3, 128.0, 127.93, 127.87, 127.8, 127.7, 127.6, 118.7, 114.8, 99.9, 99.5, 98.8, 97.4, 79.7, 76.8, 75.2, 74.6, 73.9, 73.7, 73.6, 73.5, 73.22, 73.15, 73.1, 72.9, 72.5, 71.5, 71.0, 69.9, 68.6, 68.3, 67.3, 62.5, 62.1, 59.5, 56.1, 53.5, 50.5, 23.61, 23.56, 21.6, 21.4, 21.3, 21.1, 16.9; HRMS calcd for $C_{90}H_{103}O_{28}N_5SNa$ (M + Na) 1756.6408, found 1756.6387.

4-Methoxyphenyl (2-Amino-6-*O*-benzyl-2-deoxy-2,3-*N*,*O*-(2-oxoethylidene)-*β*-D-galactopyranosyl)-(1→4)-[2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl]-(1→3)-(2-acetamido-6-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside) (40). Compound **21** (167 mg, 0.13 mmol) was dissolved in toluene (2.0 mL) and Bu_2SnO (42 mg, 0.17 mmol), and molecular sieves (85 mg, 4 Å, activated) were added. The mixture was stirred at 80 °C for 8 h, then Bu_4NBr (50 mg, 0.16 mmol) and *tert*-butyl bromoacetate (0.2 mL, 1.35 mmol) were added. The stirring was continued at 80 °C for 4 h, and the mixture was filtered through a short column (SiO_2, 1:1 toluene−acetone plus 1% Et_3N). The crude product was dissolved in AcOH (15 mL), activated zinc dust (2.0 g) was added, and the mixture was stirred for 4 h, filtered through Celite, and co-concentrated with toluene. The residue was dissolved in MeOH (15 mL), and MeONa−MeOH (1 M) was added until the pH reached 9. The mixture was stirred for 1 h, neutralized with AcOH, and concentrated. The residue was chromatographed (SiO_2, 2:1 toluene−acetone) to give **40** (78 mg, 52%): $[\alpha]^{20}_D$ −51 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) *δ* 7.25−7.40 (m, 25 H, Ar), 6.85 (bs, 1 H, NH′), 6.75−6.95 (m, 4 H, OPMP), 6.10 (d, 1 H, *J* = 6.9 Hz, NH), 5.43 (d, 1 H, *J* = 7.4 Hz, H-1), 5.14 (d, 1 H, *J* = 3.5 Hz, H-1″), 4.95, 4.60 (ABq, 1 H each, *J* = 11.2 Hz, OBn), 4.93, 4.67 (ABq, 1 H each, *J* = 11.7 Hz, OBn), 4.81, 4.75 (ABq, 1 H each, *J* = 11.6 Hz, OBn), 4.63, 4.47 (ABq, 1 H each, *J* = 12.0 Hz, OBn), 4.51 (s, 2 H, OBn), 4.43 (d, 1 H, *J* = 8.3 Hz, H-1′), 4.42 (t, 1 H, *J* = 8.6 Hz, H-3), 4.32, 4.17 (ABq, 1 H each, *J* = 16.8 Hz, OCH_2CO), 4.29 (t, 1 H, *J* = 7.4 Hz, H-5″), 4.06−4.13 (m, 3 H, H-4,4′,2″), 4.00 (dd, 1 H, *J* = 10.5, 2.9 Hz, H-4″), 3.50−3.85 (m, 9 H, H-2,3,5,6,2′,5′,6′), 3.77 (s, 3 H, OMe), 3.14, (dd, 1 H, *J* = 10.1, 2.7 Hz, H-3′), 2.45 (b s, 1 H, OH), 1.73 (s, 3 H, NHAc), 1.10 (d, 3 H, *J* = 6.5 Hz, H-6″); ^{13}C NMR ($CDCl_3$) *δ* 170.8, 168.9, 155.7, 151.7, 139.2, 139.1, 139.0, 138.3, 138.0, 129.00, 128.98, 128.9, 128.8, 128.68, 128.65, 128.5, 128.4, 128.3, 128.2, 128.0, 99.4, 99.1, 97.6, 80.0, 77.1, 76.9, 76.1, 75.4, 75.0, 74.9, 74.4, 74.0, 73.9, 72.8, 69.2, 68.8, 68.4, 67.3, 66.5, 57.4, 56.1, 52.2, 23.7, 17.4; HRMS calcd for $C_{64}H_{72}O_{16}N_2Na$ (M + Na) 1147.4780, found 1147.4778.

