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J. Org. Chem., **Just Accepted Manuscript** • Publication Date (Web): 25 Sep 2012

Just Accepted

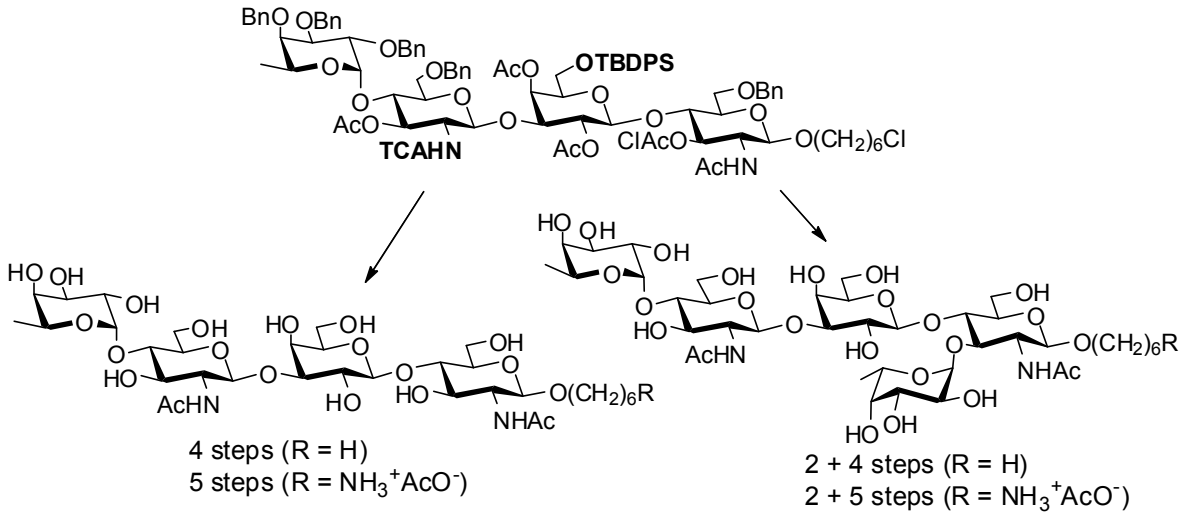
The Journal of Organic Chemistry is published by the American Chemical Society.
1155 Sixteenth Street N.W., Washington, DC 20036

Challenging Deprotection Steps During the Synthesis of Tetra- and Pentasaccharide Fragments of the Le^aLe^x Tumor-Associated Hexasaccharide Antigen

*Mickaël Guillemineau, France-Isabelle Auzanneau**

Department of Chemistry, University of Guelph, Guelph, Ontario, N1G 2W1 Canada.

fauzanne@uoguelph.ca



Abstract

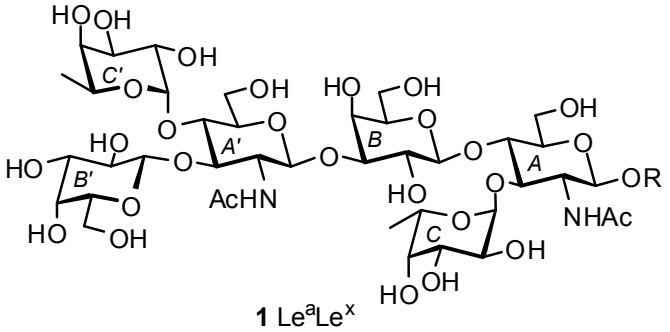
We report the convergent synthesis of two novel tetrasaccharide and two novel pentasaccharide fragments of the Le^aLe^x TACA: the tetrasaccharides contain neither the galactose at the Le^a non-reducing end nor the fucose at the Le^x reducing end; the pentasaccharides only lack the galactose residue at the Le^a non-reducing end. Two of the analogues were prepared as hexyl glycosides to be used in NMR experiments and as soluble

inhibitors in binding studies, and two as 6-aminohexyl glycosides to be conjugated to carrier proteins. Our strategy relied on stepwise extensions using excess monosaccharide glycosyl donors (trichloroacetimidates and thioglycosides) in sequential glycosylation reactions. The protecting groups were chosen to limit the number of deprotection steps required to obtain the final derivatives. While this strategy ensured that all glycosylation reactions proceeded in very good yields (70–84%), deprotection of the oligosaccharide intermediates was challenging. Global deprotection using Birch metal dissolving conditions did not remove the *t*-butyldiphenylsilyl group which indeed was incompatible with such reaction conditions. Attempts to remove the TBDPS with tetrabutylammonium fluoride was unsuccessful and led to a complex mixture of compounds that could not be separated. The desired hexyl and aminohexyl tetrasaccharides were finally obtained after 4 and 5 steps deprotection sequences, respectively. Deprotection of the pentasaccharide intermediate to give the hexyl and aminohexyl analogues also led to unexpected results. Indeed, during Zemplén deacylation, a chloroacetamide chlorine atom was displaced by methoxide ions leading to the corresponding methoxyacetamide. Once the chloroacetamide was fully reduced to an acetamide the pentasaccharides were obtained in 4 and 5 steps, respectively.

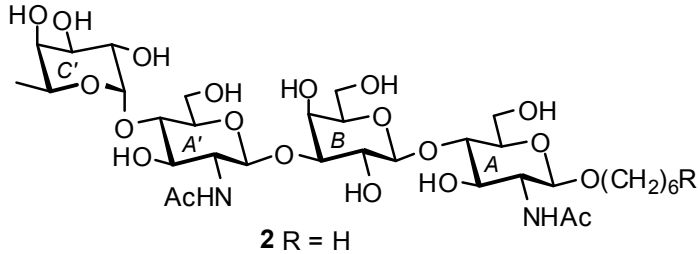
Introduction

Targeting tumor-associated carbohydrate antigens (TACAs) to develop anti-cancer vaccines is an area of intensive research and the advances made in this exciting field have been recently summarized in multiple reviews.[1] Even though the TACA Le^aLe^x hexasaccharide (**1**) has long been associated with lung cancer and particularly squamous lung carcinoma,[2] it has yet to be used in the development of anti-cancer vaccines. In this context, our research aims at

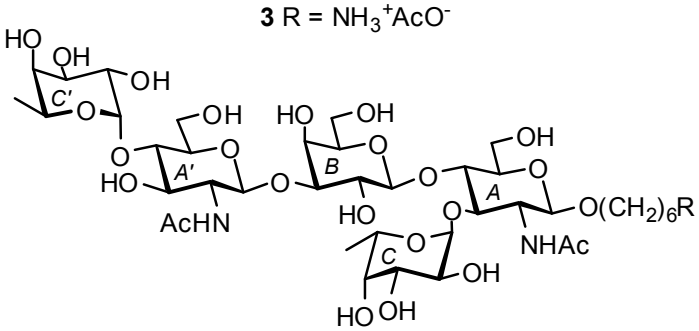
discovering a therapeutic anti-cancer vaccine based on the Le^aLe^x hexasaccharide. Unfortunately, while the expression of the Le^aLe^x hexasaccharide is highly localized to squamous lung carcinoma (SLC) cells, it has been well-established that the Le^a trisaccharide expressed at the non-reducing end of this large structure was displayed at the surface of many non-cancerous cells.[2a,3] Thus, immunization with the Le^aLe^x TACA will likely trigger an immune response against the Le^a trisaccharide and, in turn, lead to the destruction of numerous healthy cells. Most important to our program is the work by Olsson *et al.* who after immunization of mice with SLC cells cloned a monoclonal antibody named 43-9F which was shown to specifically recognize Le^aLe^x while it only weakly bound to the Le^a trisaccharide.[2a-c] Such finding supports that the Le^aLe^x TACA displays internal epitopes that do not involve the Le^a trisaccharide and that can therefore be targeted for anti-cancer vaccine development. In search of truncated structures that would retain internal epitopes such as that recognized by mAb 43-9F but no-longer carry the Le^a trisaccharide, we report here the preparation of tetra- and pentasaccharides **2**–**5**. Tetrasaccharides **2** and **3** contain neither the galactose moiety at the Le^a non-reducing end nor the fucose moiety at the Le^x reducing end,



1 Le^aLe^x



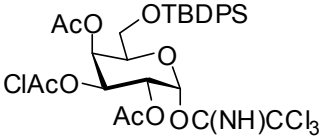
2 R = H
3 R = $NH_3^+AcO^-$



4 R = H
5 R = $NH_3^+AcO^-$

while pentasaccharides **4** and **5** only lack the galactose residue at the Le[a] non-reducing end. While analogues **2** and **4** were obtained as hexyl glycosides to be used in NMR experiments and binding studies, derivatives **3** and **5** were prepared as the corresponding 6-aminohexyl glycosides that will be conjugated to carrier proteins such as Bovine Serum Albumin or Tetanus Toxoid. Relying on our recent success in preparing analogues of dimLe[x],[4] we embarked on the synthesis of fragments **2**–**5** following a stepwise approach that employed monosaccharide glycosyl donors in sequential glycosylation reactions. The choice of protecting groups was made with the intention to limit the number of deprotection steps required to obtain the final derivatives. We intended to carry out a one-step deprotection in Birch metal dissolving conditions[4-5] to obtain the hexyl glycosides **2** and **4** and a two-steps deprotection involving first the reduction of the non-reducing end trichloroacetamide followed by a deprotection in metal dissolving conditions to prepare 6-aminohexyl glycosides **3** and **5**. As shown below, the use of a *t*-butyldiphenylsilyl ether (TBDPS) protecting group to selectively protect O-6*B* impeded these strategies and dictated the sequence of the multi-step deprotection sequences that were required to prepare analogues **2**–**5**.

Results and Discussion



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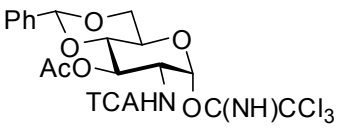

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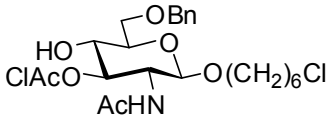

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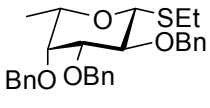

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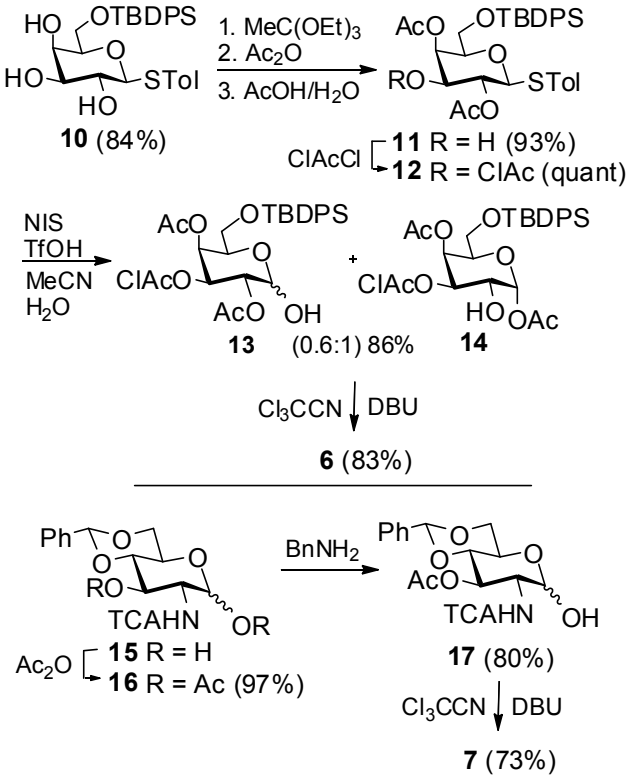
The desired analogues were prepared using novel building blocks **6** and **7** and known monosaccharides **8**[5c] and **9**[6]. Galactosyl donor **6** was prepared in 5 steps from known[7] *p*-thiotolyl β-D-galactopyranoside (Scheme 1). Selective silylation at O-6 gave the known[8] triol **10** which was

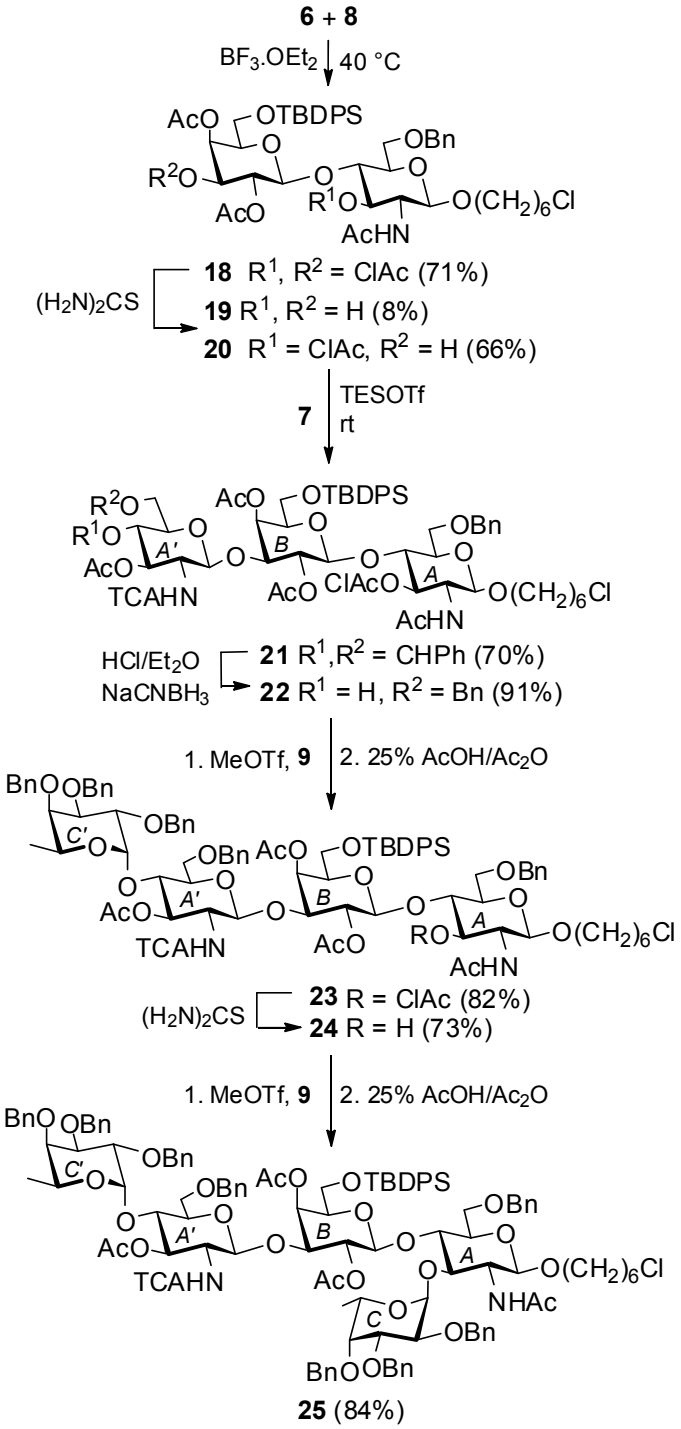
fully characterized. In turn, triol **10** was converted to the corresponding 3,4-orthoacetate that was acetylated *in situ* at position 2 and treated in mild acidic conditions to give alcohol **11** in excellent yield. Chloroacetylation at O-3 gave monosaccharide **12** which was submitted to the hydrolysis of the anomeric thioglycoside to give hemiacetal **13**.[9] Not surprisingly,[4,10] such reaction led to alcohol **14** as the major product while the desired hemiacetal **13** was only formed as the minor product (**13**/**14** ratio 0.6:1) and obtained as an α/β mixture (ratio 1:0.5). Analytical samples of **13** and **14** were isolated for characterization purposes and the remaining mixture of **13** and **14** was engaged in the next step. As expected,[4,10] under treatment with DBU in the presence of trichloroacetonitrile, the anomeric acetate in monosaccharide **14** underwent migration to O-2 and the desired trichloroacetimidate donor **6** was formed from both compounds **13** and **14** and isolated in excellent yield as the α anomer ($J_{H\text{-}1,\ H\text{-}2}$ = 3.6 Hz). Glucosamine glycosyl donor **7** was prepared in 3 steps from the known[11] benzylidene **15**. Thus diol **15** was acetylated giving di-acetate **16**, which was submitted to selective deacetylation at the anomeric position with benzylamine leading to the α/β anomeric mixture (ratio 1:0.25) of hemiacetal **17** in excellent yield. In turn, treatment of this anomeric

SCHEME 1. Synthesis of building blocks 6, 7



mixture with DBU and trichloroacetonitrile gave the desired glucosyl donor **7** as its α-anomer ($J_{H\text{-}1,\ H\text{-}2}$ = 3.7 Hz).

SCHEME 2. Synthesis of tetrasaccharide 23 and pentasaccharide 25



The stepwise synthesis of linear tetrasaccharide **23** and subsequent pentasaccharide **25** is outlined on Scheme 2 and began by the coupling of acceptor **8** with galactosyl donor **6**. This coupling was performed under the conditions developed in our group[12] to promote efficient glycosylation at O-4 of N-acetylglucosamine acceptors. Thus, acceptor **8** was reacted with galactosyl donor **6** (4 equiv) in the presence of an excess of $BF_3{\cdot}OEt_2$ (2 equiv) in CH_2Cl_2 at 40 °C and the desired disaccharide **18** was isolated in good yield. Selective removal of the O-3' chloroacetate with thiourea was carried out using similar conditions to those that we have previously described.[5b,c] A small

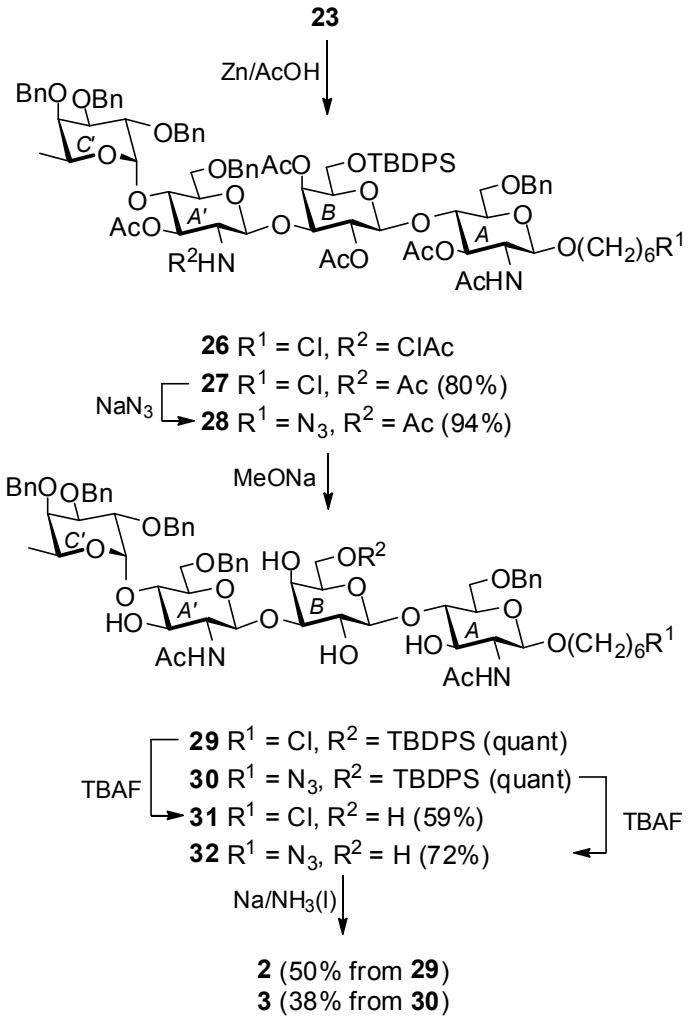
excess of thiourea (1.2 equiv) in a 2:1 pyridine/EtOH mixture at 55 °C led to the disappearance followed by TLC of di-chloroacetate **18** within 4.5 h and gave only a small amount of diol **19** (8%) while desired alcohol **20** was isolated in 66% yield. The position of the free hydroxyl group in acceptor **20** was confirmed by ^{1}H NMR comparing the chemical shifts of the non-reducing end H-3' in product **20** ($\delta_{\text{H-3'}}$ = 3.57 ppm) to the same signal in starting material **18** ($\delta_{\text{H-3'}}$ = 4.84 ppm). Glycosylation of acceptor **20** with donor **7** was then performed at room temperature in CH_2Cl_2 under activation with two equiv of TESOTf as recommended by Jacquinet[11] to prevent the formation of the undesired donor oxazoline. Under these conditions the desired trisaccharide **21** was obtained in good yield as the expected β anomer ($J_{\text{H-1}A', \text{H-2}A'}$ = 7.9 Hz). Regioselective reductive opening of the 4,6-*O*-benzylidene in trisaccharide **21** ($NaCNBH_3$-HCl/Et_2O, THF, rt) provided trisaccharide acceptor **22** free at O-4*A'* as confirmed by ^{1}H NMR which showed the presence of a doublet corresponding to OH-4*A'* ($J_{\text{OH-4}A', \text{H-4}A'}$ = 2.9 Hz) at 3.25 ppm. Trisaccharide acceptor **22** was engaged in a glycosylation reaction (CH_2Cl_2) with an excess of known[6] fucosyl donor **9** (2 equiv) activated by MeOTf (5 equiv) at room temperature. After treatment of the crude mixture with 25% AcOH in Ac_2O to convert any expected[13] methyl imidate formed into *N*-acetyl group, the desired tetrasaccharide **23** was isolated in excellent yield. As the anomeric signal for H-1*C'* was not resolved in the ^{1}H NMR spectrum, the stereochemistry of the newly formed fucosidic bond was established by measuring the coupling constant between C-1*C'* and H-1*C'* in a coupled HSQC experiment. This coupling constant ($J_{\text{H-1}C', \text{C-1}C'}$ = 170 Hz) supported[14] an expected α configuration for the newly introduced fucosyl unit. A fraction of tetrasaccharide **23** was set aside to prepare deprotected analogues **2** and **3** (Scheme 3), while the remaining tetrasaccharide was engaged in the synthesis of pentasaccharide **25**. Thus, tetrasaccharide **23** was converted to acceptor **24** free at O-*3A* in good yield by

treatment with thiourea (10 equiv) in a 2:1 pyridine/EtOH at 65 °C. MeOTf-promoted coupling of tetrasaccharide acceptor **24** and fucosyl donor **9** was then achieved using the same (two steps) reaction conditions as those described above for the synthesis of tetrasaccharide **23**. The desired pentasaccharide **25** was obtained in excellent yield and the α configuration of the newly introduced fucosidic bond at O-3*A* was confirmed by measuring the coupling constant between H-1 and H-2 of the fucosyl unit ($J_{\text{H-1}C',\ \text{H-2}C'}$ = 3.6 Hz).

