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Convergent Preparation of DimLe^x Hexasaccharide Analogues

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We report the convergent preparation of four hexasaccharides to be used towards the synthesis of a safe anticancer vaccine based on the tumor-associated carbohydrate antigen dimLe^x. A common trisaccharide intermediate was first synthesized as a precursor to the tetrasaccharide backbones. These tetrasaccharides were then converted into diol acceptors and fucosylated at O-3 of both glucosamine residues. The conditions required to promote fucosylation at O-3 of the reducing end glucosamine units led to some loss of the fucosyl units already introduced at O-3 of the nonreducing end glucosamine residues. Despite this hurdle, optimization of the glycosylation conditions provided the desired hexasaccharides in sufficient quantities to prepare the final analogues. Propyl glycosides and cysteamine adducts were prepared easily in two steps from the protected allyl glycoside hexasaccharides, and a one-step deprotection under metal-dissolving conditions was key to our deprotection strategy.

Introduction

The dimeric Le^x hexasaccharide (dimLe^x, Figure 1) has been identified as a tumor-associated carbohydrate antigen (TACA) in colon and liver carcinoma and has been associated with the progression of colorectal cancer.[1] However, the Le^x antigenic determinant or X determinant {β-D-Gal*p*(1→4)-[α-L-Fuc*p*(1→3)]-D-GlcNAc*p*} displayed at the nonreducing end of dimLe^x is also present on normal cells and tissues such as kidney tubules, gastrointestinal epithelial cells, and cells of the spleen and brain.[2] Thus, using TACA dimLe^x as a target candidate for anticancer vaccine development is precarious, as such a structure is likely to elicit an immune response against the X determinant that would eventually lead to the destruction of healthy cells. In this context, our research program aims at discovering analogues of the dimLe^x hexasaccharide that would retain internal epitopes displayed on the surface of cancer cells by dimLe^x (see ref.[1a,1f]) but no longer possess epitopes associated with the Le^x trisaccharide *A′(B′)C′*. Indeed we recently reported[3] that a Le^x analogue in which the galactose residue (*C*) was replaced by a glucose unit was no longer recognized by the anti-Le^x antibody SH1.[1f] Thus, we postulate that a vaccine candidate displaying an analogue of dimLe^x in which the nonreducing end galactosyl residue (*C′*) is replaced by a glucose unit (Figure 1) will no longer trigger the production of antibodies that cross-react with Le^x. Most importantly, because the galactose residue C-4 *C′* hydroxy group is not likely involved in the internal epitopes displayed by the TACA dimLe^x,[1a,1f] we may expect that this vaccine candidate will trigger the production of antibodies that are cross-reactive with the internal epitopes presented by the TACA dimLe^x. Thus, we report here the synthesis of dimLe^x analogues **2** and **3** (Figure 1) in which the nonreducing end galactosyl residue (*C′*) has been replaced by a glucose unit; these analogues will be further referred to as GlcLe^{x}Le^x derivatives for short. Whereas propyl glycoside **2** will be employed as a soluble inhibitor in binding studies, cysteamine adduct **3** will be used to prepare[3,4] BSA (bovine serum albumin) and tetanous toxoid based glycoconjugates. In addition to analogues **2** and **3**,

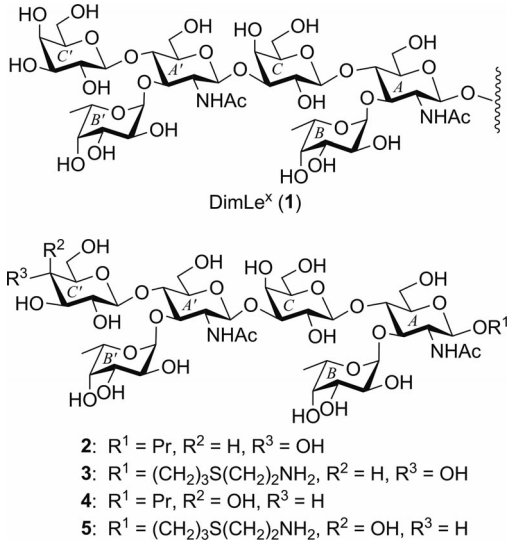

Figure 1. DimLe^x and the analogues synthesized in this study..

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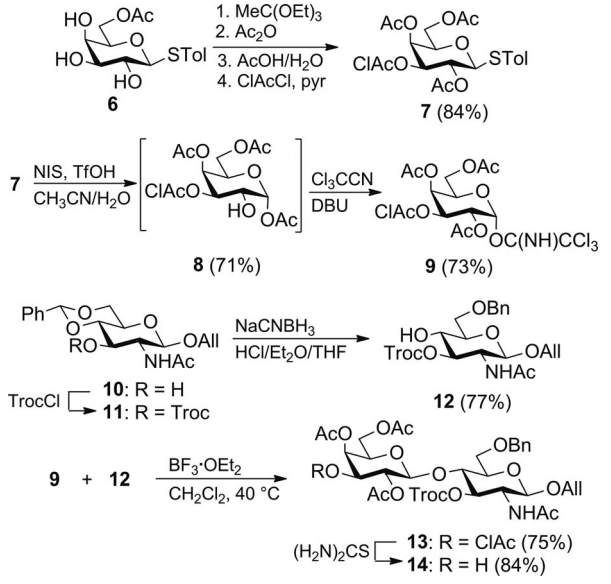
we also report here the preparation of dimLe^x derivatives **4** and **5** to be used as soluble inhibitors for propyl glycoside **4** and hapten in the preparation of glycoconjugates for cysteamine adduct **5**.

Results and Discussion

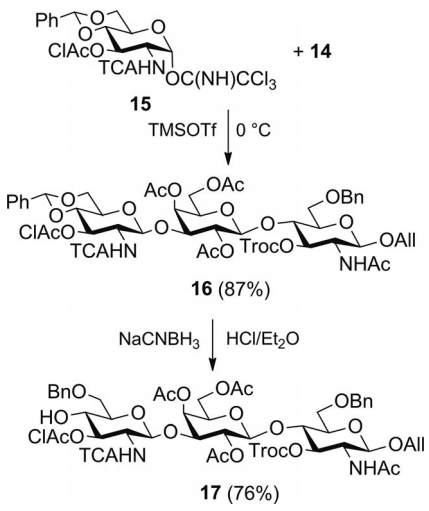
Two general strategies have been used to prepare dimLe^x analogues: a block synthesis[5] involving the coupling of two Le^x trisaccharides usually prepared in a convergent approach, and a linear synthesis[6] that involves the difucosylation of a dilactosamine tetrasaccharide acceptor. Because we aimed at preparing both GlcLe^{x}Le^x analogues **2** and **3** and dimLe^x derivatives **4** and **5** in a convergent synthesis, we prepared trisaccharide **17** as the common intermediate for all four final targets. Trisaccharide **17** was prepared stepwise from monosaccharide building blocks **9**,[7] **12**, and **15**[8] (Schemes 1 and 2). We report an improved synthesis of donor **9** from known[9] thioglycoside **6**. Thus, triol **6** was converted into the corresponding 3,4-orthoacetate, then acetylated at O-2, and the orthoacetate was opened in situ to the corresponding C-4 acetate. The remaining 3-OH was then chloroacetylated to give fully protected intermediate **7** in 84% yield over the four steps (Scheme 1).



Scheme 1.

This represents an improvement over our reported synthesis of **7**, which required five steps (64% overall) from the analogous 3,4-*O*-isopropylidene *p*-thiotolyl galactoside.[7] Thiotolyl galactoside **7** was then converted into trichloroacetimidate donor **9** by using the same conditions as those we have described:[7] hydrolysis of the thioglycoside and conversion of the expected hemiacetal into a trichloroacetimidate. Interestingly, full ^{1}H NMR spectroscopic characterization of the compound formed after hydrolysis revealed that intermediate **8** carried an α-acetate at the anomeric position ($\delta_{1\text{-H}}$ = 6.31 ppm, $J_{1\text{-H},2\text{-H}}$ = 3.8 Hz) and a free equatorial hydroxy group at C-2 ($\delta_{2\text{-H}}$ = 4.22 ppm). We propose that compound **8** resulted from the opening at C-1 of a 1,2-hemiorthoacetate likely formed upon attack of water on the intermediate cyclic acetoxonium ion. We had, indeed, overlooked this migration in our previous study, because when intermediate **8** is treated with DBU and trichloroacetonitrile it promptly undergoes base-catalyzed O-1 to O-2 acetyl migration concurrently to the formation of desired trichloroacetimidate **9** (Scheme 1).

Acceptor **12** was prepared in two steps from known[10] allyl glycoside **10**: treatment with 2,2,2-trichloroethyl chloroformate gave Troc-protected intermediate **11**, which was submitted without purification to the regioselective reductive opening at O-6 of the benzylidene acetal (Scheme 1). It is well known that the hydroxy group at C-4 of *N*-acetylglucosamine is a poor nucleophile and has reduced reactivity towards glycosylation when compared to other acceptors.[11] However, we have reported the efficient glycosylation of such acceptors by using peracetylated trichloroacetimidate donors (5 equiv.) activated at 20–40 °C with $BF_3{\cdot}OEt_2$ (2 equiv.).[12] Thus, acceptor **12** was treated under these conditions with donor **9** (5 equiv.) at 40 °C and desired disaccharide **13** was isolated in 87% yield. Whereas higher yields were achieved when using 5 equiv. of the donor, larger-scale couplings were performed by using only 3 equiv. of high value-added donor **9** and gave **13** in acceptable yield (Scheme 1). Treatment of disaccharide **13** with thiourea gave disaccharide acceptor **14**, which was, in turn, glycosylated with trichloroacetimidate donor **15**[8] under TMSOTf (2.0 equiv.) activation at 0 °C (Scheme 2).

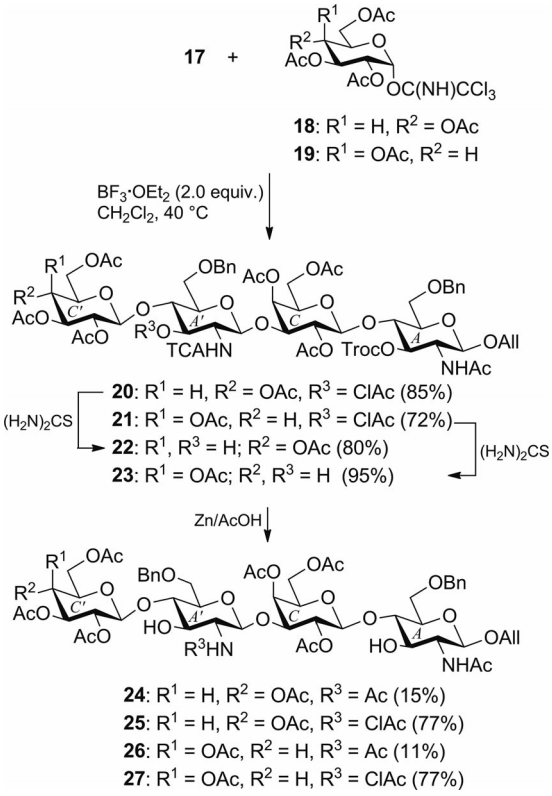


Scheme 2.

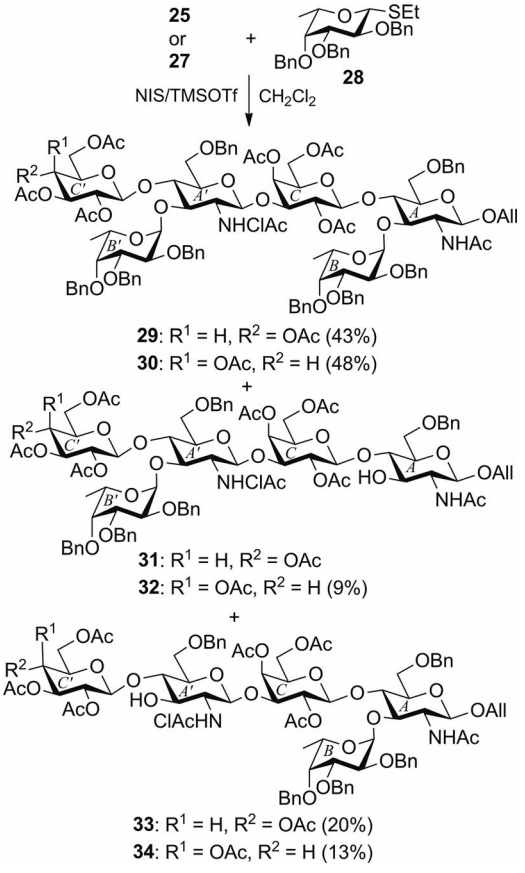
Desired trisaccharide **16** was obtained in 87% yield after precipitation from EtOAc/hexanes (1:1, 54%) and chromatography of the mother liquors (33%). Reductive opening of the benzylidene acetal in **16** gave trisaccharide acceptor **17** free at O-4′′ and precursor to hexasaccharides **2**–**5** (Scheme 3). Trisaccharide acceptor **17** was coupled with the known[13] trichloroacetimidate glucosyl and galactosyl donors **18** and **19** by applying once again the conditions used above for the preparation of disaccharide **13**.[12] Under

these conditions, glucosylation of acceptor **17** with donor **18** gave desired tetrasaccharide **20** in good yields after 45 min of reaction. In contrast, galactosylation of acceptor **17** with donor **19** was difficult to follow by TLC, as degradation products (from donor **19**) co-migrated with acceptor **17**. To ensure maximum conversion into the tetrasaccharide, an additional amount of the donor (1.5 equiv.) was added, and the reaction was left to proceed an additional hour. Under these conditions, desired tetrasaccharide **21** was obtained pure in 72% yield upon purification by flash chromatography and RP-HPLC. Tetrasaccharides **20** and **21** were then treated with an excess amount of thiourea to give acceptors **22** and **23**, respectively, free at O-3 of the nonreducing end glucosamine residue (*A′*). In turn, the simultaneous removal of the Troc group and reduction of the *N*-trichloroacetate to an acetamido in **22** and **23** was attempted by treatment with freshly activated zinc in acetic acid. However, while the trichloroethoxy carbonate groups were quickly removed under these conditions, the conversion of the *N*-trichloroacetyl groups into *N*-acetyl groups was more difficult. For example, extended reaction time, higher temperature (up to 80 °C), and repeated additions of zinc only gave desired *N*-acetylated acceptor **24** in 37% yield, whereas chloroacetamido analogue **25** was obtained in 57% yield. Revising our strategy, we thus decided to use *N*-chloroacetylated analogues **25** and **27** as the acceptors in the fucosylation reactions (Scheme 4) and optimized this reaction to maximize their formation. Thus, tetrasaccharides **22** and **23** were treated with an excess amount of zinc in AcOH at 40 °C for 1 h and diol acceptors **25** and **27** were isolated in 77% yield, whereas chloroacetamido analogues **24** and **26** were isolated in 15 and 11% yield, respectively (Scheme 3).

Difucosylation of diol **25** was first attempted by using known[14] fucosyl donor **28** activated with $CuBr_2$ and tetrabutylammonium bromide; a method that we have applied successfully to the synthesis of various Le^x derivatives.[7,12b] However, no fucosylation was observed under these conditions. Indeed, after an extended reaction time, using up to 4 equiv. of donor and raising the temperature to 35 °C, unreacted acceptor **25** was recovered and no fucosylated product was isolated. Thus, we investigated the activation of donor **28** (4 equiv.) with NIS (5 equiv.) and TMSOTf (0.3 equiv.) while running the reaction at 0 °C for 1 h before quenching with NEt_3. Following workup and purification (CH_2Cl_2/MeOH = 100:1 to 20:1), some unreacted tetrasaccharide **25** was recovered (ca. 20%) and two new products were isolated. These products were identified by NMR spectroscopy and HRMS as hexasaccharide **29** (ca. 10%) and pentasaccharide **31** (ca. 50%). The chemical shifts ($\Delta\delta_{NH}$ = ca. 1 ppm) measured for the NH signals of *N*-acetylated residue *A* and *N*-chloroacetylated residue *A′* were key to determine accurate chemical shifts for 2-H and 3-H of the two residues *A* and *A′*. Thus, fucosylation at O-3 of both glucosamine residues (*A* and *A′*) in hexasaccharide **29** led to a ca. 0.2 ppm downfield shift of both 3*A*-H and 3*A′*-H (Table 1) when compared to these signals in diol acceptor **25**. In pentasaccharide **31**, the nonreducing end



Scheme 3.



Scheme 4.

3A'-H underwent a ca. 0.2 ppm downfield shift when compared to the same signal in acceptor **25**, whereas 3A-H was found at the same chemical shift as that in acceptor **25**.

Table 1. Selected ^{1}H and ^{13}C NMR chemical shifts for compounds **25**, **27**, and **29**–**34**.

