Mapping the reactivity and selectivity of 2-azidofucosyl donors for the efficient assembly of N-acetyl fucosamine containing bacterial oligosaccharides

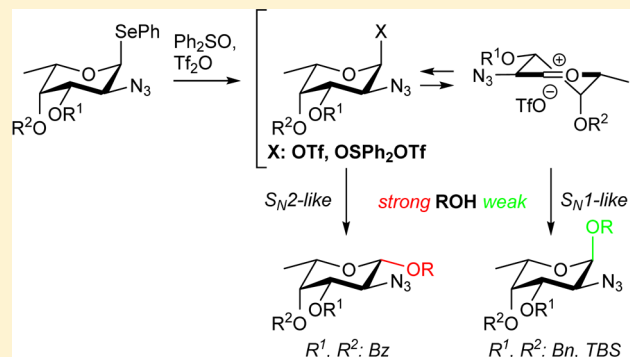Hagen, B.; Ali, S.; Overkleeft, H.S.; Marel, G.A. van der; Codee, J.D.C.

Mapping the Reactivity and Selectivity of 2-Azidofucosyl Donors for the Assembly of *N*-Acetylfucosamine-Containing Bacterial Oligosaccharides

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ⓢ Supporting Information

ABSTRACT: The synthesis of complex oligosaccharides is often hindered by a lack of knowledge on the reactivity and selectivity of their constituent building blocks. We investigated the reactivity and selectivity of 2-azidofucosyl ($FucN_3$) donors, valuable synthons in the synthesis of 2-acetamido-2-deoxyfucose (FucNAc) containing oligosaccharides. Six $FucN_3$ donors, bearing benzyl, benzoyl, or *tert*-butyldimethylsilyl protecting groups at the C3-*O* and C4-*O* positions, were synthesized, and their reactivity was assessed in a series of glycosylations using acceptors of varying nucleophilicity and size. It was found that more reactive nucleophiles and electron-withdrawing benzoyl groups on the donor favor the formation of β-glycosides, while poorly reactive nucleophiles and electron-donating protecting groups on the donor favor α-glycosidic bond formation. Low-temperature NMR activation studies of Bn- and Bz-protected donors revealed the formation of covalent $FucN_3$ triflates and oxosulfonium triflates. From these results, a mechanistic explanation is offered in which more reactive acceptors preferentially react via an S_N2-like pathway, while less reactive acceptors react via an S_N1-like pathway. The knowledge obtained in this reactivity study was then applied in the construction of α-$FucN_3$ linkages relevant to bacterial saccharides. Finally, a modular synthesis of the *Staphylococcus aureus* type 5 capsular polysaccharide repeating unit, a trisaccharide consisting of two FucNAc units, is described.

INTRODUCTION

The rare sugar 2-acetamido-2-deoxyfucose (FucNAc) is a constituent monosaccharide of several bacterial capsular polysaccharides (CPS).[1,2] Both D- and L-enantiomers are found in Nature, and they can be linked through either α- or β-glycosidic linkages (see Chart 1). For example, the repeating trisaccharide of the type 5 CPS of *Staphylococcus aureus* features both a β-D-FucNAc residue and an α-L-FucNAc moiety, while the type 8 CPS of *S. aureus* has D- and L-FucNAc constituents that are both 1,2-*cis*-linked.[3] The *S. aureus* strain M is built up from trisaccharide repeats,[4,5] which are composed of two galactosaminuronic acid (GalNAcA) residues and an α-D-FucNAc monosaccharide. Various O-antigens of *Escherichia coli* contain FucNAc residues as exemplified by the structures in Chart 1.[6,7]
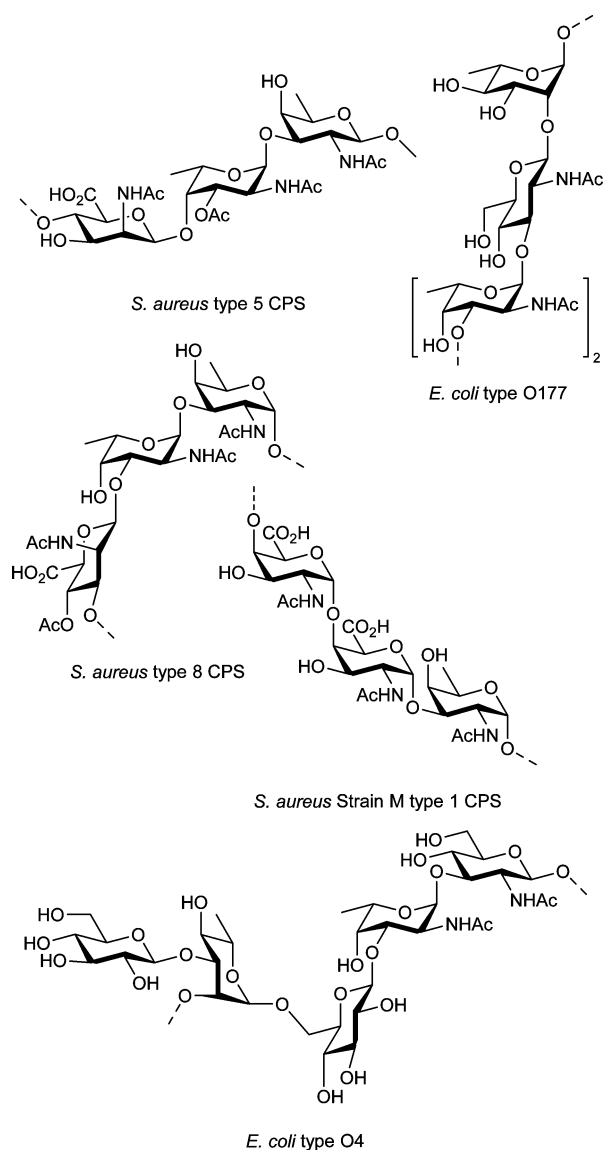
Well-defined fragments of bacterial polysaccharides have been used extensively in the development of (semi)-synthetic vaccines, as part of diagnostic tools, to unravel binding and interactions with carbohydrate binding receptors and as probes for bacterial CPS-biomachinery enzymes.[8] Organic synthesis can deliver these fragments as well-defined single molecules, devoid of any bacterial impurity and functionalized at predetermined sites with, for example, a conjugation handle for further manipulation.[9,10] The synthesis of complex oligosaccharides, such as those depicted in Chart 1, however, can be an arduous task, requiring a significant time and labor investment.

This is largely due to the complexity associated with the stereoselective construction of glycosidic linkages.[11−14] Few studies have been directed at the incorporation of fucosamine residues in oligosaccharides, and there is no general method to install the challenging α-fucosamine linkage. There have been reports on the assembly of the trisaccharide repeating units of *S. aureus* type 5 and 8,[15−18] but the syntheses reported were developed to target a single trisaccharide providing little insight into the reactivity and selectivity of fucosamine building blocks in a broader context, thus making it difficult to transpose the outcome of these studies to other relevant oligosaccharide targets or synthetic approaches.

To facilitate the effective assembly of fucosamine-containing bacterial oligosaccharides, we here report an in-depth study of the reactivity and selectivity of a variety of fucosazide building blocks with the goal to understand and control the stereoselectivity of these donors. We investigated reactive intermediates formed upon activation of fucosazide donor synthons and we have formulated a mechanistic rationale to account for the stereoselectivity observed in fucosaminylation reactions. We applied the generated insight in the construction of several relevant 1,2-*cis*-fucosamine linkages as well as a modular synthesis of the *S. aureus* type 5 trisaccharide.

Chart 1. Structures of the Repeating Units of FucNAc-Containing Polysaccharides

S. aureus type 5 CPS

E. coli type O177

S. aureus type 8 CPS

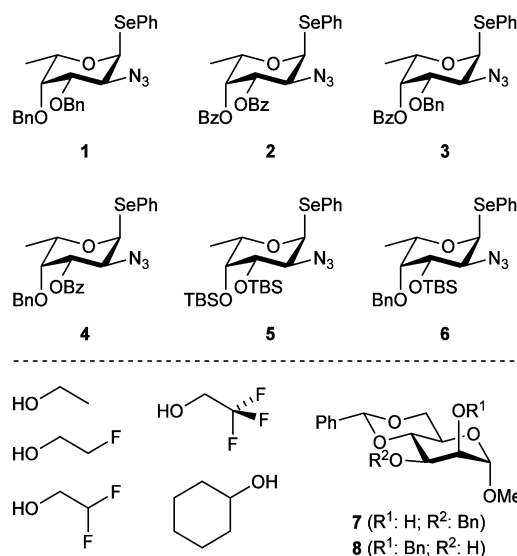*S. aureus* Strain M type 1 CPS

E. coli type O4

■ RESULTS AND DISCUSSION

To achieve the stereoselective introduction of 1,2-*cis* glycosamine linkages, the C2 amino functionality of a donor glycoside is generally masked as the nonparticipating azide.[19] To generate a series of fucosazide (FucN$_3$) donors, we decided to target phenylseleno fucosazides because selenoglycosides[20,21] are generally very potent glycosyl donors and phenylseleno fucosazides can be effectively generated from readily available fucal precursors.[22] To map the reactivity and selectivity of fucosazide donors, we investigated a set of donors having different protecting groups. Whereas the glycosylating properties of fucosazide donors have received relatively little attention, there is a large body of data available on the stereoselective introduction of fucosyl linkages.[23−34]

It appears that the α-fucosyl linkage can be installed with relative ease. For the stereoselective construction of this linkage, fucosyl building blocks, bearing acyl protecting groups at C3 and/or C4, are commonly used, and it is often assumed that these groups are capable of "remote participation".[23] Of note, tri-*O*-benzyl-protected fucosyl donors have also been
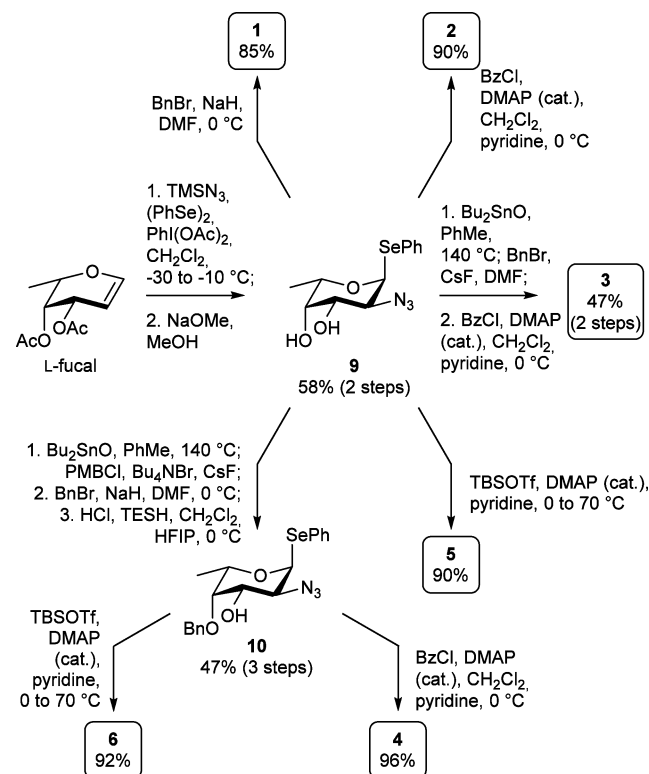
employed, and these have also been reported to provide the desired 1,2-*cis* fucosyl linkages with good selectivity.[25,26] No mechanistic rationale has been forwarded to account for this striking selectivity.

For our study, we generated six L-FucN$_3$ donors (**1−6**, Chart 2) from L-fucal, featuring benzyl, benzoyl, or *tert*-butyldimethylsilyl

Chart 2. Structures of L-FucN$_3$ Donors 1−6 and Model Acceptors

7 (R^1: H; R^2: Bn)
8 (R^1: Bn; R^2: H)

groups. We probed these donor fucosides in a series of glycosylation reactions using a preactivation protocol in which the donor glycosides were activated with the diphenyl sulfoxide (Ph$_2$SO)−triflic anhydride (Tf$_2$O) reagent couple.[35−37] This reagent combination provides a very powerful electrophile for activation of thio- and selenoglycosides, and it allows for the detection of reactive intermediates by low-temperature NMR spectroscopy to provide insight into the glycosylation mechanism of the preactivated donor glycosides.[38]

The synthesis of L-FucN$_3$ donors **1−6** is depicted in Scheme 1. Homogeneous azidoselenylation[22] of easily accessible L-fucal[17] installed the azide and the anomeric phenylseleno moiety in one step in the desired α-fucosyl configuration, accompanied by minor amounts of inseparable isomers. Deacetylation of the crude product mixture allowed separation, yielding diol **9** in 58% yield over two steps. Donors **1**, **2**, and **5** could be accessed in one step each from diol **9** by benzylation (BnBr, NaH in DMF, 85% yield), benzoylation (BzCl and a catalytic amount of DMAP in a mixture of CH$_2$Cl$_2$ and pyridine, 90% yield), and silylation (TBSOTf and a catalytic amount of DMAP in pyridine at elevated temperature, 85% yield), respectively. In the last case, standard silylation conditions employing TBSCl as the silylating agent and either imidazole in DMF, or DMAP and pyridine, failed to give the disilylated product. Donor **3**, bearing C3-*O*-benzyl and C4-*O*-benzoyl protection, was procured by Bu$_2$SnO-mediated, regioselective benzylation on the C3-*O* position followed by benzoylation of the remaining C4-*O* position using similar conditions as described for **2** to give **3** in 47% yield over two steps. A more elaborate protection sequence was required to access C4-*O*-benzyl donors **4** and **6**, owing to the less reactive nature of the C4 position. Thus, regioselective, Bu$_2$SnO-mediated *p*-methoxybenzylation of the C3-*O* position, benzylation of the remaining free C4 alcohol, followed by acid-mediated cleavage of the C3-*O*-PMB ether, using HCl in a mixture of

Scheme 1. Synthesis of L-FucN₃ Donors 1−6

Figure 1. Generation of reactive species from donors **1** and **2** (A). Partial ¹H NMR spectra (400 MHz, 193 K) of reactive species from **1** using 1.3 and 2.0 equiv of Ph₂SO (B and C, respectively) and **2** (1.3 equiv of Ph₂SO, D).

CH₂Cl₂ and hexafluoroisopropanol (HFIP),[39] gave key intermediate **10** in 47% yield over three steps. The use of oxidative conditions to remove the PMB group was avoided, owing to the potentially oxidation-sensitive phenylseleno moiety. With **10** in hand, donors **4** and **6** were obtained after benzoylation and silylation using conditions described above, in 96% and 92% yield, respectively.

We started our investigation with the detection of the reactive intermediates, generated upon activation of two different donor synthons: di-O-benzyl- and di-O-benzoyl fucosazides **1** and **2**, respectively. Thus, a mixture of **1** and Ph₂SO (1.3 equiv) in CD₂Cl₂ was treated with Tf₂O (1.3 equiv) at −80 °C (Figure 1A). After a ¹H NMR spectrum (Figure 1B) was recorded, two new anomeric signals appeared (δ 6.06 and 6.10 ppm), which were assigned as α-triflate **11** (J = 3.2 Hz) and α-oxosulfonium triflate **13** (J = 3.2 Hz), respectively, based on their chemical shift.[38] While the formation of the anomeric triflate was anticipated, oxosulfonium triflate formation under these conditions is quite surprising. The oxosulfonium species likely arises from reaction of the anomeric triflate with Ph₂SO present in the reaction mixture.[40,41] Because the amount of oxosulfonium fucosazide **13** is higher than what could be expected based on the excess of Ph₂SO (0.3 equiv), it appears that the selenodonor **1** does not require a full equivalent of Ph₂SO for complete activation. To account for complete activation of donor **1**, we assume that the electrophile, generated upon reaction of the anomeric phenylselenol group with the diphenylsulfonium bis-triflate activator (PhSe−SPh₂OTf), is reactive enough to activate the nucleophilic phenylselenium moiety. Addition of more Ph₂SO to the reaction mixture resulted in an increase of the signal at δ 6.10 ppm (Figure 1C), reinforcing the presence of oxosulfonium triflate **11**. In order to assess the stability of the two reactive intermediates, the NMR probe was gradually warmed with increments of 10 °C. Both triflate **11** and oxosulfonium triflate
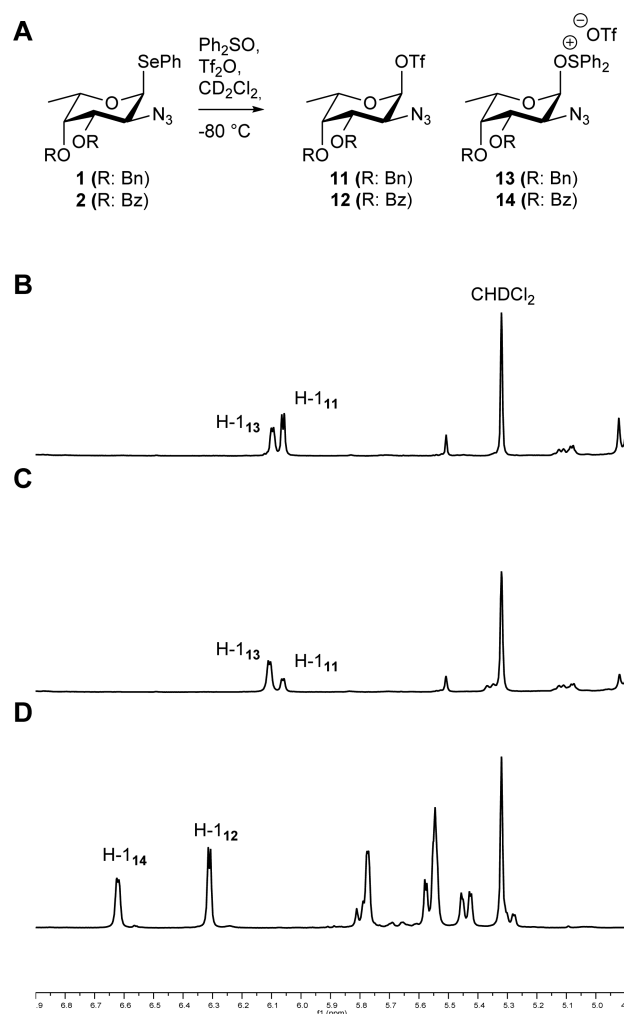
13 started to decompose at −20 °C. The activation of dibenzoyl donor **2** proceeded in a similar manner to provide α-triflate **12** and oxosulfonium triflate **14** (Figure 1D). These reactive intermediates proved to be more stable than their dibenzyl counterparts, with decomposition setting in around 0 °C.

Next, we investigated the behavior of donor fucosazides **1−6** in a series of glycosylation reactions. To this end, we applied a unified glycosylation protocol to all condensation reactions, involving preactivation of the donor glycoside at low temperature (in the presence of the non-nucleophilic base 2,4,6-tri-tert-butylpyrimidine (TTBP)[42]), then acceptor addition, subsequently warming the reaction mixture slowly to −40 °C, and finally quenching the reaction at this temperature. We used the set of model acceptors depicted in Chart 2 to map the selectivity of the fucosazide donors **1−6**. To study the dependency of acceptor nucleophilicity on the outcome of the glycosylation reactions a set of partially fluorinated ethanols was used.[43] In addition, three secondary alcohol acceptors were used: cyclohexanol, mannoside **7**, having an axial C2-OH, and mannoside **8**, with an equatorial C3-OH.[44,45]

Glycosylation of donors **1−6** with the series of ethanols (Table 1, rows A−D) revealed a clear dependency of the stereochemical outcome of the glycosylations on the nucleophilicity

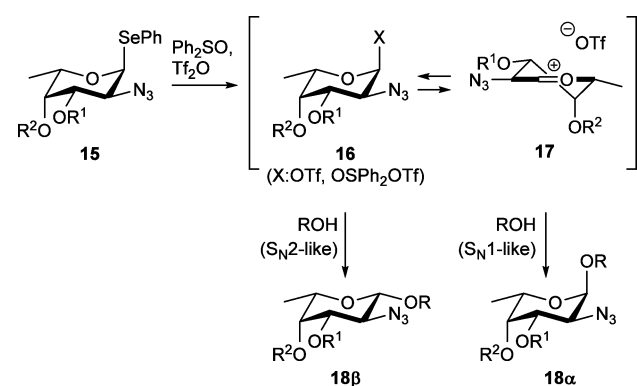**Table 1. Glycosylations of L-FucN$_3$ Donors 1−6 with Model Acceptors**

	A, Et (%)	B, FEt (%)	C, F$_2$Et (%)	D, F$_3$Et (%)	E, Cy (%)	F, 2-Man (%)	G, 3-Man (%)
1 (R^1, R^2: Bn)	88 (1:1)	72 (1:1)	81 (2:1)	80 (19:1)	75 (2:1)	68 (19:1)	72 (19:1)
2 (R^1, R^2: Bz)	59 (1:3)	34 (1:2)	74 (3:2)	50 (10:1)	38 (1:9)	38 (4:1)	64 (19:1)
3 (R^1: Bn; R^2: Bz)	61 (1:3)	56 (1:1)	76 (3:1)	77 (7:1)	75 (1:4)	58 (10:1)	54 (19:1)
4 (R^1: Bz; R^2: Bn)	58 (1:3)	60 (2:3)	80 (1:1)	45 (19:1)	71 (1:4)	68 (4:1)	64 (10:1)
5 (R^1, R^2: TBS)	63 (2:5)	81 (2:3)	75 (5:2)	84 (19:1)	84 (1:3)	67 (19:1)	73 (19:1)
6 (R^1: TBS; R^2: Bn)	81 (1:1)	80 (1:1)	87 (2:1)	90 (19:1)	80 (1:2)	74 (19:1)	64 (9:1)

^{a}Isolated yields reported; α/β ratios in parentheses.

of the acceptor alcohols. All donors showed the same trend: with decreasing nucleophilicity (increasing amount of fluorine atoms in the acceptors) α-selectivity increased. While the more reactive donors (**1**, **5**, and **6**) reacted in a nonselective manner with the most nucleophilic acceptor, ethanol (row A), the less reactive, benzoyl-bearing fucosazide donors reacted with moderate β-selectivity. With the reactive secondary alcohol, cyclohexanol (row E), a similar picture emerged: less reactive donors provided more β-product than the reactive fucosaminylating agents. The condensations of the secondary carbohydrate acceptors **7** and **8** (rows F and G) all proceeded with good to excellent α-selectivity, again with the more reactive donors providing better α-selectivity than their less reactive counterparts. Across the board, donors **1**, **5**, and **6** outperformed the benzoylated donors **2**−**4** in terms of yield of the glycosylation reactions.

The observed β-selectivity in the condensation reactions of the benzoylated fucosazide donors with ethanol and cyclohexanol strongly argue against a remote participation scenario for these donors.[23] The selectivity in these reactions is better explained with the α-anomeric triflates or oxosulfonium triflates **16** as glycosylating species (Scheme 2). The presence of benzoyl

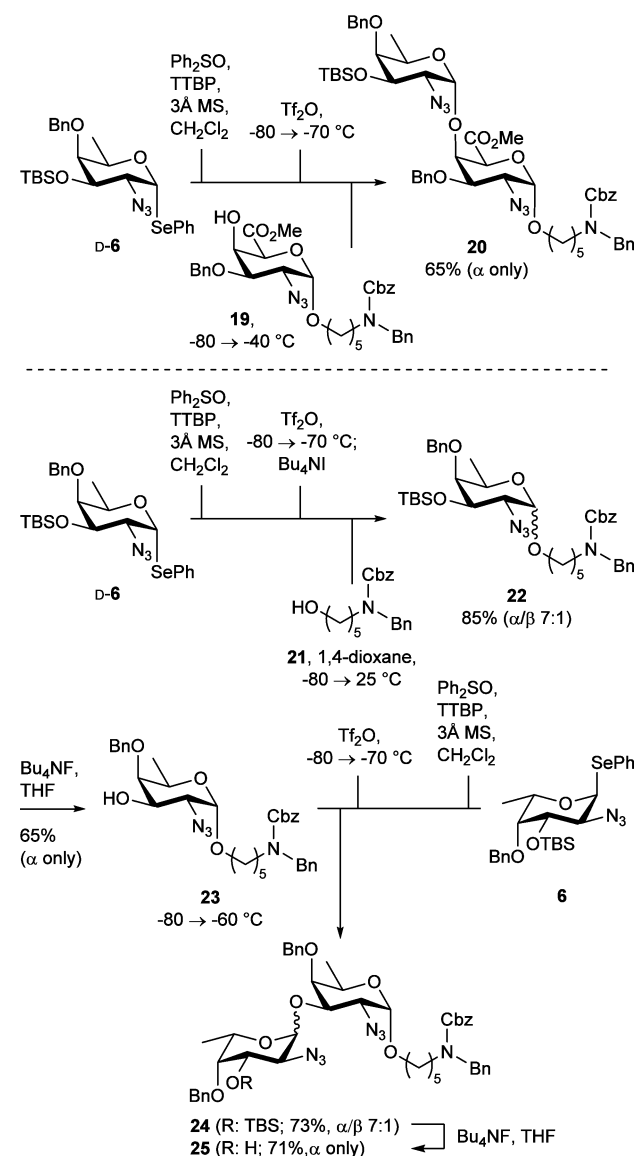**Scheme 2. Mechanistic Explanation for Observed Stereoselectivities**

groups on the fucosazide donors stabilizes these intermediates, as judged from the higher decomposition temperature found in the variable temperature NMR measurements. Strong nucleophiles can substitute the covalent α-triflates/oxosulfonium triflates with

inversion of configuration to provide the β-linked products (**18β**). Weaker nucleophiles, such as di- and trifluoroethanol and the carbohydrate alcohols (also featuring two or three electron withdrawing atoms at a β-position with respect to the alcohol function), are unable to directly displace a covalently bound leaving group and require a more electrophilic glycosylating agent to react. The covalent triflate/oxosulfonium species can serve as a reservoir for a more reactive oxocarbenium ion **17** with a loosely associated triflate counterion.[46,47] It is now well established that the geometry of an oxocarbenium ion can be decisive for the stereochemical course of a glycosylation reaction.[48−53] The fucosazide oxocarbenium ions that can form from the covalent triflates/oxosulfonium triflates can adopt a $^3H_4$-like conformation (as in **17**) in which the substituents at C2 and C4 are positioned properly to allow for stabilization of the electron depleted anomeric center, while the groups at C3 and C5 are positioned in sterically favorable pseudo-equatorial positions.[54] This oxocarbenium ion is preferentially attacked on the diastereotopic face that leads to the product via an energetically favorable chairlike transition state, leading to the 1,2-cis product **18α**. This reaction trajectory is sterically relatively unhindered, and it can account for the selective formation of the 1,2-cis-products as observed here. The fact that more electron-rich donors provide higher α-selectivity strongly supports this rationale.[55] It also provides an adequate explanation for glycosylations of highly reactive per-benzylated fucosyl donors previously reported in literature.[25,26]

The reactivity study described above has revealed a clear dependence of the stereochemical course of the glycosylations on both the reactivity of the donor glycoside and the reactivity of the acceptor alcohol. The best 1,2-cis selectivity is obtained with reactive fucosazide donors, bearing benzyl or silyl ether protecting groups and relatively weak nucleophiles, such as secondary carbohydrate alcohols.

Building on this knowledge, we set out to investigate the construction of a series of relevant glycosidic linkages, present in capsular polysaccharides of S. aureus. The repeating unit of the S. aureus strain M CPS (Figure 1) contains an α-D-FucNAc unit linked to two α-linked N-acetylgalactosaminuronic acid (GalNAcA) residues.[4,5] We anticipated that the glycosylation between a galacturonic acid C4-OH acceptor, generally considered to be a weak nucleophile, and a reactive fucosamine donor, would likely lead to a highly α-selective glycosylation.

Scheme 3. Synthesis of Protected *S. aureus* Strain M and Type 8 CPS Disaccharides 20 and 25

more reactive. Nucleophiles can displace the β-iodide in an S_N2-like fashion, leading to the selective formation of the α-product. When D-**6** was glycosylated with **21** using a slight modification of Bennett's protocol, product **22** was obtained in 85% yield with good α-selectivity. Removal of the TBS group facilitated separation of the anomers, giving pure **23** in 65% yield. In the next glycosylation event, the reactive L-fucosazide donor **6** was paired with D-fucosazide acceptor **23** in a Ph₂SO/Tf₂O-mediated preactivation glycosylation event to provide disaccharide **24** in 73% yield and high stereoselectivity. Removal of the TBS group under the agency of Bu₄NF allowed chromatographic separation of the two anomers, yielding the α-linked disaccharide **25** in 71% yield.

As a final endeavor, we set out to synthesize the repeating unit of the *S. aureus* type 5 CPS repeating unit (Scheme 4). Target trisaccharide **26** consists of a rare *N*-acetylmannosaminuronic acid (ManNAcA), a central α-linked L-FucNAc residue, and a terminal β-D-FucNAc connected to an aminopentanol spacer for future conjugation purposes. The central L-FucNAc contains a 3-*O* acetate group. The synthesis of this repeating unit has previously been reported by the groups of Adamo,[16] Boons,[17] and very recently, Demchenko.[15] Adamo and co-workers relied on a strategy starting from the nonreducing end and using glucosyl and rhamnosyl synthons to form the ManNAcA and FucNAc units, respectively. The final glycosylation between the L-FucN₃-containing disaccharide and a D-FucNAc unit proceeded with modest stereoselectivity. Demchenko and co-workers used a similar approach with glucosyl and fucosyl synthons. Boons and co-workers built the trisaccharide repeating unit, starting from the reducing end, using FucN₃ building blocks. The installation of the glycosidic linkage between the two FucN₃ units proved problematic, proceeding in low yield or with relatively poor stereoselectivity. The ManNAcA unit was installed using a nonoxidized 2-azidomannosyl (ManN₃) donor.[60]

Our strategy is presented in Scheme 4. In order to differentiate the C3′-*O* position from the other alcohols in the trisaccharide, this position was protected as an ester in fully protected intermediate **27**, while the others were masked as benzyl ethers. Based on the reactivity/selectivity study described above, we reasoned that the β-fucosamine linkage could be constructed using a disarmed fucosazide donor, such as D-**4**. For the pivotal α-glycosidic linkage between the L-FucN₃ and D-FucN₃ moieties, the use of reactive 3,4-di-*O*-TBS donor **5** was anticipated because of the highly α-selective glycosylations of this donor (Table 1). We thus aimed to use a FucN₃ donor for the installation of both the 1,2-*cis* and 1,2-*trans* fucosamine linkages. This will shorten the sequence of protecting group manipulations at the trisaccharide stage. For the introduction of the mannosaminuronic unit, we selected 2-azidomannuronate donor **28** because of the excellent β-selectivity observed with this class of donors as we have disclosed previously.[61,62] The use of a "pre-oxidized" mannosaminuronic acid synthon circumvents the necessity of a late-stage oxidation step in the assembly sequence.

