Modular Synthesis of Heparin Oligosaccharides

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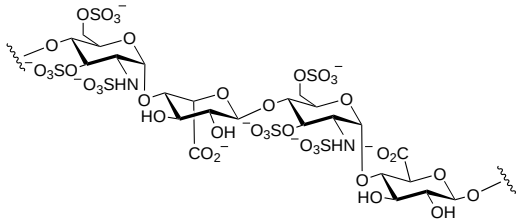
Abstract: A general, modular strategy for the first completely stereoselective synthesis of defined heparin oligosaccharides is described. Six monosaccharide building blocks (four differentially protected glucosamines, one glucuronic and one iduronic acid) were utilized to prepare di- and trisaccharide modules in a fully selective fashion. Installation of the α-glucosamine linkage was controlled by placing a conformational constraint on the uronic acid glycosyl acceptors thereby establishing a new concept for stereochemical control. Combination of disaccharide modules to form *trans*-uronic acid linkages was completely selective by virtue of C2 participating groups. Coupling reactions between disaccharide modules exhibited sequence dependence. While the union of many glucosamine uronic acid disaccharide modules did not meet any problems, certain sequences proved not accessible. Elaboration of glucosamine uronic acid disaccharide building blocks to trisaccharide modules by addition of either one additional glucosamine or uronic acid allowed for stereoselective access to oligosaccharides as demonstrated on the example of a hexasaccharide resembling the ATIII-binding sequence. Final deprotection and sulfation yielded the fully synthetic heparin oligosaccharides.

Keywords: carbohydrates · glycosylation · heparin · oligosaccharides

Introduction

Proteoglycans are complex protein–carbohydrate assemblies that consist of a core protein and one or more covalently attached glycosaminoglycan chains.[1] These linear polysaccharides range in length from ≈20 to 200 disaccharide repeat units, each composed of an amino sugar and an uronic acid moiety (Scheme 1). Heparin-like glycosaminoglycans (HLGAGs) are the most acidic naturally occurring biopolymers. These complex polysaccharides, found in the extra cellular matrix, play a key role in regulating the biological activity of several proteins in the coagulation cascade along with many other processes of biomedical importance including growth factor interactions, virus entry, and angiogenesis.[2] Heparin, isolated from the mast cells of pigs, is currently produced in multi-ton quantities and used in a variety of medical applications.[3] Most prominent is the use of heparin as an anticoagulant in heart disease where it has served as a therapeutic agent since the late 1930s. The heterogeneity of heparin results in many severe side effects, making this inexpensive drug dangerous and necessitates close monitoring.[4]



Scheme 1. Schematic view of heparin.

The heparin-antithrombin III (AT-III) interaction is responsible for heparin's anticoagulant activity and is the only system where the exact sequence of heparin that associates with the protein has been identified. Extensive structure–activity studies using synthetic oligosaccharides[5] as well as NMR[6] and X-ray crystallography[7] have been performed.

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Based on these studies, a concerted drug development effort has been undertaken and resulted in the development of a synthetic pentasaccharide heparin analogue for use in humans.[8] With the exception of the AT-III–heparin interaction, the structure and function relationship of HLGAGs is still very poorly understood due to the complexity and heterogeneity of these polymers. Defined HLGAG oligosaccharides constitute valuable molecular tools to gain a detailed understanding of the sequences of HLGAGs responsible for binding to a particular protein and modulating its biological activity.[1] Determination of the structure–activity relationships of HLGAGs creates an opportunity for the discovery of novel therapeutic interventions for a host of disease states.

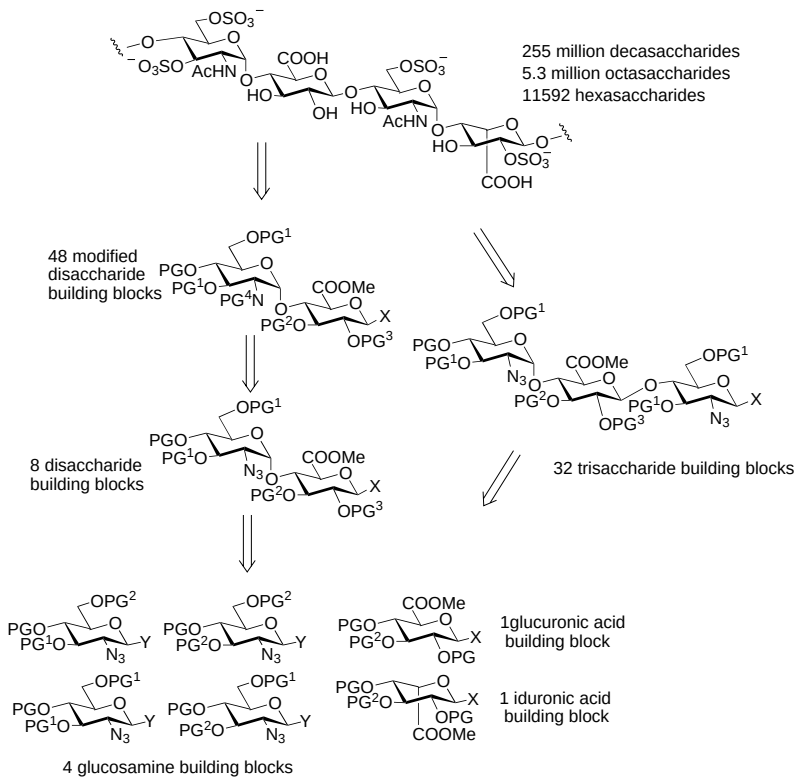
Over the past two decades, a variety of synthetic methods directed at the preparation of HLGAG oligosaccharides have been disclosed[9] and heroic total syntheses have resulted in the assembly of AT-III-binding HLGAG oligosaccharides.[10] More recently, longer oligosaccharide HLGAG analogues exhibiting impressive biological activity have been prepared using simplified syntheses.[11] Still, the procurement of specific HLGAG sequences required a new total synthesis for each oligosaccharide.

A modular, highly convergent synthetic approach for the rapid assembly of defined HLGAG oligosaccharide sequences and eventually even libraries of defined glycosaminoglycans and non-natural analogues would be ideal. Such an approach requires careful consideration of the many synthetic challenges presented by the great diversity of native structures. The sulfation patterns mandate the placement of specific protecting groups in all positions to carry sulfates and different protection on hydroxyls that remain unaltered. The amine portion of the glucosamine component has been found to be acetylated, sulfated and found to exist as the free amine,[12] thus requiring a protecting group scheme that allows for the differentiation of this position.

In addition to the installation of a host of protective groups, the creation of the glycosidic linkages making up the backbone of HLGAGs poses several challenges. The use of uronic acid derivatives as glycosidating agents has received little attention[13] and is often circumvented[9b–d, 10b, c] due to the inherent low reactivity imposed by the C5 ester. Stereocontrol during the fashioning of the α-glucosamine linkage is difficult as anchimeric assistance cannot be exploited, thus resulting in the formation of mixtures of glycosides.[9d] Separation of such anomeric mixtures often necessitates very difficult chromatographic steps. Finally, the preparation of iduronic acid monosaccharides requires lengthy synthetic procedures. A successful synthetic strategy will have to find appropriate solutions to all these challenges, enable high convergency without compromising generality and ideally provide a modular approach that can be readily transferred to the automated solid-phase assembly of defined HLGAG structures.

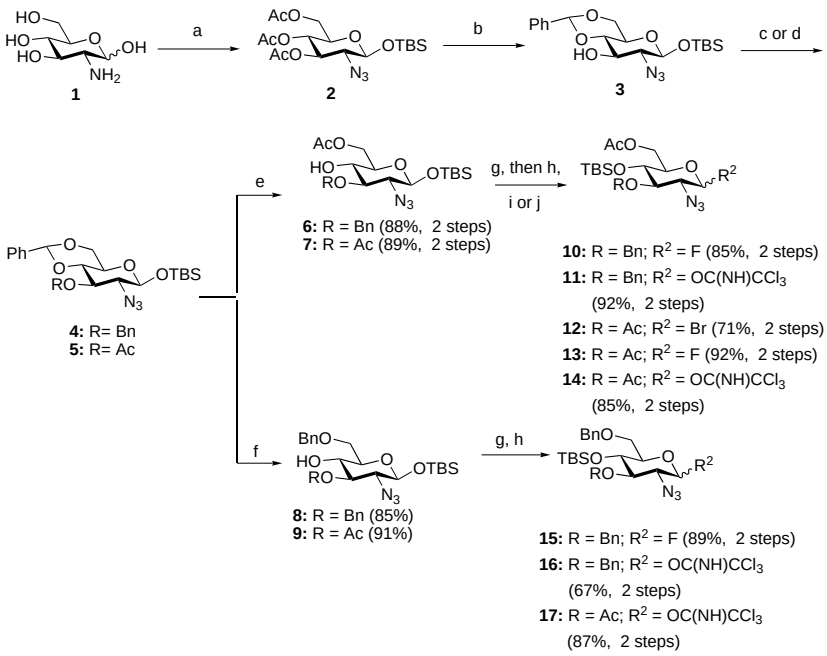
Results and Discussion

Synthetic strategy: In contemplating the challenges and rewards of a synthetic strategy for the rapid assembly of defined HLGAG oligosaccharide sequences we designed a modular, highly convergent synthetic plan. A set of four glucosamine monosaccharide building blocks exhibiting protecting group patterns representative of the different forms of sulfation found in native structures will be derived from glucosamine. Glucuronic and iduronic acid monomers will be prepared through a common route from diacetone glucose. Coupling of glucosamine and uronic acid monomers will furnish a set of disaccharide modules. Introduction of a new method to control the stereoselectivity of glycosylation reactions by conformationally constraining the uronic acid acceptor will render the desired disaccharide modules with complete selectivity.[14] These disaccharides can be further modified by protecting group manipulations to allow for variable substitution of the amino group. A simple two step elongation cycle involving the union of disaccharide units will result in larger heparin oligosaccharides (Scheme 2). The



Scheme 2. Retrosynthetic analysis of a general, modular approach to the preparation of heparin-like glycosaminoglycans.

overall scheme can also accommodate trisaccharide modules prepared by coupling of monosaccharides and disaccharides. Established procedures facilitate the final stages of the synthesis as removal of temporary acetate protecting groups followed by sulfation of the exposed hydroxyls and final deprotection followed by N-sulfation will yield the target molecules.[9b, c]

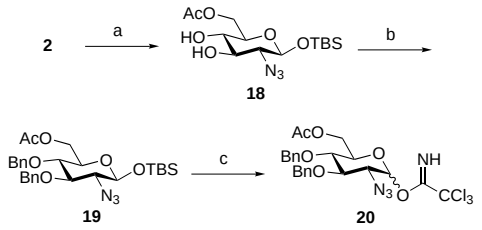


Scheme 3. Synthesis of differentially protected glucosamine monosaccharide building blocks. a) 1. TfN_3, H_2O, K_2CO_3, CH_2Cl_2, MeOH, $CuSO_4$; 2. Ac_2O, pyridine, DMAP; 3. NH_3, MeOH, THF; 4. TBSCl, imidazole, CH_2Cl_2, 57% (four steps); b) 1. NaOMe, MeOH; 2. $PhCH(OMe)_2$, pTsOH, CH_3CN, 86% (two steps); c) BnBr, Ag_2O, 4 Å molecular sieves, CH_2Cl_2, 95%; d) Ac_2O, DMAP, pyridine, 95%; e) 1. TFA (60% aq.), CH_2Cl_2; 2. AcCl, collidine, $-40\,^{\circ}C$; f) TES, TFA, CH_2Cl_2; g) 1. TBSOTf, lutidine, CH_2Cl_2; 2. TBAF, AcOH, THF; h) $NCCCl_3$, DBU, CH_2Cl_2; i) DAST, CH_2Cl_2, $0\,^{\circ}C$; j) $SOBr_2$, imidazole, THF.

Preparation of the monosaccharide building blocks: The first challenge to be tackled in trying to reduce such a general approach to HLGAG synthesis to practice is the procurement of large amounts of differentially protected monosaccharide building blocks. In order to access large quantities of all monosaccharides, a convergent synthesis from inexpensive starting materials is needed that can be performed on large scale with a minimal number of chromatographic steps. While a host of synthetic methods for the preparation of glucosamine donors had been explored previously[15] we decided to focus on an approach that allows access to all glucosamine monomers from common advanced intermediates. To identify the building blocks most suitable for installation of the desired α-glucosamine linkage, different anomeric leaving groups replaced an anomeric silyl ether during the late stages of the synthesis. A set of glucosamine building blocks was prepared from glucosamine **1** (Scheme 3). Conversion of the 2-amino group into the corresponding azide, necessary for α-selective glycosylations, was followed by acetylation and anomeric silylation to afford crystalline **2** in 57% yield over four steps.[16] Deacetylation and installation of the 4,6-benzylidene acetal furnished common precursor **3**. Benzylation of the 3-hydroxyl to fashion **4** or acetylation to afford **5** was followed by either removal of the 4,6-benzylidene protection and placement of 6-acetates to provide **6** and **7** or selective opening of the benzylidene acetal to furnish **8** and **9**. These maneuvers provided access to the skeleton of glucosamine building blocks containing 4-*O*-silyl ethers as temporary protecting groups. The TBS groups will be removed later during the preparation of oligosaccharides utilizing disaccharide modules.

With the desired protecting group patterns in place we turned our attention to the installation of different anomeric leaving groups. Less reactive glycosyl fluorides **10**, **13**, and **15**, glycosyl bromide **12** exhibiting intermediate reactivity, and highly reactive glycosyl trichloroacetimidates **11**, **14**, **16** and **17** were prepared for couplings with uronic acid acceptors.

In addition to glucosamine units that act as acceptors during oligosaccharide formation, glucosamine "cap" monosaccharides will be required to mark the non-reducing end of the target oligosaccharide. A 4-*O*-benzyl ether was readily introduced by dibenzylation of diol **18** followed by transformation into glycosyl trichloroacetimidate **20** (Scheme 4).



Scheme 4. Synthesis of a glucosamine monosaccharide building block as non-reducing end terminus. a) 1. NaOMe, MeOH; 2. AcCl, collidine, $-40\,^{\circ}C$, 93% (two steps); b) BnBr, Ag_2O, 4 Å molecular sieves, CH_2Cl_2, 80%; c) 1. THF, AcOH, TBAF; 2. CCl_3CN, DBU, CH_2Cl_2, 88% (two steps).

Although we focused our efforts exclusively on cap **20** as a proof of principle, three other cap building blocks with different permutations of acetates and benzyl groups can be synthesized in the same fashion.

After establishing a route for the preparation of glucosamine building blocks from a common precursor, a reliable and efficient path for the synthesis of uronic acid building blocks was needed. Traditionally, the preparation of iduronic acid has been particularly difficult since no direct precursor can be obtained from natural sources.[17] Efficiency, scalability and the avoidance of excessive chromatography is mandatory for the procurement of large amounts of these starting materials. Under this premise, we developed a route to

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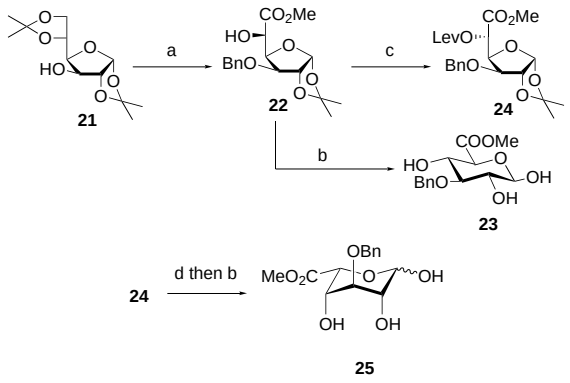
differentially protected glucuronic acid and iduronic acid monosaccharides via a common intermediate (Scheme 5). Commercially available diacetone glucose **21** was converted to crystalline glucuronic acid furanoside **22** through an eight-step procedure that was easily scalable to 100 g starting material and did not require purification of any intermediates.[18] Access to iduronic acid furanoside **24** was readily achieved by inversion of the C5 stereocenter of the triflate derived from **22**. Treatment of **22** and **24** with trifluoroacetic acid resulted in deprotection and formation of the uronic acid pyranosides **23** and **25**.



Scheme 5. Synthesis of glucuronic acid and iduronic acid monosaccharide building blocks. a) 1. NaH, BnBr, THF, Bu_4NI; 2. aq. HOAc (66%), 40 °C; 3. TBSCl, DMAP, CH_2Cl_2, pyridine; 4. Ac_2O, DMAP, pyridine; 5. HF/pyridine, THF; 6. TEMPO (cat.), KBr, Bu_4NBr, $NaHCO_3$, NaOCl, CH_2Cl_2/H_2O; 7. 4 M NaOH, MeOH; 8. MeI, $KHCO_3$, DMF, 65% (eight steps); b) TFA (90% aq.), quant; c) 1. Tf_2O, pyridine, CH_2Cl_2; 2. LevONa, DMF, 80 °C, 82% (two steps); d) N_2H_4, HOAc, pyridine, 91%.

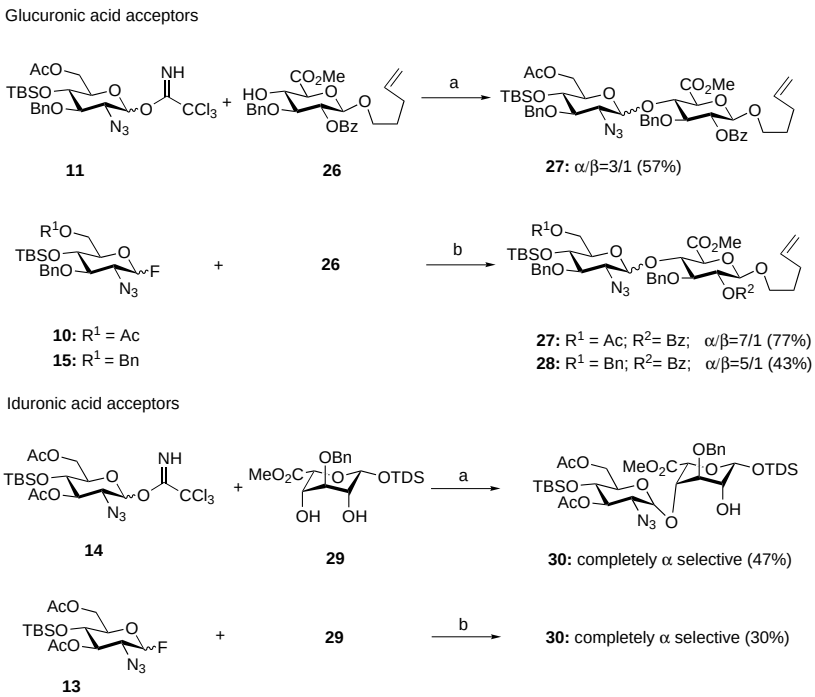
Disaccharide formation—Stereocontrol of glycosylation reactions by conformational locking of the glycosyl acceptor: With both differentially protected glucosamine as well as glucuronic and iduronic monosaccharides at hand, a set of disaccharide building blocks was to be assembled by creation of an α-glucosamine linkage. While *trans*-glycosidic linkages are readily installed with complete stereoselectivity by virtue of a C2 participating group using a host of anomeric leaving groups, stereoselective formation of *cis*-glycosides is generally more difficult since anchimeric assistance cannot be exploited.[19]

In order to form α-glucosamine linkages that are ubiquitous in nature,[20] the C2 amino group of glucosamine is typically masked in form of a nonparticipating azide.[9, 21] Anomeric selectivities vary greatly depending upon the coupling partners involved and often require difficult separations. Couplings involving C2-azido glucosamine trichloroacetimidate **11** and fluoride donors (**10**, **15**[22]) with glucuronic acid acceptor **26**[22] yielded anomeric mixtures of **27** and **28** (Scheme 6). These results were in agreement with previous studies involving other glucuronic acid acceptors.[10a,c, 23] Interestingly, when the C5 epimer of glucuronic acid, iduronic acid **29**,[17b] served as glycosyl acceptor, exclusively α-glucosamine linkages were obtained.[5b, 14, 24] Contrary to findings reported by others,[17b] glycosylation of **29** was not completely regioselective but afforded trisaccharide by concomitant glycosylation of the C2 hydroxyl group.

The marked differences in the stereoselectivity of these coupling reactions prompted us to investigate how the observed effect could be harnessed to establish the desired linkage with complete stereoselectivity. Electronic effects[25] and conformational constraint[26] of the glycosidating agent have been utilized to control the stereochemical outcome of glycosylations. Manipulation of the steric and electronic nature of the glycosyl acceptor to direct glycosylations had received less attention.

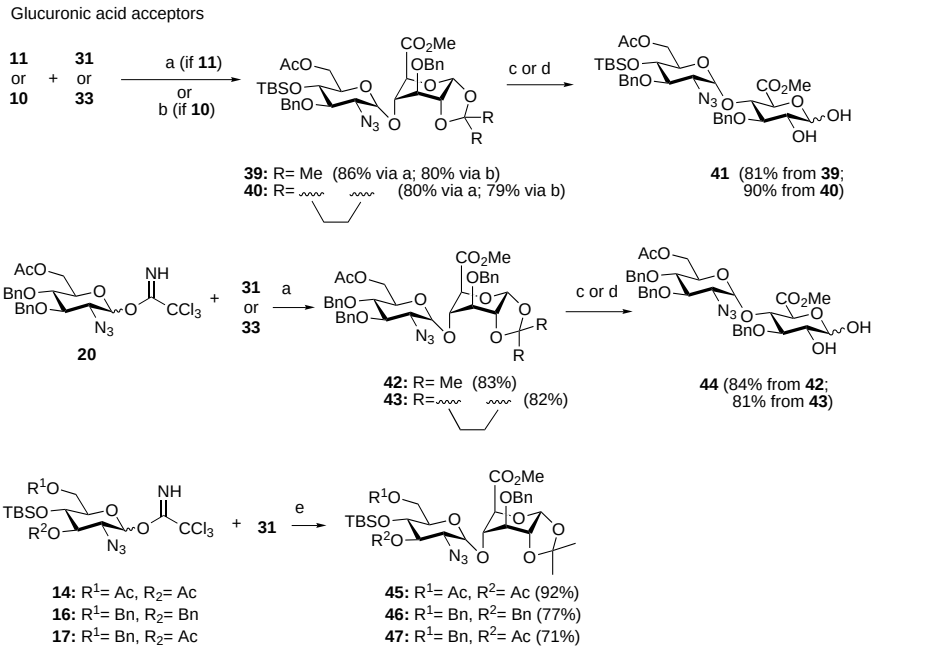
The conformation of the different acceptors suggested a possible explanation for the different behavior of glucuronic and iduronic acid acceptors. Glucuronic acid preferentially adopts a $^4C_1$ conformation with an equatorial C4 hydroxyl group. Iduronic acid in contrast adopts either a $^1C_4$ conformation or a skewed boat $^2S_0$ conformation in oligosaccharide sequences depending upon the substituents on the ring.[27, 28] In the $^1C_4$ conformation the C4 hydroxyl occupies an axial position.[19, 29] Apparently, the conformation is responsible for the observed α-selectivity of glycosylations without anchimeric assistance.

Based on these observations we engineered a conformational constraint into glycosyl acceptors to control the stereochemistry during disaccharide formation (Scheme 7).[14] NMR

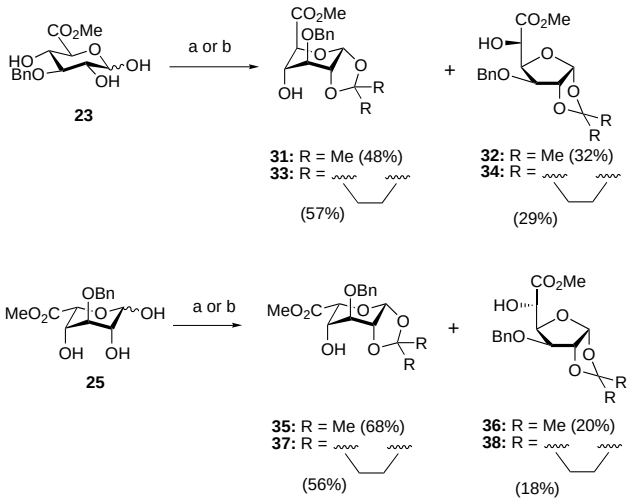


Scheme 6. Synthesis of disaccharides using uronic acid acceptors. a) TBSOTf, CH_2Cl_2, −78 °C → room temperature; b) $AgClO_4$, $SnCl_2$, Et_2O, 4 Å molecular sieves, 0 °C → room temperature.

analysis of glucuronic acid (**31**, **33**) carrying cyclic isopropylidene protecting groups revealed a $^1C_4$ conformation as judged by the coupling constants ($J_{4,5} \approx 3.5$ Hz ($^4C_1$: $J_{4,5} > 8$ Hz) and $J_{1,2} \approx 2.7$ Hz). Differentially protected glucuronic acid monomers (**31**, **33**) were prepared from triol **23** by formation of isopropylidene[30] or cyclopentylidene[31] acetals upon reaction with 2-methoxypropene or methoxycyclopentene under kinetic control (Scheme 7). The corresponding furanoside by-products (**32**, **34**) were also obtained and were recycled by cleavage of the acetal protective group and resubmission to 1,2-acetal formation. With conformationally constrained glucuronic acid acceptors **31** and **33** in hand, the stereochemical outcome of the coupling reactions was investigated (Scheme 8). Both glycosyl trichloroacetimidates (e.g. **11**) and glycosyl fluorides (e.g. **10**) resulted exclusively in the formation of α-linked disaccharides **39** and **40** in very good



Scheme 8. Synthesis of disaccharides using "locked" glucuronic acid acceptors. a) TBSOTf, 4 Å molecular sieves, CH_2Cl_2, $-78\,^\circ C \rightarrow$ room temperature; b) $AgClO_4$, $SnCl_2$, Et_2O, 4 Å molecular sieves, $0\,^\circ C \rightarrow$ room temperature; c) dichloroacetic acid (75 % aq.); d) dichloroacetic acid (50 % aq.); e) TBSOTf, 4 Å molecular sieves, CH_2Cl_2, $-25\,^\circ C \rightarrow$ room temperature.

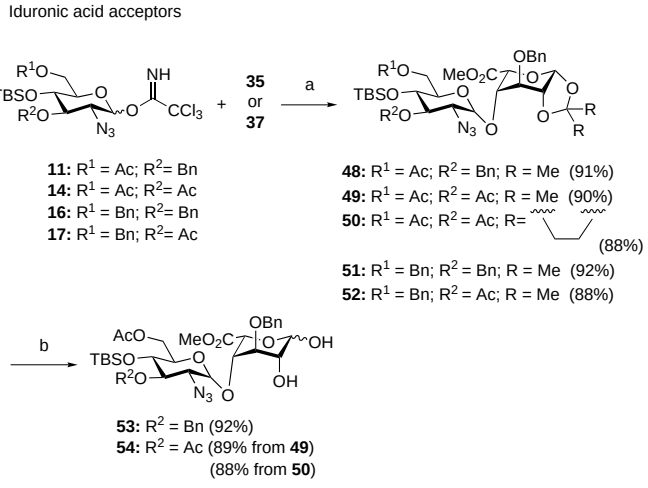


Scheme 7. Installation of 1,2-acetal protecting groups as molecular locks of uronic acid monosaccharides. a) 2-methoxypropene, DMF, CSA; b) methoxycyclopentene, DMF, CSA.

yield upon coupling with glucuronic acid acceptors. The nature of the cyclic protecting group (isopropylidene or cyclopentylidene) and the anomeric leaving group had no influence on the selectivity of the coupling reaction. Subsequently, glycosyl trichloroacetimidates were employed in couplings since they performed slightly better than glycosyl fluorides and disaccharides **42**, **43**, **45**–**47** were formed.

In addition to their use as molecular locks 1,2-acetals are convenient for differential protection of monosaccharides and were applied to iduronic acid acceptors. In an analoguos fashion to glucuronic acid, differentially protected iduronic acid **35** and **37** were prepared from the triol **25**. As expected, **35** and **37** adopted a $^1C_4$ conformation. The corresponding furanoside by-products **36** and **38** were recycled analogously to **32** and **34** (Scheme 7). Coupling of glycosyl donors **11**, **14**, **16** and **17** with iduronic acid acceptors **35** and **37** furnished disaccharides **48**–**52** (Scheme 9).

After the cyclic acetal protecting groups served their purpose, they were readily removed to yield disaccharide diols **41**, **44**, **53**, and **54** (Schemes 8 and 9). Complete α-



Scheme 9. Synthesis of disaccharides using "locked" iduronic acid acceptors. a) TBSOTf, 4 Å molecular sieves, CH_2Cl_2, $-30\,^\circ C \rightarrow$ room temperature; b) dichloroacetic acid (60 % aq.).

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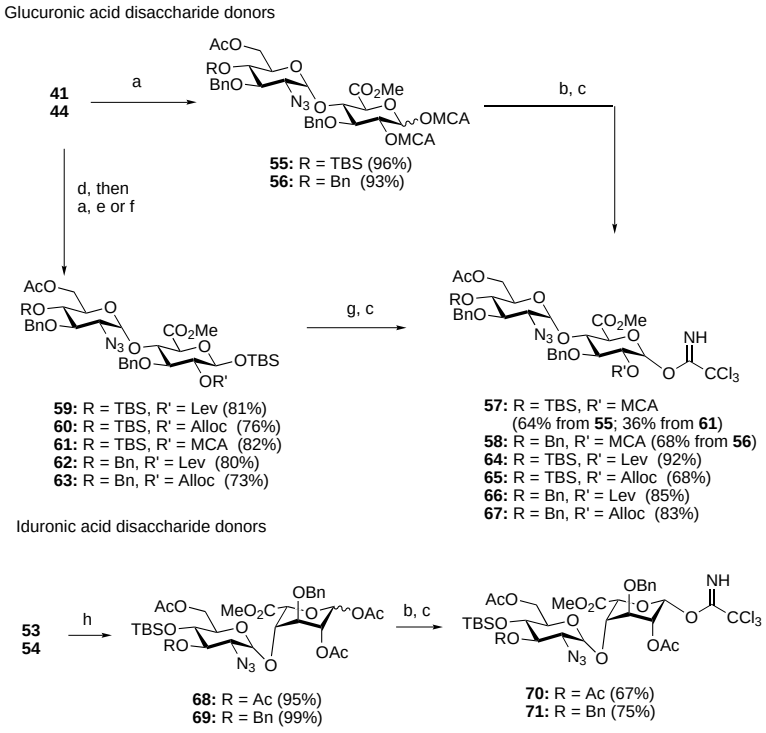
selectivity of the coupling reactions greatly simplified access to the nine disaccharide modules (**39**, **42**, **45**–**47**, **48**, **49**, **51**, **52**) needed for heparin assembly and purification of the reaction products.

After the α-glucosamine linkages had been stereoselectively formed, the resulting disaccharides had to be converted into competent glycosylating agents. In accordance with our modular assembly strategy for heparin oligosaccharides, different C2 participating groups had to be introduced in the uronic acid portion. To account for the presence of uronic acid C2 hydroxyl or sulfate groups, participating protective groups orthogonal to acetates were needed. Levulinoyl (Lev),[32] allyloxycarbonate (Alloc),[33] and monochloroacetate (MCA)[34] groups were installed in a variety of disaccharides. These groups can be replaced by permanent benzyl ether protection at the appropriate stage of the synthesis. The selective introduction of 2-hydroxyl protective groups was accomplished via two different routes (Scheme 10). Diacetylation of disaccharide diols **41** and **44** using monochloroacetyl chloride and selective cleavage of the anomeric MCA group from **55** and **56** was followed by conversion to the corresponding glycosyl trichloroacetimidates **57** and **58**.[35] For protecting groups that do not allow for selective anomeric cleavage, anomeric silylation,[36] protection of the 2-hydroxyl group, desilylation and preparation of the glycosyl trichloroacetimidates furnished disaccharide modules **64**–**67**. Synthesis of iduronic acid containing disaccharide modules **70** and **71** were accomplished from **53** and **54**.

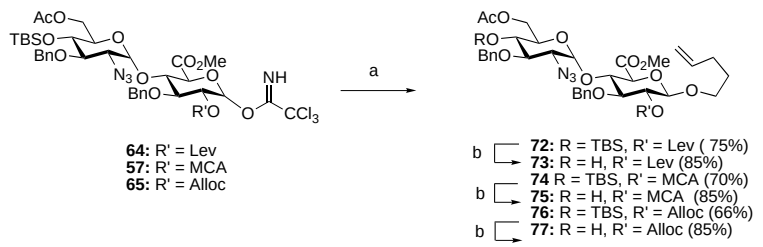


Scheme 10. Preparation of uronic acid containing disaccharide building blocks. a) $(MCA)_2O$, CH_2Cl_2, DMAP, pyridine; b) $BnNH_2$, Et_2O, 0 °C; c) $NCCCl_3$, DBU, CH_2Cl_2, 0 °C; d) TBSCl, imidazole, CH_2Cl_2, 0 °C; e) $(LevO)_2O$, DMAP, CH_2Cl_2; f) AllocCl, DMAP, CH_2Cl_2; g) TBAF, HOAc, THF; h) Ac_2O, CH_2Cl_2, DMAP, pyridine.

Oligosaccharide assembly: Convergent routes to monosaccharide building blocks and selective α-glucosamine glycoside formation by conformational locking of uronic acid acceptors provided ready access to a set of key disaccharide modules. The use of di- and trisaccharide building blocks in the assembly of defined heparin tetra- and hexasaccharides was the next goal of our investigation.

Several key issues had to be addressed to enable our approach based on the assembly of di- and trisaccharide modules. 1) A versatile reducing end moiety mimicking the solid-phase situation and allowing for further functionalization was identified; 2) uronic acid glycosyl donors were employed to avoid difficult late stage oxidations;[9b–d, 10b, c, 24e] 3) products of the modular oligosaccharide assembly carry protecting group patterns analogous to previous total syntheses to enable established deprotection and sulfation protocols.[9b, 10a, 37]

We began oligosaccharide assembly by preparing the reducing end. *n*-Pentenyl glycosides served to protect the reducing terminus during oligosaccharide synthesis mimicking an octenediol linker used in automated solid-phase oligosaccharide synthesis.[38] Furthermore the *n*-pentenyl group can function as glycosidating agent or may be converted into convenient handles for attachment to proteins or surfaces.[39] Three reducing end modules (**73**, **75**, and **77**) were obtained by coupling disaccharide glycosyl trichloroacetimidates **64**, **57**, **65**, and *n*-pentenyl alcohol followed by removal of the silyl protecting group from the C4 hydroxyl moiety (Scheme 11).



Scheme 11. Synthesis of reducing end disaccharides. a) 4-penten-1-ol, TMSOTf, CH_2Cl_2, 0 °C; b) HF/pyridine, HOAc, THF.

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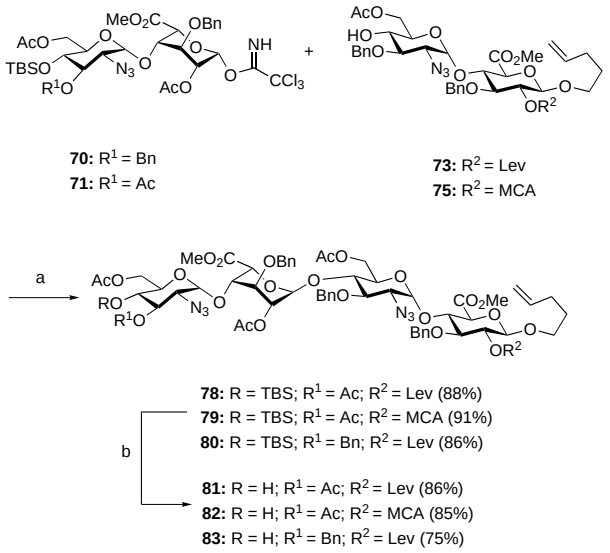
Oligosaccharide assembly using disaccharide modules: Next, the elongation of heparin oligosaccharide sequences by combining disaccharide building blocks with reducing end modules was explored. Coupling of disaccharide donors, **70** and **71**, with reducing end modules, **73** and **75**, furnished tetrasaccharides **78**–**80** in excellent yield. Removal of the silyl ether protecting group from the C4 hydroxyl group of **78**–**80** produced tetrasaccharides **81**–**83** as acceptors for further elongation (Scheme 12).



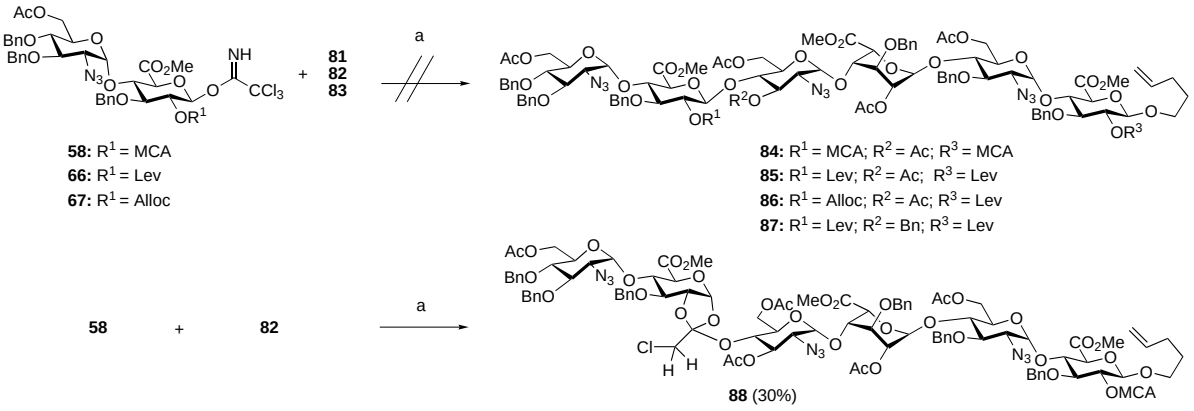
Scheme 12. Synthesis of tetrasaccharides by coupling of two disaccharides. a) TMSOTf, CH_2Cl_2, $-25\,^{\circ}C$; b) HF/pyridine, AcOH, THF.

Encouraged by the success of the couplings between disaccharides, the preparation of defined heparin hexasaccharides by addition of a further disaccharide module was attempted. Disaccharides **58**, **66**, and **67** containing different C2 protecting groups, were employed in coupling with the tetrasaccharides **81** and **82** under a variety of glycosylation conditions (Scheme 13). The formation of the hexasaccharides **84** and **86** was never detected in appreciable yield. Not unexpectedly, activation of monochloroacetate protected donor **58** afforded hexasaccharide orthoester **88**. Treatment of **88** with acid to procure rearranged product **84** did not succeed.[40] Tetrasaccharide **83** containing a 3-*O*-benzyl ether was employed as acceptor to explore if a 3-*O*-acetate protecting group was responsible for the failure to couple. Again, the desired union to form hexasaccharide **87** did not occur. Even benzylation of the 4-hydroxyl group of **81** failed!

To investigate the low reactivity of the C4 hydroxyl group of the tetrasaccharide acceptors and rationalize the unexpected results observed during the coupling of di- and tetrasaccharides we performed model coupling experiments involving acceptors containing the sequence GlcN-IdoA. The reaction of glucosamine trichloroacetimidate **90** and iduronic acid **35** afforded disaccharide **91**. Removal of the isopropylidene group produced **92** before anomeric silylation, acetylation and selective removal of the levulinoyl group afforded disaccharide acceptor **93**. The coupling between glucuronic acid trichloroacetimidate **94** and GlcN-IdoA acceptor **93** did not afford the desired trisaccharide, but rather the starting materials were recovered (Scheme 14). Similarly, no pentasaccharide product was obtained when disaccharide donor **97** and trisaccharide **98** where treated under glycosidation conditions (Scheme 15).

To determine if the $^1C_4$ conformation of the iduronic acid unit is responsible for the poor coupling behavior of the GlcN-IdoA sequence, we prepared disaccharide **101** containing a glucuronic acid locked in the $^1C_4$ conformation (Scheme 15). Glycosylation of **101** with glucuronic acid trichloroacetimidate **94** and iduronic acid trichloroacetimidate **103** afforded the expected coupling products **102** and **104** in good yield (Scheme 16). Based on these results, the conformation of the acceptor itself is not responsible of the low reactivity of the C4 hydroxyl group of GlcN-IdoA. Although we are currently not able to explain the low reactivity of the C4 hydroxyl group of the GlcN-IdoA sequence, these results clearly illustrated that our initial strategy had to be amended to allow for the incorporation of GlcN-IdoA sequences in the assembly of bigger structures.

