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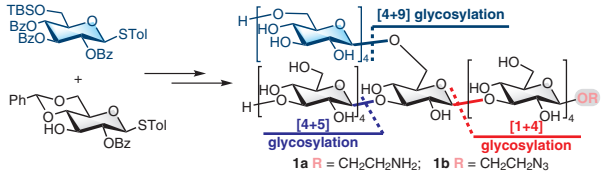
Convergent Synthesis of Branched β-Glucan Tridecasaccharides Ready for Conjugation

Xin Zhou[a]
Qing Long[a]
Dongwei Li[a]
Jingru Gao[a]
Qikai Sun[a]
Shaozi Sun[a]
Yong Su[a]
Peng Wang[a]
Wenjie Peng[*b]
Ming Li[*a,c]

[a] Key Laboratory of Marine Medicine, Chinese Ministry of Education, School of Medicine and Pharmacy, Ocean University of China, Qingdao 266003, P. R. of China
lmsnouc@ouc.edu.cn
[b] Laboratory of Systems Biomedicine, Chinese Ministry of Education, Shanghai Center for Systems Biomedicine, Shanghai Jiao Tong University, Shanghai 200240, P. R. of China
wenjiep@sjtu.edu.cn
[c] Laboratory for Marine Drugs and Bioproducts, Pilot National Laboratory for Marine Science and Technology, Qingdao 266237, P. R. of China



- convergent synthesis based on catalytic glycosylation of glycosyl trichloroacetimidates
- in 4.7% and 3.9% overall yield and in the longest linear sequence of 16 and 17 steps
- gram-scale access to the nonasaccharide main chain
- installation of the tetrasaccharide branch via orthoester rearrangement

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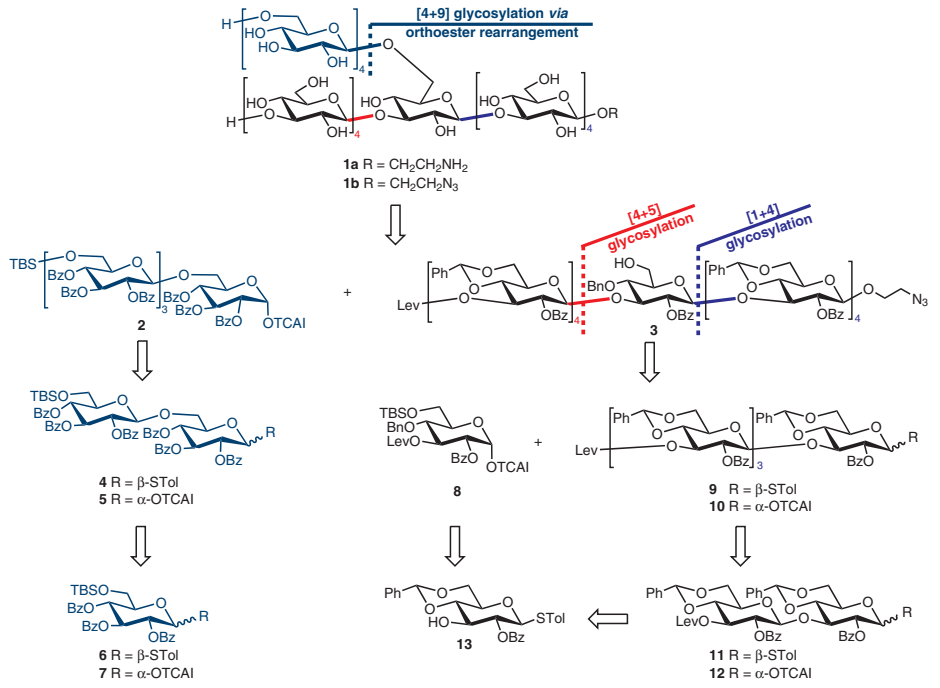
Abstract Structurally defined and pure oligosaccharides corresponding to β-glucans have attracted great attention because of their potential properties as immunostimulating agents and as antigens of vaccine candidates. We herein describe a convergent synthesis of ready-to-conjugate tridecasaccharides composed of a β-1,3-glucan nonasaccharide backbone and a β-1,6-glucan tetrasaccharide branch. The assembly was achieved by employing trichloroacetimidate glycosylations and features the gram-scale preparation of the nonasaccharide backbone and installation of the tetrasaccharide branch involving orthoester rearrangement to the glycoside.

Key words β-glucans, glycosyl trichloroacetimidates, oligosaccharide synthesis, orthoester rearrangement, convergent synthesis

β-D-Glucans are fundamental structural members of the cell wall or reserve polysaccharides of yeasts, algae, and high plants. They are composed of a β-1,3-glucan backbone decorated frequently with branches consisting of β-1,3- or β-1,6-linked short glucans that are usually attached to C6-OHs of glucosyl units of the main chain.[1] β-Glucans have been shown to possess anti-inflammatory, anticancer, antimicrobial, and antidiabetic activities, among others.[2] The immunostimulating properties of β-glucans have been applied to enhance the natural immune system and to relieve the side effects resulting from chemotherapy.[3] The absence of β-1,3-glucans in mammals makes such glucans and structurally related oligosaccharides promising antigens of carbohydrate–protein conjugate vaccine candidates for the prevention and treatment of mycotic infections and cancers.[4]

The heterogeneity of isolates from natural sources results in difficulties in acquiring pure homogeneous glycoforms of β-1,3-glucans, thus complicating the establishment of structure–activity relationships. To overcome these obstacles, much effort has been devoted to the chemical synthesis and biological evaluation of β-1,3-glucan fragments and derivatives with a rigorously defined structure and a high degree of purity.[5] Among these precedents, impressive achievements are the automated assembly of a dodeca- and tridecasaccharide[6,7] and the one-pot synthesis of 6-*O*-branched tridecasaccharides based on the preactivation of thioglycosides.[8] Regioselective glycosylation featuring step economy was successfully applied in the synthesis of a linear tridecasaccharide[9] and branched heptadecasaccharide.[10,11] Chromatography-free synthesis of a β-1,6-hexaglucan[12] and β-1,3-glucan[13] laminarihexaose was achieved relying on hydrophobic tag assisted, liquid-phase ionic liquid supported synthesis technologies. Gold-catalyzed glycosylation of *o*-alkynylbenzoates represents a mild method to construct various glycosidic linkages.[14] The reaction was employed to assemble hexadeca- and tetradecasaccharides of glucans.[15] Very recently, Crich and co-workers described the synthesis of 1,5-dithia- and thioether-linked carbocyclic mimics as β-1,3-glucan oligomers.[16] Biological activities of the synthesized β-1,3-glucan oligomers and derivatives have been evaluated including binding affinity to dectin-1,[6,7,10,11,14–17] the possibility as antibody epitopes,[7] and the ability to stimulate phagocytosis and pinocytosis,[16]

Georg Thieme Verlag KG, Rüdigerstraße 14, 70469 Stuttgart, Germany



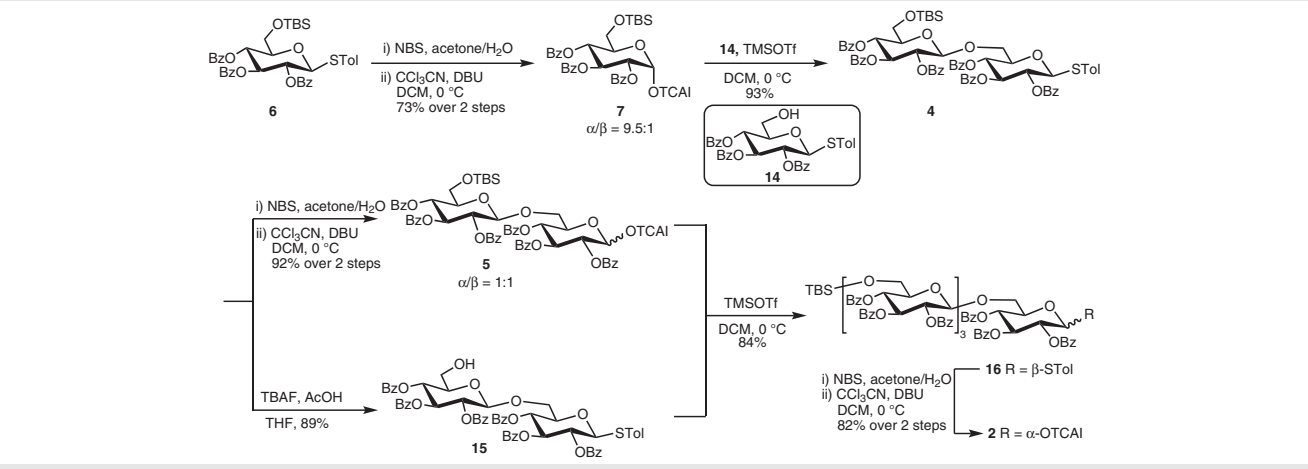
Scheme 1 Strategy for the synthesis of tridecasaccharides **1a** and **1b**

which show potential applications in carbohydrate-based medicines. In addition, the conjugate of 2-aminoethyl β-glucan tridecasaccharide **1a** (Scheme 1) with keyhole limpet hemocyanin (KLH) has been shown to be a promising antifungal vaccine candidate.[18] Herein, we describe the assembly of **1a** and its azido congener **1b** (Scheme 1). Either the amino or azido group could serve as a handle to couple with functional devices through amide bond formation or click chemistry, thus giving access to chemical probes for use in biological studies.

Synthetic Plan. The Schmidt glycosylation has been recognized as one of the most popular reactions to construct various glycosidic bonds because of the easy preparation of glycosyl trichloroacetimidates and high-yielding coupling with nucleophiles under mild conditions with catalytic Lewis acids such as trimethylsilyl trifluoromethanesulfonate (TMSOTf) and boron trifluoride etherate ($BF_3{\cdot}OEt_2$) as the promoters.[19] As such, we wanted to assemble the target molecules following a convergent strategy based on the Schmidt glycosylation.

Structurally, tridecasaccharides **1a** and **1b** are composed of a β-1,3-nonaglucan backbone and a β-1,6-tetraglucan branch appended to C6-OH of the central glucosyl unit of the backbone. Since a primary hydroxy group such as C6-OH of glucose is generally more accessible than a secondary hydroxy group such as C3-OH, we aimed to reach the target by assembling the β-1,3-glucan nonasaccharide backbone prior to the introduction of β-1,6-glucan branching. Furthermore, in order to ensure the formation of 1,2-*trans*-β-glucosidic bonds by means of anchimeric assistance, benzoyl was selected as the protecting group at C2-OH of glucosyl units.

With these considerations in mind, the target molecules **1a** and **1b** could be disconnected into β-1,6-linked tetrasaccharide **2** as the branch and β-1,3-connected linear nonasaccharide **3** as the backbone (Scheme 1). Tetrasaccharide **2** could be prepared by the coupling of disaccharide trichloroacetimidate (TCAI) **5** with thioglycoside **4**, both of which could originate from thioglucoside **6** and glucosyl TCAI donor **7**. The bulky *tert*-butyldimethylsilyl (TBS) was selected as the protecting group of C6-OH of **6** in recognition of its reliability and proven record in highly preferential installation at primary hydroxy groups over secondary ones and orthogonal removal in the presence of benzoates for ensuing sugar chain extension at this position. 4,6-*O*-Benzylidene acetal as the C4- and C6-OHs of glucosyl building blocks has witnessed successes in several syntheses of β-1,3-glucans.[6,8–11,13,15,20] Accordingly, the nonasaccharide **3** could be divided into the monosaccharide TCAI donor **8** and the tetrasaccharide fragments **9** and **10**. Building block **8** is characterized by the C6 TBS ether and C3 levulinoyl (Lev) ester that mark the branching and the elongating sites. Disaccharides **11** and **12** *en route* to tetrasaccharides **9** and **10** could be traced to readily available 4,6-*O*-benzylidene-protected thioglucoside **13**, with Lev and benzoyl differentiating C3- and C2-OH. Thioglycoside **13** also could serve as the

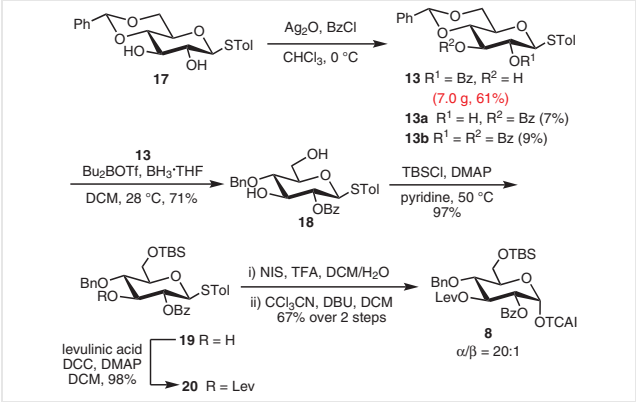


Scheme 2 Synthesis of β-1,6-glucan tetrasaccharide building block **2**

precursor to orthogonally protected TCAI donor **8** which entails protecting group manipulations to decorate C6-OH with a TBS group.

Synthesis of β-1,6-Glucan Tetrasaccharide 2. Our study toward convergent synthesis of β-1,6-glucan tetramer **2** (Scheme 2) commenced with the preparation of glucosyl TCAI donor **7**, which would be employed as the glycosylating agent. Thus, treatment of thioglycoside **6**[21] with *N*-bromosuccinimide in aqueous acetone followed by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)-catalyzed addition of the resulting hemiacetal to trichloroacetonitrile afforded **7** in 73% yield over two steps. TMSOTf-catalyzed orthogonal glycosylation of acceptor alcohol **14**,[21] readily prepared by selective removal of the TBS group at position C6 of thioglycoside **6**, with TCAI donor **7** smoothly provided the desired disaccharide **4** in 93% yield. With disaccharide **4** in hand, we then converted the disaccharide into TCAI donor **5** and acceptor alcohol **15** by anomeric functional group manipulations and selective cleavage of the TBS ether with AcOH-buffered tetrabutylammonium fluoride in 92% and 89% yield, respectively. 1,6-Linked β-tetraglucan **16** was stereoselectively achieved in 84% yield by coupling **5** with **15**. Conversion of thioglycoside **16** into the corresponding TCAI donor **2** was accomplished in 82% yield over two steps.

