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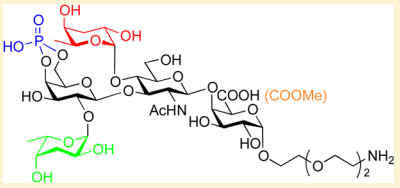
Chemical Synthesis of the Galacturonic Acid Containing Pentasaccharide Antigen of the O-Specific Polysaccharide of *Vibrio cholerae* O139 and Its Five Fragments

Xiaowei Lu and Pavol Kováč*

Section on Carbohydrates, Laboratory of Bioorganic Chemistry, National Institute of Diabetes and Digestive and Kidney Diseases, National Institutes of Health, 8 Center Drive, Bethesda, Maryland 20892-0815, United States

Supporting Information

ABSTRACT: Three pentasaccharides, two tetrasaccharides, and a trisaccharide fragment of the O-specific antigen of *Vibrio cholerae* O139 were synthesized by applying 1 + 1, 2 + 1, 3 + 1, and 4 + 1 coupling strategies. The most challenging tasks involved were the synthesis of the 1,2-*cis*-glycosidic linkage between galactose and the linker (spacer) molecule and final purification of the target multicharged substances. Difficulties with final deprotection by hydrogenation/hydrogenolysis caused by the presence of galacturonic acid were overcome by protecting the acid with a group inert to the treatment with hydrogen. Some intermediates described previously as incompletely characterized amorphous materials were obtained in the crystalline condition and were fully characterized for the first time.



INTRODUCTION

Cholera is a potentially epidemic, life-threatening infectious disease caused by the Gram-negative bacteria *Vibrio cholerae* O1 and O139. The main symptoms of the disease are severe diarrhea and dehydration, which can be fatal within hours if left untreated. Cholera is endemic in more than 50 countries. Management of patients with cholera involves aggressive fluid replacement and treatment with antibiotics. Prevention of cholera depends on access to safe water and sanitation. Cholera vaccines that provide long-term protection are needed to prevent infections, transmission, and severity of the disease.[1−3] Among types of possible vaccines for cholera, carbohydrate−protein conjugate vaccines are a promising remedy for young children, for whom the whole cell vaccines are either not effective or often toxic.[4−6]

Historically, only the O1 serogroup of *V. cholerae* has been associated with cholera epidemics. However, in 1992 an epidemic caused by O139 serogroup was reported. *V. cholerae* O139, which is in many aspects indistinguishable from *V. cholerae* O1[7,8] arose from a *V. cholerae* O1 strain by genetic mutation.[9] The main difference is the constitution of the cell surface. *V. cholerae* O1 is not encapsulated, and its outer-membrane lipopolysaccharide (LPS) has a long O-side chain identified as a homopolymer of 4-(2-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannose.[10,11] Although it has the same core−lipid A backbone as *V. cholerae* O1, *V. cholerae* O139 LPS has a hexasaccharide O-side chain (Figure 1) and produces a polysaccharide capsule (CPS) the repeating unit of which is identical to the O-side chain.

A detailed antigenicity study of *V. cholerae* O139 O-antigen is part of our ongoing effort to develop a potent glycoconjugate vaccine for cholera. Such work requires fragments of O-antigen and determination of their binding ability with the homologous antibodies, as well as of their conformation. Syntheses of

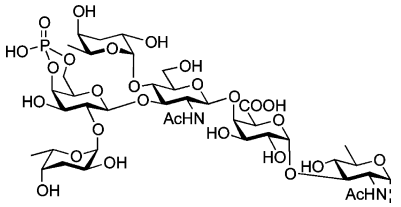


Figure 1. Structure of O-side chain in the LPS of *V. cholerae* O139.

colitose-, galactose-, and glucosamine-containing di-, tri-, and tetrasaccharide fragments of the O-antigen have already been reported.[12−18] Here we describe the first synthesis of the related galacturonic acid-containing pentasaccharide **1** and its five fragments, **2**−**6**.

RESULTS AND DISCUSSION

The O-specific antigen of *V. cholerae* O139 is unique among bacterial polysaccharides in that, unlike the usual scenario, it does not consist of multiples of repeating units. The hexasaccharide shown in Figure 1 is the complete O-specific antigen. The structure was proposed[19] and determined[20] in 1995, but the hexasaccharide has never been synthesized. The target molecule of this paper, compound **1**, is the largest fragment of the title O-specific antigen synthesized to date. It is a complex structure with some features that make its preparation synthetically very demanding. Further difficulty lies in final purification of the very polar, multicharged substances **1**−**6**. The construction of the cyclic phosphate present in the title pentasaccharide **1** was solved during independent syntheses of O-specific antigen fragments that

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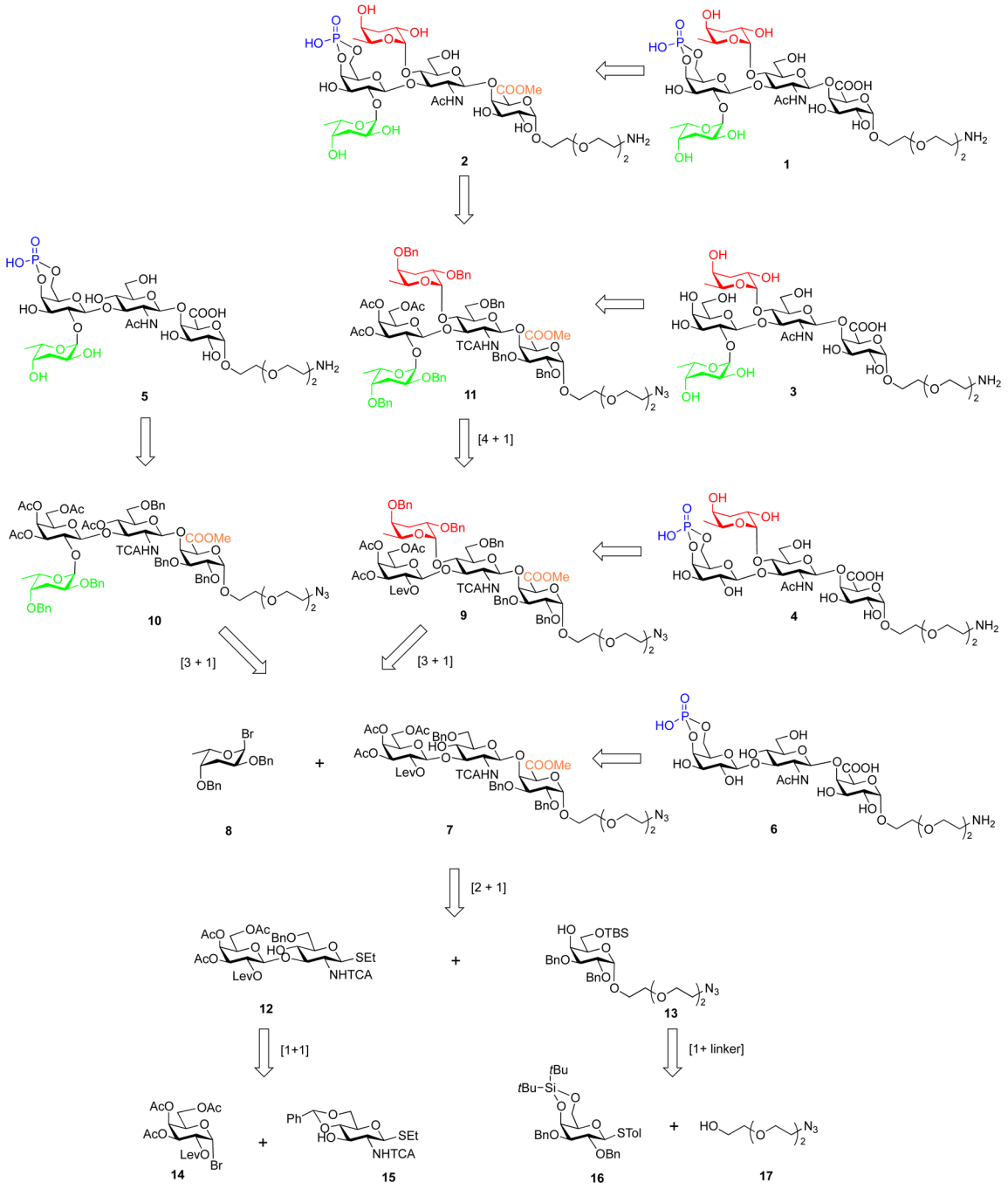

Figure 2. Retrosynthetic analysis.

were described earlier.[12−16,18] Here we show how we have been able to deal successfully with the two aforementioned problems involved.

The overall synthetic strategy toward compounds **1**−**6** is outlined in the retrosynthetic analysis (Figure 2). The strategy involves blocking groups that allow final deprotection, except saponification of the methyl ester, through one step hydrogenation/hydrogenolysis (see below for the importance to keep the methyl ester functionality intact through the reductive treatment). The central intermediate **7** was converted through hydroxyl group manipulation either to its phosphorylated analog **6** or through chain extension with donor **8**[16] to higher oligosaccharides **9**−**11**. The linker-equipped building block **7** was obtained by 2 + 1 coupling of the hydroxyl-group-containing donor **12** with alcohol **13**. Arriving at intermediate **7** required solving two essential tasks, namely, preparation of the orthogonally protected disaccharide donor **12** and installation of a linker moiety at the anomeric center of a precursor of the galacturonic acid residue with high α-stereoselectivity. Having succeeded in doing that, two 1 + 1 couplings, **14**[21] with **15**[22] and **16**[23] with **17**,[14] respectively, provided the required synthons to assemble **7**.

In oligosaccharide synthesis, it is advisible, for obvious reasons, to avoid chemical manipulations with larger molecules. Difficulties with formation of the α-glycosidic linkage between D-galactose and the very reactive primary hydroxyl group[24] in linker **17**[14] could be anticipated. Therefore, unlike in the synthesis of a related tetrasaccharide,[13] the buildup of **1** started

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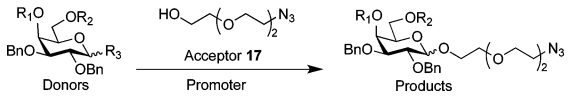
from the downstream[25] end with the linker-equipped galactose moiety. With the aforementioned strategy in mind, the task that we had to solve first was the construction of the downstream α-galactosyl → spacer linkage.

Initial attempts to attach the linker molecule to D-galactose in 1,2-cis manner involved glycosylations of linker **17**[14] with donors **18**,[26] **19**, or **20**.[26] Mainly β-isomers were formed (Table 1, entries 1−3). More successful were glycosylations of linker

Table 1. Glycosylation Results for Coupling of Donors 18−23 with Acceptor 17



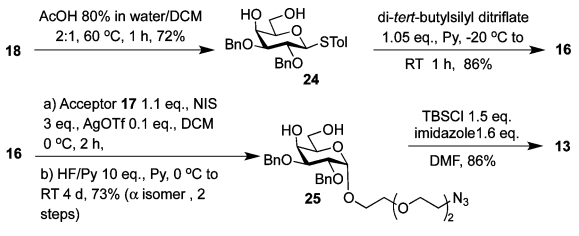
entry	donor[b]	promoter[b] and temp	products[a]
1	**18**:[26] R_1, R_2 = CHPMP; R_3 = β-STol	NIS, DCM −40 °C to rt	mainly β
2	**19**: R_1, R_2 = CHPMP; R_3 = α-Cl	$AgClO_4$, Et_2O −30 to −10 °C	mainly β
3	**20**:[26] R_1 = H, R_2 = PMB, R_3 = β-STol	NIS, DCM 0 °C	mainly β
4	**21**:[27] R_1 = R_2 = Ac, R_3 = β-STol	NIS, AgOTf, DCM 0 °C	α/β = 1.7:1
5	**22**: R_1 = R_2 = Ac, R_3 = α-Cl	$AgClO_4$, Et_2O 0 °C	α/β = 1.5:1
6	**23**: R_1 = H, R_2 = Bz, R_3 = β-STol	NIS, AgOTf, DCM 0 °C	α/β = 0.3:1

[a]The α- and β-isomers were separated by preparative TLC and characterized by NMR and MS. The α/β ratios were identified before purification, from the NMR spectra of the mixtures of two isomers formed. [b]PMP = *p*-methoxyphenyl, STol = *p*-toluenethiol, PMB = *p*-methoxybenzyl, NIS = *N*-iodosuccinimide, AgOTf = silver trifluoromethanesulfonate, rt = room temperature.

17[14] with the less reactive donors **21**,[27] **22**, and **23** (Table 1, entries 4, 5, and 6, respectively; experiments listed in Table 1 are considered preliminary and are not described in the Experimental Section).

In attempts to further improve the α-stereoselectivity, we applied an α-selective galactosylation methodology involving the α-directing di-*tert*-butylsilylene (DTBS) group.[28−30] It was very gratifying to observe that when alcohol **17**[14] was galactosylated with donor **16**,[23] obtained through **24** (Scheme 1),[32] the α-isomer was formed almost exclusively (see the Experimental Section). To avoid the difficult separation of a small amount of β-anomer formed during the glycosylation, purification of the critically needed α-product of the **16** + **17** coupling was put off until after 4,6-O-deprotection (Scheme 1). The product, compound **25**, was obtained in this way in 73%

Scheme 1. Synthesis of Acceptor 13[a]



[a]AcOH = acetic acid, Py = pyridine.

yield (for two steps). To obtain acceptor **13** (86%), the bulky *tert*-butyldimethylsilyl (TBS) group was selectively installed at the primary hydroxyl group of diol **25** by treatment with TBSCl.

Disaccharide donor **12** was needed for installation of colitose at position O-2 of D-galactose and O-4 of glucosamine at a later stage of the synthesis. Its preparation required an orthogonally protected, β-directing galactosyl donor with a selectively removable protecting group at O-2. Such a donor, **14**,[21] was readily obtained (77% for two steps) by levulinylation at O-2 of the known α-D-galactopyranose 1,3,4,6-tetraacetate **26**[33] followed by conventional treatment[34] of the formed, fully protected substance **27** with HBr in HOAc (Scheme 2).

With the donor **14**[21] at hand, we could proceed with the synthesis of disaccharide **28**. Because AgOTf normally does not activate thioglycosides, treatment of thioglycosides with AgOTf does not result in their self-glycosylation. Thus, glycosylation of thioglycoside acceptors with glycosyl halides in the presence of AgOTf is possible. However, because acceptor **15**[22] is more reactive (armed)[35] than the disarmed donor **14**,[21] their AgOTf-promoted condensation resulted, in addition to formation of the desired **28**, also in formation of a product of aglycon transfer.[36−39] The formation of the latter could be minimized when the inverse glycosylation procedure[40] was applied, whereby a solution of donor **14**[21] in DCM was added dropwise into a precooled solution of acceptor **15**,[22] promoter, and base at −35 °C. The presence of the acid-labile benzylidene group in **15**[22] required careful optimization of the reaction conditions, namely, the proper choice and amount of acid scavenger for TfOH generated during the AgOTf-mediated condensation. It is also important to note that these conversions require base-deficient reaction conditions[41,42] to facilitate the rearrangement of the orthoester intermediate of the glycosidation. When Soliman and Kováč glycosylated[43] acceptor **15**[22] with 1,2,3,4,6-penta-*O*-acetyl-α-D-galactopyranose, they replaced the mixture of *sym*-collidine and 4 Å molecular sieves, suggested by Sherman et al.,[22] with 1,1,3,3-tetramethylurea. It resulted in considerably an improved, almost theoretical yield of the desired product, compared to the 60% originally reported.[22] Those conditions,[43] however, were not suitable in our situation: the benzylidene group was cleaved under the base-deficient glycosylation conditions. We solved the problem by the use of *sym*-collidine as base and careful control of reaction conditions. By using 1.5 equiv of donor **14**[21] (Scheme 2) and also avoiding[43] the use of molecular sieves, disaccharide **28** was eventually obtained in 83% yield.

Our attempt to obtain trisaccharide **29** in acceptable yield by NIS/AgOTf-mediated reaction of **13** and **28** (Scheme 2) was not successful, apparently due to the ill-matched protecting groups (benzylidene and NHTCA) in donor **28**. When the condensation was conducted under less acidic conditions, to prevent the cleavage of the benzylidene group, the main product was not the desired trisaccharide **29** but oxazoline **30**. Structure **30** was deduced from MS and NMR spectral data for the characteristic[44,45] structure (see Experimental Section). Under base-deficient conditions, on the other hand, the donor carrying the acid-labile, benzylidene group was cleaved almost completely. The next plan was to regioselectively open the benzylidene group in **28** to obtain **12** and to install a selectively removable protecting group at its O-4[I]. However, the 4[I]-OH in **12** resisted derivatization with TBSCl (Scheme 2), and the desired disaccharide **31** could not be obtained. This observation prompted us to try to turn the unreactivity of 4[I]-OH in

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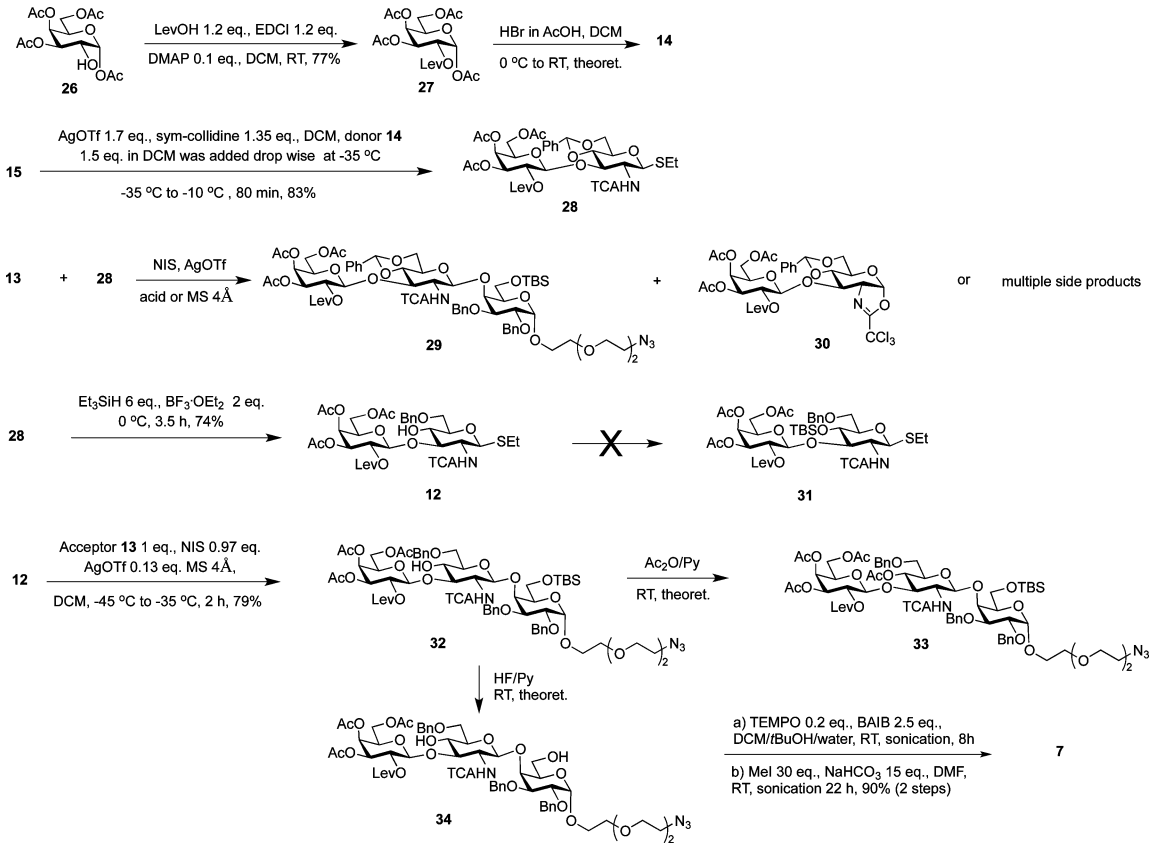
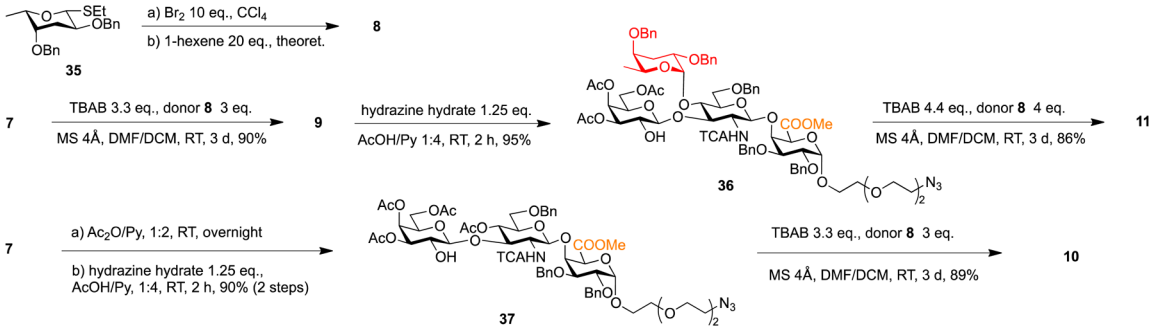
Scheme 2. Synthesis of Trisaccharide 7[a]



[a]TFA = trifluoroacetic acid, LevOH = levulinic acid, EDCI = *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride, DMAP = 4-dimethylaminopyridine, NHTCA = trichloroacetamido, MS = molecular sieve, TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy, BAIB = diacetoxyiodobenzene.

Scheme 3. Syntheses of Tetrasaccharides 9 and 10 and Pentasaccharide 11[a]



[a]TBAB = tetra-*n*-butylammonium bromide.

disaccharide **12** to our advantage. Accordingly, presuming that **12** would not self-condense, we used alcohol **12** as a glycosyl donor. Its reaction with acceptor **13** at low temperature was successful and yielded trisaccharide **32** in 79% yield. The presence of the free 4^{I}-OH group in product **32** was confirmed after acetylation, giving acetate **33**, the H-4^{II} of which showed a characteristic downfield shift. Desilylation (HF−Py complex)[46] of **32** furnished diol **34** that was selectively oxidized (TEMPO, BAIB).[47] Esterification (MeI, $NaHCO_3$)[48,49] of the resulting carboxyl group gave trisaccharide **7** in 90% yield (for three steps, Scheme 2).

Installation of colitose residues into structures related to the O-specific polysaccharide (O-SP) of *V. cholerae* O139 became less demanding after Ruttens[50] improved the synthesis of the acetylated analog of thioglycoside **35**,[50] thereby making different colitose donors more easily accessible. The latter thioglycoside can be transformed readily to the corresponding α-bromide, which is a powerful reagent in the Lemieux's halide-assisted 1,2-*cis*-glycosidation,[51] known to occur with complete stereoselectivity. Thus, bromide **8**[16] was freshly prepared from **35**[50] and treated[16] with acceptor **7** (Scheme 3) to readily give tetrasaccharide **9** in 90% yield. The levulinoyl group present in tetrasaccharide **9** was removed by treatment with hydrazine hydrate in pyridine/acetic acid[52] to give **36** (95%), which was colitosylated[16] to give pentasaccharide **11** in 86% yield. Successive acetylation and delevulinoylation of trisaccharide **7**

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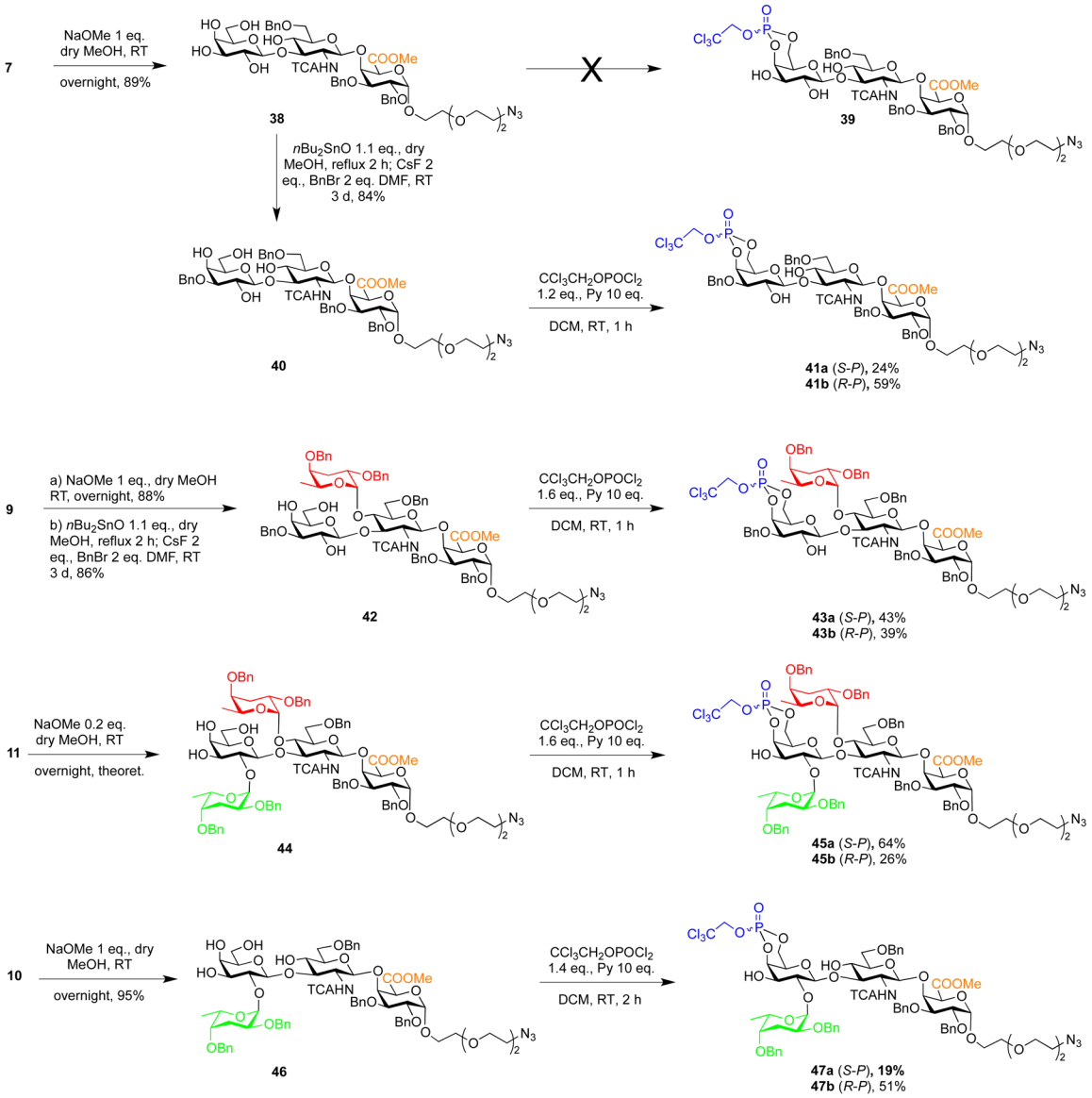
Scheme 4. Preparation of Phosphate Triesters



gave acceptor **37** (90% for two steps), which was converted to tetrasaccharide **10** in 89% yield, following the established colitosylation conditions described above.

Next we explored possibilities to shorten routes to the targeted phosphorylated products, compared to approaches described previously, where the benzyl group was installed at the 3-OH of galactose before introduction of the 4,6-cyclic phosphate.[13,16] Deacetylation of trisaccharide **7** gave pentaol **38** (89%), but the subsequent phosphorylation gave a mixture of products and could not be made into a preparatively useful way to produce **39** (cf. Scheme 4). On the other hand, trisaccharide **40**, obtained by selective benzylation of **38**, was phosphorylated uneventfully and gave two phosphate triesters **41a** and **41b** in overall 83% yield. The configuration at phosphorus was assigned on the basis of the chemical shift of ^{31}P observed in the NMR spectra. The signal for ^{31}P in an equatorial P═O appears more downfield than that of the isomer with an axial P═O.[53,54] The synthetic strategy just described, where the two-isomer-forming phosphorylation is carried out just before the hydrogenation/hydrogenolysis deprotection,[17] was followed also in syntheses of all other target compounds described here.

Succesive deacetylation and regioselective benzylation[17] at 3-OH of the galactose residue in tetrasaccharide **9** gave tetrasaccharide **42** (76% for two steps), which was phosphorylated to give two the isomeric phosphate triesters **43a** and **43b** in 82% combined yield (Scheme 4). Soliman[18] showed that 2-O-substituted galactose triols can be selectively 4,6-O-phosphorylated. Thus, triol **44**, obtained from **11** by deacetylation, was directly phosphorylated to give phosphate triesters **45a** and **45b** in combined 90% yield over two steps. Tetraol **46**, obtained from tetrasaccharide **10** (95%) by deacetylation, was treated as **44**, giving phosphate triesters **47a** and **47b** in 70% overall yield.

The syntheses reported here were designed to allow transformation by catalytic (Pd/C) treatment with hydrogen of the benzyl ethers, the trichloroethyl and trichloroacetyl groups, and the azido group in one step. The pH of the reaction mixture was controlled (1 M buffer, pH 7), to neutralize the HCl generated during the process, thereby preventing the cleavage of the acid-labile glycosidic linkages. At this point, it

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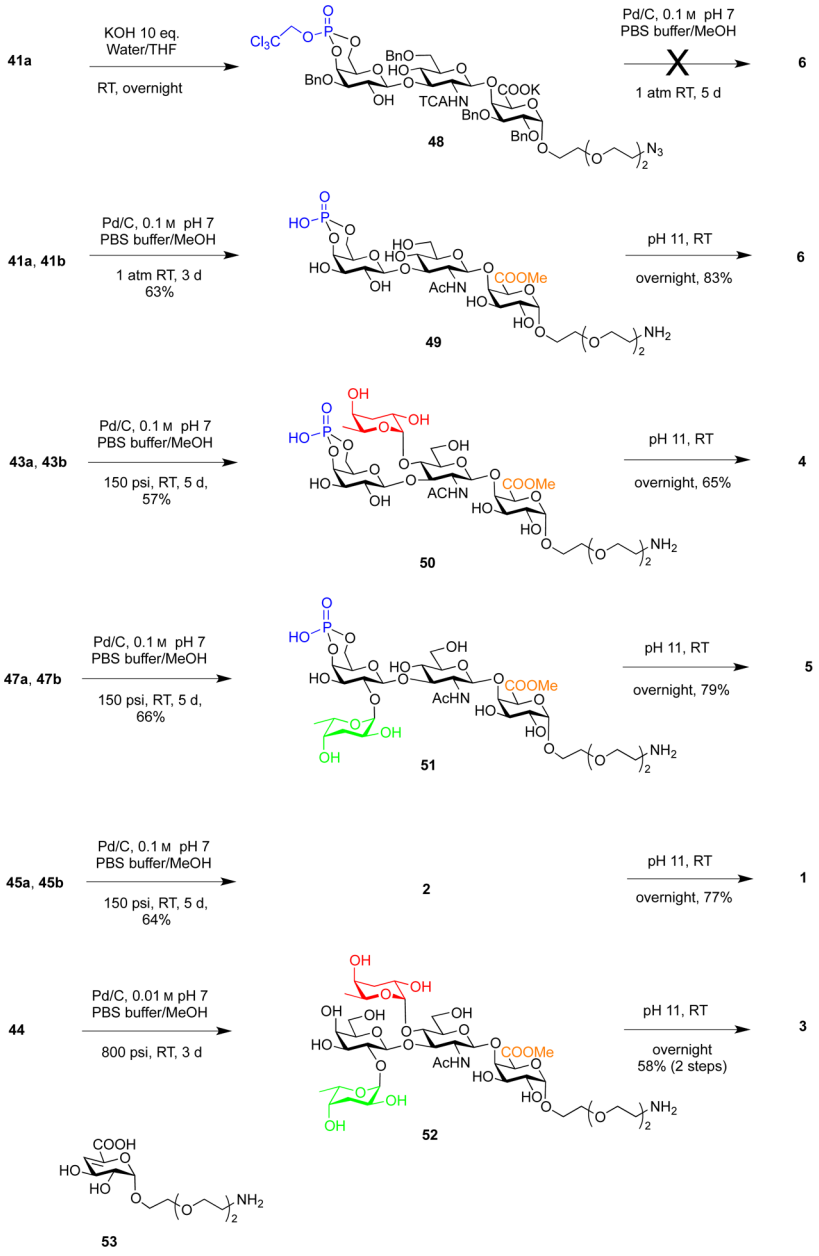
Scheme 5. Deprotections Using Hydrogenolysis/Hydrogenation and Saponification



was important to establish whether the hydrogenolysis should be performed before or after saponification of the methyl ester. To that end, exploratory hydrogenolyses were performed with methyl ester **41a,b** and carboxylate **48**, and the results were compared (Scheme 5). Monitoring of the progress of the hydrogenolysis of **48** by NMR spectroscopy showed the absence of aromatic protons, the absence of the trichloroethyl group, and presence of the acetamido group. However, the desired product **6** was not present (TLC). On the other hand, when the same hydrogenolysis conditions were applied to an isomeric mixture of trisaccharides **41a** and **41b**, the desired compound **49** was obtained after chromatography in 63% yield. The above results suggested that, in the series of compounds described here, successful hydrogenolysis could be expected when the carboxylate in galacturonic acid is protected with a group that is inert to hydrogenolysis. Accordingly, hydrogenolysis of a mixture of **43a** and **43b** at rt/150 psi followed by HPLC purification gave tetrasaccharide **50** (57%). The isomeric tetrasaccharide **51** (66%) was obtained in a similar way from **47a** and **47b**. Pentasaccharide **2** (64%) was produced likewise from pentasaccharides **45a** and **45b**.

