JOC The Journal of Organic Chemistry

FEATURED ARTICLE

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Stereoselective Synthesis of 2,3-Diamino-2,3-dideoxy-β-D-mannopyranosyl Uronates

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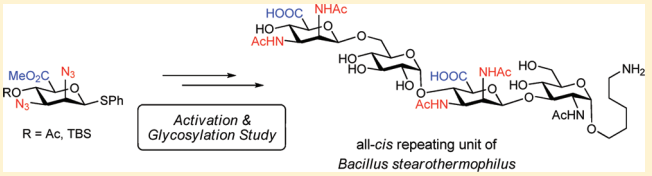
Supporting Information

ABSTRACT: With the aim to find an efficient synthetic procedure for the construction of 2,3-diamino-2,3-dideoxy-β-D-mannuronic acids, we evaluated three mannosyl donors: (*S*)-phenyl 4,6-di-*O*-acetyl-2,3-diazido mannopyranoside, (*S*)-phenyl 2,3-diazido-4,6-*O*-benzylidene mannopyranoside, and (*S*)-phenyl 2,3-diazido mannopyranosyl methyl uronate. The first two mannosylating agents are rather unselective or slightly α-selective in their condensation with three different acceptors. The mannuronic acid donor on the other hand reliably provides the desired β-mannosidic linkage. A mechanistic rationale is put forward to account for the different behavior of the three donor types. Suitably protected 2,3-diazido mannuronic acids were employed to construct the all-*cis*-linked tetrasaccharide repeating unit of the capsular polysaccharide of *Bacillus stearothermophilus*, featuring two 2,3-diacetamido-2,3-dideoxy-β-D-mannuronic acids.



INTRODUCTION

Functional groups on a glycosyl donor play a decisive role on the stereochemical course of its glycosylation reactions. In our studies toward the synthesis of anionic (bacterial) oligosaccharides, we have recently disclosed that glycosylations of mannuronic acid ester donors, that is, mannopyranosides of which the C-6 is oxidized to a carboxylic acid ester, such as **1** (Figure 1), proceed with a very high degree of β-selectivity.[1] Initially, we postulated that the observed β-selectivity was the result of the S_N2-like reaction of an intermediate α-triflate (**2**), in line with the seminal work of Crich and co-workers on 4,6-*O*-benzylidene directed β-mannosylations.[2] We reasoned that the C-5 carboxylic ester is sufficiently electron-withdrawing to stabilize the anomeric triflate with respect to the oxacarbenium−triflate ion pair to allow for a β-selective displacement reaction. However, we were at that time unable to spectroscopically detect a single anomeric triflate species. Examination of the activation of a series of 2-azido-2-deoxy mannuronic acid ester donors, including thiomannoside **3**, revealed that an anomeric triflate was formed from these donors and that it exists as a mixture of $^4C_1$ and $^1C_4$ conformers, **4a** and **4b**, respectively, in which the latter species, having an equatorially positioned triflate, surprisingly prevailed.[3] Although these studies showed the intermediacy of an anomeric triflate species, the fact that this triflate species prefers to adopt an "inverted" chair conformation lends support to an alternative mechanistic rationale for the β-selectivity which invokes the $^3H_4$ mannuronic acid ester oxacarbenium ion **5** as the product forming intermediate (Figure 1).[4] In line with the detailed studies of Woerpel and co-workers on the stereochemical alkylation of oxacarbenium ions,[5] this intermediate is preferentially attacked by an incoming nucleophile from the β-face,

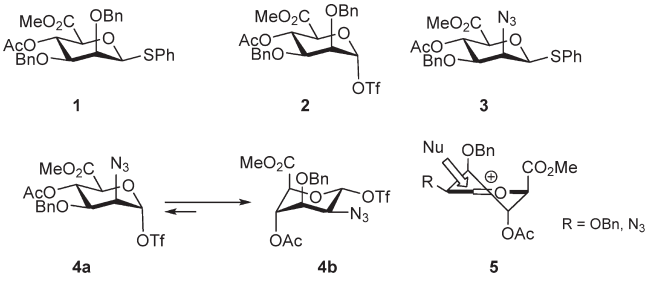


Figure 1. Mannopyranosyl uronic esters studied previously.

explaining the observed β-selectivity. It was reasoned that the C-5 carboxylate was at the basis of this unusual conformational behavior. It also became apparent in our studies of the C-2 azido mannuronic acid series that the introduction of the C-2 azide functionality in **3** did not significantly alter the β-selectivity of the glycosylation reaction with respect to the glycosylations of its C-2 benzyloxy counterpart **1**.[3b] Notably, this contrasts with the 4,6-*O*-benzylidene β-mannosylation system in which the selectivity has been shown to be sensitive to the nature of the C-2 substituent.[6] Work from our laboratory has revealed that condensations involving 2-azido-2-deoxy-4,6-*O*-benzylidene mannosyl donors proceed somewhat less β-selective than couplings with its C-2-*O*-benzyl counterpart.[7] To further investigate the influence of different substitution patterns on glycosylation with mannosyl and mannuronic acid ester donors, we here report the results

Received: June 7, 2011
Published: July 27, 2011

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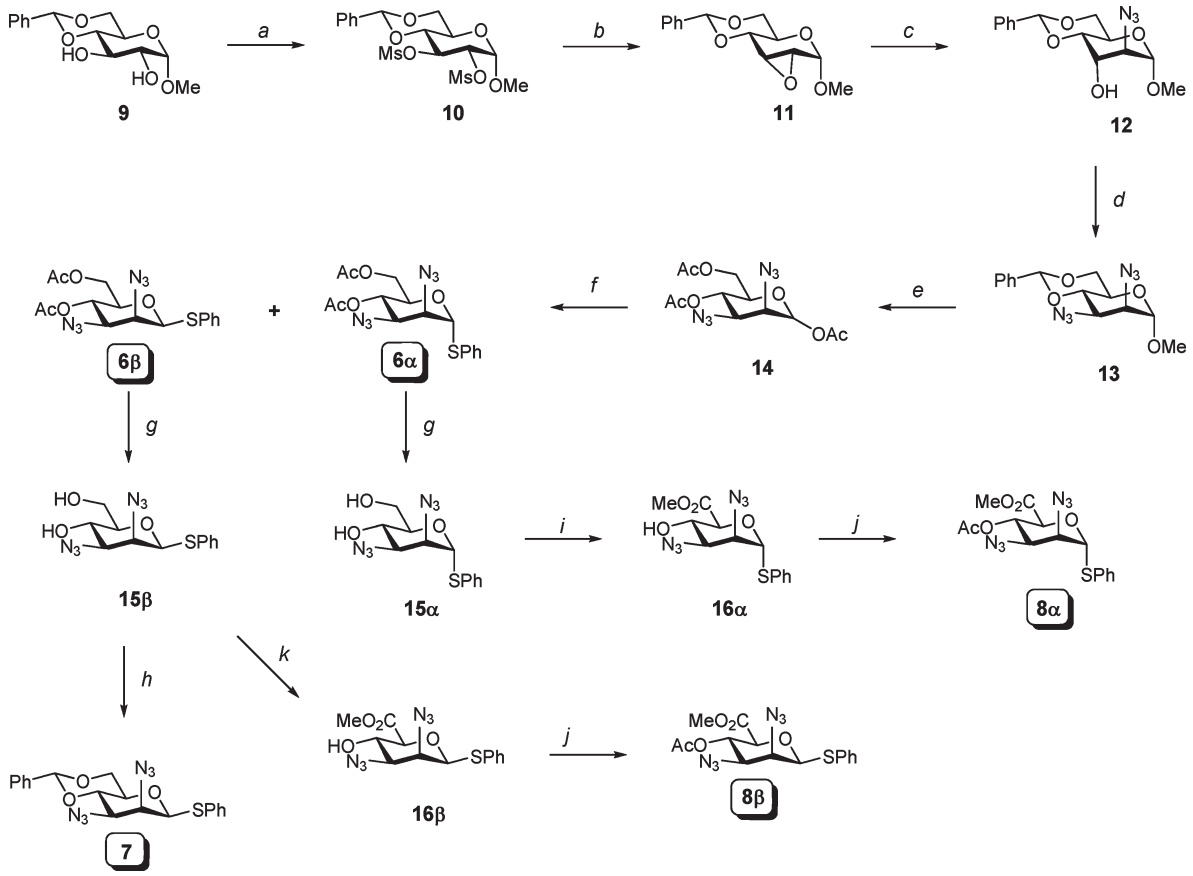
of our study of 2,3-diazido-2,3-dideoxy mannopyranosyl[8] and mannopyranosyl uronate donors. 2,3-Diacetamido-dideoxy mannopyranosyl uronates are found in various bacterial capsular polysaccharides,[9] in which they are usually linked in a 1,2-*cis* fashion to the next sugar residue. An efficient route of synthesis toward these rare bacterial carbohydrates can help to elucide their role in biology and immunology. We also report the stereoselective assembly of the tetrasaccharide repeating unit of the capsular polysaccharide of *Bacillus stearothermophilus*, containing two 2,3-diacetamido-2,3-dideoxy-β-mannopyranosyl uronates (**47**, Scheme 2).[10]

RESULTS AND DISCUSSION

We investigated three types of 2,3-diazido mannosyl donors, the 4,6-di-*O*-acetyl mannosides **6α** and **6*β***, the 4,6-*O*-benzylidene mannoside **7**, and the mannuronic acid esters **8α** and **8*β*** (Scheme 1). The first two donors were selected because we previously reported that the installment of electron-withdrawing groups such as an *O*-acetate on C-4 and C-6 of a 2-azido mannosyl donor also provides β-selective condensation reactions, depending on the nature of the acceptor used.[11] More recently, Kim and co-workers reported on the stereodirecting effect of electron-withdrawing groups at C-3, C-4, and C-6 in mannosylations.[12] Donors **6**, **7**, and **8** were synthesized as depicted in Scheme 1. Key intermediate **13** was obtained following an adaptation of the procedure described by Guthrie and Murphy.[13] Starting from 4,6-*O*-benzylidene-protected methyl glucoside **9**,[14] double methanesulfonylation toward compound **10** and subsequent epoxidation using potassium hydroxide in THF/MeOH resulted in crystalline compound **11** in 62% over two steps. Selective *trans*-diaxial opening of the epoxide with sodium azide in DMF at reflux temperature gave 2-azido-2-deoxy-altropyranoside **12** in 93%.

Subsequent triflation of C-3-OH and S_N2 substitution with NaN_3 in DMF at 80 °C resulted in diazido-containing mannopyranoside **13** via inversion of configuration at C-3.[15] In one step, the benzylidene and anomeric methyl function were hydrolyzed with concomitant acetylation of the liberated alcohols to afford compound **14** as an anomeric mixture (α/β = 5:1). Treatment of compound **14** with PhSH and $BF_3\cdot Et_2O$ in DCE at 50 °C resulted in α-thio donor **6α** (24%) and β-thio donor **6*β*** (58%), which were readily separated. Subsequent deacetylation under Zemplén conditions gave diols **15α/*β***. Crystalline benzylidene donor **7** was obtained from diol **15*β*** using benzaldehyde dimethylacetal and a catalytic amount of *p*-TsOH in 69% yield. To obtain the mannuronic acid donors **8α/*β***, diols **15α/*β*** were subjected to regio- and chemoselective oxidation at C-6 using the TEMPO/BAIB reagent combination.[16,17] From diol **15α**, compound **16α** was obtained in 76% yield after oxidation and ensuing methylation. Under similar conditions, diol **15*β*** was

Scheme 1. Synthesis of Donors 6−8[a]



[a] Reagents and conditions: (a) MsCl, pyridine; (b) KOH, THF/MeOH (**11**, 62% over two steps); (c) NaN_3, NH_4Cl, DMSO, 80 °C (**12**, 93%); (d) (*i*) Tf_2O, pyridine; (*ii*) NaN_3, NH_4Cl, DMF, 80 °C (**13**, 75%); (e) H_2SO_4, Ac_2O (**14**, 98%); (f) PhSH, $BF_3\cdot Et_2O$, DCE, 50 °C (**6α**, 24%; **6*β***, 58%); (g) NaOMe, MeOH (**15α**, 100%; **15*β***, 98%); (h) $PhCH(OMe)_2$, *p*-TsOH, MeCN (**7**, 69%); (i) (*i*) TEMPO, BAIB, DCM/H_2O; (*ii*) MeI, K_2CO_3, DMF (**16α**, 76%); (j) Ac_2O, pyridine (**8α**, 91%; **8*β***, 100%); (k) (*i*) TEMPO, BAIB, EtOAc/H_2O; (*ii*) MeI, K_2CO_3, DMF (**16*β***, 91%).

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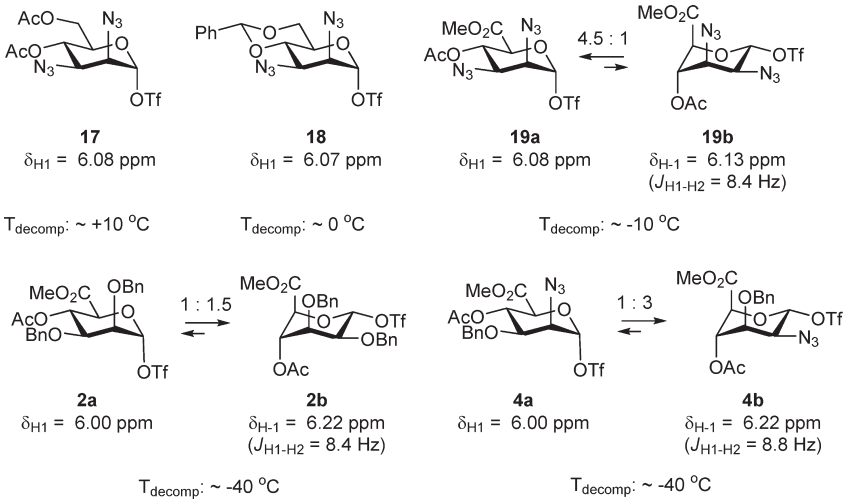


Figure 2. Overview of mannopyranosyl triflates.

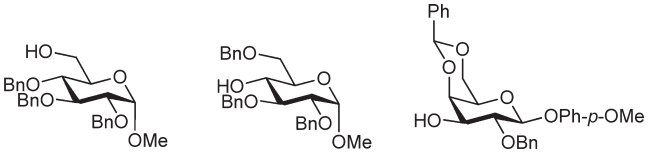
transformed into **16*β*** in a somewhat lower yield (50%). Changing the organic solvent of the biphasic oxidation mixture from dichloromethane to ethyl acetate, in which the crystalline **15*β*** proved to be more soluble, led to an increased yield (91%) of compound **16*β***. Methyl mannuronates **16α** and **16*β*** were acetylated using Ac_2O in pyridine to give donors **8α** and **8*β***.

With the five donors, **6α**/**6*β***, **7**, and **8α**/**8*β***, in hand, we first investigated their activation in low-temperature NMR experiments. Upon treatment of diacyl donor **6*β*** with Ph_2SO and Tf_2O[18,19] in DCM-d_2 at −80 °C, α-triflate **17** was rapidly formed (see Figure 2). This species proved to be stable to +10 °C. α-Configured donor **6α** provided the same triflate but required a higher temperature for complete activation (−40 °C). Using the same activator system,[20] benzylidene donor **7** was rapidly transformed at −80 °C into α-triflate **18**, which was stable up to 0 °C. Similarly, *β*-diazido mannuronic acid donor **8*β*** was completely transformed into the corresponding anomeric triflate **19** at −80 °C. In analogy to the monoazido mannuronic acid triflate **4**, this species exists as a mixture of $^4C_1$ and $^1C_4$ conformers ($^4C_1/^1C_4 \sim 4.5{:}1$). Decomposition of this triflate started around −10 °C, making this species the least stable of the three diazido mannosidic triflates, in contrast to what could be expected based on the electron-withdrawing capacity of the different functional groups. The result is in line, however, with the relatively low decomposition temperatures for mannuronic acid triflates **2** and **4**, as depicted in Figure 2.[3] From the decomposition temperatures of the three different mannuronates, **2**, **4**, and **19**, it is clear that the extra C-3 azide group in **19** has a stabilizing effect, as expected on the basis of its electron-withdrawing capacity (*F* value ∼0.48).[21] The last donor in the series, α-mannuronic acid **8α**, required a significantly higher temperature (−10 °C) for complete activation than its *β*-configured counterpart. As in the case of the monoazido mannuronic acid **3**, the temperature required for complete activation of the α-isomer **8α** matched the decomposition temperature of the anomeric triflate.

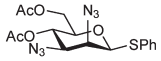
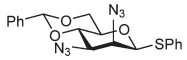
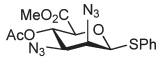
Next, *β*-thio donors **6*β***, **7**, and **8*β*** were surveyed in a set of glycosylation reactions with primary acceptor **20** and secondary acceptors **21** and **22**. To this end, the donors were preactivated (Ph_2SO−Tf_2O) for 20 min at −80 °C before the addition of the acceptor alcohols and warming to 0 °C. The results of the condensations are summarized in Table 1. As can be seen from entries 1−3, the condensations with diacetyl diazido mannoside **6*β*** proceeded with very little selectivity. Entries 4−6 show that the benzylidene donor **7** is moderately α-selective. Clearly, these results oppose the results obtained with 2,3-di-*O*-benzyl benzylidene mannose.[2] As described above, we have previously studied 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene mannosyl donors and found them to be moderately *β*-selective. More recently, Crich and co-workers have reported on the condensations of an α-(*S*)-phenyl 3-azido-2-*O*-benzyl-4,6-*O*-alkylidene mannopyranosyl donor,[22] which also proceed with moderate *β*-selectivity. The substitution of a single *O*-benzyl group for an azide functionality thus already causes a drop in selectivity. The introduction of two azides leads to further erosion of *β*-selectivity, providing moderate α-selectivity in two of the three cases studied here. Crich and co-workers have rationalized the erosion of *β*-selectivity, observed with small substituents at the C-2 or C-3 position, through the observation that formation of the benzylidene mannosyl $^4H_3$ oxacarbenium ion from the corresponding α-triflate proceeds with concomitant compression of the R2−C-2−C-3−R3 torsion angle, which is easier if the substituents R2 and R3 are smaller.[6a,23] The diazido case studied here supports this mechanistic rationale: the presence of the two small azides (*A* value ∼0.45−0.62 kcal mol^{-1})[24] allows the mannosyl triflate to readily collapse into the α-selective $^4H_3$ oxacarbenium ion. It should be noted that the electron-withdrawing effect of the azide does not counterbalance this steric effect, which has also been found for C-3-*O*-benzyl-C-2-fluoro- and C-2-*O*-benzyl-C-3-fluorobenzylidene mannosides.[6a] A similar rationale can account for the poor selectivity obtained with donor **6*β***. Furthermore, Kim and co-workers have argued that participation of a remote C-6-*O*-acetate can also account for the formation of α-linked products from otherwise benzylated mannosides.[12] In the present case, we cannot exclude such a mechanism to contribute to the formation of the α-mannosides.

