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Solid-phase synthesis of glycopeptide carrying a tetra-*N*-acetyllactosamine-containing core 2 decasaccharide

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ABSTRACT

A novel synthesis of tetralactosaminyl *O*-glycoamino acid is described. The stereoselective assemblage of a lactosaminyl unit was performed by 2-trichloroacetamido group-assisted β-glycosylation. Initial investigation into the synthesis of decasaccharyl threonine **2** showed limited success because of the low yield in the step concerning the removal of 4-*O*-chloroacetyl groups. In contrast, 4-*O*-benzylated decasaccharyl threonine **50** was efficiently synthesized from key LacNAc derivative **35** carrying a 3-*O*-allyl protecting group at the Gal residue by reiterative glycosylation using the (*N*-phenyl)trifluoroacetimidate method. Decasaccharide **50** was used as a building block in the solid-phase synthesis of a MUC1-related glycopeptide. Synthetic glycopeptide was obtained through two acidic processes: cleavage from resin with reagent K at a lowered temperature and debenzylation with a diluted cocktail of low-acidity TfOH. Desired glycopeptide **54** was isolated as the major product, while a series of the saccharide-shortened minor products were generated due to the acid-labile property of the β-GlcNAc glycosidic linkages.

1. Introduction

N-Acetyllactosamine, [β-D-Gal-(1→4)-β-D-GlcNAc], is a common disaccharide component of the *N*- and *O*-linked oligosaccharides of glycoproteins, and serves as a scaffold for LeX and SLex epitopes of biological significance. In addition, several numbers of the disaccharide units are often assembled linearly to form a so-called poly-*N*-acetyllactosamine structure. It has been reported that *N*-acetyllactosamine is an essential structural unit recognized by the galectins of an animal lectin family and that the recognitions are enhanced based on galectin species by the multivalent *N*-acetyllactosamines present in branched *N*-glycan or repeated *N*-acetyllactosamine chains.[1] In order to gain better insight into such carbohydrate-mediated biological mechanisms and to tackle such inaccessible complex structures, efforts have been made to obtain synthetic homogeneous samples. Syntheses of oligosaccharides carrying repeated *N*-acetyllactosamines have previously been reported by several groups, where the *N*-phthaloylated,[2–8] *N*-tetrachlorophthaloylated[9] or *N*-trichloroethoxycarbonylated[10] lactosaminyl derivatives were used as glycosyl donors to achieve β-selective glycosylation.[11,12] In contrast, we have recently developed new synthetic procedures for the core 2,[13] core 3,[14] core 4,[15] and core 6[14] *O*-glycans of glycoprotein, employing benzylidene- and/or benzyl-protected *N*-trichloroacetyllactosaminyl fluorides with high β-selectivity. The oligosaccharides thus prepared were successfully introduced into the glycopeptides through solid-phase peptide synthesis (SPPS) followed by debenzylation under the conditions of low-acidity trifluoromethanesulfonic acid (TfOH). The high potencies of the *N*-trichloroacetyllactosaminyl fluoride in terms of reactivity and β-selectivity prompted us to synthesize this complex molecule as core 2 *O*-glycan with a tetrameric *N*-acetyllactosamine motif (**2**), which would allow us to apply in the solid-phase glycopeptide synthesis. It should be noted that the related decasaccharide has already been synthesized in an earlier study, but the most difficult task concerning deprotection of the oligosaccharide was not realized.[4b] Apart from the chemical approach, a chemoenzymatic synthesis of the same structural framework was recently reported.[12a] We wish to describe here a novel synthesis of the tetra-*N*-acetyllactosamine-containing core 2 *O*-glycan and the solid-phase synthesis of a glycopeptide carrying decasaccharide.

2. Synthesis of decasaccharyl threonine building block

In our initial synthesis planning shown in Scheme 1, the route to the properly protected decasaccharyl threonine **2** was designed to couple tetralactosaminyl intermediate **3** and known disaccharyl threonine **4**[13a,b] on the basis of our benzyl-protection strategy.[13–15] It has been established that glycosylation of **4** and the related 4,6-dihydroxy disaccharide preferentially occur at the more reactive 6-*O*-position.[13a,b,16] We envisioned that the lactosamine

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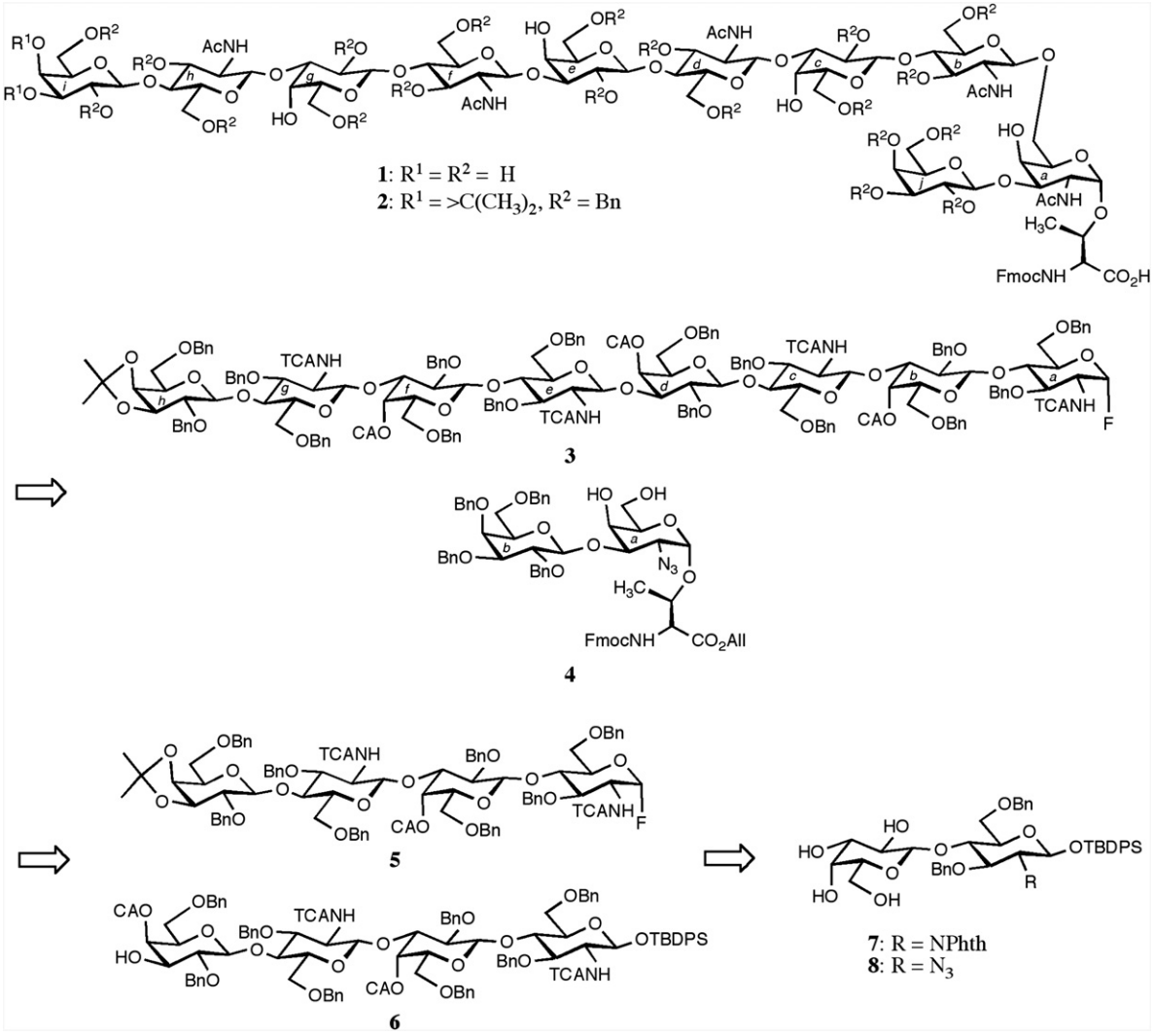


Scheme 1. Retrosynthetic scheme to the tetralactosaminyl *O*-glycothreonine in the initial synthesis planning.

tetramer could be obtained by coupling di-lactosaminyl donor **5** and acceptor **6**, which could be prepared from known disaccharide **7**[16] or **8**[13b] (see Scheme 1).

Isopropylidenation of **7** with acetone and an acid catalyst afforded a mixture of **9** (70%) and **10** (24%), and the structures of which were determined by the NMR data of corresponding diacetate **11** and **12**. The shifted proton signals for H-2b of **11** appeared at 4.93 ppm, while H-2b and H-3b of **12** were observed at 5.27 and 4.75 ppm, respectively. The major isomer **9** was benzylated to **13** (84%), which was heated with ethylenediamine in *n*-BuOH to give **19** (90%). Compound **19** was alternatively prepared from **8** in a comparable overall yield. Isomers **14** (60%) and **15** (18%) were obtained by reacting **8** with acetone. The structures of **14** and **15** were also determined after acetylation to **16** and **17**. Benzylation of **14** followed by reduction of the azido group with Zn and AcOH yielded **19** (85% in two steps). Subsequently, 2-amino sugar **19** was then trichloroacetylated to give key disaccharide **20** (97%). Desilylation of **20** with tetra-*n*-butylammonium fluoride (TBAF)/THF in the presence of AcOH was followed by treatment with diethylaminosulfur trifluoride (DAST) to afford glycosyl donor **22** (83% in two steps). Glycosyl acceptor **23** was obtained via the deisopropylidenation of **20**. Regioselective glycosylation of diol **23** (1.2 equiv) with glycosyl donor **22** was examined under the $Cp_2Zr(ClO_4)_2$/CH_2Cl_2 conditions.[17] The donor was consumed at −15 °C within 2 h. However, desired tetrasaccharide **25** [$(M+Na)^+$: *m*/*z* 1973.54] was obtained only in 25% yield. Hexasaccharide **27** [$(M+Na)^+$: *m*/*z* 2840.35, 23%] and a trace amount of tetrasaccharide isomer [$(M+Na)^+$: *m*/*z* 1974.56] were also found in the reaction mixture. The structure of **25** was confirmed by conversion to 4-*O*-chloroacetate **26**, which exhibited a characteristic lower-field shifted proton signal for H-4b at 5.48 ppm. We recently observed similar insufficient regioselectivity, when glycosylation of a 3,4-unprotected galactose derivative was performed with a highly reactive glycosyl donor carrying a 2-trichloroacetamido group.[15] A modified procedure, employing the slow addition of **22** by a syringe pump into the more diluted reaction mixture containing excess acceptor **23** (1.5 equiv), improved the yield of **25** (72%). However, the byproducts were also generated in 5–7% yields. To avoid the formation these byproduct, 4-*O*-chloroacetate **24** was prepared by regioselective cleavage of the corresponding 3,4-*O*-orthoester and reacted with **22**. The reaction proceeded smoothly to give tetrasaccharide **26** in 85% yield. Glycosyl donor **5** was then prepared from **26** by desilylation and fluorination (79%), while glycosyl acceptor **6** was obtained through deisopropylidenation and 4-*O*-chloroacetylation (65%).

The coupling reaction of **5** and **6** under similar conditions was successful in producing octasaccharide **30** in 73% yield. Conversion of **30** into glycosyl fluoride **3** was achieved straightforwardly by desilylation and fluorination. Glycosylation of **4** with **3** using a zirconium promoter resulted in the formation of **32** (86%) as the

sole decasaccharide product. The decasaccharide structure was evident from ^{1}H-, ^{13}C NMR and mass spectral data [$(M+Na)^{+}$: m/z 4700.3]. Having the necessary decasaccharide framework, we attempted to manipulate the protecting groups to suite the SPPS. A conventional dechloroacetylation condition consisting of heating with thiourea at 70 °C in DMF was examined using **32**. However, the reaction produced the desired **33** in only 36% yield, and the remaining part of **32** was converted into complex materials with high polarity. The use of other dechloroacetyl agents such as aq pyridine or 1-selenocarbamoylpiperidine[18] did not offer any improvement. Although the optimal conditions were not attained for the selective removal of chloroacetyl groups, the study was

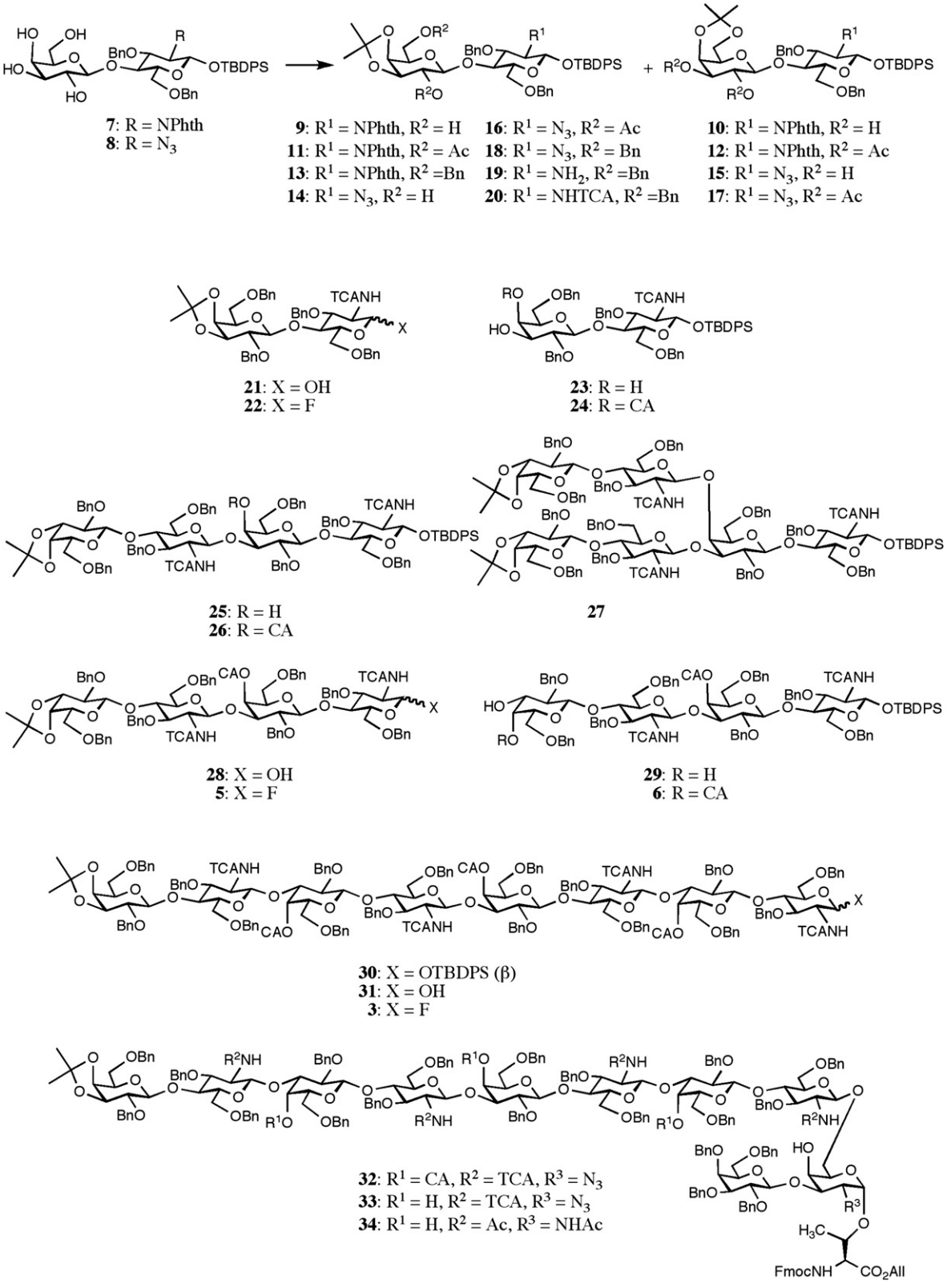


Figure 1. Intermediates in the synthesis of tetralactosaminyl *O*-glycothreonine **2**.

progressed to achieve necessary deprotection. Upon Zn reduction accelerated by microwave irradiation[15] and subsequent acetylation, compound **33** was converted to **34** (86%), which was then treated with $Pd(PPh_3)_4$ and dimedone in THF to quantitatively produce **2**. Our observation of the structure of **2** was supported by the NMR and mass spectral data.

As only limited success was achieved from the above mentioned procedure, we explored an alternative route to the $(LacNAc)_4$-containing core 2 *O*-glycoamino acid by omitting 4-*O*-chloroacetyl protection. We recently reported the facile synthesis of allyl and benzyl-protected LacNAc derivative **35** by propionitrile-mediated β-selective galactosylation.[19] The disaccharide **35** was considered optimal for the preparation of a series of $(LacNAc)_n$ glycosyl donors and acceptors. In addition, we found that the 3-*O*-allyl protecting group was removable when exposed to the low-acidity TfOH conditions used for the ultimate deprotection of synthetic glycopeptides. Accordingly, 3-*O*-allyl-protected oligosaccharides are usable in our benzyl-based protocol of solid-phase glycopeptide synthesis without specific deallylative processing. By desilylation and subsequent fluorination, the disaccharyl fluoride **37** was obtained in 96% yield (two steps). In contrast, selective removal of the allyl group of **35** was readily performed by iridium-catalyzed olefin migration followed by hydrolysis to give glycosyl acceptor **39** (97%). The coupling reaction of **37** and **39** with $Cp_2Zr(ClO_4)_2$ in CH_2Cl_2 gave a complex mixture of products, from which the desired tetrasaccharide **40** [$(M+Na)^+$: *m*/*z* 2153.97] was isolated in only 29% yield. A byproduct with larger molecular weight corresponding to hexasaccharide **43** [$(M+Na)^+$: *m*/*z* 3078.97] was also generated in 16% yield. This result presents a remarkable contrast to the high-yielding case of **26**. The 4-*O*-benzylated Gal residue may enhance the armed nature of GlcNTCA residue, and thus strong Lewis acid may permit the departure of the *t*-butyldiphenylsilyloxy group from initially formed **40** to form a tetrasaccharyl glycosyl donor leading to **43**. Regeneration of **35** (9%) in the byproducts partly supported the occurrence of the cleavage of the *t*-butyldiphenylsilyloxy group. We have previously observed that reactivity of LacNTCA fluoride is considerably influenced by the protecting groups at the Gal residue.[15] The LacNTCA fluoride carrying 2,3,4,6-tetra-*O*-benzyl Gal was more reactive than that carrying 2,3-di-*O*-benzyl-4,6-*O*-benzylidene Gal. In order to reduce such side reactions, glycosylation that could be promoted by a catalytic Lewis acid was exploited. Thus, we selected the glycosyl imidate method reported by Yu and Tao.[20] By treatment with (*N*-phenyl)-trifluoroacetimidoyl chloride[21] and K_2CO_3, hemiacetal **36** was

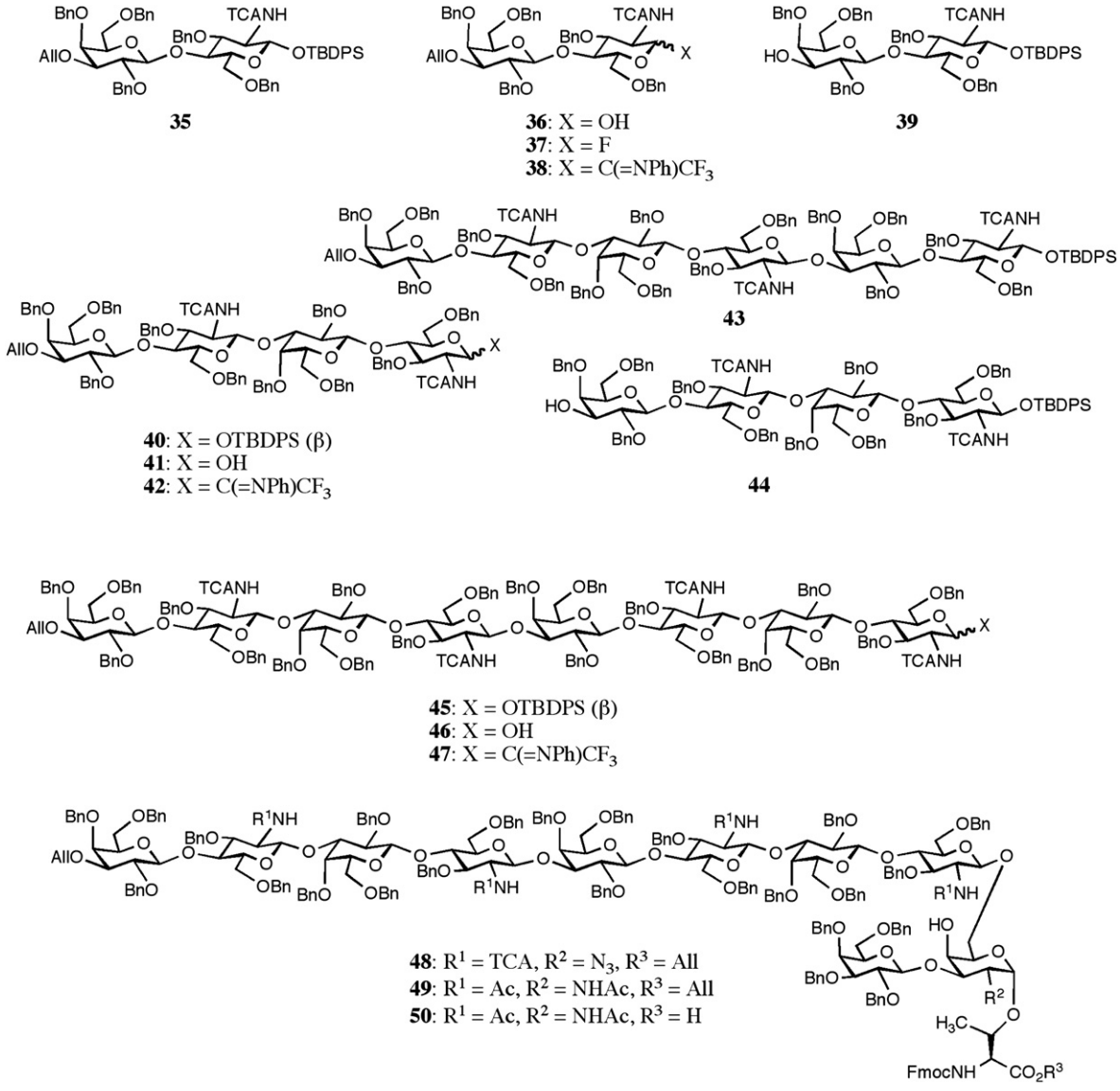


Figure 2. Compounds in the second synthesis of tetralactosaminyl *O*-glycothreonine **50**.

readily converted to a stable (*N*-Phenyl)trifluoroacetimidate **38** (94%), which was reacted with **39** in the presence of TMSOTf (0.05 equiv) to give an excellent yield of **40** (93%). The tetrasaccharide was then transformed into the subsequent coupling partners for octasaccharide. Desilylation of **40**, followed by imidate formation afforded glycosyl donor **42** (94% in two steps), while deallylation of **40** gave glycosyl acceptor **44** (97%). The coupling of **42** and **44** was smoothly promoted by catalytic TMSOTf to afford **45** in 93% yield, which was converted to glycosyl imidate **47** (98%) in an analogous manner. Reacting **4** and **47** under the same glycosylation conditions, the desired tetralactosaminyl *O*-glycothreonine **48** was obtained in 85% yield. Expeditious reduction of the azido group and dehalogenation of the trichloroacetyl group proceeded by reaction with Zn and AcOH under microwave irradiation within 1 h, and subsequent acetylation of the generated 2-aminogalactosyl moiety readily produced penta-acetamido decasaccharide **49** (88%). Allyl ester was selectively cleaved by Pd(0)-catalyzed reaction to provide the desired **50** (83%). The tetralactosaminyl core 2 glycothreonine in a suitably protected form for solid-phase glycopeptide synthesis was thus obtained in better overall yield than that by the initial procedure (**2**) (Fig. 2).