Oligosaccharide assembly using trisaccharide modules: Based on the observations outlined above, the modular synthesis of heparin oligosacharides was expanded to draw from di- and trisaccharide modules to access all possible structures. The overall strategy remains efficient as the linkage between



Scheme 13. Attempted synthesis of a hexasaccharide by coupling of tetra- and disaccharides. a) TMSOTf, CH_2Cl_2, $-25\,^{\circ}C$.

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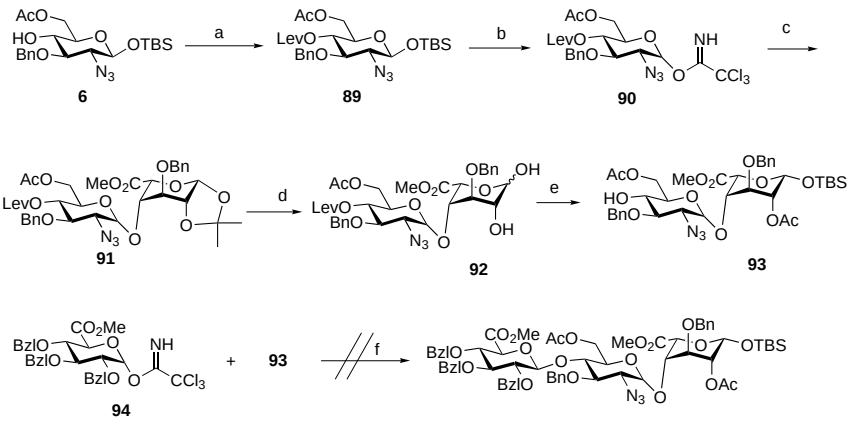
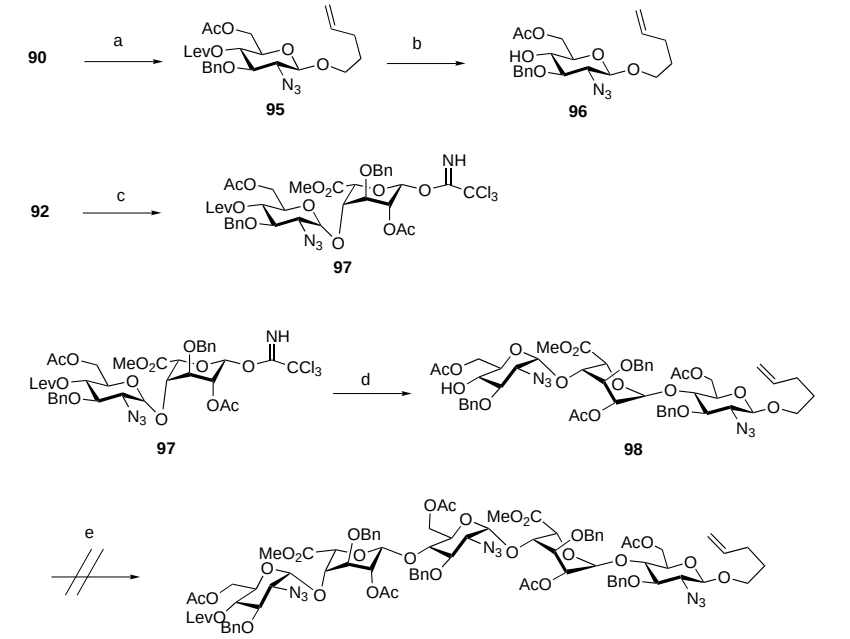


Scheme 14. Preparation of disaccharides to investigate the sequence dependence of coupling reactions. a) Lev_2O, DMAP, CH_2Cl_2, 96%; b) 1. THF, AcOH, TBAF; 2. $NCCCl_3$, DBU, CH_2Cl_2, 87% (two steps); c) **35**, TBSOTf, 4 Å molecular sieves, CH_2Cl_2, $-78\,^{\circ}C \rightarrow$ room temperature, 83%; d) dichloroacetic acid (60% aq.), 91%; e) 1. TBSCl, imidazole, CH_2Cl_2, $-15\,^{\circ}C$; 2. Ac_2O, DMAP, pyridine, CH_2Cl_2; 3. $NH_2NH_2 \cdot H_2O$, AcOH, pyridine, 60% (three steps); f) TMSOTf, CH_2Cl_2, $-20\,^{\circ}C$.



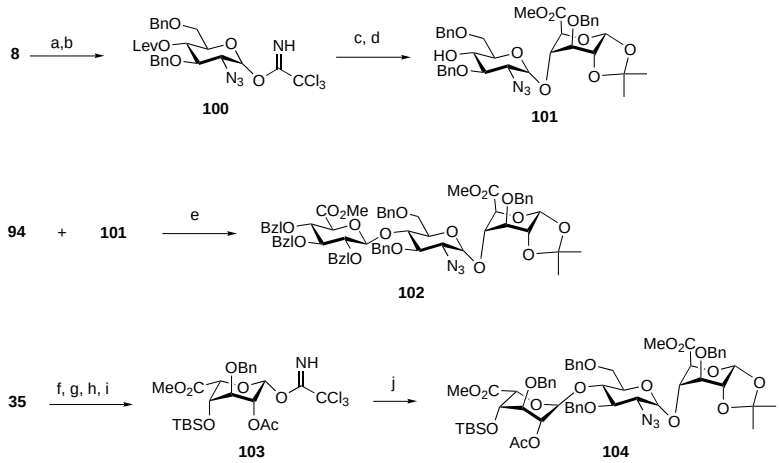
Scheme 15. Synthesis of trisaccharide models to investigate coupling reactions. a) 4-penten-1-ol, $BF_3 \cdot Et_2O$, CH_2Cl_2/hexane, $-78\,^{\circ}C \rightarrow$ room temperature, 75%; b) $NH_2NH_2 \cdot H_2O$, AcOH, pyridine, 91%; c) 1.Ac_2O, DMAP, pyridine, CH_2Cl_2; 2. $BnNH_2$, Et_2O, $0\,^{\circ}C$; 3. $NCCCl_3$, DBU, CH_2Cl_2, $0\,^{\circ}C$, 87% (three steps); d) 1. **96**, TMSOTf, CH_2Cl_2, $-20\,^{\circ}C$; 2. $NH_2NH_2 \cdot H_2O$, AcOH, pyridine, 45% (two steps); e) **97**, TMSOTf, CH_2Cl_2, $-45\,^{\circ}C \rightarrow$ room temperature.

glucosamine and iduronic acid can be established selectively and in high yield.[14] Trisaccharide modules were readily accessed from the set of disaccharides as exemplified by the synthesis of **105** and **107** (Scheme 17). The resulting trisaccharides can be readily converted into glycosyl acceptors (e.g. **106**) or glycosylating agents (e.g. **108**) for the modular assembly of oligosaccharides. This approach was successfully demonstrated for the synthesis of hexasaccharide **109** by coupling trisaccharide modules **106** and **108** in 62% yield (Scheme 18).

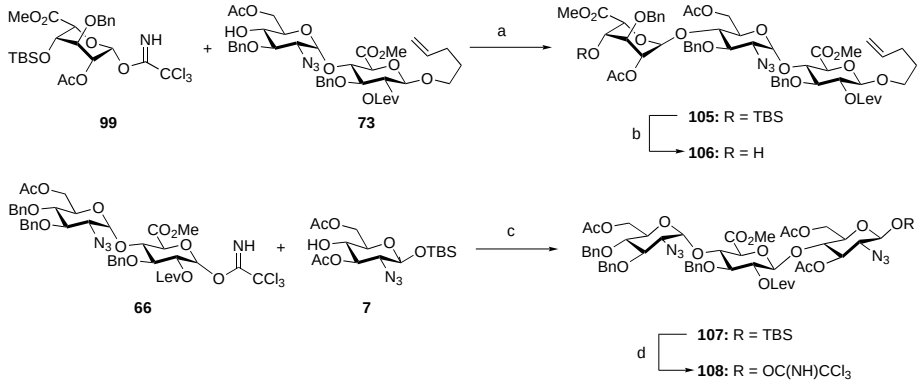
Sulfation and final deprotection: After establishing a general synthesis of heparin oligosaccharides based on di- and trisaccharide modules by preparing tetra- and hexasaccharides, installation of the desired sulfation patterns had to be demonstrated. From the outset of the synthesis acetates marked positions to be sulfated and benzyl ethers designated free hydroxyl groups. Thus, late stage manipulations could follow precedent from earlier total syntheses.[9b, 10a–c, 37] Still, the placement of different C2 protection groups on uronic acid donors had to be illustrated. Tetrasaccharides **81** and **82** served to demonstrate the final deprotection and sulfation steps (Scheme 19). Selective removal of the monochloroacetate group in **81**[41] and levulinoyl group in **82**[32] was achieved in high yield. Permanent protection of the free hydroxyl group was readily accomplished by benzylation to furnish **110**. Alternatively, after saponification of **111** the unprotected hydroxyl groups can be sulfated by reaction with Et_3NSO_3.[9b, 10a–c, 37] Cleavage of all benzyl ether protective groups and selective N-sulfation furnished fully functionalized heparin tetrasaccharide **112**.[9b, 10a–c]

Conclusion

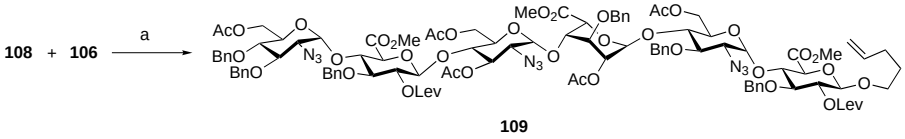
In summary, we have developed a general, modular strategy for the first completely stereoselective synthesis of defined heparin oligosaccharides. Di- and trisaccharide modules were derived from just six monosaccharide building blocks in a fully selective fashion by placing a conformational constraint on uronic acid glycosyl acceptors. We demonstrated a new concept for stereochemical control of α-glucosamine glycoside formation. Locking the conformation of the glucuronic acid acceptor allowed for completely selective preparation of the desired *cis*-glycosides. This innovation greatly simplified the key step in the preparation of disaccharide building blocks. Combination of disaccharide modules to form *trans*-uronic acid linkages proved also completely selective by virtue of C2 participating groups. Coupling reactions between modules exhibited sequence dependence. Trisaccharide modules allowed for stereoselective access to oligosaccharides as demonstrated on the



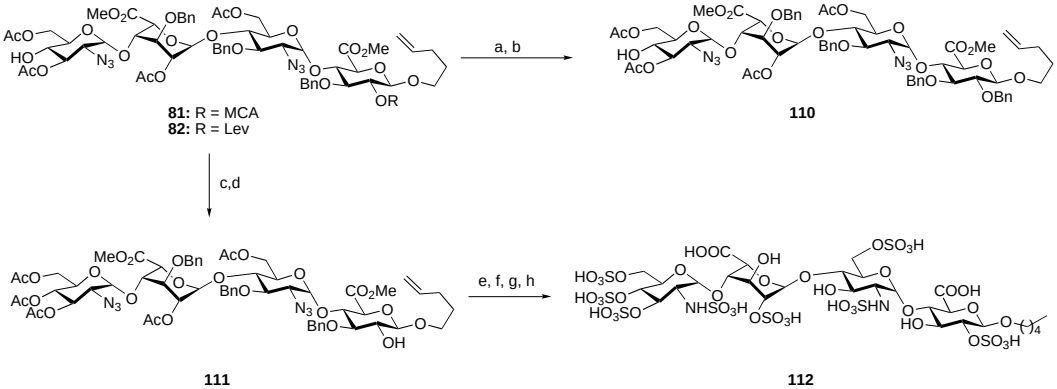
Scheme 16. Investigation of the sequence dependence of coupling reactions. a) 1. Lev_2O, DMAP, CH_2Cl_2, 98%; b) 1. THF, AcOH, TBAF; 2. $NCCCl_3$, DBU, CH_2Cl_2, 0 °C, 86% (two steps); c) **31**, TBSOTf, CH_2Cl_2, −25 °C → room temperature, 89%; d) $NH_2NH_2 \cdot H_2O$, AcOH, pyridine, 77%; e) TMSOTf, CH_2Cl_2, −20 °C → room temperature, 59%; f) 1. TBSOTf, lutidine, CH_2Cl_2, 98%; g) dichloroacetic acid (60% aq.), 92%; g) Ac_2O, DMAP, pyridine, CH_2Cl_2, 98%; h) $BnNH_2$, Et_2O, 0 °C, 75%; i) $NCCCl_3$, DBU, CH_2Cl_2, 0 °C, 92%; j) **101**, TMSOTf, CH_2Cl_2, −25 °C → room temperature, 71%.



Scheme 17. Synthesis of trisaccharides by coupling mono- and disaccharides. a) TMSOTf, CH_2Cl_2, −25 °C, 93%; b) HF/pyridine, AcOH, THF, 82%; c) TMSOTf, CH_2Cl_2, −25 °C, 63%; d) 1. TBAF, AcOH, THF; 2. $NCCCl_3$, DBU, CH_2Cl_2, 0 °C, 87% (two steps).



Scheme 18. Synthesis of a hexasaccharide by coupling trisaccharides. a) TMSOTf, CH_2Cl_2, −25 °C, 62%.



Scheme 19. Protecting group modifications, sulfation and final deprotection of a tetrasaccharide. a) Thiourea, DMF, pyridine, room temperature, 24 h, 90%; b) BnBr, Ag_2O, 4 Å molecular sieves, CH_2Cl_2, room temperature, overnight, 76%; c) Ac_2O, pyridine, quant.; d) $NH_2NH_2 \cdot H_2O$, pyridine, AcOH, 90%; e) 1. LiOH (0.7 M aq.), H_2O_2 (50% aq.), THF overnight; 2. 4 M NaOH, room temperature overnight, 82% (two steps); f) Et_3NSO_3, DMF, 50 °C, overnight, 50%; g) H_2, Pd/C, EtOH, water, quant.; h) $Py \cdot SO_3$, H_2O, 60%.

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example of a hexasaccharide. Final deprotection and sulfation yielded the fully synthetic heparin oligosaccharides.

Utilizing the synthetic approach presented here, we are now preparing heparin oligosaccharides to elucidate the exact structures responsible for protein interactions involved in growth factor signaling and viral entry. This general strategy is expected to allow for the synthesis of heparin oligosaccharides on solid support using a repetitive coupling/deprotection cycle. The assembly of other classes of glycosaminoglycans of medical importance such as hyaluronic acid and chondroitin has come within reach. Investigations in these areas are currently underway and will be reported in due course.

Experimental Section

General methods: All chemicals used were reagent grade and used as supplied except where noted otherwise. Anhydrous methanol (MeOH) and dimethylformamide (DMF) were purchased from Aldrich in SureSeal bottles. Dichloromethane (CH_2Cl_2), diethyl ether, toluene and tetrahydrofuran (THF) were purchased from J. T. Baker (Cycletainer) and passed through a neutral alumina column prior to use. Pyridine, 2,4,6-collidine, and acetonitrile (CH_3CN) were heated under reflux over calcium hydride and distilled prior to use. Analytical thin-layer chromatography was performed on E. Merck silica gel 60 F_{254} glass plates (0.25 mm). Compounds were visualized by dipping the plates in a cerium sulfate-ammonium molybdate solution followed by heating. Liquid column chromatography was performed using forced flow of the indicated solvent on Silicycle 230–400 mesh (60 Å pore diameter) silica gel. ^{1}H NMR spectra were obtained on a Varian VXR-500 (500 MHz) or a Varian-300 (300 MHz) spectrometer and are reported in parts per million (δ) relative to $CHCl_3$ (7.27 ppm). Coupling constants (J) are reported in Hertz. ^{13}C NMR spectra were obtained on a Varian VXR-500 (125 MHz) or a Varian-300 (75 MHz) spectrometer and are reported in δ relative to $CDCl_3$ (77.23 ppm) as an internal reference.

tert*-Butyldimethylsilyl 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-β-D-glucopyranoside (2)**: *Preparation of TfN_3*: CH_2Cl_2 (250 mL) was added to a solution of NaN_3 (59.5 g, 0.92 mol) in water (150 mL) at 0 °C. The mixture was stirred vigorously and treated with trifluoromethanesulfonic anhydride (31.0 mL, 0.19 mol) over a period of 3 h at 0 °C. After the complete addition of trifluoromethanesulfonic anhydride, the reaction mixture was stirred at 0 °C for 2.5 h. The aqueous phase was extracted with CH_2Cl_2 (2 × 100 mL) and the combined organic layers washed with saturated Na_2CO_3 and saved for use in the next step. [Caution***: TfN_3 is explosive when not in solution!] $CuSO_4$ (140 mg, 0.88 mmol) and K_2CO_3 (19.2 g, 0.14 mol) were added to a solution of glucosamine hydrochloride (**1**) (20.0 g, 0.092 mol) in water (300 mL). Methanol (600 mL) was added to the reaction mixture followed by the addition of the TfN_3 solution. Methanol was added until the solution was homogeneous (≈300 mL). The clear blue solution was allowed to stir for 24 h at room temperature. Glycine (70 g) was added and the reaction mixture was again allowed to stir for 24 h. The glycine was filtered off and the solvent was removed in vacuo to afford a brown oil. The oil was taken up in pyridine (95 mL), cooled to 0 °C and DMAP (≈30 mg) and acetic anhydride (86 mL, 0.91 mol) were added. The solution was stirred for 12 h at room temperature. The reaction was quenched with saturated $NaHCO_3$ and the aqueous phase was extracted with CH_2Cl_2 (3 × 1000 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent was removed in vacuo to yield a brown oil. Warm ethanol was added until the solution was homogeneous. The resulting solution was cooled to −20 °C and a white precipitate formed. Cold water was then added, the white precipitate was filtered and washed with water and cold ethanol to afford 1,3,4,6-tetra-*O*-acetyl-2-azido-2-deoxy-β-D-glucopyranose (23.8 g, 0.063 mol, 68 %) as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.55 (d, J = 8.6 Hz, 1H), 5.15–5.00 (m, 2H), 4.31 (dd, J = 4.6, 12.5 Hz, 1H), 4.08 (dd, J = 2.1, 12.5 Hz, 1H), 3.75 (ddd, J = 2.1, 4.4, 6.3 Hz, 1H), 3.65–3.72 (m, 1H), 2.20 (s, 3H), 2.10 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H); IR (thin film): $\tilde{\nu}$ = 2959, 2112, 1747 cm^{-1}. Flash chromatography of the mother liquor (hexanes/EtOAc 7:3) afforded a colorless oil (mixture of α/β) (5.6 g, 0.015 mmol, 17 %). The spectral data was in agreement with the reported data.[16b]

1,3,4,6-Tetra-*O*-acetyl-2-azido-2-deoxy-α/β-D-glucopyranose (30.2 g, 80 mmol) was coevaporated twice with toluene and dissolved in THF and methanol (7:3, 300 mL). The solution was cooled to 0 °C and gaseous anhydrous ammonia was bubbled through at a modest rate. After 15 min, nitrogen was bubbled through the solution to remove excess ammonia and the solvent was removed in vacuo to afford a brown oil. The residue was coevaporated twice with toluene and dissolved in CH_2Cl_2 (150 mL). Imidazole (10.9 g, 160 mmol) and *tert*-butyldimethylsilyl chloride (13.3 g, 88 mmol) were added. After 2 h, the mixture was diluted with EtOAc, washed with water, 1N HCl (2 ×) and water. The organic layer was dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. Crystallization from ethanol afforded **2** (29.8 g, 67 mmol, 84 %) as colorless crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.00–4.90 (m, 2H), 4.63 (d, J = 7.6 Hz, 1H), 4.20 (dd, J = 5.9, 12.1 Hz, 1H), 4.09 (dd, J = 2.6, 12.1 Hz, 1H), 3.70–3.64 (m, 1H), 3.48–3.40 (m, 1H), 2.10 (s, 3H), 2.08 (s, 3H), 2.00 (s, 3H), 0.95 (s, 9H), 0.15 (s, 6H). The spectral data was in agreement with the reported data.[42]

***tert*-Butyldimethylsilyl 2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (3)**: Compound **2** (36.9 g, 82.8 mmol) was dissolved in methanol (300 mL) and NaOMe (25 % in MeOH, 5.4 mL) was added. After 15 min, DOWEX-50 acidic resin was added and the mixture was stirred until the pH reached 6. The DOWEX resin was filtered off and the solvent was removed in vacuo to afford a yellow oil. The residue was coevaporated twice with toluene and dissolved in acetonitrile (400 mL). Benzaldehyde dimethyl acetal (24.8 mL, 165 mmol) and *p*-toluenesulfonic acid monohydrate (400 mg, 2.1 mmol) were added. After stirring overnight at room temperature, triethylamine (5 mL) was added and the solvents evaporated. Flash chromatography on silica gel (hexanes/EtOAc 95:5 → 9:1) afforded **3** (29.0 g, 71.2 mmol, 86 %) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55–7.45 (m, 2H), 7.45–7.38 (m, 3H), 5.52 (s, 1H), 4.65 (d, J = 7.65 Hz, 1H), 4.29 (dd, J = 4.9, 10.4 Hz, 1H), 3.77 (t, J = 10.1 Hz, 1H), 3.60–3.30 (m, 4H), 2.91 (s, 1H), 1.00 (s, 9H), 0.19 (s, 6H). The spectral data was in agreement with the reported data.[43]

***tert*-Butyldimethylsilyl 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (4)**: *tert*-Butyldimethylsilyl 2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (**3**; 28.1 g, 68.97 mmol) was dissolved in CH_2Cl_2 (250 mL). Powdered, freshly activated 4 Å molecular sieves (45 g) and benzyl bromide (20.5 mL, 172 mmol) were added and the mixture was stirred for 30 min. Silver(I)oxide (47 g, 203 mmol) was added and the reaction vessel was covered in aluminum foil to exclude light. After 8 h, the reaction mixture was filtered through Celite and the filtrate was concentrated in vacuo. Flash chromatography on silica (hexanes/EtOAc 50:1) afforded **4** (32.6 g, 65.5 mmol, 95 %) as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.28 (m, 10H), 5.51 (s, 1H), 4.98 (d, J = 11.5 Hz, 1H), 4.84 (d, J = 11.5 Hz, 1H), 4.63 (d, J = 7.5 Hz, 1H), 4.33 (dd, J = 5.0, 9.4 Hz, 1H), 3.89–3.73 (m, 2H), 3.60–3.35 (m, 3H), 0.98 (s, 9H), 0.17 (s, 6H). The spectral data was in agreement with the reported data.[43]

***tert*-Butyldimethylsilyl 3-*O*-acetyl-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (5)**: Compound **3** (9.5 g, 23.3 mmol) was dissolved in CH_2Cl_2 (150 mL) and pyridine (21 mL), DMAP (280 mg, 2.3 mmol) and acetic anhydride (10 mL, 106 mol) were added. The reaction mixture was stirred overnight, water was added and stirred for 1 h. The organic layer was extracted with water, 1N HCl, water and saturated $NaHCO_3$. The organic phase was dried over $MgSO_4$, filtered and the solvent was removed in vacuo. Flash chromatography on silica gel (hexanes/EtOAc 50:1 → 5:1) afforded **5** (9.96 g, 22.1 mmol, 95 %) as a colorless crystalline solid. $[\alpha]_D^{24}$ = −72.1 (c = 0.99, CH_2Cl_2); IR (thin film): $\tilde{\nu}$ = 2111, 1751, 1370, 1222, 1099, 841 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.33 (m, 5H), 5.49 (s, 1H), 5.13 (dd, J = 9.7, 9.9 Hz, 1H), 4.72 (d, J = 7.6 Hz, 1H), 4.31 (dd, J = 4.9, 10.5 Hz, 1H), 3.80 (dd, J = 10.2, 10.3 Hz, 1H), 3.65 (dd, J = 9.4, 9.5 Hz, 1H), 3.49 (ddd, J = 4.9, 9.6, 9.6 Hz, 1H), 3.42 (dd, J = 7.5, 10.1 Hz, 1H), 2.14 (s, 3H), 0.95 (s, 9H), 0.19 (s, 3H), 0.18 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.9, 136.9, 129.3, 128.4, 126.3, 101.7, 97.8, 78.9, 71.1, 68.7, 67.4, 66.8, 25.8, 21.2, 18.2, −4.1, −4.9; FAB MS: m/z: calcd for $C_{21}H_{31}N_3O_6Si$: 449.1982; found: 449.1876 $[M]^+$.

***tert*-Butyldimethylsilyl 6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-β-D-glucopyranoside (6)**: Compound **4** (32.6 g, 65.5 mmol) was dissolved in CH_2Cl_2 (1.5 L) and trifluoroacetic acid (60 % aq., 54 mL) was added. The resulting

mixture was stirred vigorously at room temperature for 8.5 h and saturated $NaHCO_3$ was added carefully. After phase separation, the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered and the solvents were removed in vacuo. Flash chromatography on silica (hexanes/EtOAc 4:1 → 1:1) afforded *tert*-butyldimethylsilyl 2-azido-3-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside (25 g, 61 mmol, 92 %) as a colorless oil. $[\alpha]_D^{24} = -30.4$ ($c = 1.00$, CH_2Cl_2); IR (thin film): $\tilde{\nu} = 3415, 2110, 1361, 1079\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.44-7.30$ (m, 5H), 4.97 (d, $J = 11.4$ Hz, 1H), 4.72 (d, $J = 11.4$ Hz, 1H), 4.58 (d, $J = 7.5$ Hz, 1H), 3.84 (dd, $J = 3.7, 11.8$ Hz, 1H), 3.75 (dd, $J = 4.8, 11.8$ Hz, 1H), 3.59 (dd, $J = 8.7, 9.5$ Hz, 1H), 3.36–3.26 (m, 2H), 3.22 (dd, $J = 8.6, 9.9$ Hz, 1H), 0.96 (s, 9H), 0.19 (s, 3H), 0.18 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 138.2, 128.9, 128.34, 128.26, 97.5, 82.5, 75.3, 75.2, 70.7, 68.5, 62.8, 25.8, 18.1, -4.0, -4.9$; FAB MS: *m/z*: calcd for $C_{19}H_{31}N_3O_5Si$: 409.2033; found: 409.2029 $[M]^+$. The spectral data was in agreement with the reported data.[44]

Acetyl chloride (4.5 mL, 63.3 mmol) was added dropwise to a solution of *tert*-butyldimethylsilyl 2-azido-3-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside (25 g, 61 mmol) in 2,4,6-collidine (110 mL) under nitrogen at −40 °C. After stirring at −40 °C overnight, water was added. The mixture was poured into EtOAc and extracted with 1N HCl, brine and saturated $NaHCO_3$. The organic phase was dried over Na_2SO_4, filtered and the solvents were removed in vacuo to afford **6** (26.5 g, 58.7 mmol, 96 %) as a colorless solid. $[\alpha]_D^{24} = -27.1$ ($c = 1.00$, CH_2Cl_2); IR (thin film): $\tilde{\nu} = 3482, 2110, 1743, 1255\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.43-7.30$ (m, 5H), 4.96 (d, $J = 11.4$ Hz, 1H), 4.73 (d, $J = 11.4$ Hz, 1H), 4.55 (d, $J = 7.6$ Hz, 1H), 4.34–4.27 (m, 2H), 3.50–3.38 (m, 2H), 3.33 (dd, $J = 7.6, 9.9$ Hz, 1H), 3.21 (dd, $J = 8.3, 9.9$ Hz, 1H), 2.59–2.46 (brs, 1H), 2.09 (s, 3H), 0.96 (s, 9H), 0.18 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 171.5, 138.1, 128.8, 128.31, 128.28, 97.4, 82.2, 75.3, 73.8, 70.3, 68.3, 63.5, 25.8, 21.1, 18.3, -4.1, -5.0$; FAB MS: *m/z*: calcd for $C_{21}H_{33}N_3O_6Si$: 451.2138; found: 451.2135 $[M]^+$.

***tert*-Butyldimethylsilyl 3,6-di-*O*-acetyl-2-azido-2-deoxy-*β*-D-glucopyranoside (7)**: Compound **5** (9.5 g, 21.1 mmol) was dissolved in CH_2Cl_2 (500 mL) and trifluoroacetic acid (60 % aq., 17 mL) was added. The resulting mixture was stirred vigorously at room temperature overnight and saturated $NaHCO_3$ was added carefully. After phase separation, the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered and the solvents were removed in vacuo. Flash chromatography on silica gel (hexanes/EtOAc 4:1 → 1:1) afforded *tert*-butyldimethylsilyl 3-*O*-acetyl-2-azido-2-deoxy-*β*-D-glucopyranoside (7.25 g, 20 mmol, 95 %) as a colorless solid. $[\alpha]_D^{24} = -26.4$ ($c = 1.00$, CH_2Cl_2); IR (thin film): $\tilde{\nu} = 3387, 2112, 1748, 1254\ cm^{-1}$; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 4.77$ (dd, $J = 9.2, 9.5$ Hz, 1H), 4.64 (d, $J = 7.6$ Hz, 1H), 3.90 (dd, $J = 3.7, 11.9$ Hz, 1H), 3.81 (dd, $J = 4.9, 11.9$ Hz, 1H), 3.66 (dd, $J = 9.5, 9.5$ Hz, 1H), 3.41–3.36 (m, 1H), 3.34 (dd, $J = 7.6, 10.4$ Hz, 1H), 3.08–2.92 (brs, 1H), 2.15–1.92 (brs, 1H), 2.19 (s, 3H), 0.94 (s, 9H), 0.174 (s, 3H), 0.168 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 172.2, 97.2, 76.0, 75.8, 70.1, 66.2, 62.6, 25.7, 21.2, 18.1, -4.1, -5.0$; FAB MS: *m/z*: calcd for $C_{14}H_{27}N_3O_6Si$: 361.1669; found: 361.1677 $[M]^+$.

Acetyl chloride (1.5 mL, 21.1 mmol) was added slowly to a solution of *tert*-butyldimethylsilyl 3-*O*-acetyl-2-azido-2-deoxy-*β*-D-glucopyranoside (7.25 g, 20 mmol) in 2,4,6-collidine (47 mL) under nitrogen at −40 °C. After stirring at −40 °C overnight, water was added. The mixture was poured into EtOAc and extracted with 1N HCl, brine and saturated $NaHCO_3$. The organic phase was dried over Na_2SO_4, filtered and the solvents were removed in vacuo. Flash chromatography on silica gel (hexanes/EtOAc 5:1 → 4:1) afforded **7** (7.59 g, 18.8 mmol, 94 %) as a colorless solid. $[\alpha]_D^{24} = -31.6$ ($c = 1.00$, CH_2Cl_2); IR (thin film on NaCl): $\tilde{\nu} = 3459, 2112, 1747, 1233, 1042, 841\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 4.81-4.74$ (m, 1H), 4.62 (d, $J = 7.6$ Hz, 1H), 4.37–4.31 (m, 2H), 3.75–3.46 (m, 2H), 3.53 (dd, $J = 7.7, 10.3$ Hz, 1H), 3.13–3.09 (m, 1H), 2.18 (s, 3H), 2.10 (s, 3H), 0.94 (s, 9H), 0.17 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 171.8, 171.5, 97.2, 75.5, 74.3, 69.8, 66.0, 63.4, 25.8, 21.2, 21.1, 18.2, -4.2, -5.0$; FAB MS: *m/z*: calcd for $C_{16}H_{29}N_3O_7Si$: 403.1775; found: 403.1779 $[M]^+$.

***tert*-Butyldimethylsilyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside (8)**: Compound **4** (3.6 g, 7.24 mmol) and triethylsilane (6.5 mL, 43.4 mmol) were dissolved in anhydrous CH_2Cl_2 (70 mL) under nitrogen at 0 °C and trifluoroacetic acid (3.3 mL, 43.4 mmol) was added dropwise over 5 min. The reaction mixture was slowly warmed to room temperature, stirred for 5 h and quenched with saturated $NaHCO_3$. After addition of CH_2Cl_2 and phase separation, the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$, filtered and the solvents were removed in vacuo. Flash chromatography on silica gel (hexanes/EtOAc 8:1 → 6:1) afforded **8** (3.1 g, 6.2 mmol, 85 %) as a colorless oil. $[\alpha]_D^{24} = -33.9$ ($c = 1.00$, CH_2Cl_2); IR (thin film): $\tilde{\nu} = 3472, 2111, 1257, 1113, 1069\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.45-7.28$ (m, 10H), 4.93 (d, $J = 11.4$ Hz, 1H), 4.77 (d, $J = 11.4$ Hz, 1H), 4.61 (d, $J = 12.1$ Hz, 1H), 4.56 (d, $J = 12.1$ Hz, 1H), 4.55 (d, $J = 7.5$ Hz, 1H), 3.73 (d, $J = 4.8$ Hz, 2H), 3.65 (dd, $J = 8.5, 9.7$ Hz, 1H), 3.46–3.39 (m, 1H), 3.33 (dd, $J = 7.5, 10.0$ Hz, 1H), 3.23 (dd, $J = 8.5, 10.0$ Hz, 1H), 0.95 (s, 9H), 0.18 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 138.3, 137.9, 128.8, 128.6, 128.23, 128.16, 127.9, 127.8, 97.4, 82.5, 75.2, 74.1, 73.9, 72.2, 70.6, 68.3, 25.9, 18.3, -4.0, -5.0$; FAB MS: *m/z*: calcd for $C_{26}H_{37}N_3O_5Si$: 499.2502; found: 499.2513. The spectral data was in agreement with the reported data.[43]

***tert*-Butyldimethylsilyl 3-*O*-acetyl-2-azido-6-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside (9)**: Compound **5** (42.0 mg, 0.093 mmol) and triethylsilane (75 μL, 0.47 mmol) were dissolved in CH_2Cl_2 (930 μL) under argon at 0 °C and trifluoroacetic acid (36 μL, 0.47 mmol) was added dropwise over 6 min. The reaction mixture was slowly warmed to room temperature, stirred for 3 h and quenched with saturated $NaHCO_3$. After addition of CH_2Cl_2 and phase separation, the aqueous phase was extracted three times with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$, filtered and the solvents were removed in vacuo. Flash chromatography on silica gel (hexanes/EtOAc 8:1 → 6:1) furnished **9** (38.1 mg, 91 %) as a colorless oil. $[\alpha]_D^{24} = -21.6$ ($c = 1.00$, CH_2Cl_2); IR (thin film): $\tilde{\nu} = 3434, 2111, 1749, 1252\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.40-7.28$ (m, 5H), 4.80 (dd, $J = 9.1$ Hz, 10.3 Hz, 1H), 4.61 (d, $J = 7.7$ Hz, 1H), 4.61–4.57 (m, 2H), 3.75 (dd, $J = 1.6, 4.9$ Hz, 1H), 3.69 (ddd, $J = 3.5, 9.3, 9.3$ Hz, 1H), 3.53–3.45 (m, 1H), 3.36 (dd, $J = 7.7, 10.3$ Hz, 1H), 3.00 (d, $J = 3.7$ Hz, 1H), 2.18 (s, 3H), 0.95 (s, 9H), 0.178 (s, 3H), 0.175 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 171.5, 137.7, 128.6, 128.0, 127.8, 97.3, 75.4, 74.4, 73.9, 71.1, 70.3, 66.1, 25.8, 21.3, 18.2, -4.1, -5.0$; FAB MS: *m/z*: calcd for $C_{21}H_{33}N_3O_6Si$: 451.2138; found: 451.2131 $[M]^+$.

6-*O*-Acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*α*/*β*-D-glucopyranosyl fluoride (10*α*): *tert*-Butyldimethylsilyl trifluormethanesulfonate (3.4 mL, 14.8 mmol) was added to a solution of compound **6** (5.15 g, 11.4 mmol) and 2,6-lutidine (3.3 mL, 28.3 mmol) in CH_2Cl_2 (50 mL) at −20 °C. The reaction was allowed to warm to room temperature and stir for 1 h. The mixture was poured into EtOAc and the aqueous layer was extracted with 1N HCl, brine and saturated $NaHCO_3$. The organic layer was dried over Na_2SO_4, filtered and the solvents were removed in vacuo. Flash chromatography on silica gel (hexanes/EtOAc 199:1 → 98:2) afforded *tert*-butyldimethylsilyl 6-*O*-acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*β*-D-glucopyranoside (5.8 g, 10.3 mmol, 90 %) as a colorless oil. $[\alpha]_D^{24} = +36.1$ ($c = 1.00$, CH_2Cl_2); IR (thin film): $\tilde{\nu} = 2110, 1748, 1112\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.40-7.28$ (m, 5H), 4.93 (d, $J = 11.1$ Hz, 1H), 4.71 (d, $J = 11.1$ Hz, 1H), 4.56 (d, $J = 7.6$ Hz, 1H), 4.42 (dd, $J = 2.2$, 11.6 Hz, 1H), 4.07 (dd, $J = 6.6$, 11.6 Hz, 1H), 3.59 (dd, $J = 8.3, 9.5$ Hz, 1H), 3.45 (ddd, $J = 2.2, 6.6, 9.5$ Hz, 1H), 3.34 (dd, $J = 7.6, 9.9$ Hz, 1H), 3.20 (dd, $J = 8.3, 9.9$ Hz, 1H), 2.08 (s, 3H), 0.94 (s, 9H), 0.89 (s, 9H), 0.164 (s, 3H), 0.160 (s, 3H), 0.05 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 170.8, 138.4, 128.5, 127.7, 127.6, 97.4, 83.0, 75.2, 74.6, 71.3, 69.2, 63.6, 26.1, 25.8, 21.1, 18.3, -3.5, -4.1, -4.6, -5.0$; FAB MS: *m/z*: calcd for $C_{27}H_{47}N_3O_6Si_2$: 565.3003; found: 565.3011 $[M]^+$.

tert-Butyldimethylsilyl 6-*O*-acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*β*-D-glucopyranoside (4.0 g, 7.07 mmol) was dissolved in THF (60 mL) and cooled to 0 °C. Glacial acetic acid (500 μL, 8.7 mmol) and TBAF (1M in THF, 8.2 mL, 8.2 mmol) were added simultaneously. After 30 min, the mixture was poured into Et_2O (200 mL) and washed three times with brine. The organic layer was dried over Na_2SO_4, filtered and the solvents were removed in vacuo. The residue was coevaporated with toluene, dissolved in anhydrous THF (20 mL) and cooled to −30 °C. DAST (1.2 mL, 9.08 mmol) was added dropwise and the mixture was stirred for 5 min at −30 °C and 30 min at room temperature. The reaction mixture was cooled to −30 °C and anhydrous methanol (500 μL) was added. After warming to room temperature, the mixture was poured into EtOAc (300 mL) and washed with saturated $NaHCO_3$, water and brine. The organic layer was dried over Na_2SO_4, filtered and the solvents were removed in vacuo. Flash chromatography on silica gel (hexanes/EtOAc 95:5) afforded a mixture (5:1) of **10*α*** and **10*β*** (3.0 g, 6.62 mmol, 94 %) as a crystalline solid. **10*α***: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.45-7.28$ (m, 5H),

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5.68 (dd, $J = 2.7$, 52.7, 1H), 4.92 (d, $J = 11.0$ Hz, 1H), 4.84 (d, $J = 11.0$ Hz, 1H), 4.45 (dd, $J = 1.9$, 12.1 Hz, 1H), 4.11 (dd, $J = 4.7$, 12.1 Hz, 1H), 4.04–3.94 (m, 1H), 3.83–3.71 (m, 2H), 3.74–3.36 (m, 1H), 2.11 (s, 3H), 0.92 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 170.7$, 137.7, 128.5, 127.8, 127.5, 107.6, 104.6, 80.1, 75.6, 73.14, 73.08, 70.4, 64.3, 64.0, 62.5, 26.1, 21.1, 18.3, −3.4, −4.7. **10*β***: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.45–7.28$ (m, 5H), 5.68 (dd, $J = 2.7$, 52.7 Hz, 1H), 4.92 (d, $J = 11.0$ Hz, 1H), 4.84 (d, $J = 11.0$ Hz, 1H), 4.45 (dd, $J = 1.9$, 12.1 Hz, 1H), 4.11 (dd, $J = 4.7$, 12.1 Hz, 1H), 4.04–3.94 (m, 1H), 3.83–3.71 (m, 2H), 3.74–3.36 (m, 1H), 2.11 (s, 3H), 0.92 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 170.7$, 137.7, 128.6, 128.5, 128.2, 127.9, 127.6, 109.6, 106.7, 82.4, 82.3, 75.4, 74.8, 74.7, 70.2, 66.6, 66.3, 62.8, 26.0, 21.1, 18.2, −3.5, −4.7.

