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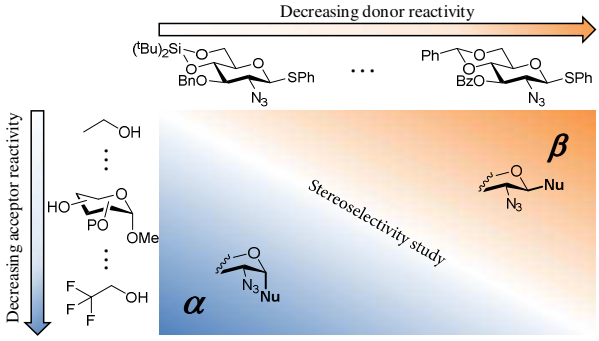
Stereoselectivity of conformationally restricted glucosazide donors

Stefan van der Vorm, Herman S. Overkleeft, Gijsbert A. van der Marel, Jeroen D. C. Codée*

Leiden Institute of Chemistry, Leiden University, Einsteinweg 55, 2333 CC Leiden, The Netherlands

*e-mail: jcodee@chem.leidenuniv.nl



ABSTRACT

Glycosylations of 4,6-tethered glucosazide donors with a panel of model acceptors reveal the effect of acceptor nucleophilicity on the stereoselectivity of these donors. The difference in reactivity between the donors is evaluated in competitive glycosylation reactions and their relative reactivity is reflected in the stereoselectivity in glycosylations with a set of fluorinated alcohols as well as carbohydrate acceptors. The 2-azido-2-deoxy moiety is more β-directing than its C-2-*O*-benzyl counterpart, as a consequence of increased destabilization of anomeric charge development by the electron withdrawing azide. Additional disarming groups further decrease α-selectivity of the studied donors, while substitution of the 4,6-benzylidene acetal with a 4,6-di-*tert*-butyl silylidene led to a slight increase in α-selectivity. The C-2-dinitropyridone group was also explored as an alternative for the non-participating azide group but this protecting group significantly increases β-selectivity. All studied donors show the same acceptor-dependent selectivity trend, and good α-selectivity can be obtained with the weakest acceptors and most reactive donors.

Introduction

Glucosamine is a key constituent in numerous important oligosaccharides and glycoconjugates, where it can be either α- or β-linked.[1–5] While the former type of linkage can be reliably installed by the use of neighboring group participation of an C-2-amide or carbamate based protecting group, the latter type continues to present a synthetic challenge.[6–8] A thorough understanding of the glycosylation mechanism and the influence of both reaction partners and reaction conditions on glycosylation stereoselectivity is needed to enable reliable and predictable glycosylation reactions. The in-depth research conducted on conformationally restricted benzylidene mannose and glucose donors has provided important insight into the glycosylation mechanisms of this type of 1,2-*cis* selective donors.[9–17] To construct 1,2-*cis* linkages of glucosamine donors, the C-2-amino group is most commonly masked as the non-particpating azide.[18,19] Notably, benzylidene glucosazides have not been systematically investigated with respect to the stereoselectivity of glycosylations in which they are employed. The extrapolation of the stereoselectivity of benzylidene glucose donors to their glucosazide counterparts suggests that benzylidene or analogously protected glucosazides may represent an attractive class of 1,2-*cis* selective glucosamine donor synthons.[20,21]

Recently, we have advocated the use of a comprehensive set of partially fluorinated ethanols, of gradually decreasing nucleophilicity, that can be used to map how the stereoselectivity of a given glycosylation system is dependent on the nucleophilicity of the acceptor.[22] The stereoselectivity of the benzylidene glucose donor system proved to be greatly affected by the reactivity of the nucleophile.[23–27] In light of the demand for 1,2-*cis* selective glucosaminylations but also with the aim in mind to further our understanding of the stereo-electronic effects exerted by the azido group we set out to systematically evaluate a series of glucosazide donors in a set of glycosylation reactions involving the toolset of partially fluorinated ethanols and a selection of carbohydrate acceptors. As we describe here, changes in the structure and reactivity of the donor can be effectively mapped using our panel of model acceptors, and we observed a clear reactivity-selectivity relationship for the stereoselectivity of the glycosylations of all donors studied. Differences between the donors and the stereochemical variation in the glycosylation outcome are explained using competition experiments and the characterization of the reactive intermediates involved.

Results and discussion

The set of (partially) fluorinated ethanol acceptors, which we recently employed to relate the glycosylation stereoselectivity to the acceptor nucleophilicity, is depicted in Figure 1 (compounds **6-11**). Glycosylating these acceptors with benzylidene mannose, benzylidene glucose, mannuronic acid donors, as well as fucosazide donors bearing various protecting groups, established the dependence of the stereoselectivity of the glycosylations with these donors on the nucleophilicity of the acceptor.[22,28] For benzylidene protected glucose donor **1**, the gradual decrease in acceptor nucleophilicity going from ethanol, monofluoroethanol (MFE), difluoroethanol (DFE), trifluoroethanol (TFE) to hexafluoro-*iso*-propanol (HFIP) led to a gradual shift of the stereoselecivity from high β- to exclusive α-selectivity (See Table 3). Here we present our results in investigating the set of conformationally restricted glucosamine donors depicted in Figure 1 (**1**-**5**). Variation in the structure of these donors is found in the cyclic protecting groups (benzylidene *vs* silylidene), in the functionality at the C-3-OH (benzyl *vs* benzoyl) and the nature of the C-2-*N*-protecting group (azide *vs* the dinitropyridone (DNPY) group). The DNPY is introduced here as a non-participating *N*-protecting group.[29,30] The reactivity and selectivity of the set of glucosamine donors is related to the well studied benzylidene glucose donor **1**.[9,22]

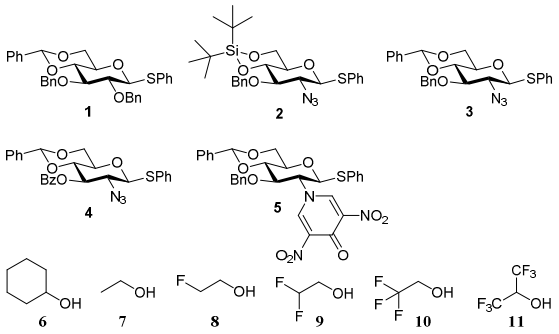
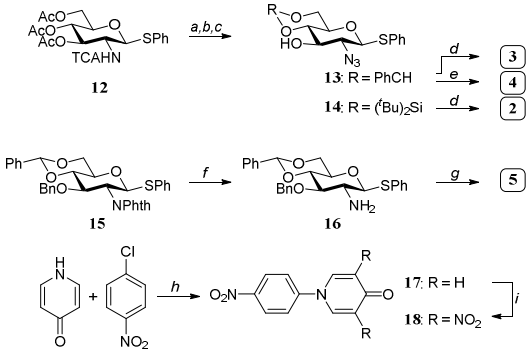


Figure 1: Glucose-configured donors 1-5 and model acceptors 6-11 used in this study.

Synthesis

We prepared benzylidene protected glucosazide donors **3**[31] and **4**[32] with either an *O*-benzyl or *O*-benzoyl at C-3, and a silylidene protected donor **2**, from common building block **12**[33] as depicted in Scheme 1. Hydrolysis of all acetyl esters and the trichloroacetamide was followed by a diazotransfer to install the desired C-2-azide.[34] Subsequent introduction of the di-*tert*-butylsilylidene (DTBS) or the benzylidene acetal gave intermediates **13**[31] and **14**. Benzylation of **14** and **13** and benzoylation of **13** gave the target donor compounds **2**, **3**, and **4**, respectively. Donor **5** was prepared in two steps from thioglucoside **15**[35] by exchange of the phthaloyl group for the DNPY functionality. To this end, compound **15** was treated with ethylenediamine to give amine **16**, wich was treated with DNPY reagent **18**[30,36] to furnish the target donor.

Scheme 1. Preparation of donors 2-5[a]

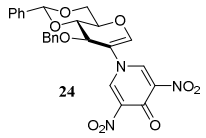


[a]Reagents and conditions: (a) *i.* K_2CO_3, EtOH, H_2O; *ii.* $CuSO_4$•$5H_2O$, imidazole-1-sulfonyl azide hydrochloride[34]; (b) di-*tert*-butylsilyl bis(trifluoromethanesulfonate), pyridine, **14**: 71% (three steps); (c) $PhCH(OMe)_2$, *p*-TsOH•H_2O, **13**: 78% (three steps); (d) BnBr, NaH, DMF, **2**: 80%, **3**: 89%; (e) BzCl, DMAP, pyridine, DCM, 90%; (f) ethylenediamine, EtOH, 88%; (g) **18**, AcOH/pyridine (1/16, v/v), 98%; (h) K_2CO_3, NMP, 85% ; i) HNO_3, H_2SO_4, 60%.

Observation of anomeric triflates

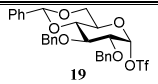
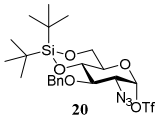
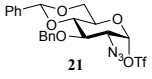
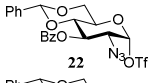
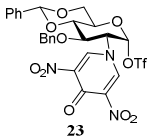
With these five donors in hand, we investigated the formation of potential covalent reactive intermediates in low-temperature NMR studies.[37] The donors were treated with the diphenyl sulfoxide/triflic anhydride (Ph_2SO/Tf_2O)[38] combination of reagents in deuterated dichloromethane. Figure 2 shows the results of these studies and Table 1 summarizes the anomeric chemical shifts of the observed triflates and the temperature at which decomposition starts (T_{decomp}) (See also SI). Activation of reference donor **1** led

to the formation of two species, beside the anomeric triflate **19**[9] also the oxosulfonium triflate **19α*** (6.68 ppm, 3.6 Hz) is formed as was confirmed by the activation of a sample containing additional Ph_2SO (See SI). Donors **2** and **3** are cleanly converted to their anomeric α-triflates **20** and **21** respectively by treatment with the activation couple at -80°C. Activation of donor **4** proceeded more slowly and raising the temperature from -80°C to -35°C was required for complete activation. Donor **5** proved difficult to study by low-temperature NMR due to significant line-broadening in the resonance sets for both the donor and the products formed upon activation. Complete activation of the thioglycoside could only be achieved at -40°C, but at this temperature decomposition of the reactive intermediates also sets in. Two anomeric signals can be discriminated in the spectrum of the activated DNPY donor **5** (Figure 2) and we assign these as the intermediate triflate (6.06 ppm) and oxosulfonium triflate (6.54 ppm). Unfortunately complete characterization is hampered by the severe line broadening.[39] The reactive intermediates formed all decomposed to give the glucal product **24**. The formation of the glucal double bond is relatively fast as the proton at C-2 is readily eliminated to provide the enol ether double bond that is conjugated to the DNPY aromatic ring.



24

Table 1: Anomeric triflates observed.

Entry	Triflate	^{1}H δ (ppm) $^3J_{H1\text{-}H2}$ [a]	^{13}C δ (ppm)	T_{decomp} (°C)
1	 **19**	6.09 3.4 Hz	106.1	-20
2	 **20**	6.00 3.4 Hz	104.8	-30
3	 **21**	6.07 3.5 Hz	105.0	-20
4	 **22**	6.23 3.5 Hz	104.5	-10
5	 **23**	6.06	102.2	-40

[a]values determined at -40°C

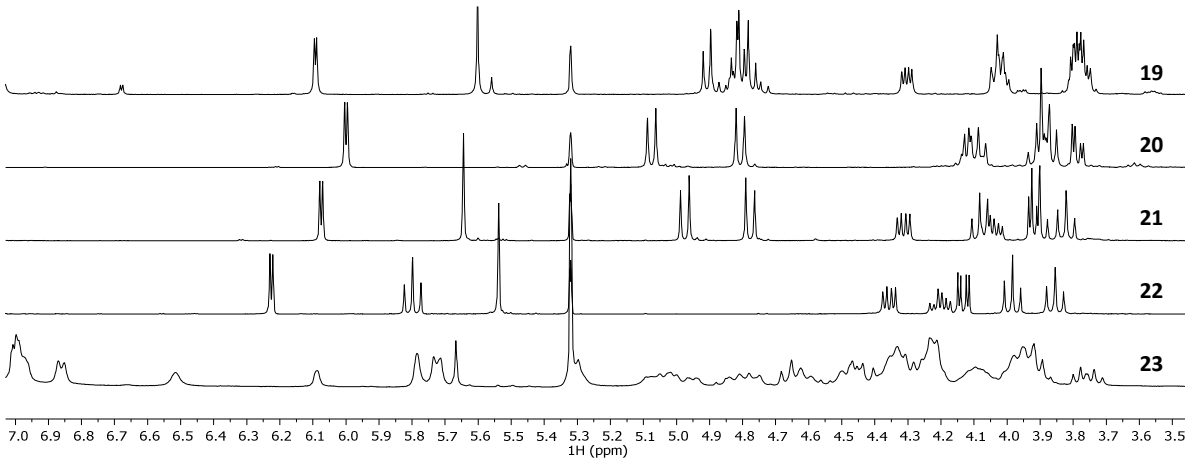
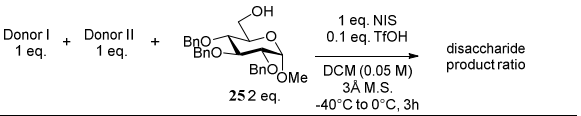


Figure 2: ^{1}H-NMR spectra of activated donors 1-5 showing their respective anomeric triflates 19-23.

Competitive glycosylations and relative reactivities.

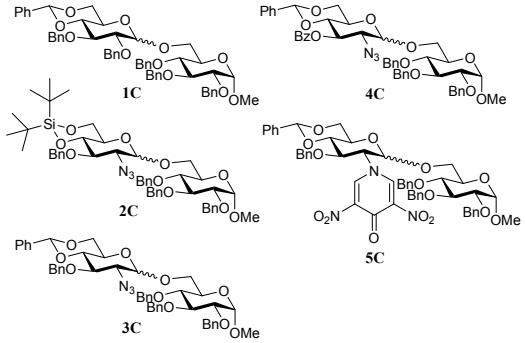
To investigate the reactivity of donors **1-5** a series of competitive glycosylations were performed between the different thioglycosides.[40–44] In these competition experiments we used an *in situ* activation protocol, employing NIS/TfOH as activator and 2,3,4-tri-*O*-benzyl-α-*O*-methyl glucose **25** as the acceptor, as is commonly done to determine the reactivity of thioglycoside donors.[45,46] It should be noted however that the reactivity of the thiophenyl donor does not directly compare with the reactivity of an intermediate triflate in the glycosylation, but it does give an indication of the relative disarming or arming nature of the protecting groups present on the different donors. It is apparent from Table 2 that the azide has a profound effect on the reactivity of donor **3** as it is completely outcompeted by the C-2-*O*-benzyl donor **1**.[46] Silylidene donor **2** is more reactive than donor **3**, and the disaccharide products derived from donor **2** and **3** are formed in a 6 : 1 ratio. C-3-*O*-benzyl donor **3** in turn outcompetes benzoylated donor **4** slightly, as a result of the electron withdrawing nature of the benzoate, giving a 1.6 : 1 ratio of the addition products **3C** and **4C**.[47–49] DNPY protected donor **5** is the least reactive of the set of donors as it does not provide any disaccharide product in the competition experiment with donor **4**.

Table 2: Competitive donor activations.



Entry	Donor I	Donor II	Products[a]	Yield[b]
1	**1**	**2**	**1C** : **2C**, 14 : 1	65 %
2	**1**	**3**	**1C** : **3C**, 1 : 0	80 %
3	**2**	**3**	**2C** : **3C**, 6 : 1	37 %
4	**3**	**4**	**3C** : **4C**, 1.6 : 1	39 %
5[c]	**4**	**5**	**4C** : **5C**, 1 : 0	64 %

[a]Determined by ^{1}H-NMR of the isolated disaccharide. [b]The disaccharide fraction was quantified after isolation by size-exclusion chromatography and related to the limiting amount of NIS (see experimental section). [c]Combined donor concentration 0.1 M, triflic acid was added at -20°C and the reaction heated to +15°C overnight, then quenched (Et_3N).

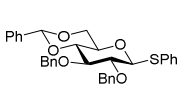
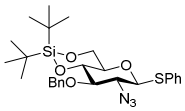
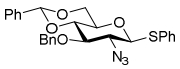
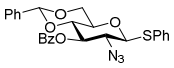
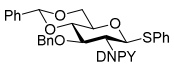
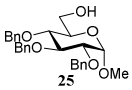
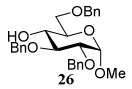
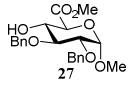
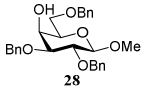
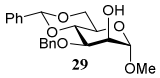


Glycosylations

With the reactivity of these five donors established the series of glycosylations with model acceptors **6-11** and carbohydrate acceptors **25-29**[50–52] was undertaken using the Ph_2SO/Tf_2O pre-activation procedure. Table 3 list all glycosylations ordered by acceptor and donor reactivity. A clear relation between acceptor nucleophilicity and stereochemical outcome of the glycosylation reactions of all studied glucosamine donors was observed, in line with the results previously obtained with donor **1**. When comparing the outcome of the coupling reactions of glucosazide **3** to the results obtained with C-2-*O*-benzyl donor **1** it becomes apparent that the latter donor reacts with higher α-selectivity. Donor **2**, bearing the DTBS group, overall provides slightly more of the α-linked products than its benzylidene counterpart **3**. The stereoselectivity of the condensations of donor **4**, bearing an additional electron withdrawing protecting group (*i.e.* the C-3-*O*-benzoyl) group is very similar to the stereoselectivity observed with C-3-*O*-benzyl donor **3**. Finally, donor **5**, carrying the strongly electron withdrawing DNPY group, is the most β-selective of the series of donors listed in Table 3.[53]

The selectivities of glycosylations with carbohydrate acceptors also proceed in a nucleophilicity-dependent fashion. The primary perbenzylated acceptor **25** reacts like ethanol **7** to give primarily the β-linked products for all glucosamine donors studied. Secondary carbohydrate acceptors that are less nucleophilic show variation in the selectivity with the proportion of α-product increasing with decreasing acceptor reactivity. In line with our previous studies the nucleophilicity of the secondary equatorial carbohydrate alcohols falls somewhere in between the reactivity of MFE and DFE, with the reactivity of the axial hydroxyls approaching the reactivity of TFE. The differences in the reactivity of the donors are reflected both in the stereoselectivity of the glycosylation that involve the model acceptors as well as the glycosylations with the carbohydrate acceptors. A recurring trend is apparent for all acceptors, with the most reactive donor **1** providing most and the least reactive donor **5** giving least α-linked product.

Table 3: Glycosylations of donors 1-5 with model acceptors 6-11 and carbohydrate acceptors 25-29.

		 **1** Product[a] α : β (yield)[b]	 **2** Product α : β (yield)	 **3** Product α : β (yield)	 **4** Product α : β (yield)	 **5** Product α : β (yield)
A	 **7**	**1A** 1 : 10 (68 %)	**2A** < 1 : 20 (65 %)	**3A** < 1 : 20 (83 %)	**4A** < 1 : 20 (86 %)	**5A** < 1 : 20 (59 %)
B	 **6**	**1B** 1 : 5.1 (71 %)	**2B** < 1 : 20 (77 %)	**3B** < 1 : 20 (93 %)	**4B** < 1 : 20 (91 %)	**5B** < 1 : 20 (63 %)
C	 **25**	**1C** 1 : 2.7 (81 %)	**2C** 1 : 14 (92 %)	**3C** < 1 : 20 (89 %)	**4C** 1 : 14 (79 %)	**5C** < 1 : 20 (57 %)
D	 **8**	**1D** 1 : 2.8 (70 %)	**2D** 1 : 5 (79 %)	**3D** 1 : 6.7 (90 %)	**4D** 1 : 6.5 (83 %)	**5D** < 1 : 20 (43 %)
E	 **26**	**1E** 1 : 1 (79 %)	**2E** 1 : 3 (81 %)	**3E** 1 : 7 (88 %)	**4E** 1 : 6 (71 %)	**5E** 1 : 20 (55 %)
F	 **27**	**1F** 5 : 1 (90 %)	**2F** 3.3 : 1 (84 %)	**3F** 1.1 : 1 (93 %)	**4F** 1 : 1.4 (59 %)	**5F** 1 : 3.6 (30 %)
G	 **9**	**1G** 5 : 1 (70 %)	**2G** 2.7 : 1 (76 %)	**3G** 2.9 : 1 (64 %)	**4G** 2.7 : 1 (84 %)	**5G** 1 : 1 (59 %)
H	 **28**	**1H** > 20 : 1 (83 %)	**2H** 7 : 1 (52 %)	**3H** 9 : 1 (75 %)	**4H** 4 : 1 (51 %)	**5H** < 1 : 20 (52 %)
I	 **29**	**1I** > 20 : 1 (80 %)	**2I** > 20 : 1 (85 %)	**3I** 9 : 1 (74 %)	**4I** 5 : 1 (73 %)	**5I** 1 : 1.3 (53 %)
J	 **10**	**1J** > 20 : 1 (64 %)	**2J** > 20 : 1 (82 %)	**3J** > 20 : 1 (94 %)	**4J** > 20 : 1 (86 %)	**5J** 4 : 1 (58 %)
K	 **11**	**1K** > 20 : 1 (65 %)	**2K** > 20 : 1 (34 %)	**3K** > 20 : 1 (53 %)	-[c]	32% **24**

[a]Glycosylation results of donor **1**, previously reported in van der Vorm *et al.*[22] [b]Ratio and yield of isolated product after column chromatography, anomers were not separated. [c]Only hydrolysed donor was found.

Mechanistic discussion

Two major trends become apparent from the table of glycosylations. First, with decreasing acceptor nucleophilicity the α/β-ratio increases; and second, decreasing donor reactivity corresponds with a decrease in the α/β-ratio. These trends have also come to the fore during our previous studies involving benzylidene glucose, mannose, mannuronic acid and fucosazide donors.[22,28] The reactive intermediates that can play a role in the glycosylations of the confromationally restricted glucosamine donors and the reaction trajectories of the incoming nucleophiles are presented in Figure 3. Previous studies by the group of Crich have indicated that substitutions on the benzylidene glucosyl triflate **19** proceed in an S_N2-like manner. In these mechanistic studies, that involved the determination of kinetic isotope effects and cation-clock methodology, *iso*-propanol was used as an acceptor.[12,14] In the kinetic scenario that was proposed the relatively stable α-trilfate (observed by low temperature NMR studies) is in equilibrium with its more reactive β-counterpart. In both species the triflate can be displaced by alcohols if they are nucleophilic enough. The higher β-selectivity that is seen for the glucosazide and DNPY-glucosamine donors in comparison to donor **1** can be accounted for by the stronger electron withdrawing effect of the azide with respect to the benzyl ether. This leads to a more stable covalent α-triflate and favors an associative displacement mechanism. A similar effect has been observed by the group of Crich in glycosylations of the analogous 2-deoxy-2-fluoro benzylidene glucosides.[54] The DNPY group is even more electron withdrawing, leading to a further increase of β-selectivity via associative displacement. However, an S_N2-like reaction pathway is less likely for

the weaker nucleophiles, such as TFE and HFIP. The high α-selectivity for these acceptors can be explained perhaps more precisely by considering the involvement of more electrophilic intermediates such as the glycosyl oxocarbenium ion. The benzylidene and silylidene protecting groups restrict the conformational space that the donor pyranosides can adopt and the intermediate oxocarbenium ion likely adopt a $^{3}E/^{3}H_{4}$–like conformation.[55,56] Nucleophiles attack this envelope/half chair conformer preferentially from the bottom face to lead to the α-linked prodcuts *via* a chair-like transition state.[57] The more reactive donors more readily dissociate to form an oxocarbenium ion and this accounts for the increased α-selectivity for these donors. Donor **2**, bearing the silylidene group is the most reactive of the studied glucosamine donors. It also is slightly more flexible than the benzylidene restricted donors and these two factors allow the activated donor to more readily form a flattened oxocarbenium ion-like intermediate. Consequently, it is the most α-selective of the studied glucosamine donors. Finally, it is notable that the C-3-*O*-benzoyl protected glucosazide **4** reacts in a slightly more β-selective fashion than its C-3-*O*-benzyl counterpart **3**. In light of the discussion above this makes sense as the electron withdrawing benzoyl stabilizes the anomeric α-triflate. It contrasts however with the behavior of acyl groups at the C-3 position of benzylidene mannosyl donors. The 1,2-*cis* selectivity generally observed for these donors can be completely changed to selectively give the α-linked products by installing a C-3-acyl group in the donor.[58,59] The difference between the benzylidene mannose and benzylidene glucose series may be found in the different geometries that the oxocarbenium ions adopts. For the benzylidene mannose system a $B_{2,5}$-like structure is one of the lower energy oxocarbenium ion conformers.[12,55,56] In this constellation, the C-3-benzoate can fold over to the electron depleted anomeric center to provide stabilization, without a major skeletal rearrangement. For the benzylidene glucose on the other hand, a $B_{2,5}$-like structure such as **32** is significantly less favorable because this puts the C-2-azide in a flag-pole position. Given the selectivities observed for this donor, influences arising from this boat conformation do not play a significant role here.