Entries 7−9 show that the three diazido mannuronate disaccharides **29**, **30**, and **31** were all formed in a *β*-selective fashion. Secondary alcohol **21** gave the poorest selectivity and yield in the series, which parallels the results of condensations of this acceptor with other mannuronate donors.[3a] Introduction of two azides on the mannuronic acid core thus has little influence on the selectivity of the mannuronic acid type donors, in contrast to the other two types of donors studied here. A possible explanation for this

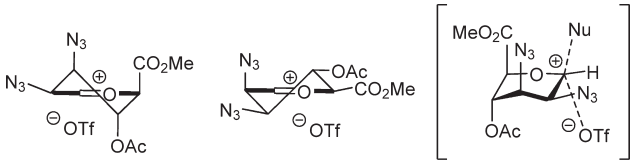
Table 1. Glycosylation Study of Donors 6β, 7, and 8β[a]



20 21 22

Entry	Donor	Acceptor	Product	Ratio α : β	Yield (%)
1		**20**	**23**	1 : 1	75
2		**21**	**24**	2 : 1	45
3	**6β**	**22**	**25**	2.5 : 1	66
4		**20**	**26**	3 : 1	79
5		**21**	**27**	5 : 1	66
6	**7**	**22**	**28**	1 : 1	81
7		**20**	**29**	1 : 5.5	94
8		**21**	**30**	1 : 3.5	49
9	**8β**	**22**	**31**	1 : 7.5	89

[a] Conditions: donor **6β** or **7**, Tf_2O (1.3 equiv), Ph_2SO (1.3 equiv), TTBP (2.5 equiv), DCM (0.05) at −80 °C, then add acceptor (1.5 equiv). Donor **8β**, Tf_2O (1.3 equiv), Ph_2SO (1.3 equiv), TTBP (2.5 equiv), DCM (0.05) at −80 → −60 °C, then add acceptor (1.5 equiv).



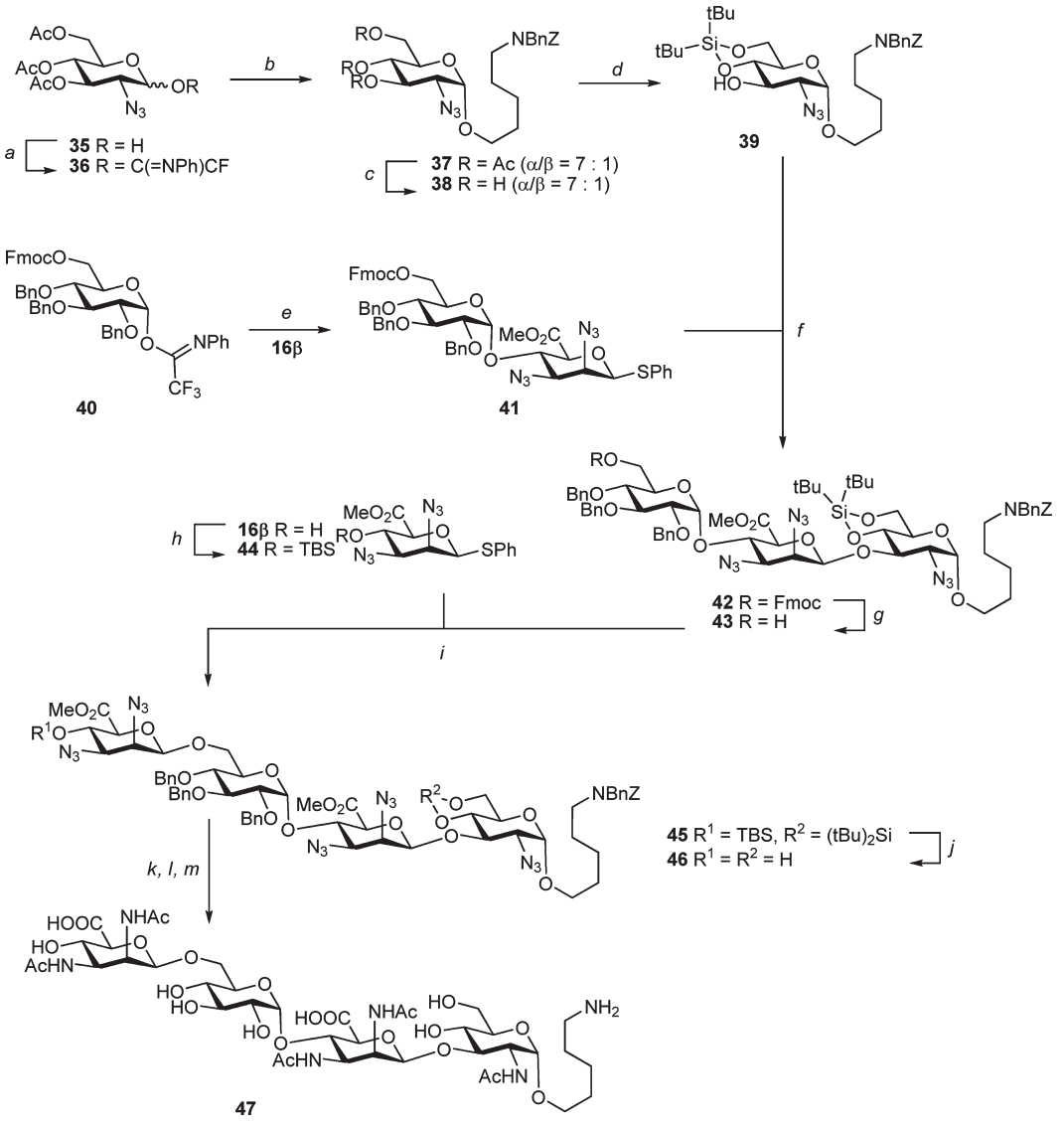
32 33 34

Figure 3. 2,3-Diazido mannuronate oxacarbenium ions.

observation can be found in the preferred conformation of the mannuronate oxacarbenium ions, in which the C-5 carboxylic acid ester prefers to occupy a pseudoaxial position (as in **5**, Figure 1), making the $^3H_4$ oxacarbenium ion energetically favored over its $^4H_3$ counterpart. Nucleophilic attack at the $^3H_4$ oxacarbenium ion leads to the preferential formation of the β-product. Woerpel and co-workers have established that an azido group follows the preference of an *O*-alkyl substituent to occupy an axial orientation in an oxacarbenium ion intermediate.[5a] The relative stabilities of the diazido mannuronic acid $^3H_4$ and $^4H_3$ oxacarbenium ions **32** and **33** thus mirror those of the 2,3-di-*O*-benzyl mannuronic acid, making the former favored over the latter and providing a positive contribution to the formation of the β-linked product (Figure 3). The same line of reasoning can be applied to a product forming exploded transition state (**34**) in which the triflate dissociates from the diazido mannuronic acid core leading to partial oxacarbenium ion character at C-1, which is best accommodated in a $^3H_4$-like conformation. S_N2-like reaction of this species provides the β-linked product. Although it could be reasoned that installment of two azides and the C-5 carboxylic acid ester would provide a highly disarmed donor, which would be difficult to activate, the yields obtained in the condensations of donor **8β** with alcohols **20** and **22** clearly show this not to be the case: the donors can be activated at temperatures as low as −80 °C to provide reactive glycosylating species. The conformational behavior of the mannuronates could be at the basis of this unexpected reactivity.[25]

Having established that the diazido mannuronic acid donor **8β** is the donor of choice for the introduction of the 2,3-diamino-2,3-dideoxy β-mannosidic bond, we sought to explore its utility in the construction of a complex oligosaccharide. To this end, we selected the repeating unit of the secondary cell wall polysaccharide of *Bacillus stearothermophilus*, [→4)-β-D-Man*p*A2,3(NAc)$_2$-(1→6)-α-D-Glc*p*-(1→4)-β-D-Man*p*A2,3(NAc)$_2$-(1→3)-α-D-Glc*p*NAc-(1→],[9] as a synthetic target (Scheme 2). This all-*cis*-linked oligosaccharide features two β-linked diacetamino mannuronic acids in addition to an α-glucose and an α-glucosamine moiety. We decided to construct tetrasaccharide **47**, having an aminopentanol spacer at its reducing end, from three building blocks: reducing end glucosamine **39**, glucose mannuronic acid disaccharide **41**, and terminal mannuronic acid **44**. We based our synthesis on the use of the central disaccharide **41** because this type of disaccharide performed well in the construction of *Micrococcus luteus* oligomers, composed of repeating [→6)-α-D-Glc*p*-(1→4)-β-D-Man*p*A2(NAc)-(1→] units.[3b] The synthesis of these building blocks and the full assembly of the tetrasaccharide is depicted in Scheme 2. The synthesis of acceptor **39** started from hemiacetal **35**,[26a,b] which was transformed into *N*-phenyltrifluoroacetimidate **36**[26c] in 96% yield. The stereoselective condensation of this donor with *N*-(benzyl)benzyloxycarbonyl-5-aminopentanol required some optimization. When a mixture of **36** and the acceptor in DCM was treated with a catalytic amount of TfOH at 0 °C, compound **37** was formed as an α/β mixture, with a slight preference for the α-anomer. The addition of thiophene to the reaction mixture as prescribed by Boons et al.[27] to enhance the α-selectivity did not result in a better selectivity. By using diethyl ether as the solvent and lowering the reaction temperature to −40 °C, the stereoselectivity of the reaction was enhanced to provide product **37** in 77% yield and a 7:1 α/β ratio. Separation of the two anomers was troublesome at this stage, and therefore, **37** was transformed into alcohol **39** by subsequent deacetylation and silylidene formation. After this sequence of reactions, pure α-configured acceptor **39**

Scheme 2. Construction of Tetrasaccharide 47[a]



[a] Reagents and conditions: (a) $C(NPh)CF_3-Cl$, K_2CO_3, acetone/H_2O (96%, α/β = 1.4:1); (b) *N*-(benzyl)benzyloxycarbonyl-5-aminopentanol, TfOH (cat.), Et_2O, −40 → −10 °C (77%, α/β = 7:1); (c) NaOMe, MeOH (quant.); (d) $(tBu)_2Si(OTf)_2$, DMF (76%); (e) **40**, **16*β***, TfOH (cat.), Et_2O, −40 → −10 °C (96%); (f) **41**, Ph_2SO, Tf_2O, DCM, −80 → −60 °C, then **39**, −80 → −10 °C (99%); (g) Et_3N, pyridine (94%); (h) TBSOTf, Et_3N, DCM, (88%); (i) **44**, Ph_2SO, Tf_2O, TTBP, DCM, −80 °C, then **43**, −30 °C overnight, (74%); (j) (*i*) TBAF, HOAc (96%); (*ii*) TBAF, HOAc (75%); (k) KOH, H_2O_2, THF, H_2O; (l) (*i*) Zn, AcOH, THF; (*ii*) Ac_2O, $NaHCO_3$, THF, H_2O; (m) H_2, Pd/C, H_2O, THF, HCl (20%).

could be isolated in 76% yield. The disaccharide **41** was constructed using 6-*O*-Fmoc-protected glucose imidate donor **40** and (*S*)-phenyl diazido mannuronic acid **16*β*** using conditions we previously established for the α-selective condensation of **40** and the monoazido mannuronic acid counterpart of **16*β***.[3b,28] The key disaccharide **41** was obtained in excellent yield as a single anomer. Next, dimer **41** and glucosamine **39** were fused using our standard Ph_2SO-Tf_2O preactivation protocol in the absence of any base to prevent undesired Fmoc cleavage. All-*cis*-linked trisaccharide **42** was obtained in near quantitative yield as a single diastereomer, highlighting the apt glycosylating capacity of the diazido mannuronic acid donor. Liberation of the 6″-OH under mild basic conditions then set the stage for the final coupling, in which the trisaccharide acceptor **43** was condensed with C-4-*O*-TBS-protected diazido mannuronic acid **44**, obtained from **16*β*** by treatment with TBSOTf and Et_3N in 88% yield. The stereochemical outcome of this reaction did not pose any problems, but to obtain a profitable yield, some experimentation was required. After trying different reaction temperatures and times, the best conditions (reaction at −30 °C overnight) provided the fully protected tetrasaccharide **45** in 74% yield. It is of interest to note that the replacement of the electron-withdrawing C-4-*O*-acetyl in **8*β*** by the less electron poor TBS ether in **44** does not adversely affect the *β*-selectivity of the diazido mannuronic acid donor.

Deprotection of the tetrasaccharide started with the removal of the silyl groups. It was found that the silylidene group could be removed without affecting the C-4‴-*O*-TBS ether.[29] In fact, removal of this latter silyl ether was extremely sluggish and deprotection of the C-4‴-OH required 72 h for completion. Next, the carboxylic acid esters were saponified using KOOH in H_2O/THF to

dx.doi.org/10.1021/jo201179p |*J. Org. Chem.* 2011, 76, 7301–7315

provide the diacid. Initially, we tried to simultaneously reduce the five azide groups and benzyl ethers and benzylcarbonate functionality under Birch conditions.[3b] Unfortunately, this led to partial fragmentation of the oligosaccharide through cleavage of the β-mannuronic acid bonds, a side reaction we have also observed in our synthesis of *M. luteus* [→6)-α-D-Glc*p*-(1→4)-β-D-Man*p*A2(NAc)-(1→]$_n$ oligomers. We therefore resorted to a stepwise reduction procedure, in which first the four azides were reduced using zinc in acetic acid,[30] followed by aqueous acetylation of the liberated amines. Removal of the benzyl ethers and benzyloxycarbonyl groups by treatment with H_2 over Pd/C in the presence of aqueous HCl completed the synthesis of the target tetrasaccharide. The fully deprotected tetramer **47** was purified by HPLC and isolated in 20% overall yield.

CONCLUSIONS

Three different 2,3-diazido-2,3-dideoxy mannosylating agents were evaluated for their potential to provide β-mannosidic bonds: the 4,6-di-*O*-acetyl- and 4,6-*O*-benzylidene-2,3-diazido-2,3-dideoxy mannopyranosyl donors proved to be rather unselective or slightly α-selective. In contrast, 2,3-diazido-2,3-dideoxy mannuronic acid esters provided the desired β-linked product with good selectivity. The observed differences in stereochemical outcome suggest that different mechanistic pathways take place: the 4,6-di-*O*-acetyl- and 4,6-*O*-benzylidene systems react through an α-selective $^4H_3$-oxacarbenium ion-type intermediate (or corresponding transition state), while the reactions of the mannuronate donors involve a transition state with $^3H_4$ oxacarbenium ion-like character. The profitable β-mannosylating properties of the diazido mannuronates were exploited in the stereoselective synthesis of an all-*cis*-linked *Bacillus stearothermophilus* tetrasaccharide, featuring two β-mannuronic acid linkages. It is expected that the methodology described here can be readily applied in the synthesis of diamino mannuronic acid containing polysaccharides of different bacteria,[31] such as *Bordetella pertussis*, *Pseudomonas aeruginosa*, and *Neisseria meningitides*. Current research is aimed at further unravelling the reaction mechanism(s) underlying the β-selectivity and reactivity of mannuronic acids.

EXPERIMENTAL SECTION

General Procedure for the Low-Temperature NMR Experiments. A mixture of the donor (30 μmol) and Ph_2SO (39 μmol)[20] was coevaporated with toluene (2×). The residue was dissolved in DCM-d_2 (0.6 mL) and transferred to an NMR tube under an argon atmosphere. The tube was stoppered and sealed. The NMR magnet was cooled to −80 °C, locked, and shimmed. In an acetone bath (−80 °C), the sample was treated with Tf_2O (39 μmol), shaken three times, and placed back in the NMR magnet. The first ^{1}H spectrum was immediately recorded. Further temperature changes were executed depending on the spectra recorded but always with multiples of 10 °C.

General Procedure for the Ph_2SO/Tf_2O-Mediated Glycosylations. A mixture of the donor (1 equiv), Ph_2SO (1.3 equiv), and TTBP (2.5 equiv) was coevaporated twice with toluene. While the mixture was under an argon atmosphere, freshly distilled DCM (0.05 M) was added, followed by the addition of activated molecular sieves (3 Å). The resulting mixture was stirred for 30 min at room temperature and cooled to the activation temperature. Tf_2O (1.3 equiv) was added in one portion, and the activation progress was monitored by TLC analysis. In the case of uronic acid donor **8β**, the temperature was raised to −60 °C in 20 min and cooled back to −80 °C. Then a solution of the acceptor (0.3−0.5 M in DCM) was slowly added via the wall of the flask. The mixture was allowed to warm to 0 °C, after which Et_3N or pyridine was added to quench the reaction. Aqueous workup, passage of the residue through a column of Sephadex LH-20 (eluted with DCM/MeOH, 1/1, v/v), and purification using flash column chromatography (silica gel) gave the coupled product.