To effect the β-selective glycosylation between donor D-**4** and spacer **21** in the absence of a participating group on the C2-position of the donor, several modifications of our standard glycosylation conditions were tested (data not shown). It was found that the use of ether as a cosolvent effectively increased the β-selectivity of the glycosylation. This is somewhat surprising given the fact that ether is commonly used to promote the formation of α-glycosidic linkages.[56,63,64]

Indeed, when D-fucosazide donor D-**6** was coupled to acceptor **19**, the α-linked disaccharide **20** was obtained as the sole product in 65% yield (Scheme 3).
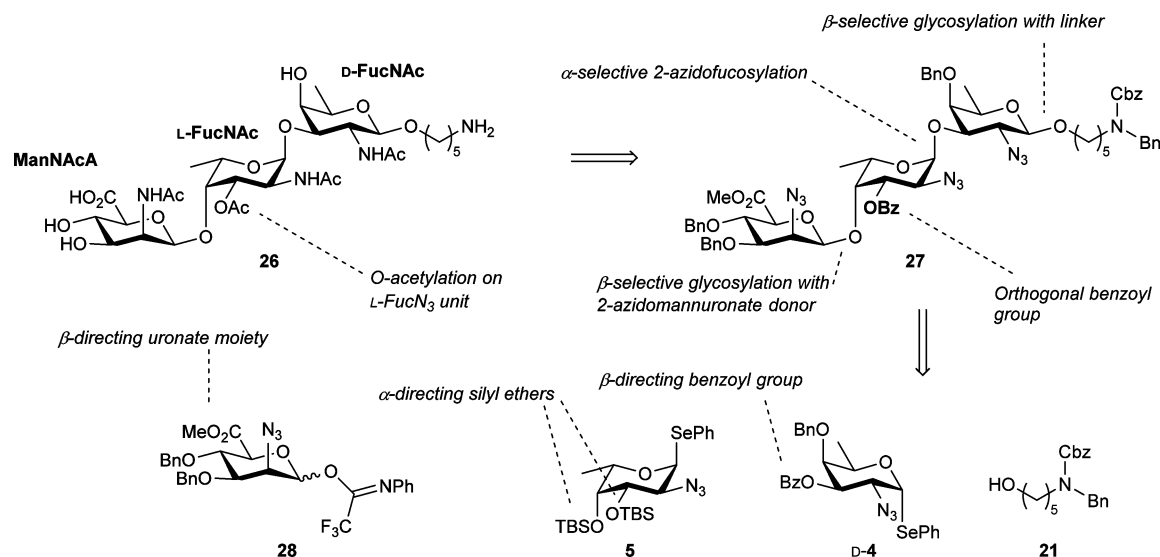
The repeating unit of *S. aureus* type 8 CPS contains two α-linked *N*-acetyl fucosamine units (Figure 1).[3] To investigate the construction of the α-linkage between the two fucosamine residues, we first generated an α-D-fucosazide acceptor bearing a spacer at its reducing end. Because the reactivity study described above indicated that nucleophilic primary alcohols react in a non- or β-selective manner with fucosazide donors we turned our attention to the use of tetrabutylammonium iodide (Bu₄NI) as a stereochemistry-directing additive[56] in the condensation of aminopentanol **21**[57] and fucosazide donor D-**6**. Bennett and co-workers have previously reported a Ph₂SO/Tf₂O-based activation protocol (in the presence of the electrophilic scavenger *N*-methylmaleimide (NMM)), utilizing an excess of Bu₄NI to generate an intermediate anomeric iodide as a reactive species.[58] As first conceived by Lemieux and co-workers,[59] an equilibrium is established between the α- and β-iodides, with the latter species being less stable but much

Scheme 4. Retrosynthetic Analysis for the *S. aureus* Type 5 CPS Trisaccharide 26

It can, however, be rationalized with the mechanistic scheme depicted in Scheme 1. The low polarity of ether (in comparison to dichloromethane) stabilizes the covalent anomeric triflate/oxosulfonium triflate because it disfavors charge separation as in oxocarbenium ion pairs. If the incoming alcohol acceptor is nucleophilic enough, it can displace the covalent reactive species in an S_N2-manner leading to the stereoselective formation of the β-FucN$_3$ bond. The use of an 1:1 mixture of CH$_2$Cl$_2$ and Et$_2$O in the glycosylation between aminopentanol 19 and disarmed FucN$_3$ donor D-4 led to a spacer containing D-fucosamine building block 29 in 80% yield and 1:7 α/β-selectivity (Scheme 5). Removal of the benzoyl group using Zemplén conditions afforded the D-FucN$_3$ acceptor 30 in 95% yield.

Next, the pivotal glycosylation between L-FucN$_3$ donor 5 and D-FucN$_3$ acceptor 30 was performed. Using the standard preactivation glycosylation protocol provided disaccharide 31 as a single anomer in 76% yield. Removal of both TBS ethers was followed by regioselective benzoylation of the C3-O' position, using Taylor's diphenylborinate catalyst 32,[65] to give disaccharide acceptor 33 in 67% yield over two steps. The final glycosylation between mannosaminuronic acid donor 28 and dimer 33 proved challenging. Mannuronic acids are relatively reactive,[66] and it was difficult to pair the reactive ManN$_3$A donor with the weakly nucleophilic FucN$_3$ alcohol. It was found that the use of an excess donor and almost an equimolar amount of Lewis acid promotor was most effective, allowing for the generation of trisaccharide 27 in 75% yield with complete stereoselectivity.[67]
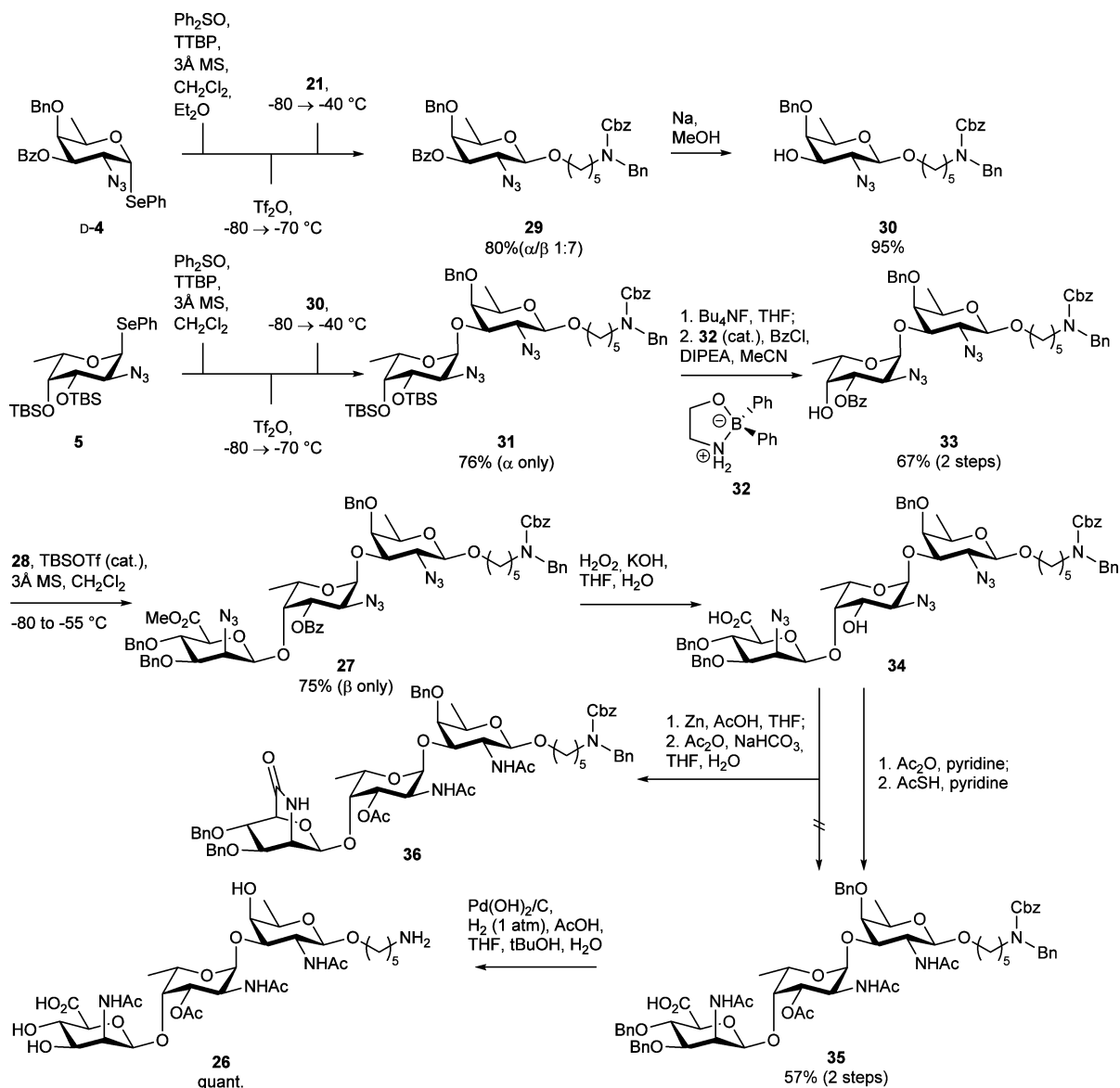
With trisaccharide 27 in hand, its optimal deprotection sequence was investigated. First, the methyl mannuronate and the benzoyl ester on the central L-FucN$_3$ unit were removed to protect the mannuronic acid moiety for potential lactamization upon exposure of the C2-amino group.[62] Next the azides in 34 were reduced using Zn in AcOH and THF.[68] It was found, however, that the subsequent O- and N-acetylation reaction resulted in a complex mixture of products, with lactam 36 as the major product. We therefore moved to an alternative reaction sequence, in which we first acetylated the free C3'−OH. Next both azides were transformed into the corresponding acetamido

functionalities using thioacetic acid (AcSH).[69] This step likely proceeds via a one-step process and circumvents formation of the free amine. Intermediate 35 was obtained in 57% yield over these two steps. The synthesis of the *S. aureus* type 5 trisaccharide 26 was finalized by hydrogenation of 35 using Pearlman's catalyst (Pd(OH)$_2$ on carbon) to remove all benzyl groups and the benzyloxycarbonyl carbamate.

■ CONCLUSION

In conclusion, we have mapped the reactivity and selectivity of a panel of phenylseleno fucosazide donors. Low-temperature NMR studies on activated donors revealed the formation of the covalent α-glycosyl triflates and oxosulfonium triflates, the stability of which depended on the protecting group pattern of the donor glycosides. Using a series of glycosylations involving a set of partially fluorinated ethanols, we were able to pinpoint how the stereoselectivity of the glycosylations of the different donors depends on the nucleophilicity of the acceptor alcohols. A mechanistic rationale was established that accounts for the stereoselectivity in glycosylations featuring fucosazide donors. Disarmed donors bearing acyl-protecting groups can selectively provide β-linked products when paired with reactive nucleophiles in an S_N2-like glycosylation reaction. Armed donors, having benzyl or silyl ether groups, on the other hand, are well suited for the installation of the challenging 1,2-*cis* fucosamine linkages, and this is rationalized with a $^3H_4$-oxocarbenium ion like reactive intermediate that is selectively attacked on its α-face. It is likely that reactions using reactive fucosyl donors proceed via similar pathways, providing a rationale for the high stereoselectivity obtained with these donors. It is anticipated that the use of the family of partially fluorinated ethanols to map reactivity−selectivity relationships for other donor types will provide valuable insight into glycosylation mechanism of these donors and significantly increase our insight how effective stereoselective glycosylation reactions can be achieved. The insight into the reactivity−selectivity of fucosazide donors generated here has paved the way for the construction of a variety of relevant glycosidic linkages and the modular assembly of the *S. aureus* type 5 repeating unit.

Scheme 5. Synthesis of Trisaccharide 26

■ EXPERIMENTAL SECTION

All reactions were carried out in oven-dried glassware (85 °C). Prior to reactions, traces of water and solvent were removed by coevaporation with toluene where appropriate. Reactions sensitive to air or moisture were carried out under an atmosphere of argon (balloon). Solvents for reactions were of reagent grade and stored over 4 Å molecular sieves (3 Å for CH_2Cl_2, MeOH, and MeCN), except pyridine and DMF. NEt_3 was stored over KOH pellets. Tf_2O used in glycosylations was dried over P_2O_5 (~3 h), followed by distillation, and stored in a Schlenk flask at −20 °C. All other chemicals were used as received. Reaction progress was monitored using aluminum-supported silica gel TLC plates (with fluorescent indicator); visualization was carried out by irradiation with UV light (λ: 254 nm), followed by spraying with 20% H_2SO_4 in EtOH (w/v) or Hanessian's stain (($NH_4)_6Mo_7O_{24}$·$4H_2O$, 25 g/L; ($NH_4)_4Ce(SO_4)_2$·$2H_2O$, 10 g/L; in 10% aq H_2SO_4). Column chromatography was carried out using silica gel (0.040−0.063 mm). Size-exclusion chromatography was carried out using Sephadex LH-20. NMR spectra were recorded on 400/100 MHz (for ^{1}H and ^{13}C, respectively) or 500/125 MHz spectrometers. Chemical shifts (δ) are reported in ppm relative to Me_4Si (δ: 0.00 ppm) or residual solvent signals. NMR spectra were recorded at ambient temperature, and samples were prepared in $CDCl_3$ unless noted otherwise.

^{13}C-APT spectra are ^{1}H decoupled. The structural assignment was achieved using HH−COSY and HSQC 2D experiments. Coupling constants of anomeric carbon atoms ($J_{H1,C1}$) were determined using HMBC-GATED experiments. Infrared spectra were recorded with an FTIR instrument with wavenumbers (ν) reported in cm^{-1}. LC−MS analyses were performed on an HPLC system equipped with a C-18 column (50 × 4.6 mm) connected to an ion-trap mass spectrometer with ESI⁺. Eluents used were MeCN and H_2O with addition of TFA (0.1%). Runtimes were 13 min with a flow rate of 1 mL/min. HRMS spectra were recorded on a LTQ-Orbitrap instrument equipped with ESI⁺ (source voltage 3.5 kV, sheath gas flow 10, capillary temperature 275 °C) with resolution R 60.000 at m/z 400 (mass range: 150−4000) and dioctyl phthalate (m/z 391.28428) as a "lock mass".

Phenyl 2-Azido-2-deoxy-1-seleno-α-L-fucopyranoside (9). A solution of 3,4-di-O-acetyl-L-fucal[17] (12.5 g, 58.4 mmol, 1.0 equiv) and (PhSe)$_2$ (18.2 g, 58.4 mmol, 1.0 equiv) in CH_2Cl_2 (300 mL, 0.2 M) was degassed by sonication (30 min) before being cooled to −30 °C. PhI(OAc)$_2$ (18.8 g, 58.4 mmol, 1.0 equiv) and TMSN$_3$ (15 mL, 116.8 mmol, 2.0 equiv) were added. The mixture was stirred for 1 h at −30 °C and subsequently at −20 °C overnight. To the mixture was added cyclohexene (~15 mL), and the mixture was allowed to warm to room temperature. The bright orange solution was concentrated *in vacuo*, and the brown residual oil was subjected to column

chromatography (PE/EtOAc, 1:0 → 9:1 v/v) to separate the lipophilic impurities from the carbohydrate fraction. The latter was concentrated and suspended in MeOH (190 mL, 0.3 M), after which NaOMe (0.31 g, 5.8 mmol, 0.1 equiv) was added. The mixture was stirred overnight, after which TLC analysis (PE/EtOAc, 1:1 v/v) showed complete conversion of the starting material. The reaction mixture was neutralized by addition of ion-exchange resin (Amberlite IR-120, H$^+$ form). The resin was filtered and the filtrate concentrated *in vacuo*. The solid thus obtained was crystallized from toluene to obtain the title compound as an amorphous solid (11.1 g, 33.8 mmol, 58%). ^{1}H NMR (400 MHz, acetone-d_6) δ: 7.62−7.57 (m, 2H, CH_{arom}); 7.32−7.28 (m, 3H, CH_{arom}); 5.96 (d, 1H, J = 5.2 Hz, H-1); 4.29 (q, 1H, J = 6.4 Hz, H-5); 4.40 (dd, 1H, J = 5.2 Hz, 10.4 Hz, H-2); 3.82− 3.79 (m, 2H, H-3, H-4); 1.17 (d, 3H, J = 6.4 Hz, H-6). ^{13}C-APT NMR (100 MHz, acetone-d_6) δ: 135.4 (CH_{arom}); 130.1 (C$_{q,arom}$); 129.8, 128.3 (CH_{arom}); 86.7 (C-1); 72.4, 72.2 (C-3, C-4); 70.2 (C-5); 62.6 (C-2); 16.5 (C-6). IR (neat) ν: 3279, 2100, 1578, 1252, 1094, 1059. HRMS: [M − N$_2$ + H]$^+$ calcd for C$_{12}$H$_{16}$NO$_3$Se 302.02899, found 302.02914. Mp: 138−140 °C.

Phenyl 2-Azido-3,4-di-*O*-benzyl-2-deoxy-1-seleno-α-L-fuco-pyranoside (1). To a stirred solution of **9** (0.66 g, 2.0 mmol, 1.0 equiv) in DMF (8 mL, 0.25 M) were added BnBr (0.71 mL, 6.0 mmol, 3.0 equiv) and Bu$_4$NI (0.15 g, 0.4 mmol, 0.2 equiv). The mixture was cooled in an ice bath, and NaH (60% w/w in oil, 0.32 g, 8.0 mmol, 4.0 equiv) was added. The mixture was stirred until TLC analysis (PE/EtOAc, 9:1 v/v) indicated complete consumption of the starting material (≤3 h). Excess NaH was quenched by slow addition of cold water until gas evolution ceased. The mixture was diluted with water and Et$_2$O, and the aqueous phase was washed twice with Et$_2$O. The combined ethereal phases were washed with brine (1×), dried over MgSO$_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (PE/Et$_2$O 1:0 → 9:1) to furnish the title compound as an oil which solidified on standing, in 85% yield (0.87 g, 1.7 mmol). ^{1}H NMR (400 MHz) δ: 7.57−7.47 (m, 2H, CH_{arom}); 7.45−7.22 (m, 13H, CH_{arom}); 5.93 (d, 1H, J = 5.2 Hz, H-1); 4.92 (d, 1H, J = 11.2 Hz, PhCHH); 4.80−4.73 (m, 2H, PhCH_2); 4.61 (d, 1H, J = 11.6 Hz, PhCHH); 4.35 (dd, 1H, J = 5.2 Hz, 9.8 Hz, H-2); 4.22 (q, 1H, J = 6.4 Hz, H-5); 3.75−3.72 (m, 2H, H-3, H-4); 1.13 (q, 3H, J = 6.4 Hz, H-6). ^{13}C-APT NMR (100 MHz) δ: 138.1, 137.4 (C$_{q,arom}$); 134.3, 129.0, 128.6, 128.3, 128.1, 128.0, 127.8, 127.7, 127.6 (CH_{arom}); 85.5 (C-1); 80.6, 75.7 (C-3, C-4); 75.0, 72.5 (PhCH_2); 69.4 (C-5); 60.9 (C-2); 16.5 (C-6). IR (neat) ν: 2882, 2112, 1474, 1298, 1101, 1063, 1047. HRMS: [M − N$_2$ + H]$^+$ calcd for C$_{26}$H$_{28}$NO$_3$Se 482.1229, found 482.1229.

Phenyl 2-Azido-3,4-di-*O*-benzoyl-2-deoxy-1-seleno-α-L-fu-copyranoside (2). To a stirred solution of **9** (0.66 g, 2.0 mmol, 1.0 equiv) in CH$_2$Cl$_2$/pyridine (3:1 v/v, 8 mL, 0.2 M) was slowly added BzCl (0.7 mL, 6.0 mmol, 3.0 equiv), followed by DMAP (0.05 g, 0.4 mmol, 0.2 equiv). The mixture was stirred until TLC analysis (PE/EtOAc, 4:1 v/v) indicated complete conversion of the starting material (~3 h). The reaction was quenched with MeOH, and the mixture was diluted with CH$_2$Cl$_2$, washed (1 M aq HCl, 2×; satd aq NaHCO$_3$, 1×; brine, 1×), dried over MgSO$_4$, filtered, and concentrated *in vacuo*. The residue was subjected to column chromatography (PE/EtOAc, 1:0 → 4:1) to furnish the title compound in 90% yield (0.96 g, 1.79 mmol). ^{1}H NMR (400 MHz) δ: 7.25−8.15 (m, 15H, CH_{arom}), 6.12 (d, 1H, J = 5.2 Hz, H-1), 5.76 (d, 1H, J = 2.8 Hz, H-4), 5.51 (dd, 1H, J = 3.2 Hz, 10.8 Hz, H-3), 4.53 (dd, 1H, J = 5.6, 10.8 Hz, H-2), 4.73 (q, 1H, J = 6.4 Hz, H-5), 1.19 (d, 3H, J = 6.4 Hz, H-6); ^{13}C-APT NMR (100 MHz) δ: 165.7, 165.4 (CO_{Bz}), 134.9− 127.2 (CH_{arom}), 84.6 (C-1), 72.4 (C-3), 70.8 (C-4), 68.0 (C-5), 59.6 (C-2), 16.0 (C-6). IR (thin film) ν: 3061, 2984, 2108, 1724, 1450, 1273, 1257, 1109, 1080, 1067, 1024. HRMS: [M − N$_2$ + H]$^+$ calcd for C$_{26}$H$_{24}$NO$_5$Se 510.0814, found 510.0819.

Phenyl 2-Azido-4-*O*-benzoyl-3-*O*-benzyl-2-deoxy-1-seleno-α-L-fucopyranoside (3). Compound **9** (0.66 g, 2.0 mmol, 1.0 equiv) was suspended in toluene (7 mL, 0.3 M). Bu$_2$SnO (0.50 g, 2.0 mmol, 1.0 equiv) was added, and the mixture was heated to 140 °C for 3 h, during which time a clear reaction mixture was obtained. The mixture was concentrated *in vacuo* and coevaporated once with dry

toluene. The mixture was dissolved in DMF (9 mL, 0.2 M), BnBr (0.26 mL, 2.2 mmol, 1.1 equiv), and CsF (0.33 g, 2.2 mmol, 1.1 equiv), and the mixture was stirred overnight, after which TLC analysis indicated conversion of the starting material (PE/EtOAc, 7:3 v/v). The reaction was diluted with H$_2$O and extracted (Et$_2$O, 3×), and the combined ethereal phases were washed (brine, 1×), dried over MgSO$_4$, filtered, and concentrated *in vacuo*. The residue was passed over a small column (PE/EtOAc, 1:0 → 4:1 v/v) to obtain the 3-*O*-benzylated intermediate (0.42 mmol, 1 mmol, 50%). ^{1}H NMR (400 MHz) δ: 7.59−7.56 (m, 2H, CH_{arom}); 7.42−7.24 (m, 8H, CH_{arom}); 5.89 (d, 1H, J = 5.2 Hz, H-1); 4.76 (d, 1H, J = 11.2 Hz, PhCHH); 4.69 (d, 1H, J = 11.2 Hz, PhCHH); 4.30 (q, 1H, J = 6.8 Hz, H-5); 4.17 (dd, 1H, J = 5.2 Hz, 10.4 Hz, H-2); 3.88 (s, 1H, H-4); 3.70 (dd, 1H, J = 3.2 Hz, 10.4 Hz, H-3); 2.36 (s, 1H, 3-OH); 1.26 (d, 3H, J = 6.8 Hz, H-6). ^{13}C-APT NMR (100 MHz, CDCl$_3$) δ: 137.1 (C$_{q,arom}$); 134.5, 129.2, 128.9, 128.5 (CH_{arom}), 128.2 (C$_{q,arom}$), 127.9 (CH_{arom}), 85.3 (C-1), 79.3 (C-3), 72.3 (CH$_2$ Bn), 68.7, 68.6 (C-4, C-5), 60.3 (C-2), 16.2 (C-6). The intermediate was dissolved in CH$_2$Cl$_2$/pyridine (4:1 v/v, 5 mL, 0.2 M), and BzCl (0.14 mL, 1.2 mmol, 1.2 equiv) and DMAP (12 mg, 0.1 mmol, 0.1 equiv) were added at 0 °C. After TLC analysis (PE/EtOAc, 9:1 v/v) indicated complete conversion of the starting material (~1 h), the mixture was quenched by the addition of water. The mixture was diluted with CH$_2$Cl$_2$ washed (1 M aq HCl, 2×; satd aq NaHCO$_3$ 1×; H$_2$O 1×; brine 1×), dried over MgSO$_4$, filtrated, and concentrated under reduced pressure. Purification by column chromatography (PE/EtOAc, 17:3 v/v) afforded the title compound (0.49 g; 0.93 mmol; 47% over two steps). ^{1}H NMR (400 MHz) δ: 8.09−8.04 (m, 4H, CH_{arom}), 7.64−7.20 (m, 11H, CH_{arom}), 6.00 (d, 1H, J = 5.2 Hz, H-1), 5.71 (d, 1H, J = 2.8 Hz, H-4), 4.85 (d, 1H, J = 10.8 Hz, PhCHH), 4.57 (d, 1H, J = 10.8 Hz, PhCHH), 4.52 (q, 1H, J = 6.4 Hz, H-5), 4.26 (dd, 1H, J = 5.2 Hz, J = 10.4 Hz, H-2), 3.90 (dd, 1H, J = 3.2 Hz, J = 10.0 Hz, H-3), 1.16 (d, 3H, J = 6.4 Hz, H-6). ^{13}C-APT NMR (100 MHz) δ: 166.0 (CO_{Bz}), 136.9 (C$_{q,arom}$), 134.7−127.7 (CH_{arom}), 85.1 (C-1), 77.5 (C-3), 71.6 (PhCH$_2$), 69.4 (C-4), 68.1 (C-5), 60.5 (C-2), 16.2 (C-6). IR (thin film) ν: 3061, 2984, 2897, 2108, 1719, 1452, 1263, 1109, 1078, 1062, 1024. HRMS: [M − N$_2$ + H]$^+$ calcd for C$_{26}$H$_{26}$NO$_4$Se 496.1022, found 496.1023.

Phenyl 2-Azido-3-*O*-benzyl-2-deoxy-1-seleno-α-L-fucopyra-noside (10). In a three-necked flask equipped with a Dean−Stark trap, a suspension of phenyl 2-azido-2-deoxy-1-seleno-α-L-fucopyrano-side (4.27 g, 13 mmol, 1.0 equiv) and Bu$_2$SnO (3.40 g, 13.7 mmol, 1.05 equiv) in toluene (65 mL, 0.2 M) was heated to 140 °C for 1 h. The resultant clear, brown solution was cooled to 60 °C, and Bu$_4$NBr (4.42 g, 13.7 mmol, 1.05 equiv), CsF (2.08 g, 13.7 mmol, 1.05 equiv), and PMBCl (1.9 mL, 13.7 mmol, 1.05 equiv) were added. The mixture was heated to 120 °C for ~2 h, after which TLC analysis (PE/EtOAc, 3:2 v/v) indicated complete conversion of the starting diol. The mixture was cooled to room temperature, KF (10% in H$_2$O, w/v) was added, and the resulting misture was stirred vigorously for ~15 min. The aqueous phase was extracted (EtOAc, 2×), and the combined organic fractions were washed (brine 1×), dried over MgSO$_4$, filtered, and concentrated in vacuo. Purification by column chromatography (PE/EtOAc, 1:0 → 4:1) furnished the 3-*O*-PMB-protected intermediate as a yellow oil in 81% yield (4.71 g, 10.5 mmol). ^{1}H NMR (400 MHz) δ: 7.58−7.56 (m, 2H, CH_{arom}); 7.34−7.24 (m, 5H, CH_{arom}); 6.93−6.87 (m, 2H, CH_{arom}); 5.87 (d, 1H, J = 5.2 Hz, H-1); 4.68 (d, 1H, J = 10.8 Hz, PhCHH); 4.62 (d, 1H, J = 10.8 Hz, PhCHH); 4.28 (q, 1H, J = 6.4 Hz, H-5); 4.14 (dd, 1H, J = 5.2 Hz, 10.2 Hz, H-2); 3.83 (d, 1H, J = 2.4 Hz, H-4); 3.81 (s, 3H, OCH_3); 3.68 (dd, 1H, J = 3.2 Hz, 10.4 Hz, H-3); 1.25 (d, 3H, J = 6.4 Hz, H-6). ^{13}C-APT NMR (100 MHz) δ: 159.6 (C$_{q,arom}$); 134.4, 134.3, 129.7, 129.0 (CH_{arom}); 129.0, 128.6 (C$_{q,arom}$); 127.7, 114.0 (CH_{arom}); 85.2 (C-1); 78.8 (C-3); 71.7 (PhCH$_2$); 68.5, 68.4 (C-4, C-5); 60.0 (C-2); 55.2 (OCH$_3$); 16.0 (C-6). IR (thin film) ν: 3441, 2897, 2106, 1612, 1512, 1246, 1088, 1063, 1031. HRMS: [M + H]$^+$ calcd for C$_{20}$H$_{24}$N$_3$O$_4$Se 450.0927, found 450.0923. A solution of the intermediate building block (1.56 g, 3.48 mmol, 1.0 equiv) and BnBr (0.83 mL, 6.96 mmol, 2.0 equiv) in DMF (12 mL, 0.3 M) was cooled to 0 °C. NaH (60% dispersion in oil, 0.21 g, 5.22 mmol, 1.5 equiv) was added, and the mixture was allowed to reach room temperature. After ~3 h, TLC analysis (PE/EtOAc, 9:1 v/v)

indicated complete conversion of the starting material, and the reaction was quenched by slow addition of water. After gas evolution had ceased, the mixture was partitioned between water and Et$_2$O. The aqueous phase was extracted (Et$_2$O, 2×), and the combined ethereal phases were washed (brine, 1×), dried over MgSO$_4$, filtered, and concentrated in vacuo. Purification by column chromatography (PE/Et$_2$O, 1:0 → 9:1) delivered the fully protected intermediate as a colorless oil (1.68 g, 3.12 mmol, 90%). ^{1}H NMR (400 MHz) δ: 7.57–7.54 (m, 2H, CH$_{arom}$); 7.36–7.23 (m, 10H, CH$_{arom}$); 6.92 (d, 2H, J = 8.8 Hz, CH$_{arom}$); 5.91 (d, 1H, J = 5.2 Hz, H-1); 4.94 (d, 1H, J = 11.6 Hz, PhCHH); 4.72–4.66 (m, 2H, PhCH$_2$); 4.60 (d, 1H, J = 11.6 Hz, PhCHH); 4.32 (dd, 1H, J = 5.2 Hz, 10.2 Hz, H-2); 4.21 (q, 1H, J = 6.4 Hz, H-5); 3.82 (s, 3H, OCH$_3$); 3.73–3.68 (m, 2H, H-3, H-4). ^{13}C-APT NMR (100 MHz) δ: 159.5, 138.2 (C$_{q,arom}$); 134.3, 129.5, 129.0 (CH$_{arom}$); 128.7 (C$_{q,arom}$); 128.3, 128.1, 127.7, 127.6, 114.0 (CH$_{arom}$); 85.6 (C-1); 80.3, 75.8 (C-3, C-4); 74.9, 72.2 (PhCH$_2$); 69.4 (C-5); 60.8 (C-2), 55.3 (OCH$_3$); 16.5 (C-6). IR (thin film) ν: 2868, 2104, 1612, 1512, 1246, 1099, 1063, 1034. HRMS: [M + H]$^+$ calcd for C$_{27}$H$_{30}$N$_3$O$_4$Se 540.1396, found 540.1394. To a stirred solution of the fully protected 2-azidofucoside (1.56 g, 2.9 mmol, 1.0 equiv) and Et$_3$SiH (0.73 mL, 8.7 mmol, 3.0 equiv) in CH$_2$Cl$_2$ (15 mL, 0.2 M) was added a solution of HCl (0.25 mL of an 37% solution, w/v in water) in HFIP (15 mL).[39] After 1 min, the mixture was poured into a solution of NaHCO$_3$ (satd aq). After separation of the layers, the aqueous phase was extracted (CH$_2$Cl$_2$, 1×), and the combined organic phases were washed (brine, 1×), dried over MgSO$_4$, filtered, and concentrated in vacuo. After column chromatography (toluene/EtOAc, 1:0 → 9:1), the C3-OH intermediate was obtained as an oil in 64% yield (0.78 g, 1.9 mmol). ^{1}H NMR (400 MHz) δ: 7.58–7.56 (m, 2H, CH$_{arom}$); 7.38–7.25 (m, 8H, CH$_{arom}$); 5.91 (d, 1H, J = 5.2 Hz, H-1); 4.81 (d, 1H, J = 11.6 Hz, PhCHH); 4.72 (d, 1H, J = 11.6 Hz, PhCHH); 4.33 (q, 1H, J = 6.4 Hz, H-5); 4.02 (dd, 1H, J = 5.2 Hz, 10.2 Hz, H-2); 3.85–3.79 (m, 1H, H-3); 3.69 (d, 1H, J = 2.8 Hz, H-4); 2.26 (d, 1H, J = 8.8 Hz, 3-OH); 1.25 (d, 3H, J = 6.8 Hz, H-6). ^{13}C-APT NMR (100 MHz) δ: 137.7 (C$_{q,arom}$); 134.3, 129.1, 128.7, 128.2, 128.1, 127.7 (CH$_{arom}$); 85.2 (C-1); 79.3 (C-4); 71.9 (C-3); 69.3 (C-5); 62.5 (C-2); 16.6 (C-6). IR (thin film) ν: 3468, 2882, 2106, 1263, 1094, 1057, 1022. HRMS: [M − N$_2$ + H]$^+$ calcd for C$_{19}$H$_{22}$NO$_3$Se 392.0759, found 392.0759.