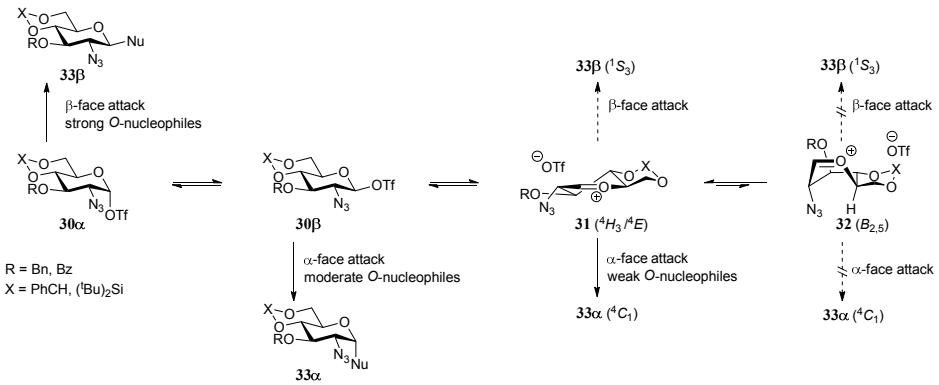


Figure 3: Reactive intermediates and reaction pathways for the 4,6-tethered glucosazide donors.

Conclusions

A set of model acceptors of gradually changing nucleophilicity has been used to investigate how the stereochemistry of glycosylations involving 4,6-tethered glucosamine donors relates to the nucleophilicity of the acceptor. The set of acceptors was complemented by a suite of carbohydrate alcohols to translate the results obtained with the model acceptors to a more relevant glycosylation setting. Four glucosamine donors were probed differing in the type of tether spanning the C-4 and C-6-alcohols, the nature of the protecting group at the C-3-OH and the amino functionality at C-2. Similar to the previously described benzylidene glucose donor **1**, the stereoselectivity of the studied glucosamine donors show a strong correlation to the nucleophilicity of the acceptor, with strong nucleophiles providing completely β-selective condensations and weak nucleophiles selectively leading to the formation of the α-linked products. Benzylidene glucosazide donors are less α-selective than their C-2-*O*-benzyl congeners, due to the increased electron withdrawal power of the azide, which retards the formation of an oxocarbenium ion species and favors a more associative mechanistic pathway. We have also introduced a novel protecting group for the C-2-amino group: the dinitropyridone functionality.[29,30,36] Although this group is easily installed and removed from the C-2-amine, its strongly electron withdrawing character limits its use. In the 4,6-benzylidene glucosamine donor studied here it disarms the donor glycoside to the extent that it turns into a suboptimal glycosyl donor. A major incentive for the reported study has been the good to excellent α-selectivity that has previously been reported for benzylidene glucose donor **1**. Unfortunately, installation of a 4,6-benzylidene on the analogous glucosazide donors does not provide a reliable donor to affect 1,2-*cis*-selective glycosylations. Only with relatively poor nucleophiles useful stereoselectivities are obtained. Changing the benzylidene for a silylidene group however turns the donor into a more reactive glycosylating agent showing improved α-selectivity. This donor, attractive because of its fully orthogonal protecting group scheme, may find application in the future assembly of oligosaccharides featuring α-glucosamines. Finally we note that this study provides another illustration of the application of the toolset of partially fluorinated ethanols to efficiently map the reactivity-selectivity relationship of a class of donor glycosides. Implementation of this methodology to investigate novel donor systems will broaden our insights into the different mechanistic pathways at play during glycosylations and eventually generate a complete picture how to tune both reaction partners to achieve stereoselective glycosylation reactions in a predictable manner.

Supporting Information

NMR spectra of all new compounds, decomposition study and identification of anomeric triflates by NMR, ^{1}H-NMR spectra of isolated disaccharide fractions of competition experiments.

Experimental Section

General experimental procedures: All chemicals were of commercial grade and used as received unless stated otherwise. DCM was stored over activated 4 Å molecular sieves for at least 24 h before use. Trifluoromethanesulfonic anhydride (Tf_2O) was distilled over P_2O_5 and stored at -20°C under an nitrogen atmosphere. Triethylamine (Et_3N) was distilled over CaH_2 and stored over KOH pellets. Overnight temperature control was achieved by a FT902 Immersion Cooler (Julabo). Flash column chromatography was performed on silica gel 60 Å (0.04 – 0.063 mm, Screening Devices B.V.). Size exclusion chromatography was performed on Sephadex™ (LH-20, GE Healthcare Life Sciences) by isocratic elution with DCM/MeOH (1/1, v/v). TLC-analysis was conducted on TLC Silica gel 60 (Kieselgel 60 F_{254}, Merck) with UV detection by (254 nm) and by spraying with 20% sulfuric acid in ethanol or by spraying with a solution of $(NH_4)_6Mo_7O_{24}\cdot H_2O$ (25 g/L) and $(NH_4)_4Ce(SO_4)_4\cdot{}_2H_2O$ (10 g/L) in 10% aq. sulfuric acid followed by charring at ±250 °C. High-resolution mass spectra (HRMS) were recorded on a Thermo Finnigan LTQ Orbitrap mass spectrometer equipped with an electrospray ion source in positive mode (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). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400, Bruker DMX-400, Bruker AV-500 NMR instrument. Chemical shifts (δ) are given in ppm relative to tetramethylsilane as internal standard or the residual signal of the deuterated solvent. Coupling constants (J) are given in Hz. All given ^{13}C-APT spectra are proton decoupled. NMR peak assignments were made using COSY and HSQC. If necessary additional NOESY, HMBC and HMBC-GATED experiments were used to further elucidate the structure. The anomeric product ratios were based on careful analysis of the crude reaction mixture and the purified reaction product by integration of representative ^{1}H NMR signals. IR spectra were recorded on a Shimadzu FTIR-8300 IR spectrometer and are reported in cm^{-1}. Specific rotations were measured on a Propol automatic polarimeter or an Anton-Paar MCP-100 modular circular polarimeter at 589 nm unless otherwise stated.

General procedure for Tf_2O/Ph_2SO mediated glycosylations: Donor (0.1 mmol), Ph_2SO (26 mg, 0.13 mmol, 1.3 eq.) and TTBP[60] (62 mg, 0.25 mmol, 2.5 eq.) were coevaporated twice with dry toluene and dissolved in dry DCM (2 mL, 0.05 M donor). Activated 3Å molecular sieves (rods, size 1/16 in.) were added and the reaction mixture stirred for 1 h at room temperature under a nitrogen atmosphere. The solution was cooled to -78°C and Tf_2O (22 µl, 0.13 mmol, 1.3 eq.) was added. The reaction mixture was allowed to warm to -60°C (donor **1**, **2**, **3**), -45°C (donor **5**), -35°C (donor **4**), followed by recooling to -78°C and addition of the acceptor (0.2 mmol, 2 eq.) in DCM (0.4 mL, 0.5 M). The reaction mixture was allowed to warm to -40°C in approximately 90 min and stirred for an additional 0-18 h depending on the acceptor. The reaction was quenched with Et_3N (0.1 mL, 0.72 mmol, 5.5 eq.) at -40 □C and diluted with DCM. The solution was transferred to a separatory funnel and water was added, the layers were separated and the water phase extracted once more with DCM. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by silica gel flash column chromatography and when needed, sephadex™ LH-20 size exclusion chromatography yielded the glycosylation product as a mixture of anomers.

General procedure for the NIS/TfOH mediated competition experiments: Donor I (0.1 mmol, 1 eq.), donor II (0.1 mmol, 1 eq.) and acceptor **25** (0.2 mmol, 2 eq.) were together coevaporated with dry toluene (2x). Dry DCM (4 mL, donor concentration 0.05 M), a Teflon stirring bar and 3Å activated molecular sieves (rods, size 1/16 in.) were added and the mixture was stirred under a nitrogen atmosphere for 1 h at room temperature. The mixture was cooled to -40°C and NIS (0.1 mmol, 1 eq.) was added. TfOH (50 µL of a freshly prepared 0.2 M stock solution in dry DCM, 0.1 eq.) was added and the mixture was allowed to warm to 0°C in 3 hours. Et_3N (0.1 mL) was added and the mixture was diluted with EtOAc, washed with sat. aq. NaS_2O_3 and brine, dried over Na_2SO_4 and concentrated *in vacuo*. Size exclusion chromatography (Sephadex™ LH-20, 1/1 DCM/MeOH) enabled isolation of the disaccharide products and the monosaccharide rests, which were both analysed with NMR spectroscopy. The yield of the disaccharide fraction was determined. For the competition between donors **4** and **5**, a 0.1 M concentration, and a starting temperature of -20°C was used, which was allowed to warm to +15°C in 18h.

General procedure for the low temperature NMR experiments: A mixture of donor (30 µmol) and Ph_2SO (39 µmol) was coevaporated with dry toluene twice (for the activation of donor 1 also TTBP (75 µmol) was added). Under a nitrogen atmosphere, CD_2Cl_2 (0.6 mL) was added and the mixture transferred to a nitrogen flushed NMR tube and closed with a NMR tube septum. The NMR magnet was cooled to -80°C, locked and shimmed and the sample was measure prior to activation. In a long narrow cold bath (EtOH, -85°C) the sample was treated with Tf_2O (39 µmol), shaken thrice and cooled again after every shake. The cold sample was wiped dry and quickly inserted back in the cold magnet. The first ^{1}H NMR spectrum was immediately recorded. The sample was then reshimmed and spectra were recorded in 10°C intervals with at least 5 min equilibration time for every temperature.

Phenyl 2-azido-4,6-*O*-benzylidene-2-deoxy-1-thio-β-D-glucopyranoside (13). To a suspension of thioglycoside **12**[33] (27.14 g, 50 mmol, 1 eq.) in EtOH (200 mL) was added K_2CO_3 (41.5 g, 300 mmol, 6 eq), and 20 mL H_2O and the mixture was refluxed overnight. The flask was cooled to r.t. and to the crude free amine[61] was added the diazo transfer reagent imidazole-1-sulfonyl azide hydrochloride[34] (13.10 g, 62.5 mmol, 1.25 eq.) in 3 equal portions followed by a catalytic amount of $CuSO_4$•5 H_2O (125 mg, 0.5 mmol, 0.01 eq.). After stirring for 5 hours, the solution was filtered and reduced to 1/4 of its volume *in vacuo*. H_2O (150 mL) and 1 M aq. HCl (150 mL) were added to obtain an acidic (pH ≈ 3) solution which was extracted with EtOAc (3x 120 mL). The combined organic layers were washed with sat. aq. $NaHCO_3$ (150 mL) and brine (150 mL), dried with $MgSO_4$ and concentrated *in vacuo* to obtain crude azide; phenyl 2-azido-2-deoxy-1-thio-β-D-glucopyranoside.[62] The crude azide (≤50 mmol) was coevaporated with toluene twice and subsequently dissolved in DMF (50 mL) and MeCN (200 mL) to which benzaldehyde dimethyl acetal (15 mL, 100 mmol, 2 eq.) and *p*-TsOH•H_2O (950 mg, 5 mmol, 0.1 eq.) were added. The reaction mixture was heated at 60°C overnight, followed by an additional 5 hours of heating at 60°C under reduced pressure (300 mbar) to reduce the volume to 1/3. The reaction was quench by the addition of triethylamine (1 mL), and diluted with EtOAc (350 mL), washed with H_2O (2x 100 mL), sat. aq. $NaHCO_3$ (1x 100 mL), and brine (1x 100 mL). The organic layer was dried ($MgSO_4$) and concentrated *in vacuo.* The crude mixture was purified by percipitation from hot EtOAc (100 mL) / heptane (300 mL) by adding petroleum ether (500 mL) while stirring and slowly cooling to 0°C to obtain the title compound as a white powder (11.38 g, 29.5 mmol, 59%). The mother liquors were purified by flash column chromatography (8/1 to 4/1 pentane/EtOAc) to obtain an additional batch of white solid product (3.8 g, 9.6 mmol, total yield = 39.1 mmol, 78%, 3 steps). A purified sample could be recrystallized from either hot MeOH or EtOAc/petroleum ether to obtain white cotton like needles. R_f: 0.50 (6/1 pentane/EtOAc). Spectroscopic data were in accord with those previously reported.[31] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.64 – 7.52 (m, 2H, CH_{arom}), 7.50 – 7.43 (m, 2H, CH_{arom}), 7.42 – 7.32 (m, 6H, CH_{arom}), 5.53 (s, 1H, C*H*Ph), 4.54 (d, 1H, J = 10.1 Hz, H-1), 4.38 (dd, 1H, J = 10.5, 4.6 Hz, H-6), 3.85 – 3.70 (m, 2H, H-3, H-6), 3.52 – 3.40 (m, 2H, H-4, H-5), 3.35 (dd, 1H, J = 10.2, 9.0 Hz, H-6), 2.75 (bs, 1H, 3-OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 136.8 (C_q CHPh), 133.8 (CH_{arom}), 130.9 (C_q SPh), 129.6, 129.3, 128.8, 128.5, 126.4 (CH_{arom}), 102.1 (CHPh), 86.9 (C-1), 80.3 (C-4), 74.2 (C-3), 70.4 (C-5), 68.5 (C-6), 65.2 (C-2); HRMS: $[M+H]^+$ calcd for $C_{19}H_{20}N_3O_4S$ 386.11690, found 386.11708.

Phenyl 2-azido-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-1-thio-β-D-glucopyranoside (14). Crude triol phenyl 2-azido-2-deoxy-1-thio-β-D-glucopyranoside (synthesized as described for compound **13**) (≤10 mmol) was dissolved in pyridine (15 mL) and cooled to 0°C. Di-*tert*-butylsilyl bis(trifluoromethanesulfonate) (3.6 mL, 11 mmol, 1.1 eq.) was slowly added and the reaction was stirred for 1 h before being quenched with MeOH. The reaction mixture was diluted with 200 mL Et_2O and washed with 1M aq. HCl (3x 60 mL), sat. aq. $NaHCO_3$ (60 mL), and brine (60 mL). The organic layer was dried with Na_2SO_4, filtered and concentrated in vacuo. Purification by flash column chromatography (1-10% Et_2O/pentane) afforded the silylidene protected title compound as a colorless oil (3.10 g, 7.1 mmol, 71% over three steps). R_f: 0.18 (19/1 pentane/Et_2O). $[\alpha]_D^{23}$ = -42.6° (c = 1.0, $CHCl_3$); IR (neat): 652, 733, 824, 1072, 1092, 1155, 1277, 1474, 2112, 2859, 2884, 2934, 2963, 3449; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC) δ 7.57 – 7.51 (m, 2H, CHarom), 7.36 – 7.31 (m, 3H, CHarom), 4.49 (d, 1H, J = 10.2 Hz, H-1), 4.21 (dd, 1H, J = 10.2, 5.1 Hz, H-6), 3.89 (t, 1H, J = 10.2 Hz, H-6), 3.64 (t, 1H, J = 9.1 Hz, H-4), 3.56 (td, 1H, J = 9.0, 1.2 Hz, H-3), 3.40 (ddd, 1H, J = 10.1, 9.3, 5.1 Hz, H-5), 3.31 (dd, 1H, J = 10.2, 9.1 Hz, H-2), 2.92 (d, 1H, J = 1.6 Hz, 3-OH), 1.04 (s, 9H, CH_3 ^{t}Bu), 0.97 (s, 9H, CH_3 ^{t}Bu); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 133.7 (CH_{arom}), 131.2 (C_q), 129.2, 128.7 (CH_{arom}), 86.8 (C-1), 77.4 (C-3), 76.6 (C-4), 74.4 (C-5), 66.0 (C-6), 64.4 (C-2), 27.5, 27.0 (CH_3 ^{t}Bu), 22.8, 20.0 (C_q ^{t}Bu); HRMS: $[M-N_2+H]^+$ calcd for $C_{20}H_{32}NO_4SSi$ 410.18213, found 410.18220.

Phenyl 2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-1-thio-β-D-glucopyranoside (2). Compound **14** (1.4 g, 3.2 mmol) was dissolved in DMF (15 mL) and cooled to 0°C. Benzyl bromide (421 µL, 3.52 mmol, 1.1 eq.) and NaH (60% dispersion in mineral oil, 166 mg, 4.16 mmol, 1.3 eq.) were added and the reaction was stirred for 2 h at 0°C and 1 h at r.t. The reaction mixture was quenched with MeOH and H_2O (100 mL) was added. The water phase was extracted three times with 30 mL Et_2O and the combined organic layers were washed with brine (2x), dried with Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography (1%-8% Et_2O/pentane) yielded compound **2** as a colorless oil (1.35 g, 2.56 mmol, 80%). Additional impurities as observed by ^{1}H NMR originating from the previous crude steps could be removed by size exclusion chromatography (Sephadex™ LH-20, 1/1 DCM/MeOH). R_f: 0.51 (19/1 pentane/Et_2O). $[\alpha]_D^{23}$ = -85.0°

(c = 1.0, $CHCl_3$); IR (neat): 654, 694, 746, 766, 826, 1059, 1078, 1099, 1159, 1474, 2110, 2859, 2884, 2934, 2963; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.55 – 7.48 (m, 2H, CHarom), 7.43 – 7.37 (m, 2H, CHarom), 7.36 – 7.27 (m, 6H, CHarom), 4.99 (d, 1H, J = 10.7 Hz, C*H*H Bn), 4.81 (d, 1H, J = 10.7 Hz, CH*H* Bn), 4.41 (d, 1H, J = 10.2 Hz, H-1), 4.21 (dd, 1H, J = 10.3, 5.1 Hz, H-6), 3.90 (t, 1H, J = 10.2 Hz, H-6), 3.87 (dd, 1H, J = 9.5, 8.7 Hz, H-4), 3.48 – 3.38 (m, 2H, H-3, H-5), 3.28 (dd, 1H, J = 10.2, 9.2 Hz, H-2), 1.07 (s, 9H, CH_3 ^{t}Bu), 1.01 (s, 9H, CH_3 ^{t}Bu); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.9 (C_q Bn), 133.9 (CH_{arom}), 130.9 (C_q SPh), 129.1, 128.7, 128.5, 128.5, 128.1 (CH_{arom}), 86.4 (C-1), 84.2 (C-3), 77.8 (C-4), 75.7 (CH_2 Bn), 74.7 (C-5), 66.2 (C-6), 64.2 (C-2), 27.5, 27.1 (CH_3 ^{t}Bu), 22.7, 20.0 (CH_3 ^{t}Bu); HRMS: $[M+H]^+$ calcd for $C_{27}H_{38}N_3O_4SSi$ 528.23468, found 528.23451. and $[M-N_2+H]^+$ calcd for $C_{27}H_{38}NO_4SSi$ 500.22853, found 500.22839.

Phenyl 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-1-thio-β-D-glucopyranoside (3). Compound **13** (4.36 g, 11.3 mmol) was coevaporated once with dry toluene and then dissolved in DMF (50 mL) and cooled to 0°C. Benzyl bromide (1.9 mL, 15.8 mmol, 1.4 eq.) and NaH (60% dispersion in mineral oil, 900 mg, 22.6 mmol, 2 eq.) were added in succession and the reaction mixture was stirred at r.t. for 4.5 h. MeOH (5 mL) was slowly added and the reaction mixture was diluted with EtOAc (150 mL) and washed with H_2O (2x 60 mL) and brine (50 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude product was purified by crystallization (10 mL hot EtOAc, addition of 100 mL petroleum ether) to yield the title compound as a white cotton like solid (4.79 g, 10.1 mmol, 89%). R_f: 0.71 (8/1 pentane/EtOAc). Spectroscopic data were in accord with those previously reported.[31] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.56 (ddt, 2H, J = 5.0, 3.4, 1.5 Hz, CH_{arom}), 7.47 (dd, 2H, J = 7.5, 2.3 Hz, CH_{arom}), 7.42 – 7.26 (m, 11H, CH_{arom}), 5.57 (s, 1H, C*H*Ph), 4.91 (d, 1H, J = 10.9 Hz, C*H*H Bn), 4.78 (d, 1H, J = 10.9 Hz, CH*H* Bn), 4.49 (d, 1H, J = 10.2 Hz, H-1), 4.39 (dd, 1H, J = 10.6, 5.0 Hz, H-6), 3.79 (t, 1H, J = 10.3 Hz, H-6), 3.71 – 3.59 (m, 2H, H-3, H-4), 3.52 – 3.42 (m, 1H, H-5), 3.41 – 3.32 (m, 1H, H-2); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.6, 137.1 (C_q), 134.0 (CH_{arom}), 130.6 (C_q SPh), 129.2, 129.2, 128.8, 128.5, 128.4, 128.4, 128.1, 126.0 (CH_{arom}), 101.3 (CHPh), 86.5 (C-1), 81.3, 81.0 (C-3, C-4), 75.3 (CH_2 Bn), 70.5 (C-5), 68.5 (C-6), 64.6 (C-2); HRMS: $[M+H]^+$ calcd for $C_{26}H_{26}N_3O_4S$ 476.16385, found 476.16375.

Phenyl 2-azido-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-1-thio-β-D-glucopyranoside (4). To a 0°C solution of compound **13** (1.34 g, 3.48 mmol) in DCM (17 mL) and pyridine (1.4 mL, 34.8 mmol, 5 eq.) was added benzoyl chloride (0.61 mL, 5.22 mmol, 1.5 eq.) and DMAP (42 mg, 0.35 mmol, 0.1 eq.). The reaction mixture was allowed to stir overnight after which H_2O and DCM were added. The organic layer was separated and washed with sat. aq. $NaHCO_3$ and brine. The organic layer was dried with $MgSO_4$ and concentrated *in vacuo*. Flash column chromatography (19/1 to 8/1 pentane/EtOAc) afforded the title compound as a white solid (1.54 g, 3.15 mmol, 90%). The product could be recrystallized from EtOAc and petroleum ether to obtain a fluffy white solid. R_f: 0.53 (8/1 pentane/EtOAc). Spectroscopic data were in accord with those previously reported.[63] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.05 (d, 2H, J = 7.3 Hz, CH_{arom}), 7.59 (dd, 2H, J = 6.5, 3.1 Hz, CH_{arom}), 7.53 (t, 1H, J = 7.4 Hz, CH_{arom}), 7.44 – 7.33 (m, 7H, CH_{arom}), 7.29 – 7.23 (m, 3H, CH_{arom}), 5.52 (t, 1H, J = 9.6 Hz, H-3), 5.46 (s, 1H, C*H*Ph), 4.69 (d, 1H, J = 10.1 Hz, H-1), 4.38 (dd, 1H, J = 10.5, 4.9 Hz, H-6), 3.79 (t, 1H, J = 10.2 Hz, H-6), 3.71 (t, 1H, J = 9.5 Hz, H-4), 3.62 – 3.53 (m, 2H, H-2, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 165.3 (C=O Bz), 136.7 (C_q), 133.7, 133.4 (CH_{arom}), 130.8 (C_q), 129.9, 129.3 (CH_{arom}), 129.2 (C_q), 129.1, 128.8, 128.5, 128.2, 126.1 (CH_{arom}), 101.3 (CHPh), 87.1 (C-1), 78.4 (C-4), 73.5 (C-3), 70.7 (C-5), 68.3 (C-6), 63.9 (C-2); HRMS: $[M+H]^+$ calcd for $C_{26}H_{24}N_3O_5S$ 490.14312, found 490.14305.