Phenyl 4,6-Di-*O*-acetyl-2,3-diazido-2,3-dideoxy-1-thio-α/β-D-mannopyranoside (6α/6β). Compound **14** (0.39 g, 1.08 mmol) and PhSH (0.13 mL, 1.25 mmol) were dissolved in DCE (5.65 mL), followed by the addition of $BF_3\cdot Et_2O$ (0.28 mL, 2.26 mmol), and the solution was heated to 50 °C (5 h). Saturated aqueous $NaHCO_3$ was added, and the mixture was diluted with EtOAc. The organic layer was washed with H_2O (2×). Purification using column chromatography (silica gel, 20% EtOAc in PE for the α-anomer, 25% EtOAc in PE for the β-anomer) yielded the pure anomers **6α** and **6β** as off-white amorphous solids (0.36 g, 0.89 mmol, 82%, α/β = 1:2.4). TLC R_f α-anomer 0.50, β-anomer 0.34 (PE/EtOAc, 2/1, v/v). spectroscopic data for the α-anomer: $[\alpha]^{20}_D$ +110.0 (*c* 1, DCM); IR (neat, cm^{-1}) 1034, 1227, 1728, 2106; ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.45−7.51 (m, 2H, CH_{arom}), 7.32−7.36 (m, 3H, CH_{arom}), 5.54 (d, 1H, *J* = 1.0 Hz, H-1), 5.31 (t, 1H, *J* = 9.9 Hz, H-4), 4.44 (ddd, 1H, *J* = 2.4, 5.6, 9.8 Hz, H-5), 4.23 (dd, 1H, *J* = 5.6, 12.3 Hz, H-6), 4.16 (dd, 1H, *J* = 1.3, 3.5 Hz, H-2), 4.09 (dd, 1H, *J* = 2.4, 12.3 Hz, H-6), 4.00 (dd, 1H, *J* = 3.5, 10.0 Hz, H-3), 2.16 (s, 3H, CH_3 Ac), 2.05 (s, 3H, CH_3 Ac); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 170.3, 169.2 (C═O Ac), 131.9 (C_q SPh), 131.9, 129.1, 128.2 (CH_{arom}), 85.5 (C-1), 69.4 (C-5), 67.2 (C-4), 63.3 (C-2), 62.0 (C-6), 60.7 (C-3), 20.4, 20.4 (CH_3 Ac); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 85.5 ($J_{C1,H1}$ = 169 Hz, C-1); HRMS $[M + NH_4]^+$ calcd for $C_{16}H_{22}N_7O_5S$ 424.13976, found 424.13994. Spectroscopic data for the β-anomer: $[\alpha]^{20}_D$ +14.4 (*c* 1, DCM); IR (neat, cm^{-1}) 1034, 1211, 1736, 2106; ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.50−7.55 (m, 2H, CH_{arom}), 7.30−7.34 (m, 3H, CH_{arom}), 5.27 (t, 1H, *J* = 10.0 Hz, H-4), 4.83 (d, 1H, *J* = 1.4 Hz, H-1), 4.21 (dd, 1H, *J* = 6.1, 12.2 Hz, H-6), 4.13−4.17 (m, 2H, H-2, H-6), 3.80 (dd, 1H, *J* = 3.7, 10.0 Hz, H-3), 3.60 (ddd, 1H, *J* = 2.8, 6.0, 9.6 Hz, H-5), 2.13 (s, 3H, CH_3 Ac), 2.08 (s, 3H, CH_3 Ac); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 170.0, 169.2 (C═O Ac), 132.9 (C_q SPh), 131.1, 128.8, 127.7 (CH_{arom}), 86.1 (C-1), 76.3 (C-5), 66.8 (C-4), 64.0 (C-2), 63.8 (C-3), 62.2 (C-6), 20.2, 20.2 (CH_3 Ac); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 86.1 ($J_{C1,H1}$ = 155 Hz, C-1); HRMS $[M + NH_4]^+$ calcd for $C_{16}H_{22}N_7O_5S$ 424.13976, found 424.13984.

Phenyl 2,3-diazido-4,6-*O*-benzylidene-2,3-dideoxy-1-thio-β-D-mannopyranoside (7). To a solution of compound **15β** (0.38 g, 1.18 mmol) in dry acetonitrile (9 mL) were added $PhCH(OMe)_2$ (0.33 mL, 2.2 mmol) and *p*-TsOH (cat). The resulting solution was stirred overnight at rt, followed by the addition of Et_3N until pH was almost neutral. EtOAc was added, and the solution was washed with saturated aqueous NaCl (2×), dried over Na_2SO_4, and concentrated in vacuo. The title compound was obtained by crystallization from EtOAc/PE as white fluffy crystals (0.33 g, 0.81 mmol, 69%): TLC R_f 0.52 (PE/EtOAc, 4/1, v/v); $[\alpha]^{20}_D$ +34.4 (*c* 1, DCM); melting point = 178−180 °C; IR (neat, cm^{-1}) 696, 978, 1078, 1096, 1263, 2099, 2151; ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.44−7.53 (m, 4H, CH_{arom}), 7.31−7.42 (m, 6H, CH_{arom}), 5.66 (s, 1H, CH Ph), 4.90 (s, 1H, H-1), 4.35 (dd, 1H, *J* = 4.9, 10.6 Hz, H-6), 4.09−4.20 (m, 2H, H-2, H-4), 3.87−3.96 (m, 2H, H-3, H-6), 3.47 (dt, 1H, *J* = 4.9, 9.5, 9.7 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 136.6 (C_q Ph), 133.2 (C_q SPh), 132.0, 129.3, 129.1, 128.3, 125.8 (CH_{arom}), 101.6 (CH Ph), 87.5 (C-1), 76.9 (C-4), 72.0 (C-5), 68.3 (C-6), 64.9 (C-2), 63.1 (C-3); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 87.5 ($J_{C1,H1}$ = 157 Hz, C-1); HRMS $[M + H]^+$ calcd for $C_{19}H_{19}N_6O_3S$ 411.12339, found 411.12343.

Methyl (Phenyl 4-*O*-acetyl-2,3-diazido-2,3-dideoxy-1-thio-α-D-mannopyranosyl uronate) (8α). Compound **16α** (0.24 g, 0.69 mmol) was treated with Ac_2O/pyridine (6 mL, 1/3, v/v) until TLC analysis indicated complete consumption of the starting material.

The mixture was diluted with EtOAc, washed with H_2O and saturated aqueous NaCl, dried over Na_2SO_4, and concentrated in vacuo. Purification using flash column chromatography (silica gel, 25% EtOAc in PE) yielded the title compound as yellowish oil (0.25 g, 0.62 mmol, 91%): TLC R_f 0.43 (PE/EtOAc, 3/1, v/v); $[\alpha]^{20}_D$ +70.6 (*c* 1, DCM); IR (neat, cm^{-1}) 748, 1049, 1211, 1751, 2106; ^1H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.53−7.58 (m, 2H, CH_{arom}), 7.30−7.36 (m, 3H, CH_{arom}), 5.55 (d, 1H, *J* = 5.1 Hz, H-1), 5.42 (t, 1H, *J* = 6.8 Hz, H-4), 4.65 (d, 1H, *J* = 6.5 Hz, H-5), 4.06 (dd, 1H, *J* = 3.4, 7.4 Hz, H-3), 4.00 (dd, 1H, *J* = 3.6, 4.9 Hz, H-2), 3.76 (s, 3H, CH_3 CO_2Me), 2.12 (s, 3H, CH_3 Ac); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 169.1, 167.3 (C═O Ac, CO_2Me), 131.9 (CH_{arom}), 131.5 (C_q SPh) 129.0, 128.1 (CH_{arom}), 83.8 (C-1), 71.3 (C-5), 68.4 (C-4), 60.7 (C-2), 60.1 (C-3), 52.6 (CH_3 CO_2Me), 20.4 (CH_3 Ac); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 83.8 ($J_{C1,H1}$ = 168 Hz, C-1); HRMS $[M + Na]^+$ calcd for $C_{15}H_{16}N_6O_5SNa$ 415.07951, found 415.07942.

Methyl (Phenyl 4-*O*-acetyl-2,3-diazido-2,3-dideoxy-1-thio-β-D-mannopyranosyl uronate) (8β). Compound **16β** (0.26 g, 0.74 mmol) was treated with Ac_2O/pyridine (6 mL, 1/3, v/v) until TLC analysis indicated complete consumption of the starting material. The mixture was diluted with EtOAc, washed with H_2O and saturated aqueous NaCl, dried over Na_2SO_4, and concentrated in vacuo. Purification using flash column chromatography (silica gel, 50% EtOAc in PE) yielded the title compound as a yellowish solid (0.29 g, 0.74 mmol, quant.): TLC R_f 0.31 (PE/EtOAc, 3/1, v/v); $[\alpha]^{20}_D$ +19.8 (*c* 1, DCM); IR (neat, cm^{-1}) 1049, 1219, 1751, 2106; ^1H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.44−7.48 (m, 2H, CH_{arom}), 7.26−7.32 (m, 3H, CH_{arom}), 5.33 (t, 1H, *J* = 10.0 Hz, H-4), 5.00 (d, 1H, *J* = 1.3 Hz, H-1), 4.26 (dd, 1H, *J* = 1.1, 3.6 Hz, H-2), 4.05 (dd, 1H, *J* = 3.4, 10.3 Hz, H-3), 4.03 (d, 1H, *J* = 9.9 Hz, H-5), 3.69 (s, 3H, CH_3 CO_2Me), 2.06 (s, 3H, CH_3 Ac); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 169.2, 166.7 (C═O Ac, CO_2Me), 132.8 (C_q SPh), 131.4, 129.0, 128.0 (CH_{arom}), 86.6 (C-1), 76.3 (C-5), 67.6 (C-4), 64.0 (C-2), 63.4 (C-3), 52.6 (CH_3 CO_2Me), 20.2 (CH_3 Ac); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 86.6 ($J_{C1,H1}$ = 156 Hz, C-1); HRMS $[M + NH_4]^+$ calcd for $C_{15}H_{20}N_7O_5S$ 410.12411, found 410.12400.

Methyl 4,6-*O*-Benzylidene-2,3-di-*O*-methanesulfonyl-α-D-glucopyranoside (10). Compound **9**[14] (17.4 g, 61.7 mmol) was dissolved in pyridine (123 mL), and methanesulfonyl chloride (14.4 mL, 186 mmol) was dropwise added. The mixture was stirred overnight and subsequently diluted with EtOAc and H_2O. The layers were separated, and the organic fraction was washed with saturated aqueous NaCl (2×), dried over Na_2SO_4, and concentrated in vacuo. Crude compound **10** was used in the next reaction step without further purification. A fraction was crystallized for analytical purposes. Spectroscopic data were in accord with those previously reported:[32] TLC R_f 0.74 (DCM/acetone, 10/1, v/v); ^1H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.41−7.48 (m, 2H, CH_{arom}), 7.35−7.40 (m, 3H, CH_{arom}), 5.56 (s, 1H, CH Ph), 5.09 (t, 1H, *J* = 9.6 Hz, H-3), 5.03 (d, 1H, *J* = 3.7 Hz, H-1), 4.63 (dd, 1H, *J* = 3.7, 9.6 Hz, H-2), 4.34 (dd, 1H, *J* = 4.8, 10.4 Hz, H-6), 3.94 (td, 1H, *J* = 4.8, 9.8, 9.9 Hz, H-5), 3.79 (t, 1H, *J* = 10.4 Hz, H-6), 3.74 (t, 1H, *J* = 9.5 Hz, H-4), 3.49 (s, 3H, OMe), 3.17 (s, 3H, CH_3 Ms), 2.97 (s, 3H, CH_3 Ms); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 136.2 (C_q Ph), 129.5, 128.4, 126.0 (CH_{arom}), 101.9 (CH Ph), 98.78 (C-1), 78.9 (C-4), 77.1 (C-3), 75.8 (C-2), 68.6 (C-6), 62.2 (C-5), 56.0 (OMe), 38.9, 38.7 (CH_3 Ms); HRMS $[M + Na]^+$ calcd for $C_{16}H_{22}O_{10}S_2Na$ 461.05466, found 461.05430.

Methyl 2,3-Anhydro-4,6-*O*-benzylidene-α-D-allopyranoside (11). Crude compound **10** (~62 mmol) was dissolved in THF/MeOH (500 mL, 2/3, v/v) followed by the addition of KOH (10.5 g, 187 mmol). The mixture was refluxed at 70 °C overnight. Then H_2O was added, the mixture diluted with EtOAc, and the organic fraction was separated and washed with H_2O (3×), dried over Na_2SO_4, and concentrated in vacuo. Crystallization (EtOAc/PE) yielded the title compound as a white fluffy solid (10.2 g, 39.5 mmol, 62% over two steps). Spectroscopic data were in accord with those previously reported:[33] TLC R_f 0.56 (PE/EtOAc, 2/3, v/v); ^1H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.47−7.52 (m, 2H, CH_{arom}), 7.35−7.40 (m, 3H, CH_{arom}), 5.57 (s, 1H, CH Ph), 4.89 (d, 1H, *J* = 2.8 Hz, H-1), 4.24 (dd, 1H, *J* = 5.0, 10.2 Hz, H-6), 4.05−4.12 (m, 1H, H-5), 3.95 (dd, 1H, *J* = 1.0, 9.1 Hz, H-4), 3.68 (t, 1H, *J* = 10.3 Hz, H-6), 3.52 (d, 1H, *J* = 4.3 Hz, H-3), 3.49 (dd, 1H, *J* = 2.8, 4.3 Hz, H-2), 3.47 (s, 3H, OMe); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 137.1 (C_q Ph), 129.2, 128.3, 126.3 (CH_{arom}), 102.7 (CH Ph), 95.3 (C-1), 77.9 (C-4), 68.9 (C-6), 60.0 (C-5), 55.8 (OMe), 53.1 (C-2), 50.7 (C-3); HRMS $[M + H]^+$ calcd for $C_{14}H_{17}O_5$ 265.10705, found 265.10718.

Methyl 2-Azido-4,6-*O*-benzylidene-2-deoxy-α-D-altropyranoside (12). Compound **11** (13.6 g, 52 mmol) was dissolved in DMSO (260 mL), followed by the addition of NaN_3 (10.1 g, 155 mmol) and NH_4Cl (24.9 g, 466 mmol). The mixture was heated overnight at 80 °C and subsequently diluted with EtOAc, washed with saturated aqueous NaCl (3×), dried over Na_2SO_4, and concentrated in vacuo. Purification using flash column chromatography (silica gel, 50% EtOAc in PE) yielded the title compound as a colorless oil (14.8 g, 48.4 mmol, 93%): TLC R_f 0.51 (PE/EtOAc, 2/3, v/v); $[\alpha]^{20}_D$ +68.9 (*c* 1, DCM); IR (neat, cm^{-1}) 1042, 1242, 1736, 2106; ^1H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.45−7.51 (m, 2H, CH_{arom}), 7.29−7.38 (m, 3H, CH_{arom}), 5.57 (s, 1H, CH Ph), 4.63 (s, 1H, H-1), 4.28 (dd, 1H, *J* = 5.2, 10.2 Hz, H-6), 4.16 (td, 1H, *J* = 5.2, 10.0, 10.0 Hz, H-5), 4.03 (s, 1H, H-3), 3.76−3.81 (m, 2H, H-2, H-4), 3.75 (t, 1H, *J* = 10.3 Hz, H-6), 3.37 (s, 3H, OMe), 3.14 (bs, 1H, 3-OH); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 136.9 (C_q Ph), 128.9, 128.0, 126.0 (CH_{arom}), 101.9 (CH Ph), 99.1 (C-1), 75.7 (C-4), 68.7 (C-6), 67.1 (C-3), 61.6 (C-2), 57.8 (C-5), 55.5 (OMe); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 99.1 ($J_{C1,H1}$ = 171 Hz, C-1); HRMS $[M + H]^+$ calcd for $C_{14}H_{18}N_3O_5$ 308.12410, found 308.12414.

Methyl 2,3-Diazido-4,6-*O*-benzylidene-2,3-dideoxy-α-D-mannopyranoside (13). A solution of compound **12** (14.85 g, 48.4 mmol) in DCE (340 mL) was treated with pyridine (91 mL, 1.13 mol) and Tf_2O (18.9 mL, 112.5 mmol). The reaction was stirred for 30 min, followed by the addition of H_2O to quench. The mixture was diluted with DCM, washed with H_2O (3×), dried over Na_2SO_4, and concentrated in the presence of toluene (2×). The crude triflate (~48 mmol) was dissolved in DMF (110 mL). NaN_3 (18.7 g, 288 mmol) and NH_4Cl (9.0 g, 168 mmol) were added, and the mixture was heated overnight at 80 °C. EtOAc and H_2O were added, and the layers were separated. The organic phase was washed with H_2O (2×), dried over Na_2SO_4, and concentrated in vacuo. Purification using column chromatography (silica gel, 50% EtOAc in PE) furnished the title compound as a white amorphous solid (12.1 g, 36.3 mmol, 75%): TLC R_f 0.75 (PE/EtOAc, 4/1, v/v); $[\alpha]^{20}_D$ +94.0 (*c* 1, DCM); IR (neat, cm^{-1}) 1041, 1735, 2106, 2931; ^1H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.47−7.52 (m, 2H, CH_{arom}), 7.35−7.41 (m, 3H, CH_{arom}), 5.65 (s, 1H, CH Ph), 4.71 (d, 1H, *J* = 1.4 Hz, H-1), 4.29 (dd, 1H, *J* = 10.6, 16.2 Hz, H-6), 4.14 (dd, 1H, *J* = 3.6, 10.2 Hz, H-3), 4.05 (dt, 1H, *J* = 1.6, 10.2 Hz, H-4), 3.90 (dd, 1H, *J* = 1.4, 3.6 Hz, H-2), 3.82−3.85 (m, 2H, H-5, H-6), 3.40 (s, 3H, OMe); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 136.8 (C_q), 129.0, 128.3, 125.8 (CH_{arom}), 101.6 (CH Ph), 99.3 (C-1), 77.5 (C-4), 68.7 (C-6), 63.8 (C-5), 62.7 (C-2), 59.2 (C-3), 55.2 (OMe); HRMS $[M + H]^+$ calcd for $C_{14}H_{17}N_6O_4$ 333.13058, found 333.13036.

Acetyl 4,6-Di-*O*-acetyl-2,3-diazido-2,3-dideoxy-α/β-D-mannopyranoside (14). Compound **13** (20.7 mmol) was dissolved in Ac_2O (35 mL) and treated with H_2SO_4 (0.3 mL) at 0 °C for 2 h. The mixture was diluted with EtOAc and quenched with saturated aqueous $NaHCO_3$. The organic fraction was washed with H_2O and saturated aqueous NaCl (2×). Purification using flash column chromatography (silica gel, 50% EtOAc in PE) furnished the title compound as a brownish oil (7.3 g, 20.5 mmol, 98%, α/β = 5:1): TLC R_f 0.45 (PE/EtOAc, 1/1, v/v); IR (neat, cm^{-1}) 1211, 1735, 2106; ^1H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 6.12 (d, 1H, *J* = 1.6 Hz, H-1α), 5.85 (d, 0.2H, *J* = 0.9 Hz, H-1β), 5.33 (t, 1H, *J* = 10.1 Hz, H-4α), 5.21 (t, 0.2H, *J* = 9.9 Hz,

H-4β), 4.22−4.27 (m, 0.2H, H-6β), 4.20 (dd, 1H, J = 4.6, 12.5 Hz, H-6α), 4.11 (d, 0.2H, J = 2.3 Hz, H-2β), 4.07−4.14 (m, 1.2H, H-6α, H-6β), 4.05−4.07 (m, 1H, H-3α), 3.95−4.00 (m, 2H, H-2α, H-5α), 3.73−3.80 (m, 0.4H, H-3β, H-5β), 2.20 (s, 0.6H, CH_3 Ac-β), 2.17 (s, 3H, CH_3 Ac-α), 2.15 (s, 3H, CH_3 Ac-α), 2.13 (s, 0.6H, CH_3 Ac-β), 2.09 (s, 3H, CH_3 Ac-α); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 170.3, 169.1, 169.1, 168.1, 167.9 (C═O Ac), 91.5 (C-1β), 90.6 (C-1α), 73.5 (C-5β), 70.4 (C-5α), 66.2 (C-4α), 65.7 (C-4β), 61.7 (C-2β), 61.5 (C-6α, C-6β), 61.3 (C-3β), 60.9 (C-2α), 59.8 (C-3α), 20.5, 20.4, 20.3, 20.3, 20.3 (CH_3 Ac); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 91.5 ($J_{C1,H1}$ = 162 Hz, C-1β), 90.6 ($J_{C1,H1}$ = 175 Hz, C-1α); HRMS $[M + Na]^+$ calcd for $C_{12}H_{16}N_6O_7Na$ 379.09727, found 379.09719.