6-*O*-Acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*α*/*β*-D-glucopyranosyl trichloroacetimidate (11): *tert*-Butyldimethylsilyl 6-*O*-acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*β*-D-glucopyranoside (1.16 g, 2.05 mmol) was dissolved in anhydrous THF (20 mL) and cooled to 0 °C. Glacial acetic acid (146 μL, 2.56 mmol) and TBAF (1M in THF) (2.25 mL, 2.25 mmol) were added simultaneously. After 30 min, the mixture was poured into Et_2O (200 mL) and washed three times with brine. The organic layer was dried over Na_2SO_4, filtered and the solvents were removed in vacuo. The residue was dissolved in CH_2Cl_2 (50 mL) and cooled to 0 °C. Trichloroacetonitrile (3.1 mL, 30.9 mmol) and DBU (30 μL, 0.2 mmol) were added and the mixture was stirred for 1 h at 0 °C and concentrated in vacuo. Flash chromatography on silica gel (hexanes/EtOAc 85:15) afforded a mixture of **11*α*** and **11*β*** (27/73) (1.12 g, 1.88 mmol, 92%) as a colorless oil. **11*α***: $[\alpha]_D^{24} = +118.6$ ($c = 1.69$, CH_2Cl_2); IR (thin film): $\tilde{\nu} =$ 3344, 2954, 2929, 2857, 2110, 1745, 1674, 1255, 1069 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.75$ (s, 1H), 7.41–7.28 (m, 5H), 6.44 (d, $J = 3.4$ Hz, 1H), 4.92 (d, $J = 11.3$ Hz, 1H), 4.86 (d, $J = 11.0$ Hz, 1H), 4.40 (dd, $J = 12.2$, 2.1 Hz, 1H), 4.08 (dd, $J = 12.2$, 4.6 Hz, 1H), 3.95–3.99 (m, 1H), 3.77–3.82 (m, 2H), 3.66–3.71 (m, 1H), 2.06 (s, 3H), 0.91 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 170.8$, 160.9, 137.9, 128.5, 127.8, 127.6, 94.8, 80.5, 75.5, 73.3, 70.8, 63.7, 62.7, 26.1, 21.0, 18.2, −3.5, −4.8; FAB MS: *m*/*z*: calcd for $C_{23}H_{33}Cl_3N_4O_6Si$: 594.1235; found: 594.1219. **11*β***: $[\alpha]_D^{24} = +43.6$ ($c = 1.11$, CH_2Cl_2); IR (thin film): $\tilde{\nu} = 3329$, 2928, 2857, 2113, 1745, 1676, 1063 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.74$ (s, 1H), 7.48–7.28 (m, 5H), 5.66 (d, $J = 8.2$ Hz, 1H), 4.94 (d, $J = 11.3$ Hz, 1H), 4.79 (d, $J =$ 11.3 Hz, 1H), 4.42 (dd, $J = 11.9$, 2.4 Hz, 1H), 4.13 (dd, $J = 12.2$, 4.9 Hz, 1H), 3.77 (dd, $J = 9.5$, 8.5 Hz, 1H), 3.69 (dd, $J = 9.8$, 8.2 Hz, 1H), 3.60 (ddd, $J =$ 9.5, 4.9, 2.4 Hz, 1H), 3.36 (dd, $J = 9.5$, 8.5 Hz, 1H), 2.08 (s, 3H), 0.90 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 170.9$, 161.2, 138.1, 128.6, 127.9, 127.6, 97.1, 83.4, 75.5, 75.4, 70.4, 66.2, 62.8, 26.0, 21.1, 18.2, −3.5, −4.8; FAB MS: *m*/*z*: calcd for $C_{23}H_{33}Cl_3N_4O_6Si$: 594.1235; found: 594.1222 $[M]^+$.

3,6-Di-*O*-acetyl-2-azido-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*α*-D-glucopyranosyl bromide (12): *tert*-Butyldimethylsilyl trifluoromethanesulfonate (4.1 mL, 17.9 mmol) was added to a solution of compound **7** (4.70 g, 11.65 mmol) and 2,6-lutidine (3.5 mL, 30 mmol) in CH_2Cl_2 (25 mL) at −20 °C. The reaction was allowed to warm to room temperature and stirred for 1 h. The mixture was poured into EtOAc and extracted with 1N HCl, brine and saturated $NaHCO_3$. The organic layer was dried over Na_2SO_4, filtered and solvents removed in vacuo. Flash chromatography on silica gel (hexanes/EtOAc 199:1 → 98:2) afforded *tert*-butyldimethylsilyl 3,6-di-*O*-acetyl-2-azido-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*β*-D-glucopyranoside (5.61 g, 10.8 mmol, 93%) as a colorless oil. $[\alpha]_D^{24} = -3.1$ ($c = 1.00$, CH_2Cl_2); IR (thin film): $\tilde{\nu} = 2111$, 1750, 1363, 1221 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.87$ (dd, $J = 8.8$, 10.4 Hz, 1H), 4.63 (d, $J = 7.6$ Hz, 1H), 4.39 (dd, $J = 2.2$, 11.7 Hz, 1H), 4.08 (dd, $J = 6.2$, 11.7 Hz, 1H), 3.67 (dd, $J = 9.1$, 9.2 Hz, 1H), 3.54–3.46 (m, 1H), 3.27 (dd, $J = 7.6$, 10.4 Hz, 1H), 2.14 (s, 3H), 2.08 (s, 3H), 0.92 (s, 9H), 0.83 (s, 9H), 0.15 (s, 3H), 0.14 (s, 3H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 170.7$, 169.9, 97.1, 74.6, 74.5, 69.6, 66.8, 63.1, 25.80, 25.75, 21.6, 21.1, 18.2, 18.1, −3.9, −4.3, −4.6, −5.0; FAB MS: *m*/*z*: calcd for $C_{22}H_{43}N_3O_7Si_2$: 517.2639; found: 517.2635 $[M]^+$.

TBAF (1.0M in THF, 6.4 mL) and glacial acetic acid (350 μL, 5.9 mmol) were added dropwise to a solution of *tert*-butyldimethylsilyl 3,6-di-*O*-acetyl-2-azido-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*β*-D-glucopyranoside (2.90 g, 5.6 mmol) in THF (60 mL) under nitrogen at 0 °C. The reaction mixture was warmed to room temperature, stirred for 1.5 h and quenched with saturated $NaHCO_3$. After extracting three times with CH_2Cl_2, the combined organic phases were dried over $MgSO_4$, filtered and the solvents were removed in vacuo. The crude material was evaporated three times with toluene, dried under vacuum for 1 h and dissolved in THF (17 mL). The resulting solution was added to a suspension of $SOBr_2$ (760 μL, 9.6 mmol) and imidazole (585 mg, 8.6 mmol) in anhydrous THF (55 mL) at 0 °C. The resulting suspension was stirred for 1 h, diluted with anhydrous Et_2O, filtered over a pad of florisil and ground $Na_2S_2O_3$ and concentrated to furnish **12** as a yellow solid (2.1 g, 4.5 mmol, 76%) which was used without further purification. $[\alpha]_D^{24} = +5.8$ ($c = 1.00$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 2929$, 2859, 2113, 1746, 1473, 1235, 1006 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.40$ (d, $J = 3.9$ Hz, 1H), 5.43 (dd, $J = 8.8$, 10.4 Hz, 1H), 4.41 (dd, $J = 2.1$, 12.5 Hz, 1H), 4.17–4.11 (m, 2H), 3.87 (t, $J = 8.8$ Hz, 1H), 3.58 (dd, $J = 3.9$, 10.4 Hz, 1H), 2.17 (s, 3H), 2.10 (s, 3H), 0.86 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 170.6$, 169.6, 88.1, 75.1, 73.7, 68.6, 63.4, 61.9, 25.8, 21.5, 20.9, 18.1, −3.8, −4.8; FAB MS: *m*/*z*: calcd for $C_{16}H_{28}BrN_3O_7Si$: 465.0930; found: 465.0940 $[M]^+$.[45]

3,6-*O*-Acetyl-2-azido-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*α*/*β*-D-glucopyranosyl fluoride (13): *tert*-Butyldimethylsilyl-3,6-*O*-acetyl-2-azido-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*α*/*β*-D-glucopyranoside (202 mg, 0.39 mmol) was dissolved in THF (4 mL) and cooled to 0 °C. Glacial acetic acid (25 μL, 0.43 mmol) and TBAF (1M, in THF, 0.43 μL, 0.43 mmol) were added simultaneously. After 30 min, the mixture was poured into Et_2O (200 mL) and washed three times with brine. The organic layer was dried over Na_2SO_4, filtered and the solvent were removed in vacuo. The residue was coevaporated with toluene, dissolved in anhydrous CH_2Cl_2 (3 mL) and cooled to −30 °C. DAST (0.06 mL, 0.45 mmol) was added dropwise and the mixture was stirred for 5 min at −30 °C and 30 min at room temperature. The reaction mixture was cooled to −30 °C and anhydrous methanol (0.1 mL) was added. After warming to room temperature, the mixture was poured into EtOAc (100 mL) and washed with saturated $NaHCO_3$, water and brine. The organic layer was dried over Na_2SO_4, filtered and the solvent were removed in vacuo. Flash chromatograpy on silica gel (hexanes/EtOAc 9:1) afforded an anomeric mixture (6:1) of **13** (145 mg, 92%) as a crystalline solid. FAB MS: *m*/*z*: calcd for $C_{16}H_{28}FN_3O_6Si$: 405.1731; found: 405.1758 $[M]^+$.

3,6-Di-*O*-acetyl-2-azido-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*α*/*β*-D-glucopyranosyl trichloroacetimidate (14): TBAF (1.0M in THF, 1.4 mL) and glacial acetic acid (80 μL, 5.9 mmol) were added dropwise to a solution of *tert*-butyldimethylsilyl 3,6-di-*O*-acetyl-2-azido-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*β*-D-glucopyranoside (590 mg, 1.14 mmol) in THF (12 mL) under nitrogen at 0 °C. The reaction mixture was warmed to room temperature, stirred for 1.5 h and quenched with saturated $NaHCO_3$ solution. After extracting three times with CH_2Cl_2, the combined organic phases were dried over $MgSO_4$, filtered and the solvents were removed in vacuo. The crude material was dried by coevaporation three times with toluene and under vacuum for 1 h and dissolved in CH_2Cl_2 (25 mL). Trichloroacetonitrile (1.3 mL, 12.50 mmol) and freshly activated 4 Å powdered molecular sieves (300 mg) were added and the mixture was stirred for 30 minutes at room temperature. After cooling to 0 °C, DBU (30 μL, 0.2 mmol) was added and the temperature was allowed to rise to room temperature. After 1 h, the mixture was filtered through Celite and the solvents were removed in vacuo. Flash chromatography on silica gel (hexanes/EtOAc 85:15) afforded **14*α*** (437 mg, 0.80 mmol, 70%) and **14*β*** (94 mg, 0.17 mmol, 15%). **14*α***: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.81$ (s, 1H, NH), 6.44 (d, $J = 3.6$ Hz, 1H), 5.43 (dd, $J = 8.8$, 10.4 Hz, 1H), 4.41 (dd, $J = 1.9$, 12.0 Hz, 1H), 4.12–3.99 (m, 2H), 3.87 (t, $J = 9.1$ Hz, 1H), 3.58 (dd, $J = 3.6$, 10.7 Hz, 1H), 2.17 (s, 3H), 2.01 (s, 3H), 0.86 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 170.5$, 169.7, 160.8, 94.7, 72.77, 69.1, 62.5, 61.5, 25.9, 21.6, 21.0, 18.2, −3.8, −4.6. **14*β***: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.81$ (s, 1H), 5.73 (d, $J = 8.2$ Hz, 1H), 5.03 (dd, $J = 8.8$, 9.8 Hz, 1H), 4.40 (dd, $J =$ 2.1, 11.9 Hz, 1H), 4.13 (dd, $J = 4.2$, 11.9 Hz, 1H), 3.87 (t, $J = 9.5$ Hz, 1H), 3.58 (m, 2H), 2.17 (s, 3H), 2.08 (s, 3H), 0.84 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 170.7$, 169.9, 160.8, 96.6, 75.3, 68.8, 64.1, 62.4, 25.9, 25.8, 25.8, 21.5, 21.1, 18.1, −3.9, −4.8.

2-Azido-3,6-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*α*/*β*-D-glucopyranosyl fluoride (15): A mixture of tetrabutylammonium fluoride (1.0M in THF, 203 μL) and glacial acetic acid (12 μL, 0.203 mmol) was added dropwise to a solution of *tert*-butyldimethylsilyl 3,6-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*α*/*β*-D-glucopyranosyide (104 mg, 0.169 mmol) in THF (1.7 mL) under nitrogen at 0 °C. The reaction mixture was warmed to room temperature, stirred for 1.5 h and quenched with brine. After dilution with CH_2Cl_2, the two phases were separated. The organic phase

was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude material was coevaporated three times with toluene and dried under vacuum for 1 h. CH_2Cl_2 (1.4 mL) was added and a solution of DAST (29 μL, 0.22 mmol) in CH_2Cl_2 (300 μL) was added dropwise to the reaction mixture. After stirring at room temperature for 2.5 h, the reaction mixture was diluted with CH_2Cl_2 and washed with water. The organic phase was dried over Na_2SO_4 and after filtration the solvent was removed under reduced pressure. Column chromatography on silica gel (hexanes/EtOAc 20:1) afforded **15** (80.1 mg, 89%) as a colorless oil. FAB MS: *m/z*: calcd for $C_{26}H_{36}FN_3O_4Si$: 501.2459; found: 501.2439 $[M]^+$.

2-Azido-3,6-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-D-glucopyranosyl trichloroacetimidate (16): *tert*-Butyldimethylsilyl trifluoromethanesulfonate (244 μL, 1.06 mmol) was added under argon at room temperature to a solution of compound **8** (353.7 mg, 0.708 mmol) and 2,6-lutidine (206 μL, 1.77 mmol) in CH_2Cl_2 (800 μL). The reaction mixture was stirred for 1 h and quenched with saturated $NaHCO_3$. After addition of CH_2Cl_2 and phase separation the aqueous phase was extracted four times with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$, filtered and solvents removed in vacuo. Flash chromatography on silica gel (hexanes/EtOAc 25:1) afforded *tert*-butyldimethylsilyl 2-azido-3,6-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-β-D-glucopyranoside (420 mg, 97%) as a colorless solid. $[\alpha]_D^{24} = +31.1$ ($c = 1.00$, CH_2Cl_2); IR (thin film): $\tilde{\nu} = 2109$, 1472, 1360, 1107, 1066 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.40-7.28$ (m, 5H), 4.93 (d, $J = 11.1$ Hz, 1H), 4.72 (d, $J = 11.1$ Hz, 1H), 4.64 (d, $J = 12.2$ Hz, 1H), 4.58 (d, $J = 7.7$ Hz, 1H), 4.53 (d, $J = 12.2$ Hz, 1H), 3.78–3.64 (m, 2H), 3.59 (dd, $J = 5.5$, 10.8 Hz, 1H), 3.44–3.39 (m, 1H), 3.34 (dd, $J = 8.5$, 9.8 Hz, 1H), 3.19 (dd, $J = 8.5$, 9.8 Hz, 1H), 0.96 (s, 9H), 0.87 (s, 9H), 0.20 (s, 3H), 0.19 (s, 3H), 0.03 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 138.7$, 138.5, 128.50, 128.46, 127.63, 127.60, 97.5, 83.4, 76.6, 75.0, 73.5, 71.0, 69.3, 69.2, 26.1, 25.8, 18.23, 18.19, −3.6, −4.0, −4.6, −5.0; FAB MS: *m/z*: calcd for $C_{32}H_{51}N_3O_5Si_2$: 613.3367; found: 613.3359 $[M]^+$.

tert-Butyldimethylsilyl 2-azido-3,6-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-β-D-glucopyranoside (0.121 mg, 0.197 mmol) was dissolved in anhydrous THF (1.5 mL) and cooled to 0 °C. Glacial acetic acid (20.0 μL, 0.256 mmol) and TBAF (1.0 M in THF, 240 μL, 0.240 mmol) were added simultaneously. After 30 min, the mixture was poured into EtOAc (50 mL) and washed with sat. $NaHCO_3$. The organic layer was dried over Na_2SO_4, filtered and the solvents were removed in vacuo. The residue was dissolved in CH_2Cl_2 (1 mL) and cooled to 0 °C. Trichloroacetonitrile (1.0 mL) and DBU (5 μL, 0.03 mmol) were added and the mixture was stirred for 1 h at 0 °C, diluted with CH_2Cl_2 (30 mL), passed through a plug of silica and concentrated in vacuo. Flash chromatography on silica gel (hexanes/EtOAc 5:1) afforded **16*α*** and **16*β*** (87.5 mg, 0.137 mmol, 69%) as an inseparable 1:1 mixture. ^1H NMR (500 MHz, $CDCl_3$) $\delta = 8.76$ (s, 1H), 8.73 (s, 1H), 7.40–7.27 (m, 15H), 6.48 (d, $J = 3.6$ Hz, 1H), 8.24 (d, $J = 8.2$, 1H), 4.94 (d, $J = 11.6$ Hz, 1H), 4.91 (d, $J = 11.9$ Hz, 1H), 4.85 (d, $J = 11.0$ Hz, 1H), 4.78 (d, $J = 11.3$ Hz, 1H), 4.66 (d, $J = 12.2$ Hz, 1H), 4.60 (d, $J = 12.2$ Hz, 1H), 4.53 (d, $J = 12.5$ Hz, 1H), 4.50 (d, $J = 11.9$ Hz, 1H), 3.95–3.90 (m, 1H), 3.86 (app t, $J = 9.0$ Hz, 1H), 3.81–3.73 (m, 3H), 3.71–3.64 (m, 5H), 3.60–3.57 (m, 2H), 3.38 (app t, $J = 9.0$ Hz, 1H), 0.88 (s, 9H), 0.87 (s, 9H), 0.06–0.02 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 161.2$, 161.0, 138.4, 138.3, 138.1, 128.5, 128.5, 128.5, 127.8, 127.7, 127.6, 97.1, 95.2, 83.5, 80.6, 77.7, 75.4, 75.2, 73.3, 70.6, 70.4, 68.4, 66.3, 63.9, 26.2, 26.1, 18.2, 18.2, −3.5, −3.6, −4.6.

6-*O*-Benzyl-2-azido-3-*O*-acetyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*α*/*β*-D-glucopyranosyl trichloroacetimidate (17): *tert*-Butyldimethylsilyl trifluoromethanesulfonate (9.5 μL, 0.041 mmol) was added to a solution of compound **9** (12.4 mg, 0.027 mmol) and 2,6-lutidine (8.0 μL, 0.069 mmol) in CH_2Cl_2 (200 μL) under argon at room temperature. The reaction mixture was stirred for 1 h and quenched with saturated $NaHCO_3$. After addition of CH_2Cl_2 and phase separation, the aqueous phase was extracted three times with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$, filtered and the solvents were removed in vacuo. Flash chromatography on silica gel (hexanes/EtOAc 30:1) afforded *tert*-butyldimethylsilyl 3-*O*-acetyl-2-azido-6-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-β-D-glucopyranoside (15.3 mg, 98%) as a colorless solid. $[\alpha]_D^{24} = -11.3$ ($c = 0.71$, CH_2Cl_2); IR (thin film): $\tilde{\nu} = 2109$, 1752, 1473, 1221, 1107, 899 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.38-7.29$ (m, 5H), 4.87 (dd, $J = 9.0$, 10.5 Hz, 1H), 4.65 (d, $J = 12.4$ Hz, 1H), 4.64 (d, $J = 7.8$ Hz, 1H), 4.53 (d, $J = 12.4$ Hz, 1H), 3.79 (dd, $J = 9.3$, 9.1 Hz, 1H), 3.70–3.60 (m, 2H), 3.45–3.38 (m, 1H), 2.15 (s, 3H), 0.95 (s, 9H), 0.82 (s, 9H), 0.18 (s, 3H), 0.17 (s, 3H), 0.06 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 170.1$, 138.3, 128.5, 127.7, 127.6, 97.2, 76.4, 74.9, 73.5, 69.1, 68.5, 67.0, 25.9, 25.8, 21.7, 18.2, 18.1, −3.9, −4.1, −4.5, −5.0; FAB MS: *m/z*: calcd for $C_{27}H_{47}N_3O_6Si_2$: 565.3003; found: 565.3011 $[M]^+$.

tert-Butyldimethylsilyl 6-*O*-benzyl-2-azido-3-*O*-acetyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-β-D-glucopyranoside (0.170 g, 0.30 mmol) was dissolved in anhydrous THF (3 mL) and cooled to 0 °C. Glacial acetic acid (20 μL, 0.35 mmol) and TBAF (1 M in THF) (330 μL, 0.33 mmol) were added simultaneously. After 30 min, the mixture was poured into Et_2O (50 mL) and washed three times with brine. The organic layer was dried over Na_2SO_4, filtered and the solvents were removed in vacuo. The residue was dissolved in CH_2Cl_2 (3 mL) and cooled to 0 °C. Trichloroacetonitrile (770 μL, 7.67 mmol) and DBU (5 μL, 0.03 mmol) were added and the mixture was stirred for 1 h at 0 °C and concentrated in vacuo. Flash chromatography on silica gel (hexanes/EtOAc 85:15) afforded a mixture of **17*α*** and **17*β*** (2.7:1) (0.160 g, 0.27 mmol, 89%) as a colorless oil. **17*α*** ^1H NMR (500 MHz, $CDCl_3$): $\delta = 8.77$ (s, 1H, NH), 7.36–7.27 (m, 5H), 6.50 (d, $J = 3.4$ Hz, 1H), 5.43 (dd, $J = 7.9$, 10.7 Hz, 1H), 4.58 (d, $J = 11.9$ Hz, 1H), 4.51 (d, $J = 11.9$ Hz, 1H), 4.01–3.95 (m, 2H), 3.75 (dd, $J = 3.3$, 11.3 Hz, 1H), 3.65 (dd, 1H), 3.48 (dd, $J = 3.4$, 10.4 Hz, 1H), 2.17 (s, 3H), 0.84 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 170.0$, 161.0, 138.1, 128.5, 127.8, 127.7, 95.2, 74.7, 73.6, 73.1, 68.7, 68.0, 61.7, 25.9, 21.6, 18.2, −4.0, −4.6; **17*β*** ^1H NMR (500 MHz, $CDCl_3$): $\delta = 8.78$ (s, 1H), 7.34–7.27 (m, 5H), 5.76 (d, $J = 8.5$ Hz, 1H), 5.03 (dd, $J = 8.8$, 10.0 Hz, 1H), 4.64 (d, $J = 12.2$ Hz, 1H), 4.53 (d, $J = 12.3$ Hz, 1H), 3.91 (t, $J = 9.1$ Hz, 1H), 3.68–3.58 (m, 4H), 2.16 (s, 3H), 0.82 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H).

***tert*-Butyldimethylsilyl-6-*O*-acetyl-2-azido-2-deoxy-β-D-glucopyranoside (18)**: Compound **2** (1.23 g, 2.77 mmol) was dissolved in methanol (10 mL). NaOMe (25% in methanol, 170 μL) was added. After 15 min DOWEX-50 acidic resin was added and the mixture was stirred until the pH reached 6. The DOWEX resin was filtered off and the solvent was removed under reduced pressure to afford a yellow oil. The residue was coevaporated twice with toluene, dissolved in 2,4,6-collidine (7 mL), cooled to −40 °C and acetyl chloride (196 μL, 2.74 mmol) was added. After stirring the reaction mixture for 3 h, a second portion of acetyl chloride (42 μL, 0.6 mmol) was added. The mixture was stirred for another 1 h at −40 °C and for 1 h at room temperature and then quenched with saturated $NaHCO_3$. After addition of CH_2Cl_2 and phase separation the aqueous phase was extracted three times with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$, filtered and the solvents were removed in vacuo. Flash chromatography (hexanes/EtOAc 4:1) on silica afforded **18** (933 mg, 2.58 mmol, 93%) as a colorless syrup. $[\alpha]_D^{24} = -7.0$ ($c = 1.00$, $CHCl_3$); IR (thin film): $\tilde{\nu} = 3412$, 2929, 2958, 2111, 1741, 1463, 1370, 1257, 1177 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 4.55$ (d, $J = 7.5$ Hz), 4.38–4.26 (m, 2H), 4.13 (br s, 2H), 3.45–3.20 (m, 4H), 2.06 (s, 3H), 0.93 (s, 9H), 0.15 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 171.9$, 97.3, 74.5, 73.8, 70.6, 68.2, 63.7, 25.7, 21.0, 18.1, −3.5, −4.6; FAB MS: *m/z*: calcd for $C_{14}H_{27}N_3O_6Si$: 361.1669; found: 361.1680 $[M]^+$.

***tert*-Butyldimethylsilyl-6-*O*-acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (19)**: Compound **18** (7.1 g, 19.64 mmol) was dissolved in CH_2Cl_2 (100 mL). Powdered, freshly activated 4 Å molecular sieves (20 g) and benzyl bromide (12 mL, 100 mmol) were added and this mixture stirred for 30 min. Silver(I)oxide (26.4 g, 114 mmol) was added and light was excluded from the reaction mixture. After 48 h, the reaction mixture was filtered over Celite and the filtrate was concentrated under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 97:3) afforded **19** (8.5 g, 15.7 mmol, 80%) as a colorless oil. $[\alpha]_D^{24} = -4.7$ ($c = 1.40$, CH_2Cl_2); IR (thin film): $\tilde{\nu} = 3031$, 2955, 2858, 2109, 1745, 1454, 1252, 1042, cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.43-7.29$ (m, 10H), 4.95 (d, $J = 11.0$ Hz, 1H), 4.89 (d, $J = 11.0$ Hz, 1H), 4.82 (d, $J = 10.7$ Hz, 1H), 4.61 (d, $J = 11.0$ Hz, 1H), 4.56 (d, $J = 7.6$ Hz, 1H), 4.36 (dd, $J = 11.9$, 1.5 Hz, 1H), 4.17 (dd, $J = 11.9$, 5.8 Hz, 1H), 3.55–3.49 (m, 2H), 3.47–3.43 (m, 1H), 3.38 (dd, $J = 9.8$, 7.6 Hz, 1H), 2.06 (s, 3H), 0.98 (s, 9H), 0.20 (s, 3H), 0.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 170.8$, 138.0, 137.7, 128.7, 128.6, 128.2, 128.2, 128.1, 97.3, 83.1, 77.7, 75.7, 75.2, 73.2, 68.8, 63.2, 25.8, 21.0, 18.2, −4.2, −5.1; FAB MS: *m/z*: calcd for $C_{28}H_{39}N_3O_6Si$: 541.2608; found: 541.2606 $[M]^+$.

6-*O*-Acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-*α*/*β*-D-glucopyranosyl trichloroacetimidate (20): Glacial acetic acid (100 μL, 1.75 mmol) and TBAF (1 M in THF, 1.55 mL, 1.55 mmol) were added simultaneously to a solution of **19** (756 mg, 1.4 mmol) in anhydrous THF (15 mL) at 0 °C. After 30 min this mixture was poured into Et_2O (150 mL) and extracted three times with

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brine. The organic layer was dried over Na_2SO_4, filtered and the solvents were removed in vacuo. The residue was dissolved in anhydrous CH_2Cl_2 (50 mL) and cooled in an ice bath. Trichloroacetonitrile (2.1 mL, 21 mmol) and DBU (21 μL, 0.14 mmol) were added. After 45 min, the solvents were removed in vacuo. Flash chromatography on silica gel (hexanes/EtOAc 85:15 → 8:2) afforded a mixture (58:42) of **20*α*** and **20*β*** (708 mg, 1.24 mmol, 88 %) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.76 (s, 1H, NH), 7.44–7.26 (m, 10H, arom. H), 6.42 (d, J = 3.4 Hz, 1H), 5.64 (d, J = 8.2 Hz, 1H), 4.97–4.86 (m, 4H), 4.64–4.60 (m, 1H), 4.35–4.24 (m, 2H), 4.10–4.06 (m, 1H), 3.73–3.57 (m, 2H), 2.03 (s, 3H).

Methyl 3-*O*-benzyl-1,2-*O*-isopropylidene-*α*-D-glucofuranosyluronate (22): 1,2:5,6-Di-*O*-isopropylidene-*α*-D-glucofuranose (**21**; 52.06 g, 200 mmol) was dissolved in THF (500 mL) and NaH (60 % in mineral oil, washed with pentanes) (9.6 g, 240 mmol) was added in portions. After the evolution of hydrogen ceased, tetrabutylammonium iodide (500 mg, 1.35 mmol) and benzyl bromide (25 mL, 210 mmol) were added and the mixture stirred for 10 h at room temperature. Water was added slowly to the reaction mixture and the organic solvents were removed in vacuo. The aqueous phase was extracted three times with EtOAc. The combined organic phases were dried over Na_2SO_4, filtered through a plug of silica gel and the solvents were removed in vacuo.

Aqueous acetic acid (66 %, 300 mL) was added to the resulting oil and the mixture was stirred for 14 h at room temperature and for 6 h at 40 °C. After removal of the solvents, the remaining residue was dissolved in CH_2Cl_2 and extracted with saturated $NaHCO_3$. After phase separation, the aqueous layer was extracted with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4, filtered and the solvents were removed in vacuo.

The residual oil was dissolved in CH_2Cl_2 (750 mL) and pyridine (80 mL), before DMAP (3.5 g, 28.6 mmol) and *tert*-butyldimethylsilyl chloride (32 g, 212 mmol) were added. After stirring at room temperature for 19 h, the mixture was extracted with water, 1N HCl, brine and saturated $NaHCO_3$. The organics were dried over Na_2SO_4, filtered and the solvents were removed in vacuo. The residue was dissolved in anhydrous pyridine (170 mL) and DMAP (1 g, 8.2 mmol) was added. The mixture was cooled to 0 °C and acetic anhydride (38 mL, 403 mmol) was added dropwise. After stirring overnight at room temperature, the solvents were removed in vacuo. The residue was dissolved in EtOAc and extracted with water, 1N HCl, brine and saturated $NaHCO_3$. The organic layer was dried over Na_2SO_4, filtered and the solvents were removed in vacuo.

The residue (91.2 g, max. 195 mmol) was dissolved in THF (300 mL) and cooled to 0 °C. To this solution, HF/pyridine (24 mL) in pyridine (80 mL) was added and stirred overnight at room temperature. The reaction mixture was poured into water and extracted three times with EtOAc. The combined organic phases were extracted with water, 1N HCl, water, saturated $NaHCO_3$, dried over Na_2SO_4, filtered and the solvents were removed in vacuo.

The residue was dissolved in CH_2Cl_2 (400 mL) and TEMPO (800 mg, 5.1 mmol) was added. A mixture of saturated $NaHCO_3$ (700 mL), water (200 mL), KBr (2.25 g, 18.9 mmol) and tetrabutylammonium bromide (3.45 g, 10.7 mmol) was added and the resulting mixture was cooled to 0 °C. With vigorous stirring, bleach (6.15% sodium hypochlorite, 700 mL) was added in 100 mL portions every 10 min. After complete addition, stirring was continued for 30 min and methanol was added until the mixture was decolorized. After 20 min, the aqueous layer was extracted with CH_2Cl_2 followed by the dropwise addition of conc. HCl to pH 1. The aqueous layer was extracted three times with CH_2Cl_2. The organic layers were dried over Na_2SO_4, filtered and the solvents were removed in vacuo.

The residue was dissolved in methanol (280 mL), 4N NaOH (42 mL) was added and the mixture was stirred overnight at room temperature. The mixture was acidified with conc. HCl and extracted five times with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4, filtered and the solvents were removed in vacuo.

The residue was dissolved in anhydrous DMF (200 mL) and powdered $KHCO_3$ (27.4 g, 274 mmol) and methyl iodide (17 mL, 273 mmol) were added. After stirring at room temperature overnight, the mixture was poured into Et_2O and extracted twice with water, saturated Na_2SO_3, and water. The organic phase was dried over Na_2SO_4, filtered and the solvents were removed in vacuo to afford **22** (44 g, 130 mmol, 65 %) as a slightly yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.27 (m, 5H), 6.04 (d, J = 3.9 Hz, 1H), 4.70–4.52 (m, 4H), 4.41 (dd, J = 6.2, 3.8 Hz, 1H), 4.16 (d, J = 3.8 Hz, 1H), 3.76 (s, 3H), 3.34 (d, J = 9.1 Hz, 1H), 1.50 (s, 3H), 1.34 (s, 3H). The spectral data was in agreement with the reported data.[18]

Methyl 3-*O*-benzyl-D-glucopyranosyluronate (23): Compound **22** (3.43 g, 10.14 mmol) was dissolved in 90 % aqueous trifluoroacetic acid (20 mL) and stirred for 15 min at room temperature. The solvent was evaporated and the residue coevaporated twice with water and twice with toluene to afford **23**, which was used without further purification. The spectral data was in agreement with the reported data.[18]

Methyl 3-*O*-benzyl-1,2-*O*-isopropylidene-5-*O*-levulinoyl-*β*-L-idofuranosyluronate (24): A solution of trifluoromethanesulfonic anhydride (13 mL) in CH_2Cl_2 (250 mL) was added dropwise to a mixture of pyridine (13 mL) and CH_2Cl_2 (132 mL) at −20 °C. The mixture was allowed to warm to −10 °C and a solution of compound **22** (12 g, 35.5 mmol) in CH_2Cl_2 (123 mL) was added dropwise. After 1 h at −10 °C, the mixture was poured into ice cold water containing $NaHCO_3$ and stirred for 1 h. The organic layer was washed with 3 % HCl, water, dried over $MgSO_4$, filtered and the solvents were removed in vacuo. Sodium levulinate (9.8 g, 71 mmol) was added to a solution of the crude residue in DMF (65 mL) and the resulting mixture was stirred overnight at 80 °C and cooled to room temperature. After dilution with EtOAc, the mixture was washed with water and the organic phase was dried over $MgSO_4$, filtered and the solvents were removed in vacuo. Flash chromatography on silica gel (toluene/EtOAc 9:1 → 7:3) afforded **24** (12.8 g, 29.3 mmol, 82 %) as an amorphous solid. $[\alpha]_D^{24} = -4.2$ (c = 1, $CHCl_3$); IR (thin film): $\tilde{\nu}$ = 2512, 1751, 1718, 1025 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36–7.28 (m, 5H), 5.97 (d, J = 3.9 Hz, 1H), 5.53 (d, J = 7.0 Hz, 1H), 4.66–4.62 (m, 3H), 4.50 (d, J = 11.4 Hz, 1H), 4.16 (d, 1H), 3.69 (s, 3H), 2.73–2.63 (m, 4H), 2.12 (s, 3H), 1.59 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 205.3, 171.9, 168.5, 137.2, 128.6, 128.4, 128.0, 112.7, 105.1, 83.1, 82.7, 72.5, 70.9, 52.8, 38.0, 30.0, 28.0, 27.3, 26.8; FAB MS: m/z: calcd for $C_{22}H_{28}O_9$: 436.1733; found: 436.1742 $[M]^+$.

Methyl 3-*O*-benzyl-L-idopyranosyluronate (25): Hydrazine hydrate (7.3 mL, 146 mmol) was added to a solution of compound **23** (12.8 g, 29.3 mmol) in pyridine/acetic acid (3:2, 290 mL) at 0 °C. After 15 min, acetone (1.2 mL) was added, and the mixture was stirred at room temperature for 15 min. After removal of the solvents in vacuo, the crude product was dissolved in aqueous trifluoroacetic acid (90 %, 70 mL). The mixture was stirred for 15 min, the solvents removed in vacuo and coevaporated twice with water to give a white solid, which was recrystallized from ethyl acetate/hexanes to afford **25** (8.0 g, 26.8 mmol, 91 %). Analytical data was in agreement with reported data.[18]

***n*-Pentenyl (6-*O*-acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*α*/*β*-D-glucopyranosyl)-(1 → 4)-methyl 2-*O*-benzoyl-3-*O*-benzyl-*β*-D-glucopyranosyluronate (27)**

By coupling 11 and 26: Compounds **11** (27.0 mg, 0.045 mmol) and **26** (16.1 mg, 0.035 mmol) were coevaporated three times with toluene and dissolved in CH_2Cl_2 (1 mL). Freshly activated powdered 4 Å molecular sieves (100 mg) were added and the mixture was stirred at room temperature for 1 h. The reaction mixture was cooled to −78 °C and *tert*-butyldimethylsilyl trifluoromethanesulfonate (2.0 μL, 0.009 mmol) was added dropwise. The reaction mixture was warmed to room temparature over 2.5 h. Triethylamine (0.5 mL) was added, the mixture was filtered through a pad of Celite and the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 95:5) afforded **27** (18 mg, 0.02 mmol, 57 %) as a yellow oil.

By coupling 10 and 26: Compounds **10** (57.3 mg, 0.126 mmol) and **26** (82.4 mg, 0.175 mmol) were coevaporated three times with toluene, dissolved in Et_2O (4.0 mL) and cooled to 0 °C. Freshly activated powdered 4 Å molecular sieves (140 mg), $SnCl_2$ (28.4 mg, 0.152 mmol) and $AgClO_4$ (31.5 mg, 0.152 mmol) were added to this mixture. After stirring for 90 min at 0 °C, the mixture was warmed to 12 °C over 22 h, filtered through a pad of Celite, washed with sat. $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4 and after filtration the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 25:1 → 1:1) afforded **27** (87.7 mg, 0.097 mmol, 77 %) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.06–8.03 (m, 2H), 7.92–7.89 (m, 2H), 7.61–7.04 (m, 13H), 5.71–5.59 (m, 1H), 5.57 (d, J = 3.5 Hz), 5.36 (dd, J = 8.6, 7.3 Hz), 5.23 (dd, J = 8.6, 7.6 Hz), 4.93–4.60 (m, 7H), 4.48 (d, J = 7.8 Hz), 4.40–4.25 (m, 2H), 4.15–3.80 (m, 7H), 3.65–3.18 (m, 5H), 2.11 (s, 3H, CH_3), 1.98–1.84 (m, 2H), 1.67–1.53 (m, 2H), 0.91 (s, 9H), 0.90 (s, 9H), 0.01 (s, 3H).

***n*-Pentenyl (2-azido-3,6-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*α*/*β*-D-glucopyranosyl)-(1 → 4)-methyl 2-*O*-benzoyl-3-*O*-benzyl-*β*-D-glucopyranosyluronate (28)**: Tin(II) triflate (140 mg, 0.336 mmol) was added to freshly activated powdered 4 Å molecular sieves (100 mg) under argon in a glove box. Et_2O (2.0 mL) was added and the reaction mixture was cooled to −10 °C before di-*tert*-butylpyridine (64 mg, 0.33 mmol) was added to the reaction. Compound **15** (25.6 mg, 0.051 mmol) and **26** (31.8 mg, 0.068 mmol) were coevaporated three times with toluene and dissolved in Et_2O (1.0 mL). The resulting solution was added dropwise to the reaction mixture at −10 °C. The reaction was stirred for one hour at −10 °C and then for three hours at room temperature. After dilution with CH_2Cl_2 and filtration through a pad of Celite, the solution was quenched with sat. $NaHCO_3$. The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 20:1 → 3:1) afforded **28** (21.1 mg, 0.022 mmol, 43 %) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92 – 7.89 (m, 2H), 7.60 – 7.15 (m, 8H), 5.71 – 5.60 (m, 1H), 5.59 (d, J = 3.6 Hz), 5.38 (t, J = 7.8 Hz), 5.26 (t, J = 7.5 Hz), 4.84 – 4.47 (m, 9H), 4.39 – 4.23 (m, 1H), 4.14 – 4.01 (m, 2H), 3.93 – 3.56 (m, 8H), 3.52 – 3.34 (m, 2H), 3.28 (dd, J = 3.6, 10.2 Hz), 3.19 (at, J = 8.7 Hz, 1H), 2.02 – 1.93 (m, 2H), 1.66 – 1.54 (m, 2H), 0.88 (s, 9H), 0.86 (s, 9H), 0.05 (s, 3H, CH_3), 0.03 (s, 3H, CH_3).