Products of reductive treatment of the fully protected intermediates yielded the desired products as methyl galacturonates. Treatment of such substances even with mild base is likely to be accompanied by β-elimination.[55,56] Because the driving force for the elimination is the electron-withdrawing alkoxycarbonyl group, the saponification had to be conducted under mild conditions to minimize such side reaction and also to keep the cyclic phosphate intact. These conditions were provided[55] by slow addition of a dilute solution of KOH. It was established in preliminary experiments that when the basicity of the reaction mixtures was adjusted to pH 11 and the mixtures were kept at room temperature, the saponifications were complete within 16 h (TLC, *i*PrOH/water 1:1. Interestingly, the products of saponification moved faster than the starting methyl esters). Saponifications of methyl esters **49**–**51** and **2**

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(Scheme 5) were followed by HPLC purification (for details, see the Experimental Section), to give the desired products in ~80% yields. The yield of tetrasaccharide **4** was lower because more elimination side product was formed. All saponifications were accompanied by β-elimination to some degree. The elimination product **53** isolated from several separations was combined and identified by spectroscopy (NMR and HRMS). Structure **53** was deduced from MS and NMR spectral data, the latter showing chemical shifts for C-4 (108.38) and C-5 (145.29) characteristic of olefins.

Compared to treatment with hydrogen of other intermediates described here, hydrogenolysis/hydrogenation of pentasaccharide **44** turned out to be the most difficult to complete. When the conversion was performed at 800 psi at room temperature, the presence of aromatic protons could be still detected (NMR) after 3 weeks. When the conversion was performed at 1 atm at temperatures up to 50 °C, NMR showed that aromatic protons and the trichloroethyl group were absent and that the conversion of NHTCA→NHAc was complete, but the amount of desired product **52** formed was small (TLC). Changing methanol for another water-miscible solvent (isopropyl alcohol, *tert*-butyl alcohol, DMF, or acetonitrile), using fresh catalyst, and increasing the pressure up to 800 psi did not change the situation appreciably. Eventually, presuming that the salts present might deactivate the catalyst, decreasing the concentration of the buffer from 0.1 to 0.01 M largely solved the problem. The reaction was complete within 3 days when the reaction was carried out at 800 psi at room temperature. It was very gratifying to observe that the glycosidic linkages remained intact, including the colitosyl linkages, despite the increased acidity of the mixture (pH ~2). That conclusion is supported by the fact that the yield of **52** was similar to the yield of colitose-containing compounds that were prepared using 0.1 M buffer, when the alkalinity had been kept at pH ~7. Unexpectedly, purification of ester **52** turned out to be problematic, because the compound was not retained on either a C18 or an amide HPLC column. Deprotonation of the amine by the use of basic mobile phase was prohibited, lest the methyl ester present might react as well. Therefore, products of hydrogenation/hydrogenolysis were subjected to saponification directly without purification. The crude product, containing the desired compound **3**, was resolved using an amide HPLC column to give pure **3** in ~60% yield (over two steps).

CONCLUSIONS

Because of the complexity of their structures, syntheses of oligosaccharides related to the O-SP of *V. cholerae* O139 include many challenging synthetic tasks. The difficulty of the synthesis of the pentasaccharide fragment **1** is magnified by the presence of the D-galacturonic moiety at the downstream end, which has to be attached to the linker with high α-selectivity. This problem was solved by the use of a 4,6-*O*-DTBS-group-protected galactosyl donor, which proved to be strongly α-directing, even when the glycosyl acceptor was a highly reactive primary, aliphatic alcohol. Another hurdle encountered during the synthesis, the aglycon transfer, which occurred during glycosidation of donor **14**[21] with a thioglycoside **15**,[22] was solved by the proper mode of addition of reagents. The protecting group incompatibility during preparation of trisaccharide **29**, arising from the presence of the acid-labile benzylidene and oxazoline-forming NHTCA groups in donor **28**, the latter requiring base-deficient glycosylation conditions, was solved by the use of the unreactive, hydroxyl-group-containing thioglycoside donor **12**. The colitosylations according to protocols developed in this laboratory transformed the key intermediate **7** into tetrasaccharides **9** and **10** and pentasaccharide **11**. Likewise, applying strategies developed in this laboratory, cyclic phosphate group were installed into tri-, tetra-, and pentasaccharides. Subjecting methyl esters to reductive deprotection (H_2, Pd/C) and performing saponification of methyl esters as the last deprotection step solved unexpected difficulties encountered during deprotection by catalytic hydrogenation/hydrogenolysis observed when carboxylates were present in the intermediates. All deprotected, highly polar, multiply charged oligosaccharides were obtained in pure state (HPLC, NMR), using C18 and amide HPLC columns. Overall, more than 20 mg of each pure (TLC, HPLC, NMR) compound (**1**–**6**) was obtained. Results of antigenicity studies with a wide spectrum of fragments of the O-SP of *V. cholerae* O139, performed with the aim to determine minimum structural requirements to elicit protective responses in laboratory animals immunized with the respective glycoconjugates, will be reported in due time.

EXPERIMENTAL SECTION

General Procedures. HPLC-grade solvents were used, and reactions requiring anhydrous conditions were carried out under nitrogen or argon. A Parr mini benchtop reactor was used for reactions under pressurized H_2. The density ($d \approx 1.7$ g/mL at 20 °C) of 2,2,2-trichloroethyl phosphorodichloridate was determined by differential weighing of 1 mL of reagent. The palladium-on-charcoal catalyst used was purchased from Engelhard Industries (Escat 103, lot# FC96303). Reactions were monitored by thin-layer chromatography (TLC) on silica gel 60 glass slides. Spots were visualized by charring with H_2SO_4 in EtOH (5% v/v). Melting points were determined with a Kofler hot stage. Optical rotations were measured with an automatic polarimeter. Sonication was performed with the laboratory sonicator. NMR spectra were measured at 25 °C, at 162 MHz for ^{13}P, at 600 MHz for ^{1}H and at 150 MHz for ^{13}C. Assignments of NMR signals were aided by 1D and 2D experiments (APT, COSY, TOCSY, HSQC, HMQC, and HMBC) run with the software supplied with the spectrometers. With $CDCl_3$ as solvent, ^{1}H, ^{13}C, and ^{31}P chemical shifts were referenced to signals of tetramethylsilane (0 ppm), $CDCl_3$ (77.23 ppm), and H_3PO_4 (0 ppm). With D_2O as solvent, ^{1}H, ^{13}C, and ^{31}P chemical shifts were referenced to signals of H_2O (4.80 ppm), MeOH (external, 49.50 ppm), and H_3PO_4 (0 ppm). 2,2,2-Trichloroethyl phosphorodichloridate[57] used was from our older stock, originally purchased from Aldrich/Sigma Chemical Co. For monitoring the progress of the global deprotection by NMR spectroscopy, a portion of the reaction mixture was withdrawn and centrifuged, the supernatant was concentrated and freeze-dried, and the residue was dissolved in D_2O (or CD_3OD) for NMR spectroscopy. The reactions were terminated when the spectra showed that aromatic protons and those associated with the trichloroethyl group (4.45–4.67 ppm) were no longer present. In addition, the completion of the reaction was indicated when integration of the singlet (~2 ppm) for the NHAc group showed the presence of three protons. Mixtures of isomeric *R*/*S* cyclic phosphates formed by phosphorylation were resolved and fully characterized. For hydrogenolysis, pure isomers were combined and treated with hydrogen as descried below. Yields are listed as "virtually theoretical" within the description of reactions when complete conversion of the key reagent took place for one-product transformations. Samples for combustion analysis and neutral silica gel were prepared as described.[58] A solution of chlorine in CCl_4 was prepared by passing chlorine through the solvent at 0–5 °C, and the concentration was determined by differential weighing. Solutions in organic solvents were dried with anhydrous Na_2SO_4 or $MgSO_4$ and concentrated with a rotary evaporator at <40 °C/2 kPa, unless stated otherwise.

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*4-Methylphenyl 2,3-Di-O-benzyl-(S)-4,6-O-(4-methoxybenzylidene)-1-thio-β-D-galactopyranoside (**18**).* Preparation of this substance has been reported,[26] but the crystalline compound has now been obtained for the first time and fully characterized: mp 143.5−144.5 °C (DCM/EtOH 3:1, white needles); R_f = 0.59 (EtOAc/hexane 4:1); $[\alpha]_D^{22}$ − 10.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR and ^{13}C NMR agree with published assignments;[26] HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{35}H_{37}O_6S$ 585.2311, found 585.2300. Anal. Calcd for $C_{35}H_{36}O_6S$: C, 71.89; H, 6.26. Found: C, 72.16; H, 6.39.

*2,3-Di-O-benzyl-(S)-4,6-O-(4-methoxybenzylidene)-α-D-galactopyranosyl Chloride (**19**).* Thioglycoside **18**[26] (1.30 g, 2.23 mol) was dissolved in dry DCM (20 mL). Chlorine in CCl_4 (1.1 mL, 2.4 M, 2.45 mmol) was added at 0 °C and the mixture was stirred at room temperature for 1 h, when TLC (R_f of **18** and **19**, 0.19 and 0.43, respectively, hexane/EtOAc/DCM 5:1:1) confirmed that the reaction was complete. After concentration, chromatography on activated silica gel (100 g, hexane/EtOAc/DCM 7:1:1) yielded monosaccharide **19** (0.75 g, 1.51 mmol, 68%). Crystallization (DCM/Et_2O) gave white crystal: mp 103−123 °C (dec.); R_f 0.43 (hexane/EtOAc/DCM 5:1:1); $[\alpha]_D^{22}$ +133.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.27 (m, 12H, H_{arom}), 6.90−6.87 (m, 2H, H_{arom}), 6.22 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 5.46 (s, 1H, C*H*PMP), 4.87−4.71 (m, 4H, CH_2Ph), 4.26−4.20 (m, 3H, H-4, H-6a, H-2), 4.06−3.99 (m, 2H, H-3, H-6b), 3.93 (bs, 1H, H-5), 3.81 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.64, 138.12, 130.31, 128.67, 128.59, 128.13, 127.93, 127.77 (C_{arom}), 101.20 (*C*HPMP), 95.56 (C-1), 75.65 (C-3), 75.45 (C-4), 74.24 (C-2), 73.59 (CH_2Ph), 72.62 (CH_2Ph), 69.03 (C-6), 65.87 (C-5), 55.54 (OCH_3); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{28}H_{30}O_6Cl$ 497.1731, found 497.1736. Anal. Calcd for $C_{28}H_{29}O_6Cl$: C, 67.67; H, 5.88. Found: C, 67.97; H, 5.87.

*4-Methylphenyl 2,3-Di-O-benzyl-6-O-(4-methoxybenzyl)-1-thio-β-D-galactopyranoside (**20**).* Preparation of this substance has been reported,[26] but the crystalline compound has now been obtained for the first time and fully characterized: mp 99.5−100.0 °C (EtOH); R_f 0.47 (hexane/DCM/EtOAc 3:1:1); $[\alpha]_D^{22}$ −5.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR and ^{13}C NMR assignments agreed with those published;[26] HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{35}H_{38}O_6NaS$ 609.2281, found 609.2280. Anal. Calcd for $C_{35}H_{38}O_6S$: C, 71.65; H, 6.53. Found: C, 71.51; H, 6.51.

*4,6-Di-O-acetyl-2,3-di-O-benzyl-α-D-galactopyranosyl Chloride (**22**).* Thioglycoside **21**[27] (0.80g, 1.45 mmol) was dissolved in dry DCM (10.0 mL). Chlorine in CCl_4 (1.5 mL, 2.4 M, 3.60 mmol) was added at 0 °C. Yellow color became faint as the reaction progressed. When TLC (R_f 0.17 and 0.24 for **21** and **22**, respectively, hexane/EtOAc/DCM 8:1:1) showed the disappearance of the trisaccharide **21**, the mixture was concentrated, and chromatography of the residue (40 g activated silica, hexane/EtOAc/DCM 8:1:1) yielded amorphous compound **22** (0.53 g, 1.14 mmol, 78%): R_f 0.24 (hexane/EtOAc/DCM 8:1:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36−7.27 (m, 10 H, H_{arom}), 6.10 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 5.59 (dd, 1H, $J_{3,4}$ = 3.3 Hz, $J_{4,5}$ = 1.3 Hz, H-4), 4.80 (d, 1H, *J* = 11.8 Hz, CH_2Ph), 4.74 (d, 1H, *J* = 11.2 Hz, CH_2Ph), 4.69 (d, 1H, *J* = 11.8 Hz, CH_2Ph), 4.58 (d, 1H, *J* = 11.2 Hz, CH_2Ph), 4.42 (m, 1H, H-5), 4.16 (dd, 1H, $J_{5,6a}$ = 5.9 Hz, $J_{6a,6b}$ = 11.5 Hz, H-6a), 4.07 (dd, 1H, $J_{5,6b}$ = 7.0 Hz, H-6b), 4.00 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-3), 3.95 (m, dd, 1H, H-2), 2.11 (s, 3H, CH_3), 2.07 (s, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.67, 170.24 ($COCH_3$),137.90, 137.87, 128.67, 128.59, 128.17, 128.05, 128.00 (C_{arom}), 94.09 (C-1), 75.53 (C-3), 75.40 (C-2), 73.56, 72.65 (CH_2Ph), 70.04 (C-5), 67.22 (C-4), 61.90 (C-6), 20.97, 20.91 (CH_3); HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{24}H_{27}O_7NaCl$ 485.1343, found 485.1342.

*4-Methylphenyl 6-O-Benzoyl-2,3-di-O-benzyl-1-thio-β-D-galactopyranoside (**23**).* Benzoyl chloride (0.24 mL, 2.02 mmol) was added to a mixture of **24**[31,32] (0.93 g, 2.00 mmol) and pyridine (0.32 mL, 36.00 mmol) in DCM (4.00 mL) at 0 °C and the mixture was stirred for 1 h. The mixture was poured into H_2O (100 mL), the layers were separated, and the aqueous layer was extracted with EtOAc (3 × 70 mL). The combined organic layers were washed with brine (100 mL) and concentrated. Crystallization from DCM/EtOH (twice) gave compound **23** (0.95 g, 1.66 mmol, 83%, white needles): mp 166−167 °C; R_f 0.59 (hexane/EtOAc 3:2); $[\alpha]_D^{22}$ −1.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05−8.02 (m, 2 H, H_{arom}), 7.60 (m, 1 H, H_{arom}), 7.48−7.41 (m, 6 H, H_{arom}), 7.38−7.29 (m, 8 H, H_{arom}), 6.96−6.93 (m, 2 H, H_{arom}), 4.88 (d, 1H, *J* = 10.3 Hz, CH_2Ph), 4.76 (d, overlapped, *J* = 10.3 Hz, CH_2Ph), 4.76−4.67 (d, overlapped, 2 × CH_2Ph), 4.64−4.54 (m, overlapped, H-6a, H-6b), 4.58 (m, overlapped, H-1), 4.04 (t, 1H, $J_{3,4}$ = 2.3 Hz, $J_{4,5}$ = 2.3 Hz, H-4), 3.75 (m, overlapped, H-5), 3.72 (m, overlapped, H-2), 3.59 (dd, 1H, $J_{2,3}$ = 8.9 Hz, H-3), 2.46 (m, 1H, OH-4), 2.26 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.58 (COPh), 133.36, 132.61, 130.25, 130.10, 130.02, 129.80, 128.82, 128.61, 128.59, 128.51, 128.34, 128.14, 128.08 (C_{arom}), 88.42 (C-1), 82.54 (C-3), 77.31 (C-2), 76.04 (CH_2Ph), 75.98 (C-5), 72.75 (CH_2Ph), 67.16 (C-4), 64.14 (C-6), 21.32 (CH_3); HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{34}H_{34}O_6NaS$ 593.1968, found 593.1969. Anal. Calcd for $C_{34}H_{34}O_6S$: C, 71.56; H, 6.00. Found: C, 71.27; H, 5.89.

*4-Methylphenyl 2,3-Di-O-benzyl-1-thio-β-D-galactopyranoside (**24**).* Preparation of this substance has been reported[32] but the crystalline compound has now been obtained for the first time and fully characterized: mp 151.0−151.5 °C (EtOH); R_f 0.07 (hexane/EtOAc 2:1); $[\alpha]_D^{22}$ −5.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.09 (m, 14H, H_{arom}), 4.84 (d, 1H, *J* = 10.4 Hz, CH_2Ph), 4.74 (d, 1H, *J* = 10.4 Hz, CH_2Ph), 4.73−4.66 (m, 2H, CH_2Ph), 4.58 (d, 1H, $J_{1,2}$ = 9.6 Hz, H-1), 4.04−4.03 (m, 1H, H-4), 3.98−3.92 (m, 1H, H-6a), 3.81−3.75 (m, 1H, H-6b), 3.71 (t, 1H, $J_{2,3}$ = 9.4 Hz, H-2), 3.57 (dd, 1H, $J_{3,4}$ = 3.2 Hz, H-3), 3.47−3.44 (m, 1H, H-5), 2.64 (d, 1H, $J_{4,OH-4}$ = 1.1 Hz, OH-4) 2.31 (s, 3H, CH_3(STol)), 2.25 (dd, 1H, $J_{6a,OH-6}$ = 4.1 Hz, $J_{6b,OH-6}$ = 8.7 Hz, OH-6), agreed with data published;[31,32] ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.36, 137.98, 137.73, 132.73, 129.93, 129.85, 128.78, 128.58, 128.45, 128.28, 128.11, 128.03 (C_{arom}), 88.06 (C-1), 82.64 (C-3), 78.15 (C-5), 77.20 (C-2), 75.92 (CH_2Ph), 72.45 (CH_2Ph), 67.53 (C-4), 62.93 (C-6), 21.31 (CH_3(STol)), agreed with references;[31] HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{27}H_{30}O_5NaS$ 489.1712, found 489.1716. Anal. Calcd for $C_{27}H_{30}O_5S$: C, 69.50; H, 6.48. Found: C, 69.25; H, 6.39.

*4-Methylphenyl 2,3-Di-O-benzyl-4,6-O-di-tert-butylsilanediyl-1-thio-β-D-galactopyranoside (**16**).* Preparation of this substance has been reported,[23] but the crystalline compound has now been obtained for the first time and fully characterized: mp 118−118.5 °C (white needles, EtOH); R_f 0.32 (toluene); $[\alpha]_D^{22}$ +10.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48−7.06 (m, 14 H, H_{arom}), 4.93−4.87 (m, 2H, CH_2Ph), 4.77 (d, 1H, *J* = 12.0 Hz, CH_2Ph), 4.69 (d, 1H, *J* = 12.0 Hz, CH_2Ph), 4.58 (d, 1H, $J_{1,2}$ = 9.8 Hz, H-1), 4.48 (d, 1H, $J_{3,4}$ = 2.7 Hz, H-4), 4.20 (dd, 1H, $J_{5,6a}$ = 1.6 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6a), 4.15 (dd, 1H, $J_{5,6b}$ = 2.2 Hz, H-6b), 3.83 (t, 1H, $J_{2,3}$ = 9.6 Hz, H-2), 3.46 (dd, 1H, H-3), 3.23 (bs, 1H, H-5), 2.31 (s, 3H, CH_3(STol)), 1.14 (s, 9H, $C(CH_3)_3$), 1.08 (s, 9H, $C(CH_3)_3$);[23] ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.65, 138.61, 137.70, 133.07, 131.17, 129.70, 128.65, 128.62, 128.50, 128.00, 127.90 (C_{arom}), 89.27 (C-1), 83.06 (C-3), 77.53 (C-2), 76.10 (CH_2Ph), 74.95 (C-5), 71.20 (CH_2Ph), 70.19 (C-4), 67.61 (C-6), 27.91 ($C(CH_3)_3$), 27.85 ($C(CH_3)_3$), 23.63 ($C(CH_3)_3$), 21.33 (CH_3(STol)), 20.94 ($C(CH_3)_3$), agreed with references;[23] HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{35}H_{47}O_5SSi$ 607.2914, found 607.2903. Anal. Calcd for $C_{35}H_{46}O_5SSi$: C, 69.27; H, 7.64. Found: C, 69.52; H, 7.64.

*2-[2-(2-Azidoethoxy)ethoxy]ethyl 2,3-Di-O-benzyl-1-thio-α-D-galactopyranoside (**25**).* AgOTf (0.26 g, 1.00 mmol) was added at 0 °C slowly in four portions to a solution of thioglycoside **16**[23] (6.06 g, 10.00 mmol), linker **17**[14] (1.93 g, 11.00 mmol), and *N*-iodosuccinimide (6.76 g, 30.00 mmol) in DCM (100 mL), contained in a flask equipped with a thermometer immersed in the reaction mixture. Reaction temperature was monitored and kept at 0 °C for 2 h. After dilution with DCM (200 mL), the yellow precipitate (AgI) was removed by filtration, and the filtrate was washed with a 1:1 mixture of saturated, aqueous solutions of $Na_2S_2O_3$/$NaHCO_3$. The aqueous layer was backwashed with DCM (3 × 100 mL), and the DCM layer was dried and concentrated. Chromatography (120 g of silica, toluene/acetone 15:1) yielded an anomeric mixture in which the α-isomer largely predominated. With the aid of pyridine (total volume, 12 mL), the mixture was transferred into an HF-resistant vessel and cooled to 0

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°C, HF in pyridine (70 wt %, 4.5 mL) was added dropwise with stirring, and the stirring at room temperature was continued for 4 d, when TLC (DCM/acetone 4:1) showed that the reaction was complete. For monitoring of the progress of the reaction, a portion (50 μL) was transferred into an HF-resistant tube, and EtOAc (0.5 mL) was added. The solution was washed successively with $NaHCO_3$ (aq sat.) and with $CuSO_4$ (aq sat.). The reaction mixture was diluted with EtOAc (150 mL) and washed with water (150 mL). The aqueous layer was backwashed with EtOAc (3 × 75 mL), and the organic layers were combined, washed with brine (2 × 200 mL), $CuSO_4$ (aq sat., 2 × 100 mL), brine (50 mL), and (aq sat.) $NaHCO_3$/brine 1:1 (2 × 100 mL). Chromatography of the residue obtained after drying and concentration [160 g of silica, 10→25% acetone in DCM, ∼15 column volumes (CV)] yielded first a small amount (<1 mg) of a mixture where one substance predominated. The main component in the mixture, combined from several experiments, was purified by preparative TLC and identified by NMR and mass spectroscopy as the β-anomer of **25**, 2-[2-(2-azidoethoxy)ethoxy]ethyl 2,3-di-*O*-benzyl-1-thio-β-D-galactopyranoside: R_f 0.23 (DCM/acetone 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.28 (m, 10 H, H_{arom}), 4.94 (d, 1H, J = 11.2 Hz, CH_2Ph), 4.43 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1), 4.75−4.68 (m, 3H, CH_2Ph), 4.04 (dt, 1H, J = 4.3 Hz, J = 10.7 Hz, CH_2(linker)), 3.99−3.93 (m, 2H, H-4, H-6a), 3.87−3.77 (m, 2H, H-6b, CH_2(linker)), 3.71 (t, 2H, J = 4.5 Hz, 2 × CH_2(linker)), 3.67−3.58 (m, 7H, H-2, 6 × CH_2(linker)), 4.50 (dd, 1H, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 3.4 Hz, H-3), 3.47−3.45 (m, 1H, H-5), 3.33 (t, 2H, J = 5.2 Hz, CH_2(linker)), 2.63 (bs, 1H, OH-4), 2.29−2.26 (m, 1H, OH-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.87, 137.98,128.62, 128.43, 128.21, 128.07, 128.00, 120.73 (C_{arom}), 104.08 (C-1), 80.50 (C-3), 78.93 (C-2), 75.11(CH_2Ph), 74.15 (C-5), 72.65 (CH_2Ph), 70.83, 70.77, 70.68, 70.11 69.27 (CH_2(linker)), 67.52 (C-4), 62.51 (C-6), 50.76 (CH_2(linker)); HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{26}H_{39}N_4O_8$ 535.2768, found 535.2770.

Continued elution gave the α-isomer **25** (3.80 g, 7.35 mmol, 73% over two steps). R_f 0.34 (DCM/acetone 4:1); $[\alpha]_D^{22}$ +56.7 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.28 (m, 10 H, H_{arom}), 4.90 (d, 1H, $J_{1,2}$ = 4.9 Hz, H-1), 4.82−4.78 (m, 2H, CH_2Ph), 4.71−4.65 (m, 2H, CH_2Ph), 4.07 (m, 1H, H-4), 3.90 (m, overlapped, H-5), 3.89 (m, overlapped, H-3), 3.86 (m, overlapped, H-6a), 3.85 (m, overlapped, H-2), 3.76 (m, overlapped, H-6b), 3.81−3.59 (m, overlapped, 10 × CH_2(linker)), 3.35 (t, 2H, J = 5.3 Hz, 2 × CH_2(linker)), 2.68 (t, 1H, $J_{4,OH\text{-}4}$ = 2.7 Hz, OH-4), 2.52 (dd, 1H, $J_{6a,OH\text{-}6}$ = 4.2 Hz, $J_{6b,OH\text{-}6}$ = 8.4 Hz, OH-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.62, 138.30, 128.64, 128.53, 128.04, 127.94, 127.90 (C_{arom}), 97.74 (C-1), 77.54 (C-3), 75.93 (C-2), 73.29, 72.95 (CH_2Ph), 70.88, 70.65, 70.58, 70.15 (CH_2(linker)), 69.40 (C-5), 69.04 (C-4), 67.42 (CH_2(linker)), 63.07 (C-6), 50.77 (CH_2(linker)); HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{26}H_{39}N_4O_8$ 535.2768, found 535.2772. Anal. Calcd for $C_{26}H_{35}N_3O_8$: C, 60.34; H, 6.82. Found: C, 60.64; H, 6.90.

*2-[2-(2-Azidoethoxy)ethoxy]ethyl 2,3-Di-O-benzyl-6-O-tert-butyldimethylsilyl-α-D-galactopyranoside (**13**).* TBDMSCl (3.40 g, 22.50 mmol) was added at 0 °C to a solution of monosaccharide **25** (7.80 g, 15.08 mmol) and imidazole (1.70 g, 24.97 mmol) in DMF (anhydrous, 30 mL). The cooling was removed and the mixture was stirred at room temperature overnight. MeOH (3 mL) was added and, after stirring for 30 min, the solvent was removed, the residue was partitioned between brine and EtOAc. Chromatography (60 g of silica, toluene/acetone 15:1) yielded monosaccharide **13** (8.20 g, 13.0 mmol, 86%): R_f 0.28 (toluene/acetone 15:1); $[\alpha]_D^{22}$ +39.6 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.18 (m, 10 H, H_{arom}), 4.82 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 4.76−4.59 (m, 4H, CH_2Ph), 4.00 (bs, 1H, H-4), 3.81 (m, overlapped, H-2), 3.81 (m, overlapped, H-3), 3.77 (m, overlapped, H-6a), 3.69 (m, overlapped, H-6b), 3.73 (m, overlapped, H-5), 3.74−3.52 (m, overlapped, 10 × CH_2(linker)), 3.27 (t, 2H, J = 3.3 Hz, CH_2(linker)) 0.82 (s, 9H, C(CH_3)$_3$), 0.00 (s, 6H, 2 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.75, 138.55, 128.56, 128.46, 127.97, 127.89, 127.86, 127.78 (C_{arom}), 97.60 (C-1), 77.87 (C-2), 76.06 (C-3), 73.19 (CH_2Ph), 72.78 (CH_2Ph), 70.83, 70.79, 70.40, 70.17 (CH_2(linker)), 69.83 (C-5), 67.75 (C-4), 67.01 (CH_2(linker)), 62.70 (C-6), 50.78 (CH_2(linker)), 26.01 (C(CH_3)$_3$), 18.42 (C(CH_3)$_3$), −5.27 ($SiCH_3$), −5.33 ($SiCH_3$); HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{32}H_{53}N_4O_8Si$ 649.3633, found 649.3629. Anal. Calcd for $C_{32}H_{49}N_3O_8Si$: C, 60.83; H, 7.82; N, 6.65. Found: C, 60.89; H, 7.72; N, 6.71.

*1,3,4,6-Tetra-O-acetyl-2-O-levulinoyl-α-D-galactopyranose (**27**).* LevOH (7.10 mL, 8.05 g, 69.32 mmol) was added to a solution of monosaccharide **26**[33] (20.00 g, 57.45 mmol), EDCI (13.20 g, 68.85 mol), and DMAP (0.70 g, 5.73 mmol) in DCM (100 mL). The reaction was stirred at room temperature overnight. The mixture was diluted with DCM (500 mL) and washed successively with brine (500 mL), $NaHCO_3$ (500 mL), and brine (500 mL). Chromatography of the residue obtained upon concentration of the organic phase (500 g of silica, toluene/acetone 9:1) gave monosaccharide **27** (27.00 g, 44.25 mmol, 77%): R_f 0.23 (toluene/acetone 9:1); $[\alpha]_D^{22}$ +93.0 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 (d, 1H, $J_{1,2}$ = 3.3 Hz, H-1), 5.49 (dd, 1H, $J_{4,5}$ = 1.2 Hz, H-4), 5.37 (dd, 1H, $J_{3,4}$ = 3.0 Hz, H-3), 5.32 (dd, 1H, $J_{2,3}$ = 10.9 Hz, H-2), 4.34 (ddd, 1H, $J_{5,6a}$ = 6.8 Hz, $J_{5,6b}$ = 6.8 Hz, H-5), 4.14−4.06 (m, 2H, H-6a, H-6b), 2.83−2.41 (m, 4H, CH_2(Lev)), 2.17 (s, 3H, CH_3(Ac)), 2.17 (s, 3H, CH_3(Lev)), 2.16 (s, 3H, CH_3(Ac)), 2.04 (s, 3H, CH_3(Ac)), 2.04 (s, 3H, CH_3(Ac)), agreed with ref 21; ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.12 (CH_2COCH_3), 171.88, 170.52, 170.43, 170.28, 169.13 (4 × $OCOCH_3$, $OCOCH_2$), 89.82 (C-1), 68.94 (C-5), 67.65 (C-4), 67.37 (C-3), 66.86 (C-2), 61.42 (C-6), 37.84 (CH_2(Lev)), 29.89 (CH_3(Lev)), 27.79 (CH_2(Lev)), 21.09, 20.84, 20.81, 20.79 (CH_3(Ac)); HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{19}H_{30}NO_{12}$ 464.1768, found 464.1775. Anal. Calcd for $C_{19}H_{26}O_{12}$: C, 51.12; H, 5.87. Found: C, 51.29; H, 5.86.