Before applying **50** to the solid-phase synthesis, we examined the deprotection of such large oligosaccharide covered by 24 benzyl groups and an allyl group using our protocol of low-acidity TfOH. A limited amount of TfOH was used to optimize the deprotection reaction, since it is known that the LacNAc glycosides tend to split under debenzylation conditions with excess TfOH.[13b,15] Sample **50** was dissolved in a mixture of trifluoroacetic acid (TFA)/dimethyl sulfide (DMS)/*m*-cresol [5:3:1] and cooled at −15 °C. The mixture was treated with TfOH (6 equiv/benzyl and allyl groups) for 4 h at −15 °C, and the product was precipitated from diethyl ether. HPLC analysis of the product is shown in Figure 3. The major fraction (peak 1) corresponds to desired oligosaccharide **1** [$(M+Na)^+$: *m*/*z* 2189.4]. This result shows that the allyl group in the decasaccharide was sufficiently susceptible to the acidic deprotection. A LacNAc-deleted octasaccaride [peak 2, $(M+Na)^+$: *m*/*z* 1824.2] and other degraded oligosaccharides were also detected in the less mobile fractions. Attempts to suppress the LacNAc cleavage by lowering the temperature or by reducing the amount of TfOH resulted in incomplete deprotection. Decasaccharide **1** was isolated by reversed-phase preparative HPLC in 19% yield.

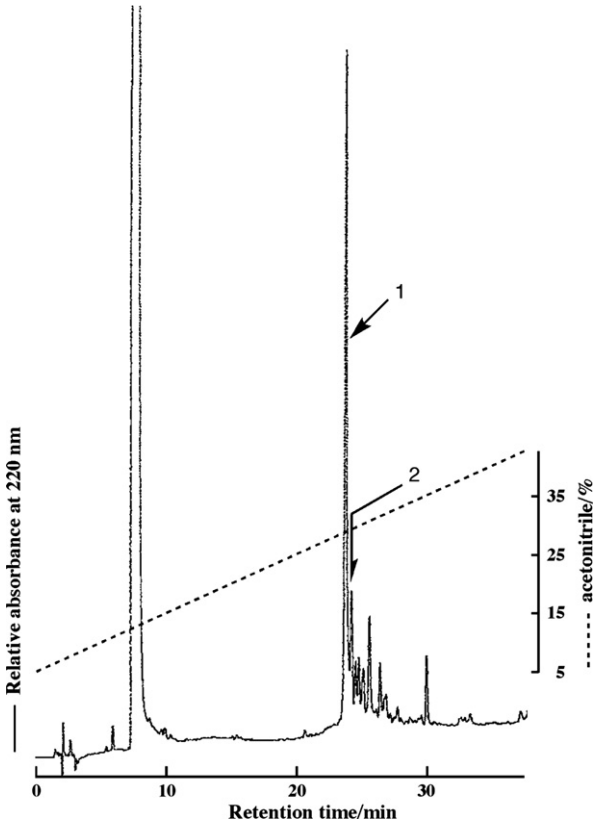
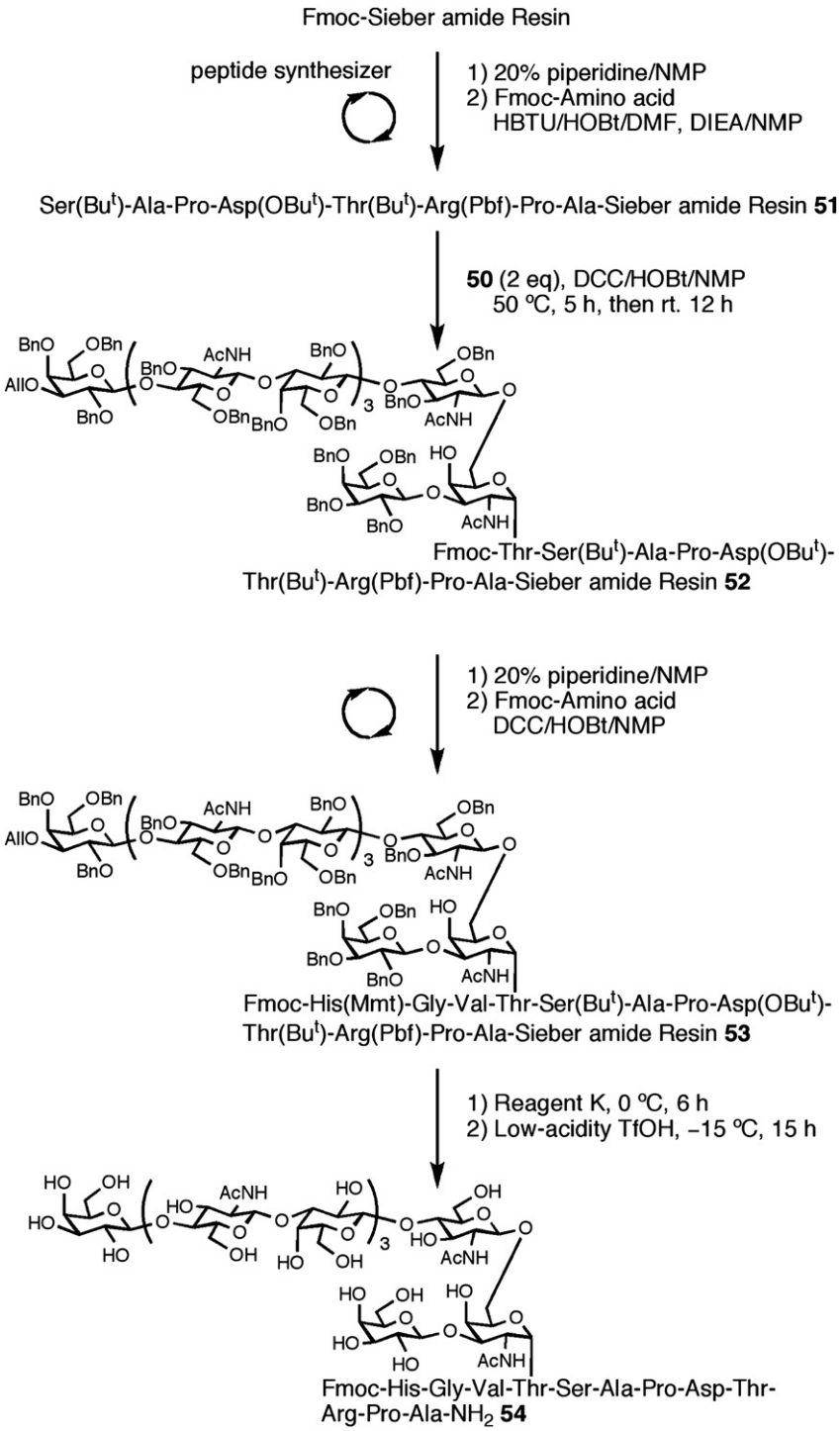


Figure 3. HPLC profile of the products by treatment of **50** with low-acidity TfOH. Peak 1 and 2 correspond to desired **1** and the LacNAc-deleted analog, respectively. Conditions: column, Mightysil KANTO RP-18, 4.6×150 (5 μm); eluent A, distilled water containing 0.1% TFA, eluent B, acetonitrile containing 0.1% TFA; flow rate, 1 ml/min.

3. Solid-phase synthesis of glycopeptide

With the suitably protected glyco-threonine **50** in hand, we next studied solid-phase glycopeptide synthesis and deprotection of the product with low-acidity TfOH. A glycosylated (*) MUC1 fragment (HGVT*SAPDTRPA) **54** was chosen as a synthetic model. An octapeptide (SAPDTRPA) was synthesized on commercial Fmoc-Sieber amide resin using a peptide synthesizer under a tailor-made program (*FastMoc*) for Fmoc chemistry. Each Fmoc amino acid was activated with a mixture of *O*-benzotriazol-1-yl-*N*, *N*, *N*′, *N*′-tetramethyluronium hexafluorophosphate (HBTU), 1-hydroxybenzotriazole (HOBt), and diisopropylethylamine (DIEA) in 1-methyl-2-pyrrolidinone (NMP), and then condensed with the growing peptide on resin, while *N*-deprotection was performed with 20% piperidine/NMP before the condensation (Scheme 2).

To protect side-chain functional groups, 2,2,4,6,7-pentamethyldihydrobenzofuran-5-sulfonyl (Pbf) group was employed for arginine, and a *t*-butyl group for threonine, serine and aspartic acid, respectively. A part of the machine-made peptide resin **51** was subjected to manual condensation with **50** (2 equiv). The reaction was performed at an elevated temperature (50 °C) with *N*, *N*'-dicyclohexylcarbodiimide (DCC)/HOBt in NMP using a vortex mixer. Subsequently, the three N-terminal amino acids were introduced with DCC/HOBt in NMP by manual operation. 4-Methoxytrityl (Mmt) was used as a protective group for histidine. After completion of the peptide assembly, the synthesized glycopeptide **53** was cleaved from the resin. To avoid undesired scission of the labile LacNAc glycosidic linkages, the resin was treated with reagent K (TFA/H_2O/thioanisole/1,2-ethanedithiol/phenol)[22] at a lowered temperature (0 °C) for 6 h. The product precipitated from diethyl ether was collected by centrifugation, and then subjected to the debenzylation reaction without isolation of the intermediates. The final deprotection was performed at −15 °C for 15 h with a reduced amount of TfOH (calculated 1.5 equiv/benzyl and allyl groups) in a more diluted cocktail [TFA/DMS/*m*-cresol/TfOH (5:3:1:0.3)] than for the deprotection of **50** (vide supra), since excess TfOH brought about uncontrolled cleavage of the LacNAc glycosides and benzyl ethers. An HPLC elution profile of the crude product is shown in Figure 4. The chromatogram was more complicated than that in the model experiment with **50**. The major peak (1) corresponds to desired glycopeptide **54** [$(M+H)^+$: *m*/*z* 3255.1], which was separated by reversed-phase preparative HPLC. Purity of isolated **54** was supported by HPLC (Fig. 4b) and the mass spectrum. The yield of **54** was estimated as 4.8% based on the value of Gly in the amino acid-analysis data of the acid-hydrolyzed sample. The accompanying byproducts were derived by cleavage predominantly at the β-LacNAc linkages. Mass spectral data of the following fractions exhibited side-production of a series of dodecapeptides carrying octasaccharide [peak 2: $(M+H)^+$ *m*/*z* 2889.68; **54**-LacNAc], hexasaccharide [peak 3: $(M+H)^+$ *m*/*z* 2524.98; **54**—$(LacNAc)_2$], tetrasaccharide [peak 4: $(M+H)^+$ *m*/*z* 2159.82; **54**–$(LacNAc)_3$], and disaccharide [peak 5: $(M+H)^+$ *m*/*z* 1794.39; **54**–$(LacNAc)_4$]. A trace amount of the non-glycosylated dodecapeptide [peak 7: $(M+H)^+$ *m*/*z* 1429.66] was also observed in the products. In contrast, peak 6



Scheme 2. Solid-phase synthesis of glycopeptide **54**.

demonstrated a mass spectral value (m/z 1019.47) coinciding with an unusual DCC adduct to the C-terminal octapeptide, probably generated by the forced conditions (50 °C, 5 h) in the step to introduce **50**. Amino-acid analysis supported its octapeptidyl structure. No other byproducts corresponding to the shorter peptides were detected. It was therefore clear that building block **50** was introduced into the resin-supported peptide with high efficiency and that the bulk of the settled decasaccharide posed little obstacle to further elongation of the peptide chain.

In conclusion, we have synthesized a linear tetralactosaminyl oligosaccharide by taking advantage of the 2-trichloroacetamido group-assisted β-stereoselective glycosylation and constructed a core 2 *O*-linked decasaccharyl threonine with the $(LacNAc)_4$ substituent in an *N*-Fmoc-, *O*-benzyl- and *O*-allyl-protected form. The bulky glycothreonine was successfully introduced into a MUC1-related dodecapeptide, even when a reduced amount (2 equiv) of the building block was used in the solid-phase synthesis. Both acidic conditions for releasing the synthetic glycopeptide from resin with reagent K and for its deprotection with low-acidity TfOH were carefully examined to suppress scission of the acid-labile glycosidic linkages. The reagent K reaction at a lower reaction temperature needed a longer reaction period than usual to

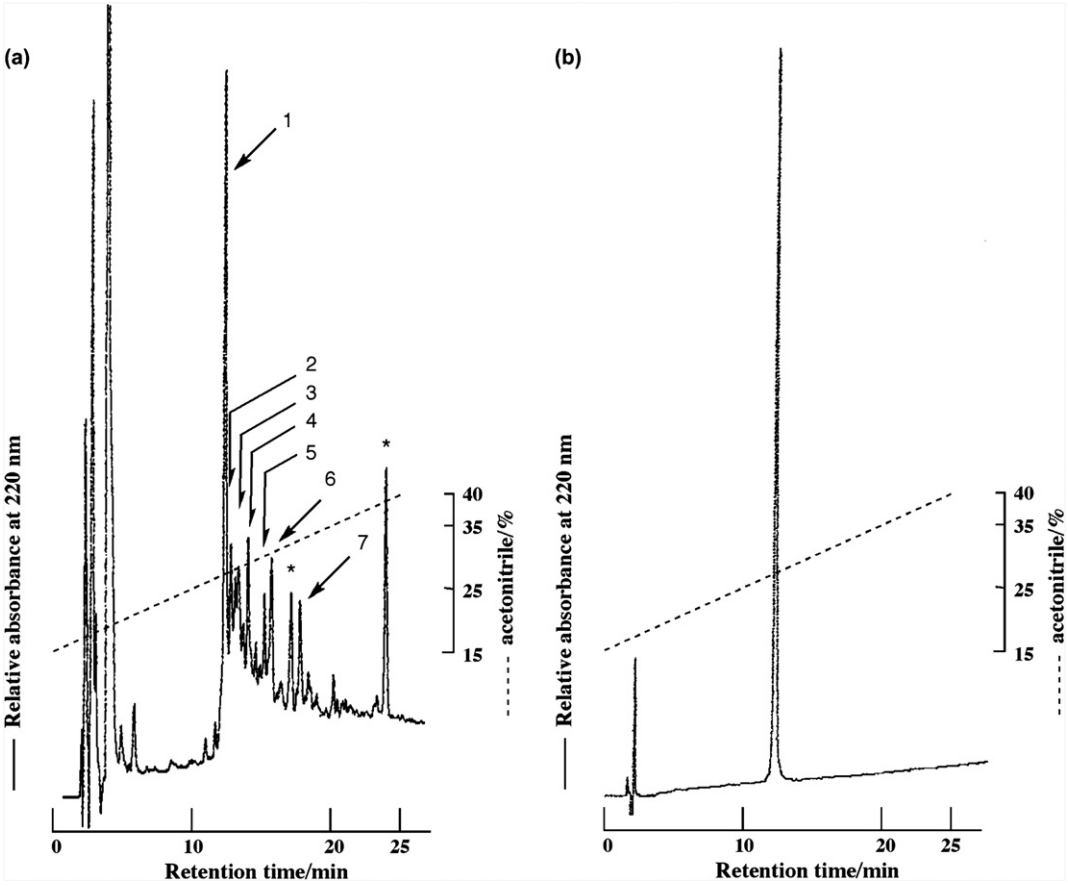


Figure 4. HPLC profile of synthetic glycopeptide **54** (**a**-**1**) and isolated **54** (**b**) Conditions: column, Mightysil KANTO RP-18, 4.6×150 (5 μm); eluent A, distilled water containing 0.1% TFA, eluent B, acetonitrile containing 0.1% TFA; flow rate 1 ml/min.

complete removal of the peptide protecting groups. The benzyl and allyl groups in the oligosaccharide part were finally cleaved by treatment with a reduced amount of TfOH in the cleavage cocktail at −15 °C by extending the reaction time. Since considerable damage to the oligosaccharide moiety could not be eliminated after the optimization studies, such heavily benzylated glycopeptides containing the accumulated acid-labile linkages as **53** may lie virtually within the limitations of deprotection when the low-acidity TfOH method is employed.

4. Experimental

4.1. General

Optical rotation values were determined with a Jasco DIP-370 polarimeter at 20±2 °C for solutions in $CHCl_3$, unless noted otherwise. Column chromatography was performed on silica gel PSQ 100B (Fuji Silysia), while TLC and HPTLC were performed on silica gel 60 F_{254} (E. Merck). ^{1}H- and ^{13}C NMR spectra were recorded with a Jeol AL400 spectrometer (^{1}H at 400 MHz and ^{13}C at 100 MHz). Chemical shifts are expressed in ppm downfield from the signal for internal Me_4Si for solutions in $CDCl_3$. For description of the NMR data, each sugar residue in oligosaccharide is indicated by alphabetical mark as shown in Figure 1 MALDI TOF mass spectra were obtained with a PerSeptive Voyager-DE PRO spectrometer (2,5-dihydroxybenzoic acid was used as a matrix) Automated solid-phase peptide synthesis was performed with an Applied Biosystems 433A peptide synthesizer. Manual solid-phase reactions were undertaken in capped polypropylene test tubes equipped with a filter and three-way stopcock by stirring on an EYELA CM-1000 vortex mixer. HPLC was performed in Mightysil RP-18 (4.6×150 mm for analysis, 10×250 mm and 20×250 mm for preparation, Kanto Chemical Co.). Fmoc-Sieber-amide resin was purchased from NOVAbiochem. The yield of glycopeptide was determined by amino acid analysis after the samples were hydrolyzed in a sealed tube with 20% HCl and 0.5% phenol at 150 °C for 2 h. Amino acids were analyzed by a Hitachi L-8500 amino acid analyzer, in which Val was separated with GlcNAc (1/4 sensitivity).