Phenyl 2-Azido-3-O-benzoyl-4-O-benzyl-2-deoxy-1-seleno-α-L-fucopyranoside (4). To a stirred solution of **10** (0.21 g, 0.5 mmol, 1.0 equiv) in CH$_2$Cl$_2$/pyridine (1.6 mL, 0.3 M, 1:1 v/v) were added BzCl (0.12 mL, 1.0 mmol, 2 equiv) and DMAP (6 mg, 0.05 mmol, 0.1 equiv) at 0 °C. After TLC analysis indicated complete conversion of the starting material (typically, the reaction mixture was left overnight), the reaction was quenched by addition of MeOH. The mixture was diluted with CH$_2$Cl$_2$, washed with CuSO$_4$·5H$_2$O (in H$_2$O, 10% w/v, 2×), water (1×), and brine (1×), dried over MgSO$_4$, filtered, and concentrated in vacuo. Purification by column chromatography (PE/Et$_2$O, 1:0 → 9:1) furnished the title compound in 96% yield (0.25 g, 0.48 mmol). ^{1}H NMR (400 MHz) δ: 8.09 (d, 2H, J = 7.6 Hz, CH$_{arom}$); 7.63–7.58 (m, 3H, CH$_{arom}$); 7.48 (t, 2H, J = 7.6 Hz, CH$_{arom}$); 7.41–7.23 (m, 8H, CH$_{arom}$); 6.01 (d, 1H, J = 5.2 Hz, H-1); 5.29 (dd, 1H, J = 2.8 Hz, 11.0 Hz, H-3); 4.67 (d, 1H, J = 11.2 Hz, PhCHH); 4.58 (dd, 1H, J = 5.2 Hz, 11.2 Hz, H-2); 4.53 (d, 1H, J = 11.6 Hz, PhCHH); 4.43 (q, 1H, J = 6.4 Hz, H-5); 4.01 (d, 1H, J = 2.0 Hz, H-4); 1.17 (d, 3H, J = 6.4 Hz, H-6). ^{13}C-APT NMR (100 MHz) δ: 165.7 (CO$_{Bz}$); 137.4 (C$_{q,arom}$); 134.5, 133.7, 129.9, 129.1 (CH$_{arom}$); 129.0 (C$_{q,arom}$); 128.6 (CH$_{arom}$); 128.4 (C$_{q,arom}$); 128.3, 128.1, 127.9, 127.8 (CH$_{arom}$); 84.9 (C-1); 76.6 (C-4); 75.6 (PhCH$_2$); 75.1 (C-3); 69.1 (C-5); 59.6 (C-2); 16.3 (C-6). IR (thin film) ν: 2936, 2108, 1722, 1267, 1107, 1086, 1070. HRMS: [M + Na]$^+$ calcd for C$_{26}$H$_{25}$N$_3$O$_4$SeNa 546.0903, found 546.0902.

Phenyl 2-Azido-2-deoxy-3,4-di-O-(tert-butyldimethylsilyl)-1-seleno-α-L-fucopyranoside (5). A 100 mL, three-necked flask was equipped with a septum, a gas inlet, and a Liebig condenser fitted with a drying tube. Under a flow of N$_2$ gas, the flask was charged with a solution of phenyl 2-azido-2-deoxy-1-seleno-α-L-fucopyranoside (1.31 g, 4.0 mmol, 1.0 equiv) in pyridine (20 mL, 0.2 M). At 0 °C, DMAP (98 mg, 0.8 mmol, 0.2 equiv) was added followed by TBSOTf (3.7 mL, 16.0 mmol, 4.0 equiv, in a dropwise fashion). The mixture

was heated to 70 °C and stirred for 16 h, after which TLC analysis (PE/Et$_2$O, 19:1 v/v) showed complete conversion of the starting material. The reaction mixture was cooled to rt, quenched with MeOH, and diluted with EtOAc. The mixture was washed with 10% aq CuSO$_4$ solution (2×), H$_2$O, and brine, dried over MgSO$_4$, filtered, and concentrated in vacuo. Purification by column chromatography (PE/Et$_2$O, 1:0 → 49:1 v/v) furnished the title compound as a light-yellow oil in 85% yield (3.4 mmol, 1.90 g). ^{1}H NMR (CD$_2$Cl$_2$, 193 K) δ: 7.53 (d, 2H, J = 7.6 Hz, CH$_{arom}$); 7.27–7.25 (m, 3H, CH$_{arom}$); 5.89 (d, 1H, J = 5.2 Hz, H-1); 4.21 (q, 1H, J = 6.4 Hz, H-5); 4.06 (dd, 1H, J = 4.8 Hz, 10.0 Hz, H-2); 3.70–3.67 (m, 2H, H-3, H-4); 1.06 (d, 3H, J = 6.0 Hz, H-6); 0.90, 0.82 (s, 9H, CH$_{3,tBu}$); 0.14, 0.11, 0.09, 0.03 (s, 3H, CH$_{3,Me}$). ^{13}C-APT NMR (CD$_2$Cl$_2$, 193 K) δ: 134.3, 128.7 (CH$_{arom}$); 128.0 (C$_{q,arom}$); 127.4 (CH$_{arom}$); 85.3 (C-1); 73.6, 72.9 (C-3, C-4); 69.5 (C-2); 61.6 (C-5); 25.5, 25.3 (CH$_{3,tBu}$); 18.1, 17.8 (C$_{q,tBu}$); 16.6 (C-6); −4.3, −4.7, −5.3, −5.3 (CH$_{3,Me}$). IR (thin film) ν: 2953, 2930, 2856, 2106, 1472, 1252, 1115, 1067, 1022. HRMS: [M − N$_2$ + H]$^+$ calcd C$_{24}$H$_{44}$NO$_3$SeSi$_2$ 530.2020, found 530.2017.

Phenyl 2-Azido-4-O-benzyl-2-deoxy-3-O-(tert-butyldimethylsilyl)-1-seleno-α-L-fucopyranoside (6). A 50 mL, three-necked flask was equipped with a septum, a gas inlet, and a Liebig condenser fitted with a drying tube. Under a flow of N$_2$ gas, the flask was charged with a solution of **10** (0.63 g, 1.5 mmol, 1.0 equiv) in pyridine (7.5 mL, 0.2 M). At 0 °C, DMAP (4 mg, 0.3 mmol, 0.2 equiv) was added followed by TBSOTf (0.69 mL, 3.0 mmol, 2.0 equiv, in a dropwise fashion). The mixture was heated to 70 °C and stirred for 16 h, after which TLC analysis (PE/Et$_2$O, 19:1 v/v) showed complete conversion of the starting material. The reaction mixture was cooled to rt, quenched with MeOH, and diluted with EtOAc. The mixture was washed with 10% aq CuSO$_4$ solution (2×), H$_2$O and brine, dried over MgSO$_4$, filtered and concentrated in vacuo. Purification by column chromatography (PE/Et$_2$O, 1:0 → 19:1 v/v) furnished the title compound as a light yellow oil in 92% yield (0.73 g, 1.38 mmol). ^{1}H NMR (400 MHz) δ: 7.57–7.55 (m, 2H, CH$_{arom}$); 7.39–7.26 (m, 8H, CH$_{arom}$); 5.96 (d, 1H, J = 4.8 Hz, H-1); 5.06 (d, 1H, J = 11.2 Hz, PhCHH); 4.59 (d, 1H, J = 11.2 Hz, PhCHH); 4.27 (q, 1H, J = 6.4 Hz, H-5); 4.22 (dd, 1H, J = 5.2 Hz, 10.0 Hz, H-2); 3.88 (dd, 1H, J = 2.4 Hz, 10.0 Hz, H-3); 3.53 (bs, 1H, H-4); 1.15 (d, 3H, J = 6.4 Hz, H-6); 0.99 (s, 9H, (CH$_3$)$_3$CSi); 0.25, 0.22 (s, 3H, CH$_3$Si). ^{13}C-APT NMR (100 MHz) δ: 138.5 (C$_{q,arom}$); 134.3, 129.0, 128.3, 127.8, 127.7, 127.6 (CH$_{arom}$); 85.6 (C-1); 80.1 (C-4); 75.6 (PhCH$_2$); 74.2 (C-3); 69.4 (C-5); 62.9 (C-2); 26.0 ((CH$_3$)$_3$CSi); 16.5 (C-6). IR (thin film) ν: 2953, 2930, 2886, 2857, 2106, 1472, 1260, 1111, 1080, 1062, 1042, 1022. HRMS: [M + H]$^+$ calcd for C$_{25}$H$_{36}$N$_3$O$_3$SeSi 534.1686, found 534.1688.

General Procedure for Generation of Glycosyl Triflates and Oxosulfonium Triflates. A mixture of glycosyl donor (0.038 mmol, 1.0 equiv) and Ph$_2$SO (10 mg, 0.049 mmol, 1.3 equiv; 15 mg, 0.076 mmol, 2.0 equiv; or 31 mg, 0.152 mmol, 4.0 equiv) was dried by coevaporation with toluene (3×) followed by three vacuum/argon purges. The mixture was dissolved in CD$_2$Cl$_2$ (0.75 mL, 0.05 M) and transferred to a dry NMR tube, which was subsequently capped with a septum. The tube was placed in the probe of a NMR magnet and cooled to −80 °C, after which a ^{1}H NMR spectrum was recorded. The tube was removed from the magnet and placed in a acetone/N$_2$ (l) bath (temperature ≤−80 °C). Tf$_2$O (8 μL, 0.049 mmol, 1.3 equiv) was added with a microliter syringe, and after rapid mixing and recooling, the tube was placed back in the NMR instrument. A ^{1}H NMR spectrum was recorded, which revealed the formation of reactive intermediate(s). After further characterization (^{13}C-APT NMR, HH–COSY, and HSQC) the temperature of the sample was increased by increments of 10 °C until decomposition of the intermediate(s) was observed.

General Procedure for Glycosylations of 2-Azido-2-deoxy Donors 1−6 with Model Acceptors. To a mixture of donor (0.1 mmol, 1.0 equiv), Ph$_2$SO (26 mg, 0.13 mmol, 1.3 equiv), and TTBP (62 mg, 0.25 mmol, 2.5 equiv) in dry CH$_2$Cl$_2$ (2 mL, 0.05 M) were added flame-dried 3 Å molecular sieves. The mixture was subsequently stirred for 30 min before being cooled to −80 °C. At this temperature, Tf$_2$O (22 μL, 0.13 mmol, 1.3 equiv) was added via

syringe, and the temperature was raised to −60 °C over the course of ~30 min. After the temperature was recooled to −80 °C, the acceptor (0.2 mmol, 2.0 equiv, 0.4 mL of a 0.5 M stock solution in CH_2Cl_2) was added at −80 °C, and the reaction mixture was allowed to warm to −40 °C, after which the reaction was quenched by addition of NEt_3 (0.1 mL) and subsequently diluted with CH_2Cl_2. The mixture was filtered through a small bed of Celite, the residue was washed with CH_2Cl_2, and the filtrate was washed once with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification by ordinary column chromatography and/or size-exclusion chromatography afforded the corresponding O-glycoside(s).

Ethyl 2-Azido-3,4-di-O-benzyl-2-deoxy-α/β-L-fucopyranoside (A1). The title compounds (α/β 1:1) were obtained after column chromatography (hexane/Et₂O, 1:0 → 9:1) in 88% yield (35 mg, 0.088 mmol). ¹H NMR (400 MHz) δ: 7.43−7.25 (m, 18H, CH_{arom}); 4.95−4.92 (m, 1.8H, PhCHHα, PhCHHβ); 4.90 (d, 0.8H, J = 4.0 Hz, H-1α); 4.74−4.60 (m, 5.4H, PhCH₂α, PhCH₂β); 4.18 (d, 1H, J = 8.0 Hz, H-1β); 3.99−3.78 (m, 4.2H, H-2α, H-2β, H-3α, H-5α, CHHCH₃α); 3.75−3.67 (m, 1.8H, H-4β, CHHCH₃β); 3.60−3.50 (m, 2.8H, H-4β, CHHCH₃α, CHHCH₃β); 3.41 (q, 1H, J = 6.4 Hz, H-5β); 3.30 (dd, 1H, J = 2.8 Hz, 10.4 Hz, H-3β); 1.28−1.16 (m, 10.8H, H-6α, H-6β, CH₂CH_3α, CH₂CH_3β). ¹³C-APT NMR (100 MHz) δ: 138.3, 137.7 ($C_{q,arom}$); 128.5, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6 (CH_{arom}); 102.0 (C-1β); 97.9 (C-1α); 81.1 (C-3β); 78.0 (C-3α); 76.3 (C-4α); 74.9 (C-4β); 74.9, 74.6, 72.6, 72.4 (PhCH₂); 70.5 (C-5β); 66.5 (C-5α); 65.3 (CH₂CH₃); 63.7 (CH₂CH₃); 63.0 (C-2β); 59.6 (C-2α); 16.9, 16.7 (C-6); 15.0, 15.0 (CH₂CH₃). IR (thin film) ν: 2893, 2106, 1454, 1356, 1099, 1063. HRMS: $[M + NH_4]^+$ calcd for $C_{22}H_{31}N_4O_4$ 415.2340, found 415.2339.

Ethyl 2-Azido-3,4-di-O-benzoyl-2-deoxy-α/β-L-fucopyranoside (A2). The title compounds (α/β 1:4) were obtained after column chromatography (hexane/EtOAc, 1:0 → 4:1 v/v) in 39% yield (25 mg, 0.059 mmol). ¹H NMR (400 MHz) δ: 8.09−8.03 (m, 10H, CH_{arom}); 7.89−7.86 (m, 9H, CH_{arom}); 7.64−7.59 (m, 6H, CH_{arom}); 7.53−7.46 (m, 17H, CH_{arom}); 7.35−7.31 (m, 10H, CH_{arom}); 5.78 (dd, 1H, J = 3.2 Hz, 10.8 Hz, H-3α); 5.71 (dd, 1H, J = 1.2 Hz, 3.2 Hz, H-4α); 5.59 (dd, 4H, J = 0.8 Hz, 3.2 Hz, H-4β); 5.17 (dd, 4H, J = 3.6 Hz, 10.8 Hz, H-3β); 5.13 (d, 1H, J = 3.6 Hz, H-1α); 4.51 (d, 4H, J = 8.0 Hz, H-1β); 4.37 (q, 1H, J = 6.4 Hz, H-5α); 4.10 (dq, 4H, J = 7.2 Hz, 9.6 Hz, CHHCH₃β); 3.98−3.90 (m, 8H, H-2β, H-5β); 3.88−3.84 (m, 2H, H-2α, CHHCH₃α); 3.76−3.63 (m, 6H, CHHCH₃α, CHHCH₃β); 1.37−1.21 (m, 30H, H-6α, H-6β, CH₂CH_3α, CH₂CH_3β). ¹³C-APT NMR (100 MHz) δ: 165.8, 165.8, 165.4 (CO$_{Bz}$); 133.4, 133.4, 133.3, 133.2, 129.9, 129.7 (CH_{arom}); 129.2, 129.1 ($C_{q,arom}$); 128.5, 128.5, 128.3, 128.3 (CH_{arom}); 102.2 (C-1β); 98.1 (C-1α); 72.0 (C-3β); 71.4 (C-4α); 70.3 (C-4β); 69.5 (C-5β); 69.3 (C-3α); 66.2 (CH₂CH₃); 65.1 (C-5α); 64.3 (CH₂CH₃); 61.2 (C-2β); 57.9 (C-2α); 16.3 (C-6β); 16.1 (C-6α); 15.1 (CH₂CH₃β); 15.0 (CH₂CH₃α). IR (thin film) ν: 1980, 2927, 2110, 1724, 1450, 1261, 1175, 1109, 1094, 1067, 1026. HRMS: $[M + Na]^+$ calcd for $C_{22}H_{23}N_3O_6Na$ 448.1479, found 448.1478.

Ethyl 2-Azido-4-O-benzoyl-3-O-benzyl-2-deoxy-α/β-L-fucopyranoside (A3). The title compounds (α/β 1:3) were obtained after column chromatography (hexane/Et₂O, 1:0 → 4:1 v/v) in 61% yield (25 mg, 0.061 mmol). ¹H NMR (400 MHz) δ: 8.15−8.07 (m, 8H, CH_{arom}); 7.60−7.56 (m, 4H, CH_{arom}); 7.48−7.44 (m, 8H, CH_{arom}); 7.36−7.24 (m, 20H, CH_{arom}); 5.68 (d, 1H, J = 2.4 Hz, H-4α); 5.54 (dd, 3H, J = 0.8 Hz, 3.2 Hz, H-4β); 4.98 (d, 1H, J = 3.6 Hz, H-1α); 4.83 (d, 1H, J = 10.8 Hz, PhCHHα); 4.79 (d, 3H, J = 11.6 Hz, PhCHHβ); 4.56−4.53 (m, 4H, PhCHHα, PhCHHβ); 4.28 (d, 4H, J = 8.0 Hz, H-1β); 4.18 (q, 1H, J = 6.8 Hz, H-5α); 4.11 (dd, 1H, J = 3.2 Hz, 10.4 Hz, H-3α); 4.06−3.99 (m, 3H, CHHCH₃α); 3.78−3.60 (m, 11H, H-2α, H-2β, H-5β, CHHCH₃α, CHHCH₃β); 3.45 (dd, 3H, J = 3.2 Hz, 10.4 Hz, H-3β); 1.59−1.26 (m, 21H, H-6β, CH₂CH_3α, CH₂CH_3β); 1.22 (d, 3H, J = 6.8 Hz, H-6α). ¹³C-APT NMR (100 MHz) δ: 166.2 (CO$_{Bz}$); 137.2, 137.1 ($C_{q,arom}$); 133.3, 133.2, 130.0, 129.8 (CH_{arom}); 129.4 ($C_{q,arom}$); 128.5, 128.4, 128.4, 128.4, 128.2, 128.4, 1f27.9, 127.8 (CH_{arom}); 102.0 (C-1β); 97.9 (C-1α); 77.6 (C-3β); 74.4 (C-3α); 71.5 (PhCH₂β); 71.5 (PhCH₂α); 70.0 (C-4α); 69.5 (C-5β); 68.9 (C-4β); 65.9 (CH₂CH₃β); 65.1 (C-5α);

64.0 (CH₂CH₃α); 62.6 (C-2β); 59.3 (C-2α); 16.5 (C-6β); 16.3 (C-6α); 15.1 (CH₂CH₃β); 15.0 (CH₂CH₃α). IR (thin film) ν: 2980, 2870, 2108, 1721, 1452, 1265, 1175, 1111, 1065, 1026. HRMS: $[M + H]^+$ calcd for $C_{22}H_{26}N_3O_5$ 412.1867, found 412.1870.

Ethyl 2-Azido-3-O-benzoyl-4-O-benzyl-2-deoxy-α/β-L-fucopyranoside (A4). The title compounds (α/β 2:5) were obtained after column chromatography (hexane/Et₂O 1:0 → 9:1) in 58% yield (24 mg, 0.058 mmol). ¹H NMR (400 MHz) δ: 8.10−8.06 (m, 14H, CH_{arom}); 7.62−7.58 (m, 7H, CH_{arom}); 7.49−7.45 (m, 14H, CH_{arom}); 7.26−7.19 (m, 35H, CH_{arom}); 5.57 (dd, 2H, J = 3.0 Hz, 11.0 Hz, H-3α); 5.00 (d, 2H, J = 3.6 Hz, H-1α); 4.95 (dd, 5H, J = 3.0 Hz, 11.0 Hz, H-3β); 4.72−4.68 (m, 7H, PhCHHα, PhCHHβ); 4.57−4.52 (m, 7H, PhCHHβ); 4.37 (d, 5H, J = 8.0 Hz, H-1β); 4.11 (q, 2H, J = 6.8 Hz, H-5α); 4.05−3.94 (m, 14H, H-2α, H-2β, H-4α, CHHCH₃β); 3.82−3.74 (m, 7H, H-4β, CHHCH₃α); 3.68−3.56 (m, 12H, H-5β, CHHCH₃α, CHHCH₃β); 1.31−1.20 (m, 42H, H-6α, H-6β, CH₂CH_3α, CH₂CH_3β). ¹³C-APT NMR (100 MHz) δ: 165.9 (CO Bz); 137.6, 137.5 ($C_{q,arom}$); 133.5, 133.5, 129.9 (CH_{arom}); 129.2 ($C_{q,arom}$); 128.5, 128.3, 128.2, 128.1, 127.8, 127.8, 127.6 (CH_{arom}); 101.9 (C-1β); 98.0 (C-1α); 77.4 (C-4α); 76.0 (C-4β); 75.5 (PhCH₂); 75.4 (PhCH₂); 75.0 (C-3β); 72.3 (C-3α); 70.5 (C-5β); 66.2 (C-5α); 65.6 (CH₂CH₃); 63.9 (CH₂CH₃); 61.2 (C-2β); 58.0 (C-2α); 16.6, 16.4, 15.0, 15.0 (CH₂CH₃, C-6α, C-6β). IR (thin film) ν: 2978, 2932, 2108, 1721, 1452, 1265, 1175, 1094, 1069, 1026. HRMS: $[M + NH_4]^+$ calcd for $C_{22}H_{29}N_4O_5$ 429.2133, found 429.2134.

Ethyl 2-Azido-2-deoxy-3,4-di-O-(tert-butyldimethylsilyl)-α/β-L-fucopyranoside (A5). The title compounds (α/β 2:5) were obtained after column chromatography (hexane/Et₂O, 1:0 → 19:1) along with a minor amount of inseparable, hydrolyzed donor in 63% yield (28 mg, 0.063 mmol). ¹H NMR (400 MHz) δ: 4.91 (d, 2H, J = 3.6 Hz, H-1α); 4.19 (d, 5H, J = 8.0 Hz, H-1β); 4.01−3.95 (m, 7H, H-3α, OCHHCH₃); 3.88 (q, 2H, J = 6.4 Hz, H-5α); 3.73−3.70 (m, 6H, H-2α, H-4α, OCHHCH₃α); 3.62−3.52 (m, 17H, H-2β, H-4β, OCHHCH₃α; OCHHCH₃β); 3.45 (q, 5H, J = 6.4 Hz, H-5β); 3.35 (dd, 5H, J = 2.4 Hz, 10.4 Hz, H-3β); 1.29−1.18 (m, 42H, H-6α, H-6β, CH₂CH_3α, CH₂CH_3β); 0.96−0.93 (m, 126H, (CH_3)₃CSiα, (CH_3)₃CSiβ); 0.19−0.09 (m, 84H, CH_3Siα, CH_3Siβ). ¹³C-APT NMR (100 MHz) δ: 102.5 (C-1β); 97.7 (C-1α); 75.2 (C-4α); 74.5 (C-3β); 74.0 (C-4β); 71.3 (C-3α); 71.2 (C-5β); 67.7 (C-5α); 65.5 (OCH₂CH₃); 63.8 (C-2β); 63.4 (OCH₂CH₃α); 61.1 (C-2α); 26.3, 26.2, 26.1 ((CH₃)₃CSi); 18.6, 18.5 (C_qSi); 17.6, 17.3 (OCH₂CH₃); 15.1, 15.0 (C-6α, C-6β); −3.5, −3.6, −4.2, −4.4 (CH₃Si). IR (thin film) ν: 2928, 2857, 2112, 1252, 1117, 1069. HRMS: $[M + NH_4]^+$ calcd for $C_{20}H_{47}N_4O_4Si_2$ 463.3130, found 463.3129.

Ethyl 2-Azido-4-O-benzyl-2-deoxy-3-O-(tert-butyldimethylsilyl)-α/β-L-fucopyranoside (A6). The title products (α/β 1:1) were obtained after column chromatography (hexane/Et₂O, 1:0 → 19:1 v/v) in 81% yield (34 mg, 0.081 mmol). ¹H NMR (400 MHz) δ: 7.39−7.26 (m, 10H, CH_{arom}); 5.05−5.02 (m, 2H, PhCHHα, PhCHHβ); 4.91 (d, 1H, J = 3.6 Hz, H-1α); 4.61−4.56 (m, 2H, PhCHHα, PhCHHβ); 4.19 (d, 1H, J = 8.0 Hz, H-1β); 4.12 (dd, 1H, J = 2.8 Hz, 10.0 Hz, H-3α); 3.98−3.93 (m, 2H, H-5α, OCHHCH₃); 3.74−3.50 (m, 8H, H-2α, H-2β, H-3β, H-4α, H-5β, OCHHCH₃, 2× OCHHCH₃); 3.37 (d, 1H, J = 2.4 Hz, H-4β); 1.27−1.19 (m, 12H, H-6α, H-6β, OCH₂CH_3α, OCH₂CH_3β); 0.98, 0.96 (s, 9H, (CH_3)₃CSi); 0.24 (s, 3H, CH_3Si); 0.18 (m, 6H, CH_3Si); 0.15 (s, 3H, CH_3Si). ¹³C-APT NMR (100 MHz) δ: 138.6, 138.6 ($C_{q,arom}$); 128.3, 128.1, 128.1, 127.9, 127.6, 127.5 (CH_{arom}); 102.1 (C-1β); 97.8 (C-1α); 80.9 (C-4α); 79.2 (C-4β); 75.6, 75.3 (PhCH₂); 74.9 (C-3β or C-5β); 71.5 (C-3α); 70.3 (C-3β or C-5β); 66.5 (C-5α); 65.4 (OCH₂CH₃); 64.6 (C-2β); 63.6 (OCH₂CH₃); 61.5 (C-2α); 25.9, 25.9 ((CH₃)₃CSi); 18.2, 18.1 (C_qSi); 16.8, 16.7 (C-6α, C-6β); 15.1, 15.0 (OCH₂CH₃α, OCH₂CH₃β); −4.0, −4.3, −4.7, −5.0 (CH₃Si). IR (thin film) ν: 2930, 2891, 2857, 2108, 1254, 1171, 1117, 1067, 1047. HRMS: $[M + NH_4]^+$ calcd for $C_{21}H_{39}N_4O_4Si$ 439.2735, found 439.2732.

2-Fluoroethyl 2-Azido-3,4-di-O-benzyl-2-deoxy-α/β-L-fucopyranoside (B1). The title products (α/β 1:1) were obtained after column chromatography (hexane/EtOAc, 1:0 → 4:1) in 72% yield (30 mg, 0.072 mmol). ¹H NMR (400 MHz) δ: 7.66−7.63 (m, 2H, CH_{arom});

7.46−7.25 (m, 18H, CH$_{arom}$); 4.95−4.91 (m, 3H, H-1α, 2× PhCHH); 4.74−4.50 (m, CH$_2$Fα, CH$_2$Fβ, 2× PhCHH; 4x PhCHH); 4.26 (d, 1H, J = 8.0 Hz, H-1β); 4.02−3.73 (m, 9H, H-2α, H-2β, H-3α; H-4α, H-5α, CH$_2$CH$_2$Fα, CH$_2$CH$_2$Fβ); 3.54 (d, 1H, J = 2.4 Hz, H-4β); 3.42 (q, 1H, J = 6.4 Hz, H-5β); 3.31 (dd, 1H, J = 2.8 Hz, 10.4 Hz, H-3β); 1.20−1.17 (m, 6H, H-6α, H-6β). ^{13}C-APT NMR (100 MHz) δ: 138.2, 137.6 (C$_{q,arom}$); 131.0, 129.9, 128.5, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.7, 124.7 (CH$_{arom}$); 102.3 (C-1β); 98.4 (C-1α); 82.7 (d, J = 168 Hz, CH$_2$F); 82.5 (d, J = 168 Hz, CH$_2$F); 80.9 (C-3β); 77.8 (C-3α); 76.1 (C-4α); 74.9 (PhCH$_2$); 74.8 (C-4β); 72.7, 72.4 (PhCH$_2$); 70.6 (C-5β); 68.3 (d, 20 Hz, CH$_2$CH$_2$F) 67.1 (d, 20 Hz, CH$_2$CH$_2$F); 66.7 (C-5α); 62.9 (C-2β); 59.5 (C-2α); 16.8, 16.7 (C-6α, C-6β). IR (thin film) ν: 2876, 2108, 1726, 1358, 1109, 1062, 1045. HRMS: [M + NH$_4$]$^+$ calcd for C$_{22}$H$_{30}$FN$_4$O$_4$ 433.2246, found 433.2242.

2-Fluoroethyl 2-Azido-3,4-di-O-benzoyl-2-deoxy-α/β-L-fucopyranoside (B2). The title compounds (α/β 1:2) were obtained after column chromatography (hexane/EtOAc, 1:0 → 4:1) in 34% yield (15 mg, 0.034 mmol). ^{1}H NMR (400 MHz) δ: 8.08−8.03 (m, 6H, CH$_{arom}$); 7.89−7.86 (m, 6H, CH$_{arom}$); 7.63−7.60 (m, 3H, CH$_{arom}$); 7.53−7.46 (m, 9H, CH$_{arom}$); 7.35−7.31 (m, 6H, CH$_{arom}$); 5.78 (dd, 1H, J = 3.2 Hz, 11.2 Hz, H-3α); 5.72 (d, 1H, J = 3.2 Hz, H-4α); 5.59 (d, 2H, J = 3.2 Hz, H-4β); 5.19−5.16 (m, 3H, H-1α, H-3β); 4.77−4.60 (m, 6H, CH$_2$Fα, CH$_2$Fβ, H-1β); 4.58 (d, 2H, J = 8.4 Hz, H-1β); 4.42 (q, 1H, J = 6.8 Hz, H-5α); 4.25−3.89 (m, 11H, H-2α, H-2β, H-5β, CH$_2$CH$_2$Fα, CH$_2$CH$_2$Fβ); 1.31 (d, 6H, J = 6.4 Hz, H-6β); 1.25 (d, 3H, J = 6.4 Hz, H-6α). ^{13}C-APT NMR (100 MHz) δ: 165.8, 165.4 (CO$_{Bz}$); 133.5, 133.4, 133.3, 133.3, 129.9, 129.8 (CH$_{arom}$); 129.3, 129.2, 129.0 (C$_{q,arom}$); 128.6, 128.3 (CH$_{arom}$); 102.5 (C-1β); 98.6 (C-1α); 82.6 (d, J = 169 Hz, CH$_2$CH$_2$Fβ); 82.4 (d, J = 170 Hz, CH$_2$CH$_2$Fα); 72.0 (C-3β); 71.3 (C-4β); 70.2 (C-4β); 69.7 (C-5β); 69.2 (C-3α); 69.1 (d, J = 21 Hz, CH$_2$CH$_2$Fβ); 67.5 (d, J = 20 Hz, CH$_2$CH$_2$Fα); 65.4 (C-5α); 61.3 (C-2β); 58.0 (C-2α); 16.3 (C-6β); 16.1 (C-6α). IR (thin film) ν: 2984, 2924, 2110, 1721, 1450, 1260, 1169, 1107, 1094, 1067, 1026. HRMS: [M + Na]$^+$ calcd for C$_{22}$H$_{22}$FN$_3$O$_6$Na 466.1385, found 466.1384.