Phenyl 2,3-Diazido-2,3-dideoxy-1-thio-α-D-mannopyranoside (15α). Compound **6α** (0.78 g, 2.0 mmol) was suspended in MeOH (10 mL) and treated with NaOMe (39 mg, 0.72 mmol) for 2 h. The mixture was neutralized by the addition of Amberlite-H^+, filtered, and reduced in volume. The residue was taken up in EtOAc, washed with saturated aqueous NaCl (2×), dried over Na_2SO_4, and concentrated in vacuo. The product was obtained as a yellow oil (0.65 g, 2.0 mmol, quant.): TLC R_f 0.16 (PE/EtOAc, 2/1, v/v); $[\alpha]^{20}_D$ +72.1 (c 1, DCM); IR (neat, cm^{-1}) 727, 905, 1065, 2102, 3337; ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.42−7.46 (m, 2H, CH_{arom}), 7.29−7.35 (m, 3H, CH_{arom}), 5.46 (s, 1H, H-1), 4.36 (bs, 1H, 4-OH), 4.05−4.15 (m, 3H, H-2, H-4, H-5), 3.86−3.92 (m, 2H, H-3, H-6), 3.79 (dd, 1H, J = 1.3, 12.3 Hz, H-6), 3.04 (bs, 1H, 6-OH); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 132.4 (C_q SPh), 132.1, 129.2, 128.2 (CH_{arom}), 86.1 (C-1), 73.3 (C-4), 66.4 (C-5), 63.8 (C-2), 62.9 (C-3), 61.3 (C-6); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 86.1 ($J_{C1,H1}$ = 168 Hz, C-1); HRMS $[M + NH_4]^+$ calcd for $C_{12}H_{18}N_7O_3S$ 340.11863, found 340.11869.

Phenyl 2,3-Diazido-2,3-dideoxy-1-thio-β-D-mannopyranoside (15β). Compound **6β** (3.22 g, 7.93 mmol) was suspended in MeOH (40 mL) and treated with NaOMe (43 mg, 0.79 mmol) for 1.5 h, after which time the mixture was neutralized by the addition of Amberlite-H^+, filtered, and concentrated in vacuo. The title compound was obtained as an off-white fluffy solid (2.50 g, 7.76 mmol, 98%): TLC R_f 0.39 (PE/EtOAc, 1/1, v/v); $[\alpha]^{20}_D$ +22.7 (c 1, MeOH); IR (neat, cm^{-1}) 1074, 2104, 3211, 3366; ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.45−7.50 (m, 2H, CH_{arom}), 7.30−7.37 (m, 3H, CH_{arom}), 4.87 (s, 1H, H-1), 4.10 (d, 1H, J = 3.3 Hz, H-2), 4.06 (t, 1H, J = 9.7 Hz, H-4), 3.90 (dd, 1H, J = 3.2, 12.3 Hz, H-6), 3.84 (dd, 1H, J = 4.0, 12.2 Hz, H-6), 3.69 (dd, 1H, J = 3.5, 9.9 Hz, H-3), 3.30−3.36 (m, 1H, H-5), 1.39 (bs, 2H, 4-OH, 6-OH); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 133.4 (C_q SPh), 131.2, 129.1, 127.9 (CH_{arom}), 86.4 (C-1), 80.9 (C-5), 66.2 (C-3), 65.6 (C-4), 64.7 (C-2), 61.3 (C-6); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 86.4 ($J_{C1,H1}$ = 155 Hz, C-1); HRMS $[M + Na]^+$ calcd for $C_{12}H_{14}N_6O_3SNa$ 345.07403, found 345.07380.

Methyl (Phenyl 2,3-diazido-2,3-deoxy-1-thio-α-D-mannopyranosyl uronate) (16α). Diol **15α** (0.37 g, 1.15 mmol) was dissolved in DCM (4 mL), and H_2O (2 mL) was added. The mixture was cooled to 0 °C, followed by the addition of TEMPO (36 mg, 0.23 mmol) and BAIB (0.93 g, 2.88 mmol). The resulting emulsion was stirred at rt for 1.5 h. The reaction was quenched by the addition of saturated aqueous $Na_2S_2O_3$, and the organic layer was washed with saturated aqueous NaCl (2×), dried over $MgSO_4$, and concentrated in vacuo. The crude product was dissolved in dry DMF (10 mL) and treated with MeI (0.2 mL, 3.45 mmol) and K_2CO_3 (0.48 g, 3.45 mmol) at rt overnight. The mixture was diluted with EtOAc and H_2O, and the organic layer was washed with saturated aqueous NaCl (2×), dried over $MgSO_4$, and concentrated in vacuo. Purification using flash column chromatography (silica gel, 25% EtOAc in PE) gave the title compound as a yellowish oil (0.29 g, 0.82 mmol, 71%): TLC R_f 0.70 (PE/EtOAc, 1/1, v/v); $[\alpha]^{20}_D$ +86.4 (c 1, DCM); IR (neat, cm^{-1}) 727, 1078, 1250, 1439, 1734, 2102, 3487; ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.47−7.52 (m, 2H, CH_{arom}), 7.28−7.36 (m, 3H, CH_{arom}), 5.50 (d, 1H, J = 1.3 Hz, H-1), 4.71 (d, 1H, J = 9.1 Hz, H-5), 4.26 (t, 1H, J = 9.0 Hz, H-4), 4.09 (s, 1H, H-2), 3.91 (dd, 1H, J = 3.4, 9.4 Hz, H-3), 3.81 (s, 3H, CH_3 CO_2Me), 3.68 (d, 1H, J = 1.9 Hz, 4-OH); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 170.0 (C═O CO_2Me), 132.1 (C_q SPh), 132.0, 129.2, 128.3 (CH_{arom}), 86.2 (C-1), 71.6 (C-5), 68.2 (C-4), 62.7 (C-2), 61.7 (C-3), 52.9 (CH_3 CO_2Me); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 86.2 ($J_{C1,H1}$ = 169 Hz, C-1); HRMS $[M + NH_4]^+$ calcd for $C_{13}H_{18}N_7O_4S$ 368.11355, found 368.11356.

Methyl (Phenyl 2,3-diazido-2,3-dideoxy-1-thio-β-D-mannopyranosyl uronate) (16β). Diol **15β** (0.51 g, 1.58 mmol) was dissolved in EtOAc (6 mL), and H_2O (3 mL) was added. The mixture was cooled to 0 °C, followed by the addition of TEMPO (50 mg, 0.32 mmol) and BAIB (1.27 g, 3.95 mmol). The resulting emulsion was stirred at rt for 1 h. The reaction was quenched by the addition of saturated aqueous $Na_2S_2O_3$, and the organic layer was washed with saturated aqueous NaCl (2×), dried over $MgSO_4$, and concentrated in vacuo. The crude product was dissolved in dry DMF (9 mL) and treated with MeI (0.3 mL, 4.74 mmol) and K_2CO_3 (0.66 g, 4.74 mmol) at rt overnight. The mixture was diluted with EtOAc and H_2O, and the organic layer was washed with saturated aqueous NaCl (2×), dried over $MgSO_4$, and concentrated in vacuo. Purification using flash column chromatography (silica gel, 33% EtOAc in PE) gave the title compound as an off-white solid (0.50 g, 1.43 mmol, 91%): TLC R_f 0.29 (PE/EtOAc, 2/1, v/v); $[\alpha]^{20}_D$ −13.8 (c 1, DCM); IR (neat, cm^{-1}) 1034, 1265, 1288, 1736, 2106, 3741; ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.49−7.55 (m, 2H, CH_{arom}), 7.28−7.36 (m, 3H, CH_{arom}), 4.84 (s, 1H, H-1), 4.22 (t, 1H, J = 9.6 Hz, H-4), 4.08 (d, 1H, J = 2.9 Hz, H-2), 3.81−3.86 (m, 4H, H-5, CH_3 CO_2Me), 3.72 (dd, 1H, J = 3.5, 9.7 Hz, H-3), 3.60 (bs, 1H, 4-OH); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 169.2 (C═O CO_2Me), 133.1 (C_q SPh), 131.8, 129.1, 128.2 (CH_{arom}), 87.2 (C-1), 77.8 (C-5), 67.7 (C-4), 65.2 (C-3), 63.8 (C-2), 53.0 (CH_3 CO_2Me); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 87.2 ($J_{C1,H1}$ = 155 Hz, C-1); HRMS $[M + Na]^+$ calcd for $C_{13}H_{14}N_6O_4SNa$ 373.06894, found 373.06854.

Methyl 6-*O*-(4,6-Di-*O*-acetyl-2,3-diazido-2,3-dideoxy-α/β-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (23). Donor **6β** and acceptor **20** were condensed using the general protocol for Ph_2SO/Tf_2O-mediated glycosylations to yield disaccharide **23** (75%, α/β = 1:1). TLC R_f α 0.44, β 0.15 (toluene/EtOAc, 2/3, v/v); IR (neat, cm^{-1}) 1042, 1227, 1744, 2098, 2924. Spectroscopic data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.24−7.40 (m, 15H, CH_{arom}), 5.22 (t, 1H, J = 10.0 Hz, H-4′), 5.02 (d, 1H, J = 10.8 Hz, C*H*H Bn), 4.98 (d, 1H, J = 11.6 Hz, C*H*H Bn), 4.89 (d, 1H, J = 1.0 Hz, H-1′), 4.80 (d, 1H, J = 10.6 Hz, CH*H* Bn), 4.80 (d, 1H, J = 12.5 Hz, C*H*H Bn), 4.69 (d, 1H, J = 12.1 Hz, CH*H* Bn), 4.60 (d, 1H, J = 3.0 Hz, H-1), 4.59 (d, 1H, J = 12.0 Hz, CH*H* Bn), 3.98−4.06 (m, 2H, H-3, H-6′), 3.96 (dd, 1H, J = 2.4, 12.4 Hz, H-6′), 3.82−3.90 (m, 3H, H-2′, H-3′, H-6), 3.73−3.78 (m, 2H, H-5, H-5′), 3.65 (dd, 1H, J = 1.6, 11.2 Hz, H-6), 3.52 (dd, 1H, J = 3.6, 9.6 Hz, H-2), 3.46 (t, 1H, J = 9.2 Hz, H-4), 3.38 (s, 3H, OMe), 2.09 (s, 3H, CH_3 Ac), 2.02 (s, 3H, CH_3 Ac); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 170.6, 169.3 (C═O Ac), 138.4, 138.0, 137.9 (C_q Bn), 128.5, 128.4, 128.0, 127.4 (CH_{arom}), 97.9 (C-1), 97.7 (C-1′), 82.0 (C-3), 79.9 (C-2), 77.2 (C-4), 75.8, 74.7, 73.3 (CH_2 Bn), 69.5, 68.7 (C-5, C-5′), 66.8 (C-4′), 66.5 (C-6), 62.1 (C-2′), 61.9 (C-6′), 60.3 (C-3′), 55.3 (OMe), 20.6, 20.6 (CH_3 Ac); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 97.9 ($J_{C1,H1}$ = 163 Hz, C-1), 97.7 ($J_{C1,H1}$ = 173 Hz, C-1′). Spectroscopic data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.25−7.39 (m, 15H, CH_{arom}), 5.12 (t, 1H, J = 9.9 Hz, H-4′), 5.00 (d, 1H, J = 10.9 Hz, C*H*H Bn), 4.88 (d, 1H, J = 11.6 Hz, C*H*H Bn), 4.81 (d, 1H, J = 10.8 Hz, CH*H* Bn), 4.79 (d, 1H, J = 12.0 Hz, C*H*H Bn), 4.64 (d, 1H, J = 12.0 Hz, CH*H* Bn), 4.59 (d, 1H, J = 11.7 Hz, CH*H* Bn), 4.56 (d, 1H, J = 3.5 Hz, H-1), 4.33 (s, 1H, H-1′), 4.20 (dd, 1H, J = 5.2, 12.3 Hz, H-6′), 4.06−4.14 (m, 2H, H-6, H-6′), 4.02 (t, 1H, J = 9.2 Hz, H-3), 3.83 (ddd, 1H, J = 1.4, 5.7, 9.7 Hz, H-5), 3.71 (d, 1H, J = 3.3 Hz,

H-2′), 3.53 (dd, 1H, J = 5.9, 10.4 Hz, H-6), 3.49 (dd, 1H, J = 3.5, 9.7 Hz, H-2), 3.43−3.47 (m, 1H, H-5′), 3.35−3.41 (m, 5H, H-3′, H-4, OMe), 2.10 (s, 3H, CH_3 Ac), 2.03 (s, 3H, CH_3 Ac); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 170.7, 169.2 (C═O Ac), 138.6, 138.4, 138.0 (C_q Bn), 128.4, 128.1, 128.0, 127.9, 127.8, 127.6 (CH_{arom}), 100.3 (C-1′), 97.9 (C-1), 82.0 (C-3), 79.9 (C-2), 77.3 (C-4), 75.7, 74.5, 73.4 (CH_2 Bn), 73.0 (C-5′), 69.5 (C-5), 68.8 (C-6), 66.7 (C-4′), 62.5 (C-2′), 62.3 (C-6′), 61.4 (C-3′), 55.2 (OMe), 20.7, 20.6 (CH_3 Ac); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 100.3 ($J_{C1,H1}$ = 156 Hz, C-1′), 97.9 ($J_{C1,H1}$ = 162 Hz, C-1); HRMS $[M + Na]^+$ calcd for $C_{38}H_{44}N_6O_{11}Na$ 783.29603, found 783.29585.

Methyl 4-*O*-(4,6-Di-*O*-acetyl-2,3-diazido-2,3-dideoxy-α/β-D-mannopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (24). Donor **6*β*** and acceptor **21** were condensed using the general protocol for Ph_2SO/Tf_2O-mediated glycosylations to yield disaccharide **24** (45%, α/β = 2:1). TLC R_f 0.24, 0.38 (PE/EtOAc, 2/1, v/v); IR (neat, cm^{-1}) 1042, 1234, 1744, 2106, 2924. Spectroscopic data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.25−7.41 (m, 15H, CH_{arom}), 5.19 (t, 1H, J = 10.0 Hz, H-4′), 5.15 (d, 1H, J = 1.7 Hz, H-1′), 5.11 (d, 1H, J = 11.5 Hz, C*H*H Bn), 4.74 (d, 1H, J = 12.0 Hz, C*H*H Bn), 4.58−4.65 (m, 4H, CH_2 Bn, H-1), 4.51 (d, 1H, J = 12.0 Hz, CH*H* Bn), 4.03 (dd, 1H, J = 4.6, 12.3 Hz, H-6′), 3.92 (t, 1H, J = 9.1 Hz, H-3), 3.77−3.87 (m, 3H, H-3′, H-5′, H-6′), 3.73−3.77 (m, 1H, H-5), 3.71 (t, 1H, J = 8.7 Hz, H-4), 3.65−3.68 (m, 2H, H-6), 3.55 (dd, 1H, J = 3.5, 9.6 Hz, H-2), 3.50 (dd, 1H, J = 1.9, 3.3 Hz, H-2′), 3.41 (s, 3H, OMe), 2.10 (s, 3H, CH_3 Ac), 2.03 (s, 3H, CH_3 Ac); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 170.6, 169.3 (C═O Ac), 138.0, 137.8, 137.6 (Cq Bn), 128.7, 128.5, 128.4, 128.1, 128.0, 127.7, 127.5 (CH_{arom}), 99.5 (C-1′), 97.7 (C-1), 80.9 (C-3), 80.3 (C-2), 77.8 (C-4), 75.5, 73.5, 73.2 (CH_2 Bn), 69.5, 69.4 (C-5, C-5′), 69.0 (C-6), 67.0 (C-4′), 62.1 (C-6′), 62.0 (C-2′), 60.3 (C-3′), 55.4 (OMe), 20.7, 20.6 (CH_3 Ac); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 99.5 ($J_{C1,H1}$ = 171 Hz, C-1′), 97.7 ($J_{C1,H1}$ = 163 Hz, C-1). Spectroscopic data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.26−7.42 (m, 15H, CH_{arom}), 5.06 (t, 1H, J = 10.0 Hz, H-4′), 4.99 (d, 1H, J = 11.3 Hz, C*H*H Bn), 4.86 (d, 1H, J = 11.3 Hz, CH*H* Bn), 4.77 (d, 1H, J = 12.3 Hz, C*H*H Bn), 4.74 (d, 1H, J = 13.2 Hz, C*H*H Bn), 4.58−4.63 (m, 2H, CH*H* Bn, H-1), 4.54 (d, 1H, J = 1.1 Hz, H-1′), 4.39 (d, 1H, J = 12.1 Hz, CH*H* Bn), 4.02 (dd, 1H, J = 4.3, 12.4 Hz, H-6′), 3.91 (t, 1H, J = 8.8 Hz, H-3), 3.89 (t, 1H, J = 8.8 Hz, H-4), 3.80 (dd, 1H, J = 2.6, 12.4 Hz, H-6′), 3.72−3.77 (m, 2H, H-5, H-6), 3.61−3.65 (m, 1H, H-6), 3.51 (dd, 1H, J = 3.6, 9.1 Hz, H-2), 3.38 (s, 3H, OMe), 3.37 (dd, 1H, J = 0.7, 3.4 Hz, H-2′), 3.16 (ddd, 1H, J = 2.6, 4.2, 9.7 Hz, H-5′), 2.94 (dd, 1H, J = 3.5, 10.2 Hz, H-3′), 2.08 (s, 3H, CH_3 Ac), 1.97 (s, 3H, CH_3 Ac); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 170.6, 169.1 (C═O Ac), 139.2, 128.0, 137.5 (C_q Bn), 128.7, 128.6, 128.4, 128.2, 128.1, 127.9, 127.3 (CH_{arom}), 100.1 (C-1′), 98.2 (C-1), 80.0 (C-3), 79.2 (C-2), 77.7 (C-4), 74.9, 73.7, 73.4 (CH_2 Bn), 72.9 (C-5′), 69.3 (C-5), 68.1 (C-6), 66.2 (C-4′), 62.6 (C-2′), 61.8 (C-6′), 61.5 (C-3′), 55.4 (OMe), 20.7, 20.6 (CH_3 Ac); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 100.1 ($J_{C1,H1}$ = 155 Hz, C-1′), 98.2 ($J_{C1,H1}$ = 164 Hz, C-1); HRMS $[M + Na]^+$ calcd for $C_{38}H_{44}N_6O_{11}Na$ 783.29603, found 783.29586.