With tetra- and pentasaccharides **23** and **25** in hands, we investigated deprotection reactions to prepare the desired analogues **2**–**5**. Focusing on the deprotection of tetrasaccharide **23** to obtain analogue **2**, we first attempted its global deprotection in metal dissolving conditions ($NH_{3(l)}$/Na, THF) at –78 °C. While it is known[4-5] that in such conditions benzyl ethers, acetates, and trichloroacetamides will be removed and the chlorohexyl chain reduced to the hexyl chain, the behavior of the TBDPS group at O-6*B* was unknown. After quenching the reaction with MeOH and acetylation *in situ* of the expected C-2*A'* free amine the poorly water soluble crude product was analyzed by TLC and NMR. It was found to be a complex mixture of compounds containing ethylenic protons which likely came from the partial reduction of the aromatic rings in the TBDPS group. Concluding that the silyl group at O-6*B* could not be removed in metal dissolving conditions, we then attempted to remove it first with TBAF in THF at room temperature. However, while the silyl group was removed in these conditions a complex mixture of compounds was isolated. Since it has been well established that trichloroacetamides are removed in Zemplén conditions occasionally leading to the formation of undesired methyl carbamates,[15] we then engaged trisaccharide **23** in a deprotection strategy (Scheme 3) which first involved the reduction of the trichloroacetamide prior to Zemplén deacetylation. Reduction of the C-2*A'* trichloroacetamide was first attempted using an excess of freshly activated zinc

powder (100 equiv) in AcOH at 50 °C for 20 h. While TLC showed disappearance of the starting material, two new products were formed and isolated together in 79% yield. Analytical reverse phase HPLC showed that these compounds were present in a 35:65 ratio. An analytical sample of the minor compound could be isolated and was identified as chloroacetamide **26** (estimated yield 27%), while the major product (estimated yield 52%) was identified as acetamide **27**. In both compounds the chloroacetate at O-3*A* had been reduced to an acetate. Since acetamide **27** was the major product of this reaction, we optimized its formation by increasing the temperature of reaction to 65 °C. Indeed, after 5 h at this temperature, tetrasaccharide **27** was isolated in an excellent (80%) yield. Before engaging tetrasaccharide **27** into further deprotection steps towards analogue **2** a fraction of this intermediate was converted to the 6-azidohexyl tetrasaccharide **28** *via* nucleophilic displacement of the chlorine atom with sodium azide (DMF, 80 °C). In turn, the 6-chlorohexyl and 6-azidohexyl tetrasaccharides **27** and **28** were engaged into the final deprotection steps to lead to the desired analogues **2** and **3**, respectively. Zemplén deacetylation (MeONa/MeOH, rt) first led

SCHEME 3. Deprotection steps to analogues 2 and 3

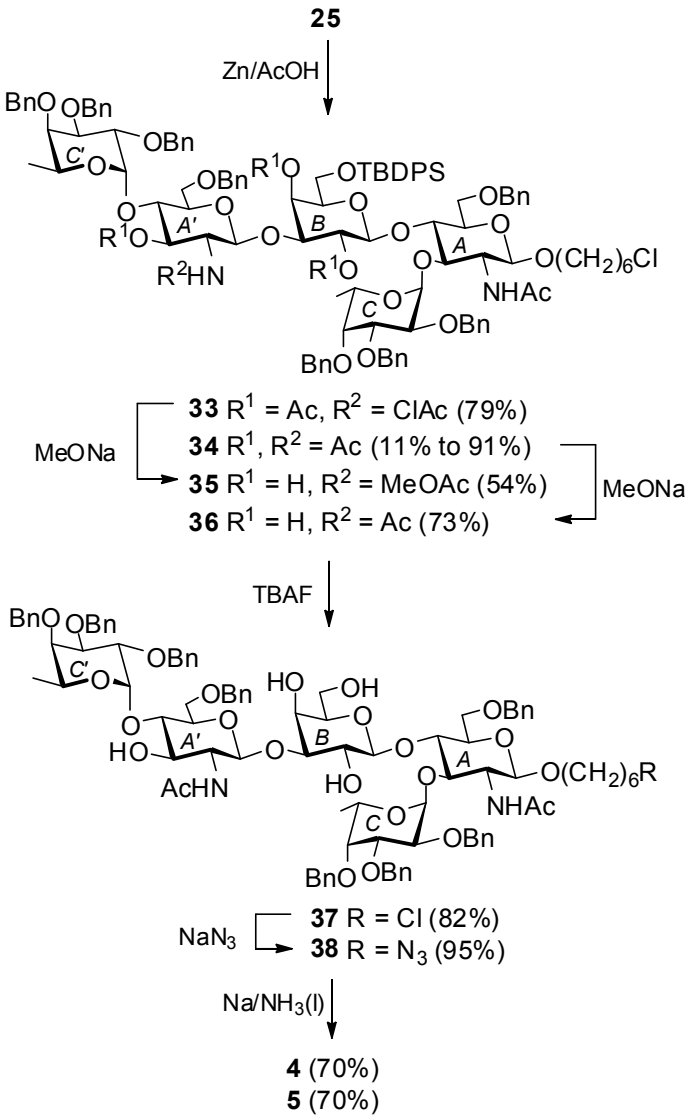


quantitatively to triols **29** and **30** which were treated with TBAF in THF at room temperature to give the 6-chlorohexyl tetrasaccharide **31** and 6-azidohexyl tetrasaccharide **32**, in 59 and 72% yield, respectively. These rather moderate yields resulted from the challenging purifications required to obtain the desired tetrasaccharides free of tetrabutylammonium salts. Thus, we minimized purification steps and attempted in subsequent reactions to engage tetrasaccharides **31** and **32** still contaminated with tetrabutylammonium salts into the final deprotection step in metal dissolving conditions ($NH_{3(l)}$/Na, THF, –78 °C). These reactions were quenched with MeOH, neutralized with AcOH and the final compounds were purified by size exclusion chromatography on Biogel P2® eluted with water for hexyl glycoside **2** and 0.05 M aqueous ammonium acetate for aminohexyl glycoside **3**. Following these last two deprotection steps, the desired final compounds **2** and **3** were obtained pure in 50 and 38% yield from protected tetrasaccharide **29** and **30**, respectively. Mass spectrometry ($[M + Na]^+$ = 839.3668) along with ^{1}H NMR showing a triplet at 0.86 ppm corresponding to the terminal methyl group, coming from the reduction of the chlorine, confirmed the structure of tetrasaccharide **2**. Similarly, the structure of tetrasaccharide **3** was confirmed by mass spectrometry ($[M + H]^+$ = 832.3906) and by the presence of a triplet at 2.97 ppm in ^{1}H NMR corresponding to the terminal methylene group ($CH_2NH_3^+$).

The deprotection of pentasaccharide **25** to yield the desired final pentasaccharides **4** and **5** is outlined in Scheme 4 and followed the strategy that we had established for the conversion of tetrasaccharide **23** to the final compounds **2** and **3**. Thus, the first step in this sequential deprotection was the reduction of the C-2*A'* trichloroacetamide with zinc in acetic acid. However, since fucosyl residues at O-3 of glucosamine units are known[16] to be unstable when treated in acidic conditions, this reduction was left to proceed at room temperature rather than heated to 50 or 60 °C. After 7 h of reaction at this temperature, TLC showed complete

disappearance of the starting material and formation of one major and one minor product. The major product was identified as chloroacetamide **33** (79%), and the minor product was characterized as the fully reduced acetamide **34** isolated in 11% yield. Since we expected the chloroacetamide to be easily reduced to the acetamide in the last step ($Na/NH_{3(l)}$)[4] and unaffected by the subsequent reactions, we engaged pentasaccharide **33** in a Zemplén deacetylation step in 0.25 M sodium methoxide in methanol. This reaction was first left to proceed at room temperature for 2 h at which time TLC showed the formation of a major product. However, work up of the reaction and ^{1}H NMR of the crude product showed that the O-4*B* acetyl group had not been removed ($\delta_{H\text{-}4B}$ = 5.47 ppm, bd). Therefore, this crude product was re-engaged in Zemplén deacetylation conditions and the reaction was left to proceed at room temperature for 18 h, at which time TLC showed the formation of a new major compound. Surprisingly, this new compound was isolated in 54% yield and characterized

SCHEME 4. Deprotection steps to analogues 4 and 5



by NMR as being the methoxyacetamide **35** (Scheme 4). The first indication that the chloroacetamide had been modified in these conditions was given by the downfield shift observed for the NH*A'* signal found at almost 7 ppm in the ^{1}H NMR spectrum while the same signal in chloroacetamides **26** and **33** was found at 6.3 ppm. In addition, the chloroacetamide methylene carbon signal found at 42.7 ppm in the ^{13}C NMR spectra of chloroacetamide derivatives **26** and **33** was replaced by a methylene signal found at 72 ppm in pentasaccharide **35**. We also observed the presence of an additional *O*-methyl group in pentasaccharide **35** which gave signals at 3.33 ppm and 59.3 ppm in the ^{1}H and ^{13}C NMR spectra, respectively. An HMBC experiment showed correlations between the methylene hydrogens (~3.8 ppm) and this *O*-methyl carbon (59.3 ppm) as well as a correlation between the methyl hydrogens (3.33 ppm) and the methylene carbon (72 ppm). These correlations confirmed that the methylene and methyl group were linked to the same oxygen and suggested that during this Zemplén deacetylation, the chloroacetamide chlorine atom in pentasaccharide **33** had undergone nucleophilic displacement by a methoxide ion leading to the unexpected methoxyacetamide pentasaccharide **35**. The structure of pentasaccharide **35** was eventually confirmed by HRMS. While trichloroacetamides are sensitive to Zemplén conditions, the nucleophilic displacement of a chloroacetamide chlorine atom by methoxide ions has, to our knowledge, not been previously observed in such conditions. Indeed, Zemplén deacetylations of chloroacetamide intermediates have been reported.[17] In our case, the extended reaction time that was required to deacetylate O-4*B* led to the formation of pentasaccharide **35** that could not be prevented. Thus, we decided to explore reactions conditions that would lead to the total reduction of the trichloroacetamide to an acetamide in pentasaccharide **25** prior to engaging the product into the Zemplén deacetylation. Running the reaction (Zn/AcOH) at 65 °C for 3 h increased the yield of desired acetamide **34** but it was only

isolated in 23% yield while chloroacetamide **33** was obtained in 69% yield. Thus, we attempted to perform the reaction under sonication[18] and left it to proceed for 4 h at 65 °C. At this time, TLC showed that all starting material had been consumed and that acetamide **34** had become the major product formed. Additional zinc (100 equiv) was added, the reaction was allowed to proceed at 65 °C under sonication during an additional 3 h and the desired acetamide **34** was isolated in an excellent 91% yield. In turn, Zemplén deacetylation (MeONa/MeOH, rt) of acetamide **34** gave the desired triol **36** in good yield after purification by RP-HPLC (CH_3CN/H_2O). Rather than engaging a portion of 6-chlorohexyl pentasaccharide **36** into a nucleophilic displacement with sodium azide prior to the removal of the TBDPS group at O-6*B* (as was done for the preparation of tetrasaccharide **3**), we decided to first treat **36** with TBAF (THF, rt) and prepare pentasaccharide **37**. Fortunately, even though pentasaccharides **36** and **37** co-migrated on TLC, sufficient reaction time (16 h) provided the desired pentasaccharide **37** pure and in very good yield despite requiring two successive purification by silica gel chromatography and RP HPLC. At this time, a fraction of the 6-chlorohexyl pentasaccharide **37** was converted to the 6-azidohexyl pentasaccharide **38** (NaN_3/DMF, 80 °C) which was obtained in excellent yield. Both pentasaccharide **37** and **38** were then treated in metal dissolving conditions ($NH_{3(l)}$/Na, THF, –78 °C) to give the desired hexyl and 6-aminohexyl pentasaccharides **4** and **5**, both in 70% yield after purification by size exclusion column chromatography on Biogel P2®. Mass spectrometry ($[M + H]^+ = 963.4435$) along with ^1H NMR showing a triplet at 0.85 ppm corresponding to the terminal methyl group confirmed the structure of pentasaccharide **4**. The structure of the pentasaccharide **5** was confirmed by mass spectrometry ($[M + H]^+ = 978.4522$) and by the presence of a triplet at 2.97 ppm in ^1H NMR corresponding to the terminal $CH_2NH_3^+$.

Conclusion

In conclusion, we report here the convergent synthesis of two novel tetrasaccharide and two novel pentasaccharide fragments of the Le^aLe^x TACA. Our strategy relied on stepwise monosaccharide extensions using excess equivalents (up to 4 equiv) of the relatively cheap monosaccharide glycosyl donors. This strategy ensured that all glycosylation reactions proceeded in very good yields (70–84%) even when preparing the largest structures. Thus the protected tetra- and pentasaccharide intermediates **23** and **25** were obtained in 25% yield over 6 steps and 15% yield over 8 steps, respectively. In contrast, the deprotection of the tetra- and pentasaccharide intermediates turned out to be challenging as we met numerous unforeseen difficulties. Indeed, working on tetrasaccharide **23** to prepare the 6-hexyl derivative **3** gave us the first indication that such deprotection steps were not as straightforward as the protecting groups chosen would have led us to believe. Investigating whether a global deprotection strategy using Birch metal dissolving conditions[4,5b,c] would be applicable here revealed that the TBDPS group was not removed and incompatible with such reaction conditions. Our results subsequently indicated that that the removal of this silyl group with fluoride ions led to partial migration of the O-4*B* acetyl group as well as to the formation of other uncharacterized products. Once the trichloroacetamide was reduced to an acetamide, deprotection steps involving TBAF and MeONa proceeded in good yields giving the desired tetrasaccharides **2** and **3** in 40% (4 steps) and 28% (5 steps) yield, respectively, from tetrasaccharide **23**. Evidence of the reactivity of halogenated acetamides with nucleophiles was obtained when chloroacetamide pentasaccharide **33** was submitted to Zemplén deacetylation conditions. As a result of the extended reaction time required to remove all acetates, we observed the unexpected nucleophilic displacement of the chloroacetamide chlorine atom by methoxide ions leading to the methoxyacetamide **35**. Full

reduction of the chloroacetamide to an acetamide in pentasaccharide **34** allowed for efficient subsequent deprotection steps leading to pentasaccharide **4** in 38% yield (4 steps from **34**) and aminohexyl analogue **5** in 36% yield (5 steps from **34**). To conclude, the combined presence of the TBDPS at O-6*B* and trichloroacetamide at C-2*A'* in the protected intermediates were not compatible with efficient deprotection steps.

Experimental Section

***p*-Tolyl 6-*O*-*tert*-butyldiphenylsilyl-β-1-thio-D-galactopyranoside (10).** Imidazole (6.5 g, 95 mmol, 2.5 equiv) was added to a solution of known[7] β-thiotolyl galactopyranoside (10.9 g, 38 mmol) in anhyd DMF (93 mL) at rt under N_2. TBDPSCl (12 mL, 46 mmol, 1.2 equiv) was then slowly added and the reaction was left under stirring for 22 h at rt. The solvent was evaporated and the residue was dissolved in CH_2Cl_2 (500 mL) and washed with HCl 2 N (3 × 500 mL). The aq layer was re-extracted with CH_2Cl_2 (5 × 200 mL) and the combined organic layers were dried and concentrated. Column chromatography (EtOAc/hexanes, 6:4–7:3) gave the known[8] silylated intermediate **10** (16.8 g, 84%) pure as a white amorphous foam. $[\alpha]_D$ –24.5 (*c* 1.0, MeOH). ^{1}H NMR (400 MHz, $CDCl_3$, 296 K): δ_H 7.73–7.65 (m, 4 H, Ar), 7.45–7.33 (m, 8 H, Ar), 7.03 (d, J = 8.0 Hz, 2 H, Ar), 4.43 (d, J = 9.6 Hz, 1 H, H-1), 4.07 (m, 1 H, H-4), 3.96–3.87 (m, 2 H, H-6a, H-6b), 3.59–3.50 (m, 2 H, H-3, H-5), 3.37 (d, J = 5.1 Hz, 1 H, OH-3), 3.05 (d, J = 3.6 Hz, 1 H, OH-4), 2.98 (br s, 1 H, OH-2), 2.28 (s, 3 H, CH_3 tolyl), 1.04 (s, 9 H, C(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 296 K): δ_C 138.0 (quat Ar), 135.6, 135.5, 132.8 (Ar), 132.7 (quat Ar), 129.9, 129.7 (Ar), 128.5 (quat Ar), 127.8 (Ar), 88.8 (C-1), 78.1 (C-5), 74.9 (C-3), 69.8 (C-2), 69.4 (C-4), 63.7 (C-6), 26.7 (C(*C*H$_3$)$_3$), 21.1 (CH_3 tolyl), 19.1 (*C*(CH$_3$)$_3$). HRMS (ESI-TOF) *m/z*: calcd for $C_{29}H_{36}O_5SSiNa$ $[M+Na]^+$ 547.1950, found 547.1978.

***p*-Tolyl 2,4-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-β-1-thio-D-galactopyranoside (11).** Triethylorthoacetate (33 mL, 181 mmol, 4 equiv) and CSA (842 mg, 3.62 mmol, 0.08 equiv) were added to a solution of triol **10** (23.8 g, 45 mmol) in anhyd MeCN (650 mL) under N_2. The solution was stirred at rt for 15 min, anhyd pyridine (183 mL, 2.26 mol, 50 equiv) and Ac_2O (107 mL, 1.13 mol, 25 equiv) were then added, and the mixture was heated to 50 °C for 1.5 h. The mixture was co-concentrated with toluene (4 × 150 mL), and the resulting oily residue was left under high vacuum overnight. It was dissolved in a mixture of AcOH and H_2O (8:2, 200 mL), stirred for 10 min, then diluted with CH_2Cl_2 (300 mL) and washed sequentially with satd aq $NaHCO_3$ (2 × 500 mL) and HCl 2 N (2 × 500 mL). The aq layers were re-extracted with CH_2Cl_2 (2 × 100 mL) and the combined organic layers were dried and concentrated. Column chromatography (EtOAc/hexanes, 4:6) gave alcohol **11** (25.7 g, 93%) pure as a white amorphous glass. $[\alpha]_D$ +8.0 (*c* 1.0, MeOH). ^{1}H NMR (400 MHz, $CDCl_3$, 295 K): δ_H 7.64–7.58 (m, 4 H, Ar), 7.45–7.32 (m, 8 H, Ar), 7.03 (d, *J* = 7.9 Hz, 2 H, Ar), 5.44 (d, *J* = 3.3 Hz, 1 H, H-4), 4.95 (t, *J* = 9.8 Hz, 1 H, H-2), 4.58 (d, *J* = 10.0 Hz, 1 H, H-1), 3.85 (ddd, *J* = 3.5, 5.3, 9.1 Hz, 1 H, H-3), 3.74 (dd, *J* = 4.5, 8.0 Hz, 1 H, H-6a), 3.71–3.61 (m, 2 H, H-5, H-6b), 2.43 (d, *J* = 5.3 Hz, 1 H, OH-3), 2.29 (s, 3 H, CH_3 tolyl), 2.14, 2.00 (2 s, 6 H, 2 $OCOCH_3$), 1.01 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 295 K): δ_C 171.2, 170.7 (C=O), 138 (quat Ar), 135.6 (Ar), 133.0 (quat Ar), 132.7, 129.9, 129.8, 129.6 (Ar), 129.2 (quat Ar), 127.8, 127.7 (Ar), 86.8 (C-1), 77.4 (C-5), 72.9 (C-3), 70.9 (C-2), 70.0 (C-4), 61.8 (C-6), 26.7 ($C(CH_3)_3$), 21.1, 21.0, 20.7 (CH_3 tolyl, $OCOCH_3$), 19.1 ($C(CH_3)_3$). HRMS (ESI-TOF) *m/z* calcd for $C_{33}H_{40}O_7SSiNa$ $[M+Na]^+$ 631.2162, found 631.2162.

***p*-Tolyl 2,4-di-*O*-acetyl-3-*O*-chloroacetyl-6-*O*-*tert*-butyldiphenylsilyl-1-thio-β-D-galactopyranoside (12).** Chloroacetylchloride (6.7 mL, 84 mmol, 2 equiv) was slowly added to

a solution of alcohol **11** (25.7 g, 42 mmol) in anhyd CH_2Cl_2 (420 mL) containing anhyd pyridine (17 mL, 211 mmol, 5 equiv) at rt under N_2. The reaction mixture was stirred for 15 min then diluted with CH_2Cl_2 (50 mL) and washed sequentially with HCl 2 N (2 × 500 mL) and satd aq $NaHCO_3$ (2 × 500 mL). The organic layer was dried and concentrated to give chloroacetate **12** (29 g, quant) pure as a yellow amorphous glass. $[\alpha]_D$ +12.8 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 296 K): δ_H 7.62–7.55 (m, 4 H, Ar), 7.45–7.32 (m, 8 H, Ar), 7.05 (d, *J* = 8.0 Hz, 2 H, Ar), 5.54 (d, *J* = 3.0 Hz, 1 H, H-4), 5.18 (t, *J* = 9.9 Hz, 1 H, H-2), 5.10 (dd, *J* = 3.2, 9.9 Hz, 1 H, H-3), 4.63 (d, *J* = 9.8 Hz, 1 H, H-1), 3.94 (s, 2 H, COC*H*$_2$Cl), 3.80–3.73 (m, 2 H, H-5, H-6a), 3.61 (dd, *J* = 9.4, 11.8 Hz, 1 H, H-6b), 2.30 (s, 3 H, CH_3 tolyl), 2.07, 1.96 (2 s, 6 H, 2 OCOCH_3), 1.00 (s, 9 H, C(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 296 K): δ_C 170.2, 169.4, 166.6 (C=O), 138.3 (quat Ar), 135.6, 132.8 (Ar), 132.8 (quat Ar), 132.7 (quat Ar), 129.9, 129.8, 129.7 (Ar), 128.8 (quat Ar), 127.8 (Ar), 87.1 (C-1), 77.0 (C-5), 74.2 (C-3), 67.2, 67.0 (C-2, C-4), 61.2 (C-6), 40.5 (CO*C*H$_2$Cl), 26.7 (C(*C*H$_3$)$_3$), 21.1, 20.8, 20.6 (CH_3 tolyl, OCO*C*H$_3$), 19.0 (*C*(CH$_3$)$_3$). HRMS (ESI-TOF) *m/z* calcd for $C_{35}H_{41}ClO_8SSiNa$ $[M+Na]^+$ 707.1878, found 707.1937 and for $C_{35}H_{41}ClO_8SSiK$ $[M+K]^+$ 723.1617, found 723.1650.

2,4-Di-*O*-acetyl-3-*O*-chloroacetyl-6-*O*-*tert*-butyldiphenylsilyl-α,β-D-galactopyranose (13) and acetyl 4-*O*-acetyl-3-*O*-chloroacetyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-galactopyranose (14). NIS (11 g, 46 mmol, 1.1 equiv) and TfOH (374 µL, 4.2 mmol, 0.1 equiv) were added to a solution of chloroacetate **12** (29 g, 42 mmol) in a mixture of MeCN (650 mL) and H_2O (6.50 mL) at rt. The reaction mixture was stirred for 5 min at rt, then quenched with NEt_3 (1.5 mL, 11 mmol, 0.25 equiv) and concentrated. The residue was dissolved in CH_2Cl_2 (500 mL) and was washed with a 20% w/w solution of aq $Na_2S_2O_3$ (400 mL). The aq layer was re-extracted with CH_2Cl_2 (2 × 100 mL) and the combined organic layers were dried and

concentrated. Column chromatography (EtOAc/hexanes, 4:6) of the residue gave a 0.6:1 mixture of alcohols **13** and **14** (21 g, 86%). For analytical purpose, a small amount of the mixture containing **13** and **14** was submitted to further chromatography to afford analytical samples of **13(α,β)** and **14**.