*Ethyl 3,4,6-Tri-O-acetyl-2-O-levulinoyl-β-D-galactopyranosyl-(1→3)-(R)-4,6-O-benzylidene-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (**28**).* A solution of donor **14**[21] (2.74 g, 5.88 mmol) in DCM (anhydrous, 12 mL) was added dropwise to a mixture of acceptor **15**[22] (1.78 g, 3.92 mmol), *sym*-collidine (0.70 mL, 0.64 g, 5.29 mmol), and AgOTf (1.71 g, 6.66 mmol) in DCM (anhydrous, 46 mL) while the inner temperature of the reaction mixture was kept between −35 and −30 °C. When the addition was complete, the temperature was increased during 80 min to −10 °C. TEA (0.84 mL, 0.61 g, 6.00 mmol) was added, and the mixture was diluted with DCM (150 mL) and filtered through a Celite pad. After concentration of the filtrate, chromatography (120 g of silica, 16% EtOAc−toluene, 10 CV, 16% →30% EtOAc in toluene, 10 CV) gave disaccharide **28** (2.73 g, 3.25 mmol, 83%): R_f 0.17 (hexane/acetone 2:1); $[\alpha]_D^{22}$ −20.0 (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (d, 1H, J = 7.6 Hz, NH), 7.52−7.33 (m, 5 H, H_{arom}), 5.57 (s, 1H, C*H*Ph), 5.40 (d, 1H, $J_{1,2}$ = 10.5 Hz, H-1), 5.36 (bd, 1H, $J_{3',4'}$ = 3.0 Hz, H-4′), 5.21 (dd, 1H, $J_{1',2'}$ = 8.1 Hz, $J_{2',3'}$ = 10.6 Hz, H-2′), 4.94 (dd, 1H, H-3′), 4.74 (t, 1H, J = 9.2 Hz, H-3), 4.60 (d, 1H, H-1′), 4.36 (dd, 1H, $J_{5,6a}$ = 4.8 Hz, $J_{6a,6b}$ = 10.6 Hz, H-6a), 4.21 (dd, 1H, $J_{5',6'a}$ = 7.8 Hz, $J_{6'a,6'b}$ = 11.1 Hz, H-6′a), 3.99 (dd, 1H, $J_{5',6'b}$ = 6.0 Hz, H-6′b), 3.88 (m, 1H, H-5′), 3.76 (bt, 1H, $J_{5,6b}$ = 10.0 Hz, H-6b), 3.64 (t, $J_{4,5}$ = 9.4 Hz, H-4), 3.60 (dt, H-5), 3.50 (dt, 1H, H-2), 3.08 (m, 1H, CH_2(Lev)), 2.82−2.70 (m, overlapped, CH_2 (SEt)), 2.73 (m, overlapped, CH_2(Lev)), 2.28 (m, overlapped, CH_2(Lev)), 2.25 (s, overlapped, CH_3(Lev)), 2.09 (s, 3H,CH_3(Ac)), 2.00 (s, 3H, CH_3(Ac)), 1.96 (s, 3H, CH_3(Ac)), 1.29 (t, 2H, J = 7.5 Hz, CH_3(SEt)); ^{13}C NMR (150 MHz, $CDCl_3$) δ 209.55 (CH_2COCH_3), 101.73, 170.62, 170.53, 170.25 (3 × $OCOCH_3$, $OCOCH_2$), 162.40 (NHCO), 137.42, 129.12, 128.25, 126.17 (C_{arom}), 101.69 (C-1′), 100.87 (C*H*Ph), 92.67 (CCl_3) 82.03 (C-1), 79.37 (C-4), 77.02 (C-3), 70.94 (C-3′), 70.82 (C-5), 70.64 (C-5′), 69.62 (C-2′), 68.68 (C-6), 66.96 (C-4′), 61.17 (C-6′), 58.68 (C-2), 38.12 (CH_2(Lev)), 30.23 (CH_3(Lev)), 27.79 (CH_2(Lev)), 24.71 (CH_2(SEt)), 20.91, 20.88 20.82 (CH_3(Ac)), 15.44 (CH_3(SEt)); HRMS (ESI) m/z [M + NH_4]$^+$ calcd for $C_{34}H_{46}N_2O_{15}SCl_3$ 859.1684, found 859.1685. Anal. Calcd for $C_{34}H_{42}NO_{15}SCl_3$: C, 48.43; H, 5.02; N,1.66. Found: C, 48.37; H, 5.13; N, 1.62.

*2-[2-(2-Azidoethoxy)ethoxy]ethyl 3,4,6-Tri-O-acetyl-2-O-levulinoyl-β-D-galactopyranosyl-(1→3)-(R)-4,6-O-benzylidene-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1→4)-2,3-di-O-benzyl-6-O-tert-butyldimethylsilyl-α-D-galactopyranoside (**29**).* Donor **28**

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(84.1 mg, 0.10 mmol), acceptor **13**, molecular sieves (4 Å, 0.01 g), and DCM (2 mL) were stirred at room temperature for 0.5 h. The mixture was cooled to −30 °C, and *N*-iodosuccinimide (16.8 mg, 0.075 mmol) and AgOTf (6.4 mg, 0.025 mmol) were added. The reaction temperature was increased to −5 °C within 1.5 h, and TEA (0.05 mL, 36.3 mg, 0.36 mmol) was added. After concentration, preparative TLC (toluene/EtOAc 5:1, three developments) gave trisaccharide **29** (40.0 mg, 0.028 mmol, 28%) and oxazoline **30** (8.0 mg, 0.010 mmol, 10%). Further elution gave acceptor **13** (8.0 mg, 0.013 mmol, 13%). Data for trisaccharide **29**: R_f 0.17 (toluene/EtOAc 4:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (d, 1H, J = 7.3 Hz, NH), 7.53−7.26 (m, 15 H, H_{arom}), 5.55 (s, 1H, C*H*Ph), 5.32 (d, 1H, $J_1{}^{II}{}_{,2}{}^{II}$ = 8.3 Hz, H-1^{II}), 5.35 (d, 1H, $J_3{}^{III}{}_{,4}{}^{III}$ = 3.1 Hz, H-4^{III}), 5.18 (dd, 1H, $J_1{}^{III}{}_{,2}{}^{III}$ = 7.9 Hz, $J_2{}^{III}{}_{,3}{}^{III}$ = 10.5 Hz, H-2^{III}), 4.94 (d, overlapped, $J_1{}^{I}{}_{,2}{}^{I}$ = 3.6 Hz, H-1^I), 4.92 (dd, 1H, H-3^{III}), 4.84 (d, 1H, J = 12.1 Hz, C*H*$_2$Ph), 4.71 (d, 1H, J = 11.6 Hz, C*H*$_2$Ph), 4.64 (m, overlapped, H-3^{II}), 4.62 (m, overlapped, 1 × C*H*$_2$Ph), 4.61 (m, overlapped, 1 × C*H*$_2$Ph), 4.61 (m, overlapped, H-1^{III}), 4.24 (dd, 1H, $J_5{}^{II}{}_{,6a}{}^{II}$ = 4.8 Hz, $J_{6a}{}^{II}{}_{,6b}{}^{II}$ = 10.3 Hz, H-6a^{II}), 4.18 (dd, 1H, $J_5{}^{III}{}_{,6a}{}^{III}$ = 7.8 Hz, $J_{6a}{}^{III}{}_{,6b}{}^{III}$ = 10.9 Hz, H-6a^{III}), 4.01 (dd, 1H, $J_5{}^{III}{}_{,6b}{}^{III}$ = 5.9 Hz, H-6b^{III}), 3.92 (dd, 1H, $J_2{}^{I}{}_{,3}{}^{I}$ = 9.8 Hz, H-2^I), 3.84 (m, 1H, H-5^{III}), 3.82 (m, overlapped, H-3^I), 3.79 (m, overlapped, H-4^I), 3.76 (m, overlapped, 1 × CH_2(linker)), 3.69 (m, overlapped, H-5^I), 3.68 (m, overlapped, H-6b^{II}), 3.60 (m, overlapped, H-4^{II}), 3.64−3.58 (m, overlapped, H-6a^I, H-6b^I), 3.70−3.56 (m, overlapped, 9 × CH_2(linker)), 3.40 (m, overlapped, H-5^{II}), 3.39 (m, overlapped, H-2^{II}), 3.32 (t, 2H, J = 5.3 Hz, CH_2(linker)), 2.95 (ddd, 1H, J = 3.0, 10.0, 18.7 Hz, CH_2(Lev)), 2.73 (ddd, 1H, J = 3.0, 10.2, 17.2 Hz, CH_2(Lev)), 2.64 (ddd, 1H, J = 3.1, 6.3, 18.7 Hz, CH_2(Lev)), 2.35 (ddd, 1H, J = 3.3, 6.4, 17.2 Hz, CH_2(Lev)), 2.15, 2.09, 2.00 1.97 (CH_3(Lev), CH_3(Ac)), 0.88 (S, 9H, SiC$(CH_3)_3$), 0.04 (s, 3H, $SiCH_3$), 0.03 (s, 3H, $SiCH_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 208.42 (CH_2COCH_3), 171.83, 170.56, 170.48, 170.27 (3 × O $COCH_3$, $OCOCH_2$), 162.02 ($NHCOCH_3$), 139.13, 138.89, 137.47, 129.11, 128.61, 128.57, 128.43, 128.24, 127.99, 127.66, 127.54, 126.18 (C_{arom}), 101.45 (C-1^{III}), 100.89 (*C*HPh), 99.13 (C-1^{II}), 97.36 (C-1^I), 93.02 (CCl_3), 79.34 (C-4^{II}), 77.79 (C-3^I), 77.38 (C-2^I), 76.46 (C-3^{II}), 74.53 (C-4^I), 73.81, 72.94 (CH_2Ph), 71.31 (C-5^I), 70.88, 70.79 (CH_2(linker)), 70.94 (C-3^{III}), 70.64 (C-5^{III}), 70.38 (CH_2(linker)), 70.18 (CH $_2$(linker)), 69.67 (C-2^{III}), 68.74 (C-6^{II}), 67.04 (C-4^{III}), 66.91 (CH_2(linker)), 65.86 (C-5 ^{II}), 63.53 (C-6^I), 61.16 (C-6^{III}), 59.80 (C-2^{II}), 50.81 (CH_2(linker)), 37.97 (CH_2(Lev)), 30.01 (CH_3(Lev)), 27.77 (CH_2(Lev)), 26.12 (C(*C*H$_3$)$_3$), 20.87, 20.84, 20.76 (CH_3(Ac)), 18.50 (C(*C*H$_3$) $_3$), −4.9 (Si(*C*H$_3$)$_2$). HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{64}H_{89}N_5O_{23}SiCl_3$ 1428.4773, found 1428.4778.

When base was used in a similar glycosylation, oxazoline **30** was the major product: ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.35 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1^I); ^{13}C NMR (150 MHz, $CDCl_3$) δ 105.79 (C-1^I); HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{32}H_{37}NO_{15}Cl_3$ 780.1229, found 780.1228.

*Ethyl 3,4,6-Tri-O-acetyl-2-O-levulinoyl-β-D-galactopyranosyl-(1→3)-6-O-benzyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (**12**).* Et_3SiH (11.36 mL, 71.12 mmol) and BF_3·OEt_2 (2.91 mL, 3.35 g, 23.60 mmol) were added at 0 °C to a solution of disaccharide **28** (9.90 g, 11.77 mmol) in DCM (180 mL). The mixture was stirred at 0 °C for 3.5 h, neutralized with Et_3N (3.61 mL, 2.62 g, 25.89 mmol), diluted with DCM (300 mL), and washed with a 1:1 mixture of saturated aqueous solutions of $Na_2S_2O_3$ and $NaHCO_3$ (500 mL). The aqueous layer was backwashed with DCM (3 × 200 mL). After drying of CH_2Cl_2 solutions and concentration, chromatography (120 g of silica, acetone in toluene 11%→13%, 15 CV) yielded disaccharide **12** (6.70 g, 7.95 mmol, 67%). Further elution gave **28** (1.00 g, 1.19 mmol, 10%), raising the yield of **12** to 74% (based on the starting material consumed): R_f 0.34 (toluene/acetone 6:1); $[\alpha]_D^{22}$ +14.9 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, 1H, J = 7.2 Hz, NH), 7.37−7.26 (m, 5 H, H_{arom}), 5.38 (dd, 1H, $J_{4',5'}$ = 0.9 Hz, $J_{3',4'}$ = 3.4 Hz, H-4′), 5.35 (d, 1H, $J_{1,2}$ = 10.4 Hz, H-1), 5.24 (dd, 1H, $J_{1',2'}$ = 8.1 Hz, $J_{3',2'}$ = 10.7 Hz, H-2′), 4.92 (dd, 1H, H-3′), 4.64−4.58 (m, 2H, C*H*$_2$Ph), 4.51 (d, 1H, H-1′), 4.43 (dd, 1H, $J_{2,3}$ = 7.1 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 4.13−4.11 (m, 2H, H-6′a, H-6′b), 4.00 (ddd, 1H, $J_{5',6'a}$ = 7.1 Hz, $J_{5',6'b}$ = 6.0 Hz, H-5′), 3.87 (dd, 1H, $J_{5,6a}$ = 1.1 Hz, $J_{6a,6b}$ = 10.7 Hz, H-6a), 3.68 (dd, 1H, $J_{5,6b}$ = 4.3 Hz, H-6b), 3.60−3.63 (m, 3H, OH-4, H-5, H-4), 3.45−3.38 (m, 1H, H-2), 3.16−3.11 (m, 1H, CH_2(Lev), 2.84−2.67 (m, 3H, CH_2(Lev), 2 × CH_2(SEt)), 2.60−2.53 (m, 1H, CH_2(Lev)), 2.31−2.24 (m, 4H, CH_2(Lev), CH_3(Lev)), 2.13 (s, 3H, CH_3(OAc)), 2.05 (s, 3H, CH_3(OAc)), 1.96 (s, 3H, CH_3(OAc)), 1.30 (t, 2H, CH_3(SEt)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.38 (CH_3COCH_2), 101.71, 170.66, 170.26, 170.11 (OCO), 162.36 (NHCO), 138.61, 128.49, 127.76, 127.66 (C_{arom}), 101.42 (C-1′), 82.32 (C-3), 80.92 (C-1), 79.73 (C-5), 73.62 (C*H*$_2$Ph), 71.25 (C-5′), 70.55 (C-3′), 69.89 (C-6), 69.55 (C-4), 68.84 (C-2′), 67.03 (C-4′), 61.32 (C-6′), 57.88 (C-2), 37.95 (CH_2(Lev)), 30.27 (CH_3(Lev)), 27.65 (CH_2(Lev)), 24.55 (CH_2(SEt)), 20.77 (2 × CH_3(OAc)), 20.72 (CH_3(OAc)), 15.48 (CH_3(SEt)); HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{34}H_{48}N_2O_{15}SCl_3$ 861.1841, found 861.1831. Anal. Calcd for $C_{34}H_{44}NO_{15}SCl_3$: C, 48.32; H, 5.25; N,1.66. Found: C, 48.28; H, 5.30; N, 1.65.

*2-[2-(2-Azidoethoxy)ethoxy]ethyl 3,4,6-Tri-O-acetyl-2-O-levulinoyl-β-D-galactopyranosyl-(1→3)-6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→4)-2,3-di-O-benzyl-6-O-tert-butyldimethylsilyl-α-D-galactopyranoside (**32**).* A mixture of donor **12** (3.40 g, 4.03 mmol), acceptor **13** (2.55 g, 4.03 mmol), molecular sieves (4 Å, 7.06 g), and DCM (130 mL) was stirred at room temperature for 15 min. The mixture was cooled to −50 °C, and *N*-iodosuccinimide (0.87 g, 3.87 mmol) was added. A solution of AgOTf (5.28 mL, 0.1 M in toluene, 0.14 g, 0.53 mmol) was added dropwise. The reaction temperature was increased to −35 °C within 2 h, and TEA (0.62 mL, 0.45 g, 4.44 mmol) was added. After addition of DCM (200 mL), the precipitate that formed (AgI) was filtered off, and the filtrate was washed with a 1:1 mixture of saturated aqueous solutions of $Na_2S_2O_3$ and $NaHCO_3$). The aqueous layer was backwashed with DCM (3 × 100 mL), the combined DCM solutions were dried and concentrated, and chromatography (40 g of silica, 14% acetone in toluene) yielded trisaccharide **32** (4.48 g, 3.17 mmol, 79%) and acceptor **13** (0.16 g, 0.25 mmol, 6%): R_f 0.32 (toluene/acetone 6:1); $[\alpha]_D^{22}$ +31.2 (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, 1H, J = 7.0 Hz, NH), 7.37−7.22 (m, 15 H, H_{arom}), 5.36 (dd, 1H, $J_3{}^{III}{}_{,4}{}^{III}$ = 3.4 Hz, $J_4{}^{III}{}_{,5}{}^{III}$ = 0.9 Hz, H-4^{III}), 5.25 (d, 1H, $J_1{}^{II}{}_{,2}{}^{II}$ = 8.5 Hz, H-1^{II}), 5.20 (dd, 1H, $J_1{}^{III}{}_{,2}{}^{III}$ = 8.0 Hz, $J_2{}^{III}{}_{,3}{}^{III}$ = 10.7 Hz, H-2^{III}), 4.97 (d, 1H, $J_1{}^{I}{}_{,2}{}^{I}$ = 3.3 Hz, H-1^I), 4.89 (dd, 1H, H-3^{III}), 4.77 (d, 1H, J = 12.1 Hz, C*H*$_2$Ph), 4.70 (d, 1H, J = 11.8 Hz, C*H*$_2$Ph), 4.64 (d, 1H, J = 11.8 Hz, C*H*$_2$Ph), 4.61 (d, 1H, J = 12.1 Hz, C*H*$_2$Ph), 4.56−4.52 (m, 2H, C*H*$_2$Ph), 4.46 (d, 1H, H-1^{III}), 4.21 (dd, 1H, $J_2{}^{II}{}_{,3}{}^{II}$ = 10.0 Hz, $J_3{}^{II}{}_{,4}{}^{II}$ = 8.0 Hz, H-3^{II}), 4.14 (dd, 1H, $J_5{}^{III}{}_{,6a}{}^{III}$ = 7.5 Hz, $J_{6a}{}^{III}{}_{,6b}{}^{III}$ = 11.5 Hz, H-6a^{III}), 4.10 (dd, 1H, $J_5{}^{III}{}_{,6b}{}^{III}$ = 5.8 Hz, H-6b^{III}), 3.97−3.96 (m, 1H, H-5^{III}), 3.96 (d, 1H, H-4^I), 3.87 (dd, 1H, $J_2{}^{I}{}_{,3}{}^{I}$ = 10.0 Hz, H-2^I), 3.83 (dd, 1H, $J_3{}^{I}{}_{,4}{}^{I}$ = 2.7 Hz, H-3^I), 3.80 (dd, 1H, $J_5{}^{II}{}_{,6a}{}^{II}$ = 1.7 Hz, $J_{6a}{}^{II}{}_{,6b}{}^{II}$ = 10.9 Hz, H-6a^{II}), 3.74 (m, overlapped, H-5^I), 3.78−3.71 (m, overlapped, H-6a^I, H-6b^I), 3.67−3.55 (m, 10H, CH_2(linker)), 3.60 (m, overlapped, H-6b^{II}), 3.48 (dd, 1H, $J_4{}^{II}{}_{,5}{}^{II}$ = 10.0 Hz, H-4^{II}), 3.42 (ddd, 1H, $J_5{}^{II}{}_{,6b}{}^{II}$ = 5.9 Hz, H-5^{II}), 3.37 (ddd, 1H, H-2^{II}), 3.29 (t, 2H, J = 5.3 Hz, CH_2(linker)), 2.94 (ddd, 1H, J = 3.4, 10.0, 18.7 Hz, CH_2(Lev)), 2.80 (ddd, 1H, J = 3.4, 10.0, 17.4 Hz, CH_2(Lev)), 2.63 (ddd, 1H, J = 3.5, 6.4, 18.7 Hz, CH_2(Lev)), 2.36 (ddd, 1H, J = 3.5, 6.4, 17.4 Hz, CH_2(Lev)), 2.18, 2.12, 2.05, 1.99 (CH_3(Lev), 3 × CH $_3$(Ac)), 0.85 (S, 9H, C$(CH_3)_3$), 0.00 (s, 6H, 2 × CH $_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 208.15 (CH_2COCH_3), 171.87, 170.65, 170.30 × 2 (3 × $OCOCH_3$, $OCOCH_2$), 162.00 ($NHCOCH_3$), 139.17, 138.95, 138.57, 128.57, 128.55, 128.46, 128.44, 127.87, 127.65, 127.58 (C_{arom}), 101.25 (C-1^{III}), 98.58 (C-1^{II}), 97.23 (C-1^I), 93.09 (CCl_3(TCA)), 82.12 (C-3^{II}), 77.82 (C-3^I), 77.48 (C-2^I), 75.28 (C-5^{II}), 74.32 (C-4^I), 73.78, 73.41, 73.00 (*C*H$_2$Ph), 71.62 (C-5^I), 71.21 (C-5^{III}), 70.92, 70.85 (CH_2(linker)), 70.58 (C-3^{III}), 70.39 (CH_2(linker)), 70.32 (C-6 ^{II}), 70.21 (CH_2(linker)), 69.56 (C-4^{II}), 68.71 (C-2^{III}), 67.02 (C-4^{III}), 66.86 (CH_2(linker)), 64.19 (C-6^I), 61.32 (C-6^{III}), 58.47 (C-2^{II}), 50.85 (CH_2(linker)), 37.92 (CH_2(Lev)), 30.22 (CH_3(Lev)), 27.74 (CH_2(Lev)), 26.11 (C(*C*H$_3$)$_3$), 2 × 20.84, 20.75 (3 × CH $_3$(Ac)), 18.47 (*C*(CH$_3$)$_3$), 0.21 (Si(CH_3)$_2$); HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{64}H_{91}N_5O_{23}SiCl_3$ 1430.4934, found 1430.4944. Anal. Calcd for $C_{64}H_{87}N_4O_{23}SiCl_3$: C, 54.33; H, 6.20; N, 3.96. Found: C, 54.62; H, 6.25; N, 3.91.

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*2-[2-(2-Azidoethoxy)ethoxy]ethyl 3,4,6-Tri-O-acetyl-2-O-levulinoyl-β-D-galactopyranosyl-(1→3)-4-O-acetyl-6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→4)-2,3-di-O-benzyl-6-O-tert-butyldimethylsilyl-α-D-galactopyranoside (**33**).* Trisaccharide **32** (20.0 mg, 0.014 mmol) was acetylated with pyridine (0.2 mL) and Ac_2O (0.1 mL) conventionally. The crude product was eluted from a small column of silica gel and dried at 50 °C/2 kPa overnight to give trisaccharide **33** (20.4 mg, 0.014 mmol) in virtually theoretical yield: R_f 0.20 (toluene/acetone 8:1); $[\alpha]_D^{22}$ +27.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, 1H, *J* = 6.15 Hz, NH), 7.35−7.22 (m, 15 H, H_{arom}), 5.31 (bd, 1H, $J_{3^{III},4^{III}}$ = 3.4 Hz, H-4^{III}), 5.19 (d, 1H, $J_{1^{II},2^{II}}$ = 8.4 Hz, H-1^{II}), 5.02 (dd, 1H, $J_{1^{III},2^{III}}$ = 7.9 Hz, $J_{2^{III},3^{III}}$ = 10.5 Hz, H-2^{III}), 4.95 (d, 1H, $J_{1^{I},2^{I}}$ = 3.5 Hz, H-1^{I}), 4.84 (dd, overlapped, H-4^{II}), 4.83 (dd, 1H, H-3^{III}), 4.78 (d, 1H, *J* = 11.9 Hz, CH_2Ph), 4.67 (d, 1H, *J* = 11.5 Hz, CH_2Ph), 4.63 (d, 1H, *J* = 11.18 Hz, CH_2Ph), 4.61 (d, 1H, *J* = 10.1 Hz, CH_2Ph), 4.47−4.44 (m, 2H, CH_2Ph), 4.45 (d, overlapped, H-1^{III}), 4.37 (t, 1H, $J_{2^{II},3^{II}}$ = 9.3 Hz, $J_{3^{II},4^{II}}$ = 9.3 Hz, H-3^{II}), 4.10 (dd, 1H, $J_{5^{III},6a^{III}}$ = 6.4 Hz, $J_{6a^{III},6b^{III}}$ = 10.9 Hz, H-6a^{III}), 4.07 (dd, 1H, $J_{5^{III},6b^{III}}$ = 7.4 Hz, H-6b^{III}), 3.88 (d, 1H, $J_{3^{I},4^{I}}$ = 3.0 Hz, H-4^{I}), 3.87 (dd, 1H, $J_{2^{I},3^{I}}$ = 10.0 Hz, H-2^{I}), 3.83 (dd, 1H, $J_{3^{I},4^{I}}$ = 3.5 Hz, H-3^{I}), 3.77−3.74 (m, 1H, CH_2(linker)), 3.73−3.70 (m, 1H, H-5^{I}), 3.68−3.67 (m, 2H, H-6a^{I}, H-6b^{I}), 3.66−3.65 (m, 1H, CH_2(linker)), 3.51 (dd, 1H, $J_{5^{II},6a^{II}}$ = 3.3 Hz, $J_{6a^{II},6b^{II}}$ = 10.6 Hz, H-6a^{II}), 3.61−3.57 (m, 2H, CH_2(linker)), 3.59 (m, overlapped, H-5^{II}), 3.56−3.54 (m, 2H, CH_2(linker)), 3.48 (dd, 1H, $J_{5^{II},6a^{II}}$ = 5.6 Hz, H-6b^{II}), 3.42 (bdt, 1H, H-2^{II}), 3.28 (t, 2H, *J* = 5.2 Hz, CH_2(linker)), 2.94−2.88 (m, 1H, CH_2(Lev)), 2.73−2.64 (m, 2H, CH_2(Lev)), 2.38−2.33 (m, 1H, CH_2(Lev)), 2.15, 2.10, 2.04, 1.95, 1.94 (CH_3(Lev), 4 × CH_3(Ac)), 0.84 (S, 9H, C$(CH_3)_3$), 0.00 (s, 6H, 2 × CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 208.04 (CH_2COCH_3), 171.47, 170.48, 170.29, 170.28, 169.72 (4 × $OCOCH_3$, $OCOCH_2$), 161.82 ($NHCOCH_3$), 139.06, 138.88, 137.98, 128.56, 128.54, 128.48, 128.40, 127.91, 127.87, 127.63, 127.55 (C_{arom}), 101.16 (C-1^{III}), 98.67 (C-1^{II}), 97.08 (C-1^{I}), 92.86 (CCl_3(TCA)), 77.74 (C-3^{I}), 77.44 (C-2^{I}), 76.6 (C-3^{II}), 74.67 (C-4^{I}), 73.77, 73.58 (CH_2Ph), 73.16 (C-5^{II}), 72.74 (CH_2Ph), 71.46 (C-5^{I}), 70.86 (C-3^{III}), 70.86 (C-6^{II}), 70.77, (CH_2(linker)), 70.56 (C-5^{III}), 70.36 (CH_2(linker)), 70.31 (C-4^{II}), 70.15 (CH_2(linker)), 69.13 (C-2^{III}), 66.97 (C-4^{III}), 66.79 (CH_2(linker)), 64.08 (C-6^{I}), 61.07 (C-6^{III}), 58.99 (C-2^{II}), 50.85 (CH_2(linker)), 38.08 (CH_2(Lev)), 30.01 (CH_3(Lev)), 27.76 (CH_2(Lev)), 26.08 C$(CH_3)_3$), 21.01, 20.84, 20.80, 20.68 (3 × CH_3(Ac)), 18.44 C$(CH_3)_3$); HRMS (ESI-TOF) *m*/*z* $[M + NH_4]^+$ calcd for $C_{66}H_{93}N_5O_{24}SiCl_3$ 1472.5045, found 1472.5051. Anal. Calcd for $C_{66}H_{89}N_4O_{24}SiCl_3$: C, 54.41; H, 6.16; N, 3.85. Found: C, 54.55; H, 6.21; N, 3.78.

*2-[2-(2-Azidoethoxy)ethoxy]ethyl 3,4,6-Tri-O-acetyl-2-O-levulinoyl-β-D-galactopyranosyl-(1→3)-6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→4)-2,3-di-O-benzyl-α-D-galactopyranoside (**34**).* A solution of trisaccharide **32** (8.50 g, 6.02 mmol) in pyridine (16 mL) was treated with HF (in pyridine, 70 wt %, 4 mL) as described above for preparation of **25**. After workup, elution from a small silica gel column, and drying at (40 °C, 0.3 atm) for 2 d, trisaccharide **34** (7.80 g, 6.00 mmol) was obtained in virtually theoretical yield: R_f 0.14 (toluene/acetone 6:1); $[\alpha]_D^{22}$ +32.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (d, 1H, *J* = 6.9 Hz, NH), 7.42−7.24 (m, 15 H, H_{arom}), 5.38 (dd, 1H, $J_{3^{III},4^{III}}$ = 3.3 Hz, $J_{4^{III},5^{III}}$ = 0.8 Hz, H-4^{III}), 5.15 (d, 1H, $J_{1^{II},2^{II}}$ = 8.5 Hz, H-1^{II}), 5.20 (dd, 1H, $J_{1^{III},2^{III}}$ = 8.0 Hz, $J_{2^{III},3^{III}}$ = 10.7 Hz, H-2^{III}), 4.90 (dd, 1H, H-3^{III}), 4.88 (d, 1H, $J_{1^{I},2^{I}}$ = 1.6 Hz, H-1^{I}), 4.80 (d, 1H, *J* = 12.4 Hz, CH_2Ph), 4.73 (d, 1H, *J* = 12.0 Hz, CH_2Ph), 4.67 (d, 1H, *J* = 12.4 Hz, CH_2Ph), 4.60 (d, 1H, *J* = 8.8 Hz, CH_2Ph), 4.58 (d, 1H, *J* = 8.8 Hz, CH_2Ph), 4.49 (d, 1H, *J* = 12.0 Hz, CH_2Ph), 4.47 (d, 1H, H-1^{III}), 4.30 (dd, 1H, $J_{2^{II},3^{II}}$ = 10.0 Hz, $J_{3^{II},4^{II}}$ = 8.2 Hz, H-3^{II}), 4.15 (dd, 1H, $J_{5^{III},6a^{III}}$ = 7.5 Hz, $J_{6a^{III},6b^{III}}$ = 11.5 Hz, H-6a^{III}), 4.11 (dd, 1H, $J_{5^{III},6b^{III}}$ = 5.7 Hz, H-6b^{III}), 3.98−3.96 (m, 2H, H-4^{I}, H-5^{III}, in that order), 3.86 (m, 2H, H-2^{I}, H-3^{I}), 3.88−3.77 (m, 2H. H-5^{I}, H-6a^{I}), 3.74−3.57 (m, 10H, CH_2(linker)), 3.83 (dd, 1H, $J_{5^{II},6a^{II}}$ = 2.1 Hz, $J_{6a^{II},6b^{II}}$ = 10.3 Hz, H-6a^{II}), 3.58 (m, overlapped, H-5^{II}), 3.53 (dd, 1H, $J_{5^{II},6b^{II}}$ = 8.2 Hz, H-6b^{II}), 3.47−3.41 (m, 2H, H-6b ^{I}, H-2^{II}, in that order), 3.39 (dd, 1H, $J_{4^{II},5^{II}}$ = 9.4 Hz, H-4^{II}), 3.31 (t, 2H, *J* = 5.0 Hz, CH_2(linker)), 2.98 (ddd, 1H, *J* = 3.3, 10.5, 18.7 Hz, CH_2(Lev)), 2.82 (ddd, 1H, *J* = 3.3, 10.5, 17.6 Hz, CH_2(Lev)), 2.63 (ddd, 1H, *J* = 3.3, 6.2, 18.6 Hz, CH_2(Lev)), 2.36 (ddd, 1H, *J* = 3.3, 6.2, 17.6 Hz, CH_2(Lev)), 2.18, 2.13, 2.06, 1.98 (CH_3(Lev), 3 × CH_3(OAc)); ^{13}C NMR (150 MHz, $CDCl_3$) δ 208.33 (CH_2COCH_3), 171.76, 170.61, 2 × 170.21 (O$COCH_3$ × 3, $OCOCH_2$), 162.15 ($NHCOCH_3$), 128.60, 128.58, 128.46, 128.25, 128.02, 127.95, 127.70, 127.57 (C_{arom}), 101.23 (C-1^{III}), 99.61 (C-1^{II}), 99.75 (C-1^{I}), 92.93 (CCl_3(TCA)), 81.70 (C-3^{II}), 77.49, 76.86 (C-3^{I}, C-2^{I}), 74.32 (C-5^{II}), 74.88 (C-4^{I}), 73.70, 73.30, 73.26 (CH_2Ph), 71.28 (C-5^{III}), 70.91, 70.85 (CH_2(linker)), 70.49 (C-3^{III}), 70.43 (CH_2(linker)), 70.17 (CH_2(linker)), 70.12 (C-4^{II}), 70.07 (C-6^{II}), 69.32 (C-5^{I}), 68.64 (C-2^{III}), 67.37 (CH_2(linker)), 66.97 (C-4^{III}), 61.31 (C-6^{III}), 59.51 (C-6^{I}), 58.20 (C-2^{II}), 50.79 (CH_2(linker)), 30.20 (CH_3(Lev)), 37.83 (CH_2(Lev)), 27.67 (CH_2(Lev)), 20.80, 20.77, 20.71 (CH_3(Ac)); HRMS (ESI-TOF) *m*/*z* $[M + NH_4]^+$ calcd for $C_{58}H_{77}N_5O_{23}Cl_3$ 1316.4075, found 1316.4064. Anal. Calcd for $C_{58}H_{73}N_4O_{23}Cl_3$: C, 53.56; H, 5.66; N, 4.31. Found: C, 53.40; H, 5.63; N, 4.24.