2-Fluoroethyl 2-Azido-4-O-benzoyl-3-O-benzyl-2-deoxy-α/β-L-fucopyranoside (B3). The products (α/β 1:1) were obtained after column chromatography (hexane/EtOAc, 1:0 → 9:1) and size-exclusion chromatography (CH$_2$Cl$_2$/MeOH, 1:1 v/v) in 56% yield (24 mg, 0.056 mmol), accompanied by a small amount of inseparable, hydrolyzed donor. ^{1}H NMR (400 MHz) δ: 8.14−8.07 (m, 4H, CH$_{arom}$); 7.60−7.56 (m, 2H, CH$_{arom}$); 7.49−4.44 (m, 4H, CH$_{arom}$); 7.35−7.25 (m, 10H, CH$_{arom}$); 5.70 (d, 1H, J = 2.8 Hz, H-4α); 5.55 (d, 1H, J = 3.2 Hz, H-4β); 5.02 (d, 1H, J = 3.6 Hz, H-1α); 4.85−4.53 (m, 8H, CH$_2$Fα, CH$_2$Fβ, PhCH$_2$α, PhCH$_2$β); 4.36 (d, 1H, J = 8.0 Hz, H-1β); 4.24 (q, 1H, J = 6.4 Hz, H-5α); 4.15−3.71 (m, 8H, H-2α, H-2β, H-3α, H-5β, CH$_2$CH$_2$Fα, CH$_2$CH$_2$Fβ); 3.47 (dd, 1H, J = 3.2 Hz, 10.2 Hz, H-3β); 1.28−1.21 (m, 6H, H-6α, H-6β). ^{13}C-APT NMR (100 MHz) δ: 166.2, 166.1 (CO$_{Bz}$); 137.1, 137.0 (C$_{q,arom}$); 133.4, 133.3, 130.2, 130.0, 129.8, 129.4 (CH$_{arom}$); 129.4 (C$_{q,arom}$); 128.5, 128.4, 128.2, 128.0, 127.9, 127.8 (CH$_{arom}$); 102.3 (C-1β); 98.4 (C-1α); 82.7 (d, J = 169 Hz, CH$_2$Fβ); 82.5 (d, J = 170 Hz, CH$_2$Fα); 77.5 (C-3β); 74.3 (C-3α); 71.6 (PhCH$_2$β); 71.5 (PhCH$_2$α); 69.8 (C-4α); 69.6 (C-5β); 68.8 (d, J = 20 Hz, CH$_2$CH$_2$Fβ); 68.8 (C-4β); 67.4 (d, J = 20 Hz, CH$_2$CH$_2$Fα); 65.4 (C-5α); 62.6 (C-2β); 59.2 (C-2α); 16.5, 16.3 (C-6α, C-6β). IR (thin film) ν: 2926, 2110, 1721, 1452, 1267, 1169, 1111, 1067, 1026. HRMS: [M + H − N$_2$]$^+$ calcd for C$_{22}$H$_{25}$FNO$_5$ 402.1711, found 402.1711.

2-Fluoroethyl 2-Azido-3-O-benzoyl-4-O-benzyl-2-deoxy-α/β-L-fucopyranoside (B4). The products (α/β 2:3) were obtained after column chromatography (hexane/EtOAc, 1:0 → 9:1) and size-exclusion chromatography (CH$_2$Cl$_2$/MeOH, 1:1 v/v) in 60% yield (26 mg, 0.060 mmol). ^{1}H NMR (400 MHz) δ: 8.10−8.06 (m, 10H, CH$_{arom}$); 7.62−7.58 (m, 5H, CH$_{arom}$); 7.49−7.45 (m, 10H, CH$_{arom}$); 7.26−7.20 (m, 25H, CH$_{arom}$); 5.58 (dd, 2H, J = 2.8 Hz, 11.2 Hz, H-3α); 5.05 (d, 2H, J = 3.6 Hz, H-1α); 4.95 (dd, 3H, J = 3.2 Hz, 10.8 Hz, H-3β); 4.73−4.52 (m, 20H, CHCH$_2$F, PhCH$_2$); 4.43 (d, 3H, J = 8.0 Hz, H-1β); 4.17−3.78 (m, 22H, H-2α, H-2β, H-4α, H-4β, H-5α, CH$_2$CH$_2$F); 3.67 (q, 3H, J = 6.4 Hz, H-5β); 1.26−1.21 (m, 15H,

H-6α, H-6β). ^{13}C-APT NMR (100 MHz) δ: 165.8 (CO$_{Bz}$); 137.5, 137.4 (C$_{q,arom}$); 133.6, 133.5, 129.9 (CH$_{arom}$); 129.3, 129.1 (C$_{q,arom}$); 128.6, 128.3, 128.3, 128.1, 127.9, 127.9 (CH$_{arom}$); 102.3 (C-1β); 98.5 (C-1α); 82.6 (d, J = 168 Hz, CH$_2$CH$_2$Fβ); 82.4 (d, J = 169 Hz, CH$_2$CH$_2$Fα); 77.2 (C-4α); 75.9 (C-4β); 75.6 (PhCH$_2$α); 75.4 (PhCH$_2$β); 74.9 (C-3β); 72.2 (C-3α); 70.6 (C-5β); 68.6 (d, J = 21 Hz, CH$_2$CH$_2$Fβ); 67.3 (d, J = 20 Hz, CH$_2$CH$_2$Fα); 66.5 (C-5α); 61.2 (C-2β); 58.0 (C-2α); 16.6 (C-6β); 16.4 (C-6α). IR (thin film) ν: 2934, 2110, 1721, 1452, 1267, 1171, 1096, 1069, 1026. HRMS: [M + NH$_4$]$^+$ calcd for C$_{22}$H$_{28}$FN$_4$O$_5$ 447.2038, found 447.2038.

2-Fluoroethyl 2-Azido-2-deoxy-3,4-di-O-(tert-butyldimethylsilyl)-α/β-L-fucopyranoside (B5). The products (α/β 2:3) were obtained after column chromatography (hexane/Et$_2$O, 1:0 → 9:1) in 82% yield (38 mg, 0.082 mmol). ^{1}H NMR (400 MHz) δ: 4.94 (d, 2H, J = 3.6 Hz, H-1α); 4.66−4.51 (m, 10H, CH$_2$Fα, CH$_2$Fβ); 4.26 (d, 3H, J = 8.0 Hz, H-1β); 4.15−4.01 (m, 5H, H-3α, CHHCH$_2$Fβ); 3.94−3.68 (m, 13H, H-2α, H-4α, H-5α, CH$_2$CH$_2$Fα, CHHCH$_2$Fβ); 3.59−3.55 (m, 6H, H-2β, H-4β); 3.47 (q, 3H, J = 6.4 Hz, H-5β); 3.36 (dd, 3H, J = 2.4 Hz, 10.2 Hz, H-3β); 1.23 (d, 9H, J = 6.4 Hz, H-6β); 1.19 (d, 6H, J = 6.4 Hz, H-6α), 0.96−0.93 (m, 90H, (CH$_3$)$_3$CSi); 0.19−0.08 (m, 60H, CH$_3$Si). ^{13}C-APT NMR (100 MHz) δ: 102.8 (C-1β); 98.3 (C-1α); 82.8 (d, J = 168 Hz, CH$_2$CH$_2$Fβ); 82.6 (d, J = 168 Hz, CH$_2$CH$_2$Fα); 75.1 (C-4α); 74.4 (C-3β); 73.9 (C-4β); 71.3 (C-5β); 71.2 (C-3α); 68.3 (d, J = 20 Hz, CH$_2$CH$_2$Fβ); 66.9 (d, J = 20 Hz, CH$_2$CH$_2$Fα); 63.8 (C-2β); 61.1 (C-2α); 26.3, 26.1, 26.1 ((CH$_3$)$_3$CSi); 18.6, 18.6, 18.5 (C$_q$Si); 17.5 (C-6β); 17.3 (C-6α); −3.5, −3.5, −3.6, −3.7, −4.3, −4.5, −4.5, −4.7 (CH$_3$Si). IR (thin film) ν: 2930, 2857, 2108, 1252, 1177, 1119, 1069, 1045, 1028. HRMS: [M + NH$_4$]$^+$ calcd for C$_{20}$H$_{46}$FN$_4$O$_4$Si$_2$ 481.3036, found 481.3034.

2-Fluoroethyl 2-Azido-4-O-benzyl-2-deoxy-3-O-(tert-butyldimethylsilyl)-α/β-L-fucopyranoside (B6). The title products (α/β 1:1) were isolated after column chromatography (hexane/Et$_2$O, 1:0 → 9:1) in 80% yield (35 mg, 0.080 mmol). ^{1}H NMR (400 MHz) δ: 7.39−7.26 (m, 10H, CH$_{arom}$); 5.05−5.02 (m, 2H, 2× PhCHH); 4.94 (d, 1H, J = 3.6 Hz, H-1α); 4.67−5.51 (m, 6H, 2× PhCHH, CH$_2$Fα, CH$_2$Fβ); 4.26 (d, 1H, J = 8.0 Hz, H-1β); 4.13 (dd, 1H, J = 2.8 Hz, 10.4 Hz, H-3α); 4.00−3.76 (m, 7H, H-2α, H-2β; H-5α; CH$_2$CH$_2$Fα, CH$_2$CH$_2$Fβ); 3.52−3.48 (m, 3H, H-3β, H-4α, H-5β); 3.38 (d, 1H, J = 2.8 Hz, H-4β); 1.21−1.18 (m, 6H, H-6α, H-6β); 0.98, 0.97 (s, 9H, (CH$_3$)$_3$CSi); 0.24 (s, 3H, CH$_3$Si); 0.20 (s, 6H, 2× CH$_3$Si); 0.16 (s, 3H, CH$_3$Si). ^{13}C-APT NMR (100 MHz) δ: 138.5, 138.5 (C$_{q,arom}$); 128.3, 128.2, 128.1, 127.9, 127.6, 127.6 (CH$_{arom}$); 102.5 (C-1β); 98.4 (C-1α); 82.7 (d, J = 168 Hz, CH$_2$Fβ); 82.6 (d, J = 168 Hz, CH$_2$Fα); 80.7 (C-4α); 79.0 (C-4β); 75.6, 75.4 (PhCH$_2$); 74.8 (C-5β); 71.4 (C-3α); 70.5 (C-3β); 68.4 (d, J = 20 Hz, CH$_2$CH$_2$F); 67.1 (d, J = 20 Hz, CH$_2$CH$_2$F); 66.8 (C-5α); 64.6 (C-2β); 61.4 (C-2α); 25.9, 25.9 ((CH$_3$)$_3$CSi); 18.1, 18.0 (C$_q$Si); 16.7, 16.6 (C-6α, C-6β); −4.0, −4.3, −4.8, −5.1 (CH$_3$Si). IR (thin film) ν: 2930, 2886, 2857, 2108, 1254, 1169, 1119, 1065, 1045. HRMS: [M + NH$_4$]$^+$ calcd for C$_{21}$H$_{38}$FN$_4$O$_4$Si 457.2643, found 457.2636.

2,2-Difluoroethyl 2-Azido-3,4-di-O-benzyl-2-deoxy-α/β-L-fucopyranoside (C1). The products (α/β 3:2) were obtained after column chromatography (toluene/EtOAc, 1:0 → 9:1 v/v) in 81% yield (35 mg, 0.081 mmol). ^{1}H NMR (400 MHz) δ: 7.43−7.25 (m, 50H, CH$_{arom}$); 6.08−5.78 (m, 5H, CHF$_2$α, CHF$_2$β); 4.95−4.91 (m, 7H, H-1α, PhCHHα, PhCHHβ); 4.74−4.59 (m, 14H, PhCH$_2$); 4.24 (d, 2H, J = 8.0 Hz, H-1β); 4.01−3.73 (m, 24H, H-2α, H-2β, H-3α, H-4α, H-5α, CH$_2$CHF$_2$α, CH2CHF$_2$β); 3.54 (d, 2H, J = 2.4 Hz, H-4β); 3.43 (q, 2H, J = 6.4 Hz, H-5β); 3.31 (dd, 2H, J = 2.8 Hz, 10.0 Hz, H-3β); 1.20−1.17 (m, 15H, H-6α, H-6β). ^{13}C-APT NMR (100 MHz) δ: 138.1, 138.0, 137.5, 137.5 (C$_{q,arom}$); 128.6, 128.5, 128.3, 128.3, 128.2, 128.0, 127.8, 127.8, 127.8, 127.6 (CH$_{arom}$); 114.3 (CHF$_2$β); 113.9 (CHF$_2$α); 102.4 (C-1β); 99.0 (C-1α); 80.8 (C-3β); 77.6 (C-3α or C-5α); 75.9 (C-4α); 75.0 (PhCH$_2$α); 74.7 (PhCH$_2$β); 74.6 (C-4β); 72.8 (PhCH$_2$β); 72.4 (PhCH$_2$α); 70.9 (C-5β); 68.3 (t, J = 29 Hz, CH$_2$CHF$_2$β); 67.2 (C-3α or C-5α); 67.2 (t, J = 29 Hz, CH$_2$CHF$_2$β); 62.8 (C-2β); 59.4 (C-2α); 16.7, 16.6 (C-6α, C-6β). IR (thin film) ν: 2926, 2110, 1738, 1454, 1360, 1109, 1069. HRMS: [M + NH$_4$]$^+$ calcd for C$_{22}$H$_{29}$F$_2$N$_4$O$_4$ 451.2151, found 451.2150.

2,2-Difluoroethyl 2-Azido-3,4-di-O-benzoyl-2-deoxy-α/β-L-fucopyranoside (C2). The title compounds (α/β 3:2) were obtained after column chromatography (toluene/EtOAc, 1:0 → 9:1 v/v) in 74% yield (34 mg, 0.074 mmol). 8.07−8.02 (m, 5.4H, CH_{arom}); 7.89−7.86 (m, 5.4H, CH_{arom}); 7.64−7.60 (m, 2.7H, CH_{arom}); 7.53−7.46 (m, 8.1H, CH_{arom}); 7.35−7.31 (m, 5.4H, CH_{arom}); 6.17−5.87 (m, 2.7H, CHF₂α, CHF₂β); 5.76−5.73 (m, 3.4H, H-3α, H-4α); 5.60 (d, 1H, J = 3.2 Hz, H-4β); 5.19−5.16 (m, 2.7H, H-1α, H-3β); 4.56 (d, 1H, J = 8.0 Hz, H-1β); 4.38 (q, 1H, J = 6.4 Hz, H-5α); 4.17−3.86 (m, 9.1H, H-2α, H-2β, H-5β, $CH_2CH_2Fα$, $CH_2CH_2Fβ$); 1.32−1.23 (m, 8.1H, H-6α, H-6β). ¹³C-APT NMR (100 MHz) δ: 165.7, 165.7, 165.4 (CO_{Bz}); 133.5, 133.5, 133.4, 133.3, 129.9, 129.8 (CH_{arom}); 129.2, 129.1, 129.0 ($C_{q,arom}$); 129.0, 128.6, 128.4, 128.3 (CH_{arom}); 114.0 (t, J = 240 Hz, CHF₂β); 113.7 (t, J = 240 Hz, CHF₂α); 102.6 (C-1β); 99.1 (C-1α); 71.9 (C-3β); 71.1 (C-3α or C-4α); 70.0, 69.9 (C-4β, C-5β); 69.0 (C-3α or C-4α); 68.8 (t, J = 30 Hz, $CH_2CH_2Fβ$); 67.4 (t, J = 30 Hz, $CH_2CH_2Fα$); 65.8 (C-5α); 61.2 (C-2β); 57.9 (C-2α); 16.2 (C-6β); 16.0 (C-6α). IR (thin film) ν: 2926, 2110, 1726, 1450, 1261, 1163, 1107, 1094, 1067. HRMS: $[M + Na]^+$ calcd for $C_{22}H_{21}F_2N_3O_6Na$ 484.1291, found 484.1289.

2,2-Difluoroethyl 2-Azido-4-O-benzoyl-3-O-benzyl-2-deoxy-α/β-L-fucopyranoside (C3). The products (α/β 3:1) were obtained after column chromatography (toluene/EtOAc, 1:0 → 19:1) in 76% yield (34 mg, 0.076 mmol), accompanied by a small amount of inseparable, hydrolyzed donor. ¹H NMR (400 MHz) δ: 8.12−8.07 (m, 8H, CH_{arom}); 7.60−7.58 (m, 4H, CH_{arom}); 7.49−7.44 (m, 10H, CH_{arom}); 7.35−7.25 (m, 18H, CH_{arom}); 6.12−5.82 (m, 4H, CHF₂α, CHF₂β); 5.70 (d, 3H, J = 2.8 Hz, H-4α); 5.45 (d, 1H, J = 2.8 Hz, H-4β); 5.01 (d, 3H, J = 3.6 Hz, H-1α); 4.83 (d, 3H, J = 10.8 Hz, PhCHHα); 4.79 (d, 1H, J = 11.6 Hz, PhCHHβ); 4.56−4.53 (d, 4H, PhCHHα, PhCHHβ); 4.33 (d, 1H, J = 8.0 Hz, H-1β); 4.19 (q, 3H, J = 6.4 Hz, H-5α); 4.08 (dd, 3H, J = 3.2 Hz, 10.8 Hz, H-3α); 4.03−3.69 (m, 13H, H-2α, H-2β, H-5β, $CH_2CHF_2α$, $CH_2CHF_2β$); 3.47 (dd, 1H, J = 3.6 Hz, 10.8 Hz, H-3β); 1.31−1.22 (m, 12H, H-6α, H-6β). ¹³C-APT NMR (100 MHz) δ: 166.1, 166.0 (CO_{Bz}); 137.0, 136.9 ($C_{q,arom}$); 133.4, 133.3, 130.0, 129.9, 129.5, 129.4, 129.2 (CH_{arom}); 128.6, 128.5 ($C_{q,arom}$); 128.4, 128.4, 128.3, 128.2, 128.0, 127.9, 127.6 (CH_{arom}); 114.2 (t, J = 240 Hz, CHF₂β); 113.8 (t, J = 240 Hz, CHF₂α); 102.4 (C-1β); 99.0 (C-1α); 77.5 (C-3β); 74.1 (C-3α); 71.6 (PhCH₂β); 71.5 (PhCH₂α); 69.8 (C-5β); 69.6 (C-4α); 68.6 (C-4β); 64.6 (t, J = 30 Hz, $CH_2CHF_2β$); 67.4 (t, J = 28 Hz, $CH_2CHF_2α$); 65.8 (C-5α); 62.5 (C-2β); 59.1 (C-2α); 16.4, 16.3 (C-6α, C-6β). IR (thin film) ν: 2924, 2110, 1721, 1452, 1265, 1167, 1109, 1067, 1053, 1026. HRMS: $[M + H−N_2]^+$ calcd for $C_{22}H_{24}F_2NO_5$ 420.1617, found 420.1617.

2,2-Difluoroethyl 2-Azido-3-O-benzoyl-4-O-benzyl-2-deoxy-α/β-L-fucopyranoside (C4). The title compounds (α/β 1:1) were obtained after column chromatography (toluene/EtOAc, 1:0 → 9:1) in 80% yield (36 mg, 0.080 mmol). ¹H NMR (400 MHz) δ: 8.10−8.06 (m, 4H, CH_{arom}); 7.63−7.59 (m, 2H, CH_{arom}); 7.49−7.46 (m, 4H, CH_{arom}); 7.26−7.20 (m, 10H, CH_{arom}); 6.11−5.82 (m, 2H, CHF₂α, CHF₂β); 5.54 (dd, 1H, J = 3.2 Hz, 11.2 Hz, H-3α); 5.04 (d, 1H, J = 3.6 Hz, H-1α); 4.95 (dd, 1H, J = 2.8 Hz, 10.8 Hz, H-3β); 4.72−4.69 (d, 2H, J = 11.6 Hz, 2× PhCHH); 4.57−4.52 (m, 2H, 2× PhCHH); 4.42 (d, 1H, J = 8.8 Hz, H-1β); 4.14−4.3.78 (m, 9H, H-2α, H-2β, H-4α, H-4β, H-5α, $CH_2CHF_2α$, $CH_2CHF_2β$); 3.68 (q, 1H, J = 6.4 Hz, H-5β); 1.30−1.20 (m, 6H, H-6α, H-6β). ¹³C-APT NMR (100 MHz) δ: 165.8 (CO_{Bz}); 137.4, 137.3 ($C_{q,arom}$); 133.6, 133.6, 130.2, 129.9 (CH_{arom}); 129.3 ($C_{q,arom}$); 129.0, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9 (CH_{arom}); 114.1 (t, J = 240 Hz, CHF₂); 113.8 (t, J = 240 Hz, CHF₂); 102.4 (C-1β); 99.0 (C-1α); 77.0, 75.7 (C-4α, C-4β); 75.6, 75.5 (PhCH₂); 74.7 (C-3β); 71.9 (C-3α); 70.9 (C-5β); 68.7−67.3 (m, 2C, $CH_2CHF_2α$, $CH_2CHF_2β$); 66.9 (C-5α); 61.1 (C-2β); 57.9 (C-2α); 16.5, 16.3 (C-6α, C-6β). IR (thin film) ν: 2924, 2110, 1721, 1452, 1265, 1169, 1096, 1069, 1026. HRMS: $[M + NH_4]^+$ calcd for $C_{22}H_{27}F_2N_4O_5$ 465.1944, found 465.1943.

2,2-Difluoroethyl 2-Azido-2-deoxy-3,4-di-O-(tert-butyldimethyl-silyl)-α/β-L-fucopyranoside (C5). The title products (α/β 5:2) were obtained after column chromatography (hexane/Et₂O, 1:0 → 19:1 v/v) in 75% yield (36 mg, 0.075 mmol). ¹H NMR (400 MHz) δ: 6.09−5.79 (m, 7H, CHF₂α, CHF₂β) 4.93 (d, 5H, J = 3.2 Hz, H-1α); 4.26 (d, 2H, J = 8.0 Hz, H-1β); 4.01−3.73 (m, 27H, H-2α, H-3α, H-5α, $OCH_2CHF_2α$, $OCH_2CHF_2β$); 3.71 (d, 5H, J = 2.0 Hz, H-4α); 3.58−3.53 (m, 4H, H-2β, H-4β); 3.47 (q, 2H, J = 6.4 Hz, H-5β); 3.36 (dd, 2H, J = 2.4 Hz, 10.4 Hz, H-3β); 1.23 (d, 6H, J = 6.4 Hz, H-6β); 1.19 (d, 15H, J = 6.4 Hz, H-6α); 0.96−0.89 (m, 126H, (($CH_3)_3CSi$); 0.18−0.09 (m, 84H, CH_3Si). ¹³C-APT NMR (100 MHz) δ: 114.4 (t, J = 240 Hz, CHF₂β); 114.1 (t, J = 240 Hz, CHF₂α); 102.8 (C-1β); 98.9 (C-1α); 75.0 (C-4α); 74.3 (C-3β); 73.8 (C-4β); 71.5 (C-5β); 71.1 (C-3α); 68.5 (C-5α); 68.2 (t, J = 29 Hz, $CH_2CHF_2β$); 67.1 (t, J = 29 Hz, $CH_2CHF_2α$); 63.8 (C-2β); 61.0 (C-2α); 26.3, 26.1 (($CH_3)_3CSi$); 18.6, 18.5 (C_qSi); 17.4, (C-6β); 17.3 (C-6α); −3.5, −3.5, −3.8, −4.4, −4.5, −4.7 (CH_3Si). IR (thin film) ν: 2930, 2859, 2108, 1252, 1177, 1113, 1069, 1043, 1028. HRMS: $[M + H−N_2]^+$ calcd for $C_{20}H_{42}F_2NO_4Si_2$ 454.2615, found 454.2613.

2,2-Difluoroethyl 2-Azido-4-O-benzyl-2-deoxy-3-O-(tert-butyldimethylsilyl)-α/β-L-fucopyranoside (C6). The title products (α/β 2:1) were obtained after chromatography (hexane/Et₂O, 1:0 → 9:1 v/v) in 87% yield (40 mg, 0.087 mmol). ¹H NMR (400 MHz) δ: 7.39−7.25 (m, 7.5H, CH_{arom}); 6.08−5.81 (m, 1.5H, CHF₂α, CHF₂β); 5.05−5.02 (d, 1.5H, J = 11.2 Hz, PhCHHα, PhCHHβ); 4.93 (d, 1H, J = 3.6 Hz, H-1α); 4.62−4.56 (m, 1.5H, PhCHHα, PhCHHβ); 4.25 (d, 0.5H, J = 8.0 Hz, H-1β); 4.08 (dd, 1H, J = 2.8 Hz, 10.4 Hz, H-3α); 3.94 (q, 1H, J = 6.4 Hz, H-5α); 3.82−3.73 (m, 4H, H-2α, $CH_2CHF_2α$, $CH_2CHF_2β$); 3.66 (dd, 0.5H, J = 8.0 Hz, 10.4 Hz, H-2β); 3.52−3.50 (m, 2H, H-3β, H-4α, H-5β); 3.39 (d, 0.5H, J = 2.4 Hz, H-4β), 1.26−1.18 (m, 4.5H, H-6α, H-6β); 0.98 (s, 9H, ($CH_3)_3CSi$); 0.97 (s, 4.5H, ($CH_3)_3CSi$); 0.24 (s, 3H, CH_3Si); 0.20 (s, 4.5H, $CH_3Siα$, $CH_3Siβ$); 0.16 (s, 1.5H, CH_3Si). ¹³C-APT NMR (100 MHz) δ: 138.4, 138.4 ($C_{q,arom}$); 128.3, 128.2, 128.1, 127.9, 127.7, 127.7 (CH_{arom}); 114.3 (t, J = 240 Hz, CHF₂β); 114.0 (t, J = 240 Hz, CHF₂α); 102.6 (C-1β); 99.0 (C-1α); 80.5 (C-4α); 78.9 (C-4β); 75.7, 75.5 (PhCH₂); 74.7 (C-3β or C-5β); 71.3 (C-3α); 70.7 (C-3β or C-5β); 68.4 (t, J = 27 Hz, $CH_2CHF_2β$); 67.3 (t, J = 29 Hz, $CH_2CHF_2α$); 67.3 (C-5α); 64.5 (C-2β); 61.3 (C-2α); 25.9, 25.8 (($CH_3)_3CSi$); 18.1, 18.0 (C_qSi); 16.7, 16.6 (C-6, C-6′); −4.1, −4.3, −4.8, −5.1 (CH_3Si). IR (thin film) ν: 2930, 2110, 1260, 1169, 1115, 1070, 1047. HRMS: $[M + NH_4]^+$ calcd for $C_{21}H_{37}F_2N_4O_4Si$ 475.2546, found 475.2547.

2,2,2-Trifluoroethyl 2-Azido-3,4-di-O-benzyl-2-deoxy-α-L-fucopyranoside (D1). The title compound was obtained after column chromatography (hexane/Et₂O 1:0 → 9:1 v/v) in 80% yield (36 mg, 0.080 mmol, 80%). ¹H NMR (400 MHz) δ: 7.44−7.25 (m, 10H, CH_{arom}); 4.96−4.92 (m, 2H, PhCHH, H-1); 4.75 (s, 2H, PhCH₂); 4.60 (d, 1H, J = 11.6 Hz, PhCHH); 3.99−3.88 (m, 5H, H-2, H-3, H-5, CH_2CF_3); 3.54 (d, 1H, J = 2.4 Hz, H-4); 1.18 (d, 3H, J = 6.4 Hz, H-6). ¹³C-APT NMR (100 MHz) δ: 138.0, 137.5 ($C_{q,arom}$); 128.6, 128.3, 128.3, 128.0, 127.8, 127.8 (CH_{arom}); 123.6 (q, J = 277 Hz, CF₃); 99.0 (C-1); 77.4 (C-3 or C-5); 75.9 (C-4); 75.0, 72.5 (PhCH₂); 67.5 (C-3 or C-5); 64.9 (q, J = 35 Hz, CH_2CF_3); 59.2 (C-2); 16.7 (C-6). ¹³C-GATED NMR (100 MHz) δ: 99.0 (d, J = 170 Hz, C-1). IR (thin film) ν: 2927, 2108, 1454, 1356, 1279, 1163, 1082, 1051. HRMS: $[M + Na]^+$ calcd for $C_{22}H_{24}F_3N_3O_4Na$ 474.1611, found 474.1609.

2,2,2-Trifluoroethyl 2-Azido-3,4-di-O-benzoyl-2-deoxy-α/β-L-fucopyranoside (D2). The title compounds (α/β 10:1) were isolated after column chromatography (hexane/EtOAc. 1:0 → 4:1) in 50% yield (24 mg, 0.050 mmol). NMR data are reported for the α-product only. ¹H NMR (400 MHz) δ: 8.04−8.02 (m, 2H, CH_{arom}); 7.89−7.86 (m, 2H, CH_{arom}); 7.66−7.61 (m, 1H, CH_{arom}); 7.54−7.45 (m, 3H, CH_{arom}); 7.36−7.32 (m, 2H, CH_{arom}); 5.77−7.73 (m, 2H, H-3, H-4); 5.20 (d, 1H, J = 3.6 Hz, H-1); 4.37 (q, 1H, J = 6.4 Hz, H-5); 4.08 (q, 2H, J = 8.4 Hz, CH_2CF_3); 3.95 (dd, 1H, J = 3.2 Hz, 11.4 Hz, H-2); 1.26 (d, 3H, J = 6.8 Hz, H-6). ¹³C-APT NMR (100 MHz) δ: 165.6, 165.3 (CO_{Bz}); 133.5, 133.4, 129.9, 129.8 (CH_{arom}); 129.2, 129.0 ($C_{q,arom}$); 128.6, 128.3 (CH_{arom}); 123.4 (q, J = 276 Hz, CF₃); 99.2 (C-1); 71.0 (C-3); 68.8 (C-4); 65.8 (C-5); 65.3 (q, J = 35 Hz, CH_2CF_3); 57.7 (C-2); 16.0 (C-6). IR (thin film) ν: 2928, 2110, 1724, 1452, 1273, 1261, 1157, 1109, 1094, 1069, 1026. HRMS: $[M + Na]^+$ calcd for $C_{22}H_{20}F_3N_3O_6Na$ 502.1196, found 502.1195.