4.1.1. tert-Butyldiphenylsilyl 3,4-O-isopropylidene-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside ***9***. To a solution of **7** (423 mg, 0.48 mmol) in anhydrous acetone (250 ml) were added dried $CuSO_4$ (1.47 g) and *p*-$TsOH\cdot H_2O$ (71 mg). The mixture was stirred at room temperature for 5 h. Then the reaction mixture was neutralized with satd $NaHCO_3$ aq, and the precipitate was filtered off through Celite. The filtrate was concentrated in vacuo, and the residual product was extracted with EtOAc. The extract was successively washed with satd $NaHCO_3$ aq, water, and brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was chromatographed on silica gel with toluene–EtOAc (1:1) to give **9** (311 mg, 70%) and **10** (107 mg, 24%). Compound **9**: $[\alpha]_D$ +7.4 (*c* 1). R_f 0.53 (1:1 toluene–EtOAc). ^{1}H NMR: δ 7.67–6.86 (m, 24H, Ar), 5.18 (m, 1H, H-1a), 4.81 (d, 1H, *J*=12.0 Hz, –C*H*$_2$Ph), 4.61 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.45 (d, 1H, *J*=12.0 Hz, –C*H*$_2$Ph), 4.44 (d, 1H, *J*=8.0 Hz, H-1b), 4.38 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.32–4.26 (m, 2H, H-2a, H-3a), 4.08 (m, 1H, H-4a), 4.02 (dd, 1H, *J*=1.7, 5.6 Hz, H-4b), 3.97 (dd, 1H, *J*=5.6, 6.8 Hz, H-3b), 3.76 (dd, 1H, *J*=3.2, 12.5 Hz, H-6a), 3.70 (m, 1H, H-6b), 3.66–3.63 (m, 2H, H-5b, –O*H*), 3.51–3.45 (m, 2H, H-6a, H-2b), 3.25 (br d, 1H, *J*=10.0 Hz, H-5a), 2.92 (d, 1H, *J*=2.5 Hz, –O*H*), 1.48 (s, 3H, –C*H*$_3$), 1.31 (s, 3H, –C*H*$_3$), 0.88 (s, 9H, ^{t}Bu). MALDI

TOF MS: calcd for $C_{53}H_{59}NO_{12}Si$ $(M+Na)^+$ *m/z* 952.38. Found: 952.26. Anal. calcd for $C_{53}H_{59}NO_{12}Si$: C, 68.44; H, 6.39; N, 1.51. Found: C, 68.56; H, 6.46; N, 1.35. Compound **10**: $[\alpha]_D$ +44.6 (*c* 1). R_f 0.16 (1:1 toluene–EtOAc). ^{1}H NMR: δ 7.78–6.84 (m, 24H, Ar), 5.17 (d, 1H, *J*=7.8 Hz, H-1a), 4.85 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.62 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.54 (d, 1H, *J*=7.3 Hz, H-1b), 4.49 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.45 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.36 (dd, 1H, *J*=8.3, 10.5 Hz, H-3a), 4.29 (dd, 1H, *J*=7.8, 10.5 Hz, H-2a), 4.12 (m, 1H, H-4a), 4.01 (br d, 1H, *J*=2.9 Hz, H-4b), 3.89 (dd, 1H, *J*=2.9, 12.0 Hz, H-6a), 3.83 (dd, 1H, *J*=2.2, 12.7 Hz, H-6b), 3.75 (dd, 1H, *J*=1.2, 12.7 Hz, H-6b), 3.62–3.68 (m, 2H, H-2b, –O*H*), 3.47–3.43 (m, 2H, H-6a, H-3b), 3.24 (br d, 1H, *J*=10.0 Hz, H-5a), 2.94 (br s, 1H, H-5b), 2.44 (d, 1H, *J*=8.3 Hz, –O*H*), 1.38 (s, 3H, –C*H*$_3$), 1.34 (s, 3H, –C*H*$_3$), 0.88 (s, 9H, ^{t}Bu). MALDI TOF MS: calcd for $C_{53}H_{59}NO_{12}Si$ $(M+Na)^+$ *m/z* 952.38. Found: 952.53. Anal. calcd for $C_{53}H_{59}NO_{12}Si$: C, 68.44; H, 6.39; N, 1.51. Found: C, 68.34; H, 6.46; N, 1.47.

4.1.2. tert-Butyldiphenylsilyl 2,6-di-O-acetyl-3,4-O-isopropylidene-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside ***11***. Compound **9** was stirred with Ac_2O (10 equiv) in pyridine at room temperature overnight. The crude product was chromatographed on silica gel with toluene–EtOAc (7:3) to give **11**. ^{1}H NMR: δ 7.77–6.78 (m, 24H, Ar), 5.18 (d, 1H, *J*=8.0 Hz, H-1a), 4.93 (dd, 1H, *J*=7.6, 8.3 Hz, H-2b), 4.76 (d, 1H, *J*=12.5 Hz, –C*H*$_2$Ph), 4.67 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.49 (d, 1H, *J*=8.3 Hz, H-1b), 4.41 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.39 (d, 1H, *J*=12.5 Hz, –C*H*$_2$Ph), 4.30–4.22 (m, 2H, H-6b, H-2a), 4.19 (dd, 1H, *J*=4.6, 11.7 Hz, H-6b), 4.14 (dd, 1H, *J*=8.5, 10.7 Hz, H-3a), 4.09–3.97 (m, 3H, H-4a, H-3b, H-4b), 3.84 (m, 1H, H-5b), 3.67 (dd, 1H, *J*=3.2, 11.2 Hz, H-6a), 3.44 (dd, 1H, *J*=1.5, 11.2 Hz, H-6a), 3.16 (br d, 1H, *J*=9.8 Hz, H-5a), 2.07 (s, 3H, Ac), 2.02 (s, 3H, Ac), 1.50 (s, 3H, –C*H*$_3$), 1.30 (s, 3H, –C*H*$_3$), 0.88 (s, 9H, ^{t}Bu).

4.1.3. tert-Butyldiphenylsilyl 2,3-di-O-acetyl-4,6-O-isopropylidene-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside ***12***. Compound **10** was acetylated as described for **11** to give **12**. ^{1}H NMR: δ 7.66–6.79 (m, 24H, Ar), 5.27 (dd, 1H, *J*=8.1, 10.3 Hz, H-2b), 5.18 (d, 1H, *J*=7.8 Hz, H-1a), 4.91 (d, 1H, *J*=12.5 Hz, –C*H*$_2$Ph), 4.75 (dd, 1H, *J*=3.7, 10.5 Hz, H-3b), 4.63 (d, 1H, *J*=8.0 Hz, H-1b), 4.63 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.50 (d, 1H, *J*=12.5 Hz, –C*H*$_2$Ph), 4.38 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.27–4.11 (m, 3H, H-2a, H-3a, H-4b), 4.06 (br t, 1H, *J*=9.0 Hz, H-4a), 3.90 (m, 2H, H-6b×2), 3.66 (dd, 1H, *J*=3.3, 11.2 Hz, H-6a), 3.44 (br d, 1H, *J*=11.0 Hz, H-6a), 3.17–3.14 (m, 2H, H-5a, H-5b), 2.05 (s, 3H, Ac), 1.98 (s, 3H, Ac), 1.31 (s, 3H, –C*H*$_3$), 1.29 (s, 3H, –C*H*$_3$), 0.87 (s, 9H, ^{t}Bu).

4.1.4. tert-Butyldiphenylsilyl 2,6-di-O-benzyl-3,4-O-isopropylidene-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside ***13***. To a stirred mixture of **9** (201 mg, 0.22 mmol) and 60% NaH/mineral oil (35 mg, 0.87 mmol) in anhydrous DMF (15 ml) was added benzyl bromide (103 μl, 0.87 mmol) at 0 °C under Ar. Then, the cooling bath was removed and the mixture was stirred at room temperature for 4 h. The reaction was quenched with a careful addition of a few piece of ice. The mixture was diluted with ether–EtOAc (1:1), successively washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was chromatographed on silica gel with toluene–EtOAc (9:1) to afford **13** (201 mg, 84%). $[\alpha]_D$ +37.4 (*c* 1). R_f 0.46 (9:1 toluene–EtOAc). ^{1}H NMR: δ 7.80–6.82 (m, 34H, Ar), 5.19 (d, 1H, *J*=8.0 Hz, H-1a), 4.78 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.76 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.68 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.57 (d, 1H, *J*=12.0 Hz, –C*H*$_2$Ph), 4.50 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.46 (d, 1H, *J*=8.0 Hz, H-1b), 4.42 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.40 (d, 1H, *J*=12.0 Hz, –C*H*$_2$Ph), 4.36 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.31 (dd, 1H, *J*=8.1, 10.8 Hz, H-2a), 4.21 (dd, 1H, *J*=8.3, 10.7 Hz, H-3a), 4.14–4.03 (m, 3H, H-4a, H-3b, H-4b), 3.78–3.75 (m, 2H, H-6a, H-5b), 3.68 (dd, 1H, *J*=5.9, 10.0 Hz, H-6b), 3.60 (dd, 1H, *J*=6.5, 10.0 Hz, H-6b), 3.42 (br d, 1H, *J*=10.7 Hz, H-6a), 3.32 (br t, 1H, *J*=7.5 Hz, H-2b), 3.18 (br d, 1H, *J*=8.8 Hz, H-5a), 1.34 (s, 3H, –C*H*$_3$), 1.32 (s, 3H, –C*H*$_3$), 0.89 (s, 9H, ^{t}Bu.). MALDI TOF MS: calcd for $C_{67}H_{71}NO_{12}Si$ $(M+Na)^+$ *m/z* 1132.47. Found: 1132.70. Anal. calcd for $C_{67}H_{71}NO_{12}Si$: C, 72.47; H, 6.45; N, 1.26. Found: C, 72.64; H, 6.55; N, 1.12.

4.1.5. tert-Butyldiphenylsilyl 3,4-O-isopropylidene-β-D-galactopyranosyl-(1→4)-2-azido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranoside ***14***. To a solution of **8** (1.69 g, 2.15 mmol) in anhydrous acetone (300 ml) were added well-dried $CuSO_4$ (8.0 g) and *p*-TsOH·H_2O (70 mg). The mixture was stirred at room temperature for 3 h. Then the reaction mixture was neutralized with satd $NaHCO_3$, and the precipitate was filtered off through Celite. The filtrate was concentrated in vacuo, and the residual product was extracted with EtOAc. The extract was successively washed with satd $NaHCO_3$, water, and brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was chromatographed on silica gel with toluene–EtOAc (1: 1) to give **14** (1.12 g, 60%) and **15** (0.35 g, 18%). Compound **14**: $[\alpha]_D$ +6.5 (*c* 1). R_f 0.46 (1:1 hexane–EtOAc). ^{1}H NMR: δ 7.73–7.68, 7.52–7.05 (m, 20H, Ar), 4.88 (d, 1H, *J*=10.5 Hz, –C*H*$_2$Ph), 4.78 (d, 1H, *J*=10.7 Hz, –C*H*$_2$Ph), 4.49 (d, 1H, *J*=12.0 Hz, –C*H*$_2$Ph), 4.35–4.29 (m, 3H, H-1a, H-1b, –C*H*$_2$Ph), 3.98–3.90 (m, 3H, H-4a, H-4b, H-3b), 3.65–3.56 (m, 3H, H-6a, H-6b, H-6b), 3.52–3.47 (m, 2H, H-2a, H-5b), 3.43 (m, 1H, H-2b), 3.32–3.26 (m, 2H, H-3a, H-6a), 2.96–2.92 (m, 2H, H-5a, –O*H*), 1.49 (s, 3H, –C*H*$_3$), 1.31 (s, 3H, –C*H*$_3$), 1.12 (s, 9H, ^{t}Bu). MALDI TOF MS: calcd for $C_{45}H_{55}N_3O_{10}Si$ $(M+Na)^+$ *m/z* 848.35. Found: 848.13. Anal. calcd for $C_{45}H_{55}N_3O_{10}Si$: C, 65.43; H, 6.71; N, 5.09. Found: C, 65.53; H, 6.74; N, 5.03. Compound **15**: $[\alpha]_D$ −6.2 (*c* 1). R_f 0.18 (1:1 hexane–EtOAc). ^{1}H NMR: δ 7.72–7.67, 7.43–7.15 (m, 20H, Ar), 4.96 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.87 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.51 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.47 (d, 1H, *J*=7.8 Hz, H-1b), 4.35 (d, 1H, *J*=7.8 Hz, H-1a), 4.32 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.00 (t, 1H, *J*=9.3 Hz, H-4a), 3.98 (d, 1H, *J*=4.4 Hz, H-4b), 3.78–3.74 (m, 2H, H-6a, H-6b), 3.67 (dd, 1H, *J*=1.5, 12.7 Hz, H-6b), 3.57–3.47 (m, 3H, –O*H*, H-2a, H-2b), 3.40 (dt, 1H, *J*=3.9, 8.3 Hz, H-3b), 3.35 (t, 1H, *J*=9.8 Hz, H-3a), 3.26 (dd, 1H, *J*=1.9, 12.1 Hz, H-6a), 2.93 (m, 1H, H-5a), 2.76 (br s, 1H, H-5b), 2.42 (d, 1H, *J*=8.3 Hz, –O*H*), 1.39 (s, 3H, –C*H*$_3$), 1.38 (s, 3H, –C*H*$_3$), 1.11 (s, 9H, ^{t}Bu). MALDI TOF MS: calcd for $C_{45}H_{55}N_3O_{10}Si$ $(M+Na)^+$ *m/z* 848.36. Found: 848.36. Anal. calcd for $C_{45}H_{55}N_3O_{10}Si$: C, 65.43; H, 6.71; N, 5.09. Found: C, 65.29; H, 6.73; N, 5.02.

4.1.6. tert-Butyldiphenylsilyl 2,6-di-O-acetyl-3,4-O-isopropylidene-β-D-galactopyranosyl-(1→4)-2-azido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranoside ***16***. Compound **14** was acetylated with Ac_2O in pyridine to give **16**. ^{1}H NMR: δ 7.74–7.68 (m, 4H, Ar), 7.43–7.20 (m, 16H, Ar), 4.95 (d, 1H, *J*=10.7 Hz, –C*H*$_2$Ph), 4.89 (br t, 1H, *J*=7.9 Hz, H-2b), 4.68 (d, 1H, *J*=10.7 Hz, –C*H*$_2$Ph), 4.55 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.44 (d, 1H, *J*=8.3 Hz, H-1b), 4.33 (d, 1H, *J*=7.8 Hz, H-1a), 4.28 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.23 (br t, 1H, *J*=6.4 Hz, H-6b), 4.13 (dd, 1H, *J*=7.0, 11.7 Hz, H-6b), 4.04 (m, 1H, H-4b), 3.98–3.93 (m, 2H, H-4a, H-3b), 3.74 (m, 1H, H-5b), 3.56 (dd, 1H, *J*=2.9, 11.3 Hz, H-6a), 3.45 (dd, 1H, *J*=7.8, 9.7 Hz, H-2a), 3.28–3.24 (m, 2H, H-3a, H-6a), 2.85 (br d, 1H, *J*=9.7 Hz, H-5a), 1.99 (s, 3H, Ac), 1.95 (s, 3H, Ac), 1.51 (s, 3H, –C*H*$_3$), 1.30 (s, 3H, –C*H*$_3$), 1.10 (s, 9H, ^{t}Bu).

4.1.7. tert-Butyldiphenylsilyl 2,3-di-O-acetyl-4,6-O-isopropylidene-β-D-galactopyranosyl-(1→4)-2-azido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranoside ***17***. Compound **15** was acetylated with Ac_2O in pyridine to give **17**. ^{1}H NMR: δ 7.73–7.68 (m, 4H, Ar), 7.51 (br d, 2H, *J*=7.0 Hz, Ar), 7.42–7.18 (m, 14H, Ar), 5.22 (dd, 1H, *J*=8.0, 10.5 Hz, H-2b), 5.06 (d, 1H, *J*=10.5 Hz, –C*H*$_2$Ph), 4.74 (d, 1H, *J*=10.5 Hz, –C*H*$_2$Ph), 4.70 (dd, 1H, *J*=3.9, 7.8 Hz, H-3b), 4.58 (d, 1H, *J*=8.0 Hz, H-1b), 4.51 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.32 (d, 1H, *J*=7.8 Hz, H-1a), 4.25 (d, 1H, *J*=12.0 Hz, –C*H*$_2$Ph), 4.21 (d, 1H, *J*=3.6 Hz, H-4b), 3.96 (br t, 1H, *J*=9.3 Hz, H-4a), 3.84–3.79 (m, 2H, H-6b), 3.57 (dd, 1H, *J*=3.1,

11.4 Hz, H-6a), 3.45 (dd, 1H, *J*=8.0, 9.7 Hz, H-2a), 3.31–3.25 (m, 2H, H-3a, H-6a), 3.02 (br s, 1H, H-5b), 2.84 (br d, 1H, *J*=8.5 Hz, H-5a), 2.04 (s, 3H, Ac), 1.91 (s, 3H, Ac), 1.40 (s, 3H, –C*H*$_3$), 1.34 (s, 3H, –C*H*$_3$), 1.10 (s, 9H, ^{t}Bu).

4.1.8. tert-Butyldiphenylsilyl 2,6-di-O-benzyl-3,4-O-isopropylidene-β-D-galactopyranosyl-(1→4)-2-azido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranoside ***18****.* To a stirred mixture of **14** (1.12 g, 1.36 mmol) and 60% NaH/mineral oil (217 mg, 5.43 mmol) in anhydrous THF (50 ml) was added benzyl bromide (0.66 ml 5.42 mmol) under Ar. The stirred mixture was heated at 60 °C for 6 h and then cooled to ambient temperature. A few piece of ice was carefully added to the mixture, which was concentrated in vacuo. The residual product was extracted with ether–EtOAc (1:1), successively washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was chromatographed on silica gel with toluene–EtOAc (9:1) to afford **18** (1.18 g, 86%). $[\alpha]_D$ +2.4 (*c* 1). R_f 0.53 (4:1 hexane–EtOAc). ^{1}H NMR: δ 7.73–7.69, 7.44–7.14 (m, 30H, Ar), 4.92 (d, 1H, *J*=10..0 Hz, –C*H*$_2$Ph), 4.73 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.65 (d, 1H, *J*=10.3 Hz, –C*H*$_2$Ph), 4.61 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.51 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.42 (d, 1H, *J*=12.0 Hz, –C*H*$_2$Ph), 4.40 (d, 1H, *J*=8.1 Hz, H-1b), 4.31 (d, 1H, *J*=7.6 Hz, H-1a), 4.27–4.23 (m, 2H, –C*H*$_2$Ph×2), 4.12 (dd, 1H, *J*=1.9, 5.4 Hz, H-4b), 4.09–3.97 (m, 2H, H-3a, H-4a), 3.74–3.62 (m, 3H, H-5b, H-6a, H-6b), 3.53 (dd, 1H, *J*=5.9, 9.3 Hz, H-6b), 3.38–3.20 (m, 4H, H-2a, H-2b, H-6a, H-3a), 2.87 (m, 1H, H-5a), 1.38 (s, 3H, –C*H*$_3$), 1.34 (s, 3H, –C*H*$_3$), 1.10 (s, 9H, ^{t}Bu). MALDI TOF MS: calcd for $C_{59}H_{67}N_3O_{10}Si$ $(M+Na)^+$ *m*/*z* 1028.45. Found: 1028.51. Anal. calcd for $C_{59}H_{67}N_3O_{10}Si$: C, 70.42; H, 6.71; N, 4.18. Found: C, 70.22; H, 6.79; N, 4.08.

4.1.9. tert-Butyldiphenylsilyl 2,6-di-O-benzyl-3,4-O-isopropylidene-β-D-galactopyranosyl-(1→4)-2-amino-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranoside ***19****. Procedure A* (*dephthaloylation of* **13**). A mixture of **13** (1.91 g, 1.73 mmol) and ethylenediamine (5.19 ml, 77.6 mmol) in *n*-BuOH (90 ml) was stirred at 90 °C under Ar for 46 h, before being concentrated in vacuo. The residual product was extracted with $CHCl_3$, successively washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was chromatographed on silica gel with $CHCl_3$–EtOAc (19:1) to give **19** (1.56 g, 90%). $[\alpha]_D$ +2.5 (*c* 1). R_f 0.36 (9:1 toluene–EtOAc). ^{1}H NMR: δ 7.72–7.67 (m, 4H, Ar), 7.39–7.06 (m, 26H, Ar), 5.06 (d, 1H, *J*=10.5 Hz, –C*H*$_2$Ph), 4.75 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.65 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.54 (d, 1H, *J*=12.0 Hz, –C*H*$_2$Ph), 4.52 (d, 1H, *J*=10.5 Hz, –C*H*$_2$Ph), 4.43 (d, 1H, *J*=12.0 Hz, –C*H*$_2$Ph), 4.43 (d, 1H, *J*=8.0 Hz, H-1a), 4.34 (d, 1H, *J*=12.0 Hz, –C*H*$_2$Ph), 4.20 (d, 1H, *J*=12.0 Hz, –C*H*$_2$Ph), 4.11 (dd, 1H, *J*=1.7, 5.7 Hz, H-4b), 4.06 (t, 1H, *J*=9.3 Hz, H-4a), 4.03 (dd, 1H, *J*=5.7, 6.6 Hz, H-3b), 3.74 (dt, 1H, *J*=1.7, 6.3 Hz, H-5b), 3.70–3.66 (m, 2H, H-6a, H-6b), 3.57 (dd, 1H, *J*=6.1, 9.5 Hz, H-6b), 3.22 (dd, 1H, *J*=7.1, 8.0 Hz, H-2a), 3.28 (t, 1H, *J*=9.5 Hz, H-3a), 3.27 (dd, 1H, *J*=1.3, 11.5 Hz, H-6a), 2.96 (m, 1H, H-5a), 2.95 (dd, 1H, *J*=7.8, 9.8 Hz, H-2b), 1.34 (s, 3H, –C*H*$_3$), 1.33 (s, 3H, –C*H*$_3$), 1.09 (s, 9H, ^{t}Bu). MALDI TOF MS: calcd for $C_{59}H_{69}NO_{10}Si$ $(M+Na)^+$ *m*/*z* 1002.46. Found: 1002.53. Anal. calcd for $C_{59}H_{69}NO_{10}Si$: C, 72.29; H, 7.09; N, 1.43. Found: C, 72.24; H, 7.07; N, 1.35.