A sample of **40** was conventionally acetylated, which gave a ^{1}H NMR signal at *δ* 5.43 (bs, 1 H, H-4′).

4-Methylphenyl 4,6-*O*-Benzylidene-3-*O*-(methoxyethanoyl)-1-thio-*β*-D-glucopyranoside (41). Compound **26** (3.80 g, 10.09 mmol) and Bu_2SnO (2.89 g, 11.6 mmol) were dissolved in MeOH (120 mL). The mixture was refluxed for 75 min and then co-concentrated with toluene. The residue was dissolved in toluene (40 mL), and *tert*-butyl bromoacetate (5.95 mL, 40.4 mmol), Bu_4NBr (3.41 g, 10.6 mmol), and molecular sieves (500 mg, 3 Å, activated) were added. The mixture was refluxed for 3 h, filtered, and concentrated. The residue was dissolved in MeONa−MeOH (120 mL, 0.05 M), and the mixture was stirred for 1 h and neutralized with Amberlite IR 120 H^+. The mixture was filtered and concentrated, and the residue was chromatographed (SiO_2, 40:1 → 20:1 toluene−acetone) to give **41** (3.23 g, 72%). A sample was crystallized from heptane−EtOAc: $[\alpha]^{20}_D$ −11 (*c* 1.1, $CHCl_3$); mp 122−124 °C; ^{1}H NMR ($CDCl_3$) *δ* 7.10−7.50 (m, 9 H, Ar), 5.53 (s, 1 H, ArCH), 4.61 (m, 1 H, virtual coupling as in entry 19 in ref 26, H-1), 4.44, 4.37 (ABq, 1 H each, *J* = 16.8 Hz, OCH_2CO), 4.38 (d, 1 H, *J* = 5.5 Hz, H-6), 3.79 (t, 1 H, *J* = 10.2 Hz, H-6), 3.73 (s, 3 H, OMe), 3.60−3.65 (m, 1 H, H-4), 3.55 (q, 1 H, *J* = 8.3 Hz, H-3), 3.54 (d, 1 H, *J* = 9.4 Hz, H-2), 3.46 (dt, 1 H, *J* = 9.9, 5.0 Hz, H-5), 2.36 (s, 3 H, Me); ^{13}C NMR ($CDCl_3$) *δ* 173.3, 139.0, 137.5, 134.4, 130.1, 129.6, 129.5, 128.8, 128.7, 128.1, 126.4, 101.8, 88.9, 84.6, 81.3, 71.7, 70.8, 69.3, 69.0, 52.7, 21.6; HRMS calcd for $C_{23}H_{26}O_7SNa$ (M + Na) 469.1297, found 469.1296.

4-Methylphenyl 2-*O*-Acetyl-4,6-*O*-benzylidene-3-*O*-(methoxyethanoyl)-1-thio-*β*-D-glucopyranoside (42). Compound **41** (1.95 g, 14.4 mmol) was dissolved in pyridine (80 mL), and Ac_2O (65 mL) was added dropwise, followed by (dimethylamino)pyridine (DMAP, 20 mg). The mixture was stirred for 40 min and co-concentrated with toluene. The residue was chromatographed (SiO_2, 40:1 toluene−acetone) to give **42** (2.09 g, 98%). A sample was crystallized from heptane−EtOAc: $[\alpha]^{20}_D$ −11 (*c* 1.1, $CHCl_3$); mp 147.5−148 °C; ^{1}H NMR ($CDCl_3$) *δ* 7.13−7.46 (m, 9 H, Ar), 5.52 (s, 1 H, ArCH), 4.99 (dd, 1 H, *J* = 10.1, 8.5 Hz, H-2), 4.70 (d, 1 H, *J* = 10.1 Hz, H-1), 4.38 (dd, 1 H, *J* = 10.5, 5.0 Hz, H-6), 4.37, 4.31 (ABq, 1 H each, *J* = 16.8 Hz, OCH_2CO), 3.69−3.82 (m, 3 H, H-3,4,6), 3.61 (s, 3 H, OMe), 3.44−3.51 (m, 1 H, H-5), 2.36 (s, 3 H, Me), 2.22 (s, 3 H, OAc); ^{13}C NMR ($CDCl_3$) *δ* 170.04, 170.00, 139.1, 137.3, 134.2, 130.2, 129.6, 128.7, 128.3, 126.5, 101.7, 87.1, 81.7, 71.1, 70.5, 69.4, 69.0, 52.0, 21.6, 21.5; HRMS calcd for $C_{25}H_{28}O_8SNa$ (M + Na) 511.1403, found 511.1407.