Compound	3A-H[a]	3A'-H[a]	C-4A[b]	C-4A'[b]
25	3.90	3.95	81.1[c]	81.3[c]
27	3.90	3.98	81.1[c]	81.4[c]
29	4.07	4.15	73.7[c]	74.8[c]
30	4.08	4.18	73.7[c]	74.3[c]
31	3.92	4.14	81.2	74.8
32	3.90	4.18	81.2	74.2
33	4.10	3.95	73.8	81.4
34	4.10	3.98	73.8[d]	81.4

[a] δ_H in ppm. [b] δ_C in ppm. [c] Assignments C-4A and C-4A' may be reversed. [d] Alternate chemical shift possible: δ = 74.2 or δ = 74.1 ppm.

Interestingly, the chemical shift measured for C-4 of the glucosamine residues (A or A') was greatly affected by the presence or absence of a fucose on the vicinal O-3. As shown in Table 1, C-4A was found at $\delta \approx 81$ ppm when the vicinal OH group was not fucosylated in acceptor **25** or pentasaccharide **31**, whereas the same signal was found at $\delta \approx 74$ ppm upon fucosylation in hexasaccharide **29**. Similarly, C-4A' was found at δ = 81.3 ppm in acceptor **25**, whereas it gave a signal upfield at δ = 74.8 ppm in both hexasaccharide **29** and pentasaccharide **31**. Indeed, this feature was characteristic in all derivatives described here: the C-4 signal of *N*-acylated glucosamine units carrying a free OH at C-3 was found at $\delta \approx 81$ ppm, whereas the C-4 signal in glucosamine residues that were protected (Troc or ClAc) or fucosylated at O-3 was found between δ = 73 ppm and δ = 77 ppm.

Although we did isolate desired hexasaccharide **29** in small amounts, the fact that the major product of this reaction was the pentasaccharide fucosylated at the nonreducing end glucosamine suggested that these conditions were not efficient to promote fucosylation at the hindered 3-OH group of the reducing end glucosamine. Therefore, this reaction was repeated starting at 0 °C with NIS (1.7 equiv.), TMSOTf (0.2 equiv.), and donor **28** (1.5 equiv.) and left to proceed at 0 °C for 1.5 h to allow fucosylation at O-3A'. Additional amount of NIS (4.5 equiv.) and donor (4.5 equiv.) were then added, and the reaction was placed at room temperature for 2 h to promote fucosylation at the less-reactive O-3A. TLC showed the formation of three products that were purified by a combination of flash chromatography and RP-HPLC. These three products were identified as hexasaccharide **29** (ca. 35%), pentasaccharide **33** (ca. 20%), and pentasaccharide **31** (ca. 6%). Fucosylation at the reducing end glucosamine residue (A) in pentasaccharide **33** was confirmed by the chemical shift of 3A-H that underwent a ca. 0.2 ppm downfield shift when compared to the same signal in acceptor **25**. In addition, the chemical shift measured for C-4A was found at δ = 73.8 ppm, whereas that of C-4A' was found at δ = 81.4 ppm (Table 1), indicating that C-3A' carried a free OH group, whereas C-3A did not. The results of these two reactions suggest that at low temperature pentasaccharide **31** was formed first and then slowly fucosylated at O-3A when the temperature was increased, giving hexasaccharide **29**. However, the conditions that were required to complete the fucosylation at O-3A and maximize the yield of desired hexasaccharide **29** led, in turn, to the loss of the fucosyl residue first introduced at O-3A' and gave pentasaccharide **33**. On the basis of observations reported previously by us[3,12a] and others,[15] the poor stability observed for the α-fucosyl unit at O-3 of a glucosamine residue was not surprising. Numerous conditions, varying the temperature, time of reaction, concentration of fucosyl donor, and amounts of NIS and TMSOTf, were investigated to optimize the yield of hexasaccharide **29** while minimizing that of pentasaccharide **33**. In all cases the desired hexasaccharide was never isolated in better than 40–45% yield after multiple purifications on silica gel and RP-HPLC. In our hands, the best results were obtained when the reaction was carried out at room temperature by using 5 and 0.3 equiv. of NIS and TMSOTf, respectively, to activate 4 equiv. of donor **28** for 40 min, then adding an one additional equivalent of donor and allowing the reaction to proceed for another 20 min. Under these reaction conditions, desired hexasaccharide **29** was isolated in 43% yield and pentasaccharide **33** was obtained in 20% yield, whereas no pentasaccharide **31** was recovered.

Galactosylated acceptor **27** was thus submitted to difucosylation at O-3A and O-3A' by applying the optimized conditions described above for the glycosylation of analogue **25**. After RP-HPLC, protected dimeric Le^x hexasaccharide **30** was obtained in 48% yield, and pentasaccharides **32** and **34** were isolated in 9 and 13% yield, respectively. The structure of hexasaccharide **30** and those of pentasaccharides **32** and **34** were confirmed by HRMS and NMR spectroscopy. The position of the fucosyl residues at O-3A' and O-3A in pentasaccharides **32** and **34**, respectively, was confirmed by looking at the chemical shifts measured for 3A-H and 3A'-H as well as that of C-4A and C-4A' as described above for the characterization of pentasaccharides **31** and **33** (Table 1). It is interesting to notice that, in contrast to the results obtained with fucosylating acceptor **25**, not all pentasaccharide **32** was converted into hexasaccharide **30** and then further degraded to pentasaccharide **34**. Although difficult to rationalize, this observation suggests an overall lower reactivity of acceptors **27** and **32** towards fucosylation and degradation when compared to that of acceptors **25** and **31**.

Even though protected hexasaccharides **29** and **30** were obtained in rather moderate yield, enough material was isolated in both cases to allow the preparation of GlcLe^{x}Le^x analogues **2** and **3** and dimLe^x derivatives **4** and **5**. The syntheses of propyl GlcLe^{x}Le^x (**2**) and dimLe^x (**4**) were accomplished in two steps: (1) Reduction of the allyl group (H_2, 10% Pd/C) to a propyl group. (2) Full deprotection/reduction under dissolving-metal reduction conditions [Na/$NH_{3(l)}$ –78 °C, in THF]. Indeed, dissolving-metal conditions were shown to efficiently and concurrently remove protecting groups such as benzyl, benzylidene, acyl, and tri-

chloroacetamido and also reduce azido groups to amino groups.[3,7,16] After such reactions, GlcLe^{x}Le^x propyl glycoside (**2**) and dimLe^x propyl glycoside (**4**) were purified by size-exclusion chromatography on a Biogel P2 column and obtained pure in 71 and 65% yield, respectively. Fortunately, these Birch reduction conditions led to the reduction of the *N*-chloroacetates to *N*-acetates, rather than to their transamidation leading to free amines that would require re-acetylation. Thus, we could follow a similar one-step deprotection strategy to prepare free amine analogues **3** and **5** from protected analogues **29** and **30**. UV-promoted addition of cysteamine hydrochloride to allyl hexasaccharides **29** and **30** afforded the corresponding protected 3-(2-aminoethylthio)propyl glycosides, which were obtained free of excess cysteamine by washing with 1 M NaOH. The crude adducts were then submitted to metal-dissolving deprotection to fully remove all protecting groups and reduce the chloroacetamido groups. To prevent adsorption on the Biogel support, adducts **3** and **5** were purified on a P2 column eluted with 0.1 M aqueous ammonium acetate and repeated freeze-drying from water provided the acetate salts of analogues **3** and **5** in 75 and 65% yield, respectively, over the two steps.

Conclusions

The synthetic strategy adopted in this work was shown to be efficient to prepare dimLe^x derivatives **4** and **5** and closely related new GlcLe^{x}Le^x analogues **2** and **3**, which carry a glucose residue at the nonreducing end replacing the galactose unit present in the naturally occurring TACA. Our stepwise preparation of the tetrasaccharide backbones by using an excess amount of the cheaper monosaccharide glycosyl donors was shown to produce the desired compounds in excellent overall yields. The tetrasaccharides were then converted into diol acceptors ready for difucosylation at O-3 of both glucosamine residues. Characterization of the fucosylated products by NMR spectroscopy showed that all fucosylations proceeded stereoselectively to give α-fucosidic linkages. However, difucosylations proved to be challenging reactions due to the difference in reactivities of the two glucosamine hydroxy groups at the 3-position. Our results suggest that fucosylation at the nonreducing *A′* ring happened first followed by fucosylation of the reducing end *A* glucosamine, which occurred slowly. Thus, despite the presence of an electron-withdrawing *N*-chloroacetate at the nonreducing end glucosamine residue (*A′*), this residue was more rapidly fucosylated than the reducing end *N*-acetylated glucosamine unit. We propose that steric hindrance around the hydroxy group at C-3 of the reducing end glucosamine residue (*A*) reduced its reactivity toward fucosylation when compared to that of the nonreducing end glucosamine unit. The conditions that most efficiently led to desired hexasaccharides **29** and **30** in usable yields also led to some loss of the more labile nonreducing end fucosyl residue (*B′*) that had been introduced first. Interestingly, it appears that the presence or absence of substituents (protecting groups or sugar residue) at C-3 of the glucosamine residues has a large impact on the chemical shifts measured for the vicinal C-4 carbon atoms in the ^{13}C NMR spectra. This signal was found at $\delta \approx 80$–81 ppm for 3-OH analogues, whereas it was found between $\delta = 75$ ppm and $\delta = 77$ ppm in the 3 *O*-substituted derivatives. Hexasaccharides **29** and **30** were, in turn, easily and efficiently converted into final target analogues **2**–**5**. The allyl aglycones were either hydrogenated to propyl glycosides or submitted to addition of cysteamine hydrochloride, and the resulting intermediates were submitted without further purification to full deprotection and reduction of the *N*-chloroacetate by using metal-dissolving reduction conditions. From the protected hexasaccharides, propyl hexasaccharides **2** and **4** were obtained in 71 and 65%, respectively, and cysteamine adducts **3** and **5** were isolated in 75 and 65% yield, respectively. Thus, we have established an efficient convergent synthesis of new GlcLe^{x}Le^x hexasaccharide analogues **2** and **3** as well as that of dimLe^x analogues **4** and **5**, which were all obtained in a very acceptable ca. 7% overall yield from the protected monosaccharide building blocks by using trisaccharide **7** as a common intermediate for all final targets.

Experimental Section

General: ^{1}H NMR (400.13 and 600.13 MHz) and ^{13}C NMR (100.6 and 150.9 MHz) spectra were recorded in $CDCl_3$ (internal standard, for ^{1}H residual $CHCl_3$ $\delta_H = 7.24$ ppm; for ^{13}C: $CDCl_3$ $\delta_C = 77.0$ ppm), CD_3OD (internal standard, for ^{1}H residual CH_3OD $\delta_H = 3.30$ ppm; for ^{13}C: CD_3OD $\delta_C = 49.0$ ppm), D_2O (external standard, sodium 2,2-dimethyl-2-silapentane-5-sulfonate, DSS, δ_H and $\delta_C = 0.0$ ppm), or [D$_6$]DMSO (internal standard, for ^{1}H residual Me_2SO $\delta_H = 2.49$ ppm; for ^{13}C: [D$_6$]DMSO $\delta_C = 39.5$ ppm). Coupling constants (*J*) were obtained from first-order analysis of 1D spectra. Assignments of proton and carbon resonances were based on 2D ^{1}H–^{1}H COSY and ^{13}C–^{1}H HSQC correlation experiments as well as 1D TOCSY experiments. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). Analytical thin-layer chromatography (TLC) was performed by using silica gel 60 F_{254} precoated plates (250 μm) with visualization under UV light and/or charring with 10% H_2SO_4 in EtOH. Flash chromatography was performed by using silica gel 60 (230–400 mesh) from EM science. All reactions were carried out under a nitrogen atmosphere with anhydrous freshly distilled solvents unless otherwise noted. Solvents were distilled and dried according to standard procedures,[17] and organic solutions were dried with Na_2SO_4 and concentrated under reduced pressure. Molecular sieves were activated by flame drying under reduced pressure. All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Reverse-phase HPLC purifications were carried out with Prep Nova Pak HR C18, 6 μm 60 Å columns by using mixtures of acetonitrile and water as eluent. Purifications by gel permeation chromatography were carried out with a Biogel P2 column (95 cm × 1.5 cm) eluted with water unless otherwise stated. UV irradiation was accomplished with a Rayonet photochemical reactor. Optical rotations were measured at 298 K and are uncorrected. Purity and structure of all new compounds were confirmed by NMR (see Supporting Information) and HRMS. HRESI mass spectra were recorded by the analytical services of the McMaster Regional Center for Mass Spectrometry, Hamilton, Ontario.

Propyl 2-Acetamido-2-deoxy-3-*O*-(α-L-fucopyranosyl)-4-*O*-{3-*O*-[2-acetamido-2-deoxy-3-*O*-(α-L-fucopyranosyl)-4-*O*-(β-D-gluco-

pyranosyl)-β-D-glucopyranosyl]-β-D-galactopyranosyl}-β-D-glucopyranoside (2): To a solution of hexasaccharide **29** (29 mg, 0.014 mmol) dissolved in MeOH (1 mL) was added 10% Pd/C (13 mg), and the mixture was stirred under an atmosphere of H_2. After 18 h, the reaction mixture was filtered, the solids were washed with MeOH (5 × 10 mL), and the filtrate was concentrated to give the crude propyl hexasaccharide. A solution of the crude hexasaccharide in THF (5 mL) was added at –78 °C to a solution of liquid NH_3 (ca. 20 mL) containing Na (60 mg, 2.6 mmol, 186 equiv.). After 1 h at –78 °C, the reaction was quenched with MeOH (10 mL), and ammonia was allowed to evaporate at room temperature. The remaining solution was neutralized with AcOH (202 μL, ca. 1.1 equiv. to Na) and the solvent was evaporated. The resulting solid was dissolved in water and passed through a Biogel P2 column eluted with H_2O. After freeze-drying, propyl glycoside **2** (11 mg, 71%) was obtained pure as a white amorphous powder. $[\alpha]_D$ = –52 (c = 0.5, H_2O). ^{1}H NMR (600 MHz, D_2O, 295 K): δ = 5.13 (d, J = 4.0 Hz, 1 H, 1B′-H), 5.09 (d, J = 4.0 Hz, 1 H, 1B-H), 4.81 (m, 1 H, 5B-H), 4.74 (m, 1 H, 5B′-H), 4.69 (d, J = 8.5 Hz, 1 H, 1A′-H), 4.53 (d, J = 7.9 Hz, 2 H, 1A-H, 1C′-H), 4.42 (d, J = 7.9 Hz, 1 H, 1C-H), 4.09 (d, J = 3.4 Hz, 1 H, 4C-H), 4.00–3.92 (m, 5 H, 6Aa-H, 2A′-H, 4A′-H, 6Aa′-H, 6Cb′-H), 3.91–3.80 (m, 9 H, 2A-H, 3A-H, 4A-H, 6Ab-H, 3B-H, 3A′-H, 6Ab′-H, 3B′-H, OC*H*HCH$_2$CH$_3$), 3.76 (br. s, 2 H, 4B-H, 4B′-H), 3.74–3.65 (m, 5 H, 2B-H, 3C-H, 6Cab-H, 2B′-H), 3.60–3.52 (m, 5 H, 5A-H, 5C-H, 5A′-H, 6ca′-H, OC*H*HCH$_2$CH$_3$), 3.48 (t, J = 9.2 Hz, 2 H, 2C-H, 3C′-H), 3.42 (m, 1 H, 5C′-H), 3.22–3.16 (m, 2 H, 2C′-H, 4C′-H), 2.02, 2.01 (2 s, 6 H, 2 COCH$_3$), 1.54 (m, 2 H, OCH$_2$C*H*$_2$CH$_3$), 1.17 (d, J = 6.7 Hz, 3 H, 6B′-H), 1.14 (d, J = 6.6 Hz, 3 H, 6B-H), 0.86 (t, J = 7.5 Hz, 3 H, OCH$_2$CH$_2$C*H*$_3$) ppm. ^{13}C NMR (150 MHz, D_2O, 295 K): δ = 174.6, 174.3 (C=O), 102.5 (C-1A′), 101.7 (C-1C), 101.2 (C-1C′), 100.8 (C-1A), 98.7 (C-1B, C-1B′), 81.6 (C-3C), 76.0 (C-5C′), 75.4 (C-3C′), 75.3, 75.0, 74.9, 74.4 (C-3A,C-5A, C-5C, C-3A′, C-5A′), 73.6 (C-4C′), 73.3, 73.0 (C-4A, C-4A′), 72.4 (OC*H*$_2$CH$_2$CH$_3$), 71.9, 71.8 (C-4B, C-4B′), 70.4 (C-2C, C-2C′), 69.2, 69.1 (C-3B, C-3B′), 68.2 (C-4C), 67.6 (C-2B, C-2B′), 66.6, 66.4 (C-5B, C-5B′), 61.6, 61.4, (C-6C, C-6C′), 59.7, 59.5 (C-6A,C-6A′), 55.9 (C-2A, C-2A′), 22.2 (OCH$_2$*C*H$_2$CH$_3$), 22.1, 22.0 (CO*C*H$_3$), 15.3, 15.2 (C-6B, C-6B′), 9.5 (OCH$_2$CH$_2$*C*H$_3$) ppm. HRMS: calcd. for $C_{43}H_{74}N_2O_{29}$ [M + H]$^+$ 1083.4456; found 1083.4485.