Procedure B (*reduction of* **18**). A mixture of **18** (1.18 g, 1.17 mmol), AcOH (1.41 ml, 23.4 mmol), and Zn (3 g, 45.9 mmol) in CH_2Cl_2 (30 ml) was stirred at room temperature for 3 h. Then the mixture was filtered through Celite and the filtrate was concentrated with toluene in vacuo. The residual product was extracted with $CHCl_3$, successively washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. Chromatography of the crude product on silica gel with $CHCl_3$–EtOAc (19:1) to give **19** (1.13 g, 99%).

4.1.10. tert-Butyldiphenylsilyl 2,6-di-O-benzyl-3,4-O-isopropylidene-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside ***20****.* To a stirred solution of **19** (130 mg, 0.35 mmol) in pyridine (5 ml) was added trichloroacetyl chloride (45 μl, 0.41 mmol) at 0 °C. The mixture was stirred at 0 °C for 2 h to complete the reaction, and concentrated in vacuo. The residual product was extracted with ether–EtOAc (1:1), successively washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was chromatographed on silica gel with hexane–EtOAc (3:1) to afford **20** (150 mg, 97%). $[\alpha]_D$ +9.8 (*c* 1). R_f 0.43 (3:1 hexane–EtOAc). ^{1}H NMR: δ 7.70–7.63 (m, 4H, Ar), 7.40–7.14 (m, 26H, Ar), 6.90 (d, 1H, *J*=7.8 Hz, –N*H*), 4.91 (d, 1H, *J*=7.3 Hz, H-1a), 4.84 (d, 1H, *J*=10.3 Hz, –C*H*$_2$Ph), 4.72 (d, 1H, *J*=11.9 Hz, –C*H*$_2$Ph), 4.63 (d, 1H, *J*=11.9 Hz, –C*H*$_2$Ph), 4.57 (d, 1H, *J*=10.3 Hz, –C*H*$_2$Ph), 4.48 (d, 1H, *J*=12.0 Hz, –C*H*$_2$Ph), 4.42 (d, 1H, *J*=7.8 Hz, H-1b), 4.41 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.30 (d, 1H, *J*=11.9 Hz, –C*H*$_2$Ph), 4.25 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.14–4.02 (m, 3H, H-4a, H-3b, H-4b), 3.88 (t, 1H, *J*=9.5 Hz, H-3a), 3.76–3.62 (m, 4H, H-2a, H-6a, H-5b, H-6b), 3.51 (dd, 1H, *J*=6.5, 9.6 Hz, H-6b), 3.34–3.28 (m, 2H, H-2b, H-6a), 3.10 (br d,1H, *J*=9.0 Hz, H-5a), 1.34 (s, 3H, –C*H*$_3$), 1.33 (s, 3H, –C*H*$_3$), 1.06 (s, 9H, ^{t}Bu). MALDI TOF MS: calcd for $C_{61}H_{68}Cl_3NO_{11}Si$ $(M+Na)^+$ *m*/*z* 1146.35. Found: 1146.53. Anal. calcd for $C_{61}H_{68}Cl_3NO_{11}Si$: C, 65.09; H, 6.09; N, 1.24; Cl, 9.45. Found: C, 64.84; H, 6.08; N, 1.21; Cl, 9.53.

4.1.11. 2,6-Di-O-benzyl-3,4-O-isopropylidene-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-α/β-D-glucopyranose ***21****.* To a stirred mixture of **20** (407 mg, 0.36 mmol) and AcOH (0.21 ml, 3.62 mmol) in distilled THF (5 ml) was added 1 M TBAF/THF (1.45 ml. 1.45 mmol) on an ice-water bath. The mixture was allowed to stir overnight at room temperature. Then the mixture was diluted with enough volume of $CHCl_3$, washed successively with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was chromatographed on silica gel with toluene–EtOAc (4:1) to give **21** (304 mg, 95%, α/β=>10). R_f 0.31 (α) and 0.15 (β) (4:1 toluene–EtOAc). ^{1}H NMR: δ 7.34–7.24 (m, 20H, Ar), 6.83 (d, 1H, *J*=8.6 Hz, –N*H*), 5.38 (br s, 1H, H-1a), 4.91 (d, 1H, *J*=10.7 Hz, –C*H*$_2$Ph), 4.80 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.69 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.64 (d, 1H, *J*=10.7 Hz, –C*H*$_2$Ph), 4.56 (d, 1H, *J*=12.0 Hz, –C*H*$_2$Ph), 4.46 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.39 (d, 1H, *J*=12.0 Hz, –C*H*$_2$Ph), 4.31 (d, 1H, *J*=8.1 Hz, H-1b), 4.29 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 1.40 (s, 3H, –C*H*$_3$), 1.34 (s, 3H, –C*H*$_3$). MALDI TOF MS: calcd for $C_{45}H_{50}Cl_3NO_{11}$ $(M+Na)^+$, *m*/*z* 908.24. Found: 908.59. Anal. calcd for $C_{45}H_{50}Cl_3NO_{11}$: C, 60.92; H, 5.68; N, 1.58; Found: C, 60.87; H, 5.68; N, 1.53.

4.1.12. 2,6-Di-O-benzyl-3,4-O-isopropylidene-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-α/β-D-glucopyranosyl fluoride ***22****.* To a stirred solution of **21** (357 mg, 0.40 mmol) in distilled THF (10 ml) was added DAST (0.11 ml, 0.80 mmol) on an ice-water bath under Ar. The mixture was stirred at 0 °C for 1 h, before the reaction was quenched by addition of a few drops of CH_3OH. The mixture was concentrated in vacuo to the residue, which was dissolved in $CHCl_3$. The extract was washed successively with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was chromatographed on silica gel with toluene–EtOAc (9:1) to give 22 (312 mg, 87%, α/β=19). R_f 0.68 (α) and 0.67 (β) (7:3 toluene–EtOAc). ^{1}H NMR: δ 7.36–7.24 (m, 20H, Ar), 6.62 (d, 1H, *J*=7.8 Hz, –N*H*), 5.76 (dd, 1H, *J*=2.7, 53.7 Hz, H-1a), 4.92 (d, 1H, *J*=11.0 Hz, –C*H*$_2$Ph), 4.80 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.68 (d, 1H, *J*=12.0 Hz, –C*H*$_2$Ph), 4.67 (d, 1H, *J*=11.0 Hz, –C*H*$_2$Ph), 4.59 (d, 1H, *J*=11.9 Hz, –C*H*$_2$Ph), 4.49 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.41 (d, 1H, *J*=12.0 Hz, –C*H*$_2$Ph), 4.34 (d, 1H, *J*=7.8 Hz, H-1b), 4.32 (d, 1H, *J*=12.0 Hz, –C*H*$_2$Ph), 4.17 (br t, 1H, *J*=9.5 Hz, H-4a), 4.11–4.05 (m, 2H, H-2a, H-4b), 4.00 (br t, 1H, *J*=6.2 Hz, H-3b), 3.94 (dd, 1H, *J*=2.9, 11.0 Hz, H-6b), 3.99 (m, 1H, H-5a), 3.75 (dd, 1H, *J*=9.0, 10.7 Hz, H-3a), 3.71–5.59 (m, 3H, H-6a, H-5b, H-6b), 3.52 (dd, 1H, *J*=6.4, 9.8 Hz, H-6a), 3.35 (dd, 1H, *J*=6.8,

8.0 Hz, H-2b), 1.40 (s, 3H, –C*H*$_3$), 1.34 (s, 3H, –C*H*$_3$). MALDI TOF MS: calcd for $C_{45}H_{49}Cl_3FNO_{10}$ (M+Na)$^+$ *m*/*z* 910.23. Found: 911.67. Anal. calcd for $C_{45}H_{49}Cl_3FNO_{10}$: C, 60.78; H, 5.55; N, 1.58; F, 2.14. Found: C, 60.87; H, 5.68; N, 1.53; F, 2.17.

4.1.13. tert-Butyldiphenylsilyl 2,6-di-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside ***23****.* A solution of **20** (365 mg, 0.32 mmol) in CH_2Cl_2 (10 ml) was stirred with 80% TFA aq (2 ml) at 0 °C for 1 h. The mixture was concentrated with toluene in vacuo to the residue, which was chromatographed on silica gel with toluene–EtOAc (7:3) to afford **23** (303 mg, 86%). $[\alpha]_D$ +7.4 (*c* 1). R_f 0.35 (7:3 toluene–EtOAc). ^{1}H NMR: δ 7.69 (br d, 2H, *J*=7.9 Hz, Ar), 7.63 (m, 2H, Ar), 7.39–7.13 (m, 26H, Ar), 6.89 (d, 1H, *J*=8.0 Hz, –N*H*), 4.94 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.91 (d, 1H, *J*=8.0 Hz, H-1a), 4.73 (d, 1H, *J*=11.5 Hz, –C*H*$_2$Ph), 4.60 (d, 1H, *J*=10.5 Hz, –C*H*$_2$Ph), 4.59 (d, 1H, *J*=11.5 Hz, –C*H*$_2$Ph), 4.45 (d, 1H, *J*=7.3 Hz, H-1b), 4.42 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.41 (d, 1H, *J*=11.9 Hz, –C*H*$_2$Ph), 4.36 (d, 1H, *J*=12.0 Hz, –C*H*$_2$Ph), 4.26 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.10 (br t, 1H, *J*=8.5 Hz, H-4a), 3.94 (br d, 1H, *J*=2.5 Hz, H-4b), 3.89 (br t, 1H, *J*=9.0 Hz, H-3a), 3.76 (dd, 1H, *J*=7.8, 9.5 Hz, H-2a), 3.65 (dd, 1H, *J*=3.2, 11.2 Hz, H-6a), 3.59 (dd, 1H, *J*=6.3, 10.0 Hz, H-6b), 3.37 (m, 3H, H-2b, H-5b, H-6b), 3.33 (dd, 1H, *J*=2.2, 11.2 Hz, H-6a), 3.06 (m, 1H, H-5a), 1.06 (s, 9H, ^{t}Bu). MALDI TOF MS: calcd for $C_{58}H_{64}Cl_3NO_{11}Si$ (M+Na)$^+$ *m*/*z* 1106.33. Found: 1106.18. Anal. calcd for $C_{58}H_{64}Cl_3NO_{11}Si$: C, 64.17; H, 5.94; N, 1.29; Cl, 9.80. Found: C, 63.87; H, 5.91; N, 1.28; Cl, 9.87.

4.1.14. tert-Butyldiphenylsilyl 2,6-di-O-benzyl-4-O-chloroacetyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside ***24****.* A mixture of **20** (332 mg, 0.31 mmol), triethyl orthochloroacetate (291 μl, 1.53 mmol), and a catalytic amount of *p*-TsOH·H$_2$O in CH_2Cl_2 (5 ml) was stirred at room temperature for 30 min. The reaction was quenched by adding satd $NaHCO_3$ aq and the mixture was extracted with $CHCl_3$. The extract was washed successively with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was dissolved in 80% AcOH aq (10 ml) and stirred at room temperature overnight before being concentrated in vacuo. The crude product was chromatographed on silica gel with toluene–EtOAc (4:1) to give **24** (348 mg, 99%). $[\alpha]_D$ −12.7 (*c* 1). R_f 0.39 (4:1 toluene–EtOAc). ^{1}H NMR: δ 7.70–7.13 (m, 30H, Ar), 6.89 (d, 1H, *J*=7.8 Hz, –N*H*), 5.40 (d, 1H, *J*=2.9 Hz, H-4b), 4.95 (d, 1H, *J*=7.8 Hz, H-1a), 4.92 (d, 1H, *J*=12.5 Hz, –C*H*$_2$Ph), 4.71 (d, 1H, *J*=11.5 Hz, –C*H*$_2$Ph), 4.57 (d, 2H, *J*=11.2 Hz, –C*H*$_2$Ph×2), 4.49 (d, 1H, *J*=7.8 Hz, H-1b), 4.45–4.42 (m, 2H, –C*H*$_2$Ph×2), 4.26 (d, 1H, *J*=12.0 Hz, –C*H*$_2$Ph), 4.25 (d, 1H, *J*=12.0 Hz, –C*H*$_2$Ph), 4.10 (br t, 1H, *J*=8.3 Hz, H-4a), 3.95–3.82 (m, 3H, H-3a, C*H*$_2$Cl), 3.68 (m, 1H, H-2a), 3.70–3.63 (m, 2H, H-6a, H-6b), 3.59–3.56 (m, 1H, H-3b), 3.35–3.26 (m, 4H, H-6a, H-2b, H-5b, H-6b), 3.05–3.08 (m, 1H, H-5a), 1.06 (s, 9H, ^{t}Bu). MALDI TOF MS: calcd for $C_{60}H_{65}Cl_4NO_{12}Si$ (M+Na)$^+$ *m*/*z* 1182.29. Found 1182.51. Anal. calcd for $C_{60}H_{65}Cl_4NO_{12}Si$: C, 62.01; H, 5.64; N, 1.21. Found: C, 61.67; H, 5.37; N, 1.21.

4.1.15. tert-Butyldiphenylsilyl 2,6-di-O-benzyl-3,4-O-isopropylidene-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside ***25****. Procedure A*: A mixture of **23** (107 mg, 0.10 mmol), Cp_2ZrCl_2 (69 mg, 0.23 mmol), $AgClO_4$ (98 mg, 0.47 mmol), and dried MS 4A (300 mg) in anhydrous CH_2Cl_2 (5 ml) was stirred at −15 °C under Ar for 30 min. Then, a solution of **22** (73 mg, 0.08 mmol) in anhydrous CH_2Cl_2 (3 ml) was added to the mixture. The mixture was stirred for 2 h, before the reaction was quenched with satd $NaHCO_3$ aq. The mixture was diluted with $CHCl_3$ and filtered through Celite. The filtrate was washed successively with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was chromatographed on silica gel with toluene–EtOAc (4:1) to give **27** (52 mg, 23%) and **25** (41 mg, 25%). Further chromatography of the less mobile fraction by preparative TLC gave isomer of **25** (5 mg. 3%). *Compound* **25**: $[\alpha]_D$ +6.1 (*c* 1). R_f 0.40 (4:1 toluene–EtOAc). ^{1}H NMR: δ 7.66 (br d, 2H, *J*=7.3 Hz, Ar), 7.62 (br d, 2H, *J*=7.3 Hz, Ar), 7.39–7.11 (m, 46H, Ar), 6.89 (d, 1H, *J*=8.0 Hz, –N*H*), 6.84 (d, 1H, *J*=7.6 Hz, –N*H*), 5.10 (d, 1H, *J*=7.4 Hz, H-1c), 4.90 (d, 1H, *J*=10.2 Hz, –C*H*$_2$Ph), 4.86 (d, 1H, *J*=7.4 Hz, H-1a), 4.79 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.69 (d, 1H, *J*=11.5 Hz, –C*H*$_2$Ph), 4.60 (br s, 2H, –C*H*$_2$Ph×2), 4.56–4.46 (m, 3H, –C*H*$_2$Ph×3), 4.43–4.36 (m, 4H, H-1b, H-1d, –C*H*$_2$Ph×2), 4.19 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 2.92 (br d, 1H, *J*=9.1 Hz, H-5a), 1.37 (s, 3H, –C*H*$_3$), 1.34 (s, 3H, –C*H*$_3$), 1.04 (s, 9H, ^{t}Bu). ^{13}C NMR: δ 92.1 and 92.4 (–*C*OCCl$_3$×2), 94.7 (C-1a), 99.0 (C-1c), 102.1 (C-1b, C-1d), 109.8 [(CH$_3$)$_2$*C*<]. MALDI TOF MS: calcd for $C_{103}H_{112}Cl_6N_2O_{21}Si$ (M+Na)$^+$ *m*/*z* 1973.57. Found 1973.54. Anal. calcd for $C_{103}H_{112}Cl_6N_2O_{21}Si$: C, 63.29; H, 5.77; N, 1.43. Found: C, 63.27; H, 5.76; N, 1.27. *Compound* **27**: R_f 0.55 (4:1 toluene–EtOAc). ^{1}H NMR: δ 5.24 (d, 1H, *J*=8.3 Hz, GlcNTCA H-1), 5.03 (d, 1H, *J*=7.8 Hz, GlcNTCA H-1), 4.81 (d, 1H, *J*=7.6 Hz, GlcNTCA H-1). ^{13}C NMR: δ 92.1, 92.6, and 92.9 (–*C*OCCl$_3$×2), 94.9 (C-1a), 100.1, and 100.2 (C-1c and C-1e), 102.0, 102.2, and 102.6 (C-1b, C-1d, and C-1f). MALDI TOF MS: calcd for $C_{148}H_{160}Cl_9N_3O_{31}Si$ (M+Na)$^+$ *m*/*z* 2840.79. Found 2840.35. Isomer of **25**: R_f 0.28 (4:1 toluene–EtOAc). ^{1}H NMR: δ 7.07 (d, 1H, *J*=7.8 Hz, –N*H*), 6.92 (d, 1H, *J*=7.8 Hz, –N*H*), 5.13 (d, 1H, *J*=7.8 Hz, H-1c), 4.92 (d, 1H, *J*=7.3 Hz, H-1a). MALDI TOF MS: Found 1974.56.

Procedure B: A mixture of **23** (211 mg, 0.20 mmol), Cp_2ZrCl_2 (76 mg, 0.26 mmol), $AgClO_4$ (108 mg, 0.52 mmol), and dried MS 4A (550 mg) in anhydrous CH_2Cl_2 (16 ml) was stirred at −5 °C under Ar for 30 min. To the mixture was added a solution of **22** (115 mg, 0.13 mmol) in anhydrous CH_2Cl_2 (6 ml) dropwise over a period of 1 h using a syringe pump. The mixture was allowed to stir for another 4 h, and worked up as mentioned above. Chromatography of the crude product on silica gel with toluene–EtOAc (4:1) afforded **27** (19 mg, 5%) and **25** (183 mg, 72%). From the less mobile fraction, the tetrasaccharide isomer (17 mg, 7%) was obtained.

4.1.16. tert-Butyldiphenylsilyl 2,6-di-O-benzyl-3,4-O-isopropylidene-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-4-O-chloroacetyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside ***26****. By chloroacetylation of* **25**: To a stirred solution of **25** (62 mg, 32 μmol) in a mixture of anhydrous CH_2Cl_2 (5 ml) and pyridine (3 ml) was added chloroacetyl chloride (35 μl, 0.42 mmol) at 0 °C. The mixture was stirred at 0 °C to room temperature for 6 h, before adding satd $NaHCO_3$ aq to quench the reaction. The mixture was extracted with $CHCl_3$. The extract was successively washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed on silica gel with toluene–EtOAc (4:1) to give **26** (59 mg, 91%). $[\alpha]_D$ −0.8 (*c* 1). R_f 0.20 (9:1 toluene–EtOAc). ^{1}H NMR: δ 7.66 (m, 4H, Ar), 7.63 (m, 2H, Ar), 7.38–7.10 (m, 46H, Ar), 6.88 (d, 1H, *J*=8.1 Hz, –N*H*), 6.67 (d, 1H, *J*=8.0 Hz, –N*H*), 5.48 (d, 1H, *J*=3.4 Hz, H-4b), 5.02 (d, 1H, *J*=7.3 Hz, H-1c), 4.87 (d, 1H, *J*=7.8 Hz, H-1a), 1.37 (s, 3H, –C*H*$_3$), 1.33 (s, 3H, –C*H*$_3$), 1.04 (s, 9H, ^{t}Bu). ^{13}C NMR: δ 92.3 and 92.5 (–*C*OCCl$_3$), 94.7 (C-1a), 99.1 (C-1c), 102.0, and 102.1 (C-1b and C-1d), 109.7 [(CH$_3$)$_2$*C*<]. MALDI TOF MS: calcd for $C_{105}H_{113}Cl_7N_2O_{22}Si$ (M+Na)$^+$ *m*/*z* 2049.52. Found 2050.30. Anal. calcd for $C_{105}H_{113}Cl_7N_2O_{22}Si$: C, 62.09; H, 5.61; N, 1.38. Found: C, 62.07; H, 5.61; N, 1.38.

