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Synthesis of the Tetrasaccharide Repeating Unit of the β-Kdo-Containing Exopolysaccharide from *Burkholderia pseudomallei* and *B. cepacia* Complex

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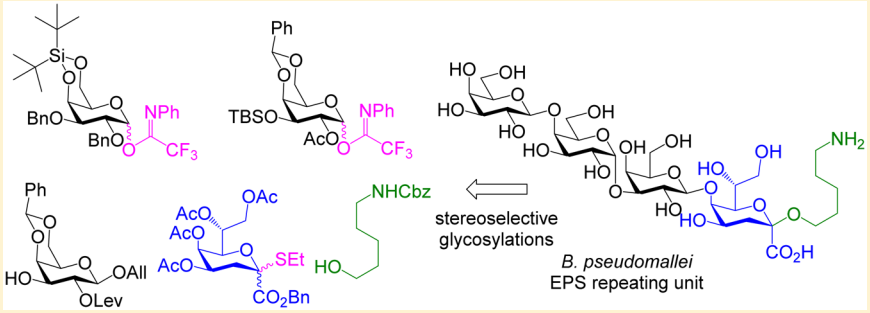
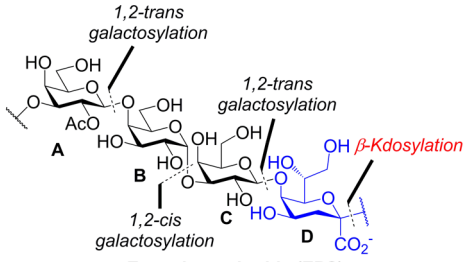
Supporting Information



ABSTRACT: The synthesis of the repeating unit of the immunogenic β-Kdo-containing exopolysaccharide produced by *Burkholderia pseudomallei* and bacteria of the *B. cepacia* complex is described. The target tetrasaccharide was synthesized via stereoselective 1,2-*cis*- and 1,2-*trans*-galactosylations and β-Kdosylation. A [3 + 1] coupling reaction between a trigalactosyl *N*-phenyl-2,2,2-trifluoroacetimidate donor and a Kdo acceptor has been successfully achieved for the assembly of the tetrasaccharide skeleton.

Burkholderia pseudomallei is a Gram-negative bacteria that causes a tropical disease called melioidosis, an often fatal illness when not diagnosed in time.[1] Because of its high infectivity via the respiratory tract and experimental use as a biological warfare agent, *B. pseudomallei* has recently been classified as a Tier 1 Select Agent by the US.[2] Currently, no approved vaccine is available to prevent melioidosis infections. Progress on this front is related to the development of live attenuated, killed whole cell, DNA, and subunit vaccines.[3] In the last few years, studies have highlighted the importance of polysaccharides expressed by *B. pseudomallei* as virulence factors and protective antigens.[4] Together with a lipopolysaccharide and a capsular polysaccharide, *B. pseudomallei* produces a high molecular weight (>150 kDa) exopolysaccharide (EPS) of unusual structure consisting of a linear heteropolymer of repeating tetrasaccharide units composed of three galactose residues (**A**, **B**, and **C**) and a 3-deoxy-D-*manno*-2-octulosonic acid (Kdo, **D**). The structure of the EPS is defined as follows: [→3)-2-*O*-Ac-β-D-Gal*p*-(1→4)-α-D-Gal*p*-(1→3)-β-D-Gal*p*-(1→5)-β-D-Kdo*p*-(2→]$_n$ (Figure 1).[5,6]

In 1995, Steinmetz[7] showed that this EPS was strongly reactive with sera of patients infected with melioidosis and constitutively expressed among *B. pseudomallei* strains of different geographical regions. Furthermore, a monoclonal



Exopolysaccharide (EPS)

[→3)-2-*O*-Ac-β-D-Gal*p*-(1→4)-α-D-Gal*p*-(1→3)-β-D-Gal*p*-(1→5)-β-D-Kdo*p*-(2→]$_n$

Figure 1. Structure of the EPS tetrasaccharide unit from *B. pseudomallei*.

IgG (mAb 3015) with specificity for this EPS was isolated and exhibited no cross-reactivity with other *Burkholderia* species with the exception of the closely genetically related *B. mallei*, the causative agent of glanders. This EPS is thus seen as a promising target for the development of diagnostics and/or subunit vaccines against melioidosis.[8,9] Interestingly, this β-Kdo-containing EPS has also been isolated from the human

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pathogenic *B. oklahomensis* E0147 strain[10] as well as from four different species of the *B. cepacia* complex (Bcc), that is, *B. ambifaria*, *B. cepacia*, *B. dolosa*, and *B. stabilis*.[11,12] Cystic fibrosis patients are strongly susceptible to Bcc infections, known as the Cepacia syndrome, leading to rapid death in 20% of infected patients. Noteworthily, vaccination is currently unavailable to prevent Bcc infections.[3]

The presence of a common immunogenic EPS within these highly pathogenic *Burkholderia* species together with its unusual chemical structure motivated us to undertake the synthesis of the repeating unit. From an organic chemistry perspective, one could anticipate diverse challenges and hurdles related to the total synthesis of *B. pseudomallei* EPS fragments (Figure 1): (1) the 1,2-*cis* linkage between Gal **B** and **C**, (2) the uncommon and thermodynamically unfavorable β-Kdo linkage on residue **D**, (3) the galactosylation of the less reactive axial groups on residues **B** and **D**, and (4) the choice of both the glycosylation sequence and the nature of sugar at the reducing end. As depicted in Figure 2, unacetylated tetrasaccharide **1** was chosen

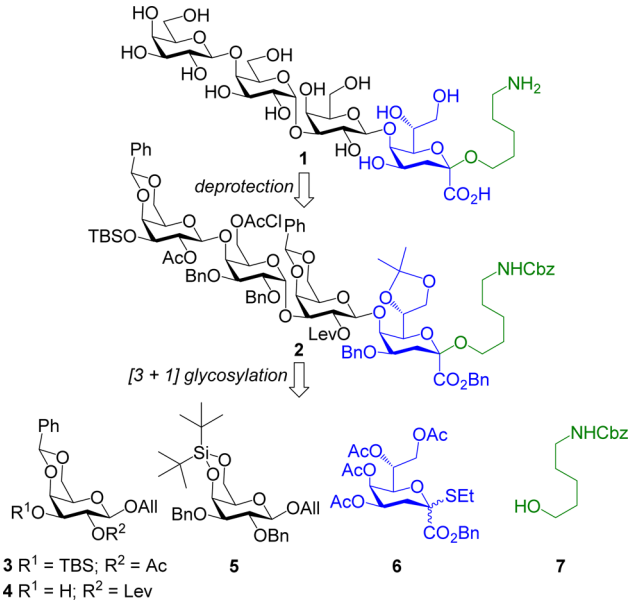
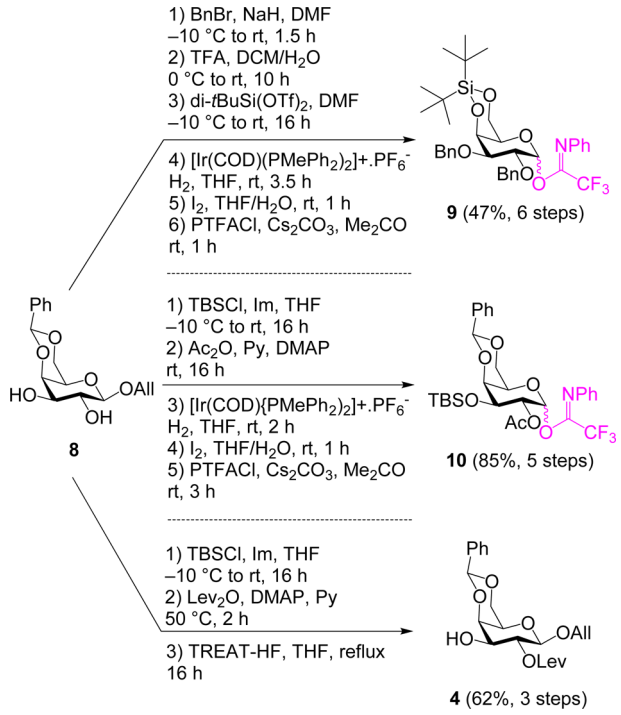


Figure 2. Retrosynthetic analysis of tetrasaccharide **1**.

as the first target. Incorporation of an amino linker should allow its conjugation, for instance, with an immunogenic carrier protein. To streamline the synthesis of **1**, the expensive and synthetically challenging Kdo residue was positioned at the reducing end. Fully protected tetrasaccharide **2** would come from a [3 + 1] glycosylation between a trigalactoside **ABC** and Kdo acceptor **D**. The latter would be obtained by coupling between peracetylated β-thioglycoside **6** and alcohol **7** via a stereoselective Kdosylation. Formation of the 1,2-*cis* glycosidic linkage **BC** would be ensured by the use of a di-*tert*-butylsilylene (DTBS)[13] group, and we could take advantage of the neighboring group participation effect of acetyl and levulinoyl (Lev) groups for the stereoselective 1,2-*trans* glycosylations connecting **AB** and **CD**. Galactopyranose derivatives **3**−**5** bearing an allyl group at the anomeric position, which could be orthogonally deprotected before activation into the highly efficient *N*-phenyl-2,2,2-trifluoroacetimidate (PTFA)[14] donors, would come from commercially available D-galactose.

According to Scheme 1, galactose acceptor **4** and PTFA donors **9** and **10** were synthesized starting from the common

Scheme 1. Synthesis of Galactose Donors and Acceptor



intermediate **8**, which is readily accessible in four steps from D-galactose. Diol **8**[15] was benzylated, and the benzylidene group was hydrolyzed under acidic conditions (TFA) and replaced by an α-directing DTBS group. Then, isomerization of the allyl group using an iridium-based Crabtree catalyst[16] followed by iodine-promoted deprotection led to a hemiacetal, which was activated into PTFA donor **9** using standard conditions. Following this sequence, donor **9** was synthesized in 47% yield over six steps and three chromatographic purifications. Regioselective silylation at the C-3 position of diol **8** gave an alcohol, which was either acetylated or levulinoylated at C-2. Deallylation and activation according to the above-mentioned conditions provided PTFA donor **10** in 85% yield over five steps, whereas cleavage of the TBS group using TREAT-HF allowed the formation of acceptor **4** in 62% yield over three steps. The novel galactose derivatives **4**, **9**, and **10** were all synthesized at the gram-scale and proved stable for months when stored at 4 °C.

Stereoselective synthesis of trisaccharide **14** was the next task (Scheme 2). Glycosylation of an α/β-mixture of donor **9** (1.1 equiv) with acceptor **4** under the promotion of TMSOTf in DCE afforded disaccharide **11** in 87% yield. The steric hindrance of the DTBS group directed the glycosylation toward the α-anomer,[13] which was formed exclusively as shown by ^{1}H NMR (br s, H-1$_B$). Performing the reaction with pure α- or β-donor **9** led to similar yields with no difference in anomeric stereoselectivity. The DTBS group of disaccharide **11** was then deprotected with TREAT-HF, giving diol **12** in 83% yield. Noteworthily, strictly anhydrous conditions were essential to ensure the stability of the benzylidene group. We then planned to protect the H-6$_B$ position of diol **12** with a benzyl group. Unfortunately, silver-promoted benzylation under neutral conditions gave only low and unreproducible

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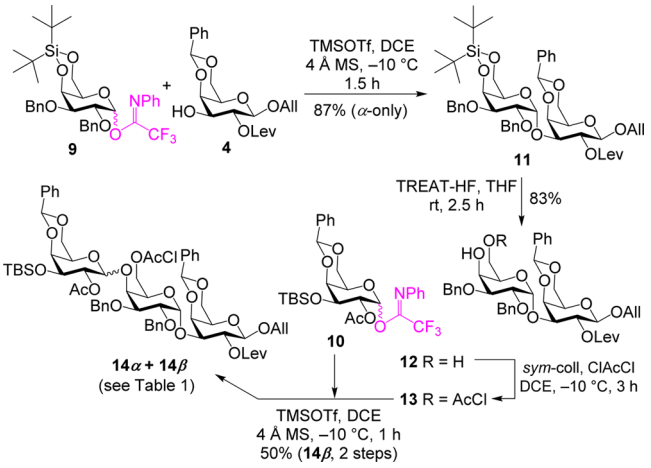
Scheme 2. Synthesis of Trisaccharide 14



yields of C-4 alcohol. Yamamoto regioselective acetylation[17] of diol **12** using *sym*-collidine and ClAcCl at −10 °C was more rewarding and furnished crude alcohol **13** with good conversion and selectivity. However, the chloroacetyl group migrated during the silica gel purification, leading to an inseparable mixture of C-4 and C-6 acylated derivatives. Glycosylation with donor **10** was thus performed on crude alcohol **13** to yield trisaccharide **14**.

Screening of the glycosylation conditions for the formation of trisaccharide **14** was examined next (Table 1). Using

Table 1. Optimization of the Synthesis of Trisaccharide 14β

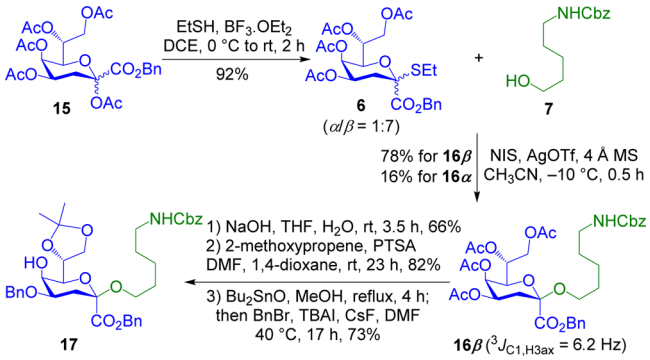
			yield (%, 2 steps)[a]	
entry	promoter	solvent, *T* (°C)	**14α**	**14β**
1	TBSOTf	DCE, *−10*	nd[b]	nd
2	TMSOTf	DCM, *−78*	nd	nd
3	TMSOTf	DCE, *−10*	13	46
4	TMSOTf	CH_3CN, *−10*	8	31
5	TMSOTf	DCE, +60	22	18
6	TMSOTf	DCE, *−10*	18	**50**[c]

[a]Isolated yields. [b]No reaction. [c]Donor **10** was used at 1.8 equiv.

TBSOTf as the promoter was not effective (entry 1). Performing the glycosylation in DCM at a cryogenic temperature (−78 °C) led to donor degradation without formation of **14** (entry 2). Switching DCM for DCE and increasing the reaction temperature to −10 °C provided target trisaccharide **14β** in 46% yield over two steps along with the minor (13%) α-anomer **14α** according to NMR and HRMS (entry 3). The formation of undesired 1,2-*cis* linkage during the synthesis of galactosides bearing a 4,6-*O*-benzylidene group is not unprecedented. First highlighted by Kováč in 1985 in the course of the synthesis of (1→3)-β-D-oligogalactosides,[18] this has been later shown to be a common issue, even in the presence of acyl participating groups.[19−21] To increase the yield of **14β**, we then tried to take advantage of the so-called "nitrile-effect"[22] but did not see any improvement (entry 4). Performing the reaction at 60 °C led to an increased yield of the thermodynamically favored **14α** (entry 5). A glycosylation was also conducted using a fluoride donor under the promotion of $SnCl_2$ or Cp_2ZrCl_2 in combination with AgOTf, but the yields and selectivities were not satisfying (data not shown). We finally found that increasing the number of equivalents of donor **10** to 1.8 allowed for the formation of trisaccharide **14β** in a satisfying 50% yield over two steps from diol **12** (entry 6). Anomers **14α** and **14β** were readily separable by silica gel chromatography.