4-Methylphenyl 2-*O*-Acetyl-6-*O*-benzyl-3-*O*-(methoxyethanoyl)-1-thio-*β*-D-glucopyranoside (43). Compound **42** (2.91 g, 6.0 mmol) was dissolved in THF (60 mL), and the mixture was cooled to 0 °C. $NaBH_3CN$ (3.75 g, 60 mmol) and molecular sieves (4.5 g, 4 Å) were added. Et_2O (nondried)

saturated with HCl (g) was added to the reaction mixture until the pH (moist litmus paper) was approximately 2. The mixture was stirred at 0 °C for 1.5 h, diluted with Et_2O, and filtered through Celite. The mixture was washed with saturated aqueous $NaHCO_3$ solution and H_2O, dried (Na_2SO_4), and concentrated. The residue was chromatographed (SiO_2, 40:1 → 20:1 toluene−acetone) to give **43** (2.35 g, 80%). A sample was crystallized from heptane−EtOAc: $[\alpha]^{20}_D$ −49 (*c* 0.9, $CHCl_3$); mp 100−100.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.00−7.45 (m, 9 H, Ar), 4.96 (dd, 1 H, J = 10.0, 9.1 Hz, H-2), 4.60 (s, 2 H, OBn), 4.57 (d, 1 H, J = 10.0 Hz, H-1), 4.40, 4.14 (ABq, 1 H each, J = 17.6 Hz, OCH_2CO), 3.92 (dd, 1 H, J = 10.7, 2.3 Hz, H-6), 3.79 (s, 3 H, OMe), 3.74 (dd, 1 H, J = 10.8, 6.1 Hz, H-6), 3.64 (t, 1 H, J = 8.9 Hz, H-4), 3.52 (dt, 1 H, J = 7.9, 2.5 Hz, H-5), 3.40 (t, 1 H, J = 9.0 Hz, H-3), 2.31 (s, 3 H, Me), 2.18 (s, 3 H, OAc); ^{13}C NMR ($CDCl_3$) δ 173.5, 169.8, 138.8, 138.5, 133.2, 130.1, 129.5, 128.1, 128.0, 87.4, 86.6, 80.1, 74.0, 72.3, 70.3, 70.0, 68.8, 52.9, 21.6, 21.5; HRMS calcd for $C_{25}H_{30}O_8SNa$ (M + Na) 513.1559, found 513.1567.

4-Methylphenyl 2-*O*-Acetyl-4-azido-6-*O*-benzyl-4-deoxy-3-*O*-(methoxyethanoyl)-1-thio-*β*-D-galactopyranoside (44). Compound **43** (2.15 g, 4.4 mmol) was dissolved in CH_2Cl_2 (21 mL), and the mixture was cooled to 0 °C. Pyridine (1.48 mL) and trifluoromethansulfonic anhydride (1.37 mL, 9.9 mmol) were added. The temperature was increased to ∼22 °C, and the solution was stirred for 3 h and then diluted with CH_2Cl_2. The organic phase was washed with saturated aqueous $NaHCO_3$ solution, dried (Na_2SO_4), concentrated, and dried under vacuum. The residue was dissolved in DMF (9 mL), and NaN_3 (1.65 g, 25.4 mmol) was added. The mixture was stirred for 15 h and then diluted with CH_2Cl_2, filtered through a short column (SiO_2, 1:1 heptane−EtOAc), and then chromatographed (SiO_2, 3:1 heptane−EtOAc), to give **44** (1.76 g, 75%): $[\alpha]^{20}_D$ −28 (*c* 1.0, $CHCl_3$); mp 92.5−93 °C; ^{1}H NMR ($CDCl_3$) δ 7.07−7.40 (m, 9 H, Ar), 5.20 (t, 1 H, J = 9.7 Hz, H-2), 4.58, 4.55 (ABq, 1 H each, J = 12.1 Hz, OBn), 4.52 (d, 1 H, J = 10.0 Hz, H-1), 4.32 (d, 1 H, J = 3.6 Hz, H-4), 4.30, 4.20 (ABq, 1 H each, J = 16.9 Hz, OCH_2CO), 3.76 (s, 3 H, OMe), 3.65−3.74 (m, 4 H, H-3,5,6), 2.33 (s, 3 H, Me), 2.17 (s, 3 H, OAc); ^{13}C NMR ($CDCl_3$) δ 170.9, 169.9, 138.5, 138.1, 133.2, 130.1, 129.5, 128.9, 128.4, 87.4, 82.3, 76.4, 74.2, 70.1, 69.1, 68.2, 60.8, 52.4, 21.6, 21.5; HRMS calcd for $C_{25}H_{29}O_7N_3SNa$ (M + Na) 538.1624, found 538.1644.