Analytical data for 13: Yellow foam, α/β ratio (1:0.5), ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ_H 7.61–7.55 (m, 6 H, Ar), 7.44–7.33 (m, 9 H, Ar), 5.62 (dd, J = 1.0, 3.2 Hz, 1 H, H-4α), 5.58 (d, J = 3.3 Hz, 0.5 H, H-4β), 5.48 (dd, J = 3.3, 10.8 Hz, 1 H, H-3α), 5.40 (d, J = 2.9 Hz, 1 H, H-1α), 5.15–5.10 (m, 1.5 H, H-2α, H-3β), 5.03 (dd, J = 7.8, 10.4 Hz, 0.5 H, H-2β), 4.60 (t, J = 7.4 Hz, 0.5 H, H-1β), 4.32 (t, J = 7.5 Hz, 1 H, H-5α), 3.97 (s, 3 H, COCH_2Cl), 3.80–3.71 (m, 1 H, H-5β, H-6aβ), 3.68–3.56 (m, 2.5 H, H-6aα, H-6bα, H-6bβ), 3.43 (br s, 0.5 H, OH-1β), 2.85 (br s, 1 H, OH-1α), 2.07, 2.06, 2.00, 1.99 (4 s, 9 H, 4 $OCOCH_3$), 1.00 (s, 13.5 H, C(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 297 K): δ_C 171.2, 170.3 170.2, 166.6, 166.5 (C=O), 135.6, 135.5 (Ar), 132.9, 132.8, 132.6 (quat Ar), 129.9, 129.8, 127.8, 127.7 (Ar), 95.8 (C-1β), 90.6 (C-1α), 73.2 (C-5β), 72.4 (C-2α), 71.1 (C-2β), 69.5 (C-3α), 68.5 (C-3β), 68.3 (C-5α), 67.8 (C-4α), 66.7 (C-4β), 61.2 (C-6α), 60.7 (C-6β), 40.5 (COCH$_2$Clα), 40.4 (COCH$_2$Clβ), 26.7 (C(CH$_3$)$_3$), 20.8, 20.6 ($OCOCH_3$), 19.0 (C(CH$_3$)$_3$). HRMS (ESI-TOF) *m/z* calcd for $C_{28}H_{35}ClO_9SiNa$ $[M+Na]^+$ 601.1637, found 601.1614.

Analytical data for 14: Yellow foam, $[\alpha]_D$ +68.5 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 296 K): δ_H 7.60–7.54 (m, 4 H, Ar), 7.44–7.32 (m, 6 H, Ar), 6.22 (d, J = 3.9 Hz, 1 H, H-1), 5.62 (dd, J = 1.1, 3.1 Hz, 1 H, H-4), 5.24 (dd, J = 3.2, 10.5 Hz, 1 H, H-3), 4.12 (ddd, J = 3.9, 7.7, 11.1 Hz, 1 H, H-2), 4.09–4.03 (m, 3 H, H-5, COCH_2Cl), 3.66 (dd, J = 5.7, 10.0 Hz, 1 H, H-6a), 3.57 (dd, J = 8.5, 9.9 Hz, 1 H, H-6b), 2.14, 1.98 (2 s, 6 H, 2 $OCOCH_3$), 2.08 (d, J = 7.7 Hz, 1 H, OH-

2), 1.00 (s, 9 H, C(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 296 K): δ_C 170.1, 169.4, 167.1 (C=O), 135.6 (Ar), 132.8, 132.7 (quat Ar), 129.9, 127.8 (Ar), 91.8 (C-1), 72.7 (C-3), 71.0 (C-5), 67.1 (C-4), 66.0 (C-2), 60.8 (C-6), 40.7 (CO*C*H$_2$Cl), 26.7 (C(*C*H$_3$)$_3$), 21.0, 20.5 (OCO*C*H$_3$), 19.0 (*C*(CH$_3$)$_3$). HRMS (ESI-TOF) *m/z* calcd for $C_{28}H_{35}ClO_9SiNa$ $[M+Na]^+$ 601.1637, found 601.1597.

2,4-Di-*O*-acetyl-3-*O*-chloroacetyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-galactopyranosyl trichloroacetimidate (6). Trichloroacetonitrile (11 mL, 109 mmol, 3 equiv) was added to a solution of alcohols **13** and **14** (21.0 g, 36.3 mmol) in anhyd CH_2Cl_2 (350 mL) at rt under N_2. DBU (1.4 mL, 9.08 mmol, 0.25 equiv) was then slowly added to the mixture, which was stirred at rt for 3 h. The reaction mixture was then concentrated and column chromatography of the residue (EtOAc/hexanes, 3:7 with 0.1% NEt_3) gave trichloroacetimidate **6** (21.8 g, 83%) pure as a slightly yellowish amorphous foam. $[\alpha]_D$ –50.2 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 296 K): δ_H 8.60 (s, 1 H, NH), 7.60–7.54 (m, 4 H, Ar), 7.44–7.32 (m, 6 H, Ar), 6.54 (d, *J* = 3.6 Hz, 1 H, H-1), 5.71 (d, *J* = 3.1 Hz, 1 H, H-4), 5.51 (dd, *J* = 3.2, 10.8 Hz, 1 H, H-3), 5.35 (dd, *J* = 3.7, 10.8 Hz, 1 H, H-2), 4.29 (t, *J* = 7.2 Hz, 1 H, H-5), 4.00 (s, 2 H, COC*H*$_2$Cl), 4.20 (dd, *J* = 6.0, 10.1 Hz, 1 H, H-6a), 4.12 (dd, *J* = 8.0, 10.1 Hz, 1 H, H-6b), 2.03, 2.00 (2 s, 6 H, 2 OCOCH$_3$), 0.98 (s, 9 H, C(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 296 K): δ_C 170.2, 170.0, 166.5 (C=O), 160.9 (C=N), 135.5 (Ar), 132.8, 132.7 (quat Ar), 129.9, 127.8, 127.7 (Ar), 93.5 (C-1), 71.3 (C-5), 69.7 (C-3), 67.1 (C-4), 67.0 (C-2), 61.0 (C-6), 40.5 (CO*C*H$_2$Cl), 26.6 (C(*C*H$_3$)$_3$), 20.6, 20.5 (OCO*C*H$_3$), 19.0 (*C*(CH$_3$)$_3$). HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{35}Cl_4NO_9SiNa$ $[M+Na]^+$ 744.0733, found 744.0737.

1,3-Di-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-trichloroacetamido-α,β-D-glucopyranoside (16). Known[11] diol **15** (9.07 g, 21.71 mmol) was treated with a mixture of pyridine and Ac_2O (1:1, 90 mL) at 50 °C for 2 h. The reaction mixture was co-concentrated with toluene (4 × 100 mL) and the residue was dissolved in CH_2Cl_2 (200 mL) and washed sequentially with HCl (2 N, 2 × 200 mL) and satd aq $NaHCO_3$ (2 × 200 mL). The aqueous layers were re-extracted with CH_2Cl_2 (2 × 50 mL) and the combined organic layers were dried and concentrated. Column chromatography (CH_2Cl_2/MeOH, 50:1) gave diacetate **16** (10.55 g, 97%) pure (α/β ratio, 1:0.21) as white amorphous powder. ^{1}H NMR (600 MHz, $CDCl_3$, 295 K): δ_H 7.53 (d, J = 9.7 Hz, 0.21 H, NHβ), 7.46–7.41 (m, 2.42 H, Ar), 7.37–7.32 (m, 3.63 H, Ar), 7.09 (d, J = 8.4 Hz, 1 H, NHα), 6.24 (d, J = 3.9 Hz, 1 H, H-1α), 5.80 (d, J = 8.7 Hz, 0.21 H, H-1β), 5.57–5.53 (m, 1,21 H, H-3β, >PhC*H*α), 5.51–5.46 (m, 1.21 H, H-3α, >PhC*H*β), 4.36–4.29 (m, 2 H, H-2α, H-6aα), 4.26 (m, 0.21 H, H-2β), 3.96 (td, J = 4.9, 9.9 Hz, 1 H, H-5α), 3.88 (dd, J = 4.9, 10.3 Hz, 0.21 H, H-6aβ), 3.82 (t, J = 9.7 Hz, 1 H, H-4α), 3.78 (t, J = 10.4 Hz, 1 H, H-6bα), 3.72 (t, J = 9.5 Hz, 0.21 H, H-4β), 3.62 (t, J = 10.1 Hz, 0.21 H, H-6bβ), 3.54 (td, J = 4.9, 9.6 Hz, 0.21 H, H-5β), 2.09, 2.05 (2 s, 1.26 H, 2 OCOCH_3β), 2.08, 2.04 (2 s, 6 H, 2 COCH_3α). ^{13}C NMR (125 MHz, $CDCl_3$, 295 K): δ_C 171.8, 168.6, 162.1 (C=Oα), 171.2, 168.9, 162.5 (C=Oβ), 136.6 (quat Ar), 129.3, 128.3, 126.1 (Ar), 101.7 (>Ph*C*Hαβ), 92.5 (C-1β), 92.3 (CCl_3β), 91.8 (CCl_3α), 90.0 (C-1α), 78.1 (C-4α, C-4β), 71.0 (C-3β), 69.2 (C-3α), 68.4 (C-6α), 67.9 (C-6β), 67.3 (C-5β), 64.9 (C-5α), 55.2 (C-2β), 53.8 (C-2α), 20.8, 20.7, 20.5 (OCO*C*H_3). HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{20}Cl_3NO_8Na$ $[M+Na]^+$ 518.0152, found 518.0170.

3-*O*-Acetyl-4,6-*O*-benzylidene-2-deoxy-2-trichloroacetamido-α,β-D-glucopyranose (17). To a solution of the diacetate **16** (2.38 g, 4.74 mmol) in THF (70 mL) was added $BnNH_2$ (1 mL, 9.49 mmol, 2 equiv) at rt and the mixture was left under stirring for 66 h. The mixture was

poured into water (70 mL), extracted with CH_2Cl_2 (5 × 40 mL) and the combined organic layers were dried and concentrated. Column chromatography (toluene/EtOAc, 5:1) gave hemiacetal **17** (1.74 g, 80%) pure (α/β ratio, 1:0.25) as a white amorphous glass. ^{1}H NMR (600 MHz, $CDCl_3$, 295 K): δ_H 7.46–7.41 (m, 2.50 H, NHβ, Ar), 7.38–7.32 (m, 4 H, Ar), 7.11 (d, *J* = 9.1 Hz, 1 H, NHα), 5.53 (m, 1.25 H, >PhC*H*α, >PhC*H*β), 5.48 (t, *J* = 10.1 Hz, 1 H, H-3α), 5.37 (t, *J* = 3.5 Hz, 1 H, H-1α) , 5.26 (t, *J* = 10.0 Hz, 0.25 H, H-3β), 4.79 (t, *J* = 8.6 Hz, 0.25 H, H-1β), 4.38 (dd, *J* = 5.0, 10.5 Hz, 0.25 H, H-6aβ), 4.28 (dd, *J* = 4.9, 10.3 Hz, 1 H, H-6aα), 4.22 (ddd, *J* = 3.5, 9.1, 10.3 Hz, 1 H, H-2α), 4.16 (td, *J* = 4.9, 10.0 Hz, 1 H, H-5α), 4.03 (d, *J* = 9.0 Hz, 0.25 H, OH-1β), 3.93 (m, 0.25 H, H-2β), 3.83 (t, *J* = 10.3 Hz, 0.25 H, H-6bβ), 3.80–3.73 (m, 2.25 H, H-4α, H-6bα, H-4β), 3.50 (td, *J* = 4.9, 9.7 Hz, 0.25 H, H-5β), 2.95 (d, *J* = 1.9 Hz, 1 H, OH-1α), 2.09 (s, 0.75 H, $OCOCH_3$β), 2.05 (s, 3 H, $COCH_3$α). ^{13}C NMR (125 MHz, $CDCl_3$, 295 K): δ_C 172.3, 164.3 (C=Oβ), 171.4, 162.2 (C=Oα), 136.8 (quat Ar α), 136.8 (quat Ar β), 129.2, 128.3, 126.2 (Ar α), 129.3, 128.3, 126.1 (Ar β), 101.7 (>Ph*C*Hα), 101.6 (>Ph*C*Hβ), 97.2 (C-1β), 92.0 (CCl_3α), 91.7 (C-1α), 78.7 (C-4α), 78.2 (C-4β), 70.8 (C-3β), 69.3 (C-3α), 68.7 (C-6α), 68.4 (C-6β), 66.8 (C-5β), 62.9 (C-5α), 59.0 (C-2β), 54.8 (C-2α), 20.8 ($OCOCH_3$). HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{18}Cl_3NO_7Na$ $[M+Na]^+$ 476.0047, found 476.0042.

3-*O*-Acetyl-4,6-*O*-benzylidene-2-deoxy-2-trichloroacetamido-α-D-glucopyranosyl trichloroacetimidate (7). A solution of hemiacetal **17** (6.38 g, 13.9 mmol) in anhyd CH_2Cl_2 (175 mL) under N_2 was cooled to 0 °C, Cl_3CCN (7 mL, 69.4 mmol, 5 equiv) was added to the solution, followed by the dropwise addition of DBU (520 μL, 3.47 mmol, 0.25 equiv) over a period of 3 min. The reaction was left at 0 °C for 3 h and the solvent was evaporated. Column chromatography (EtOAc/hexanes, 25:75 with 0.1 % NEt_3) gave trichloroacetimidate **7** (6.09 g, 73%) pure as a slightly yellowish foam. $[\alpha]_D$ +53.2 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$,

296 K): δ_H 7.47–7.43 (m, 2 H, Ar), 7.38–7.34 (m, 3 H, Ar), 7.11 (d, *J* = 8.4 Hz, 1 H, NH), 6.46 (d, *J* = 3.7 Hz, 1 H, H-1), 5.57 (s, 1 H, >PhC*H*), 5.53 (t, *J* = 10.2 Hz, 1 H, H-3), 4.42 (ddd, *J* = 3.7, 8.5, 10.6 Hz, 1 H, H-2), 4.36 (dd, *J* = 4.9, 10.5 Hz, 1 H, H-6a), 4.08 (td, *J* = 4.9, 9.9 Hz, 1 H, H-5), 3.88 (t, *J* = 9.7 Hz, 1 H, H-4), 3.82 (t, *J* = 10.3 Hz, 1 H, H-6b), 2.09 (s, 3 H, $OCOCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 296 K): δ_C 171.5, 162.2 (C=O), 160.3 (C=N), 136.5 (quat Ar), 129.3, 128.3, 126.1 (Ar), 101.7 (>Ph*C*H), 94.1 (C-1), 91.7, 90.5 (CCl_3), 78.0 (C-4), 69.0 (C-3), 68.4 (C-6), 65.5 (C-5), 54.6 (C-2), 20.8 ($OCOCH_3$). HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{18}Cl_6N_2O_7Na$ $[M+Na]^+$ 618.9143, found 618.9172.

6-Chlorohexyl 2-acetamido-4-*O*-(2,4-di-*O*-acetyl-3-*O*-chloroacetyl-6-*O*-*tert*-butyldiphenylsilyl-β-D-galactopyranosyl)-6-*O*-benzyl-3-*O*-chloroacetyl-2-deoxy-β-D-glucopyranoside (18). A stirred solution of known[5c] alcohol **8** (1.86 g, 3.67 mmol) and galactosyl trichloroacetimidate **6** (10.61 g, 14.67 mmol, 4 equiv) in anhyd CH_2Cl_2 (95 mL) was heated to 40 °C under N_2. Freshly distilled $BF_3{\cdot}OEt_2$ (921 μL, 7.33 mmol, 2 equiv) was added to the mixture, which was stirred for 1 h at 40 °C. The reaction was quenched with NEt_3 (1.2 mL, 8.80 mmol, 2.4 equiv), the mixture diluted with CH_2Cl_2 (100 mL) and washed with satd aq $NaHCO_3$ (200 mL). The aq layer was re-extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic layers were dried and concentrated. Column chromatography (EtOAc/hexanes, 4:6–5:5) gave disaccharide **18** (2.77 g, 71%) pure as a slightly yellowish amorphous foam. $[\alpha]_D$ –4.8 (*c* 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$, 297 K): δ_H 7.61–7.52 (m, 4 H, Ar), 7.46–7.30 (m, 11 H, Ar), 5.57 (d, *J* = 9.3 Hz, 1 H, NHA), 5.40 (d, *J* = 3.0 Hz, 1 H, H-4B), 5.03 (dd, *J* = 8.8, 10.1 Hz, 1 H, H-3A), 4.91 (dd, *J* = 7.7, 10.3 Hz, 1 H, H-2B), 4.84 (dd, *J* = 3.3, 10.4 Hz, 1 H, H-3B), 4.74 (d, *J* = 12.0 Hz, 1 H, C*H*HPh), 4.44–4.40 (m, 2 H, H-1, CH*H*Ph), 4.31 (d, *J* = 7.7 Hz, 1 H, H-1B), 3.96–3.61 (m, 10 H, H-2A, H-4A, H-6Aa, H-6Ab, H-6Ba, 2 COCH_2Cl , OC*H*HCH_2),

3.53–3.36 (m, 6 H, H-5A, H-5B, H-6Bb, CH_2Cl, OCH*H*(CH_2), 1.97, 1.93 (2 s, 6 H, 2 $OCOCH_3$), 1.90 (s, 3 H, NHCOC*H*$_3$), 1.73 (m, 2 H, $O(CH_2)_4CH_2CH_2Cl$), 1.55 (m, 2 H, $OCH_2CH_2(CH_2)_3CH_2Cl$), 1.40 (m, 2 H, $O(CH_2)_3CH_2(CH_2)_2Cl$), 1.32 (m, 2 H, $O(CH_2)_2CH_2(CH_2)_3Cl$), 1.02 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 297 K): δ_C 170.3, 170.1, 168.9, 167.2, 166.6 (C=O), 137.7 (quat Ar), 135.5 (Ar), 132.5, 132.4 (quat Ar), 130.1, 128.6, 128.2, 128.1, 127.9 (Ar), 100.9 (C-1A), 100.0 (C-1B), 74.5 (C-3A), 74.4 (C-4A), 74.3 (C-5A), 73.6 (CH_2Ph), 72.9 (C-3B), 72.7 (C-5B), 69.3 (OCH_2CH_2), 69.1 (C-2B), 67.3 (C-6A), 66.4 (C-4B), 60.6 (C-6B), 53.4 (C-2A), 45.0 (CH_2Cl), 40.7, 40.5 ($COCH_2Cl$), 32.4 ($O(CH_2)_4CH_2CH_2Cl$), 29.2 ($OCH_2CH_2(CH_2)_3CH_2Cl$), 26.7 ($C(CH_3)_3$), 26.5 ($O(CH_2)_3CH_2(CH_2)_2Cl$), 25.2 ($O(CH_2)_2CH_2(CH_2)_3Cl$), 23.3 ($NHCOCH_3$), 20.7, 20.6 ($OCOCH_3$), 19.0 ($C(CH_3)_3$). HRMS (ESI-TOF) *m/z* calcd for $C_{51}H_{67}Cl_3NO_{15}Si$ $[M+H]^+$ 1066.336, found 1066.326.

6-Chlorohexyl 2-acetamido-4-*O*-(2,4-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-β-D-galactopyranosyl)-6-*O*-benzyl-2-deoxy-β-D-glucopyranoside (19) and 6-Chlorohexyl 2-acetamido-4-*O*-(2,4-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-β-D-galactopyranosyl)-6-*O*-benzyl-3-*O*-chloroacetyl-2-deoxy-β-D-glucopyranoside (20). Disaccharide **18** (2.27 g, 2.13 mmol) was dissolved in a mixture of pyridine and EtOH (2:1, 54 mL), thiourea (195 mg, 2.56 mmol, 1.2 equiv) was added and the solution was heated to 55 °C for 4.5 h, then allowed to cool to rt. The reaction mixture was diluted with $CHCl_3$ (100 mL) and washed with HCl 2 N (200 mL). The aq layer was re-extracted with $CHCl_3$ (5 × 100 mL) and the combined organic layers were dried and concentrated. Column chromatography ($CHCl_3$/MeOH, 30:1) gave pure alcohol **19** (2.12 g, 66%) and pure diol **20** (155 mg, 8%).

Analytical data for 19: White foam, $[\alpha]_D$ –15.6 (*c* 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$, 297 K): δ_H 7.61–7.55 (m, 4 H, Ar), 7.45–7.28 (m, 11 H, Ar), 5.49 (d, *J* = 7.8 Hz, 1 H, NHA), 5.33 (d, *J* = 3.2 Hz, 1 H, H-4B), 4.90 (dd, *J* = 8.1, 9.8 Hz, 1 H, H-2B), 4.74 (d, *J* = 8.2 Hz, 1 H, H-1A), 4.67 (d, *J* = 12.1 Hz, 1 H, C*H*HPh), 4.50 (d, *J* = 12.1 Hz, 1 H, CH*H*Ph), 4.42 (d, *J* = 8.0 Hz, 1 H, H-1B), 4.02 (d, *J* = 1.2 Hz, 1 H, OH-3A), 3.96 (t, *J* = 9.5 Hz, 1 H, H-3A), 3.82 (m, 1 H, OC*H*HCH$_2$), 3.77–3.38 (m, 11 H, H-3B, H-4A, H-5A, H-5B, H-6Aa, H-6Ab, H-6Ba, H-6Bb, CH_2Cl, OCH*H*CH$_2$), 3.32 (m, 1 H, H-2A), 2.63 (d, *J* = 5.1 Hz, 1 H, OH-3B), 2.03, 1.99 (2 s, 6 H, 2 OCOCH$_3$), 1.87 (s, 3 H, NHCOC*H*$_3$), 1.74 (m, 2 H, O(CH$_2$)$_4$C*H*$_2$CH$_2$Cl), 1.55 (m, 2 H, OCH$_2$C*H*$_2$(CH$_2$)$_3$CH$_2$Cl), 1.42 (m, 2 H, O(CH$_2$)$_3$C*H*$_2$(CH$_2$)$_2$Cl), 1.34 (m, 2 H, O(CH$_2$)$_2$C*H*$_2$(CH$_2$)$_3$Cl), 1.02 (s, 9 H, C(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 297 K): δ_C 171.1, 170.7, 170.3 (C=O), 138.2 (quat Ar), 135.6, 135.5 (Ar), 132.7, 132.4 (quat Ar), 130.0, 129.9, 128.4, 127.9, 127.7, 127.6 (Ar), 100.9 (C-1B), 100.1 (C-1A), 80.8 (C-4A), 74.0, 73.8 (C-5A, C-5B), 73.5 (*C*H$_2$Ph), 72.6 (C-2B), 71.4 (C-3B), 71.3 (C-3A), 69.4 (C-4B), 69.3 (O*C*H$_2$CH$_2$), 68.3 (C-6A), 61.3 (C-6B), 57.0 (C-2A), 45.0 (*C*H$_2$Cl), 32.5 (O(CH$_2$)$_4$*C*H$_2$CH$_2$Cl), 29.3 (OCH$_2$*C*H$_2$(CH$_2$)$_3$CH$_2$Cl), 26.7 (C(*C*H$_3$)$_3$), 26.5 (O(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$Cl), 25.2 (O(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$Cl), 23.6 (NHCO*C*H$_3$), 20.9, 20.7 (OCO*C*H$_3$), 19.0 (*C*(CH$_3$)$_3$). HRMS (ESI-TOF) *m/z* calcd for $C_{47}H_{64}ClNO_{13}SiNa$ $[M+Na]^+$ 936.3733, found 936.3698.