The preparation of challenging β-Kdo acceptor **17** was then studied. Although the synthesis of the more stable α-Kdo anomers has been thoroughly reported in the literature, studies toward the synthesis of β-Kdo glycosides are rather scarce.[23] On the basis of work of Ling,[24] the Mong group recently reported the stereoselective formation of β-Kdo glycosides promoted by NIS via the use of 4,5:7,8-di-*O*-isopropylidene Kdo glycal.[25] This elegant methodology gives good yields and selectivities but requires the synthesis of the Kdo glycal in nine steps for D-mannose or in four steps from Kdo.[26] Moreover, an additional reductive deiodination step is necessary after the glycosylation. In 1992, van Boom showed in two seminal papers that using pure peracetylated β-Kdo thiodonors leads to the exclusive formation of β-Kdo glycosides.[27,28] This approach was recently revisited by Oscarson who showed that activation with DMTST or IBr/AgOTf can also provide good β-Kdo selectivities.[29] Following these previous studies, we synthesized peracetylated thioglycoside **6** in 92% yield (1:7 α/β ratio) from **15** that was reacted with ethanethiol in the presence of $BF_3{\cdot}OEt_2$ (Scheme 3). Ester **15**[30] was prepared in 67% yield over

Scheme 3. Synthesis of Kdo Acceptor 17



two steps from crystalline Kdo ammonium salt.[31] Screening of the reaction conditions indicated that glycosylation between donor **6** and acceptor **7** under the promotion of NIS/AgOTf[32] in acetonitrile gave excellent yields of β-Kdo glycoside **16β** (78%) along with the α-anomer as a minor compound (**16α**, 16%). Contrasting with the results of Oscarson,[29] we were pleased to find that, under NIS/AgOTf activation, no Kdo glycal was detected in the reaction mixture. Importantly, using acetonitrile instead of DCE or Et_2O was essential to avoid the formation of the undesirable glycal. The anomeric configuration of glycoside **16β** was ascertained via undecoupled ^{13}C NMR ($^3J_{C1,H3ax}$ = 6.2 Hz).[33] Deacetylation of **16β** was best performed with NaOH in THF/H_2O (66%), whereas Zemplén deacetylation or reaction with PTSA/MeOH led to benzyl ester *trans*-esterification. Then, the resulting tetraol was protected at C-7/C-8 with an isopropylidene group (82%), and the C-4 position was benzylated via stannylene acetal chemistry giving target Kdo acceptor **17** in 73% yield.

The final steps toward the synthesis of tetrasaccharide **1** are depicted in Scheme 4. Trisaccharide **14β** was deallylated and activated at the anomeric position to give PTFA donor **18** (58% over three steps). The demanding glycosylation between trisaccharide donor **18** and Kdo acceptor **17** was performed

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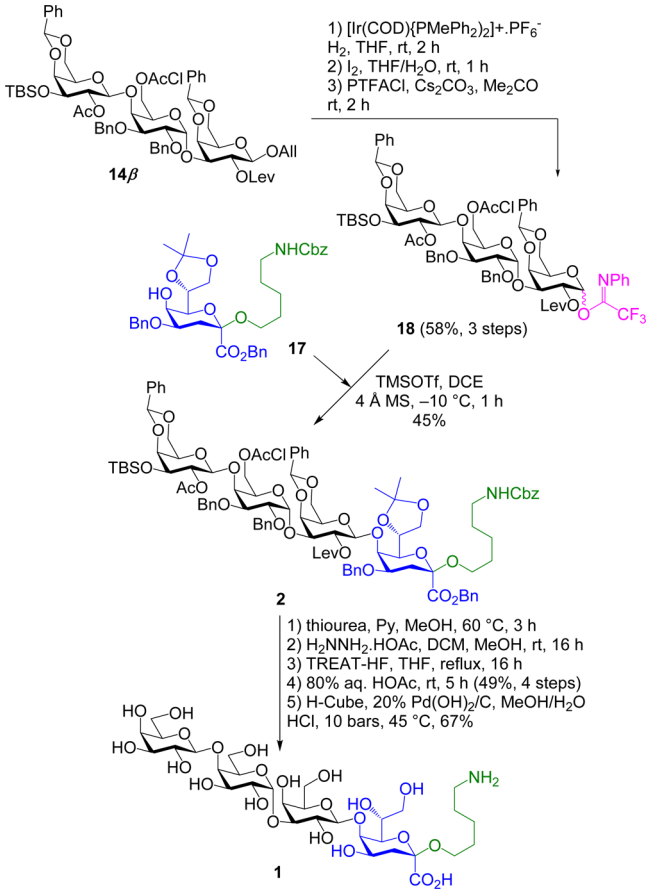
Scheme 4. Final Steps in the Synthesis of Tetrasaccharide 1



using the conditions previously optimized for the synthesis of trisaccharide **14*β***, i.e., TMSOTf in DCE at −10 °C, providing fully protected tetrasaccharide **2** in 45% yield along with some unreacted Kdo acceptor **17**. Global deprotection of tetrasaccharide **2** was the next task. We tried to selectively cleave the isopropylidene group using TFA in DCM/H_2O as shown by Boons[34] on a similar Kdo-containing oligosaccharide. Unfortunately, the reaction led to a complex mixture of products; a compound corresponding to the deprotection of the three acetals along with the TBS group was isolated in moderate yield (~50%). We thus decided to follow a different sequence consisting of (1) thiourea deprotection of the chloroacetyl, (2) hydrazine cleavage of the levulinoyl, (3) TREAT-HF removal of TBS group, and (4) acidic cleavage of the isopropylidene using HOAc instead of TFA. According to this route, the tetrasaccharide pentaol was isolated in 49% yield over four steps after one chromatographic purification. $Pd(OH)_2/C$ catalyzed hydrogenolysis of the latter under microfluidic conditions (H-Cube) cleanly gave tetrasaccharide **1** in 67% yield following C_{18} purification and freeze-drying. Acidic conditions (2.0 equiv of HCl) were needed to ensure the full deprotection, which explained the loss of the acetyl group as revealed by NMR and HRMS. ^1H and ^{13}C NMR data of tetrasaccharide **1** were in good agreement with those published for the natural EPS.[5]

In summary, the synthesis of the tetrasaccharide repeating unit of the *β*-Kdo-containing EPS from human pathogenic *Burkholderia* species has been accomplished for the first time. The challenging 1,2-*cis*-galactosylation was achieved via the stereodirecting effect of the DTBS group, and the synthesis of the *β*-Kdo linkage was performed using a newly developed thioethyl donor activated with NIS/AgOTf. Tetrasaccharide **1** represents a promising antigen for the development of glycoconjugate vaccines and diagnostics against melioidosis and Bcc infections.

EXPERIMENTAL SECTION

General Methods. All starting materials and reagents were purchased from commercial sources and used as received without further purification. Air and water sensitive reactions were performed in heat gun-dried glassware under an Ar atmosphere. Moisture sensitive reagents were introduced via a dry syringe. Anhydrous solvents were supplied over molecular sieves and used as received. Petroleum ether (PE) refers to the 40−60 °C boiling fraction. Powdered 4 Å molecular sieves (MS) were activated before use by heating with a heat gun for ~5 min under high vacuum. Reactions were monitored by thin-layer chromatography (TLC) with silica gel 60 F_{254} 0.25 mm precoated aluminum foil plates. Compounds were visualized by using UV_{254} and/or orcinol (1 mg mL^{-1}) in a 10% H_2SO_4(aq) solution and/or Hanessian's stain [2.5 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 1.0 g $Ce(NH_4)_4(SO_4)_4\cdot 2H_2O$, 90 mL H_2O, 10 mL H_2SO_4] with heating. Normal-phase flash column chromatography was performed on silica gel 60 Å (15−40 *μ*m). Reversed-phase flash column chromatography was performed on C_{18} silica gel (fully capped, 25−40 *μ*m). NMR spectra were recorded at 297 K in the indicated solvent (acetone-d_6, $CDCl_3$, D_2O) with 400 or 600 MHz instruments employing standard software provided by the manufacturer. ^1H and ^{13}C NMR spectra were referenced to internal tetramethylsilane (TMS, $\delta_H = \delta_C = 0.00$ ppm) for spectra in $CDCl_3$ and acetone-d_6 or to internal acetone ($\delta_H = 2.225$ ppm; $\delta_C = 31.07$ ppm) for spectra in D_2O. Assignments were based on ^1H, ^{13}C, undecoupled ^{13}C, DEPT-135, COSY, HSQC, and undecoupled HSQC and HMBC experiments. Interchangeable assignments are marked with an asterisk. High-resolution mass spectra (HRMS) were recorded on an ESI-Q-TOF mass spectrometer.

*Allyl 4,6-O-Benzylidene-2-O-levulinoyl-β-D-galactopyranoside (**4**).* Diol **8** (2.00 g, 6.49 mmol, 1.0 equiv) was dissolved in anhydrous THF (32 mL) with gentle heating. The solution was cooled to −10 °C; then, imidazole (486 mg, 7.14 mmol, 1.1 equiv) followed by TBSCl (1.08 g, 7.14 mmol, 1.1 equiv) were added. The mixture was stirred for 16 h under Ar while gradually being warmed to rt. The solvents were concentrated under reduced pressure, and the residue was purified by silica gel flash chromatography (PE/EtOAc 1:0 to 6:4) to give an inseparable mixture of 3-OTBS and 2-OTBS regioisomers (2.18 g, 79%, ratio 3-OTBS:2-OTBS = 9:1) as a sticky colorless solid. Analytical data for 3-OTBS: ^1H NMR (400 MHz, $CDCl_3$) δ 7.54−7.50 (m, 2H, C*H*-Ar), 7.38−7.31 (m, 3H, C*H*-Ar), 6.00−5.90 (m, 1H, H-2_{All}), 5.52 (s, 1H, C*H*-acetal), 5.31 (ddd, J = 17.2, 3.2, 1.7 Hz, 1H, H-$3a_{All}$), 5.20 (ddd, J = 10.4, 2.8, 1.2 Hz, 1H, H-$3b_{All}$), 4.42 (ddt, J = 10.8, 5.2, 1.5 Hz, 1H, H-$1a_{All}$), 4.35 (d, $J_{1,2}$ = 7.7 Hz, 1H, H-1), 4.34 (dd, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6a}$ = 1.5 Hz, 1H, H-6a), 4.13 (ddt, J = 12.8, 4.1, 1.3 Hz, 1H, H-$1b_{All}$), 4.07 (dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6b}$ = 1.9 Hz, 1H, H-6b), 4.03 (dd, $J_{3,4}$ = 3.7 Hz, $J_{4,5}$ = 0.9 Hz, 1H, H-4), 3.85 (dd, $J_{2,3}$ = 9.5 Hz, $J_{1,2}$ = 7.7 Hz, 1H, H-2), 3.72 (dd, $J_{2,3}$ = 9.4 Hz, $J_{3,4}$ = 3.7 Hz, 1H, H-3), 3.43−3.41 (m, 1H, H-5), 0.91 (s, 9H, $C(CH_3)_3$), 0.13, 0.12 (2 × s, 6H, 2 × CH_3Si); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0 (C-Ar), 134.2 (C-2_{All}), 128.8, 128.1, 126.3 (CH-Ar), 117.9 (C-3_{All}), 101.9 (C-1), 101.0 (CH-acetal), 76.6 (C-4), 74.3 (C-3), 71.0 (C-2), 70.0 (C-1_{All}), 69.4 (C-6), 66.8 (C-5), 25.9 ($C(CH_3)_3$), 18.4 ($C(CH_3)_3$), −4.2, −4.5 (2 × CH_3Si); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{22}H_{35}O_6Si$ 423.2197, found 423.2196; m/z $[M + NH_4]^+$ calcd for $C_{22}H_{38}NO_6Si$ 440.2463, found 440.2462; m/z $[M + Na]^+$ calcd for $C_{22}H_{34}NaO_6Si$ 445.2017, found 445.2014. To a solution of the regioisomers (5.65 g, 13.4 mmol, 1.0 equiv) in anhydrous py (100 mL) was added DMAP (8.17 g, 66.9 mmol, 5.0 equiv). A solution of levulinic anhydride[35] (12.9 g, 60.2 mmol, 4.5 equiv) in anhydrous py (50 mL) was slowly added over 10 min to the former mixture. The mixture was warmed to 50 °C and stirred under N_2 for 2 h. The solvents were concentrated under reduced pressure, and the residue