4-Methoxyphenyl [2-*O*-Acetyl-4-azido-6-*O*-benzyl-4-deoxy-3-*O*-(methoxy ethanoyl)-*β*-D-galactopyranosyl]-(1→4)-[2-deoxy-6-*O*-benzyl-2-(tetrachlorophthalimido)-*β*-D-glucopyranoside] (45). To a solution of **44** (806 mg, 1.52 mmol) and **15**[1] (651 mg, 1.01 mmol) in CH_2Cl_2 (7.8 mL) at −78 °C under Ar was added a solution of AgOTf (670 mg, 3.03 mmol) in MeCN (4.1 mL). After 5 min, a 4 M solution of methylsulfenyl bromide[15] in 1,2-dichloroethane (0.635 mL) was added during 30 min, the mixture was stirred for 1.5 h, and then isopropylamine (0.65 mL) was added. The mixture was stirred at −78 °C for 1.5 h, filtered through a short column (SiO_2, 1:1 heptane−EtOAc), and concentrated. The residue was chromatographed (SiO_2, 30:1 toluene−acetone) to give **45** (715 mg, 67%): $[\alpha]^{20}_D$ −6 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.15−7.35 (m, 10, Ar), 6.70−6.90 (m, 4 H, OPMP), 5.63 (d, 1 H, J = 8.4 Hz, H-1), 5.21 (dd, 1 H, J = 9.9, 8.0 Hz, H-2), 4.70 (ABq, 1 H, J = 12.0 Hz, OBn), 4.38−4.55 (m, 6 H, H-2,3,4′,-OBn), 4.43 (d, 1 H, J = 8.0 Hz, H-1′), 4.32, 4.17 (ABq, 1 H each, J = 16.9 Hz, OCH_2CO), 4.26 (d, 1 H, J = 3.1 Hz, H-4′), 3.60−3.75 (m, 8 H, H-4,5,6,3′,5′,6′), 3.77 (s, 3 H, OMe), 3.73 (s, 3 H, OMe), 2.10 (s, 3 H, OAc); ^{13}C NMR ($CDCl_3$) δ 170.9, 169.6, 155.9, 150.9, 140.6, 138.7, 137.6, 128.81, 128.77, 128.20, 128.15, 128.1, 127.9, 118.9, 114.8, 101.8, 97.4, 82.0, 81.4, 74.8, 74.03, 74.00, 72.6, 71.5, 69.9,69.3, 68.5, 68.4, 60.3, 56.8, 56.0, 52.5, 21.4; HRMS calcd for $C_{46}H_{44}O_{15}N_4Cl_4Na$ (M + Na) 1055.1455, found 1055.1463.