Synthesis of β-1,3-Glucan Nonasaccharide 3. According to our synthetic plan, we assembled β-1,3-glucan nonasaccharide backbone **3** following a [4+(1+4)] strategy. Thus, the synthesis proceeded from preparation of the key monosaccharide building block **13** bearing a benzoyl protecting group at C2-OH (Scheme 3). Motivated by the protocol of Ye and Chang, whose groups independently described Ag_2O-mediated site-selective benzoylation of sugars,[22,23] we employed the reaction to selectively protect benzylidene-protected thioglucoside **17**.[22] The desired 2-*O*-benzoylthioglucoside **13** was obtained, accompanied by 3-*O*-benzoyl isomer **13a** and 2,3-di-*O*-benzoylglucoside **13b** as the unwanted products. Several features of the transformation warrant comments. Monitoring the reaction process by thin-layer chromatography revealed conversion of kinetically formed benzoate **13a** into thermodynamic product **13** through migration of the benzoyl group from C3-OH to C2-OH. Separation of the desired product **13** from regioisomer **13a** with very close polarity could be readily achieved by crystallization in toluene; however, it was crucial to remove the silver species and dibenzoate **13b** using flash chromatography on a short silica gel column prior to the crystallization because their presence resulted in decomposition or difficulty in the isolation of **13**. Following this procedure, 7.0 g of **13** could be obtained in 61% yield in one batch, setting a solid foundation for the assembly of nonasaccharide **3**.



Scheme 3 Synthesis of monosaccharide TCAI donor **8**

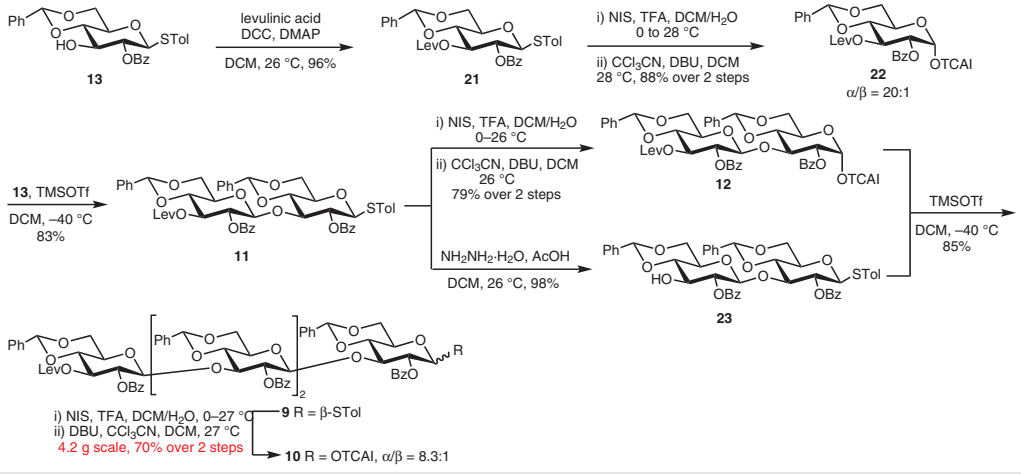
With sufficient **13** in hand, we turned our attention to the synthesis of mono- and tetrasaccharide TCAI donors **8** and **10**, two key intermediates to reach nonasaccharide **3**. As shown in Scheme 3, regioselective reductive ring opening of the benzylidene acetal on **13** using the combination of borane–tetrahydrofuran complex (BH_3·THF)/dibutylboryl trifluoromethanesulfonate (Bu_2BOTf)[24] delivered 71% of 4-

O-benzyl ether **18** with C3- and C6-OH free. Silylation at C6-OH with TBSCl (→ **19**) and then levulinoylation at C3-OH using *N*,*N*′-dicyclohexylcarbodiimide-mediated esterification afforded orthogonally protected thioglycoside **20**. Finally, the expected TCAI donor **8** was obtained in a satisfactory yield by a two-step reaction sequence involving *N*-iodosuccinimide-mediated hydrolysis of **20** and addition of the resulting hemiacetal to trichloroacetonitrile in the presence of DBU.

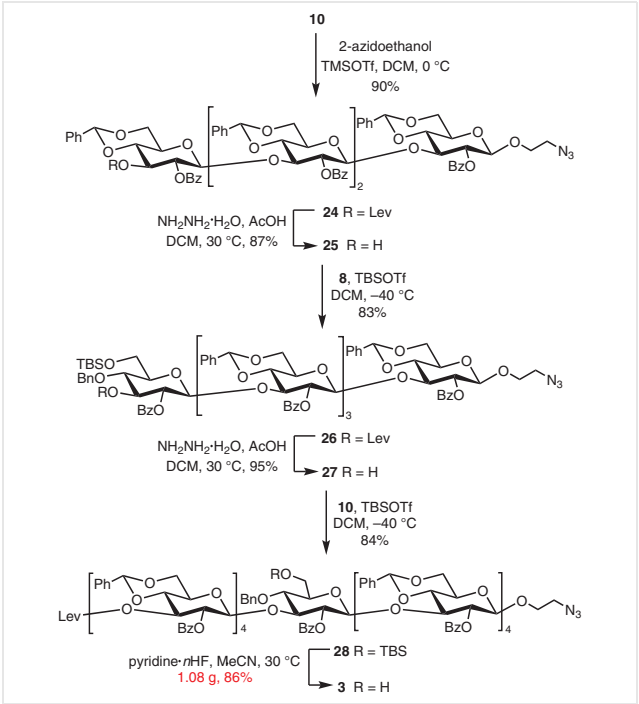
The preparation of tetrasaccharide TCAI donor **10** is outlined in Scheme 4. Thioglycoside **13** evolved into TCAI donor **22** in overall 84% yield involving levulinoylation of C3-OH (→ **21**) and subsequent conversion of thioglycoside into the corresponding TCAI donor **22**. With the building blocks **22** and **13** secured, TMSOTf-catalyzed chemoselective activation coupling efficiently furnished disaccharide thioglycoside **11** in 83% yield and in significant quantities (5.65 g scale). Next, **11** was split and transformed in parallel to disaccharide TCAI donor **12** and acceptor alcohol **23** as follows. As usual, TCAI donor **12** was obtained in 79% yield through *N*-iodosuccinimide-mediated hydrolysis of thioglycoside followed by reaction with trichloroacetonitrile. Selective removal of Lev using hydrazine-mediated aminolysis[25] in the presence of AcOH allowed for the preparation of **23** in almost quantitative yield. Coupling of **12** and **23** at –40 °C by the action of TMSOTf (0.1 equiv) exclusively gave β-linked tetrasaccharide **9**, which was further converted into the corresponding TCAI donor **10** (4.2 g scale) in 70% yield over two steps.

With TCAI donors **8** and **10** available, we set out to assemble the nonasaccharide following the [4+(1+4)] strategy. As shown in Scheme 5, TMSOTf-promoted glycosylation of TCAI donor **10** with 2-azidoethanol at 0 °C furnished β-1,3-glucan tetramer **24** in 90% yield. It should be pointed out that attempts to couple tetrasaccharide thioglycoside **9** with 2-azidoethanol produced **24** in a lower yield of 61%. Cleavage of the Lev group uneventfully resulted in acceptor alcohol **25** in 87% yield. Unexpectedly, sugar chain extension at C3-OH of **25** using monosaccharide donor **8** is not trivial. The initial reaction promoted by TMSOTf as the conventional catalyst resulted in a complicated mixture. To our delight, after evaluating various Lewis acids, we found that a switch of the activator from TMSOTf to TBSOTf yielded the desired pentasaccharide **26** in 83% yield at –40 °C. TBSOTf has proven to be a superior catalyst to TMSOTf for glycosylations of TCAI donors with substrates difficult to glycosylate.[26] Iterative coupling of TCAI **10** with **27**, prepared by removing Lev from compound **26**, under the promotion of TBSOTf (0.2 equiv) smoothly furnished nonasaccharide **28** (2.25 g scale) in excellent 84% yield. Deprotection of the TBS ether with pyridinium poly(hydrofluoride) (pyridine·*n*HF) in acetonitrile efficiently liberated C6-OH of the central glucose unit and left the eight benzylidene acetals untouched. As such, the gram-scale synthesis of 1,3-linked nonasaccharide **3** (1.08 g scale) was achieved in 86% yield, ready for next installation of the β-(1,6)-glucan tetrasaccharide branch.

Synthesis of β-Glucan Tridecasaccharides 1a and 1b. With β-1,6-glucan tetrasaccharide TCAI donor **2** and β-1,3-glucan nonasaccharide acceptor alcohol **3** in hand, the assembly of tridecasaccharide **30** was performed. We first evaluated the possibility of the coupling of **2** with **3** catalyzed by TMSOTf or TBSOTf. We were, however, unrewarded and hydrolysis of **2** was found to take place as the major side reaction. These unwanted results might originate from the unmatched reactivity of **2** with **3** due to steric hindrance of the acceptor alcohol. Inspired by the reports using silver triflate (AgOTf) as a mild activator in the Schmidt glycosylation reaction,[27] we opted to apply this catalyst to the coupling between **2** and **3**. The reaction promoted by AgOTf resulted in a clean transformation in toluene in the presence of 5 Å molecular sieves. The isolated product was,



Scheme 4 Synthesis of β-1,3-glucan tetrasaccharide building blocks **9** and **10**

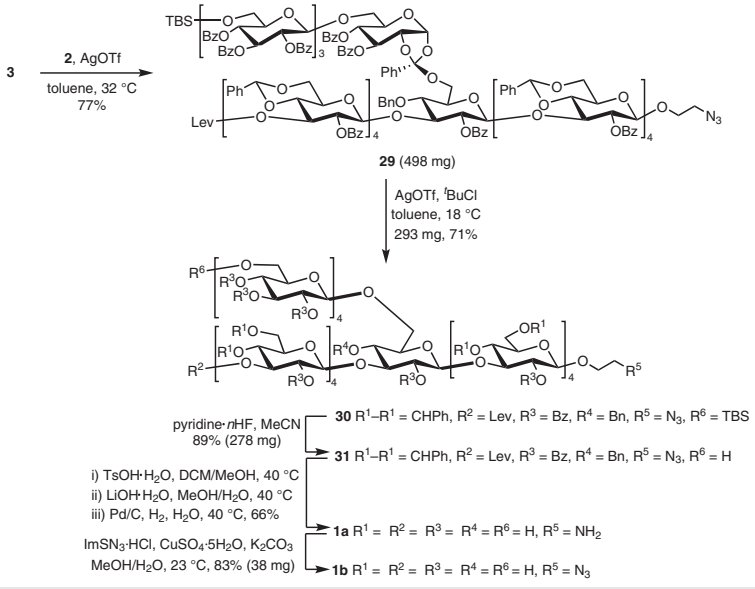


Scheme 5 Synthesis of β-1,3-glucan nonasaccharide backbone **3**

however, determined to be orthoester **29** (Scheme 6) rather than the expected glycoside. The structure of **29** was evident from the ^{1}H and ^{13}C NMR spectroscopic data. The anomeric proton associated with the newly formed glycosidic bond was found to resonate at 5.77 ppm as a doublet with a coupling constant of $^{3}J_{H1-H2}$ = 4.9 Hz, implying the presence of an α-configured glycosidic bond. In addition, a quaternary carbon signal in the ^{13}C NMR spectrum appeared at 121.3 ppm, data diagnostic of an orthoester quaternary carbon.

Although circuitous, protic acid promoted rearrangement of orthoesters has proven to be an efficient method to gain access to glycosides.[28] Gratifyingly, treatment of orthoester **29** with TfOH, generated *in situ* by reacting AgOTf and ^{t}BuCl, afforded tridecasaccharide **30** in 71% yield. However, attempts to directly reach **30** by treating acceptor alcohol **3** with TCAI donor **2** in the presence of TfOH failed.

With fully protected **30** in hand, synthesis of tridecasaccharides **1a** and **1b** was carried out as shown in Scheme 6. After desilylation of **30** with pyridine·*n*HF resulted in tridecasaccharide **31**, we initially tended to employ lithium-mediated Birch reduction in liquid ammonia to globally remove all protecting groups, including the eight benzylidene acetals, one benzyl group, 21 benzoyl groups, and one Lev, along with concomitant reduction of the azido substituent. Unfortunately, the reaction was messy and ESI-MS analysis of the crude reaction mixture did not show a peak corresponding to the anticipated oligosaccharide. Next, we turned to a stepwise manner to deprotect **31** involving a three-step sequence of reactions, composed of removal of the benzylidene acetals with a mixture of MeOH and DCM in the presence of *p*-toluenesulfonic acid hydrate at 40 °C, hydrolysis of the esters using LiOH·H_2O as the base in aqueous MeOH, and then palladium-catalyzed hydrogenolysis of the benzyl group along with hydrogenation of the azido group, which provided the desired target molecule **1a** in overall 66% yield. Reversal of the manipulation order of acetal and ester hydrolysis is not suggested because the benzylidene-protected polyalcohol arising from saponification was found to be very poorly soluble in either pure MeOH or aqueous MeOH. Amine **1a** was transformed to azide **1b** in



Scheme 6 Synthesis of branched β-glucan tridecasaccharides **1a** and **1b**

83% yield using imidazole-1-sulfonyl azide hydrochloride ($ImSN_3$·HCl)[29] as diazo transfer agent in the presence of $CuSO_4$·5 H_2O and K_2CO_3 in MeOH/H_2O.