By coupling of **22** and **24**: As described for **25** (*procedure A*), a solution of **22** (226 mg, 0.25 mmol) in anhydrous CH_2Cl_2 (4 ml)

was added to a stirred mixture of **24** (348 mg, 0.30 mmol), Cp_2ZrCl_2 (148 mg, 0.51 mmol), $AgClO_4$ (210 mg, 1.01 mmol), and dried MS 4A (500 mg) in anhydrous CH_2Cl_2 (4 ml) at −15 °C under Ar. The mixture was stirred at −15 °C for 1 h to complete the reaction, and worked up. Chromatography of the crude product on silica gel with toluene–EtOAc (9:1) gave **26** (435 mg, 85%).

4.1.17. 2,6-Di-O-benzyl-3,4-O-isopropylidene-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-4-O-chloroacetyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-(α)-D-glucopyranose ***28****.* To a stirred mixture of **26** (120 mg, 59 μmol) and AcOH (34 μl, 0.59 mmol) in freshly distilled THF (3 ml) was added 1 M TBAF/THF (236 μl, 0.24 mmol) under Ar. The mixture was stirred at room temperature for 30 h. THF was co-evaporated with toluene to the residue, which was extracted with EtOAc, washed successively with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was chromatographed on silica gel with toluene–EtOAc (1:1) to afford **28** as an α-isomer rich mixture (103 mg, 97%). R_f 0.48 (1:1 toluene–EtOAc). ^{1}H NMR: δ 7.51–7.04 (m, 40H, Ar), 6.81 (d, 1H, *J*=8.5 Hz, –N*H*), 6.70 (d, 1H, *J*=8.1 Hz, –N*H*), 5.48 (d, 1H, *J*=3.4 Hz, H-4b), 5.35 (d, *J*=3.7 Hz, H-1aα), 5.04 (d, 1H, *J*=7.1 Hz, H-1c), 1.38 (s, 3H, –C*H*$_3$), 1.34 (s, 3H, –C*H*$_3$). ^{13}C NMR: δ 90.7 (C-1a), 92.1, and 92.2 (–*C*OCCl$_3$), 99.0 (C-1c), 102.0, and 102.1 (C-1b and C-1d), 109.5 [(CH$_3$)$_2$*C*<]. MALDI TOF MS: calcd for $C_{89}H_{95}Cl_7N_2O_{22}$ $(M+Na)^+$ *m*/*z* 1811.40. Found 1811.23. Anal. calcd for $C_{89}H_{95}Cl_7N_2O_{22}\cdot 4H_2O$: C, 57.32; H, 5.57; N, 1.50. Found: C, 57.40; H, 5.47; N, 1.34.

4.1.18. 2,6-Di-O-benzyl-3,4-O-isopropylidene-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-4-O-chloroacetyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-(α)-D-glucopyranosyl fluoride ***5****.* To a stirred solution of **28** (119 mg, 0.07 mmol) was added DAST (17 μl, 0.13 mmol) at 0 °C. The mixture was stirred for 1 h before adding a few drops of CH_3OH to destroy excess reagent. The mixture was concentrated in vacuo to the residue, which was dissolved in $CHCl_3$. The extract was washed successively with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by gel-permeation chromatography on LH-60 with $CHCl_3$–CH_3OH (3:2) to give **5** as an α-isomer rich mixture (96 mg, 81%, α/β=10/1). R_f 0.62 (7:3 toluene–EtOAc). ^{1}H NMR: δ 7.66–7.04 (m, 40H, Ar), 6.75 (d, 1H, *J*=8.1 Hz, –N*H*), 6.60 (d, 1H, *J*=8.1 Hz, –N*H*), 5.72 (dd, 1H, *J*=2.0, 53.7 Hz, H-1a), 5.49 (d, 1H, *J*=2.7 Hz, H-4b), 5.05 (d, 1H, *J*=7.1 Hz, H-1c), 1.37 (s, 3H, –C*H*$_3$), 1.34(s, 3H, –C*H*$_3$). ^{13}C NMR: δ 91.8 and 92.0 (–*C*OCCl$_3$), 99.0 (C-1c), 101.8 and 102.0 (C-1b and C-1d) 105.3 (d, J_{CF}=221.7 Hz, C-1a), 109.5 [(CH$_3$)$_2$*C*<]. MALDI TOF MS: calcd for $C_{89}H_{94}Cl_7FN_2O_{21}$ $(M+Na)^+$ *m*/*z* 1813.40. Found 1814.48. Anal. calcd for $C_{89}H_{94}Cl_7FN_2O_{21}$: C, 59.56; H, 5.28; N, 1.56. Found: C, 59.62; H, 5.45; N, 1.51.

4.1.19. tert-Butyldiphenylsilyl 2,6-di-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-4-O-chloroacetyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside ***29****.* A solution of **26** (214 mg, 0.11 mmol) in CH_2Cl_2 (2 ml) was stirred with 80% TFA aq (4 ml) at 0 °C for 1 h. The mixture was neutralized with satd $NaHCO_3$ aq and extracted with $CHCl_3$. The extract was washed successively with satd $NaHCO_3$ aq, water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed on silica gel with toluene–EtOAc (2:1) to afford **29** (185 mg, 86%). $[\alpha]_D$ +3.8 (*c* 1). R_f 0.57 (1:1 toluene–EtOAc). ^{1}H NMR: δ 7.68–7.61 (m, 4H, Ar), 7.49–7.10 (m, 46H, Ar), 6.88 (d, 1H, *J*=8.1 Hz, –N*H*), 6.66 (d, 1H, *J*=8.1 Hz, –N*H*), 5.50 (d, 1H, *J*=3.7 Hz, H-4b), 5.02 (d, 1H, *J*=7.3 Hz, H-1a), 4.87 (d, 1H, *J*=7.6 Hz, H-1c), 1.05 (s, 9H, ^{t}Bu). ^{13}C NMR: δ 92.1 and 92.3 (–*C*OCCl$_3$), 94.5 (C-1a), 98.8 (C-1c), 101.8 and 102.5 (C-1b and C-1d). MALDI TOF MS: calcd for $C_{102}H_{109}Cl_7N_2O_{22}Si$ $(M+Na)^+$ *m*/*z* 2009.49. Found 2010.04. Anal. calcd for $C_{102}H_{109}Cl_7N_2O_{22}Si$: C, 61.52; H, 5.52; N, 1.41. Found: C, 61.25; H, 5.47; N, 1.37.

4.1.20. tert-Butyldiphenylsilyl 2,6-di-O-benzyl-4-O-chloroacetyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-4-O-chloroacetyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside ***6****.* As described for **24**, compound **29** (85 mg, 42 μmol) was converted to a 3,4-*O*-cyclic orthoester by transesterification with triethyl orthochloroacetate (40 μl, 212 μmol) and *p*-TsOH·H$_2$O (cat.) in CH_2Cl_2 (5 ml). The orthoester was treated with 80% AcOH aq (5 ml) overnight. The product was purified by chromatography on silica gel with toluene–EtOAc (4:1) to give **6** (67 mg, 76%). $[\alpha]_D$ −0.5 (*c* 1). R_f 0.34 (4:1 toluene–EtOAc). ^{1}H NMR: δ 7.68–7.61 (m, 4H, Ar), 7.38–7.11 (m, 46H, Ar), 6.92 (d, 1H, *J*=7.8 Hz, –N*H*), 6.72 (d, 1H, *J*=8.1 Hz, –N*H*), 5.49 (d, 1H, *J*=3.1 Hz), and 5.39 (d, 1H, *J*=2.9 Hz) (H-4b and H-4d), 5.06 (d, 1H, *J*=7.4 Hz, H-1c), 1.08 (s, 9H, ^{t}Bu). ^{13}C NMR: δ 92.1 and 92.3 (–*C*OCCl$_3$), 94.5 (C-1a), 98.7 (C-1c), 101.9 and 102.3 (C-1b and C-1d). MALDI TOF MS: calcd for $C_{104}H_{110}Cl_8N_2O_{23}Si$ $(M+Na)^+$ *m*/*z* 2085.47. Found 2086.28. Anal. calcd for $C_{104}H_{110}Cl_8N_2O_{23}Si$: C, 60.41; H, 5.36; N, 1.35. Found: C, 61.13; H, 5.36; N, 1.35.

4.1.21. tert-Butyldiphenylsilyl 2,6-di-O-benzyl-3,4-O-isopropylidene-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-4-O-chloroacetyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-4-O-chloroacetyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-4-O-chloroacetyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside ***30****.* Coupling reaction of **6** (96 mg, 47 μmol) and **5** (77 mg, 43 μmol) was promoted using Cp_2ZrCl_2 (25 mg, 86 μmol), $AgClO_4$ (36 mg, 172 μmol) and MS 4A (300 mg) in anhydrous CH_2Cl_2 (6 ml) at −15 °C as describe above for **25** (*procedure A*). The mixture was stirred for 4 h and worked up. The product was chromatographed using a column of LH-60 with $CHCl_3$–CH_3OH (3:2) to give **30** (120 mg, 73%). $[\alpha]_D$ −3.4 (*c* 1). R_f 0.72 (7:3 toluene–EtOAc). ^{1}H NMR: δ 7.67–7.61 (m, 4H, Ar), 7.40–7.09 (m, 86H, Ar), 6.87 (d, 1H, *J*=8.1 Hz, –N*H*), 6.69–6.63 (m, 3H, -N*H*×3), 5.51–5.46 (m, 3H, H-4b, H-4d, and H-4f), 5.05–4.98 (m, 3H, H-1c, H-1e, H-1 g), 4.87 (d, 1H, *J*=7.6 Hz, H-1a), 1.38 (s, 3H, –C*H*$_3$), 1.34 (s, 3H, –C*H*$_3$), 1.05 (s, 9H, ^{t}Bu). ^{13}C NMR: δ 92.0, 92.1, and 92.3 (–*C*OCCl$_3$), 94.5 ($^1J_{CH}$=168.2 Hz, C-1a), 98.8 and 99.0 ($^1J_{CH}$=165.9 Hz, C-1c, C-1e and C-1 g), 101.8, 101.9, 102.0, and 102.1 ($^1J_{CH}$=163.4 Hz, C-1b, C-1d, C-1f, C-1 h), 109.5 [(CH$_3$)$_2$*C*<]. MALDI TOF MS: calcd for $C_{193}H_{203}Cl_{15}N_4O_{44}Si$ [average, $(M+Na)^+$] *m*/*z* 3865.87. Found 3865.57. Anal. calcd for $C_{193}H_{203}Cl_{15}N_4O_{44}Si$: C, 60.33; H, 5.32; N, 1.46. Found: C, 60.18; H, 5.35; N, 1.41.

4.1.22. 2,6-Di-O-benzyl-3,4-O-isopropylidene-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-4-O-chloroacetyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-4-O-chloroacetyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-4-O-chloroacetyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-(α)-D-glucopyranose ***31****.* Desilylation of octasaccharide **30** (162 mg, 42 μmol) was performed for three days in a similar manner described for **24**. The crude product was purified through a column of LH-20 with $CHCl_3$–CH_3OH (3:2) to give **31**

(134 mg, 89%). R_f 0.27 (4:1 toluene–EtOAc). ^{1}H NMR: δ 7.49–7.11 (m, 80H, Ar), 6.81 (d, 1H, J=8.5 Hz, –N*H*), 6.69–6.65 (m, 3H, -N*H*×3), 5.51 (d, 1H, J=3.4 Hz), 5.49 (d, 1H, J=3.2 Hz), and 5.45 (d, 1H, J=3.1 Hz) (H-4b, H-4d, and H-4f), 5.33 (d, 1H, J=2.9 Hz, H-1a), 5.04 (d, 1H, J=7.1 Hz), 5.01 (d, 1H, J=7.1 Hz), and 4.99 (d, 1H, J=6.8 Hz) (H-1c, H-1e, H-1g), 1.37 (s, 3H, –C*H*$_3$), 1.34 (s, 3H, –C*H*$_3$). ^{13}C NMR: δ 90.6 (C-1a), 92.1, and 92.3 (–*C*OCCl$_3$), 98.9, and 99.0 (C-1c, C-1e, and C-1), 101.9 and 102.1 (C-1b, C-1d, C-1f, and C-1h), 109.5 [(CH$_3$)$_2$*C*<]. MALDI TOF MS: calcd for $C_{177}H_{185}Cl_{15}N_4O_{44}$ [average, (M+Na)$^+$] m/z 3627.14. Found 3626.94. Anal. calcd for $C_{177}H_{185}Cl_{15}N_4O_{44}$: C, 58.98; H, 5.17; N, 1.55. Found: C, 59.03; H, 5.35; N, 1.47.

*4.1.23. 2,6-Di-O-benzyl-3,4-O-isopropylidene-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-4-O-chloroacetyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-4-O-chloroacetyl–β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-4-O-chloroacetyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-(α)-D-glucopyranosyl fluoride **3**.* Compound **31** (92 mg, 0.03 mmol) was fluorinated with DAST in THF and purified by gel-permeation chromatography as described for **5** to afford **3** as a mixture of α and β anomers (88 mg, 94%, α/β=5). R_f 0.66 (7:3 toluene–EtOAc). ^{1}H NMR: δ 7.37–7.18 (m, 80H, Ar), 6.77–6.66 (m, 3H, –N*H*×3), 5.71 (dd, 1H, J=2.9, 55.9 Hz, H-1aα), 5.51 (d, 1H, J=3.4 Hz), 5.49 (d, 1H, J=3.4 Hz), and 5.48 (d, 1H, J=3.4 Hz) (H-4b, H-4d, and H-4f), 5.04 (d, 1H, J=7.0 Hz), and 5.01 (d, 2H, J=7.2 Hz) (H-1c, H-1e, and H-1g), 1.38 (s, 3H, –C*H*$_3$), 1.34 (s, 3H, –C*H*$_3$). ^{13}C NMR: δ 92.0 and 92.3 (–*C*OCCl$_3$), 99.0, 99.1, and 99.2 (C-1c, C-1e, and C-1g), 102.0, 102.1, and 102.3 (C-1b, C-1d, C-1f, and C-1h), 105.2 ($^1J_{CF}$=221.0 Hz, C-1a), 109.7 [(CH$_3$)$_2$*C*<]. MALDI TOF MS: calcd for $C_{177}H_{184}Cl_{15}FN_4O_{43}$ [average, (M+Na)$^+$] m/z 3629.13. Found 3629.19. Anal. calcd for $C_{177}H_{184}Cl_{15}FN_4O_{43}$: C, 58.95; H, 5.14; N, 1.55. Found: C, 59.07; H, 5.31; N, 1.53.

*4.1.24. N-(9-Fluorenylmethoxycarbonyl)-O-{2,6-di-O-benzyl-3,4-O-isopropylidene-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-4-O-chloroacetyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deox-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-4-O-chloroacetyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-4-O-chloroacetyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→6)-[2,3,4,6-tetra-O-benzyl-β-D-galactopyranosyl-(1→3)]-2-azido-2-deoxy-α-D-galactopyranosyl}-L-threonine allyl ester **32**.* Coupling reaction of **3** (84 mg, 23 μmol) and **4** (31 mg, 28 μmol) was promoted using Cp$_2$ZrCl$_2$ (13 mg, 46 μmol), AgClO$_4$ (19 mg, 92 μmol) and MS 4A (500 mg) in anhydrous CH$_2$Cl$_2$ (3.5 ml) at −15 °C as describe above for **25** (*procedure A*). The mixture was stirred for 5 h before adding satd NaHCO$_3$ aq to quench the reaction, and worked up. The product was chromatographed using a column of LH-60 with CHCl$_3$–CH$_3$OH (3:2) to give **32** (92 mg, 86%). [α]$_D$ +11.9 (*c* 1). R_f 0.63 (7:3 toluene–EtOAc). ^{1}H NMR: δ 7.74 (br d, 2H, J=7.6 Hz, Ar), 7.58 (m, 2H, Ar), 7.41–7.20 (m, 104H, Ar), 6.95 (d, 1H, J=7.0 Hz, TCAN*H*), 6.68–6.65 (m, 3H, TCAN*H*×3), 5.91 (m, 1H, –C*H*=CH$_2$), 5.65 (d, 1H, J=9.3 Hz, FmocN*H*), 5.50–5.47 (m, 3H, H-4c, H-4e, H-4 g), 5.33 (br d, 1H, J=17.3 Hz, –CH$_2$=C*H*$_2$), 5.22 (br d, 1H, J=10.3 Hz, –CH$_2$=C*H*$_2$), 5.05–4.99 (m, 4H, H-1d, H-1f, H-1 h, –C*H*$_2$Ph), 4.96 (d, 1H, J=2.9 Hz, H-1a), 1.38 (s, 3H, –C*H*$_3$), 1.34 (s, 3H, –C*H*$_3$), 1.31 (d, 3H, J=5.9 Hz, Thr-γH). ^{13}C NMR: δ 92.1 and 92.3 (–*C*OCCl$_3$), 98.8 and 99.0 (C-1d, C-1f, and C-1h), 99.4 (C-1a), 99.5 (C-1b), 102.0, and 102.1 (C-1c, C-1e, C-1g, and C-1i), 103.7 (C-1j), 109.5 [(CH$_3$)$_2$*C*<]. MALDI TOF MS: calcd for $C_{239}H_{249}Cl_{15}N_8O_{57}$ [average, (M+Na)$^+$] m/z 4700.33. Found 4700.31. Anal. calcd for $C_{239}H_{249}Cl_{15}N_8O_{57}$: C, 61.37; H, 5.37; N, 2.40. Found: C, 61.39; H, 5.37; N, 2.24.

*4.1.25. N-(9-Fluorenylmethoxycarbonyl)-O-{2,6-di-O-benzyl-3,4-O-isopropylidene-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→6)-[2,3,4,6-tetra-O-benzyl-β-D-galactopyranosyl-(1→3)]-2-azido-2-deoxy-α-D-galactopyranosyl}-L-threonine allyl ester **33**.* A mixture of **32** (68 mg, 15 μmol) and thiourea (17 mg, 218 μmol) in anhydrous DMF (3 ml) was heated with stirring under Ar at 70 °C overnight. The mixture was concentrated in vacuo to remove most DMF, and the residue was dissolved in ether–EtOAc (1:1). The extract was washed successively with water and brine, dried over Na$_2$SO$_4$, and concentrated in vacuo. The residue was chromatographed on silica gel with toluene–EtOAc (7:3) to give **33** (25 mg, 36%). [α]$_D$ +19.1 (*c* 0.9). R_f 0.37 (7:3 toluene–EtOAc). ^{1}H NMR: δ 7.74 (d, 2H, J=7.3 Hz, Ar), 7.59 (m, 2H, Ar), 7.40–7.22 (m, 104H, Ar), 6.98 (d, 1H, J=6.8 Hz, TCAN*H*), 6.94–6.89 (m, 3H, TCAN*H*×3), 5.91 (m, 1H, –C*H*=CH$_2$), 5.66 (d, 1H, J=10.0 Hz, FmocN*H*), 5.33 (d, 1H, J=17.1 Hz, –CH=C*H*$_2$), 5.22 (d, 1H, J=10.3 Hz, –CH=C*H*$_2$), 5.13 (d, 1H, J=7.1 Hz), 5.09 (d, 1H, J=7.3 Hz) and 5.07 (d, 1H, J=7.3 Hz) (H-1d, H-1f, and H-1h), 4.94 (d, 1H, J=3.7 Hz, H-1a), 1.38 (s, 3H, –C*H*$_3$), 1.35 (s, 3H, –C*H*$_3$), 1.30 (d, 3H, J=6.3 Hz, Thr-γH). ^{13}C NMR: δ 92.0 (–*C*OCCl$_3$), 98.7, and 98.8 (C-1d, C-1f, and C-1h), 99.5 (C-1a), 99.6 (C-1b), 102.2, 102.4, and 102.6 (C-1c, C-1e, C-1g, and C-1i), 103.7 (C-1j), 109.7 [(CH$_3$)$_2$*C*<]. MALDI TOF MS: calcd for $C_{233}H_{246}Cl_{12}N_8O_{54}$ [average, (M+Na)$^+$] m/z 4448.90. Found 4449.30. Anal. calcd for $C_{233}H_{246}Cl_{12}N_8O_{54}$: C, 62.92; H, 5.57; N, 2.52. Found: C, 62.81; H, 5.68; N, 2.24.