*2-[2-(2-Azidoethoxy)ethoxy]ethyl 3,4,6-Tri-O-acetyl-2-O-levulinoyl-β-D-galactopyranosyl-(1→3)-6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→4)-(methyl 2,3-di-O-benzyl-α-D-galactopyranosid)uronate (**7**).* Diacetoxyiodobenzene (4.96 g, 15.40 mmol) and 2,2,6,6-tetramethyl-1-piperidinyloxy (0.19 g, 1.23 mmol) were added at room temperature to a solution of trisaccharide **34** (8.00 g, 6.16 mmol) in DCM (16 mL), *t*BuOH (16 mL), and water (8 mL). The mixture was sonicated for 8 h at room temperature. When TLC (R_f 0.43 and 0.33 for **34** and the intermediate acid, respectively, toluene/acetone/AcOH 15:15:1) showed the disappearance of the trisaccharide **34**, the mixture was diluted with EtOAc (160 mL) and washed with a 1:1 mixture of saturated aqueous solutions of $Na_2S_2O_3$ and NaH_2PO_4 (3 × 80 mL). The combined aqueous layer was backwashed with EtOAc (5 × 80 mL). After drying, the combined organic layers were concentrated; the residue was coevaporated with toluene (3 × 15 mL) and dissolved in DMF (30 mL). $NaHCO_3$ (7.75 g, 92.25 mmol) and MeI (5.76 mL, 13.13 g, 92.50 mmol) were added, and the mixture was sonicated at room temperature for 14 h with a needle in a septum as outlet. Another portion of MeI (5.76 mL, 13.13 g, 92.50 mmol) was added and the sonication at room temperature was continued for 8 h or more. The volatiles were removed, and the residue was partitioned between EtOAc (200 mL) and water (100 mL). The organic layer was collected, the water layer was backwashed with EtOAc (5 × 100 mL); the organic layers were combined, dried, concentrated; and chromatography (400 g of silica gel, (16% acetone in toluene, 5 CV, 16%→35% acetone, 15 CV) gave trisaccharide **7** (7.68 g, 5.79 mmol, 94%): R_f 0.12 (toluene/acetone 5:1); $[\alpha]_D^{22}$ +31.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (60 0 MHz, $CDCl_3$) δ 8.13 (d, 1H, *J* = 6.9 Hz, NH), 7.32−7.16 (m, 15 H, H_{arom}), 5.29 (dd, 1H, $J_{3^{III},4^{III}}$ = 3.3 Hz, $J_{4^{III},5^{III}}$ = 0.7 Hz, H-4^{III}), 5.22 (d, 1H, $J_{1^{II},2^{II}}$ = 8.5 Hz, H-1^{II}), 5.14 (dd, 1H, $J_{1^{III},2^{III}}$ = 7.9 Hz, $J_{2^{III},3^{III}}$ = 10.6 Hz, H-2^{III}), 4.95 (d, 1H, $J_{1^{I},2^{I}}$ = 3.1 Hz, H-1^{I}), 4.83 (dd, 1H, H-3^{III}), 4.73 (d, 1H, *J* = 12.2 Hz, CH_2Ph), 4.65 (d, 1H, *J* = 11.6 Hz, CH_2Ph), 4.59 (d, 1H, *J* = 12.3 Hz, CH_2Ph), 4.51 (d, 1H, *J* = 11.6 Hz, CH_2Ph), 4.50 (d, 1H, *J* = 12.1 Hz, CH_2Ph), 4.48 (d, 1H, *J* = 12.1 Hz, CH_2Ph), 4.42 (d, 1H, $J_{4^{I},5^{I}}$ = 1.6 Hz, H-5^{I}), 4.40 (d, 1H, H-1^{III}), 4.27 (t, 1H, H-4^{I}), 4.23 (dd, 1H, $J_{2^{II},3^{II}}$ = 9.9 Hz, $J_{3^{II},4^{II}}$ = 8.3 Hz, H-3^{II}), 4.08 (dd, 1H, $J_{5^{III},6a^{III}}$ = 7.4 Hz, $J_{6a^{III},6b^{III}}$ = 11.4 Hz, H-6a^{III}), 4.03 (dd, 1H, $J_{5^{III},6b^{III}}$ = 5.9 Hz, H-6b^{III}), 3.90 (dd, 1H, H-5^{III}), 3.86 (dd, 1H, $J_{2^{I},3^{I}}$ = 10.0 Hz, $J_{3^{I},4^{I}}$ = 3.2 Hz, H-2^{I}), 3.83 (dd, 1H, H-3^{I}), 3.74 (dd, 1H, $J_{5^{II},6a^{II}}$ = 1.7 Hz, $J_{6a^{II},6b^{II}}$ = 10.8 Hz, H-6a^{II}), 3.68−3.64 (m, 1H, CH_2(linker)), 3.57 (s, overlapped, $COOCH_3$), 3.57 (m, overlapped, H-6b^{II}), 3.58−3.45 (m, 9H, 9 × CH_2(linker)), 3.44 (dd, overlapped, H-4^{II}), 3.35 (ddd, 1H, $J_{4^{II},5^{II}}$ = 9.6 Hz, $J_{5^{II},6b^{II}}$ = 5.4 Hz, H-5^{II}), 3.25 (ddd, overlapped, H-2^{II}), 3.21 (t, 2H, *J* = 5.0 Hz, CH_2(linker)), 2.88 (ddd, 1H, *J* = 3.9, 10.2, 18.5 Hz, CH_2(Lev)), 2.70 (ddd, 1H, *J* = 3.4, 9.2, 17.0 Hz, CH_2(Lev)), 2.58 (ddd, 1H, *J* = 3.9, 6.8, 18.5 Hz, CH_2(Lev)), 2.38 (ddd, 1H, *J* = 3.4, 6.8, 17.0 Hz, CH_2(Lev)), 2.15, 2.05, 1.98, 1.90 (CH_3(Lev), 3 × CH_3(Ac)); ^{13}C NMR (150 MHz, $CDCl_3$) δ 208.14 (CH_2COCH_3), 171.79, 170.63, 170.29 × 2 (3 × $OCOCH_3$, $OCOCH_2$), 168.51, 161.90 (C-6^{I}, $NHCOCH_3$), 138.83, 138.60, 138.52, 128.61, 128.52, 128.43, 127.98, 127.83, 127.69, 127.67, 127.61 (C_{arom}), 101.23 (C-1^{III}), 98.65 (C-1^{II}), 97.68 (C-1^{I}), 92.96 (CCl_3(TCA)), 81.81 (C-3^{II}), 76.90 (C-2^{I}), 76.72

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(C-3^{I}), 75.06 (C-5^{II}), 74.69 (C-4^{I}), 73.50, 73.43, 73.27 (CH_2Ph), 71.20 (C-5^{III}), 70.84, 70.82 (CH_2(linker)), 70.59 (C-3^{III}), 70.36 (CH_2(linker)), 70.33 (C-5^{I}), 70.20 (CH_2(linker)), 69.82 (C-6^{II}), 69.19 (C-4^{II}), 68.64 (C-2^{III}), 67.90 (CH_2(linker)), 67.00 (C-4^{III}), 61.30 (C-6^{III}), 58.60 (C-2^{II}), 50.79 (CH_2(linker)), 52.38 ($COOCH_3$) 37.94 (CH_2(Lev)), 30.22 (CH_3(Lev)), 27.77 (CH_2(Lev)), 2 × 20.81, 20.73 (3 × CH_3(Ac)); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{59}H_{73}N_4O_{24}Cl_3Na$ 1349.3573, found 1349.3581. Anal. Calcd for $C_{59}H_{73}N_4O_{24}Cl_3$: C, 53.34; H, 5.54; N, 4.22. Found: C, 53.09; H, 5.44; N, 4.25.

*2-[2-(2-Azidoethoxy)ethoxy]ethyl [2,4-Di-O-benzyl-3,6-dideoxy-α-L-xylo-hexopyranosyl-(1→4)]-[3,4,6-tri-O-acetyl-2-O-levulinoyl-β-D-galactopyranosyl-(1→3)]-6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→4)-(methyl 2,3-di-O-benzyl-α-D-galactopyranosid)uronate (**9**).* A mixture of acceptor 7 (1.00 g, 0.75 mmol), molecular sieves (4 Å, 1.80 g), tetrabutylammonium bromide (0.80 g, 2.48 mmol), and DMF (anhydrous, 2 mL) was stirred at room temperature for 30 min. Donor **8**[16] (0.88 g, 2.26 mmol in 10 mL anhydrous DCM) was added, and the mixture was stirred at room temperature for 3 d. After filtration through a Celite pad and concentration, chromatography (120 g of silica, 15% acetone in toluene, 15 CV) yielded tetrasaccharide **9** (1.11 g, 0.68 mmol, 90%): R_f 0.21 (hexane/acetone 2:1); $[\alpha]_D^{22}$ +9.6 (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (bs, 1H, NH), 7.35−7.23 (m, 25 H, H_{arom}), 5.32 (dd, 1H, $J_{3^{III},4^{III}}$ = 3.5 Hz, $J_{4^{III},5^{III}}$ = 0.8 Hz, H-4^{III}), 5.16 (d, 1H, $J_{1^{II},2^{II}}$ = 8.4 Hz, H-1^{II}), 5.09 (dd, 1H, $J_{1^{III},2^{III}}$ = 8.1 Hz, $J_{2^{III},3^{III}}$ = 10.0 Hz, H-2^{III}), 5.02 (d, 1H, $J_{1^{I},2^{I}}$ = 3.1 Hz, H-1^{I}), 5.02 (d, 1H, $J_{1^{IV},2^{IV}}$ = 2.2 Hz, H-1^{IV}), 4.93 (dd, 1H, $J_{3^{III},4^{III}}$ = 3.7 Hz, H-3^{III}), 4.83 (d, 1H, H-1^{III}), 4.68 (d, 1H, J = 11.5 Hz, CH_2Ph), 4.67 (d, 1H, J = 11.4 Hz, CH_2Ph), 4.65 (d, 1H, J = 12.2 Hz, CH_2Ph), 4.58 (d, 1H, J = 11.4 Hz, CH_2Ph), 4.57 (d, 1H, J = 12.4 Hz, CH_2Ph), 4.51−4.45 (m, 6H, H-5^{IV}, H-5^{I}, 4 × CH_2Ph), 4.38 (m, 1H, H-5^{II}), 4.31 (d, 1H, J = 12.5 Hz, CH_2Ph), 4.27 (dd, 1H, $J_{4^{I},5^{I}}$ = 1.6 Hz, $J_{3^{I},4^{I}}$ = 2.8 Hz, H-4^{I}), 4.11−4.06 (m, 2H, H-6a^{III}, H-6b^{III}), 3.95 (t, J = 7.0 Hz, H-4^{II}), 3.92 (dd, 1H, $J_{2^{I},3^{I}}$ = 9.9 Hz, H-2^{I}), 3.87 (m, overlapped, 1H, H-3^{I}), 3.86 (dd, 1H, H-5^{III}), 3.85 (m, overlapped, H-2^{IV}), 3.85 (m, overlapped, 1 × CH_2(linker)), 3.72 (m, 1H, CH_2(linker)), 3.59 (s, overlapped, $COOCH_3$), 3.64−3.53 (m, 9H, CH_2(linker)), 3.64−3.61 (m, overlapped, H-3^{II}, H-6a^{II}, H-6b^{II}), 3.50 (m, 1H, H-2^{II}), 3.35 (m, 1H, H-4^{IV}) 3.30 (t, 2H, J = 5.1 Hz, CH_2(linker)), 2.80 (t, 2H, J = 6.0 Hz, CH_2(Lev)), 2.62 (ddd, 1H, J = 5.1, 6.5, 17.1 Hz, CH_2(Lev)), 2.53 (ddd, 1H, J = 6.1, 6.1, 17.1 Hz, CH_2(Lev)), 2.18 (s, 3H, CH_3(Lev)), 2.11 (ddd, 1H, $J_{2^{IV},3eq^{IV}}$ = 3.6 Hz, $J_{3eq^{IV},4^{IV}}$ = 3.6 Hz, $J_{3ax^{IV},3eq^{IV}}$ = 12.8 Hz, H-3$_{eq}^{IV}$), 2.11 (s, 3H, CH_3(Ac)), 1.99 (s, 3H, CH_3(Ac)), 1.80 (s, 3H, CH_3(Ac)), 1.77 (m, 1H, H-3$_{ax}^{IV}$), 1.23 (d, 3H, $J_{5^{IV},6^{IV}}$ = 6.2 Hz, H-6^{IV}); ^{13}C NMR (150 MHz, $CDCl_3$) δ 207.33 (CH_2COCH_3), 171.78 170.46, 170.36, 170.09 (3 × $OCOCH_3$, $OCOCH_2$), 168.43, 161.63 (C-6^{I}, $NHCOCH_3$), 138.69, 138.54, 138.37, 138.34, 138.13, 128.68, 128.60, 128.58, 128.48, 128.38, 128.13, 128.09, 127.93, 127.92, 127.84 (C_{arom}), 100.15 (C-1^{III}), 99.44 (C-1^{II}), 97.54 (C-1^{I}), 96.88 (C-1^{IV}), 92.75 (CCl_3(TCA)), 76.90 (C-2^{I}), 76.75 (C-3^{I}), 76.70 (C-3^{II}), 75.97 (C-5^{II}), 75.90 (C-4^{IV}), 75.36 (C-4^{I}), 73.89, 73.74, 73.44 (CH_2Ph), 72.91 (C-4^{II}), 71.55 (CH_2Ph), 71.17 (C-2^{IV}), 70.90 (CH_2Ph), 70.88 (2 × CH_2(linker)), 70.82 (C-5^{III}), 70.76 (C-3^{III}), 70.45 (CH_2(linker)), 70.34 (C-5^{I}), 70.23 (CH_2(linker)), 68.91 (C-6^{II}), 68.76 (C-2^{III}), 67.95 (CH_2(linker)), 67.29 (C-4^{III}), 66.46 (C-5^{IV}), 60.74 (C-6^{III}), 59.04 (C-2^{II}), 52.56 ($COOCH_3$), 50.84 (CH_2(linker)), 38.19 (CH_2(Lev)), 29.95 (CH_3(Lev)), 28.04 (CH_2(Lev)), 27.04 (C-3^{IV}), 20.88, 20.72, 20.63 (CH_3 (Ac)), 16.75 (C-6^{IV}); HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{79}H_{99}N_5O_{27}Cl_3$ 1654.5588, found 1654.5597. Anal. Calcd for $C_{79}H_{95}N_4O_{27}Cl_3$: C, 57.89; H, 5.84; N, 3.42. Found: C, 57.65; H, 6.00; N, 3.31.

*2-[2-(2-Azidoethoxy)ethoxy]ethyl [2,4-Di-O-benzyl-3,6-dideoxy-α-L-xylo-hexopyranosyl-(1→4)]-[3,4,6-tri-O-acetyl-β-D-galactopyranosyl-(1→3)]-6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→4)-(methyl 2,3-di-O-benzyl-α-D-galactopyranosid)uronate (**36**).* A solution of tetrasaccharide **9** (0.78 g, 0.48 mmol) in pyridine (6 mL) was treated dropwise with a mixture of AcOH (1.5 mL) and hydrazine hydrate (118 μl, 25 wt % in water, 29.84 mg, 0.60 mmol), and the mixture was stirred at room temperature for 2 h. Acetone (1 mL) was added and mixture was stirred at room temperature for 30 min. After concentration, chromatography (80 g, silica, 15% acetone in toluene, 15 CV) gave tetrasaccharide **36** (0.70 g, 0.45 mmol, 95%): R_f 0.24 (hexane/acetone 2:1); $[\alpha]_D^{22}$ +24.9 (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35−7.26 (m, 25 H, H_{arom}), 5.32 (dd, 1H, $J_{3^{III},4^{III}}$ = 3.6 Hz, $J_{4^{III},5^{III}}$ = 1.1 Hz, H-4^{III}), 5.24 (d, 1H, $J_{1^{II},2^{II}}$ = 7.6 Hz, H-1^{II}), 4.99 (d, 1H, $J_{1^{IV},2^{IV}}$ = 3.2 Hz, H-1^{IV}), 4.97 (d, 1H, $J_{1^{I},2^{I}}$ = 2.7 Hz, H-1^{I}), 4.83 (dd, 1H, $J_{2^{III},3^{III}}$ = 10.2 Hz, H-3^{III}), 4.77 (d, 1H, J = 11.9 Hz, CH_2Ph), 4.68 (d, 1H, J = 11.4 Hz, CH_2Ph), 4.67 (d, 1H, J = 11.9 Hz, CH_2Ph), 4.59 (d, 1H, J = 11.4 Hz, CH_2Ph), 4.55 (d, 1H, J = 12.1 Hz, CH_2Ph), 4.50 (d, 1H, $J_{4^{I},5^{I}}$ = 1.4 Hz, H-5^{I}), 4.46 (d, 1H, $J_{1^{III},2^{III}}$ = 7.8 Hz, H-1^{III}), 4.44−4.42 (m, 4H, CH_2Ph), 4.38 (dd, 1H, $J_{3^{I},4^{I}}$ = 2.0 Hz, H-4^{I}), 4.34 (d, 1H, J = 12.9 Hz, CH_2Ph), 4.34 (m, overlapped, H-3^{II}), 4.32 (m, overlapped, H-5^{IV}), 4.10 (dd, 1H, $J_{5^{III},6a^{III}}$ = 6.1 Hz, $J_{6a^{III},6b^{III}}$ = 11.2 Hz, H-6a^{III}), 4.03 (dd, 1H, $J_{5^{III},6b^{III}}$ = 7.2 Hz, H-6b^{III}), 3.98 (t, 1H, J = 8.4 Hz, H-4^{II}), 3.93−3.89 (m, 4H, CH_2(linker), H-6a^{II}, H-2^{I}, H-3^{I}), 3.83 (m, overlapped, H-5^{III}), 3.83 (m, overlapped, H-2^{IV}), 3.72 (m, overlapped, CH_2(linker)), 3.71 (dd, overlapped, $J_{5^{II},6b^{II}}$ = 2.4 Hz, $J_{6a^{II},6b^{II}}$ = 10.5 Hz, H-6b^{II}), 3.65 (dd, 1H, H-2^{III}), 3.61 (s, overlapped, $COOCH_3$), 3.67−3.53 (m, overlapped, 9 × CH_2(linker)), 3.59 (m, overlapped, H-2^{II}), 3.54 (m, overlapped, H-5^{II}), 3.39 (bs, 1H, H-4^{IV}) 3.31 (dd, 2H, J = 4.6, 5.6 Hz, CH_2(linker)), 2.13 (ddd, 1H, $J_{2^{IV},3eq^{IV}}$ = 3.6 Hz, $J_{3eq^{IV},4^{IV}}$ = 3.6 Hz, $J_{3ax^{IV},3eq^{IV}}$ = 12.9 Hz, H-3$_{eq}^{IV}$), 2.06 (s, 3H, CH_3 (OAc)), 2.00 (s, 3H, CH_3 (OAc)), 1.92 (s, 3H, CH_3 (OAc)), 1.80 (ddd, 1H, $J_{3ax^{IV},4^{IV}}$ = 2.1 Hz, $J_{2^{IV},3ax^{IV}}$ = 12.9 Hz, H-3$_{ax}^{IV}$), 1.18 (d, 3H, $J_{5^{IV},6^{IV}}$ = 6.5 Hz, H-6^{IV}); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.74 170.45, 170.13 ($OCOCH_3$), 168.52, 162.05 (C-6^{I}, $NHCOCH_3$), 138.62, 138.52, 138.42, 138.20, 138.18, 128.68, 128.66, 128.59, 128.57, 128.55, 128.40, 128.31, 128.13, 128.10, 127.97, 127.95, 127.88, 127.84, 127.82, 127.80 (C_{arom}), 100.31 (C-1^{III}), 99.32 (C-1^{II}), 97.51 (C-1^{I}), 96.62 (C-1^{IV}), 92.59 (CCl_3(TCA)), 77.94 (C-3^{II}), 76.86, 76.77 (C-2^{I}, C-3^{I}), 75.85 (C-4^{IV}), 75.43 (C-5^{II}), 75.26 (C-4^{I}), 74.11 (C-4^{II}), 73.93 (CH_2Ph), 73.36 (CH_2Ph), 72.93 (CH_2Ph), 72.67 (C-3^{III}), 71.43 (CH_2Ph), 71.36 (C-5^{III}), 71.17 (CH_2Ph), 71.10 (C-2^{IV}), 70.84 (2 × CH_2(linker)), 70.43 (CH_2(linker)), 70.28 (C-5^{I}), 70.22 (CH_2(linker)), 68.59 (C-6^{II}), 68.54 (C-2^{III}), 67.92 (CH_2(linker)), 67.30 (C-4^{III}), 67.00 (C-5^{IV}), 61.76 (C-6^{III}), 57.83 (C-2^{II}), 52.53 ($COOCH_3$), 50.82 (CH_2(linker)), 27.01 (C-3^{IV}), 20.95, 20.94, 20.68 (CH_3 (Ac)), 16.83 (C-6^{IV}); HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{74}H_{93}N_5O_{25}Cl_3$ 1556.5220, found 1556.5227. Anal. Calcd for $C_{74}H_{89}N_4O_{25}Cl_3$: C, 57.68; H, 5.82; N, 3.64. Found: C, 57.41; H, 5.90; N, 3.56.

*2-[2-(2-Azidoethoxy)ethoxy]ethyl [2,4-Di-O-benzyl-3,6-dideoxy-α-L-xylo-hexopyranosyl-(1→2)-3,4,6-tri-O-acetyl-β-D-galactopyranosyl]-(1→3)-(2,4-di-O-benzyl-3,6-dideoxy-α-L-xylo-hexopyranosyl)-(1→4)-6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→4)-(methyl 2,3-di-O-benzyl-α-D-galactopyranosid)uronate (**11**).* Acceptor **36** (0.54 g, 0.35 mmol), molecular sieves (4 Å, 0.81 g), tetrabutylammonium bromide (0.50 g, 1.55 mmol), and DMF (anhydrous, 0.9 mL) were mixed and stirred at room temperature for 30 min. Donor **8**[16] (0.55 g, 1.41 mmol in 4.5 mL anhydrous DCM) was added, and the mixture was stirred at room temperature for 3 d. After filtration through a Celite pad and concentration of the filtrate, purification (60 g of silica, 5% acetone in toluene, 1 CV, 5%→20% acetone, 10 CV, 20% acetone, 5 CV) yielded pentasaccharide **11** (0.45 g, 0.24 mmol, 68% or 86% based on acceptor consumed) and acceptor **36** (0.11 g, 0.07 mmol, 21%): R_f 0.31 (hexane/acetone 2:1); $[\alpha]_D^{22}$ +4.0 (c 0.7, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34−7.20 (m, 35 H, H_{arom}), 7.00 (d, 1H, $J_{NH^{II},2^{II}}$ = 7.6 Hz, H-NH^{II}), 5.27 (dd, 1H, $J_{3^{III},4^{II}}$ = 3.4 Hz, $J_{4^{III},5^{III}}$ = 1.0 Hz, H-4^{III}), 5.12 (d, 1H, $J_{1^{V},2^{V}}$ = 3.3 Hz, H-1^{V}), 5.09 (d, 1H, $J_{1^{II},2^{II}}$ = 8.3 Hz, H-1^{II}), 5.03 (d, 1H, $J_{1^{IV},2^{IV}}$ = 3.3 Hz, H-1^{IV}), 5.01 (d, 1H, $J_{1^{I},2^{I}}$ = 2.6 Hz, H-1^{I}), 4.88 (dd, 1H, $J_{2^{III},3^{III}}$ = 10.1 Hz, H-3^{III}), 4.75 (d, 1H, J = 11.9 Hz, CH_2Ph), 4.72 (d, 1H, $J_{1^{III},2^{III}}$ = 7.9 Hz, H-1^{III}), 4.66 (d, 1H, J = 11.3 Hz, CH_2Ph), 4.63 (d, 1H, J = 11.9 Hz, CH_2Ph), 4.62 (m, overlapped, H-5^{IV}), 4.58 (d, 1H, J = 12.4 Hz, CH_2Ph), 4.57 (d, 1H, J = 11.5 Hz, CH_2Ph), 4.57 (d, 1H, J = 12.4 Hz, CH_2Ph), 4.50 (d, 1H, J = 12.0 Hz, CH_2Ph), 4.49 (m, overlapped, H-3^{II}), 4.47−4.44 (m, 4H, 4 × CH_2Ph), 4.46 (m, overlapped, H-5^{I}), 4.40 (d, 1H, J = 11.9 Hz, CH_2Ph), 4.38 (d, 1H, J = 11.9 Hz, CH_2Ph), 4.32 (m, overlapped, H-5^{V}), 4.29 (d, 1H, J = 12.4 Hz, CH_2Ph), 4.28 (t, overlapped, $J_{2^{I},3^{I}}$ = 1.8

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Hz, $J_{3,4}^{I,I}$ = 1.8 Hz, H-4^{I}), 4.07 (dd, 1H, $J_{5,6a}^{III,III}$ = 5.9 Hz, $J_{6a,6b}^{III,III}$ = 11.1 Hz, H-6a^{III}), 4.02 (dd, 1H, $J_{5,6b}^{III,III}$ = 8.1 Hz, H-6b^{III}), 4.00 (m, overlapped, H-6a^{II}), 3.91 (t, 1H, J = 8.7 Hz, H-4^{II}), 3.88 (m, overlapped, H-2^{IV}), 3.87 (m, overlapped, H-2^{I}), 3.86 (m, overlapped, H-3^{I}), 3.86 (m, overlapped, H-2^{V}), 3.85 (dd, 1H, H-2^{III}), 3.76 (ddd, 1H, H-5^{III}), 3.72 (m, overlapped, CH_2(linker)), 3.68 (dd, 1H, $J_{5,6b}^{II,II}$ = 2.1 Hz, $J_{6a,6b}^{II,II}$ = 10.7 Hz, H-6b^{II}), 3.64−3.52 (m, overlapped, 9 × CH_2(linker)), 3.59 (m, overlapped, H-4^{V}), 3.50 (m, overlapped, H-2^{II}, H-5^{II}), 3.50 (s, overlapped, $COOCH_3$), 3.34 (bs, 1H, H-4^{IV}), 3.30 (dd, 2H, J = 4.9, 5.3 Hz, CH_2(linker)), 2.16−2.12 (m, 2H, H-3$_{eq}^{IV}$, H-3$_{eq}^{V}$, in this order), 2.02 (s, 3H, CH_3(Ac)), 1.93 (ddd, 1H, $J_{3ax,4}^{V,V}$ = 2.0 Hz, $J_{2,3ax}^{V,V}$ = 12.3 Hz, $J_{3ax,3eq}^{V,V}$ = 12.3 Hz, H-3$_{ax}^{V}$), 1.81 (ddd, 1H, $J_{3ax,4}^{IV,IV}$ = 2.0 Hz, $J_{2,3ax}^{IV,IV}$ = 12.8 Hz, $J_{3ax,3eq}^{IV,IV}$ = 12.8 Hz H-3$_{ax}^{IV}$), 1.76 (s, 3H, CH_3(Ac)), 1.68 (s, 3H, CH_3(Ac)), 1.24 (d, overlapped, $J_{5,6}^{V,V}$ = 6.4 Hz, H-6^{V}), 1.23 (d, overlapped, $J_{5,6}^{IV,IV}$ = 6.1 Hz, H-6^{IV}); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.53 169.99, 169.94 ($OCOCH_3$), 168.50, 161.25 (C-6^{I}, NHCO), 138.73, 138.70, 138.59, 138.58, 138.31, 138.10 128.71, 128.67, 128.57, 128.55, 128.52, 128.48, 128.37, 128.14, 128.12, 128.00, 127.91, 127.87, 127.77, 127.72, (C_{arom}), 101.54 (C-1^{III}), 99.59 (C-1^{II}), 98.04 (C-1^{V}), 97.47 (C-1^{I}), 97.15 (C-1^{IV}), 92.70 (CCl_3(TCA)), 77.06 (C-2^{I}), 76.56 (C-3^{I}), 76.35 (C-4^{V}), 75.81 (C-4^{IV}), 75.68 (C-5^{II}), 75.52 (C-4^{I}), 75.40 (C-3^{II}), 73.84 (CH_2Ph), 73.42 (C-3^{III}), 73.35 (C-4^{II}), 73.09 (CH_2Ph), 72.88 (C-2^{III}), 72.82 (CH_2Ph), 71.61 (CH_2Ph), 71.58 (C-2^{V}), 71.58 (CH_2Ph), 71.34 (C-2^{IV}), 70.86 (2 × CH_2(linker)), 70.69 (CH_2Ph), 70.62 (C-5^{III}), 70.44 (C-5^{I}), 70.42 (CH_2(linker)), 70.31 (CH_2Ph), 70.22 (CH_2(linker)), 68.10 (C-6^{II}), 67.92 (CH_2(linker)), 67.67 (C-4^{III}), 67.30 (C-5^{V}), 66.30 (C-5^{IV}), 60.83 (C-6^{III}), 59.85 (C-2^{II}), 52.41 ($COOCH_3$), 50.83 (CH_2(linker)), 26.90 (C-3^{V}), 26.59 (C-3^{IV}), 20.0 20.77, 20.61 (CH_3(Ac)), 16.72 (C-6^{IV}), 16.43 (C-6^{V}); HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{94}H_{115}N_5O_{28}Cl_3$ 1866.6789, found 1866.6796. Anal. Calcd for $C_{94}H_{111}N_4O_{28}Cl_3$: C, 60.99; H, 6.04; N, 3.03. Found: C, 60.84; H, 6.18; N, 3.07.

*2-[2-(2-Azidoethoxy)ethoxy]ethyl 3,4,6-Tri-O-acetyl-β-D-galactopyranosyl-(1→3)-4-O-acetyl-6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→4)-(methyl 2,3-di-O-benzyl-α-D-galactopyranosid)uronate (**37**).* Trisaccharide **7** (0.40 g, 0.30 mmol) was acetylated with pyridine (2 mL) and Ac_2O (1 mL) conventionally, and a solution of the crude product in pyridine (4 mL) was treated with a mixture of AcOH (1 mL) and hydrazine hydrate (74 μL, 25% wt. in water, 18.78 mg, 0.38 mmol), as described above for preparation of **36**. Chromatography (40 g, silica, 20% acetone in toluene, 15 CV) of the crude product gave trisaccharide **37** (0.34 g, 0.27 mmol, 90%): R_f 0.35 (toluene/acetone 3:1); $[\alpha]_D^{22}$ + 38.3 (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40−7.29 (m, 15 H, H_{arom}), 7.22 (d, 1H, J = 6.4 Hz, NH), 5.33 (dd, 1H, $J_{3,4}^{III,III}$ = 3.2 Hz, $J_{5,4}^{III,III}$ = 0.3 Hz, H-4^{III}), 5.10 (d, 1H, $J_{1,2}^{I,I}$ = 3.6 Hz, H-1^{I}), 4.93 (m, overlapped, H-4^{II}), 4.93 (d, overlapped, $J_{1,2}^{II,II}$ = 8.2 Hz, H-1^{II}), 4.89 (d, 1H, J = 10.9 Hz, CH_2Ph), 4.70 (dd, 1H, $J_{3,2}^{III,III}$ = 10.2 Hz, H-3^{III}), 4.66 (d, overlapped, J = 11.0 Hz, CH_2Ph), 4.65−4.60 (m, overlapped, 2 × CH_2Ph), 4.59 (d, 1H, $J_{4,5}^{I,I}$ = 1.6 Hz, H-5^{I}), 4.53−4.49 (m, 2H, 2 × CH_2Ph), 4.40 (dd, 1H, $J_{3,4}^{I,I}$ = 3.2 Hz, $J_{4,5}^{I,I}$ = 1.8 Hz, H-4^{I}), 4.21 (dd, 1H, $J_{5,6a}^{III,III}$ = 6.2 Hz, $J_{6a,6b}^{III,III}$ = 11.2 Hz, H-6a^{III}), 4.12 (d, 1H, $J_{1,2}^{III,III}$ = 7.5 Hz, H-1^{III}), 4.04 (dd, 1H, $J_{5,6b}^{III,III}$ = 7.4 Hz, H-6b^{III}), 4.02 (dd, overlapped, $J_{2,3}^{I,I}$ = 9.8 Hz, H-3^{I}), 3.95 (dd, 1H, H-2^{I}), 3.82 (m, overlapped, H-3^{II}), 3.80 (m, overlapped, H-2^{II}), 3.78 (m, overlapped, H-5^{III}), 3.74 (m, overlapped, 1xCH$_2$(linker)), 3.67 (s, 3H, $COOCH_3$), 3.67−3.53 (m, overlapped, 9 × CH_2(linker)), 3.62 (m, overlapped, H-2^{III}), 3.61 (m, overlapped, H-5^{II}), 3.59 (m, overlapped, H-6a^{II}), 3.57 (m, overlapped, H-6b^{II}), 3.35−3.29 (m, 2H, CH_2(linker)), 2.66 (d, 1H, J = 1.9 Hz, OH-2^{III}), 2.09, 2.08, 2.01, 1.97 (CH_3(Ac)); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.71, 170.64, 170.21, 169.73 ($OCOCH_3$), 168.26, 162.73 (C-6^{I}, $NHCOCH_3$), 138.48, 138.12, 137.88, 128.93, 128.90, 128.88, 128.65, 128.63 128.59, 128.05, 128.03, 127.77 (C_{arom}), 103.06 (C-1^{III}), 100.58 (C-1^{II}), 97.20 (C-1^{I}), 92.28 (CCl_3(TCA)), 79.23 (C-3^{II}), 77.10 (C-3^{I}), 76.91 (C-2^{I}), 76.54 (C-4^{I}), 74.91, 73.78 (CH_2Ph), 73.78 (C-5^{II}), 72.89 (C-3^{III}), 72.22 (CH_2Ph), 70.87, 70.86 (CH_2(linker), C-6^{II}), 70.74 (C-5^{III}), 70.47, 70.25 (CH_2(linker)), 70.00 (C-5^{I}), 69.60 (CH_2(linker)), 69.58 (C-4^{II}), 68.82 (C-2^{III}), 67.90 (CH_2(linker)), 67.02 (C-4^{III}), 61.32 (C-6^{III}), 57.69 (C-2^{II}), 50.85 (CH_2(linker)), 52.59 ($COOCH_3$), 21.07, 20.91, 20.75, 20.00 (CH_3(Ac)); HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{56}H_{73}N_5O_{23}Cl_3$ 1288.3762, found 1288.3757. Anal. Calcd for $C_{56}H_{69}Cl_3N_4O_{23}$: C, 52.86; H, 5.47; N, 4.40. Found: C, 52.57; H, 5.45; N, 4.21.

