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Reactivity and selectivity in glycosylation reactions

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Chapter 4

Stereoselectivity of conformationally restricted glucosazide donors

Introduction

Glucosamine is a key constituent in numerous important oligosaccharides and glycoconjugates, where it can be either α - or β -linked.^{1–5} Whereas the former type of linkage can be reliably installed through 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 donor.^{9–17} To construct 1,2-*cis*-linkages of glucosamine donors, the C-2-amino group is most commonly masked as the nonparticipating 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 might represent an attractive class of 1,2-*cis*-selective glucosamine donor synthons.^{20,21}

In Chapter 3 a comprehensive set of partially fluorinated ethanol, 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, was introduced.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 of furthering the understanding of the stereoelectronic effects exerted by the azido group, this chapter sets out to systematically evaluate a series of glucosazide donors in a set of glycosylation reactions involving the toolset of partially fluorinated ethanol and a selection of carbohydrate acceptors. As is described here, changes in the structure and reactivity of the donor can be effectively mapped using the panel of model acceptors, and a clear reactivity-selectivity relationship for the stereoselectivity of the glycosylations, emerges for all donors studied. Differences among the donors and the stereochemical variation in the glycosylation outcome can be explained on the basis of competition experiments and the characterization of the reactive intermediates involved.

Results and discussion

The set of (partially) fluorinated ethanol acceptors that was employed in Chapter 3, 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, and mannuronic acid donors, as well as fucosazide donors bearing various protecting groups, established the dependence of the stereoselectivity of the

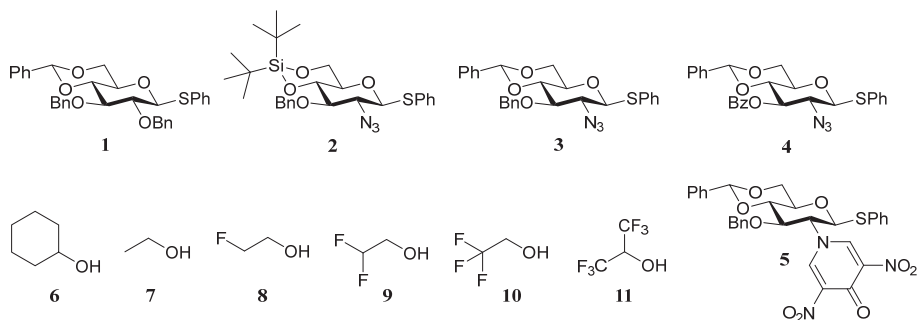


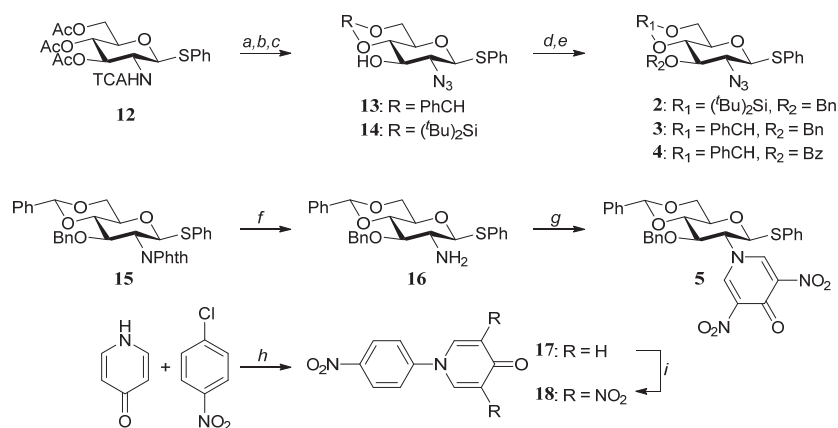
Figure 1. Glucose-configured donors **1–5** and model acceptors **6–11** used in this study.

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), and hexafluoro-*iso*-propanol (HFIP) led to a gradual shift of the stereoselectivity from high β -selectivity to exclusive α -selectivity (See Table 3 below). Here, the results from investigating the set of conformationally restricted glucosamine donors depicted in Figure 1 (1-5) is presented. 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 in the nature of the C-2-*N*-protecting group (azide vs the dinitropyridone [DNPY] group). The DNPY is introduced here as a nonparticipating *N*-protecting group.^{29,30} The reactivity and selectivity of the set of glucosamine donors are related to the corresponding properties of well-studied benzylidene glucose donor **1**.^{9,22}

Synthesis

Benzylidene-protected glucosazide donors **3**³¹ and **4**³² with an *O*-benzyl and an *O*-benzoyl, respectively, at C-3, as well as silylidene-protected donor **2**, were prepared 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

Scheme 1. Preparation of donors 2-5.



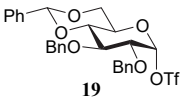
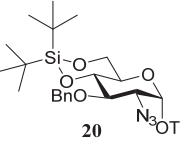
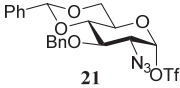
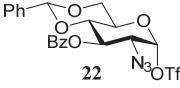
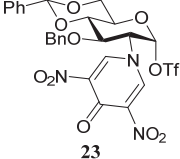
Reagents and conditions: (a) i. K_2CO_3 , EtOH, H_2O ; ii. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, imidazole-1-sulfonyl azide hydrochloride³⁴; (b) di-*tert*-butylsilyl bis(trifluoromethanesulfonate), pyridine, **14**: 71% (three steps); (c) PhCH(OMe)_2 , *p*-TsOH· H_2O , **13**: 78% (three steps); (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%.

Subsequent introduction of the di-*tert*-butylsilylidene (DTBS) and the benzylidene acetal gave intermediates **13**³¹ and **14**, respectively. Benzylation of **14** and **13** and benzylation 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**, which was treated with DNPY reagent **18**^{30,36} to furnish the target donor.

Observation of anomeric triflates

With these five donors in hand, the formation of potential covalent reactive intermediates was investigated by low-temperature NMR studies.³⁷ The donors were treated with the diphenyl sulfoxide/triflic anhydride (Ph₂SO/Tf₂O)³⁸ combination of reagents in deuterated dichloromethane. Figure 3 shows the results of these studies and Table 1 summarizes the anomeric chemical shifts of the observed triflates and the temperatures at which decomposition starts (*T*_{decomp}). Activation of reference donor **1** led

Table 1. Anomeric triflates observed.

Entry	Triflate	¹ H δ (ppm)	³ J _{H1-H2} ^a (Hz)	¹³ C δ (ppm)	<i>T</i> _{decomp} (°C)
1		6.09	3.4	106.1	-20
2		6.00	3.4	104.8	-30
3		6.07	3.5	105.0	-20
4		6.23	3.5	104.5	-10
5		6.06	n/a	102.2	-40

^avalues determined at -40°C

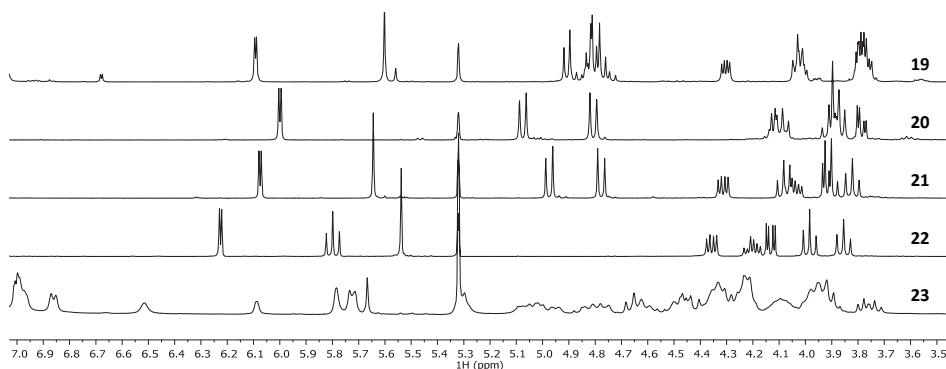


Figure 3. ^1H -NMR spectra at -40°C of activated donors **1-5** showing their respective anomeric triflates **19-23**.

to the formation of two species: In addition to the anomeric triflate **19**,⁹ the oxosulfonium triflate **19 α^*** (6.68 ppm, 3.6 Hz) was also formed, as was confirmed by the activation of a sample containing additional Ph_2SO . Donors **2** and **3** were cleanly converted to their anomeric α -triflates **20** and **21** respectively, by treatment at -80°C with the activation couple. Activation of donor **4** proceeded more slowly, and an increase of the temperature from -80°C to -35°C was required for complete activation. Donor **5** proved difficult to study by low-temperature NMR spectroscopy because of 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 set in. Two anomeric signals can be discriminated in the spectrum of the activated DNPY donor **5** (Figure 3), and these were tentatively assigned as the intermediate triflate (6.06 ppm) and oxosulfonium triflate (6.54 ppm). Unfortunately, complete characterization was hampered by the severe line broadening.³⁹ The reactive intermediates formed all decomposed to give the glucal product **24** (Figure 2). 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.

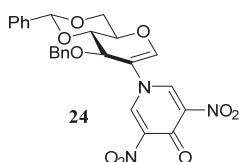
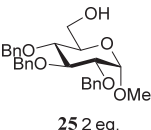
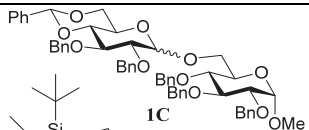
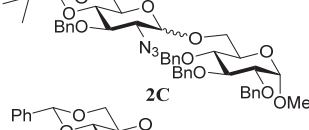
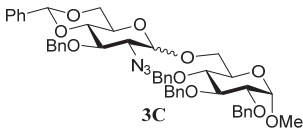
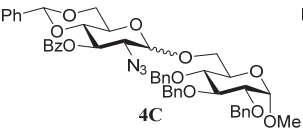
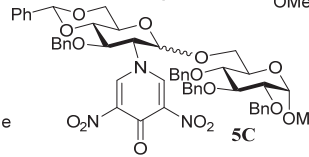


Figure 2. Structure of DNPY glucal **24**, cleanly forms as a decomposition product of activated donor **5**.

Competitive glycosylations and relative reactivities.

To investigate the reactivities of donors **1-5**, a series of competitive glycosylations were performed between the different thioglycosides.^{40–44} In these competition experiments, an *in situ* activation protocol was used, employing *N*-iodosuccinimide (NIS)/trifluoromethanesulfonic acid (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 reactivities 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, although it does provide 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

Table 2. Competitive donor activations.

<div style="display: flex; align-items: center; justify-content: space-around;"> <div> Donor I 1 eq. Donor II 1 eq. </div> <div>+</div> <div>  25 2 eq. </div> <div> $\xrightarrow[\text{DCM (0.05 M), 3A M.S., -40}^{\circ}\text{C to } 0^{\circ}\text{C, 3h}]{\text{1 eq. NIS, 0.1 eq. TfOH}}$ </div> <div> disaccharide product ratio </div> </div>					
			 1C		
			 2C		
			 3C		
			 4C		
			 5C		
Entry	Donor I	Donor II	Products ^a	Ratios	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

^aDetermined by ¹H-NMR of the isolated disaccharide. ^bThe disaccharide fraction was quantified after isolation by size-exclusion chromatography and related to the limiting amount of NIS (see experimental section). ^cThe combined donor concentration for entry 5 was 0.1 M, triflic acid was added at -20°C and the reaction mixture was heated to +15°C overnight, and then the reaction was quenched (Et₃N).


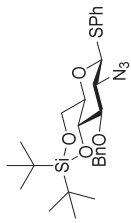

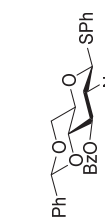
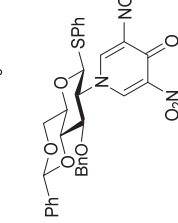

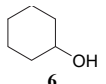
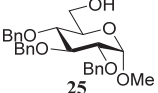
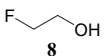
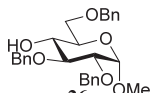
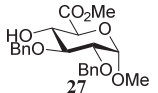
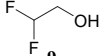
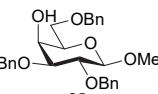
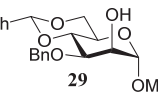
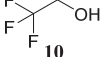
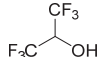
formed in a 6:1 ratio. C-3-O-Benzyl donor **3** in turn outcompetes benzoylated donor **4** slightly, as a result of the electron-withdrawing nature of the benzoate, giving a 1.6:1 ratio of the addition products **3C** and **4C**.^{47–49} DNPY-protected donor **5** is the least reactive of the set of donors, as it did not provide any disaccharide product in the competition experiment with donor **4**.

Glycosylations

With the reactivities 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 Ph₂SO/Tf₂O preactivation 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**. Upon comparison of the outcomes of the coupling reactions of glucosazide **3** with 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), 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 were also found to vary in a nucleophilicity-dependent fashion. The primary perbenzylated acceptor **25** reacts similarly to ethanol **7** to give primarily the β -linked products for all glucosamine donors studied. Secondary carbohydrate acceptors that were less nucleophilic showed variations in selectivity with the proportion of α -product increasing with decreasing acceptor reactivity. In line with the results from Chapter 3, the nucleophilicities of the secondary equatorial carbohydrate alcohols fall somewhere between the reactivities of MFE and DFE, with the reactivities of the axial hydroxyls approaching the reactivity of TFE. The differences in the reactivities of the donors are reflected in the stereoselectivities of both the glycosylations that involve the model acceptors and the glycosylations with the carbohydrate acceptors. A recurring trend is apparent for all acceptors, with the most reactive donor **1** providing most α -linked product 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	2	3	4	5
	Acceptor	Product ^a $\alpha:\beta$ (yield) ^b	Product $\alpha:\beta$ (yield)	Product $\alpha:\beta$ (yield)	Product $\alpha:\beta$ (yield)	Product $\alpha:\beta$ (yield)
A		1A 1 : 10 (68 %)	2A < 1 : 20 (65 %)	3A < 1 : 20 (83 %)	4A < 1 : 20 (86 %)	5A < 1 : 20 (59 %)
B		1B 1 : 5.1 (71 %)	2B < 1 : 20 (77 %)	3B < 1 : 20 (93 %)	4B < 1 : 20 (91 %)	5B < 1 : 20 (63 %)
C		1C 1 : 2.7 (81 %)	2C 1 : 14 (92 %)	3C < 1 : 20 (89 %)	4C 1 : 14 (79 %)	5C < 1 : 20 (57 %)
D		1D 1 : 2.8 (70 %)	2D 1 : 5 (79 %)	3D 1 : 6.7 (90 %)	4D 1 : 6.5 (83 %)	5D < 1 : 20 (43 %)
E		1E 1 : 1 (79 %)	2E 1 : 3 (81 %)	3E 1 : 7 (88 %)	4E 1 : 6 (71 %)	5E 1 : 20 (55 %)
F		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		1G 5 : 1 (70 %)	2G 2.7 : 1 (76 %)	3G 2.9 : 1 (64 %)	4G 2.7 : 1 (84 %)	5G 1 : 1 (59 %)
H		1H > 20 : 1 (83 %)	2H 7 : 1 (52 %)	3H 9 : 1 (75 %)	4H 4 : 1 (51 %)	5H < 1 : 20 (52 %)
I		1I > 20 : 1 (80 %)	2I > 20 : 1 (85 %)	3I 9 : 1 (74 %)	4I 5 : 1 (73 %)	5I 1 : 1.3 (53 %)
J		1J > 20 : 1 (64 %)	2J > 20 : 1 (82 %)	3J > 20 : 1 (94 %)	4J > 20 : 1 (86 %)	5J 4 : 1 (58 %)
K		1K > 20 : 1 (65 %)	2K > 20 : 1 (34 %)	3K > 20 : 1 (53 %)	32% 24	

^aGlycosylation results of donor **1**, are also reported in Chapter 2 of this thesis. ^bRatio and yield of isolated product after column chromatography, anomers were not separated. ^cOnly 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. Second, decreasing donor reactivity corresponds to a decrease in the α/β ratio. These trends also emerged in Chapter 3 and the work on fucosazide donors.^{22,28} The reactive intermediates that can play a role in the glycosylations of the conformationally restricted glucosamine donors and the reaction trajectories of the incoming nucleophiles are presented in Figure 4. 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, which involved the determination of kinetic isotope effects and cation-clock methodology, isopropanol was used as an acceptor.^{12,14} In the kinetic scenario that was proposed the relatively stable α -triflate (observed by low-temperature NMR spectroscopy) 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 explained 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 in β -selectivity through associative displacement. However, an S_N2 -like reaction pathway is

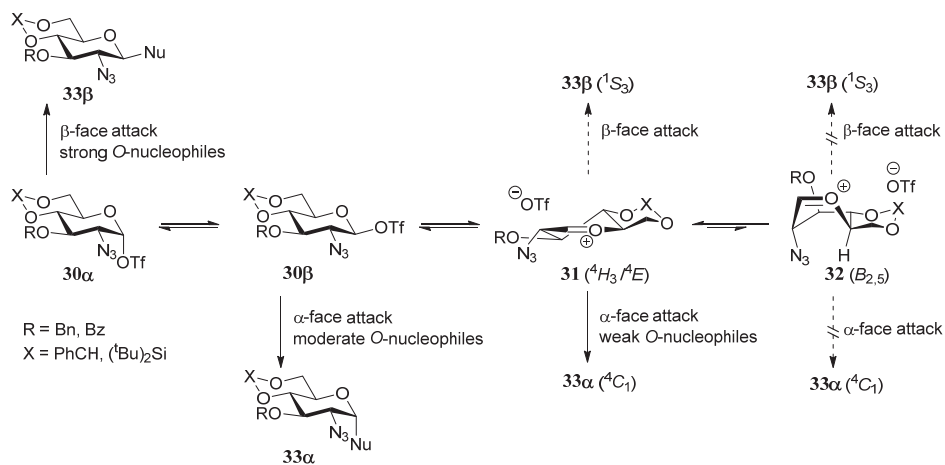


Figure 4. Reactive intermediates and reaction pathways for the 4,6-tethered glucosazide donors.