In conclusion, we have developed an efficient convergent synthesis of branched β-glucan tridecasaccharides bearing a 2-amino- or 2-azidoethyl linker. The synthesis takes advantage of Lewis acid catalyzed Schmidt glycosylation and features the preparation of a β-1,3-nonasaccharide backbone on a gram scale and the installation of a β-1,6-tetrasaccharide branch relying on TfOH-catalyzed rearrangement of an orthoester intermediate to the corresponding glycoside. The ready availability of tridecasaccharides sets a solid foundation for conjugation to biological devices for use in biological studies.

All reactions were carried out under argon with magnetic stirring unless otherwise indicated. All commercially obtained reagents were used as received, except where specified otherwise. NBS, NIS, TMSOTf, TBSOTf, AgOTf, BH_3·THF, TBSCl, DMAP, DCC, NH_2NH_2·H_2O, and *p*-TsOH·H_2O were purchased from Energy Chemical; trichloroacetonitrile, DBU, TBAF, levulinic acid, pyridine·*n*HF, and $CuSO_4$·5 H_2O were purchased from Macklin Biochemical; Bu_2BOTf, ^{t}BuCl, and LiOH·H_2O were purchased from Aladdin; Pd/C was purchased from Sigma-Aldrich and used without further purification. Anhydrous DCM and toluene were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Pyridine was refluxed over CaH_2 and distilled before use. Acetone and MeOH were used without further purification. Flash column chromatography was performed on Silica Gel H (300–400 mesh, Qingdao, China). Analytical TLC was performed on SiliCycle SiliaPlate glass-backed plates coated with silica gel (60 mesh pore size, F-254 indicator) and visualized by exposure to UV light and/or staining with 8% H_2SO_4 in MeOH. Optical rotations were determined with a JASCO P-1020 digital polarimeter. NMR spectra were recorded on an Agilent DD2 400 or 500 MHz NMR spectrometer and calibrated by using residual undeuterated chloroform (δ_H = 7.26 ppm) and $CDCl_3$ (δ_C = 77.16 ppm) as internal references. The following abbreviations are used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet. High-resolution mass spectra were obtained using a Thermo LTQ Orbitrap XL high resolution mass spectrometer.

2,3,4-Tri-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-α-D-glucopyranosyl Trichloroacetimidate (7)

NBS (1.50 g, 8.42 mmol, 2.0 equiv) was added to a solution of tolyl glycoside **6** (3.0 g, 4.21 mmol, 1.0 equiv) in a mixture of acetone/H_2O (30 mL, 9:1 v/v) at 0 °C. The reaction was allowed to proceed under stirring for 2 h at rt and quenched with Et_3N, and the mixture was concentrated. The residue was dissolved in DCM (30 mL) and washed with 20% (w/w) aqueous $Na_2S_2O_3$ (30 mL). The aqueous layer was re-extracted with DCM (2 × 30 mL) and the combined organic layers were dried and concentrated; the crude hemiacetal was used in the next step without further purification. Trichloroacetonitrile (2.11 mL, 21.05 mmol, 5.0 equiv) was added to a solution of the hemiacetal in anhydrous DCM (30 mL) stirred at rt under N_2. DBU (315 μL, 2.11 mmol, 0.5 equiv) was then added slowly, and the mixture was stirred at 0 °C for 12 h. The reaction mixture was concentrated, and purified by silica gel column chromatography (petroleum ether/EtOAc, 7:1) to afford **7** (2.3 g, 3.07 mmol, 73% over 2 steps, α/β = 9.5:1) as a slightly yellow foam.

$[\alpha]_D^{15}$ +0.88 (*c* 1.75, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.8 Hz, 4 H), 7.87 (d, *J* = 7.5 Hz, 2 H), 7.50 (t, *J* = 6.7 Hz, 2 H), 7.45–7.27 (m, 5 H), 7.29 (t, *J* = 7.6 Hz, 2 H), 6.84 (d, *J* = 3.2 Hz, 1 H), 6.23 (t, *J* = 10.0 Hz, 1 H), 5.73 (t, *J* = 10.0 Hz, 1 H), 5.55 (dd, *J* = 10.2, 3.4 Hz, 1 H), 4.35 (d, *J* = 10.1 Hz, 1 H), 3.91–3.81 (m, 2 H), 0.86 (s, 9 H), 0.00 (s, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.9, 165.6, 165.2, 160.7, 133.6, 133.4, 133.3, 130.0, 129.94, 129.86, 129.23, 129.18, 128.8, 128.5, 128.4, 93.5, 91.0, 73.6, 71.1, 70.6, 68.6, 62.2, 25.9, 18.4, –5.32, –5.33.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{35}H_{42}Cl_3N_2O_9Si$: 767.1720; found: 767.1704.

p-Tolylthio (2,3,4-Tri-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (4)

A mixture of trichloroacetimidate **7** (2.0 g, 2.67 mmol, 1.0 equiv) and acceptor **14** (1.84 g, 3.07 mmol, 1.15 equiv) in anhydrous DCM (50 mL) was stirred for 30 min in the presence of activated 5 Å molecular sieves (5.0 g). Then the mixture was cooled to 0 °C followed by addition of TMSOTf (49 μL, 0.27 mmol, 0.1 equiv). After being stirred for 4 h at 0 °C, the reaction mixture was filtered through a Celite pad, and the filtrate was sequentially washed with saturated aqueous $NaHCO_3$ and brine. The collected organic layers were dried over Na_2SO_4. The solid was filtered off, and the filtrate was concentrated. The residue was purified by silica gel chromatography (petroleum ether/DCM/EtOAc, 8:1:1) to afford **4** (2.94 g, 2.48 mmol, 93%) as a white foam.

$[\alpha]_D^{15}$ +0.07 (*c* 3.25, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.95–7.91 (m, 6 H), 7.85 (d, 7.4 Hz, 4 H), 7.74 (d, *J* = 7.4 Hz, 2 H), 7.55–7.45 (m, 4 H), 7.45–7.22 (m, 16 H), 7.17 (d, *J* = 7.8 Hz, 2 H), 5.83 (t, *J* = 9.6 Hz, 1 H), 5.77 (t, *J* = 9.5 Hz, 1 H), 5.52–5.42 (m, 2 H), 5.34 (t, *J* = 9.7 Hz, 1 H), 5.27 (t, *J* = 9.7 Hz, 1 H), 4.97 (d, *J* = 7.9 Hz, 1 H), 4.80 (d, *J* = 9.9 Hz, 1 H), 4.06–3.97 (m, 2 H), 3.92–3.88 (m, 1 H), 3.85–3.73 (m, 3 H), 2.37 (s, 3 H), 0.83 (s, 9 H), –0.04 (d, *J* = 6.7 Hz, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 165.9, 165.8, 165.40, 165.37, 165.2, 165.1, 138.9, 134.1, 133.6, 133.4, 133.26, 133.22, 133.20, 129.96, 129.95, 129.92, 129.85, 129.78, 129.5, 129.4, 129.3, 129.1, 128.9, 128.8, 128.50, 128.47, 128.40, 128.36, 128.32, 127.7, 101.2, 86.1, 78.4, 75.4, 74.3, 73.5, 72.1, 70.6, 69.69, 69.65, 68.4, 62.7, 25.9, 21.3, 18.4, –5.26, –5.29.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{67}H_{70}NO_{16}SSi$: 1204.4179; found: 1204.4158.

(2,3,4-Tri-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-D-glucopyranosyl Trichloroacetimidate (5)

Following the procedure for **7**, treatment of **4** (2.0 g, 1.69 mmol, 1.0 equiv) with NBS (601 mg, 3.38 mmol, 2.0 equiv) in acetone/H_2O (30 mL, 9:1 v/v) at 0 °C afforded the crude hemiacetal, which was treated with trichloroacetonitrile (847 μL, 8.45 mmol, 5.0 equiv) and DBU (126 μL, 0.85 mmol, 0.5 equiv) at 0 °C to afford **5** (1.9 g, 1.55 mmol, 92% over 2 steps, α/β = 1:1) as a white foam after purification by silica gel column chromatography (petroleum ether/EtOAc, 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.62 (s, 1 H), 8.31 (s, 1 H), 8.01 (d, *J* = 7.8 Hz, 2 H), 7.97 (d, *J* = 7.9 Hz, 2 H), 7.94–7.86 (m, 12 H), 7.83–7.76 (m, 8 H), 7.52–7.18 (m, 36 H), 6.68 (d, *J* = 3.0 Hz, 1 H), 6.21–6.14 (m, 1 H), 6.08 (d, *J* = 7.9 Hz, 1 H), 5.90–5.80 (m, 3 H), 5.70 (t, *J* = 8.6 Hz, 1 H), 5.57–5.38 (m, 7 H), 5.06 (d, *J* = 7.8 Hz, 1 H), 4.92 (d, *J* = 7.5 Hz, 1 H), 4.46 (dd, *J* = 10.2, 5.4 Hz, 1 H), 4.25–4.18 (m, 1 H), 4.17–4.05 (m, 3 H), 3.94 (dd, *J* = 11.7, 7.5 Hz, 1 H), 3.85–3.75 (m, 6 H), 0.82 (d, *J* = 3.6 Hz, 18 H), –0.04 (d, *J* = 8.9 Hz, 12 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 166.02, 165.98, 165.7, 165.41, 165.37, 165.32, 165.24, 165.22, 165.14, 164.9, 164.3, 163.8, 160.7, 160.3, 133.7, 133.60, 133.57, 133.45, 133.43, 133.38, 133.33, 133.26, 133.25, 133.23, 133.1, 130.1, 130.02, 129.95, 129.87, 129.82, 129.78, 129.57, 129.55, 129.25, 129.23, 129.04, 129.03, 129.01, 128.97, 128.70, 128.68, 128.64, 128.54, 128.49, 128.46, 128.41, 128.39, 128.35, 128.26, 100.9, 100.6, 95.8, 92.9, 75.5, 75.4, 73.43, 73.39, 72.8, 72.1, 71.99, 71.97, 71.91, 70.84, 70.82, 70.2, 69.7, 69.5, 69.2, 68.7, 67.6, 67.5, 62.7, 62.6, 29.8, 25.88, 25.86, 18.4, –5.29, –5.30, –5.32, –5.35.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{62}H_{64}Cl_3N_2O_{17}Si$: 1241.3034; found: 1241.3042.

p-Tolylthio (2,3,4-Tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (15)

To a stirred solution of **4** (3.5 g, 2.95 mmol, 1.0 equiv) in AcOH (675 μL, 11.80 mmol, 4.0 equiv) and THF (44 mL) was added TBAF (1 M in THF, 5.9 mL, 5.9 mmol, 2.0 equiv). After the mixture was stirred at rt for 12 h, DCM (50 mL) and saturated aqueous $NaHCO_3$ (50 mL) were successively added. The organic phase was separated and washed with brine (50 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/DCM/EtOAc, 6:3:1) to afford **15** (2.81 g, 2.62 mmol, 89%) as a white foam.

$[\alpha]_D^{15}$ –0.15 (*c* 1.55, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96–7.90 (m, 8 H), 7.82 (d, *J* = 7.7 Hz, 2 H), 7.76 (d, *J* = 7.7 Hz, 2 H), 7.57–7.46 (m, 5 H), 7.45–7.33 (m, 12 H), 7.32–7.22 (m, 3 H), 7.15 (d, *J* = 7.9 Hz, 2 H), 5.87 (t, *J* = 9.7 Hz, 1 H), 5.79 (t, *J* = 9.5 Hz, 1 H), 5.45–5.27 (m, 4 H), 4.97 (d, *J* = 7.9 Hz, 1 H), 4.83 (d, *J* = 10.0 Hz, 1 H), 4.06 (d, *J* = 10.2 Hz, 1 H), 4.03–3.91 (m, 2 H), 3.82–3.72 (m, 2 H), 3.62 (d, *J* = 12.6 Hz, 1 H), 2.83 (brs, 1 H), 2.36 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.97, 165.87, 165.85, 165.81, 165.2, 165.1, 139.0, 134.2, 133.75, 133.70, 133.38, 133.33, 133.32, 133.28, 130.05, 130.02, 129.97, 129.84, 129.40, 129.38, 128.99, 128.93, 128.91, 128.74, 128.65, 128.60, 128.48, 128.41, 128.35, 127.5, 100.7, 86.2, 77.9, 74.8, 74.2, 72.97, 71.7, 70.6, 70.1, 69.5, 68.1, 61.4, 21.4.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{61}H_{56}NO_{16}S$: 1090.3314; found: 1090.3284.

p-Tolylthio (2,3,4-Tri-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (16)

Following the procedure for **4**, trichloroacetimidate **5** (1.04 g, 0.85 mmol, 1.0 equiv) and acceptor alcohol **15** (1.03 g, 0.96 mmol, 1.13 equiv) were treated with TMSOTf (15 μL, 0.085 mmol, 0.1 equiv) in anhydrous DCM (17 mL) to afford **16** (1.52 g, 0.71 mmol, 84%) as a white foam after purification by silica gel column chromatography (petroleum ether/DCM/EtOAc, 6:3:1).