2,2,2-Trifluoroethyl 2-Azido-4-O-benzoyl-3-O-benzyl-2-deoxy-α-L-fucopyranoside (D3). The title compound was obtained after column chromatography (hexane/Et₂O 1:0 → 9:1 v/v) in 45% yield

(21 mg, 0.045 mmol, $\alpha/\beta \geq$ 19:1). NMR data are reported for the α-isomer only. ^{1}H NMR (400 MHz) δ: 8.08 (d, 2H, J = 7.2 Hz, CH_{arom}); 7.59 (t, 1H, J = 7.6 Hz, CH_{arom}); 7.46 (t, 2H, J = 8.0 Hz, CH_{arom}); 7.34−7.24 (m, 5H, CH_{arom}); 5.72 (d, 1H, J = 2.8 Hz, H-4); 5.05 (d, 1H, J = 3.6 Hz, H-1); 4.85 (d, 1H, J = 10.4 Hz, PhCHH); 4.55 (d, 1H, J = 10.8 Hz, PhCHH); 4.19 (q, 1H, J = 6.4 Hz, H-5); 4.11 (dd, 1H, J = 2.8 Hz, 10.4 Hz, H-3); 4.01 (q, 2H, J = 8.4 Hz, CH_2CF_3); 3.80 (dd, 1H, J = 3.6 Hz, 10.4 Hz, H-2); 1.24 (d, 3H, J = 6.8 Hz, H-6). ^{13}C-APT NMR (100 MHz) δ: 166.0 (CO_{Bz}); 137.0 ($C_{q,arom}$); 133.4, 129.8 (CH_{arom}); 129.5 ($C_{q,arom}$); 128.5, 128.4, 128.3, 127.9 (CH_{arom}); 123.5 (q, J = 277 Hz, CF_3); 99.1 (C-1); 74.1 (C-3); 71.6 (PhCH$_2$); 69.6 (C-4); 66.2 (C-5); 65.3 (q, J = 35 Hz, CH_2CF_3); 58.9 (C-2); 16.3 (C-6). IR (thin film) ν: 2924, 2110, 1721, 1452, 1267, 1157, 1111, 1084, 1055, 1026. HRMS: $[M + H]^+$ calcd for $C_{22}H_{23}F_3N_3O_5$ 466.1584, found 466.1581.

2,2,2-Trifluoroethyl 2-Azido-3-O-benzoyl-4-O-benzyl-2-deoxy-α/β-L-fucopyranoside (D4). The title compounds (α/β 7:1) were obtained after column chromatography (hexane/Et$_2$O 1:0 → 4:1 v/v) in 77% yield (36 mg, 0.077 mmol). ^{1}H NMR (400 MHz) δ: 8.10−8.06 (m, 2.3H, CH_{arom}); 7.63−7.59 (m, 1.2H, CH_{arom}); 7.49−7.46 (m, 2.5H, CH_{arom}); 7.29−7.21 (m, 6H, CH_{arom}); 5.54 (dd, 1H, J = 2.8 Hz, 11.2 Hz, H-3α); 5.07 (d, 1H, J = 3.6 Hz, H-1α); 4.95 (dd, 0.15H, J = 2.8 Hz, 11.2 Hz, H-3β); 4.72−4.69 (m, 1.15H, PhCH$H\alpha$, PhCH$H\beta$); 4.57−4.52 (m, 1.15H, PhCH$H\alpha$, PhCH$H\beta$); 4.48 (d, 0.15H, J = 8.0 Hz, H-1β); 4.11 (q, 1H, J = 6.8 Hz, H-5α); 4.07−3.95 (m, 4.45H, H-2α, H-4α, $CH_2CF_3\alpha$, H-2β, $CH_2CF_3\beta$); 3.82 (d, 0.15H, J = 2.8 Hz, H-4β); 3.68 (q, 0.15H, J = 6.8 Hz, H-5β); 1.26−1.22 (m, 3.45H, H-6α, H-6β). ^{13}C-APT NMR (100 MHz) δ: 165.8 (CO Bz); 137.3 ($C_{q,arom}$); 133.6, 129.9 (CH_{arom}); 129.1 ($C_{q,arom}$); 128.6, 128.4, 128.3, 128.2, 128.0 (CH_{arom}); 123.5 (q, J = 277 Hz, $CF_3\alpha$); 102.0 (C-1β); 99.1 (C-1α); 76.9 (C-4α); 75.6 (PhCH$_2\alpha$); 75.6 (C-4β); 75.5 (PhCH$_2\beta$); 74.6 (C-3β); 71.8 (C-3α); 71.0 (C-5β); 67.2 (C-5α); 65.0 (q, J = 35 Hz, $CH_2CF_3\alpha$); 61.1 (C-2β); 57.6 (C-2α); 16.4 (C-6β); 16.3 (C-6α). IR (thin film) ν: 2924, 2110, 1721, 1452, 1267, 1155, 1105, 1096, 1070, 1045, 1026. HRMS: $[M + NH_4]^+$ calcd for $C_{22}H_{26}F_3N_4O_5$ 483.1850, found 483.1849.

2,2,2-Trifluoroethyl 2-Azido-2-deoxy-3,4-di-O-(tert-butyldimethylsilyl)-α/β-L-fucopyranoside (D5). The title compounds (α/β 19:1) were isolated after column chromatography (hexane/Et$_2$O, 1:0 → 49:1) in 84% yield (42 mg, 0.084 mmol). NMR data are reported for the α-isomer only. ^{1}H NMR (400 MHz) δ: 4.97 (d, 1H, J = 3.2 Hz, H-1); 4.01 (dd, 1H, J = 2.0 Hz, 10.4 Hz, H-3); 3.98−3.88 (m, 3H, H-5, CH_2CF_3); 3.79 (dd, 1H, J = 3.6 Hz, 10.4 Hz, H-2); 3.72 (d, 1H, J = 1.2 Hz, H-4); 1.20 (d, 3H, J = 6.4 Hz, H-6); 0.96, 0.94 (s, 9H, (CH$_3$)$_3$CSi); 0.19 (s, 3H, CH_3Si); 0.16−0.15 (m, 6H, CH_3Si); 0.07 (s, 3H, CH_3Si). ^{13}C-APT NMR (100 MHz) δ: 123.7 (q, J = 276 Hz, CF_3); 98.8 (C-1); 74.9 (C-4); 70.9 (C-3); 68.8 (C-5); 64.7 (q, J = 35 Hz, CH_2CF_3); 60.8 (C-2); 26.2, 26.1 ((CH$_3$)$_3$CSi); 18.6, 18.5 (C$_q$Si); 17.2 (C-6); −3.5, −3.8, −4.5, −4.8 (CH_3Si). IR: 2932, 2859, 2108, 1279, 1256, 1177, 1045. HRMS: $[M + H−N_2]^+$ calcd for $C_{20}H_{41}F_3NO_4Si_2$ 472.2521, found 472.2518.

2,2,2-Trifluoroethyl 2-Azido-4-O-benzyl-2-deoxy-3-O-(tert-butyldimethylsilyl)-α-L-fucopyranoside (D6). The title product was obtained after column chromatography (hexane/Et$_2$O, 1:0 → 9:1 v/v) in 90% yield (43 mg, 0.090 mmol). ^{1}H NMR (400 MHz) δ: 7.39−7.25 (m, 5H, CH_{arom}); 5.04 (d, 1H, J = 11.2 Hz, PhCHH); 4.96 (d, 1H, J = 3.6 Hz, H-1); 4.57 (d, 1H, J = 11.2 Hz, PhCHH); 4.10 (dd, 1H, J = 2.4 Hz, 10.2 Hz, H-3); 3.97−3.91 (m, 3H, H-5, CH_2CF_3); 3.81 (dd, 1H, J = 3.6 Hz, 10.0 Hz, H-2); 3.53 (d, 1H, J = 2.0 Hz, H-4); 1.20 (d, 3H, J = 6.4 Hz, H-6); 0.98 (d, 9H, (CH$_3$)$_3$CSi); 0.24, 0.20 (s, 3H, CH_3Si). ^{13}C-APT NMR (100 MHz) δ: 138.4 ($C_{q,arom}$); 128.3, 128.1, 127.9 (CH_{arom}); 123.6 (q, J = 277 Hz, CF_3); 99.0 (C-1); 8.4 (C-4); 75.7 (PhCH$_2$); 71.1 (C-3); 67.7 (C-5); 64.9 (q, J = 35 Hz, CH_2CF_3); 61.1 (C-2); 25.9 ((CH$_3$)$_3$CSi); 18.1 (C$_q$Si); 16.5 (C-6); −4.1, −5.1 (CH_3Si). IR (thin film) ν: 2930, 2859, 2108, 1279, 1261, 1163, 1121, 1084, 1045. HRMS: $[M + NH_4]^+$ calcd for $C_{21}H_{36}F_3N_4O_4Si$ 493.2452, found 493.2452.

Cyclohexyl 2-Azido-3,4-di-O-benzyl-2-deoxy-α/β-L-fucopyranoside (E1). The title compounds (α/β 1:2) were obtained after column chromatography (hexane/Et$_2$O 1:0 → 9:1 v/v) in 75% yield (34 mg,

0.075 mmol). ^{1}H NMR (400 MHz) δ: 7.44−7.25 (m, 30H, CH_{arom}); 5.02 (d, 1H, J = 3.6 Hz, H-1α); 4.94−4.91 (m, 3H, PhCH$H\alpha$, PhCH$H\beta$); 4.77−4.60 (m, 12H, PhCH$_2\alpha$, PhCH$_2\beta$); 4.28 (d, 2H, J = 8.0 Hz, H-1β); 4.02−3.96 (m, 2H, H-3α, H-5α); 3.81−374 (m, 4H, H-2α, H-2β, H-4α); 3.65 (tt, 2H, J = 7.6 Hz, 9.6 Hz, CH_{Cy}); 3.58 (tt, 1H, J = 7.6 Hz, 9.6 Hz, CH_{Cy}); 3.51 (d, 2H, J = 2.4 Hz, H-4β); 3.38 (q, 2H, J = 6.4 Hz, H-5β); 3.26 (dd, 2H, J = 2.8 Hz, 10.4 Hz, H-3β), 1.90−1.62 (m, 12H, $CH_{2,Cy}$); 1.50−1.34 (m, 10H, $CH_{2,Cy}$); 1.25−1.15 (m, 15H, H-6α, H-6β, $CH_{2,Cy}$). ^{13}C-APT NMR (100 MHz) δ: 138.2, 137.8 ($C_{q,arom}$); 128.5, 128.5, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.4, 127.6 (CH_{arom}); 100.3 (C-1β); 96.6 (C-1α); 80.9 (C-3β); 77.6 (C-3α); 77.2 ($CH_{Cy}\beta$); 76.2 (C-4α); 76.1 ($CH_{Cy}\alpha$); 74.8 (C-4β); 74.5, 72.6, 72.2 (PhCH$_2$); 70.4 (C-5β); 66.5 (C-5α); 63.2 (C-2β); 59.4 (C-2α); 33.3, 31.5, 31.4, 25.6, 25.5, 24.1, 23.9, 23.8 ($CH_{2,Cy}$); 17.0 (C-6β); 16.7 (C-6α). IR (thin film) ν: 2932, 2855, 2106, 1454, 1359, 1107, 1067, 1038. HRMS: $[M + NH_4]^+$ calcd for $C_{26}H_{37}N_4O_4$ 469.2809, found 469.2810.

Cyclohexyl 2-Azido-3,4-di-O-benzoyl-2-deoxy-α/β-L-fucopyranoside (E2). The title compounds (α/β 1:9) were obtained after column chromatography (hexane/EtOAc 1:0 → 9:1 v/v) in 38% yield (18 mg, 0.038 mmol). NMR data are reported only for the β-glycoside. ^{1}H NMR (400 MHz) δ: 8.09−8.07 (m, 2H, CH_{arom}); 7.89−7.85 (m, 2H, CH_{arom}); 7.64−7.60 (m, 1H, CH_{arom}); 7.52−7.45 (m, 3H, CH_{arom}); 7.32 (t, 2H, J = 7.6 Hz, CH_{arom}); 5.56 (d, 1H, J = 3.6 Hz, H-4); 5.15 (dd, 1H, J = 3.6 Hz, 10.8 Hz, H-3); 4.61 (d, 1H, J = 8.0 Hz, H-1); 3.95−3.88 (m, 2H, H-2, H-5); 3.79 (tt, 1H, J = 7.6 Hz, 9.6 Hz, CH_{Cy}); 2.03−2.01 (m, 2H, $CH_{2,Cy}$); 1.81−1.79 (m, 2H, $CH_{2,Cy}$); 1.57−1.43 (m, 3H, $CH_{2,Cy}$); 1.37−1.22 (m, 8H, H-6, $CH_{2,Cy}$). ^{13}C-APT NMR (100 MHz) δ: 165.9, 165.4 (CO_{Bz}); 133.4, 133.3, 129.9, 129.7 (CH_{arom}); 129.3, 129.1 ($C_{q,arom}$); 128.5, 128.3 (CH_{arom}); 100.5 (C-1); 78.3 (CH_{Cy}); 71.9 (C-3); 70.3 (C-4); 69.4 (C-5); 61.5 (C-2); 33.5, 31.6, 25.5, 24.1, 23.9 ($CH_{2,Cy}$); 16.4 (C-6). IR (thin film) ν: 2934, 2857, 2110, 1724, 1450, 1281, 1263, 1173, 1107, 1096, 1069, 1026. HRMS: $[M + Na]^+$ calcd for $C_{26}H_{29}N_3NaO_6$ 502.1949, found 502.1948.

Cyclohexyl 2-Azido-4-O-benzoyl-3-O-benzyl-2-deoxy-α/β-L-fucopyranoside (E3). The title compounds (α/β 1:4) were obtained after column chromatography (hexane/Et$_2$O 1:0 → 9:1 v/v) in 71% yield (33 mg, 0.071 mmol). ^{1}H NMR (400 MHz) δ: 8.14−8.07 (m, 2.5H, CH_{arom}); 7.60−7.56 (m, 1.25H, CH_{arom}); 7.48−7.44 (m, 2.5H, CH_{arom}); 7.35−7.24 (m, 6.25H, CH_{arom}); 5.70 (d, 0.25H, J = 2.4 Hz, H-4α); 5.52 (dd, 1H, J = 0.8 Hz, 3.2 Hz, H-4β); 5.11 (d, 0.25H, J = 3.6 Hz, H-1α); 4.84 (d, 0.25H, J = 10.4 Hz, PhCH$H\alpha$); 4.78 (d, 1H, J = 11.6 Hz, PhCH$H\beta$); 4.56−4.52 (m, 1.25H, PhCHH); 4.39 (d, 1H, J = 8.4 Hz, H-1β); 4.26 (q, 0.25H, J = 7.2 Hz, H-5α); 4.13 (dd, 0.25H, J = 3.6 Hz, 10.6 Hz, H-3α); 3.74−3.60 (m, 3.5H, H-2α, H-2β, H-5β, CH_{Cy}); 3.41 (dd, 1H, J = 3.2 Hz, 10.2 Hz, H-3β); 1.98−1.77 (m, 5H, $CH_{2,Cy}$); 1.55−1.43 (m, 4H, $CH_{2,Cy}$); 1.31−1.20 (m, 7.25H, H-6α, H-6β, $CH_{2,Cy}$). ^{13}C-APT (100 MHz) δ: 166.30 (CO_{Bz}); 137.2 ($C_{q,arom}$); 133.3, 133.2, 130.1, 129.8 (CH_{arom}); 129.5 ($C_{q,arom}$); 128.4, 128.4, 128.2, 128.1, 127.8, 127.8, 127.8 (CH_{arom}); 100.3 (C-1β); 96.7 (C-1α); 78.0 (CH_{Cy}); 77.5 (C-3β); 74.1 (C-3α); 71.5 (PhCH$_2\alpha$); 70.1 (C-4α); 69.4 (C-5β); 69.0 (C-4β); 65.2 (C-5α); 62.9 (C-2β); 59.2 (C-2α); 33.5, 33.3, 31.6, 31.5, 25.5, 24.1, 23.9, 23.8 ($CH_{2,Cy}$); 16.6 (C-6β); 16.3 (C-6α). IR (thin film) ν: 2922, 2110, 1720, 1446, 1265, 1107, 1068. HRMS: $[M + H]^+$ calcd for $C_{26}H_{32}N_3O_5$ 466.2337, found 466.2335.

Cyclohexyl 2-Azido-3-O-benzoyl-4-O-benzyl-2-deoxy-α/β-L-fucopyranoside (E4). The title compounds (α/β 1:4) were obtained after column chromatography (hexane/Et$_2$O 1:0 → 9:1 v/v) in 71% yield (35 mg, 0.075 mmol). ^{1}H NMR (400 MHz) δ: 8.10−8.06 (m, 10H, CH_{arom}); 7.62−7.58 (m, 5H, CH_{arom}); 7.48−7.45 (m, 11H, CH_{arom}); 7.25−7.18 (m, 28H, CH_{arom}); 5.59 (dd, 1H, J = 2.4 Hz, 11.2 Hz, H-3α); 5.13 (d, 1H, J = 3.2 Hz, H-1α); 4.93 (dd, 4H, J = 2.8 Hz, 10.8 Hz, H-3β); 4.71−4.69 (m, 5H, PhCHH); 4.57−4.52 (m, 5H, PhCHH); 4.47 (d, 4H, J = 8.0 Hz, H-1β); 4.19 (q, 1H, J = 6.4 Hz, H-5α); 3.98−3.93 (m, 5H, H-2β, H-4α); 3.88 (dd, 1H, J = 3.4 Hz, 11.2 Hz, H-2α); 3.76−3.70 (m, 8H, H-4β, $CH_{Cy}\beta$); 3.66−3.61 (m, 5H, H-5β, $CH_{Cy}\alpha$); 1.93−1.75 (m, 22H, $CH_{2,Cy}$); 1.52−1.43 (m, 18H, $CH_{2,Cy}$); 1.32−1.18 (m, 38H, H-6α, H-6β, $CH_{2,Cy}$). ^{13}C-APT NMR

(100 MHz) δ: 165.8 (CO Bz); 137.6, 137.5 (C$_{q,arom}$); 133.5, 129.9 (CH$_{arom}$); 129.2 (C$_{q,arom}$); 128.5, 128.3, 128.2, 128.2, 127.8, 127.8 (CH$_{arom}$); 100.3 (H-1β); 96.7 (H-1α); 77.6 (CH$_{Cy}$β); 77.4 (H-4α); 76.5 (CH$_{Cy}$α); 75.9 (C-4β); 75.5 (PhCH$_2$α); 75.3 (PhCH$_2$β); 74.8 (C-3β); 72.0 (C-3α); 70.4 (C-5β); 66.2 (C-5α); 61.4 (C-2β); 57.8 (C-2α); 33.4, 33.3, 31.4, 29.7, 25.5, 23.9, 23.8 (CH$_{2,Cy}$); 16.7 (C-6β); 16.4 (C-6α). IR (thin film) ν: 2932, 2857, 2108, 1452, 1265, 1173, 1096, 1069, 1038, 1026. HRMS: [M + NH$_4$]$^+$ calcd for C$_{26}$H$_{35}$N$_4$O$_5$ 483.2602, found 483.2602.

Cyclohexyl 2-Azido-2-deoxy-3,4-di-O-(tert-butyldimethylsilyl)-α/β-L-fucopyranoside (E5). The products (α/β 1:3) were obtained after column chromatography (hexane/Et$_2$O, 1:0 → 9:1) in 80% yield (40 mg, 0.080 mmol). ^{1}H NMR (400 MHz) δ: 5.04 (d, 1H, J = 3.6 Hz, H-1α); 4.28 (d, 3H, J = 7.6 Hz, H-1β); 4.05 (dd, 1H, J = 2.4 Hz, 10.4 Hz, H-3α); 3.94 (q, 1H, J = 6.8 Hz, H-5α); 3.69−3.56 (m, 6H, H-2α, H-4α, OCH$_{Cy}$α, OCH$_{Cy}$β); 3.55 (d, 3H, J = 2.4 Hz, H-4β); 3.51 (dd, 3H, J = 8.0 Hz, 10.2 Hz, H-2β); 3.42 (q, 3H, J = 6.4 Hz, H-5β); 3.33 (dd, 3H, J = 2.4 Hz, 10.4 Hz, H-3β); 1.97−1.25 (m, 40H, CH$_{2,Cy}$); 1.22 (d, 9H, J = 6.4 Hz, H-6β); 1.17 (d, 3H, J = 6.4 Hz, H-6α); 0.96−0.90 (m, 72H, (CH$_3$)$_3$CSi); 0.18−0.08 (m, 48H, CH$_3$Si). ^{13}C-APT NMR (100 MHz) δ: 100.6 (C-1β); 96.3 (C-1α); 77.4 (CH$_{Cy}$β); 75.6 (CH$_{Cy}$α); 74.5 (C-3β); 74.0 (C-4β); 71.2 (C-3α); 71.0 (C-5β); 67.8 (C-5α); 64.2 (C-2β); 60.9 (C-2α); 33.5, 33.3, 31.8, 31.4 (CH$_{2,Cy}$); 26.2, 26.1 ((CH$_3$)CSi); 25.7, 25.6, 24.1, 24.0, 23.9, 23.7 (CH$_{2,Cy}$); 18.6, 18.5 (C$_q$Si); 17.7 (C-6β); 17.3 (C-6α); −3.4, −3.6, −4.3, −4.4, −4.5, −4.7 (CH$_3$Si). IR (thin film) ν: 2930, 2857, 2110, 1252, 1115, 1069, 1026. HRMS: [M + Na]$^+$ calcd for C$_{24}$H$_{49}$N$_3$O$_4$Si$_2$Na 522.3154, found 522.3151.

Cyclohexyl 2-Azido-4-O-benzyl-3-O-(tert-butyldimethylsilyl)-2-deoxy-α/β-L-fucopyranoside (E6). The title compounds (α/β 1:2) were obtained after column chromatography (hexane/Et$_2$O, 1:0 → 19:1) in 80% yield (38 mg, 0.080 mmol). ^{1}H NMR (400 MHz) δ: 7.39−7.26 (m, 15H, CH$_{arom}$); 5.03−5.01 (m, 4H, H-1α, PhCHHα, PhCHHβ); 4.61−4.55 (m, 3H, PhCHHα, PhCHHβ); 4.28 (d, 2H, J = 8.0 Hz, H-1β); 4.14 (broad doublet, J = 8.4 Hz, H-3α); 4.00 (q, 1H, J = 6.4 Hz, H-5α); 3.67−3.43 (m, 11H, H-2α, H-2β, H-3β, H-4α, H-5β, OCH$_{Cy}$α, OCH$_{Cy}$β); 3.36 (bs, 2H, H-4β); 1.89−1.11 (m, 39H, CH$_{2,Cy}$α/β, H-6α, H-6β); 0.98 (s, 9H, (CH$_3$)$_3$CSiα, 0.96 (s, 18H, (CH$_3$)$_3$CSiβ); 0.23−0.15 (m, 18H, CH$_3$Siα/β).^{13}C-APT NMR (100 MHz) δ: 138.7 (C$_{q,arom}$); 128.2, 128.2, 128.1, 127.9, 127.5, 127.5 (CH$_{arom}$); 100.4 (C-1β); 96.6 (C-1α); 81.0 (C-4α); 79.2 (C-4β); 77.3 (OCH$_{Cy}$β); 76.0 (OCH$_{Cy}$α); 75.6 (PhCH$_2$α); 75.3 (PhCH$_2$β); 74.9 (C-3β or C-5β); 71.3 (C-3α); 70.2 (C-3β or C-5β); 66.6 (C-5α); 64.9 (C-2β); 61.2 (C-2α); 33.4, 33.3, 31.5 (CH$_{2,Cy}$); 25.9, 25.6 (CH$_3$)$_3$CSiα/β); 24.1, 23.9, 23.8 (CH$_{2,Cy}$); 16.9 (C-6β); 16.7 (C-6α); −3.9, −4.3, −4.7, −5.0 (CH$_3$Si). IR (thin film) ν: 2930, 2857, 2108, 1254, 1115, 1067, 1040. HRMS: [M + NH$_4$]$^+$ calcd for C$_{25}$H$_{45}$N$_4$O$_4$Si 493.3205, found 493.3202.

Methyl 2-O-(2-Azido-3,4-di-O-benzoyl-2-deoxy-α/β-L-fucopyranosyl)-3-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside (F1). The product was obtained after size-exclusion chromatography (CH$_2$Cl$_2$/MeOH, 1:1 v/v) in 68% yield (49 mg, 0.068 mmol). NMR data are reported for the α-linked fucoside only. ^{1}H NMR (400 MHz) δ: 7.53−7.50 (m, 2H, CH$_{arom}$); 7.44−7.23 (m, 18H, CH$_{arom}$); 5.64 (s, 1H, PhCH); 4.95 (d, 1H, J = 3.6 Hz, H-1′); 4.90 (d, 1H, J = 11.2 Hz, PhCHH); 4.79−4.69 (m, 5H, H-1, PhCH$_2$); 4.59 (d, 1H, J = 11.6 Hz, PhCHH); 4.37 (q, 1H, J = 6.4 Hz, H-5′); 4.25 (dd, 1H, J = 4.8 Hz, 10.2 Hz, H-6); 4.19−4.13 (m, 3H, H-2, H-4, H-3′); 3.98 (dd, 1H, J = 3.6 Hz, 10.0 Hz, H-3); 3.89 (t, 1H, J = 10.4 Hz, H-6); 3.78 (dt, 1H, J = 4.8 Hz, 9.2 Hz, H-5); 3.74 (d, 1H, J = 1.2 Hz, H-4′); 3.70 (dd, 1H, J = 3.2 Hz, 10.8 Hz, H-2′); 3.36 (s, 3H, OCH$_3$); 1.70 (d, 3H, J = 6.8 Hz, H-6′). ^{13}C-APT NMR (100 MHz) δ: 138.2, 137.6, 137.5 (C$_{q,arom}$); 128.8, 128.5, 128.3, 128.2, 128.2, 128.1, 127.9, 127.9, 127.7, 127.6, 127.5, 126.1 (CH$_{arom}$); 101.5 (PhCH); 98.8 (C-1); 97.3 (C-1′); 78.5 (C-4); 76.5 (C-2 or C-3′); 76.0 (C-4′); 75.0 (PhCH$_2$); 74.8 (C-3); 73.5 (C-2 or C-3′); 72.7, 71.9 (PhCH$_2$); 68.8 (C-6); 67.1 (C-5′); 64.1 (C-5); 58.9 (C-2′); 55.0 (OCH$_3$); 16.7 (C-6′). ^{13}C-GATED (100 MHz) δ: 98.8 (^{C,H}J = 168 Hz, C-1); 97.3 (^{C,H}J = 170 Hz, C-1′). IR (thin film) ν: 2909, 2108, 1454, 1371, 1101, 1059, 1040, 1003. HRMS: [M + Na]$^+$ calcd for C$_{41}$H$_{45}$N$_3$O$_9$Na 746.3048, found 746.3048.

Methyl 2-O-(2-Azido-3,4-di-O-benzoyl-2-deoxy-α/β-L-fucopyranosyl)-3-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside (F2). The title compounds (α/β 4:1) were obtained after size-exclusion chromatography (CH$_2$Cl$_2$/MeOH, 1:1 v/v), followed by column chromatography (toluene/acetone, 1:0 → 49:1 v/v) in 38% yield (29 mg, 0.038 mmol). ^{1}H NMR (400 MHz, for the α-isomer) δ: 8.12−8.09 (m, 2H, CH$_{arom}$); 7.60−7.22 (m, 18H, CH$_{arom}$); 5.72−5.69 (m, 2H, H-3′, PhCH); 5.03 (d, 1H, J = 3.6 Hz, H-1′); 4.85 (d, 1H, J = 12.0 Hz, PhCHH); 4.77 (d, 1H, J = 1.2 Hz, H-1); 4.71−4.65 (m, 2H, PhCH$_2$); 4.56 (q, 1H, J = 6.4 Hz, H-5′); 4.51 (d, 1H, J = 11.2 Hz, PhCHH); 4.30−4.20 (m, H-4, H-6); 4.17 (dd, 1H, J = 1.6 Hz, 3.2 Hz, H-2); 3.98 (dd, 1H, J = 3.6 Hz, 10.2 Hz, H-3); 3.92−3.87 (m, 2H, H-4′, H-6); 3.85−3.75 (m, 2H, H-2′, H-5); 3.76 (s, 3H, OCH$_3$); 0.98 (d, 3H, J = 6.4 Hz, H-6′). Diagnostic peaks for the β-anomer: 5.62 (s, 0.25H, PhCH); 3.54 (q, 0.25H, J = 6.4 Hz, H-5′); 1.22 (d, 0.75H, J = 6.4 Hz, H-6′). ^{13}C-APT NMR 100 MHz, for the α-isomer) δ: 165.8 (CO$_{Bz}$); 137.7, 137.4 (C$_{q,arom}$); 135.5, 129.9 (CH$_{arom}$); 129.2 (C$_{q,arom}$); 128.7, 128.5, 128.2, 128.1, 128.1, 127.8, 127.6, 127.5, 127.3, 127.1, 126.0 (CH$_{arom}$); 101.4 (PhCH); 98.9 (C-1); 97.4 (C-1′); 78.8 (C-4); 77.5 (C-4′); 75.6 (PhCH$_2$); 74.6 (C-3); 74.3 (C-2); 73.0 (PhCH$_2$); 71.2 (C-3′); 68.7 (C-6); 66.7 (C-5′); 64.1 (C-5); 57.6 (C-2′); 54.9 (OCH$_3$); 16.1 (C-6′). IR (thin film) ν: 2936, 2110, 1726, 1452, 1273, 1261, 1101, 1070, 1045, 1026, 1006. HRMS: [M + Na]$^+$ calcd for C$_{41}$H$_{41}$N$_3$O$_{11}$Na 774.2631, found 774.2633.

Methyl 2-O-(2-Azido-4-O-benzoyl-3-O-benzyl-2-deoxy-α/β-L-fucopyranosyl)-3-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside (F3). The title compound (α/β 10:1) was obtained after size-exclusion chromatography (CH$_2$Cl$_2$/MeOH, 1:1 v/v) and column chromatography (toluene/acetone, 1:0 → 49:1 v/v) in 58% yield (43 mg, 0.058 mmol). NMR data are reported for the α-isomer only. ^{1}H NMR (400 MHz) δ: 8.07−8.05 (m, 2H, CH$_{arom}$); 7.58−7.25 (m, 18H, CH$_{arom}$); 5.66 (s, 1H, PhCH); 5.65 (d, 1H, J = 2.4 Hz, H-4′); 5.03 (d, 1H, J = 3.2 Hz, H-1′); 4.88−4.80 (m, 2H, PhCHH 2×, H-1); 4.72 (d, 1H, J = 12.0 Hz, PhCHH); 4.65 (q, 1H, J = 6.4 Hz, H-5′); 4.54 (d, 1H, J = 10.8 Hz, PhCHH); 4.29−4.23 (m, 2H, H-6, H-3′); 4.20−4.15 (m, 2H, H-2, H-4); 4.02 (dd, 1H, J = 3.2 Hz, 10.0 Hz, H-3); 3.90 (t, 1H, J = 10.4 Hz, H-6); 3.80 (dt, 1H, J = 4.8 Hz, 9.6 Hz, H-5); 3.59 (dd, 1H, J = 3.6 Hz, 10.8 Hz, H-2′); 3.39 (s, 3H, OCH$_3$); 1.04 (d, 3H, J = 6.8 Hz, H-6′). ^{13}C-APT NMR (100 MHz) δ: 166.1 (CO$_{Bz}$); 138.1, 137.6, 137.1 (C$_{q,arom}$); 133.2, 130.0, 129.8 (CH$_{arom}$); 129.6 (C$_{q,arom}$); 128.9, 128.4, 128.4, 128.3, 128.2, 128.2, 127.8, 127.8, 127.7, 127.1, 126.1 (CH$_{arom}$); 101.5 (PhCH); 98.8 (C-1); 97.3 (C-1′); 78.7 (C-2 or C-4); 74.5 (C-3); 74.2 (C-2 or C-4); 73.2 (C-3′); 73.1 (PhCH$_2$); 71.3 (PhCH$_2$); 69.8 (C-4′); 68.8 (C-6); 65.7 (C-5′); 64.1 (C-5); 58.7 (C-2′); 55.0 (OCH$_3$); 16.2 (C-6′). IR (thin film) ν: 2932, 2108, 1721, 1452, 1373, 1267, 1175, 1101, 1074, 1061, 1045, 1026, 1003. HRMS: [M + Na]$^+$ calcd for C$_{41}$H$_{43}$N$_3$O$_{10}$Na 760.2841, found 760.2839.