*2-[2-(2-Azidoethoxy)ethoxy]ethyl 2,4-Di-O-benzyl-3,6-dideoxy-α-L-xylo-hexopyranosyl-(1→2)-3,4,6-tri-O-acetyl-β-D-galactopyranosyl-(1→3)-4-O-acetyl-6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→4)-(methyl 2,3-di-O-benzyl-α-D-galactopyranosid)uronate (**10**).* A mixture of acceptor **37** (0.33 g, 0.26 mmol), molecular sieves (4 Å, 0.6 g), tetrabutylammonium bromide (0.28 g, 0.86 mmol), and DMF (anhydrous, 0.68 mL) was stirred at room temperature for 30 min. A solution of donor **8**[16] (0.30 g, 0.78 mmol in 3.32 mL anhydrous DCM) was added, and the mixture was stirred at room temperature for 3 d. Workup, as described above for similar reactions, and purification (40 g of silica, 12% acetone in toluene→15% acetone, 2 CV, 15% acetone, 10 CV, 15%→25% acetone, 1 CV, 25% acetone, 5 CV) yielded tetrasaccharide **10** (0.31 g, 0.20 mmol, 77%, 89% based on acceptor consumed) and acceptor **37** (45 mg, 0.035 mmol, 14%): R_f 0.38 (toluene/acetone 5:1); $[\alpha]_D^{22}$ +17.1 (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36−7.22 (m, 25 H, H_{arom}), 6.95 (d, 1H, $J_{NH,2}^{II,II}$ = 7.4 Hz, H-NH^{II}), 5.31 (dd, 1H, $J_{3,4}^{III,III}$ = 3.3 Hz, $J_{4,5}^{III,III}$ = 0.9 Hz, H-4^{III}), 5.18 (d, 1H, $J_{1,2}^{IV,IV}$ = 3.3 Hz, H-1^{IV}), 5.14 (d, 1H, $J_{1,2}^{II,II}$ = 8.4 Hz, H-1^{II}), 5.03 (d, 1H, $J_{1,2}^{I,I}$ = 3.4 Hz, H-1^{I}), 4.87 (dd, overlapped, $J_{2,3}^{III,III}$ = 10.1 Hz, H-3^{III}), 4.84 (t, overlapped, J = 8.9 Hz, H-4^{II}), 4.81 (d, 1H, J = 11.9 Hz, CH_2Ph), 4.67 (d, 2H, J = 11.7 Hz, CH_2Ph), 4.60 (d, 1H, J = 12.0 Hz, CH_2Ph), 4.58 (d, 1H, J = 11.4 Hz, CH_2Ph), 4.52 (m, overlapped, H-5^{I}), 4.48 (d, overlapped, $J_{1,2}^{III,III}$ = 7.6 Hz, H-1^{III}), 4.52−4.46 (d, overlapped, 3 × CH_2Ph), 4.42−4.37 (m, overlapped, 2 × CH_2Ph), 4.40 (m, overlapped, H-3^{II}), 4.32 (dd, 1H, $J_{4,5}^{I,I}$ = 1.7 Hz, $J_{3,4}^{I,I}$ = 2.8 Hz, H-4^{I}), 4.24 (m, 1H, H-5^{IV}), 4.18 (dd, 1H, $J_{5,6a}^{III,III}$ = 7.2 Hz, $J_{6a,6b}^{III,III}$ = 11.1 Hz, H-6a^{III}), 4.06 (dd, 1H, $J_{5,6b}^{III,III}$ = 7.6 Hz, H-6b^{III}), 3.92 (dd, $J_{3,2}^{I,I}$ = 9.4 Hz, H-3^{I}), 3.88 (m, overlapped, H-2^{I}), 3.87 (m, overlapped, H-2^{III}), 3.84 (m, overlapped, H-2^{IV}), 3.78 (m, 1H, H-5^{III}), 3.75−3.71 (m, 1H, CH_2(linker)), 3.65 (s, 1H, $COOCH_3$), 3.62 (m, overlapped, H-5^{II}), 3.64−3.52 (m, overlapped, 9 × CH_2(linker)), 3.57 (m, overlapped H-4^{IV}), 3.56−3.52 (m, overlapped, H-6a^{II}, H-6b^{II}), 3.48 (m, 1H, H-2^{II}), 3.31 (dd, 2H, J = 4.7, 5.6 Hz, CH_2(linker)), 2.10 (ddd, 1H, $J_{2,3eq}^{IV,IV}$ = 3.6 Hz, $J_{3eq,4}^{IV,IV}$ = 3.6 Hz, $J_{3ax,3eq}^{IV,IV}$ = 13.4 Hz, H-3$_{eq}^{IV}$), 2.04 (s, 3H, CH_3 (OAc)), 2.06 (s, 3H, CH_3 (OAc)), 1.98 (s, 3H, CH_3 (OAc)), 1.91 (ddd, 1H, $J_{3ax,4}^{IV,IV}$ = 2.3 Hz, $J_{2,3ax}^{IV,IV}$ = 13.0 Hz, H-3$_{ax}^{IV}$), 1.81 (s, 3H, CH_3 (OAc)), 1.25 (d, 3H, $J_{5,6}^{IV,IV}$ = 6.6 Hz, H-6^{IV}); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.64, 170.29, 170.08, 169.63 ($OCOCH_3$ × 4), 168.45 (C-6^{I}), 161.56 ($NHCOCH_3$), 139.07, 138.81, 138.68, 138.59, 138.00, 128.76, 128.60, 128.52, 128.51, 128.48, 128.24, 127.99, 127.98, 127.90, 127.79, 127.68, 127.64, 127.53 (C_{arom}), 101.54 (C-1^{III}), 99.59 (C-1^{II}), 97.49 (C-1^{I}), 97.12 (C-1^{IV}), 92.61 (CCl_3(TCA)), 77.06 (C-2^{I}), 76.64 (C-3^{I}), 76.38 (C-4^{IV}), 75.77 (C-4^{I}), 75.03 (C-3^{II}), 74.01 (CH_2Ph), 73.45 (C-5^{II}), 73.87 (C-3^{III}), 73.64 (CH_2Ph), 72.88 (CH_2Ph), 72.18 (C-2^{III}), 71.66 (C-2^{IV}), 71.64 (CH_2Ph), 70.88 (2 × CH_2(linker)), 70.71 (C-5^{III}), 70.45 (CH_2(linker)), 70.38 (CH_2Ph), 70.25 (CH_2(linker)), 70.23 (C-5^{I}), 69.93 (C-4^{II}), 69.60 (C-6^{II}), 67.96 (CH_2(linker)), 67.60 (C-4^{III}), 67.11 (C-5^{IV}), 61.05 (C-6^{III}), 59.01 (C-2^{II}), 52.48 ($COOCH_3$), 50.86 (CH_2(linker)), 27.21 (C-3^{IV}), 21.05, 20.91, 20.86, 20.80 (CH_3 (Ac)), 16.48 (C-6^{IV}); HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{76}H_{95}N_5O_{26}Cl_3$ 1598.5331, found 1598.5345. Anal. Calcd for $C_{76}H_{91}N_4O_{26}Cl_3$: C, 57.67; H, 5.79; N, 3.54. Found: C, 57.94; H, 5.78; N, 3.43.

*2-[2-(2-Azidoethoxy)ethoxy]ethyl 3-O-Benzyl-β-D-galactopyranosyl-(1→3)-6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→4)-(methyl 2,3-di-O-benzyl-α-D-galactopyranosid)uronate (**40**).* Trisaccharide **7** (400 mg, 0.30 mmol) was deacylated at room temperature with NaOMe (0.30 mmol, 16.20 mg, 1 M in MeOH) in anhydrous MeOH, to give, after isolation of the product by preparative TLC (DCM/MeOH 20:1), trisaccharide **38** (296 mg, 89%). The foregoing product was subjected to selective benzylation, following the reported procedure,[17] and preparative TLC (hexane/acetone 3:2, 3 developments) gave the unchanged trisaccharide **38** (41 mg, 0.037 mmol, 14%) and trisaccharide **40** (229 mg, 0.19 mmol, 71%, 84% based on **38** consumed): R_f 0.38 (DCM/MeOH 20:1); $[\alpha]_D^{22}$

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+38.6 (*c* 1.0, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.36−7.26 (m, 20 H, H_{arom}), 5.09 (d, 1H, $J_{1^I,2^I}$ = 3.4 Hz, H-1^I), 4.84 (d, overlapped, *J* = 11.0 Hz, CH_2Ph), 4.84 (d, overlapped, $J_{1^{II},2^{II}}$ = 8.7 Hz, H-1^{II}), 4.77−4.73 (m, 2H, 2 × CH_2Ph), 4.66 (d, 1H, *J* = 11.1 Hz, CH_2Ph), 4.61 (d, overlapped, *J* = 11.3 Hz, CH_2Ph), 4.58 (m, overlapped, CH_2Ph), 4.56 (m, overlapped, H-5^I), 4.56 (d, overlapped, *J* = 12.0 Hz, CH_2Ph), 4.53 (d, 1H, *J* = 12.0 Hz, CH_2Ph), 4.48 (bs, 1H, OH-4^{II}), 4.03 (d, 1H, $J_{1^{III},2^{III}}$ = 7.7 Hz, H-1^{III}), 4.39 (dd, 1H, $J_{3^I,4^I}$ = 3.1 Hz, $J_{4^I,5^I}$ = 1.8 Hz, H-4^I), 3.98 (dd, 1H, $J_{2^I,3^I}$ = 9.9 Hz, H-3^I), 3.94 (m, overlapped, H-2^I), 3.93 (m, overlapped, H-6a^{III}), 3.82 (m, overlapped, H-2^{II}), 3.88 (m, 1H, H-4^{III}), 3.83 (m, overlapped, H-6a^{II}), 3.81 (m, overlapped, H-2^{III}), 3.79 (m, overlapped, H-6b^{III}), 3.67 (s, overlapped, $COOCH_3$), 3.66 (m, overlapped, H-6b^{II}), 3.73 (m, 1H, CH_2(linker)), 3.66−3.54 (m, overlapped, 9 × CH_2(linker)), 3.51 (m, overlapped, H-4^{II}), 3.48 (m, overlapped, H-5^{III}), 3.45 (m, overlapped, H-3^{II}), 3.42 (ddd, 1H, $J_{5^{II},6a^{II}}$ = 1.5 Hz, $J_{5^{II},6b^{II}}$ = 5.6 Hz, $J_{4^{II},5^{II}}$ = 7.2 Hz, H-5^{II}), 3.31−3.29 (m, 3H, 2 × CH_2(linker), H-3^{III}), 3.09 (d, 1H, *J* = 1.9 Hz, OH-2^{III}), 2.96 (bs, 1H, OH-4^{III}), 2.68 (dd, 1H, *J* = 4.7 Hz, 6.5 Hz, OH-6^{III}); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.35, 162.97 (C-6^I, $NHCOCH_3$), 138.57, 137.38, 138.06, 138.03, 128.94, 128.73, 128.66, 128.56, 128.54 128.20, 128.10, 127.92, 127.80, 127.78, 127.71 (C_{arom}), 103.93 (C-1^{III}), 100.67 (C-1^{II}), 97.09 (C-1^I), 92.55 (CCl_3(TCA)), 88.16 (C-3^{II}), 79.81 (C-3^{III}), 77.27 (C-3^I), 76.89 (C-2^I), 75.98 (C-4^I), 75.77 (C-5^{II}), 75.19 (C-5^{III}), 74.88, 73.63, 72.32, 72.11 (CH_2Ph), 70.92 (C-2^{III}), 70.82 (2 × CH_2(linker)), 70.41, 70.21 (CH_2(linker)), 69.98 (C-5^I), 70.13 (C-6^{II}), 69.28 (C-4^{II}), 67.85 (CH_2(linker)), 67.57 (C-4^{III}), 62.40 (C-6^{III}), 56.85 (C-2^{II}), 52.51 ($COOCH_3$), 50.81 (CH_2(linker)); HRMS (ESI-TOF) *m*/*z* [M + NH_4]$^+$ calcd for $C_{55}H_{71}N_5O_{19}Cl_3$ 1210.3809, found 1210.3812. Anal. Calcd for $C_{55}H_{67}N_4O_{19}Cl_3$: C, 55.30; H, 5.65; N, 4.69. Found: C, 55.19; H, 5.62; N, 4.68.

*2-[2-(2-Azidoethoxy)ethoxy]ethyl 3-O-Benzyl-β-D-galactopyranosyl-(S)-(P)-4,6-cyclic 2,2,2-trichloroethyl phosphate-(1→3)-6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→4)-(methyl 2,3-di-O-benzyl-α-D-galactopyranosid)uronate (41a) and 2-[2-(2-Azidoethoxy)ethoxy]ethyl 3-O-Benzyl-β-D-galactopyranosyl-(R)-(P)-4,6-cyclic 2,2,2-trichloroethyl phosphate-(1→3)-6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→4)-(methyl 2,3-di-O-benzyl-α-D-galactopyranosid)uronate (**41b**).* A solution of 2,2,2-trichloroethyl phosphorodichloridate (33.8 μL, 57.46 mg, 0.22 mmol) in pyridine (142 μL, 0.14 g, 1.76 mmol) was added dropwise at room temperature to a stirred solution of trisaccharide **40** (0.21 g, 0.176 mmol) in DCM (anhydrous, 5.3 mL). Stirring at room temperature was continued for 1 h, when TLC showed that the reaction was complete and that two products were formed. MeOH (0.5 mL) was added, and the mixture was concentrated after 30 min. A solution of the residue in DCM (10 mL) was washed with brine (10 mL) and the aqueous layer was backwashed with DCM (3 × 4 mL). The combined organic layer was dried, filtered, and concentrated, and the residue was purified by preparative TLC (hexane/EtOAc 1:2, three developments) to give trisaccharide **41a** (58 mg, 0.0419 mmol, 24%) and trisaccharide **41b** (143 mg, 0.103 mmol, 59%). Data for trisaccharide **41a**: R_f 0.41 (toluene/acetone 3:1); $[\alpha]_D^{22}$ +33.3 (*c* 0.4, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.38−7.24 (m, 20 H, H_{arom}), 5.10 (d, 1H, $J_{1^I,2^I}$ = 3.4 Hz, H-1^I), 4.90 (d, $J_{1^{II},2^{II}}$ = 8.2 Hz, H-1^{II}), 4.84 (d, overlapped, *J* = 11.4 Hz, CH_2Ph), 4.77 (s, 2H, 2 × CH_2Ph), 4.73 (d, 1H, $J_{3^{III},4^{III}}$ = 3.0 Hz, H-4^{III}), 4.67−4.45 (m, 5 × CH_2Ph, 2 × CH_2CCl_3), 4.55 (d, overlapped, $J_{4^I,5^I}$ = 1.5 Hz, H-5^I), 4.54−4.44 (m, overlapped, H-6a^{III}, H-6b^{III}), 4.39 (dd, 1H, $J_{3^I,4^I}$ = 2.5 Hz, H-4^I), 4.20 (d, 1H, $J_{1^{III},2^{III}}$ = 7.8 Hz, H-1^{III}), 3.98 (m, overlapped, H-3^I), 3.96 (m, overlapped, H-2^I), 3.94 (m, overlapped, H-2^{III}), 3.82 (dd, 1H, $J_{5^{II},6a^{II}}$ = 2.3 Hz, $J_{6a^{II},6b^{II}}$ = 10.8 Hz, H-6a^{II}), 3.78 (bs, 1H, OH-4^{II}), 3.74 (m, 1H, CH_2(linker)), 3.69 (m, overlapped, H-2^{II}), 3.68 (m, overlapped, H-3^{II}), 3.68 (m, overlapped, H-6b^{II}), 3.68 (s, overlapped, $COOCH_3$), 3.71−3.54 (m, overlapped, 9 × CH_2(linker)), 3.55 (m, overlapped, H-4^{II}), 3.53 (m, overlapped, H-5^{III}), 3.40 (m, overlapped, H-5^{II}), 3.39 (m, overlapped, H-3^{III}), 3.31 (m, 2H, 2 × CH_2(linker)), 3.15 (bs, 1H, OH-2^{III}); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.38, 162.96 (C-6^I, $NHCOCH_3$), 138.63, 137.39, 138.25, 137.68, 128.80, 128.77, 128.63, 128.61, 128.59 128.23, 128.21, 128.20, 128.00, 127.92, 127.77 (C_{arom}), 103.65 (C-1^{III}), 100.24 (C-1^{II}), 97.30 (C-1^I), 95.21 (d, $J_{C,P}$ = 10.5 Hz, CH_2CCl_3), 92.62 (CCl_3(TCA)), 84.77 (C-3^{II}), 77.29 (C-3^I), 77.21 (d, $J_{C,P}$ = 7.4 Hz, CH_2CCl_3) 76.99 (C-2^I), 76.73 (d, $J_{C,P}$ = 7.2 Hz, C-4^{III}), 76.68 (d, $J_{C,P}$ = 7.0 Hz, C-3^{III}), 75.75 (C-4^I), 75.31 (C-5^{II}), 74.64, 73.81, 72.43, 72.42 (CH_2Ph), 70.86 (2 × CH_2(linker)), 70.48 (CH_2(linker)), 70.46 (d, $J_{C,P}$ = 4.7 Hz, C-6^{III}), 70.24 (CH_2(linker)), 70.13 (C-5^I), 70.10 (C-6^{II}), 69.87 (C-2^{III}), 69.51 (C-4^{II}), 67.89 (CH_2(linker)), 66.80 (d, $J_{C,P}$ = 6.6 Hz, C-5^{III}), 57.26 (C-2^{II}), 52.58 ($COOCH_3$), 50.85 (CH_2(linker)); ^{31}P NMR (162 MHz, $CDCl_3$) δ −10.80; HRMS (ESI-TOF) *m*/*z* [M + NH_4]$^+$ calcd for $C_{57}H_{71}N_5O_{21}PCl_6$ 1402.2510, found 1402.2505. Anal. Calcd for $C_{57}H_{67}N_4O_{21}PCl_6$: C, 49.33; H, 4.87; N, 4.04. Found: C, 49.39; H, 5.06; N, 3.92. Data for trisaccharide **41b**: R_f 0.32 (toluene/acetone 3:1); $[\alpha]_D^{22}$ +36.0 (*c* 1.0, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.37−7.25 (m, 20 H, H_{arom}), 5.10 (d, 1H, $J_{1^I,2^I}$ = 3.5 Hz, H-1^I), 4.89 (d, 1H, $J_{3^{III},4^{III}}$ = 3.0 Hz, H-4^{III}), 4.87 (d, $J_{1^{II},2^{II}}$ = 9.2 Hz, H-1^{II}), 4.87−4.84 (m, 2H, 2 × CH_2Ph), 4.81 (d, 1H, *J* = 12.5 Hz, CH_2Ph), 4.71 (d, 1H, *J* = 12.3 Hz, CH_2Ph), 4.68 (ddd, overlapped, $J_{5^{III},6a^{III}}$ = 2.5 Hz, $J_{6a^{III},P^{III}}$ = 4.0 Hz, $J_{6a^{III},6b^{III}}$ = 12.6 Hz, H-6a^{III}), 4.66−4.54 (m, 6 × CH_2Ph, 2 × CH_2CCl_3), 4.57 (m, overlapped, H-5^I) 4.46 (ddd, 1H, $J_{5^{III},6b^{III}}$ = 1.3 Hz, $J_{6b^{III},P^{III}}$ = 19.8 Hz, H-6b^{III}), 4.40 (dd, 1H, $J_{3^I,4^I}$ = 3.0 Hz, $J_{4^I,5^I}$ = 1.9 Hz, H-4^I), 4.19 (d, 1H, $J_{1^{III},2^{III}}$ = 7.6 Hz, H-1^{III}), 3.99 (dd, 1H, $J_{2^I,3^I}$ = 9.8 Hz, H-3^I), 3.95 (dd, 1H, H-2^I), 3.86 (ddd, 1H, $J_{2^{III},3^{III}}$ = 9.4 Hz, $J_{OH\text{-}2^{III},2^{III}}$ = 1.5 Hz Hz, H-2^{III}), 3.81 (dd, 1H, $J_{5^{II},6a^{II}}$ = 1.9 Hz, $J_{6a^{II},6b^{II}}$ = 10.8 Hz, H-6a^{II}), 3.71 (m, overlapped, H-2^{II}), 3.66 (m, overlapped, H-6b^{II}), 3.67 (s, overlapped, $COOCH_3$), 3.67−3.54 (m, overlapped, 10 × CH_2(linker)), 3.62 (m, overlapped, H-5^{III}), 3.58 (m, overlapped, H-3^{II}), 3.52 (t, 1H, $J_{3^{II},4^{II}}$ = 9.2 Hz, $J_{4^{II},5^{II}}$ = 9.2 Hz, H-4^{II}), 3.41 (ddd, $J_{3^{III},P^{III}}$ = 4.0 Hz, H-3^{III}), 3.37 (ddd, 1H, $J_{5^{II},6b^{II}}$ = 5.5 Hz, H-5^{II}), 3.31 (m, 2H, 2 × CH_2(linker)), 3.01 (d, 1H, OH-2^{III}); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.33, 162.93 (C-6^I, $NHCOCH_3$), 138.55, 137.31, 138.23, 137.37, 128.83, 128.79, 128.62, 128.31, 128.29 128.00, 127.91, 127.79, 127.75 (C_{arom}), 103.45 (C-1^{III}), 100.39 (C-1^{II}), 97.23 (C-1^I), 94.60 (d, $J_{C,P}$ = 10.6 Hz, CH_2CCl_3), 92.52 (CCl_3(TCA)), 85.47 (C-3^{II}), 78.04 (d, $J_{C,P}$ = 5.2 Hz, CH_2CCl_3) 77.30 (C-3^I), 76.96 (C-2^I), 76.64 (d, $J_{C,P}$ = 6.5 Hz, C-3^{III}), 75.92 (C-4^I), 75.53 (C-5^{II}), 75.43 (d, $J_{C,P}$ = 5.3 Hz, C-4^{III}), 74.80, 73.76, 72.28, 72.10 (CH_2Ph), 70.85, 70.84, 70.46, 70.24 (CH_2(linker)), 70.05 (d, $J_{C,P}$ = 2.6 Hz, C-2^{III}), 70.04 (C-5^I), 69.88 (d, $J_{C,P}$ = 6.7 Hz, C-6^{III}), 69.86 (C-6^{II}), 69.26 (C-4^{II}), 67.88 (CH_2(linker)), 67.25 (d, $J_{C,P}$ = 7.5 Hz, C-5^{III}), 57.09 (C-2^{II}), 52.55 ($COOCH_3$), 50.84 (CH_2(linker)); ^{31}P NMR (162 MHz, $CDCl_3$) δ −8.26; HRMS (ESI-TOF) *m*/*z* [M + NH_4]$^+$ calcd for $C_{57}H_{71}N_5O_{21}PCl_6$ 1402.2510, found 1402.2523. Anal. Calcd for $C_{57}H_{67}N_4O_{21}PCl_6$: C, 49.33; H, 4.87; N, 4.04. Found: C, 49.38; H, 4.78; N, 3.96.

*2-[2-(2-Azidoethoxy)ethoxy]ethyl [2,4-Di-O-benzyl-3,6-dideoxy-α-L-xylo-hexopyranosyl-(1→4)]-[3-O-benzyl-β-D-galactopyranosyl-(1→3)]-6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→4)-(methyl 2,3-di-O-benzyl-1-D-galactopyranosid)-uronate (**42**).* Tetrasaccharide **9** (0.42 g, 0.26 mmol) was treated with NaOMe in anhydrous MeOH as described for **38**. Preparative TLC (DCM/MeOH 15:1) gave the corresponding tetraol (0.32 g, 0.23 mmol, 88%), which was subjected to selective benzylation following the reported procedure.[17] Chromatography (24 g of silica gel, toluene/EtOAc 1:1) of the crude product gave tetrasaccharide **42** (0.3 g, 0.20 mmol, 86%): R_f 0.27 (DCM/MeOH 30:1); $[\alpha]_D^{22}$ +20.2 (*c* 0.5, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, 1H, $J_{NH^{II},H\text{-}2^{II}}$ = 6.5 Hz, NH^{II}), 7.35−7.24 (m, 30 H, H_{arom}), 5.13 (d, 1H, $J_{1^{II},2^{II}}$ = 7.9 Hz, H-1^{II}), 5.04 (d, 1H, $J_{1^{IV},2^{IV}}$ = 3.2 Hz, H-1^{IV}), 5.03 (d, 1H, $J_{1^I,2^I}$ = 3.2 Hz, H-1^I), 4.81 (d, 1H, *J* = 12.2 Hz, CH_2Ph), 4.74 (d, 1H, *J* = 11.7 Hz, CH_2Ph), 4.73 (d, 1H, *J* = 12.5 Hz, CH_2Ph), 4.67 (d, 1H, *J* = 11.4 Hz, CH_2Ph), 4.65 (d, 1H, *J* = 11.7 Hz, CH_2Ph), 4.59 (d, 1H, *J* = 11.4 Hz, CH_2Ph), 4.51 (d, 1H, *J* = 11.7 Hz, CH_2Ph), 4.51 (d, 1H, $J_{4^I,5^I}$ = 1.3 Hz, H-5^I), 4.45−4.41 (m, 4H, CH_2Ph), 4.38 (d, 1H, *J* = 12.2 Hz, CH_2Ph), 4.34 (dd, 1H, $J_{3^I,4^I}$ = 2.5 Hz, H-4^I), 4.31 (m, overlapped, H-5^{IV}), 4.30 (d, 1H, $J_{1^{III},2^{III}}$ = 7.7 Hz, H-1^{III}), 4.22 (t, 1H, $J_{2^{II},3^{II}}$ = 7.9 Hz, $J_{3^{II},4^{II}}$ = 7.9 Hz, H-3^{II}), 3.99 (t, 1H, $J_{4^{II},5^{II}}$ = 7.9 Hz, H-4^{II}), 3.93 (dd, 1H, $J_{2^I,3^I}$ = 9.9 Hz, H-2^I), 3.90 (dd, overlapped, H-3^I), 3.89 (m, overlapped, H-6a^{III}), 3.86 (m, overlapped, H-4^{III}), 3.84 (m, overlapped, H-2^{IV}), 3.83 (m, overlapped, H-6a^{II}), 3.74 (m, overlapped, H-6b^{III}), 3.74 (m, overlapped, H-6b^{II}), 3.71 (m, overlapped, H-2^{III}), 3.67 (m,

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overlapped, H-2^{II}), 3.60 (s, overlapped, $COOCH_3$), 3.70−3.53 (m, overlapped, 10 × CH_2(linker)), 3.57 (m, overlapped, H-5^{II}), 3.41 (bs, 1H, H-4^{IV}), 3.39 (m, 1H, H-5^{III}), 3.32 (dd, 1H, $J_{3}^{III,4}{}^{III}$ = 3.4 Hz, $J_{2}^{III,3}{}^{III}$ = 9.2 Hz, H-3^{III}), 3.31 (m, overlapped, 2 × CH_2(linker)), 2.09 (ddd, 1H, $J_{2}^{IV,3eq}{}^{IV}$ = 3.6 Hz, $J_{3eq}^{IV,4}{}^{IV}$ = 3.6 Hz, $J_{3ax}^{V,3eq}{}^{IV}$ = 12.9 Hz, H-3$_{eq}^{IV}$), 1.84 (ddd, 1H, $J_{3ax}^{IV,4}{}^{IV}$ = 2.2 Hz, $J_{2}^{IV,3ax}{}^{IV}$ = 12.9 Hz H-3$_{ax}^{IV}$), 1.15 (d, 3H, $J_{5}^{IV,6}{}^{IV}$ = 6.6 Hz, H-6^{IV}); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.72, 162.12 (C-6^{I}, NHCOCH$_3$), 138.70, 138.69, 138.34, 138.21, 138.17, 129.24, 128.75, 128.71, 128.66, 128.59, 128.57, 128.50, 128.43, 128.37, 128.26, 128.17, 128.14, 128.11, 128.05, 127.99, 127.91, 127.83, 127.80, 125.50 (C_{arom}), 102.02 (C-1^{III}), 99.70 (C-1^{II}), 97.54 (C-1^{I}), 97.45 (C-1^{IV}), 92.65 (CCl_3(TCA)), 79.87 (C-3^{III}), 78.53 (C-3^{II}), 76.88 (C-3^{I}), 76.81 (C-2^{I}), 76.35 (C-4^{IV}), 75.78 (C-5^{II}), 75.56 (C-4^{I}), 74.94 (C-5^{III}), 74.06 (C-4^{II}), 73.94, 73.28, 72.87, 72.67, 71.73 (CH_2Ph), 71.58 (C-2^{IV}), 71.31 (CH_2Ph), 71.16 (C-2^{III}), 70.86 (2 × CH_2(linker)), 70.50 (CH_2(linker)), 70.41 (C-5^{I}), 70.23 (CH_2(linker)), 68.83 (C-6^{II}), 67.93 (CH_2(linker)), 67.85 (C-4^{III}), 67.09 (C-5^{IV}), 62.72 (C-6^{III}), 58.13 (C-2^{II}), 52.58 ($COOCH_3$), 50.84 (CH_2(linker)), 27.38 (C-3^{IV}), 16.73 (C-6^{IV}); HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{75}H_{93}N_5O_{22}Cl_3$ 1520.5378, found 1520.5391. Anal. Calcd for $C_{75}H_{89}N_4O_{22}Cl_3$: C, 59.86; H, 5.96; N, 3.72. Found: C, 60.02; H, 6.07; N, 3.56.