Phenyl 2-amino-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-1-thio-β-D-glucopyranoside (16). Fully protected glycoside **15**[35] (9.11 g, 15.7 mmol) was dissolved in 160 ml EtOH and heated to reflux upon which ethylene diamine (52 mL, 785 mmol, 50 eq.) was added in three portions and reflux was maintained overnight. The reaction mixture was concentrated under reduced pressure and mixed with toluene (100 mL) and 45 g of silica gel, and the mixture evaporated to dryness. Column chromatography (8/2 to 2/1 pentane/EtOAc) gave the free amine as a white solid (6.19 g, 13.76 mmol, 88%) which could be recrystallized in EtOAc/petroleum ether. R_f: 0.40 (2/1 pentane/EtOAc). m.p. 136.1-137.5 °C. $[\alpha]_D^{20}$ = -33.5° (c = 0.57, $CHCl_3$); IR (thin film): 698, 748, 1026, 1069, 1123, 1371, 1452, 1583, 2870, 3030, 3059; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.56 – 7.44 (m, 4H, CH_{arom}), 7.42 – 7.24 (m, 11H, CH_{arom}), 5.59 (s, 1H, C*H*Ph), 4.99 (d, 1H, J = 11.3 Hz, C*H*H Bn), 4.68 (d, 1H, J = 11.2 Hz, CH*H* Bn), 4.58 (d, 1H, J = 9.9 Hz, H-1), 4.38 (dd, 1H, J = 10.5, 5.0 Hz, H-6), 3.81 (t, 1H, J = 10.3 Hz, H-6), 3.72 (t, 1H, J = 9.2 Hz, H-4), 3.59 (t, 1H, J = 9.0 Hz, H-3), 3.52 (td, 1H, J = 9.7, 4.9 Hz, H-5), 2.91 (t, 1H, J = 9.4 Hz, H-2), 1.75 (bs, 2H, NH_2); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.2, 137.4 (C_q), 133.0 (CH_{arom}), 131.8 (C_q SPh), 129.1, 128.6, 128.4, 128.3, 128.3, 128.0, 126.0 (CH_{arom}), 101.3 (CHPh), 89.6 (C-1), 82.2, 82.2 (C3, C-4), 75.1 (CH_2 Bn), 70.7 (C-5), 68.8 (C-6), 55.5 (C-2); HRMS: $[M+H]^+$ calcd for $C_{26}H_{28}NO_4S$ 450.17336, found 450.17238.

1-(4-nitrophenyl)-4-pyridone (17). Following the procedure of You and Twieg[64] 4-hydroxypyridine (14.3 g, 150 mmol), 4-chloronitrobenzene (22.9 g, 145 mmol) and K_2CO_3 (20.7 g, 150 mmol) were suspended in *N*-methyl-2-pyrrolidone (110 mL) and heated at 150°C for 2 h. The hot solution was then poured directly onto ice and allowed to precipitate until all the ice had melted. The suspension was then filtered and washed four times with cold H_2O. The resulting solid was dried under vacuum at 100°C until dry. Yield: 26.6 g, 123 mmol, 85%. IR (neat): 606, 692, 741, 752, 843, 1015, 1111, 1198, 1285, 1339, 1495, 1514, 1582, 1638, 3071; ^{1}H NMR (DMSO, 400 MHz, HH-COSY, HSQC): δ 8.38 (d, 2H, J = 9.1 Hz), 8.14 (d, 2H, J = 7.8 Hz), 7.86 (d, 2H, J = 9.1 Hz), 6.29 (d, 2H, J = 7.8 Hz); ^{13}C-APT NMR (DMSO, 101 MHz, HSQC): δ 177.6, 147.1, 145.9, 139.2, 125.3, 123.2, 118.3; HRMS: $[M+H]^+$ calcd for $C_{11}H_9N_2O_3$ 217.06077, found 217.06074.

3,5-dinitro-1-(4-nitrophenyl)-4-pyridone (18). Modification of the procedure from Matsumura *et al*.[30], an ice cooled three-neck flask equipped with a condenser was charged with 120 mL H_2SO_4 (30% SO_3) followed by the slow addition of 120 mL fuming 99% HNO_3. To the cold mixture pyridone **17** (21.6 g, 100 mmol) was added in small portions. When addition was complete the mixture was slowly brought to 130°C and stirred for 40 h. The cooled down mixture was then poured over ice, stirred for 3 h, filtered, and washed three times with cold water. Yield: 18.4 g, 60 mmol, 60%. Purity (NMR): 90%. Tetra-nitro (3,5-dinitro-1-(2,4-dinitrophenyl)-4-pyridone ^{1}H NMR (DMSO, 400 MHz): δ 9.42 (s, 2H), 9.05 (d, 1H, J = 2.6 Hz), 8.87 (dd, 1H, J = 8.8, 2.6 Hz), 8.32 (d, 1H, J = 8.7 Hz)) and di-nitro (3-nitro-1-(4-nitrophenyl)-4-pyridone ^{1}H NMR (DMSO, 400 MHz): δ 9.18 (d, 1H, J = 2.5 Hz), 8.43 (d, 2H, J = 9.0 Hz), 8.26 (dd, 1H, J = 7.8, 2.5 Hz), 7.99 (d, 2H, J = 9.1 Hz), 6.68 (d, 1H, J = 7.9 Hz)) impurities are present (ratios vary slightly upon repetition). IR (neat): 717, 768, 789, 853, 910, 1141, 1261, 1306, 1350, 1449, 1514, 1591, 1672, 3076; ^{1}H NMR (DMSO, 400 MHz): δ 9.38 (s, 1H), 8.47 (d, 1H, J = 9.0 Hz), 8.05 (d, 1H, J = 9.1 Hz); ^{13}C-APT NMR (DMSO, 101 MHz): δ 159.3, 147.6, 145.5, 142.1, 141.6, 125.7, 125.1; HRMS: $[M+H]^+$ calcd for $C_{11}H_7N_4O_7$ 307.03093, found 307.03123.

Phenyl 2-(3,5-dinitro-4-pyridone)-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-1-thio-β-D-glucopyranoside (5). Free amine **16** (3.6 g, 8 mmol) and reagent **18** (2.7 g, 8.8 mmol, 1.1 eq.) were dissolved in pyridine (48 mL) and AcOH (4 mL) and left to stir for 30 min. The mixture was diluted with EtOAc and washed with 1M aq. HCl (5x) and once with sat.aq. $NaHCO_3$. The organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. Column chromatography: DCM until all the nitroanaline had been removed, then 1% to 5% acetone in DCM. Yield 4.84 g, 7.8 mmol (98%) as a yellow solid. R_f: 0.21 (DCM), $[\alpha]_D^{20}$ = 10.5° (c = 0.5, $CHCl_3$); IR (thin film): 604, 696, 746, 989, 1055, 1094, 1211, 1300, 1329, 1516, 1674, 2856, 2926, 3034, 3059; ^{1}H NMR (Acetone-d_6, 400 MHz, HH-COSY, HSQC): δ 8.74 (s, 2H, CH pyridone), 7.63 – 7.54 (m, 2H, CH_{arom}), 7.51 – 7.39 (m, 5H, CH_{arom}), 7.39 – 7.31 (m, 3H, CH_{arom}), 7.21 – 7.14 (m, 3H, CH_{arom}), 7.14 – 7.07 (m, 2H, CH_{arom}), 5.84 (s, 1H, C*H*Ph), 5.73 (d, 1H, J = 10.4 Hz, H-1), 4.84 (d, 1H, J = 12.1 Hz, C*H*H Bn), 4.62 (d, 1H, J = 12.1 Hz, CH*H* Bn), 4.55 – 4.47 (m, 1H, H-3), 4.44 – 4.39 (m, 1H, H-6), 4.39 (t, 1H, J = 8.9 Hz, H-2), 4.06 – 3.91 (m, 3H, H-4, H-5, H-6); ^{13}C-APT NMR (Acetone-d_6, 101 MHz, HSQC): δ 159.9 (C=O pyridone), 143.1 (C_q NO_2), 138.5, 137.8 (C_q), 133.4 (CH_{arom}), 131.7 (C_q SPh), 130.3, 129.7, 129.5, 129.2, 129.0, 129.0, 127.0 (CH_{arom}), 102.0 (CHPh), 85.9 (C-1), 83.0 (C-4), 77.0 (C-3), 74.7 (CH_2 Bn), 71.6 (C-2), 70.9 (C-5), 68.8 (C-6); HRMS: $[M+H]^+$ calcd for $C_{31}H_{28}N_3O_9S$ 618.15408 found 618.15375.

Trifluoromethanesulfonyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (19).[9] ^{1}H NMR (CD_2Cl_2, T = 213 K, 400 MHz, HH-COSY, HSQC): δ 6.08 (d, 1H, J = 3.5 Hz, H-1), 5.59 (s, 1H, C*H*Ph), 4.89 (d, 1H, J = 11.0 Hz, C*H*H Bn), 4.85 – 4.69 (m, 3H, CH*H* Bn, CH_2 Bn), 4.29 (dd, 1H, J = 10.3, 4.8 Hz, H-6), 4.09 – 3.94 (m, 2H, H-3, H-5), 3.86 – 3.70 (m, 3H, H-2, H-4, H-6); ^{13}C-APT NMR (CD_2Cl_2, T = 213 K, 101 MHz, HSQC): δ 106.1 (C-1), 100.8 (CHPh), 79.6 (C-4), 77.0 (C-3), 76.3 (C-2), 75.0, 74.1 (CH_2 Bn), 67.4 (C-6), 65.8 (C-5).

Trifluoromethanesulfonyl 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (20). ^{1}H NMR (CD_2Cl_2, T = 243 K, 400 MHz, HH-COSY, HSQC): δ 6.08 (d, 1H, J = 3.5 Hz, H-1), 5.64 (s, 1H, C*H*Ph), 4.98 (d, 1H, J = 10.6 Hz, C*H*H Bn), 4.78 (d, 1H, J = 10.6 Hz, CH*H* Bn), 4.32 (dd, 1H, J = 10.4, 4.9 Hz, H-6), 4.11 – 4.00 (m, 2H, H-3, H-5), 3.94 – 3.86 (m, 2H, H-2, H-4), 3.82 (t, 1H, J = 10.3 Hz, H-6); ^{13}C-APT NMR (CD_2Cl_2, T = 243 K, 101 MHz, HSQC): δ 137.2, 136.7 (C_q), 130.5, 128.4, 128.4, 125.9 (CH_{arom}), 105.0 (C-1), 101.3 (CHPh), 80.6 (C-4), 76.4 (C-3), 75.3 (CH_2 Bn), 67.6 (C-6), 66.2 (C-5), 61.4 (C-2).

Trifluoromethanesulfonyl 2-azido-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (21). ^{1}H NMR (CD_2Cl_2, T = 243 K , 400 MHz, HH-COSY, HSQC): δ 6.23 (d, 1H, J = 3.5 Hz, H-1), 5.80 (t, 1H, J = 10.0 Hz, H-3), 5.54 (s, 1H, C*H*Ph), 4.36 (dd, 1H, J = 10.4, 4.9 Hz, H-6), 4.21 (td, 1H, J = 9.9, 4.9 Hz, H-5), 4.12 (dd, 1H, J = 10.2, 3.5 Hz, H-2), 3.98 (t, 1H, J = 9.8 Hz, H-4), 3.86 (t, 1H, J = 10.3 Hz, H-6); ^{13}C-APT NMR (CD_2Cl_2, T = 243 K, 101 MHz, HSQC): δ 104.5 (C-1), 101.8 (CHPh), 77.5 (C-4), 69.3 (C-3), 67.6 (C-6), 66.4 (C-5), 60.9 (C-2).

Trifluoromethanesulfonyl 2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-α-D-glucopyranoside (22). ^{1}H NMR (CD_2Cl_2, T = 233 K, 400 MHz, HH-COSY, HSQC, HMBC): δ 6.00 (d, 1H, J = 3.4 Hz, H-1), 5.08 (d, 1H, J = 10.1 Hz, C*H*H Bn), 4.81 (d, 1H, J = 10.2 Hz, CH*H* Bn), 4.15 – 4.06 (m, 2H, H-4, H-6), 3.95 – 3.84 (m, 3H, H-3, H-5, H-6), 3.79 (dd, 1H, J = 10.1, 3.4 Hz, H-2), 1.07 (s, 9H, CH_3 ^{t}Bu), 1.00 (s, 9H, CH_3 ^{t}Bu); ^{13}C-APT NMR (CD_2Cl_2, T = 233 K, 101 MHz, HSQC, HMBC): δ 118.9 (q, J = 317.6 Hz, CF_3), 104.8 (C-1), 78.8 (C-3), 76.9 (C-4), 75.7 (CH_2 Bn), 70.0 (C-5), 65.3 (C-6), 60.6 (C-2), 27.0, 26.4 (CH_3 ^{t}Bu), 22.5, 19.7 (C_q ^{t}Bu); ^{13}C-HMBC NMR (CD_2Cl_2, 101 MHz): δ 104.8 ($J_{C1\text{-}H1}$ = 187 Hz, C-1).

3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)-D-glucal (24). Off-white solid. R_f: 0.20 (7/3 pentane/EtOAc). $[\alpha]_D^{23}$ = +85.9° (*c* = 0.32, DCM); IR (thin film): 698, 720, 753, 1007, 1059, 1095, 1192, 1247, 1304, 1351, 1516, 1679, 2880, 2924, 3072; ^{1}H NMR (Acetone-d_6, 500 MHz, HH-COSY, HSQC): δ 8.72 (s, 2H, CH pyridone), 7.62 – 7.53 (m, 2H, CH_{arom}), 7.49 – 7.37 (m, 4H, CH_{arom}, H-1), 7.29 – 7.14 (m, 5H, CH_{arom}), 5.88 (s, 1H, C*H*Ph), 4.93 – 4.88 (m, 2H, C*H*H Bn, H-3), 4.68 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.46 (dd, 1H, *J* = 10.5, 5.2 Hz, H-6), 4.37 (dd, 1H, *J* = 10.4, 6.9 Hz, H-4), 4.30 (td, 1H, *J* = 10.2, 5.1 Hz, H-5), 4.03 (t, 1H, *J* = 10.3 Hz, H-6); ^{13}C-APT NMR (Acetone-d_6, 101 MHz, HSQC): δ 160.0 (C=O pyridone), 149.3 (C-1), 144.7 (CH pyridone), 142.8 (C_q NO_2), 138.4 (C_q Bn, Ph), 129.8, 129.2, 129.1, 129.0, 128.8, 127.0 (CH_{arom}), 122.1 (C-2), 101.9 (CHPh), 80.2 (C-4), 74.7 (CH_2 Bn), 74.6 (C-3), 70.7 (C-5), 68.2 (C-6); HRMS: $[M+H]^+$ calcd for $C_{25}H_{22}N_3O_9$ 508.13506, found 508.13465.

Ethyl 2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-β-D-glucopyranoside (2A). Donor **2** and ethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations and purified by flash column chromatography (0% to 5% Et_2O in pentane) to yield glycosylation product **2A** (30 mg, 65 µmol, 65%, α:β = < 1:20) as a colorless oil. R_f: 0.35 (5% Et_2O in pentane). $[\alpha]_D^{23}$ = -69.6° (*c* = 0.5, $CHCl_3$); IR (neat): 652, 768, 827, 962, 1082, 1161, 1474, 2112, 2859, 2932; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.46 – 7.40 (m, 2H, CH_{arom}), 7.39 – 7.27 (m, 3H, CH_{arom}), 4.99 (d, 1H, *J* = 11.0 Hz, C*H*H Bn), 4.81 (d, 1H, *J* = 10.9 Hz, CH*H* Bn), 4.31 (dd, 1H, *J* = 7.7, 1.7 Hz, H-1), 4.16 (dd, 1H, *J* = 10.3, 5.0 Hz, H-6), 3.98 – 3.87 (m, 3H, C*H*H-CH_3 Et, H-4, H-6), 3.61 (dq, 1H, *J* = 9.5, 7.1 Hz, CH*H*-CH_3 Et), 3.41 – 3.28 (m, 3H, H-2, H-3, H-5), 1.26 (t, 3H, *J* = 7.1 Hz, CH_3 Et), 1.08 (s, 9H, CH_3 ^{t}Bu), 1.01 (s, 9H, CH_3 ^{t}Bu); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.3 (C_q), 128.5, 128.4, 128.0 (CH_{arom}), 102.1 (C-1), 82.4 (C-3), 78.1 (C-4), 75.4 (CH_2 Bn), 70.5 (C-5), 66.4 (C-6), 66.1 (CH_2 Et), 65.6 (C-2), 27.6, 27.2 (CH_3 ^{t}Bu), 22.8, 20.1 (C_q ^{t}Bu), 15.2 (CH_3 Et); HRMS: $[M-N_2+H]^+$ calcd for $C_{23}H_{38}NO_5Si$ 436.25138, found 436.25132.

Cyclohexyl 2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-β-D-glucopyranoside (2B). Donor **2** and cyclohexanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations and purified by flash column chromatography (4/1 to 0/1 pentane/toluene) to yield glycosylation product **2B** (40 mg, 77 µmol, 77%, α:β = < 1 : 20) as a colorless oil. R_f: 0.43 (5% Et_2O in pentane). $[\alpha]_D^{20}$ = -44.3° (*c* = 1.0, $CHCl_3$); IR (thin film): 696, 768, 827, 961, 1080, 1163, 1364, 2112, 2859, 2934; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.45 – 7.40 (m, 2H, CH_{arom}), 7.38 – 7.27 (m, 3H, CH_{arom}), 4.97 (d, 1H, *J* = 11.1 Hz, C*H*H Bn), 4.81 (d, 1H, *J* = 11.1 Hz, CH*H* Bn), 4.42 (d, 1H, *J* = 7.8 Hz, H-1), 4.15 (dd, 1H, *J* = 10.3, 5.0 Hz, H-6), 3.99 – 3.89 (m, 2H, H-3, H-6), 3.64 (tt, 2H, *J* = 9.2, 3.8 Hz, CH Cy), 3.40 – 3.24 (m, 3H, H-2, H-4, H-5), 1.96 – 1.83 (m, 2H, CH_2 Cy), 1.80 – 1.71 (m, 2H, CH_2 Cy), 1.55 – 1.48 (m, 1H, CH_2 Cy), 1.47 – 1.37 (m, 2H, CH_2 Cy), 1.34 – 1.20 (m, 3H, CH_2 Cy), 1.08 (s, 9H, ^{t}Bu), 1.01 (s, 9H, ^{t}Bu); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.4 (C_q), 128.5, 128.3, 127.9 (CH_{arom}), 100.7 (C-1), 82.3 (C-4), 78.3 (CH Cy), 78.0 (C-3), 75.4 (CH_2 Bn), 70.5 (C-5), 66.4 (C-6), 65.8 (C-2), 33.6, 31.7 (CH_2 Cy), 27.6, 27.2 (CH_3 ^{t}Bu), 25.6 (CH_2 Cy), 24.1, 23.9 (Cq ^{t}Bu), 22.8, 20.1 (CH_2 Cy); HRMS: $[M-N_2+H]^+$ calcd for $C_{27}H_{44}NO_5Si$ 490.29833, found 490.29811.

Methyl 6-*O*-(2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-α/β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (2C). Donor **2** and acceptor **25** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 hours at -40°C) and purified by flash column chromatography (1/0 to 9/1 pentane/EtOAc) to yield glycosylation product **2C** (81 mg, 92 µmol, 92%, α:β = 1:14) as a white solid. R_f: 0.42 (4/1 pentane/EtOAc). $[\alpha]_D^{23}$ = -18.6° (*c* = 1.0, $CHCl_3$); IR (thin film): 654, 969, 735, 827, 962, 1028, 1070, 1161, 1362, 1454, 2112, 2859, 2931; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.45 – 7.39 (m, 2H, CH_{arom}), 7.38 – 7.25 (m, 18H, CH_{arom}), 4.99 (d, 1H, *J* = 11.0 Hz, C*H*H Bn), 4.98 (d, 1H, *J* = 10.9 Hz, C*H*H Bn), 4.94 (d, 1H, *J* = 11.1 Hz, C*H*H Bn), 4.85 – 4.76 (m, 3H, C*H*H Bn, 2xCH*H* Bn), 4.66 (d, 1H, *J* = 11.1 Hz, CH*H* Bn), 4.64 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.60 (d, 1H, *J* = 3.6 Hz, H-1), 4.17 (d, 1H, *J* = 7.9 Hz, H-1'), 4.15 – 4.10 (m, 1H, H-6'), 4.05 – 3.96 (m, 2H, H-3, H-6), 3.96 – 3.87 (m, 2H, H-4', H-6'), 3.76 (ddd, 1H, *J* = 9.9, 4.2, 1.7 Hz, H-5), 3.70 (dd, 1H, *J* = 10.7, 4.2 Hz, H-6), 3.59 (t, 1H, *J* = 9.5 Hz, H-4), 3.54 (dd, 1H, *J* = 9.6, 3.5 Hz, H-2), 3.40 (dd, 1H, *J* = 9.7, 7.9 Hz, H-2'), 3.37 – 3.26 (m, 5H, CH_3 Ome, H-3', H-5'), 1.07 (s, 9H, CH_3 ^{t}Bu), 1.01 (s, 9H, CH_3 ^{t}Bu); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 138.9, 138.6, 138.2, 138.1 (C_q), 128.6, 128.5, 128.5, 128.4, 128.3, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7 (CH_{arom}), 102.2 (C-1'), 98.3 (C-1), 82.5 (C-3'), 82.2 (C-3), 79.9 (C-2), 77.9 (C-4'), 77.7 (C-4), 75.9, 75.4, 75.0, 73.6 (CH_2 Bn), 70.6 (C-5'), 69.7 (C-5), 68.6 (C-6), 66.3 (C-6'), 65.6 (C-2'), 55.3 (OMe), 27.5, 27.1 (CH_3 ^{t}Bu), 22.8, 20.1 (C_q ^{t}Bu); Diagnostic peaks α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.87 (d, 1H, *J* = 3.6 Hz, H-1'), 4.52 (d, 1H, *J* = 3.4 Hz, H-1); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 98.1, 98.0, 68.3; HRMS: $[M+NH_4]^+$ calcd for $C_{49}H_{67}N_4O_{10}Si$ 899.46210, found 899.46246.

2-Fluoroethyl 2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-α/β-D-glucopyranoside (2D). Donor **2** and 2-fluoroethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations and purified by flash column chromatography (1/0 to 0/1 pentane/toluene to 2% Et_2O in toluene) to yield glycosylation product **2D** (37.8 mg, 79 µmol, 79%, α:β = 1:5.5) as a colorless oil. R_f: 0.20 (toluene). Reported as a 1.00 : 0.18 mixture of anomers: IR (neat): 654, 768, 827, 962, 1080, 1161, 1472, 2112, 2859, 2932; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.45 – 7.40 (m, 2.36H, CH_{arom}), 7.39 – 7.27 (m, 3.54H, CH_{arom}), 5.06 (d, 0.18H, *J* = 10.7 Hz, C*H*H Bn_α), 4.99 (d, 1H, *J* = 10.9 Hz, C*H*H Bn_β), 4.86 (d, 0.18H, *J* = 3.6 Hz, $H\text{-}1_\alpha$), 4.82 (d, 0.18H, *J* = 10.6 Hz, CH*H* Bn_α), 4.82 (d, 1H, *J* = 10.9 Hz, CH*H* Bn_β), 4.71 – 4.61 (m, 1.18H, C*H*HF_α, C*H*HF_β), 4.58 – 4.47 (m, 1.18H, CH*H*F_α, CH*H*F_β), 4.37 (d, 1H, *J* = 7.6 Hz, $H\text{-}1_\beta$), 4.17 (dd, 1H, *J* = 10.3, 5.1 Hz, $H\text{-}6_\beta$), 4.12 – 3.78 (m, 5.26H, CH_2-CH_2F_α, CH_2-CH_2F_β, $H\text{-}3_\alpha$, $H\text{-}4_\alpha$, $H\text{-}4_\beta$, $H\text{-}5_\alpha$, $H\text{-}6_\alpha$, $H\text{-}6_\alpha$, $H\text{-}6_\beta$), 3.44 – 3.29 (m, 3.18H, $H\text{-}2_\alpha$, $H\text{-}2_\beta$, $H\text{-}3_\beta$, $H\text{-}5_\beta$), 1.09 (s, 1.62H, CH_3 ^{t}Bu_α), 1.08 (s, 9H, CH_3 ^{t}Bu_β), 1.03 (s, 1.62H CH_3 ^{t}Bu_α), 1.01 (s, 9H, CH_3 ^{t}Bu_β); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.3 ($C_{q,\alpha}$), 138.2 ($C_{q,\beta}$), 128.6 (CH_{arom} Bn_α), 128.5 (CH_{arom} Bn_β), 128.5 (CH_{arom} Bn_α), 128.4 (CH_{arom} Bn_β), 128.0 (CH_{arom} $Bn_{\alpha,\beta}$), 102.4 ($C\text{-}1_\beta$), 98.3 ($C\text{-}1_\alpha$), 82.7 (d, *J* = 170.0 Hz, CH_2F_β), 82.4 (d, *J* = 170.6 Hz, CH_2F_α), 82.3 ($C\text{-}3_\beta$), 79.3, 79.0 ($C\text{-}3_\alpha$, $C\text{-}4_\alpha$), 78.0 ($C\text{-}4_\beta$), 75.6 (CH_2 Bn_α), 75.5 (CH_2 Bn_β), 70.6 ($C\text{-}5_\beta$), 69.0 (d, *J* = 20.3 Hz, CH_2-CH_2F_β), 67.3 (d, *J* = 20.1 Hz, CH_2-CH_2F_α), 66.8 ($C\text{-}5_\alpha$), 66.7 ($C\text{-}6_\alpha$), 66.3 ($C\text{-}6_\beta$), 65.5 ($C\text{-}2_\beta$), 62.5 ($C\text{-}2_\alpha$), 27.5, 27.1 (CH_3 ^{t}$Bu_{\alpha,\beta}$), 23.1 (C_q ^{t}Bu_α), 22.8 (C_q ^{t}Bu_β), 20.1 (C_q ^{t}Bu_α), 20.1 (C_q ^{t}Bu_β); HRMS: $[M-N_2+H]^+$ calcd for $C_{23}H_{37}FNO_5Si$ 454.24195, found 454.24188.