Methyl 2-O-(2-Azido-3-O-benzoyl-4-O-benzyl-2-deoxy-α/β-L-fucopyranosyl)-3-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside (F4). The disaccharides (α/β 4:1) were isolated after size-exclusion chromatography (CH$_2$Cl$_2$/MeOH, 1:1 v/v) and column chromatography (toluene/acetone, 1:0 → 49:1 v/v) in 68% yield (50 mg, 0.068 mmol). ^{1}H NMR (400 MHz, for the α-anomer) δ: 8.11 (d, 2H, J = 7.2 Hz, CH$_{arom}$); 7.60−7.22 (m, 18H, CH$_{arom}$); 5.72−5.69 (m, 2H, H-3′, PhCH); 5.03 (d, 1H, J = 3.6 Hz, H-1′); 4.85 (d, 1H, J = 4.85 Hz, PhCHH); 4.70 (d, 1H, J = 1.2 Hz, H-1); 4.70−4.65 (m, 2H, PhCH$_2$); 4.56 (q, 1H, J = 6.4 Hz, H-5′); 4.51 (d, 1H, J = 11.2 Hz, PhCHH); 4.30−4.20 (m, 2H, H-4, H-6); 4.17 (dd, 1H, J = 1.6 Hz, 3.2 Hz, H-2); 3.98 (dd, 1H, J = 3.2 Hz, 10.2 Hz, H-3); 3.92−3.87 (m, 2H, H-4′, H-6); 3.92−3.75 (m, 2H, H-2′, H-5); 3.38 (s, 3H, OCH$_3$); 0.98 (d, 3H, J = 6.4 Hz, H-6′). Diagnostic peaks for the β-anomer: 5.62 (s, 0.25H, PhCH); 3.54 (q, 0.25H, J = 6.4 Hz, H-5′); 3.35 (s, 0.75H, OCH$_3$); 1.22 (d, 0.75H, J = 6.4 Hz, H-6′). ^{13}C-APT NMR (100 MHz, for the α-anomer) δ: 165.8 (CO$_{Bz}$); 138.4, 137.7, 137.4 (C$_{q,arom}$); 133.5, 129.9 (CH$_{arom}$); 129.2 (C$_{q,arom}$); 128.8, 128.5, 128.2, 128.1, 127.8, 127.6, 127.5, 127.3, 127.1, 126.0 (CH$_{arom}$); 101.4 (PhCH); 98.9 (C-1); 97.4 (C-1′); 78.8 (C-4); 77.5 (C-4′); 75.6 (PhCH$_2$); 74.6 (C-3); 74.3 (C-2); 73.0 (PhCH$_2$); 71.2 (C-3′); 68.7 (C-6); 66.7 (C-5′); 64.1 (C-5); 57.6 (C-2′); 54.9 (OCH$_3$); 16.1 (C-6′). IR (thin film) ν: 2934, 2909, 2110, 1722, 1452, 1373, 1269, 1103, 1074,

1043, 1028. HRMS: $[M + Na]^+$ calcd for $C_{41}H_{43}N_3O_{10}Na$ 760.2841, found 760.2838.

Methyl 2-O-(2-Azido-2-deoxy-3,4-di-O-(tert-butyldimethylsilyl)-α-L-fucopyranosyl)-3-O-benzyl-4,6-O-benzylidene-α-D-mannopyrano-side (F5). The title compound was obtained after column chromatography (hexane/Et₂O, 1:0 → 9:1) as the sole product in 67% yield (52 mg, 0.067 mmol). ¹H NMR (400 MHz) δ: 7.50–7.49 (m, 2H, CH_arom); 7.39–7.25 (m, 13H, CH_arom); 5.59 (s, 1H, PhCH); 4.95 (d, 1H, J = 3.6 Hz, H-1′); 4.80 (d, 1H, J = 12.4 Hz, PhCHH); 4.74–4.70 (m, 2H, H-1, PhCHH); 4.29–4.25 (m, H-5′, H-6); 4.17 (dd, 1H, J = 2.4 Hz, 10.4 Hz, H-3′); 4.12–4.05 (m, H-2′, H-4); 3.96 (dd, 1H, J = 3.2 Hz, 9.8 Hz, H-3); 3.86–3.76 (m, 2H, H-5, H-6); 3.71 (dd, 1H, J = 3.2 Hz, 10.4 Hz, H-2′); 3.61 (d, 1H, J = 1.6 Hz, H-4′); 3.36 (s, 3H, OCH₃); 1.01–0.99 (m, 12H, H-6′, (CH₃)₃CSi); 0.91 (s, 9H, (CH₃)₃CSi); 0.22, 0.16, 0.15, 0.14 (4x s, 3H, CH₃Si). ¹³C-APT NMR (100 MHz) δ: 138.4, 137.6 (C_q,arom); 128.8, 128.3, 128.1, 127.5, 127.4, 126.1 (CH_arom); 101.5 (PhCH); 99.1 (C-1); 97.3 (C-1′); 79.0 (C-4); 75.3 (C-4′); 74.5 (C-3); 73.6 (C-2); 72.3 (PhCH₂); 70.9 (C-3′); 69.0 (C-6); 68.4 (C-5′); 64.0 (C-5); 60.9 (C-2′); 55.0 (OCH₃); 26.2, 26.1 ((CH₃)₃CSi); 18.6, 18.6 (C_qSi); 17.2 (C-6′); –3.4, –3.4, –4.6, –4.7 (CH₃Si). IR (thin film) ν: 2930, 2857, 2108, 1254, 1177, 1103, 1061, 1042, 1028, 1004. HRMS: $[M + Na]^+$ calcd for $C_{39}H_{61}N_3O_9Si_2Na$ 794.3839, found 794.3839.

Methyl 2-O-(2-Azido-4-O-benzyl-2-deoxy-3-O-(tert-butyldime-thylsilyl)-α-L-fucopyranosyl)-3-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside (F6). The title disaccharide was isolated after column chromatography (hexane/Et₂O, 1:0 → 4:1) as the sole product in 74% yield (55 mg, 0.074 mmol). ¹H NMR (400 MHz) δ: 7.51–7.50 (m, 2H, CH_arom); 7.40–7.24 (m, 13H, CH_arom); 5.62 (s, 1H, PhCH); 5.00 (d, 1H, J = 11.2 Hz, PhCHH); 4.95 (d, 1H, J = 3.2 Hz, H-1′); 4.81–4.70 (m, 3H, H-1, PhCH₂); 4.53 (d, 1H, J = 11.2 Hz, PhCHH); 4.37 (q, 1H, J = 6.4 Hz, H-5′); 4.29–4.24 (m, 2H, H-3′, H-6); 4.14–4.09 (m, 2H, H-2, H-4); 3.97 (dd, 1H, J = 3.2 Hz, 10.0 Hz, H-3); 3.86 (t, 1H, J = 10.4 Hz, H-6); 3.78 (dt, 1H, J = 4.4 Hz, 9.6 Hz, H-5); 3.64 (dd, 1H, J = 3.2 Hz, 10.4 Hz, H-2′); 3.44 (d, 1H, J = 2.4 Hz, H-4′); 3.36 (s, 3H, OCH₃); 1.04 (d, 3H, J = 6.4 Hz, H-6′); 0.99 (s, 9H, (CH₃)₃CSi); 0.26 (s, 3H, CH₃Si); 0.21 (s, 3H, CH₃Si). ¹³C-APT NMR (100 MHz) δ: 138.6, 138.3, 137.6 (C_q,arom); 128.8, 128.3, 128.2, 128.1, 127.8, 127.6, 127.5, 127.0, 126.1 (CH_arom); 101.5 (PhCH); 98.9 (C-1); 97.4 (C-1′); 81.0 (C-4′); 78.8 (C-4); 75.6 (PhCH₂); 74.6 (C-3); 73.5 (C-2); 72.5 (PhCH₂); 70.7 (C-3′); 68.9 (C-6); 67.1 (C-5′); 64.1 (C-5); 61.0 (C-2′); 55.0 (OCH₃); 25.8 ((CH₃)₃CSi); 18.1 (C_qSi); 16.6 (C-6′); –3.6, –5.0 (CH₃Si). IR (thin film) ν: 2928, 2857, 2106, 1454, 1371, 1258, 1171, 1101, 1040, 1004. HRMS: $[M + Na]^+$ calcd for $C_{40}H_{53}N_3O_9SiNa$ 770.3443, found 770.3441.

Methyl 3-O-(2-Azido-3,4-di-O-benzyl-2-deoxy-α-L-fucopyrano-syl)-2-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside (G1). The title compound was obtained after size-exclusion chromatography (CH₂Cl₂/MeOH, 1:1 v/v) and column chromatography (toluene/acetone, 1:0 → 9:1 v/v) in 72% yield (52 mg, 0.072 mmol). ¹H NMR (400 MHz) δ: 7.39–7.22 (m, 20H, CH_arom); 4.95–4.91 (m, 2H, H-1′, PhCHH); 4.86 (d, 1H, J = 11.6 Hz, PhCHH); 4.72 (d, 1H, J = 12.0 Hz, PhCHH); 4.69–4.63 (m, 3H, H-1, PhCH₂); 4.53 (d, 1H, J = 11.6 Hz, PhCHH); 4.23 (dd, 1H, J = 4.0 Hz, 9.6 Hz, H-6); 4.16–4.09 (m, 3H, H-3, H-4, H-5′); 4.00 (m, 2H, H-2′, H-3′); 3.88–3.77 (m, 3H, H-2, H-5, H-6); 3.56 (s, 1H, H-4′); 3.31 (s, 3H, OCH₃); 0.88 (d, 3H, J = 6.4 Hz, H-6′). ¹³C-APT NMR (100 MHz) δ: 138.3, 138.1, 137.7, 137.6 (C_q,arom); 128.9, 128.6, 128.4, 128.4, 128.2, 128.1, 127.8, 127.8, 127.6, 127.4, 126.2, 125.9 (CH_arom); 101.8 (PhCH); 100.3 (C-1); 95.7 (C-1′); 78.3 (C-3′); 77.1 (C-3 or C-4); 76.3 (C-4′); 75.4 (C-2); 74.8, 73.8 (PhCH₂); 73.4 (C-2); 72.1 (PhCH₂); 68.9 (C-6); 66.6 (C-5′); 64.2 (C-5); 59.9 (C-2′); 54.8 (OCH₃); 16.3 (C-6′). IR (thin film) ν: 2930, 2108, 1454, 1098, 1057, 1026. HRMS: $[M + Na]^+$ calcd for $C_{41}H_{45}N_3O_9Na$ 746.3048, found 746.3041.

Methyl 3-O-(2-Azido-3,4-di-O-benzoyl-2-deoxy-α-L-fucopyrano-syl)-2-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside (G2). The title compound was obtained after size-exclusion chromatography (CH₂Cl₂/MeOH, 1:1 v/v) and column chromatography (toluene/acetone, 1:0 → 49:1 v/v) in 64% yield (48 mg, 0.064 mmol).

¹H NMR (400 MHz) δ: 8.00–7.98 (m, 2H, CH_arom); 7.90–7.87 (m, 2H, CH_arom); 7.60–7.24 (m, 16H, CH_arom); 5.79 (dd, 1H, J = 3.2 Hz, 10.0 Hz, H-3′); 5.64 (s, 1H, PhCH); 5.55 (d, 1H, J = 2.0 Hz, H-4′); 5.14 (d, 1H, J = 3.6 Hz, H-1′); 4.96 (d, 1H, J = 12.0 Hz, PhCHH); 4.78 (d, 1H, J = 12.0 Hz, PhCHH); 4.70 (d, 1H, J = 1.6 Hz, H-1); 4.57 (q, 1H, J = 6.4 Hz, H-5′); 4.27 (dd, 1H, J = 4.4 Hz, 9.6 Hz, H-6); 4.22–4.18 (m, 2H, H-3, H-4); 4.10 (dd, 1H, J = 3.6 Hz, 11.0 Hz, H-2′); 3.93–3.88 (m, 3H, H-2, H-5, H-6); 3.35 (s, 3H, OCH₃); 0.76 (d, 3H, J = 6.4 Hz, H-6′). ¹³C-APT NMR (100 MHz) δ: 165.7, 165.3 (CO_Bz); 138.1, 137.4 (C_q,arom); 133.3, 133.2, 129.7 (CH_arom); 129.5, 129.2 (C_q,arom); 129.1, 128.5, 128.4, 128.3, 128.2, 128.0, 127.7, 126.3 (CH_arom); 102.1 (PhCH); 100.4 (C-1); 96.3 (C-1′) 77.1 (C-3 or C-4); 75.8 (C-2); 74.8 (C-3 or C-4); 73.9 (PhCH₂); 71.4 (C-4′); 70.1 (C-3′); 68.8 (C-6); 65.2 (C-5′); 64.4 (C-5); 58.8 (C-2′); 54.9 (OCH₃); 15.4 (C-6′). IR (thin film) ν: 2932, 2108, 1724, 1452, 1275, 1261, 1098, 1065, 1026, 1005. HRMS: $[M + Na]^+$ calcd for $C_{41}H_{41}N_3O_{11}Na$ 774.2633, found 774.2629.

Methyl 3-O-(2-Azido-4-O-benzoyl-3-O-benzyl-2-deoxy-α-L-fuco-pyranosyl)-2-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside (G3). The title compound was obtained after size-exclusion chromatography (CH₂Cl₂/MeOH, 1:1 v/v) and column chromatography (toluene/acetone, 1:0 → 49:1 v/v) in 54% yield (40 mg, 0.054 mmol). ¹H NMR (400 MHz) δ: 8.08–8.06 (m, 2H, CH_arom); 7.61–7.59 (m, 1H, CH_arom); 7.47–7.19 (m, 17H, CH_arom); 5.59 (s, 1H, PhCH); 5.52 (d, 1H, J = 2.8 Hz, H-4′); 5.02 (d, 1H, J = 3.6 Hz, H-1′); 4.94 (d, 1H, J = 11.6 Hz, PhCHH); 4.81–4.75 (m, 2H, PhCH₂); 4.68 (d, 1H, J = 1.2 Hz, H-1); 4.50 (d, 1H, J = 10.8 Hz, PhCHH); 4.41 (q, 1H, J = 6.4 Hz, H-5′); 4.25 (dd, 1H, J = 3.6 Hz, 9.4 Hz, H-6); 4.17–4.12 (m, H-3, H-4, H-3′); 3.91–3.80 (m, 4H, H-2, H-5, H-6, H-2′); 3.33 (s, 3H, OCH₃); 0.83 (d, 3H, J = 6.4 Hz, H-6′). ¹³C-APT NMR (100 MHz) δ: 166.1 (CO_Bz); 138.1, 137.6, 137.1 (C_q,arom); 133.2, 129.8 (CH_arom); 129.7 (C_q,arom); 129.2, 128.4, 128.3, 128.3, 128.1, 127.8, 127.8, 26.2 (CH_arom); 102.1 (PhCH); 100.4 (C-1); 96.0 (C-1′); 77.1, 75.6, 75.0, 74.2 (C-2, C-3, C-4, C-4′); 73.8, 71.4 (PhCH₂); 70.0 (C-4′); 68.9 (C-6); 65.2 (C-5′); 64.3 (C-5); 59.6 (C-2′); 54.9 (OCH₃); 15.8 (C-6′). IR (thin film) ν: 2930, 2110, 1721, 1454, 1269, 1110, 1099, 1059, 1026, 1003. HRMS: $[M + Na]^+$ calcd for $C_{41}H_{43}N_3O_{10}Na$ 760.2841, found 760.2839.

Methyl 3-O-(2-Azido-3-O-benzoyl-4-O-benzyl-2-deoxy-α/β-L-fu-copyranosyl)-2-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside (G4). The products (α/β 10:1) were obtained after size-exclusion chromatography (CH₂Cl₂/MeOH, 1:1 v/v) and column chromatography (toluene/acetone, 1:0 → 49:1 v/v) in 64% yield (47 mg, 0.064 mmol). ¹H NMR (400 MHz) δ: 8.08–8.06 (m, 2H, CH_arom); 7.61–7.17 (m, 18H, CH_arom); 5.61–5.57 (m, 2H, H-3′, PhCH); 5.03 (d, 1H, J = 3.6 Hz, H-1′); 4.93 (d, 1H, J = 12.0 Hz, PhCHH); 4.73 (d, 1H, J = 12.0 Hz, PhCHH); 4.66 (d, 1H, J = 1.6 Hz, H-1); 4.58 (d, 1H, J = 11.2 Hz, PhCHH); 4.46 (d, 1H, J = 11.2 Hz, PhCHH); 4.32 (q, 1H, J = 6.4 Hz, H-5′); 4.25 (dd, 1H, J = 4.0 Hz, 9.8 Hz, H-6); 4.21–4.13 (m, H-3, H-4, H-2′); 3.88 (t, 1H, J = 10.0 Hz, H-6); 3.83–3.78 (m, 3H, H-2, H-5, H-4′); 3.32 (s, 3H, OCH₃); 0.82 (d, 3H, J = 6.4 Hz, H-6′). ¹³C-APT NMR (100 MHz) δ: 165.8 (CO_Bz); 138.1, 137.6 (C_q,arom); 133.5, 129.8 (CH_arom); 129.3 (C_q,arom); 128.9, 128.7, 128.5, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7 (CH_arom); 102.0 (PhCH); 100.4 (C-1); 96.2 (C-1′); 77.5 77.1, 75.7, 74.2 (C-2, C-3, C-4, C-4′); 75.6, 73.8 (PhCH₂); 73.0 (C-3′); 68.8 (C-6); 66.4 (C-5′); 64.3 (C-5); 58.8 (C-2′); 54.8 (OCH₃); 15.8 (C-6′). IR (thin film) ν: 2932, 2108, 1722, 1452, 129, 1098, 1067, 1026. $[M + Na]^+$ calcd for $C_{41}H_{43}N_3O_{10}$ 760.2841, found 760.2836.

Methyl 3-O-(2-Azido-2-deoxy-3,4-di-O-(tert-butyldimethylsilyl)-α/β-L-fucopyranosyl)-2-O-benzyl-4,6-O-benzylidene-α-D-mannopyra-noside (G5). The title product was obtained after column chromatography (hexane/Et₂O, 1:0 → 4:1) in 73% yield (56 mg, 0.073 mmol). ¹H NMR (400 MHz) δ: 7.45–7.25 (m, 10H, CH_arom); 5.58 (s, 1H, PhCH); 4.98–4.95 (m, 2H, H-1, PhCHH), 4.78 (d, 1H, J = 11.6 Hz, PhCHH); 4.69 (d, 1H, J = 1.6 Hz, H-1); 4.24 (dd, 1H, J = 4.0 Hz, 9.6 Hz, H-6); 4.14–4.12 (m, 2H, H-3, H-4); 4.07–4.02 (m, 2H, H-3′, H-5′); 3.88–3.82 (m, H-2, H-2′, H-5, H-6); 3.55 (d, 1H, J = 1.6 Hz, H-4′); 3.32 (s, 3H, OCH₃); 0.94 (s, 9H, (CH₃)₃CSi); 0.90 (s, 9H, (CH₃)₃CSi); 0.79 (d, 3H, J = 6.4 Hz, H-6′); 0.16, 0.13, 0.13,

0.03 (4x s, 3H, CH$_3$Si). ^{13}C-APT NMR (100 MHz) δ: 138.4, 137.8 (C$_{q,arom}$); 128.9, 128.3, 128.1, 127.9, 127.7, 126.2, 125.8 (CH$_{arom}$); 101.9 (PhCH); 100.7 (C-1); 96.1 (C-1′); 77.3 (C-3, C-4); 75.7 (C-2, C-5); 75.3 (C-4′); 73.9 (C-3, C-4); 73.9 (PhCH$_2$); 71.4 (C-3′, C-5′); 68.9 (C-6); 68.0 (C-3′, C-5′); 64.4 (C-2, C-5); 61.8 (C-2′); 54.8 (OCH$_3$); 26.3, 26.1 ((CH$_3$)$_3$CSi); 18.6, 18.5 (C$_q$Si); 16.8 (C-6′); −3.4, −4.0, −4.5, −4.6 (CH$_3$Si). IR (thin film) ν: 2953, 2857, 2106, 1254, 1179, 1121, 1099, 1049, 1028. HRMS: [M + Na]$^+$ calcd for C$_{39}$H$_{61}$N$_3$O$_9$Si$_2$Na 794.3839, found 794.3839.

Methyl 3-O-(2-Azido-4-O-benzyl-2-deoxy-3-O-(tert-butyldimethylsilyl)-α/β-L-fucopyranosyl)-2-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside (G6). The title compounds (α/β 10:1) were obtained after column chromatography (hexane/Et$_2$O, 1:0 → 4:1) in 64% yield (48 mg, 0.064 mmol). NMR data are reported for the α-isomer only. ^{1}H NMR (400 MHz) δ: 7.46−7.24 (m, 15H, CH$_{arom}$); 5.58 (s, 1H, PhCH); 5.00−4.92 (m, 3H, H-1′, 2× PhCHH); 4.78 (d, 1H, J = 11.6 Hz, PhCHH); 4.70 (d, 1H, J = 1.6 Hz, H-1); 4.50 (d, 1H, J = 10.8 Hz, PhCHH); 4.42 (dd, 1H, J = 4.0 Hz, 9.6 Hz, H-6); 4.16−4.06 (m, 4H, H-3, H-3′, H-4, H-5′); 3.90 (dd, 1H, J = 3.2 Hz, 10.2 Hz, H-2′); 3.88−3.79 (m, 3H, H-2, H-5, H-6); 3.36−3.32 (m, 4H, H-4′, OCH$_3$); 0.96 (s, 9H, (CH$_3$)$_3$Si); 0.80 (d, 3H, J = 6.4 Hz, H-6′); 0.21 (s, 3H, CH$_3$Si); 0.15 (s, 3H, CH$_3$Si). ^{13}C-APT NMR (100 MHz) δ: 138.7, 138.3, 137.7 (C$_{q,arom}$); 128.9, 128.6, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5, 127.4, 126.2, 125.8 (CH$_{arom}$); 101.9 (PhCH); 100.5 (C-1); 96.5 (C-1′); 81.0 (C-4′); 77.2 (C-4); 75.8 (C-2); 75.6 (PhCH$_2$); 74.4 (C-3 or C-3′); 73.8 (PhCH$_2$); 71.8 (C-3 or C-3′); 68.9 (C-6); 66.9 (C-5′); 63.3 (C-5); 62.3 (C-2′); 54.8 (OCH$_3$); 25.9 ((CH$_3$)$_3$CSi); 18.0 (C$_q$Si); 16.1 (C-6′); −4.2, −5.0 (CH$_3$Si). IR (thin film) ν: 2930, 2857, 2106, 1454, 1364, 1260, 1117, 1098, 1047, 1028. HRMS: [M + Na]$^+$ calcd for C$_{40}$H$_{53}$N$_3$NaO$_9$Si 770.3443, found 770.3442.

5-(Benzyl(benzyloxycarbonyl)amino)pentyl methyl(2-azido-4-O-(2-azido-4-O-benzyl-2-deoxy-3-O-(tert-butyldimethylsilyl)-α-D-fucopyranosyl)-3-O-benzyl-2-deoxy-α-D-galactopyranosiduronate) (20). To a solution of D-6 (0.29 g, 0.54 mmol, 2.0 equiv), Ph$_2$SO (0.11 g, 0.54 mmol, 2.0 equiv), and TTBP (0.27 g, 1.08 mmol, 4.0 equiv) in CH$_2$Cl$_2$ (5.4 mL, 0.1 M relative to donor) were added flame-dried, rod-shaped, 3 Å MS. After ~30 min, the mixture was cooled to −80 °C, Tf$_2$O (91 μL, 0.54 mmol, 2.0 equiv) was added, and the mixture was warmed to −70 °C. The mixture was recooled to −80 °C, and a solution of acceptor 19 (0.17 g, 0.27 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (0.54 mL, 0.5 M) was added via the wall of the flask. The mixture was warmed to −40 °C and kept at this temperature for ~2 h, after which the reaction was quenched by addition of pyridine (0.4 mL), filtered over a pad of Celite, washed with brine, dried over MgSO$_4$, filtered, and concentrated in vacuo. Purification by column chromatography (hexane/EtOAc, 19:1 → 7:3 v/v) yielded the title disaccharide in 68% yield (0.17 g, 0.167 mmol). ^{1}H NMR (500 MHz, 323 K) δ: 7.43−7.23 (m, 20H, CH$_{arom}$); 5.16 (s, 2H, PhCH$_2$); 5.05 (d, 1H, J = 3.0 Hz, H-1); 4.99−4.97 (m, 2H, H-1′, PhCHH); 4.82 (d, 1H, J = 11.5 Hz, PhCHH); 4.66 (d, 1H, J = 12.0 Hz, PhCHH); 4.60 (s, 1H, H-4); 4.51−4.48 (m, 3H, PhCH$_2$); 4.31 (s, 1H, H-5); 4.17 (q, 1H, J = 6.5 Hz, H-5′); 4.07 (dd, 1H, J = 2.5 Hz, 10.5 Hz, H-3′); 3.90 (bd, 1H, J = 10.5 Hz, H-3); 3.81 (s, 3H, CO$_2$CH$_3$); 3.74 (dd, 1H, J = 3.5 Hz, 10.5 Hz, H-2′); 3.63 (bs, 1H, OCHH$_{pentyl}$); 3.61 (dd, 1H, J = 3.5 Hz, 10.5 Hz, H-2); 3.47 (bs, 1H, OCHH$_{pentyl}$); 3.40 (s, 1H, H-4′); 3.22 (bs, 2H, NCH$_{2,pentyl}$); 1.52 (bs, 4H, CH$_{2,pentyl}$); 1.34−1.27 (m, 2H, CH$_{2,pentyl}$); 0.99−0.93 (m, 12H, H-6′, C(CH$_3$)$_3$Si); 0.21, 0.18 (s, 3H, CH$_3$Si). ^{13}C-APT NMR (125 MHz, 323 K) δ: 168.6 (C-6); 138.7, 138.0, 137.3 (C$_{q,arom}$); 128.8, 128.5, 128.4, 128.4, 128.2, 127.9, 127.8, 127.8, 127.7, 127.5, 127.2 (CH$_{arom}$); 99.2 (C-1′); 98.2 (C-1); 81.0 (C-4); 75.6 (PhCH$_2$); 75.0 (C-3); 73.8 (C-4); 72.0 (PhCH$_2$); 71.1 (C-3′); 70.1 (C-5); 68.8 (OCH$_{2,pentyl}$); 67.6 (C-5′); 67.1 (PhCH$_2$); 62.0 (C-2′); 59.4 (C-2); 52.4 (CO$_2$CH$_3$); 50.5 (PhCH$_2$); 29.0 (CH$_{2,pentyl}$); 25.9 (C(CH$_3$)$_3$Si); 23.2 (CH$_{2,pentyl}$); 18.1 (C$_q$Si); 16.5 (C-6′); −3.9, −5.0 (CH$_3$Si). ^{13}C-GATED NMR (125 MHz, 323 K) δ: 99.2 (d, J = 170 Hz, C-1′); 98.2 (d, J = 172 Hz, C-1). IR (thin film) ν: 2930, 2106, 1730, 1697, 1454, 1254, 1125, 1067, 1042. HRMS: [M + Na]$^+$ calcd for C$_{53}$H$_{69}$N$_7$NaO$_{11}$Si 1030.4717, found 1030.4721.

5-(Benzyl(benzyloxycarbonyl)amino)pentyl 2-Azido-4-O-benzyl-2-deoxy-α-D-fucopyranoside (23). To a stirred solution of donor D-6 (0.80 g, 1.5 mmol, 1.0 equiv), Ph$_2$SO (0.39 g, 1.95 mmol, 1.3 equiv), N-methylmaleimide (0.25 g, 2.25 mmol, 1.5 equiv), and TTBP (0.93 g, 3.75 mmol, 2.5 equiv) in CH$_2$Cl$_2$ (30 mL, 0.05 M) were added, flame-dried, rod-shaped, 3 Å MS. After being stirred for ~30 min, the mixture was cooled to −80 °C, Tf$_2$O (0.33 mL, 1.95 mmol, 1.3 equiv) was added, and the mixture was warmed to −70 °C, after which TLC analysis (toluene/EtOAc, 9:1 v/v) indicated complete activation of the donor. The mixture was recooled to −80 °C, after which Bu$_4$NI (as a 1 M solution in CH$_2$Cl$_2$, 7.5 mL, 7.5 mmol, 5.0 equiv) was added, upon which the reaction mixture assumed a maroon color. After 5 min at −80 °C, a solution of acceptor 21 (as a 0.5 M solution in CH$_2$Cl$_2$/1,4-dioxane, 1:1 v/v, 3.0 mmol, 2.0 equiv) was slowly added via the wall of the flask, and the mixture was allowed to warm to room temperature. After the mixture was stirred for ~18 h, TLC analysis (toluene/EtOAc, 9:1 v/v) indicated complete conversion of the starting material. The reaction was quenched by addition of NEt$_3$, diluted with CH$_2$Cl$_2$, filtered over a pad of Celite, washed (brine, 1×), dried over MgSO$_4$, filtered, and concentrated in vacuo. Purification by column chromatography (toluene/Et$_2$O, 1:0 → 9:1) delivered 22 (α/β ~ 7:1) as an inseparable mixture in 85% yield (0.90 g, 1.27 mmol). To a stirred solution of 22 (0.90 g, 1.27 mmol, 1.0 equiv) in THF (4 mL, 0.3 M) was added Bu$_4$NF (as a 1 M solution in THF, 2.5 mL, 2.5 mmol, 2.0 equiv). After TLC analysis (PE/EtOAc, 7:3 v/v) indicated complete consumption of the starting material (~2 h), the reaction was quenched by addition of NaHCO$_3$ (satd aq) and extracted with EtOAc (3×). The combined organic phases were washed (H$_2$O 1×, brine 1×), dried over MgSO$_4$, filtered, and concentrated in vacuo. Purification by column chromatography (PE/EtOAc, 19:1 → 4:1 v/v) delivered the title compound as an oil in 63% yield (0.47 g, 0.80 mmol). ^{1}H NMR (500 MHz, 323 K) δ: 7.36−7.20 (m, 15H, CH$_{arom}$); 5.17 (s, 2H, PhCH$_2$); 4.82 (d, 1H, J = 3.0 Hz, H-1); 4.77 (d, 1H, J = 11.5 Hz, PhCHH); 4.70 (d, 1H, J = 11.5 Hz, PhCHH); 4.48 (s, 2H, PhCH$_2$); 4.03 (bd, 1H, J = 8.0 Hz, H-3); 3.92 (q, 1H, J = 6.0 Hz, H-5); 3.62−3.56 (m, 2H, H-4, OCHH$_{pentyl}$); 3.15−3.39 (m, H-2, OCHH$_{pentyl}$); 3.24 (bs, NCH$_{2,pentyl}$); 1.54 (bs, 4H, CH$_{2,pentyl}$); 1.31 (bs, 2H, CH$_{2,pentyl}$); 1.24 (d, 3H, J = 6.5 Hz, H-6). ^{13}C-APT NMR (125 MHz, 323 K) δ: 138.0, 136.9 (C$_{q,arom}$); 128.6, 128.5, 128.4, 128.0, 127.9, 127.8, 127.5, 127.2, 126.9 (CH$_{arom}$); 98.2 (C-1); 80.3 (C-4); 76.1 (PhCH$_2$); 68.5 (C-3); 68.1 (OCH$_{2,pentyl}$); 67.2 (PhCH$_2$); 66.5 (C-5); 61.0 (C-2); 50.5 (NCH$_{2,pentyl}$); 29.1, 23.4 (CH$_{2,pentyl}$); 16.7 (C-6). ^{13}C-GATED NMR (125 MHz, 323 K) δ: 98.2 (d, J = 170 Hz, C-1). IR (thin film) ν: 2934, 2108, 1690, 1454, 1421, 1229, 1171, 1067. HRMS: [M + H]$^+$ calcd for C$_{33}$H$_{41}$N$_4$O$_6$ 589.3021, found 589.3022.