Analytical data for 20: White foam, $[\alpha]_D$ –12.4 (*c* 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$, 297 K): δ_H 7.62–7.55 (m, 4 H, Ar), 7.45–7.28 (m, 11 H, Ar), 5.72 (d, *J* = 9.2 Hz, 1 H, NHA), 5.29 (d, *J* = 3.3 Hz, 1 H, H-4B), 5.06 (t, *J* = 9.9 Hz, 1 H, H-3A), 4.75–4.66 (m, 2 H, H-2B, C*H*HPh), 4.49–4.40 (m, 2 H, H-1A, CH*H*Ph), 4.28 (d, *J* = 7.9 Hz, 1 H, H-1B), 3.96–3.70 (m, 7 H, H-2A, H-4A, H-6Aa, H-6Ab, COC*H*$_2$Cl, OC*H*HCH$_2$), 3.66–3.33 (m, 8 H, H-3B, H-5A, H-5B, H-6Ba, H-6Bb, CH_2Cl, OCH*H*CH$_2$), 2.61 (br s, 1 H, OH-3B), 2.02, 2.00 (2 s, 6 H, 2

OCOCH$_3$), 1.91 (s, 3 H, NHCOC*H$_3$*), 1.73 (m, 2 H, O(CH$_2$)$_4$C*H$_2$*CH$_2$Cl), 1.55 (m, 2 H, OCH$_2$C*H$_2$*(CH$_2$)$_3$CH$_2$Cl), 1.40 (m, 2 H, O(CH$_2$)$_3$C*H$_2$*(CH$_2$)$_2$Cl), 1.33 (m, 2 H, O(CH$_2$)$_2$C*H$_2$*(CH$_2$)$_3$Cl), 1.04 (s, 9 H, C(C*H$_3$*)$_3$). ^{13}C NMR (100 MHz, CDCl$_3$, 297 K): δ_C 171.1, 170.9, 170.4, 167.3 (C=O), 137.8 (quat Ar), 135.5 (Ar), 132.7, 132.6 (quat Ar), 130.1, 130.0, 128.5, 127.9 (Ar), 100.9 (C-1A), 100.0 (C-1B), 74.5 (C-3A, C-4A), 74.4 (C-5A), 73.6 (*C*H$_2$Ph), 73.1 (C-2B), 73.0 (C-5B), 71.5 (C-3B), 69.4 (C-4B), 69.3 (O*C*H$_2$CH$_2$), 67.5 (C-6A), 61.1 (C-6B), 53.4 (C-2A), 45.0 (*C*H$_2$Cl), 40.8 (CO*C*H$_2$Cl), 32.4 (O(CH$_2$)$_4$*C*H$_2$CH$_2$Cl), 29.2 (OCH$_2$*C*H$_2$(CH$_2$)$_3$CH$_2$Cl), 26.7 (C(*C*H$_3$)$_3$), 26.5 (O(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$Cl), 25.2 (O(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$Cl), 23.2 (NHCO*C*H$_3$), 21.0, 20.7 (OCO*C*H$_3$), 19.1 (*C*(CH$_3$)$_3$). HRMS (ESI-TOF) *m/z* calcd for C$_{49}$H$_{66}$Cl$_2$NO$_{14}$Si [M+H]$^+$ 990.3630, found 990.3546.

6-Chlorohexyl 2-acetamido-4-*O*-[2,4-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-β-D-galactopyranosyl]-6-*O*-benzyl-3-*O*-chloroacetyl-2-deoxy-β-D-glucopyranoside (21). Disaccharide acceptor **20** (1.94 g, 1.96 mmol) and glycosyl donor **7** (3.54 g, 5.87 mmol, 3 equiv) were dissolved in anhyd CH$_2$Cl$_2$ (100 mL) under N$_2$. Freshly distilled TESOTf (885 μL, 3.91 mmol, 2 equiv) was added to the reaction mixture, which was stirred at rt for 45 min. The reaction was quenched with NEt$_3$ (655 μL, 4.70 mmol, 2.4 equiv) and the mixture was diluted with CH$_2$Cl$_2$ (50 mL) and washed with satd aq NaHCO$_3$ (150 mL). The aq layer was re-extracted with CH$_2$Cl$_2$ (3 × 40 mL) and the combined organic layers were dried and concentrated. Column chromatography (EtOAc/hexanes, 45:55–6:4) gave trisaccharide **21** (1.99 g, 70%) pure as a yellowish amorphous foam. [α]$_D$ –21.8 (*c* 1.0, CH$_2$Cl$_2$). ^{1}H NMR (600 MHz, CDCl$_3$, 295 K): δ_H 7.63–7.57 (m, 4 H, Ar), 7.46–7.25 (m, 16 H, Ar), 7.05 (d, *J* = 9.8 Hz, 1 H, NHA'), 5.78 (d, *J* = 9.4 Hz, 1 H, NHA), 5.51 (s, 1 H, >C*H*Ph), 5.39 (t, *J* = 10.0 Hz, 1 H, H-3A'), 5.35 (d, *J* = 3.4 Hz,

1 H, H-4B), 4.99 (t, *J* = 8.3 Hz, 1 H, H-3A), 4.84 (dd, *J* = 8.1, 9.8 Hz, 1 H, H-2B), 4.70 (d, *J* = 12.1 Hz, 1 H, C*H*HPh), 4.57 (d, *J* = 7.9 Hz, 1 H, H-1A'), 4.50 (d, *J* = 12.0 Hz, 1 H, C*H*HPh), 4.37 (d, *J* = 7.2 Hz, 1 H, H-1A), 4.32 (d, *J* = 8.0 Hz, 1 H, H-1B), 4.27 (dd, *J* = 4.9, 10.4 Hz, 1 H, H-6Aa'), 4.03 (m, 1 H, H-2A), 3.91–3.61 (m, 10 H, H-4A, H-6Aab, H-6Ba, H-2A', H-4A', H-6Ab', COCH_2Cl, OC*H*HCH$_2$), 3.56–3.47 (m, 5 H, H-3B, H-6Bb, H-5A', CH$_2$Cl), 3.47–3.41 (m, 2 H, H-5A, H-5B), 3.38 (m, 1 H, OCH*H*CH$_2$), 2.02, 2.01, 1.92 (3 s, 9 H, 3 OCOCH$_3$), 1.91 (s, 3 H, NHCOC*H*$_3$), 1.72 (m, 2 H, O(CH$_2$)$_4$CH_2CH$_2$Cl), 1.54 (m, 2 H, OCH$_2$CH_2(CH$_2$)$_3$CH$_2$Cl), 1.40 (m, 2 H, O(CH$_2$)$_3$CH_2(CH$_2$)$_2$Cl), 1.32 (m, 2 H, O(CH$_2$)$_2$CH_2(CH$_2$)$_3$Cl), 1.06 (s, 9 H, C(CH_3)$_3$). ^{13}C NMR (125 MHz, CDCl$_3$, 295 K): δ_C 171.3, 170.0, 169.8, 168.6, 167.1, 161.9 (C=O), 137.9, 136.9 (quat Ar), 135.6, 135.5 (Ar), 132.8, 132.7 (quat Ar), 130.0, 129.1, 128.4, 128.3, 128.0, 127.9, 127.8, 126.0 (Ar), 101.1 (>*C*HPh) 100.9 (C-1A), 100.4 (C-1A'), 100.2 (C-1B), 92.3 (CCl$_3$), 78.3 (C-4A'), 75.2 (C-3B), 74.6 (C-5A), 74.1 (C-3A), 73.8 (C-4A), 73.7 (*C*H$_2$Ph), 73.6 (C-5B), 71.2 (C-2B), 70.8 (C-3A'), 69.2 (O*C*H$_2$CH$_2$), 68.6 (C-4B), 68.3 (C-6A'), 67.6 (C-6A), 66.1 (C-5A'), 61.1 (C-6B), 56.5 (C-2A'), 52.2 (C-2A), 45.0 (*C*H$_2$Cl), 40.7 (CO*C*H$_2$Cl), 32.4 (O(CH$_2$)$_4$*C*H$_2$CH$_2$Cl), 29.2 (OCH$_2$*C*H$_2$(CH$_2$)$_3$CH$_2$Cl), 26.8 (C(*C*H$_3$)$_3$), 26.5 (O(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$Cl), 25.2 (O(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$Cl), 23.2 (NHCO*C*H$_3$), 21.0, 20.8, 20.7 (OCO*C*H$_3$), 19.1 (*C*(CH$_3$)$_3$). HRMS (ESI-TOF) *m/z* calcd for $C_{66}H_{82}Cl_5N_2O_{20}Si$ $[M+H]^+$ 1425.367, found 1425.367.

6-Chlorohexyl 2-acetamido-4-*O*-[2,4-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-β-D-galactopyranosyl]-6-*O*-benzyl-3-*O*-chloroacetyl-2-deoxy-β-D-glucopyranoside (22). A solution of the benzylidene acetal **21** (962 mg, 0.672 mmol) in anhyd THF (17 mL) containing freshly activated molecular sieves 3 Å (2.55 g), NaCNBH$_3$ (633 mg, 10.1 mmol, 15 equiv) and

methyl orange indicator (2 mg) was stirred under N_2 for 45 min at rt and cooled to 0 °C. A 2 M solution of HCl in Et_2O (5 mL, 10.1 mmol, 15 equiv) 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 was stirred at rt for 1 h, then filtered over Celite®. The solids were washed with THF (2 × 50 mL) and the combined filtrate and washings were concentrated. The residue was dissolved in CH_2Cl_2 (100 mL) and washed with satd aq $NaHCO_3$ (100 mL). The aq layer was re-extracted with CH_2Cl_2 (3 × 30 mL) and the combined organic layers were dried and concentrated. Column chromatography (CH_2Cl_2/MeOH, 100:1–30:1) gave alcohol **22** (877 mg, 91%) pure as an amorphous white foam. $[\alpha]_D$ –16.0 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 295 K): δ_H 7.61–7.55 (m, 4 H, Ar), 7.44–7.24 (m, 16 H, Ar), 6.84 (d, *J* = 8.7 Hz, 1 H, NHA'), 5.76 (d, *J* = 9.4 Hz, 1 H, NHA), 5.41 (d, *J* = 3.5 Hz, 1 H, H-4B), 5.14 (dd, *J* = 9.0, 10.8 Hz, 1 H, H-3A'), 4.98 (t, *J* = 8.8 Hz, 1 H, H-3A), 4.83 (dd, *J* = 8.1, 9.9 Hz, 1 H, H-2B), 4.68 (d, *J* = 12.1 Hz, 1 H, C*H*HPh), 4.64 (d, *J* = 8.0 Hz, 1 H, H-1A'), 4.57 (d, *J* = 11.8 Hz, 1 H, C*H*HPh), 4.51 (d, *J* = 11.8 Hz, 1 H, C*H*HPh), 4.45 (d, *J* = 12.1 Hz, 1 H, C*H*HPh), 4.37 (d, *J* = 7.4 Hz, 1 H, H-1A), 4.20 (d, *J* = 8.0 Hz, 1 H, H-1B), 3.97 (m, 1 H, H-2A), 3.88–3.51 (m, 14 H, H-4A, H-6Aab, H-3B, H-6Bab, H-2A', H-4A', H-5A', H-6Aab', COC*H*$_2$Cl, OC*H*HCH$_2$), 3.49 (t, *J* = 6.7 Hz, 2 H, CH_2Cl), 3.45–3.36 (m, 3 H, H-5A, H-5B, OCH*H*CH$_2$), 3.25 (d, *J* = 2.9 Hz, OH-4A'), 2.04, 1.97, 1.94 (3 s, 9 H, 3 $OCOCH_3$), 1.90 (s, 3 H, NHCOC*H*$_3$), 1.72 (m, 2 H, O(CH$_2$)$_4$C*H*$_2$CH$_2$Cl), 1.53 (m, 2 H, OCH$_2$C*H*$_2$(CH$_2$)$_3$CH$_2$Cl), 1.40 (m, 2 H, O(CH$_2$)$_3$C*H*$_2$(CH$_2$)$_2$Cl), 1.31 (m, 2 H, O(CH$_2$)$_2$C*H*$_2$(CH$_2$)$_3$Cl), 1.03 (s, 9 H, C(C*H*$_3$)$_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 295 K): δ_C 171.8, 170.1, 169.8, 168.9, 167.2, 161.7 (C=O), 137.8, 137.3 (quat Ar), 135.6, 135.5 (Ar), 132.7, 132.6 (quat Ar), 130.0, 128.5, 128.0, 127.9, 127.8, 127.7 (Ar), 100.9 (C-1A), 100.2 (C-1B), 99.7 (C-1A'), 92.3 (CCl_3), 75.2 (C-3B), 74.4 (C-5A), 74.1 (C-

3A), 74.0 (C-5A'), 73.9 (C-4A, *C*H_2Ph), 73.7 (C-3A'), 73.6 (C-5B, *C*H_2Ph), 71.3 (C-2B), 71.0 (C-4A'), 70.7 (C-6A'), 69.2 (O*C*$H_2$$CH_2$), 68.4 (C-4B), 67.5 (C-6A), 61.3 (C-6B), 56.2 (C-2A'), 52.5 (C-2A), 45.0 (*C*H_2Cl), 40.7 (CO*C*H_2Cl), 32.4 (O$(CH_2)_4$*C*$H_2$$CH_2$Cl), 29.2 (OC$H_2$*C*$H_2$$(CH_2)_3$$CH_2$Cl), 26.8 (C(*C*$H_3)_3$), 26.5 (O$(CH_2)_3$*C*$H_2$$(CH_2)_2$Cl), 25.2 (O$(CH_2)_2$*C*$H_2$$(CH_2)_3$Cl), 23.2 (NHCO*C*$H_3$), 21.0, 20.9, 20.6 (OCO*C*H_3), 19.0 (*C*$(CH_3)_3$). HRMS (ESI-TOF) *m/z* calcd for $C_{66}H_{84}Cl_5N_2O_{20}Si$ $[M+H]^+$ 1427.384, found 1427.383.

6-Chlorohexyl 2-acetamido-4-*O*-{2,4-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-[4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl]-β-D-galactopyranosyl}-6-*O*-benzyl-3-*O*-chloroacetyl-2-deoxy-β-D-glucopyranoside (23). A solution of glycosyl acceptor **22** (550 mg, 3.84 mmol) and known[6] thioglycoside donor **9** (367 mg, 7.67 mmol, 2 equiv) in anhyd CH_2Cl_2 (19 mL) containing freshly activated molecular sieves 4 Å (1.9 g) was stirred under N_2 for 3 h at rt. MeOTf (217 μL, 1.92 mmol, 5 equiv) was added to the reaction mixture, which was stirred at rt for 30 min. The reaction was quenched with NEt_3 (321 μL, 2.30 mmol, 6 equiv) and filtered over Celite®. The solids were washed with CH_2Cl_2 (2 × 30 mL) and the combined filtrate and washings were washed with satd aq $NaHCO_3$ (80 mL). The aq layer was re-extracted with CH_2Cl_2 (3 × 30 mL) and the combined organic layers were dried and concentrated. The resulting residue was dissolved in a mixture of Ac_2O and AcOH (3:1, 36 mL) and the solution was stirred at rt for 18 h, then co-concentrated with toluene (3 × 25 mL). Column chromatography (EtOAc/hexanes, 45:55–1:1) gave tetrasaccharide **23** (585 mg, 82%) pure as white amorphous glass. $[\alpha]_D$ –37.1 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 295 K): δ_H 7.61–7.55 (m, 4 H, Ar), 7.43–7.15 (m, 31 H, Ar), 6.55 (d, *J* = 8.8 Hz, 1 H, NHA'), 5.71 (d, *J* = 9.4 Hz, 1 H, NHA), 5.47 (d, *J* = 3.5 Hz, 1 H, H-4B), 5.12 (dd, *J* = 7.7, 10.6 Hz, 1 H, H-3A'), 4.97–4.89 (m, 3 H, H-

3A, H-1C', C*H*HPh), 4.82–4.66 (m, 5 H, H-2B, 4 C*H*HPh), 4.63–4.58 (m, 2 H, 2 C*H*HPh), 4.56 (d, *J* = 7.9 Hz, 1 H, H-1A'), 4.43 (d, *J* = 12.2 Hz, 1 H, C*H*HPh), 4.38–4.33 (m, 2 H, H-1A, C*H*HPh), 4.27 (d, *J* = 11.9 Hz, 1 H, C*H*HPh), 4.15–4.11 (m, 2 H, H-1B, H-6Aa'), 4.02–3.94 (m, 2 H, H-2A, H-2C'), 3.85–3.76 (m, 5 H, H-4A, H-3C', H-5C', COC*H*HCl, OC*H*HCH$_2$), 3.74–3.56 (m, 10 H, H-6Aab, H-3B, H-6Ba, H-2A', H-4A', H-5A', H-6Ab', H-4C', COCH*H*Cl), 3.54 (dd, *J* = 7.3, 10.0 Hz, 1 H, H-6Bb), 3.50 (t, *J* = 6.7 Hz, 2 H, CH$_2$Cl), 3.45–3.35 (m, 3 H, H-5A, H-5B, OCH*H*CH$_2$), 1.98 (2 s, 6 H, 2 OCOCH$_3$), 1.90 (2 s, 6 H, NHCOC*H*$_3$, OCOCH$_3$), 1.73 (m, 2 H, O(CH$_2$)$_4$C*H*$_2$CH$_2$Cl), 1.53 (m, 2 H, OCH$_2$C*H*$_2$(CH$_2$)$_3$CH$_2$Cl), 1.40 (m, 2 H, O(CH$_2$)$_3$C*H*$_2$(CH$_2$)$_2$Cl), 1.32 (m, 2 H, O(CH$_2$)$_2$C*H*$_2$(CH$_2$)$_3$Cl), 1.06-1.00 (m, 12 H, H-6C', C(C*H*$_3$)$_3$). ^{13}C NMR (125 MHz, CDCl$_3$, 295 K): δ_C 171.6, 170.0, 169.8, 168.7, 167.1, 161.6 (C=O), 138.6, 138.5, 138.4, 138.3, 137.7 (quat Ar), 135.6, 135.5 (Ar), 132.7, 132.6 (quat Ar), 130.0, 129.9, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.4 (Ar), 100.9 (C-1A), 100.4 (C-1C'), 100.1 (C-1B), 99.6 (C-1A'), 92.2 (CCl$_3$), 79.0 (C-3C'), 77.5 (C-4A', C-4C'), 76.5 (C-2C'), 75.4 (C-5A'), 74.9 (*C*H$_2$Ph), 74.3 (C-5A, C-3B), 74.1 (C-3A), 73.9, 73.7 (*C*H$_2$Ph), 73.6 (C-4A, C-5B), 73.4 (*C*H$_2$Ph), 73.0 (C-3A'), 72.8 (*C*H$_2$Ph), 71.4 (C-2B), 70.0 (C-6A'), 69.2 (O*C*H$_2$CH$_2$), 68.7 (C-4B), 67.8 (C-5C'), 67.4 (C-6A), 61.3 (C-6B), 56.5 (C-2A'), 52.4 (C-2A), 45.0 (*C*H$_2$Cl), 40.6 (CO*C*H$_2$Cl), 32.4 (O(CH$_2$)$_4$*C*H$_2$CH$_2$Cl), 29.2 (OCH$_2$*C*H$_2$(CH$_2$)$_3$CH$_2$Cl), 26.8 (C(*C*H$_3$)$_3$), 26.5 (O(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$Cl), 25.2 (O(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$Cl), 23.2 (NHCO*C*H$_3$), 21.2, 21.0, 20.7 (OCO*C*H$_3$), 19.0 (*C*(CH$_3$)$_3$), 16.3 (C-6C'). HRMS (ESI-TOF) *m/z* calcd for C$_{93}$H$_{112}$Cl$_5$N$_2$O$_{24}$Si [M+H]$^+$ 1843.582, found 1843.585.

6-Chlorohexyl 2-acetamido-4-*O*-{2,4-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-[4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl]-β-D-galactopyranosyl}-6-*O*-benzyl-2-deoxy-β-D-

glucopyranoside (24). Tetrasaccharide **23** (348 mg, 0.188 mmol) was dissolved in a mixture of pyridine and EtOH (2:1, 15 mL), thiourea (143 mg, 1.88 mmol, 10 equiv) was added and the solution was heated to 65 °C for 23 h, then allowed to come to rt. The reaction mixture was diluted with CH_2Cl_2 (150 mL) and washed with HCl 2 N (150 mL). The aq layer was re-extracted with CH_2Cl_2 (5 × 20 mL) and the combined organic layers were dried and concentrated. Column chromatography (CH_2Cl_2/MeOH, 9:1) gave alcohol **24** (243 mg, 73%) pure as a white amorphous foam. $[\alpha]_D$ –36.5 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 295 K): δ_H 7.57 (t, *J* = 6.4 Hz, 4 H, Ar), 7.43–7.16 (m, 31 H, Ar), 6.56 (d, *J* = 8.8 Hz, 1 H, NHA'), 5.42 (d, *J* = 3.2 Hz, 1 H, H-4B), 5.39 (d, *J* = 8.0 Hz, 1 H, NHA), 5.08 (dd, *J* = 8.0, 10.7 Hz, 1 H, H-3A'), 5.01 (dd, *J* = 8.3, 9.8 Hz, 1 H, H-2B), 4.92 (d, *J* = 11.5 Hz, 1 H, C*H*HPh), 4.88 (d, *J* = 3.5 Hz, 1 H, H-1C'), 4.78–4.65 (m, 5 H, H-1A, 4 C*H*HPh), 4.63–4.58 (m, 2 H, 2 C*H*HPh), 4.55 (d, *J* = 8.0 Hz, 1 H, H-1A'), 4.46 (d, *J* = 12.2 Hz, 1 H, C*H*HPh), 4.33 (d, *J* = 12.1 Hz, 1 H, C*H*HPh), 4.28 (d, *J* = 7.8 Hz, 1 H, H-1B), 4.25 (d, *J* = 12.0 Hz, 1 H, C*H*HPh), 4.13-4.07 (m, 2 H, H-6Aa', OH-3A), 3.96 (dd, *J* = 3.5, 10.2 Hz, 1 H, H-2C'), 3.89 (td, *J* = 1.8, 9.8 Hz, 1 H, H-3A), 3.85–3.75 (m, 4 H, H-3B, H-3C', H-5C', OC*H*HCH$_2$), 3.69–3.52 (m, 11 H, H-4A, H-6Aab, H-5B, H-6Bab, H-2A', H-4A', H-5A', H-6Ab', H-4C'), 3.49 (t, *J* = 6.7 Hz, 2 H, CH_2Cl), 3.46–3.36 (m, 3 H, H-2A, H-5A, OCH*H*CH$_2$), 1.98, 1.97, 1.95 (3 s, 9 H, 3 OCOCH$_3$), 1.82 (s, 3 H, NHCOC*H$_3$*), 1.73 (m, 2 H, O(CH$_2$)$_4$C*H$_2$*CH$_2$Cl), 1.55 (m, 2 H, OCH$_2$C*H$_2$*(CH$_2$)$_3$CH$_2$Cl), 1.41 (m, 2 H, O(CH$_2$)$_3$C*H$_2$*(CH$_2$)$_2$Cl), 1.32 (m, 2 H, O(CH$_2$)$_2$C*H$_2$*(CH$_2$)$_3$Cl), 1.04–0.97 (m, 12 H, H-6C', C(C*H$_3$*)$_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 295 K): δ_C 171.7, 170.1, 169.9, 168.9, 161.7 (C=O), 138.5, 138.4, 138.3, 138.2 (quat Ar), 135.6, 135.5 (Ar), 132.7, 132.4 (quat Ar), 129.9, 129.8, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.4, 127.3 (Ar), 101.1 (C-1B), 100.4 (C-1C'), 100.2 (C-1A), 99.8 (C-1A'), 92.2 (CCl_3), 80.5 (C-4A), 78.9 (C-3C'), 77.4 (C-4A', C-

4C'), 76.5 (C-2C'), 75.4 (C-5A'), 74.9 (*C*H_2Ph), 74.1 (C-5A, C-3B, C-5B), 73.9, 73.6, 73.3 (*C*H_2Ph), 73.2 (C-3A'), 72.7 (*C*H_2Ph), 71.5 (C-3A), 71.1 (C-2B), 69.9 (C-6A'), 69.2 (O*C*H_2CH_2), 68.8 (C-4B), 68.0 (C-6A), 67.8 (C-5C'), 61.8 (C-6B), 56.3 (C-2A, C-2A'), 45.0 (*C*H_2Cl), 32.5 (O$(CH_2)_4$*C*H_2CH_2Cl), 29.3 (OCH_2*C*$H_2(CH_2)_3CH_2$Cl), 26.8 (C(*C*$H_3)_3$), 26.5 (O$(CH_2)_3$*C*$H_2(CH_2)_2$Cl), 25.2 (O$(CH_2)_2$*C*$H_2(CH_2)_3$Cl), 23.5 (NHCO*C*H_3), 21.1, 21.0, 20.6 (OCO*C*H_3), 19.0 (*C*$(CH_3)_3$), 16.3 (C-6C'). HRMS (ESI-TOF) *m/z* calcd for $C_{91}H_{111}Cl_4N_2O_{23}Si$ $[M+H]^+$ 1767.61, found 1767.608.