Methyl 4-*O*-(2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-α/β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (2E). Donor **2** and acceptor **26** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 hours at -40°C) and purified by flash column chromatography (1/0 to 9/1 pentane/EtOAc) to yield glycosylation product **2E** (72 mg, 82 µmol, 82%, α:β = 1:3) as a colorless oil. R_f: 0.23 and 0.41 (9/1 pentane/EtOAc). IR (thin film): 654, 696, 735, 768, 827, 962, 1090, 1159, 1271, 1362, 1454, 2110, 2859, 2932; Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.44 – 7.39 (m, 2H, CH_{arom}), 7.39 – 7.21 (m, 18H, CH_{arom}), 4.98 (d, 1H, *J* = 10.8 Hz, C*H*H Bn), 4.83 – 4.74 (m, 4H, CH*H* Bn, CH_2 Bn, CH*H* Bn), 4.68 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.62 (d, 1H, *J* = 12.2 Hz, CH*H* Bn) 4.59 (d, 1H, *J* = 3.6 Hz, H-1), 4.44 (d, 1H, *J* = 11.9 Hz, CH*H* Bn), 4.23 (d, 1H, *J* = 8.0 Hz, H-1'), 3.97 (dd, 1H, *J* = 10.6, 3.0 Hz, H-6), 3.94 – 3.73 (m, 5H, H-3, H-4, H-4', H-5, H-6'), 3.71 – 3.66 (m, 1H, H-6), 3.55 – 3.47 (m, 2H, H-2, H-6'), 3.38 (s, 3H, CH_3 OMe), 3.27 – 3.21 (m, 1H, H-2'), 3.20 – 3.14 (m, 1H, H-3'), 3.06 (td, 1H, *J* = 9.9, 5.1 Hz, H-5'), 1.06 (s, 9H, CH_3 ^{t}Bu), 0.97 (s, 9H, CH_3 ^{t}Bu); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 139.4, 138.4, 138.1, 137.9 (C_q), 128.5, 128.5, 128.5, 128.4, 128.4, 128.2, 128.1, 128.0, 128.0, 127.9, 127.4, 127.3 (CH_{arom}), 101.0 (C-1'), 98.4 (C-1), 82.6 (C-3'), 80.2 (C-3), 79.2 (C-2), 78.1 (C-4'), 77.0 (C-4), 75.3, 75.3, 73.6, 73.6 (CH_2 Bn), 70.2 (C-5'), 69.7 (C-5), 68.3 (C-6), 66.2 (C-6'), 66.1 (C-2'), 55.4 (OMe), 27.6, 27.1 (CH_3 ^{t}Bu), 22.7, 20.0 (C_q tBu); Diagnostic peaks α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.67 (d, 1H, *J* = 4.0 Hz, H-1), 5.11 (d, 1H, *J* = 10.6 Hz, C*H*H Bn), 5.06 (d, 1H, *J* = 10.6 Hz, C*H*H Bn), 4.87 (d, 1H, *J* = 10.6 Hz, CH*H* Bn), 4.79 (d, 1H, *J* = 10.6 Hz, CH*H* Bn), 4.75 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.09 (t, 1H, *J* = 9.0 Hz, H-3), 3.56 (dd, 1H, *J* = 9.6, 3.5 Hz, H-2), 3.38 (s, CH_3 OMe), 3.21 (dd, 1H, J = 10.2, 4.0 Hz, H-2'), 1.06 (s, 9H, CH_3 ^{t}Bu), 1.04 (s, 9H, CH_3 ^{t}Bu); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 138.8, 138.3, 138.2, 138.0, 128.6, 128.4, 128.3, 128.1, 128.0, 128.0, 128.0, 127.9, 127.7, 127.6, 127.4, 127.3, 97.9, 97.7 (C-1, C-1'), 82.1 (C-3), 80.6 (C-2), 79.1, 79.0, 75.6, 75.1, 73.7, 73.4, 69.6, 69.2, 67.5, 66.5, 62.3 (C-2'), 55.4, 27.6, 27.2, 22.8, 20.1; HRMS: $[M+NH_4]^+$ calcd for $C_{49}H_{67}N_4O_{10}Si$ 899.46210, found 899.46246.

Methyl (methyl 4-*O*-[2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-α/β-D-glucopyranosyl]-2,3-di-*O*-benzyl-α-D-glucopyranosyl uronate) (2F). Donor **2** and acceptor **27** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 hours at -40°C) and purified by flash column chromatography (1/0 to 9/1 pentane/EtOAc) to yield glycosylation product **2F** (69 mg, 84 µmol, 84%, α:β = 3.3:1) as a white solid. R_f: 0.36 and 0.39 (9/1 pentane/EtOAc). IR (thin film): 654, 696, 735, 827, 1042, 1144, 1387, 1751, 2108, 2859, 2934; Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.43 – 7.38 (m, 2H, CH_{arom}), 7.37 – 7.25 (m, 13H, CH_{arom}), 5.45 (d, 1H, *J* = 4.1 Hz, H-1'), 5.07 – 5.02 (m, 2H, 2x*CH*H Bn), 4.90 (d, 1H, *J* = 10.6 Hz, CH*H* Bn), 4.84 – 4.78 (m, 1H, CH*H* Bn), 4.75 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.59 (d, 1H, *J* = 12.2 Hz, CH*H* Bn), 4.57 (d, 1H, *J* = 3.5 Hz, H-1), 4.21 – 4.17 (m, 1H, H-5), 4.09 – 4.01 (m, 3H, H-3, H-4, H-6'), 3.91 – 3.85 (m, 1H, H-4'), 3.83 – 3.73 (m, 5H, CH_3 CO_2Me, H-3', H-6'), 3.62 (td, 1H, *J* = 10.1, 5.0 Hz, H-5'), 3.58 – 3.53 (m, 1H, H-2), 3.41 (s, 3H, CH_3 OMe), 3.23 (dd, 1H, *J* = 10.2, 4.1 Hz, H-2'), 1.07 (s, 9H, CH_3 ^{t}Bu), 1.05 (s, 9H, CH_3 ^{t}Bu); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 169.2 (C=O CO_2Me), 138.7, 138.2, 137.8 (C_q), 128.7, 128.5, 128.5, 128.5, 128.3, 128.2, 128.0, 127.7, 127.6 (CH_{arom}), 98.5, 98.4 (C-1, C-1'), 81.0 (C-3), 79.9 (C-2), 79.0, 79.0 (C-3', C-4'), 76.2 (C-4), 75.5, 75.4, 73.6 (CH_2 Bn), 70.2 (C-5), 67.0 (C-5'), 66.4 (C-6'), 62.4 (C-2'), 55.9 (OMe), 52.9 (CO_2Me), 27.6, 27.2 (CH_3 ^{t}Bu), 22.9, 20.0 (C_q ^{t}Bu); Diagnostic peaks β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.98 (d, 1H, *J* = 10.9 Hz, C*H*H Bn), 4.39 (d, 1H, *J* = 7.7 Hz, H-1'), 4.02 – 3.96 (m, 1H), 3.82 (s, 3H, CH_3 CO_2Me), 3.52 (dd, 1H, *J* = 9.5, 3.6 Hz, H-2), 1.05 (s, 9H, CH_3 ^{t}Bu), 0.97 (s, 9H, CH_3, ^{t}Bu); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 170.2, 139.1, 138.1, 138.1, 128.6, 128.5, 128.4, 128.3, 128.3, 128.1, 128.0, 127.5, 127.3, 101.9 (C-1'), 98.9 (C-1), 82.5, 79.6, 79.4, 78.8, 78.0, 75.4, 73.9, 70.4, 69.9, 66.1, 55.9, 52.8, 27.5, 27.1, 22.8, 20.0; HRMS: $[M+NH_4]^+$ calcd for $C_{43}H_{61}N_4O_{11}Si$ 837.41006, found 837.41042.

2,2-Difluoroethyl 2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-α/β-D-glucopyranoside (2G). Donor **2** and 2,2-difluoroethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations and purified by flash column chromatography (1/0 to 0/1 pentane/toluene to 2% Et_2O in toluene) to

yield glycosylation product **2G** (38.1 mg, 76 µmol, 76%, α:β = 2.7:1) in two fractions (24.3 mg α only, 13.8 mg α:β = 0.3:1) as white solids. R_f: 0.43 β, 0.31 α (toluene). IR (neat): 654, 766, 826, 1070, 1474, 2108, 2860, 2934; Data for the α-anomer: $[\alpha]_D^{23}$ = +35.6° (*c* = 0.86, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.45 – 7.40 (m, 2H, CH_{arom}), 7.39 – 7.27 (m, 3H, CH_{arom}), 5.95 (tt, 1H, *J* = 55.2, 4.1 Hz, C*H*F_2), 5.06 (d, 1H, *J* = 10.6 Hz, C*H*H Bn), 4.85 (d, 1H, *J* = 3.6 Hz, H-1), 4.82 (d, 1H, *J* = 10.7 Hz, CH*H* Bn), 4.13 – 4.08 (m, 1H, H-6), 3.98 – 3.92 (m, 1H, H-3/4), 3.92 – 3.72 (m, 5H, CH_2-CHF_2, H-3/4, H-5, H-6), 3.35 (dd, 1H, *J* = 10.1, 3.6 Hz, H-2), 1.09 (s, 9H, CH_3 ^{t}Bu), 1.03 (s, 9H, CH_3 ^{t}Bu); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.1 (C_q), 128.6, 128.5, 128.1 (CH_{arom}), 113.8 (t, *J* = 241.6 Hz, CHF_2), 98.7 (C-1), 79.0, 78.9 (C-3, C-4), 75.7 (CH_2 Bn), 67.3 (t, *J* = 28.6 Hz, *C*H_2-CHF_2), 67.1 (C-5), 66.6 (C-6), 62.4 (C-2), 27.5, 27.1 (CH_3 ^{t}Bu), 22.8, 20.1 (C_q ^{t}Bu); Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.44 – 7.39 (m, 2H, CH_{arom}), 7.38 – 7.29 (m, 3H, CH_{arom}), 5.92 (tdd, 1H, *J* = 55.3, 5.1, 3.4 Hz, C*H*F_2), 4.99 (d, 1H, *J* = 10.9 Hz, C*H*H Bn), 4.81 (d, 1H, *J* = 11.0 Hz, CH*H* Bn), 4.35 (s, 1H, *J* = 7.7 Hz, H-1), 4.17 (dd, 1H, *J* = 10.3, 5.0 Hz, H-6), 4.02 – 3.74 (m, 4H, CH_2-CHF_2, H-4, H-6), 3.42 – 3.30 (m, 3H, H-2, H-3, H-5), 1.09 (s, 9H, CH_3 ^{t}Bu), 1.01 (s, 9H, CH_3, ^{t}Bu); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.1 (C_q), 128.5, 128.4, 128.1 (CH_{arom}), 114.1 (t, *J* = 241.4 Hz, CHF_2), 102.5 (C-1), 82.2 (C-3), 77.9 (C-4), 75.5 (CH_2 Bn), 70.7 (C-5), 68.8 (dd, *J* = 29.3, 28.8 Hz, *C*H_2-CHF_2), 66.2 (C-6), 65.4 (C-2), 27.5, 27.1 (CH_3 ^{t}Bu), 22.8, 20.1 (C_q ^{t}Bu); HRMS: $[M\text{-}N_2\text{+}H]^+$ calcd for $C_{23}H_{36}F_2NO_5Si$ 472.23253, found 472.23239.

Methyl 4-*O*-(2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-α/β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-β-D-galactopyranoside (2H). Donor **2** and acceptor **28** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 hours at -40°C) and purified by flash column chromatography (1/0 to 9/1 pentane/EtOAc) to yield glycosylation product **2H** (46 mg, 52 µmol, 52%, α:β = 7:1) as a colorless oil. R_f: 0.33 and 0.51 (9/1 pentane/EtOAc). IR (thin film): 652, 696, 735, 826, 1001, 1036, 1206, 1364, 1454, 2108, 2859, 2932; Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.46 – 7.41 (m, 2H, CH_{arom}), 7.41 – 7.23 (m, 18H, CH_{arom}), 5.10 (d, 1H, *J* = 10.3 Hz, C*H*H Bn), 4.89 – 4.81 (m, 3H, CH*H* Bn, 2xC*H*H Bn), 4.79 (d, 1H, *J* = 3.7 Hz, H-1'), 4.72 (d, 1H, *J* = 10.6 Hz, CH*H* Bn), 4.68 (d, 1H, *J* = 13.0 Hz, CH*H* Bn), 4.58 – 4.44 (m, 3H, CH_2 Bn, H-5'), 4.23 (d, 1H, *J* = 7.6 Hz, H-1), 4.07 – 3.99 (m, 2H, H-4, H-6), 3.99 – 3.88 (m, 3H, H-3', H-4', H-6'), 3.76 (t, 1H, *J* = 10.1 Hz, H-6'), 3.67 – 3.58 (m, 2H, H-2, H-6), 3.56 (s, 3H, CH_3 OMe), 3.48 (dd, 1H, *J* = 8.9, 5.5 Hz, H-5), 3.38 (dd, 1H, *J* = 10.0, 2.9 Hz, H-3), 3.33 (dd, 1H, *J* = 9.7, 3.7 Hz, H-2'), 1.06 (s, 9H, CH_3 ^{t}Bu), 1.02 (s, 9H, CH_3 ^{t}Bu); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 138.8, 138.4, 138.2, 137.7 (C_q), 128.6, 128.6, 128.5, 128.5, 128.5, 128.3, 128.2, 127.9, 127.8 (CH_{arom}), 105.1 (C-1), 99.2 (C-1'), 79.9, 79.9 (C-2, C-3'), 79.6, 79.4 (C-3, C-4'), 75.7, 75.6 (CH_2 Bn), 75.0 (C-4), 73.6 (CH_2 Bn), 72.9 (C-5), 72.6 (CH_2 Bn), 67.1, 67.0 (C-6, C-6'), 66.9 (C-5'), 63.2 (C-2'), 57.5 (OMe), 27.5, 27.3 (CH_3 ^{t}Bu), 22.7, 20.2 (C_q ^{t}Bu); Diagnostic peaks β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.94 (d, 0.14H, *J* = 11.1 Hz, C*H*H Bn), 4.27 (d, 0.14H, *J* = 7.7 Hz, H-1), 3.22 – 3.16 (m, 0.28H), 3.20 – 3.09 (m, 2H); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 105.1 (C-1), 102.0 (C-1'), 82.3, 78.0, 75.4, 75.3, 73.7, 73.7, 73.5, 73.4, 70.4, 69.6, 66.4, 65.6, 57.3, 27.6, 27.2, 22.8, 20.1; HRMS: $[M+NH_4]^+$ calcd for $C_{49}H_{67}N_4O_{10}Si$ 899.46210, found 899.46243.

Methyl 2-*O*-(2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-α-D-glucopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (2I). Donor **2** and acceptor **29** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 hours at -40°C) and purified by flash column chromatography (1/0 to 9/1 pentane/EtOAc) to yield glycosylation product **2I** (67 mg, 85 µmol, 85%, α:β = > 20:1) as a white solid. R_f: 0.54 (9/1 pentane/EtOAc). $[\alpha]_D^{20}$ = +44.3° (*c* = 1.34, $CHCl_3$); IR (thin film): 696, 827, 937, 1040, 1088, 1130, 1364, 2108, 2859, 2957; Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.54 – 7.47 (m, 2H, CH_{arom}), 7.46 – 7.41 (m, 2H, CH_{arom}), 7.41 – 7.22 (m, 11H, CH_{arom}), 5.65 (s, 1H, C*H*Ph), 5.23 (d, 1H, *J* = 3.6 Hz, H-1'), 5.09 (d, 1H, *J* = 10.6 Hz, C*H*H Bn), 4.89 – 4.82 (m, 2H, CH*H* Bn, C*H*H Bn), 4.74 – 4.65 (m, 2H, C*H*H Bn, H-1), 4.31 – 4.21 (m, 2H, H-4, H-6), 4.11 – 3.92 (m, 5H, H-2, H-3, H-3', H-4', H-6'), 3.92 – 3.76 (m, 4H, H-5, H-5', H-6, H-6'), 3.36 (s, 3H, CH_3 OMe), 3.27 (dd, 1H, *J* = 10.0, 3.7 Hz, H-2'), 1.09 (s, 9H), 1.05 (s, 9H); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 138.6, 138.4, 137.7 (C_q), 129.0, 128.5, 128.5, 128.4, 128.3, 128.3, 128.0, 127.6, 127.5, 127.4, 126.2, 126.1 (CH_{arom}), 101.7 (CHPh), 101.0 (C-1), 99.4 (C-1'), 79.3 (C-4), 79.1, 78.9 (C-3', C-4'), 76.0, 75.6 (C-2, C-3), 75.6, 73.0 (CH_2 Bn), 69.0 (C-6), 67.2 (C-5'), 66.6 (C-6'), 64.1 (C-5), 62.6 (C-2'), 55.2 (CH_3 OMe), 27.5, 27.2 (CH_3 ^{t}Bu), 22.8, 20.2 (C_q ^{t}Bu); Diagnostic peaks β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.60 (s, 1H, C*H*Ph), 4.98 (d, 1H, *J* = 11.3 Hz, C*H*H Bn), 4.39 (d, 1H, *J* = 8.2 Hz, H-1'), 3.57 – 3.48 (m, 1H); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 101.6, 99.6, 81.8, 78.5, 77.8, 76.4, 75.2, 74.4, 72.3, 70.9, 65.7, 55.1, 27.5, 27.1; HRMS: $[M+NH_4]^+$ calcd for $C_{42}H_{59}N_4O_{10}Si$ 807.39950, found 807.39931.

2,2,2-Trifluoroethyl 2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-α-D-glucopyranoside (2J). Donor **2** and 2,2,2-trifluoroethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 30 min at -40°C) and purified by flash column chromatography (1/0 to 0/1 pentane/toluene to 2% Et_2O in toluene) to yield glycosylation product **2J** (42.4 mg, 82 µmol, 82%, α:β = > 20:1) as a colorless oil. R_f: 0.36 (toluene). $[\alpha]_D^{23}$ = +32.6° (*c* = 1.0, $CHCl_3$); IR (neat): 654, 766, 826, 1036, 1082, 1159, 1279, 1472, 2108, 2859, 2930; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.45 – 7.39 (m, 2H, CH_{arom}), 7.38 – 7.27 (m, 3H, CH_{arom}), 5.07 (d, 1H, *J* = 10.6 Hz, C*H*H Bn), 4.88 (d, 1H, *J* = 3.6 Hz, H-1), 4.82 (d, 1H, *J* = 10.6 Hz, CH*H* Bn), 4.14 – 4.07 (m, 1H, H-6), 4.03 – 3.93 (m, 3H, CH_2-CF_3, H-4), 3.92 – 3.80 (m, 3H, H-3, H-5, H-6), 3.36 (dd, 1H, *J* = 10.0, 3.6 Hz, H-2), 1.09 (s, 9H, CH_3 ^{t}Bu), 1.03 (s, 9H, CH_3 ^{t}Bu); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.1 (C_q), 128.6, 128.5, 128.1 (CH_{arom}), δ 123.5 (q, *J* = 278.4 Hz, CF3), 98.8 (C-1), 78.9 (C-3), 78.8 (C-4), 75.7 (CH_2 Bn), 67.4 (C-5), 66.5 (C-6), 65.2 (q, *J* = 35.4 Hz, *C*H_2-CF_3), 62.2 (C-2), 27.5, 27.1 (CH_3 ^{t}Bu), 22.8, 20.1 (C_q ^{t}Bu); HRMS: $[M\text{-}N_2\text{+}H]^+$ calcd for $C_{23}H_{35}F_3NO_5Si$ 490.22311, found 490.22292.

1,1,1,3,3,3-Hexafluoro-2-propyl 2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-α-D-glucopyranoside (2K). Donor **2** and 1,1,1,3,3,3-hexafluoro-2-propanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 72 hours at -40°C) and purified by flash column chromatography (4/1 to 0/1 pentane/toluene) to yield glycosylation product **2K** (20 mg, 34 µmol, 34%, α:β = > 20:1) as a white solid. R_f: 0.38 (9/1 pentane/Et_2O). $[\alpha]_D^{20}$ = +31.2° (*c* = 0.50, $CHCl_3$); IR (thin film): 689, 827, 1030, 1098, 1221, 1288, 1368, 2112, 2860, 2934; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC, NOESY): δ 7.45 – 7.28 (m, 5H, CH_{arom}), 5.12 – 5.04 (m, 2H, C*H*H Bn, H-1), 4.83 (d, 1H, *J* = 10.5 Hz, CH*H* Bn), 4.40 (hept, 1H, *J* = 5.7 Hz, C*H* HFIP), 4.09 (dd, 1H, *J* = 9.4, 4.0 Hz, H-6), 4.03 – 3.91 (m, 2H, H-4, H-5), 3.91 – 3.83 (m, 2H, H-3, H-6), 3.42 (dd, 1H, *J* = 10.2, 3.8 Hz, H-2), 1.08 (s, 9H, CH_3 ^{t}Bu), 1.03 (s, 9H, CH_3 ^{t}Bu); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 138.0 (C_q), 128.6, 128.5, 128.2 (CH_{arom}), 100.4 (C-1), 78.7 (C-3), 78.4 (C-4), 75.8 (CH_2 Bn), 73.3 (p, *J* = 33.2 Hz), 68.1 (C-5), 66.1 (C-6), 61.9 (C-2), 27.5, 27.0 (CH_3 ^{t}Bu), 22.8, 20.1 (C_q ^{t}Bu); HRMS: $[M\text{-}N_2\text{+}H]^+$ calcd for $C_{24}H_{34}F_6NO_5Si$ 558.21050, found 558.21009.

Ethyl 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (3A). Donor **3** and ethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations and purified by flash column chromatography (1/0 to 0/1 hexane/toluene to 5% EtOAc in toluene) to yield glycosylation product **3A** (34.3 mg, 83 µmol, 83%, α:β = < 1:20) as a white solid. R_f: 0.58 (9/1 toluene/EtOAc). $[\alpha]_D^{23}$ = -79.6° (*c* = 0.69, $CHCl_3$); IR (neat): 692, 993, 1098, 1186, 1267, 1365, 1452, 2111, 2878, 2979; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.50 – 7.46 (m, 2H, CH_{arom}), 7.41 – 7.28 (m, 8H, CH_{arom}), 5.57 (s, 1H, C*H*Ph), 4.91 (d, 1H, *J* = 11.2 Hz, C*H*H Bn), 4.79 (d, 1H, *J* = 11.3 Hz, CH*H* Bn), 4.37 (d, 1H, *J* = 8.2 Hz, H-1), 4.34 (dd, 1H, *J* = 10.6, 5.0 Hz, H-6), 3.96 (dq, 1H, *J* = 9.7, 7.1 Hz, C*H*H Et), 3.80 (t, 1H, *J* = 10.3 Hz, H-6), 3.70 (t, 1H, *J* = 9.0 Hz, H-4), 3.66 (dq, 1H, *J* = 9.7, 7.2 Hz, CH*H* Et), 3.54 (t, 1H, *J* = 9.3 Hz, H-3), 3.44 (dd, 1H, *J* = 9.5, 8.0 Hz, H-2), 3.39 (td, 2H, *J* = 9.8, 5.0 Hz, H-5), 1.29 (t, 3H, *J* = 7.1 Hz, CH_3 Et); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.0, 137.2 (C_q), 129.2, 128.5, 128.4, 128.3, 128.0, 126.1 (CH_{arom}), 102.5 (C-1), 101.4 (CHPh), 81.7 (C-4), 79.1 (C-3), 75.0 (CH_2 Bn), 68.7 (C-6), 66.3 (CH_2 Et), 66.3, 66.2 (C-2, C-5), 15.2 (CH_3 Et); ^{13}C-HMBC-GATED NMR ($CDCl_3$, 101 MHz): δ 102.5 ($J_{C1,H1}$ = 161 Hz, C-1); HRMS: $[M+NH_4]^+$ calcd for $C_{22}H_{29}N_4O_5$ 429.21325, found 429.21321.