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 $^4E/^4H_3$ -like conformation.^{55,56} Nucleophiles attack this envelope/half-chair conformer preferentially from the bottom face to lead to the α -linked products through 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 can 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 flagpole position. Given the selectivities observed for this donor, influences arising from this boat conformation do not play a significant role here.

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

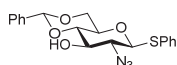
the model acceptors to a more relevant glycosylation setting. Four glucosamine donors were probed that differed in the type of tether spanning the C-4 and C-6-alcohols, the nature of the protecting group at the C-3-OH, and the amino functionality at C-2. Similarly to the previously described benzylidene 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, because of the increased electron-withdrawing power of the azide, which retards the formation of an oxocarbenium ion species and favors a more associative mechanistic pathway. This chapter 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 was 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 are useful stereoselectivities 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, might find application in the future assembly of oligosaccharides featuring α -glucosamines. Finally, it is prudent to 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 the insight 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.

Experimental section

General procedure for Tf₂O/Ph₂SO mediated glycosylations: Donor (0.1 mmol), Ph₂SO (26 mg, 0.13 mmol, 1.3 eq.) and TTBP⁶⁰ (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 Tf₂O (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 Et₃N (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 MgSO₄, filtered, and concentrated *in vacuo*. Purification by silica gel flash column chromatography and when needed, sephadexTM LH-20 size exclusion chromatography yielded the glycosylation product as a mixture of anomers.

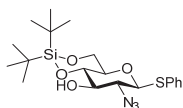
General procedure for the NIS/TfOH mediated competition experiments: Donor I (0.1 mmol, 1 eq.), donor II (0.1 mmol, 1 eq.) and acceptor **25** (0.2 mmol, 2 eq.) were together coevaporated with dry toluene (2x). Dry DCM (4 mL, donor concentration 0.05 M), a Teflon stirring bar and 3Å activated molecular 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. Et₃N (0.1 mL) was added and the mixture was diluted with EtOAc, washed with sat. aq. Na₂S₂O₃ and brine, dried over Na₂SO₄ 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 Ph₂SO (39 µmol) was coevaporated with dry toluene twice (for the activation of donor 1 also TTBP (75 µmol) was added). Under a nitrogen atmosphere, CD₂Cl₂ (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 Tf₂O (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 ¹H NMR spectrum was immediately recorded. The sample was then reshimmied and spectra were recorded in 10°C intervals with at least 5 min equilibration time for every temperature.

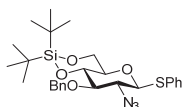


Phenyl 2-azido-4,6-O-benzylidene-2-deoxy-1-thio-β-D-glucopyranoside (13**).** To a suspension of thioglycoside **12**³³ (27.14 g, 50 mmol, 1 eq.) in EtOH (200 mL) was added K₂CO₃ (41.5 g, 300 mmol, 6 eq), and 20 mL H₂O and the mixture was refluxed overnight. The flask was cooled to r.t. and to the crude free amine⁶¹ was added the diazo transfer reagent imidazole-1-sulfonyl azide hydrochloride³⁴ (13.10 g, 62.5 mmol, 1.25 eq.) in 3 equal portions followed by a catalytic amount of CuSO₄·5 H₂O (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*. H₂O (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. NaHCO₃ (150 mL) and brine (150 mL), dried with MgSO₄ 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·H₂O (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 H₂O (2x 100 mL), sat. aq. NaHCO₃ (1x 100 mL), and brine (1x 100 mL). The organic layer was dried (MgSO₄) and concentrated *in vacuo*. The crude mixture was purified by percolation 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

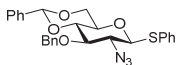
data were in accord with those previously reported.³¹ ¹H NMR (CDCl₃, 400 MHz, HH-COSY, HSQC): δ 7.64 – 7.52 (m, 2H, CH_{arom}), 7.50 – 7.43 (m, 2H, CH_{arom}), 7.42 – 7.32 (m, 6H, CH_{arom}), 5.53 (s, 1H, CHPh), 4.54 (d, 1H, *J* = 10.1 Hz, H-1), 4.38 (dd, 1H, *J* = 10.5, 4.6 Hz, H-6), 3.85 – 3.70 (m, 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); ¹³C-APT NMR (CDCl₃, 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 C₁₉H₂₀N₃O₄S 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 Et₂O and washed with 1M aq. HCl (3x 60 mL), sat. aq. NaHCO₃ (60 mL), and brine (60 mL). The organic layer was dried with Na₂SO₄, filtered and concentrated in vacuo. Purification by flash column chromatography (1-10% Et₂O/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/Et₂O). [α]_D²³ = -42.6° (c = 1.0, CHCl₃); IR (neat): 652, 733, 824, 1072, 1092, 1155, 1277, 1474, 2112, 2859, 2884, 2934, 2963, 3449; ¹H NMR (CDCl₃, 400 MHz, HH-COSY, HSQC) δ 7.57 – 7.51 (m, 2H, CH_{arom}), 7.36 – 7.31 (m, 3H, CH_{arom}), 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, CH₃ ^tBu), 0.97 (s, 9H, CH₃ ^tBu); ¹³C-APT NMR (CDCl₃, 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 (CH₃ ^tBu), 22.8, 20.0 (C_q ^tBu); HRMS: [M-N₂+H]⁺ calcd for C₂₀H₃₂N₂O₄Si 410.18213, found 410.18220.

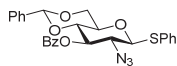


Phenyl 2-azido-3-O-benzyl-2-deoxy-4,6-O-di-tert-butylsilylidene-1-thio-β-D-glucopyranoside (2). Compound **14** (1.4 g, 3.2 mmol) was dissolved in DMF (15 mL) and cooled to 0°C. Benzyl bromide (421 μL, 3.52 mmol, 1.1 eq.) and NaH (60% dispersion in mineral oil, 166 mg, 4.16 mmol, 1.3 eq.) were added 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 H₂O (100 mL) was added. The water phase was extracted three times with 30 mL Et₂O and the combined organic layers were washed with brine (2x), dried with Na₂SO₄ and concentrated under reduced pressure. Purification by flash column chromatography (1%-8% Et₂O/pentane) yielded compound **2** as a colorless oil (1.35 g, 2.56 mmol, 80%). Additional impurities as observed by ¹H NMR originating from the previous crude steps could be removed by size exclusion chromatography (SephadexTM LH-20, 1/1 DCM/MeOH). R_f: 0.51 (19/1 pentane/Et₂O). [α]_D²³ = -85.0° (c = 1.0, CHCl₃); IR (neat): 654, 694, 746, 766, 826, 1059, 1078, 1099, 1159, 1474, 2110, 2859, 2884, 2934, 2963; ¹H NMR (CDCl₃, 400 MHz, HH-COSY, HSQC): δ 7.55 – 7.48 (m, 2H, CH_{arom}), 7.43 – 7.37 (m, 2H, CH_{arom}), 7.36 – 7.27 (m, 6H, CH_{arom}), 4.99 (d, 1H, *J* = 10.7 Hz, CHH Bn), 4.81 (d, 1H, *J* = 10.7 Hz, CHH 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, CH₃ ^tBu), 1.01 (s, 9H, CH₃ ^tBu); ¹³C-APT NMR (CDCl₃, 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 (CH₂ Bn), 74.7 (C-5), 66.2 (C-6), 64.2 (C-2), 27.5, 27.1 (CH₃ ^tBu), 22.7, 20.0 (CH₃ ^tBu); HRMS: [M+H]⁺ calcd for C₂₇H₃₈N₃O₄Si 528.23468, found 528.23451. and [M-N₂+H]⁺ calcd for C₂₇H₃₈N₂O₄Si 500.22853, found 500.22839.

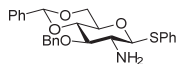


Phenyl 2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy-1-thio-β-D-glucopyranoside (3). Compound **13** (4.36 g, 11.3 mmol) was coevaporated once with dry toluene and then dissolved in DMF (50 mL) and cooled to 0°C. Benzyl bromide (1.9 mL, 15.8 mmol, 1.4 eq.) and NaH (60% dispersion in mineral oil, 900 mg, 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 H₂O (2x 60 mL) and brine (50 mL). The organic layer was dried (MgSO₄), 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 ¹H NMR (CDCl₃, 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, CHPh), 4.91 (d, 1H, *J* = 10.9 Hz, CHH Bn), 4.78 (d, 1H, *J* = 10.9 Hz, CHH 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); ¹³C-APT NMR (CDCl₃, 101 MHz, HSQC): δ 137.6, 137.1 (C_q), 134.0 (CH_{arom}), 130.6 (C_q SPh), 129.2,

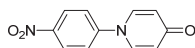
129.2, 128.8, 128.5, 128.4, 128.4, 128.1, 126.0 (CH_{arom}), 101.3 (CHPh), 86.5 (C-1), 81.3, 81.0 (C-3, C-4), 75.3 (CH₂ Bn), 70.5 (C-5), 68.5 (C-6), 64.6 (C-2); HRMS: [M+H]⁺ calcd for C₂₆H₂₆N₃O₄S 476.16385, found 476.16375.



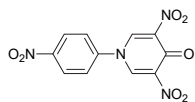
Phenyl 2-azido-3-O-benzoyl-4,6-O-benzylidene-2-deoxy-1-thio-β-D-glucopyranoside (4). To a 0°C solution of compound **13** (1.34 g, 3.48 mmol) in DCM (17 mL) and pyridine (1.4 mL, 34.8 mmol, 5 eq.) was added benzoyl chloride (0.61 mL, 5.22 mmol, 1.5 eq.) and DMAP (42 mg, 0.35 mmol, 0.1 eq.). The reaction mixture was allowed to stir overnight after which H₂O and DCM were added. The organic layer was separated and washed with sat. aq. NaHCO₃ and brine. The organic layer was dried with MgSO₄ 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 ¹H NMR (CDCl₃, 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, CHPh), 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); ¹³C-APT NMR (CDCl₃, 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 C₂₆H₂₄N₃O₅S 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. [α]_D²⁰ = -33.5° (*c* = 0.57, CHCl₃); IR (thin film): 698, 748, 1026, 1069, 1123, 1371, 1452, 1583, 2870, 3030, 3059; ¹H NMR (CDCl₃, 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, CHPh), 4.99 (d, 1H, *J* = 11.3 Hz, CHH Bn), 4.68 (d, 1H, *J* = 11.2 Hz, CHH 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, NH₂); ¹³C-APT NMR (CDCl₃, 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 (C-3, C-4), 75.1 (CH₂ Bn), 70.7 (C-5), 68.8 (C-6), 55.5 (C-2); HRMS: [M+H]⁺ calcd for C₂₆H₂₈NO₄S 450.17336, found 450.17238.

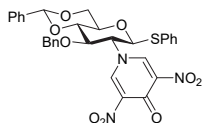


1-(4-nitrophenyl)-4-pyridone (17). Following the procedure of You and Twieg⁶⁴ 4-hydroxypyridine (14.3 g, 150 mmol), 4-chloronitrobenzene (22.9 g, 145 mmol) and K₂CO₃ (20.7 g, 150 mmol) were suspended in *N*-methyl-2-pyrrolidone (110 mL) and heated at 150°C for 2 h. The hot solution was then poured directly onto ice and allowed to precipitate until all the ice had melted. The suspension was then filtered and washed four times with cold H₂O. 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; ¹H 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); ¹³C-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 C₁₁H₉N₂O₃ 217.06077, found 217.06074.



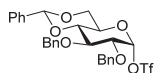
3,5-dinitro-1-(4-nitrophenyl)-4-pyridone (18). Modification of the procedure from Matsumura *et al.*³⁰, an ice cooled three-neck flask equipped with a condenser was charged with 120 mL H₂SO₄ (30% SO₃) followed by the slow addition of 120 mL fuming 99% HNO₃. To the cold mixture pyridone **17** (21.6 g, 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 ¹H 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 ¹H 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; ¹H 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); ¹³C-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 C₁₁H₇N₄O₇ 307.03093, found 307.03123.

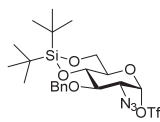


Phenyl 2-(3,5-dinitro-4-pyridone)-3-O-benzyl-4,6-O-benzylidene-2-deoxy-1-thio-β-D-glucopyranoside (5). Free amine **16** (3.6 g, 8 mmol) and reagent **18** (2.7 g, 8.8 mmol, 1.1 eq.) were dissolved in pyridine (48 mL) and AcOH (4 mL) and left to stir for 30 min. The mixture was diluted with EtOAc and washed with 1M aq. HCl (5x) and once with sat. aq. NaHCO₃. The organic layer was dried (MgSO₄), filtered and concentrated under reduced

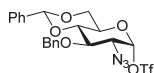
pressure. Column chromatography: DCM until all the nitroanaline had been removed, then 1% to 5% acetone in DCM. Yield 4.84 g, 7.8 mmol (98%) as a yellow solid. R_f: 0.21 (DCM), [α]_D²⁰ = 10.5° (*c* = 0.5, CHCl₃); IR (thin film): 604, 696, 746, 989, 1055, 1094, 1211, 1300, 1329, 1516, 1674, 2856, 2926, 3034, 3059; ¹H 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, CHPh), 5.73 (d, 1H, *J* = 10.4 Hz, H-1), 4.84 (d, 1H, *J* = 12.1 Hz, CHH Bn), 4.62 (d, 1H, *J* = 12.1 Hz, CHH 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); ¹³C-APT NMR (Acetone-*d*₆, 101 MHz, HSQC): δ 159.9 (C=O pyridone), 143.1 (C_q NO₂), 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 (CH₂ Bn), 71.6 (C-2), 70.9 (C-5), 68.8 (C-6); HRMS: [M+H]⁺ calcd for C₃₁H₂₈N₃O₉S 618.15408 found 618.15375.