6-Chlorohexyl 2-acetamido-4-*O*-{2,4-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-[4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-trichloroacetamido-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 (25). A solution of glycosyl acceptor **24** (243 mg, 0.137 mmol) and known[6] thioglycoside donor **9** (197 mg, 0.411 mmol, 3 equiv) in anhyd CH_2Cl_2 (10 mL) containing freshly activated molecular sieves 4 Å (1 g) was stirred under N_2 for 3 h at rt. MeOTf (77 μL, 0.685 mmol, 5 equiv) was added and the reaction mixture was stirred at rt for 30 min. The reaction was quenched with NEt_3 (115 μL, 0.822 mmol, 6 equiv) and the mixture filtered over Celite®. The solids were washed with CH_2Cl_2 (3 × 20 mL) and the combined filtrate and washings were washed with satd aq $NaHCO_3$ (80 mL). The aq layer was re-extracted with CH_2Cl_2 (3 × 25 mL) and the combined organic layers were dried and concentrated. The resulting residue was dissolved in a mixture of Ac_2O and AcOH (3:1, 28 mL) and the solution was stirred at rt for 18 h, then co-concentrated with toluene (4 × 20 mL). Column chromatography (EtOAc/hexanes, 4:6–1:1) gave pentasaccharide **25** (252 mg, 84%) pure as an amorphous white foam. $[\alpha]_D$ –61.6 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 295 K): δ_H 7.55–7.49 (m, 4 H, Ar), 7.37–7.10 (m, 46 H, Ar), 6.52 (d, *J* = 8.9 Hz, 1 H, NHA'), 6.01

(d, J = 7.9 Hz, 1 H, NHA), 5.62 (d, J = 3.5 Hz, 1 H, H-4B), 5.08 (dd, J = 8.1, 10.7 Hz, 1 H, H-3A'), 5.00 (d, J = 3.6 Hz, 1 H, H-1C), 4.95–4.88 (m, 3 H, H-2B, H-1C', C*H*HPh), 4.85 (d, J = 11.7 Hz, 1 H, C*H*HPh), 4.78–4.71 (m, 2 H, 2 C*H*HPh), 4.70–4.64 (m, 4 H, H-1A, 3 C*H*HPh), 4.63–4.58 (m, 2 H, 2 C*H*HPh), 4.57 (d, J = 7.9 Hz, 1 H, H-1A'), 4.56–4.47 (m, 3 H, 3 C*H*HPh), 4.41–4.36 (m, 3 H, 3 C*H*HPh), 4.31 (d, 1 H, C*H*HPh), 4.26 (d, J = 8.2 Hz, 1 H, H-1B), 4.15 (d, J = 10.3 Hz, 1 H, H-6Aa'), 4.03–3.93 (m, 4 H, H-3A, H-2C, H-5C, H-2C'), 3.85 (dd, J = 3.6, 10.0 Hz, 1 H, H-3B), 3.82–3.76 (m, 4 H, H-4A, H-6Aa, H-3C', H-5C'), 3.74–3.56 (m, 11 H, H-2A, H-6Ab, H-6Bab, H-3C, H-2A', H-4A', H-5A', H-6Ab', H-4C', OC*H*HCH$_2$), 3.54 (m, 1 H, H-5A), 3.48–3.42 (m, 3 H, H-5B, CH$_2$Cl), 3.38 (s, 1 H, H-4C), 3.33 (m, 1 H, OCH*H*CH$_2$), 1.99, 1.98, 1.95 (3 s, 9 H, 3 OCOCH$_3$), 1.76 (s, 3 H, NHCOC*H*$_3$), 1.66 (m, 2 H, O(CH$_2$)$_4$C*H*$_2$CH$_2$Cl), 1.44 (m, 2 H, OCH$_2$C*H*$_2$(CH$_2$)$_3$CH$_2$Cl), 1.31 (m, 2 H, O(CH$_2$)$_3$C*H*$_2$(CH$_2$)$_2$Cl), 1.24 (m, 2 H, O(CH$_2$)$_2$C*H*$_2$(CH$_2$)$_3$Cl), 1.03 (d, J = 6.4 Hz, 3 H, H-6C'), 0.97 (s, 9 H, C(C*H*$_3$)$_3$), 0.92 (d, J = 6.4 Hz, 3 H, H-6C). ^{13}C NMR (125 MHz, CDCl$_3$, 295 K): δ_C 171.8, 170.0, 169.6, 169.2, 161.7 (C=O), 138.8, 138.7, 138.6, 138.4, 138.3, 138.0 (quat Ar), 135.7, 135.6, 135.4 (Ar), 132.7, 132.4 (quat Ar), 129.9, 129.8, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2 (Ar), 101.4 (C-1C'), 99.7 (C-1A'), 99.6 (C-1A), 99.3 (C-1B), 96.6 (C-1C), 92.2 (CCl$_3$), 79.5 (C-3C), 79.0 (C-3C'), 77.5 (C-4C'), 77.4 (C-4C, C-4A'), 76.5 (C-2C'), 76.3 (C-2C), 75.6 (C-5A'), 74.9, 74.5 (*C*H$_2$Ph), 74.0 (C-5A), 73.9 (*C*H$_2$Ph), 73.8 (C-3B), 73.5 (*C*H$_2$Ph), 73.4 (C-5B, *C*H$_2$Ph), 73.3 (C-4A), 73.2 (C-3A'), 73.0, 72.8 (*C*H$_2$Ph), 72.7 (C-3A), 71.6 (C-2B), 70.1 (C-6A'), 69.0 (C-6A, OCH$_2$CH$_2$), 68.5 (C-4B), 67.8 (C-5C'), 66.5 (C-5C), 60.6 (C-6B), 56.3 (C-2A'), 52.9 (C-2A), 45.0 (*C*H$_2$Cl), 32.5 (O(CH$_2$)$_4$*C*H$_2$CH$_2$Cl), 29.2 (OCH$_2$*C*H$_2$(CH$_2$)$_3$CH$_2$Cl), 26.8 (C(*C*H$_3$)$_3$), 26.6 (O(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$Cl), 25.2 (O(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$Cl), 23.1 (NHCO*C*H$_3$),

21.1, 20.8 (OCO*C*H_3), 18.9 (*C*$(CH_3)_3$), 16.4 (C-6C), 16.3 (C-6C'). HRMS (ESI-TOF) *m/z* calcd for $C_{118}H_{139}Cl_4N_2O_{27}SiNa$ $[M+H+Na]^{2+}$ 1103.3988, found 1103.4086.

6-Chlorohexyl 2-acetamido-4-*O*-{2,4-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-[4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-3-*O*-acetyl-6-*O*-benzyl-2-chloroacetamido-2-deoxy-β-D-glucopyranosyl]-β-D-galactopyranosyl}-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-β-D-glucopyranoside (26) and 6-chlorohexyl 2-acetamido-4-*O*-{2,4-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-[4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-acetamido-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-β-D-glucopyranosyl]-β-D-galactopyranosyl}-3-acetyl-6-*O*-benzyl-2-deoxy-β-D-glucopyranoside (27).

Method A: To a solution of tetrasaccharide **23** (31 mg, 0.017 mmol) dissolved in AcOH (1 mL) was added freshly activated Zn (109 mg, 1.7 mmol, 100 equiv). The reaction mixture was heated to 50 °C for 20 h, then filtered over Celite®. The solids were washed with CH_2Cl_2 (2 × 15 mL) and the combined filtrate and washings were washed with satd aq $NaHCO_3$ (2 × 20 mL). The aq layers were re-extracted with CH_2Cl_2 (3 × 10 mL) and the combined organic layers were dried and concentrated. Column chromatography (CH_2Cl_2/MeOH, 100:1–30:1) gave the two products **26** and **27** as a mixture (23 mg, 79%). Analytical RP-HPLC (CH_3CN/H_2O, 80:20) showed a ratio **26**/**27** of 35:65. A small sample of the pure chloroacetamido **26** was obtained pure as a white foam by further column chromatography (CH_2Cl_2/MeOH, 60:1–30:1).

Method B: Freshly activated Zn (441 mg, 6.75 mmol, 100 equiv) was added to a solution of tetrasaccharide **23** (125 mg, 0.0675 mmol) in AcOH (4 mL). The reaction mixture was stirred at 65 °C for 5 h, then filtered over Celite®. The solids were washed with CH_2Cl_2 (2 × 15 mL) and the combined filtrate and washings were washed with satd aq $NaHCO_3$ (2 × 40 mL). The aq

layers were re-extracted with CH_2Cl_2 (5 × 15 mL) and the combined organic layers were dried and concentrated. Column chromatography (CH_2Cl_2/MeOH, 60:1–30:1) gave acetamido **27** (93 mg, 80%) pure as white amorphous foam.

Analytical data for 26: $[\alpha]_D$ –30.5 (*c* 0.2, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 295 K): δ_H 7.59–7.54 (m, 4 H, Ar), 7.41–7.19 (m, 31 H, Ar), 6.34 (d, *J* = 8.5 Hz, 1 H, NHA'), 5.52 (d, *J* = 3.4 Hz, 1 H, H-4B), 5.45 (d, *J* = 9.4 Hz, 1 H, NHA), 5.18 (dd, *J* = 8.1, 10.7 Hz, 1 H, H-3A'), 4.94–4.81 (m, 4 H, H-3A, H-2B, H-1C', C*H*HPh), 4.77–4.65 (m, 4 H, 4 C*H*HPh), 4.62–4.57 (m, 2 H, H-1A', C*H*HPh), 4.44 (d, *J* = 12.2 Hz, 1 H, C*H*HPh), 4.35 (d, *J* = 11.9 Hz, 1 H, C*H*HPh), 4.31–4.27 (m, 2 H, H-1A, C*H*HPh), 4.17–4.12 (m, 2 H, H-1B, H-6Aa'), 4.02 (d, *J* = 15.1 Hz, 1 H, COC*H*HCl), 3.97–3.93 (m, 2 H, H-2A, H-2C'), 3.87 (d, *J* = 15.1 Hz, 1 H, COCH*H*Cl), 3.82–3.76 (m, 4 H, H-4A, H-3C', H-5C', OC*H*HCH$_2$), 3.66–3.48 (m, 11 H, H-6Aab, H-3B, H-6Bab, H-4A', H-5A', H-6Ab', H-4C', CH_2Cl), 3.47–3.34 (m, 4 H, H-5A, H-5B, H-2A', OCH*H*CH$_2$), 2.00, 1.98, 1.93 (3 s, 9 H, 3 $OCOCH_3$), 1.89 (1 s, 3 H, NHCOC*H$_3$*), 1.75-1.70 (m, 5 H, O(CH$_2$)$_4$C*H$_2$*CH$_2$Cl, OCOC*H$_3$*), 1.52 (m, 2 H, OCH$_2$C*H$_2$*(CH$_2$)$_3$CH$_2$Cl), 1.40 (m, 2 H, O(CH$_2$)$_3$C*H$_2$*(CH$_2$)$_2$Cl), 1.31 (m, 2 H, O(CH$_2$)$_2$C*H$_2$*(CH$_2$)$_3$Cl), 1.03-0.98 (m, 12 H, H-6C', C(C*H$_3$*)$_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 295 K): δ_C 171.5, 170.7, 169.9, 169.6, 169.3, 166.2 (C=O), 138.6, 138.4, 137.8 (quat Ar), 135.6, 135.5 (Ar), 132.9, 132.8 (quat Ar), 129.9, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4 (Ar), 101.2 (C-1A), 100.4 (C-1C'), 100.4 (C-1A'), 100.0 (C-1B), 79.0 (C-3C'), 77.9 (C-4A'), 77.6 (C-4C'), 76.6 (C-2C'), 75.4 (C-5A'), 75.3 (C-3B), 74.9 (*C*H$_2$Ph), 74.7 (C-5A), 74.1 (C-4A), 73.8, 73.7, 73.5 (*C*H$_2$Ph), 73.4 (C-5B), 73.1 (C-3A'), 72.8 (*C*H$_2$Ph), 72.4 (C-3A), 71.3 (C-2B), 70.2 (C-6A'), 69.1 (O*C*H$_2$CH$_2$), 68.9 (C-4B), 67.8 (C-5C'), 67.6 (C-6A), 61.2 (C-6B), 55.6 (C-2A'), 52.9 (C-2A), 45.0 (*C*H$_2$Cl), 42.7 (CO*C*H$_2$Cl), 32.5 (O(CH$_2$)$_4$*C*H$_2$CH$_2$Cl), 29.2 (OCH$_2$*C*H$_2$(CH$_2$)$_3$CH$_2$Cl), 26.8

(C(CH_3)$_3$), 26.5 (O(CH_2)$_3$$CH_2$($CH_2$)$_2$Cl), 25.2 (O($CH_2$)$_2$$CH_2$($CH_2$)$_3$Cl), 23.2 (NHCO$CH_3$), 21.2, 21.1, 20.8, 20.5 (OCOCH_3), 19.0 (C(CH_3)$_3$), 16.3 (C-6C'). HRMS (ESI-TOF) *m/z* calcd for $C_{93}H_{115}Cl_2N_2O_{24}Si$ $[M+H]^+$ 1741.699, found 1741.705.

Analytical data for 27: $[\alpha]_D$ –25.6 (*c* 0.9, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 295 K): δ_H 7.59–7.54 (m, 4 H, Ar), 7.41–7.19 (m, 31 H, Ar), 5.50 (d, *J* = 3.5 Hz, 1 H, H-4B), 5.47 (d, *J* = 9.3 Hz, 1 H, NHA), 5.25 (d, *J* = 8.3 Hz, 1 H, NHA'), 5.19 (dd, *J* = 8.2, 10.2 Hz, 1 H, H-3A'), 4.93–4.86 (m, 3 H, H-3A, H-1C', C*H*HPh), 4.84 (dd, *J* = 8.2, 9.9 Hz, 1 H, H-2B), 4.75–4.64 (m, 5 H, H-1A', 4 C*H*HPh), 4.62–4.57 (m, 2 H, 2 C*H*HPh), 4.44 (d, *J* = 12.2 Hz, 1 H, C*H*HPh), 4.37–4.27 (m, 3 H, H-1A, 2 C*H*HPh), 4.17 (d, *J* = 8.0 Hz, 1 H, H-1B), 4.10 (m, 1 H, H-6Aa'), 3.97–3.92 (m, 2 H, H-2A, H-2C'), 3.83–3.75 (m, 4 H, H-4A, H-3C', H-5C', OC*H*HCH$_2$), 3.69–3.47 (m, 11 H, H-6Aab, H-3B, H-6Bab, H-4A', H-5A', H-6Ab', H-4C', CH_2Cl), 3.46–3.32 (m, 4 H, H-5A, H-5B, H-2A', OCH*H*CH$_2$), 1.98, 1.97, 1.95 (3 s, 9 H, 3 OCOCH_3), 1.89, 1.81 (2 s, 6 H, 2 NHCOCH_3), 1.75-1.70 (m, 5 H, O(CH_2)$_4$C$H_2$$CH_2Cl, OCOCH_3$), 1.53 (m, 2 H, OCH$_2CH_2$($CH_2$)$_3$$CH_2$Cl), 1.40 (m, 2 H, O($CH_2$)$_3CH_2$($CH_2$)$_2$Cl), 1.30 (m, 2 H, O($CH_2$)$_2CH_2$($CH_2$)$_3$Cl), 1.04–0.98 (m, 12 H, H-6C', C(CH_3)$_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 295 K): δ_C 171.3, 170.6, 170.2, 169.8, 169.5, 169.4 (C=O), 138.6, 138.4, 138.3, 137.7 (quat Ar), 135.6, 135.5 (Ar), 132.8 (quat Ar), 129.8, 128.5, 128.4, 128.3, 128.2, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4 (Ar), 101.1 (C-1A), 100.1 (C-1C'), 100.0 (C-1B), 99.9 (C-1A'), 79.0 (C-3C'), 77.6 (C-4A', C-4C'), 76.6 (C-2C'), 75.1 (C-3B, C-5A'), 74.9 (CH$_2$Ph), 74.7 (C-5A), 74.0 (C-4A), 73.8, 73.7 (CH$_2$Ph), 73.6 (C-5B, C-3A'), 73.4, 72.8 (CH$_2$Ph), 72.4 (C-3A), 71.7 (C-2B), 70.2 (C-6A'), 69.1 (OCH$_2$CH$_2$), 68.9 (C-4B), 67.7 (C-5C'), 67.6 (C-6A), 61.3 (C-6B), 55.6 (C-2A'), 52.8 (C-2A), 45.0 (CH$_2$Cl), 32.5 (O(CH_2)$_4$$CH_2CH_2$Cl), 29.2 (OCH$_2$$CH_2$($CH_2$)$_3$$CH_2$Cl), 26.8 (C($CH_3$)$_3$), 26.5 (O($CH_2$)$_3$$CH_2$($CH_2$)$_2$Cl), 25.2 (O($CH_2$)$_2$$CH_2$($CH_2$)$_3$Cl), 23.3, 23.2 (NHCO$CH_3$),

21.3, 21.1, 20.7, 20.6 (OCO*C*H_3), 19.0 (*C*$(CH_3)_3$), 16.3 (C-6C'). HRMS (ESI-TOF) *m/z* calcd for $C_{93}H_{116}ClN_2O_{24}Si$ $[M+H]^+$ 1707.738, found 1707.734.

6-Azido 2-acetamido-4-*O*-{2,4-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-[4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-acetamido-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-β-D-glucopyranosyl]-β-D-galactopyranosyl}-3-acetyl-6-*O*-benzyl-2-deoxy-β-D-glucopyranoside (28). Sodium azide (38 mg, 0.584 mmol, 10 equiv) was added to a solution of tetrasaccharide **27** (100 mg, 0.0584 mmol) in DMF (4 mL) and the reaction mixture was stirred at 80 °C for 20 h. The solvent was evaporated, the residue dissolved in CH_2Cl_2 (50 mL) and washed with water (2 × 30 mL). The aq layers were re-extracted with CH_2Cl_2 (5 × 10 mL) and the combined organic layers were dried and concentrated. Column chromatography (CH_2Cl_2/MeOH, 30:1) gave azido **28** (94 mg, 94%) pure as a white foam. $[\alpha]_D$ –42.6 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 295 K): δ_H 7.60–7.55 (m, 4 H, Ar), 7.41–7.20 (m, 31 H, Ar), 5.55 (d, *J* = 9.4 Hz, 1 H, NHA), 5.50 (d, *J* = 3.5 Hz, 1 H, H-4B), 5.32 (d, *J* = 8.3 Hz, 1 H, NHA'), 5.19 (dd, *J* = 8.2, 10.2 Hz, 1 H, H-3A'), 4.94–4.86 (m, 3 H, H-3A, H-1C', C*H*HPh), 4.84 (dd, *J* = 8.2, 9.9 Hz, 1 H, H-2B), 4.76–4.65 (m, 5 H, H-1A', 4 C*H*HPh), 4.62–4.58 (m, 2 H, 2 C*H*HPh), 4.44 (d, *J* = 12.2 Hz, 1 H, C*H*HPh), 4.37–4.28 (m, 3 H, H-1A, 2 C*H*HPh), 4.17 (d, *J* = 7.9 Hz, 1 H, H-1B), 4.10 (m, 1 H, H-6Aa'), 3.97–3.93 (m, 2 H, H-2A, H-2C'), 3.84–3.76 (m, 4 H, H-4A, H-3C', H-5C', OC*H*HCH$_2$), 3.70–3.49 (m, 9 H, H-6Aab, H-3B, H-6Bab, H-4A', H-5A', H-6Ab', H-4C'), 3.46–3.32 (m, 4 H, H-5A, H-5B, H-2A', OCH*H*CH$_2$), 3.22 (t, *J* = 6.9 Hz, 2 H, CH_2N_3), 1.98, 1.97, 1.94 (3 s, 9 H, 3 OCOC*H*$_3$), 1.89, 1.81 (2 s, 6 H, 2 NHCOC*H*$_3$), 1.72 (s, 3 H, $OCOCH_3$), 1.58-1.50 (m, 4 H, $O(CH_2)_4CH_2CH_2N_3$, $OCH_2CH_2(CH_2)_3CH_2N_3$), 1.36–1.29 (m, 4 H, $O(CH_2)_3CH_2(CH_2)_2N_3$, $O(CH_2)_2CH_2(CH_2)_3N_3$), 1.04–0.98 (m, 12 H, H-6C', C(C*H*$_3$)$_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 295 K): δ_C 171.3, 170.6, 170.2, 169.8, 169.5, 169.4 (C=O), 138.6, 138.4,

138.3, 137.7 (quat Ar), 135.6, 135.5 (Ar), 132.8 (quat Ar), 129.8, 128.5, 128.4, 128.3, 128.2, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4 (Ar), 101.1 (C-1A), 100.1 (C-1C'), 100.0 (C-1B), 99.9 (C-1A'), 79.0 (C-3C'), 77.6 (C-4A', C-4C'), 76.5 (C-2C'), 75.1 (C-3B, C-5A'), 74.9 (CH$_2$Ph), 74.6 (C-5A), 74.0 (C-4A), 73.8, 73.7 (CH$_2$Ph), 73.5 (C-5B, C-3A'), 73.4, 72.8 (CH$_2$Ph), 72.4 (C-3A), 71.6 (C-2B), 70.1 (C-6A'), 69.0 (OCH$_2$CH$_2$), 68.9 (C-4B), 67.7 (C-5C'), 67.6 (C-6A), 61.3 (C-6B), 55.6 (C-2A'), 52.8 (C-2A), 51.3 (CH$_2$N$_3$), 29.2 (OCH$_2C$H$_2$(CH$_2$)$_3$CH$_2$N$_3$), 28.7 (O(CH$_2$)$_4C$H$_2$CH$_2$N$_3$), 26.8 (C(CH$_3$)$_3$), 26.4 (O(CH$_2$)$_3C$H$_2$(CH$_2$)$_2$N$_3$), 25.5 (O(CH$_2$)$_2C$H$_2$(CH$_2$)$_3$N$_3$), 23.2, 23.1 (NHCOCH$_3$), 21.2, 21.0, 20.7, 20.5 (OCOCH$_3$), 19.0 (C(CH$_3$)$_3$), 16.3 (C-6C'). HRMS (ESI-TOF) *m/z* calcd for $C_{93}H_{116}N_5O_{24}Si$ $[M+H]^+$ 1714.778, found 1714.771.