Cyclohexyl 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (3B). Donor **3** and cyclohexanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations and purified by flash column chromatography (1/1 to 0/1 hexane/toluene to 5% EtOAc in toluene) to yield glycosylation product **3B** (43 mg, 93 µmol, 93%, α:β = < 1 : 20) as a white solid. R_f: 0.23 (toluene). $[\alpha]_D^{23}$ = -60.5° (*c* = 0.86, DCM); IR (neat): 696, 748, 998, 1092, 1275, 1365, 1452, 2108, 2858, 2933; Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.50 – 7.44 (m, 2H, CH_{arom}), 7.42 – 7.27 (m, 8H, CH_{arom}), 5.56 (s, 1H, C*H*Ph), 4.90 (d, 1H, *J* = 11.4 Hz, C*H*H Bn), 4.79 (d, 1H, *J* = 11.4 Hz, CH*H* Bn), 4.47 (d, 1H, *J* = 7.8 Hz, H-1), 4.32 (dd, 1H, *J* = 10.5, 5.0 Hz, H-6), 3.79 (t, 1H, *J* = 10.3 Hz, H-6), 3.74 – 3.64 (m, 2H, H-4, CH Cyc), 3.50 (t, 1H, *J* = 9.2 Hz, H-3), 3.44 (dd, 1H, *J* = 9.6, 7.8 Hz, H-2), 3.36 (td, 1H, *J* = 9.7, 5.0 Hz, H-5), 1.99 – 1.87 (m, 2H, CH_2 Cyc), 1.82 – 1.72 (m, 2H, *J* = 15.2, 4.4 Hz, CH_2 Cyc), 1.56 – 1.37 (m, 3H, CH_2 Cyc), 1.36 – 1.20 (m, 3H, CH_2 Cyc); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.0, 137.3 (C_q), 129.1, 128.5, 128.4, 128.3, 127.9, 126.1 (CH_{arom}), 101.4 (CHPh), 101.0 (C-1), 81.6 (C-4), 79.0 (C-3), 78.5 (CH Cyc), 75.0 (CH_2 Bn), 68.8 (C-6), 66.5 (C-2), 66.3 (C-5), 33.6, 31.8, 25.6, 24.1, 23.9 (CH_2 Cyc); Diagnostic peaks α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.59 (s, 0.04H, C*H*Ph), 5.03 (d, 0.04H, *J* = 3.7 Hz, H-1), 4.12 (t, 0.04H, *J* = 9.5 Hz, H-3), 4.00 (td, 0.04H, *J* = 9.9, 4.8 Hz, H-5), 3.28 (dd, 0.04H, *J* = 10.0, 3.7 Hz, H-2); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 101.4 (CHPh), 97.1 (C-1), 76.0 (C-3), 63.8 (C-2), 62.9 (C-5); HRMS: $[M+NH_4]^+$ calcd for $C_{26}H_{35}N_4O_5$ 483.26020 found 483.25991.

Methyl 6-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (3C). Donor **3** and acceptor **25** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 h at -40°C) and purified by flash column chromatography (19/1 to 4/1 pentane/EtOAc) to yield glycosylation product **3C** (73.7 mg, 89 µmol, 89%, α:β = < 1:20) as a white solid. R_f: 0.42 (4/1 pentane/EtOAc). Spectroscopic data were in accord with those previously reported.[38] $[\alpha]_D^{23}$ = -32.2° (*c* = 1.0, $CHCl_3$); IR (neat): 696, 737, 999, 1028, 1070, 1090, 1277, 1362, 1497, 2108, 2876, 2926; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.47 (dd, 2H, *J* = 7.3, 2.5 Hz, CH_{arom}), 7.42 – 7.25 (m, 23H, CH_{arom}), 5.55 (s, 1H, C*H*Ph), 4.99 (d, 1H, *J* = 10.9 Hz, C*H*H 3-OBn), 4.95 (d, 1H, *J* = 11.2 Hz, C*H*H 4-OBn), 4.91 (d, 1H, *J* = 11.2 Hz, C*H*H 3'-OBn), 4.85 – 4.76 (m, 3H, CH*H* 3-OBn, C*H*H 2-OBn, CH*H* 3'-OBn), 4.70 – 4.63 (m, 2H, CH*H* 4-OBn, CH*H* 2-OBn), 4.61 (d, 1H, *J* = 3.6 Hz, H-1), 4.30 (dd, 1H, *J* = 10.5, 5.0 Hz, H-6'), 4.23 (d, 1H, *J* = 7.9 Hz, H-1'), 4.07 (d, 1H, *J* = 8.9 Hz, H-6), 4.00 (t, 1H, *J* = 9.3 Hz, H-3), 3.81 – 3.72 (m, 3H, H-5, H-6, H-6'), 3.69 (t, 1H, *J* = 9.1 Hz, H-4'), 3.60 (t, 1H, *J* = 9.3 Hz, H-4), 3.59 – 3.46 (m, 3H, H-2, H-2', H-

3'), 3.37 (s, 3H, CH_3 OMe), 3.36 – 3.29 (m, 1H, H-5'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 138.8, 138.5, 138.2, 137.8, 137.2 (C_q), 129.2, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 128.1, 128.1, 128.0, 127.9, 127.9, 127.7, 126.1 (CH_{arom}), 102.4 (C-1'), 101.4 (CHPh), 98.4 (C-1), 82.2 (C-3), 81.5 (C-4'), 79.8 (C-2), 79.3 (C-3'), 77.6 (C-4), 75.9 (CH_2 3-OBn), 75.0, 75.0 (CH_2 3'-OBn, 4-OBn), 73.6 (CH_2 2-OBn), 69.6 (C-5), 68.7, 68.6 (C-6, C-6'), 66.3 (C-5'), 66.1 (C-2'), 55.4 (OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{55}N_4O_{10}$ 847.39127, found 847.39224.

2-Fluoroethyl 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranoside (3D). Donor **3** and 2-fluoroethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations and purified by flash column chromatography (1/0 to 0/1 pentane/toluene to 5% EtOAc in toluene) to yield glycosylation product **3D** (38.5 mg, 90 µmol, 90%, α:β = 1:6.7) as a white solid. R_f: 0.40 (19/1 toluene/EtOAc). IR (neat): 696, 748, 996, 1028, 1072, 1091, 1174, 1276, 1368, 1454, 2108, 2873, 2917; Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.50 – 7.46 (m, 2H, CH_{arom}), 7.41 – 7.36 (m, 5H, CH_{arom}), 7.36 – 7.25 (m, 3H, CH_{arom}), 5.57 (s, 1H, C*H*Ph), 4.91 (d, 1H, *J* = 11.2 Hz, C*H*H Bn), 4.79 (d, 1H, *J* = 11.3 Hz, CH*H* Bn), 4.69 – 4.64 (m, 1H, C*H*HF), 4.55 (dt, 1H, *J* = 4.6, 2.9 Hz, CH*H*F), 4.42 (d, 1H, *J* = 7.9 Hz, H-1), 4.34 (dd, 1H, *J* = 10.5, 5.0 Hz, H-6), 4.11 (ddd, 0.5H, *J* = 12.2, 4.8, 2.9 Hz, C*H*H-CFH_2), 4.03 (ddd, 0.5H, *J* = 12.2, 4.7, 3.0 Hz, C*H*H-CFH_2), 3.92 (ddd, 0.5H, *J* = 12.2, 5.9, 3.2 Hz, CH*H*-CFH_2), 3.86 (ddd, 0.5H, *J* = 12.2, 6.0, 3.3 Hz, CH*H*-CFH_2), 3.80 (t, 1H, *J* = 10.3 Hz, H-6), 3.71 (t, 1H, *J* = 9.2 Hz, H-4), 3.56 (t, 1H, *J* = 9.2 Hz, H-3), 3.48 (dd, 1H, *J* = 9.5, 7.9 Hz, H-2), 3.39 (td, 1H, *J* = 9.7, 4.9 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.8, 137.1 (C_q), 129.2, 128.5, 128.4, 128.3, 128.0, 126.1 (CH_{arom}), 102.7 (C-1), 101.4 (CHPh), 82.6 (d, *J* = 170.1 Hz, CFH_2), 81.5 (C-4), 79.0 (C-3), 75.1 (CH_2 Bn), 69.3 (d, *J* = 20.1 Hz, CH_2-CFH_2), 68.6 (C-6), 66.3 (C-5), 66.1 (C-2); ^{13}C-HMBC-GATED NMR ($CDCl_3$, 101 MHz): δ 102.7 ($J_{C1,H1}$ = 162 Hz, C-1); Diagnostic peaks α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 5.58 (s, 0.15H, C*H*Ph), 4.96 (d, 0.15H, *J* = 10.9 Hz, C*H*H Bn), 4.95 (d, 0.15H, *J* = 3.7 Hz, H-1), 4.81 (d, 0.15H, *J* = 11.0 Hz, CH*H* Bn), 4.29 (dd, 0.15H, *J* = 10.2, 4.9 Hz, H-6); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 101.5 (CHPh), 98.8 (C-1), 82.8 (C-4), 76.2 (C-3), 75.2 (CH_2 Bn), 68.9 (C-6), 63.0, 62.9 (C-2, C-5); ^{13}C-HMBC-GATED NMR ($CDCl_3$, 101 MHz): δ 98.8 ($J_{C1,H1}$ = 172 Hz, C-1); HRMS: $[M+NH_4]^+$ calcd for $C_{22}H_{28}FN_4O_5$ 447.20382 found 447.20355.

Methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (3E). Donor **3** and acceptor **26** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 h at -40°C) and purified by flash column chromatography (19/1 to 4/1 pentane/EtOAc) to yield glycosylation product **3E** (73.3 mg, 88 µmol, 88%, α:β = 1:7) as a white solid. R_f: 0.51 α, 0.43 β (4/1 pentane/EtOAc). IR (neat): 696, 737, 1049, 1092, 1362, 1454, 2110, 2868; Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, TOCSY): δ 7.68 – 7.60 (m, 2H, CH_{arom}), 7.52 – 7.18 (m, 23H, CH_{arom}), 5.47 (s, 1H, C*H*Ph), 4.89 (d, 1H, *J* = 11.2 Hz, C*H*H Bn), 4.87 (d, 1H, *J* = 10.9 Hz, C*H*H Bn), 4.81 (d, 1H, *J* = 10.9 Hz, CH*H* Bn), 4.78 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.75 (d, 1H, *J* = 11.2 Hz, CH*H* Bn), 4.71 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.63 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.60 (d, 1H, *J* = 3.7 Hz, H-1), 4.41 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.19 (d, 1H, *J* = 7.6 Hz, H-1'), 4.11 (dd, 1H, *J* = 10.6, 5.0 Hz, H-6'), 4.00 – 3.90 (m, 2H, H-4, H-6), 3.85 (t, 1H, *J* = 9.3 Hz, H-3), 3.75 (dt, 1H, *J* = 9.8, 2.4 Hz, H-5), 3.69 (dd, 1H, *J* = 10.8, 1.9 Hz, H-6), 3.56 (t, 1H, *J* = 9.0 Hz, H-4'), 3.51 (dd, 1H, *J* = 9.5, 3.7 Hz, H-2), 3.45 – 3.38 (m, 4H, H-6', CH_3 OMe), 3.36 – 3.27 (m, 2H, H-2', H-3'), 3.00 (td, 1H, *J* = 9.8, 5.0 Hz, H-5'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 139.3, 138.3, 137.8, 137.8, 137.3 (C_q), 131.1, 129.4, 128.6, 128.4, 128.3, 128.2, 128.2, 128.1, 128.1, 127.9, 127.9, 127.6, 126.0, 124.8 (CH_{arom}), 101.3, 101.2 (CHPh, C-1'), 98.4 (C-1), 81.7 (C-4'), 80.1 (C-3), 79.2 (C-3'), 79.0 (C-2), 76.9 (C-4), 75.4, 74.7, 73.6, 73.5 (CH_2 Bn), 69.7 (C-5), 68.6 (C-6'), 68.0 (C-6), 66.6 (C-2'), 65.8 (C-5'), 55.4 (OMe); Diagnostic peaks α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.71 (d, 1H, *J* = 4.0 Hz, H-1'), 5.53 (s, 1H, C*H*Ph), 5.11 (d, 1H, *J* = 10.7 Hz, C*H*H Bn), 4.95 (d, 1H, *J* = 10.9 Hz, C*H*H Bn); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 98.1, 97.8, 82.7, 82.1, 80.5, 76.2, 75.1, 73.3, 73.0, 69.4, 69.1, 68.7, 63.4, 62.9; HRMS: $[M+Na]^+$ calcd for $C_{48}H_{51}N_3O_{10}Na$ 852.34667, found 852.34668.

Methyl (Methyl 4-*O*-[2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl]-2,3-di-*O*-benzyl-α-D-glucopyranosyl uronate) (3F). Donor **3** and acceptor **27** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 h at -40°C) and purified by flash column chromatography (19/1 to 4/1 pentane/EtOAc) to yield glycosylation product **3F** (71.8 mg, 93 µmol, 93%, α:β = 1.1:1) as a white solid. R_f: 0.54 (4/1 pentane/EtOAc). Spectroscopic data were in accord with those previously reported.[21] IR (neat): 696, 735, 914, 989, 1028, 1045, 1090, 1267, 1369, 1454, 1749, 2108, 2870, 2916; Reported as a 1 : 1 mixture of anomers: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.48 – 7.41 (m, 4H, CH_{arom}), 7.41 – 7.24 (m, 36H, CH_{arom}), 5.53 (s, 1H, C*H*Ph_α), 5.51 (d, 1H, *J* = 3.9 Hz, H-1'$_\alpha$), 5.47 (s, 1H, C*H*Ph_β), 5.04 (d, 1H, *J* = 10.5 Hz, C*H*H Bn), 4.94 (d, 1H, *J* = 11.0 Hz, C*H*H Bn), 4.91 – 4.82 (m, 4H, 2xCH*H* Bn, 2xC*H*H Bn), 4.81 – 4.72 (m, 4H, 2xCH*H* Bn, 2xC*H*H Bn), 4.64 – 4.58 (m, 2H, 2xCH*H* Bn), 4.57 (d, 2H, *J* = 3.5 Hz, H-1$_{\alpha,\beta}$), 4.43 (d, 1H, *J* = 8.1 Hz, H-1'$_\beta$), 4.26 (dd, 1H, *J* = 10.3, 4.8 Hz, H-6'$_\alpha$), 4.24 – 4.19 (m, 2H, H-5$_\alpha$, H-5$_\beta$), 4.09 – 3.99 (m, 4H, H-3$_\beta$, H-4$_\alpha$, H-4$_\beta$, H-6'$_\beta$), 3.97 (t, 1H, *J* = 9.5 Hz, H-3'$_\alpha$), 3.89 (t, 1H, *J* = 9.2 Hz, H-3$_\alpha$), 3.82 (s, 3H, CH_3 CO_2Me), 3.81 (s, 3H, CH_3 CO_2Me), 3.72 – 3.56 (m, 4H, H-2$_\beta$, H-4'$_\alpha$, H-4'$_\beta$, H-6'$_\alpha$), 3.56 – 3.46 (m, 3H, H-2$_\alpha$, H-3'$_\beta$, H-5'$_\alpha$), 3.46 – 3.38 (m, 7H, 2xCH_3 OMe, H-6'$_\beta$), 3.36 – 3.29 (m, 2H, H-2'$_\alpha$, H-2'$_\beta$), 3.26 (td, 1H, *J* = 9.7, 5.0 Hz, H-5'$_\beta$); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 170.0, 170.0 (C=O CO_2Me), 139.1, 138.5, 138.0, 137.9, 137.9, 137.8, 137.4, 137.2 (C_q), 129.2, 129.1, 128.7, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 128.0, 128.0, 127.8, 127.7, 127.5, 127.4, 126.1, 126.1 (CH_{arom}), 102.3 (C-1'$_\beta$), 101.4 (CHPh$_\beta$), 101.3 (CHPh$_\alpha$), 98.9, 98.6 (C-1$_\alpha$, C-1$_\beta$), 98.5 (C-1'$_\alpha$), 82.4 (C-4'$_\alpha$), 81.6 (C-4'$_\beta$), 81.1 (C-3$_\beta$), 79.6 (C-2$_\beta$, C-4$_\beta$), 79.5 (C-3$_\alpha$), 79.4 (C-3'$_\beta$), 78.7 (C-2$_\alpha$), 76.3 (C-3'$_\alpha$), 75.6 (CH_2 Bn), 75.5 (C-4$_\alpha$), 75.1, 75.0, 73.9, 73.7 (CH_2 Bn), 70.0, 69.9 (C-5$_\alpha$, C-5$_\beta$), 68.5, 68.5 (C-6$_\alpha$, C-6$_\beta$), 66.7 (C-2'$_\beta$), 66.2 (C-5'$_\beta$), 63.0 (C-5'$_\alpha$), 62.8 (C-2'$_\alpha$), 55.9, 55.9 (OMe), 53.0, 52.8 (CO_2Me); HRMS: $[M+NH_4]^+$ calcd for $C_{42}H_{49}N_4O_{11}$ 785.33923, found 785.34007.

2,2-Difluoroethyl 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranoside (3G). Donor **3** and 2,2-difluoroethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations and purified by flash column chromatography (1/0 to 0/1 pentane/toluene to 5% EtOAc in toluene) to yield glycosylation product **3G** (28.8 mg, 64 µmol, 64%, α:β = 2.9:1) as a white solid. R_f: 0.15 and 0.18 (toluene). IR (neat): 698, 747, 998, 1070, 1093, 1372, 1454, 2109, 2867, 2934; Reported as a 1 : 0.35 mixture of anomers: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.52 – 7.45 (m, 2.70H, CH_{arom}), 7.43 – 7.26 (m, 10.80H, CH_{arom}), 5.95 (tt, 1H, *J* = 55.2, 4.2 Hz, CF_2H_α), 5.94 (tt, 0.35H, *J* = 55.3, 3.8 Hz, CF_2H_β), 5.58 (s, 1H, C*H*Ph$_\alpha$), 5.57 (s, 0.35H, C*H*Ph$_\beta$), 4.96 (d, 1H, *J* = 10.9 Hz, C*H*H Bn$_\alpha$), 4.93 (d, 1H, *J* = 3.9 Hz, H-1$_\alpha$), 4.92 (d, 0.35H, *J* = 11.3 Hz, C*H*H Bn$_\beta$), 4.80 (d, 1H, *J* = 11.0 Hz, CH*H* Bn$_\alpha$), 4.79 (d, 0.35H, *J* = 11.3 Hz, CH*H* Bn$_\beta$), 4.40 (d, 0.35H, *J* = 7.9 Hz, H-1$_\beta$), 4.34 (dd, 0.35H, *J* = 10.5, 5.0 Hz, H-6$_\beta$), 4.29 (dd, 1H, *J* = 10.2, 4.8 Hz, H-6$_\alpha$), 4.08 (t, 1H, *J* = 9.5 Hz, H-3$_\alpha$), 4.02 – 3.67 (m, 6.4H, H-4$_\alpha$, H-4$_\beta$, H-5$_\alpha$, H-6$_\alpha$, H-6$_\beta$, C*H*$_2$-CF_2H_α, C*H*$_2$-CF_2H_β), 3.56 (t, 0.35H, *J* = 9.2 Hz, H-3$_\beta$), 3.50 – 3.35 (m, 1.70H, H-2$_\alpha$, H-2$_\beta$, H-5$_\beta$); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.8, 137.8, 137.1, 137.1 (C_q), 129.4, 129.3, 129.1, 128.6, 128.5, 128.5, 128.4, 128.1, 126.1 (CH_{arom}), 114.0 (t, *J* = 241.5 Hz, CF_2H_β), 113.8 (t, *J* = 241.6 Hz, CF_2H_α), 102.8 (C-1$_\beta$), 101.6 (CHPh$_\alpha$), 101.5 (CHPh$_\beta$), 99.3 (C-1$_\alpha$), 82.6 (C-4$_\alpha$), 81.4 (C-4$_\beta$), 78.9 (C-3$_\beta$), 76.0 (C-3$_\alpha$), 75.3 (CH_2 Bn$_\alpha$), 75.1 (CH_2 Bn), 69.0 (t, *J* = 29.0 Hz, *C*H_2-CF_2H_β), 68.8 (C-6), 68.5 (C-6), 67.5 (t, *J* = 28.7 Hz, *C*H_2-CF_2H_α), 66.4 (C-5$_\beta$), 66.0 (C-2$_\beta$), 63.3 (C-5$_\alpha$), 62.9 (C-2$_\alpha$); HRMS: $[M+H]^+$ calcd for $C_{22}H_{24}F_2N_3O_5$ 448.16785, found 448.16761.

Methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-β-D-galactopyranoside (3H). Donor **3** and acceptor **28** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 h at -40°C) and purified by flash column chromatography (19/1 to 4/1 pentane/EtOAc) to yield glycosylation product **3H** (62.2 mg, 75 µmol, 75%, α:β = 9:1) as a white solid. R_f: 0.52 (4/1 pentane/EtOAc). IR (neat): 696, 735, 995, 1030, 1072, 1090, 1368, 1454, 1497, 2106, 2862, 2920; Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.50 – 7.46 (m, 2H, CH_{arom}), 7.42 – 7.25 (m, 23H, CH_{arom}), 5.51 (s, 1H, C*H*Ph), 4.98 (d, 1H, *J* = 10.7 Hz, C*H*H 3'-OBn), 4.90 (d, 1H, *J* = 11.0 Hz, C*H*H 2-OBn), 4.88 (d, 1H, *J* = 3.7 Hz, H-1'), 4.84 – 4.76 (m, 3H, CH*H* 2-OBn, CH*H* 3'-OBn, CH*H* 3-OBn), 4.69 (d, 1H, *J* = 12.4 Hz, CH*H* 3-OBn), 4.59 – 4.51 (m, 2H, CH_2 6-OBn), 4.30 (td, 1H, *J* = 10.1, 4.9 Hz, H-5'), 4.25 (d, 1H, *J* = 7.6 Hz, H-1), 4.14 – 4.07 (m, 2H, H-3', H-4), 4.03 (t, 1H, *J* = 8.9 Hz, H-6), 3.80 (dd, 1H, *J* = 10.2, 4.9 Hz, H-6'), 3.70 – 3.60 (m, 3H, H-2, H-4', H-6), 3.55 (s, 3H, CH_3 OMe), 3.54 – 3.48 (m, 2H, H-5, H-6'), 3.44 – 3.36 (m, 2H, H-2', H-3); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 138.7, 138.3, 138.1, 137.7, 137.6 (C_q), 129.0, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 128.3, 128.2, 128.0, 127.7, 127.6, 126.1 (CH_{arom}), 105.3 (C-1), 101.2 (CHPh), 99.4 (C-1'), 83.1 (C-4'), 80.1 (C-3), 78.9 (C-2), 77.0 (C-3'), 75.3 (CH_2 3'-OBn), 75.1 (CH_2 2-OBn), 74.7 (C-4), 73.6 (CH_2 6-OBn), 73.0 (CH_2 3-OBn), 72.9 (C-5), 68.9 (C-6'), 67.1 (C-6), 63.8 (C-2'), 62.9 (C-5'), 57.4 (OMe); Diagnostic peaks β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.54 (s, 1H, C*H*Ph), 3.92 (dd, 1H, *J* = 9.7, 7.7 Hz, H-2), 3.76 – 3.71 (m, 1H, H-6), 3.22 (td, 1H, *J* = 9.7, 4.8 Hz, H-5'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 105.1 (C-1), 102.6 (C-1'), 101.4, 81.5, 81.3, 79.5, 79.0, 74.0, 73.4, 69.4, 68.6, 66.3, 66.0, 57.4; HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{55}N_4O_{10}$ 847.39127, found 847.39206.