$[\alpha]_D^{15}$ –0.86 (*c* 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.06–7.94 (m, 6 H), 7.94–7.85 (m, 12 H), 7.83 (d, *J* = 7.7 Hz, 4 H), 7.71 (d, *J* = 7.6 Hz, 2 H), 7.57–7.14 (m, 38 H), 7.10 (d, *J* = 7.7 Hz, 2 H), 6.08 (t, *J* = 9.7 Hz, 1 H), 5.92–5.81 (m, 3 H), 5.58 (t, *J* = 9.7 Hz, 1 H), 5.55–5.45 (m, 3 H), 5.45–5.39 (m, 1 H), 5.38–5.23 (m, 3 H), 4.99 (t, *J* = 9.0 Hz, 2 H), 4.93 (d, *J* = 7.9 Hz, 1 H), 4.72 (d, *J* = 7.8 Hz, 1 H), 4.12–3.96 (m, 5 H), 3.91–3.74 (m, 6 H), 3.45–3.36 (m, 1 H), 2.33 (s, 3 H), 0.83 (s, 9 H), –0.06 (s, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 165.9, 165.77, 165.73, 165.71, 165.5, 165.25, 165.22, 165.19, 165.18, 165.06, 165.02, 138.9, 133.98, 133.5, 133.4, 133.20, 133.17, 133.16, 133.08, 132.97, 130.1, 130.00, 129.95, 129.93, 129.91, 129.83, 129.79, 129.70, 129.54, 129.52, 129.48, 129.42, 129.21, 129.14, 129.10, 129.05, 128.98, 128.88, 128.87, 128.83, 128.7, 128.5, 128.43, 128.36, 128.27, 128.25, 128.1, 101.7, 100.93, 100.91, 86.9, 78.6, 75.4, 74.2, 73.9, 73.1, 72.97, 72.90, 72.5, 72.1, 71.96, 70.8, 70.6, 69.9, 69.8, 69.7, 69.2, 68.3, 68.1, 62.9, 60.4, 25.9, 21.2, 18.3, –5.3, –5.4.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{121}H_{114}NO_{32}SSi$: 2153.6887; found: 2153.6838.

(2,3,4-Tri-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranosyl Trichloroacetimidate (2)

Following the procedure for **7**, treatment of **16** (1.0 g, 0.47 mmol, 1.0 equiv) with NBS (167 mg, 0.94 mmol, 2.0 equiv) in acetone/H_2O (11 mL, 9:1 v/v) at 0 °C afforded the crude hemiacetal, which was treated with trichloroacetonitrile (235 μL, 2.35 mmol, 5.0 equiv) and DBU (35 μL, 0.235 mmol, 0.5 equiv) at 0 °C to afford **2** (837 mg, 0.39 mmol, 82% over 2 steps) as a white foam after purification by silica gel column chromatography (petroleum ether/DCM/EtOAc, 8:4:1).

$[\alpha]_D^{24}$ –8.9 (*c* 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.48 (s, 1 H), 8.03 (d, *J* = 7.4 Hz, 2 H), 8.01–7.92 (m, 8 H), 7.91–7.84 (m, 8 H), 7.82 (d, *J* = 7.4 Hz, 2 H), 7.78 (d, *J* = 7.3 Hz, 2 H), 7.73 (d, *J* = 7.4 Hz, 2 H), 7.57–7.14 (m, 34 H), 7.05 (t, *J* = 7.8 Hz, 2 H), 6.82 (d, *J* = 3.5 Hz, 1 H), 6.28 (t, *J* = 9.9 Hz, 1 H), 6.07 (t, *J* = 9.7 Hz, 1 H), 5.93 (t, *J* = 9.6 Hz, 1 H), 5.82–5.7 (m, 2 H), 5.65 (dd, *J* = 10.2, 3.5 Hz, 1 H), 5.55 (t, *J* = 9.7 Hz, 1 H), 5.49 (dd, *J* = 9.7, 8.0 Hz, 1 H), 5.41 (dd, *J* = 9.6, 8.0 Hz, 1 H), 5.37–5.25 (m, 3 H), 5.04 (d, *J* = 7.8 Hz, 1 H), 4.81 (d, *J* = 7.8 Hz, 2 H), 4.49–4.42 (m, 1 H), 4.15–4.07 (m, 3 H), 4.02–3.98 (m, 1 H), 3.88–3.73 (m, 5 H), 3.72–3.65 (m, 1 H), 3.50 (dd, *J* = 11.6, 5.7 Hz, 1 H), 0.83 (s, 9 H), –0.04 (s, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 165.9, 165.77, 165.74, 165.68, 165.4, 165.31, 165.30, 165.26, 165.21, 165.16, 165.08, 165.07, 160.4, 133.6, 133.5, 133.38, 133.35, 133.18, 133.11, 132.98, 130.1, 130.0, 129.91, 129.88, 129.80, 129.77, 129.74, 129.63, 129.57, 129.51, 129.15, 129.07, 129.06, 128.97, 128.92, 128.87, 128.83, 128.81, 128.76, 128.62, 128.57, 128.48, 128.44, 128.36, 128.30, 128.27, 128.23, 128.17, 101.3, 100.75, 100.71, 93.2, 77.4, 77.2, 75.2, 74.0, 73.96, 73.2, 72.95, 72.8, 72.4, 72.3, 72.0, 71.9, 70.9, 69.99, 69.6, 69.5, 69.2, 68.6, 67.9, 67.3, 62.8, 25.8, 18.3, –5.3, –5.4.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{116}H_{108}Cl_3N_2O_{33}Si$: 2189.5664; found: 2189.5633.

p-Tolylthio 2-*O*-Benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (13), *p*-Tolylthio 3-*O*-Benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (13a), and *p*-Tolylthio 2,3-Di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (13b)

To a stirred solution of **17** (9.0 g, 24.0 mmol, 1.0 equiv) in $CHCl_3$ (350 mL) were added freshly prepared Ag_2O (8.34 g, 36.0 mmol, 1.5 equiv), BzCl (3.7 mL, 31.2 mmol, 1.3 equiv) at –20 °C. After the reaction mix-

ture was stirred for 8 h at 0 °C, the mixture was filtered through a small pad of Celite, and washed with DCM. The collected filtrate was concentrated and the residue was purified by flash chromatography on a silica gel column (petroleum ether/DCM/EtOAc, 6:3:1) to give **13b** (1.25 g, 2.16 mmol, 9%) and a mixture of **13** and **13a**. Pure **13** (7.0 g, 14.64 mmol, 61%) was isolated by recrystallization from toluene and analytically pure **13a** (0.8 g, 1.68 mmol, 7%) was separated from the mother liquid.

13: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 7.6 Hz, 2 H), 7.61 (t, *J* = 7.4 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 4 H), 7.41–7.32 (m, 5 H), 7.11 (d, *J* = 7.8 Hz, 2 H), 5.55 (s, 1 H), 5.12 (t, *J* = 9.4 Hz, 1 H), 4.83 (d, *J* = 10.0 Hz, 1 H), 4.41 (dd, *J* = 10.5, 4.7 Hz, 1 H), 4.03 (t, *J* = 8.8 Hz, 1 H), 3.81 (t, *J* = 10.1 Hz, 1 H), 3.63–3.51 (m, 2 H), 2.89 (s, 1 H), 2.35 (s, 3 H).

13a: $[\alpha]_D^{23}$ –113.6 (*c* 0.667, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 7.2 Hz, 2 H), 7.56 (t, *J* = 7.4 Hz, 1 H), 7.51–7.38 (m, 6 H), 7.34–7.28 (m, 3 H), 7.17 (d, *J* = 7.9 Hz, 2 H), 5.59–5.46 (m, 2 H), 4.72 (d, *J* = 9.7 Hz, 1 H), 4.42 (dd, *J* = 10.5, 4.9 Hz, 1 H), 3.80 (m, 2 H), 3.73–3.57 (m, 2 H), 3.00 (d, *J* = 3.1 Hz, 1 H), 2.38 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.7, 138.9, 136.8, 133.9, 133.3, 130.0, 129.6, 129.1, 128.4, 128.2, 127.3, 126.1, 101.5, 89.4, 78.4, 75.6, 71.7, 70.9, 68.6, 21.3.

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{27}H_{30}NO_6S$: 496.1788; found: 496.1783.

13b: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 7.2 Hz, 4 H), 7.51 (m, 2 H), 7.45–7.29 (m, 11 H), 7.13 (d, *J* = 7.9 Hz, 2 H), 5.80 (t, *J* = 9.5 Hz, 1 H), 5.54 (s, 1 H), 5.46 (t, *J* = 9.6 Hz, 1 H), 4.98 (d, *J* = 10.0 Hz, 1 H), 4.47 (dd, *J* = 10.5, 4.8 Hz, 1 H), 3.89 (m, 2 H), 3.74 (m, 1 H), 2.36 (s, 3 H). The data are indentical with the reported.[30]

p-Tolylthio 2-*O*-Benzoyl-4-*O*-benzyl-β-D-glucopyranoside (18)

A solution of BH_3·THF (1 M, 100 mL, 100 mmol, 10.0 equiv) was added to a 250 mL dry flask containing **13** (4.79 g, 10 mmol, 1.0 equiv) at 0 °C. After the resulting solution was stirred for 5 min, a solution of Bu_2BOTf (1 M in DCM, 5 mL, 5 mmol, 0.5 equiv) was then added to the clear solution slowly. After being stirred for 2 h at 28 °C, the starting material had disappeared (TLC monitoring). Et_3N (1.4 mL, 10 mmol, 1.0 equiv) was added to quench the reaction, then MeOH was slowly added until the evolution of H_2 had ceased while cooling in an ice bath. The reaction mixture was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 3:1) to afford **18** (3.40 g, 7.07 mmol, 71%) as a white foam.

$[\alpha]_D^{19}$ –15.0 (*c* 0.95, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.1 Hz, 2 H), 7.60 (t, *J* = 7.5 Hz, 1 H), 7.48 (t, *J* = 7.7 Hz, 2 H), 7.38–7.28 (m, 7 H), 7.09 (d, *J* = 8.0 Hz, 2 H), 4.98 (t, *J* = 10.0 Hz, 1 H), 4.85 (d, *J* = 11.3 Hz, 1 H), 4.79–4.71 (m, 2 H), 3.99–3.90 (m, 2 H), 3.79–3.70 (m, 1 H), 3.56 (t, *J* = 9.2 Hz, 1 H), 3.49–3.43 (m, 1 H), 2.78 (d, *J* = 3.3 Hz, 1 H), 2.33 (s, 3 H), 2.07 (brs, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.5, 138.7, 138.0, 133.6, 133.5, 130.2, 129.9, 129.6, 128.7, 128.6, 128.3, 128.2, 85.9, 79.4, 77.8, 77.4, 75.1, 73.6, 62.2, 21.3.

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{27}H_{32}NO_6S$: 498.1945; found: 498.1960.

p-Tolylthio 2-*O*-Benzoyl-4-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranoside (19)

To a solution of **18** (3.40 g, 7.07 mmol, 1.0 equiv) in anhydrous pyridine (68 mL) were added TBSCl (1.60 g, 10.6 mmol, 1.5 equiv) and DMAP (87 mg, 0.71 mmol, 0.1 equiv). The resulting mixture was stirred for 4 h at 50 °C. At this stage the solution was concentrated *in vacuo*, and the resultant solid was dissolved in DCM, and sequentially washed with 1 M HCl and brine. The aqueous layer was extracted with DCM and the combined organic layers were dried over Na_2SO_4. The solid was filtered off and the filtrate was concentrated. The obtained residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 5:1) to afford **19** (4.08 g, 6.86 mmol, 97%) as a white foam.

$[\alpha]_D^{19}$ –33.0 (*c* 1.1, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.3 Hz, 2 H), 7.60 (t, *J* = 7.4 Hz, 1 H), 7.47 (t, *J* = 7.8 Hz, 2 H), 7.40–7.33 (m, 6 H), 7.32–7.27 (m, 1 H), 7.07 (d, *J* = 7.9 Hz, 2 H), 4.94 (t, *J* = 9.5 Hz, 1 H), 4.84 (d, *J* = 11.2 Hz, 1 H), 4.78–4.70 (m, 2 H), 4.00–3.87 (m, 3 H), 3.64 (t, *J* = 9.3 Hz, 1 H), 3.44–3.37 (m, 1 H), 2.65 (brs, 1 H), 2.33 (s, 3 H), 0.96 (s, 9 H), 0.14 (s, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 166.4, 138.4, 138.3, 133.7, 133.5, 130.1, 129.8, 129.7, 128.7, 128.56, 128.53, 128.2, 128.1, 85.8, 80.2, 77.8, 77.4, 75.1, 73.5, 62.3, 26.1, 21.3, 18.5, –4.9, –5.2.

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{33}H_{46}NO_6SSi$: 612.2810; found: 612.2825.

p-Tolylthio 2-*O*-Benzoyl-4-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-levulinoyl-β-D-glucopyranoside (20)

A solution of **19** (4.17 g, 7.01 mmol, 1.0 equiv) and levulinic acid (1.22 g, 10.5 mmol, 1.5 equiv) in DCM (60 mL) was treated with DMAP (86 mg, 0.70 mmol, 0.1 equiv) and DCC (2.60 g, 12.6 mmol, 1.8 equiv) at 0 °C. The solution was allowed to stir at rt for 3 h. A white precipitate slowly formed, and the solution turned slightly pink. After complete conversion of the starting material, the mixture was filtered through a Celite pad and the filtrate was evaporated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 4:1) to afford **20** (4.76 g, 6.87 mmol, 98%) as a colorless oil.

$[\alpha]_D^{19}$ –10.2 (*c* 1.23, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 7.3 Hz, 2 H), 7.58 (t, *J* = 7.4 Hz, 1 H), 7.45 (t, *J* = 7.7 Hz, 2 H), 7.39–7.24 (m, 7 H), 7.07 (d, *J* = 8.0 Hz, 2 H), 5.41 (t, *J* = 9.4 Hz, 1 H), 5.08 (t, *J* = 9.7 Hz, 1 H), 4.75 (d, *J* = 10.0 Hz, 1 H), 4.69–4.62 (m, 2 H), 3.98–3.85 (m, 2 H), 3.79 (t, *J* = 9.5 Hz, 1 H), 3.47–3.43 (m, 1 H), 2.52–2.25 (m, 7 H), 1.99 (s, 3 H), 0.96 (s, 9 H), 0.15 (s, 3 H), 0.12 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 205.9, 172.0, 165.4, 138.4, 138.1, 133.7, 133.4, 130.1, 129.71, 129.68, 128.55, 128.54, 128.46, 128.1, 127.96, 86.1, 80.4, 76.5, 75.4, 74.8, 71.2, 62.1, 37.9, 29.7, 28.1, 26.1, 21.3, 18.5, –4.9, –5.2.