Aminoethylthiopropyl 2-Acetamido-2-deoxy-3-*O*-(α-L-fucopyranosyl)-4-*O*-{3-*O*-[2-acetamido-2-deoxy-3-*O*-(α-L-fucopyranosyl)-4-*O*-(β-D-glucopyranosyl)-β-D-glucopyranosyl]-β-D-galactopyranosyl}-β-D-glucopyranoside (3): MeOH (600 μL) and 2-aminoethanethiol hydrochloride (94 mg, 0.86 mmol, 45 equiv.) were added to a solution of allyl glycoside **29** (39 mg, 0.018 mmol) dissolved in a minimum amount of CH_2Cl_2 (200 μL) and placed into a quartz tube. The mixture was stirred until full dissolution and irradiated by UV light for 90 min. The solution was then diluted with $CHCl_3$ (50 mL) and washed with 1 M NaOH (5 × 50 mL). The aqueous layers were re-extracted with $CHCl_3$ (50 mL), and the organic layers were combined, dried, filtered, and concentrated to give the crude cysteamine adduct (39 mg). A solution of this adduct in THF (5 mL) was added at –78 °C to a solution of liquid NH_3 (ca. 20 mL) containing Na (60 mg, 2.6 mmol, 145 equiv.). After 50 min at –78 °C, the reaction was quenched with MeOH (10 mL), and the ammonia was allowed to evaporate at room temperature. The remaining solution was neutralized with AcOH (260 μL, ca. 1.1 equiv. to Na), and the solvent was evaporated. The resulting solid was dissolved in 0.1 M ammonium acetate solution and was passed through a Biogel P2 column eluted with 0.1 M ammonium acetate. The fractions containing hexasaccharide **3** were combined and lyophilized, and the resulting powder was freeze-dried from water an additional two times to remove the excess amount of ammonium acetate. The ammonium salt of cysteamine adduct **3** (15 mg, 75%) was obtained pure as a white solid. $[\alpha]_D$ = –62 (c = 0.5, H_2O). ^{1}H NMR (600 MHz, D_2O, 295 K): δ = 5.12 (d, J = 4.0 Hz, 1 H, 1B′-H), 5.08 (d, J = 4.0 Hz, 1 H, 1B-H), 4.81 (m, 1 H, 5B-H), 4.75 (m, 1 H, 5B′-H), 4.69 (d, J = 8.4 Hz, 1 H, 1A′-H), 4.52 (m, 2 H, 1A-H, 1C′-H), 4.42 (d, J = 7.9 Hz, 1 H, 1C-H), 4.09 (d, J = 3.4 Hz, 1 H, 4C-H), 4.00–3.91 (m, 6 H, 6aA-H, 2A′-H, 4A′-H, 6Aa′-H, 6bC′-H, OC*H*HCH$_2$), 3.91–3.79 (m, 8 H, 2A-H, 3A-H, 4A-H, 6Ab-H, 3B-H, 3A′-H, 6Ab′-H, 3B′-H), 4.76 (br. s, 2 H, 4B-H, 4B′-H), 3.72–3.64 (m, 5 H, 2B-H, 3C-H, 6abC-H, 2B′-H), 3.60–3.54 (m, 5 H, 5A-H, 5C-H, 5A′-H, 6Ca′-H, OC*H*HCH$_2$), 3.50 (t, J = 8.9 Hz, 2 H, 2C-H, 3C′-H), 3.42 (m, 1 H, 5C′-H), 3.22–3.17 (m, 4 H, 2C′-H, 4C′-H, SCH$_2$C*H*$_2$N), 2.83 (m, 2 H, SC*H*$_2$CH$_2$N), 2.60 (m, 2 H, OCH$_2$CH$_2$C*H*$_2$S), 2.03, 2.01 (2 s, 6 H, 2 COCH$_3$), 1.84 (m, 2 H, OCH$_2$C*H*$_2$CH$_2$S), 1.17 (d, J = 6.7 Hz, 3 H, 6B′-H), 1.14 (d, J = 6.6 Hz, 3 H, 6B-H) ppm. ^{13}C NMR (150 MHz, D_2O, 295 K): δ = 174.6, 174.2 (C=O), 102.5 (C-1A′), 101.7 (C-1C), 101.2 (C-1A), 101.0 (C-1C′), 98.7 (C-1B, C-1B′), 81.6 (C-3C), 76.0 (C-5C′), 75.4 (C-3C′), 75.3, 75.0, 74.9, 74.8, 74.4 (C-3A, C-5A, C-5C, C-3A′, C-5A′), 73.6 (C-4C′), 73.3, 73.0 (C-4A, C-4A′), 71.9, 71.8 (C-4B, C-4B′), 70.4 (C-2C, C-4C′), 69.2, 69.1 (C-3B, C-3B′), 68.6 (O*C*H$_2$CH$_2$), 68.2 (C-4C), 67.6 (C-2B, C-2 B′), 66.7, 66.4 (C-5B, C-5B′), 61.6, 61.4, (C-6C, C-6C′), 59.7, 59.5 (C-6A, C-6A′), 55.9 (C-2A, C-2A′), 38.2 (SCH$_2$*C*H$_2$N), 28.4 (OCH$_2$*C*H$_2$CH$_2$S), 28.1 (S*C*H$_2$CH$_2$N), 26.9 (OCH$_2$CH$_2$*C*H$_2$S), 22.2 (CO*C*H$_3$), 15.3, 15.2 (C-6B, C-6B′) ppm. HRMS: calcd. for $C_{45}H_{79}N_3O_{29}S$ [M + H]$^+$ 1158.1800; found 1158.4637.

Propyl 2-Acetamido-2-deoxy-3-*O*-(α-L-fucopyranosyl)-4-*O*-{3-*O*-[2-acetamido-2-deoxy-3-*O*-(α-L-fucopyranosyl)-4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranosyl]-β-D-galactopyranosyl}-β-D-glucopyranoside (4): Reduction of the allyl aglycon and deprotection of hexasaccharide **30** (21 mg, 0.01 mmol) to give analogue **4** was carried out as described for the preparation of compound **2** from hexasaccharide **29**. After freeze-drying, propyl glycoside **4** (7 mg, 65%) was obtained pure as an amorphous white solid. $[\alpha]_D$ = –59 (c = 0.5, H_2O). ^{1}H NMR (600 MHz, D_2O, 295 K): δ = 5.13 (d, J = 4.0 Hz, 1 H, 1B′-H), 5.09 (d, J = 4.0 Hz, 1 H, 1B-H), 4.82 (m, 2 H, 5B-H, 5B′-H), 4.69 (d, J = 8.5 Hz, 1 H, 1A′-H), 4.53 (br. d, J = 8.2 Hz, 1 H, 1A-H), 4.46 (d, J = 7.9 Hz, 1 H, 1C′-H), 4.43 (d, J = 7.9 Hz, 1 H, 1C-H), 4.09 (d, J = 3.3 Hz, 1 H, 4C-H), 3.99–3.92 (m, 4 H, 6Aa-H, 2A′-H, 4A′-H, 6Aa′-H), 3.92–3.81 (m, 10 H, 2A-H, 3A-H, 4A-H, 6Ab-H, 3B-H, 3A′-H, 6Ab′-H, 3B′-H, 4C′-H, OC*H*HCH$_2$CH$_3$), 3.78 (br. d, J = 3.8 Hz, 1 H, 4B′-H), 3.76 (br. d, J = 3.8 Hz, 1 H, 4B-H), 3.75–3.66 (m, 7 H, 2B-H, 3C-H, 6Cab-H, 2B′-H, 6Cab′-H), 3.64 (dd, J = 9.9, 3.4 Hz, 1 H, 3C′-H), 3.61–3.52 (m, 4 H, 5A-H, 5C-H, 5A′-H, 5C′-H, OC*H*HCH$_2$CH$_3$), 3.49 (m, 2 H, 2C-H, 2C′-H), 2.02 (s, 6 H, 2 COCH$_3$), 1.54 (m, 2 H, OCH$_2$C*H*$_2$CH$_3$), 1.16 (d, 3 H, J = 6.7 Hz, 6B′-H), 1.14 (d, J = 6.7 Hz, 3 H, 6B-H), 0.86 (t, J = 7.4 Hz, 3 H, OCH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (150 MHz, D_2O, 295 K): δ = 174.6, 174.3 (C=O), 102.5 (C-1A′), 101.7 (C-1C, C-1C′), 100.9 (C-1A), 98.7 (C-1B), 98.5 (C-1B′), 81.5 (C-3C), 75.3, 75.0, 74.9, 74.7, 74.4 (C-3A, C-5A, C-5C, C-3A′, C-5A′, C-5C′), 73.0, 72.9 (C-4A, C-4A′), 72.4 (C-3C′), 72.3 (O*C*H$_2$CH$_2$CH$_3$), 71.8 (C-4B, C-4B′), 71.0, 70.5 (C-2C, C-2C′), 69.1 (C-3B, C-3B′), 68.3, 68.2 (C-4C, C-4C′), 67.6 (C-2B, C-2B′), 66.6 (C-5B, C-5B′), 61.5, 61.4 (C-6C, C-6C′), 59.7, 59.5 (C-6A, C-6A′), 55.9 (C-2A, C-2A′), 22.1 (CO*C*H$_3$), 22.0 (OCH$_2$*C*H$_2$CH$_3$), 15.2 (C-6B, C-6B′), 9.5 (OCH$_2$CH$_2$*C*H$_3$) ppm. HRMS: calcd. for $C_{43}H_{74}N_2O_{29}$ [M + Na]$^+$ 1105.4275; found 1105.4281.

Aminoethylthiopropyl 2-Acetamido-2-deoxy-3-*O*-(α-L-fucopyranosyl)-4-*O*-{3-*O*-[2-acetamido-2-deoxy-3-*O*-(α-L-fucopyranosyl)-4-*O*-

(β-D-galactopyranosyl)-β-D-glucopyranosyl]-β-D-galactopyranosyl}-β-D-glucopyranoside (5): Cysteamine addition and deprotection of hexasaccharide **30** (23 mg, 0.011 mmol) to give analogue **5** was carried out as described for the preparation of compound **3** from hexasaccharide **29**. After freeze-drying, cysteamine adduct **5** (8 mg, 65%) was obtained pure as an amorphous white solid. $[\alpha]_D$ = –54 (c = 0.5, H_2O). ^1H NMR (600 MHz, D_2O, 295 K): δ = 5.12 (d, J = 4.0 Hz, 1 H, 1B′-H), 5.09 (d, J = 3.9 Hz, 1 H, 1B-H), 4.81 (m, 2 H, 5B-H, 5B′-H), 4.69 (d, J = 8.4 Hz, 1 H, 1A′-H), 4.52 (br. d, J = 8.2 Hz, 1 H, 1A-H), 4.45 (d, J = 7.8 Hz, 1 H, 1C′-H), 4.42 (d, J = 7.9 Hz, 1 H, 1C-H), 4.09 (d, J = 3.3 Hz, 1 H, 4C-H), 4.04–3.91 (m, 5 H, 6Aa-H, 2A′-H, 4A′-H, H6Aa′, OC*H*HCH$_2$), 3.91–3.80 (m, 9 H, 2A-H, 3A-H, 4A-H, 6Ab-H, 3B-H, 3A′-H, 6Ab′-H, 3B′-H, 4C′-H), 3.78 (d, J = 2.9 Hz, 1 H, 4B′-H), 3.76 (d, J = 2.4 Hz, 1 H, 4B-H), 3.75–3.66 (m, 8 H, 2B-H, 3C-H, 6Cab-H, 2B′-H, 6Cab′-H, OC*H*HCH$_2$), 3.64 (dd, J = 9.9, 3.4 Hz, 1 H, 3C′-H), 3.61–3.54 (m, 4 H, 5A-H, 5C-H, 5A′-H, 5C′-H), 3.49 (m, 2 H, 2C-H, 2C′-H), 3.20 (t, J = 6.7 Hz, 2 H, SCH$_2$C*H*$_2$N), 2.83 (m, 2 H, SC*H*$_2$CH$_2$N), 2.60 (m, 2 H, OCH$_2$CH$_2$C*H*$_2$S), 2.03, 2.01 (2 s, 6 H, 2 COCH$_3$), 1.84 (m, 2 H, OCH$_2$C*H*$_2$CH$_2$S), 1.17 (d, J = 6.7 Hz, 3 H, 6B′-H), 1.14 (d, J = 6.7 Hz, 3 H, 6B-H) ppm. ^{13}C NMR (150 MHz, D_2O, 295 K): δ = 174.6, 174.2 (C=O), 102.4 (C-1A′), 101.7 (C-1C, C-1C′), 101.0 (C-1A), 98.7 (C-1B), 98.5 (C-1B′), 81.6 (C-3C), 75.3, 75.0, 74.8, 74.7, 74.4 (C-3A, C-5A, C-5C, C-3A′, C-5A′, C-5C′), 72.9 (C-4A, C-4A′), 72.4 (C-3C′), 71.8 (C-3B, C-3B′), 71.0 (C-2C, C-2C′), 69.1 (C-3B, C-3B′), 68.6 (O*C*H$_2$CH$_2$), 68.3, 68.2 (C-4C, C-4C′), 67.6, 67.5 (C-2B, C-2B′), 66.6 (C-5B, C-5B′), 61.5 (C-6C, C-6C′), 59.7, 59.5 (C-6A, C-6A′), 55.9 (C-2A, C-2A′), 38.2 (SCH$_2$*C*H$_2$N), 28.4 (OCH$_2$*C*H$_2$CH$_2$S), 28.1 (S*C*H$_2$CH$_2$N), 26.9 (OCH$_2$CH$_2$*C*H$_2$S), 22.2 (CO*C*H$_3$), 15.2 (C-6B, C-6B′) ppm. HRMS: calcd. for $C_{45}H_{79}N_3O_{29}S$ [M + H]$^+$ 1158.1800; found 1158.4630.

2,4,6-Tri-*O*-acetyl-3-*O*-chloroacetyl-α-D-galactopyranosyl trichloroacetimidate (9): Triethylorthoacetate (17.9 mL, 100 mmol, 4.0 equiv.) and CSA (1.1 g, 0.16 equiv.) were added to a solution of known[9] triol **6** (8.0 g, 24.4 mmol) in anhydrous MeCN (400 mL) under an atmosphere of N_2. The solution was stirred at room temperature for 30 min, pyridine (96 mL) and Ac_2O (56 mL) were then added, and the mixture was stirred 2 h at 50 °C. The mixture was co-concentrated with toluene (4 × 100 mL), and the resulting oily residue was left under high vacuum overnight. It was dissolved in a mixture of AcOH (76 mL) and H_2O (19 mL), and the mixture was stirred for 10 min, then poured into sat. aq. $NaHCO_3$ (200 mL). The solution was extracted with CH_2Cl_2 (3 × 100 mL), and the combined organic layers were dried, filtered, and concentrated to give the corresponding triacetate (8.6 g, 86% from **6**) as a white amorphous powder. Chloroacetyl chloride (4.0 mL, 2.0 equiv.) was added to a mixture of the triacetate in anhydrous CH_2Cl_2 (245 mL) and pyridine (10.0 mL, 5.0 equiv.) at 0 °C. The reaction mixture was stirred for 15 min, the solvent were evaporated, and the residue was co-concentrated with toluene (2 × 50 mL). The resulting residue was dissolved in CH_2Cl_2 (400 mL) and washed sequentially with 8% HCl (200 mL), sat. aq. $NaHCO_3$ (200 mL), and brine (200 mL). The combined organic layers were dried, filtered, and concentrated to give chloroacetate **7** (10.1 g, 98%) as a white amorphous powder. NIS (6.4 g, 1.1 equiv.) and TfOH (0.40 mL, 0.2 equiv.) were added to a solution of chloroacetate **7** (10.1 g, 20.9 mmol) in a mixture of MeCN (300 mL) and H_2O (3 mL) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C, the reaction was quenched with Et_3N (0.52 mL, 3.7 mmol), and the solvents were evaporated. The residue was dissolved in CH_2Cl_2 (300 mL) and was washed with a 20% w/w solution of aq. $Na_2S_2O_3$ (100 mL). The organic layer was dried, filtered, and concentrated. Flash chromatography of the residue (EtOAc/hexanes = 1:1) gave alcohol **8** (6.6 g, 71%) pure as a colorless glass. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.31 (d, J = 3.8 Hz, 1 H, 1-H), 5.47 (d, J = 3.4 Hz, 1 H, 4-H), 5.26 (dd, J = 10.5, 3.3 Hz, 1 H, 3-H), 4.31 (t, J = 9.2 Hz, 1 H, 5-H), 4.22 (dd, J = 10.6, 4.0 Hz, 1 H, 2-H), 4.13–4.05 (m, 4 H, 6ab-H, CH_2Cl), 2.19, 2.15, 2.04 (3s, 9 H, 3 COCH$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 170.3, 169.4, 167.1 (C=O), 91.8 (C-1), 72.1 (C-3), 68.5 (C-5), 67.2 (C-4), 65.7 (C-2), 61.1 (C-6), 40.4 (CH_2Cl), 20.9, 20.6 (CO*C*H$_3$) ppm. Trichloroacetonitrile (10.4 mL, 6.1 equiv.) and DBU (1.0 mL, 0.4 equiv.) were added a solution of alcohol **8** (6.6 g, 17.3 mmol) in anhydrous CH_2Cl_2 (90 mL) at room temperature under an atmosphere of N_2. The reaction was stirred at room temperature for 1 h, the solvent was evaporated, and flash chromatography of the residue (EtOAc/hexanes = 4:6 with 0.1% Et_3N) gave trichloroacetimidate **9** as a yellow amorphous powder (6.6 g, 73%). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.66 (s, 1 H, NH), 6.59 (d, J = 3.6 Hz, 1 H, 1-H), 5.53 (d, J = 3.2 Hz, 1 H, 4-H), 5.47 (dd, J = 10.8, 3.2 Hz, 1 H, 3-H), 5.38 (dd, J = 10.8, 3.6 Hz, 1 H, 2-H), 4.42 (t, J = 6.7 Hz, 1 H, 5-H), 4.15 (dd, J = 11.3, 6.7 Hz, 1 H, 6a-H), 4.07 (dd, J = 11.3, 6.7 Hz, 1 H, 6b-H), 3.97 (s, 2 H, ClCH$_2$CO), 2.14, 2.00 (2 s, 6 H, 2 COCH$_3$) ppm. The NMR spectroscopic data are in agreement with those reported previously.[7]