Methyl 2-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (3I). Donor **3** and acceptor **29** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 h at -40°C) and purified by flash column chromatography (19/1 to 4/1 pentane/EtOAc) to yield glycosylation product **3I** (54.7 mg, 74 µmol, 74%, α:β = 9:1) as a white solid. R_f: 0.74 (7/2 pentane/EtOAc). IR (neat): 696, 746, 997, 1036, 1074, 1090, 1128, 1371, 1454, 2106, 2862, 2922; Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HSQC, HMBC): δ 7.54 – 7.47 (m, 4H, CH_{arom}), 7.44 – 7.25 (m, 16H, CH_{arom}), 5.66 (s, 1H, C*H*Ph), 5.60 (s, 1H, C*H*Ph'), 5.39 (d, 1H, *J* = 3.7 Hz, H-1'), 5.00 (d, 1H, *J* = 11.0 Hz, C*H*H Bn), 4.90 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.84 (d, 1H, *J* = 10.9 Hz, CH*H* Bn), 4.73 – 4.66 (m, 2H, H-1, CH*H* Bn), 4.34 – 4.24 (m, 3H, H-4, H-6, H-6'), 4.17 (dd, 1H, *J* = 10.2, 9.0 Hz, H-3'), 4.09 (dd, 1H, *J* = 3.1, 1.7 Hz, H-2), 4.00 (dd, 1H, *J* = 9.9, 3.1 Hz, H-3), 3.95 – 3.86 (m, 2H, H-5', H-6), 3.83 – 3.70 (m, 3H, H-4', H-5, H-6'), 3.36 (s, 3H, CH_3 OMe), 3.32 (dd, 1H, *J* = 10.2, 3.8 Hz, H-2'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 138.7, 138.0, 137.7, 137.2 (C_q), 129.2, 129.0, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.6, 127.4, 126.2, 126.0 (CH_{arom}), 101.7 (CHPh), 101.5 (CHPh'), 101.0 (C-1), 99.8 (C-1'), 82.9 (C-4'), 79.4 (C-4), 75.9 (C-3), 75.6 (C-3'), 75.5 (C-2), 75.3, 73.3 (CH_2 Bn), 69.0, 68.9 (C-6, C-6'), 64.1 (C-5), 63.3 (C-5'), 63.0 (C-2'), 55.0 (OMe); Diagnostic peaks β-anomer: ^{1}H NMR ($CDCl_3$, 400

MHz): δ 4.43 (d, 0.1H, *J* = 8.0 Hz, H-1'), 3.62 (dd, 0.1H, *J* = 9.6, 8.0 Hz, H-2'), 3.51 (t, 0.1H, *J* = 9.3 Hz, H-4); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 102.0 (C-1'), 78.5 (C-4), 66.4 (C-2'); HRMS: $[M+NH_4]^+$ calcd for $C_{41}H_{47}N_4O_{10}$ 755.32867, found 755.32921.

2,2,2-Trifluoroethyl 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (3J). Donor **3** and 2,2,2-trifluoroethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 1 h at -40°C) and purified by flash column chromatography (1/0 to 0/1 pentane/toluene to 5% EtOAc in toluene) to yield glycosylation product **3J** (44 mg, 94 µmol, 94%, α:β = > 20:1) as a colorless oil. R_f: 0.24 (toluene). $[\alpha]_D^{23}$ = +25.9° (*c* = 0.88, DCM); IR (neat): 697, 747, 1001, 1034, 1090, 1165, 1279, 1373, 2108, 2865, 2934; Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.51 – 7.48 (m, 2H, CH_{arom}), 7.42 – 7.28 (m, 8H, CH_{arom}), 5.58 (s, 1H, C*H*Ph), 4.99 – 4.94 (m, 2H, C*H*H Bn, H-1), 4.80 (d, 1H, *J* = 10.9 Hz, CH*H* Bn), 4.29 (dd, 1H, *J* = 10.2, 4.8 Hz, H-6), 4.10 (dd, 1H, *J* = 10.0, 9.0 Hz, H-3), 3.98 (qd, 2H, *J* = 8.5, 3.1 Hz, C*H*$_2$-CF$_3$), 3.91 (td, 1H, *J* = 9.9, 4.8 Hz, H-5), 3.79 – 3.70 (m, 2H, H-4, H-6), 3.43 (dd, 1H, *J* = 10.0, 3.7 Hz, H-2); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.8, 137.1 (C_q), 129.3, 128.6, 128.5, 128.3, 128.1, 126.1 (CH_{arom}), 123.5 (q, *J* = 278.5 Hz), 101.6 (CHPh), 99.4 (C-1), 82.5 (C-4), 75.9 (C-3), 75.3 (CH_2 Bn), 68.7 (C-6), 65.4 (q, *J* = 35.4 Hz), 63.5 (C-5), 62.7 (C-2); ^{13}C-HMBC-GATED NMR ($CDCl_3$, 101 MHz): δ 102.5 ($J_{C1,H1}$ = 173 Hz, C-1); Diagnostic peaks β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.44 (d, 0.03H, *J* = 7.9 Hz, H-1), 4.34 (dd, 0.03H, *J* = 10.8, 5.3 Hz, H-6), 3.56 (t, 0.03H, *J* = 9.2 Hz), 3.48 (dd, 0.03H, *J* = 10.0, 7.9 Hz, H-2); ^{13}C-HMBC-GATED NMR ($CDCl_3$, 101 MHz): δ 102.4 (J_{C-H} = 150 Hz, C-1); HRMS: $[M+NH_4]^+$ calcd for $C_{22}H_{26}F_3N_4O_5$ 483.18498 found 483.18463.

1,1,1,3,3,3-Hexafluoro-2-propyl 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (3K). Donor **3** and 1,1,1,3,3,3-hexafluoroisopropanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 72 h at -40°C) and purified by flash column chromatography (1/0 to 9/1 pentane/EtOAc) to yield glycosylation product **3K** (28.1 mg, 53 µmol, 53%, α:β = > 20:1) as a colorless oil. $[\alpha]_D^{23}$ = +25.8° (*c* = 0.5, $CHCl_3$); IR (neat): 689, 748, 999, 1092, 1196, 1219, 1287, 1368, 2108, 2868, 2928; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.54 – 7.45 (m, 2H, CH_{arom}), 7.44 – 7.27 (m, 8H, CH_{arom}), 5.59 (s, 1H, C*H*Ph), 5.13 (d, 1H, *J* = 3.9 Hz, H-1), 4.99 (d, 1H, *J* = 10.8 Hz, C*H*H Bn), 4.82 (d, 1H, *J* = 10.8 Hz, CH*H* Bn), 4.40 (hept, 1H, *J* = 5.9 Hz, CH HFIP), 4.26 (dd, 1H, *J* = 10.3, 4.9 Hz, H-6), 4.10 (dd, 1H, *J* = 10.0, 9.1 Hz, H-3), 3.98 (td, 1H, *J* = 10.0, 4.9 Hz, H-5), 3.80 – 3.73 (m, 2H, H-4, H-6), 3.51 (dd, 1H, *J* = 10.1, 3.9 Hz, H-2); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.6, 136.9 (C_q), 129.3, 128.6, 128.5, 128.4, 128.2, 126.1 (CH_{arom}), 120.9 (q, *J* = 283 Hz, CF_3), 101.6 (CHPh), 101.0 (C-1), 82.1 (C-4), 75.9 (C-3), 75.5 (CH_2 Bn), 74.0, 73.7 (hept, *J* = 32.8 Hz, CH HFIP), 68.3 (C-6), 64.2 (C-5), 62.5 (C-2); HRMS: $[M+H]^+$ calcd for $C_{23}H_{21}F_6N_3O_5$ 534.14582, found 534.14569.

Ethyl 2-azido-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (4A). Donor **4** and ethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations and purified by flash column chromatography (1/1/0 to 0/1/0 to 0/19/1 pentane/toluene/EtOAc) to yield glycosylation product **4A** (36 mg, 85 µmol, 85%, α:β = < 1:20) as a white solid. R_f: 0.44 (19/1 toluene/EtOAc). $[\alpha]_D^{23}$ = -53.7° (*c* = 1.04, DCM); IR (thin film): 709, 1001, 1026, 1070, 1094, 1180, 1263, 1375, 1726, 2110, 2872; Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.11 – 8.05 (m, 2H, CH_{arom}), 7.60 – 7.55 (m, 1H, CH_{arom}), 7.48 – 7.43 (m, 2H, CH_{arom}), 7.40 – 7.35 (m, 2H, CH_{arom}), 7.32 – 7.27 (m, 3H, CH_{arom}), 5.50 (s, 1H, C*H*Ph), 5.40 (t, 1H, *J* = 9.8 Hz, H-3), 4.59 (d, 1H, *J* = 7.9 Hz, H-1), 4.38 (dd, 1H, *J* = 10.6, 5.0 Hz, H-6), 4.02 (dq, 1H, *J* = 9.5, 7.1 Hz, C*H*H Et), 3.83 (t, 1H, *J* = 10.3 Hz, H-6), 3.80 – 3.67 (m, 2H, H-4, CH*H* Et), 3.64 (dd, 1H, *J* = 10.0, 7.9 Hz, H-2), 3.56 (td, 1H, *J* = 9.7, 5.0 Hz, H-5), 1.32 (t, 3H, *J* = 7.1 Hz, CH_3 Et); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 165.5 (C=O Bz), 136.9 (C_q), 133.4, 130.1 (CH_{arom}), 129.7 (C_q), 129.2, 128.6, 128.3, 126.2 (CH_{arom}), 102.8 (C-1), 101.6 (CHPh), 79.0 (C-4), 71.8 (C-3), 68.7 (C-6), 66.6, 66.6 (C-5, CH_2 Et), 65.0 (C-2), 15.2 (CH_3 Et); Diagnostic peaks α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 5.88 (t, 0.03H, *J* = 9.9 Hz, H-3), 5.53 (s, 0.03H, C*H*Ph), 5.06 (d, 0.03H, *J* = 3.6 Hz, H-1), 4.32 (dd, 0.03H, *J* = 10.4, 4.9 Hz, H-6), 3.32 (dd, 0.03H, *J* = 10.3, 3.6 Hz, H-2); HRMS: $[M+NH_4]^+$ calcd for $C_{22}H_{27}N_4O_6$ 443.19251 found 443.19234.

Cyclohexyl 2-azido-3-*O*-benozyl-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (4B). Donor **4** and cyclohexanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations and purified by flash column chromatography (1/1/0 to 0/1/0 to 0/19/1 pentane/toluene/EtOAc) to yield glycosylation product **4B** (43.6 mg, 91 µmol, 91%, α:β = < 1:20) as a white solid. R_f: 0.18 (toluene). $[\alpha]_D^{23}$ = -41.2° (*c* = 0.87, DCM); IR (thin film): 613, 708, 999, 1096, 1263, 1730, 2110, 2859, 2934; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.11 – 8.05 (m, 2H, CH_{arom}), 7.61 – 7.54 (m, 1H, CH_{arom}), 7.49 – 7.42 (m, 2H, CH_{arom}), 7.41 – 7.35 (m, 2H, CH_{arom}), 7.31 – 7.27 (m, 3H, CH_{arom}), 5.50 (s, 1H, C*H*Ph), 5.38 (t, 1H, *J* = 9.9 Hz, H-3), 4.70 (d, 1H, *J* = 7.9 Hz, H-1), 4.37 (dd, 1H, *J* = 10.6, 5.0 Hz, H-6), 3.89 – 3.71 (m, 3H, H-4, H-6, C*H*O Cyc), 3.64 (dd, 1H, *J* = 10.1, 7.9 Hz, H-2), 3.55 (td, 1H, *J* = 9.8, 5.0 Hz, H-5), 2.04 – 1.90 (m, 2H, 2xC*H*H Cyc), 1.85 – 1.73 (m, 2H, 2xC*H*H Cyc), 1.58 – 1.40 (m, 3H, C*H*H Cyc, 2xCH*H* Cyc), 1.39 – 1.20 (m, 3H, 3xCH*H* Cyc); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 165.5 (C=O Bz), 136.9 (C_q), 133.4, 130.0 (CH_{arom}), 129.7 (C_q), 129.2, 128.5, 128.3, 126.2 (CH_{arom}), 101.6 (CHPh), 101.2 (C-1), 79.0 (C-4), 78.8 (CH Cyc), 71.8 (C-3), 68.7 (C-6), 66.6 (C-5), 65.2 (C-2), 33.7, 31.7, 25.6, 24.1, 23.9 (CH_2 Cyc); HRMS: $[M+NH_4]^+$ calcd for $C_{26}H_{33}N_4O_6$ 497.23946 found 497.23932.

Methyl 6-*O*-(2-azido-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (4C). Donor **4** and acceptor **25** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 h at -40°C) and purified by flash column chromatography (19/1 to 3/1 pentane/EtOAc) to yield glycosylation product **4C** (67 mg, 79 µmol, 79%, α:β = 1:14) as a white solid. R_f: 0.24 (4/1 pentane/EtOAc). $[\alpha]_D^{20}$ = -17.5° (*c* = 1.34, $CHCl_3$); IR (thin film): 696, 748, 1002, 1028, 1068, 1092, 1263, 1313, 1369, 1452, 1730, 2110, 2872, 2918; Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.09 – 8.04 (m, 2H, CH_{arom}), 7.60 – 7.53 (m, 1H, CH_{arom}), 7.48 – 7.41 (m, 2H, CH_{arom}), 7.40 – 7.24 (m, 20H, CH_{arom}), 5.47 (s, 1H, C*H*Ph), 5.42 (t, 1H, *J* = 9.8 Hz, H-3'), 5.00 (d, 1H, *J* = 10.9 Hz, C*H*H Bn), 4.95 (d, 1H, *J* = 11.1 Hz, C*H*H Bn), 4.84 (d, 1H, *J* = 11.0 Hz, CH*H* Bn), 4.80 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.68 – 4.63 (m, 2H, 2xCH*H* Bn), 4.61 (d, 1H, *J* = 3.5 Hz, H-1), 4.43 (d, 1H, *J* = 8.0 Hz, H-1'), 4.33 (dd, 1H, *J* = 10.5, 5.0 Hz, H-6'), 4.12 (d, 1H, *J* = 9.1 Hz, H-6), 4.02 (t, 1H, *J* = 9.3 Hz, H-3), 3.84 – 3.72 (m, 4H, H-4', H-5, H-6, H-6'), 3.69 (dd, 1H, *J* = 9.9, 8.0 Hz, H-2'), 3.57 (t, 1H, *J* = 9.2 Hz, H-4), 3.54 (dd, 1H, *J* = 9.7, 3.6 Hz, H-2), 3.49 (td, 1H, *J* = 9.8, 5.0 Hz, H-5'), 3.39 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 165.4 (C=O), 138.7, 138.3, 138.2, 136.7 (CH_{arom}), 133.5, 130.0 (CH_{arom}), 129.4 (C_q Bz), 129.1, 128.6, 128.6, 128.5, 128.5, 128.3, 128.3, 128.1, 128.0, 128.0, 127.9, 127.9, 127.7, 126.1 (CH_{arom}), 102.6 (C-1'), 101.5 (CHPh), 98.3 (C-1), 82.1 (C-3), 79.8 (C-2), 78.7 (C-4'), 77.7 (C-4), 75.8, 75.0, 73.6 (CH_2 Bn), 71.9 (C-3'), 69.7 (C-5), 68.9 (C-6), 68.5 (C-6'), 66.6 (C-5'), 65.2 (C-2'), 55.4 (CH_3 OMe); Diagnostic peaks α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.79 (t, 0.07H, *J* = 9.9 Hz, H-3'), 5.50 (s, 0.07H, C*H*Ph), 5.08 (d, 0.07H, *J* = 3.5 Hz, H-1'), 4.24 (dd, 0.07H, *J* = 10.3, 4.8 Hz, H-6'), 3.41 (s, 0.21H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 101.7 (CHPh), 99.3 (C-1'), 98.1 (C-1), 82.1, 80.0, 79.7, 77.6, 75.8, 75.2, 70.0, 69.4, 67.0, 62.8, 62.1, 55.4; HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{53}N_4O_{11}$ 861.37053, found 861.37064.

2-Fluoroethyl 2-azido-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranoside (4D). Donor **4** and 2-fluoroethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations and purified by flash column chromatography (1/1/0 to 0/1/0 to 0/16/1 pentane/toluene/EtOAc) to yield glycosylation product **4D** (36.6 mg, 83 µmol, 83%, α:β = 1:6.5) as a white solid. R_f: 0.41 (19/1 toluene/EtOAc). IR (thin film): 700, 748, 879, 1001, 1026, 1070, 1093, 1179, 1261, 1722, 2108, 2868; Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.10 – 8.05 (m, 2H, CH_{arom}), 7.61 – 7.54 (m, 1H, CH_{arom}), 7.49 – 7.43 (m, 2H, CH_{arom}), 7.41 – 7.36 (m, 2H, CH_{arom}), 7.33 – 7.27 (m, 3H, CH_{arom}), 5.50 (s, 1H, C*H*Ph), 5.41 (t, 1H, *J* = 9.8 Hz, H-3), 4.69 (ddt, 1H, *J* = 4.6, 3.2, 1.8 Hz, C*H*H-CH_2F), 4.65 (d, 1H, *J* = 7.9 Hz, H-1), 4.58 (ddt, 1H, *J* = 4.5, 3.3, 1.8 Hz, CH*H*-CH_2F), 4.38 (dd, 1H, *J* = 10.5, 4.9 Hz, H-6), 4.14 (dddd, 1H, *J* = 30.3, 11.9, 4.6, 3.1 Hz, C*H*HF), 3.95 (dddd, 1H, *J* = 27.1, 12.1, 5.5, 3.4 Hz, CH*H*F), 3.83 (t, 1H, *J* = 10.3 Hz, H-6), 3.79 (t, 1H, *J* = 9.5 Hz, H-4), 3.69 (dd, 1H, *J* = 10.0, 7.9 Hz, H-2), 3.57 (td, 1H, *J* = 9.7, 5.0 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 165.4 (C=O), 136.8 (C_q Ph), 133.5, 130.0 (CH_{arom}), 129.5 (C_q Bz), 129.2, 128.6, 128.5, 128.3, 126.3, 126.2 (CH_{arom}), 103.0 (C-1), 101.6 (CHPh), 82.5 (d, *J* = 170.5 Hz, *C*H$_2$F), 78.8 (C-4), 71.7 (C-3), 69.5 (d, *J* = 20.2 Hz, *C*H$_2$-CH$_2$F), 68.5 (C-6), 66.7 (C-5), 64.9 (C-2); Diagnostic peaks α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.89 (t, 0.17H, *J* = 9.9 Hz, H-3), 5.53 (s, 0.17H, C*H*Ph), 5.12 (d, 0.17H, *J* = 3.6 Hz, H-1), 4.33 (dd, 0.17H, *J* = 10.4, 5.0 Hz, H-6), 3.38 (dd, 0.17H, *J* = 10.4, 3.6 Hz, H-2); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 101.8, 99.5 (C-1), 82.4 (d, *J* = 170.8 Hz), 79.6, 68.9, 67.8 (d, *J* = 20.2 Hz), 63.1, 61.8; HRMS: $[M+NH_4]^+$ calcd for $C_{22}H_{26}FN_4O_6$ 461.18309 found 461.18292.

Methyl 4-*O*-(2-azido-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (4E). Donor **4** and acceptor **26** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 h at -40°C) and purified by flash column chromatography (19/1 to 4/1 pentane/EtOAc) to yield glycosylation product **4E** (60 mg, 71 µmol, 71%, α:β = 1:6) as a white solid. R_f: 0.67 (4/1 pentane/EtOAc). IR (thin film): 696, 733, 914, 999, 1026, 1045, 1090, 1177, 1263, 1314, 1366, 1452, 1730, 2108, 2866, 2899; Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.10 – 8.04 (m, 2H, CH_{arom}), 7.61 – 7.53 (m, 1H, CH_{arom}), 7.49 – 7.24 (m, 22H, CH_{arom}), 5.40 (s, 1H, C*H*Ph), 5.19 (t, 1H, *J* = 9.8 Hz, H-3'), 4.90 (d, 1H, *J* = 10.8 Hz, C*H*H Bn), 4.83 (d, 1H, *J* = 10.8 Hz, CH*H* Bn), 4.81 – 4.73 (m, 2H, 2xC*H*H Bn), 4.67 – 4.60 (m, 2H, CH*H* Bn, H-1), 4.42 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.31 (d, 1H, *J* = 8.0 Hz, H-1'), 4.17 (dd, 1H, *J* = 10.6, 5.0 Hz, H-6'), 4.08 – 3.98 (t, 1H, *J* = 9.4 Hz, H-4), 3.96 (dd, 1H, *J* = 10.8, 2.4 Hz, H-6), 3.86 (t, 1H, *J* = 9.3 Hz, H-3), 3.79 – 3.74 (m, 1H, H-5), 3.71 (dd, 1H, *J* = 10.7, 1.7 Hz, H-6), 3.61 (t, 1H, *J* = 9.5 Hz, H-4'), 3.54 (dd, 1H, *J* = 9.6, 3.7 Hz, H-2), 3.52 – 3.45 (m, 2H, H-2', H-6'), 3.39 (s, 3H, CH_3 OMe), 3.08 (td, 1H, *J* = 9.7, 5.0 Hz, H-5'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 165.3 (C=O), 139.3, 138.3, 137.6, 136.9 (C_q), 133.4, 129.9 (CH_{arom}), 128.9 (C_q Bz), 128.6, 128.5, 128.5, 128.3, 128.3, 128.2, 127.9, 127.8, 126.2 (CH_{arom}), 101.5, 101.4 (CHPh, C-1'), 98.4 (C-1), 80.1 (C-3), 79.1 (C-2), 78.9 (C-4'), 76.8 (C-4), 75.6, 73.7, 73.6 (CH_2 Bn), 72.0 (C-3'), 69.7 (C-5), 68.6 (C-6'), 67.8 (C-6), 66.1 (C-5'), 65.6 (C-2'), 55.5 (OMe); Diagnostic peaks α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.91 (d, 0.17H, *J* = 3.9 Hz, H-1'), 5.80 (t, 0.17H, *J* = 10.0 Hz, H-3'), 5.47 (s, 0.17H, C*H*Ph), 5.15 (d, 0.17H, *J* = 10.7 Hz, C*H*H Bn), 4.74 (d, 0.17H, *J* = 12.0 Hz, C*H*H Bn), 4.09 (t, 0.17H, *J* = 9.2 Hz), 3.29 (dd, 0.17H, *J* = 10.5, 3.9 Hz, H-2'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 165.6, 138.6, 138.1,

137.9, 137.0, 133.4, 130.0, 129.6, 129.0, 128.6, 128.6, 128.5, 128.4, 128.2, 128.1, 127.6, 127.6, 127.4, 101.6 (CHPh), 98.6 (C-1'), 97.7 (C-1), 82.1, 80.7, 79.5, 75.0, 73.6, 73.3, 72.8, 69.5, 69.3, 68.9, 68.7, 63.7, 61.9, 55.5; HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{53}N_4O_{11}$ 861.37053, found 861.37081.