p*-Methoxyphenyl 3-*O*-(4,6-di-*O*-acetyl-2,3-diazido-2,3-dideoxy-α/β-D-mannopyranosyl)-2-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside (25).** Donor **6*β and acceptor **22** were condensed using the general protocol for Ph_2SO/Tf_2O-mediated glycosylations to yield disaccharide **25** (66%, α/β = 2.5:1). TLC R_f α 0.75, β 0.50 (toluene/EtOAc, 1/1, v/v); IR (neat, cm^{-1}) 1049, 1219, 1504 1744, 2106, 2924, 3742. Spectroscopic data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.52−7.56 (m, 2H, CH_{arom}), 7.39−7.43 (m, 3H, CH_{arom}), 7.30−7.36 (m, 5H, CH_{arom}), 7.06 (d, 2H, J = 9.1 Hz, CH_{arom}), 6.83 (d, 1H, J = 9.1 Hz, CH_{arom}), 5.57 (s, 1H, CH Ph), 5.24 (t, 1H, J = 10.1 Hz, H-4′), 5.08 (d, 1H, J = 11.0 Hz, C*H*H Bn), 5.02 (d, 1H, J = 1.1 Hz, H-1′), 4.90 (d, 1H, J = 7.7 Hz, H-1), 4.73 (d, 1H, J = 11.1 Hz, CH*H* Bn), 4.37 (dd, 1H, J = 1.2, 12.4 Hz, H-6), 4.30 (d, 1H, J = 3.5 Hz, H-4), 4.02−4.11 (m, 3H, H-2, H-5′, H-6), 3.94 (dd, 1H, J = 2.4, 12.6 Hz, H-6′), 3.82−3.92 (m, 4H, H-2′, H-3, H-3′, H-6′), 3.77 (s, 3H, OMe), 3.47 (s, 1H, H-5), 2.06 (s, 3H, CH_3 Ac), 2.03 (s, 3H, CH_3 Ac); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 170.6, 169.3 (C═O Ac), 155.5, 151.3, 138.0, 137.4 (C_q Ph, Bn), 129.2, 128.4, 128.2, 128.1, 127.9, 126.3, 118.8, 114.5 (CH_{arom}), 103.4 (C-1), 101.1 (CH Ph), 93.2 (C-1′), 76.2 (C-2), 75.1 (CH_2 Bn), 74.0 (C-3), 71.1 (C-4), 69.1 (C-6), 68.6 (C-5′), 66.6 (C-4′), 66.2 (C-5), 62.0 (C-2′), 61.5 (C-6′), 60.5 (C-3′), 55.6 (OMe), 20.7, 20.6 (CH_3 Ac); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 103.4 ($J_{C1,H1}$ = 159 Hz, C-1), 93.2 ($J_{C1,H1}$ = 171 Hz, C-1′); HRMS $[M + Na]^+$ calcd for $C_{37}H_{40}N_6O_{12}Na$ 783.25964, found 783.25923.

Methyl 6-*O*-(2,3-Diazido-4,6-*O*-benzylidene-2,3-dideoxy-α/β-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (26). Donor **7** and acceptor **20** were condensed using the general protocol for Ph_2SO/Tf_2O-mediated glycosylations to yield disaccharide **26** (79%, α/β = 3:1). TLC R_f 0.65 (PE/EtOAc, 2/1, v/v); IR (neat, cm^{-1}) 698, 743, 1030, 1067, 1072, 2106. Spectroscopic data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.43−7.49 (m, 2H, CH_{arom}), 7.25−7.40 (m, 18H, CH_{arom}), 5.62 (s, 1H, CH Ph), 5.01 (d, 1H, J = 10.8 Hz, C*H*H Bn), 4.95 (d, 1H, J = 11.1 Hz, C*H*H Bn), 4.77−4.84 (m, 3H, CH_2 Bn, H-1′), 4.68 (d, 1H, J = 12.1 Hz, CH*H* Bn), 4.60 (d, 1H, J = 11.1 Hz, CH*H* Bn), 4.59 (d, 1H, J = 3.5 Hz, H-1), 4.17 (dd, 1H, J = 3.2, 8.8 Hz, H-6′), 3.98−4.05 (m, 3H, H-3, H-3′, H-4′), 3.85 (d, 1H, J = 2.8 Hz, H-2′), 3.71−3.83 (m, 4H, H-5, H-5′, H-6, H-6′), 3.63 (dd, 1H, J = 1.5, 11.3 Hz, H-6), 3.52 (dd, 1H, J = 3.5, 9.6 Hz, H-2), 3.46 (t, 1H, J = 9.4 Hz, H-4), 3.37 (s, 3H, OMe); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 138.5, 137.9, 137.8, 136.8 (C_q), 129.0, 128.5, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7, 125.8 (CH_{arom}), 101.6 (CH Ph), 98.6 (C-1′), 97.9 (C-1), 82.0 (C-3), 79.9 (C-2), 77.5 (C-4′), 77.1 (C-4), 75.7, 74.9, 73.3 (CH_2 Bn), 69.6 (C-5), 68.5 (C-6′), 66.5 (C-6), 64.1 (C-5′), 62.6 (C-2′), 59.1 (C-3′), 55.3 (OMe); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 98.6 ($J_{C1,H1}$ = 174 Hz, C-1′), 97.9 ($J_{C1,H1}$ = 171 Hz, C-1); HRMS $[M + NH_4]^+$ calcd for $C_{41}H_{48}N_7O_9$ 782.35080, found 782.35125.

Methyl 4-*O*-(2,3-Diazido-4,6-*O*-benzylidene-2,3-dideoxy-α/β-D-mannopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (27). Donor **7** and acceptor **21** were condensed using the general protocol for Ph_2SO/Tf_2O-mediated glycosylations to yield disaccharide **27** (66%, α/β = 5:1). TLC R_f 0.40 (PE/EtOAc, 3/1, v/v); IR (neat, cm^{-1}) 698, 737, 1028, 1047, 1096, 2106, 2928. Spectroscopic data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.44−7.49 (m, 2H, CH_{arom}), 7.23−7.41 (m, 18H, CH_{arom}), 5.59 (s, 1H, CH Ph), 5.16 (s, 1H, H-1′), 5.11 (d, 1H, J = 11.4 Hz, C*H*H Bn), 4.74 (d, 1H, J = 12.1 Hz, C*H*H Bn), 4.60−4.68 (m, 3H, CH*H* Bn, CH*H* Bn, H-1), 4.57 (d, 1H, J = 12.0 Hz, C*H*H Bn), 4.52 (d, 1H, J = 11.9 Hz, CH*H* Bn), 4.05 (dd, 1H, J = 4.7, 10.3 Hz, H-6′), 3.98−4.01 (m, 2H, H-3′, H-4′), 3.94 (t, 1H, J = 9.1 Hz, H-3), 3.80−3.86 (m, 1H, H-5′), 3.79 (t, 1H, J = 9.2 Hz, H-4), 3.63−3.74 (m, 4H, H-5, H-6, H-6, H-6′), 3.53−3.58 (m, 2H, H-2, H-2′), 3.39 (s, 3H, OMe); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 138.1, 137.7, 136.9 (C_q), 129.0, 128.9, 128.8, 128.7, 128.5, 128.3, 128.2, 128.1, 128.0, 127.6, 127.0, 125.8 (CH_{arom}), 101.6 (CH Ph), 100.0 (C-1′), 97.7 (C-1), 81.2 (C-3), 80.3 (C-2), 77.3 (C-4′), 76.7 (C-4), 75.5, 73.6, 73.2 (CH_2 Bn), 69.4 (C-5), 68.8, 68.5 (C-6, C-6′), 64.8 (C-5′), 62.6 (C-2′), 59.2 (C-3′), 55.4 (OMe); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 100.0 ($J_{C1,H1}$ = 176 Hz, C-1′), 97.7 ($J_{C1,H1}$ = 167 Hz); HRMS $[M + NH_4]^+$ calcd for $C_{41}H_{48}N_7O_9$ 782.35080, found 782.35123.

***p*-Methoxyphenyl 3-*O*-(2,3-Diazido-4,6-*O*-benzylidene-2,3-dideoxy-α/β-D-mannopyranosyl)-2-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside (28).** Donor **7** and acceptor **22** were condensed using the general protocol for Ph_2SO/Tf_2O-mediated glycosylations to yield disaccharide **28** (81%, α/β = 1:1): TLC R_f 0.44 (PE/EtOAc, 2/1, v/v); IR (neat, cm^{-1}) 696, 729, 1057, 1078, 1219, 1506, 2104; ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.51−7.60 (m, 4H, CH_{arom}), 7.32−7.48

(m, 26H, CH_{arom}), 7.06 (d, 4H, J = 9.0 Hz, CH_{arom}), 6.80−6.85 (m, 4H, CH_{arom}), 5.61 (s, 1H, CH Ph-α), 5.59 (s, 1H, CH Ph-β), 5.56 (s, 1H, CH Ph-α), 5.55 (s, 1H, CH Ph-β), 5.10 (d, 1H, J = 11.5 Hz, C*H*H Bn-β), 4.98 (s, 1H, H-1′α), 4.98 (d, 1H, J = 10.8 Hz, C*H*H Bn-α), 4.93 (s, 1H, H-1′β), 4.90 (d, 1H, J = 7.8 Hz, H-1), 4.90 (d, 1H, J = 7.7 Hz, H-1), 4.79 (d, 1H, J = 10.9 Hz, CH*H* Bn-α), 4.67 (d, 1H, J = 11.6 Hz, CH*H* Bn-β), 4.36 (dd, 2H, J = 3.4, 12.2 Hz, H-6α, H-6β), 4.26−4.32 (m, 3H, H-4α, H-4β, H-6′β), 4.00−4.22 (m, 8H, H-2α, H-2β, H-3′α, H-4′α, H-5′α, H-6α, H-6β, H-6′β), 3.81−3.90 (m, 5H, H-2′α, H-3α, H-3β, H-4′β, H-6′α), 3.73−3.78 (m, 7H, H-6′α, CH_3 OMe-α, CH_3 OMe-β), 3.51 (s, 1H, H-5), 3.46 (s, 1H, H-5), 3.30 (d, 1H, J = 3.5 Hz, H-2′β), 3.23−3.27 (m, 1H, H-5′β), 3.21 (dd, 1H, J = 3.6, 10.1 Hz, H-3′β); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 155.4, 155.4, 151.3, 138.5, 137.8, 137.6, 137.4, 137.0, 136.5 (C_q), 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.3, 128.1, 127.9, 126.3, 126.2, 126.0, 125.8, 125.3, 118.9, 118.7, 114.5, 114.4 (CH_{arom}), 103.4, 103.2 (C-1α, C-1β), 101.6, 101.5, 101.4 (C-1′β, CH Ph, CH Ph), 101.1, 100.5 (CH Ph), 93.8 (C-1′α), 79.1 (C-2), 77.5 (C-4′α), 77.2, 76.7 (C-3), 76.2 (C-2), 75.6 (C-4), 75.5, 75.5 (CH_2 Bn), 73.8 (C-4′β), 70.9 (C-4), 69.1, 68.8 (C-6), 68.4, 68.3 (C-6′α, C-6′β), 68.0 (C-5′β), 66.6, 66.1 (C-5α, C-5β), 63.9 (C-5′α), 62.5, 62.4 (C-2′α, C-2′β), 60.3 (C-3′β), 59.1 (C-3′α), 55.6 (OMe); 13C-HMBC ($CDCl_3$, 100 MHz) δ 103.4 ($J_{C1,H1}$ = 161 Hz, C-1), 103.2 ($J_{C1,H1}$ = 159 Hz, C-1), 101.4 ($J_{C1,H1}$ = 164 Hz, C-1′β), 93.8 ($J_{C1,H1}$ = 171 Hz, C-1′α); HRMS $[M + NH_4]^+$ calcd for $C_{40}H_{44}N_7O_{10}$ 782.31442, found 782.31459.

Methyl 6-*O*-(Methyl 4-*O*-acetyl-2,3-diazido-2,3-dideoxy-α/β-D-mannopyranosyl uronate)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (29). Donor **8*β*** and acceptor **20** were condensed using the general protocol for Ph_2SO/Tf_2O-mediated glycosylations to yield disaccharide **29** (94%, α/β = 1:5.5). TLC R_f α 0.55, β 0.45 (toluene/EtOAc, 3/1, v/v); IR (neat, cm^{-1}) 1065, 1751,2106, 2916. Spectroscopic data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.26−7.38 (m, 15H, CH_{arom}), 5.24 (t, 1H, J = 9.8 Hz, H-4′), 5.00 (d, 1H, J = 10.9 Hz, C*H*H Bn), 4.87 (d, 1H, J = 11.7 Hz, C*H*H Bn), 4.81 (d, 1H, J = 10.9 Hz, CH*H* Bn), 4.78 (d, 1H, J = 12.0 Hz, C*H*H Bn), 4.64 (d, 1H, J = 12.1 Hz, CH*H* Bn), 4.58 (d, 1H, J = 11.7 Hz, CH*H* Bn), 4.55 (d, 1H, J = 3.5 Hz, H-1), 4.34 (s, 1H, H-1′), 4.08−4.13 (m, 1H, H-6), 4.01 (t, 1H, J = 9.2 Hz, H-3), 3.77−3.84 (m, 1H, H-5), 3.79 (d, 1H, J = 9.6 Hz, H-5′), 3.73 (s, 3H, CH_3 CO_2Me), 3.71 (d, 1H, J = 3.5 Hz, H-2′), 3.46−3.53 (m, 2H, H-3′, H-6), 3.45 (dd, 1H, J = 3.6, 10.2 Hz, H-2), 3.36 (t, 1H, J = 9.2 Hz, H-4), 3.35 (s, 3H, OMe), 2.08 (s, 3H, CH_3 Ac); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 169.1, 166.8 (C═O Ac, CO_2Me), 138.6, 138.3, 138.0 (C_q Bn), 128.4, 128.3, 128.1, 128.0, 127.9, 127.7, 127.6 (CH_{arom}), 100.2 (C-1′), 97.8 (C-1), 81.9 (C-3), 79.9 (C-2), 77.2 (C-4), 75.7, 74.5 (CH_2 Bn), 73.7 (C-5 or C-5′), 73.4 (CH_2 Bn), 69.4 (C-5 or C-5′), 68.9 (C-6), 67.4 (C-4′), 62.2 (C-2′), 60.9 (C-3′), 55.1 (OMe), 52.8 (CH_3 CO_2Me), 20.5 (CH_3 Ac); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 100.2 ($J_{C1,H1}$ = 159 Hz, C-1′), 97.8 ($J_{C1,H1}$ = 172 Hz, C-1); HRMS $[M + Na]^+$ calcd for $C_{37}H_{42}N_6O_{11}Na$ 769.28038, found 769.28029.