*4.1.26. N-(9-Fluorenylmethoxycarbonyl)-O-{2,6-di-O-benzyl-3,4-O-isopropylidene-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranosyl-(1→6)-[2,3,4,6-tetra-O-benzyl-β-D-galactopyranosyl-(1→3)]-2-acetamido-2-deoxy-α-D-galactopyranosyl}-L-threonine allyl ester **34**.* A mixture of **33** (17 mg, 3.9 μmol), powdered Zn (76 mg, 1.2 mmol), and AcOH (77 μl, 1.4 mmol) in EtOAc (1 ml) was placed in a round-bottom flask equipped with a reflux condenser. The atmosphere was replaced with a balloon of Ar. The reaction mixture was stirred under microwave irradiation at 150 W for 1 h. The microwave machine was controlled so as to continuously irradiate the flask during this period. The mixture was diluted with EtOAc, filtered through Celite, and the filtrate was concentrated in vacuo. The residue was dissolved in EtOAc, successively washed with satd NaHCO$_3$ aq, water, and brine, dried over Na$_2$SO$_4$, and concentrated in vacuo. The residue was dissolved in a mixture of CH$_2$Cl$_2$ (0.4 ml) and MeOH (0.1 ml), and stirred with Ac$_2$O (40 μl) at room temperature for 2 h. The mixture was concentrated in vacuo to the residue, which was chromatographed on Bio-beads *S*-X1 with toluene–EtOAc (1:1) and then by recycled HPLC [JAIGEL-2H with CHCl$_3$] to afford **34** (13.5 mg, 86%). [α]$_D$ +24.0 (*c* 0.7). R_f 0.21 (1:9 toluene–EtOAc). ^{1}H NMR: δ 7.75 (d, 2H, J=7.4 Hz, Ar), 7.61 (br d, 2H, J=7.3 Hz, Ar), 7.40–7.21 (m, 104H, Ar), 5.82 (m, 1H, –C*H*=CH$_2$), 5.71 (d, 1H, J=9.3 Hz, –N*H*), 5.66 (d, 1H, J=9.3 Hz, –N*H*), 5.61 (d, 1H,

J=8.3 Hz, –N*H*), 5.30 (d, 1H, *J*=17.6 Hz, –CH=C*H*$_2$), 1.81, 1.66, 1.47, and 1.25 (br s, 15H, –COC*H*$_3$×5), 1.39 (s, 3H, –C*H*$_3$), 1.34 (s, 3H, –C*H*$_3$), 1.14 (br s, 3H, Thr-γH). MALDI TOF MS: calcd for $C_{235}H_{262}N_6O_{55}$ [average, $(M+Na)^+$ and $(M+K)^+$] *m*/*z* 4073.59 and 4089.70. Found 4071.66 and 4087.46.

*4.1.27. N-(9-Fluorenylmethoxycarbonyl)-O-{2,6-di-O-benzyl-3,4-O-isopropylidene-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2,6-di-O-benzyl-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranosyl-(1→6)-[2,3,4,6-tetra-O-benzyl-β-D-galactopyranosyl-(1→3)]-2-acetamido-2-deoxy-α-D-galactopyranosyl}-L-threonine **2***. A mixture of **34** (13 mg, 3.2 μmol), $Pd(PPh_3)_4$ (1 mg, 0.8 μmol), and dimedone (5,5-dimethyl-1,3-cyclohexanedione, 9 mg, 0.06 mmol) in anhydrous THF (2 ml) was stirred at room temperature under Ar for 30 min, and the concentrated in vacuo. The residue was subjected to gel-permeation chromatography on LH-20 with $CHCl_3$–CH_3OH (3:2) to afford **2** quantitatively. $[\alpha]_D$ +28.0 (*c* 0.3). R_f 0.48 (90:10:1 $CHCl_3$–CH_3OH–AcOH). ^{1}H NMR: δ 1.47, 1.38, 1.34, and 1.25 (br s, 21H, –COC*H*$_3$×5, –C*H*$_3$×2), 0.85 (d, 3H, *J*=6.3 Hz, Thr-γH). MALDI TOF MS: calcd for $C_{232}H_{258}N_6O_{55}$ [average, $(M+Na)^+$ and $(M+K)^+$] *m*/*z* 4033.53 and 4049.63. Found 4031.95 and 4046.96.

*4.1.28. 3-O-Allyl-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-D-glucopyranose **36***. Compound **35** (92.7 mg, 76 μmol) was desilylated with 1 M TBAF/THF (0.31 ml, 0.31 mmol) and AcOH (44 μl, 0.76 mmol) in freshly distilled THF (1 ml) as described for **21**. The crude product was chromatographed on silica gel with toluene–EtOAc (7:1–4:1) to afford **36** (73.9 mg, 99%). Mp 125.5–127.0 °C (recrystallized from hexane–EtOAc). R_f 0.42 (4:1 toluene–EtOAc). ^{1}H NMR: δ 7.34–7.12 (m, 25H, Ar), 6.84 (d, 1H, *J*=8.3 Hz, –N*H*), 5.93 (m, 1H, –C*H*=CH$_2$), 5.38 (br t, 1H, *J*=3.7 Hz, H-1a), 5.32 (dd, 1H, *J*=1.5, 17.1 Hz, –CH=C*H*$_2$), 5.18 (dd, 1H, *J*=1.5, 10.2 Hz, –CH=C*H*$_2$), 5.02 (d, 1H, *J*=10.7 Hz, –C*H*$_2$Ph), 4.94 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.82 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.76 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.60 (d, 1H, *J*=10.7 Hz, –C*H*$_2$Ph), 4.52 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.51 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.34 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.34 (d, 1H, *J*=7.8 Hz, H-1b), 4.30 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.20 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.16 (dd, 2H, *J*=1.5, 5.4 Hz, –C*H*$_2$CH=CH$_2$), 4.12 (m, 1H, H-2a), 4.03–3.94 (m, 2H, H-5a, H-4a), 3.84 (br d, 1H, *J*=2.9 Hz, H-4b), 3.81 (m, 1H, H-6a), 3.79 (dd, 1H, *J*=7.8, 10.2 Hz, H-3a), 3.71 (dd, 1H, *J*=7.8, 9.3 Hz, H-2b), 3.60 (br d, 1H, *J*=10.2 Hz, H-6a), 3.43 (br t, 1H, *J*=8.0 Hz, H-6b), 3.37–3.25 (m, 3H, H-5b, H-6b, H-3b), 2.95 (dd, 1H, *J*=1.5, 3.4 Hz, –O*H*). ^{13}C NMR: δ 161.7 (Cl_3CCONH), 134.9 (–C*H*=CH$_2$), 116.4 (–CH=C*H*$_2$), 103.0 (C-1b), 92.5 (C-1a), 90.8 (-CCl_3), 82.2 (C-3b), 79.8 (C-2b), 77.3 (C-3a), 77.0 (C-4a), 75.3 (–C*H*$_2$Ph), 74.5 (–C*H*$_2$Ph), 74.5 (–C*H*$_2$Ph), 73.5 (C-4b), 73.4 (–C*H*$_2$Ph), 73.1 (–C*H*$_2$Ph), 73.1 (C-5b), 71.5 (–C*H*$_2$CH=CH$_2$), 70.9 (C-5a), 68.1 (C-6b), 68.1 (C-6a), 54.6 (C-2a). MALDI TOF MS: calcd for $C_{52}H_{56}NO_{11}Cl_3$ $(M+Na)^+$, *m*/*z* 998.28. Found: 998.17. Anal. calcd for $C_{52}H_{56}NO_{11}Cl_3$: C, 63.90; H, 5.78; N, 1.43. Found: C, 63.90; H, 5.80; N, 1.44.

*4.1.29. 3-O-Allyl-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-D-glucopyranosyl fluoride **37***. Compound **36** (91.3 mg, 93 μmol) was fluorinated with DAST (25 μl, 0.19 mmol) in THF (2 ml) as described for **22**. The crude product was chromatographed on silica gel with hexane–EtOAc (7:1) to give **37** as a mixture of anomers (88.1 mg, 97%, α/β=>9). R_f 0.46 (2:1 hexane–EtOAc). ^{1}H NMR: δ 7.34–7.14 (m, 25H, Ar), 6.66 (d, 1H, *J*=7.8 Hz, –N*H*), 5.94 (m, 1H, –C*H*=CH$_2$), 5.75 (dd, 1H, *J*=2.4, 53.7 Hz, H-1a), 5.34 (dd, 1H, *J*=1.0, 17.2 Hz, –CH=C*H*$_2$), 5.19 (dd, 1H, *J*=1.0, 10.7 Hz, –CH=C*H*$_2$), 5.04 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.95 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.82 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.72 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.64 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.55 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.53 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.38 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.37 (d, 1H, *J*=7.8 Hz, H-1b), 4.33 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.24 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.18–4.07 (m, 4H, –C*H*$_2$CH=CH$_2$, H-4a, H-2a), 3.91 (dd, 1H, *J*=2.4, 10.7 Hz, H-6a), 3.86 (br d, 1H, *J*=2.4 Hz, H-4b), 3.84 (m, 1H, H-5a), 3.73 (br t, 1H, *J*=9.8 Hz, H-3a), 3.72 (dd, 1H, *J*=7.8, 9.3 Hz, H-2b), 3.57 (br d, 1H, *J*=10.2 Hz, H-6a), 3.47 (br t, 1H, *J*=6.6 Hz, H-6b), 3.39–3.32 (m, 2H, H-5b, H-6b), 3.28 (dd, 1H, *J*=2.4, 9.3 Hz, H-3b). ^{13}C NMR: δ 161.9 (Cl_3CCONH), 134.9 (–C*H*=CH$_2$), 116.5 (–CH=C*H*$_2$), 105.5 (d, $^1J_{CF}$=222.7 Hz, C-1a, α-F), 102.7 (C-1b), 92.1 (–CCl_3), 82.2 (C-3b), 79.7 (C-2b), 76.4 (C-3a), 75.5 (C-4a), 75.4 (–CH_2Ph), 74.6 (–C*H*$_2$Ph), 74.5 (–C*H*$_2$Ph), 73.4 (C-4b), 73.4 (C-5a), 73.4 (–C*H*$_2$Ph), 73.1 (–C*H*$_2$Ph), 73.1 (C-5b), 71.4 (–C*H*$_2$CH=CH$_2$), 68.1 (C-6b), 66.9 (C-6a), 54.5 (d, $^2J_{CF}$=24.8 Hz, C-2a). MALDI TOF MS: calcd for $C_{52}H_{55}NO_{10}Cl_3F$ $(M+Na)^+$ *m*/*z* 1000.28. Found: 1000.25. Anal. calcd for $C_{52}H_{55}NO_{10}Cl_3F$: C, 63.77; H, 5.66; N, 1.43. Found: C, 63.81; H, 5.72; N, 1.49.

*4.1.30. 3-O-Allyl-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-D-glucopyranosyl (N-phenyl)-2,2,2-trifluoroacetimidate **38***. A suspension of **36** (108.3 mg, 0.11 mmol), (*N*-Phenyl)-2,2,2-trifluoroacetimidoyl chloride (46 mg, 0.22 mmol), and K_2CO_3 (30.6 mg, 0.22 mmol) in acetone (2 ml) was stirred at room temperature for 3 h. The reaction mixture was filtrated and concentrated in vacuo. The crude product was chromatographed on silica gel with toluene–EtOAc (19:1) to afford **38** (119.2 mg, 94%). R_f 0.51 (7:1 toluene–EtOAc). ^{1}H NMR: δ 7.36–7.16 (m, 27H, Ar), 7.08 (br t, 1H, *J*=7.6 Hz, =N*Ph*), 6.76 (d, 2H, *J*=7.8 Hz, =N*Ph*), 6.61 (d, 1H, *J*=7.3 Hz, –N*H*), 6.45 (br s, 1H, H-1a), 5.94 (m, 1H, –C*H*=CH$_2$), 5.34 (dd, 1H, *J*=1.5, 17.1 Hz, –CH=C*H*$_2$), 5.19 (dd, 1H, *J*=1.5, 10.7 Hz, –CH=C*H*$_2$), 5.00 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.95 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.84 (d, 1H, *J*=10.7 Hz, –C*H*$_2$Ph), 4.74 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.64 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.53 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.53 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.39 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.38 (d, 1H, *J*=7.8 Hz, H-1b), 4.34 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.26 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.22–4.16 (m, 3H, H-2a, –C*H*$_2$CH=CH$_2$), 4.12 (br t, 1H, *J*=9.0 Hz, H-4a), 3.87 (dd, 1H, *J*=3.4, 10.7 Hz, H-6a), 3.86 (br d, 1H, *J*=2.9 Hz, H-4b), 3.83–3.77 (m, 2H, H-3a, H-5a), 3.73 (dd, 1H, *J*=7.8, 9.8 Hz, H-2b), 3.56 (br d, 1H, *J*=10.7 Hz, H-6a), 3.48 (br t, 1H, *J*=6.0 Hz, H-6b), 3.40–3.34 (m, 2H, H-5b, H-6b), 3.30 (dd, 1H, *J*=2.9, 9.8 Hz, H-3b). ^{13}C NMR: δ 161.8 (Cl_3CCONH), 143.0 (>*C*=NPh), 134.9 (–C*H*=CH$_2$), 124.6 (=N*Ph*), 119.3 (=N*Ph*), 116.5 (–CH=C*H*$_2$), 102.8 (C-1b), 92.1 (–CCl_3), 82.3 (C-3b), 79.7 (C-2b), 76.4 (C-3a), 75.6 (C-4a), 75.4 (–CH_2Ph), 74.5 (–C*H*$_2$Ph), 74.4 (–C*H*$_2$Ph), 73.9 (C-5a), 73.4 (–C*H*$_2$Ph), 73.4 (C-4b), 73.2 (–C*H*$_2$Ph), 73.2 (C-5b), 71.5 (–C*H*$_2$CH=CH$_2$), 68.2 (C-6b), 67.2 (C-6a), 53.6 (C-2a). Anal. calcd for $C_{60}H_{60}N_2O_{11}Cl_3F_3$: C, 62.75; H, 5.27; N, 2.44. Found: C, 62.80; H, 5.33; N, 2.36.

*4.1.31. tert-Butyldiphenylsilyl 2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside **39***. A mixture of $Ir(COD)(PMe_2Ph)_2PF_6$ (5 mg, 6 μmol) in freshly distilled THF (5 ml) was stirred at room temperature for 15 min under H_2, and the atmosphere was replaced by Ar. To the mixture of activated Ir complex in THF was added a solution of **35** (250 mg, 0.21 mmol) in THF (5 ml) under Ar. The mixture was stirred for 30 min before adding water (2 ml) and iodine (104 mg, 0.41 mmol), and stirred for 10 min. The reaction mixture was diluted EtOAc, successively washed with satd $Na_2S_2O_3$ aq, water, and brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was

chromatographed on silica gel with toluene–EtOAc (19:1–9:1) to afford **39** (240 mg, 99%).

Mp 100.0–101.0 °C (recrystallized from hexane–EtOAc). $[\alpha]_D$ −4.5 (*c* 1). R_f 0.34 (9:1 toluene–EtOAc). ^{1}H NMR: δ 7.69 (d, 1H, *J*=6.8 Hz, Ar), 7.69 (d, 1H, *J*=7.8 Hz, Ar), 7.64 (d, 1H, *J*=6.8 Hz, Ar), 7.64 (d, 1H, *J*=8.3 Hz, Ar), 7.40–7.13 (m, 31H, Ar), 6.90 (d, 1H, *J*=7.8 Hz, –N*H*), 4.95 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.93 (d, 1H, *J*=7.8 Hz, H-1a), 4.75 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.72 (d, 1H, *J*=10.2 Hz, –C*H*$_2$Ph), 4.60 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.57 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.57 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.56 (d, 1H, *J*=10.2 Hz, –C*H*$_2$Ph), 4.44 (d, 1H, *J*=7.8 Hz, H-1b), 4.40 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.37 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.37 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.26 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.26 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.07 (br t, 1H, *J*=8.5 Hz, H-4a), 3.89 (br t, 1H, *J*=9.0 Hz, H-3a), 3.83 (d, 1H, *J*=3.4 Hz, H-4b), 3.75 (dd, 1H, *J*=7.8, 9.8 Hz, H-2a), 3.63 (dd, 1H, *J*=2.9, 10.7 Hz, H-6a), 3.57–3.43 (m, 4H, H-5b, H-6b, H-2b, H-3b), 3.36 (dd, 1H, *J*=3.9, 8.3 Hz, H-6b), 3.34 (dd, 1H, *J*=2.4, 10.7 Hz, H-6a), 3.08 (br d, 1H, *J*=8.8 Hz, H-5a), 2.17 (d, 1H, *J*=8.8 Hz, –O*H*), 1.06 (s, 9H, ^{t}Bu). ^{13}C NMR: δ 161.5 (Cl_3CCONH), 102.7 (C-1b), 94.8 (C-1a), 92.6 (-*C*Cl$_3$), 80.4 (C-3b), 77.7 (C-3a), 76.1 (C-4a), 75.8 (C-4b), 75.2 (C-5a), 75.0 (–*C*H$_2$Ph), 74.9 (–*C*H$_2$Ph), 74.0 (C-5b), 73.9 (–*C*H$_2$Ph), 73.3 (C-2b), 73.3 (–*C*H$_2$Ph), 73.2 (–*C*H$_2$Ph), 68.0 (C-6b), 67.6 (C-6a), 59.4 (C-2a), 26.8 [–C(*C*H$_3$)$_3$], 19.1 [–*C*(CH$_3$)$_3$]. MALDI TOF MS: calcd for $C_{65}H_{70}NO_{11}Cl_3Si$ $(M+Na)^+$ *m*/*z* 1196.37. Found: 1196.55. Anal. calcd for $C_{65}H_{70}NO_{11}Cl_3Si$: C, 66.40; H, 6.00; N, 1.19. Found: C, 66.16; H, 6.00; N, 1.19.

4.1.32. tert-Butyldiphenylsilyl 3-O-allyl-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside ***40****. Procedure A* (*glycosylation of* **39** with **37**). A mixture of Cp_2ZrCl_2 (12 mg, 42 μmol), $AgClO_4$ (17 mg, 84 μmol), and dried MS 4A powder (70 mg) in anhydrous CH_2Cl_2 (1 ml) was stirred at room temperature under Ar for 30 min and then cooled at −40 °C. To the stirred mixture was added a mixture of **37** (41 mg, 42 μmol) and **39** (41 mg, 42 μmol) in anhydrous CH_2Cl_2 (1 ml). Then the temperature was raised to −15 °C during the period of 30 min and stirring was continued for further 2.5 h, before the reaction was quenched with aq $NaHCO_3$. The mixture was diluted with EtOAc and filtered through Celite. The filtrate was successively washed with satd $NaHCO_3$ aq, water, and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by preparative TLC, which was eluted twice with toluene–EtOAc (19:1) to give **40** (22 mg, 29%). Hexasaccharide **43** (8 mg, 16%) and fully protected disaccharide **35** (5 mg, 9%) were obtained from the more polar band and the less polar band, respectively. *Compound* **40**: $[\alpha]_D$ −14.0 (*c* 1). R_f 0.41 (9:1 toluene–EtOAc). ^{1}H NMR: δ 7.66 (d, 2H, *J*=6.8 Hz, Ar), 7.62 (d, 2H, *J*=6.8 Hz, Ar), 7.45–7.08 (m, 56H, Ar), 6.88 (d, 1H, *J*=7.3 Hz, –N*H*), 6.63 (d, 1H, *J*=7.8 Hz, –N*H*), 5.93 (m, 1H, –C*H*=CH$_2$), 5.33 (dd, 1H, *J*=1.5, 17.1 Hz, –CH=C*H*$_2$), 5.18 (dd, 1H, *J*=1.5, 10.7 Hz, –CH=C*H*$_2$), 5.08 (d, 1H, *J*=7.3 Hz, H-1c), 4.96 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.94 (d, 2H, *J*=9.8 Hz, –C*H*$_2$Ph×2), 4.88 (d, 1H, *J*=10.2 Hz, –C*H*$_2$Ph), 4.84 (d, 1H, *J*=7.3 Hz, H-1a), 4.81 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.77 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.66 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.63 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.52 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.50 (d, 1H, *J*=10.2 Hz, –C*H*$_2$Ph), 4.47 (d, 2H, *J*=11.7 Hz, –C*H*$_2$Ph×2), 4.45 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.42 (d, 1H, *J*=7.8 Hz, Gal H-1), 4.38 (d, 1H, *J*=7.3 Hz, Gal H-1), 4.37 (d, 1H, *J*=10.2 Hz, –C*H*$_2$Ph), 4.36 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.31 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.28 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.21–4.14 (m, 5H, –C*H*$_2$Ph×3, –C*H*$_2$CH=CH$_2$), 4.03 (br t, 1H, *J*=8.0 Hz, H-4c), 4.01 (br t, 1H, *J*=8.0 Hz, H-4a), 3.90 (d, 1H, *J*=2.4 Hz, Gal H-4), 3.85 (d, 1H, *J*=2.9 Hz, Gal H-4), 3.85–3.63 (m, 9H, H-6c, GlcNTCA H-3×2, Gal H-3, GlcNTCA H-2×2, H-6c, Gal H-2×2), 3.52–3.41 (m, 5H, H-6a, H-5c, Gal H-6×2, Gal H-5), 3.38–3.25 (m, 4H, Gal H-5, Gal H-3, Gal H-6×2), 3.19 (br d, 1H, *J*=11.2 Hz, H-6a), 2.87 (br d, 1H, *J*=8.8 Hz, H-5a), 1.04 (s, 9H, ^{t}Bu). ^{13}C NMR: δ 161.6 and 161.5 (Cl_3CCONH×2), 134.9 (–*C*H=CH$_2$), 116.5 (–CH=*C*H$_2$), 103.0, and 102.5 (C-1b and C-1d), 100.2 (C-1c), 94.8 (C-1a), 92.6, and 92.4 (–*C*Cl$_3$×2), 82.2 (C-3d), 71.5 (–*C*H$_2$–CH=CH$_2$), 59.3 (C-2a), 57.7 (C-2c), 26.8 [–C(*C*H$_3$)$_3$], 19.1 [–*C*(CH$_3$)$_3$]. MALDI TOF MS: calcd for $C_{117}H_{124}N_2O_{21}Cl_6Si$ $(M+Na)^+$ *m*/*z* 2153.65. Found: 2153.97. Anal. calcd for $C_{117}H_{124}N_2O_{21}Cl_6Si$: C, 65.82; H, 5.85; N, 1.31. Found: C, 65.61; H, 5.88; N, 1.29.