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was purified by silica gel flash chromatography (PE/EtOAc 9:1 to 7:3) to give an inseparable mixture of 3-OTBS and 2-OTBS regioisomers (6.60 g, 95%, ratio 3-OTBS:2-OTBS = 9:1) as a yellow oil. Analytical data for 3-OTBS: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.51 (m, 2H, C*H*-Ar), 7.38−7.31 (m, 3H, C*H*-Ar), 5.93−5.82 (m, 1H, H-2$_{All}$), 5.52 (s, 1H, C*H*-acetal), 5.29−5.22 (m, 2H, H-2, H-3a$_{All}$), 5.17 (ddd, J = 10.4, 3.1, 1.4 Hz, 1H, H-3b$_{All}$), 4.45 (d, $J_{1,2}$ = 8.1 Hz, 1H, H-1), 4.37−4.31 (m, 2H, H-6a, H-1a$_{All}$), 4.14−4.03 (m, 3H, H-6b, H-1b$_{All}$, H-4), 3.85 (dd, $J_{2,3}$ = 9.7 Hz, $J_{3,4}$ = 3.7 Hz, 1H, H-3), 3.42 (br s, 1H, H-5), 2.79−2.73 (m, 2H, CH_{2Lev}), 2.65−2.59 (m, 2H, CH_{2Lev}), 2.19 (s, 3H, COCH_{3Lev}), 0.85 (s, 9H, C(CH_3)$_3$), 0.07, 0.06 (2 × s, 6H, 2 × CH_3Si); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.6 (CO_{Lev}), 171.4 ($COCH_{2Lev}$), 137.9 (C-Ar), 134.2 (C-2$_{All}$), 128.9, 128.2, 128.2, 126.4 (CH-Ar), 117.2 (C-3$_{All}$), 101.1 (CH-acetal), 100.0 (C-1), 76.6 (C-4), 72.3 (C-3), 71.8 (C-2), 69.3, 69.2 (C-6, C-1$_{All}$), 66.8 (C-5), 38.1 (CH_{2Lev}), 30.1 ($COCH_{3Lev}$), 28.2 (CH_{2Lev}), 25.7 (C(CH_3)$_3$), 18.2 (C(CH_3)$_3$), −4.4, −4.5 (2 × CH_3Si); HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{27}H_{44}NO_8Si$ 538.2831, found 538.2833; m/z [M + Na]$^+$ calcd for $C_{27}H_{40}NaO_8Si$ 543.2385, found 543.2382. To a solution of the regioisomers (5.53 g, 10.6 mmol, 1.0 equiv) in anhydrous THF (106 mL) was added TREAT-HF (4.53 mL, 31.9 mmol, 3.0 equiv). The mixture was refluxed for 2 h under Ar; then, additional TREAT-HF (4.53 mL, 31.9 mmol, 3.0 equiv) was added, and the mixture was refluxed for 14 h. The solution was cooled to rt and diluted with EtOAc (250 mL). The organic phase was washed with a saturated $NaHCO_3$(aq) solution (100 mL) and brine (100 mL). The solvents of the dried ($MgSO_4$) solution were concentrated, and the residue was purified by silica gel flash chromatography (PE/EtOAc 5:5 to 3:7) to give **4** (3.52 g, 82%) along with its 2-OH regioisomer (391 mg, 9%), both as white foams. Analytical data for **4**: $[\alpha]_D^{20}$ −1.6 (c 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.48 (m, 2H, C*H*-Ar), 7.38−7.34 (m, 3H, C*H*-Ar), 5.95−5.84 (m, 1H, H-2$_{All}$), 5.54 (s, 1H, C*H*-acetal), 5.28 (ddd, J = 17.3, 3.4, 1.7 Hz, 1H, H-3a$_{All}$), 5.19 (ddd, J = 10.5, 3.0, 1.4 Hz, 1H, H-3b$_{All}$), 5.14 (dd, $J_{2,3}$ = 9.9 Hz, $J_{1,2}$ = 8.0 Hz, 1H, H-2), 4.48 (d, $J_{1,2}$ = 8.0 Hz, 1H, H-1), 4.37 (ddt, J = 13.2, 4.8, 1.6 Hz, 1H, H-1a$_{All}$), 4.32 (dd, $J_{6a,6b}$ = 12.5 Hz, $J_{5,6a}$ = 1.3 Hz, 1H, H-6a), 4.20 (br d, $J_{3,4}$ = 3.8 Hz, 1H, H-4), 4.11 (ddt, J = 13.2, 6.0, 1.4 Hz, 1H, H-1b$_{All}$), 4.07 (dd, $J_{6a,6b}$ = 12.0 Hz, $J_{5,6b}$ = 1.4 Hz, 1H, H-6b), 3.78−3.71 (m, 1H, H-3), 3.46 (br s, 1H, H-5), 2.79−2.74 (m, 2H, CH_{2Lev}), 2.74−2.69 (m, 1H, O*H*), 2.67−2.62 (m, 2H, CH_{2Lev}), 2.17 (s, 3H, COCH_{3Lev}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.8 (CO_{Lev}), 172.4 ($COCH_{2Lev}$), 137.4 (C-Ar), 134.0 (C-2$_{All}$), 129.3, 128.3, 126.5 (CH-Ar), 117.3 (C-3$_{All}$), 101.5 (CH-acetal), 99.6 (C-1), 75.6 (C-4), 72.5 (C-2), 71.6 (C-3), 69.6 (C-1$_{All}$), 69.0 (C-6), 66.6 (C-5), 38.2 (CH_{2Lev}), 29.9 ($COCH_{3Lev}$), 28.2 (CH_{2Lev}); HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{21}H_{30}NO_8$ 424.1966, found 424.1968; m/z [M + Na]$^+$ calcd for $C_{21}H_{26}NaO_8$ 429.1520, found 429.1519. Analytical data for the 2-OH regioisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.49 (m, 2H, C*H*-Ar), 7.39−7.33 (m, 3H, C*H*-Ar), 6.01−5.90 (m, 1H, H-2$_{All}$), 5.51 (s, 1H, C*H*-acetal), 5.33 (ddd, J = 17.3, 3.1, 1.6 Hz, 1H, H-3a$_{All}$), 5.23 (ddd, J = 10.4, 2.7, 1.2 Hz, 1H, H-3b$_{All}$), 4.91 (dd, $J_{2,3}$ = 10.2 Hz, $J_{3,4}$ = 3.7 Hz, 1H, H-3), 4.45 (ddt, J = 12.7, 5.2, 1.5 Hz, 1H, H-1a$_{All}$), 4.43 (d, $J_{1,2}$ = 7.8 Hz, 1H, H-1), 4.33 (dd, $J_{3,4}$ = 3.7 Hz, $J_{4,5}$ = 0.8 Hz, 1H, H-4), 4.32 (dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 1.5 Hz, 1H, H-6a), 4.15 (ddt, J = 12.7, 6.5, 1.2 Hz, 1H, H-1b$_{All}$), 4.07 (dd, $J_{6a,6b}$ = 12.5 Hz, $J_{5,6b}$ = 1.7 Hz, 1H, H-6b), 4.03 (dd, $J_{2,3}$ = 10.2 Hz, $J_{1,2}$ = 7.7 Hz, 1H, H-2), 3.50 (br s, 1H, H-5), 2.78−2.74 (m, 2H, CH_{2Lev}), 2.68−2.64 (m, 2H, CH_{2Lev}), 2.09 (s, 3H, COCH_{3Lev}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9 (CO_{Lev}), 172.7 ($COCH_{2Lev}$), 137.8 (C-Ar), 133.8 (C-2$_{All}$), 129.1, 128.2, 126.5 (CH-Ar), 118.3 (C-3$_{All}$), 101.9 (C-1), 101.1 (CH-acetal), 73.9 (C-3), 73.6 (C-4), 70.3 (C-1$_{All}$), 69.1 (C-6), 68.6 (C-2), 66.6 (C-5), 38.2 (CH_{2Lev}), 29.9 ($COCH_{3Lev}$), 28.4 (CH_{2Lev}); HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{21}H_{27}O_8$ 407.1700, found 407.1695; m/z [M + NH_4]$^+$ calcd for $C_{21}H_{30}NO_8$ 424.1966, found 424.1964; m/z [M + Na]$^+$ calcd for $C_{21}H_{26}NaO_8$ 429.1520, found 429.1515.

*Allyl 2-O-Acetyl-4,6-O-benzylidene-3-O-tert-butyldimethylsilyl-β-D-galactopyranoside (**3**).* To a solution of 3-OTBS and 2-OTBS regioisomers (1.01 g, 2.39 mmol, 1.0 equiv, see previous experiment for details) in anhydrous py (10 mL) was added Ac_2O (10 mL) followed by DMAP (3.0 mg, 24 μmol, 0.01 equiv). The mixture was stirred for 16 h at rt, then concentrated under reduced pressure and coevaporated with toluene (3×). The residue was purified by silica gel flash chromatography (PE/EtOAc 1:0 to 8:2) to give **3** (951 mg, 86%) as a white amorphous solid along with its 2-OTBS regioisomer (136 mg, 12%) as a colorless oil. Analytical data for **3**: $[\alpha]_D^{20}$ +19.0 (c 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.51 (m, 2H, C*H*-Ar), 7.40−7.32 (m, 3H, C*H*-Ar), 5.91−5.80 (m, 1H, H-2$_{All}$), 5.52 (s, 1H, C*H*-acetal), 5.29−5.23 (m, 2H, H-2, H-3a$_{All}$), 5.16 (ddd, J = 10.4, 3.1, 1.4 Hz, 1H, H-3b$_{All}$), 4.46 (d, $J_{1,2}$ = 8.1 Hz, 1H, H-1), 4.38−4.32 (m, 2H, H-6a, H-1a$_{All}$), 4.14−4.03 (m, 3H, H-6b, H-1b$_{All}$, H-4), 3.85 (dd, $J_{2,3}$ = 9.7 Hz, $J_{3,4}$ = 3.7 Hz, 1H, H-3), 3.42 (br s, 1H, H-5), 2.08 (s, 3H, COCH_3), 0.86 (s, 9H, C(CH_3)$_3$), 0.07, 0.05 (2 × s, 6H, 2 × CH_3Si); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5 ($COCH_{3Ac}$), 137.9 (C-Ar), 134.2 (C-2$_{All}$), 128.9, 128.2, 126.4 (CH-Ar), 117.1 (C-3$_{All}$), 101.1 (CH-acetal), 100.0 (C-1), 76.7 (C-4), 72.4 (C-3), 71.5 (C-2), 69.2, 69.1 (C-6, C-1$_{All}$), 66.8 (C-5), 25.6 (C(CH_3)$_3$), 21.2 ($COCH_{3Ac}$), 18.1 (C(CH_3)$_3$), −4.4, −4.6 (2 × CH_3Si); HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{24}H_{40}NO_7Si$ 482.2569, found 482.2571; m/z [M + Na]$^+$ calcd for $C_{24}H_{36}NaO_7Si$ 487.2123, found 487.2120. Analytical data for the 2-OTBS regioisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.48 (m, 2H, C*H*-Ar), 7.40−7.34 (m, 3H, C*H*-Ar), 6.00−5.89 (m, 1H, H-2$_{All}$), 5.48 (s, 1H, C*H*-acetal), 5.29 (ddd, J = 17.3, 3.0, 1.4 Hz, 1H, H-3a$_{All}$), 5.18 (ddd, J = 10.4, 2.8, 1.2 Hz, 1H, H-3b$_{All}$), 4.79 (dd, $J_{2,3}$ = 9.7 Hz, $J_{3,4}$ = 3.7 Hz, 1H, H-3), 4.42 (ddt, J = 12.3, 5.4, 1.4 Hz, 1H, H-1a$_{All}$), 4.36−4.29 (m, 3H, H-1, H-4, H-6a), 4.11−4.03 (m, 2H, H-1b$_{All}$, H-6b), 3.96 (dd, $J_{2,3}$ = 9.7 Hz, $J_{1,2}$ = 7.5 Hz, 1H, H-2), 3.47 (br s, 1H, H-5), 2.10 (s, 3H, COCH_{3Ac}), 0.86 (s, 9H, C(CH_3)$_3$), 0.10, 0.09 (2 × s, 6H, 2 × CH_3Si); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0 ($COCH_{3Ac}$), 137.9 (C-Ar), 134.2 (C-2$_{All}$), 129.1, 128.2, 126.5 (CH-Ar), 117.8 (C-3$_{All}$), 102.7 (C-1), 101.1 (CH-acetal), 75.3 (C-3), 73.8 (C-4), 70.5 (C-1$_{All}$), 69.5 (C-2), 69.3 (C-6), 66.3 (C-5), 25.9 (C(CH_3)$_3$), 21.3 ($COCH_{3Ac}$), 18.3 (C(CH_3)$_3$), −4.0, −4.7 (2 × CH_3Si); HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{24}H_{37}O_7Si$ 465.2303, found 465.2302; m/z [M + NH_4]$^+$ calcd for $C_{24}H_{40}NO_7Si$ 482.2569, found 482.2570; m/z [M + Na]$^+$ calcd for $C_{24}H_{36}NaO_7Si$ 487.2123, found 487.2119.

*2-O-Acetyl-4,6-O-benzylidene-3-O-tert-butyldimethylsilyl-α,β-D-galactopyranosyl N-Phenyl-2,2,2-trifluoroacetimidate (**10**).* 1,5-Cyclooctadiene-bis(methyldiphenylphosphine)iridium(I) hexafluorophosphate (58 mg, 68 μmol, 0.03 equiv) was dissolved in anhydrous THF (11 mL), and the resulting red solution was degassed under Ar. Hydrogen was bubbled through the solution for 5 min, and then the resulting yellow solution was once again degassed under Ar. A solution of benzylidene **3** (1.05 g, 2.26 mmol, 1.0 equiv) in anhydrous THF (11 mL) was added to the former solution. The mixture was stirred for 2 h at rt under Ar. Then, a solution of iodine (1.15 g, 4.52 mmol, 2.0 equiv) in THF/H_2O (13.5 mL, 4:1 v/v) was added to the mixture, which was stirred for another 1 h at rt. The excess of iodine was then quenched by adding a freshly prepared 10% $Na_2S_2O_3$(aq) solution. The mixture was concentrated to 1/3 volume, and the aqueous phase was extracted with EtOAc (3 × 25 mL). The combined organic layers were washed with brine (25 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (PE/EtOAc 8:2 to 5:5) to give a hemiacetal (952 mg, 99%, two steps, ratio α/β = 2.6:1.0) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.51 (m, 2H, C*H*-Ar), 7.40−7.30 (m, 3H, C*H*-Ar), 5.55−5.51 (m, 1.7H, H-1α, C*H*-acetalα, C*H*-acetalβ), 5.15 (ddd, $J_{2,3}$ = 10.1 Hz, $J_{1,2}$ = 3.6 Hz, $^4J_{2,OH}$ = 0.6 Hz, 0.7H, H-2α), 5.06 (dd, $J_{2,3}$ = 9.7 Hz, $J_{1,2}$ = 8.1 Hz, 0.3H, H-2β), 4.57 (dd, $J_{1,OH}$ = 11.0 Hz, $J_{1,2}$ = 8.2 Hz, 0.3H, H-1β), 4.37 (dd, $J_{6a,6b}$ = 12.5. Hz, $J_{5,6a}$ = 1.5 Hz, 0.3H, H-6aβ), 4.28−4.24 (m, 1.4H, H-3α, H-6aα), 4.10−4.02 (m, 2H, H-4α, H-4β, H-6bβ, H-6bα), 3.92 (br s, 0.7H, H-5α), 3.87 (dd, $J_{2,3}$ = 9.7 Hz, $J_{3,4}$ = 3.7 Hz, 0.3H, H-3β), 3.79 (d, $J_{OH,1}$ = 11.0 Hz, 0.3H, O*H*β), 3.48 (dd, $J_{5,6b}$ = 2.8 Hz, $J_{5,6a}$ = 1.7 Hz, 0.3H, H-5β), 3.28 (dd, $J_{OH,1}$ = 3.5 Hz, $^4J_{OH,2}$ = 1.0 Hz, 0.7H, O*H*α), 2.12 (s, 0.9H, COC$H_3\beta$), 2.10 (s, 2.1H, COC$H_3\alpha$), 0.89 (s, 6.3H, C(CH_3)$_3\alpha$), 0.88 (s, 2.7H, C(CH_3)$_3\beta$), 0.10, 0.10 (s, 4.2H, 2 × CH_3Si), 0.09, 0.08 (2 × s, 1.8H, 2 × CH_3Si); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7 ($COCH_3\beta$), 170.5 ($COCH_3\alpha$), 138.0 (C-Ar), 128.9−126.2 (CH-Ar), 100.7 (CH-acetal), 96.3 (C-1β),

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91.4 (C-1α), 77.3 (C-4α), 76.5 (C-4β), 74.5 (C-2β), 71.6 (C-2α), 71.5 (C-3β), 69.5 (C-6α), 69.2 (C-6β), 67.3 (C-3α), 67.0 (C-5β), 62.8 (C-5α), 25.7 ($C(CH_3)_3\alpha$), 25.6 ($C(CH_3)_3\beta$), 21.2 ($COCH_3$), 18.2 ($C(CH_3)_3\alpha$), 18.1 ($C(CH_3)_3\beta$), −4.4, −4.5 (2 × $CH_3Si\alpha$), −4.5, −4.5 (2 × $CH_3Si\beta$); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{21}H_{32}NaO_7Si$ 447.1810, found 447.1813. To a solution of the hemiacetal (597 mg, 1.14 mmol, 1.0 equiv) in acetone (14 mL) was added Cs_2CO_3 (504 mg, 1.55 mmol, 1.1 equiv) followed by PTFACl (584 mg, 2.81 mmol, 2.0 equiv). The mixture was stirred for 3 h at rt; then, the suspension was filtered and rinsed with DCM. The solvents were concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (PE/EtOAc 1:0 to 8:2 + 1% Et_3N) to give **10** (840 mg, quant, ratio α/β = 1.4:1.0) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, partial) δ 7.59−6.77 (m, 10H, H-Ar), 5.56 (s, 1.8H, C*H*-acetalα), 5.52 (s, 1.2H, C*H*-acetalβ), 5.48 (t, $J_{1,2} \approx J_{2,3} \approx$ 8.5 Hz, 0.4H, H-2β), 5.34 (d, $J_{2,3}$ = 7.9 Hz, 0.6H, H-2α), 4.37−4.23 (m, 1.6H, H-3α, H-6aα, H-6aβ), 4.18 (br s, 0.6H, H-4α), 4.09−4.00 (m, 1.4H, H-4β, H-6bα, H-6bβ), 3.93−3.74 (m, 1H, H-3β, H-5α), 2.09 (s, 1.2H, $COCH_3\beta$), 2.08 (s, 1.8H, $COCH_3\alpha$), 0.90 (s, 5.4H, $C(CH_3)_3\alpha$), 0.87 (s, 3.6H, $C(CH_3)_3\beta$), 0.12 (s, 1.8H, $CH_3Si\alpha$), 0.10 (s, 1.8H, $CH_3Si\alpha$), 0.08 (s, 1.2H, $CH_3Si\beta$), 0.07 (s, 1.2H, $CH_3Si\beta$); ^{13}C NMR (100 MHz, $CDCl_3$, partial) δ 170.0 ($COCH_3\alpha$), 168.9 ($COCH_3\beta$), 143.6 (C-Arβ), 143.5 (C-Arα), 137.7 (C-Arα), 137.6 (C-Arβ), 136.5 (d, $J_{C,F}$ = 136.5 Hz, CF_3), 129.5−119.5 (CH-Ar), 101.1 (CH-acetalβ), 100.9 (CH-acetalα), 76.8 (C-4α), 76.2 (C-4β), 72.2 (C-3β), 70.5 (C-2β), 69.8 (C-2α), 69.0 (C-6α), 68.8 (C-6β), 67.6 (C-3α), 65.4 (C-5α), 25.7 ($C(CH_3)_3\alpha$), 25.6 ($C(CH_3)_3\beta$), 20.90 ($COCH_3\beta$), 20.87 ($COCH_3\alpha$), 18.2 ($C(CH_3)_3\alpha$), 18.1 ($C(CH_3)_3\beta$), −4.4, −4.5, −4.60, −4.61 (4 × $CH_3Si\alpha\beta$); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{29}H_{36}F_3NNaO_7Si$ 618.2105, found 618.2109.