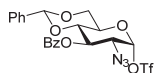
Trifluoromethanesulfonyl 2,3-di-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (19).⁹ ¹H NMR (CD₂Cl₂, *T* = 213 K, 400 MHz, HH-COSY, HSQC): δ 6.08 (d, 1H, *J* = 3.5 Hz, H-1), 5.59 (s, 1H, CHPh), 4.89 (d, 1H, *J* = 11.0 Hz, CHH Bn), 4.85 – 4.69 (m, 3H, CHH Bn, CH₂ Bn), 4.29 (dd, 1H, *J* = 10.3, 4.8 Hz, H-6), 4.09 – 3.94 (m, 2H, H-3, H-5), 3.86 – 3.70 (m, 3H, H-2, H-4, H-6); ¹³C-APT NMR (CD₂Cl₂, *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 (CH₂ Bn), 67.4 (C-6), 65.8 (C-5).



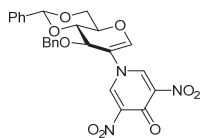
Trifluoromethanesulfonyl 2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (20). ¹H NMR (CD₂Cl₂, *T* = 243 K, 400 MHz, HH-COSY, HSQC): δ 6.08 (d, 1H, *J* = 3.5 Hz, H-1), 5.64 (s, 1H, CHPh), 4.98 (d, 1H, *J* = 10.6 Hz, CHH Bn), 4.78 (d, 1H, *J* = 10.6 Hz, CHH Bn), 4.32 (dd, 1H, *J* = 10.4, 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); ¹³C-APT NMR (CD₂Cl₂, *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 (CH₂ 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). ¹H NMR (CD₂Cl₂, *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, CHPh), 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); ¹³C-APT NMR (CD₂Cl₂, *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).

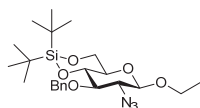


Trifluoromethanesulfonyl 2-azido-3-O-benzyl-2-deoxy-4,6-O-di-tert-butylsilylidene-α-D-glucopyranoside (22). ¹H NMR (CD₂Cl₂, *T* = 233 K, 400 MHz, HH-COSY, HSQC, HMBC): δ 6.00 (d, 1H, *J* = 3.4 Hz, H-1), 5.08 (d, 1H, *J* = 10.1 Hz, CHH Bn), 4.81 (d, 1H, *J* = 10.2 Hz, CHH Bn), 4.15 – 4.06 (m, 2H, H-4, 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, CH₃ ^tBu), 1.00 (s, 9H, CH₃ ^tBu); ¹³C-APT NMR (CD₂Cl₂, *T* = 233 K, 101 MHz, HSQC, HMBC): δ 118.9 (q, *J* = 317.6 Hz, CF₃), 104.8 (C-1), 78.8 (C-3), 76.9 (C-4), 75.7 (CH₂ Bn), 70.0 (C-5), 65.3 (C-6), 60.6 (C-2), 27.0, 26.4 (CH₃ ^tBu), 22.5, 19.7 (C_q ^tBu); ¹³C-HMBC NMR (CD₂Cl₂, 101 MHz): δ 104.8 (*J*_{C1-H1} = 187 Hz, C-1).



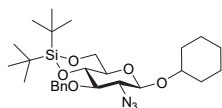
3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)-D-glucal (24). Off-white solid. R_f: 0.20 (7/3 pentane/EtOAc). [α]_D²³ = +85.9° (*c* = 0.32, DCM); IR (thin film): 698, 720, 753, 1007, 1059, 1095, 1192, 1247, 1304, 1351, 1516, 1679, 2880, 2924, 3072; ¹H NMR (Acetone-*d*₆, 500 MHz, HH-COSY, 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, CHPh), 4.93 – 4.88 (m, 2H, CHH Bn, H-3), 4.68 (d, 1H, *J* = 11.8 Hz, CHH 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); ¹³C-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 NO₂), 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 (CH₂ Bn), 74.6 (C-3), 70.7 (C-5), 68.2 (C-6); HRMS: [M+H]⁺ calcd for C₂₅H₂₂N₃O₉ 508.13506, found 508.13465.



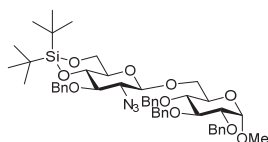
Ethyl 2-azido-3-O-benzyl-2-deoxy-4,6-O-di-tert-butylsilylidene-β-D-glucopyranoside (2A).

Donor **2** and ethanol were condensed using the general procedure for Tf₂O/Ph₂SO mediated glycosylations and purified by flash column chromatography (0% to 5% Et₂O 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% Et₂O in pentane). [α]_D²³ = -69.6° (c = 0.5, CHCl₃); IR (neat): 652, 768, 827, 962, 1082, 1161, 1474, 2112, 2859, 2932; ¹H NMR (CDCl₃, 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, CHH Bn), 4.81 (d, 1H, J = 10.9 Hz, CHH 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, CHH-CH₃ Et, H-4, H-6), 3.61 (dq, 1H, J = 9.5, 7.1 Hz, CHH-CH₃ Et), 3.41 – 3.28 (m, 3H, H-2, H-3, H-5), 1.26 (t, 3H, J = 7.1 Hz, CH₃ Et), 1.08 (s, 9H, CH₃ ^tBu), 1.01 (s, 9H, CH₃ ^tBu); ¹³C-APT NMR (CDCl₃, 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 (CH₂ Bn), 70.5 (C-5), 66.4 (C-6), 66.1 (CH₂ Et), 65.6 (C-2), 27.6, 27.2 (CH₃ ^tBu), 22.8, 20.1 (C_q ^tBu), 15.2 (CH₃ Et); HRMS: [M-N₂+H]⁺ calcd for C₂₃H₃₈NO₅Si 436.25138, found 436.25132.



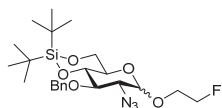
Cyclohexyl 2-azido-3-O-benzyl-2-deoxy-4,6-O-di-tert-butylsilylidene-β-D-glucopyranoside (2B).

Donor **2** and cyclohexanol were condensed using the general procedure for Tf₂O/Ph₂SO 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% Et₂O in pentane). [α]_D²⁰ = -44.3° (c = 1.0, CHCl₃); IR (thin film): 696, 768, 827, 961, 1080, 1163, 1364, 2112, 2859, 2934; ¹H NMR (CDCl₃, 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, CHH Bn), 4.81 (d, 1H, J = 11.1 Hz, CHH 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, CH₂ Cy), 1.80 – 1.71 (m, 2H, CH₂ Cy), 1.55 – 1.48 (m, 1H, CH₂ Cy), 1.47 – 1.37 (m, 2H, CH₂ Cy), 1.34 – 1.20 (m, 3H, CH₂ Cy), 1.08 (s, 9H, ^tBu), 1.01 (s, 9H, ^tBu); ¹³C-APT NMR (CDCl₃, 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 (CH₂ Bn), 70.5 (C-5), 66.4 (C-6), 65.8 (C-2), 33.6, 31.7 (CH₂ Cy), 27.6, 27.2 (CH₃ ^tBu), 25.6 (CH₂ Cy), 24.1, 23.9 (C_q ^tBu), 22.8, 20.1 (CH₂ Cy); HRMS: [M-N₂+H]⁺ calcd for C₂₇H₄₄NO₅Si 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).

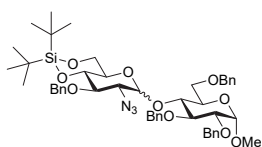
Donor **2** and acceptor **25** were condensed using the general procedure for Tf₂O/Ph₂SO mediated glycosylations (for an additional 18 hours at -40°C) and purified by flash column chromatography (1/0 to 9/1 pentane/EtOAc) to yield glycosylation product **2C** (81 mg, 92 μmol, 92%, α:β = 1:14) as a white solid. R_f: 0.42 (4/1 pentane/EtOAc). [α]_D²³ = -18.6° (c = 1.0, CHCl₃); IR (thin film): 654, 969, 735, 827, 962, 1028, 1070, 1161, 1362, 1454, 2112, 2859, 2931; ¹H NMR (CDCl₃, 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, CHH Bn), 4.98 (d, 1H, J = 10.9 Hz, CHH Bn), 4.94 (d, 1H, J = 11.1 Hz, CHH Bn), 4.85 – 4.76 (m, 3H, CHH Bn, 2xCHH Bn), 4.66 (d, 1H, J = 11.1 Hz, CHH Bn), 4.64 (d, 1H, J = 12.1 Hz, CHH 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, CH₃ Ome, H-3', H-5'), 1.07 (s, 9H, CH₃ ^tBu), 1.01 (s, 9H, CH₃ ^tBu); ¹³C-APT NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 138.9, 138.6, 138.2, 138.1 (C_q), 128.6, 128.5, 128.3, 128.4, 128.3, 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 (CH₂ 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 (CH₃ ^tBu), 22.8, 20.1 (C_q ^tBu); Diagnostic peaks α-anomer: ¹H NMR (CDCl₃, 400 MHz): δ 4.87 (d, 1H, J = 3.6 Hz, H-1'), 4.52 (d, 1H, J = 3.4 Hz, H-1'); ¹³C-APT NMR (CDCl₃, 101 MHz): δ 98.1, 98.0, 68.3; HRMS: [M+NH₄]⁺ calcd for C₄₉H₆₇N₄O₁₀Si 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).

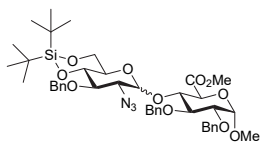
Donor **2** and 2-fluoroethanol were condensed using the general procedure for Tf₂O/Ph₂SO mediated glycosylations and purified by flash column chromatography (1/0 to 0/1 pentane/toluene to 2% Et₂O in toluene) to yield glycosylation product **2D** (37.8 mg, 79 μmol, 79%, α:β = 1:5.5) as a colorless oil. 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; ¹H NMR (CDCl₃, 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, CHH Bn_α), 4.99 (d, 1H, *J* = 10.9 Hz, CHH Bn_β), 4.86 (d, 0.18H, *J* = 3.6 Hz, H-1_α), 4.82 (d, 0.18H, *J* = 10.6 Hz, CHH Bn_α), 4.82 (d, 1H, *J* = 10.9 Hz, CHH Bn_β), 4.71 – 4.61 (m, 1.18H, CHHF_α, CHHF_β), 4.58 – 4.47 (m, 1.18H, CHHF_α, CHHF_β), 4.37 (d, 1H, *J* = 7.6 Hz, H-1_β), 4.17 (dd, 1H, *J* = 10.3, 5.1 Hz, H-6_β), 4.12 – 3.78 (m, 5.26H, CH₂-CH₂F_α, CH₂-CH₂F_β, H-3_α, H-4_α, H-4_β, H-5_α, H-6_α, H-6_β), 3.44 – 3.29 (m, 3.18H, H-2_α, H-2_β, H-3_β, H-5_β), 1.09 (s, 1.62H, CH₃ ^tBu_α), 1.08 (s, 9H, CH₃ ^tBu_β), 1.03 (s, 1.62H CH₃ ^tBu_α), 1.01 (s, 9H, CH₃ ^tBu_β); ¹³C-APT NMR (CDCl₃, 101 MHz, HSQC): δ 138.3 (C_{q,α}), 138.2 (C_{q,β}), 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_{α,β}), 102.4 (C-1_β), 98.3 (C-1_α), 82.7 (d, *J* = 170.0 Hz, CH₂F_β), 82.4 (d, *J* = 170.6 Hz, CH₂F_α), 82.3 (C-3_β), 79.3, 79.0 (C-3_α, C-4_α), 78.0 (C-4_β), 75.6 (CH₂ Bn_α), 75.5 (CH₂ Bn_β), 70.6 (C-5_β), 69.0 (d, *J* = 20.3 Hz, CH₂-CH₂F_β), 67.3 (d, *J* = 20.1 Hz, CH₂-CH₂F_α), 66.8 (C-5_α), 66.7 (C-6_α), 66.3 (C-6_β), 65.5 (C-2_β), 62.5 (C-2_α), 27.5, 27.1 (CH₃ ^tBu_{α,β}), 23.1 (C_q ^tBu_α), 22.8 (C_q ^tBu_β), 20.1 (C_q ^tBu_α), 20.1 (C_q ^tBu_β); HRMS: [M-N₂+H]⁺ calcd for C₂₃H₃₇FNO₅Si 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 Tf₂O/Ph₂SO 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

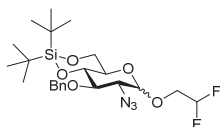
pentane/EtOAc). IR (thin film): 654, 696, 735, 768, 827, 962, 1090, 1159, 1271, 1362, 1454, 2110, 2859, 2932; Data for the β-anomer: ¹H NMR (CDCl₃, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.44 – 7.39 (m, 2H, CH_{arom}), 7.39 – 7.21 (m, 18H, CH_{arom}), 4.98 (d, 1H, *J* = 10.8 Hz, CHH Bn), 4.83 – 4.74 (m, 4H, CHH Bn, CH₂ Bn, CHH Bn), 4.68 (d, 1H, *J* = 11.9 Hz, CHH Bn), 4.62 (d, 1H, *J* = 12.2 Hz, CHH Bn), 4.59 (d, 1H, *J* = 3.6 Hz, H-1), 4.44 (d, 1H, *J* = 11.9 Hz, CHH 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, CH₃ 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, CH₃ ^tBu), 0.97 (s, 9H, CH₃ ^tBu); ¹³C-APT NMR (CDCl₃, 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 (CH₂ 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 (CH₃ ^tBu), 22.7, 20.0 (C_q ^tBu); Diagnostic peaks α-anomer: ¹H NMR (CDCl₃, 400 MHz): δ 5.67 (d, 1H, *J* = 4.0 Hz, H-1), 5.11 (d, 1H, *J* = 10.6 Hz, CHH Bn), 5.06 (d, 1H, *J* = 10.6 Hz, CHH Bn), 4.87 (d, 1H, *J* = 10.6 Hz, CHH Bn), 4.79 (d, 1H, *J* = 10.6 Hz, CHH Bn), 4.75 (d, 1H, *J* = 12.0 Hz, CHH 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, CH₃ OMe), 3.21 (dd, 1H, *J* = 10.2, 4.0 Hz, H-2'), 1.06 (s, 9H, CH₃ ^tBu), 1.04 (s, 9H, CH₃ ^tBu); ¹³C-APT NMR (CDCl₃, 101 MHz): δ 138.8, 138.3, 138.2, 138.0, 128.6, 128.4, 128.3, 128.1, 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+NH₄]⁺ calcd for C₄₉H₆₇N₄O₁₀Si 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 Tf₂O/Ph₂SO 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

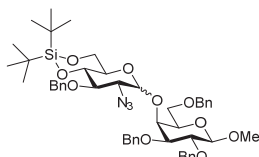
(9/1 pentane/EtOAc). IR (thin film): 654, 696, 735, 827, 1042, 1144, 1387, 1751, 2108, 2859, 2934; Data for the α-anomer: ¹H NMR (CDCl₃, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.43 – 7.38 (m, 2H, CH_{arom}), 7.37 – 7.25 (m, 13H, CH_{arom}), 5.45 (d, 1H, *J* = 4.1 Hz, H-1'), 5.07 – 5.02 (m, 2H, 2xCHH Bn), 4.90 (d, 1H, *J* = 10.6 Hz, CHH Bn), 4.84 – 4.78 (m, 1H, CHH Bn), 4.75 (d, 1H, *J* = 12.0 Hz, CHH Bn), 4.59 (d, 1H, *J* = 12.2 Hz, CHH 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, CH₃ CO₂Me, 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, CH₃ OMe), 3.23 (dd, 1H, *J* = 10.2, 4.1 Hz, H-2'), 1.07 (s, 9H, CH₃ ^tBu), 1.05 (s, 9H, CH₃ ^tBu); ¹³C-APT NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 169.2 (C=O CO₂Me), 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 (CH₂ Bn), 70.2 (C-5), 67.0 (C-5'), 66.4 (C-6'), 62.4 (C-2'), 55.9 (OMe), 52.9 (CO₂Me), 27.6, 27.2 (CH₃ ^tBu), 22.9, 20.0 (C_q ^tBu); Diagnostic peaks β-anomer: ¹H NMR (CDCl₃, 400 MHz): δ 4.98 (d, 1H, *J* = 10.9 Hz, CHH Bn), 4.39 (d, 1H, *J* = 7.7 Hz, H-1'), 4.02 – 3.96 (m, 1H), 3.82 (s, 3H, CH₃ CO₂Me), 3.52 (dd, 1H, *J* = 9.5, 3.6 Hz, H-2), 1.05 (s, 9H, CH₃ ^tBu), 0.97 (s, 9H, CH₃ ^tBu); ¹³C-APT NMR (CDCl₃, 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.