*2-[2-(2-Azidoethoxy)ethoxy]ethyl [3-O-Benzyl-β-D-galactopyranosyl-(S)-(P)-4,6-cyclic 2,2,2-trichloroethyl phosphate-(1→3)]-[2,4-di-O-benzyl-3,6-dideoxy-α-L-xylo-hexopyranosyl-(1→4)]-6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→4)-(methyl 2,3-di-O-benzyl-α-D-galactopyranosiduronate (**43a**) and 2-[2-(2-Azidoethoxy)ethoxy]ethyl [3-O-Benzyl-β-D-galactopyranosyl-(R)-(P)-4,6-cyclic 2,2,2-trichloroethyl phosphate-(1→3)]-[2,4-di-O-benzyl-3,6-dideoxy-α-L-xylo-hexopyranosyl-(1→4)]-6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→4)-(methyl 2,3-di-O-benzyl-α-D-galactopyranosid)uronate (**43b**).* Tetrasaccharide **42** (0.25 g, 0.16 mmol) was phosphorylated in DCM with pyridine (0.13 mL, 0.13 g, 1.64 mmol) and 2,2,2-trichloroethyl phosphorodichloridate (41.9 μL, 71.17 mg, 0.26 mmol), which was divided into two portions (31.4 μL, 10.5 μL, successively) and added 30 min apart. When the reaction was complete (TLC), workup, as described above, and preparative TLC (toluene/EtOAc 2:3, 3 developments) gave tetrasaccharide **43a** (0.12 g, 0.070 mmol, 43%) and tetraasaccharide **43b** (0.11 mg, 0.064 mmol, 39%). Data for tetrasaccharide **43a**: R_f 0.49 (toluene/EtOAc 2:3); $[\alpha]_D^{22}$ +14.4 (*c* 0.4, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36−7.20 (m, 30 H, H_{arom}), 5.13 (d, 1H, $J_{1}^{II,2}{}^{II}$ = 7.8 Hz, H-1^{II}), 5.04 (d, 1H, $J_{1}^{I,2}{}^{I}$ = 3.4 Hz, H-1^{I}), 5.00 (d, overlapped, $J_{1}^{IV,2}{}^{IV}$ = 3.3 Hz, H-1^{IV}), 4.78−4.73 (m, overlapped, 3 × CH_2Ph), 4.70 (d, 1H, $J_{3}^{III,4}{}^{III}$ = 3.1 Hz, H-4^{III}), 4.68−4.57 (m, overlapped, 5 × CH_2Ph), 4.65−4.61 (m, overlapped, 2 × CH_2CCl$_3$), 4.53 (m, overlapped, H-6a^{III}), 4.50 (m, overlapped, H-6b^{III}), 4.51−4.43 (m, overlapped, 4 × CH_2Ph), 4.50 (m, overlapped, H-5^{I}), 4.49 (m, overlapped, H-5^{IV}), 4.45 (d, overlapped, $J_{1}^{III,2}{}^{III}$ = 7.8 Hz, H-1^{III}), 4.41 (m, overlapped, H-3^{II}), 4.31 (dd, 1H, $J_{3}^{I,4}{}^{I}$ = 3.0 Hz, $J_{4}^{I,5}{}^{I}$ = 1.4 Hz, H-4^{I}), 4.00 (t, 1H, *J* = 8.6 Hz, H-4^{II}), 3.94 (dd, overlapped, $J_{5}^{II,6a}{}^{II}$ = 3.6 Hz, $J_{6a}^{II,6b}{}^{II}$ = 10.6 Hz, H-6a^{II}), 3.93 (m, overlapped, H-2^{I}), 3.90 (dd, overlapped, $J_{2}^{I,3}{}^{I}$ = 9.8 Hz, H-3^{I}), 3.79 (bs, 1H, H-4^{IV}), 3.87 (m, overlapped, H-2^{IV}), 3.85 (m, overlapped, H-2^{III}), 3.69 (m, dd, 1H, $J_{5}^{II,6b}{}^{II}$ = 2.5 Hz, H-6b^{II}), 3.63 (m, overlapped, H-2^{II}), 3.60 (s, overlapped, $COOCH_3$), 3.52 (ddd, 1H, H-5^{II}), 3.75−3.52 (m, overlapped, 10 × CH_2(linker)), 3.40 (bs, 1H, H-5^{III}), 3.37 (m, 1H, H-3^{III}), 3.31 (t, 2H, *J* = 5.2 Hz, CH_2(linker)), 3.03 (bs, 1H, OH-2^{III}), 2.07 (ddd, 1H, $J_{3eq}^{IV,4}{}^{IV}$ = 3.7 Hz, $J_{3eq}^{IV,2}{}^{IV}$ = 3.7 Hz, $J_{3eq}^{IV,3ax}{}^{IV}$ = 12.7 Hz, H-3$_{eq}^{IV}$), 1.82 (ddd, 1H, $J_{3ax}^{IV,4}{}^{IV}$ = 2.3 Hz, $J_{3ax}^{IV,2}{}^{IV}$ = 12.7 Hz, H-3$_{ax}^{IV}$), 1.24 (d, 3H, $J_{5}^{IV,6}{}^{IV}$ = 6.7 Hz, H-6^{IV}); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.63, 161.79 (C-6^{I}, NHCO), 139.35, 138.66, 138.51, 138.35, 138.10, 137.61, 128.83, 128.64, 128.62, 128.57, 128.43, 128.38, 128.29, 128.19, 128.12, 128.04, 127.99, 127.93, 127.98, 127.78, 127.52, (C_{arom}), 102.15 (C-1^{III}), 99.17 (C-1^{II}), 97.51 (C-1^{I}), 97.39 (C-1^{IV}), 95.19 (d, $J_{C,P}$ = 10.6 Hz, CH_2CCl_3), 92.66 (CCl_3(TCA)), 77.07 (d, $J_{C,P}$ = 4.1 Hz, CH_2CCl_3), 77.21 (C-3^{II}), 77.00 (C-3^{III}), 76.95 (C-4^{IV}), 76.88 (C-2^{I}, C-3^{I}), 76.75 (d, $J_{C,P}$ = 7.0 Hz, C-4^{III}), 75.60 (C-5^{II}), 75.13 (C-4^{I}), 74.01, 73.34 (CH_2Ph), 73.14 (C-4^{II}), 72.80, 72.61, 72.34 (CH_2Ph), 71.27 (CH_2Ph), 71.41 (C-2^{IV}), 70.99 (d, $J_{C,P}$ = 7.7 Hz, C-6^{III}), 70.86 (2 × CH_2(linker)), 70.46 (CH_2(linker)), 70.42 (C-5^{I}), 70.23 (CH_2(linker)), 70.04 (C-2^{III}), 68.36 (C-6^{II}), 67.94 (CH_2(linker)), 66.64 (d, $J_{C,P}$ = 6.5 Hz, C-5^{III}), 66.06 (C-5^{IV}), 58.95 (C-2^{II}), 52.74 ($COOCH_3$), 50.84 (CH_2(linker)), 27.63(C-3^{IV}), 16.61 (C-6^{IV}); ^{31}P NMR (162 MHz, $CDCl_3$) δ −10.67; HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{77}H_{93}N_5O_{24}PCl_6$ 1712.4079, found 1712.4064. Anal. Calcd for $C_{77}H_{89}N_4O_{24}PCl_6$: C, 54.46; H, 5.28; N, 3.30. Found: C, 54.46; H, 5.41; N, 3.26. Data for tetrasaccharide **43b**: R_f 0.16 (toluene/EtOAc 2:3); $[\alpha]_D^{22}$ +18.5 (*c* 0.9, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39−7.21 (m, 30 H, H_{arom}), 5.26 (d, 1H, $J_{1}^{II,2}{}^{II}$ = 7.6 Hz, H-1^{II}), 5.00 (d, 1H, $J_{1}^{I,2}{}^{I}$ = 3.5 Hz, H-1^{I}), 4.98 (d, 1H, $J_{1}^{IV,2}{}^{IV}$ = 3.3 Hz, H-1^{IV}), 4.87 (d, 1H, $J_{3}^{III,4}{}^{III}$ = 3.2 Hz, H-4^{III}), 4.80 (d, 1H, *J* = 12.3 Hz, CH_2Ph), 4.72 (d, 1H, *J* = 12.3 Hz, CH_2Ph), 4.69 (m, overlapped, CH_2Ph), 4.57 (d, 1H, $J_{1}^{III,2}{}^{III}$ = 7.7 Hz, H-1^{III}), 4.60 (m, overlapped, CH_2CCl$_3$), 4.42 (m, overlapped, H-3^{II}), 4.68 (m, overlapped, CH_2Ph), 4.65 (m, overlapped, CH_2Ph), 4.63 (m, overlapped, H-6a^{III}), 4.62−4.59 (m, overlapped, CH_2CCl$_3$), 4.57 (m, overlapped, CH_2Ph), 4.48 (m, overlapped, H-5^{I}), 4.45 (m, overlapped, H-6b^{III}), 4.50−4.38 (m, overlapped, 6 × CH_2Ph), 4.29 (dd, 1H, $J_{4}^{I,5}{}^{I}$ = 1.3 Hz, H-4^{I}), 4.22 (dd, 1H, $J_{5}^{IV,6}{}^{IV}$ = 6.6 Hz, $J_{4}^{IV,5}{}^{IV}$ = 12.9 Hz, H-5^{IV}), 4.00 (t, 1H, *J* = 7.3 Hz, H-4^{II}), 3.92 (dd, 1H, $J_{2}^{I,3}{}^{I}$ = 9.9 Hz, H-2^{I}), 3.87 (dd, 1H, $J_{3}^{I,4}{}^{I}$ = 3.1 Hz, H-3^{I}), 3.84 (m, overlapped, H-6a^{II}), 3.83 (m, overlapped, H-2^{IV}), 3.80 (m, overlapped, H-2^{III}), 3.72 (m, 1H, CH_2(linker)), 3.68 (dd, 1H, $J_{5}^{II,6b}{}^{II}$ = 3.5 Hz, $J_{6a}^{II,6b}{}^{II}$ = 10.3 Hz, H-6b^{II}), 3.64 (m, overlapped, H-5^{II}), 3.61 (m, overlapped, H-2^{II}), 3.61 (s, 3H, $COOCH_3$), 3.65−3.53 (m, overlapped, 9 × CH_2(linker)), 3.54 (m, overlapped, H-5^{III}), 3.48 (m, 1H, H-3^{III}), 3.45 (bs, 1H, H-4^{IV}), 3.31 (t, 2H, *J* = 5.4 Hz, CH_2(linker)), 2.12 (ddd, 1H, $J_{3eq}^{IV,4}{}^{IV}$ = 3.8 Hz, $J_{3eq}^{IV,2}{}^{IV}$ = 3.8 Hz, $J_{3eq}^{IV,3ax}{}^{IV}$ = 12.9 Hz, H-3$_{eq}^{IV}$), 1.78 (ddd, 1H, $J_{3ax}^{IV,4}{}^{IV}$ = 1.8 Hz, $J_{3ax}^{IV,2}{}^{IV}$ = 12.9 Hz, H-3$_{ax}^{IV}$), 1.18 (d, 3H, H-6^{IV}); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.69, 161.65 (C-6^{I}, NHCO), 138.67, 138.64 138.48, 138.23, 138.17 137.53, 128.83, 128.69, 128.60, 128.57, 128.36, 128.29, 128.26, 128.18, 128.12, 127.96, 127.93, 127.87, 127.81 (C_{arom}), 101.10 (C-1^{III}), 99.19 (C-1^{II}), 97.67 (C-1^{I}), 97.58 (C-1^{IV}), 94.70 (d, $J_{C,P}$ = 9.9 Hz, CH_2CCl_3), 92.62 (CCl_3(TCA)), 76.83 (C-3^{I}), 76.70 (C-2^{I}), 76.29 (C-4^{IV}), 78.02 (C-3^{II}), 77.90 (d, $J_{C,P}$ = 4.2 Hz, CH_2CCl_3), 77.27 (C-3^{III}), 75.90 (C-5^{II}), 75.26 (C-4^{I}), 75.25 (m, C-4^{III}), 74.38 (C-4^{II}), 73.69 (CH_2Ph), 73.29 (CH_2Ph), 73.14 (CH_2Ph), 72.18 (CH_2Ph), 71.68 (CH_2Ph), 71.38 (CH_2Ph), 71.20 (C-2^{IV}), 70.85 (2 × CH_2(linker)), 70.44 (CH_2(linker)), 70.36 (C-5^{I}), 70.22 (CH_2(linker)), 70.34 (C-6^{III}), 69.93 (C-2^{III}), 68.93 (C-6^{II}), 67.99 (CH_2(linker)), 67.38 (C-5^{IV}), 67.04 (d, $J_{C,P}$ = 6.0 Hz, C-5^{III}), 57.61 (C-2^{II}), 52.61 ($COOCH_3$), 50.84 (CH_2(linker)), 27.50 (C-3^{IV}), 16.71 (C-6^{IV}); ^{31}P NMR (162 MHz, $CDCl_3$) δ −5.4; HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{77}H_{93}N_5O_{24}PCl_6$ 1712.4079, found 1712.4076. Anal. Calcd for $C_{77}H_{89}N_4O_{24}PCl_6$: C, 54.46; H, 5.28; N, 3.30. Found: C, 54.26; H, 5.45; N, 3.23.

*2-[2-(2-Azidoethoxy)ethoxy]ethyl [2,4-Di-O-benzyl-3,6-dideoxy-α-L-xylo-hexopyranosyl-(1→2)-β-D-galactopyranosyl-(S)-(P)-4,6-cyclic 2,2,2-trichloroethyl phosphate-(1→3)]-[2,4-di-O-benzyl-3,6-dideoxy-α-L-xylo-hexopyranosyl-(1→4)]-6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→4)-methyl 2,3-di-O-benzyl-α-D-galactopyranosid)uronate (**45a**) and 2-[2-(2-Azidoethoxy)ethoxy]ethyl [2,4-Di-O-benzyl-3,6-dideoxy-α-L-xylo-hexopyranosyl-(1→2)-β-D-galactopyranosyl-(R)-(P)-4,6-cyclic 2,2,2-trichloroethyl phosphate-(1→3)]-[2,4-di-O-benzyl-3,6-dideoxy-α-L-xylo-hexopyranosyl-(1→4)]-6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→4)-(methyl 2,3-di-O-benzyl-1-α-D-galactopyranosid)uronate (**45b**).* Pentasaccharide **11** (0.39 g, 0.21 mmol) was deacetylated with NaOMe in anhydrous MeOH at 0 °C as described above, and after usual workup, the crude product was dried in vacuum at 40 °C overnight to give pentasaccharide **44** in virtually theoretical yield (0.36 g, 0.21 mmol). It was treated with pyridine (0.17 mL, 166.11 mg, 2.10 mmol) and 2,2,2-trichloroethyl phosphorodichloridate (52 μL, 88.6 mg, 0.34 mmol), which was divided into two portions (33 μL, 19 μL, successively) and added 30 min apart. When the reaction was complete (TLC), workup, as described above, and chromatography (24 g of silica, 12%→17% acetone in toluene, 15 CV) gave pentasaccharide **45a** (257 mg, 0.134 mmol, 64%) and pentasaccharide **45b** (103 mg, 0.054 mmol, 26%). Data for pentasaccharide **45a**: R_f 0.51 (toluene/acetone 5:1); $[\alpha]_D^{22}$ −4.0 (*c* 0.7, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37−7.21 (m, 35 H, H_{arom}), 7.05 (d, 1H, $J_{NH}^{II,2}{}^{II}$ = 6.8 Hz, H-NH^{II}), 5.29 (d, 1H,

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$J_{1}^{II},_{2}^{II}$ = 8.4 Hz, H-1^{II}), 5.18 (d, 1H, $J_{1}^{I},_{2}^{I}$ = 3.0 Hz, H-1^{V}), 5.01 (d, overlapped, $J_{1}^{I},_{2}^{I}$ = 3.1 Hz, H-1^{I}), 5.00 (d, overlapped, $J_{1}^{IV},_{2}^{IV}$ = 3.1 Hz, H-1^{IV}), 4.77 (d, 1H, $J_{3}^{III},_{4}^{III}$ = 3.2 Hz, H-4^{III}), 4.73 (m, overlapped, H-3^{II}), 4.73 (d, 1H, J = 12.1 Hz, CH_2Ph), 4.68 (d, overlapped, J = 11.6 Hz, CH_2Ph), 4.68 (m, overlapped, H-5^{IV}), 4.66 (m, overlapped, CH_2CCl$_3$), 4.65 (m, overlapped, H-1^{III}), 4.61 (d, overlapped, J = 12.1 Hz, CH_2Ph), 4.60 (d, overlapped, J = 11.4 Hz, CH_2CCl$_3$), 4.58 (d, 1H, J = 11.6 Hz, CH_2Ph), 4.57 (m, overlapped, H-6a^{III}), 4.57 (d, 1H, J = 12.9 Hz, CH_2Ph), 4.55 (m, overlapped, H-6b^{III}), 4.55 (d, overlapped, J = 11.9 Hz, 2 × CH_2Ph), 4.52 (d, overlapped, J = 12.1 Hz, CH_2 Ph), 4.51 (d, overlapped, J = 11.9 Hz, CH_2 Ph), 4.48 (d, overlapped, J = 11.8 Hz, CH_2 Ph), 4.47 (d, overlapped, J = 12.6 Hz, CH_2 Ph), 4.45 (d, overlapped, J = 12.1 Hz, CH_2 Ph), 4.45 (m, overlapped, H-5^{I}), 4.43 (d, overlapped, J = 12.1 Hz, CH_2 Ph), 4.37 (d, overlapped, J = 12.6 Hz, CH_2 Ph), 4.36 (bs, 1H, OH-3^{III}), 4.31 (t, 1H, J = 1.9 Hz, H-4^{I}), 4.17 (m 1H, H-5^{V}), 3.95 (m, overlapped, H-2^{V}), 3.93 (m, overlapped, H-4^{II}), 3.92 (m, overlapped, H-4^{IV}), 3.91 (m, overlapped, H-6a^{II}), 3.89 (m, overlapped, H-2^{IV}), 3.86 (m, overlapped, H-3^{I}), 3.85 (m, overlapped, H-2^{I}), 3.78 (dd, 1H, $J_{1}^{III},_{2}^{III}$ = 8.2 Hz, $J_{2}^{III},_{3}^{III}$ = 9.7 Hz, H-2^{III}), 3.72 (m, 1H, CH$_2$(linker)), 3.68 (m, overlapped, H-6b^{II}), 3.67 (m, overlapped, H-3^{III}), 3.65−3.51 (m, overlapped, 9 × CH$_2$(linker)), 3.54 (s, 3H, COOCH$_3$), 3.51 (m, overlapped, H-4^{V}), 3.50 (m, overlapped, H-5^{II}), 3.48 (m, overlapped, H-5^{III}), 3.40 (m, 1H, H-2^{II}), 3.30 (t, 2H, J = 5.0 Hz, CH$_2$(linker)), 2.16 (ddd, 1H, $J_{3eq}^{V},_{4}^{V}$ = 3.9 Hz, $J_{3eq}^{V},_{2}^{V}$ = 3.6 Hz, $J_{3eq}^{V},_{3ax}^{V}$ = 12.7 Hz, H-3$_{eq}^{V}$), 2.07 (ddd, 1H, $J_{3eq}^{IV},_{4}^{IV}$ = 3.9 Hz, $J_{3eq}^{IV},_{2}^{IV}$ = 3.6 Hz, $J_{3eq}^{IV},_{3ax}^{IV}$ = 12.6 Hz, H-3$_{eq}^{IV}$), 1.87 (m, overlapped, H-3$_{ax}^{V}$), 1.85 (m, overlapped, H-3$_{ax}^{IV}$), 1.27 (d, 3H, $J_{5}^{IV},_{6}^{IV}$ = 6.6 Hz, H-6^{IV}), 1.25 (d, 3H $J_{5}^{V},_{6}^{V}$ = 6.5 Hz, H-6^{V}); ^{13}C NMR (150 MHz, CDCl$_3$) δ 168.45, 160.99 (NHCO, C-6^{I}), 139.72, 138.79, 138.60, 138.55, 138.50, 138.21, 137.25, 128.88, 128.61, 128.59, 128.58, 128.53, 128.51, 128.42, 128.39, 128.37, 128.32, 128.28, 128.27, 128.13, 128.08, 127.96, 127.90, 127.86, 127.70, 127.65, 127.59, 127.35 (C$_{arom}$), 101.63 (C-1^{III}), 99.58 (C-1^{V}), 98.21 (C-1^{II}), 97.57 (C-1^{I}), 96.98 (C-1^{IV}), 95.19 (d, $J_{C,P}$ = 10.4 Hz, CH$_2$CCl$_3$), 93.04 (CCl$_3$(TCA)), 78.60 (d, $J_{C,P}$ = 7.0 Hz, C-4^{III}), 78.29 (C-2^{III}), 77.20 (C-4^{IV}), 77.04 (C-2^{I}), 77.03 (CH$_2$CCl$_3$), 76.69 (C-3^{I}), 75.65 (C-4^{V}), 75.49 (C-5^{II}), 75.20 (C-3^{II}), 74.33 (C-4^{I}), 73.62, 73.10, 73.03, 72.71 (CH$_2$Ph), 72.64 (C-4^{II}), 72.25 (C-2^{V}), 72.03 (d, $J_{c,P}$ = 7.4 Hz, C-3^{III}), 71.77 (CH$_2$Ph), 71.46 (CH$_2$Ph), 71.43 (C-2^{IV}), 71.18 (CH$_2$Ph), 71.11 (d, $J_{C,P}$ = 7.4 Hz, C-6^{III}), 70.87, 70.85 (CH$_2$(linker)), 70.48 (C-5 ^{I}), 70.40 (CH$_2$(linker)), 70.22 (CH$_2$(linker)), 68.26 (C-5^{V}), 68.08 (C-6^{II}), 67.93 (CH$_2$(linker)), 66.71 (C-5^{IV}), 66.58 (d, $J_{C,P}$ = 6.4 Hz, C-5^{III}), 60.92 (C-2^{II}), 52.57 (COOCH$_3$), 50.83 (CH$_2$(linker)), 27.61 (C-3^{IV}), 27.21 (C-3^{V}), 16.82 (C-6^{V}), 16.57 (C-6^{IV}); ^{31}P NMR (162 MHz, CDCl$_3$) δ −10.3; HRMS (ESI-TOF) m/z [M + NH$_4$]$^+$ calcd for C$_{90}$H$_{109}$N$_5$O$_{27}$PCl$_6$ 1932.5179, found 1932.5172. Anal. Calcd for C$_{90}$H $_{105}$N$_4$O$_{27}$PCl$_6$: C, 56.34; H, 5.52; N, 2.92. Found: C, 56.15; H, 5.52; N, 2.89. Data for pentasaccharide **45b**: R_f 0.26 (toluene/acetone 5:1); $[\alpha]_D^{22}$ −8.3 (c 0.7, CHCl$_3$); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.36−7.21 (m, 35 H, H$_{arom}$), 5.33 (d, 1H, $J_{1}^{II},_{2}^{II}$ = 8.3 Hz, H-1^{II}), 5.15 (d, 1H, $J_{1}^{V},_{2}^{V}$ = 2.8 Hz, H-1^{V}), 5.02 (d, 1H, $J_{1}^{I},_{2}^{I}$ = 3.5 Hz, H-1^{IV}), 5.00 (d, 1H, $J_{1}^{I},_{2}^{I}$ = 1.7 Hz, H-1^{I}), 4.90 (d, 1H, $J_{3}^{III},_{4}^{III}$ = 3.1 Hz, H-4^{III}), 4.73 (d, 1H, $J_{1}^{III},_{2}^{III}$ = 7.5 Hz, H-1^{III}), 4.69 (m, overlapped, H-6a^{III}), 4.67 (d, overlapped, J = 12.5 Hz, CH_2Ph), 4.65 (m, overlapped, 2 × CH_2Ph), 4.64 (m, overlapped, CH_2CCl$_3$), 4.58 (m, overlapped, CH_2Ph), 4.58 (m, overlapped, H-3^{II}), 4.57 (m, overlapped, CH_2CCl$_3$), 4.57−4.36 (m, overlapped, 9 × CH_2Ph), 4.51 (m, overlapped, H-5^{IV}), 4.47 (d, overlapped, J = 11.2 Hz, CH_2Ph), 4.46 (m, overlapped, OH-3^{III}), 4.45 (m, overlapped, H-6b^{III}), 4.43 (m, overlapped, H-5^{I}), 4.31 (m, 1H, H-4^{I}), 4.15 (m, 1H, H-5^{V}), 3.97 (t, 1H, J = 7.4 Hz, H-4^{II}), 3.93 (ddd, 1H, $J_{3eq}^{V},_{2}^{V}$ = 3.7 Hz, $J_{3ax}^{V},_{2}^{V}$ = 12.7 Hz, H-2^{V}), 3.85 (m, overlapped, H-2^{I}, H-3^{I}), 3.85 (m, overlapped, H-6a^{II}), 3.84 (m, overlapped, H-2^{IV}), 3.76 (m, overlapped, H-3^{III}), 3.72 (m, overlapped, CH$_2$(linker)), 3.72 (m, overlapped, H-2^{III}), 3.67 (m, overlapped, H-6b^{II}), 3.66 (m, overlapped, H-5^{II}), 3.56 (m, overlapped, H-5^{III}), 3.55 (s, 3H, COOCH$_3$), 3.69−3.51 (m, overlapped, 9 × CH$_2$(linker)), 3.54 (m, overlapped, H-4^{IV}), 3.53 (m, overlapped, H-2^{II}), 3.50 (m, overlapped, H-4^{V}), 3.29 (t, 2H, J = 5.1 Hz, CH$_2$(linker)), 2.14 (m, overlapped, H-3$_{eq}^{V}$), 2.13 (m, overlapped, H-3$_{eq}^{IV}$), 1.87 (ddd, 1H, $J_{3ax}^{V},_{4}^{V}$ = 2.2 Hz, $J_{2}^{V},_{3ax}^{V}$ = 12.7 Hz, $J_{3ax}^{V},_{3eq}^{V}$ = 12.7 Hz, H-3$_{ax}^{V}$), 1.81 (ddd, 1H, $J_{3ax}^{IV},_{4}^{IV}$ = 1.7 Hz, $J_{3ax}^{IV},_{2}^{IV}$ = 12.6 Hz, $J_{3eq}^{IV},_{3ax}^{IV}$ = 12.6 Hz, H-3$_{ax}^{IV}$), 1.24 (d, 3H $J_{5}^{V},_{6}^{V}$ = 6.6 Hz, H-6^{V}), 1.22 (d, 3H, $J_{5}^{IV},_{6}^{IV}$ = 6.6 Hz, H-6^{IV}); ^{13}C NMR (150 MHz, CDCl$_3$) δ 168.27, 161.31 (C-6^{I}, NHCO), 139.01, 138.73, 138.55 138.44, 138.40, 138.23 137.40, 128.87, 128.65, 128.60, 128.56, 128.53, 128.45, 128.39, 128.26, 128.06 127.91, 127.89, 127.86 (C$_{arom}$), 101.50 (C-1^{III}), 99.56 (C-1^{V}), 98.58 (C-1^{II}), 97.54 (C-1^{I}), 96.84 (C-1^{IV}), 94.82 (d, $J_{C,P}$ = 7.9 Hz, CH$_2$CCl$_3$), 92.88 (CCl$_3$(TCA)), 77.82 (d, $J_{C,P}$ = 3.0 Hz, CH$_2$CCl$_3$), 78.42 (C-2^{III}), 77.57 (d, $J_{C,P}$ = 4.1 Hz, C-4^{III}), 76.86, 76.84 (C-2^{I}, C-3^{I}), 76.71 (C-4^{IV}), 76.56 (C-5^{II}, C-3^{II}, in this order), 75.76 (C-4^{V}), 74.91 (C-4^{I}), 73.50 (CH$_2$Ph), 73.33 (C-4^{II}), 73.23 (CH$_2$Ph), 72.96 (CH$_2$Ph), 72.19 (d, $J_{C,P}$ = 7.5 Hz, C-3^{III}), 71.73 (CH$_2$Ph), 71.42 (C-6^{III}), 71.37, 71.27 (CH$_2$Ph), 72.00 (C-2^{V}), 71.08 (C-2^{IV}), 70.87 (2 × CH$_2$(linker)), 70.41 (CH$_2$(linker)), 70.41 (CH$_2$Ph), 70.31 (C-5^{I}), 70.23 (CH$_2$(linker)), 68.75 (C-6^{II}), 68.28 (C-5^{V}), 67.98 (CH$_2$(linker)), 67.34 (d, $J_{C,P}$ = 5.8 Hz, C-5^{III}), 66.75 (C-5^{IV}), 60.20 (C-2^{II}), 52.51 (COOCH$_3$), 50.84 (CH$_2$(linker)), 27.44 (C-3^{IV}), 27.25 (C-3^{V}), 16.79 (C-6^{V}), 16.70 (C-6^{IV}); ^{31}P NMR (162 MHz, CDCl$_3$) δ −2.4; HRMS (ESI-TOF) m/z [M + NH$_4$]$^+$ calcd for C$_{90}$H$_{109}$N$_5$O$_{27}$PCl$_6$ 1932.5179, found 1932.5193. Anal. Calcd for C$_{90}$H$_{105}$N$_4$O$_{27}$PCl$_6$: C, 56.34; H, 5.52; N, 2.92. Found: C, 56.16; H, 5.57; N, 2.86.

*2-[2-(2-Azidoethoxy)ethoxy]ethyl 2,4-Di-O-benzyl-3,6-dideoxy-α-L-xylo-hexopyranosyl-(1→2)-β-D-galactopyranosyl-(S)-(P)-4,6-cyclic 2,2,2-trichloroethyl phosphate-(1→3)-6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→4)-methyl 2,3-di-O-benzyl-α-D-galactopyranosyluronate (**47a**) and 2-[2-(2-Azidoethoxy)-ethoxy]ethyl 2,4-Di-O-benzyl-3,6-dideoxy-α-L-xylo-hexopyranosyl-(1→2)-β-D-galactopyranosyl-(R)-(P)-4,6-cyclic 2,2,2-trichloroethyl phosphate-(1→3)-6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1→4)-(methyl 2,3-di-O-benzyl-1-α-D-galactopyranosid)uronate (**47b**).* Tetrasaccharide **10** (212 mg, 0.134 mmol) was deacetylated with NaOMe in anhydrous MeOH as described above for a similar reaction to give tetraol **46** (0.18 g, 0.127 mmol, 95%), which was phosphorylated in DCM (anhydrous, 3.8 mL) with pyridine (0.10 mL, 0.10g, 1.27 mmol) and 2,2,2-trichloroethyl phosphorodichloridate (28.5 μL, 47.49 mg, 0.18 mmol). The reagent was divided into two portions (24.5 μL, 4 μL, successively) and added 30 min apart, as described above for a similar reaction. When the reaction was complete (TLC), work up, as described above, and preparative TLC (hexane/acetone 3:2, twice) gave tetrasaccharide **47a** (39 mg, 0.024 mmol, 19%) and tetrasaccharide **47b** (103 mg, 0.064 mmol, 51%). Data for tetrasaccharide **47a**: R_f 0.58 (toluene/acetone 2:1); $[\alpha]_D^{22}$ +14.6 (c 0.4, CHCl$_3$); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.39−7.23 (m, 25 H, H$_{arom}$), 6.96 (d, 1H, $J_{NH}^{II},_{2}^{II}$ = 7.0 Hz, H-NH^{II}), 5.15 (d, 1H, $J_{1}^{II},_{2}^{II}$ = 8.3 Hz, H-1^{II}), 5.08 (d, 1H, $J_{1}^{IV},_{2}^{IV}$ = 2.8 Hz, H-1^{IV}), 5.03 (d, 1H, $J_{1}^{I},_{2}^{I}$ = 2.7 Hz, H-1^{I}), 4.77 (d, overlapped, $J_{3}^{III},_{4}^{III}$ = 3.1 Hz, H-4^{III}), 4.77 (d, 1H, J = 12.0 Hz, CH_2Ph), 4.69 (d, overlapped, J = 11.4 Hz, CH_2Ph), 4.67 (m, overlapped, CH$_2$CCl$_3$ × 1), 4.66 (d, overlapped, J = 11.8 Hz, CH_2Ph), 4.59 (m, overlapped, CH$_2$CCl$_3$ × 1), 4.55 (m, overlapped, H-6a^{III}), 4.52 (m, overlapped, H-6b^{III}), 4.52 (m, overlapped, $J_{1}^{III},_{2}^{III}$ = 7.9 Hz, H-1^{III}), 4.60−4.51 (m, 6 × CH_2Ph), 4.49 (m, overlapped, H-5^{I}), 4.41 (d, overlapped, J = 11.8 Hz, CH_2Ph), 4.40 (m, overlapped, H-3^{II}), 4.29 (bs, 1H, H-4^{I}), 4.10 (dd 1H, $J_{4}^{IV},_{5}^{IV}$ = 9.6 Hz, $J_{5}^{IV},_{6}^{IV}$ = 6.0 Hz, H-5^{IV}), 3.93 (m, overlapped, H-2^{IV}), 3.92 (m, overlapped, H-2^{III}), 3.88 (m, overlapped, H-2^{I}, H-3^{I}), 3.80 (dd, 1H, $J_{5}^{II},_{6a}^{II}$ = 1.4 Hz, $J_{6a}^{II},_{6b}^{II}$ = 10.9 Hz, H-6a^{II}), 3.69 (m, overlapped, H-6b^{II}), 3.66 (s, 3H, COOCH$_3$), 3.66 (m, overlapped, H-3^{III}), 3.62 (m, overlapped, H-5^{III}), 3.74−3.53 (m, overlapped, 10 × CH$_2$(linker)), 3.55 (m, overlapped, H-4^{II}), 3.44 (bs, 1H, H-4^{IV}), 3.42 (ddd, 1H, $J_{5}^{II},_{6b}^{II}$ = 9.9 Hz, $J_{4}^{II},_{5}^{II}$ = 5.0 Hz, H-5^{II}), 3.36 (ddd, 1H, $J_{2}^{II},_{3}^{II}$ = 9.9 Hz H-2^{II}), 3.30 (t, 2H, J = 5.1 Hz, CH$_2$(linker)), 2.12 (ddd, 1H, $J_{3eq}^{IV},_{4}^{IV}$ = 3.9 Hz, $J_{3eq}^{IV},_{2}^{IV}$ = 3.6 Hz, $J_{3eq}^{IV},_{3ax}^{IV}$ = 13.0 Hz, H-3$_{eq}^{IV}$), 1.85 (ddd, 1H, $J_{3ax}^{IV},_{4}^{IV}$ = 2.0 Hz, $J_{3ax}^{IV},_{2}^{IV}$ = 13.0 Hz, H-3$_{ax}^{IV}$), 1.19 (d, 3H, H-6^{IV}); ^{13}C NMR (150 MHz, D$_2$O) δ 168.52, 161.45 (NHCO, C-6^{I}), 138.80, 138.61, 138.48, 138.40, 137.02, 128.95, 128.69, 128.64, 128.60, 128.56, 128.41, 128.02, 127.99 127.88, 127.75, 127.71 (C$_{arom}$), 100.50 (C-1^{III}), 99.55 (C-1^{IV}), 99.29 (C-1^{II}), 97.62 (C-1^{I}), 95.17 (d, $J_{C,P}$ = 10.4 Hz, CH$_2$CCl$_3$), 93.01 (CCl$_3$(TCA)), 78.92 (C-3^{II}), 78.68 (d, $J_{C,P}$ = 7.4 Hz, C-4^{III}), 78.20 (C-2^{III}), 77.12 (d, $J_{C,P}$ = 4.2 Hz, CH$_2$CCl$_3$), 77.00, 76.74 (C-2^{I}, C-3^{I}), 75.64 (C-4^{IV}), 75.20 (C-4^{I}), 75.17 (C-5^{II}), 73.80, 73.58, 73.11, (3 × CH$_2$Ph), 72.56 (C-2^{IV}), 71.98 (d, $J_{C,P}$ = 7.5