*Allyl 2,3-Di-O-benzyl-4,6-O-(di-tert-butylsilylene)-β-D-galactopyranoside (**5**).* To a cooled solution (0 °C) of diol **8** (1.73 g, 5.60 mmol, 1.0 equiv) in anhydrous DMF (22 mL) was slowly added NaH (60% oil dispersion, 561 mg, 14.0 mmol, 2.5 equiv). The suspension was stirred for 1 h while being gradually warmed to rt. The mixture was cooled to −10 °C; then, BnBr (1.67 mL, 14.0 mmol, 2.5 equiv) was added dropwise. The mixture was stirred for 1.5 h under Ar while being gradually warmed to rt. Then, the mixture was cooled to 0 °C, and a few drops of MeOH were added to quench the excess of base. The mixture was allowed to stir for 30 min while being gradually warmed to rt. The solution was diluted with EtOAc (200 mL), and the organic phase was extracted with H_2O (3 × 60 mL). The combined organic layers were washed with a saturated NH_4Cl(aq) solution (60 mL) and brine (60 mL). The solvents of the dried ($MgSO_4$) solution were concentrated under reduced pressure and placed under high vacuum. A portion of the crude benzylidene (2.64 g, 5.40 mmol, 1.0 equiv) was dissolved in DCM (216 mL), and the solution was cooled to 0 °C. A solution of TFA/H_2O (1:1 v/v, 22 mL) was added, and the mixture was vigorously stirred for 10 h while being gradually warmed to rt. Then, the organic phase was washed with a saturated $NaHCO_3$(aq) solution (3 × 100 mL). The aqueous phase was back-extracted with DCM (100 mL), and the combined organic layers were washed with brine (100 mL). The solvents of the dried ($MgSO_4$) solution were concentrated under reduced pressure and placed under high vacuum. The crude diol (2.16 g, 5.40 mmol, 1.0 equiv) was dissolved in anhydrous DMF (21.6 mL), and the solution was cooled to −10 °C. Di-*t*BuSi(OTf)$_2$ (1.76 mL, 5.40 mmol, 1.0 equiv) was added, and the mixture was stirred for 16 h while being gradually warmed to rt. Py (1.3 mL, 3.0 equiv) was added to quench the reaction, and the solution was diluted with EtOAc (150 mL). The organic phase was washed with H_2O (3 × 85 mL) and brine (50 mL). The solvents of the dried ($MgSO_4$) solution were concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (PE/EtOAc 1:0 to 9:1) to give **5** (1.97 g, 67%, over three steps) as a yellow oil that solidified upon standing. $[\alpha]_D^{20}$ +9.8 (*c* 0.93, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.38 (m, 4H, C*H*-Ar), 7.34−7.25 (m, 6H, C*H*-Ar), 6.00−5.90 (m, 1H, H-2$_{All}$), 5.32 (ddd, J = 17.2, 3.4, 1.6 Hz, 1H, H-3a$_{All}$), 5.17 (ddd, J = 10.4, 2.9, 1.6 Hz, 1H, H-3b$_{All}$), 4.91 (d, J = 10.8 Hz, 1H, C*H*HPh), 4.79 (d, J = 10.9 Hz, 1H, C*H*HPh), 4.76 (d, J = 12.7 Hz, 1H, C*H*HPh), 4.71 (d, J = 12.1 Hz, 1H, C*H*HPh), 4.43−4.39 (m, 3H, H-1, H-4, H-1a$_{All}$), 4.20 (d, J = 1.8 Hz, 2H, H-6ab), 4.14 (ddt, J = 13.0, 6.0, 1.4 Hz, 1H, H-1b$_{All}$), 3.78 (dd, $J_{2,3}$ = 9.6 Hz, $J_{1,2}$ = 7.7 Hz, 1H, H-2), 3.40 (dd, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 3.1 Hz, 1H, H-3), 3.24 (br s, 1H, H-5), 1.09, 1.07 (2 × s, 18H, 2 × $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 138.7 (2 × C-Ar), 134.7 (C-2$_{All}$), 128.5−127.6 (CH-Ar), 116.9 (C-3$_{All}$), 102.8 (C-1), 81.1 (C-3), 78.4 (C-2), 75.5 (CH_2Ph), 71.3 (CH_2Ph), 71.2 (C-5), 70.3 (C-4), 70.0 (C-1$_{All}$), 67.4 (C-6), 27.7, 27.6 (2 × $C(CH_3)_3$), 23.5, 20.9 (2 × $C(CH_3)_3$); HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{31}H_{48}NO_6Si$ 558.3245, found 558.3246; m/z [M + Na]$^+$ calcd for $C_{31}H_{44}NaO_6Si$ 563.2800, found 563.2797.

*2,3-Di-O-benzyl-4,6-O-(di-tert-butylsilylene)-α,β-D-galactopyranosyl N-Phenyl-2,2,2-trifluoroacetimidate (**9**).* 1,5-Cyclooctadiene-bis(methyldiphenylphosphine)iridium(I) hexafluorophosphate (78 mg, 92 μmol, 0.05 equiv) was dissolved in anhydrous THF (9.2 mL), and the resulting red solution was degassed under Ar. Hydrogen was bubbled through the solution for 5 min, and then the resulting yellow solution was once again degassed under Ar. A solution of silylene **5** (1.00 g, 1.85 mmol, 1.0 equiv) in anhydrous THF (9.2 mL) was added to the former solution. The mixture was stirred for 3.5 h at rt under Ar. Then, a solution of iodine (939 mg, 3.70 mmol, 2.0 equiv) in THF/H_2O (11 mL, 4:1 v/v) was added to the mixture, which was stirred for another 1 h at rt. The excess of iodine was then quenched by adding a freshly prepared 10% $Na_2S_2O_3$(aq) solution (20 mL). The mixture was concentrated to 1/3 volume, and the aqueous phase was extracted with EtOAc (3 × 25 mL). The combined organic layers were washed with brine (25 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (PE/EtOAc 8:2 to 6:4) to give an hemiacetal (748 mg, 81%, two steps, ratio α/β = 3.6:1.0) as a yellow foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.27 (m, 10H, C*H*-Ar), 5.20 (d, $J_{1,2}$ = 3.7 Hz, 0.8H, H-1α), 4.90 (d, J = 11.7 Hz, 1H, C*H*HPh), 4.79−4.68 (m, 3.2H, 3 × C*H*HPh, H-1β), 4.52 (d, $J_{3,4}$ = 2.6 Hz, 0.8H, H-4α), 4.46 (d, $J_{3,4}$ = 2.8 Hz, 0.2H, H-4β), 4.21 (dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 1.9 Hz, 1H, H-6a), 4.13 (dd, $J_{6a,6b}$ = 12.5 Hz, $J_{5,6b}$ = 1.6 Hz, 1H, H-6b), 3.98 (dd, $J_{2,3}$ = 9.8 Hz, $J_{1,2}$ = 3.7 Hz, 0.8H, H-2α), 3.84 (br s, 0.8H, H-5α), 3.77 (dd, $J_{2,3}$ = 9.8 Hz, $J_{3,4}$ = 3.0 Hz, 0.8H, H-3α), 3.71 (dd, $J_{2,3}$ = 9.5 Hz, $J_{1,2}$ = 7.7 Hz, 0.2H, H-2β), 3.45 (dd, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 3.1 Hz, 0.2H, H-3β), 3.33 (br s, 0.2H, H-5β), 1.08, 1.08 (s, 3.6H, 2 × $C(CH_3)_3\beta$), 1.06, 1.01 (s, 14.4H, 2 × $C(CH_3)_3\alpha$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 138.2 (2 × C-Ar), 128.5−127.6 (CH-Ar), 97.5 (C-1β), 92.2 (C-1α), 81.1 (C-3β), 79.2 (C-2β), 77.5 (C-3α), 75.3 ($CH_2Ph\beta$), 74.8 (C-2α), 74.0 ($CH_2Ph\alpha$), 71.5 (C-5β), 71.1 ($CH_2Ph\beta$), 70.9 ($CH_2Ph\alpha$), 70.7 (C-4α), 70.0 (C-4β), 67.5 (C-5α), 67.3 (C-6α), 67.2 (C-6β), 27.7, 27.6, 27.5, 27.3 (2 × $C(CH_3)_3\alpha\beta$), 23.4, 23.4, 20.8, 20.7 (2 × $C(CH_3)_3\alpha\beta$); HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{28}H_{44}NO_6Si$ 518.2932, found 518.2933; m/z [M + Na]$^+$ calcd for $C_{28}H_{40}NaO_6Si$ 523.2486, found 523.2485. To a solution of the hemiacetal (292 mg, 583 μmol, 1.0 equiv) in acetone (5.8 mL) was added Cs_2CO_3 (209 mg, 641 μmol, 1.1 equiv) followed by PTFACl (242 mg, 1.17 mmol, 2.0 equiv). The mixture was stirred for 1 h at rt; then, the suspension was filtered and rinsed with DCM. The solvents were concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (PE/EtOAc 1:0 to 9:1 + 1% Et_3N) to give the less polar α-anomer **9α** (221 mg, 56%) as a white foam along with the more polar β-anomer **9β** (120 mg, 31%) as a colorless oil. Analytical data for **9α**: ^{1}H NMR (400 MHz, $CDCl_3$, partial) δ 7.45−7.22 (m, 12H, C*H*-Ar), 7.10−7.05 (m, 1H, C*H*-Ar), 6.77−6.71 (m, 2H, C*H*-Ar), 6.54 (br s, 1H, H-1), 4.86 (d, J = 11.7 Hz, 1H, C*H*HPh), 4.79−4.71 (m, 3H, 3 × C*H*HPh), 4.58 (br s, 1H, H-4), 4.25−4.11 (m, 3H, H-6a, H-6b, H-2), 3.89−3.84 (m, 2H, H-3, H-5), 1.06 (s, 9H, $C(CH_3)_3$), 0.98 (br s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$, partial) δ 143.9 (C = N), 138.8, 138.8, 138.3 (3 × C-Ar), 129.6−119.6 (CH-Ar), 77.4 (C-3), 73.9 (CH_2Ph), 73.7 (C-2), 71.3 (CH_2Ph), 70.8 (C-4), 70.1 (C-5), 67.0 (C-6), 27.8, 27.4 (2 × $C(CH_3)_3$), 23.5, 20.8 (2 × $C(CH_3)_3$). Analytical data for **9β**: ^{1}H NMR (400 MHz, $CDCl_3$, partial) δ 7.43−7.23 (m, 12H, C*H*-Ar), 7.10−7.04 (m, 1H, C*H*-Ar), 6.85−6.80 (m, 2H, C*H*-Ar), 5.66 (br s, 1H, H-1), 4.87 (d, J = 10.7 Hz, 1H, C*H*HPh), 4.80 (d, J = 10.7 Hz, 1H, C*H*HPh), 4.77 (d, J = 12.7 Hz, 1H, C*H*HPh), 4.69 (d, J = 12.1 Hz,

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1H, C*H*HPh), 4.43 (br s, 1H, H-4), 4.18 (br s, 2H, H-6a, H-6b), 4.00 (m, 1H, H-2), 3.44 (m, 1H, H-3), 1.08, 1.07 (2 × s, 18H, 2 × C(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$, partial) δ 143.8 (C=N), 138.4, 138.4, 138.3 (3 × C-Ar), 128.7−119.5 (*C*H-Ar), 97.2 (C-1), 81.1 (C-3), 76.9 (C-2), 75.8 (CH_2Ph), 72.1, 71.3 (CH_2Ph), 69.9 (C-4), 66.9 (C-6), 27.8, 27.5 (2 × C(CH_3)$_3$), 23.6, 20.9 (2 × *C*(CH_3)$_3$); HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{36}H_{44}F_3NNaO_6Si$ 694.2782, found 694.2785.

*Allyl 2,3-Di-O-benzyl-4,6-O-(di-tert-butylsilylene)-α-D-galactopyranosyl-(1→3)-4,6-O-benzylidene-2-O-levulinoyl-β-D-galactopyranoside (**11**).* To a solution of acceptor **4** (258 mg, 635 μmol, 1.0 equiv) and donor **9** (469 mg, 698 μmol, 1.1 equiv, ratio α/β 2.4:1.0) in anhydrous DCE (12.7 mL) was added freshly activated 4 Å molecular sieves (1.00 g). The suspension was stirred for 1 h at rt under Ar. The solution was cooled to −10 °C, and TMSOTf (34 μL, 190 μmol, 0.3 equiv) was added, keeping rigorous anhydrous conditions. The mixture was stirred for 1.5 h at −10 °C under Ar and then quenched with Et_3N (200 μL). The mixture was filtered and rinsed with DCM, and the solvents were concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (PE/EtOAc 8:2 to 6:4) to give **11** (493 mg, 87%) as a white foam. $[\alpha]_D^{20}$ +81.9 (*c* 0.53, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.49 (m, 2H, C*H*-Ar), 7.41−7.11 (m, 13H, C*H*-Ar), 5.92−5.79 (m, 1H, H-2$_{All}$), 5.47 (br s, 1H, C*H*-acetal), 5.40−5.34 (m, 1H, H-2), 5.25 (br d, *J* = 17.0 Hz, 1H, H-3a$_{All}$), 5.16 (d, *J* = 10.1 Hz, 1H, H-3b$_{All}$), 4.99 (br s, 1H, H-1′), 4.78−4.64 (m, 4H, C*H*HPh, CH_2Ph, H-4), 4.56 (d, *J* = 11.2 Hz, 1H, C*H*HPh), 4.45 (br d, $J_{1,2}$ = 6.3 Hz, 1H, H-1), 4.38−4.23 (m, 4H, H-1a$_{All}$, H-6a, H-6a′, H-3′), 4.15−3.79 (m, 7H, H-6b′, H-1b$_{All}$, H-6b, H-2′, H-4′, H-5′, H-3), 3.37 (br s, 1H, H-5), 2.90−2.76 (m, 1H, C*H*H$_{Lev}$), 2.67−2.55 (m, 1H, C*H*H$_{Lev}$), 2.52−2.43 (m, 2H, CH_{2Lev}), 2.13 (s, 3H, COCH_{2Lev}), 1.06, 1.00 (2 × s, 18H, 2 × C(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4 (CO_{Lev}), 171.3 ($COCH_{2Lev}$), 139.2, 139.0, 137.7 (3 × C-Ar), 134.1 (C-2$_{All}$), 128.9−126.5 (*C*H-Ar), 117.2 (C-3$_{All}$), 101.1 (C*H*-acetal), 100.1 (C-1), 96.7 (C-1′), 77.1 (C-4′), 75.2 (C-3), 74.1 (C-2′), 72.7 (CH_2Ph), 72.6 (C-3′), 71.0 (C-4), 70.8 (CH_2Ph), 70.4 (C-2), 69.4, 69.3 (C-6, C-1$_{All}$), 68.1 (C-5′), 67.3 (C-6′), 66.7 (C-5), 37.7 (CH_{2Lev}), 30.2 (COCH_{3Lev}), 28.1 (CH_{2Lev}), 27.8, 27.4 (2 × C(CH_3)$_3$), 23.5, 20.7 (2 × *C*(CH_3)$_3$); HRMS (ESI-TOF) *m*/*z* [M + NH_4]$^+$ calcd for $C_{49}H_{68}NO_{13}Si$ 906.4454, found 906.4461; *m*/*z* [M + Na]$^+$ calcd for $C_{49}H_{64}NaO_{13}Si$ 911.4008, found 911.4009.