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{38}H_{52}NO_8SSi$: 710.3177; found: 710.3194.

2-*O*-Benzoyl-4-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-levulinoyl-α-D-glucopyranosyl Trichloroacetimidate (8)

NIS (3.11 g, 13.83 mmol, 2.0 equiv) and TFA (565 µL, 7.60 mmol, 1.1 equiv) were added to a solution of **20** (4.79 g, 6.91 mmol, 1.0 equiv) in a mixture of DCM/H_2O (66 mL, 10:1 v/v) at 0 °C. The reaction was allowed to proceed under stirring for 2 h at rt and quenched with Et_3N. The mixture was concentrated, and then the residue was dissolved in DCM (50 mL) and washed with 20% (w/w) aqueous $Na_2S_2O_3$ (50 mL)

and saturated aqueous $NaHCO_3$ (50 mL). The organic layer was separated and the aqueous layer was reextracted with DCM (2 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The resultant hemiacetal was treated with trichloroacetonitrile (3.47 mL, 34.6 mmol, 5.0 equiv) in anhydrous DCM (50 mL) in the presence of DBU (517 µL, 3.46 mmol, 0.5 equiv). After being stirred at rt for 12 h, the reaction mixture was concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 6:1) to afford **8** (3.39 g, 4.64 mmol, 67% over 2 steps, α/β = 20:1) as a white foam.

$[\alpha]_D^{19}$ +82.8 (*c* 0.94, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.47 (s, 1 H), 7.97 (d, *J* = 8.2 Hz, 2 H), 7.55 (t, *J* = 7.4 Hz, 1 H), 7.41 (t, *J* = 7.8 Hz, 2 H), 7.37–7.32 (m, 4 H), 7.32–7.27 (m, 1 H), 6.66 (d, *J* = 3.5 Hz, 1 H), 5.85 (t, *J* = 9.5 Hz, 1 H), 5.22 (dd, *J* = 10.2, 3.6 Hz, 1 H), 4.73 (s, 2 H), 4.05–3.93 (m, 3 H), 3.89 (d, *J* = 11.1 Hz, 1 H), 2.58–2.50 (m, 2 H), 2.43–2.33 (m, 2 H), 2.00 (s, 3 H), 0.95 (s, 9 H), 0.12 (s, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 205.8, 171.98, 165.7, 160.8, 138.0, 133.5, 130.1, 129.1, 128.59, 128.53, 128.3, 128.0, 93.8, 75.09, 75.06, 74.5, 72.1, 71.3, 61.5, 37.9, 29.7, 28.1, 26.1, 18.5, –4.9, –5.2.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{33}H_{46}Cl_3N_2O_9Si$: 747.2033; found: 747.2046.

p-Tolylthio 2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-levulinoyl-β-D-glucopyranoside (21)

Following the procedure for **20**, **13** (9.0 g, 18.8 mmol, 1.0 equiv) and levulinic acid (3.28 g, 28.2 mmol, 1.5 equiv) were treated with DCC (6.97 g, 33.8 mmol, 1.8 equiv) and DMAP (230 mg, 1.88 mmol, 0.1 equiv) in anhydrous DCM (20 mL) to afford **21** (10.4 g, 18.1 mmol, 96%) as a white foam after purification by silica gel column chromatography (petroleum ether/DCM/EtOAc, 6:3:1).

$[\alpha]_D^{24}$ –12.3 (*c* 1.1, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 7.1 Hz, 2 H), 7.60 (t, *J* = 7.4 Hz, 1 H), 7.52–7.41 (m, 4 H), 7.39–7.31 (m, 5 H), 7.11 (d, *J* = 8.0 Hz, 2 H), 5.57–5.46 (m, 2 H), 5.26 (t, *J* = 9.5 Hz, 1 H), 4.88 (d, *J* = 10.0 Hz, 1 H), 4.42 (dd, *J* = 10.5, 4.9 Hz, 1 H), 3.83 (t, *J* = 10.2 Hz, 1 H), 3.74 (t, *J* = 9.5 Hz, 1 H), 3.68–3.59 (m, 1 H), 2.58–2.41 (m, 4 H), 2.34 (s, 3 H), 1.98 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 205.8, 171.9, 165.3, 138.9, 136.9, 133.9, 133.5, 130.1, 129.9, 129.5, 129.2, 128.6, 128.3, 127.96, 126.3, 101.6, 87.2, 78.3, 73.1, 71.2, 70.9, 68.6, 38.0, 29.6, 28.1, 21.3.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{32}H_{36}NO_8S$: 594.2156; found: 594.2173.

2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-levulinoyl-α-D-glucopyranosyl Trichloroacetimidate (22)

Following the procedure for **8**, treatment of **21** (4.20 g, 7.28 mmol, 1.0 equiv) with NIS (4.09 g, 18.2 mmol, 2.5 equiv) and TFA (595 µL, 8.01 mmol, 1.1 equiv) in DCM/H_2O (154 mL, 9:1 v/v) at 0 °C afforded crude the hemiacetal, which was treated with trichloroacetonitrile (3.65 mL, 36.4 mmol, 5 equiv) and DBU (544 µL, 3.64 mmol, 0.5 equiv) at rt to afford **22** (3.94 g, 6.41 mmol, 88% over 2 steps, α/β = 20:1) as a white foam after purification by silica gel column chromatography (petroleum ether/DCM/EtOAc, 6:3:1).

$[\alpha]_D^{19}$ +38.8 (*c* 0.33, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.58 (s, 1 H), 8.01 (d, *J* = 7.2 Hz, 2 H), 7.57 (t, *J* = 7.4 Hz, 1 H), 7.52–7.46 (m, 2 H), 7.44–7.33 (m, 5 H), 6.69 (d, *J* = 3.8 Hz, 1 H), 5.89 (t, *J* = 9.9 Hz, 1 H), 5.59 (s, 1 H), 5.38 (dd, *J* = 9.9, 3.8 Hz, 1 H), 4.40 (dd, *J* = 10.4, 4.9 Hz, 1 H), 4.22–4.17 (m, 1 H), 3.91–3.81 (m, 2 H), 2.68–2.46 (m, 4 H), 1.99 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 205.7, 171.8, 165.2, 138.7, 136.7, 133.7, 133.4, 130.0, 129.7, 129.3, 129.1, 128.5, 128.2, 127.8, 126.1, 101.4, 87.1, 78.2, 73.0, 71.1, 70.8, 68.5, 37.9, 28.0, 21.2.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{27}H_{30}Cl_3N_2O_9$: 631.1011; found: 631.1012.

p-Tolylthio (2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-levulinoyl-β-D-glucopyranosyl)-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (11)

Following the procedure for **4**, trichloroacetimidate **22** (5.4 g, 8.78 mmol, 1.2 equiv) and **13** (3.5 g, 7.32 mmol, 1.0 equiv) were treated with TMSOTf (132 µL, 0.73 mmol, 0.1 equiv) in anhydrous DCM (120 mL) at –40 °C to afford **11** (5.65 g, 6.07 mmol, 83%) as a white foam after purification by silica gel column chromatography (petroleum ether/EtOAc, 3:1).

$[\alpha]_D^{19}$ +16.1 (*c* 1.59, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 7.6 Hz, 2 H), 7.62–7.46 (m, 6 H), 7.43–7.31 (m, 10 H), 7.30–7.21 (m, 4 H), 7.05 (d, *J* = 7.8 Hz, 2 H), 5.58 (s, 1 H), 5.34–5.16 (m, 4 H), 4.92 (d, *J* = 7.0 Hz, 1 H), 4.75 (d, *J* = 10.0 Hz, 1 H), 4.39 (dd, *J* = 10.4, 4.6 Hz, 1 H), 4.26–4.12 (m, 2 H), 3.88–3.75 (m, 3 H), 3.68 (t, *J* = 10.2 Hz, 1 H), 3.59–3.53 (m, 1 H), 3.46–3.39 (m, 1 H), 2.53–2.26 (m, 7 H), 1.94 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 205.8, 171.8, 164.9, 164.7, 138.6, 137.1, 136.9, 133.4, 133.1, 132.9, 129.9, 129.8, 129.14, 129.07, 128.47, 128.41, 128.25, 128.21, 126.20, 126.14, 101.6, 101.3, 100.7, 87.6, 79.6, 79.3, 77.9, 72.96, 72.1, 70.8, 68.6, 66.2, 37.9, 29.6, 28.0, 21.2.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{52}H_{54}NO_{14}S$: 948.3260; found: 948.3279.

(2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-levulinoyl-β-D-glucopyranosyl)-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranosyl Trichloroacetimidate (12)

Following the procedure for **8**, treatment of **11** (2.8 g, 3.0 mmol, 1.0 equiv) with NIS (1.69 g, 7.5 mmol, 2.5 equiv) and TFA (245 µL, 3.3 mmol, 1.1 equiv) in DCM/H_2O (66 mL, 10:1 v/v) at 0 °C afforded the crude hemiacetal, which was treated with trichloroacetonitrile (1.5 mL, 15.0 mmol, 5.0 equiv) and DBU (224 µL, 1.5 mmol, 0.5 equiv) at rt to afford **12** (2.30 g, 2.37 mmol, 79% over 2 steps) as a white foam after purification by silica gel column chromatography (DCM/EtOAc, 30:1).

$[\alpha]_D^{19}$ +46.2 (*c* 0.99, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.50 (s, 1 H), 7.72 (d, *J* = 7.6 Hz, 2 H), 7.61–7.51 (m, 5 H), 7.49–7.28 (m, 11 H), 7.18 (t, *J* = 7.7 Hz, 2 H), 6.55 (d, *J* = 3.9 Hz, 1 H), 5.64 (s, 1 H), 5.42–5.34 (m, 2 H), 5.31–5.22 (m, 2 H), 5.05 (d, *J* = 7.2 Hz, 1 H), 4.48 (t, *J* = 9.4 Hz, 1 H), 4.39–4.31 (m, 2 H), 4.12–4.06 (m, 1 H), 3.92–3.73 (m, 4 H), 3.65–3.57 (m, 1 H), 2.53–2.33 (m, 4 H), 1.94 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 205.8, 171.9, 165.0, 160.7, 137.0, 136.9, 133.5, 133.1, 129.81, 129.75, 129.4, 129.2, 128.9, 128.6, 128.47, 128.38, 128.32, 128.30, 126.28, 126.15, 101.51, 101.46, 101.36, 93.6, 79.1, 78.1, 76.0, 72.98, 72.3, 72.1, 68.7, 68.6, 66.5, 65.3, 37.97, 29.6, 28.1.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{47}H_{48}N_2O_{15}Cl_3$: 985.2115; found: 985.2113.

***p*-Tolylthio (2-*O*-Benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (23)**

Compound **11** (2.5 g, 2.68 mmol, 1.0 equiv) was dissolved in DCM (40 mL), followed by addition of AcOH (15.3 mL, 268 mmol, 100.0 equiv) and $NH_2NH_2{\cdot}H_2O$ (650 μL, 13.4 mmol, 5.0 equiv). The resulting reaction mixture was stirred at rt for 3 h and quenched with acetone. The mixture was diluted with DCM and washed with saturated aqueous $NaHCO_3$. The collected organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/DCM/EtOAc, 9:2:2, to DCM/EtOAc, 30:1) to afford **23** (2.19 g, 2.63 mmol, 98%) as a white foam.

$[\alpha]_D^{24}$ –6.0 (*c* 1.1, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 7.6 Hz, 2 H), 7.68 (d, *J* = 7.6 Hz, 2 H), 7.58–7.48 (m, 4 H), 7.44–7.24 (m, 14 H), 7.06 (d, *J* = 7.9 Hz, 2 H), 5.56 (s, 1 H), 5.31 (s, 1 H), 5.24 (t, *J* = 9.3 Hz, 1 H), 5.07 (t, *J* = 7.4 Hz, 1 H), 4.91 (d, *J* = 7.0 Hz, 1 H), 4.78 (d, *J* = 9.9 Hz, 1 H), 4.39 (dd, *J* = 10.5, 4.8 Hz, 1 H), 4.23 (t, *J* = 8.9 Hz, 1 H), 4.15 (dd, *J* = 10.4, 4.9 Hz, 1 H), 3.88–3.73 (m, 3 H), 3.66 (t, *J* = 9.6 Hz, 2 H), 3.61–3.55 (m, 1 H), 3.38–3.32 (m, 1 H), 2.64 (brs, 1 H), 2.32 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 165.6, 164.8, 138.6, 137.2, 137.0, 133.6, 133.2, 133.1, 129.91, 129.90, 129.8, 129.6, 129.46, 129.36, 129.30, 128.44, 128.43, 128.36, 128.28, 126.3, 126.2, 101.71, 101.67, 100.4, 87.5, 80.5, 79.4, 79.2, 75.5, 72.7, 72.4, 70.8, 68.71, 68.68, 66.1, 21.3.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{47}H_{48}NO_{12}S$: 850.2892; found: 850.2907.

***p*-Tolylthio (2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-levulinoyl-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (9)**

Following the procedure for **4**, trichloroacetimidate **12** (1.39 g, 1.43 mmol, 1.1 equiv) and alcohol **23** (1.08 g, 1.3 mmol, 1.0 equiv) were treated with TMSOTf (24 μL, 0.13 mmol, 0.1 equiv) in anhydrous DCM (24 mL) at –40 °C to afford **9** (1.82 g, 1.11 mmol, 85%) as a white foam after purification by silica gel column chromatography (DCM/EtOAc, 15:1).