5-(Benzyl(benzyloxycarbonyl)amino)pentyl 2-Azido-3-O-(2-azido-4-O-benzyl-2-deoxy-α-L-fucopyranosyl)-4-O-benzyl-α-D-fucopyranoside (25). To a stirred solution of donor 6 (0.43 g, 0.80 mmol, 2.0 equiv), Ph$_2$SO (0.16 g, 0.80 mmol, 2.0 equiv), and TTBP (0.40 g, 1.60 mmol, 4.0 equiv) in CH$_2$Cl$_2$ (8 mL, 0.1 M relative to donor) were added flame-dried, rod-shaped, 3 Å MS. After being stirred for ~30 min, the mixture was cooled to −80 °C, and Tf$_2$O (0.13 mL, 0.80 mmol, 2.0 equiv) was added. After the mixture was allowed to warm to −70 °C, it was recooled to −80 °C, and a solution of acceptor 23 (0.40 mmol, 1.0 equiv, in 0.8 mL CH$_2$Cl$_2$, dried by triple coevaporation with toluene) was added via the wall of the flask. The mixture was warmed to −60 °C, left at this temperature for 15 min, and the reaction was quenched by addition of NEt$_3$. The bright yellow solution was filtered over Celite, washed (brine, 1×), dried over MgSO$_4$, filtered, and concentrated in vacuo. Purification by size-exclusion chromatography (CH$_2$Cl$_2$/MeOH, 1:1 v/v) yielded 24 as a mixture of disaccharides (α/β ~ 7:1) in 73% yield (0.27 g, 0.28 mmol). ^{1}H NMR for the α-anomer (500 MHz, 323 K) δ: 7.41−7.21 (m, 20H, CH$_{arom}$); 5.24 (d, 1H, J = 3.5 Hz, H-1′); 5.16 (bs, 2H, PhCH$_2$); 5.03 (d, 1H, J = 11.5 Hz, PhCHH); 4.91 (d, 1H, J = 11.5 Hz, PhCHH); 4.88 (d, 1H, J = 3.5 Hz, H-1); 4.62 (d, 1H, J = 11.0 Hz, PhCHH); 4.55 (d, 1H, J = 11.0 Hz, PhCHH); 4.48 (bs, 2H, PhCH$_2$); 4.10 (dd, 1H, J = 3.0 Hz, 10.5 Hz, H-3′); 4.06 (dd, 1H, J = 3.0 Hz, 11.0 Hz, H-3); 3.99, 3.92 (q, 1H, J = 6.5 Hz, H-5, H-5′); 3.84−3.81 (m, 2H, H-2, H-2′); 3.60−3.56 (m, 2H, H-4, OCHH$_{pentyl}$);

3.47 (d, 1H, J = 1.5 Hz, H-4'); 3.40 (bs, 1H, OCHH_{pentyl}); 3.23 (bs, 2H, NC$H_{2,pentyl}$); 1.53 (m, 4H, C$H_{2,pentyl}$); 1.30 (m, 2H, C$H_{2,pentyl}$); 1.20, 1.16 (d, 3H, J = 6.5 Hz, H-6, H-6'); 0.96 (s, 9H, (CH_3)$_3$CSi); 0.20, 0.14 (s, 3H, CH_3Si). ^{13}C-APT NMR (125 MHz, 323 K) δ: 138.7, 138.5, 138.1 (C$_{q,arom}$); 128.5, 128.4, 128.4, 128.3, 127.9, 127.9, 127.8, 127.7, 127.6, 127.6, 127.3 (CH$_{arom}$); 99.5 (C-1'); 98.3 (C-1); 80.8 (C-4'); 79.9 (C-4); 76.2 (C-3); 75.6, 75.2 (PhCH$_2$); 71.5 (C-3'); 68.3 (OCH$_{2,pentyl}$); 67.8 (C-5 or C-5'); 67.2 (PhCH$_2$); 66.9 (C-5 or C-5'); 61.8, 60.4 (C-2, C-2'); 29.2 (CH$_{2,pentyl}$); 25.9 ((CH$_3$)$_3$CSi); 23.4 (CH$_{2,pentyl}$); 18.1 (C$_q$Si); 16.8, 16.7 (C-6, C-6'); −4.1, −5.0 (CH$_3$Si). Diagnostic ^{1}H NMR signal for the β-anomer (500 MHz, 323 K) δ: 4.32 (d, 1H, J = 8.0 Hz, H-1'). Disaccharide **24** was dissolved in dry THF (1.4 mL, 0.2 M), and Bu$_4$NF (as 1 M solution in THF, 0.34 mL, 0.34 mmol, 1.2 equiv) was added. After 4 h, TLC analysis (PE/EtOAc, 7:3 v/v) indicated complete consumption of the starting material and the appearance of two more polar products. The reaction was quenched by addition of satd aq NaHCO$_3$, the mixture was extracted (CH$_2$Cl$_2$, 3×), and the combined organics were washed (H$_2$O, 1×; brine, 1×), dried over MgSO$_4$, and concentrated in vacuo. Purification by column chromatography (hexane/EtOAc, 19:1 → 4:1 v/v) furnished the title disaccharide in 71% yield (0.17 g, 0.20 mmol). ^{1}H NMR (500 MHz, 323 K) δ: 7.36−7.19 (m, 20H, CH$_{arom}$); 5.20 (d, 1H, J = 4.0 Hz, H-1'); 5.17 (bs, 2H, PhCH$_2$); 4.89 (d, 1H, J = 3.0 Hz, H-1); 4.79 (d, 1H, J = 11.5 Hz, PhCHH); 4.75 (d, 1H, J = 11.5 Hz, PhCHH); 4.72−4.67 (m, 2H, 2× PhCHH); 4.49 (bs, 2H, PhCH$_2$); 4.04 (dd, 1H, J = 3.0 Hz, 10.8 Hz, H-3); 3.93−3.90 (m, 3H, H-3', H-5, H-5'); 3.84 (dd, 1H, J = 3.5 Hz, 10.5 Hz, H-2); 3.59 (bs, 1H, OCHH_{pentyl}); 3.55 (d, 1H, J = 2.5 Hz, H-4); 3.52 (d, 1H, J = 2.5 Hz, H-4'); 3.49 5(dd, 1H, J = 3.5 Hz, 10.8 Hz, H-2'); 3.41 (bs, 1H, OCHH_{pentyl}); 3.24 (bs, 2H, NC$H_{2,pentyl}$); 1.55 (bs, 4H, 2× C$H_{2,pentyl}$); 1.31 (bs, 2H, C$H_{2,pentyl}$); 1.23−1.20 (m, 6H, H-6, H-6'). ^{13}C-APT NMR (125 MHz, 323 K) δ: 138.4, 138.0, 137.9, 136.9 (C$_{q,arom}$); 128.6, 128.5, 128.4, 128.4, 128.1, 128.1, 127.9, 127.8, 127.7, 127.6, 127.3 (CH$_{arom}$); 99.8 (C-1'); 98.2 (C-1); 80.4 (C-4); 79.8 (C-4'); 76.2 (C-3); 76.0, 75.5 (PhCH$_2$); 68.7 (C-3', C-5 or C-5'); 68.2 (OCH$_{2,pentyl}$); 67.4 (C-3', C-5 or C-5'); 67.2 (PhCH$_2$); 67.0 (C-3', C-5 or C-5'); 61.0 (C-2'); 60.4 (C-2); 29.1 (2× CH$_{2,pentyl}$); 23.4 (CH$_{2,pentyl}$); 16.8, 16.8 (C-6, C-6'). ^{13}C-GATED NMR (125 Hz) δ: 99.8 (d, J = 170 Hz, C-1'); 98.2 (d, J = 168 Hz, C-1). IR (thin film) ν: 2936, 2106, 1694, 1454, 1422, 1092, 1036, 1028. HRMS: [M + NH$_4$]$^+$ calcd for C$_{46}$H$_{59}$N$_8$O$_9$ 867.4400, found 867.4403.

Methyl (2-Azido-3,4-di-O-benzyl-2-deoxy-1-O-(N-phenyl-2,2,2-trifluoroacetimidoyl)-α/β-D-mannopyranosiduronate) (28). To a stirred, ice-cooled solution of phenyl 2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy-1-thio-α-D-mannopyranoside[60] (4.9 g, 10.3 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (30 mL, 0.3 M) was added, under argon, BH$_3$·THF (as 1 M solution in THF, 30 mL, 3.0 equiv), followed by Bu$_2$BOTf (as 1 M solution in CH$_2$Cl$_2$, 10 mL, 1.0 equiv) and the reaction mixture was kept at 0 °C. After 1 h, TLC analysis (PE/EtOAc, 4:1 v/v) indicated complete conversion of the starting material, and the reaction was quenched by sequential addition of NEt$_3$ (4 mL) and MeOH (added dropwise until gas evolution ceased). The mixture was concentrated in vacuo and the residue was coevaporated with MeOH (3×). Purification by column chromatography (PE/EtOAc, 19:1 → 9:1 v/v) delivered phenyl 2-azido-3,4-di-O-benzyl-2-deoxy-1-thio-α-D-mannopyranoside as a colorless oil (4.6 g, 9.7 mmol, 94% yield). ^{1}H NMR (400 MHz) δ: 7.42−7.22 (m, 15H, CH$_{arom}$); 5.40 (s, 1H, H-1); 4.90 (d, 1H, J = 10.8 Hz, PhCHH); 4.75 (s, 2H, PhCH$_2$); 4.66 (d, 1H, J = 11.2 Hz, PhCHH); 4.15−4.04 (m, 3H, H-2, H-3, H-5); 3.92 (t, 1H, J = 9.6 Hz, H-4); 3.77 (bs, 2H, H-6); 1.88 (bs, 1H, 6-OH). ^{13}C-APT NMR (100 MHz) δ: 137.9, 137.3, 132.9 (C$_{q,arom}$); 132.1, 129.2, 128.6, 128.4, 128.1, 128.0, 127.9 (CH$_{arom}$); 86.2 (C-1); 79.8 (C-2, C-3 or C-5); 75.4 (PhCH$_2$); 74.2 (C-4); 73.2 (C-2, C-3 or C-5); 72.7 (PhCH$_2$); 62.7 (C-2, C-3 or C-5); 61.7 (C-6). IR (thin film) ν: 2872, 2102, 1454, 1265, 1096, 1084, 1026. HRMS: [M + Na]$^+$ calcd for C$_{26}$H$_{27}$N$_3$NaO$_4$S 500.1615, found 500.1611. The primary alcohol (1.17 g, 2.6 mmol, 1.0 equiv) was dissolved in CH$_2$Cl$_2$ (8 mL), and H$_2$O (4 mL) and *tert*-butyl alcohol (1 mL, final concentration 0.2 M) were added. Under vigorous stirring were added AcOH (15 μL, 0.26 mmol, 0.1 equiv), TEMPO (81 mg, 0.52 mmol, 0.2 equiv), and

PhI(OAc)$_2$ (2.09 g, 6.5 mmol, 2.5 equiv), and the resulting red mixture was stirred until TLC analysis (PE/EtOAc/AcOH, 75:20:5 v/v/v) indicated complete conversion of the starting material into a lower running spot (∼90 min). The reaction was quenched by addition of satd aq Na$_2$S$_2$O$_3$, and the resulting light yellow mixture was extracted (CH$_2$Cl$_2$, 2×). The combined organic fractions were washed (H$_2$O 1×, brine 1×), dried over MgSO$_4$, filtered, and concentrated in vacuo. After coevaporation with toluene (1×), the residue was dissolved in DMF (9 mL, 0.3 M), and MeI (0.32 mL, 5.2 mL, 2.0 equiv) and K$_2$CO$_3$ (0.72 g, 5.2 mmol, 2.0 equiv) were added. The reaction was stirred overnight, after which TLC analysis (PE/EtOAc/AcOH, 70:30:5 v/v/v) indicated complete conversion of the starting material. The reaction mixture was partitioned between Et$_2$O and H$_2$O, and after separation, the aqueous phase was extracted with Et$_2$O (2×). The combined ethereal phases were washed (brine 1×), dried over MgSO$_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc, 1:0 → 9:1 v/v) to deliver methyl (phenyl 2-azido-3,4-di-O-benzyl-2-deoxy-1-thio-α-D-mannopyranosiduronate) as an oil in 79% yield (1.04 g, 2.06 mmol). ^{1}H NMR (400 MHz) δ: 7.62−7.60 (m, 2H, CH$_{arom}$); 7.38−7.25 (m, 13H, CH$_{arom}$); 5.61 (d, 1H, J = 7.6 Hz, H-1); 4.69−4.59 (m, 5H, H-5, PhCH$_2$); 4.21 (dd, 1H, J = 4.4 Hz, 5.6 Hz, H-4); 3.93 (dd, 1H, J = 3.2 Hz, 5.6 Hz, H-3); 3.72 (dd, J = 2.4 Hz, 7.6 Hz, H-2); 3.54 (s, 3H, OCH$_3$). ^{13}C-APT NMR (100 MHz) δ: 169.3 (C-6); 137.3, 136.8 (C$_{q,arom}$); 132.4 (CH$_{arom}$); 132.0 (C$_{q,arom}$); 128.9, 128.5, 128.4, 128.1, 128.0, 127.8, 127.7); 74.6 (C-4); 73.0 (PhCH$_2$); 72.9 (C-5); 58.7 (C-2); 52.2 (OCH$_3$). The C-1 and C-3 were not observable at room temperature due to signal broadening. IR (thin film) ν: 2870, 2102, 1749, 1454, 1439, 1265, 1119, 1094, 1078, 1024. HRMS: [M + Na]$^+$ calcd for C$_{27}$H$_{27}$N$_3$NaO$_5$S 528.1564, found 528.1559. To a solution of the methyl uronate (0.56 g, 1.12 mmol, 1.0 equiv) in acetone (8.4 mL) was added H$_2$O (2.8 mL, final concentration 0.1 M). At 0 °C, NBS (0.60 g, 3.35 mmol, 3.0 equiv) was added, and the reaction mixture assumed an orange-brown color. After ∼90 min, a second portion of NBS (0.60 g, 3.35 mmol, 3.0 equiv) was added, and the mixture was stirred for an additional 15 min, after which TLC (PE/EtOAc, 7:3 v/v) indicated complete conversion of the starting material. The reaction was quenched by addition of satd aq Na$_2$SO$_3$, and the mixture was extracted (EtOAc, 3×). The combined organic phases were washed (H$_2$O 1×, brine 1×), dried over MgSO$_4$, filtered, and concentrated in vacuo. Methyl 2-azido-3,4-di-O-benzyl-2-deoxy-α/β-D-mannopyranosiduronate was obtained after column chromatography (PE/EtOAc, 9:1 → 7:3 v/v), with the β-product predominating (α/β ∼ 1:9) in 82% yield (0.38 g, 0.92 mmol). NMR data are reported for the β-isomer only. ^{1}H NMR (400 MHz, 323 K) δ: 7.29−7.22 (m, 10H, CH$_{arom}$); 5.42 (d, 1H, J = 3.6 Hz, H-1); 4.65 (s, 2H, PhCH$_2$); 4.62−4.54 (m, 2H, PhCH$_2$); 4.49 (d, 1H, J = 5.6 Hz, H-5); 4.33 (bs, 1H, 1-OH); 4.12 (t, 1H, J = 5.6 Hz, H-4); 3.96 (bd, 1H, J = 3.2 Hz, H-3); 3.76 (bs, 1H, H-2); 3.55 (s, 3H, OCH$_3$). ^{13}C-APT NMR (100 MHz, 323 K) δ: 169.7 (C-6); 137.5, 137.3 (C$_{q,arom}$); 128.5, 128.4, 128.3, 128.1, 127.9, 127.7 (CH$_{arom}$); 92.1 (C-1); 77.4 (C-3); 75.2 (C-4); 73.5, 72.8 (PhCH$_2$); 72.3 (C-5); 61.0 (C-2); 52.1 (OCH$_3$). ^{13}C-GATED NMR (100 MHz, 323 K) δ: 92.1 (d, J = 170 Hz, H-1). IR (thin film) 3439, 2104, 1747, 1454, 1437, 1281, 1240, 1123, 1093, 1072, 1024. HRMS: [M + Na]$^+$ calcd for C$_{21}$H$_{23}$N$_3$NaO$_6$ 436.1479, found 436.1476. To a solution of the reducing sugar (0.30 g, 0.73 mmol, 1.0 equiv) in acetone (2.5 mL, 0.3 M) were added N-phenyl 2,2,2-trifluoroimidoyl chloride (0.17 mL, 1.1 mmol, 1.5 equiv) and Cs$_2$CO$_3$ (0.29 g, 0.88 mmol, 1.2 equiv), and the mixture was stirred until TLC analysis (PE/EtOAc, 4:1 v/v) indicated complete conversion of the starting material (∼2 h). The reaction mixture was diluted with acetone, filtered, and concentrated in vacuo. Purification of the residue by column chromatography (PE/EtOAc/NEt$_3$, 100:0:1 → 90:10:1) delivered the title compound as a mixture of anomers and/or conformers, in 88% yield (0.38 g, 0.64 mmol). ^{1}H NMR (major isomer, 400 MHz, 323 K) δ: 7.34−7.25 (m, 13H, CH$_{arom}$); 7.11 (t, 1H, J = 7.6 Hz, CH$_{arom}$); 6.80 (d, 2H, J = 8.0 Hz, CH$_{arom}$); 6.30 (bs, 1H, H-1); 4.77−4.64 (m, 4H, PhCH$_2$); 4.38 (d, 1H, J = 7.2 Hz, H-5); 4.18 (t, 1H, J = 7.6 Hz, H-4); 4.02 (dd, 1H, J = 2.8 Hz, 7.6 Hz, H-3); 3.87 (bs, 1H, H-2); 3.66 (s, 3H, OCH$_3$). ^{13}C-APT NMR (100 MHz, 323 K) δ: 168.5 (C-6); 143.1, 137.5, 137.1 (C$_{q,arom}$); 128.8, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0,

127.8, 124.6, 124.4, 119.4 (CH$_{arom}$); 94.4 (C-1); 77.8 (C-3); 74.9 (C-4); 74.6 (PhCH$_2$); 73.8 (C-5); 73.5 (PhCH$_2$); 59.8 (C-2); 52.4 (OCH$_3$). Diagnostic ^{1}H NMR signals for the minor isomer (400 MHz, 323 K) δ: 6.00 (bs, 0.2H, H-1); 4.30 (t, 0.2H, J = 6.8 Hz, H-4); 3.91 (bs, 0.2H, H-2); 3.62 (s, 0.6H, OCH$_3$). IR (thin film) ν: 2110, 1751, 1717, 1317, 1207, 1161, 1115, 1026. HRMS: [M + Na]$^+$ calcd for C$_{29}$H$_{27}$F$_3$N$_4$NaO$_6$ 607.1775, found 607.1777.

5-(Benzyl(benzyloxycarbonyl)amino)pentyl 2-Azido-3-O-benzoyl-4-O-benzyl-2-deoxy-β-D-fucopyranoside (29). A three-necked, 250 mL flask, equipped with a thermometer, rubber septa, an argon balloon, and a gas outlet, was charged with a solution of donor D-4 (2.86 g, 5.5 mmol, 1.0 equiv), Ph$_2$SO (1.44 g, 7.1 mmol, 1.3 equiv), and TTBP (3.39 g, 13.4 mmol, 2.5 equiv) in CH$_2$Cl$_2$/Et$_2$O (110 mL, 1:1 v/v, 0.05 M). Flame-dried 3 Å MS were added, and the mixture was stirred at room temperature for ~30 min. After the mixture was cooled to −80 °C, Tf$_2$O (1.2 mL, 7.1 mmol, 1.3 equiv) was added and the mixture was allowed to warm to −60 °C. After the mixture was recooled to −80 °C, a solution of 21 (3.58 g, 10.9 mmol, 2.0 equiv) in CH$_2$Cl$_2$/Et$_2$O (20 mL, 1:1 v/v) was added via cannula transfer (reaction mixture temperature did not exceed −70 °C during addition). The mixture was allowed to warm to −40 °C, after which the reaction was quenched by addition of NEt$_3$ (4 mL), filtered over a pad of Celite, diluted with CH$_2$Cl$_2$, washed with brine, dried over MgSO$_4$, filtered, and concentrated in vacuo. Column chromatography (PE/EtOAc, 49:1 →9:1 v/v) first furnished a mixture of α/β products (0.77 g, 1.1 mmol, 20% yield, α/β 1:3); when all higher-running α-product had eluted off, further elution (PE/EtOAc, 4:1 v/v) delivered pure β-product as a colorless oil (2.43 g, 3.5 mmol, 60%). NMR data are reported for the pure β-isomer. ^{1}H NMR (400 MHz, 323 K) δ: 8.06 (d, 2H, J = 7.6 Hz, CH$_{arom}$); 7.59 (t, 1H, J = 7.6 Hz, CH$_{arom}$); 7.46 (t, 2H, J = 7.6 Hz, CH$_{arom}$); 7.30−7.17 (m, 14H, CH$_{arom}$); 5.17 (bs, 2H, PhCH$_2$); 4.93 (dd, 1H, J = 2.8 Hz, 10.8 Hz, H-3); 4.68 (d, 1H, J = 11.6 Hz, PhCHH); 4.55 (d, 1H, J = 11.6 Hz, PhCHH); 4.49 (s, 2H, PhCH$_2$); 4.29 (d, 1H, J = 8.0 Hz, H-1); 3.96−3.91 (m, 2H, H-2, OCHH$_{pentyl}$); 3.78 (d, 1H, J = 2.0 Hz, H-4); 3.63 (q, 1H, J = 6.4 Hz, H-5); 3.48 (bs, 1H, OCHH$_{pentyl}$); 3.23 (CH$_2$N$_{pentyl}$); 1.61 (bs, 4H, 2× CH$_{2,pentyl}$); 1.35 (bs, 2H, 2H, CH$_{2,pentyl}$); 1.25 (d, 3H, J = 6.4 Hz, H-6). ^{13}C-APT NMR (100 MHz, 323 K) δ: 165.9 (CO$_{Bz}$); 138.1, 137.7 (C$_{q,arom}$); 133.5, 129.9 (CH$_{arom}$); 129.4 (C$_{q,arom}$); 128.6, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.3 (CH$_{arom}$); 102.3 (C-1); 76.3 (C-4); 75.5 (PhCH$_2$); 75.0 (C-3); 70.6 (C-5); 69.8 (OCH$_{2,pentyl}$); 67.2 (PhCH$_2$); 61.6 (C-2); 50.7 (PhCH$_2$); 29.2, 23.3 (CH$_{2,pentyl}$); 16.7 (C-6). IR (thin film) ν: 2937, 2110, 1719, 1695, 1452, 1421, 1265, 1096, 1069, 1026. HRMS: [M + Na]$^+$ calcd for C$_{40}$H$_{44}$N$_4$NaO$_7$ 715.3102, found 715.3097.

5-(Benzyl(benzyloxycarbonyl)amino)pentyl 2-Azido-4-O-benzyl-2-deoxy-β-D-fucopyranoside (30). To a stirred solution of 29 (2.43 g, 3.5 mmol, 1.0 equiv) in dry MeOH (18 mL, 0.2 M) was added a chip of Na metal. The reaction mixture was stirred at room temperature until TLC analysis (PE/EtOAc, 7:3 v/v) indicated complete conversion of the starting material. The reaction mixture was neutralized by addition of Amberlite IR-120 (H$^+$ form), filtered, and concentrated in vacuo. The title compound was obtained after column chromatography (PE/EtOAc) as a colorless oil in 95% yield (1.94 g, 3.3 mmol). ^{1}H NMR (400 MHz, 323 K) δ: 7.36−7.22 (m, 15H, CH$_{arom}$); 5.17 (s, 2H, PhCH$_2$); 4.80 (d, 1H, J = 11.6 Hz, PhCHH); 4.72 (d, 1H, J = 11.6 Hz, PhCHH); 4.48 (s, 2H, PhCH$_2$); 4.16 (d, 1H, J = 7.2 Hz, H-1); 3.86 (bs, 1H, OCHH$_{pentyl}$); 3.53−3.43 (m, 5H, OCHH$_{pentyl}$, H-2, H-3, H-4, H-5); 3.23 (bs, 2H, NCH$_{2,pentyl}$); 2.17 (d, 1H, J = 9.2 Hz, 3-OH); 1.57−1.53 (m, 4H, CH$_{2,pentyl}$); 1.44−1.43 (m, 2H, CH$_{2,pentyl}$); 1.26 (d, 3H, J = 7.2 Hz, H-6). ^{13}C-APT NMR (100 MHz, 323 K) δ: 138.1 (C$_{q,arom}$); 128.5, 128.5, 128.4, 128.2, 128.0, 127.9, 127.3 (CH$_{arom}$); 102.3 (C-1); 78.6 (C-3, C-4, or C-5); 76.0 (PhCH$_2$); 73.2, 70.9 (C-3, C-4 or C-5); 69.7 (OCH$_{2,pentyl}$); 67.2 (PhCH$_2$); 64.8 (C-2); 29.3, 23.3 (CH$_{2,pentyl}$); 16.9 (C-6). IR (thin film) ν: 2934, 2108, 1690, 1454, 1421, 1229, 1171, 1067. HRMS: [M + Na]$^+$ calcd for C$_{33}$H$_{40}$N$_4$NaO$_6$ 611.2840, found 611.2833.

5-(Benzyl(benzyloxycarbonyl)amino)pentyl 2-Azido-3-O-(2-azido-2-deoxy-3,4-di-O-(tert-butyldimethylsilyl)-α-L-fucopyranosyl)-4-O-benzyl-β-D-fucopyranoside (31). To a stirred solution of 5

(1.22 g, 2.2 mmol, 2.0 equiv), Ph$_2$SO (0.44 g, 2.2 mmol, 2.0 equiv), and TTBP (1.09 g, 4.4 mmol, 4.0 equiv) in CH$_2$Cl$_2$ (22 mL, 0.1 M relative to donor) were added flame-dried, rod-shaped, 3 Å molecular sieves. After 30 min at room temperature, the reaction mixture was cooled to −80 °C, after which Tf$_2$O (0.37 mL, 2.2 mmol, 2.0 equiv) was added. The reaction mixture was allowed to warm to −70 °C, after which it was recooled to −80 °C. A solution of acceptor 30 (dried by triple coevaporation with toluene, 0.65 g, 1.1 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (2.2 mL) was added via the wall of the flask, and the mixture was allowed to warm to −60 °C, after which it was stirred at this temperature for 15 min. The reaction was stopped by addition of NEt$_3$ (1 mL), and the mixture filtered over a pad of Celite, washed with brine (1×), dried over MgSO$_4$, filtered, and concentrated in vacuo. Purification of the residue by column chromatography (toluene/EtOAc, 1:0 → 9:1 v/v) and size-exclusion chromatography (CH$_2$Cl$_2$/MeOH, 1:1 v/v) furnished the title compound as an oil (0.83 g, 0.84 mmol, 76%). ^{1}H NMR (400 MHz, 323 K) δ: 7.34−7.21 (m, 15H, CH$_{arom}$); 5.36 (d, 1H, J = 3.6 Hz, H-1′); 5.16 (s, 2H, PhCH$_2$); 4.97 (d, 1H, J = 11.6 Hz, PhCHH); 4.58 (d, 1H, J = 11.2 Hz, PhCHH); 4.48 (s, 2H, PhCH$_2$); 4.17 (d, 1H, J = 8.0 Hz, H-1); 4.99 (bd, 1H, J = 10.0 Hz, H-3′); 3.94 (q, 1H, J = 6.8 Hz, H-5′); 3.85−3.80 (m, 2H, OCHH$_{pentyl}$, H-2); 3.77−3.71 (m, 2H, H-2′, H-4′); 3.52−3.42 (m, 4H, OCHH$_{pentyl}$, H-3, H-4, H-5); 3.23 (bs, 2H, NCH$_{2,pentyl}$); 1.53 (bs, 4H, 2× CH$_{2,pentyl}$); 1.34 (bs, 2H, CH$_{2,pentyl}$); 1.23 (d, 3H, J = 6.4 Hz, H-6 or H-6′); 1.19 (d, 3H, J = 6.4 Hz, H-6 or H-6′); 0.93, 0.93 (s, 9H, CH$_{3,tBuSi}$); 0.16, 0.14, 0.11, 0.09 (s, 3H, CH$_{3,MeSi}$). ^{13}C-APT NMR (100 MHz, 323 K) δ: 151.5 (CO$_{Cbz}$); 138.3, 138.1 (C$_{q,arom}$); 128.5, 128.4, 128.3, 127.9, 127.9, 127.8, 127.7, 127.2 (CH$_{arom}$); 102.8 (C-1); 99.3 (C-1′); 78.8, 78.7 (C-4, C-5); 75.0 (PhCH$_2$); 74.9 (C-4); 71.4 (C-3′); 70.8 (C-3); 69.7 (OCH$_{2,pentyl}$); 69.0 (C-5′); 67.2 (PhCH$_2$); 63.8 (C-2); 61.2 (C-2′); 50.5 (PhCH$_2$); 29.2 (CH$_{2,pentyl}$); 26.2, 26.1 (CH$_{3,tBuSi}$); 23.3 (PhCH$_2$); 18.6, 18.5 (C$_{q,tBuSi}$); 17.3, 16.9 (C-6, C-6′); −3.4, −3.6, −4.5, −4.6 (CH$_{3,MeSi}$). IR (thin film) ν: 2930, 2857, 2114, 1697, 1252, 1177, 1105, 1067, 1042, 1026. HRMS: [M + Na]$^+$ calcd for C$_{51}$H$_{77}$N$_7$NaO$_9$Si$_2$ 1010.5214, found 1010.5216.