*Allyl 2,3-Di-O-benzyl-α-D-galactopyranosyl-(1→3)-4,6-O-benzylidene-2-O-levulinoyl-β-D-galactopyranoside (**12**).* To a solution of disaccharide **11** (206 mg, 232 μmol, 1.0 equiv) in anhydrous THF (4.6 mL) was added TREAT-HF (38 μL, 232 μmol, 1.0 equiv). The mixture was stirred for 2.5 h at rt under Ar. The solution was diluted with EtOAc (25 mL), and the organic phase was washed with a saturated $NaHCO_3$(aq) solution (10 mL) and brine (10 mL). The solvents of the dried ($MgSO_4$) solution were concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (EtOAc/MeOH 1:0 to 98:2) to give **12** (144 mg, 83%) as a white amorphous powder. $[\alpha]_D^{20}$ −43.6 (*c* 0.55, $CHCl_3$); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.54−7.49 (m, 2H, C*H*-Ar), 7.42−7.37 (m, 2H, C*H*-Ar), 7.33−7.22 (m, 6H, C*H*-Ar), 7.20−7.14 (m, 5H, C*H*-Ar), 5.96−5.86 (m, 1H, H-2$_{All}$), 5.67 (s, 1H, C*H*-acetal), 5.36−5.23 (m, 3H, H-2, H-1′, H-3a$_{All}$), 5.12 (ddd, *J* = 10.6, 3.1, 1.4 Hz, 1H, H-3b$_{All}$), 4.77 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.72 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.66−4.56 (m, 4H, CH_2Ph, H-4, H-1), 4.35−4.27 (m, 2H, H-5′, H-1a$_{All}$), 4.23 (br d, $J_{6a,6b}$ = 12.2 Hz, 1H, H-6a), 4.16 (br d, $J_{6a,6b}$ = 12.2 Hz, 1H, H-6b), 4.13−4.07 (m, 2H, H-1b$_{All}$, H-3), 4.02−3.90 (m, 3H, H-4′, H-3′, H-2′), 3.81−3.64 (m, 5H, H-6a′, H-6b′, H-5, 2 × O*H*), 2.85−2.76 (m, 1H, C*H*H$_{Lev}$), 2.71−2.61 (m, 2H, CH_{2Lev}), 2.52−2.43 (m, 1H, C*H*H$_{Lev}$), 2.12 (s, 3H, COCH_{3Lev}); ^{13}C NMR (100 MHz, acetone-d_6) δ 206.9 (CO_{Lev}), 172.0 ($COCH_{2Lev}$), 140.4, 140.2, 139.7 (3 × C-Ar), 135.5 (C-2$_{All}$), 129.3−127.3 (*C*H-Ar), 116.6 (C-3$_{All}$), 101.4, 101.3 (*C*H-acetal, C-1), 94.5 (C-1′), 78.4 (C-3′), 76.4 (C-2′), 74.1 (C-3), 72.6 (C-4), 72.4, 72.2 (2 × CH_2Ph), 71.9 (C-4′), 70.8 (C-2), 70.0, 69.8 (C-6, C-1$_{All}$), 68.2 (C-5′), 67.5 (C-5), 62.6 (C-6′), 38.1 (CH_{2Lev}), 29.9 (COCH_{3Lev}), 28.7 (CH_{2Lev}); HRMS (ESI-TOF) *m*/*z* [M + NH_4]$^+$ calcd for $C_{41}H_{52}NO_{13}$ 766.3433, found 766.3436; *m*/*z* [M + Na]$^+$ calcd for $C_{41}H_{48}NaO_{13}$ 771.2987, found 771.2985.

*Allyl 2,3-Di-O-benzyl-6-O-chloroacetyl-α-D-galactopyranosyl-(1→3)-4,6-O-benzylidene-2-O-levulinoyl-β-D-galactopyranoside (**13**).* To a cooled solution (−10 °C) of diol **12** (619 mg, 827 μmol, 1.0 equiv) in *sym*-collidine (33 mL) was added a freshly prepared solution of chloroacetyl chloride in DCE (72 μL in 2.0 mL, 910 μmol, 1.1 equiv) over a period of 20 min under N_2. Then, additional chloroacetyl chloride in DCE solution was added after 2 h (1.1 equiv), and the mixture was stirred at −10 °C until TLC showed completion. The reaction was quenched by adding a few drops of MeOH. The solution was diluted with EtOAc (250 mL), and the organic phase was washed with a 10% HCl(aq) solution (3 × 100 mL), a saturated $NaHCO_3$(aq) solution (100 mL), and brine (100 mL). The solvents of the dried ($MgSO_4$) solution were concentrated under reduced pressure and coevaporated with toluene (3×) to give crude **13** (736 mg) as a white foam, which was used without purification for the glycosylation step. $[\alpha]_D^{20}$ +57.7 (*c* 0.70, $CHCl_3$); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.54−7.50 (m, 2H, C*H*-Ar), 7.41−7.37 (m, 2H, C*H*-Ar), 7.33−7.22 (m, 6H, C*H*-Ar), 7.19−7.14 (m, 5H, C*H*-Ar), 5.96−5.86 (m, 1H, H-2$_{All}$), 5.75 (s, 1H, C*H*-acetal), 5.38−5.32 (m, 2H, H-2, H-1′), 5.27 (ddd, *J* = 17.3, 3.6, 1.8 Hz, 1H, H-3a$_{All}$), 5.14 (ddd, *J* = 10.5, 3.3, 1.5 Hz, 1H, H-3b$_{All}$), 4.78 (d, *J* = 11.7 Hz, 1H, C*H*HPh), 4.72 (d, *J* = 11.7 Hz, 1H, C*H*HPh), 4.69 (d, $J_{3,4}$ = 3.4 Hz, 1H, H-4), 4.65−4.61 (m, 2H, C*H*HPh, H-1), 4.56 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.47−4.36 (m, 3H, H-6a′, H-6b′, H-4′), 4.34−4.27 (m, 4H, H-1a$_{All}$, H-5′, CH_2Cl), 4.25 (dd, $J_{6a,6b}$ = 12.2 Hz, $J_{5,6a}$ = 1.5 Hz, 1H, H-6a), 4.20 (dd, $J_{6a,6b}$ = 12.2 Hz, $J_{5,6b}$ = 1.6 Hz, 1H, H-6b), 4.14−4.08 (m, 2H, H-1b$_{All}$, H-3), 4.02 (dd, $J_{2',3'}$ = 10.0 Hz, $J_{3',4'}$ = 3.1 Hz, 1H, H-3′), 3.98 (dd, *J* = 3.2, 1.1 Hz, 1H, 4-O*H*), 3.93 (dd, $J_{2',3'}$ = 10.0 Hz, $J_{1',2'}$ = 3.6 Hz, 1H, H-2′), 3.70 (br s, 1H, H-5), 2.91−2.81 (m, 1H, C*H*H$_{Lev}$), 2.73−2.61 (m, 2H, 2 × C*H*H$_{Lev}$), 2.47−2.38 (m, 1H, C*H*H$_{Lev}$), 2.13 (s, 3H, COCH_{3Lev}); ^{13}C NMR (100 MHz, acetone-d_6) δ 207.1 (CO_{Lev}), 172.1 ($COCH_{2Lev}$), 167.8 ($COCH_2Cl$), 140.3, 140.1, 139.6 (3 × C-Ar), 135.5 (C-2$_{All}$), 129.4−127.3 (*C*H-Ar), 116.8 (C-3$_{All}$), 101.5, 101.3 (*C*H-acetal, C-1), 93.6 (C-1′), 78.1 (C-3′), 76.0 (C-2′), 73.4 (C-3), 72.6 (CH_2Ph), 72.1 (C-4), 72.1 (CH_2Ph), 70.5 (C-2), 70.0 (C-1b$_{All}$), 69.8 (C-6), 69.4 (C-5′), 68.0 (C-4′), 67.5 (C-5), 66.3 (C-6′), 41.7 ($COCH_2Cl$), 38.0 (CH_{2Lev}), 30.1 (COCH_{3Lev}), 28.5 (CH_{2Lev}); HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{43}H_{49}ClNaO_{14}$ 847.2703, found 847.2698.

*Allyl 2-O-Acetyl-4,6-O-benzylidene-3-O-tert-butyldimethylsilyl-β-D-galactopyranosyl-(1→4)-2,3-di-O-benzyl-6-O-chloroacetyl-α-D-galactopyranosyl-(1→3)-4,6-O-benzylidene-2-O-levulinoyl-β-D-galactopyranoside (**14β**) and Allyl 2-O-Acetyl-4,6-O-benzylidene-3-O-tert-butyldimethylsilyl-α-D-galactopyranosyl-(1→4)-2,3-di-O-benzyl-6-O-chloroacetyl-α-D-galactopyranosyl-(1→3)-4,6-O-benzylidene-2-O-levulinoyl-β-D-galactopyranoside (**14α**).* To a solution of crude acceptor **13** (581 mg, 705 μmol, 1.0 equiv) and donor **10** (756 mg, 1.27 mmol, 1.8 equiv, ratio α/β = 1.4:1.0) dissolved in anhydrous DCE (14.1 mL) was added freshly activated 4 Å molecular sieves (2.3 g). The suspension was stirred for 1 h at rt under Ar. The solution was cooled to −10 °C; then, TMSOTf (38 μL, 211 μmol, 0.3 equiv) was added, keeping rigorous anhydrous conditions. The mixture was stirred for 1 h under Ar while being warmed to rt and then quenched with Et_3N (100 μL). The mixture was filtered over Celite and rinsed with DCM, and the solvents were concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (PE/EtOAc 8:2 to 65:35) to give α-anomer **14α** (157 mg, 18%, two steps from **12**) along with β-anomer **14β** (436 mg, 50%, two steps from **12**), both as white amorphous powders. Analytical data for **14β**: $[\alpha]_D^{20}$ +52.5 (*c* 2.1, $CHCl_3$); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.56−7.47 (m, 6H, C*H*-Ar), 7.39−7.22 (m, 10H, C*H*-Ar), 7.16−7.07 (m, 4H, C*H*-Ar), 5.96−5.85 (m, 1H, H-2$_{All}$), 5.77 (s, 1H, C*H*-acetal), 5.66 (s, 1H, C*H*-acetal), 5.35 (dd, $J_{2,3}$ = 10.5 Hz, $J_{1,2}$ = 8.0 Hz, 1H, H-2), 5.31 (d, $J_{1',2'}$ = 3.7 Hz, 1H, H-1′), 5.27 (ddd, *J* = 17.3, 3.5, 1.8 Hz, 1H, H-3a$_{All}$), 5.17−5.10 (m, 2H, H-2″, H-3b$_{All}$), 4.82 (d, *J* = 11.1 Hz, 1H, C*H*HPh), 4.81 (d, $J_{1'',2''}$ = 8.2 Hz, 1H, H-1″), 4.76 (d, *J* = 11.6 Hz, 1H, C*H*HPh), 4.71−4.65 (m, 2H, H-6a′, H-4), 4.63 (d, $J_{1,2}$ = 8.0 Hz, 1H, H-1), 4.59 (d, *J* = 11.9 Hz, 1H, C*H*HPh), 4.49−4.45 (m, 2H, C*H*HPh, H-4′), 4.34−4.28 (m, 6H, H-6b′, H-5′, H-4″, H-1a$_{All}$, CH_2Cl), 4.25−4.14 (m, 4H, H-6a, H-6b, H-6a″, H-6b″), 4.14−4.06 (m, 4H, H-1b$_{All}$, H-3, H-3′, H-3″), 3.82 (dd, $J_{2',3'}$ = 10.2 Hz, $J_{1',2'}$ = 3.7

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Hz, 1H, H-2′), 3.70 (br s, 2H, H-5, H-5″), 2.97−2.87 (m, 1H, CHH$_{Lev}$), 2.77−2.60 (m, 2H, 2 × CHH$_{Lev}$), 2.43−2.36 (m, 1H, CHH$_{Lev}$), 2.13 (s, 3H, COCH$_{3Lev}$), 1.71 (s, 3H, COCH$_{3Ac}$), 0.87 (s, 9H, C(CH$_3$)$_3$), 0.15, 0.09 (2 × s, 6H, 2 × CH$_3$Si); ^{13}C NMR (100 MHz, acetone-d_6) δ 207.5 (CO$_{Lev}$), 172.2 (COCH$_{2Lev}$), 170.1 (COCH$_{3Ac}$), 167.8 (COCH$_2$Cl), 140.4, 140.0, 139.9, 139.7 (4 × C-Ar), 135.4 (C-2$_{All}$), 129.4−127.0 (CH-Ar), 116.8 (C-3$_{All}$), 103.3 (C-1″), 101.6, 101.3, 101.3 (2 × CH-acetal, C-1), 93.2 (C-1′), 78.0 (C-3′), 77.3 (C-4″), 77.1, 77.1 (C-4′, C-2′), 73.5 (CH$_2$Ph), 73.1, 72.7 (C-3″, C-3), 72.5 (C-2″), 72.4 (CH$_2$Ph), 71.9 (C-4), 70.4 (C-2), 70.0 (C-1$_{All}$), 69.8, 69.7 (C-6, C-6″), 69.4 (C-5′), 67.5, 67.2 (C-5, C-5″), 66.9 (C-6′), 41.8 (CH$_2$Cl), 38.0 (CH$_{2Lev}$), 29.9 (COCH$_{3Lev}$), 28.4 (CH$_{2Lev}$), 26.0 (C(CH$_3$)$_3$), 21.4 (COCH$_{3Ac}$), 18.6 (C(CH$_3$)$_3$), −4.4, −4.6 (2 × CH$_3$Si); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{64}H_{79}ClNaO_{20}Si$ 1253.4515, found 1253.4472. Analytical data for **14*α***: $[\alpha]_D^{20}$ +68.3 (*c* 0.66, CHCl$_3$); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.58−7.54 (m, 2H, CH-Ar), 7.47−7.41 (m, 4H, CH-Ar), 7.37−7.25 (m, 14H, CH-Ar), 5.96−5.86 (m, 1H, H-2a$_{All}$), 5.80 (s, 1H, CH-acetal), 5.47 (s, 1H, CH-acetal), 5.40 (d, $J_{1',2'}$ = 3.5 Hz, 1H, H-1′), 5.34 (dd, $J_{2,3}$ = 10.4 Hz, $J_{1,2}$ = 8.1 Hz, 1H, H-2), 5.27 (ddd, J = 17.3, 3.6, 1.8 Hz, 1H, H-3a$_{All}$), 5.18 (dd, $J_{2'',3''}$ = 10.2 Hz, $J_{1'',2''}$ = 3.3 Hz, 1H, H-2′′), 5.14 (ddd, J = 10.5, 3.3, 1.4 Hz, 1H, H-3b$_{All}$), 5.05 (d, $J_{1'',2''}$ = 3.4 Hz, 1H, H-1″), 4.86 (d, J = 12.1 Hz, 1H, CHHPh), 4.76−4.69 (m, 2H, H-4, CHHPh), 4.68−4.61 (m, 3H, H-1, CH$_2$Ph), 4.53 (dd, $J_{6a',6b'}$ = 10.0 Hz, $J_{5,6a'}$ = 7.0 Hz, 1H, H-6a′), 4.48 (d, $J_{3',4'}$ = 2.6 Hz, 1H, H-4′), 4.40 (t, $J_{5',6a'} \approx J_{5',6b'} \approx$ 6.0 Hz, 1H, H-5′), 4.36−4.28 (m, 4H, H-6b′, CH$_2$Cl, H-1a$_{All}$), 4.27−4.07 (m, 8H, H-6a, H-6b, H-3, H-3′, H-3″, H-4″, H-5″, H-1b$_{All}$), 3.94 (dd, $J_{2',3'}$ = 10.4 Hz, $J_{1',2'}$ = 3.5 Hz, 1H, H-2′), 3.71 (br s, 1H, H-5), 3.54 (dd, $J_{6a'',6b''}$ = 12.6 Hz, $J_{5'',6a''}$ = 1.8 Hz, 1H, H-6a″), 3.41 (dd, $J_{6a'',6b''}$ = 12.5 Hz, $J_{5'',6b''}$ = 1.3 Hz, 1H, H-6b″), 2.93−2.84 (m, 1H, CHH$_{Lev}$), 2.74−2.61 (m, 2H, 2 × CHH$_{Lev}$), 2.44−2.37 (m, 1H, CHH$_{Lev}$), 2.15, 2.09 (s, 6H, 2 × COCH$_3$), 0.87 (s, 9H, C(CH$_3$)$_3$), 0.09, 0.07 (2 × s, 6H, 2 × CH$_3$Si); ^{13}C NMR (100 MHz, acetone-d_6) δ 207.5 (CO$_{Lev}$), 172.1 (COCH$_{2Lev}$), 170.6 (COCH$_{3Ac}$), 167.8 (COCH$_2$Cl), 140.3, 139.9, 139.9, 139.6 (4 × C-Ar), 135.5 (C-2$_{All}$), 129.4−127.0 (CH-Ar), 116.7 (C-3$_{All}$), 101.5 (CH-acetal), 101.3 (C-1), 100.9 (CH-acetal), 100.0 (C-1″), 93.3 (C-1′), 78.0, 77.8 (C-4″, C-3′), 77.1 (C-4′), 75.2 (C-2′), 73.5 (C-3), 73.1 (CH$_2$Ph), 72.1 (C-4), 71.7 (CH$_2$Ph), 71.7 (C-2″), 70.5 (C-2), 70.0 (C-1$_{All}$), 69.8 (C-6), 69.6 (C-5′), 69.4 (C-6″), 68.6 (C-3″), 67.5 (C-5), 64.8 (C-6′), 64.0 (C-5″), 41.7 (CH$_2$Cl), 38.0 (CH$_{2Lev}$), 29.9 (COCH$_{3Lev}$), 28.4 (CH$_{2Lev}$), 26.0 (C(CH$_3$)$_3$), 21.3 (COCH$_{3Ac}$), 18.7 (C(CH$_3$)$_3$), −4.3, −4.4 (2 × CH$_3$Si); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{64}H_{79}ClNaO_{20}Si$ 1253.4515, found 1253.4505.