Methyl 4-*O*-(Methyl 4-*O*-acetyl-2,3-diazido-2,3-dideoxy-α/β-D-mannopyranosyl uronate)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (30). Donor **8*β*** and acceptor **21** were condensed using the general protocol for Ph_2SO/Tf_2O-mediated glycosylations to yield disaccharide **30** (49%, α/β = 1:3.5). TLC R_f 0.27, 0.38 (PE/EtOAc, 2/1, v/v); IR (neat, cm^{-1}) 1041, 1751, 2106, 2924. Spectroscopic data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.22−7.45 (m, 15H, CH_{arom}), 5.10 (t, 1H, J = 10.0 Hz, H-4′), 5.02 (d, 1H, J = 11.4 Hz, C*H*H Bn), 4.84 (d, 1H, J = 11.4 Hz, CH*H* Bn), 4.78 (d, 1H, J = 12.1 Hz, C*H*H Bn), 4.72 (d, 1H, J = 12.1 Hz, C*H*H Bn), 4.60 (d, 1H, J = 3.7 Hz, H-1), 4.57 (d, 1H, J = 12.2 Hz, CH*H* Bn), 4.53 (d, 1H, J = 0.9 Hz, H-1′), 4.36 (d, 1H, J = 12.1 Hz, CH*H* Bn), 3.93 (t, 1H, J = 9.0 Hz, H-3), 3.87 (t, 1H, J = 9.2 Hz, H-4), 3.72−3.77 (m, 2H, H-5, H-6), 3.62 (dd, 1H, J = 2.2, 10.8 Hz, H-6), 3.49−3.53 (m, 5H, H-2, H-5′, CH_3 CO_2Me), 3.38 (s, 3H, OMe), 3.27 (dd, 1H, J = 0.4, 3.3 Hz, H-2′), 2.98 (dd, 1H, J = 3.4, 10.2 Hz, H-3′), 2.07 (s, 3H, CH_3 Ac); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 169.2, 166.6 (C═O Ac, CO_2Me), 139.3, 138.0, 137.6 (C_q Bn), 128.8, 128.7, 128.4, 128.1, 127.8, 127.3, 127.1 (CH_{arom}), 100.2 (C-1′), 98.2 (C-1), 80.0 (C-4), 79.3 (C-2), 78.4 (C-3), 75.0 (CH_2 Bn), 73.8 (C-5′), 73.7, 73.4 (CH_2 Bn), 68.9 (C-5), 68.0 (C-6), 67.4 (C-4′), 62.5 (C-2′), 60.9 (C-3′), 55.4 (OMe), 52.6 (CH_3 CO_2Me), 20.5 (CH_3 Ac); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 100.2 ($J_{C1,H1}$ = 159 Hz, C-1′), 98.2 ($J_{C1,H1}$ = 168 Hz, C-1); Spectroscopic data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.28−7.40 (m, 15H, CH_{arom}), 5.40 (d, 1H, J = 3.3 Hz, H-1′), 5.29 (t, 1H, J = 8.2 Hz, H-4′), 5.11 (d, 1H, J = 11.3 Hz, C*H*H Bn), 4.74 (d, 1H, J = 11.9 Hz, C*H*H Bn), 4.69 (d, 1H, J = 11.2 Hz, CH*H* Bn), 4.61−4.65 (m, 2H, CH*H* Bn, H-1), 4.55 (d, 1H, J = 11.8 Hz, C*H*H Bn), 4.48 (d, 1H, J = 11.8 Hz, CH*H* Bn), 4.24 (d, 1H, J = 7.9 Hz, H-5′), 3.97 (t, 1H, J = 9.1 Hz, H-3), 3.93 (dd, 1H, J = 3.5, 8.6 Hz, H-3′), 3.87 (t, 1H, J = 9.3 Hz, H-4), 3.65−3.77 (m, 3H, H-5, H-6), 3.59 (s, 3H, CH_3 CO_2Me), 3.55−3.57 (m, 1H, H-2), 3.52 (t, 1H, J = 3.4 Hz, H-2′), 3.39 (s, 3H, OMe), 2.09 (s, 3H, CH_3 Ac); HRMS $[M + Na]^+$ calcd for $C_{37}H_{42}N_6O_{11}Na$ 769.28038, found 769.28022.

p*-Methoxyphenyl 3-*O*-(Methyl 4-*O*-acetyl-2,3-diazido-2,3-dideoxy-α/β-D-mannopyranosyl uronate)-2-*O*-benzyl-4,6-O-benzylidene-β-D-galactopyranoside (31).** Donor **8*β and acceptor **22** were condensed using the general protocol for Ph_2SO/Tf_2O-mediated glycosylations to yield disaccharide **31** (89%, α/β = 1:7.5). TLC R_f α 0.55, β 0.45 (toluene/EtOAc, 2/1, v/v); IR (neat, cm^{-1}) 1057, 1219, 1504, 1751, 2106. Spectroscopic data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.52−7.56 (m, 2H, CH_{arom}), 7.28−7.44 (m, 8H, CH_{arom}), 7.06 (d, 2H, J = 9.1 Hz,CH_{arom}), 6.83 (d, 1H, J = 9.1 Hz, CH_{arom}), 5.59 (s, 1H, CH Ph), 5.13 (t, 1H, J = 10.0 Hz, H-4′), 5.09 (d, 1H, J = 11.6 Hz, C*H*H Bn), 4.87−4.89 (m, 2H, H-1, H-1′), 4.66 (d, 1H, J = 11.6 Hz, CH*H* Bn), 4.32−4.38 (m, 2H, H-4, H-6), 4.18 (dd, 1H, J = 7.8, 9.9 Hz, H-2), 4.07 (dd, 1H, J = 1.4, 12.4 Hz, H-6), 3.88 (dd, 1H, J = 3.5, 9.9 Hz, H-3), 3.78 (s, 3H, OMe), 3.72 (s, 3H, CH_3 CO_2Me), 3.69 (d, 1H, J = 9.7 Hz, H-5′), 3.50 (s, 1H, H-5), 3.32 (d, 1H, J = 3.3 Hz, H-2′) 3.02 (dd, 1H, J = 3.5, 10.2 Hz, H-3′), 2.07 (s, 3H, CH_3 Ac); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 169.2, 166.9 (C═O Ac, CO_2Me), 155.3, 151.3, 138.6, 137.6 (C_q Ph, Bn), 128.7, 128.6, 128.3, 128.2, 127.8, 126.3, 126.2, 118.5, 114.4 (CH_{arom}), 103.0 (C-1), 100.6 (C-1′), 100.4 (CH Ph), 79.2 (C-2), 77.0 (C-3), 75.4 (CH_2 Bn), 75.4 (C-4), 73.5 (C-5′), 68.7 (C-6), 67.4 (C-4′), 66.5 (C-5), 61.6 (C-2′), 61.0 (C-3′), 55.5 (OMe), 52.8 (CH_3 CO_2Me), 22.4 (CH_3 Ac); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 103.0 ($J_{C1,H1}$ = 158 Hz, C-1), 100.6 ($J_{C1,H1}$ = 161 Hz, C-1′); HRMS $[M + Na]^+$ calcd for $C_{36}H_{38}N_6O_{12}Na$ 769.24399, found 769.24405.

3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-1-*O*-(*N*-[phenyl]trifluoroacetimidoyl)-α/β-D-glucopyranoside (36). Compound **35**[26a,b] (0.95 g, 2.87 mmol) was dissolved in acetone (25 mL), followed by the addition of *N*-(phenyl)trifluoroacetimidoyl chloride[34] (0.87 mL, 5.73 mmol), K_2CO_3 (0.48 g, 3.44 mmol), and H_2O (1 mL). After stirring for 1.5 h at rt, the mixture was diluted with EtOAc and the organic layer was washed with saturated aqueous NaCl (2×), dried over Na_2SO_4, and concentrated in vacuo. Purification using flash column chromatography (silica gel, 33% EtOAc in PE) yielded the title product as a yellowish oil (1.38 g, 2.76 mmol, 96%, α/β = 1.4:1); TLC R_f 0.65 (PE/EtOAc, 2/1, v/v); IR (neat, cm^{-1}) 727, 907, 1209, 1747, 2114; ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC, T = 328 K) δ 7.27−7.33 (m, 4.8H, CH_{arom}), 7.09−7.15 (m, 2.4H, CH_{arom}), 6.82−6.87 (m, 4.8H, CH_{arom}), 6.43 (d, 1.4H, J = 2.6 Hz, H-1α), 5.59 (d, 1H, J = 8.2 Hz, H-1β), 5.48 (t, 1.4H, J = 9.9 Hz, H-3α), 5.11 (t, 1.4H, J = 9.7 Hz, H-4α), 5.00−5.08 (m, 2H, H-3β, H-4β), 4.21−4.30 (m, 2.4H, H-6α, H-6β), 4.07−4.14 (m, 3.8H, H-5α, H-6α, H-6β), 3.69−3.76 (m, 2.4H, H-2α, H-2β), 3.63−3.69 (m, 1H, H-5β), 2.09 (s, 4.2H, CH_3 Ac-α), 2.08 (s, 3H, CH_3 Ac-β), 2.06 (s, 4.2H, CH_3 Ac-α), 2.04 (s, 7.2H, CH_3 Ac-α, CH_3 Ac-β), 1.99 (s, 3H, CH_3 Ac-β); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 170.0, 169.9, 169.4, 169.4, 169.2,

169.1 (C═O Ac), 142.6 (C_q Ph), 128.6, 124.4, 118.9, 118.8 (CH_{arom}), 115.6 (q, J = 284 Hz, CF_3), 155.5 (q, J = 283 Hz, CF_3), 94.9 (C-1β), 92.8 (C-1α), 72.3, 72.1 (C-4), 70.2, 69.8 (C-3, C-5), 67.5, 67.5 (C-3, C-5), 62.4 (C-2), 61.1 (C-6, C-6), 60.1 (C-2), 20.1, 20.1, 20.5, 20.0 (CH_3 Ac); HRMS [M(hemiacetal)+Na]$^+$ calcd for $C_{12}H_{17}N_3O_8Na$ 354.09079, found 354.09059.

***N*-(Benzyl)benzyloxycarbonyl-5-aminopentyl *O*-3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α/β-D-glucopyranoside (37).** Donor **36** (0.52 g, 1.04 mmol) and *N*-(benzyl)benzyloxycarbonyl-5-aminopentanol (0.51 g, 1.56 mmol) were together coevaporated with toluene (2×), dissolved in dry Et_2O (21 mL), and stirred on activated MS for 30 min at rt. The solution was cooled to −40 °C, and TfOH (18 μL, 0.21 mmol) was added. The mixture was allowed to warm to −10 °C in 1 h followed by the addition of Et_3N (0.1 mL). EtOAc was added, and the organic phase was washed with saturated aqueous NaCl (2×), dried over Na_2SO_4, and concentrated in vacuo. The residue was dissolved in pyridine (6 mL) and treated with Ac_2O (2 mL) for 2 h, followed by the addition of EtOAc. The solution was washed with saturated aqueous NaCl (2×), dried over Na_2SO_4, and concentrated in vacuo. Purification using flash column chromatography (silica gel, 50% EtOAc in PE) gave the title compound as a yellowish oil (0.64 g, 0.99 mmol, 95%, α/β = 7.4:1). TLC R_f 0.41 (PE/EtOAc, 3/2, v/v); IR (neat, cm^{-1}) 698, 1030, 1219, 1694, 1746, 2108, 2922. Spectroscopic data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.13−7.40 (m, 10H, CH_{arom}), 5.47 (t, 1H, J = 9.9 Hz, H-3), 5.18 (d, 2H, J = 13.1 Hz, CH_2 Z), 5.04 (t, 1H, J = 9.8 Hz, H-4), 4.93 (d, 1H, J = 12.0 H, H-1), 4.50 (bs, 2H, CH_2 Bn), 4.28 (dd, 1H, J = 3.5, 12.2 Hz, H-6), 4.06 (d, 1H, J = 12.5 Hz, H-6), 3.94−4.02 (m, 1H, H-5), 3.60−3.75 (m, 1H, CH_2), 3.35−3.50 (m, 1H, CH_2), 3.26 (dd, 1H, J = 3.5, 10.6 Hz, H-2), 3.18−3.30 (m, 2H, CH_2), 2.08 (s, 3H, CH_3 Ac), 2.07 (s, 3H, CH_3 Ac), 2.03 (s, 3H, CH_3 Ac), 1.45−1.70 (m, 4H, CH_2), 1.24−1.42 (m, 2H, CH_2); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 170.2, 169.7, 169.3 (C═O Ac), 156.1 (d, J = 50 Hz, C═O Z), 137.7 (Cq Z), 136.6 (d, J = 10 Hz, Cq Bn), 128.3, 127.6, 127.0 (CH_{arom}), 97.5 (C-1), 70.0 (C-3), 68.3 (C-4), 68.3 (CH_2), 67.3 (C-5), 66.8 (CH_2 Z), 61.6 (C-6), 60.5 (C-2), 50.1 (d, J = 32 Hz, CH_2 Bn), 46.3 (d, J = 91 Hz, CH_2), 28.7 (CH_2), 27.3 (d, J = 48 Hz, CH_2), 23.0 (CH_2), 20.4, 20.3 (CH_3 Ac); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 97.5 ($J_{C1,H1}$ = 171 Hz, C-1). Diagnostic peak for the β-anomer: ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 101.7 (C-1); HRMS [M + Na]$^+$ calcd for $C_{32}H_{40}N_4O_{10}Na$ 663.26366, found 663.26356.

***N*-(Benzyl)benzyloxycarbonyl-5-aminopentyl *O*-2-Azido-2-deoxy-α-D-glucopyranoside (38).** Compound **37** (0.64 g, 0.99 mmol) was dissolved in MeOH (10 mL) and treated with NaOMe (cat.) for 4 h until full consumption of the starting material was indicated by TLC analysis. The mixture was neutralized by the addition of Amberlite-H$^+$, filtered, and concentrated in vacuo. The title compound was used in the next reaction step without further purification. TLC R_f 0.18 (PE/EtOAc, 1/3, v/v); IR (neat, cm^{-1}) 1028, 1682, 2106, 2930, 3552. Spectroscopic data for the α-anomer: ^{1}H NMR (MeOH-d_4, 400 MHz, HH−COSY, HSQC) δ 7.64−7.71 (m, 2H, CH_{arom}), 7.08−7.33 (m, 8H, CH_{arom}), 5.10 (d, 1H, J = 17.1 Hz, CH_2 Z), 4.80 (bs, 1H, H-1), 4.43 (bs, 2H, CH_2 Bn), 3.85 (t, 1H, J = 9.5 Hz, H-3), 3.77 (d, 1H, J = 11.9 Hz, H-6), 3.69 (dd, 1H, J = 5.0, 11.9 Hz, H-6), 3.49−3.64 (m, 2H, H-5, CH_2), 3.36 (t, 1H, J = 9.3 Hz, H-4), 3.25−3.32 (m, 1H, CH_2), 3.12−3.24 (m, 2H, CH_2), 3.02 (dd, 1H, J = 2.9, 10.4 Hz, H-2), 1.39−1.60 (m, 4H, CH_2), 1.20−1.38 (m, 2H, CH_2); ^{13}C-APT NMR (MeOH-d_4, 100 MHz, HSQC) δ 157.8 (d, J = 53 Hz, C═O Z), 138.7 (d, J = 9 Hz, C_q Z), 137.5 (d, J = 11 Hz, C_q Bn), 129.3, 128.6, 128.4, 128.1, 128.0 (CH_{arom}), 99.0 (C-1), 73.3 (C-5), 72.1 (C-3), 71.7 (C-4), 68.5, 68.2 (CH_2, CH_2 Z), 64.0 (C-2), 62.1 (C-6), 51.2 (d, J = 19 Hz, CH_2 Bn), 47.6 (d, J = 88 Hz, CH_2), 29.8 (CH_2), 28.4 (d, J = 46 Hz, CH_2), 24.1 (CH_2). Diagnostic peak for the β-anomer: ^{13}C-APT NMR (MeOH-d_4, 100 MHz, HSQC) δ 102.9 (C-1); HRMS [M + Na]$^+$ calcd for $C_{26}H_{34}N_4O_7Na$ 537.23197, found 537.23153.

***N*-(Benzyl)benzyloxycarbonyl-5-aminopentyl *O*-2-Azido-4,6-*O*-di-*tert*-butylsilylidene-2-deoxy-α-D-glucopyranoside (39).** Compound **38** (0.52 mmol) was coevaporated with toluene (2×) and dissolved in dry DMF (5 mL) under an argon atmosphere. The solution was cooled to −40 °C, and di-*tert*-butylsilylbistriflate (0.19 mL, 0.6 mmol) was dropwise added. The reaction was stirred for 1.5 h, followed by the addition of pyridine (0.2 mL). The mixture was diluted with EtOAc, washed with saturated aqueous NaCl (2×), dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification using flash column chromatography (silica gel, 14% EtOAc in PE) gave the title compound as a colorless oil (0.26 g, 0.39 mmol, 76%): TLC R_f 0.64 (PE/EtOAc, 3/1, v/v); $[\alpha]^{20}_D$ +52.2 (*c* 1, DCM); IR (neat, cm^{-1}) 827, 1088, 1688, 2108, 2858, 2934, 3429; ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC, T = 328 K) δ 7.16−7.34 (m, 10H, CH_{arom}), 5.17 (s, 2H, CH_2 Z), 4.75 (d, 1H, J = 3.4 Hz, H-1), 4.48 (s, 2H, CH_2 Bn), 4.07 (dd, 1H, J = 4.6, 9.6 Hz, H-6), 3.97 (dd, 1H, J = 8.6, 10.1 Hz, H-3), 4.83 (t, 1H, J = 10.0 Hz, H-6), 3.75 (ddd, 1H, J = 4.5, 9.4, 9.4 Hz, H-5), 3.65 (t, 1H, J = 8.8 Hz, H-4), 3.57−3.63 (m, 1H, CH_2), 3.36−3.44 (m, 1H, CH_2), 3.18−3.27 (m, 2H, CH_2), 3.14 (dd, 1H, J = 3.6, 10.2 Hz, H-2), 2.85 (bs, 1H, 3-OH), 1.48−1.62 (m, 4H, CH_2), 1.25−1.38 (m, 2H, CH_2), 1.06 (s, 9H, CH_3*t*Bu), 0.99 (s, 9H, CH_3*t*Bu); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 156.3 (d, J = 48 Hz, C═O Z), 137.7, 136.7 (C_q Bn), 128.4, 128.3, 127.8, 127.7, 127.1 (CH_{arom}), 98.0 (C-1), 77.9 (C-4), 71.3 (C-3), 68.1 (CH_2), 67.0 (CH_2 Z), 66.3 (C-6), 66.0 (C-5), 62.1 (C-2), 50.3 (d, J = 30 Hz, CH_2 Bn), 46.5 (d, J = 95 Hz, CH_2), 28.9, 27.7 (CH_2), 27.3, 26.8 (CH_3*t*Bu), 23.3 (CH_2), 22.5, 19.8 (C_q*t*Bu); HRMS [M + Na]$^+$ calcd for $C_{34}H_{50}N_4O_7SiNa$ 677.33410, found 677.33397.

Methyl (Phenyl 4-*O*-[2,3,4-tri-*O*-benzyl-6-*O*-{9-fluorenylmethoxycarbonyl}-α-D-glucopyranosyl]-2,3-diazido-2,3-dideoxy-1-thio-β-D-mannopyranosyl Uronate) (41). Imidate **40**[3b] (0.55 g, 0.65 mmol) and acceptor **16β** (0.18 g, 0.5 mmol) were together coevaporated with dry toluene (2×). Et_2O (13 mL, dried over 4 Å MS prior to use) was added, and the mixture was cooled to −40 °C. TfOH (9 μL, 0.1 mmol) was added, and the mixture was allowed to warm to −10 °C. Then pyridine (0.1 mL) was added, and the mixture was diluted with EtOAc and washed with saturated aqueous NaCl (2×). The organic layer was dried over Na_2SO_4, concentrated in vacuo, and purified using column chromatography (silica gel, 20% EtOAc in PE) to yield the title compound as a colorless oil (0.48 g, 0.48 mmol, 96%): TLC R_f 0.54 (PE/EtOAc, 3/1, v/v); $[\alpha]^{20}_D$ +36.6 (*c* 1, DCM); IR (neat, cm^{-1}) 696, 737, 1070, 1252, 1744, 2106; ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.75 (d, 2H, J = 7.6 Hz, CH_{arom}), 7.59 (dd, 2H, J = 7.6, 11.1 Hz, CH_{arom}), 7.20−7.45 (m, 24H, CH_{arom}), 5.00 (d, 1H, J = 3.9 Hz, H-1′), 4.99 (d, 1H, J = 11.4 Hz, C*H*H Bn), 4.89 (d, 1H, J = 4.89 Hz, C*H*H Bn), 4.67−4.81 (m, 4H, CH*H* Bn, CH_2 Bn, H-1), 4.57 (d, 1H, J = 10.8 Hz, CH*H* Bn), 4.33−4.44 (m, 3H, CH_2 Fmoc, H-6′), 4.30 (dd, 1H, J = 2.5, 11.9 Hz, H-6′), 4.22 (t, 1H, J = 7.3 Hz, CH Fmoc), 4.12−4.17 (m, 2H, H-2, H-4), 3.94 (t, 1H, J = 9.4 Hz, H-3′), 3.80 (d, 1H, J = 9.4 Hz, H-5), 3.72−3.77 (m, 4H, H-5′, CH_3 CO_2Me), 3.70 (dd, 1H, J = 3.5, 9.8 Hz, H-3), 3.60 (t, 1H, J = 9.5 Hz, H-4′), 3.52 (dd, 1H, J = 3.3, 9.8 Hz, H-2′); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 166.7 (C═O CO_2Me), 154.8 (C═O Fmoc), 143.3, 143.1, 141.1 (C_q Fmoc), 138.5, 137.9, 137.8 (C_q Bn), 133.2 (C_q SPh), 131.3, 129.2, 128.3, 127.9, 127.8, 127.6, 127.1, 125.0, 125.0, 119.9 (CH_{arom}), 99.6 (C-1′), 87.3 (C-1), 81.0 (C-3′), 79.9, 79.9 (C-2′, C-5),76.5, 76.3 (C-4, C-4′), 75.5, 75.1, 73.5 (CH_2 Bn), 70.1 (C-5′), 69.7 (CH_2 Fmoc), 65.8 (C-3), 65.7 (C-6′), 64.4 (C-2), 52.9 (CH_3 CO_2Me), 46.6 (CH Fmoc); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 99.6 ($J_{C1,H1}$ = 172 Hz, C-1′), 87.3 ($J_{C1,H1}$ = 155 Hz, C-1); HRMS [M + Na]$^+$ calcd for $C_{55}H_{52}N_6O_{11}SNa$ 1027.33070, found 1027.33138.