4-Methoxyphenyl [2-*O*-Acetyl-4-azido-6-*O*-benzyl-4-deoxy-3-*O*-(methoxy ethanoyl)-*β*-D-galactopyranosyl]-(1→4)-(2-acetamido-6-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside) (46). Compound **45** (292 mg, 0.28 mmol) was dissolved in dry EtOH (20 mL), and diaminoethane[12] (0.022 mL, 0.33 mmol) was added during 30 min. The mixture was heated at 60 °C for 15 h and then co-concentrated with toluene. The residue was dissolved in MeOH−H_2O−Ac_2O (8.5, 1.7, 2.6 mL), and the mixture was stirred for 1 h and then co-concentrated with toluene. The residue was chromatographed (SiO_2, 4:1 toluene-acetone) to give **46** (161 mg, 70%): $[\alpha]^{20}_D$ −24 (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.25−7.40 (m, 10 H, Ar), 6.75−6.97 (m, 4 H, OPMP), 5.69 (d, 1 H, J = 8.1 Hz, NH), 5.21 (d, 1 H, J = 8.0 Hz, H-1), 5.17 (dd, 1 H, J = 9.9, 8.1 Hz, H-2′), 4.67, 4.49 (ABq, 1 H each, J = 12.0 Hz, OBn), 4.59, 4.53 (ABq, 1 H each, J = 11.9 Hz, OBn), 4.37 (d, 1 H, J = 8.0 Hz, H-1′), 4.29, 4.17 (ABq, 1 H, J = 17.1 Hz, OCH_2CO), 4.26 (d, 1 H, J = 3.5 Hz, H-4′), 4.03 (b dd, 1 H, J = 9.2, 7.9 Hz, H-3), 3.57−3.77 (m, 10 H, H-2,4,5,6,3′,4′,5′,6′), 3.78 (s, 3 H, OMe), 3.76 (s, 3 H, OMe), 2.07, 2.00 (s, 3 H each, OAc, NHAc); ^{13}C NMR ($CDCl_3$) δ 170.9, 169.7, 155.7, 151.8, 138.7, 137.7, 129.0, 128.8, 128.5, 128.4, 128.2, 128.1, 119.0, 114.9, 101.7, 100.1, 81.4, 81.3, 74.6, 74.2, 74.0, 72.5, 72.0, 71.5, 68.7, 68.4, 60.3, 57.0, 56.1, 52.5, 24.1, 21.3; HRMS calcd for $C_{40}H_{48}O_{14}N_4Na$ (M + Na) 831.3065, found 831.3073.

4-Methoxyphenyl (2-*O*-Acetyl-4-azido-6-*O*-benzyl-4-deoxy-3-*O*-(methoxyethanoyl)-*β*-D-galactopyranosyl)-(1→4)-[2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl]-(1→3)-(2-acetamido-6-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside) (47). Ethyl 2,3,4-tri-*O*-benzyl-1-thio-α-L-fucopyranoside[16] (**18**, 171 mg, 0.36 mmol) was dissolved in dry CH_2Cl_2 (2.0 mL), and a solution of freshly distilled Br_2 (0.050 mL) in CH_2Cl_2 (0.450 mL) was added. The mixture was stirred for 15 min, and cyclohexene was added until the color of Br_2 disappeared. The solvent was evaporated, the residue was dissolved in dry CH_2Cl_2 (2.16 mL), and the solution was then added to a mixture of **46** (126 mg, 0.15 mmol), molecular sieves (850 mg, 4 Å), and Bu_4NBr (126 mg, 0.39 mmol) in CH_2Cl_2−DMF (5:3, 2.16 mL). The mixture was stirred for 3 d, pyridine (1.2 mL) was added, and the stirring was continued for 3 h. The mixture was filtered through Celite and co-concentrated with toluene. The residue was chromatographed (SiO_2, 1:1 heptane−EtOAc) to give **47** (181 mg, 82%): $[\alpha]^{20}_D$ −57 (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.15−7.40 (m, 25 H, Ar), 6.72−6−91 (m, 4 H, OPMP), 6.15 (d, 1 H, J = 7.8 Hz, NH), 5.34 (d, 1 H, J = 4.7 Hz, H-1), 5.13 (d, 1 H, J = 3.6 Hz, H-1″), 5.10 (dd, 1 H, J = 9.7, 7.9 Hz, H-2′), 4.96, 4.65 (ABq, 1 H each, J = 11.6 Hz, OBn), 4.83, 4.71 (ABq, 1 H each, J = 11.9 Hz, OBn), 4.79, 4.70 (ABq, 1 H each, J = 12.0 Hz, OBn), 4.50 (s, 2 H, OBn), 4.39, 4.28 (ABq, 1 H each, J = 12.0 Hz, OBn), 4.36 (d, 1 H, J = 8.2 Hz, H-1′), 4.31 (s, 1 H, H-4′), 4.30, 4.18 (ABq, 1 H each, J = 16.8 Hz, OCH_2CO), 3.50−4.10 (m, 15 H, H-2,3,4,5,6,3′,4′,5′,6′,2″,3″,-4″,5″), 3.79 (s, 3 H OMe), 3.75 (s, 3 H, OMe), 2.06 (s, 3 H, OAc), 1.86 (s, 3 H, NHAc), 1.06 (d, 3 H, J = 6.4 Hz, H-6″); ^{13}C NMR ($CDCl_3$) δ 170.9, 170.7, 170.1, 155.3, 151.7, 139.3, 139.2, 139.0, 138.5, 137.9, 129.0, 128.9, 128.82, 128.77, 128.6, 128.5, 128.4, 128.3, 128.1, 128.02, 127.99, 127.9, 127.7, 118.6, 114.8, 99.8, 98.9, 97.4, 80.9, 79.7, 76.8, 75.2, 74.6, 74.1, 73.7, 73.6, 73.4, 73.1, 72.8, 72.2, 71.8, 69.6, 68.5, 68.3, 67.3, 60.7, 56.1, 52.5, 23.6, 21.4, 16.9; HRMS calcd for $C_{67}H_{76}O_{18}N_4Na$ (M + Na) 1247.5053, found 1247.5045.