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Hz, C-3^{III}), 71.98 (CH_2Ph), 71.76 (CH_2Ph), 70.89 (CH_2(linker)), 70.88 (d, $J_{C,P}$ = 6.7 Hz, C-6^{III}), 70.87 (CH_2(linker)), 70.44 (CH_2(linker)), 70.33 (C-5^{I}), 70.24 (CH_2(linker)), 69.67 (C-6^{II}), 68.64 (C-4^{II}), 68.25 (C-5^{IV}), 67.97 (CH_2(linker)), 66.69 (d, $J_{c,p}$ = 6.9 Hz, C-5^{III}), 58.70 (C-2^{II}), 52.47 (COOCH $_3$), 50.85 (CH_2(linker)), 27.22 (C-3^{IV}), 16.98 (C-6^{IV}); HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{70}H_{87}N_5O_{24}PCl_6$ 1622.3610, found 1622.3606. Anal. Calcd for $C_{70}H_{83}N_4O_{24}PCl_6$: C, 52.28; H, 5.20; N, 3.48. Found: C, 52.06; H, 5.40; N, 3.41. Data for tetrasaccharide **47b**: R_f 0.26 (toluene/acetone 2:1); $[\alpha]_D^{22}$ +17.6 (c 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37−7.23 (m, 25 H, H_{arom}), 6.96 (d, 1H, $J_{2^{II},NH^{II}}$ = 7.0 Hz, H-NH^{II}), 5.14 (d, 1H, $J_{1^{II},2^{II}}$ = 8.3 Hz, H-1^{II}), 5.10 (d, 1H, $J_{1^{IV},2^{IV}}$ = 2.9 Hz, H-1^{IV}), 5.04 (d, 1H, $J_{1^{I},2^{I}}$ = 3.2 Hz, H-1^{I}), 4.88 (d, 1H, $J_{3^{III},4^{III}}$ = 2.7 Hz, H-4^{III}), 4.77 (d, overlapped, J = 12.1 Hz, CH_2Ph), 4.68 (d, overlapped, J = 11.5 Hz, CH_2Ph), 4.65 (d, overlapped, J = 12.2 Hz, CH_2Ph), 4.66 (m, overlapped, H-6a^{III}), 4.61 (m, overlapped, 1 × CH_2CCl$_3$), 4.60 (m, overlapped, 1 × CH_2CCl$_3$), 4.53 (m, overlapped, H-1^{III}), 4.60−4.50 (m, overlapped, 6 × CH_2Ph), 4.50 (m, overlapped, H-6b^{III}), 4.50 (d, 1H, $J_{4^{I},5^{I}}$ = 1.2 Hz, H-5^{I}), 4.42 (m, overlapped, H-3^{II}), 4.41 (d, overlapped, J = 12.0 Hz, CH_2Ph), 4.31 (bs, 1H, H-4^{I}), 4.12 (m, 1H, H-5^{IV}), 3.92 (ddd, 1H, $J_{3eq^{IV},2^{IV}}$ = 3.8 Hz, $J_{3ax^{IV},2^{IV}}$ = 12.0 Hz, H-2^{IV}), 3.90 (m, overlapped, H-3^{I}), 3.87 (m, overlapped, H-2^{I}), 3.86 (m, overlapped, H-2^{III}), 3.78 (dd, 1H, $J_{5^{II},6a^{II}}$ = 1.5 Hz, $J_{6a^{II},6b^{II}}$ = 10.7 Hz, H-6a^{II}), 3.75−3.52 (m, overlapped, 10 × CH_2(linker)), 3.70 (m, overlapped, H-5^{III}), 3.67 (m, overlapped, H-6b^{II}), 3.67 (m, overlapped, H-3^{III}), 3.65 (s, 3H, $COOCH_3$), 3.51 (m, overlapped, H-4^{II}), 3.45 (m, overlapped, H-4^{IV}), 3.41 (ddd, 1H, $J_{5^{II},6b^{II}}$ = 9.7 Hz, $J_{4^{II},5^{II}}$ = 4.9 Hz, H-5^{II}), 3.32 (ddd, overlapped, $J_{2^{II},3^{II}}$ = 10.3 Hz, H-2^{II}), 3.30 (t, 2H, J = 5.0 Hz, CH_2(linker)), 2.13 (ddd, 1H, $J_{3eq^{IV},3ax^{IV}}$ = 12.6 Hz, $J_{3eq^{IV},4^{IV}}$ = 3.6 Hz, $J_{3eq^{IV},2^{IV}}$ = 3.6 Hz, H-3$_{eq}^{IV}$), 1.84 (ddd, 1H, $J_{3ax^{IV},4^{IV}}$ = 2.3 Hz, H-3$_{ax}^{IV}$), 1.20 (d, 3H $J_{5^{IV},6^{IV}}$ = 6.5 Hz, H-6^{IV}); ^{13}C NMR (150 MHz, D_2O) δ 168.53, 161.49 (C-6^{I}, NHCO), 138.72, 138.60 138.42, 138.38, 137.12, 128.91, 128.64, 128.63, 128.57, 128.44, 128.37, 128.01, 127.98, 127.91, 127.80, 127.73, 127.64,127.43 (C_{arom}), 100.34 (C-1^{III}), 99.70 (C-1^{IV}), 99.26 (C-1^{II}), 97.59 (C-1^{I}), 94.87 (d, $J_{C,P}$ = 9.8 Hz, CH_2CCl_3), 92.93 (CCl_3(TCA)), 78.63 (C-3^{II}), 78.33 (C-2^{III}), 78.00 (d, $J_{C,P}$ = 5.0 Hz, C-4^{III}), 77.98 (d, $J_{C,P}$ = 4.6 Hz, CH_2CCl_3), 77.04 (C-2^{I}), 76.71 (C-3^{I}), 75.67 (C-4^{IV}), 75.18 (C-5^{II}), 75.12 (C-4^{I}), 73.83 (CH_2Ph), 73.58 (CH_2Ph), 73.08 (CH_2Ph), 72.26 (d, $J_{C,P}$ = 6.7 Hz, C-3^{III}), 71.86, 71.78 (CH_2Ph), 72.40 (C-2^{IV}), 70.86 (2 × CH_2(linker)), 70.43 (CH_2(linker)), 70.30 (C-5^{I}), 70.23 (CH_2(linker)), 70.10 (d, $J_{C,P}$ = 5.8 Hz, C-6^{III}), 69.64 (C-6^{II}), 68.87 (C-4^{II}), 68.03 (C-5^{IV}), 67.96 (CH_2(linker)), 67.21 (d, $J_{C,P}$ = 8.1 Hz, C-5^{III}), 58.69 (C-2^{II}), 52.46 ($COOCH_3$), 50.84 (CH_2(linker)), 27.07 (C-3^{IV}), 16.95 (C-6^{IV}); HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{70}H_{87}N_5O_{24}PCl_6$ 1622.3610, found 1622.3613. Anal. Calcd for $C_{70}H_{83}N_4O_{24}PCl_6$: C, 52.28; H, 5.20; N, 3.48. Found: C, 52.08; H, 5.33; N, 3.49.

*2-[2-(2-Aminoethoxy)ethoxy]ethyl β-D-Galactopyranosyl-4,6-cyclic phosphate-(1→3)-2-deoxy-2-acetamido-β-D-glucopyranosyl-(1→4)-(methyl α-D-galactopyranosid)uronate (**49**).* A mixture of trisaccharide **41a** and **41b** (0.20 g, 0.145 mmol), palladium-on-charcoal (0.20 g), and potassium phosphate buffer (0.1 M, pH 7, 50 mL/mmol, 7.3 mL) in MeOH (7.3 mL) was stirred at room temperature at ambient pressure for 3 d. The progress of the conversion was monitored by NMR spectroscopy, and the reaction was deemed complete when aromatic protons were no longer present and the integration of the singlet for the NHAc group (~2 ppm) reached three protons. Palladium-on-charcoal was removed by centrifugation (6000 rpm for 10 min) and the supernatant was collected. The catalyst was washed with water/MeOH 9:1 (10 × 3 mL), and the combined washings were centrifuged, to yield a clear supernatant, which was collected and concentrated, to give a crude produce. A solution of the crude product in water (1.5 mL) was purified in six runs by HPLC (C18 column, Phenomenex, 5 μm, 250 × 21.20 mm), with acetonitrile in water (0% 15 min, 3% 30 min, 10 mL/min) as mobile phase to give trisaccharide **49** (70.2 mg, 0.092 mmol, 63%): t_R 37.4 min; R_f 0.38 (*i*PrOH/water 1:1); $[\alpha]_D^{22}$ +12.4 (c 0.6, H_2O); ^{1}H NMR (600 MHz, D_2O) δ 5.09 (d, 1H, $J_{1^{I},2^{I}}$ = 3.9 Hz, H-1^{I}), 4.77 (d, $J_{1^{II},2^{II}}$ = 8.1 Hz, H-1^{II}), 4.74 (d, 1H, $J_{4^{I},5^{I}}$ = 0.8 Hz, H-5^{I}), 4.64 (d, 1H, $J_{3^{III},4^{III}}$ = 3.5 Hz, H-4^{III}), 4.55 (d, 1H, $J_{1^{III},2^{III}}$ = 7.8 Hz, H-1^{III}), 4.51 (dd, 1H, $J_{3^{I},4^{I}}$ = 2.8 Hz, H-4^{I}), 4.46 (bd, 1H, $J_{6a^{III},6b^{III}}$ = 12.9 Hz, H-6a^{III}), 4.30 (ddd, 1H, $J_{5^{III},6b^{III}}$ = 1.5 Hz, $J_{6b^{III},P^{III}}$ = 20.3 Hz, H-6b^{III}), 4.09 (dd, 1H, $J_{2^{I},3^{I}}$ = 10.3 Hz, H-3^{I}), 3.94 (dd, overlapped, $J_{6a^{II},6b^{II}}$ = 12.3 Hz, $J_{5^{II},6a^{II}}$ = 2.1 Hz, H-6a^{II}), 3.87 (s, overlapped, $COOCH_3$), 3.85 (m, overlapped, H-2^{II}), 3.90−3.72 (m, overlapped, 10 × CH_2(linker)), 3.82 (m, overlapped, H-3^{II}), 3.82 (m, overlapped, H-6b^{II}), 3.80 (m, overlapped, H-3^{III}), 3.80 (m, overlapped, H-5^{III}), 3.74 (m, overlapped, H-2^{I}), 3.65 (dd, 1H, $J_{2^{III},3^{III}}$ = 9.9 Hz, H-2^{III}), 3.59 (dd, 1H, $J_{3^{II},4^{II}}$ = 8.7 Hz, $J_{4^{II},5^{II}}$ = 9.9 Hz, H-4^{II}), 3.44 (ddd, 1H, $J_{5^{II},6b^{II}}$ = 5.2 Hz, H-5^{II}), 3.26 (t, 2H, J = 4.9 Hz, 2 × CH_2(linker)), 2.08 (s, 3H, $NCOCH_3$); ^{13}C NMR (150 MHz, D_2O) δ 175.49, 175.37 (C-6^{I}, $NHCOCH_3$), 103.55 (C-1^{III}), 102.52 (C-1^{II}), 99.32 (C-1^{I}), 82.88 (C-3^{II}), 78.56 (C-4^{I}), 76.58 (d, $J_{C,P}$ = 5.24 Hz, C-4^{III}), 75.81 (C-5^{II}), 71.62 (d, $J_{C,P}$ = 7.53 Hz, C-3^{III}), 70.86 (C-5^{I}), 70.41 (C-2^{III}), 70.38, 70.25, 70.12 (CH_2(linker)), 69.43 (C-3^{I}), 68.91 (d, $J_{C,P}$ = 5.65 Hz, C-6^{III}), 68.84 (C-4^{II}), 68.59 (C-2^{I}), 68.89 (CH_2(linker)), 67.96 (d, $J_{C,P}$ = 4.95 Hz, C-5^{III}), 67.02 (CH_2(linker)), 61.47 (C-6^{II}), 55.27 (C-2^{II}), 53.59 ($COOCH_3$), 39.75 (CH_2(linker)), 23.06 ($NHCOCH_3$); ^{31}P NMR (162 MHz, D_2O, with coupling) δ −4.0124 ($^3J_{P,H}$ = 21.98 Hz); HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{27}H_{48}N_2O_{21}P$ 767.2487, found 767.2498.

*2-[2-(2-Aminoethoxy)ethoxy]ethyl [β-D-Galactopyranosyl-4,6-cyclic phosphate)-(1→3)]-[3,6-dideoxy-α-L-xylo-hexopyranosyl-(1→4)]-2-deoxy-2-acetamido-β-D-glucopyranosyl-(1→4)-(methyl α-D-galactopyranosid)uronate (**50**).* Tetrasaccharides **43a** and **43b** (0.18 g, 0.106 mmol) were treated at room temperature with hydrogen at 150 psi for 5 d in the presence of Pd/C, as described for similar conversions. A solution of the crude product in water (0.5 mL) was purified in five runs by preparative C18 column (Phenomenex, 5 μm, 250 × 21.20 mm), with 4% MeOH in water (10 mL/min) as mobile phase to yield tetrasaccharide **50** (t_R = 43 min, 54.5 mg, 0.061 mmol, 57%). R_f 0.20 (*i*PrOH/water 3:2); $[\alpha]_D^{22}$ −9.3 (c 0.3, H_2O); ^{1}H NMR (600 MHz, D_2O) δ 5.09 (d, 1H, $J_{1^{I},2^{I}}$ = 3.8 Hz, H-1^{I}), 4.98 (d, 1H, $J_{1^{IV},2^{IV}}$ = 3.8 Hz, H-1^{IV}), 4.84 (dd, 1H, $J_{4^{IV},5^{IV}}$ = 13.9 Hz, $J_{5^{IV},6^{IV}}$ = 7.0 Hz, H-5^{IV}), 4.73 (m, overlapped, H-1^{II}), 4.62 (d, 1H, $J_{3^{III},4^{III}}$ = 3.5 Hz, H-4^{III}), 4.59 (d, 1H, $J_{1^{III},2^{III}}$ = 7.9 Hz, H-1^{III}), 4.49 (d, 1H, $J_{4^{I},5^{I}}$ = 1.7 Hz, H-4^{I}), 4.45 (dd, 1H, $J_{6a^{III},6b^{III}}$ = 12.2 Hz, H-6a^{III}), 4.73 (m, overlapped, H-5^{I}), 4.34 (dd, overlapped, $J_{6b^{III},P^{III}}$ = 22.2 Hz, H-6b^{III}), 4.17 (m, 1H, H-4^{IV}), 4.08 (dd, 1H, $J_{3^{I},4^{I}}$ = 2.8 Hz, $J_{2^{I},3^{I}}$ = 10.2 Hz, H-3^{I}), 4.05 (m, overlapped, H-2^{IV}), 4.04 (m, overlapped, H-3^{II}), 3.99 (dd, overlapped, $J_{6a^{II},6b^{II}}$ = 12.1 Hz, $J_{5^{II},6a^{II}}$ = 2.0 Hz, H-6a^{II}), 3.91 (m, overlapped, H-2^{II}), 3.90 (m, overlapped, H-6b^{II}), 3.87 (m, overlapped, 1 × CH_2(linker)), 3.88 (s, overlapped, $COOCH_3$), 3.81−3.73 (m, overlapped, 9 × CH_2(linker)), 3.77 (m, overlapped, H-4^{II}), 3.76 (m, overlapped, H-3^{III}), 3.75 (m, overlapped, H-2^{I}), 3.66 (s, 1H, H-5^{III}), 3.57 (dd, 1H, $J_{2^{III},3^{III}}$ = 9.8 Hz, H-2^{III}), 3.51 (ddd, 1H, $J_{5^{II},6b^{II}}$ = 4.0 Hz, $J_{5^{II},4^{II}}$ = 9.8 Hz, H-5^{II}), 3.26 (t, 2H, J = 5.2 Hz, 2 × CH_2(linker)), 2.08 (s, overlapped, $NCOCH_3$), 2.04 (ddd, 1H, $J_{3ax^{IV},4^{IV}}$ = 2.6 Hz, $J_{2^{IV},3ax^{IV}}$ = 12.6 Hz, $J_{3ax^{IV},3eq^{IV}}$ = 12.6 Hz, H-3$_{ax}^{IV}$), 1.92 (ddd, 1H, $J_{3eq^{IV},4^{IV}}$ = 4.4 Hz, $J_{2^{IV},3eq^{IV}}$ = 4.4 Hz, H-3$_{eq}^{IV}$), 1.17 (d, 3H, $J_{5^{IV},6^{IV}}$ = 6.7 Hz, H-6^{IV}); ^{13}C NMR (150 MHz, D_2O) δ 175.26 (C-6^{I}), 171.53 ($NHCOCH_3$), 103.56 (C-1^{III}), 102.54 (C-1^{II}), 99.33 (C-1^{I}), 98.46 (C-1^{IV}), 78.85 (C-4^{I}), 77.51 (C-3^{II}), 76.54 (d, $J_{C,P}$ = 4.9 Hz, C-4^{III}), 75.86 (C-5^{II}), 73.21 (C-4^{II}), 71.82 (d, $J_{C,P}$ = 7.6 Hz, C-3^{III}), 70.84 (C-5^{I}), 70.29 (C-2^{III}), 70.38, 70.26, 70.13 (CH_2(linker)), 69.43 (C-3^{I}), 69.28 (d, $J_{C,P}$ = 5.8 Hz, C-6^{III}), 68.83 (C-4^{IV}), 68.61 (C-2^{I}), 67.98 (d, $J_{C,P}$ = 4.6 Hz, C-5^{III}), 67.90 (CH_2(linker)), 67.22 (C-5^{IV}), 67.03 (CH_2(linker)), 63.81 (C-2^{IV}), 60.51 (C-6^{II}), 56.57 (C-2^{II}), 53.59 ($COOCH_3$), 39.76 (CH_2(linker)), 33.27 (C-3^{IV}), 23.13 ($NHCOCH_3$), 16.09 (C-6^{IV}); ^{31}P NMR (162 MHz, D_2O, with coupling) δ −3.80 ($^3J_{P,H}$ = 21.25 Hz); HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{33}H_{58}N_2O_{24}$ P 897.3117, found 897.3125.

*2-[2-(2-Aminoethoxy)ethoxy]ethyl 3,6-Dideoxy-α-L-xylo-hexopyranosyl-(1→2)-β-D-galactopyranosyl-4,6-cyclic phosphate-(1→3)-2-deoxy-2-acetamido-β-D-glucopyranosyl-(1→4)-(methyl-α-D-galactopyranosid)uronate (**51**).* Hydrogenation/hydrogenolysis of mixture of tetrasaccharides **47a** and **47b** (266 mg, 0.165 mmol) in presence of palladium-on-charcoal (266 mg), potassium phosphate buffer (0.1 M, pH 7, 8.3 mL), and MeOH (8.3 mL) was conducted at room temperature/150 psi for 5 d, when NMR (see preparation of **49**) showed that the conversion was complete. After workup, a solution of

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the crude product in water (1 mL), divided into 10 portions, was purified by HPLC (Phenomenex, C18, 5 μm, 250 × 21.20 mm; elution time, 36 min), with 7% MeOH in water (10 mL/min) as mobile phase, to give tetrasaccharide **51** (98.0 mg, 0.109 mmol, 66%): R_f 0.23 (*i*PrOH/water 3:2); $[\alpha]_D^{22}$ −4.9 (*c* 0.4, H_2O); ^{1}H NMR (600 MHz, D_2O) δ 5.15 (d, 1H, $J_{1^{IV},2^{IV}}$ = 3.8 Hz, H-1^{IV}), 5.08 (d, 1H, $J_{1^{I},2^{I}}$ = 3.8 Hz, H-1^{I}), 4.76 (d, 1H, $J_{1^{III},2^{III}}$ = 7.8 Hz, H-1^{III}), 4.73 (t, 1H, $J_{4^{I},5^{I}}$ = 0.9 Hz, $J_{5^{I},6b^{I}}$ = 0.9 Hz, H-5^{I}), 4.63 (d, 1H, $J_{3^{III},4^{III}}$ = 3.2 Hz, H-4^{III}), 4.63 (m, overlapped, $J_{1^{II},2^{II}}$ = 7.6 Hz, H-1^{II}), 4.46 (m, overlapped, H-6a^{III}), 4.45 (m, overlapped, H-4^{I}), 4.36 (ddd, overlapped, $J_{6b^{III},P^{III}}$ = 22.1 Hz, $J_{6a^{III},6b^{III}}$ = 12.3 Hz, $J_{5^{III},6b^{III}}$ = 0.9 Hz, H-6b^{III}), 4.27 (dd 1H, $J_{4^{IV},5^{IV}}$ = 13.2 Hz, $J_{5^{IV},6^{IV}}$ = 6.6 Hz, H-5^{IV}), 4.08 (dd, 1H, $J_{3^{I},4^{I}}$ = 3.0 Hz, $J_{2^{I},3^{I}}$ = 10.2 Hz, H-3^{I}), 4.05 (ddd, 1H, $J_{2^{IV},3eq^{IV}}$ = 3.8 Hz, $J_{2^{IV},3ax^{IV}}$ = 12.1 Hz, H-2^{IV}), 3.99 (ddd, 1H, $J_{2^{III},3^{III}}$ = 9.8 Hz, $J_{3^{III},P^{III}}$ = 3.2 Hz, H-3^{III}), 3.94 (m, overlapped, H-6a^{II}), 3.93 (m, overlapped, H-3^{II}), 3.87 (s, overlapped, $COOCH_3$), 3.89−3.72 (m, overlapped, 10 × CH_2(linker)), 3.83 (m, overlapped, H-6b^{II}), 3.82 (m, overlapped, H-4^{IV}), 3.80 (m, overlapped, H-5^{III}), 3.80 (m, overlapped, H-2^{II}), 3.75 (m, overlapped, H-2^{III}), 3.68 (dd, 1H, H-2^{I}), 3.54 (t, 1H, $J_{3^{II},4^{II}}$ = 9.8 Hz, $J_{4^{II},5^{II}}$ = 9.8 Hz, H-4^{II}), 3.45 (ddd, 1H, $J_{5^{II},6a^{II}}$ = 2.0 Hz, $J_{5^{II},6b^{II}}$ = 4.8 Hz, H-5^{II}), 3.25 (t, 2H, *J* = 4.8 Hz, 2 × CH_2(linker)), 2.11 (s, 3H, $NCOCH_3$), 1.97 (ddd, 1H, $J_{3eq^{IV},4^{IV}}$ = 4.1 Hz, $J_{3ax^{IV},3eq^{IV}}$ = 12.9 Hz, H-3$_{eq}^{IV}$), 1.85 (ddd, 1H, $J_{3ax^{IV},4^{IV}}$ = 2.8 Hz, H-3$_{ax}^{IV}$), 1.21 (d, 3H, $J_{5^{IV},6^{IV}}$ = 6.7 Hz, H-6^{IV}); ^{13}C NMR (150 MHz, D_2O) δ 175.79,175.56 (C-6^{I}, $NHCOCH_3$), 103.42 (C-1^{II}), 100.82 (C-1^{III}), 99.66 (C-1^{IV}), 99.34 (C-1^{I}), 79.10 (C-3^{II}), 78.93 (C-4^{I}), 77.11 (d, $J_{C,P}$ = 5.05 Hz, C-4^{III}), 76.19 (C-2^{III}), 75.87 (C-5^{II}), 72.68 (d, $J_{C,P}$ = 7.37 Hz, C-3^{III}), 70.84 (C-5^{I}), 70.34, 70.27, 70.12 (CH_2(linker)), 69.29 (C-3^{I}), 69.12 (C-4^{IV}), 68.78 (C-4^{II}), 68.79 (d, $J_{C,P}$ = 6.07 Hz, C-6^{III}), 68.60 (C-2^{I}), 67.95 (CH_2(linker)), 67.83 (d, $J_{C,P}$ = 4.95 Hz, C-5^{III}), 67.03 (CH_2(linker)), 66.91 (C-5^{IV}), 63.77 (C-2^{IV}), 61.37 (C-6^{II}), 55.34 (C-2^{II}), 53.65 ($COOCH_3$), 39.74 (CH_2(linker)), 33.35 (C-3^{IV}), 23.02 ($NHCOCH_3$), 15.98 (C-6^{IV}); ^{31}P NMR (162 MHz, D_2O, with coupling) δ −4.04 ($^3J_{P,H}$ = 21.59 Hz); HRMS (ESI-TOF) *m*/*z* [M + H]$^+$ calcd for $C_{33}H_{58}N_2O_{24}$ P 897.3117, found 897.3122.

*2-[2-(2-Aminoethoxy)ethoxy]ethyl [(3,6-Dideoxy-α-L-xylo-hexopyranosyl)-(1→2)-β-D-galactopyranosyl-4,6-cyclic phosphate-(1→3)]-[3,6-dideoxy-α-L-xylo-hexopyranosyl)-(1→4)]-2-deoxy-2-acetamido-β-D-glucopyranosyl-(1→4)-(methyl α-D-galactopyranosid)-uronate (**2**).* Palladium-on-charcoal (228 mg) was added to a solution of pentasaccharide **45a** and **45b** (228 mg, 0.12 mmol) in a mixture of potassium phosphate buffer (0.1 M, pH 7, 6 mL) and MeOH (6 mL), and the mixture was stirred at room temperature under hydrogen (150 psi) for 5 d, when NMR (see preparation of **49**) showed that the conversion was complete. After workup, a solution of the crude product (226 mg) in water (1 mL) was chromatographed in four runs (preparative HPLC, C18 column, Phenomenex, 5 μm, 250 × 21.20 mm), with 5% acetonitrile in water (10 mL/min) as a mobile phase. Pentasaccharide **2** eluted at 14.5 min (79.0 mg, 0.077 mmol, 64%): R_f 0.37 (*i*PrOH/water 1:1); $[\alpha]_D^{22}$ −20.1 (*c* 0.4, H_2O); ^{1}H NMR (600 MHz, D_2O) δ 5.09 (d, 1H, $J_{1^{I},2^{I}}$ = 3.9 Hz, H-1^{I}), 5.07 (d, 1H, $J_{1^{V},2^{V}}$ = 3.6 Hz, H-1^{V}), 4.98 (d, 1H, $J_{1^{IV},2^{IV}}$ = 3.4 Hz, H-1^{IV}), 4.82 (dd, overlapped, $J_{4^{IV},5^{IV}}$ = 13.6 Hz, $J_{5^{IV},6^{IV}}$ = 6.7, H-5^{IV}), 4.77 (d, 1H, $J_{1^{III},2^{III}}$ = 8.0 Hz, H-1^{III}), 4.73 (m, 1H, H-5^{I}), 4.62 (m, overlapped, H-4^{III}), 4.61 (d, overlapped, $J_{1^{II},2^{II}}$ = 8.1 Hz, H-1^{II}), 4.46 (m, overlapped, H-6a^{III}), 4.44 (m, overlapped, H-4^{I}), 4.38 (m, overlapped, H-6b^{III}), 4.34 (dd, overlapped, $J_{4^{V},5^{V}}$ = 13.5 Hz, $J_{5^{V},6^{V}}$ = 6.6 Hz, H-5^{V}), 4.25 (m, 1H, H-4^{IV}), 4.07 (dd, overlapped, $J_{2^{I},3^{I}}$ = 10.4 Hz, $J_{3^{I},4^{I}}$ = 2.9 Hz, H-3^{I}), 4.06 (m, overlapped, H-3^{II}), 4.05 (m, overlapped, H-2^{IV}), 4.02 (m, overlapped, H-2^{V}), 3.98 (dd, overlapped, $J_{6a^{II},6b^{II}}$ = 12.0 Hz, $J_{5^{II},6a^{II}}$ = 1.9 Hz, H-6a^{II}), 3.95 (m, overlapped, H-3^{III}), 3.92 (dd, overlapped, $J_{5^{II},6b^{II}}$ = 3.9 Hz, H-6b^{II}), 3.88 (s, overlapped, $COOCH_3$), 3.86 (m, overlapped, H-2^{II}), 3.81 (m, overlapped, H-4^{V}), 3.91−3.73 (m, overlapped, 10 × CH_2(linker)), 3.75 (m, overlapped, H-4^{II}), 3.68 (m, overlapped, H-2^{I}), 3.67 (m, overlapped, H-5^{III}, H-2^{III}, in this order), 3.48 (ddd, 1H, $J_{5^{II},6a/b^{II}}$ = 3.3 Hz, $J_{5^{II},6a/b^{II}}$ = 2.4 Hz, $J_{5^{II},4^{II}}$ = 9.5 Hz, H-5^{II}), 3.25 (t, 2H, *J* = 5.2 Hz, CH_2(linker)), 2.12 (s, overlapped, $NCOCH_3$), 2.09 (ddd, overlapped, $J_{3ax^{IV},4^{IV}}$ = 2.5 Hz, $J_{2^{IV},3ax^{IV}}$ = 12.9 Hz, $J_{3ax^{IV},3eq^{IV}}$ = 12.9 Hz, H-3$_{ax}^{IV}$), 1.95 (m, overlapped, H-3$_{ax}^{V}$), 1.91 (m, overlapped, H-3$_{eq}^{IV}$), 1.90 (m, overlapped, H-3$_{eq}^{V}$), 1.26 (d, 3H, H-6^{V}), 1.25 (d, 3H, H-6^{IV}); ^{13}C NMR (150 MHz, D_2O) δ 174.76, 171.58 (C-6^{I}, $NHCOCH_3$), 103.40 (C-1^{II}), 101.60 (C-1^{III}), 99.99 (C-1^{V}), 99.33 (C-1^{I}), 98.22 (C-1^{IV}), 79.16 (C-4^{I}), 76.95 (d, $J_{C,P}$ = 4.8 Hz, C-4^{III}), 76.85 (C-2^{III}),76.05 (C-3^{II}), 75.91 (C-5^{II}), 73.04 (d, $J_{C,P}$ = 7.2 Hz, C-3^{III}), 72.87 (C-4^{II}), 70.79 (C-5^{I}), 70.33, 70.26, 70.11 (CH_2(linker)), 69.32 (C-4^{V}), 69.24 (d, $J_{C,P}$ = 4.7 Hz, C-6^{III}), 69.23 (C-3^{I}), 68.97 (C-4^{IV}), 68.60 (C-2^{I}), 67.94 (d, $J_{C,P}$ = 5.6 Hz, C-5^{III}), 67.94 (CH_2(linker)), 67.23 (C-5^{IV}), 67.06 (CH_2(linker)), 66.70 (C-5^{V}), 64.11 (C-2^{V}), 63.89 (C-2^{IV}), 60.30 (C-6^{II}), 56.32 (C-2^{II}), 53.63 ($COOCH_3$), 39.74 (CH_2(linker)), 33.33 (C-3^{V}), 33.18 (C-3^{IV}), 23.05 ($NHCOCH_3$), 16.13 (C-6^{IV}), 16.03 (C-6^{V}); ^{31}P NMR (162 MHz, D_2O, with coupling) δ −3.68 ($^3J_{P,H}$ = 21.29 Hz); HRMS (ESI-TOF) *m*/*z* [M − H]$^-$ calcd for $C_{39}H_{66}N_2O_{27}P$ 1025.3591, found 1025.3593.