$[\alpha]_D^{19}$ +36.1 (*c* 0.97, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 7.8 Hz, 2 H), 7.77 (d, *J* = 7.7 Hz, 4 H), 7.65 (d, *J* = 7.8 Hz, 2 H), 7.60 (t, *J* = 7.3 Hz, 1 H), 7.56–7.20 (m, 32 H), 7.14 (t, *J* = 7.3 Hz, 1 H), 7.07 (d, *J* = 7.9 Hz, 2 H), 5.48 (s, 1 H), 5.42–5.34 (m, 2 H), 5.27–5.21 (m, 2 H), 5.14 (s, 1 H), 5.03 (t, *J* = 7.6 Hz, 2 H), 4.85–4.81 (m, 2 H), 4.76 (t, *J* = 9.3 Hz, 1 H), 4.66 (d, *J* = 10.1 Hz, 1 H), 4.51 (s, 1 H), 4.33 (dd, *J* = 10.4, 4.8 Hz, 1 H), 4.24–4.16 (m, 2 H), 4.15–4.05 (m, 3 H), 3.96–3.88 (m, 2 H), 3.81–3.54 (m, 6 H), 3.54–3.38 (m, 4 H), 3.13 (t, *J* = 9.4 Hz, 1 H), 2.57–2.36 (m, 4 H), 2.32 (s, 3 H), 1.97 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 205.9, 171.8, 165.1, 164.97, 164.67, 164.64, 138.4, 137.40, 137.39, 137.2, 137.0, 133.7, 133.39, 133.31, 133.28, 132.8, 129.96, 129.93, 129.81, 129.76, 129.57, 129.54, 129.51, 129.48, 129.28, 129.18, 129.12, 129.10, 128.91, 128.87, 128.59, 128.51, 128.45, 128.38, 128.27, 128.0, 126.6, 126.3, 126.2, 102.1, 101.4, 101.1, 100.7, 99.8, 97.8, 97.3, 88.0, 78.9, 78.6, 78.3, 77.9, 77.3, 75.3, 74.9, 73.3, 73.0, 72.9, 72.8, 72.1, 70.8, 68.8, 68.7, 68.6, 66.3, 65.97, 65.4, 38.1, 29.6, 28.1, 21.2.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{92}H_{86}NaO_{26}S$: 1661.5020; found: 1661.5022.

(2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-levulinoyl-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-D-glucopyranosyl Trichloroacetimidate (10)

Following the procedure for **8**, treatment of **9** (5.8 g, 3.54 mmol, 1.0 equiv) with NIS (1.59 g, 7.07 mmol, 2.0 equiv) and TFA (289 μL, 3.89 mmol, 1.1 equiv) in DCM/H_2O (77 mL, 10:1 v/v) at 0 °C afforded the hemiacetal, which was treated with trichloroacetonitrile (1.77 mL, 17.7 mmol, 5.0 equiv) and DBU (265 μL, 1.77 mmol, 0.5 equiv) at rt to afford **10** (4.19 g, 2.50 mmol, 70% over 2 steps, α/β = 8.3:1) as a white foam after purification by silica gel column chromatography (petroleum ether/DCM/EtOAc, 5:2:2).

$[\alpha]_D^{24}$ +35.6 (*c* 1.1, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.48 (s, 1 H), 7.83 (d, *J* = 7.7 Hz, 2 H), 7.80–7.66 (m, 6 H), 7.63–7.57 (m, 3 H), 7.53–7.22 (m, 28 H), 7.15 (t, *J* = 7.4 Hz, 1 H), 6.43 (d, *J* = 3.2 Hz, 1 H), 5.58 (s, 1 H), 5.39–5.32 (m, 2 H), 5.27–5.23 (m, 2 H), 5.19 (s, 1 H), 5.06 (d, *J* = 6.5 Hz, 1 H), 5.02–4.98 (m, 2 H), 4.88 (s, 1 H), 4.57–4.50 (m, 2 H), 4.41 (t, *J* = 9.5 Hz, 1 H), 4.32 (dd, *J* = 10.4, 4.9 Hz, 1 H), 4.23–4.17 (m, 3 H), 4.02–3.87 (m, 4 H), 3.80–3.43 (m, 9 H), 3.35–3.22 (m, 1 H), 2.53–2.36 (m, 4 H), 1.95 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 205.9, 171.8, 165.1, 164.9, 164.7, 164.5, 160.7, 137.36, 137.30, 137.0, 136.9, 133.55, 133.52, 133.4, 133.2, 129.9, 129.82, 129.74, 129.65, 129.48, 129.47, 129.27, 129.19, 129.07, 128.9, 128.78, 128.74, 128.51, 128.47, 128.43, 128.40, 128.26, 128.22, 128.02, 126.6, 126.25, 126.22, 126.1, 102.2, 101.3, 101.1, 100.8, 99.9, 98.1, 97.4, 93.5, 78.9, 78.3, 78.2, 78.0, 77.3, 75.1, 73.5, 72.97, 72.94, 72.8, 72.1, 71.1, 68.8, 68.7, 68.64, 68.55, 66.2, 66.0, 65.4, 65.3, 60.5, 37.97, 29.6, 28.1.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{87}H_{80}{}^{37}ClCl_2NNaO_{27}$: 1700.3846; found: 1700.3830.

2-Azidoethyl (2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-levulinoyl-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (24)

Following the procedure for **4**, trichloroacetimidate **10** (1.81 g, 1.08 mmol, 1.0 equiv) and 2-azidoethanol (563 mg, 6.47 mmol, 6.0 equiv) were treated with TMSOTf (39 μL, 0.216 mmol, 0.2 equiv) in anhydrous DCM (40 mL) to afford **24** (1.55 g, 0.97 mmol, 90%) as a white foam after purification by silica gel column chromatography (petroleum ether/DCM/EtOAc, 2:1:1).

$[\alpha]_D^{24}$ +13.2 (*c* 1.1, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 7.7 Hz, 2 H), 7.78 (d, *J* = 7.9 Hz, 4 H), 7.67 (d, *J* = 7.7 Hz, 2 H), 7.61–7.16 (m, 32 H), 5.51 (s, 1 H), 5.42–5.37 (m, 2 H), 5.28 (t, *J* = 8.1 Hz, 1 H), 5.21 (t, *J* = 6.0 Hz, 1 H), 5.10–4.99 (m, 3 H), 4.88–4.86 (d, *J* = 8.0 Hz, 3 H), 4.68 (s, 1 H), 4.55 (d, *J* = 7.6 Hz, 1 H), 4.34 (dd, *J* = 10.2, 4.6 Hz, 1 H), 4.26–4.07 (m, 5 H), 3.95 (t, *J* = 8.2 Hz, 2 H), 3.89–3.83 (m, 1 H), 3.81–3.43 (m, 11 H), 3.31–3.22 (m, 3 H), 2.58–2.36 (m, 4 H), 1.97 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 205.9, 171.7, 165.1, 164.7, 164.62, 164.56, 137.3, 137.2, 136.96, 133.4, 133.20, 133.18, 129.9, 129.8, 129.74, 129.70, 129.48, 129.41, 129.38, 129.2, 129.10, 129.09, 129.04, 128.96, 128.7, 128.6, 128.43, 128.38, 128.32, 128.21, 128.18, 128.0, 126.5, 126.28, 126.22, 126.1, 101.9, 101.33, 101.31, 100.98, 100.92, 99.5, 98.1, 97.3, 78.7, 78.6, 78.3, 77.7, 77.5, 77.4, 74.8, 74.5, 73.9, 73.2, 72.8, 72.7, 72.1, 68.76, 68.73, 68.6, 67.9, 66.6, 66.2, 65.8, 65.5, 50.7, 37.98, 29.6, 28.1.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{87}H_{83}N_3NaO_{27}$: 1624.5106; found: 1624.5095.

2-Azidoethyl (2-*O*-Benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (25)

Following the procedure for **23**, tetrasaccharide **24** (3.01 g, 1.88 mmol, 1.0 equiv) was treated with $NH_2NH_2{\cdot}H_2O$ (455 μL, 9.39 mmol, 5.0 equiv) and AcOH (10.7 mL, 188 mmol, 100 equiv) in DCM (50 mL) to afford **25** (2.45 g, 1.63 mmol, 87%) as a white foam after purification by silica gel column chromatography (petroleum ether/DCM/EtOAc, 5:2:2).

$[\alpha]_D^{24}$ +4.4 (*c* 1.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 7.3 Hz, 2 H), 7.86 (d, *J* = 7.2 Hz, 2 H), 7.79 (d, *J* = 7.3 Hz, 2 H), 7.66 (d, *J* = 7.3 Hz, 2 H), 7.58–7.48 (m, 5 H), 7.47–7.43 (m, 3 H), 7.42–7.31 (m, 19 H), 7.31–7.17 (m, 5 H), 5.54 (s, 1 H), 5.42 (s, 1 H), 5.22–5.13 (m, 2 H), 5.05 (d, *J* = 7.4 Hz, 1 H), 4.99 (d, *J* = 5.3 Hz, 1 H), 4.93 (t, *J* = 8.1 Hz, 1 H), 4.89–4.79 (m, 3 H), 4.76 (s, 1 H), 4.56 (d, *J* = 7.6 Hz, 1 H), 4.34 (dd, *J* = 10.4, 4.8 Hz, 1 H), 4.20 (dd, *J* = 10.4, 4.9 Hz, 1 H), 4.17–4.05 (m, 4 H), 4.01–3.91 (m, 3 H), 3.90–3.87 (m, 1 H), 3.76–3.64 (m, 3 H), 3.62–3.35 (m, 9 H), 3.32–3.20 (m, 2 H), 2.63 (brs, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.9, 164.68, 164.65, 164.61, 137.31, 137.24, 137.1, 137.0, 133.6, 133.4, 133.2, 133.1, 129.9, 129.8, 129.72, 129.68, 129.44, 129.41, 129.36, 129.30, 129.25, 129.1, 129.04, 128.95, 128.66, 128.59, 128.40, 128.37, 128.32, 128.29, 128.1, 126.4, 126.33, 126.31, 126.1, 101.9, 101.8, 101.3, 101.2, 100.8, 98.8, 98.4, 97.1, 80.8, 78.7, 78.3, 77.5, 77.3, 77.1, 76.9, 75.1, 74.9, 74.4, 73.8, 73.5, 72.7, 72.5, 68.70, 68.66, 68.64, 67.9, 66.6, 66.0, 65.6, 50.7.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{82}H_{81}N_4O_{25}$: 1521.5184; found: 1521.5186.

2-Azidoethyl (4-*O*-Benzyl-2-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-levulinoyl-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (26)

A mixture of trichloroacetimidate **8** (1.45 g, 1.98 mmol, 1.5 equiv) and tetrasaccharide **25** (1.99 g, 1.32 mmol, 1.0 equiv) in anhydrous DCM (50 mL) was stirred for 30 min in the presence of freshly activated 5 Å molecular sieves (2.5 g). Then the mixture was cooled to –40 °C followed by addition of TBSOTf (61 μL, 0.264 mmol, 0.2 equiv). After being stirred for 2 h at –40 °C, the reaction mixture was filtered through a Celite pad, and the filtrate was sequentially washed with saturated aqueous $NaHCO_3$ and brine. The collected organic layers were dried over Na_2SO_4. The solid was filtered off, and the filtrate was concentrated. The residue was purified by silica gel chromatography (toluene/EtOAc, 6:1) to afford **26** (2.28 g, 1.10 mmol, 83%) as a white foam.

$[\alpha]_D^{24}$ +29.7 (*c* 1.1, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99–7.87 (m, 6 H), 7.79 (d, *J* = 7.7 Hz, 2 H), 7.69 (d, *J* = 7.7 Hz, 2 H), 7.64 (d, *J* = 7.6 Hz, 2 H), 7.55–7.23 (m, 37 H), 7.16 (t, *J* = 7.4 Hz, 1 H), 5.54 (s, 1 H), 5.39 (t, *J* = 9.4 Hz, 1 H), 5.22–5.09 (m, 3 H), 5.04–4.95 (m, 2 H), 4.95–4.84 (m, 4 H), 4.81 (t, *J* = 6.8 Hz, 1 H), 4.71–4.60 (m, 4 H), 4.55 (d, *J* = 7.7 Hz, 1 H), 4.33 (dd, *J* = 10.4, 4.7 Hz, 1 H), 4.21–4.02 (m, 7 H), 3.93 (dd, *J* = 8.2, 3.9 Hz, 1 H), 3.90–3.66 (m, 6 H), 3.65–3.58 (m, 1 H), 3.58–3.34 (m, 8 H), 3.32–3.22 (m, 2 H), 3.16 (t, *J* = 9.3 Hz, 1 H), 3.02 (t, *J* = 8.8 Hz, 1 H), 2.52–2.47 (m, 2 H), 2.40–2.27 (m, 2 H), 2.01 (s, 3 H), 0.87 (s, 9 H), 0.01 (s, 3 H), –0.05 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 206.0, 171.8, 165.3, 164.8, 164.7, 164.6, 164.5, 138.2, 137.33, 137.27, 137.21, 133.96, 133.49, 133.44, 133.2, 129.88, 129.87, 129.69, 129.65, 129.46, 129.40, 129.24, 129.18, 129.06, 129.01, 128.80, 128.74, 128.71, 128.5, 128.44, 128.40, 128.36, 128.31, 128.2, 128.1, 128.0, 127.8, 127.7, 126.6, 126.4, 126.3, 102.2, 101.6, 101.2, 100.88, 100.82, 97.9, 97.3, 96.9, 96.7, 78.6, 78.2, 78.1, 77.5, 76.1, 75.7, 75.4, 75.2, 74.6, 74.5, 74.3, 73.99, 73.7, 73.5, 72.6, 72.4, 72.1, 68.9, 68.7, 68.59, 68.55, 67.9, 66.5, 65.7, 65.4, 65.1, 61.6, 50.7, 37.9, 29.6, 28.1, 25.9, 18.3, –4.7, –5.6.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{113}H_{121}N_4O_{33}Si$: 2089.7677; found: 2089.7622.