*2-O-Acetyl-4,6-O-benzylidene-3-O-tert-butyldimethylsilyl-β-D-galactopyranosyl-(1→4)-2,3-di-O-benzyl-6-O-chloroacetyl-α-D-galactopyranosyl-(1→3)-4,6-O-benzylidene-2-O-levulinoyl-α-D-galactopyranosyl N-Phenyl-2,2,2-trifluoroacetimidate (**18**).* 1,5-Cyclooctadiene-bis(methyldiphenylphosphine)iridium(I) hexafluorophosphate (8.9 mg, 11 μmol, 0.03 equiv) was dissolved in anhydrous THF (2.0 mL), and the resulting red solution was degassed under Ar. Hydrogen was bubbled through the solution for 5 min, and then the resulting yellow solution was once again degassed under Ar. A solution of trisaccharide **14*β*** (418 mg, 339 μmol, 1.0 equiv) in anhydrous THF (2.0 mL) was added to the former solution. The mixture was stirred for 2 h at rt under Ar. Then, a solution of iodine (172 mg, 679 μmol, 2.0 equiv) in THF/H$_2$O (6.0 mL, 4:1 v/v) was added to the mixture, which was stirred for 1 h at rt. The excess of iodine was then quenched by adding a freshly prepared 10% Na$_2$S$_2$O$_3$(aq) solution (10 mL). The mixture was diluted with EtOAc (150 mL) and H$_2$O (25 mL), and the aqueous layer was extracted with EtOAc (2 × 75 mL). The organic phase was dried over MgSO$_4$ and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (PE/EtOAc 6:4 to 4:6) to give a hemiacetal (300 mg, 74%, two steps, ratio α/β = 6:1) as a yellow solid. ^{1}H NMR (400 MHz, acetone-d_6) δ 7.56−7.08 (m, 20H, H-Ar), 5.93 (dd, $J_{OH,1}$ = 4.1 Hz, $J_{OH,2}$ = 0.9 Hz, 1H, 1-OH), 5.74 (s, 1H, CH-acetal), 5.65 (s, 1H, CH-acetal), 5.38 (t, $J_{1,2} \approx J_{OH,1} \approx$ 3.8 Hz, 1H, H-1), 5.32 (d, $J_{1',2'}$ = 3.8 Hz, 1H, H-1′), 5.25 (dd, $J_{2,3}$ = 10.8 Hz, $J_{1,2}$ = 3.5 Hz, 1H, H-2), 5.14 (dd, $J_{2'',3''}$ = 9.8 Hz, $J_{1'',2''}$ = 8.0 Hz, 1H, H-2″), 4.83−4.73 (m, 3H, CH$_2$Ph, H-6a′), 4.70 (d, $J_{3,4}$ = 3.3 Hz, 1H, H-4), 4.61 (d, J = 11.8 Hz, 1H, CHHPh), 4.52−4.44 (m, 2H, CHHPh, CHHCl), 4.42 (dd, $J_{2,3}$ = 10.8 Hz, $J_{3,4}$ = 3.4 Hz, 1H, H-3), 4.39−4.24 (m, 5H, H-4′, H-4″, H-5′, H-6b′, CHHCl), 4.24−4.00 (m, 7H, H-6a, H-6b, H-6a′, H-6b′, H-3′, H-3″, H-5), 3.83 (dd, $J_{2',3'}$ = 10.1 Hz, $J_{1',2'}$ = 3.6 Hz, 1H, H-2′), 3.71 (br s, 1H, H-5″), 2.90−2.79 (m, 1H, CHH$_{Lev}$), 2.74−2.58 (m, 2H, 2 × CHH$_{Lev}$), 2.50−2.42 (m, 1H, CHH$_{Lev}$), 2.13 (s, 3H, COCH$_{3Lev}$), 1.73 (s, 3H, COCH$_{3Ac}$), 0.87 (s, 9H, C(CH$_3$)$_3$), 0.14, 0.09 (2 × s, 6H, 2 × CH$_3$Si); ^{13}C NMR (100 MHz, acetone-d_6) δ 207.1 (CO$_{Lev}$), 173.2 (COCH$_{2Lev}$), 170.1 (COCH$_{3Ac}$), 168.2 (COCH$_2$Cl), 140.3, 140.0, 139.9, 139.8 (4 × C-Ar), 129.4−127.1 (CH-Ar), 103.2 (C-1″), 101.41, 101.35 (2 × CH-acetal), 93.0 (C-1′), 91.5 (C-1), 78.2 (C-3′), 77.3, 77.2, 77.1 (C-2′, C-4′, C-4″), 73.6 (CH$_2$Ph), 72.7 (C-3″, C-4), 72.6 (C-2″), 72.5 (CH$_2$Ph), 70.3 (C-2), 70.0 (C-6*), 69.7 (C-6″*, C-5′), 68.6 (C-3), 67.2 (C-5″), 67.0 (C-6′), 63.2 (C-5), 41.9 (CH$_2$Cl), 38.3 (CH$_{2Lev}$), 30.4 (COCH$_{3Lev}$), 28.4 (CH$_{2Lev}$), 26.0 (C(CH$_3$)$_3$), 21.4 (COCH$_{3Ac}$), 18.6 (C(CH$_3$)$_3$), −4.4, −4.6 (2 × CH$_3$Si); HRMS (ESI-TOF) m/z [M + NH$_4$]$^+$ calcd for $C_{61}H_{79}ClNO_{20}Si$ 1208.4648, found 1208.4646. To a solution of the hemiacetal (299 mg, 251 μmol, 1.0 equiv) in acetone (3.0 mL) was added Cs$_2$CO$_3$ (91 mg, 280 μmol, 1.1 equiv) followed by PTFACl (104 mg, 502 μmol, 2.0 equiv). The mixture was stirred for 2 h at rt; then, the suspension was filtered and rinsed with acetone. The solvents were concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (PE/EtOAc 67:33 to 2:8 + 1% Et$_3$N) to give **18** (233 mg, 78%, ratio α/β = 4:1) as a white foam. ^{1}H NMR (400 MHz, acetone-d_6, partial) δ 7.57−6.90 (m, 25H, H-Ar), 5.71 (s, 1H, CH-acetal), 5.65 (s, 1H, CH-acetal), 5.42 (br d, $J_{2,3}$ = 9.2 Hz, 1H, H-2), 5.33 (d, $J_{1',2'}$ = 3.5 Hz, 1H, H-1′), 5.15 (dd, $J_{2'',3''}$ = 9.8 Hz, $J_{1'',2''}$ = 7.9 Hz, 1H, H-2″), 4.84−4.77 (m, 4H, H-1″, H-4, CH$_2$Ph), 4.67−4.51 (m, 3H, H-6a′, CH$_2$Ph), 4.48−4.02 (m, 14H, H-3, H-3′, H-3″, H-4′, H-4″, H-5, H-5′, H-6a, H-6b, H-6b′, H-6a″, H-6b″, CH$_2$Cl), 3.87 (dd, $J_{2',3'}$ = 10.1 Hz, $J_{1',2'}$ = 3.5 Hz, 1H, H-2′), 3.68 (br s, 1H, H-5″), 2.76−2.45 (m, 3H, CH$_{2Lev}$, CHH$_{Lev}$), 2.38 (ddd, J = 17.1, 6.6, 4.9 Hz, 1H, CHH$_{Lev}$), 2.13 (s, 3H, COCH$_{3Lev}$), 1.74 (s, 3H, COCH$_{3Ac}$), 0.87 (s, 9H, C(CH$_3$)$_3$), 0.15, 0.10 (2 × s, 6H, 2 × CH$_3$Si); ^{13}C NMR (100 MHz, acetone-d_6, partial) δ 207.1 (CO$_{Lev}$), 173.0 (COCH$_{2Lev}$), 170.1 (COCH$_{3Ac}$), 167.7 (COCH$_2$Cl), 140.2, 140.0, 139.9, 139.4, 140.3 (5 × C-Ar), 129.7−120.3 (CH-Ar), 103.2 (C-1″), 101.4, 101.3 (2 × CH-acetal), 94.6 (C-1′), 78.2 (C-3′), 77.3, 77.2 (C-2′, C-4′*), 76.8 (C-4″*), 73.4 (CH$_2$Ph), 73.0 (CH$_2$Ph), 72.78, 72.76 (C-3″, C-4), 72.6 (C-2″), 70.2 (C-3), 69.6 (C-6″), 69.4 (C-5′, C-6), 68.6 (C-2), 67.3 (C-5″), 66.4 (C-5), 66.2 (C-6′), 41.6 (CH$_2$Cl), 38.2 (CH$_{2Lev}$), 29.7 (COCH$_{3Lev}$), 28.4 (CH$_{2Lev}$), 26.0 (C(CH$_3$)$_3$), 21.4 (COCH$_{3Ac}$), 18.6 (C(CH$_3$)$_3$), −4.4, −4.6 (2 × CH$_3$Si); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{69}H_{79}ClF_3NNaO_{20}Si$ 1384.4498, found 1384.4513.

*Benzyl (2,4,5,7,8-Penta-O-acetyl-3-deoxy-β-D-manno-oct-2-ulopyranosid)onate (**15**).* Crystalline ammonium 3-deoxy-D-*manno*-oct-2-ulopyranosylonate (ammonium Kdo)[31] was synthesized according to the procedure recently reported by Kosma and co-workers. Ammonium Kdo (1.39 g, 5.45 mmol, 1.0 equiv) was suspended in anhydrous py (55 mL), and then Ac$_2$O (55 mL) followed by DMAP (6.6 mg, 54 μmol, 0.01 equiv) were added. The suspension was stirred for 16 h at rt under Ar after which time the solution was found to be homogeneous. The mixture was concentrated under reduced pressure, keeping the temperature below 50 °C, and coevaporated with toluene (3×). The residue was purified by silica gel flash chromatography (DCM/MeOH 1:0 to 6:4) to give ammonium 2,4,5,7,8-penta-*O*-acetyl-3-deoxy-D-*manno*-oct-2-ulopyranosylonate[33] (2.40 g, 95%, α/β mixture) as a yellow oil. To a solution of the latter compound (1.36 g, 2.92 mmol, 1.0 equiv) in anhydrous DMF (15 mL) was added BnBr (762 μL, 6.42 mmol, 2.2 equiv) followed by Cs$_2$CO$_3$ (380 mg, 1.17 mmol, 0.4 equiv). The mixture was stirred for 2 h at rt under Ar. The suspension was filtered over Celite, rinsed, and diluted with EtOAc (50 mL). The organic phase was washed with a saturated NH$_4$Cl (aq) solution (25 mL) and H$_2$O (25 mL). The aqueous phase was back extracted with EtOAc (25 mL). The combined organic layers were dried over MgSO$_4$, and the solvents were concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (PE/EtOAc 85:15 to 6:4) to give benzyl ester **15** (1.06 g, 67%, α/β

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mixture) as a white foam. The physical and analytical data of **15**[30] were in agreement with those published in the literature.

*Benzyl (Ethyl 4,5,7,8-Tetra-O-acetyl-3-deoxy-2-thio-β-D-manno-oct-2-ulopyranosid)onate (**6**).* To a solution of benzyl ester **15** (1.04 g, 1.93 mmol, 1.0 equiv) in anhydrous DCE (10 mL) was added EtSH (286 μL, 3.86 mmol, 2.0 equiv). The solution was cooled to 0 °C; then, $BF_3{\cdot}OEt_2$ (357 μL, 2.90 mmol, 1.5 equiv) was slowly added. The mixture was stirred for 2 h under Ar while gradually being warmed to rt. The solution was diluted with DCM, and a saturated $NaHCO_3$(aq) solution was added for neutralization. Then, iodine was added until a dark red color persisted. The excess iodine was reduced by washing the organic phase with a freshly prepared 10% $Na_2S_2O_3$(aq) solution until the red color disappeared. The solution was poured into a separatory funnel, and the aqueous layer was extracted with DCM. The pooled organic phases were dried over $MgSO_4$ and filtered, and the solvents were concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (PE/EtOAc 85:15 to 75:25) to give thioglycoside **6** (956 mg, 92%, ratio α/β = 1:7) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.32 (m, 5H, C*H*-Ar), 5.31−5.16 (m, 4H, H-5, H-7, CH_2Ph), 4.89 (ddd, $J_{3ax,4}$ = 12.5 Hz, $J_{3eq,4}$ = 4.7 Hz, $J_{4,5}$ = 3.0 Hz, 1H, H-4), 4.33−4.30 (m, 2H, H-8ab), 3.95 (dd, $J_{6,7}$ = 9.6 Hz, $J_{5,6}$ = 1.3 Hz, 1H, H-6), 2.75−2.66 (m, 1H, SC*H*H), 2.54 (dd, $J_{3eq,3ax}$ = 12.6 Hz, $J_{3eq,4}$ = 4.7 Hz, 1H, H-3eq), 2.48−2.39 (m, 1H, SC*H*H), 2.17 (t, $J_{3ax,3eq} \approx J_{3ax,4} \approx$ 12.6 Hz, 1H, H-3ax), 2.10, 2.09, 1.99, 1.98 (all s, 12H, 4 × COCH_3), 1.14 (t, J = 7.5 Hz, 3H, SCH$_2$CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.7, 169.9, 169.8 (4 × *C*OCH$_3$), 167.9 (C-1), 135.1 (C-Ar), 128.8, 128.8, 128.4 (*C*H-Ar), 84.3 (C-2), 72.1 (C-6), 68.0 (C-7), 67.9 (CH_2Ph), 67.3 (C-4), 64.1 (C-5), 62.6 (C-8), 32.6 (C-3), 23.4 (S*C*H$_2$), 20.9, 20.9, 20.9, 20.8 (4 × CO*C*H$_3$), 14.2 (SCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{25}H_{36}NO_{11}S$ 558.2004, found 558.2006; m/z [M + Na]$^+$ calcd for $C_{25}H_{32}NaO_{11}S$ 563.1558, found 563.1556.