Allyl 2-Acetamido-6-*O*-benzyl-2-deoxy-3-*O*-trichloroethyloxylcarbonyl-β-D-glucopyranoside (12): A solution of known[10] alcohol **10** (1.8 g, 5.16 mmol) in pyridine (40 mL) was cooled to 0 °C under an atmosphere of N_2. 2,2,2-Trichloroethyl chloroformate (1.2 mL, 8.98 mmol, 1.7 equiv.) was added slowly to the stirred mixture over 15 min, and the mixture was allowed to warm up slowly to room temperature and was stirred for 2 h. The mixture was co-concentrated with toluene (2 × 100 mL), and the crude residue containing benzylidene acetal **11** was dried under high vacuum overnight and dissolved in anhydrous THF (90 mL). Activated 3 Å molecular sieves (4.5 g), $NaCNBH_3$ (3.2 g, 51 mmol, 10 equiv.), and methyl orange indicator were added, and the mixture was stirred for 2 h under an atmosphere of N_2 and cooled to 0 °C. A 2 M solution of HCl in Et_2O (ca. 20 mL) was added dropwise to the reaction mixture at 0 °C until the methyl orange indicator turned pink, remained as such for 10 min, and H_2(g) was no longer generated. The reaction mixture was stirred for 1 h at room temperature and filtered through Celite, and the solids were washed with THF; the pooled filtrate and washings were concentrated. Flash chromatography (CH_2Cl_2/MeOH = 50:1) of the crude residue gave alcohol **12** (2.07 g, 77%) pure as a colorless glass. $[\alpha]_D$ = –33 (c = 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.25 (m, 5 H, Ar), 5.86–5.78 (m, 2 H, NH, C*H*=CH$_2$), 5.24 (m, 2 H, CH=C*H*$_2$), 5.17 (t, J = 10.0 Hz, 1 H, 3-H), 4.83 (d, J = 11.9 Hz, 1 H, C*H*HCCl$_3$), 4.78 (d, J = 8.2 Hz, 1 H, 1-H), 4.67 (d, J = 11.9 Hz, 1 H, C*H*HCCl$_3$), 4.56 (2d, J = 12.0 Hz, 2 H, C*H*$_2$Ph), 4.31 (m, 1 H, C*H*HCH=CH$_2$), 4.04 (m, 1 H, C*H*HCH=CH$_2$), 3.80–3.63 (m, 4 H, 2-H, 4-H, 6ab-H), 3.57 (m, 1 H, 5-H), 3.19 (br. d, J = 3.2 Hz, 1 H, OH), 1.90 (s, 3 H, COCH$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 154.5 (C=O), 137.5 (quat. Ar), 133.6 (CH$_2$=*C*H), 128.5, 127.9, 127.7 (Ar), 117.6 (*C*H$_2$=CH), 99.2 (C-1), 94.4 (CCl_3), 79.7 (C-3), 76.9 (*C*H$_2$CCl$_3$), 73.7 (*C*H$_2$Ph), 73.6 (C-5), 70.8 (C-4), 70.1 (*C*H$_2$CH=CH$_2$), 69.9 (C-6), 55.0 (C-2), 23.4 (CO*C*H$_3$) ppm. HRMS: calcd. for $C_{21}H_{26}Cl_3NO_8$ [M + H]$^+$ 526.0802; found 526.0756.

Allyl 2-Acetamido-4-*O*-(2,4,6-tri-*O*-acetyl-3-*O*-chloroacetyl-β-D-galactopyranosyl)-6-*O*-benzyl-2-deoxy-3-*O*-trichloroethyloxylcarbonyl-β-D-glucopyranoside (13): A stirred solution of alcohol **12** (680 mg, 1.29 mmol) and galactosyl trichloroacetimidate **9** (2.10 g, 3.08 mmol, 3.1 equiv.) in CH_2Cl_2 (62 mL) was warmed up to 40 °C in a round-bottomed flask equipped with drying tube containing

Drierite. $BF_3{\cdot}OEt_2$ (325 μL, 2.0 equiv.) was added to the mixture, which was stirred for 1 h at 40 °C. More donor **9** (0.10 g, 0.19 mmol, 0.15 equiv.) was added, and the reaction was left to proceed for an additional 30 min. The reaction was quenched with Et_3N (430 μL) and diluted with CH_2Cl_2 (50 mL). The mixture was washed with sat. aq. $NaHCO_3$ (50 mL), the aqueous layer was re-extracted with CH_2Cl_2 (2 × 20 mL), and the combined organic layers were dried, filtered, and concentrated. Column chromatography (EtOAc/hexanes = 45:55 → 70:30) of the residue gave disaccharide **13** (860 mg, 75%) pure as a colorless glass. $[\alpha]_D$ = +5 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42–7.22 (m, 5 H, Ar), 5.85 (m, 1 H, C*H*=CH), 5.77 (d, *J* = 8.5 Hz, 1 H, NH), 5.29–5.14 (m, 4 H, 3-H, 4′-H, CH_2=CH), 5.04 (dd, *J* = 10.4, 8.0 Hz, 1 H, 2′-H), 4.92 (d, *J* = 11.8 Hz, 1 H, C*H*HCCl$_3$), 4.88 (dd, *J* = 10.4, 3.5 Hz, 1 H, 3′-H), 4.75 (m, 2 H, 1-H, C*H*HPh), 4.66 (d, *J* = 11.9 Hz, 1 H, C*H*HCCl$_3$), 4.45 (d, *J* = 12.1 Hz, 1 H, C*H*HPh), 4.42 (d, *J* = 8.0 Hz, 1 H, 1′-H), 4.32 (m, 1 H, OC*H*HCH=CH$_2$), 4.14–4.03 (m, 3 H, 6ab′-H, OC*H*HCH=CH$_2$), 4.01–3.91 (m, 3 H, 4-H, CH_2Cl), 3.78 (q, *J* = 8.4 Hz, 1 H, 2-H), 3.73 (s, 2 H, 6ab-H), 3.69 (m, 1 H, 5′-H), 3.53 (m, 1 H, 5-H), 2.13, 2.03, 1.96, 1.92 (4s, 12 H, 4 $COCH_3$) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.4, 170.3, 169.2, 166.5, 153.7 (C=O), 137.7 (quat. Ar), 133.6 (*C*H=CH$_2$), 128.6, 128.1 (Ar), 117.6 (*C*H$_2$=CH), 100.3 (C-1′), 99.0 (C-1), 94.4 (CCl_3), 76.8 (C-3, CH_2CCl_3), 75.2 (C-4), 74.1 (C-5), 73.7 (*C*H$_2$Ph), 72.5 (C-3′), 70.3 (C-5′), 69.8 (O*C*H$_2$CH=CH$_2$), 68.7 (C-2′), 67.4 (C-6), 66.5 (C-4′), 60.5 (C-6′), 54.6 (C-2), 40.3 (CH_2Cl), 23.3, 20.7, 20.6 (CO*C*H$_3$) ppm. HRMS: calcd. for $C_{35}H_{43}Cl_4NO_{17}$ [M + H]$^+$ 890.1363; found 890.1371.

Allyl 2-Acetamido-4-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-6-*O*-benzyl-2-deoxy-3-*O*-trichloroethyloxylcarbonyl-β-D-glucopyranoside (14): To a solution of disaccharide **13** (850 mg, 0.954 mmol) dissolved in pyridine/EtOH (1:1, 20 mL) was added thiourea (362 mg, 5 equiv.), and the solution was stirred at 80 °C for 2 h. The solvents were evaporated, and the residue was co-concentrated with toluene (3 × 50 mL). The residue was dissolved in CH_2Cl_2 and washed with 2 M HCl (100 mL), $NaHCO_3$ (50 mL), and brine (50 mL), and the aqueous layers were re-extracted with CH_2Cl_2 (50 mL). The combined organic layers were dried, filtered, and concentrated. Column chromatography (EtOAc/hexanes = 7:3) of the residue gave alcohol **14** (660 mg, 84%) pure as a colorless glass. $[\alpha]_D$ = –22 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.40–7.25 (m, 5 H, Ar), 5.85 (m, 1 H, C*H*=CH$_2$), 5.69 (d, *J* = 8.5 Hz, 1 H, NH), 5.28–5.13 (m, 4 H, 3-H, 4′-H, CH_2=CH-), 4.91 (d, *J* = 11.9 Hz, 1 H, C*H*HCCl$_3$), 4.78 (dd, *J* = 10.1, 8.0 Hz, 1 H, 2′-H), 4.72 (d, *J* = 7.9 Hz, 1 H, 1-H),4.70 (d, *J* = 12.2 Hz, 1 H, C*H*HPh), 4.62 (d, *J* = 11.8 Hz, 1 H, C*H*HCCl$_3$), 4.47 (d, *J* = 12.1 Hz, 1 H, C*H*HPh), 4.40 (d, *J* = 8.0 Hz, 1 H, 1′-H),4.30 (m, 1 H, CH*H*CH=CH$_2$), 4.09 (m, 3 H, 6ab′-H, CH*H*CH=CH$_2$), 3.94 (t, *J* = 8.7 Hz, 1 H, 4-H), 3.81–3.70 (m, 3 H, 2-H, 6ab-H), 3.67–3.59 (m, 2 H, 3′-H, 5′-H), 3.52 (m, 1 H, 5-H), 2.52 (d, *J* = 6.1 Hz, 1 H, OH), 2.12, 2.02, 2.01, 1.92 (4s, 12 H, 4 $COCH_3$) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 171.0, 170.8, 170.5, 170.2, 153.7 (C=O), 137.9 (quat. Ar), 133.6 (*C*H=CH$_2$), 128.8, 128.6 (Ar), 117.6 (CH=*C*H$_2$), 100.4 (C-1′), 99.1 (C-1), 94.5 (*C*Cl$_3$), 77.3 (C-3), 76.7 (*C*H$_2$CCl$_3$), 75.3 (C-4), 74.3 (C-5), 73.6 (*C*H$_2$Ph), 72.7 (C-2′), 71.3 (C-3′), 70.6 (C-5′), 69.8 (*C*H$_2$CH=CH$_2$), 69.2 (C-4′), 67.6 (C-6), 61.1 (C-6′), 54.6 (C-2), 23.3, 21.9, 20.8, 20.7 (CO*C*H$_3$) ppm. HRMS: calcd. for $C_{33}H_{42}Cl_3NO_{16}$ [M + H]$^+$ 814.1647; found 814.1605.

Allyl 2-Acetamido-4-*O*-[2,4,6-tri-*O*-acetyl-3-*O*-(4,6-*O*-benzylidene-3-chloroacetyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-β-D-galactopyranosyl]-6-*O*-benzyl-2-deoxy-3-*O*-trichloroethyloxylcarbonyl-β-D-glucopyranoside (16): Disaccharide acceptor **14** (480 mg, 0.589 mmol) and known[8] donor **15** (1.18 g, 1.77 mmol, 3.0 equiv.) were dissolved in CH_2Cl_2 (30 mL) under an atmosphere of N_2. The mixture was cooled to 0 °C and freshly distilled TMSOTf (212 μL, 1.18 mmol, 3.0 equiv.) was added. After stirring at 0 °C for 45 min, the reaction was quenched with Et_3N (200 μL. 1.41 mmol), the solids were filtered off and washed with CH_2Cl_2, and the combined filtrate and washing were concentrated. A mixture of EtOAc/hexanes (1:1, ca. 50 mL) was added to the residue, and a white amorphous solid was filtered off and washed with EtOAc/hexanes (1:1). It was identified as pure trisaccharide **16** (400 mg, 54%). The mother liquor and washing were combined and concentrated, and column chromatography (CH_2Cl_2/MeOH = 50:1) on the residue gave additional trisaccharide **16** (250 mg, 33%) pure as a white amorphous powder. $[\alpha]_D$ = –65 (*c* = 0.5, DMSO). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 9.00 (d, *J* = 9.2 Hz, 1 H, NH′′), 8.00 (d, *J* = 9.1 Hz, 1 H, NH), 7.30 (m, 10 H, Ar), 5.83 (m, 1 H, OCH$_2$C*H*=CH$_2$), 5.65 (s, 1 H, C*H*Ph), 5.44 (t, *J* = 9.9 Hz, 1 H, 3′′-H), 5.30 (br. d, *J* = 3.7 Hz, 1 H, 4′-H), 5.20 (m, 1 H, -CH=C*H*H), 5.11 (m, 1 H, CH=C*H*H), 5.00 (d, *J* = 12.3 Hz, 1 H, C*H*HCCl$_3$), 4.91 (d, *J* = 7.9 Hz, 1 H, 1′′-H), 4.83 (t, *J* = 9.8 Hz, 1 H, 3-H), 4.76 (dd, *J* = 10.5, 8.3 Hz, 1 H, 2′-H), 4.67 (d, *J* = 12.3 Hz, 1 H, C*H*HCl$_3$), 4.59 (d, *J* = 12.2 Hz, 1 H, C*H*HPh), 4.55 (d, *J* = 8.4 Hz, 1 H, 1-H), 4.49 (d, *J* = 12.2 Hz, 1 H, C*H*HPh), 4.46–4.40 (m, 2 H, 1′-H, C*H*HCl), 4.21–4.15 (m, 3 H, 6a′′-H, C*H*HCl, C*H*HCH=CH$_2$), 4.01–3.96 (m, 2 H, 6a′-H, C*H*HCH=CH$_2$), 3.92 (dd, *J* = 10.3, 3.2 Hz, 1 H, 3′-H), 3.89–3.66 (m, 8 H, 2-H, 4-H, 6a-H, 5′-H, 6b′-H, 2′′-H, 4′′-H, 6b′′-H), 3.58 (dd, *J* = 11.0, 4.5 Hz, 1 H, 6b-H), 3.49 (m, 1 H, 5-H), 3.40 (m, 1 H, 5′′-H), 2.00, 1.97, 1.94, 1.66 (4s, 12 H, 4 $COCH_3$) ppm. ^{13}C NMR (150 MHz, [D$_6$]DMSO): δ = 170.1, 169.7, 169.1, 168.7, 166.7, 161.5, 153.0 (C=O), 138.1, 137.1 (quat. Ar), 134.4 (*C*H=CH$_2$), 128.9, 128.4, 128.1, 127.6, 127.5, 126.1, 126.0 (Ar), 116.4 (*C*H$_2$=CH-CH$_2$), 100.2 (*C*HPh), 100.1 (C-1′), 99.3 (C-1), 98.7 (C-1′′), 94.8, 92.5 (CCl_3), 78.3 (C-3), 77.3 (C-4′′), 75.9 (*C*H$_2$CCl$_3$), 75.7 (C-4, C-3′), 73.7 (C-5), 72.7 (C-3′′), 72.4 (*C*H$_2$Ph), 70.1 (C-5′), 69.7 (C-2′), 69.0 (*C*H$_2$CH=CH$_2$), 67.7 (C-6), 67.6 (C-4′), 67.3 (C-6′′), 65.8 (C-5′′), 61.5 (C-6′), 55.9 (C-2′′), 53.0 (C-2), 40.7 (CH_2Cl), 22.7, 20.7, 20.6 (CO*C*H$_3$) ppm. HRMS: calcd. for $C_{50}H_{57}Cl_7N_2O_{22}$ [M + H]$^+$ 1283.1300; found 1283.1344.