2-Azidoethyl (4-*O*-Benzyl-2-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (27)

Following the procedure for **23**, pentasaccharide **26** (3.81 g, 1.84 mmol, 1.0 equiv) was treated with $NH_2NH_2{\cdot}H_2O$ (446 μL, 9.2 mmol, 5.0 equiv) in AcOH (10.5 mL, 184 mmol, 100 equiv) and DCM (50 mL) at 30 °C to afford **27** (3.45 g, 1.75 mmol, 95%) as a white foam after purification by silica gel column chromatography (petroleum ether/DCM/EtOAc, 2:1:1).

$[\alpha]_D^{24}$ +99.9 (*c* 0.9, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 7.7 Hz, 2 H), 7.93 (d, *J* = 7.8 Hz, 4 H), 7.81 (d, *J* = 7.9 Hz, 2 H), 7.71 (d, *J* = 7.9 Hz, 2 H), 7.64 (d, *J* = 7.7 Hz, 2 H), 7.56–7.43 (m, 10 H), 7.43–7.22 (m, 27 H), 7.17 (t, *J* = 7.3 Hz, 1 H), 5.54 (s, 1 H), 5.19 (s, 1 H), 5.15–5.03 (m, 3 H), 5.01–4.73 (m, 9 H), 4.70 (s, 1 H), 4.61–4.52 (m, 2 H), 4.34 (dd, *J* = 10.1, 4.5 Hz, 1 H), 4.25–4.03 (m, 7 H), 3.98–3.93 (m, 1 H), 3.92–3.82 (m, 4 H), 3.78 (d, *J* = 11.5 Hz, 1 H), 3.72–3.62 (m, 3 H), 3.61–3.21 (m, 10 H), 3.15 (t, *J* = 9.4 Hz, 1 H), 2.96 (t, *J* = 9.0 Hz, 1 H), 0.85 (s, 9 H), –0.01 (s, 3 H), –0.07 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 166.3, 165.0, 164.8, 164.7, 164.6, 138.5, 137.4, 137.30, 137.23, 134.13, 133.56, 133.49, 133.2, 129.99, 129.94, 129.73, 129.71, 129.6, 129.5, 129.4, 129.3, 129.2, 129.09, 129.07, 128.89, 128.80, 128.66, 128.57, 128.51, 128.47, 128.45, 128.35, 128.25, 128.10, 128.06, 127.9, 127.8, 126.6, 126.5, 126.4, 126.3, 102.2, 101.8, 101.3, 100.86, 100.79, 97.9, 97.1, 96.84, 96.79, 78.6, 78.2, 77.94, 77.91, 77.6, 75.7, 75.4, 74.9, 74.7, 74.6, 74.2, 74.1, 73.99, 73.5, 72.6, 72.2, 68.88, 68.80, 68.62, 68.56, 67.98, 66.6, 65.8, 65.4, 65.2, 61.98, 50.7, 25.9, 18.3, –4.7, –5.6.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{108}H_{115}N_4O_{31}Si$: 1991.7309; found: 1991.7260.

2-Azidoethyl (2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-levulinoyl-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(4-*O*-benzyl-2-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (28)

Following the procedure for **26**, trichloroacetimidate **10** (1.66 g, 0.99 mmol, 1.3 equiv) and pentasaccharide **27** (1.50 g, 0.76 mmol, 1.0

equiv) were treated with TBSOTf (35 μL, 0.15 mmol, 0.2 equiv) in anhydrous DCM (20 mL) at –40 °C to afford **28** (2.25 g, 0.64 mmol, 84%) as a white foam after purification by silica gel column chromatography (petroleum ether/DCM/EtOAc, 5:2:2).

$[\alpha]_D^{19}$ +61.7 (*c* 0.9, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91–7.73 (m, 10 H), 7.71–7.66 (m, 4 H), 7.62–7.56 (m, 6 H), 7.55–7.15 (m, 70 H), 5.51 (s, 1 H), 5.42–5.35 (m, 2 H), 5.30 (s, 1 H), 5.26 (t, *J* = 8.1 Hz, 1 H), 5.11 (t, *J* = 5.4 Hz, 1 H), 5.07–5.03 (m, 2 H), 4.99 (s, 1 H), 4.96–4.75 (m, 14 H), 4.73–4.65 (m, 3 H), 4.54 (d, *J* = 7.8 Hz, 2 H), 4.32 (dd, *J* = 10.1, 4.4 Hz, 1 H), 4.30–3.83 (m, 18 H), 3.81–3.61 (m, 7 H), 3.59–3.22 (m, 21 H), 3.13 (t, *J* = 9.4 Hz, 1 H), 3.02 (t, *J* = 8.8 Hz, 1 H), 2.56–2.38 (m, 4 H), 1.97 (s, 3 H), 0.80 (s, 9 H), –0.07 (s, 3 H), –0.11 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 205.9, 171.7, 165.1, 164.72, 164.68, 164.65, 164.51, 164.49, 138.8, 137.4, 137.3, 137.25, 137.20, 136.89, 133.88, 133.46, 133.37, 133.18, 133.11, 129.85, 129.82, 129.74, 129.69, 129.64, 129.59, 129.52, 129.44, 129.32, 129.28, 128.98, 128.96, 128.8, 128.7, 128.57, 128.54, 128.42, 128.39, 128.36, 128.30, 128.28, 128.23, 128.16, 128.07, 128.04, 127.8, 127.5, 126.50, 126.49, 126.32, 126.29, 126.16, 126.05, 102.1, 101.7, 101.4, 101.3, 101.22, 101.15, 100.84, 100.79, 99.5, 99.0, 98.5, 97.95, 97.4, 97.1, 96.9, 96.3, 79.6, 78.7, 78.5, 78.31, 78.27, 78.1, 77.58, 77.51, 77.27, 77.22, 75.6, 75.5, 74.9, 74.7, 74.3, 74.2, 73.95, 73.65, 73.62, 73.54, 73.47, 72.7, 72.5, 72.0, 68.75, 68.68, 68.58, 67.9, 66.5, 66.24, 66.17, 65.8, 65.61, 65.56, 65.4, 65.2, 62.8, 50.7, 37.9, 29.5, 28.0, 25.9, 18.3, –5.0, –5.4.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{193}H_{193}N_4O_{57}Si$: 3506.2090; found: 3506.2053.

2-Azidoethyl (2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-levulinoyl-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(4-*O*-benzyl-2-*O*-benzoyl-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (3)

Pyridine·*n*HF (255 μL, 7.45 mmol, 20.0 equiv) was added to a solution of nonasaccharide **28** (1.3 g, 0.372 mmol, 1.0 equiv) in MeCN (20 mL) at 0 °C. The reaction was allowed to proceed under stirring for 2 h at rt. The mixture was poured into H_2O and the aqueous phase was extracted with DCM. The combined organic layers were washed with saturated aqueous $NaHCO_3$ and dried over Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/DCM/EtOAc, 3:2:2) to afford **3** (1.08 g, 0.32 mmol, 86%) as a white foam.

$[\alpha]_D^{19}$ +24.9 (*c* 1.21, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 7.6 Hz, 2 H), 7.77 (d, *J* = 7.0 Hz, 4 H), 7.72–7.55 (m, 14 H), 7.56–7.19 (m, 70 H), 5.52 (s, 1 H), 5.41–5.34 (m, 2 H), 5.28–5.23 (m, 2 H), 5.11 (t, *J* = 5.4 Hz, 1 H), 5.04 (d, *J* = 7.5 Hz, 1 H), 4.96–4.70 (m, 20 H), 4.55 (d, *J* = 7.5 Hz, 1 H), 4.34 (dd, *J* = 10.2, 4.6 Hz, 1 H), 4.26 (dd, *J* = 9.9, 4.2 Hz, 1 H), 4.23–4.06 (m, 8 H), 4.06–3.99 (m, 2 H), 3.98–3.84 (m, 7 H), 3.76–3.63 (m, 4 H), 3.60–3.34 (m, 22 H), 3.34–3.21 (m, 4 H), 2.56–2.35 (m, 4 H), 1.96 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 205.97, 171.8, 165.1, 164.78, 164.74, 164.72, 164.69, 164.63, 164.62, 164.59, 164.50, 138.4, 137.38, 137.36, 137.34, 137.28, 137.27, 137.23, 136.99, 133.63, 133.57, 133.55, 133.53, 133.45, 133.27, 133.22, 133.21, 129.91, 129.86, 129.79, 129.73, 129.6, 129.5, 129.4, 129.3, 129.20, 129.17, 129.16, 129.14, 129.13, 129.08, 128.73, 128.68, 128.65, 128.62, 128.56, 128.49, 128.45, 128.41, 128.37, 128.33, 128.28, 128.26, 128.21, 128.18, 128.0, 127.8, 126.54, 126.45, 126.43, 126.39, 126.38, 126.25, 126.15, 102.05, 101.5, 101.38, 101.35, 101.26, 101.22, 100.9, 99.24, 99.17, 98.4, 97.7, 97.6, 97.5, 96.99, 79.0, 78.80, 78.77, 78.41, 78.38, 78.13, 78.05, 77.7, 77.6, 77.4, 75.6, 75.4, 75.11, 75.10, 75.0, 74.97, 74.8, 74.5, 74.38, 74.35, 73.9, 73.68, 73.67, 73.65, 73.42, 73.35, 73.2, 73.07, 73.05, 72.62, 72.59, 72.1, 68.79, 68.72, 68.68, 68.0, 66.6, 66.4, 66.3, 65.70, 65.68, 65.65, 65.59, 62.2, 50.8, 38.0, 29.6, 28.1.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{187}H_{179}N_4O_{57}$: 3392.1226; found: 3392.1195.

2-Azidoethyl (2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-levulinoyl-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-{4-*O*-benzyl-2-*O*-benzoyl-6-*O*-[(2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-(3,4-di-*O*-benzoyl-1,2-*O*-α-D-glucopyranosyl Orthobenzoate]-β-D-glucopyranosyl}-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (29)

Trichloroacetimidate **2** (391 mg, 0.18 mmol, 1.5 equiv) and nonasaccharide **3** (403 mg, 0.12 mmol, 1.0 equiv) were dissolved in anhydrous toluene (15 mL). The mixture was stirred for 15 min at rt in the presence of flame-activated 5 Å molecular sieves (1.8 g). At this point, AgOTf (154 mg, 0.60 mmol, 5.0 equiv) was added. After being stirred for 3 h at 32 °C with the exclusion of light, the reaction was quenched with Et_3N. The solid was filtered off, and the filtrate was concentrated. The resulting residue was purified by silica gel column chromatography (petroleum ether/DCM/EtOAc, 7:2:1 to 2:1:1) to afford **29** (498 mg, 92.4 μmol, 77%) as a white foam.

$[\alpha]_D^{24}$ +20.1 (*c* 1.1, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03–7.84 (m, 20 H), 7.80–7.70 (m, 18 H), 7.69–6.93 (m, 112 H), 6.04 (t, *J* = 9.7 Hz, 1 H), 5.81 (t, *J* = 9.5 Hz, 1 H), 5.77 (d, *J* = 4.9 Hz, 1 H), 5.75–5.71 (m, 1 H)', 5.57–5.20 (m, 12 H), 5.18–5.08 (m, 2 H), 5.03 (d, *J* = 7.7 Hz, 2 H), 4.96–4.88 (m, 7 H), 4.88–4.69 (m, 12 H), 4.67–4.61 (m, 2 H), 4.59–4.48 (m, 3 H), 4.34 (dd, *J* = 10.2, 4.6 Hz, 1 H), 4.25–4.08 (m, 7 H), 4.06–3.65 (m, 23 H), 3.64–3.16 (m, 29 H), 3.06 (s, 1 H), 2.57–2.30 (m, 4 H), 1.96 (s, 3 H), 0.83 (s, 9 H), –0.04 (s, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 205.95, 171.8, 165.9, 165.8, 165.6, 165.43, 165.40, 165.37, 165.32, 165.16, 165.12, 164.98, 164.84, 164.79, 164.71, 164.65, 164.64, 164.49, 138.5, 137.44, 137.39, 137.33, 137.28, 137.0, 135.1, 133.8, 133.6, 133.54, 133.50, 133.4, 133.3, 133.22, 133.17, 133.15, 133.09, 133.04, 133.03, 132.84, 132.82, 130.2, 130.1, 130.03, 129.98, 129.91, 129.84, 129.80, 129.75, 129.6, 129.51, 129.46, 129.42, 129.35, 129.26, 129.19, 129.16, 129.08, 129.01, 128.8, 128.63, 128.59, 128.50, 128.45, 128.41, 128.34, 128.30, 128.26, 128.21, 128.18, 128.0, 127.9, 127.6, 126.9, 126.65, 126.57, 126.49, 126.43, 126.40, 126.3, 126.2, 121.3, 102.1, 101.93, 101.90, 101.6, 101.4, 101.3, 101.2, 100.96, 100.92, 99.2, 98.5, 98.4, 97.6, 97.5, 97.4, 96.9, 95.9, 79.21, 79.20, 79.05, 78.8, 78.44, 78.40, 78.3, 78.2, 77.67, 77.63, 77.36, 75.32, 75.28, 75.09, 75.02, 75.01, 74.99, 74.8, 74.44, 74.35, 73.96, 73.81, 73.78, 73.6, 73.5, 73.29, 73.23, 73.19, 73.05, 72.75, 72.66, 72.62, 72.5, 72.3, 72.1, 71.98, 71.64, 70.58, 69.7, 69.4, 69.1, 68.8, 68.7, 68.5, 68.3, 68.0, 67.7, 66.6, 66.4, 66.3, 65.7, 65.6, 65.5, 64.5, 62.9, 50.8, 38.1, 29.6, 28.1, 25.9, 18.4, –5.23, –5.29.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{301}H_{281}N_4O_{89}Si$: 5402.7349; found: 5402.7302.