6-Chlorohexyl 2-acetamido-4-*O*-{6-*O*-*tert*-butyldiphenylsilyl-3-*O*-[4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-acetamido-6-*O*-benzyl-2-deoxy-β-D-glucopyranosyl]-β-D-galactopyranosyl}-6-*O*-benzyl-2-deoxy-β-D-glucopyranoside (29). A solution of tetrasaccharide **27** (105 mg, 0.0613 mmol) in 0.25 M NaOMe in MeOH (8 mL) was stirred at rt for 2 h, then deionized with Dowex 50 (H^+) resin. The resin was filtered off, washed with MeOH (4 × 20 mL) and the combined filtrate and washings were concentrated to give compound **29** (95 mg, quant) pure as a white amorphous foam. $[\alpha]_D$ –33.7 (*c* 1.0, MeOH). ^{1}H NMR (600 MHz, CD_3OD, 295 K): δ_H 7.68–7.63 (m, 4 H, Ar), 7.42–7.08 (m, 31 H, Ar), 4.99 (d, J = 3.2 Hz, 1 H, H-1C'), 4.90 (d, J = 11.3 Hz, 1 H, CHHPh), 4.79–4.75 (m, 2 H, 2 CHHPh), 4.71 (d, J = 11.7 Hz, 1 H, CHHPh), 4.64–4.57 (m, 4 H, H-1A', 3 CHHPh), 4.54 (d, J = 11.8 Hz, 1 H, CHHPh), 4.38 (d, J = 8.3 Hz, 1 H, H-1A), 4.31–4.25 (m, 3 H, H-1B, H-5C', CHHPh), 4.20 (d, J = 11.9 Hz, 1 H, CHHPh), 4.04 (d, J = 2.3 Hz, 1 H, H-4B), 3.98–3.91 (m, 2 H, H-2C', H-3C'), 3.90–3.76 (m, 7 H, H-6Aab, H-6Bab, H-6Aa', H-4C', OCHHCH$_2$), 3.75–3.49 (m, 12 H, H-2A, H-3A, H-4A, H-5A,

H-2B, H-2A', H-3A', H-4A', H-5A', H-6Ab', CH_2Cl), 3.48–3.42 (m, 3 H, H-3B, H-5B, OCH*H*CH_2), 1.99, 1.90 (2 s, 6 H, 2 NHCOC*H*$_3$), 1.72 (m, 2 H, $O(CH_2)_4CH_2CH_2Cl$), 1.55 (m, 2 H, $OCH_2CH_2(CH_2)_3CH_2Cl$), 1.41 (m, 2 H, $O(CH_2)_3CH_2(CH_2)_2Cl$), 1.36 (m, 2 H, $O(CH_2)_2CH_2(CH_2)_3Cl$), 1.14 (d, J = 6.4 Hz, 3 H, H-6C'), 1.01 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (125 MHz, CD_3OD, 295 K): δ_C 174.4, 173.3 (C=O), 140.0, 139.8, 139.4 (quat Ar), 136.7, 135.6 (Ar), 134.4, 134.3 (quat Ar), 131.0, 130.9, 129.4, 129.3, 129.2, 128.9, 128.8, 128.7, 128.6, (Ar), 105.1 (C-1B), 104.1 (C-1A'), 102.8 (C-1A), 100.2 (C-1C'), 83.5 (C-3B), 81.2 (C-4A), 80.5 (C-3C'), 79.6 (C-4A'), 79.2 (C-4C'), 77.3 (C-2C'), 76.2 (CH_2Ph), 76.2 (C-5A'), 76.0 (C-5B), 75.7 (C-5A), 75.2 (CH_2Ph), 74.5 (C-3A'), 74.4 (CH_2Ph), 73.9 (C-3A), 73.4 (CH_2Ph), 71.4 (C-2B), 70.5 (OCH_2CH_2), 69.9 (C-6A), 69.7 (C-6A'), 69.3 (C-4B), 68.6 (C-5C'), 63.6 (C-6B), 57.7 (C-2A'), 56.6 (C-2A), 45.7 (CH_2Cl), 33.8 ($O(CH_2)_4CH_2CH_2Cl$), 30.5 ($OCH_2CH_2(CH_2)_3CH_2Cl$), 27.6 ($O(CH_2)_3CH_2(CH_2)_2Cl$), 27.5 ($C(CH_3)_3$), 26.4 ($O(CH_2)_2CH_2(CH_2)_3Cl$), 23.1, 23.0 ($NHCOCH_3$), 20.0 ($C(CH_3)_3$), 16.9 (C-6C'). HRMS (ESI-TOF) *m/z* calcd for $C_{85}H_{107}ClN_2O_{20}SiNa$ $[M+Na]^+$ 1561.677, found 1561.679.

6-Azido 2-acetamido-4-*O*-{6-*O*-*tert*-butyldiphenylsilyl-3-*O*-[4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-acetamido-6-*O*-benzyl-2-deoxy-β-D-glucopyranosyl]-β-D-galactopyranosyl}-6-*O*-benzyl-2-deoxy-β-D-glucopyranoside (30). Tetrasaccharide **28** (90 mg, 0.0522 mmol) was de-acetylated as described above for the preparation of tetrasaccharide **29**. After work up, as described above, tetrasaccharide **30** (81 mg, quant) was obtained pure as a colorless amorphous glass. $[\alpha]_D$ –31.2 (*c* 1.0, MeOH). ^{1}H NMR (600 MHz, CD_3OD, 295 K): δ_H 7.68–7.63 (m, 4 H, Ar), 7.42–7.08 (m, 31 H, Ar), 4.99 (d, J = 3.4 Hz, 1 H, H-1C'), 4.90 (d, J = 11.3 Hz, 1 H, C*H*HPh), 4.80–4.76 (m, 2 H, 2 C*H*HPh), 4.72 (d, J = 11.6 Hz, 1 H, C*H*HPh), 4.64–4.58 (m, 4 H, H-1A', 3 C*H*HPh), 4.55 (d, J = 11.8 Hz, 1 H, C*H*HPh), 4.38 (d, J = 8.3 Hz, 1 H, H-

1A), 4.31–4.25 (m, 3 H, H-1B, H-5C', C*H*HPh), 4.20 (d, *J* = 11.9 Hz, 1 H, C*H*HPh), 4.04 (d, *J* = 3.2 Hz, 1 H, H-4B), 3.98–3.91 (m, 2 H, H-2C', H-3C'), 3.89–3.76 (m, 7 H, H-6Aab, H-6Bab, H-6Aa', H-4C', OC*H*HCH$_2$), 3.74–3.50 (m, 10 H, H-2A, H-3A, H-4A, H-5A, H-2B, H-2A', H-3A', H-4A', H-5A', H-6Ab'), 3.48–3.42 (m, 3 H, H-3B, H-5B, OCH*H*CH$_2$), 3.24 (t, *J* = 6.8 Hz, 2 H, CH$_2$N$_3$), 1.98, 1.90 (2 s, 6 H, 2 NHCOC*H*$_3$), 1.58–1.51 (m, 4 H, O(CH$_2$)$_4$C*H*$_2$CH$_2$N$_3$, OCH$_2$C*H*$_2$(CH$_2$)$_3$CH$_2$N$_3$), 1.39–1.33 (m, 4 H, O(CH$_2$)$_3$C*H*$_2$(CH$_2$)$_2$N$_3$, O(CH$_2$)$_2$C*H*$_2$(CH$_2$)$_3$N$_3$), 1.13 (d, *J* = 6.5 Hz, 3 H, H-6C'), 1.02 (s, 9 H, C(C*H*$_3$)$_3$). ^{13}C NMR (125 MHz, CD$_3$OD, 295 K): δ_C 174.4, 173.3 (C=O), 140.0, 139.8, 139.5 (quat Ar), 136.7, 135.6 (Ar), 134.4, 134.3 (quat Ar), 131.0, 130.9, 129.4, 129.3, 129.2, 128.9, 128.8, 128.7, 128.6, (Ar), 105.1 (C-1B), 104.1 (C-1A'), 102.8 (C-1A), 100.2 (C-1C'), 83.5 (C-3B), 81.2 (C-4A), 80.5 (C-3C'), 79.6 (C-4A'), 79.2 (C-4C'), 77.3 (C-2C'), 76.2 (*C*H$_2$Ph), 76.2 (C-5A'), 76.0 (C-5B), 75.7 (C-5A), 75.2 (*C*H$_2$Ph), 74.5 (C-3A'), 74.4 (*C*H$_2$Ph), 73.9 (C-3A), 73.4 (*C*H$_2$Ph), 71.4 (C-2B), 70.5 (O*C*H$_2$CH$_2$), 69.9 (C-6A), 69.7 (C-6A'), 69.3 (C-4B), 68.6 (C-5C'), 63.6 (C-6B), 57.7 (C-2A'), 56.6 (C-2A), 52.4 (*C*H$_2$N$_3$), 30.5 (OCH$_2$*C*H$_2$(CH$_2$)$_3$CH$_2$N$_3$), 29.9 (O(CH$_2$)$_4$*C*H$_2$CH$_2$N$_3$), 27.5 (C(*C*H$_3$)$_3$), 27.2 (O(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$N$_3$), 26.6 (O(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$N$_3$), 23.1, 23.0 (NHCO*C*H$_3$), 20.0 (*C*(CH$_3$)$_3$), 16.9 (C-6C'). HRMS (ESI-TOF) *m/z* calcd for C$_{85}$H$_{108}$N$_5$O$_{20}$Si [M+H]$^+$ 1546.736, found 1546.735.

6-Chlorohexyl 2-acetamido-4-*O*-{3-*O*-[4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-acetamido-6-*O*-benzyl-2-deoxy-β-D-glucopyranosyl]-β-D-galactopyranosyl}-6-*O*-benzyl-2-deoxy-β-D-glucopyranoside (31). To a solution of tetrasaccharide **29** (28 mg, 0.0180 mmol) in THF (2 mL) was added a 1 M solution of TBAF in THF (18 μL, 0.0180 mmol, 1 equiv) and the reaction was stirred at rt for 1 h. After evaporation of the solvent, column chromatography (CH$_2$Cl$_2$/MeOH, 100:1 then 30:1 then 9:1) followed by RP HPLC (CH$_3$CN/H$_2$O, 45:70, 30 min)

of the residue gave tetrasaccharide **31** (14 mg, 59%) pure as an amorphous white foam. $[\alpha]_D$ –41.5 (*c* 1.0, MeOH). ^{1}H NMR (600 MHz, CD_3OD, 295 K): δ_H 7.41–7.38 (m, 2 H, Ar), 7.36–7.22 (m, 23 H, Ar), 5.01 (d, *J* = 3.6 Hz, 1 H, H-1C'), 4.90 (d, *J* = 11.2 Hz, 1 H, C*H*HPh), 4.81–4.75 (m, 2 H, 2 C*H*HPh), 4.72 (d, *J* = 11.7 Hz, 1 H, C*H*HPh), 4.65–4.60 (m, 3 H, 3 C*H*HPh), 4.58 (d, *J* = 8.4 Hz, 1 H, H-1A'), 4.53 (d, *J* = 11.8 Hz, 1 H, C*H*HPh), 4.38 (d, *J* = 8.4 Hz, 1 H, H-1A), 4.37–4.25 (m, 4 H, H-1B, H-5C', 2 C*H*HPh), 3.98 (dd, *J* = 3.6, 10.3 Hz, 1 H, H-2C'), 3.96–3.92 (m, 2 H, H-4B, H-3C'), 3.90 (dd, *J* = 4.2, 6.8 Hz, 1 H, H-6Aa'), 3.86–3.81 (m, 3 H, H-6Ab', H-4C', OC*H*HCH$_2$), 3.77 (d, *J* = 3.2 Hz, 2 H, H-6Aab), 3.75–3.69 (m, 3 H, H-2A, H-6Ba, H-2A'), 3.67–3.40 (m, 13 H, H-3A, H-4A, H-5A, H-2B, H-3B, H-5B, H-6Bb, H-3A', H-4A', H-5A', OCH*H*CH$_2$, CH$_2$Cl), 1.98, 1.95 (2 s, 6 H, 2 NHCOC*H*$_3$), 1.73 (m, 2 H, O(CH$_2$)$_4$C*H*$_2$CH$_2$Cl), 1.55 (m, 2 H, OCH$_2$C*H*$_2$(CH$_2$)$_3$CH$_2$Cl), 1.43 (m, 2 H, O(CH$_2$)$_3$C*H*$_2$(CH$_2$)$_2$Cl), 1.37 (m, 2 H, O(CH$_2$)$_2$C*H*$_2$(CH$_2$)$_3$Cl), 1.14 (d, *J* = 6.5 Hz, 3 H, H-6C'). ^{13}C NMR (125 MHz, CD_3OD, 295 K): δ_C 174.4, 173.4 (C=O), 140.1, 139.8, 139.7, 139.6 (quat Ar), 129.4, 129.3, 128.9, 128.8, 128.7, 128.6, (Ar), 104.9 (C-1B), 104.1 (C-1A'), 102.8 (C-1A), 100.3 (C-1C'), 83.4 (C-3B), 80.5 (C-4A, C-3C'), 80.0 (C-4A'), 79.2 (C-4C'), 77.4 (C-2C'), 76.8 (C-5B), 76.3 (*C*H$_2$Ph), 75.9 (C-5A), 75.8 (C-5A'), 75.2 (*C*H$_2$Ph), 74.6 (C-3A'), 74.4, 74.3 (*C*H$_2$Ph), 74.1 (C-3A), 73.4 (*C*H$_2$Ph), 71.6 (C-2B), 70.5 (O*C*H$_2$CH$_2$), 70.2 (C-4B), 69.8 (C-6A), 69.7 (C-6A'), 68.7 (C-5C'), 62.6 (C-6B), 57.7 (C-2A'), 56.7 (C-2A), 45.7 (*C*H$_2$Cl), 33.8 (O(CH$_2$)$_4$*C*H$_2$CH$_2$Cl), 30.5 (OCH$_2$*C*H$_2$(CH$_2$)$_3$CH$_2$Cl), 27.6 (O(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$Cl), 26.4 (O(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$Cl), 23.1, 23.0 (NHCO*C*H$_3$), 16.9 (C-6C'). HRMS (ESI-TOF) *m/z* calcd for $C_{69}H_{90}ClN_2O_{20}$ $[M+H]^+$ 1301.578, found 1301.572.

***n*-Hexyl 2-acetamido-2-deoxy-4-*O*-{3-*O*-[2-acetamido-2-deoxy-4-*O*-(α-L-fucopyranosyl)-β-D-glucopyranosyl]-β-D-galactopyranosyl}-β-D-glucopyranoside (2).** To a

solution of tetrasaccharide **29** (71 mg, 0.0455 mmol) in THF (5 mL) was added a 1 M solution of TBAF in THF (45 μL, 0.0455 mmol, 1 equiv) and the reaction was stirred at rt for 1 h. After evaporation of the solvent, column chromatography (CH_2Cl_2/MeOH, 100:1–9:1) of the residue gave tetrasaccharide **31**, contaminated with tetrabutyl ammonium salts, which was directly dissolved in anhyd THF (5 mL) and added at –78 °C to a deep blue solution of liquid ammonia (25 mL) containing a piece of sodium (60 mg, 2.61 mmol, 57 equiv). The mixture was stirred for 1 h at –78 °C, quenched with MeOH (5 mL) and the ammonia was allowed to evaporate at rt for 3 h. The remaining solution was neutralized with AcOH (500 μL), the solvent was evaporated and the residue was dissolved in milli-Q water and passed twice through a Biogel P2 size exclusion column eluted with Milli-Q water. After lyophilization, hexyl glycoside **2** (19 mg, 50% over two steps) was obtained pure as a white amorphous powder. $[\alpha]_D$ –43.5 (*c* 1.0, H_2O). ^{1}H NMR (D_2O, 600 MHz, 295 K): δ_H 4.94 (d, *J* = 3.8 Hz, 1 H, H-1C'), 4.67 (d, *J* = 8.5 Hz, 1 H, H-1A'), 4.51 (d, *J* = 7.7 Hz, 1 H, H-1A), 4.44 (d, *J* = 7.9 Hz, 1 H, H-1B), 4.35 (m, 1 H, H-5C'), 4.14 (d, *J* = 3.2 Hz, 1 H, H-4B), 4.00–3.84 (m, 4 H, H-6Aa, H-6Aab', OC*H*HCH$_2$), 3.83–3.63 (m, 13 H, H-2A, H-3A, H-4A, H-6Ab, H-3B, H-5B, H-6Bab, H-2A', H-3A', H-2C', H-3C',H-4C'), 3.60–3.55 (m, 4 H, H-5A, H-2B, H-4A', OCH*H*CH$_2$), 3.53 (m, 1 H, H-5A'), 2.03, 2.02 (2 s, 6 H, 2 OCOCH$_3$), 1.53 (m, 2 H, OCH$_2$C*H*$_2$(CH$_2$)$_3$CH$_3$), 1.33–1.22 (m, 6 H, OCH$_2$CH$_2$(C*H*$_2$)$_3$CH$_3$), 1.15 (d, *J* = 6.6 Hz, 3 H, H-6C'), 0.86 (t, *J* = 6.6 Hz, 3 H, O(CH$_2$)$_5$C*H*$_3$). ^{13}C NMR (125 MHz, D_2O, 295 K): δ_C 177.6, 177.2 (C=O), 105.6 (C-1B), 105.5 (C-1A'), 103.4 (C-1A), 102.3 (C-1C'), 84.7 (C-3B), 81.2 (C-4), 79.7 (C-4A'), 77.8 (C-5A'), 77.6 (C-5B), 77.5 (C-5A), 75.2 (C-3A), 75.1 (C-3A'), 74.6 (C-4C'), 73.3 (O*C*H$_2$CH$_2$), 72.7 (C-2B), 72.1 (C-3C'), 71.0 (C-4B), 70.8 (C-2C'), 69.7 (C-5C'), 63.7 (C-6B), 62.8 (C-6A), 62.5 (C-6A'), 58.9 (C-2A'), 57.8 (C-2A) 31.3 (OCH$_2$*C*H$_2$(CH$_2$)$_3$CH$_3$), 33.4, 27.5, 24.8 (OCH$_2$CH$_2$(*C*H$_2$)$_3$CH$_3$), 24.9

(NHCO*C*H_3), 18.0 (C-6C'), 16.1 (O(CH_2)$_5$*C*H_3). HRMS (ESI-TOF) *m/z*: Calcd for $C_{34}H_{60}N_2O_{20}Na$ $[M + Na]^+$ 839.3637, found 839.3668.

6-Azido 2-acetamido-4-*O*-{3-*O*-[4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-acetamido-6-*O*-benzyl-2-deoxy-β-D-glucopyranosyl]-β-D-galactopyranosyl}-6-*O*-benzyl-2-deoxy-β-D-glucopyranoside (32). Tetrasaccharide **30** (33 mg, 0.0209 mmol) was treated for 45 min with TBAF (0.0420 mmol, 2 equiv) as described above for the preparation of tetrasaccharide **31**. After concentration and two columns chromatography (CH_2Cl_2/MeOH, 100:1–90:10, then CH_2Cl_2/MeOH, 90:3–90:10) tetrasaccharide **32** (20 mg, 72%) was isolated pure as an amorphous white foam. $[\alpha]_D$ –43.5 (*c* 1.0, MeOH). ^{1}H NMR (600 MHz, CD_3OD, 295 K): δ_H 7.41–7.38 (m, 2 H, Ar), 7.36–7.22 (m, 23 H, Ar), 5.01 (d, *J* = 3.5 Hz, 1 H, H-1C'), 4.90 (d, *J* = 11.2 Hz, 1 H, C*H*HPh), 4.80–4.76 (m, 2 H, 2 C*H*HPh), 4.72 (d, *J* = 11.7 Hz, 1 H, C*H*HPh), 4.65–4.60 (m, 3 H, 3 C*H*HPh), 4.58 (d, *J* = 8.4 Hz, 1 H, H-1A'), 4.53 (d, *J* = 11.8 Hz, 1 H, C*H*HPh), 4.38 (d, *J* = 8.3 Hz, 1 H, H-1A), 4.36–4.25 (m, 4 H, H-1B, H-5C', 2 C*H*HPh), 3.98 (dd, *J* = 3.6, 10.3 Hz, 1 H, H-2C'), 3.96–3.92 (m, 2 H, H-4B, H-3C'), 3.90 (dd, *J* = 4.2, 6.8 Hz, 1 H, H-6Aa'), 3.87–3.81 (m, 3 H, H-6Ab', H-4C', OC*H*HCH$_2$), 3.77 (d, *J* = 2.7 Hz, 2 H, H-6Aab), 3.75–3.69 (m, 3 H, H-2A, H-6Ba, H-2A'), 3.67–3.40 (m, 11 H, H-3A, H-4A, H-5A, H-2B, H-3B, H-5B, H-6Bb, H-3A', H-4A', H-5A', OCH*H*CH$_2$), 3.25 (t, *J* = 6.8 Hz, 3 H, CH_2N_3), 1.98, 1.95 (2 s, 6 H, 2 NHCOC*H*$_3$), 1.59–1.52 (m, 4 H, O(CH_2)$_4$C*H*$_2$$CH_2N_3$, OCH$_2$C*H*$_2$($CH_2$)$_3$$CH_2N_3$), 1.40–1.34 (m, 4 H, O($CH_2$)$_3$C*H*$_2$($CH_2$)$_2$$N_3$, O($CH_2$)$_2$C*H*$_2$($CH_2$)$_3$$N_3$), 1.14 (d, *J* = 6.5 Hz, 3 H, H-6C'). ^{13}C NMR (125 MHz, CD_3OD, 295 K): δ_C 174.4, 173.4 (C=O), 140.1, 139.8, 139.7, 139.6 (quat Ar), 129.4, 129.3, 128.9, 128.8, 128.7, 128.6, (Ar), 104.9 (C-1B), 104.1 (C-1A'), 102.8 (C-1A), 100.3 (C-1C'), 83.4 (C-3B), 80.5 (C-4A, C-3C'), 80.0 (C-4A'), 79.2 (C-4C'), 77.4 (C-2C'), 76.8 (C-5B), 76.3 (*C*H$_2$Ph), 75.9 (C-5A), 75.8 (C-5A'), 75.2 (*C*H$_2$Ph), 74.6 (C-3A'), 74.4, 74.3 (*C*H$_2$Ph), 74.1