*Benzyl [2-(5-Amino-N-benzyloxycarbonyl-1-pentyl) 4,5,7,8-Tetra-O-acetyl-3-deoxy-β-D-manno-oct-2-ulopyranosid]onate (**16β**) and Benzyl [2-(5-Amino-N-benzyloxycarbonyl-1-pentyl) 4,5,7,8-Tetra-O-acetyl-3-deoxy-α-D-manno-oct-2-ulopyranosid]onate (**16α**).* To a solution of donor **6** (1.14 g, 2.10 mmol, 1.0 equiv), acceptor **7** (998 mg, 4.21 mmol, 2.0 equiv), and NIS (946 mg, 4.21 mmol, 2.0 equiv) in anhydrous CH_3CN (35 mL) was added freshly activated 4 Å molecular sieves (4.5 g). The mixture was stirred for 45 min at rt under Ar. Then, the suspension was cooled to −10 °C; the flask was protected from light, and AgOTf (540 mg, 2.10 mmol, 1.0 equiv) was added. The mixture was stirred for 30 min at −10 °C under Ar. Et_3N (585 μL, 4.21 mmol, 2.0 equiv) was added to quench the reaction. The suspension was filtered over Celite and rinsed with DCM, and the solvents were concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (PE/EtOAc 8:2, then 7:3) to give β-anomer **16β** (1.17 g, 78%) along with α-anomer **16α** (236 mg, 16%), both as yellow oils. Analytical data for **16β**: $[\alpha]_D^{20}$ +14.6 (c 4.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.29 (m, 10H, C*H*-Ar), 5.27 (d, J = 11.6 Hz, 1H, C*H*HPh), 5.27−5.26 (m, 1H, H-5), 5.20−5.15 (m, 1H, H-7), 5.17 (d, J = 11.8 Hz, 1H, C*H*HPh), 5.10 (br s, 2H, CO_2CH_2Ph), 4.86 (ddd, $J_{3ax,4}$ = 13.2 Hz, $J_{3eq,4}$ = 4.6 Hz, $J_{4,5}$ = 3.0 Hz, 1H, H-4), 4.38 (dd, $J_{8a,8b}$ = 12.3 Hz, $J_{7,8a}$ = 2.5 Hz, 1H, H-8a), 4.31 (dd, $J_{8a,8b}$ = 12.3 Hz, $J_{7,8b}$ = 4.7 Hz, 1H, H-8b), 4.18 (dd, $J_{6,7}$ = 9.5 Hz, $J_{5,6}$ = 1.3 Hz, 1H, H-6), 3.70 (dt, $J_{1a,1b}$ = 12.7 Hz, $J_{1a,2a} \approx J_{1a,2b} \approx$ 6.3 Hz, 1H, H-1a$_{linker}$), 3.20−3.10 (m, 3H, H-1b$_{linker}$, H-5ab$_{linker}$), 2.39 (ddd, $J_{3ax,3eq}$ = 12.6 Hz, $J_{3eq,4}$ = 4.6 Hz, $^4J_{3eq,5}$ = 0.8 Hz, 1H, H-3eq), 2.09 (t, $J_{3ax,3eq} \approx J_{3ax,4} \approx$ 12.9 Hz, 1H, H-3ax), 2.09, 2.07, 2.00, 1.98 (4 × s, 12H, 4 × COCH_3), 1.53−1.39 (m, 4H, H-2ab$_{linker}$, H-4ab$_{linker}$), 1.31−1.20 (m, 2H, H-3ab$_{linker}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.5, 169.8, 169.8 (4 × $COCH_3$), 167.8 (C-1, $^3J_{1,3ax}$ = 6.2 Hz, $^3J_{1,CHHPh} \approx {}^3J_{1,CHHPh} \approx$ 3.2 Hz), 156.4 (CO_2CH_2Ph), 136.7, 134.9 (2 × C-Ar), 128.8−128.1 (*C*H-Ar), 99.4 (C-2), 70.7 (C-6), 68.1 (C-7), 67.6 (CH_2Ph), 67.0 (C-4), 66.6 (CO_2CH_2Ph), 64.4 (C-1$_{linker}$), 64.1 (C-5), 62.6 (C-8), 40.9 (C-5$_{linker}$), 32.5 (C-3), 29.5 (C-4$_{linker}$), 29.0 (C-2$_{linker}$), 23.0 (C-3$_{linker}$), 20.8, 20.7, 20.7, 20.7 (4 × $COCH_3$); HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{36}H_{46}NO_{14}$ 716.2913, found 716.2913; m/z [M + NH_4]$^+$ calcd for $C_{36}H_{49}N_2O_{14}$ 733.3178, found 733.3176; m/z [M + Na]$^+$ calcd for $C_{36}H_{45}NNaO_{14}$ 738.2732, found 738.2727. Analytical data for **16α**: $[\alpha]_D^{20}$ +37.8 (c 3.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.28 (m, 10H, H-Ar), 5.36 (br s, 1H, H-5), 5.33 (ddd, $J_{3ax,4}$ = 12.0 Hz, $J_{3eq,4}$ = 5.1 Hz, $J_{4,5}$ = 3.1 Hz, 1H, H-4), 5.28−5.17 (m, 3H, H-7, CH_2Ph), 5.09 (br s, 2H, CH_2Cbz), 4.90−4.84 (m, 1H, N*H*), 4.60 (dd, $J_{8a,8b}$ = 12.3 Hz, $J_{7,8a}$ = 2.4 Hz, 1H, H-8a), 4.14 (dd, $J_{8a,8b}$ = 12.3 Hz, $J_{7,8b}$ = 3.7 Hz, 1H, H-8b), 4.07 (br d, $J_{6,7}$ = 9.9 Hz, 1H, H-6), 3.44 (dt, $J_{1a,1b}$ = 9.1 Hz, $J_{1a,2a} \approx J_{1a,2b} \approx$ 6.1 Hz, 1H, H-1a$_{linker}$), 3.23−3.10 (m, 3H, H-1b$_{linker}$, H-5ab$_{linker}$), 2.19 (dd, $J_{3ax,3eq}$ = 12.9 Hz, $J_{3eq,4}$ = 5.0 Hz, 1H, H-3eq), 2.07 (s, 3H, COCH_3), 2.05 (t, $J_{3ax,3eq} \approx J_{3ax,4} \approx$ 12.9 Hz, 1H, H-3ax), 2.03, 1.99, 1.96 (all s, 9H, 3 × COCH_3), 1.56−1.40 (m, 4H, H-2ab$_{linker}$, H-4ab$_{linker}$), 1.34−1.24 (m, 2H, H-3ab$_{linker}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.4, 170.0, 169.7 (4 × $COCH_3$), 167.1 (C-1, $^3J_{1,CHHPh} \approx {}^3J_{1,CHHPh} \approx$ 3.5 Hz), 136.7, 135.1 (2 × C-Ar), 128.8−128.1 (*C*H-Ar), 98.8 (C-2), 68.2 (C-6), 67.7 (C-7), 67.4 (CH_2Ph), 66.6 (CH_2Cbz), 66.5 (C-4), 64.4 (C-5), 63.8 (C-1$_{linker}$), 62.1 (C-8), 40.9 (C-5$_{linker}$), 32.0 (C-3), 29.7, 29.0 (C-2$_{linker}$, C-4$_{linker}$), 23.3 (C-3$_{linker}$), 20.8, 20.75, 20.68, 20.68 (4 × $COCH_3$); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{36}H_{45}NNaO_{14}$ 738.2732, found 738.2746.

*Benzyl [2-(5-Amino-N-benzyloxycarbonyl-1-pentyl) 4-O-Benzyl-3-deoxy-7,8-O-isopropylidene-β-D-manno-oct-2-ulopyranosid]onate (**17**).* To a solution of peracetylated **16β** (25.5 mg, 35 μmol, 1.0 equiv) in THF/H_2O (1.75 mL, 4:1 v/v) was added NaOH (7.8 mg, 195 μmol, 5.6 equiv). The mixture was stirred for 1 h at rt; then, additional NaOH (7.1 mg, 178 μmol, 5.0 equiv) was added, and the mixture was stirred for 1.5 h at rt. The solution was diluted with EtOAc (25 mL), and the organic phase was washed with a 10% HCl(aq) solution (3 × 10 mL), a saturated $NaHCO_3$(aq) solution (25 mL), and brine (25 mL). The organic layer was dried over $MgSO_4$, and the solvents were concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (PE/EtOAc 6:4 then DCM/MeOH 9:1) to give a tetraol (12.6 mg, 66%) as a yellow oil. $[\alpha]_D^{20}$ −41.7 (c 0.60, MeOH/$CHCl_3$ 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.27 (m, 10H, H-Ar), 5.25 (d, J = 12.1 Hz, 1H, C*H*HPh), 5.12 (d, J = 12.1 Hz, 1H, C*H*HPh), 5.06 (br s, 2H, CH_2Cbz), 4.97−4.90 (m, 1H, N*H*), 4.11−3.91 (m, 2H, H-5, H-7), 3.82−3.76 (m, 2H, H-8a, H-8b), 3.66−3.57 (m, 2H, H-1a$_{linker}$, H-4), 3.47 (d, $J_{6,7}$ = 8.7 Hz, 1H, H-6), 3.14−3.03 (m, 3H, H-1b$_{linker}$, H-5ab$_{linker}$), 2.45 (dd, $J_{3ax,3eq}$ = 12.6 Hz, $J_{3eq,4}$ = 4.3 Hz, 1H, H-3eq), 1.94 (t, $J_{3ax,3eq} \approx J_{3ax,4} \approx$ 12.6 Hz, 1H, H-3ax), 1.44−1.32 (m, 4H, H-2ab$_{linker}$, H-4ab$_{linker}$), 1.26−1.11 (m, 2H, H-3ab$_{linker}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1 (C-1), 156.6 (NHCO), 136.7, 135.0 (2 × C-Ar), 128.9−128.2 (*C*H-Ar), 99.5 (C-2), 74.2 (C-6), 69.9 (C-7), 67.8 (CH_2Ph), 67.4 (C-4), 66.7 (CH_2Cbz), 66.0 (C-5), 64.4 (C-8), 64.1 (C-1$_{linker}$), 41.0 (C-5$_{linker}$), 35.1 (C-3), 29.6, 29.1 (C-2$_{linker}$, C-4$_{linker}$), 23.1 (C-3$_{linker}$); HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{28}H_{38}NO_{10}$ 548.2490, found 548.2497; m/z [M + Na]$^+$ calcd for $C_{28}H_{37}NNaO_{10}$ 570.2310, found 570.2322. To a solution of the tetraol (192 mg, 351 μmol, 1.0 equiv) in anhydrous DMF (3.5 mL) and 1,4-dioxane (1.7 mL) was added 2-methoxypropene (67 μL, 694 μmol, 2.0 equiv) followed by PTSA (13 mg, 68 μmol, 0.2 equiv). The mixture was stirred for 23 h at rt under Ar. Then, the reaction was neutralized by adding Et_3N (250 μL); the solvents were concentrated under reduced pressure and coevaporated with toluene (3×). The residue was purified by silica gel flash chromatography (DCM/MeOH 97:3) to give a diol (168 mg, 82%) as a colorless oil. $[\alpha]_D^{20}$ +31.2 (c 3.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.29 (m, 10H, H-Ar), 5.27 (d, J = 12.0 Hz, 1H, C*H*HPh), 5.15 (d, J = 12.1 Hz, 1H, C*H*HPh), 5.09 (br s, 2H, CH_2Cbz), 4.77 (t, $J_{NH,5a} \approx J_{NH,5b} \approx$ 5.3 Hz, 1H, N*H*), 4.30 (ddd, $J_{6,7}$ = 8.2 Hz, $J_{7,8a}$ = 6.1 Hz, $J_{7,8b}$ = 5.0 Hz, 1H, H-7), 4.11 (dd, $J_{8a,8b}$ = 8.6 Hz, $J_{7,8a}$ = 6.3 Hz, 1H, H-8a), 4.05 (dd, $J_{8a,8b}$ = 8.6 Hz, $J_{7,8b}$ = 4.9 Hz, 1H, H-8b), 3.90 (br d, J = 1.9 Hz, 1H, H-5), 3.68 (dt, $J_{1a,1b}$ = 9.2 Hz, $J_{1a,2a} \approx J_{1a,2b} \approx$ 6.5 Hz, 1H, H-1a$_{linker}$), 3.62 (ddd, $J_{3ax,4}$ = 12.1 Hz, $J_{3eq,4}$ = 4.7 Hz, J = 3.4 Hz, 1H, H-4), 3.49 (dd, $J_{6,7}$ = 8.3 Hz, $J_{5,6}$ = 1.0 Hz, 1H, H-6), 3.21 (dt, $J_{1a,1b}$ = 9.2 Hz, $J_{1b,2a} \approx J_{1b,2b} \approx$ 6.5 Hz, 1H, H-1b$_{linker}$), 3.17−3.09 (m, 2H, H-5ab$_{linker}$), 2.47 (dd, $J_{3ax,3eq}$ = 12.7 Hz, $J_{3eq,4}$ = 4.7 Hz, 1H, H-3eq), 1.90 (t, $J_{3ax,3eq} \approx J_{3ax,4} \approx$ 12.6 Hz, 1H, H-3ax), 1.52−1.38 (m, 4H, H-2ab$_{linker}$, H-4ab$_{linker}$), 1.36, 1.36 (2 × s, 6H, 2 × CH_3), 1.31−1.22 (m, 2H, H-3ab$_{linker}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5 (C-1), 156.5 (NHCO), 136.7, 135.2 (2 × C-