Allyl 2-Acetamido-4-*O*-[2,4,6-tri-*O*-acetyl-3-*O*-(6-*O*-benzyl-3-chloroacetyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-β-D-galactopyranosyl]-6-*O*-benzyl-2-deoxy-3-*O*-trichloroethyloxylcarbonyl-β-D-glucopyranoside (17): Benzylidene acetal **16** (300 mg, 0.233 mmol) was reductively opened as described for the synthesis of acceptor **12**. Flash chromatography (CH_2Cl_2/MeOH = 100:1→40:1) of the crude residue gave alcohol **17** (228 mg, 76%) pure as a colorless glass. $[\alpha]_D$ = –21 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41–7.25 (m, 10 H, Ar), 6.84 (d, *J* = 8.7 Hz, 1 H, NH′′), 5.81 (m, 1 H, C*H*=CH$_2$), 5.75 (d, *J* = 8.9 Hz, 1 H, NH), 5.34 (br. d, *J* = 3.4 Hz, 1 H, 4′-H), 5.26–5.21 (m, 2 H, 3′′-H, CH=C*H*H), 5.15 (m, 1 H, CH=C*H*H), 5.05 (t, *J* = 9.8 Hz, 1 H, 3-H), 4.96 (t, *J* = 8.2 Hz, 1 H, 2′-H), 4.86 (d, *J* = 11.9 Hz, 1 H, C*H*HCCl$_3$), 4.70 (d, *J* = 8.1 Hz, 1 H, 1′′-H), 4.67 (d, *J* = 12.1 Hz, 1 H, C*H*HPh), 4.66–4.60 (m, 3 H, 1-H, C*H*HPh, C*H*HCCl$_3$), 4.54 (d, *J* = 11.8 Hz, 1 H, C*H*HPh), 4.46 (d, *J* = 12.1 Hz, 1 H, C*H*HPh), 4.30 (d, *J* = 8.1 Hz, 1 H, 1′-H), 4.28 (m, 1 H, C*H*H=CH$_2$), 4.12–3.89 (m, 7 H, 2-H, 4-H, 6a′-H, 6b′-H, C*H*H=CH$_2$, CH_2Cl), 3.82 (dd, *J* = 10.1, 5.0 Hz, 1 H, 6a′′-H), 3.78–3.62 (m, 7 H, 6a-H, 6b-H, 3′-H, 5′-H, 2′′-H, 4′′-H, 6b′′-H), 3.58 (m, 1 H, 5′′-H), 3.52 (m, 1 H, 5-H), 3.15 (d, *J* = 3.5 Hz, OH), 2.09, 2.00, 1.90 (3s, 12 H, 3 $COCH_3$) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.5, 170.1, 170.0, 169.3, 168.0, 162.0, 153.5 (C=O), 137.9, 137.3 (quat. Ar), 133.5 (*C*H=CH$_2$), 128.6, 128.5, 128.1, 127.9, 127.8 (Ar), 117.4

(CH=CH_2), 100.4 (C-1′), 99.4 (C-1′′), 99.1 (C-1), 94.4, 92.1 (CCl_3), 77.1 (CH_2CCl_3), 76.7 (C-3), 75.5 (C-3′′), 75.1 (C-4′′), 74.5 (C-4), 74.3 (C-5), 73.9 (C-5′′), 73.8, 73.6 (CH_2Ph), 70.9 (C-3′, C-5′), 70.6 (C-2′), 70.1 (C-6′′), 69.6 (CH_2=$CHCH_2$), 68.4 (C-4′), 67.8 (C-6), 61.4 (C-6′), 56.1 (C-2′′), 53.3 (C-2), 40.6 (CH_2Cl), 23.3, 21.1, 20.8, 20.7 ($COCH_3$) ppm. HRMS: calcd. for $C_{50}H_{59}Cl_7N_2O_{22}$ $[M + H]^+$ 1285.1460; found 1285.1431.

Allyl 2-Acetamido-4-*O*-{2,4,6-tri-*O*-acetyl-3-*O*-[4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-*O*-benzyl-3-chloroacetyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl]-β-D-galactopyranosyl}-6-*O*-benzyl-2-deoxy-3-*O*-trichloroethyloxylcarbonyl-β-D-glucopyranoside (20): A stirred solution of alcohol **17** (115 mg, 0.09 mmol) and glucosyl trichloroacetimidate **18**[13] (221 mg, 0.45 mmol, 5.0 equiv.) in CH_2Cl_2 (5.0 mL) was warmed up to 40 °C. BF_3·OEt_2 (23 μL, 2.0 equiv.) was added, and the reaction mixture was stirred for 45 min at 40 °C. The reaction was quenched with Et_3N (29 μL) and diluted with CH_2Cl_2 (20 mL). The mixture was washed with sat. aq. $NaHCO_3$ (20 mL), the aqueous layer was re-extracted with CH_2Cl_2 (2 × 20 mL), and the combined organic layers were dried, filtered, and concentrated. Column chromatography (EtOAc/hexanes = 6:4) gave tetrasaccharide **20** (126 mg, 85%) pure as a colorless glass. $[\alpha]_D$ = –11 (c = 1.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.39–7.21 (m, 10 H, Ar), 6.52 (d, J = 8.6 Hz, 1 H, NHA′), 5.81 (m, 1 H, CH=CH_2), 5.70 (d, J = 8.8 Hz, 1 H, NHA), 5.37 (d, J = 3.1 Hz, 1 H, 4C-H), 5.27–5.19 (m, 2 H, 3A′-H, CH=CH), 5.15 (m, 1 H, CH=CH), 5.06 (dd, J = 8.5, 7.8 Hz, 1 H, 3A-H), 5.05–4.95 (m, 3 H, 2C-H, 3C′-H, 4C′-H), 4.87 (d, J = 11.9 Hz, 1 H, C$H$$HCCl_3$), 4.82 (t, J = 8.2 Hz, 1 H, 2C′-H), 4.77 (d, J = 11.9 Hz, 1 H, CHHPh), 4.70–4.62 (m, 4 H, 1A-H, 1A′-H, CHHPh, C$H$$HCCl_3$), 4.53–4.46 (m, 3 H, 1C′-H, 2 CHHPh), 4.43 (dd, J = 12.7, 3.9 Hz, 1 H, 6aC′-H), 4.33 (d, J = 8.0 Hz, 1 H, 1C-H), 4.29 (m, 1 H, OCH_2CH=CH_2), 4.13 (d, J = 15.4 Hz, 1 H, CHHCl), 4.09 (dd, J = 11.4, 6.8 Hz, 1 H, 6aC-H), 4.05–3.89 (m, 7 H, 2A-H, 4A-H, 6bC-H, 4A′-H, 6bC-H, CHHCl, OCHHCH=CH_2), 3.78–3.69 (m, 7 H, 6abA-H, 3C-H, 5C-H, 2A′-H, 6abA′-H), 3.53 (m, 1 H, 5A-H), 3.43 (m, 2 H, 5A′-H, 5C′-H), 2.09, 2.06, 1.97, 1.95, 1.94, 1.89 (8s, 24 H, 8 $COCH_3$) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.5, 170.4, 170.2, 170.1, 170.0, 169.3, 169.1, 168.8, 167.1, 161.9, 153.6 (C=O), 138.0, 137.6 (quat. Ar), 133.6 (CH=CH_2), 128.7, 128.5, 128.3, 128.1, 127.9 (Ar), 117.4 (CH=CH_2), 100.5 (C-1 C), 100.3 (C-1C′), 99.7 (C-1A′), 99.1 (C-1A), 94.4 (CCl_3), 76.9 (C-3A, CH_2CCl_3), 75.4 (C-3 C), 74.94 (C-5A′), 74.6, 74.5 (C-4A, C-4A′), 74.3 (C-5A), 73.7, 73.6 (CH_2Ph), 72.9 (C-3C′), 72.6 (C-3A′), 72.0 (C-5C′), 71.4 (C-2C′), 71.1 (C-5C), 70.9 (C-2C), 69.6 (OCH_2CH=CH_2), 68.5 (C-4C), 67.9 (C-6A or C-6A′), 67.4 (C-4C′), 66.9 (C-6A or C-6A′), 61.6 (C-6C), 61.1 (C-6C′), 56.3 (C-2A′), 53.4 (C-2A), 40.4 (CH_2Cl), 23.3, 21.2, 20.8, 20.7 20.6, 20.5 ($COCH_3$) ppm. HRMS: calcd. for $C_{64}H_{77}Cl_7N_2O_{31}$ $[M + H]^+$ 1615.4210; found 1615.2452.

Allyl 2-Acetamido-4-*O*-{2,4,6-tri-*O*-acetyl-3-*O*-[4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-6-*O*-benzyl-3-chloroacetyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl]-β-D-galactopyranosyl}-6-*O*-benzyl-2-deoxy-3-*O*-trichloroethyloxylcarbonyl-β-D-glucopyranoside (21): Alcohol **17** (120 mg, 0.09 mmol) was coupled to donor **19**[13] (229 mg, 0.605 mmol, 5.0 equiv.) in CH_2Cl_2 (5.0 mL) as described above for the preparation of tetrasaccharide **20**. After 1 h of reaction at 40 °C, additional donor **19** (60 mg, 1.5 equiv.) was added, and the reaction was left to proceed for another 1 h at 40 °C. The reaction was quenched with Et_3N (29 μL) and worked up as described above for the preparation of compound **20**. Column chromatography (EtOAc/hexanes = 6:4), followed by RP HPLC (CH_3CN/H_2O = 60:40 → 100:0) gave tetrasaccharide **21** (108 mg, 72%) pure as a colorless glass. $[\alpha]_D$ = –10 (c = 0.8, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41–7.25 (m, 10 H, Ar), 6.70 (d, J = 8.6 Hz, 1 H, NHA′), 5.82 (m, 1 H, CH=CH_2), 5.74 (d, J = 8.9 Hz, 1 H, NHA), 5.36 (d, J = 3.2 Hz, 1 H, 4C-H), 5.29–5.20 (m, 3 H, 3A′-H, 4C′-H, CHH=CH), 5.15 (m, 1 H, CHH=CH-), 5.06 (br. t, J = 8.3 Hz, 1 H, 3A-H), 5.00 (dd, J = 10.0, 8.1 Hz, 1 H, 2C-H), 4.97 (dd, J = 10.4, 8.0 Hz, 1 H, 2C′-H), 4.87 (d, J = 11.9 Hz, 1 H, C$H$$HCCl_3$), 4.82 (dd, J = 10.4, 3.5 Hz, 1 H, 3C′-H), 4.75 (d, J = 11.9 Hz, 1 H, C$H$$HCCl_3$), 4.70–4.60 (m, 4 H, 1A-H, 1A′-H, 2 CHHPh), 4.52–4.45 (m, 2 H, 2 CHHPh), 4.43 (d, J = 8.0 Hz, 1 H, 1C′-H), 4.31 (d, J = 8.0 Hz, 1 H, 1C-H), 4.28 (m, 1 H, CHHCH=CH_2), 4.10–3.88 (m, 10 H, 2A-H, 4A-H, 6abC-H, 4A′-H, 6abC′-H, CH_2Cl, CHHCH=CH_2), 3.77–3.64 (m, 8 H, 6abA-H, 3C-H, 5C-H, 2A′-H, 6abA′-H, 5C′-H), 3.53 (m, 1 H, 5A-H or 5A′-H), 3.46 (m, 1 H, 5A-H or 5A′-H), 2.11, 2.10, 2.06, 1.99, 1.97, 1.94, 1.91 (8s, 24 H, 8 $COCH_3$) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.5, 170.4, 170.2, 170.1, 170.0, 169.2, 168.9, 166.9, 161.8, 153.5 (C=O), 137.9, 137.5 (quat. Ar), 133.5 (CH=CH_2), 128.7, 128.5, 128.4, 128.2, 128.0, 127.9, 127.8, 127.5 (Ar), 117.4 (CH=CH_2), 100.4 (C-1C, C-1C′), 99.6 (C-1A′), 99.1 (C-1A), 94.4, 92.0 (CCl_3), 76.7 (C-3A, C$H$$CCl_3$), 75.4 (C-3C), 74.9, 74.5, 74.3 (C-4A, C-4A′, C-5A, C-5A′), 73.6 (CH_2Ph), 72.8 (C-3A′), 71.0, 70.9, 70.8, 70.7 (C-2C, C-5C, C-3C′, C-5C′), 69.6 (CH_2CH=CH_2), 69.0 (C-2C′), 68.4 (C-4C), 67.8, 67.0 (C-6A, C-6A′), 66.8 (C-4C′), 61.5, 61.1 (C-6C, C-6C′), 56.0 (C-2A′), 53.3 (C-2A), 40.5 (CH_2Cl), 23.3, 21.2, 20.8, 20.7 ($COCH_3$) ppm. HRMS: calcd. for $C_{64}H_{77}Cl_7N_2O_{31}$ $[M + H]^+$ 1615.2410; found 1615.2451.

Allyl 2-Acetamido-4-*O*-{2,4,6-tri-*O*-acetyl-3-*O*-[4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-*O*-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl]-β-D-galactopyranosyl}-6-*O*-benzyl-2-deoxy-3-*O*-trichloroethyloxylcarbonyl-β-D-glucopyranoside (22): To a solution of tetrasaccharide **20** (126 mg, 0.077 mmol) dissolved in pyridine/EtOH (1:1, 10 mL) was added thiourea (58 mg, 10 equiv.), and the solution was heated at 80 °C for 24 h. The mixture was co-concentrated with toluene (2 × 20 mL), and the residue was dissolved in CH_2Cl_2 (100 mL) and washed with 1 M HCl (100 mL), $NaHCO_3$ (50 mL), and brine (50 mL). The aqueous layers were re-extracted with CH_2Cl_2 (50 mL), and the combined organic layers were dried, filtered, and concentrated. Column chromatography (CH_2Cl_2/MeOH = 60:1) of the residue gave alcohol **22** (97 mg, 80%) pure as a colorless glass. $[\alpha]_D$ = +5 (c = 1.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41–7.25 (m, 10 H, Ar), 6.71 (d, J = 7.4 Hz, 1 H, NHA′), 5.81 (m, 1 H, CH=CH_2), 5.71 (d, J = 8.8 Hz, 1 H, NHA), 5.37 (d, J = 3.4 Hz, 1 H, 4C-H), 5.24 (m, 1 H, CHH=CH), 5.17–5.11 (m, 2 H, 3C′-H, CHH=CH), 5.06 (br. t, J = 8.5 Hz, 1 H, 3A-H), 4.99 (dd, J = 10.0, 8.0 Hz, 1 H, 2C-H), 4.97–4.91 (m, 3 H, 1A′-H, 2C′-H, 4C′-H), 4.86 (d, J = 11.9 Hz, 1 H, C$H$$HCCl_3$), 4.71 (d, J = 12.0 Hz, 1 H, CHHPh), 4.68–4.61 (m, 3 H, 1A-H, CHHPh, C$H$$HCCl_3$), 4.54–4.45 (m, 3 H, 1C′-H, 2 CHHPh), 4.31–4.15 (m, 2 H, 1C′-H, OCHHCH=CH_2), 4.15 (dd, J = 12.3, 2.5 Hz, 1 H, 6aC′-H), 4.10–3.90 (m, 7 H, 2A-H, 4A-H, 6abC-H, 3A′-H, 6bC′-H, CHHCH=CH_2), 3.88 (d, J = 1.6 Hz, 1 H, OH), 3.76–3.58 (m, 8 H, 6abA-H, 3C-H, 5C-H, 4A′-H, 6abA′-H, 5C′-H), 3.53 (m, 1 H, 5A-H or 5A′-H), 3.48 (m, 1 H, 5A-H or 5A′-H), 3.37 (m, 1 H, 2A′-H), 2.05, 1.98, 1.97, 1.94, 1.93, 1.91, 1.90, 1.87 (8s, 24 H, 8 $COCH_3$) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.5, 170.0, 169.3, 169.2, 169.1, 161.7, 153.5 (C=O), 138.0, 137.9 (quat. Ar), 133.5 (CH=CH_2), 128.1 (Ar), 117.4 (CH=CH_2), 101.1 (C-1C′), 100.5 (C-1C), 99.1 (C-1A), 99.0 (C-1A′), 94.4 (CCl_3), 81.4 (C-4A′), 77.1 (CH_2CCl_3), 76.7 (C-3A), 75.4 (C-3C), 74.4 (C-4A), 74.3, 74.1 (C-5A, C-5A′), 73.7, 73.6 (CH_2Ph), 72.5, 72.01 (C-5C or C-5C′, C-3C′), 71.1 (C-5C or C-5C′, C-2C), 70.7 (C-2C′), 70.3 (C-3A′), 69.6 (CH_2CH=CH_2), 68.8 (C-4C), 68.3

(C-4C′), 67.9 (C-6A, C-6A′), 61.9 (C-6C′), 61.6 (C-6C), 58.8 (C-2A′), 53.3 (C-2A), 23.3, 21.2, 20.9, 20.6 (CO*C*H$_3$) ppm. HRMS: calcd. for $C_{62}H_{76}Cl_6N_2O_{30}$ [M + H]$^+$ 1539.2656; found 1539.2692.