***N*-(Benzyl)benzyloxycarbonyl-5-aminopentyl *O*-(Methyl 4-*O*-[2,3,4-tri-*O*-benzyl-6-*O*-{9-fluorenylmethoxycarbonyl}-α-D-glucopyranosyl]-2,3-diazido-2,3-dideoxy-β-D-mannopyranosyl Uronate)-2-azido-4,6-*O*-di-*tert*-butylsilylidene-2-deoxy-α-D-glucopyranoside (42).** Compound **41** (0.29 g, 0.29 mmol) and Ph_2SO (70 mg, 0.35 mmol) were together coevaporated with toluene (2×). Freshly distilled DCM (5.8 mL) and activated molecular sieves (3 Å)

were added under an argon atmosphere, and the resulting mixture was stirred at rt for 20 min, followed by cooling to −80 °C. Tf_2O (59 μL, 0.35 mmol) was added, and the mixture was allowed to warm to −60 °C in 15 min. After cooling back to −80 °C, a solution of compound **39** (0.26 g, 0.39 mmol) in DCM (2 mL) was added. The reaction was warmed to −10 °C in 4 h, after which time pyridine (0.2 mL) was added. The mixture was diluted with EtOAc, washed with saturated aqueous NaCl (2×), dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by size-exclusion chromatography (Sephadex LH-20, eluted with DCM/MeOH, 1/1, v/v) gave the title compound as a colorless oil (0.45 g, 0.29 mmol, >98%): TLC R_f 0.36 (PE/EtOAc, 3/1, v/v); $[\alpha]^{20}_D$ +30.8 (*c* 1, DCM); IR (neat, cm^{-1}) 698, 739, 1043, 1072, 1094, 1256, 1697, 1749, 2108, 2934; ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC, *T* = 328 K) δ 7.71 (d, 2H, *J* = 7.6 Hz, CH_{arom}), 7.57 (t, 2H, *J* = 7.6 Hz, CH_{arom}), 7.18−7.40 (m, 29H, CH_{arom}), 5.17 (s, 2H, CH_2 Z), 5.09 (d, 1H, *J* = 3.1 Hz, H-1″), 4.97 (d, 1H, *J* = 11.1 Hz, C*H*H Bn), 4.92 (s, 1H, H-1′), 4.87 (d, 1H, *J* = 10.9 Hz, C*H*H Bn), 4.78 (d, 2H, *J* = 11.4 Hz, H-1, CH*H* Bn), 4.70−4.75 (m, 2H, CH_2 Bn), 4.58 (d, 1H, *J* = 10.9 Hz, CH*H* Bn), 4.49 (s, 2H, CH_2 Bn), 4.35−4.42 (m, 3H, H-6″, CH_2 Fmoc), 4.31 (dd, 1H, *J* = 2.1, 11.8 Hz, H-6″), 4.21 (t, 1H, *J* = 7.5 Hz, CH Fmoc), 4.16 (t, 1H, *J* = 9.4 Hz, H-4′), 4.01−4.08 (m, 2H, H-2′, H-6), 3.89−3.96 (m, 2H, H-3, H-3″), 3.78−3.89 (m, 3H, H-4, H-5′, H-6), 3.69−3.78 (m, 2H, H-5, H-5″), 3.67 (s, 3H, CH_3 CO_2Me), 3.55−3.62 (m, 2H, H-4″, C*H*H CH_2), 3.48−3.54 (m, 2H, H-2″, H-3′), 3.36−3.45 (m, 1H, CH*H* CH_2), 3.27 (dd, 1H, *J* = 3.4, 10.1 Hz, H-2), 3.20−3.26 (m, 2H, CH_2), 1.48−1.64 (m, 4H, CH_2), 1.26−1.38 (m, 2H, CH_2), 1.04 (s, 9H, CH_3*t*Bu), 0.97 (s, 9H, CH_3*t*Bu); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 166.9 (C═O CO_2Me), 156.3 (d, *J* = 50 Hz, C═O Z), 154.8 (C═O Fmoc), 143.3, 143.1, 141.1, 141.1 (C_q Fmoc), 138.5, 137.8, 137.8, 137.7 (C_q Bn), 136.7 (d, *J* = 17 Hz, C_q Bn), 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.5, 127.2, 127.0 (CH_{arom}), 125.0, 124.9, 119.9 (CH_{arom} Fmoc), 101.0 (C-1′), 99.1 (C-1″), 97.4 (C-1), 80.9 (C-3″), 79.7 (C-2″), 79.4 (C-3), 76.7 (C-5′), 76.4 (C-4″), 76.0 (C-4), 75.5 (C-4′), 75.4, 75.0, 73.3 (CH_2 Bn), 69.9 (C-5″), 69.7 (CH_2 Fmoc), 68.1 (CH_2), 67.0 (CH_2 Z), 66.6 (C-5), 66.3 (C-6), 65.6 (C-6″), 63.4 (C-3′), 62.6 (C-2′), 62.5 (C-2), 52.6 (CH_3 CO_2Me), 50.3 (d, *J* = 24 Hz, CH_2 Bn), 46.6 (CH Fmoc), 46.4 (d, *J* = 109 Hz, CH_2), 28.8 (CH_2), 27.5 (d, *J* = 33 Hz, CH_2), 27.2, 26.8 (CH_3*t*Bu), 23.3 (CH_2), 22.5, 19.7 (C_q*t*Bu); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 101.0 ($J_{C1,H1}$ = 158 Hz, C-1′), 99.1 ($J_{C1,H1}$ = 170 Hz, C-1″), 97.4 ($J_{C1,H1}$ = 170 Hz, C-1); HRMS $[M + NH_4]^+$ calcd for $C_{83}H_{100}N_{11}O_{18}Si$ 1566.70116, found 1566.70311.

***N*-(Benzyl)benzyloxycarbonyl-5-aminopentyl *O*-(Methyl 4-*O*-[2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl]-2,3-diazido-2,3-dideoxy-β-D-mannopyranosyl Uronate)-2-azido-4,6-*O*-di-*tert*-butylsilylidene-2-deoxy-α-D-glucopyranoside (43).** Compound **42** (0.39 g, 0.25 mmol) was dissolved in pyridine (5 mL) and treated with triethylamine (0.53 mL, 3.79 mmol) for 3 h, followed by addition of EtOAc. The organic phase was washed with H_2O (1×) and saturated aqueous NaCl (2×), dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification using flash column chromatography (silica gel, 33% EtOAc in PE) furnished the title compound as a colorless oil (0.32 g, 0.24 mmol, 94%): TLC R_f 0.36 (PE/EtOAc, 2/1, v/v); $[\alpha]^{20}_D$ +18.8 (*c* 1, DCM); IR (neat, cm^{-1}) 1028, 1072, 1686, 1751, 2108, 2858, 2934; ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC, *T* = 328 K) δ 7.18−7.40 (m, 25H, CH_{arom}), 5.17 (s, 2H, CH_2 Z), 5.00 (d, 1H, *J* = 3.4 Hz, H-1″), 4.93 (d, 1H, *J* = 11.2 Hz, C*H*H Bn), 4.91 (d, 1H, *J* = 0.8 Hz, H-1′), 4.84 (d, 1H, *J* = 11.1 Hz, C*H*H Bn), 4.81 (d, 1H, *J* = 3.3 Hz, H-1), 4.77 (d, 1H, *J* = 11.2 Hz, CH*H* Bn), 4.71 (s, 2H, CH_2 Bn), 4.60 (d, 1H, *J* = 11.2 Hz, CH*H* Bn), 4.50 (bs, 2H, CH_2 Bn), 4.14 (t, 1H, *J* = 9.4 Hz, H-4′), 4.05 (dd, 1H, *J* = 4.6, 9.8 Hz, H-6), 4.02 (d, 1H, *J* = 3.1 Hz, H-2′), 3.78−3.93 (m, 5H, H-3, H-3″, H-5′, H-5″, H-6), 3.70−3.78 (m, 2H, H-5, H-6″), 3.66 (s, 3H, CH_3 CO_2Me), 3.55−3.64 (m, 3H, H-4, H-6″, C*H*H CH_2), 3.53 (dd, 1H, *J* = 3.3, 9.7 Hz, H-3′), 3.35−3.47 (m, 3H, H-2″, H-4″, CH*H* CH_2), 3.28 (dd, 1H, *J* = 3.5, 10.0 Hz, H-2), 3.20−3.27 (m, 2H, CH_2), 2.02 (bs, 1H, 6″−OH), 1.48−1.63 (m, 4H, CH_2), 1.25−1.38 (m, 2H, CH_2), 1.04 (s, 9H, CH_3*t*Bu), 0.97 (s, 9H, CH_3*t*Bu); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 167.1 (C═O CO_2Me), 156.2 (d, *J* = 53 Hz, C═O Z), 138.5, 137.9, 137.7 (C_q Bn), 136.6 (d, *J* = 17 Hz, C_q Bn), 128.4, 128.3, 128.2, 127.8, 127.6, 127.4, 127.1, 127.0 (CH_{arom}), 100.9 (C-1′), 98.7 (C-1″), 97.3 (C-1), 80.8 (C-3″), 79.7 (C-2″), 79.4 (C-3), 77.2 (C-4″), 76.8 (C-5′), 75.9 (C-5″), 75.4 (CH_2 Bn), 74.9 (C-4′), 74.9, 73.3 (CH_2 Bn), 72.6 (C-4), 68.0 (CH_2), 67.0 (CH_2 Z), 66.5 (C-5), 66.3 (C-6), 63.1 (C-3′), 62.5 (C-2′), 62.4 (C-2), 61.4 (C-6″), 52.5 (CH_3 CO_2Me), 50.2 (d, *J* = 25 Hz, CH_2 Bn), 46.4 (d, *J* = 108 Hz, CH_2), 28.8 (CH_2), 27.4 (d, *J* = 34 Hz, CH_2), 27.1, 26.8 (CH_3*t*Bu), 23.2 (d, *J* = 11 Hz, CH_2), 22.4, 19.6 (C_q*t*Bu); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 100.9 ($J_{C1,H1}$ = 160 Hz, C-1′), 98.7 ($J_{C1,H1}$ = 169 Hz, C-1″), 97.3 ($J_{C1,H1}$ = 170 Hz, C-1); HRMS $[M + Na]^+$ calcd for $C_{68}H_{86}N_{10}O_{16}SiNa$ 1349.58847, found 1349.58962.

Methyl (Phenyl 2,3-diazido-4-*O*-*tert*-butyldimethylsilyl-2,3-dideoxy-1-thio-β-D-mannopyranosyl Uronate) (44). Compound **16β** (0.35 g, 1.0 mmol) was dissolved in dry DCM (20 mL) and cooled to 0 °C, followed by the addition of Et_3N (0.84 mL, 6 mmol) and TBS−OTf (0.45 mL, 2 mmol). The resulting solution was stirred overnight at rt. Saturated aqueous $NaHCO_3$ was added, and the mixture was diluted with EtOAc. The organic fraction was separated, washed with saturated aqueous NaCl (2×), dried over Na_2SO_4, and concentrated in vacuo. Purification using flash column chromatography (silica gel, 10% EtOAc in PE) yielded the title compound as amorphous white solids (0.41 g, 0.88 mmol, 88%): TLC R_f 0.67 (PE/EtOAc, 4/1, v/v); $[\alpha]^{20}_D$ −10.6 (*c* 1, DCM); IR (neat, cm^{-1}) 827, 1057, 1441, 1742, 2106, 2927; ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC) δ 7.38−7.43 (m, 2H, CH_{arom}), 7.24−7.30 (m, 3H, CH_{arom}), 4.87 (s, 1H, H-1), 4.20 (d, 1H, *J* = 3.2 Hz, H-2), 4.04 (t, 1H, *J* = 9.3 Hz, H-4), 3.78 (d, 1H, *J* = 9.2 Hz, H-5), 3.73 (s, 3H, CH_3 CO_2Me), 3.56 (dd, 1H, *J* = 3.5, 9.5 Hz, H-3), 0.83 (s, 9H, CH_3*t*Bu), 0.18 (s, 3H, CH_3 Me), 0.01 (s, 3H, CH_3 Me); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 167.3 (C═O CO_2Me), 133.4 (C_q SPh), 131.2, 129.1, 127.9 (CH_{arom}), 87.2 (C-1), 80.8 (C-5), 68.1 (C-3), 67.6 (C-2), 64.8 (C-4), 52.4 (CH_3 CO_2Me), 25.5 (CH_3*t*Bu), 17.8 (C_q*t*Bu), −4.8, −5.3 (CH_3 Me); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 87.2 ($J_{C1,H1}$ = 155 Hz, C-1); HRMS $[M + NH_4]^+$ calcd for $C_{19}H_{32}N_7O_4SSi$ 482.20003, found 482.20002.

***N*-(Benzyl)benzyloxycarbonyl-5-aminopentyl 3-*O*-(Methyl 4-*O*-[6-O-{methyl 2,3-diazido-4-*O*-*tert*-butyldimethylsilyl-2,3-dideoxy-β-D-mannopyranosyl Uronate}-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl]-2,3-diazido-2,3-dideoxy-β-D-mannopyranosyl Uronate)-2-azido-4,6-*O*-di-*tert*-butylsilylidene-2-deoxy-α-D-glucopyranoside (45).** Compound **44** (30 mg, 65 μmol), Ph_2SO (13 mg, 65 μmol), and TTBP (32 mg, 130 μmol) were together coevaporated with toluene (2×). Freshly distilled DCM (1.5 mL) and activated molecular sieves (3 Å) were added under an argon atmosphere, and the resulting mixture was stirred at rt for 20 min, followed by cooling to −80 °C. Tf_2O (11 μL, 65 μmol) was added, and the mixture was stirred at −80 °C for 20 min. Then a solution of compound **43** (95 mg, 71 μmol) in DCM (1 mL) was added. The reaction was stirred overnight at −30 °C and subsequently warmed to −10 °C, followed by the addition of triethylamine (0.1 mL). The mixture was diluted with EtOAc, washed with saturated aqueous NaCl (2×), dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash column chromatography (silica gel, 20% EtOAc in PE) and subsequent size-exclusion chromatography (Sephadex LH-20, eluted with DCM/MeOH, 1/1, v/v) to remove hydrolyzed donor gave the title compound as a colorless oil (81 mg, 48 μmol, 74%): TLC R_f 0.33 (PE/EtOAc, 4/1, v/v); $[\alpha]^{20}_D$ +10.9 (*c* 1, DCM); IR (neat, cm^{-1}) 696, 727, 907, 1692, 1751, 2106, 2931; ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC, *T* = 328 K, tentatively assigned based on ^{1}H NMR of compound **42**) δ 7.13−7.36 (m, 25H, CH_{arom}), 5.15 (s, 2H, CH_2 Z), 5.02 (d, 1H, *J* = 3.4 Hz, H-1″), 4.92 (d, 1H, *J* = 11.2 Hz, C*H*H Bn), 4.87 (s, 1H, H-1′), 4.76−4.83 (m, 2H, H-1, C*H*H Bn), 4.72 (d, 1H, *J* = 11.2 Hz, CH*H* Bn), 4.63−4.69 (m, 2H, CH_2 Bn), 4.58 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.47

(s, 2H, CH_2 Bn), 4.32 (s, 1H, H-1‴), 4.07 (t, 1H, J = 9.5 Hz, H-4′), 3.96−4.03 (m, 2H, H-2′, H-6), 3.89−3.96 (m, 2H, H-4‴, H-6″), 3.75−3.89 (m, 5H, H-3, H-3″, H-5′, H-5″, H-6), 3.65−3.75 (m, 5H, H-2‴, H-5, CH_3 CO_2Me), 3.54−3.64 (m, 7H, H-4, H-5‴, H-6″, CH_2, CH_3 CO_2Me), 3.43−3.48 (m, 2H, H-3′, H-4″), 3.35−3.42 (m, 2H, H-2″, CH_2), 3.26 (dd, 1H, J = 3.6, 9.9 Hz, H-2), 3.17−3.24 (m, 2H, CH_2), 3.12 (dd, 1H, J = 3.5, 9.5 Hz, H-3‴), 1.46−1.63 (m, 4H, CH_2), 1.25−1.37 (m, 2H, CH_2), 1.01 (s, 9H, CH_3*t*Bu), 0.94 (s, 9H, CH_3*t*Bu), 0.83 (s, 9H, CH_3*t*Bu), 0.14 (s, 3H, CH_3 Me), −0.03 (s, 3H, CH_3 Me); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC, tentatively assigned based on ^{13}C-APT NMR of compound **42**) δ 167.7, 167.0 (C═O CO_2Me), 156.3 (d, J = 53 Hz, C═O Z), 138.6, 138.5, 137.9, 137.8 (C_q Bn), 136.7 (d, J = 18 Hz, C_q Bn), 128.3, 127.9, 127.8, 127.7, 127.5, 127.1 (CH_{arom}), 101.0 (C-1′), 100.0 (C-1‴), 98.8 (C-1″), 97.4 (C-1), 81.1 (C-3″), 79.6 (C-2″, C-3), 77.5 (C-5‴), 76.9 (C-5″), 76.0, 75.9 (C-4″, C-5′), 75.3 (CH_2 Bn), 74.7 (C-4′), 74.4, 73.4 (CH_2 Bn), 70.9 (C-4), 68.2 (CH_2), 67.7 (C-4‴), 67.2, 67.1 (C-6″, CH_2 Z), 66.6 (C-5), 66.4 (C-6), 64.9 (C-3‴), 63.3 (C-3′), 62.7 (C-2′), 62.5, 62.4 (C-2, C-2‴), 52.7, 52.3 (CH_3 CO_2Me), 50.3 (d, J = 26 Hz, CH_2 Bn), 46.5 (d, J = 107 Hz, CH_2), 28.9 (d, J = 7 Hz, CH_2), 27.5 (d, J = 35 Hz, CH_2), 27.2, 26.9, 25.5 (CH_3*t*Bu), 23.3 (d, J = 10 Hz, CH_2), 22.5, 19.7, 17.9 (C_q*t*Bu), −4.7, −5.3 (CH_3 Me); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 101.0 ($J_{C1,H1}$ = 157 Hz, C-1′), 100.0 ($J_{C1,H1}$ = 160 Hz, C-1‴), 98.8 ($J_{C1,H1}$ = 168 Hz, C-1″), 97.4 ($J_{C1,H1}$ = 169 Hz, C-1); HRMS $[M + NH_4]^+$ calcd for $C_{81}H_{112}N_{17}O_{20}Si_2$ 1698.78026, found 1698.78165.