Byproduct **43**: ^{1}H NMR: δ 6.86 (d, 1H, *J*=7.8 Hz, –N*H*), 6.66 (d, 1H, *J*=7.3 Hz, –N*H*), 6.60 (br d, 1H, *J*=7.8 Hz, –N*H*), 5.94 (m, 1H, –C*H*=CH$_2$), 1.03 (s, 9H, ^{t}Bu). MALDI TOF MS calcd for $C_{166}H_{174}N_3O_{31}Cl_9Si$ $(M+Na)^+$: *m*/*z* 3077.31. Found: 3078.97.

Procedure B (*glycosylation of* **39** with **38**). A mixture of **39** (1.36 g, 1.15 mmol), **38** (1.39 g, 1.21 mmol), and dried MS AW-300 powder (3.5 g) in anhydrous CH_2Cl_2 (35 ml) was cooled at −78 °C with stirring under Ar for 10 min. To the cold mixture was added TMSOTf (10 μl, 0.06 mmol). The mixture was stirred at −78 °C for 1 h, before the reaction was quenched with aq $NaHCO_3$. The mixture was diluted with EtOAc and filtered through Celite. The filtrate was successively washed with satd $NaHCO_3$ aq, water, and brine, dried over $MgSO_4$, and concentrated in vacuo. The crude product was chromatographed on Bio-beads *S*-X3 with toluene–EtOAc (3:1) and then on silica gel with toluene–EtOAc (14:1–9:1) to give **40** (2.32 g, 94%).

4.1.33. 3-O-Allyl-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-D-glucopyranose ***41****.* Compound **40** (978 mg, 0.46 mmol) was desilylated with 1 M TBAF/THF (1.8 ml, 1.83 mmol) and AcOH (0.26 ml, 4.58 mmol) in THF (5 ml) as described for **21**. The crude product was chromatographed on silica gel with toluene–EtOAc (5:1–4:1–2:1) to afford **41** (850 mg, 98%). R_f 0.40 and 0.22 (4:1 toluene–EtOAc). ^{1}H NMR: δ 7.37–7.08 (m, 50H, Ar), 6.82 (d, 1H, *J*=8.8 Hz, –N*H*), 6.64 (d, 1H, *J*=7.8 Hz, –N*H*), 5.93 (m, 1H, –C*H*=CH$_2$), 5.36–5.30 (m, 2H, –CH=C*H*$_2$ and H-1a), 5.19 (dd, 1H, *J*=1.5, 10.2 Hz, –CH=C*H*$_2$), 5.09 (m, 1H, H-1c), 4.98 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.96 (d, 1H, *J*=10.7 Hz, –C*H*$_2$Ph), 4.94 (d, 2H, *J*=11.2 Hz, –C*H*$_2$Ph×2), 4.83 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.80 (m, 1H, –C*H*$_2$Ph), 4.78 (d, 1H, *J*=10.7 Hz, –C*H*$_2$Ph), 4.71 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.54 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.52 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.51 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.48 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.47 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.45 (d, 1H, *J*=10.2 Hz, –C*H*$_2$Ph), 4.42 (d, 1H, *J*=7.8 Hz, Gal H-1), 4.37 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.28 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.27 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.26 (m, 1H, Gal H-1), 4.25 (d, 1H, *J*=10.2 Hz, –C*H*$_2$Ph), 4.19 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.20–4.15 (m, 2H, –C*H*$_2$CH=CH$_2$), 4.14 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.10–3.99 (m, 2H, H-2a, H-4c), 3.93 (br t, 1H, *J*=9.3 Hz, H-4a), 3.90 (s, 1H, Gal H-4), 3.86 (d, 1H, *J*=2.4 Hz, Gal H-4), 3.83–3.78 (m, 4H, H-5a, H-6c, H-3c, H-2c), 3.75–3.65 (m, 6H, H-6c, Gal H-2×2, H-3a, Gal H-3, H-6a), 3.55 (m, 1H, H-5c), 3.46–3.30 (m, 7H, H-6a, Gal H-6, -O*H*, Gal H-5×2, Gal H-6, Gal H-3), 3.28–3.25 (m, 2H, Gal H-6×2). ^{13}C NMR: δ 161.7 and 161.6 (Cl_3CCONH×2), 134.9 (–*C*H=CH$_2$), 116.5 (–CH=*C*H$_2$), 103.0 and 102.8 (C-1b, C-1d), 100.3 (C-1c), 92.5 and 92.3 (–*C*Cl$_3$×2), 90.7 (C-1a), 82.2 (C-3d), 71.5 (–*C*H$_2$–CH=CH$_2$), 57.5 (C-2c), 54.4 (C-2a). MALDI TOF MS: calcd for $C_{101}H_{106}N_2O_{21}Cl_6$ $(M+Na)^+$ *m*/*z* 1915.53. Found: 1915.87. Anal. calcd for $C_{101}H_{106}N_2O_{21}Cl_6$: C, 63.96; H, 5.63; N, 1.48. Found: C, 64.00; H, 5.72; N, 1.53.

4.1.34. 3-O-Allyl-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-

benzyl-2-deoxy-2-trichloroacetamido-D-glucopyranosyl (N-phenyl)-2,2,2-trifluoroacetimidate ***42***. Compound **41** (739 mg, 0.39 mmol) was reacted with (*N*-Phenyl)-2,2,2-trifluoroacetimidoyl chloride (162 mg, 0.78 mmol) and K_2CO_3 (270 mg, 1.95 mmol) in acetone (5 ml) as described for **38**. The crude product was chromatographed on Bio-beads *S*-X3 with toluene–EtOAc (3:1) to afford **42** (774 mg, 96%). R_f 0.41 (7:1 toluene–EtOAc). ^{1}H NMR: δ 7.38–7.05 (m, 53H, Ar), 6.75–6.71 (m, 3H, =NPh×2, –N*H*), 6.59 (d, 1H, *J*=7.8 Hz, –N*H*), 6.43 (br s, 1H, H-1a), 5.94 (m, 1H, –C*H*=CH$_2$), 5.34 (dd, 1H, *J*=1.5, 17.1 Hz, –CH=C*H*$_2$), 5.19 (dd, 1H, *J*=1.5, 10.2 Hz, –CH=C*H*$_2$), 5.12 (d, 1H, *J*=7.3 Hz, H-1c), 4.98 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.96–4.92 (m, 3H, –C*H*$_2$Ph×3), 4.84 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.80–4.75 (m, 2H, –C*H*$_2$Ph×2), 4.71 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.58 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.54 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.52 (d, 2H, *J*=11.2 Hz, –C*H*$_2$Ph×2), 4.47 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.47 (d, 1H, *J*=10.2 Hz, –C*H*$_2$Ph), 4.43 (d, 1H, *J*=7.3 Hz, Gal H-1), 4.38 (d, 1H, *J*=10.2 Hz, –C*H*$_2$Ph), 4.35 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.31 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.30 (d, 1H, *J*=7.3 Hz, Gal H-1), 4.29 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.20 (d, 2H, *J*=11.7 Hz, –C*H*$_2$Ph×2), 4.21–4.11 (m, 3H, –C*H*$_2$CH=CH$_2$, H-2a), 4.09 (br t, 1H, *J*=9.8 Hz, GlcNTCA H-4), 4.04 (br t, 1H, *J*=8.6 Hz, GlcNTCA H-4), 3.93 (br s, 1H, Gal H-4), 3.87–3.83 (m, 3H, Gal H-4, GlcNTCA H-3, GlcNTCA H-6), 3.80–3.70 (m, 7H, H-2c, Gal H-2×2, Gal H-3, GlcNTCA H-3, GlcNTCA H-6×2), 3.62–3.57 (m, 2H, GlcNTCA H-5×2), 3.48–3.32 (m, 7H, Gal H-6, GlcNTCA H-6, Gal H-6×2, Gal H-5×2, Gal H-3), 3.27 (dd, 1H, *J*=4.9, 8.3 Hz, Gal H-6). ^{13}C NMR: δ 161.8 (Cl$_3$CCONH), 161.6 (Cl$_3$CCONH), 143.0 (>*C*=NPh), 134.9 (–*C*H=CH$_2$), 116.5 (–CH=*C*H$_2$), 103.1 and 102.6 (C-1b and C-1d), 100.3 (C-1c), 92.4 and 92.1 (–*C*Cl$_3$×2), 82.2 (C-3d), 71.6 (–*C*H$_2$–CH=CH$_2$), 57.7 (C-2c), 53.5 (C-2a). Anal. calcd for $C_{109}H_{110}N_3O_{21}Cl_6F_3$: C, 63.31; H, 5.36; N, 2.03. Found: C, 63.50; H, 5.40; N, 2.04.

4.1.35. tert-Butyldiphenylsilyl 2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside ***44***. Compound **40** (877 mg, 0.41 mmol) was deallylated by Ir-catalyzed olefin isomerization and hydroiodination as described for **39**. The crude product was chromatographed on silica gel with toluene–EtOAc (7:1) to afford **44** (837 mg, 97%). $[\alpha]_D$ −14.3 (*c* 1). R_f 0.50 (4:1 toluene–EtOAc). ^{1}H NMR: δ 7.66 (d, 1H, *J*=6.3 Hz, Ar), 7.66 (d, 1H, *J*=7.8 Hz, Ar), 7.62 (d, 1H, *J*=6.8 Hz, Ar), 7.62 (d, 1H, *J*=8.3 Hz, Ar), 7.39–7.09 (m, 56H, Ar), 6.88 (d, 1H, *J*=7.8 Hz, –N*H*), 6.65 (d, 1H, *J*=8.3 Hz, –N*H*), 5.11 (d, 1H, *J*=7.3 Hz, H-1c), 4.97 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.94 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.89 (d, 1H, *J*=10.2 Hz, –C*H*$_2$Ph), 4.85 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.84 (d, 1H, *J*=8.3 Hz, H-1a), 4.75 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.70 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.67 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.63 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.58 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.53 (d, 1H, *J*=10.7 Hz, –C*H*$_2$Ph), 4.51 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.50 (d, 1H, *J*=10.2 Hz, –C*H*$_2$Ph), 4.46 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.42 (d, 1H, *J*=9.8 Hz, H-1d), 4.40 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.39 (d, 1H, *J*=8.3 Hz, H-1b), 4.37 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.33 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.31 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.22 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.19 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.16 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.07 (br t, 1H, *J*=8.5 Hz, H-4c), 4.02 (br t, 1H, *J*=8.5 Hz, H-4a), 3.91 (d, 1H, *J*=2.9 Hz, H-4b), 3.86–3.80 (m, 3H, H-4d, H-6c, H-3c), 3.78–3.70 (m, 5H, H-3a, H-3b, H-6c, H-2c, H-2a), 3.66 (dd, 1H, *J*=7.8, 9.3 Hz, H-2b), 3.52–3.42 (m, 8H, H-5c, H-3d, H-2d, H-6a, H-6b, H-6d, H-5b, H-5d), 3.36–3.29 (m, 2H, H-6b, H-6d), 3.19 (dd, 1H, *J*=2.0, 11.2 Hz, H-6a), 2.87 (br d, 1H, *J*=9.3 Hz, H-5a), 2.20 (d, 1H, *J*=4.9 Hz, –O*H*), 1.04 (s, 9H, ^{t}Bu). ^{13}C NMR: δ 161.6 and 161.5 (Cl$_3$CCONH×2), 102.9 ($^1J_{CH}$ 161.9 Hz, C-1d), 102.5 ($^1J_{CH}$ 161.1 Hz, C-1b), 100.1 ($^1J_{CH}$ 166.2 Hz, C-1c), 94.8 ($^1J_{CH}$ 164.5 Hz, C-1a), 92.6 and 92.4 (-*C*Cl$_3$×2), 75.2 (C-3d), 59.3 (C-2a), 57.7 (C-2c), 26.8 [–C(*C*H$_3$)$_3$], 19.1 [–*C*(CH$_3$)$_3$]. MALDI TOF MS: calcd for $C_{114}H_{120}N_2O_{21}Cl_6Si$ (M+Na)$^+$ *m*/*z* 2113.61. Found: 2114.21. Anal. calcd for $C_{114}H_{120}N_2O_{21}Cl_6Si$: C, 65.36; H, 5.77; N, 1.34. Found: C, 65.41; H, 5.84; N, 1.40.

4.1.36. tert-Butyldiphenylsilyl 3-O-allyl-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside ***45***. A mixture of **42** (702 mg, 0.34 mmol), **44** (647 mg, 0.31 mmol), and dried MS AW-300 (1 g) in anhydrous CH_2Cl_2 (10 ml) was cooled at −78 °C with stirring under Ar for 10 min. To the cold mixture was added TMSOTf (3 μl, 15 μmol). Then the temperature was raised to −40 °C over a period of 30 min and stirring was continued for further 1.5 h, before the reaction was quenched with satd $NaHCO_3$ aq. The mixture was diluted with EtOAc and filtered through Celite. The filtrate was successively washed with satd $NaHCO_3$ aq, water, and brine, dried over $MgSO_4$, and concentrated in vacuo. The crude product was chromatographed on Bio-beads *S*-X1 with toluene–EtOAc (1:1) and then by recycled HPLC [Mightysil Si 60 (20×250 mm, 5 μm, Kanto Chemical Co.) with $CHCl_3$–EtOAc (87:13)] to give **45** (1.14 g, 93%). $[\alpha]_D$ −20.7 (*c* 1). R_f 0.20 (9:1 toluene–EtOAc). ^{1}H NMR: δ 7.65 (d, 1H, *J*=6.3 Hz, Ar), 7.65 (d, 1H, *J*=7.8 Hz, Ar), 7.61 (d, 1H, *J*=6.8 Hz, Ar), 7.61 (d, 1H, *J*=7.8 Hz, Ar), 7.39–7.05 (m, 106H, Ar), 6.87 (d, 1H, *J*=7.8 Hz, –N*H*), 6.68 (d, 1H, *J*=7.3 Hz, –N*H*), 6.64 (d, 1H, *J*=7.8 Hz, –N*H*), 6.60 (d, 1H, *J*=7.8 Hz, –N*H*), 5.94 (m, 1H, –C*H*=CH$_2$), 5.33 (dd, 1H, *J*=1.5, 17.1 Hz, –CH=C*H*$_2$), 5.19 (dd, 1H, *J*=1.5, 10.7 Hz, –CH=C*H*$_2$), 5.11 (d, 1H, *J*=7.3 Hz, GlcNTCA H-1), 5.04 (m, 1H, GlcNTCA H-1), 5.01 (m, 1H, GlcNTCA H-1), 5.00–4.92 (m, 5H, –C*H*$_2$Ph×5), 4.89–4.69 (m, 10H, –C*H*$_2$Ph×9, H-1a), 4.64 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.61 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.53–4.45 (m, 10H, –C*H*$_2$Ph×10), 4.43–4.25 (m, 13H, –C*H*$_2$Ph×9, Gal H-1×4), 4.24–4.12 (m, 7H, –C*H*$_2$Ph×5, –C*H*$_2$CH=CH$_2$×2), 4.06–3.98 (m, 4H, GlcNTCA H-4×4), 3.91 (d, 1H, *J*=2.4 Hz, Gal H-4), 3.87–3.86 (m, 3H, Gal H-4×3), 3.84–3.23 (m, 38H, GlcNTCA H-2×4, GlcNTCA H-3×4, GlcNTCA H-5×3, GlcNTCA H-6×7, Gal H-2×4, Gal H-3×4, Gal H-5×4, Gal H-6×8), 3.18 (dd, 1H, *J*=2.0, 11.2 Hz, H-6a), 2.86 (br d, 1H, *J*=8.8 Hz, H-5a), 1.03 (s, 9H, ^{t}Bu). ^{13}C NMR: δ 161.6 (Cl$_3$CCONH×2), 161.5, and 161.4 (Cl$_3$CCONH×2), 134.9 (–*C*H=CH$_2$), 116.5 (–CH=*C*H$_2$), 103.0, 102.9, 102.8, and 102.5 (Gal C-1×4), 100.2 (C-1), 100.1 and 100.1 (GlcNTCA C-1×3), 94.8 (C-1a), 92.6 (–*C*Cl$_3$), 92.3 (–*C*Cl$_3$×3), 82.2 (C-3h), 71.5 (–CH$_2$–CH=CH$_2$), 59.2 (C-2a), 57.6 (GlcNTCA C-2), 57.5 (GlcNTCA C-2×2), 26.8 [–C(*C*H$_3$)$_3$], 19.1 [–*C*(CH$_3$)$_3$]. MALDI TOF MS: calcd for $C_{215}H_{224}N_4O_{41}Cl_{12}Si$ (M+Na)$^+$ *m*/*z* 3996.15 (100%). Found: 3996.72. Anal. calcd for $C_{215}H_{224}N_4O_{41}Cl_{12}Si$: C, 64.99; H, 5.68; N, 1.41. Found: C, 64.89; H, 5.78; N, 1.43.

4.1.37. 3-O-Allyl-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-D-glucopyranose ***46***. Compound **45** (908 mg, 0.23 mmol) was desilylated with 1 M TBAF/THF (0.9 ml, 0.91 mmol) and AcOH (0.13 ml, 2.29 mmol) in freshly distilled THF (5 ml) as described for **21**. The crude product was chromatographed on Bio-beads *S*-X1 with toluene–EtOAc (1:1) to quantitatively afford **46** (854 mg). R_f 0.40 and 0.18 (4:1 toluene–EtOAc). ^{1}H NMR: δ 7.38–7.03 (m, 100H, Ar), 6.83 (d, 1H, *J*=8.8 Hz, –N*H*), 6.70 (d, 1H, *J*=7.8 Hz, –N*H*), 6.68 (d, 1H, *J*=9.8 Hz, –N*H*), 6.63 (d, 1H, *J*=7.8 Hz, –N*H*), 5.94

(m, 1H, –C*H*=CH_2), 5.34 (dq, 1H, *J*=1.5, 17.1 Hz, –CH=C*H*$_2$), 5.29 (br t, 1H, *J*=3.2 Hz, H-1a), 5.19 (br dd, 1H, *J*=1.5, 10.2 Hz, –CH=C*H*$_2$), 5.11 (br d, 1H, *J*=6.8 Hz, GlcNTCA H-1), 5.04 (d, 1H, *J*=7.3 Hz, GlcNTCA H-1), 5.02 (d, 1H, *J*=7.3 Hz, GlcNTCA H-1), 4.98 (d, 1H, *J*=12.2 Hz, –C*H*$_2$Ph), 4.97–4.93 (m, 5H, –C*H*$_2$Ph×5), 4.88 (d, 1H, *J*=10.2 Hz, –C*H*$_2$Ph), 4.87 (d, 1H, *J*=10.7 Hz, –C*H*$_2$Ph), 4.83 (d, 1H, *J*=11.2 Hz, –C*H*$_2$Ph), 4.82 (d, 1H, *J*=11.7 Hz, –C*H*$_2$Ph), 4.83–4.67 (m, 6H, –C*H*$_2$Ph×6), 4.53–4.11 (m, 30H, –C*H*$_2$Ph×24, Gal H-1×4, –C*H*$_2$CH=CH_2×2), 4.06–3.26 (m, 49H, GlcNTCA H-2×4, GlcNTCA H-3×4, GlcNTCA H-4×4, GlcNTCA H-5×4, GlcNTCA H-6×8, Gal H-2×4, Gal H-3×4, Gal H-4×4, Gal H-5×4, Gal H-6×8, –O*H*). ^{13}C NMR: δ 161.6, 161.6, and 161.6 (Cl_3CCONH×4), 134.8 (–*C*H=CH_2), 116.5 (–CH=*C*H_2), 103.0 (Gal C-1), 102.8 (Gal C-1×2), 102.7 (Gal C-1), 100.2 (GlcNTCA C-1×2), 100.1 (GlcNTCA C-1), 92.5 (–*C*Cl_3), 92.3 (–*C*Cl_3×3), 90.7 (C-1a), 82.1 (C-3h), 71.5 (–*C*H_2CH=CH_2), 57.6, 57.4, and 57.4 (GlcNTCA C-2×3), 54.4 (C-2a). MALDI TOF MS: calcd for $C_{199}H_{206}N_4O_{41}Cl_{12}$ $(M+Na)^+$ *m*/*z* 3758.03 (100%). Found: 3758.85. Anal. calcd for $C_{199}H_{206}N_4O_{41}Cl_{12}$+$H_2O$; C, 63.68; H, 5.59; N, 1.49. Found: C, 63.57; H, 5.64; N, 1.61.