Allyl 2-Acetamido-4-*O*-{2,4,6-tri-*O*-acetyl-3-*O*-[4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-*O*-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl]-β-D-galactopyranosyl}-6-*O*-benzyl-2-deoxy-3-*O*-trichloroethyloxylcarbonyl-β-D-glucopyranoside (23): Tetrasaccharide **21** (70 mg, 0.043 mmol) was dechloroacetylated as described for the synthesis of acceptor **22**. Column chromatography (CH_2Cl_2/MeOH = 60:1 → 20:1) of the crude residue gave alcohol **23** (64 mg, 95%) pure as a colorless glass. $[\alpha]_D$ = +10 (*c* = 0.7, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42–7.23 (m, 10 H, Ar), 6.75 (d, *J* = 7.3 Hz, 1 H, NHA′), 5.82 (m, 1 H, C*H*=CH$_2$), 5.75 (d, *J* = 8.8 Hz, 1 H, NHA), 5.36 (d, *J* = 3.5 Hz, 1 H, 4C-H), 5.33 (d, *J* = 3.5 Hz, 1 H, 4C′-H), 5.24 (m, 1 H, C*H*H=CH), 5.18–5.12 (m, 2 H, 2C′-H, C*H*H=CH), 5.05 (br. d, *J* = 8.6 Hz, 1 H, 3A-H), 4.98 (dd, *J* = 10.0, 7.9 Hz, 1 H, 2C-H), 4.96 (d, *J* = 8.1 Hz, 1 H, 1A′-H), 4.92 (dd, *J* = 10.7, 3.3 Hz, 1 H, 3C′-H), 4.86 (d, *J* = 11.9 Hz, 1 H, C*H*HCCl$_3$), 4.71 (d, *J* = 12.0 Hz, 1 H, C*H*HPh), 4.68 (d, *J* = 12.1 Hz, 1 H, C*H*HPh), 4.63 (d, *J* = 7.2 Hz, 1 H, 1A-H), 4.61 (d, *J* = 12.1 Hz, 1 H, C*H*HCCl$_3$), 4.51 (d, *J* = 11.9 Hz, 1 H, C*H*HPh), 4.48 (d, *J* = 8.3 Hz, 1 H, 1C′-H), 4.46 (d, *J* = 12.1 Hz, 1 H, C*H*HPh), 4.29 (m, 2 H, 1C-H, C*H*HCH=CH$_2$), 4.12–3.89 (m, 10 H, 2A-H, 4A-H, 5C-H, 6abC-H, 3A′-H, 6abC′-H, C*H*HCH=CH$_2$, OH), 3.76–3.57 (m, 7 H, 6abA-H, 3C-H, 4A′-H, 6abA′-H, 5C′-H), 3.55–3.48 (m, 2 H, 5A-H, 5A′-H), 3. 24 (m, 1 H, 2A′-H), 2.15, 2.12, 2.04, 2.01, 1.99, 1.98, 1.94 (8s, 24 H, 8 CO*C*H$_3$) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.5, 170.4, 170.1, 170.0, 169.9, 169.2, 161.7, 153.5 (C=O), 138.0, 137.9 (quat. Ar), 133.6 (*C*H=CH$_2$), 128.6, 128.5, 128.4, 128.2, 128.0, 127.9, 127.7, 127.4 (Ar), 117.4 (CH=*C*H$_2$), 101.5 (C-1C′), 100.5 (C-1C), 99.1 (C-1A), 99.0 (C-1A′), 94.4, 92.4 (*C*Cl$_3$), 81.5 (C-4A′), 76.8 (*C*H$_2$CCl$_3$), 76.7 (C-3A), 75.5 (C-3C), 74.4 (C-4A), 74.2, 74.1 (C-5A, C-5A′), 73.7, 73.6 (*C*H$_2$Ph), 71.3, 71.0 (C-5C, C-5C′), 70.7 (C-2C, C-3C′), 70.1 (C-3A′), 69.6 (*C*H$_2$CH=CH$_3$), 68.8 (C-4C), 68.6 (C-2C′), 67.9, 67.8 (C-6A, C-6A′), 66.8 (C-4C′), 61.6 (C-6C, C-6C′), 58.8 (C-2A′), 53.3 (C-2A), 23.3, 21.2, 20.9, 20.7, 20.6 (CO*C*H$_3$) ppm. HRMS: calcd. for $C_{62}H_{76}Cl_6N_2O_{30}$ [M + H]$^+$ 1539.2692; found 1539.2692.

Allyl 2-Acetamido-4-*O*-{2,4,6-tri-*O*-acetyl-3-*O*-[2-acetamido-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-*O*-benzyl-2-deoxy-β-D-glucopyranosyl]-β-D-galactopyranosyl}-6-*O*-benzyl-2-deoxy-β-D-glucopyranoside (24) and allyl 2-acetamido-4-*O*-{2,4,6-tri-*O*-acetyl-3-*O*-[4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-*O*-benzyl-2-chloroacetamido-2-deoxy-β-D-glucopyranosyl]-β-D-galactopyranosyl}-6-*O*-benzyl-2-deoxy-β-D-glucopyranoside (25): To a solution of tetrasaccharide **22** (30 mg, 0.020 mmol) dissolved in AcOH (1.2 mL) was added activated Zn (140 mg, 100 equiv.). The mixture was heated to 40 °C for 1 h, diluted with EtOAc (10 mL), and filtered. The solids were washed with EtOAc (2 × 10 mL) and CH_2Cl_2 (2 × 10 mL), and the combined filtrate and washings were concentrated. Column chromatography (CH_2Cl_2/MeOH = 60:1) of the residue gave *N*-chloroacetamido **25** (19 mg, 77%) pure as a colorless glass, followed by *N*-acetamido **24** (3 mg, 15%) pure as a colorless glass. Data for **24**: $[\alpha]_D$ = –12 (*c* = 0.5, MeOH). ^{1}H NMR (600 MHz, CD_3OD): δ = 7.49–7.20 (m, 10 H, Ar), 5.90 (m, 1 H, C*H*=CH$_2$), 5.42 (d, *J* = 3.4 Hz, 1 H, 4C-H), 5.25 (m, 1 H, C*H*H=CH-), 5.18 (t, *J* = 9.5 Hz, 1 H, 3C′-H), 5.13 (m, 1 H, C*H*H=CH), 5.01 (dd, *J* = 10.0, 8.5 Hz, 1 H, 2C-H), 4.99 (t, *J* = 9.8 Hz, 1 H, 4C′-H), 4.88 (dd, *J* = 9.8, 8.2 Hz, 1 H, 2C′-H), 4.72 (m, 2 H, 1C′-H, C*H*HPh), 4.68 (d, *J* = 12.0 Hz, 1 H, C*H*HPh), 4.56 (d, *J* = 11.8 Hz, 1 H, C*H*HPh), 4.54–4.47 (m, 3 H, 1C-H, 1A-H, C*H*HPh), 4.40 (d, *J* = 8.5 Hz, 1 H, 1A′-H), 4.29 (m, 1 H, C*H*H-CH=CH$_2$), 4.21 (dd, *J* = 12.4, 5.5 Hz, 1 H, 6aC′-H), 4.13 (dd, *J* = 12.4, 2.4 Hz, 1 H, 6bC′-H), 4.10 (dd, *J* = 11.7, 4.6 Hz, 1 H, H6aC), 4.65 (m, 1 H, C*H*H-CH=CH$_2$), 3.98 (dd, *J* = 11.5, 8.2 Hz, 1 H, 6bC-H), 3.89 (m, 1 H, 5C-H), 3.83 (dd, *J* = 10.0, 3.5 Hz, 1 H, 3C-H), 3.81 (m, 1 H, 5C′-H), 3.78–3.68 (m, 5 H, 2A′-H, 6abA-H, 6abA′-H), 3.65 (dd, *J* = 10.3, 8.5 Hz, 1 H, 3A-H), 3.60–3.54 (m, 3 H, 4A-H, 3A′-H, 4A′-H), 3.51 (dd, *J* = 10.4, 8.5 Hz, 1 H, 2A-H), 3.49–3.42 (m, 2 H, 5A-H, 5A′-H), 2.13, 2.05, 2.04, 2.02, 2.00, 1.97, 1.96, 1.95, 1.93 (9s, 27 H, 9 CO*C*H$_3$) ppm. ^{13}C NMR (150 MHz, CD_3OD): δ = 173.6, 173.5, 172.5, 172.1, 171.7, 171.4, 171.1 (C=O), 139.9, 139.8 (quat. Ar), 135.6 (*C*H=CH$_2$), 129.8, 129.7, 129.3, 129.1 (Ar), 117.2 (CH=*C*H$_2$), 103.2 (C-1C), 102.5 (C-1A), 102.0 (C-1A′), 101.8 (C-1C′), 81.9, 81.6 (C-4A, C-4A′), 78.3 (C-3C), 75.7 (C-5A, C-5A′), 75.0, 74.8 (*C*H$_2$Ph), 74.3 (C-3C′), 74.1 (C-3A′), 73.2 (C-3A), 73.1 (C-5C), 73.0 (C-5C′), 72.9 (C-2C′), 71.9 (C-2C), 71.4 (C-4C), 71.0 (*C*H$_2$CH=CH$_2$) 69.9 (C-4C′), 69.8, 69.5 (C-6A, C-6A′), 63.6 (C-6C′), 63.1 (C-6C), 57.3 (C-2A′), 56.6 (C-2A), 23.3, 23.0, 21.4, 20.9, 20.8 (CO*C*H$_3$) ppm. HRMS: calcd. for $C_{59}H_{78}N_2O_{28}$ [M + H]$^+$ 1263.4819; found 1263.4850. Data for **25**: $[\alpha]_D$ = –8 (*c* = 0.6, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.23 (m, 10 H, Ar), 6.51 (d, *J* = 8.7 Hz, 1 H, NHA′), 5.85 (m, 1 H, C*H*=CH$_2$), 5.58 (d, *J* = 8.9 Hz, 1 H, NHA), 5.33 (br. d, *J* = 3.4 Hz, 1 H, 4C-H), 5.23 (m, 1 H, C*H*H=CH), 5.15 (m, 1 H, C*H*H=CH), 5.13 (t, *J* = 9.3 Hz, 1 H, 3C′-H), 5.07 (dd, *J* = 9.7, 8.1 Hz, 1 H, 2C-H), 4.97 (t, *J* = 9.7 Hz, 1 H, 4C′-H), 4.94 (dd, *J* = 9.7, 8.1 Hz, 1 H, 2C′-H), 4.85 (d, *J* = 8.0 Hz, 1 H, 1A′-H), 4.75–4.65 (m, 3 H, 1A-H, 2 C*H*HPh), 4.54–4.46 (m, 3 H, 1C′-H, 2 C*H*HPh), 4.34–4.26 (m, 2 H, 1C-H, C*H*HCH=CH$_2$), 4.16–3.85 (m, 9 H, 3A-H, 6abC-H, 3A′-H, 6abC′-H, CH$_2$Cl, C*H*HCH=CH$_2$), 3.74–3.42 (m, 12 H, 2A-H, 4A-H, 5A-H, 6abA-H, 3C-H, 5C-H, 4A′-H, 5A′-H, 6abA′-H, 5C′-H), 3.25 (m, 1 H, 2′′-H), 2.16, 2.13, 2.06, 2.03, 2.02, 1.99, 1.97 (8s, 24 H, 8 CO*C*H$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 170.4, 170.1, 170.0, 169.3, 169.0, 166.1 (C=O), 138.2, 138.0 (quat. Ar), 133.9 (*C*H=CH$_2$), 128.6, 128.4, 127.9, 127.7, 127.6 (Ar), 117.5 (CH=*C*H$_2$), 101.2 (C-1C), 101.0 (C-1C′), 99.9 (C-1A′), 99.3 (C-1A), 81.3, 81.1 (C-4A, C-4A′), 76.0 (C-3C), 74.0 (C-5A, C-5A′), 73.6 (*C*H$_2$Ph) 72.5 (C-3C′), 72.0, 71.7, 71.3 (C-5A, C-3A or C-3A′, C-5A′), 71.1 (C-2C′), 70.5 (C-3A or C-3A′, C-2C), 69.7 (*C*H$_2$CH=CH$_2$), 69.0 (C-4C), 68.2 (C-4C′), 68.0 (C-6A, C-6A′), 62.2, 61.8 (C-6C, C-6C′), 57.5 (C-2A′), 56.5 (C-2A), 42.6 (CH$_2$Cl), 23.5, 21.0, 20.7, 20.5 (CO*C*H$_3$) ppm. HRMS: calcd. for $C_{59}H_{77}ClN_2O_{28}$ [M + H]$^+$ 1297.4430; found 1297.4458.

Allyl 2-Acetamido-4-*O*-{2,4,6-tri-*O*-acetyl-3-*O*-[2-acetamido-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-6-*O*-benzyl-2-deoxy-β-D-glucopyranosyl]-β-D-galactopyranosyl}-6-*O*-benzyl-2-deoxy-β-D-glucopyranoside (26) and allyl 2-acetamido-4-*O*-{2,4,6-tri-*O*-acetyl-3-*O*-[4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-6-*O*-benzyl-2-chloroacetamido-2-deoxy-β-D-glucopyranosyl]-β-D-galactopyranosyl}-6-*O*-benzyl-2-deoxy-β-D-glucopyranoside (27): Tetrasaccharide **23** (65 mg, 0.042 mmol) was treated with Zn in AcOH as described for the synthesis of diol **25**. Column chromatography (CH_2Cl_2/MeOH = 60:1) gave *N*-chloroacetamido **27** (42 mg, 77%) pure as a colorless class, followed by *N*-acetamido **26** (5 mg, 11%) pure as a colorless glass. Data for **26**: $[\alpha]_D$ = –12 (*c* = 0.8, CH_2Cl_2). ^{1}H NMR (600 MHz, CD_3OD): δ = 7.38–7.16 (m, 10 H, Ar), 5.87 (m, 1 H, C*H*=CH$_2$), 5.42 (d, *J* = 3.7 Hz, 1 H, 4C-H), 5.35 (d, *J* = 2.2 Hz, 1 H, 4C′-H), 5.25 (m, 1 H, C*H*H=CH$_2$), 5.13 (m, 1 H, C*H*H=CH$_2$), 5.09–5.05 (m, 2 H, 2C′-H, 3C′-H), 5.01 (dd, *J* = 10.0, 8.2 Hz, 1 H, 2C-H), 4.75–4.66 (m, 3 H, 1C′-H, 2 C*H*HPh), 4.57 (d, *J* = 11.9 Hz, 1 H, C*H*HPh), 4.53–4.48 (m, 3 H, 1C-H, 1A-H, C*H*HPh), 4.41 (d, *J* = 8.5 Hz, 1 H, 1A′-H), 4.29 (m, 1 H, C*H*HCH=CH$_2$), 4.16–4.02 (m, 5 H, 6aC-H, 5C′-H, 6abC′-H, C*H*HCH=CH$_2$), 4.98 (dd, *J* = 11.5, 8.2 Hz, 1 H, 6bC-H), 3.90 (m,