(C-3A), 73.4 (*C*H_2Ph), 71.6 (C-2B), 70.5 (O*C*$H_2$$CH_2$), 70.2 (C-4B), 69.8 (C-6A), 69.7 (C-6A'), 68.7 (C-5C'), 62.6 (C-6B), 57.7 (C-2A'), 56.7 (C-2A), 52.4 (*C*$H_2$$N_3$), 30.5 (OCH$_2$*C*H$_2$(CH$_2$)$_3CH_2N_3$), 29.9 (O(CH$_2$)$_4$*C*H$_2CH_2N_3$), 27.2 (O(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2N_3$), 26.6 (O(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3N_3$), 23.1, 23.0 (NHCO*C*H$_3$), 16.9 (C-6C'). HRMS (ESI-TOF) *m/z* calcd for $C_{69}H_{90}N_5O_{20}$ $[M+H]^+$ 1308.618, found 1308.616

6-Aminohexyl 2-acetamido-2-deoxy-4-*O*-{3-*O*-[2-acetamido-2-deoxy-4-*O*-(α-L-fucopyranosyl)-β-D-glucopyranosyl]-β-D-galactopyranosyl}-β-D-glucopyranoside (3). Tetrasaccharide **30** (79 mg, 0.0511 mmol) was treated with TBAF (1 equiv) as described above for the preparation of crude intermediate **31**. After work up and chromatography as described above for compound **31**, crude tetrasaccharide **32**, contaminated with tetrabutyl ammonium salts was isolated. It was submitted to metal dissolving conditions (Na, 60 mg; NH_3(l), 25 mL; –78 °C) as described above for the preparation of deprotected tetrasaccharide **2**. Work up, as described above, and two successive size exclusion chromatography columns (Biogel P2, 0.05 M $AcONH_4$) gave deprotected tetrasaccharide **3** (17 mg, 38%) pure as a white amorphous powder. $[\alpha]_D$ –28.5 (*c* 1.0, H_2O). ^{1}H NMR (D_2O, 600 MHz, 295 K): δ_H 4.94 (d, *J* = 3.8 Hz, 1 H, H-1C'), 4.67 (d, *J* = 8.5 Hz, 1 H, H-1A'), 4.50 (d, *J* = 7.8 Hz, 1 H, H-1A), 4.45 (d, *J* = 7.9 Hz, 1 H, H-1B), 4.35 (m, 1 H, H-5C'), 4.14 (d, *J* = 3.1 Hz, 1 H, H-4B), 4.00–3.84 (m, 4 H, H-6Aa, H-6Aab', OC*H*HCH$_2$), 3.83–3.63 (m, 13 H, H-2A, H-3A, H-4A, H-6Ab, H-3B, H-5B, H-6Bab, H-2A', H-3A', H-2C', H-3C',H-4C'), 3.60–3.55 (m, 4 H, H-5A, H-2B, H-4A', OCH*H*CH$_2$), 3.53 (m, 1 H, H-5A'), 2.97 (t, *J* = 7.6 Hz, 2 H, C*H*$_2$$NH_3^+$), 2.03, 2.02 (2 s, 6 H, 2 OCOCH$_3$), 1.91 (s, 3 H, OCOCH$_3$), 1.64 (m, 2 H, O(CH$_2$)$_4$C*H*$_2$CH$_2$$NH_3^+$), 1.55 (m, 2 H, OCH$_2$C*H*$_2$(CH$_2$)$_3CH_2$$NH_3^+$), 1.40–1.31 (m, 4 H, O(CH$_2$)$_3$C*H*$_2$(CH$_2$)$_2$$NH_3^+$, O(CH$_2$)$_2$C*H*$_2$(CH$_2$)$_3$$NH_3^+$), 1.15 (d, *J* = 6.6 Hz, 3 H, H-6C'). ^{13}C NMR (125 MHz, D_2O, 295 K): δ_C 177.6, 177.1 (C=O), 105.6 (C-1B), 105.5 (C-1A'),

103.8 (C-1A), 102.3 (C-1C'), 84.7 (C-3B), 81.2 (C-4), 79.7 (C-4A'), 77.8 (C-5A'), 77.6 (C-5B), 77.5 (C-5A), 75.2 (C-3A), 75.1 (C-3A'), 74.6 (C-4C'), 73.2 (OCH_2CH_2), 72.7 (C-2B), 72.1 (C-3C'), 71.0 (C-4B), 70.8 (C-2C'), 69.7 (C-5C'), 63.7 (C-6B), 62.8 (C-6A), 62.5 (C-6A'), 58.9 (C-2A'), 57.8 (C-2A), 42.1 ($CH_2NH_3^+$), 31.1 ($OCH_2CH_2(CH_2)_3CH_2NH_3^+$), 29.4 ($O(CH_2)_4CH_2CH_2NH_3^+$), 28.0 ($O(CH_2)_3CH_2(CH_2)_2NH_3^+$), 27.4 ($O(CH_2)_2CH_2(CH_2)_3NH_3^+$), 24.9 ($NHCOCH_3$), 17.9 (C-6C'). HRMS (ESI-TOF) *m/z*: Calcd for $C_{34}H_{62}N_3O_{20}$ $[M + H]^+$ 832.3927, found 832.3906.

6-Chlorohexyl 2-acetamido-4-*O*-{2,4-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-[4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-3-*O*-acetyl-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) and 6-chlorohexyl 2-acetamido-4-*O*-{2,4-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-[4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-acetamido-3-*O*-acetyl-6-*O*-benzyl-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 (34).

Method A: To a solution of pentasaccharide **25** (30 mg, 0.0137 mmol) dissolved in AcOH (1.0 mL) was added freshly activated Zn (89 mg, 1.37 mmol, 100 equiv) at rt. The reaction mixture was stirred for 7 h at rt, then filtered over Celite®. The solids were washed with CH_2Cl_2 (3 × 10 mL) and the combined filtrate and washings were washed with satd aq $NaHCO_3$ (20 mL). The aq layer was re-extracted with CH_2Cl_2 (3 × 10 mL) and the combined organic layers were dried and concentrated. Column chromatography (EtOAc/hexanes, 6:4 then CH_2Cl_2/MeOH, 30:1) of the residue gave chloroacetamido **33 (**23 mg, 79%) and acetamido **34 (**3.2 mg, 11%).

Method B: Freshly activated Zn (298 mg, 4.56 mmol, 100 equiv) was added to a solution of pentasaccharide **25** (100 mg, 0.0456 mmol) in AcOH (5 mL). The reaction mixture was heated to 50 °C under sonication for 4 h. More Zn (298 mg, 4.56 mmol, 100 equiv) was added and the reaction was left to proceed at 50 °C under sonication for an additional 3 h, then filtered over Celite®. Work up as described above for the preparation of tetrasaccharide **27**, and chromatography (EtOAc/hexanes, 6:4 then CH_2Cl_2/MeOH, 30:1) gave acetamido **34** (87 mg, 91%) pure as a white amorphous foam.

Analytical data for 33: White foam, $[\alpha]_D$ –58.5 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 295 K): δ_H 7.55–7.48 (m, 4 H, Ar), 7.39–7.12 (m, 44 H, Ar), 7.06–7.03 (m, 2 H, Ar), 6.33 (d, *J* = 8.7 Hz, 1 H, NHA'), 5.79 (d, *J* = 7.6 Hz, 1 H, NHA), 5.61 (d, *J* = 3.5 Hz, 1 H, H-4B), 5.15 (dd, *J* = 8.2, 10.7 Hz, 1 H, H-3A'), 4.96 (d, *J* = 3.6 Hz, 1 H, H-1C), 4.94–4.90 (m, 2 H, H-1C', C*H*HPh), 4.88–4.80 (m, 3 H, H-1A, H-2B, C*H*HPh), 4.76–4.58 (m, 8 H, 8 C*H*HPh), 4.55 (d, *J* = 8.0 Hz, 1 H, H-1A'), 4.52 (d, *J* = 11.7 Hz, 1 H, C*H*HPh), 4.43–4.36 (m, 3 H, 3 C*H*HPh), 4.34–4.30 (m, 2 H, 2 C*H*HPh), 4.28 (d, *J* = 8.2 Hz, 1 H, H-1B), 4.22 (m, 1 H, H-5C), 4.16 (d, *J* = 10.4 Hz, 1 H, H-6Aa'), 4.05–4.01 (m, 4 H, H-3A, H-2C, H-2C', COC*H*HCl), 3.86 (d, *J* = 15.1 Hz, 1 H, COCH*H*Cl), 3.83–3.76 (m, 3 H, H-4A, H-3C', H-5C'), 3.75–3.54 (m, 12 H, H-6Aab, H-3B, H-6Bab, H-3C, H-2A', H-4A', H-5A', H-6Ab', H-4C', OC*H*HCH$_2$), 3.48–3.41 (m, 5 H, H-2A, H-5A, H-5B, CH_2Cl), 3.40 (s, 1 H, H-4C), 3.35 (m, 1 H, OCH*H*CH$_2$), 1.99, 1.96, 1.95 (3 s, 9 H, 3 $OCOCH_3$), 1.71–1.65 (m, 5 H, O(CH$_2$)$_4$C*H*$_2$CH$_2$Cl, NHCOC*H*$_3$), 1.46 (m, 2 H, OCH$_2$C*H*$_2$(CH$_2$)$_3$CH$_2$Cl), 1.34 (m, 2 H, O(CH$_2$)$_3$C*H*$_2$(CH$_2$)$_2$Cl), 1.24 (m, 2 H, O(CH$_2$)$_2$C*H*$_2$(CH$_2$)$_3$Cl), 1.02 (d, *J* = 6.4 Hz, 3 H, H-6C'), 0.99 (d, *J* = 6.4 Hz, 3 H, H-6C), 0.96 (s, 9 H, C(C*H*$_3$)$_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 295 K): δ_C 171.5, 170.0, 169.5, 169.3, 166.1 (C=O), 138.8, 138.7, 138.6, 138.5, 138.4, 137.8 (quat Ar), 135.6, 135.4 (Ar), 132.7, 132.4 (quat

Ar), 129.8, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2 (Ar), 100.5 (C-1A'), 100.4 (C-1C'), 99.4 (C-1A), 99.3 (C-1B), 97.0 (C-1C), 79.8 (C-3C), 79.0 (C-3C'), 77.7 (C-4C'), 77.5 (C-4C, C-4A'), 76.5 (C-2C'), 76.3 (C-2C), 75.5 (C-5A'), 75.1 (C-3B), 74.9, 74.6 (CH$_2$Ph), 74.3 (C-5A), 73.8 (C-4A, CH$_2$Ph), 73.6, 73.5, 73.4 (CH$_2$Ph), 73.3 (C-5B), 73.2 (C-3A'), 73.0 (C-3A), 72.8, 72.6 (CH$_2$Ph), 71.1 (C-2B), 70.3 (C-6A'), 69.2 (OCH$_2$CH$_2$), 68.8 (C-4B), 68.3 (C-6A), 67.8 (C-5C'), 66.4 (C-5C), 60.5 (C-6B), 55.3 (C-2A, C-2A'), 45.0 (CH$_2$Cl), 42.7 (COCH$_2$Cl), 32.5 (O(CH$_2$)$_4C$H$_2$CH$_2$Cl), 29.2 (OCH$_2C$H$_2$(CH$_2$)$_3$CH$_2$Cl), 26.7 (C(CH$_3$)$_3$), 26.6 (O(CH$_2$)$_3C$H$_2$(CH$_2$)$_2$Cl), 25.2 (O(CH$_2$)$_2C$H$_2$(CH$_2$)$_3$Cl), 23.1 (NHCOCH$_3$), 21.2, 21.0, 20.9 (OCOCH$_3$), 18.9 (C(CH$_3$)$_3$), 16.4 (C-6C), 16.3 (C-6C'). HRMS (ESI-TOF) *m/z* calcd for $C_{118}H_{145}Cl_2N_3O_{27}Si$ $[M+H+NH_4]^{2+}$ 1066.9601, found 1066.9556.

Analytical data for 34: $[\alpha]_D$ –46.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 295 K): δ_H 7.55–7.48 (m, 4 H, Ar), 7.38–7.11 (m, 44 H, Ar), 7.08–7.05 (m, 2 H, Ar), 5.82 (d, J = 7.6 Hz, 1 H, NHA), 5.58 (d, J = 3.0 Hz, 1 H, H-4B), 5.26 (d, J = 8.5 Hz, 1 H, NHA'), 5.13 (t, J = 8.4 Hz, 1 H, H-3A'), 4.97 (d, J = 3.4 Hz, 1 H, H-1C), 4.93–4.90 (m, 2 H, H-1C', CHHPh), 4.89–4.83 (m, 2 H, H-2B, CHHPh), 4.81 (d, J = 5.7 Hz, 1 H, H-1A), 4.75–4.69 (m, 3 H, 3 CHHPh), 4.67–4.57 (m, 6 H, H-1A', 5 CHHPh), 4.53 (d, J = 11.7 Hz, 1 H, CHHPh), 4.43 (d, J = 11.3 Hz, 1 H, CHHPh), 4.38 (m, 2 H, 2 CHHPh) 4.33 (m, 2 H, 2 CHHPh), 4.28 (d, J = 8.2 Hz, 1 H, H-1B), 4.19 (m, 1 H, H-5C), 4.11 (d, J = 10.7 Hz, 1 H, H-6Aa'), 4.04 (t, J = 6.9 Hz, 1 H, H-3A), 4.00–3.93 (m, 2 H, H-2C, H-2C'), 3.83–3.54 (m, 14 H, H-4A, H-6Aab, H-3B, H-6Bab, H-3C, H-4A', H-5A', H-6Ab', H-3C', H-4C', H-5C', OCHHCH$_2$), 3.51–3.39 (m, 7 H, H-2A, H-5A, H-5B, H-4C, H-2A', CH$_2$Cl), 3.30 (m, 1 H, OCHHCH$_2$), 1.98, 1.91 (3 s, 9 H, 3 OCOCH$_3$), 1.81 (s, 3 H, NHCOCH_3), 1.71–1.65 (m, 5 H, O(CH$_2$)$_4$CH_2CH$_2$Cl, NHCOCH_3), 1.46 (m, 2 H,

OCH$_2$C*H$_2$*(CH$_2$)$_3$CH$_2$Cl), 1.34 (m, 2 H, O(CH$_2$)$_3$C*H$_2$*(CH$_2$)$_2$Cl), 1.24 (m, 2 H, O(CH$_2$)$_2$C*H$_2$*(CH$_2$)$_3$Cl), 1.02 (d, *J* = 6.4 Hz, 3 H, H-6C'), 0.98 (d, *J* = 6.4 Hz, 3 H, H-6C), 0.96 (s, 9 H, C(C*H$_3$*)$_3$). ^{13}C NMR (125 MHz, CDCl$_3$, 295 K): δ_C 171.4, 170.2, 170.1, 169.5, 169.3 (C=O), 138.8, 138.7, 138.6, 138.5, 138.4, 137.8 (quat Ar), 135.6, 135.4 (Ar), 132.7, 132.5 (quat Ar), 129.9, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2 (Ar), 100.0 (C-1A', C-1C'), 99.4 (C-1A), 99.3 (C-1B), 97.0 (C-1C), 79.8 (C-3C), 79.0 (C-3C'), 77.6 (C-4C'), 77.4 (C-4C, C-4A'), 76.5 (C-2C'), 76.3 (C-2C), 75.1 (C-5A'), 74.9 (*C*H$_2$Ph), 74.8 (C-3B), 74.5 (*C*H$_2$Ph), 74.3 (C-5A), 73.8 (*C*H$_2$Ph), 73.7 (C-4A, C-5B, C-3A'), 73.5, 73.4 (*C*H$_2$Ph), 73.0 (C-3A), 73.0, 72.9 (*C*H$_2$Ph), 71.1 (C-2B), 70.2 (C-6A'), 69.2 (O*C*H$_2$CH$_2$), 68.8 (C-4B), 68.4 (C-6A), 67.7 (C-5C'), 66.4 (C-5C), 60.6 (C-6B), 55.2 (C-2A, C-2A'), 45.0 (*C*H$_2$Cl), 32.5 (O(CH$_2$)$_4$*C*H$_2$CH$_2$Cl), 29.2 (OCH$_2$*C*H$_2$(CH$_2$)$_3$CH$_2$Cl), 26.7 (C(*C*H$_3$)$_3$), 26.6 (O(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$Cl), 25.2 (O(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$Cl), 23.1 (NHCO*C*H$_3$), 21.2, 21.1, 20.8 (OCO*C*H$_3$), 18.9 (*C*(CH$_3$)$_3$), 16.4 (C-6C), 16.3 (C-6C'). HRMS (ESI-TOF) *m/z* calcd for C$_{118}$H$_{143}$ClN$_2$O$_{27}$Si [M+2H]$^{2+}$ 1041.4663, found 1041.4661.

6-Chlorohexyl 2-acetamido-4-*O*-{6-*O*-*tert*-butyldiphenylsilyl-3-*O*-[4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-6-*O*-benzyl-2-deoxy-2-methoxyacetamido-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 (35). A solution of pentasaccharide **33** (21 mg, 0.010 mmol) in 0.25 M NaOMe in MeOH (1.5 mL) was stirred at rt for 2 h, then deionized with Dowex 50 (H$^+$) resin. The resin was filtered off, washed with MeOH (3 × 10 mL) and the combined filtrate and washings were concentrated. ^{1}H NMR of the crude product showed that the acetate at O-4*B* had not been removed. Thus, this crude product was again dissolved in 0.25 M NaOMe in MeOH (1.5 mL) and stirred at room temperature for 18 h. TLC showed the formation of a new major compound

which after work up, as described above, was purified by column chromatography (EtOAc/hexanes, 9:1). This compound was identified as methoxyacetamido **35** (11 mg, 54%) pure as a colorless amorphous glass. $[\alpha]_D$ –26.6 (*c* 0.9, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 295 K): δ_H 7.65 (d, *J* = 7.1 Hz, 2 H, Ar), 7.59 (d, *J* = 7.1 Hz, 2 H, Ar), 7.38–7.16 (m, 44 H, Ar), 6.98–6.95 (m, 3 H, NHA', Ar), 5.72 (d, *J* = 6.6 Hz, 1 H, NHA), 5.05–5.00 (m, 2 H, H-1A, H-1A'), 4.97 (d, *J* = 3.7 Hz, 1 H, H-1C'), 4.94 (d, *J* = 11.6 Hz, 1 H, C*H*HPh), 4.90 (d, *J* = 3.5 Hz, 1 H, H-1C), 4.82 (d, *J* = 11.8 Hz, 1 H, C*H*HPh), 4.80–4.74 (m, 3 H, 3 C*H*HPh), 4.72 (d, *J* = 11.8 Hz, 1 H, C*H*HPh), 4.66–4.59 (m, 3 H, 3 C*H*HPh), 4.54 (d, *J* = 11.8 Hz, 1 H, C*H*HPh), 4.47–4.41 (m, 3 H, H-5C, 2 C*H*HPh), 4.37–4.38 (m, 2 H, H-1B, C*H*HPh), 4.22–4.17 (m, 3 H, H-3A, CH_2Ph), 4.14–4.09 (m, 2 H, H-4B, H-5C'), 4.04 (dd, *J* = 3.7, 10.2 Hz, 1 H, H-2C'), 3.96–3.68 (m, 14 H, H-4A, H-6Aab, H-6Bab, H-2C, H-3C, H-3A', H-6Aab', H-3C', NHCOC*H*$_2$, OC*H*HCH_2), 3.66 (s, 1 H, H-4C'), 3.65–3.43 (m, 9 H, H-5A, H-2B, H-3B, H-4C, H-2A', H-4A', H-5A', CH_2Cl), 3.39 (m, 1 H, OCH*H*CH_2), 3.37–3.32 (m, 2 H, H-5B, OCH_3), 3.05 (m, 1 H, H-2A), 2.50 (bs, 1 H, OH-4B), 1.70 (m, 2 H, O$(CH_2)_4$C*H*$_2$$CH_2$Cl), 1.53–1.45 (m, 5 H, NHCOC*H*$_3$, OCH$_2$C*H*$_2$$(CH_2)_3CH_2$Cl), 1.37 (m, 2 H, O$(CH_2)_3$C*H*$_2$$(CH_2)_2$Cl), 1.25 (m, 2 H, O$(CH_2)_2$C*H*$_2$$(CH_2)_3$Cl), 1.12 (d, *J* = 6.5 Hz, 3 H, H-6C'), 1.07 (d, *J* = 6.5 Hz, 3 H, H-6C), 0.96 (s, 9 H, C(C*H*$_3$)$_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 295 K): δ_C 171.2, 170.2 (C=O), 138.9, 138.8, 138.5, 138.4, 138.3, (quat Ar), 135.6, 135.4 (Ar), 132.8, 132.7 (quat Ar), 129.9, 129.8, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 127.4 (Ar), 100.9 (C-1A'), 100.6 (C-1B), 99.5 (C-1C'), 99.3 (C-1A), 98.2 (C-1C), 82.0 (C-3B), 80.3 (C-4A'), 79.9 (C-3C), 79.2 (C-3C'), 77.7 (C-4C), 77.4 (C-4C'), 76.2 (C-2C), 75.8 (C-2C'), 75.3 (C-3A), 75.1, 74.9 (*C*H_2Ph), 74.8 (C-5A), 74.6 (C-5A'), 74.3 (C-4A), 74.2, 73.9 (*C*H_2Ph), 75.8 (C-5B), 73.5 (C-3A'), 73.4, 73.1, 72.8 (*C*H_2Ph), 72.0 (NHCOC*H*$_2$), 71.9 (*C*H_2Ph), 71.2 (C-2B), 69.4 (O*C*$H_2$$CH_2$), 68.6 (C-

6A, C-6A'), 67.7 (C-5C'), 67.1 (C-4B), 66.5 (C-5C), 61.0 (C-6B), 59.3 (OCH_3), 59.0 (C-2A), 57.3 (C-2A'), 45.0 (CH_2Cl), 32.5 ($O(CH_2)_4CH_2CH_2Cl$), 29.2 ($OCH_2CH_2(CH_2)_3CH_2Cl$), 26.7 ($C(CH_3)_3$), 26.6 ($O(CH_2)_3CH_2(CH_2)_2Cl$), 25.2 ($O(CH_2)_2CH_2(CH_2)_3Cl$), 23.2 ($NHCOCH_3$), 19.1 ($C(CH_3)_3$), 16.7 (C-6C'), 16.6 (C-6C). HRMS (ESI-TOF) *m/z* calcd for $C_{113}H_{139}ClN_2O_{25}Si$ $[M+2H]^{2+}$ 993.4562, found 993.4559.