2-Azidoethyl (2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-levulinoyl-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-{4-*O*-benzyl-2-*O*-benzoyl-6-*O*-[(2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)]-(1→6)-β-D-glucopyranosyl}-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (30)

Orthoester **29** (412 mg, 76.5 μmol, 1.0 equiv) was dissolved in anhydrous toluene (6 mL). The mixture was stirred for 15 min at rt in the presence of flame-activated 5 Å molecular sieves (0.6 g). At this point, AgOTf (98 mg, 382.5 μmol, 5.0 equiv) and ^{t}BuCl (11 μL, 99.5 μmol, 1.3 equiv) were added. After being stirring for 2 h at 18 °C with the exclusion of light, the reaction was quenched with Et_3N. The solid was filtered off, and the filtrate was concentrated. The resultant residue was purified by silica gel column chromatography (petroleum ether/DCM/EtOAc, 5:2:2) to afford **30** (293 mg, 54.4 μmol, 71%) as a white foam.

$[\alpha]_D^{24}$ –4.1 (*c* 0.6, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99–7.75 (m, 28 H), 7.69 (d, *J* = 7.8 Hz, 2 H), 7.66–7.60 (m, 9 H), 7.58–7.11 (m, 111 H), 6.03 (t, *J* = 9.6 Hz, 1 H), 5.85 (t, *J* = 9.5 Hz, 1 H), 5.74 (t, *J* = 9.6 Hz, 2 H), 5.57 (s, 1 H), 5.51 (t, *J* = 9.7 Hz, 1 H), 5.47–5.36 (m, 5 H), 5.33–5.19 (m, 5 H), 5.15 (t, *J* = 9.7 Hz, 1 H), 5.10 (t, *J* = 5.4 Hz, 1 H), 5.05 (d, *J* = 7.4 Hz, 1 H), 4.97 (t, *J* = 8.6 Hz, 3 H), 4.94–4.61 (m, 18 H), 4.61–4.50 (m, 4 H), 4.36 (dd, *J* = 10.6, 4.8 Hz, 1 H), 4.28–4.07 (m, 9 H), 4.05–3.18 (m, 50 H), 3.09 (t, *J* = 8.3 Hz, 1 H), 2.58–2.37 (m, 4 H), 1.95 (s, 3 H), 0.82 (s, 9 H), –0.06 (s, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 205.96, 171.8, 165.88, 165.84, 165.7, 165.5, 165.34, 165.27, 165.26, 165.23, 165.21, 165.15, 165.11, 164.74, 164.67, 164.61, 164.55, 164.1, 138.6, 137.48, 137.42, 137.37, 137.35, 137.29, 137.0, 133.55, 133.51, 133.45, 133.43, 133.41, 133.37, 133.32, 133.24, 133.20, 133.1, 133.0, 130.13, 130.10, 129.92, 129.88, 129.85, 129.83, 129.78, 129.6, 129.51, 129.44, 129.38, 129.33, 129.29, 129.27, 129.20, 129.17, 129.14, 129.07, 128.98, 128.62, 128.57, 128.52, 128.47, 128.39, 128.36, 128.33, 128.26, 128.23, 128.18, 128.09, 127.73, 127.65, 126.5, 126.4, 126.28, 126.26, 126.15, 101.99, 101.41, 101.39, 101.27, 101.07, 101.03, 100.99, 100.90, 100.7, 99.6, 99.1, 98.7, 98.5, 98.3, 97.56, 97.45, 96.76, 79.3, 78.95, 78.7, 78.6, 78.4, 77.97, 77.66, 77.63, 77.4, 76.7, 75.6, 75.5, 75.3, 75.1, 74.99, 74.8, 74.0, 73.9, 73.7, 73.64, 73.58, 73.4, 73.26, 73.17, 73.08, 73.03, 72.9, 72.8, 72.6, 72.3, 72.1, 71.99, 71.8, 70.5, 70.4, 69.81, 69.76, 69.3, 68.8, 68.7, 68.6, 68.4, 68.3, 68.0, 66.6, 66.4, 66.3, 65.72, 65.68, 65.5, 62.9, 60.5, 50.8, 38.0, 29.8, 28.1, 25.9, 18.4, –5.3, –5.4.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{301}H_{281}N_4O_{89}Si$: 5402.7349; found: 5402.7307.

2-Azidoethyl (2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-levulinoyl-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-{4-*O*-benzyl-2-*O*-benzoyl-6-*O*-[(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)]-(1→6)-β-D-glucopyranosyl}-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (31)

Following the procedure for **3**, treatment of **30** (320 mg, 59.4 μmol, 1.0 equiv) with pyridine·*n*HF (41 μL, 1.2 mmol, 20.2 equiv) in MeCN (4 mL) afforded **31** (278 mg, 52.7 μmol, 89%) as a white foam after purification by silica gel column chromatography (petroleum ether/DCM/EtOAc, 2:1:1).

$[\alpha]_D^{24}$ –0.5 (*c* 1.1, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 7.8 Hz, 2 H), 7.93 (d, *J* = 8.5 Hz, 12 H), 7.83 (d, *J* = 7.6 Hz, 12 H), 7.77 (d, *J* = 7.8 Hz, 2 H), 7.69 (d, *J* = 7.7 Hz, 2 H), 7.67–7.12 (m, 120 H), 5.97 (t, *J* = 9.7 Hz, 1 H), 5.87 (t, *J* = 9.5 Hz, 1 H), 5.73 (t, *J* = 9.6 Hz, 2 H), 5.57 (s, 1 H), 5.47–5.22 (m, 11 H), 5.18 (t, *J* = 9.8 Hz, 1 H), 5.10 (t, *J* = 5.4 Hz, 1 H), 5.06 (d, *J* = 7.5 Hz, 1 H), 5.03–4.56 (m, 23 H), 4.51 (t, *J* = 6.9 Hz, 2 H), 4.42–4.33 (m, 1 H), 4.25–4.07 (m, 9 H), 4.02 (t, *J* = 9.2 Hz, 3 H), 3.96–3.83 (m, 11 H), 3.81–3.21 (m, 36 H), 3.13 (t, *J* = 8.1 Hz, 1 H), 3.03 (s, 1 H), 2.56–2.37 (m, 4 H), 1.95 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 205.9, 171.7, 165.86, 165.82, 165.77, 165.64, 165.45, 165.36, 165.30, 165.11, 164.71, 164.66, 164.58, 164.57, 164.54, 164.52, 164.35, 164.26, 164.1, 138.5, 137.47, 137.40, 137.33, 137.31, 137.27, 137.24, 136.97, 133.54, 133.52, 133.47, 133.39, 133.36, 133.35, 133.27, 133.18, 133.14, 133.09, 133.0, 130.1, 130.0, 129.90, 129.86, 129.81, 129.74, 129.67, 129.56, 129.52, 129.49, 129.47, 129.42, 129.38, 129.36, 129.34, 129.32, 129.26, 129.24, 129.19, 129.17, 129.13, 129.09, 129.08, 129.05, 129.02, 128.99, 128.8, 128.65, 128.59, 128.53, 128.49, 128.48, 128.42, 128.37, 128.31, 128.22, 128.19, 128.15, 128.13, 128.04, 127.7, 127.6, 126.50, 126.48, 126.36, 126.26, 126.22, 126.12, 101.95, 101.44, 101.41, 101.35, 101.31, 101.2, 101.1, 100.95, 100.86, 100.78, 100.77, 100.74, 99.4, 99.1, 98.7, 98.5, 98.2, 97.54, 97.50, 97.4, 96.7, 79.1, 78.9, 78.7, 78.5, 78.4, 77.9, 77.65, 77.61, 77.4, 77.3, 76.6, 75.55, 75.53, 75.09, 74.99, 74.76, 74.67, 73.88, 73.82, 73.69, 73.61, 73.3, 73.23, 73.16, 73.06, 72.98, 72.93, 72.8, 72.70, 72.69, 72.57, 72.1, 71.9, 71.8, 71.7, 70.6, 70.3, 69.4, 68.75, 68.65, 68.57, 68.49, 68.34, 68.32, 67.96, 66.5, 66.4, 66.2, 65.67, 65.62, 65.46, 65.43, 61.36, 50.7, 37.99, 29.6, 28.1.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{295}H_{267}N_4O_{89}$: 5288.6484; found: 5288.6446.

2-Aminoethyl (β-D-Glucopyranosyl)-(1→3)-(β-D-glucopyranosyl)-(1→3)-(β-D-glucopyranosyl)-(1→3)-(β-D-glucopyranosyl)-(1→3)-{6-*O*-[(β-D-glucopyranosyl)-(1→6)-(β-D-glucopyranosyl)-(1→6)-(β-D-glucopyranosyl)-(1→6)-(β-D-glucopyranosyl)]-(1→6)-β-D-glucopyranosyl}-(1→3)-(β-D-glucopyranosyl)-(1→3)-(β-D-glucopyranosyl)-(1→3)-(β-D-glucopyranosyl)-(1→3)-β-D-glucopyranoside (1a)

Tridecasaccharide **31** (278 mg, 52.7 μmol, 1.0 equiv) was dissolved in DCM/MeOH (24 mL, 1:2 v/v), followed by addition of *p*-TsOH·H_2O (40.1 mg, 210.8 μmol, 4.0 equiv). After being stirred at 40 °C for 4 h, the reaction was quenched with Et_3N. The volatiles were removed, the resulting residue was dissolved in MeOH/H_2O (60 mL, 1:1 v/v), and LiOH·H_2O (195 mg, 4.64 mmol, 88.0 equiv) was added in portions. The mixture was heated at 40 °C for 12 h, and the solution was neutralized with resin (H^+). The solid was filtered off, and the filtrate was concentrated. The whole amount of residue and 10% Pd/C (90 mg) in H_2O (10 mL) was stirred under H_2 atmosphere (1 atm) overnight at 40 °C. Then the solid was filtered off through a Celite pad. The filtrate was concentrated and the residue was purified by silica gel column chromatography (^{i}PrOH/H_2O/NH_4OH, 2:1:1) to afford **1a** (75 mg, 34.6 μmol, 66% over 3 steps) as a white foam.

$[\alpha]_D^{24}$ –4.6 (*c* 0.2, H_2O).

^{1}H NMR (500 MHz, D_2O): δ = 4.91–4.70 (m, 9 H), 4.55–4.49 (m, 4 H), 4.26–4.18 (m, 3 H), 4.16–4.08 (m, 1 H), 4.01–3.21 (m, 78 H).

^{13}C NMR (126 MHz, D_2O): δ = 102.9, 102.79, 102.71, 102.4, 101.8, 84.7, 84.12, 84.05, 83.97, 83.8, 75.9, 75.8, 75.5, 74.8, 74.45, 73.35, 73.2, 73.1, 72.95, 72.7, 69.5, 69.3, 68.7, 68.5, 67.99, 65.86, 60.6, 60.4, 39.3.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{80}H_{138}NO_{66}$: 2168.7467; found: 2168.7441.

2-Azidoethyl (β-D-Glucopyranosyl)-(1→3)-(β-D-glucopyranosyl)-(1→3)-(β-D-glucopyranosyl)-(1→3)-(β-D-glucopyranosyl)-(1→3)-{6-*O*-[(β-D-glucopyranosyl)-(1→6)-(β-D-glucopyranosyl)-(1→6)-(β-D-glucopyranosyl)-(1→6)-(β-D-glucopyranosyl)]-(1→6)-β-D-glucopyranosyl}-(1→3)-(β-D-glucopyranosyl)-(1→3)-(β-D-glucopyranosyl)-(1→3)-(β-D-glucopyranosyl)-(1→3)-β-D-glucopyranoside (1b)

To a solution of **1a** (46 mg, 21.2 μmol, 1.0 equiv) in MeOH/H_2O (5 mL, 1:1 v/v) were added imidazole-1-sulfonyl azide hydrochloride (44.4 mg, 212 μmol, 10.0 equiv), K_2CO_3 (58.6 mg, 424 μmol, 20.0 equiv), and $CuSO_4$·5 H_2O (1.06 mg, 4.24 μmol, 0.2 equiv). The reaction mixture was stirred at rt for 10 h. Thereafter, the solvent was evaporated, and the residue was purified by silica gel chromatography (^{i}P-rOH/H_2O/NH_4OH, 2:1:1) to afford the white sticky solid **1b** (38 mg, 17.6 μmol, 83%).

$[\alpha]_D^{24}$ –19.6 (*c* 0.5; H_2O/MeOH, 1:1).

^{1}H NMR (500 MHz, D_2O): δ = 5.00–4.69 (m, 9 H), 4.57–4.49 (m, 4 H), 4.26–4.18 (m, 3 H), 4.08–4.02 (m, 1 H), 4.01–3.25 (m, 78 H).

^{13}C NMR (126 MHz, D_2O): δ = 102.92, 102.89, 102.80, 102.72, 102.4, 102.0, 84.7, 84.1, 83.98, 83.96, 83.8, 75.9, 75.8, 75.5, 74.8, 73.4, 73.20, 73.15, 73.06, 72.97, 72.8, 69.53, 69.48, 69.4, 69.3, 68.8, 68.7, 68.5, 68.0, 60.6, 50.4.

HRMS (ESI): *m*/*z* $[M - 2H]^+/2$ calcd for $C_{80}H_{133}N_3O_{66}$: 1095.8577; found: 1095.8564.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

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