1 H, 5C-H), 3.84 (dd, J = 10.1, 3.6 Hz, 1 H, 3C-H), 3.79–3.68 (m, 5 H, 2A′-H, 6abA-H, 6abA′-H), 3.66 (dd, J = 10.3, 8.5 Hz, 1 H, 3A-H), 3.60–3.51 (m, 4 H, 2A-H, 4A-H, 3A′-H, 4A′-H), 3.48 (m, 1 H, 5A′-H), 3.44 (m, 1 H, 5A-H), 2.03, 2.02, 1.96, 1.92, 1.89, 1.85, 1.84, 1.83 (9s, 27 H, 9 $COCH_3$) ppm. ^{13}C NMR (150 MHz, CD_3OD): δ = 173.5, 173.3, 172.3, 172.2, 171.9, 171.8, 171.3, 171.2, 171.0 (C=O), 139.8, 139.7 (quat. Ar), 135.5 (CH=CH_2), 129.7, 129.6, 129.5, 129.3, 129.1, 129.0, 128.9, 128.8, 128.7 (Ar), 117.1 (CH=CH_2), 103.1 (C-1A, C-1C), 102.2 (C-1C′), 101.8 (C-1A′), 81.8, 81.7 (C-4A, C-4A′), 78.2 (C-3C), 75.6, 75.5 (C-5A, C-5A′), 74.9, 74.7 (CH_2Ph), 74.0 (C-3A′), 73.1 (C-3A), 72.9 (C-5C), 72.3 (C-2C′ or C-3C′, C-5C′), 71.8 (C-2C), 71.2 (C-4C′), 70.9 (CH_2CH=CH_2), 70.4 (C-2C′ or C-3C′), 69.7, 69.4 (C-6A, C-6A′), 68.7 (C-4C′), 63.5 (C-6C), 62.6 (C-6C′), 57.1 (C-2A), 56.5 (C-2A′), 23.1, 22.9, 21.3, 20.8 ($COCH_3$) ppm. HRMS: calcd. for $C_{59}H_{78}N_2O_{28}$ [M + H]$^+$ 1263.4820; found 1263.4814. Data for **27**: $[\alpha]_D$ = –7 (c = 1.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41–7.22 (m, 10 H, Ar), 6.53 (d, J = 7.6 Hz, 1 H, NHA′), 5.85 (m, 1 H, CH=CH_2), 5.55 (d, J = 8.0 Hz, 1 H, NHA), 5.33 (d, J = 3.4 Hz, 2 H, 4C-H, 4C′-H), 5.24 (m, 1 H, CH=CH), 5.18–5.12 (m, 2 H, 2C′-H, CH=CH_2), 5.07 (dd, J = 10.0, 8.5 Hz, 1 H, 2C-H), 4.93 (dd, J = 10.4, 3.4 Hz, 1 H, 3C′-H), 4.87 (d, J = 8.0 Hz, 1 H, 1A′-H), 4.72–4.66 (m, 3 H, 1A-H, 2 CHHPh), 4.54–4.47 (m, 3 H, 1C′-H, 2 CHHPh), 4.33–4.27 (m, 2 H, 1C-H, CHHCH=CH_2), 4.20–3.89 (m, 12 H, 3A-H, 5C-H, 6abC-H, 3A′-H, 6abC′-H, 2 OH, CH_2Cl, CHHCH=CH_2), 3.76–3.43 (m, 11 H, 6abA-H, 2A-H, 4A-H, 5A-H, 3C-H, 4A′-H, 5A′-H, 6abA′-H, 5C′-H), 3.24 (m, 1 H, 2A′-H), 2.14, 2.13, 2.05, 2.02, 1.99, 1.97 (8s, 24 H, 8 $COCH_3$) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.6, 170.4, 170.1, 170.0, 169.9, 169.3, 169.2, 166.1 (C=O), 138.2, 138.1 (quat. Ar), 133.8 (CH=CH_2), 128.5, 128.4, 128.3, 127.9, 127.8, 127.7, 127.6, 127.3 (Ar), 117.5 (CH=CH_2), 101.4 (C-1C′), 101.2 (C-1C), 99.9 (C-1A′), 99.2 (C-1A), 81.4, 81.1 (C-4A, C-4A′), 76.0 (C-3C), 74.0 (C-5A, C-5A′), 73.6 (2 CH_2Ph), 71.7, 71.6 (C-5C, C-5C′), 71.2 (C-3A), 70.6 (C-3A′), 70.5 (C-3C′), 70.4 (C-2C), 69.7 (CH_2CH=CH_2), 69.0 (C-4C), 68.7 (C-2C′), 68.0, 67.9 (C-6A, C-6A′), 66.8 (C-4C′), 62.2, 61.5 (C-6C, C-6C′), 57.5 (C-2A′), 56.5 (C-2A), 42.6 (CH_2Cl), 23.6, 21.0, 20.7, 20.6, 20.5 ($COCH_3$) ppm. HRMS: calcd. for $C_{59}H_{77}ClN_2O_{28}$ [M + H]$^+$ 1297.4430; found 1297.4443.

Allyl 2-Acetamido-4-*O*-{2,4,6-tri-*O*-acetyl-3-*O*-[4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-chloroacetamido-2-deoxy-β-D-glucopyranosyl]-β-D-galactopyranosyl}-6-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-deoxy-β-D-glucopyranoside (29); allyl 2-acetamido-4-*O*-{2,4,6-tri-*O*-acetyl-3-*O*-[4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-chloroacetamido-2-deoxy-β-D-glucopyranosyl]-β-D-galactopyranosyl}-6-*O*-benzyl-2-deoxy-β-D-glucopyranoside (31); and allyl 2-acetamido-4-*O*-{2,4,6-tri-*O*-acetyl-3-*O*-[4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-*O*-benzyl-2-chloroacetamido-2-deoxy-β-D-glucopyranosyl]-β-D-galactopyranosyl}-6-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-deoxy-β-D-glucopyranoside (33)

Method 1: A mixture of acceptor **25** (20 mg, 0.015 mmol), thioglycoside **28**[14] (11 mg, 0.023 mmol, 1.5 equiv.) and activated powdered 4 Å molecular sieves (0.1 g) in CH_2Cl_2 (2 mL) was stirred for 1 h at room temperature under an atmosphere of N_2 and then cooled to 0 °C. NIS (6 mg, 1.7 equiv.) and 10 μL of a 50 μL/mL solution of TMSOTf in CH_2Cl_2 (0.5 μL of TMSOTf, 0.003 mmol, 0.2 equiv.) were added, and the mixture was stirred at 0 °C for 1.5 h. More NIS (15 mg, 4.5 equiv.) followed by a solution of donor **28** (32 mg, 0.067 mmol, 4.5 equiv.) in CH_2Cl_2 (1 mL) were added, and the reaction was allowed to proceed for an additional 2 h at room temperature. The reaction was quenched with Et_3N (2 μL), the mixture was filtered through Celite, and the solids were washed with CH_2Cl_2 (15 mL). The combined filtrate and washing were washed with 20% $Na_2S_2O_3$ (15 mL), and the aqueous layer was re-extracted with CH_2Cl_2 (15 mL). The combined organic layers were dried, filtered, and concentrated. Flash chromatography (EtOAc/hexanes = 1:1) gave first semipure hexasaccharide **29** (13 mg, ca. 85% pure as assessed by ^{1}H NMR, 35%) followed by a mixture of pentasaccharides **31** and **33**. Flash chromatography (EtOAc/hexanes = 6:4) on the pentasaccharide mixture gave first pentasaccharide **33** (6.2 mg, ca. 85% pure as assessed by ^{1}H NMR, 21%) followed by pure pentasaccharide **31** (1.5 mg, 6%). Both hexasaccharide **29** and pentasaccharide **33** were obtained pure after RP HPLC (CH_3CN/ H_2O = 60:40 → 100:0).

Method 2: A mixture of acceptor **25** (24 mg, 0.019 mmol), thioglycoside **28** (35 mg, 0.074 mmol, 4.0 equiv.) and activated powdered 4 Å molecular sieves (100 mg) in CH_2Cl_2 (2 mL) was stirred for 2 h at room temperature under an atmosphere of N_2. NIS (21 mg, 5.0 equiv.) and 10 μL of a 100 μL/mL solution of TMSOTf in CH_2Cl_2 (1 μL of TMSOTf, 0.005 mmol, 0.3 equiv.) were added, and the mixture was stirred at room temperature for 40 min. Additional donor **28** (9 mg, 1 equiv.) was added to the mixture and the reaction was allowed to proceed for an additional 20 min. The reaction was quenched and worked up as described above in Method 1. A first chromatography (CH_2Cl_2/MeOH = 50:1) of the crude residue gave a mixture of hexa- and pentasaccharides (45 mg), which were submitted to a second flash chromatography (EtOAc/hexanes = 6:4) to give first semipure hexasaccharide **29** (20 mg, ca. 85% pure as assessed by ^{1}H NMR, 43%) followed by pure pentasaccharide **33** (6 mg, 20%). Hexasaccharide **29** was obtained pure as a colorless glass by RP HPLC (CH_3CN/H_2O = 60:40 → 100:0).

29: $[\alpha]_D$ = –3 (c = 0.6, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.43–7.10 (m, 40 H, Ar), 6.52 (d, J = 8.6 Hz, 1 H, NHA′), 6.01 (d, J = 8.9 Hz, 1 H, NHA), 5.77 (m, 1 H, CH=CH_2), 5.34 (d, J = 3.5 Hz, 1 H, 4C-H), 5.24 (m, 1 H, CH=CHH), 5.11–5.07 (m, 3 H, 1B-H, 1B′-H, CH=CHH), 5.15 (t, J = 9.4 Hz, 1 H, 3C′-H), 4.99 (dd, J = 9.8, 8.5 Hz, 1 H, 2C-H), 4.96–4.91 (m, 3 H, 1A′-H, 2 CHHPh), 4.88 (t, J = 9.8 Hz, 1 H, 4C′-H), 4.85–4.68 (m, 12 H, 1A-H, 1C′-H, 2C′-H, 4 CH_2Ph, CHHPh), 4.66–4.62 (m, 2 H, 2 CHHPh), 4.58–4.48 (m, 4 H, 5B-H, CH_2Ph, CHHPh), 4.42 (dd, J = 12.7, 4.2 Hz, 1 H, 6aC′-H), 4.38 (d, J = 12.1 Hz, 1 H, CHHPh), 4.36 (d, J = 8.1 Hz, 1 H, 1C-H), 4.19–4.10 (m, 4 H, 6aC-H, 3A′-H, 5B′-H, CHHCH=CH_2), 4.10–4.04 (m, 3 H, 3A-H, 2B-H, 2B′-H), 4.02–3.77 (m, 10 H, 4A-H, 6aA-H, 3B-H, 6bC-H, 4A′-H, 6aA′-H, 3B′-H 6bC′-H, CHHCH=CH_2, CHHCl), 3.77–3.64 (m, 6 H, 2A-H, 6bA-H, 4B-H or 4B′-H, 3C-H, 6bA′-H, CHHCl), 3.62–3.55 (m, 3 H, 5A-H, 4B-H or 4B′-H, 5C-H), 3.44 (m, 1 H, 2A′-H), 3.39 (m, 1 H, 5A′-H), 3.34 (m, 1 H, 5C′-H), 1.98, 1.97, 1.95, 1.94, 1.90, 1.85, 1.81 (7s, 24 H, 8 $COCH_3$), 1.20 (d, J = 6.5 Hz, 3 H, 6B′-H), 1.09 (d, J = 6.4 Hz, 3 H, 6B-H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.3, 170.2, 170.1, 169.8, 169.5, 168.7, 166.0 (C=O), 138.9, 138.8, 138.7, 138.6, 138.1, 137.9 (quat. Ar), 133.9 (CH=CH_2), 128.6, 128.4, 128.3, 128.2, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 126.9 (Ar), 117.0 (CH_2=CH), 99.4 (C-1A, C-1C), 99.1 (C-1A′), 98.6 (C-1C′), 97.5, 97.0 (C-1B, C-1B′), 79.7, 79.5 (C-3B, C-3B′), 78.1 (C-3C), 77.2 (C-4B or C-4B′), 76.4, 76.3 (C-2B, C-2B′), 75.2 (C-5A′), 75.0 (C-4B or C-4B′), 74.8 (C-4A or C-4A′), 74.7, 74.5 (CH_2Ph), 74.0, 73.9 (C-3A′), 73.9 (C-5A), 73.7 (C-4A or C-4A′), 73.5, 73.4, 73.2 (CH_2Ph), 73.0 (C-3C′), 72.8 (C-3A), 72.7 (CH_2Ph), 72.0 (C-5C′), 71.3, 71.2 (C-5C, C-2C′), 70.8 (C-2C), 69.4 (CH_2CH=CH_2), 69.0 (C-6A′), 68.8 (C-4C), 67.8 (C-4C′), 67.6 (C-6A), 66.7, 66.5 (C-5B, C-5B′), 61.6, 61.5 (C-6C, C-

6C′), 58.4 (C-2A′), 53.2 (C-2A), 42.4 (CH_2Cl), 23.2, 21.0, 20.7, 20.6 ($CO\mathit{C}H_3$), 16.7, 16.6 (C-6B, C-6B′) ppm. HRMS: calcd. for $C_{113}H_{133}N_2ClO_{36}$ [M + H]$^+$ 2129.8410; found 2129.8398.

31: $[\alpha]_D$ = –6 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.43–7.11 (m, 25 H, Ar), 6.58 (d, *J* = 7.4 Hz, 1 H, NHA′), 5.85 (m, 1 H, C*H*=CH_2), 5.52 (d, *J* = 8.0 Hz, 1 H, NHA), 5.31 (d, *J* = 3.5 Hz, 1 H, 4C-H), 5.24 (m, 1 H, C*H*H=CH_2), 5.16 (m, 1 H, C*H*H=CH_2), 5.11–5.05 (m, 2 H, 2C-H, 1B′-H), 5.02–4.96 (m, 2 H, 1A′-H, 3C′-H), 4.94 (d, *J* = 11.4 Hz, 1 H, C*H*HPh), 4.88 (t, *J* = 9.8 Hz, 1 H, 4C′-H), 4.86–4.79 (m, 2 H, 2C′-H, C*H*HPh), 4.78–4.73 (m, 2 H, 2 C*H*HPh), 4.72–4.63 (m, 5 H, 1A-H, 1C′-H, 3 C*H*HPh), 4.58–4.46 (m, 4 H, 5B′-H, 3 C*H*HPh), 4.43 (dd, *J* = 12.5, 4.1 Hz, 1 H, 6aC′-H), 4.34–4.27 (m, 2 H, 1C-H, C*H*HCHCH$_2$), 4.18–4.12 (m, 2 H, 6aC-H, 3A′-H), 4.09 (dd, *J* = 10.1, 3.7 Hz, 1 H, 2B′-H), 4.05 (m, 1 H, C*H*HCHCH$_2$), 3.99 (br. t, *J* = 8.7 Hz, 1 H, 4A′-H), 3.97–3.87 (m, 3 H, 3A-H, 3B′-H, H6bC), 3.86–3.78 (m, 3 H, 6aA′-H, 6bC′-H, CHCl), 3.76–3.69 (m, 4 H, 3C-H, 5C-H, 6bA′-H, CHCl), 3.68–3.58 (m, 3 H, 6abA-H, 4B′-H), 3.56 (br. t, *J* = 8.7 Hz, 1 H, 4A-H), 3.51 (m, 1 H, 2A-H), 3.47 (m, 1 H, 5A-H), 3.46–3.38 (m, 2 H, 2A′-H, 5A′-H), 3.33 (m, 1 H, 5C′-H), 2.06, 2.02, 1.98, 1.97, 1.92, 1.85 (8s, 24 H, 8 $COCH_3$), 1.20 (d, *J* = 6.5 Hz, 3 H, 6B′-H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.6, 170.4, 170.3, 170.2, 169.5, 169.4, 168.7, 166.0 (C=O), 138.6, 138.2, 137.8 (quat. Ar), 133.8 (*C*H=CH_2), 128.2, 128.1, 127.9, 127.6, 127.4, 127.2 (Ar), 117.6 (CH=*C*H$_2$), 101.3 (C-1C), 99.5, 99.3, 99.2 (C-1A, C-1A′ C-1C′), 97.5 (C-1B′), 81.2 (C-4A), 79.8 (C-3B′), 78.1 (C-4B′), 76.5 (C-2B′), 75.4 (C-3C), 75.1 (C-5A′), 74.8 (C-4A′, *C*H$_2$Ph), 74.1 (C-5A, C-3A′), 73.6, 73.5, 73.4 (*C*H$_2$Ph), 73.0 (C-3C′), 72.6 (*C*H$_2$Ph), 72.0 (C-5C′), 71.8, 71.7 (C-3A, C-5C), 71.3 (C-2C′), 70.5 (C-2C), 69.8 (*C*H$_2$CH=CH$_2$), 68.8 (C-4C), 68.1 (C-6A), 67.8 (C-4C′), 67.6 (C-6A′), 66.6 (C-5B′), 62.3 (C-6C), 61.5 (C-6C′), 58.5 (C-2A′), 56.5 (C-2A), 42.4 (CH_2Cl), 23.6, 21.0, 20.7, 20.6 ($CO\mathit{C}H_3$), 16.7 (C-6B′) ppm. HRMS: calcd. for $C_{86}H_{105}ClN_2O_{32}$ [M + H]$^+$ 1713.6426; found 1713.6417.