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Ar), 128.9−128.2 (*C*H-Ar), 109.7 ($C(CH_3)_2$), 99.5 (C-2), 75.8 (C-6), 73.5 (C-7), 67.6, 67.5 (CH_2Ph, C-8), 67.2 (C-4), 66.8 (CH_2Ph), 66.5 (C-5), 64.0 (C-1_{linker}), 41.1 (C-5_{linker}), 35.5 (C-3), 29.5, 29.1 (C-2_{linker}, C-4_{linker}), 26.9, 25.3 (2 × CH_3), 23.1 (C-3_{linker}); HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{31}H_{41}NNaO_{10}$ 610.2623, found 610.2612. To a solution of the diol (159 mg, 271 μmol, 1.0 equiv) in MeOH (4.0 mL) was added Bu_2SnO (74 mg, 298 μmol, 1.1 equiv). The mixture was refluxed for 4 h under Ar. Then, the solvents were concentrated under reduced pressure and coevaporated with toluene (3×). The residue was dissolved in anhydrous DMF (3.0 mL). BnBr (35 μL, 298 μmol, 1.1 equiv), TBAI (110 mg, 298 μmol, 1.1 equiv), and CsF (45 mg, 298 μmol, 1.1 equiv) were added successively, and the mixture was stirred overnight at 40 °C under Ar. The solution was cooled to 0 °C, filtered over Celite, and rinsed with EtOAc. The solvents were concentrated under reduced pressure and coevaporated with toluene (3×). The residue was purified by silica gel flash chromatography (PE/EtOAc 7:3 to 6:4) to give alcohol **17** (133 mg, 73%) as a colorless oil. $[\alpha]_D^{20}$ +21.6 (*c* 2.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.27 (m, 15H, H-Ar), 5.22 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 5.14 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 5.09 (br s, 2H, CH_2Cbz), 4.76 (t, $J_{NH,5a} \approx J_{NH,5b} \approx 5.1$ Hz, 1H, N*H*), 4.54 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.51 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.37 (ddd, $J_{6,7}$ = 8.4 Hz, $J_{7,8a}$ = 6.2 Hz, $J_{7,8b}$ = 5.2 Hz, 1H, H-7), 4.11 (dd, $J_{8a,8b}$ = 8.6 Hz, $J_{7,8a}$ = 6.3 Hz, 1H, H-8a), 4.04 (dd, $J_{8a,8b}$ = 8.6 Hz, $J_{7,8b}$ = 5.2 Hz, 1H, H-8b), 4.03−4.01 (m, 1H, H-5), 3.68 (dt, $J_{1a,1b}$ = 9.2 Hz, $J_{1a,2a} \approx J_{1a,2b} \approx$ 6.4 Hz, 1H, H-1a$_{linker}$), 3.46−3.42 (m, 1H, H-6), 3.41 (ddd, $J_{3ax,4}$ = 12.4 Hz, $J_{3eq,4}$ = 4.6 Hz, $J_{4,5}$ = 2.9 Hz, 1H, H-4), 3.24 (dt, $J_{1a,1b}$ = 9.2 Hz, $J_{1b,2a} \approx J_{1b,2b} \approx$ 6.6 Hz, 1H, H-1b$_{linker}$), 3.17−3.11 (m, 2H, H-5ab$_{linker}$), 2.50 (dd, $J_{3eq,3ax}$ = 12.6 Hz, $J_{3eq,4}$ = 4.6 Hz, 1H, H-3eq), 2.27 (br s, 1H, 5-O*H*), 2.03 (t, $J_{3ax,3eq} \approx J_{3ax,4} \approx$ 12.4 Hz, 1H, H-3ax), 1.51−1.39 (m, 4H, H-2ab$_{linker}$, H-4ab$_{linker}$), 1.37 (br s, 6H, 2 × CH_3), 1.32−1.21 (m, 2H, H-3ab$_{linker}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6 (C-1), 156.5 (NHCO), 137.6, 136.8, 135.3 (3 × C-Ar), 128.8−127.8 (*C*H-Ar), 109.5 ($C(CH_3)_2$), 99.5 (C-2), 75.8 (C-6), 74.1 (C-4), 73.3 (C-7), 70.3 (CH_2Ph), 67.5 (C-8), 67.4 (CH_2Ph), 66.7 (CH_2Cbz), 64.0 (C-5), 63.9 (C-1$_{linker}$), 41.1 (C-5$_{linker}$), 32.4 (C-3), 29.6, 29.2 (C-2_{linker}, C-4_{linker}), 26.9, 25.3 (2 × CH_3), 23.2 (C-3$_{linker}$); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{38}H_{48}NO_{10}$ 678.3273, found 678.3271; *m*/*z* $[M + Na]^+$ calcd for $C_{38}H_{47}NNaO_{10}$ 700.3092, found 700.3091.

*2-O-Acetyl-4,6-O-benzylidene-3-O-tert-butyldimethylsilyl-β-D-galactopyranosyl-(1→4)-2,3-di-O-benzyl-6-O-chloroacetyl-α-D-galactopyranosyl-(1→3)-4,6-O-benzylidene-2-O-levulinoyl-β-D-galactopyranosyl-(1→5)-benzyl [2-(5-Amino-N-benzyloxycarbonyl-1-pentyl) 4-O-Benzyl-3-deoxy-7,8-O-isopropylidene-β-D-manno-oct-2-ulopyranosid]onate (**2**).* To a solution of crude acceptor **17** (25.5 mg, 38 μmol, 1.0 equiv) and donor **18** (61.4 mg, 45 μmol, 1.2 equiv) dissolved in anhydrous DCE (750 μL) was added freshly activated 4 Å molecular sieves (100 mg). The suspension was stirred for 1 h at rt under Ar. The solution was cooled to −10 °C; then, TMSOTf (2.0 μL, 11 μmol, 0.3 equiv) was added, keeping rigorous anhydrous conditions. The mixture was stirred at −10 °C for 30 min under Ar and then quenched with Et_3N (50 μL, 10 equiv). The mixture was filtered over Celite and rinsed with DCM, and the solvents were concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (PE/acetone 95:5 to 63:27) to give tetrasaccharide **2** (31 mg, 45%) as a white amorphous powder. $[\alpha]_D^{20}$ −112 (*c* 0.13, $CHCl_3$); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.56−7.07 (m, 35H, H-Ar), 6.31 (t, $J_{NH,5a} \approx J_{NH,5b} \approx$ 4.9 Hz, 1H, N*H*), 5.75 (s, 1H, C*H*-acetal), 5.65 (s, 1H, C*H*-acetal), 5.33 (dd, $J_{2,3}$ = 10.3 Hz, $J_{1,2}$ = 7.9 Hz, 1H, H-2), 5.31 (s, 1H, H-1′), 5.21 (d, *J* = 12.3 Hz, 1H, C*H*HPh), 5.16 (d, *J* = 12.5 Hz, 1H, C*H*HPh), 5.14 (dd, $J_{2'',3''}$ = 9.0 Hz, $J_{1'',2''}$ = 8.0 Hz, 1H, H-2″), 5.04 (br s, 2H, CH_2Cbz), 4.93 (d, $J_{1,2}$ = 7.9 Hz, 1H, H-1), 4.81 (d, $J_{1'',2''}$ = 7.9 Hz, 1H, H-1″), 4.79 (d, *J* = 11.6 Hz, 1H, C*H*HPh), 4.74 (d, *J* = 11.6 Hz, 1H, C*H*HPh), 4.67 (d, *J* = 12.6 Hz, 1H, C*H*HPh), 4.64−4.56 (m, 4H, 2 × C*H*HPh, H-4, H-6a′), 4.51−4.42 (m, 3H, H-7$_{Kdo}$, C*H*HPh, H-4′), 4.38−4.14 (m, 11H, H-6b′, H-5′, H-4″, H-6a, H-6a″, H-5$_{Kdo}$, H-8a$_{Kdo}$, CH_2Cl, H-6b, H-6b″), 4.14−4.02 (m, 4H, H-8b$_{Kdo}$, H-3, H-3′, H-3″), 3.82 (dd, $J_{2',3'}$ = 10.2 Hz, $J_{1',2'}$ = 3.5 Hz, 1H, H-2′), 3.72−3.66 (m, 3H, H-5*, H-6$_{Kdo}$, H-1a$_{linker}$), 3.62 (br s, 1H, H-5″*), 3.56 (ddd, $J_{3ax,4}$ = 12.4 Hz, $J_{3eq,4}$ = 3.9 Hz, $J_{4,5}$ = 2.1 Hz, 1H, H-4$_{Kdo}$), 3.36 (dt, $J_{1a,1b}$ = 9.4 Hz, $J_{1b,2a} \approx J_{1b,2b} \approx$ 6.5 Hz, 1H, H-1b$_{linker}$), 3.17−3.10 (m, 2H, H-5ab$_{linker}$), 2.93−2.86 (m, 1H, C*H*H$_{Lev}$), 2.68−2.54 (m, 2H, 2 × C*H*H$_{Lev}$), 2.44−2.36 (m, 2H, C*H*H$_{Lev}$, H-3eq$_{Kdo}$), 2.09 (s, 3H, CH_{3Lev}), 2.03 (t, $J_{3ax,3eq} \approx J_{3ax,4} \approx$ 12.2 Hz, 1H, H-3ax$_{Kdo}$), 1.70 (s, 3H, CH_{3Ac}), 1.53−1.44 (m, 4H, H-2ab$_{linker}$, H-4ab$_{linker}$), 1.37−1.29 (m, 2H, H-3ab$_{linker}$), 1.30 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 0.87 (s, 9H, $C(CH_3)_3$), 0.14 (s, 3H, $SiCH_3$), 0.09 (s, 3H, $SiCH_3$); ^{13}C NMR (100 MHz, acetone-d_6) δ 207.56 (CO_{Lev}), 172.3 ($COCH_{2Lev}$), 170.1 ($COCH_{3Ac}$), 169.4 (C-1$_{Kdo}$), 167.6 ($COCH_2Cl$), 157.1 (NHCO), 140.4, 140.1, 139.9, 139.7, 139.5, 138.6, 136.8 (7 × C-Ar), 129.4−127.1 (*C*H-Ar), 108.9 ($C(CH_3)_2$), 103.3 (C-1″), 102.0 (C-1), 101.8, 101.3 (2 × *C*H-acetal), 100.4 (C-2$_{Kdo}$), 93.8 (C-1′), 78.0 (C-3′), 77.3 (C-4″), 77.1 (C-2′), 77.0 (C-4′), 76.6 (C-6$_{Kdo}$), 76.1 (C-4$_{Kdo}$), 75.8 (C-7$_{Kdo}$), 73.5 (CH_2Ph), 73.0, 72.7 (C-3, C-3′), 72.5 (C-2″), 72.3 (CH_2Ph), 71.9 (C-4, C-5$_{Kdo}$), 71.2 (C-2), 71.1 (CH_2Ph), 69.8, 69.7 (C-6, C-6″), 69.2 (C-5′), 67.5 (CH_2Ph), 67.3, 67.2 (C-5, C-5″), 66.7 (C-8$_{Kdo}$), 66.6 (C-6′), 66.3 (CH_2Cbz), 64.3 (C-1$_{linker}$), 41.7 (CH_2Cl), 41.5 (C-5$_{linker}$), 38.2 (CH_{2Lev}), 33.1 (C-3$_{Kdo}$), 30.4, 30.3 (C-2_{linker}, C-4_{linker}), 30.0 ($COCH_{3Lev}$), 28.6 (CH_{2Lev}), 27.0 (CH_3), 26.0 ($C(CH_3)_3$), 25.8 (CH_3), 23.9 (C-3$_{linker}$), 21.4 (CH_{3Ac}), 18.6 ($C(CH_3)_3$), −4.43, −4.57 (2 × CH_3Si); HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{99}H_{120}ClNNaO_{29}Si$ 1872.7296, found 1872.7325.

*β-D-Galactopyranosyl-(1→4)-α-D-galactopyranosyl-(1→3)-β-D-galactopyranosyl-(1→5)-[2-(5-amino-1-pentyl) 3-Deoxy-β-D-manno-oct-2-ulopyranosid]onate (**1**).* To a solution of tetrasaccharide **2** (23.0 mg, 12.4 μmol, 1.0 equiv) in anhydrous MeOH/py (1.2 mL, 1:1 v/v) was added thiourea (19 mg, 248 μmol, 20 equiv). The mixture was stirred at 60 °C for 3.5 h under Ar. Then, the solvents were concentrated under reduced pressure, and the residue was dissolved with EtOAc (60 mL). The organic phase was washed with a 10% HCl(aq) solution (25 mL), a saturated $NaHCO_3$(aq) solution (25 mL), and brine (25 mL). The organic phase was dried over $MgSO_4$, and the solvents were concentrated under reduced pressure. HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{97}H_{119}NNaO_{28}Si$ 1796.7580, found 1796.7630. The residue was dissolved in anhydrous DCM/MeOH (1.55 mL, 4:1 v/v), and hydrazine acetate (2.3 mg, 25 μmol, 2.0 equiv) was added. The mixture was stirred overnight at rt under Ar; the solvents were concentrated under reduced pressure and coevaporated with toluene (3×). HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{92}H_{113}NNaO_{26}Si$ 1698.7212, found 1698.7205. The residue was dissolved in anhydrous THF (1.24 mL), and TREAT-HF (102 μL, 620 μmol, 50 equiv) was added. The mixture was refluxed for 16 h under Ar; then, the solution was cooled to rt and diluted with EtOAc (30 mL). The organic phase was washed with a saturated $NaHCO_3$(aq) solution (2 × 10 mL) and brine (10 mL). The organic layer was dried over $MgSO_4$, and the solvents were concentrated under reduced pressure. HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{86}H_{99}NNaO_{26}$ 1584.6348, found 1584.6399. The residue was dissolved in AcOH/H_2O (1.63 mL, 4:1 v/v), and the mixture was stirred for 5 h from 0 °C to rt. Then, the solvents were concentrated under reduced pressure, and the residue was purified by silica gel flash chromatography (DCM/MeOH 1:0 to 98:2) to give a pentaol (9.3 mg, 49%, four steps from **2**) as a white amorphous powder. HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{83}H_{95}NNaO_{26}$ 1544.6035, found 1544.6009. A solution of the pentaol (9.3 mg, 6.1 μmol, 1.0 equiv) in MeOH/H_2O (7.4 mL, 5:1 v/v) containing concentrated HCl (1.0 μL, 12 μmol, 2.0 equiv) was passed through a 20% $Pd(OH)_2$/C cartridge (CatCart30) using a H-Cube continuous flow hydrogenation system in the control mode (10 bar). The temperature was set at 45 °C, and the flow rate was fixed at 1.0 mL min^{-1}. After one run, the cartridge was rinsed with MeOH/H_2O (5:1 v/v). The solutions were concentrated under reduced pressure, keeping the bath temperature below 40 °C. The residue was subjected to C_{18} reversed-phase flash chromatography (H_2O/MeOH 10:0 to 9:1) followed by freeze-drying to give tetrasaccharide **1** (3.3 mg, 67%) as a white amorphous solid. ^{1}H NMR (600 MHz, D_2O) δ 5.15 (d, $J_{1,2}$ = 3.3 Hz, 1H, H-1′), 4.67 (d, $J_{1,2}$ = 7.5 Hz, 1H, H-1), 4.60 (d, $J_{1,2}$ = 7.6 Hz, 1H, H-1″), 4.30−4.24 (m, 2H), 4.17−4.14 (m, 2H), 4.10−4.04 (m, 2H), 3.98−3.57 (m, 19H), 3.42 (dd, *J* = 16.2, 7.3 Hz, 1H, H-1b$_{linker}$), 3.00 (dd, *J* = 13.7, 6.3 Hz, 2H, H-5ab$_{linker}$), 2.47 (dd, $J_{3eq,3ax}$ = 12.1 Hz, $J_{3eq,4}$ = 4.5 Hz, 1H, H-

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3eq$_{Kdo}$), 1.87 (t, $J_{3eq,3ax} \approx J_{3ax,4} \approx$ 12.1 Hz, 1H, H-3ax$_{Kdo}$), 1.72−1.63 (m, 2H, H-4ab$_{linker}$), 1.62−1.56 (m, 2H, H-2ab$_{linker}$), 1.45−1.38 (m, 2H, H-3ab$_{linker}$); ^{13}C NMR (150 MHz, D_2O) δ 174.4 (C-1$_{Kdo}$), 105.3 (C-1″), 105.0 (C-1′), 102.2 (C-2$_{Kdo}$), 96.5 (C-1), 79.1, 78.4, 76.0, 75.7, 75.5, 74.1, 73.7, 72.3, 70.8, 70.6, 69.9, 69.5, 69.4, 68.6, 65.8, 65.2 (C-1$_{linker}$), 64.6, 62.2, 61.8, 61.3, 40.2 (C-5$_{linker}$), 36.7 (C-3$_{Kdo}$), 29.0 (C-4$_{linker}$), 27.1 (C-2$_{linker}$), 22.9 (C-3$_{linker}$); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{31}H_{55}NNaO_{23}$ 832.3057, found 832.3069.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01823.

NMR spectra for new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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