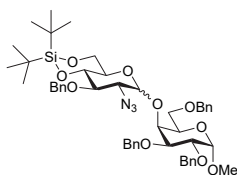
2,2-Difluoroethyl 2-azido-3-O-benzyl-2-deoxy-4,6-O-di-tert-butylsilylidene- α/β -D-glucopyranoside (2G). Donor **2** and 2,2-difluoroethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations and purified by flash column chromatography (1/0 to 0/1 pentane/toluene to 2% Et_2O in toluene) to yield glycosylation product **2G** (38.1 mg, 76 μ mol, 76%, $\alpha:\beta = 2.7:1$) in two fractions (24.3 mg

α only, 13.8 mg $\alpha:\beta = 0.3:1$) 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: $[\alpha]_D^{25} = +35.6^\circ$ ($c = 0.86$, $CHCl_3$); 1H 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, CHF_2), 5.06 (d, 1H, $J = 10.6$ Hz, CHH Bn), 4.85 (d, 1H, $J = 3.6$ Hz, H-1), 4.82 (d, 1H, $J = 10.7$ Hz, CHH 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 tBu), 1.03 (s, 9H, CH_3 tBu); ^{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, CH_2-CHF_2), 67.1 (C-5), 66.6 (C-6), 62.4 (C-2), 27.5, 27.1 (CH_3 tBu), 22.8, 20.1 (C_q tBu); Data for the β -anomer: 1H 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, CHF_2), 4.99 (d, 1H, $J = 10.9$ Hz, CHH Bn), 4.81 (d, 1H, $J = 11.0$ Hz, CHH 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 tBu), 1.01 (s, 9H, CH_3 tBu); ^{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, CH_2-CHF_2), 66.2 (C-6), 65.4 (C-2), 27.5, 27.1 (CH_3 tBu), 22.8, 20.1 (C_q tBu); HRMS: $[M+N+H]^+$ 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 $-40^\circ C$) and purified by flash column chromatography (1/0 to 9/1 pentane/ $EtOAc$) to yield glycosylation product **2H** (46 mg, 52 μ mol, 52%, $\alpha:\beta = 7:1$) as a colorless oil. R_f : 0.33 and 0.51

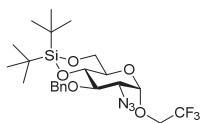
(9/1 pentane/ $EtOAc$). IR (thin film): 652, 696, 735, 826, 1001, 1036, 1206, 1364, 1454, 2108, 2859, 2932; Data for the α -anomer: 1H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.46–7.41 (m, 2H, CH_{arom}), 7.41–7.23 (m, 18H, CH_{arom}), 5.10 (d, 1H, $J = 10.3$ Hz, CHH Bn), 4.89–4.81 (m, 3H, CHH Bn, 2x CHH Bn), 4.79 (d, 1H, $J = 3.7$ Hz, H-1'), 4.72 (d, 1H, $J = 10.6$ Hz, CHH Bn), 4.68 (d, 1H, $J = 13.0$ Hz, CHH 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 tBu), 1.02 (s, 9H, CH_3 tBu); ^{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 tBu), 22.7, 20.2 (C_q tBu); Diagnostic peaks β -anomer: 1H NMR ($CDCl_3$, 400 MHz): δ 4.94 (d, 0.14H, $J = 11.1$ Hz, CHH 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 $-40^\circ C$) and purified by flash column chromatography (1/0 to 9/1 pentane/ $EtOAc$) to yield glycosylation product **2I** (67 mg, 85 μ mol, 85%, $\alpha:\beta = > 20:1$) as a white solid. R_f : 0.54 (9/1 pentane/ $EtOAc$). $[\alpha]_D^{20} = +44.3^\circ$ ($c = 1.34$, $CHCl_3$); IR (thin film): 696, 827, 937, 1040, 1088, 1130, 1364,

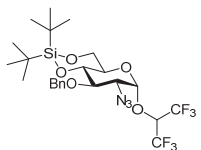
2108, 2859, 2957; Data for the α -anomer: 1H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.54–7.47 (m, 2H, CH_{arom}), 7.46–7.41 (m, 2H, CH_{arom}), 7.41–7.22 (m, 11H, CH_{arom}), 5.65 (s, 1H, $CHPh$), 5.23 (d, 1H, $J = 3.6$ Hz, H-1'), 5.09 (d, 1H, $J = 10.6$ Hz, CHH Bn), 4.89–4.82 (m, 2H, CHH Bn, CHH Bn), 4.74–4.65 (m, 2H, CHH 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 (CH₂ Bn), 69.0 (C-6), 67.2 (C-5'), 66.6 (C-6'), 64.1 (C-5), 62.6 (C-2'), 55.2 (CH₃ OMe), 27.5, 27.2 (CH₃ ¹Bu), 22.8, 20.2 (C_q ¹Bu); Diagnostic peaks β-anomer: ¹H NMR (CDCl₃, 400 MHz): δ 5.60 (s, 1H, CHPh), 4.98 (d, 1H, J = 11.3 Hz, CHH Bn), 4.39 (d, 1H, J = 8.2 Hz, H-1'), 3.57 – 3.48 (m, 1H); ¹³C-APT NMR (CDCl₃, 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+NH₄]⁺ calcd for C₄₂H₅₉N₄O₁₀Si 807.39950, found 807.39931.



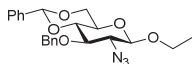
2,2,2-Trifluoroethyl 2-azido-3-O-benzyl-2-deoxy-4,6-O-di-tert-butylsilylidene-α-D-glucopyranoside (2I).

Donor **2** and 2,2,2-trifluoroethanol were condensed using the general procedure for Tf₂O/Ph₂SO 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% Et₂O in toluene) to yield glycosylation product **2I** (42.4 mg, 82 μmol, 82%, α:β = >20:1) as a colorless oil. R_f: 0.36 (toluene). [α]_D²³ = +32.6° (c = 1.0, CHCl₃); IR (neat): 654, 766, 826, 1036, 1082, 1159, 1279, 1472, 2108, 2859, 2930; ¹H NMR (CDCl₃, 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, CHH Bn), 4.88 (d, 1H, J = 3.6 Hz, H-1), 4.82 (d, 1H, J = 10.6 Hz, CHH Bn), 4.14 – 4.07 (m, 1H, H-6), 4.03 – 3.93 (m, 3H, CH₂-CF₃, 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, CH₃ ¹Bu), 1.03 (s, 9H, CH₃ ¹Bu); ¹³C-APT NMR (CDCl₃, 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 (CH₂ Bn), 67.4 (C-5), 66.5 (C-6), 65.2 (q, J = 35.4 Hz, CH₂-CF₃), 62.2 (C-2), 27.5, 27.1 (CH₃ ¹Bu), 22.8, 20.1 (C_q ¹Bu); HRMS: [M-N₂+H]⁺ calcd for C₂₃H₃₅F₃NO₅Si 490.22311, found 490.22292.



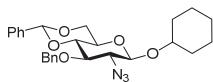
1,1,1,3,3,3-Hexafluoro-2-propyl 2-azido-3-O-benzyl-2-deoxy-4,6-O-di-tert-butylsilylidene-α-D-glucopyranoside (2K).

Donor **2** and 1,1,1,3,3,3-hexafluoro-2-propanol were condensed using the general procedure for Tf₂O/Ph₂SO 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/Et₂O). [α]_D²⁰ = +31.2° (c = 0.50, CHCl₃); IR (thin film): 689, 827, 1030, 1098, 1221, 1288, 1368, 2112, 2860, 2934; ¹H NMR (CDCl₃, 400 MHz, HH-COSY, HSQC, HMBC, NOESY): δ 7.45 – 7.28 (m, 5H, CH_{arom}), 5.12 – 5.04 (m, 2H, CHH Bn, H-1), 4.83 (d, 1H, J = 10.5 Hz, CHH Bn), 4.40 (hept, 1H, J = 5.7 Hz, CH 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, CH₃ ¹Bu), 1.03 (s, 9H, CH₃ ¹Bu); ¹³C-APT NMR (CDCl₃, 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 (CH₂ Bn), 73.3 (p, J = 33.2 Hz), 68.1 (C-5), 66.1 (C-6), 61.9 (C-2), 27.5, 27.0 (CH₃ ¹Bu), 22.8, 20.1 (C_q ¹Bu); HRMS: [M-N₂+H]⁺ calcd for C₂₄H₃₄F₆NO₅Si 558.21050, found 558.21009.



Ethyl 2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy-β-D-glucopyranoside (3A).

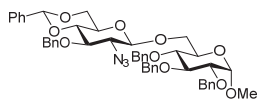
Donor **3** and ethanol were condensed using the general procedure for Tf₂O/Ph₂SO mediated glycosylations and purified by flash column chromatography (1/0 to 0/1 hexane/toluene to 5% EtOAc in toluene) to yield glycosylation product **3A** (34.3 mg, 83 μmol, 83%, α:β = <1:20) as a white solid. R_f: 0.58 (9/1 toluene/EtOAc). [α]_D²³ = -79.6° (c = 0.69, CHCl₃); IR (neat): 692, 993, 1098, 1186, 1267, 1365, 1452, 2111, 2878, 2979; ¹H NMR (CDCl₃, 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, CHPh), 4.91 (d, 1H, J = 11.2 Hz, CHH Bn), 4.79 (d, 1H, J = 11.3 Hz, CHH 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, CHH 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, CHH 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, CH₃ Et); ¹³C-APT NMR (CDCl₃, 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 (CH₂ Bn), 68.7 (C-6), 66.3 (CH₂ Et), 66.3, 66.2 (C-2, C-5), 15.2 (CH₃ Et); ¹³C-HMBC-GATED NMR (CDCl₃, 101 MHz): δ 102.5 (J_{C1,H1} = 161 Hz, C-1); HRMS: [M+NH₄]⁺ calcd for C₂₂H₂₉N₄O₅ 429.21325, found 429.21321.



Cyclohexyl 2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy-β-D-glucopyranoside (3B).

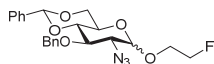
Donor **3** and cyclohexanol were condensed using the general procedure for Tf₂O/Ph₂SO mediated glycosylations and purified by flash column chromatography (1/1 to 0/1 hexane/toluene to 5% EtOAc in toluene) to yield glycosylation product **3B** (43 mg, 93 μmol, 93%, α:β = <1:20) as a white solid. R_f: 0.23 (toluene). [α]_D²³ = -60.5° (c = 0.86, DCM); IR (neat): 696, 748, 998, 1092, 1275, 1365, 1452, 2108, 2858, 2933; Data for the β-anomer: ¹H NMR (CDCl₃, 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, CHPh), 4.90 (d, 1H, J = 11.4 Hz, CHH Bn), 4.79 (d, 1H, J

= 11.4 Hz, CHH 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, CH₂ Cyc), 1.82 – 1.72 (m, 2H, J = 15.2, 4.4 Hz, CH₂ Cyc), 1.56 – 1.37 (m, 3H, CH₂ Cyc), 1.36 – 1.20 (m, 3H, CH₂ Cyc); ¹³C-APT NMR (CDCl₃, 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 (CH₂ Bn), 68.8 (C-6), 66.5 (C-2), 66.3 (C-5), 33.6, 31.8, 25.6, 24.1, 23.9 (CH₂ Cyc); Diagnostic peaks α-anomer: ¹H NMR (CDCl₃, 400 MHz): δ 5.59 (s, 0.04H, CHPh), 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); ¹³C-APT NMR (CDCl₃, 101 MHz): δ 101.4 (CHPh), 97.1 (C-1), 76.0 (C-3), 63.8 (C-2), 62.9 (C-5); HRMS: [M+NH₄]⁺ calcd for C₂₆H₃₅N₄O₅ 483.26020 found 483.25991.



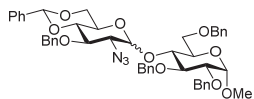
Methyl 6-O-(2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy-β-D-glucopyranosyl)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (3C). Donor **3** and acceptor **25** were condensed using the general procedure for Tf₂O/Ph₂SO mediated glycosylations (for an additional 18 h at -40°C) and purified by flash column chromatography (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 [α]_D²³ = -32.2° (c = 1.0, CHCl₃); IR (neat): 696, 737, 999, 1028, 1070, 1090, 1277, 1362, 1497, 2108, 2876, 2926; ¹H NMR (CDCl₃, 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, CHPh), 4.99 (d, 1H, J = 10.9 Hz, CHH 3-OBn), 4.95 (d, 1H, J = 11.2 Hz, CHH 4-OBn), 4.91 (d, 1H, J = 11.2 Hz, CHH 3'-OBn), 4.85 – 4.76 (m, 3H, CHH 3-OBn, CHH 2-OBn, CHH 3'-OBn), 4.70 – 4.63 (m, 2H, CHH 4-OBn, CHH 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, CH₃ OMe), 3.36 – 3.29 (m, 1H, H-5'); ¹³C-APT NMR (CDCl₃, 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 (CH₂ 3-OBn), 75.0, 75.0 (CH₂ 3'-OBn, 4-OBn), 73.6 (CH₂ 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+NH₄]⁺ calcd for C₄₈H₅₅N₄O₁₀ 847.39127, found 847.39224.



2-Fluoroethyl 2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy-α/β-D-glucopyranoside (3D).