33: $[\alpha]_D$ = –8 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42–7.10 (m, 25 H, Ar), 6.48 (d, *J* = 7.7 Hz, 1 H, NHA′), 5.95 (d, *J* = 8.0 Hz, 1 H, NHA), 5.78 (m, 1 H, C*H*=CH), 5.35 (d, *J* = 3.5 Hz, 1 H, 4C-H), 5.23 (m, 1 H, C*H*H=CH), 5.14 (t, *J* = 9.5 Hz, 1 H, 3C′-H), 5.09 (m, 1 H, C*H*HCH$_2$), 5. 07 (d, *J* = 3.7 Hz, 1 H, 1B-H), 5.01–4.90 (m, 4 H, 2C-H, 2C′-H, 4C′-H, C*H*HPh), 4.84–4.66 (m, 7 H, 1A-H, 1A′-H, 2 C*H*$_2$Ph C*H*HPh), 4.64 (d, *J* = 11.8 Hz, 1 H, C*H*HPh), 4.58–4.45 (m, 3 H, 1C-H, 2 C*H*HPh), 4.38 (d, *J* = 12.1 Hz, 1 H, C*H*HPh), 4.46 (d, *J* = 8.1 Hz, 1 H, 1C′-H), 4.22–4.06 (m, 7 H, 3A-H, 6aC-H, 6abC′-H, 2B-H, 5B-H, C*H*HCH=CH$_2$), 4.03–3.79 (m, 8 H, 6aA-H, 6bC-H, 3A′-H, 4A-H, 3B-H, O-C*H*HCH=CH$_2$, CH_2Cl), 3.75 (dd, *J* = 10.3, 3.9 Hz, 1 H, 6bA-H), 3.71–3.52 (m, 9 H, 2A-H, 4A′-H, 5A-H, 4B-H, 3C-H, 5C-H, 6abA′-H, 5C′-H), 3.47 (m, 1 H, 5A′-H), 3.25 (m, 1 H, 2A′-H), 2.05, 2.02, 1.98, 1.96, 1.90, 1.78 (8s, 24 H, 8 $COCH_3$), 1.10 (d, *J* = 6.5 Hz, 3 H, 6B-H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.5, 170.2, 170.1, 170.0, 169.8, 169.6, 169.3, 169.1, 166.1 (C=O), 138.9, 138.8, 138.5, 138.1, 138.0, 136.3 (quat. Ar), 133.9 (C*H*=CH_2), 128.5, 128.4, 127.9, 127.8, 127.5, 127.3 (Ar), 117.1 (C*H*$_2$=CH), 101.0 (C-1C or C-1C′), 99.8 (C-1A′), 99.4 (C-1C or C-1C′), 98.6 (C-1A), 97.0 (C-1B), 81.4 (C-4A′), 81.3 (C-4), 79.7 (C-3B), 77.1 (C-4B), 76.3 (C-2B), 75.6 (C-3C), 74.5 (*C*H$_2$Ph), 74.1, 74.0 (C-5A, C-5A′), 73.8 (C-4A), 73.7, 73.4, 73.3 (*C*H$_2$Ph), 72.9 (C-3A), 72.6 (*C*H$_2$Ph), 72.5 (C-3C′), 72.0 (C-5C), 71.1, 71.0, 70.7, 70.6 (C-2C, C-3A′, C-2C′, C-5C′), 69.5 (*C*H$_2$CH=CH$_2$), 69.0 (C-4C), 68.6 (C-6A or C-6A′), 68.2 (C-4C′), 67.8 (C-6A or C-6A′), 66.6 (C-5B), 61.8, 61.5 (C-6C, C-6C′), 57.4 (C-2A′), 54.1 (C-2A), 42.6 (CH_2Cl), 23.2, 21.0, 20.7, 20.6, 20.5 ($CO\mathit{C}H_3$), 16.6 (C-6B) ppm. HRMS: calcd. for $C_{86}H_{105}ClN_2O_{32}$ [M + H]$^+$1713.6447; found 1713.6417.

Allyl 2-Acetamido-4-*O*-{2,4,6-tri-*O*-acetyl-3-*O*-[4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-6-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-chloroacetamido-2-deoxy-β-D-glucopyranosyl]-β-D-galactopyranosyl}-6-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-deoxy-β-D-glucopyranoside (30); allyl 2-acetamido-4-*O*-{2,4,6-tri-*O*-acetyl-3-*O*-[4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-6-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-chloroacetamido-2-deoxy-β-D-glucopyranosyl]-β-D-galactopyranosyl}-6-*O*-benzyl-2-deoxy-β-D-glucopyranoside (32); and Allyl 2-Acetamido-4-*O*-{2,4,6-tri-*O*-acetyl-3-*O*-[4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-6-*O*-benzyl-2-chloroacetamido-2-deoxy-β-D-glucopyranosyl]-β-D-galactopyranosyl}-6-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-deoxy-β-D-glucopyranoside (33): Alcohol **27** (42 mg, 0.032 mmol) was coupled to donor **28** (77 mg, 0.16 mmol, 5.0 equiv.) in CH_2Cl_2 (3.5 mL) at room temperature as described above in Method 2 for the preparation of hexasaccharide **29**. Column chromatography of the residue (EtOAc/hexanes = 4:6 → 7:3) gave hexasaccharide **30** contaminated with succinimide (37 mg) followed by a mixture containing pentasaccharides **32** and **34** (14 mg, 25%). Additional purification of the hexasaccharide was achieved using RP HPLC (60:40 → 100:0 CH_3CN/H_2O) to give **30** pure as a colorless glass (33 mg, 48%). RP HPLC (60:40 → 100:0 CH_3CN/H_2O) provided pure pentasaccharides **34** (7 mg, 13%) and **32** (5 mg, 9%). Data for **30**: $[\alpha]_D$ = –9 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42–7.15 (m, 40 H, Ar), 6.50 (d, *J* = 7.6 Hz, 1 H, NHA′), 6.01 (d, *J* = 8.2 Hz, 1 H, NHA), 5.77 (m, 1 H, C*H*=CH_2), 5.35 (d, *J* = 3.6 Hz, 1 H, 4C-H), 5.27–5.21 (m, 2 H, 4C′-H, C*H*H=CH$_2$), 5.12–5.08 (m, 3 H, 1B-H, 1B′-H, C*H*H=CH$_2$), 5.03–4.98 (m, 3 H, 1A′-H, 2C-H, 2C′-H), 4.97–4.93 (br. d, 2 H, 2 C*H*HPh), 4.85–4.59 (m, 15 H, 1A-H, 5B-H or 5-B′-H, 1C′-H, 3C′-H, 4 C*H*$_2$Ph, 3 C*H*HPh), 4.55 (d, *J* = 11.9 Hz, 1 H, C*H*HPh), 4.51 (d, *J* = 12.0 Hz, 1 H, C*H*HPh), 4.41 (d, *J* = 12.0 Hz, 1 H, C*H*HPh), 4. 38 (d, *J* = 8.1 Hz, 1 H, 1C-H), 4.23–4.08 (m, 8 H, 3A-H, 2B-H, 5B-H or 5B′-H, 6aC-H, 3A′-H, 2B′-H, 6aC′-H, C*H*HCH=CH$_2$), 4.02–3.78 (m, 10 H, 4A-H, 6aA-H, 3B-H, 6bC-H, 4A′-H, 6aA′-H, 3B′-H, 6bC′-H, C*H*HCl, C*H*HCH=CH$_2$), 3.78–3.73 (m, 4 H, 2A-H, 6bA-H, 6bA′-H, C*H*HCl), 3.71–3.67 (m, 2 H, 3C-H, 4B-H or 4B′-H), 3.62–3.54 (m, 4 H, 5A′-H, 4B-H or 4B′-H, 5C-H, 5C′-H), 3.44–3.35 (m, 2 H, 2A′-H, 5A-H), 1.99, 1.98, 1.96, 1.94, 1.90, 1.82 (8s, 24 H, 8 $COCH_3$), 1.20, 1.10 (2d, *J* = 6.5 Hz, 6 H, 6B-H, 6B′-H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.3, 170.1, 170.0, 169.8, 168.8, 166.1 (C=O), 138.9, 138.8, 138.7, 138.6, 138.2, 137.9 (quat. Ar), 134.0 (*C*H=CH$_2$), 127.4, 127.3 (Ar), 117.1 (*C*H$_2$=CH), 99.7 (C-1C′), 99.5 (C-1C), 99.1 (C-1A′), 98.6 (C-1A), 97.6, 97.0 (C-1B, C-1B′), 80.1, 79.6 (C-3, C-3B′), 77.0, 76.8 (4B, 4B′), 76.3, 75.9 (C-2B, C-2B′), 75.3 (C-5A), 75.1 (C-3C), 74.5 (*C*H$_2$Ph), 74.3 (C-4A or C-4A′), 74.2 (*C*H$_2$Ph), 74.0 (C-5A′), 73.7 (C-4A or C-4A′), 73.6, 73.5, 73.4, 73.2 (*C*H$_2$Ph), 73.2 (C-3A′), 72.8 (C-3A), 72.7, 72.5 (2 *C*H$_2$Ph), 71.2 (C-5C or C-5C′), 70.8 (C-3C′, C-2C or C-2C′), 70.4 (C-5C or C-5C′), 69.4 (*C*H$_2$CH=CH$_2$), 69.0 (C-6A or C-6A′), 68.9, 68.8 (C-2C or C-2C′, C-4C), 67.5 (C-6A or C-6A′), 66.6 (C-5B or C-5B′, C-4C′), 66.4 (C-5B or C-5B′), 61.6, 60.1 (C-6C, C-6C′), 58.7 (C-2A′), 53.1 (C-2A), 42.4 (CH_2Cl), 23.2, 21.1, 20.7 ($CO\mathit{C}H_3$), 16.7, 16.6 (C-6B, C-6B′) ppm. HRMS: calcd. for $C_{113}H_{133}N_2ClO_{36}$ [M + H]$^+$ 2129.8410; found 2129.8379. Data for **32**: $[\alpha]_D$ = –9 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42–7.21 (m, 25 H, Ar), 6.52 (d, *J* = 7.4 Hz, 1 H, NHA′), 5.85 (m, 1 H, C*H*=CH$_2$), 5.50 (d, *J* = 8.0 Hz, 1 H, NHA), 5.31 (d, *J* = 3.5 Hz, 1 H, 4C-H), 5.27–5.22 (m, 2 H, 4C′-H, C*H*H=CH), 5.15 (m, 1 H, C*H*H=CH), 5.09 (dd, *J* = 9.8, 8.3 Hz, 1 H, 2C-H), 5.06 (d, *J* = 3.7 Hz, 1 H, 1B′-H), 5.01 (br. d, *J* = 7.8 Hz, 1 H, 1A′-H), 4.98 (d, *J* = 10.3, 8.3 Hz, 1 H, 2C′-H), 4.93 (d, *J* = 11.8 Hz, 1 H, C*H*HPh), 4.85 (d, *J* = 12.0 Hz, 1 H, C*H*HPh), 4.81–

4.56 (m, 9 H, 1A-H, 1C′-H, 3C′-H, 6 C*H*HPh), 4.59 (m, 1 H, 5B′-H), 4.51–4.36 (m, 2 H, 2 C*H*HPh), 4.34–4.26 (m, 2 H, 1C-H, C*H*HCH=CH_2), 4.20–3.85 (m, 10 H, 3A-H, 4A′-H, 6abC-H, 3A′-H, 2B′-H, 3B′-H, 6abC′-H, C*H*HCH_2=CH_2), 3.85–3.44 (m, 13 H, 2A-H, 5A-H, 6abA-H, 3C-H, 5C-H, 6abA′-H, 4A-H, 4B′-H, 5C′-H, CH_2Cl), 3.38 (m, 2 H, 2A′-H, 5A′-H), 2.06, 2.01, 1.99, 1.98, 1.93, 1.92, 1.81, 1.56 (8s, 24 H, 8 $COCH_3$), 1.19 (d, J = 6.5 Hz, 3 H, 6B′-H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.6, 170.4, 170.1, 170.0, 169.8, 169.4, 168.8, 166.0 (C=O), 138.7, 138.5, 138.3, 137.8 (quat. Ar), 133.8 (*C*H=CH_2), 128.6, 128.4, 128.2, 128.1, 127.7, 127.6, 127.3, 127.1, 127.0 (Ar), 117.6 (*C*H_2=CH), 101.3 (C-1C), 99.7 (C-1C′), 99.3 (C-1A), 99.1 (C-1A′), 97.6 (C-1B), 81.2 (C-4A), 80.1 (C-3B′), 77.0 (C-4B′), 76.0 (C-2B′), 75.4 (C-3C), 75.2 (C-5A′), 74.3 (*C*H_2Ph), 74.2 (C-4A′), 74.1 (C-5A), 73.6, 73.6, 73.4 (3 *C*H_2Ph), 73.3 (C-3A′), 72.5 (*C*H_2Ph), 71.8, 77.7 (C-3A′, C-5C or C-5C′), 70.8 (C-3C′), 70.6 (C-2C), 70.4 (C-5C or C-5C′), 69.8 (O*C*H_2CH=CH_2), 68.8 (C-4C, C-2C′), 68.1, 67.5 (C-6A, C-6A′), 66.7 (C-4C′), 66.3 (C-5B′), 62.3, 60.1 (C-6C, C-6C′), 58.9 (C-2A′), 56.5 (C-2A), 42.4 (CH_2Cl), 23.6, 21.0, 20.7, 20.6, 20.5 (CO*C*H_3), 16.7 (C-6B′) ppm. HRMS: calcd. for $C_{86}H_{105}ClN_2O_{32}$ [M + H]$^+$ 1713.6417; found 1713.6384. Data for **34**: $[\alpha]_D$ = –13 (c = 0.4, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41–7.12 (m, 25 H, Ar), 6.49 (d, J = 7.7 Hz, 1 H, NHA′), 5.95 (d, J = 8.0 Hz, 1 H, NHA), 5.79 (m, 1 H, C*H*=CH_2), 5.36 (d, J = 3.6 Hz, 1 H, 4C-H), 5.34 (d, J = 3.6 Hz, 1 H, 4C′-H), 5.22 (m, 1 H, CH=C*H*H), 5.16 (dd, J = 10.4, 8.0 Hz, 1 H, 2C′-H), 5.09 (m, 1 H, CH=C*H*H), 5.08 (d, J = 3.7 Hz, 1 H, 1B′-H), 4.99–4.91 (m, 3 H, 2C-H, 3C′-H, C*H*HPh), 4.86–4.69 (m, 7 H, 1A-H, 1A′-H, 5 C*H*HPh), 4.64 (d, J = 11.8 Hz, 1 H, C*H*HPh), 4.57 (d, J = 12.0 Hz, 1 H, C*H*HPh), 4.53 (d, J = 12.1 Hz, 1 H, C*H*HPh), 4.50 (d, J = 8.0 Hz, 1 H, 1C′-H), 4.39 (d, J = 12.3 Hz, 1 H, C*H*HPh), 4.36 (d, J = 8.4 Hz, 1 H, 1C-H), 4.23–4.15 (m, 1 H, 5B-H, C*H*HCH=CH_2), 4.14–4.04 (m, 5 H, 3A-H, 2B-H, 6abC-H or 6abC′-H, 6aC-H or 6aC′-H), 4.03–3.82 (m, 9 H, 4A-H, 6aA-H, 3B-H, 5C-H, 6bC-H or 6bC′-H, 3A′-H, CH_2Cl, C*H*HCH=CH_2), 3.75 (dd, J = 10.4, 3.9 Hz, 2 H, 6bA-H), 3.69–3.51 (m, 8 H, 2A-H, 5A-H, 4B-H, 3C-H, 4A′-H, 6abA′-H, 5C′-H), 3.49 (m, 1 H, 5A′-H), 3.24 (m, 1 H, 2A′-H), 2.13, 2.03, 2.01, 1.97, 1.96, 1.90, 1.78 (8s, 24 H, 8 $COCH_3$), 1.10 (d, J = 6.5 Hz, 3 H, 6B-H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.5, 170.3, 170.2, 170.1, 170.0, 169.8, 169.6, 169.3, 166.1 (C=O), 138.9, 138.6, 138.2, 138.1 (quat. Ar), 134.0 (*C*H=CH_2), 128.6, 128.4, 127.9, 127.8, 127.7, 127.6, 127.4 (Ar), 117.1 (CH=*C*H_2), 101.5 (C-1C′), 99.9 (C-1A or C-1A′), 99.4 (C-1C), 98.6 (C-1A or C-1A′), 97.1 (C-1B), 81.5 (C-4A′), 79.7 (C-3B), 76.9 (C-4B), 76.3 (C-2B), 75.7 (C-3C), 74.5 (*C*H_2Ph), 74.2, 74.1, 73.8 (C-5A, C-4A, C-5A′), 73.7, 73.4, 73.3 (3 *C*H_2Ph), 72.9 (C-3A), 72.6 (*C*H_2Ph), 71.3, 71.1, (C-5C, C-5C′), 70.7, 70.6 (C-2C, C-3A′, C-3C′), 69.5 (*C*H_2CH=CH_2), 69.0 (C-4C), 68.7 (C-2C′), 68.0 (C-6A, C-6A′), 66.8 (C-4C′), 66.6 (C-5B), 61.6, 61.5 (C-6C, C-6C′), 57.5 (C-2A′), 54.0 (C-2A), 42.7 (CH_2Cl), 23.2, 21.1, 20.8, 20.7, 20.6 (CO*C*H_3), 16.6 (C-6B) ppm. HRMS: calcd. for $C_{86}H_{105}ClN_2O_{32}$ [M + Na]$^+$ 1735.6237; found 1735.6288.

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H and ^{13}C NMR spectra for compounds **2**–**5**, **12**–**14**, **16**, **17**, **20**–**27**, and **29**–**34**.

Acknowledgments

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