*2-[2-(2-Aminoethoxy)ethoxy]ethyl β-D-Galactopyranosyl-4,6-cyclic phosphate-(1→3)-2-deoxy-2-acetamido-β-D-glucopyranosyl-(1→4)-α-D-galactopyranuronic Acid (**6**).* To a solution of trisaccharide **49** (58 mg, 0.0756 mmol) in water (5.7 mL) was added KOH (0.25 mmol, 13.8 mg, 0.1 M solution, 2.5 mL) in several portions, to adjust the pH to ∼11, and the mixture was kept at room temperature, while the progress of saponification was monitored intermittently by TLC (*i*PrOH/water 1:1, R_f of trisaccharides **49** and **6**, 0.38 and 0.71, respectively). When the reaction was complete (∼8 h), CO_2 was passed through the mixture, to adjust the pH to 6. After lyphilization, the residue was dissolved in water (0.4 mL) and centrifuged (6000 rpm, 5 min) before purification, in four runs, by preparative HPLC (C18 column, Phenomenex, C18, 5 μm, 250 × 21.20 mm), with pure water (12 mL/min) as mobile phase. Salt eluted at 3.7 min and trisaccharide **6** at 4.6 min (47.2 mg, 0.0627 mmol, 83%). R_f 0.71 (*i*PrOH/water 1:1); $[\alpha]_D^{22}$ +16.1 (*c* 0.6, H_2O); ^{1}H NMR (600 MHz, D_2O) δ 5.03 (d, 1H, $J_{1^{I},2^{I}}$ = 4.0 Hz, H-1^{I}), 4.68 (d, $J_{1^{II},2^{II}}$ = 8.3 Hz, H-1^{II}), 4.64 (d, 1H, $J_{3^{III},4^{III}}$ = 3.4 Hz, H-4^{III}), 4.56 (d, 1H, $J_{1^{III},2^{III}}$ = 7.8 Hz, H-1^{III}), 4.46 (ddd, 1H, $J_{6a^{III},6b^{III}}$ = 12.8 Hz, $J_{5^{III},6a^{III}}$ = 1.6 Hz, $J_{P^{III},6a^{III}}$ = 1.6 Hz H-6a^{III}), 4.38 (dd, 1H, $J_{3^{I},4^{I}}$ = 3.1 Hz, $J_{4^{I},5^{I}}$ = 0.9 Hz, H-4^{I}), 4.32 (d, overlapped, H-5^{I}), 4.30 (ddd, overlapped, $J_{6b^{III}-P^{III}}$ = 21.9 Hz, H-6b^{III}, $J_{5^{III},6b^{III}}$ = 1.6 Hz), 4.01 (dd, 1H, $J_{3^{I},4^{I}}$ = 3.1 Hz, $J_{2^{I},3^{I}}$ = 10.3 Hz, H-3^{I}), 3.91 (dd, overlapped, $J_{6a^{II},6b^{II}}$ = 10.3 Hz, $J_{5^{II},6a^{II}}$ = 2.0 Hz, H-6a^{II}), 3.89 (m, overlapped, H-2^{II}), 3.88 (m, overlapped, 1 × CH_2(linker)), 3.83−3.73 (m, overlapped, 9 × CH_2(linker)), 3.82 (m, overlapped, H-3^{II}), 3.80 (m, overlapped, H-3^{III}), 3.80 (m, overlapped, H-5^{III}), 3.77 (m, overlapped, H-2^{I}), 3.75 (m, overlapped, H-6b^{II}), 3.65 (dd, 1H, $J_{2^{III},3^{III}}$ = 9.9 Hz, H-2^{III}), 3.56 (dd, 1H, $J_{3^{II},4^{II}}$ = 8.6 Hz, $J_{4^{II},5^{II}}$ = 9.8 Hz, H-4^{II}), 3.42 (ddd, 1H, $J_{5^{II},6b^{II}}$ = 6.6 Hz, H-5^{II}), 3.24 (m, 2H, CH_2(linker)), 2.08 (s, 3H, $NCOCH_3$); ^{13}C NMR (150 MHz, D_2O) δ 175.74, 175.51 (C-6^{I}, $NHCOCH_3$), 103.40 (C-1^{III}), 102.65 (C-1^{II}), 99.17 (C-1^{I}), 82.88 (C-3^{II}), 80.15 (C-4^{I}), 76.59 (d, $J_{C,P}$ = 5.07 Hz, C-4^{III}), 75.75 (C-5^{II}), 71.80 (C-5^{I}), 71.63 (d, $J_{C,P}$ = 7.44 Hz, C-3^{III}), 70.58 (CH_2(linker)), 70.40 (C-3^{I}, C-2^{III}), 70.24, 70.18 (CH_2(linker)), 69.17 (C-4^{II}), 68.95 (C-2^{I}), 68.92 (d, $J_{C,P}$ = 5.78 Hz, C-6^{III}), 67.96 (d, $J_{C,P}$ = 4.87 Hz, C-5^{III}), 67.76, 67.22 (CH_2(linker)), 61.90 (C-6^{II}), 55.39 (C-2^{II}), 39.78 (CH_2(linker)), 23.03 ($NHCOCH_3$); ^{31}P NMR (162 MHz, D_2O, with coupling) δ −3.99 ($^3J_{P,H}$ = 22.07 Hz); HRMS (ESI-TOF) *m*/*z* [M − H]$^-$ calcd for $C_{26}H_{44}N_2O_{21}$ P 751.2174, found 751.2184.

*2-[2-(2-Aminoethoxy)ethoxy]ethyl [β-D-Galactopyranosyl-4,6-cyclic phosphate)-(1→3)]-[3,6-dideoxy-α-L-xylo-hexopyranosyl-(1→4)]-2-deoxy-2-acetamido-β-D-glucopyranosyl-(1→4)-α-D-galactopyranuronic Acid (**4**).* A solution of tetrasaccharide **50** (15 mg, 0.01674 mmol) in water (1.26 mL) was treated with KOH (0.054 mmol, 3.0 mg, 0.1 M solution, 0.54 mL) for 16 h, as described above for similar saponifications (R_f of tetrasaccharide **50**, 0.20, cf. R_f 0.43 for **4**, *i*PrOH/water 3:2). After processing with CO_2 and lyphylization as described above, a mixture of crude tetrasaccharide and buffer salts was obtained. MeOH (0.5 mL) followed by acetonitrile (1.5 mL) was added to a solution of the crude product in water (0.5 mL). The solution was centrifuged (6000 rpm, 5 min), and the material in the supernatant was resolved, in 0.83 mL portions, by HPLC (Waters XBridge BEH Preparative Amide 5 μm, 250 × 19 mm column). Before the run, the column was equilibrated with water/acetonitrile 2:3 (70 mL/CV, 50 CV, 3.5 L, 20 mL/min, in order to coat the column-packing surface with water, and then with water/MeOH/acetonitrile 1:1:3 (20 CV, 1.4 L, 20 mL/min). Solvent mixtures were mixed ahead

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of time and allowed to warm to room temperature. Elution of the 0.83 mL samples from the HPLC column was done with water/MeOH/acetonitrile 1:1:3 (15 mL/min). Tetrasaccharide **4** eluted at 17 min as a wide peak. Before the next run, the column was equilibrated with water/acetonitrile 2:3 (10 CV, 20 mL/min), in order to wash out the salt and recoat the column-packing surface with water, and then with water/MeOH/acetonitrile 1:1:3 (10 CV, 20 mL/min) to give eventually tetrasaccharide **4** (9.53 mg, 0.011 mmol, 65%): R_f 0.43 (*i*PrOH/water 3:2); $[\alpha]_D^{22}$ −14.1 (*c* 0.5, H_2O); ^{1}H NMR (600 MHz, D_2O) δ 5.03 (d, 1H, $J_{1^{I},2^{I}}$ = 3.7 Hz, H-1^{I}), 4.89 (d, 1H, $J_{1^{IV},2^{IV}}$ = 3.7 Hz, H-1^{IV}), 4.83 (m, overlapped, H-5^{IV}), 4.68 (d, 1H, $J_{1^{II},2^{II}}$ = 8.2 Hz, H-1^{II}), 4.61 (d, 1H, $J_{3^{III},4^{III}}$ = 3.6 Hz, H-4^{III}), 4.59 (d, 1H, $J_{1^{III},2^{III}}$ = 7.9 Hz, H-1^{III}), 4.45 (dd, 1H, $J_{6a^{III},6b^{III}}$ = 12.3 Hz, H-6a^{III}), 4.37 (m, overlapped, H-4^{I}), 4.34 (m, overlapped, H-6b^{III}), 4.31 (m, overlapped, H-5^{I}), 4.15 (m, 1H, H-4^{IV}), 4.04 (m, overlapped, H-2^{IV}), 4.03 (m, overlapped, H-3^{II}), 4.02 (m, overlapped, H-3^{I}), 3.98 (dd, overlapped, $J_{6a^{II},6b^{II}}$ = 12.3 Hz, $J_{5^{II},6a^{II}}$ = 1.9 Hz, H-6a^{II}), 3.94 (m, overlapped, H-2^{II}), 3.88 (m, 1H, CH_2(linker)), 3.82 (m, overlapped, H-6b^{II}), 3.82−3.71 (m, overlapped, 9 × CH_2(linker)), 3.76 (m, overlapped, H-3^{III}), 3.76 (m, overlapped, H-2^{I}), 3.73 (m, overlapped, H-4^{II}), 3.66 (s, 1H, H-5^{III}), 3.56 (dd, 1H, $J_{2^{III},3^{III}}$ = 9.7 Hz, H-2^{III}), 3.47 (ddd, 1H, $J_{5^{II},4^{II}}$ = 1.9 Hz, $J_{5^{II},6b^{II}}$ = 5.2 Hz, $J_{5^{II},4^{II}}$ = 9.1 Hz, H-5^{II}), 3.26 (dd, 2H, *J* = 5.4 Hz, 4.9 Hz, CH_2(linker)), 2.08 (s, overlapped, $NCOCH_3$), 2.04 (ddd, overlapped, $J_{3ax^{IV},4^{IV}}$ = 2.6 Hz, $J_{3ax^{IV},3eq^{IV}}$ = 12.9 Hz, $J_{2^{IV},3ax^{IV}}$ = 12.9 Hz, H-3$_{ax}^{IV}$), 1.92 (ddd, 1H, $J_{3eq^{IV},4^{IV}}$ = 4.2 Hz, $J_{2^{IV},3eq^{IV}}$ = 4.2 Hz, H-3$_{eq}^{IV}$), 1.17 (d, 3H, $J_{5^{IV},6^{IV}}$ = 6.8 Hz, H-6^{IV}); ^{13}C NMR (150 MHz, D_2O) δ 175.78, 175.36 (C-6^{I}, $NHCOCH_3$), 103.53 (C-1^{III}), 102.54 (C-1^{II}), 99.19 (C-1^{I}), 98.59 (C-1^{IV}), 80.06 (C-4^{I}), 77.64 (C-3^{II}), 76.54 (d, $J_{C,P}$ = 5.1 Hz, C-4^{III}), 75.96 (C-5^{II}), 73.81 (C-4^{II}), 71.80 (d, $J_{C,P}$ = 7.4 Hz, C-3^{III}), 71.90 (C-5^{I}), 70.61, 70.26, 70.19 (CH_2(linker)), 70.37 (C-3^{I}), 70.30 (C-2^{III}), 69.27 (d, $J_{C,P}$ = 5.1 Hz, C-6^{III}), 68.96 (C-2^{I}), 68.86 (C-4^{IV}), 67.97 (d, $J_{C,P}$ = 5.2 Hz, C-5^{III}), 67.78 (CH_2(linker)), 67.20 (C-5^{IV}), 67.05 (CH_2(linker)), 63.81 (C-2^{IV}), 60.95 (C-6^{II}), 56.70 (C-2^{II}), 39.78 (CH_2(linker)), 33.25 (C-3^{IV}), 23.10 ($NHCOCH_3$), 16.07 (C-6^{IV}); ^{31}P NMR (162 MHz, D_2O, with coupling) δ −3.81 ($^3J_{P,H}$ = 21.38 Hz); HRMS (ESI-TOF) *m*/*z* [M + H]$^+$ calcd for $C_{32}H_{56}N_2O_{24}$ P 883.2961, found 883.2971.

*2-[2-(2-Aminoethoxy)ethoxy]ethyl 3,6-Dideoxy-α-L-xylo-hexopyranosyl-(1→2)-β-D-galactopyranosyl-4,6-cyclic phosphate-(1→3)-2-deoxy-2-acetamido-β-D-glucopyranosyl-(1→4)-α-D-galactopyranuronic Acid (**5**).* A solution of tetrasaccharide **51** (15 mg, 0.01674 mmol) in water (1.26 mL) was treated with KOH (0.054 mmol, 3.0 mg, 0.1 M solution, 0.54 mL) for 16 h, as described above for similar saponifications, until TLC (*i*PrOH/water 3:2) showed complete conversion of the starting material (R_f 0.23) into product (R_f 0.55). After processing, as described above for the preparation of **4**, a solution of the crude product in water/MeOH/acetonitrile (1:1:3, 0.83 mL) was subjected to HPLC (Waters XBridge BEH Preparative Amide 5 μm, 250 × 19 mm column, column equilibration as above for the purification of **4**, water/MeOH/acetonitrile 1:1:3, 15 mL/min). Tetrasaccharide **5** was eluted at 10 min as a wide peak. Tetrasaccharide **5** (8.4 mg, pure; 4.1 mg, slightly impure) was obtained in three runs. The impure material was dissolved in water (100 ul) and purified by HPLC (C18 column, Phenomenex, C18, 5 μm, 250 × 21.20 mm, 5% acetonitrile in water, 10 mL/min), to give pure **5** (3.2 mg, combined yield 11.6 mg, 0.0131 mmol, 79%). R_f 0.55 (*i*PrOH/water 3:2); $[\alpha]_D^{22}$ −3.6 (*c* 0.4, H_2O); ^{1}H NMR (600 MHz, D_2O) δ 5.15 (d, 1H, $J_{1^{IV},2^{IV}}$ = 3.6 Hz, H-1^{IV}), 5.02 (d, 1H, $J_{1^{I},2^{I}}$ = 3.7 Hz, H-1^{I}), 4.76 (d, 1H, $J_{1^{III},2^{III}}$ = 7.8 Hz, H-1^{III}), 4.63 (d, 1H, $J_{3^{III},4^{III}}$ = 3.3 Hz, H-4^{III}), 4.57 (d, 1H, $J_{1^{II},2^{II}}$ = 8.4 Hz, H-1^{II}), 4.46 (d, 1H, $J_{6a^{III},6b^{III}}$ = 12.6 Hz, H-6a^{III}), 4.36 (dd, overlapped, $J_{6b^{III},P^{III}}$ = 22.05 Hz, H-6b^{III}), 4.33 (m, overlapped, H-4^{I}), 4.31 (m, overlapped, H-5^{I}), 4.27 (dd 1H, $J_{4^{IV},5^{IV}}$ = 6.7 Hz, $J_{5^{IV},6^{IV}}$ = 13.5 Hz, H-5^{IV}), 4.04 (ddd, overlapped, $J_{2^{IV},3eq^{IV}}$ = 4.4 Hz, $J_{2^{IV},3ax^{IV}}$ = 12.5 Hz, H-2^{IV}), 4.01 (m, overlapped, H-3^{I}), 3.98 (ddd, overlapped, $J_{2^{III},3^{III}}$ = 9.7 Hz, $J_{3^{III},P^{III}}$ = 3.3 Hz, H-3^{III}), 3.92 (m, overlapped, H-3^{II}), 3.91 (m, overlapped, H-6a^{II}), 3.90−3.72 (m, overlapped, 10 × CH_2(linker)), 3.84 (m, overlapped, H-2^{II}), 3.82 (m, overlapped, H-4^{IV}), 3.80 (m, overlapped, H-5^{III}), 3.75 (m, overlapped, H-2^{III}), 3.73 (m, overlapped, H-6b^{II}), 3.72 (m, overlapped, H-2^{I}), 3.49 (dd, 1H, $J_{3^{II},4^{II}}$ = 8.6 Hz, $J_{4^{II},5^{II}}$ = 9.8 Hz, H-4^{II}), 3.43 (ddd, 1H, $J_{5^{II},6a^{II}}$ = 2.0 Hz, $J_{5^{II},6b^{II}}$ = 6.9 Hz, H-5^{II}), 3.21 (t, 2H, *J* = 5.1 Hz, CH_2(linker)), 2.10 (s, 3H, $NCOCH_3$), 1.97 (ddd, 1H, $J_{3eq^{IV},4^{IV}}$ = 4.1, $J_{3ax^{IV},3eq^{IV}}$ = 13.0 Hz, H-3$_{eq}^{IV}$), 1.84 (ddd, 1H, $J_{3ax^{IV},4^{IV}}$ = 2.7, H-3$_{ax}^{IV}$), 1.20 (d, 3H, $J_{5^{IV},6^{IV}}$ = 6.7 Hz, H-6^{IV}); ^{13}C NMR (150 MHz, D_2O) δ 175.77, 174.89 (C-6^{I}, $NHCOCH_3$), 103.36 (C-1^{II}), 100.89 (C-1^{III}), 99.60 (C-1^{IV}), 99.19 (C-1^{I}), 80.30 (C-4^{I}), 79.31 (C-3^{II}), 77.10 (d, $J_{C,P}$ = 4.5 Hz, C-4^{III}), 76.10 (C-2^{III}), 75.80 (C-5^{II}), 72.72 (d, $J_{C,P}$ = 7.2 Hz, C-3^{III}), 71.85 (C-5^{I}), 70.55 (CH_2(linker)), 70.29 (C-3^{I}), 70.22, 70.18 (CH_2(linker)), 69.37 (C-4^{II}), 69.05 (C-4^{IV}), 68.95 (C-2^{I}), 68.78 (d, $J_{C,P}$ = 6.0 Hz, C-6^{III}), 67.83 (d, $J_{C,P}$ = 5.5 Hz, C-5^{III}), 67.80 (CH_2(linker)), 67.48 (CH_2(linker)), 66.94 (C-5^{IV}), 63.79 (C-2^{IV}), 62.00 (C-6^{II}), 55.46 (C-2^{II}), 39.81 (CH_2(linker)), 33.32 (C-3^{IV}), 22.99 ($NHCOCH_3$), 15.95 (C-6^{IV}); ^{31}P NMR (162 MHz, D_2O, with coupling) δ −4.039 ($^3J_{P,H}$ = 21.42 Hz); HRMS (ESI-TOF) *m*/*z* [M − H]$^-$ calcd for $C_{32}H_{54}N_2O_{24}P$ 881.2804, found 881.2796,

*2-[2-(2-Aminoethoxy)ethoxy]ethyl [(3,6-Dideoxy-α-L-xylo-hexopyranosyl)-(1→2)-β-D-galactopyranosyl-4,6-cyclic phosphate-(1→3)]-[3,6-dideoxy-α-L-xylo-hexopyranosyl-(1→4)]-2-deoxy-2-acetamido-β-D-glucopyranosyl-(1→4)-α-D-galactopyranosiduronic Acid (**1**).* A solution of pentasaccharide **2** (28 mg, 0.0273 mmol) in water (2 mL) was treated with KOH (0.088 mmol, 4.9 mg, 0.1 M solution, 0.88 mL) for 16 h, as described above, until TLC (*i*PrOH/water 1:1, R_f of pentasaccharides **1** and **2**, 0.69 and 0.37, respectively) showed the completion of the reaction. After processing, as described above for preparation of **4**, a solution of the crude product in water/MeOH/acetonitrile (1:1:3, 1 mL) was subjected to HPLC (Waters XBridge BEH Preparative Amide 5 μm, 250 × 19 mm column, column equilibration as above for the purification of **4**, water/MeOH/acetonitrile 1:1:3, 15 mL/min). Pentasaccharide **1** eluted at 16 min as a wide peak. Before each next run, the column was equilibrated as described above, to give pentasaccharide **1** (21.2 mg, 0.021 mmol, 77%, total from five runs): R_f 0.69 (*i*PrOH/water 1:1); $[\alpha]_D^{22}$ −30.8 (*c* 0.4, H_2O). ^{1}H NMR (600 MHz, D_2O) δ 5.06 (d, 1H, $J_{1^{V},2^{V}}$ = 3.5 Hz, H-1^{V}), 5.02 (d, 1H, $J_{1^{I},2^{I}}$ = 3.2 Hz, H-1^{I}), 4.86 (d, 1H, $J_{1^{IV},2^{IV}}$ = 3.2 Hz, H-1^{IV}), 4.82 (m, overlapped, H-5^{IV}), 4.76 (d, 1H, $J_{1^{III},2^{III}}$ = 8.0 Hz, H-1^{III}), 4.61 (d, 1H, $J_{4^{III},3^{III}}$ = 4.0 Hz, H-4^{III}), 4.57 (d, 1H, $J_{1^{II},2^{II}}$ = 8.4 Hz, H-1^{II}), 4.46 (d, 1H, $J_{6a^{III},6b^{III}}$ = 12.4 Hz, H-6a^{III}), 4.38 (dd, $J_{P^{III},6b^{III}}$ = 22.2 Hz, H-6b^{III}), 4.34 (m, overlapped, H-5^{V}), 4.33 (d, overlapped, $J_{3^{I},4^{I}}$ = 2.6 Hz, H-4^{I}), 4.31 (bs, overlapped, H-5^{I}), 4.24 (m, 1H, H-4^{IV}), 4.06 (m, overlapped, H-3^{II}), 4.04 (m, overlapped, H-2^{IV}), 4.02 (m, overlapped, H-3^{I}, H-2^{V}, in this order), 3.98 (m, overlapped, H-6a^{II}), 3.95 (ddd, overlapped, $J_{3^{III},2^{III}}$ = 9.6 Hz, $J_{3^{III},OH^{III}}$ = 4.0 Hz, H-3^{III}), 3.90 (m, overlapped, H-2^{II}), 3.83 (m, overlapped, H-4^{V}), 3.82 (m, overlapped, H-6b^{II}), 3.90−3.71 (m, overlapped, 10 × CH_2(linker)), 3.70 (dd, overlapped, $J_{3^{I},2^{I}}$ = 10.5 Hz, H-2^{I}), 3.68 (m, overlapped, H-4^{II}), 3.67 (m, overlapped, H-2^{III}, H-5^{III}, in this order), 3.46 (m, 1H, H-5^{II}), 3.25 (t, 2H, *J* = 5.0 Hz, 2 × CH_2(linker)), 2.11 (s, overlapped, $NCOCH_3$), 2.10 (ddd, overlapped, $J_{3ax^{IV},4^{IV}}$ = 2.5 Hz, $J_{2^{IV},3ax^{IV}}$ = 12.9 Hz, $J_{3ax^{IV},3eq^{IV}}$ = 12.9 Hz, H-3$_{ax}^{IV}$), 1.93 (m, overlapped, H-3$_{ax}^{V}$), 1.91 (m, overlapped, H-3$_{eq}^{IV}$), 1.89 (m, overlapped, H-3$_{eq}^{V}$), 1.25 (d, 3H, $J_{5^{V},6^{V}}$ = 6.3 Hz, H-6^{V}), 1.24 (d, 3H, $J_{5^{IV},6^{IV}}$ = 6.5 Hz, H-6^{IV}); ^{13}C NMR (150 MHz, D_2O) δ 175.76, 174.79 (C-6^{I}, $NHCOCH_3$), 103.28 (C-1^{II}), 101.66 (C-1^{III}), 99.94 (C-1^{V}), 99.21 (C-1^{I}), 98.45 (C-1^{IV}), 80.22 (C-4^{I}), 76.97 (d, $J_{c,}$ = 3.76 Hz, C-4^{III}), 76.59 (C-2^{III}), 76.17 (C-3^{II}), 76.10 (C-5^{II}), 73.76 (C-4^{II}), 73.06 (d, $J_{C,P}$ = 7.2 Hz, C-3^{III}), 71.93 (C-5^{I}), 70.57, 70.25, 70.21 (CH_2(linker)), 70.27 (C-3^{I}), 69.26 (d, $J_{C,P}$ = 6.3 Hz, C-6^{III}), 69.26 (C-4^{V}), 68.98 (C-4^{IV}), 68.95 (C-2^{I}), 67.93 (d, $J_{C,P}$ = 4.0 Hz, C-5^{III}), 67.83 (CH_2(linker)), 67.24 (C-5^{IV}), 67.05 (CH_2(linker)), 66.76 (C-5^{V}), 64.13 (C-2^{V}), 63.89 (C-2^{IV}), 60.96 (C-6^{II}), 56.45 (C-2^{II}), 39.76 (CH_2(linker)), 33.32 (C-3^{V}), 33.18 (C-3^{IV}), 23.03 ($NHCOCH_3$), 16.12 (C-6^{IV}), 15.99 (C-6^{V}); ^{31}P NMR (162 MHz, D_2O, with coupling) δ −3.67 ($^3J_{P,H}$ = 22.47 Hz); HRMS (ESI-TOF) *m*/*z* [M + H]$^+$ calcd for $C_{38}H_{66}N_2O_{27}$ P 1013.3589, found 1013.3591.

*2-[2-(2-Aminoethoxy)ethoxy]ethyl [(3,6-Dideoxy-α-L-xylo-hexopyranosyl)-(1→2)-β-D-galactopyranosyl-(1→3)]-[3,6-dideoxy-α-L-xylo-hexopyranosyl-(1→4)]-2-deoxy-2-acetamido-β-D-glucopyranosyl-(1→4)-α-D-galactopyranuronic Acid (**3**).* A mixture of pentasaccharide **44** (50 mg, 0.029 mmol), palladium-on-charcoal (50 mg), potassium phosphate buffer (0.01 M, pH 7, 1.45 mL), and

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MeOH (1.45 mL) was stirred under hydrogen, at room temperature at 800 psi, until monitoring by NMR spectroscopy showed that the reaction was complete (~3 d, cf. above). After workup, as described for the preparation of **49**, the crude product was dissolved in water (10 mL), KOH (0.1 M) was added to adjust the pH to ~11, and the mixture was kept at room temperature for 16 h, when TLC (*i*PrOH/water 1:1, R_f of pentasaccharides **52** and **3**, 0.10 and 0.44, respectively) showed that the reaction was complete. CO_2 was passed through the mixture to adjust the pH to 6, and the residue obtained by lyophilization was dissolved in water (1.8 mL). MeOH (1.8 mL) and acetonitrile (5.4 mL) were added, and the solution was centrifuged (6000 rpm, 5 min) before loading on the HPLC column (in 9 portions, Waters XBridge BEH Preparative Amide 5 μm, 250 × 19 mm), which was conditioned as described above for the preparation of **4**. Pentasaccharide **3** was eluted at 18 min (16.1 mg, 0.0169 mmol, 58.2%): R_f 0.44 (*i*PrOH/water 1:1); $[\alpha]_D^{22}$ −21.6 (*c* 0.5, H_2O); ^{1}H NMR (600 MHz, D_2O) δ 5.12 (d, 1H, $J_{1^V,2^V}$ = 3.4 Hz, H-1^V), 5.02 (d, 1H, $J_{1^I,2^I}$ = 4.0 Hz, H-1^I), 4.88 (d, 1H, $J_{1^{IV},2^{IV}}$ = 3.4 Hz, H-1^{IV}), 4.82 (m, overlapped, H-5^{IV}), 4.73 (d, 1H, $J_{1^{III},2^{III}}$ = 7.7 Hz, H-1^{III}), 4.58 (d, 1H, $J_{1^{II},2^{II}}$ = 8.4 Hz, H-1^{II}), 4.32 (m, overlapped, H-4^I, H-5^V, in this order), 4.30 (m, overlapped, H-5^I), 4.17 (t, $J_{3^{II},2^{II}}$ = 9.6 Hz, $J_{3^{II},4^{II}}$ = 9.6 Hz, H-3^{II}), 4.06 (m, overlapped, H-2^{IV}), 4.02 (m, overlapped, H-3^I, H-2^V, in this order), 3.97 (m, overlapped, H-6a^{II}), 3.90 (m, overlapped H-4^{IV}), 3.89 (m, overlapped, H-4^{III}), 3.88 (m, overlapped, H-2^{II}), 3.87 (m, overlapped, 1 × CH_2(linker)), 3.84 (m, overlapped, H-3^{III}), 3.82 (m, overlapped, H-6a^{III}, H-4^V, in this order), 3.79 (m, overlapped, H-6b^{II}), 3.75 (m, overlapped, H-6b^{III}), 3.79–3.71 (m, overlapped, 9 × CH_2(linker)), 3.70 (m, overlapped, H-2^I), 3.68 (m, overlapped, H-4^{II}), 3.67 (m, overlapped, H-2^{III}), 3.62 (m, overlapped, H-5^{III}), 3.47 (m, 1H, H-5^{II}), 3.22 (t, 2H, *J* = 4.8 Hz, 2 × CH_2(linker)), 2.12 (s, overlapped, $NCOCH_3$), 2.10 (ddd, overlapped, $J_{3ax^{IV},4^{IV}}$ = 2.5 Hz, $J_{2^{IV},3ax^{IV}}$ = 12.8 Hz, $J_{3ax^{IV},3eq^{IV}}$ = 12.8 Hz, H-3$_{ax}^{IV}$), 1.95 (m, overlapped, H-3$_{eq}^{IV}$), 1.94 (m, overlapped, H-3$_{eq}^{V}$), 1.89 (ddd, 1H, $J_{3ax^V,4^V}$ = 2.4 Hz, $J_{2^V,3ax^V}$ = 12.8 Hz, $J_{3ax^V,3eq^V}$ = 12.8 Hz, H-3$_{ax}^{V}$), 1.24 (d, 3H, $J_{5^V,6^V}$ = 7.4 Hz, H-6^V), 1.23 (d, 3H, $J_{5^{IV},6^{IV}}$ = 6.5 Hz, H-6^{IV}); ^{13}C NMR (150 MHz, D_2O) δ 175.81, 174.78 (C-6^I, $NHCOCH_3$), 103.35 (C-1^{II}), 101.40 (C-1^{III}), 99.51 (C-1^V), 99.22 (C-1^I), 98.05 (C-1^{IV}), 80.24 (C-4^I), 76.86 (C-2^{III}), 76.17 (C-3^{II}), 76.06 (C-5^{II}), 75.42 (C-5^{III}), 74.45 (C-3^{III}), 73.48 (C-4^{II}), 71.91 (C-5^I), 70.56, 70.24, 70.21 (CH_2(linker)), 70.28 (C-3^I), 69.52 (C-4^{III}), 69.35 (C-4^{IV}), 69.21 (C-4^V), 68.98 (C-2^I), 67.82 (CH_2(linker)), 67.49 (CH_2(linker)), 67.10 (C-5^{IV}), 66.68 (C-5^V), 64.08 (C-2^V), 63.71 (C-2^{IV}), 62.29 (C-6^{III}), 61.07 (C-6^{II}), 56.47 (C-2^{II}), 39.83 (CH_2(linker)), 33.35 (C-3^V), 33.10 (C-3^{IV}), 23.05 ($NHCOCH_3$), 16.10 (C-6^{IV}), 16.05 (C-6^V); HRMS (ESI-TOF) *m*/*z* [M + H]$^+$ calcd for $C_{38}H_{67}N_2O_{25}$ 951.4033, found 951.4042.

*2-[2-(2-Aminoethoxy)ethoxy]ethyl α-D-4-Deoxy-hex-4-en-galactopyranuronicic Acid (**53**).* The β-elimination product **53** isolated from several separations was combined and purified by HPLC (C18 column, Phenomenex, C18, 5 μm, 150 × 4.6 mm), with 5% acetonitrile in water (1 mL/min) as mobile phase. Monosaccharide **53** was eluted at 2.0 min: ^{1}H NMR (600 MHz, D_2O) δ 5.83 (d, 1H, $J_{3,4}$ = 3.1 Hz, H-4), 5.18 (d, 1H, $J_{1,2}$ = 2.6 Hz, H-1), 4.38 (d, 1H, $J_{3,2}$ = 7.5 Hz, H-3), 4.07 (ddd, 1H, *J* = 3.7, 4.6, 11.9 Hz, CH_2(linker)), 3.90 (ddd, 1H, *J* = 5.6, 3.9, 11.8 Hz, CH_2(linker)), 3.84 (dd, 1H, H-2), 3.80–7.17 (m, 8H, CH_2(linker)), 3.22 (t, 2H, *J* = 4.8 Hz, CH_2(linker)); ^{13}C NMR (150 MHz, D_2O) δ 169.80 (C-6), 145.29 (C-5), 108.36 (C-4), 99.93 (C-1), 70.76 (C-2), 70.35, 70.23, 70.18, 69.03, 67.32 (CH_2(linker)), 66.81 (C-3), 39.81 (CH_2NH_2); HRMS (ESI-TOF) *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{22}NO_8$ 308.1345, found 308.1350.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01019.

Preparation of the buffer for hydrogenolysis and 1D and 2D NMR spectra for all new compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kpn@helix.nih.gov

Notes

The authors declare no competing financial interest.

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