***N*-(Benzyl)benzyloxycarbonyl-5-aminopentyl 3-*O*-(Methyl 4-*O*-[6-O-{methyl 2,3-diazido-2,3-dideoxy-β-D-mannopyranosyl Uronate}-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl]-2,3-diazido-2,3-dideoxy-β-D-mannopyranosyl Uronate)-2-azido-2-deoxy-α-D-glucopyranoside (46).** A solution of compound **45** (69 mg, 41 μmol) in THF (1 mL) was cooled to 0 °C and treated with acetic acid (9 μL, 0.16 mmol) and tetrabutylammonium fluoride (1 M in THF, 82 μL, 82 μmol). The resulting solution was stirred for 3 h, followed by the addition of H_2O and EtOAc. The organic phase was washed with saturated aqueous NaCl (2×), dried over Na_2SO_4, concentrated in vacuo, and purified using flash column chromatography (silica gel, 50% EtOAc in PE) to yield the 4‴-OTBS-protected intermediate as a colorless oil (60 mg, 39 μmol, 96%). Spectroscopic data are reported for the 4‴-OTBS-protected intermediate: TLC R_f 0.44 (PE/EtOAc, 1/1, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC, T = 328 K) δ 7.19−7.41 (m, 25H, CH_{arom}), 5.20 (s, 2H, CH_2 Z), 5.06 (d, 1H, J = 3.3 Hz, H-1″), 4.97 (d, 1H, J = 11.1 Hz, C*H*H Bn), 4.83−4.93 (m, 3H, C*H*H Bn, H-1, H-1′), 4.78 (d, 1H, J = 11.3 Hz,CH*H* Bn), 4.75 (d, 1H, J = 11.9 Hz, C*H*H Bn), 4.69 (d, 1H, J = 11.7 Hz, CH*H* Bn), 4.63 (d, 1H, J = 11.8 Hz, CH*H* Bn), 4.52 (s, 2H, CH_2 Bn), 4.33 (s, 1H, H-1‴), 4.16 (t, 1H, J = 8.7 Hz, H-4′), 4.10 (d, 1H, J = 1.2 Hz, H-2′), 4.05 (d, 1H, J = 8.4 Hz, H-5′), 3.85−4.02 (m, 4H, H-3, H-3″, H-6, H-6″), 3.77−3.82 (m, 1H, H-6), 3.74 (s, 6H, CH_3 CO_2Me), 3.54−3.72 (m, 9H, H-2‴, H-3′, H-4, H-4‴, H-5, H-5″, H-5‴, H-6″, CH_2), 3.40−3.50 (m, 3H, H-2″, H-4″, CH_2), 3.37 (dd, 1H, J = 3.4, 10.2 Hz, H-2), 3.28 (bt, 2H, J = 5.6 Hz, CH_2), 3.17 (dd, 1H, J = 3.5, 9.5 Hz, H-3‴), 1.52−1.68 (m, 4H, CH_2), 1.32−1.40 (m, 2H, CH_2), 0.88 (s, 9H, CH_3*t*Bu), 0.20 (s, 3H, CH_3 Me), 0.02 (s, 3H, CH_3 Me); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC) δ 167.7, 167.2 (C═O CO_2Me), 156.4 (d, J = 50 Hz, C═O Z), 138.5, 138.4, 137.9, 137.8 (C_q), 136.7 (d, J = 23 Hz, C_q Bn), 128.5, 128.5, 128.3, 128.2, 128.0, 127.9, 127.8, 127.6, 127.2 (CH_{arom}), 100.6 (C-1′), 100.2 (C-1‴), 98.2 (C-1″), 97.0 (C-1), 83.8 (C-3), 81.1 (C-3″), 79.7 (C-2″), 77.5 (C-5‴), 76.2 (C-5′), 75.8 (C-4″), 75.4, 74.5 (CH_2 Bn), 74.1 (C-4′), 73.5 (CH_2 Bn), 71.3, 71.0 (C-4, C-5″), 69.6 (C-5), 67.9 (CH_2), 67.7 (C-4‴), 67.4 (C-6″), 67.1 (CH_2 Z), 64.9 (C-3‴), 62.7 (C-3′), 62.4 (C-2‴), 62.4 (C-6), 62.1, 62.0 (C-2, C-2′), 53.2, 52.4 (CH_3 CO_2Me), 50.3 (d, J = 20 Hz, CH_2 Bn), 46.4 (d, J = 111 Hz, CH_2), 28.8 (CH_2), 28.0 (d, J = 51 Hz, CH_2), 25.5 (CH_3*t*Bu), 23.2 (CH_2), 17.9 (C_q*t*Bu), −4.7, −5.2 (CH_3Me); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 100.6 ($J_{C1,H1}$ = 162 Hz, C-1′), 100.2 ($J_{C1,H1}$ = 160 Hz, C-1‴), 98.2 ($J_{C1,H1}$ = 171 Hz, C-1″), 97.0 ($J_{C1,H1}$ = 169 Hz, C-1). The 4‴-OTBS-protected intermediate (84 mg, 55 μmol) was dissolved in THF (0.5 mL) and treated with acetic acid (13 μL, 0.22 mmol) and tetrabutylammonium fluoride (1 M solution in THF, 0.17 mL, 0.17 mmol) at 0 °C. The resulting mixture was stirred at rt for 2 days, after which time H_2O and EtOAc were added. The organic phase was washed with saturated aqueous NaCl (2×), dried over Na_2SO_4, and concentrated in vacuo. Purification using flash column chromatography (silica gel, 75% EtOAc in PE) yielded the title compound as a colorless foam (60 mg, 42 μmol, 75%): TLC R_f 0.31 (PE/EtOAc, 1/2, v/v); $[\alpha]^{20}_D$ +28.1 (c 1, DCM); IR (neat, cm^{-1}) 698, 731, 1028, 1070, 1683, 1749, 2102, 2927, 3495; ^{1}H NMR ($CDCl_3$, 400 MHz, HH−COSY, HSQC, T = 328 K) δ 7.14−7.39 (m, 25H, CH_{arom}), 5.17 (s, 2H, CH_2 Z), 5.07 (d, 1H, J = 3.4 Hz, H-1″), 4.95 (d, 1H, J = 11.1 Hz, C*H*H Bn), 4.89 (d, 1H, J = 0.9 Hz, H-1′), 4.83−4.87 (m, 2H, C*H*H Bn, H-1), 4.76 (d, 1H, J = 11.2 Hz, CH*H* Bn), 4.73 (d, 1H, J = 11.9 Hz, C*H*H Bn), 4.67 (d, 1H, J = 11.8 Hz, CH*H* Bn), 4.60 (d, 1H, J = 11.8 Hz, CH*H* Bn), 4.50 (s, 2H, CH_2 Bn), 4.31 (s, 1H, H-1‴), 4.16 (t, 1H, J = 8.6 Hz, H-4′), 4.06−4.10 (m, 2H, H-2′, H-5′), 4.02 (t, 1H, J = 9.5 Hz, H-4‴), 3.96−4.01 (m, 1H, H-6″), 3.83−3.95 (m, 3H, H-3, H-3″, H-6), 3.77−3.80 (m, 4H, H-6, CH_3 CO_2Me), 3.75 (s, 3H, CH_3 CO_2Me), 3.63−3.72 (m, 5H, H-2‴, H-5, H-5″, H-5‴, H-6″), 3.53−3.62 (m, 3H, H-3′, H-4, CH_2), 3.38−3.47 (m, 3H, H-2″, H-4″, CH_2), 3.35 (dd, 1H, J = 3.4, 7.1 Hz, H-2), 3.33 (dd, 1H, J = 3.3, 6.7 Hz, H-3‴), 3.26 (bt, 2H, J = 5.7 Hz, CH_2), 1.52−1.65 (m, 4H, CH_2), 1.30−1.40 (m, 2H, CH_2); ^{13}C-APT NMR ($CDCl_3$, 100 MHz, HSQC, tentatively assigned based on ^{13}C-APT NMR of compound **45**) δ 169.4, 167.5 (C═O CO_2Me), 156.5 (d, J = 50 Hz, C═O Z), 138.5, 138.4, 137.9, 137.8 (C_q Bn), 136.7 (d, J = 31 Hz, C_q Bn), 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.6 (CH_{arom}), 100.6 (C-1′), 100.1 (C-1‴), 98.2 (C-1″), 97.0 (C-1), 83.7 (C-3), 81.2 (C-3″), 79.6 (C-2″), 76.1 (C-4″, C-5′), 75.5 (CH_2 Bn), 74.8 (C-5‴), 74.5 (CH_2 Bn), 73.9 (C-4′), 73.6 (CH_2 Bn), 71.0 (C-5, C-5″), 69.7 (C-4), 68.0 (C-6″), 67.8 (d, J = 9 Hz, CH_2), 67.4 (C-4‴), 67.2 (CH_2 Z), 62.7 (C-3′), 62.5 (C-6), 62.4 (C-3‴), 62.2 (C-2, C-3′), 61.9 (C-2′, C-2‴), 53.2, 52.8 (CH_3 CO_2Me), 50.3 (d, J = 18 Hz, CH_2 Bn), 46.5 (d, J = 114 Hz, CH_2), 28.9 (CH_2), 27.5 (d, J = 50 Hz, CH_2), 23.2 (CH_2); ^{13}C-GATED ($CDCl_3$, 100 MHz) δ 100.6 ($J_{C1,H1}$ = 162 Hz, C-1′), 100.1 ($J_{C1,H1}$ = 159 Hz, H-1‴), 98.2 ($J_{C1,H1}$ = 166 Hz, C-1″), 97.0 ($J_{C1,H1}$ = 169 Hz, C-1); HRMS $[M + NH_4]^+$ calcd for $C_{67}H_{82}N_{17}O_{20}$ 1444.59165, found 1444.59310.

5-Aminopentyl 3-*O*-(4-*O*-[6-O-{2,3-Di-*N*-acetamido-2,3-dideoxy-β-D-mannopyranosyl Uronate}-α-D-glucopyranosyl]-2,3-di-*N*-acetamido-2,3-dideoxy-β-D-mannopyranosyl Uronate)-2-*N*-acetamido-2-deoxy-α-D-glucopyranoside (47). Compound **46** (85 mg, 60 μmol) was dissolved in THF (1 mL) and treated with a freshly prepared solution of aqueous KOOH (0.36 mL, 0.5 M, KOH/H_2O_2 = 1:2) at 0 °C. The resulting solution was stirred at +4 °C overnight, after which time the mixture was neutralized by the addition of 1 M aqueous HCl (pH ∼7). EtOAc was added, and the organic phase was washed with saturated aqueous NaCl (2×). The combined aqueous layers were extracted with EtOAc (1×), and the organic fractions were together dried over Na_2SO_4 and concentrated in vacuo to give the crude diacid as a colorless oil (83 mg, 59 μmol): TLC R_f 0.09 (EtOAc/MeOH, 9/1, v/v + 1% AcOH); $[\alpha]^{20}_D$ +42.0 (c 0.2, DCM); IR (neat, cm^{-1}) 698, 735, 1028, 1072, 1605, 1694, 2106, 2924, 3437. The presence of two uronic acid moieties resulted in such broadening of the NMR signals that accurate assignment was impossible; however, the disappearance of the CO_2Me-signals was confirmed: HRMS $[M + H]^+$ calcd for $C_{65}H_{75}N_{16}O_{20}$ 1399.53380, found 1399.53576. The crude diacid (∼83 mg) was dissolved in THF/acetic acid (6 mL, 4/1, v/v) and treated with zinc dust (0.29 g, 4.43 mmol) overnight. Full conversion to the free amine-containing product was verified using LC-MS (R_t = 6.91 min, 10% → 90% B in C). The mixture was subsequently filtrated over a Whatmann filter-containing glass-filter funnel using DCM/MeOH, and the

filtrate was concentrated in vacuo. The residue was dissolved in THF/H_2O (4 mL, 1/1), and the mixture was basicified by the addition of solid $NaHCO_3$ (pH > 8). Acetic anhydride (0.11 mL, 1.18 mmol) was added, and the reaction was allowed to stir at rt until LC-MS analysis indicated complete conversion to the penta-*N*-acetamido intermediate (R_t = 9.00 min, 10% → 90% B in C). The mixture was diluted with DCM, washed with saturated aqueous NaCl (1×), dried over Na_2SO_4, and concentrated in vacuo. The residue was dissolved in THF/H_2O (4 mL, 1/1) and treated with 0.45 M aqueous KOH (0.13 mL) to remove any *O*-acetyls. The mixture was then acidified by the addition of 1 M aqueous HCl (pH < 5) and purged with argon. Palladium on activated charcoal (10 wt %, ~20 mg) was added, and the resulting suspension was consecutively purged with argon and H_2(g). The mixture was allowed to stir at rt under a blanket of H_2. When analysis by LC-MS indicated no further conversion to the product, extra palladium black was added and H_2 was again applied. Subsequently, the mixture was filtered through a Whatmann filter-containing glass-filter funnel, neutralized by the addition of saturated aqueous $NaHCO_3$, and concentrated in vacuo. Purification using HPLC and lyophilization resulted in the title compound as a white fluffy solid (12 mg, 12 μmol, 20% over five steps): ^{1}H NMR (D_2O, 600 MHz, HH−COSY, HSQC, T = 313 K) δ 5.25 (d, 1H, J = 3.5 Hz, H-1″), 5.09 (s, 1H, H-1$_{Man}$), 5.04 (s, 1H, H-1$_{Man}$), 4.97 (d, 1H, J = 3.0 Hz, H-1), 4.63 (d, 1H, J = 2.3 Hz, H-2$_{Man}$), 4.42−4.47 (m, 2H, H-2$_{Man}$, H-3$_{Man}$), 4.22 (dd, 1H, J = 3.5, 10.6 Hz, H-3$_{Man}$), 4.12−4.18 (m, 2H, H-2, H-6″), 4.04−4.08 (m, 3H, H-4$_{Man}$, H-5$_{Man}$, H-6″), 3.97−4.04 (m, 3H, H-3, H-5$_{Man}$, H-6), 3.88−3.95 (m, 2H, H-5″, H-6), 3.79−3.87 (m, 3H, H-4$_{Man}$, H-5, C*H*H O−CH_2), 3.74 (t, 1H, J = 10.7 Hz, H-3″), 3.70 (t, 1H, J = 9.5 Hz, H-4), 3.63−3.67 (m, 1H, C*H*H O−CH_2), 3.59 (t, 1H, J = 9.6 Hz, H-4″), 3.53 (dd, 1H, J = 3.6, 9.8 Hz, H-2″), 3.17 (t, 2H, J = 7.4 Hz, CH_2-NH_2), 2.21 (s, 3H, CH_3 Ac), 2.21 (s, 3H, CH_3 Ac), 2.19 (s, 3H, CH_3 Ac), 2.11 (s, 3H, CH_3 Ac), 2.09 (s, 3H, CH_3 Ac), 1.74−1.88 (m, 4H, CH_2), 1.56−1.67 (m, 2H, CH_2); ^{13}C-APT NMR (D_2O, 150 MHz, HSQC) δ 176.7, 176.1, 175.7, 175.7, 175.4, 175.2, 175.1 (C═O Ac, COOH), 100.8 (C-1$_{Man}$), 100.5 (C-1$_{Man}$), 99.5 (C-1″), 97.9 (C-1), 82.2 (C-3), 79.5 (C-5$_{Man}$, C-5$_{Man}$), 73.5 (C-3″), 72.7 (C-5), 72.4 (C-4$_{Man}$), 72.2 (C-2″), 71.8 (C-5″), 69.6 (C-4), 69.5 (C-4″), 68.7 (C-6″), 68.6 (O−CH_2) 67.5 (C-4$_{Man}$), 61.5 (C-6), 54.5 (C-3$_{Man}$), 54.4 (C-3$_{Man}$), 53.3 (C-2), 52.6 (C-2$_{Man}$), 51.9 (C-2$_{Man}$), 40.4 (CH_2−NH_2), 29.1, 27.5, 23.5 (CH_2), 22.9, 22.8, 22.7 (CH_3 Ac); ^{13}C-HMBC (D_2O, 150 MHz) δ 100.8 ($J_{C1,H1}$ = 162 Hz, C-1$_{Man}$), 100.5 ($J_{C1,H1}$ = 164 Hz, C-1$_{Man}$), 99.5 ($J_{C1,H1}$ = 171 Hz, C-1″), 97.9 ($J_{C1,H1}$ = 172 Hz, C-1); HRMS $[M + H]^+$ calcd for $C_{39}H_{65}N_6O_{23}$ 985.40956, found 985.41023.

■ ASSOCIATED CONTENT

Supporting Information. NMR spectra of low-temperature experiments and all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

We thank C. Erkelens and F. Lefeber for their assistance with executing the NMR experiments. This research was supported by Top Institute Pharma and The Netherlands Organization of Scientific Research (NWO, Vidi grant). We thank Joris van Dam for the journal cover art.

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