6-Chlorohexyl 2-acetamido-4-*O*-{6-*O*-*tert*-butyldiphenylsilyl-3-*O*-[4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-acetamido-6-*O*-benzyl-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 (36). Deacetylation of tetrasaccharide **34** (42 mg, 0.0204 mmol) in 0.25 M NaOMe in MeOH was performed (12 h) as as described above for the preparation of **29**. Work up of the reaction was carried out as described above and RP HPLC (CH_3CN/H_2O, 90:100, 30 min) of the residue gave **36** (29 mg, 73%) pure as a colorless amorphous glass. $[\alpha]_D$ –57.6 (*c* 1.0, MeOH). ^{1}H NMR (600 MHz, CD_3OD, 295 K): δ_H 7.71 (d, *J* = 6.7 Hz, 2 H, Ar), 7.60 (d, *J* = 6.9 Hz, 2 H, Ar), 7.43–7.16 (m, 44 H, Ar), 6.77 (d, *J* = 7.2 Hz, 2 H, Ar), 5.10 (d, *J* = 2.5 Hz, 1 H, H-1C), 5.03 (d, *J* = 2.9 Hz, 1 H, H-1C'), 4.93 (d, *J* = 11.2 Hz, 1 H, C*H*HPh), 4.84 (m, 1 H, H-5C), 4.81–4.77 (m, 2 H, 2 C*H*HPh), 4.74 (d, *J* = 12.8 Hz, 1 H, C*H*HPh), 4.72–4.67 (m, 4 H, H-1A', 3 C*H*HPh), 4.65 (d, *J* = 11.3 Hz, 1 H, C*H*HPh), 4.58 (d, *J* = 11.3 Hz, 1 H, C*H*HPh), 4.54 (d, *J* = 11.9 Hz, 1 H, C*H*HPh), 4.51–4.41 (m, 4 H, H-1A, H-1B, 2 C*H*HPh), 4.39 (d, *J* = 11.7 Hz, 1 H, C*H*HPh), 4.30 (m, 1 H, H-5C'), 4.28 (d, *J* = 2.9 Hz, 1 H, H-4B), 4.22 (d, *J* = 11.7 Hz, 1 H, C*H*HPh), 4.16 (t, *J* = 8.9 Hz, 1 H, H-6Ba), 4.10–3.95 (m, 7 H, H-3A, H-4A, H-6Aa, H-2C', H-3C', 2 C*H*HPh), 3.91 (dd, *J* = 3.5, 11.1 Hz, 1 H, H-6Aa'), 3.89–3.74 (m, 9 H, H-2A, H-6Ab, H-6Bb, H-2C, H-3C, H-4C, H-2A', H-4C', OC*H*HCH$_2$), 3.69 (t, *J* = 9.1 Hz, 1 H, H-4A'), 3.66–3.58 (m, 3 H, H-2B, H-3A', H-6Ab'), 3.57–3.40 (m, 7 H, H-5A, H-5B, H-5A', H-3B, CH_2Cl

OCH*H*CH$_2$), 2.03, 1.90 (2 s, 6 H, NHCOC*H$_3$*), 1.75 (m, 2 H, O(CH$_2$)$_4$C*H$_2$*CH$_2$Cl), 1.57 (m, 2 H, OCH$_2$C*H$_2$*(CH$_2$)$_3$CH$_2$Cl), 1.44 (m, 2 H, O(CH$_2$)$_3$C*H$_2$*(CH$_2$)$_2$Cl), 1.38 (m, 2 H, O(CH$_2$)$_2$C*H$_2$*(CH$_2$)$_3$Cl), 1.17 (d, J = 6.5 Hz, 3 H, H-6C'), 1.12 (d, J = 6.5 Hz, 3 H, H-6C), 0.96 (s, 9 H, C(C*H$_3$*)$_3$). ^{13}C NMR (125 MHz, CD$_3$OD, 295 K): δ_C 174.5, 173.2 (C=O), 140.3, 140.0, 139.8, 139.7, 139.5, (quat Ar), 136.8, 136.6 (Ar), 134.1, 134.0 (quat Ar), 131.0, 130.9, 129.5, 129.4, 129.3, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.2 (Ar), 104.0 (C-1A'), 103.4 (C-1B), 102.6 (C-1A), 100.1 (C-1C'), 98.3 (C-1C), 84.1 (C-3B), 80.6 (C-3C'), 79.8 (C-4C), 79.7 (C-3C), 79.2 (C-4A', C-4C'), 77.4 (C-2C'), 76.5 (C-5A, *C*H$_2$Ph), 76.3 (C-2C), 76.2 (C-5A', *C*H$_2$Ph), 75.8 (C-4A), 75.3 (C-5B, *C*H$_2$Ph), 74.7 (C-3A, *C*H$_2$Ph), 74.4 (C-3A'), 74.0, 73.6, 73.4, 73.2 (*C*H$_2$Ph), 72.2 (C-2B), 70.4 (O*C*H$_2$CH$_2$), 69.7 (C-6A'), 69.4 (C-6A), 68.5 (C-5C'), 67.9 (C-4B), 67.6 (C-5C), 62.4 (C-6B), 58.2 (C-2A), 57.9 (C-2A'), 45.7 (*C*H$_2$Cl), 33.8 (O(CH$_2$)$_4$*C*H$_2$CH$_2$Cl), 30.5 (OCH$_2$*C*H$_2$(CH$_2$)$_3$CH$_2$Cl), 27.6 (O(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$Cl), 27.3 (C(*C*H$_3$)$_3$), 26.4 (O(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$Cl), 23.4, 23.1 (NHCO*C*H$_3$), 20.0 (*C*(CH$_3$)$_3$), 16.9 (C-6C, C-6C'). HRMS (ESI-TOF) *m/z* calcd for $C_{112}H_{136}ClN_2O_{24}Si$ $[M+H]^+$ 1955.8940, found 1955.8965.

6-Chlorohexyl 2-acetamido-4-*O*-{3-*O*-[4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-acetamido-6-*O*-benzyl-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 (37). Pentasaccharide **36** (29 mg, 0.0153 mmol) was treated for 16 h with TBAF (0.0305 mmol, 2 equiv) as described above for the preparation of tetrasaccharide **31**. After concentration, column chromatography (CH_2Cl_2/MeOH, 100:1–95:5) then RP HPLC (CH_3CN/H_2O, 70:90) of the residue, gave pentasaccharide **37** (21 mg, 82%) pure as an amorphous white foam. $[\alpha]_D$ –70.3 (*c* 1.0, MeOH). ^{1}H NMR (600 MHz, CD$_3$OD, 295 K): δ_H 7.40–7.14 (m, 40 H, Ar), 5.30 (d, J = 3.7 Hz, 1 H, H-

1C), 5.00 (d, J = 3.6 Hz, 1 H, H-1C'), 4.92–4.75 (m, 8 H, H-5C, 7 C*H*HPh), 4.72 (d, J = 11.5 Hz, 1 H, C*H*HPh), 4.68 (d, J = 11.9 Hz, 1 H, C*H*HPh), 4.65–4.60 (m, 2 H, 2 C*H*HPh), 4.57–4.48 (m, 4 H, H-1A', 3 C*H*HPh), 4.39–4.35 (m, 2 H, H-1A, H-1B), 4.32–4.26 (m, 3 H, H-5C', 2 C*H*HPh), 4.14 (m, 1 H, H-3A), 4.10 (dd, J = 2.8, 10.3 Hz, 1 H, H-3C'), 4.03–3.90 (m, 8 H, H-2A, H-4A, H-6Ba, H-6Aa', H-2C, H-3C, H-2C', H-4C'), 3.88–3.82 (m, 3 H, H-4B, H-4C, OC*H*HCH$_2$), 3.80–3.70 (m, 4 H, H-6Aab, H-2A', H-6Ab'), 3.57–3.47 (m, 8 H, H-5A, H-2B, H-6Bb, H-3A', H-4A', H-5A', CH$_2$Cl), 3.44 (m, 1 H, OCH*H*CH$_2$), 3.33–3.20 (m, 2 H, H-3B, H-5B), 1.97 (2 s, 6 H, NHCOC*H$_3$*), 1.74 (m, 2 H, O(CH$_2$)$_4$C*H$_2$*CH$_2$Cl), 1.55 (m, 2 H, OCH$_2$C*H$_2$*(CH$_2$)$_3$CH$_2$Cl), 1.42 (m, 2 H, O(CH$_2$)$_3$C*H$_2$*(CH$_2$)$_2$Cl), 1.37 (m, 2 H, O(CH$_2$)$_2$C*H$_2$*(CH$_2$)$_3$Cl), 1.16–1.11 (m, 6 H, H-6C, H-6C'). ^{13}C NMR (125 MHz, CD$_3$OD, 295 K): δ_C 174.5, 173.2 (C=O), 140.6, 140.3, 140.1, 139.8, 139.7, 139.6 (quat Ar), 129.6, 129.5, 129.4, 129.3, 129.2, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4 (Ar), 104.0 (C-1A'), 103.4 (C-1B), 103.2 (C-1A), 100.4 (C-1C'), 98.0 (C-1C), 84.0 (C-3B), 80.5 (C-3C), 80.2 (C-4C'), 80.1 (C-4A'), 80.0 (C-3C'), 79.3 (C-4C), 77.4 (C-2C'), 77.1 (C-2C), 76.9 (C-5B), 76.6 (C-5A, *C*H$_2$Ph), 76.3 (*C*H$_2$Ph), 75.9 (C-5A'), 75.5 (C-4A), 75.2 (*C*H$_2$Ph), 74.5 (C-3A'), 74.3 (C-3A, *C*H$_2$Ph), 74.2, 73.7, 73.6, 73.5 (*C*H$_2$Ph), 72.0 (C-2B), 70.6 (O*C*H$_2$CH$_2$), 69.9 (C-6A, C-4B), 69.3 (C-6A'), 68.7 (C-5C'), 67.8 (C-5C), 63.6 (C-6B), 57.7 (C-2A'), 57.6 (C-2A), 45.7 (*C*H$_2$Cl), 33.8 (O(CH$_2$)$_4$*C*H$_2$CH$_2$Cl), 30.5 (OCH$_2$*C*H$_2$(CH$_2$)$_3$CH$_2$Cl), 27.7 (O(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$Cl), 26.4 (O(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$Cl), 23.6, 23.1 (NHCO*C*H$_3$), 16.9 (C-6C, C-6C'). HRMS (ESI-TOF) *m/z* calcd for C$_{96}$H$_{118}$ClN$_2$O$_{24}$ [M+H]$^+$ 1717.7763, found 1717.7841.

n-Hexyl 2-acetamido-2-deoxy-3-*O*-(α-L-fucopyranosyl)-4-*O*-{3-*O*-[2-acetamido-2-deoxy-4-*O*-(α-L-fucopyranosyl)-β-D-glucopyranosyl]-β-D-galactopyranosyl-β-D-glucopyranoside (4). Pentasaccharide **37** (20 mg, 0.01162 mmol) was submitted to metal

dissolving conditions (Na, 60 mg; NH_3(l), 25 mL; –78 °C) as described above for the preparation of deprotected tetrasaccharide **2**. Work up of the reaction mixture (as described for tetrasaccharide **2**) followed by size exclusion chromatography (2 × Biogel P2, Milli-Q water) gave pentasaccharide **4** (7.8 mg, 70%) pure as a white amorphous powder upon freeze drying. $[\alpha]_D$ –42.5 (*c* 0.4, H_2O). ^{1}H NMR (D_2O, 600 MHz, 295 K): δ_H 5.08 (d, *J* = 3.9 Hz, 1 H, H-1C), 4.95 (d, *J* = 3.8 Hz, 1 H, H-1C'), 4.80 (m, 1 H, H-5C), 4.66 (d, *J* = 8.4 Hz, 1 H, H-1A'), 4.51 (d, *J* = 8.0 Hz, 1 H, H-1A), 4.42 (d, *J* = 7.8 Hz, 1 H, H-1B), 4.35 (m, 1 H, H-5C'), 4.08 (d, *J* = 3.2 Hz, 1 H, H-4B), 4.00–3.74 (m, 14 H, H-2A, H-3A, H-4A, H-6Aab, H-3C, H-4C, H-2A', H-6Aab', H-2C', H-3C', H-4C', OC*H*HCH$_2$), 3.73–3.63 (m, 5 H, H-3B, H-6Bab, H-2C, H-3A'), 3.60–3.48 (m, 6 H, H-5A, H-2B, H-5B, H-4A', H-5A', OCH*H*CH$_2$), 2.02, 2.01 (2 s, 6 H, 2 OCOCH$_3$), 1.52 (m, 2 H, OCH$_2$C*H*$_2$(CH$_2$)$_3$CH$_3$), 1.33–1.23 (m, 6 H, OCH$_2$CH$_2$(C*H*$_2$)$_3$CH$_3$), 1.17–1.12 (m, 6 H, H-6C, H-6C'), 0.85 (t, *J* = 6.6 Hz, 3 H, O(CH$_2$)$_5$C*H*$_3$). ^{13}C NMR (125 MHz, D_2O, 295 K): δ_C 177.6, 177.0 (C=O), 105.4 (C-1A'), 104.5 (C-1B), 103.7 (C-1A), 102.3 (C-1C), 101.5 (C-1C'), 84.3 (C-3B), 79.8 (C-4A'), 78.1 (C-5B), 77.7 (C-3A, C-5A'), 77.2 (C-5A), 75.8 (C-4A), 75.0 (C-3A'), 74.6 (C-4C, C-4C'), 73.4 (OCH$_2$CH$_2$), 73.2 (C-2B), 72.1 (C-3C'), 71.9 (C-3C), 71.0 (C-4B), 70.8 (C-2C'), 70.4 (C-2C), 69.7 (C-5C'), 69.5 (C-5C), 64.2 (C-6B), 62.5 (C-6A, C-6A'), 58.9 (C-2A'), 58.6 (C-2A), 31.3 (OCH$_2$CH$_2$(CH$_2$)$_3$CH$_3$), 33.5, 27.6, 24.8 (OCH$_2$CH$_2$(CH$_2$)$_3$CH$_3$), 25.0, 24.9 (NHCOCH$_3$), 18.0 (C-6C'), 17.9 (C-6C), 16.1 (O(CH$_2$)$_5$CH$_3$). HRMS (ESI-TOF) *m/z*: Calcd for $C_{40}H_{71}N_2O_{24}$ $[M + H]^+$ 963.4397, found 963.4435.

6-Azido 2-acetamido-4-*O*-{3-*O*-[4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-acetamido-6-*O*-benzyl-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 (38). Pentasaccharide **37** (20 mg, 0.01190 mmol) was treated NaN_3 (7.7 mg, 0.1190 mmol, 10 equiv) as described

above for the preparation of azido tetrasaccharide **28**. Work up as described above for **28** and purification of the crude product by column chromatography (CH_2Cl_2/MeOH, 95:5) gave the azido **38** (19 mg, 95%) pure as a white foam. $[\alpha]_D$ –68.2 (*c* 1.0, MeOH). ^{1}H NMR (600 MHz, CD_3OD, 295 K): δ_H 7.41–7.19 (m, 39 H, Ar), 7.16 (m, 1 H, Ar), 5.30 (d, *J* = 3.7 Hz, 1 H, H-1C), 5.01 (d, *J* = 3.6 Hz, 1 H, H-1C'), 4.92–4.75 (m, 8 H, H-5C, 7 C*H*HPh), 4.72 (d, *J* = 11.6 Hz, 1 H, C*H*HPh), 4.67 (d, *J* = 11.9 Hz, 1 H, C*H*HPh), 4.65–4.60 (m, 2 H, 2 C*H*HPh), 4.57–4.48 (m, 4 H, H-1A', 3 C*H*HPh), 4.39–4.35 (m, 2 H, H-1A, H-1B), 4.32–4.26 (m, 3 H, H-5C', 2 C*H*HPh), 4.14 (m, 1 H, H-3A), 4.10 (dd, *J* = 2.9, 10.3 Hz, 1 H, H-3C'), 4.03–3.91 (m, 8 H, H-2A, H-4A, H-6Ba, H-6Aa', H-2C, H-3C, H-2C', H-4C'), 3.88–3.82 (m, 3 H, H-4B, H-4C, OC*H*HCH$_2$), 3.81–3.70 (m, 4 H, H-6Aab, H-2A', H-6Ab'), 3.57–3.47 (m, 6 H, H-5A, H-2B, H-6Bb, H-3A', H-4A', H-5A'), 3.44 (m, 1 H, OCH*H*CH$_2$), 3.33–3.23 (m, 4 H, H-3B, H-5B, CH_2N_3), 1.97 (2 s, 6 H, NHCOC*H*$_3$), 1.60–1.52 (m, 4 H, O(CH$_2$)$_4$C*H*$_2$CH$_2$N$_3$, OCH$_2$C*H*$_2$(CH$_2$)$_3$CH$_2$N$_3$), 1.40–1.35 (m, 4 H, O(CH$_2$)$_3$C*H*$_2$(CH$_2$)$_2$N$_3$, O(CH$_2$)$_2$C*H*$_2$(CH$_2$)$_3$N$_3$), 1.16–1.11 (m, 6 H, H-6C, H-6C'). ^{13}C NMR (125 MHz, CD_3OD, 295 K): δ_C 174.5, 173.2 (C=O), 140.5, 140.3, 140.1, 139.8, 139.6, 139.5 (quat Ar), 129.6, 129.5, 129.4, 129.3, 129.2, 128.8, 128.7, 128.6, 128.5, 128.4 (Ar), 104.0 (C-1A'), 103.4 (C-1B), 103.2 (C-1A), 100.4 (C-1C'), 97.9 (C-1C), 84.0 (C-3B), 80.4 (C-3C), 80.1 (C-4C'), 80.0 (C-4A', C-3C'), 79.2 (C-4C), 77.4 (C-2C'), 77.1 (C-2C), 76.9 (C-5B), 76.6 (C-5A), 76.5 (*C*H$_2$Ph), 76.3 (*C*H$_2$Ph), 75.9 (C-5A'), 75.5 (C-4A), 75.2 (*C*H$_2$Ph), 74.5 (C-3A'), 74.3 (C-3A), 74.2, 73.7, 73.6, 73.4 (*C*H$_2$Ph), 72.0 (C-2B), 70.5 (O*C*H$_2$CH$_2$), 69.5 (C-6A, C-4B), 69.2 (C-6A'), 68.7 (C-5C'), 67.8 (C-5C), 63.6 (C-6B), 57.7 (C-2A'), 57.6 (C-2A), 52.4 (*C*H$_2$N$_3$), 30.6 (OCH$_2$*C*H$_2$(CH$_2$)$_3$CH$_2$N$_3$), 29.9 (O(CH$_2$)$_4$*C*H$_2$CH$_2$N$_3$), 27.5 (O(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$N$_3$), 26.7 (O(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$N$_3$), 23.5, 23.1 (NHCO*C*H$_3$), 16.9 (C-6C, C-6C'). HRMS (ESI-TOF) *m/z* calcd for $C_{96}H_{118}N_5O_{24}$ $[M+H]^+$ 1724.8167, found 1724.8164.

***n*-Aminohexyl 2-acetamido-2-deoxy-3-*O*-(α-L-fucopyranosyl)-4-*O*-{3-*O*-[2-acetamido-2-deoxy-4-*O*-(α-L-fucopyranosyl)-β-D-glucopyranosyl]-β-D-galactopyranosyl-β-D-glucopyranoside (5).** The azidopentasaccharide **38** (18 mg, 0.01042 mmol) was submitted to metal dissolving conditions as described above for the preparation of pentasaccharide **4** (Na, 60 mg; NH_3(l) 25 mL; –78 °C). Work up of the reaction mixture was performed as described for the preparation of tetrasaccharide **2**. The crude residue was submitted twice to size exclusion chromatography (Biogel P2, 0.05 M $AcONH_4$) and pentasaccharide **5** (7.6 mg, 70%) was obtained pure as a white amorphous powder upon freeze drying. $[\alpha]_D$ –44.1 (*c* 0.7, H_2O). ^{1}H NMR (D_2O, 600 MHz, 295 K): δ_H 5.08 (d, *J* = 3.8 Hz, 1 H, H-1C), 4.95 (d, *J* = 3.9 Hz, 1 H, H-1C'), 4.80 (m, 1 H, H-5C), 4.66 (d, *J* = 8.4 Hz, 1 H, H-1A'), 4.51 (d, *J* = 8.2 Hz, 1 H, H-1A), 4.42 (d, *J* = 7.8 Hz, 1 H, H-1B), 4.35 (m, 1 H, H-5C'), 4.08 (d, *J* = 3.2 Hz, 1 H, H-4B), 4.00–3.74 (m, 14 H, H-2A, H-3A, H-4A, H-6Aab, H-3C, H-4C, H-2A', H-6Aab', H-2C', H-3C', H-4C', OC*H*HCH$_2$), 3.73–3.63 (m, 5 H, H-3B, H-6Bab, H-2C, H-3A'), 3.60–3.48 (m, 6 H, H-5A, H-2B, H-5B, H-4A', H-5A', OCH*H*CH$_2$), 2.97 (t, *J* = 7.5 Hz, 2 H, C*H*$_2$NH$_3^+$), 2.03, 2.01 (2 s, 6 H, 2 OCOCH$_3$), 1.90 (s, 3 H, $^-$OCOCH$_3$), 1.64 (m, 2 H, O(CH$_2$)$_4$C*H*$_2$CH$_2$NH$_3^+$), 1.54 (m, 2 H, OCH$_2$C*H*$_2$(CH$_2$)$_3$CH$_2$NH$_3^+$), 1.40–1.31 (m, 4 H, O(CH$_2$)$_3$C*H*$_2$(CH$_2$)$_2$NH$_3^+$, O(CH$_2$)$_2$C*H*$_2$(CH$_2$)$_3$NH$_3^+$), 1.17–1.12 (m, 6 H, H-6C, H-6C'). ^{13}C NMR (125 MHz, D_2O, 295 K): δ_C 177.6, 176.9 (C=O), 105.4 (C-1A'), 104.5 (C-1B), 103.7 (C-1A), 102.3 (C-1C), 101.5 (C-1C'), 84.3 (C-3B), 79.8 (C-4A'), 78.1 (C-5B), 77.7 (C-3A, C-5A'), 77.2 (C-5A), 75.8 (C-4A), 75.0 (C-3A'), 74.6 (C-4C, C-4C'), 73.3 (C-2B, OC*H*$_2$CH$_2$), 72.1 (C-3C'), 71.9 (C-3C), 71.0 (C-4B), 70.8 (C-2C'), 70.4 (C-2C), 69.7 (C-5C'), 69.5 (C-5C), 64.2 (C-6B), 62.5 (C-6A, C-6A'), 58.9 (C-2A'), 58.6 (C-2A), 42.1 (*C*H$_2$NH$_3^+$), 31.1 (OCH$_2$*C*H$_2$(CH$_2$)$_3$CH$_2$NH$_3^+$), 29.4 (O(CH$_2$)$_4$*C*H$_2$CH$_2$NH$_3^+$), 28.0 (O(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$NH$_3^+$), 27.4 (O(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$NH$_3^+$), 25.0,

24.9 (NHCO*C*H$_3$), 18.0 (C-6C), 17.9 (C-6C'). HRMS (ESI-TOF) *m/z*: Calcd for $C_{40}H_{72}N_3O_{24}$ [M + H]$^+$ 978.4506, found 978.4522.

Acknowledgement. We thank the National Science and Engineering Research Council of Canada for financial support of this work.

Supporting Information Available. General Experimental Procedures, ^{1}H, COSY, ^{13}C and HSQC NMR spectra for compounds **2–7**, **10–14, 16–38** are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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