Dimethylthexylsilyl (3,6-di-*O*-acetyl-2-azido-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*α*-D-glucopyranosyl)-(1 → 4)-methyl 3-*O*-benzyl-*β*-D-idopyranosyluronate (30)

By coupling 14 and 29: Compound **14** (100 mg, 0.18 mmol) and **29** (119 mg, 0.27 mmol) were coevaporated with toluene (3 ×) and dissolved in CH_2Cl_2 (50 mL). Freshly activated powdered 4 Å molecular sieves (100 mg) were added and the mixture was stirred at room temperature for 1 h. The reaction mixture was cooled to −78 °C and *tert*-butyldimethylsilyl trifluoromethanesulfonate (72 μL, 0.314 mmol) was added dropwise. The mixture was warmed to room temperature over 2.5 h. Triethylamine (3 mL) was added, the mixture was filtered through a pad of Celite and the solvent was removed under reduced pressure. Flash chromatography on silica gel (toluene/EtOAc 99:1 → 9:1) afforded **30** (71 mg, 0.09 mmol, 47 %), both as a colorless foam.

By coupling 13 and 29: Compound **13** (100 mg, 0.250 mmol) and **29** (154 mg, 0.350 mmol) were coevaporated three times with toluene, dissolved in Et_2O (1.5 mL) and cooled to 0 °C. Freshly activated powdered 4 Å molecular sieves (100 mg), $SnCl_2$ (48 mg, 0.250 mmol) and $AgClO_4$ (52 mg, 0.250 mmol) were added to this mixture. After stirring for 5 h at 0 °C the mixture was warmed to 12 °C over 22 h, filtered through a pad of Celite, washed with sat. $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4 and after filtration the solvent was removed under reduced pressure. Flash chromatography on silica gel (toluene/EtOAc 99:1 → 9:1) afforded **30** (60 mg, 0.07 mmol, 30 %) as a colorless foam. ^{1}H NMR (500 MHz, CDCl3): δ = 7.38 – 7.35 (m, 5H), 5.19 (dd, J = 8.0, 10.8 Hz, 1H), 5.11 (d, J = 3.6 Hz, 1H), 5.04 (d, J = 0.8 Hz, 1H), 4.61 (d, 3H), 4.37 (d, 1H), 4.13 – 4.06 (m, 2H), 3.82 (s, 3H), 3.81 – 3.71 (m, 3H), 3.63 (br s, 1H), 3.24 (dd, J = 3.3, 10.4 Hz, 1H), 2.80 (br s, 1H), 2.12 (s, 3H), 2.10 (s, 3H), 1.98 (s, 3H), 0.90 – 0.84 (m, 7H), 0.24 (s, 3H), 0.18 (s, 3H), 0.05 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.6, 169.5, 169.4, 137.2, 128.7, 128.3, 127.8, 94.5, 73.9, 73.1, 72.9, 72.6, 70.6, 69.8, 69.0, 68.5, 62.6, 61.8, 52.5, 34.3, 25.8, 25.2, 21.6, 21.2, 20.6, 20.3, 18.9, 18.7, 18.1, −1.7, −3.0, −3.7, −4.7; FAB MS: *m*/*z*: calcd for $C_{38}H_{63}N_3O_{13}Si_2$: 825.3899; found: 825.3888 $[M]^+$.

Methyl 3-*O*-benzyl-1,2-*O*-isopropylidene-*α*-D-glucopyranosyluronate (31): Compound **23** (3.02 g, 10.14 mmol) was dissolved in DMF (10 mL) and 2-methoxypropene (10 mL, 100 mmol) was added and cooled to 0 °C. A solution of (1*S*)-(+)-camphorsulfonic acid (230 mg, 1 mmol) in DMF (2 mL) was added and stirring was continued at 0 °C for 1 h and at room temperature overnight. Methanol (15 mL) was added and the mixture was stirred for 3 h at room temperature. Triethylamine (3 mL) was added and the mixture was concentrated. The residue was dissolved in Et_2O and washed with water and twice with brine. The organic layer was dried over Na_2SO_4 and after filtration the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 9:1) afforded **31** (1.65 g, 4.88 mmol, 48 %) as a colorless oil. $[\alpha]_D^{24}$ = +22.3 (c = 1.13, CH_2Cl_2); IR (thin film on NaCl): $\tilde{\nu}$ = 3520, 3037, 2987, 1752, 1455, 1169, 1105 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34 – 7.26 (m, 5H), 5.87 (d, J = 2.7 Hz, 1H), 4.63 (d, J = 11.9 Hz, 1H), 4.54 (d, J = 11.6 Hz, 1H), 4.54 (d, J = 3.7 Hz, 1H), 4.24 – 4.20 (m, 1H), 4.11 – 4.09 (m, 1H), 4.00 (dd, J = 3.1, 3.4 Hz, 1H), 3.58 (s, 3H), 3.51 (d, J = 10.4 Hz, 1H), 1.60 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.3, 137.2, 128.6, 128.2, 127.8, 111.4, 94.4, 75.8, 75.5, 73.7, 72.4, 67.0, 52.2, 28.0, 25.9; FAB MS: *m*/*z*: calcd for $C_{17}H_{22}O_7$: 338.1366; found: 338.1377 $[M]^+$. Further elution (hexanes/EtOAc 7:3) afforded **32** (1.1 g, 32 %) as a colorless oil.

Methyl 3-*O*-benzyl-1,2-*O*-cyclopentylidene-*α*-D-glucopyranosyluronate (33) and methyl 3-*O*-benzyl-1,2-*O*-cyclopentylidene-*α*-D-glucofuranosyluronate (34): Compound **23** (2.94 g, 9.87 mmol) was dissolved in DMF (10 mL) and methoxycyclopentene (7.1 g, 72 mmol) and cooled to 0 °C. A solution of (1*S*)-(+)-camphorsulfonic acid (244 mg, 1.05 mmol) in DMF (2 mL) was added and stirring was continued at 0 °C for 1 h and at room temperature overnight. Methanol (5 mL) was added and the mixture was stirred for 30 min at room temperature. Triethylamine (3 mL) was added and the mixture was concentrated. The residue was dissolved in Et_2O and washed with water and twice with brine. The organic layer was dried over Na_2SO_4 and after filtration the solvent was removed under reduced pressure. Flash chromatography on silica gel (toluene/EtOAc 98.5:1.5) afforded **33** (2.05 g, 57 %) as a colourless oil. $[\alpha]_D^{24}$ = +33.9 (c = 1.48, CH_2Cl_2); IR (thin film on NaCl): $\tilde{\nu}$ = 3510, 3032, 2955, 2873, 1750, 1454, 1436, 1206 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37 – 7.27 (m, 5H), 5.84 (d, J = 2.8 Hz, 1H), 4.66 (d, J = 11.6 Hz, 1H), 4.57 (d, J = 11.9 Hz, 1H), 4.52 (d, J = 4.3 Hz, 1H), 4.23 – 4.19 (m, 1H), 4.04 (dd, J = 3.0, 2.4 Hz, 1H), 4.00 (dd, J = 3.4, 3.1 Hz, 1H), 3.63 (s, 3H), 3.40 (d, J = 9.5 Hz, 1H), 2.14 – 2.08 (m, 1H), 1.92 – 1.86 (m, 1H), 1.79 – 1.62 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.5, 137.3, 128.6, 128.2, 127.8, 94.2, 75.9, 75.0, 74.2, 72.4, 67.4, 52.3, 37.7, 36.8, 23.5, 23.2; FAB MS: *m*/*z*: calcd for $C_{19}H_{24}O_7$: 364.1522; found: 364.1534 $[M]^+$. Further elution (toluene/EtOAc 9:1) afforded **34** (1.04 g, 2.85 mmol, 29 %) as a colorless oil. $[\alpha]_D^{24}$ = +0.7 (c = 1.37, CH_2Cl_2); IR (thin film on NaCl): $\tilde{\nu}$ = 3470, 2955, 2875, 1738, 1455, 1208 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 – 7.27 (m, 5H), 5.98 (d, J = 4.0 Hz, 1H), 4.66 (d, J = 11.5 Hz, 1H), 4.63 – 4.52 (m, 3H), 4.43 (dd, J = 6.0, 4.0 Hz, 1H), 4.16 (d, J = 4.0 Hz, 1H), 3.73 (s, 3H), 3.36 (br s, 1H), 2.00 – 1.93 (m, 1H), 1.86 – 1.76 (m, 1H), 1.74 – 1.60 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.1, 136.9, 128.7, 128.3, 128.1, 121.9, 105.3, 83.3, 82.7, 80.1, 72.8, 70.1, 52.5, 37.1, 36.7, 23.4, 23.2; FAB MS: *m*/*z*: calcd for $C_{19}H_{24}O_7$: 364.1522; found: 364.1530 $[M]^+$.

Methyl 3-*O*-benzyl-1,2-*O*-isopropylidene-*β*-L-idopyranosyluronate (35): Methyl 3-*O*-benzyl-L-idopyranosyluronate (**25**; 1.7 g, 5.70 mmol) was dissolved in DMF (6 mL) and 2-methoxypropene (10.7 mL, 114 mmol) was added. The mixture was cooled at 0 °C and (1*S*)-(+)-camphorsulfonic acid (132 mg, 0.57 mmol) in DMF (2 mL) was added dropwise under stirring. The mixture was stirred for 6 h at 0 °C, then methanol (2 mL) was added and stirred for 30 min at 0 °C before the reaction was quenched by addition of triethylamine After dilution with EtOAc, the solution was washed with water. The organic layer was dried over $MgSO_4$ and evaporated. Flash chromatography on silica gel (toluene/EtOAc 99:1 → 96:4) afforded **35** (1.3 g, 3.84 mmol, 68 %) as a yellow oil. $[\alpha]_D^{24}$ = −29.5 (c = 1.00, $CHCl_3$); IR (thin film on NaCl): $\tilde{\nu}$ = 2937, 1764, 1374, 843 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40 – 7.30 (m, 5H), 5.35 (d, J = 1.9 Hz, 1H), 4.71 (d, J = 11.7 Hz, 1H), 4.63 (d, J = 11.7 Hz, 1H), 4.49 (s, 1H), 4.12 – 4.10 (m, 1H), 4.0 (d, J = 1.8 Hz, 1H), 3.97 (dd, J = 1.9, 3.7 Hz, 1H), 3.80 (s, 3H), 3.12 (d, J = 11.6 Hz, 1H), 1.63 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.4, 137.1, 128.8, 128.5, 128.0, 112.1, 96.5, 75.5, 73.4, 72.9, 72.2, 67.4, 52.6, 28.4, 25.7; FAB MS: *m*/*z*: calcd for $C_{17}H_{22}O_7$: 338.1365; found: 338.1357. Further elution (toluene/EtOAc 9:1) afforded **36** (382 mg, 20 %) as a colorless oil.

Methyl 3-*O*-benzyl-1,2-*O*-cyclopentylidene-*β*-L-idopyranosyluronate (37) and methyl 3-*O*-benzyl-1,2-*O*-cyclopentylidene-*β*-L-idofuranosyluronate (38): A mixture of (1*S*)-(+)-camphorsulfonic acid (77 mg, 0.33 mmol) and methoxycyclopentylidene (3.3 g, 33.5 mmol) in DMF (2 mL) was cooled to 0 °C. A solution of **25** (1.0 g, 3.35 mmol) in DMF (1 mL) was added dropwise under stirring. The mixture was stirrred for 3 h at 0 °C and overnight at room temperature, after which methanol (2 mL) was added and stirred 30 minutes. The reaction was quenched by adding triethylamine. After dilution with EtOAc, the solution was washed with water and dried over $MgSO_4$. After filtration the solvent was removed under reduced pressure and the syrup was purified by flash chromatography on silica gel (toluene/EtOAc 99:1 → 98:2) to yield **37** (684 mg, 1.88 mmol, 56 %) as a yellow syrup. $[\alpha]_D^{24}$ = +10.9 (c = 1.00, $CHCl_3$); IR (thin film on NaCl): $\tilde{\nu}$ = 3534, 2954, 2111, 1764, 1437, 1336, 1120 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40 – 7.30 (m, 5H), 5.35 (d, J = 1.9 Hz, 1H), 4.70 (d, J = 11.7 Hz, 1H), 4.63 (d, J = 11.7 Hz, 1H), 4.50 (s, 1H), 4.11 – 4.09 (m, 1H), 4.07 (d, J =

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1.6 Hz, 1H), 3.88 (dd, $J = 2.1$, 3.6 Hz, 1H), 3.80 (s, 3H), 3.10 (d, $J = 11.9$ Hz, 1H), 2.14–2.08 (m, 1H), 2.23–2.16 (m, 1H), 1.86–1.61 (m, 6H), ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 169.4$, 137.2, 128.8, 128.5, 128.0, 121.5, 96.1, 75.7, 73.5, 72.9, 72.1, 67.4, 52.6, 38.3, 36.6, 23.5, 23.4; FAB MS: *m/z*: calcd for $C_{19}H_{24}O_7$: 364.1522; found: 364.1530 $[M]^+$.

Further elution (toluene/EtOAc 9:1) afforded **38** (219 mg, 0.6 mmol, 18%) as a colorless oil. $[\alpha]_D^{24} = -13.9$ ($c = 1.00$, $CHCl_3$); IR (thin film on NaCl): $\tilde{\nu} = 3485$, 2954, 2874, 1738, 1453, 1338, 1120 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.38–7.30$ (m, 5H), 5.97 (d, $J = 4.1$ Hz, 1H), 4.74 (d, $J = 11.6$ Hz, 1H), 4.64 (dd, $J = 1.2$, 4.1 Hz, 1H), 4.57–4.50 (m, 2H), 4.53 (d, $J = 11.4$ Hz, 1H), 4.20 (dd, $J = 1.5$, 4.7 Hz, 1H), 3.74 (s, 3H), 3.30 (d, $J = 3.3$ Hz, 1H), 2.00–1.91 (m, 1H), 1.81–1.65 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 172.3$, 137.0, 128.7, 128.3, 128.1, 122.2, 105.1, 83.5, 83.0, 80.4, 72.5, 70.1, 52.8, 37.3, 37.1, 23.4, 23.3; FAB MS: *m/z*: calcd for $C_{19}H_{24}O_7$: 364.1522; found: 364.1534 $[M]^+$.

6-*O*-Acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucopyranosyluronate (39)

By coupling 11 and 31: Compounds **11** (1.87 g, 3.14 mmol) and **31** (850 mg, 2.51 mmol) were coevaporated three times with toluene and dissolved in CH_2Cl_2 (50 mL). Freshly activated powdered 4 Å molecular sieves (1 g) were added and the mixture was stirred at room temperature for 1 h. The reaction mixture was cooled to −78 °C and *tert*-butyldimethylsilyl trifluoromethanesulfonate (72 μL, 0.314 mmol) was added dropwise. The mixture was warmed to room temperature over 2.5 h. Triethylamine (3 mL) was added, the mixture was filtered through a pad of Celite and the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 85:15) afforded **39** (1.68 g, 2.18 mmol, 86%) as a colorless foam.

By coupling 10 and 31: Compounds **10** (540 mg, 1.19 mmol) and **31** (362 mg, 1.07 mmol) were coevaporated three times with toluene, dissolved in Et_2O (20 mL) and cooled to 0 °C. To this mixture freshly activated 4 Å molecular sieves (1 g), $SnCl_2$ (229 mg, 1.21 mmol) and $AgClO_4$ (250 mg, 1.21 mmol) were added. This mixture was stirred for 90 min at 0 °C, then warmed to 12 °C over 22 h. The mixture was filtered through a pad of Celite, washed with sat. $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4 and after filtration the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 9:1) afforded **39** (660 mg, 0.86 mmol, 80%) as a colorless foam. $[\alpha]_D^{24} = +97.2$ ($c = 2.55$, CH_2Cl_2); IR (thin film on NaCl): $\tilde{\nu} = 3032$, 2953, 2930, 2858, 2106, 1746, 1455, 1372, 1250 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.40–7.27$ (m, 10H), 5.78 (d, $J = 3.7$ Hz, 1H), 5.17 (d, $J = 3.7$ Hz, 1H), 4.88 (d, $J = 11.0$ Hz, 1H), 4.78 (d, $J = 11.0$ Hz, 1H), 4.68 (s, 2H), 4.59 (d, $J = 6.1$ Hz, 1H), 4.38 (dd, $J = 2.1$, 11.9 Hz, 1H), 4.25–4.21 (m, 2H), 4.09–4.05 (m, 2H), 3.89–3.85 (m, 1H), 3.74 (dd, $J = 8.5$, 10.4 Hz, 1H), 3.71 (s, 3H), 3.63 (dd, $J = 8.5$, 9.8 Hz, 1H), 3.25 (dd, $J = 3.7$, 10.4 Hz, 1H), 2.08 (s, 3H), 1.63 (s, 3H), 1.39 (s, 3H), 0.89 (s, 9H), 0.02 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (MHz, $CDCl_3$): $\delta = 170.9$, 170.1, 138.1, 137.3, 128.6, 128.4, 128.2, 128.0, 127.7, 127.5, 111.0, 98.2, 95.7, 80.0, 76.0, 75.6, 75.1, 73.9, 72.3, 71.9, 71.3, 71.2, 63.6, 62.9, 52.5, 27.6, 26.0, 25.9, 21.0, 18.1, −3.6, −4.8; FAB MS: *m/z*: calcd for $C_{38}H_{53}N_3O_{12}Si$: 771.3399; found: 771.3386 $[M]^+$.

6-*O*-Acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 3-*O*-benzyl-1,2-*O*-cyclopentylidene-α-D-glucopyranosyluronate (40)

By coupling 11 and 33: Compounds **11** (870 mg, 1.46 mmol) and **33** (425 mg, 1.17 mmol) were coevaporated three times with toluene and dissolved in CH_2Cl_2 (20 mL). Freshly activated powdered 4 Å molecular sieves (500 mg) were added and the mixture was stirred at room temperature for 30 min. The mixture was cooled to −25 °C and *tert*-butyldimethylsilyl trifluoromethanesulfonate (33 μL, 0.146 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred overnight. Triethylamine (3 mL) was added, the mixture was filtered through a pad of Celite and the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 95:5→9:1) afforded **40** (744 mg, 0.93 mmol, 80%) as a colorless foam.

By coupling 10 and 33: Compounds **10** (610 mg, 1.35 mmol) and **33** (402 mg, 1.10 mmol) were coevaporated three times with toluene, dissolved in Et_2O (20 mL) and cooled to 0 °C. To this mixture freshly activated powdered 4 Å molecular sieves (1 g), $SnCl_2$ (260 mg, 1.37 mmol) and $AgClO_4$ (290 mg, 1.40 mmol) were added. The mixture was stirred for 8 h at 0 °C, then warmed to 12 °C over 8 h. The mixture was filtered through a pad of Celite, washed with sat. $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4 and after filtration the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 95:5→9:1) afforded **40** (693 mg, 0.87 mmol, 79%) as a colorless foam. $[\alpha]_D^{24} = +87.5$ ($c = 1.20$, CH_2Cl_2); IR (thin film on NaCl): $\tilde{\nu} = 3025$, 2954, 2849, 2105, 1746, 1455, 1250 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.40–7.27$ (m, 10H), 5.74 (d, $J = 4.0$ Hz, 1H), 5.15 (d, $J = 3.4$ Hz, 1H), 4.87 (d, $J = 11.0$ Hz, 1H), 4.79 (d, $J = 11.0$ Hz, 1H), 4.70 (d, $J = 11.6$ Hz, 1H), 4.67 (d, $J = 11.9$ Hz, 1H), 4.59 (d, $J = 6.7$ Hz, 1H), 4.38 (dd, $J = 2.1$, 11.9 Hz, 1H), 4.26 (dd, $J = 3.1$, 6.7 Hz, 1H), 4.14 (dd, $J = 3.4$, 4.0 Hz, 1H), 4.08–4.04 (m, 2H), 3.89–3.84 (m, 1H), 3.74 (dd, $J = 8.5$, 10.4 Hz, 1H), 3.71 (s, 3H), 3.64 (dd, $J = 9.2$, 8.9 Hz, 1H), 3.24 (dd, $J = 3.7$, 10.4 Hz, 1H), 2.08–2.00 (m, 5H), 1.79–1.62 (m, 6H), 0.89 (s, 9H), 0.02 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 171.0$, 170.2, 138.1, 137.3, 128.7, 128.5, 128.2, 128.0, 127.8, 127.5, 120.6, 98.0, 95.5, 80.0, 75.7, 75.3, 75.2, 74.0, 72.3, 71.4, 71.2, 71.2, 63.6, 62.9, 52.6, 37.0, 36.9, 26.0, 23.8, 23.3, 21.1, 18.1, −3.5, −4.8; FAB MS: *m/z*: calcd for $C_{40}H_{55}N_3O_{12}Si$: 797.3555; found: 797.3578 $[M]^+$.

6-*O*-Acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 3-*O*-benzyl-D-syluronate (41): Compound **39** (1.68 g, 2.18 mmol) was dissolved in dichloroacetic acid (75% aqueous, 20 mL) and stirred at room temperature for 1 h. The reaction mixture was added slowly to sat. $NaHCO_3$ and extracted three times with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and after filtration the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 1:1) afforded **41** (1.29 g, 1.86 mmol, 81%) colorless foam. Compound **40** (1.19 g, 1.49 mmol) was dissolved in dichloroacetic acid (50% aqueous, 15 mL) and stirred at room temperature for 2 h. The reaction mixture was added slowly to sat. $NaHCO_3$ and extracted three times with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and after filtration the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 1:1) afforded **41** (980 mg, 1.34 mmol, 90%) as a colorless foam. FAB MS: *m/z*: calcd for $C_{35}H_{49}N_3O_{12}Si$: 731.3086; found: 731.3107 $[M]^+$.

6-*O*-Acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucopyranosyluronate (42): Compound **20** (946 mg, 1.65 mmol) and **31** (451 mg, 1.33 mmol) were coevaporated three times with toluene and dissolved in CH_2Cl_2 (30 mL). Freshly activated powdered 4 Å molecular sieves (700 mg) were added and the mixture was stirred at room temperature for 1 h. The mixture was cooled to −78 °C and *tert*-butyldimethylsilyl trifluoromethanesulfonate (38 μL, 0.165 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred overnight. Triethylamine (3 mL) was added and the mixture was filtered through a pad of Celite and the solvent was removed under reduced pressure. Flash chromatography (hexanes/EtOAc 8:2) afforded **42** (828 mg, 1.11 mmol, 83%) as a colorless oil. $[\alpha]_D^{24} = +58.0$ ($c = 1.53$, CH_2Cl_2); IR (thin film on NaCl): $\tilde{\nu} = 3029$, 2938, 2017, 1743, 1454 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.41–7.27$ (m, 15H), 5.72 (d, $J = 4.0$ Hz, 1H), 5.14 (d, $J = 3.7$ Hz, 1H), 4.90 (d, $J = 10.7$ Hz, 1H), 4.87 (d, $J = 10.7$ Hz, 1H), 4.86 (d, $J = 11.0$ Hz, 1H), 4.70 (s, 2H), 4.59 (d, $J = 11.0$ Hz, 1H), 4.48 (d, $J = 7.3$ Hz, 1H), 4.30 (dd, $J = 2.4$, 11.9 Hz, 1H), 4.28–4.22 (m, 3H), 4.06 (at, $J = 3.7$ Hz, 1H), 4.00–3.92 (m, 2H), 3.73 (s, 3H), 3.54 (dd, $J = 8.8$, 10.1 Hz, 1H), 3.30 (dd, $J = 3.7$, 10.4 Hz, 1H), 2.05 (s, 3H), 1.62 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 171.4$, 170.7, 138.4, 138.2, 137.9, 129.3, 129.2, 128.8, 128.7, 128.7, 128.6, 128.5, 111.7, 98.3, 96.7, 80.5, 78.5, 77.1, 76.3, 76.1, 75.7, 74.4, 72.8, 72.1, 70.6, 63.9, 63.2, 53.2, 28.0, 26.5, 21.5; FAB MS: *m/z*: calcd for $C_{39}H_{45}N_3O_{12}$: 747.3003; found: 747.3001 $[M]^+$.

6-*O*-Acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 3-*O*-benzyl-1,2-*O*-cyclopentylidene-α-D-glucopyranosyluronate (43): Compound **20** (855 mg, 1.50 mmol) and **33** (436 mg, 1.20 mmol) were coevaporated three times with toluene and dissolved in CH_2Cl_2 (20 mL). Freshly activated powdered 4 Å molecular sieves (250 mg) were added and the mixture was stirred at room temperature for 1 h. The mixture was cooled to −20 °C and *tert*-butyldimethylsilyl trifluoromethanesulfonate (100 μL, 0.44 mmol) was added dropwise. The reaction mixture was stirred for 2.5 h at −20 °C. Triethylamine (3 mL) was added, the mixture was filtered through a pad of Celite and the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 85:15→8:2) afforded **43** (760 mg, 0.98 mmol, 82%) as a colorless oil. $[\alpha]_D^{24} = +62.3$ ($c = 1.07$, CH_2Cl_2); IR (thin film on NaCl): $\tilde{\nu} = 2948$, 2107, 1743, 1454, 1362 cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40–7.27 (m, 15H), 5.69 (d, J = 4.0 Hz, 1H), 5.12 (d, J = 3.7 Hz, 1H), 4.90 (d, J = 10.7 Hz, 1H), 4.87 (d, J = 10.7 Hz, 1H), 4.86 (d, J = 11.3 Hz, 1H), 4.70 (s, 2H), 4.60 (d, J = 11.0 Hz, 1H), 4.48 (d, J = 7.3 Hz, 1H), 4.31 (dd, J = 2.1, 12.2 Hz, 1H), 4.28–4.24 (m, 2H), 4.18 (dd, J = 3.7, 4.0 Hz, 1H), 4.06 (at, J = 3.4 Hz, 1H), 4.01–3.93 (m, 2H), 3.74 (s, 3H), 3.55 (dd, J = 8.8, 10.0 Hz, 1H), 3.29 (dd, J = 3.7, 10.4 Hz, 1H), 2.09–2.03 (m, 5H), 1.79–1.68 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.4, 170.7, 138.4, 138.2, 137.9, 129.3, 129.2, 128.8, 128.7, 128.7, 128.6, 128.5, 121.2, 98.1, 96.4, 80.5, 78.5, 76.8, 76.1, 76.0, 75.7, 74.5, 72.8, 71.6, 70.6, 63.8, 63.2, 53.2, 37.4, 37.3, 24.4, 23.8, 21.5; FAB MS: m/z: calcd for $C_{41}H_{47}N_3O_{12}$: 773.3160; found: 773.3179 $[M]^+$.

6-*O*-Acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-methyl-3-*O*-benzyl-D-glucopyranosyluronate (44): From **42**: Compound **42** (315 mg, 0.42 mmol) was dissolved in dichloroacetic acid (75% aqueous, 4 mL) and stirred at room temperature for 2 h. The reaction mixture was added slowly to sat. $NaHCO_3$ and extracted three times with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and after filtration the solvent was remove under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 1:1) afforded **44** (250 mg, 0.35 mmol, 84%) as a colorless foam. From **43**: Compound **43** (836 mg, 1.08 mmol) was dissolved in dichloroacetic acid (50% aqueous, 12 mL) and stirred at room temperature for 2 h. The reaction mixture was added slowly to sat. $NaHCO_3$ and extracted three times with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and after filtration the solvent was removed under reduced pressure. Flash chromatography (hexanes/EtOAc 1:1) afforded **44** (619 mg, 0.87 mmol, 81%) as a colorless foam. FAB MS: m/z: calcd for $C_{36}H_{41}N_3O_{12}$: 707.2690; found: 707.2678 $[M]^+$.

3,6-Di-*O*-acetyl-2-azido-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 3-*O*-benzyl-1,2-*O*-isopropylidene-α-L-glucopyranosyluronate (45): Compound **14** (215 mg, 0.39 mmol) and **31** (102 mg, 0.30 mmol) were coevaporated three times with toluene and dissolved in CH_2Cl_2 (3 mL). Freshly activated powdered 4 Å molecular sieves (100 mg) were added and the mixture was stirred at room temperature for 1 h. The mixture was cooled to −25 °C and *tert*-butyldimethylsilyl trifluoromethanesulfonate (0.1M in CH_2Cl_2, 300 μL, 0.030 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 30 minutes. Triethylamine (3 mL) was added and the mixture was filtered through a pad of Celite and the solvent was removed under reduced pressure. Flash chromatography (hexanes/EtOAc 4:1) afforded **45** (201 mg, 0.279 mmol, 92%) as a colorless oil. $[\alpha]_D^{24} = +90$ (c = 0.7, $CHCl_3$); IR (thin film on NaCl): $\tilde{\nu}$ = 2932, 2110, 1747, 1372, 1221 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35–7.26 (m, 5H), 5.73 (d, J = 4.0 Hz, 1H), 5.32 (dd, J = 8.5, 10.5 Hz, 1H), 5.19 (d, J = 4.0 Hz, 1H), 4.68–4.66 (A part of AB system, J = 11.5 Hz, 1H), 4.65–4.62 (B part of AB system, J = 11.5 Hz, 1H), 4.55 (d, J = 6.5 Hz, 1H), 4.38–4.35 (A part of ABX, J = 2.0, 12.0 Hz, 1H), 4.22 (dd, J = 4.0, 6.5 Hz, 1H), 4.19 (t, J = 3.0 Hz, 1H), 4.10–4.06 (m, 2H), 3.92–3.88 (m, 1H), 3.70 (t, J = 9.0 Hz, 1H), 3.68 (s, 3H), 2.95 (dd, J = 3.5, 11.0 Hz, 1H), 2.13 (s, 3H), 2.06 (s, 3H), 1.59 (s, 3H), 1.35 (s, 3H), 0.82 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.7, 170.2, 170.0, 137.3, 128.6, 128.2, 128.0, 111.2, 98.1, 95.9, 76.3, 75.7, 74.0, 72.5, 72.3, 71.6, 70.8, 69.4, 62.7, 61.3, 52.5, 27.4, 25.9, 25.7, 21.5, 20.9, −3.96, −4.82; ES MS: m/z: calcd for $C_{33}H_{49}N_3NaO_{13}Si$: 746.2927; found: 746.2901 $[M-Na]^+$.

2-Azido-3,6-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 3-*O*-benzyl-1,2-*O*-isopropylidene-α-L-glucopyranosyluronate (46): Compound **16** (39 mg, 0.06 mmol) and **31** (16 mg, 0.05 mmol) were coevaporated three times with toluene and dissolved in CH_2Cl_2 (0.7 mL). Freshly activated powdered 4 Å molecular sieves (16 mg) were added and the mixture was stirred at room temperature for 1 h. The mixture was cooled to −25 °C and *tert*-butyldimethylsilyl trifluoromethanesulfonate (0.1M in CH_2Cl_2, 48 μL, 0.005 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 30 minutes. Triethylamine was added and the mixture was filtered through a pad of Celite and the solvent was removed under reduced pressure. Flash chromatography (hexanes/EtOAc 6:1) afforded **46** (31 mg, 0.04 mmol, 77%) as a colorless oil. $[\alpha]_D^{24} = +86.5$ (c = 1.1, $CHCl_3$); IR (thin film on NaCl): $\tilde{\nu}$ = 2928, 2105, 1751, 837 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39–7.25 (m, 15H), 5.83 (d, J = 3.5 Hz, 1H), 5.19 (d, J = 3.5 Hz, 1H), 4.89–4.86 (A part of AB system, J = 11.0 Hz, 1H), 4.78–4.76 (B part of AB system, J = 11.0 Hz, 1H), 4.69 (d, J = 5.0 Hz, 1H), 4.66 (s, 2H), 4.58–4.55 (A part of AB system, J = 12.0 Hz, 1H), 4.51–4.49 (B part of AB system, J = 12.0 Hz, 1H), 4.24 (dd, J = 3.5, 5.0 Hz, 1H), 4.20 (t, J = 3.5 Hz, 1H), 4.09 (t, J = 3.0 Hz, 1H), 3.85–3.82 (m, 1H), 3.77–3.71 (m, 2H), 3.67–3.64 (A part of ABX, J = 4.5, 10.5 Hz, 1H), 3.63–3.61 (m, 4H), 3.27 (dd, J = 3.5, 10.0 Hz, 1H), 1.64 (s, 3H), 1.40 (s, 3H), 0.82 (s, 9H), 0.02 (s, 3H), −0.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.2, 138.2, 137.4, 128.7, 128.5, 128.4, 128.2, 128.0, 127.7, 127.8, 127.6, 127.5, 111.1, 98.6, 95.5, 80.2, 75.7, 75.6, 74.8, 73.9, 73.5, 72.7, 72.4, 72.3, 71.0, 68.7, 63.7, 52.4, 27.8, 26.1, 18.2, −3.58, −4.68; ES MS: m/z: calcd for $C_{43}H_{57}N_3NaO_{11}Si$: 842.3654; found: 842.3638 $[M+Na]^+$.

3-*O*-Acetyl-2-azido-6-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 3-*O*-benzyl-1,2-*O*-isopropylidene-α-L-glucopyranosyluronate (47): Compound **17** (49 mg, 0.09 mmol) and **31** (23 mg, 0.07 mmol) were coevaporated three times with toluene and dissolved in CH_2Cl_2 (0.7 mL). Freshly activated powdered 4 Å molecular sieves (23 mg) were added and the mixture was stirred at room temperature for 1 h. The mixture was cooled to −25 °C and *tert*-butyldimethylsilyl trifluoromethanesulfonate (0.1M in CH_2Cl_2, 68 μL, 0.007 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 30 minutes. Triethylamine was added and the mixture was filtered through a pad of Celite and the solvent was removed under reduced pressure. Flash chromatography (hexanes/EtOAc 4:1) afforded **47** (37 mg, 0.05 mmol, 71%) as a colorless oil. $[\alpha]_D^{24} = +93.3$ (c = 1.7, $CHCl_3$); IR (thin film on NaCl): $\tilde{\nu}$ = 2928, 2110, 1751, 1224 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37–7.26 (m, 10H), 5.77 (d, J = 4.0 Hz, 1H), 5.34 (dd, J = 7.5, 10.5, 1H), 5.23 (d, J = 3.5 Hz, 1H), 4.69–4.66 (A part of AB system, J = 11.5 Hz, 1H), 4.66–4.64 (B part of AB system, J = 11.5 Hz, 1H), 4.62 (d, J = 6.5 Hz, 1H), 4.58–4.56 (A part of AB system, J = 12.5 Hz, 1H), 4.53–4.50 (B part of AB system, J = 12.5 Hz, 1H), 4.24 (dd, J = 4.0, 6.0 Hz, 1H), 4.20 (t, J = 3.5 Hz, 1H), 4.10 (t, J = 3.0 Hz, 1H), 3.88–3.80 (m, 2H), 3.73–3.70 (A part of ABX, J = 3.5, 10.5 Hz, 1H), 3.63 (s, 3H), 3.62–3.60 (B part of ABX, J = 2.0, 10.5 Hz, 1H), 2.97 (dd, J = 3.5, 10.5 Hz, 1H), 2.14 (s, 3H), 1.62 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 0.81 (s, 9H), 0.04 (s, 3H, CH_3), 0.03 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.3, 170.1, 138.1, 137.4, 128.7, 128.5, 128.2, 128.0, 127.8, 127.7, 111.2, 98.4, 95.8, 76.3, 75.8, 73.9, 73.6, 72.9, 72.3, 71.9, 69.1, 68.2, 61.4, 52.5, 27.6, 26.1, 25.8, 21.6, 18.2, −4.05, −4.66; ES MS: m/z: calcd for $C_{38}H_{53}N_3NaO_{12}Si$: 794.3281; found: 794.3275 $[M+Na]^+$.

6-*O*-Acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 3-*O*-benzyl-1,2-*O*-isopropylidene-α-L-idopyranosyluronate (48): A mixture of **11** (1.38 g, 2.32 mmol) and **35** (627 mg, 1.9 mmol) was coevaporated three times with toluene and dried under vacuum for 1 h. The mixture was dissolved in CH_2Cl_2 (20 mL) and was stirred for 30 min at room temperature under argon in the presence of freshly activated powdered 4 Å molecular sieves (800 mg). After cooling the mixture to −30 °C, *tert*-butyldimethylsilyl trifluoromethanesulfonate (1M in CH_2Cl_2, 230 μL, 0.23 mmol) was added dropwise. The mixture was warmed to room temperature over 1 h. Triethylamine (4 mL) was added, the mixture was filtered through a pad of Celite and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (toluene/EtOAc 95:5→92:8) to yield **48** (1.30 g, 1.68 mmol, 91%) as a colorless glass. $[\alpha]_D^{24} = +93.3$ (c = 1, $CHCl_3$); IR (thin film on NaCl): $\tilde{\nu}$ = 2890, 2100, 1740, 1020 cm − 1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38–1.20 (m, 10H), 5.28 (d, J = 2.4 Hz, 1H), 4.93 (d, J = 3.0 Hz, 1H), 4.76 (d, J = 11.0 Hz, 1H), 4.65 (d, J = 11.0 Hz, 1H), 4.61 (s, 2H), 4.41–4.36 (m, 2H), 4.13 (t, J = 2.1 Hz, 1H), 3.99 (s, 1H), 3.95 (dd, J = 3.0, 12.2 Hz, 1H), 3.91 (m, 2H), 3.74–3.71 (m, 1H), 3.71 (s, 3H), 3.61–3.59 (m, 2H), 3.30 (dd, J = 3.3, 9.5 Hz, 1H), 2.08 (s, 3H), 1.98 (s, 3H), 1.57 (s, 3H), 1.33 (s, 3H), 0.78 (s, 9H), −0.10 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.8, 169.0, 138.2, 137.1, 128.8, 128.4, 128.0, 127.9, 127.7, 127.6, 112.2, 98.1, 97.1, 80.1, 97.3, 75.4, 75.2, 73.5, 72.9, 72.8, 71.5, 71.3, 70.6, 68.9, 64.6, 62.5, 52.5, 28.3, 26.3, 26.0, 21.1, 18.1, −3.6, −5.0; FAB MS: m/z: calcd for $C_{38}H_{53}N_3O_{12}Si$: 771.3399; found: 771.3415 $[M]^+$.

3,6-Di-*O*-acetyl-2-azido-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 3-*O*-benzyl-1,2-*O*-isopropylidene-β-L-idopyranosyluronate (49): A mixture of **14** (500 mg, 0.91 mmol) and **35** (241 mg, 0.71 mmol) was coevaporated three times with toluene and dried under vacuum for 1 h. The mixture was dissolved in CH_2Cl_2 (15 mL) and was stirred for 30 min at room temperature under argon in the presence of freshly activated powdered 4 Å molecular sieves (400 mg). After cooling the mixture to −30 °C, *tert*-butyldimethylsilyl trifluoromethanesulfonate (0.1M in CH_2Cl_2, 1 mL, 0.1 mmol) was added dropwise. The mixture was warmed to 0 °C over 1 h. Triethylamine (1.8 mL) was added, the mixture was filtered through a pad of Celite and the solvent was removed under

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reduced pressure. The residue was purified by silica gel column chromatography (toluene/EtOAc 95:5 → 92:8) to yield **49** (463 mg, 0.64 mmol, 90 %) as a colorless glass. $[\alpha]_D^{24} = +87.4$ ($c = 1.00$, $CHCl_3$); IR (thin film on NaCl): $\tilde{\nu} = 2880, 2086, 1731, 1440, 1054\ cm^{-1}$; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.38-7.32$ (m, 5H), 5.34 (d, $J = 2.1$ Hz, 1H), 5.32–5.36 (dd, 1H), 4.93 (d, $J = 3.0$ Hz, 1H), 4.70 (d, $J = 11.6$ Hz, 1H), 4.67 (d, $J = 11.6$ Hz, 1H), 4.50 (dd, $J = 2.1$, 12.5 Hz, 1H), 4.42 (d, $J = 1.5$ Hz, 1H), 4.27 (t, $J = 2.1$ Hz, 1H), 4.06–4.02 (m, 2H), 3.98–3.94 (m, 2H), 3.80–3.74 (m, 1H), 3.79 (s, 3H), 3.17 (dd, $J = 10.7$, 3.4 Hz, 1H), 2.08 (s, 3H), 2.00 (s, 3H), 1.64 (s, 3H), 1.39 (s, 3H), 0.81 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 170.6$, 169.8, 169.1, 137.3, 128.8, 128.4, 128.1, 112.5, 99.1, 97.3, 75.7, 74.8, 73.9, 73.0, 72.8, 71.3, 71.3, 68.9, 62.4, 62.3, 52.7, 28.1, 26.2, 25.7, 21.5, 21.1, 18.0, −3.9, −4.9; FAB MS: *m*/*z*: calcd for $C_{33}H_{49}N_3O_{13}Si$: 723.3035; found: 723.3058 $[M]^+$.