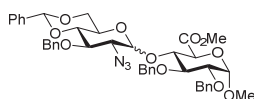
Donor **3** and 2-fluoroethanol were condensed using the general procedure for Tf₂O/Ph₂SO mediated glycosylations and purified by flash column chromatography (1/0 to 0/1 pentane/toluene to 5% EtOAc in toluene) to yield glycosylation product **3D** (38.5 mg, 90 μmol, 90%, α:β = 1:6.7) as a white solid. 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: ¹H NMR (CDCl₃, 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, CHPh), 4.91 (d, 1H, J = 11.2 Hz, CHH Bn), 4.79 (d, 1H, J = 11.3 Hz, CHH Bn), 4.69 – 4.64 (m, 1H, CHHF), 4.55 (dt, 1H, J = 4.6, 2.9 Hz, CHHF), 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, CHH-CF₂), 4.03 (ddd, 0.5H, J = 12.2, 4.7, 3.0 Hz, CHH-CF₂), 3.92 (ddd, 0.5H, J = 12.2, 5.9, 3.2 Hz, CHH-CF₂), 3.86 (ddd, 0.5H, J = 12.2, 6.0, 3.3 Hz, CHH-CF₂), 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); ¹³C-APT NMR (CDCl₃, 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, CF₂), 81.5 (C-4), 79.0 (C-3), 75.1 (CH₂ Bn), 69.3 (d, J = 20.1 Hz, CH₂-CF₂), 68.6 (C-6), 66.3 (C-5), 66.1 (C-2); ¹³C-HMBC-GATED NMR (CDCl₃, 101 MHz): δ 102.7 ($J_{C1,H1}$ = 162 Hz, C-1); Diagnostic peaks α-anomer: ¹H NMR (CDCl₃, 400 MHz, HH-COSY, HSQC): δ 5.58 (s, 0.15H, CHPh), 4.96 (d, 0.15H, J = 10.9 Hz, CHH Bn), 4.95 (d, 0.15H, J = 3.7 Hz, H-1), 4.81 (d, 0.15H, J = 11.0 Hz, CHH Bn), 4.29 (dd, 0.15H, J = 10.2, 4.9 Hz, H-6); ¹³C-APT NMR (CDCl₃, 101 MHz, HSQC): δ 101.5 (CHPh), 98.8 (C-1), 82.8 (C-4), 76.2 (C-3), 75.2 (CH₂ Bn), 68.9 (C-6), 63.0, 62.9 (C-2, C-5); ¹³C-HMBC-GATED NMR (CDCl₃, 101 MHz): δ 98.8 ($J_{C1,H1}$ = 172 Hz, C-1); HRMS: [M+NH₄]⁺ calcd for C₂₂H₂₈FN₄O₅ 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 Tf₂O/Ph₂SO mediated glycosylations (for an additional 18 h at -40°C) and purified by flash column chromatography (19/1

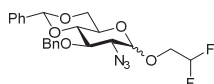
to 4/1 pentane/EtOAc) to yield glycosylation product **3E** (73.3 mg, 88 μmol, 88%, α:β = 1:7) as a white solid. R_f: 0.51 α, 0.43 β (4/1 pentane/EtOAc). IR (neat): 696, 737, 1049, 1092, 1362, 1454, 2110, 2868; Data for the β-anomer: ¹H NMR (CDCl₃, 400 MHz, HH-COSY, HSQC, TOCSY): δ 7.68 – 7.60 (m, 2H, CH_{arom}), 7.52 – 7.18 (m, 23H, CH_{arom}), 5.47 (s, 1H, CHPh), 4.89 (d, 1H, J = 11.2 Hz, CHH Bn), 4.87 (d, 1H, J = 10.9 Hz, CHH Bn), 4.81 (d, 1H, J = 10.9 Hz, CHH Bn), 4.78

(d, 1H, J = 12.2 Hz, CHH Bn), 4.75 (d, 1H, J = 11.2 Hz, CHH Bn), 4.71 (d, 1H, J = 12.0 Hz, CHH Bn), 4.63 (d, 1H, J = 12.1 Hz, CHH Bn), 4.60 (d, 1H, J = 3.7 Hz, H-1), 4.41 (d, 1H, J = 12.0 Hz, CHH 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', CH₃ OMe), 3.36 – 3.27 (m, 2H, H-2', H-3'), 3.00 (td, 1H, J = 9.8, 5.0 Hz, H-5'); ¹³C-APT NMR (CDCl₃, 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 (CH₂ 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: ¹H NMR (CDCl₃, 400 MHz): δ 5.71 (d, 1H, J = 4.0 Hz, H-1'), 5.53 (s, 1H, CHPh), 5.11 (d, 1H, J = 10.7 Hz, CHH Bn), 4.95 (d, 1H, J = 10.9 Hz, CHH Bn); ¹³C-APT NMR (CDCl₃, 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 C₄₈H₅₁N₃O₁₀Na 852.34667, found 852.34668.



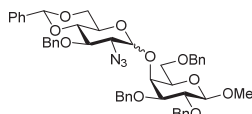
Methyl (Methyl 4-O-[2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy-α/β-D-glucopyranosyl]-2,3-di-O-benzyl-α-D-glucopyranosyl uronate) (3F). Donor **3** and acceptor **27** were condensed using the general procedure for Tf₂O/Ph₂SO mediated glycosylations (for an additional 18 h at -40°C) and purified by 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: ¹H NMR (CDCl₃, 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, CHPh_a), 5.51 (d, 1H, J = 3.9 Hz, H-1'_a), 5.47 (s, 1H, CHPh_b), 5.04 (d, 1H, J = 10.5 Hz, CHH Bn), 4.94 (d, 1H, J = 11.0 Hz, CHH Bn), 4.91 – 4.82 (m, 4H, 2xCHH Bn, 2xCHH Bn), 4.81 – 4.72 (m, 4H, 2xCHH Bn, 2xCHH Bn), 4.64 – 4.58 (m, 2H, 2xCHH Bn), 4.57 (d, 2H, J = 3.5 Hz, H-1_{aβ}), 4.43 (d, 1H, J = 8.1 Hz, H-1'_β), 4.26 (dd, 1H, J = 10.3, 4.8 Hz, H-6'_a), 4.24 – 4.19 (m, 2H, H-5_a, H-5_β), 4.09 – 3.99 (m, 4H, H-3_β, H-4_a, H-4_β, H-6'_β), 3.97 (t, 1H, J = 9.5 Hz, H-3'_a), 3.89 (t, 1H, J = 9.2 Hz, H-3_a), 3.82 (s, 3H, CH₃ CO₂Me), 3.81 (s, 3H, CH₃ CO₂Me), 3.72 – 3.56 (m, 4H, H-2_β, H-4'_a, H-4'_β, H-6'_a), 3.56 – 3.46 (m, 3H, H-2_a, H-3'_β, H-5'_a), 3.46 – 3.38 (m, 7H, 2xCH₃ OMe, H-6'_β), 3.36 – 3.29 (m, 2H, H-2'_a, H-2'_β), 3.26 (td, 1H, J = 9.7, 5.0 Hz, H-5'_β); ¹³C-APT NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 170.0, 170.0 (C=O CO₂Me), 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, 128.3, 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'_β), 101.4 (CHPh_β), 101.3 (CHPh_a), 98.9, 98.6 (C-1_a, C-1_β), 98.5 (C-1'_a), 82.4 (C-4'_a), 81.6 (C-4'_β), 81.1 (C-3_β), 79.6 (C-2_β, C-4_β), 79.5 (C-3_a), 79.4 (C-3'_β), 78.7 (C-2_a), 76.3 (C-3'_a), 75.6 (CH₂ Bn), 75.5 (C-4_a), 75.1, 75.0, 73.9, 73.7 (CH₂ Bn), 70.0, 69.9 (C-5_a, C-5_β), 68.5, 68.5 (C-6_a, C-6_β), 66.7 (C-2'_β), 66.2 (C-5'_β), 63.0 (C-5'_a), 62.8 (C-2'_a), 55.9, 55.9 (OMe), 53.0, 52.8 (CO₂Me); HRMS: [M+NH₄]⁺ calcd for C₄₂H₄₉N₄O₁₁ 785.33923, found 785.34007.



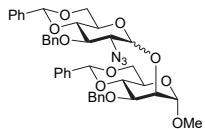
2,2-Difluoroethyl 2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy-α/β-D-glucopyranoside (3G). Donor **3** and 2,2-difluoroethanol were condensed using the general procedure for Tf₂O/Ph₂SO mediated glycosylations and purified by flash column chromatography (1/0 to 0/1 pentane/toluene to 5% EtOAc in toluene) 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: ¹H NMR (CDCl₃, 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, CF₂H_a), 5.94 (tt, 0.35H, J = 55.3, 3.8 Hz, CF₂H_β), 5.58 (s, 1H, CHPh_a), 5.57 (s, 0.35H, CHPh_β), 4.96 (d, 1H, J = 10.9 Hz, CHH Bn_a), 4.93 (d, 1H, J = 3.9 Hz, H-1_a), 4.92 (d, 0.35H, J = 11.3 Hz, CHH Bn_β), 4.80 (d, 1H, J = 11.0 Hz, CHH Bn_a), 4.79 (d, 0.35H, J = 11.3 Hz, CHH Bn_β), 4.40 (d, 0.35H, J = 7.9 Hz, H-1_β), 4.34 (dd, 0.35H, J = 10.5, 5.0 Hz, H-6_β), 4.29 (dd, 1H, J = 10.2, 4.8 Hz, H-6_a), 4.08 (t, 1H, J = 9.5 Hz, H-3_a), 4.02 – 3.67 (m, 6.4H, H-4_a, H-4_β, H-5_a, H-6_a, H-6_β, CH₂-CF₂H_a, CH₂-CF₂H_β), 3.56 (t, 0.35H, J = 9.2 Hz, H-3_β), 3.50 – 3.35 (m, 1.70H, H-2_a, H-2_β, H-5_β); ¹³C-APT NMR (CDCl₃, 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, CF₂H_β), 113.8 (t, J = 241.6 Hz, CF₂H_a), 102.8 (C-1_β), 101.6 (CHPh_a), 101.5 (CHPh_β), 99.3 (C-1_a), 82.6 (C-4_a), 81.4 (C-4_β), 78.9 (C-3_β), 76.0 (C-3_a), 75.3 (CH₂ Bn_a), 75.1 (CH₂ Bn), 69.0 (t, J = 29.0 Hz, CH₂-CF₂H_β), 68.8 (C-6), 68.5 (C-6), 67.5 (t, J = 28.7 Hz, CH₂-CF₂H_a), 66.4 (C-5_β), 66.0 (C-2_β), 63.3 (C-5_a), 62.9 (C-2_a); HRMS: [M+H]⁺ calcd for C₂₂H₂₄F₂N₃O₅ 448.16785, found 448.16761.



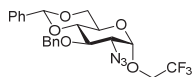
Methyl 4-O-(2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy- α/β -D-glucopyranosyl)-2,3,6-tri-O-benzyl- β -D-galactopyranoside (3H).

Donor **3** and acceptor **28** were condensed using the general procedure for $\text{Ti}_2\text{O}/\text{Ph}_2\text{SO}$ 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%, $\alpha:\beta = 9:1$) 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: ^1H 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, CHPh), 4.98 (d, 1H, $J = 10.7$ Hz, $\text{CHH } 3'\text{-OBn}$), 4.90 (d, 1H, $J = 11.0$ Hz, $\text{CHH } 2\text{-OBn}$), 4.88 (d, 1H, $J = 3.7$ Hz, $\text{H-1}'$), 4.84 – 4.76 (m, 3H, $\text{CHH } 2\text{-OBn}$, $\text{CHH } 3'\text{-OBn}$, $\text{CHH } 3\text{-OBn}$), 4.69 (d, 1H, $J = 12.4$ Hz, $\text{CHH } 3\text{-OBn}$), 4.59 – 4.51 (m, 2H, CH_2 6-OBn), 4.30 (td, 1H, $J = 10.1$, 4.9 Hz, $\text{H-5}'$), 4.25 (d, 1H, $J = 7.6$ Hz, H-1), 4.14 – 4.07 (m, 2H, $\text{H-3}'$, H-4), 4.03 (t, 1H, $J = 8.9$ Hz, H-6), 3.80 (dd, 1H, $J = 10.2$, 4.9 Hz, $\text{H-6}'$), 3.70 – 3.60 (m, 3H, H-2 , $\text{H-4}'$, H-6), 3.55 (s, 3H, CH_3 OMe), 3.54 – 3.48 (m, 2H, H-5 , $\text{H-6}'$), 3.44 – 3.36 (m, 2H, $\text{H-2}'$, 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, 128.2, 128.0, 127.7, 127.6, 126.1 (CH_{arom}), 105.3 (C-1), 101.2 (CHPh), 99.4 ($\text{C-1}'$), 83.1 ($\text{C-4}'$), 80.1 (C-3), 78.9 (C-2), 77.0 ($\text{C-3}'$), 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 ($\text{C-6}'$), 67.1 (C-6), 63.8 ($\text{C-2}'$), 62.9 ($\text{C-5}'$), 57.4 (OMe); Diagnostic peaks β -anomer: ^1H NMR (CDCl_3 , 400 MHz): δ 5.54 (s, 1H, CHPh), 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, $\text{H-5}'$); ^{13}C -APT NMR (CDCl_3 , 101 MHz): δ 105.1 (C-1), 102.6 ($\text{C-1}'$), 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: $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{48}\text{H}_{55}\text{N}_4\text{O}_{10}$ 847.39127, found 847.39206.



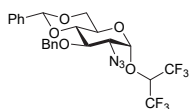
Methyl 2-O-(2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy- α/β -D-glucopyranosyl)-3-O-benzyl-4,6-O-benzylidene- α -D-mannopyranoside (3I).

Donor **3** and acceptor **29** were condensed using the general procedure for $\text{Ti}_2\text{O}/\text{Ph}_2\text{SO}$ 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%, $\alpha:\beta = 9:1$) 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: ^1H NMR (CDCl_3 , 400 MHz, HH-COSY, HSQC, HMBC): δ 7.54 – 7.47 (m, 4H, CH_{arom}), 7.44 – 7.25 (m, 16H, CH_{arom}), 5.66 (s, 1H, CHPh), 5.60 (s, 1H, CHPh'), 5.39 (d, 1H, $J = 3.7$ Hz, $\text{H-1}'$), 5.00 (d, 1H, $J = 11.0$ Hz, CHH Bn), 4.90 (d, 1H, $J = 12.2$ Hz, CHH Bn), 4.84 (d, 1H, $J = 10.9$ Hz, CHH Bn), 4.73 – 4.66 (m, 2H, H-1 , CHH Bn), 4.34 – 4.24 (m, 3H, H-4 , H-6 , $\text{H-6}'$), 4.17 (dd, 1H, $J = 10.2$, 9.0 Hz, $\text{H-3}'$), 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, $\text{H-5}'$, H-6), 3.83 – 3.70 (m, 3H, $\text{H-4}'$, H-5 , $\text{H-6}'$), 3.36 (s, 3H, CH_3 OMe), 3.32 (dd, 1H, $J = 10.2$, 3.8 Hz, $\text{H-2}'$); ^{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 ($\text{C-1}'$), 82.9 ($\text{C-4}'$), 79.4 (C-4), 75.9 (C-3), 75.6 ($\text{C-3}'$), 75.5 (C-2), 75.3, 73.3 (CH_2 Bn), 69.0, 68.9 (C-6 , $\text{C-6}'$), 64.1 (C-5), 63.3 ($\text{C-5}'$), 63.0 ($\text{C-2}'$), 55.0 (OMe); Diagnostic peaks β -anomer: ^1H NMR (CDCl_3 , 400 MHz): δ 4.43 (d, 0.1H, $J = 8.0$ Hz, $\text{H-1}'$), 3.62 (dd, 0.1H, $J = 9.6$, 8.0 Hz, $\text{H-2}'$), 3.51 (t, 0.1H, $J = 9.3$ Hz, H-4); ^{13}C -APT NMR (CDCl_3 , 101 MHz): δ 102.0 ($\text{C-1}'$), 78.5 (C-4), 66.4 ($\text{C-2}'$); HRMS: $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{41}\text{H}_{47}\text{N}_4\text{O}_{10}$ 755.32867, found 755.32921.

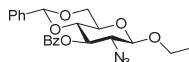


2,2,2-Trifluoroethyl 2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy- α -D-glucopyranoside (3J).

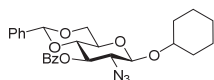
Donor **3** and 2,2,2-trifluoroethanol were condensed using the general procedure for $\text{Ti}_2\text{O}/\text{Ph}_2\text{SO}$ mediated glycosylations (for an additional 1 h at -40°C) and purified by flash column chromatography (1/0 to 0/1 pentane/toluene to 5% EtOAc in toluene) to yield glycosylation product **3J** (44 mg, 94 μmol , 94%, $\alpha:\beta = >20:1$) as a colorless oil. R_f : 0.24 (toluene). $[\alpha]_D^{23} = +25.9^\circ$ ($c = 0.88$, DCM); IR (neat): 697, 747, 1001, 1034, 1090, 1165, 1279, 1373, 2108, 2865, 2934; Data for the α -anomer: ^1H 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, CHPh), 4.99 – 4.94 (m, 2H, CHH Bn , H-1), 4.80 (d, 1H, $J = 10.9$ Hz, CHH 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, $\text{CH}_2\text{-CF}_3$), 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 ($J_{\text{C-1,H-1}} = 173$ Hz, C-1); Diagnostic peaks β -anomer: ^1H 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 ($J_{\text{C-H}} = 150$ Hz, C-1); HRMS: $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{22}\text{H}_{26}\text{F}_3\text{N}_4\text{O}_5$ 483.18498 found 483.18463.