Methyl (Methyl 4-*O*-[2-azido-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl]-2,3-di-*O*-benzyl-α-D-glucopyranosyl uronate) (4F). Donor **4** and acceptor **27** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 h at -40°C) and purified by flash column chromatography (19/1 to 4/1 pentane/EtOAc) to yield glycosylation product **4F** (46 mg, 59 µmol, 59%, α:β = 1:1.4) as a white solid. R_f: 0.56 (4/1 pentane/EtOAc). IR (thin film): 698, 750, 991, 1026, 1047, 1092, 1178, 1263, 1452, 1730, 2110, 2868, 2938; Reported as a 0.7 : 1 mixture of anomers: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.09 – 8.03 (m, 3.4H, CH_{arom}), 7.61 – 7.52 (m, 1.7H, CH_{arom}), 7.49 – 7.25 (m, 28.9H, CH_{arom}), 5.76 (dd, 0.7H, *J* = 9.5, 10.3 Hz, H-3'$_\alpha$), 5.70 (d, 0.7H, *J* = 3.9 Hz, H-1'$_\alpha$), 5.47 (s, 0.7H, C*H*Ph$_\alpha$), 5.41 (s, 1H, C*H*Ph$_\beta$), 5.36 (t, 1H, *J* = 9.8 Hz, H-3'$_\beta$), 5.10 (d, 0.7H, *J* = 10.6 Hz, C*H*H Bn$_\alpha$), 4.93 (d, 1H, *J* = 10.9 Hz, C*H*H Bn$_\beta$), 4.87 (d, 1H, *J* = 10.9 Hz, CH*H* Bn$_\beta$), 4.83 (d, 0.7H, *J* = 10.6 Hz, CH*H* Bn$_\alpha$), 4.79 (d, 1H, *J* = 13.6 Hz, C*H*H Bn$_\beta$), 4.76 (d, 0.7H, *J* = 13.6 Hz, C*H*H Bn$_\alpha$), 4.66 – 4.62 (m, 2H, CH*H* Bn$_\beta$, H-1'$_\beta$), 4.61 – 4.58 (m, 2.4H, CH*H* Bn$_\alpha$, H-1$_\alpha$, H-1$_\beta$), 4.31 (dd, 0.7H, *J* = 10.0, 4.6 Hz, H-6'$_\alpha$), 4.28 (d, 0.7H, *J* = 9.7 Hz, H-5$_\alpha$), 4.23 (d, 1H, *J* = 9.9 Hz, H-5$_\beta$), 4.19 – 4.06 (m, 3.4H, H-3$_\alpha$, H-4$_\alpha$, H-4$_\beta$, H-6'$_\beta$), 3.91 (t, 1H, *J* = 9.2 Hz, H-3), 3.85 (s, 2.1H, CH_3 CO_2Me_α), 3.83 (s, 3H, CH_3 CO_2Me_β), 3.79 – 3.59 (m, 3.8H, H-2$_\alpha$, H-4'$_\alpha$, H-4'$_\beta$, H-5'$_\alpha$, H-6'$_\alpha$), 3.59 – 3.44 (m, 4H, H-2$_\beta$, H-2'$_\beta$, H-5'$_\beta$, H-6'$_\beta$), 3.43 (s, 3H, CH_3 OMe$_\beta$), 3.42 (s, 2.1H, CH_3 OMe$_\alpha$), 3.31 (dd, 1H, *J* = 10.4, 3.9 Hz, H-2'$_\alpha$); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 170.2, 169.9 (C=O CO_2Me), 165.5, 165.3 (C=O Bz), 139.1, 138.4, 138.0, 137.7, 137.0, 136.8 (C_q Bn, CHPh), 133.4, 133.4, 130.0, 130.0 (CH_{arom}), 129.5, 129.5 (C_q Bz), 129.1, 129.1, 128.7, 128.6, 128.5, 128.5, 128.5, 128.3, 128.3, 128.2, 128.1, 127.8, 127.7, 127.6, 127.5, 126.2, 126.2 (CH_{arom}), 102.3 (C-1'$_\beta$), 101.7 (CHPh$_\alpha$), 101.5 (CHPh$_\beta$), 99.0 (C-1'$_\alpha$), 98.8 (C-1$_\beta$), 98.5 (C-1$_\alpha$), 81.1 (C-3$_\alpha$), 79.9 (C-2$_\alpha$), 79.5, 79.5 (C-3$_\beta$, C-4$_\beta$), 79.2 (C-4'$_\alpha$), 78.9, 78.7 (C-2$_\beta$, C-4'$_\beta$), 75.7, 75.4 (CH_2 Bn), 75.2 (C-4$_\alpha$), 73.9, 73.6 (CH_2 Bn), 71.9 (C-3'$_\beta$), 69.8, 69.8 (C-5$_\alpha$, C-5$_\beta$), 69.6 (C-3'$_\alpha$), 68.5, 68.4 (C-6'$_\alpha$, C-6'$_\beta$), 66.5 (C-5'$_\beta$), 65.6 (C-2'$_\beta$), 63.2 (C-5'$_\alpha$), 61.7 (C-2'$_\alpha$), 56.0, 56.0 (CH_3 OMe), 53.1, 53.0 (CH_3 CO_2Me); HRMS: $[M+NH_4]^+$ calcd for $C_{42}H_{47}N_4O_{12}$ 799.31850, found 799.31869.

2,2-Difluoroethyl 2-azido-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranoside (4G). Donor **4** and 2,2-difluoroethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations and purified by flash column chromatography (1/1/0 to 0/1/0 to 0/19/1 pentane/toluene/EtOAc) to yield glycosylation product **4G** (38.6 mg, 84 µmol, 84%, α:β = 2.7:1) as a white solid. R_f: 0.49 (19/1 toluene/EtOAc). IR (thin film): 709, 997, 1026, 1069, 1094, 1265, 1726, 2108, 2870; Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.11 – 8.05 (m, 2H, CH_{arom}), 7.63 – 7.53 (m, 1H, CH_{arom}), 7.50 – 7.36 (m, 4H, CH_{arom}), 7.34 – 7.27 (m, 3H, CH_{arom}), 6.02 (tt, 1H, *J* = 55.1, 4.2 Hz, C*H*F_2), 5.91 – 5.81 (m, 1H, H-3), 5.53 (s, 1H, C*H*Ph), 5.11 (d, 1H, *J* = 3.6 Hz, H-1), 4.33 (dd, 1H, *J* = 10.4, 4.9 Hz, H-6), 4.07 (ddd, 1H, *J* = 14.8, 6.4, 3.7 Hz, H-5), 3.99 – 3.77 (m, 4H, H-4, H-6), 3.42 (dd, 1H, *J* = 10.4, 3.6 Hz, H-2); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 165.5 (C=O Bz), 136.8 (C_q), 133.5, 130.1 (CH_{arom}), 129.5 (C_q Bz), 128.5, 128.3, 126.2 (CH_{arom}), 113.7 (t, *J* = 241.7 Hz, CHF_2), 101.8 (CHPh), 99.8 (C-1), 79.4 (C-4), 69.3 (C-3), 68.7 (C-6), 67.6 (t, *J* = 29.0 Hz, CH_2-CHF_2), 63.5 (C-5), 61.8 (C-2); Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.97 (tdd, 0.37H, *J* = 55.2, 4.8, 3.5 Hz, C*H*F_2), 5.51 (s, 0.37H, C*H*Ph), 5.42 (t, 0.37H, *J* = 9.8 Hz, H-3), 4.63 (d, 0.37H, *J* = 7.9 Hz, H-1), 4.38 (dd, 0.37H, *J* = 10.5, 5.0 Hz, H-6), 4.12 – 3.99 (m, 0.37H, C*H*H-CHF_2), 3.98 – 3.76 (m, 1.11H, CH*H*-CHF_2, H-4, H-6), 3.69 (dd, 0.37H, *J* = 10.0, 7.9 Hz, H-2), 3.58 (td, 0.37H, *J* = 9.8, 5.0 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 165.4, 136.7, 133.5, 130.0, 129.4, 129.2, 128.6, 126.2, 113.8 (t, *J* = 241.5 Hz), 103.1, 101.7, 78.7 (C-4), 71.5 (C-3), 69.1 (t, *J* = 29.0 Hz, CH_2-CHF_2), 68.4 (C-6), 66.8 (C-5), 64.9 (C-2); HRMS: $[M+H]^+$ calcd for $C_{22}H_{22}F_2N_3O_6$ 462.14712, found 462.14699.

Methyl 4-*O*-(2-azido-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-β-D-galactopyranoside (4H). Donor **4** and acceptor **28** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 h at -40°C) and purified by flash column chromatography (19/1 to 4/1 pentane/EtOAc) to yield glycosylation product **4H** (43 mg, 52 µmol, 52%, α:β = 4:1) as a white solid. R_f: 0.36 (4/1 pentane/EtOAc). IR (thin film): 698, 737, 997, 1072, 1094, 1265, 1452, 1730, 2106, 2862, 2930; Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.12 – 8.05 (m, 2H, CH_{arom}), 7.57 (t, 1H, *J* = 7.4 Hz, CH_{arom}), 7.45 (t, 2H, *J* = 7.7 Hz, CH_{arom}), 7.42 – 7.20 (m, 20H, CH_{arom}), 5.85 (t, 1H, *J* = 9.9 Hz, H-3'), 5.44 (s, 1H, C*H*Ph), 5.07 (d, 1H, *J* = 3.9 Hz, H-1'), 4.93 (d, 1H, *J* = 11.0 Hz, C*H*H Bn), 4.84 (d, 1H, *J* = 10.9 Hz, CH*H* Bn), 4.79 (d, 1H, *J* = 12.4 Hz, C*H*H Bn), 4.74 (d, 1H, *J* = 12.4 Hz, CH*H* Bn), 4.55 (s, 2H, CH_2 Bn), 4.46 (td, 1H, *J* = 9.9, 4.9 Hz, H-5'), 4.26 (d, 1H, *J* = 7.6 Hz, H-1), 4.17 (d, 1H, *J* = 3.1 Hz, H-4), 3.93 (t, 1H, *J* = 9.1 Hz, H-6), 3.85 (dd, 1H, *J* = 10.2, 5.0 Hz, H-6'), 3.81 – 3.70 (m, 2H, H-2, H-4'), 3.64 (dd, 2H, *J* = 9.1, 5.4 Hz, H-6), 3.57 – 3.50 (m, 5H, CH_3 OMe, H-5, H-6'), 3.47 (dd, 1H, *J* = 10.4, 3.9 Hz, H-2'), 3.42 (dd, 1H, *J* = 10.0, 3.0 Hz, H-3); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 165.3 (C=O Bz), 138.7, 138.3, 137.6, 137.2 (C_q), 133.3, 130.0 (CH_{arom}), 129.8 (C_q), 128.9, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.2, 128.1, 127.9, 127.7, 127.6, 127.6, 126.3, 126.2 (CH_{arom}), 105.2 (C-1), 101.4 (CHPh), 99.4 (C-1'), 80.0 (C-4'), 79.8 (C-3), 79.0 (C-2), 75.2 (CH_2 Bn), 74.4 (C-4), 73.6, 73.2 (CH_2 Bn), 72.6 (C-5), 70.2 (C-3'), 68.8 (C-6'), 67.1 (C-6), 62.8, 62.7 (C-2', C-5'), 57.0 (OMe); Diagnostic peaks β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.47 (s, 0.25H, C*H*Ph), 5.34 (t, 0.25H, *J* = 9.8 Hz, H-3'), 4.30 (d, 0.25H, *J* = 7.7 Hz, H-1'), 4.09 (d, 0.25H, *J* = 2.7 Hz, H-4); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 105.1 (C-1), 102.7 (C-1'), 101.5 (CHPh), 81.2, 79.6, 78.9, 75.3, 74.6, 73.9, 73.6, 73.3, 71.7, 69.4, 68.5, 66.2, 65.0, 57.3; HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{53}N_4O_{11}$ 861.37053, found 861.37067.

Methyl 2-*O*-(2-azido-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (4I). Donor **4** and acceptor **29** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 h at -40°C) and purified by flash column chromatography (19/1 to 3/1 pentane/EtOAc) to yield glycosylation product **4I** (55 mg, 73 µmol, 73%, α:β = 5:1) as a white solid. R_f: 0.36 (4/1 pentane/EtOAc). IR (thin film): 671, 750, 1037, 1092, 1265, 1373, 1730, 2108, 2913; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.15 – 8.04 (m, 2H, CH_{arom}), 7.59 – 7.53 (m, 1H, CH_{arom}), 7.53 – 7.25 (m, 17H, CH_{arom}), 5.92 (dd, 1H, *J* = 10.4, 9.5 Hz, H-3'), 5.67 (s, 1H, C*H*Ph), 5.54 (s, 1H, C*H*Ph'), 5.51 (d, 1H, *J* = 3.8 Hz, H-1'), 4.94 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.73 (d, 1H, *J* = 1.5 Hz, H-1), 4.69 (d, 1H, *J* = 12.2 Hz, CH*H* Bn), 4.39 (t, 1H, *J* = 9.7 Hz, H-4), 4.32 (dd, 1H, *J* = 10.4, 4.9 Hz, H-6'), 4.27 (dd, 1H, *J* = 10.3, 4.7 Hz, H-6), 4.14 (dd, 1H, *J* = 3.1, 1.6 Hz, H-2), 4.06 – 3.99 (m, 2H, H-3, H-5'), 3.95 (t, 1H, *J* = 10.3 Hz, H-6), 3.86 – 3.77 (m, 3H, H-4', H-5, H-6'), 3.38 – 3.33 (m, 4H, CH_3 OMe, H-2'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 165.5 (C=O Bz), 138.8, 137.7, 136.8 (C_q), 133.4, 130.1 (CH_{arom}), 129.6 (C_q), 129.2, 128.9, 128.5, 128.4, 128.3, 128.3, 128.3, 128.3, 127.6, 127.6, 127.4, 126.2, 126.2, 126.2, 126.1 (CH_{arom}), 101.7, 101.6 (CHPh), 100.9 (C-1), 100.1 (C-1'), 79.7 (C-4'), 79.5 (C-4), 75.9, 75.9 (C-2, C-3), 73.6 (CH_2 Bn), 69.2 (C-3'), 68.9 (C-6), 68.8 (C-6'), 64.1 (C-5), 63.3 (C-5'), 61.9 (C-2'), 54.9 (OMe); Diagnostic peaks β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.60 (s, 0.2H, C*H*Ph), 5.50 (s, 0.2H, C*H*Ph), 5.40 (t, 0.2H, *J* = 9.8 Hz, H-3'), 4.87 (d, 0.2H, *J* = 1.4 Hz, H-1), 4.80 (d, 0.2H, *J* = 12.3 Hz, C*H*H Bn), 3.57 (td, 0.2H, *J* = 9.9, 4.3 Hz), 3.40 (s, 0.6H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 101.8 (C-1'), 100.0 (CHPh), 99.4 (C-1), 78.7, 78.5, 76.4, 74.4, 72.4, 71.5, 68.9, 68.5, 66.9, 65.1, 64.2, 55.2; HRMS: $[M+NH_4]^+$ calcd for $C_{41}H_{45}N_4O_{11}$ 769.30793, found 769.30780.

2,2,2-Trifluoroethyl 2-azido-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (4J). Donor **4** and 2,2,2-trifluoroethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 30 min at -40°C) and purified by flash column chromatography (19/1 to 17/3 pentane/EtOAc) to yield glycosylation product **4J** (41 mg, 86 µmol, 86%, α:β = > 20:1) as a white solid. R_f: 0.15 (toluene). $[\alpha]_D^{20}$ = +78.9° (*c* = 1.03, $CHCl_3$); IR (thin film): 702, 989, 1085, 1177, 1275, 1717, 2112, 2864; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.13 – 8.03 (m, 2H, CH_{arom}), 7.60 – 7.53 (m, 1H, CH_{arom}), 7.48 – 7.38 (m, 4H, CH_{arom}), 7.33 – 7.28 (m, 3H, CH_{arom}), 5.87 (t, 1H, *J* = 10.0 Hz, H-3), 5.53 (s, 1H, C*H*Ph), 5.14 (d, 1H, *J* = 3.6 Hz, H-1), 4.33 (dd, 1H, *J* = 10.4, 4.9 Hz, H-6), 4.14 – 3.97 (m, 4H, CH_2CF_3, H-5), 3.84 (t, 1H, *J* = 9.5 Hz, H-4), 3.80 (t, 1H, *J* = 10.3 Hz, H-6), 3.44 (dd, 1H, *J* = 10.4, 3.6 Hz, H-2); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 165.5 (C=O), 136.7 (C_q), 133.5, 130.0 (CH_{arom}), 129.5 (C_q Bz), 129.2, 128.5, 127.6, 126.2 (CH_{arom}), 123.42 (q, *J* = 278.6 Hz), 101.8 (CHPh), 99.9 (C-1), 79.3 (C-4), 69.1 (C-3), 68.6 (C-6), 65.41 (q, *J* = 35.6 Hz), 63.7 (C-5), 61.6 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{22}H_{24}F_3N_4O_6$ 497.16425 found 497.16425.

Ethyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)-β-D-glucopyranoside (5A). Donor **5** and ethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 1 hour at -40°C) and purified by flash column chromatography (19/1 to 8/2 pentane/EtOAc) to yield glycosylation product **5A** (32 mg, 59 µmol, 59%, α:β = <1:20) as a yellow solid alongside donor 5 (14 mg). R_f: 0.60 (7/3 pentane/EtOAc). $[\alpha]_D^{23}$ = +156.9° (*c* = 0.64, $CHCl_3$); IR (thin film): 698, 998, 1093, 1213, 1303, 1330, 1516, 1679, 2930; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.58 (s, 2H, CH pyridone), 7.56 (dd, 2H, *J* = 7.4, 2.2 Hz, CH_{arom}), 7.45 – 7.38 (m, 3H, CH_{arom}), 7.06 – 6.97 (m, 5H, CH_{arom}), 5.66 (s, 1H, C*H*Ph), 5.32 (d, 1H, *J* = 8.3 Hz, H-1), 4.70 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.57 (dd, 1H, *J* = 10.2, 8.7 Hz, H-3), 4.53 (d, 1H, *J* = 11.6 Hz, CH*H* Bn), 4.43 (dd, 1H, *J* = 10.3, 4.6 Hz, H-6), 3.99 – 3.81 (m, 4H, C*H*H Et, H-4, H-5, H-6), 3.72 (dd, 1H, *J* = 10.3, 8.3 Hz, H-2), 3.60 (dq, 1H, *J* = 9.9, 7.1 Hz, CH*H* Et), 1.08 (t, 3H, *J* = 7.1 Hz, CH_3 Et); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 160.6 (C=O pyridone), 141.7 (C_q NO_2 pyridone), 141.4 (CH pyridone), 137.1, 136.6 (C_q), 129.4, 128.9, 128.7, 128.5, 128.5, 126.3 (CH_{arom}), 101.9 (CHPh), 99.3 (C-1), 82.8 (C-4), 75.4 (C-3), 74.9 (CH_2 Bn), 73.8 (C-2), 68.7 (C-6), 66.5 (CH_2 Et), 65.7 (C-5), 15.1 (CH_3 Et); HRMS: $[M+H]^+$ calcd for $C_{27}H_{28}N_3O_{10}$ 554.17692, found 554.17642.

Cyclohexyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)-β-D-glucopyranoside (5B). Donor **5** and cyclohexanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 1 hour at -40°C) and purified by flash column chromatography (19/1 to 8/2 pentane/EtOAc) to yield 51 mg of glycosylation product **5B** as an inseperable mixture with donor 5 (13 mg 5, 38 mg **5B**, 63 µmol, 63%, α:β =< 1:20) as a yellow solid. R_f: 0.75 (7/3 pentane/EtOAc). R_f: 0.55 (7/3 pentane/EtOAc); IR: (thin film): 697, 718, 749, 789, 910, 997, 1092, 1212, 1302, 1330, 1516, 1623, 1674, 2931; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.60 (s, 2H, CH pyridone), 7.56 (d, 2H, *J* = 4.7 Hz, CH_{arom}), 7.48 – 7.33 (m, 3H, CH_{arom}), 7.10 – 6.96 (m, 5H, CH_{arom}), 5.65 (s, 1H, C*H*Ph), 5.41 (d, 1H, *J* = 8.2 Hz, H-1), 4.71 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.66 – 4.50 (m, 2H, CH*H* Bn, H-3), 4.44 (dd, 1H, *J* = 10.6, 5.2 Hz, H-6), 3.98 – 3.80 (m, 3H, H-4, H-5, H-6), 3.79 – 3.61 (m, 2H, C*H* Cy, H-2), 1.91 – 1.77 (m, 1H, CH_2 Cy), 1.71 – 1.54 (m, 2H, CH_2 Cy), 1.54 – 1.45 (m, 1H, CH_2 Cy), 1.43 – 0.96 (m, 6H, CH_2 Cy); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 160.5 (C=O pyridone), 141.6 (C_q NO_2 pyridone), 141.4 (CH pyridone), 137.1, 136.7 (C_q), 128.8, 128.6, 128.4,

126.3 (CH_{arom}), 101.9 (CHPh), 98.1 (C-1), 82.7 (C-4), 78.8 (CH Cy), 75.6 (C-3), 74.8 (CH_2 Bn), 74.0 (C-2), 68.8 (C-6), 65.7 (C-5), 33.3, 31.7, 25.3, 23.9, 23.6 (CH_2 Cy); HRMS: $[M+H]^+$ calcd for $C_{31}H_{34}N_3O_{10}$ 608.22387, found 608.22352.

Methyl 6-*O*-(3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (3C). Donor **5** and acceptor **25** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 hours at -40°C) and purified by flash column chromatography (9/1 to 7/3 pentane/EtOAc) to yield glycosylation product **5C** (55 mg, 54 µmol, 54%, α:β = <1:20) as a yellow solid. R_f: 0.45 (7/3 pentane/EtOAc). $[\alpha]_D^{20}$ = +90.5° (*c* = 0.92, $CHCl_3$); IR (thin film): 698, 1001, 1069, 1094, 1213, 1331, 1454, 1522, 1678, 2868; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.19 (s, 2H, CH pyridone), 7.54 (dd, 2H, *J* = 7.6, 2.1 Hz, CH_{arom}), 7.45 – 7.38 (m, 3H, CH_{arom}), 7.34 – 7.22 (m, 13H, CH_{arom}), 7.20 – 7.12 (m, 5H, CH_{arom}), 7.04 (dd, 2H, *J* = 6.6, 2.9 Hz, CH_{arom}), 5.66 (s, 1H, C*H*Ph), 4.92 (d, 1H, *J* = 11.0 Hz, C*H*H Bn), 4.85 (d, 1H, *J* = 8.3 Hz, H-1'), 4.83 – 4.66 (m, 2H, 2xC*H*H Bn), 4.72 (d, 1H, *J* = 10.9 Hz, CH*H* Bn), 4.69 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.60 (d, 1H, *J* = 12.2 Hz, CH*H* Bn), 4.60 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.46 (d, 1H, *J* = 3.4 Hz, H-1), 4.39 (dd, 1H, *J* = 10.6, 5.0 Hz, H-6'), 4.34 (d, 1H, *J* = 11.3 Hz, CH*H* Bn), 4.10 (t, 1H, *J* = 7.9 Hz, H-3'), 4.01 (dd, 1H, *J* = 10.8, 1.8 Hz, H-6), 3.91 (t, 1H, *J* = 9.2 Hz, H-3), 3.89 – 3.82 (m, 2H, H-4', H-6), 3.77 – 3.69 (m, 2H, H-2', H-5), 3.65 (td, 1H, *J* = 9.7, 5.0 Hz, H-5'), 3.52 (dd, 1H, *J* = 10.8, 7.1 Hz, H-6), 3.39 (dd, 1H, *J* = 9.6, 3.5 Hz, H-2), 3.21 (s, 3H, CH_3 OMe), 3.13 (dd, 1H, *J* = 9.9, 8.9 Hz, H-4); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 159.4 (C=O pyridone), 141.7 (C_q NO_2 pyridone), 140.2 (CH pyridone), 138.6, 138.0, 138.0, 136.7, 135.8 (C_q), 129.5, 129.1, 129.0, 128.6, 128.5, 128.5, 128.5, 128.2, 128.1, 128.0, 128.0, 127.9, 127.7, 127.6, 126.1 (CH_{arom}), 101.8 (CHPh), 100.1 (C-1'), 97.9 (C-1), 82.3 (C-4'), 81.6 (C-3), 79.8 (C-2), 78.2 (C-4), 75.7, 74.8, 74.3, (CH_2 Bn), 74.0 (C-3'), 73.3 (CH_2 Bn), 72.7 (C-2'), 70.4 (C-6), 69.3 (C-5), 68.4 (C-6'), 66.1 (C-5'), 55.1 (OMe); ^{13}C-HMBC-GATED NMR ($CDCl_3$, 101 MHz): δ 100.1 (*J* = 163 Hz, C-1'); HRMS: $[M+H]^+$ calcd for $C_{53}H_{54}N_3O_{15}$ 972.35494, found 972.35546.

2-Fluoroethyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)-β-D-glucopyranoside (5D). Donor **5** and 2-fluoroethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 1 hour at -40°C) and purified by flash column chromatography (19/1 to 8/2 pentane/EtOAc) to yield glycosylation product **5D** (24 mg, 43 µmol, 43%, α:β =< 1:20) as a yellow solid alongside donor 5 (15.6 mg). R_f: 0.42 (3/2 pentane/EtOAc). $[\alpha]_D^{23}$ = +142.9° (*c* = 0.48, $CHCl_3$); IR (thin film): 698, 752, 1070, 1096, 1213, 1304, 1331, 1518, 1680, 2870, 3064; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.58 (s, 2H, CH pyridone), 7.63 – 7.49 (m, 2H, CH_{arom}), 7.47 – 7.36 (m, 3H, CH_{arom}), 7.09 – 6.96 (m, 5H, CH_{arom}), 5.66 (s, 1H, C*H*Ph), 5.46 (d, 1H, *J* = 8.3 Hz, H-1), 4.71 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.57 (dd, 1H, *J* = 10.3, 8.7 Hz, H-3), 4.53 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.48 – 4.42 (m, 2H, C*H*HF, H-6), 4.33 (t, 1H, *J* = 4.1 Hz, CH*H*F), 4.09 – 3.81 (m, 5H, C*H*$_2$-CH_2F, H-4, H-5, H-6), 3.77 (dd, 1H, *J* = 10.3, 8.4 Hz, H-2); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 160.6 (C=O pyridone), 141.5, 141.5 (C_q NO_2, CH pyridone), 137.0, 136.6 (C_q), 129.4, 129.0, 128.7, 128.6, 128.5, 126.3 (CH_{arom}), 101.9 (CHPh), 99.8 (C-1), 82.7 (C-4), 82.5 (d, *J* = 169.4 Hz, CH_2F), 75.3 (C-3), 74.9 (CH_2 Bn), 73.6 (C-2), 69.5 (d, *J* = 19.5 Hz, *C*H_2-CH_2F), 68.6 (C-6), 65.8 (C-5); HRMS: $[M+H]^+$ calcd for $C_{27}H_{27}FN_3O_{10}$ 572.16760, found 572.16705.