3,6-Di-*O*-acetyl-2-azido-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1 → 4)-methyl 3-*O*-benzyl-1,2-*O*-cyclopentylidene-β-L-idopyranosyluronate (50): A mixture of **14** (200 mg, 0.36 mmol) and **37** (95 mg, 0.28 mmol) was coevaporated three times with toluene and dried under vacuum for 1 h. The mixture was dissolved in CH_2Cl_2 (5 mL) and was stirred for 30 min at room temperature under argon in the presence of freshly activated powdered 4 Å molecular sieves (150 mg). After cooling the mixture to −30 °C, *tert*-butyldimethylsilyl trifluoromethanesulfonate (0.1 M in dry CH_2Cl_2, 0.4 mL, 0.04 mmol) was added dropwise. The mixture was warmed to 0 °C over 1 h. Triethylamine (0.7 mL) was added, the mixture was filtered through a pad of Celite and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (toluene/EtOAc 96:3 → 90:10) to yield **50** (217 mg, 0.29 mmol, 88 %) as a colorless glass. $[\alpha]_D^{24} = +75.6$ ($c = 1.00$, CH_2Cl_2); IR (thin film on NaCl): $\tilde{\nu} = 2955, 2858, 2109, 1744, 1455\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.38-7.30$ (m, 5H), 5.34–5.29 (m, 2H), 4.68 (t, $J = 12.0$ Hz, 2H), 4.51 (m, 1H), 4.46 (d, $J = 1.5$ Hz 1H), 4.28 (dd, $J = 2.1$, 2.9 Hz, 1H), 4.13 (t, 1H), 4.07–4.02 (m, 2H), 3.87 (t, 1H), 3.80–3.74 (m, 1H), 3.77 (s, 3H), 3.07 (dd, $J = 3.4$, 10.6 Hz, 1H), 2.13 (s, 3H), 2.06 (s, 3H), 2.09–2.04 (m, 2H), 1.78–1.63 (m, 6H), 0.82 (s, 9H), 0.04 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 170.6$, 169.8, 169.1, 137.3, 128.7, 128.3, 121.7, 98.9, 96.9, 76.9, 75.8, 74.4, 74.1, 73.0, 72.7, 71.1, 71.0, 68.9, 62.3, 62.1, 52.6, 37.6, 36.9, 25.7, 23.5, 21.5, 21.0, 18.0, −3.9, −4.9; FAB MS: *m*/*z*: calcd for $C_{35}H_{51}N_3O_{13}Si$: 749.3191; found: 749.3197 $[M]^+$.

3,6-Di-*O*-benzyl-2-azido-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1 → 4)-methyl 3-*O*-benzyl-1,2-*O*-isopropylidene-β-L-idopyranosyluronate (51): A mixture of **16** (50 mg, 0.08 mmol) and **35** (25 mg, 0.074 mmol) was coevaporated three times with toluene and dried under vacuum for 1 h. The mixture was dissolved in CH_2Cl_2 (1 mL) and was stirred for 30 min at room temperature under argon in the presence of freshly activated powdered 4 Å molecular sieves (20 mg). After cooling the mixture to −30 °C, *tert*-butyldimethylsilyl trifluoromethanesulfonate (0.1 M in CH_2Cl_2, 80 μL, 0.08 mmol) was added dropwise. The mixture was warmed to room temperature over 1 h. Triethylamine was added, the mixture was filtered through a pad of Celite and the solvent was removed under reduce pressure. The residue was purified by silica gel column chromatography (toluene/EtOAc 95:5 → 92:8) to yield **51** (55 mg, 0.067 mmol, 92 %) as a colorless glass. $[\alpha]_D^{24} = +91$ ($c = 1$, $CHCl_3$); IR (thin film on NaCl): $\tilde{\nu} = 2935, 2110, 1766, 1017\ cm^{-1}$; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.39-7.28$ (m, 15H), 5.35 (d, $J = 2.4$ Hz, 1H), 4.98 (d, $J = 3.4$ Hz, 1H), 4.84 (d, $J = 11.3$ Hz, 1H), 4.73 (d, $J = 11.3$ Hz, 1H), 4.68 (s, 2H), 4.59 (d, $J = 11.9$ Hz, 1H), 4.46 (d, $J = 11.6$ Hz, 1H), 4.45 (d, $J = 1.5$ Hz, 1H), 4.27 (t, $J = 2.4$ Hz, 1H), 4.11 (s, 1H), 3.98 (s, 1H), 3.80–3.73 (m, 2H), 3.71 (s, 3H), 3.80–3.63 (m, 3H), 3.39 (dd, $J = 10.4$, 3.4 Hz, 1H), 1.65 (s, 3H), 1.41 (s, 3H), 0.84 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 169.1$, 138.3, 138.2, 137.3, 128.8, 128.5, 128.4, 128.1, 127.9, 127.7, 127.6, 127.5, 112.3, 97.9, 97.1, 80.3, 75.5, 74.9, 73.4, 73.0, 72.9, 72.8, 72.4, 71.3, 70.5, 68.1, 64.4, 52.4, 28.2, 26.3, 26.1, 18.1, −3.6, −4.8; FAB MS: *m*/*z*: calcd for $C_{33}H_{49}N_3NaO_{13}Si$: 842.3654; found: 842.3696 $[M+Na]^+$.

6-*O*-Benzyl-2-azido-3-*O*-acetyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1 → 4)-methyl 3-*O*-benzyl-1,2-*O*-isopropylidene-α-L-idopyranosyluronate (52): A mixture of **17** (50 mg, 0.084 mmol) and **35** (25 mg, 0.074 mmol) was coevaporated three times with toluene and dried under vacuum for 1 h. The mixture was dissolved in CH_2Cl_2 (1 mL) and was stirred for 30 min at room temperature under argon in the presence of freshly activated powdered 4 Å molecular sieves (20 mg). After cooling the mixture to −30 °C, *tert*-butyldimethylsilyl trifluoromethanesulfonate (0.1 M in CH_2Cl_2, 84 μL, 0.084 mmol) was added dropwise. The mixture was warmed to room temperature over 1 h. Triethylamine was added, the mixture was filtered through a pad of Celite and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (toluene/EtOAc 95:5 → 92:8) to yield **52** (50 mg, 0.065 mmol, 88 %) as a colorless glass. $[\alpha]_D^{24} = +85$ ($c = 1.0$, $CHCl_3$); IR (thin film on NaCl): $\tilde{\nu} = 2940, 2106, 1740, 1766, 1017\ cm^{-1}$; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.38-7.26$ (m, 10H), 5.32 (m, 2H), 4.97 (d, $J = 3.0$ Hz, 1H), 4.69 (d, $J = 11.6$ Hz, 1H), 4.65 (d, $J = 11.9$ Hz, 1H), 4.60 (d, $J = 12.2$ Hz, 1H), 4.46 (d, $J = 11.9$ Hz, 1H), 4.42 (d, $J = 1.5$ Hz, 1H), 4.29 (t, $J = 2.7$ Hz, 1H), 4.07 (s, 1H), 3.98 (s, 1H), 3.91–3.86 (m, 2H), 3.71 (dd, $J = 2.4$, 11.0 Hz, 1H), 3.68 (s, 3H), 3.63 (dd, $J = 1.8$, 10.4 Hz, 1H), 3.18 (dd, $J = 10.4$, 3.0 Hz, 1H), 2.12 (s, 3H), 1.65 (s, 3H), 1.39 (s, 3H), 0.81 (s, 9H), −0.04 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 170.0$, 169.0, 138.2, 137.3, 128.7, 128.5, 128.4, 128.3, 128.1, 127.9, 112.5, 99.0, 97.3, 75.8, 74.4, 73.7, 73.4, 73.0, 72.9, 72.8, 71.2, 68.7, 67.7, 62.4, 52.4, 28.1, 26.2, 25.8, 21.6, 18.0, −4.1, −4.8; FAB MS: *m*/*z*: calcd for $C_{38}H_{53}N_3NaO_{12}Si$: 794.3291; found: 794.3298 $[M+Na]^+$.

6-*O*-Acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1 → 4)-methyl 3-*O*-benzyl-L-idopyranosyluronate (53): A solution of **48** (1.20 g, 1.55 mmol) in dichloroacetic acid (40 mL, 60 % aq) was stirred at room temperature for 3 h, diluted with water and neutralized with $NaHCO_3$ (24 g). The aqueous phase was extracted three times with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$. After filtration the solvent was removed under reduced pressure to afford **53** (1.05 g, 1.4 mmol, 92 %) as an essentially pure white solid. Compound **53** can be further purified by silica gel column chromatography (hexanes/EtOAc 70:30). FAB MS: *m*/*z*: calcd for $C_{35}H_{49}N_3O_{12}Si$: 731.3086; found: 731.3002 $[M]^+$.

3,6-Di-*O*-acetyl-2-azido-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1 → 4)-methyl 3-*O*-benzyl-L-idopyranosyluronate (54)

From 49: A solution of **49** (770 mg, 1.06 mmol) in dichloroacetic acid (10 mL, 60 % aq) was stirred at room temperature for 3 h, diluted with water and neutralized with $NaHCO_3$ (7 g). The aqueous phase was extracted three times with CH_2Cl_2 and the combined organic phases were dried over $MgSO_4$. After filtration the solvent was removed under reduced pressure to afford **54** (647 mg, 0.95 mmol, 89 %) as a white solid. Compound **54** can be further purified by silica gel column chromatography (hexanes/EtOAc 70:30). FAB MS: *m*/*z*: calcd for $C_{30}H_{45}N_3O_{13}Si$: 683.2722; found: 683.2743 $[M]^+$.

From 50: A solution of **50** (200 mg, 0.27 mmol) in dichloroacetic acid (3 mL, 60 % aq) was stirred at room temperature for 3 h, diluted with water and neutralized with $NaHCO_3$ (7 g). The aqueous phase was washed three times with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$. After filtration the solvent was removed under reduced pressure to afford **54** (160 mg, 0.23 mmol, 88 %) as an essentially pure white solid.

6-*O*-Acetyl-2-azido 3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1 → 4)-methyl-3-*O*-benzyl-1,2-*O*-monochloroacetyl-α/β-D-glucopyranosyluronate (55): Pyridine (2.1 mL, 24 mmol), monochloroacetic anhydride (3.0 g, 9.00 mmol) and DMAP (19 mg, 0.157 mmol) were added to a solution of **41** (1.3 g, 1.57 mmol) in CH_2Cl_2 (21 mL). The solution was stirred at room temperature for 6 h, water was added and the mixture was stirred for one additional hour. The organic phase was washed with sat. $NaHCO_3$, water and aqueous HCl (10 %), dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (hexanes/EtOAc 90:20) to yield **55** (1.5 g, 1.7 mmol, 96 %) as a colorless syrup. FAB MS: *m*/*z*: calcd for $C_{39}H_{51}Cl_2N_3O_{14}Si$: 883.2517; found: 883.2506 $[M]^+$.

6-*O*-Acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1 → 4)-methyl 3-*O*-benzyl-1,2-*O*-monochloroacetyl-α/β-D-glucopyranosyluronate (56): Pyridine (0.65 mL, 7.4 mmol), monochloroacetic anhydride (820 mg, 2.5 mmol) and DMAP (7 mg, 0.06 mmol) were added to a solution of **44** (400 mg, 0.6 mmol) in CH_2Cl_2 (6.5 mL). The solution was stirred at room temperature for 6 h, water was added and the mixture was stirred for one additional hour. The organic phase was washed with saturated solution of $NaHCO_3$, water and 10 % HCl, dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (hexanes/EtOAc 90:20) to yield **56** (452 mg, 0.53 mmol 93 %) as a colorless syrup. FAB MS: *m*/*z*: calcd for $C_{40}H_{43}Cl_2N_3O_{14}$: 859.2122; found: 859.2113 $[M]^+$.

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6-*O*-Acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 3-*O*-benzyl-2-*O*-monochloroacetyl-α-D-glucopyranosyluronate trichloroacetimidate (57)

From 55: Benzylamine (70 μL, 0.63 mmol) was added in three portions, every 2 h, to a solution of **55** (1 g, 1.2 mmol) Et_2O (40 mL) at 0 °C and kept overnight at −20 °C. The mixture was diluted with CH_2Cl_2, filtered and washed with aqueous HCl (10%). The organic phase was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 90:10→80:20) afforded 6-*O*-acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 3-*O*-benzyl-2-*O*-monochloroacetyl-D-glucopyranosyluronate (704 mg, 0.87 mmol, 75%) as a white solid. FAB MS: *m*/*z*: calcd for $C_{37}H_{50}ClN_3O_{13}Si$: 807.2801; found: 807.2796 $[M]^+$.

From 61: A mixture of tetrabutylammonium fluoride (1.0 M in THF, 0.6 mL) and glacial acetic acid (55 μL, 0.9 mmol) was added dropwise to a solution of **61** (539 mg, 0.58 mmol) in THF (6 mL) under nitrogen at 0 °C. The reaction mixture was warmed to room temperature, stirred for 1.5 h and quenched with brine. After dilution with CH_2Cl_2, the two phases were separated. The organic phase was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude material was purified by silica gel column chromatography (hexane/EtOAc 90:10→80:20) to yield 6-*O*-acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 3-*O*-benzyl-2-*O*-monochloroacetyl-α/β-D-glucopyranosyluronate (198 mg, 43%) as a white solid.

A solution of 6-*O*-acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 3-*O*-benzyl-2-*O*-monochloroacetyl-D-glucopyranosyluronate (540 mg, 0.7 mmol) and trichloroacetonitrile (2 mL, 19.2 mmol) in CH_2Cl_2 (14 mL) containing freshly activated 4 Å molecular sieves (100 mg), was stirred 30 minutes at room temperature. After cooling to 0 °C, DBU (45 μL, 0.3 mmol) was added. The mixture was allowed to reach room temperature after 1 h the mixture was filtered through a pad of Celite and concentrated. The residue was purified by silica gel column chromatography (hexanes/EtOAc 85:15) to yield **57** (546 mg, 0.57 mmol, 85%) as a white solid. $[\alpha]_D^{24} = +81.5$ ($c = 1.00$, $CHCl_3$); IR (thin film on NaCl): $\tilde{\nu} = 2930, 2106, 1745, 1678, 1252, 1029\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.69$ (s, 1H), 7.36–7.26 (m, 10H), 6.56 (d, $J = 3.2$ Hz), 5.60 (d, $J = 3.6$ Hz, 1H), 5.14–5.19 (m, 1H), 4.96–4.78 (m, 4H), 4.49 (d, 1H), 4.35 (dd, $J = 11.8$ Hz, 1H), 4.28–4.25 (m, 2H), 4.04 (dd, $J = 3.8, 12.1$ Hz, 1H), 3.99 (d, $J = 9.5$ Hz, 1H), 3.84–3.76 (m, 2H), 3.79 (s, 3H), 3.72–3.61 (m, 2H), 3.50 (m, 1H), 3.26 (dd, $J = 3.6, 10.2$ Hz, 1H), 2.10 (s, 3H), 0.88 (s, 9H), −0.01 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 171.0, 168.5, 166.5, 160.8, 138.0, 137.9, 128.8, 128.5, 128.1, 127.8, 127.5, 127.4, 98.2, 92.9, 80.1, 79.6, 75.5, 75.3, 75.0, 74.3, 72.6, 71.3, 70.9, 63.7, 62.5, 53.1, 40.3, 26.0, 21.1, 18.2, −3.5, −4.8$; FAB MS: *m*/*z*: calcd for $C_{39}H_{50}Cl_4N_4O_{13}Si$: 950.1898; found: 950.1892 $[M]^+$.

6-*O*-Acetyl-2-azido 3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl-3-*O*-benzyl-2-*O*-monochloroacetyl-α-D-glucopyranosyluronate trichloroacetimidate (58): Benzylamine (70 μL, 0.63 mmol) was added in three portions, every 2 h, to a solution of **56** (400 mg, 0.46 mmol) in Et_2O (25 mL) at 0 °C and kept overnight at −20 °C. The mixture was diluted with CH_2Cl_2, filtered and washed with aqueous HCl (10%). The organic phase was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 90:10→80:20) afforded 6-*O*-acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 3-*O*-benzyl-2-*O*-monochloroacetyl-D-glucopyranosyluronate (277 mg, 0.35 mmol, 76%) as a white solid. FAB MS: *m*/*z*: calcd for $C_{38}H_{42}ClN_3O_{13}Si$: 783.2406; found: 783.2400 $[M]^+$.

A solution of 6-*O*-acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 3-*O*-benzyl-2-*O*-monochloroacetyl-D-glucopyranosyluronate (226 mg, 0.292 mmol) and trichloroacetonitrile (0.790 mL, 7.6 mmol) in CH_2Cl_2 (7 mL) containing freshly activated 4 Å molecular sieves (100 mg), was stirred 30 minutes at room temperature. After cooling to 0 °C, DBU (5 μL, 0.03 mmol) was added. The mixture was allowed to reach room temperature and after 1 h it was filtered through a pad of Celite and concentrated. The residue was purified by silica gel column chromatography (hexanes/EtOAc 85:15) to yield **58** (240 mg, 0.26 mmol, 90%) as a white solid. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 8.70$ (s, 1H), 7.38–7.27 (m, 15H), 6.56 (d, $J = 3.4$ Hz, 1H), 5.53 (d, $J = 3.7$ Hz, 1H), 5.17–5.14 (m, 1H), 4.99–4.78 (m, 5H), 4.46–4.42 (m, 2H), 4.28–4.19 (m, 4H), 3.97–3.90 (m, 1H), 3.84–3.70 (m, 2H), 3.77 (s, 3H), 3.62–3.49 (m, 2H), 3.32 (dd, $J = 3.8, 10.4$ Hz, 1H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 170.8, 168.4, 166.5, 160.7, 137.9, 137.8, 137.7, 137.6, 129.0, 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.5, 98.4, 92.9, 90.7, 80.1, 79.3, 77.6, 77.5, 75.7, 75.6, 75.2, 75.1, 73.5, 72.6, 70.1, 63.3, 62.3, 53.2, 40.3, 21.0$; FAB MS: *m*/*z*: calcd for $C_{40}H_{42}Cl_4N_4O_{13}Si$: 926.1502; found: 926.1514 $[M]^+$.

***tert*-Butyldimethylsilyl (6-*O*-acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-2-*O*-levulinoyl-β-D-glucopyranosyluronate (59)**: Compound **41** (1.12 g, 1.53 mmol) and imidazole (208 mg, 3.05 mmol) were dissolved in CH_2Cl_2 (10 mL) and cooled to −15 °C. *tert*-Butyldimethylsilylchloride (253 mg, 1.68 mmol) was added to the mixture and stirring was continued at −15 °C. After 5 h *tert*-butyldimethylsilylchloride (125 mg, 0.83 mmol) was added and after 6 h imidazole (100 mg, 1.47 mmol) and *tert*-butyldimethylsilylchloride (253 mg, 1.68 mmol) were added. After 18 h one additional portion of *tert*-butyldimethylsilylchloride (70 mg, 0.46 mmol) was added. After 40 h, water was added and the mixture was warmed to room temperature. After dilution with EtOAc the mixture was washed with sat. $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4 and after filtration the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 9:1→8:2) afforded *tert*-butyldimethylsilyl (6-*O*-acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-β-D-glucopyranosyluronate (1.08 g, 1.28 mmol, 84%) as a colorless foam. $[\alpha]_D^{24} = +65.9$ ($c = 1.55$, CH_2Cl_2); IR (thin film on NaCl): $\tilde{\nu} = 3475, 3031, 2953, 2857, 2106, 1747, 1472, 1254\ cm^{-1}$; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.41–7.27$ (m, 10H), 5.64 (d, $J = 3.7$ Hz, 1H), 5.07 (d, $J = 11.0$ Hz, 1H), 4.89 (d, $J = 11.0$ Hz, 1H), 4.83 (d, $J = 11.0$ Hz, 1H), 4.81 (d, $J = 11.0$ Hz, 1H), 4.59 (d, $J = 7.3$ Hz, 1H), 4.35 (dd, $J = 2.1, 11.9$ Hz, 1H), 4.14 (dd, $J = 8.8, 9.5$ Hz, 1H), 4.07 (dd, $J = 3.7, 12.2$ Hz, 1H), 3.99 (d, $J = 9.8$ Hz, 1H), 3.79 (s, 3H), 3.76 (at, $J = 8.8$ Hz, 1H), 3.69–3.63 (m, 2H), 3.57 (ddd, $J = 9.5, 9.2, 2.1$ Hz, 1H), 3.52–3.49 (m, 1H), 3.28–3.22 (m, 1H), 2.31 (d, $J = 2.1$ Hz, 1H), 2.10 (s, 3H), 0.92 (s, 9H), 0.89 (s, 9H), 0.15 (s, 6H), 0.00 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 171.0, 168.8, 138.5, 138.1, 128.6, 128.5, 127.9, 127.8, 127.7, 127.5, 98.0, 97.7, 83.9, 80.2, 76.6, 75.2, 74.9, 74.8, 74.7, 71.0, 70.8, 63.8, 62.6, 52.8, 26.0, 25.9, 21.1, 18.2, 18.1, −3.5, −4.1, −4.9, −5.0$; FAB MS: *m*/*z*: calcd for $C_{41}H_{63}N_3O_{12}Si_2C_{41}H_{63}N_3O_{12}Si_2$: 845.3950; found: 845.3925 $[M]^+$.

tert-Butyldimethylsilyl (6-*O*-acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-β-D-glucopyranosyluronate (998 mg, 1.18 mmol) and DMAP (432 mg, 3.54 mmol) were dissolved in CH_2Cl_2 (10 mL) and a solution of levulinic anhydride (500 mg, 2.34 mmol) in CH_2Cl_2 (5 mL) was added. The reaction mixture was stirred for 2 h at room temperature and concentrated. Flash chromatography on silica gel (hexanes/EtOAc 8:2) afforded **59** (1.08 g, 1.14 mmol, 97%) as a colorless foam. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.39–7.24$ (m, 10H), 5.53 (d, $J = 3.6$ Hz, 1H), 5.04 (dd, $J = 7.3, 8.8$ Hz, 1H), 4.90–4.73 (m, 5H), 4.37 (dd $J = 1.8, 11.9$ Hz, 1H), 4.26 (at, $J = 9.2, 9.0$ Hz, 1H), 4.07–4.00 (m, 2H), 3.86 (dd, $J = 8.8, 8.7$ Hz, 1H), 3.79 (s, 3H), 3.68–3.61 (m, 2H), 3.55–3.52 (m, 1H), 3.25 (dd, $J = 3.7, 9.9$ Hz, 1H), 2.68–2.63 (m, 2H), 2.53–2.48 (m, 2H), 2.12 (s, 3H), 2.08 (s, 3H), 0.89 (s, 9H), 0.87 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H), 0.00 (s, 3H), −0.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 206.0, 171.2, 170.8, 168.5, 138.0, 137.9, 128.5, 128.4, 127.8, 127.7, 127.6, 127.4, 97.5, 96.1, 82.5, 80.2, 75.2, 75.1, 74.7, 74.5, 74.1, 71.1, 70.8, 63.8, 62.5, 52.7, 37.8, 29.9, 28.0, 26.0, 25.6, 21.0, 18.1, 17.9, −3.6, −4.2, −5.0, −5.2$; FAB MS: *m*/*z*: calcd for $C_{46}H_{69}N_3O_{14}Si_2$: 943.4318; found: 943.4332 $[M]^+$.

***tert*-Butyldimethylsilyl (6-*O*-acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-methyl 2-*O*-allyloxycarbonyl-3-*O*-benzyl-β-D-glucopyranosyluronate (60)**: *tert*-Butyldimethylsilyl (6-*O*-acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-β-D-glucopyranosyluronate (for the synthesis see the procedure to prepare compound **59**) (350 mg, 0.414 mmol) and DMAP (1.01 g, 8.28 mmol) were dissolved in CH_2Cl_2 (10 mL) and cooled to −70 °C. Allyloxycarbonylchloride (800 μL, 7.54 mmol) was added in three equal portions every 2 h. After the addition was complete the mixture was warmed to room temperature and stirred overnight. The mixture was poured into EtOAc and washed with 1N HCl, brine and sat. $NaHCO_3$. The organic layer was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 9:1→85:15) afforded **60** (347 mg, 0.373 mmol, 90%) as a colorless oil. $[\alpha]_D^{24} = +82.6$ ($c = 1.04$, CH_2Cl_2); IR

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(thin film on NaCl): $\tilde{\nu}$ = 3037, 2929, 2857, 2106, 1758, 1454, 1252 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39–7.26 (m, 10H), 5.91–5.82 (m, 1H), 5.55 (d, J = 3.7 Hz, 1H), 5.35–5.30 (m, 1H), 5.25–5.22 (m, 1H), 4.89–4.71 (m, 6H), 4.62–4.53 (m, 2H), 4.34 (dd, J = 2.1, 11.9 Hz, 1H), 4.22 (dd, J = 9.5, 9.2 Hz, 1H), 4.05 (dd, J = 3.7, 12.2 Hz, 1H), 3.99 (d, J = 9.8 Hz, 1H), 3.85 (d, J = 9.2 Hz, 1H), 3.80 (s, 3H), 3.68–3.61 (m, 2H), 3.52–3.49 (m, 1H), 3.29–3.25 (m, 1H), 2.10 (s, 3H), 0.89 (s, 9H), 0.87 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H), 0.00 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.0, 168.5, 154.1, 138.0, 137.8, 131.4, 128.6, 128.5, 127.9, 127.8, 127.7, 127.5, 119.6, 97.8, 96.1, 82.6, 80.2, 79.1, 75.3, 75.0, 74.8, 74.6, 71.1, 70.8, 69.0, 63.9, 62.5, 52.9, 26.0, 25.6, 21.1, 18.1, 18.0, −3.5, −4.1, −4.9, −5.3; FAB MS: m/z: calcd for $C_{45}H_{67}N_3O_{14}Si_2$: 929.4162; found: 929.4122 $[M]^+$.

***tert*-Butyldimethylsilyl (6-*O*-acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-2-*O*-monochloroacetyl-β-D-glucopyranosyluronate (61)**: Pyridine (0.5 mL, 6 mmol), monochloroacetic anhydride (360 mg, 1.00 mmol) and DMAP (9 mg, 0.05 mmol) were added to a solution of *tert*-butyldimethylsilyl (6-*O*-acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-methyl-3-*O*-benzyl-β-D-glucopyranosyluronate (see the procedure to prepare **59**) (439 mg, 0.52 mmol) in CH_2Cl_2 (5 mL). The solution was stirred at room temperature for 3 h, water was added and the mixture was stirred for one additional hour. The organic phase was washed with sat. $NaHCO_3$, water and aqueous HCl (10%), dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (hexanes/EtOAc 90:20) to yield **61** (470 mg, 0.51 mmol, 98%) as a colorless syrup. $[\alpha]_D^{24}$ = +30.1 (c = 1.00, $CHCl_3$); IR (thin film on NaCl): $\tilde{\nu}$ = 2932, 2107, 1745, 1254, 1029, 839 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37–7.28 (m, 10H), 5.50 (d, J = 3.4 Hz, 1H), 5.05 (dd, J = 7.9, 9.1 Hz), 4.74 (d, J = 7.3 Hz), 4.86 (d, J = 11.0 Hz, 2H), 4.79 (d, J = 11.3 Hz, 1H), 4.68 (d, J = 11.3 Hz, 1H), 4.35 (dd, J = 1.5, 11.9 Hz, 1H), 4.29–4.23 (m, 1H), 4.04 (dd, J = 3.7, 12.2 Hz, 1H), 3.99 (d, J = 9.5 Hz, 1H), 3.89–3.83 (m, 2H), 3.79 (s, 3H), 3.78 (d, J = 14.9 Hz, 1H), 3.60–3.67 (m, 2H), 3.53-3.51 (m, 1H), 3.28 (dd, J = 3.0, 9.2 Hz, 1H), 2.10 (s, 3H), 0.86 (s, 9H), 0.85 (s, 9H), 0.10 (s, 3H), 0.82 (s, 3H), −0.01 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.0, 168.4, 165.8, 138.0, 137.8, 128.7, 128.5, 128.0, 127.8, 127.7, 127.5, 97.8, 96.0, 82.6, 80.2, 76.4, 75.3, 75.2, 74.7, 74.6, 71.3, 70.8, 63.9, 62.5, 52.9, 26.1, 25.6, 21.1, 18.2, 17.9, −3.5, −4.1, −4.9, −5.1; FAB MS: m/z: calcd for $C_{43}H_{64}ClN_3O_{13}Si$: 921.3666; found: 921.366 $[M]^+$.

***tert*-Butyldimethylsilyl (6-*O*-acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-methyl-3-*O*-benzyl-2-*O*-levulinyl-β-D-glucopyranosyluronate (62)**: Compound **44** (813 mg, 1.15 mmol) and imidazole (310 mg, 4.55 mmol) were dissolved in CH_2Cl_2 (10 mL) and cooled to −15 °C. To this mixture *tert*-butyldimethylsilylchloride (241 mg, 1.60 mmol) was added and stirring was continued at −15 °C. After 5 h *tert*-butyldimethylsilylchloride (50 mg, 0.33 mmol) was added followed after 16 h by another portion of *tert*-butyldimethylsilylchloride (100 mg, 0.66 mmol). After 40 h, water was added and the mixture was warmed to room temperature. After dilution with EtOAc the mixture was washed with sat. $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4 and after filtration the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 9:1→8:2) afforded *tert*-butyldimethylsilyl (6-*O*-acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-β-D-glucopyranosyluronate (752 mg, 0.92 mmol, 80%) as a colorless foam. $[\alpha]_D^{24}$ = +26.2 (c = 1.02, CH_2Cl_2); IR (thin film on NaCl): $\tilde{\nu}$ = 3376, 3049, 2919, 2861, 2107, 1744, 1454, 1362, 1252 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42–7.26 (m, 15H), 5.60 (d, J = 4.0 Hz, 1H), 5.08 (d, J = 11.0 Hz, 1H), 4.92–4.89 (m, 2H), 4.86 (d, J = 10.7 Hz, 1H), 4.84 (d, J = 11.0 Hz, 1H), 4.58 (d, J = 7.3 Hz, 1H), 4.57 (d, J = 10.7 Hz, 1H), 4.27–4.25 (m, 2H), 4.14 (dd, J = 8.9, 9.5 Hz, 1H), 3.96 (d, J = 9.8 Hz, 1H), 3.91 (dd, J = 8.9, 10.4 Hz, 1H), 3.77 (s, 3H), 3.73 (dd, J = 9.2, 8.9 Hz, 1H), 3.65–3.61 (m, 1H), 3.59–3.52 (m, 2H), 3.30 (dd, J = 4.0, 10.4 Hz, 1H), 2.33 (d, J = 2.4 Hz, 1H), 2.04 (s, 3H), 0.93 (s, 9H), 0.16 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.9, 168.6, 138.6, 137.8, 137.7, 128.7, 128.6, 128.3, 128.2, 128.2, 128.1, 127.9, 127.8, 98.0, 97.8, 83.9, 80.2, 77.6, 76.5, 75.6, 75.3, 75.1, 74.9, 74.7, 69.7, 63.5, 62.4, 52.8, 25.8, 21.0, 18.2, −4.1, −5.0; FAB MS: m/z: calcd for $C_{42}H_{55}N_3O_{12}Si$: 821.3555; found: 821.3549 $[M]^+$.

tert-Butyldimethylsilyl (6-*O*-acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-β-D-glucopyranosyluronate (748 mg, 0.41 mmol) and DMAP (334 mg, 2.73 mmol) were dissolved in CH_2Cl_2 (5 mL) and a solution of levulinic anhydride (390 mg, 1.82 mmol) in CH_2Cl_2 (5 mL) was added. The reaction mixture was stirred for 2 h at room temperature and concentrated. Flash chromatography on silica gel (hexanes/EtOAc 8:2) afforded **62** (834 mg, 0.91 mmol, quant.) as a colorless foam. $[\alpha]_D^{24}$ = +18.9 (c = 1.01, CH_2Cl_2); IR (thin film on NaCl): $\tilde{\nu}$ = 3036, 2929, 2857, 2108, 1747, 1720, 1454, 1362 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40–7.26 (m, 15H), 5.50 (d, J = 3.7 Hz, 1H), 5.03 (dd, J = 7.3, 8.8 Hz, 1H), 4.89 (s, 2H), 4.83 (d, J = 10.7 Hz, 2H), 4.74 (d, J = 11.3 Hz, 1H), 4.73 (d, J = 7.3 Hz, 1H), 4.56 (d, J = 11.0 Hz, 1H), 4.27–4.23 (m, 3H), 3.97 (d, J = 9.5 Hz, 1H), 3.89 (dd, J = 8.8, 10.1 Hz, 1H), 3.82 (dd, J = 8.9, 8.5 Hz, 1H), 3.77 (s, 3H), 3.66–3.62 (m, 1H), 3.53 (dd, J = 10.1, 8.8 Hz, 1H), 3.31 (dd, J = 3.7, 10.4 Hz, 1H), 2.69–2.65 (m, 2H), 2.54–2.49 (m, 2H), 2.14 (s, 3H), 2.04 (s, 3H), 0.86 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 206.2, 171.3, 170.8, 168.5, 138.0, 137.7, 137.7, 128.7, 128.5, 128.2, 128.2, 128.2, 128.1, 127.8, 127.7, 97.7, 96.1, 82.6, 80.2, 77.6, 75.7, 75.2, 75.2, 75.2, 74.5, 74.4, 69.8, 63.5, 62.4, 52.9, 37.9, 30.0, 28.1, 25.6, 21.0, 18.0, −4.2, −5.2; FAB MS: m/z: calcd for $C_{47}H_{61}N_3O_{14}Si$: 919.3923; found: 919.3914 $[M]^+$.

***tert*-Butyldimethylsilyl (6-*O*-acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-methyl 2-*O*-allyloxycarbonyl-3-*O*-benzyl-β-D-glucopyranosyluronate (63)**: *tert*-Butyldimethylsilyl (6-*O*-acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-methyl-3-*O*-benzyl-β-D-glucopyranosyluronate (see the procedure to prepare **62**), (190 mg, 0.231 mmol) and DMAP (780 mg, 6.38 mmol) were dissolved in CH_2Cl_2 (5 mL) and cooled to −70 °C. Allyloxycarbonylchloride (600 μL, 5.65 mmol) was added in three equal portions every 2 h. After the addition was complete the mixture was warmed to room temperature and stirred overnight. The mixture was poured into EtOAc and washed with 1N HCl, brine and sat. $NaHCO_3$. The organic layer was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 9:1→85:15) afforded **63** (190 mg, 0.21 mmol, 91%) as a colorless oil. $[\alpha]_D^{24}$ = +21.9 (c = 1.25, CH_2Cl_2); IR (thin film on NaCl): $\tilde{\nu}$ = 3026, 2929, 2858, 2108, 1756, 1252 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41–7.26 (m, 15H), 5.92–5.84 (m, 1H), 5.52 (d, J = 3.7 Hz, 1H), 5.36–5.32 (m, 1H), 5.26–5.23 (m, 1H), 4.92–4.81 (m, 5H), 4.79–4.73 (m, 2H), 4.63–4.54 (m, 3H), 4.29–4.26 (m, 2H), 4.22 (dd, J = 9.5, 8.9 Hz, 1H), 3.97 (d, J = 9.5 Hz, 1H), 3.90 (dd, J = 8.8, 10.4 Hz, 1H), 3.84 (dd, J = 9.2, 8.8 Hz, 1H), 3.78 (s, 3H), 3.65–3.61 (m, 1H), 3.54 (dd, J = 8.9, 10.1 Hz, 1H), 3.32 (dd, J = 3.7, 10.4 Hz, 1H), 2.05 (s, 3H), 0.88 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.8, 168.3, 154.0, 137.9, 137.7, 137.6, 131.4, 128.7, 128.7, 128.5, 128.3, 128.2, 128.2, 128.1, 127.9, 127.7, 119.6, 97.8, 96.1, 82.5, 80.2, 79.1, 77.6, 75.7, 75.4, 75.2, 74.9, 74.5, 69.8, 69.0, 63.5, 62.4, 52.9, 25.6, 21.0, 18.0, −4.1, −5.4; FAB MS: m/z: calcd for $C_{46}H_{59}N_3O_{14}Si$: 905.3766; found: 905.3751 $[M]^+$.

6-*O*-Acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 2-*O*-levulinyl-3-*O*-benzyl-α-D-glucopyranosyluronate trichloroacetimidate (64): Compound **59** (1.06 g, 1.12 mmol) was dissolved in THF (10 mL) and cooled to 0 °C. Glacial acetic acid (90 μL, 1.57 mmol) and TBAF (1M in THF, 1.30 mL, 1.30 mmol) were added in sequence. After 30 min the mixture was poured into Et_2O (100 mL) and washed three times with brine. The organic layer was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (20 mL) and cooled to 0 °C. Trichloroacetonitrile (1.7 mL, 17.0 mmol) and DBU (15 μL, 0.1 mmol) were added and the mixture was stirred at 0 °C for 1 h and at room temperature for 3 h. After removal of the solvent under reduced pressure, flash chromatography on silica gel (hexanes/EtOAc 85:15→70:30) afforded **64** (1.0 g, 1.03 mmol, 92%) as a colorless foam. $[\alpha]_D^{24}$ = +108.9 (c = 1.69, CH_2Cl_2); IR (thin film on NaCl): $\tilde{\nu}$ = 3337, 3031, 2954, 2929, 2857, 2105, 1746, 1720, 1678, 1454 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.71 (s, 1H), 7.26–7.40 (m, 10H), 6.54 (d, J = 3.7 Hz, 1H), 5.63 (d, J = 3.7 Hz, 1H), 5.12–5.16 (m, 1H), 4.80–4.92 (m, 4H), 4.48 (d, J = 9.5 Hz, 1H), 4.35 (dd, J = 2.1, 11.9 Hz, 1H), 4.21–4.29 (m, 2H), 4.04 (dd, J = 4.0, 12.2 Hz, 1H), 3.79 (s, 3H), 3.69 (dd, J = 8.5, 10.1 Hz, 1H), 3.64 (dd, J = 9.5, 8.5 Hz, 1H), 3.45–3.49 (m, 1H), 3.23 (dd, J = 4.0, 10.1 Hz, 1H), 2.61–2.71 (m, 2H), 2.35–2.50 (m, 2H), 2.14 (s, 3H), 2.10 (s, 3H), 0.88 (s, 9H), 0.00 (s, 3H), −0.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 206.1, 172.0, 171.0, 168.7, 160.7, 138.1, 137.9, 128.7, 128.5, 128.0, 127.7, 127.6, 127.4, 98.1, 93.3, 90.9, 80.1, 79.7, 75.3, 75.3, 74.1, 72.5, 72.4, 71.2, 70.9, 63.7, 62.6, 53.1, 37.8, 30.0, 27.7, 26.0, 21.1, 18.1, −3.5, −4.9; FAB MS: m/z: calcd for $C_{42}H_{55}Cl_3N_4O_{14}Si$: 972.2550; found: 972.2579 $[M]^+$.