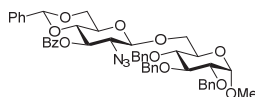
1,1,1,3,3,3-Hexafluoro-2-propyl glucopyranoside (3K). Donor **3** and 1,1,1,3,3,3-hexafluoroisopropanol were condensed using the general procedure for Tf₂O/Ph₂SO mediated glycosylations (for an additional 72 h at -40°C) and purified by flash column chromatography (1/0 to 9/1 pentane/EtOAc) to yield glycosylation product **3K** (28.1 mg, 53 μmol, 53%, α:β = >20:1) as a colorless oil. [α]_D²³ = +25.8° (c = 0.5, CHCl₃); IR (neat): 689, 748, 999, 1092, 1196, 1219, 1287, 1368, 2108, 2868, 2928; ¹H NMR (CDCl₃, 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, CHPh), 5.13 (d, 1H, J = 3.9 Hz, H-1), 4.99 (d, 1H, J = 10.8 Hz, CHH Bn), 4.82 (d, 1H, J = 10.8 Hz, CHH 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); ¹³C-APT NMR (CDCl₃, 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, CF₃), 101.6 (CHPh), 101.0 (C-1), 82.1 (C-4), 75.9 (C-3), 75.5 (CH₂ 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 C₂₃H₂₁F₆N₃O₅ 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 Tf₂O/Ph₂SO 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). [α]_D²³ = -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: ¹H NMR (CDCl₃, 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, CHPh), 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, CHH Et), 3.83 (t, 1H, J = 10.3 Hz, H-6), 3.80 – 3.67 (m, 2H, H-4, CHH 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, CH₃ Et); ¹³C-APT NMR (CDCl₃, 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, CH₂ Et), 65.0 (C-2), 15.2 (CH₃ Et); Diagnostic peaks α-anomer: ¹H NMR (CDCl₃, 400 MHz, HH-COSY, HSQC): δ 5.88 (t, 0.03H, J = 9.9 Hz, H-3), 5.53 (s, 0.03H, CHPh), 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+NH₄]⁺ calcd for C₂₂H₂₇N₄O₆ 443.19251 found 443.19234.

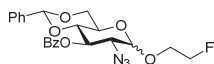


Cyclohexyl 2-azido-3-O-benzoyl-4,6-O-benzylidene-2-deoxy-β-D-glucopyranoside (4B). Donor **4** and cyclohexanol were condensed using the general procedure for Tf₂O/Ph₂SO mediated glycosylations and purified by flash column chromatography (1/1/0 to 0/1/0 to 0/19/1 pentane/toluene/EtOAc) to yield glycosylation product **4B** (43.6 mg, 91 μmol, 91%, α:β = <1:20) as a white solid. R_f: 0.18 (toluene). [α]_D²³ = -41.2° (c = 0.87, DCM); IR (thin film): 613, 708, 999, 1096, 1263, 1730, 2110, 2859, 2934; ¹H NMR (CDCl₃, 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, CHPh), 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, CH₂ 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, 2xCHH Cyc), 1.85 – 1.73 (m, 2H, 2xCHH Cyc), 1.58 – 1.40 (m, 3H, CHH Cyc, 2xCHH Cyc), 1.39 – 1.20 (m, 3H, 3xCHH Cyc); ¹³C-APT NMR (CDCl₃, 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 (CH₂ Cyc); HRMS: [M+NH₄]⁺ calcd for C₂₆H₃₃N₄O₆ 497.23946 found 497.23932.



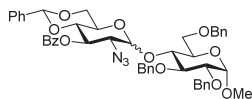
Methyl 6-O-(2-azido-3-O-benzoyl-4,6-O-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2,3,4-tri-O-benzylidene-α-D-glucopyranoside (4C). Donor **4** and acceptor **25** were condensed using the general procedure for Tf₂O/Ph₂SO mediated glycosylations (for an additional 18 h at -40°C) and purified by flash column 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). [α]_D²⁰ = -17.5° (c = 1.34, CHCl₃); IR (thin film): 696, 748, 1002, 1028, 1068, 1092, 1263, 1313, 1369, 1452, 1730, 2110, 2872, 2918; Data for the β-anomer: ¹H NMR (CDCl₃, 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, CHPh), 5.42 (t, 1H, J = 9.8 Hz, H-3'), 5.00 (d, 1H, J = 10.9 Hz, CHH Bn), 4.95 (d, 1H, J = 11.1 Hz, CHH Bn), 4.84 (d, 1H, J = 11.0 Hz, CHH Bn), 4.80 (d, 1H, J = 12.2 Hz, CHH Bn), 4.68 – 4.63 (m, 2H, 2xCHH 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, CH₃ OMe); ¹³C-APT NMR (CDCl₃, 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 (CH₂ 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 (CH₃ OMe); Diagnostic peaks α -anomer: ¹H NMR (CDCl₃, 400 MHz): δ 5.79 (t, 0.07H, $J = 9.9$ Hz, H-3'), 5.50 (s, 0.07H, CHPh), 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, CH₃ OMe); ¹³C-APT NMR (CDCl₃, 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+NH₄]⁺ calcd for C₄₈H₅₃N₄O₁₁ 861.37053, found 861.37064.



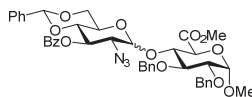
2-Fluoroethyl 2-azido-3-O-benzoyl-4,6-O-benzylidene-2-deoxy- α/β -D-glucopyranoside (4D). Donor **4** and 2-fluoroethanol were condensed using the general procedure for Tf₂O/Ph₂SO mediated glycosylations and purified by flash column chromatography

(1/1/0 to 0/1/0 to 0/16/1 pentane/toluene/EtOAc) to yield glycosylation product **4D** (36.6 mg, 83 μ mol, 83%, $\alpha:\beta = 1:6.5$) 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: ¹H NMR (CDCl₃, 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, CHPh), 5.41 (t, 1H, $J = 9.8$ Hz, H-3), 4.69 (ddt, 1H, $J = 4.6$, 3.2, 1.8 Hz, CHH-CH₂F), 4.65 (d, 1H, $J = 7.9$ Hz, H-1), 4.58 (ddt, 1H, $J = 4.5$, 3.3, 1.8 Hz, CHH-CH₂F), 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, CHHF), 3.95 (dddd, 1H, $J = 27.1$, 12.1, 5.5, 3.4 Hz, CHHF), 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); ¹³C-APT NMR (CDCl₃, 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, CH₂F), 78.8 (C-4), 71.7 (C-3), 69.5 (d, $J = 20.2$ Hz, CH₂-CH₂F), 68.5 (C-6), 66.7 (C-5), 64.9 (C-2); Diagnostic peaks α -anomer: ¹H NMR (CDCl₃, 400 MHz): δ 5.89 (t, 0.17H, $J = 9.9$ Hz, H-3), 5.53 (s, 0.17H, CHPh), 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); ¹³C-APT NMR (CDCl₃, 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+NH₄]⁺ calcd for C₂₂H₂₆FN₄O₆ 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 Tf₂O/Ph₂SO mediated glycosylations (for an additional 18 h at -40°C) and purified by flash column

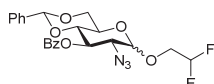
chromatography (19/1 to 4/1 pentane/EtOAc) to yield glycosylation product **4E** (60 mg, 71 μ mol, 71%, $\alpha:\beta = 1:6$) as a white solid. R_f: 0.67 (4/1 pentane/EtOAc). IR (thin film): 696, 733, 914, 999, 1026, 1045, 1090, 1177, 1263, 1314, 1366, 1452, 1730, 2108, 2866, 2899; Data for the β -anomer: ¹H NMR (CDCl₃, 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, CHPh), 5.19 (t, 1H, $J = 9.8$ Hz, H-3'), 4.90 (d, 1H, $J = 10.8$ Hz, CHH Bn), 4.83 (d, 1H, $J = 10.8$ Hz, CHH Bn), 4.81 – 4.73 (m, 2H, 2XCHH Bn), 4.67 – 4.60 (m, 2H, CHH Bn, H-1), 4.42 (d, 1H, $J = 12.0$ Hz, CHH 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, CH₃ OMe), 3.08 (td, 1H, $J = 9.7$, 5.0 Hz, H-5'); ¹³C-APT NMR (CDCl₃, 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 (CH₂ 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: ¹H NMR (CDCl₃, 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, CHPh), 5.15 (d, 0.17H, $J = 10.7$ Hz, CHH Bn), 4.74 (d, 0.17H, $J = 12.0$ Hz, CHH Bn), 4.09 (t, 0.17H, $J = 9.2$ Hz), 3.29 (dd, 0.17H, $J = 10.5$, 3.9 Hz, H-2'); ¹³C-APT NMR (CDCl₃, 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+NH₄]⁺ calcd for C₄₈H₅₃N₄O₁₁ 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 Tf₂O/Ph₂SO mediated glycosylations (for an additional 18 h at -40°C) and purified by flash column

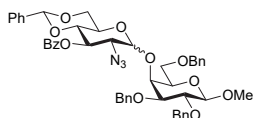
chromatography (19/1 to 4/1 pentane/EtOAc) to yield glycosylation product **4F** (46 mg, 59 μ mol, 59%, $\alpha:\beta = 1:1.4$) as

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: ¹H NMR (CDCl₃, 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'_α), 5.70 (d, 0.7H, *J* = 3.9 Hz, H-1'_α), 5.47 (s, 0.7H, CHPh_α), 5.41 (s, 1H, CHPh_β), 5.36 (t, 1H, *J* = 9.8 Hz, H-3'_β), 5.10 (d, 0.7H, *J* = 10.6 Hz, CHH Bn_α), 4.93 (d, 1H, *J* = 10.9 Hz, CHH Bn_β), 4.87 (d, 1H, *J* = 10.9 Hz, CHH Bn_β), 4.83 (d, 0.7H, *J* = 10.6 Hz, CHH Bn_α), 4.79 (d, 1H, *J* = 13.6 Hz, CHH Bn_β), 4.76 (d, 0.7H, *J* = 13.6 Hz, CHH Bn_α), 4.66–4.62 (m, 2H, CHH Bn_β, H-1'_β), 4.61–4.58 (m, 2.4H, CHH Bn_α, H-1_α, H-1_β), 4.31 (dd, 0.7H, *J* = 10.0, 4.6 Hz, H-6'_α), 4.28 (d, 0.7H, *J* = 9.7 Hz, H-5_α), 4.23 (d, 1H, *J* = 9.9 Hz, H-5_β), 4.19–4.06 (m, 3.4H, H-3_α, H-4_α, H-4_β, H-6'_β), 3.91 (t, 1H, *J* = 9.2 Hz, H-3), 3.85 (s, 2.1H, CH₃ CO₂Me_α), 3.83 (s, 3H, CH₃ CO₂Me_β), 3.79–3.59 (m, 3.8H, H-2_α, H-4'_α, H-4'_β, H-5'_α, H-6'_α), 3.59–3.44 (m, 4H, H-2_β, H-2'_β, H-5'_β, H-6'_β), 3.43 (s, 3H, CH₃ OMe_β), 3.42 (s, 2.1H, CH₃ OMe_α), 3.31 (dd, 1H, *J* = 10.4, 3.9 Hz, H-2'_α); ¹³C-APT NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 170.2, 169.9 (C=O CO₂Me), 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'_β), 101.7 (CHPh_α), 101.5 (CHPh_β), 99.0 (C-1'_α), 98.8 (C-1_β), 98.5 (C-1_α), 81.1 (C-3_α), 79.9 (C-2_α), 79.5, 79.5 (C-3_β, C-4_β), 79.2 (C-4'_α), 78.9, 78.7 (C-2_β, C-4'_β), 75.7, 75.4 (CH₂ Bn), 75.2 (C-4_α), 73.9, 73.6 (CH₂ Bn), 71.9 (C-3'_β), 69.8, 69.8 (C-5_α, C-5_β), 69.6 (C-3'_α), 68.5, 68.4 (C-6'_α, C-6'_β), 66.5 (C-5'_β), 65.6 (C-2'_β), 63.2 (C-5'_α), 61.7 (C-2'_α), 56.0, 56.0 (CH₃ OMe), 53.1, 53.0 (CH₃ CO₂Me); HRMS: [M+NH₄]⁺ calcd for C₄₂H₄₇N₄O₁₂ 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

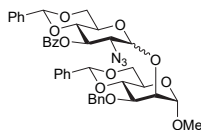
general procedure for Tf₂O/Ph₂SO mediated glycosylations and purified by flash column chromatography (1/1/0 to 0/1/0 to 0/19/1 pentane/toluene/EtOAc) to yield glycosylation product **4G** (38.6 mg, 84 μmol, 84%, α:β = 2.7:1) as a white solid. *R*_f: 0.49 (19/1 toluene/EtOAc). IR (thin film): 709, 997, 1026, 1069, 1094, 1265, 1726, 2108, 2870; Data for the α-anomer: ¹H NMR (CDCl₃, 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, CHF₂), 5.91–5.81 (m, 1H, H-3), 5.53 (s, 1H, CHPh), 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); ¹³C-APT NMR (CDCl₃, 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, CHF₂), 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, CH₂-CHF₂), 63.5 (C-5), 61.8 (C-2); Data for the β-anomer: ¹H NMR (CDCl₃, 400 MHz): δ 5.97 (tdd, 0.37H, *J* = 55.2, 4.8, 3.5 Hz, CHF₂), 5.51 (s, 0.37H, CHPh), 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, CHH-CHF₂), 3.98–3.76 (m, 1.11H, CHH-CHF₂, 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); ¹³C-APT NMR (CDCl₃, 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, CH₂-CHF₂), 68.4 (C-6), 66.8 (C-5), 64.9 (C-2); HRMS: [M+H]⁺ calcd for C₂₂H₂₂F₂N₃O₆ 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

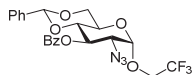
acceptor **28** were condensed using the general procedure for Tf₂O/Ph₂SO mediated glycosylations (for an additional 18 h at -40°C) and purified by flash column chromatography (19/1 to 4/1 pentane/EtOAc) to yield glycosylation product **4H** (43 mg, 52 μmol, 52%, α:β = 4:1) as a white solid. *R*_f: 0.36 (4/1 pentane/EtOAc). IR (thin film): 698, 737, 997, 1072, 1094, 1265, 1452, 1730, 2106, 2862, 2930; Data for the α-anomer: ¹H NMR (CDCl₃, 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, CHPh), 5.07 (d, 1H, *J* = 3.9 Hz, H-1'), 4.93 (d, 1H, *J* = 11.0 Hz, CHH Bn), 4.84 (d, 1H, *J* = 10.9 Hz, CHH Bn), 4.79 (d, 1H, *J* = 12.4 Hz, CHH Bn), 4.74 (d, 1H, *J* = 12.4 Hz, CHH Bn), 4.55 (s, 2H, CH₂ 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, CH₃ 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); ¹³C-APT NMR (CDCl₃, 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 (CH₂ Bn), 74.4 (C-4), 73.6, 73.2 (CH₂ 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: ¹H NMR (CDCl₃, 400 MHz): δ 5.47 (s, 0.25H, CHPh), 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: $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{48}\text{H}_{53}\text{N}_4\text{O}_{11}$ 861.37053, found 861.37067.



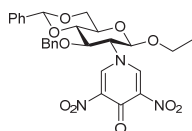
Methyl 2-O-(2-azido-3-O-benzoyl-4,6-O-benzylidene-2-deoxy- α / β -D-glucopyranosyl)-3-O-benzyl-4,6-O-benzylidene- α -D-mannopyranoside (4I). Donor **4** and acceptor **29** were condensed using the general procedure for $\text{TiF}_2\text{O}/\text{Ph}_2\text{SO}$ mediated glycosylations (for an additional 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; ^1H 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, CHPh), 5.54 (s, 1H, CHPh '), 5.51 (d, 1H, J = 3.8 Hz, H-1'), 4.94 (d, 1H, J = 12.2 Hz, CHH Bn), 4.73 (d, 1H, J = 1.5 Hz, H-1), 4.69 (d, 1H, J = 12.2 Hz, CHH 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, 128.3, 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: ^1H NMR (CDCl_3 , 400 MHz): δ 5.60 (s, 0.2H, CHPh), 5.50 (s, 0.2H, CHPh '), 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, CHH 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: $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{41}\text{H}_{45}\text{N}_4\text{O}_{11}$ 769.30793, found 769.30780.