*4.1.38. 3-O-Allyl-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-D-glucopyranosyl (N-phenyl)-2,2,2-trifluoroacetimidate **47**.* Compound **46** (101 mg, 27 μmol) was reacted with (*N*-Phenyl)-2,2,2-trifluoroacetimidoyl chloride (11 mg, 54 μmol) and K_2CO_3 (19 mg, 135 μmol) in acetone (0.5 ml) as described for **38**. The crude product was chromatographed on Bio-beads *S*-X1 with toluene–EtOAc (1:1) to afford **47** (104 mg, 98%). R_f 0.19 (7:1 toluene–EtOAc). ^{1}H NMR: δ 7.38–7.03 (m, 103H, Ar), 6.75–6.68 (m, 5H, =N*Ph*×2, –N*H*×3), 6.61 (d, 1H, *J*=7.3 Hz, –N*H*), 6.43 (br s, 1H, H-1a), 5.94 (m, 1H, –C*H*=CH_2), 5.34 (dd, 1H, *J*=1.5, 17.1 Hz, –CH=C*H*$_2$), 5.18 (br d, 1H, *J*=10.2 Hz, –CH=C*H*$_2$), 5.13 (d, 1H, *J*=6.8 Hz, GlcNTCA H-1), 5.07 (br d, 2H, *J*=6.8 Hz, GlcNTCA H-1×2), 5.01–4.69 (m, 15H, –C*H*$_2$Ph×15), 4.59–4.25 (m, 25H, –C*H*$_2$Ph×21, Gal H-1×4), 4.21–3.99 (m, 11H, –C*H*$_2$Ph×4, H-2a, –C*H*$_2$CH=CH_2×2, GlcNTCA H-4×4), 3.93–3.25 (m, 43H, GlcNTCA H-2×3, GlcNTCA H-3×4, GlcNTCA H-5×4, GlcNTCA H-6×8, Gal H-2×4, Gal H-3×4, Gal H-4×4, Gal H-5×4, Gal H-6×8). ^{13}C NMR: δ 161.7, 161.5 (Cl_3CCONH×4), 142.9 (>*C*=NPh), 134.8 (–*C*H=CH_2), 124.4, and 119.2 (=N*Ph*), 116.4 (–CH=*C*H_2), 103.0 (Gal C-1), 102.8 (Gal C-1×2), 102.4 (Gal C-1), 100.2 (GlcNTCA C-1×2), 100.1 (GlcNTCA C-1), 92.3 (–*C*Cl_3×3), 92.0 (–*C*Cl_3), 82.1 (C-3h), 71.5 (–*C*H_2CH=CH_2), 57.5 (GlcNTCA C-2×2), 57.4 (GlcNTCA C-2), 53.4 (C-2a). Anal. calcd for $C_{207}H_{210}N_5O_{41}Cl_{12}F_3$: C, 63.65; H, 5.42; N, 1.79. Found: C, 63.83; H, 5.50; N, 1.89.

*4.1.39. N-(9-Fluorenylmethoxycarbonyl)-O-{3-O-allyl-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→6)-[2,3,4,6-tetra-O-benzyl-β-D-galactopyranosyl-(1→3)]-2-azido-2-deoxy-α-D-galactopyranosyl}-L-threonine allyl ester **48**.* A mixture of **4** (95 mg, 87 μmol), **47** (309 mg, 79 μmol), and dried MS AW-300 (400 mg) in anhydrous CH_2Cl_2 (4 ml) was cooled at −78 °C with stirring under Ar for 10 min. To the cold mixture was added 5% TMSOTf/CH_2Cl_2 (0.7 μl, 4 μmol). Then the temperature was raised to −40 °C over a period of 30 min and stirring was continued for further 1.5 h, before the reaction was quenched with aq $NaHCO_3$. The mixture was diluted with EtOAc and filtered through Celite. The filtrate was successively washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The crude product was chromatographed on Bio-beads *S*-X1 with toluene–EtOAc (1:1) and then by recycled HPLC on JAIGEL-2H with CH_2Cl_2 to give **48** (324 mg, 85%). $[\alpha]_D$ −2.1 (*c* 1). R_f 0.39 (4:1 toluene–EtOAc). ^{1}H NMR: δ 7.73 (d, 2H, *J*=7.8 Hz, Ar), 7.60 (d, 1H, *J*=6.8 Hz, Ar), 7.58 (d, 1H, *J*=6.8 Hz, Ar), 7.39–7.05 (m, 124H, Ar), 6.99 (d, 1H, *J*=7.8 Hz, TCAN*H*), 6.69 (d, 1H, *J*=7.8 Hz, TCAN*H*), 6.68 (d, 1H, *J*=7.3 Hz, TCAN*H*), 6.63 (d, 1H, *J*=6.8 Hz, TCAN*H*), 5.92 (m, 2H, –C*H*=CH_2×2), 5.67 (d, 1H, *J*=9.3 Hz, FmocN*H*), 5.36–5.31 (m, 2H, –OCH_2CH=C*H*$_2$ and –CO_2CH_2CH=C*H*$_2$), 5.24–5.17 (m, 2H, –CO_2CH_2CH=C*H*$_2$ and –OCH_2CH=C*H*$_2$), 5.12 (br d, 1H, *J*=6.8 Hz, GlcNTCA H-1), 5.07–5.03 (m, 2H, GlcNTCA H-1×2), 5.02 (d, 1H, *J*=10.7 Hz, –C*H*$_2$Ph), 4.98–4.85 (m, 11H, –C*H*$_2$Ph×10, GlcNTCA H-1), 4.82–4.65 (m, 14H, –C*H*$_2$Ph×11, $GalN_3$ H-1, –CO_2C*H*$_2$CH=CH_2×2), 4.58–4.34 (m, 24H, –C*H*$_2$Ph×17, Gal H-1×4, Thr-βH, –C*H*$_2$$CHAr_2$, Thr-αH), 4.32–4.13 (m, 14H, –C*H*$_2$Ph×9, Gal H-1, –C*H*$_2$$CHAr_2$, –$CH_2$C*H*$Ar_2$, –$OCH_2$CH=$CH_2$×2), 4.11–3.26 (m, 60H, $GalN_3$ H-2, $GalN_3$ H-3, $GalN_3$ H-4, $GalN_3$ H-5, $GalN_3$ H-6×2, GlcNTCA H-2×4, GlcNTCA H-3×4, GlcNTCA H-4×4, GlcNTCA H-5×4,, GlcNTCA H-6×8, Gal H-2×5, Gal H-3×5, Gal H-4×5, Gal H-5×5, Gal H-6×10), 3.05 (br s, 1H, –O*H*), 1.31 (d, 3H, *J*=6.3 Hz, Thr-γH). ^{13}C NMR: δ 169.9 (–*C*O_2All), 161.6 (Cl_3*C*CONH), 161.5 (Cl_3CCONH×2), 161.5 (Cl_3CCONH), 156.7 (–*O*CONH), 134.8 (–OCH_2*C*H=CH_2), 131.3 (–CO_2CH_2*C*H=CH_2), 119.4 (–CO_2CH_2CH=*C*H_2), 116.5 (–OCH_2CH=*C*H_2), 103.9 (C-1j), 103.0 and 102.8 (Gal C-1×2), 102.8 (Gal C-1×2), 100.2 (GlcNTCA C-1), 100.1 (GlcNTCA C-1×2), 99.8 (C-1a), 99.7 (C-1b), 92.4 (–*C*Cl_3), 92.3 (–*C*Cl_3×3), 82.1 (C-3i), 75.8 (Thr C-3), 71.5 (–*O*CH_2CH=CH_2), 67.4 (–*C*$H_2$$CHAr_2$), 66.4 (–$CO_2$*C*$H_2$CH=$CH_2$), 59.0 (C-2b), 58.7 (Thr C-2), 57.5 and 57.4 (GlcNTCA C-2×3), 57.0 (C-2a), 47.0 (–CH_2*C*HAr_2), 18.7 (Thr C-4). Anal. calcd for $C_{261}H_{270}N_8O_{54}Cl_{12}$: C, 65.19; H, 5.66; N, 2.33. Found: C, 65.24; H, 5.75; N, 2.33.

*4.1.40. N-(9-Fluorenylmethoxycarbonyl)-O-{3-O-allyl-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranosyl-(1→6)-[2,3,4,6-tetra-O-benzyl-β-D-galactopyranosyl-(1→3)]-2-acetamido-2-deoxy-α-D-galactopyranosyl}-L-threonine allyl ester **49**.* Compound **48** (324 mg, 67 μmol) was reduced with powdered Zn (1.32 g, 20.22 mmol), and AcOH (1.35 ml, 23.6 mmol) in EtOAc (17 ml) under microwave irradiation at 150 W for 1 h, and the crude product was treated with Ac_2O (0.7 ml) in a mixture of CH_2Cl_2 (5.6 ml) and MeOH (1.4 ml) at room temperature for 2 h as described for **34**. The resulting product was chromatographed on Bio-beads *S*-X1 with toluene–EtOAc (1:1) and then by recycled HPLC on JAIGEL-2H with $CHCl_3$ to afford **49** (261 mg, 88%). $[\alpha]_D$ +9.2 (*c* 1). R_f 0.30 (1:4 toluene–EtOAc). ^{1}H NMR: δ 7.74 (d, 2H, *J*=7.3 Hz, Ar), 7.61 (d, 1H, *J*=7.3 Hz, Ar), 7.39–7.14 (m, 125H, Ar), 5.98–5.76 (m, 4H, –C*H*=CH_2×2, AcN*H*×2), 5.66 (br d, 1H, *J*=8.8 Hz, FmocN*H*), 5.33 (dd, 1H, *J*=1.5, 17.1 Hz, –OCH_2CH=C*H*$_2$), 5.30 (br d, 1H, *J*=17.1 Hz, –CO_2CH_2CH=C*H*$_2$), 5.24 (dd, 1H, *J*=1.0, 10.2 Hz, –CO_2CH_2CH=C*H*$_2$), 5.18 (dd, 1H, *J*=1.5, 10.2 Hz, –OCH_2CH=C*H*$_2$), 5.17–5.15 (m, 3H, AcN*H*×3), 5.01–4.60 (m, 25H, –C*H*$_2$Ph×19, GlcNAc H-1×4, GalNAc H-1, –C*H*$_2$$CHAr_2$), 4.54–4.14 (m, 42H, –C*H*$_2$Ph×29, Gal H-1×5, –C*H*$_2$$CHAr_2$, –$CH_2$C*H*$Ar_2$, Thr-αH, Thr-βH, C*H*$_2$CH=$CH_2$×4), 1.66 (s, 3H, –COC*H*$_3$), 1.44 (s, 9H, –COC*H*$_3$×3), 1.29–1.23 (m, 6H, –COC*H*$_3$, Thr-γH). ^{13}C NMR: δ 170.4, 170.0, 169.7, and 165.5 (–*C*O_2All, –NHCOCH_3×5), 156.3 (–*O*CONH), 134.7 (–OCH_2*C*H=CH_2), 130.9

(–CO_2CH_2CH=CH_2), 124.8, 119.7 (–CH_2CHAr_2), 119.3 (–CO_2CH_2CH=CH_2), 116.2 (–OCH_2CH=CH_2), 102.8, 102.8 (Gal C-1×5), 101.6 (GlcNTCA C-1×4), 99.4 (GalNAc C-1), 75.6 (Thr C-3), 71.3 (–OCH_2CH=CH_2), 67.0 (–CO_2CH_2CH=CH_2), 65.9 (–CH_2CHAr_2), 58.4 (Thr C-2), 55.9 (GlcNTCA C-2), 46.9 (–CH_2CHAr_2), 29.4 (Thr C-4), 22.9 (–$COCH_3$). MALDI TOF MS: calcd for $C_{263}H_{286}N_6O_{55}$ [average, $(M+Na)^+$] *m/z* 4434.08. Found: 4434.42. Anal. calcd for $C_{263}H_{286}N_6O_{55}\cdot 2H_2O$: C, 71.03; H, 6.57; N, 1.89. Found: C, 71.05; H, 6.55; N, 1.93.

4.1.41. N-(9-Fluorenylmethoxycarbonyl)-O-{3-O-allyl-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranosyl-(1→6)-[2,3,4,6-tetra-O-benzyl-β-D-galactopyranosyl-(1→3)]-2-acetamido-2-deoxy-α-D-galactopyranosyl}-L-threonine ***50***. A mixture of **49** (53 mg, 0.012 mmol), dimedone (34 mg, 0.24 mmol), and $Pd(PPh_3)_4$ (0.7 mg, 0.6 μmol) in freshly distilled THF (0.5 ml) was stirred under Ar at room temperature for 30 min, before concentrated in vacuo. The crude product was chromatographed on Bio-beads *S*-X1 with toluene–EtOAc (1:1) and then by recycled HPLC on JAIGEL-2H with $CHCl_3$ to give **50** (43 mg, 83%). $[\alpha]_D$ +10.4 (*c* 2). R_f 0.39 (9:1 $CHCl_3$–MeOH, 1% AcOH). ^{1}H NMR (DMSO-d_6): δ 12.88 (br s, 1H, –CO_2H), 7.89–7.86 (m, 7H, Ar×2, AcN*H*×5), 7.73–7.70 (m, 2H, Ar, FmocN*H*), 7.38–7.12 (m, 125H, Ar), 5.96 (m, 1H, –*CH*=CH_2), 5.35 (br d, 1H, *J*=17.1 Hz, –CH=*CH*$_2$), 5.16 (br d, 1H, *J*=9.8 Hz, –CH=*CH*$_2$), 5.00–4.66 (m, 19H, –*CH*$_2$Ph×15, GlcNAc H-1×4), 4.66–4.08 (m, 46H, –*CH*$_2$Ph×33, Gal H-1×5, GalNAc H-1, –*CH*$_2$CHAr$_2$×2, –CH_2*CH*Ar$_2$, Thr-αH, Thr-βH, *CH*$_2$CH=CH_2×2), 1.78 (s, 3H, –COC*H*$_3$), 1.67 (s, 3H, –COC*H*$_3$), 1.58 and 1.57 (s×2, 9H, –COC*H*$_3$×3), 1.08 (d, 3H, *J*=5.9 Hz, Thr-γH). ^{13}C NMR ($CDCl_3$): δ 193.1 (–*C*O$_2$H), 169.9, 169.0, and 165.7 (, –NH*C*OCH$_3$×5), 156.5 (–O*C*ONH), 135.5 (–*C*H=CH_2), 125.3, 120.1 (–CH_2CHAr_2×2), 115.9 (–CH=*C*H$_2$), 104.9, 102.7, 102.2, and 101.6 (Gal C-1×5, GlcNTCA C-1×4), 98.8 (GalNAc C-1), 70.5 (–*C*H$_2$CH=CH_2), 65.7 (–CH_2CHAr_2), 46.8 (–CH_2CHAr_2), 29.4 (Thr C-4), 23.0 and 22.8 (–$COCH_3$×5). MALDI TOF MS: calcd for $C_{260}H_{282}N_6O_{55}$ [100% $(M+Na)^+$] *m/z* 4392.94. Found: 4392.81. Anal. calcd for $C_{260}H_{282}N_6O_{55}\cdot 4H_2O$: C, 70.28; H, 6.58; N, 1.89. Found: C, 70.28; H, 6.55; N, 1.92.

4.1.42. N-(9-Fluorenylmethoxycarbonyl)-O-{β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-[β-D-galactopyranosyl-(1→3)]-2-acetamido-2-deoxy-α-D-galactopyranosyl}-L-threonine ***1*** *(Deprotection of decasaccharyl threonine* ***50****).* Decasaccharide **50** (10 mg, 2.4 μmol) was dissolved in a mixture of TFA/DMS/*m*-cresol (5:3:1, 270 μl), and the mixture was cooled at −15 °C. TfOH (30 μl, 0.34 mmol) was added dropwise to the mixture. The reaction mixture was stirred at −15 °C for 4 h, before the reaction was terminated by the addition of diethyl ether preliminarily cooled at −80 °C. The mixture was centrifuged to precipitate the product, which was washed three times with diethyl ether and centrifuged as mentioned above. The crude product was purified by preparative HPLC on Mightysil (KANTO) RP-18 (5 μm, 250×20 mm) with a gradient elution of aq CH_3CN (26%–34%/16 min) containing 0.1% TFA (flow rate: 7 ml/min). The collected major fraction was lyophilized to afford **1** (1.0 mg, 19%). MALDI TOF MS: calcd for $C_{89}H_{134}N_6O_{55}$ $(M+Na)^+$ *m/z* 2189.78. Found: 2189.41.

Glycopeptide **54**. Commercial Fmoc-Sieber amide resin (294 mg, 0.1 mmol) was subjected to an automated synthesis of the peptide to produce an octapeptide (SAPDTRPA)-resin by the *Fastmoc* program of the synthesizer, using 20% piperidine/NMP for *N*-deprotection and HBTU/HOBt as the condensing agent. 2,2,4,6,7-Pentamethyldihydrobenzofuran-5-sulfonyl (Pbf) group was employed for the protection of Arg, and *t*-Bu groups were used for the protection of Thr, Ser and Asp, respectively. A part of the octapeptide resin (5 μmol) was transferred into a polypropylene test tube, to which a mixture of **50** (44 mg, 10 μmol), 0.1 M HOBt/NMP (40 μl, 40 μmol) and 0.1 M DCC/NMP (40 μl, 40 μmol) was added. The mixture was heated for 5 h at 50 °C in an oven with stirring by a vortex mixer and then at room temperature for 12 h, and filtered. The resin was washed with CH_2Cl_2–MeOH (1:1) and several times with NMP. The N-terminal three amino acids were introduced manually using Fmoc amino acid (20 μmol), 0.1 M HOBt/NMP (30 μl, 30 μmol) and 0.1 M DCC/NMP (30 μl, 30 μmol) to give dodecaglycopeptide (HGVTSAPDTRPA)-resin (27 mg). 4-Methoxytrityl (Mmt) group was employed for the protection of His. To a part of the resin (9 mg) was added an ice-cooled solution of reagent K (TFA/phenol/water/thioanisole/ethanedithiol, 33:2:2:2:1, 150 μl), and the mixture stirred at 0 °C for 6 h. Then the resin was filtered off, and the volatile materials in the mixture were evaporated in a stream of N_2. Diethyl ether was added to the residue to precipitate the product, which was separated by centrifugation. The precipitate was washed several times by suspending in diethyl ether and then centrifuging to give a crude product, to which was added a mixture of TFA/DMS/*m*-cresol (5:3:1, 107 μl), and the mixture was cooled at −15 °C. A mixture of TFA/DMS/*m*-cresol/TfOH (5:3:1:1, 51 μl) was added to the mixture. The reaction mixture was stirred at −15 °C for 15 h, before the reaction was terminated by the addition of diethyl ether preliminarily cooled at −80 °C. The mixture was centrifuged to separate the debenzylated product, which was washed three times with diethyl ether and centrifuged as mentioned above to give a precipitate. The crude product was dissolved in 50% CH_3CN aq and purified by preparative HPLC on a column of Mightysil (KANTO) RP-18 (5 μm, 250×10 mm) with a gradient elution of aq CH_3CN (23%–33%/20 min) containing 0.1% TFA (flow rate: 2.5 ml/min). The major fraction was collected and lyophilized to afford **54** (0.5 mg, 4.8% overall yield based on the value of Gly in the amino-acid analysis). MALDI TOF MS: calcd for $C_{135}H_{207}N_{23}O_{69}$ $(M+H)^+$ *m/z* 3255.35. Found: 3255.16. Amino-acid analysis: $Asp_{0.92}$ $Thr_{1.63}$ $Ser_{0.92}$ $Pro_{1.82}$ $Gly_{1.00}$ $Ala_{1.79}$ $Val(+GlcNAc)_{1.98}$ $His_{0.78}$ $Arg_{0.93}$.

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