5-(Benzyl(benzyloxycarbonyl)amino)pentyl 2-Azido-3-O-(2-azido-3-O-benzoyl-2-deoxy-α-L-fucopyranosyl)-4-O-benzyl-β-D-fucopyranoside (33). To a stirred solution of disaccharide 31 (0.83 g, 0.84 mmol, 1.0 equiv) in THF (4 mL, 0.2 M) was added Bu$_4$NF (as 1 M solution in THF, 2.0 mL, 2.4 equiv), and the resulting yellow reaction mixture was stirred until TLC analysis (toluene/EtOAc, 4:1 v/v) indicated complete conversion of the starting material (~2 h). The mixture was diluted with EtOAc, and the reaction quenched by addition of satd aq NaHCO$_3$. After separation of the layers, the aqueous layer was extracted with EtOAc (1×), and the combined organics were washed (H$_2$O, 1×; brine, 1×), dried over MgSO$_4$, filtered, and concentrated in vacuo. The residue was coevaporated once with dry MeCN before dissolution in MeCN (4 mL, 0.2 M). Added were, in succession, 2-aminoethyl diphenylborinate 30 (18 mg, 0.08 mmol, 0.1 equiv), DIPEA (0.3 mL, 1.68 mmol, 2.0 equiv) and BzCl (0.2 mL, 1.68 mmol, 2.0 equiv). The reaction vessel was stirred, under exclusion of light, until TLC analysis (toluene/EtOAc, 4:1 v/v) indicated complete conversion of the starting material (~16 h). The reaction mixture was diluted with EtOAc, washed (H$_2$O, 2×; brine, 1×), dried over MgSO$_4$, filtered, and concentrated in vacuo. Purification by column chromatography (toluene/EtOAc, 1:0 → 17:3 v/v) furnished the title compound as a colorless oil in 67% yield over two steps (0.48 g, 0.56 mmol). ^{1}H NMR (500 MHz, 323 K) δ: 8.10−8.09 (m, 2H, CH$_{arom}$); 7.59 (t, 1H, J = 7.5 Hz, CH$_{arom}$); 7.48−7.21 (m, 17H, CH$_{arom}$); 5.46 (dd, 1H, J = 3.0 Hz, 11.5 Hz, H-3′); 5.42 (d, 1H, J = 3.5 Hz, H-1′); 5.16 (bs, 2H, PhCH$_2$); 4.93 (d, 1H, J = 12.0 Hz, PhCHH); 4.77 (d, 1H, J = 11.5 Hz, PhCHH); 4.48 (bs, 2H, PhCH$_2$); 4.20 (d, 1H, J = 7.5 Hz, H-1); 3.99 (bs, 1H, H-4′); 3.95 (q, 1H, J = 6.5 Hz, H-5′); 3.90−3.86 (m, 2H, H-2, OCHH$_{pentyl}$); 3.82 (dd, 1H, J = 3.5 Hz, 11.3 Hz, H-2′); 3.55−3.45 (m, 4H, H-3, H-4, H-5, OCHH$_{pentyl}$); 3.22 (bs, 2H, NCH$_{2,pentyl}$); 1.59−1.21 (m, 6H, 3× CH$_{2,pentyl}$); 1.22 (d, 3H, J = 6.5 Hz, H-6); 1.14 (d, 3H, J = 6.5 Hz, H-6′). ^{13}C-APT NMR (125 MHz, 323 K) δ: 165.5 (CO$_{Bz}$); 138.2, 138.1 (C$_{q,arom}$); 133.5, 129.9 (CH$_{arom}$); 129.5 (C$_{q,arom}$); 128.6, 128.5, 128.4, 128.1, 127.9, 127.8, 127.3 (CH$_{arom}$); 102.8 (C-1); 99.8 (C-1′);

78.9, 78.3 (C-3, C-4 or C-5); 75.2 (PhCH$_2$); 71.4 (C-3′); 71.0 (C-3, C-4 or C-5); 70.2 (C-4′); 69.8 (OCH$_2$,pentyl); 67.2 (PhCH$_2$); 66.5 (C-5′); 63.8 (C-2); 57.4 (C-2′); 29.3, 23.3 (CH$_2$,pentyl); 17.1. 16.1 (C-6, C-6′). IR (thin film) ν: 2117, 1717, 1273, 1072. HRMS: [M + Na]$^+$ calcd for C$_{46}$H$_{53}$N$_7$NaO$_{10}$ 886.3746, found 886.3743.

5-(Benzyl(benzyloxycarbonyl)amino)pentyl 2-Azido-3-O-(2-azido-3-O-benzoyl-2-deoxy-4-O-(methyl 2-azido-3,4-di-O-benzyl-2-deoxy-β-D-mannopyranosiduronate)-α-L-fucopyranosyl)-4-O-benzyl-2-deoxy-β-D-fucopyranoside (27). To a stirred solution of donor **28** (0.75 g, 1.28 mmol, 4.0 equiv) and acceptor **33** (0.28 g, 0.32 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (3.2 mL, 0.1 M) were added flame-dried, rod-shaped, 3 Å MS. After ~30 min, the mixture was cooled to −80 °C, and TBSOTf (60 μL, 0.26 mmol, 0.8 equiv) was added. The reaction mixture was allowed to warm to −55 °C and was stirred at this temperature using an immersion cooler. After the mxiture was stirred for ~5.5 h, TLC analysis (toluene/acetone, 4:1 v/v) indicated complete disappearance of the acceptor, and the reaction was quenched by addition of NEt$_3$ (0.2 mL). The mixture was diluted with CH$_2$Cl$_2$, filtered over a small bed of Celite, washed (brine, 1×), dried over MgSO$_4$, filtered, and concentrated in vacuo. Purification by size-exclusion chromatography (CH$_2$Cl$_2$/MeOH, 1:1v/v) followed by column chromatography (toluene/EtOAc, 1:0 → 9:1) furnished the title trisaccharide as a colorless oil in 65% yield (260 mg, 0.21 mmol). ^{1}H NMR (500 MHz, 323 K) δ: 8.11−8.09 (m, 2H, CH$_{arom}$); 7.57 (t, 1H, J = 7.5 Hz, CH$_{arom}$); 7.47−7.14 (m, 27H, CH$_{arom}$); 5.41−5.39 (m, 2H, H-1′, H-3′); 5.16 (bs, 2H, PhCH$_2$); 4.95 (d, 1H, J = 11.5 Hz, PhCHH); 4.76 (d, 1H, J = 11.0 Hz, PhCHH); 4.72−4.68 (m, 3H, PhCH$_2$); 4.55 (d, 1H, J = 11.0 Hz, PhCHH); 4.49−4.48 (m, 3H, H-1″, PhCH$_2$); 4.21 (d, 1H, J = 3.0 Hz, H-4′); 4.18 (d, 1H, J = 8.0 Hz, H-1); 4.02−3.96 (m, 3H, H-2, H-2″, H-5′); 3.94 (t, 1H, J = 9.0 Hz, H-4″); 3.86 (bs, 1H, OCHH$_{pentyl}$); 3.83 (dd, 1H, J = 8.0 Hz, 10.5 Hz, H-2); 3.55 (d, 1H, J = 10.0 Hz, H-5″); 3.52−3.46 (m, 5H, H-3, H-3″, H-4, H-5, OCHH$_{pentyl}$); 3.22 (bs, 2H, NCH$_2$,pentyl); 3.13 (s, 3H, OCH$_3$); 1.58−1.38 (m, 6H, CH$_2$,pentyl); 1.30 (d, 3H, J = 6.0 Hz, H-6); 1.16 (d, 3H, J = 7.0 Hz, H-6′). ^{13}C-APT NMR (125 MHz, 323 K) δ: 166.9, 166.1 (C-6″, CO$_{Bz}$); 138.2, 138.1, 137.4 (C$_{q,arom}$); 133.0, 130.1 (CH$_{arom}$); 129.9 (C$_{q,arom}$); 128.6, 128.5, 128.5, 128.4, 1283, 128.2, 128.1, 127.9, 127.9, 127.7, 127.7, 127.5, 127.3 (CH$_{arom}$); 102.8 (C-1); 101.2 (C-1″); 99.5 (C-1′); 79.9 (C-3″); 79.0 (C-3); 78.3 (C-4); 76.5 (C-4′); 75.3, 75.2 (PhCH$_2$); 75.2, 75.2 (C-4″; C-5″); 72.3 (PhCH$_2$); 70.9 (C-5); 69.8 (OCH$_2$,pentyl); 69.5 (C-3′); 67.2 (PhCH$_2$); 66.4 (C-5′); 63.8 (C-2); 61.3 (C-2″); 57.4 (C-2′); 51.9 (OCH$_{3,methyl}$); 50.9 (NCH$_2$,pentyl); 29.3, 23.3 (CH$_2$,pentyl); 17.1 (C-6); 16.6 (C-6′). ^{13}C-GATED NMR (125 MHz, 323 K) δ: 102.8 (d, J = 159 Hz, C-1); 101.2 (d, J = 160 Hz, C-1″); 99.5 (d, J = 173 Hz, C-1′). IR (thin film) ν: 2934, 2110, 1749, 1717, 1699, 1273, 1103, 1069, 1038. HRMS: [M + Na]$^+$ calcd for C$_{67}$H$_{74}$N$_{10}$NaO$_{15}$ 1281.5227, found 1281.5228.

5-Aminopentyl 2-Acetamido-3-O-(2-acetamido-3-O-acetyl-4-O-(2-acetamido-2-deoxy-β-D-mannopyranosiduronyl)-2-deoxy-α-L-fucopyranosyl)-2-deoxy-β-D-fucopyranoside (26). A solution of **27** (50 mg, 0.040 mmol, 1.0 equiv) in THF was treated with a freshly prepared solution of KOOH (H$_2$O$_2$, 30% w/w in H$_2$O, was added to 0.5 M aq KOH solution), and the slightly turbid mixture was allowed to stir for 2 days until TLC analysis (toluene/EtOAc/AcOH, 60:40:5 v/v/v) indicated complete conversion of the starting material. The mixture was acidified to pH 3 with 1 M aq HCl and extracted (CH$_2$Cl$_2$, 5×), and the combined organic fractions were washed (brine, 1×), dried over MgSO$_4$, filtered, and concentrated in vacuo. Purification by column chromatography (toluene/EtOAc/AcOH, 90:10:5 → 70:30:5 v/v/v) gave free uronic acid **34** as a milky solid (30 mg, 0.026 mmol, 66%). ^{1}H NMR (500 MHz, 323 K, CD$_3$CN + acetic acid-d4) δ: 7.40−7.18 (m, 25H, CH$_{arom}$); 5.22 (d, 1H, J = 3.5 Hz, H-1′); 5.12 (s, 2H, PhCH$_2$); 4.85 (d, 1H, J = 11.0 Hz, PhCHH); 4.77−4.75 (m, 3H, H-1″, PhCH$_2$); 4.66−4.61 (m, 3H, PhCH$_2$); 4.46 (s, 2H, PhCH$_2$); 4.34 (d, 1H, J = 2.5 Hz, H-2″); 4.24 (d, 1H, J = 7.0 Hz, H-1); 4.03 (q, 1H, J = 6.5 Hz, H-5′); 3.96 (d, 1H, J = 9.0 Hz, H-5″); 3.94−3.89 (m, 2H, H-3′, H-4′); 3.87 (t, 1H, J = 9.5 Hz, H-4″); 3.78 (dd, 1H, J = 3.5 Hz, 9.0 Hz, H-3″); 3.75−3.74 (m, 1H, OCHH$_{pentyl}$); 3.63−3.54 (m, 4H, H-2, H-3, H-4, H-5); 3.48−3.36 (m, 1H, OCHH$_{pentyl}$); 3.39 (dd, 1H, J = 3.5 Hz, 10.5 Hz, H-2′);

3.27 (t, 2H, J = 7.5 Hz, NCH$_2$,pentyl); 1.53−1.50 (m, 4H, CH$_2$,pentyl); 1.34−1.20 (m, 8H, H-6, H-6′, CH$_2$,pentyl). HRMS: [M + H]$^+$ calcd for C$_{59}$H$_{69}$N$_{10}$O$_{14}$ 1141.4989, found 1141.4994. The uronic acid **32** (17 mg, 0.015 mmol, 1.0 equiv) was dissolved in pyridine (0.6 mL), and at 0 °C, Ac$_2$O (0.15 mL) was slowly added. The mixture was stirred until TLC analysis (toluene/EtOAc/AcOH, 60:40:5 v/v/v) indicated complete conversion of the starting material. The reaction was quenched by slow addition of water, and after ~15 min, the mixture was extracted (CH$_2$Cl$_2$, 5×). The organic phases were washed (brine, 1×), dried over MgSO$_4$, filtered, and concentrated in vacuo. The residue was coevaporated with toluene (2×) to remove excess acetic acid and pyridine. ^{1}H NMR (500 MHz, CD$_3$CN + acetic acid-d$_4$) δ: 7.39−7.22 (m, 25H, CH$_{arom}$); 5.32 (d, 1H, J = 3.5 Hz, H-1′); 5.14 (dd, 1H, J = 3.0 Hz, 11.5 Hz, H-3′); 5.10 (bs, 2H, PhCH$_2$); 4.87 (d, 1H, J = 10.0 Hz, PhCHH); 4.79−4.74 (m, 2H, PhCH$_2$); 4.67 (d, 1H, J = 1.0 Hz, H-1″); 4.65−4.60 (m, 2H, PhCH$_2$); 4.54 (d, 1H, J = 11.0 Hz, PhCHH); 4.44 (s, 2H, PhCH$_2$); 4.31 (d, 1H, J = 2.5 Hz, H-2″); 4.24 (bs, 1H, H-1); 4.11 (d, 1H, J = 3.0 Hz, H-4′); 4.08 (q, 1H, J = 6.5 Hz, H-5′); 3.83−3.70 (m, 5H, H-2′, H-3″, H-4″, H-5″, OCHH$_{pentyl}$); 3.58−3.53 (m, 4H, H-2, H-3, H-4, H-5); 3.44 (bs, 2H, OCHH$_{pentyl}$); 3.20 (bs, 2H, NCH$_2$,pentyl); 2.01 (s, 3H, CH$_{3,Ac}$); 1.51−1.49 (m, 4H, CH$_2$,pentyl); 1.32−1.19 (m, 8H, H-6, H-6′, CH$_2$,pentyl). The crude O-acetate (12 mg, 0.01 mmol, 1.0 equiv) was dissolved in pyridine (0.5 mL, degassed by sonication before use), and added was freshly distilled AcSH (0.5 mL). The reaction was stirred for 3 days after which LC−MS analysis (MeCN/H$_2$O/TFA, 50:50:0.1 → 90:10:0.1 v/v/v, t_R: 6.80 min) indicated complete conversion of the starting material. The mixture was diluted with pyridine (~1 mL) and concentrated in vacuo. The crude mixture was subjected to size-exclusion chromatography (CH$_2$Cl$_2$/MeOH, 1:1 v/v) to isolate the intermediate **35** in 57% yield (7 mg, 0.0057 mmol). ^{1}H NMR (500 MHz, 323 K, CD$_3$CN + acetic acid-d$_4$) δ: 7.42−7.21 (m, 25H, CH$_{arom}$); 5.11 (s, 2H, PhCH$_2$); 4.97−4.90 (m, 4H, H-1″, H-2″, H-3′, PhCHH); 4.79−4.77 (m, 2H, PhCH$_2$); 4.69−4.67 (m, 2H, H-1′, PhCHH); 4.58 (d, 1H, J = 10.5 Hz, PhCHH); 4.48−4.46 (m, 3H, PhCH$_2$); 4.41 (dd, 1H, J = 3.5 Hz, 11.5 Hz, H-2′); 4.25 (d, 1H, J = 9.0 Hz, H-1); 4.10−4.05 (m, 3H, H-2, H-4′, H-5′); 3.81−3.60 (m, 6H, H-3, H-3″, H-4″, H-5, H-5″, OCHH$_{pentyl}$); 3.56 (d, 1H, J = 2.5 Hz, H-4); 3.37−3.35 (m, 1H, OCHH$_{pentyl}$); 3.21 (t, 1H, J = 7.0 Hz, NCH$_2$,pentyl); 2.03, 1.95, 1.91, 1.81 (CH$_{3,Ac}$); 1.50−1.45 (m, 4H, CH$_2$,pentyl); 1.27−1.18 (m, 8H, H-6, H-6′, CH$_2$,pentyl). ^{13}C-APT NMR (125 MHz, 323 K, CD$_3$CN + acetic acid-d$_4$) δ: 171.9 (C-6″); 129.6, 129.5, 129.4, 129.4, 129.3, 129.0, 129.0, 128.8, 128.8, 128.6, 128.3 (CH$_{arom}$); 102.3 (C-1); 101.5 (C-1′); 100.4 (C-1″); 80.9 (C-3″, C-4″ or C-5″); 80.4 (C-4); 78.8 (C-3); 77.3, 77.0 (C-4 and C-3″, C-4″ or C-5″); 76.2, 75.8 (PhCH$_2$); 75.6 (C-3″, C-4″ or C-5″); 72.0 (PhCH$_2$); 71.5 (C-5); 71.0 (C-3′); 69.9 (OCH$_2$,pentyl); 68.1 (C-5′); 67.9 (PhCH$_2$); 53.0 (C-2); 50.3 (C-2″); 47.8 (C-2′); 30.1, 24.1 (CH$_2$,pentyl); 23.5, 23.3, 23.3, 21.3 (CH$_{3,Ac}$); 17.5, 16.8 (C-6, C-6′). HRMS: [M + H]$^+$ calcd for C$_{67}$H$_{83}$N$_4$O$_{18}$ 1231.5697, found 1231.5704. The trisaccharide **33** (4 mg, 0.003 mmol) was dissolved in THF, tert-butyl alcohol, and H$_2$O (1:1:3 v/v/v, 0.002 M). Added was a drop of AcOH and the mixture was degassed (freeze−thaw, 3 cycles) and backfilled with argon. Pd(OH)$_2$ (20 weight% on carbon, 50% H$_2$O) was added and the mixture was purged with argon (balloon), followed by H$_2$ (balloon). After purging, the mixture was stirred under H$_2$ atmosphere for 2 days. The mixture was filtered over a fritted syringe filled with Celite, the residue was washed with THF/H$_2$O (1:1 v/v) and concentrated in vacuo. After ^{1}H NMR analysis revealed no aromatic signals, the crude trisaccharide was purified by passing over a C18 solid-phase extraction column (MeCN/H$_2$O, 0:1 → 1:9) and subsequently lyophilized to obtain the product **26** (2.5 mg, 0.003 mmol) as a white solid. ^{1}H NMR (500 MHz, D$_2$O) δ: 5.03 (dd, 1H, J = 3.0 Hz, 12.0 Hz, H-3′); 5.01 (d, 1H, J = 4.0 Hz, H-1′); 4.74 (bs, 1H, H-1″); 4.59 (d, 1H, J = 4.5 Hz, H-2″); 4.41 (d, 1H, J = 8.5 Hz, H-1); 4.38 (dd, 1H, J = 4.0, 11.5 Hz, H-2′); 4.22 (d, 1H, J = 2.5 Hz, H-4′); 4.19 (q, 1H, J = 6.5 Hz, H-5′); 3.99 (t, 1H, J = 8.5 Hz, H-2); 3.91−3.86 (m, 1H, OCHH$_{pentyl}$); 3.82−3.77 (m, 4H, H-3, H-3″, H-4, H-5); 3.65 (t, 1H, J = 9.5 Hz, H-4″); 3.60−3.56 (m, 2H, H-5″, OCHH$_{pentyl}$); 2.14, 2.09, 2.01, 1.99 (s, 3H, CH$_{3,Ac}$); 1.66 (t, 2H,

J = 7.5 Hz, $CH_{2,pentyl}$); 1.62−1.56 (m, 2H, $CH_{2,pentyl}$); 1.41−1.38 (m, 2H, $CH_{2,pentyl}$); 1.28 (d, 3H, J = 6.5 Hz, H-6); 1.25 (d, 3H, J = 6.5 Hz, H-6′). ^{13}C-APT NMR (125 MHz, D_2O) δ: 175.7, 175.6, 174.3, 174.1, 173.9 (C-6″, CO_{Ac}); 101.6 (C-1); 99.9 (C-1″); 99.1 (C-1′); 78.7 (C-5″); 71.1 (C-3, C-3″, C-4 or C-5); 71.7, 70.8, 70.5 (C-3, C-3″, C-4, C-5); 70.1 ($OCH_{2,pentyl}$); 69.9 (C-3′); 69.6 (C-4″); 66.9 (C-5); 53.1 (C-2″); 51.4 (C-2); 47.2 (C-2′); 39.4 ($NCH_{2,pentyl}$); 28.2, 26.5 ($CH_{2,pentyl}$); 22.2, 22.2, 22.1 ($CH_{3,Ac}$); 22.0 ($CH_{2,pentyl}$); 20.4 ($CH_{3,Ac}$); 15.4, 15.3 (C-6, C-6′). HRMS: $[M + H]^+$ calcd for $C_{31}H_{53}N_4O_{16}$ 737.3451, found 737.3452.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02593.

NMR spectra of new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Emmadi, M.; Kulkarni, S. S. *Nat. Prod. Rep.* **2014**, *31*, 870−879.

(2) Berti, F.; Ravenscroft, N. In *Carbohydrate-Based Vaccines: Methods and Protocols*; Lepenies, B., Ed.; Springer: New York, 2015; pp 189−209.

(3) Jones, C. *Carbohydr. Res.* **2005**, *340*, 1097−1106.

(4) Liau, D. F.; Hash, J. H. *J. Bacteriol.* **1977**, *131*, 194−200.

(5) Murthy, S. V. K. N.; Melly, M. A.; Harris, T. M.; Hellerqvist, C. G.; Hash, J. H. *Carbohydr. Res.* **1983**, *117*, 113−123.

(6) Jann, B.; Shashkov, A. S.; Kochanowski, H.; Jann, K. *Carbohydr. Res.* **1993**, *248*, 241−250.

(7) Svensson, M. V.; Weintraub, A.; Widmalm, G. *Carbohydr. Res.* **2011**, *346*, 2300−2303.

(8) Anish, C.; Schumann, B.; Pereira, C. L.; Seeberger, P. H. *Chem. Biol.* **2014**, *21*, 38−50.

(9) Seeberger, P. H.; Werz, D. B. *Nature* **2007**, *446*, 1046−1051.

(10) Fernández-Tejada, A.; Cañada, F. J.; Jiménez-Barbero, J. *Chem. - Eur. J.* **2015**, *21*, 10616−10628.

(11) Crich, D. *Acc. Chem. Res.* **2010**, *43*, 1144−1153.

(12) Zhu, X.; Schmidt, R. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 1900−1934.

(13) Nigudkar, S. S.; Demchenko, A. V. *Chem. Sci.* **2015**, *6*, 2687−2704.

(14) Mydock, L. K.; Demchenko, A. V. *Org. Biomol. Chem.* **2010**, *8*, 497−510.

(15) Yasomanee, J. P.; Visansirikul, S.; Pornsuriyasak, P.; Thompson, M.; Kolodziej, S. A.; Demchenko, A. V. *J. Org. Chem.* **2016**, *81*, 5981−5987.

(16) Danieli, E.; Proietti, D.; Brogioni, G.; Romano, M. R.; Cappelletti, E.; Tontini, M.; Berti, F.; Lay, L.; Costantino, P.; Adamo, R. *Bioorg. Med. Chem.* **2012**, *20*, 6403−6415.

(17) Gagarinov, I. A.; Fang, T.; Liu, L.; Srivastava, A. D.; Boons, G.-J. *Org. Lett.* **2015**, *17*, 928−931.

(18) Visansirikul, S.; Yasomanee, J. P.; Pornsuriyasak, P.; Kamat, M. N.; Podvalnyy, N. M.; Gobble, C. P.; Thompson, M.; Kolodziej, S. A.; Demchenko, A. V. *Org. Lett.* **2015**, *17*, 2382−2384.

(19) Banoub, J.; Boullanger, P.; Lafont, D. *Chem. Rev.* **1992**, *92*, 1167−1195.

(20) Mehta, S.; Pinto, B. M. *Tetrahedron Lett.* **1991**, *32*, 4435−4438.

(21) Szeja, W.; Grynkiewicz, G.; Field, R. A. In *Handbook of Chemical Glycosylation*; Demchenko, A. V., Ed.; Wiley-VCH, 2008; pp 329−379.

(22) Mironov, Y. V.; Sherman, A. A.; Nifantiev, N. E. *Tetrahedron Lett.* **2004**, *45*, 9107−9110.

(23) Komarova, B. S.; Ustyuzhanina, N. E.; Tsvetkov, Y. E.; Nifantiev, N. E. In *Modern Synthetic Methods in Carbohydrate Chemistry*; Werz, D. B., Vidal, S., Eds.; Wiley-VCH, 2013; pp 125−159.

(24) Arafuka, S.; Koshiba, N.; Takahashi, D.; Toshima, K. *Chem. Commun.* **2014**, *50*, 9831−9834.

(25) Guillemineau, M.; Auzanneau, F.-I. *J. Org. Chem.* **2012**, *77*, 8864−8878.

(26) Mong, K.-K. T.; Wong, C.-H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4087−4090.

(27) Krylov, V. B.; Kaskova, Z. M.; Vinnitskiy, D. Z.; Ustyuzhanina, N. E.; Grachev, A. A.; Chizhov, A. O.; Nifantiev, N. E. *Carbohydr. Res.* **2011**, *346*, 540−550.

(28) Gerbst, A. G.; Ustuzhanina, N. E.; Grachev, A. A.; Zlotina, N. S.; Khatuntseva, E. A.; Tsvetkov, D. E.; Shashkov, A. S.; Usov, A. I.; Nifantiev, N. E. *J. Carbohydr. Chem.* **2002**, *21*, 313−324.

(29) Gerbst, A. G.; Ustuzhanina, N. E.; Grachev, A. A.; Khatuntseva, E. A.; Tsvetkov, D. E.; Whitfield, D. M.; Berces, A.; Nifantiev, N. E. *J. Carbohydr. Chem.* **2001**, *20*, 821−831.

(30) Gerbst, A. G.; Ustuzhanina, N. E.; Grachev, A. A.; Tsvetkov, D. E.; Khatuntseva, E. A.; Nifant'ev, N. E. *Mendeleev Commun.* **1999**, *9*, 114−116.

(31) Daly, R.; McCabe, T.; Scanlan, E. M. *J. Org. Chem.* **2013**, *78*, 1080−1090.

(32) Zong, C.; Li, Z.; Sun, T.; Wang, P.; Ding, N.; Li, Y. *Carbohydr. Res.* **2010**, *345*, 1522−1532.

(33) Hua, Y.; Du, Y.; Yu, G.; Chu, S. *Carbohydr. Res.* **2004**, *339*, 2083−2090.

(34) Kasai, A.; Arafuka, S.; Koshiba, N.; Takahashi, D.; Toshima, K. *Org. Biomol. Chem.* **2015**, *13*, 10556−10568.

(35) Garcia, B. A.; Poole, J. L.; Gin, D. Y. *J. Am. Chem. Soc.* **1997**, *119*, 7597−7598.

(36) Garcia, B. A.; Gin, D. Y. *J. Am. Chem. Soc.* **2000**, *122*, 4269−4279.

(37) Codée, J. D. C.; Litjens, R. E. J. N.; Den Heeten, R.; Overkleeft, H. S.; Van Boom, J. H.; Van der Marel, G. A. *Org. Lett.* **2003**, *5*, 1519−1522.

(38) Frihed, T. G.; Bols, M.; Pedersen, C. M. *Chem. Rev.* **2015**, *115*, 4963−5013.

(39) Volbeda, A. G.; Kistemaker, H. A. V; Overkleeft, H. S.; Van der Marel, G. A.; Filippov, D. V.; Codée, J. D. C. *J. Org. Chem.* **2015**, *80*, 8796−8806.

(40) Fascione, M. A.; Adshead, S. J.; Mandal, P. K.; Kilner, C. A.; Leach, A. G.; Turnbull, W. B. *Chem. - Eur. J.* **2012**, *18*, 2987−2997.

(41) Fascione, M. A.; Brabham, R.; Turnbull, W. B. *Chem. - Eur. J.* **2016**, *22*, 3916−3928.

(42) Crich, D.; Smith, M.; Yao, Q.; Picione, J. *Synthesis* **2001**, *2001*, 323−326.

(43) Beaver, M. G.; Woerpel, K. A. *J. Org. Chem.* **2010**, *75* (4), 1107−1118.

(44) Ennis, S. C.; Cumpstey, I.; Fairbanks, A. J.; Butters, T. D.; Mackeen, M.; Wormald, M. R. *Tetrahedron* **2002**, *58*, 9403−9411.

(45) Szurmai, Z.; Balatoni, L.; Lipták, A. *Carbohydr. Res.* **1994**, *254*, 301−309.

(46) Bohé, L.; Crich, D. *Carbohydr. Res.* **2015**, *403*, 48−59.

(47) Bohé, L.; Crich, D. *C. R. Chim.* **2011**, *14*, 3−16.

(48) Smith, D. M.; Woerpel, K. A. *Org. Biomol. Chem.* **2006**, *4*, 1195−1201.

(49) Romero, J. A. C.; Tabacco, S. A.; Woerpel, K. A. *J. Am. Chem. Soc.* **2000**, *122*, 168−169.

(50) Ayala, L.; Lucero, C. G.; Romero, J. A. C.; Tabacco, S. A.; Woerpel, K. A. *J. Am. Chem. Soc.* **2003**, *125*, 15521−15528.

(51) Woods, R. J.; Andrews, C. W.; Bowen, J. P. *J. Am. Chem. Soc.* **1992**, *114*, 859−864.

(52) Van Rijssel, E. R.; Van Delft, P.; Lodder, G.; Overkleeft, H. S.; Van Der Marel, G. a.; Filippov, D. V.; Codée, J. D. C. *Angew. Chem., Int. Ed.* **2014**, *53*, 10381−10385.

(53) Walvoort, M. T. C.; Dinkelaar, J.; Van den Bos, L. J.; Lodder, G.; Overkleeft, H. S.; Codée, J. D. C.; Van der Marel, G. A. *Carbohydr. Res.* **2010**, *345*, 1252−1263.

(54) Codée, J. D. C.; van den Bos, L. J.; de Jong, A.-R.; Dinkelaar, J.; Lodder, G.; Overkleeft, H. S.; van der Marel, G. A. *J. Org. Chem.* **2009**, *74*, 38−47.

(55) The 1,2-*cis* selectivity can also be accounted for with a kinetic scenario that is based on the in situ anomerization of an α-triflate into the corresponding β-triflate and subsequent displacement of this more reactive covalent species. However, we found that addition of extra triflate ions in the condensation of **1** with cyclohexanol enhances the rate of anomerization of the reactive intermediates, leading to the formation of more β-product (α/β 2:5, compared to a ratio of 1:1 using unmodified conditions (Table 1)).

(56) Mulani, S. K.; Hung, W.-C.; Ingle, A. B.; Shiau, K.-S.; Mong, K.-K. T. *Org. Biomol. Chem.* **2014**, *12*, 1184−1197.

(57) Noti, C.; de Paz, J. L.; Polito, L.; Seeberger, P. H. *Chem. - Eur. J.* **2006**, *12*, 8664−8686.

(58) Chu, A.-H. A.; Nguyen, S. H.; Sisel, J. A.; Minciunescu, A.; Bennett, C. S. *Org. Lett.* **2013**, *15*, 2566−2569.

(59) Lemieux, R. U.; Hendriks, K. B.; Stick, R. V.; James, K. *J. Am. Chem. Soc.* **1975**, *97*, 4056−4062.

(60) Litjens, R. E. J. N.; Leeuwenburgh, M. A.; Van der Marel, G. A.; Van Boom, J. H. *Tetrahedron Lett.* **2001**, *42*, 8693−8696.

(61) Walvoort, M. T. C.; Lodder, G.; Mazurek, J.; Overkleeft, H. S.; Codée, J. D. C.; Van der Marel, G. A. *J. Am. Chem. Soc.* **2009**, *131*, 12080−12081.

(62) Walvoort, M. T. C.; Lodder, G.; Overkleeft, H. S.; Codée, J. D. C.; Van der Marel, G. A. *J. Org. Chem.* **2010**, *75*, 7990−8002.

(63) Demchenko, A. V.; Stauch, T.; Boons, G.-J. *Synlett* **1997**, *1997*, 818−820.

(64) Hashimoto, S.; Hayashi, M.; Noyori, R. *Tetrahedron Lett.* **1984**, *25*, 1379−1382.

(65) Lee, D.; Taylor, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 3724−3727.

(66) Walvoort, M. T. C.; de Witte, W.; van Dijk, J.; Dinkelaar, J.; Lodder, G.; Overkleeft, H. S.; Codée, J. D. C.; van der Marel, G. A. *Org. Lett.* **2011**, *13*, 4360−4363.

(67) The hydrolyzed donor could be partially recovered after the glycosylation.

(68) Walvoort, M. T. C.; Moggré, G.-J.; Lodder, G.; Overkleeft, H. S.; Codée, J. D. C.; van der Marel, G. A. *J. Org. Chem.* **2011**, *76*, 7301−7315.

(69) Shangguan, N.; Katukojvala, S.; Greenberg, R.; Williams, L. J. *J. Am. Chem. Soc.* **2003**, *125*, 7754−7755.