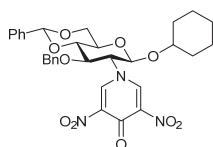
2,2,2-Trifluoroethyl 2-azido-3-O-benzoyl-4,6-O-benzylidene-2-deoxy- α -D-glucopyranoside (4J). Donor **4** and 2,2,2-trifluoroethanol were condensed using the general procedure for

$\text{TiF}_2\text{O}/\text{Ph}_2\text{SO}$ 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; ^1H 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, CHPh), 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: $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{22}\text{H}_{24}\text{F}_3\text{N}_4\text{O}_6$ 497.16425 found 497.16425.



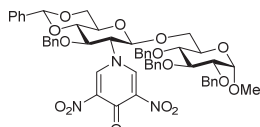
Ethyl 3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)- β -D-glucopyranoside (5A). Donor **5** and ethanol were condensed using the general procedure for $\text{TiF}_2\text{O}/\text{Ph}_2\text{SO}$ mediated glycosylations (for an additional 1 hour at -40°C) and purified by flash column 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; ^1H 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, CHPh), 5.32 (d, 1H, J = 8.3 Hz, H-1), 4.70 (d, 1H, J = 11.7 Hz, CHH Bn), 4.57 (dd, 1H, J = 10.2, 8.7 Hz, H-3), 4.53 (d, 1H, J = 11.6 Hz, CHH Bn), 4.43 (dd, 1H, J = 10.3, 4.6 Hz, H-6), 3.99 – 3.81 (m, 4H, CHH 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, CHH 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: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{28}\text{N}_8\text{O}_{10}$ 554.17692, found 554.17642.

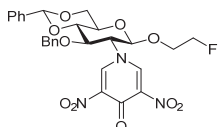


Cyclohexyl 3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)- β -D-glucopyranoside (5B). Donor **5** and cyclohexanol were condensed using the general procedure for $\text{TiF}_2\text{O}/\text{Ph}_2\text{SO}$ mediated glycosylations (for an additional 1 hour at -40°C) and purified by flash column chromatography (19/1 to 8/2 pentane/EtOAc) to yield 51 mg of glycosylation product **5B** as an inseparable mixture with donor **5** (13 mg 5, 38 mg

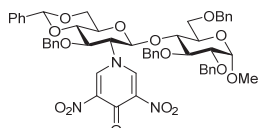
58, 63 μmol , 63%, $\alpha:\beta = <1:20$) as a yellow solid. R_f : 0.75 (7/3 pentane/EtOAc). R_f : 0.55 (7/3 pentane/EtOAc); IR: (thin film): 697, 718, 749, 789, 910, 997, 1092, 1212, 1302, 1330, 1516, 1623, 1674, 2931; ^1H NMR (CDCl_3 , 400 MHz, HH-COSY, HSQC): δ 8.60 (s, 2H, CH pyridone), 7.56 (d, 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, CHPh), 5.41 (d, 1H, $J = 8.2$ Hz, H-1), 4.71 (d, 1H, $J = 11.7$ Hz, CHH Bn), 4.66 – 4.50 (m, 2H, CHH 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, CH Cy , H-2), 1.91 – 1.77 (m, 1H, $\text{CH}_2 \text{ Cy}$), 1.71 – 1.54 (m, 2H, $\text{CH}_2 \text{ Cy}$), 1.54 – 1.45 (m, 1H, $\text{CH}_2 \text{ Cy}$), 1.43 – 0.96 (m, 6H, $\text{CH}_2 \text{ Cy}$); ^{13}C -APT NMR (CDCl_3 , 101 MHz, HSQC): δ 160.5 (C=O pyridone), 141.6 ($\text{C}_q \text{ NO}_2$ 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 ($\text{CH}_2 \text{ Bn}$), 74.0 (C-2), 68.8 (C-6), 65.7 (C-5), 33.3, 31.7, 25.3, 23.9, 23.6 ($\text{CH}_2 \text{ Cy}$); HRMS: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{31}\text{H}_{34}\text{N}_3\text{O}_{10}$ 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 (5C). Donor **5** and acceptor **25** were condensed using the general procedure for $\text{Tf}_2\text{O}/\text{Ph}_2\text{SO}$ 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%, $\alpha:\beta = <1:20$) as a yellow solid. R_f : 0.45 (7/3 pentane/EtOAc). $[\alpha]_D^{20} = +90.5^\circ$ ($c = 0.92$, CHCl_3); IR (thin film): 698, 1001, 1069, 1094, 1213, 1331, 1454, 1522, 1678, 2868; ^1H 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, CHPh), 4.92 (d, 1H, $J = 11.0$ Hz, CHH Bn), 4.85 (d, 1H, $J = 8.3$ Hz, H-1'), 4.83 – 4.66 (m, 2H, $2\times\text{CHH Bn}$), 4.72 (d, 1H, $J = 10.9$ Hz, CHH Bn), 4.69 (d, 1H, $J = 12.0$ Hz, CHH Bn), 4.60 (d, 1H, $J = 12.2$ Hz, CHH Bn), 4.60 (d, 1H, $J = 12.0$ Hz, CHH 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, CHH 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, $\text{CH}_3 \text{ OMe}$), 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 ($\text{C}_q \text{ NO}_2$ 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, 128.2, 128.1, 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, ($\text{CH}_2 \text{ Bn}$), 74.0 (C-3'), 73.3 ($\text{CH}_2 \text{ Bn}$), 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: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{53}\text{H}_{54}\text{N}_4\text{O}_{15}$ 972.35494, found 972.35546.

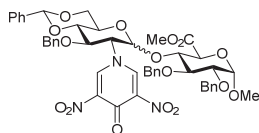


2-Fluoroethyl 3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)-β-D-glucopyranoside (5D). Donor **5** and 2-fluoroethanol were condensed using the general procedure for $\text{Tf}_2\text{O}/\text{Ph}_2\text{SO}$ mediated glycosylations (for an additional 1 hour at -40°C) and purified by flash column chromatography (19/1 to 8/2 pentane/EtOAc) to yield glycosylation product **5D** (24 mg, 43 μmol , 43%, $\alpha:\beta = <1:20$) as a yellow solid alongside donor **5** (15.6 mg). R_f : 0.42 (3/2 pentane/EtOAc). $[\alpha]_D^{23} = +142.9^\circ$ ($c = 0.48$, CHCl_3); IR (thin film): 698, 752, 1070, 1096, 1213, 1304, 1331, 1518, 1680, 2870, 3064; ^1H 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, CHPh), 5.46 (d, 1H, $J = 8.3$ Hz, H-1), 4.71 (d, 1H, $J = 11.7$ Hz, CHH Bn), 4.57 (dd, 1H, $J = 10.3$, 8.7 Hz, H-3), 4.53 (d, 1H, $J = 11.7$ Hz, CHH Bn), 4.48 – 4.42 (m, 2H, CHHF , H-6), 4.33 (t, 1H, $J = 4.1$ Hz, CHHF), 4.09 – 3.81 (m, 5H, $\text{CH}_2\text{-CH}_2\text{F}$, 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 ($\text{C}_q \text{ NO}_2$, 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 ($\text{CH}_2 \text{ Bn}$), 73.6 (C-2), 69.5 (d, $J = 19.5$ Hz, $\text{CH}_2\text{-CH}_2\text{F}$), 68.6 (C-6), 65.8 (C-5); HRMS: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{27}\text{FN}_3\text{O}_{10}$ 572.16760, found 572.16705.



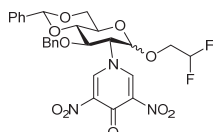
Methyl 4-O-(3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)-β-D-glucopyranosyl)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (5E). Donor **5** and acceptor **26** were condensed using the general procedure for $\text{Tf}_2\text{O}/\text{Ph}_2\text{SO}$ mediated glycosylations (for an additional 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%, $\alpha:\beta = <1:20$) as a yellow solid. R_f : 0.37 (7/3 pentane/EtOAc). $[\alpha]_D^{23} = +83.3^\circ$ ($c = 0.84$, CHCl_3); IR (thin film): 696, 734, 997, 1028, 1039, 1092, 1209, 1302, 1327, 1454, 1522, 1682, 2862, 2900, 3030, 3065; ^1H 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, CHPh), 4.90 (d, 1H, $J = 11.7$ Hz, CHH Bn), 4.83 (d, 1H, $J = 8.3$ Hz, H-1'), 4.81 – 4.64 (m, 2H, $2\times\text{CHH Bn}$), 4.72 (d, 1H, $J = 10.9$ Hz, CHH Bn), 4.69 (d, 1H, $J = 12.0$ Hz, CHH Bn), 4.60 (d, 1H, $J = 12.2$ Hz, CHH Bn), 4.60 (d, 1H, $J = 12.0$ Hz, CHH 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, CHH 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, $\text{CH}_3 \text{ OMe}$), 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 ($\text{C}_q \text{ NO}_2$ 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, 128.2, 128.1, 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, ($\text{CH}_2 \text{ Bn}$), 74.0 (C-3'), 73.3 ($\text{CH}_2 \text{ Bn}$), 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: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{53}\text{H}_{54}\text{N}_4\text{O}_{15}$ 972.35494, found 972.35546.

Bn), 4.77 (d, 1H, $J = 12.1$ Hz, *CHH* Bn), 4.74 (d, 1H, $J = 12.3$ Hz, *CHH* Bn), 4.69 (d, 1H, $J = 11.7$ Hz, *CHH* Bn), 4.66 (d, 1H, $J = 12.0$ Hz, *CHH* Bn), 4.63 (d, 1H, $J = 12.1$ Hz, *CHH* Bn), 4.56 (d, 1H, $J = 12.3$ Hz, *CHH* 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, *CHH* 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_2 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, 128.5, 128.4, 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: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{53}\text{H}_{54}\text{N}_3\text{O}_{15}$ 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).

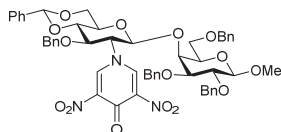
Donor **5** and acceptor **27** were condensed using the general procedure for $\text{Tf}_2\text{O}/\text{Ph}_2\text{SO}$ mediated glycosylations (for an additional 18 hours at -40°C) and purified by flash column chromatography (9/1 to 7/3 pentane/EtOAc) to yield glycosylation product **5F** (27 mg, 30 μmol , 30%, $\alpha/\beta = 1:3.6$) 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: ^1H 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, CHPh), 5.17 (d, 1H, $J = 8.2$ Hz, H-1'), 4.92 (d, 1H, $J = 11.3$ Hz, *CHH* Bn), 4.82–4.72 (m, 3H, *CHH* Bn, 2*xCHH* Bn), 4.61–4.55 (m, 2H, 2*xCHH* 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, 127.7, 127.7, 126.1, 126.0, 125.7 (CH_{arom}), 101.7 (CHPh), 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: ^1H 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, CHPh), 5.03 (d, 0.28H, $J = 12.7$ Hz, *CHH* Bn), 4.70 (d, 0.28H, $J = 12.3$ Hz), 4.62 (d, 0.28H, $J = 12.2$ Hz, *CHH* Bn), 4.46 (d, 0.28H, $J = 12.3$ Hz, *CHH* 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: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{47}\text{H}_{48}\text{N}_3\text{O}_{16}$ 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).

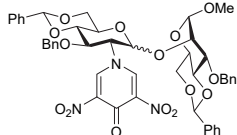
Donor **5** and 2,2-difluoroethanol were condensed using the general procedure for $\text{Tf}_2\text{O}/\text{Ph}_2\text{SO}$ mediated glycosylations (for an additional 1 hour at -40°C) and purified by flash column chromatography (19/1 to 8/2 pentane/EtOAc) to yield glycosylation product **5G** (17.3 mg, 29 μmol α anomer, 17.8 mg 30 μmol β anomer. $\alpha/\beta = 1:1$, 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: ^1H 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, CHF_2), 5.83 (s, 1H, CHPh), 5.56 (d, 1H, $J = 3.7$ Hz, H-1), 4.91 (d, 1H, $J = 11.9$ Hz, *CHH* Bn), 4.79 (dd, 1H, $J = 10.7$, 3.7 Hz, H-2), 4.71–4.62 (m, 2H, *CHH* Bn, H-3), 4.37 (dd, 1H, $J = 10.1$, 4.9 Hz, H-6), 4.18–4.06 (m, 2H, *CHH*- CHF_2 , H-5), 4.03 (dd, 1H, $J = 9.6$, 8.6 Hz, H-4), 3.96–3.83 (m, 2H, *CHH*- 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, CH_2 - CHF_2), 63.9 (C-5); Data for the β -anomer: ^1H 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, CHF_2), 5.65 (s, 1H, CHPh), 5.59 (d, 1H, $J = 8.3$ Hz, H-1), 4.76–4.64 (m, 2H, *CHH* Bn, H-3), 4.50 (d, 1H, $J = 11.6$ Hz, *CHH* 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, CH_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 (CH₂ Bn), 73.7 (C-2), 68.9 (t, $J = 27.8$ Hz, CH₂-CHF₂), 68.6 (C-6), 65.8 (C-5); HRMS: [M+H]⁺ calcd for C₂₇H₂₆F₂N₃O₁₀ 590.15808, found 590.15741.



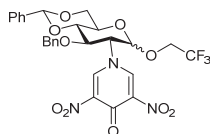
Methyl 4-O-(3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)-β-D-glucopyranosyl)-2,3,6-tri-O-benzyl-β-D-galactopyranoside (5H). Donor **5** and acceptor **28** were condensed using the general procedure for Tf₂O/Ph₂SO mediated glycosylations (for an additional 18 hours at -40°C) and purified by flash column chromatography (9/1 to 7/3 pentane/EtOAc) to yield glycosylation