6-*O*-Acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 2-*O*-allyloxycarbonyl-3-*O*-benzyl-α-D-glucopyranosyluronate trichloroacetimidate (65): Compound **60** (271 mg, 0.291 mmol) was dissolved in anhydrous THF (5 mL) and cooled to 0 °C. Glacial acetic acid (21 μL, 0.367 mmol) and TBAF (1.0 M in THF, 320 μL, 0.32 mmol) were added in sequence. After 30 min the mixture was poured into Et_2O (50 mL) and washed three times with brine. The organic layer was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (11 mL) and cooled to 0 °C. Trichloroacetonitrile (450 μL, 4.49 mmol) and DBU (5 μL, 0.033 mmol) were added and the mixture was stirred overnight at room temperature. After removal of the solvent under reduced pressure, flash chromatography on silica gel (hexanes/EtOAc 85:15) afforded **65** (190 mg, 0.198 mmol, 68 %) as a colorless foam. $[\alpha]_D^{24} = +114.0$ ($c = 1.37$, CH_2Cl_2); IR (thin film on NaCl): $\tilde{\nu}$ = 3340, 3026, 2953, 2857, 2105, 1754, 1679, 1454, 1367 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.74 (s, 1H), 7.40–7.26 (m, 10H), 6.63 (d, J = 3.4 Hz, 1H), 5.91–5.82 (m, 1H), 5.65 (d, J = 3.7 Hz, 1H), 5.34–5.30 (m, 1H), 5.27–5.23 (m, 1H), 5.01 (dd, J = 3.4, 9.5 Hz, 1H), 4.93–4.85 (m, 3H), 4.82 (d, J = 11.0 Hz, 1H), 4.65–4.57 (m, 2H), 4.50 (d, J = 9.5 Hz, 1H), 4.37 (dd, J = 1.8, 12.2 Hz, 1H), 4.29–4.22 (m, 2H), 4.05 (dd, J = 4.0, 12.2 Hz, 1H), 3.80 (s, 3H), 3.71 (dd, J = 10.1, 8.5 Hz, 1H), 3.65 (dd, J = 9.2, 8.5 Hz, 1H), 3.50–3.46 (m, 1H), 3.23 (dd, J = 3.7, 10.1 Hz, 1H), 2.11 (s, 3H), 0.89 (s, 9H), 0.00 (s, 3H), −0.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 171.0, 168.6, 160.7, 154.2, 138.0, 137.6, 131.2, 128.6, 128.4, 128.0, 127.8, 127.7, 127.4, 119.4, 98.2, 93.2, 90.8, 80.0, 79.4, 75.8, 75.4, 75.2, 74.1, 72.4, 71.2, 70.9, 69.2, 63.6, 62.5, 53.0, 26.0, 21.0, 18.1, −3.6, −4.9; FAB MS: m/z: calcd for $C_{41}H_{53}Cl_3N_4O_{14}Si$: 958.2393; found: 958.2392 $[M]^+$.

6-*O*-Acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 3-*O*-benzyl-2-*O*-levulinoyl-α-D-glucopyranosyluronate trichloroacetimidate (66): Compound **62** (345 mg, 0.376 mmol) was dissolved in THF (10 mL) and cooled to 0 °C. Glacial acetic acid (27 μL, 0.472 mmol) and tetrabutylammoniumfluoride (1.0 M in THF, 415 μL, 0.415 mmol) were added sequentially. After 40 min this mixture was poured into EtOAc (50 mL) and washed with sat. $NaHCO_3$. The organic layer was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (10 mL) and cooled to 0 °C. Trichloroacetonitrile (750 μL, 7.48 mmol) and DBU (30 μL) were added and the mixture was stirred for 2 h. After removal of the solvent under reduced pressure, flash chromatography on silica gel (hexanes/EtOAc 8:2→6:4) afforded **66** as a colorless foam (302 mg, 0.32 mmol, 85 %). $[\alpha]_D^{24} = +79.8$ ($c = 1.72$, CH_2Cl_2); IR (thin film on NaCl): $\tilde{\nu}$ = 3337, 3063, 3030, 2953, 2108, 1746, 1719, 1677, 1497, 1363 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.71 (s, 1H), 7.40–7.25 (m, 15H), 6.53 (d, J = 3.4 Hz, 1H), 5.55 (d, J = 3.7 Hz, 1H), 5.14–5.11 (m, 1H), 4.95–4.82 (m, 5H), 4.57 (d, J = 11.0 Hz, 1H), 4.46–4.42 (m, 1H), 4.28–4.20 (m, 4H), 3.94 (dd, J = 8.5, 10.4 Hz, 1H), 3.77 (s, 3H), 3.62–3.58 (m, 1H), 3.51 (dd, J = 8.8, 10.1 Hz, 1H), 3.30 (dd, J = 3.7, 10.4 Hz, 1H), 2.70–2.60 (m, 2H), 2.51–2.36 (m, 2H), 2.14 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 206.1, 172.0, 170.9, 168.6, 160.7, 138.0, 137.8, 137.7, 128.7, 128.7, 128.7, 128.2, 128.1, 127.9, 127.6, 98.3, 93.2, 90.9, 80.1, 79.4, 77.6, 75.7, 75.4, 75.2, 75.0, 72.5, 72.4, 70.0, 63.3, 62.4, 53.2, 37.8, 30.0, 27.7, 21.0; FAB MS: m/z: calcd for $C_{43}H_{47}Cl_3N_4O_{14}$: 948.2154; found: 948.2118 $[M]^+$.

6-*O*-Acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 2-*O*-allyloxycarbonyl-3-*O*-benzyl-α/β-D-glucopyranosyluronate trichloroacetimidate (67): Compound **63** (74 mg, 0.082 mmol) was dissolved in THF (2 mL) and cooled to 0 °C. Glacial acetic acid (6 μL, 0.1 mmol) and TBAF (1 M in THF, 90 μL, 0.09 mmol) were added. After 30 min the mixture was poured into Et_2O (50 mL) and washed three times with brine. The organic layer was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (2 mL) and cooled to 0 °C. Trichloroacetonitrile (120 μL, 1.19 mmol) and DBU (1.2 μL, 0.008 mmol) were added and the mixture was stirred overnight at room temperature. After removal of the solvent under reduced pressure, flash chromatography on silica gel (hexanes/EtOAc 85:15) afforded **67** (63 mg, 0.07 mmol, 83 %) as a colorless foam. FAB MS: m/z: calcd for $C_{42}H_{45}Cl_3N_4O_{14}$: 934.1998; found: 934.1989 $[M]^+$.

3,6-Di-*O*-acetyl-2-azido-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 1,2-*O*-acetyl-3-*O*-benzyl-α/β-L-idopyranosyluronate (68): Pyridine (2.0 mL, 24 mmol), acetic anhydride (1.4 mL, 15 mmol) and DMAP (12 mg, 0.1 mmol) were added to a solution of **53** (700 mg, 1.02 mmol) in CH_2Cl_2 (16 mL). The solution was stirred at room temperature for 1 h, water was added and the mixture was stirred for one additional hour. The organic phase was washed with sat. $NaHCO_3$, water, and aqueous HCl (10 %), dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (hexane/EtOAc 90:20) to yield **68** (707 mg, 0.92 mmol, 95 %) as a colorless syrup. FAB MS: m/z: calcd for $C_{34}H_{49}N_3O_{15}Si$: 767.2933; found: 767.2951 $[M]^+$.

6-*O*-Acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 1,2-*O*-acetyl-3-*O*-benzyl-L-idopyranosyluronate (69): Pyridine (1.5 mL, 18 mmol), acetic anhydride (1 mL, 11 mmol) and DMAP (10 mg, 0.08 mmol) were added to a solution of **54** (560 mg, 0.77 mmol) in CH_2Cl_2 (10 mL). The solution was stirred at room temperature for 1 h, water was added and the mixture was stirred for one additional hour. The organic phase was washed with sat. $NaHCO_3$, water and aqueous HCl (10 %), dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (hexanes/EtOAc 90:20) to yield **69** (619 mg, 0.76 mmol, 99 %) as a colorless syrup. FAB MS: m/z: calcd for $C_{39}H_{53}N_3O_{14}Si$: 815.3297; found: 815.3270 $[M]^+$.

3,6-Di-*O*-acetyl-2-azido-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 2-*O*-acetyl-3-*O*-benzyl-β-L-idopyranosyluronate trichloroacetimidate (70): Benzylamine (2.0 mL, 18.3 mmol) was added to a solution of **68** (650 mg, 0.85 mmol) in Et_2O (50 mL) at 0 °C. After stirring at 0 °C for 4 h the mixture was diluted with CH_2Cl_2, filtered and washed with HCl (10 %). The organic phase was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 90:10→80:20) afforded 3,6-di-*O*-acetyl-2-azido-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 2-*O*-acetyl-3-*O*-benzyl-α/β-L-idopyranosyluronate (443 mg, 72 %) as a white solid. FAB MS: m/z: calcd for $C_{32}H_{47}N_3O_{14}Si$: 725.2827; found: 725.2811 $[M]^+$.

A solution of 3,6-di-*O*-acetyl-2-azido-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 2-*O*-acetyl-3-*O*-benzyl-α/β-L-idopyranosyluronate (335 mg, 0.46 mmol) and trichloroacetonitrile (1.3 mL, 12.5 mmol) in CH_2Cl_2 (10 mL) containing freshly activated powdered 4 Å molecular sieves (100 mg) was stirred 30 minutes at room temperature. After cooling the solution to 0 °C, DBU (30 μL, 0.2 mmol) was added. The temperature was allowed to rise and after 1 h stirring, the mixture was filtered through a pad of Celite and concentrated. The residue was purified by silica gel column chromatography (hexanes/EtOAc 85:15) yielding **70** (373 mg, 0.43 mmol, 93 %) as a white solid. $[\alpha]_D^{24} = +53.4$ ($c = 1.00$, $CHCl_3$); IR (thin film on NaCl): $\tilde{\nu}$ = 2935, 2693, 2109, 1744, 1675, 1372 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.68 (s, 1H), 7.36–7.30 (m, 5H), 6.41 (s, 1H), 5.26 (dd, J = 8.5, 10.4 Hz, 1H), 5.17 (s, 1H), 5.00 (d, J = 3.4 Hz, 1H), 4.98 (d, J = 1.8 Hz, 1H), 4.81 (d, J = 11.6 Hz, 1H), 4.65 (d, J = 11.6 Hz, 1H), 4.46 (dd, J = 2.1, 12.5 Hz, 1H), 4.27 (s, 1H), 4.09–4.06 (m, 2H), 4.00–3.81 (m, 1H), 3.80 (s, 3H), 3.81–3.79 (m, 1H), 3.05 (dd, J = 3.3, 10.7 Hz, 1H), 2.20 (s, 3H), 2.14 (s, 3H), 2.10 (s, 3H), 0.84 (s, 9H), 0.49 (s, 3H), 0.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.7, 170.3, 169.9, 169.1, 160.3, 137.2, 128.6, 128.1, 128.0, 98.3, 95.7, 73.7, 72.8, 72.7, 72.3, 71.1, 69.2, 68.9, 65.4, 62.4, 61.9, 52.8, 25.8, 21.5, 21.0, 20.9, 18.1, −4.0, −4.8; FAB MS: m/z: calcd for $C_{34}H_{47}Cl_3N_4O_{14}Si$: 868.1924; found: 868.1938 $[M]^+$.

6-*O*-Acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 2-*O*-acetyl-3-*O*-benzyl-β-L-idopyranosyluronate) trichloroacetimidate (71): Benzylamine (0.6 mL, 5.5 mmol) was added to a solution of **69** (600 mg, 0.73 mmol) in Et_2O (15 mL) at 0 °C. After stirring at 0 °C for 5 h the mixture was diluted with CH_2Cl_2, filtered and washed with HCl (10 %). The organic phase was dried over Na_2SO_4 and after filtration purified by silica gel column chromatography (hexanes/AcOEt 90:10→80:20) to yield 6-*O*-acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 2-*O*-acetyl-3-*O*-benzyl-α/β-L-idopyranosyluronate (415 mg, 0.54 mmol, 77 %) as a white solid. FAB MS: m/z: calcd for $C_{37}H_{51}N_3O_{13}Si$: 773.3191; found: 773.3201 $[M]^+$.

A solution of 6-*O*-acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 2-*O*-acetyl-3-*O*-benzyl-α/β-L-idopyranosyluronate (90 mg, 0.12 mmol) and trichloroacetonitrile (0.34 mL, 3.3 mmol) in CH_2Cl_2 (3 mL) containing freshly activated powdered 4 Å molecular sieves (50 mg) was stirred 30 minutes at room

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temperature. After cooling the solution to 0 °C, DBU (2 μL, 0.012 mmol) was added. The temperature was allowed to rise and after 1 h stirring, the mixture was filtered through a pad of Celite and concentrated. The residue was purified by silica gel column chromatography (hexanes/EtOAc 85:15) yielding **71** (104 mg, 0.113 mmol, 97 %) as a white solid. $[\alpha]_D^{24} = +70.3$ ($c = 1.00$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.70$ (s, 1H), 7.36–7.27 (m, 10H), 6.43 (s, 1H), 5.16 (s, 1H), 4.93 (d, $J = 3.4$ Hz, 1H), 5.00 (d, $J = 2.1$ Hz, 1H), 4.84 (d, $J = 11.0$ Hz, 1H), 4.83 (d, $J = 11.6$ Hz, 1H), 4.76 (d, $J = 11.0$ Hz, 1H), 4.67 (d, $J = 11.6$ Hz, 1H), 4.41 (dd, $J = 2.1$, 12.2 Hz), 4.21 (s, 1H), 3.82 (s, 3H), 4.07–4.02 (m, 2H), 3.75–3.70 (m, 1H), 3.68–3.62 (m, 3H), 3.35 (dd, $J = 3.5$, 9.7 Hz, 1H), 2.17 (s, 3H), 2.07 (s, 3H), 0.88 (s, 9H), 0.05 (s, 3H), −0.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 170.9$, 170.1, 168.9, 160.3, 137.9, 137.2, 128.6, 128.5, 128.2, 127.9, 127.8, 127.4, 97.1, 95.4, 80.3, 75.2, 72.6, 72.1, 71.3, 70.8, 70.8, 69.3, 65.4, 64.0, 62.7, 52.7, 26.3, 21.1, 21.0, 18.1, −3.5, −4.8; FAB MS: *m/z*: calcd for $C_{34}H_{47}Cl_3N_4O_{14}Si$: 916.2287; found: 916.2246 $[M]^+$.

***n*-Pentenyl (6-*O*-acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-2-*O*-levulinoyl-*β*-D-glucopyranosyluronate (72)**: Compound **64** (292 mg, 0.30 mmol) was coevaporated three times with toluene, dried under vacuum for 1 h, dissolved in toluene (5 mL) and 4-penten-1-ol (300 μL, 3.00 mmol) was added. After cooling the mixture to 0 °C, TMSOTf (0.1 M in toluene, 300 μL, 0.03 mmol) was added dropwise. The mixture was warmed to room temperature and stirred for 2 h. Triethylamine (0.6 mL) was added and the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 85:15) afforded **72** (203 mg, 0.60 mmol, 75 %) as a colorless gum. $[\alpha]_D^{24} = +53.1$ ($c = 1.18$, CH_2Cl_2); IR (thin film on NaCl): $\tilde{\nu} = 2930$, 2858, 2106, 1747, 1362, 1237 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.25–7.39$ (m, 10H), 5.75–5.84 (m, 1H), 5.54 (d, $J = 3.7$ Hz, 1H), 5.07 (dd, $J = 7.3$, 8.5 Hz, 1H), 4.95–5.04 (m, 2H), 4.88 (d, $J = 11.0$ Hz, 1H), 4.74–4.82 (m, 3H), 4.48 (d, $J = 7.3$ Hz, 1H), 4.35 (dd, $J = 2.1$, 11.9 Hz, 1H), 4.25 (at, $J = 9.2$ Hz, 1H), 4.02–4.07 (m, 2H), 3.84–3.89 (m, 2H), 3.79 (s, 3H), 3.61–3.67 (m, 2H), 3.43–3.51 (m, 2H), 3.23–3.26 (m, 1H), 2.67–2.71 (m, 2H), 2.44–2.58 (m, 2H), 2.14 (s, 3H), 2.03–2.12 (m, 5H), 1.60–1.72 (m, 2H), 0.88 (s, 9H), 0.00 (s, 3H), −0.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 206.7$, 172.0, 171.5, 169.3, 138.7, 138.6, 138.3, 129.1, 129.0, 128.4, 128.3, 128.3, 127.9, 115.7, 101.7, 98.1, 83.1, 80.7, 75.8, 75.0, 75.0, 74.9, 74.1, 71.7, 71.4, 70.0, 64.4, 63.1, 53.4, 38.5, 30.6, 30.5, 29.2, 28.6, 26.6, 21.6, 18.7, −3.0, −4.4; FAB MS: *m/z*: calcd for $C_{45}H_{63}N_3O_{14}Si$: 897.4079; found: 897.4067 $[M]^+$.

***n*-Pentenyl (6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-2-*O*-levulinoyl-*β*-D-glucopyranosyluronate (73)**: Compound **72** (674 mg, 0.75 mmol) was dissolved in THF (80 mL). Glacial acetic acid (20 mL) and HF/pyridine complex (12 mL) were added and the solution was stirred at room temperature for 93 h. The mixture was poured into EtOAc and washed with brine, water, sat. $NaHCO_3$ and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 8:2→6:4) afforded **73** (500 mg, 0.64 mmol, 85 %) as a colorless oil. $[\alpha]_D^{24} = +0.3$ ($c = 1.20$, CH_2Cl_2); IR (thin film on NaCl): $\tilde{\nu} = 3484$, 3037, 2924, 2109, 1746, 1719, 1363 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.43–7.25$ (m, 10H), 5.84–5.75 (m, 1H), 5.50 (d, $J = 3.7$ Hz, 1H), 5.07 (dd, $J = 7.3$, 8.5 Hz, 1H), 5.04–4.95 (m, 2H), 4.90 (d, $J = 11.3$ Hz, 1H), 4.88 (d, $J = 11.3$ Hz, 1H), 4.81 (d, $J = 10.7$ Hz, 1H), 4.75 (d, $J = 10.7$ Hz, 1H), 4.57 (dd, $J = 3.1$, 12.5 Hz, 1H), 4.48 (d, $J = 7.3$ Hz, 1H), 4.24 (dd, $J = 9.2$, 8.9 Hz, 1H), 4.12 (dd, $J = 1.8$, 12.5 Hz, 1H), 4.01 (d, $J = 9.5$ Hz, 1H), 3.88–3.83 (m, 2H), 3.78 (s, 3H), 3.74 (dd, $J = 8.8$, 10.0 Hz, 1H), 3.50–3.38 (m, 3H), 3.23 (dd, $J = 3.7$, 10.4 Hz, 1H), 3.05 (d, $J = 3.4$ Hz, 1H), 2.71–2.68 (m, 2H), 2.59–2.45 (m, 2H), 2.15 (s, 3H), 2.11–2.04 (m, 5H), 1.72–1.60 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 206.2$, 172.5, 171.5, 168.9, 138.1, 138.0, 137.8, 128.8, 128.6, 128.4, 128.3, 127.9, 127.8, 115.2, 101.2, 97.8, 82.5, 79.1, 75.5, 74.6, 74.5, 74.5, 73.7, 70.9, 70.5, 69.5, 62.9, 62.6, 52.9, 38.0, 30.1, 30.0, 28.7, 28.1, 21.0; FAB MS: *m/z*: calcd for $C_{39}H_{49}N_3O_{14}$: 783.3215; found: 783.3206 $[M]^+$.

***n*-Pentenyl (6-*O*-acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-2-*O*-monochloroacetyl-*β*-D-glucopyranosyluronate (74)**: Compound **57** (816 mg, 0.856 mmol) was coevaporated three times with toluene, dried in vacuo for 1 h, dissolved in toluene (30 mL) and 4-penten-1-ol (450 μL, 4.36 mmol) was added. After cooling the mixture to 0 °C, TMSOTf (0.1 M in toluene, 1.72 mL, 0.17 mmol) was added dropwise. The mixture was warmed to room temperature and stirred for 48 h. Triethylamine (1.7 mL) was added and the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 85:15) afforded **74** (527 mg, 0.60 mmol, 70 %) as a colorless gum. $[\alpha]_D^{24} = +45.5$ ($c = 1.00$, $CHCl_3$); IR (thin film on NaCl): $\tilde{\nu} = 2954$, 2109, 1745, 1223, 1072 cm^{-1} ;^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.37–7.28$ (m, 10H), 5.79–5.74 (m, 1H), 5.50 (d, $J = 3.7$ Hz, 1H), 5.09 (dd, $J = 7.6$, 8.8 Hz, 1H), 5.07–4.95 (m, 2H), 4.74 (d, $J = 7.3$ Hz, 1H), 4.87 (d, $J = 11.3$ Hz, 2H), 4.86 (d, $J = 11.0$ Hz, 2H), 4.80 (d, $J = 11.3$ Hz, 1H), 4.70 (d, $J = 11.0$ Hz, 1H), 4.48 (d, 1H), 4.35 (dd, $J = 2.1$, 11.9 Hz, 1H), 4.04 (t, 1H), 4.05–4.00 (m, 2H), 3.89–3.80 (m, 4H), 3.79 (s, 3H), 3.65–3.64 (m, 2H), 3.50–3.42 (m, 2H), 3.28 (dd, $J = 4.0$, 10.1 Hz, 1H), 2.09 (s, 3H), 1.07–1.03 (m, 2H), 1.69–1.58 (m, 2H), 0.88 (s, 9H), −0.01 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 171.0$, 168.6, 166.0, 137.9, 137.7, 137.4, 129.0, 128.7, 128.5, 128.1, 128.0, 127.9, 127.75, 127.7, 127.4, 115.0, 100.9, 97.7, 82.5, 80.2, 75.3, 74.9, 74.8, 74.6, 74.5, 71.3, 70.8, 69.5, 63.8, 62.5, 52.9, 44.0, 42.8, 40.6, 30.0, 28.6, 26.0, 21.0, 18.1, −3.5, −4.9; FAB MS: *m/z*: calcd for $C_{42}H_{36}ClN_3O_{13}Si$: 875.3427; found: 875.3432 $[M]^+$.

***n*-Pentenyl (6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-2-*O*-monochloroacetyl-*β*-*O*-pentenyl-D-glucopyranosyluronate (75)**: Compound **74** (250 mg, 0.285 mmol) was dissolved in THF (33 mL). Glacial acetic acid (8 mL) and HF/pyridine complex (4.8 mL) were added and the solution was stirred at room temperature for 4 d. The mixture was poured into Et_2O and washed with brine, sat. $NaHCO_3$ and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 7:3) afforded **75** (186 mg, 0.244 mmol, 85 %) as a colorless foam. $[\alpha]_D^{24} = +10.8$ ($c = 1.0$, $CHCl_3$); IR (thin film on NaCl): $\tilde{\nu} = 3485$, 2925, 2109, 1747, 1454, 1028 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.43–7.27$ (m, 10H), 5.98–5.70 (m, 1H), 5.47 (d, $J = 3.8$ Hz), 5.09 (t, 1H), 5.08–4.97 (m, 2H), 4.95–4.93 (m, 3H), 4.69 (d, $J = 10.7$ Hz, 1H), 4.40–4.35 (m, 1H), 4.59 (dd, $J = 2.7$, 12.4 Hz, 1H), 4.48 (d, $J = 7.7$ Hz, 1H), 4.24 (t, 1H), 4.11 (dd, $J = 1.9$, 12.4 Hz, 1H), 4.0 (d, $J = 5.5$ Hz, 1H), 3.89–3.79 (m, 4H), 3.79 (s, 3H), 3.78–3.70 (m, 1H), 3.50–3.38 (m, 3H), 3.27 (dd, $J = 3.8$, 10.4 Hz, 1H), 2.98 (brs, 1H), 2.03–2.01 (m, 2H), 2.12 (s, 3H), 1.73–1.59 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 172.5$, 168.6, 165.9, 138.0, 137.9, 137.7, 128.8, 128.7, 128.4, 128.3, 128.1, 127.7, 115.3, 101.0, 98.0, 82.5, 79.0, 75.5, 75.1, 75.0, 74.8, 74.6, 71.1, 70.5, 69.6, 62.9, 62.6, 53.0, 40.6, 30.0, 28.6, 21.0; FAB MS: *m/z*: calcd for $C_{36}H_{44}ClN_3O_{13}$: 761.2563; found: 761.2557 $[M]^+$.

***n*-Pentenyl (6-*O*-acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-methyl 2-*O*-allyloxycarbonyl-3-*O*-benzyl-*β*-D-glucopyranosyluronate (76)**: Compound **65** (93 mg, 0.097 mmol) was coevaporated three times with toluene, dried under vacuum for 1 h, dissolved in toluene (5 mL) and 4-penten-1-ol (50 μL, 0.484 mmol) was added. After cooling the mixture to 0 °C, TMSOTf (0.1 M in toluene, 200 μL, 0.019 mmol) was added dropwise. The mixture was warmed to room temperature and stirred for 30 min. Triethylamine (200 μL) was added and the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 85:15) afforded **76** (57 mg, 0.064 mmol, 66 %) as a colorless gum. $[\alpha]_D^{24} = +64.1$ ($c = 1.65$, CH_2Cl_2); IR (thin film on NaCl): $\tilde{\nu} = 3065$, 2953, 2857, 2106, 1755, 1454, 1369 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.26–7.39$ (m, 10H), 5.73–5.92 (m, 2H), 5.55 (d, $J = 3.7$ Hz, 1H), 5.32–5.37 (m, 1H), 5.19–5.25 (m, 1H), 4.96–5.04 (m, 2H), 4.76–4.90 (m, 5H), 4.55–4.64 (m, 2H), 4.49 (d, $J = 7.6$ Hz, 1H), 4.35 (dd, $J = 2.1$, 11.9 Hz, 1H), 4.21 (at, $J = 9.2$ Hz, 1H), 4.05 (dd, $J = 4.0$, 12.2 Hz, 1H), 4.00 (d, $J = 9.5$ Hz, 1H), 3.86–3.95 (m, 2H), 3.80 (s, 3H), 3.62–3.70 (m, 2H), 3.45–3.50 (m, 2H), 3.29–3.24 (m, 1H), 2.00–2.16 (m, 5H), 1.60–1.77 (m, 2H), 0.89 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 171.0$, 168.6, 154.0, 138.1, 138.0, 137.7, 131.4, 128.6, 128.5, 128.0, 127.8, 127.7, 127.4, 119.6, 115.2, 101.2, 97.8, 82.6, 80.2, 77.4, 75.3, 74.9, 74.7, 74.5, 71.2, 70.9, 69.7, 69.1, 63.9, 62.5, 52.9, 30.0, 28.7, 26.0, 21.1, 18.1, −3.5, −4.9; FAB MS: *m/z*: calcd for $C_{44}H_{61}N_3O_{14}Si$: 883.3923; found: 883.3930 $[M]^+$.

***n*-Pentenyl (6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-methyl 2-*O*-allyloxycarbonyl-3-*O*-benzyl-*β*-D-glucopyranosyluronate (77)**: Compound **76** (55 mg, 0.062 mmol) was dissolved in THF (7 mL). Glacial acetic acid (1.75 mL) and HF/pyridine complex (1 mL) were added and the solution was stirred at room temperature for 5 days. The mixture was poured into EtOAc and washed with brine, water, sat. $NaHCO_3$ and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 7:3) afforded **77** (41 mg, 0.053 mmol, 85 %) as a colorless oil. $[\alpha]_D^{24} = +11.3$ ($c = 1.02$, CH_2Cl_2); IR (thin film on NaCl): $\tilde{\nu} = 3470$, 2922, 2109, 1752, 1454, 1367, 1255 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.43–$

7.27 (m, 10H), 5.92–5.84 (m, 1H), 5.82–5.74 (m, 1H), 5.51 (d, J = 3.7 Hz, 1H), 5.37–5.31 (m, 1H), 5.23–5.26 (m, 1H), 5.04–4.95 (m, 2H), 4.90–4.79 (m, 4H), 4.77 (d, J = 10.7 Hz, 1H), 4.65–4.56 (m, 3H), 4.49 (d, J = 7.7 Hz, 1H), 4.21 (dd, J = 8.9, 9.4 Hz, 1H), 4.11 (dd, J = 1.9, 12.6 Hz, 1H), 3.99 (d, J = 9.5 Hz, 1H), 3.92–3.87 (m, 1H), 3.86 (at, J = 9.0 Hz, 1H), 3.79 (s, 3H), 3.74 (dd, J = 8.6, 10.3 Hz, 1H), 3.51–3.45 (m, 2H), 3.41 (dd, J = 10.0, 8.7 Hz, 1H), 3.25 (dd, J = 3.7, 10.4 Hz, 1H), 2.98 (br s, 1H), 2.21–2.06 (m, 5H), 1.74–1.60 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.5, 168.7, 154.0, 138.1, 138.0, 137.7, 131.4, 128.8, 128.6, 128.4, 128.3, 128.0, 127.8, 119.6, 115.2, 101.3, 98.0, 82.6, 79.1, 75.6, 75.1, 74.9, 74.5, 71.0, 70.5, 69.7, 69.1, 62.9, 62.6, 53.0, 30.0, 28.7, 21.0; FAB MS: m/z: calcd for $C_{38}H_{47}N_3O_{14}$: 769.3058; found: 769.3051 $[M]^+$.

***n*-Pentenyl (3,6-di-*O*-acetyl-2-azido-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(methyl 2-*O*-acetyl-3-*O*-benzyl-*β*-L-idopyranosyluronate)-(1→4)-(6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-2-*O*-levulinyl-*β*-D-glucopyranosyluronate (78)**: Compound **71** (290 mg, 0.33 mmol) and **73** (173 mg, 0.22 mmol) were coevaporated with toluene and dried under vacuum for 1 h. The mixture was dissolved in CH_2Cl_2 (3 mL) and after cooling to −25 °C, TMSOTf (330 μL, 0.1 M in CH_2Cl_2) was added. The mixture was stirred for 4 h and then diluted with CH_2Cl_2 and filtered through a pad of Celite. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (toluene/EtOAc 90:10→80:20) to yield **78** (289 mg, 88%) as a syrup. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.37–7.15 (m, 15H), 5.83–5.75 (m, 1H), 5.47 (d, J = 4.0 Hz, 1H), 5.35 (d, J = 4.9 Hz, 1H), 5.24 (dd, J = 8.8, 10.7 Hz, 1H), 5.13 (d, J = 3.3 Hz, 1H), 5.08–5.03 (m, 1H), 4.99–4.90 (m, 4H), 4.80–4.67 (m, 5H), 4.58 (d, J = 4.9 Hz, 1H), 4.47 (d, J = 7.3 Hz, 1H), 4.37–4.31 (m, 2H), 4.25–4.18 (m, 2H), 4.10 (at, J = 6.1 Hz, 1H), 4.06 (dd, J = 3.7, 12.2 Hz, 1H), 4.02–3.98 (m, 2H), 3.94–3.91 (m, 1H), 3.88–3.80 (m, 3H), 3.79–3.69 (m, 2H), 3.68 (s, 3H), 3.65 (s, 3H), 3.56–3.54 (m, 1H), 3.48–3.43 (m, 1H), 3.28 (dd, J = 6.9, 10.3 Hz, 1H), 3.00 (dd, J = 3.3, 10.7 Hz, 1H), 2.68 (t, J = 6.7 Hz, 1H), 2.57–2.44 (m, 2H), 2.26–2.01 (m, 17H), 1.71–1.61 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 206.2, 171.4, 170.6, 170.2, 170.0, 169.8, 168.9, 138.1, 138.0, 137.8, 137.5, 129.2, 128.7, 128.6, 128.4, 128.2, 128.1, 127.9, 127.7, 125.5, 115.1, 101.2, 98.3, 98.2, 97.3, 82.5, 78.1, 76.2, 76.0, 75.1, 74.5, 74.4, 74.3, 73.5, 73.0, 72.5, 70.9, 70.4, 70.3, 69.6, 69.4, 68.9, 63.2, 62.4, 61.8, 61.5, 52.8, 52.3, 37.9, 30.0, 29.9, 28.7, 28.0, 25.7, 21.6, 21.5, 21.0, 20.9, 18.0, −3.9, −4.9; FAB MS: m/z: calcd for $C_{71}H_{94}N_6NaO_{27}Si$: 1513.5834; found: 1513.5793 $[M+Na]^+$.

***n*-Pentenyl (3,6-di-*O*-acetyl-2-azido-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(methyl 2-*O*-acetyl-3-*O*-benzyl-*α*-L-idopyranosyluronate)-(1→4)-(6-*O*-acetyl-3-*O*-benzyl-2-azido-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-2-*O*-monochloroacetyl-*β*-D-glucopyranosyluronate (79)**: Compound **71** (360 mg, 0.41 mmol) and **75** (186 mg, 0.24 mmol) were coevaporated with toluene and dried under vacuum for 1 h. The mixture was dissolved in CH_2Cl_2 (3 mL) and after cooling to −25 °C, TMSOTf (370 μL, 0.1 M in CH_2Cl_2) was added. The mixture was stirred for 4 h and then diluted with CH_2Cl_2 and filtered through a pad of Celite. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (toluene/EtOAc 90:10→80:20) to yield **79** (331 mg, 0.22 mmol, 91%) as a syrup. $[\alpha]_D^{24}$ = +40.0 (c = 1.00, $CHCl_3$); IR (thin film on NaCl): $\tilde{\nu}$ = 2930, 2107, 1728, 1538, 1362 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39–7.27 (m, 20H), 5.77–5.74 (m, 1H), 5.43 (d, J = 3.7 Hz, 1H), 5.35 (d, J = 4.9 Hz, 1H), 5.23 (t, J = 10.4 Hz, 1H), 5.12 (d, J = 3.7 Hz, 1H), 5.07 (t, 1H), 5.01–4.84 (m, 6H), 4.73–4.64 (m, 4H), 4.57 (d, J = 4.6 Hz, 1H), 4.47 (d, J = 7.6 Hz, 1H), 4.34 (m, 2H), 4.24–4.18 (m, 2H), 4.09 (t, 1H), 4.05 (dd, J = 3.3, 12.2 Hz, 1H), 4.00 (m, 2H), 3.92–3.81 (m, 6H), 3.79–3.72 (m, 2H), 3.69 (s, 3H), 3.67 (s, 3H), 3.56–3.54 (m, 1H), 3.45–3.42 (m, 1H), 3.31 (dd, J = 3.7, 10.7 Hz, 1H), 3.00 (dd, J = 3.7, 10.7 Hz, 1H), 2.13 (s, 6H), 2.10 (s, 3H), 2.05–2.01 (m, 2H), 2.03 (s, 3H), 1.69–1.60 (m, 2H), 0.84 (s, 9H), 0.04 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.0, 170.7, 170.2, 169.8, 168.6, 165.9, 137.9, 137.7, 137.5, 128.7, 128.4, 128.2, 128.1, 128.0, 127.9, 127.7, 127.3, 115.3, 101.0, 98.2, 97.7, 82.5, 78.2, 76.0, 75.1, 75.0, 74.7, 74.6, 74.4, 73.0, 72.6, 71.0, 69.8, 69.6, 69.0, 63.3, 62.4, 61.6, 52.4, 40.7, 30.0, 28.7, 26.6, 25.7, 21.8, 21.2, 18.0, −3.9, −4.8; FAB MS: m/z: calcd for $C_{68}H_{89}ClN_6O_{26}Si$: 1468.5284; found: 1468.5361 $[M]^+$.

***n*-Pentenyl (6-*O*-acetyl-2-azido-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*α*-D-glucopyranosyl-(1→4)-(methyl 2-*O*-acetyl-3-*O*-benzyl-*α*-L-idopyranosyluronate)-(1→4)-(6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl-(1→4)-methyl 3-*O*-benzyl-2-*O*-levulinoyl-*β*-*O*-D-glucopyranosyluronate (80)**: Compound **70** (85 mg, 0.09 mmol) and **73** (60 mg, 0.07 mmol) were coevaporated with toluene and dried under vacuum for 1 h. The mixture was dissolved in CH_2Cl_2 (2 mL) and after cooling to −25 °C, TMSOTf (90 μL, 0.1 M in CH_2Cl_2) was added. The mixture was stirred for 4 h and then diluted with CH_2Cl_2 and filtered through a pad of Celite. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (toluene/EtOAc 90:10→80:20) to yield **80** (107 mg, 86%) as a syrup. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.37–7.25 (m, 20H), 5.82–5.74 (m, 1H), 5.47 (d, J = 3.6 Hz, 1H), 5.26 (d, J = 4.6 Hz, 1H), 5.07–5.02 (m, 3H), 4.99–4.88 (m, 3H), 4.83–4.65 (m, 8H), 4.47 (d, J = 7.3 Hz, 1H), 4.35–4.32 (m, 2H), 4.25–4.18 (m, 2H), 4.07–3.95 (m, 4H), 3.87–3.82 (m, 3H), 3.80–3.73 (m, 2H), 3.72–3.64 (m, 4H), 3.61 (s, 3H), 3.59–3.55 (m, 2H), 3.47–3.43 (m, 1H), 3.27 (dd, J = 3.9, 10.3 Hz, 1H), 3.23 (dd, J = 3.3, 10.1, 1H), 2.68 (t, J = 6.7 Hz, 2H), 2.57–2.44 (m, 2H), 2.18 (s, 3H), 2.14 (s, 3H), 2.13–2.05 (m, 5H), 2.02 (s, 3H), 1.70–1.61 (m, 2H), 0.89 (m, 9H), −0.01 (s, 3H), −0.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 206.2, 171.4, 170.9, 170.8, 170.1, 169.6, 168.9, 138.1, 137.9, 137.8, 137.7, 137.5, 128.7, 128.6, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7, 127.4, 115.2, 101.2, 98.2, 97.7, 97.4, 82.6, 80.2, 78.1, 75.9, 75.2, 75.0, 74.8, 74.5, 74.0, 73.6, 72.7, 71.2, 70.8, 70.2, 70.0, 69.7, 69.5, 63.7, 63.2, 62.6, 61.9, 52.9, 52.1, 38.0, 30.1, 30.0, 28.7, 28.0, 26.0, 21.1, 21.0, 18.1, −3.53, −4.87; FAB MS: m/z: calcd for $C_{76}H_{98}N_6O_{26}Si$: 1538.6300; found: 1538.6249 $[M]^+$.

***n*-Pentenyl (3,6-di-*O*-acetyl-2-azido-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(methyl 2-*O*-acetyl-3-*O*-benzyl-*α*-L-idopyranosyluronate)-(1→4)-(6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-2-*O*-levulinyl-*β*-D-glucopyranosyluronate (81)**: Compound **78** (170 mg, 0.11 mmol) was dissolved in THF (13 mL). Glacial acetic acid (3 mL) and HF/pyridine complex (1.88 mL) were added and the solution was stirred at room temperature for three days. The mixture was poured into EtOAc and washed with brine, water, sat. $NaHCO_3$ and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 5:3) afforded **81** (135 mg, 86%) as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.37–7.15 (m, 15H), 5.82–5.74 (m, 1H), 5.47 (d, J = 3.6 Hz, 1H), 5.29 (d, J = 4.3 Hz, 1H), 5.21 (t, J = 10.1 Hz, 1H), 5.07–5.02 (m, 2H), 4.98–4.90 (m, 3H), 4.79–4.68 (m, 5H), 4.61 (d, J = 4.3 Hz, 1H), 4.50–4.46 (m, 2H), 4.32–4.30 (m, 1H), 4.25–4.14 (m, 3H), 4.07 (t, J = 5.2 Hz, 1H), 3.98 (d, J = 9.5 Hz, 1H), 3.95 (t, J = 5.5 Hz, 1H), 3.90–3.82 (m, 4H), 3.74 (t, J = 10.1 Hz, 1H), 3.67 (s, 3H), 3.66 (s, 3H), 3.56–3.54 (m, 1H), 3.47–3.42 (m, 2H), 3.27 (dd, J = 3.6, 10.3 Hz, 1H), 3.17 (dd, J = 3.6, 10.7 Hz, 1H), 3.01 (br s, 1H), 2.68 (t, J = 6.7 Hz, 2H), 2.57–2.43 (m, 2H), 2.26–2.08 (m, 17H), 1.70–1.60 (m, 2H); FAB MS: m/z: calcd for $C_{65}H_{80}N_6NaO_{27}$: 1399.4969; found: 1399.9923 $[M+Na]^+$.