4-Methoxyphenyl (2-*O*-Acetyl-4-amino-6-*O*-benzyl-4-deoxy-4,3-*N*,*O*-(2-oxoethylidene)-*β*-D-galactopyranosyl)-(1→4)-[2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl]-(1→3)-(2-acetamido-6-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside) (48). H_2S(g) was bubbled through a solution of **47** (177 mg, 0.14 mmol) in pyridine−Et_3N−MeOH (8.0, 4.0, 4.0 mL) at 0 °C for 1 h. The mixture was kept under H_2S at room temperature for 15 h. Residual H_2S was removed by a stream of N_2 for 1 h, and the mixture was co-concentrated with toluene. The residue was chromatographed (SiO_2, 4:1 toluene−acetone) to give **48** (165 mg, 98%): $[\alpha]^{20}_D$ −48 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.20−7.40 (m, 25 H, Ar), 6.75−6.95 (m, 4 H, OPMP), 6.60 (bs, 1 H, NH), 6.01 (d, 1 H, J = 8.2 Hz, NH), 5.40 (d, 1 H, J = 5.6 Hz, H-1), 5.24 (dd, 1 H, J = 9.9, 7.9 Hz, H-2′), 5.11 (d, 1 H, J = 3.4 Hz, H-1″), 4.95, 4.65 (ABq, 1 H each, J = 11.4 Hz, OBn), 4.88, 4.74 (ABq, 1 H each, J = 11.7 Hz, OBn), 4.76, 4.72 (ABq, 1 H each, J = 12.0 Hz, OBn), 4.56, 4.43 (ABq, 1 H each, J = 12.0 Hz, OBn), 4.54 (d, 1 H, J = 8.1 Hz, H-1′), 4.49, 4.33 (ABq, 1 H each, J = 11.8 Hz, OBn), 4.38, 4.17 (ABq, 1 H each, J = 17.8 Hz, OCH_2CO), 4.19−4.24 (m, 2

H, H-3,5″), 4.13 (dd, 1 H, J = 10.0, 3.7 Hz, H-2″), 4.02 (t, 1 H, J = 6.1 Hz, H-4), 3.65−3.95 (m, 10 H, H-2, H-5, 2*H-6, H-3′, H-4′, H-6′, H-2″, H-3″, H-4″), 3.76 (s, 3 H, OMe), 3.59 (dd, 1 H, J = 10.2, 6.2 Hz, H-6′), 3.35 (bt, 1 H, J = 5.5 Hz, H-5′), 2.10 (s, 3 H, OAc), 1.80 (s, 3 H, NHAc), 1.12 (d, 3 H, J = 6.4 Hz, H-6″); ^{13}C NMR ($CDCl_3$) δ 170.8, 170.3, 168.6, 155.5, 151.7, 139.2, 138.5, 137.0, 129.2, 128.94, 128.86, 128.79, 128.6, 128.21, 128.17, 128.1, 127.9, 127.7, 118.9, 114.8, 100.2, 99.1, 98.1, 79.8, 78.5, 76.9, 75.5, 74.7, 74.3, 74.1, 73.9, 73.7, 72.9, 72.0, 70.9, 69.4, 68.7, 67.4, 66.5, 62.9, 56.1, 52.4, 23.7, 21.2, 17.0; HRMS calcd for $C_{66}H_{74}O_{17}N_2Na$ (M + Na) 1189.4885, found 1189.4906.

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Supporting Information Available: ^{1}H NMR spectra for all title compounds described in the Experimental Section (39 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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