Methyl 4-*O*-(3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)-β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (5E). Donor **5** and acceptor **26** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 hours at -40°C) and purified by flash column chromatography (9/1 to 7/3 pentane/EtOAc) to yield glycosylation product **5E** (54 mg, 56 µmol, 56%, α:β = <1:20) as a yellow solid. R_f: 0.37 (7/3 pentane/EtOAc). $[\alpha]_D^{23}$ = +83.3° (*c* = 0.84, $CHCl_3$); IR (thin film): 696, 734, 997, 1028, 1039, 1092, 1209, 1302, 1327, 1454, 1522, 1682, 2862, 2900, 3030, 3065; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC, HMBC, NOESY): δ 7.74 (s, 2H, CH pyridone), 7.57 – 7.53 (m, 2H, CH_{arom}), 7.49 – 7.38 (m, 8H, CH_{arom}), 7.36 – 7.25 (m, 13H, CH_{arom}), 7.04 – 7.00 (m, 2H, CH_{arom}), 5.57 (s, 1H, C*H*Ph), 4.90 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.77 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.74 (d, 1H, *J* = 12.3 Hz, C*H*H Bn), 4.69 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.66 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.63 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.56 (d, 1H, *J* = 12.3 Hz, CH*H* Bn), 4.54 (d, 1H, *J* = 3.6 Hz, H-1), 4.35 (d, 1H, *J* = 8.2 Hz, H-1'), 4.27 – 4.20 (m, 2H, CH*H* Bn, H-6'), 3.92 (t, 1H, *J* = 9.5 Hz, H-4), 3.70 (t, 1H, *J* = 9.3 Hz, H-3), 3.67 (t, 1H, *J* = 9.0 Hz, H-4'), 3.58 (t, 1H, *J* = 10.4 Hz, H-6'), 3.53 – 3.45 (m, 2H, H-2, H-3'), 3.43 (dd, 1H, *J* = 11.4, 1.5 Hz, H-6), 3.40 – 3.34 (m, 1H, H-5), 3.31 (s, 2H, CH_3 OMe), 3.18 (dd, 1H, *J* = 10.5, 8.3 Hz, H-2'), 3.04 (dd, 1H, *J* = 11.3, 2.6 Hz, H-6), 2.92 (td, 1H, *J* = 9.8, 5.1 Hz, H-5'); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC, HMBC): δ 159.3 (C=O pyridone), 141.8 (C_q NO_2 pyridone), 139.6 (CH pyridone), 139.4, 138.1, 137.8, 136.8, 135.7 (C_q), 129.6, 129.3, 129.2, 129.0, 128.9, 128.6, 128.6, 128.5, 128.4, 128.1, 128.1, 127.8, 126.1 (CH_{arom}), 101.8 (CHPh), 98.1 (C-1), 97.6 (C-1'), 82.4 (C-4'), 79.7 (C-2), 79.2 (C-3), 75.3 (CH_2 Bn), 74.4 (C-4), 73.9, 73.6, 73.5 (CH_2 Bn), 73.0 (C-3'), 72.5 (C-2'), 69.2 (C-5), 68.4 (C-6'), 68.1 (C-6), 65.6 (C-5'), 55.7 (OMe); HRMS: $[M+H]^+$ calcd for $C_{53}H_{54}N_3O_{15}$ 972.35494, found 972.35519.

Methyl (Methyl 4-*O*-[3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)-α/β-D-glucopyranosyl]-2,3-di-*O*-benzyl-α-D-glucopyranosyl uronate) (5F). Donor **5** and acceptor **27** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 hours at -40°C) and purified by flash column chromatography (9/1 to 7/3 pentane/EtOAc) to yield glycosylation product **5F** (27 mg, 30 µmol, 30%, α:β = 1:3.6) as a yellow solid. R_f: 0.51 (7/3 pentane/EtOAc). IR (thin film): 648, 698, 733, 789, 910, 995, 1090, 1171, 1209, 1302, 1331, 1454, 1520, 1678, 1744, 2932; Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC, HMBC): δ 8.06 (s, 2H, CH pyridone), 7.50 (dd, 2H, *J* = 7.3, 2.0 Hz, CH_{arom}), 7.45 – 7.35 (m, 6H, CH_{arom}), 7.33 – 7.18 (m, 9H, CH_{arom}), 7.03 (dd, 2H, *J* = 6.9, 2.2 Hz, CH_{arom}), 6.96 (dd, 1H, *J* = 14.5, 6.9 Hz, CH_{arom}), 5.55 (s, 1H, C*H*Ph), 5.17 (d, 1H, *J* = 8.2 Hz, H-1'), 4.92 (d, 1H, *J* = 11.3 Hz, C*H*H Bn), 4.82 – 4.72 (m, 3H, CH*H* Bn, 2xC*H*H Bn), 4.61 – 4.55 (m, 2H, 2xCH*H* Bn), 4.51 (d, 1H, *J* = 3.3 Hz, H-1), 4.14 (dd, 1H, *J* = 10.6, 4.8 Hz, H-6'), 3.97 – 3.88 (m, 2H, H-3', H-4), 3.83 (d, 1H, *J* = 9.7 Hz, H-5), 3.82 – 3.73 (m, 2H, H-3, H-4'), 3.54 – 3.43 (m, 6H, CH_3 CO_2Me, H-2, H-2', H-5'), 3.42 – 3.36 (m, 4H, CH_3 OMe, H-6'); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC, HMBC): δ 170.0 (C=O CO_2Me), 159.5 (C=O pyridone), 141.5 (C_q NO_2 pyridone), 140.4 (CH pyridone), 139.1, 137.8, 136.7, 135.7 (C_q), 129.5, 129.2, 129.2, 129.1, 129.0, 128.9, 128.7, 128.7, 128.6, 128.5, 128.4, 128.2, 128.2, 127.7, 127.7, 126.1, 126.0, 125.7 (CH_{arom}), 101.7 (*C*HPh), 98.8 (C-1'), 98.3 (C-1), 82.3 (C-4'), 79.1 (C-3), 78.8 (C-2), 77.8 (C-4), 75.5, 74.2 (CH_2 Bn), 74.0 (C-3'), 73.7 (CH_2 Bn), 72.9 (C-2'), 68.8 (C-5), 68.2 (C-6'), 65.9 (C-5'), 56.1 (OMe), 52.9 (CO_2Me); ^{13}C-HMBC-GATED NMR ($CDCl_3$, 101 MHz): δ 98.8 (*J* = 167 Hz, C-1'); Diagnostic peaks α-anomer: ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 5.74 (d, 0.28H, *J* = 3.9 Hz, H-1'), 5.61 (s, 0.28H, C*H*Ph), 5.03 (d, 0.28H, *J* = 12.7 Hz, C*H*H Bn), 4.70 (d, 0.28H, *J* = 12.3 Hz), 4.62 (d, 0.28H, *J* = 12.2 Hz, C*H*H Bn), 4.46 (d, 0.28H, *J* = 12.3 Hz, CH*H* Bn), 4.37 (dd, 0.28H, *J* = 10.5, 4.9 Hz, H-6'), 4.29 (d, 0.28H, *J* = 9.9 Hz, H-5), 4.08 (t, 0.28H, *J* = 9.4 Hz), 3.69 (dd, 0.28H, *J* = 10.6, 3.9 Hz, H-2'); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 169.7, 159.2, 141.2, 101.8 (CHPh), 96.8 (C-1'), 82.6, 80.7, 79.8, 74.5, 74.4, 73.1, 72.2, 69.6, 69.5, 68.1, 63.0, 56.1, 53.3; ^{13}C-HMBC-GATED NMR ($CDCl_3$, 101 MHz): δ 96.8 (*J* = 181 Hz, C-1'); HRMS: $[M+H]^+$ calcd for $C_{47}H_{48}N_3O_{16}$ 910.30291, found 910.30315.

2,2-Difluoroethyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)-α/β-D-glucopyranoside (5G). Donor **5** and 2,2-difluoroethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 1 hour at -40°C) and purified by flash column chromatography (19/1 to 8/2 pentane/EtOAc) to yield glycosylation product **5G** (17.3 mg, 29 µmol α anomer, 17.8 mg 30 µmol β anomer. α:β = 1:1, 59%) as a yellow solids alongside donor 5 (11 mg). R_f: 0.12 and 0.30 (7/3 pentane/EtOAc). IR (thin film): 698, 997, 1069, 1094, 1211, 1300, 1339, 1520, 1684, 2922; Data for the α-anomer: ^{1}H NMR (Acetone-d_6, 400 MHz, HH-COSY, HSQC): δ 8.91 (s, 2H, CH pyridone), 7.61 – 7.53 (m, 2H, CH_{arom}), 7.48 – 7.37 (m, 3H, CH_{arom}), 7.25 – 7.10 (m, 5H, CH_{arom}), 6.16 (tt, 1H, *J* = 55.0, 3.7 Hz, C*H*F_2), 5.83 (s, 1H, C*H*Ph), 5.56 (d, 1H, *J* = 3.7 Hz, H-1), 4.91 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.79 (dd, 1H, *J* = 10.7, 3.7 Hz, H-2), 4.71 – 4.62 (m, 2H, CH*H* Bn, H-3), 4.37 (dd, 1H, *J* = 10.1, 4.9 Hz, H-6), 4.18 – 4.06 (m, 2H, C*H*H-CHF_2, H-5), 4.03 (dd, 1H, *J* = 9.6, 8.6 Hz, H-4), 3.96 – 3.83 (m, 2H, CH*H*-CHF_2, H-6); ^{13}C-APT NMR (Acetone-d_6, 101 MHz, HSQC): δ 160.0 (C=O pyridone), 142.9 (C_q NO_2 pyridone), 142.6 (CH pyridone), 138.6, 138.5 (C_q), 129.8, 129.2, 129.0, 129.0, 128.9, 127.0 (CH_{arom}), 115.0 (t, *J* = 239.2 Hz, CHF_2), 102.1 (CHPh), 98.8 (C-1), 83.5 (C-4), 75.0 (CH_2 Bn), 74.7 (C-3), 69.9 (C-2), 68.9 (C-6), 67.93 (t, *J* = 27.3 Hz, *C*H_2-CHF_2), 63.9 (C-5); Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.67 (s, 2H, CH pyridone), 7.60 – 7.52 (m, 2H, CH_{arom}), 7.46 – 7.37 (m, 3H, CH_{arom}), 7.03 – 6.93 (m, 5H, CH_{arom}), 5.75 (tt, 1H, *J* = 54.9, 3.9 Hz, C*H*F_2), 5.65 (s, 1H, C*H*Ph), 5.59 (d, 1H, *J* = 8.3 Hz, H-1), 4.76 – 4.64 (m, 2H, C*H*H Bn, H-3), 4.50 (d, 1H, *J* = 11.6 Hz, CH*H* Bn), 4.45 (dd, 1H, *J* = 10.4, 4.9 Hz, H-6), 4.05 (td, 1H, *J* = 9.7, 5.0 Hz, H-5), 4.00 – 3.80 (m, 4H, C*H*$_2$-CHF_2, H-4, H-6), 3.77 (dd, 1H, *J* = 10.3, 8.4 Hz, H-2); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 160.9 (C=O pyridone), 141.7 (C_q NO_2 pyridone), 141.5 (CH pyridone), 137.0, 136.7 (C_q), 129.4, 128.8, 128.6, 128.5, 128.4, 126.4 (CH_{arom}), 113.4 (t, *J* = 241.5 Hz, 102.0 (CHPh), 99.9 (C-1), 82.6 (C-4), 75.5 (C-3), 75.1 (CH_2 Bn), 73.7 (C-2), 68.9 (t, *J* = 27.8 Hz, *C*H_2-CHF_2), 68.6 (C-6), 65.8 (C-5); HRMS: $[M+H]^+$ calcd for $C_{27}H_{26}F_2N_3O_{10}$ 590.15808, found 590.15741.

Methyl 4-*O*-(3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)-β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-β-D-galactopyranoside (5H). Donor **5** and acceptor **28** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 hours at -40°C) and purified by flash column chromatography (9/1 to 7/3 pentane/EtOAc) to yield glycosylation product **5H** (51 mg, 52 µmol, 52%, α:β = <1:20) as a yellow solid. R_f: 0.49 (7/3 pentane/EtOAc). $[\alpha]_D^{20}$ = +35.5° (*c* = 0.85, $CHCl_3$); IR (thin film): 698, 750, 999, 1072, 1094, 1213, 1454, 1522, 1682, 2868; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.20 (s, 2H, CH pyridone), 7.55 – 7.49 (m, 2H, CH_{arom}), 7.47 – 7.40 (m, 3H, CH_{arom}), 7.40 – 7.15 (m, 18H, CH_{arom}), 7.07 – 7.00 (m, 2H, CH_{arom}), 5.63 (s, 1H, C*H*Ph), 5.03 (d, 1H, *J* = 8.3 Hz, H-1'), 4.80 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.64 (d, 1H, *J* = 10.4 Hz, C*H*H Bn), 4.61 (d, 1H, *J* = 12.3 Hz, C*H*H Bn), 4.57 (d, 1H, *J* = 12.2 Hz, CH*H* Bn), 4.50 (s, 2H, CH_2 Bn), 4.47 (d, 1H, *J* = 12.3 Hz, CH*H* Bn), 4.29 (d, 1H, *J* = 10.4 Hz, CH*H* Bn), 4.20 (dd, 1H, *J* = 10.5, 5.0 Hz, H-6'), 4.13 (d, 1H, *J* = 7.6 Hz, H-1), 3.91 (d, 1H, *J* = 2.6 Hz, H-4), 3.88 – 3.78 (m, 2H, H-3', H-4'), 3.74 (t, 1H, *J* = 10.3 Hz, H-6'), 3.70 (dd, 1H, *J* = 9.9, 8.4 Hz, H-2'), 3.66 – 3.52 (m, 2H, H-6, H-6), 3.46 (s, 4H, CH_3 OMe, H-5), 3.41 – 3.33 (m, 2H, H-3, H-5'), 2.93 (dd, 1H, *J* = 9.6, 7.6 Hz, H-2); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 159.4 (C_q pyridone), 141.6 (C_q NO_2 pyridone), 140.5 (CH pyridone), 138.2, 138.0, 137.6, 136.6, 135.6 (C_q), 129.6, 129.3, 129.1, 129.1, 128.9, 128.7, 128.6, 128.6, 128.4, 128.4, 128.1, 128.0, 127.7, 127.5, 126.1 (CH_{arom}), 104.8 (C-1), 101.8 (CHPh), 99.6 (C-1'), 82.3 (C-4'), 80.2, 80.2 (C-2, C-3), 75.4 (CH_2 Bn), 74.6 (C-4),

74.5, 74.4 (CH_2 Bn), 74.2 (C-3'), 73.5 (CH_2 Bn), 72.5 (C-5), 72.3 (C-2'), 68.6 (C-6), 68.2 (C-6'), 66.2 (C-5'), 57.3 (OMe); ^{13}C-HMBC-GATED NMR ($CDCl_3$, 101 MHz): δ 104.8 (J = 159 Hz, C-1), 99.6 (J = 165 Hz, C-1'); HRMS: $[M+H]^+$ calcd for $C_{53}H_{54}N_3O_{15}$ 972.35494, found 972.35542.

Methyl 2-*O*-(3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)-α/β-D-glucopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (5I). Donor **5** and acceptor **29** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 hours at -40°C) and purified by flash column chromatography (9/1 to 7/3 pentane/EtOAc) to yield glycosylation product **5I** (47 mg, 53 µmol, 53%, α:β = 1:1.3) as a yellow solid. R_f: 0.34 and 0.49 (7/3 pentane/EtOAc). IR: (thin film): 646, 696, 731, 789, 908, 997, 1090, 1123, 1211, 1302, 1333, 1454, 1518, 1624, 1674, 2910; Reported as a 0.8 : 1 mixture of anomers. ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.48 (s, 2H, pyridone$_\beta$), 8.33 (s, 1.6H, pyridone$_\alpha$), 7.58 – 7.26 (m, 22.8H, CH_{arom}), 7.23 – 7.01 (m, 11.8H, CH_{arom}), 6.99 – 6.94 (m, 1.6H, CH_{arom}), 5.67 (s, 1.8H, C*H*Ph'$_\alpha$, C*H*Ph'$_\beta$), 5.62 (s, 0.8H, C*H*Ph$_\alpha$), 5.53 (s, 1H, C*H*Ph$_\beta$), 5.27 (d, 0.8H, J = 3.9 Hz, H-1'$_\alpha$), 5.24 (d, 1H, J = 8.3 Hz, H-1'$_\beta$), 4.84 (d, 1H, J = 12.1 Hz, C*H*H Bn$_\beta$), 4.79 (d, 0.8H, J = 12.2 Hz, C*H*H Bn$_\alpha$), 4.75 (d, 1H, J = 12.1 Hz, C*H*H Bn$_\beta$), 4.70 (d, 1H, J = 12.2 Hz, CH*H* Bn$_\beta$), 4.67 (d, 0.8H, J = 1.1 Hz, H-1$_\alpha$), 4.64 (d, 1H, J = 12.1 Hz, CH*H* Bn$_\beta$), 4.57 (d, 0.8H, J = 12.2 Hz, CH*H* Bn$_\alpha$), 4.52 (d, 0.8H, J = 11.1 Hz, CH*H* Bn$_\alpha$), 4.50 (dd, 1H, J = 10.3, 8.2 Hz, H-3'$_\beta$), 4.46 – 4.41 (m, 1H, H-6'$_\beta$), 4.33 (d, 0.8H, J = 11.1 Hz, CH*H* Bn$_\alpha$), 4.34 – 4.26 (m, 1.6H, H-6$_\alpha$, H-6'$_\alpha$), 4.22 – 4.15 (m, 2.8H, H-1$_\beta$, H-2$_\beta$, H-3'$_\alpha$), 4.10 – 3.96 (m, 4.4H, H-2$_\alpha$, H-2'$_\alpha$, H-2'$_\beta$, H-5'$_\alpha$, H-6$_\beta$), 3.95 – 3.83 (m, 8.2H, H-3$_\alpha$, H-3$_\beta$, H-4$_\beta$, H-4'$_\alpha$, H-4'$_\beta$, H-5'$_\beta$, H-6$_\alpha$, H-6'$_\alpha$, H-6'$_\beta$), 3.81 – 3.74 (m, 1.6H, H-4$_\alpha$, H-5$_\alpha$), 3.61 (dq, 1H, J = 9.0, 4.5 Hz, H-5$_\beta$), 3.50 (t, 1H, J = 10.3 Hz, H-6$_\beta$), 3.38 (s, 2.4H, CH_3 OMe$_\alpha$), 3.15 (s, 3H, CH_3 OMe$_\beta$); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 159.9, 159.7 (C=O pyridone), 142.1 (CH pyridone$_\alpha$), 141.7 (C_q NO_2 pyridone), 140.9 (CH pyridone$_\beta$), 140.8 (C_q NO_2 pyridone), 138.2, 137.6, 137.4, 137.4, 136.8, 136.6, 136.5, 136.0 (C_q), 129.6, 129.4, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 128.3, 127.8, 127.8, 127.6, 126.2, 126.1, 126.1 (CH_{arom}), 101.9, 101.8 (CHPh'$_{\alpha,\beta}$), 101.6, 101.6 (CHPh$_{\alpha,\beta}$), 100.7 (C-1$_\alpha$), 99.8 (C-1'$_\alpha$), 99.2 (C-1$_\beta$), 98.8 (C-1'$_\beta$), 83.1 (C-4'$_\alpha$), 82.4 (C-4'$_\beta$), 79.6 (C-4$_\alpha$), 79.1 (C-2$_\alpha$), 78.5 (C-4$_\beta$), 76.1 (C-2$_\beta$), 75.0 (C-3$_\alpha$), 74.5, 74.5, 74.3 (CH_2 Bn), 74.2 (C-3$_\beta$, C-3'$_\beta$), 72.9 (C-2'$_\beta$), 72.7 (CH_2 Bn), 72.5 (C-3'$_\alpha$), 69.9 (C-2'$_\alpha$), 68.5, 68.5, 68.4 (C-6$_{\alpha,\beta}$, C-6'$_{\alpha,\beta}$), 66.1 (C-5'$_\beta$), 63.7 (C-5$_\beta$), 63.3 (C-5$_\alpha$), 63.1 (C-5'$_\alpha$), 55.1, 55.1 (OMe); ^{13}C-HMBC-GATED NMR ($CDCl_3$, 101 MHz): δ 99.8 (J = 176 Hz, C-1'$_\alpha$), 98.8 (J = 164 Hz, C-1'$_\beta$); HRMS: $[M+H]^+$ calcd for $C_{46}H_{46}N_3O_{15}$ 880.29234, found 880.29252.

2,2,2-Trifluoroethyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)-α/β-D-glucopyranoside (5J). Donor **5** and 2,2,2-trifluoroethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 1 hour at -40°C) and purified by flash column chromatography (19/1 to 8/2 pentane/EtOAc) to yield glycosylation product **5J** (28 mg, 46 µmol α anomer and 7 mg, 12 µmol β anomer. α:β = 4:1, 58%) as a yellow solids alongside glucal 24 (4 mg) and donor 5 (13 mg). R_f: 0.15 and 0.67 (7/3 pentane/EtOAc). IR (thin film): 698, 754, 1001, 1071, 1096, 1169, 1215, 1279, 1304, 1331, 1520, 1680, 2855, 2924, 3065; Data for the α-anomer: ^{1}H NMR (Acetone-d_6, 400 MHz, HH-COSY, HSQC): δ 8.92 (s, 2H, CH pyridone), 7.60 – 7.54 (m, 2H, CH_{arom}), 7.47 – 7.37 (m, 3H, CH_{arom}), 7.24 – 7.13 (m, 5H, CH_{arom}), 5.84 (s, 1H, C*H*Ph), 5.65 (d, 1H, J = 3.7 Hz, H-1), 4.92 (d, 1H, J = 11.8 Hz, C*H*H Bn), 4.84 (dd, 1H, J = 10.7, 3.7 Hz, H-2), 4.73 (dd, 1H, J = 10.7, 8.4 Hz, H-3), 4.70 (d, 1H, J = 11.8 Hz, CH*H* Bn), 4.51 – 4.38 (m, 1H, C*H*H-CF_3), 4.38 (dd, 1H, J = 10.1, 4.7 Hz, H-6), 4.30 – 4.17 (m, 1H, CH*H*-CF_3), 4.12 (dd, 1H, J = 9.8, 4.7 Hz, H-5), 4.09 – 4.02 (m, 1H, H-4), 3.93 (t, 1H, J = 10.0 Hz, H-6); ^{13}C-APT NMR (Acetone-d_6, 101 MHz, HSQC): δ 160.0 (C=O pyridone), 142.9 (C_q NO_2 pyridone), 142.6 (CH pyridone), 138.6, 138.5 (C_q), 129.8, 129.2, 129.0, 129.0, 128.9, 127.0 (CH_{arom}), 124.72 (q, J = 277.4 Hz, CF_3), 102.1 (CHPh), 98.8 (C-1), 83.4 (C-4), 75.1 (CH_2 Bn), 74.6 (C-3), 69.8 (C-2), 68.8 (C-6), 65.84 (q, J = 35.0 Hz, *C*H_2-CF_3), 64.1 (C-5); Diagnostic peaks β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.61 (s, 2H, CH pyridone), 7.56 (dd, 2H, J = 6.6, 2.9 Hz, CH_{arom}), 7.41 (dd, 3H, J = 5.0, 1.7 Hz, CH_{arom}), 7.00 (s, 5H, CH_{arom}), 5.66 (s, 1H, C*H*Ph), 5.58 (d, 1H, J = 8.3 Hz, H-1), 4.75 – 4.62 (m, 2H, C*H*H Bn, H-3), 4.52 (d, 1H, J = 11.7 Hz, CH*H* Bn), 4.46 (dd, 1H, J = 10.5, 4.8 Hz, H-6), 4.17 – 3.99 (m, 3H, C*H*$_2$-CF_3, H-5), 3.91 – 3.82 (m, 2H, H-4, H-6), 3.78 (dd, 1H, J = 10.0, 8.5 Hz, H-2); HRMS: $[M+H]^+$ calcd for $C_{27}H_{25}F_3N_3O_{10}$ 608.14865, found 608.14825.

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