***n*-Pentenyl (3,6-di-*O*-acetyl-2-azido-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(methyl 2-*O*-acetyl-3-*O*-benzyl-*α*-L-idopyranosyluronate)-(1→4)-(6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-2-*O*-monochloroacetyl-*β*-D-glucopyranosyluronate (82)**: Compound **79** (60 mg, 0.21 mmol) was dissolved in THF (26 mL). Glacial acetic acid (6.4 mL) and HF/pyridine complex (3.8 mL) were added and the solution was stirred at room temperature for three days. The mixture was poured into EtOAc and washed with brine, water, sat. $NaHCO_3$ and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 5:3) afforded **82** (247 mg, 85%). $[\alpha]_D^{24}$ = +20.4 (c = 1.00, $CHCl_3$); IR (thin film on NaCl): $\tilde{\nu}$ = 3510, 2924, 2109, 1742 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39–7.27 (m, 20H), 5.80–5.75 (m, 1H), 5.44 (d, J = 3.7 Hz, 1H), 5.31 (d, J = 4.9 Hz, 1H), 5.22 (t, J = 10.2 Hz, 1H), 5.16–5.12 (m, 2H), 5.07–4.83 (m, 5H), 4.73–4.64 (m, 5H), 4.57–4.52 (d, 1H), 4.37 (d, 1H), 4.34–4.25 (m, 3H), 4.08 (m, 1H), 4.00–3.95 (m, 3H), 3.90–3.81 (m, 6H), 3.80–3.72 (m, 2H), 3.69 (s, 3H), 3.67 (s, 3H), 3.60–3.53 (m, 1H), 3.51–3.42 (m, 1H), 3.27 (dd, J = 3.7, 10.7 Hz, 1H), 3.17 (dd, J = 3.7, 10.7 Hz, 1H), 3.07 (br s, 1H), 2.14 (s, 3H), 2.13 (s, 3H), 2.12 (s, 3H), 2.05–2.01 (m, 2H), 2.08 (s, 3H), 1.74–1.60 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.9, 171.3, 171.1, 170.3, 169.7, 168.6, 165.9, 138.0, 137.7, 137.4, 115.3, 100.9, 98.6, 98.4, 97.6, 82.5, 78.2, 75.8, 75.7, 75.1, 75.0, 74.9, 74.7, 74.6, 74.0, 73.8, 72.4, 71.4, 70.2, 70.1, 69.8, 69.5, 68.9, 63.3, 62.5, 61.9, 61.1, 52.9, 52.4, 40.6, 30.0, 28.7, 21.0, 21.0, 20.9; FAB MS: m/z: calcd for $C_{62}H_{75}ClN_6O_{26}$: 1354.4420; found: 1354.441 $[M]^+$.

***n*-Pentenyl (6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(methyl 2-*O*-acetyl-3-*O*-benzyl-*α*-L-idopyranosyluronate)-(1→4)-(6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-**

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methyl 3-*O*-benzyl-2-*O*-levulinoyl-*β*-*O*-pentenyl-D-glucopyranosyluronate (83): Compound **80** (70 mg, 0.045 mmol) was dissolved in THF (5.3 mL). Glacial acetic acid (1.3 mL) and HF/pyridine complex (0.8 mL) were added and the solution was stirred at room temperature for three days. The mixture was poured into EtOAc and washed with brine, water, sat. $NaHCO_3$ and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 5:3) afforded **83** (50 mg, 75 %). ^{1}H NMR (500 MHz, $CDCl_3$) $\delta =$ 7.40–7.25 (m, 20H), 5.82–5.76 (m, 1H), 5.48 (d, $J = 3.6$ Hz, 1H), 5.25 (d, $J = 4.6$ Hz, 1H), 5.07–4.89 (m, 6H), 4.84 (s, 2H), 4.80–4.68 (m, 5H), 4.63 (d, $J = 4.3$ Hz, 1H), 4.51 (dd, $J = 3.5$, 12.5 Hz, 1H), 4.47 (d, $J = 7.3$ Hz, 1H), 4.34–4.32 (m, 1H), 4.26–4.20 (m, 2H), 4.09 (dd, $J = 2.1$, 12.5 Hz, 1H), 4.04 (t, $J = 5.5$ Hz, 1H), 4.00 (d, $J = 9.5$ Hz, 1H), 3.95 (t, $J = 5.5$ Hz, 1H), 3.88–3.82 (m, 3H), 3.78–3.71 (m, 3H), 3.69–3.64 (m, 4H), 3.57 (s, 3H), 3.48–3.43 (m, 2H), 3.27 (d, $J = 3.6$, 10.1 Hz, 1H), 3.21 (d, $J = 3.4$, 10.1 Hz, 1H), 2.91 (d, $J = 4.0$ Hz, 1H), 2.68 (t, $J = 6.7$ Hz, 2H), 2.56–2.45 (m, 2H), 2.14 (s, 6H), 2.12–2.05 (m, 8H), 1.69–1.62 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta =$ 206.2, 172.1, 171.4, 171.0, 170.0, 169.6, 168.9, 138.1, 138.0, 137.9, 137.5, 129.2, 129.0, 128.8, 128.7, 128.6, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 115.1, 101.2, 98.4, 98.2, 97.4, 82.5, 78.8, 78.2, 77.4, 75.7, 75.3, 75.2, 75.0, 74.5, 74.4, 73.9, 73.6, 73.4, 71.1, 70.5, 70.2, 70.0, 69.7, 69.4, 63.2, 62.8, 62.7, 61.9, 52.8, 52.2, 37.9, 30.0, 28.7, 28.0, 21.1, 20.9; FAB MS: *m*/*z*: calcd for $C_{70}H_{84}N_6NaO_{26}$: 1447.5327; found: 1447.5378 $[M+Na]^+$.

***n*-Pentenyl (6-*O*-acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-*α*-D-glucopyranosyluronate 1,2)-(3,6-di-*O*-acetyl-2-azido-2-deoxy-*α*-D-glucopyranos-4-yl-monochloro orthoacetate)-(1→4)-(methyl 2-*O*-acetyl-3-*O*-benzyl-*α*-L-idopyranosyluronate)-(1→4)-(6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-2-*O*-monochloroacetyl-*β*-D-glucopyranosyluronate (88)**: Compounds **58** (82 mg, 0.09 mmol) and **82** (70 mg, 0.05 mmol) were coevaporated with toluene and dried under vacuum for 1 h. The mixture was dissolved in CH_2Cl_2 (1 mL) and after cooling to $-25\,^\circ$C, TMSOTf (20 μL, 0.1M in CH_2Cl_2) was added. The mixture was stirred for 2 h and then diluted with CH_2Cl_2 and filtered through a pad of Celite. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (toluene/EtOAc 95:5→80:20) to yield **88** (33 mg, 30 %) as a syrup. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta =$ 7.39–7.16 (m, 30H), 6.43 (d, $J = 3.7$ Hz, 1H), 6.10 (d, $J = 3.4$ Hz, 1H), 5.73–5.82 (m, 1H), 5.34 (d, $J = 4.6$ Hz, 1H), 5.30 (t, 1H), 5.09–5.01 (m, 1H), 4.98–4.82 (m, 8H), 4.71–4.56 (m, 8H), 4.47 (dd, $J = 0.9$, 7.3 Hz, 1H), 4.40 (dd, 1H), 4.39–4.14 (m, 8H), 4.07 (t, 1H), 3.99–3.89 (m, 6H), 3.88–3.82 (m, 6H), 3.79–3.63 (m, 5H), 3.69 (s, 3H), 3.66 (s, 3H), 3.57–3.44 (m, 3H), 3.39 (dd, $J = 2.7$, 9.5 Hz, 1H), 3.30 (dd, $J = 3.0$, 10.3 Hz, 1H), 3.21 (dd, 1H), 2.36 (s, 3H), 2.14 (s, 3H), 2.10 (s, 3H), 2.06–2.02 (m, 2H), 2.01 (s, 3H), 1.92 (s, 3H), 1.66–1.61 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 170.6, 170.9, 169.8, 169.1, 138.5, 138.4, 138.1, 138.0, 136.9, 129.4, 129.3, 129.2, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 128.2, 127.9, 122.5, 115.8, 101.5, 99.9, 83.0, 80.6, 78.4, 78.3, 77.9, 76.3, 75.8, 75.6, 75.4, 75.1, 73.4, 71.1, 70.3, 70.1, 63.9, 63.3, 53.4, 53.2, 53.2, 53.0, 41.2, 30.5, 29.2, 21.6, 21.5, 21.4; ES MS: *m*/*z*: calcd for $C_{100}H_{115}Cl_2N_9O_{38}$: 1082.9085; found: 1082.9109 $[M+2H]^{2+}$.

***tert*-Butyldimethylsilyl 6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-levulinoyl-*β*-D-glucopyranoside (89)**: Levulinic anhydride (1.86 g, 8.71 mmol) was added to a solution of **6** (1.97 g, 4.35 mmol) and 4-(dimethylamino)-pyridine (1.59 g, 13.05 mmol) in CH_2Cl_2 (30 mL). After stirring at room temperature for 5 h, the mixture was poured into EtOAc and extracted with 1N HCl, brine and sat. $NaHCO_3$. The organic phase was dried over Na_2SO_4, filtered and the solvents were removed under reduced pressure. The crude product was purified by silica gel column chromatography (hexanes/EtOAc 99:1→90:10) to afford **89** (2.3 g, 4.18 mmol, 96 %) as a colorless oil. $[\alpha]_D^{24} = -58$ ($c = 3.00$, CH_2Cl_2); IR (thin film): $\tilde{\nu} =$ 2110, 1746, 1719, 1363 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.20–7.10 (m, 5H), 4.82–4.80 (m, 1H), 4.66–4.48 (dd, $J = 11.5$, 50 Hz, 2H), 4.39 (t, $J = 4$ Hz, 1H), 4.01–3.91 (m, 2H), 3.42–3.38 (m, 1H), 3.26–3.22 (m, 2H), 2.59–2.46 (m, 2H), 2.19–2.31 (m, 2H), 1.99 (s, 3H), 1.89 (s,9H) (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 206.5, 172.0, 171.0, 138.2, 128.8, 128.7, 128.3, 128.2, 127.4, 127.2, 97.6, 80.2, 76.0, 75.2, 72.5, 71.4, 70.4, 68.6, 67.3, 63.0, 38.2, 37.9, 30.1, 28.2, 25.9, 21.2, 18.4, −4.0, −4.9; FAB MS: *m*/*z*: calcd for $C_{26}H_{39}N_3O_8Si$: 572.2398; found: 572.2391 $[M]^+$.

6-*O*-Acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-levulinoyl-*α*/*β*-D-glucopyranosyl trichloroacetimidate (90): A solution of **89** (2.18 g, 3.97 mmol) was dissolved in THF (30 mL) and cooled to 0 °C. A solution of glacial acetic acid (280 μL, 4.79 mmol) and TBAF (1M in THF) (4.4 mL, 4.4 mmol) was added to the reaction mixture. After 30 min, the mixture was poured into Et_2O (300 mL) and washed three times with brine. The organic layer was dried over Na_2SO_4, filtered and the solvents were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (100 mL) and cooled to 0 °C. Trichloroacetonitrile (6 mL, 59.8 mmol) and DBU (60 μL, 0.4 mmol) were added at 0 °C. After stirring the mixture for 1 h at 0 °C it was concentrated under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 8:2 then 6:4) afforded **90** (2.0 g, 3.45 mmol, 87 %) as a mixture of anomers (27/73) as a colorless oil. Compounds **90*α*** and **90*β*** were separated by silica gel column chromatography (toluene/EtOAc 99:1 to 90:1). Compound **90*α***: $[\alpha]_D^{24} = 57$ ($c = 1$, CH_2Cl_2); IR (thin film): $\tilde{\nu} =$ 3300, 2112, 1744, 1152 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 8.78 (s, 1H), 7.39–7.29 (m, 5H), 6.44 (d, $J = 1.0$ Hz, 1H), 4.72–4.89 (m, 2H), 4.02–4.25 (m, 3H), 3.77 (dd, $J = 3.5$, 11.0 Hz, 1H), 2.69–2.74 (m, 2H), 2.39–2.58 (m, 2H), 2.17 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta =$ 206.3, 171.7, 170.9, 161.2, 137.6, 128.7, 128.3, 128.2, 96.7, 80.3, 75.3, 73.2, 69.7, 68.6, 68.0, 38.0, 28.0, 21.0; FAB MS: *m*/*z*: calcd for $C_{22}H_{25}Cl_3N_4O_8$: 601.0636; found: 601.0629. Compound **90*β***: $[\alpha]_D^{24} = -31$ ($c = 1.00$, CH_2Cl_2); IR (thin film): $\tilde{\nu} =$ 3329, 2111, 1744, 1718, 1676 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 8.77 (s, 1H), 7.39–7.28 (m, 5H), 5.64 (d, $J = 8.0$ Hz, 1H), 5.14 (t, $J = 10.0$ Hz, 1H), 4.84 (d, $J = 11.0$ Hz, 1H), 4.73 (d, $J = 11.0$ Hz 1H), 4.26 (dd, $J = 5.0$, 8.0 Hz, 1H), 4.12 (dd, $J = 2.0$, 10.0 Hz, 2H), 3.77–3.70 (m, 2H), 3.57 (t, $J = 9.0$ Hz, 1H), 2.77–2.63 (m, 2H), 2.54–2.33 (m, 2H), 2.17 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta =$ 206.3, 171.7, 170.9, 161.2, 137.6, 128.7, 128.3, 128.2, 96.7, 80.3, 75.3, 73.2, 69.7, 65.6, 68.0, 38.0, 28.0, 21.0; FAB MS: *m*/*z*: calcd for $C_{22}H_{25}Cl_3N_4O_8$: 601.0636; found: 601.0626 $[M]^+$.

6-*O*-Acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-levulinoyl-*α*-D-glucopyranosyl-(1→4)-methyl 3-*O*-benzyl-1,2-*O*-isopropylidene-*β*-L-idopyranosyluronate (91): Compound **90** (666 mg, 1.14 mmol) and **35** (300 mg, 0.90 mmol) were coevaporated three times with toluene and dissolved in anhydrous CH_2Cl_2 (30 mL). Freshly activated molecular sieves 4 Å (600 mg) were added and the mixture was stirred at room temperature for 1 h. The mixture was cooled to $-78\,^\circ$C and *tert*-butyldimethylsilyl trifluoromethanesulfonate 0.1M in CH_2Cl_2 (1.2 mL, 0.12 mmol) was added dropwise. This mixture was stirred for 4 h, while it was allowed to warm to room temperature. Triethylamine (3 mL) was added and the mixture was filtered through Celite and evaporated. Flash chromatography (hexanes/EtOAc 70:30) afforded **91** (558 g, 0.72 mmol, 83 %) as a colorless foam. $[\alpha]_D^{24} = 34$ ($c = 1.00$, CH_2Cl_2); IR (thin film): $\tilde{\nu} =$ 2109, 1744, 1720, 1235 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.40–7.27 (m, 10H), 5.36 (d, $J = 2.4$ Hz, 1H), 5.10 (t, 1H), 4.73 (d, $J = 11.0$ Hz, 1H), 4.44 (d, $J = 11.0$ Hz, 1H), 4.23 (t, $J = 3.0$ Hz, 1H), 4.15 (m, 2H), 4.18–4.09 (m, 2H), 3.78 (s, 3H), 3.48 (dd, $J = 3.0$, 10.0 Hz, 1H), 2.67 (t, 2H), 3.34–3.48 (m, 2H), 2.16 (s, 3H), 2.06 (s, 3H), 1.64 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 206.3, 171.6, 170.9, 169.1, 137.7, 137.1, 128.6, 128.5, 128.4, 128.1, 98.7, 97.2, 75.4, 75.0, 74.4, 73.1, 70.0, 69.4, 64.0, 62.0, 52.6, 37.9, 30.0, 28.3, 28.0, 26.3, 21.0; FAB MS: *m*/*z*: calcd for $C_{37}H_{45}N_3O_{14}$: 778.2794; found: 778.2765 $[M]^+$.

6-*O*-Acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-levulinoyl-*α*-D-glucopyranosyl-(1→4)-methyl 3-*O*-benzyl-L-idopyranosyluronate (92): A solution of **91** (500 mg, 0.66 mmol) in dichloroacetic acid (15 mL, 60 % aq) was stirred for 3 h at room temperature. After dilution with water, the solution was cooled to 0 °C and neutralized with $NaHCO_3$ (9 g). The mixture was diluted with CH_2Cl_2 and the two phases were separated. The organic phase was washed with sat. $NaHCO_3$ and dried over $MgSO_4$. After filtration the solvent was removed under reduced pressure to afford **92** (424 mg, 91 %) as a white solid. Compound **92** can be further purified by silica gel column chromatography (hexane/EtOAc 6:5). FAB MS: *m*/*z*: calcd for $C_{34}H_{41}N_3O_{14}Si$: 715.2589; found: 715.2593 $[M]^+$.

***tert*-Butyldimethylsilyl (6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-methyl-3-*O*-benzyl-2-*O*-acetyl-*β*-D-idopyranosyluronate (93)**: A solution of **92** (883 mg, 1.23 mmol) and imidazole (336 mg, 4.94 mmol) in CH_2Cl_2 (10 mL) was cooled to $-15\,^\circ$C. *tert*-Butyldimethylsilylchloride (279 mg, 1.60 mmol) was added and the reaction mixture was kept at $-15\,^\circ$C. After 5 h *tert*-butyldimethylsilylchloride (186 mg, 1.23 mmol) was added. After 40 h water was added and the reaction mixture was warmed to room temperature. After dilution with EtOAc the mixture was washed with brine. The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 85:5→70:30) afforded *tert*-butyldime-

thylsilyl (6-*O*-acetyl-2-azido-3-benzyl-4-*O*-levulinoyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-methyl-3-*O*-benzyl-β-D-idopyranosyluronate (752 mg, 0.92 mmol, 80%) as a colorless foam.

Pyridine (1.70 mL, 20.4 mmol), acetic anhydride (1.17 mL, 12.5 mmol) and DMAP (7 mg, 0.06 mmol) were added to a solution of *tert*-butyldimethylsilyl (6-*O*-acetyl-2-azido-3-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-methyl-3-*O*-benzyl-β-D-idopyranosyluronate (520 mg, 0.63 mmol) in CH_2Cl_2 (12 mL). After 6 h at room temperature, water was added and the mixture was stirred for 1 h. The organic phase was washed with sat. $NaHCO_3$, water, and HCl (10% aqueous) and dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure and the crude was purified by silica gel column chromatography (hexanes/EtOAc 90:20) to yield *tert*-butyldimethylsilyl (6-*O*-acetyl-2-azido-3-benzyl-2-deoxy-4-*O*-levulinoyl-α-D-glucopyranosyl)-(1→4)-methyl-2-*O*-acetyl-3-*O*-benzyl-β-D-idopyranosyluronate (532 mg, 97%) as a colorless syrup. Hydrazine hydrate (83 μL, 1.2 mmol) was added at 0 °C to a solution of *tert*-butyldimethylsilyl (6-*O*-acetyl-2-azido-3-benzyl-2-deoxy-4-*O*-levulinoyl-α-D-glucopyranosyl)-(1→4)-methyl-2-*O*-acetyl-3-*O*-benzyl-β-D-idopyranosyluronate (200 mg, 0.23 mmol) in pyridine/acetic acid 3:2 (4 mL). After 15 min, acetone (0.5 mL) was added, and the mixture was stirred for 15 min at room temperature. After evaporation the crude product was purified by flash chromatography on silica gel (hexanes/EtOAc 85:15) to afford **93** (138 mg, 0.18 mmol, 78%) as a colorless foam.

n*-Pentenyl-6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-levulinoyl-β-D-glucopyranoside (95)**: Compound **90*α (380 mg, 0.66 mmol) was dissolved in CH_2Cl_2 (1 mL). Hexanes (10 mL) and 4-penten-1-ol (75 μL, 0.73 mmol) were added. The reaction mixture was cooled to −10 °C before $BF_3 \cdot EtO_2$ (98.3 μL, 0.066 mmol) was added. The reaction mixture was stirred for 30 min and then triethylamine (1 mL) was added. The solvent was removed under reduced pressure and the crude was purified by flash chromatography on silica gel (hexanes/EtOAc 80:20) to obtain **95** (29 mg, 75%) as a colorless oil. $[\alpha]_D^{24} = -30$ ($c = 1.00$, CH_2Cl_2); IR (thin film): $\tilde{\nu} = 2111, 1744, 1718\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.38-7.28$ (m, 5H), 5.88–5.77 (m, 1H), 5.08–4.97 (m, 3H), 4.81 (d, $J = 11.0$ Hz, 1H), 4.66 (d, $J = 11.0$ Hz 1H), 4.29 (d, $J = 8.0$ Hz, 1H), 4.22 (dd, $J = 5.0, 7.0$ Hz, 1H), 4.10 (dd, $J = 2.0, 10.0$ Hz, 1H), 3.96–3.90 (m, 1H), 3.60–3.52 (m, 2H), 3.48–3.38 (m, 2H), 2.76–2.61 (m, 2H), 2.53–2.33 (m, 2H), 2.23–2.17 (m, 3H), 2.16 (s, 3H), 2.07 (s, 3H), 1.81–1.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 206.4, 171.7, 170.9, 138.1, 137.9, 128.6, 128.2, 128.1, 115.3, 102.4, 80.2, 75.1, 72.2, 70.2, 70.0, 66.2, 62.4, 38.0, 30.2, 30.0, 28.9, 28.0, 21.0$; FAB MS: *m*/*z*: calcd for $C_{25}H_{33}N_3O_8$: 526.2160; found: 526.2149 $[M^+$

***n*-Pentenyl-6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-β-D-glucopyranoside (96)**: A solution of hydrazine acetate (8.1 mg, 0.088 mmol) in methanol (1 mL) was added to a solution of **95** (90 mg, 0.08 mmol) in CH_2Cl_2 (8 mL). After stirring the reaction mixture under nitrogen atmosphere for 1 h, acetone (1.5 mL) was added and the solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (hexanes/EtOAc 60:40) to afford **96** (29 mg, 0.007 mmol, 91%) as a colorless oil. $[\alpha]_D^{24} = -30$ ($c = 1.00$, CH_2Cl_2); IR (thin film): $\tilde{\nu} = 3426, 2109, 1740, cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.41-7.31$ (m, 5H), 5.88–5.78 (m, 1H), 5.04–4.97 (m, 3H), 4.94 (d, $J = 11.0$ Hz, 1H), 4.76 (d, $J = 11.0$ Hz 1H), 4.45 (dd, $J = 4.0, 8.0$ Hz, 1H), 4.30–4.23 (m, 2H), 3.97–3.92 (m, 1H), 3.60–3.22 (m, 2H), 3.48–3.38 (m, 2H), 2.63 (s, 1H), 2.21–2.12 (m, 2H), 2.11 (s, 3H), 1.84-.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 129.1, 128.7, 115.5, 102.8, 82.5, 75.7, 74.1, 70.3, 66.3, 63.4, 30.5, 29.1, 21.3$; FAB MS: *m*/*z*: calcd for $C_{20}H_{27}N_3O_6$: 428.1702; found: 428.1791 $[M]^+$.

6-*O*-Acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-levulinoyl-α-D-glucopyranosyl-(1→4)-methyl 2-*O*-acetyl-3-*O*-benzyl-α/β-L-idopyranosyl) trichloroacetimidate (97): Pyridine (0.23 mL, 2.7 mmol), acetic anhydride (0.16 mL, 1.7 mmol) and DMAP (1 mg, 0.086 mmol) were added to a solution of **92** (600 mg, 0.86 mmol) in CH_2Cl_2 (15 mL). After 6 h at room temperature, water was added and the mixture was stirred for 1 h. The organic phase was washed with sat. $NaHCO_3$, water, and HCl (10% aqueous) and dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography (hexanes/EtOAc 90:20) to yield 6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-levulinoyl-α-D-glucopyranosyl-(1→4)-methyl 1,2-di-*O*-acetyl-3-*O*-benzyl-α/β-L-idopyranosyluronate (671 mg, 95%) as a colorless syrup. FAB MS: *m*/*z*: calcd for $C_{38}H_{45}N_3O_{16}$: 822.2692; found: 822.2703 $[M]^+$.

Benzylamine (250 μL, 2.25 mmol) was added in three portions, every 2 h, to a solution of 6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-levulinoyl-α-D-glucopyranosyl-(1→4)-methyl 1,2-di-*O*-acetyl-3-*O*-benzyl-α/β-L-idopyranosyluronate (300 mg, 0.37 mmol) in Et_2O (10 mL) at 0 °C and kept overnight at −20 °C. The mixture was diluted with CH_2Cl_2, filtered and washed with aqueous HCl (10%) The organic phase was dried over $MgSO_4$ and purified by silica gel column chromatography (hexanes/EtOAc 90:10→80:20) to yield 6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-levulinoyl-α-D-glucopyranosyl-(1→4)-methyl 2-*O*-acetyl-3-*O*-benzyl-α/β-L-idopyranosyluronate (226 mg, 80%).

A solution of 6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-levulinoyl-α-D-glucopyranosyl-(1→4)-methyl 2-*O*-acetyl-3-*O*-benzyl-α/β-L-idopyranosyluronate (400 mg, 0.292 mmol) and trichloroacetonitrile (1.1 mL, 10.4 mmol) in CH_2Cl_2 (15 mL) containing freshly activated powdered 4 Å molecular sieves (100 mg) was stirred 30 minutes at room temperature. After cooling the solution to 0 °C DBU (8 μL, 0.052 mmol) was added. The temperature was allowed to rise and after 1 h stirring, the mixture was filtered through a pad of Celite and concentrated. The residue was purified by silica gel column chromatography (hexanes/EtOAc 85:15) to yield **97** (281 mg, 61%) as a white solid. FAB MS: *m*/*z*: calcd for $C_{38}H_{43}Cl_3N_4O_{15}$: 923.1682; found: 923.1691 $[M]^+$.

***n*-Pentenyl (6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-(methyl 2-*O*-acetyl-3-*O*-benzyl-α-L-idopyranosyl)-(1→4)-6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranoside (98)**: A mixture of **97** (77 mg, 0.086 mmol) and **96** (60 mg, 0.066 mmol) was coevaporated three times with toluene and dried under vacuum for 1 h. The mixture was dissolved in CH_2Cl_2 (1 mL) and was stirred for 30 min at room temperature under nitrogen. After cooling the mixture to −45 °C, TMSOTf (86 μL, 0.1M in CH_2Cl_2) was added dropwise. The mixture was stirred for 1 h and triethylamine was added. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (hexanes/EtOAc 80:20→60:40) to yield *n*-pentenyl (6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-levulinoyl-β-D-glucopyranosyl)-(1→4)-(methyl 2-*O*-acetyl-3-*O*-benzyl-α-L-idopyranosyl)-(1→4)-6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranoside (44 mg, 0.038 mmol, 58%). $[\alpha]_D^{24} = 30$ ($c = 1.00$, CH_2Cl_2); IR (thin film): $\tilde{\nu} = 3430, 2110, 1742, 1233, 1037\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.41-7.28$ (m, 15H), 5.87–5.77 (m, 1H), 5.19 (d, $J = 3.0$ Hz, 1H), 5.10–4.97 (m, 3H), 4.95 (d, $J = 4.0$ Hz, 1H), 4.91 (t, $J = 3.0$ Hz, 1H), 4.79–4.63 (m, 5H), 4.46 (dd, $J = 2.0, 10.0$ Hz, 1H), 4.25 (t, $J = 1$ Hz, 1H), 4.20 (dd, $J = 2.0, 4.0$ Hz, 1H), 4.15 (d, $J = 4.0$ Hz, 1H), 4.07–4.01 (m, 2H), 3.94–3.77 (m, 6H), 3.57–3.53 (m, 1H), 3.51 (s, 3H), 3.47–3.41 (m, 2H), 3.37–3.28 (m, 2H), 2.71–2.67 (m, 2H), 2.52–2.36 (m, 2H), 2.16 (s, 3H), 2.13 (s, 3H), 2.09 (s, 3H), 2.03 (s, 3H), 1.80–1.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 206.3, 171.6, 170.9, 170.8, 170.1, 169.3, 138.2, 138.1, 137.5, 137.4, 128.7, 128.6, 128.4, 128.3, 128.3, 128.1, 128.0, 127.7, 127.6, 115.3, 102.4, 98.2, 97.4, 81.2, 77.3, 75.2, 74.8, 70.1, 69.0, 68.8, 68.4, 66.4, 62.9, 62.5, 61.7, 52.2, 37.9, 29.9, 28.8, 27.9, 21.2, 20.9$ FAB MS: *m*/*z*: calcd for $C_{56}H_{68}N_6O_{20}$: 1167.4380; found: 1167.4415 $[M]^+$.

A solution of hydrazine acetate (8.1 mg, 0.088 mmol) in methanol (1 mL) was added to a solution of *n*-pentenyl (6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-levulinoyl-β-D-glucopyranosyl)-(1→4)-(methyl 2-*O*-acetyl-3-*O*-benzyl-α-L-idopyranosyl)-(1→4)-6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranoside (90 mg, 0.08 mmol) in CH_2Cl_2 (8 mL). After stirring the reaction mixture under nitrogen atmosphere for 1 h, acetone (1.5 mL) was added and the solvent was removed under reduced pressure and the crude was purified by flash chromatography on silica gel (hexanes/EtOAc 60:40) to afford **98** (64 mg, 0.062 mmol, 77%) as a colorless foam. $[\alpha]_D^{24} = -5$ ($c = 1.00$, CH_2Cl_2); IR (thin film): $\tilde{\nu} = 3426, 2109, 1741, 1235\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.41-7.28$ (m, 15H), 5.87–5.77 (m, 1H), 5.20 (d, $J = 3.0$ Hz, 1H), 5.07–4.97 (m, 2H), 4.94 (d, $J = 4.0$ Hz, 1H), 4.91 (t, $J = 3.0$ Hz, 1H), 4.88–4.67 (m, 7H), 4.54 (dd, $J = 3.0, 11.0$ Hz, 1H), 4.44 (dd, $J = 2.0, 10.0$ Hz, 1H), 4.26–4.20 (m, 2H), 4.14–4.04 (m, 2H), 3.95–3.84 (m, 3H), 3.83–3.63 (m, 2H), 3.57–3.53 (m, 2H), 3.52 (s, 3H), 3.47–3.28 (m,4H), 3.21 (dd, $J = 4.0, 7.0$ Hz, 1H), 2.87 (d, $J = 4.0$ Hz, 1H), 2.16–2.13 (m, 1H), 2.09 (s, 3H), 2.08 (s, 6H), 1.78–1.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 172.3, 170.2, 169.5, 138.2, 138.1, 137.9, 137.5, 128.9, 128.7, 128.5, 128.5, 128.4, 128.3, 128.1, 127.9, 127.7, 115.3, 102.4, 98.3, 98.1, 81.3, 78.9, 75.3, 74.0, 73.3, 73.2, 71.2, 70.6, 69.2, 68.8, 66.4, 63.0, 62.7, 62.5, 52.2, 30.2, 28.9, 21.1, 21.0$; FAB MS: *m*/*z*: calcd for $C_{51}H_{62}N_6O_{18}$: 1069.4013; found: 1069.4055 $[M]^+$.

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2-Azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-levulinoyl-α-D-glucopyranosyl trichloroacetimidate (100): Levulinic anhydride (1.4 g, 6.5 mmol) was added to a solution of **8** (1.4 g, 3.1 mmol) and DMAP (1.2 g, 9.8 mmol) in CH_2Cl_2 (30 mL). After stirring at room temperature for 5 h, the mixture was poured into EtOAc and extracted with 1N HCl, brine and sat. $NaHCO_3$. The organic phase was dried over Na_2SO_4, filtered and the solvents were removed under reduced pressure. The mixture was purified by silica gel column chromatography (hexanes/EtOAc 8:2) to afford *tert*-butyldimethylsilyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-levulinoyl-β-D-glucopyranoside (1.81 g, 3.0 mmol, 98%) as a colorless foam. $[\alpha]_D^{24} = +22$ ($c = 1.00$, CH_2Cl_2); IR (thin film): $\tilde{\nu} = 2111$, 1468, 1365, 1752, cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.38-7.27$ (m, 10H), 4.80–4.85 (m, 1H), 4.63 (d, $J = 11.1$ Hz, 1H), 4.46 (d, $J = 11.1$ Hz, 1H), 4.42–4.31 (m, 3H), 3.40–3.35 (m,3H), 3.25–3.20 (m, 2H), 2.51–2.35(m, 2H), 2.22–2.08 (m, 2H), 1.91 (s, 3H), 0.7 (s, 9H), 0.1 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 206$, 172.0, 138.5, 138.4, 129.0, 128.8, 128.8, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 97.6, 97.6, 82.7, 80.4, 75.1, 74.1, 73.9, 72.3, 71.5, 70.0, 68.7, 68.5, 66.9, 38.3, 38.1, 30.3, 30.2, 28.4, 28.2, 26.0, 25.9, 18.4, −3.8, −4.8; FAB MS: *m*/*z*: calcd for $C_{31}H_{43}N_3NaO_7Si$: 620.2762; found: 620.2738 $[M+Na]^+$.

tert-Butyldimethylsilyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-levulinoyl-β-D-glucopyranoside (1.4 mg, 2.4 mmol) was dissolved in THF (25 mL) and cooled to 0 °C. TBAF (1.0 M in THF, 2.8 mL) and glacial acetic acid (180 μL, 2.5 mmol) were added dropwise simultaneously. The reaction mixture was warmed to room temperature, stirred for 1.5 h and after dilution with CH_2Cl_2 was washed with sat. $NaHCO_3$. The organic phase was dried over $MgSO_4$ and after filtration the solvent was removed under reduced pressure. The crude material was dried by coevaporation with toluene and under vacuum. Trichloroacetonitrile (2.6 mL, 25 mmol) and freshly activated 4 Å powdered molecular sieves (300 mg) were added at a solution of the crude material in CH_2Cl_2 (25 mL) and the mixture was stirred for 30 minutes at room temperature. The reaction mixture was cooled to 0 °C and DBU (37 μL, 0.25 mmol) was added. After five minutes the ice bath was removed and the reaction mixture was stirred for 1 h. After filtration through a pad of Celite the solvent as removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 85:15 with 5% triethylamine) afforded **100** (1.46 g, 2.34 mmol, 86%). FAB MS: *m*/*z*: calcd for $C_{27}H_{29}Cl_3N_4NaO_7$: 649.0994; found: 649.1016 $[M+Na]^+$.

2-Azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucopyranosyluronate (101): Compound **100** (242 mg, 0.39 mmol) and **31** (100 mg, 0.29 mmol) were coevaporated three times with toluene and dissolved in CH_2Cl_2 (1 mL). Freshly activated molecular sieves 4 Å (100 mg) were added and the mixture was stirred at room temperature for 1 h. This mixture was cooled to −25 °C and *tert*-butyldimethylsilyl trifluoromethanesulfonate 0.1M in anhydrous CH_2Cl_2 (39 μL, 0.039 mmol) was added dropwise. This mixture was stirred for 2.5 h, while it was allowed to warm to room temperature. Triethylamine (0.5 mL) was added and the mixture was filtered through Celite and evaporated. Flash chromatography (hexanes/EtOAc 85:15) afforded 2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-levulinoyl-α-D-glucopyranosyl-(1→4)-methyl 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucopyranosyluronate (211 mg, 0.26 mmol, 89%) as a colorless foam. $[\alpha]_D^{24} = +52$ ($c = 0.8$, CH_2Cl_2); IR (thin film on NaCl): $\tilde{\nu} = 2955$, 2935, 2858, 2110, 1753, cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.38-7.19$ (m, 15H), 5.79 (d, $J = 3.7$ Hz, 1H), 5.22–5.15 (m, 2H), 4.80 (d, $J = 11.2$ Hz, 1H), 4.66–4.58 (m, 4H), 4.48 (d, $J = 2.6$ Hz, 1H), 4.22–4.20 (m, 2H), 4.06 (t, $J = 3.7$ Hz, 1H), 4.00–3.8 (m, 2H), 3.62 (s, 3H), 3.57–3.47 (m, 2H), 3.35 (dd, $J = 3.4$, 10.1 Hz, 1H), 2.63–2.56 (m, 2H), 2.38–2.14 (m, 2H), 2.12 (s, 3H), 1.61 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (MHz, $CDCl_3$): $\delta = 206.6$, 171.8, 170.3, 138.3, 128.1, 137.5, 128.9, 128.8, 128.7, 128.5, 128.3, 128.3, 128.2, 127.9, 111.3, 98.3, 95.9, 76.0, 75.8, 74.8, 74.2, 74.0, 72.5, 72.2, 71.2, 70.1, 68.8, 63.0, 52.7, 38.1, 30.2. 28.2, 27.8, 26.2; FAB MS: *m*/*z*: calcd for $C_{42}H_{49}N_3NaO_{13}$: 826.3158; found: 826.3158 $[M]^+$.

Hydrazine hydrate (83 μL, 1.2 mmol) was added at 0 °C to a solution 2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-levulinoyl-α-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucopyranosyluronate (200 mg, 0.25 mmol) in pyridine/acetic acid 3:2 (4 mL). After 15 min, acetone (0.5 mL) was added, and the mixture was stirred for 15 min at room temperature. After evaporation the crude product was purified by flash chromatography (hexanes/EtOAc 85:15) afforded **101** (135 mg, 0.19 mmol, 77%) as a colorless foam. $[\alpha]_D^{24} = +61$ ($c = 1$, CH_2Cl_2); IR (thin film on NaCl): $\tilde{\nu} = 2953$, 2934, 2852, 2110, 1757 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.38-7.19$ (m, 15H), 5.74 (d, $J = 4.0$ Hz, 1H), 5.11 (d, $J = 3.6$ Hz, 1H), 4.88 (d, $J = 11.1$ Hz, 1H), 4.83 (d, $J = 11.1$ Hz, 1H), 4.67 (s, 2H), 4.61 (d, $J = 12.0$ Hz, 1H), 4.51 (d, $J = 12.0$ Hz, 1H), 4.49 (d, $J = 6.9$ Hz, 1H), 4.48–4.20 (m, 2H), 4.05 (t, $J = 3.7$ Hz, 1H), 3.84–3.71 (m, 4H), 3.65 (s, 3H), 3.63–3.55 (m, 1H), 3.33 (dd, $J = 3.3$, 10.1 Hz, 1H), 2.82 (s, 1H), 1.63 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (MHz, $CDCl_3$) $\delta =$ 170.2, 138.2, 137.8, 137.4, 128.8, 128.7, 128.7, 128.3, 128.2, 128.1, 127.9, 111.0, 98.0, 96.1, 79.3, 77.5, 76.9, 76.5, 75.7, 75.2, 73.9, 73.7, 72.6, 72.2, 71.6, 70.5, 69.7, 62.6, 52.6, 27.4, 25.9; FAB MS: *m*/*z*: calcd for $C_{37}H_{43}N_3NaO_{11}$: 728.2790,; found: 728.2792 $[M]^+$.

2,3,4-*O*-Benzoyl-β-D-glucopyranosyluronate-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucopyranosyluronate (102): Compounds **94** (30 mg, 0.045 mmol) and **101** (20 mg, 0.03 mmol) were coevaporated three times with toluene and dried under vacuum for 1 h. The mixture was dissolved in CH_2Cl_2 (1 mL) and was stirred for 30 min at room temperature under nitrogen. After cooling the mixture to −25 °C, anhydrous TMSOTf (45 μL, 0.1M in CH_2Cl_2) was added. The mixture was stirred for 2 h at −10 °C and overnight at −20 °C, and then diluted with CH_2Cl_2 and filtered. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (toluene/EtOAc 95:5→80:20) to yield **102** (20 mg, 59%) as a syrup. $[\alpha]_D^{24} = +91$ ($c = 1.00$, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.83-7.80$ (m, 9H), 7.54–7.27 (m, 21H), 5.61–5.57 (m, 3H), 5.52–5.47 (m, 1H), 5.27 (d, $J = 10.9$ Hz, 1H), 5.07 (d, $J = 3.7$ Hz, 1H), 4.86 (d, $J = 5.5$ Hz, 1H), 4.75 (d, $J = 8.0$ Hz, 1H), 4.67 (d, $J = 10.9$ Hz, 1H), 4.63 (s, 1H), 4.36 (d, $J = 12.1$ Hz, 1H), 4.30 (d, $J = 7.7$ Hz, 1H), 4.20–4.18 (m, 1H), 4.11–4.01 (m, 1H), 3.99–3.88 (m, 2H), 3.82–3.66 (m, 2H), 3.64–3.60 (m, 1H), 3.51 (s, 3H), 3.32 (m, 3H), 3.21 (s, 3H), 1.43 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 170.1, 167.0, 165.7, 165.3, 164.8, 137.3, 133.7, 133.6, 133.5, 130.0, 129.9, 129.9, 129.0, 128.9, 128.8, 128.7, 128.5, 128.5, 128.2, 128.1, 127.7, 110.8, 76.9, 74.0, 73.1, 72.2, 71.7, 70.8, 70.7, 70.6, 67.1, 62.6, 52.9, 52.1, 27.1, 25.8; FAB MS: *m*/*z*: calcd for $C_{65}H_{65}N_3O_{20}$: 1230.4054; found: 1230.4050 $[M]^+$.