product **5H** (51 mg, 52 μmol, 52%, $\alpha:\beta = <1:20$) as a yellow solid. R_f: 0.49 (7/3 pentane/EtOAc). [α]_D²⁰ = +35.5° ($c = 0.85$, CHCl₃); IR (thin film): 698, 750, 999, 1072, 1094, 1213, 1454, 1522, 1682, 2868; ¹H NMR (CDCl₃, 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, CHPh), 5.03 (d, 1H, $J = 8.3$ Hz, H-1'), 4.80 (d, 1H, $J = 12.2$ Hz, CHH Bn), 4.64 (d, 1H, $J = 10.4$ Hz, CHH Bn), 4.61 (d, 1H, $J = 12.3$ Hz, CHH Bn), 4.57 (d, 1H, $J = 12.2$ Hz, CHH Bn), 4.50 (s, 2H, CH₂ Bn), 4.47 (d, 1H, $J = 12.3$ Hz, CHH Bn), 4.29 (d, 1H, $J = 10.4$ Hz, CHH 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, CH₃ 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); ¹³C-APT NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 159.4 (C_q pyridone), 141.6 (C_q NO₂ 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 (CH₂ Bn), 74.6 (C-4), 74.5, 74.4 (CH₂ Bn), 74.2 (C-3'), 73.5 (CH₂ Bn), 72.5 (C-5), 72.3 (C-2'), 68.6 (C-6), 68.2 (C-6'), 66.2 (C-5'), 57.3 (OMe); ¹³C-HMBC-GATED NMR (CDCl₃, 101 MHz): δ 104.8 ($J = 159$ Hz, C-1), 99.6 ($J = 165$ Hz, C-1'); HRMS: [M+H]⁺ calcd for C₅₃H₅₄N₃O₁₅ 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 Tf₂O/Ph₂SO 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%, $\alpha:\beta = 1:1.3$) 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. ¹H NMR (CDCl₃, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.48 (s, 2H, pyridone_β), 8.33 (s, 1.6H, pyridone_α), 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, CHPh'_α, CHPh'_β), 5.62 (s, 0.8H, CHPh_α), 5.53 (s, 1H, CHPh_β), 5.27 (d, 0.8H, $J = 3.9$ Hz, H-1'_α), 5.24 (d, 1H, $J = 8.3$ Hz, H-1'_β), 4.84 (d, 1H, $J = 12.1$ Hz, CHH Bn_β), 4.79 (d, 0.8H, $J = 12.2$ Hz, CHH Bn_α), 4.75 (d, 1H, $J = 12.1$ Hz, CHH Bn_β), 4.70 (d, 1H, $J = 12.2$ Hz, CHH Bn_α), 4.67 (d, 0.8H, $J = 1.1$ Hz, H-1_α), 4.64 (d, 1H, $J = 12.1$ Hz, CHH Bn_β), 4.57 (d, 0.8H, $J = 12.2$ Hz, CHH Bn_α), 4.52 (d, 0.8H, $J = 11.1$ Hz, CHH Bn_α), 4.50 (dd, 1H, $J = 10.3$, 8.2 Hz, H-3'_β), 4.46 – 4.41 (m, 1H, H-6'_β), 4.33 (d, 0.8H, $J = 11.1$ Hz, CHH Bn_α), 4.34 – 4.26 (m, 1.6H, H-6_α, H-6'_α), 4.22 – 4.15 (m, 2.8H, H-1_β, H-2_β, H-3'_α), 4.10 – 3.96 (m, 4.4H, H-2_α, H-2'_α, H-2'_β, H-5'_α, H-6_β), 3.95 – 3.83 (m, 8.2H, H-3_α, H-3_β, H-4_β, H-4'_α, H-4'_β, H-5'_β, H-6_α, H-6'_α, H-6'_β), 3.81 – 3.74 (m, 1.6H, H-4_α, H-5_α), 3.61 (dq, 1H, $J = 9.0$, 4.5 Hz, H-5_β), 3.50 (t, 1H, $J = 10.3$ Hz, H-6_β), 3.38 (s, 2.4H, CH₃ OMe_α), 3.15 (s, 3H, CH₃ OMe_β); ¹³C-APT NMR (CDCl₃, 101 MHz, HSQC, HMBC): δ 159.9, 159.7 (C=O pyridone), 142.1 (CH pyridone_α), 141.7 (C_q NO₂ pyridone), 140.9 (CH pyridone_β), 140.8 (C_q NO₂ 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'_{α,β}), 101.6, 101.6 (CHPh_{α,β}), 100.7 (C-1_α), 99.8 (C-1'_α), 99.2 (C-1_β), 98.8 (C-1'_β), 83.1 (C-4'_α), 82.4 (C-4'_β), 79.6 (C-4_α), 79.1 (C-2_α), 78.5 (C-4_β), 76.1 (C-2_β), 75.0 (C-3_α), 74.5, 74.5, 74.3 (CH₂ Bn), 74.2 (C-3_β, C-3'_β), 72.9 (C-2'_β), 72.7 (CH₂ Bn), 72.5 (C-3'_α), 69.9 (C-2'_α), 68.5, 68.5, 68.4 (C-6_{α,β}, C-6'_{α,β}), 66.1 (C-5'_β), 63.7 (C-5_β), 63.3 (C-5_α), 63.1 (C-5'_α), 55.1, 55.1 (OMe); ¹³C-HMBC-GATED NMR (CDCl₃, 101 MHz): δ 99.8 ($J = 176$ Hz, C-1'_α), 98.8 ($J = 164$ Hz, C-1'_β); HRMS: [M+H]⁺ calcd for C₄₆H₄₆N₃O₁₅ 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 Tf₂O/Ph₂SO 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. $\alpha:\beta =$

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: ^1H 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, CHPh), 5.65 (d, 1H, J = 3.7 Hz, H-1), 4.92 (d, 1H, J = 11.8 Hz, CHH 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, CHH Bn), 4.51 – 4.38 (m, 1H, CHH-CF₃), 4.38 (dd, 1H, J = 10.1, 4.7 Hz, H-6), 4.30 – 4.17 (m, 1H, CHH-CF₃), 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 NO₂ 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, CF₃), 102.1 (CHPh), 98.8 (C-1), 83.4 (C-4), 75.1 (CH₂ Bn), 74.6 (C-3), 69.8 (C-2), 68.8 (C-6), 65.84 (q, J = 35.0 Hz, CH₂-CF₃), 64.1 (C-5); Diagnostic peaks β -anomer: ^1H NMR (CDCl₃, 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, CHPh), 5.58 (d, 1H, J = 8.3 Hz, H-1), 4.75 – 4.62 (m, 2H, CHH Bn, H-3), 4.52 (d, 1H, J = 11.7 Hz, CHH Bn), 4.46 (dd, 1H, J = 10.5, 4.8 Hz, H-6), 4.17 – 3.99 (m, 3H, CH₂-CF₃, 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: $[\text{M}+\text{H}]^+$ calcd for C₂₇H₂₅F₃N₃O₁₀ 608.14865, found 608.14825.

Footnotes and references

- (1) Capila, I.; Linhardt, R. J. *Angew. Chem. Int. Ed.* **2002**, 41 (3), 390–412.
- (2) Spillmann, D.; Lindahl, U. *Curr. Opin. Struct. Biol.* **1994**, 4 (5), 677–682.
- (3) Griffiths, A. J.; Davies, D. B. *Carbohydr. Polym.* **1991**, 14 (3), 241–279.
- (4) Griffiths, A. J.; Davies, D. B. *Carbohydr. Polym.* **1991**, 14 (4), 339–365.
- (5) Boltje, T. J.; Buskas, T.; Boons, G.-J. *Nat. Chem.* **2009**, 1 (8), 611–622.
- (6) Christina, A. E.; van der Marel, G. A.; Codée, J. D. C. In *Modern Synthetic Methods in Carbohydrate Chemistry*; Werz, D. B., Vidal, S., Eds.; Wiley-VCH Verlag GmbH & Co. KGaA, 2013; pp 97–124.
- (7) Nigudkar, S. S.; Demchenko, A. V. *Chem. Sci.* **2015**, 6 (5), 2687–2704.
- (8) Bennett, C. S. *Selective Glycosylations: Synthetic Methods and Catalysts*; Wiley VCH Verlag GmbH, 2017.
- (9) Crich, D.; Cai, W. *J. Org. Chem.* **1999**, 64 (13), 4926–4930.
- (10) Crich, D.; Sun, S. J. *Am. Chem. Soc.* **1997**, 119 (46), 11217–11223.
- (11) Crich, D.; Sun, S. J. *Org. Chem.* **1996**, 61 (14), 4506–4507.
- (12) Huang, M.; Garrett, G. E.; Birlirakis, N.; Bohé, L.; Pratt, D. A.; Crich, D. *Nat. Chem.* **2012**, 4 (8), 663–667.
- (13) Crich, D.; Chandrasekera, N. S. *Angew. Chem. Int. Ed.* **2004**, 43 (40), 5386–5389.
- (14) Adero, P. O.; Furukawa, T.; Huang, M.; Mukherjee, D.; Retaillieu, P.; Bohé, L.; Crich, D. *J. Am. Chem. Soc.* **2015**, 137 (32), 10336–10345.
- (15) Huang, M.; Furukawa, T.; Retaillieu, P.; Crich, D.; Bohé, L. *Carbohydr. Res.* **2016**, 427, 21–28.
- (16) Bohé, L.; Crich, D. *Carbohydr. Res.* **2015**, 403, 48–59.
- (17) Huang, M.; Retaillieu, P.; Bohé, L.; Crich, D. *J. Am. Chem. Soc.* **2012**, 134 (36), 14746–14749.
- (18) Bongat, A. F. G.; Demchenko, A. V. *Carbohydr. Res.* **2007**, 342 (3–4), 374–406.
- (19) For the use of C2-N-C3-O-carbamate-protected glucosamines, see, for example: ref 6 and Codée, J. D. C.; Ali, A.; Overkleef, H. S.; van der Marel, G. A. *Comptes Rendus Chim.* **2011**, 14 (2–3), 178–193.
- (20) Cid, M. B.; Alfonso, F.; Martín-Lomas, M. *Chem. – Eur. J.* **2005**, 11 (3), 928–938.
- (21) Li, J.; Dai, Y.; Li, W.; Laval, S.; Xu, P.; Yu, B. *Asian J. Org. Chem.* **2015**, 4 (8), 756–762.
- (22) van der Vorm, S.; Hansen, T.; Overkleef, H. S.; van der Marel, G. A.; Codee, J. D. C. *Chem. Sci.* **2017**, 8 (3), 1867–1875.
- (23) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, 91 (2), 165–195.
- (24) Ammer, J.; Mayr, H. *J. Phys. Org. Chem.* **2013**, 26 (1), 59–63.
- (25) Minegishi, S.; Kobayashi, S.; Mayr, H. *J. Am. Chem. Soc.* **2004**, 126 (16), 5174–5181.
- (26) Beaver, M. G.; Woerpel, K. A. *J. Org. Chem.* **2010**, 75 (4), 1107–1118.
- (27) Krumper, J. R.; Salamant, W. A.; Woerpel, K. A. *J. Org. Chem.* **2009**, 74 (21), 8039–8050.
- (28) Hagen, B.; Ali, S.; Overkleef, H. S.; van der Marel, G. A.; Codée, J. D. C. *J. Org. Chem.* **2017**, 82 (2), 848–868.
- (29) Matsumura, E.; Ariga, M.; Tohda, Y.; Kawashima, T. *Tetrahedron Lett.* **1981**, 22 (8), 757–758.
- (30) Matsumura, E.; Kobayashi, H.; Nishikawa, T.; Ariga, M.; Tohda, Y.; Kawashima, T. *Bull. Chem. Soc. Jpn.* **1984**, 57 (7), 1961–1965.
- (31) Lindberg, J.; Öhberg, L.; Garegg, P. J.; Konradsson, P. *Tetrahedron* **2002**, 58 (7), 1387–1398.

- (32) Emmadi, M.; Kulkarni, S. S. *J. Org. Chem.* **2011**, *76* (11), 4703–4709.
- (33) Coutant, C.; Jacquinet, J.-C. *J. Chem. Soc. [Perkin 1]* **1995**, No. 12, 1573–1581.
- (34) Goddard-Borger, E. D.; Stick, R. V. *Org. Lett.* **2007**, *9* (19), 3797–3800.
- (35) Chiara, J. L.; García, Á.; Cristóbal-Lumbroso, G. *J. Org. Chem.* **2005**, *70* (10), 4142–4151.
- (36) Trans-amination via double Michael addition-elimination with a nucleophilic amine ensures deprotection. Typical conditions included 0.2 M solution of DNPY-protected compound in pyridine at room temperature treated with amine (2 eq.) and stirred for 30 min. Extractive workup gave deprotected amines in excellent yield (>90%). Efficient nucleophilic amines are ethylenediamine (DNPY product water soluble), propylamine, hexylamine, and hydrazine.
- (37) Frihed, T. G.; Bols, M.; Pedersen, C. M. *Chem. Rev.* **2015**, *115* (11), 4963–5013.
- (38) Codée, J. D. C.; Litjens, R. E. J. N.; den Heeten, R.; Overkleeft, H. S.; van Boom, J. H.; van der Marel, G. A. *Org. Lett.* **2003**, *5* (9), 1519–1522.
- (39) The chemical shifts of the resonances in donor **5** are very sensitive to temperature, concentration and chemical environment. It was ensured that the sample had not precipitated during the low-temperature NMR experiments at all temperatures; the cause of the line broadening is therefore attributed to the poor solvation and mobility of the donor in dichloromethane.
- (40) Lee, J.-C.; Greenberg, W. A.; Wong, C.-H. *Nat. Protoc.* **2007**, *1* (6), 3143–3152.
- (41) Douglas, N. L.; Ley, S. V.; Lücking, U.; Warriner, S. L. *J. Chem. Soc. [Perkin 1]* **1998**, No. 1, 51–66.
- (42) Zhang, Z.; Ollmann, I. R.; Ye, X.-S.; Wischnat, R.; Baasov, T.; Wong, C.-H. *J. Am. Chem. Soc.* **1999**, *121* (4), 734–753.
- (43) Pedersen, C. M.; Marinescu, L. G.; Bols, M. *Chem. Commun.* **2008**, No. 21, 2465–2467.
- (44) Kamkhachorn, T.; Parameswar, A. R.; Demchenko, A. V. *Org. Lett.* **2010**, *12* (13), 3078–3081.
- (45) Walvoort, M. T. C.; de Witte, W.; van Dijk, J.; Dinkelaar, J.; Lodder, G.; Overkleeft, H. S.; Codée, J. D. C.; van der Marel, G. A. *Org. Lett.* **2011**, *13* (16), 4360–4363.
- (46) de Jong, A.-R.; Hagen, B.; van der Ark, V.; Overkleeft, H. S.; Codée, J. D. C.; Van der Marel, G. A. *J. Org. Chem.* **2012**, *77* (1), 108–125.
- (47) Mootoo, D. R.; Konradsson, P.; Udodong, U.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1988**, *110* (16), 5583–5584.
- (48) Andrews, C. W.; Rodebaugh, R.; Fraser-Reid, B. *J. Org. Chem.* **1996**, *61* (16), 5280–5289.
- (49) Fraser-Reid, B.; López, J. C. In *Reactivity Tuning in Oligosaccharide Assembly*; Fraser-Reid, B., Cristóbal López, J., Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg, 2011; pp 1–29.
- (50) Balmond, E. I.; Coe, D. M.; Galan, M. C.; McGarrigle, E. M. *Angew. Chem. Int. Ed.* **2012**, *51* (36), 9152–9155.
- (51) Ennis, S. C.; Cumpstey, I.; Fairbanks, A. J.; Butters, T. D.; Mackeen, M.; Wormald, M. R. *Tetrahedron* **2002**, *58* (46), 9403–9411.
- (52) Ingle, A. B.; Chao, C.-S.; Hung, W.-C.; Mong, K.-K. *T. Org. Lett.* **2013**, *15* (20), 5290–5293.
- (53) The moderate yields obtained in glycosylations with donor **5** are attributed the unidentified baseline (TLC) material when the reaction was activated and stirred at -40°C. For model acceptors **6–10** the donor was activated to -50°C and unreacted donor was consistently recovered.
- (54) Crich, D.; Li, L. *J. Org. Chem.* **2007**, *72* (5), 1681–1690.
- (55) Whitfield, D. M. *Carbohydr. Res.* **2007**, *342* (12–13), 1726–1740.
- (56) Hosoya, T.; Kosma, P.; Rosenau, T. *Carbohydr. Res.* **2015**, *411*, 64–69.
- (57) Smith, D. M.; Woerpel, K. A. *Org. Biomol. Chem.* **2006**, *4* (7), 1195–1201.
- (58) Crich, D.; Cai, W.; Dai, Z. *J. Org. Chem.* **2000**, *65* (5), 1291–1297.
- (59) This striking stereodirecting effect has been hypothesized to be caused by remote participation, but direct evidence for this type of participation on benzylidene mannose donors has not yet been found. Other stereo-electronic stabilizing effects might be responsible for the apparent stereoselectivity and await further study. For a discussion on remote participation, see: (a) Crich, D.; Hu, T.; Cai, F. *J. Org. Chem.* **2008**, *73* (22), 8942–8953. (b) Baek, J. Y.; Lee, B.-Y.; Jo, M. G.; Kim, K. S. *J. Am. Chem. Soc.* **2009**, *131* (48), 17705–17713. (c) Komarova, B. S.; Orekhova, M. V.; Tsvetkov, Y. E.; Nifantiev, N. E. *Carbohydr. Res.* **2014**, *384*, 70–86.
- (60) Crich, D.; Smith, M.; Yao, Q.; Picione, J. *Synthesis* **2001**, 2001 (02), 0323–0326.
- (61) Benakli, K.; Zha, C.; Kerns, R. J. *J. Am. Chem. Soc.* **2001**, *123* (38), 9461–9462.
- (62) Buskas, T.; Garegg, P. J.; Konradsson, P.; Maloisel, J.-L. *Tetrahedron Asymmetry* **1994**, *5* (11), 2187–2194.
- (63) Emmadi, M.; Kulkarni, S. S. *J. Org. Chem.* **2011**, *76* (11), 4703–4709.
- (64) You, F.; Twieg, R. J. *Tetrahedron Lett.* **1999**, *40* (50), 8759–8762.