Methyl 2-*O*-acetyl-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-β-L-idopyranosyluronate trichloroacetimidate (103): *tert*-Butyldimethylsilyl trifluoromethanesulfonate (448 μL, 1.95 mmol) was added under argon to a solution of methyl 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranosyluronate[2] (600 mg, 1.77 mmol) and 2,6-lutidine (522 μL, 4.48 mmol) in CH_2Cl_2 (4 mL). After stirring for 1 h at room temperature, the reaction mixture was quenched with the addition of sat. $NaHCO_3$. The mixture was diluted with CH_2Cl_2, the two phases were separated and the aqueous phase was extracted four times with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ and after filtration the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 20:1) afforded methyl 3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-1,2-*O*-isopropylidene-β-L-idopyranosyluronate (786 mg, 98%) as a colorless solid. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.39-7.32$ (m, 5H), 5.32 (d, $J = 2.4$ Hz, 1H), 4.68 (d, $J = 11.9$ Hz, 1H), 4.62 (d, $J = 11.9$ Hz, 1H), 4.38 (d, $J = 1.2$ Hz, 1H), 4.06 (m, 1H), 3.94 (br s, 1H), 3.82 (m, 1H), 3.76 (s, 3H), 1.59 (s, 3H), 1.38 (s, 3H), 0.82 (s, 9H), −0.06 (s, 3H), −0.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 169.8, 137.5, 128.8, 128.4, 128.1, 112.3, 96.9, 75.3, 75.1, 72.9, 72.7, 68.0, 52.3, 28.3, 26.6, 25.6, 18.0, −4.4, −5.3; FAB MS: *m*/*z*: calcd for $C_{23}H_{36}O_7Si$: 452.2230; found: 452.2211 $[M]^+$.

A solution of methyl 3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-1,2-*O*-isopropylidene-β-L-idopyranosyluronate (800 mg, 1.77 mmol) in dichloroacetic acid (40 mL, 60% aq) was stirred at room temperature for 3 h, diluted with water and neutralized with $NaHCO_3$ (24 g). The aqueous phase was washed three times with CH_2Cl_2 and the combined organic phases were dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure to afford methyl 3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-L-idopyranosyluronate (671 mg, 1.62 mmol, 92%) as a white solid. The compound can be further purified by silica gel column chromatography (hexanes/EtOAc 70:30). FAB MS: *m*/*z*: calcd for $C_{20}H_{32}O_7Si$: 412.1917; found: 412.1896 $[M]^+$.

Pyridine (3.0 mL, 36 mmol), acetic anhydride (2.0 mL, 21.7 mmol) and DMAP (17 mg, 0.145 mmol) were added to a solution of 3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-L-idopyranosyluronate (600 mg, 1.45 mmol) in CH_2Cl_2 (20 mL). The solution was stirred at room temperature for 6 h, water was added and the mixture was stirred for one additional hour. The organic phase was washed with saturated solution of $NaHCO_3$, water and 10% HCl, dried over $MgSO_4$ and filtered. The solvent was removed under

reduced pressure and the residue was purified by silica gel column chromatography (hexanes/EtOAc 90:20) to yield methyl 1,2-di-*O*-acetyl-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-α/β-L-idopyranosyluronate (708 mg, 1.42 mmol, 98%) as a colorless syrup. FAB MS: *m/z*: calcd for $C_{24}H_{36}O_9Si$: 496.2129; found: 496.2129 $[M]^+$.

Benzylamine (600 μL, 5.4 mmol) was added to a solution of methyl 1,2-di-*O*-acetyl-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-α/β-L-idopyranosyluronate (630 mg, 1.27 mmol) in Et_2O (40 mL) at 0 °C. After 6 h, the mixture was diluted with CH_2Cl_2, filtered and washed with aqueous HCl (10%). The organic phase was dried over $MgSO_4$ and after filtration, silica gel column chromatography (hexanes/EtOAc 90:10 → 80:20) afforded methyl 2-*O*-acetyl-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-L-idopyranosyluronate (432 mg, 0.95 mmol, 75%) as a white solid. FAB MS: *m/z*: calcd for $C_{22}H_{34}O_8Si$: 454.2023; found: 454.2016 $[M]^+$.

A solution of methyl 2-*O*-acetyl-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-L-idopyranosyluronate (500 mg, 1.10 mmol) in CH_2Cl_2 (25 mL) was cooled to 0 °C. Trichloroacetonitrile (1.7 mL, 17.0 mmol) and DBU (25 μL, 0.16 mmol) were added and after stirring the mixture at 0 °C for 1 h, the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 85:15 → 70:30) afforded **103** (606 mg, 92%) as a colorless foam. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.65 (s, 1H), 7.38–7.31 (m, 5H), 6.41 (s, 1H), 5.11 (m, 1H), 4.90 (d, J = 1.8 Hz, 1H), 4.80 (d, J = 11.9 Hz, 1H), 4.61 (d, J = 11.9 Hz, 1H), 4.12 (m, 1H), 3.78 (s, 3H), 3.66 (br s, 1H), 1.59 (s, 3H), 1.38 (s, 3H), 2.08 (s, 3H), 0.83 (s, 9H), −0.05 (s, 3H), −0.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.7, 170.0, 160.8, 138.0, 129.7, 129.1, 128.9, 128.7, 96.1, 74.2, 72.6, 71.3, 68.8, 66.1, 53.0, 26.2, 26.1, 21.7, 18.5, −3.9, −4.9; FAB MS: *m/z*: calcd for $C_{24}H_{34}Cl_3NO_8Si$: 597.119; found: 597.1143 $[M]^+$.

Methyl 2-*O*-acetyl-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-β-L-idopyranosyluronate-(1 → 4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1 → 4)-methyl 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucopyranosyluronate (104): Compounds **103** (27 mg, 0.045 mmol) and **101** (20 mg, 0.03 mmol) were coevaporated three times with toluene and dried under vacuum for 1 h. The mixture was dissolved in CH_2Cl_2 (1 mL) and was stirred for 30 min at room temperature under nitrogen. After cooling the mixture to −25 °C, TMSOTf (45 μL, 0.1M in CH_2Cl_2) was added, The mixture was stirred for 2 h at −10 °C and overnight at −20 °C, and then diluted with CH_2Cl_2 and filtered. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (toluene/EtOAc 95:5 → 80:20) to yield **104** (23 mg, 71%) as a syrup. $[\alpha]_D^{24}$ = +82 (c = 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.19 (m, 20H), 5.73 (d, J = 4.0 Hz, 1H), 5.36 (d, J = 4.9 Hz, 1H), 5.01 (d, J = 3.6 Hz, 1H), 4.92–4.86 (m, 2H), 4.68 (s, 2H), 4.65 (s, 2H), 4.60–4.52 (m, 4H), 4.21–4.16 (m, 2H), 4.04–3.94 (m, 3H), 3.84–3.68(m, 5H), 3.63–3.60 (m, 3H), 3.57 (s, 3H), 3.47 (s, 1H), 3.30 (dd, J = 3.1, 10.3 Hz, 1H), 1.82 (s, 1H), 1.56 (s, 3H), 1.35 (s, 3H), 0.77 (s, 6H), 0.1 (s, 3H), −0.1 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.4, 170.3, 170.2, 138.5, 138.3, 138.2, 137.5, 128.9, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 111.1, 98.0, 96.2, 78.1, 76.5, 75.9, 75.8, 73.8, 72.4, 71.8, 71.0, 70.0, 63.0, 52.7, 52.0, 27.7, 26.1, 25.9, 21.3, 18.2, −4.3, −4.9; FAB MS: *m/z*: calcd for $C_{59}H_{75}N_3NaO_{18}Si$: 1164.4707; found: 1164.4749 $[M+Na]^+$.

***n*-Pentenyl (methyl 2-*O*-acetyl-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-α-L-idopyranosyluronate)-(1 → 4)-(6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1 → 4)-methyl 3-*O*-benzyl-2-*O*-levulinoyl-β-D-glucopyranosiduronate (105)**: Compounds **103** (204 mg, 0.34 mmol) and **73** (206 mg, 0.26 mmol) were coevaporated three times with toluene and dissolved in anhydrous CH_2Cl_2 (3 mL). Freshly activated powdered 4 Å molecular sieves (200 mg) were added and the mixture was stirred at room temperature for 1 h. The reaction mixture was cooled to −25 °C and TMSOTf (340 μL, 0.1M in CH_2Cl_2) was added dropwise. The mixture was warmed to room temperature over 4 h. Triethylamine was added, the mixture was filtered through a pad of Celite and the solvent was removed under reduced pressure. Flash chromatography on silica gel (toluene/EtOAc 90:10 → 80:20) afforded **105** (298 mg, 0.24 mmol, 93%) as a syrup. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39–7.27 (m, 15H), 5.80–5.77 (m, 1H), 5.44 (d, J = 3.7 Hz, 1H), 5.32 (d, J = 5.8 Hz, 1H), 5.07–5.02 (m, 2H), 4.98–4.95 (m, 2H), 4.90–4.87 (m, 1H), 4.79 (d, J = 10.9 Hz, 1H), 4.73–4.66 (m, 4H), 4.49 (d, J = 5.2, 1H), 4.46 (d, J = 7.3 Hz, 1H), 4.38 (dd, 1H), 4.21–4.12 (m, 2H), 3.99–3.91 (m, 2H), 3.89–3.81 (m, 3H), 3.75 (m, 2H), 3.71 (s, 3H), 3.68 (m, 1H), 3.58 (s, 3H), 3.47–3.42 (m, 1H), 3.29 (dd, J = 3.3, 10.1 Hz, 1H), 2.68 (m, 2H), 2.56–2.43 (m, 2H), 2.14 (s, 3H), 2.12 (s, 3H), 2.07–2.04 (m, 2H), 2.00 (s, 3H), 1.57–1.17 (m, 2H), 0.83 (s, 9H), −0.01 (s, 3H), −0.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 206.2, 171.4, 170.9, 170.4, 170.1, 168.9, 138.1, 138.2, 138.0, 137.8, 129.2, 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 115.1, 101.2, 98.0, 97.3, 82.5, 77.9, 77.4, 77.2, 76.2, 75.1, 74.5, 73.9, 73.5, 73.2, 71.7, 69.8, 69.4, 62.9, 61.7, 52.8, 51.8, 37.9, 30.0, 28.7, 28.0, 25.7, 21.1, 21.0, 27.9, −4.6, −5.1; FAB MS: *m/z*: calcd for $C_{61}H_{81}N_3O_{21}Si$: 1219.5132; found: 1219.5107 $[M]^+$.

***n*-Pentenyl (methyl 2-*O*-acetyl-3-*O*-benzyl-α-L-idopyranosyluronate)-(1 → 4)-(6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1 → 4)-methyl 3-*O*-benzyl-2-*O*-levulinoyl-β-D-glucopyranosyluronate (106)**: Compound **105** (45 mg, 0.037 mmol) was dissolved in THF (5 mL). Glacial acetic acid (1.3 mL) and HF/pyridine complex (0.8 mL) were added and the solution was stirred at room temperature for three days. The mixture was poured into Et_2O and washed with brine, water, sat. $NaHCO_3$ and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc 7:3) afforded **106** (33 mg, 0.03 mmol, 82%) as a colorless foam. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39–7.27 (m, 15H), 5.49 (d, J = 3.9 Hz, 1H), 5.07–4.95 (m, 4H), 4.90 (br s, 1H), 4.85 (br s, 1H), 4.83–4.73 (m, 4H), 4.65–4.62 (m, 4H), 4.47 (d, J = 7.0 Hz, 1H), 4.35 (dd, 1H), 4.24–4.19 (m, 2H), 3.99 (d, J = 9.0 Hz, 2H), 3.96 (m, 1H), 3.87–3.81 (m, 3H), 3.74–3.71 (m, 2H), 3.66 (s, 3H), 3.58 (dd, 1H), 3.48 (s, 3H), 3.48–3.43 (m, 1H), 3.28 (dd, J = 3.7, 10.4 Hz, 1H), 2.68 (t, 2H), 2.60–2.45 (m, 3H), 2.14–2.07 (m, 11H), 1.68–1.60 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 206.2, 171.4, 170.8, 169.7, 169.3, 168.8, 138.1, 137.8, 137.8, 137.3, 129.2, 128.8, 128.6, 128.4, 128.3, 127.9, 127.7, 127.7, 115.1, 101.2, 98.3, 97.6, 82.5, 78.4, 77.4, 75.1, 75.1, 74.8, 74.7, 74.6, 74.4, 73.6, 72.9, 69.8, 69.5, 69.0, 67.9, 67.7, 63.5, 61.9, 52.8, 52.3, 37.9, 30.0, 29.9, 28.7, 28.0, 21.6, 21.1; FAB MS: *m/z*: calcd for $C_{55}H_{67}N_3O_{21}$: 1105.4267; found: 1105.4252 $[M]^+$.

***tert*-Butyldimethylsilyl (6-*O*-acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1 → 4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-β-D-glucopyranosyl)-(1 → 4)-3,6-di-*O*-acetyl-2-azido-2-deoxy-β-D-glucopyranoside (107)**: Compound **66** (365 mg, 0.38 mmol) and **7** (105 mg, 0.26 mmol) were coevaporated with toluene and dried under vacuum for 1 h. The mixture was dissolved in CH_2Cl_2 (3 mL) and after cooling to −25 °C, TMSOTf (20 μL, 0.1M in CH_2Cl_2) was added. The mixture was stirred for 4 h and then diluted with CH_2Cl_2 and filtered through a pad of Celite. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (toluene/EtOAc 95:5 → 80:20) to yield **107** (195 mg, 0.16 mmol, 63%) as a syrup. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37–7.24 (m, 15H), 5.40 (d, J = 3.7 Hz, 1H), 4.99 (t, 1H), 4.92–4.87 (m, 3H), 4.84–4.70 (m, 3H), 4.67 (d, J = 10.6 Hz, 1H), 4.60 (d, J = 7.6 Hz, 1H), 4.57 (d, J = 10.9 Hz, 1H), 4.50–4.47 (d, J = 10.4 Hz, 1H), 4.42 (d, J = 7.6 Hz, 1H), 4.27–4.12 (m, 4H), 3.90 (d, J = 9.5 Hz, 1H), 3.85 (dd, J = 8.5, 10.4 Hz, 1H), 3.78–3.75 (m, 1H), 3.76 (s, 1H), 3.73–3.60 (m, 2H), 3.55–3.50 (m, 2H), 3.32–3.27 (m, 2H), 2.74–2.63 (m, 2H), 2.59–2.54 (m, 2H), 2.12 (s, 3H), 2.11 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 0.9 (s 9H), 0.15 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 206.1, 171.7, 170.8, 170.7, 169.8, 168.1, 145.7, 141.5, 137.7, 137.7, 137.6, 128.7, 128.7, 128.6, 128.6, 128.3, 128.3, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 101.3, 97.6, 97.6, 82.5, 80.3, 76.8, 75.7, 75.2, 74.8, 74.7, 74.6, 73.1, 72.8, 71.8, 69.9, 66.5, 63.4, 62.5, 62.3, 52.9, 37.9, 37.7, 29.9, 27.8, 25.7, 21.1, 21.0, 20.9, 18.2, −4.3, −5.0; ES MS: *m/z*: calcd for $C_{57}H_{74}N_6O_{20}Si$: 1190.4727; found: 1190.4735 $[M]^+$.

6-*O*-Acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1 → 4)-methyl 3-*O*-benzyl-2-*O*-levulinoyl-β-D-glucopyranosyl-(1 → 4)-(3,6-di-*O*-acetyl-2-azido-2-deoxy-α/β-D-glucopyranosyl) trichloroacetimidate (108): A solution of **107** (80 mg, 0.07 mmol) in THF (1 mL) was cooled to 0 °C. Glacial acetic acid (10 μL, 0.17 mmol) and TBAF (1M in THF, 110 μL, 0.11 mmol) were added sequentially. After 30 min the mixture was poured into Et_2O (100 mL) and washed three times with brine. The organic layer was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (20 mL) and the solution was cooled to 0 °C. Trichloroacetonitrile (190 μL, 1.9 mmol) and DBU (5 μL, 0.03 mmol) were added and the mixture was stirred at 0 °C for 1 h and at room temperature for 3 h. After concentration, flash chromatography on silica gel (hexanes/EtOAc 85:15 → 70:30) afforded **108** (82 mg, 0.07 mmol, 87%) as a colorless foam. FAB MS: *m/z*: calcd for $C_{53}H_{60}Cl_3N_7O_{20}$: 1219.2959; found: 1219.2963 $[M]^+$.

***n*-Pentenyl (6-*O*-acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1 → 4)-(methyl 3-*O*-benzyl-2-*O*-levulinoyl-β-D-glucopyranosyl)-(1 →**

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4)-(3,6-di-*O*-acetyl-2-azido-2-deoxy-*α*/*β*-D-glucopyranosyl)-(1→4)-(methyl 2-*O*-acetyl-3-*O*-benzyl-*α*-L-idopyranosyluronate)-(1→4)-(6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-2-*O*-levulinoyl-*β*-D-glucopyranosyluronate (109): Compounds **108** (50 mg, 0.04 mmol) and **106** (30 mg, 0.03 mmol) were coevaporated with toluene and dried under vacuum for 1 h. The mixture was dissolved in toluene (1 mL) and after cooling to −25 °C, TBSOTf (20 μL, 0.1 M in CH_2Cl_2) was added. The mixture was stirred for 2 h and then diluted with CH_2Cl_2 and filtered through a pad of Celite. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (toluene/EtOAc 95:5→80:20) to yield **109** (36 mg, 0.02 mmol, 62 %) as a syrup. $[\alpha]_D^{24} = +35$ ($c = 0.70$, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.36-7.17$ (m, 30H), 5.77–5.83 (m, 1H), 5.48–5.45 (m, 2H), 5.41 (d, $J = 3.7$ Hz, 1H), 5.33 (t, 1H), 5.29 (d, $J = 3.7$ Hz, 1H), 5.17–4.90 (m, 7H), 4.87–4.80 (m, 6H), 4.78–4.61 (m, 7H), 4.57–4.53 (m, 2H), 4.45 (d, $J = 7.9$ Hz, 1H), 4.39 (d, $J = 7.9$ Hz, 1H), 4.38–4.22 (m, 2H), 4.20–4.10 (m, 2H), 3.96 (d, $J = 9.4$ Hz, 1H), 3.95–3.84 (m, 2H), 3.82–3.66 (m, 6H), 3.75 (s, 3H), 3.71 (s, 3H), 3.67 (s, 3H), 3.54–3.49 (m, 3H), 3.48–3.43 (m, 1H), 3.30 (dd, $J = 3.9$, 10.4 Hz, 1H), 3.16 (dd, $J = 3.3$, 10.1 Hz, 1H), 3.11 (dd, $J = 3.0$, 10.4, Hz, 1H), 2.69–2.63 (m, 4H), 2.58–2.48 (m, 4H), 2.16 (s, 3H), 2.14 (s, 3H), 2.12 (s, 3H), 2.04 (s, 3H), 2.09–2.02 (m, 2H), 2.02 (s, 3H), 1.87 (s, 3H), 1.66–1.60 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 207.2$, 206.2, 171.4, 171.2, 171.0, 170.8, 170.7, 170.6, 170.1, 170.0, 169.0, 168.1, 138.2, 137.8, 137.7, 137.6, 129.2, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.5, 127.3, 125.5, 115.2, 101.5, 101.2, 99.6, 98.1, 97.7, 97.4, 82.9, 82.6, 80.4, 78.0, 77.4, 76.9, 75.8, 75.6, 75.2, 74.9, 74.8, 74.6, 74.4, 74.3, 73.6, 73.1, 71.5, 71.0, 70.0, 69.5, 69.3, 63.5, 63.3, 62.3, 61.9, 61.7, 61.0, 52.9, 52.8, 52.5, 37.9, 37.5, 31.2, 30.1, 30.0, 29.2, 28.7, 28.1, 27.7, 21.7, 21.2, 21.0, 20.9, 20.8; ES MS: m/z: calcd for $C_{106}H_{125}N_9NaO_{40}$: 2186.7916; found: 2186.7984 $[M+Na]^+$.

***n*-Pentenyl (3,6-di-*O*-acetyl-2-azido-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(methyl 2-*O*-acetyl-3-*O*-benzyl-*α*-L-idopyranosyluronate)-(1→4)-(6-*O*-acetyl-3-*O*-benzyl-2-azido-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-methyl 2,3-di-*O*-benzyl-*β*-D-glucopyranosyluronate (110)**: A solution of **81** (93 mg, 0.07 mmol) and thiourea (230 mg, 3.02 mmol) in DMF/pyridine (10/1, 2 mL) was stirred for 24 h. After removal of the solvent under reduced pressure, the residue was dissolved in $CHCl_3$ and filtered. The solvent was removed under reduced pressure and flash chromatography on silica gel afforded pent-4-enyl (3,6-di-*O*-acetyl-2-azido-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(methyl 2-*O*-acetyl-3-*O*-benzyl-*α*-L-idopyranosyluronate)-(1→4)-(6-*O*-acetyl-3-*O*-benzyl-2-azido-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-*β*-D-glucopyranosyluronate (79 mg, 0.06 mmol, 90 %). $[\alpha]_D^{23} = +12.5$ ($c = 0.80$, $CHCl_3$); IR (thin film on NaCl): $\tilde{\nu} = 2914$, 2364, 2108, 1743, 1371; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.38-7.28$ (m, 15H), 5.85–5.77 (m, 1H), 5.57 (d, $J = 3.5$ Hz, 1H), 5.29 (d, $J = 4.5$ Hz, 1H), 5.22 (dd, $J = 10.5$, 9.0 Hz, 1H), 5.07 (d, $J = 3.0$ Hz, 1H), 5.02–4.97 (m, 3H), 4.93–4.90 (m, 2H), 4.82–4.80 (A part of AB system, $J_{AB} = 11.0$ Hz, 1H), 4.76–4.68 (m, 3H), 4.63 (d, $J = 4.5$ Hz, 1H), 4.49 (A part of ABX system, $J = 12.5$, 3.5 Hz, 1H), 4.31 (d, $J = 7.5$ Hz, 1H), 4.29–4.24 (m, 2H), 4.16 (B part of ABX system, $J = 12.5$, 2.0 Hz, 1H), 4.09–4.05 (m, 2H), 4.00–3.84 (m, 5H), 3.77–3.71 (m, 2H), 3.67 (s, 3H), 3.66 (s, 3H), 3.62(dt, $J = 7.5$, 2.0 Hz, 1H), 3.54–3.50 (m, 2H), 3.44(dt, $J = 9.5$, 5.0 Hz, 1H), 3.27 (dd, $J = 10.5$, 4.0 Hz, 1H), 3.17 (dd, $J = 10.5$, 3.5 Hz, 1H), 3.03 (d, $J = 5.0$ Hz, 1H), 2.34 (d, $J = 2.0$ Hz, 1H), 2.20–2.05 (m, 14H), 1.77–1.68(m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 172.0$, 171.3, 171.1, 170.3, 169.8, 169.0, 138.4, 138.2, 138.1, 137.4, 128.7, 128.6, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 115.3, 103.1, 98.6, 98.4, 97.5, 83.9, 78.2, 75.8, 75.0, 74.9, 74.8, 74.7, 74.0, 73.9, 72.4, 71.4, 70.1, 70.0, 69.9, 69.6, 69.0, 63.3, 62.6, 62.0, 61.1, 52.8, 52.4, 30.3, 28.8, 21.1, 21.0, 20.9; ES MS: m/z: calcd for $C_{60}H_{74}N_6NaO_{25}$: 1301.4601; found: 1301.4596 $[M+Na]^+$.

A solution of *n*-pentenyl (3,6-di-*O*-acetyl-2-azido-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(methyl 2-*O*-acetyl-3-*O*-benzyl-*α*-L-idopyranosyluronate)-(1→4)-(6-*O*-acetyl-3-*O*-benzyl-2-azido-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-*β*-D-glucopyranosyluronate (62 mg, 0.05 mmol) in CH_2Cl_2 (2.0 mL) was added to freshly activated powdered 4 Å molecular sieves (60 mg). Benzyl bromide (29 μL, 0.24 mmol) was added and the mixture was stirred at room temperature. After 30 minutes, Ag_2O (67 mg, 0.29 mmol) was added and the mixture was stirred overnight. The mixture was filtered and the solvent was removed under reduced pressure and flash chromatography on silica gel afforded **110** (50 mg, 0.04 mmol, 76 %) as a pale yellow oil. $[\alpha]_D^{24} = +23.9$ ($c = 1.80$, $CHCl_3$); IR (thin film on NaCl): $\tilde{\nu} =$ 2924, 2108, 1743, 1496, 1453; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.36-7.25$ (m, 20H), 5.84–5.76 (m, 1H), 5.54 (d, $J = 4.0$ Hz, 1H), 5.28 (d, $J = 4.0$ Hz, 1H), 5.21 (t, $J = 9.5$ Hz, 1H), 5.07 (d, $J = 3.5$ Hz, 1H), 5.03–4.90 (m, 6H), 4.82–4.67 (m, 5H), 4.62 (d, $J = 4.0$ Hz, 1H), 4.50–4.45 (m, 2H), 4.31–4.29 (A part of ABX system, $J = 12.0$, 1.0 Hz, 1H), 4.26–4.23 (B part of ABX system, $J = 12.0$, 3.5 Hz, 1H), 4.17–4.14 (B part of ABX system, $J = 12.5$, 2.5 Hz, 1H), 4.09–4.05 (m, 2H), 3.96–3.89 (m, 4H), 3.86 (t, $J = 9.5$ Hz, 1H), 3.76–3.73 (m, 2H), 3.67 (s, 3H), 3.65 (s, 3H), 3.57–3.49 (m, 3H), 3.44 (td, $J = 10.5$, 3.5 Hz, 1H), 3.24 (dd, $J = 4.0$, 10.0 Hz, 1H), 3.17 (dd, $J = 3.5$, 10.5 Hz, 1H), 3.02 (d, $J = 5.0$ Hz, 1H), 2.16–2.04 (m, 14H), 1.77–1.70 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 172.0$, 171.3, 171.1, 170.3, 169.7, 169.1, 138.3, 138.2, 138.1, 137.4, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.8, 127.7, 115.3, 103.9, 98.6, 98.4, 97.4, 84.1, 81.9, 78.1, 75.75, 75.74, 75.4, 75.0, 74.9, 74.8, 74.4, 74.0, 73.8, 72.4, 71.4, 70.1, 70.0, 69.9, 69.5, 68.9, 63.2, 62.6, 62.0, 61.1, 52.8, 52.4, 30.3, 29.0, 21.0, 21.1, 20.9; ES MS: m/z: calcd for $C_{67}H_{80}N_6NaO_{25}$: 1391.5070; found: 1391.5107 $[M+Na]^+$.

***n*-Pentenyl (3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(methyl 2-*O*-acetyl-3-*O*-benzyl-*α*-L-idopyranosyluronate)-(1→4)-(6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-*β*-D-glucopyranosyluronate (111)**: A solution of **82** (50 mg, 0.04 mmol), pyridine (6.3 μL, 0.08 mmol), acetic anhydride (8 μL, 0.08 mmol) and catalytic DMAP was stirred at room temperature for 6 h. After removal of the solvent under reduced pressure, flash chromatography on silica gel (hexanes/EtOAc 1.5:1) afforded *n*-pentenyl (3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(methyl 2-*O*-acetyl-3-*O*-benzyl-*α*-L-idopyranosyluronate)-(1→4)-(6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-2-*O*-levulinyl-*β*-D-glucopyranosyluronate (57 mg, 0.08 mmol, quantitative) as a yellow oil. $[\alpha]_D^{23} = +165$ ($c = 0.10$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.38-7.24$ (m, 15H), 5.82–5.74 (m, 1H), 5.48 (d, $J = 4.0$ Hz, 1H), 5.34 (t, $J = 9.5$ Hz, 1H), 5.27 (d, $J = 4.0$ Hz, 1H), 5.08 (d, $J = 4.0$ Hz, 1H), 5.06–4.88 (m, 6H), 4.79–4.66 (m, 6H), 4.47 (d, $J = 7.5$ Hz, 1H), 4.32–4.23 (m, 2H), 4.22–4.18 (m, 2H), 4.14–4.04 (m, 3H), 3.99 (d, $J = 9.5$ Hz, 1H), 3.94 (t, $J = 5.0$ Hz, 1H), 3.87–3.82 (m, 3H), 3.74 (t, $J = 10.0$ Hz, 1H), 3.67 (s, 3H), 3.64 (s, 3H), 3.57–3.55 (m, 1H), 3.47–3.43 (m, 1H), 3.29–3.26 (m, 2H), 2.68 (t, $J = 6.5$ Hz, 2H), 2.57–2.44 (m, 2H), 2.14–2.01 (m, 20H), 1.72–1.59 (m, 2H, pent-CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 206.2$, 171.4, 171.0, 170.7, 170.2, 170.1, 169.7, 169.6, 168.8, 138.1, 138.0, 137.8, 137.3, 128.7, 128.6, 128.4, 128.3, 128.2, 127.9, 127.8, 115.1, 101.2, 98.4, 98.3, 97.4, 82.5, 78.2, 75.6, 75.4, 75.0, 74.5, 74.4, 73.9, 73.6, 70.3, 69.8, 69.6, 69.4, 68.6, 68.2, 63.3, 61.9, 61.5, 61.1, 52.8, 52.4, 37.9, 30.0, 28.7, 28.0, 21.0, 20.9, 20.87, 20.83, 20.7; ES MS: m/z: calcd for $C_{67}H_{82}N_6NaO_{28}$: 1441.5069; found: 1441.5098 $[M+Na]^+$.

A solution of *n*-pentenyl (3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(methyl 2-*O*-acetyl-3-*O*-benzyl-*α*-L-idopyranosyluronate)-(1→4)-(6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-methyl 3-*O*-benzyl-2-*O*-levulinyl-*β*-D-glucopyranosyluronate (42 mg, 0.03 mmol) in pyridine/AcOH (3/2 0.3 mL) was cooled to 0 °C and hydrazine hydrate (7.4 mg, 0.15 mmol) was added. After 20 minutes acetone (2 mL) was added and the ice bath was removed. After stirring the mixture at room temperature for 30 minutes, the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (hexanes/EtOAc 1:1) to afford **111** (35 mg, 0.03 mmol, 90 %) as a pale yellow oil. $[\alpha]_D^{23} = +138$ ($c = 3.6$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.38-7.26$ (m, 15H), 5.84–5.76 (m, 1H), 5.58 (d, $J = 3.5$ Hz, 1H), 5.34 (dd, $J = 10.5$, 9.5 Hz, 1H), 5.27 (d, $J = 4.0$ Hz, 1H), 5.08 (d, $J = 3.5$ Hz, 1H), 5.05–4.97 (m, 4H), 4.92 (t, $J = 4.5$ Hz, 1H), 4.89–4.87 (A part of AB system, $J_{AB} = 10.5$ Hz, 1H), 4.82–4.79 (B part of AB system, $J_{AB} = 10.5$ Hz, 1H), 4.76–4.67 (m, 4H), 4.32–4.19 (m, 4H), 4.11–4.04 (m, 4H), 3.97–3.90 (m, 3H), 3.85 (t, $J = 9.5$ Hz, 1H), 3.77–3.71 (m, 2H), 3.67–3.60 (m, 7H), 3.55–3.49 (m, 2H), 3.29–3.25 (m, 2H), 2.40 (br s, 1H), 2.14–2.02 (m, 17H), 1.76–1.69 (m, 2H); ^{13}C NMR (500 MHz, $CDCl_3$): $\delta = 171.0$, 170.7, 170.3, 170.1, 169.8, 169.6, 168.9, 138.3, 138.1, 138.0, 137.3, 128.7, 128.6, 128.4, 128.3, 128.2, 127.9, 127.8, 115.3, 103.1, 98.4, 97.5, 83.9, 78.2, 75.6, 75.3, 74.9, 74.8, 74.7, 73.9, 70.3, 70.0, 69.5, 69.3, 68.6, 68.2, 63.3, 61.9, 61.4, 61.0, 52.8, 52.4, 30.3, 28.7, 21.1, 20.90, 20.88, 20.86, 20.79; ES MS: m/z: calcd for $C_{62}H_{76}N_6NaO_{26}$: 1338.5152; found: 1338.4932 $[M+Na]^+$.

***n*-Pentenyl (2-deoxy-2-sodium sulfonatamido-3,4,6-tri-*O*-sodium sulfonato-*α*-D glucopyranosyl)-(1→4)-(sodium 2-*O*-sodium sulfonato-*α*-D-idopyranosyluronate)-(1→4)-(2-deoxy-2-sodium sulfonatamido-6-*O*-sodium**

sulfonato-α-D-glucopyranosyl)-(1→4)-sodium 2-*O*-sodium sulfonato-β-D-glucopyranosyluronate (112): A solution of **111** (44 mg, 0.03 mmol) in THF (3.0 mL) was cooled to −13 °C and 50% H_2O_2 (1.0 mL) and 0.7 M aq. LiOH (0.8 mL) were added dropwise. The mixture was warmed to 0 °C over one hour and at room temperature overnight. Sodium hydroxide solution (4 M, 0.8 mL) was added and the mixture was stirred overnight. After acidification to pH 6.0 with 3 M HCl in MeOH, the solvent was partially removed under vacuum. The solution was diluted with EtOAc and the two phases were separated. The organic phase was washed twice with acidified aqueous sulfite (pH 3.5) and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the residue was purified on Sephadex LH20 (CH_2Cl_2/EtOH 1:1) affording *n*-pentenyl (2-azido-2-deoxy-α-D-glucopyranosyl)-(1→4)-3-*O*-benzyl-α-L-idopyranosyluronic acid)-(1→4)-(2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-3-*O*-benzyl-β-D-glucopyranosyluronic acid (27 mg, 0.024 mmol, 82%) as a colorless oil. ES MS: *m*/*z*: calcd for $C_{50}H_{62}N_6O_{21}$: 1105.3865; found: 1105.3806 $[M+Na]^+$.

A solution of *n*-pentenyl (2-azido-2-deoxy-α-D-glucopyranosyl)-(1→4)-3-*O*-benzyl-α-L-idopyranosyluronic acid)-(1→4)-(2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-3-*O*-benzyl-β-D-glucopyranosyluronic acid (35 mg, 0.03 mmol) and sulfur trioxide/triethylamine complex (88 mg, 0.48 mmol) in DMF (1.5 mmol) was stirred under nitrogen at 50 °C for 20 h. Aqueous $NaHCO_3$ (10%, 3 mL) was added at room temperature and the mixture was stirred for 3.5 h. The reaction mixture was concentrated, dissolved in MeOH and filtered through a pad of Celite. After removal of the solvent under reduced pressure, the residue was purified through a Sephadex G-25 column eluted with 0.2 N NaCl. After concentration and desalting through a Sephadex G-25 column eluted with water, *n*-pentenyl (2-azido-2-deoxy-3,4,6-tri-*O*-sodium sulfonato-α-D-glucopyranosyl)-(1→4)-(sodium 3-*O*-benzyl-2-*O*-sodium sulfonato-α-D-idopyranosyluronate)-(1→4)-(2-azido-3-*O*-benzyl-2-deoxy-6-*O*-sodium sulfonato-α-D-glucopyranosyl)-(1→4)-sodium 3-*O*-benzyl-2-*O*-sodium sulfonato-β-D-glucopyranosyluronate (25 mg, 0.015 mmol, 50%) was obtained as a colorless solid. ^{1}H NMR (500 MHz, D_2O): δ = 7.39–7.15 (m, 15H), 5.82–5.74 (m, 1H), 5.25 (d, J = 4.0 Hz, 1H), 5.17 (br s, 1H), 5.07 (d, J = 3.5 Hz, 1H), 4.99–4.87 (m, 2H), 4.72–4.66 (m, 7H), 4.42–4.38 (m, 2H), 4.32–4.28 (m, 2H), 4.20–4.10 (m, 7H), 3.96–3.69 (m, 8H), 3.55–3.50 (m, 1H), 3.43 (dd, J = 10.5, 3.5 Hz, 1H), 3.34 (dd, J = 10.0, 4.0 Hz, 1H), 2.06–2.02 (m, 2H), 1.61–1.55 (m, 2H); ^{13}C NMR (125 MHz, D_2O): δ = 139.7, 137.9, 137.4, 137.3, 129.9, 129.4, 129.2, 129.2, 128.9, 128.8, 115.4, 101.4, 98.0, 93.6, 82.8, 80.6, 78.6, 77.3, 76.5, 76.0, 75.3, 75.6, 75.3, 74.6, 73.0, 72.7, 71.4, 70.7, 70.4, 69.3, 68.6, 68.4, 67.4, 66.9, 63.6, 62.2, 29.9, 28.6; ES MS: *m*/*z*: calcd for $C_{50}H_{62}N_6O_{39}S_6$: 780.0605; found: 780.0564 $[M-2H]^{2-}$.

A solution of *n*-pentenyl (2-azido-2-deoxy-3,4,6-tri-*O*-sodium sulfonato-α-D-glucopyranosyl)-(1→4)-(sodium 3-*O*-benzyl-2-*O*-sodium sulfonato-α-D-idopyranosyluronate)-(1→4)-(2-azido-3-*O*-benzyl-2-deoxy-6-*O*-sodium sulfonato-α-D-glucopyranosyl)-(1→4)-sodium 3-*O*-benzyl-2-*O*-sodium sulfonato-β-D-glucopyranosyluronate (25 mg, 0.02 mmol) in EtOH/water (2/1, 6.0 mL) was treated with a stream of hydrogen in the presence of Pd/C catalyst (10%, 40 mg) for three days. After filtration on a pad of Celite, the solvent was removed under reduced pressure. ^{1}H NMR (500 MHz, D_2O): δ = 5.41 (br s, 1H), 5.29 (br s, 1H), 5.10 (br s, 1H), 4.78 (br s, 1H), 4.60–4.28 (m, 2H), 4.24–3.57 (m, 17H), 3.55–3.41 (m, 2H), 3.13 (br s, 1H), 1.46–1.41 (m, 2H), 1.18–1.12 (m, 4H), 0.70 (t, J = 7.0 Hz, 3H); ES MS: *m*/*z*: calcd for $C_{29}H_{50}N_2O_{39}S_6$: 620.0085; found: 620.0040 $[M-2H]^{2-}$.

The residue (20 mg, 0.02 mmol) was dissolved in water (4 mL). Sulfur trioxide/pyridine complex (101 mg, 0.6 mmol) was added in five portions every 30 minutes with the pH being maintained at 9.5 by addition of 4 N NaOH. After 3.5 h, the reaction mixture was concentrated and purified through a Sephadex G-25 column eluted with 0.2 N NaCl. After concentration and desalting through a Sephadex G-25 eluted with water, compound **112** (13 mg, 0.01 mmol, 60%) was obtained as a solid. $[\alpha]_D^{23}$ = +57 (c = 1.2, H_2O); ^{1}H NMR (500 MHz, D_2O): δ = 5.47 (d, J = 3.0 Hz, 1H), 5.42 (d, J = 3.0 Hz, 1H), 5.03 (br s, 1H), 4.48 (d, J = 8.0 Hz, 1H), 4.37–4.00 (m, 9H), 3.97 (t, J = 8.0 Hz, 1H), 3.86–3.81 (m, 2H), 3.76–3.68 (m, 4H), 3.54–3.51 (m, 2H), 3.46 (dd, J = 10.5, 3.0 Hz, 1H), 3.14 (dd, J = 10.0, 3.5 Hz, 1H), 1.50–1.45 (m, 2H), 1.22–1.16 (m, 6H), 0.74 (at, J = 7.0 Hz, 3H); HSQC anomeric cross peaks (D_2O): δ = (4.48 × 100.8), (5.03 × 99.8), (5.42 × 98.2), (5.47 × 95.4); ES MS: *m*/*z*: calcd for $C_{29}H_{44}N_2Na_6O_{45}S_8$: 1533.8; found: 1534.1.

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